

Supplementary Information

Catalyst-Controlled Regiodivergence in Enantioselective

Synthesis of Spirocyclic γ - versus δ -Lactams

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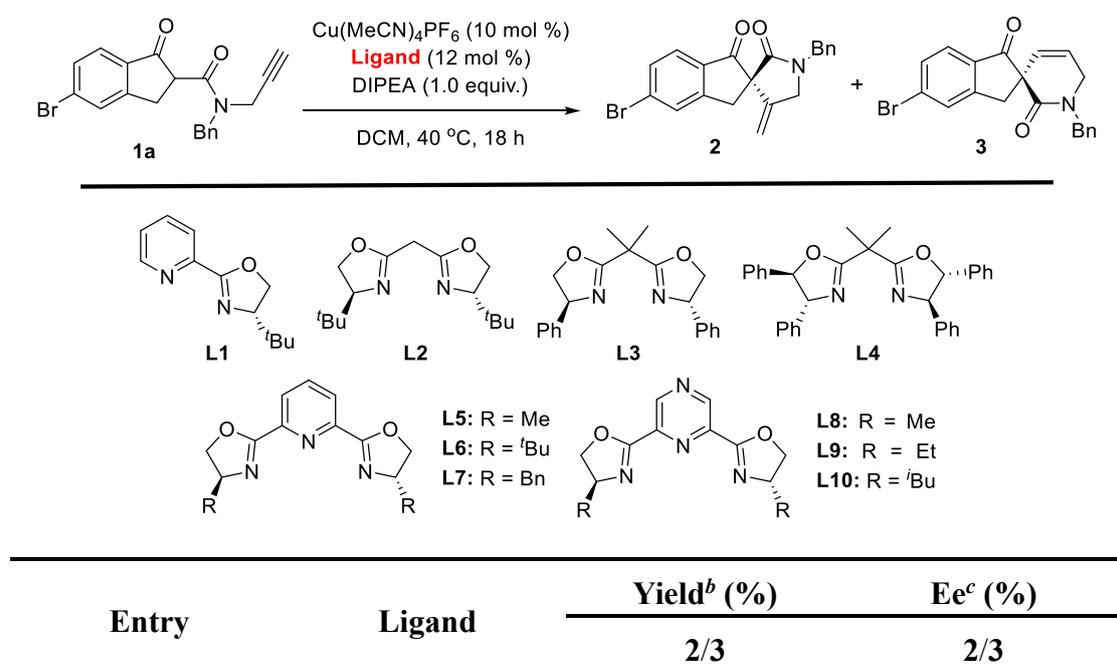
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I. General Information

All manipulations were maintained under an atmosphere of nitrogen unless otherwise stated. Commercially available reagents were used without further purification. Solvents were pre-dried over activated 4 Å molecular sieves and were refluxed over sodium-benzophenone (toluene, tetrahydrofuran), phosphorus pentoxide (chloroform) or calcium hydride (dichloromethane, dichloroethane, acetonitrile). Column chromatography was performed on silica gel (200-300 mesh). ^1H NMR spectra were recorded on a 400 spectrometer and ^{13}C NMR spectra were recorded on a 101 MHz NMR spectrometer. Infrared spectra were prepared as KBr pellets and were recorded on a Varian Excalibur 3100 series FT-IR spectrometer. Mass spectra were recorded by the mass spectrometry service of Shanghai Institute of Organic Chemistry. HPLC analyses on a Waters 1596 or Shimadzu SPD-15C. Optical rotations were measured with Rudolph Research Analytical in a 1 dm cuvette. I. **L1**¹, **L2**², **L3**³, **L4**⁴, **L5-L7**⁵ were synthesized according to the literature procedures.

II. Optimization of Reaction Conditions

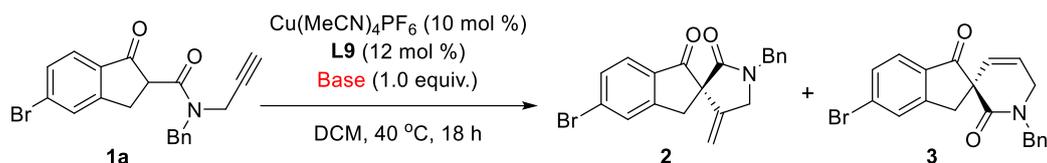
Table S1. Optimization of the Reaction Conditions (**Ligand**) for the Synthesis of γ -Lactam **2**^a



2	L2	42/-	8/-
3	L3	56/-	26/-
4	L4	67/-	34/-
5	L5	67/-	70/-
6	L6	21/-	18/-
7	L7	42/-	54/-
8	L8	58/-	70/-
9	L9	57/-	76/-
10	L10	52/-	68/-

^aReaction conditions: **1a** (0.1 mmol), Cu(MeCN)₄PF₆ (10 mol %), **Ligand** (12 mol %), DIPEA (1.0 equiv.), DCM (2 mL), 40 °C. ^bIsolated yields. ^cDetermined by HPLC analysis.

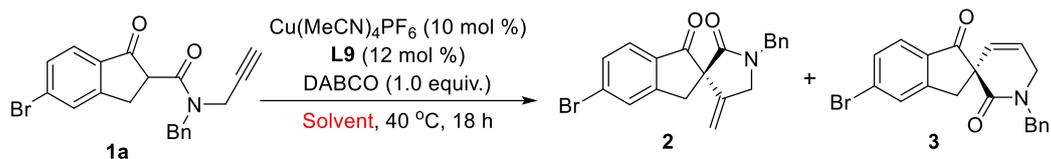
Table S2. Optimization of the Reaction Conditions (**Base**) for the Synthesis of γ -Lactam **2**^a



Entry	Base	Yield ^b (%)	Ee ^c (%)
		2/3	2/3
1	DMAP	52/-	0/-
2	Et ₃ N	78/-	88/-
3	DBU	88/-	0/-
4	DABCO	81/-	94/-
5	quinuclidine	80/-	86/-
6	^t BuOK	45/-	2/-
7	K ₂ CO ₃	36/-	4/-
8	KOH	40/-	4/-

^aReaction conditions: **1a** (0.1 mmol), Cu(MeCN)₄PF₆ (10 mol %), **L9** (12 mol %), **Base** (1.0 equiv.), DCM (2 mL), 40 °C. ^bIsolated yields. ^cDetermined by HPLC analysis.

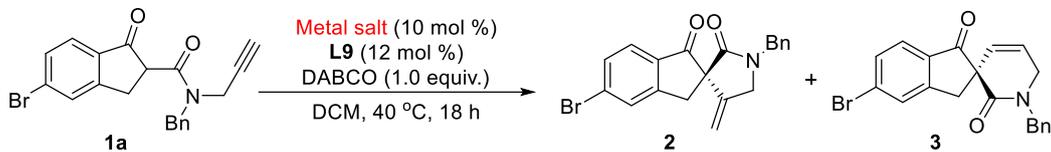
Table S3. Optimization of the Reaction Conditions (**Solvent**) for the Synthesis of γ -Lactam **2**^a



Entry	Solvent	Yield ^b (%)		Ee ^c (%)	
		2/3		2/3	
1	MeCN	70/-		48/-	
2	DCE	41/-		36/-	
3	THF	52/-		79/-	
4	toluene	50/-		42/-	
5	MeOH	26/-		38/-	
6	DCM	81/-		94/-	

^aReaction conditions: **1a** (0.1 mmol), $\text{Cu}(\text{MeCN})_4\text{PF}_6$ (10 mol %), **L9** (12 mol %), DABCO (1.0 equiv.), Solvent (2 mL), 40 °C. ^bIsolated yields. ^cDetermined by HPLC analysis.

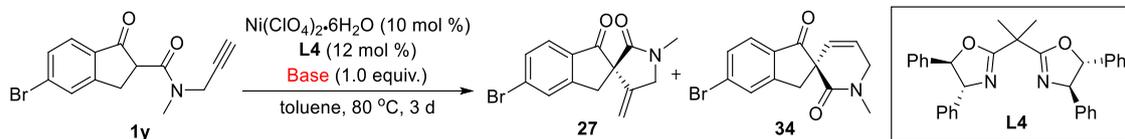
Table S4. Optimization of the Reaction Conditions (**metal salts**) for the Synthesis of γ -Lactam **2**^a



Entry	[M]	Yield ^b (%)		Ee ^c (%)	
		2/3		2/3	
1	$\text{CuBH}_4(\text{PPh}_3)_2$	99/-		0/-	
2	$\text{Cu}(\text{MeCN})_4\text{BF}_4$	89/-		94/-	
3	CuOAc	78/-		80/-	
4	CuOTf	68/-		94/-	
5	CuCl	71/-		88/-	
6	$\text{Cu}(\text{MeCN})_4\text{OTf}$	80/-		94/-	
7	$\text{Cu}(\text{OAc})_2$	54/-		0/-	
8	CuCl_2	69/-		0/-	
9	FeCl_2	-/-		-/-	
10	$\text{Fe}(\text{OAc})_2$	-/-		-/-	

^aReaction conditions: **1a** (0.1 mmol), **metal salt** (10 mol %), **L9** (12 mol %), DABCO (1.0 equiv.), DCM (2 mL), 40 °C. ^bIsolated yields. ^cDetermined by HPLC analysis.

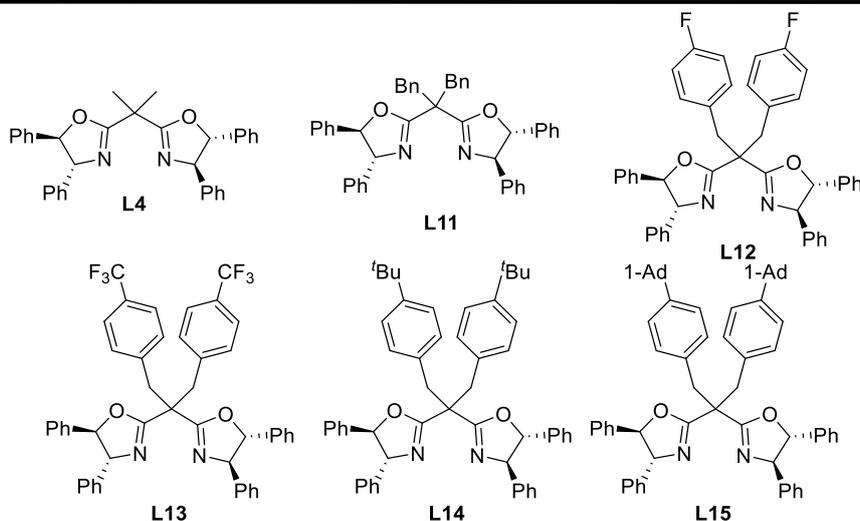
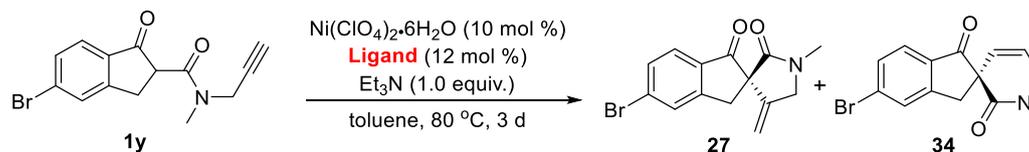
Table S5. Optimization of the Reaction Conditions (**Base**) for the Synthesis of δ -Lactam **34**^a



Entry	Base	Yield ^b (%)		Ee ^c (%)	
		27/34	27/34	27/34	27/34
1	DIPEA	-/59	-/74		
2	LiHMDS	-/25	-/32		
3	Et ₃ N	-/80	-/74		
4	DMAP	-/-	-/-		
5	Li ₂ CO ₃	-/25	-/27		

^aReaction conditions: **1y** (0.1 mmol), Ni(ClO₄)₂·6H₂O (10 mol %), **L4** (12 mol %), **Base** (1.0 equiv.), toluene (2 mL), 80 °C. ^bIsolated yields. ^cDetermined by HPLC analysis.

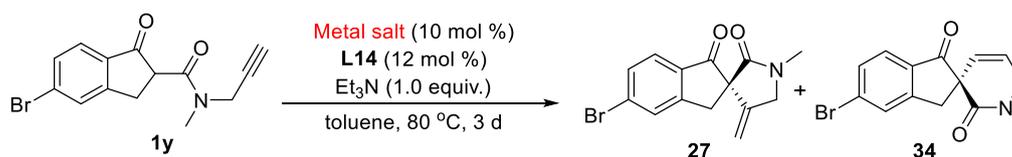
Table S6. Optimization of the Reaction Conditions (**Ligand**) for the Synthesis of δ -Lactam **34**^a



Entry	Ligand	Yield ^b (%)		Ee ^c (%)	
		27/34		27/34	
1	L4	-/80		-/74	
2	L11	-/66		-/81	
3	L12	-/53		-/75	
4	L13	-/50		-/56	
5	L14	-/87		-/86	
6	L15	-/83		-/76	

^aReaction conditions: **1y** (0.1 mmol), Ni(ClO₄)₂·6H₂O (10 mol %), **Ligand** (12 mol %), Et₃N (1.0 equiv.), toluene (2 mL), 80 °C. ^bIsolated yields. ^cDetermined by HPLC analysis.

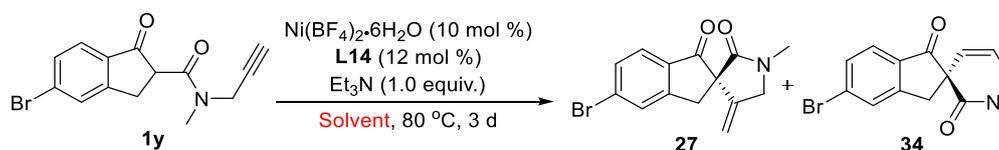
Table S7. Optimization of the Reaction Conditions (**Metal salts**) for the Synthesis of δ -Lactam **34**^a



Entry	[M]	Yield ^b (%)		Ee ^c (%)	
		27/34		27/34	
1	Ni(ClO ₄) ₂ ·6H ₂ O	-/68		-/82	
2	Ni(BF₄)₂·6H₂O	-/55		-/88	
3	NiF ₂ ·4H ₂ O	-/-		-/-	
4	Ni(OTf) ₂	-/61		-/80	
5	Ni(OTs) ₂	-/-		-/-	
6	Ni(OAc) ₂ ·2H ₂ O	-/-		-/-	

^aReaction conditions: **1y** (0.1 mmol), **Metal salt** (10 mol %), **L14** (12 mol %), Et₃N (1.0 equiv.), toluene (2 mL), 80 °C. ^bIsolated yields. ^cDetermined by HPLC analysis.

Table S8. Optimization of the Reaction Conditions (**Solvent**) for the Synthesis of δ -Lactam **34**^a

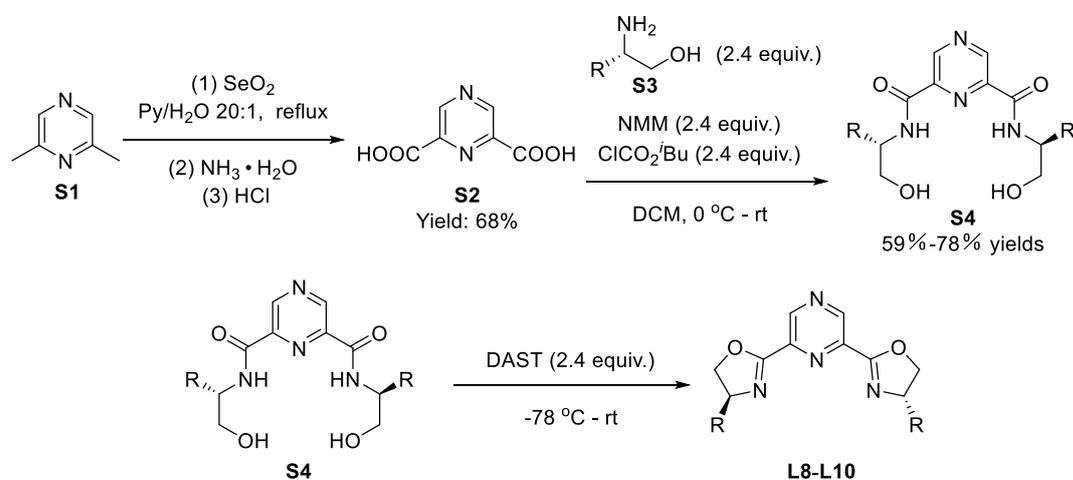


Entry	Solvent	Yield ^b (%)	Ee ^c (%)
		27/34	27/34
1	toluene	-/55	-/88
2 ^d	toluene	-/65	-/88
3 ^d	PhCF ₃	-/67	-/86
4 ^d	MeCN	-/10	-/76
5 ^d	CHCl ₃	-/8	-/80
6 ^d	THF	-/-	-/-
7 ^d	MeOH	-/-	-/-
8^d	EtOAc	-/89	-/90
9 ^d	<i>n</i> -butyl acetate	-/49	-/86
10 ^d	isopropyl acetate	-/46	-/88
11 ^d	<i>tert</i> -butyl acetate	-/35	-/90
12 ^e	EtOAc	-/80	-/90
13 ^f	EtOAc	-/45	-/89

^aReaction conditions: **1y** (0.1 mmol), Ni(BF₄)₂·6H₂O (10 mol %), **L14** (12 mol %), Et₃N (1.0 equiv.), **Solvent** (2 mL), 80 °C. ^bIsolated yields. ^cDetermined by HPLC analysis. ^dWith H₂O (5 μL). ^eWith H₂O (3 μL). ^fWith H₂O (7 μL).

III. General Procedure for the Synthesis of ligands L8-L10, L11-L15

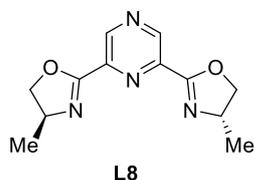
General Procedure for the Synthesis of ligands L8-L10



Step 1: 2, 6-Dimethylpyridine 1 (**S1**, 10 mmol, 1.0 equiv.) was dissolved in pyridine (20 mL, 0.5M) and water (1 mL), then SeO₂ (50 mmol, 5 equiv.) was added. The mixture was stirred at 100 °C overnight. After cooling to room temperature, dilute ammonia (8 mL of concentrated ammonia in 80 mL of water) was added to the mixture, yielding a large amount of dark green solids. After extraction, the solvent was concentrated in vacuo. 2M ammonia was added to residue. The solvent was decolorized with activated carbon, and concentrated in vacuo. 2M hydrochloric acid to was added to the mixture to precipitate a white solid, which was collected by filtration, washed with 2 M hydrochloric acid, and dried to afford **S2** in 68% yield.

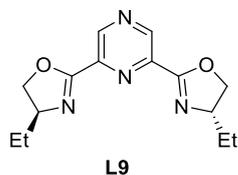
Step 2: The white solid **S2** (3 mmol, 1.0 equiv.) was dissolved in DCM (30 mL, 0.1M). The solution was cooled to 0 °C, 4-methylmorpholine (7.2 mmol, 2.4 equiv.) followed by isobutyl chloroformate (7.2 mmol, 2.4 equiv.) were added. After 5 minutes, chiral amino alcohol **S3** (7.2 mmol, 2.4 equiv.) was added to the mixture. The reaction system was slowly heated to room temperature and reacted for 12 h. The solvent was concentrated in vacuo. The **S4** obtained after recrystallization was directly used for the next reaction.

Step 3: **S4** (1 mmol, 1.0 equiv.) was dissolved in DCM (20 mL, 0.05M). DAST (2.4 mmol, 2.4 equiv.) was added at -78 °C. The reaction mixture was allowed to warm slowly to room temperature and was monitored by TLC until completion. Saturated sodium bicarbonate was added in mixture. The mixture was extracted with DCM (three times). The combined organic layer was washed with brine, dried over anhydrous MgSO₄, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate/ petroleum ether = 1: 1) to give the products **L8-L10**.

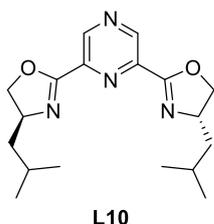


2,6-bis((S)-4-methyl-4,5-dihydrooxazol-2-yl)pyrazine (L8); TLC: $R_f = 0.20$ (petroleum ether /ethyl acetate = 1/1, v/v, UV); yellow solid (mp: 117-118 °C); yield: 30%; $[\alpha]_D^{25} = -40$ ($c = 0.1$, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 9.35 (s, 2H), 4.63 (dd, $J = 9.2, 8.4$ Hz, 2H), 4.58-4.42 (m, 2H), 4.09 (t, $J = 8.0$ Hz, 2H), 1.40 (d, $J = 6.8$

Hz, 6H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 160.7, 146.4, 141.9, 74.9, 62.7, 21.4; HRMS (ESI, m/z): calcd for $\text{C}_{12}\text{H}_{15}\text{N}_4\text{O}_2^+$ $[\text{M}+\text{H}]^+$: 247.1190, found: 247.1194.

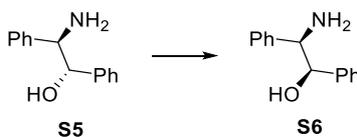


2,6-bis((S)-4-ethyl-4,5-dihydrooxazol-2-yl)pyrazine (L9); TLC: $R_f = 0.20$ (petroleum ether /ethyl acetate = 1/1, v/v, UV); white solid (mp: 58-59 °C); yield: 62%; $[\alpha]_{\text{D}}^{25} = -166$ ($c = 0.1$, CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 9.35 (s, 2H), 4.57 (dd, $J = 9.6, 8.4$ Hz, 2H), 4.38-4.26 (m, 2H), 4.14 (t, $J = 8.4$ Hz, 2H), 1.86-1.71 (m, 2H), 1.69-1.57 (m, 2H), 1.00 (t, $J = 7.2$ Hz, 6H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 160.7, 146.4, 141.9, 73.0, 68.6, 28.6, 10.2; HRMS (ESI, m/z): calcd for $\text{C}_{14}\text{H}_{19}\text{N}_4\text{O}_2^+$ $[\text{M}+\text{H}]^+$: 275.1503, found: 275.1506.

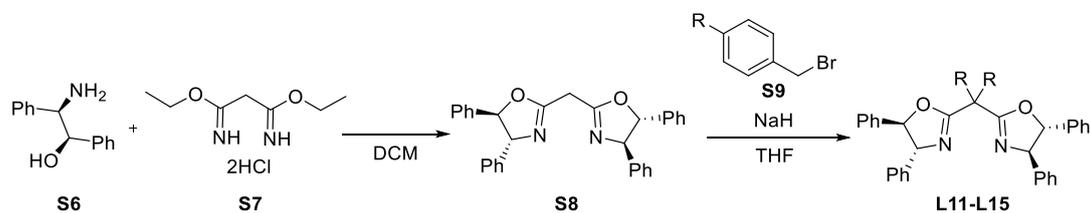


2,6-bis((S)-4-isobutyl-4,5-dihydrooxazol-2-yl)pyrazine (L10); TLC: $R_f = 0.30$ (petroleum ether /ethyl acetate = 1/1, v/v, UV); white solid (mp: 100-101 °C); yield: 30%; $[\alpha]_{\text{D}}^{25} = -98$ ($c = 0.1$, CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 9.32 (s, 2H), 4.60 (dd, $J = 9.6, 8.4$ Hz, 2H), 4.48-4.35 (m, 2H), 4.08 (t, $J = 8.4$ Hz, 2H), 1.94-1.79 (m, 2H), 1.78-1.67 (m, 2H), 1.45-1.29 (m, 2H), δ 0.98 (d, $J = 6.4$ Hz, 6H), 0.96 (d, $J = 6.4$ Hz, 6H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 160.5, 146.3, 141.9, 74.0, 65.7, 45.5, 25.5, 22.83, 22.80; HRMS (ESI, m/z): calcd for $\text{C}_{18}\text{H}_{27}\text{N}_4\text{O}_2^+$ $[\text{M}+\text{H}]^+$: 331.2129, found: 331.2126.

General Procedure for the Synthesis of ligand L11-L15

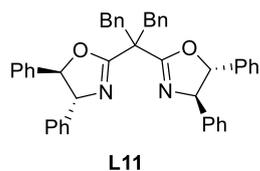


A suspension of (1*S*, 2*R*)-(+)-2-amino-1,2-diphenylethanol (**S5**, 2.0 g, 9.4 mmol) in formamide (21 mL) was heated at 150 °C for 15 min. After cooling, the solution was diluted with water (110 mL) and the crystalline formylated intermediate was separated and washed with water until free from chlorides. To thionyl chloride (2.8 mL, 38 mmol) at 0 °C was added the formylated intermediate. After 10 min at the same temperature, the reaction was allowed to rise to rt. Ice (~35 g) was added to the mixture whereby a white precipitate formed. The mixture was heated under reflux for 2 h and the clear solution was treated with charcoal and filtered. The colorless solution was made alkaline with 30% aqueous NaOH solution (9 mL). The aqueous solution was extracted three times with DCM. The combined organics was dried over MgSO₄, filtered, and concentrated to a solid **S6** (0.87 g, 44%).

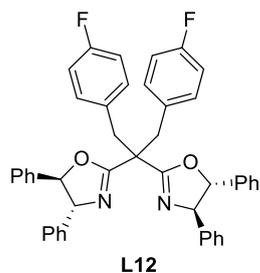


Diethyl malonimidate dihydrochloride (**S7**, 1.33 mg, 5.64 mmol) was added to a solution of (1*S*, 2*R*)-(+)-2-amino-1,2-diphenylethanol (**S6**, 2.65 g, 12.4 mmol) in DCM (50 mL) contained in a round-bottom flask under a nitrogen atmosphere. The mixture was stirred at room temperature for 7 days. It was then diluted with water and extracted with DCM. The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, and concentrated. Purification of the residue by column chromatography on silica gel (PE/EA = 1:1) afforded the product **S8** as a white solid (2.05 g, 79% yield).

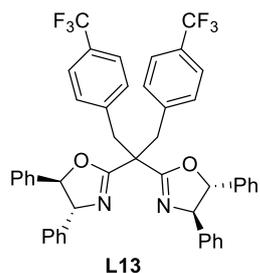
To a stirred solution of **S8** (2 mmol, 1.0 equiv.) in THF (20 mL) was carefully added NaH (60% dispersion in mineral oil, 6 mmol, 3.0 equiv.) at room temperature, and the mixture was kept for 1 h. Then **S9** (8 mmol, 4.0 equiv.) was added dropwise to the mixture at room temperature. After overnight, the resulting mixture was quenched with water (10 mL), and extracted with DCM (15 mL for three times), The organic phase was separated, washed with brine, dried over MgSO₄, and concentrated under reduced pressure. Then the residue was purified by flash chromatography (PE/EA = 10/1) to afford the desired products **L11-L15**.



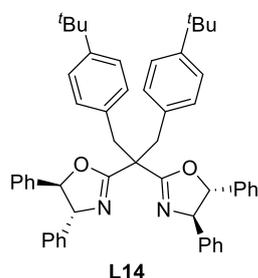
(4*R*,4'*R*,5*R*,5'*R*)-2,2'-(1,3-diphenylpropane-2,2-diyl)bis(4,5-diphenyl-4,5-dihydrooxazole) (L11); TLC: $R_f = 0.60$ (petroleum ether /ethyl acetate = 10/1, v/v, UV); white solid (mp: 154-155 °C); yield: 80%; $[\alpha]_D^{25} = 28$ ($c = 0.1$, CHCl₃); **¹H NMR (400 MHz, CDCl₃)**: δ 7.55 (dd, $J = 6.4, 3.2$ Hz, 4H), 7.41-7.31 (m, 8H), 7.31-7.17 (m, 14H), 6.81-6.74 (m, 4H), 5.14 (d, $J = 10.0$ Hz, 2H), 5.05 (d, $J = 10.0$ Hz, 2H), 3.77 (d, $J = 14.0$ Hz, 2H), 3.65 (d, $J = 14.0$ Hz, 2H); **¹³C {¹H} NMR (101 MHz, CDCl₃)**: δ 167.2, 141.0, 139.1, 137.1, 131.2, 128.9, 128.70, 128.66, 128.6, 127.6, 127.12, 127.10, 126.8, 90.3, 78.3, 49.1, 39.5; **HRMS (ESI, m/z)**: calcd for C₄₅H₃₉N₂O₂⁺ [M+H]⁺: 639.3006, found: 639.3008.



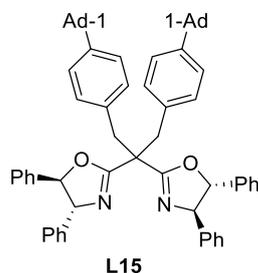
(4*R*,4'*R*,5*R*,5'*R*)-2,2'-(1,3-bis(4-fluorophenyl)propane-2,2-diyl)bis(4,5-diphenyl-4,5-dihydrooxazole) (L12); TLC: $R_f = 0.50$ (petroleum ether /ethyl acetate = 10/1, v/v, UV); white solid (mp: 61-62 °C); yield: 83%; $[\alpha]_D^{25} = 28$ ($c = 0.1$, CHCl₃); **¹H NMR (400 MHz, CDCl₃)**: δ 7.46 (dd, $J = 8.4, 5.6$ Hz, 4H), 7.39-7.32 (m, 2H), 7.30-7.17 (m, 14H), 7.02 (t, $J = 8.8$ Hz, 4H), 6.89-6.82 (m, 4H), 5.14 (d, $J = 10.0$ Hz, 2H), 5.07 (d, $J = 10.0$ Hz, 2H), 3.72 (d, $J = 14.0$ Hz, 2H), 3.56 (d, $J = 14.0$ Hz, 2H); **¹³C {¹H} NMR (101 MHz, CDCl₃)**: δ 166.9, 162.4 (d, $J = 252.5$ Hz), 141.0, 139.0, 132.6 (d, $J = 8.1$ Hz), 132.59, 129.0, 128.7, 128.7, 127.8, 126.9, 126.7, 115.4 (d, $J = 20.2$ Hz), 90.3, 78.2, 49.1, 39.4; **¹⁹F NMR (376 MHz, CDCl₃)** δ -115.9; **HRMS (ESI, m/z)**: calcd for C₄₅H₃₇F₂N₂O₂⁺ [M+H]⁺: 675.2818, found: 675.2817.



(4*R*,4'*R*,5*R*,5'*R*)-2,2'-(1,3-bis(4-(trifluoromethyl)phenyl)propane-2,2-diyl)bis(4,5-diphenyl-4,5-dihydrooxazole) (L13); TLC: $R_f = 0.50$ (petroleum ether /ethyl acetate = 10/1, v/v, UV); white solid (mp: 61-62 °C); yield: 82%; $[\alpha]_D^{25} = 32$ ($c = 0.1$, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.66-7.56 (m, 8H), 7.39-7.33 (m, 2H), 7.32-7.17 (m, 14H), 6.85 (dd, $J = 8.0, 2.0$ Hz, 4H), 5.16 (d, $J = 10.0$ Hz, 2H), 5.09 (d, $J = 10.0$ Hz, 2H), 3.82 (d, $J = 14.0$ Hz, 2H), 3.63 (d, $J = 14.0$ Hz, 2H); ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 166.5, 141.0, 140.8, 138.8, 131.5, 129.5 (q, $J = 32.5$ Hz), 129.0, 128.8, 127.9, 126.8, 126.7, 125.4 (q, $J = 3.8$ Hz), 124.4 (q, $J = 273.0$ Hz), 90.4, 78.1, 48.9, 40.4; ¹⁹F NMR (376 MHz, CDCl₃) δ -62.3; HRMS (ESI, m/z): calcd for C₄₇H₃₇F₆N₂O₂⁺ [M+H]⁺: 775.2754, found: 775.2756.



(4*R*,4'*R*,5*R*,5'*R*)-2,2'-(1,3-bis(4-(tert-butyl)phenyl)propane-2,2-diyl)bis(4,5-diphenyl-4,5-dihydrooxazole) (L14); TLC: $R_f = 0.50$ (petroleum ether /ethyl acetate = 10/1, v/v, UV); white solid (mp: 88-89 °C); yield: 88%; $[\alpha]_D^{25} = 18$ ($c = 0.1$, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.49-7.43 (m, 4H), 7.43-7.29 (m, 6H), 7.34-7.22 (m, 14H), 6.96-6.89 (m, 4H), 5.18 (d, $J = 10.4$ Hz, 2H), 5.08 (d, $J = 10.4$ Hz, 2H), 3.75 (d, $J = 14.4$ Hz, 2H), 3.53 (d, $J = 14.4$ Hz, 2H), 1.39 (s, 18H); ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 167.5, 149.8, 141.0, 139.0, 133.9, 130.9, 128.9, 128.7, 128.6, 127.7, 127.3, 126.9, 125.4, 90.2, 78.4, 49.2, 38.7, 34.7, 31.7; HRMS (ESI, m/z): calcd for C₅₃H₅₅N₂O₂⁺ [M+H]⁺: 751.4258, found: 751.4256.



(4*R*,4'*R*,5*R*,5'*R*)-2,2'-(1,3-bis(4-(tert-butyl)phenyl)propane-2,2-diyl)bis(4,5-diphenyl-4,5-dihydrooxazole) (L15); TLC: $R_f = 0.50$ (petroleum ether /ethyl acetate = 10/1, v/v, UV); white solid (mp: 125-126 °C); yield: 85%; $[\alpha]_D^{25} = 16$ ($c = 0.1$, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.51-7.45 (m, 4H), 7.40-7.33 (m, 6H), 7.33-7.24 (m,

14H), 6.97-6.91 (m, 4H), 5.18 (d, $J = 10.4$ Hz, 2H), 5.08 (d, $J = 10.4$ Hz, 2H), 3.75 (d, $J = 14.4$ Hz, 2H), 3.55 (d, $J = 14.4$ Hz, 2H), 2.15 (s, 7H), 1.99 (d, $J = 3.3$ Hz, 13H), 1.86-1.77 (m, 10H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 167.5, 150.1, 141.0, 139.1, 134.1, 130.9, 128.9, 128.7, 128.6, 127.7, 127.3, 126.9, 124.9, 90.2, 78.5, 49.2, 43.5, 38.8, 37.1, 36.2, 29.2; HRMS (ESI, m/z): calcd for $\text{C}_{65}\text{H}_{67}\text{N}_2\text{O}_2^+$ $[\text{M}+\text{H}]^+$: 907.5197, found: 907.5199.

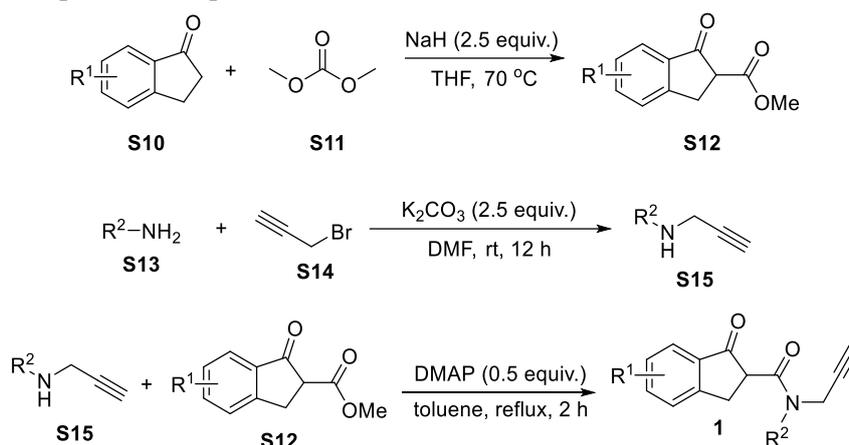
IV. General Procedure for the Synthesis of 1a-1ay

General Procedure for the Synthesis of Substrates 1a-1ay

1a-1e, 1g-1j, 1m-1o, 1s-1t, 1w, 1y, 1ad-1ae, 1aw, 1ay were synthesized according to the literature procedures⁶.

1f, 1k-1l, 1p-1r, 1u-1v, 1x, 1z-1ac, 1af-1av were synthesized by the same method⁶.

The specific operation steps are as follows:



NaH (12.5 mmol, 2.5 equiv. 60% dispersion in mineral oil) was dispersed in dry tetrahydrofuran solution. Dimethyl carbonate (**S11**, 25 mmol, 5 equiv.) was added at 0 °C, then **S10** (5 mmol, 1.0 equiv.) was dropped slowly. The mixture was stirred at 70 °C overnight. After cooling to room temperature, the mixture was quenched with HCl (aq.) and was then extracted with EtOAc (three times). The combined organic layer was washed with brine, dried over MgSO_4 , and concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/ ethyl acetate = 8:1) to give the product **S12** as yellow solid.

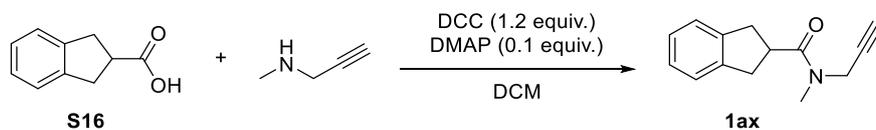
The mixture of **S13** (15 mmol, 3.0 equiv.), K_2CO_3 (17.5 mmol, 2.5 equiv.) and DMF (5 mL) was stirred at the room temperature for 15 min, and then **S14** (5 mmol,

1.0 equiv.) in DMF (5 mL) was slowly added dropwise. The mixture was stirred at room temperature for 12 h. Once the reaction was completed, water (20 mL) was added and the mixture was extracted three times with ethyl acetate (20 mL). The combined organic layer was washed with water (20 mL) and saturated brine (20 mL), dried over anhydrous Na₂SO₄, and concentrated in vacuo. The product **S15** was used directly for the next reaction.

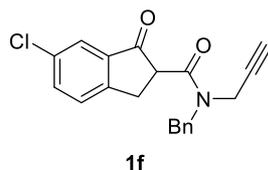
DMAP (0.5 mmol, 0.5 equiv.) and **S12** (1 mmol, 1.0 equiv.) were dissolved in dry toluene (3 mL), then **S15** (1.5 mmol) was added. The mixture was stirring at 110 °C for 2 h. After disappearance of **S12** (monitored by TLC), the mixture was cooled to room temperature and was quenched with HCl (aq.). The residue was extracted three times with ethyl acetate, and was then washed with NaHCO₃ (aq.) and dried over anhydrous MgSO₄, and concentrated in vacuo. Finally, the crude product was purified by flash chromatography on silica gel to get the desired product **1**.

General Procedure for the Synthesis of Substrate **1ax**⁷

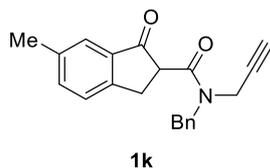
1ax were synthesized according to the literature procedures.



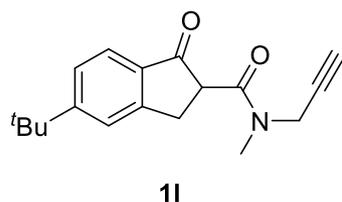
To a solution of N-Methylpropargylamine (2.0 mmol), **S16** (2.2 mmol, 1.1 equiv.) and DMAP (0.2 mmol, 0.1 equiv.) in DCM (15.0 mL), DCC (2.4 mmol, 1.2 equiv.) was added within 5 min at 0 °C under argon atmosphere. The reaction mixture was stirred overnight and the reaction temperature was slowly warmed to room temperature. After filtering through Celite and the filtrate was washed with saturated aqueous NaHCO₃ (10.0 mL) and brine (10.0 mL), dried over anhydrous Na₂SO₄. The solvent was evaporated under vacuum after filtration. Finally, the crude product was purified by flash chromatography on silica gel to get the desired product **1ax**.



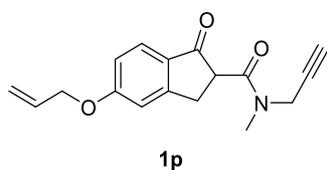
***N*-benzyl-6-chloro-1-oxo-*N*-(prop-2-yn-1-yl)-2,3-dihydro-1*H*-indene-2-carboxamide (1f)**; TLC: $R_f = 0.40$ (petroleum ether /ethyl acetate = 5/1, v/v, UV); yellow oil; yield: 67%; Enol isomerization were observed by NMR; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.66 (dd, $J = 7.2, 2.0$ Hz, 1H), 7.59-7.49 (m, 1H), 7.48-7.21 (m, 6H), 5.23 (dd, $J = 16.4, 7.2$ Hz, 1H), 4.84 (dd, $J = 19.2, 13.2$ Hz, 1H), 4.38-4.23 (m, 1.6H), 4.16 (dd, $J = 17.2, 2.4$ Hz, 0.4H), 4.06 (dd, $J = 8.0, 3.6$ Hz, 0.4H), 3.91 (dd, $J = 18.8, 2.4$ Hz, 0.6H), 3.83 (dd, $J = 17.2, 3.6$ Hz, 0.6H), 3.71 (dd, $J = 17.2, 3.6$ Hz, 0.4H), 3.35-3.05 (m, 1H), 2.35-2.18 (m, 1H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 200.5 (200.0), 167.7 (168.3), 153.0 (152.7), 136.7 (136.8), 136.3 (136.2), 135.5 (135.4), 134.0, 128.8 (129.1), 127.94 (127.96), 127.8 (127.7), 126.9 (127.6), 124.25 (124.23), 78.7 (78.5), 73.0 (72.5), 51.5 (51.4), 49.2 (50.8), 37.0 (35.4), 30.4 (30.6); HRMS (ESI, m/z): calcd for $\text{C}_{20}\text{H}_{17}\text{ClNO}_2^+$ $[\text{M}+\text{H}]^+$: 338.0942, found: 338.0943.



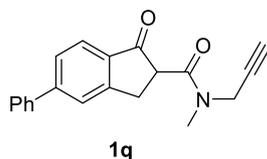
***N*-benzyl-6-methyl-1-oxo-*N*-(prop-2-yn-1-yl)-2,3-dihydro-1*H*-indene-2-carboxamide (1k)**; TLC: $R_f = 0.50$ (petroleum ether /ethyl acetate = 5/1, v/v, UV); yellow oil; yield: 68%; Enol isomerization were observed by NMR; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.52 (d, $J = 5.6$ Hz, 1H), 7.47-7.22 (m, 7H), 5.32-5.21 (m, 1H), 4.94-4.83 (m, 1H), 4.39-4.24 (m, 1.6H), 4.19 (dd, $J = 17.2, 2.4$ Hz, 0.4H), 4.04 (dd, $J = 8.0, 3.6$ Hz, 0.4H), 3.91 (dd, $J = 18.8, 2.4$ Hz, 0.6H), 3.83 (dd, $J = 17.2, 3.6$ Hz, 0.6H), 3.71 (dd, $J = 16.8, 3.6$ Hz, 0.4H), 3.34-3.08 (m, 1H), 2.40 (s, 1.8H), 2.38 (s, 1.2H), 2.33-2.20 (m, 1H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 201.8 (201.4), 168.3 (168.9), 152.3 (152.0), 137.6, 136.8 (136.7), 136.5 (136.4), 135.4 (135.5), 128.8 (129.0), 128.0 (127.9), 126.9 (127.6), 126.3 (126.2), 124.4, 78.9 (78.8), 72.8 (72.4), 51.4 (51.3), 49.1 (50.8), 37.0 (35.3), 30.4 (30.6), 21.15 (21.13); HRMS (ESI, m/z): calcd for $\text{C}_{21}\text{H}_{20}\text{NO}_2^+$ $[\text{M}+\text{H}]^+$: 318.1489, found: 318.1487.



5-(tert-butyl)-*N*-methyl-1-oxo-*N*-(prop-2-yn-1-yl)-2,3-dihydro-1*H*-indene-2-carboxamide (1l); TLC: $R_f = 0.40$ (petroleum ether /ethyl acetate = 5/1, v/v, UV); white solid (mp: 83-84 °C); yield: 79%; Enol isomerization were observed by NMR; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.63 (d, $J = 8.4$ Hz, 1H), 7.50 (d, $J = 4.0$ Hz, 1H), 7.44-7.37 (m, 1H), 5.03 (dd, $J = 18.8, 2.4$ Hz, 0.4H), 4.54 (dd, $J = 17.2, 2.8$ Hz, 0.6H), 4.20-4.06 (m, 1H), 4.08-3.95 (m, 1H), 3.85-3.67 (m, 1H), 3.39 (s, 1.8H), 3.30-3.18 (m, 1H), 3.07 (s, 1.2H), 2.35-2.21 (m, 1H), 1.34 (s, 9H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 201.0 (201.3), 168.3 (167.8), 159.8 (159.9), 155.0 (155.3), 133.0 (132.9), 125.5, 124.1 (124.2), 123.2, 78.7 (78.6), 72.1 (73.0), 51.1 (51.2), 37.2 (40.1), 35.66 (35.68), 35.5 (34.4), 31.3, 30.7 (30.8); HRMS (ESI, m/z): calcd for $\text{C}_{18}\text{H}_{22}\text{NO}_2^+$ $[\text{M}+\text{H}]^+$: 284.1645, found: 284.1646.

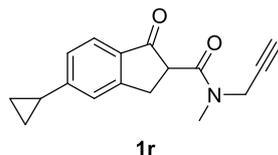


5-(allyloxy)-*N*-methyl-1-oxo-*N*-(prop-2-yn-1-yl)-2,3-dihydro-1*H*-indene-2-carboxamide (1p); TLC: $R_f = 0.50$ (petroleum ether /ethyl acetate = 4/1, v/v, UV); white solid (mp: 63-64 °C); yield: 57%; Enol isomerization were observed by NMR; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.63 (d, $J = 8.4$ Hz, 1H), 6.96-6.86 (m, 2H), 6.11-5.97 (m, 1H), 5.42 (d, $J = 17.2$ Hz, 1H), 5.32 (d, $J = 10.4$ Hz, 1H), 5.05 (dd, $J = 18.8, 2.4$ Hz, 0.4H), 4.61 (d, $J = 5.2$ Hz, 2H), 4.54 (dd, $J = 17.6, 2.4$ Hz, 0.6H), 4.18-4.07 (m, 1H), 4.06-3.94 (m, 1H), 3.83-3.65 (m, 1H), 3.39 (s, 1.8H), 3.25-3.12 (m, 1H), 3.07 (s, 1.2H), 2.38-2.18 (m, 1H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 199.4 (199.7), 168.4 (167.9), 164.9 (165.0), 157.7 (158.0), 132.4, 128.6 (128.7), 126.2 (126.3), 118.5, 116.4 (116.5), 110.49 (110.46), 78.8 (78.7), 72.1 (72.9), 69.3, 51.0 (51.1), 37.2 (40.1), 35.5 (34.4), 30.6 (30.7); HRMS (ESI, m/z): calcd for $\text{C}_{17}\text{H}_{18}\text{NO}_3^+$ $[\text{M}+\text{H}]^+$: 284.1281, found: 284.1282.

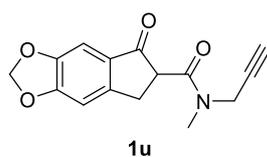


***N*-methyl-1-oxo-5-phenyl-*N*-(prop-2-yn-1-yl)-2,3-dihydro-1*H*-indene-2-carboxamide (1q)**; TLC: $R_f = 0.30$ (petroleum ether /ethyl acetate = 4/1, v/v, UV); white solid (mp: 119-120 °C); yield: 83%; Enol isomerization were observed by NMR; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.77 (d, $J = 8.0$ Hz, 1H), 7.70 (d, $J = 4.4$ Hz, 1H), 7.66-

7.55 (m, 3H), 7.51-7.37 (m, 3H), 5.04 (dd, $J = 18.8, 2.8$ Hz, 0.4H), 4.55 (dd, $J = 17.2, 2.8$ Hz, 0.6H), 4.26-4.13 (m, 1H), 4.11-3.98 (m, 1H), 3.94-3.79 (m, 1H), 3.42 (s, 1.8H), 3.38-3.22 (m, 1H), 3.10 (s, 1.2H), 2.38-2.21 (m, 1H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 200.9 (201.2), 168.2 (167.7), 155.3 (155.6), 148.6 (148.7), 140.2, 134.3 (134.1), 129.1, 128.58 (128.60), 127.7, 127.2, 125.1, 124.89 (124.93), 78.7 (78.6), 72.2 (73.0), 51.2 (51.3), 37.3 (40.1), 35.5 (34.4), 30.7 (30.8); HRMS (ESI, m/z): calcd for $\text{C}_{20}\text{H}_{18}\text{NO}_2^+$ $[\text{M}+\text{H}]^+$: 304.1332, found: 304.1333.

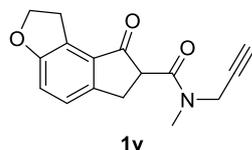


5-cyclopropyl-N-methyl-1-oxo-N-(prop-2-yn-1-yl)-2,3-dihydro-1H-indene-2-carboxamide (1r); TLC: $R_f = 0.50$ (petroleum ether /ethyl acetate = 4/1, v/v, UV); white solid (mp: 65-66 °C); yield: 91%; Enol isomerization were observed by NMR; ^1H NMR (400 MHz, CDCl_3): δ 7.57 (d, $J = 8.0$ Hz, 1H), 7.13 (s, 1H), 7.02 (d, $J = 8.0$ Hz, 1H), 5.01 (dd, $J = 18.8, 2.8$ Hz, 0.4H), 4.53 (dd, $J = 17.2, 2.8$ Hz, 0.6H), 4.18-4.04 (m, 1H), 4.07-3.94 (m, 1H), 3.81-3.63 (m, 1H), 3.38 (s, 1.8H), 3.25-3.12 (m, 1H), 3.06 (s, 1.2H), 2.37-2.18 (m, 1H), 2.01-1.90 (m, 1H), 1.08 (d, $J = 6.4$ Hz, 2H), 0.80 (d, $J = 4.4$ Hz, 2H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 200.6 (200.9), 168.3 (167.8), 155.1 (155.4), 153.4 (153.6), 133.1 (132.9), 125.5, 124.40 (124.43), 123.0, 78.74 (78.66), 72.1 (72.9), 51.0 (51.2), 37.2 (40.1), 35.4 (34.4), 30.46 (30.52), 16.32 (16.34), 10.86 (10.89), 10.8; HRMS (ESI, m/z): calcd for $\text{C}_{17}\text{H}_{18}\text{NO}_2^+$ $[\text{M}+\text{H}]^+$: 268.1332, found: 268.1335.

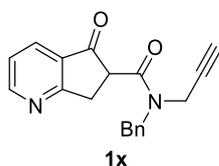


N-methyl-5-oxo-N-(prop-2-yn-1-yl)-6,7-dihydro-5H-indeno[5,6-d][1,3]dioxole-6-carboxamide (1u); TLC: $R_f = 0.50$ (petroleum ether /ethyl acetate = 4/1, v/v, UV); white solid (mp: 80-81 °C); yield: 71%; Enol isomerization were observed by NMR; ^1H NMR (400 MHz, CDCl_3): δ 7.02 (s, 1H), 6.85 (d, $J = 4.0$ Hz, 1H), 6.05 (d, $J = 3.6$ Hz, 2H), 5.01 (dd, $J = 18.8, 2.4$ Hz, 0.4H), 4.51 (dd, $J = 17.2, 2.4$ Hz, 0.6H), 4.18-4.07 (m, 1H), 4.06-3.93 (m, 1H), 3.73-3.57 (m, 1H), 3.37 (s, 1.8H), 3.17-3.07 (m, 1H), 3.05 (s, 1.2H), 2.35-2.16 (m, 1H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 199.1 (199.3), 168.2 (167.7), 154.9 (155.1), 152.6 (152.9), 148.58 (148.57), 129.9 (129.7), 105.73

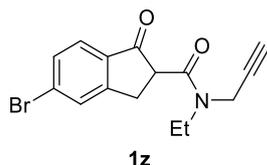
(105.74), 102.8, 102.46 (102.48), 78.7 (78.6), 72.1 (73.0), 51.2 (51.4), 37.2 (40.0), 35.4 (34.4), 30.48 (30.54); **HRMS (ESI, m/z)**: calcd for $C_{15}H_{14}NO_4^+$ $[M+H]^+$: 272.0917, found: 272.0916.



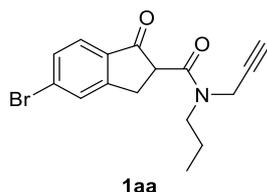
N-methyl-8-oxo-N-(prop-2-yn-1-yl)-1,6,7,8-tetrahydro-2H-indeno[5,4-b]furan-7-carboxamide (1v); TLC: $R_f = 0.40$ (petroleum ether /ethyl acetate = 4/1, v/v, UV); white solid (mp: 96-97 °C); yield: 80%; Enol isomerization were observed by NMR; **1H NMR (400 MHz, $CDCl_3$)**: δ 7.26-7.19 (m, 1H), 7.05-6.98 (m, 1H), 4.96 (dd, $J = 18.8, 2.4$ Hz, 0.4H), 4.63 (t, $J = 8.8$ Hz, 2H), 4.49 (dd, $J = 17.2, 2.4$ Hz, 0.6H), 4.19-3.95 (m, 2H), 3.76-3.61 (m, 1H), 3.46-3.35 (m, 4H), 3.28-3.14 (m, 1H), 3.07 (s, 1H), 2.38-2.18 (m, 1H); **^{13}C { 1H } NMR (101 MHz, $CDCl_3$)**: δ 201.8 (202.1), 168.3 (167.8), 160.7, 146.6 (146.9), 132.0 (131.9), 125.6, 124.7, 116.5 (116.6), 78.7 (78.5), 73.1, 72.4 (72.2), 51.6 (51.7), 37.2 (40.0), 35.4 (34.4), 30.2 (30.3), 28.5; **HRMS (ESI, m/z)**: calcd for $C_{16}H_{16}NO_3^+$ $[M+H]^+$: 270.1125, found: 270.1126.



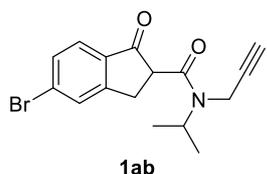
N-benzyl-5-oxo-N-(prop-2-yn-1-yl)-6,7-dihydro-5H-cyclopenta[b]pyridine-6-carboxamide (1x); TLC: $R_f = 0.20$ (petroleum ether /ethyl acetate = 1/1, v/v, UV); yellow oil; yield: 63%; Enol isomerization were observed by NMR; **1H NMR (400 MHz, $CDCl_3$)**: δ 8.88-8.78 (m, 1H), 8.05-7.96 (m, 1H), 7.45-7.23 (m, 6H), 5.31-5.19 (m, 1H), 4.94-4.77 (m, 1H), 4.43-4.26 (m, 1.5H), 4.24-4.08 (m, 1H), 4.07-3.84 (m, 1.5H), 3.54-3.27 (m, 1H), 2.35-2.21 (m, 1H); **^{13}C { 1H } NMR (101 MHz, $CDCl_3$)**: δ 200.3 (199.8), 174.1 (173.9), 167.7 (168.4), 156.6 (156.5), 136.3 (136.1), 132.9 (132.8), 128.9 (129.2), 128.6 (128.8), 128.0 (128.1), 126.9 (127.7), 122.9, 78.6 (78.5), 73.2 (72.6), 50.8 (50.9), 49.4 (50.7), 37.1 (35.5), 33.7 (33.9); **HRMS (ESI, m/z)**: calcd for $C_{19}H_{17}N_2O_2^+$ $[M+H]^+$: 305.1285, found: 305.1282.



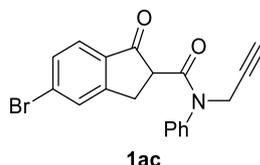
5-bromo-N-ethyl-1-oxo-N-(prop-2-yn-1-yl)-2,3-dihydro-1H-indene-2-carboxamide (1z); TLC: $R_f = 0.30$ (petroleum ether /ethyl acetate = 5/1, v/v, UV); white solid (mp: 95-96 °C); yield: 72%; Enol isomerization were observed by NMR; **^1H NMR (400 MHz, CDCl_3)**: δ 7.70 (d, $J = 4.8$ Hz, 1H), 7.61-7.53 (m, 1H), 7.54-7.47 (m, 1H), 4.96 (dd, $J = 18.8, 2.4$ Hz, 0.5H), 4.37 (dd, $J = 17.2, 2.4$ Hz, 0.5H), 4.23-4.11 (m, 1H), 4.08-3.93 (m, 1.5H), 3.86-3.72 (m, 1H), 3.71-3.57 (m, 1H), 3.55-3.41 (m, 0.5H), 3.32-3.21 (m, 1H), 2.35-2.19 (m, 1H), 1.40-1.15 (m, 3H); **^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3)**: δ 200.8 (200.2), 167.6 (167.0), 156.5 (156.3), 134.3 (134.2), 131.42 (131.39), 131.0 (130.1), 130.0 (129.9), 125.73 (125.71), 79.3 (79.1), 72.7 (71.9), 51.3 (50.6), 42.8 (42.5), 37.7 (34.9), 30.8 (30.5), 14.3 (12.8); **HRMS (ESI, m/z)**: calcd for $\text{C}_{15}\text{H}_{15}\text{BrNO}_2^+ [\text{M}+\text{H}]^+$: 320.0281, found: 320.0282.



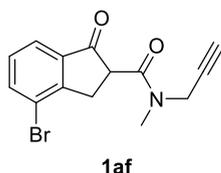
5-bromo-1-oxo-N-(prop-2-yn-1-yl)-N-propyl-2,3-dihydro-1H-indene-2-carboxamide (1aa); TLC: $R_f = 0.40$ (petroleum ether /ethyl acetate = 4/1, v/v, UV); white solid (mp: 83-84 °C); yield: 30%; Enol isomerization were observed by NMR; **^1H NMR (400 MHz, CDCl_3)**: δ 7.69 (d, $J = 3.6$ Hz, 1H), 7.60-7.52 (m, 1H), 7.50 (d, $J = 8.0$ Hz, 1H), 4.96 (dd, $J = 19.2, 2.8$ Hz, 0.5H), 4.32 (dd, $J = 17.6, 2.4$ Hz, 0.5H), 4.26-4.12 (m, 1H), 4.09-3.92 (m, 1H), 3.92-3.68 (m, 2H), 3.64-3.46 (m, 1H), 3.41-3.20 (m, 1H), 2.36-2.18 (m, 1H), 1.94-1.58 (m, 2H), 1.04-0.84 (m, 3H); **^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3)**: δ 200.2 (200.8), 167.3 (167.8), 156.6 (156.3), 134.3 (134.2), 131.40 (131.36), 131.1 (130.9), 130.0 (129.9), 125.71 (125.69), 79.3 (79.1), 72.7 (71.9), 51.3 (50.6), 49.0 (49.9), 38.0 (35.5), 30.8 (30.4), 20.9 (22.2), 11.3 (11.4); **HRMS (ESI, m/z)**: calcd for $\text{C}_{16}\text{H}_{17}\text{BrNO}_2^+ [\text{M}+\text{H}]^+$: 334.0437, found: 334.0438.



5-bromo-*N*-isopropyl-1-oxo-*N*-(prop-2-yn-1-yl)-2,3-dihydro-1*H*-indene-2-carboxamide (1ab); TLC: $R_f = 0.40$ (petroleum ether /ethyl acetate = 4/1, v/v, UV); white solid (mp: 140-141 °C); yield: 47%; Enol isomerization were observed by NMR; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.70 (s, 1H), 7.56 (d, $J = 8.0$ Hz, 1H), 7.50 (d, $J = 8.8$ Hz, 1H), 4.89-4.73 (m, 1.3H), 4.69-4.58 (m, 0.3H), 4.28 (dd, $J = 7.6, 3.2$ Hz, 0.7H), 4.21-4.07 (m, 0.7H), 4.03-3.74 (m, 2H), 3.33-3.19 (m, 1H), 2.32-2.08 (m, 1H), 1.49 (d, $J = 6.8$ Hz, 1H), 1.33 (d, $J = 6.8$ Hz, 1H), 1.27 (d, $J = 6.8$ Hz, 2H), 1.15 (d, $J = 6.8$ Hz, 2H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 201.1 (200.1), 167.6 (166.8), 156.7 (156.3), 134.28 (134.25), 131.3 (131.4), 131.01 (130.95), 130.0 (129.9), 125.69 (125.66), 80.89 (80.94), 72.1 (70.3), 51.8 (50.9), 46.2 (49.6), 31.9 (30.7), 30.6 (30.3), 21.5 (21.3), 20.21 (20.17); HRMS (ESI, m/z): calcd for $\text{C}_{16}\text{H}_{17}\text{BrNO}_2^+$ $[\text{M}+\text{H}]^+$: 334.0437, found: 334.0439.

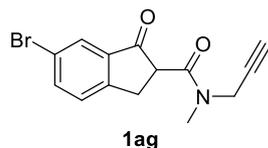


5-bromo-1-oxo-*N*-phenyl-*N*-(prop-2-yn-1-yl)-2,3-dihydro-1*H*-indene-2-carboxamide (1ac); TLC: $R_f = 0.30$ (petroleum ether /ethyl acetate = 10/1, v/v, UV); white solid (mp: 116-117 °C); yield: 46%; Enol isomerization were observed by NMR; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.61 (s, 1H), 7.58-7.49 (m, 3H), 7.49-7.43 (m, 3H), 7.43-7.35 (m, 1H), 4.73 (dd, $J = 17.2, 2.4$ Hz, 1H), 4.37 (dd, $J = 17.2, 2.4$ Hz, 1H), 3.69 (dd, $J = 8.0, 4.4$ Hz, 1H), 3.56 (dd, $J = 17.2, 4.4$ Hz, 1H), 3.11 (dd, $J = 17.2, 8.4$ Hz, 1H), 2.24 (t, $J = 2.4$ Hz, 1H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 200.2, 168.8, 155.8, 141.3, 134.5, 131.3, 130.6, 129.9, 129.7, 129.5, 129.0, 125.6, 78.8, 72.6, 51.0, 39.1, 31.2; HRMS (ESI, m/z): calcd for $\text{C}_{19}\text{H}_{15}\text{BrNO}_2^+$ $[\text{M}+\text{H}]^+$: 368.0281, found: 368.0283.

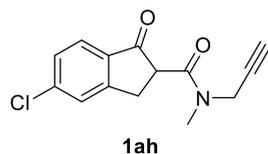


4-bromo-*N*-methyl-1-oxo-*N*-(prop-2-yn-1-yl)-2,3-dihydro-1*H*-indene-2-carboxamide (1af); TLC: $R_f = 0.30$ (petroleum ether /ethyl acetate = 4/1, v/v, UV); white solid (mp: 96-97 °C); yield: 54%; Enol isomerization were observed by NMR;

¹H NMR (400 MHz, CDCl₃): δ 7.81-7.74 (m, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.31-7.23 (m, 1H), 4.94 (dd, *J* = 18.8, 2.4 Hz, 0.4H), 4.51 (dd, *J* = 17.2, 2.4 Hz, 0.6H), 4.23-4.11 (m, 1H), 4.10-3.98 (m, 1H), 3.81-3.65 (m, 1H), 3.39 (s, 1.8H), 3.34-3.16 (m, 1H), 3.08 (s, 1.2H), 2.38-2.21 (m, 1H); **¹³C {¹H} NMR (101 MHz, CDCl₃):** δ 201.0 (200.7), 167.6 (167.2), 154.5 (154.2), 138.3 (138.2), 137.3 (137.1), 129.5, 123.37 (123.35), 122.1, 78.5 (78.4), 73.2 (72.3), 50.9 (50.7), 40.1 (37.3), 35.5 (34.5), 31.9 (31.8); **HRMS (ESI, m/z):** calcd for C₁₄H₁₃BrNO₂⁺ [M+H]⁺: 306.0124, found: 306.0125.

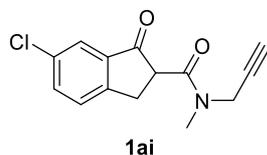


6-bromo-*N*-methyl-1-oxo-*N*-(prop-2-yn-1-yl)-2,3-dihydro-1*H*-indene-2-carboxamide (1ag); TLC: *R_f* = 0.40 (petroleum ether /ethyl acetate = 5/1, v/v, UV); white solid (mp: 76-77 °C); yield: 42%; Enol isomerization were observed by NMR; **¹H NMR (400 MHz, CDCl₃):** δ 7.82 (d, *J* = 2.0 Hz, 1H), 7.74-7.66 (m, 1H), 7.44-7.36 (m, 1H), 4.96 (dd, *J* = 18.8, 2.4 Hz, 0.4H), 4.52 (dd, *J* = 17.2, 2.8 Hz, 0.6H), 4.24-4.11 (m, 1H), 4.08-3.95 (m, 1H), 3.82-3.67 (m, 1H), 3.38 (s, 1.8H), 3.29-3.15 (m, 1H), 3.07 (s, 1.2H), 2.36-2.21 (m, 1H); **¹³C {¹H} NMR (101 MHz, CDCl₃):** δ 200.0 (200.4), 167.5 (167.1), 153.2 (153.5), 138.2 (138.3), 137.2 (137.0), 128.2, 127.38 (127.40), 121.8, 78.5 (78.4), 73.2 (72.3), 51.2 (51.3), 37.3 (40.1), 35.5 (34.5), 30.3 (30.4); **HRMS (ESI, m/z):** calcd for C₁₄H₁₃BrNO₂⁺ [M+H]⁺: 306.0124, found: 306.0125.

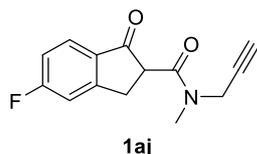


5-chloro-*N*-methyl-1-oxo-*N*-(prop-2-yn-1-yl)-2,3-dihydro-1*H*-indene-2-carboxamide (1ah); TLC: *R_f* = 0.30 (petroleum ether /ethyl acetate = 5/1, v/v, UV); white solid (mp: 74-75 °C); yield: 47%; Enol isomerization were observed by NMR; **¹H NMR (400 MHz, CDCl₃):** δ 7.61 (d, *J* = 8.4 Hz, 1H), 7.48 (s, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 4.95 (dd, *J* = 18.8, 2.4 Hz, 0.4H), 4.49 (dd, *J* = 17.2, 2.4 Hz, 0.6H), 4.21-4.08 (m, 1H), 4.07-3.94 (m, 1H), 3.85-3.66 (m, 1H), 3.37 (s, 1.8H), 3.29-3.16 (m, 1H), 3.05 (s, 1.2H), 2.41-2.19 (m, 1H); **¹³C {¹H} NMR (101 MHz, CDCl₃):** δ 199.9 (200.2), 167.6 (167.2), 156.1 (156.3), 142.0 (142.1), 133.8 (133.6), 128.48 (128.50), 126.8,

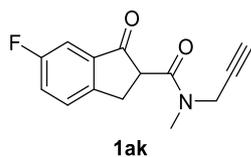
125.5 (125.6), 78.5 (78.4), 72.2 (73.2), 50.8 (51.0), 37.2 (40.0), 35.4 (34.4), 30.3 (30.4);
HRMS (ESI, m/z): calcd for C₁₄H₁₃ClNO₂⁺ [M+H]⁺: 262.0629, found: 262.0630.



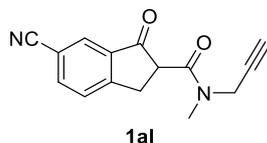
6-chloro-N-methyl-1-oxo-N-(prop-2-yn-1-yl)-2,3-dihydro-1H-indene-2-carboxamide (1ai); TLC: *R_f* = 0.40 (petroleum ether /ethyl acetate = 5/1, v/v, UV); white solid (mp: 98-99 °C); yield: 64%; Enol isomerization were observed by NMR; **¹H NMR (400 MHz, CDCl₃):** δ 7.64 (d, *J* = 2.0 Hz, 1H), 7.58-7.50 (m, 1H), 7.48-7.40 (m, 1H), 4.94 (dd, *J* = 18.8, 2.4 Hz, 0.4H), 4.50 (dd, *J* = 17.6, 2.8 Hz, 0.6H), 4.23-4.10 (m, 1H), 4.08-3.95 (m, 1H), 3.82-3.65 (m, 1H), 3.37 (s, 2H), 3.29-3.16 (m, 1H), 3.06 (s, 1H), 2.39-2.20 (m, 1H); **¹³C {¹H} NMR (101 MHz, CDCl₃):** δ 200.1 (200.5), 167.6 (167.2), 152.7 (153.0), 136.8 (136.6), 135.4 (135.5), 134.0, 127.8, 124.16 (124.19), 78.5 (78.4), 73.2 (72.3), 51.3 (51.4), 37.2 (40.0), 35.4 (34.4), 30.2 (30.3); **HRMS (ESI, m/z):** calcd for C₁₄H₁₃ClNO₂⁺ [M+H]⁺: 262.0629, found: 262.0631.



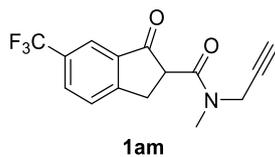
5-fluoro-N-methyl-1-oxo-N-(prop-2-yn-1-yl)-2,3-dihydro-1H-indene-2-carboxamide (1aj); TLC: *R_f* = 0.40 (petroleum ether /ethyl acetate = 5/1, v/v, UV); white solid (mp: 53-54 °C); yield: 77%; Enol isomerization were observed by NMR; **¹H NMR (400 MHz, CDCl₃):** δ 7.73-7.65 (m, 1H), 7.18-7.12 (m, 1H), 7.09-7.00 (m, 1H), 4.97 (dd, *J* = 18.8, 2.8 Hz, 0.4H), 4.49 (dd, *J* = 17.2, 2.8 Hz, 0.6H), 4.22-4.09 (m, 1H), 4.08-3.94 (m, 1H), 3.86-3.70 (m, 1H), 3.38 (s, 1.8H), 3.30-3.16 (m, 1H), 3.06 (s, 1.2H), 2.39-2.19 (m, 1H); **¹³C {¹H} NMR (101 MHz, CDCl₃):** δ 199.4 (199.7), 167.71 (167.30), 167.59 (d, *J* = 258.3 Hz) [167.66 (d, *J* = 258.5 Hz)], 157.6 (d, *J* = 10.5 Hz) [157.9 (d, *J* = 10.6 Hz)], 131.7 (d, *J* = 1.7 Hz) [131.6 (d, *J* = 1.6 Hz)], 126.79 (d, *J* = 10.7 Hz) [126.84 (d, *J* = 10.8 Hz)], 116.06 (d, *J* = 24.0 Hz) [116.08 (d, *J* = 24.0 Hz)], 113.4 (113.2), 78.5 (78.4), 72.2 (73.1), 51.0 (51.1), 37.2 (40.0), 35.4 (34.4), 30.5 (d, *J* = 2.0 Hz) [30.6 (d, *J* = 2.0 Hz)]; **¹⁹F NMR (376 MHz, CDCl₃):** δ -101.5, -101.7; **HRMS (ESI, m/z):** calcd for C₁₄H₁₃FNO₂⁺ [M+H]⁺: 246.0925, found: 246.0924.



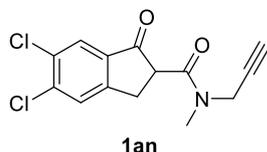
6-fluoro-*N*-methyl-1-oxo-*N*-(prop-2-yn-1-yl)-2,3-dihydro-1*H*-indene-2-carboxamide (1ak); TLC: $R_f = 0.40$ (petroleum ether /ethyl acetate = 4/1, v/v, UV); white solid (mp: 49-50 °C); yield: 76%; Enol isomerization were observed by NMR; **^1H NMR (400 MHz, CDCl_3)**: δ 7.51-7.42 (m, 1H), 7.37-7.27 (m, 2H), 4.94 (dd, $J = 18.8, 2.4$ Hz, 0.4H), 4.50 (dd, $J = 17.2, 2.8$ Hz, 0.6H), 4.25-4.12 (m, 1H), 4.08-3.95 (m, 1H), 3.80-3.67 (m, 1H), 3.37 (s, 1.8H), 3.29-3.16 (m, 1H), 3.06 (s, 1.2H), 2.39-2.21 (m, 1H); **^{13}C { ^1H } NMR (101 MHz, CDCl_3)**: δ 200.5 (d, $J = 3.0$ Hz) [200.8 (d, $J = 3.0$ Hz)], 167.7 (167.2), 162.4 (d, $J = 249.2$ Hz), 150.1 (d, $J = 2.0$ Hz) [150.3 (d, $J = 2.0$ Hz)], 137.0 (d, $J = 8.1$ Hz) [136.8 (d, $J = 8.1$ Hz)], 128.00 (d, $J = 8.2$ Hz) [128.01 (d, $J = 8.1$ Hz)], 123.2 (d, $J = 23.8$ Hz) [123.3 (d, $J = 23.9$ Hz)], 110.17 (d, $J = 22.2$ Hz) [110.19 (d, $J = 22.2$ Hz)], 78.5 (78.4), 72.2 (73.2), 51.6 (51.7), 37.2 (40.0), 35.4 (34.4), 30.0 (30.1); **^{19}F NMR (376 MHz, CDCl_3)**: δ -114.30, -114.31; **HRMS (ESI, m/z)**: calcd for $\text{C}_{14}\text{H}_{13}\text{FNO}_2^+$ [$\text{M}+\text{H}$] $^+$: 246.0925, found: 246.0926.



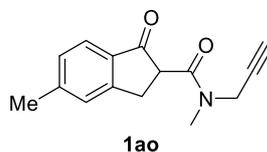
6-cyano-*N*-methyl-1-oxo-*N*-(prop-2-yn-1-yl)-2,3-dihydro-1*H*-indene-2-carboxamide (1al); TLC: $R_f = 0.30$ (petroleum ether /ethyl acetate = 4/1, v/v, UV); white solid (mp: 150-151 °C); yield: 29%; Enol isomerization were observed by NMR; **^1H NMR (400 MHz, CDCl_3)**: δ 7.99 (s, 1H), 7.85 (d, $J = 8.0$ Hz, 1H), 7.70-7.62 (m, 1H), 4.95 (dd, $J = 18.8, 2.4$ Hz, 0.4H), 4.49 (dd, $J = 17.2, 2.4$ Hz, 0.6H), 4.28-4.16 (m, 1H), 4.09-3.97 (m, 1H), 3.96-3.83 (m, 1H), 3.40 (s, 2H), 3.38-3.27 (m, 1H), 3.08 (s, 1H), 2.38-2.22 (m, 1H); **^{13}C { ^1H } NMR (101 MHz, CDCl_3)**: δ 199.4 (199.8), 167.0 (166.6), 158.7 (158.9), 137.85 (137.94), 136.0 (135.9), 128.76 (128.79), 127.9, 118.0, 112.1, 78.3 (78.2), 72.4 (73.4), 50.9 (51.1), 37.4 (40.1), 35.5 (34.6), 31.1 (31.2); **HRMS (ESI, m/z)**: calcd for $\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_2^+$ [$\text{M}+\text{H}$] $^+$: 253.0972, found: 253.0973.



***N*-methyl-1-oxo-*N*-(prop-2-yn-1-yl)-6-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxamide (1am)**; TLC: $R_f = 0.40$ (petroleum ether /ethyl acetate = 4/1, v/v, UV); white solid (mp: 53-53 °C); yield: 42%; Enol isomerization were observed by NMR; **^1H NMR (400 MHz, CDCl_3)**: δ 7.97 (s, 1H), 7.88-7.81 (m, 1H), 7.69-7.61 (m, 1H), 4.97 (dd, $J = 18.8, 2.4$ Hz, 0.4H), 4.51 (dd, $J = 17.2, 2.8$ Hz, 0.6H), 4.28-4.15 (m, 1H), 4.10-3.97 (m, 1H), 3.96-3.81 (m, 1H), 3.40 (s, 1.8H), 3.38-3.27 (m, 1H), 3.08 (s, 1.2H), 2.38-2.22 (m, 1H); **^{13}C { ^1H } NMR (101 MHz, CDCl_3)**: δ 200.2 (200.5), 167.3 (167.0), 157.9 (158.1), 135.8 (135.6), 131.9 (q, $J = 3.0\text{Hz}$) [131.80 (q, $J = 3.5\text{Hz}$)], 130.6 (q, $J = 33.3\text{Hz}$), 127.4, 123.8 (q, $J = 273.7\text{Hz}$), 121.8 (q, $J = 4.0\text{Hz}$), 78.4 (78.3), 73.3 (72.3), 51.1 (51.3), 37.3 (40.1), 35.5 (34.5), 30.8 (30.9); **^{19}F NMR (376 MHz, CDCl_3)**: δ -62.5; **HRMS (ESI, m/z)**: calcd for $\text{C}_{15}\text{H}_{13}\text{F}_3\text{NO}_2^+$ [$\text{M}+\text{H}$] $^+$: 296.0893, found: 296.0894.

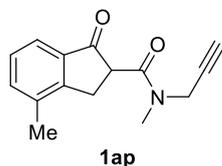


5,6-dichloro-*N*-methyl-1-oxo-*N*-(prop-2-yn-1-yl)-2,3-dihydro-1*H*-indene-2-carboxamide (1an); TLC: $R_f = 0.30$ (petroleum ether /ethyl acetate = 5/1, v/v, UV); white solid (mp: 107-108 °C); yield: 52%; Enol isomerization were observed by NMR; **^1H NMR (400 MHz, CDCl_3)**: δ 7.75 (s, 1H), 7.63 (d, $J = 4.4$ Hz, 1H), 4.93 (dd, $J = 18.8, 2.4$ Hz, 0.4H), 4.49 (dd, $J = 17.2, 2.8$ Hz, 0.6H), 4.26-4.11 (m, 1H), 4.08-3.94 (m, 1H), 3.83-3.68 (m, 1H), 3.37 (s, 2H), 3.28-3.15 (m, 1H), 3.06 (s, 1H), 2.38-2.21 (m, 1H); **^{13}C { ^1H } NMR (101 MHz, CDCl_3)**: δ 199.0 (199.3), 167.2 (166.9), 153.3 (153.6), 140.0 (140.2), 134.9 (134.8), 132.8, 128.5, 125.80 (125.83), 78.4 (78.3), 72.3 (73.3), 51.2 (51.3), 37.3 (40.0), 35.4 (34.5), 30.0 (30.1); **HRMS (ESI, m/z)**: calcd for $\text{C}_{14}\text{H}_{12}\text{Cl}_2\text{NO}_2^+$ [$\text{M}+\text{H}$] $^+$: 296.0240, found: 296.0241.



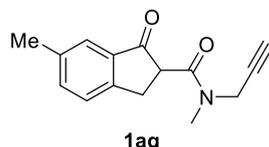
***N*,5-dimethyl-1-oxo-*N*-(prop-2-yn-1-yl)-2,3-dihydro-1*H*-indene-2-carboxamide (1ao)**; TLC: $R_f = 0.40$ (petroleum ether /ethyl acetate = 4/1, v/v, UV); white solid (mp: 97-98 °C); yield: 42%; Enol isomerization were observed by NMR; **^1H NMR (400 MHz, CDCl_3)**: δ 7.59 (d, $J = 8.0$ Hz, 1H), 7.30 (d, $J = 4.8$ Hz, 1H), 7.16 (d, $J = 8.0$ Hz, 1H), 5.01 (dd, $J = 18.8, 2.4$ Hz, 0.4H), 4.53 (dd, $J = 17.2, 2.4$ Hz, 0.6H), 4.19-4.06 (m, 1H), 4.06-3.95 (m, 1H), 3.82-3.66 (m, 1H), 3.38 (s, 1.8H), 3.28-3.14 (m, 1H), 3.07 (s,

1.2H), 2.43 (s, 3H), 2.36-2.20 (m, 1H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 200.9 (201.2), 168.2 (167.8), 155.2 (155.4), 146.8 (146.9), 133.1 (132.9), 129.0, 127.0, 124.3 (124.4), 78.7 (78.6), 72.1 (73.0), 51.0 (51.1), 37.2 (40.0), 35.5 (34.4), 30.4 (30.5), 22.2 (22.3); HRMS (ESI, m/z): calcd for $\text{C}_{15}\text{H}_{16}\text{NO}_2^+$ $[\text{M}+\text{H}]^+$: 242.1176, found: 242.1178.



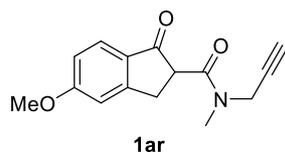
***N*,4-dimethyl-1-oxo-*N*-(prop-2-yn-1-yl)-2,3-dihydro-1*H*-indene-2-carboxamide**

(1ap); TLC: R_f = 0.30 (petroleum ether /ethyl acetate = 4/1, v/v, UV); white solid (mp: 128-129 °C); yield: 74%; Enol isomerization were observed by NMR; ^1H NMR (400 MHz, CDCl_3): δ 7.55 (d, J = 8.0 Hz, 1H), 7.44-7.38 (m, 1H), 7.29 (d, J = 7.6 Hz, 1H), 5.02 (dd, J = 18.8, 2.4 Hz, 0.4H), 4.55 (dd, J = 17.2, 2.4 Hz, 0.6H), 4.18 (dd, J = 7.6, 3.6 Hz, 0.4H), 4.12 (dd, J = 7.6, 3.6 Hz, 0.6H), 4.08-3.97 (m, 1H), 3.76-3.61 (m, 1H), 3.41 (s, 1.8H), 3.23-3.10 (m, 1H), 3.09 (s, 1.2H), 2.38 (d, J = 3.2 Hz, 3H), 2.36-2.22 (m, 1H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 201.9 (202.2), 168.3 (167.8), 153.7 (153.9), 136.02 (135.96), 135.92 (135.93), 135.2 (135.0), 127.9, 121.9 (122.0), 78.7 (78.6), 72.2 (73.0), 50.8 (50.9), 37.3 (40.1), 35.6 (34.5), 29.5 (29.6), 17.9; HRMS (ESI, m/z): calcd for $\text{C}_{15}\text{H}_{16}\text{NO}_2^+$ $[\text{M}+\text{H}]^+$: 242.1176, found: 242.1178.

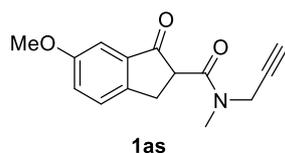


***N*,6-dimethyl-1-oxo-*N*-(prop-2-yn-1-yl)-2,3-dihydro-1*H*-indene-2-carboxamide**

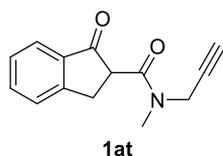
(1aq); TLC: R_f = 0.30 (petroleum ether /ethyl acetate = 5/1, v/v, UV); white solid (mp: 86-87 °C); yield: 59%; Enol isomerization were observed by NMR; ^1H NMR (400 MHz, CDCl_3): δ 7.48 (s, 1H), 7.45-7.35 (m, 2H), 4.98 (dd, J = 18.4, 2.4 Hz, 0.4H), 4.52 (dd, J = 17.2, 2.4 Hz, 0.6H), 4.18-4.07 (m, 1H), 4.06-3.96 (m, 1H), 3.80-3.64 (m, 1H), 3.38 (s, 1.8H), 3.27-3.15 (m, 1H), 3.06 (s, 1.2H), 2.37 (s, 3H), 2.35-2.21 (m, 1H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 201.5 (201.8), 168.2 (167.8), 152.0 (152.3), 137.6, 136.7 (136.8), 135.5 (135.3), 126.3, 124.32 (124.34), 78.7 (78.6), 72.1 (73.0), 51.1 (51.3), 37.2 (40.0), 35.4 (34.4), 30.2 (30.3), 21.1; HRMS (ESI, m/z): calcd for $\text{C}_{15}\text{H}_{16}\text{NO}_2^+$ $[\text{M}+\text{H}]^+$: 242.1176, found: 242.1179.



5-methoxy-*N*-methyl-1-oxo-*N*-(prop-2-yn-1-yl)-2,3-dihydro-1*H*-indene-2-carboxamide (1ar); TLC: $R_f = 0.20$ (petroleum ether /ethyl acetate = 5/1, v/v, UV); white solid (mp: 99-100 °C); yield: 71%; Enol isomerization were observed by NMR; **^1H NMR (400 MHz, CDCl_3):** δ 7.63 (d, $J = 8.4$ Hz, 1H), 6.94-6.84 (m, 2H), 5.06 (dd, $J = 18.8, 2.8$ Hz, 0.4H), 4.55 (dd, $J = 17.2, 2.4$ Hz, 0.6H), 4.20-4.08 (m, 1H), 4.07-3.94 (m, 1H), 3.88 (s, 3H), 3.83-3.68 (m, 1H), 3.40 (s, 1.8H), 3.26-3.13 (m, 1H), 3.07 (s, 1.2H), 2.35-2.20 (m, 1H); **^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3):** δ 199.5 (199.7), 168.3 (167.9), 165.9 (166.0), 157.8 (158.1), 128.6 (128.4), 126.19 (126.23), 116.0 (116.1), 109.53 (109.50), 78.72 (78.67), 72.1 (72.9), 55.8, 51.0 (51.1), 37.2 (40.0), 35.5 (34.1), 30.6 (30.7); **HRMS (ESI, m/z):** calcd for $\text{C}_{15}\text{H}_{16}\text{NO}_3^+$ $[\text{M}+\text{H}]^+$: 258.1125, found: 258.1128.

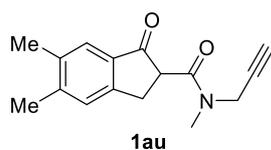


6-methoxy-*N*-methyl-1-oxo-*N*-(prop-2-yn-1-yl)-2,3-dihydro-1*H*-indene-2-carboxamide (1as); TLC: $R_f = 0.40$ (petroleum ether /ethyl acetate = 4/1, v/v, UV); white solid (mp: 107-108 °C); yield: 41%; Enol isomerization were observed by NMR; **^1H NMR (400 MHz, CDCl_3):** δ 7.42-7.34 (m, 1H), 7.23-7.15 (m, 1H), 7.11 (s, 1H), 4.96 (dd, $J = 18.8, 2.8$ Hz, 0.4H), 4.51 (dd, $J = 17.2, 2.4$ Hz, 0.6H), 4.21-4.09 (m, 1H), 4.08-3.96 (m, 1H), 3.80 (s, 3H), 3.76-3.60 (m, 1H), 3.37 (s, 1.8H), 3.28-3.13 (m, 1H), 3.07 (s, 1.2H), 2.37-2.20 (m, 1H); **^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3):** δ 201.4 (201.7), 168.2 (167.7), 159.6, 147.5 (147.8), 136.5 (136.3), 127.3, 124.9 (125.0), 105.5, 78.6 (78.5), 72.2 (73.0), 55.7, 51.5 (51.7), 37.2 (40.0), 35.4 (34.4), 29.9 (30.0); **HRMS (ESI, m/z):** calcd for $\text{C}_{15}\text{H}_{16}\text{NO}_3^+$ $[\text{M}+\text{H}]^+$: 258.1125, found: 258.1128.

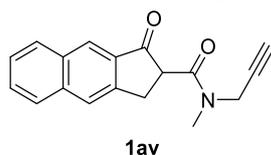


***N*-methyl-1-oxo-*N*-(prop-2-yn-1-yl)-2,3-dihydro-1*H*-indene-2-carboxamide (1at);** TLC: $R_f = 0.30$ (petroleum ether /ethyl acetate = 5/1, v/v, UV); white solid (mp: 82-

83 °C); yield: 51%; Enol isomerization were observed by NMR; **¹H NMR (400 MHz, CDCl₃)**: δ 7.71 (d, *J* = 7.6 Hz, 1H), 7.64-7.56 (m, 1H), 7.55-7.46 (m, 1H), 7.40-7.32 (m, 1H), 5.00 (dd, *J* = 18.8, 2.4 Hz, 0.4H), 4.53 (dd, *J* = 17.2, 2.4 Hz, 0.6H), 4.21-4.09 (m, 1H), 4.08-3.96 (m, 1H), 3.88-3.73 (m, 1H), 3.40 (s, 1.8H), 3.34-3.20 (m, 1H), 3.08 (s, 1.2H), 2.40-2.20 (m, 1H); **¹³C {¹H} NMR (101 MHz, CDCl₃)**: δ 201.5 (201.8), 168.1 (167.7), 154.6 (154.9), 135.4 (135.6), 135.35 (135.19), 127.7, 126.6, 124.51 (124.54), 78.6 (78.5), 72.2 (73.1), 50.8 (51.0), 37.2 (40.1), 35.5 (34.4), 30.6 (30.7); **HRMS (ESI, m/z)**: calcd for C₁₄H₁₄NO₂⁺ [M+H]⁺: 228.1019, found: 228.1021.

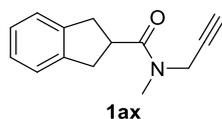


***N*,5,6-trimethyl-1-oxo-*N*-(prop-2-yn-1-yl)-2,3-dihydro-1*H*-indene-2-carboxamide (1au)**; TLC: *R_f* = 0.50 (petroleum ether /ethyl acetate = 5/1, v/v, UV); white solid (mp: 115-116 °C); yield: 69%; Enol isomerization were observed by NMR; **¹H NMR (400 MHz, CDCl₃)**: δ 7.46 (s, 1H), 7.28 (s, 1H), 5.02 (dd, *J* = 18.4, 2.8 Hz, 0.4H), 4.54 (dd, *J* = 17.2, 2.4 Hz, 0.6H), 4.17-3.94 (m, 2H), 3.78-3.62 (m, 1H), 3.38 (s, 1.8H), 3.28-3.11 (m, 1H), 3.07 (s, 1.2H), 2.36-2.30 (m, 3.4H), 2.28 (s, 3H), 2.23 (t, *J* = 2.4 Hz, 0.6H); **¹³C {¹H} NMR (101 MHz, CDCl₃)**: δ 201.1 (201.4), 168.4 (167.9), 152.9 (153.1), 145.8 (146.0), 136.6, 133.6 (133.4), 127.3, 124.75 (124.77), 78.8 (78.7), 72.1 (72.9), 51.1 (51.2), 37.2 (40.1), 35.4 (34.4), 30.19 (30.24), 20.9, 19.9; **HRMS (ESI, m/z)**: calcd for C₁₆H₁₈NO₂⁺ [M+H]⁺: 256.1332, found: 256.1335.



***N*-methyl-1-oxo-*N*-(prop-2-yn-1-yl)-2,3-dihydro-1*H*-cyclopenta[*b*]naphthalene-2-carboxamide (1av)**; TLC: *R_f* = 0.50 (petroleum ether /ethyl acetate = 4/1, v/v, UV); white solid (mp: 145-146 °C); yield: 74%; Enol isomerization were observed by NMR; **¹H NMR (400 MHz, CDCl₃)**: δ 8.28 (s, 1H), 8.00-7.81 (m, 3H), 7.62-7.54 (m, 1H), 7.52-7.44 (m, 1H), 5.02 (dd, *J* = 18.8, 2.4 Hz, 0.4H), 4.55 (dd, *J* = 17.6, 2.8 Hz, 0.6H), 4.31-4.17 (m, 1H), 4.12-4.01 (m, 1H), 4.00-3.90 (m, 1H), 3.52-3.38 (m, 2.7H), 3.17-3.04 (m, 1.3H), 2.38-2.22 (m, 1H); **¹³C {¹H} NMR (101 MHz, CDCl₃)**: δ 201.7 (202.0), 168.2 (167.8), 146.7 (146.9), 137.6 (137.7), 133.2 (133.1), 132.5, 130.5, 129.11 (129.05), 128.0, 126.3, 125.5 (125.6), 124.8, 78.7 (78.6), 72.2 (73.1), 51.6 (51.8), 37.3

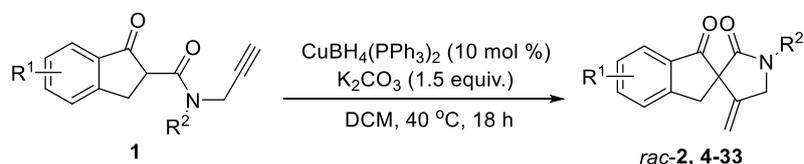
(40.1), 35.5 (34.5), 30.15 (30.21); **HRMS (ESI, m/z)**: calcd for C₁₈H₁₆NO₂⁺ [M+H]⁺: 278.1176, found: 278.1179.



N-methyl-N-(prop-2-yn-1-yl)-2,3-dihydro-1H-indene-2-carboxamide (1ax); **TLC**: R_f = 0.40 (petroleum ether / ethyl acetate = 5/1, v/v, UV); colorless oil; yield: 75%; two rotamers were observed by NMR⁸⁻¹²; **¹H NMR (400 MHz, CDCl₃)**: δ 7.22-7.13 (m, 4H), 4.28 (s, 1.3H), 4.16 (s, 0.7H), 3.65-3.48 (m, 1H), 3.39-3.27 (m, 2H), 3.21-3.10 (m, 4H), 3.05 (s, 1H), 2.40-2.19 (m, 1H); **¹³C {¹H} NMR (101 MHz, CDCl₃)**: δ 174.3 (174.5), 141.68 (141.71), 126.6, 124.3, 79.0 (78.4), 71.9 (72.9), 41.69 (41.73), 39.5, 36.7 (36.9), 36.5, 34.5 (33.7); **HRMS (ESI, m/z)**: calcd for C₁₄H₁₆NO⁺ [M+H]⁺: 214.1226, found: 214.1224.

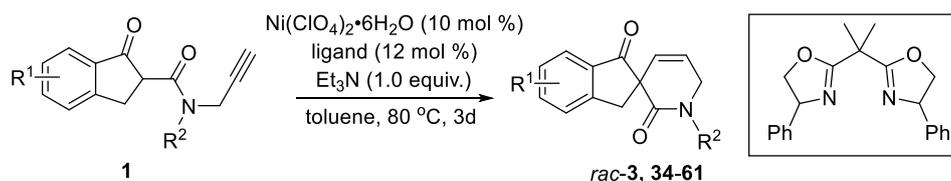
V. General Procedure for the Synthesis of Racemic Products 2 - 61

General Procedure for the Synthesis of Racemic Products 2, 4-33



A mixture of CuBH₄(PPh₃)₂ (0.01 mmol, 10 mol %), substrate **1** (0.10 mmol, 1.0 equiv.), K₂CO₃ (0.15 mmol, 1.5 equiv.) and dry DCM (2 mL) was stirred at 40 °C under a nitrogen atmosphere for 18 h. After complete consumption of substrate **1** (as monitored by TLC), the crude product was purified by flash chromatography on silica gel to afford the desired products *rac-2*, *rac-4* - *rac-33*.

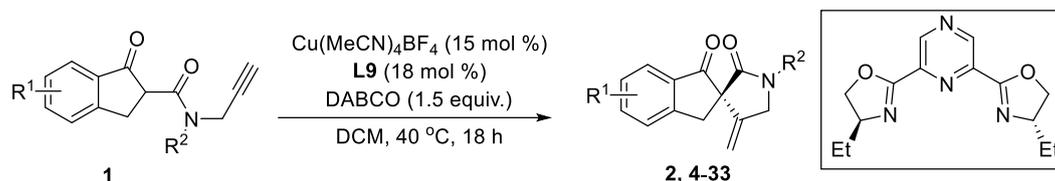
General Procedure for the Synthesis of Racemic Products 3, 34-61



A mixture of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.01 mmol, 10 mol %), ligand (0.012 mmol, 12 mol %) in dry toluene (1 mL) was stirred at 25 °C under a nitrogen atmosphere for 1.5 h. Subsequently, substrate **1** (0.10 mmol, 1.0 equiv.) and Et_3N (0.15 mmol, 1.5 equiv.) and H_2O (5 μL) and additional toluene (1 mL) were added. The reaction mixture was then stirred at 80 °C under a nitrogen atmosphere. After three days, substrate **1** had completely disappeared (as monitored by TLC). Finally, the crude product was purified by flash chromatography on silica gel to afford the desired products *rac*-**3**, *rac*-**34** - *rac*-**61**.

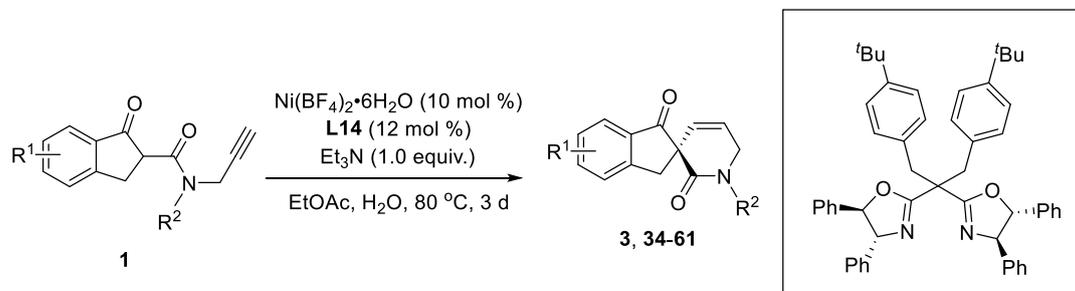
VI. General Procedure for the Synthesis of Chiral Products 2 - 61

General Procedure for the Synthesis of Chiral Products 2, 4-33

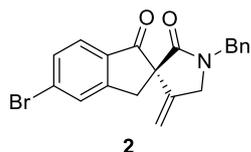


A mixture of $\text{Cu}(\text{MeCN})_4\text{BF}_4$ (0.015 mmol, 15 mol %), ligand (0.018 mmol, 18 mol %) in dry DCM (1 mL) was stirred at 25 °C under a nitrogen atmosphere for 1.5 h. Subsequently, substrate **1** (0.10 mmol, 1.0 equiv.) and DABCO (0.15 mmol, 1.5 equiv.) and additional dry DCM (1 mL) were added. The reaction mixture was then stirred at 40 °C under nitrogen. After 18 h, substrate **1** had completely disappeared (as monitored by TLC). Finally, the crude product was purified by flash chromatography on silica gel to afford the desired products **2**, **4-33**.

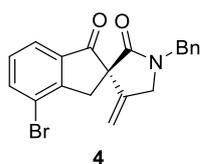
General Procedure for the Synthesis of Chiral Products 3, 34-61



A mixture of Ni(BF₄)₂•6H₂O (0.01 mmol, 10 mol %), ligand (0.012 mmol, 12 mol %) in dry EtOAc (1 mL) was stirred at 25 °C under a nitrogen atmosphere for 1.5 h. Subsequently, substrate **1** (0.10 mmol, 1.0 equiv.) and Et₃N (0.15 mmol, 1.0 equiv.) and H₂O (5 μL) and dry EtOAc (1 mL) were added. The reaction mixture was then stirred at 80 °C under nitrogen. After three days, substrate **1** had completely disappeared (as monitored by TLC). Finally, the crude product was purified by flash chromatography on silica gel to afford the desired products **3**, **34-61**.

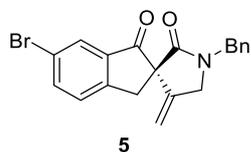


(R)-1'-benzyl-5-bromo-4'-methylenespiro[indene-2,3'-pyrrolidine]-1,2'(3H)-dione (2); TLC: R_f = 0.40 (petroleum ether /ethyl acetate = 5/1, v/v, UV); white solid (mp: 107-108 °C); yield: 92% (35.1 mg, 0.092 mmol); $[\alpha]_D^{25}$ = -35 (c = 0.1, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.74 (s, 1H), 7.64-7.52 (m, 2H), 7.42-7.27 (m, 5H), 5.03 (s, 1H), 4.87 (s, 1H), 4.75 (d, J = 15.2 Hz, 1H), 4.52 (d, J = 14.8 Hz, 1H), 4.24 (dt, J = 13.6, 2.4 Hz, 1H), 3.88-3.79 (m, 2H), 3.17 (d, J = 17.6 Hz, 1H); ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 199.9, 171.4, 155.5, 142.4, 135.6, 132.8, 131.8, 131.2, 129.8, 128.9, 128.2, 127.9, 126.5, 108.3, 64.3, 51.0, 46.9, 36.5; HRMS (ESI, m/z): calcd for C₂₀H₁₇BrNO₂⁺ [M+H]⁺: 382.0437, found: 382.0439; HPLC: Chiralpak AD-H Column, hexane/ⁱPrOH = 80/20, 1.0 mL/min, 254 nm, 25 °C; RT = 16.1 min (major), 25.6 min (minor), ee: 94%.

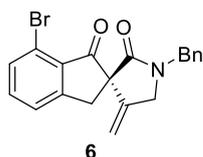


(R)-1'-benzyl-5-bromo-4'-methylenespiro[indene-2,3'-pyrrolidine]-1,2'(3H)-dione (4); TLC: R_f = 0.40 (petroleum ether /ethyl acetate = 5/1, v/v, UV); white solid (mp: 167-168 °C); yield: 90% (34.4 mg, 0.090 mmol); $[\alpha]_D^{25}$ = -13 (c = 0.1, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.81 (d, J = 7.6 Hz, 1H), 7.70 (d, J = 7.6 Hz, 1H), 7.45-7.27 (m, 6H), 5.05 (s, 1H), 4.89 (s, 1H), 4.75 (d, J = 15.2 Hz, 1H), 4.55 (d, J = 14.8 Hz, 1H), 4.26 (dt, J = 13.6, 2.4 Hz, 1H), 3.86 (dt, J = 13.6, 2.0 Hz, 1H), 3.78 (d, J = 18.0 Hz, 1H), 3.15 (d, J = 18.0 Hz, 1H); ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 200.4, 171.3,

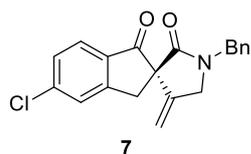
153.7, 142.3, 138.3, 135.9, 135.6, 129.9, 128.9, 128.1, 127.9, 124.2, 121.9, 108.5, 64.2, 51.0, 46.9, 38.0; **HRMS (ESI, m/z)**: calcd for $C_{20}H_{17}BrNO_2^+$ $[M+H]^+$: 382.0437, found: 382.0438; **HPLC**: Chiralpak AD-H Column, hexane/*i*PrOH = 80/20, 1.0 mL/min, 254 nm, 25 °C; RT = 13.5 min (minor), 15.0 min (major), ee: 80%.



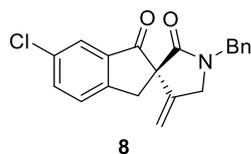
(R)-1'-benzyl-6-bromo-4'-methylenespiro[indene-2,3'-pyrrolidine]-1,2'(3H)-dione (5); **TLC**: R_f = 0.50 (petroleum ether /ethyl acetate = 5/1, v/v, UV); white solid (mp: 71-72 °C); yield: 82% (31.3 mg, 0.082 mmol); $[\alpha]_D^{25}$ = -78 (c = 0.1, $CHCl_3$); **1H NMR (400 MHz, $CDCl_3$)**: δ 7.86 (s, 1H), 7.74 (dd, J = 8.4, 2.0 Hz, 1H), 7.48-7.27 (m, 6H), 5.03 (s, 1H), 4.87 (s, 1H), 4.74 (d, J = 14.8 Hz, 1H), 4.52 (d, J = 14.8 Hz, 1H), 4.24 (dt, J = 13.6, 2.4 Hz, 1H), 3.88-3.73 (m, 2H), 3.13 (d, J = 17.6 Hz, 1H); **^{13}C { 1H } NMR (101 MHz, $CDCl_3$)**: δ 199.7, 171.3, 152.6, 142.4, 138.3, 135.8, 135.6, 128.9, 128.18, 128.17, 127.93, 127.89, 122.2, 108.4, 64.6, 50.9, 46.9, 36.5; **HRMS (ESI, m/z)**: calcd for $C_{20}H_{17}BrNO_2^+$ $[M+H]^+$: 382.0437, found: 382.0439; **HPLC**: Chiralpak AD-H Column, hexane/*i*PrOH = 80/20, 1.0 mL/min, 254 nm, 25 °C; RT = 10.1 min (major), 27.5 min (minor), ee: 89%.



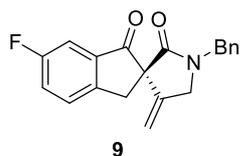
(R)-1'-benzyl-7-bromo-4'-methylenespiro[indene-2,3'-pyrrolidine]-1,2'(3H)-dione (6); **TLC**: R_f = 0.30 (petroleum ether /ethyl acetate = 5/1, v/v, UV); white solid (mp: 156-157 °C); yield: 68% (26.0 mg, 0.068 mmol); $[\alpha]_D^{25}$ = -99 (c = 0.1, $CHCl_3$); **1H NMR (400 MHz, $CDCl_3$)**: δ 7.57 (d, J = 7.6 Hz, 1H), 7.53-7.42 (m, 2H), 7.42-7.28 (m, 5H), 5.03 (s, 1H), 4.87 (s, 1H), 4.75 (d, J = 14.8 Hz, 1H), 4.53 (d, J = 14.8 Hz, 1H), 4.26 (dt, J = 13.6, 2.4 Hz, 1H), 3.86-3.77 (m, 2H), 3.14 (d, J = 17.4 Hz, 1H); **^{13}C { 1H } NMR (101 MHz, $CDCl_3$)**: δ 198.3, 171.4, 156.8, 142.4, 135.9, 135.5, 133.2, 131.3, 128.9, 128.2, 127.8, 125.4, 121.2, 108.4, 64.8, 51.0, 47.0, 35.8; **HRMS (ESI, m/z)**: calcd for $C_{20}H_{17}BrNO_2^+$ $[M+H]^+$: 382.0437, found: 382.0421; **HPLC**: Chiralpak AD-H Column, hexane/*i*PrOH = 80/20, 1.0 mL/min, 254 nm, 25 °C; RT = 10.9 min (major), 21.6 min (minor), ee: 90%.



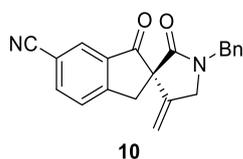
(R)-1'-benzyl-5-chloro-4'-methylenespiro[indene-2,3'-pyrrolidine]-1,2'(3H)-dione (7); TLC: $R_f = 0.50$ (petroleum ether /ethyl acetate = 5/1, v/v, UV); white solid (mp: 100-101 °C); yield: 75% (25.3 mg, 0.075 mmol); $[\alpha]_D^{25} = -61$ ($c = 0.1$, CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.67 (d, $J = 8.0$ Hz, 1H), 7.55 (s, 1H), 7.45-7.28 (m, 6H), 5.03 (s, 1H), 4.87 (s, 1H), 4.75 (d, $J = 14.8$ Hz, 1H), 4.52 (d, $J = 14.8$ Hz, 1H), 4.25 (dt, $J = 13.6, 2.4$ Hz, 1H), 3.88-3.78 (m, 2H), 3.16 (d, $J = 17.6$ Hz, 1H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 199.7, 171.4, 155.4, 142.5, 142.3, 135.6, 132.4, 129.0, 128.9, 128.2, 127.9, 126.7, 126.4, 108.3, 64.3, 51.0, 46.9, 36.5; HRMS (ESI, m/z): calcd for $\text{C}_{20}\text{H}_{17}\text{ClNO}_2^+$ $[\text{M}+\text{H}]^+$: 338.0942, found: 338.0943; HPLC: Chiralpak AD-H Column, hexane/ i PrOH = 80/20, 1.0 mL/min, 254 nm, 25 °C; RT = 13.1 min (major), 22.0 min (minor), ee: 92%.



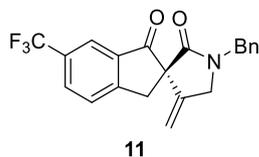
(R)-1'-benzyl-6-chloro-4'-methylenespiro[indene-2,3'-pyrrolidine]-1,2'(3H)-dione (8); TLC: $R_f = 0.50$ (petroleum ether /ethyl acetate = 5/1, v/v, UV); white solid (mp: 69-70 °C); yield: 92% (31.0 mg, 0.092 mmol); $[\alpha]_D^{25} = -97$ ($c = 0.1$, CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.70 (d, $J = 2.0$ Hz, 1H), 7.63-7.57 (m, 1H), 7.50 (d, $J = 8.0$ Hz, 1H), 7.42-7.27 (m, 5H), 5.03 (s, 1H), 4.87 (s, 1H), 4.74 (d, $J = 14.8$ Hz, 1H), 4.53 (d, $J = 14.8$ Hz, 1H), 4.24 (dt, $J = 13.6, 2.4$ Hz, 1H), 3.88-3.76 (m, 2H), 3.15 (d, $J = 17.2$ Hz, 1H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 199.9, 171.4, 152.1, 142.4, 135.59, 135.55, 135.4, 134.5, 128.9, 128.2, 127.9, 127.6, 125.1, 108.4, 64.7, 50.9, 46.9, 36.5; HRMS (ESI, m/z): calcd for $\text{C}_{20}\text{H}_{17}\text{ClNO}_2^+$ $[\text{M}+\text{H}]^+$: 338.0942, found: 338.0944; HPLC: Chiralpak AD-H Column, hexane/ i PrOH = 80/20, 1.0 mL/min, 254 nm, 25 °C; RT = 10.3 min (major), 26.9 min (minor), ee: 90%.



(R)-1'-benzyl-6-fluoro-4'-methylenespiro[indene-2,3'-pyrrolidine]-1,2'(3H)-dione (9); TLC: $R_f = 0.30$ (petroleum ether /ethyl acetate = 5/1, v/v, UV); white solid (mp: 82-83 °C); yield: 92% (29.5 mg, 0.092 mmol); $[\alpha]_D^{25} = -80$ ($c = 0.1$, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.56-7.49 (m, 1H), 7.43-7.27 (m, 7H), 5.03 (s, 1H), 4.88 (s, 1H), 4.76 (d, $J = 14.8$ Hz, 1H), 4.52 (d, $J = 14.8$ Hz, 1H), 4.25 (dt, $J = 14.0, 2.8$ Hz, 1H), 3.88-3.76 (m, 2H), 3.15 (d, $J = 17.2$ Hz, 1H); ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 200.2 (d, $J = 2.9$ Hz), 171.4, 162.8 (d, $J = 249.8$ Hz), 149.5 ($J = 2.1$ Hz), 142.5, 135.7, 135.6, 128.9, 128.2, 127.9, 127.8 ($J = 8.0$ Hz), 123.3 ($J = 23.9$ Hz), 111.1 ($J = 22.2$ Hz), 108.3, 65.0, 51.0, 46.9, 36.4; ¹⁹F NMR (376 MHz, CDCl₃): δ -113.7; HRMS (ESI, m/z): calcd for C₂₀H₁₇FNO₂⁺ [M+H]⁺: 322.1238, found: 322.1239; HPLC: Chiralpak AD-H Column, hexane/ⁱPrOH = 80/20, 1.0 mL/min, 254 nm, 25 °C; RT = 10.5 min (major), 22.1 min (minor), ee: 92%.

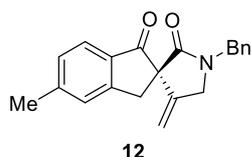


(R)-1'-benzyl-4'-methylene-1,2'-dioxo-1,3-dihydrospiro[indene-2,3'-pyrrolidine]-6-carbonitrile (10); TLC: $R_f = 0.20$ (petroleum ether /ethyl acetate = 3/1, v/v, UV); white solid (mp: 121-122 °C); yield: 71% (23.3 mg, 0.071 mmol); $[\alpha]_D^{25} = -100$ ($c = 0.1$, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 8.02 (s, 1H), 7.89 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.70 (d, $J = 8.0$ Hz, 1H), 7.43-7.28 (m, 5H), 5.07 (s, 1H), 4.87 (s, 1H), 4.74 (d, $J = 14.8$ Hz, 1H), 4.52 (d, $J = 14.8$ Hz, 1H), 4.25 (dt, $J = 14.0, 2.4$ Hz, 1H), 3.97-3.80 (m, 2H), 3.26 (d, $J = 18.4$ Hz, 1H); ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 199.2, 170.8, 157.9, 141.9, 138.0, 135.4, 134.7, 129.5, 129.0, 128.2, 128.0, 127.7, 117.8, 112.6, 108.8, 64.3, 51.0, 47.0, 37.1; HRMS (ESI, m/z): calcd for C₂₁H₁₇N₂O₂⁺ [M+H]⁺: 329.1285, found: 329.1288; HPLC: Chiralpak AD-H Column, hexane/ⁱPrOH = 80/20, 1.0 mL/min, 254 nm, 25 °C; RT = 15.3 min (major), 51.4 min (minor), ee: 80%.

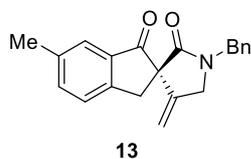


(R)-1'-benzyl-4'-methylene-6-(trifluoromethyl)spiro[indene-2,3'-pyrrolidine]-1,2'(3H)-dione (11); TLC: $R_f = 0.30$ (petroleum ether /ethyl acetate = 3/1, v/v, UV); white solid (mp: 83-84 °C); yield: 93% (34.5 mg, 0.093 mmol); $[\alpha]_D^{25} = -66$ ($c = 0.1$,

CHCl₃); **¹H NMR (400 MHz, CDCl₃):** δ 8.02 (s, 1H), 7.89 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.44-7.28 (m, 5H), 5.06 (s, 1H), 4.88 (s, 1H), 4.75 (d, *J* = 14.8 Hz, 1H), 4.53 (d, *J* = 14.8 Hz, 1H), 4.27 (dt, *J* = 13.6, 2.4 Hz, 1H), 3.99-3.82 (m, 2H), 3.26 (d, *J* = 17.6 Hz, 1H); **¹³C {¹H} NMR (101 MHz, CDCl₃):** δ 200.0, 171.2, 157.2, 142.2, 135.5, 134.4, 132.0 (q, *J* = 3.4 Hz), 131.0 (q, *J* = 33.1 Hz), 129.0, 128.2, 127.9, 127.2, 123.7 (q, *J* = 271.0 Hz), 122.6 (q, *J* = 4.0 Hz), 108.6, 64.5, 51.0, 47.0, 36.9; **¹⁹F NMR (376 MHz, CDCl₃):** δ -62.5; **HRMS (ESI, m/z):** calcd for C₂₁H₁₇F₃NO₂⁺ [M+H]⁺: 372.1206, found: 372.1209; **HPLC:** Chiralpak AD-H Column, hexane/*i*PrOH = 80/20, 1.0 mL/min, 254 nm, 25 °C; RT = 7.6 min (major), 22.7 min (minor), ee: 80%.

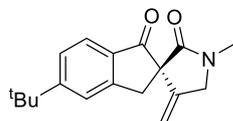


(R)-1'-benzyl-5-methyl-4'-methylenespiro[indene-2,3'-pyrrolidine]-1,2'(3H)-dione (12); TLC: *R_f* = 0.40 (petroleum ether /ethyl acetate = 5/1, v/v, UV); white solid (mp: 56-57 °C); yield: 46% (14.6 mg, 0.046 mmol); [α]_D²⁵ = -68 (*c* = 0.1, CHCl₃); **¹H NMR (400 MHz, CDCl₃):** δ 7.64 (d, *J* = 7.6 Hz, 1H), 7.42-7.28 (m, 6H), 7.22 (d, *J* = 7.6 Hz, 1H), 5.00 (s, 1H), 4.86 (s, 1H), 4.77 (d, *J* = 14.8 Hz, 1H), 4.53 (d, *J* = 14.8 Hz, 1H), 4.25 (dt, *J* = 13.6, 2.4 Hz, 1H), 3.87-3.76 (m, 2H), 3.14 (d, *J* = 17.2 Hz, 1H), 2.46 (s, 3H); **¹³C {¹H} NMR (101 MHz, CDCl₃):** δ 200.6, 172.1, 154.6, 146.9, 143.1, 135.8, 131.6, 129.4, 128.9, 128.2, 127.8, 126.8, 125.3, 107.8, 64.4, 51.0, 46.9, 36.8, 22.3; **HRMS (ESI, m/z):** calcd for C₂₁H₂₀NO₂⁺ [M+H]⁺: 318.1489, found: 318.1488; **HPLC:** Chiralpak AD-H Column, hexane/*i*PrOH = 80/20, 1.0 mL/min, 254 nm, 25 °C; RT = 13.1 min (major), 20.4 min (minor), ee: 94%.



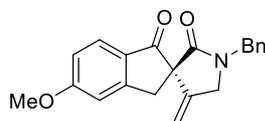
(R)-1'-benzyl-6-methyl-4'-methylenespiro[indene-2,3'-pyrrolidine]-1,2'(3H)-dione (13); TLC: *R_f* = 0.50 (petroleum ether /ethyl acetate = 5/1, v/v, UV); yellow oil; yield: 35% (11.1 mg, 0.035 mmol); [α]_D²⁵ = -55 (*c* = 0.1, CHCl₃); **¹H NMR (400 MHz, CDCl₃):** δ 7.54 (s, 1H), 7.50-7.27 (m, 7H), 5.00 (s, 1H), 4.86 (s, 1H), 4.76 (d, *J* = 14.8 Hz, 1H), 4.53 (d, *J* = 14.8 Hz, 1H), 4.25 (dt, *J* = 13.6, 2.4 Hz, 1H), 3.87-3.75 (m, 2H), 3.14 (d, *J* = 17.2 Hz, 1H), 2.40 (s, 3H); **¹³C {¹H} NMR (101 MHz, CDCl₃):** δ 201.2,

172.0, 151.5, 143.0, 138.1, 136.8, 135.8, 134.1, 128.9, 128.2, 127.8, 126.1, 125.3, 107.9, 64.6, 51.0, 46.9, 36.6, 21.2; **HRMS (ESI, m/z)**: calcd for $C_{21}H_{20}NO_2^+$ $[M+H]^+$: 318.1489, found: 318.1490; **HPLC**: Chiralpak AD-H Column, hexane/ i PrOH = 80/20, 1.0 mL/min, 254 nm, 25 °C; RT = 10.8 min (major), 18.7 min (minor), ee: 92%.



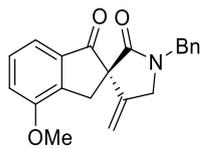
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(R)-5-(tert-butyl)-1'-methyl-4'-methylenespiro[indene-2,3'-pyrrolidine]-1,2'(3H)-dione (14); **TLC**: R_f = 0.50 (petroleum ether /ethyl acetate = 3/1, v/v, UV); white solid (mp: 94-95 °C); yield: 89% (25.2 mg, 0.089 mmol); $[\alpha]_D^{25} = -52$ ($c = 0.1$, $CHCl_3$); **1H NMR (400 MHz, $CDCl_3$)**: δ 7.64 (d, $J = 8.0$ Hz, 1H), 7.51 (s, 1H), 7.43 (d, $J = 8.0$ Hz, 1H), 5.06 (s, 1H), 4.89 (s, 1H), 4.36 (d, $J = 13.2$ Hz, 1H), 3.95 (d, $J = 13.2$ Hz, 1H), 3.74 (d, $J = 17.2$ Hz, 1H), 3.12 (d, $J = 17.2$ Hz, 1H), 3.01 (s, 3H), 1.35 (s, 9H); **^{13}C { 1H } NMR (101 MHz, $CDCl_3$)**: δ 200.9, 172.0, 159.9, 154.4, 143.4, 131.6, 125.9, 125.0, 123.0, 107.7, 64.2, 53.8, 37.2, 35.7, 31.3, 30.0; **HRMS (ESI, m/z)**: calcd for $C_{18}H_{22}NO_2^+$ $[M+H]^+$: 284.1645, found: 284.1646; **HPLC**: Chiralpak AD-H Column, hexane/ i PrOH = 80/20, 1.0 mL/min, 254 nm, 25 °C; RT = 10.4 min (major), 11.7 min (minor), ee: 92%.



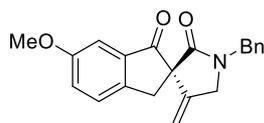
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(R)-1'-benzyl-5-methoxy-4'-methylenespiro[indene-2,3'-pyrrolidine]-1,2'(3H)-dione (15); **TLC**: R_f = 0.40 (petroleum ether /ethyl acetate = 4/1, v/v, UV); colorless oil; yield: 77% (25.6 mg, 0.077 mmol); $[\alpha]_D^{25} = -38$ ($c = 0.1$, $CHCl_3$); **1H NMR (400 MHz, $CDCl_3$)**: δ 7.67 (d, $J = 8.8$ Hz, 1H), 7.43-7.25 (m, 5H), 6.99-6.90 (m, 2H), 5.00 (s, 1H), 4.87 (s, 1H), 4.76 (d, $J = 14.8$ Hz, 1H), 4.52 (d, $J = 14.8$ Hz, 1H), 4.25 (d, $J = 13.6$ Hz, 1H), 3.90 (s, 3H), 3.86-3.74 (m, 2H), 3.13 (d, $J = 17.2$ Hz, 1H); **^{13}C { 1H } NMR (101 MHz, $CDCl_3$)**: δ 199.3, 172.2, 166.0, 157.1, 143.3, 135.8, 128.9, 128.2, 127.8, 127.1, 127.0, 116.3, 109.6, 107.7, 64.5, 55.9, 51.1, 46.9, 36.9; **HRMS (ESI, m/z)**: calcd for $C_{21}H_{20}NO_3^+$ $[M+H]^+$: 334.1438, found: 334.1439; **HPLC**: Chiralpak AD-H Column, hexane/ i PrOH = 80/20, 1.0 mL/min, 254 nm, 25 °C; RT = 15.4 min (major), 22.6 min (minor), ee: 94%.



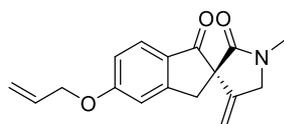
16

(R)-1'-benzyl-4-methoxy-4'-methylenespiro[indene-2,3'-pyrrolidine]-1,2'(3H)-dione (16); TLC: R_f = 0.40 (petroleum ether /ethyl acetate = 5/1, v/v, UV); yellow oil; yield: 69% (23.0 mg, 0.069 mmol); $[\alpha]_D^{25}$ = -39 (c = 0.1, CHCl_3); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.42-7.27 (m, 7H), 7.08 (d, J = 7.6 Hz, 1H), 5.01 (s, 1H), 4.89 (s, 1H), 4.77 (d, J = 14.8 Hz, 1H), 4.52 (d, J = 14.8 Hz, 1H), 4.25 (dt, J = 13.6, 2.8 Hz, 1H), 3.93 (s, 3H), 3.84 (dt, J = 13.6, 1.6 Hz, 1H), 3.73 (d, J = 17.6 Hz, 1H), 3.12 (d, J = 18.0 Hz, 1H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 201.4, 171.9, 156.8, 143.0, 142.8, 135.8, 135.3, 129.7, 128.9, 128.2, 127.8, 116.8, 115.7, 108.0, 64.1, 55.7, 51.0, 46.9, 33.9; HRMS (ESI, m/z): calcd for $\text{C}_{21}\text{H}_{20}\text{NO}_3^+$ $[\text{M}+\text{H}]^+$: 334.1438, found: 334.1439; HPLC: Chiralpak OD-H Column, hexane/ i PrOH = 80/20, 1.0 mL/min, 254 nm, 25 °C; RT = 11.5 min (minor), 15.7 min (major), ee: 88%.



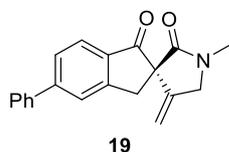
17

(R)-1'-benzyl-6-methoxy-4'-methylenespiro[indene-2,3'-pyrrolidine]-1,2'(3H)-dione (17); TLC: R_f = 0.50 (petroleum ether /ethyl acetate = 5/1, v/v, UV); yellow oil; yield: 51% (17.0 mg, 0.051 mmol); $[\alpha]_D^{25}$ = -105 (c = 0.1, CHCl_3); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.44 (d, J = 8.4 Hz, 1H), 7.41-7.29 (m, 5H), 7.28-7.21 (m, 1H), 7.17 (d, J = 2.4 Hz, 1H), 5.01 (s, 1H), 4.88 (s, 1H), 4.77 (d, J = 15.2 Hz, 1H), 4.52 (d, J = 15.2 Hz, 1H), 4.25 (dt, J = 13.6, 2.8 Hz, 1H), 3.90-3.80 (m, 4H), 3.76 (d, J = 16.8 Hz, 1H), 3.11 (d, J = 16.8 Hz, 1H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 201.2, 171.9, 160.0, 147.1, 142.9, 135.8, 135.1, 128.9, 128.2, 127.8, 127.1, 125.1, 108.0, 106.4, 65.0, 55.8, 51.0, 46.9, 36.4; HRMS (ESI, m/z): calcd for $\text{C}_{21}\text{H}_{20}\text{NO}_3^+$ $[\text{M}+\text{H}]^+$: 334.1438, found: 334.1441; HPLC: Chiralpak AD-H Column, hexane/ i PrOH = 80/20, 1.0 mL/min, 254 nm, 25 °C; RT = 12.4 min (major), 19.5 min (minor), ee: 94%.

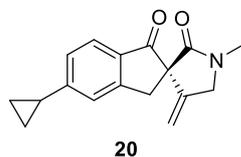


18

(R)-5-(allyloxy)-1'-methyl-4'-methylenespiro[indene-2,3'-pyrrolidine]-1,2'(3H)-dione (18); TLC: R_f = 0.40 (petroleum ether /ethyl acetate = 4/1, v/v, UV); white solid (mp: 70-71 °C); yield: 95% (26.9 mg, 0.095 mmol); $[\alpha]_D^{25}$ = -26 (c = 0.1, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.63 (d, J = 8.4 Hz, 1H), 6.97-6.89 (m, 2H), 6.11-5.97 (m, 1H), 5.42 (d, J = 17.6 Hz, 1H), 5.32 (d, J = 10.4 Hz, 1H), 5.05 (s, 1H), 4.87 (s, 1H), 4.62 (d, J = 5.2 Hz, 2H), 4.35 (d, J = 13.6 Hz, 1H), 3.94 (d, J = 13.6 Hz, 1H), 3.70 (d, J = 13.6 Hz, 1H), 3.07 (d, J = 17.6 Hz, 1H), 3.00 (s, 3H); ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 199.4, 172.0, 165.0, 157.0, 143.5, 132.3, 127.1, 127.0, 118.5, 116.7, 110.5, 107.5, 69.3, 64.2, 53.7, 37.0, 29.9; HRMS (ESI, m/z): calcd for C₁₇H₁₈NO₃⁺ [M+H]⁺: 284.1281, found: 284.1282; HPLC: Chiralpak AD-H Column, hexane/ⁱPrOH = 80/20, 1.0 mL/min, 254 nm, 25 °C; RT = 11.3 min (major), 12.3 min (minor), ee: 92%.

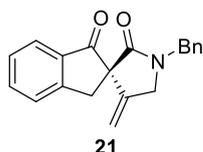


(R)-1'-methyl-4'-methylene-5-phenylspiro[indene-2,3'-pyrrolidine]-1,2'(3H)-dione (19); TLC: R_f = 0.40 (petroleum ether /ethyl acetate = 3/1, v/v, UV); white solid (mp: 156-157 °C); yield: 88% (26.7 mg, 0.088 mmol); $[\alpha]_D^{25}$ = -18 (c = 0.1, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.79 (d, J = 8.0 Hz, 1H), 7.72 (s, 1H), 7.67-7.59 (m, 3H), 7.52-7.44 (m, 2H), 7.46-7.38 (m, 1H), 5.10 (s, 1H), 4.93 (s, 1H), 4.39 (d, J = 13.6 Hz, 1H), 3.98 (d, J = 13.6 Hz, 1H), 3.83 (d, J = 17.2 Hz, 1H), 3.20 (d, J = 17.2 Hz, 1H), 3.04 (s, 3H); ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 200.8, 171.8, 154.8, 148.6, 143.3, 140.1, 132.8, 129.1, 128.6, 127.7, 127.6, 125.7, 124.9, 107.9, 64.4, 53.8, 37.1, 30.0; HRMS (ESI, m/z): calcd for C₂₀H₁₈NO₂⁺ [M+H]⁺: 304.1332, found: 304.1333; HPLC: Chiralpak AD-H Column, hexane/ⁱPrOH = 90/10, 1.0 mL/min, 254 nm, 25 °C; RT = 23.7 min (major), 28.0 min (minor), ee: 84%.

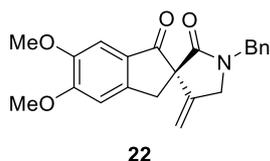


(R)-5-cyclopropyl-1'-methyl-4'-methylenespiro[indene-2,3'-pyrrolidine]-1,2'(3H)-dione (20); TLC: R_f = 0.50 (petroleum ether /ethyl acetate = 4/1, v/v, UV); white solid (mp: 151-152 °C); yield: 97% (25.9 mg, 0.097 mmol); $[\alpha]_D^{25}$ = -70 (c = 0.1, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.58 (d, J = 8.0 Hz, 1H), 7.15 (s, 1H), 7.05 (d, J = 8.0 Hz, 1H), 5.04 (s, 1H), 4.85 (s, 1H), 4.34 (dt, J = 13.6, 2.4 Hz, 1H), 3.94 (dt, J = 13.6,

2.0 Hz, 1H), 3.69 (d, $J = 17.2$ Hz, 1H), 3.06 (d, $J = 17.2$ Hz, 1H), 3.00 (s, 3H), 2.04-1.91 (m, 1H), 1.11-1.05 (m, 2H), 0.85-0.77 (m, 2H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 200.5, 171.9, 154.5, 153.6, 143.4, 131.5, 125.8, 125.2, 122.8, 107.6, 64.2, 53.7, 36.9, 29.9, 16.3, 10.9, 10.8; HRMS (ESI, m/z): calcd for $\text{C}_{17}\text{H}_{18}\text{NO}_2^+$ $[\text{M}+\text{H}]^+$: 268.1332, found: 268.1335; HPLC: Chiralpak AD-H Column, hexane/ i PrOH = 90/10, 1.0 mL/min, 254 nm, 25 °C; RT = 24.0 min (major), 29.6 min (minor), ee: 95%.

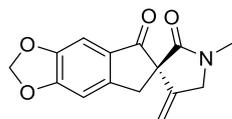


(R)-1'-benzyl-4'-methylenespiro[indene-2,3'-pyrrolidine]-1,2'(3H)-dione (21); TLC: $R_f = 0.20$ (petroleum ether /ethyl acetate = 5/1, v/v, UV); white solid (mp: 98-99 °C); yield: 78% (23.6 mg, 0.078 mmol); $[\alpha]_{\text{D}}^{25} = -93$ ($c = 0.1$, CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.76 (d, $J = 7.6$ Hz, 1H), 7.69-7.61 (m, 1H), 7.56 (d, $J = 7.6$ Hz, 1H), 7.46-7.27 (m, 6H), 5.01 (s, 1H), 4.87 (s, 1H), 4.78 (d, $J = 14.8$ Hz, 1H), 4.53 (d, $J = 14.8$ Hz, 1H), 4.26 (dt, $J = 13.6, 2.4$ Hz, 1H), 3.90-3.79 (m, 2H), 3.20 (d, $J = 17.3$ Hz, 1H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 201.1, 171.9, 154.1, 142.9, 135.8, 135.6, 133.9, 129.0, 128.2, 128.1, 127.9, 126.5, 125.5, 108.0, 64.3, 51.1, 46.9, 37.0; HRMS (ESI, m/z): calcd for $\text{C}_{20}\text{H}_{18}\text{NO}_2^+$ $[\text{M}+\text{H}]^+$: 304.1332, found: 304.1334; HPLC: Chiralpak AD-H Column, hexane/ i PrOH = 80/20, 1.0 mL/min, 254 nm, 25 °C; RT = 11.3 min (major), 16.8 min (minor), ee: 96%.



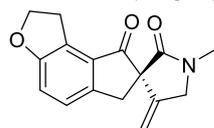
(R)-1'-benzyl-5,6-dimethoxy-4'-methylenespiro[indene-2,3'-pyrrolidine]-1,2'(3H)-dione 22; TLC: $R_f = 0.40$ (petroleum ether /ethyl acetate = 4/1, v/v, UV); white solid (mp: 51-52 °C); yield: 88% (31.9 mg, 0.088 mmol); $[\alpha]_{\text{D}}^{25} = -41$ ($c = 0.1$, CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.40-7.21 (m, 5H), 7.10 (s, 1H), 6.93 (s, 1H), 4.98 (s, 1H), 4.85 (s, 1H), 4.72 (d, $J = 15.2$ Hz, 1H), 4.48 (d, $J = 15.2$ Hz, 1H), 4.22 (d, $J = 13.2$ Hz, 1H), 3.95 (s, 3H), 3.85 (s, 3H), 3.80 (d, $J = 13.7$ Hz, 1H), 3.70 (d, $J = 17.2$ Hz, 1H), 3.05 (d, $J = 17.2$ Hz, 1H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 199.8, 172.2, 156.2, 150.1, 149.7, 143.1, 135.8, 128.9, 128.1, 127.8, 126.4, 107.7, 107.4, 105.5, 64.5, 56.4, 56.2, 51.1, 46.9, 36.8; HRMS (ESI, m/z): calcd for $\text{C}_{22}\text{H}_{22}\text{NO}_4^+$ $[\text{M}+\text{H}]^+$: 364.1543,

found: 364.1545; **HPLC**: Chiralpak AD-H Column, hexane/ⁱPrOH = 80/20, 1.0 mL/min, 254 nm, 25 °C; RT = 18.9 min (major), 31.7 min (minor), ee: 95%.



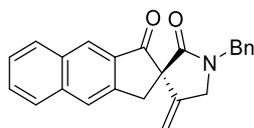
23

(R)-1'-methyl-4'-methylenespiro[indeno[5,6-d][1,3]dioxole-6,3'-pyrrolidine]-2',5(7H)-dione (23); **TLC**: $R_f = 0.30$ (petroleum ether /ethyl acetate = 2/1, v/v, UV); white solid (mp: 167-168 °C); yield: 82% (22.2 mg, 0.082 mmol); $[\alpha]_D^{25} = -58$ ($c = 0.1$, CHCl₃); **¹H NMR (400 MHz, CDCl₃)**: δ 7.03 (s, 1H), 6.88 (s, 1H), 6.06 (s, 2H), 5.06 (s, 1H), 4.88 (s, 1H), 4.34 (d, $J = 13.6$ Hz, 1H), 3.94 (d, $J = 13.6$ Hz, 1H), 3.62 (d, $J = 17.2$ Hz, 1H), 3.05-2.96 (m, 4H); **¹³C {¹H} NMR (101 MHz, CDCl₃)**: δ 199.2, 171.8, 155.1, 152.0, 148.9, 143.3, 128.3, 107.6, 105.6, 103.5, 102.6, 64.5, 53.7, 37.0, 30.0; **HRMS (ESI, m/z)**: calcd for C₁₅H₁₄NO₄⁺ [M+H]⁺: 272.0917, found: 272.0916; **HPLC**: Chiralpak AD-H Column, hexane/ⁱPrOH = 90/10, 1.0 mL/min, 254 nm, 25 °C; RT = 26.2 min (major), 39.8 min (minor), ee: 94%.



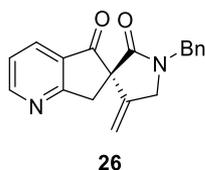
24

(R)-1'-methyl-4'-methylene-1,2-dihydrospiro[indeno[5,4-b]furan-7,3'-pyrrolidine]-2',8(6H)-dione (24); **TLC**: $R_f = 0.50$ (petroleum ether /ethyl acetate = 4/1, v/v, UV); white solid (mp: 152-153 °C); yield: 81% (21.8 mg, 0.081 mmol); $[\alpha]_D^{25} = -87$ ($c = 0.1$, CHCl₃); **¹H NMR (400 MHz, CDCl₃)**: δ 7.27 (d, $J = 8.8$ Hz, 1H), 7.06 (d, $J = 8.0$ Hz, 1H), 5.10 (s, 1H), 4.93 (s, 1H), 4.65 (t, $J = 8.8$ Hz, 2H), 4.36 (d, $J = 13.6$ Hz, 1H), 3.98 (d, $J = 13.6$ Hz, 1H), 3.71 (d, $J = 16.8$ Hz, 1H), 3.52-3.33 (m, 2H), 3.10 (d, $J = 16.8$ Hz, 1H), 3.03 (s, 3H); **¹³C {¹H} NMR (101 MHz, CDCl₃)**: δ 201.6, 171.9, 161.0, 146.0, 143.3, 130.6, 125.5, 125.4, 116.5, 107.8, 72.5, 64.8, 53.7, 36.6, 29.9, 28.5; **HRMS (ESI, m/z)**: calcd for C₁₆H₁₆NO₃⁺ [M+H]⁺: 270.1125, found: 270.1126; **HPLC**: Chiralpak AD-H Column, hexane/ⁱPrOH = 90/10, 1.0 mL/min, 254 nm, 25 °C; RT = 16.4 min (major), 22.3 min (minor), ee: 87%.

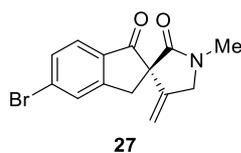


25

(R)-1'-benzyl-4'-methylenespiro[cyclopenta[b]naphthalene-2,3'-pyrrolidine]-1,2'(3H)-dione (25); TLC: $R_f = 0.30$ (petroleum ether /ethyl acetate = 5/1, v/v, UV); white solid (mp: 112-113 °C); yield: 70% (24.7 mg, 0.070 mmol); $[\alpha]_D^{25} = -84$ ($c = 0.1$, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 8.34 (s, 1H), 7.97 (d, $J = 11.6$ Hz, 2H), 7.89 (d, $J = 8.4$ Hz, 1H), 7.66-7.57 (m, 1H), 7.55-7.47 (m, 1H), 7.45-7.36 (m, 4H), 7.35-7.28 (m, 1H), 5.01 (s, 1H), 4.87 (s, 1H), 4.80 (d, $J = 14.8$ Hz, 1H), 4.57 (d, $J = 14.8$ Hz, 1H), 4.28 (dt, $J = 13.6, 2.4$ Hz, 1H), 4.05 (d, $J = 17.2$ Hz, 1H), 3.86 (dt, $J = 13.6, 2.4$ Hz, 1H), 3.37 (d, $J = 17.6$ Hz, 1H); ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 201.3, 172.0, 146.0, 143.2, 137.6, 135.8, 132.8, 131.7, 130.5, 129.3, 128.9, 128.2, 128.0, 127.8, 126.7, 126.4, 124.6, 108.2, 65.0, 51.0, 46.9, 36.4; HRMS (ESI, m/z): calcd for C₂₄H₂₀NO₂⁺ [M+H]⁺: 354.1489, found: 354.1488; HPLC: Chiralpak AD-H Column, hexane/ⁱPrOH = 80/20, 1.0 mL/min, 254 nm, 25 °C; RT = 19.5 min (major), 39.8 min (minor), ee: 90%.

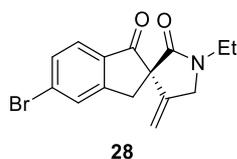


(R)-1'-benzyl-4'-methylenespiro[cyclopenta[b]pyridine-6,3'-pyrrolidine]-2',5(7H)-dione (26); TLC: $R_f = 0.20$ (petroleum ether /ethyl acetate = 1/1, v/v, UV); white solid (mp: 69-70 °C); yield: 91% (27.7 mg, 0.091 mmol); $[\alpha]_D^{25} = -60$ ($c = 0.1$, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 8.86 (s, 1H), 8.01 (dd, $J = 7.6, 1.6$ Hz, 1H), 7.42-7.24 (m, 6H), 5.06 (s, 1H), 4.92 (s, 1H), 4.76 (d, $J = 14.8$ Hz, 1H), 4.52 (d, $J = 15.2$ Hz, 1H), 4.25 (dt, $J = 13.6, 2.4$ Hz, 1H), 3.96 (d, $J = 18.0$ Hz, 1H), 3.86 (dt, $J = 13.6, 1.6$ Hz, 1H), 3.33 (d, $J = 18.0$ Hz, 1H); ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 199.7, 173.4, 171.2, 156.5, 142.2, 135.5, 133.5, 128.9, 128.2, 127.9, 123.3, 108.7, 64.0, 51.1, 46.9, 39.4; HRMS (ESI, m/z): calcd for C₁₉H₁₇N₂O₂⁺ [M+H]⁺: 305.1285, found: 305.1286; HPLC: Chiralpak AD-H Column, hexane/ⁱPrOH = 80/20, 1.0 mL/min, 254 nm, 25 °C; RT = 13.7 min (minor), 16.3 min (major), ee: 84%.

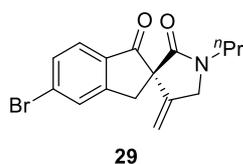


(R)-5-bromo-1'-methyl-4'-methylenespiro[indene-2,3'-pyrrolidine]-1,2'(3H)-

dione (27); TLC: $R_f = 0.50$ (petroleum ether /ethyl acetate = 2/1, v/v, UV); white solid (mp: 164-165 °C); yield: 89% (27.2 mg, 0.089 mmol); $[\alpha]_D^{25} = -43$ ($c = 0.1$, CHCl₃); **¹H NMR (400 MHz, CDCl₃)**: δ 7.72 (s, 1H), 7.62-7.50 (m, 2H), 5.09 (s, 1H), 4.88 (s, 1H), 4.36 (dt, $J = 13.6, 2.4$ Hz, 1H), 3.97 (dt, $J = 13.6, 2.0$ Hz, 1H), 3.76 (d, $J = 17.6$ Hz, 1H), 3.13 (d, $J = 17.6$ Hz, 1H), 3.02 (s, 3H); **¹³C {¹H} NMR (101 MHz, CDCl₃)**: δ 200.1, 171.3, 155.6, 142.7, 132.8, 131.8, 131.1, 129.8, 126.5, 108.2, 64.1, 53.7, 36.6, 30.0; **HRMS (ESI, m/z)**: calcd for C₁₄H₁₃BrNO₂⁺ [M+H]⁺: 306.0124, found: 306.0126; **HPLC**: Chiralpak AD-H Column, hexane/ⁱPrOH = 80/20, 1.0 mL/min, 254 nm, 25 °C; RT = 8.6 min (major), 10.1 min (minor), ee: 94%.

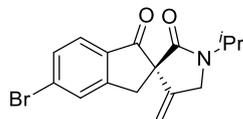


(R)-5-bromo-1'-ethyl-4'-methylenespiro[indene-2,3'-pyrrolidine]-1,2'(3H)-dione (28); TLC: $R_f = 0.40$ (petroleum ether /ethyl acetate = 2/1, v/v, UV); white solid (mp: 96-97 °C); yield: 72% (23.0 mg, 0.072 mmol); $[\alpha]_D^{25} = -35$ ($c = 0.1$, CHCl₃); **¹H NMR (400 MHz, CDCl₃)**: δ 7.72 (s, 1H), 7.61-7.50 (m, 2H), 5.10 (s, 1H), 4.88 (s, 1H), 4.37 (dt, $J = 13.6, 2.8$ Hz, 1H), 3.97 (dt, $J = 13.6, 2.0$ Hz, 1H), 3.76 (d, $J = 17.2$ Hz, 1H), 3.62-3.38 (m, 2H), 3.13 (d, $J = 17.6$ Hz, 1H), 1.22 (t, $J = 7.2$ Hz, 3H); **¹³C {¹H} NMR (101 MHz, CDCl₃)**: δ 200.1, 170.9, 155.6, 142.8, 132.8, 131.8, 131.1, 129.8, 126.5, 108.1, 64.5, 50.9, 37.7, 36.4, 12.6; **HRMS (ESI, m/z)**: calcd for C₁₅H₁₅BrNO₂⁺ [M+H]⁺: 320.0281, found: 320.0284; **HPLC**: Chiralpak AD-H Column, hexane/ⁱPrOH = 90/10, 1.0 mL/min, 254 nm, 25 °C; RT = 12.8 min (major), 17.0 min (minor), ee: 96%.



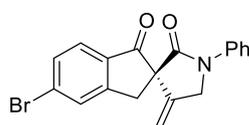
(R)-1'-propyl-4'-methylene-5-bromospiro[indene-2,3'-pyrrolidine]-1,2'(3H)-dione (29); TLC: $R_f = 0.40$ (petroleum ether /ethyl acetate = 5/1, v/v, UV); white solid (mp: 71-72 °C); yield: 94% (31.4 mg, 0.094 mmol); $[\alpha]_D^{25} = -40$ ($c = 0.1$, CHCl₃); **¹H NMR (400 MHz, CDCl₃)**: δ 7.71 (s, 1H), 7.61-7.47 (m, 2H), 5.08 (s, 1H), 4.87 (s, 1H), 4.36 (d, $J = 13.6$ Hz, 1H), 3.93 (d, $J = 13.4$ Hz, 1H), 3.76 (d, $J = 17.6$ Hz, 1H), 3.57-3.46 (m, 1H), 3.33-3.22 (m, 1H), 3.12 (d, $J = 17.6$ Hz, 1H), 1.72-1.56 (m, 2H), 0.96 (t, $J = 7.2$ Hz, 3H); **¹³C {¹H} NMR (101 MHz, CDCl₃)**: δ 200.0, 171.2, 155.6, 142.9, 132.8, 131.7,

131.0, 129.8, 126.4, 107.9, 64.5, 51.4, 44.6, 36.3, 20.6, 11.2; **HRMS (ESI, m/z)**: calcd for $C_{16}H_{17}BrNO_2^+$ $[M+H]^+$: 334.0437, found: 334.0443; **HPLC**: Chiralpak AD-H Column, hexane/*i*PrOH = 90/10, 1.0 mL/min, 254 nm, 25 °C; RT = 12.4 min (major), 18.0 min (minor), ee: 94%.



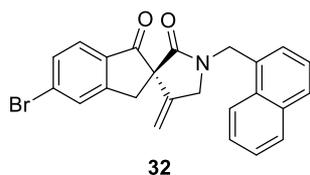
30

(R)-5-bromo-1'-isopropyl-4'-methylenespiro[indene-2,3'-pyrrolidine]-1,2'(3H)-dione (30); **TLC**: R_f = 0.40 (petroleum ether /ethyl acetate = 5/1, v/v, UV); white solid (mp: 91-92 °C); yield: 97% (32.4 mg, 0.097 mmol); $[\alpha]_D^{25} = -42$ ($c = 0.1$, $CHCl_3$); **1H NMR (400 MHz, $CDCl_3$)**: 7.71 (s, 1H), 7.60-7.46 (m, 2H), 5.09 (s, 1H), 4.87 (s, 1H), 4.53-4.38 (m, 1H), 4.28 (d, $J = 13.2$ Hz, 1H), 3.94 (d, $J = 13.2$ Hz, 1H), 3.75 (d, $J = 17.6$ Hz, 1H), 3.11 (d, $J = 17.6$ Hz, 1H), 1.26 (d, $J = 6.8$ Hz, 3H), 1.20 (d, $J = 6.8$ Hz, 3H); **^{13}C { 1H } NMR (101 MHz, $CDCl_3$)**: δ 199.9, 170.5, 155.6, 142.8, 132.8, 131.7, 131.0, 129.8, 126.4, 107.9, 64.8, 46.5, 43.4, 36.0, 20.1, 19.8; **HRMS (ESI, m/z)**: calcd for $C_{16}H_{17}BrNO_2^+$ $[M+H]^+$: 334.0437, found: 334.0442; **HPLC**: Chiralpak AD-H Column, hexane/*i*PrOH = 90/10, 1.0 mL/min, 254 nm, 25 °C; RT = 12.7 min (major), 20.5 min (minor), ee: 95%.

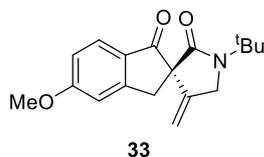


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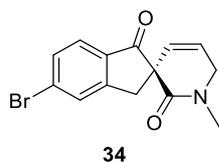
(R)-5-bromo-4'-methylene-1'-phenylspiro[indene-2,3'-pyrrolidine]-1,2'(3H)-dione (31); **TLC**: R_f = 0.50 (petroleum ether /ethyl acetate = 10/1, v/v, UV); white solid (mp: 187-188 °C); yield: 73% (26.9 mg, 0.073 mmol); $[\alpha]_D^{25} = -64$ ($c = 0.1$, $CHCl_3$); **1H NMR (400 MHz, $CDCl_3$)**: δ 7.76 (s, 1H), 7.70 (d, $J = 8.4$ Hz, 2H), 7.64-7.53 (m, 2H), 7.45-7.36 (m, 2H), 7.24-7.16 (m, 1H), 5.21 (s, 1H), 4.97 (s, 1H), 4.86 (dt, $J = 13.2, 2.4$ Hz, 1H), 4.47 (dt, $J = 13.2, 2.0$ Hz, 1H), 3.88 (d, $J = 17.6$ Hz, 1H), 3.25 (d, $J = 17.6$ Hz, 1H); **^{13}C { 1H } NMR (101 MHz, $CDCl_3$)**: δ 199.4, 170.5, 155.4, 141.3, 138.8, 132.5, 131.9, 131.3, 129.8, 129.2, 126.6, 125.4, 120.4, 108.4, 65.8, 53.0, 36.4; **HRMS (ESI, m/z)**: calcd for $C_{19}H_{15}BrNO_2^+$ $[M+H]^+$: 368.0281, found: 368.0282; **HPLC**: Chiralpak AD-H Column, hexane/*i*PrOH = 80/20, 1.0 mL/min, 254 nm, 25 °C; RT = 16.0 min (major), 26.0 min (minor), ee: 94%.



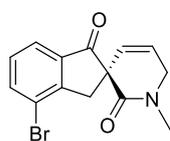
(R)-5-bromo-4'-methylene-1'-(naphthalen-2-ylmethyl)spiro[indene-2,3'-pyrrolidine]-1,2'(3H)-dione (32); TLC: $R_f = 0.30$ (petroleum ether /ethyl acetate = 1/1, v/v, UV); white solid (mp: 168-169 °C); yield: 86% (37.2 mg, 0.086 mmol); $[\alpha]_D^{25} = -16$ ($c = 0.1$, CHCl_3); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.13 (d, $J = 8.4$ Hz, 1H), 7.93-7.82 (m, 2H), 7.74 (s, 1H), 7.64-7.43 (m, 6H), 5.18 (d, $J = 14.8$ Hz, 1H), 5.01 (d, $J = 14.8$ Hz, 1H), 4.96 (s, 1H), 4.82 (s, 1H), 4.18 (d, $J = 13.6$ Hz, 1H), 3.84 (d, $J = 17.6$ Hz, 1H), 3.75 (d, $J = 13.6$ Hz, 1H), 3.14 (d, $J = 17.6$ Hz, 1H); ^{13}C { ^1H } NMR (101 MHz, CDCl_3): δ 199.8, 171.1, 155.5, 142.5, 134.0, 132.9, 131.8, 131.6, 131.13, 131.12, 129.8, 129.0, 128.8, 127.3, 126.9, 126.5, 126.3, 125.4, 123.8, 108.4, 64.4, 51.1, 45.2, 36.7; **HRMS (ESI, m/z):** calcd for $\text{C}_{24}\text{H}_{19}\text{BrNO}_2^+$ $[\text{M}+\text{H}]^+$: 432.0594, found: 432.0596; **HPLC:** Chiralpak AD-H Column, hexane/ i PrOH = 80/20, 1.0 mL/min, 254 nm, 25 °C; RT = 14.5min (major), 15.9 min (minor), ee: 94%.



(R)-1'-(tert-butyl)-5-methoxy-4'-methylenespiro[indene-2,3'-pyrrolidine]-1,2'(3H)-dione (33); TLC: $R_f = 0.40$ (petroleum ether /ethyl acetate = 5/1, v/v, UV); white solid (mp: 96-97 °C); yield: 67% (20.0 mg, 0.067 mmol); $[\alpha]_D^{25} = -34$ ($c = 0.1$, CHCl_3); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.62 (d, $J = 8.4$ Hz, 1H), 6.97-6.87 (m, 2H), 5.02 (s, 1H), 4.84 (s, 1H), 4.43 (dt, $J = 13.2, 2.8$ Hz, 1H), 4.06 (dt, $J = 13.2, 2.0$ Hz, 1H), 3.89 (s, 3H), 3.67 (d, $J = 17.2$ Hz, 1H), 3.06 (d, $J = 17.6$ Hz, 1H), 1.47 (s, 9H); ^{13}C { ^1H } NMR (101 MHz, CDCl_3): δ 199.6, 165.9, 157.2, 143.3, 127.0, 126.9, 116.1, 109.5, 106.7, 66.1, 55.9, 54.8, 50.5, 36.2, 27.9; **HRMS (ESI, m/z):** calcd for $\text{C}_{18}\text{H}_{22}\text{NO}_3^+$ $[\text{M}+\text{H}]^+$: 300.1594, found: 300.1595; **HPLC:** Chiralpak AD-H Column, hexane/ i PrOH = 90/10, 1.0 mL/min, 254 nm, 25 °C; RT = 11.2 min (major), 21.1 min (minor), ee: 91%.

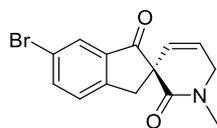


(R)-5-bromo-1'-methyl-1',6'-dihydro-2'H-spiro[indene-2,3'-pyridine]-1,2'(3H)-dione (34); TLC: R_f = 0.30 (petroleum ether /ethyl acetate = 2/1, v/v, UV); white solid (mp: 162-163 °C); yield: 88% (26.9 mg, 0.088 mmol); $[\alpha]_D^{25}$ = 88 (c = 0.1, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.68 (s, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.51 (d, J = 8.4 Hz, 1H), 6.05-5.96 (m, 1H), 5.59-5.51 (m, 1H), 4.32 (dt, J = 18.4, 2.4 Hz, 1H), 3.99-3.89 (m, 2H), 3.04 (s, 3H), 2.99 (d, J = 17.4 Hz, 1H); ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 202.1, 166.7, 156.1, 133.3, 131.5, 131.1, 129.9, 126.8, 126.3, 123.7, 58.9, 51.5, 39.2, 34.9; HRMS (ESI, m/z): calcd for C₁₄H₁₃BrNO₂⁺ [M+H]⁺: 306.0124, found: 306.0125; HPLC: Chiralpak OD-H Column, hexane/ⁱPrOH = 85/15, 1.0 mL/min, 254 nm, 25 °C; RT = 16.6 min (minor), 18.4 min (major), ee: 90%.



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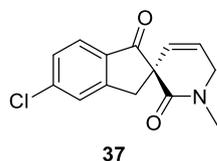
(R)-4-bromo-1'-methyl-1',6'-dihydro-2'H-spiro[indene-2,3'-pyridine]-1,2'(3H)-dione (35); TLC: R_f = 0.50 (petroleum ether /ethyl acetate = 2/1, v/v, UV); white solid (mp: 188-189 °C); yield: 85% (26.0mg, 0.085 mmol); $[\alpha]_D^{25}$ = 60 (c = 0.1, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.78 (d, J = 7.6 Hz, 1H), 7.68 (d, J = 7.2 Hz, 1H), 7.30-7.24 (m, 1H), 6.05-5.98 (m, 1H), 5.56 (d, J = 10.0 Hz, 1H), 4.32 (d, J = 17.2 Hz, 1H), 4.01-3.83 (m, 2H), 3.06 (s, 3H), 2.96 (d, J = 17.6 Hz, 1H); ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 202.7, 166.7, 154.1, 138.3, 136.5, 129.6, 126.7, 124.0, 123.7, 122.0, 58.7, 51.5, 40.7, 34.9; HRMS (ESI, m/z): calcd for C₁₄H₁₃BrNO₂⁺ [M+H]⁺: 306.0124, found: 306.0125; HPLC: Chiralpak OD-H Column, hexane/ⁱPrOH = 90/10, 1.0 mL/min, 254 nm, 25 °C; RT = 22.7 min (minor), 28.8 min (major), ee: 85%.



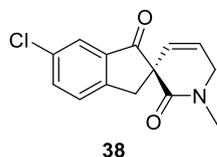
36

(R)-6-bromo-1'-methyl-1',6'-dihydro-2'H-spiro[indene-2,3'-pyridine]-1,2'(3H)-dione (36); TLC: R_f = 0.30 (petroleum ether /ethyl acetate = 2/1, v/v, UV); white solid (mp: 176-177 °C); yield: 75% (23.0 mg, 0.075 mmol); $[\alpha]_D^{25}$ = 140 (c = 0.1, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.84 (s, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.38 (d, J = 8.0 Hz, 1H), 6.04-5.97 (m, 1H), 5.55 (d, J = 9.6 Hz, 1H), 4.31 (d, J = 18.0 Hz, 1H), 4.00-3.85 (m, 2H), 3.04 (s, 3H), 2.95 (d, J = 17.2 Hz, 1H); ¹³C {¹H} NMR (101 MHz,

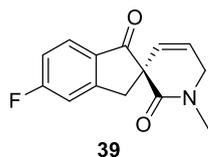
CDCl₃): δ 201.8, 166.7, 153.1, 138.2, 136.3, 128.1, 127.9, 126.7, 123.7, 121.9, 59.2, 51.5, 39.2, 34.9; **HRMS (ESI, m/z)**: calcd for C₁₄H₁₃BrNO₂⁺ [M+H]⁺: 306.0124, found: 306.0126; **HPLC**: Chiralpak AD-H Column, hexane/ⁱPrOH = 90/10, 1.0 mL/min, 254 nm, 25 °C; RT = 12.2 min (major), 30.3 min (minor), ee: 93%.



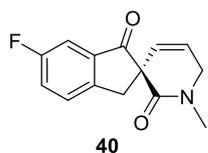
(R)-5-chloro-1'-methyl-1',6'-dihydro-2'H-spiro[indene-2,3'-pyridine]-1,2'(3H)-dione (37); **TLC**: R_f = 0.50 (petroleum ether /ethyl acetate = 2/1, v/v, UV); white solid (mp: 172-173 °C); yield: 84% (21.9 mg, 0.084 mmol); $[\alpha]_D^{25}$ = 107 (c = 0.1, CHCl₃); **¹H NMR (400 MHz, CDCl₃)**: δ 7.65 (d, J = 8.4 Hz, 1H), 7.49 (s, 1H), 7.35 (d, J = 8.0 Hz, 1H), 6.05-5.96 (m, 1H), 5.59-5.52 (m, 1H), 4.31 (dt, J = 18.0, 2.4 Hz, 1H), 3.99-3.88 (m, 2H), 3.04 (s, 3H), 2.98 (d, J = 17.2 Hz, 1H); **¹³C {¹H} NMR (101 MHz, CDCl₃)**: δ 201.8, 166.7, 155.9, 142.2, 132.9, 128.6, 126.8, 126.2, 123.7, 58.9, 51.5, 39.2, 34.9; **HRMS (ESI, m/z)**: calcd for C₁₄H₁₃ClNO₂⁺ [M+H]⁺: 262.0629, found: 262.0630; **HPLC**: Chiralpak OD-H Column, hexane/ⁱPrOH = 90/10, 1.0 mL/min, 254 nm, 25 °C; RT = 21.5 min (minor), 23.1 min (major), ee: 91%.



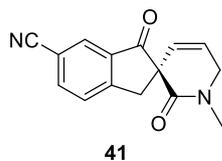
(R)-6-chloro-1'-methyl-1',6'-dihydro-2'H-spiro[indene-2,3'-pyridine]-1,2'(3H)-dione (38); **TLC**: R_f = 0.30 (petroleum ether /ethyl acetate = 2/1, v/v, UV); white solid (mp: 158-159 °C); yield: 59% (15.4 mg, 0.059 mmol); $[\alpha]_D^{25}$ = 133 (c = 0.1, CHCl₃); **¹H NMR (400 MHz, CDCl₃)**: δ 7.69 (s, 1H), 7.57 (d, J = 7.6 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 6.05-5.97 (m, 1H), 5.56 (d, J = 10.0 Hz, 1H), 4.32 (d, J = 18.4 Hz, 1H), 3.93 (d, J = 17.2 Hz, 2H), 3.05 (s, 3H), 2.98 (d, J = 17.2 Hz, 1H); **¹³C {¹H} NMR (101 MHz, CDCl₃)**: δ 202.0, 166.7, 152.6, 136.0, 135.5, 134.2, 127.7, 126.8, 124.8, 123.7, 59.4, 51.5, 39.2, 34.9; **HRMS (ESI, m/z)**: calcd for C₁₄H₁₃ClNO₂⁺ [M+H]⁺: 262.0629, found: 262.0633; **HPLC**: Chiralpak AD-H Column, hexane/ⁱPrOH = 90/10, 1.0 mL/min, 254 nm, 25 °C; RT = 11.9 min (major), 27.8 min (minor), ee: 93%.



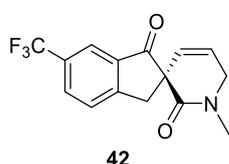
(R)-5-fluoro-1'-methyl-1',6'-dihydro-2'H-spiro[indene-2,3'-pyridine]-1,2'(3H)-dione (39); TLC: $R_f = 0.30$ (petroleum ether /ethyl acetate = 2/1, v/v, UV); white solid (mp: 151-152 °C); yield: 73% (17.9 mg, 0.073 mmol); $[\alpha]_D^{25} = 142$ ($c = 0.1$, CHCl_3); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.73 (dd, $J = 8.4, 5.2$ Hz, 1H), 7.15 (d, $J = 6.4$ Hz, 1H), 7.12-7.03 (m, 1H), 6.05-5.96 (m, 1H), 5.56 (dt, $J = 8.0, 2.0$ Hz, 1H), 4.32 (dt, $J = 18.0, 2.8$ Hz, 1H), 4.00-3.89 (m, 2H), 3.05 (s, 3H), 2.99 (d, $J = 17.2$ Hz, 1H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 201.3, 167.7 (d, $J = 258.4$ Hz), 166.9, 157.5 (d, $J = 10.5$ Hz), 130.8, 127.5 (d, $J = 10.7$ Hz), 126.9, 123.6, 116.2 (d, $J = 24.1$ Hz), 113.2 (d, $J = 23.2$ Hz), 59.1, 51.5, 39.4 (d, $J = 2.1$ Hz), 34.9; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -101.6; HRMS (ESI, m/z): calcd for $\text{C}_{14}\text{H}_{13}\text{FNO}_2^+$ $[\text{M}+\text{H}]^+$: 246.0925, found: 246.0927; HPLC: Chiralpak AD-H Column, hexane/ i PrOH = 90/10, 1.0 mL/min, 254 nm, 25 °C; RT = 13.5 min (major), 17.4 min (minor), ee: 90%.



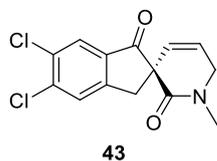
(R)-6-fluoro-1'-methyl-1',6'-dihydro-2'H-spiro[indene-2,3'-pyridine]-1,2'(3H)-dione (40); TLC: $R_f = 0.50$ (petroleum ether /ethyl acetate = 2/1, v/v, UV); white solid (mp: 152-153 °C); yield: 78% (19.1 mg, 0.078 mmol); $[\alpha]_D^{25} = 141$ ($c = 0.1$, CHCl_3); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.49-7.42 (m, 1H), 7.39-7.29 (m, 2H), 6.05-5.96 (m, 1H), 5.57 (d, $J = 9.2$ Hz, 1H), 4.39-4.24 (m, 1H), 3.99-3.89 (m, 2H), 3.05 (s, 3H), 2.97 (d, $J = 16.8$ Hz, 1H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 202.4, 166.8, 162.5 (d, $J = 249.3$ Hz), 150.0, 136.2 (d, $J = 8.1$ Hz), 127.9 (d, $J = 7.1$ Hz), 126.9, 123.5, 123.2 (d, $J = 23.6$ Hz), 110.8 (d, $J = 22.0$ Hz), 59.6, 51.5, 39.1, 34.9; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -114.3; HRMS (ESI, m/z): calcd for $\text{C}_{14}\text{H}_{13}\text{FNO}_2^+$ $[\text{M}+\text{H}]^+$: 246.0925, found: 246.0927; HPLC: Chiralpak AD-H Column, hexane/ i PrOH = 90/10, 1.0 mL/min, 254 nm, 25 °C; RT = 11.5 min (major), 23.4 min (minor), ee: 91%.



(R)-1'-methyl-1,2'-dioxo-1,1',3,6'-tetrahydro-2'H-spiro[indene-2,3'-pyridine]-6-carbonitrile (41); TLC: $R_f = 0.20$ (petroleum ether /ethyl acetate = 2/1, v/v, UV); white solid (mp: 172-173 °C); yield: 36% (9.1 mg, 0.036 mmol); $[\alpha]_D^{25} = 94$ ($c = 0.1$, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 8.00 (s, 1H), 7.85 (d, $J = 8.0$ Hz, 1H), 7.63 (d, $J = 7.6$ Hz, 1H), 6.09-6.02 (m, 1H), 5.56 (d, $J = 10.4$ Hz, 1H), 4.33 (d, $J = 18.4$ Hz, 1H), 4.03 (d, $J = 18.0$ Hz, 1H), 4.00-3.90 (m, 1H), 3.13-2.99 (m, 4H); ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 201.4, 166.2, 158.5, 137.9, 135.3, 129.3, 127.7, 126.1, 124.3, 118.0, 112.2, 59.0, 51.5, 39.9, 34.9; HRMS (ESI, m/z): calcd for C₁₅H₁₃N₂O₂⁺ [M+H]⁺: 253.0972, found: 253.0973; HPLC: Chiralpak AD-H Column, hexane/ⁱPrOH = 80/20, 1.0 mL/min, 254 nm, 25 °C; RT = 10.5 min (major), 29.3 min (minor), ee: 90%.

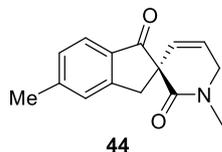


(R)-1'-methyl-6-(trifluoromethyl)-1',6'-dihydro-2'H-spiro[indene-2,3'-pyridine]-1,2'(3H)-dione (42); TLC: $R_f = 0.30$ (petroleum ether /ethyl acetate = 3/1, v/v, UV); white solid (mp: 121-122 °C); yield: 51% (15.0 mg, 0.051 mmol); $[\alpha]_D^{25} = 97$ ($c = 0.1$, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.99 (s, 1H), 7.86 (d, $J = 8.0$ Hz, 1H), 7.64 (d, $J = 8.0$ Hz, 1H), 6.12-6.00 (m, 1H), 5.58 (d, $J = 9.6$ Hz, 1H), 4.34 (d, $J = 18.8$ Hz, 1H), 4.09-3.90 (m, 2H), 3.14-3.00 (m, 4H); ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 202.1, 166.5, 157.7, 135.0, 131.9 (q, $J = 3.4$ Hz), 131.4 (q, $J = 33.2$ Hz), 127.3, 126.51 (q, $J = 273.4$), 126.46, 124.0, 122.4 (q, $J = 4.0$ Hz), 59.2, 51.5, 39.6, 34.9; ¹⁹F NMR (376 MHz, CDCl₃): δ -62.5; HRMS (ESI, m/z): calcd for C₁₅H₁₃F₃NO₂⁺ [M+H]⁺: 296.0893, found: 296.0894; HPLC: Chiralpak AD-H Column, hexane/ⁱPrOH = 90/10, 1.0 mL/min, 254 nm, 25 °C; RT = 9.0 min (major), 25.7 min (minor), ee: 82%.



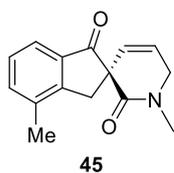
(R)-5,6-dichloro-1'-methyl-1',6'-dihydro-2'H-spiro[indene-2,3'-pyridine]-1,2'(3H)-dione (43); TLC: $R_f = 0.30$ (petroleum ether /ethyl acetate = 3/1, v/v, UV); white solid (mp: 166-167 °C); yield: 46% (13.6 mg, 0.046 mmol); $[\alpha]_D^{25} = 108$ ($c = 0.1$, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.79 (s, 1H), 7.62 (s, 1H), 6.07-5.98 (m, 1H), 5.55 (d, $J = 10.0$ Hz, 1H), 4.31 (d, $J = 18.4$ Hz, 1H), 3.99-3.87 (m, 2H), 3.04 (s, 3H),

2.96 (d, $J = 17.2$ Hz, 1H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 200.9, 166.4, 153.2, 140.2, 134.1, 133.0, 128.4, 126.4, 126.4, 124.0, 59.3, 51.5, 38.9, 34.9; HRMS (ESI, m/z): calcd for $\text{C}_{14}\text{H}_{12}\text{Cl}_2\text{NO}_2^+$ $[\text{M}+\text{H}]^+$: 296.0240, found: 296.0242; HPLC: Chiralpak AD-H Column, hexane/ i PrOH = 95/5, 1.0 mL/min, 254 nm, 25 °C; RT = 20.7 min (major), 39.9 min (minor), ee: 92%.



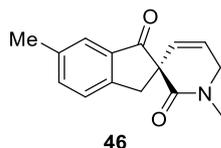
(*R*)-1',5-dimethyl-1',6'-dihydro-2'*H*-spiro[indene-2,3'-pyridine]-1,2'(3*H*)-dione

(44); TLC: $R_f = 0.40$ (petroleum ether /ethyl acetate = 2/1, v/v, UV); white solid (mp: 179-180 °C); yield: 61% (14.7 mg, 0.061 mmol); $[\alpha]_{\text{D}}^{25} = 111$ ($c = 0.1$, CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.62 (d, $J = 8.0$ Hz, 1H), 7.29 (s, 1H), 7.18 (d, $J = 8.0$ Hz, 1H), 6.02-5.93 (m, 1H), 5.56 (dt, $J = 10.0, 2.0$ Hz, 1H), 4.32 (dt, $J = 18.0, 2.4$ Hz, 1H), 3.97-3.88 (m, 2H), 3.05 (s, 3H), 2.96 (d, $J = 16.8$ Hz, 1H), 2.44 (s, 3H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 202.7, 167.3, 155.0, 146.9, 132.2, 129.1, 127.4, 126.9, 125.0, 123.2, 59.0, 51.5, 39.4, 34.9, 22.3; HRMS (ESI, m/z): calcd for $\text{C}_{15}\text{H}_{16}\text{NO}_2^+$ $[\text{M}+\text{H}]^+$: 242.1176, found: 242.1179; HPLC: Chiralpak AD-H Column, hexane/ i PrOH = 90/10, 1.0 mL/min, 254 nm, 25 °C; RT = 16.4 min (major), 21.5 min (minor), ee: 88%.

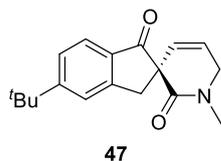


(*R*)-1',4-dimethyl-1',6'-dihydro-2'*H*-spiro[indene-2,3'-pyridine]-1,2'(3*H*)-dione

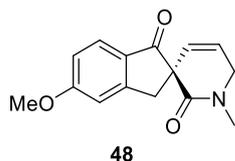
(45); TLC: $R_f = 0.20$ (petroleum ether /ethyl acetate = 2/1, v/v, UV); white solid (mp: 138-139 °C); yield: 24% (5.8 mg, 0.024 mmol); $[\alpha]_{\text{D}}^{25} = 82$ ($c = 0.1$, CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.58 (d, $J = 7.6$ Hz, 1H), 7.42 (d, $J = 7.2$ Hz, 1H), 7.33-7.25 (m, 1H), 6.03-5.96 (m, 1H), 5.57 (d, $J = 8.8$ Hz, 1H), 4.35 (d, $J = 17.6$ Hz, 1H), 4.00-3.83 (m, 2H), 3.06 (s, 3H), 2.90 (d, $J = 17.2$ Hz, 1H), 2.36 (s, 3H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 203.6, 167.3, 153.5, 136.0, 135.8, 134.3, 128.1, 127.5, 123.2, 122.6, 58.7, 51.6, 38.6, 34.9, 17.9; HRMS (ESI, m/z): calcd for $\text{C}_{15}\text{H}_{16}\text{NO}_2^+$ $[\text{M}+\text{H}]^+$: 242.1176, found: 242.1179; HPLC: Chiralpak AD-H Column, hexane/ i PrOH = 95/5, 1.0 mL/min, 254 nm, 25 °C; RT = 19.8 min (major), 31.2 min (minor), ee: 78%.



(R)-1',6-dimethyl-1',6'-dihydro-2'H-spiro[indene-2,3'-pyridine]-1,2'(3H)-dione (46); TLC: $R_f = 0.30$ (petroleum ether /ethyl acetate = 2/1, v/v, UV); white solid (mp: 151-152 °C); yield: 41% (10.0 mg, 0.041 mmol); $[\alpha]_D^{25} = 152$ ($c = 0.1$, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.53 (s, 1H), 7.43 (d, $J = 7.6$ Hz, 1H), 7.37 (d, $J = 8.0$ Hz, 1H), 6.02-5.94 (m, 1H), 5.56 (d, $J = 9.6$ Hz, 1H), 4.33 (d, $J = 18.0$ Hz, 1H), 3.99-3.88 (m, 2H), 3.05 (s, 3H), 2.96 (d, $J = 16.8$ Hz, 1H), 2.39 (s, 3H); ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 203.3, 167.3, 152.0, 137.8, 136.8, 134.7, 127.6, 126.2, 125.1, 123.2, 59.2, 51.6, 39.3, 34.9, 21.2; HRMS (ESI, m/z): calcd for calcd for C₁₅H₁₆NO₂⁺ [M+H]⁺: 242.1176, found: 242.1178; HPLC: Chiralpak AD-H Column, hexane/ⁱPrOH = 90/10, 1.0 mL/min, 254 nm, 25 °C; RT = 11.8 min (major), 21.8 min (minor), ee: 86%.

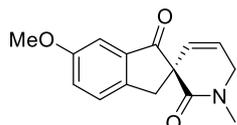


(R)-5-(tert-butyl)-1'-methyl-1',6'-dihydro-2'H-spiro[indene-2,3'-pyridine]-1,2'(3H)-dione (47); TLC: $R_f = 0.40$ (petroleum ether /ethyl acetate = 3/1, v/v, UV); yellow oil; yield: 43% (12.2 mg, 0.043 mmol); $[\alpha]_D^{25} = 72$ ($c = 0.1$, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.66 (d, $J = 8.4$ Hz, 1H), 7.49 (s, 1H), 7.42 (d, $J = 8.4$ Hz, 1H), 6.03-5.93 (m, 1H), 5.58 (d, $J = 9.6$ Hz, 1H), 4.34 (d, $J = 18.0$ Hz, 1H), 4.00-3.89 (m, 2H), 3.06 (s, 3H), 2.99 (d, $J = 17.2$ Hz, 1H), 1.36 (s, 9H); ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 202.8, 167.4, 159.9, 154.9, 132.1, 127.6, 125.7, 124.8, 123.14, 123.13, 59.1, 51.6, 39.7, 35.7, 34.9, 31.3; HRMS (ESI, m/z): calcd for C₁₈H₂₂NO₂⁺ [M+H]⁺: 284.1645, found: 284.1647; HPLC: Chiralpak AD-H Column, hexane/ⁱPrOH = 90/10, 1.0 mL/min, 254 nm, 25 °C; RT = 11.9 min (major), 14.6 min (minor), ee: 80%.



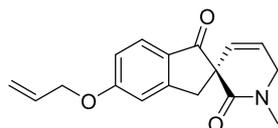
(R)-5-methoxy-1'-methyl-1',6'-dihydro-2'H-spiro[indene-2,3'-pyridine]-1,2'(3H)-dione (48); TLC: $R_f = 0.40$ (petroleum ether /ethyl acetate = 2/1, v/v, UV); white solid (mp: 126-127 °C); yield: 56% (14.4 mg, 0.056 mmol); $[\alpha]_D^{25} = 97$ ($c = 0.1$, CHCl₃); ¹H

NMR (400 MHz, CDCl₃): δ 7.65 (d, J = 8.4 Hz, 1H), 6.94-6.86 (m, 2H), 6.02-5.93 (m, 1H), 5.57 (dt, J = 10.0, 2.0 Hz, 1H), 4.33 (dt, J = 18.0, 2.4 Hz, 1H), 3.92 (d, J = 17.2 Hz, 2H), 3.88 (s, 3H), 3.05 (s, 3H), 2.95 (d, J = 16.8 Hz, 1H); **¹³C {¹H} NMR (101 MHz, CDCl₃):** δ 201.2, 167.4, 166.0, 157.6, 127.6, 127.5, 126.9, 123.1, 116.1, 109.5, 59.1, 55.8, 51.6, 39.5, 34.9; **HRMS (ESI, m/z):** calcd for C₁₅H₁₆NO₃⁺ [M+H]⁺: 258.1125, found: 258.1129; **HPLC:** Chiralpak AD-H Column, hexane/ⁱPrOH = 90/10, 1.0 mL/min, 254 nm, 25 °C; RT = 24.1 min (major), 30.6 min (minor), ee: 84%.



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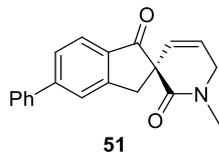
(R)-6-methoxy-1'-methyl-1',6'-dihydro-2'H-spiro[indene-2,3'-pyridine]-1,2'(3H)-dione (49); TLC: R_f = 0.20 (petroleum ether /ethyl acetate = 2/1, v/v, UV); white solid (mp: 132-133 °C); yield: 91% (23.4 mg, 0.091 mmol); $[\alpha]_D^{25}$ = 144 (c = 0.1, CHCl₃); **¹H NMR (400 MHz, CDCl₃):** δ 7.37 (d, J = 8.4 Hz, 1H), 7.20 (dd, J = 8.4, 2.4 Hz, 1H), 7.14 (s, 1H), 6.02-5.93 (m, 1H), 5.56 (d, J = 10.0 Hz, 1H), 4.31 (d, J = 18.0 Hz, 1H), 4.01-3.83 (m, 2H), 3.81 (s, 3H), 3.05 (s, 3H), 2.93 (d, J = 16.4 Hz, 1H); **¹³C {¹H} NMR (101 MHz, CDCl₃):** δ 203.2, 167.2, 159.7, 147.5, 135.6, 127.3, 127.2, 125.0, 123.1, 106.1, 59.5, 55.8, 51.5, 39.0, 34.8; **HRMS (ESI, m/z):** calcd for C₁₅H₁₆NO₃⁺ [M+H]⁺: 258.1125, found: 258.1129; **HPLC:** Chiralpak AD-H Column, hexane/ⁱPrOH = 90/10, 1.0 mL/min, 254 nm, 25 °C; RT = 17.8 min (major), 28.0 min (minor), ee: 86%.



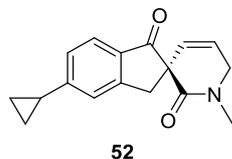
50

(R)-5-(allyloxy)-1'-methyl-1',6'-dihydro-2'H-spiro[indene-2,3'-pyridine]-1,2'(3H)-dione (50); TLC: R_f = 0.30 (petroleum ether /ethyl acetate = 2/1, v/v, UV); white solid (mp: 86-87 °C); yield: 92% (26.0 mg, 0.092 mmol); $[\alpha]_D^{25}$ = 81 (c = 0.1, CHCl₃); **¹H NMR (400 MHz, CDCl₃):** δ 7.65 (d, J = 9.2 Hz, 1H), 6.94-6.88 (m, 2H), 6.11-5.93 (m, 2H), 5.61-5.52 (m, 1H), 5.42 (d, J = 17.2 Hz, 1H), 5.32 (d, J = 10.8 Hz, 1H), 4.65-4.59 (m, 2H), 4.40-4.24 (m, 1H), 3.92 (d, J = 17.2 Hz, 2H), 3.04 (s, 3H), 2.94 (d, J = 17.2 Hz, 1H); **¹³C {¹H} NMR (101 MHz, CDCl₃):** δ 201.1, 167.4, 165.0, 157.5, 132.4, 127.7, 127.6, 126.9, 123.1, 118.4, 116.5, 110.4, 69.3, 59.1, 51.6, 39.5, 34.9; **HRMS (ESI, m/z):** calcd for C₁₇H₁₈NO₃⁺ [M+H]⁺: 284.1281, found: 284.1283; **HPLC:** Chiralpak AD-H

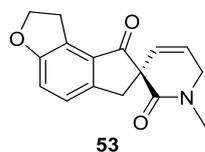
Column, hexane/ⁱPrOH = 90/10, 1.0 mL/min, 254 nm, 25 °C; RT = 27.1 min (major), 34.1 min (minor), ee: 87%.



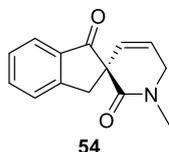
(R)-1'-methyl-5-phenyl-1',6'-dihydro-2'H-spiro[indene-2,3'-pyridine]-1,2'(3H)-dione (51); TLC: R_f = 0.40 (petroleum ether /ethyl acetate = 2/1, v/v, UV); white solid (mp: 154-155 °C); yield: 61% (18.5 mg, 0.061 mmol); $[\alpha]_D^{25}$ = 53 (c = 0.1, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.80 (d, J = 8.0 Hz, 1H), 7.68 (s, 1H), 7.66-7.57 (m, 3H), 7.51-7.37 (m, 3H), 6.06-5.97 (m, 1H), 5.61 (d, J = 10.4 Hz, 1H), 4.35 (d, J = 18.4 Hz, 1H), 4.04 (d, J = 16.8 Hz, 1H), 3.95 (dd, J = 18.0, 4.0 Hz, 1H), 3.13-3.02 (m, 4H); ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 202.8, 167.2, 155.2, 148.7, 140.3, 133.3, 129.1, 128.6, 127.7, 127.4, 127.3, 125.5, 125.0, 123.3, 59.1, 51.6, 39.6, 34.9; HRMS (ESI, m/z): calcd for C₂₀H₁₈NO₂⁺ [M+H]⁺: 304.1332, found: 304.1333; HPLC: Chiralpak AD-H Column, hexane/ⁱPrOH = 90/10, 1.0 mL/min, 254 nm, 25 °C; RT = 25.0 min (major), 37.6 min (minor), ee: 90%.



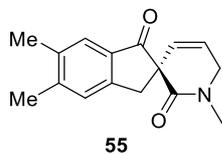
(R)-5-cyclopropyl-1'-methyl-1',6'-dihydro-2'H-spiro[indene-2,3'-pyridine]-1,2'(3H)-dione (52); TLC: R_f = 0.50 (petroleum ether /ethyl acetate = 2/1, v/v, UV); white solid (mp: 125-126 °C); yield: 89% (23.8 mg, 0.089 mmol); $[\alpha]_D^{25}$ = 90 (c = 0.1, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.59 (d, J = 8.0 Hz, 1H), 7.12 (s, 1H), 7.04 (d, J = 8.0 Hz, 1H), 6.01-5.92 (m, 1H), 5.55 (d, J = 9.6 Hz, 1H), 4.32 (d, J = 18.0 Hz, 1H), 3.96-3.86 (m, 2H), 3.04 (s, 3H), 2.94 (d, J = 16.8 Hz, 1H), 2.02-1.91 (m, 1H), 1.08 (d, J = 6.0 Hz, 2H), 0.80 (d, J = 5.2 Hz, 2H); ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 202.4, 167.3, 155.0, 153.6, 132.1, 127.5, 125.6, 125.0, 123.1, 122.9, 59.0, 51.5, 39.4, 34.9, 16.3, 10.83, 10.76; HRMS (ESI, m/z): calcd for C₁₇H₁₈NO₂⁺ [M+H]⁺: 268.1332, found: 268.1335; HPLC: Chiralpak AD-H Column, hexane/ⁱPrOH = 90/10, 1.0 mL/min, 254 nm, 25 °C; RT = 27.8 min (major), 36.8 min (minor), ee: 88%.



(R)-1'-methyl-1,1',2,6'-tetrahydro-2'H-spiro[indeno[5,4-b]furan-7,3'-pyridine]-2',8(6H)-dione (53); TLC: $R_f = 0.30$ (petroleum ether /ethyl acetate = 2/1, v/v, UV); white solid (mp: 217-218 °C); yield: 67% (18.0 mg, 0.067 mmol); $[\alpha]_D^{25} = 157$ ($c = 0.1$, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.21 (d, $J = 8.4$ Hz, 1H), 7.03 (d, $J = 8.0$ Hz, 1H), 6.03-5.94 (m, 1H), 5.58 (d, $J = 10.0$ Hz, 1H), 4.63 (t, $J = 8.8$ Hz, 2H), 4.31 (d, $J = 18.0$ Hz, 1H), 3.98-3.85 (m, 2H), 3.50-3.32 (m, 2H), 3.05 (s, 3H), 2.94 (d, $J = 16.8$ Hz, 1H); ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 203.6, 167.3, 160.8, 146.5, 131.0, 127.5, 125.5, 125.2, 123.1, 116.6, 72.5, 59.5, 51.6, 39.2, 34.9, 28.5; HRMS (ESI, m/z): calcd for C₁₆H₁₆NO₃⁺ [M+H]⁺: 270.1125, found: 270.1126; HPLC: Chiralpak AD-H Column, hexane/ⁱPrOH = 90/10, 1.0 mL/min, 254 nm, 25 °C; RT = 21.5 min (major), 24.9 min (minor), ee: 90%.

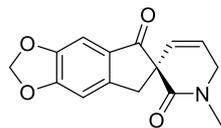


(R)-1'-methyl-1',6'-dihydro-2'H-spiro[indene-2,3'-pyridine]-1,2'(3H)-dione (54); TLC: $R_f = 0.50$ (petroleum ether /ethyl acetate = 2/1, v/v, UV); white solid (mp: 128-129 °C); yield: 84% (19.1 mg, 0.084 mmol); $[\alpha]_D^{25} = 147$ ($c = 0.1$, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.73 (d, $J = 8.0$ Hz, 1H), 7.65-7.57 (m, 1H), 7.49 (d, $J = 8.0$ Hz, 1H), 7.41-7.33 (m, 1H), 6.03-5.95 (m, 1H), 5.56 (dt, $J = 9.6, 2.0$ Hz, 1H), 4.33 (dt, $J = 18.0, 2.4$ Hz, 1H), 4.03-3.89 (m, 2H), 3.05 (s, 3H), 3.02 (d, $J = 16.8$ Hz, 1H); ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 203.2, 167.2, 154.5, 135.5, 134.4, 127.8, 127.3, 126.6, 125.2, 123.3, 58.8, 51.5, 39.6, 34.9; HRMS (ESI, m/z): calcd for C₁₄H₁₄NO₂⁺ [M+H]⁺: 228.1019, found: 228.1022; HPLC: Chiralpak AD-H Column, hexane/ⁱPrOH = 90/10, 1.0 mL/min, 254 nm, 25 °C; RT = 15.7 min (major), 22.1 min (minor), ee: 89%.



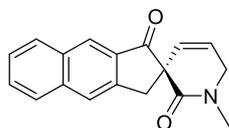
(R)-1',5,6-trimethyl-1',6'-dihydro-2'H-spiro[indene-2,3'-pyridine]-1,2'(3H)-dione (55); TLC: $R_f = 0.20$ (petroleum ether /ethyl acetate = 2/1, v/v, UV); white solid (mp: 165-166 °C); yield: 88% (22.4 mg, 0.088 mmol); $[\alpha]_D^{25} = 101$ ($c = 0.1$, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.49 (s, 1H), 7.26 (s, 1H), 6.01-5.93 (m, 1H), 5.56 (d, $J = 9.6$ Hz, 1H), 4.32 (d, $J = 18.0$ Hz, 1H), 3.98-3.84 (m, 2H), 3.05 (s, 3H), 2.92 (d, $J = 16.8$ Hz, 1H), 2.34 (s, 3H), 2.29 (s, 3H); ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 202.9,

167.4, 152.8, 146.0, 136.8, 132.6, 127.7, 127.3, 125.5, 123.1, 59.1, 51.6, 39.2, 34.9, 21.0, 19.8; **HRMS (ESI, m/z)**: calcd for $C_{16}H_{18}NO_2^+$ $[M+H]^+$: 256.1332, found: 256.1333; **HPLC**: Chiralpak AD-H Column, hexane/*i*PrOH = 90/10, 1.0 mL/min, 254 nm, 25 °C; RT = 15.2 min (major), 28.9 min (minor), ee: 88%.



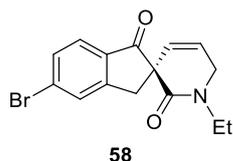
56

(R)-1'-methyl-1',6'-dihydro-2'H-spiro[indeno[5,6-d][1,3]dioxole-6,3'-pyridine]-2',5(7H)-dione (56); **TLC**: R_f = 0.50 (petroleum ether /ethyl acetate = 2/1, v/v, UV); white solid (mp: 208-209 °C); yield: 89% (24.1 mg, 0.089 mmol); $[\alpha]_D^{25}$ = 121 (c = 0.1, $CHCl_3$); **1H NMR (400 MHz, $CDCl_3$)**: δ 7.04 (s, 1H), 6.84 (s, 1H), 6.05 (d, J = 4.4 Hz, 2H), 6.01-5.92 (m, 1H), 5.55 (d, J = 9.6 Hz, 1H), 4.31 (d, J = 18.0 Hz, 1H), 3.91 (dd, J = 18.0, 4.0 Hz, 1H), 3.83 (d, J = 17.2 Hz, 1H), 3.04 (s, 3H), 2.87 (d, J = 17.2 Hz, 1H); **^{13}C { 1H } NMR (101 MHz, $CDCl_3$)**: δ 200.9, 167.2, 155.1, 152.5, 148.7, 128.9, 127.5, 123.2, 105.7, 103.4, 102.5, 59.3, 51.5, 39.4, 34.9; **HRMS (ESI, m/z)**: calcd for $C_{15}H_{14}NO_4^+$ $[M+H]^+$: 272.0917, found: 272.0916; **HPLC**: Chiralpak AD-H Column, hexane/*i*PrOH = 90/10, 1.0 mL/min, 254 nm, 25 °C; RT = 32.0 min (major), 48.7 min (minor), ee: 91%.

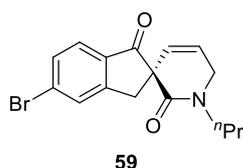


57

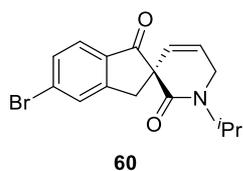
(R)-1'-methyl-1',6'-dihydro-2'H-spiro[cyclopenta[b]naphthalene-2,3'-pyridine]-1,2'(3H)-dione (57); **TLC**: R_f = 0.50 (petroleum ether /ethyl acetate = 2/1, v/v, UV); white solid (mp: 202-203 °C); yield: 55% (15.2 mg, 0.055 mmol); $[\alpha]_D^{25}$ = 122 (c = 0.1, $CHCl_3$); **1H NMR (400 MHz, $CDCl_3$)**: δ 8.32 (s, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.92-7.82 (m, 2H), 7.63-7.54 (m, 1H), 7.53-7.44 (m, 1H), 6.06-5.97 (m, 1H), 5.63 (dt, J = 9.6, 2.0 Hz, 1H), 4.35 (dt, J = 18.0, 2.4 Hz, 1H), 4.16 (d, J = 16.8 Hz, 1H), 4.02-3.91 (m, 1H), 3.20 (d, J = 16.8 Hz, 1H), 3.07 (s, 3H); **^{13}C { 1H } NMR (101 MHz, $CDCl_3$)**: δ 203.5, 167.3, 146.6, 137.8, 132.7, 132.3, 130.5, 129.1, 128.0, 127.4, 126.3, 124.7, 123.4, 59.6, 51.6, 39.1, 34.9; **HRMS (ESI, m/z)**: $C_{18}H_{16}NO_2^+$ $[M+H]^+$: 278.1176, found: 278.1178; **HPLC**: Chiralpak AD-H Column, hexane/*i*PrOH = 90/10, 1.0 mL/min, 254 nm, 25 °C; RT = 25.3 min (major), 48.4 min (minor), ee: 88%.



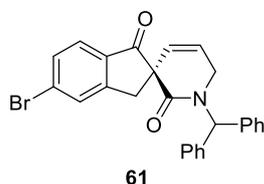
(R)-5-bromo-1'-ethyl-1',6'-dihydro-2'H-spiro[indene-2,3'-pyridine]-1,2'(3H)-dione (58); TLC: R_f = 0.40 (petroleum ether /ethyl acetate = 2/1, v/v, UV); white solid (mp: 113-114 °C); yield: 84% (26.8 mg, 0.084 mmol); $[\alpha]_D^{25}$ = 72 (c = 0.1, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.68 (s, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.53-7.48 (m, 1H), 6.08-6.00 (m, 1H), 5.59-5.51 (m, 1H), 4.33 (dt, J = 18.0, 2.4 Hz, 1H), 4.01-3.87 (m, 2H), 3.63-3.38 (m, 2H), 2.98 (d, J = 17.2 Hz, 1H), 1.17 (t, J = 7.2 Hz, 3H); ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 202.1, 166.1, 156.1, 133.3, 131.4, 131.0, 129.8, 126.7, 126.2, 124.0, 59.1, 48.8, 42.4, 39.1, 12.1; HRMS (ESI, m/z): calcd for C₁₅H₁₅BrNO₂⁺ [M+H]⁺: 320.0281, found: 320.0282; HPLC: Chiralpak OD-H Column, hexane/ⁱPrOH = 85/15, 1.0 mL/min, 254 nm, 25 °C; RT = 13.2 min (minor), 14.5 min (major), ee: 89%.



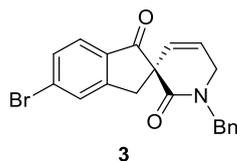
(R)-5-bromo-1'-propyl-1',6'-dihydro-2'H-spiro[indene-2,3'-pyridine]-1,2'(3H)-dione (59); TLC: R_f = 0.30 (petroleum ether /ethyl acetate = 3/1, v/v, UV); white solid (mp: 56-57 °C); yield: 80% (26.6 mg, 0.080 mmol); $[\alpha]_D^{25}$ = 71 (c = 0.1, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.67 (s, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.53-7.46 (m, 1H), 6.08-5.99 (m, 1H), 5.56 (dt, J = 10.0, 2.0 Hz, 1H), 4.34 (dt, J = 18.0, 2.4 Hz, 1H), 3.97 (d, J = 17.2 Hz, 1H), 3.94-3.86 (m, 1H), 3.62-3.48 (m, 1H), 3.33-3.21 (m, 1H), 2.98 (d, J = 17.2 Hz, 1H), 1.67-1.58 (m, 2H), 0.91 (t, J = 7.6 Hz, 3H); ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 202.1, 166.5, 156.2, 133.3, 131.4, 131.0, 129.8, 126.7, 126.2, 124.1, 59.3, 49.4, 49.1, 39.1, 20.3, 11.2; HRMS (ESI, m/z): calcd for C₁₆H₁₇BrNO₂⁺ [M+H]⁺: 334.0437, found: 334.0438; HPLC: Chiralpak OD-H Column, hexane/ⁱPrOH = 90/10, 1.0 mL/min, 254 nm, 25 °C; RT = 19.6 min (minor), 22.9 min (major), ee: 81%.



(R)-5-bromo-1'-isopropyl-1',6'-dihydro-2'H-spiro[indene-2,3'-pyridine]-1,2'(3H)-dione (60); TLC: R_f = 0.50 (petroleum ether /ethyl acetate = 3/1, v/v, UV); white solid (mp: 91-92 °C); yield: 73% (24.3 mg, 0.073 mmol); $[\alpha]_D^{25}$ = 76 (c = 0.1, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.68 (s, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.50 (d, J = 9.6 Hz, 1H), 6.13-6.04 (m, 1H), 5.60-5.52 (m, 1H), 4.90-4.77 (m, 1H), 4.19 (dt, J = 18.0, 2.4 Hz, 1H), 4.00 (d, J = 17.2 Hz, 1H), 3.91-3.81 (m, 1H), 2.97 (d, J = 17.2 Hz, 1H), 1.20 (d, J = 7.2 Hz, 3H), 1.16 (d, J = 6.8 Hz, 3H); ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 202.2, 166.1, 156.2, 133.3, 131.4, 131.0, 129.8, 126.6, 126.2, 124.4, 59.7, 45.3, 42.6, 39.1, 19.5, 19.2; HRMS (ESI, m/z): calcd for C₁₆H₁₇BrNO₂⁺ [M+H]⁺: 334.0437, found: 334.0440; HPLC: Chiralpak AD-H Column, hexane/ⁱPrOH = 97/3, 1.0 mL/min, 254 nm, 25 °C; RT = 31.3 min (major), 58.4 min (minor), ee: 89%.



(R)-1'-benzhydryl-5-bromo-1',6'-dihydro-2'H-spiro[indene-2,3'-pyridine]-1,2'(3H)-dione (61); TLC: R_f = 0.60 (petroleum ether /ethyl acetate = 5/1, v/v, UV); white solid (mp: 164-165 °C); yield: 94% (43.1 mg, 0.094 mmol); $[\alpha]_D^{25}$ = 65 (c = 0.1, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.70 (s, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.53 (d, J = 8.0 Hz, 1H), 7.42-7.27 (m, 8H), 7.25-7.15 (m, 3H), 6.05-5.95 (m, 1H), 5.60 (d, J = 9.6 Hz, 1H), 4.09 (d, J = 17.2 Hz, 1H), 4.00 (dd, J = 18.4, 2.8 Hz, 1H), 3.69 (dd, J = 18.4, 4.4 Hz, 1H), 3.06 (d, J = 17.2 Hz, 1H); ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 201.9, 167.0, 156.1, 138.3, 138.1, 133.2, 131.5, 131.2, 129.9, 129.0, 128.9, 128.73, 128.72, 127.8, 127.7, 126.5, 126.3, 124.5, 60.7, 59.9, 46.0, 39.2; HRMS (ESI, m/z): calcd for C₂₆H₂₁BrNO₂⁺ [M+H]⁺: 458.0750, found: 458.0752; HPLC: Chiralpak AD-H Column, hexane/ⁱPrOH = 90/10, 1.0 mL/min, 254 nm, 25 °C; RT = 29.9 min (major), 52.3 min (minor), ee: 81%.

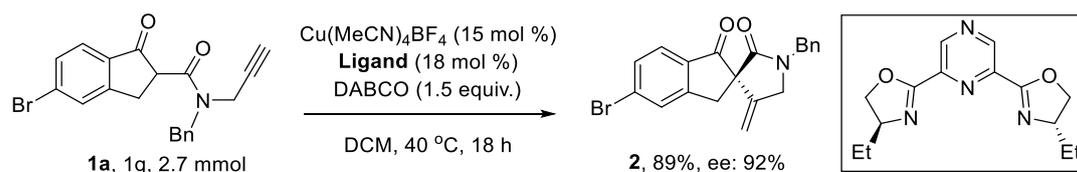


(R)-1'-benzyl-5-bromo-1',6'-dihydro-2'H-spiro[indene-2,3'-pyridine]-1,2'(3H)-dione (3); TLC: R_f = 0.30 (petroleum ether /ethyl acetate = 3/1, v/v, UV); white solid

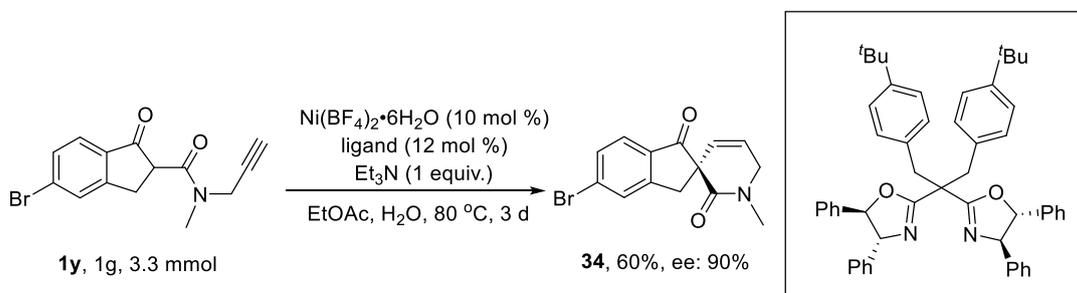
(mp: 132-133 °C); yield: 75% (28.7 mg, 0.075 mmol); $[\alpha]_D^{25} = 72$ ($c = 0.1$, CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.70 (s, 1H), 7.61 (d, $J = 8.0$ Hz, 1H), 7.53 (d, $J = 8.4$ Hz, 1H), 7.39-7.24 (m, 5H), 6.03-5.94 (m, 1H), 5.56 (d, $J = 9.6$ Hz, 1H), 4.79 (d, $J = 14.8$ Hz, 1H), 4.61 (d, $J = 14.8$ Hz, 1H), 4.22 (d, $J = 18.0$ Hz, 1H), 4.05 (d, $J = 17.2$ Hz, 1H), 3.85 (dd, $J = 18.4, 4.4$ Hz, 1H), 3.04 (d, $J = 17.2$ Hz, 1H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 202.0, 166.9, 156.1, 136.4, 133.3, 131.5, 131.2, 129.9, 128.9, 128.0, 127.7, 126.5, 126.3, 124.0, 59.2, 50.5, 48.9, 39.3; HRMS (ESI, m/z): calcd for $\text{C}_{20}\text{H}_{17}\text{BrNO}_2^+$ $[\text{M}+\text{H}]^+$: 382.0437, found: 382.0440; HPLC: Chiralpak AD-H Column, hexane/ i PrOH = 80/20, 1.0 mL/min, 254 nm, 25 °C; RT = 15.4 min (major), 26.2 min (minor), ee: 88%.

VII. Further Transformations

Scale-up synthesis

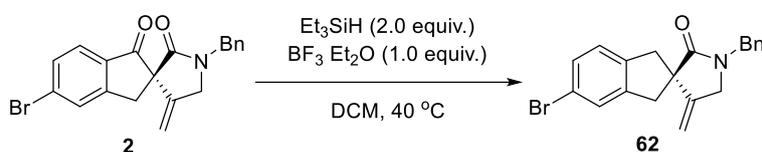


A mixture of $\text{Cu}(\text{MeCN})_4\text{BF}_4$ (0.405 mmol, 15 mol %), ligand (0.0486 mmol, 18 mol %) in dry DCM (27 mL) was stirred at 25 °C under a nitrogen atmosphere for 1.5 h. Subsequently, substrate **1a** (2.7 mmol, 1.0 equiv.) and DABCO (4.05 mmol, 1.5 equiv.) and dry DCM (27 mL) were added. The reaction mixture was then stirred at 40 °C under nitrogen. After 18 h, substrate **1** had completely disappeared (as monitored by TLC). Finally, the crude product was purified by flash chromatography on silica gel to afford the desired product **2** (890 mg, 89% yield, 92% ee).

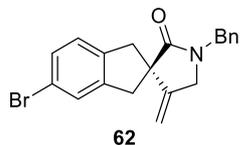


A mixture of Ni(BF₄)₂•6H₂O (0.330 mmol, 10 mol %), ligand (0.396 mmol, 12 mol %) in dry ethyl acetate (33 mL) was stirred at 25 °C under a nitrogen atmosphere for 1.5 h. Subsequently, substrate **1y** (3.3 mmol, 1.0 equiv.) and Et₃N (4.95 mmol, 1.5 equiv.) and dry EtOAc (33 mL) and H₂O (0.16 mL) were added. The reaction mixture was then stirred at 80 °C under nitrogen atmosphere. After three days, substrate **1y** had completely disappeared (as monitored by TLC). Finally, the crude product was purified by flash chromatography on silica gel to afford the desired product **34** (600 mg, 60% yield, 90% ee).

Procedure for Formation of **62**

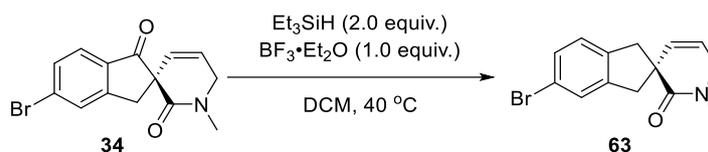


A solution of **2** (0.1 mmol, 1.0 equiv.) in DCM (2 mL) was prepared under a nitrogen atmosphere. To this solution were added triethylsilane (0.2 mmol, 2.0 equiv.) and boron trifluoride diethyl etherate (0.12 mmol, 1.2 equiv.). The reaction mixture was stirred at 40 °C until complete consumption of **2** was observed by TLC analysis. After concentration of the solvent in vacuo, the crude product was purified by flash chromatography on silica gel to afford the desired product **62**.

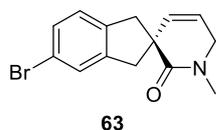


(R)-1'-benzyl-5-bromo-4'-methylene-1,3-dihydrospiro[indene-2,3'-pyrrolidin]-2'-one (62); TLC: R_f = 0.60 (petroleum ether / ethyl acetate = 5/1, v/v, UV); colorless oil; yield: 55% (20.0 mg, 0.055 mmol); $[\alpha]_D^{25}$ = 63 (c = 0.1, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.39-7.19 (m, 7H), 7.04 (d, J = 8.0 Hz, 1H), 4.78 (s, 2H), 4.54 (s, 2H), 3.85 (s, 2H), 3.58-3.44 (m, 2H), 3.01-2.89 (m, 2H); ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 176.6, 148.3, 143.8, 140.4, 136.1, 130.0, 129.0, 128.3, 127.9, 127.6, 125.9, 120.6, 106.7, 54.9, 50.1, 46.7, 44.1, 43.9; HRMS (ESI, m/z): calcd for C₂₀H₁₉BrNO⁺ [M+H]⁺: 368.0645, found: 368.0649; HPLC: Chiralpak AD-H Column, hexane/ⁱPrOH = 90/10, 1.0 mL/min, 254 nm, 25 °C; RT = 12.5 min (minor), 16.3 min (major), ee: 86%.

Procedure for Formation of **63**

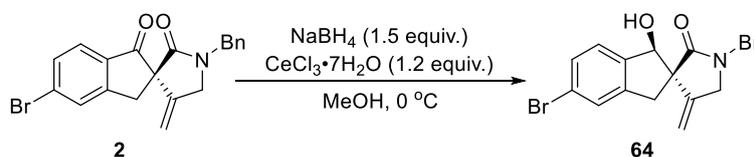


A solution of **34** (0.1 mmol, 1.0 equiv.) in DCM (2 mL) was prepared under a nitrogen atmosphere. To this solution were added triethylsilane (0.2 mmol, 2.0 equiv.) and boron trifluoride diethyl etherate (0.12 mmol, 1.2 equiv.). The mixture was stirred at 40 °C until **34** was completely consumed, as monitored by TLC. After concentration of the solvent in vacuo, the crude product was purified by flash chromatography on silica gel to afford the desired product **63**.

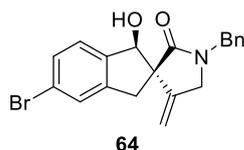


(R)-5-bromo-1'-methyl-1,1',3,6'-tetrahydro-2'H-spiro[indene-2,3'-pyridin]-2'-one (63); TLC: $R_f = 0.40$ (petroleum ether /ethyl acetate = 2/1, v/v, UV); colorless oil; yield: 76% (22.3 mg, 0.076 mmol); $[\alpha]_D^{25} = 4$ ($c = 0.1$, MeOH); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.32-7.24 (m, 2H), 7.03 (d, $J = 8.0$ Hz, 1H), 5.75 (d, $J = 10.0$ Hz, 1H), 5.61 (d, $J = 10.0$ Hz, 1H), 3.96 (s, 2H), 3.65 (dd, $J = 24.4, 16.0$ Hz, 2H), 3.04 (s, 3H), 2.85-2.74 (m, 2H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 172.4, 143.7, 140.3, 131.9, 129.8, 127.7, 126.0, 120.4, 118.1, 51.1, 49.6, 45.8, 45.5, 34.8; HRMS (ESI, m/z): calcd for $\text{C}_{14}\text{H}_{15}\text{BrNO}^+$ $[\text{M}+\text{H}]^+$: 292.0332, found: 292.0334; HPLC: Chiralpak AD-H Column, hexane/ i PrOH = 97/3, 1.0 mL/min, 254 nm, 25 °C; RT = 20.6 min (minor), 27.7 min (major), ee: 83%.

Procedure for Formation of **64**

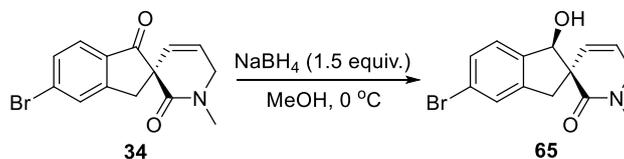


A solution of **2** (0.1 mmol, 1.0 equiv.) in methanol (2 mL) was cooled to 0 °C under a nitrogen atmosphere. To this solution were added sodium borohydride (0.15 mmol, 1.5 equiv.) and $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (0.12 mmol, 1.2 equiv.). The mixture was stirred at 0 °C until **2** was completely consumed, as monitored by TLC. After concentration of the solvent in vacuo, the crude product was purified by flash chromatography on silica gel to afford the desired product **64**.

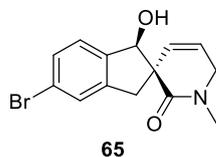


(1*R*,2*R*)-1'-benzyl-5-bromo-1-hydroxy-4'-methylene-1,3-dihydrospiro[indene-2,3'-pyrrolidin]-2'-one (64); TLC: R_f = 0.40 (petroleum ether /ethyl acetate = 3/1, v/v, UV); white solid (mp: 145-146 °C); yield: 67% (25.7 mg, 0.067 mmol); $[\alpha]_D^{25}$ = 27 (c = 0.1, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.43-7.24 (m, 8H), 5.07 (d, J = 9.2 Hz, 1H), 4.98 (s, 1H), 4.91 (s, 1H), 4.60 (d, J = 14.4 Hz, 1H), 4.50 (d, J = 14.4 Hz, 1H), 4.00 (dt, J = 14.4, 2.4 Hz, 1H), 3.88 (dt, J = 14.4, 2.4 Hz, 1H), 3.74 (d, J = 9.2 Hz, 1H), 3.58 (d, J = 16.4 Hz, 1H), 2.97 (d, J = 16.4 Hz, 1H); ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 174.8, 145.9, 143.3, 141.9, 135.6, 130.7, 129.0, 128.2, 127.9, 127.8, 126.4, 122.9, 108.2, 83.8, 58.9, 50.5, 46.5, 41.7; HRMS (ESI, m/z): calcd for C₂₀H₁₉BrNO₂⁺ [M+H]⁺: 384.0594, found: 384.0596; HPLC: Chiralpak AD-H Column, hexane/ⁱPrOH = 90/10, 1.0 mL/min, 214 nm, 25 °C; RT = 14.3 min (minor), 17.3 min (major), ee: 90%.

Procedure for Formation of 65



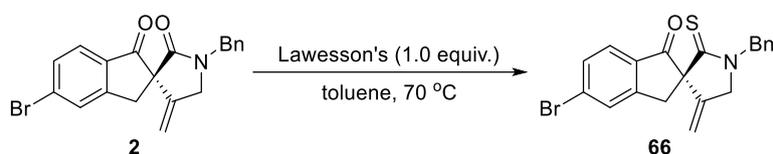
A solution of **34** (0.1 mmol, 1.0 equiv.) in methanol (2 mL) was cooled to 0 °C under a nitrogen atmosphere. To this solution was added sodium borohydride (0.15 mmol, 1.5 equiv.). The mixture was stirred at 0 °C until **34** was completely consumed, as monitored by TLC. After concentration of the solvent in vacuo, the crude product was purified by flash chromatography on silica gel to afford the desired product **65**.



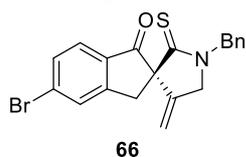
(1*R*,2*R*)-5-bromo-1-hydroxy-1'-methyl-1,1',3,6'-tetrahydro-2'*H*-spiro[indene-2,3'-pyridin]-2'-one (65); TLC: R_f = 0.40 (petroleum ether /ethyl acetate = 1/1, v/v, UV); white solid (mp: 159-160 °C); yield: 84% (25.8 mg, 0.084 mmol); $[\alpha]_D^{25}$ = 37 (c = 0.1, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.36 (d, J = 8.0 Hz, 1H), 7.32 (s, 1H), 7.25 (s, 1H), 5.80-5.73 (m, 1H), 5.70-5.63 (m, 1H), 4.87 (d, J = 7.3 Hz, 1H), 4.13 (d, J = 9.2 Hz, 1H), 3.99 (s, 2H), 3.59 (d, J = 16.4 Hz, 1H), 3.03 (s, 3H), 2.82 (d, J = 16.4

Hz, 1H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 170.9, 143.1, 142.8, 130.5, 127.8, 126.2, 122.5, 120.2, 83.5, 53.1, 50.9, 43.5, 34.5; HRMS (ESI, m/z): calcd for $\text{C}_{14}\text{H}_{15}\text{BrNO}_2^+$ $[\text{M}+\text{H}]^+$: 308.0281, found: 308.0283; HPLC: Chiralpak AD-H Column, hexane/ i PrOH = 95/5, 1.0 mL/min, 214 nm, 25 °C; RT = 21.2 min (major), 23.8 min (minor), ee: 90%.

Procedure for Formation of 66

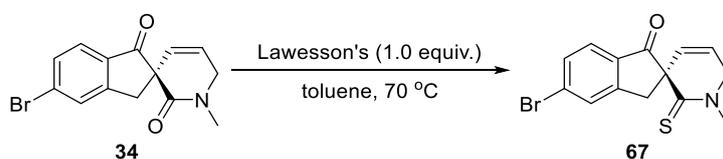


A mixture of Lawesson's reagent (0.1 mmol, 1.0 equiv.) and **2** (0.1 mmol, 1.0 equiv.) in toluene (2 mL) was stirred at 70 °C. until the starting material **2** was completely consumed (as monitored by TLC). After the solvent concentrated in vacuo, the crude product was purified by flash chromatography on silica gel to afford the desired product **66**.

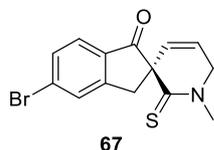


(R)-1'-benzyl-5-bromo-4'-methylene-2'-thioxospiro[indene-2,3'-pyrrolidin]-1(3H)-one (66); TLC: R_f = 0.40 (petroleum ether /ethyl acetate = 5/1, v/v, UV); white solid (mp: 169-170 °C); yield: 93% (37.2 mg, 0.093 mmol); $[\alpha]_D^{25}$ = -201 (c = 0.1, CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.75 (s, 1H), 7.63-7.52 (m, 2H), 7.43-7.31 (m, 5H), 5.29 (d, J = 14.4 Hz, 1H), 5.06-4.97 (m, 2H), 4.90 (s, 1H), 4.53 (d, J = 15.6 Hz, 1H), 4.27 (d, J = 17.6 Hz, 1H), 4.11 (d, J = 14.8 Hz, 1H), 3.25 (d, J = 17.6 Hz, 1H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 200.1, 199.2, 155.6, 142.5, 134.5, 131.9, 131.3, 129.7, 129.1, 128.4, 128.3, 126.9, 108.0, 73.5, 57.3, 52.0, 39.5; HRMS (ESI, m/z): calcd for $\text{C}_{20}\text{H}_{17}\text{BrNOS}^+$ $[\text{M}+\text{H}]^+$: 398.0209, found: 398.0212; HPLC: Chiralpak AD-H Column, hexane/ i PrOH = 90/10, 1.0 mL/min, 214 nm, 25 °C; RT = 15.0 min (major), 19.8 min (minor), ee: 88%.

Procedure for Formation of 67



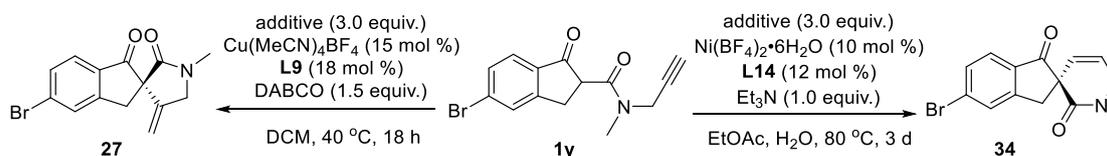
A mixture of Lawesson's reagent (0.1 mmol, 1.0 equiv.) and **34** (0.1 mmol, 1.0 equiv.) in toluene (2 mL) was stirred at 70 °C. until the starting material **34** was completely consumed (as monitored by TLC). After the solvent concentrated in vacuo, the crude product was purified by flash chromatography on silica gel to afford the desired product **67**.



(R)-5-bromo-1'-methyl-2'-thioxo-1',6'-dihydro-2'H-spiro[indene-2,3'-pyridin]-1(3H)-one (67); TLC: $R_f = 0.40$ (petroleum ether /ethyl acetate = 5/1, v/v, UV); white solid (mp: 163-164 °C); yield: 75% (25.9 mg, 0.075 mmol); $[\alpha]_D^{25} = -22$ ($c = 0.1$, CHCl_3); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.68 (s, 1H), 7.60 (d, $J = 8.4$ Hz, 1H), 7.53 (d, $J = 8.0$ Hz, 1H), 6.05-5.97 (m, 1H), 5.59 (d, $J = 10.0$ Hz, 1H), 4.60 (d, $J = 17.2$ Hz, 1H), 4.45 (dt, $J = 18.8, 2.8$ Hz, 1H), 4.14 (dd, $J = 19.2, 3.6$ Hz, 1H), 3.57 (s, 3H), 3.15 (d, $J = 17.6$ Hz, 1H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 201.5, 196.0, 155.8, 132.8, 131.6, 131.2, 129.8, 126.6, 126.5, 122.0, 63.5, 54.0, 44.5, 44.0; HRMS (ESI, m/z): calcd for $\text{C}_{14}\text{H}_{13}\text{BrNOS}^+$ $[\text{M}+\text{H}]^+$: 321.9896, found: 321.9899; HPLC: Chiralpak AD-H Column, hexane/ i PrOH = 97/3, 1.0 mL/min, 214 nm, 25 °C; RT = 19.6 min (major), 30.9 min (minor), ee: 88%.

VIII. Mechanistic Studies

VIII-I Radical inhibition experiments



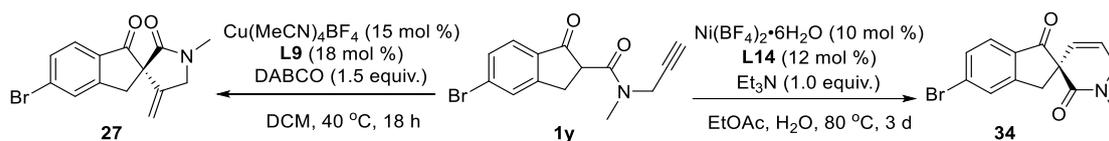
additive:	TEMPO	DPE	BHT
27:	75%, 94% ee	82%, 93% ee	82%, 93% ee
34:	trace	77%, 88% ee	36%, 80% ee

A mixture of $\text{Cu}(\text{MeCN})_4\text{BF}_4$ (0.015 mmol, 15 mol %), **L9** (0.018 mmol, 18 mol %) in dry DCM (1 mL) was stirred at 25 °C under a nitrogen atmosphere for 1.5 h. Subsequently, substrate **1y** (0.10 mmol, 1.0 equiv.) and DABCO (0.15 mmol, 1.5 equiv.)

and dry DCM (1 mL) and additive (0.30 mmol, 3.0 equiv.) were added. The reaction mixture was then stirred at 40 °C under nitrogen. After 18 h, substrate **1y** had completely disappeared (as monitored by TLC). Finally, the crude product was purified by flash chromatography on silica gel to afford the desired product **27**.

A mixture of Ni(BF₄)₂•6H₂O (0.01 mmol, 10 mol %), **L14** (0.012 mmol, 12 mol %) in dry EtOAc (1 mL) was stirred at 25 °C under a nitrogen atmosphere for 1.5 h. Subsequently, substrate **1y** (0.10 mmol, 1.0 equiv.) and Et₃N (0.15 mmol, 1.0 equiv.) and H₂O (5 μL) and dry EtOAc (1 mL) and additive (0.30 mmol, 3.0 equiv.) were added. The reaction mixture was then stirred at 80 °C under nitrogen. After three days, substrate **1y** had completely disappeared (as monitored by TLC). Finally, the crude product was purified by flash chromatography on silica gel to afford the desired product **34**.

VIII-II Nonlinear effect study



The nonlinear effect study experiments were carried out according to the general procedure:

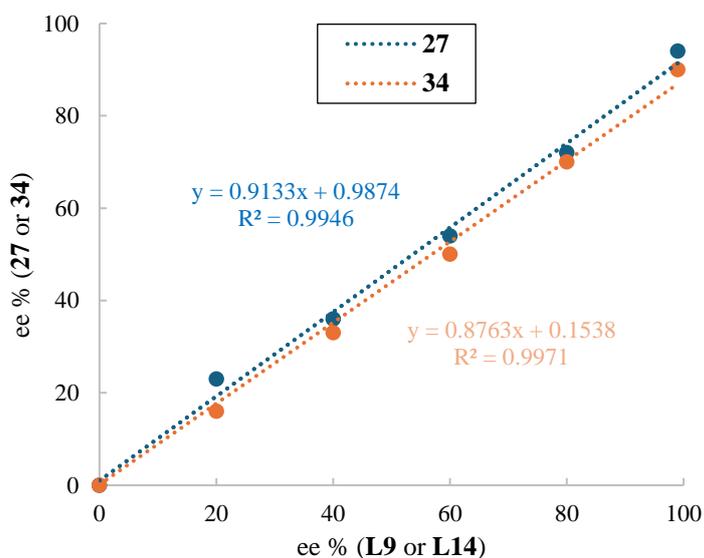
A mixture of Cu(MeCN)₄BF₄ (0.015 mmol, 15 mol %) and **L9** (0.018 mmol, 18 mol %) in dry DCM (1 mL) was stirred at 25 °C under a nitrogen atmosphere for 1.5 h. Subsequently, substrate **1y** (0.10 mmol) and DABCO (0.15 mmol, 1.5 equiv.) and dry DCM (1 mL) were added. The resulting reaction mixture was stirred at 40 °C under a nitrogen atmosphere. After 18 h, the substrate **1y** had completely disappeared (as monitored by TLC). The crude product was purified by flash chromatography on silica gel to afford the desired product **27**. And the ee values were determined by HPLC analysis.

A mixture of Ni(BF₄)₂•6H₂O (0.01 mmol, 10 mol %), **L14** (0.012 mmol, 12 mol %) in dry EtOAc (1 mL) was stirred at 25 °C under a nitrogen atmosphere for 1.5 h. Subsequently, substrate **1y** (0.10 mmol) and Et₃N (0.15 mmol, 1.5 equiv.) and H₂O (5 μL) and dry EtOAc (1 mL) were added. The resulting reaction mixture was stirred at 80 °C under a nitrogen atmosphere. After three days, the substrate **1y** had completely

disappeared (as monitored by TLC). The crude product was purified by flash chromatography on silica gel to afford the desired product **34**. And the ee values were determined by HPLC analysis.

Table S9. Nonlinear effect study comparing the ee of **L9/L14** with the ee of the product **27/34**

entry	ee of L9/L14 (%)	ee of 26 (%)	ee of 34 (%)
1	0	0	0
2	20	23	16
3	40	36	33
4	60	54	50
5	80	72	70
6	99	94	90



Supplementary Fig. 1. Nonlinear effect study comparing the ee of **L9/L14** with the ee of the products **27/34**

VIII-III The effect of ligands and metal salts on regioselectivity and stereoselectivity

A mixture of $\text{Cu}(\text{MeCN})_4\text{BF}_4$ (0.015 mmol, 15 mol %), **L14** (0.018 mmol, 18 mol %) in dry DCM (1 mL) was stirred at 25 °C under a nitrogen atmosphere for 1.5 h. Subsequently, substrate **1y** (0.10 mmol, 1.0 equiv.) and DABCO (0.15 mmol, 1.5 equiv.) and dry DCM (1 mL) were added. The reaction mixture was then stirred at 40 °C under

nitrogen atmosphere. After 18 h, the substrate **1y** had completely disappeared (as monitored by TLC). Finally, the crude product was purified by flash chromatography on silica gel to afford the desired product **27** with 78% yield and 2% ee.

A mixture of Ni(BF₄)₂•6H₂O (0.015 mmol, 15 mol %), **L9** (0.018 mmol, 18 mol %) in dry DCM (1 mL) was stirred at 25 °C under a nitrogen atmosphere for 1.5 h. Subsequently, substrate **1y** (0.10 mmol, 1.0 equiv.) and DABCO (0.15 mmol, 1.5 equiv.) and dry DCM (1 mL) were added. The reaction mixture was then stirred at 40 °C under nitrogen atmosphere. After 18 h, TLC and ¹H NMR analysis indicated that the control reactions did not proceed.

A mixture of Ni(BF₄)₂•6H₂O (0.01 mmol, 10 mol %), **L9** (0.012 mmol, 12 mol %) in dry EtOAc (1 mL) was stirred at 25 °C under a nitrogen atmosphere for 1.5 h. Subsequently, substrate **1y** (0.10 mmol, 1.0 equiv.) and Et₃N (0.15 mmol, 1.0 equiv.) and H₂O (5 μL) and dry EtOAc (1 mL) were added. The reaction mixture was then stirred at 80 °C under nitrogen atmosphere. After three days, the substrate **1y** had completely disappeared (as monitored by TLC). Finally, the crude product was purified by flash chromatography on silica gel to afford the desired product **27** with 24% yield and 38% ee.

A mixture of Cu(MeCN)₄BF₄ (0.01 mmol, 10 mol %), **L14** (0.012 mmol, 12 mol %) in dry EtOAc (1 mL) was stirred at 25 °C under nitrogen atmosphere for 1.5 h. Subsequently, substrate **1y** (0.10 mmol, 1.0 equiv.) and Et₃N (0.15 mmol, 1.0 equiv.) and H₂O (5 μL) and dry EtOAc (1 mL) were added. The reaction mixture was then stirred at 80 °C under nitrogen atmosphere. After three days, the substrate **1y** had completely disappeared (as monitored by TLC). Finally, the crude product was purified by flash chromatography on silica gel to afford the desired product **27** with 72% yield and 10% ee.

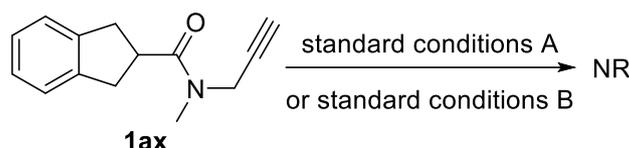
Table S10 The effect of ligands and metals on regioselectivity and stereoselectivity

Variations of reaction conditions		Yield (27/34)	ee (27/34)
standard conditions A		89%/-	94%/-
	L14 instead of L9	78%/-	2%/-
	Ni(BF ₄) ₂ •6H ₂ O instead of Cu(MeCN) ₄ BF ₄	-/-	-/-
standard conditions B		-/88%	-/90%
	L9 instead of L14	24%/-	38%/-
	Cu(MeCN) ₄ BF ₄ instead of Ni(BF ₄) ₂ •6H ₂ O	72%/-	10%/-

VIII-IV Control experiments with other substrates

A mixture of $\text{Cu}(\text{MeCN})_4\text{BF}_4$ (0.015 mmol, 15 mol %), **L9** (0.018 mmol, 18 mol %) in dry DCM (1 mL) was stirred at 25 °C under a nitrogen atmosphere for 1.5 h. Subsequently, substrate **1ax** (0.10 mmol, 1.0 equiv.) and DABCO (0.15 mmol, 1.5 equiv.) and dry DCM (1 mL) were added. The reaction mixture was then stirred at 40 °C under nitrogen. After 18 h, TLC and ^1H NMR analysis indicated that the control reactions did not proceed.

A mixture of $\text{Ni}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.01 mmol, 10 mol %), **L14** (0.012 mmol, 12 mol %) in dry EtOAc (1 mL) was stirred at 25 °C under a nitrogen atmosphere for 1.5 h. Subsequently, substrate **1ax** (0.10 mmol, 1.0 equiv.) and Et_3N (0.15 mmol, 1.0 equiv.) and H_2O (5 μL) and dry EtOAc (1 mL) were added. The reaction mixture was then stirred at 80 °C under nitrogen. After three days, TLC and ^1H NMR analysis indicated that the control reactions did not proceed.



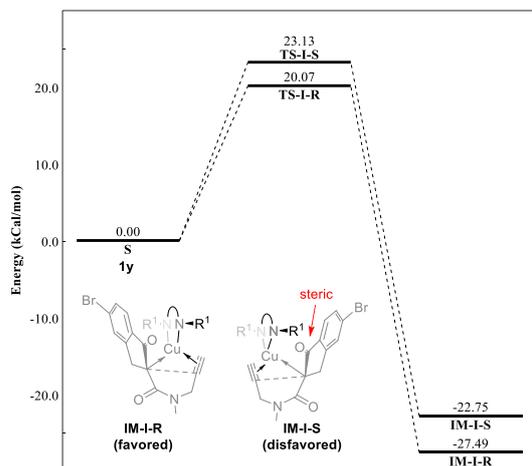
IX. DFT calculations

All quantum chemical calculations were performed using the Gaussian 16 and ORCA 6.0 program packages. The geometries of all stationary points involved on the potential-energy surface were fully optimized in solution using density functional theory (DFT) at the M06-2X/def2-SVP level of theory. Grimme's empirical dispersion correction was included to account for long-range dispersion interactions. Solvent effects were modeled by the SMD/PCM implicit solvation model as implemented in Gaussian 16, with ethyl acetate as the solvent. Frequency analyses were subsequently carried out at the same level of theory to confirm each structure as either a minimum (no imaginary frequencies) or a transition state (exactly one imaginary frequency) and to obtain thermochemical corrections.

Single-point energy refinements on the optimized geometries were then performed using ORCA 6.0 at the wb97M-V/def2-TZVP level of theory employing the RIJCOSX approximation with the def2/J auxiliary basis set to accelerate the exchange–correlation computations. Tight self-consistent-field convergence criteria (TIGHTSCF) were

applied. Solvent effects were consistently included using the SMD continuum solvation model with ethyl acetate. The reported relative Gibbs free energies were obtained by combining the electronic energies from the single-point ORCA calculations with thermal and zero-point energy corrections derived from the Gaussian frequency calculations (all referring to 298.15 K and 1 atm unless otherwise stated).

a. DFT calculations for spirocyclic γ -lactams



b. DFT calculations for spirocyclic δ -lactams

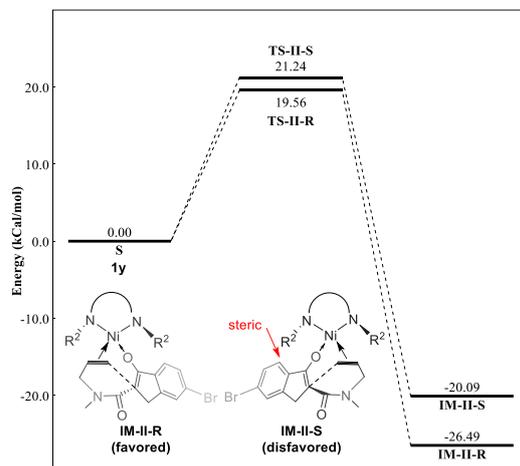
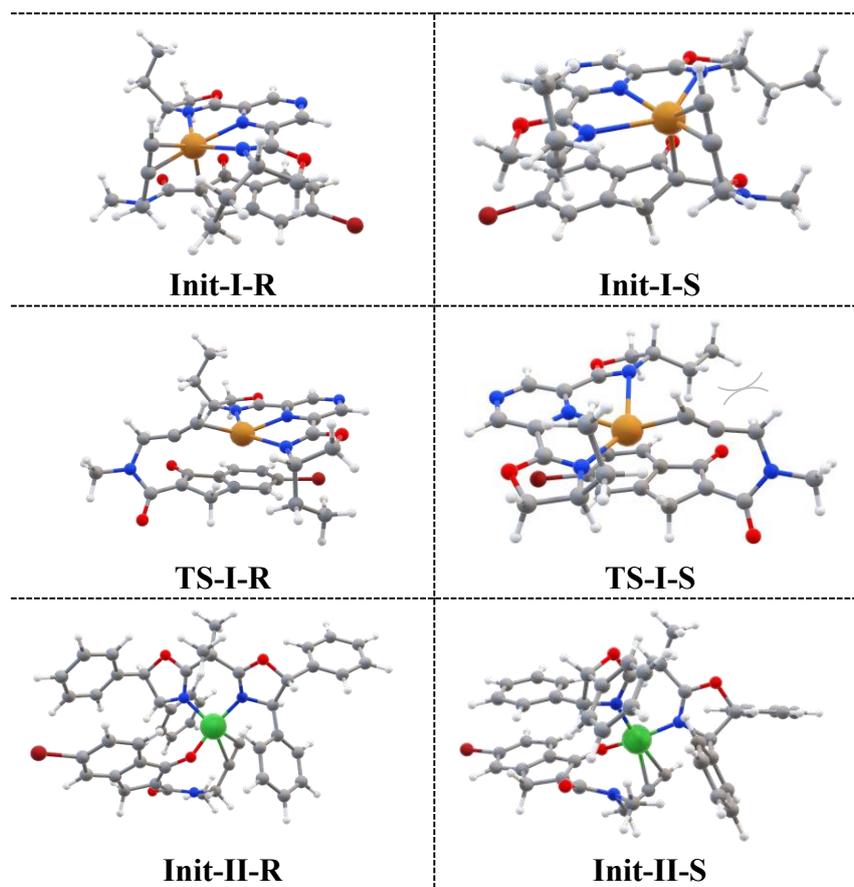
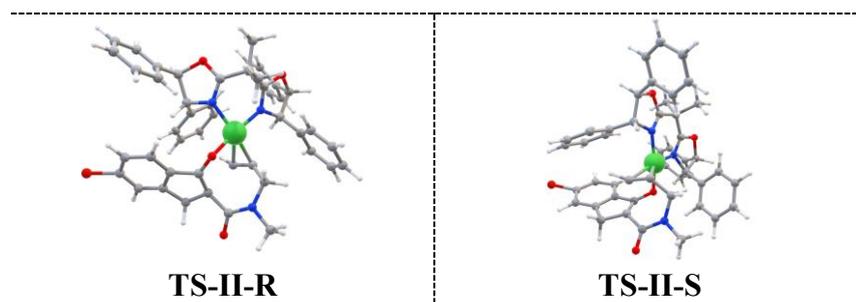


Table S11 The graphs for plausible intermediates/transition states





Init-I-R.xyz

N	-1.227000	1.237000	2.176000
O	-3.101000	0.034000	1.832000
C	-1.758000	0.137000	1.832000
C	-2.347000	2.093000	2.612000
C	-3.581000	1.372000	2.041000
C	-1.031000	-1.112000	1.516000
C	-1.673000	-2.357000	1.559000
C	-2.206000	3.566000	2.243000
C	-1.821000	3.817000	0.793000
H	-2.371000	2.026000	3.714000
H	-3.900000	1.778000	1.067000
H	-4.436000	1.341000	2.724000
H	-2.741000	-2.413000	1.784000
H	-0.807000	3.435000	0.615000
N	2.926000	-0.863000	0.599000
O	3.007000	-3.065000	0.177000
C	2.338000	-1.991000	0.590000
C	4.276000	-1.083000	0.065000
C	4.213000	-2.550000	-0.424000
C	0.922000	-2.154000	0.979000
C	0.279000	-3.395000	1.036000
C	5.337000	-0.805000	1.131000
C	5.172000	-1.644000	2.393000
H	4.411000	-0.407000	-0.790000
H	5.057000	-3.171000	-0.100000
H	4.086000	-2.608000	-1.512000

H	0.836000	-4.312000	0.830000
H	5.979000	-1.441000	3.110000
Cu	1.410000	0.717000	0.545000
N	0.264000	-1.023000	1.230000
Br	-5.267000	-0.755000	-0.981000
O	3.245000	0.637000	-2.505000
O	1.562000	-1.644000	-1.964000
N	2.531000	2.685000	-1.879000
C	1.014000	0.734000	-1.714000
C	1.860000	2.921000	0.486000
C	1.911000	2.600000	1.663000
H	1.981000	2.429000	2.724000
C	1.795000	3.454000	-0.899000
H	0.741000	3.575000	-1.175000
H	2.214000	4.470000	-0.878000
C	2.314000	1.308000	-2.063000
C	0.787000	-0.690000	-1.865000
C	-0.699000	-0.889000	-1.784000
C	-1.405000	-2.086000	-1.744000
H	-0.877000	-3.037000	-1.852000
C	-2.782000	-2.043000	-1.526000
H	-3.369000	-2.960000	-1.458000
C	-3.409000	-0.803000	-1.364000
C	-2.713000	0.404000	-1.451000
H	-3.237000	1.356000	-1.343000
C	-1.339000	0.343000	-1.667000
C	-0.332000	1.461000	-1.721000
H	-0.516000	2.117000	-0.858000
H	-0.486000	2.078000	-2.626000
C	3.884000	3.153000	-2.135000
H	4.274000	2.660000	-3.030000
H	4.569000	2.927000	-1.297000
H	5.292000	0.267000	1.383000
H	6.326000	-0.980000	0.678000

H	5.191000	-2.722000	2.170000
H	4.216000	-1.421000	2.889000
H	-1.445000	4.013000	2.901000
H	-3.157000	4.065000	2.489000
H	-1.827000	4.891000	0.565000
H	-2.505000	3.322000	0.087000
H	3.867000	4.238000	-2.297000
N	-1.013000	-3.489000	1.333000
Init-I-S.xyz			
N	-1.243000	-1.256000	1.345000
O	-3.158000	-0.135000	1.726000
C	-1.829000	-0.151000	1.558000
C	-2.279000	-2.292000	1.366000
C	-3.597000	-1.494000	1.553000
C	-1.136000	1.153000	1.587000
C	-1.793000	2.376000	1.758000
H	-4.255000	-1.529000	0.675000
H	-4.167000	-1.793000	2.444000
H	-2.869000	2.403000	1.948000
N	2.877000	0.988000	1.128000
O	2.996000	3.197000	0.746000
C	2.282000	2.108000	1.036000
C	4.304000	1.257000	0.899000
C	4.288000	2.695000	0.342000
C	0.834000	2.255000	1.280000
C	0.170000	3.480000	1.420000
H	5.061000	3.356000	0.748000
H	4.317000	2.699000	-0.758000
H	0.719000	4.420000	1.326000
Cu	1.302000	-0.625000	0.638000
N	0.173000	1.108000	1.376000
Br	-5.403000	0.398000	-1.387000
O	3.114000	-0.384000	-2.680000
O	1.431000	1.770000	-1.606000

N	2.695000	-2.434000	-1.837000
C	1.015000	-0.645000	-1.603000
C	2.131000	-2.737000	0.551000
C	2.222000	-2.424000	1.726000
H	2.354000	-2.237000	2.779000
C	2.052000	-3.258000	-0.836000
H	0.997000	-3.443000	-1.074000
H	2.538000	-4.243000	-0.845000
C	2.327000	-1.109000	-2.078000
C	0.708000	0.771000	-1.639000
C	-0.791000	0.870000	-1.644000
C	-1.577000	2.014000	-1.549000
H	-1.107000	2.999000	-1.502000
C	-2.963000	1.871000	-1.483000
H	-3.614000	2.740000	-1.384000
C	-3.518000	0.586000	-1.530000
C	-2.737000	-0.563000	-1.667000
H	-3.202000	-1.550000	-1.719000
C	-1.355000	-0.401000	-1.721000
C	-0.276000	-1.452000	-1.770000
H	-0.478000	-2.185000	-0.973000
H	-0.312000	-1.999000	-2.729000
C	4.032000	-2.840000	-2.232000
H	4.320000	-2.286000	-3.130000
H	4.779000	-2.630000	-1.446000
H	4.042000	-3.916000	-2.449000
C	4.953000	0.227000	-0.011000
H	4.774000	-0.768000	0.429000
H	4.440000	0.241000	-0.984000
C	6.448000	0.469000	-0.188000
H	6.896000	-0.302000	-0.830000
H	6.974000	0.453000	0.779000
H	6.643000	1.444000	-0.660000
H	4.804000	1.230000	1.884000

C	-1.998000	-3.327000	2.459000
H	-1.087000	-3.877000	2.179000
H	-2.823000	-4.057000	2.456000
C	-1.827000	-2.714000	3.844000
H	-2.709000	-2.126000	4.143000
H	-0.954000	-2.047000	3.868000
H	-1.680000	-3.495000	4.602000
H	-2.277000	-2.805000	0.391000
N	-1.134000	3.529000	1.676000
TS-I-R.xyz			
N	-1.555000	-1.936000	-1.404000
O	-3.726000	-2.069000	-1.974000
C	-2.675000	-1.355000	-1.557000
C	-1.803000	-3.366000	-1.657000
C	-3.185000	-3.356000	-2.343000
C	-2.880000	0.081000	-1.272000
C	-4.126000	0.723000	-1.230000
C	-1.765000	-4.140000	-0.334000
C	-2.909000	-3.810000	0.621000
H	-1.025000	-3.755000	-2.328000
H	-3.869000	-4.137000	-1.993000
H	-3.114000	-3.390000	-3.438000
H	-5.043000	0.173000	-1.451000
H	-2.999000	-2.728000	0.806000
N	0.549000	2.056000	-0.636000
O	-0.506000	3.948000	-0.055000
C	-0.542000	2.679000	-0.465000
C	1.638000	2.998000	-0.360000
C	0.888000	4.237000	0.196000
C	-1.853000	2.038000	-0.709000
C	-3.097000	2.673000	-0.638000
C	2.452000	3.265000	-1.629000
C	1.611000	3.744000	-2.806000
H	2.306000	2.555000	0.397000

H	1.145000	5.174000	-0.314000
H	1.015000	4.365000	1.279000
H	-3.169000	3.728000	-0.366000
H	2.246000	3.990000	-3.668000
Cu	0.219000	-0.209000	-0.888000
N	-1.768000	0.752000	-1.025000
Br	-3.131000	0.260000	2.300000
O	4.551000	-3.078000	1.199000
O	3.790000	0.934000	1.595000
N	5.098000	-1.345000	-0.178000
C	3.007000	-1.272000	0.925000
C	3.100000	-0.576000	-1.279000
C	2.048000	-0.687000	-1.935000
H	1.623000	-0.715000	-2.933000
C	4.528000	-0.296000	-0.998000
H	5.060000	-0.260000	-1.963000
H	4.617000	0.691000	-0.514000
C	4.268000	-1.994000	0.697000
C	2.928000	0.047000	1.469000
C	1.492000	0.235000	1.846000
C	0.878000	1.351000	2.409000
H	1.477000	2.218000	2.695000
C	-0.508000	1.348000	2.570000
H	-1.028000	2.215000	2.979000
C	-1.236000	0.221000	2.173000
C	-0.625000	-0.932000	1.673000
H	-1.216000	-1.807000	1.405000
C	0.763000	-0.916000	1.521000
C	1.704000	-2.000000	1.052000
H	1.369000	-2.429000	0.087000
H	1.747000	-2.826000	1.782000
C	6.432000	-1.818000	-0.460000
H	6.663000	-2.620000	0.249000
H	7.169000	-1.009000	-0.346000

H	2.973000	2.332000	-1.894000
H	3.228000	4.005000	-1.378000
H	1.031000	4.646000	-2.555000
H	0.902000	2.966000	-3.121000
H	-0.793000	-3.934000	0.142000
H	-1.774000	-5.216000	-0.568000
H	-2.751000	-4.297000	1.593000
H	-3.877000	-4.157000	0.233000
H	6.509000	-2.218000	-1.485000
N	-4.219000	2.010000	-0.911000
TS-I-S.xyz			
N	-1.240000	2.423000	-0.347000
O	-3.364000	3.123000	-0.515000
C	-2.465000	2.142000	-0.538000
C	-1.147000	3.881000	-0.216000
C	-2.633000	4.323000	-0.177000
C	-2.922000	0.760000	-0.801000
C	-4.259000	0.350000	-0.848000
H	-2.958000	4.646000	0.820000
H	-2.884000	5.098000	-0.912000
H	-5.068000	1.072000	-0.712000
N	0.038000	-1.826000	-1.854000
O	-1.266000	-3.583000	-1.328000
C	-1.087000	-2.263000	-1.464000
C	0.866000	-3.010000	-2.128000
C	0.044000	-4.162000	-1.510000
C	-2.243000	-1.380000	-1.195000
C	-3.581000	-1.797000	-1.203000
H	-0.051000	-5.049000	-2.145000
H	0.426000	-4.455000	-0.518000
H	-3.831000	-2.849000	-1.357000
Cu	0.112000	0.616000	-0.770000
N	-1.937000	-0.107000	-0.993000
Br	-3.276000	-1.026000	2.362000

O	4.472000	2.262000	2.221000
O	3.604000	-1.655000	1.210000
N	5.021000	1.050000	0.371000
C	2.907000	0.669000	1.374000
C	3.062000	0.729000	-1.006000
C	2.027000	1.052000	-1.612000
H	1.625000	1.394000	-2.562000
C	4.465000	0.331000	-0.756000
H	5.042000	0.577000	-1.662000
H	4.504000	-0.761000	-0.602000
C	4.182000	1.395000	1.400000
C	2.769000	-0.748000	1.371000
C	1.307000	-1.003000	1.585000
C	0.637000	-2.223000	1.643000
H	1.192000	-3.156000	1.524000
C	-0.739000	-2.228000	1.872000
H	-1.299000	-3.163000	1.910000
C	-1.401000	-1.010000	2.061000
C	-0.739000	0.218000	2.031000
H	-1.282000	1.150000	2.199000
C	0.635000	0.210000	1.784000
C	1.624000	1.352000	1.739000
H	1.321000	2.108000	0.987000
H	1.677000	1.871000	2.711000
C	6.361000	1.578000	0.275000
H	6.591000	2.090000	1.215000
H	7.091000	0.771000	0.113000
H	6.452000	2.301000	-0.553000
C	-0.332000	4.460000	-1.376000
H	0.707000	4.113000	-1.262000
H	-0.315000	5.555000	-1.263000
C	-0.865000	4.067000	-2.748000
H	-0.793000	2.979000	-2.898000
H	-0.290000	4.556000	-3.545000

H	-1.920000	4.354000	-2.877000
H	-0.644000	4.124000	0.730000
H	0.909000	-3.122000	-3.226000
C	2.286000	-2.872000	-1.603000
H	2.733000	-1.982000	-2.072000
H	2.268000	-2.667000	-0.522000
C	3.136000	-4.105000	-1.888000
H	2.723000	-5.003000	-1.403000
H	4.156000	-3.967000	-1.505000
H	3.202000	-4.306000	-2.968000
N	-4.573000	-0.926000	-1.049000

Init-II-R. xyz

Ni	1.020000	0.532000	-0.106000
O	3.598000	-2.583000	-0.376000
O	-0.394000	-2.539000	2.151000
N	2.580000	-0.649000	-0.022000
N	-0.023000	-0.819000	0.814000
C	2.551000	-1.930000	0.086000
C	4.472000	-1.643000	-1.052000
C	3.844000	-0.268000	-0.682000
H	4.488000	0.243000	0.052000
C	3.592000	0.655000	-1.850000
C	2.463000	0.480000	-2.658000
H	1.780000	-0.359000	-2.489000
C	2.185000	1.381000	-3.685000
H	1.290000	1.249000	-4.294000
C	3.053000	2.446000	-3.929000
H	2.839000	3.151000	-4.733000
C	4.199000	2.603000	-3.148000
H	4.882000	3.431000	-3.341000
C	4.464000	1.715000	-2.107000
H	5.345000	1.858000	-1.477000
C	5.899000	-1.810000	-0.620000
C	6.213000	-2.098000	0.712000

H	5.414000	-2.275000	1.436000
C	7.544000	-2.182000	1.110000
H	7.788000	-2.420000	2.146000
C	8.566000	-1.969000	0.183000
H	9.609000	-2.036000	0.497000
C	8.255000	-1.677000	-1.144000
H	9.052000	-1.518000	-1.871000
C	6.922000	-1.603000	-1.548000
H	6.678000	-1.388000	-2.591000
H	4.367000	-1.837000	-2.130000
C	1.461000	-2.812000	0.644000
C	2.061000	-3.703000	1.746000
H	2.879000	-4.300000	1.325000
H	1.286000	-4.373000	2.135000
H	2.448000	-3.100000	2.580000
C	0.905000	-3.676000	-0.512000
H	0.503000	-3.044000	-1.317000
H	0.097000	-4.314000	-0.132000
H	1.704000	-4.312000	-0.913000
C	0.326000	-1.990000	1.192000
C	-1.519000	-1.659000	2.409000
C	-1.082000	-0.338000	1.722000
H	-1.913000	0.072000	1.136000
C	-0.503000	0.746000	2.608000
C	0.724000	0.562000	3.261000
H	1.257000	-0.390000	3.177000
C	1.277000	1.590000	4.020000
H	2.227000	1.436000	4.535000
C	0.614000	2.815000	4.126000
H	1.053000	3.623000	4.713000
C	-0.611000	3.001000	3.489000
H	-1.143000	3.951000	3.548000
C	-1.170000	1.964000	2.740000
H	-2.128000	2.123000	2.241000

H	-1.590000	-1.553000	3.500000
C	-2.787000	-2.238000	1.822000
C	-3.940000	-1.443000	1.807000
H	-3.913000	-0.426000	2.207000
C	-5.128000	-1.944000	1.285000
H	-6.020000	-1.317000	1.266000
C	-5.175000	-3.241000	0.769000
H	-6.106000	-3.625000	0.352000
C	-4.031000	-4.033000	0.785000
H	-4.065000	-5.050000	0.391000
C	-2.838000	-3.536000	1.315000
H	-1.952000	-4.170000	1.350000
Br	-6.664000	-1.468000	-2.034000
O	-0.376000	1.386000	-0.904000
O	-2.309000	4.592000	1.288000
N	-0.312000	4.473000	0.248000
C	-2.181000	2.898000	-0.299000
C	-1.629000	1.724000	-0.754000
C	-2.719000	0.799000	-1.127000
C	-3.946000	1.428000	-0.888000
C	-3.690000	2.803000	-0.336000
H	-4.118000	2.942000	0.670000
H	-4.138000	3.590000	-0.965000
C	-5.138000	0.768000	-1.167000
H	-6.108000	1.238000	-1.004000
C	-5.059000	-0.535000	-1.665000
C	-3.836000	-1.180000	-1.884000
H	-3.829000	-2.201000	-2.264000
C	-2.647000	-0.504000	-1.616000
H	-1.679000	-0.979000	-1.789000
C	-1.607000	4.041000	0.454000
C	0.237000	5.487000	1.129000
H	-0.574000	5.902000	1.733000
H	0.695000	6.293000	0.535000

H	1.006000	5.057000	1.794000
C	0.610000	3.935000	-0.719000
H	1.179000	4.761000	-1.178000
C	1.588000	3.028000	-0.079000
C	2.375000	2.365000	0.571000
H	3.124000	1.912000	1.198000
H	0.087000	3.400000	-1.518000

Init-II-S. xyz

Ni	-0.606000	-0.775000	-0.456000
O	-4.142000	-1.024000	1.582000
O	-0.704000	1.366000	3.005000
N	-2.493000	-0.843000	0.111000
N	-0.242000	0.362000	1.088000
C	-2.866000	-0.835000	1.344000
C	-4.793000	-1.337000	0.318000
C	-3.709000	-0.924000	-0.720000
C	-1.968000	-0.657000	2.546000
C	-2.776000	-0.210000	3.767000
H	-3.508000	-0.983000	4.028000
H	-2.096000	-0.052000	4.613000
H	-3.312000	0.727000	3.569000
C	-1.264000	-2.008000	2.810000
H	-0.656000	-2.315000	1.946000
H	-0.608000	-1.913000	3.687000
H	-2.018000	-2.779000	3.019000
C	-0.933000	0.375000	2.168000
C	0.071000	2.347000	2.257000
C	0.744000	1.457000	1.188000
Br	8.113000	-1.587000	-0.270000
O	1.169000	-1.161000	-0.772000
O	1.216000	2.865000	-1.925000
N	-0.045000	1.084000	-2.534000
C	2.270000	0.760000	-1.792000
C	2.193000	-0.465000	-1.161000

C	3.565000	-0.934000	-0.893000
C	4.465000	0.052000	-1.314000
C	3.705000	1.216000	-1.893000
H	3.876000	2.140000	-1.316000
H	4.014000	1.429000	-2.929000
C	5.834000	-0.132000	-1.147000
H	6.558000	0.621000	-1.458000
C	6.262000	-1.320000	-0.550000
C	5.366000	-2.316000	-0.142000
H	5.752000	-3.230000	0.310000
C	3.998000	-2.123000	-0.313000
H	3.278000	-2.878000	0.005000
C	1.160000	1.656000	-2.092000
C	-1.121000	2.024000	-2.826000
H	-1.245000	2.712000	-1.983000
H	-0.894000	2.622000	-3.725000
H	-2.055000	1.469000	-2.978000
C	-0.031000	-0.129000	-3.330000
H	-0.481000	0.051000	-4.320000
C	-0.751000	-1.250000	-2.686000
C	-1.257000	-2.221000	-2.154000
H	-1.714000	-3.125000	-1.786000
H	1.006000	-0.460000	-3.488000
C	-0.875000	3.397000	1.703000
C	-2.073000	3.682000	2.371000
C	-0.540000	4.123000	0.554000
C	-2.924000	4.679000	1.896000
H	-2.331000	3.134000	3.278000
C	-1.394000	5.122000	0.086000
H	0.379000	3.925000	-0.002000
C	-2.583000	5.405000	0.755000
H	-3.850000	4.899000	2.430000
H	-1.117000	5.681000	-0.809000
H	-3.243000	6.195000	0.391000

C	2.120000	0.981000	1.600000
C	3.195000	1.850000	1.379000
C	2.344000	-0.243000	2.229000
C	4.480000	1.493000	1.774000
H	3.019000	2.807000	0.877000
C	3.634000	-0.598000	2.628000
H	1.521000	-0.942000	2.379000
C	4.703000	0.264000	2.399000
H	5.315000	2.169000	1.585000
H	3.806000	-1.564000	3.106000
H	5.713000	-0.024000	2.695000
H	0.816000	1.989000	0.234000
H	0.799000	2.776000	2.956000
C	-3.993000	0.390000	-1.409000
C	-4.499000	0.381000	-2.712000
C	-3.823000	1.609000	-0.743000
C	-4.833000	1.578000	-3.345000
H	-4.631000	-0.569000	-3.236000
C	-4.160000	2.804000	-1.375000
H	-3.412000	1.645000	0.271000
C	-4.664000	2.790000	-2.677000
H	-5.225000	1.563000	-4.363000
H	-4.016000	3.747000	-0.848000
H	-4.923000	3.727000	-3.171000
C	-5.170000	-2.793000	0.287000
C	-4.183000	-3.781000	0.414000
C	-6.500000	-3.170000	0.112000
C	-4.529000	-5.128000	0.370000
H	-3.135000	-3.498000	0.555000
C	-6.847000	-4.521000	0.059000
H	-7.274000	-2.405000	0.018000
C	-5.864000	-5.499000	0.190000
H	-3.760000	-5.894000	0.477000
H	-7.890000	-4.808000	-0.079000

H	-6.136000	-6.554000	0.153000
H	-5.681000	-0.698000	0.253000
H	-3.609000	-1.712000	-1.475000
TS-II-R. xyz			
Ni	0.856000	0.424000	-0.758000
O	4.038000	-2.117000	-0.460000
O	-0.016000	-3.540000	-0.801000
N	2.535000	-0.495000	-0.406000
N	-0.000000	-1.332000	-0.970000
C	2.854000	-1.666000	-0.826000
C	4.534000	-1.218000	0.559000
C	3.694000	0.067000	0.308000
H	3.358000	0.497000	1.260000
C	4.394000	1.135000	-0.505000
C	4.496000	1.048000	-1.896000
H	4.039000	0.214000	-2.432000
C	5.169000	2.036000	-2.616000
H	5.241000	1.961000	-3.702000
C	5.747000	3.116000	-1.950000
H	6.272000	3.889000	-2.514000
C	5.651000	3.206000	-0.561000
H	6.096000	4.051000	-0.035000
C	4.976000	2.221000	0.157000
H	4.880000	2.308000	1.242000
C	4.291000	-1.800000	1.935000
C	3.615000	-3.005000	2.130000
H	3.291000	-3.595000	1.271000
C	3.372000	-3.471000	3.424000
H	2.845000	-4.415000	3.568000
C	3.813000	-2.742000	4.526000
H	3.630000	-3.112000	5.536000
C	4.501000	-1.542000	4.334000
H	4.860000	-0.973000	5.192000
C	4.737000	-1.073000	3.045000

H	5.281000	-0.135000	2.900000
H	5.603000	-1.062000	0.366000
C	2.005000	-2.542000	-1.731000
C	2.502000	-3.988000	-1.744000
H	3.535000	-4.022000	-2.111000
H	1.863000	-4.586000	-2.405000
H	2.467000	-4.436000	-0.743000
C	2.031000	-1.934000	-3.151000
H	1.666000	-0.897000	-3.146000
H	1.391000	-2.529000	-3.815000
H	3.057000	-1.956000	-3.543000
C	0.601000	-2.443000	-1.178000
C	-1.339000	-3.147000	-0.300000
C	-1.186000	-1.610000	-0.140000
H	-2.063000	-1.092000	-0.542000
C	-0.914000	-1.107000	1.267000
C	0.310000	-1.387000	1.893000
H	1.052000	-2.022000	1.404000
C	0.607000	-0.862000	3.148000
H	1.568000	-1.092000	3.615000
C	-0.329000	-0.052000	3.799000
H	-0.102000	0.367000	4.780000
C	-1.562000	0.204000	3.198000
H	-2.306000	0.818000	3.710000
C	-1.856000	-0.323000	1.938000
H	-2.824000	-0.117000	1.475000
H	-1.463000	-3.658000	0.662000
C	-2.396000	-3.572000	-1.282000
C	-3.221000	-4.660000	-0.992000
H	-3.102000	-5.195000	-0.048000
C	-4.199000	-5.062000	-1.902000
H	-4.844000	-5.909000	-1.667000
C	-4.352000	-4.380000	-3.107000
H	-5.117000	-4.694000	-3.819000

C	-3.527000	-3.293000	-3.405000
H	-3.648000	-2.757000	-4.347000
C	-2.556000	-2.886000	-2.494000
H	-1.921000	-2.027000	-2.730000
Br	-6.974000	1.008000	1.354000
O	-0.637000	1.349000	-1.481000
O	-0.675000	5.566000	-0.209000
N	0.887000	4.324000	-1.247000
C	-1.016000	3.260000	0.013000
C	-1.369000	2.108000	-0.741000
C	-2.763000	1.755000	-0.437000
C	-3.220000	2.568000	0.605000
C	-2.177000	3.596000	0.935000
H	-1.884000	3.557000	1.998000
H	-2.532000	4.618000	0.744000
C	-4.473000	2.345000	1.167000
H	-4.847000	2.949000	1.995000
C	-5.265000	1.330000	0.622000
C	-4.838000	0.557000	-0.468000
H	-5.504000	-0.200000	-0.884000
C	-3.573000	0.769000	-1.006000
H	-3.222000	0.186000	-1.859000
C	-0.239000	4.460000	-0.467000
C	1.453000	5.542000	-1.804000
H	0.653000	6.274000	-1.949000
H	1.922000	5.312000	-2.771000
H	2.209000	5.983000	-1.133000
C	1.764000	3.174000	-1.290000
H	2.810000	3.528000	-1.310000
C	1.583000	2.297000	-0.112000
C	0.724000	2.138000	0.790000
H	0.322000	1.673000	1.688000
H	1.626000	2.585000	-2.215000

TS-II-S. xyz

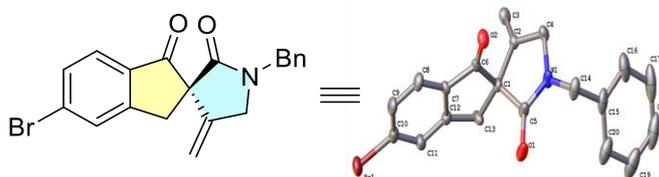
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O	2.034000	2.874000	2.161000
N	1.629000	-1.059000	0.635000
N	1.020000	1.614000	0.652000
C	2.216000	-0.791000	1.748000
C	2.556000	-3.009000	1.596000
C	1.583000	-2.526000	0.488000
C	2.484000	0.545000	2.387000
C	2.028000	0.508000	3.859000
H	2.585000	-0.270000	4.395000
H	2.229000	1.481000	4.324000
H	0.954000	0.287000	3.937000
C	4.008000	0.799000	2.301000
H	4.338000	0.843000	1.253000
H	4.247000	1.749000	2.794000
H	4.539000	-0.018000	2.805000
C	1.785000	1.670000	1.677000
C	1.218000	3.823000	1.432000
C	0.748000	2.997000	0.202000
Br	-6.388000	-1.895000	1.216000
O	-0.693000	1.221000	-1.360000
O	-1.709000	0.131000	-5.271000
N	0.272000	0.499000	-4.247000
C	-1.730000	-0.249000	-2.969000
C	-1.671000	0.484000	-1.779000
C	-2.816000	0.113000	-0.940000
C	-3.590000	-0.830000	-1.631000
C	-3.021000	-1.034000	-3.012000
H	-2.867000	-2.097000	-3.256000
H	-3.679000	-0.625000	-3.796000
C	-4.674000	-1.434000	-1.002000
H	-5.281000	-2.190000	-1.502000
C	-4.968000	-1.044000	0.306000

C	-4.225000	-0.066000	0.983000
H	-4.509000	0.216000	1.997000
C	-3.126000	0.515000	0.360000
H	-2.518000	1.266000	0.871000
C	-1.051000	0.118000	-4.248000
C	0.791000	0.984000	-5.517000
H	0.014000	1.563000	-6.026000
H	1.664000	1.622000	-5.325000
H	1.086000	0.154000	-6.181000
C	1.313000	0.090000	-3.310000
H	2.167000	-0.279000	-3.901000
C	0.902000	-0.979000	-2.369000
C	-0.220000	-1.432000	-2.006000
H	-0.846000	-2.172000	-1.515000
H	1.695000	0.964000	-2.746000
C	0.167000	-3.048000	0.621000
C	-0.173000	-4.242000	-0.026000
C	-0.814000	-2.355000	1.337000
C	-1.480000	-4.723000	0.023000
H	0.586000	-4.783000	-0.597000
C	-2.123000	-2.838000	1.388000
H	-0.573000	-1.417000	1.844000
C	-2.461000	-4.016000	0.723000
H	-1.737000	-5.647000	-0.495000
H	-2.885000	-2.289000	1.941000
H	-3.488000	-4.381000	0.754000
H	1.965000	-2.794000	-0.506000
C	3.921000	-3.427000	1.122000
C	4.565000	-2.730000	0.091000
C	4.572000	-4.495000	1.742000
C	5.848000	-3.096000	-0.306000
H	4.060000	-1.901000	-0.416000
C	5.855000	-4.866000	1.339000
H	4.073000	-5.042000	2.545000

C	6.493000	-4.166000	0.318000
H	6.344000	-2.554000	-1.111000
H	6.355000	-5.705000	1.824000
H	7.495000	-4.457000	0.001000
H	2.106000	-3.778000	2.234000
C	0.076000	4.312000	2.287000
C	-0.439000	3.543000	3.332000
C	-0.523000	5.533000	1.966000
C	-1.550000	3.990000	4.047000
H	0.036000	2.600000	3.608000
C	-1.635000	5.976000	2.679000
H	-0.117000	6.143000	1.156000
C	-2.151000	5.204000	3.720000
H	-1.943000	3.390000	4.870000
H	-2.095000	6.932000	2.426000
H	-3.017000	5.555000	4.282000
C	1.505000	3.267000	-1.081000
C	2.902000	3.165000	-1.107000
C	0.820000	3.596000	-2.253000
C	3.604000	3.381000	-2.291000
H	3.452000	2.923000	-0.192000
C	1.523000	3.821000	-3.436000
H	-0.269000	3.649000	-2.241000
C	2.913000	3.709000	-3.458000
H	4.692000	3.304000	-2.301000
H	0.979000	4.080000	-4.346000
H	3.461000	3.885000	-4.385000
H	-0.327000	3.113000	0.027000
H	1.872000	4.653000	1.137000

X. Crystallographic Data

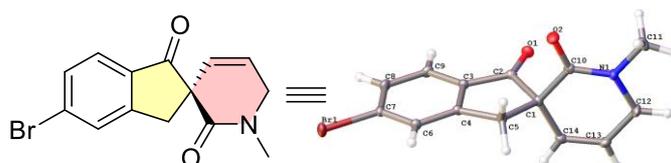
Table S12. Crystal data and structure refinement for **2** (CCDC: 2446985).



Identification code	240401cx	
Empirical formula	C ₂₀ H ₁₆ BrNO ₂	
Formula weight	382.25	
Temperature	170.00 K	
Wavelength	1.34139 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 7.1741(4) Å	a = 90°.
	b = 10.3025(6) Å	b = 92.447(2)°.
	c = 22.7770(11) Å	g = 90°.
Volume	1681.94(16) Å ³	
Z	4	
Density (calculated)	1.510 Mg/m ³	
Absorption coefficient	2.257 mm ⁻¹	
F(000)	776	
Crystal size	0.17 x 0.17 x 0.05 mm ³	
Theta range for data collection	3.379 to 54.972°.	
Index ranges	-8 ≤ h ≤ 8, -12 ≤ k ≤ 12, -26 ≤ l ≤ 27	
Reflections collected	16379	
Independent reflections	5997 [R(int) = 0.0579]	
Completeness to theta = 53.594°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7508 and 0.4593	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5997 / 190 / 476	

Goodness-of-fit on F^2	1.098
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0630$, $wR2 = 0.1806$
R indices (all data)	$R1 = 0.0740$, $wR2 = 0.1883$
Absolute structure parameter	0.061(17)
Extinction coefficient	n/a
Largest diff. peak and hole	1.398 and -0.819 e.Å ⁻³

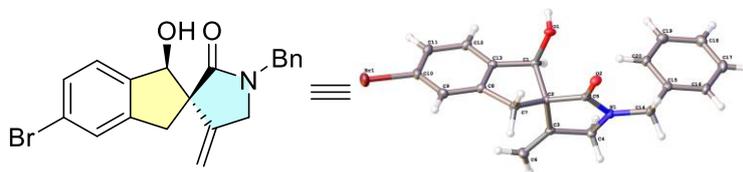
Table S13. Crystal data and structure refinement for 34 (CCDC: 2446987).



Identification code	240827wsh
Empirical formula	$C_{14}H_{12}BrNO_2$
Formula weight	306.16
Temperature	170.00 K
Wavelength	1.34139 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	$a = 7.13760(10)$ Å $a = 90^\circ$. $b = 7.65440(10)$ Å $b = 90^\circ$. $c = 22.3119(4)$ Å $g = 90^\circ$.
Volume	$1218.99(3)$ Å ³
Z	4
Density (calculated)	1.668 Mg/m ³
Absorption coefficient	3.001 mm ⁻¹
F(000)	616
Crystal size	$0.17 \times 0.17 \times 0.05$ mm ³
Theta range for data collection	3.447 to 54.947° .
Index ranges	$-8 \leq h \leq 8$, $-9 \leq k \leq 9$, $-25 \leq l \leq 27$
Reflections collected	11484
Independent reflections	2298 [$R(\text{int}) = 0.0544$]
Completeness to $\theta = 53.594^\circ$	99.2 %
Absorption correction	Semi-empirical from equivalents

Max. and min. transmission	0.7508 and 0.5422
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2298 / 0 / 164
Goodness-of-fit on F ²	1.053
Final R indices [I>2sigma(I)]	R1 = 0.0260, wR2 = 0.0649
R indices (all data)	R1 = 0.0298, wR2 = 0.0672
Absolute structure parameter	0.024(13)
Extinction coefficient	n/a
Largest diff. peak and hole	0.337 and -0.766 e.Å ⁻³

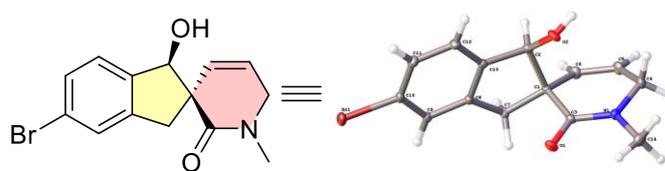
Table S14. Crystal data and structure refinement for 64 (CCDC: 2505110).



Identification code	wsh251124
Empirical formula	C ₂₀ H ₁₈ BrNO ₂
Formula weight	384.26
Temperature	170.00 K
Wavelength	1.34139 Å
Crystal system	Orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
Unit cell dimensions	a = 5.70730(10) Å a = 90° b = 13.3443(2) Å b = 90° c = 22.9961(4) Å g = 90°
Volume	1751.38(5) Å ³
Z	4
Density (calculated)	1.457 Mg/m ³
Absorption coefficient	2.238 mm ⁻¹
F(000)	784
Crystal size	0.17 x 0.07 x 0.05 mm ³
Theta range for data collection	3.331 to 60.521°
Index ranges	-7<=h<=7, -17<=k<=17, -29<=l<=29
Reflections collected	20672

Independent reflections	4026 [R(int) = 0.0489]
Completeness to theta = 53.594°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7519 and 0.5626
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4026 / 0 / 218
Goodness-of-fit on F ²	1.045
Final R indices [I > 2sigma(I)]	R1 = 0.0254, wR2 = 0.0668
R indices (all data)	R1 = 0.0284, wR2 = 0.0682
Absolute structure parameter	0.035(7)
Extinction coefficient	n/a
Largest diff. peak and hole	0.442 and -0.340 e.Å ⁻³

Table S15. Crystal data and structure refinement for 65 (CCDC: 2505111).



Identification code	251101wsh
Empirical formula	C ₁₄ H ₁₄ BrNO ₂
Formula weight	308.17
Temperature	170.00 K
Wavelength	1.34139 Å
Crystal system	Orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
Unit cell dimensions	a = 5.71060(10) Å a = 90°. b = 10.4678(2) Å b = 90°. c = 21.2022(3) Å c = 90°.
Volume	1267.41(4) Å ³
Z	4
Density (calculated)	1.615 Mg/m ³
Absorption coefficient	2.979 mm ⁻¹
F(000)	624
Crystal size	0.18 x 0.17 x 0.05 mm ³

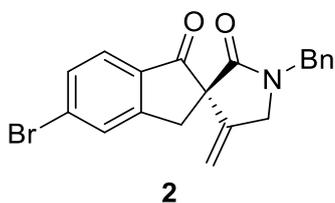
Theta range for data collection	3.627 to 68.650°.
Index ranges	-7<=h<=7, -14<=k<=13, -29<=l<=26
Reflections collected	18279
Independent reflections	3549 [R(int) = 0.0481]
Completeness to theta = 53.594°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7531 and 0.5124
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3549 / 0 / 165
Goodness-of-fit on F ²	1.035
Final R indices [I>2sigma(I)]	R1 = 0.0201, wR2 = 0.0534
R indices (all data)	R1 = 0.0203, wR2 = 0.0535
Absolute structure parameter	-0.005(6)
Extinction coefficient	n/a
Largest diff. peak and hole	0.360 and -0.244 e.Å ⁻³

XI. References

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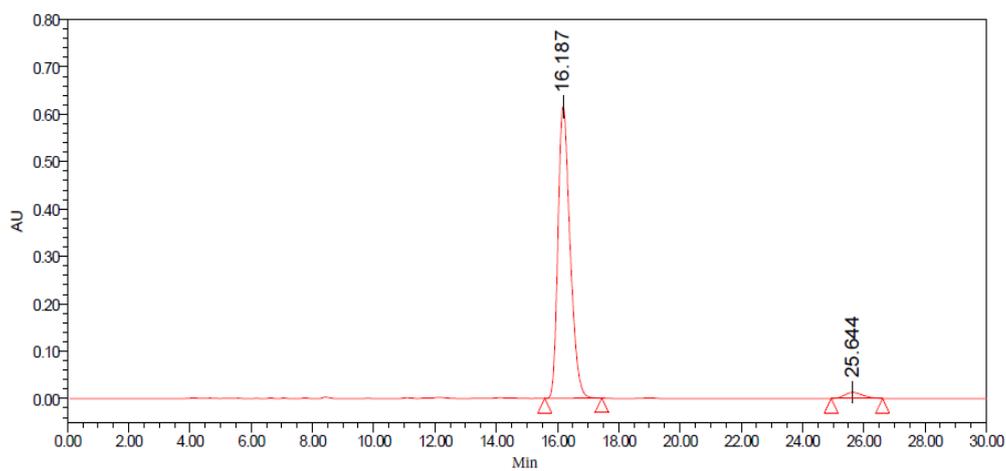
XII. Chromatographic Data for Chiral Products



HPLC Conditions

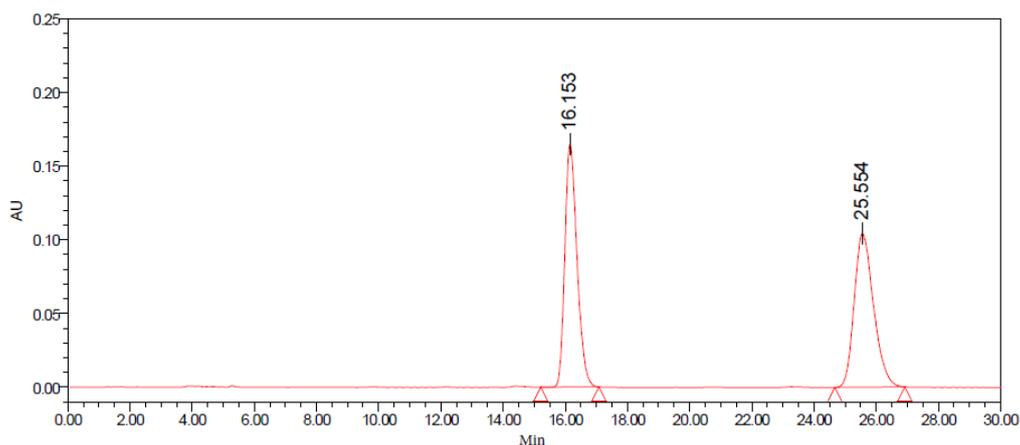
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Daicel Chemical Industries Ltd.
Eluent: Hexanes / Isopropanol (80:20)
Flow rate: 1.0 mL/min
Detection: UV 254 nm

Chiral



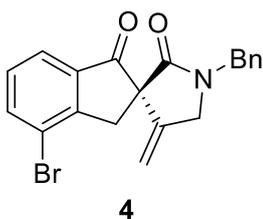
	Ret. Time	Area	% Area
1	16.187	16877854	96.98
2	25.644	525760	3.02

Racemic



	Ret. Time	Area	% Area
1	16.153	4475673	49.75
2	25.554	4520437	50.25

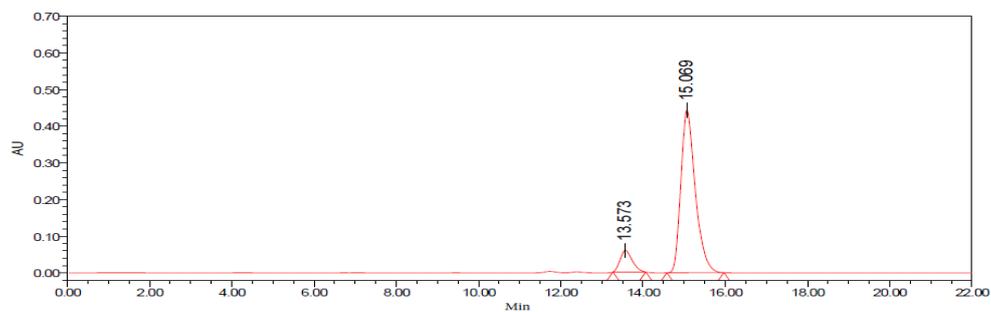
Supplementary Fig. 2. HPLC spectrum of compound 2



HPLC Conditions

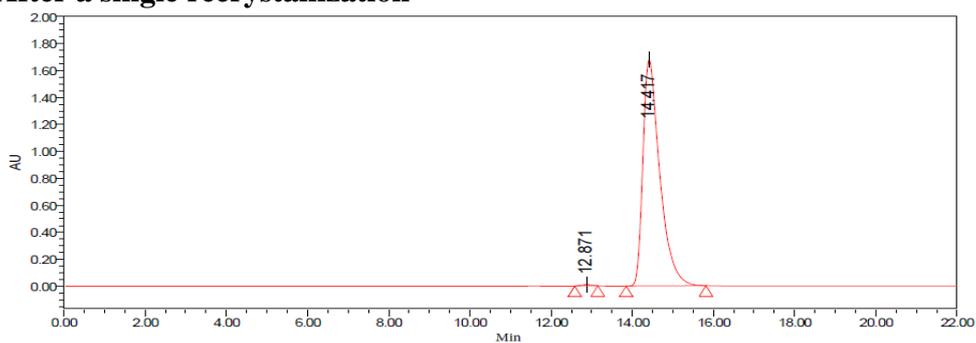
Column: Chiralpak AD-H,
Daicel Chemical Industries Ltd.
Eluent: Hexanes / Isopropanol (80:20)
Flow rate: 1.0 mL/min
Detection: UV 254 nm

Chiral



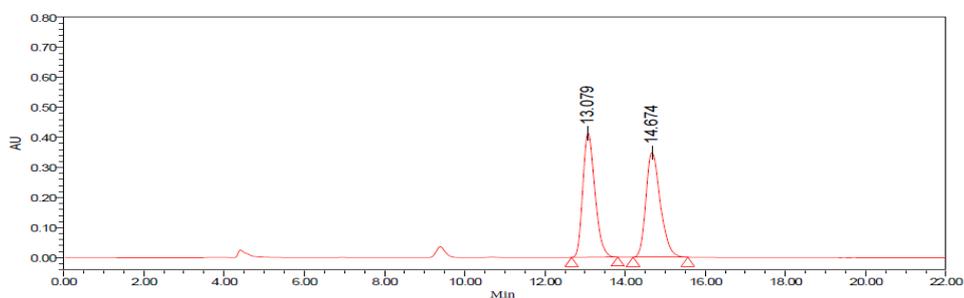
	Ret. Time	Area	% Area
1	13.573	1209854	10.07
2	15.069	10804032	89.93

After a single recrystallization



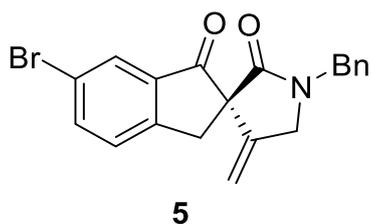
	Ret. Time	Area	% Area
1	12.871	176020	0.36
2	14.417	48490074	99.64

Racemic



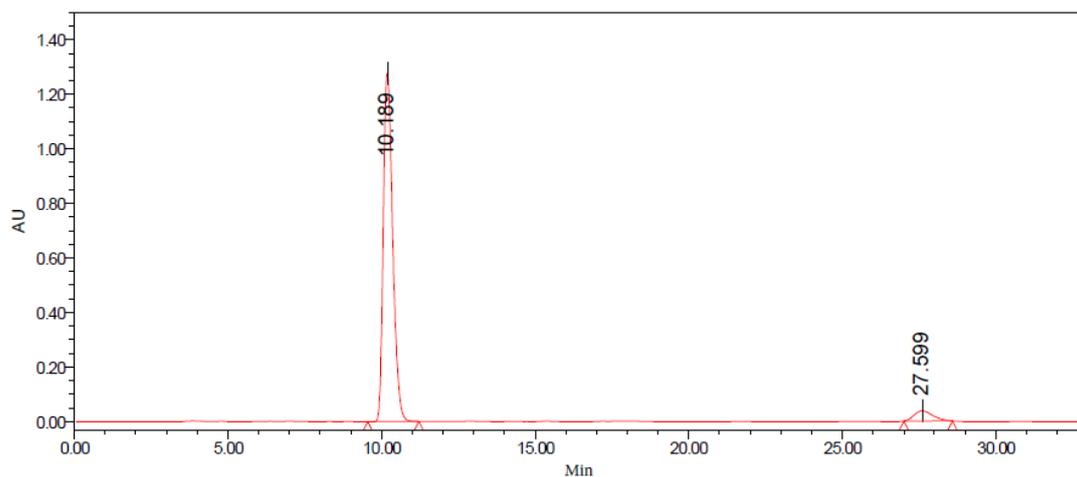
	Ret. Time	ARea	% Area
1	13.079	8676144	49.89
2	14.674	8715027	50.11

Supplementary Fig. 3. HPLC spectrum of compound 4



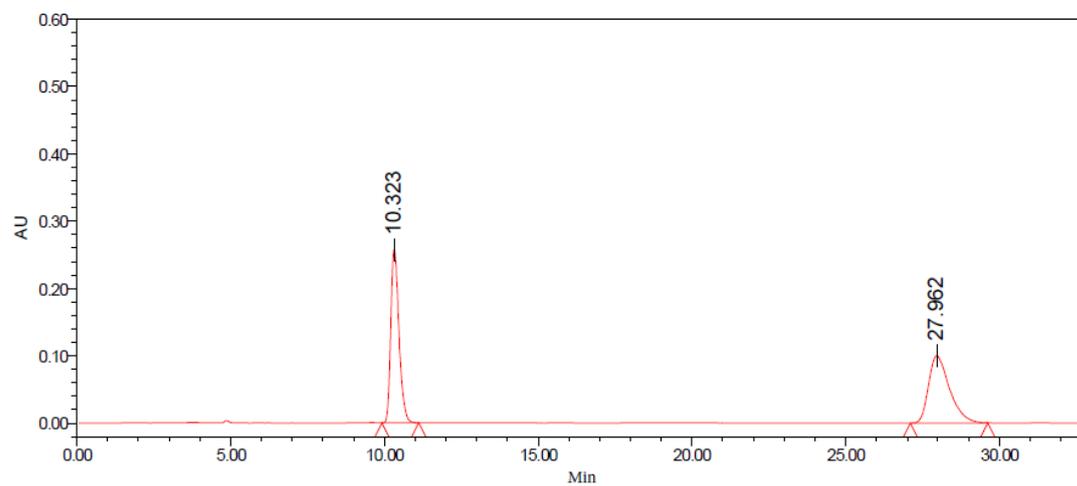
HPLC Conditions
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 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (80:20)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



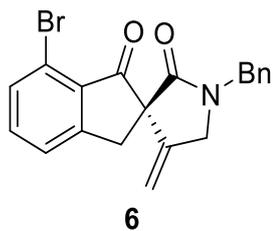
	Ret. Time	Area	% Area
1	10.189	27243401	94.49
2	27.599	1587527	5.51

Racemic



	Ret. Time	Area	% Area
1	10.323	4756242	50.11
2	27.962	4734837	49.89

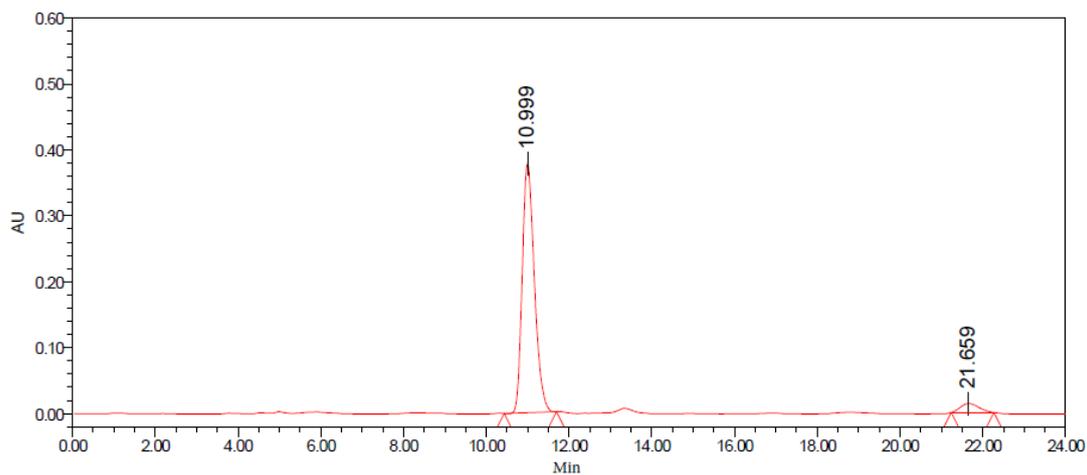
Supplementary Fig. 4. HPLC spectrum of compound 5



HPLC Conditions

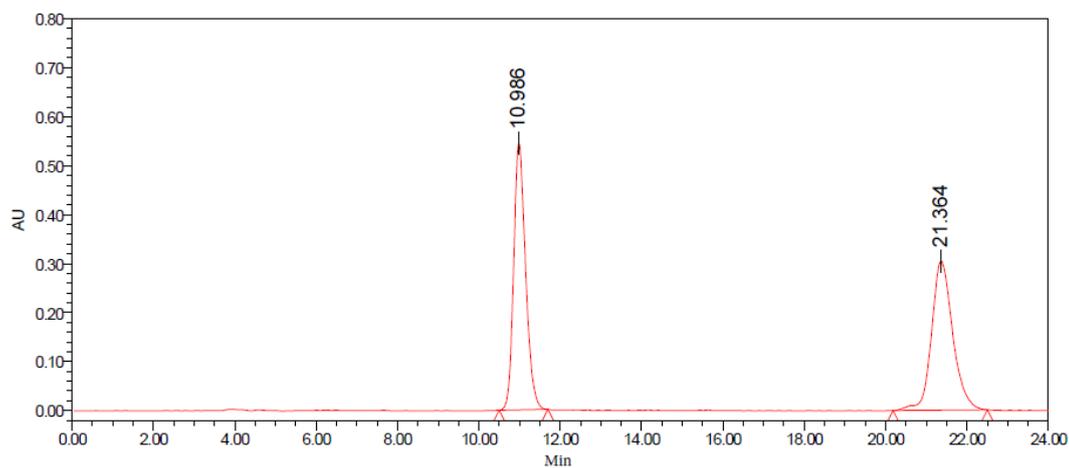
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 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



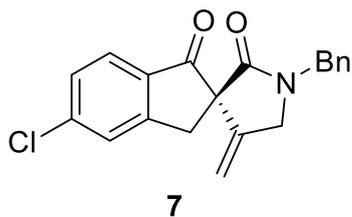
	Ret. Time	Area	% Area
1	10.999	7688372	94.77
2	21.659	424601	5.23

Racemic



	Ret. Time	Area	% Area
1	10.986	11084481	50.14
2	21.364	11023855	49.86

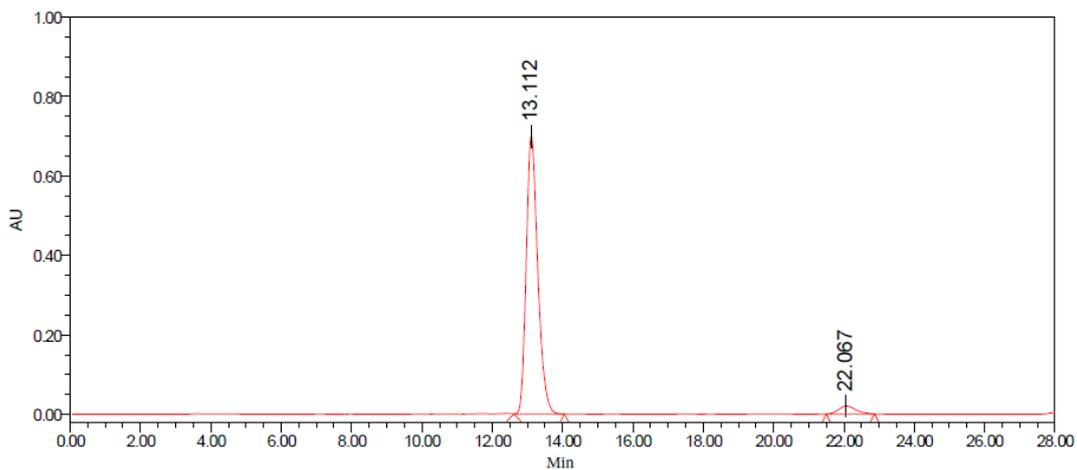
Supplementary Fig. 5. HPLC spectrum of compound **6**



HPLC Conditions

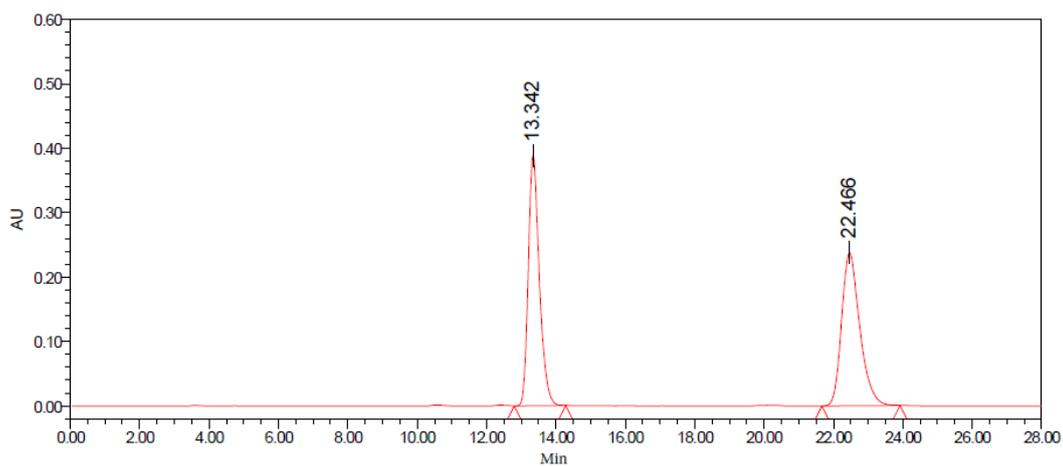
Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (80:20)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



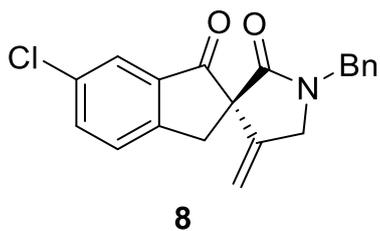
	Ret. Time	Area	% Area
1	13.112	15895159	95.93
2	22.067	673855	4.07

Racemic



	Ret. Time	Area	% Area
1	13.342	8606357	49.92
2	22.466	8634633	50.08

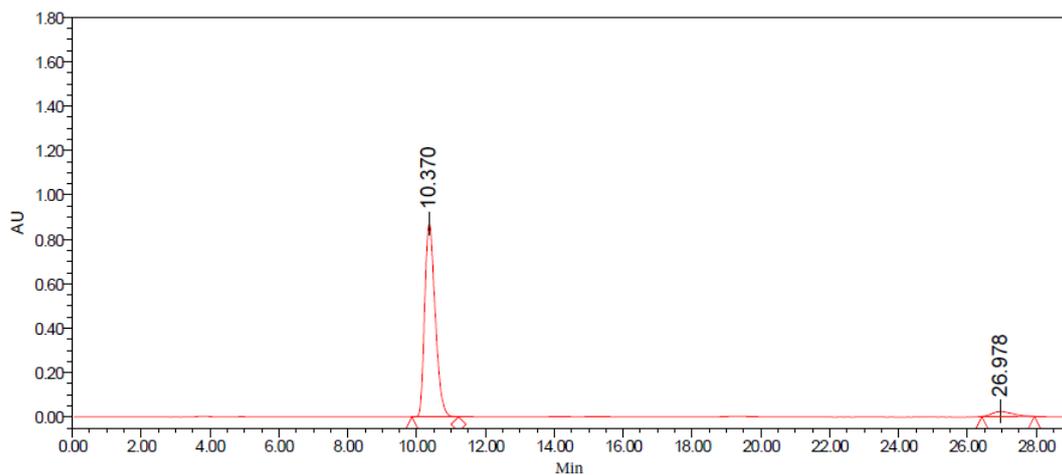
Supplementary Fig. 6. HPLC spectrum of compound **7**



HPLC Conditions

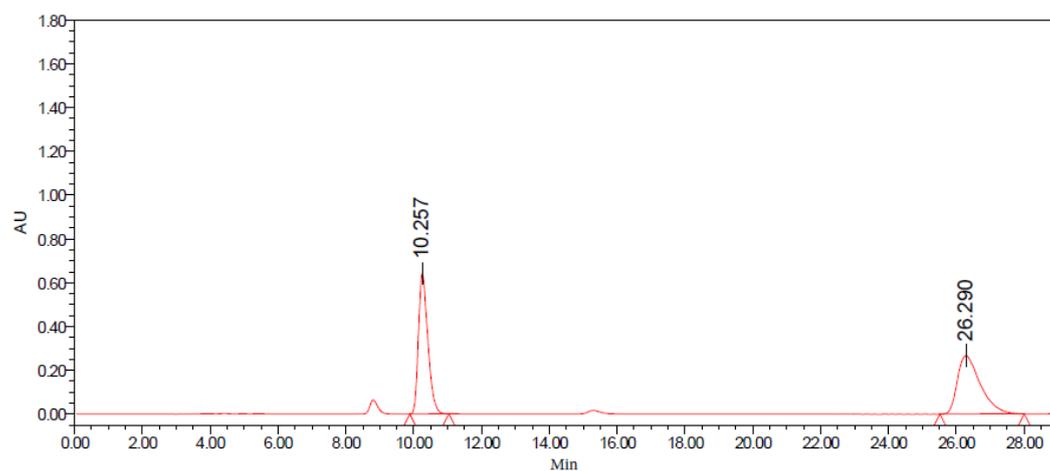
Column: Chiralpak AD-H,
Daicel Chemical Industries Ltd.
Eluent: Hexanes / Isopropanol (80:20)
Flow rate: 1.0 mL/min
Detection: UV 254 nm

Chiral



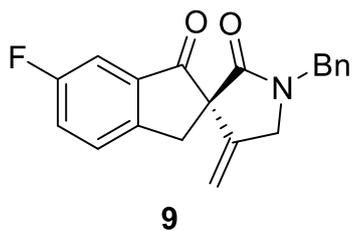
	Ret. Time	Area	% Area
1	10.370	18452713	95.14
2	26.978	943202	4.86

Racemic



	Ret. Time	Area	% Area
1	10.257	12376182	49.75
2	26.290	12498183	50.25

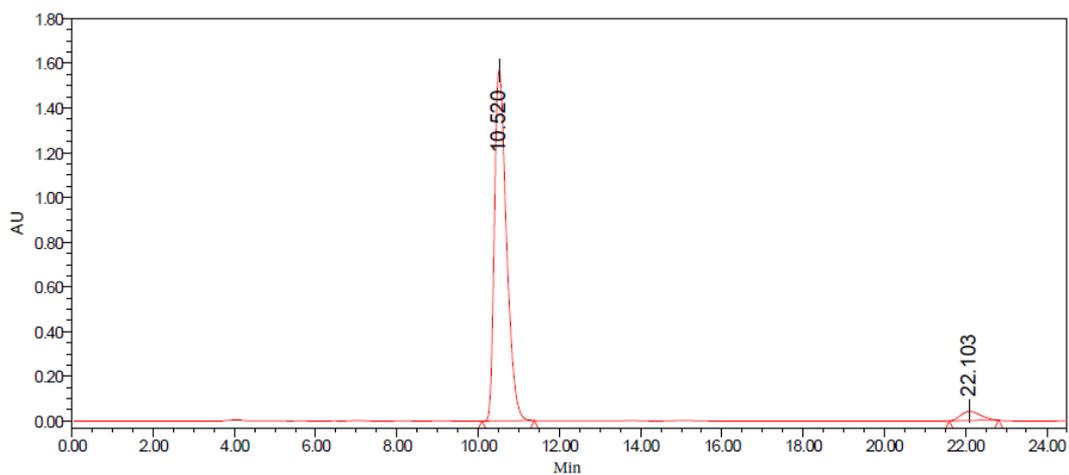
Supplementary Fig. 7. HPLC spectrum of compound 8



HPLC Conditions

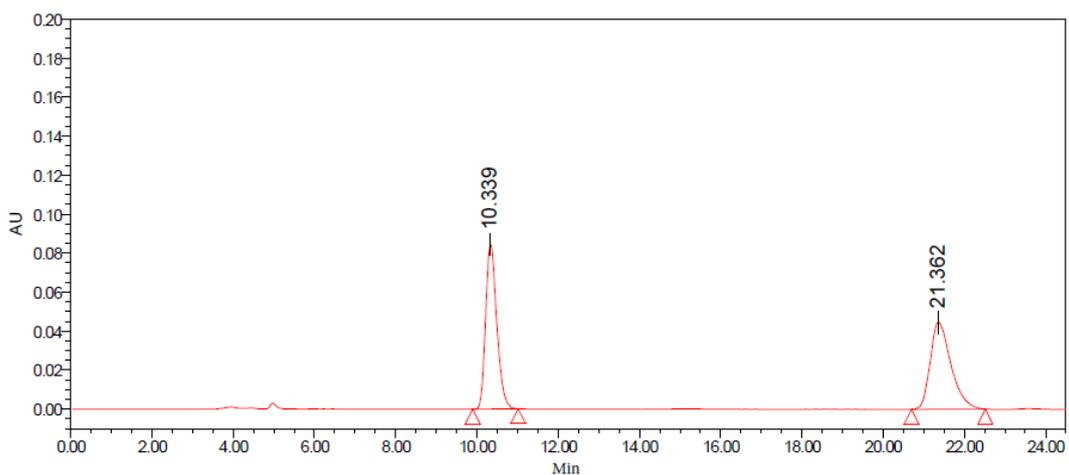
Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (80:20)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



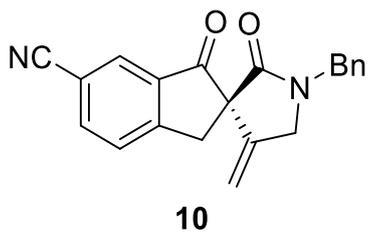
	Ret. Time	Area	% Area
1	10.520	32241374	95.85
2	22.103	1395026	4.15

Racemic



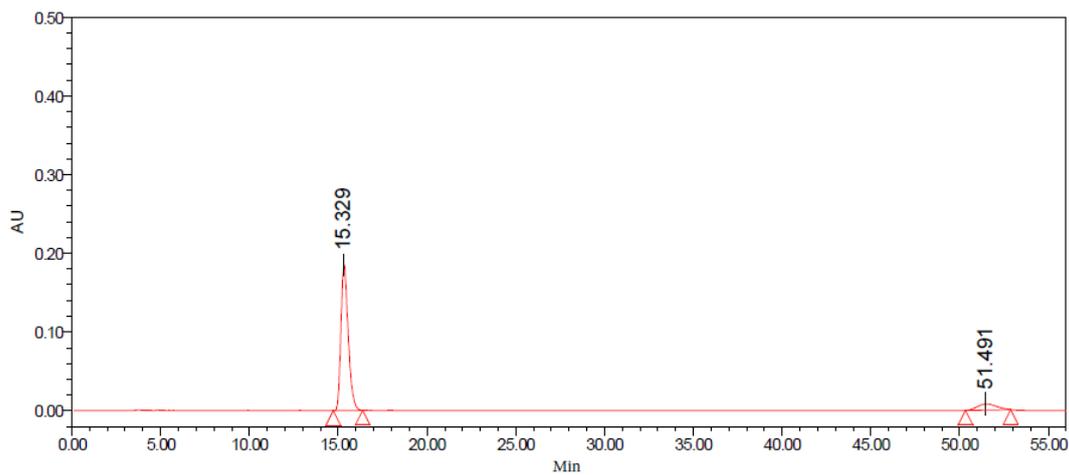
	Ret. Time	Area	% Area
1	10.339	1611397	50.49
2	21.362	1580272	49.51

Supplementary Fig. 8. HPLC spectrum of compound **9**



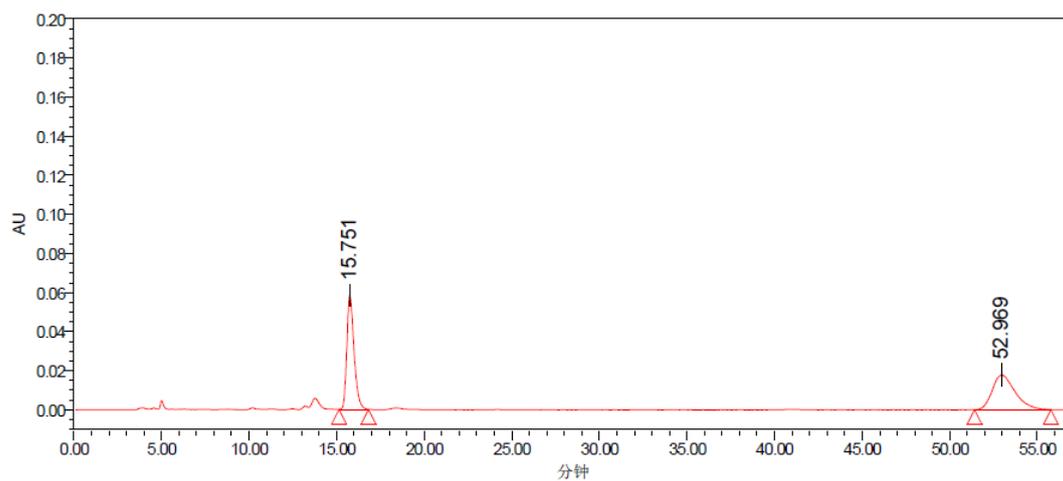
HPLC Conditions
 Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (80:20)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



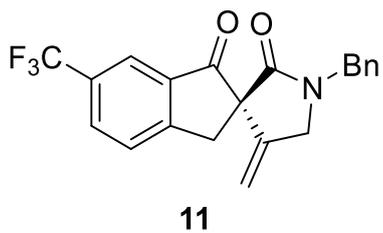
	Ret. Time	Area	% Area
1	15.329	5286278	90.06
2	51.491	583710	9.94

Racemic



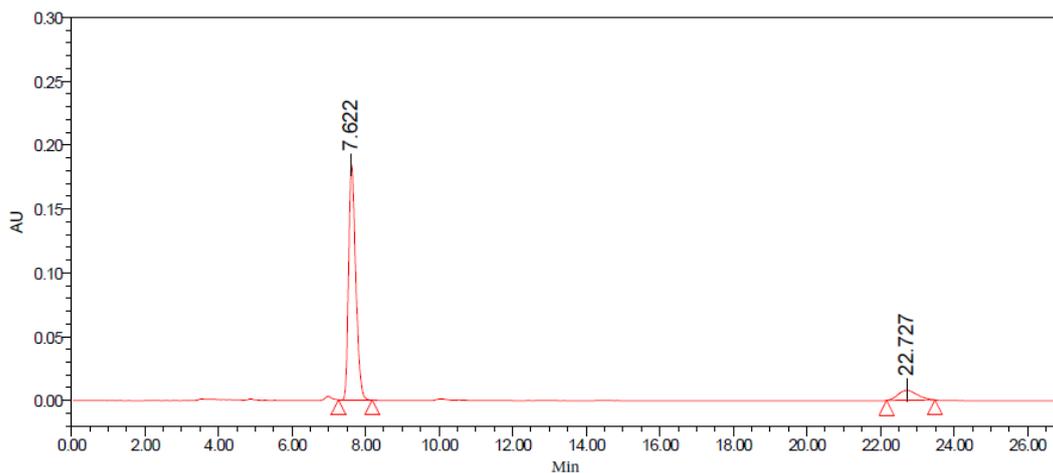
	Ret. Time	Area	% Area
1	15.751	1676121	51.04
2	52.969	1607561	48.96

Supplementary Fig. 9. HPLC spectrum of compound 10



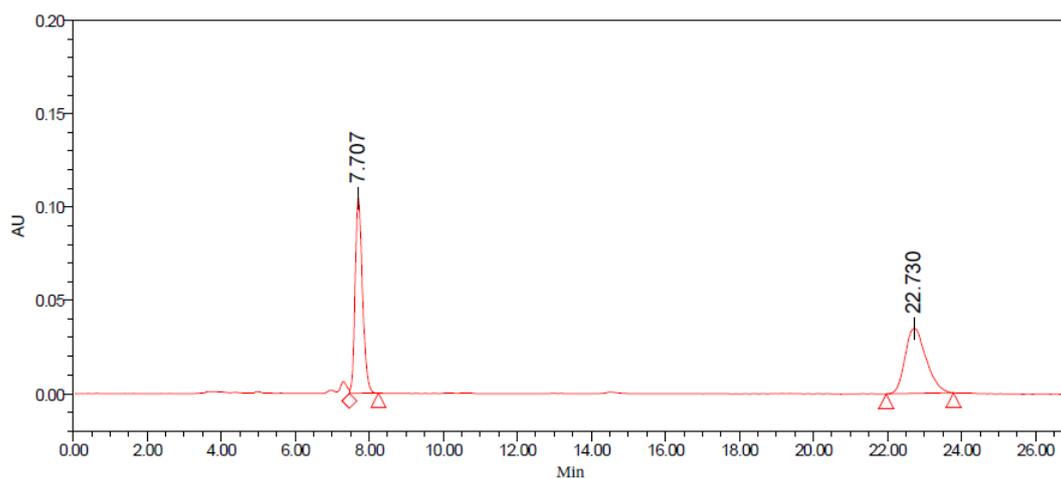
HPLC Conditions
 Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (80:20)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



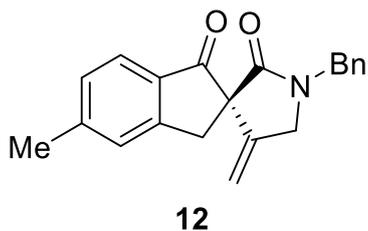
	Ret. Time	Area	% Area
1	7.622	2483193	89.83
2	22.727	281078	10.17

Racemic



	Ret. Time	Area	% Area
1	7.707	1444603	51.23
2	22.730	1375236	48.77

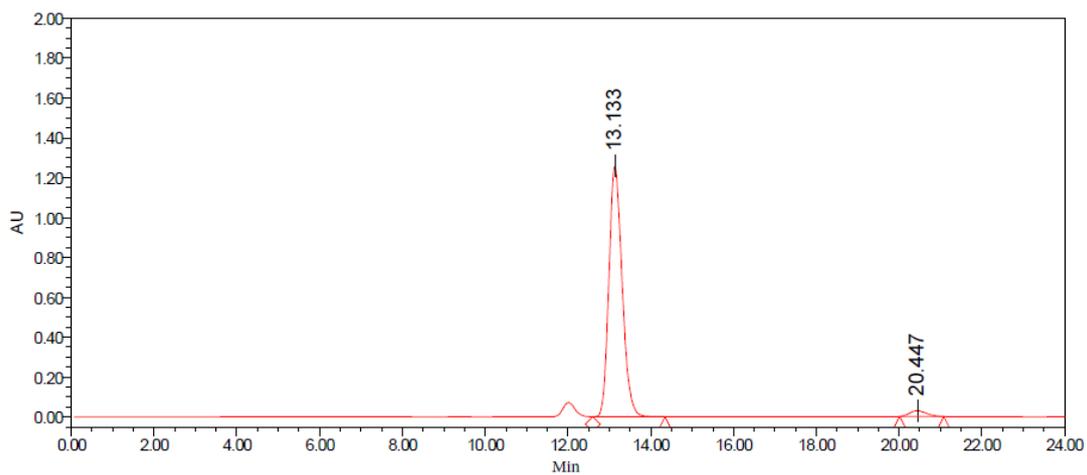
Supplementary Fig. 10. HPLC spectrum of compound **11**



HPLC Conditions

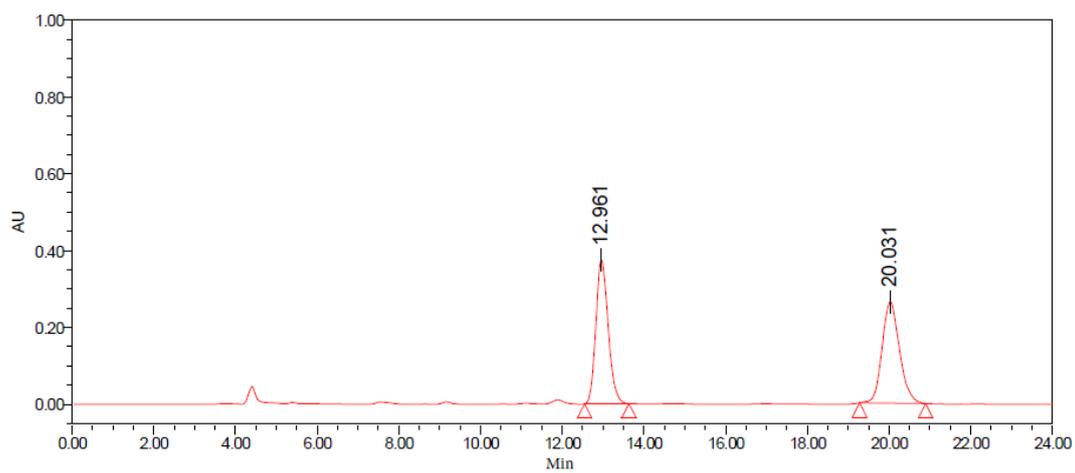
Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (80:20)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



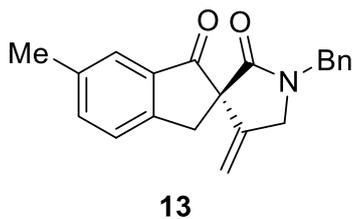
	Ret. Time	Area	% Area
1	13.133	27867563	97.15
2	20.447	818116	2.85

Racemic



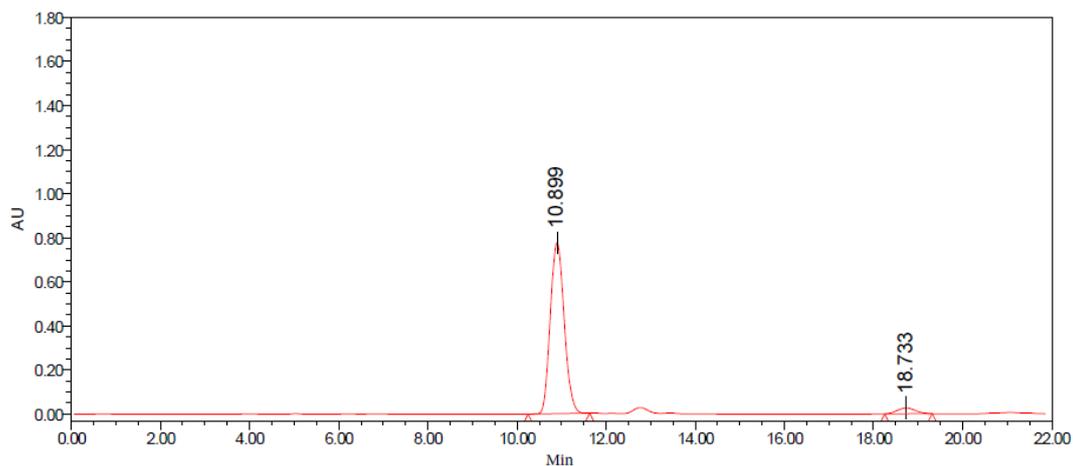
	Ret. Time	Area	% Area
1	12.961	7830335	50.07
2	20.031	7807040	49.93

Supplementary Fig. 11. HPLC spectrum of compound 12



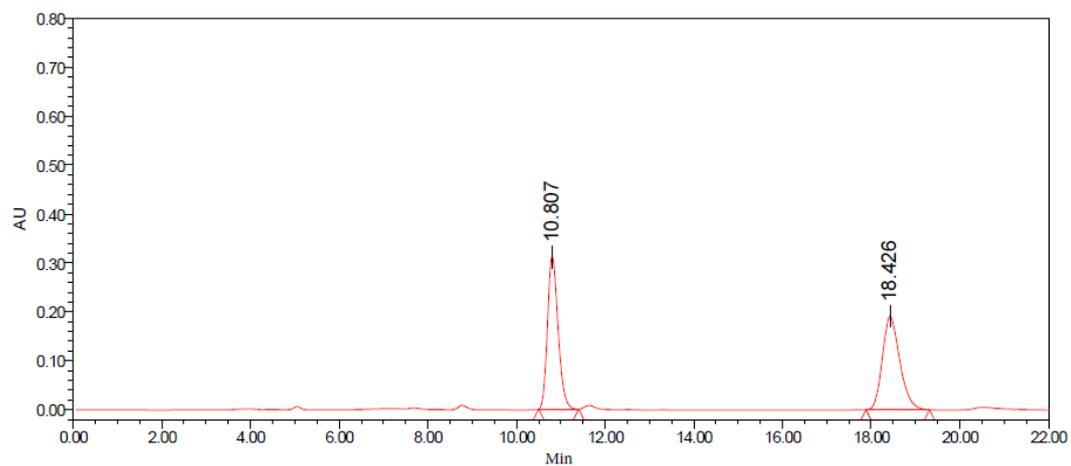
HPLC Conditions
 Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (80:20)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



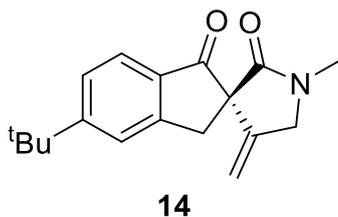
	Ret. Time	Area	% Area
1	10.899	16855946	95.74
2	18.733	749589	4.26

Racemic



	Ret. Time	Area	% Area
1	10.807	5166544	49.75
2	18.426	5218746	50.25

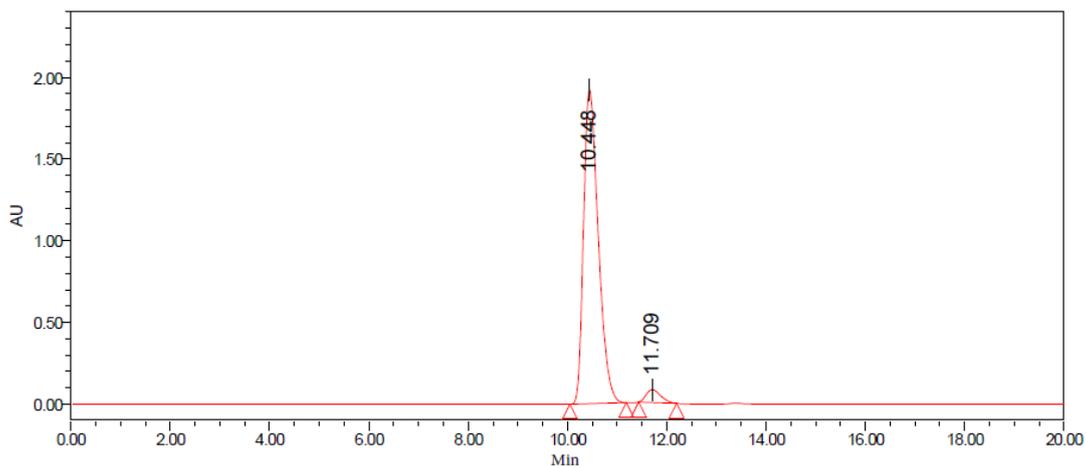
Supplementary Fig. 12. HPLC spectrum of compound **13**



HPLC Conditions

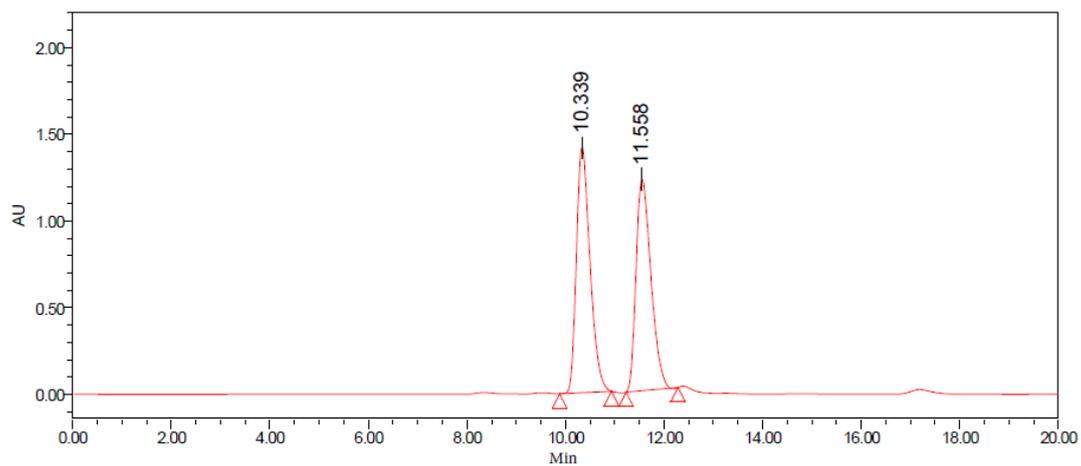
Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (80:20)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



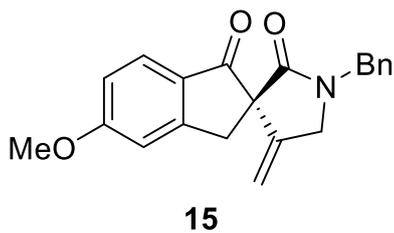
	Ret. Time	Area	% Area
1	10.448	39449720	96.08
2	11.709	1611050	3.92

Racemic



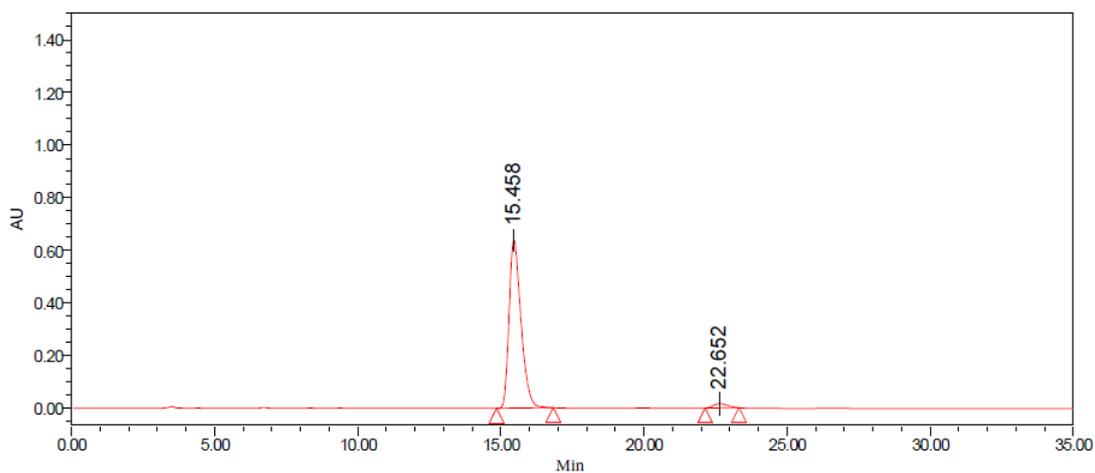
	Ret. Time	Area	% Area
1	10.339	27205936	51.50
2	11.558	25619452	48.50

Supplementary Fig. 13. HPLC spectrum of compound **14**



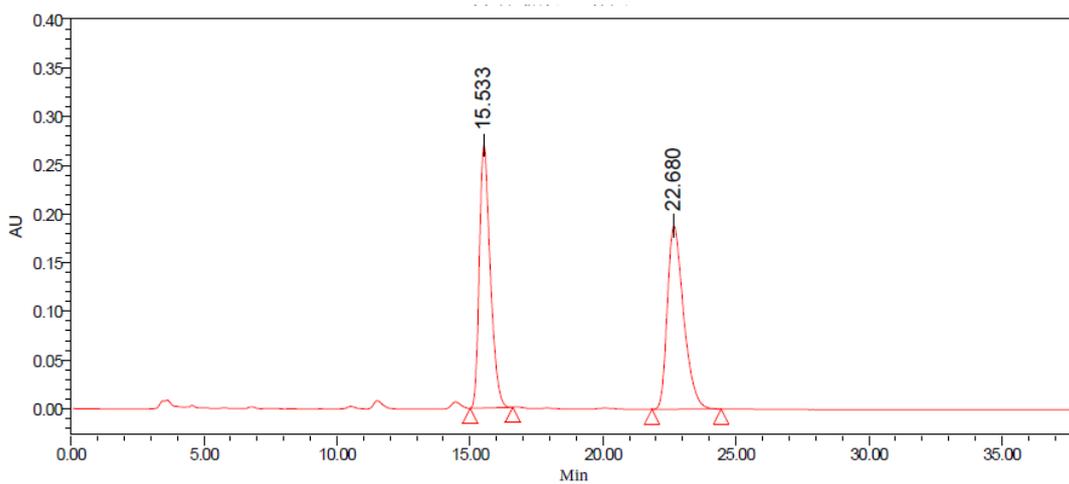
HPLC Conditions
 Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (80:20)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



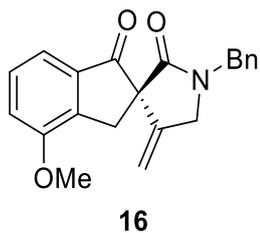
	Ret. Time	Area	% Area
1	15.458	18466717	96.97
2	22.652	577867	3.03

Racemic



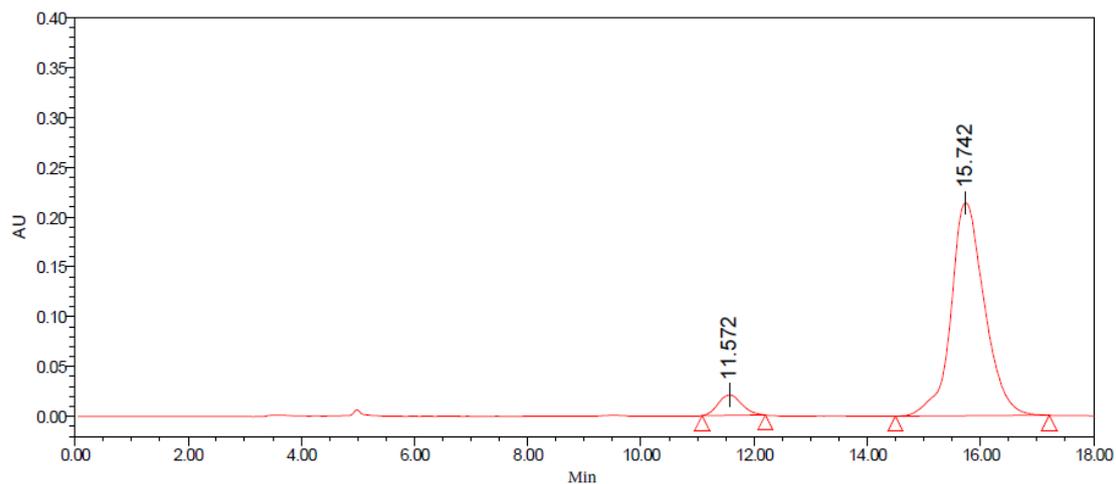
	Ret. Time	Area	% Area
1	15.533	7690266	49.03
2	22.680	7995230	50.97

Supplementary Fig. 14. HPLC spectrum of compound **15**



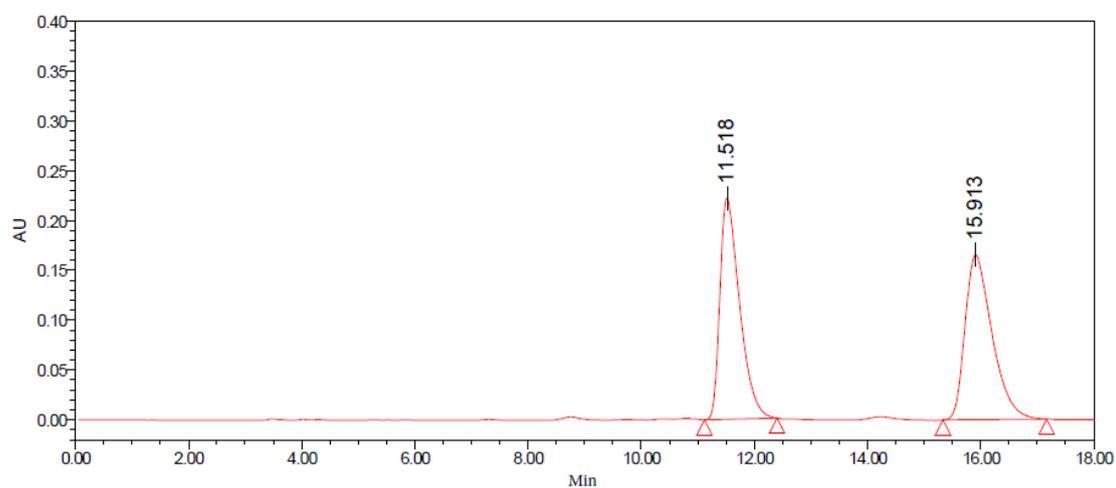
HPLC Conditions
 Column: Chiralpak OD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (80:20)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



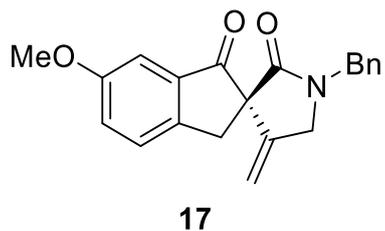
	Ret. Time	Area	% Area
1	11.572	592097	6.32
2	15.742	8771783	93.68

Racemic



	Ret. Time	Area	% Area
1	11.518	5351965	49.35
2	15.913	5492401	50.65

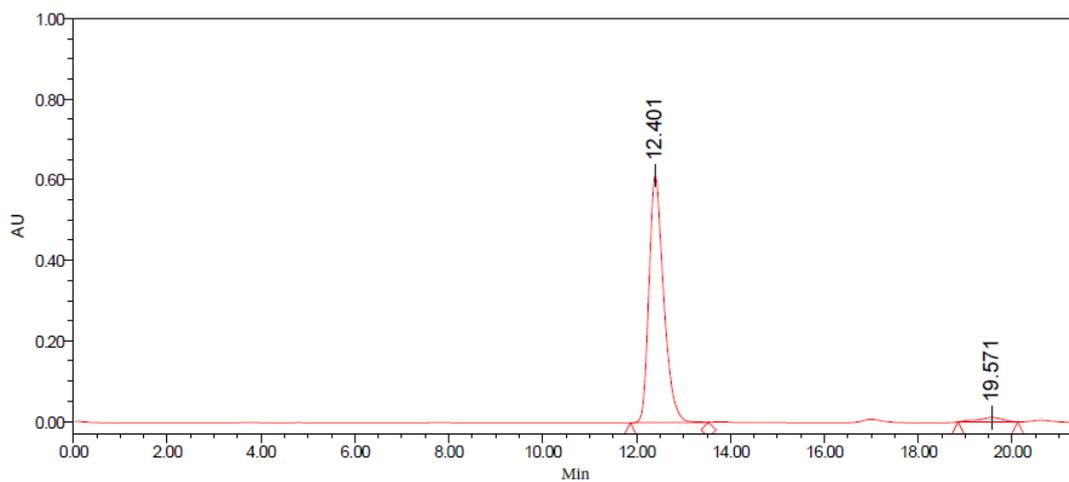
Supplementary Fig. 15. HPLC spectrum of compound 16



HPLC Conditions

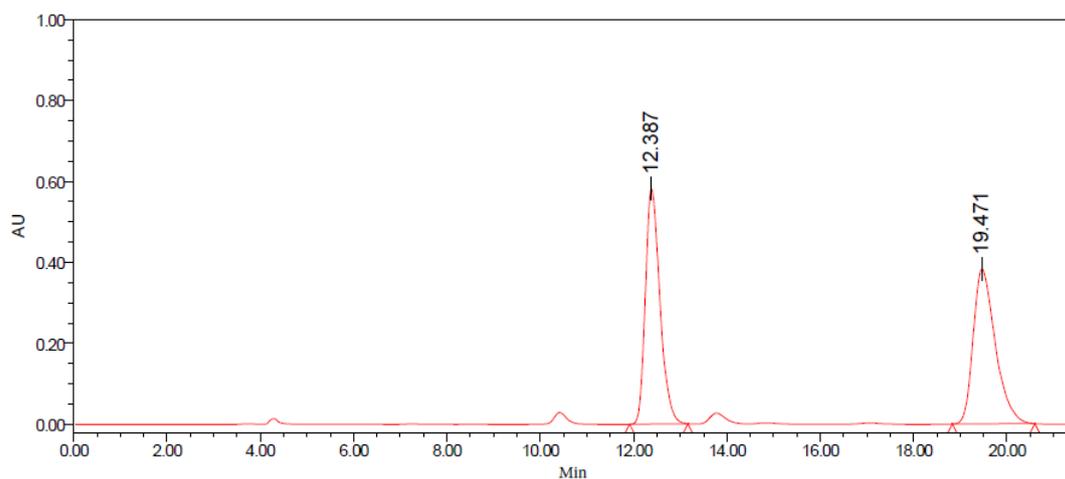
Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (80:20)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



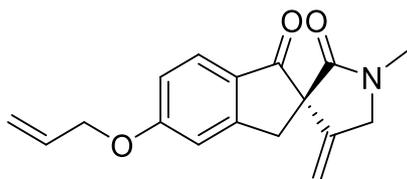
	Ret. Time	Area	% Area
1	12.401	13286349	97.13
2	19.571	392834	2.87

Racemic



	Ret. Time	Area	% Area
1	12.387	12593095	49.91
2	19.471	12640206	50.09

Supplementary Fig. 16. HPLC spectrum of compound **17**

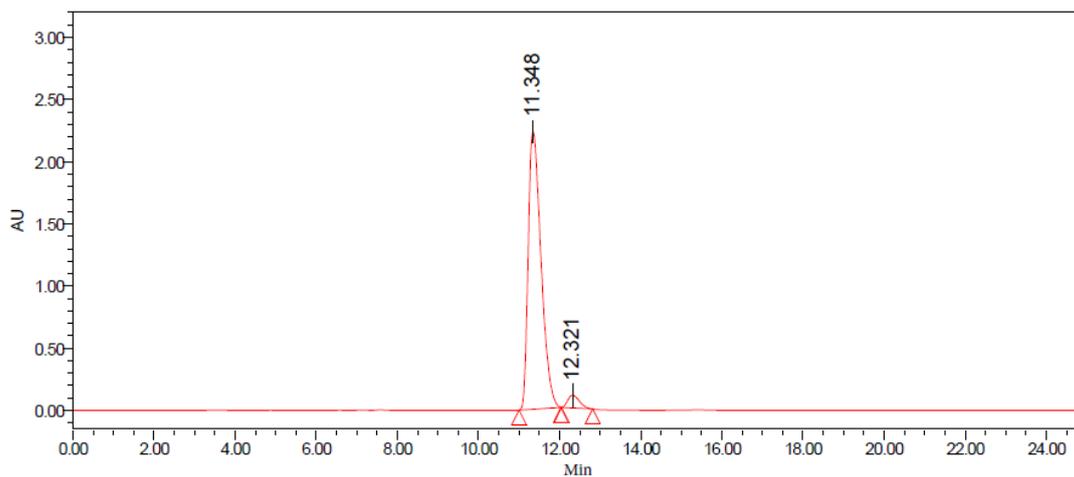


18

HPLC Conditions

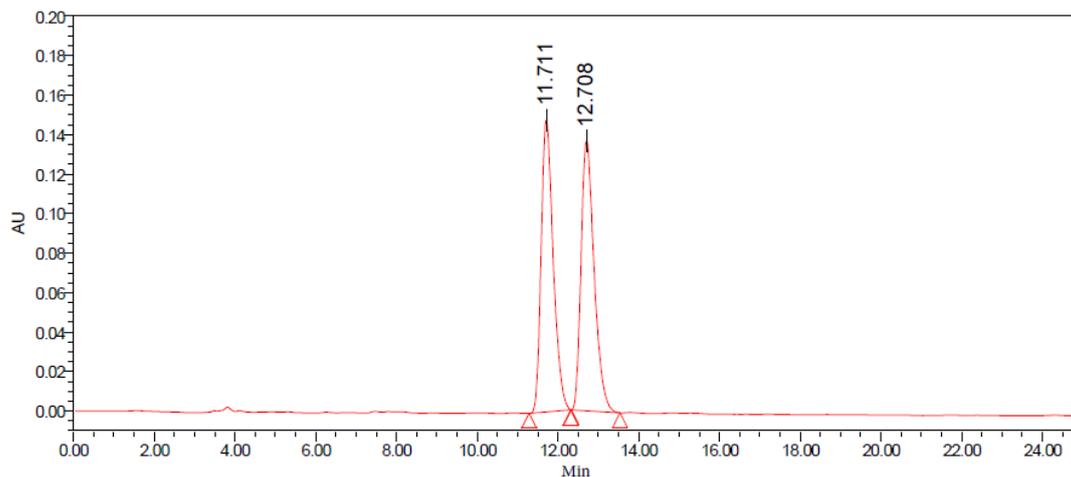
Column: Chiralpak AD-H,
Daicel Chemical Industries Ltd.
Eluent: Hexanes / Isopropanol (80:20)
Flow rate: 1.0 mL/min
Detection: UV 254 nm

Chiral



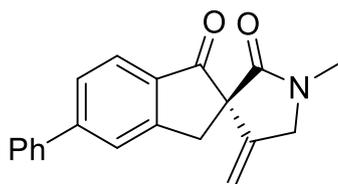
	Ret. Time	Area	% Area
1	11.348	48878348	95.98
2	12.321	2048615	4.02

Racemic



	Ret. Time	Area	% Area
1	11.711	3063909	49.98
2	12.708	3066834	50.02

Supplementary Fig. 17. HPLC spectrum of compound **18**

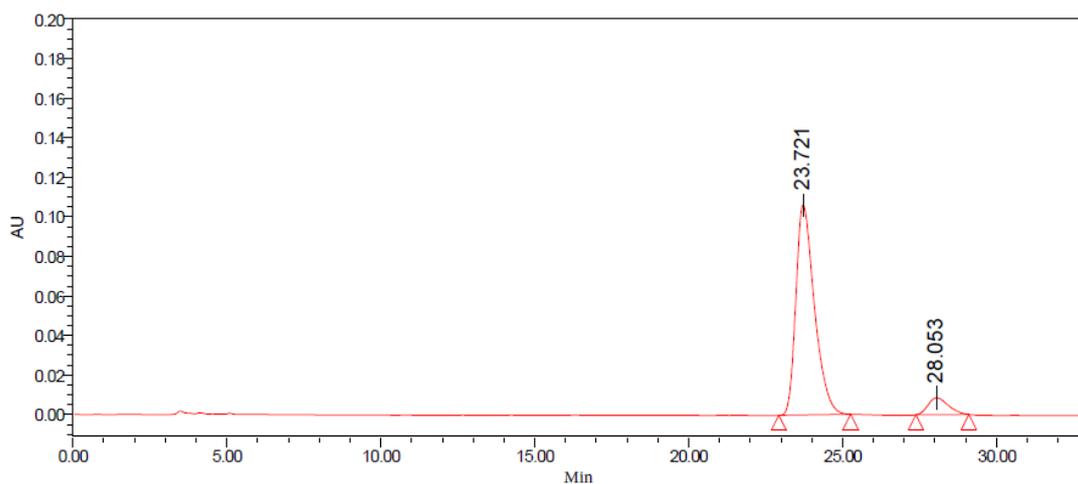


19

HPLC Conditions

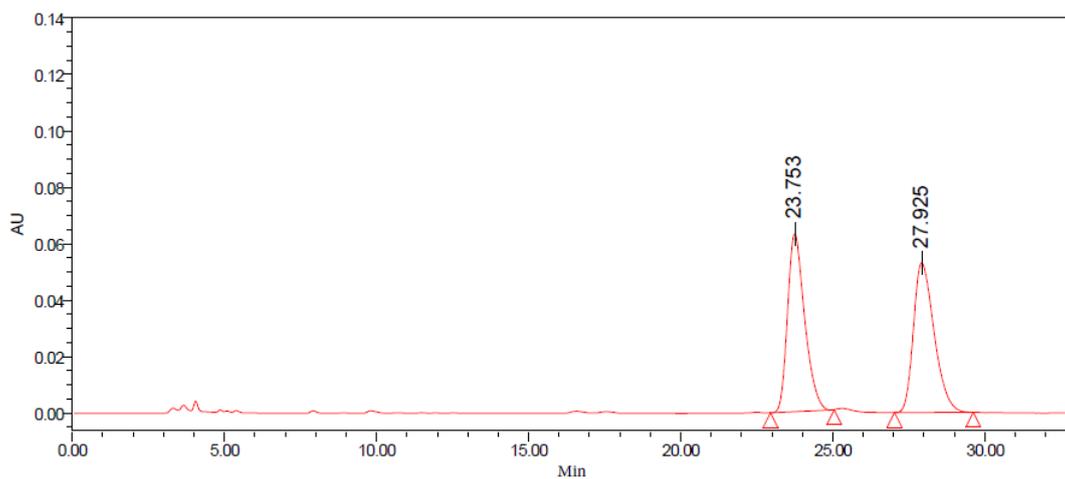
Column: Chiralpak AD-H,
Daicel Chemical Industries Ltd.
Eluent: Hexanes / Isopropanol (90:10)
Flow rate: 1.0 mL/min
Detection: UV 254 nm

Chiral



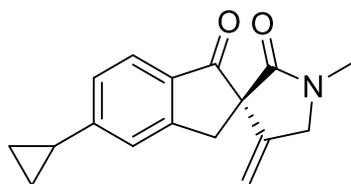
	Ret. Time	Area	% Area
1	23.721	4448232	91.92
2	28.053	391199	8.08

Racemic



	Ret. Time	Area	% Area
1	23.753	2459808	49.44
2	27.925	2515106	50.56

Supplementary Fig. 18. HPLC spectrum of compound **19**

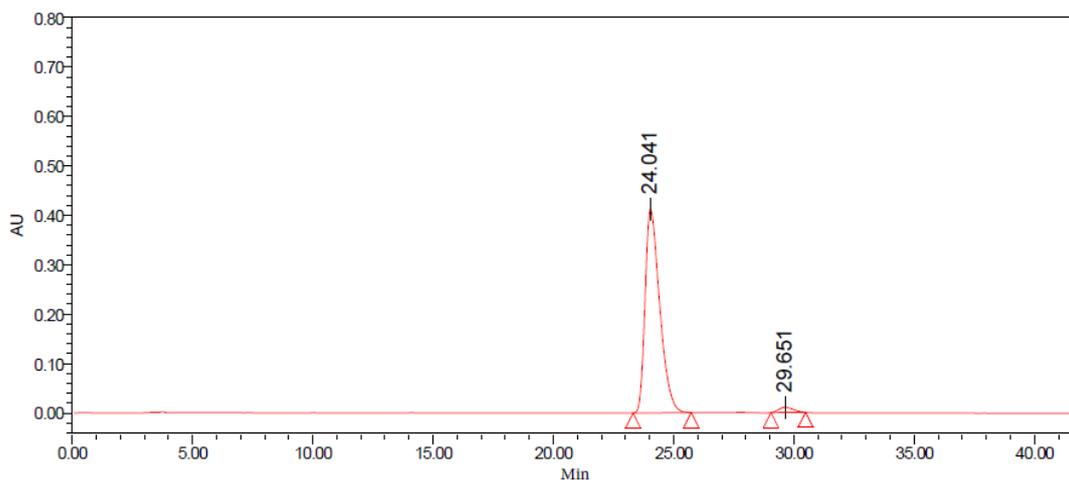


20

HPLC Conditions

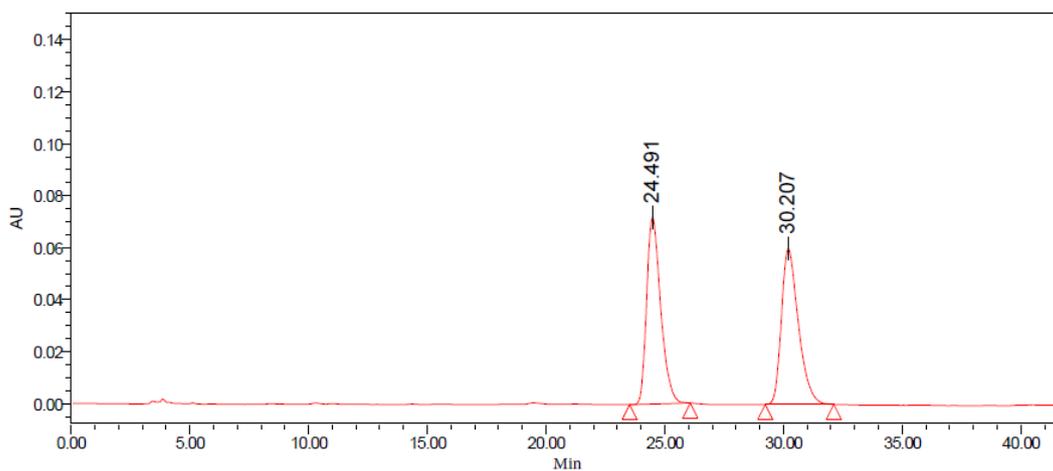
Column: Chiralpak AD-H,
Daicel Chemical Industries Ltd.
Eluent: Hexanes / Isopropanol (90:10)
Flow rate: 1.0 mL/min
Detection: UV 254 nm

Chiral



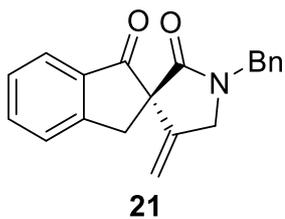
	Ret. Time	Area	% Area
1	24.041	17473554	97.51
2	29.651	446168	2.49

Racemic



	Ret. Time	Area	% Area
1	24.491	2949659	49.79
2	30.207	2974442	50.21

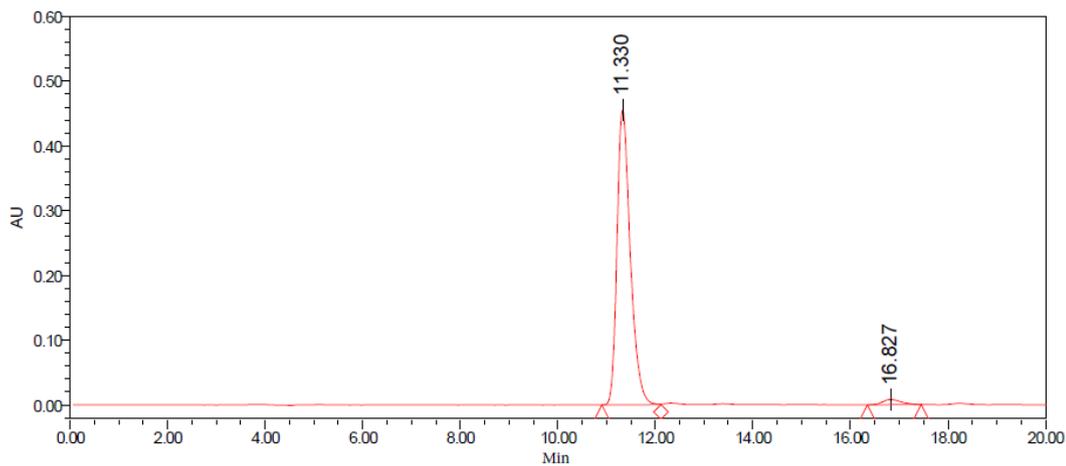
Supplementary Fig. 19. HPLC spectrum of compound **20**



HPLC Conditions

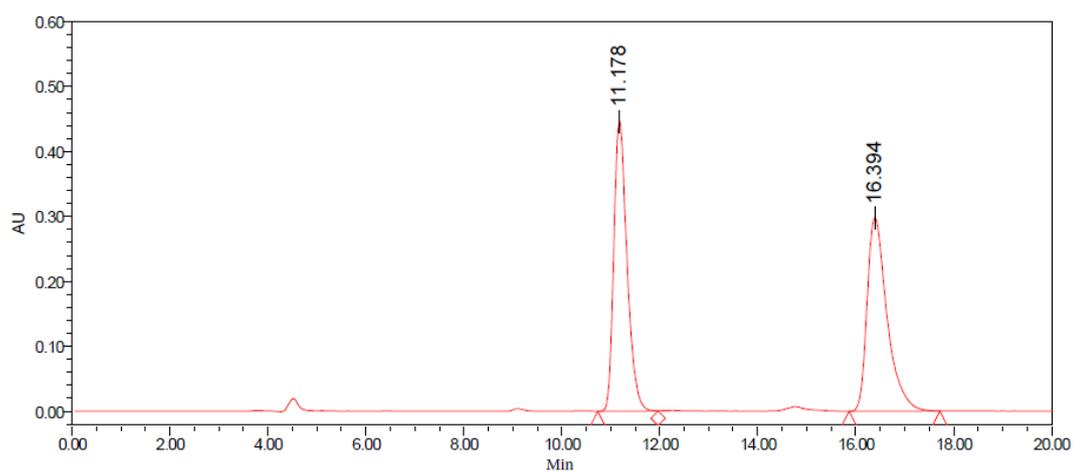
Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (80:20)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



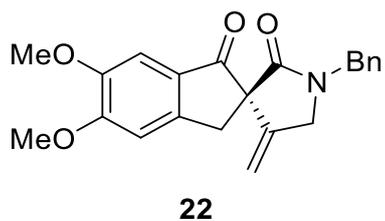
	Ret. Time	Area	% Area
1	11.330	8673890	97.61
2	16.827	212054	2.39

Racemic



	Ret. Time	Area	% Area
1	11.178	8385414	49.89
2	16.394	8421974	50.11

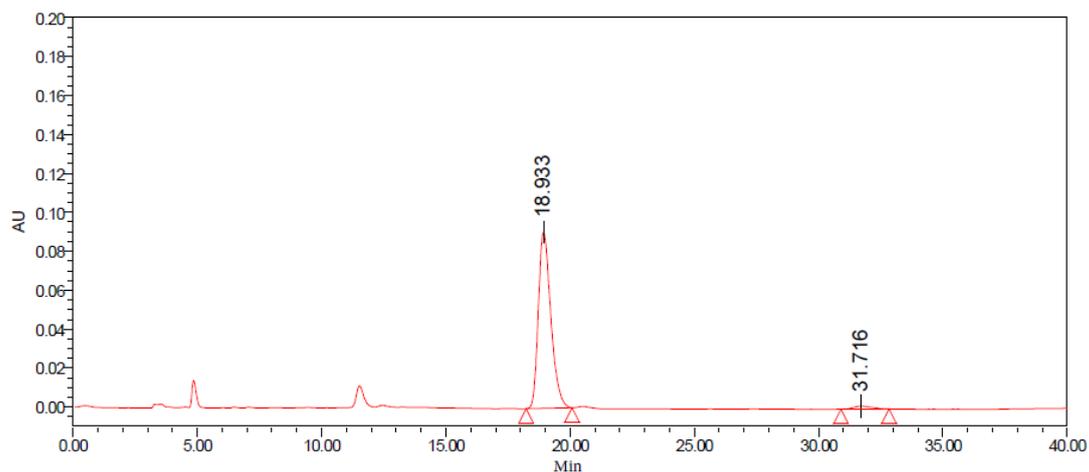
Supplementary Fig. 20. HPLC spectrum of compound **21**



HPLC Conditions

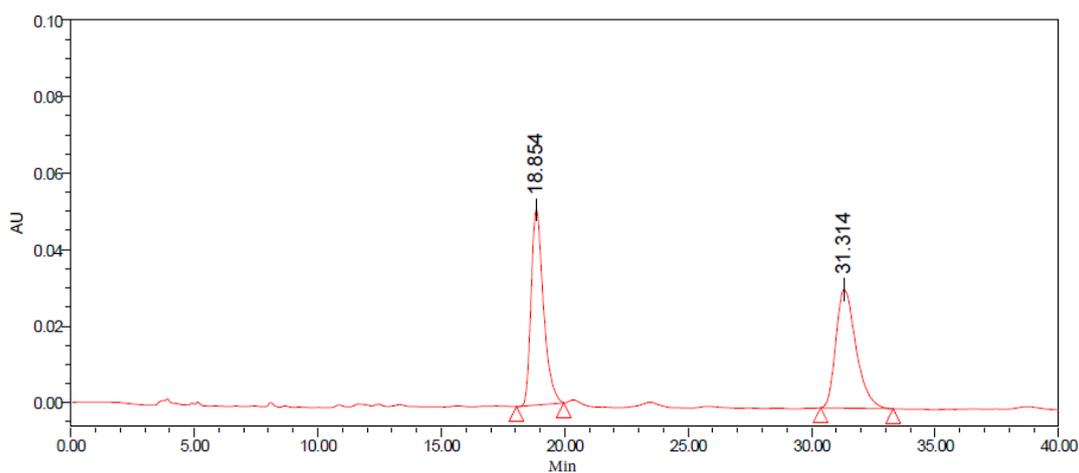
Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (80:20)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



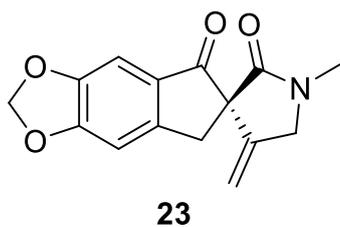
	Ret. Time	Area	% Area
1	18.933	3157770	97.50
2	31.716	80939	2.50

Racemic



	Ret. Time	Area	% Area
1	18.854	1779793	50.28
2	31.314	1759708	49.72

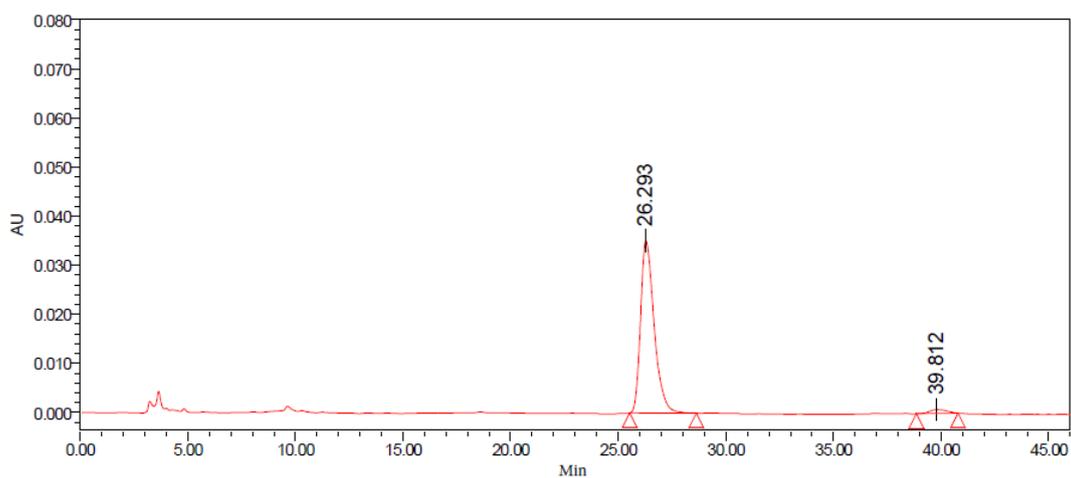
Supplementary Fig. 21. HPLC spectrum of compound 22



HPLC Conditions

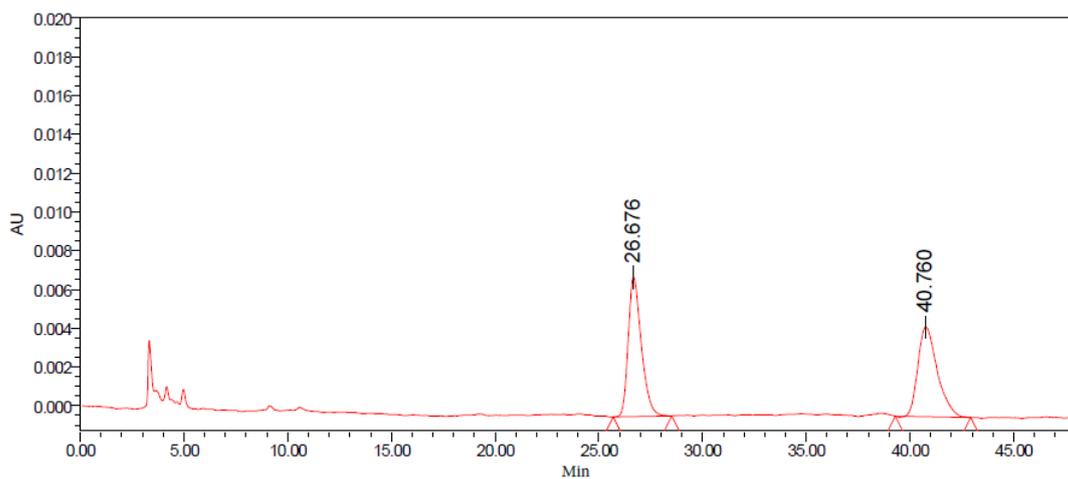
Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (90:10)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



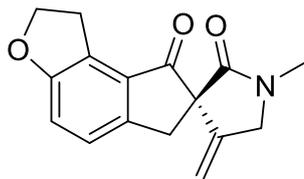
	Ret. Time	Area	% Area
1	26.293	1543469	97.22
2	39.812	44111	2.78

Racemic



	Ret. Time	Area	% Area
1	26.676	316344	51.12
2	40.760	302464	48.88

Supplementary Fig. 22. HPLC spectrum of compound **23**

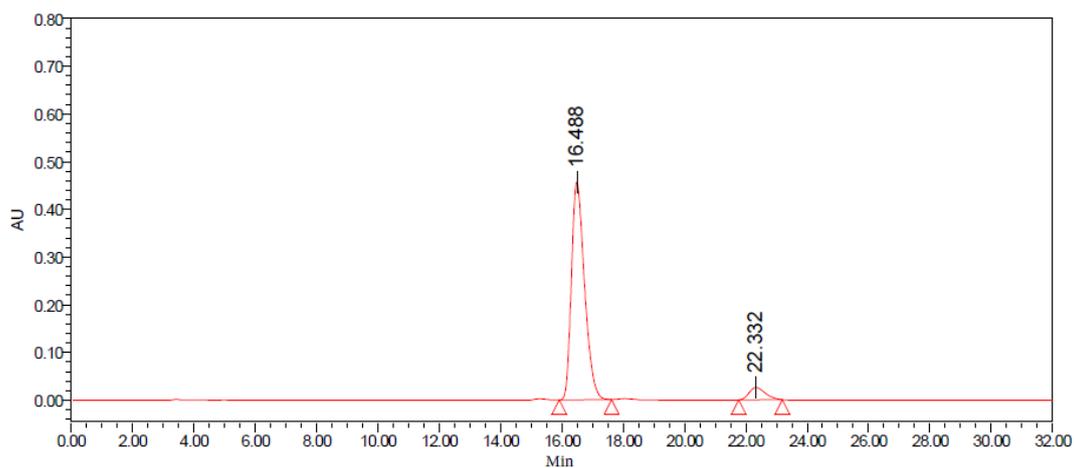


24

HPLC Conditions

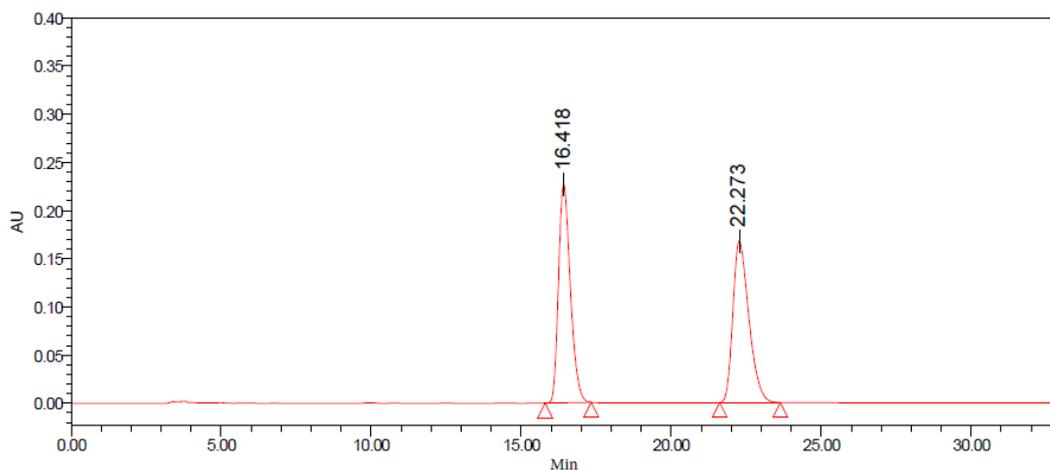
Column: Chiralpak AD-H,
Daicel Chemical Industries Ltd.
Eluent: Hexanes / Isopropanol (90:10)
Flow rate: 1.0 mL/min
Detection: UV 254 nm

Chiral



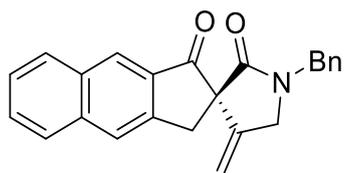
	Ret. Time	Area	% Area
1	16.488	13552121	93.46
2	22.332	947771	6.54

Racemic



	Ret. Time	Area	% Area
1	16.418	6218748	50.08
2	22.273	6199353	49.92

Supplementary Fig. 23. HPLC spectrum of compound 24

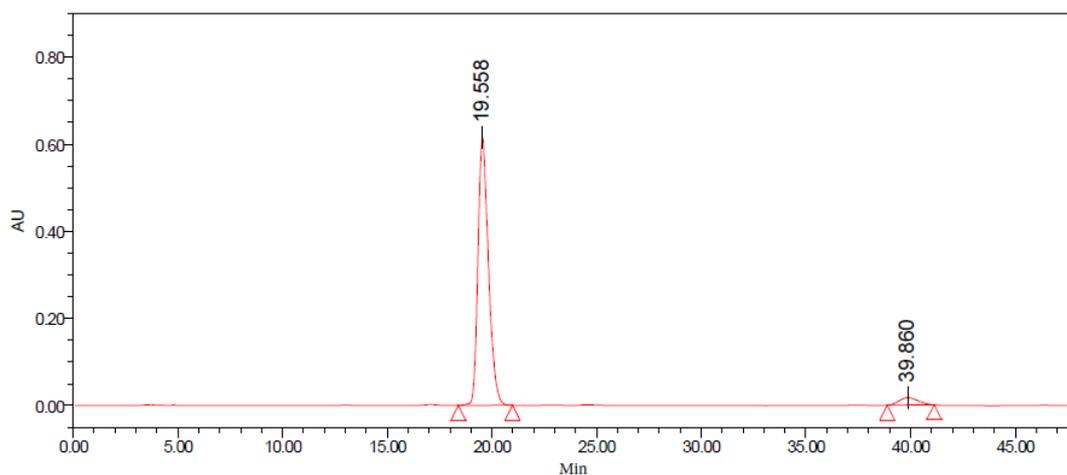


25

HPLC Conditions

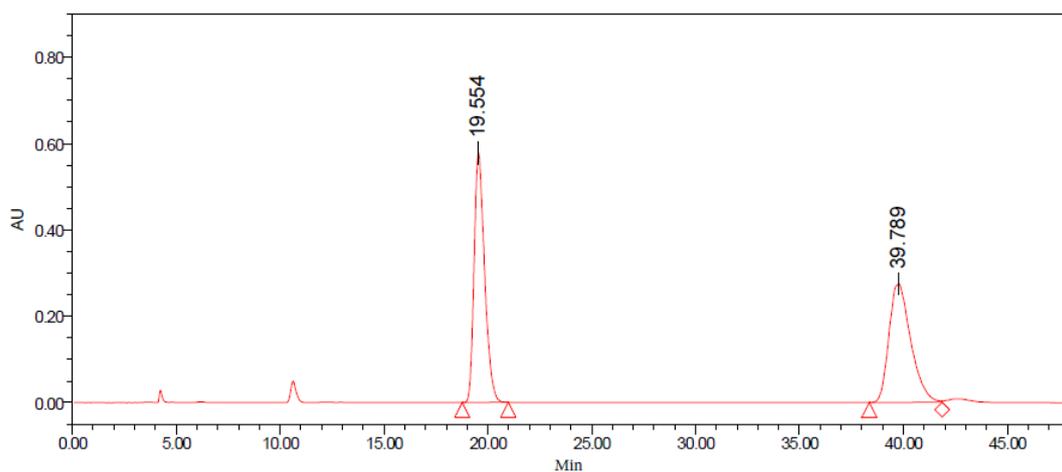
Column: Chiralpak AD-H,
Daicel Chemical Industries Ltd.
Eluent: Hexanes / Isopropanol (80:20)
Flow rate: 1.0 mL/min
Detection: UV 254 nm

Chiral



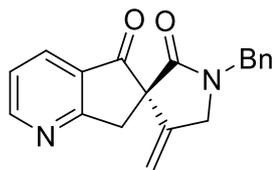
	Ret. Time	Area	% Area
1	19.558	21413253	95.18
2	39.860	1085516	4.82

Racemic



	Ret. Time	Area	% Area
1	19.554	20292389	50.27
2	39.789	20072702	49.73

Supplementary Fig. 24. HPLC spectrum of compound **25**

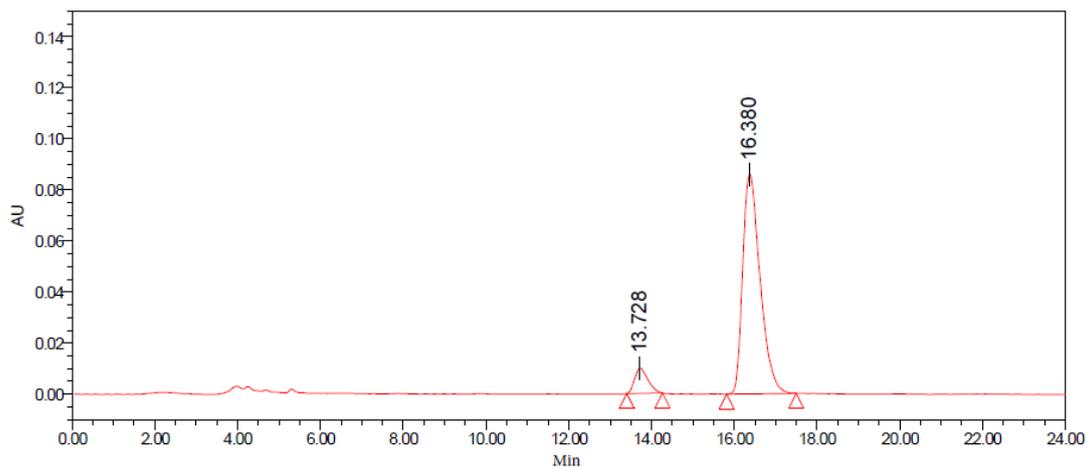


26

HPLC Conditions

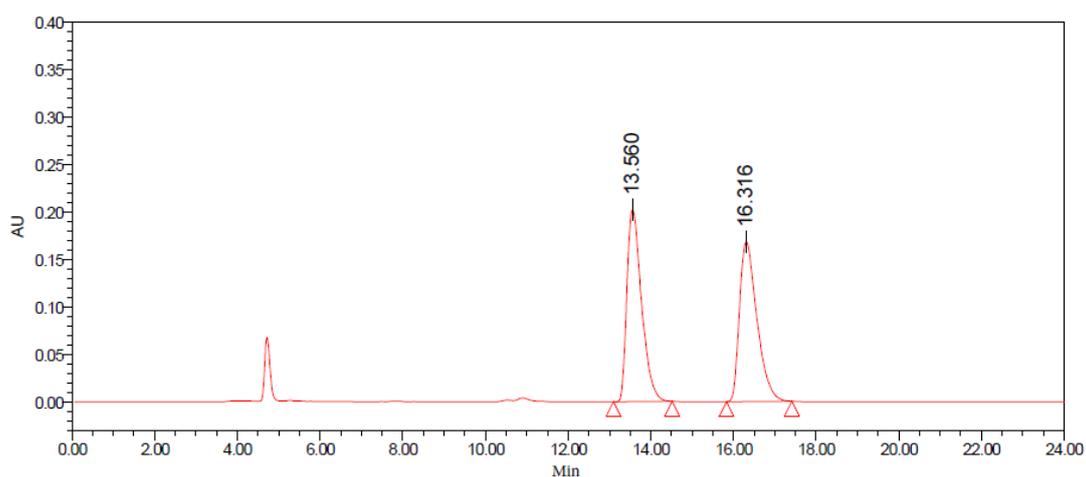
Column: Chiralpak AD-H,
Daicel Chemical Industries Ltd.
Eluent: Hexanes / Isopropanol (80:20)
Flow rate: 1.0 mL/min
Detection: UV 254 nm

Chiral



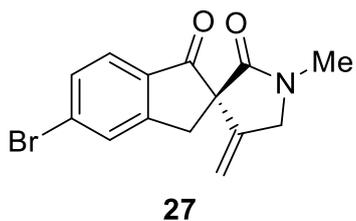
	Ret. Time	Area	% Area
1	13.728	220731	8.09
2	16.380	2507899	91.91

Racemic



	Ret. Time	Area	% Area
1	13.560	4996382	50.34
2	16.316	4928758	49.66

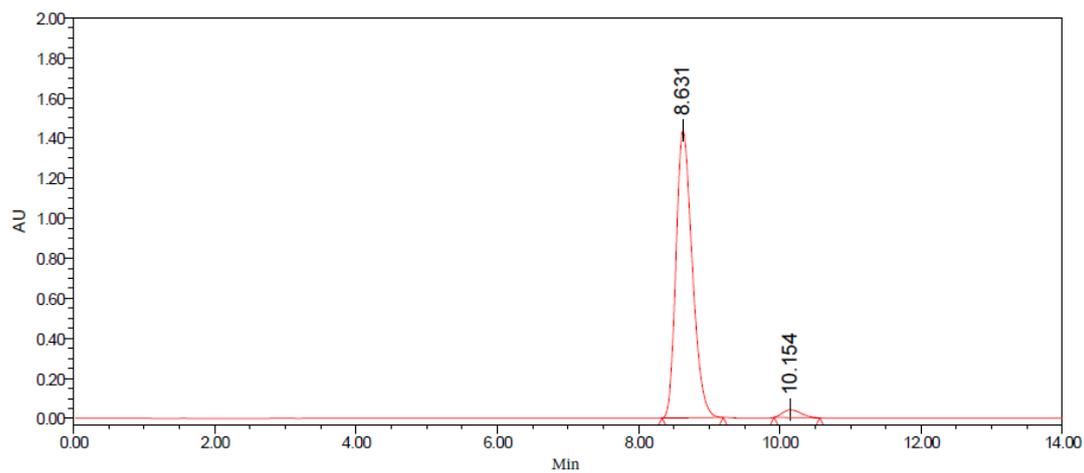
Supplementary Fig. 25. HPLC spectrum of compound 26



HPLC Conditions

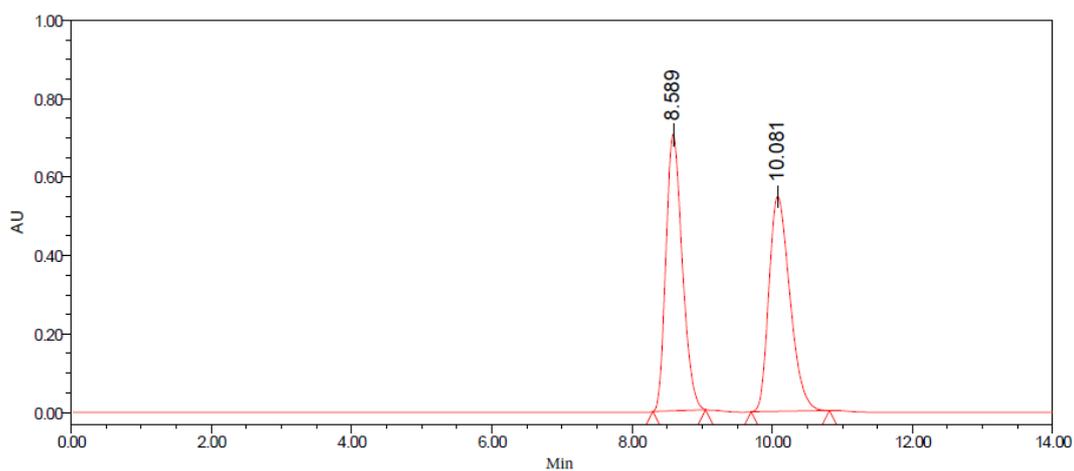
Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (80:20)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



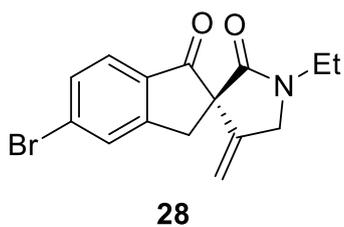
	Ret. Time	Area	% Area
1	8.631	22854833	97.00
2	10.154	707577	3.00

Racemic



	Ret. Time	Area	% Area
1	8.589	11423983	49.98
2	10.081	11431872	50.02

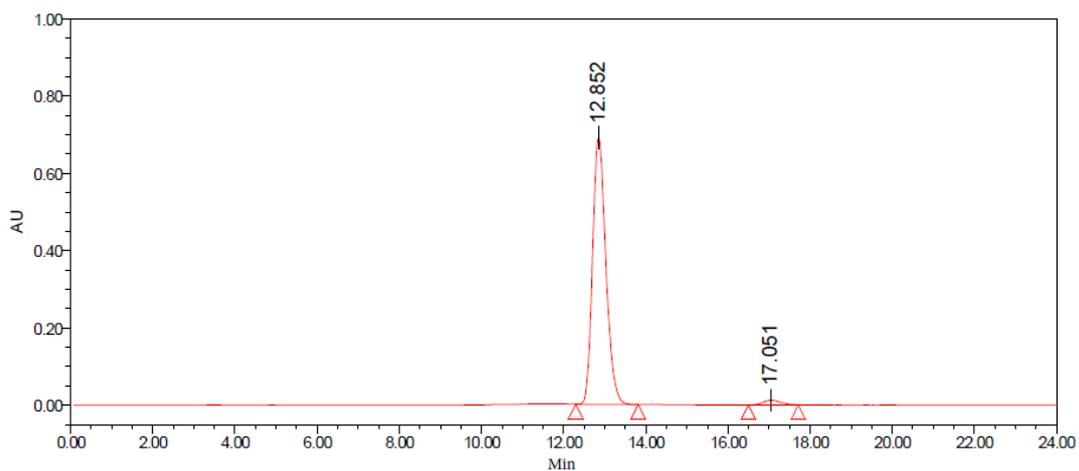
Supplementary Fig. 26. HPLC spectrum of compound 27



HPLC Conditions

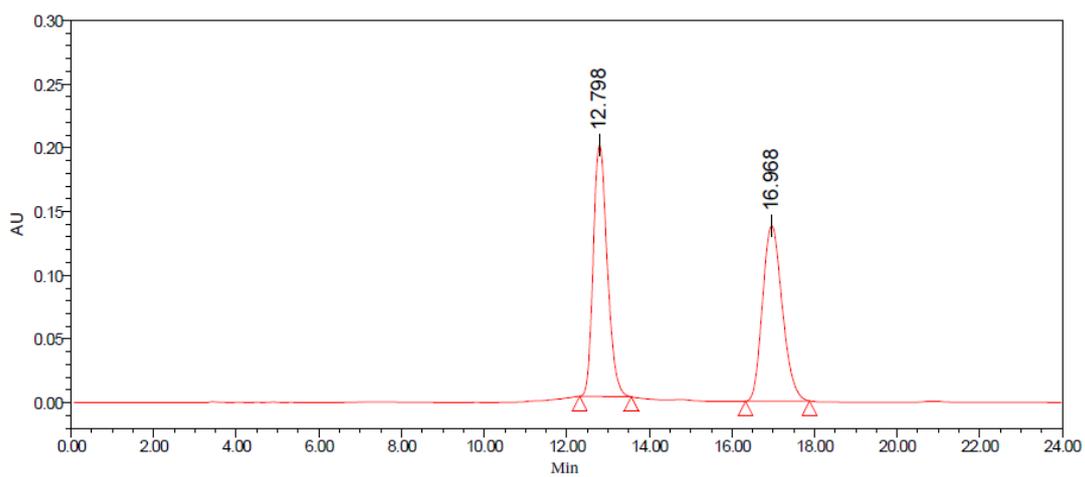
Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (90:10)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



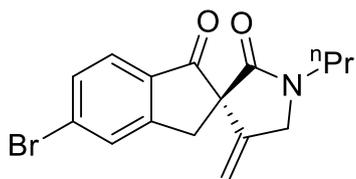
	Ret. Time	Area	% Area
1	12.852	15492694	97.73
2	17.051	360169	2.27

Racemic



	Ret. Time	Area	% Area
1	12.798	4639790	50.37
2	16.968	4572084	49.63

Supplementary Fig. 27. HPLC spectrum of compound **28**

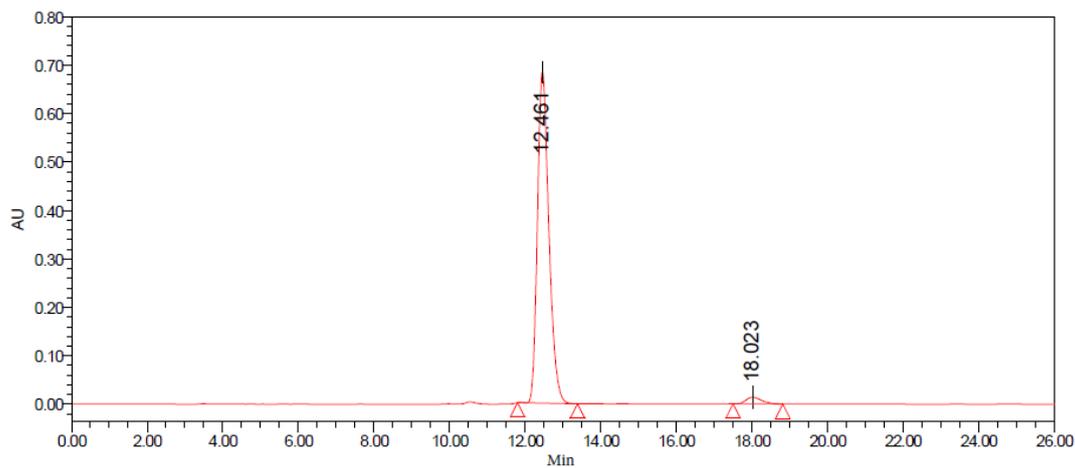


29

HPLC Conditions

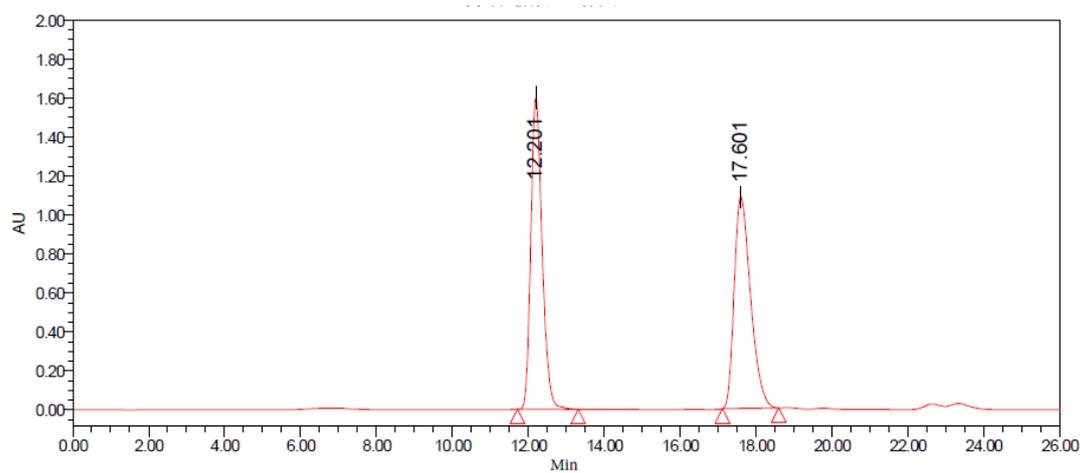
Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (90:10)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



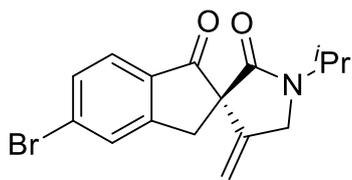
	Ret. Time	Area	% Area
1	12.461	14450329	97.28
2	18.023	404616	2.72

Racemic



	Ret. Time	Area	% Area
1	12.201	33009160	50.37
2	17.601	32529083	49.63

Supplementary Fig. 28. HPLC spectrum of compound **29**

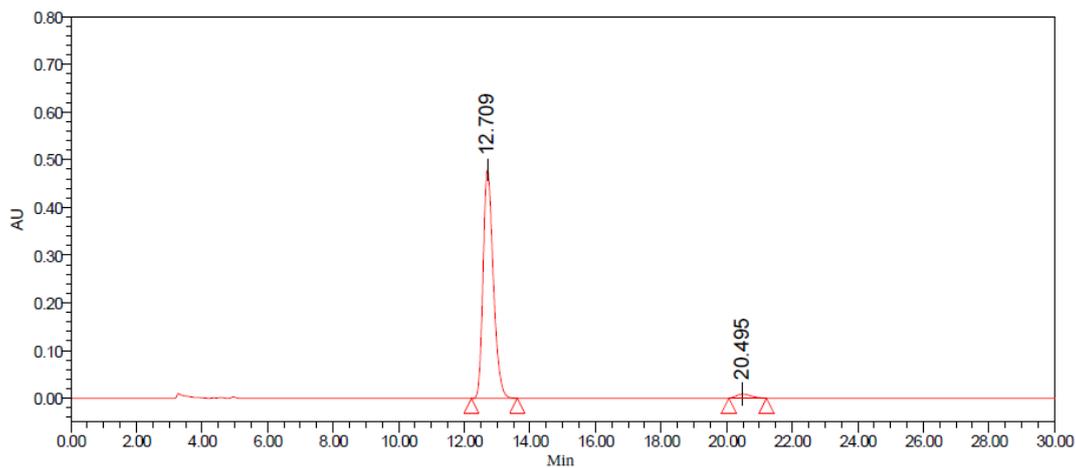


30

HPLC Conditions

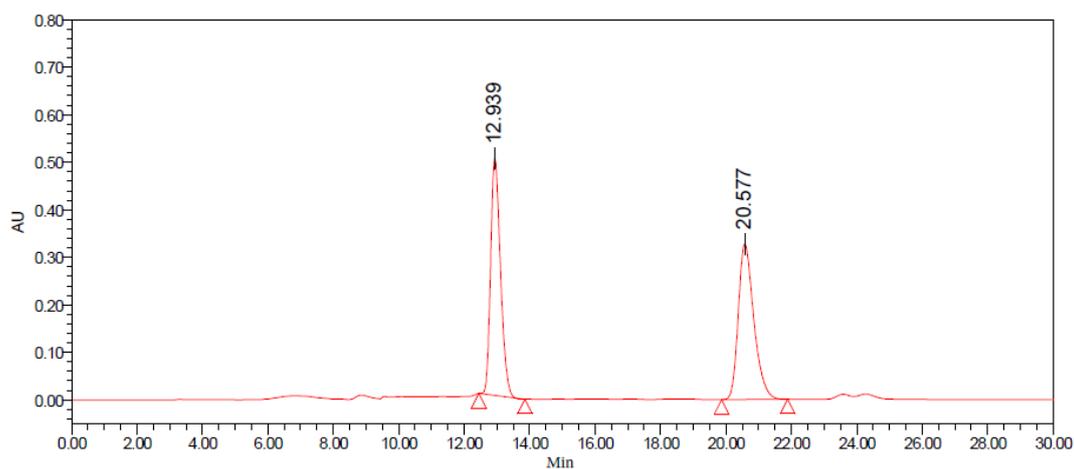
Column: Chiralpak AD-H,
Daicel Chemical Industries Ltd.
Eluent: Hexanes / Isopropanol (90:10)
Flow rate: 1.0 mL/min
Detection: UV 254 nm

Chiral



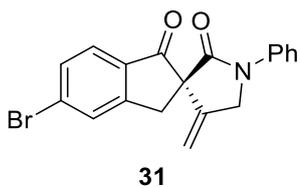
	Ret. Time	Area	% Area
1	12.709	10404231	97.49
2	20.495	268341	2.51

Racemic



	Ret. Time	Area	% Area
1	12.939	10435471	49.20
2	20.577	10774413	50.80

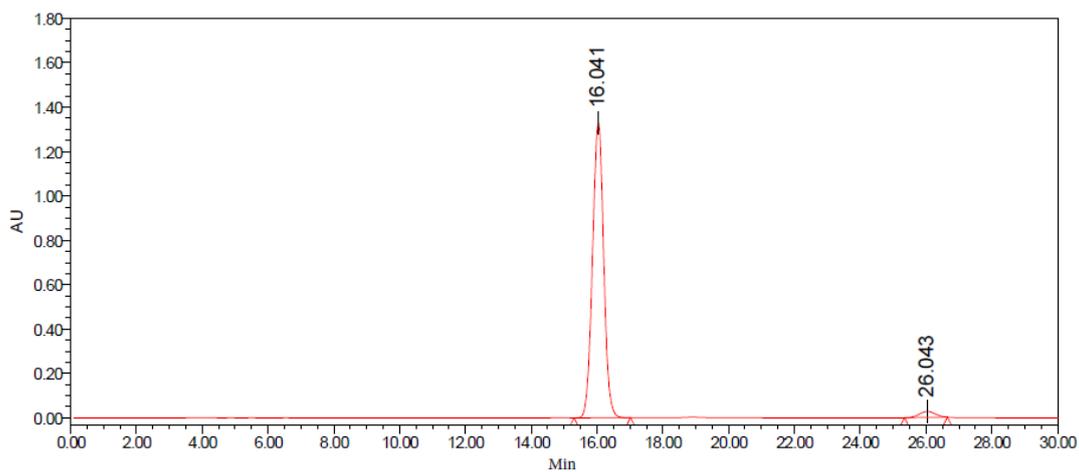
Supplementary Fig. 29. HPLC spectrum of compound 30



HPLC Conditions

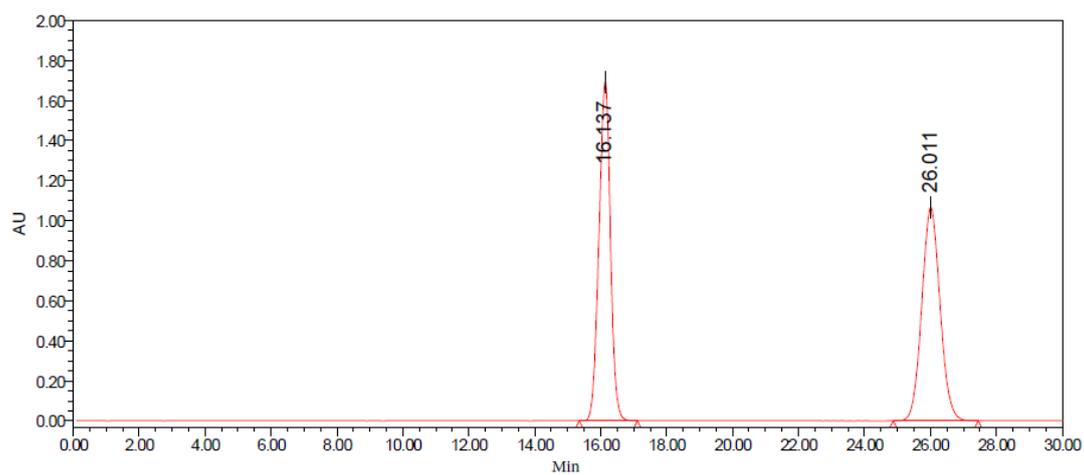
Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (80:20)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



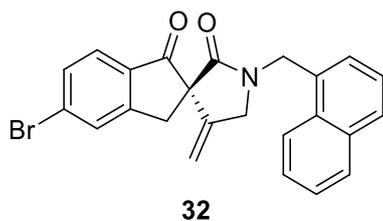
	Ret. Time	Area	% Area
1	16.041	31313394	97.13
2	26.043	925384	2.87

Racemic



	Ret. Time	Area	% Area
1	16.137	40959636	49.91
2	26.011	41109645	50.09

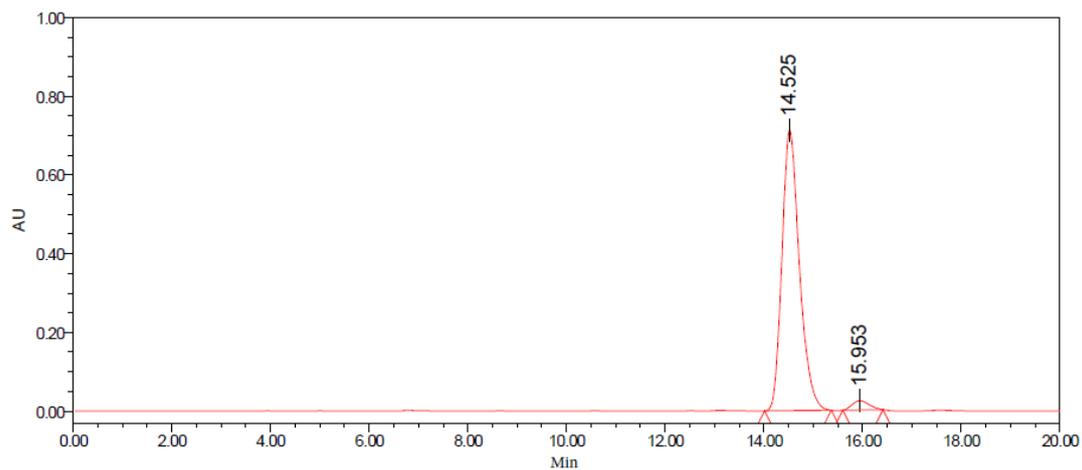
Supplementary Fig. 30. HPLC spectrum of compound 31



HPLC Conditions

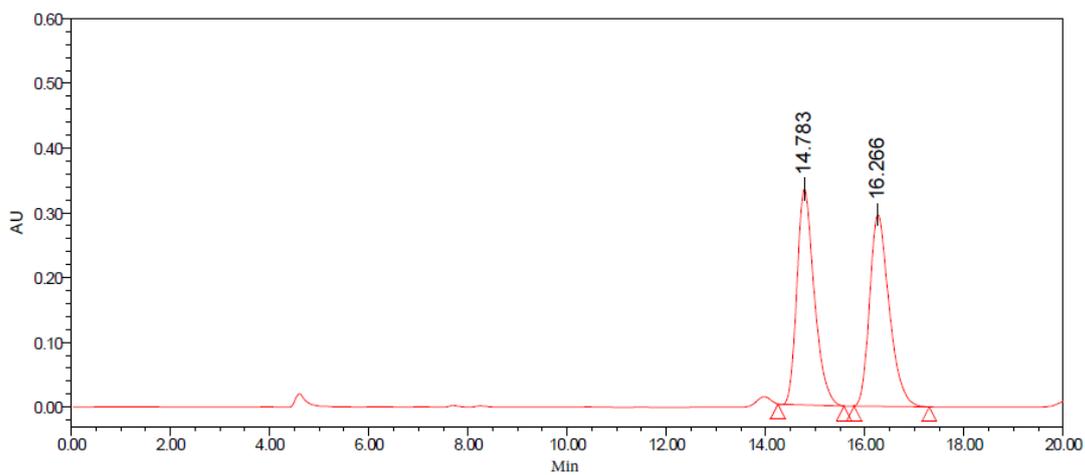
Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (80:20)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



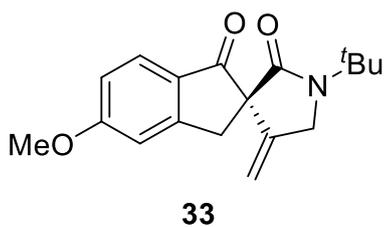
	Ret. Time	Area	% Area
1	14.525	17507621	96.87
2	15.953	566274	3.13

Racemic



	Ret. Time	Area	% Area
1	14.783	8108523	50.02
2	16.266	8101347	49.98

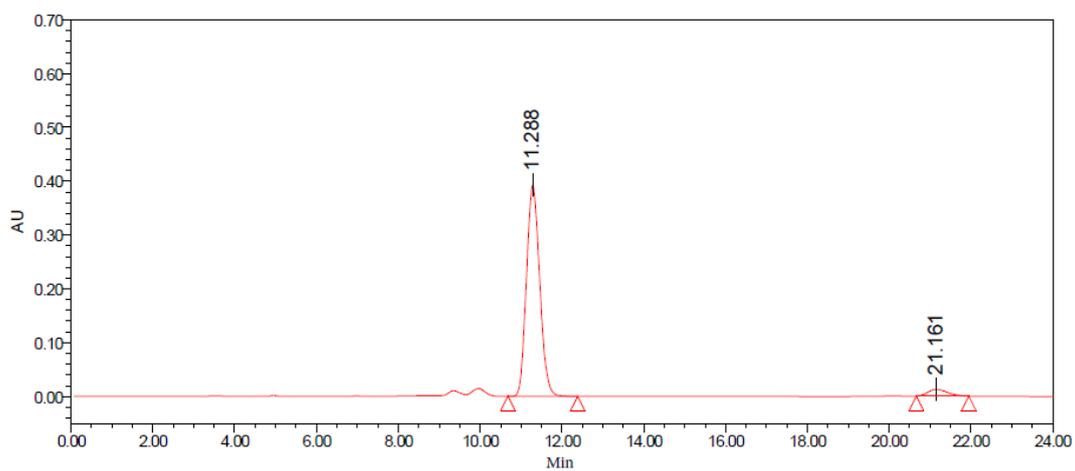
Supplementary Fig. 31. HPLC spectrum of compound **32**



HPLC Conditions

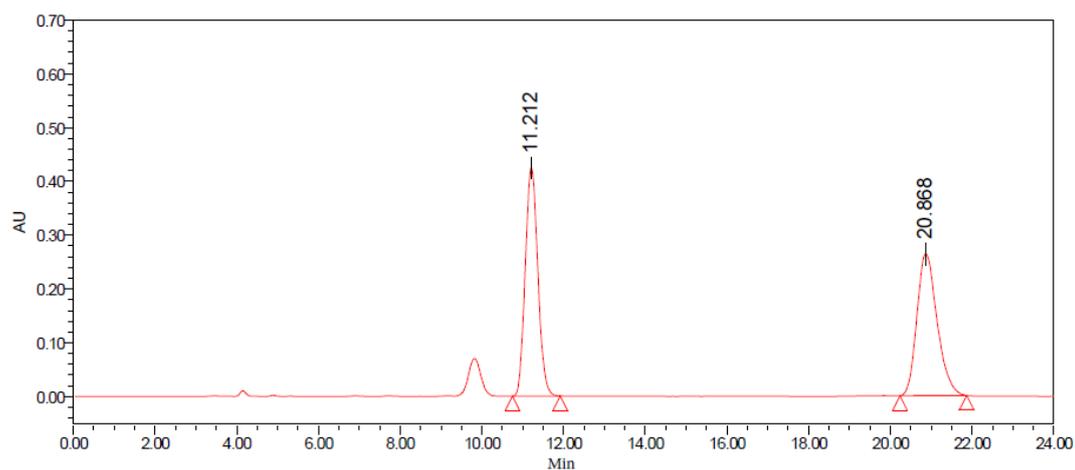
Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (90:10)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



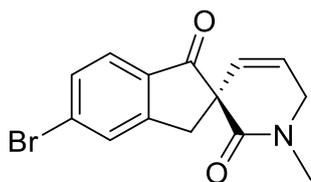
	Ret. Time	Area	% Area
1	11.288	8846862	95.48
2	21.161	419285	4.52

Racemic



	Ret. Time	Area	% Area
1	11.212	9132757	50.21
2	20.868	9056218	49.79

Supplementary Fig. 32. HPLC spectrum of compound **33**

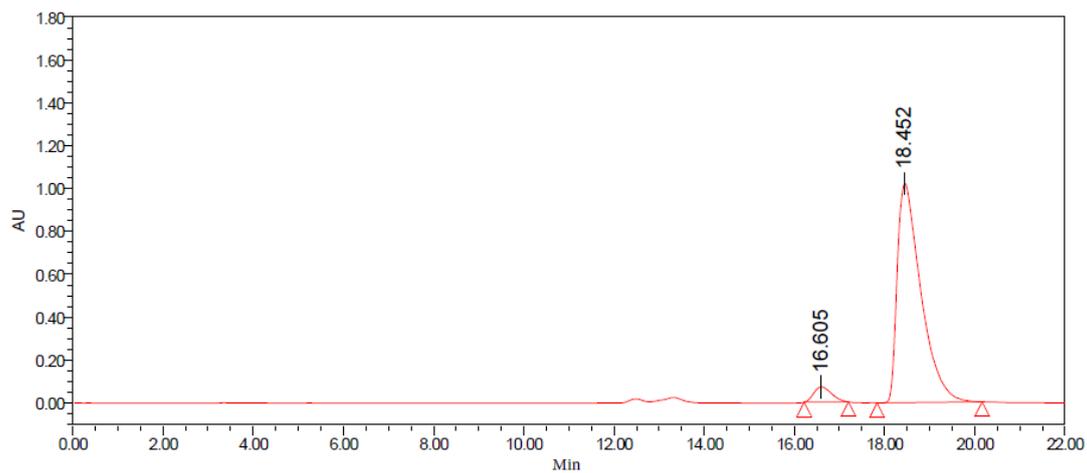


34

HPLC Conditions

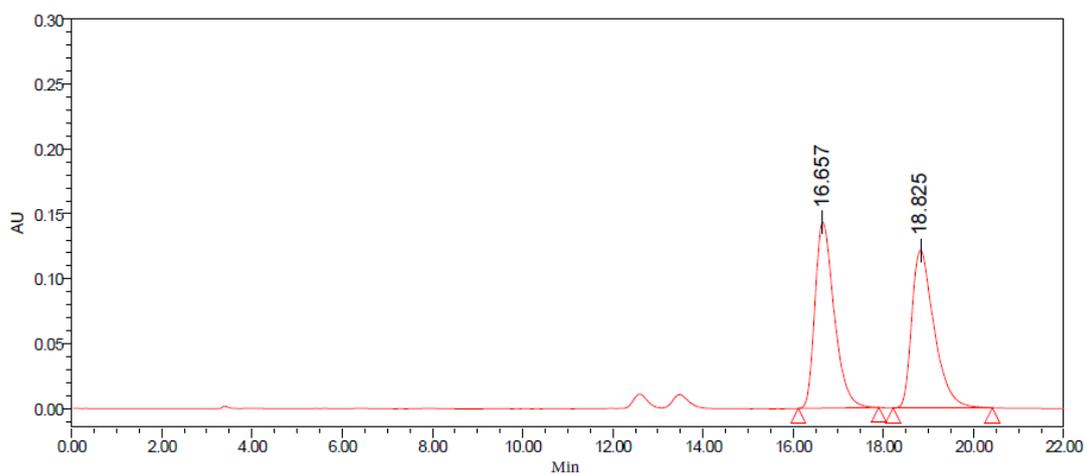
Column: Chiralpak OD-H,
Daicel Chemical Industries Ltd.
Eluent: Hexanes / Isopropanol (85:15)
Flow rate: 1.0 mL/min
Detection: UV 254 nm

Chiral



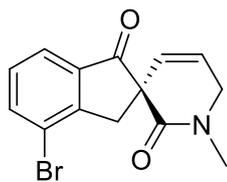
	Ret. Time	Area	% Area
1	16.605	1947626	4.97
2	18.452	37234899	95.03

Racemic



	Ret. Time	Area	% Area
1	16.657	4246515	50.37
2	18.825	4184305	49.63

Supplementary Fig. 33. HPLC spectrum of compound **34**

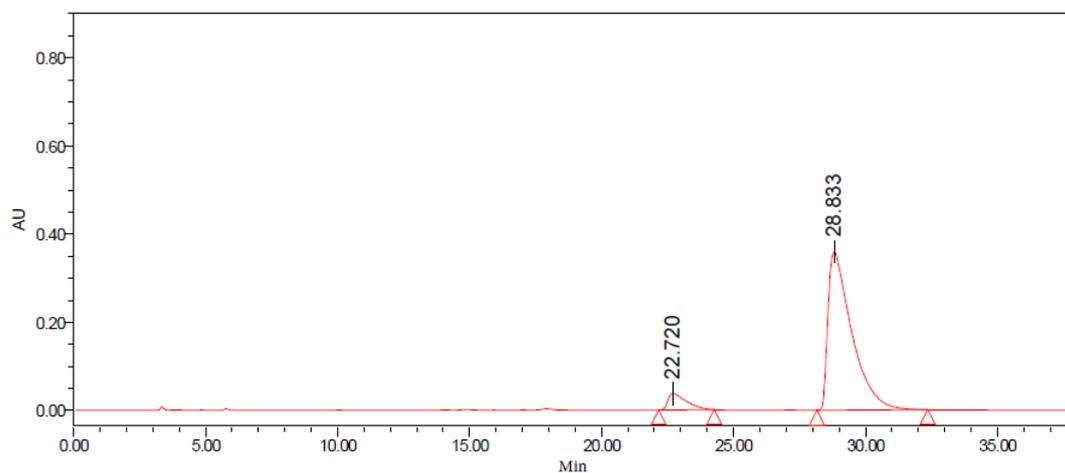


35

HPLC Conditions

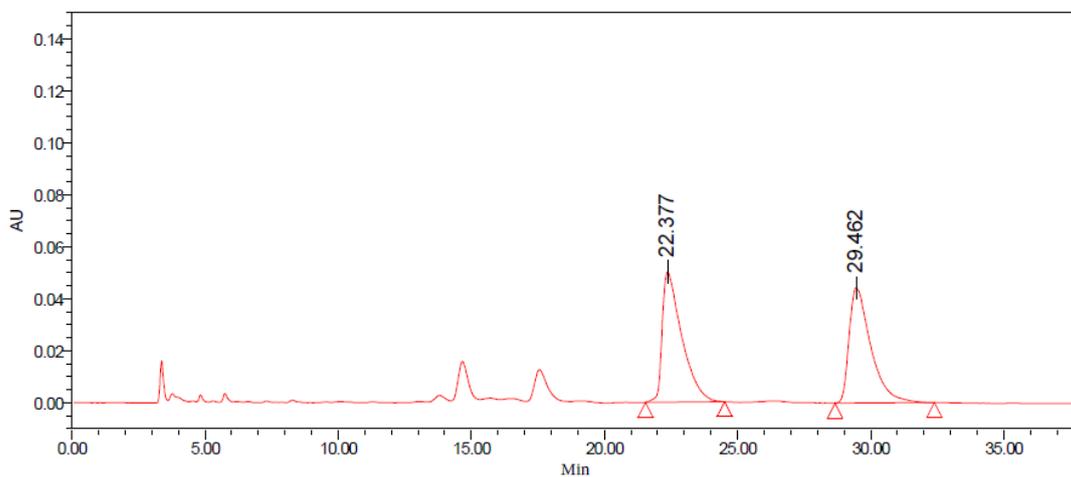
Column: Chiralpak OD-H,
Daicel Chemical Industries Ltd.
Eluent: Hexanes / Isopropanol (90:10)
Flow rate: 1.0 mL/min
Detection: UV 254 nm

Chiral



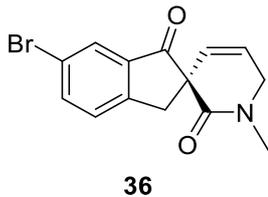
	Ret. Time	Area	% Area
1	22.720	1819521	7.50
2	28.833	22436213	92.50

Racemic



	Ret. Time	Area	% Area
1	22.377	2554483	50.47
2	29.462	2506732	49.53

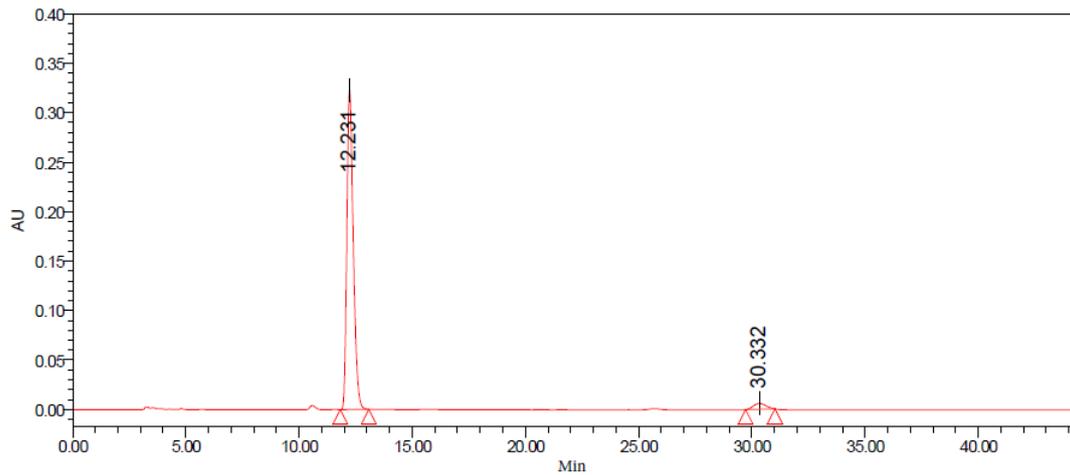
Supplementary Fig. 34. HPLC spectrum of compound **35**



HPLC Conditions

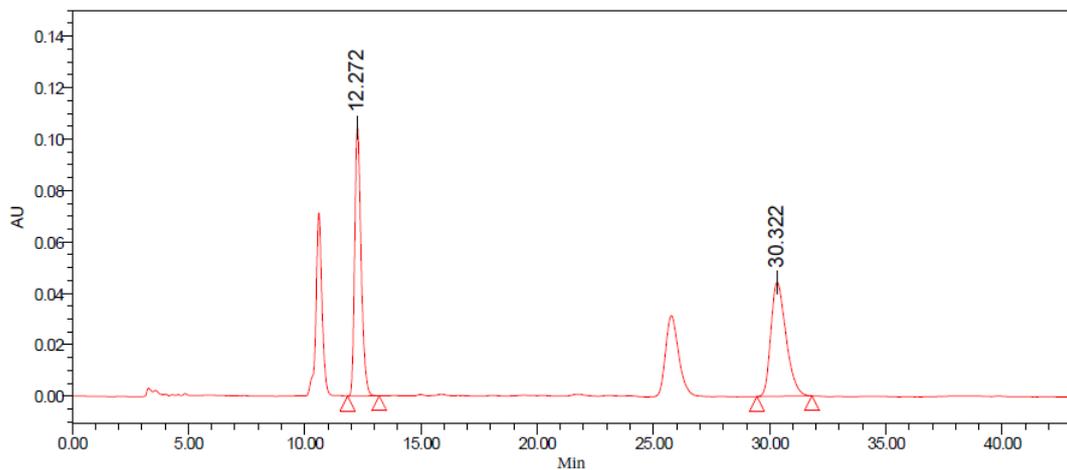
Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (90:10)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



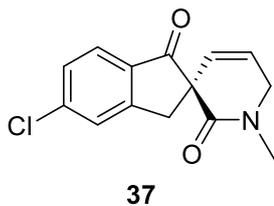
	Ret. Time	Area	% Area
1	12.231	6312592	96.47
2	30.332	230952	3.53

Racemic



	Ret. Time	Area	% Area
1	12.272	2008610	49.98
2	30.322	2009848	50.02

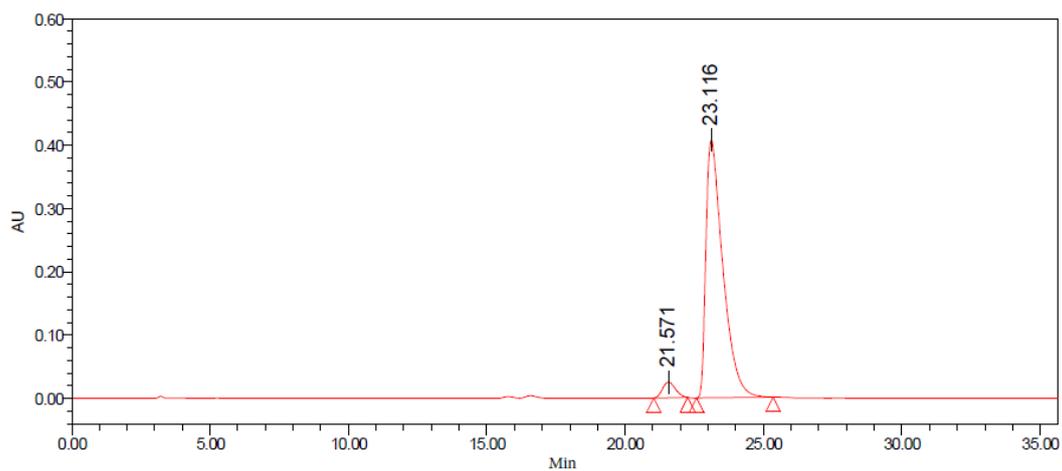
Supplementary Fig. 35. HPLC spectrum of compound **36**



HPLC Conditions

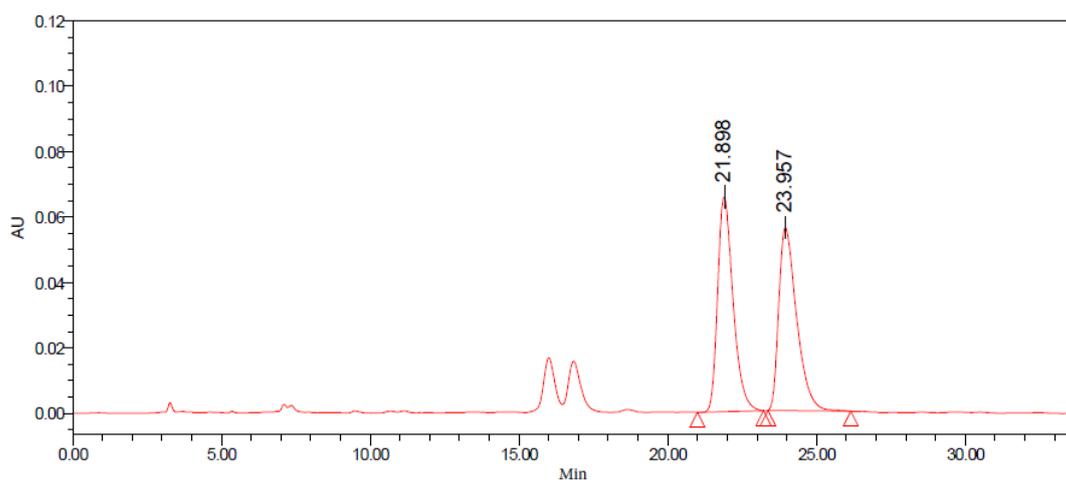
Column: Chiralpak OD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (90:10)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



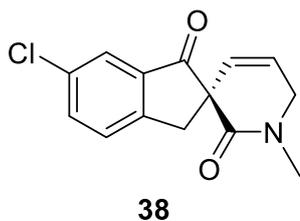
	Ret. Time	Area	% Area
1	21.571	808174	4.46
2	23.116	17318833	95.54

Racemic



	Ret. Time	Area	% Area
1	21.898	2377867	50.55
2	23.957	2326359	49.45

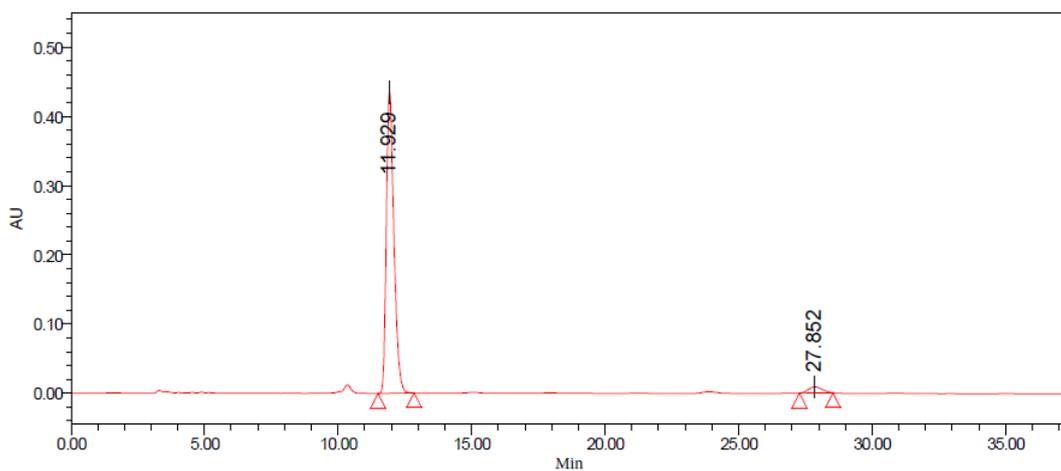
Supplementary Fig. 36. HPLC spectrum of compound **37**



HPLC Conditions

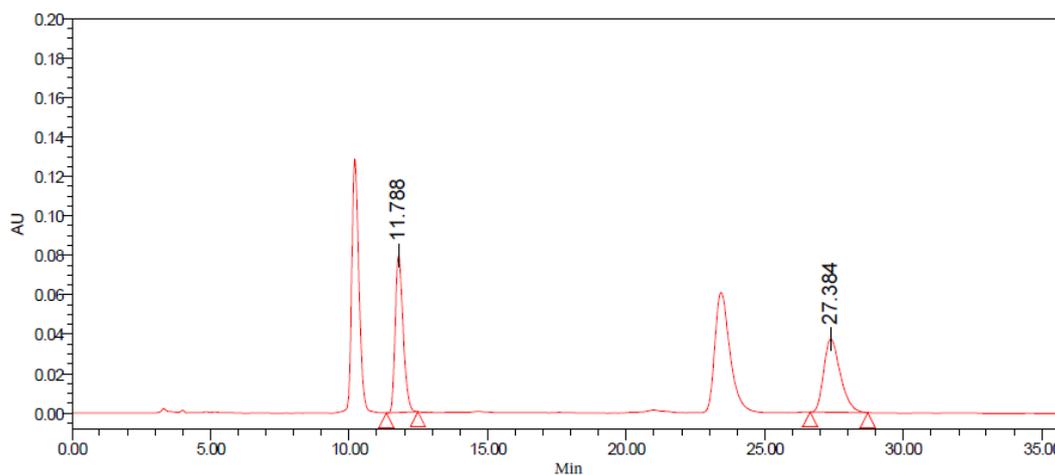
Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (90:10)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



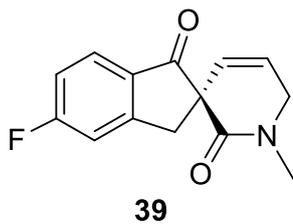
	Ret. Time	Area	% Area
1	11.929	8668327	96.46
2	27.852	317678	3.54

Racemic



	Ret. Time	Area	% Area
1	11.788	1571069	50.37
2	27.384	1547815	49.63

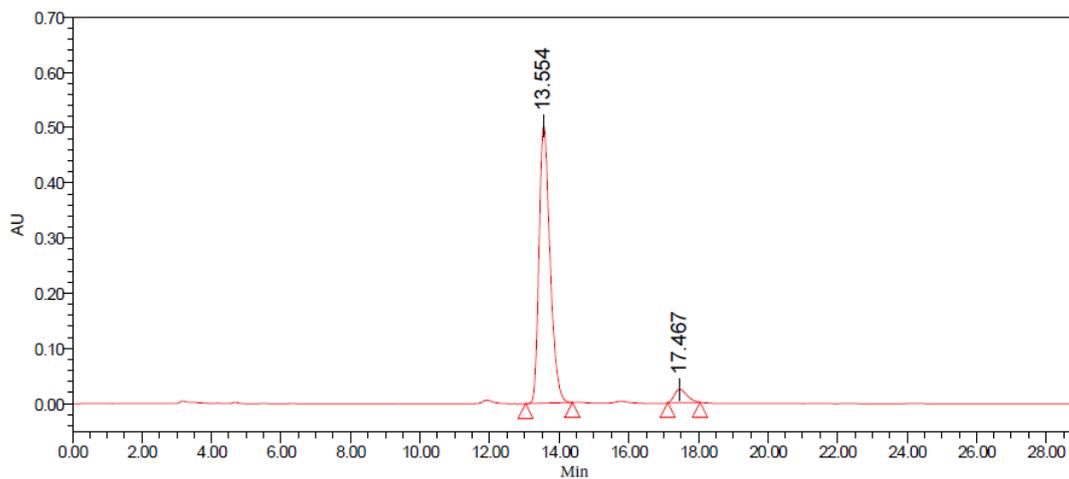
Supplementary Fig. 37. HPLC spectrum of compound **38**



HPLC Conditions

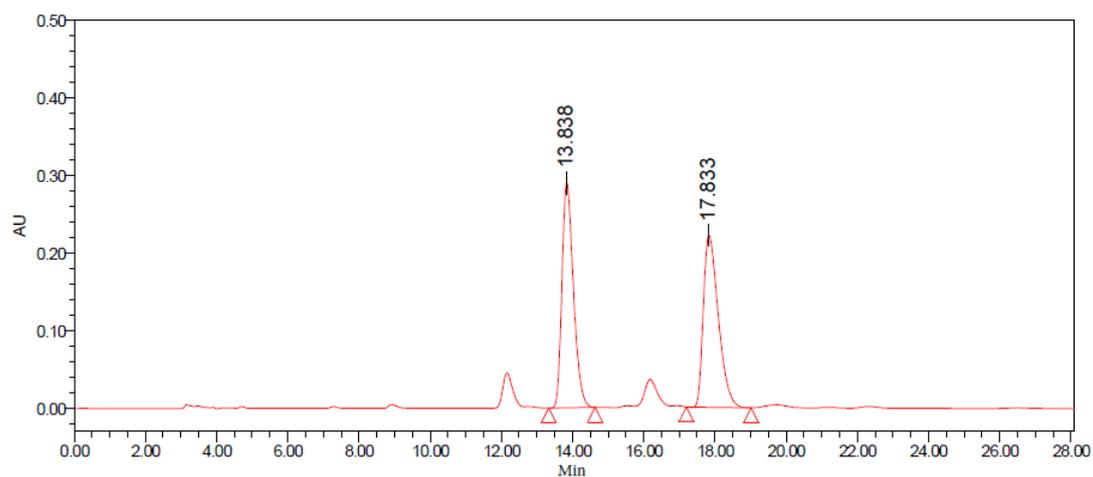
Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (90:10)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



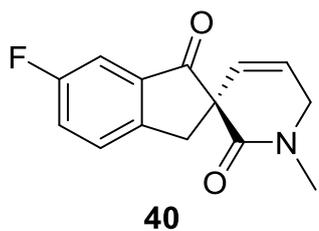
	Ret. Time	Area	% Area
1	13.554	11013434	94.80
2	17.467	604057	5.20

Racemic



	Ret. Time	Area	% Area
1	13.838	6500631	50.19
2	17.833	6451172	49.81

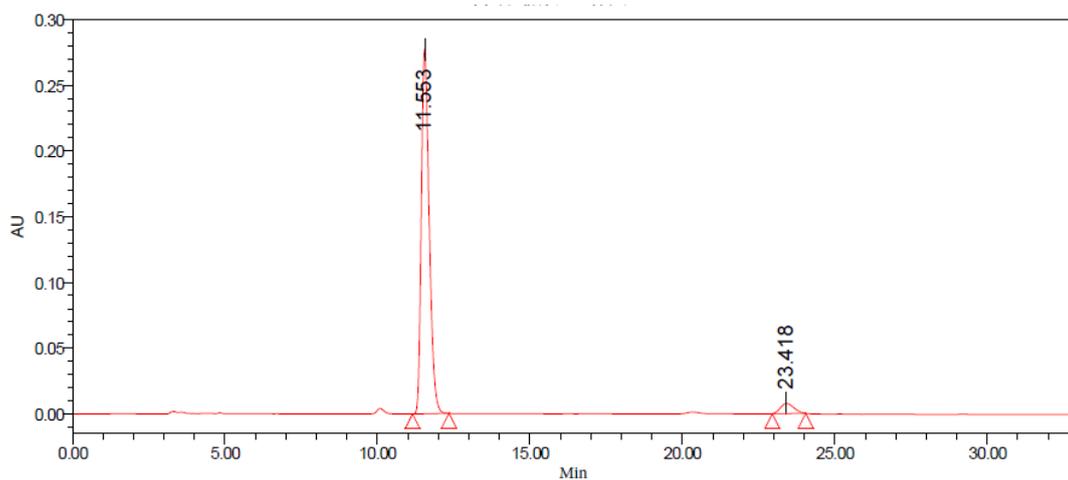
Supplementary Fig. 38. HPLC spectrum of compound **39**



HPLC Conditions

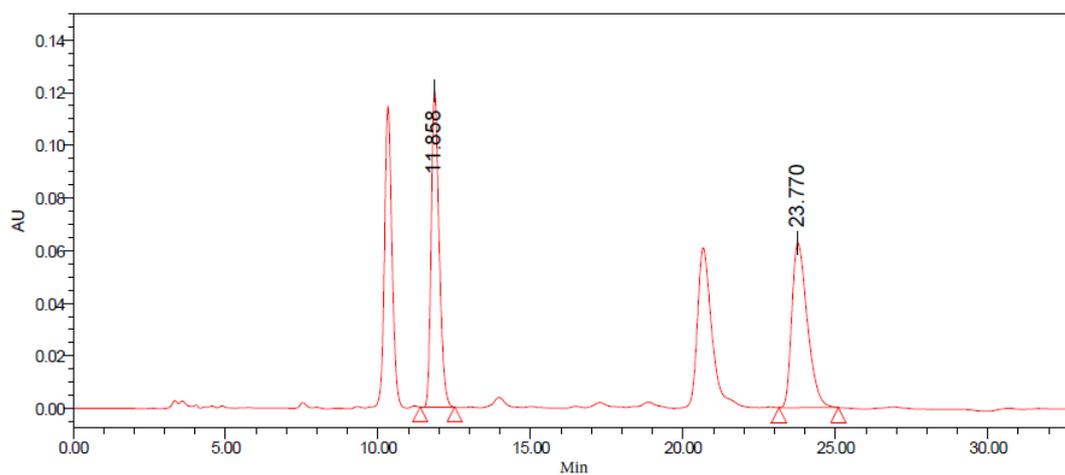
Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (90:10)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



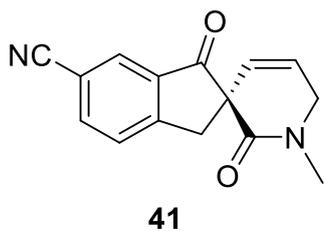
	Ret. Time	Area	% Area
1	11.553	4959485	95.48
2	23.418	234980	4.52

Racemic



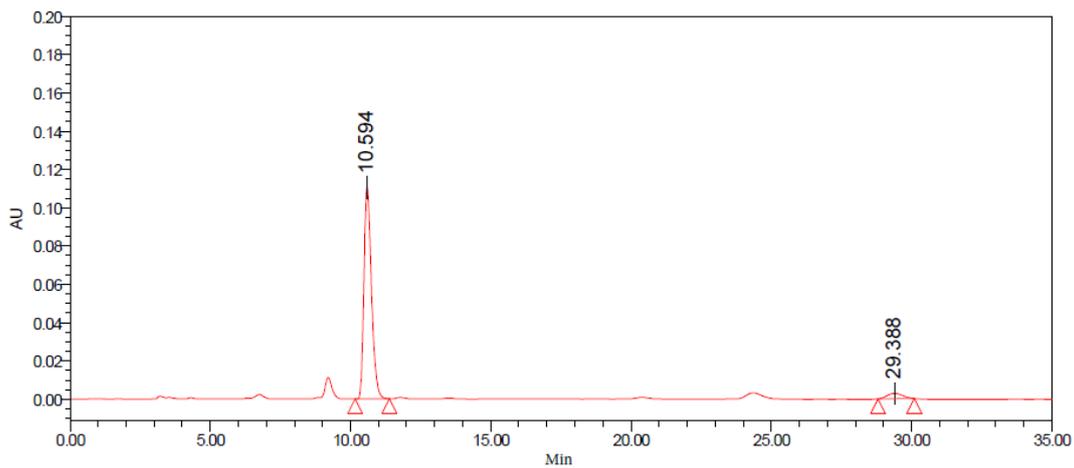
	Ret. Time	Area	% Area
1	11.858	2181169	49.68
2	23.770	2209377	50.32

Supplementary Fig. 39. HPLC spectrum of compound **40**



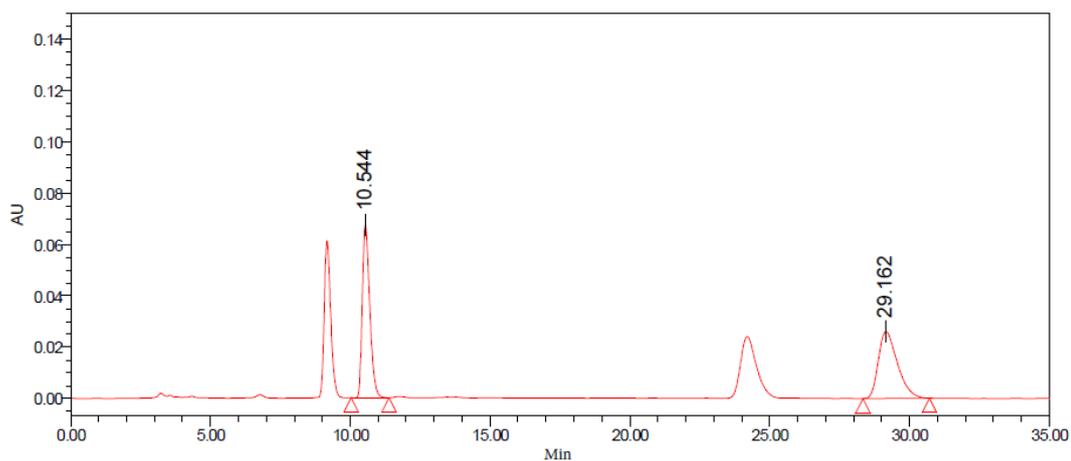
HPLC Conditions
 Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (80:20)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



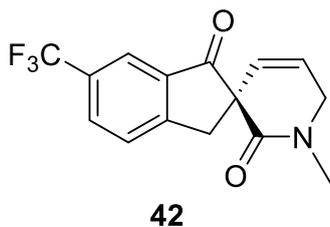
	Ret. Time	Area	% Area
1	10.594	2060628	94.97
2	29.388	109046	5.03

Racemic



	Ret. Time	Area	% Area
1	10.544	1249187	50.25
2	29.162	1236787	49.75

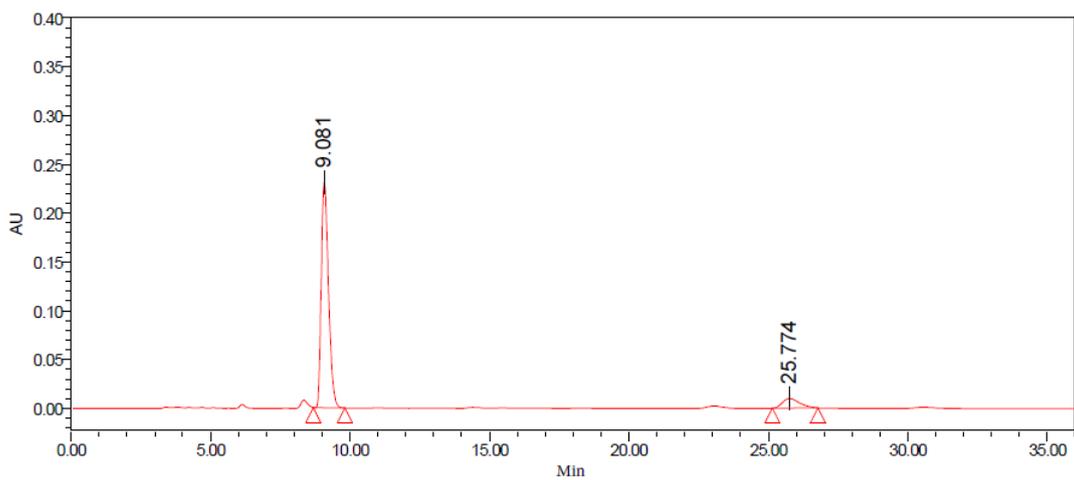
Supplementary Fig. 40. HPLC spectrum of compound **41**



HPLC Conditions

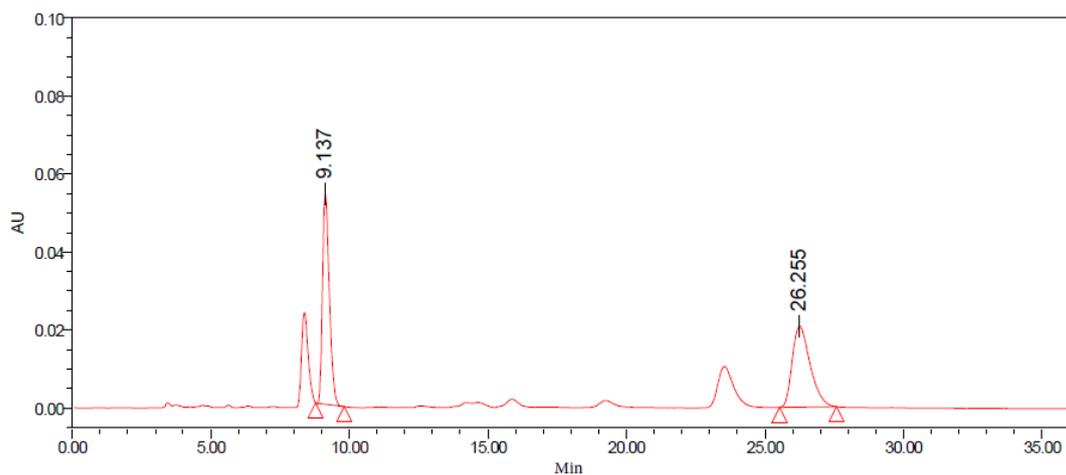
Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (90:10)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



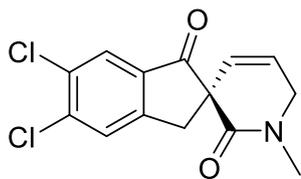
	Ret. Time	Area	% Area
1	9.081	4171020	90.90
2	25.774	417567	9.10

Racemic



	Ret. Time	Area	% Area
1	9.137	932541	50.00
2	26.255	932695	50.00

Supplementary Fig. 41. HPLC spectrum of compound 42

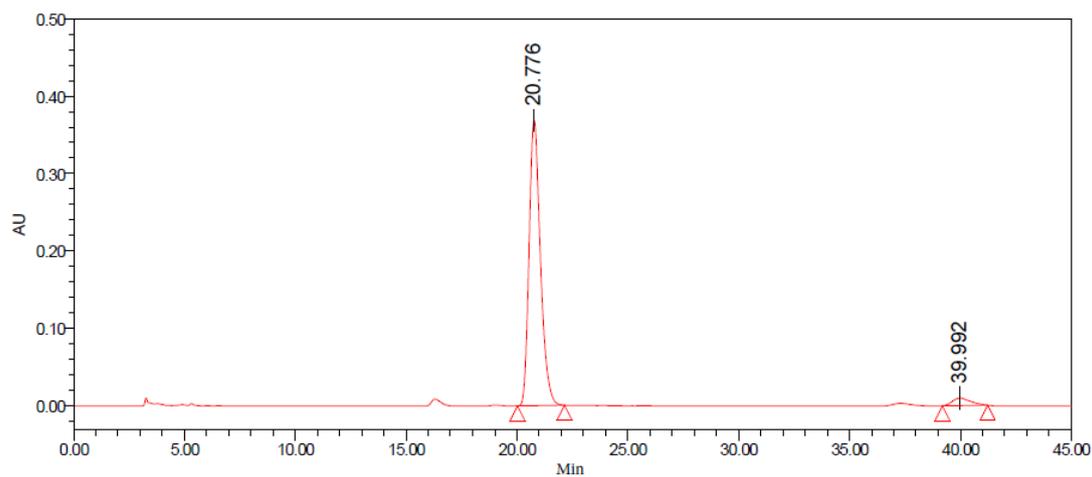


43

HPLC Conditions

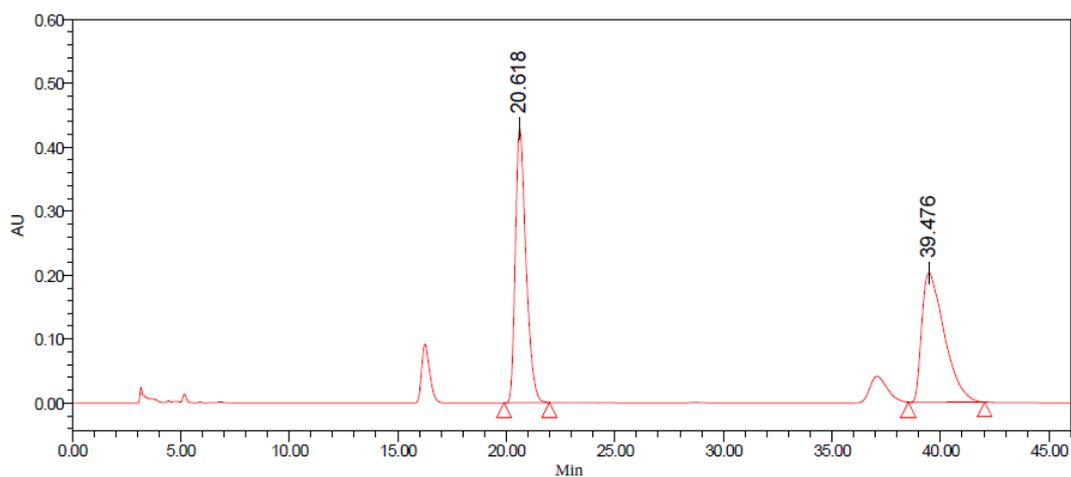
Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (95:5)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



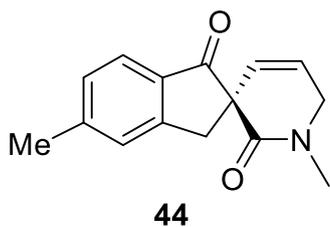
	Ret. Time	Area	% Area
1	20.776	13136664	95.98
2	39.992	550744	4.02

Racemic



	ret. Time	Area	% Area
1	20.618	14646293	50.04
2	39.476	14620023	49.96

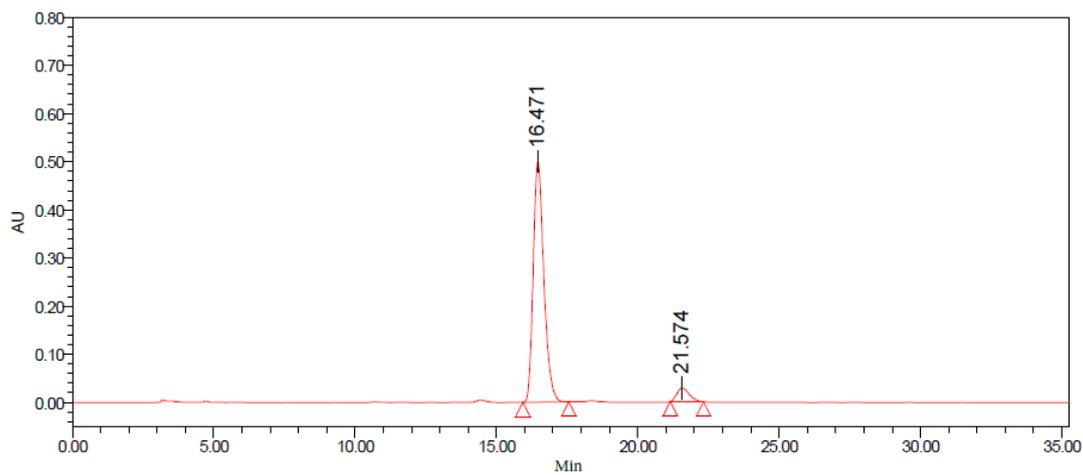
Supplementary Fig. 42. HPLC spectrum of compound 43



HPLC Conditions

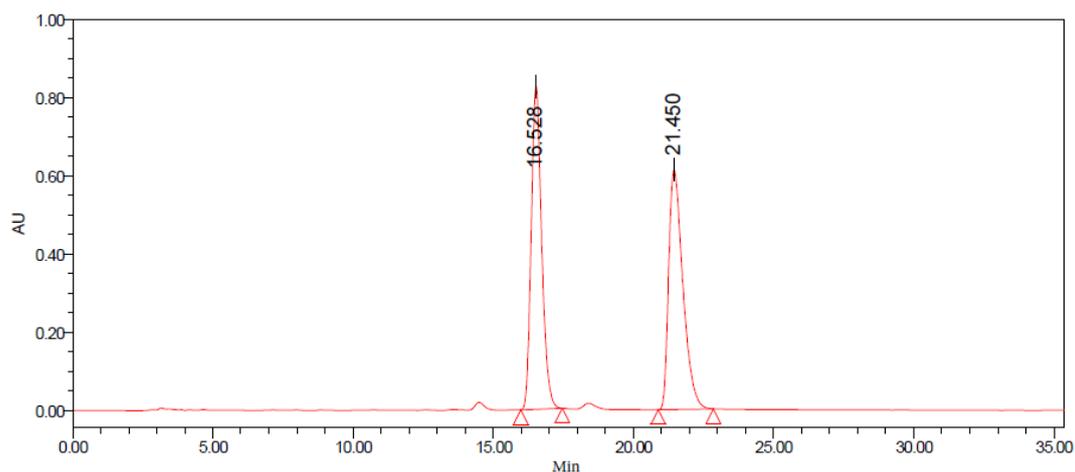
Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (90:10)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



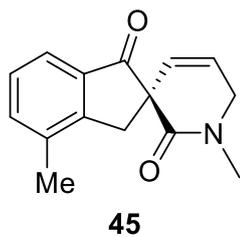
	Ret. Time	Area	% Area
1	16.471	13059300	93.78
2	21.574	866219	6.22

Racemic



	Ret. Time	Area	% Area
1	16.528	21380895	49.79
2	21.450	21559249	50.21

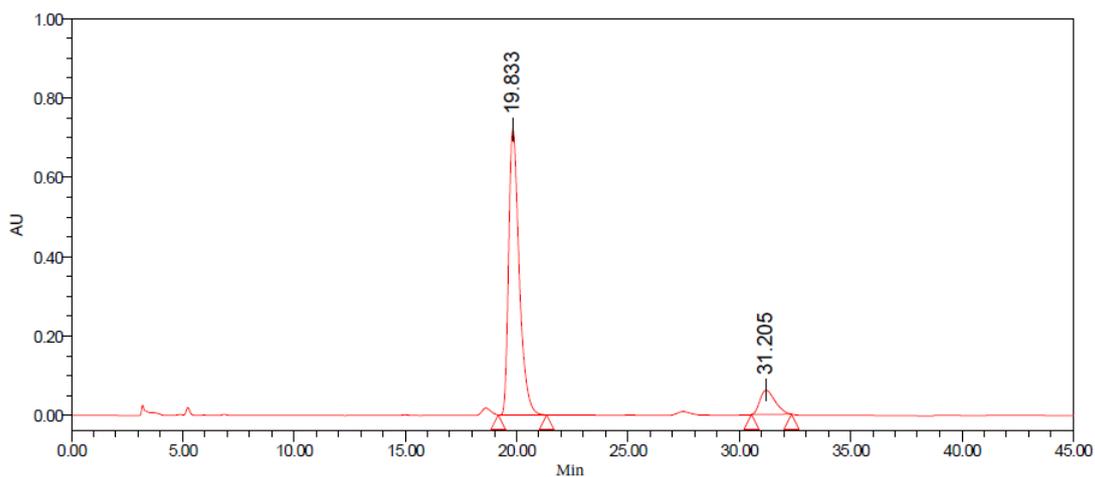
Supplementary Fig. 43. HPLC spectrum of compound **44**



HPLC Conditions

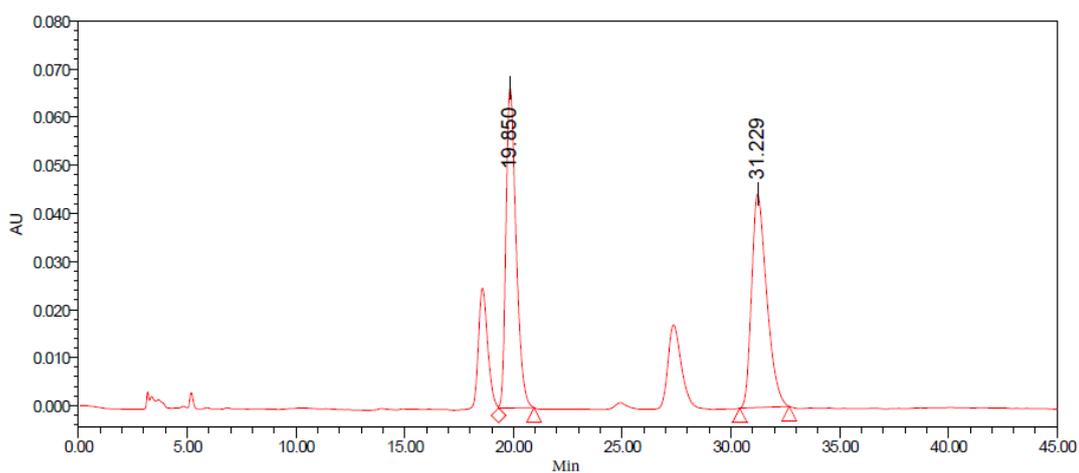
Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (95:5)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



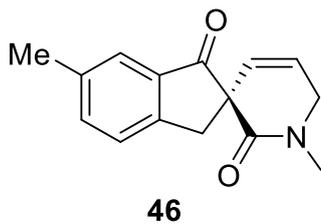
	Ret. Time	Area	% Area
1	19.833	23673681	89.06
2	31.205	2906738	10.94

Racemic



	Ret. Time	Area	% Area
1	19.850	2130386	49.91
2	31.229	2138140	50.09

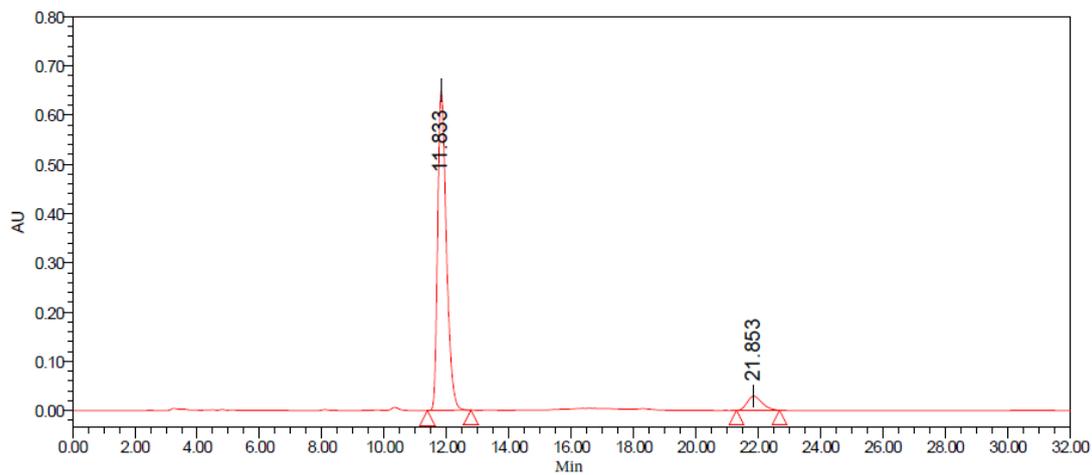
Supplementary Fig. 44. HPLC spectrum of compound 45



HPLC Conditions

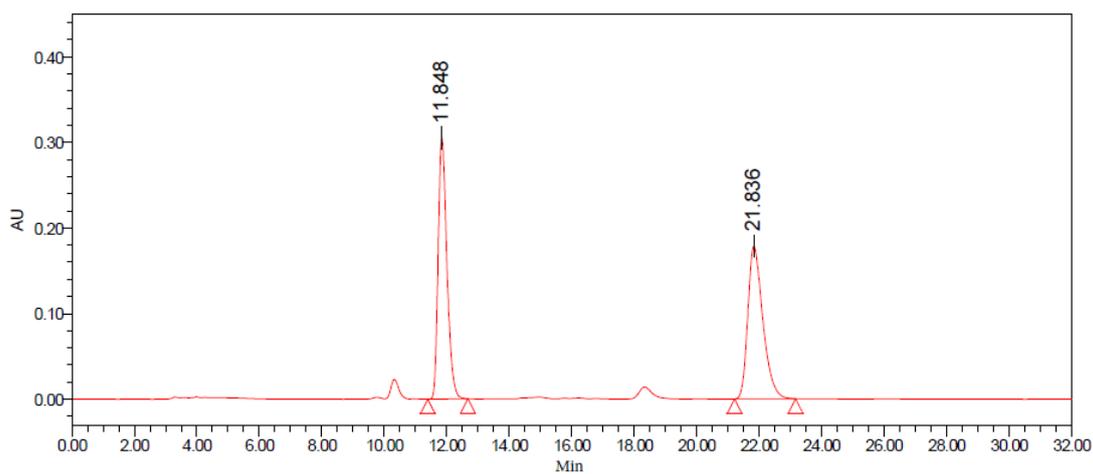
Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (90:10)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



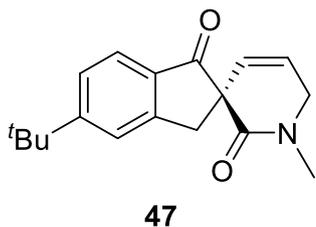
	Ret. Time	Area	% Area
1	11.833	12617366	93.08
2	21.853	938411	6.92

Racemic



	Ret. Time	Area	% Area
1	11.848	5926827	49.94
2	21.836	5942210	50.06

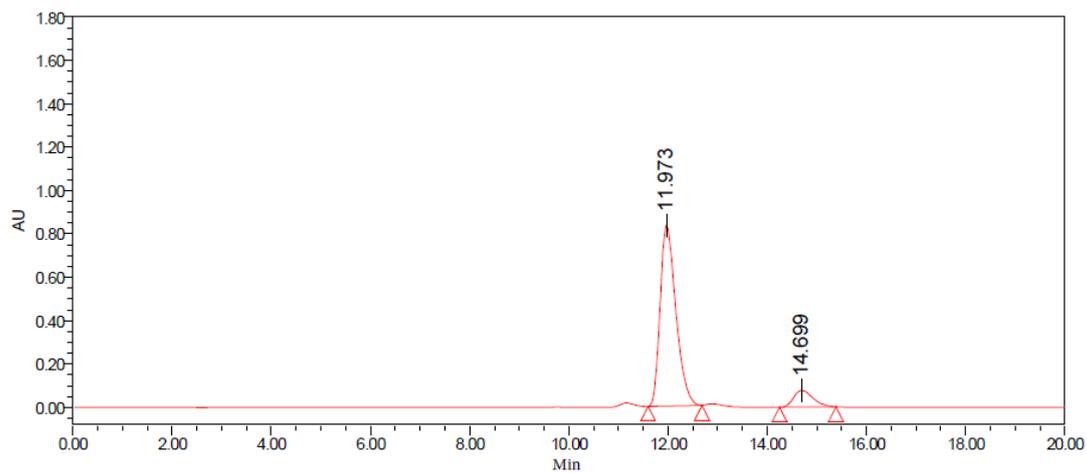
Supplementary Fig. 45. HPLC spectrum of compound **46**



HPLC Conditions

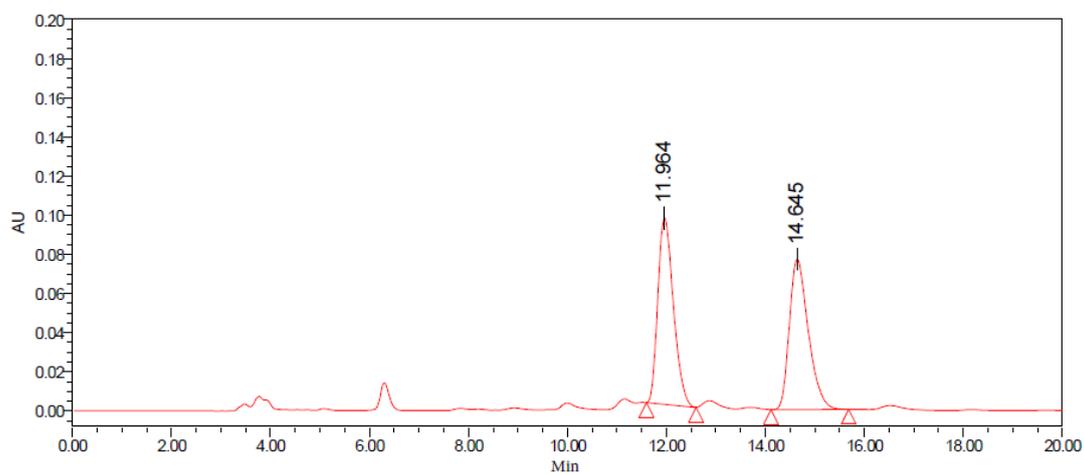
Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (90:10)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



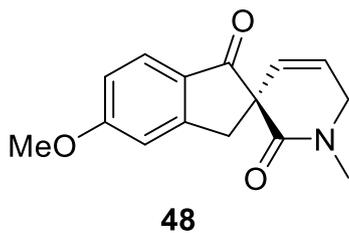
	Ret. Time	Area	% Area
1	11.973	18345461	89.91
2	14.699	2059220	10.09

Racemic



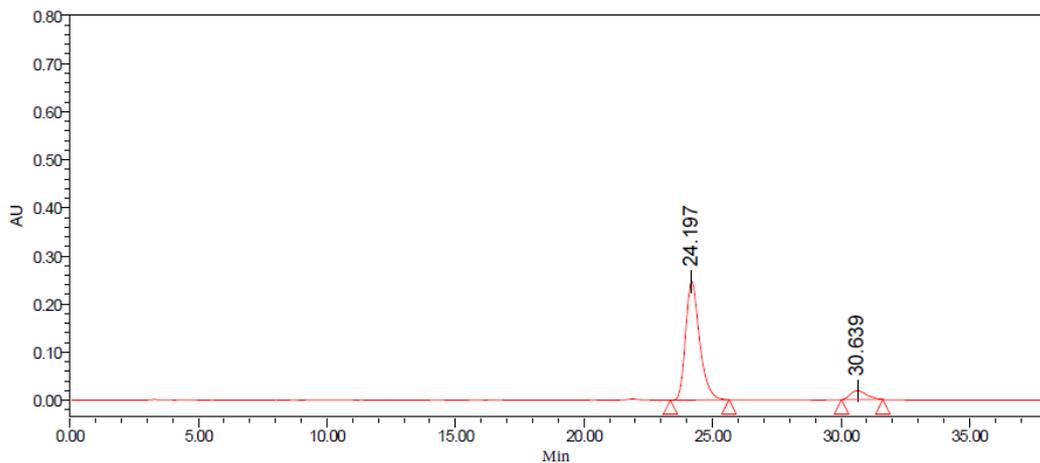
	Ret. Time	Area	% Area
1	11.964	2078652	50.39
2	14.645	2046537	49.61

Supplementary Fig. 46. HPLC spectrum of compound 47



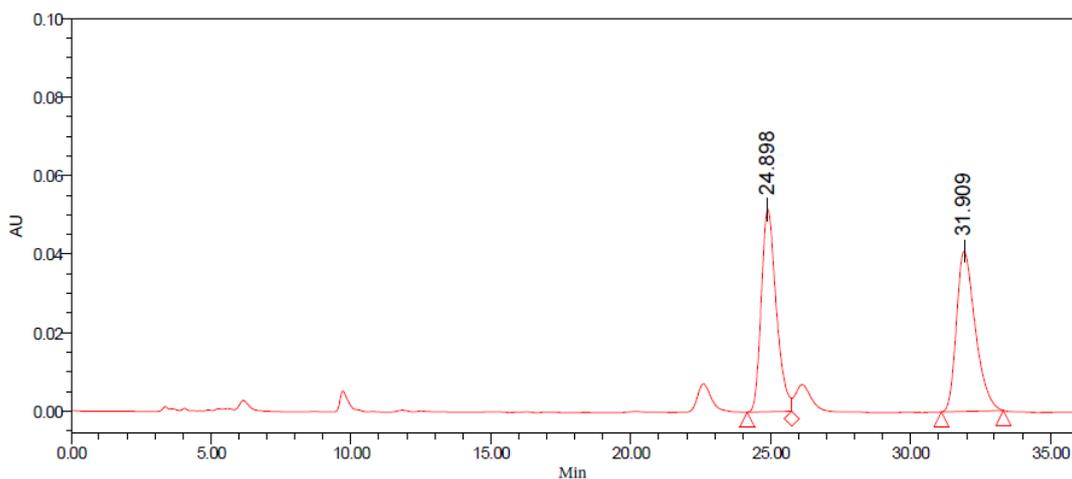
HPLC Conditions
 Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (90:10)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



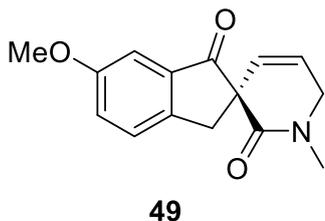
	Ret. Time	Area	% Area
1	24.197	9305648	91.88
2	30.639	822375	8.12

Racemic



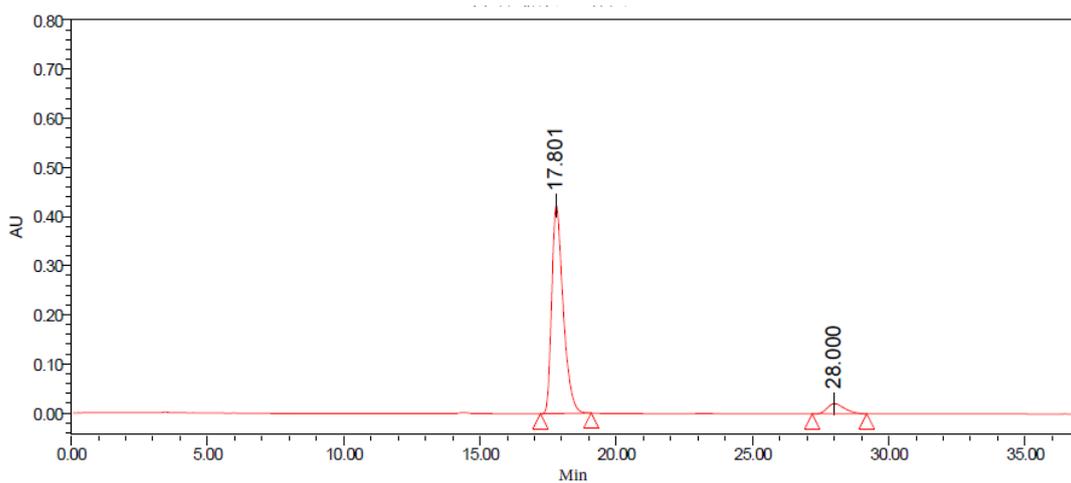
	Ret. Time	Area	% Area
1	24.898	1918091	50.14
2	31.909	1907464	49.86

Supplementary Fig. 47. HPLC spectrum of compound **48**



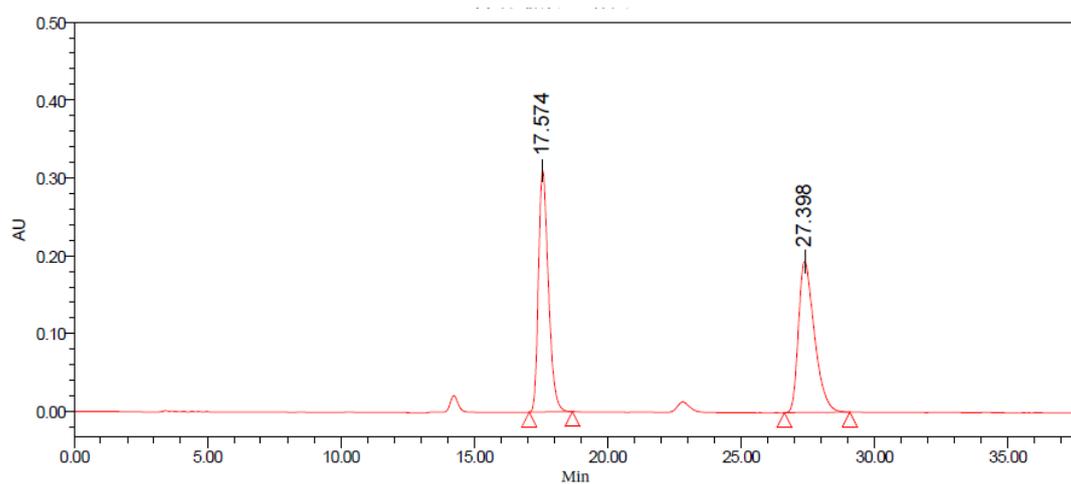
HPLC Conditions
 Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (90:10)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



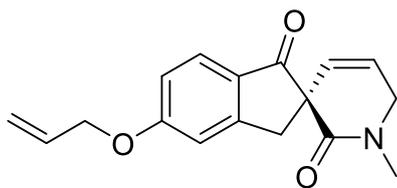
	Ret. Time	Area	% Area
1	17.801	12434636	93.07
2	28.000	925197	6.93

Racemic



	Ret. Time	Area	% Area
1	17.574	8017356	49.81
2	27.398	8079320	50.19

Supplementary Fig. 48. HPLC spectrum of compound 49

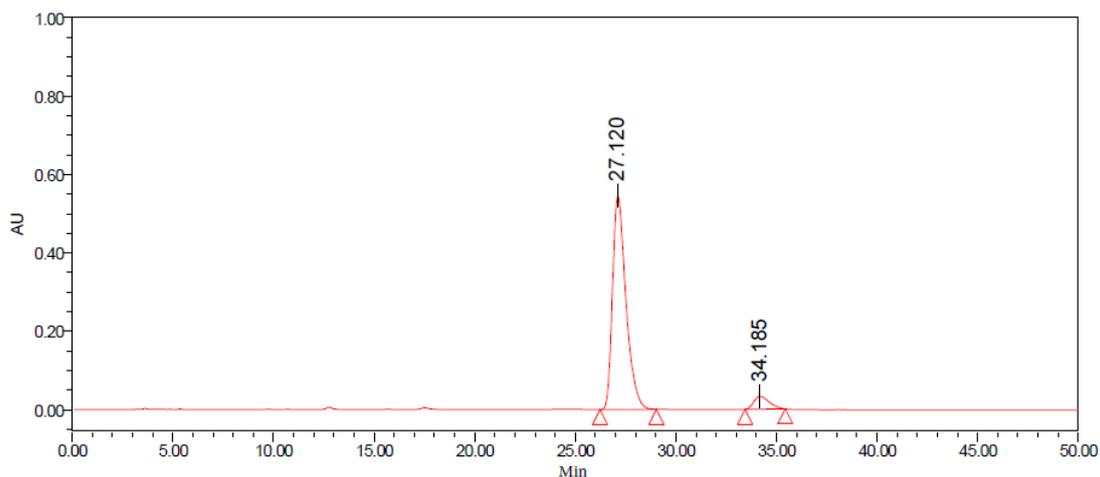


50

HPLC Conditions

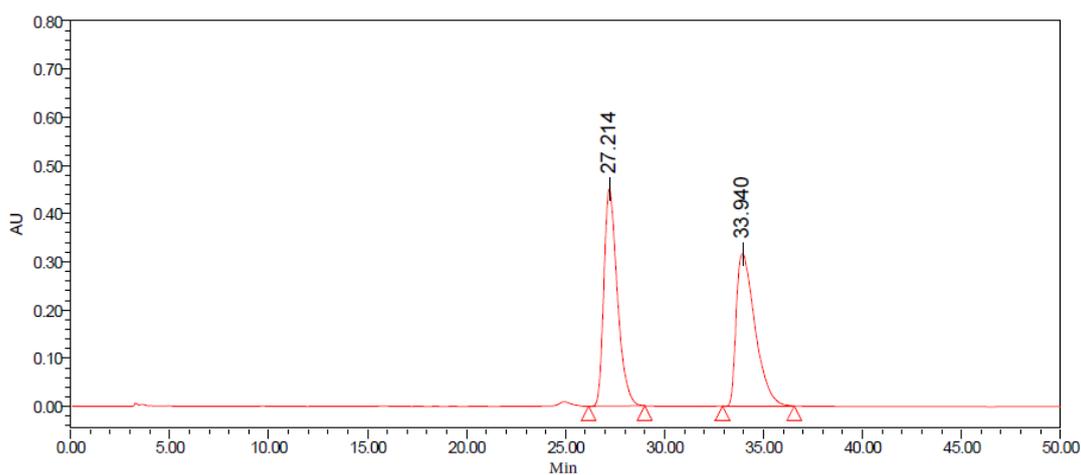
Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (90:10)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



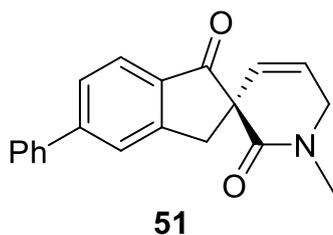
	Ret. Time	Area	% Area
1	27.120	25271420	93.47
2	34.185	1765012	6.53

Racemic



	Ret. Time	Area	% Area
1	27.214	21263159	50.52
2	33.940	20829335	49.48

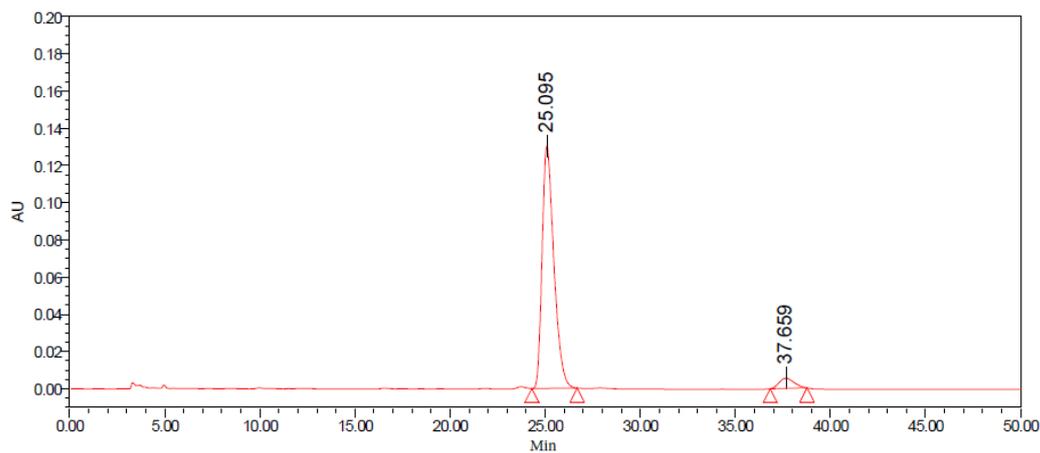
Supplementary Fig. 49. HPLC spectrum of compound **50**



HPLC Conditions

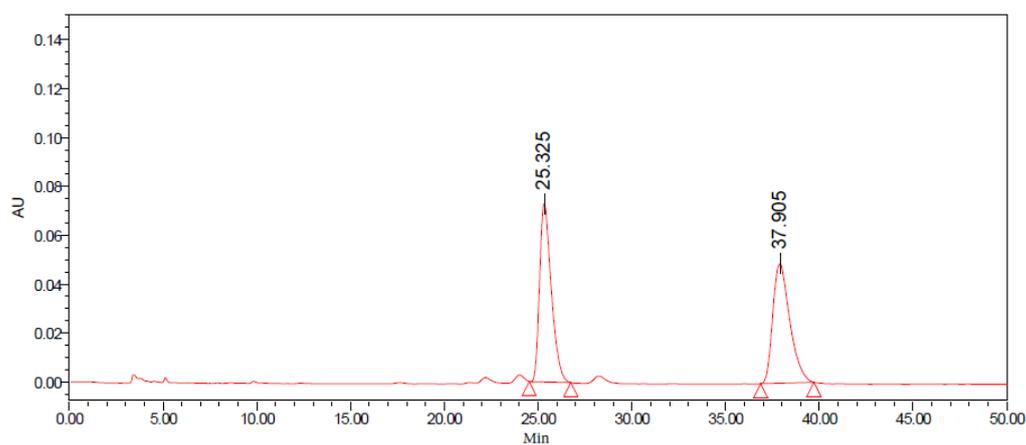
Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (90:10)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



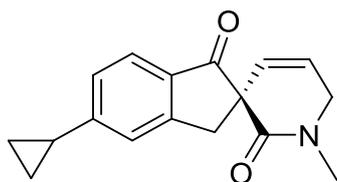
	Ret. Time	Area	% Area
1	25.095	5588584	94.90
2	37.659	300467	5.10

Racemic



	Ret. Time	Area	% Area
1	25.325	3163167	50.63
2	37.905	3084149	49.37

Supplementary Fig. 50. HPLC spectrum of compound **51**

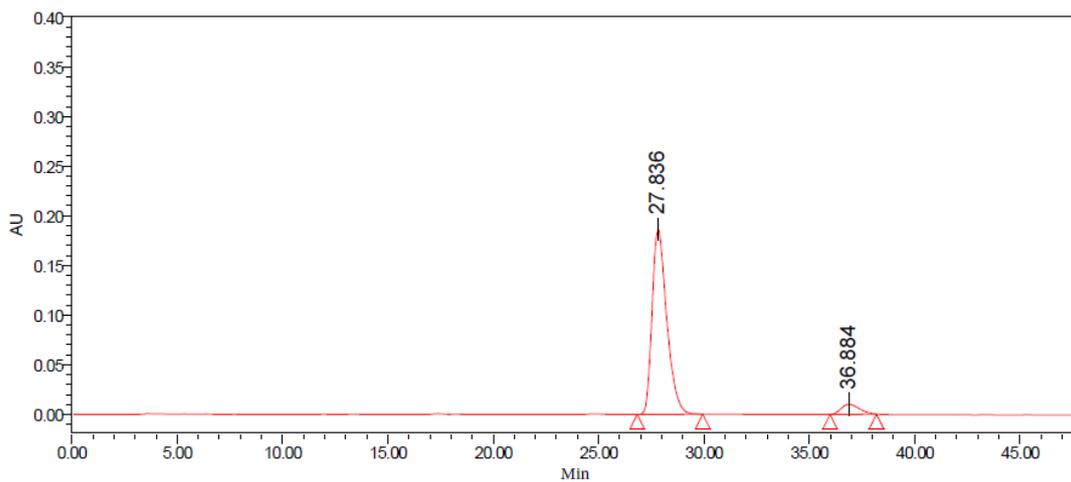


52

HPLC Conditions

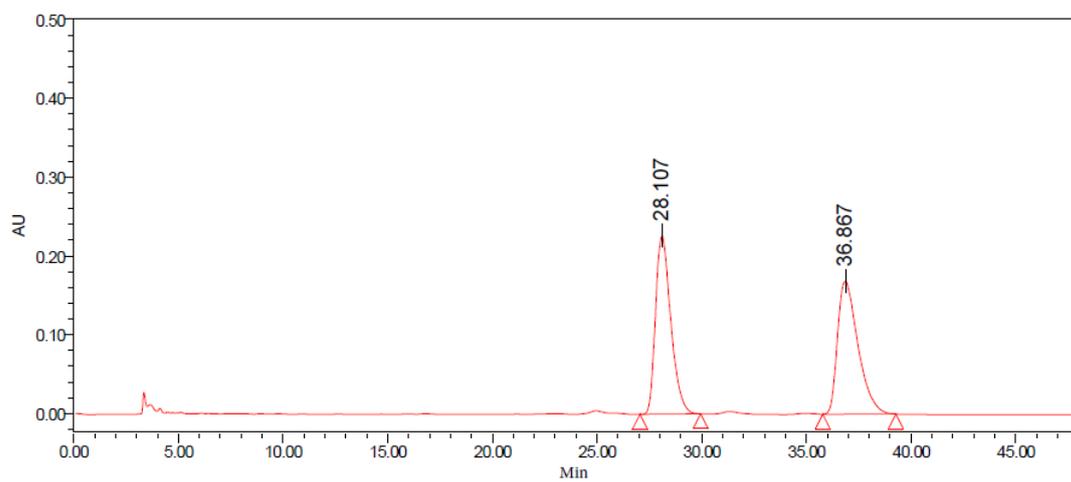
Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (90:10)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



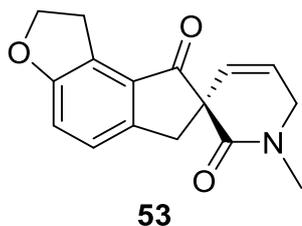
	Ret. Time	Area	% Area
1	27.836	9018378	93.81
2	36.884	595568	6.19

Racemic



	Ret. Time	Area	% Area
1	28.107	11481135	50.14
2	36.867	11417368	49.86

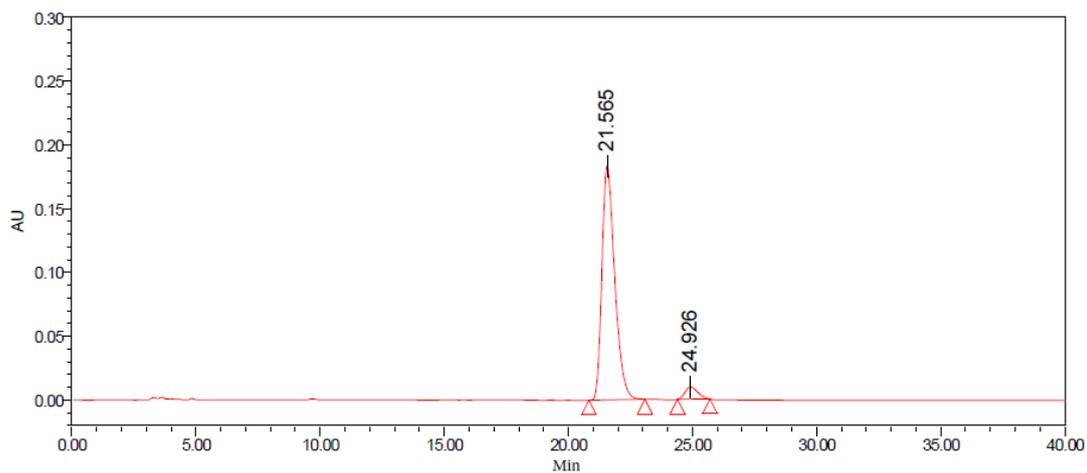
Supplementary Fig. 51. HPLC spectrum of compound **52**



HPLC Conditions

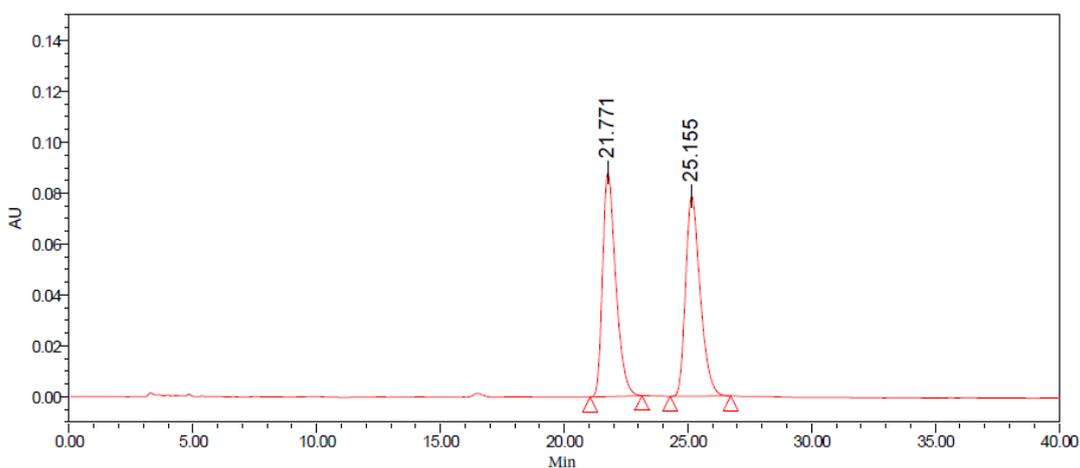
Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (90:10)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



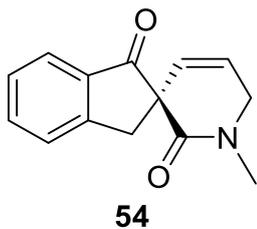
	Ret. Time	Area	% Area
1	21.565	6566952	95.00
2	24.926	345937	5.00

Racemic



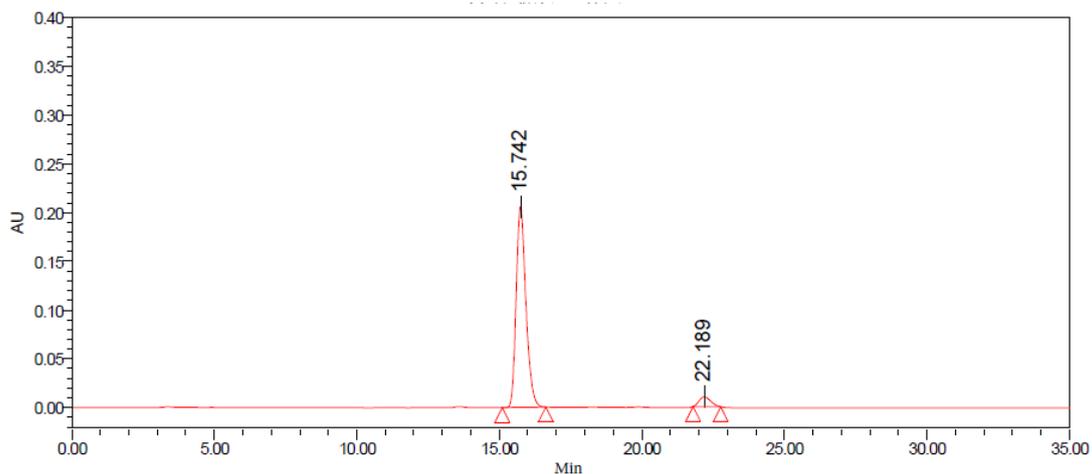
	Ret. Time	Area	% Area
1	21.771	3256408	50.25
2	25.155	3224325	49.75

Supplementary Fig. S2. HPLC spectrum of compound **53**



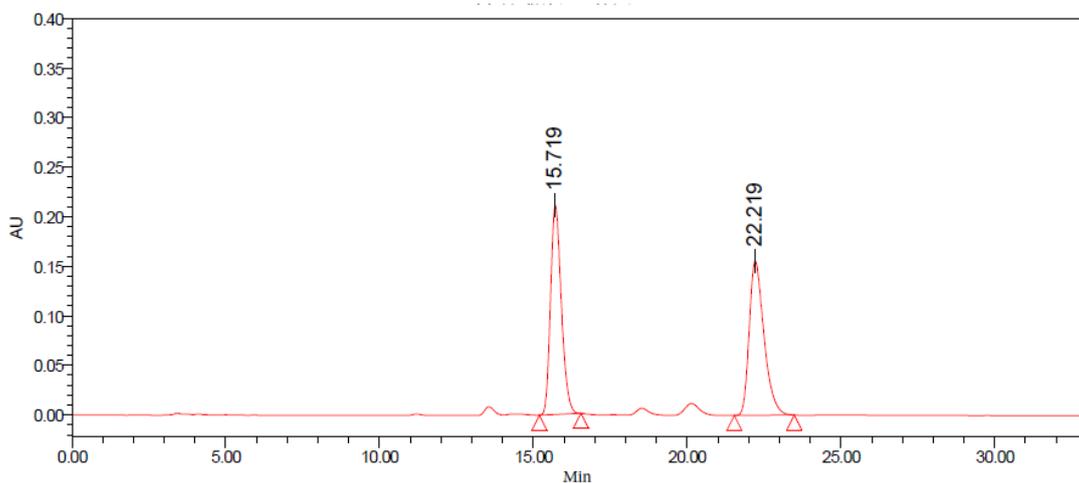
HPLC Conditions
 Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (90:10)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



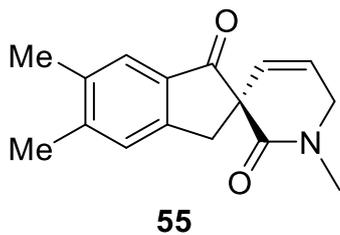
	Ret. Time	Area	% Area
1	15.742	4894365	94.49
2	22.189	285418	5.51

Racemic



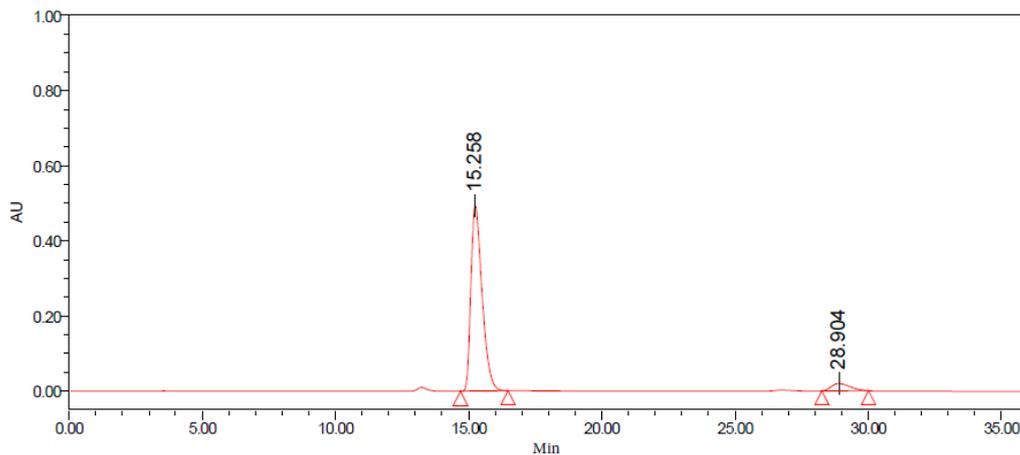
	Ret. Time	Area	% Area
1	15.719	5157193	49.83
2	22.219	5193159	50.17

Supplementary Fig. 53. HPLC spectrum of compound **54**



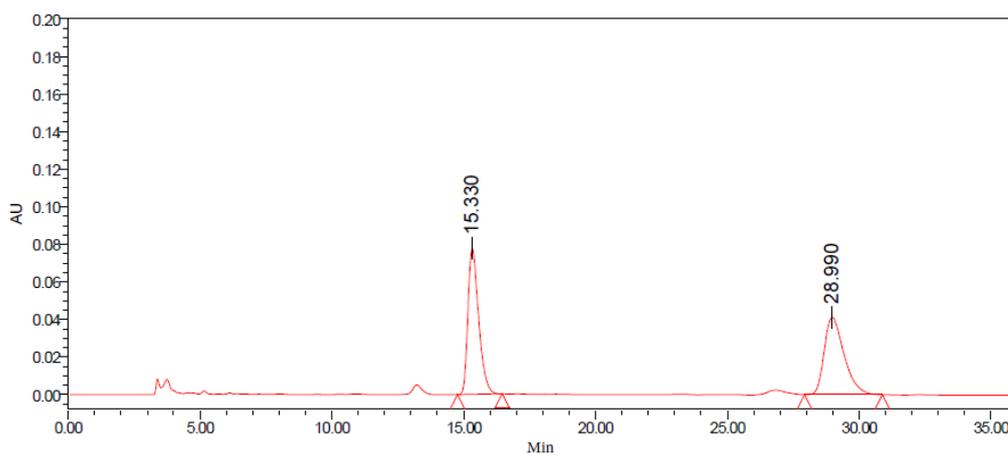
HPLC Conditions
 Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (90:10)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



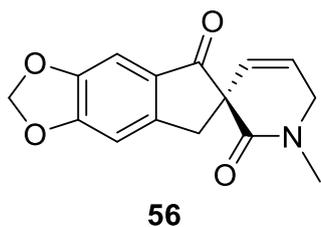
	Ret. Time	Area	% Area
1	15.258	14339186	93.86
2	28.904	938575	6.14

Racemic



	Ret. Time	Area	% Area
1	15.330	2189695	50.44
2	28.990	2151335	49.56

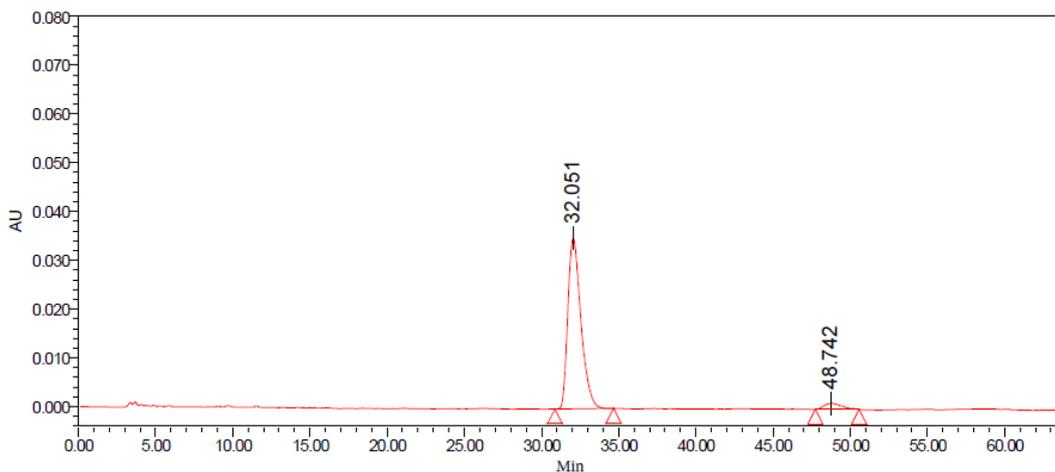
Supplementary Fig. 54. HPLC spectrum of compound **55**



HPLC Conditions

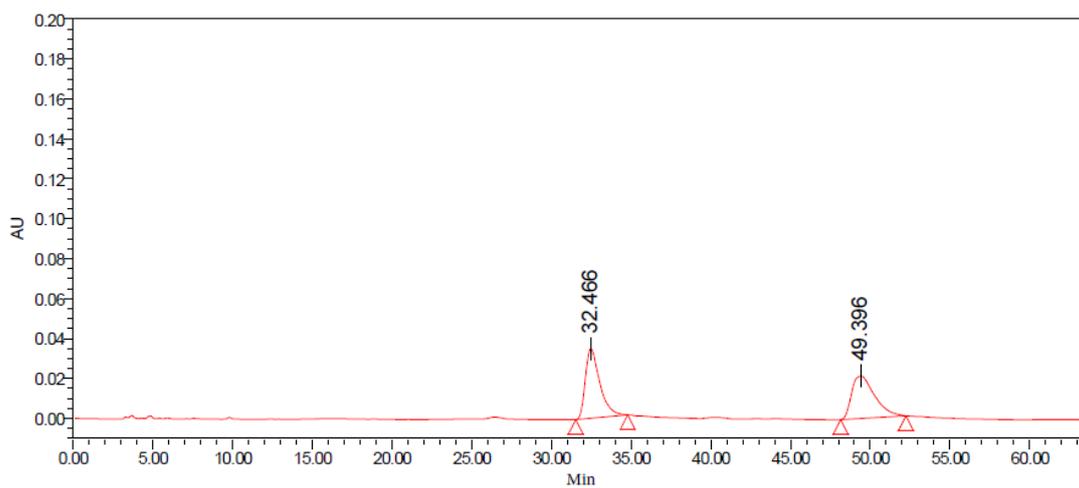
Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (90:10)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



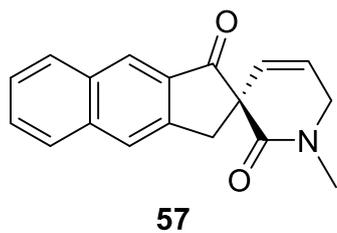
	Ret. Time	Area	% Area
1	32.051	2063181	95.44
2	48.742	98547	4.56

Racemic



	Ret. Time	Area	% Area
1	32.466	2190721	50.70
2	49.396	2130370	49.30

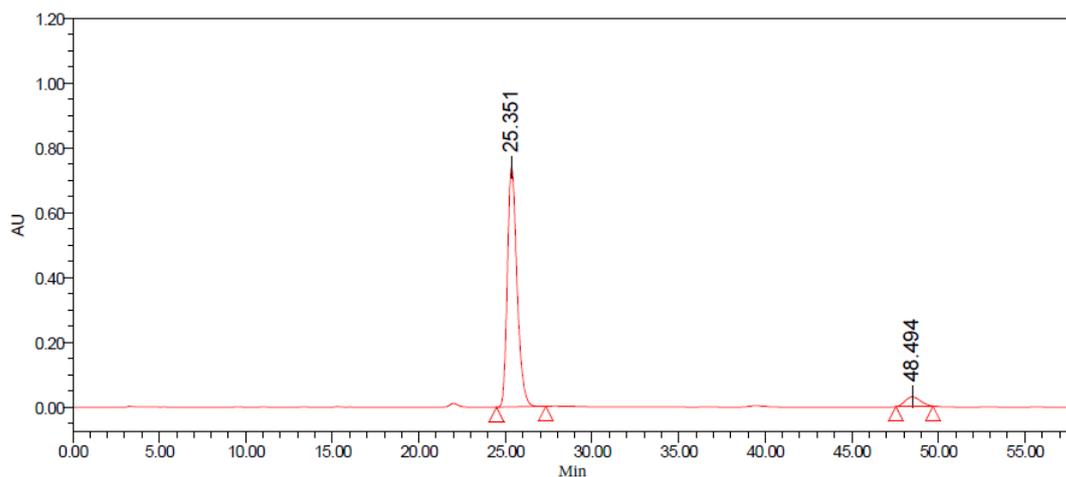
Supplementary Fig. 55. HPLC spectrum of compound **56**



HPLC Conditions

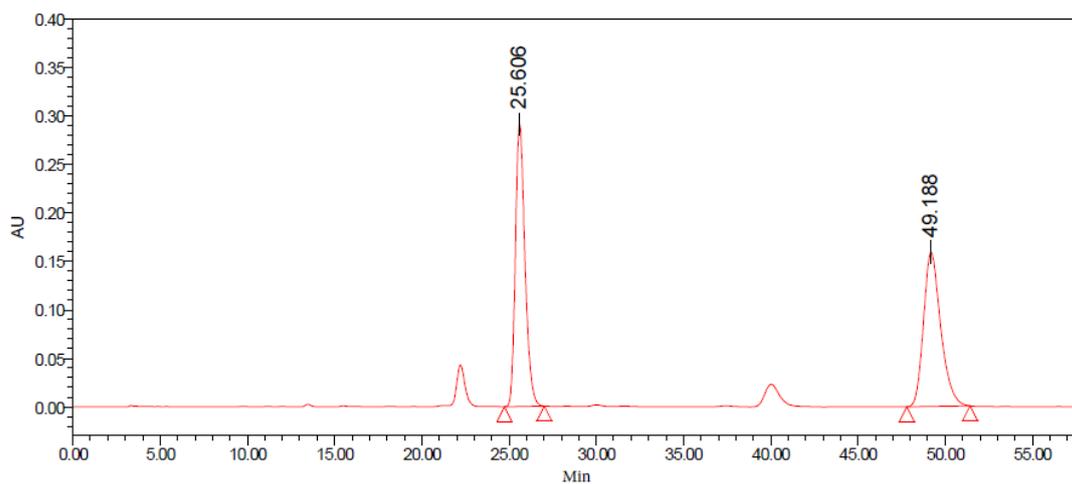
Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (90:10)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



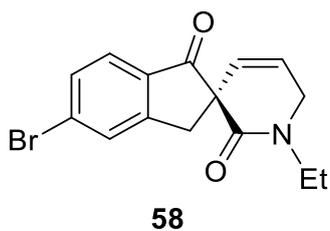
	Ret. Time	Area	% Area
1	25.351	28661350	94.08
2	48.494	1802391	5.92

Racemic



	Ret. Time	Area	% Area
1	25.606	11111116	50.49
2	49.188	10893909	49.51

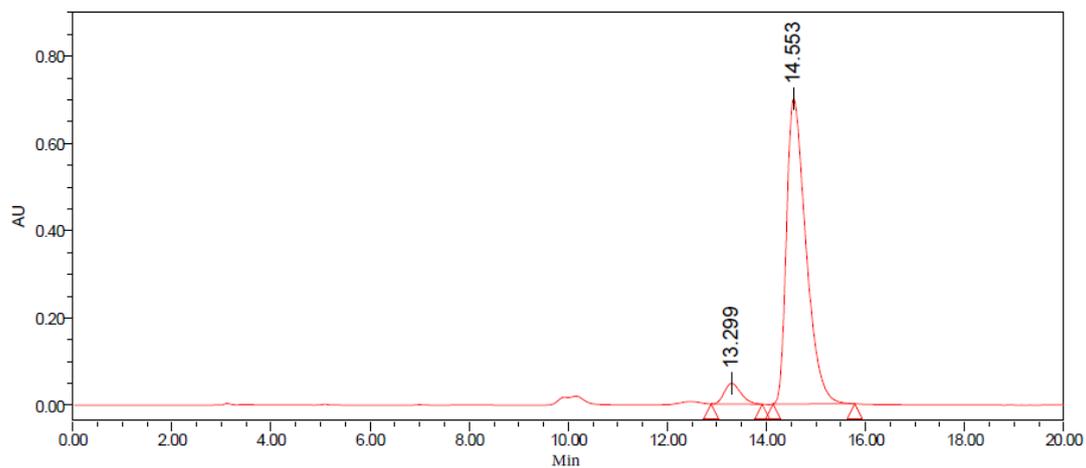
Supplementary Fig. S6. HPLC spectrum of compound 57



HPLC Conditions

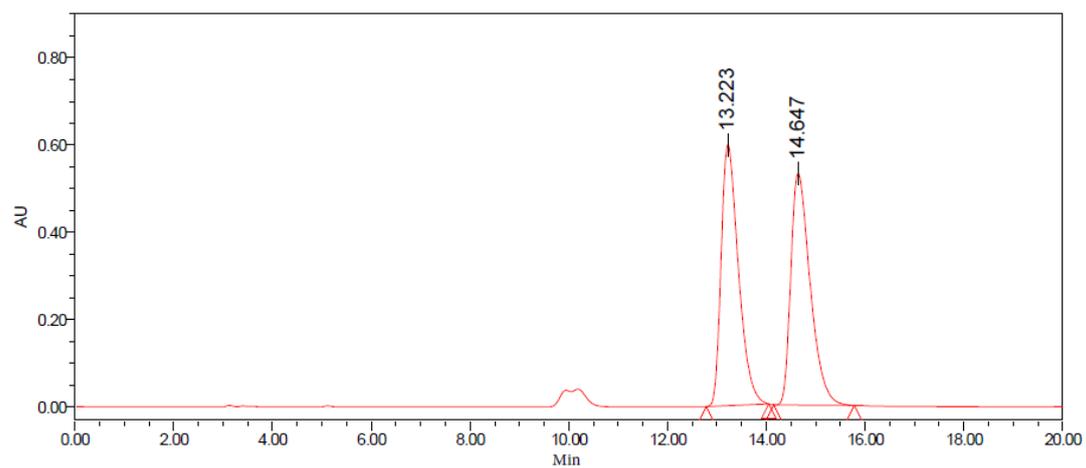
Column: Chiralpak OD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (85:15)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



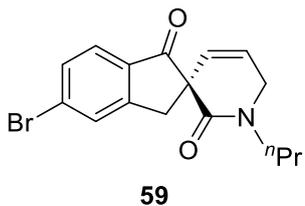
	Ret. Time	Area	% Area
1	13.299	1105763	5.47
2	14.553	19094235	94.53

Racemic



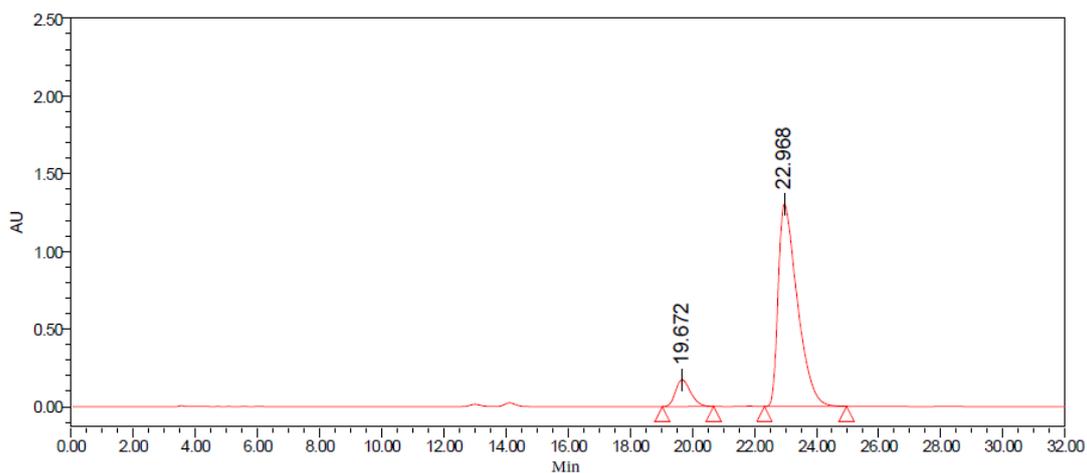
	Ret. Time	Area	% Area
1	13.223	14597805	50.17
2	14.647	14496660	49.83

Supplementary Fig. 57. HPLC spectrum of compound **58**



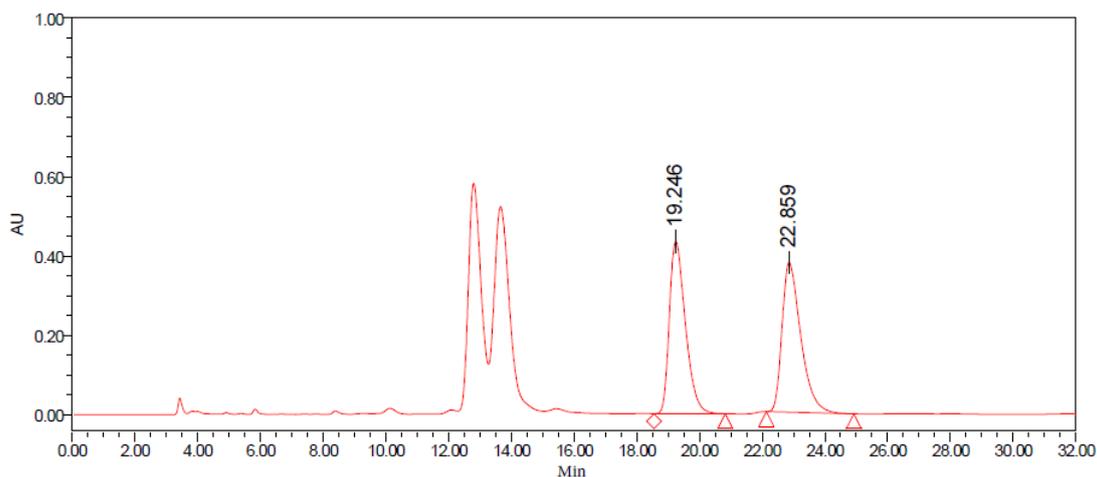
HPLC Conditions
 Column: Chiralpak OD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (90:10)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



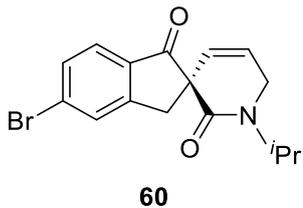
	Ret. Time	Area	% Area
1	19.672	5846648	9.50
2	22.968	55688179	90.50

Racemic



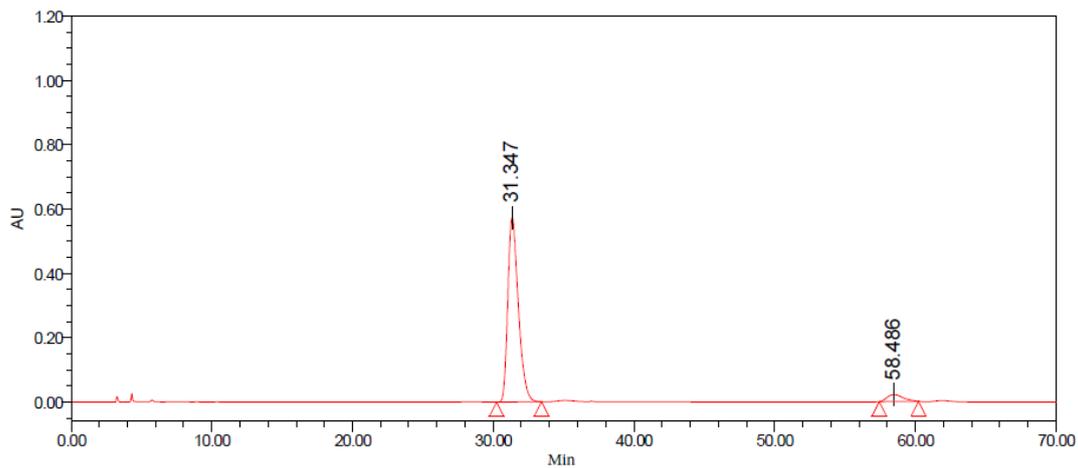
	Ret. Time	Area	% Area
1	19.246	15409128	49.61
2	22.859	15652768	50.39

Supplementary Fig. 58. HPLC spectrum of compound **59**



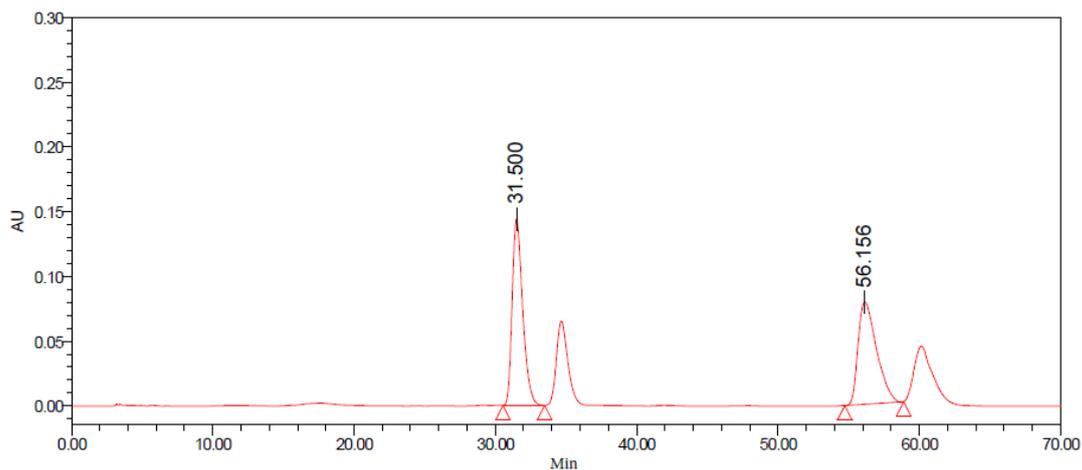
HPLC Conditions
 Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (97:3)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



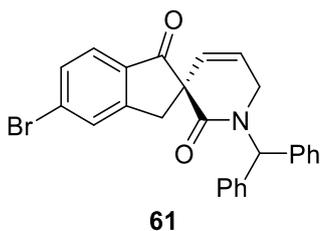
	Ret. Time	Area	% Area
1	31.347	29735081	94.51
2	58.486	1726638	5.49

Racemic



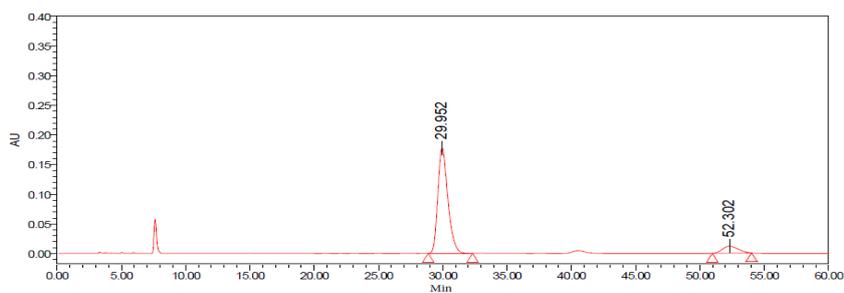
	Ret. Time	Area	% Area
1	31.500	7442724	50.99
2	56.156	7154146	49.01

Supplementary Fig. S9. HPLC spectrum of compound **60**



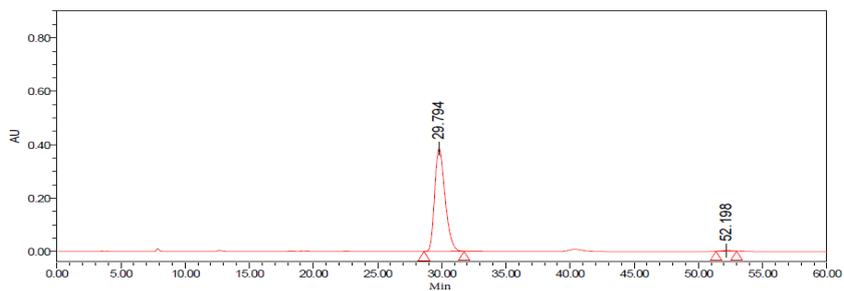
HPLC Conditions
 Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (90:10)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



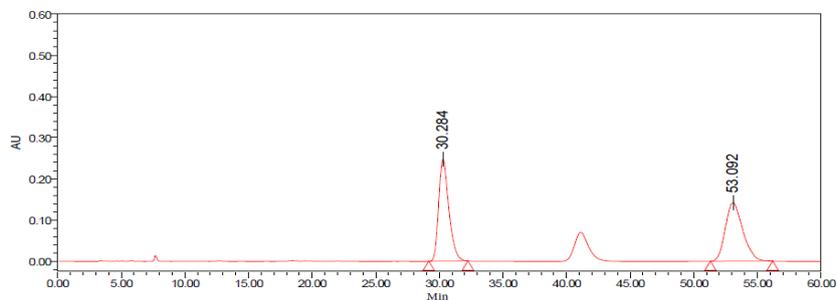
	Ret. Time	Area	% Area
1	29.952	9668700	90.50
2	52.302	1014444	9.50

After a single recrystallization



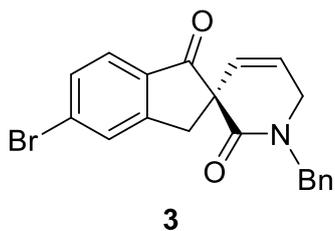
	Ret. Time	Area	% Area
1	29.794	21748507	99.42
2	52.198	127244	0.58

Racemic



	Ret. Time	Area	% Area
1	30.284	13736713	50.48
2	53.092	13473910	49.52

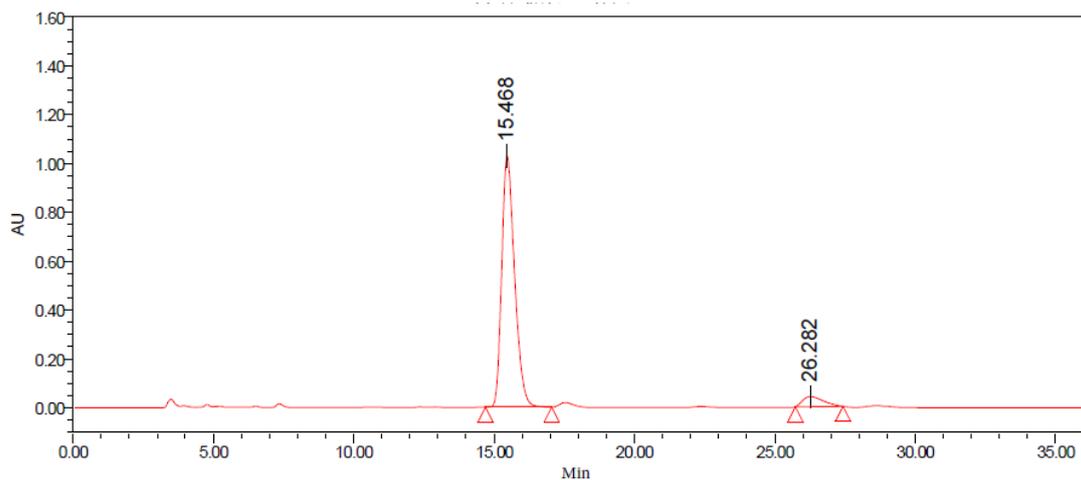
Supplementary Fig. 60. HPLC spectrum of compound 61



HPLC Conditions

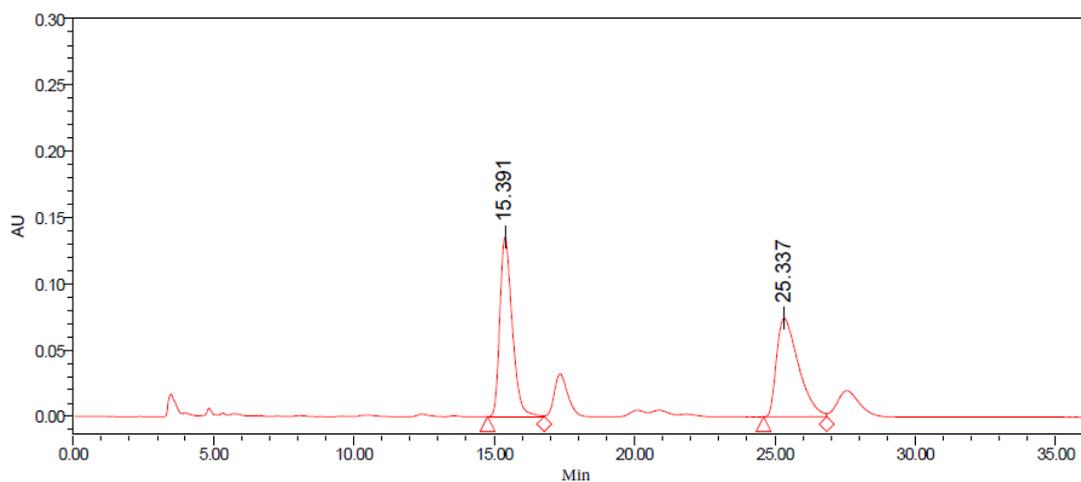
Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (80:20)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



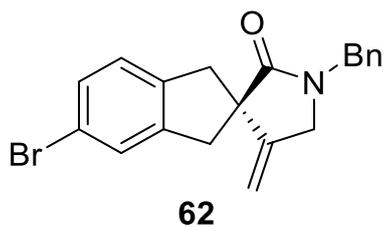
	Ret. Time	Area	% Area
1	15.468	32737361	93.88
2	26.282	2132954	6.12

Racemic



	Ret. Time	Area	% Area
1	15.391	4135197	50.66
2	25.337	4026660	49.34

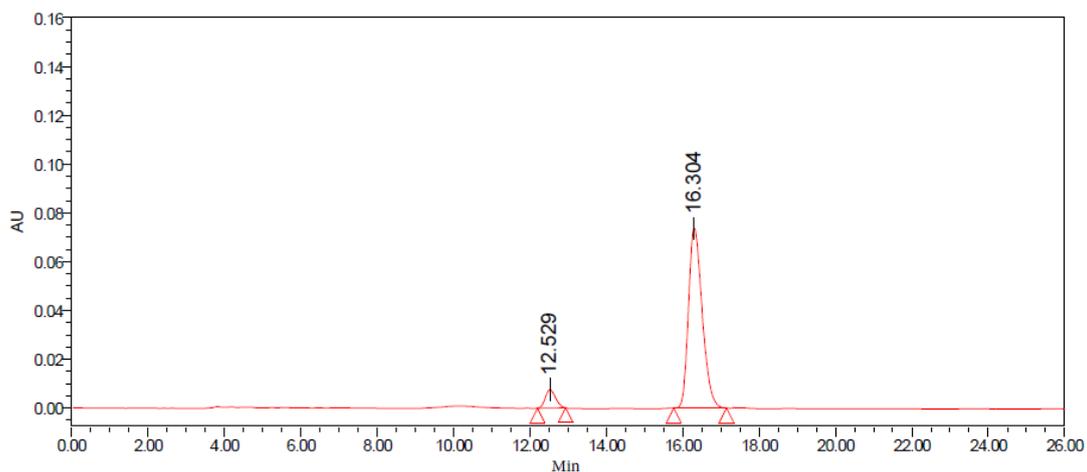
Supplementary Fig. 61. HPLC spectrum of compound **61**



HPLC Conditions

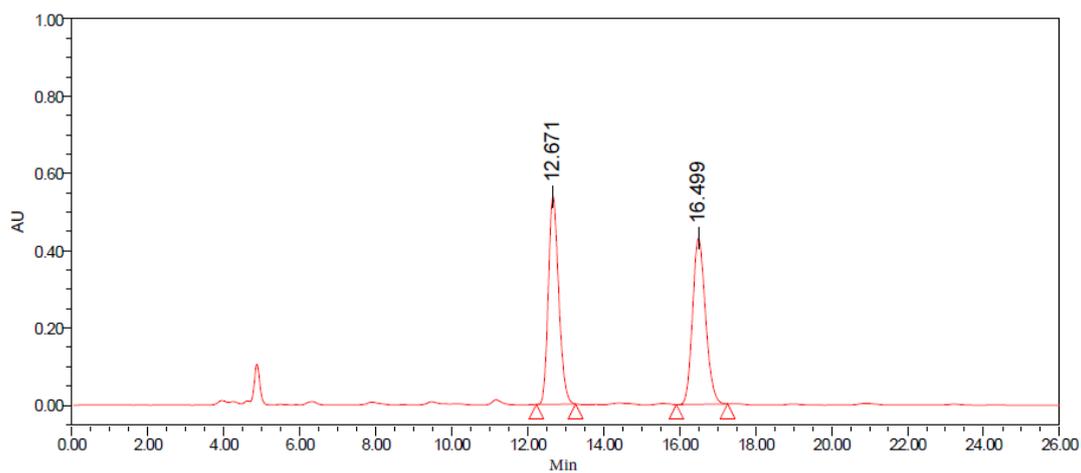
Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (90:10)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



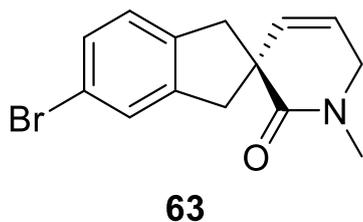
	Ret. Time	Area	% Area
1	12.529	140118	7.09
2	16.304	1836598	92.91

Racemic



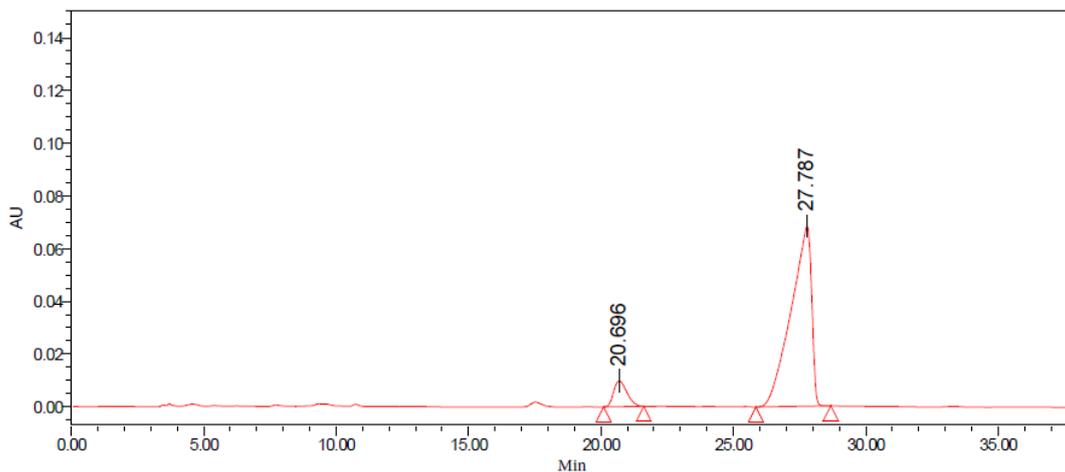
	Ret. Time	Area	% Area
1	12.671	10237124	50.07
2	16.499	10210154	49.93

Supplementary Fig. 62. HPLC spectrum of compound **62**



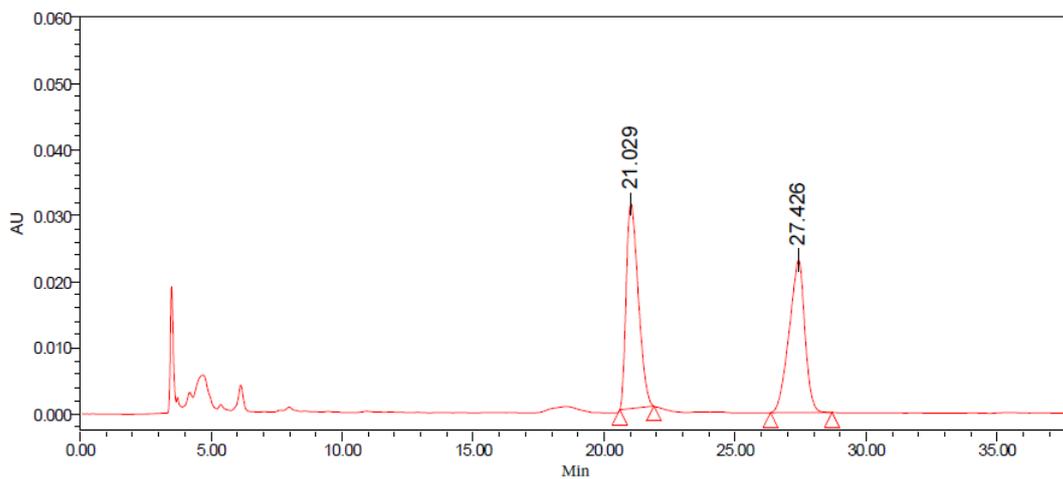
HPLC Conditions
 Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (97:3)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



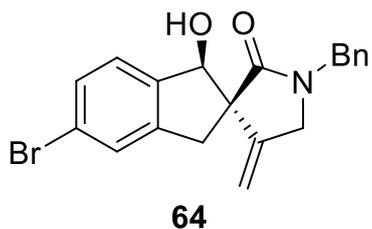
	Ret. Time	Area	% Area
1	20.696	340154	8.43
2	27.787	3694389	91.57

Racemic



	Ret. Time	Area	% Area
1	21.029	997064	50.94
2	27.426	960346	49.06

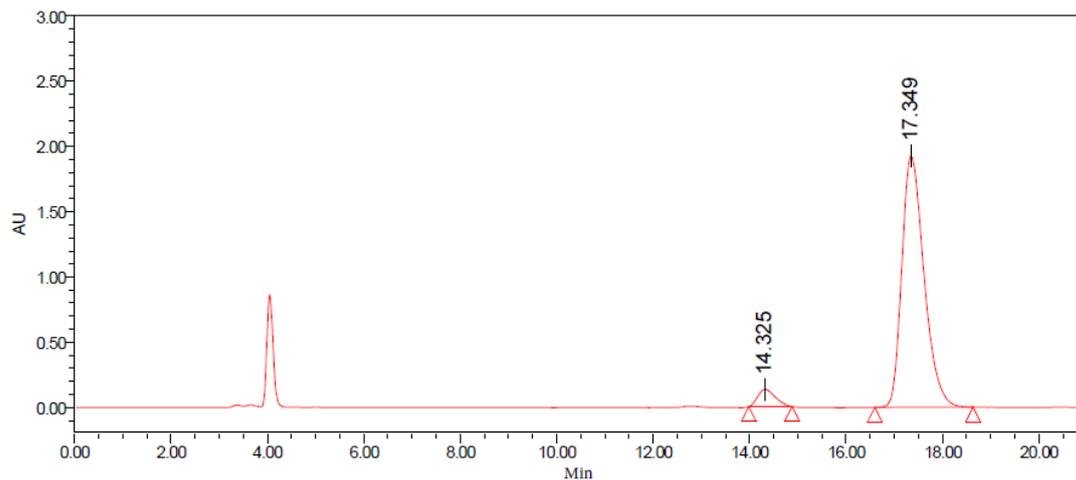
Supplementary Fig. 63. HPLC spectrum of compound **63**



HPLC Conditions

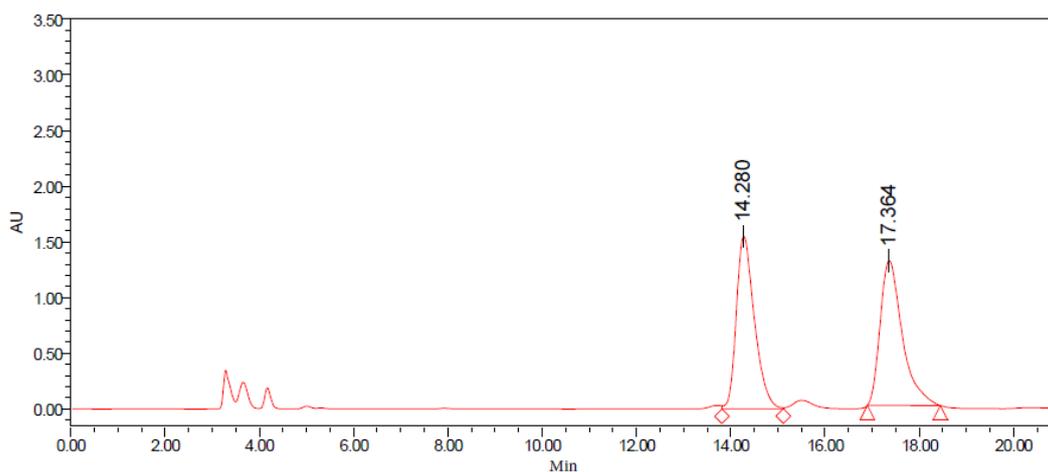
Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (90:10)
 Flow rate: 1.0 mL/min
 Detection: UV 214 nm

Chiral



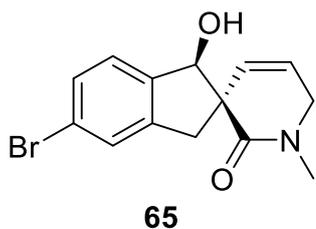
	Ret. Time	Area	% Area
1	14.325	3327619	5.12
2	17.349	61667846	94.88

Racemic



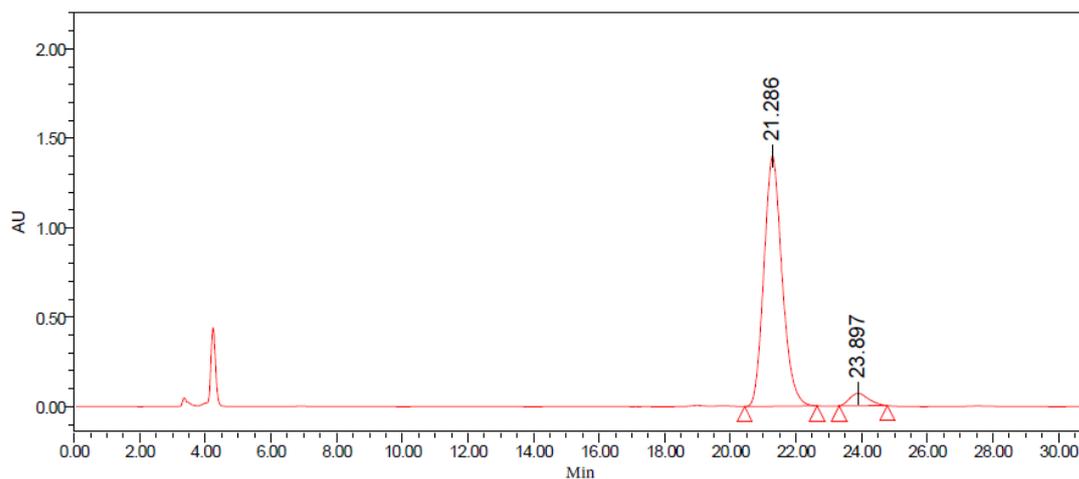
	Ret. Time	Area	% Area
1	14.280	41318030	49.35
2	17.364	42413311	50.65

Supplementary Fig. 64. HPLC spectrum of compound **64**



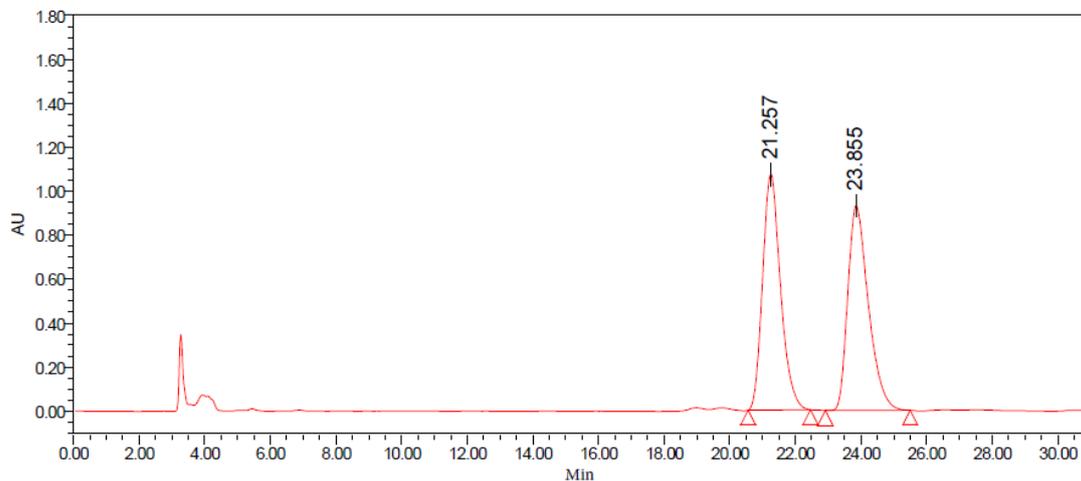
HPLC Conditions
 Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (95:5)
 Flow rate: 1.0 mL/min
 Detection: UV 214 nm

Chiral



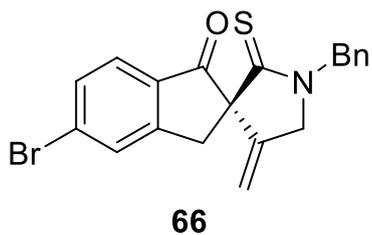
	Ret. Time	Area	% Area
1	21.286	53802829	95.09
2	23.897	2775622	4.91

Racemic



	Ret. Time	Area	% Area
1	21.257	40742151	50.07
2	23.855	40633852	49.93

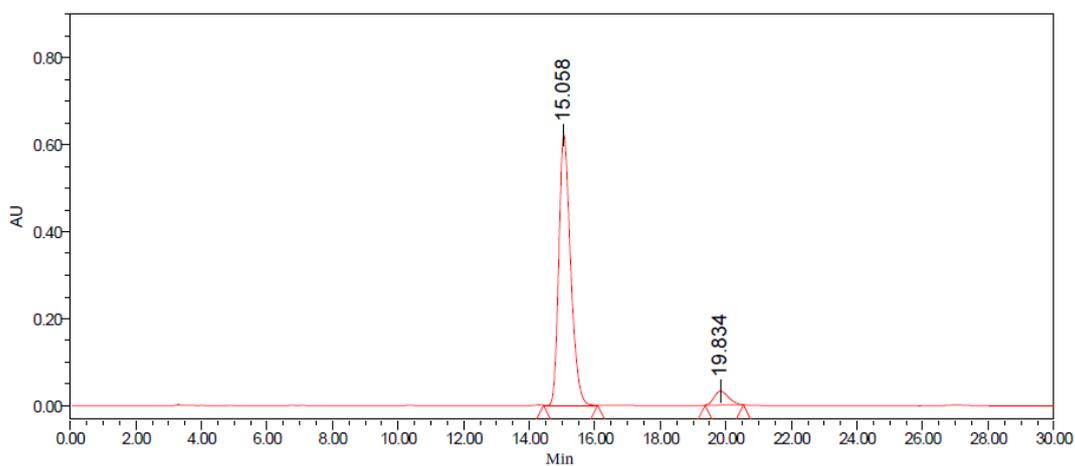
Supplementary Fig. 65. HPLC spectrum of compound **65**



HPLC Conditions

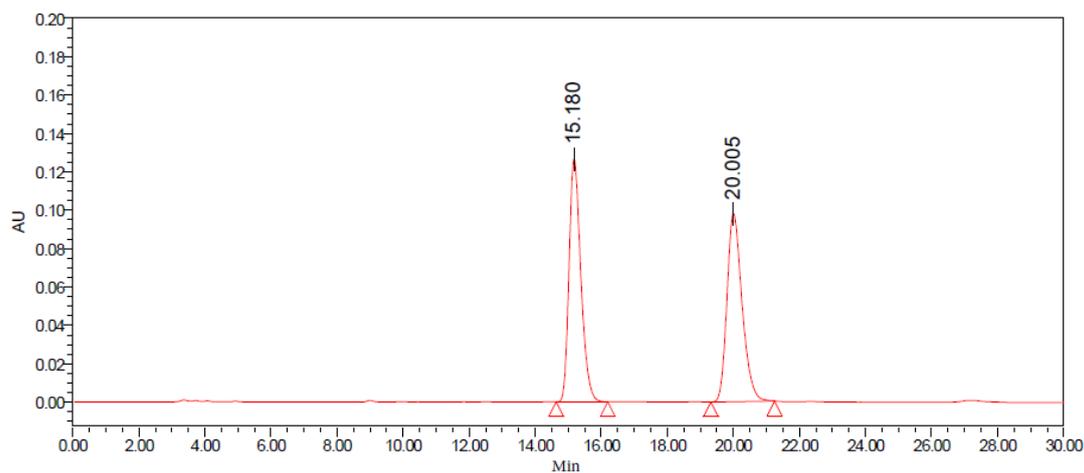
Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (90:10)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



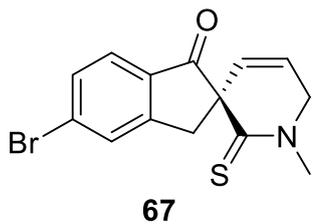
	Ret. Time	Area	% Area
1	15.058	15484531	94.03
2	19.834	982794	5.97

Racemic



	Ret. Time	Area	% Area
1	15.180	3130436	50.09
2	20.005	3118666	49.91

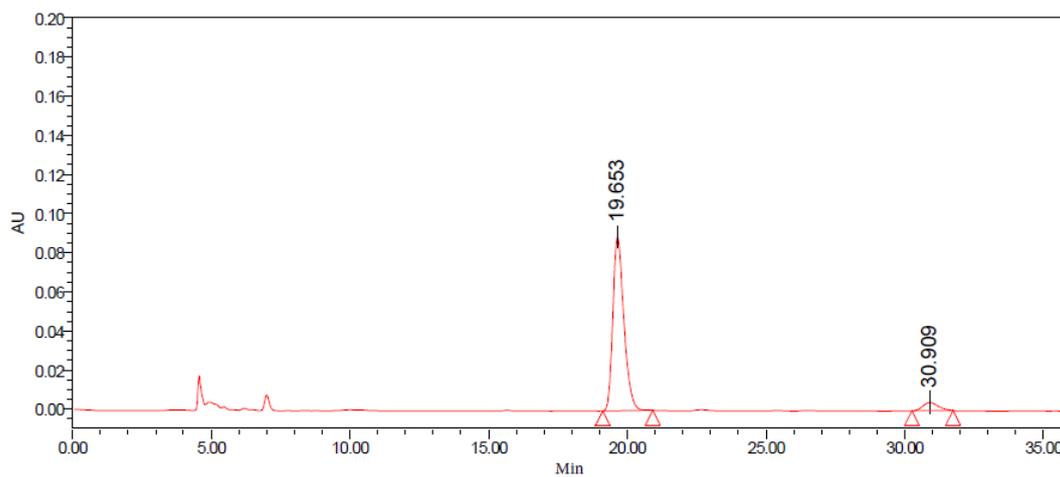
Supplementary Fig. 66. HPLC spectrum of compound 66



HPLC Conditions

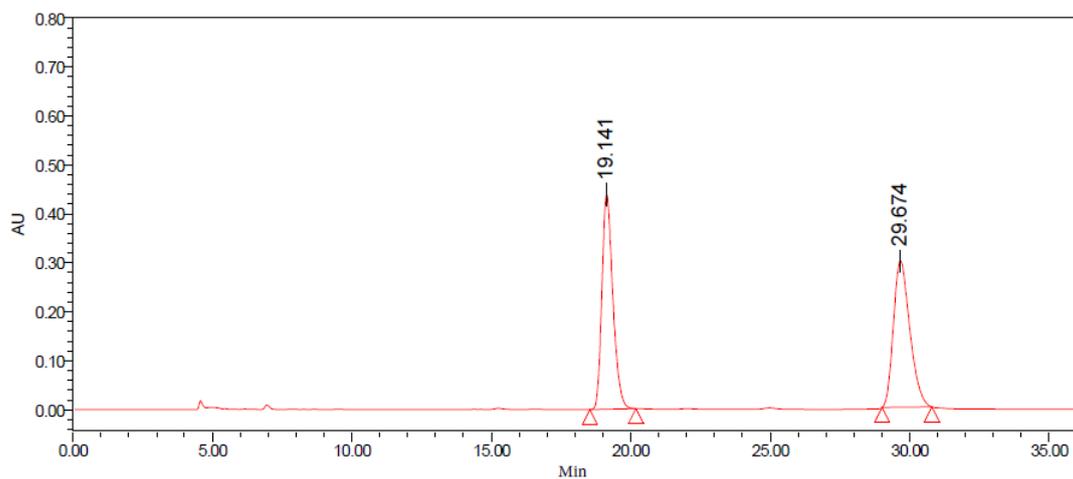
Column: Chiralpak AD-H,
 Daicel Chemical Industries Ltd.
 Eluent: Hexanes / Isopropanol (97:3)
 Flow rate: 1.0 mL/min
 Detection: UV 254 nm

Chiral



	Ret. Time	Area	% Area
1	19.653	2445942	93.82
2	30.909	161170	6.18

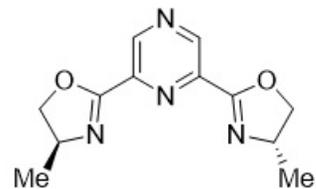
Racemic



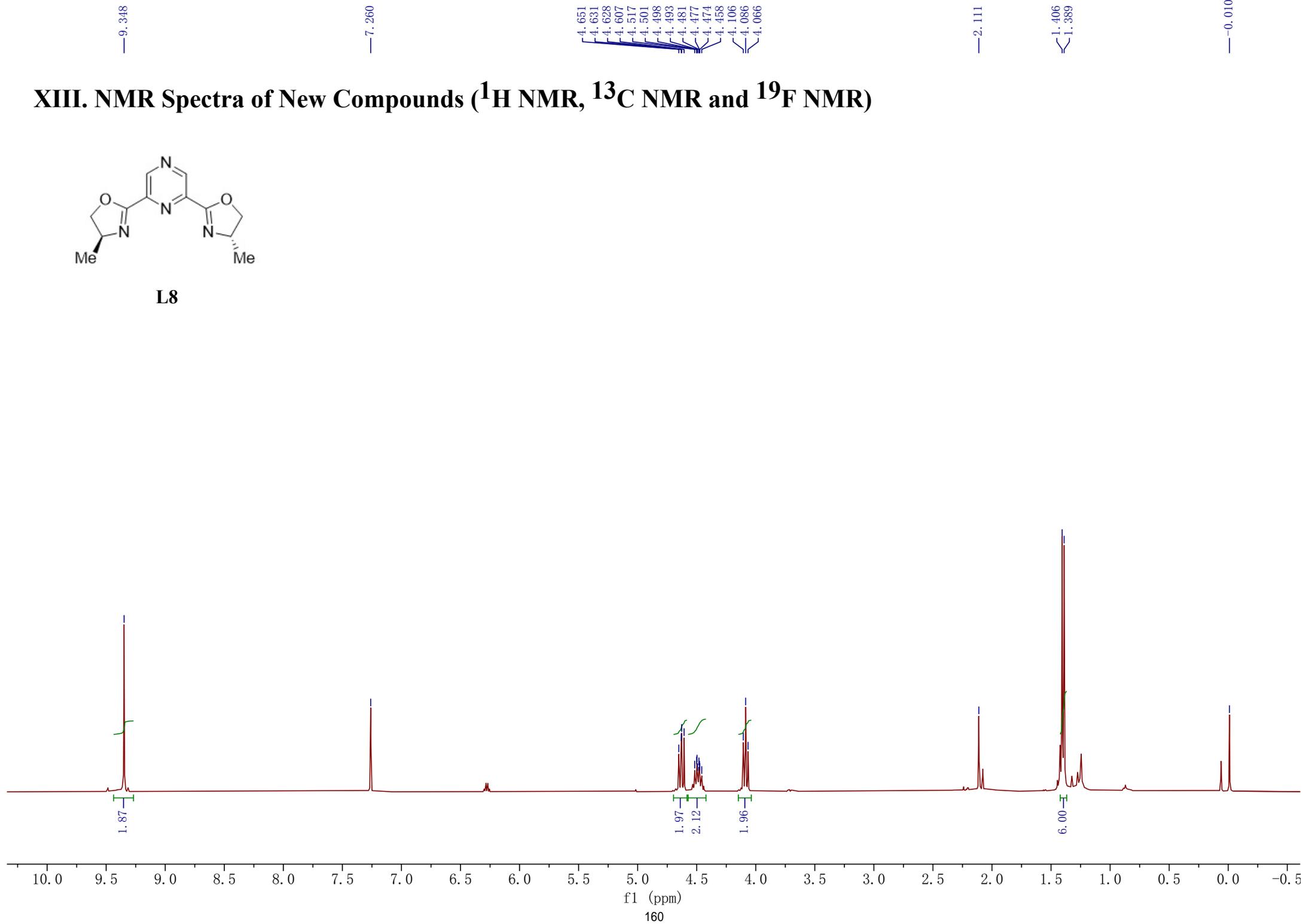
	Ret. Time	Area	% Area
1	19.141	11953155	49.41
2	29.674	12238561	50.59

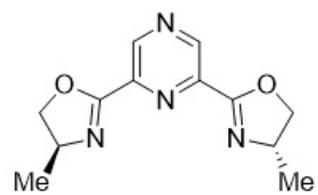
Supplementary Fig. 67. HPLC spectrum of compound **67**

XIII. NMR Spectra of New Compounds (^1H NMR, ^{13}C NMR and ^{19}F NMR)

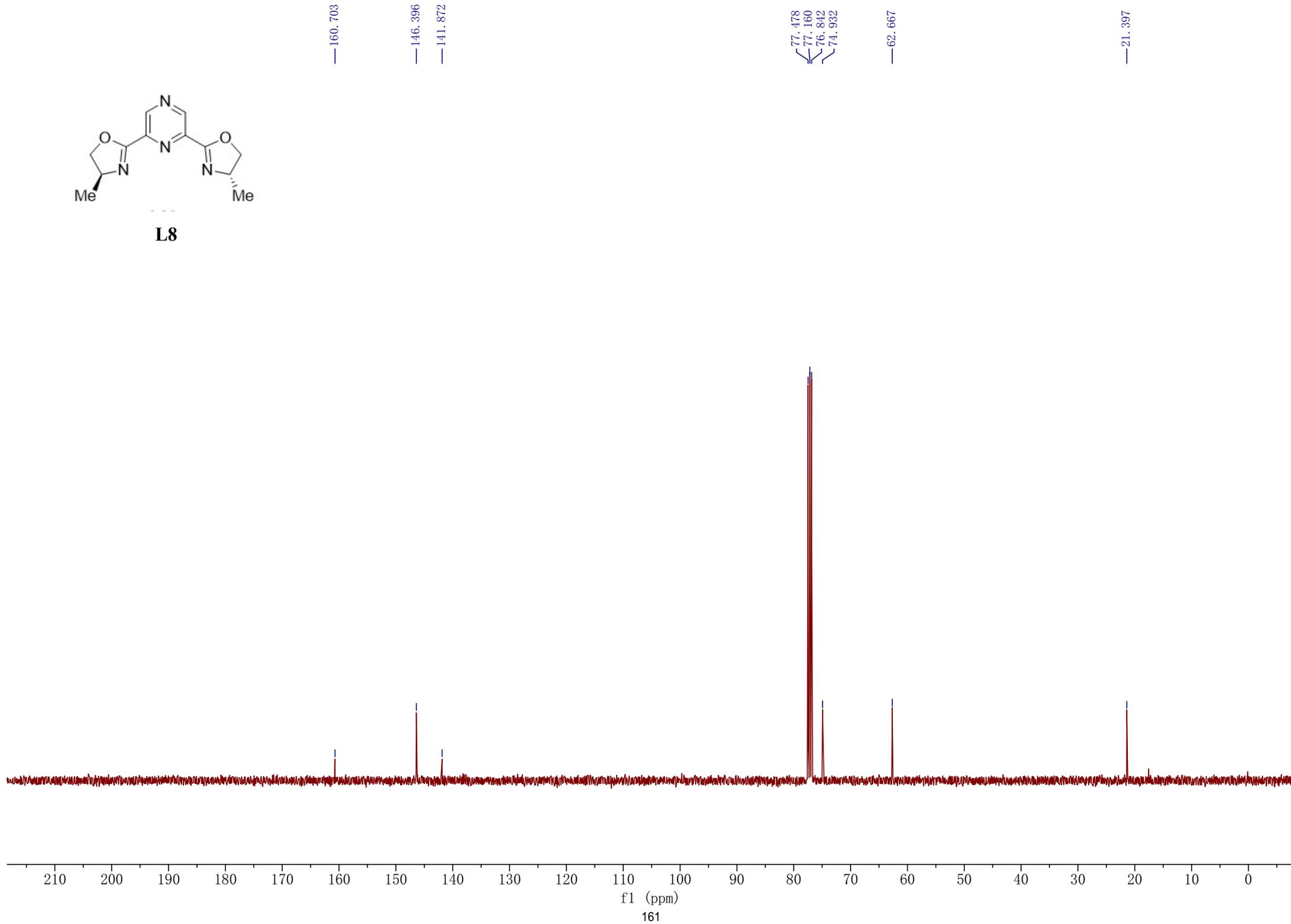


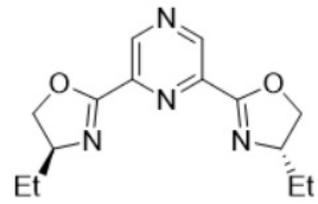
L8



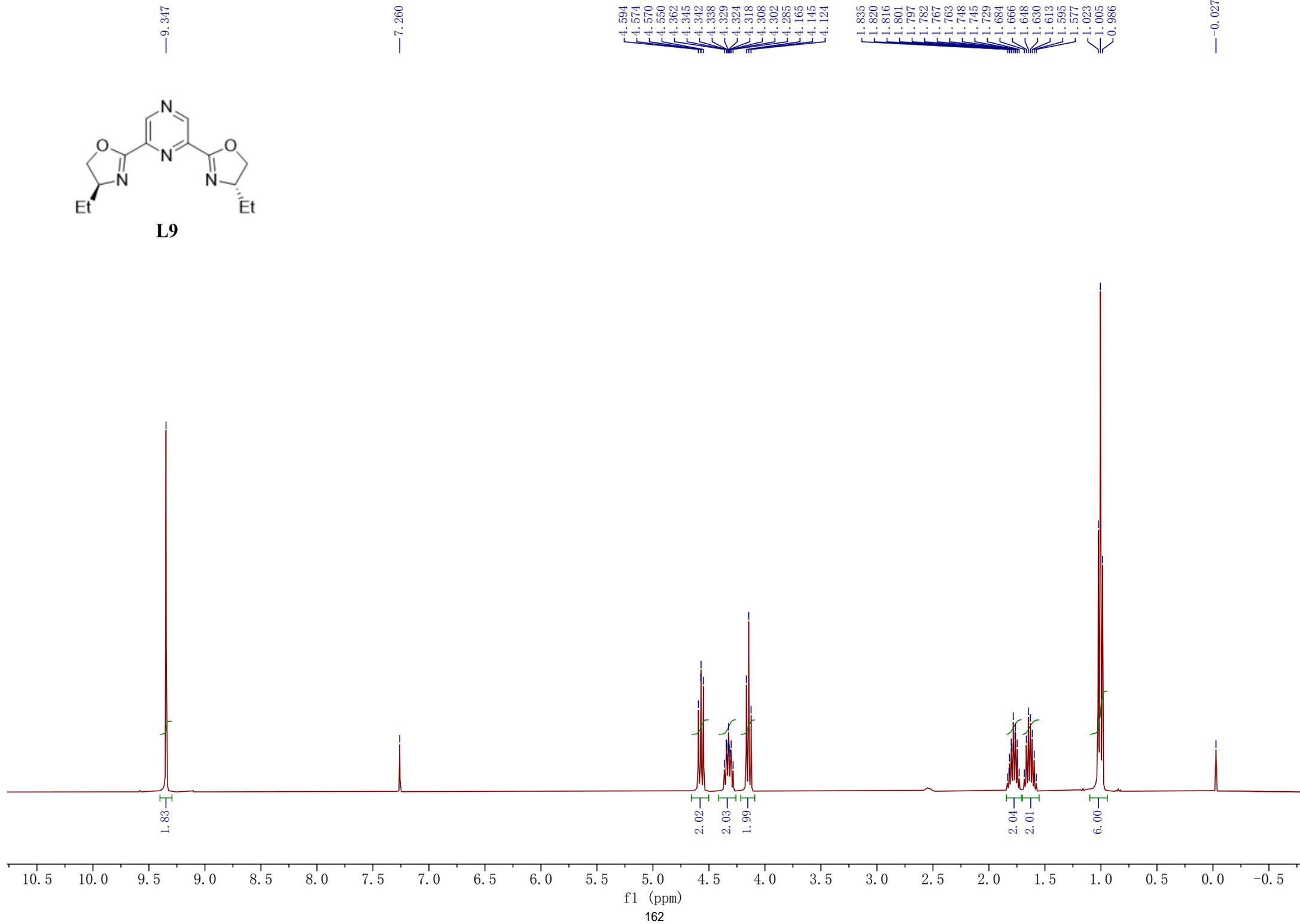


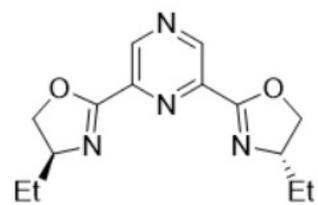
L8





L9





L9

— 160.649

— 146.384

— 141.885

77.478

77.161

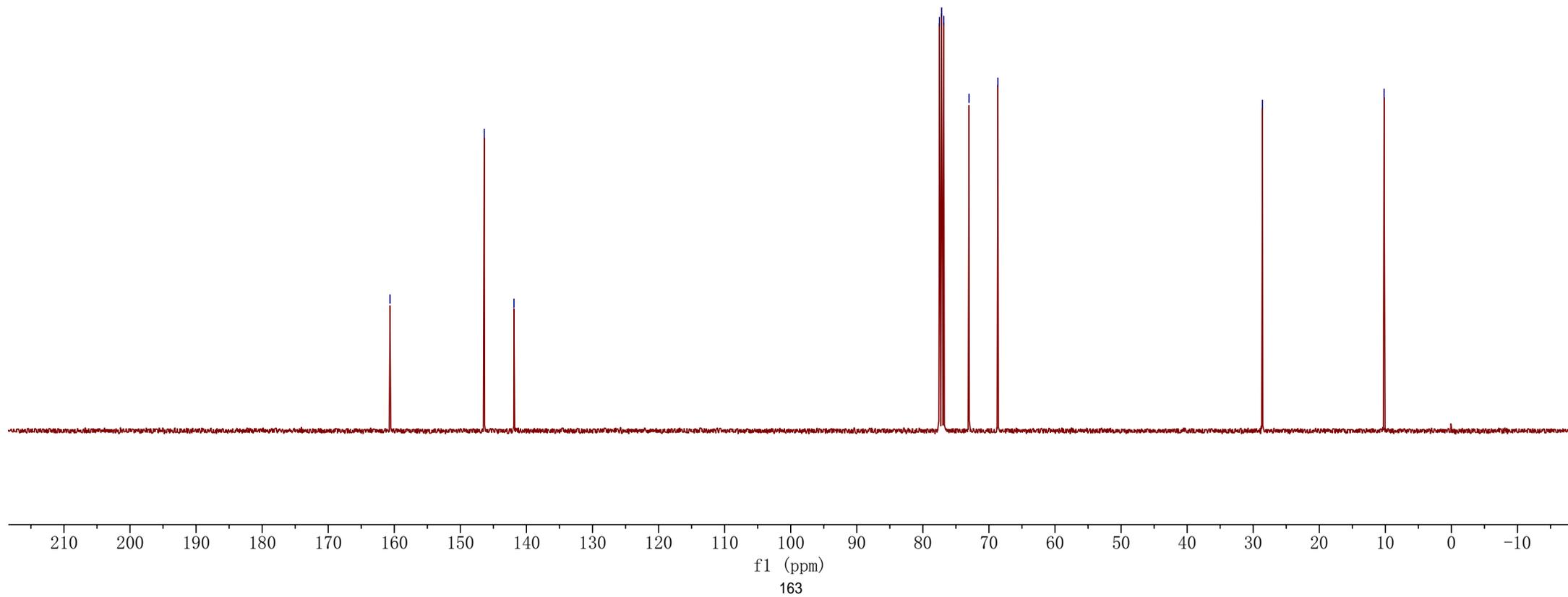
76.843

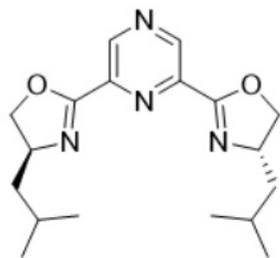
73.010

68.640

— 28.600

— 10.197





L10

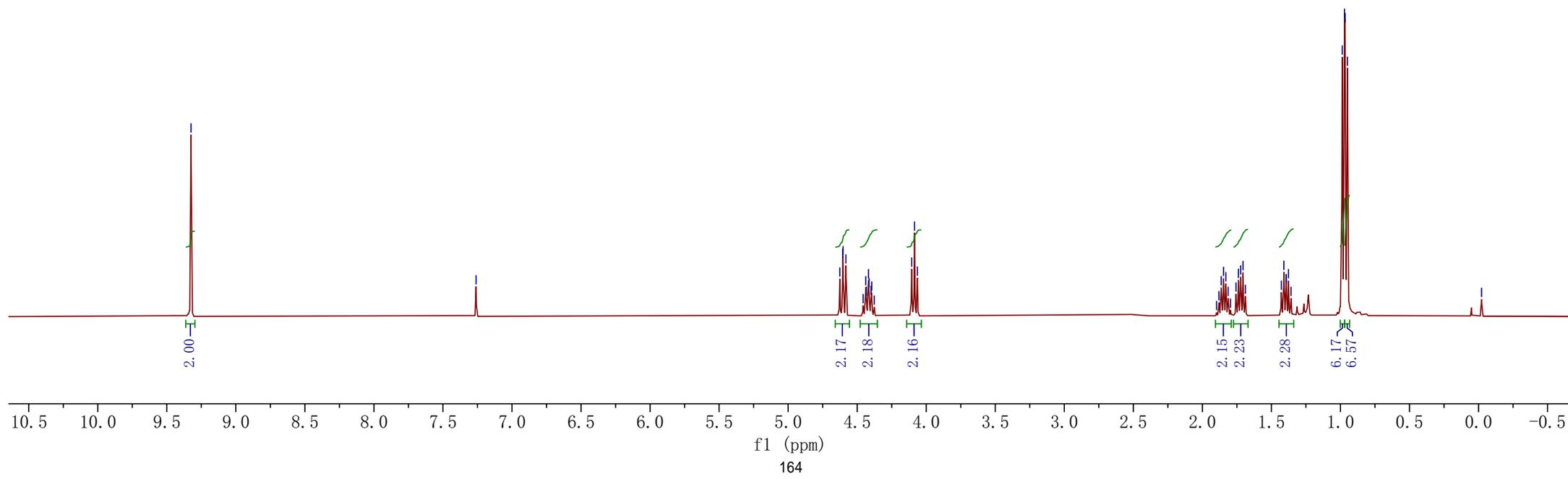
—9.324

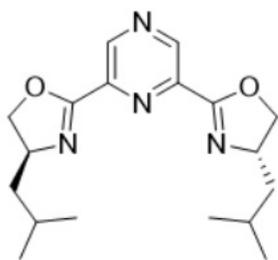
—7.260

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4.605
4.602
4.582
4.457
4.438
4.434
4.418
4.414
4.400
4.395
4.376
4.105
4.085
4.064

1.897
1.880
1.863
1.847
1.830
1.813
1.797
1.756
1.739
1.722
1.706
1.688
1.428
1.410
1.394
1.391
1.376
1.358
0.987
0.971
0.966
0.950

—0.022





L10

— 160.500

— 146.324

— 141.877

77.478

77.160

76.843

73.978

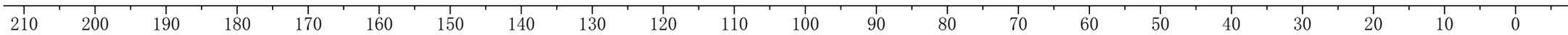
— 65.723

— 45.456

25.529

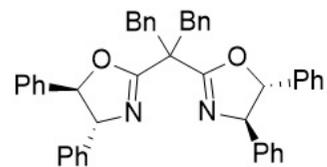
22.828

22.800



f1 (ppm)

165



L11

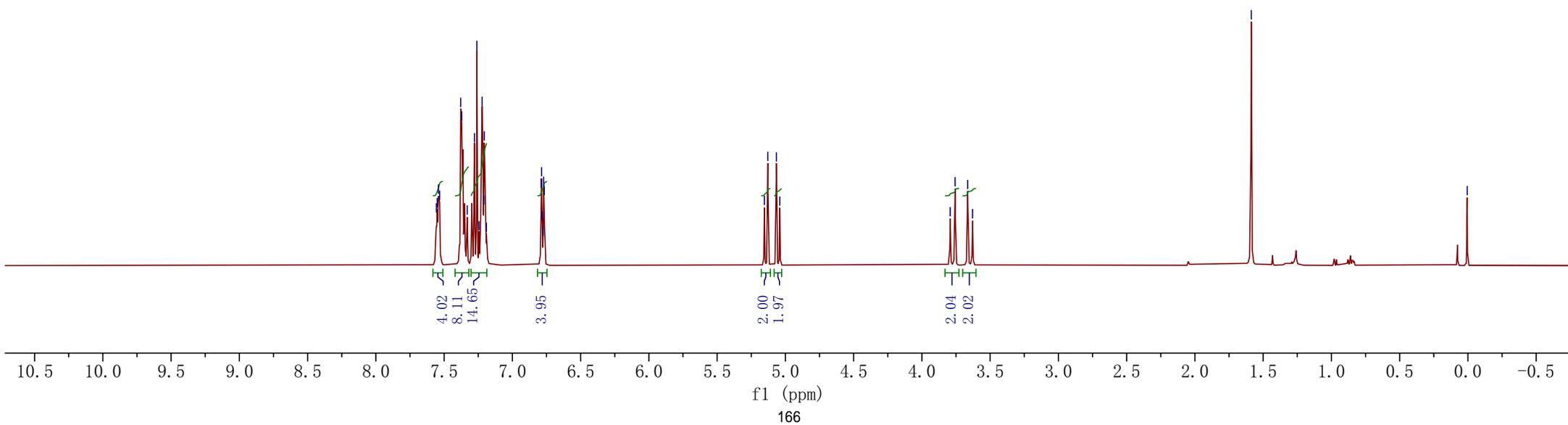
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7.550
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7.371
7.331
7.278
7.260
7.244
7.221
7.209
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7.190
6.790
6.786
6.782
6.776
6.771
6.766

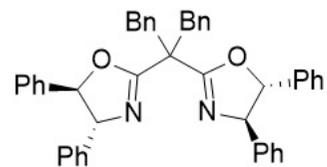
5.154
5.129
5.066
5.041

3.793
3.757
3.664
3.629

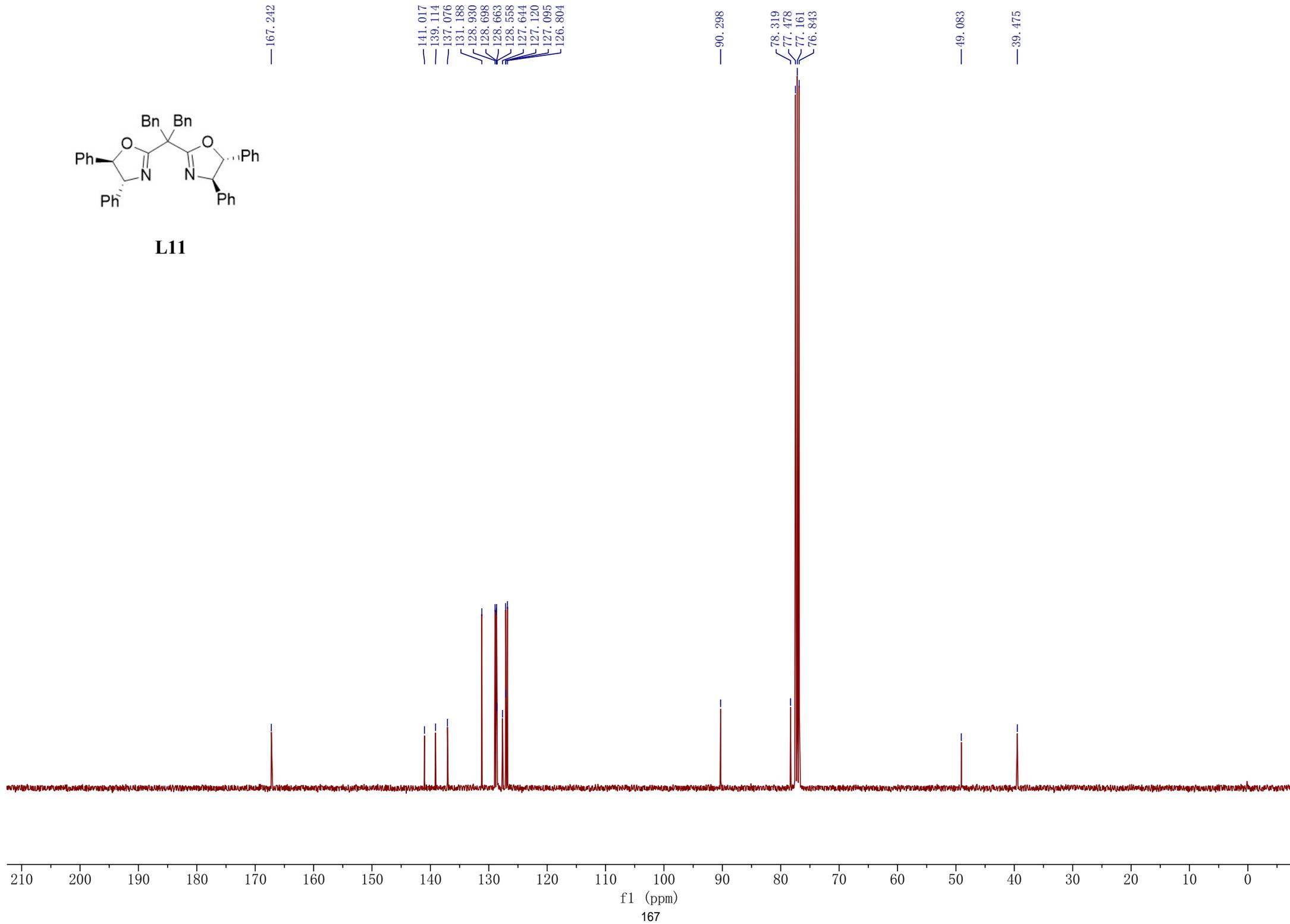
1.587

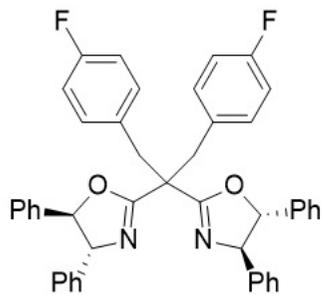
0.005





L11





L12

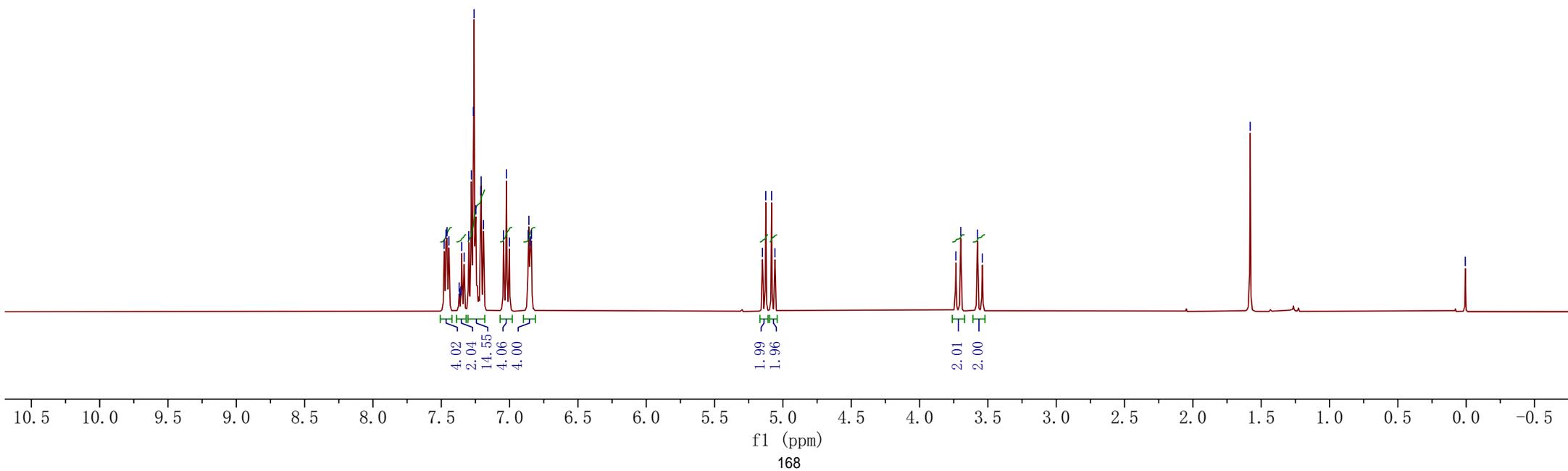
7.479
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7.365
7.356
7.351
7.333
7.299
7.280
7.264
7.260
7.247
7.211
7.208
7.191
7.045
7.023
7.001
6.864
6.859
6.847
6.846
6.840

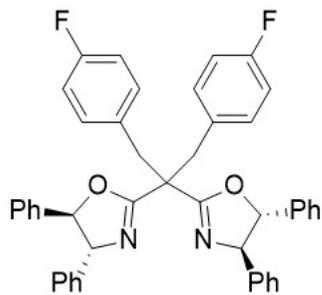
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5.083
5.058

3.734
3.699
3.576
3.540

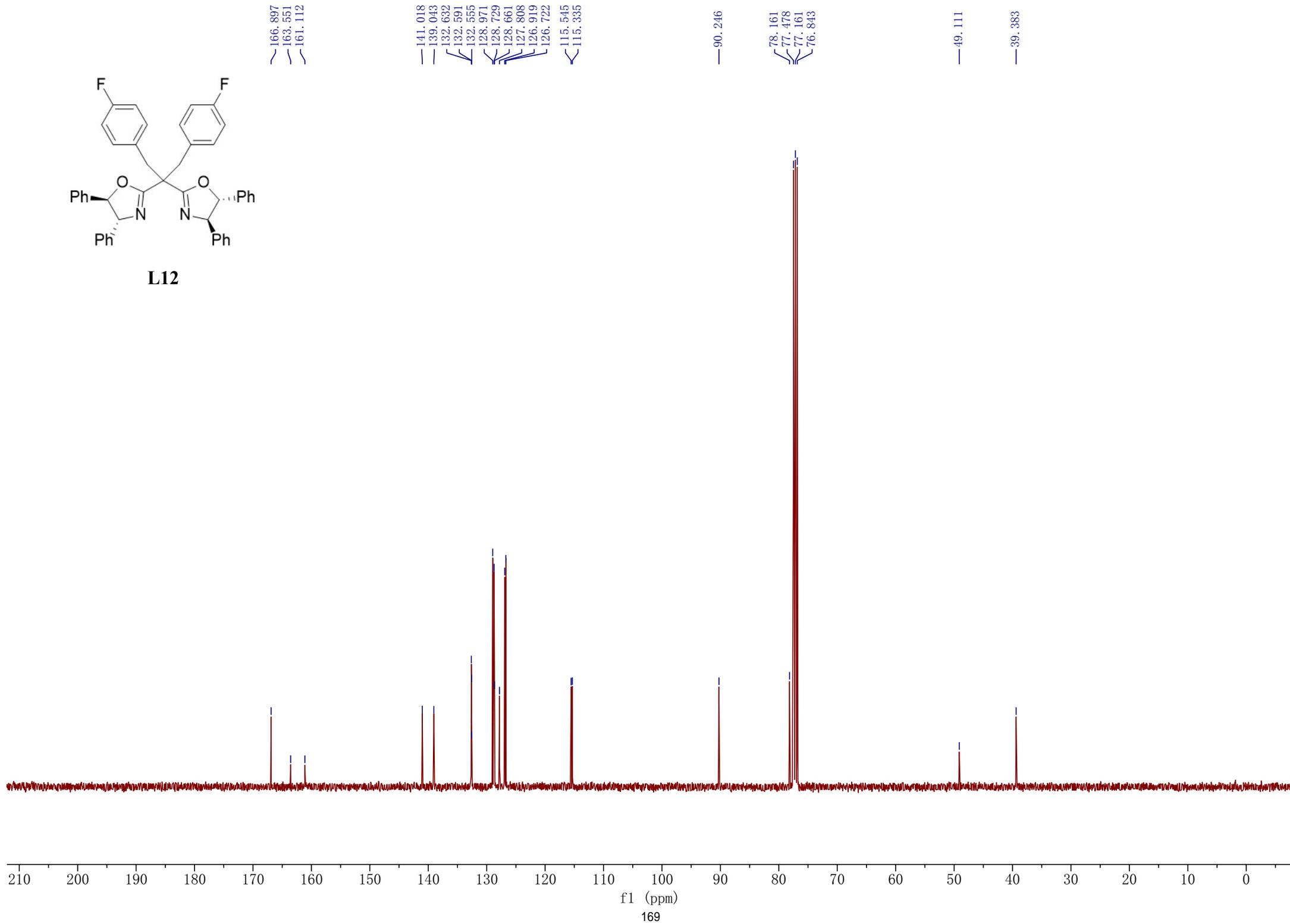
1.580

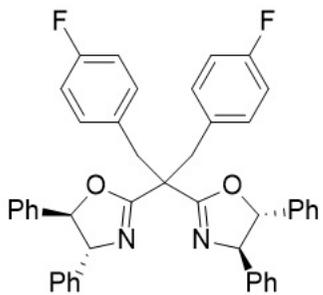
0.007





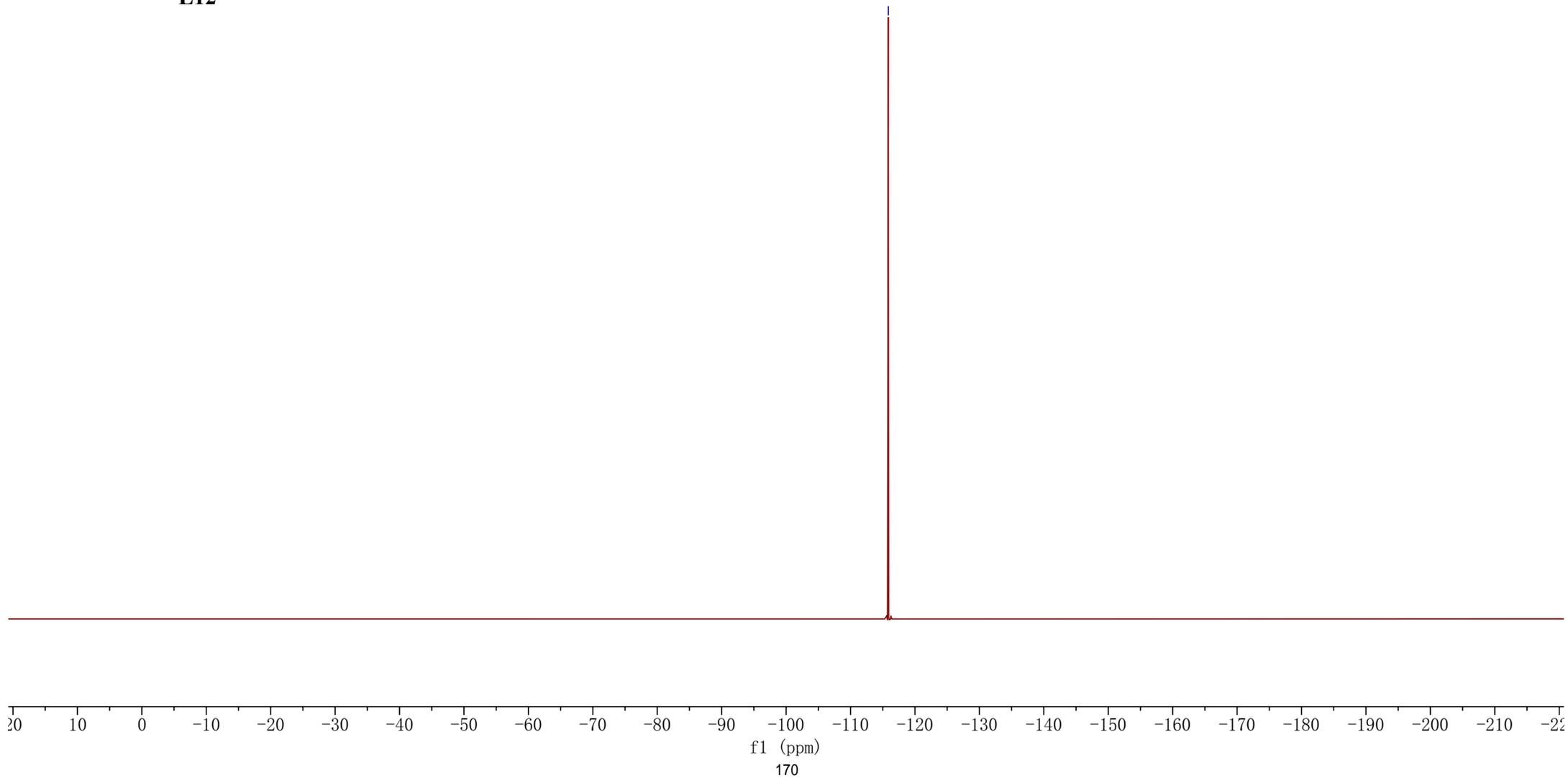
L12

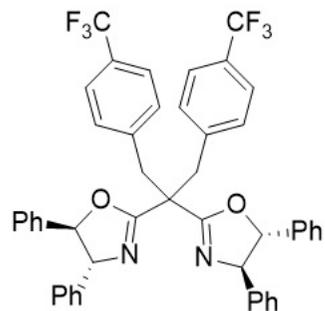




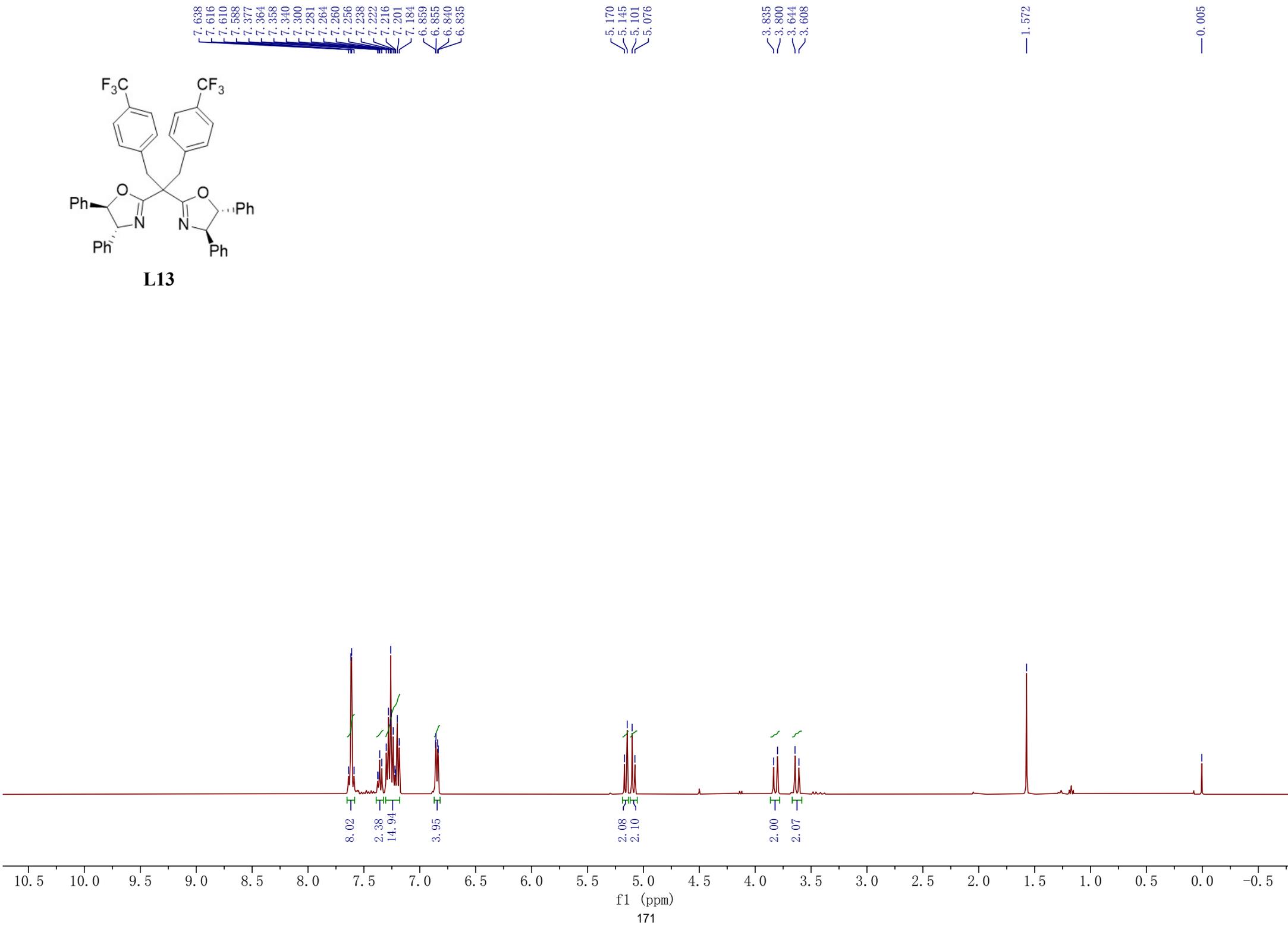
L12

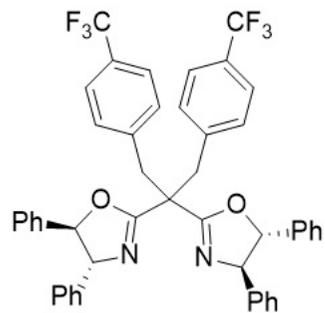
-115.868



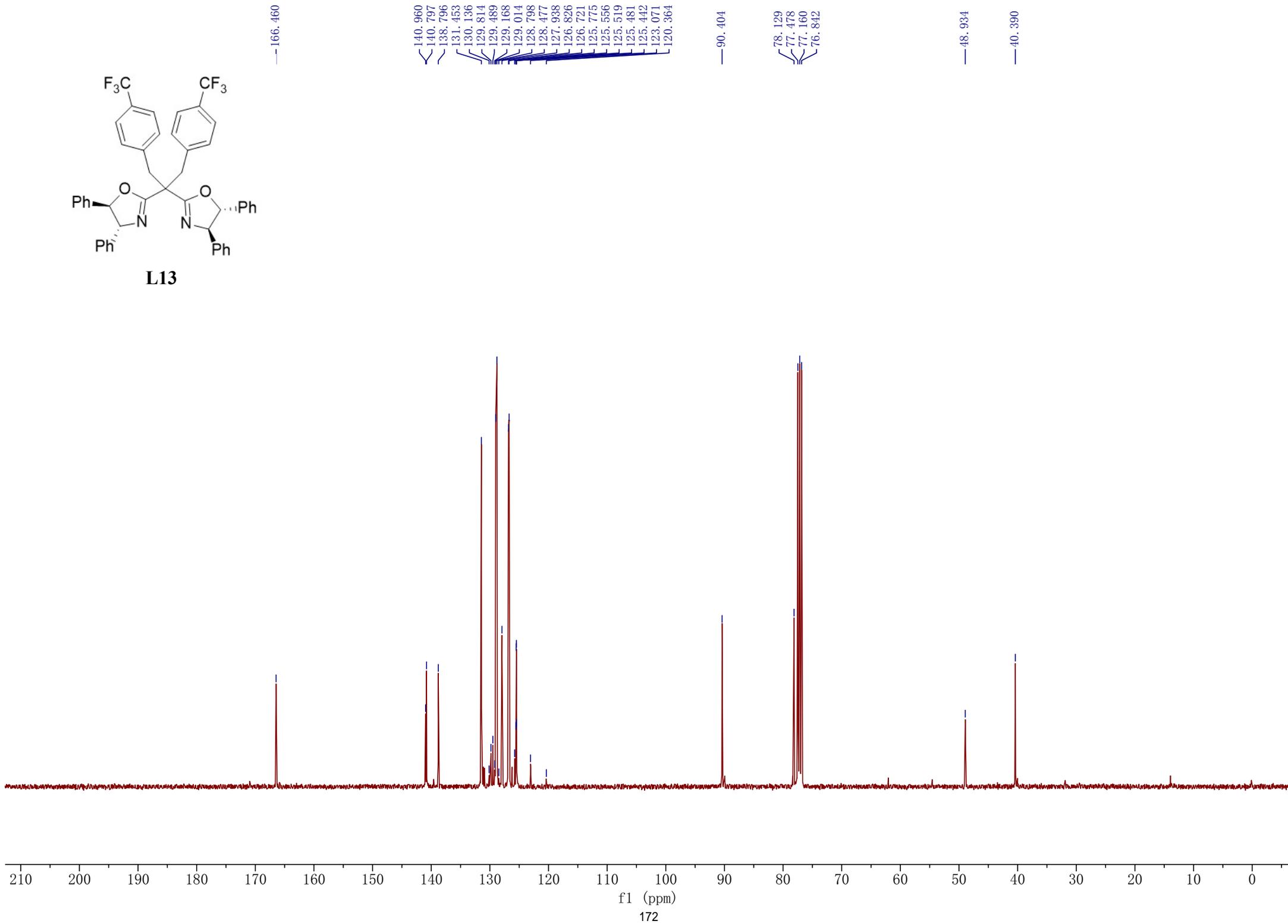


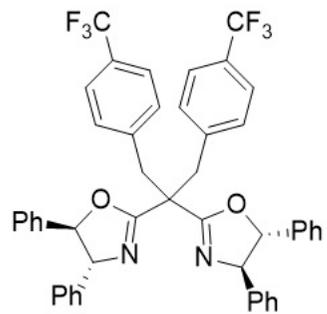
L13





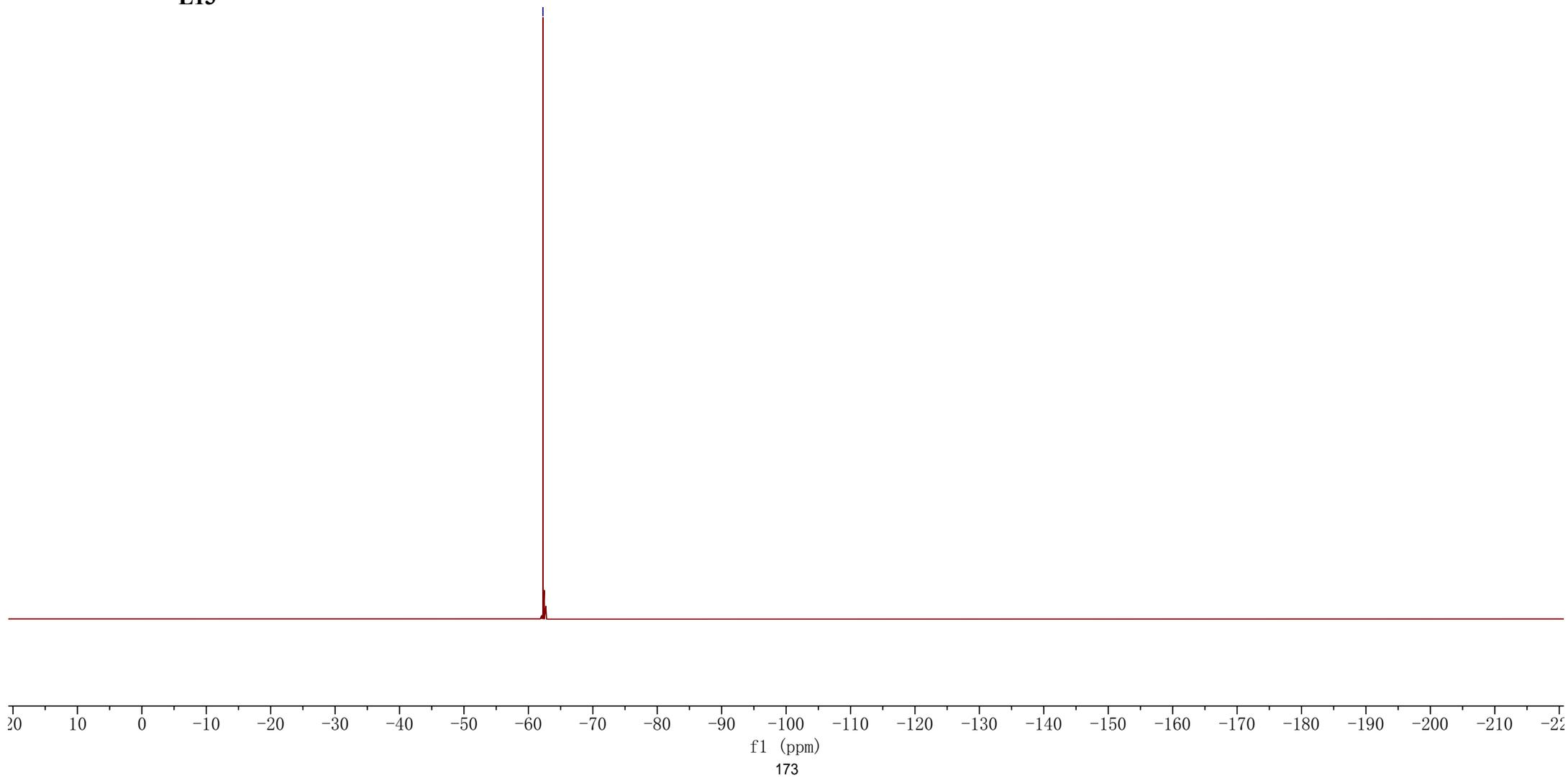
L13

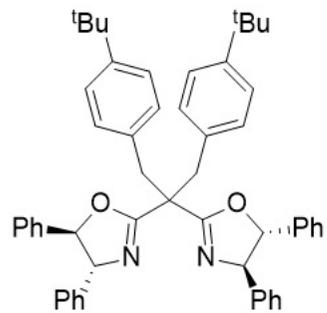




L13

— 62.256





L14

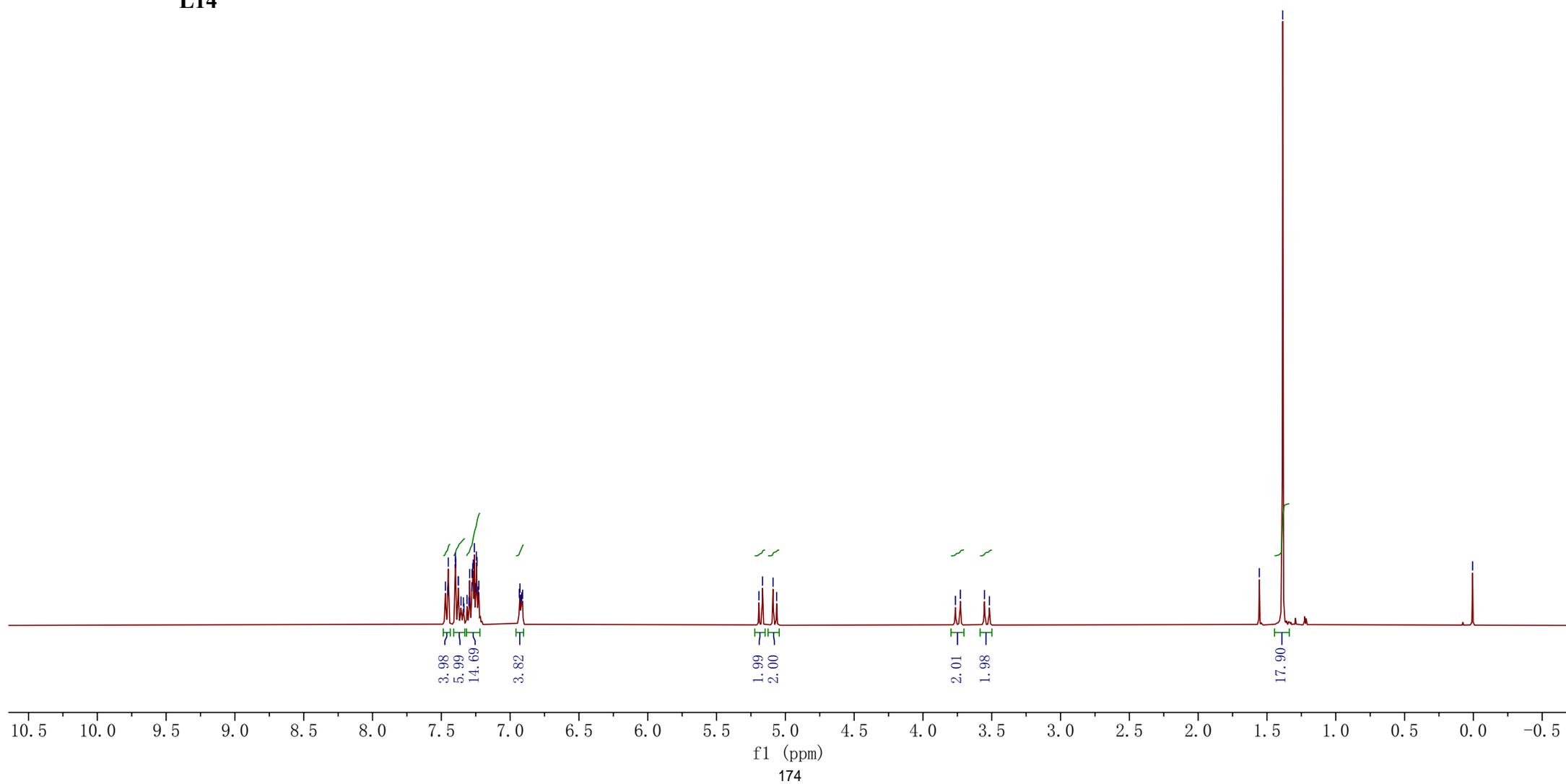
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7.357
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7.335
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7.272
7.268
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7.227
6.933
6.929
6.921
6.916
6.909

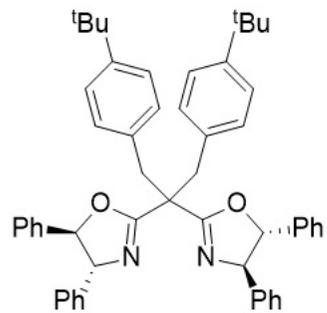
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5.063

3.764
3.728
3.553
3.517

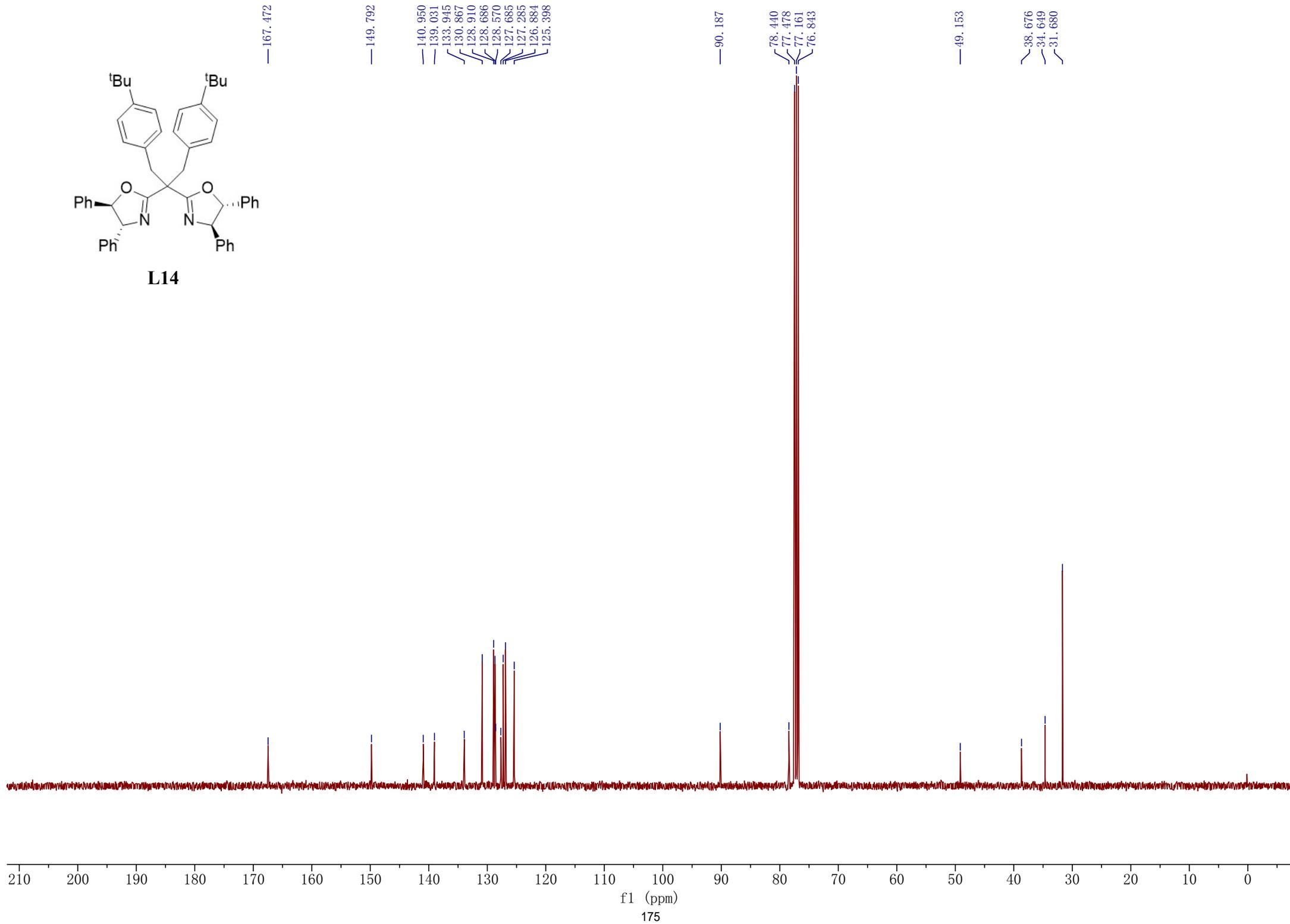
1.556
1.386

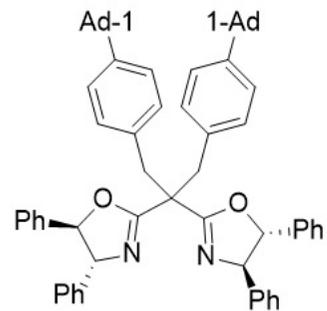
0.005





L14





L15

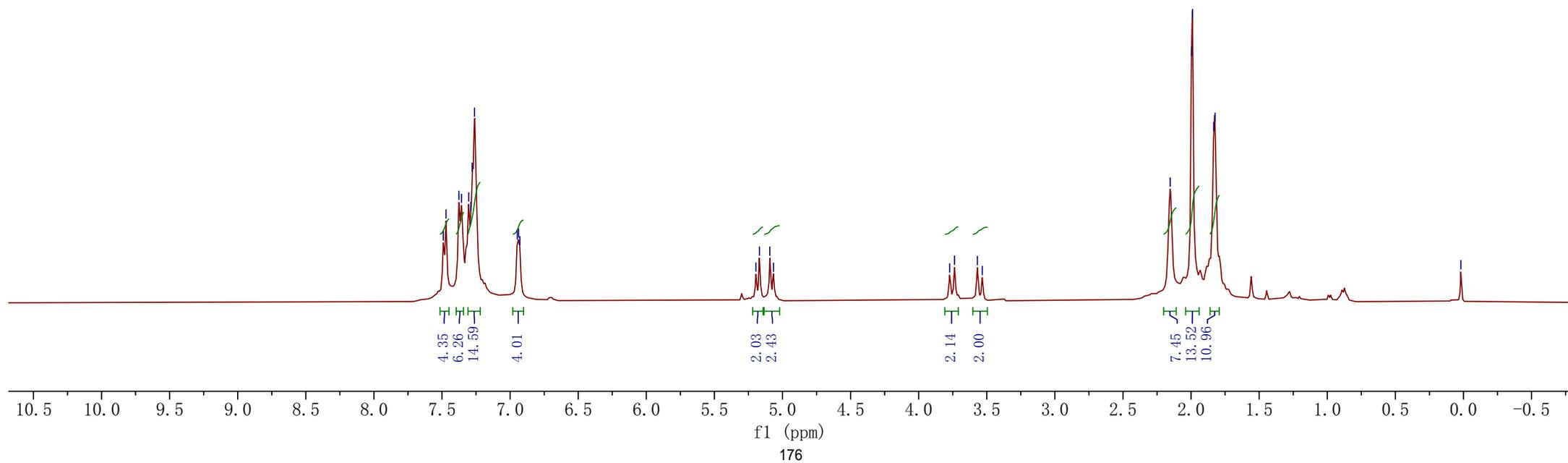
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7.278
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6.948
6.937
6.929

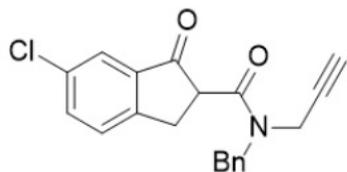
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5.066

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3.737
3.569
3.533

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1.997
1.989
1.884
1.823

0.019



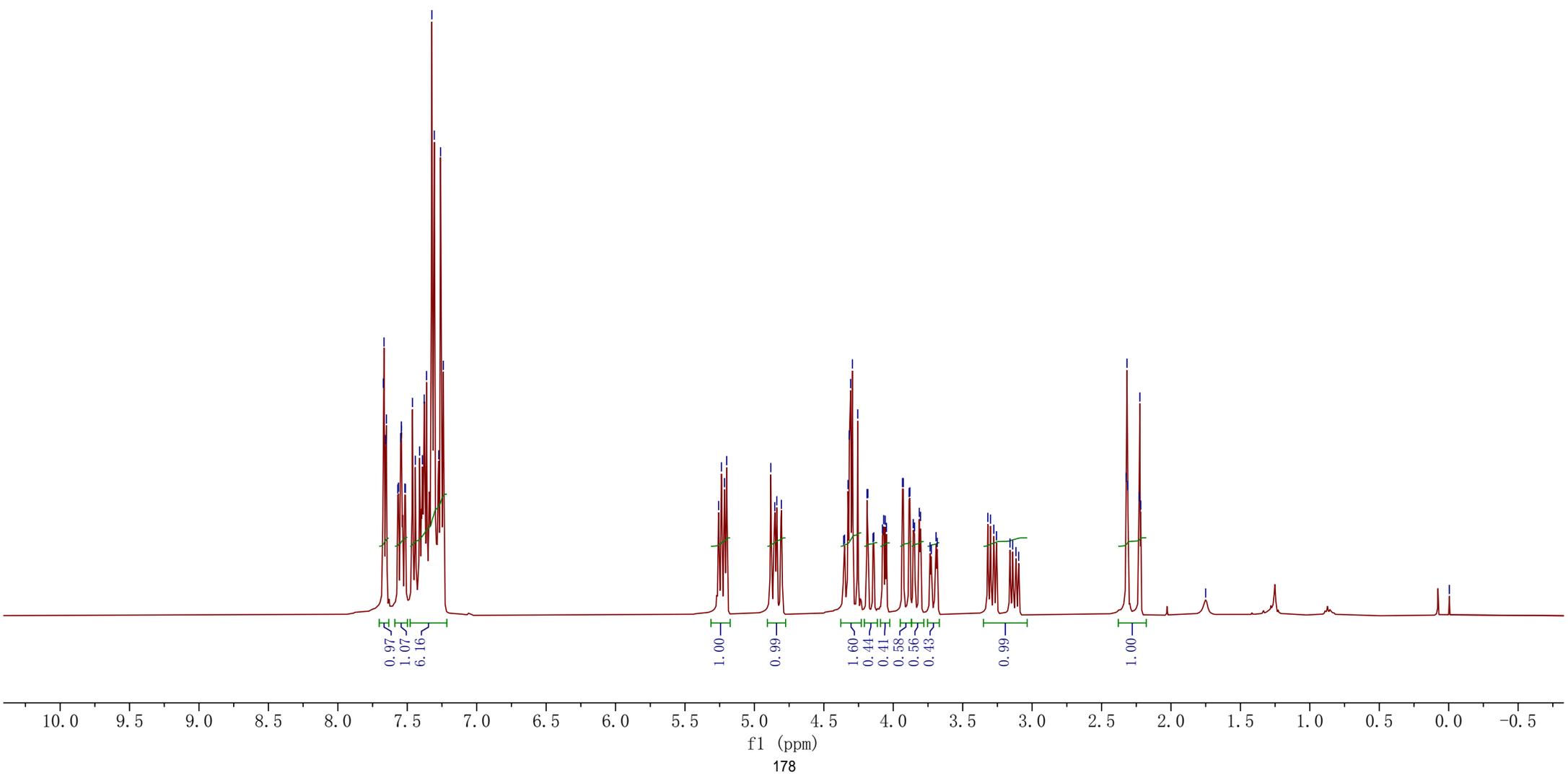


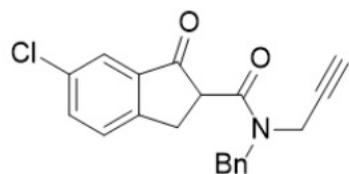
1f

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7.442
7.411
7.390
7.378
7.361
7.323
7.305
7.274
7.260
7.240

5.258
5.238
5.215
5.200
4.882
4.854
4.839
4.806

4.357
4.351
4.326
4.317
4.307
4.294
4.256
4.189
4.183
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4.140
4.078
4.069
4.058
4.049
3.933
3.927
3.886
3.880
3.856
3.847
3.813
3.804
3.735
3.726
3.692
3.683
3.319
3.300
3.276
3.256
3.159
3.140
3.116
3.097
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2.311
2.230
2.224
2.218
1.750
-0.005





1f

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200.025

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167.683

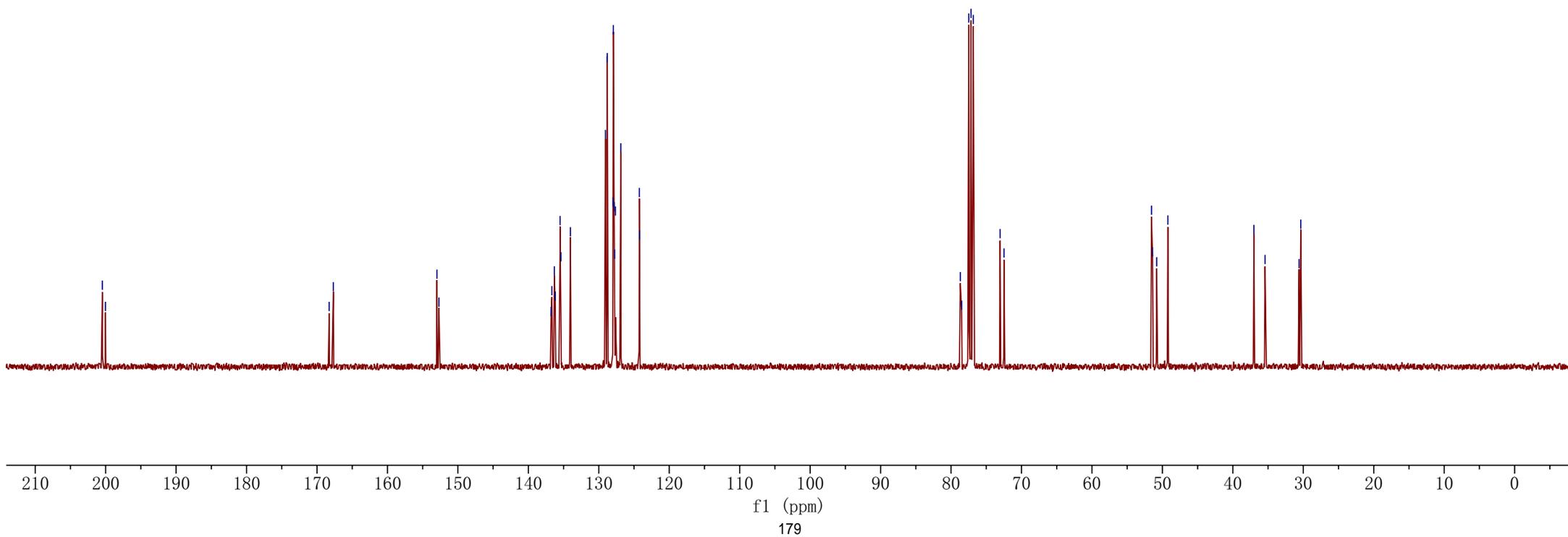
152.970
152.690

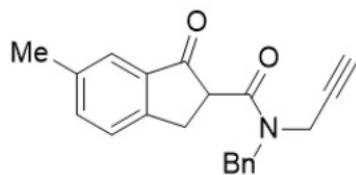
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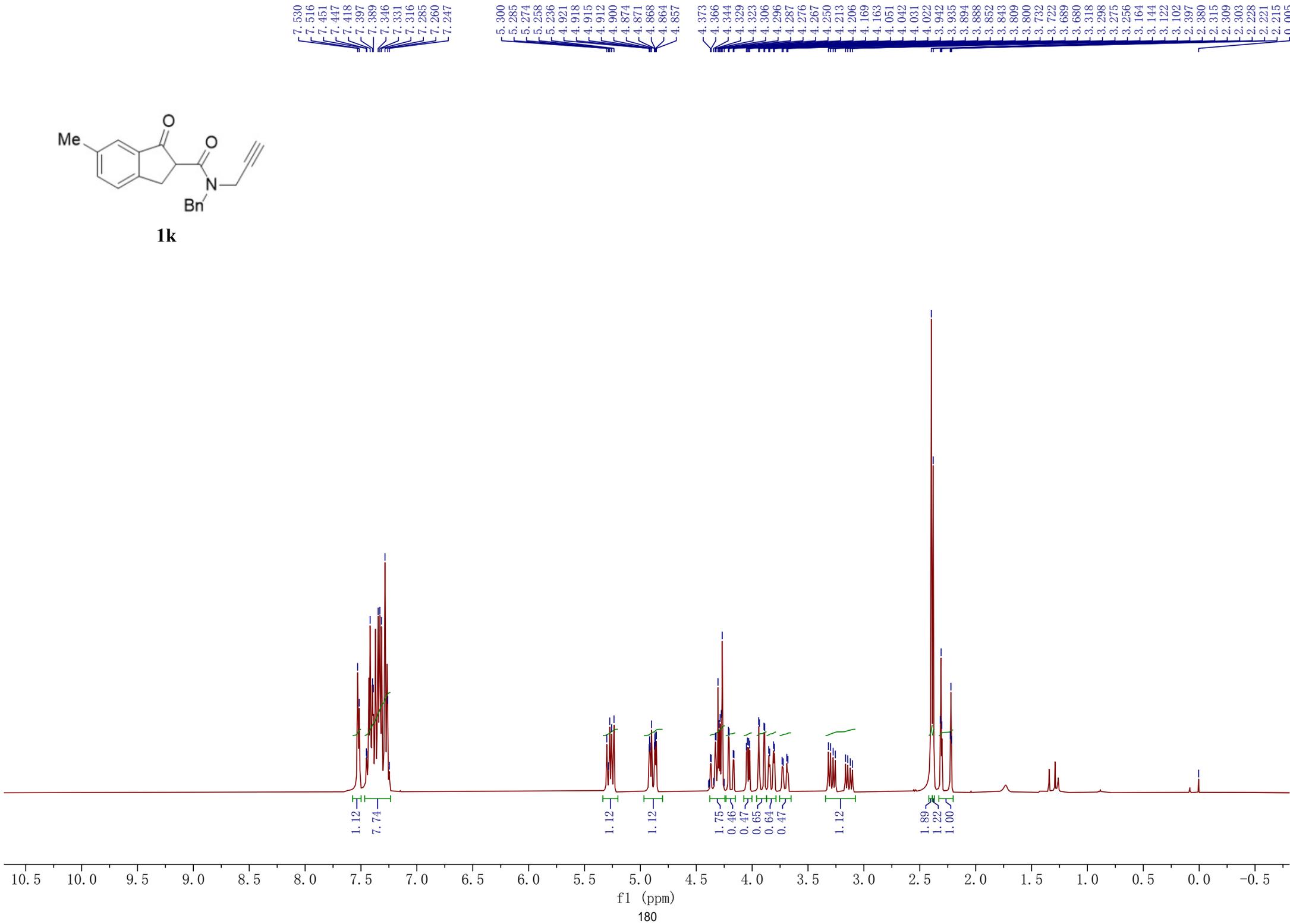
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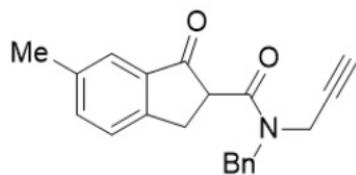
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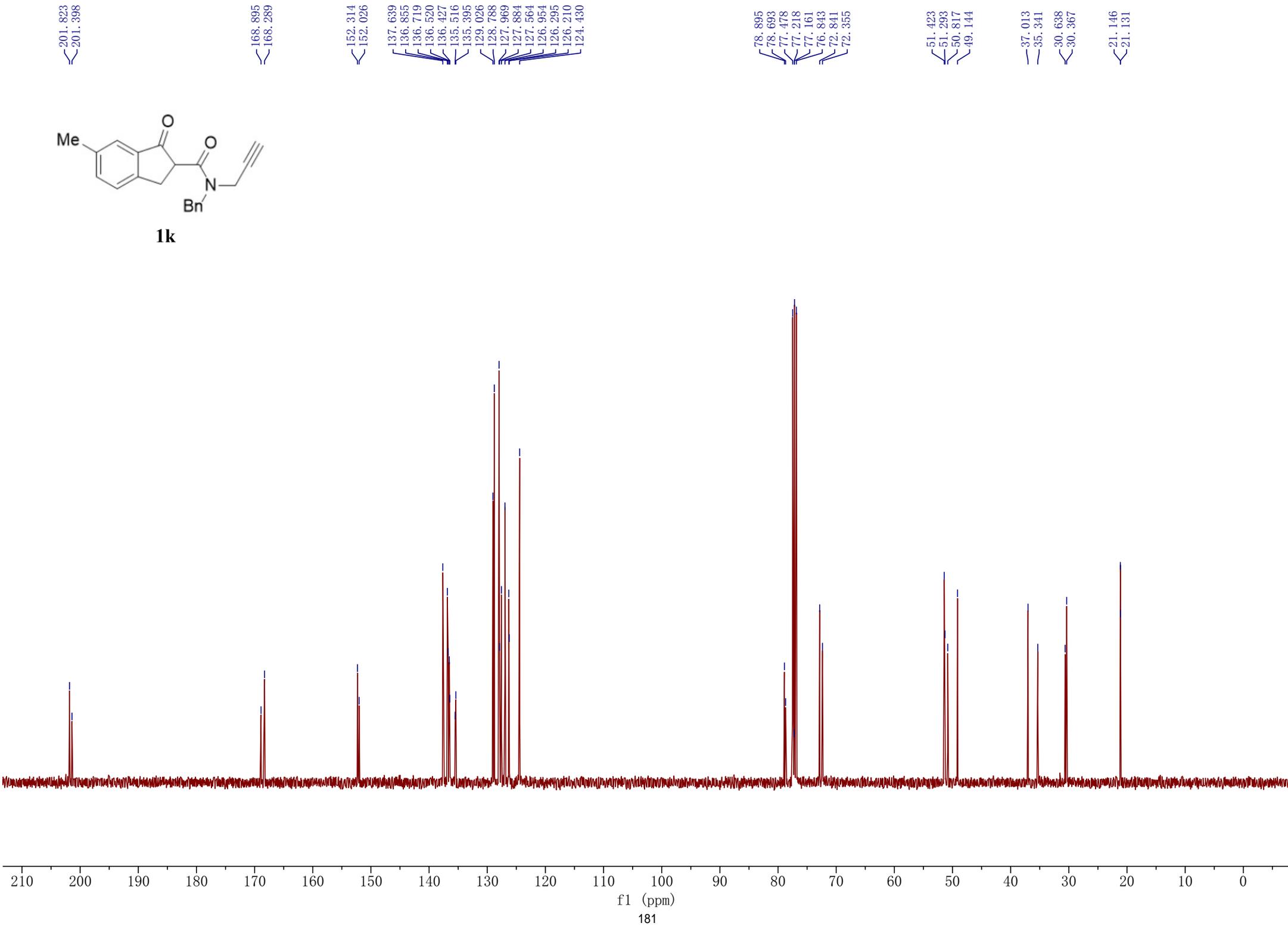


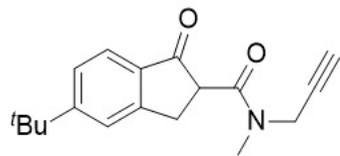
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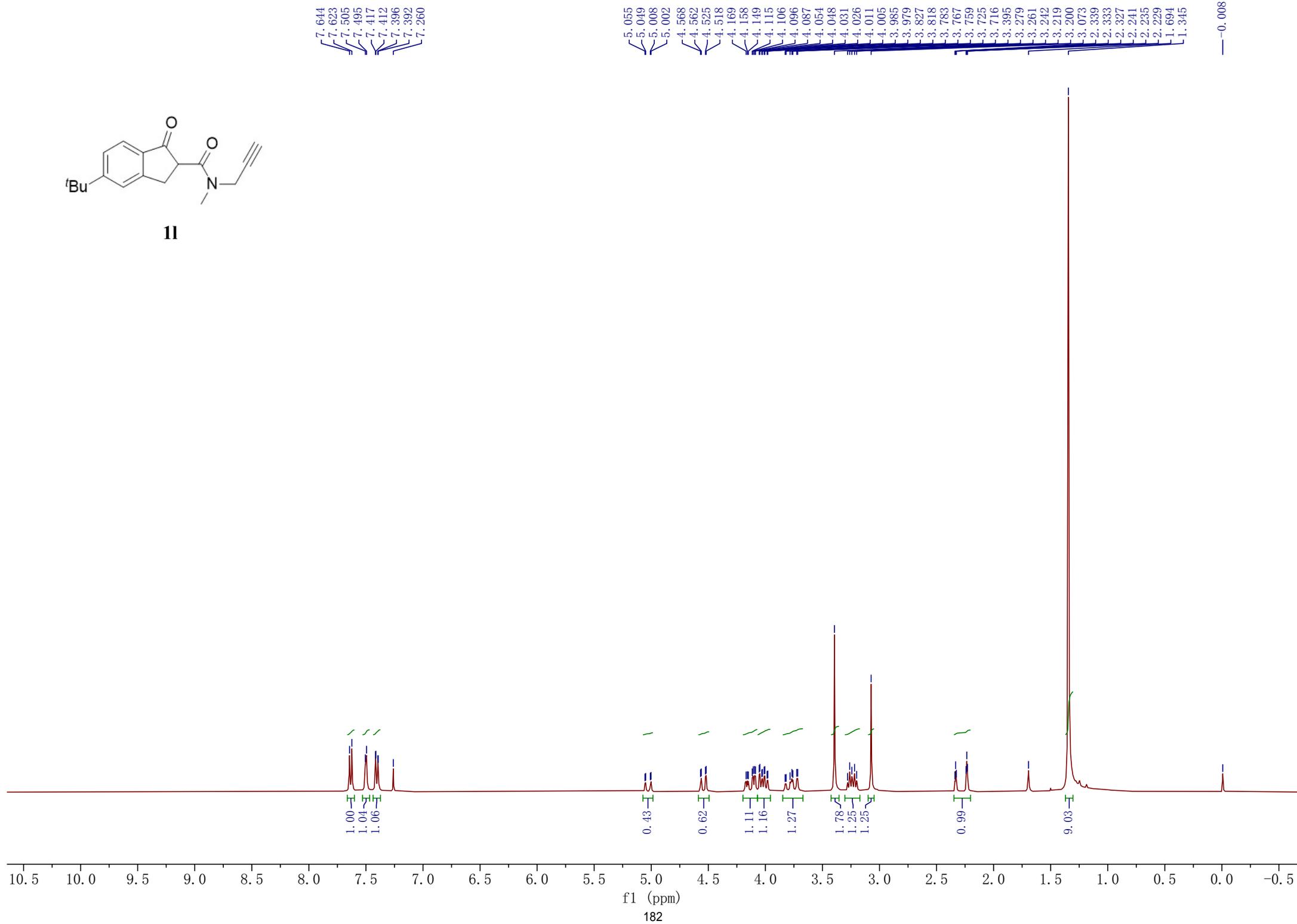


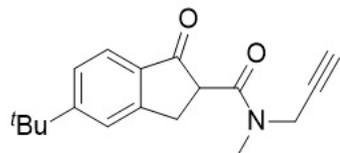
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11





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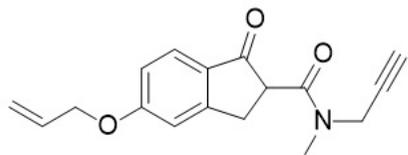
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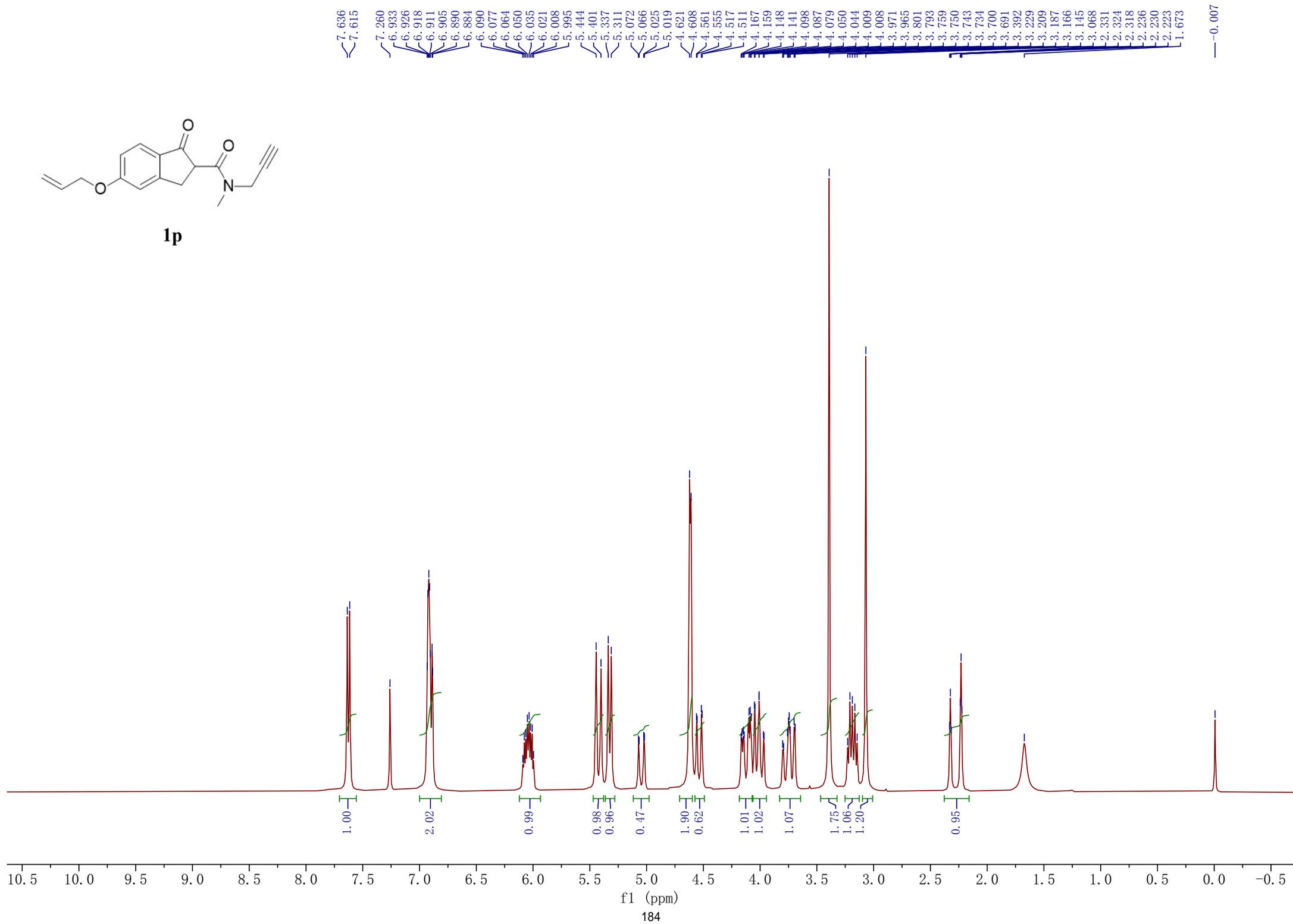
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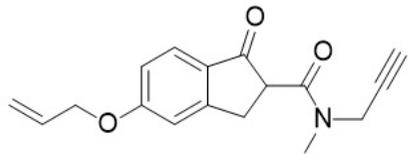
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1p

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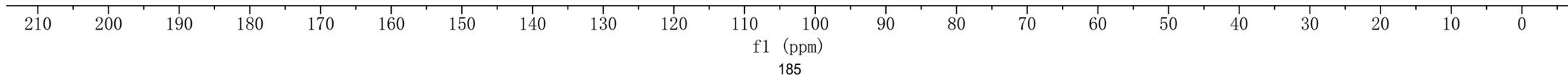
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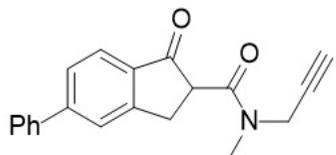
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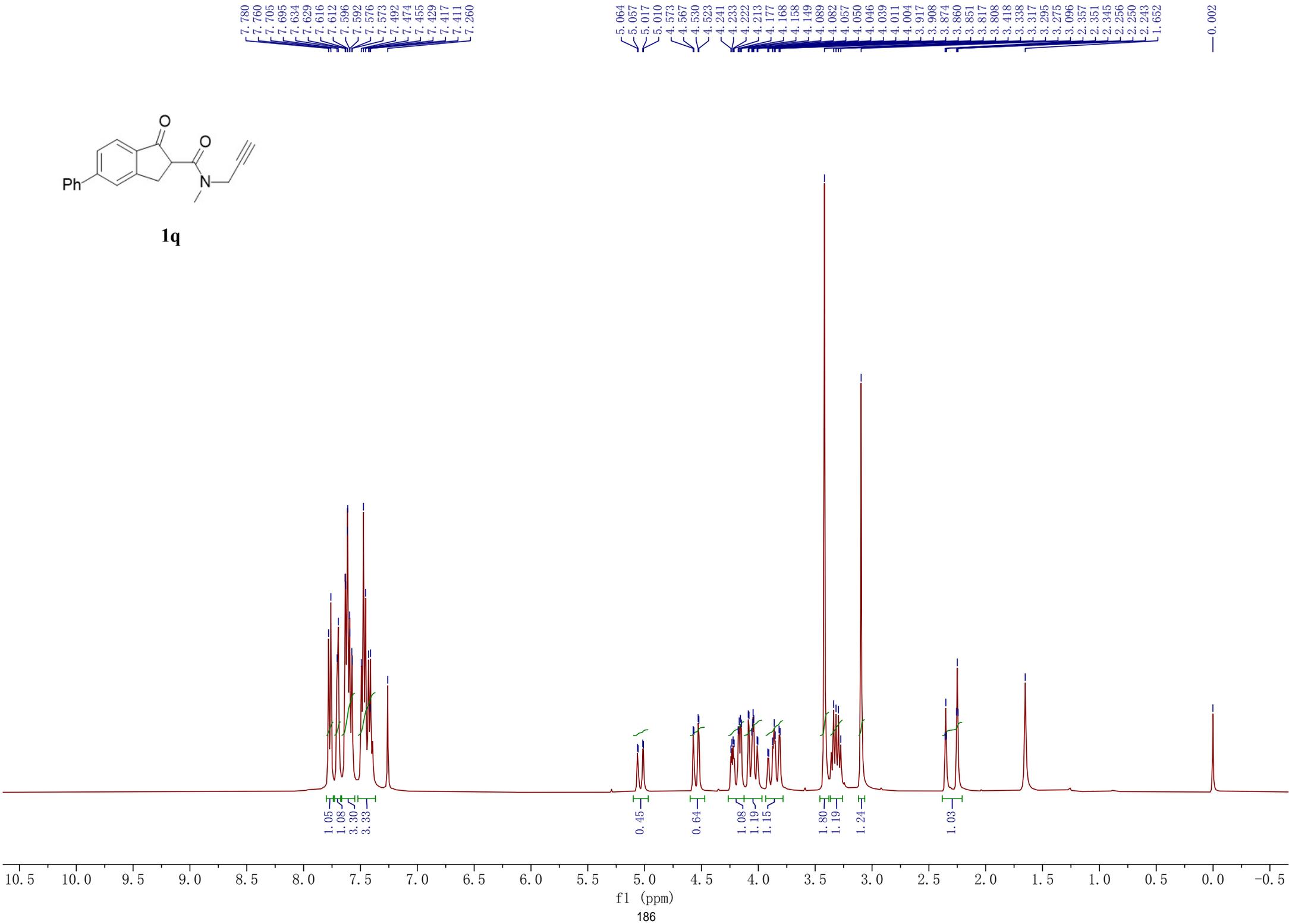


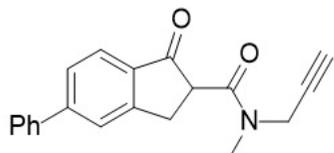
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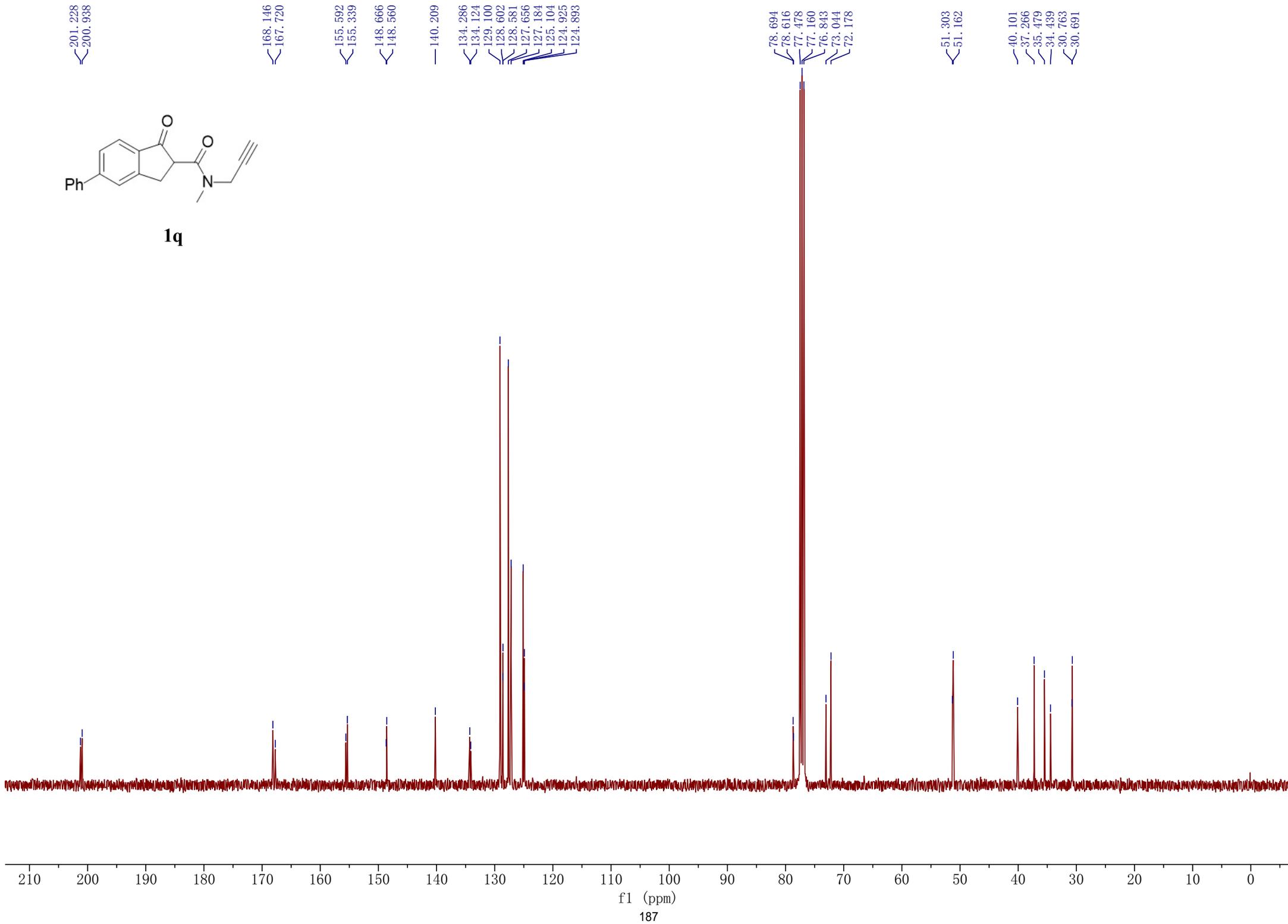
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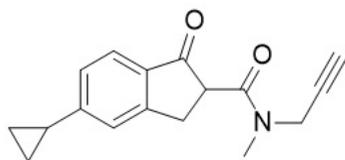
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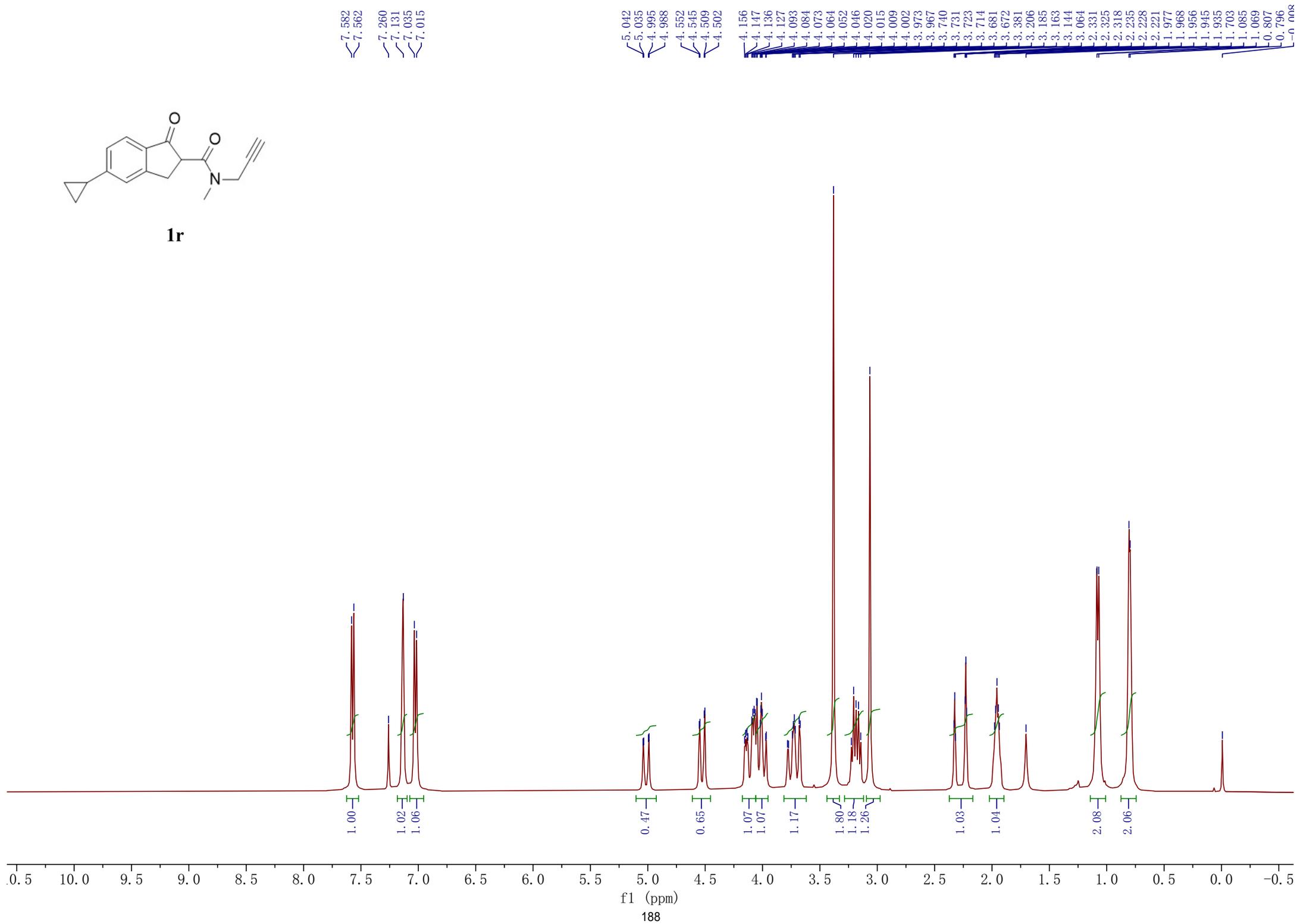


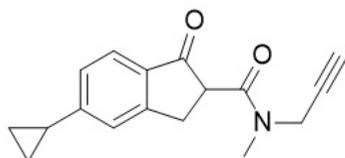
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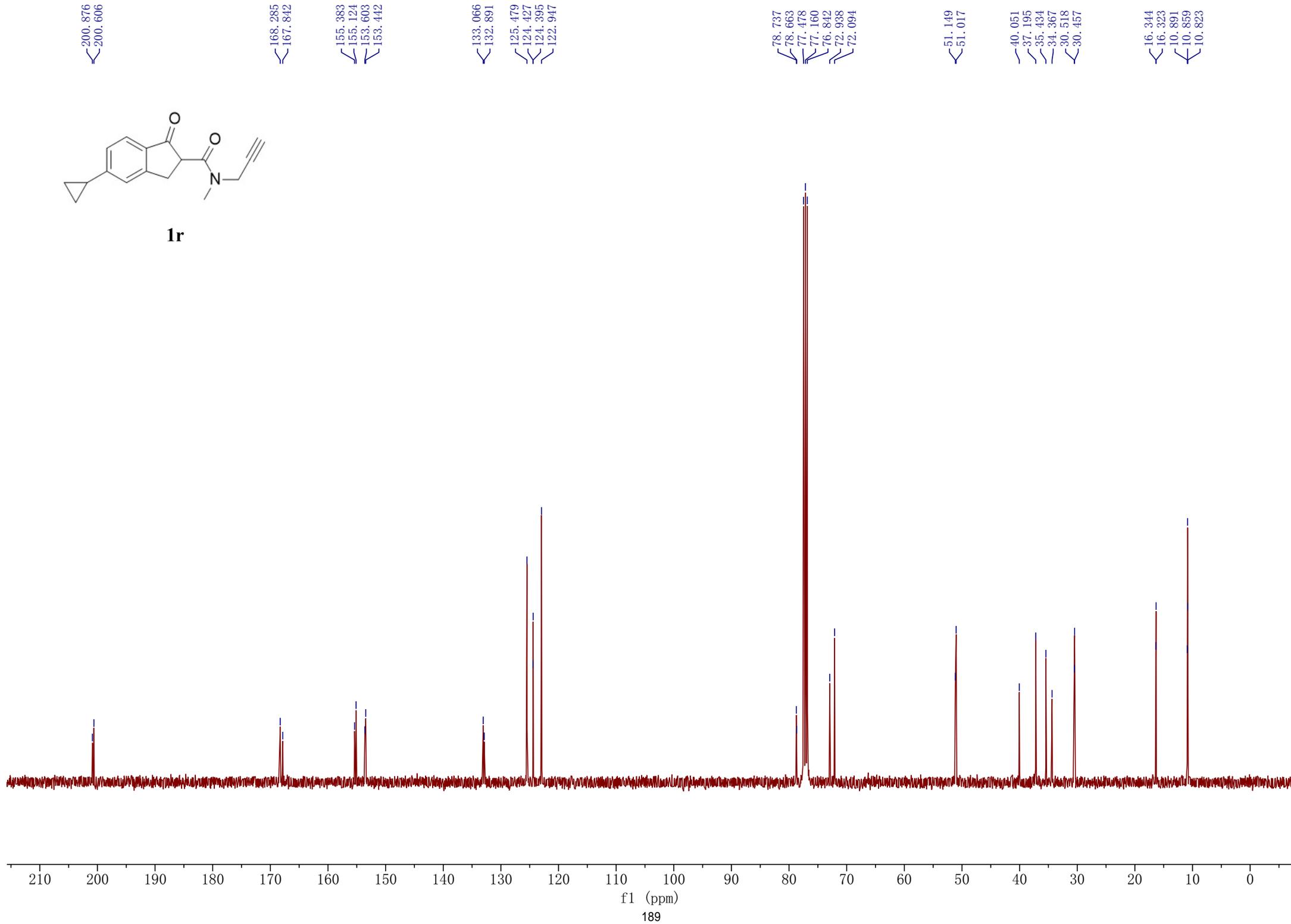


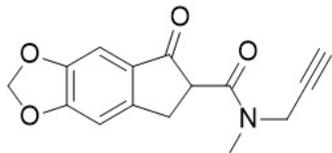
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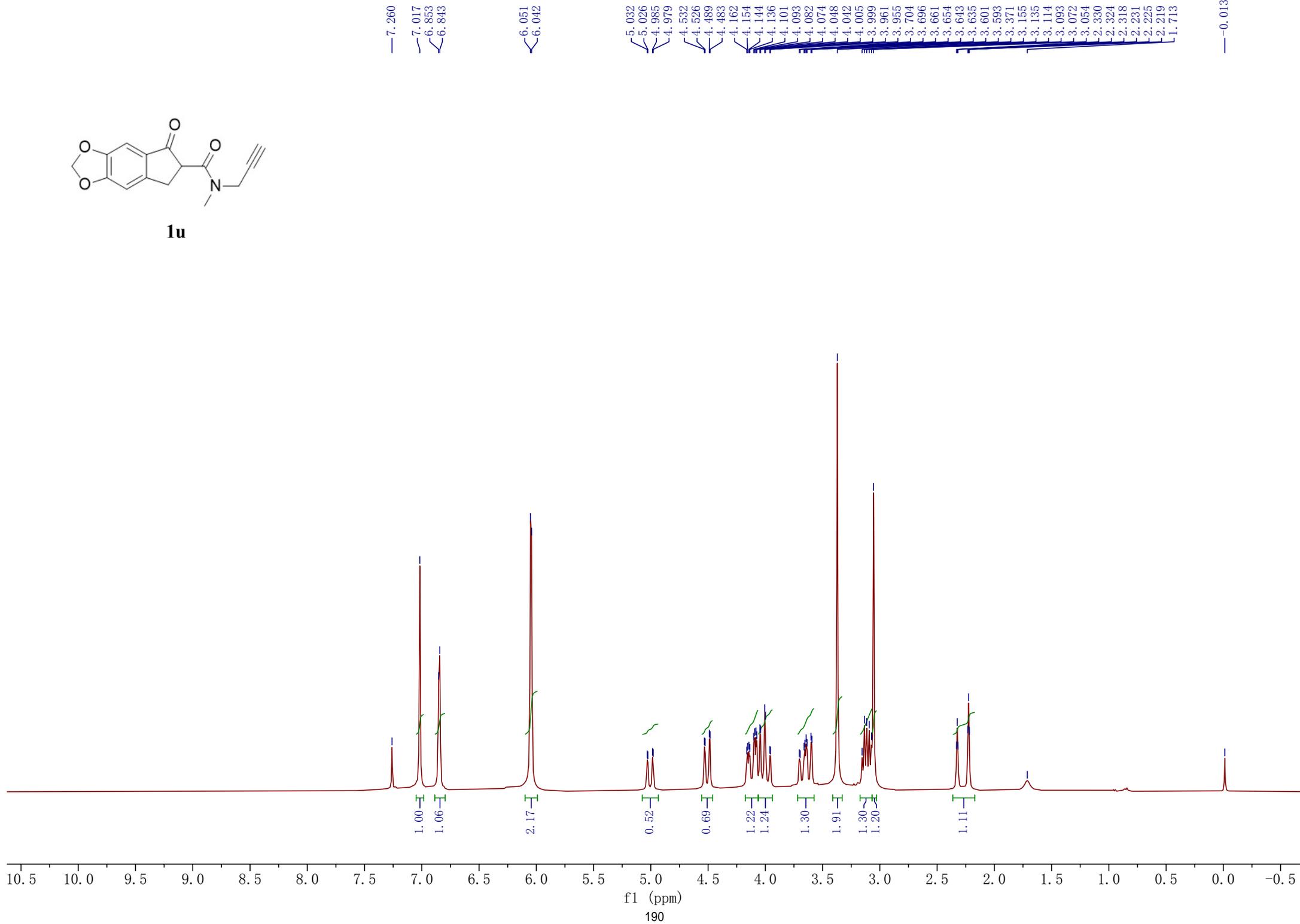


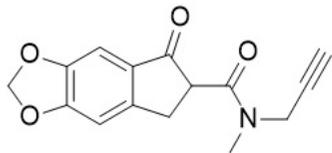
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1u





1u

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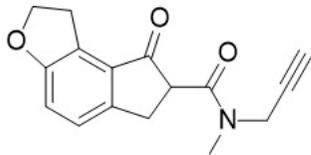
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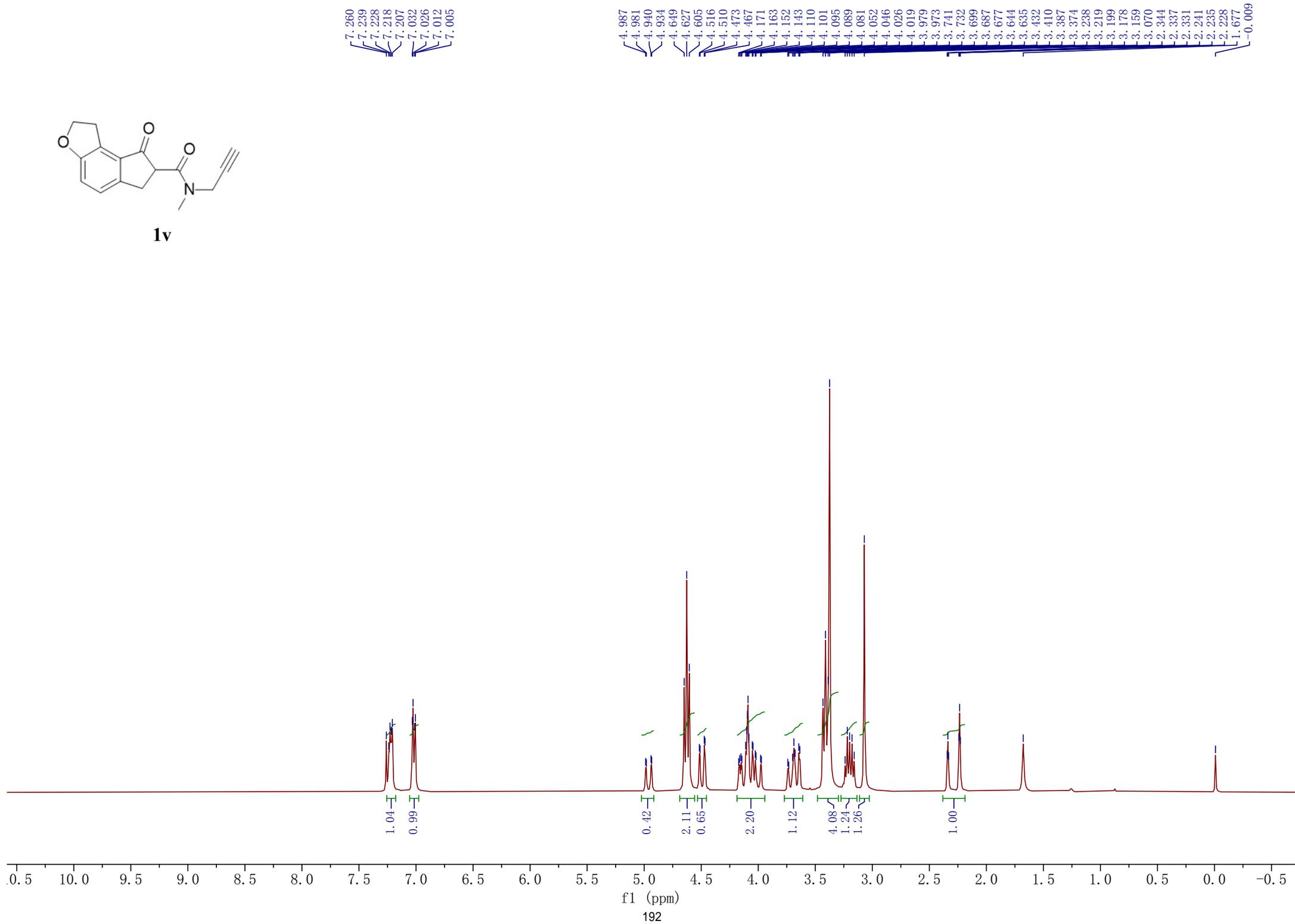
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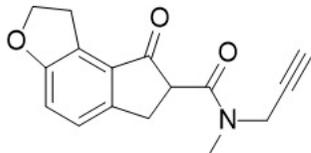


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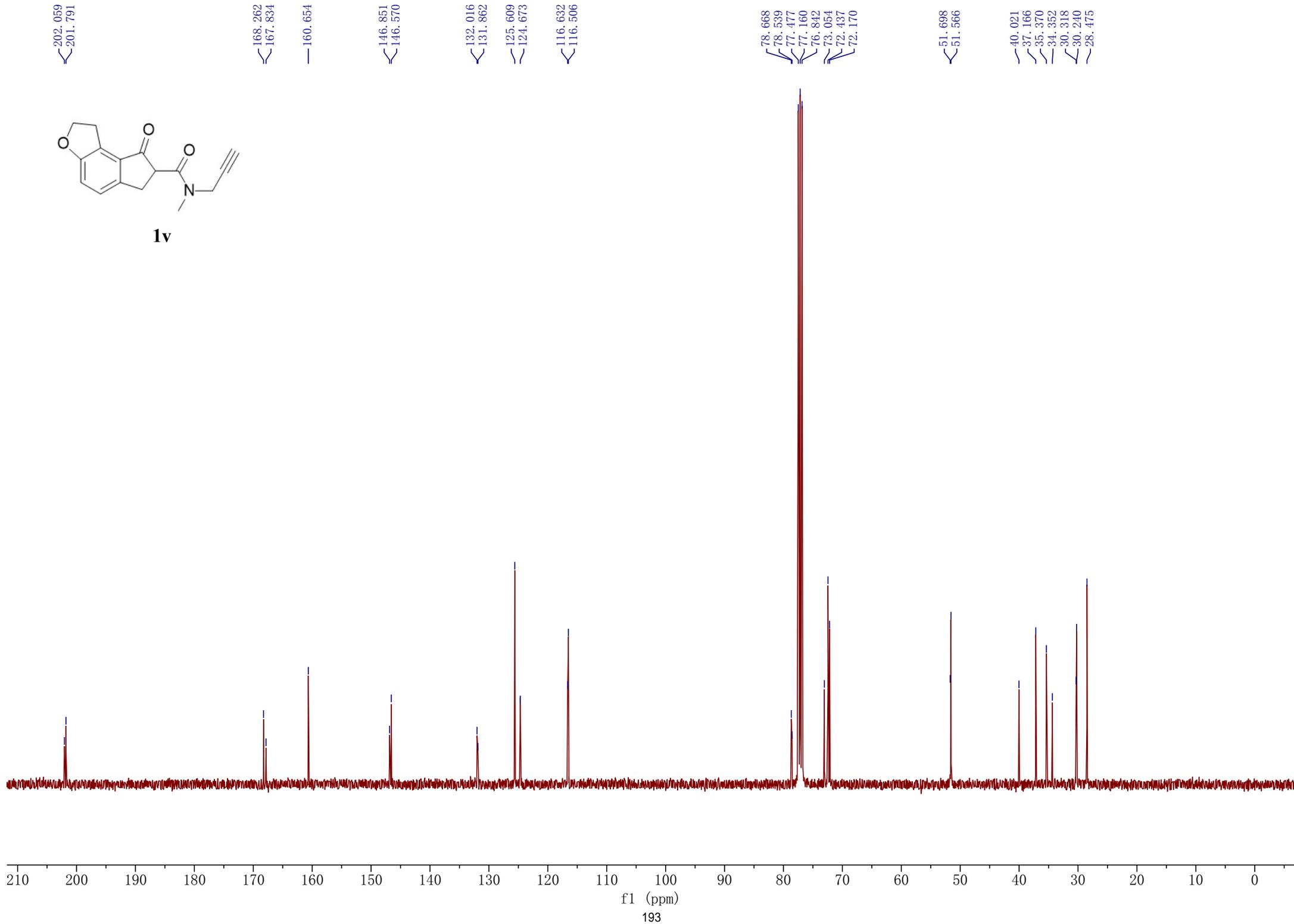


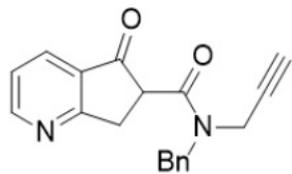
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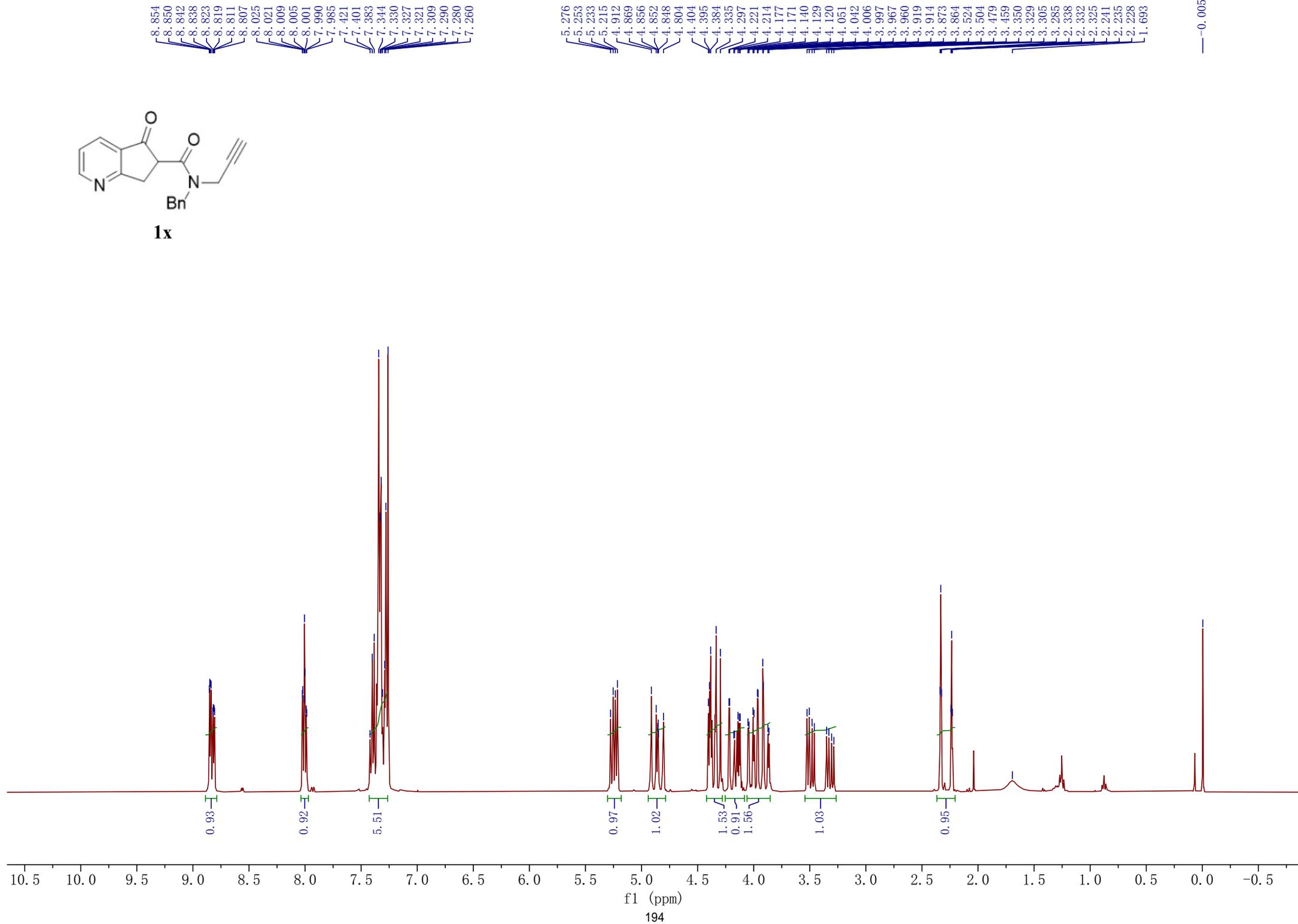


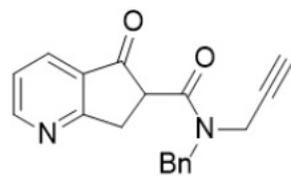
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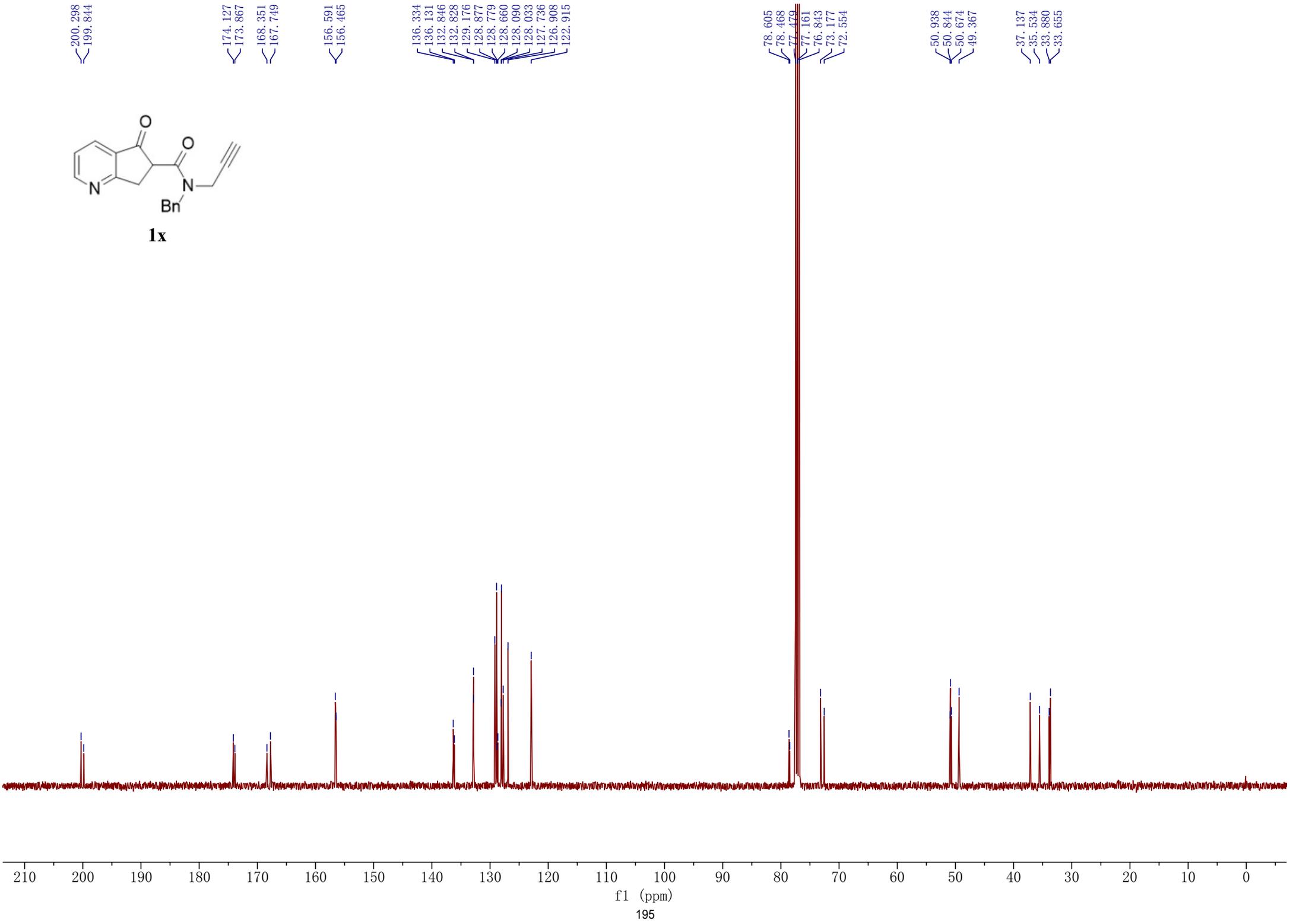


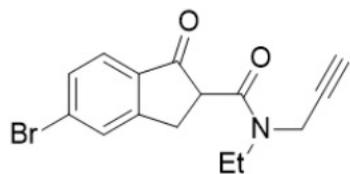
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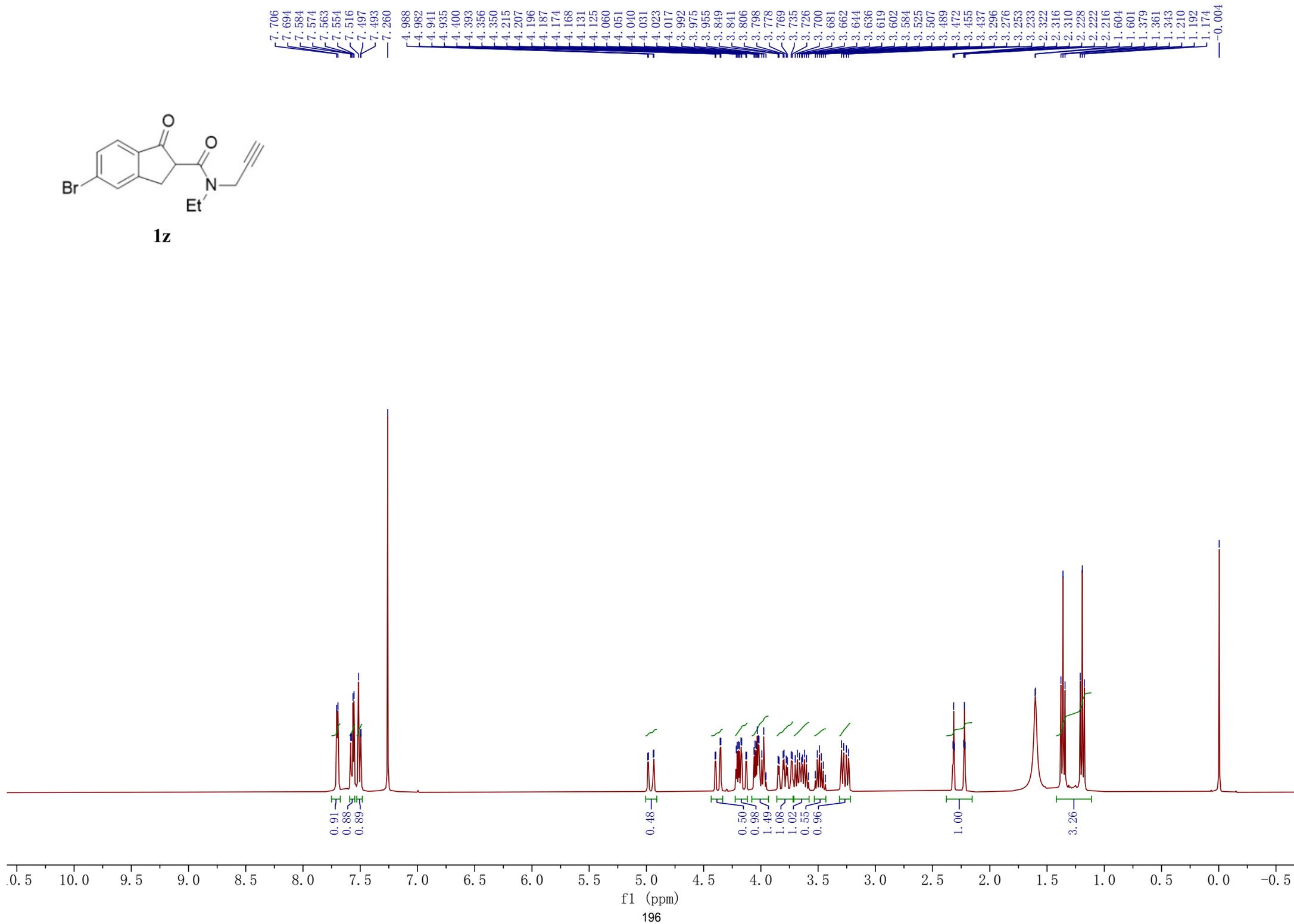


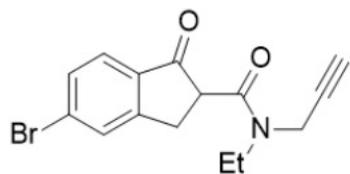
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1z





1z

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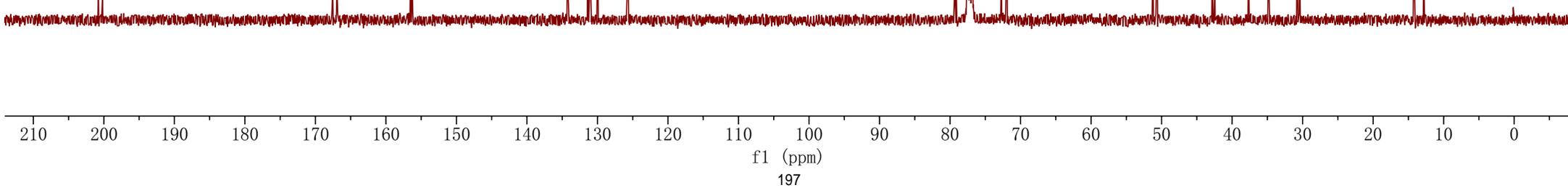
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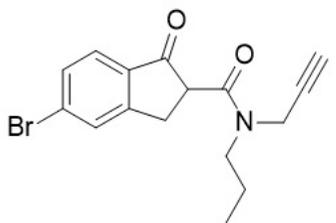
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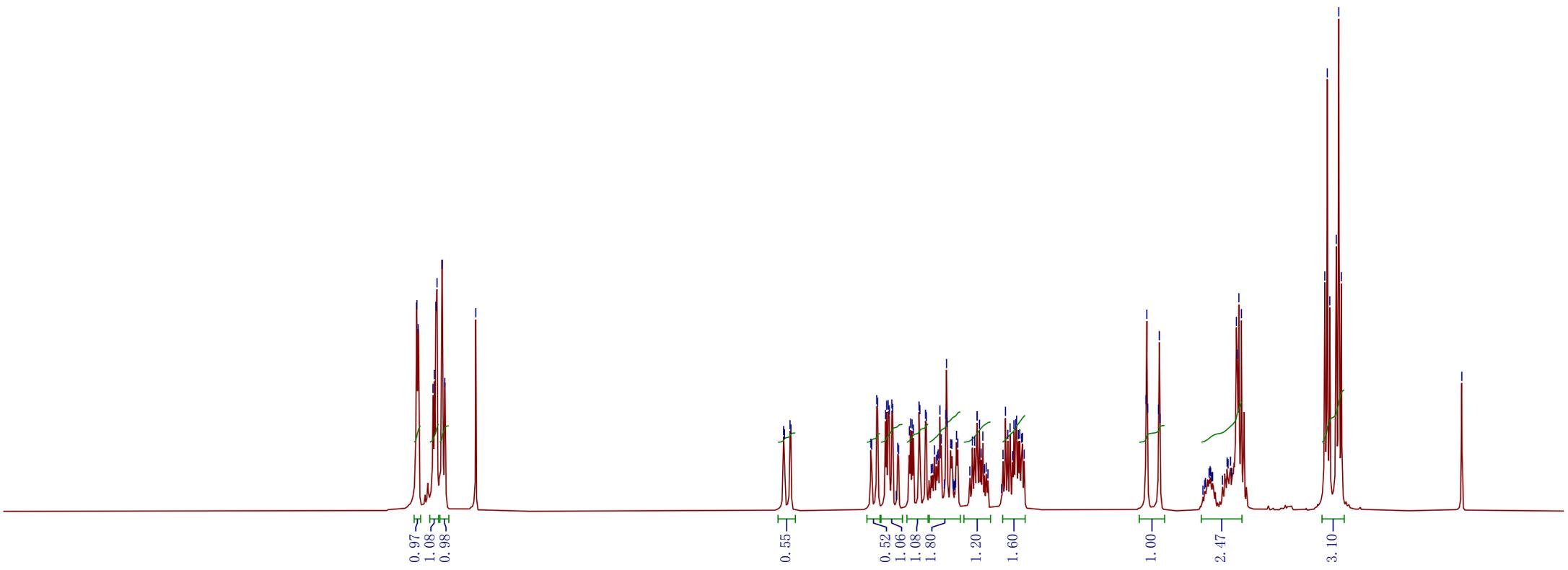
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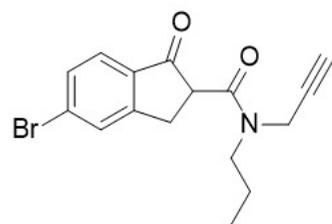


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1aa





1aa

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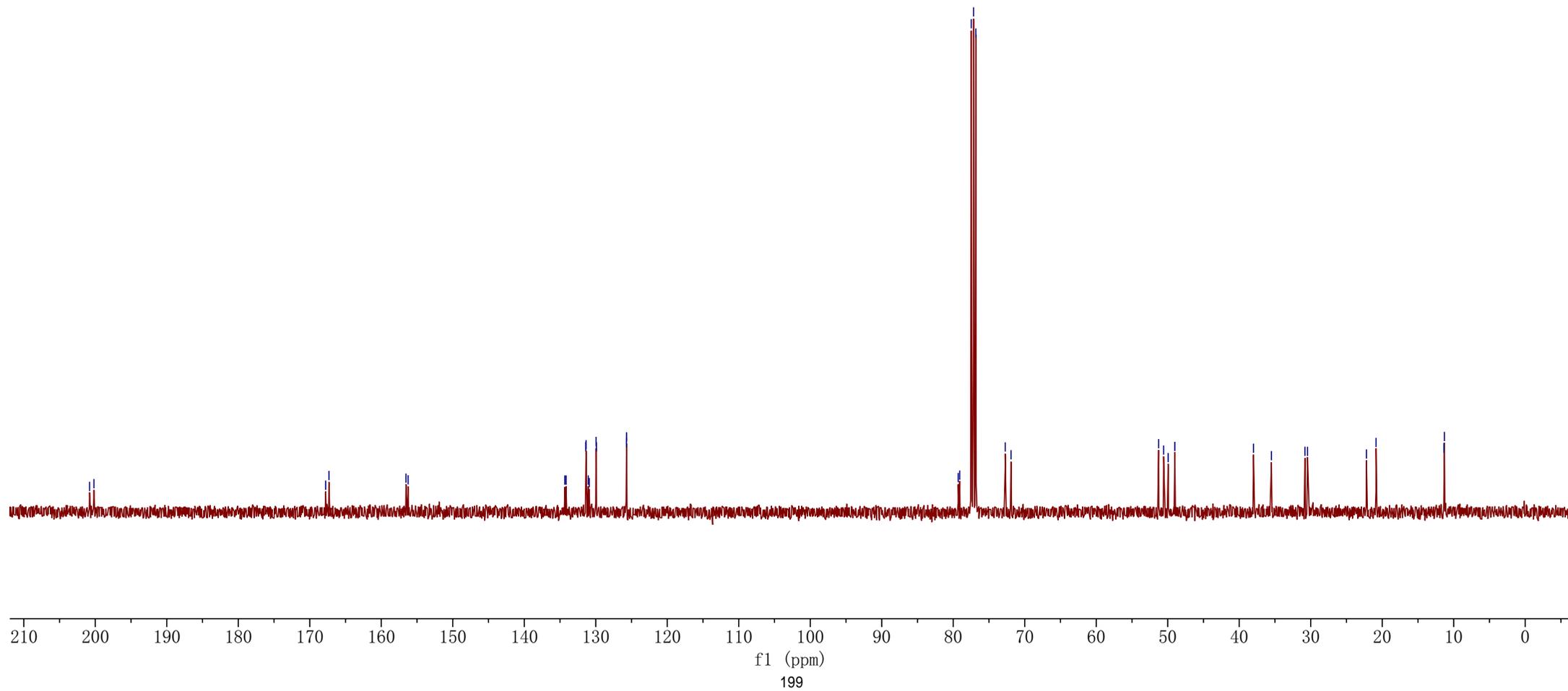
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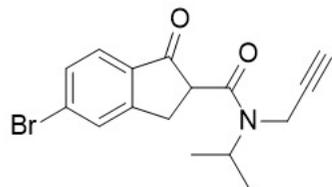
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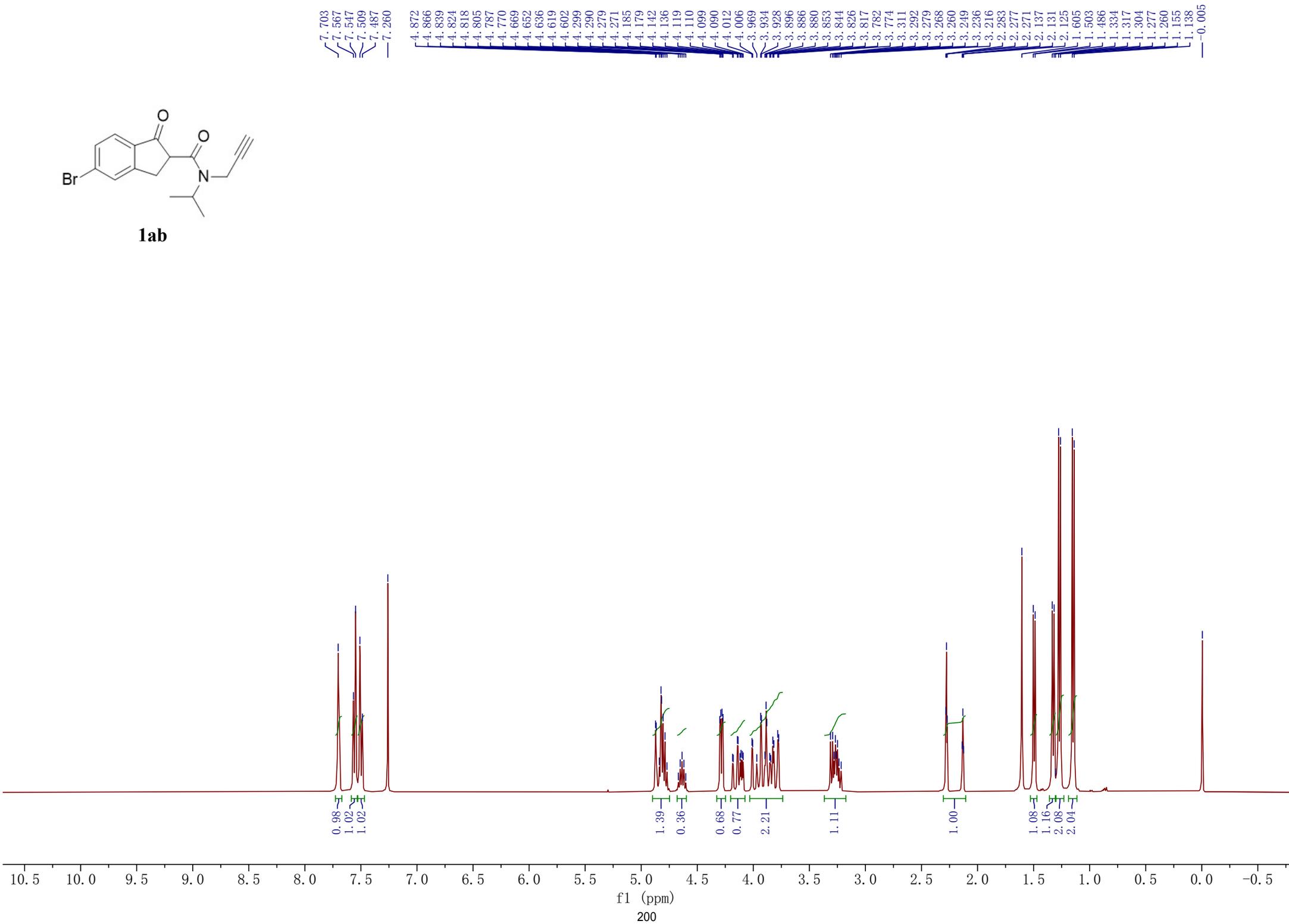
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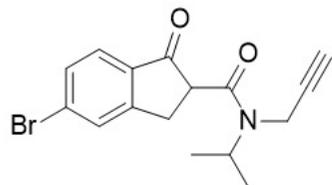
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1ab

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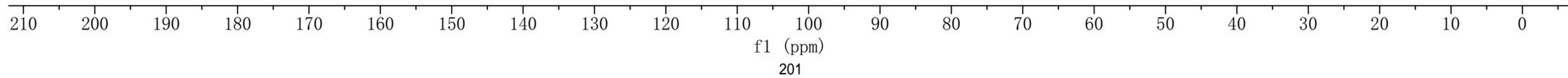
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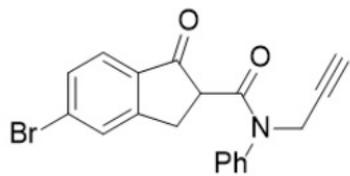
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1ac

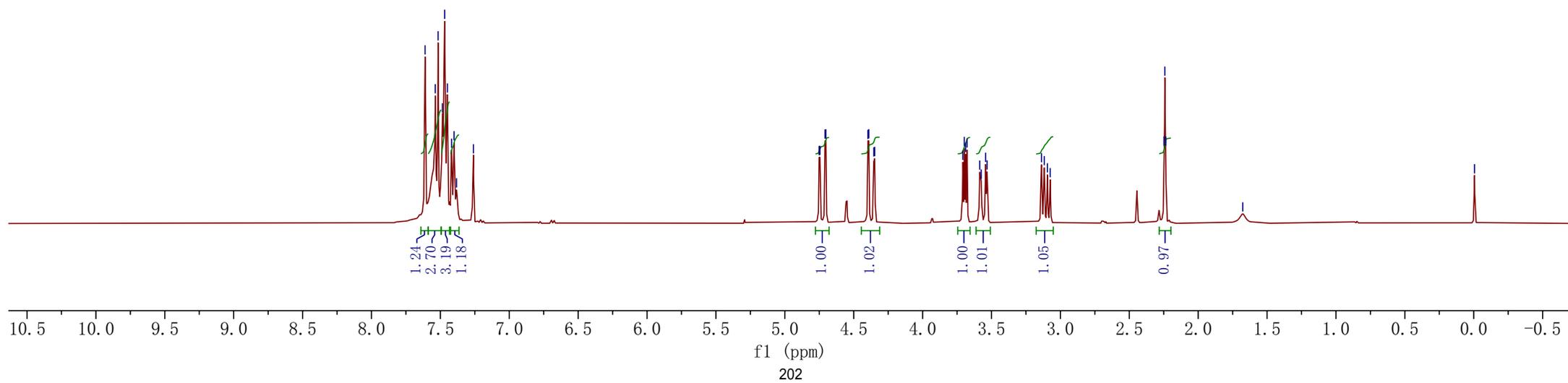
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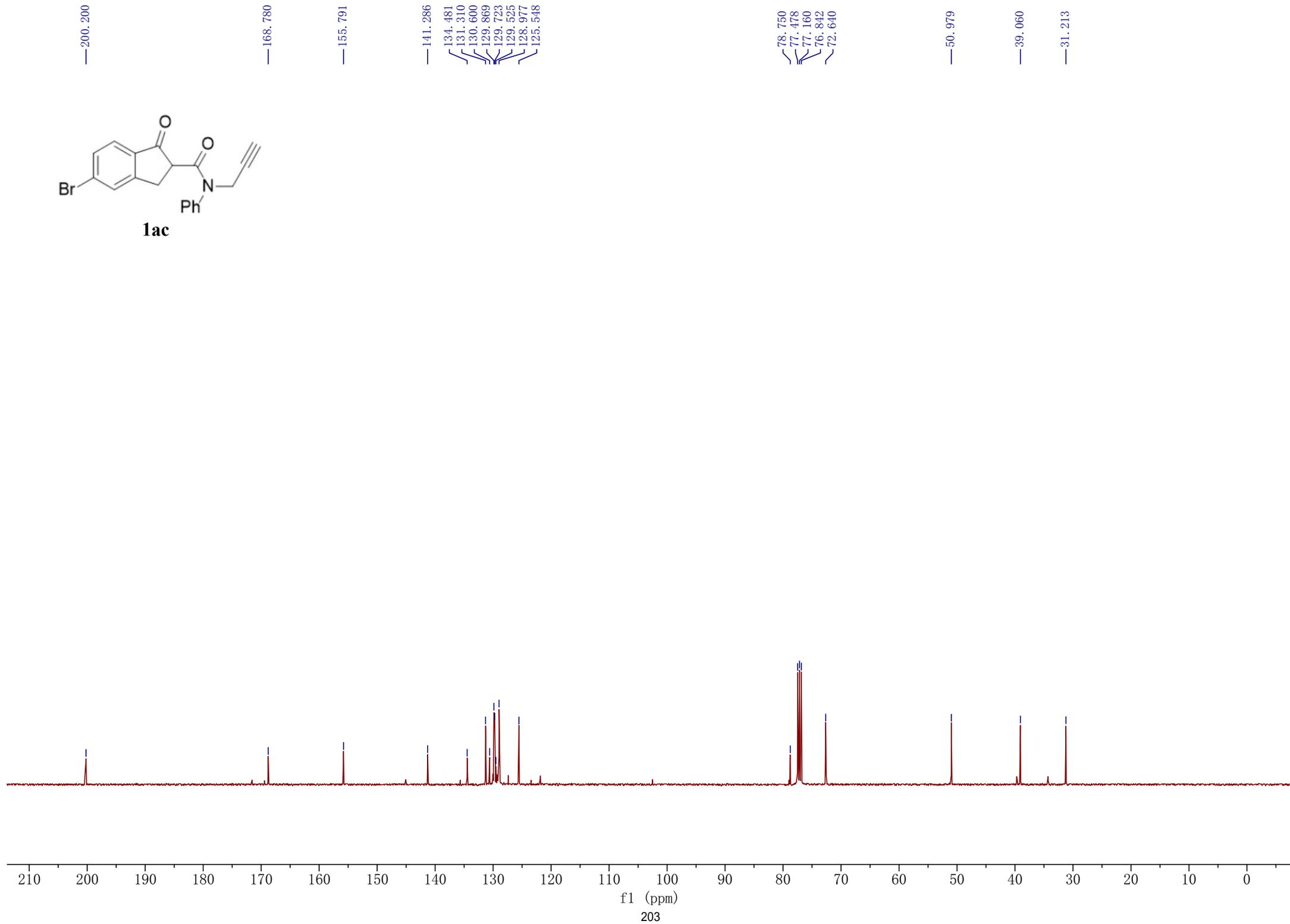
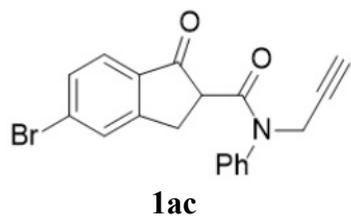
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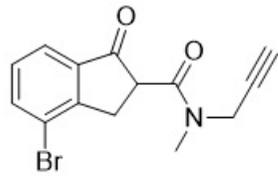
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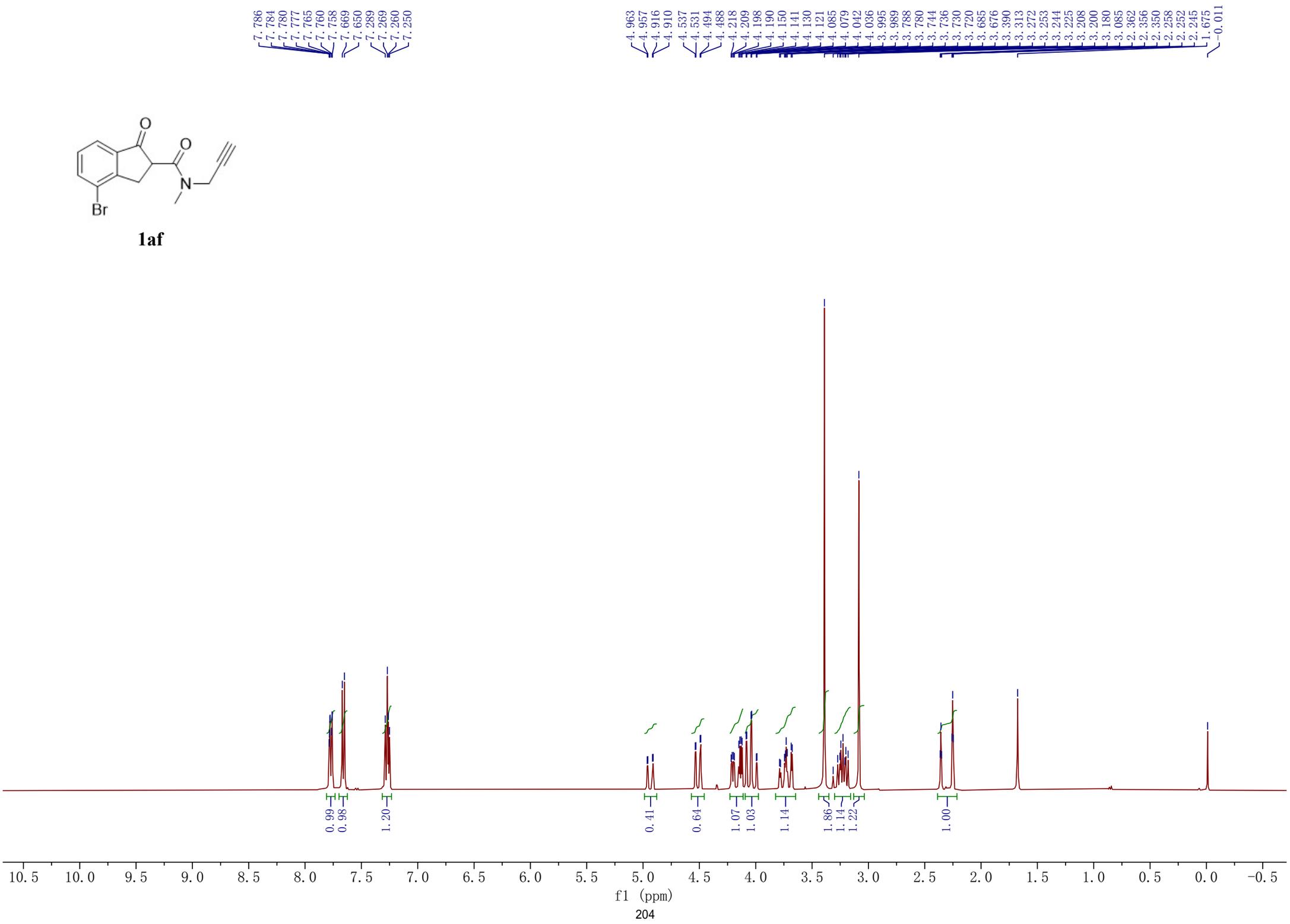
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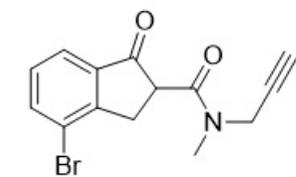




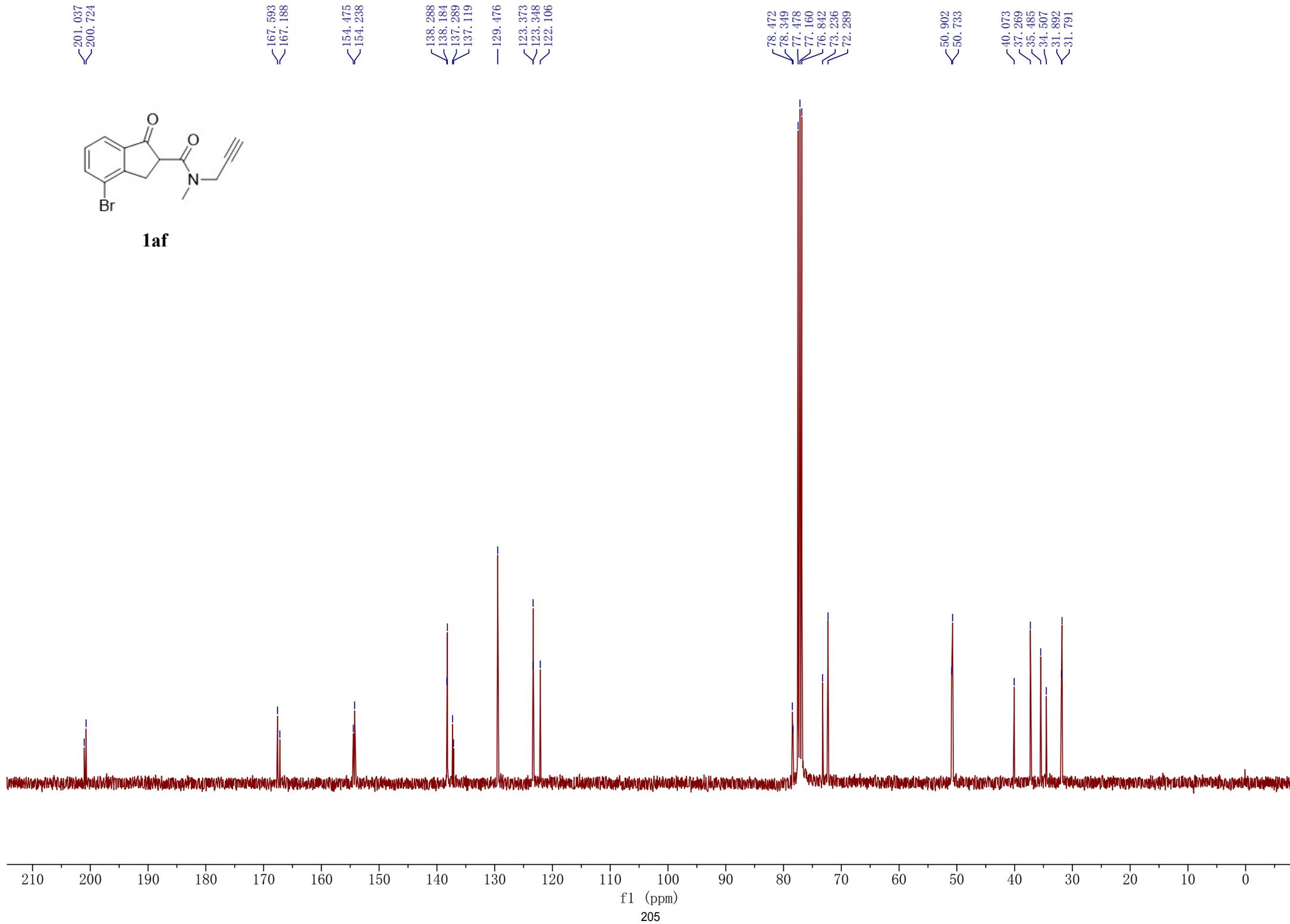


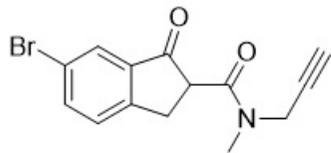
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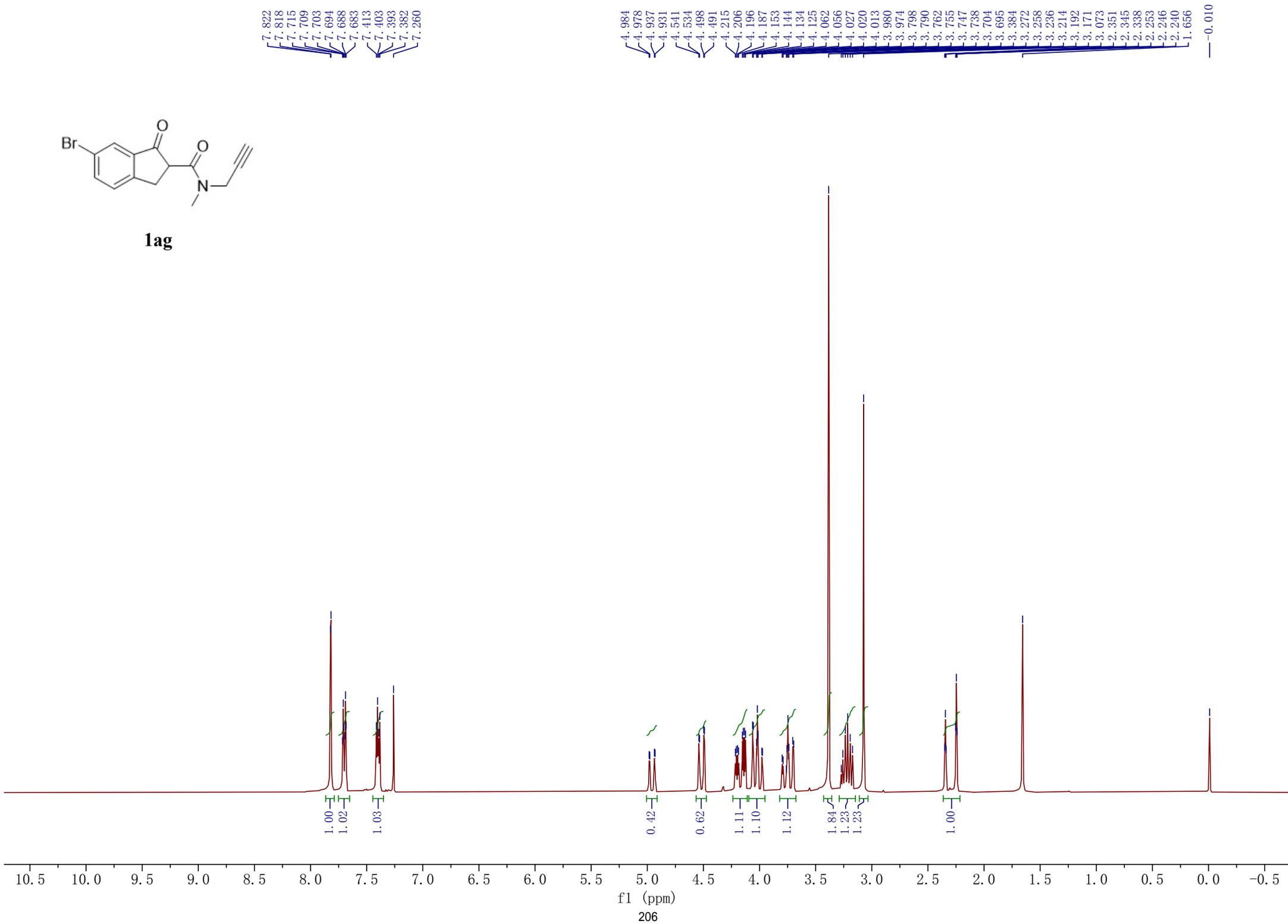


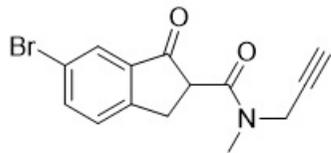
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1ag





1ag

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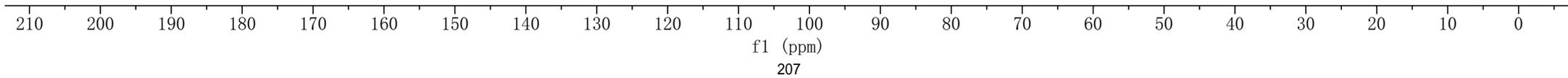
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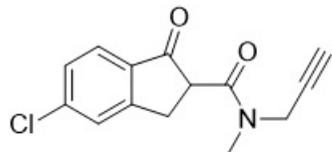
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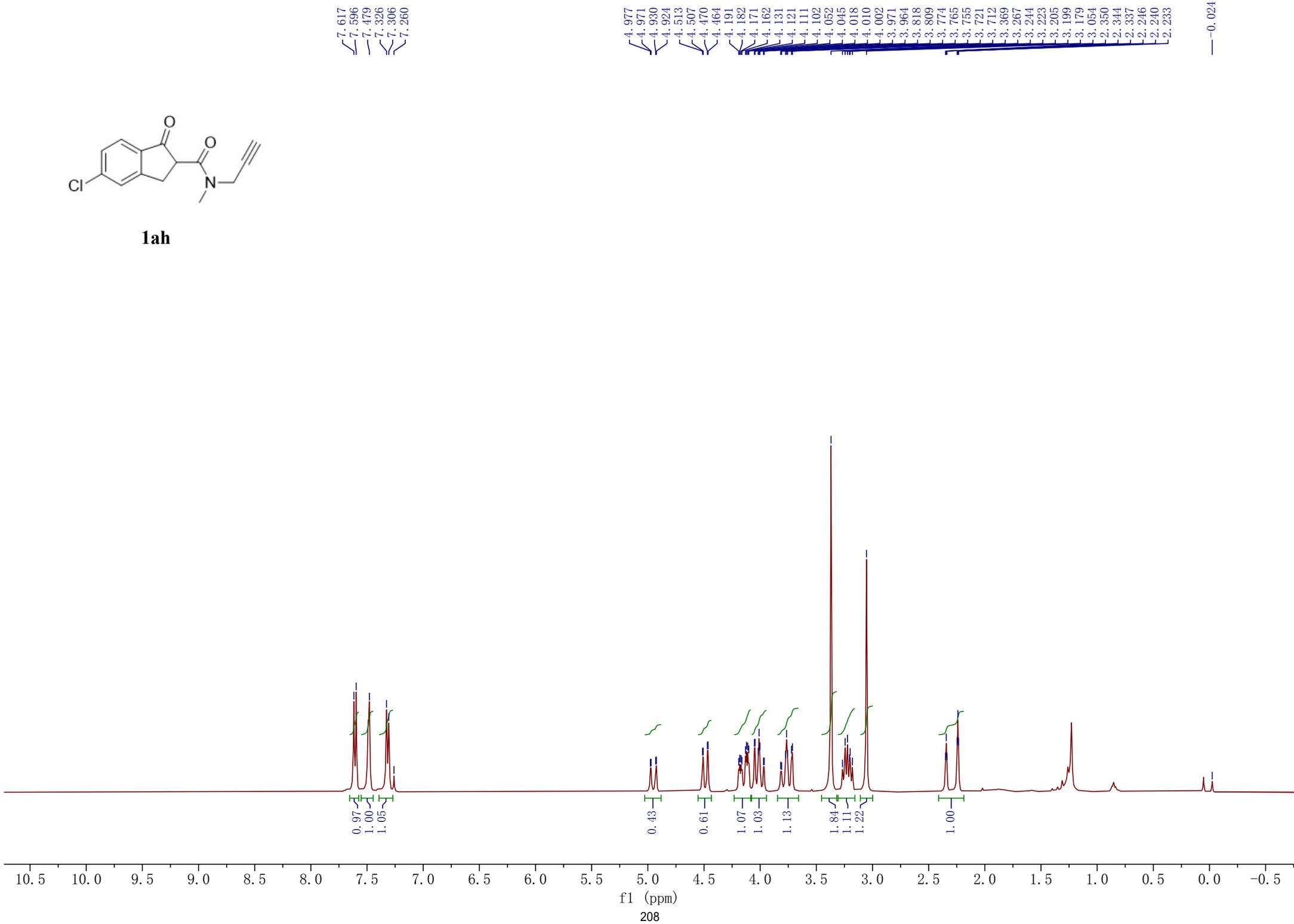
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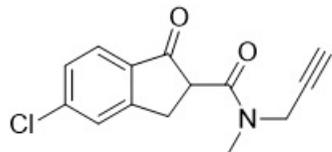
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1ah





1ah

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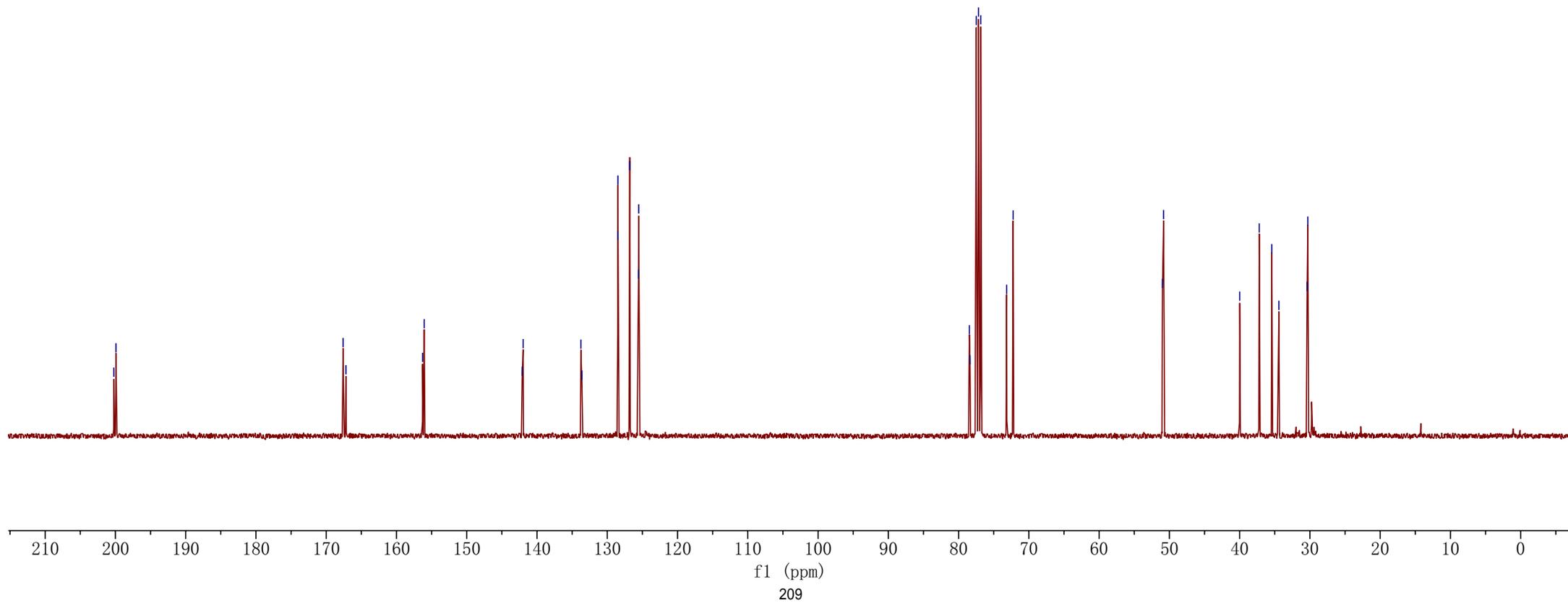
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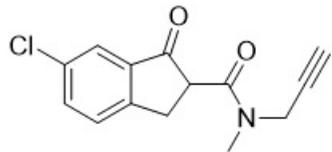
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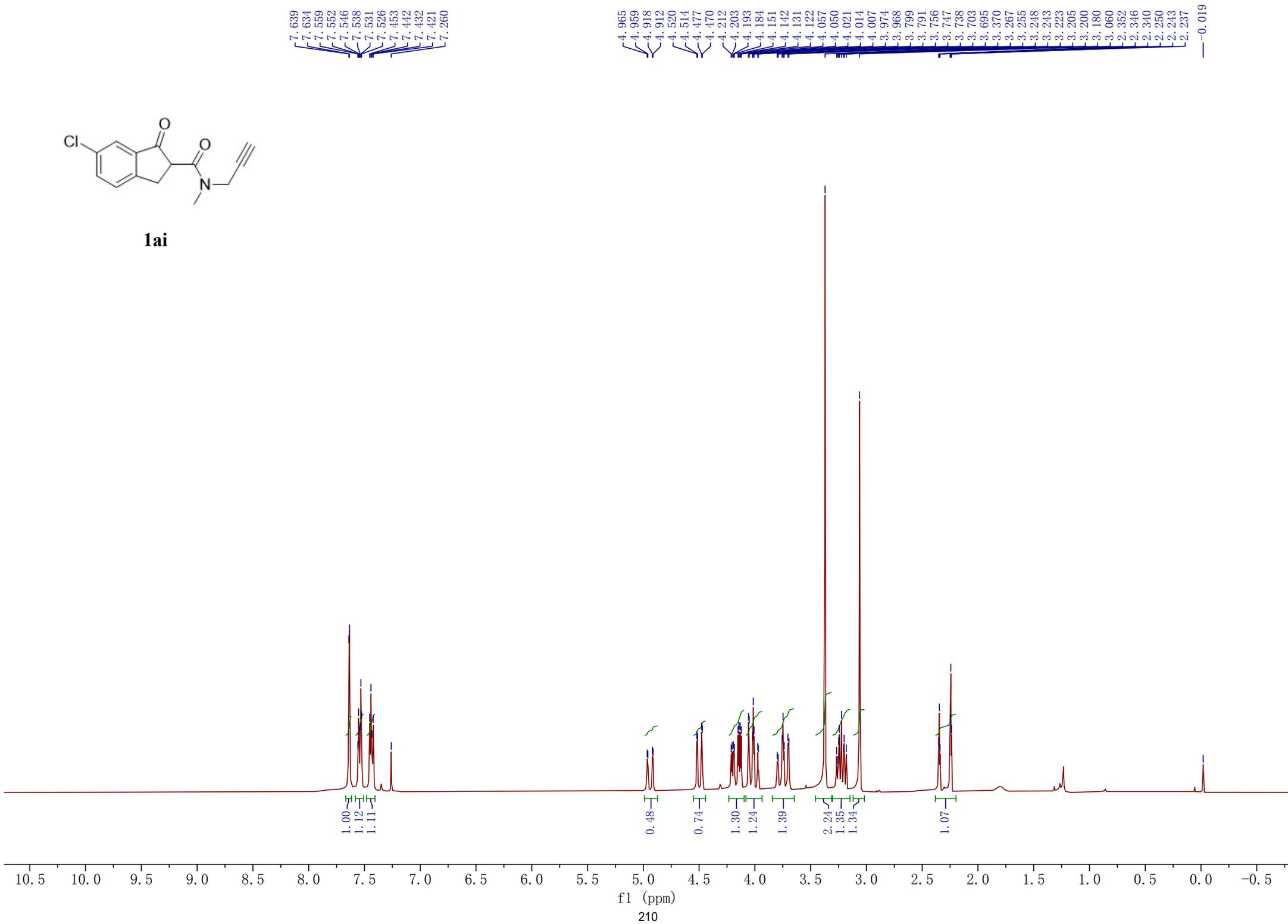
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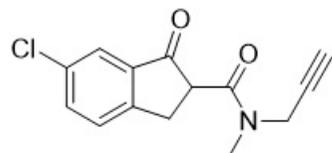
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1ai





1ai

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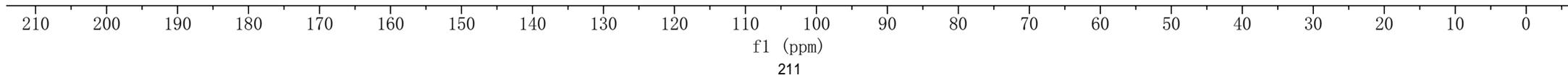
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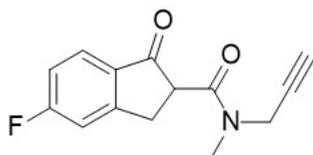
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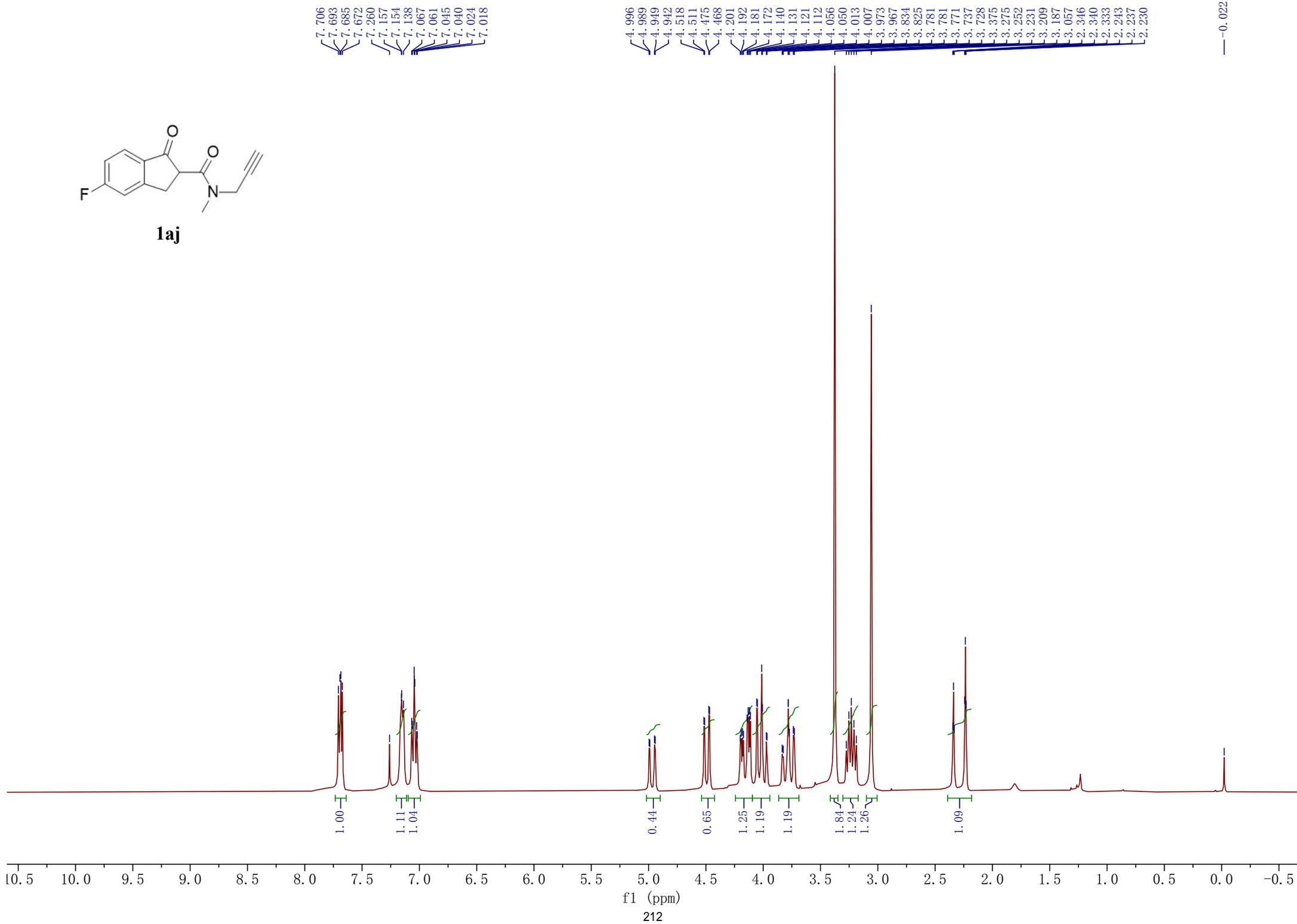
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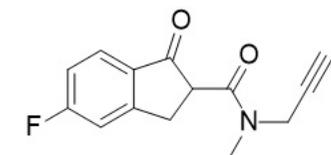
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1aj





1j

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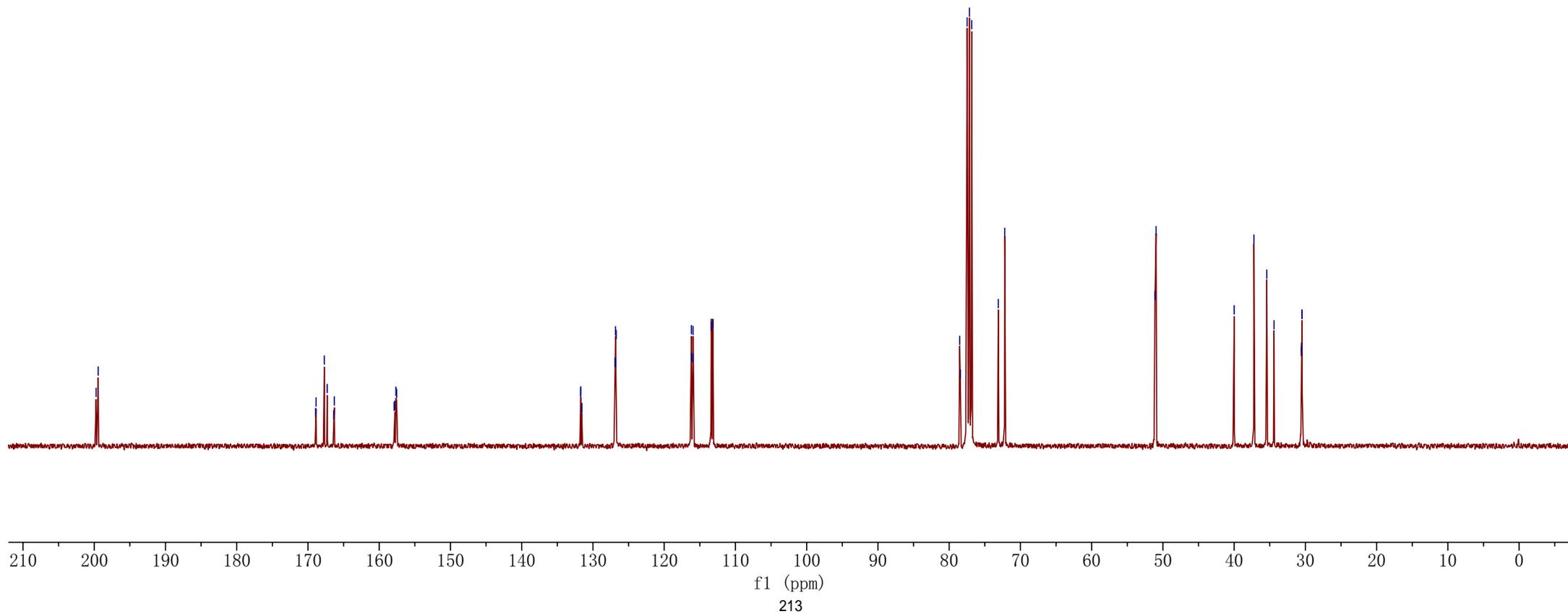
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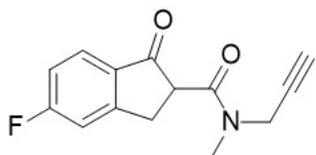
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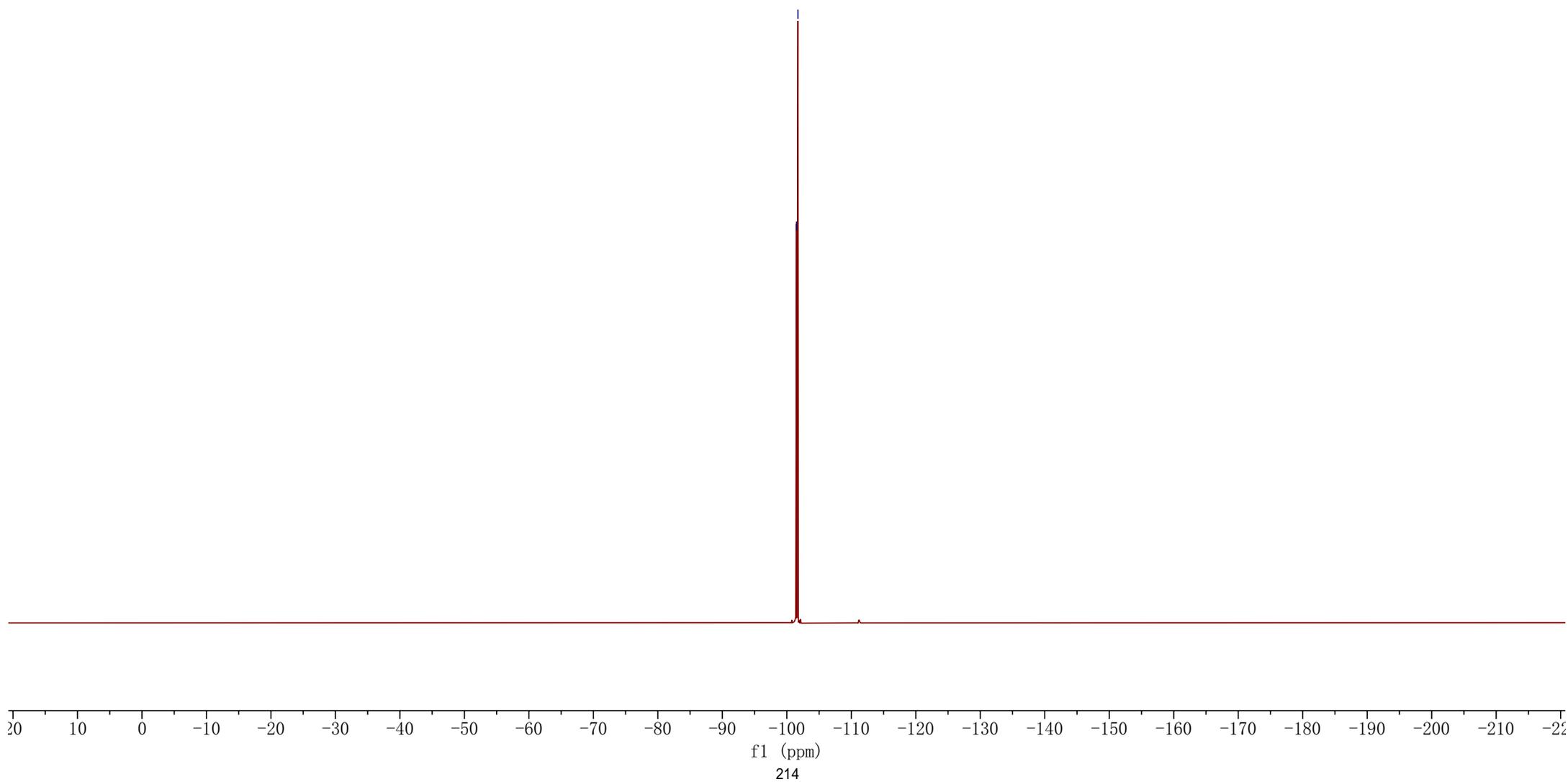
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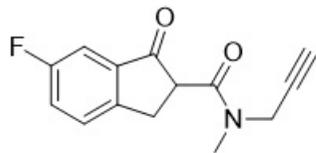




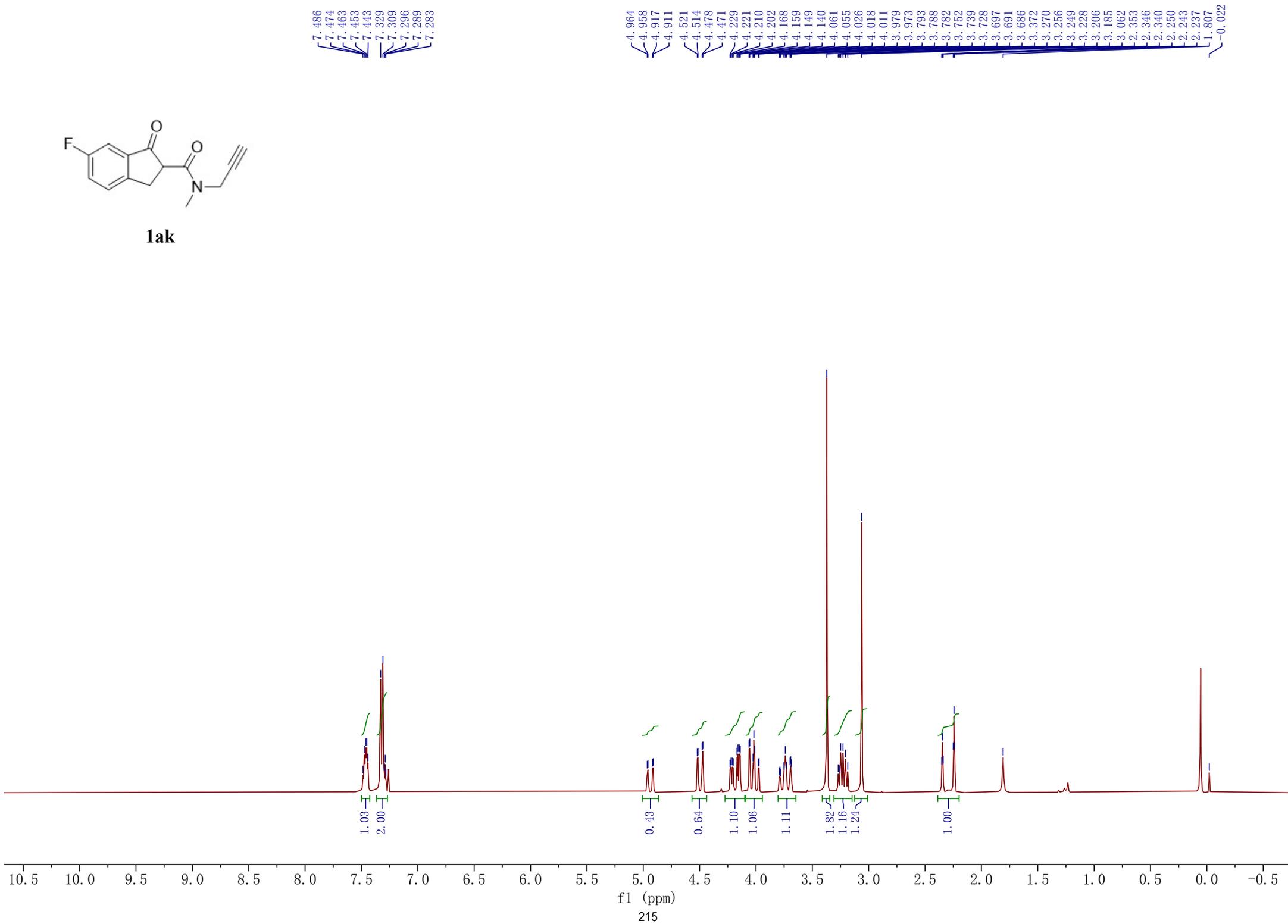
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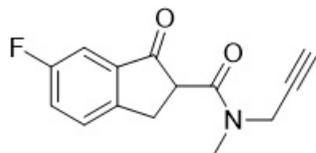
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1ak





1ak

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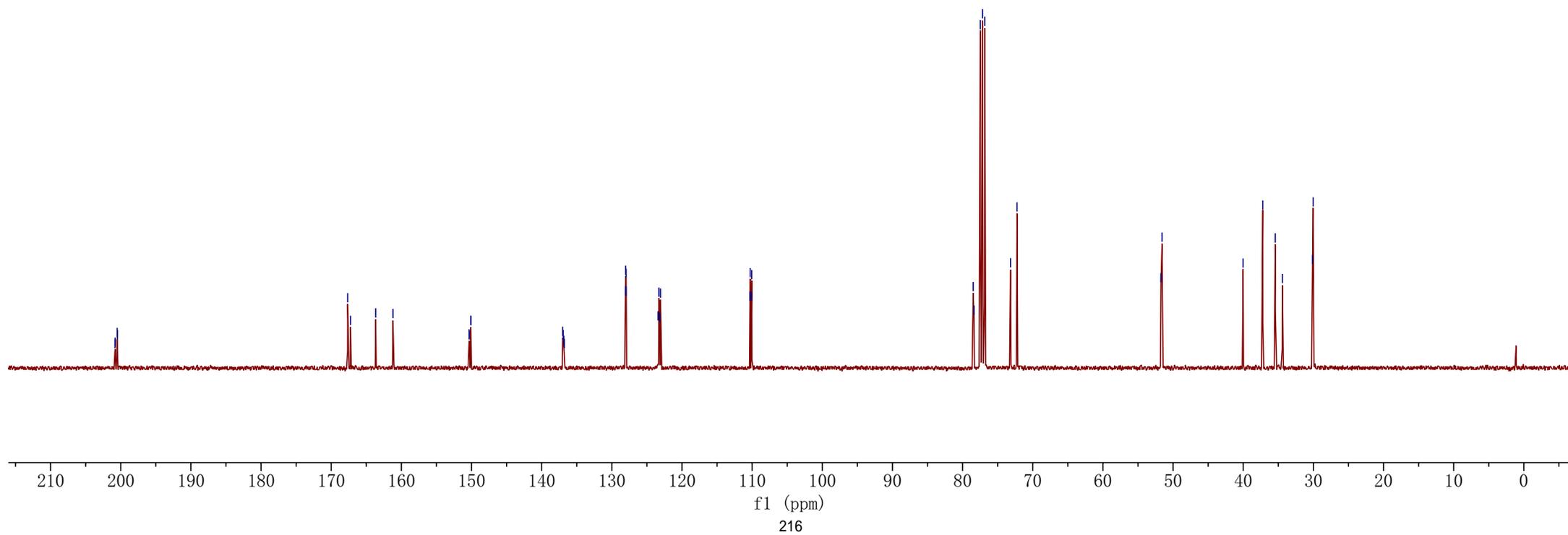
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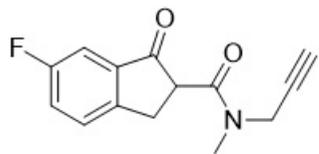
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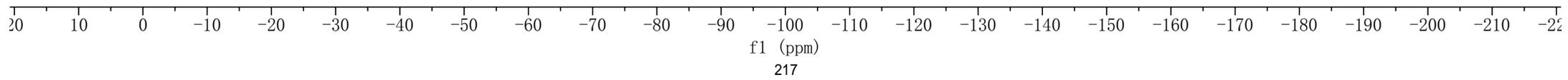
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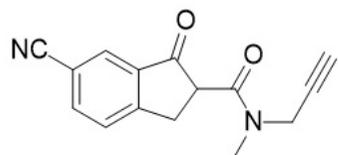




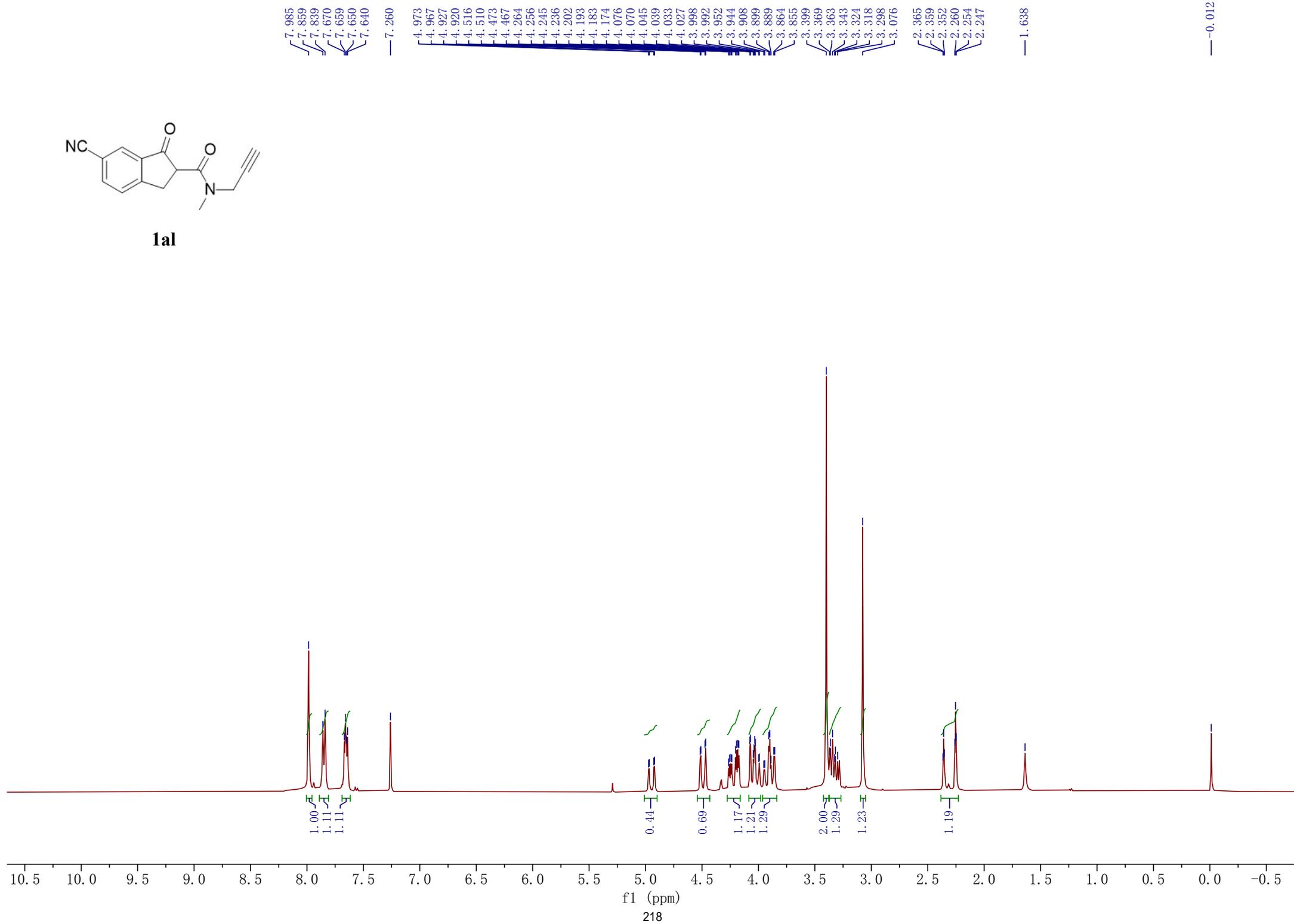
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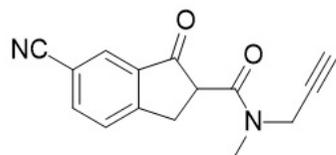
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1al





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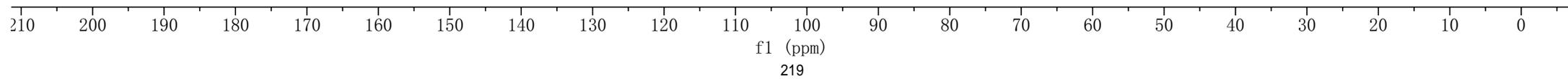
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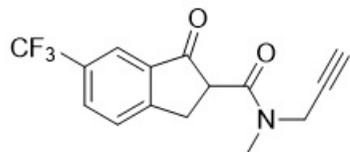
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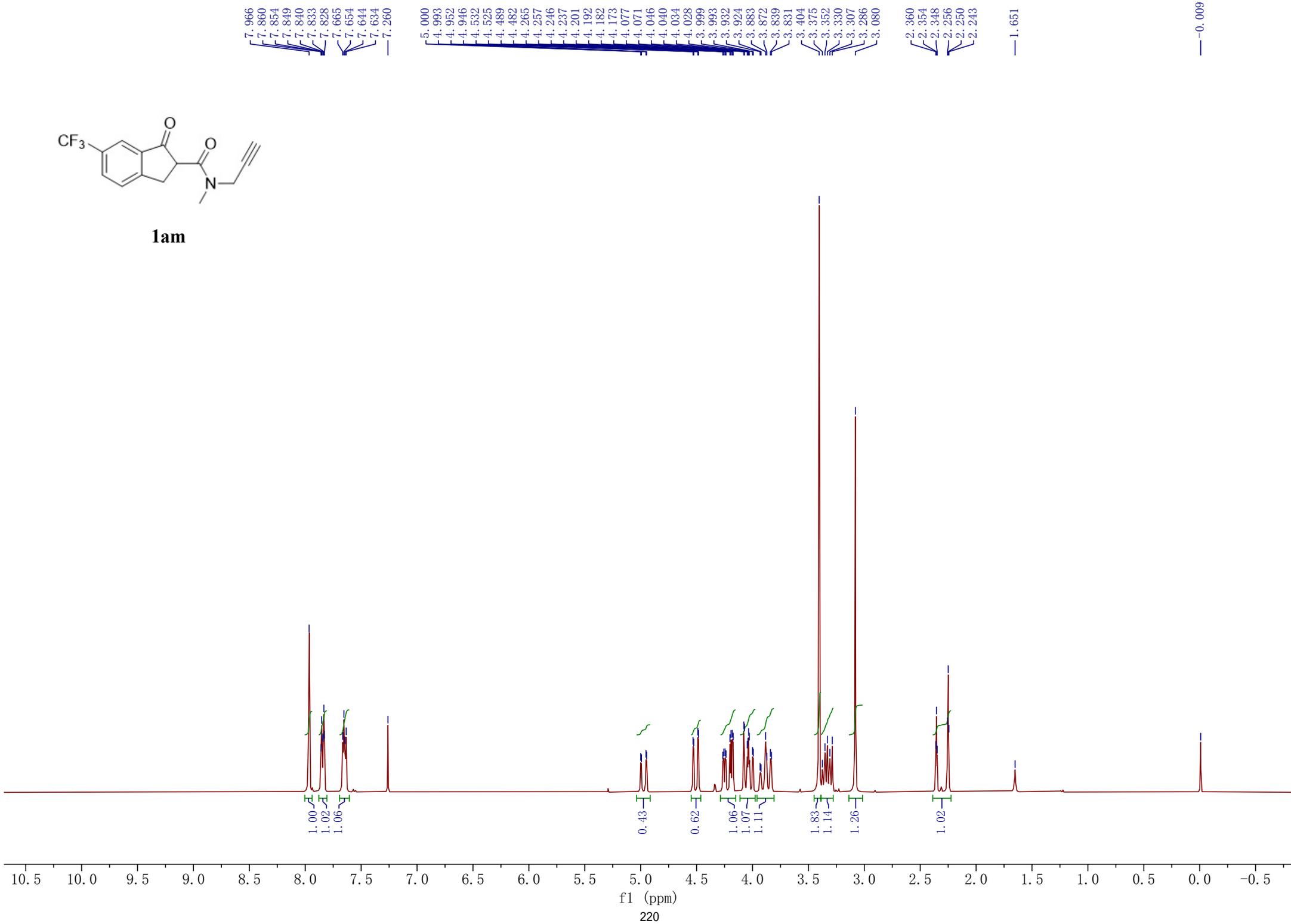
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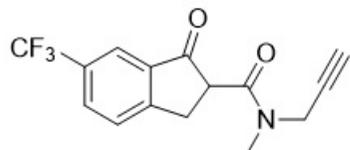
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1am

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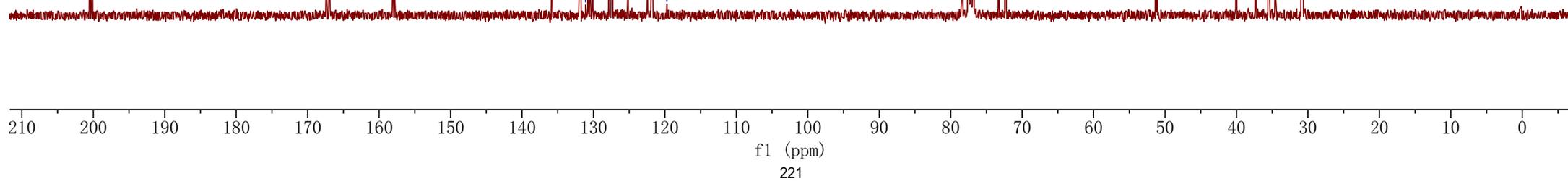
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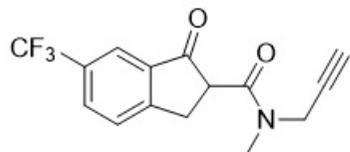
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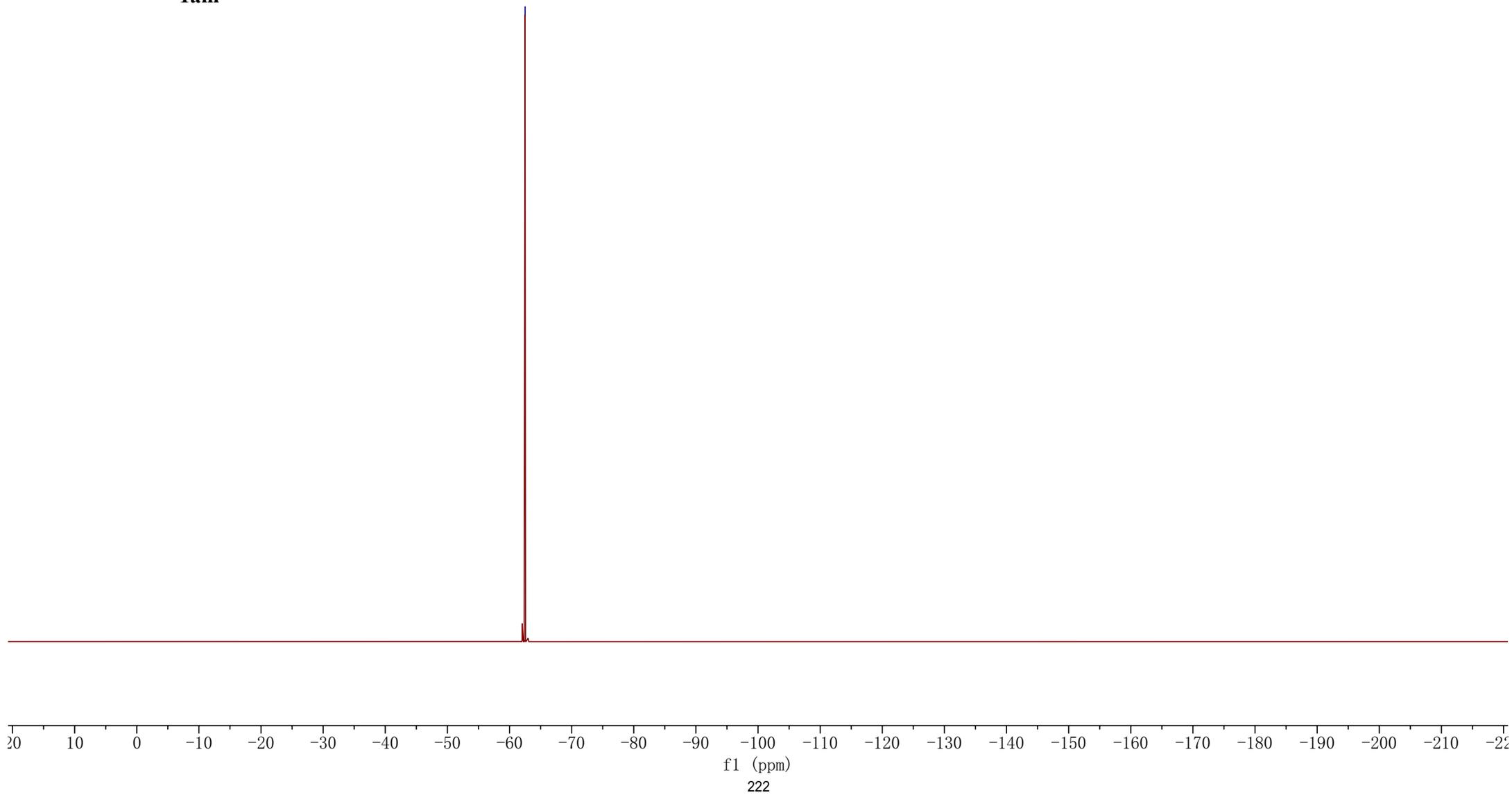
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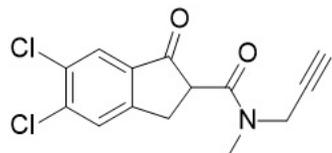




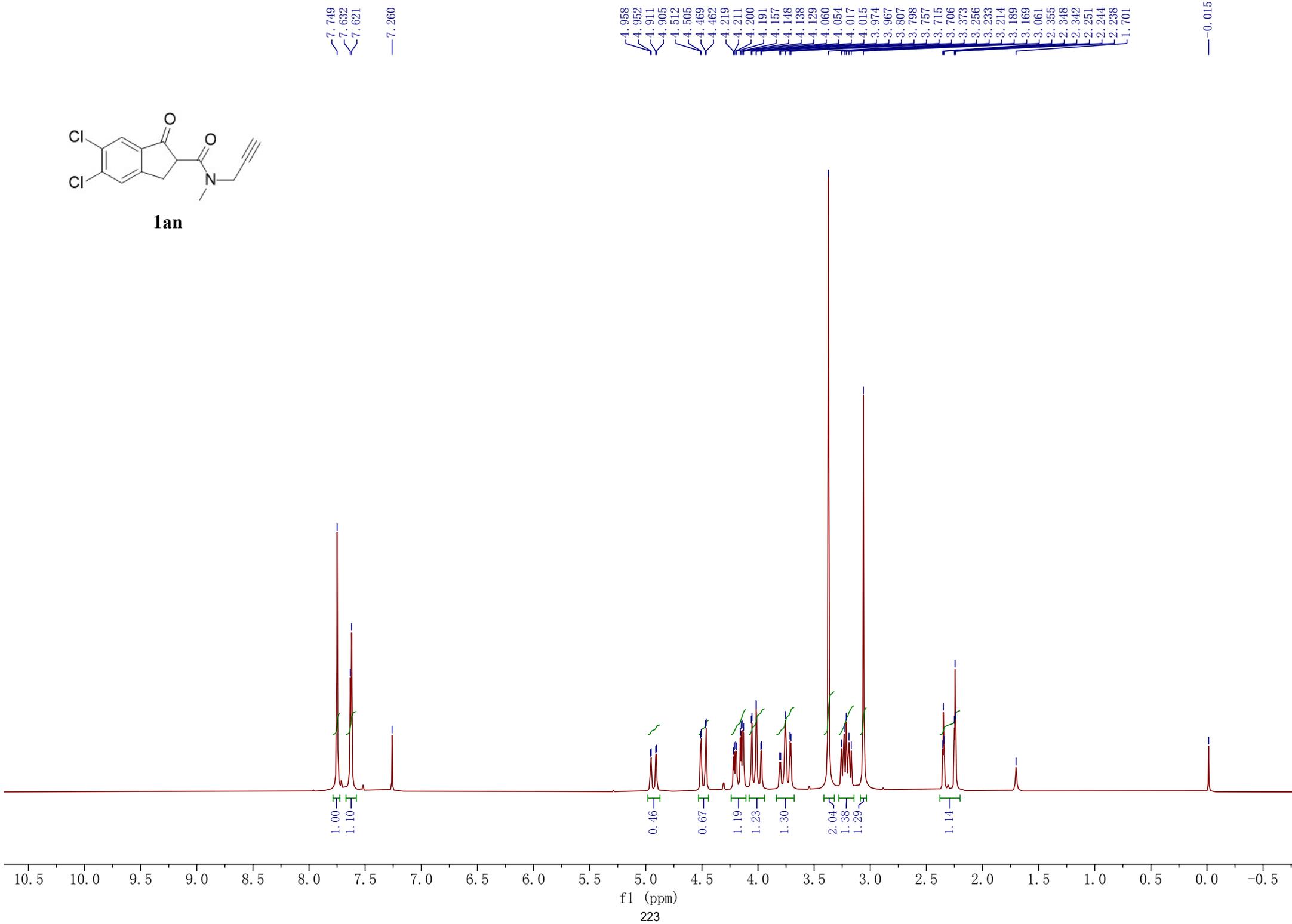
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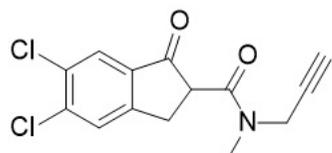
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1an

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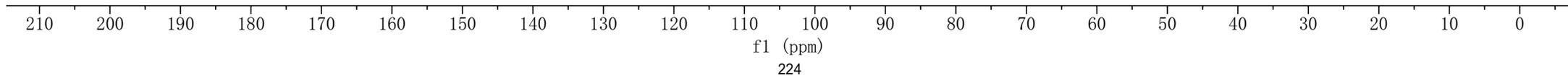
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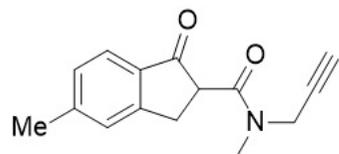
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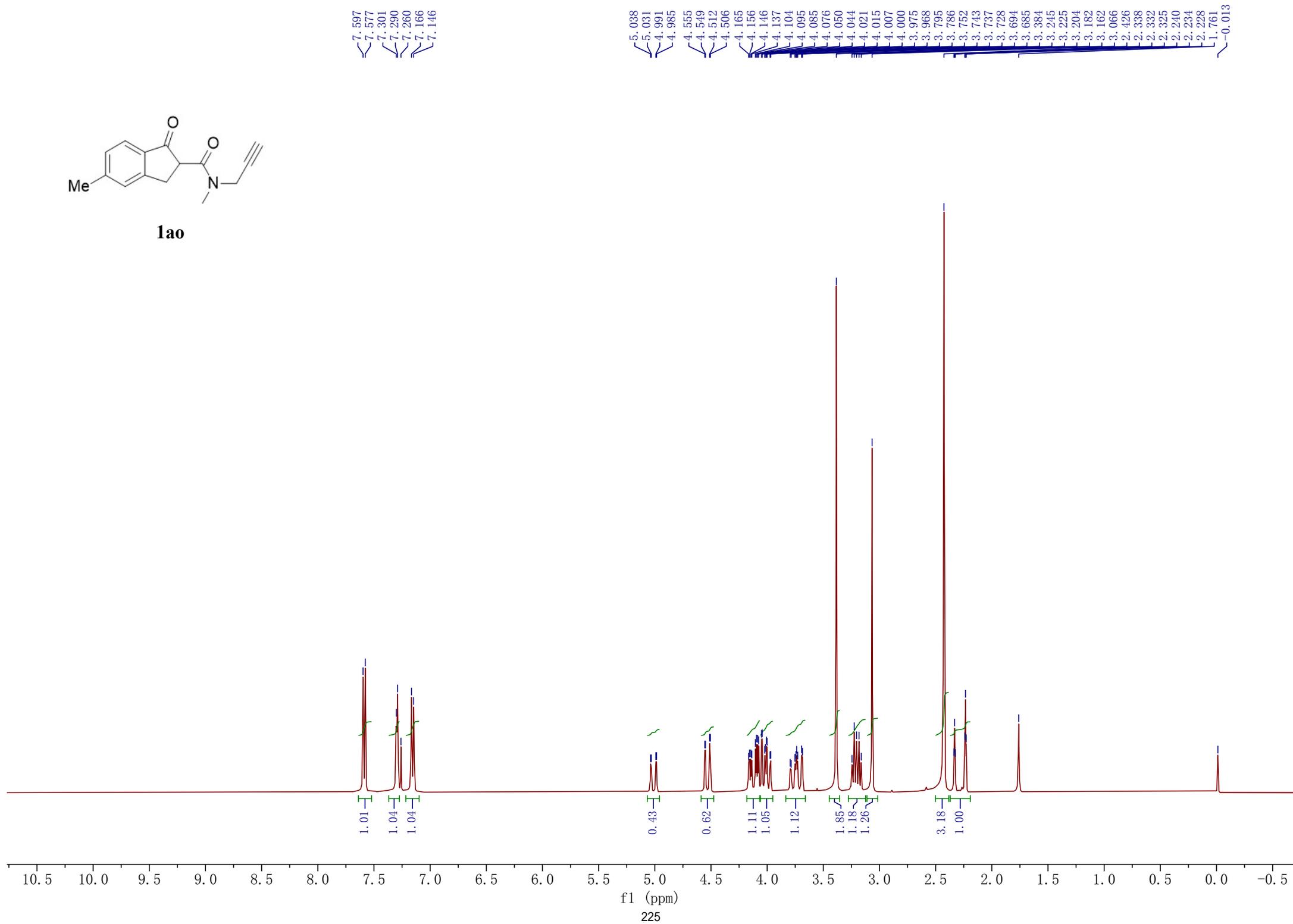
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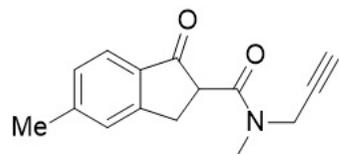
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1ao





1ao

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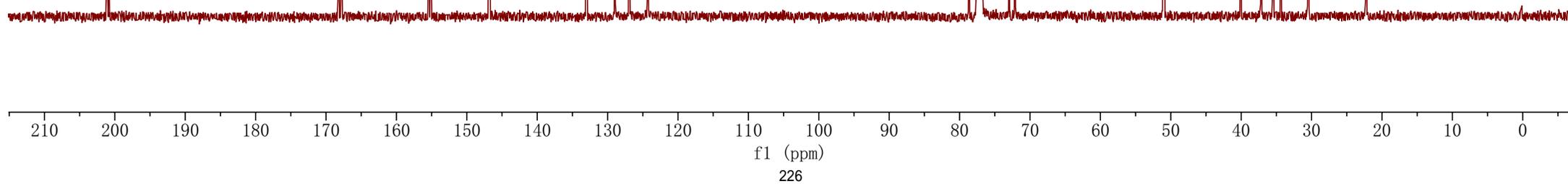
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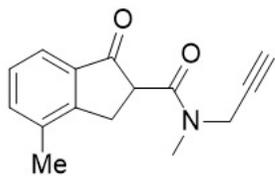
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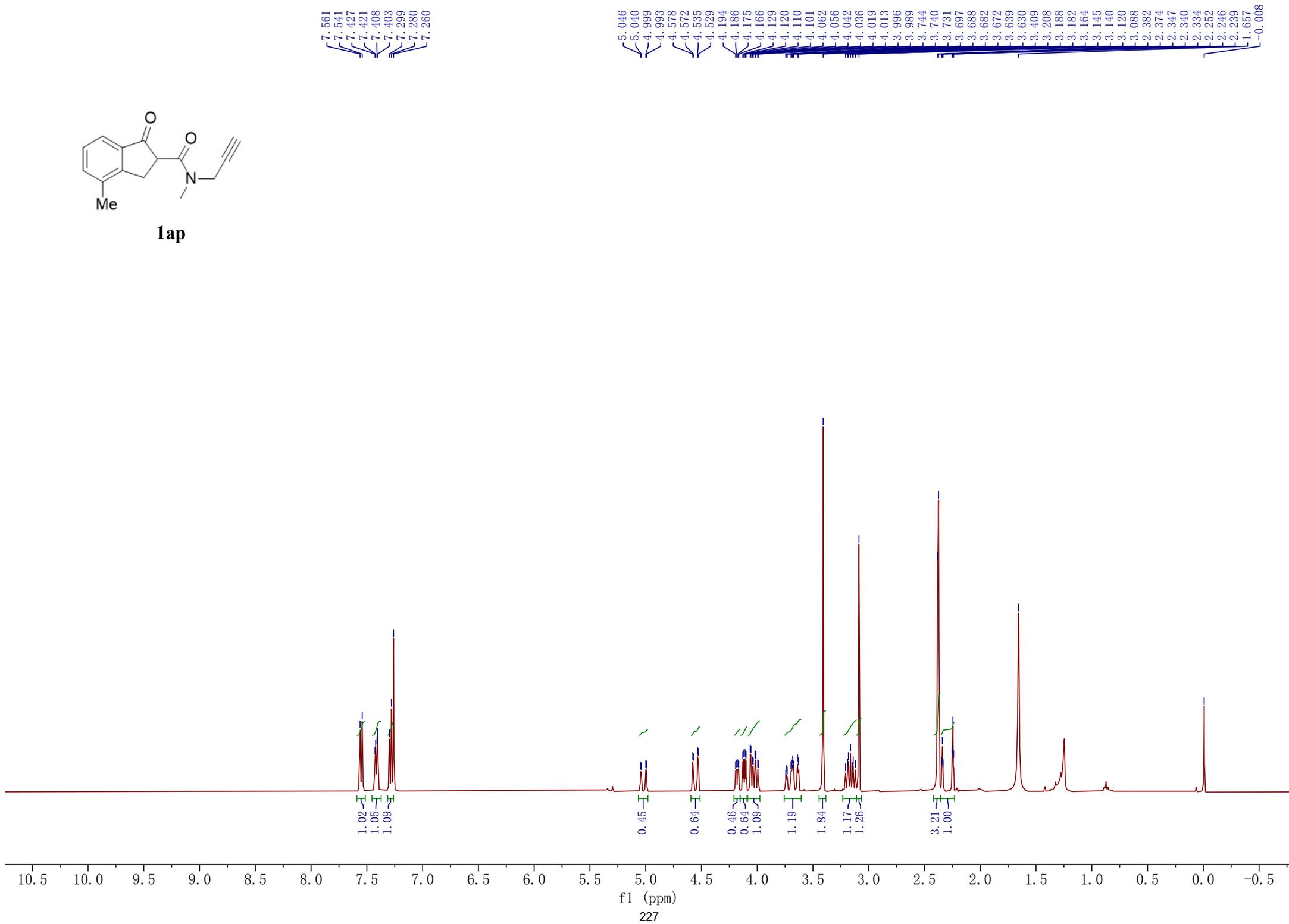
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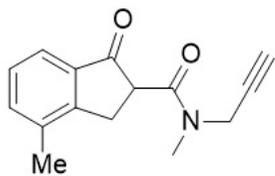
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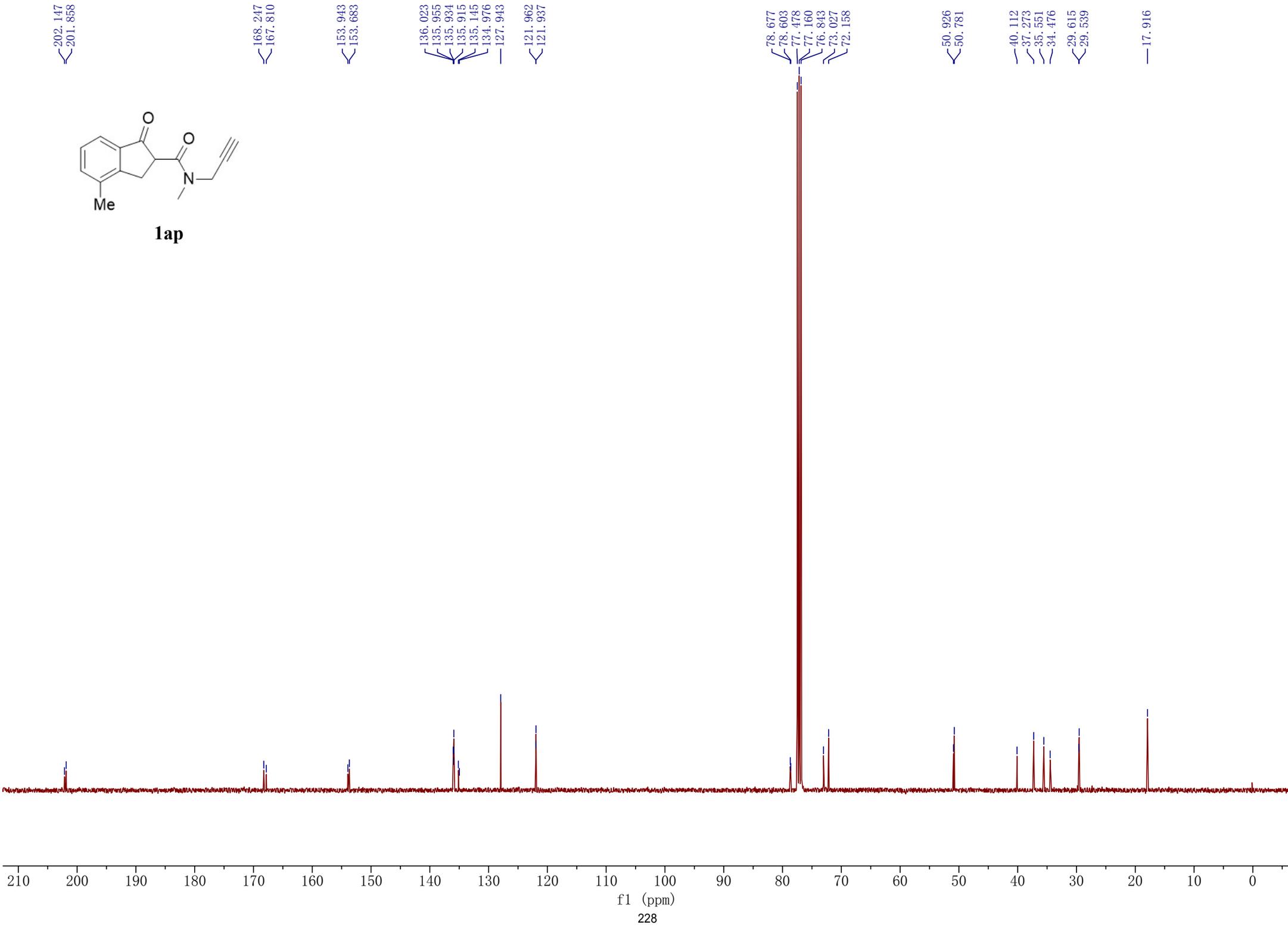


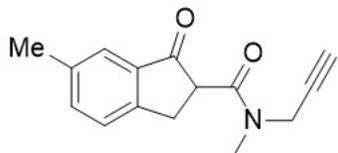
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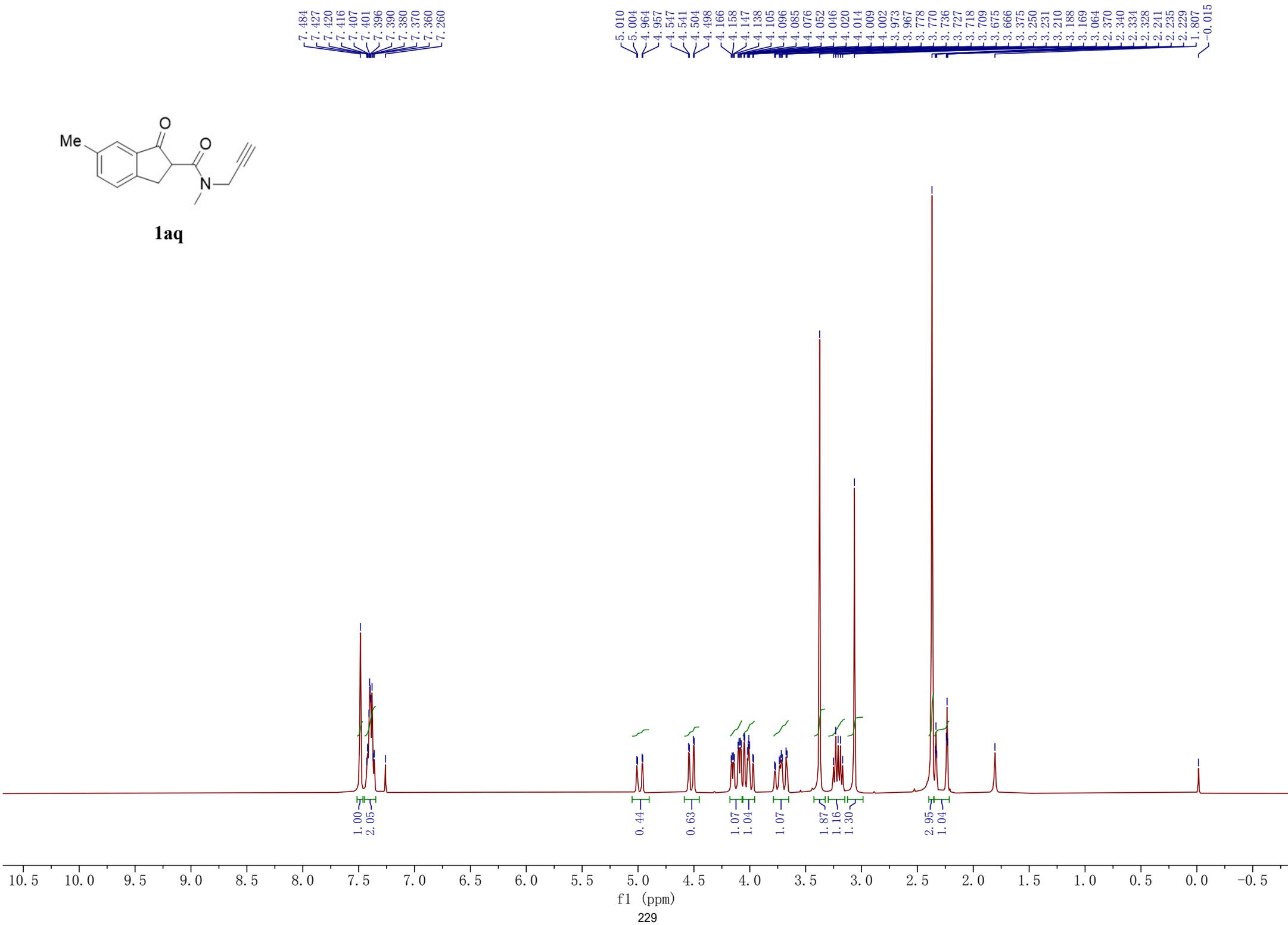


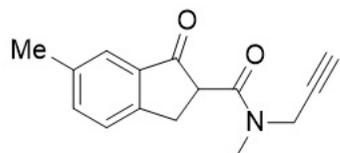
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1aq





1aq

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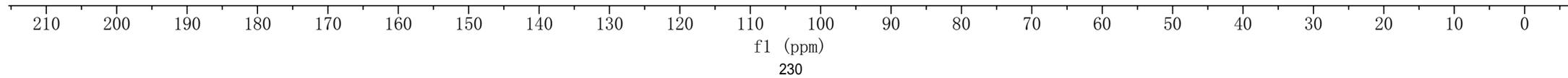
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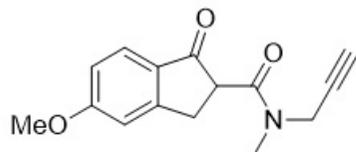
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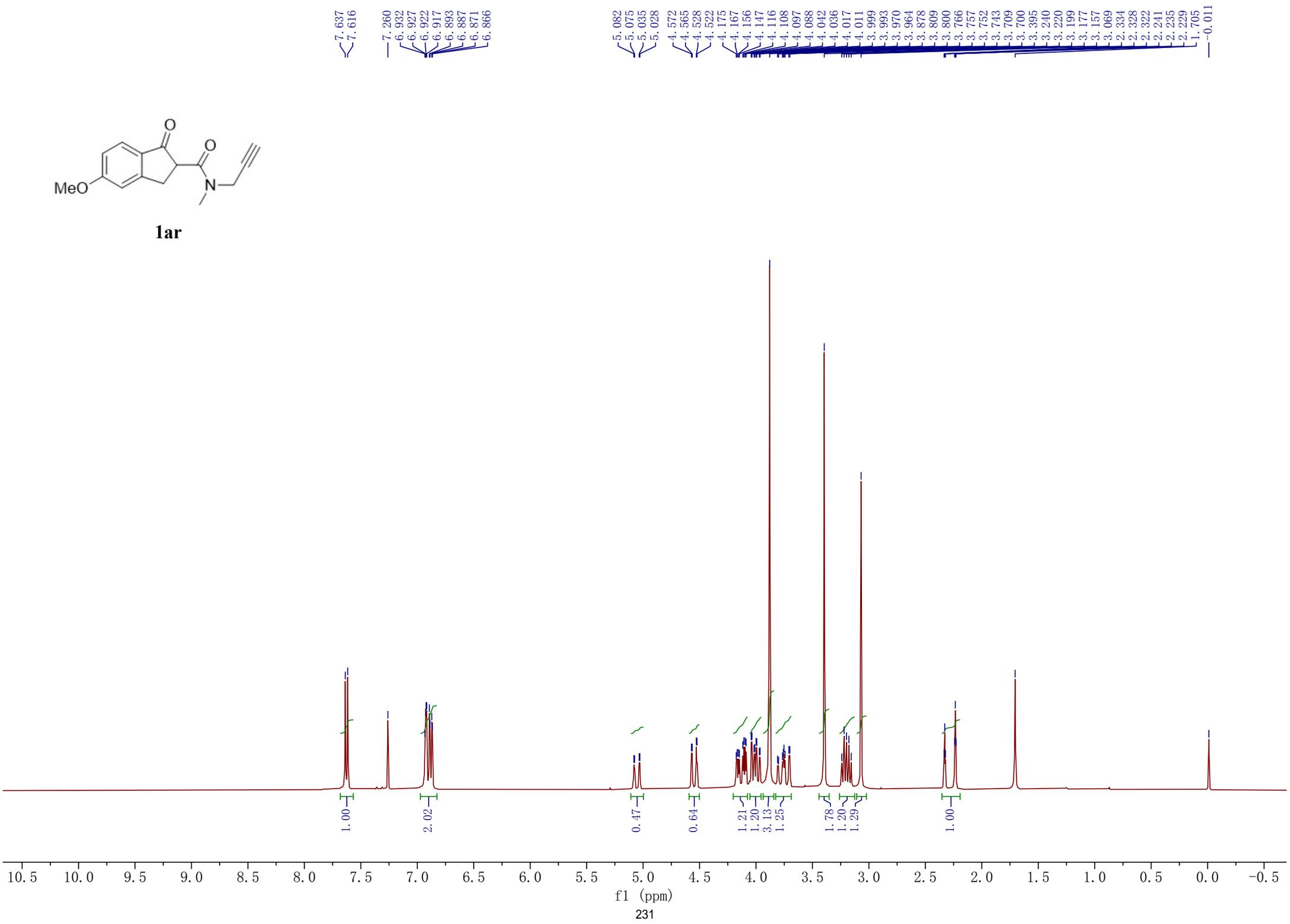
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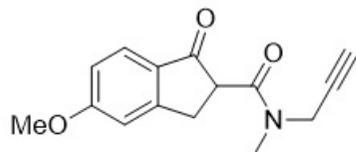
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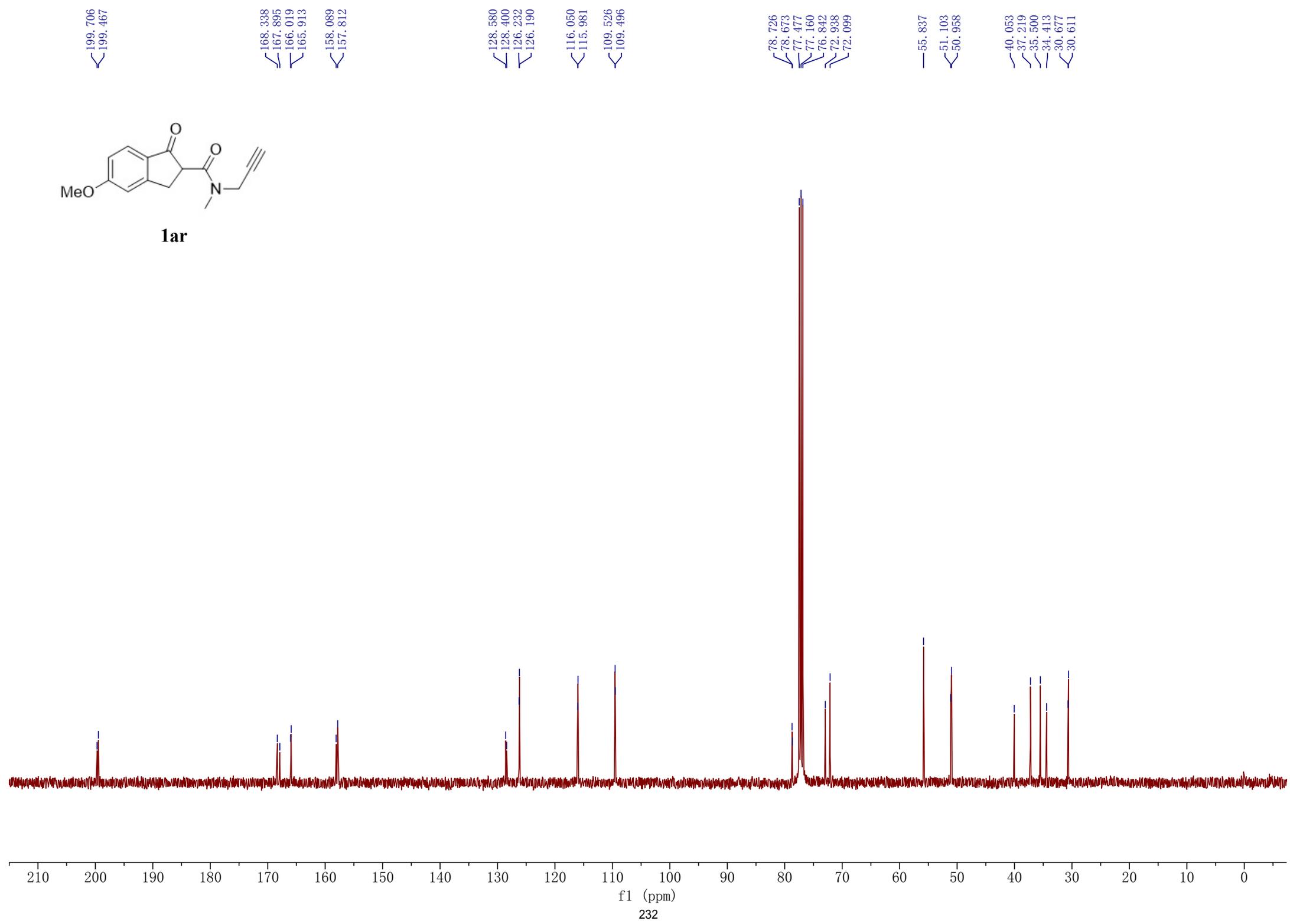


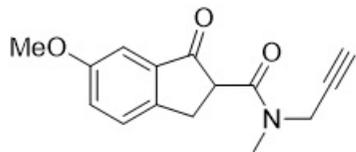
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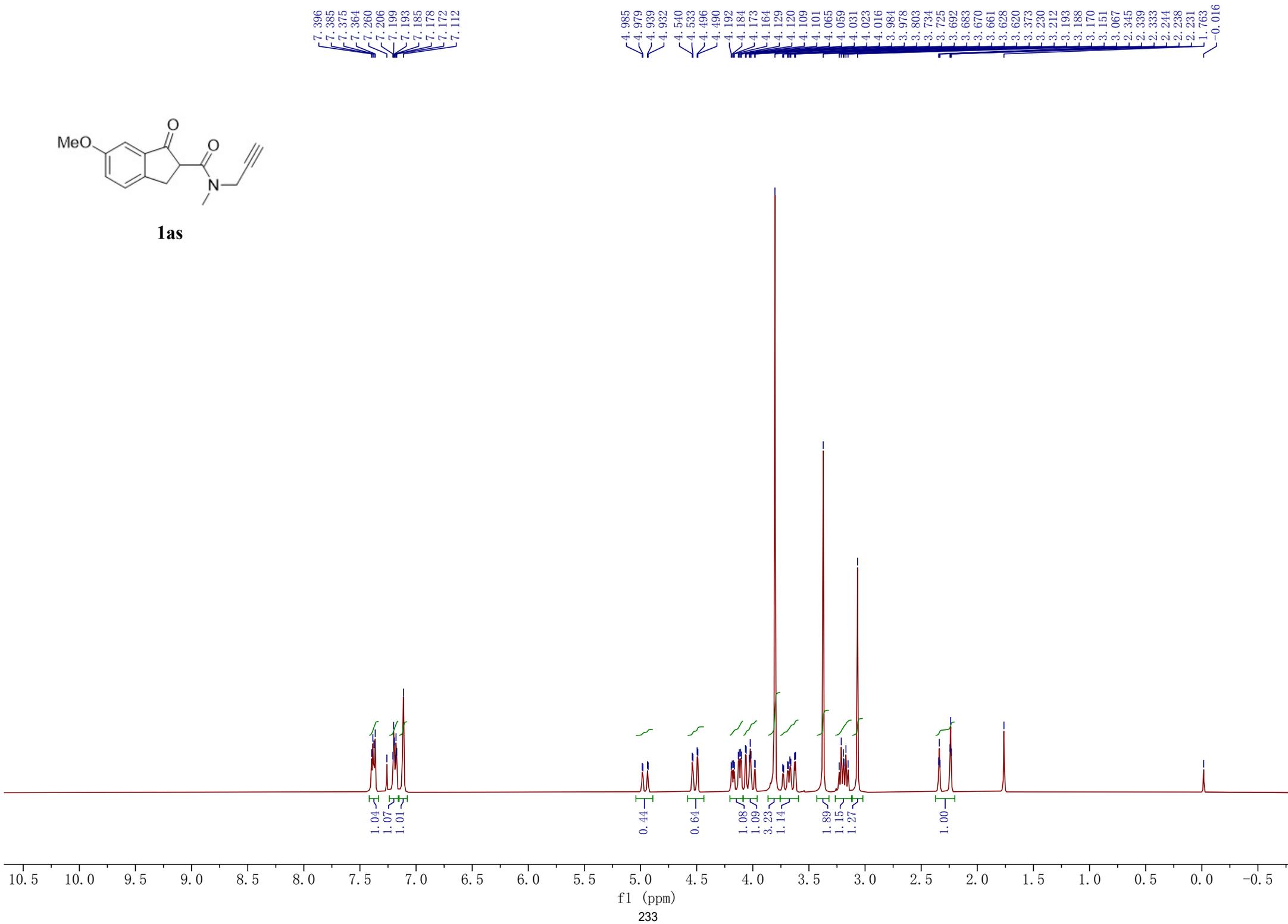


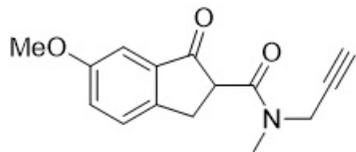
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1as





1as

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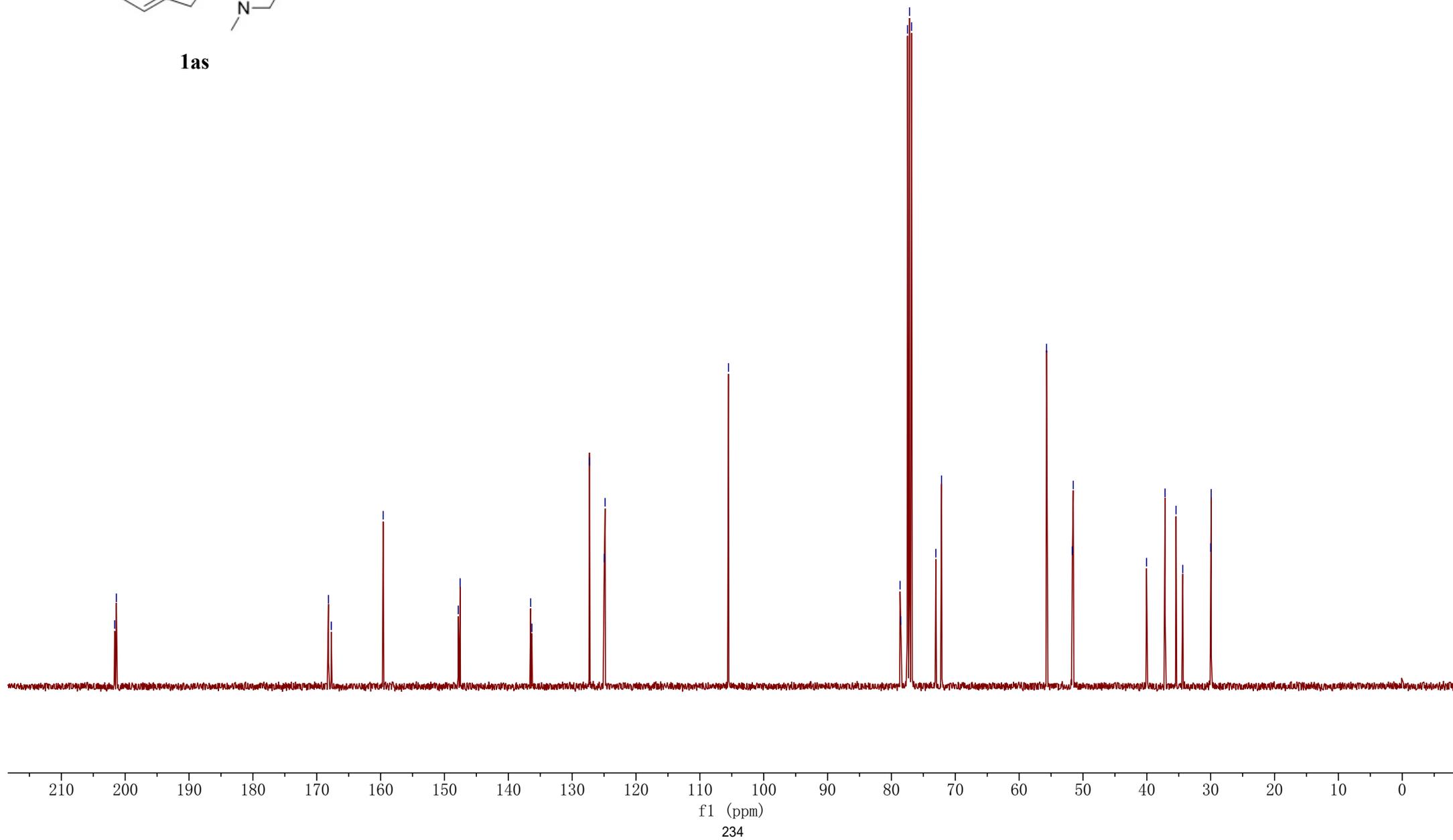
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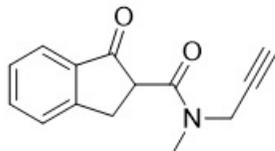
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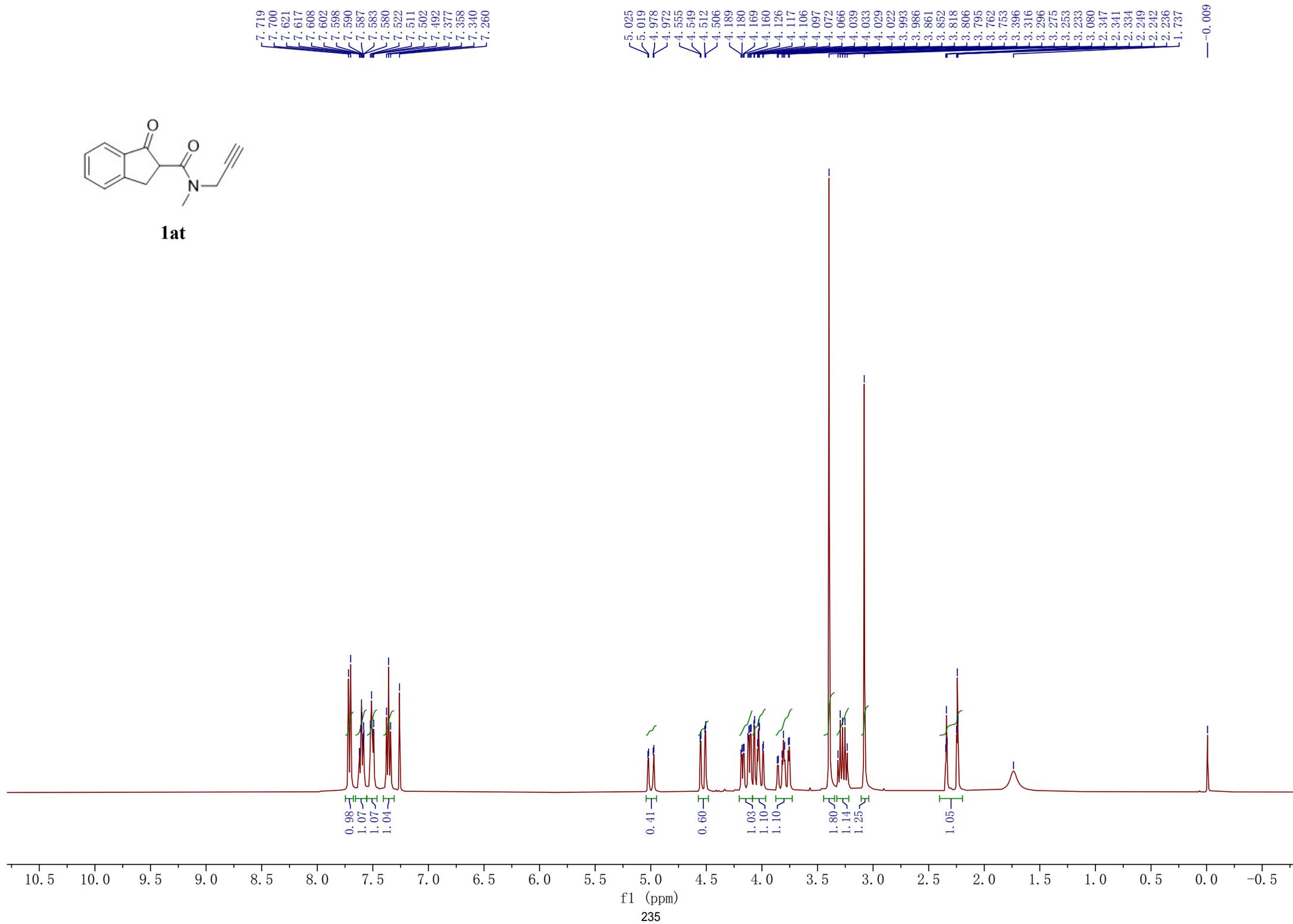
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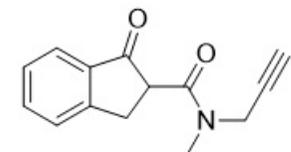
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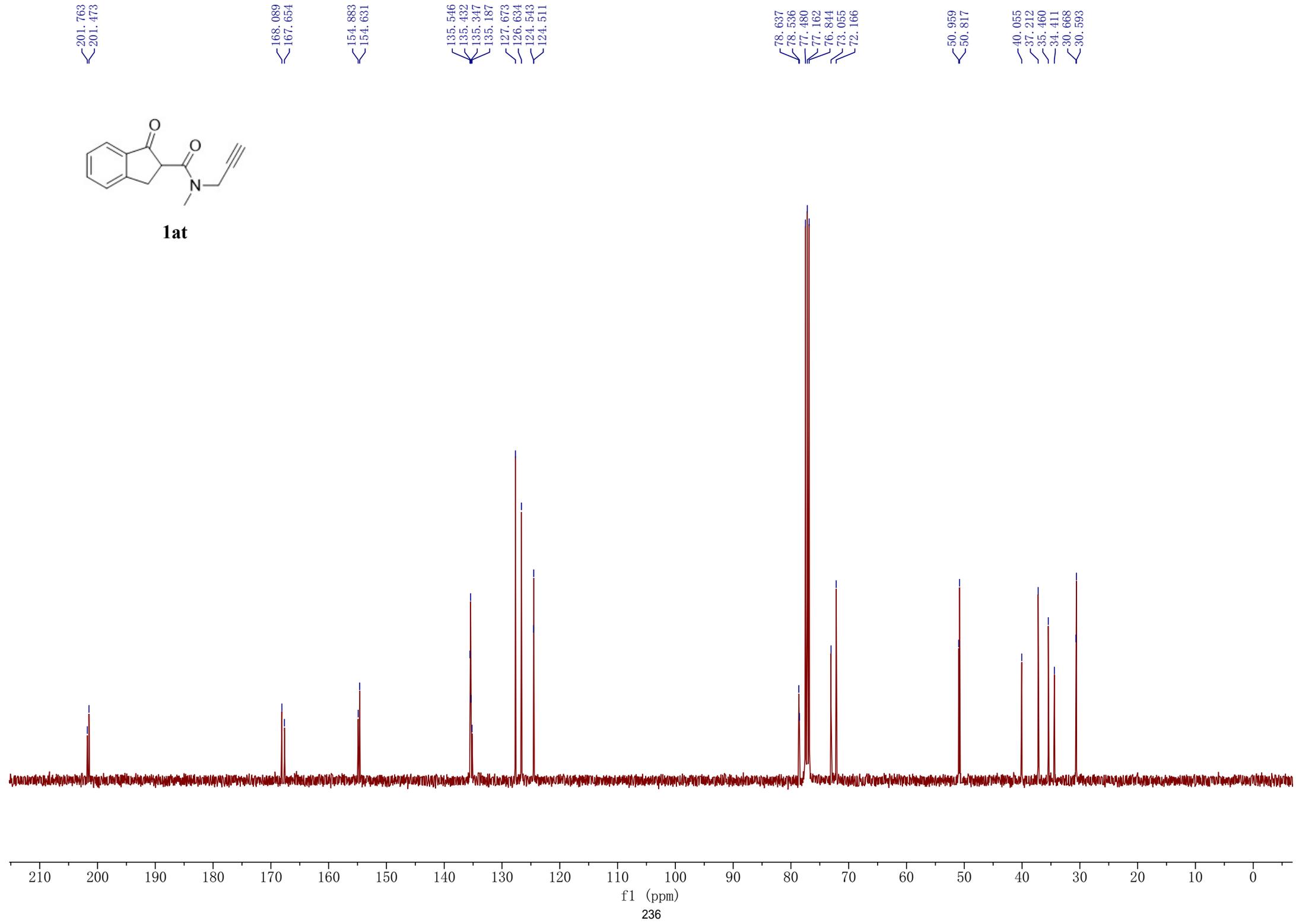


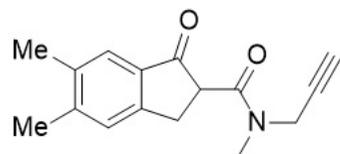
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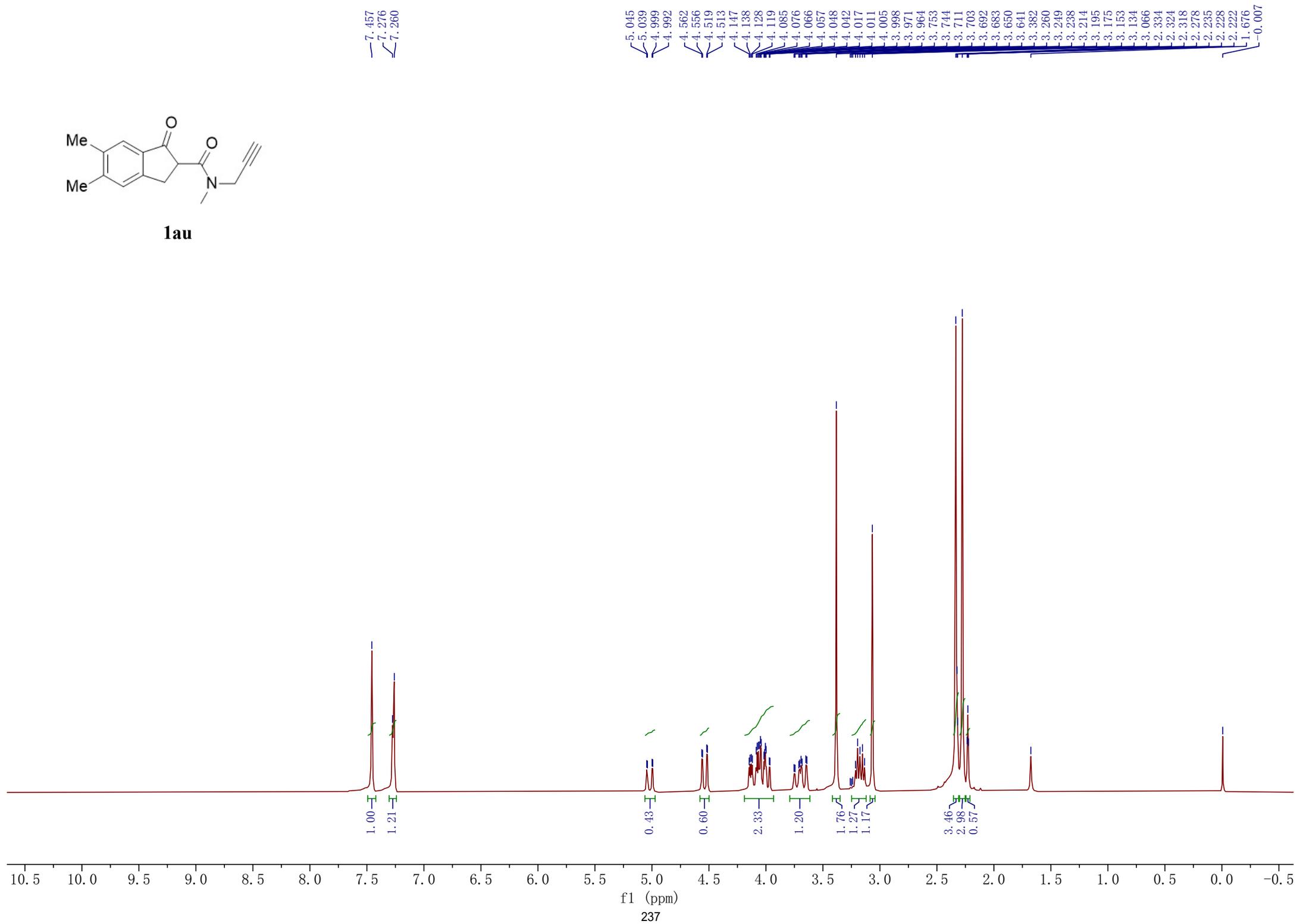


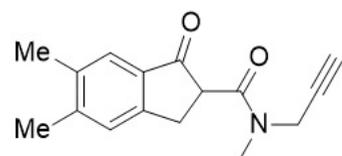
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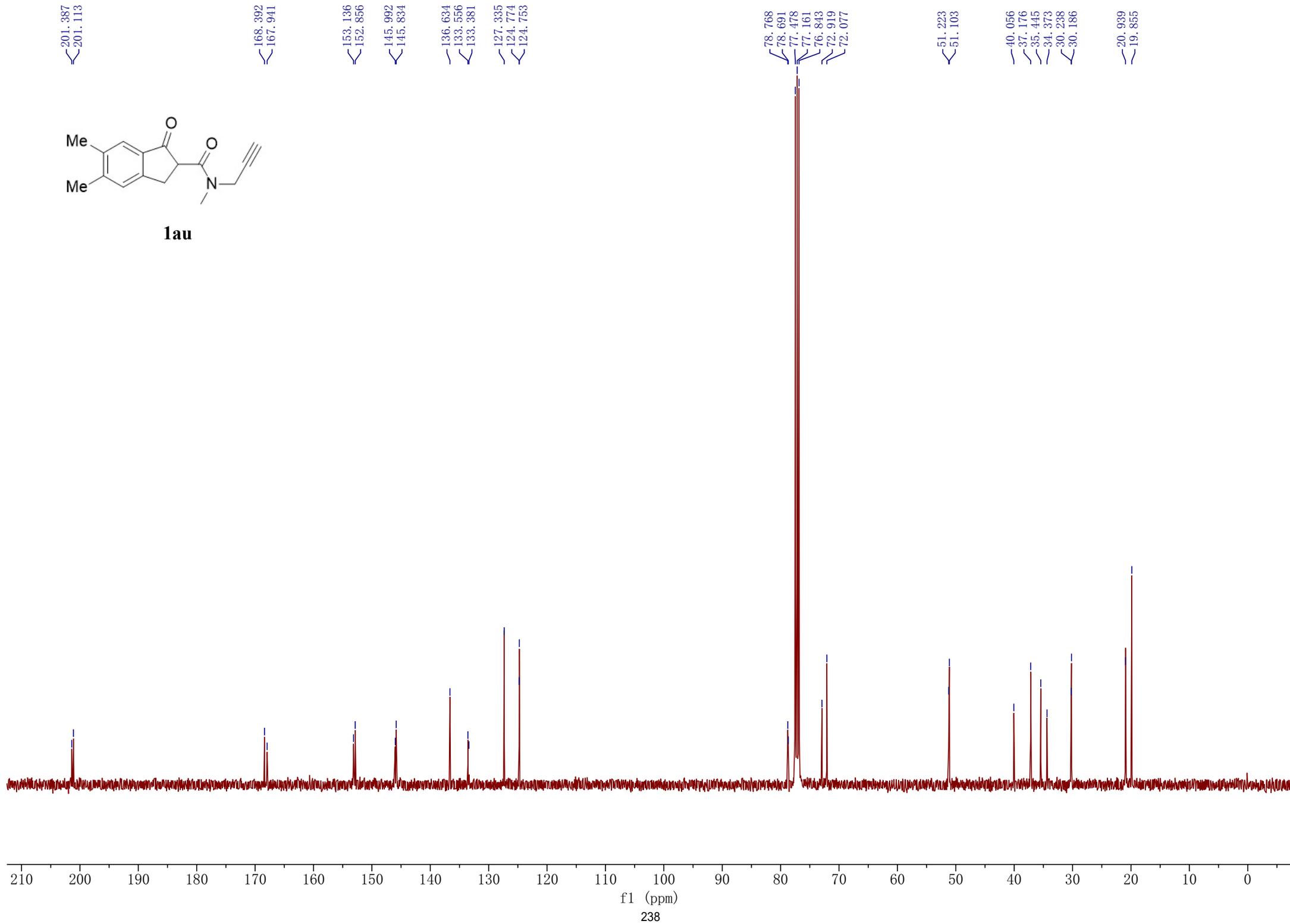


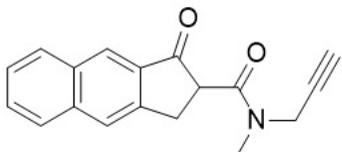
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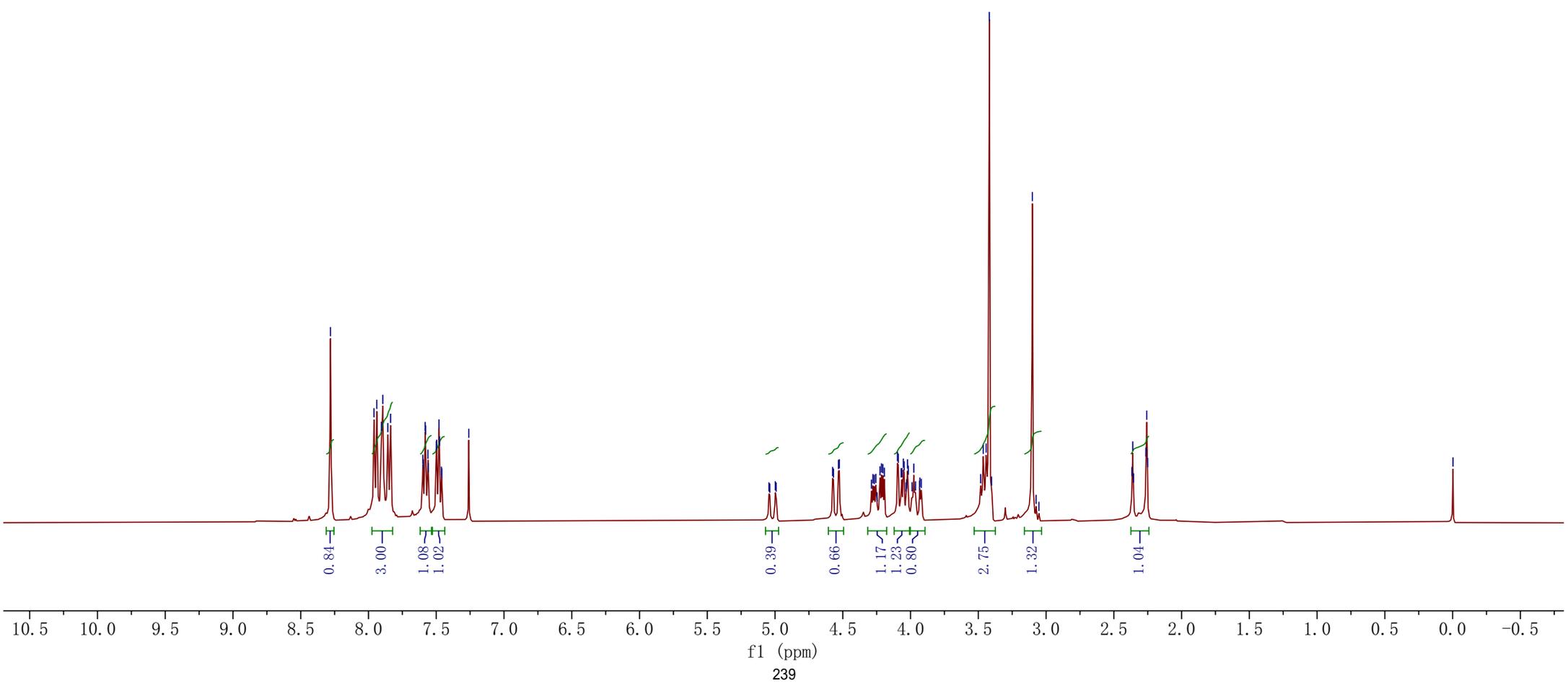


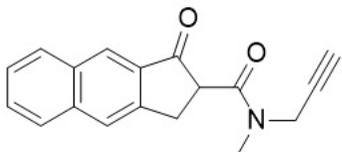


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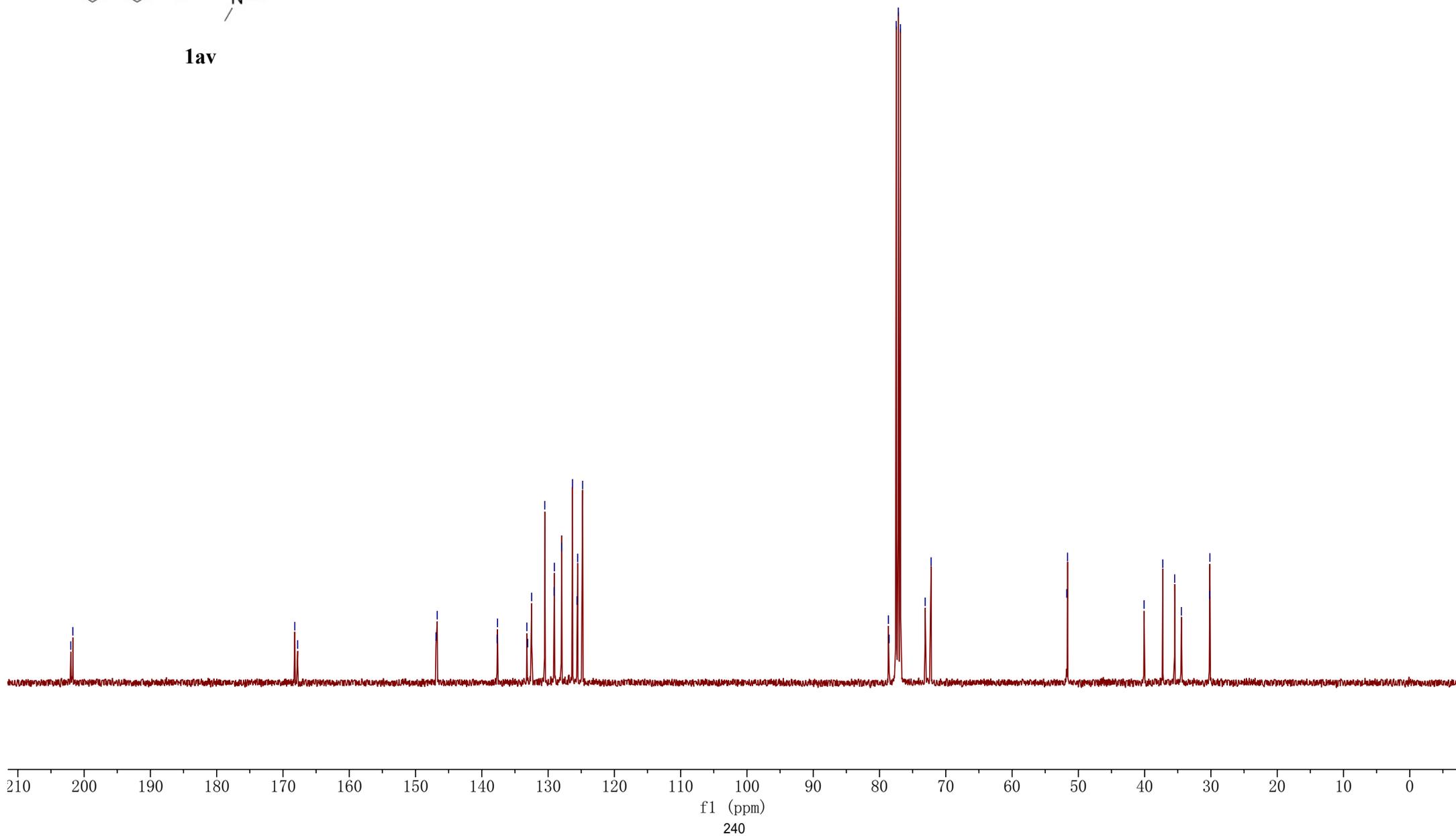
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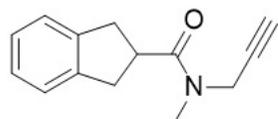
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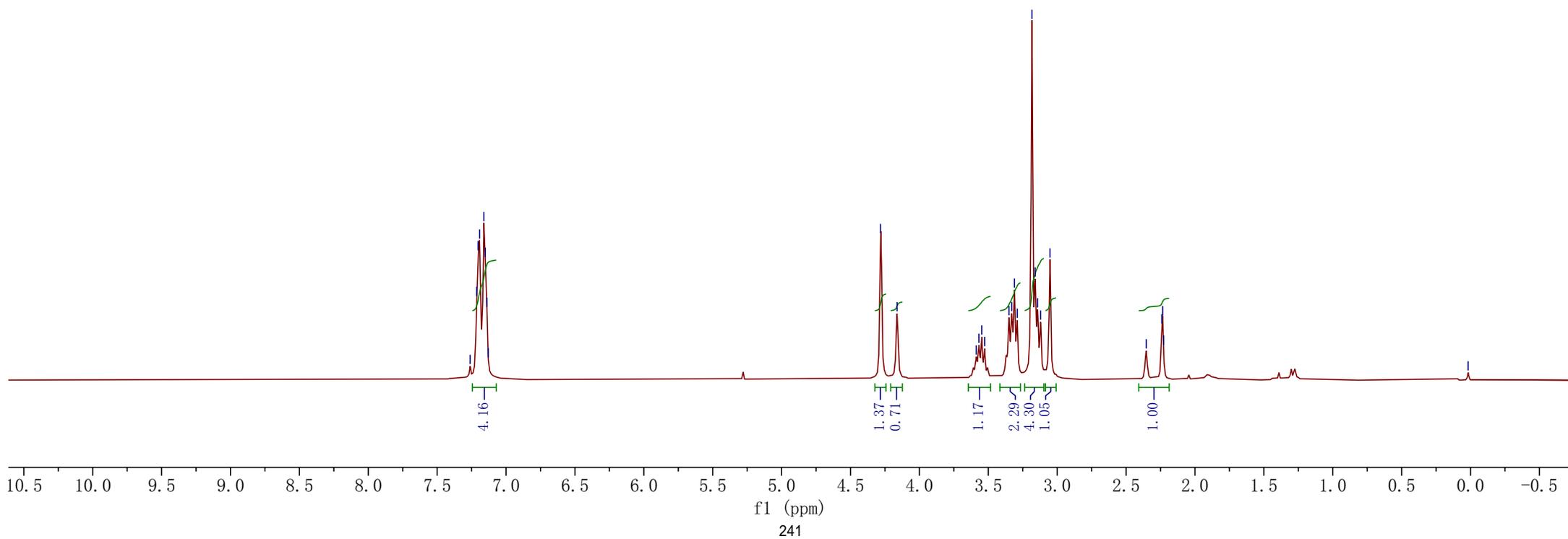


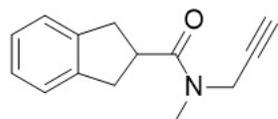
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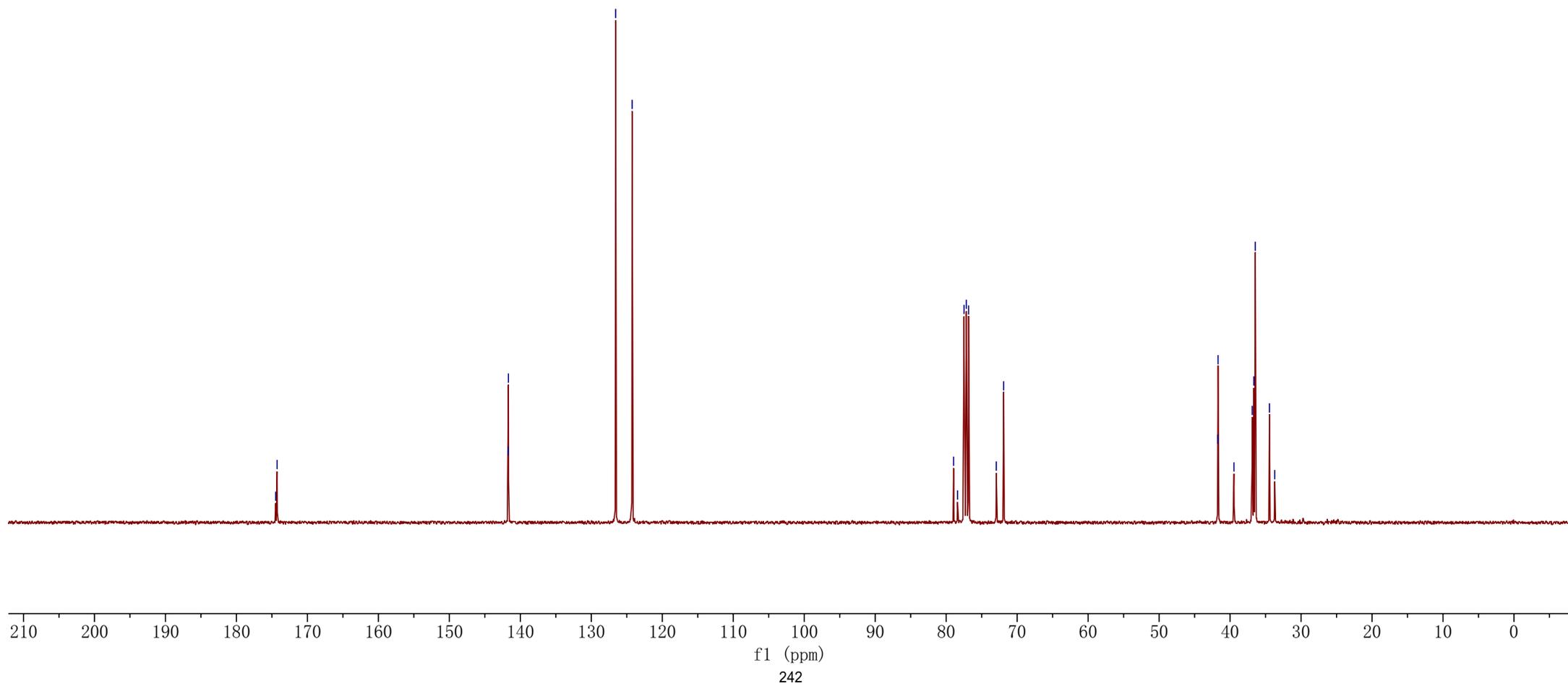
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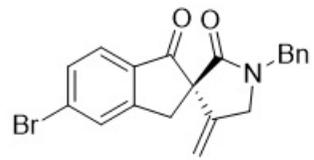
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36.449
34.451
33.703





2

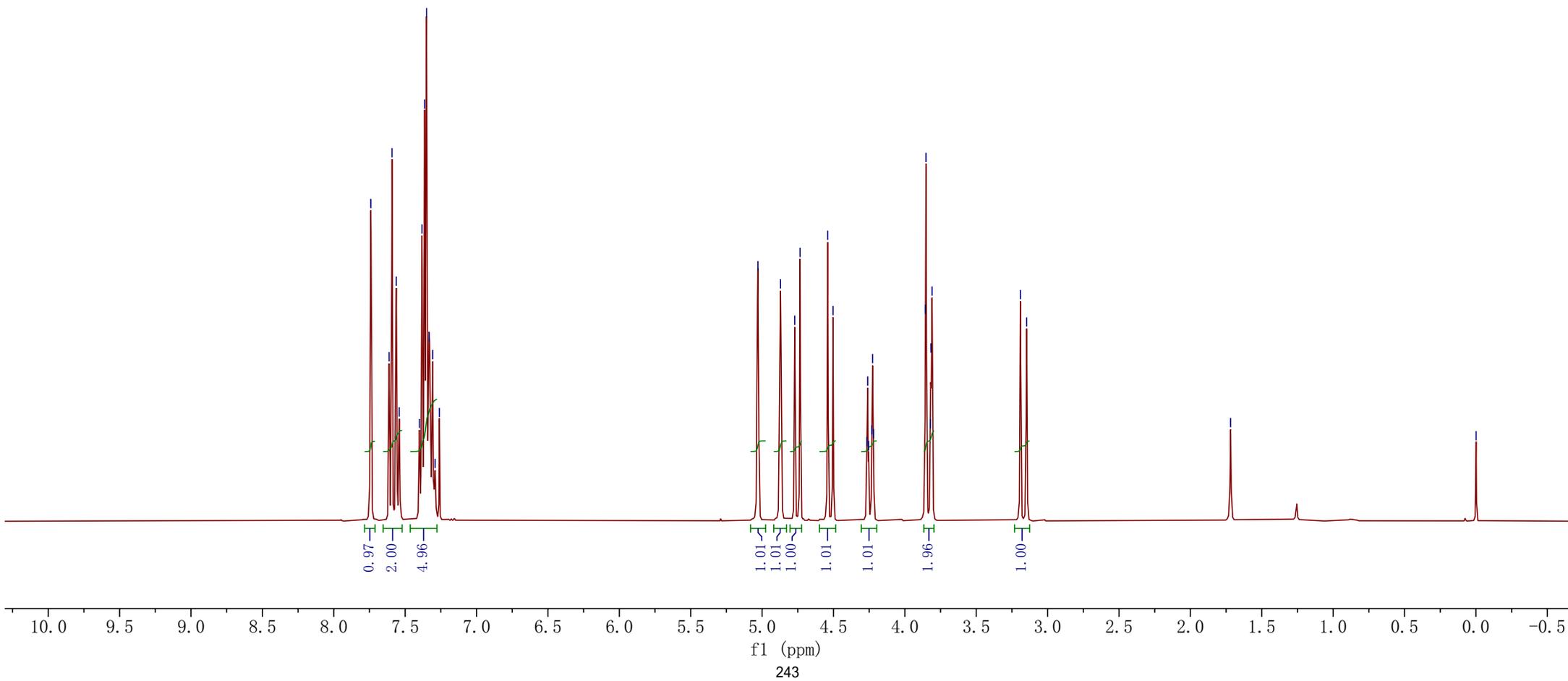
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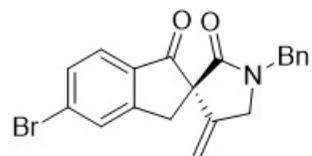
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3.852
3.822
3.817
3.809

3.191
3.147

—1.718

—-0.001





2

— 199.929
— 171.378
— 155.533
— 142.444
— 135.590
— 132.749
— 131.827
— 131.149
— 129.781
— 128.927
— 128.158
— 127.875
— 126.504

— 108.297

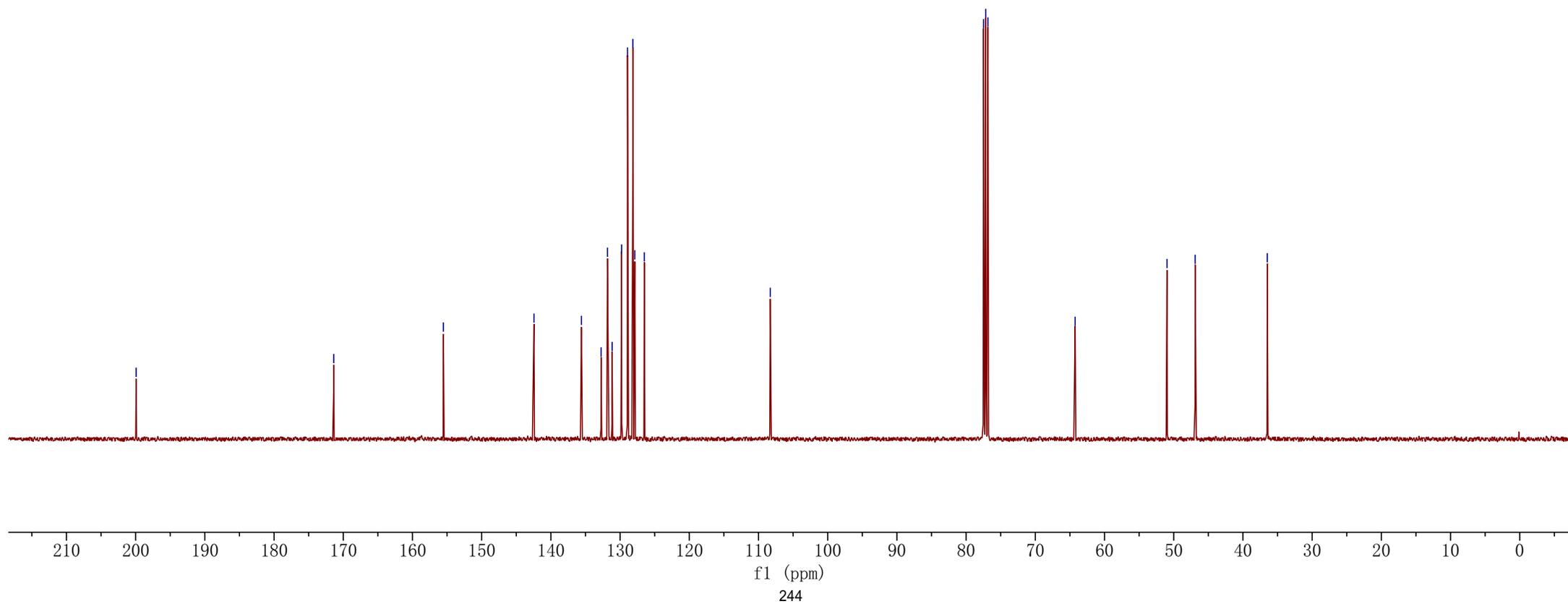
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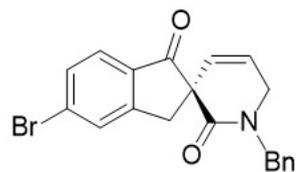
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— 50.974

— 46.908

— 36.483





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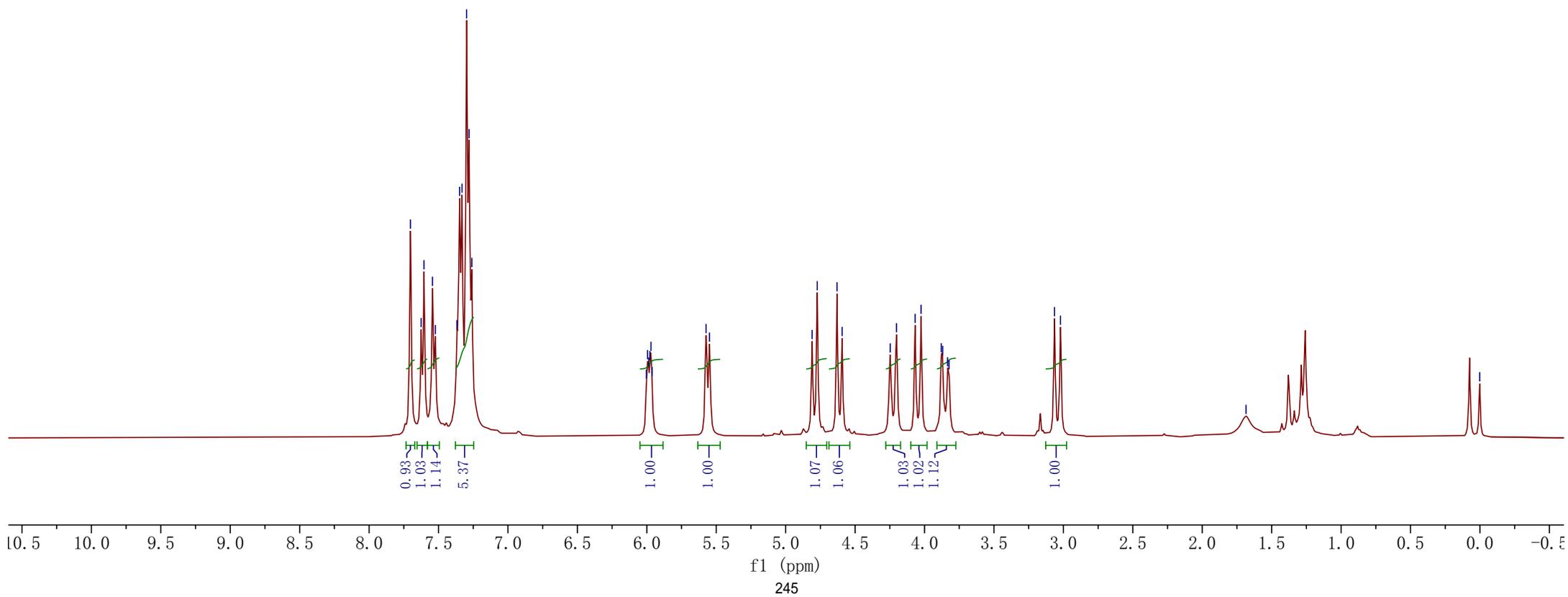
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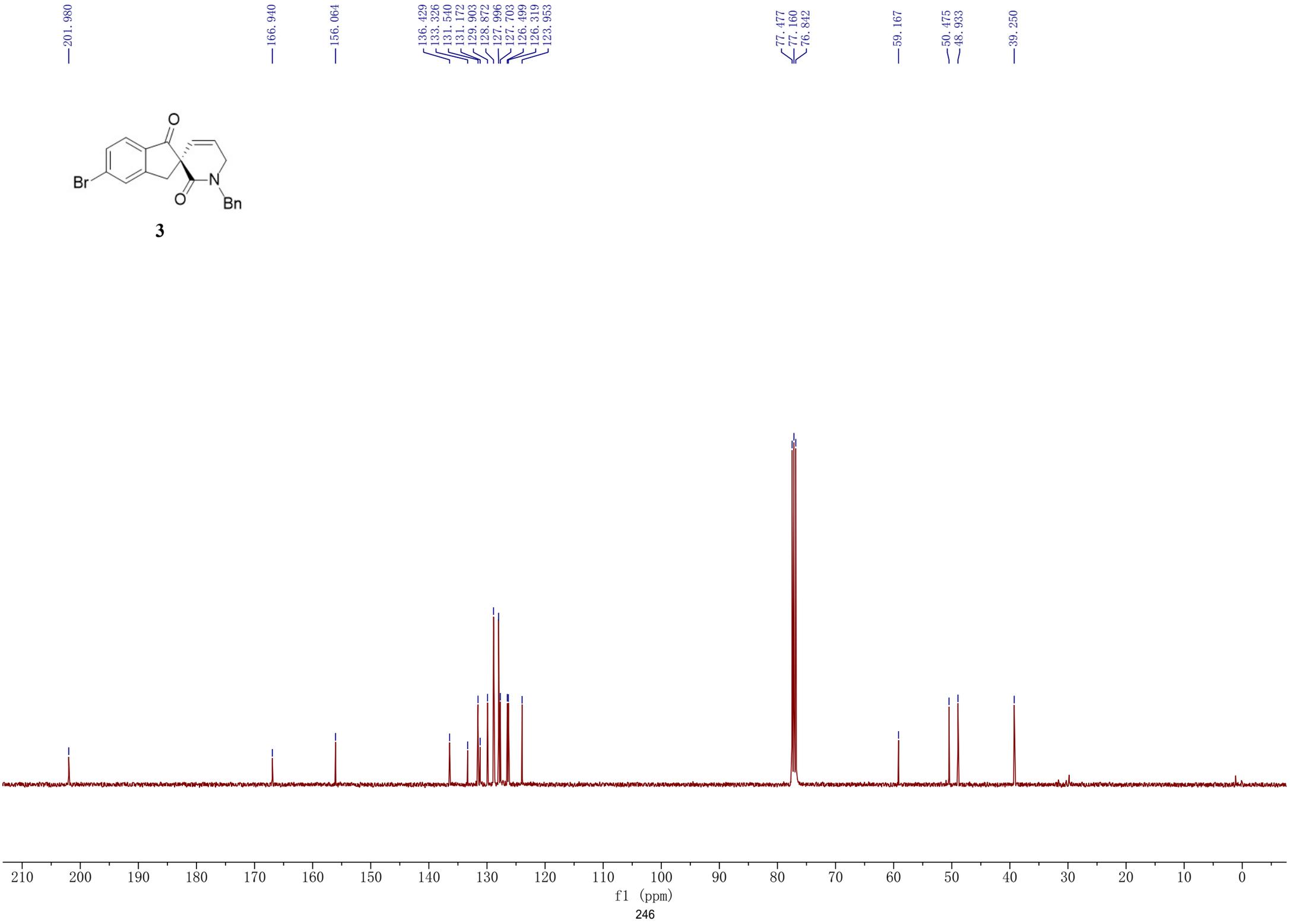
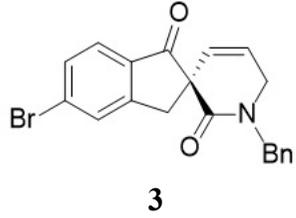
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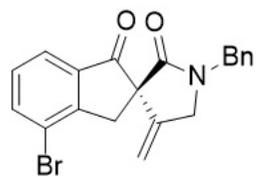
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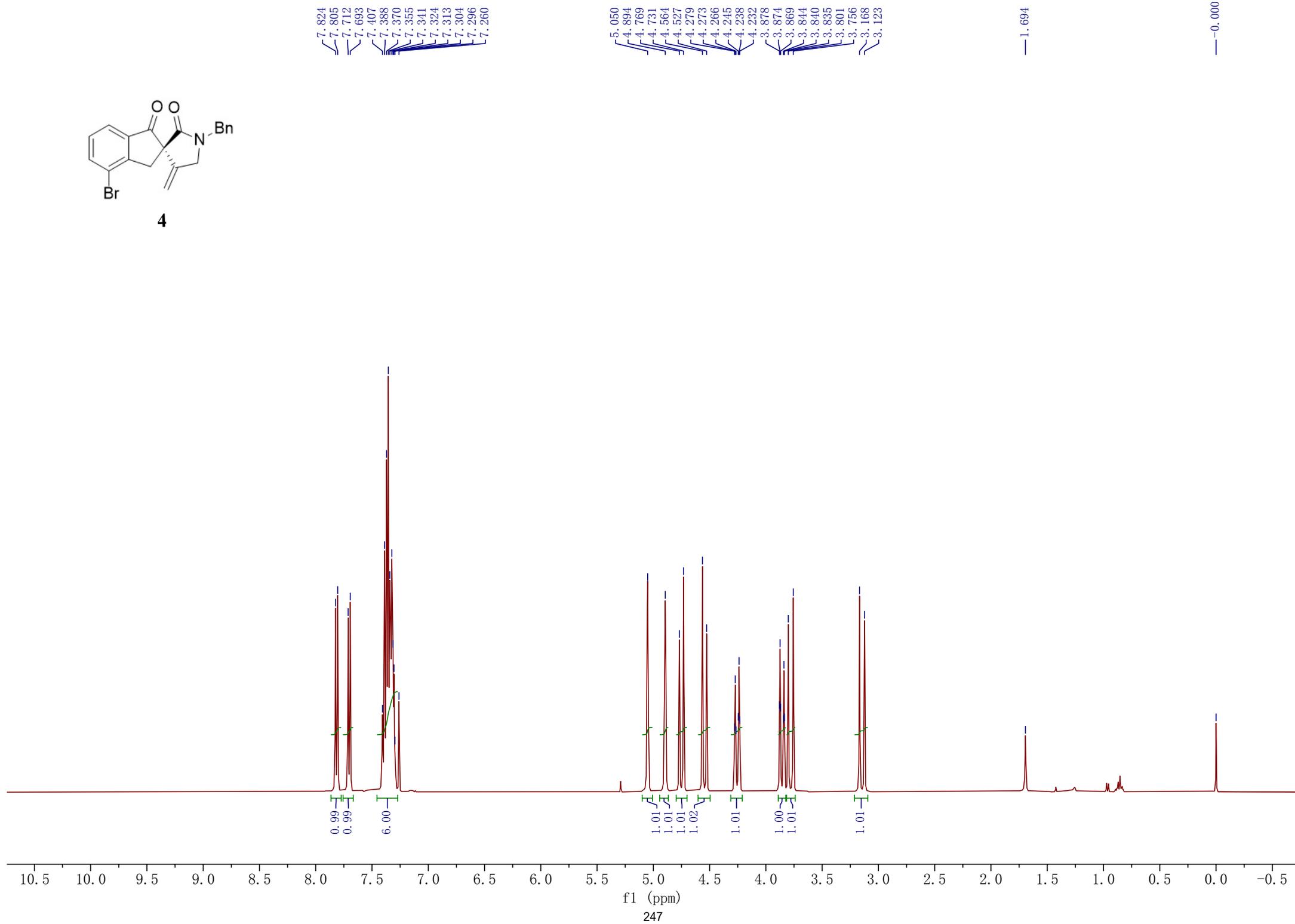
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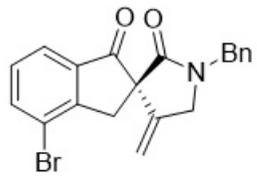






4





4

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—171.284

—153.665

—142.296

—138.294

—135.854

—135.581

—129.898

—128.927

—128.143

—127.875

—124.175

—121.889

—108.524

—77.479

—77.161

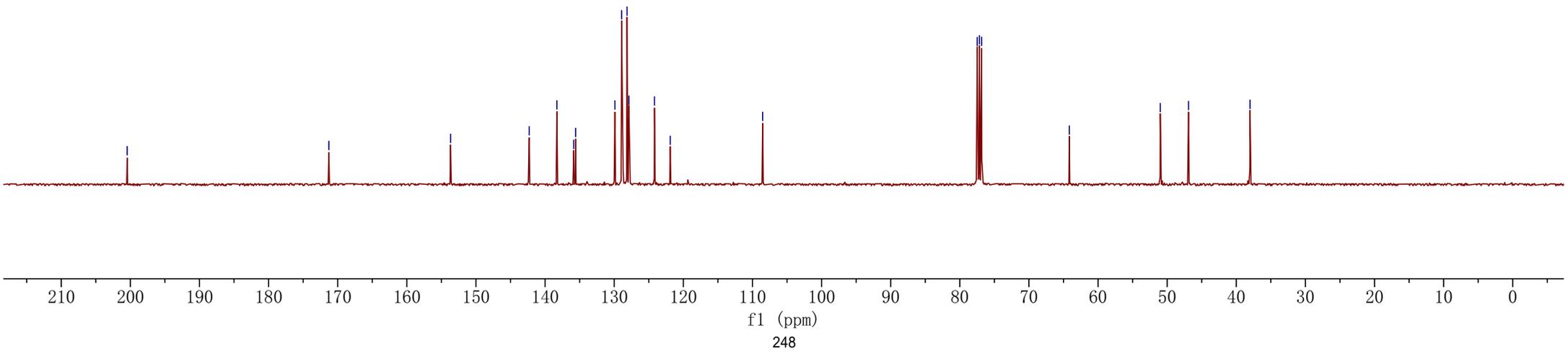
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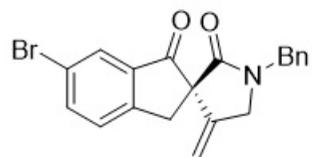
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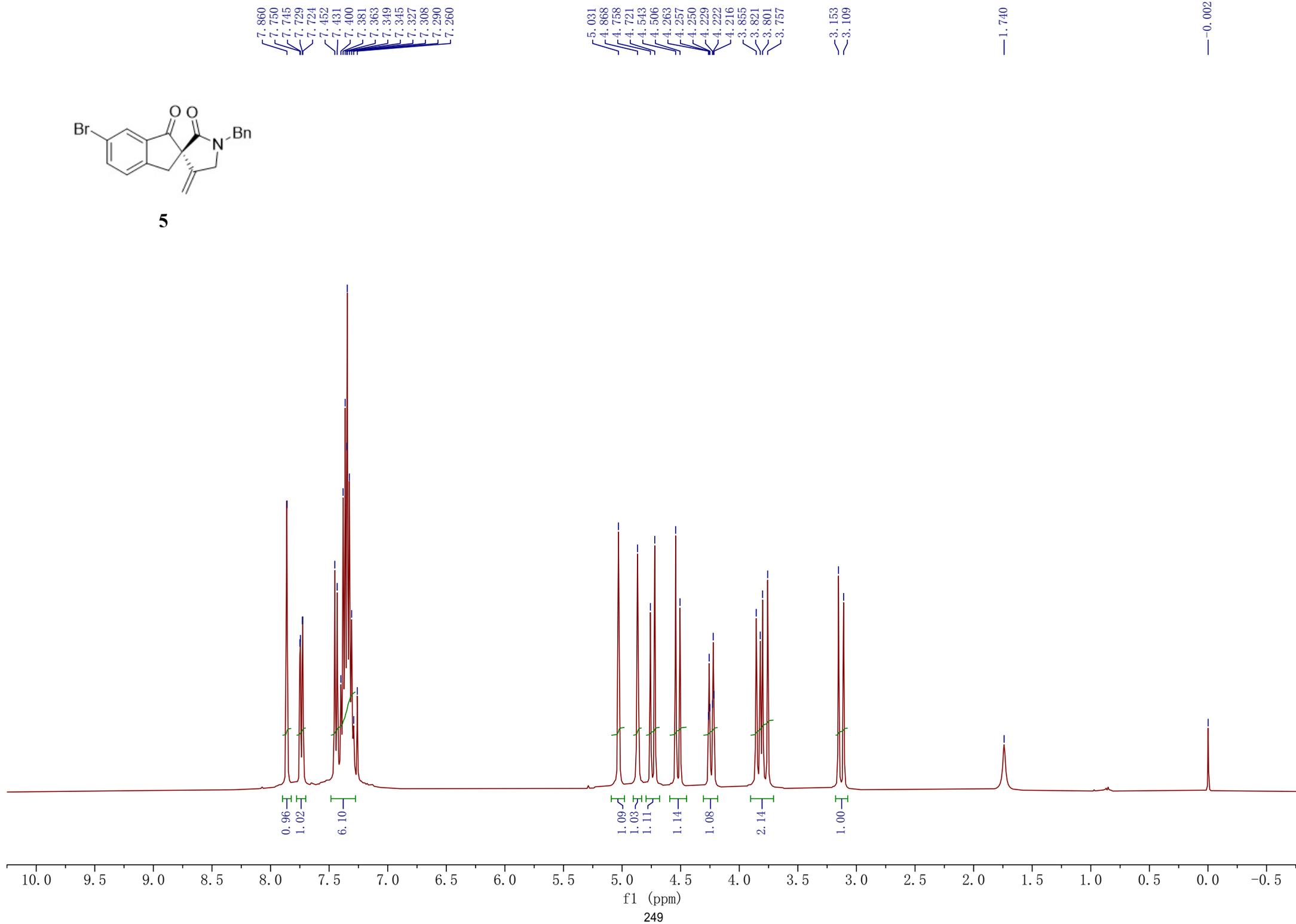
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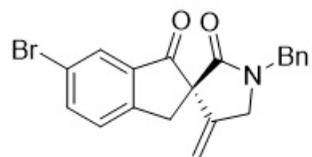
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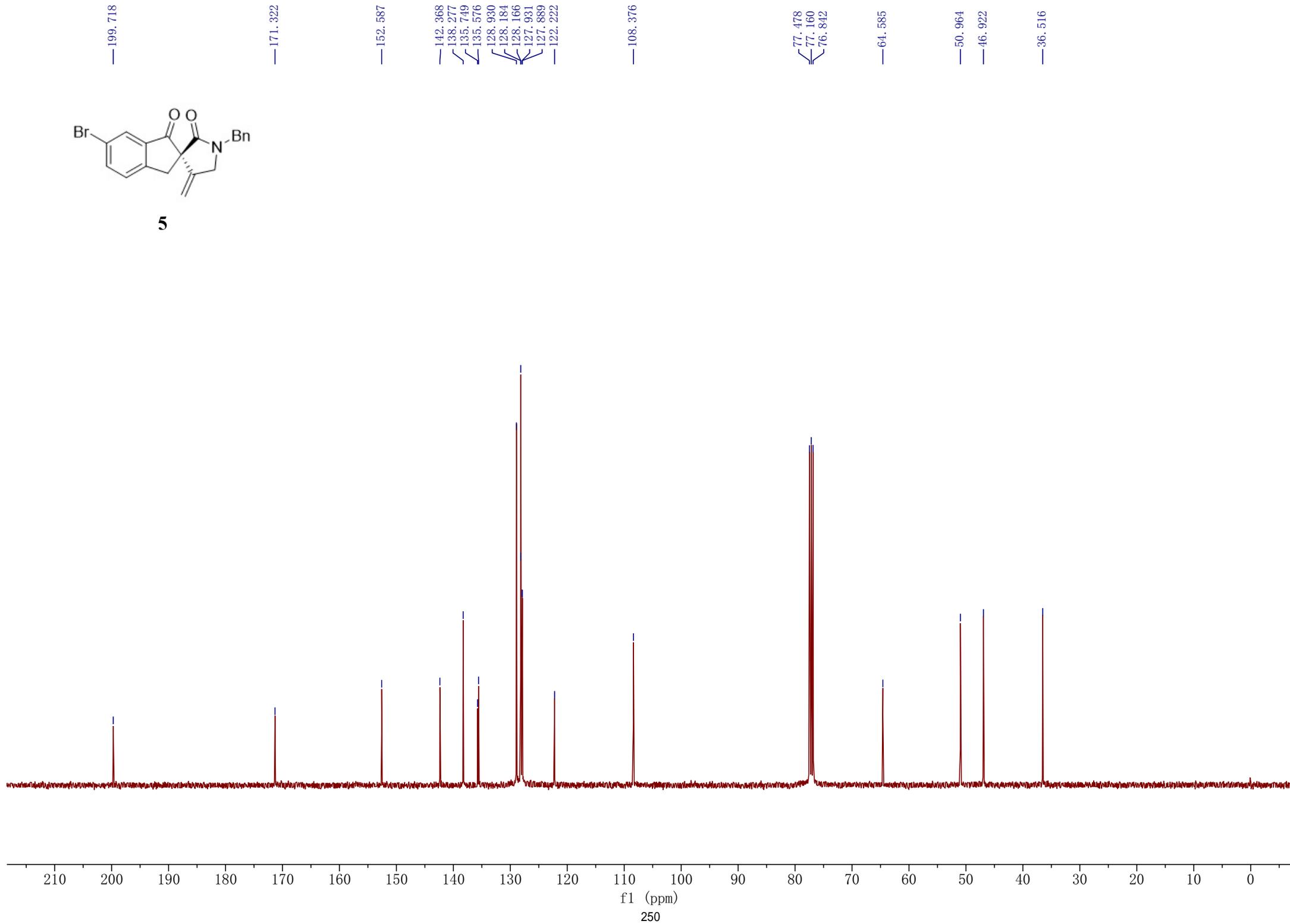


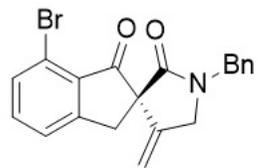
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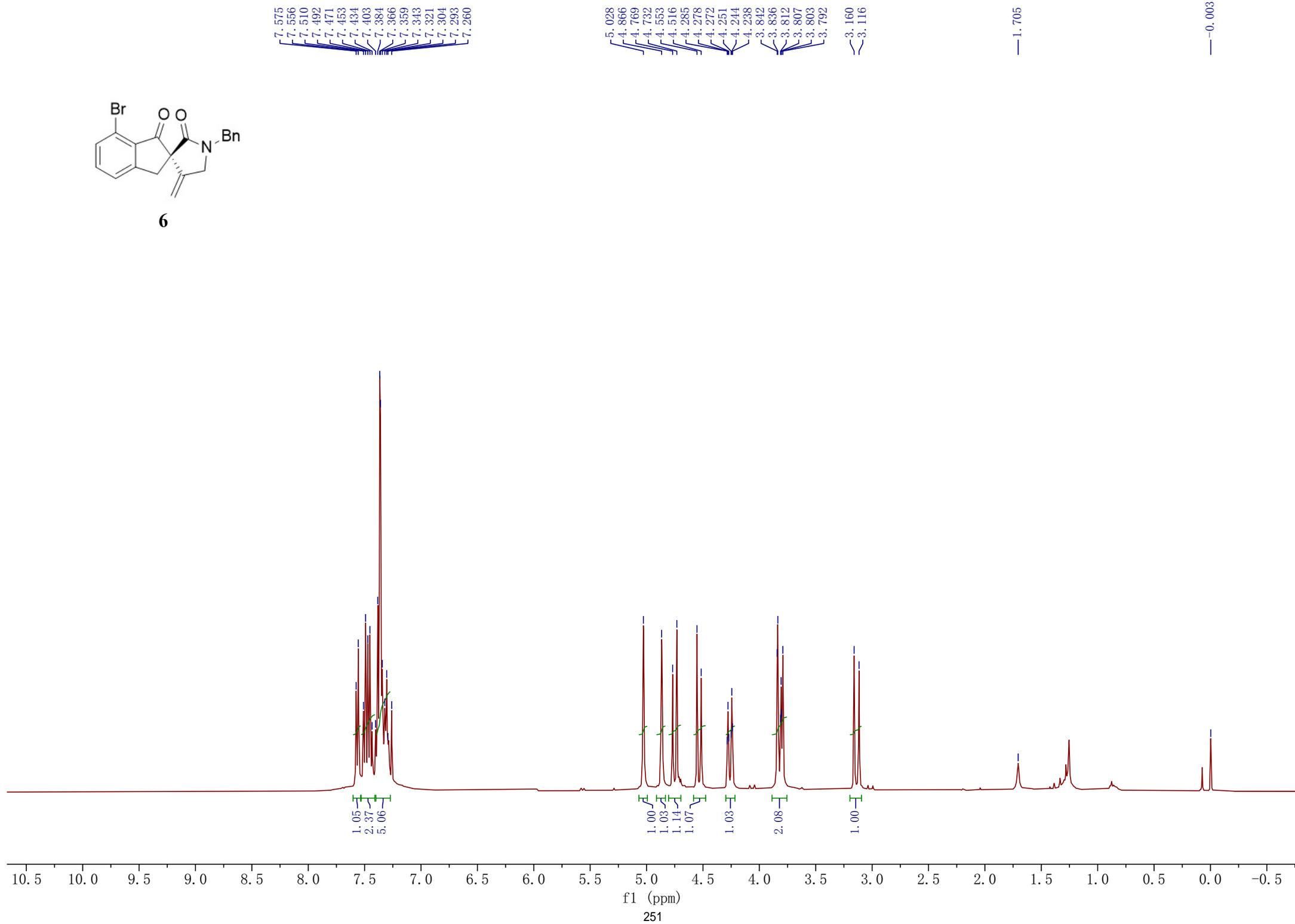


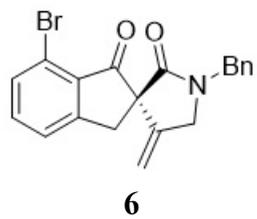
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6





— 198.272

— 171.407

— 156.792

— 142.445

135.863

135.546

133.163

131.296

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128.167

127.840

125.389

121.182

— 108.352

77.478

77.160

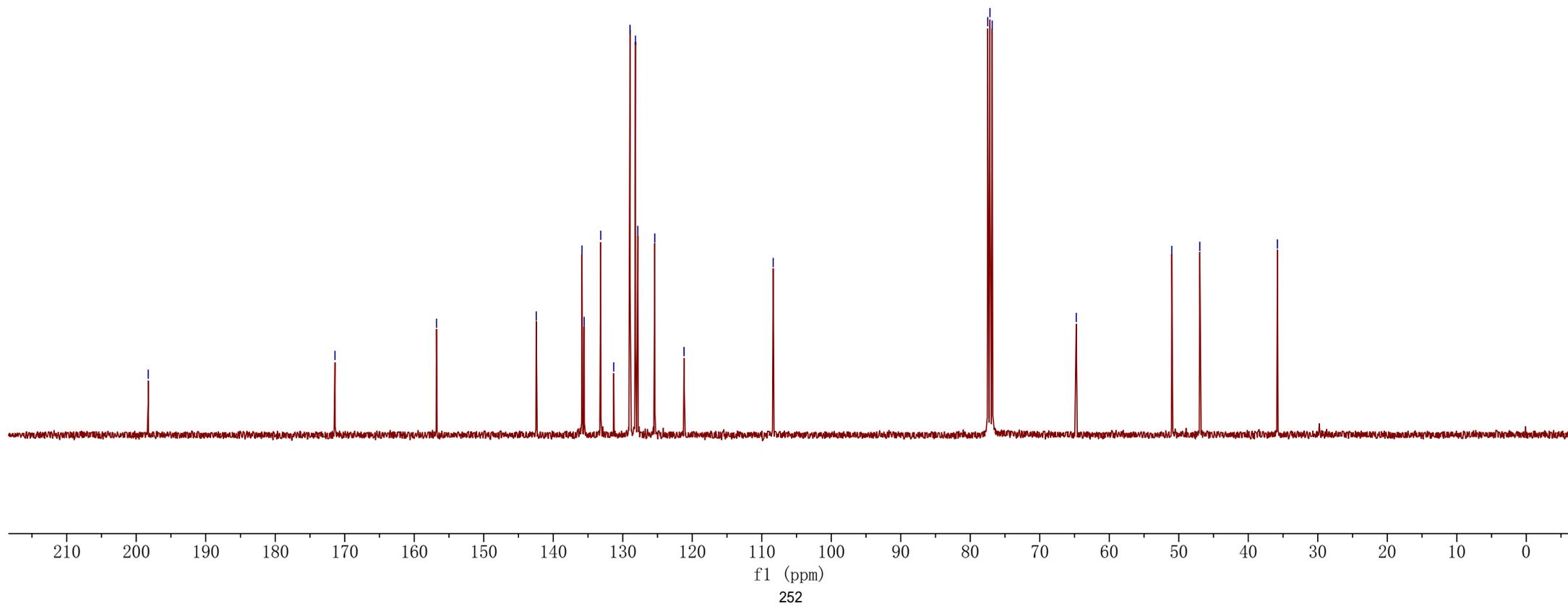
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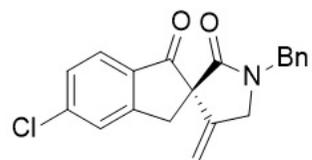
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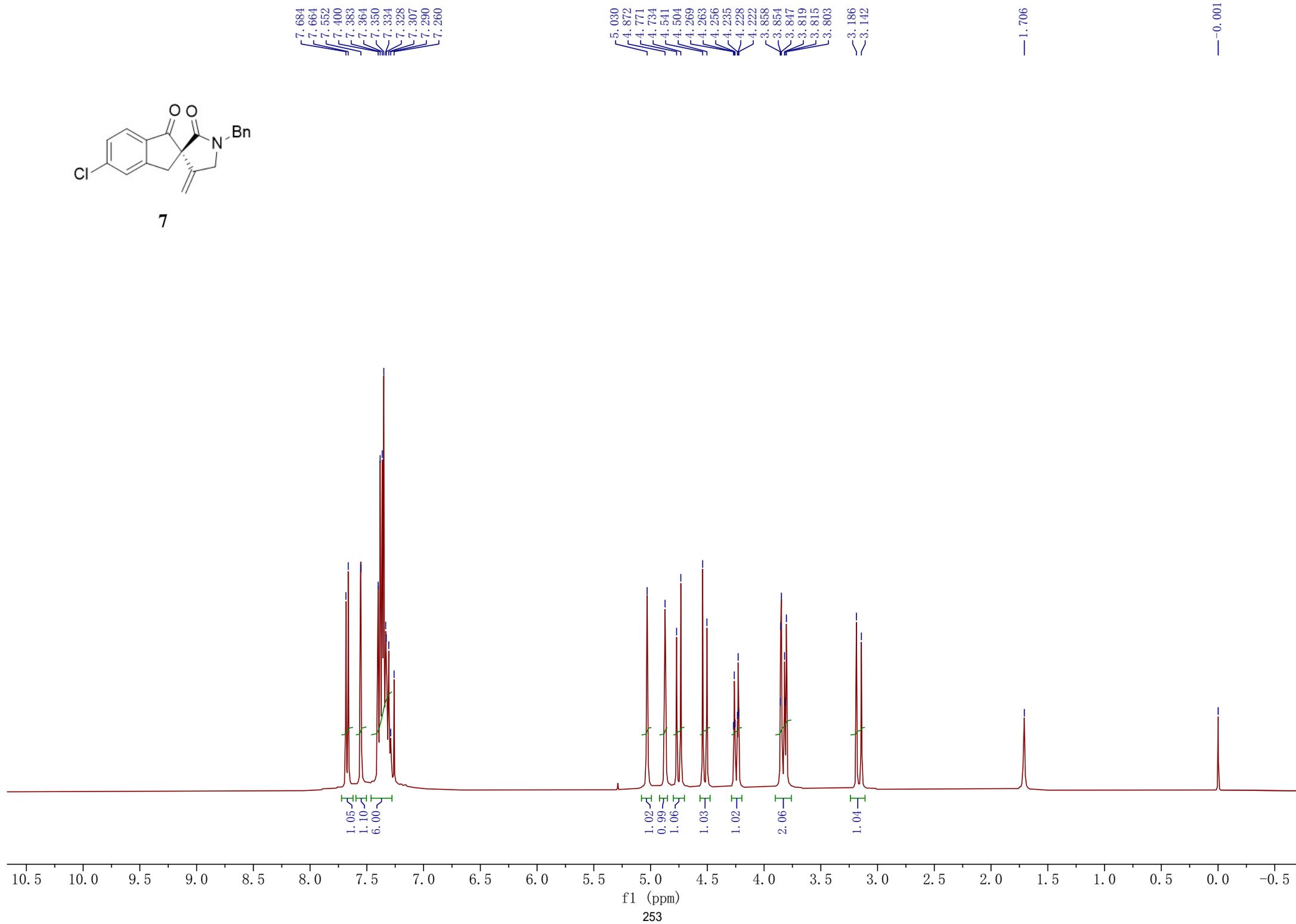
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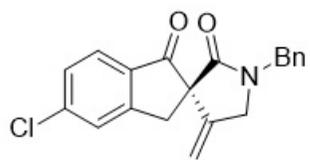
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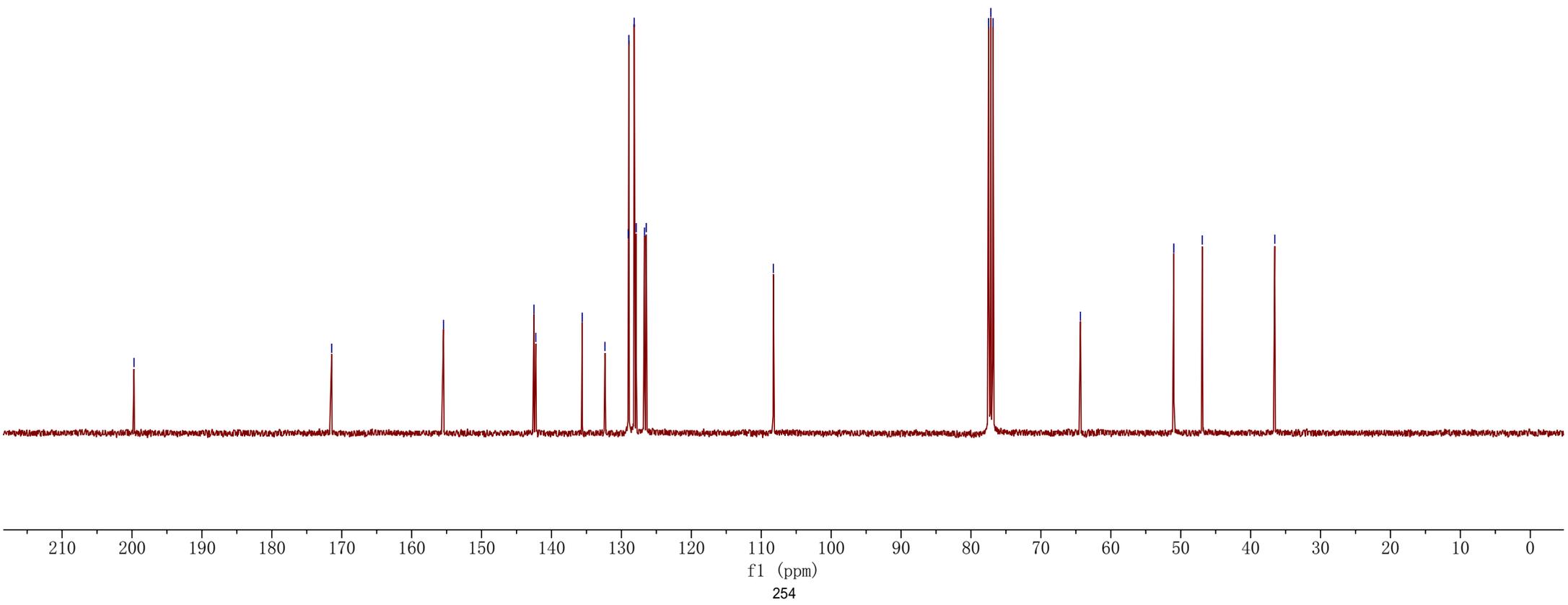


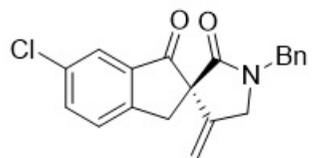


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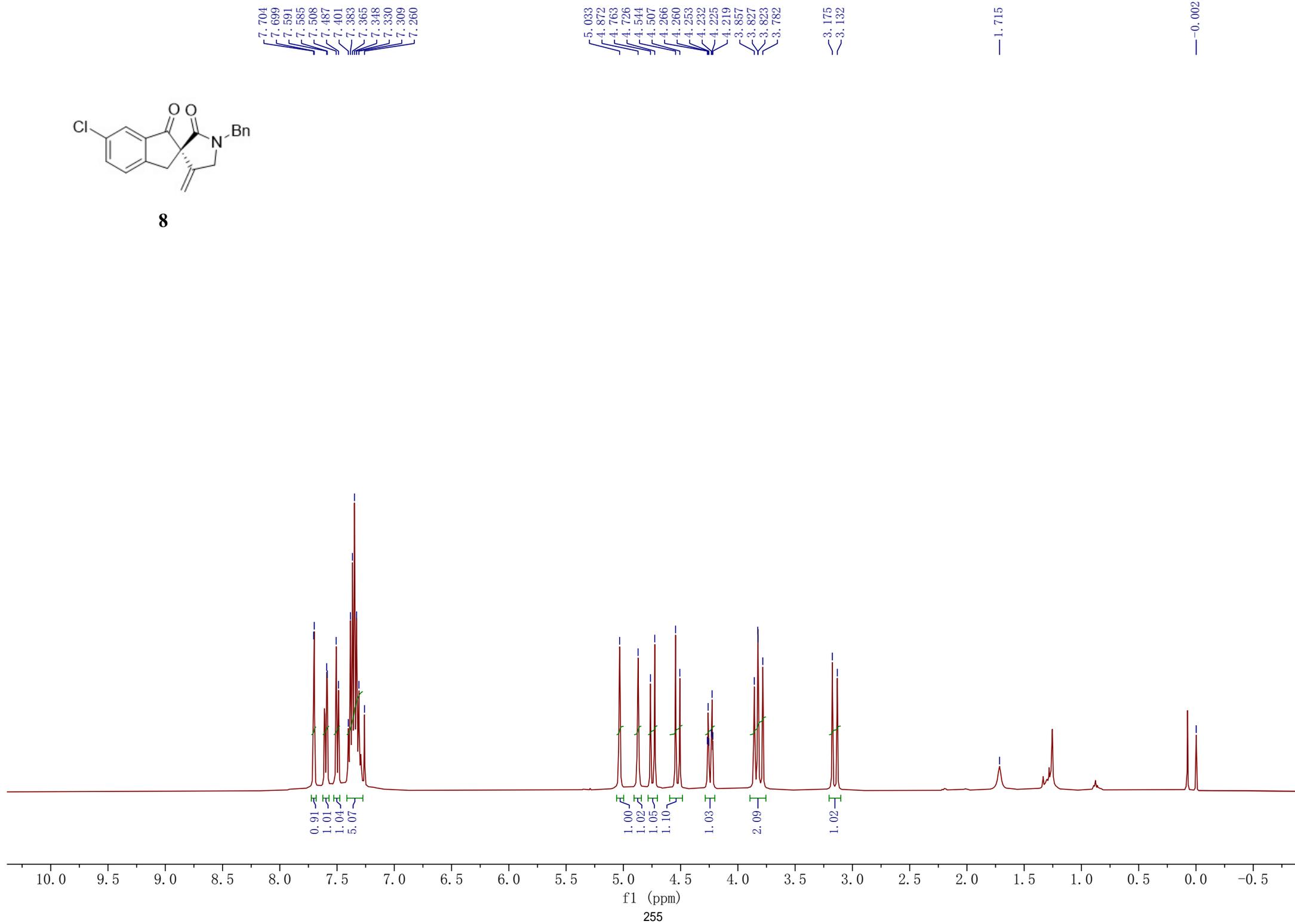
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126.443

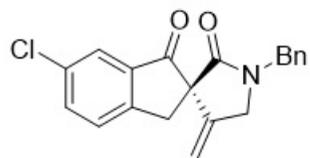
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77.478
77.160
76.842
— 64.346
— 50.992
— 46.922
— 36.544





8





8

— 199.875

— 171.360

— 152.132

— 142.396

135.589

135.551

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134.501

128.941

128.177

127.900

127.599

125.062

— 108.368

77.477

77.159

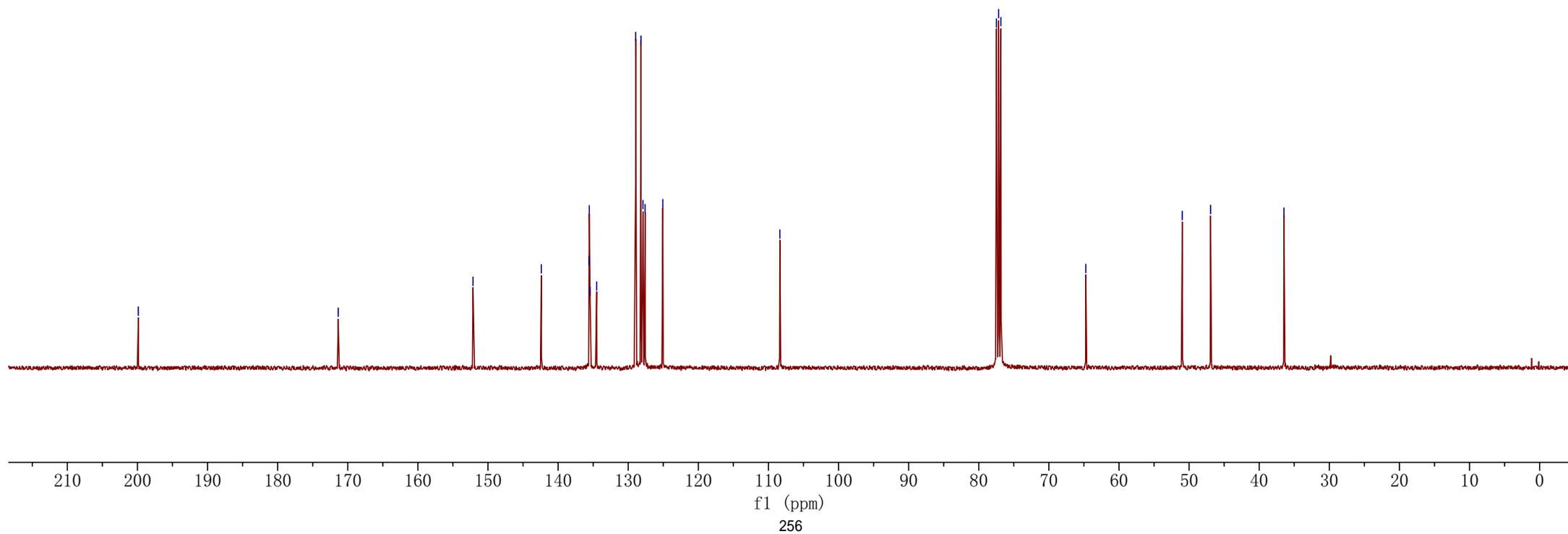
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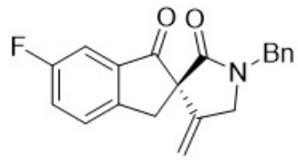
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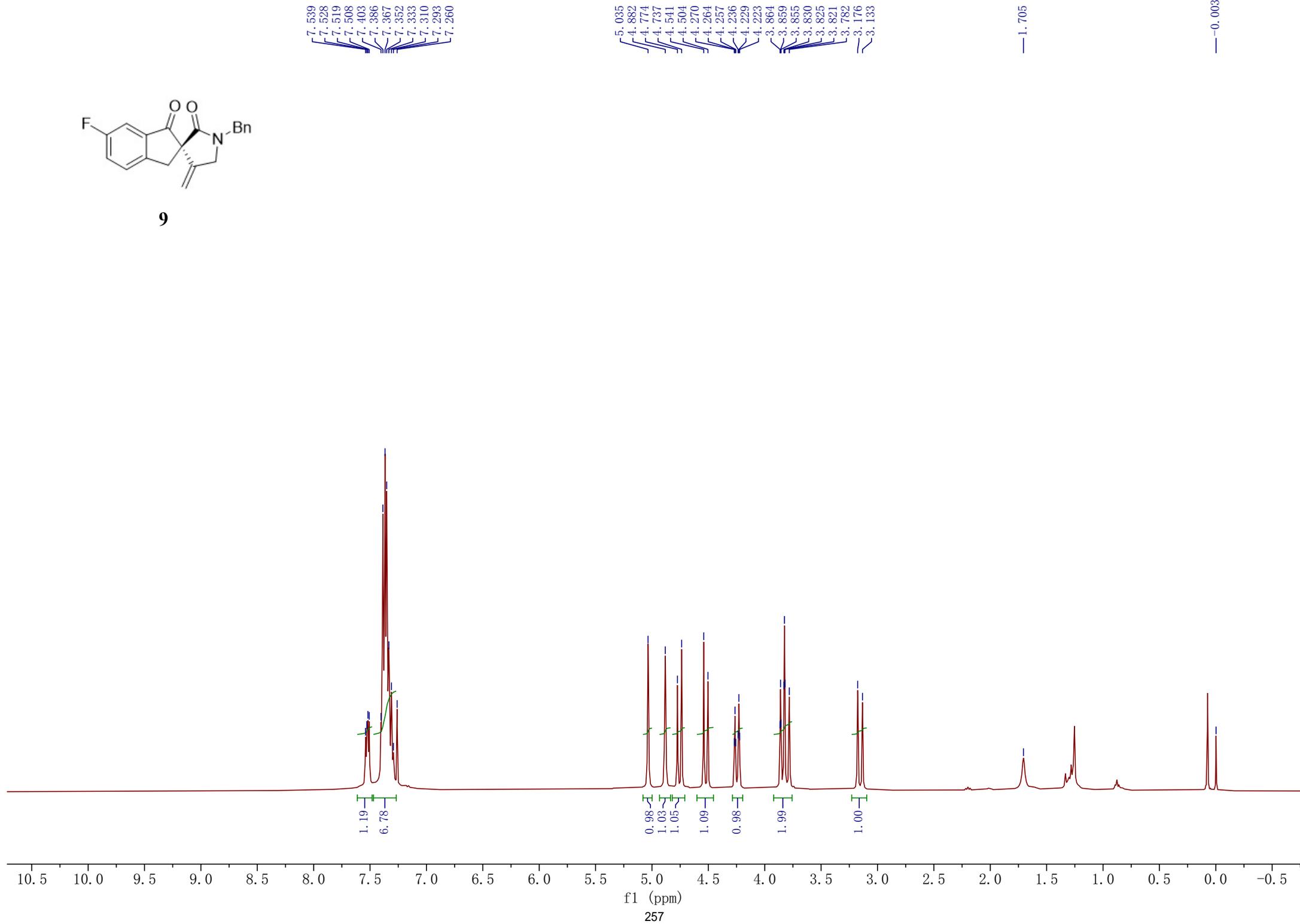
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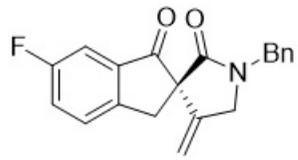
— 36.467





9





9

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149.515

142.447

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135.609

128.943

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127.826

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123.454

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77.160

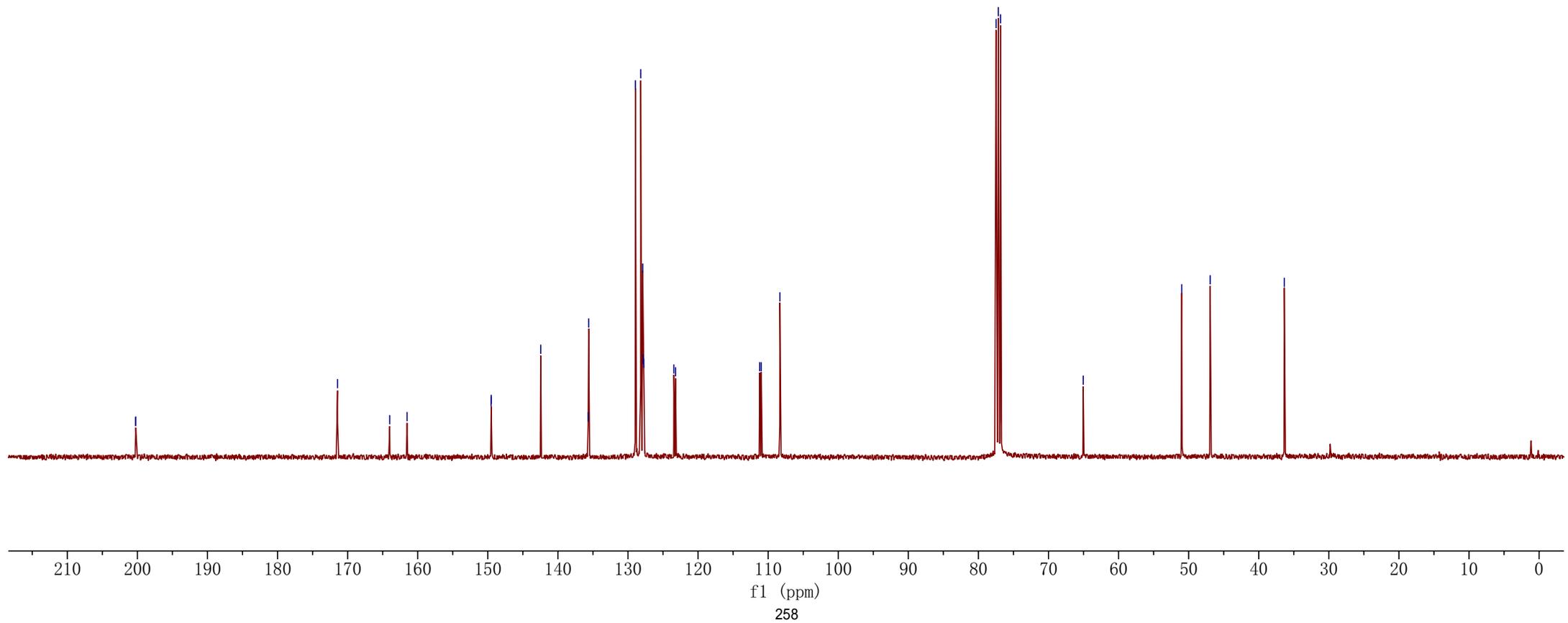
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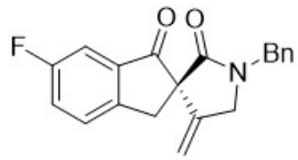
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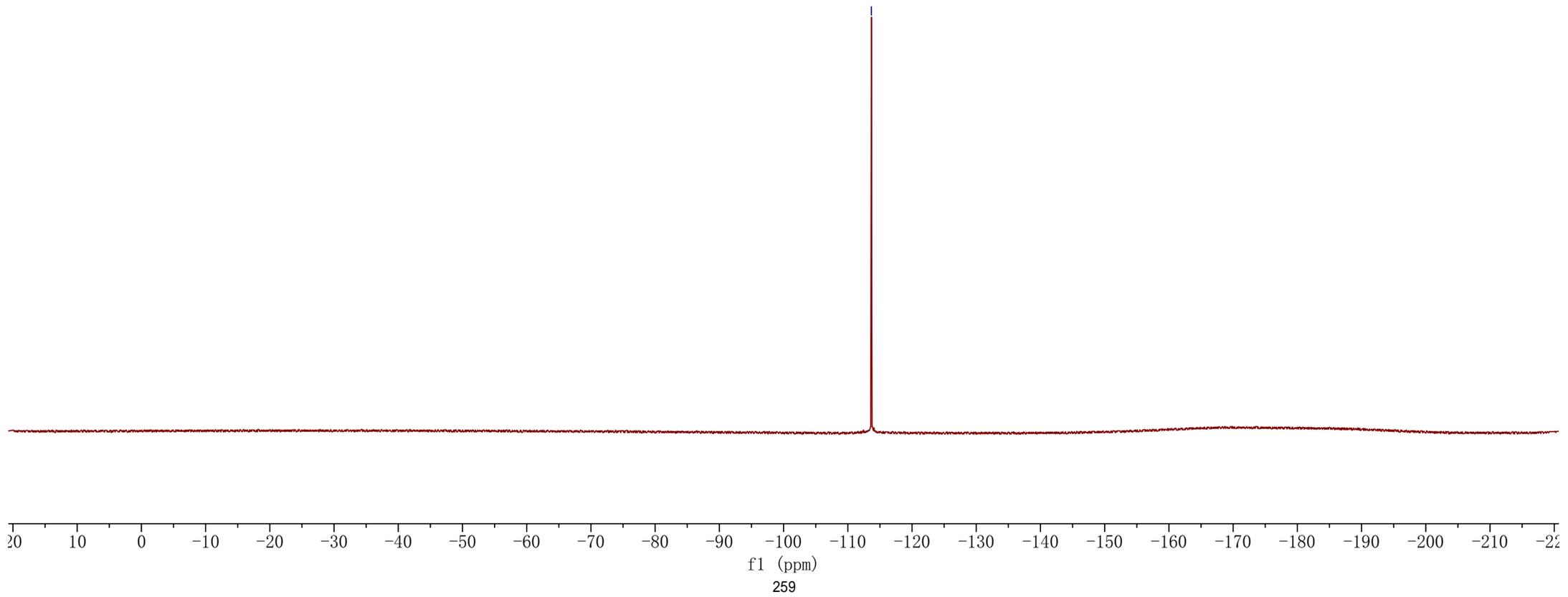
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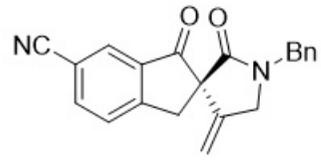




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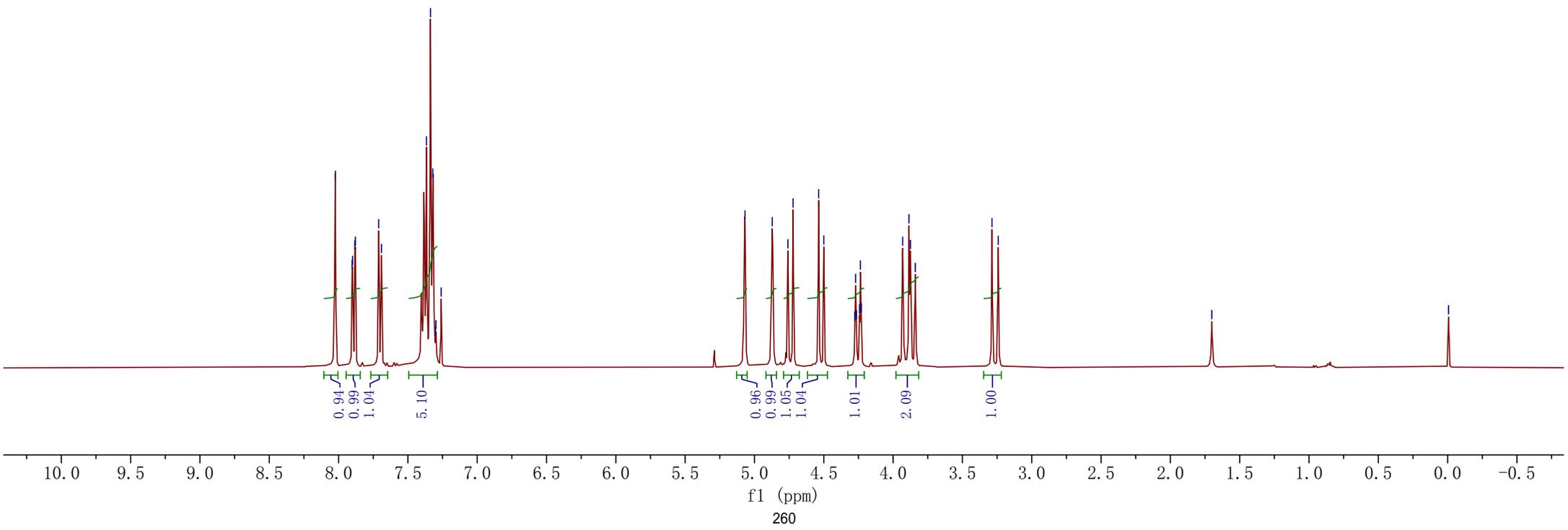
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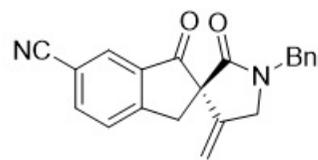
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3.241

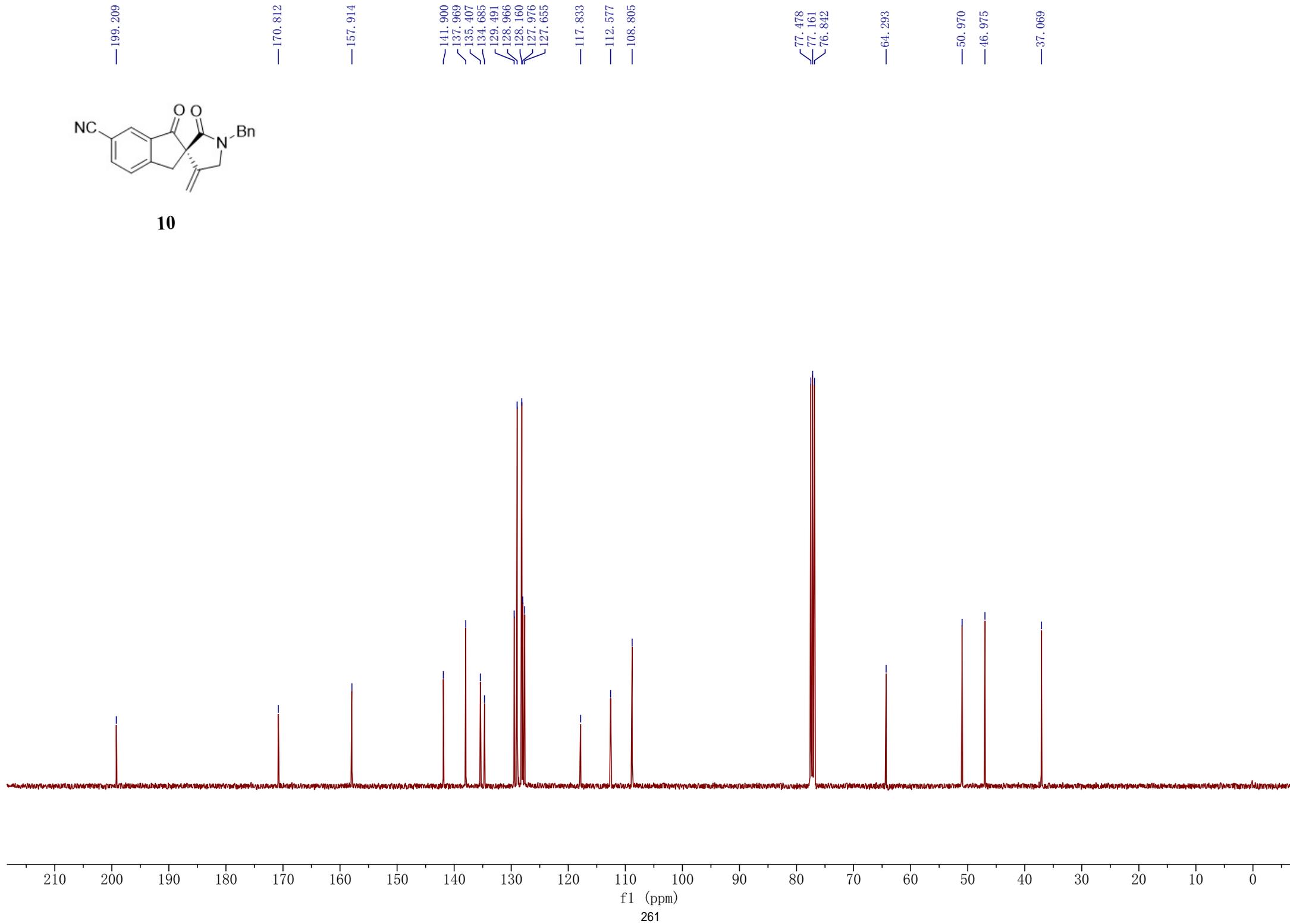
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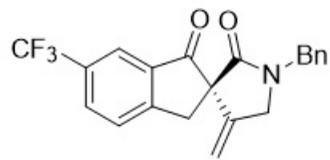
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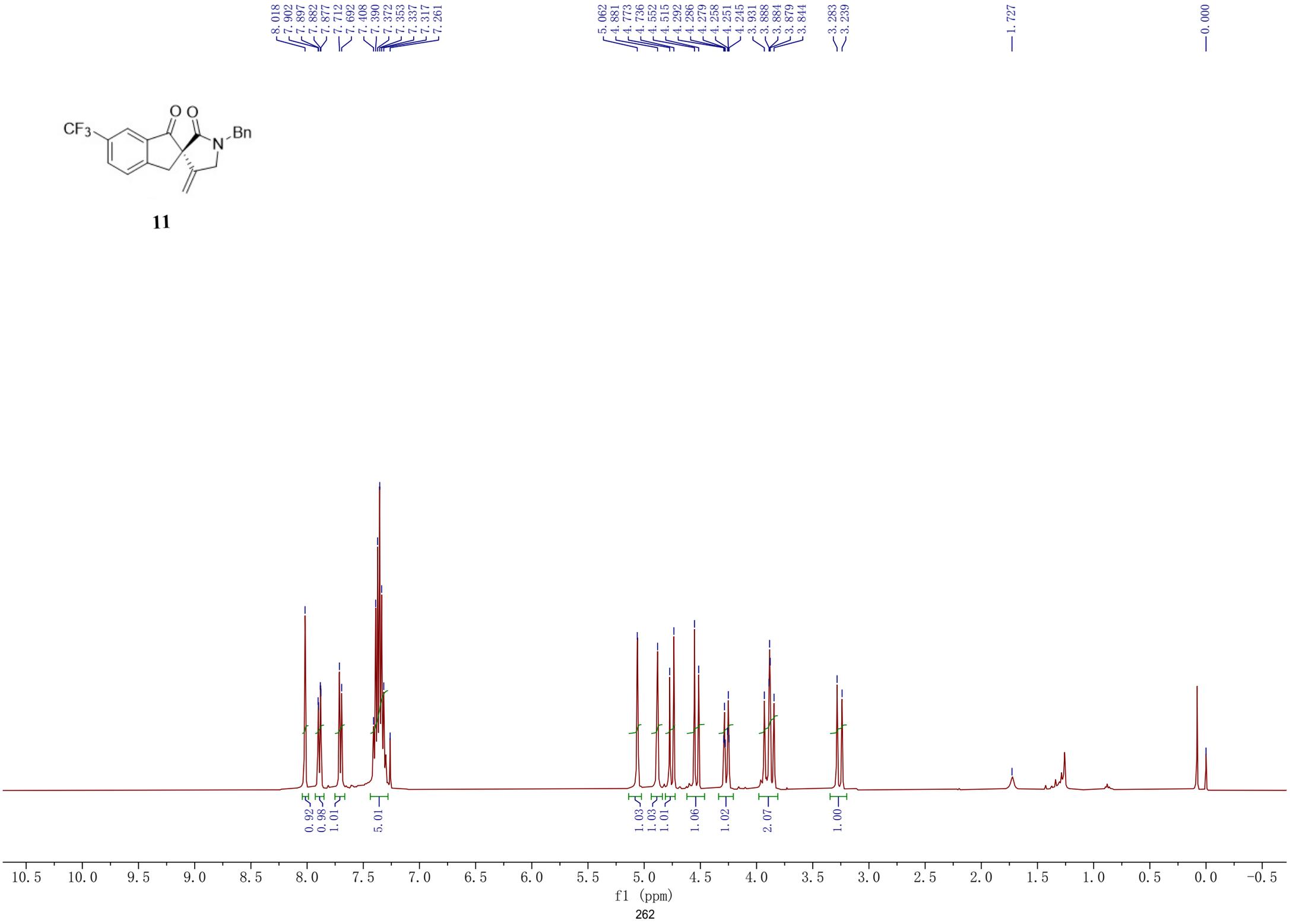


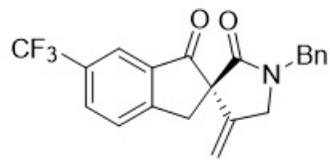
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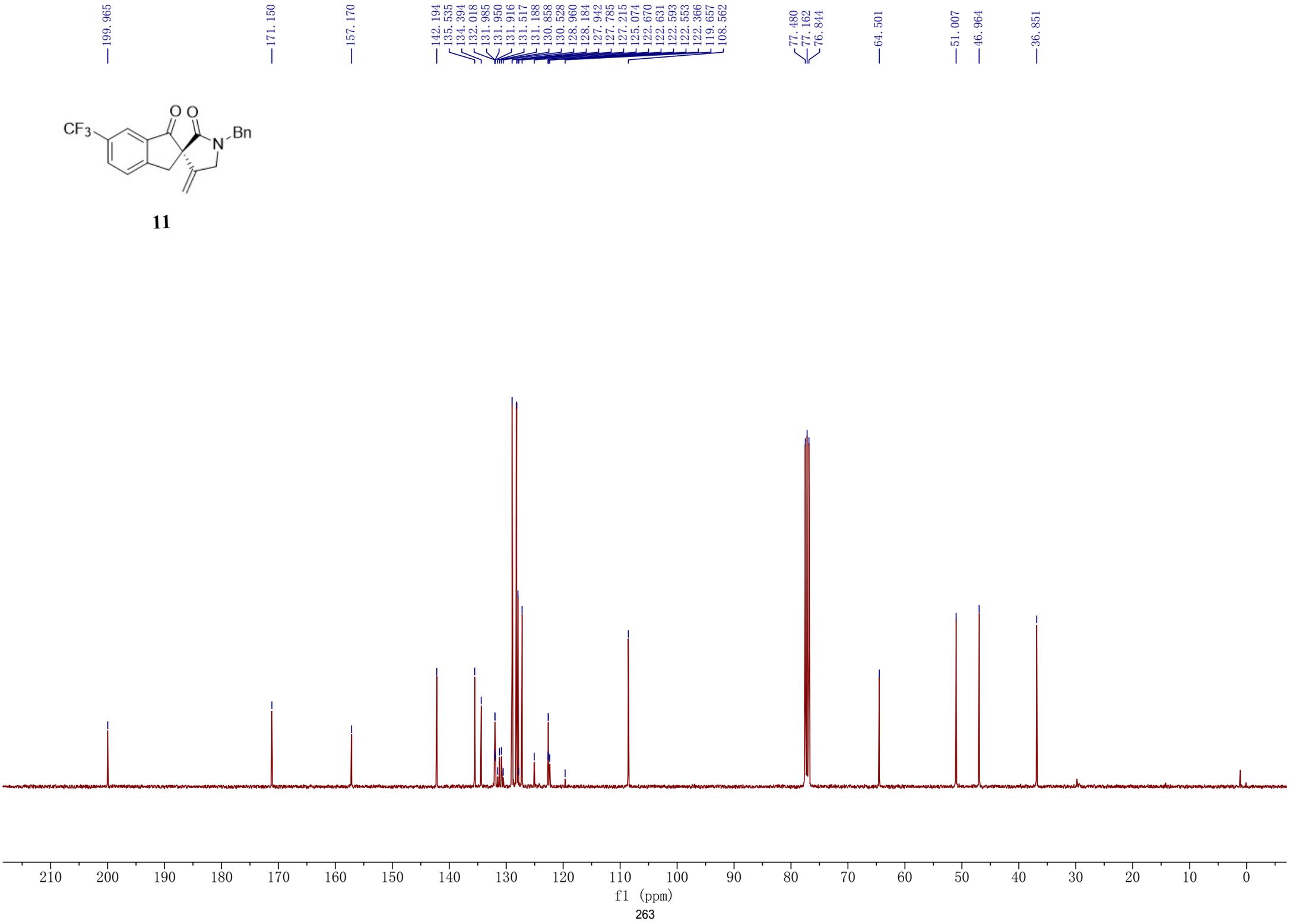


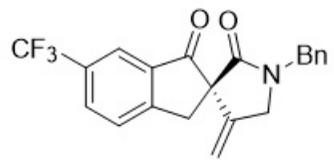
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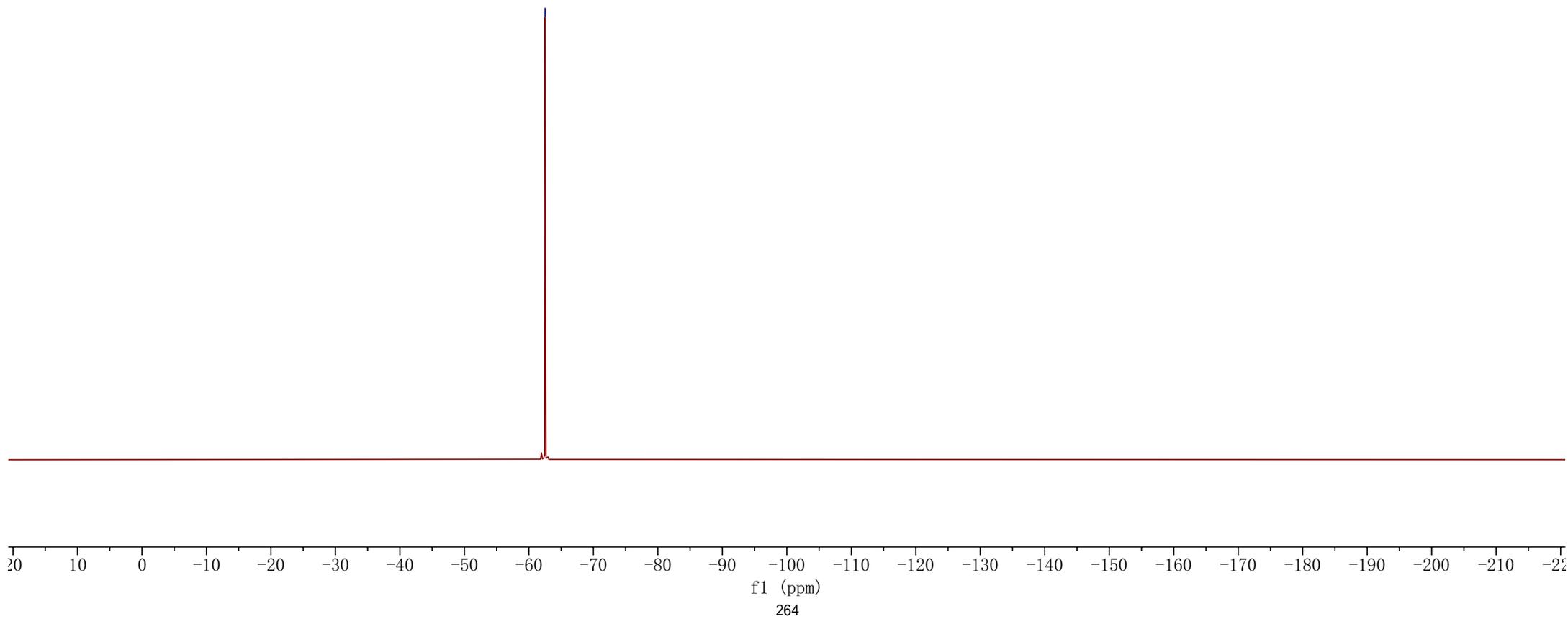
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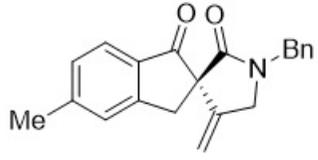




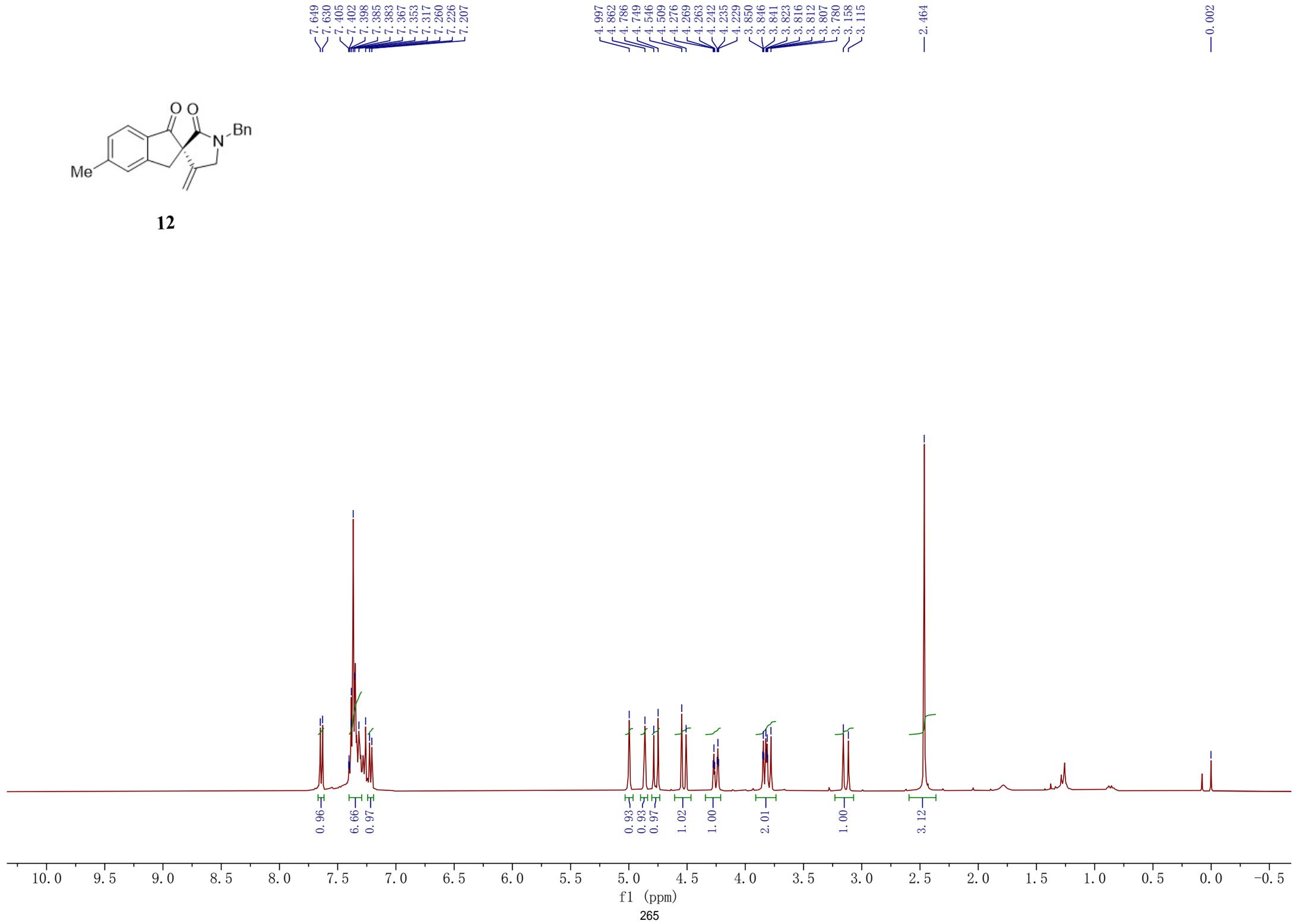
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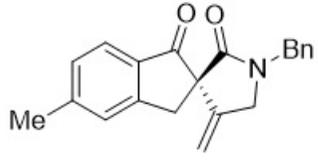
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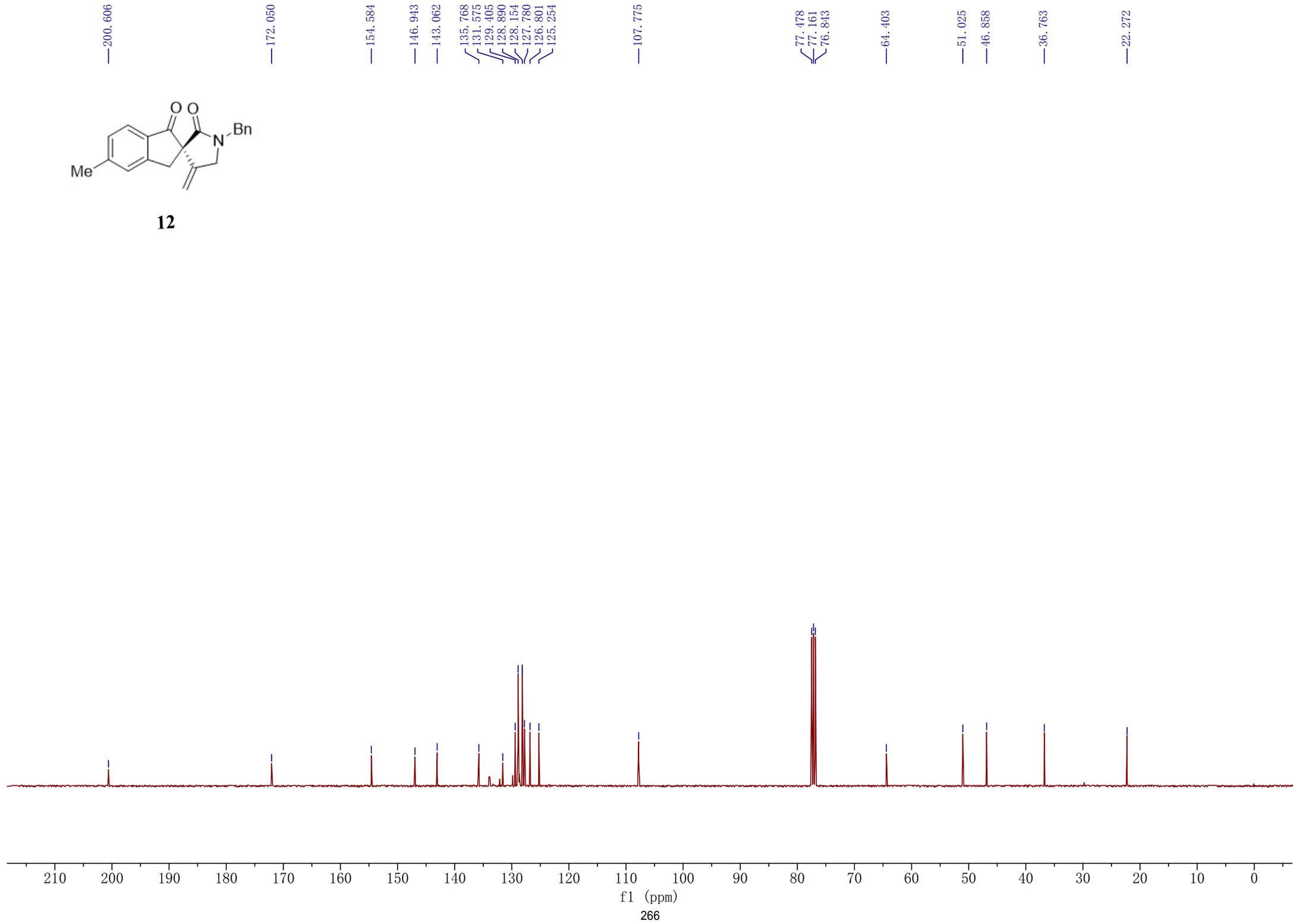


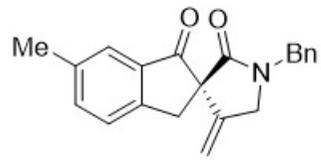
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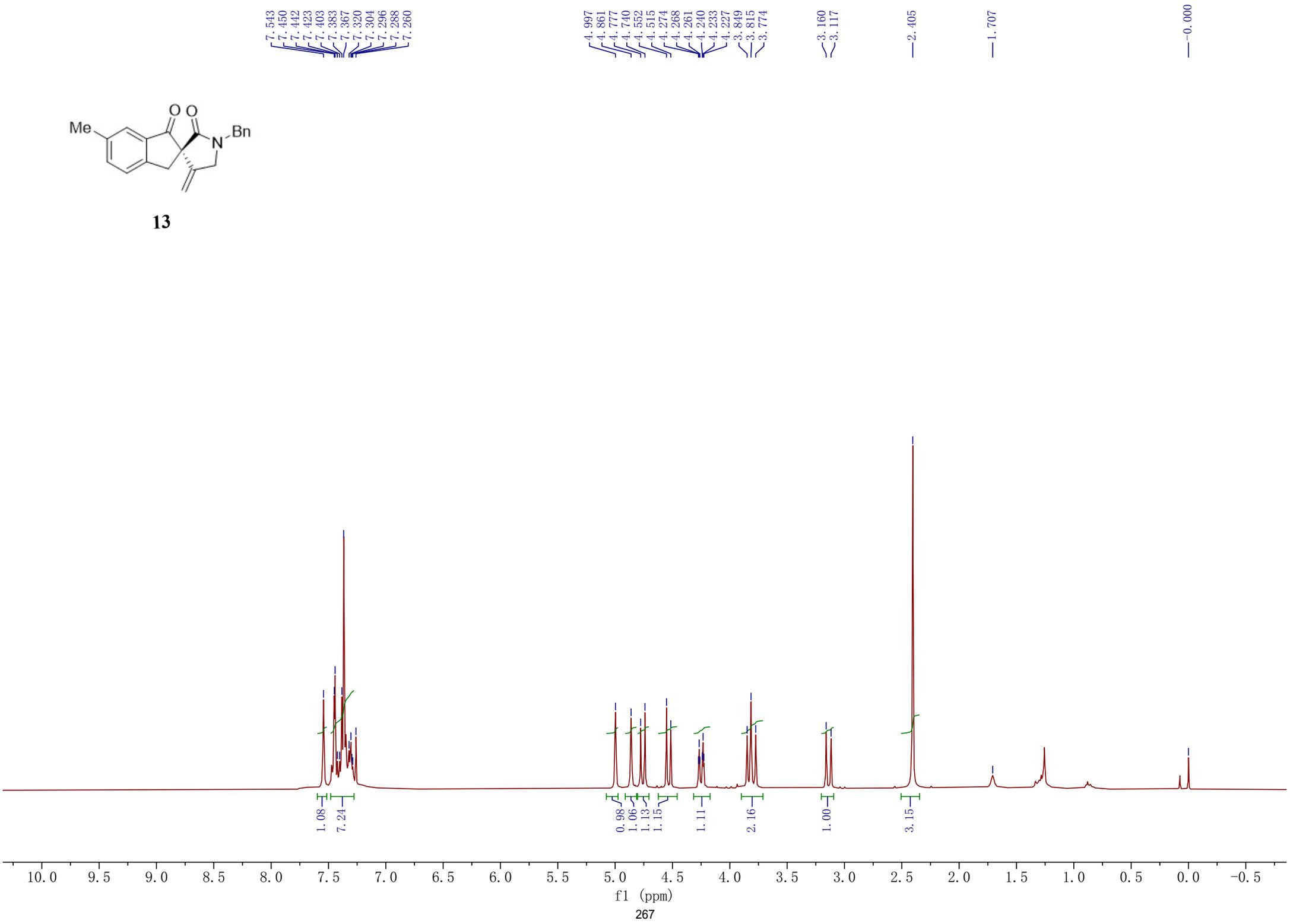


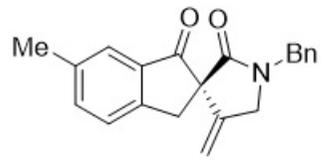
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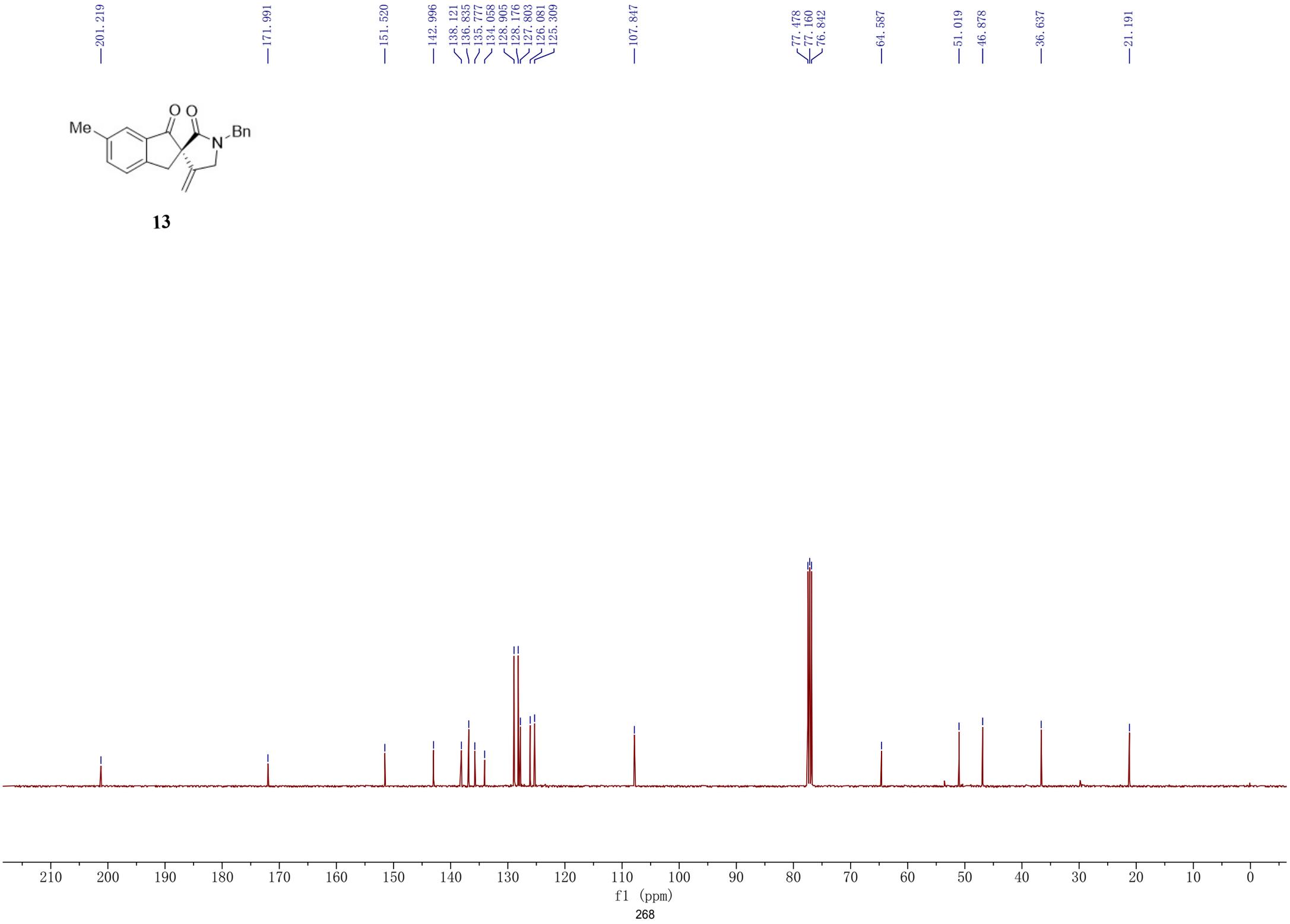


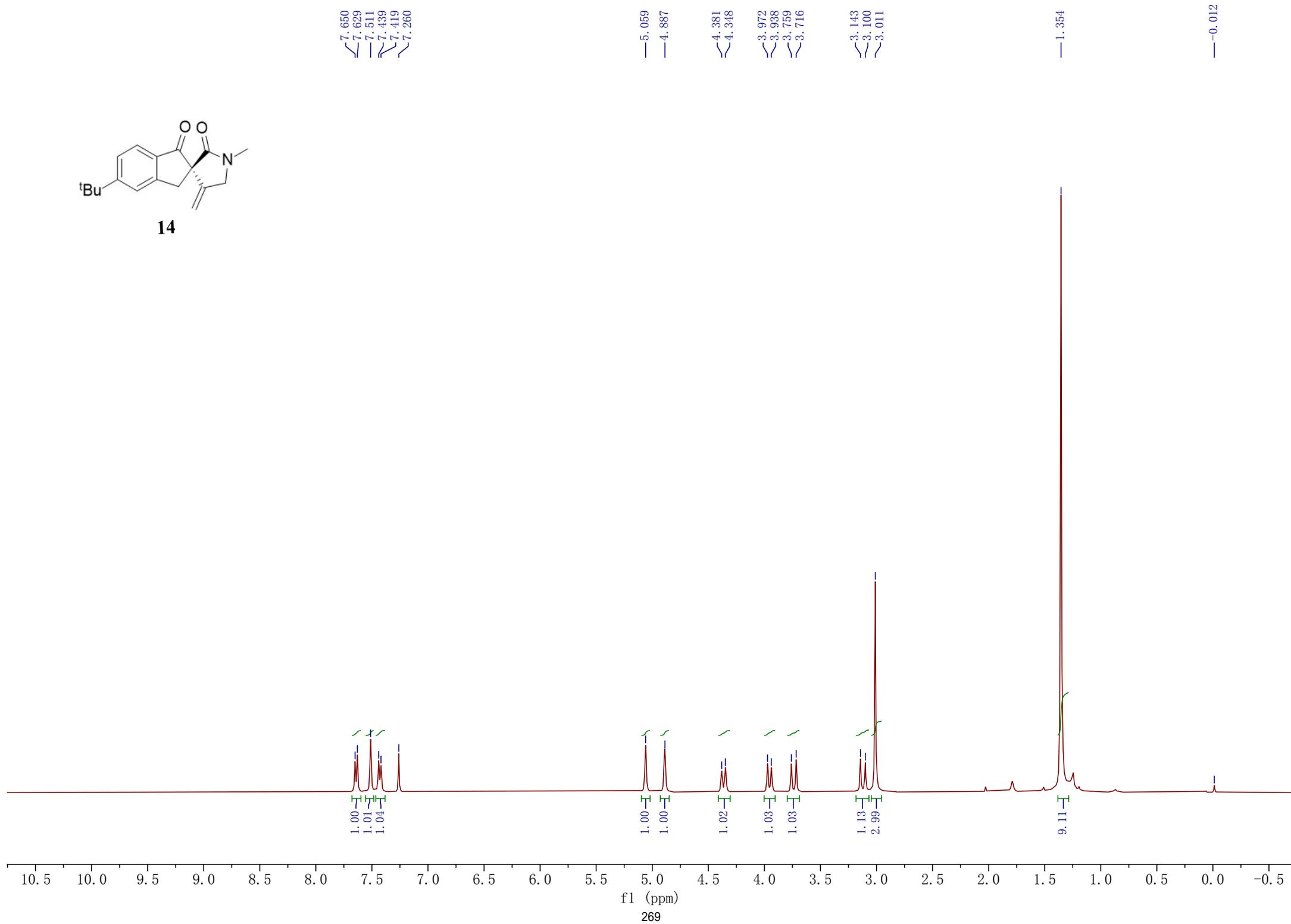
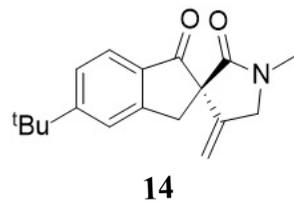
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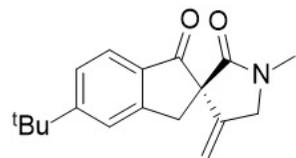




13







14

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—171.988

—159.855

—154.428

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—107.661

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76.842

—64.232

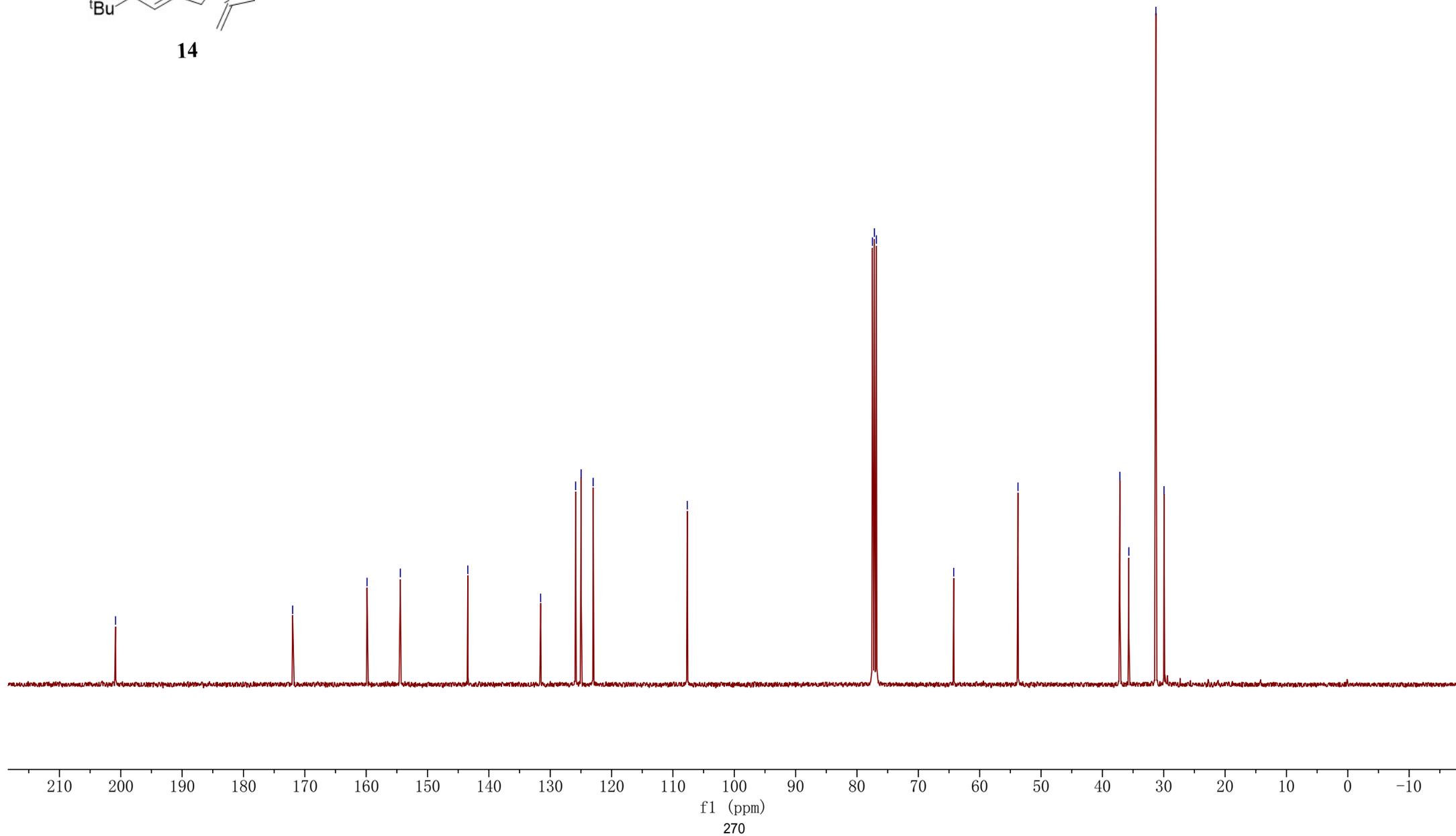
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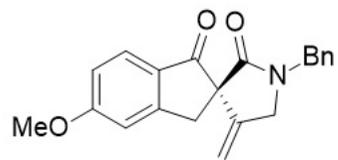
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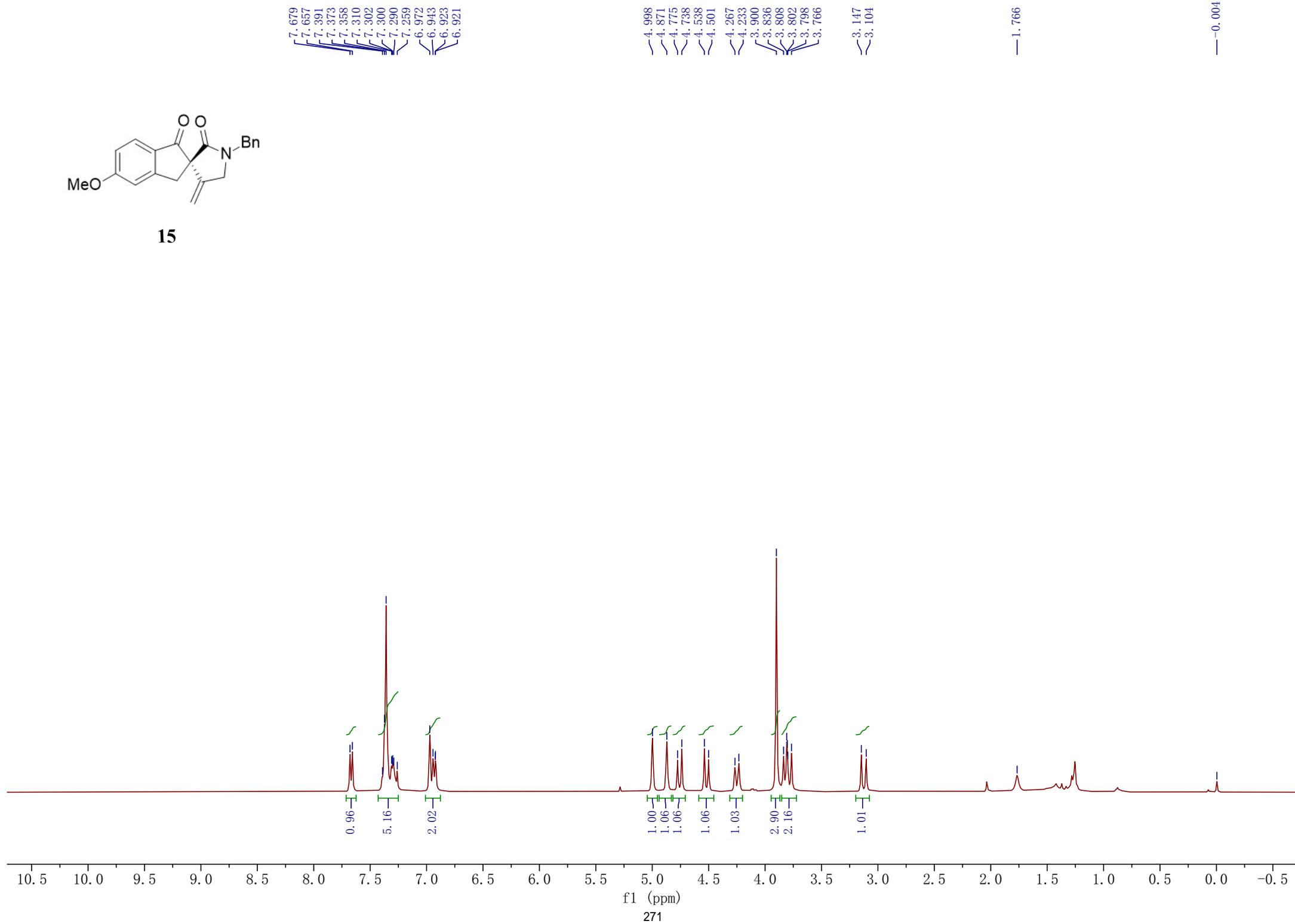
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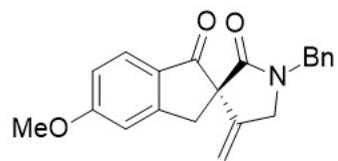
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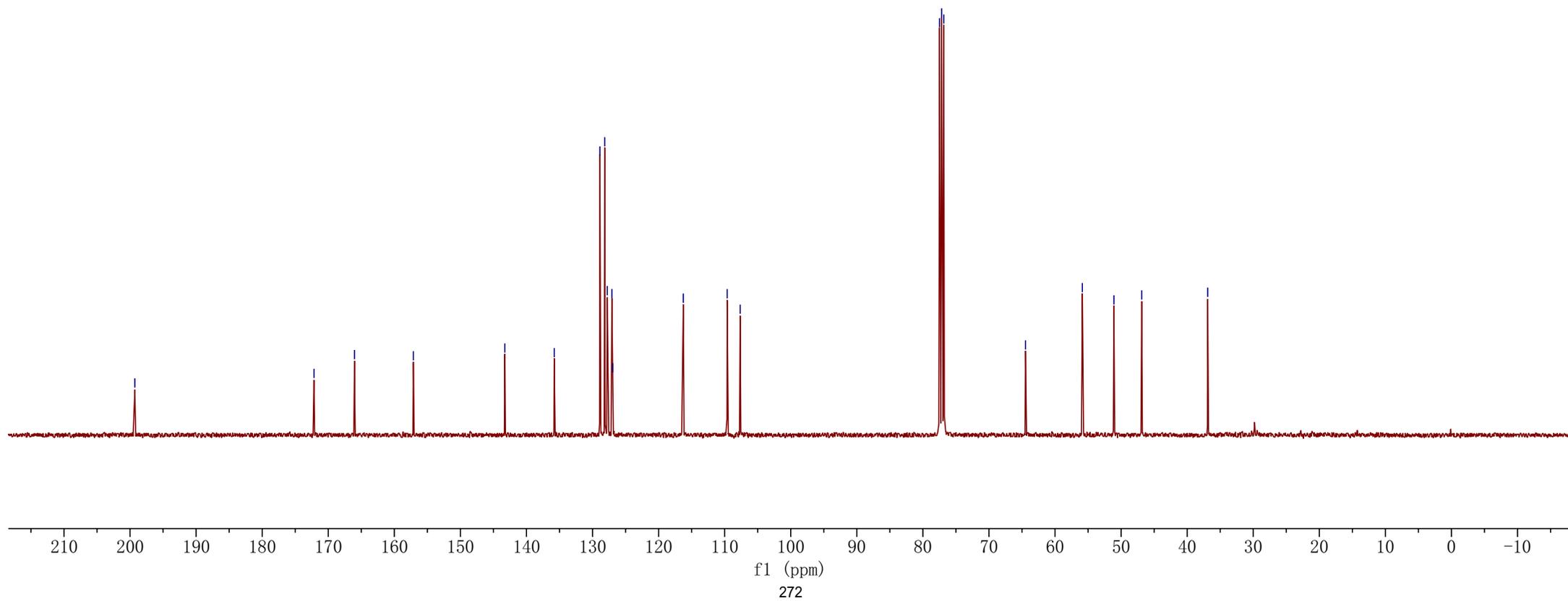


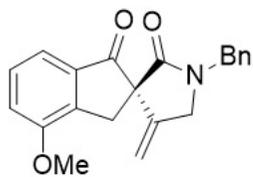


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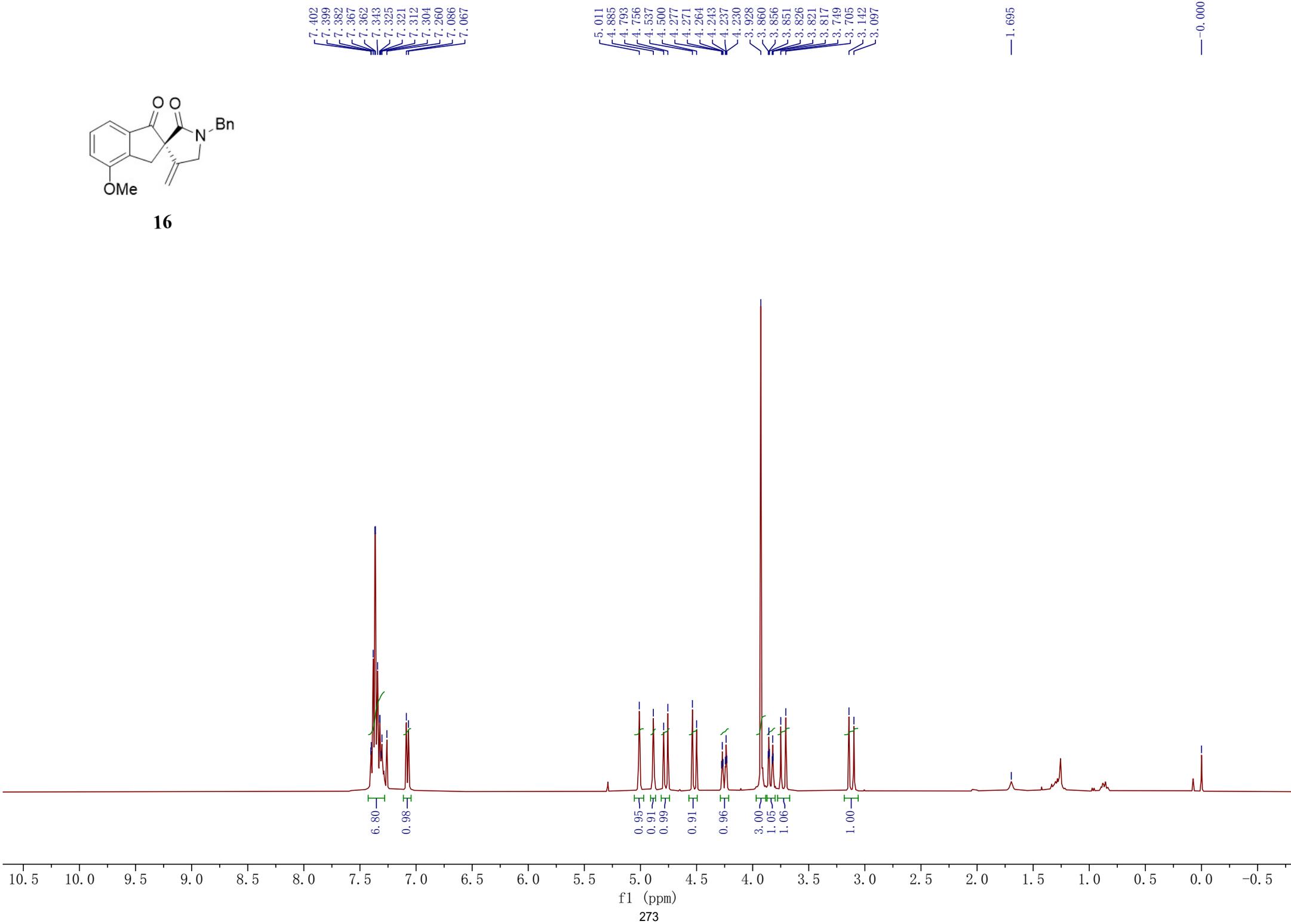
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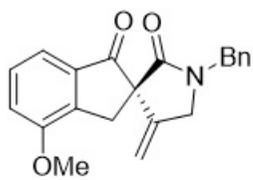
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— 36.891





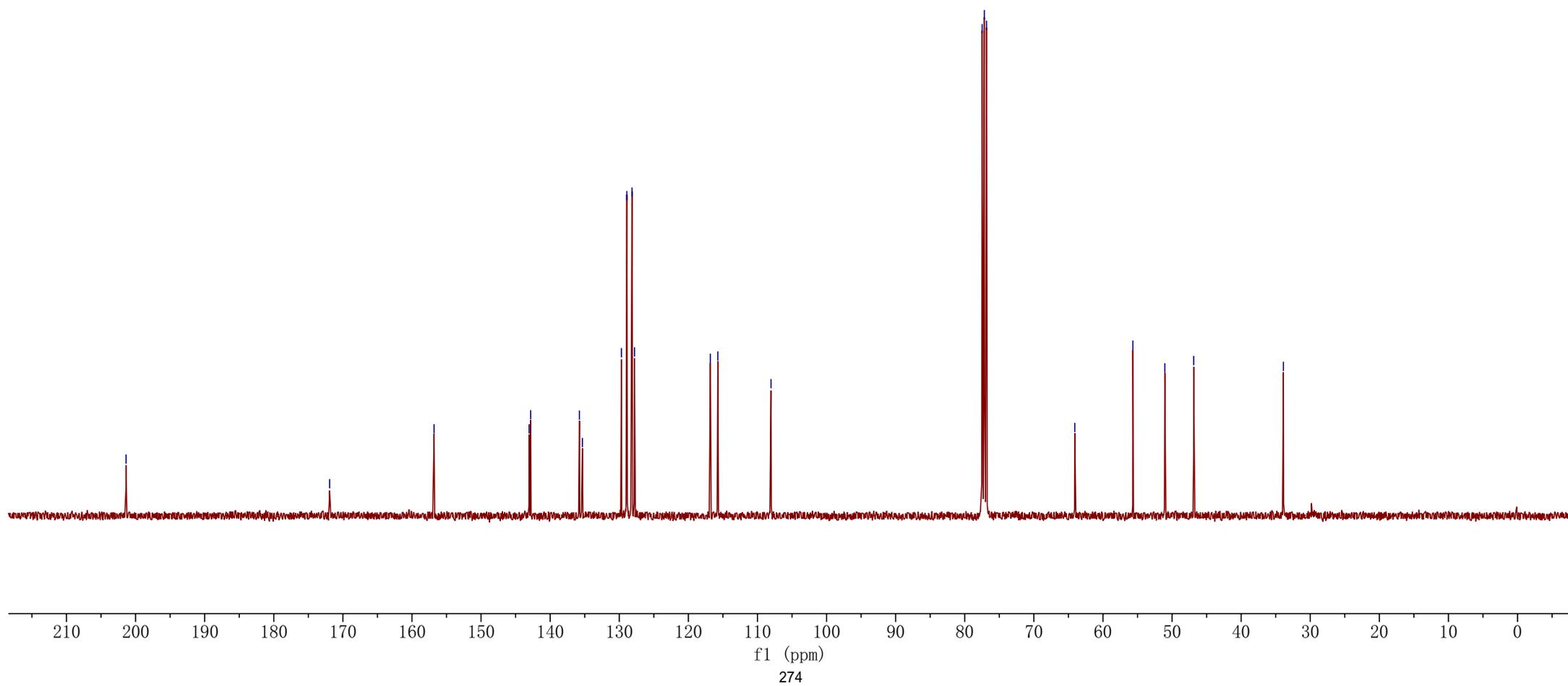
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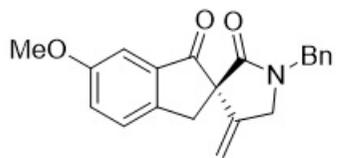




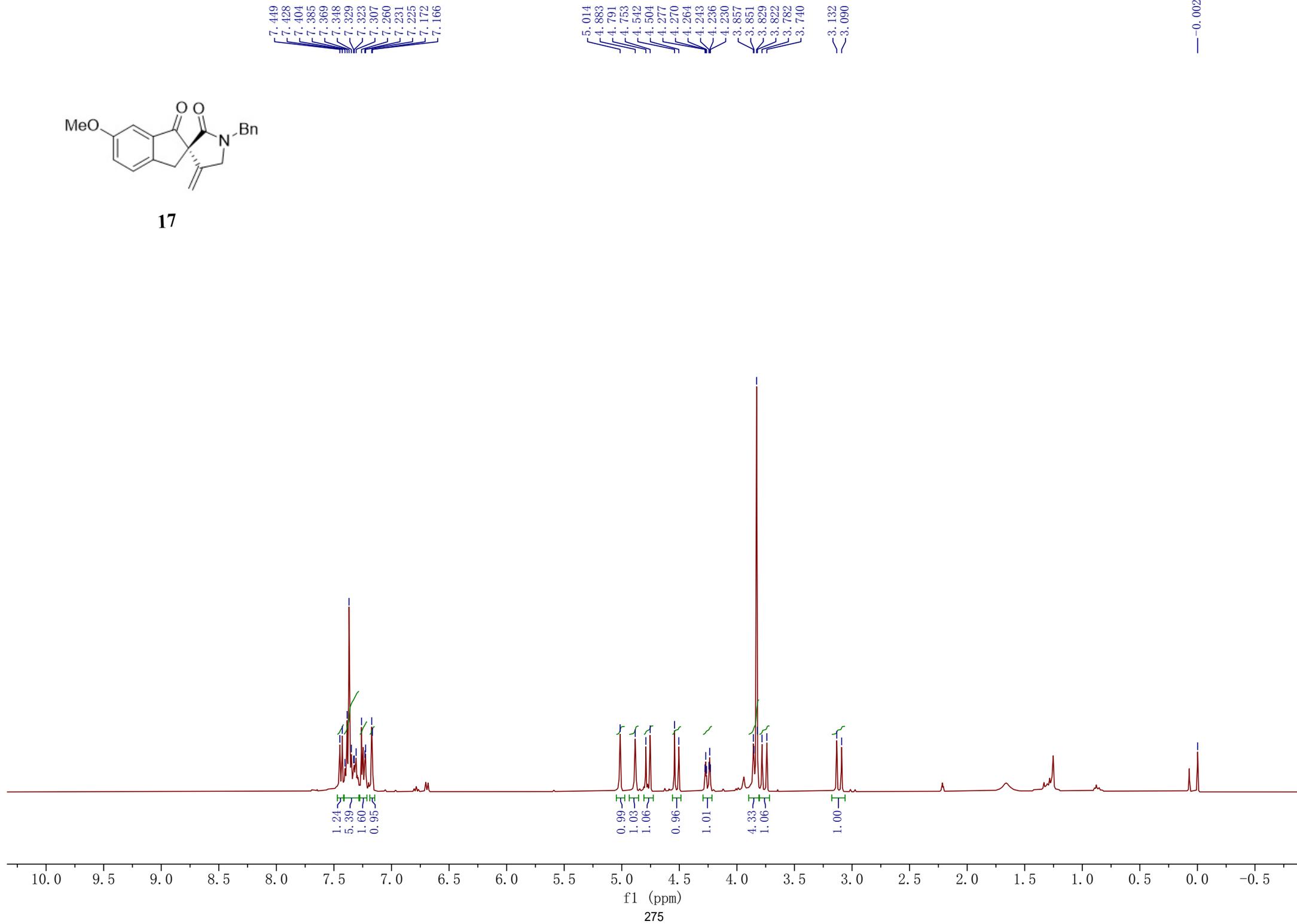
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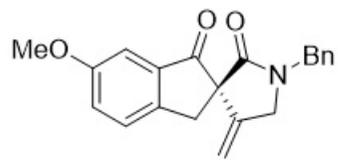
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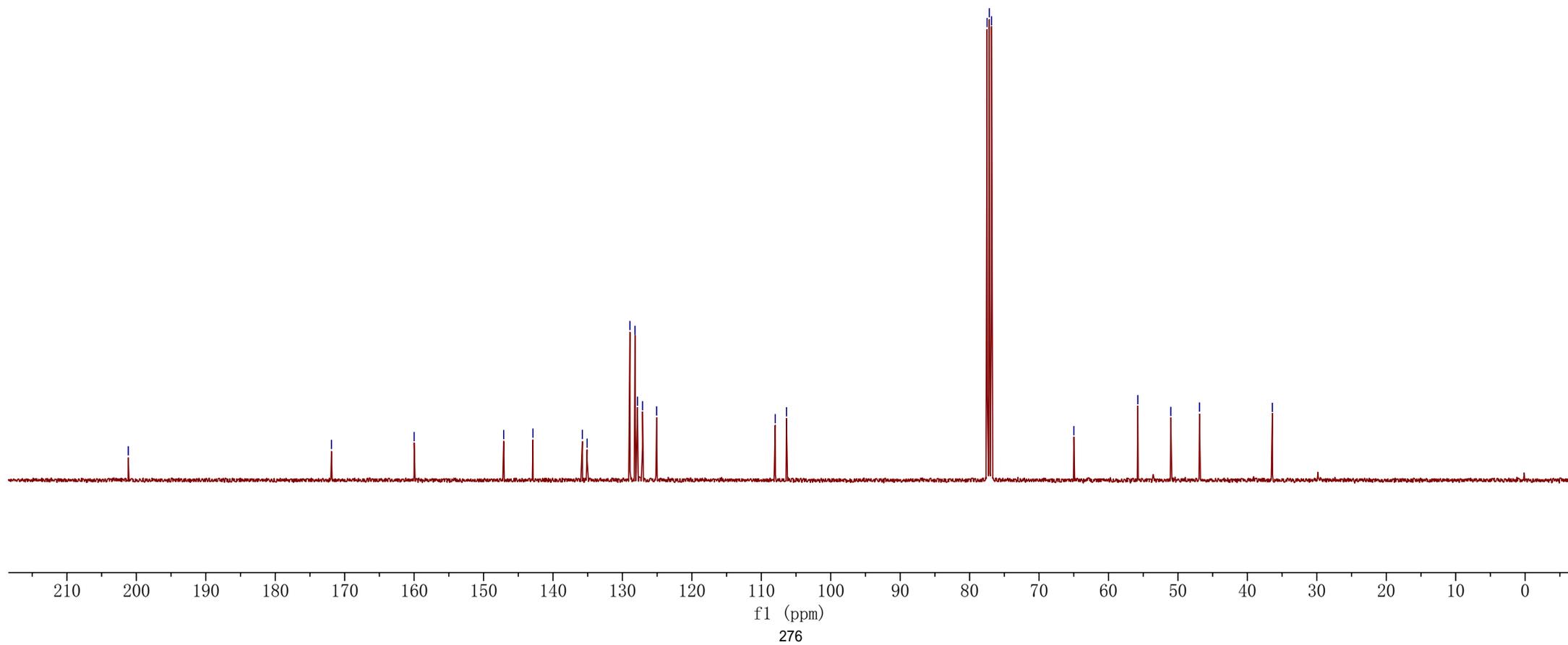
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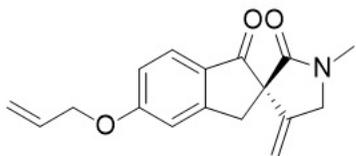




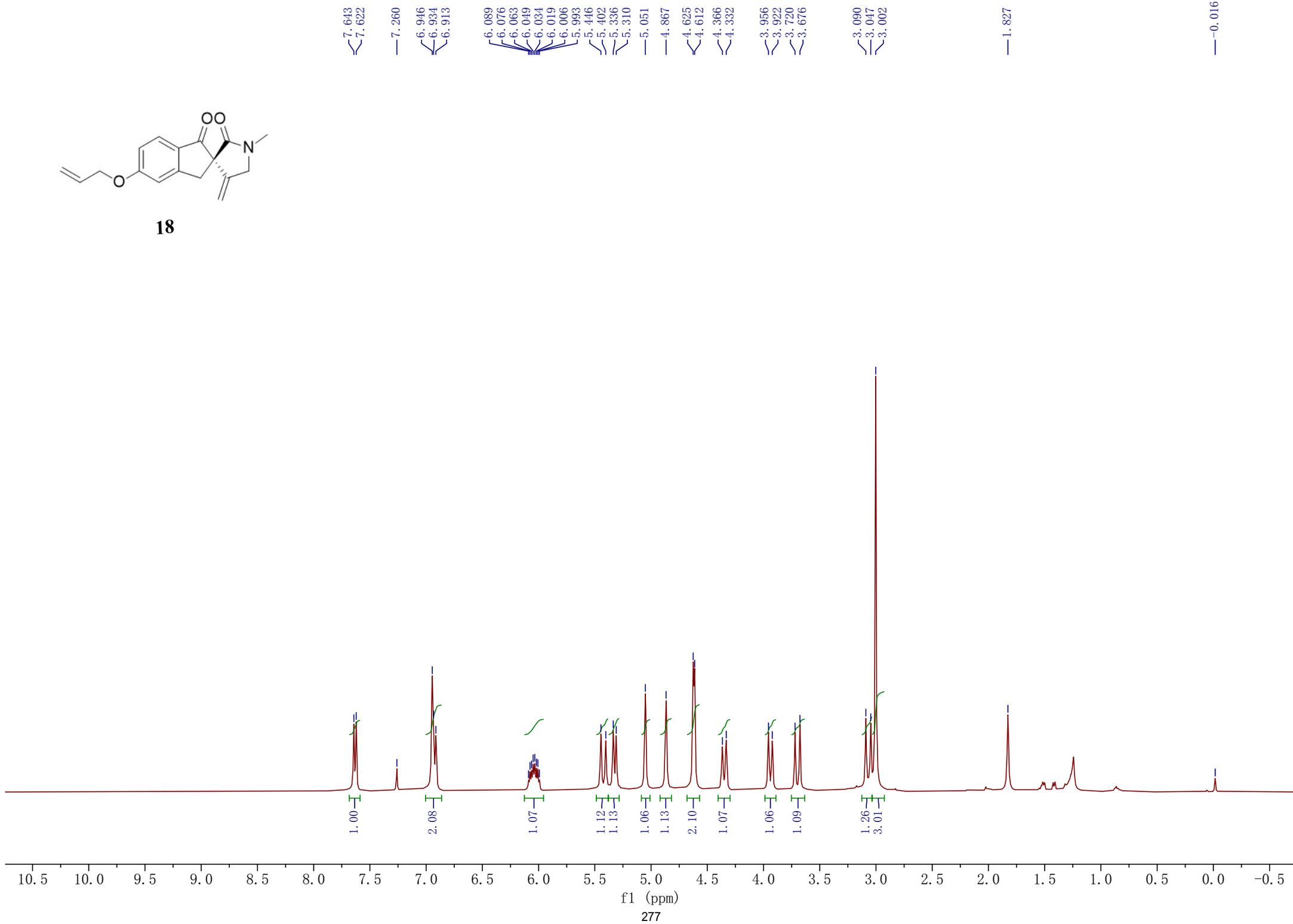
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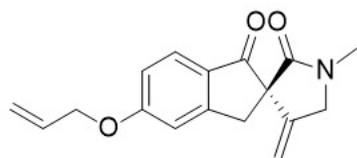
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18

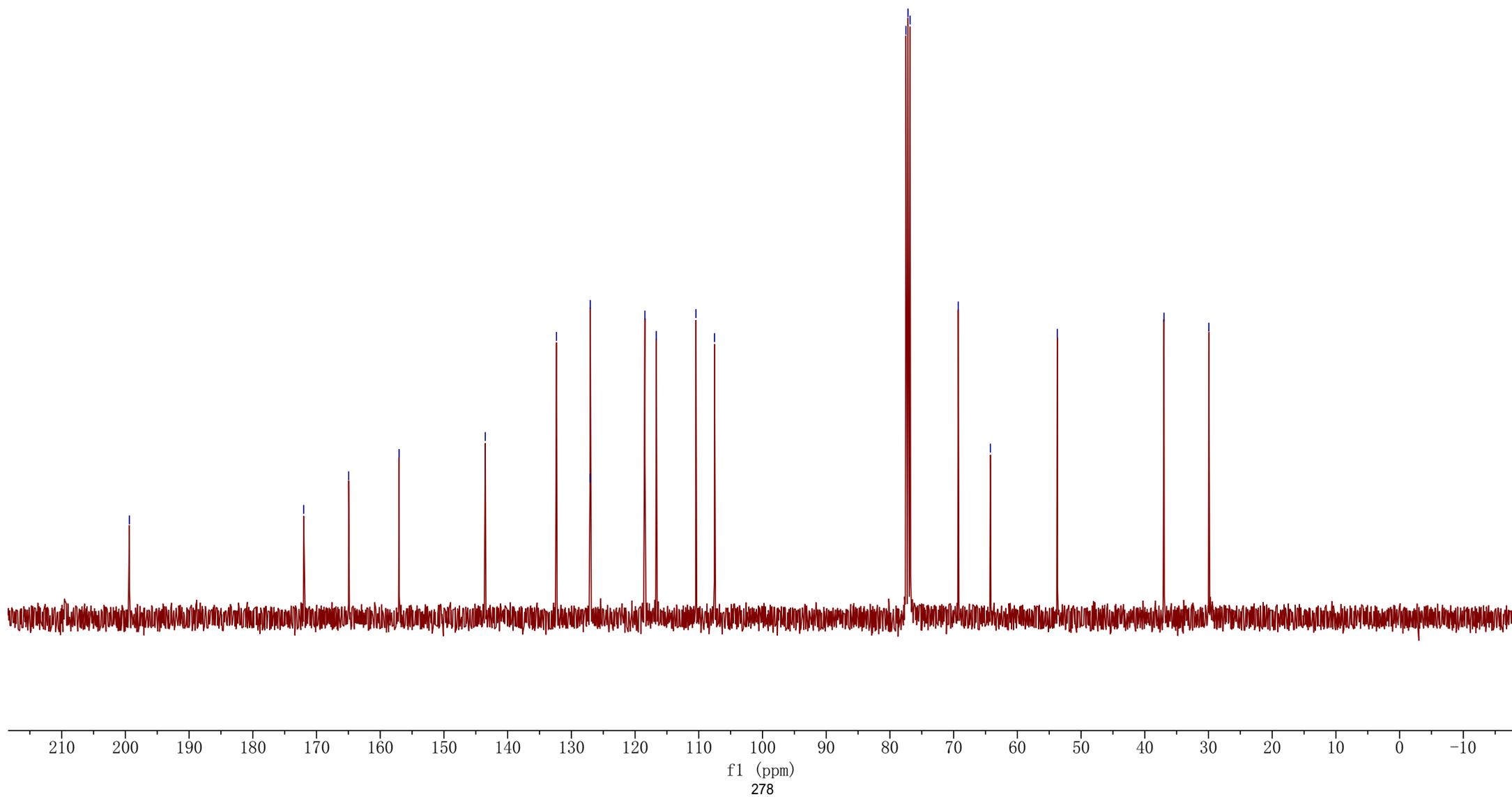


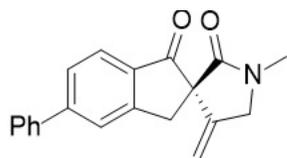


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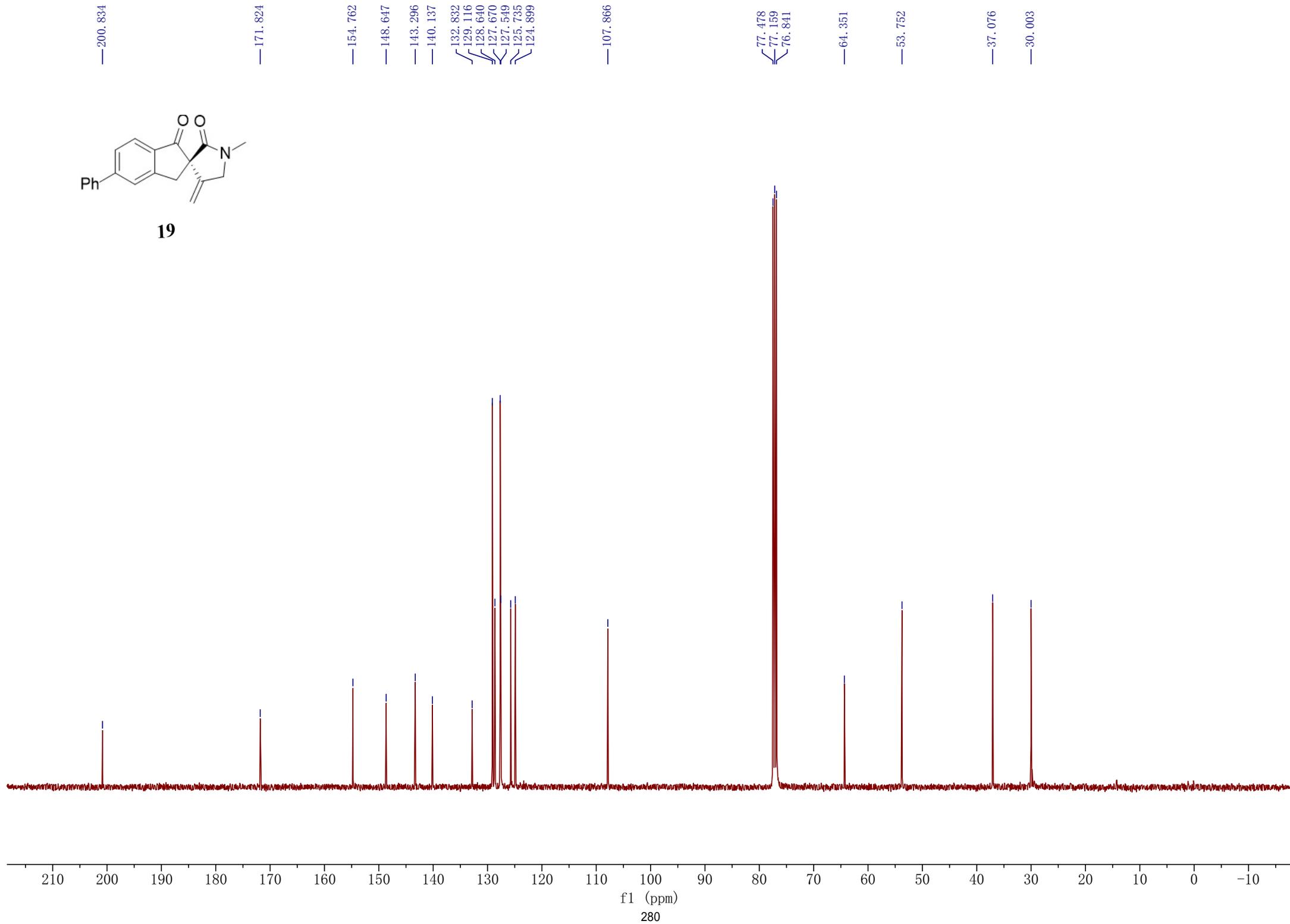
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— 157.037
— 143.512
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— 127.081
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— 118.462
— 116.674
— 110.446
— 107.532

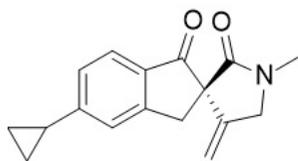
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76.842
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— 36.980
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19





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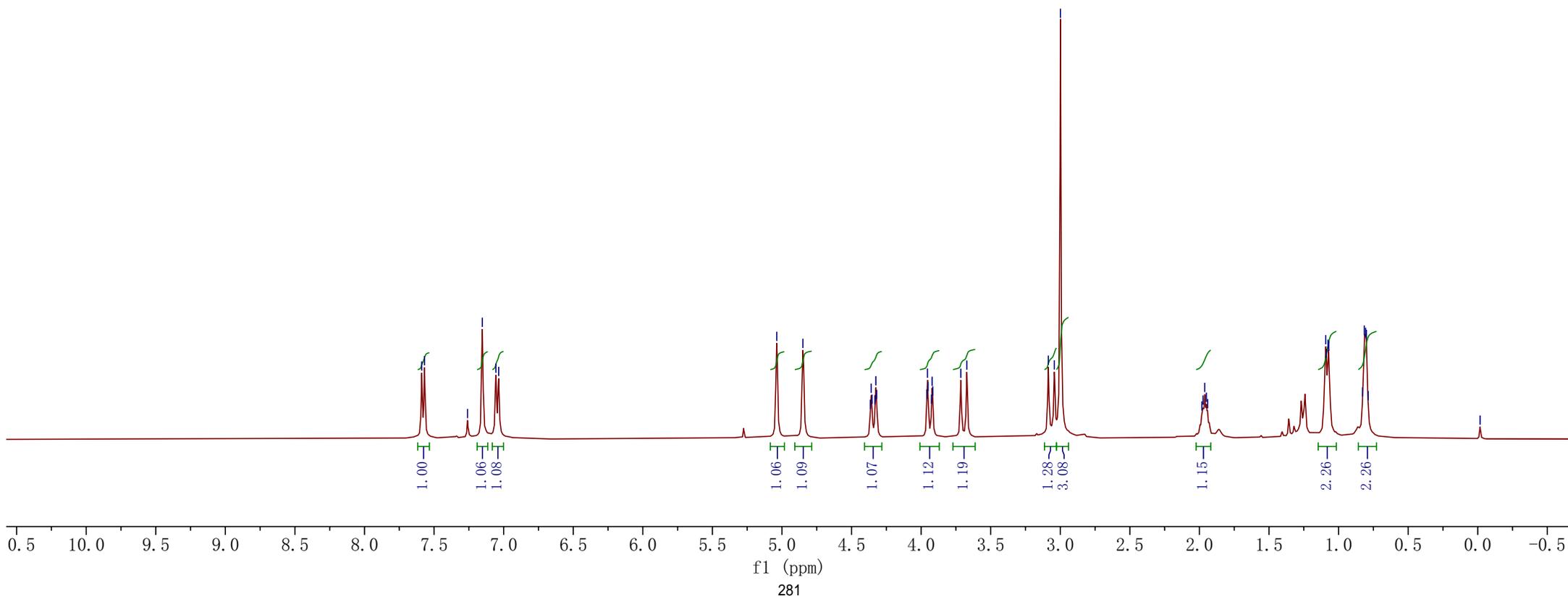
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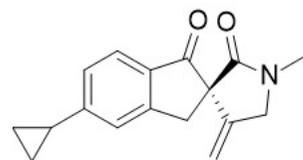
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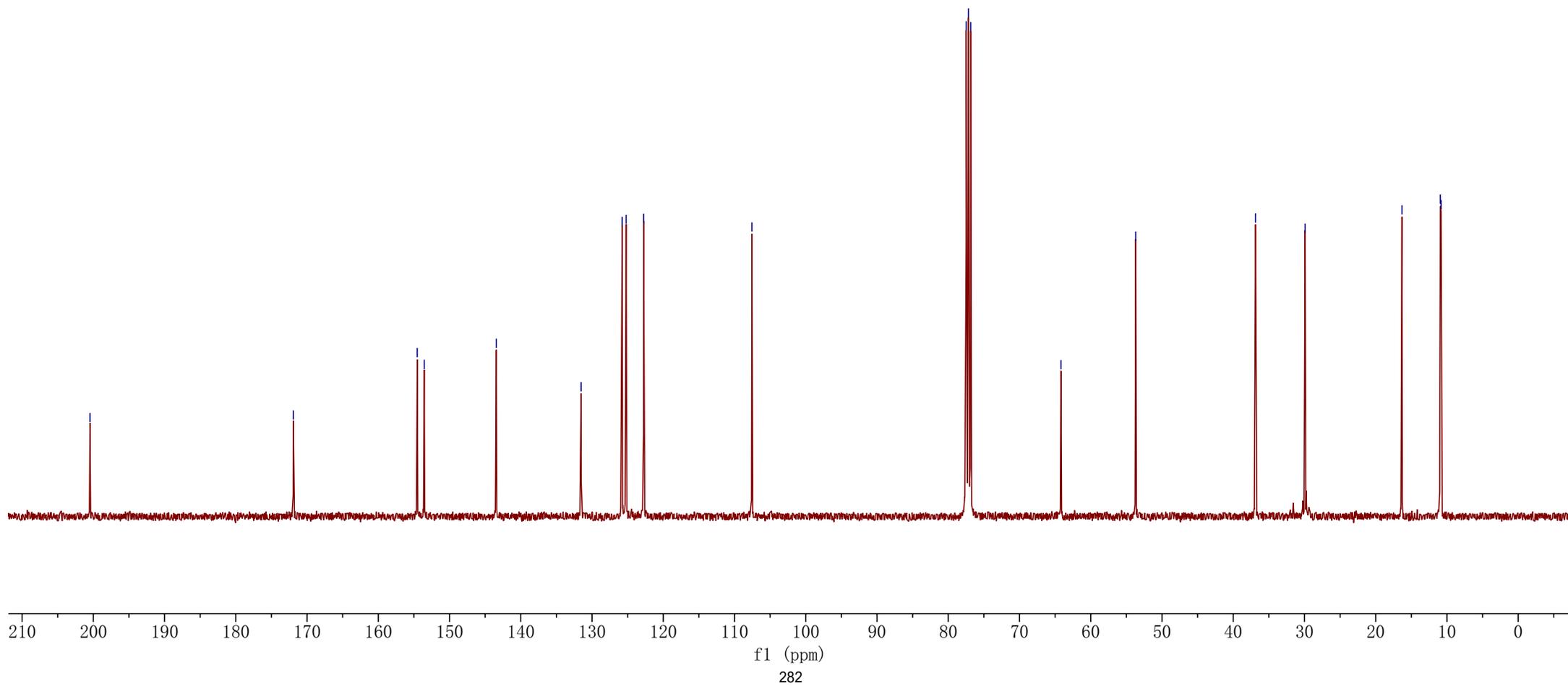
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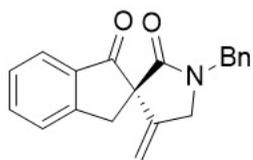




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- 29.910
- 16.318
- 10.940
- 10.825





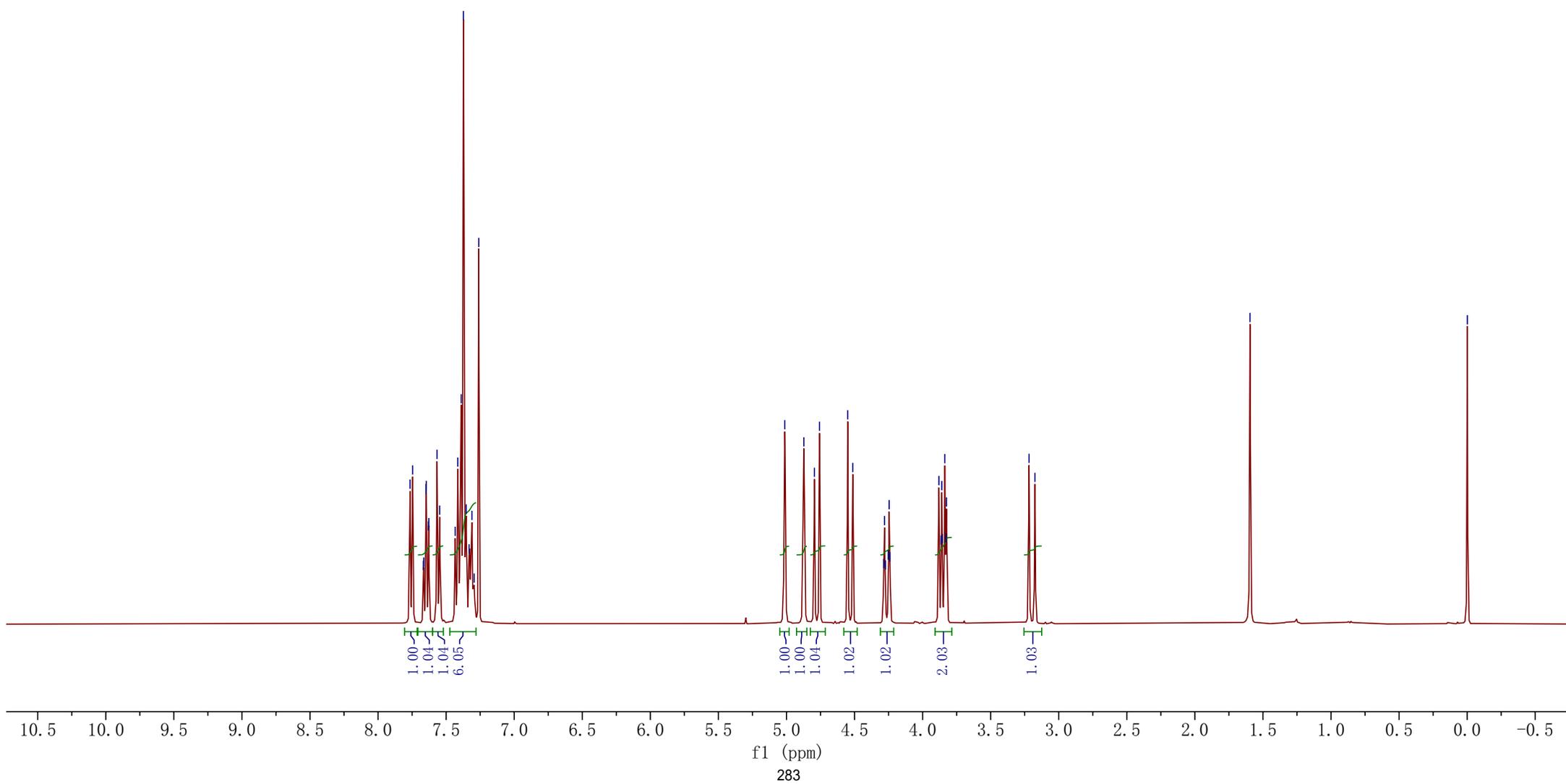
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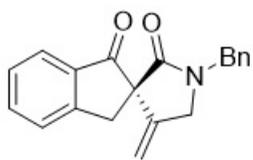
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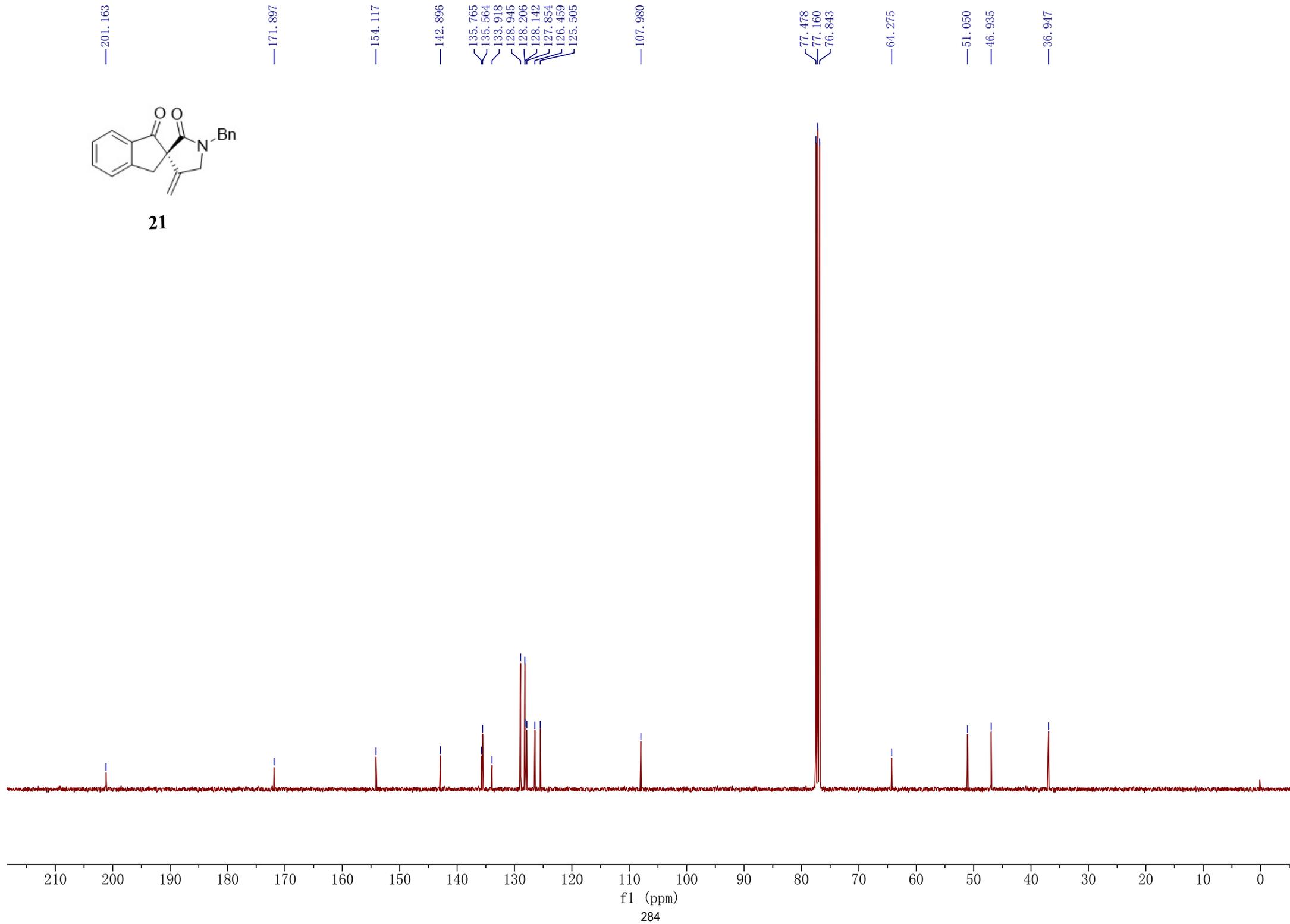
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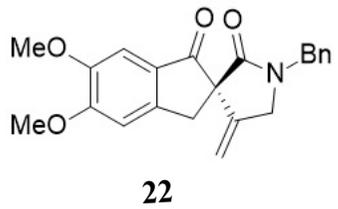
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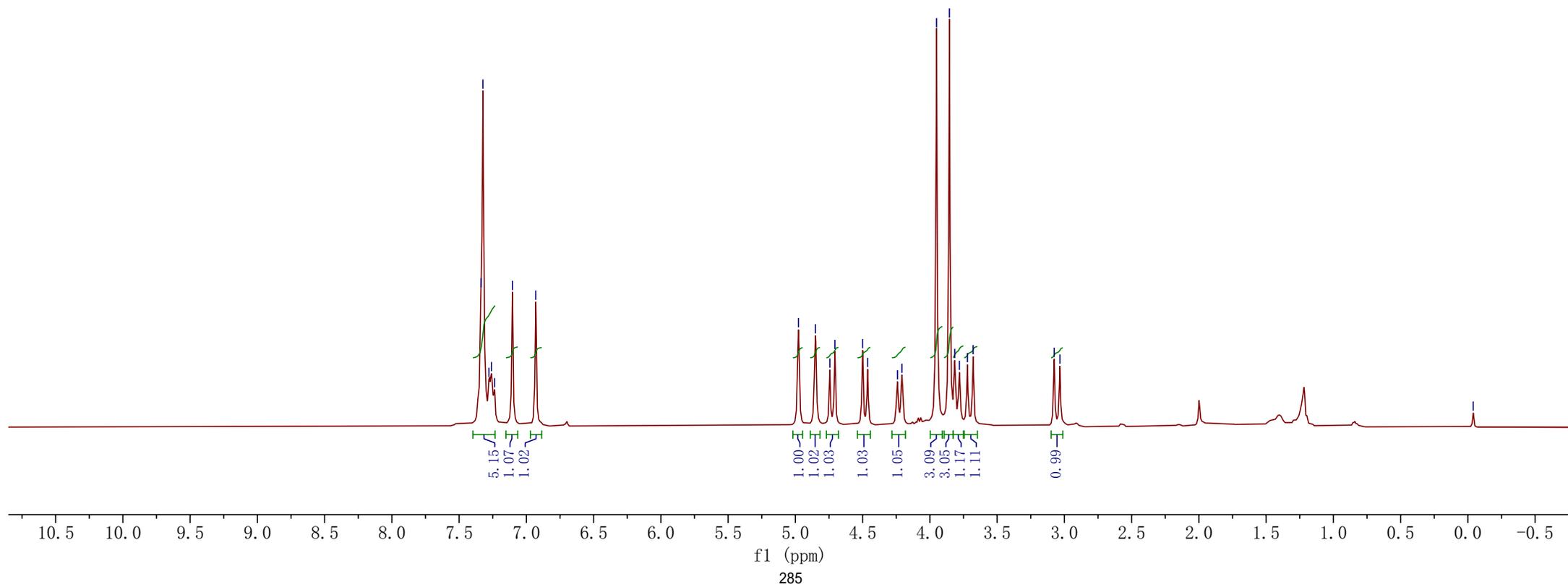


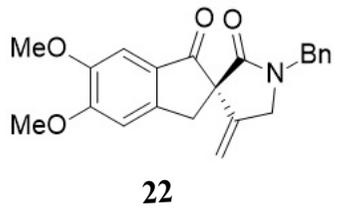
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3.721
3.678

3.076
3.033

-0.040





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—156.217

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—143.127

—135.759

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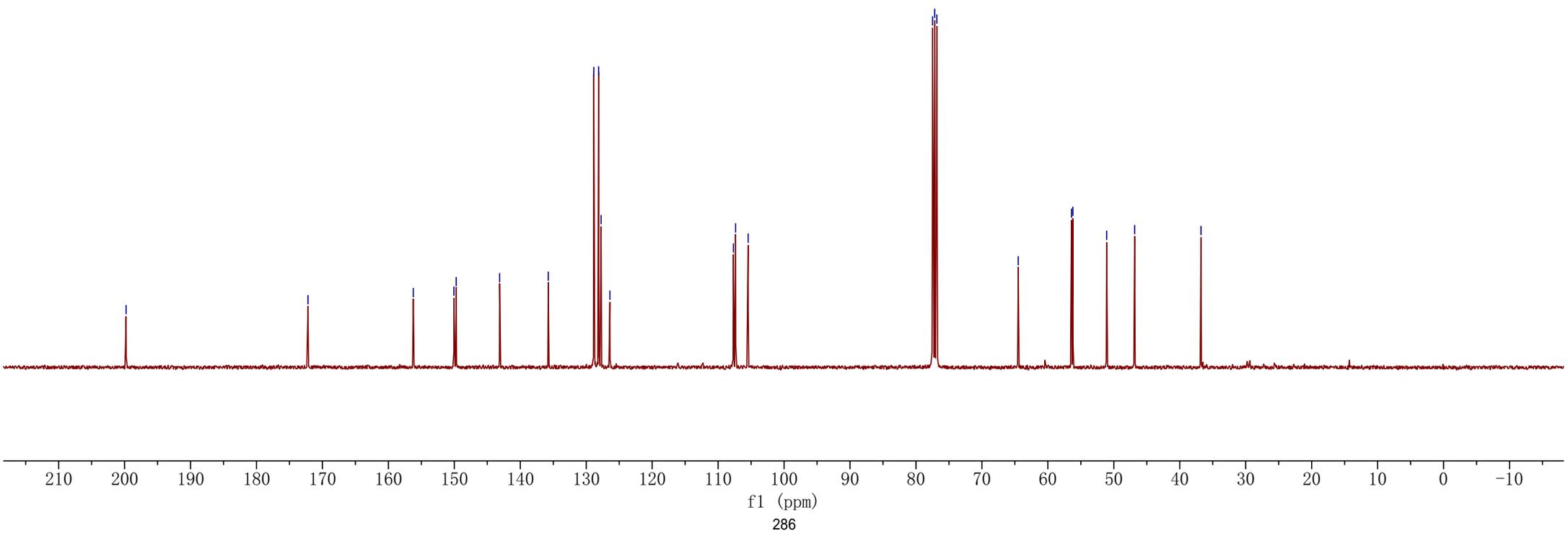
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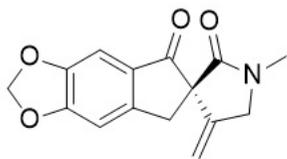
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—6.065

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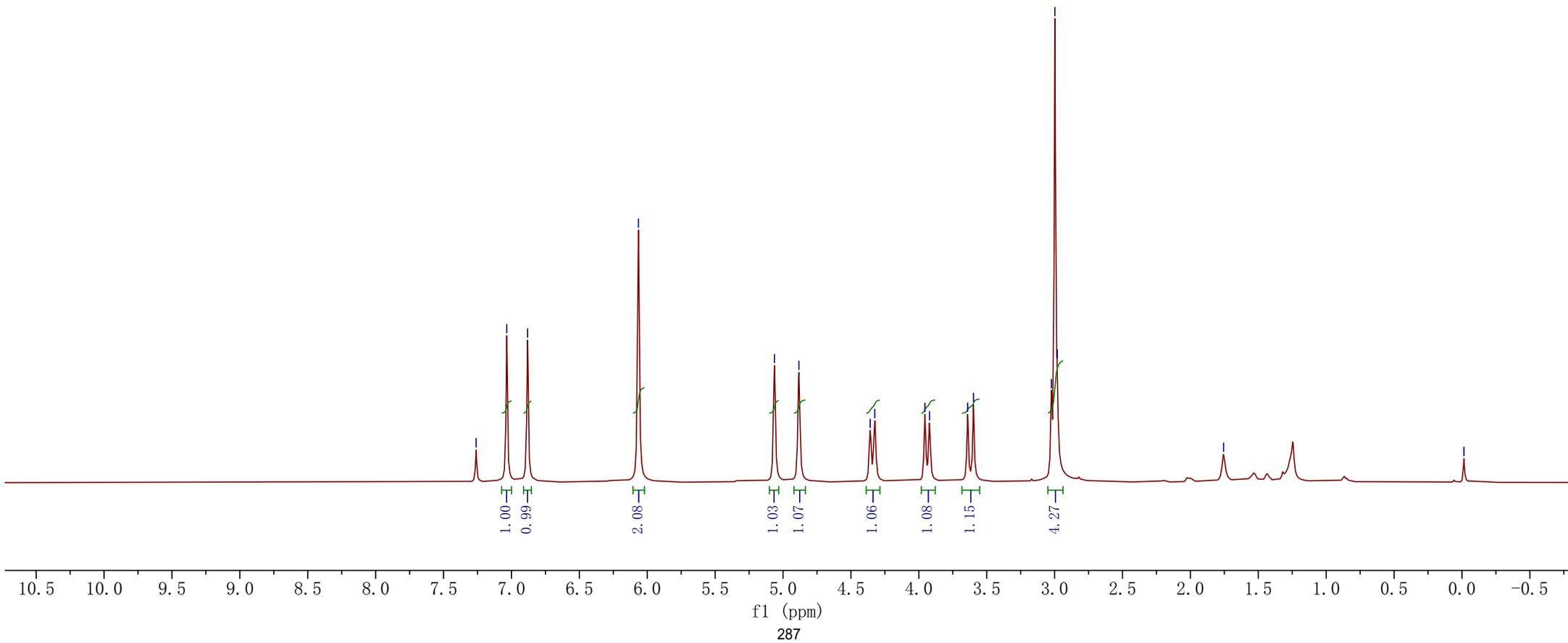
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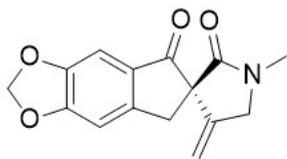
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—0.014





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—77.160

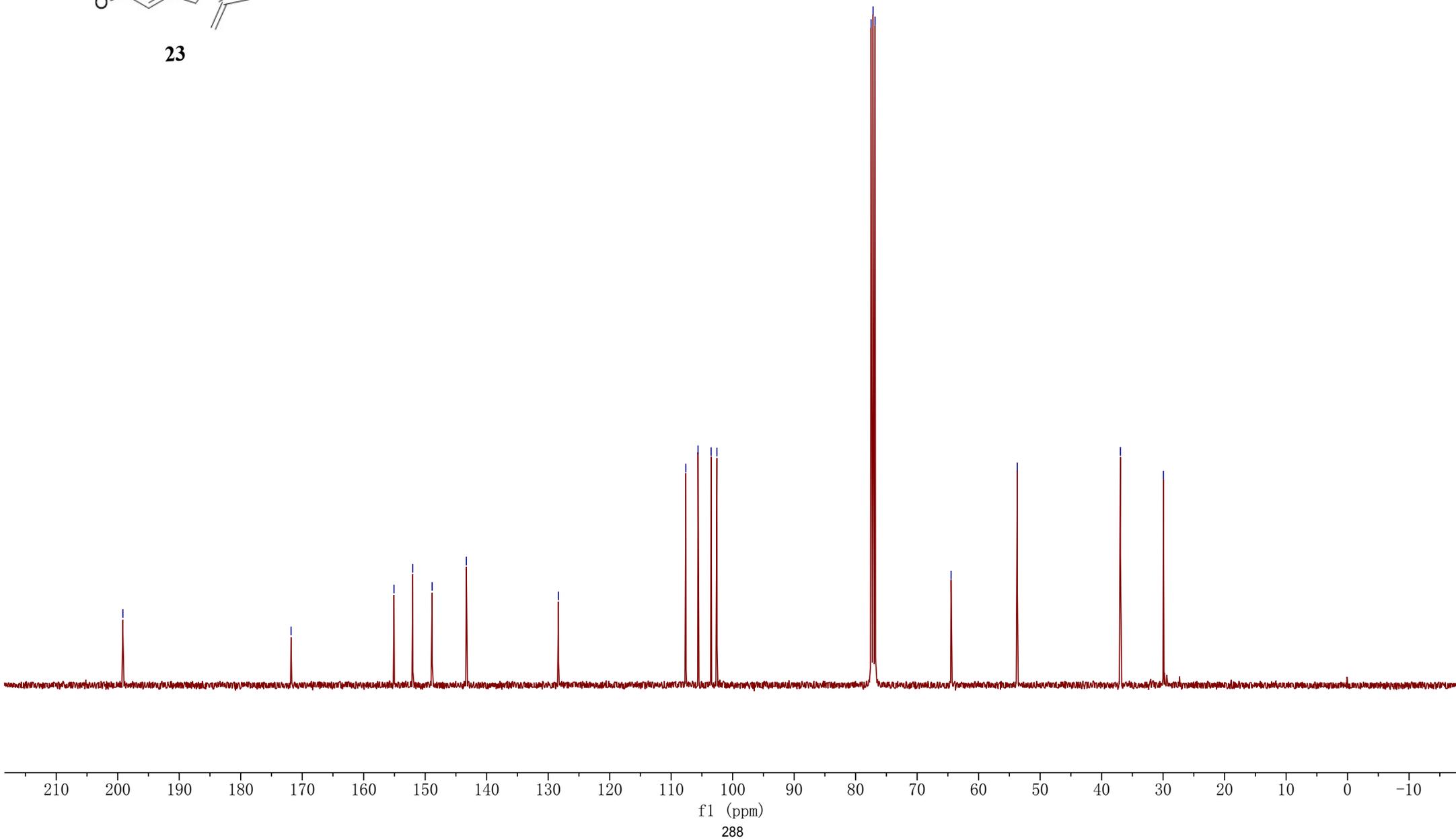
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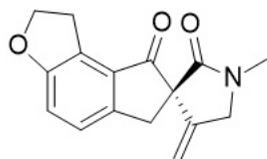
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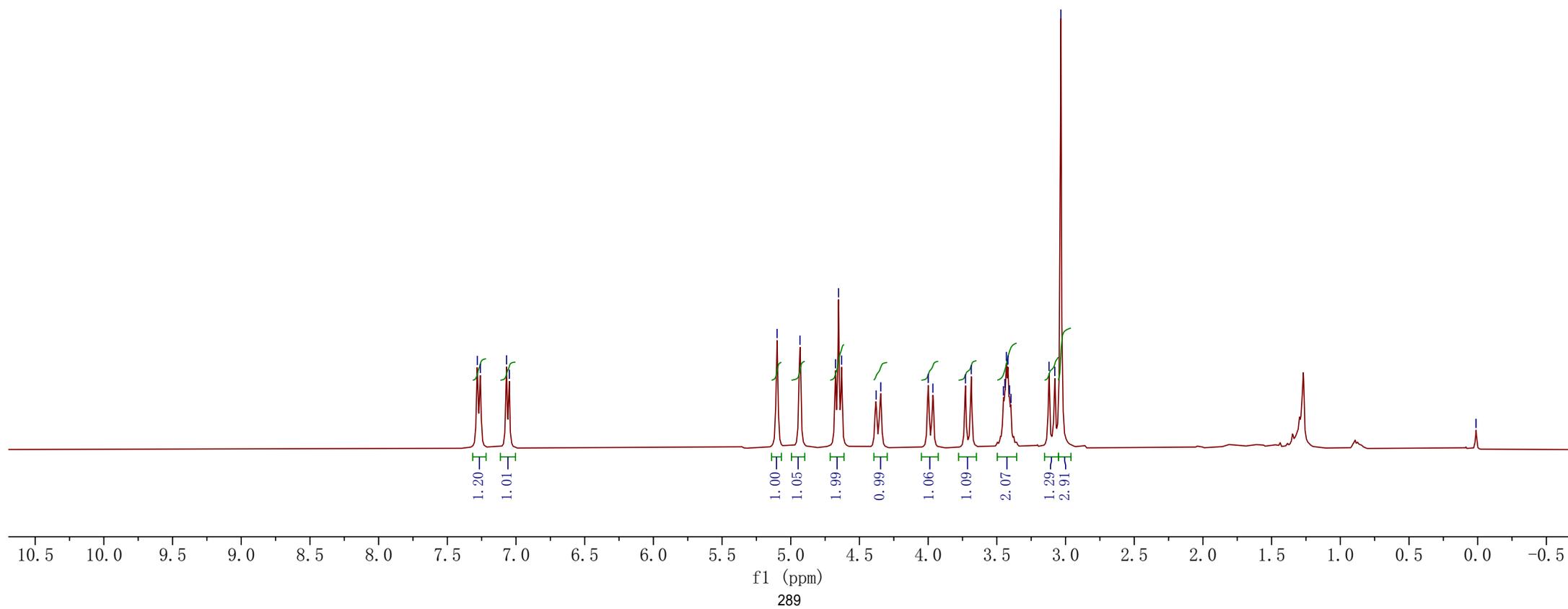
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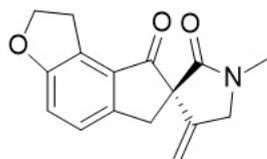
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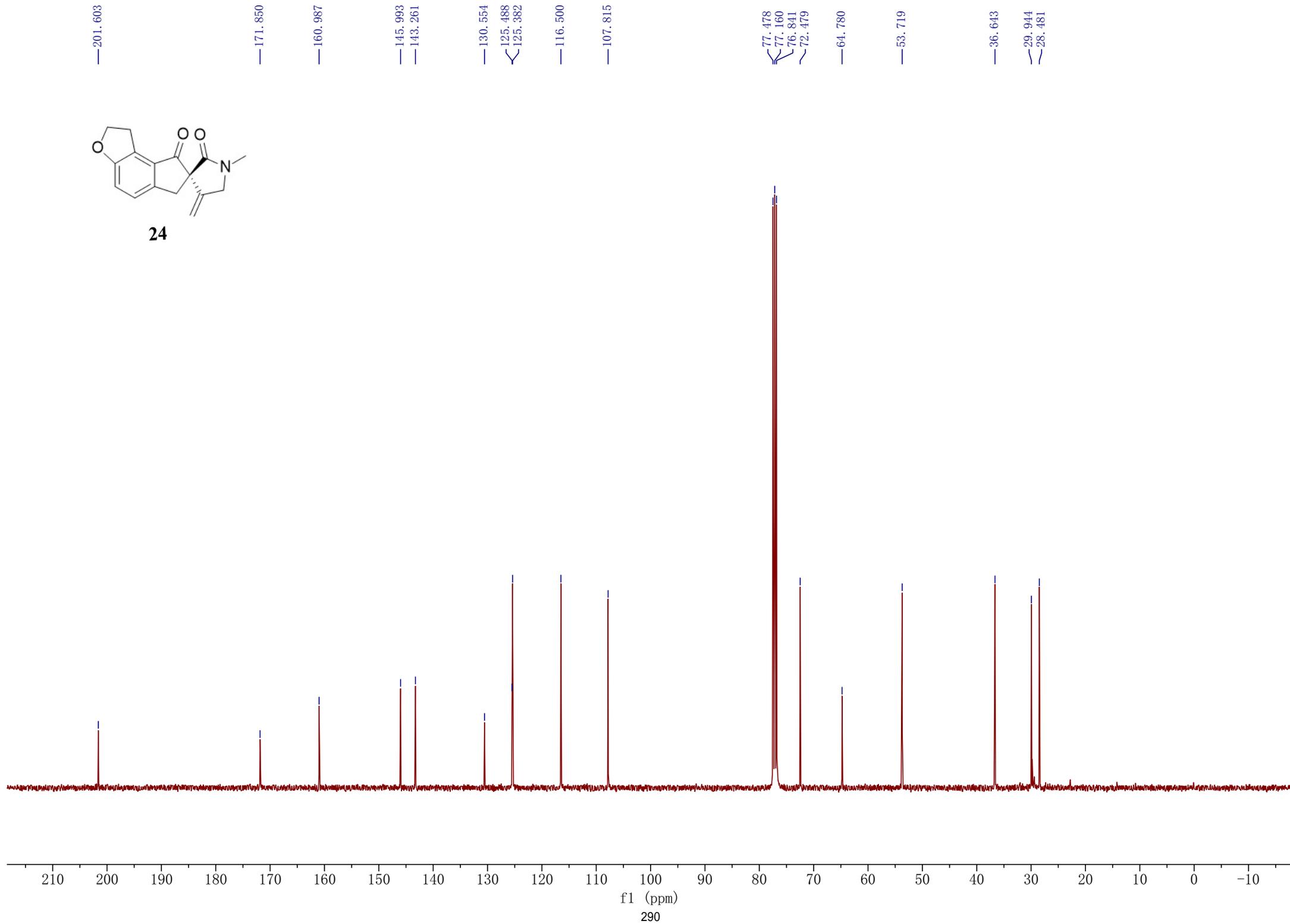
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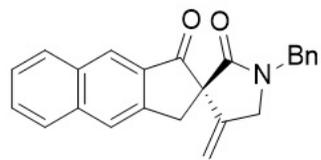
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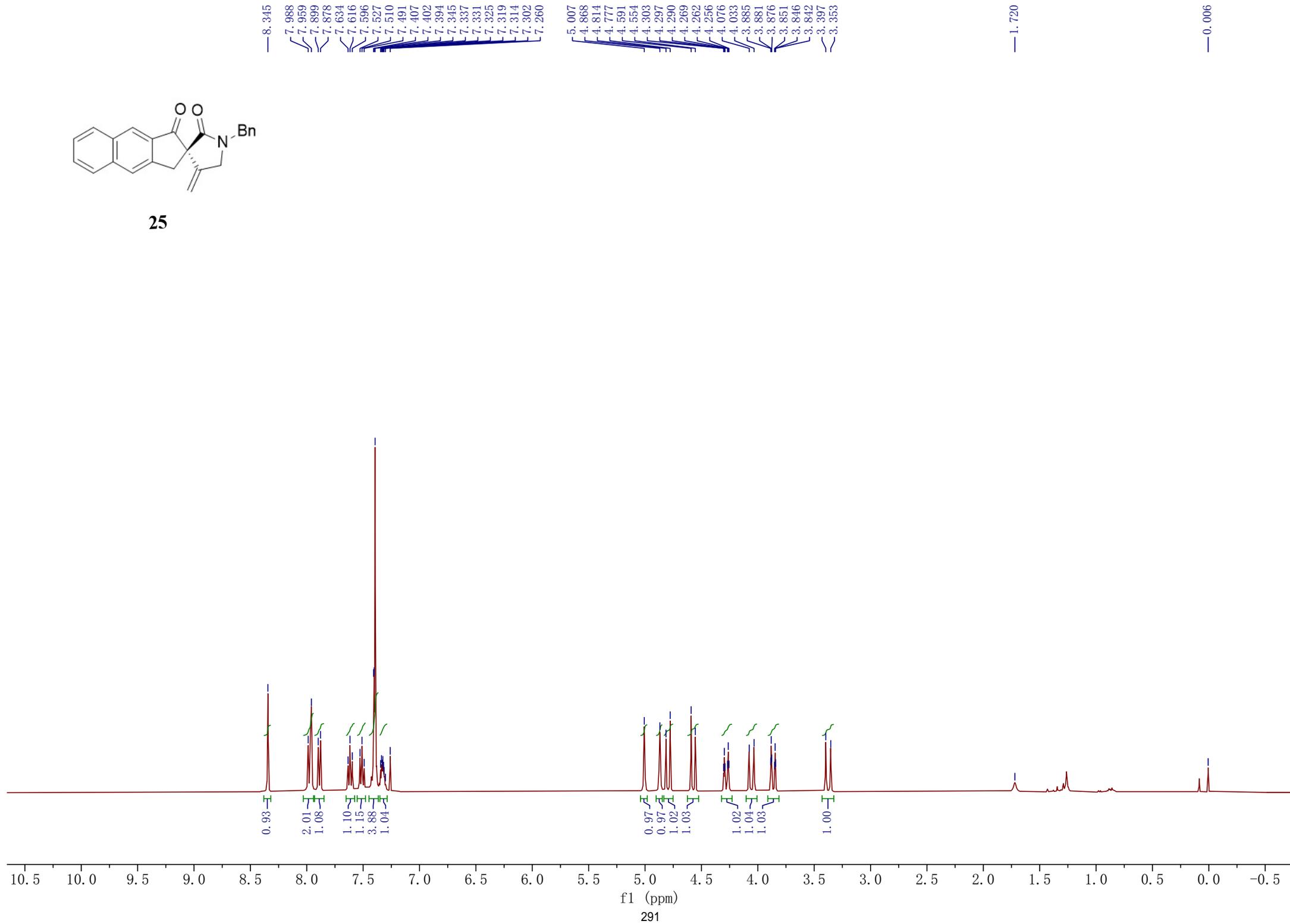


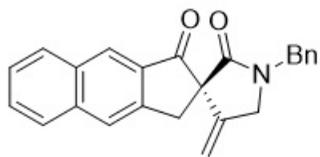
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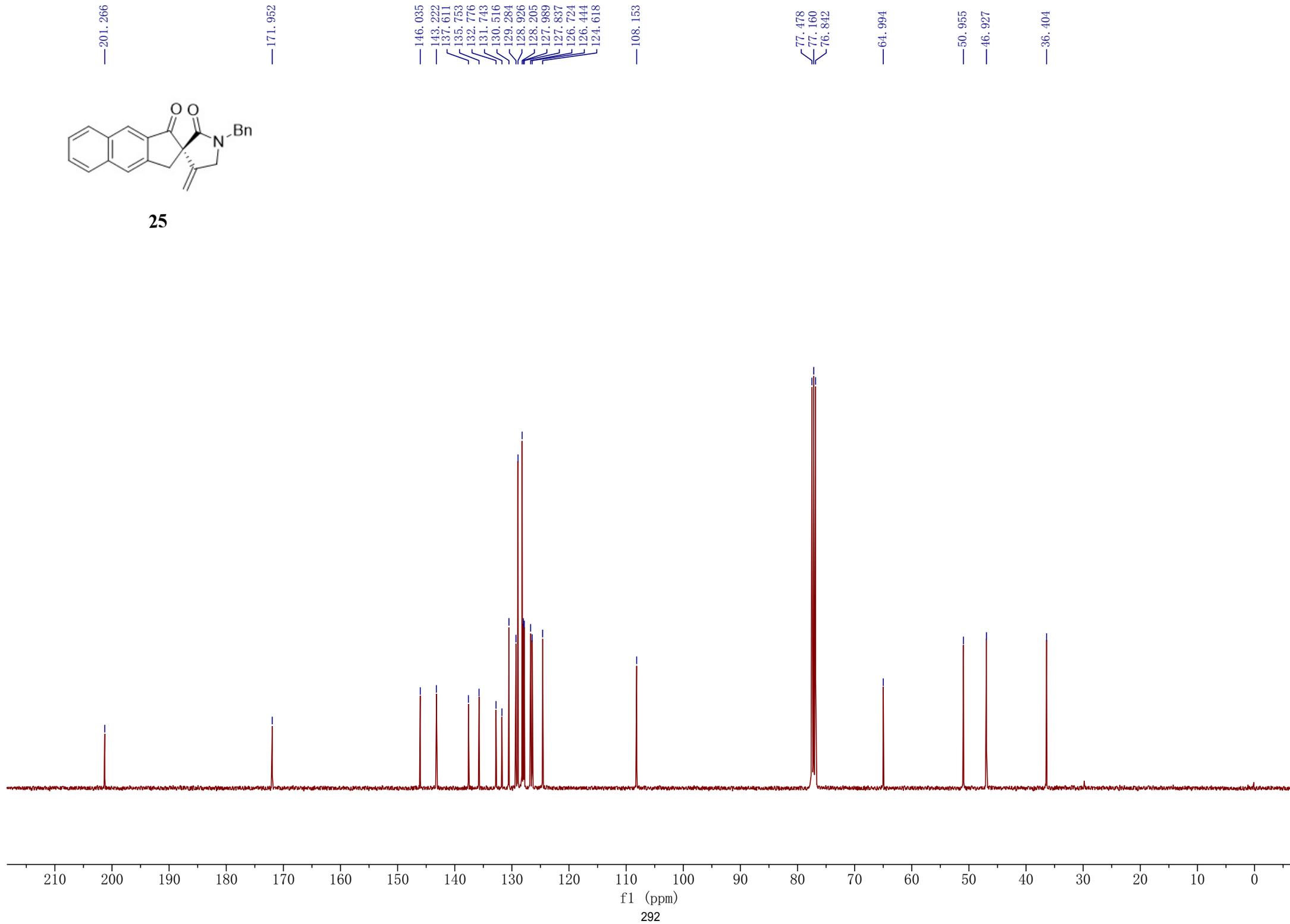


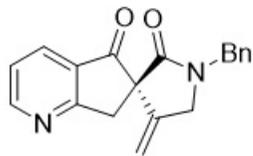
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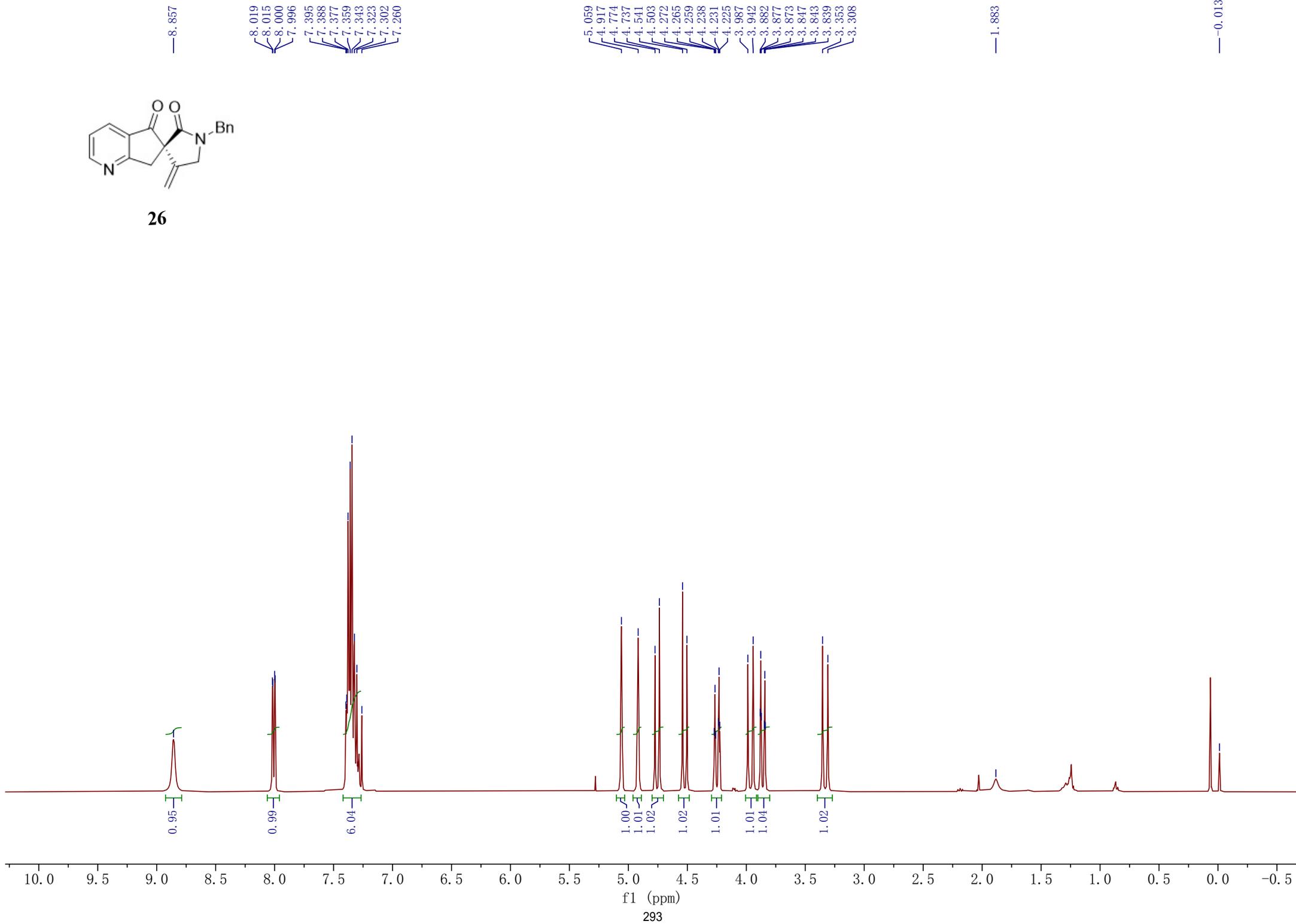


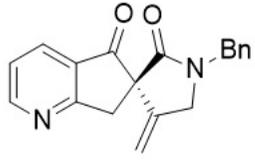
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— 123.262

— 108.656

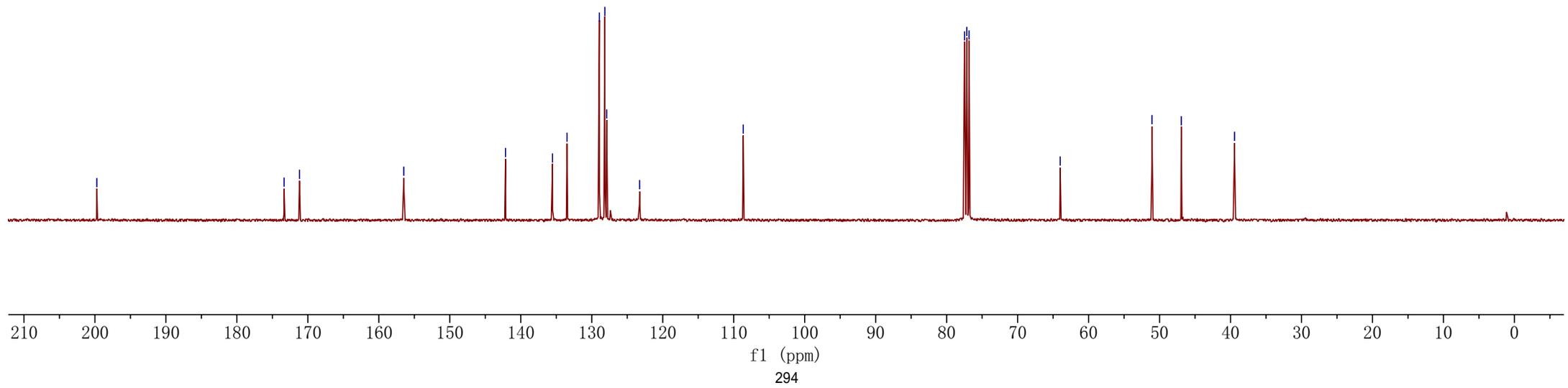
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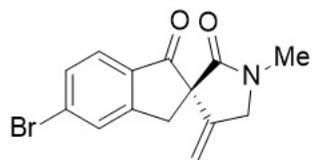
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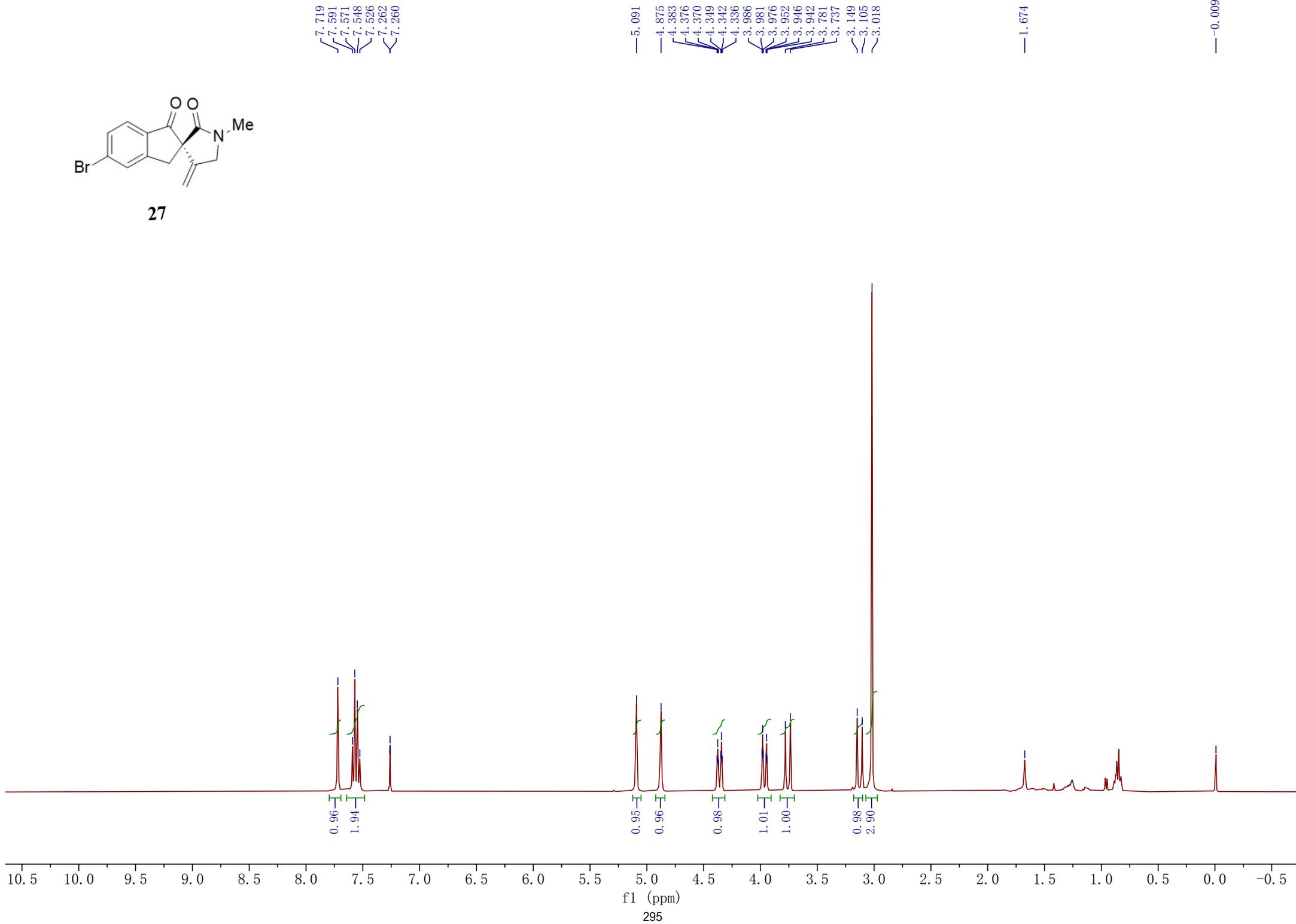
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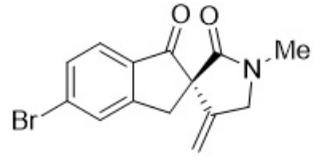
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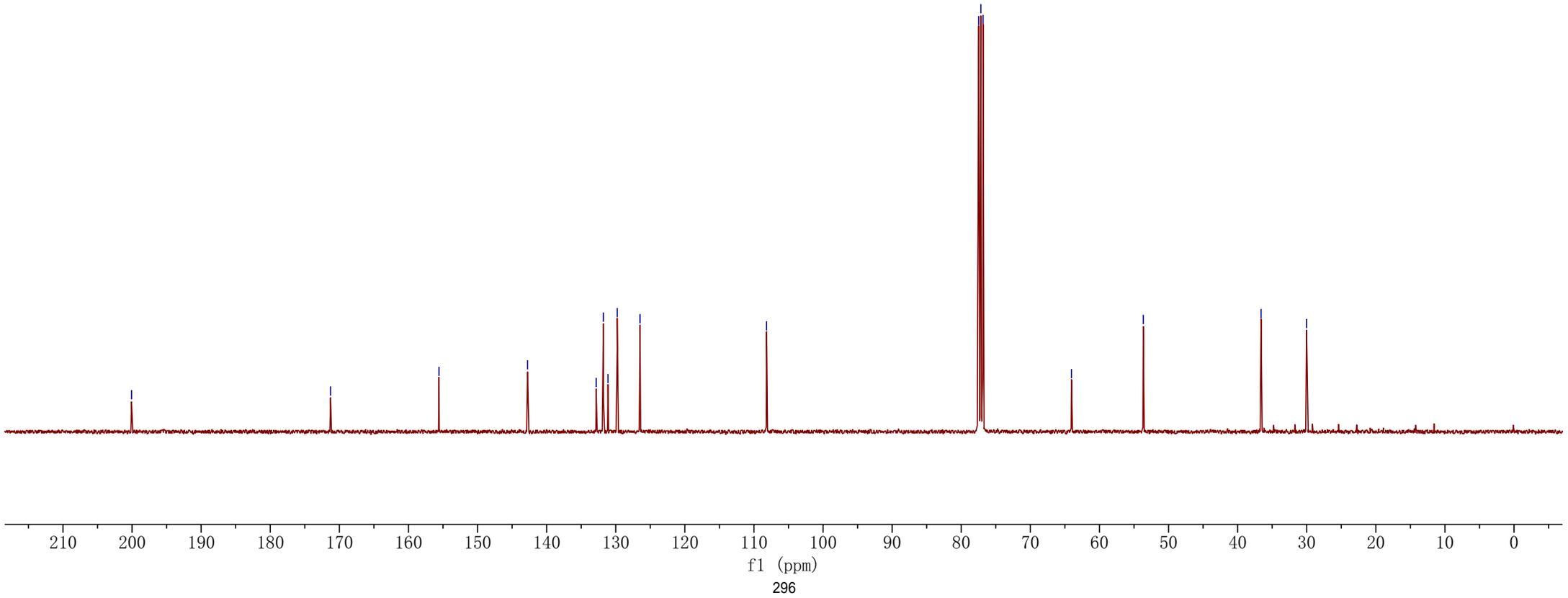
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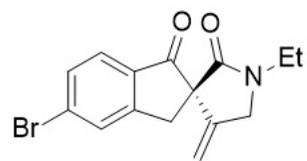
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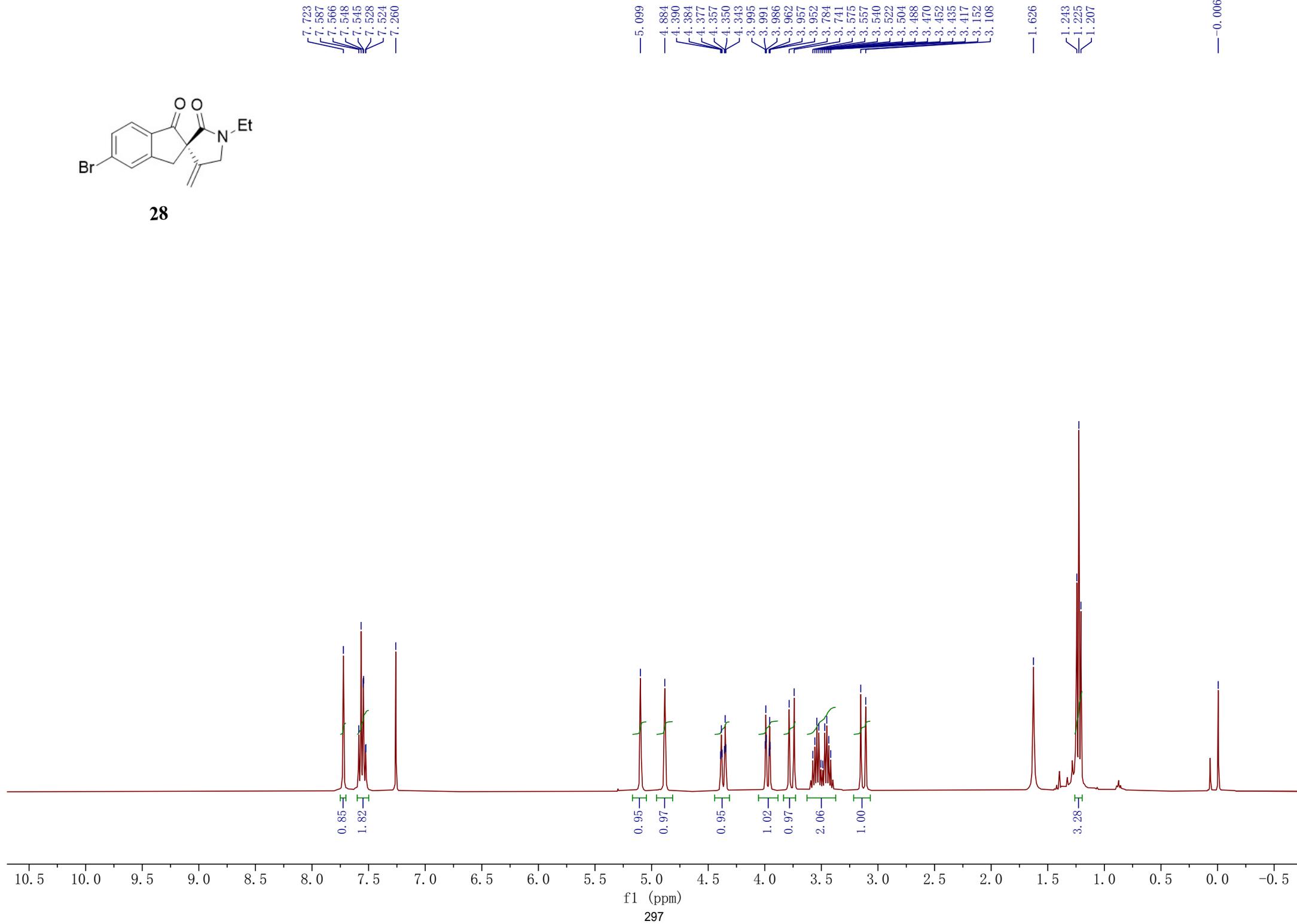
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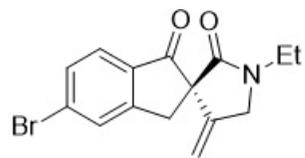
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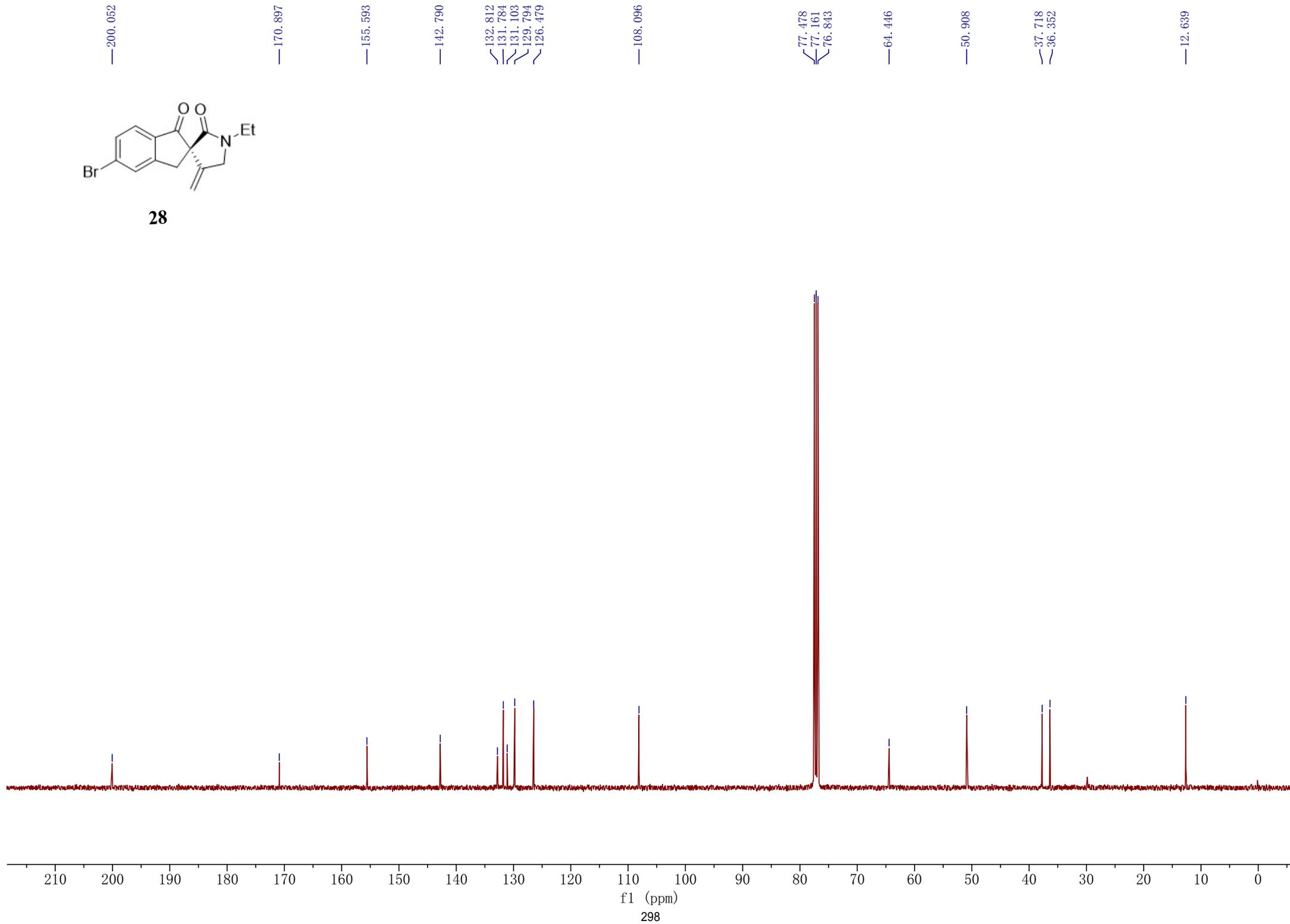


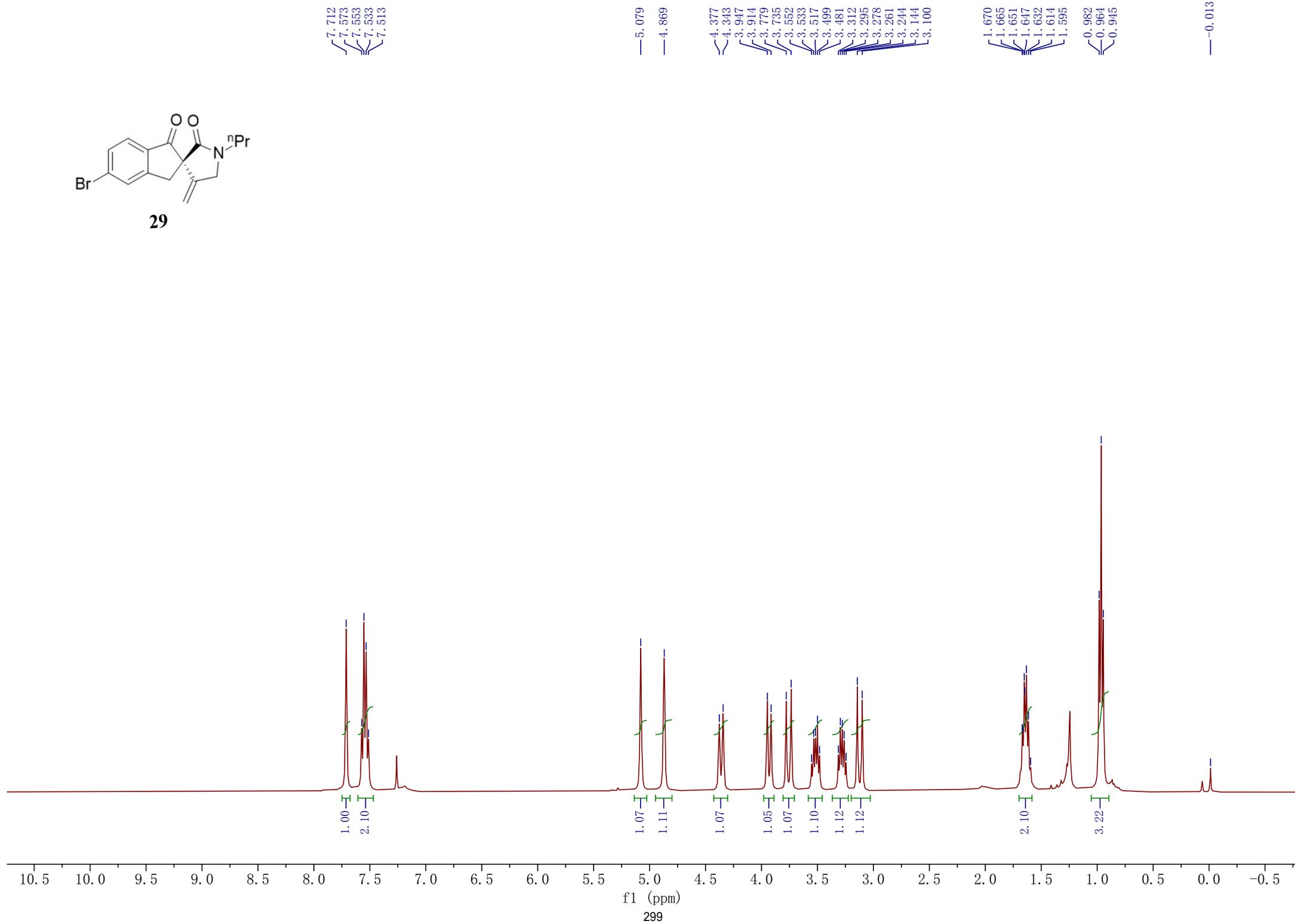
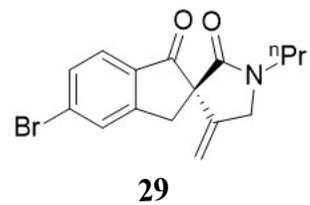
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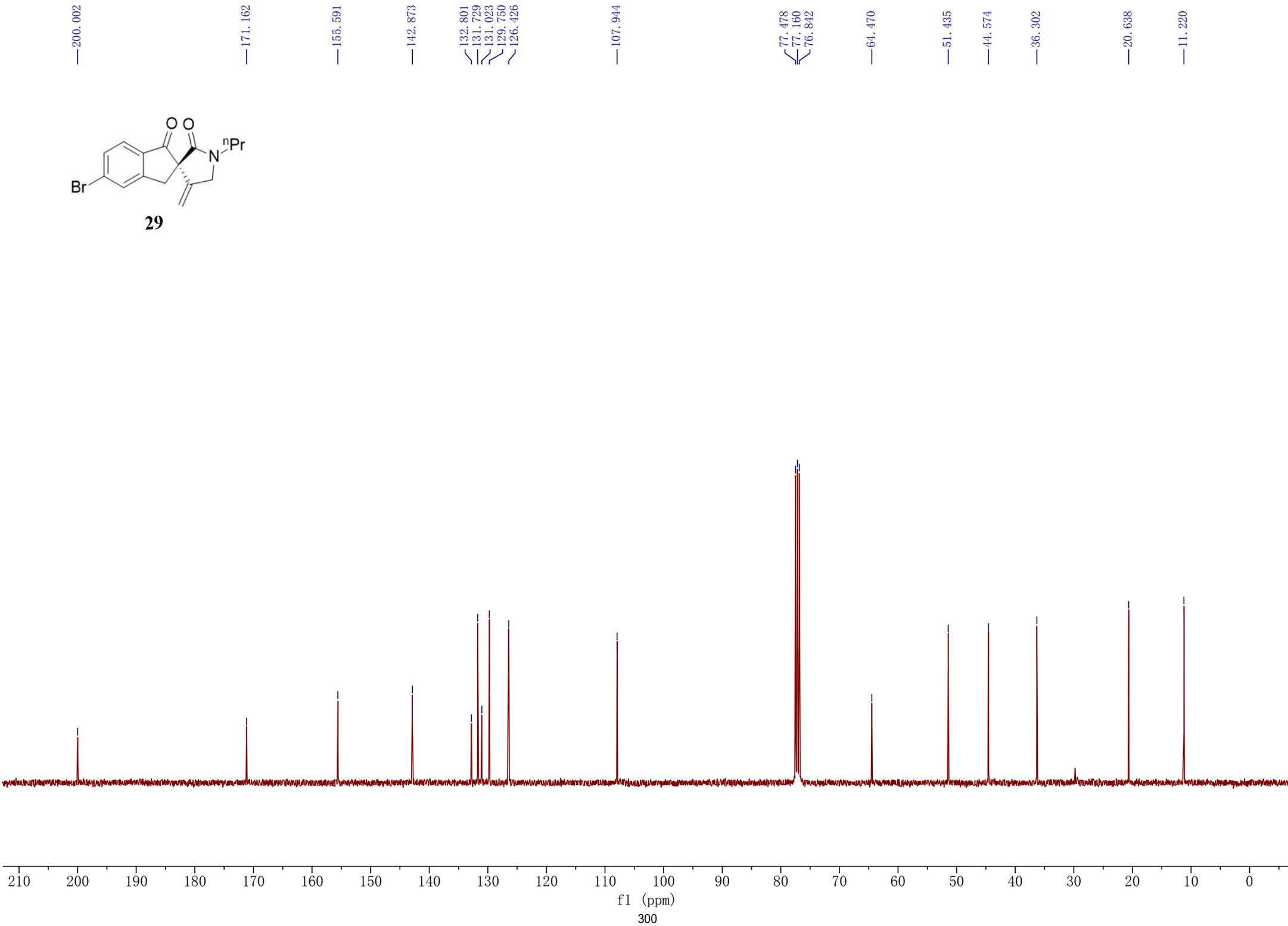
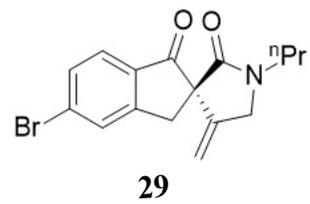


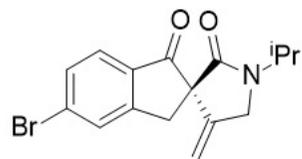


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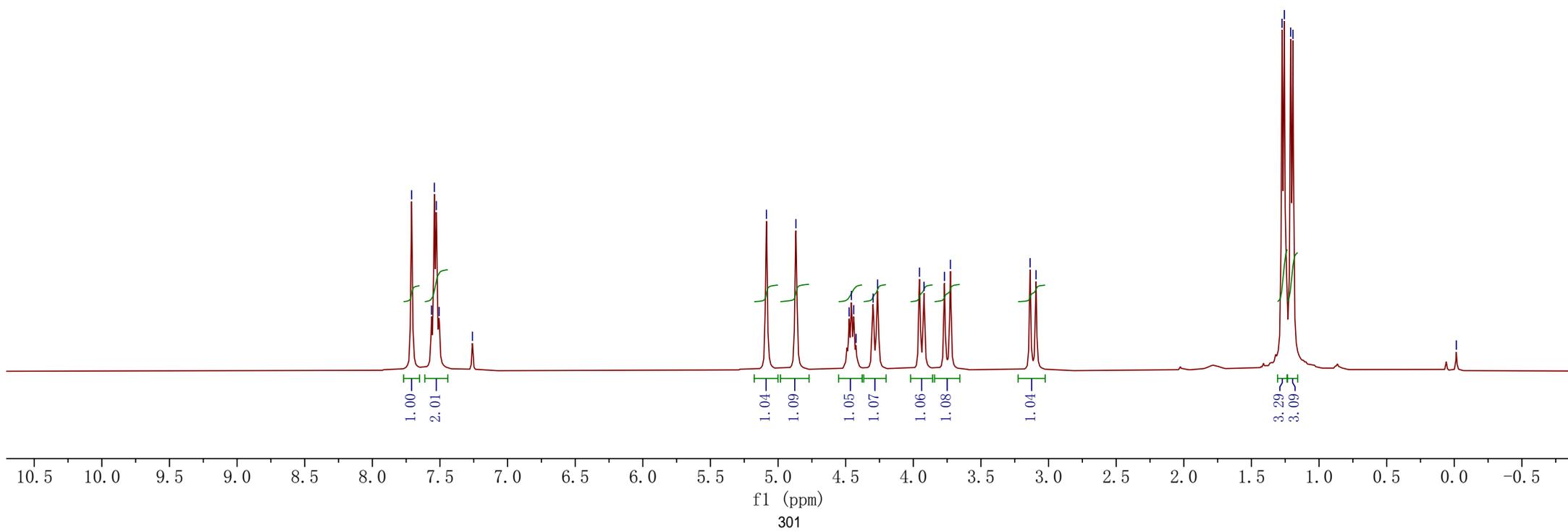
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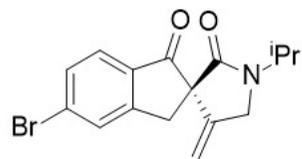
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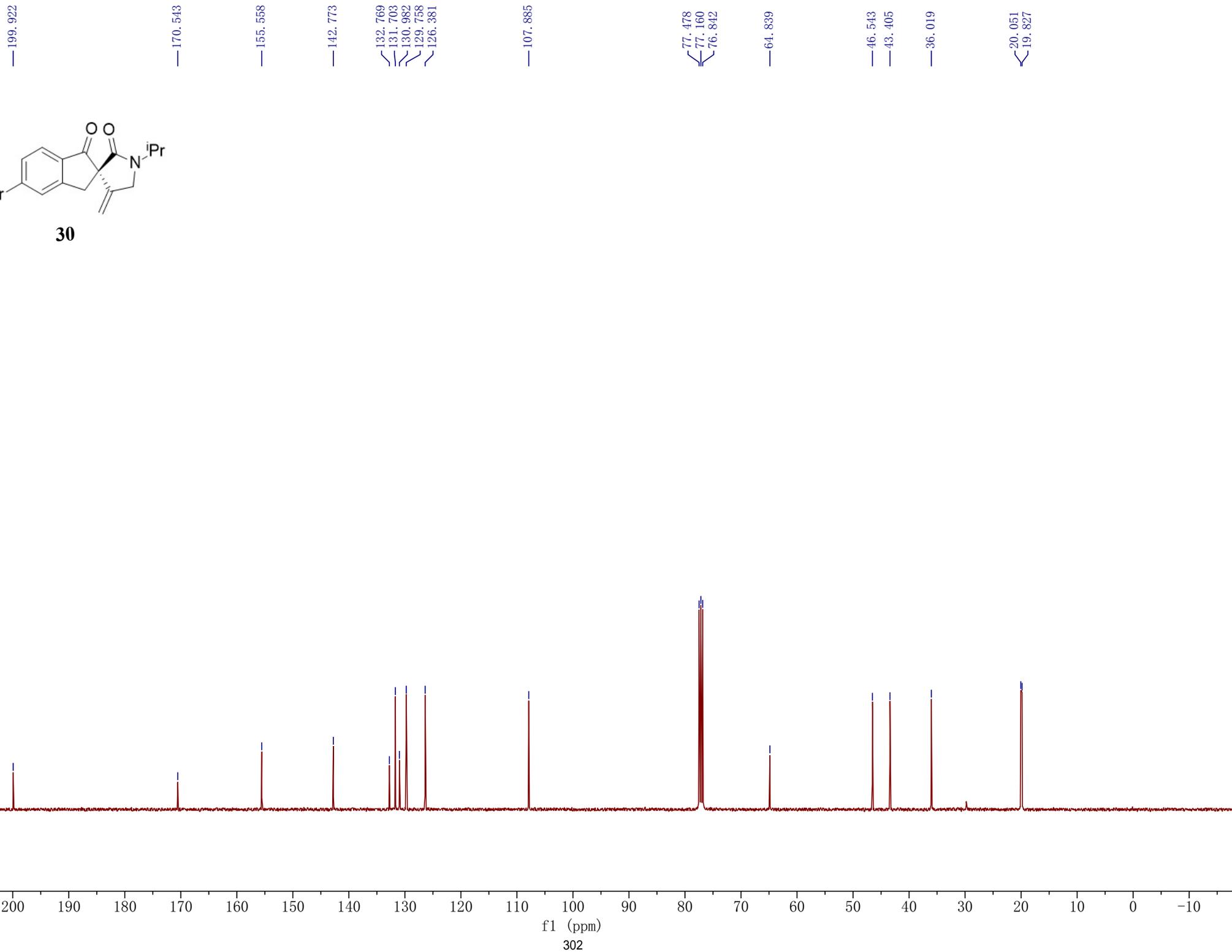
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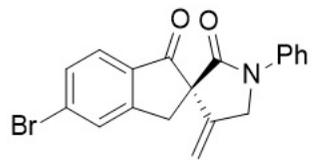
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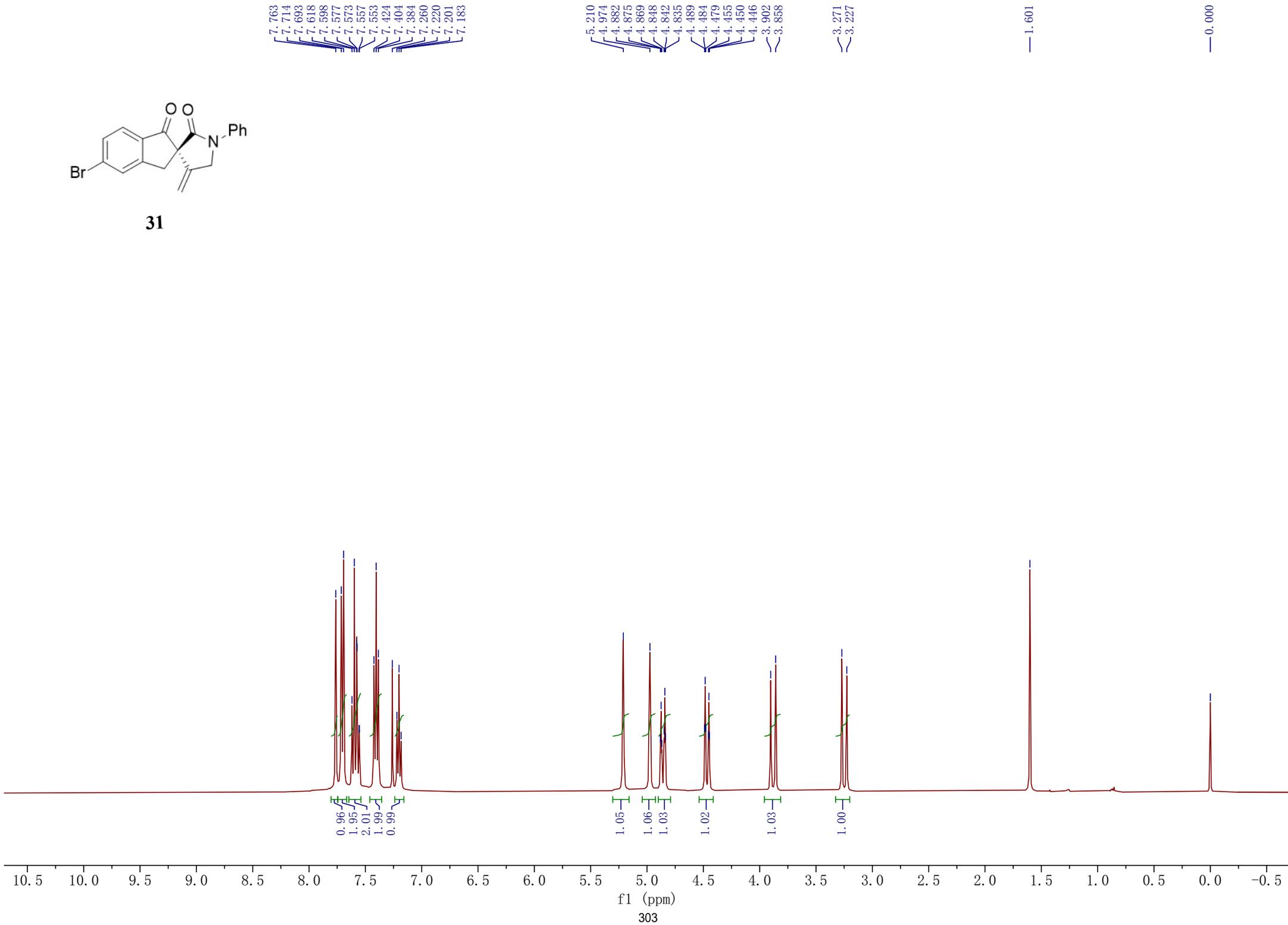


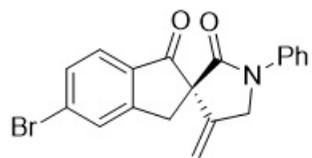
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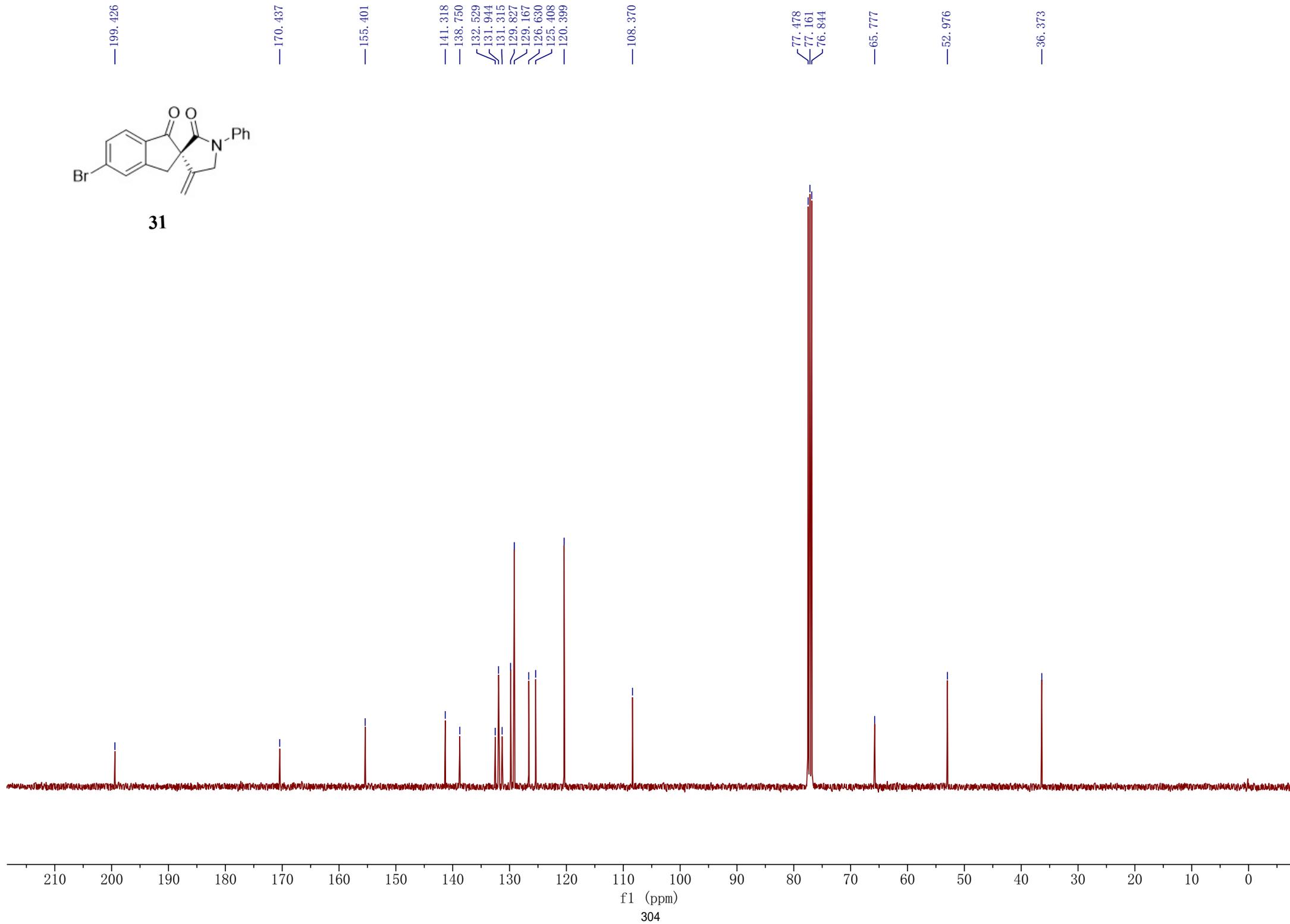


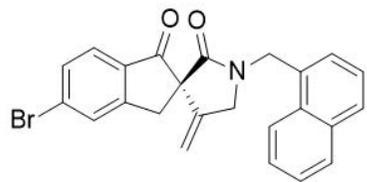
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31





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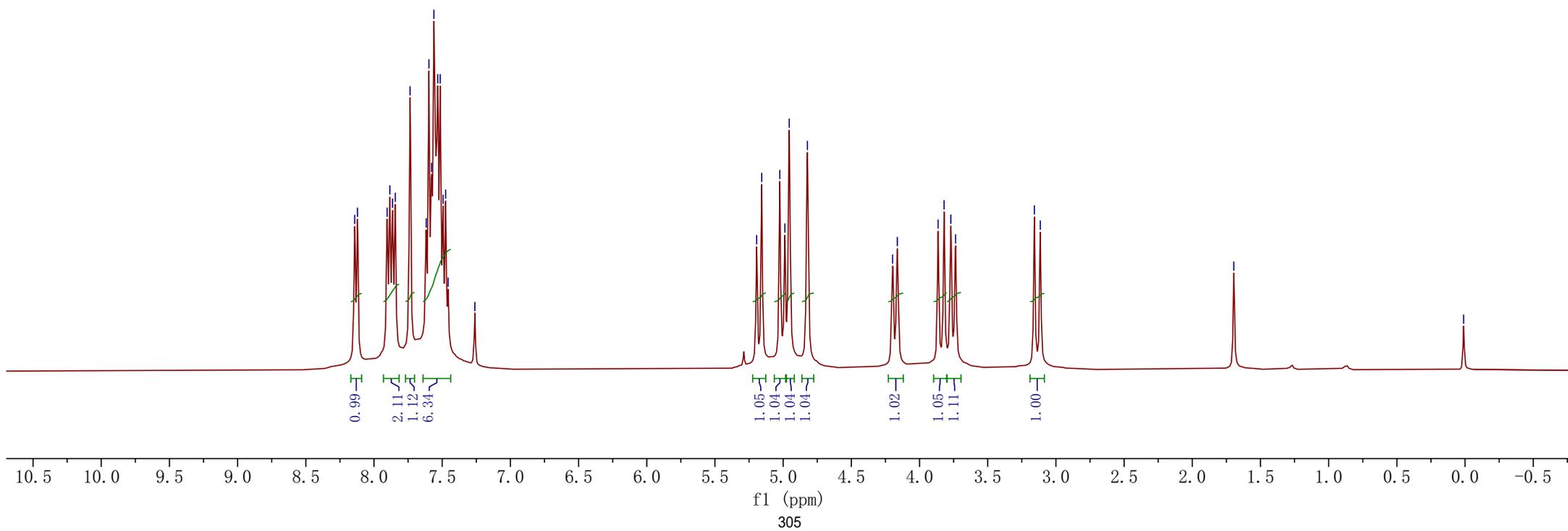
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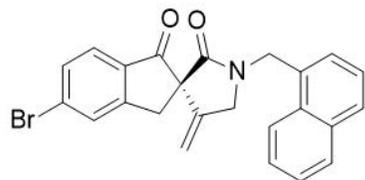
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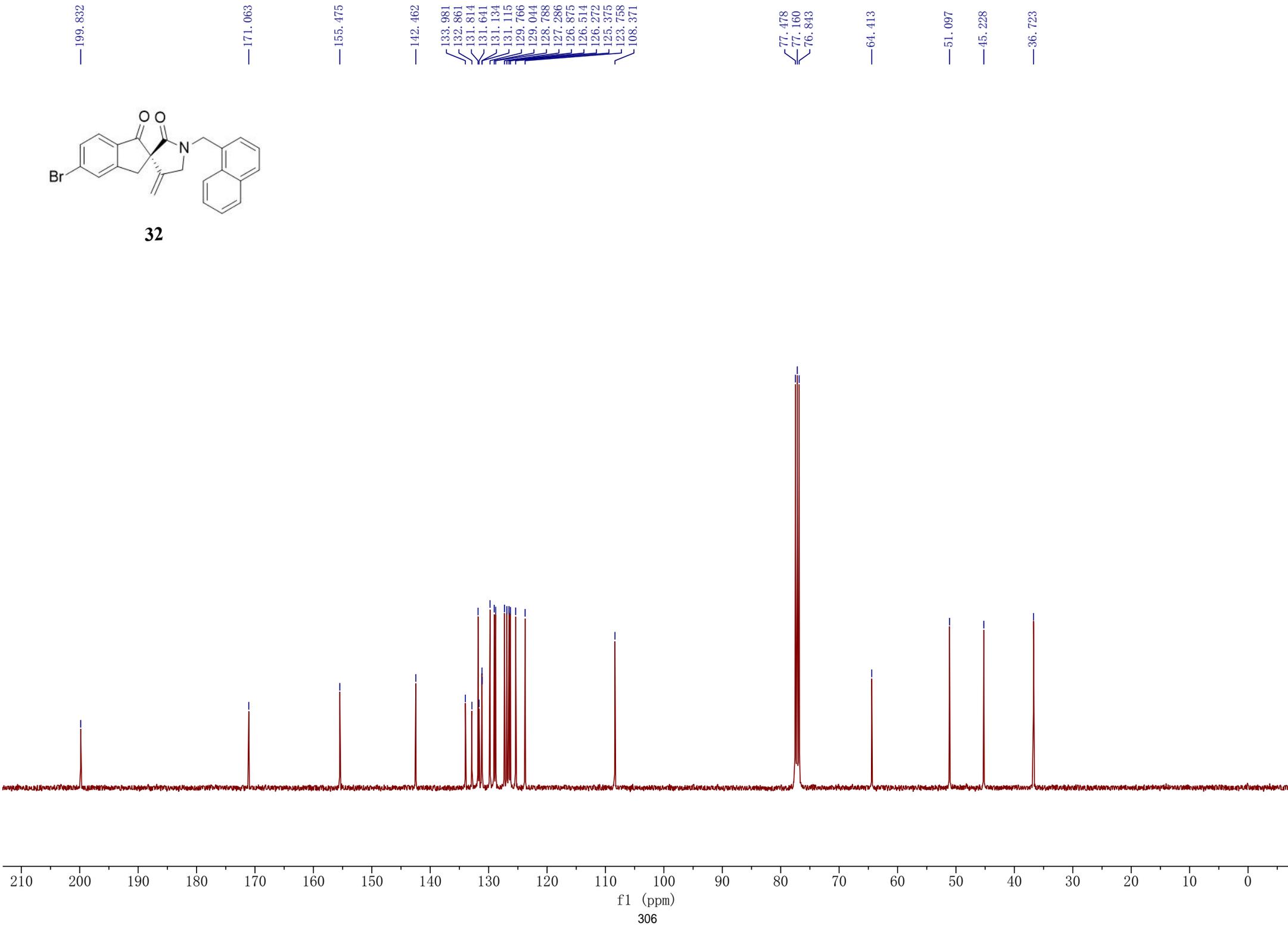
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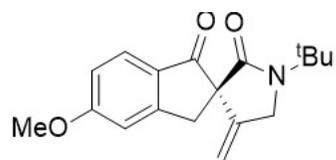
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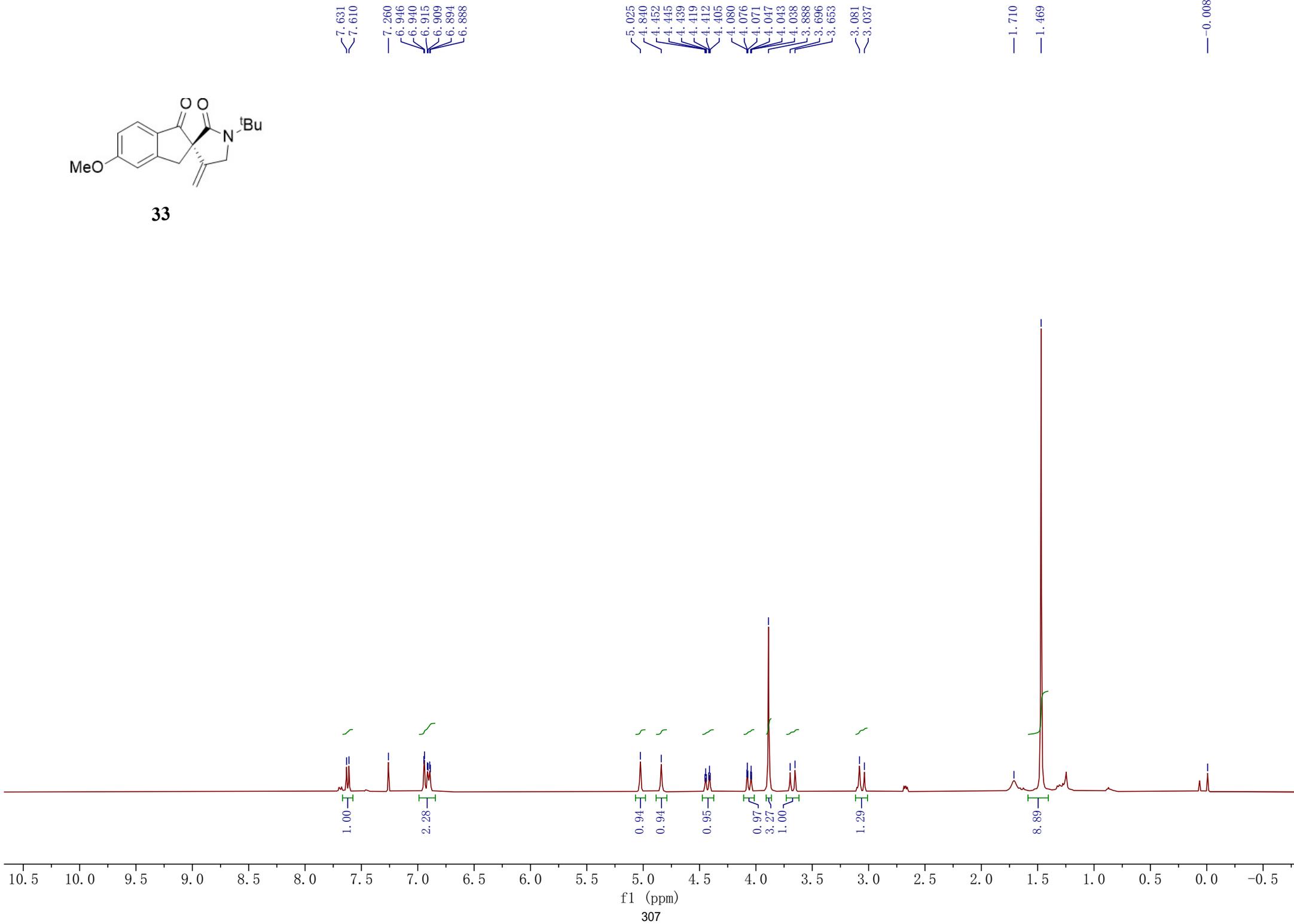


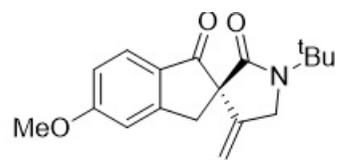
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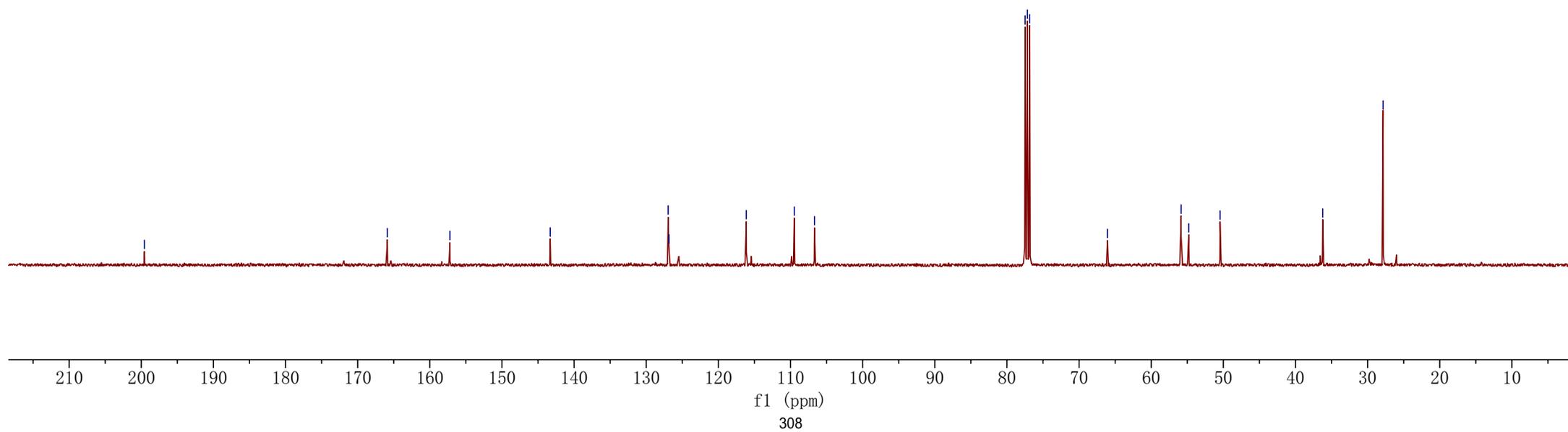
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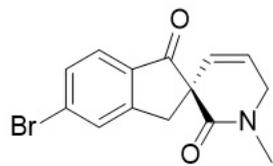
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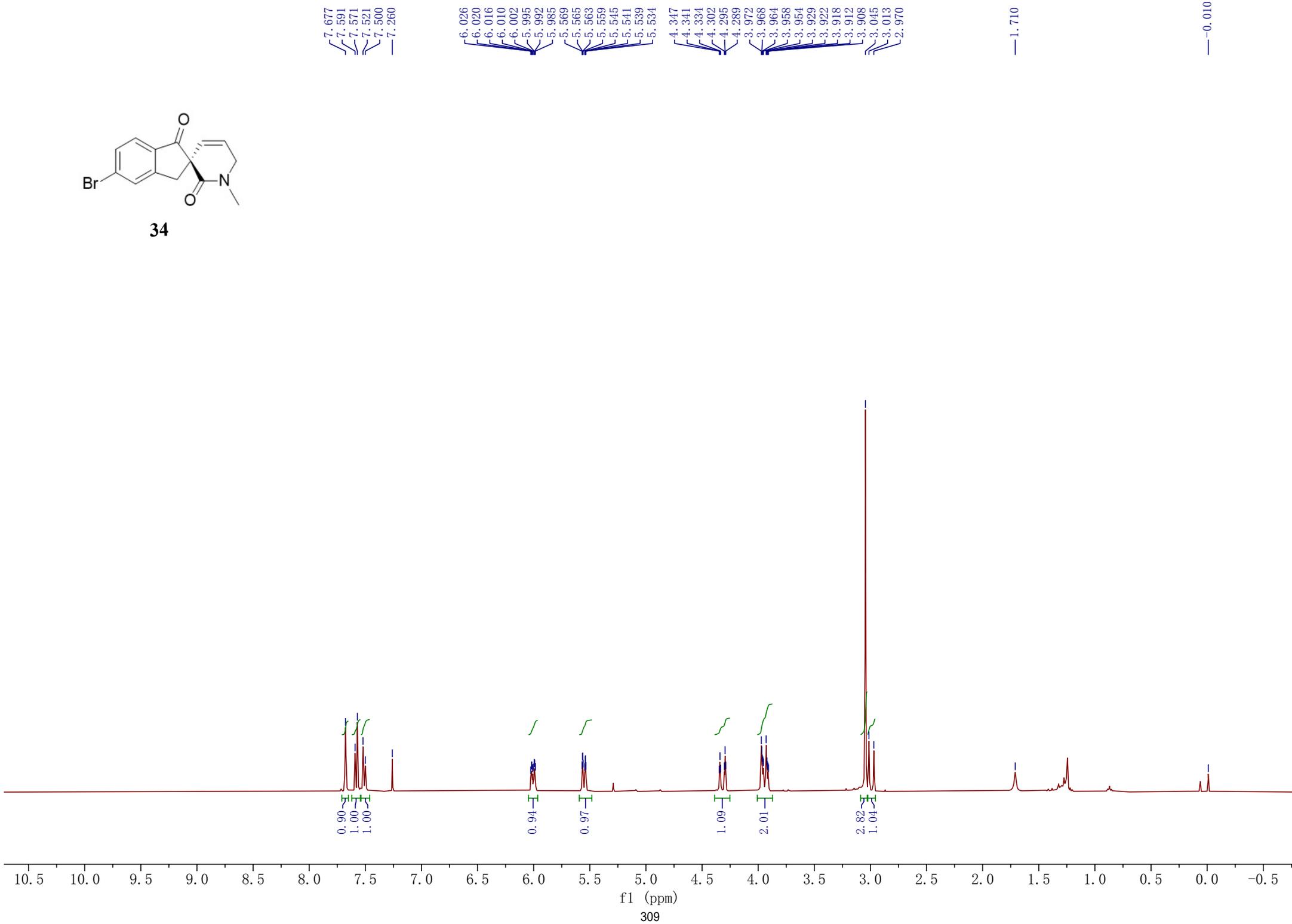
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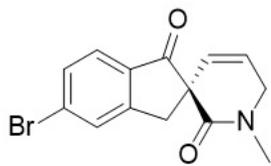
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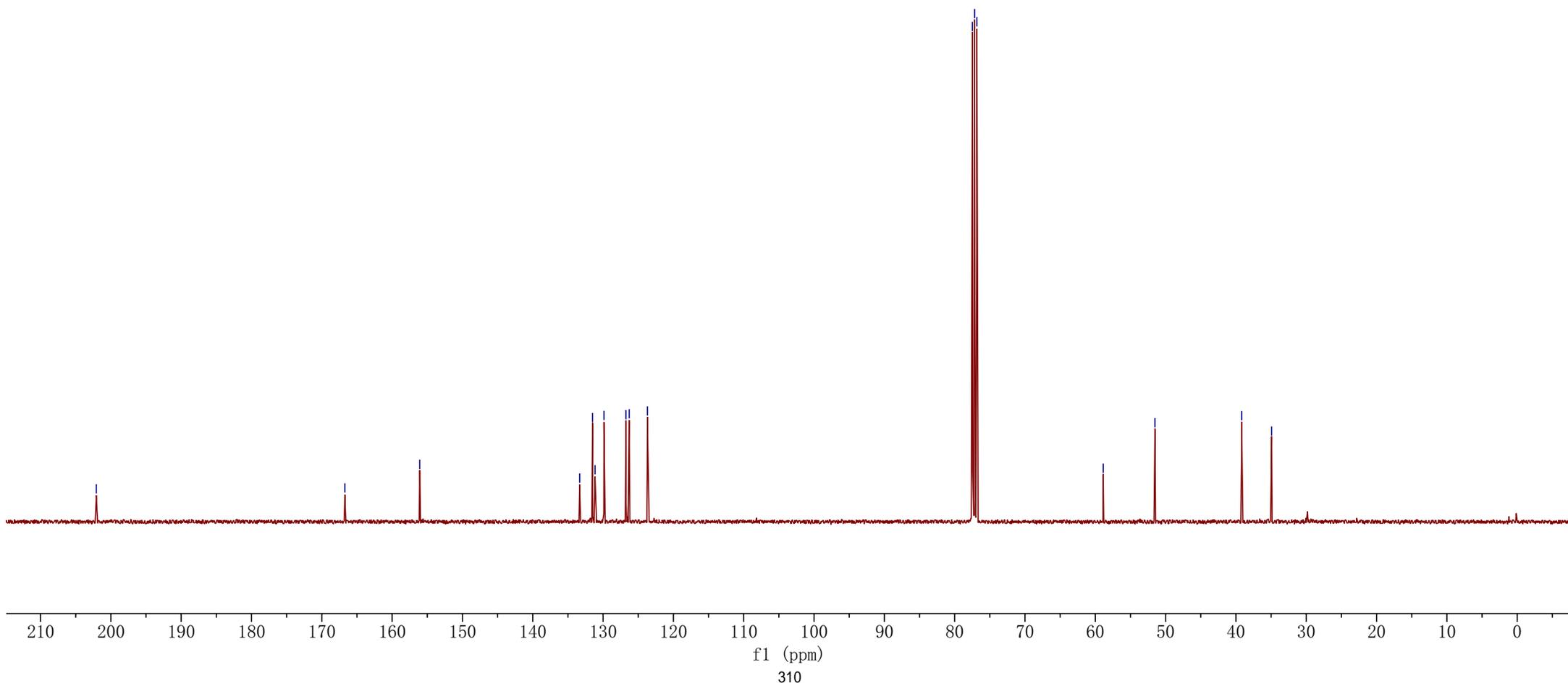
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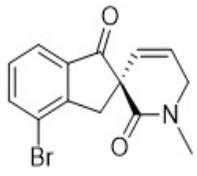
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—51.525

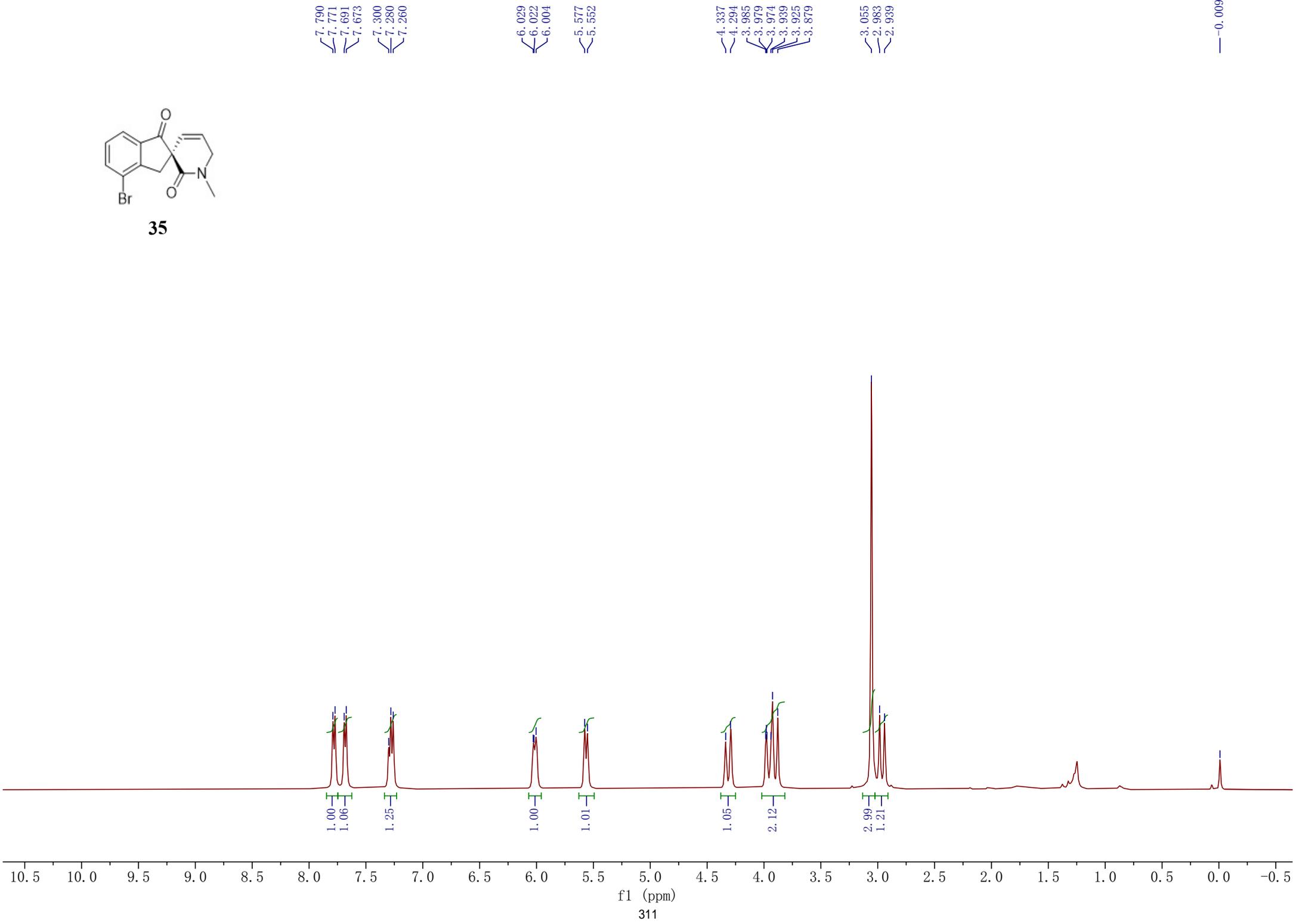
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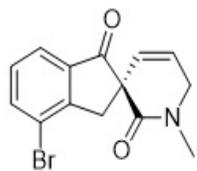
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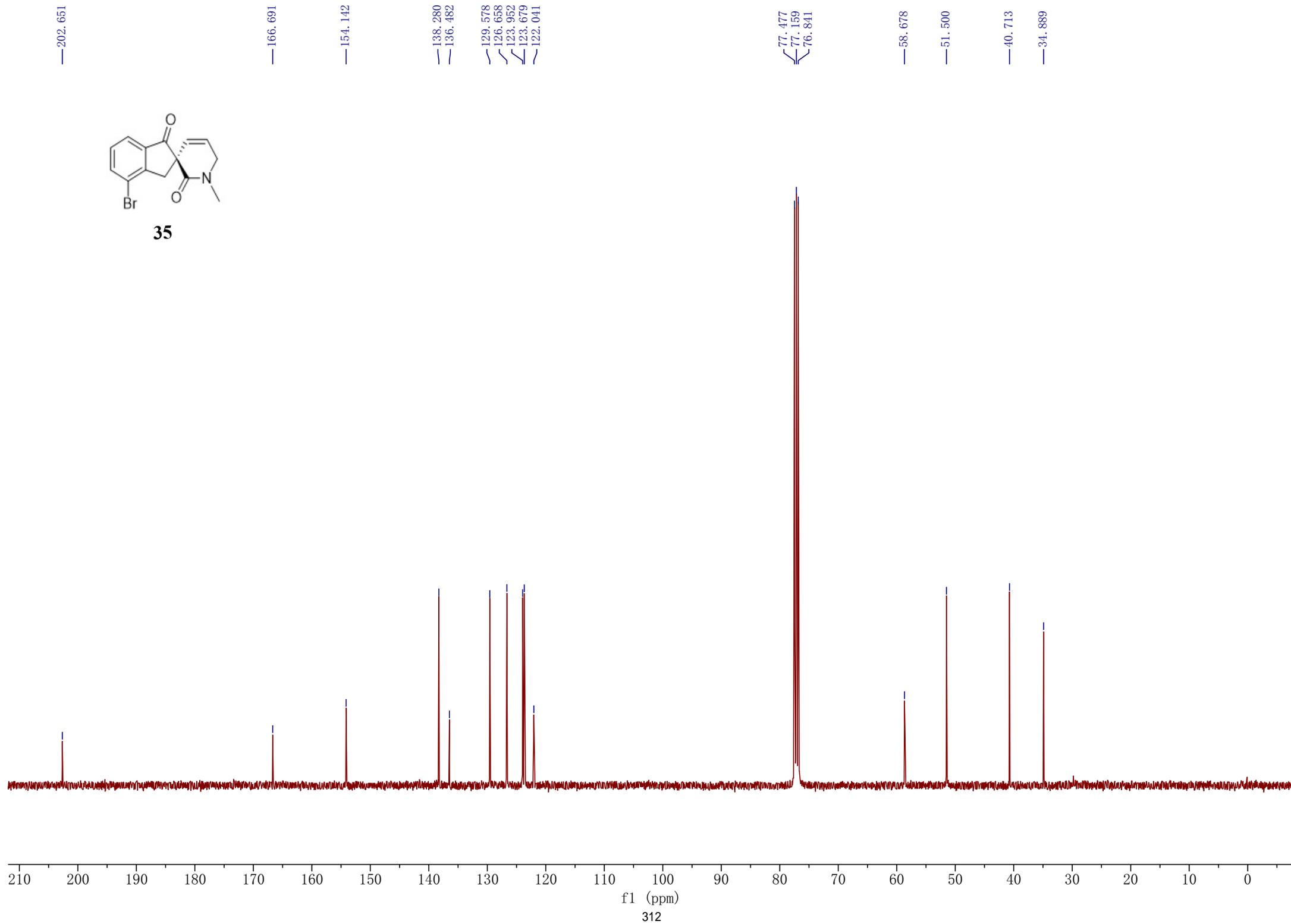


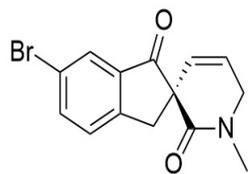
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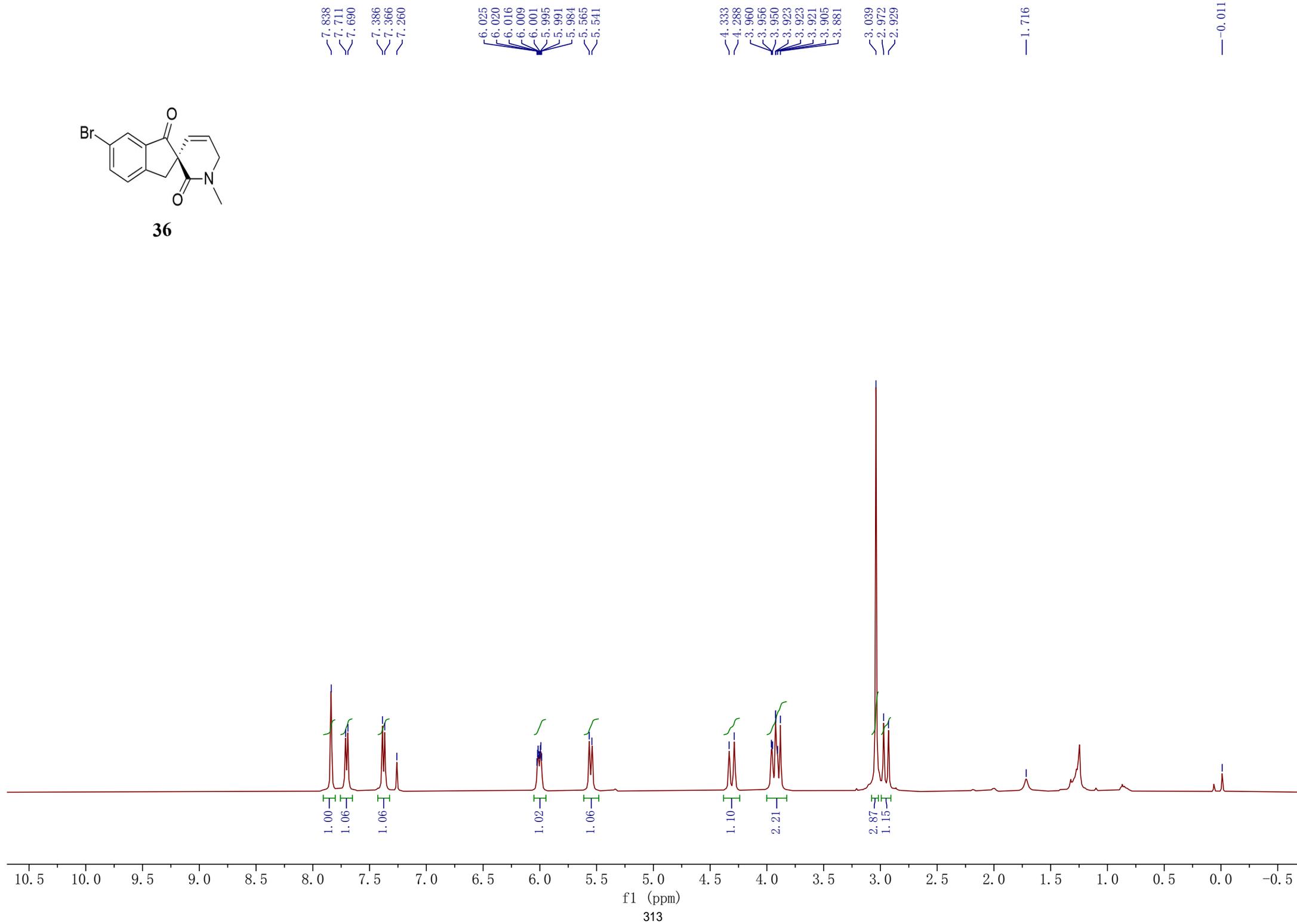


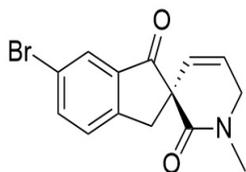
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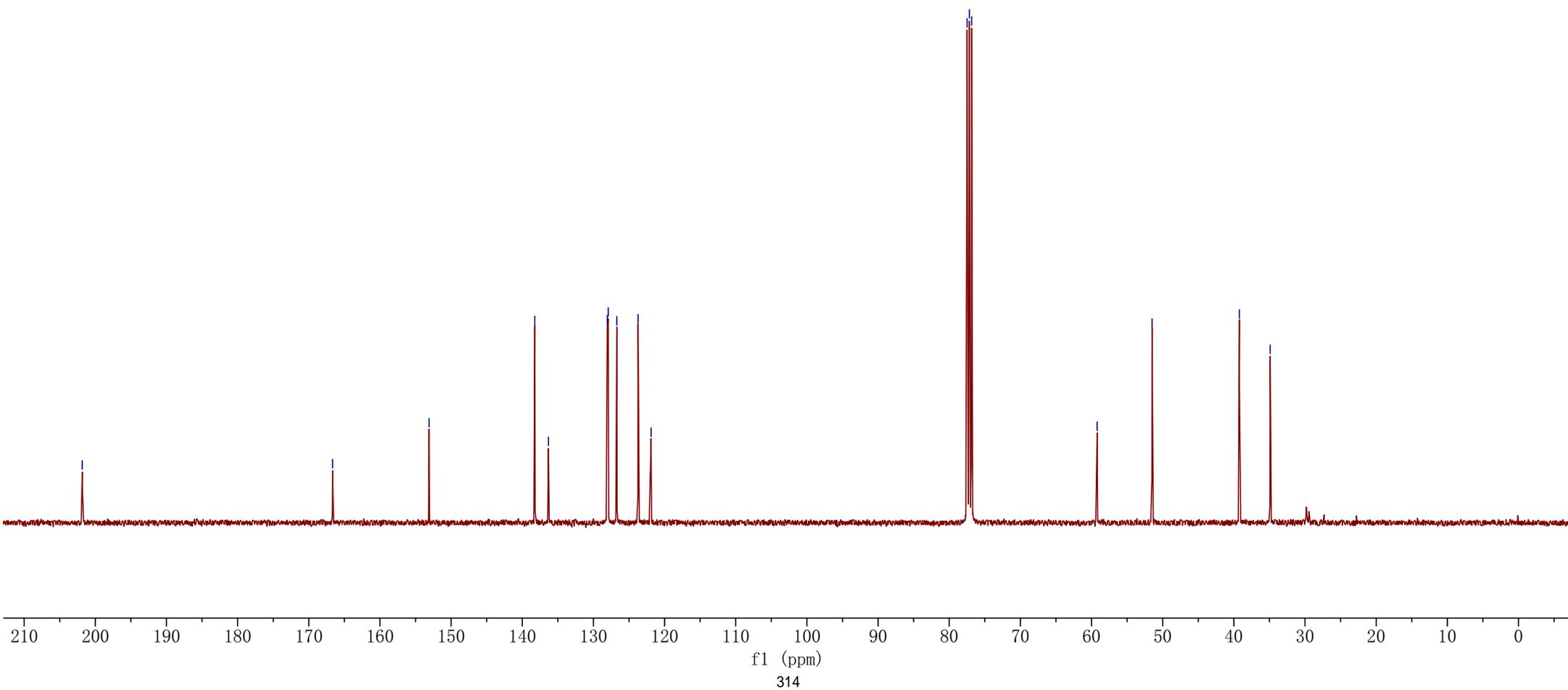
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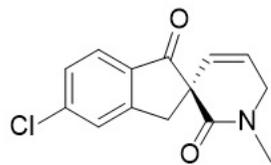




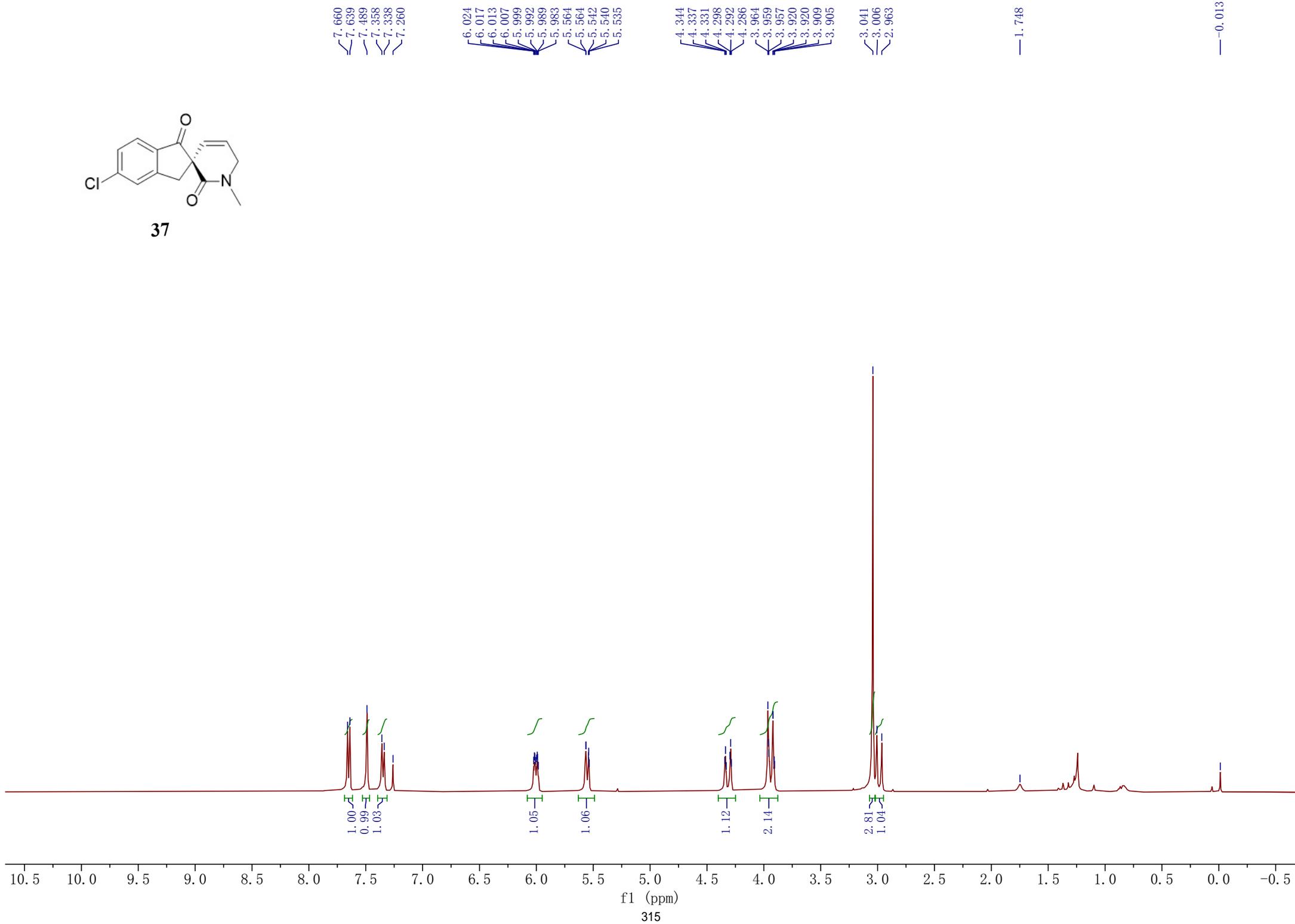
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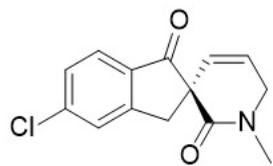
— 201.840
— 166.655
— 153.089
— 138.240
— 136.322
— 128.054
— 127.919
— 126.715
— 123.721
— 121.892
— 77.478
— 77.160
— 76.842
— 59.216
— 51.498
— 39.223
— 34.890





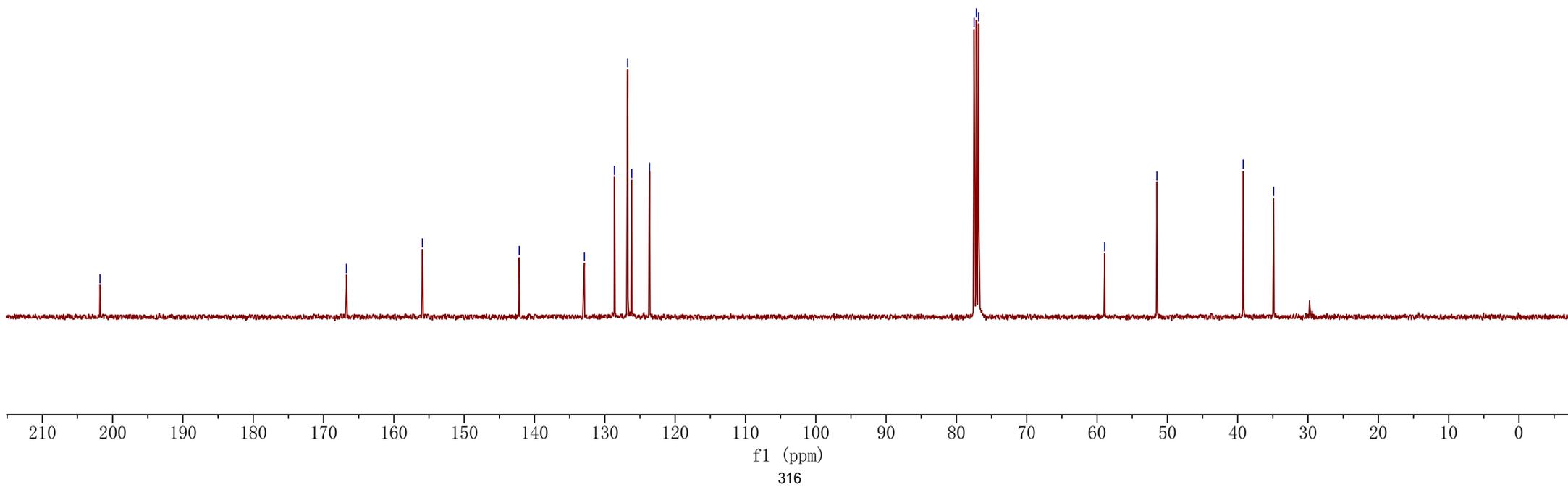
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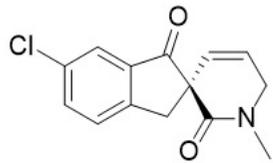




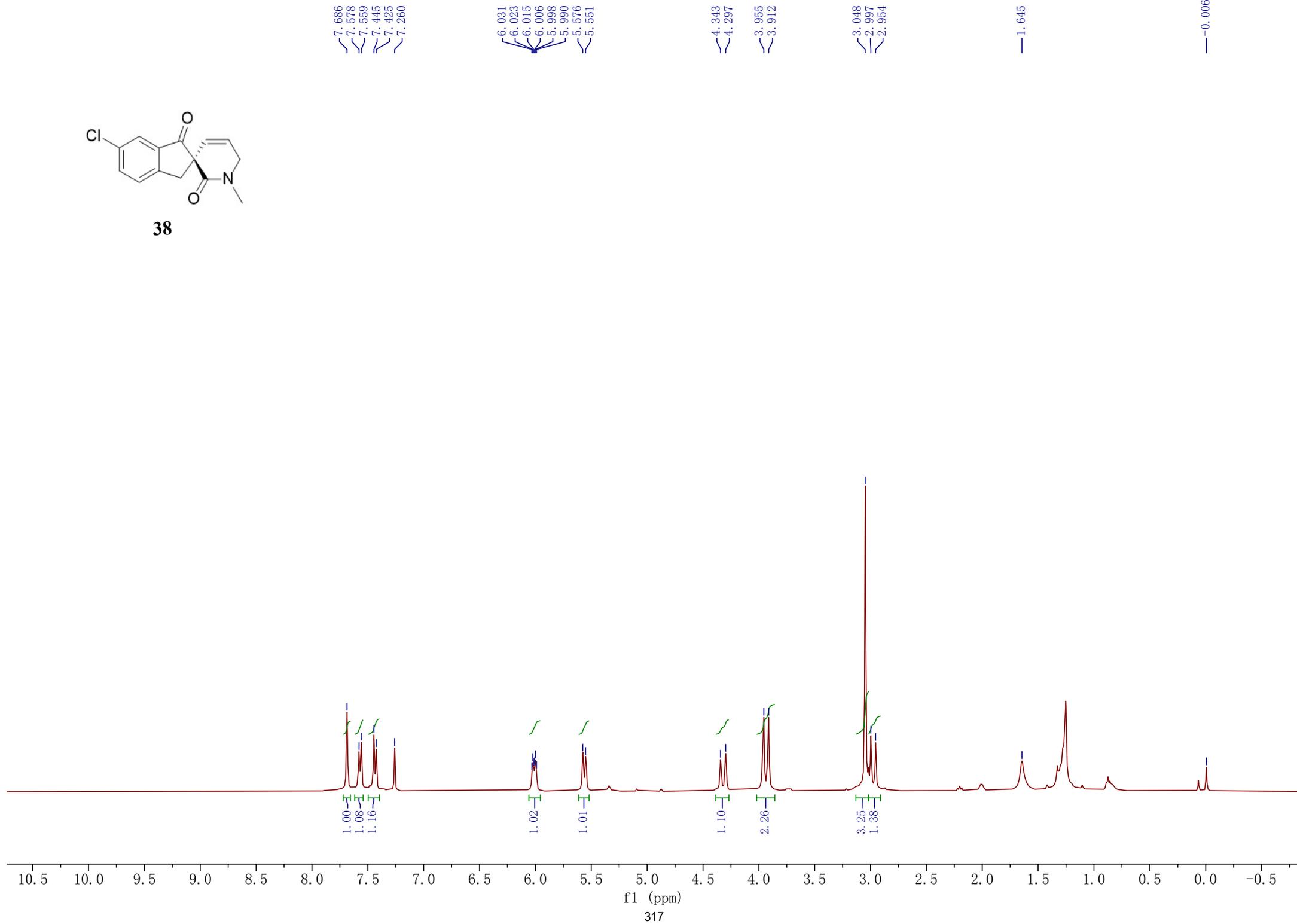
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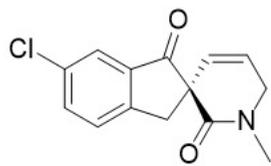
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- 166.740
- 155.941
- 142.169
- 132.909
- 128.629
- 126.754
- 126.171
- 123.649
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- 77.161
- 76.843
- 58.919
- 51.492
- 39.213
- 34.883



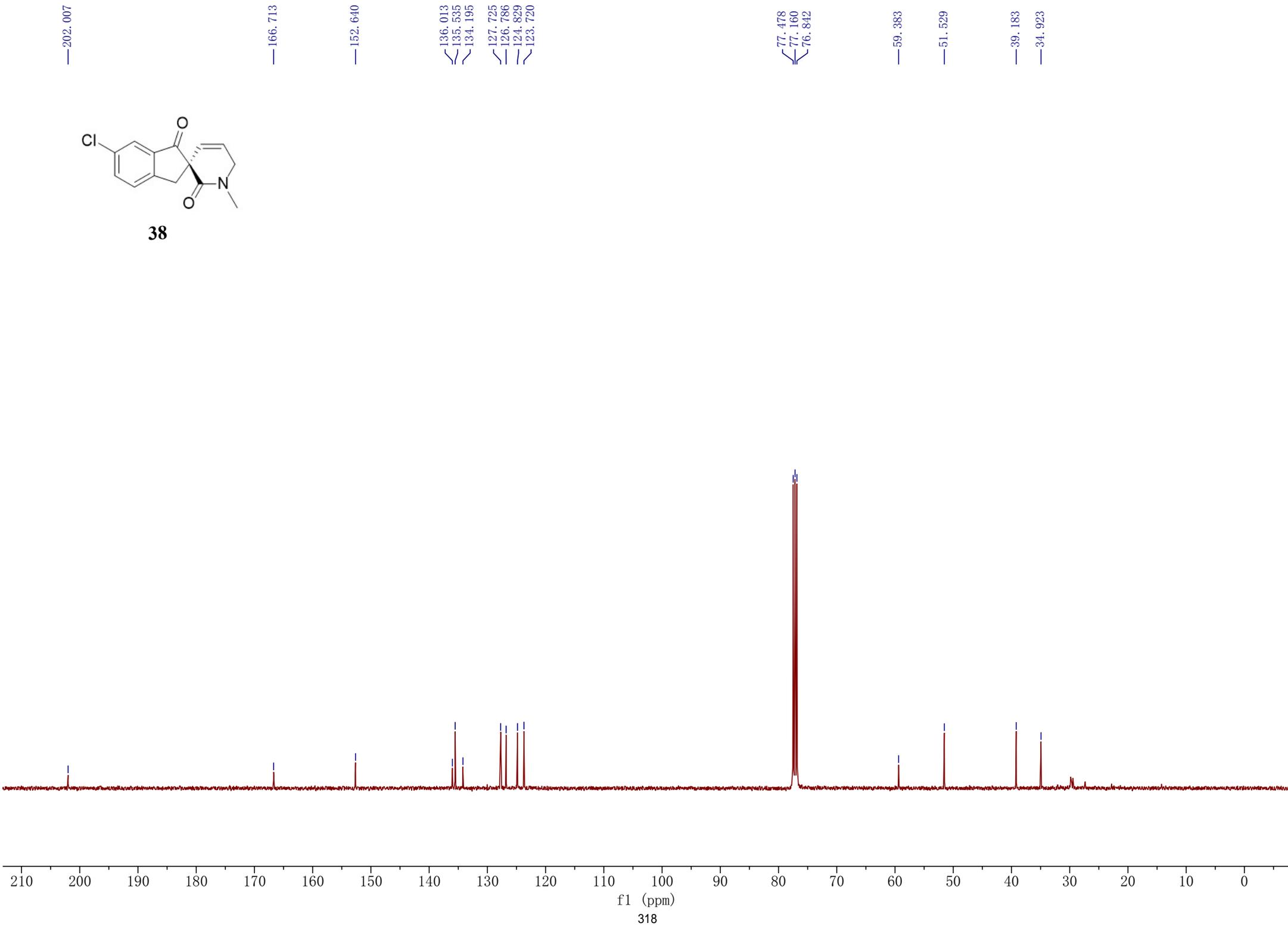


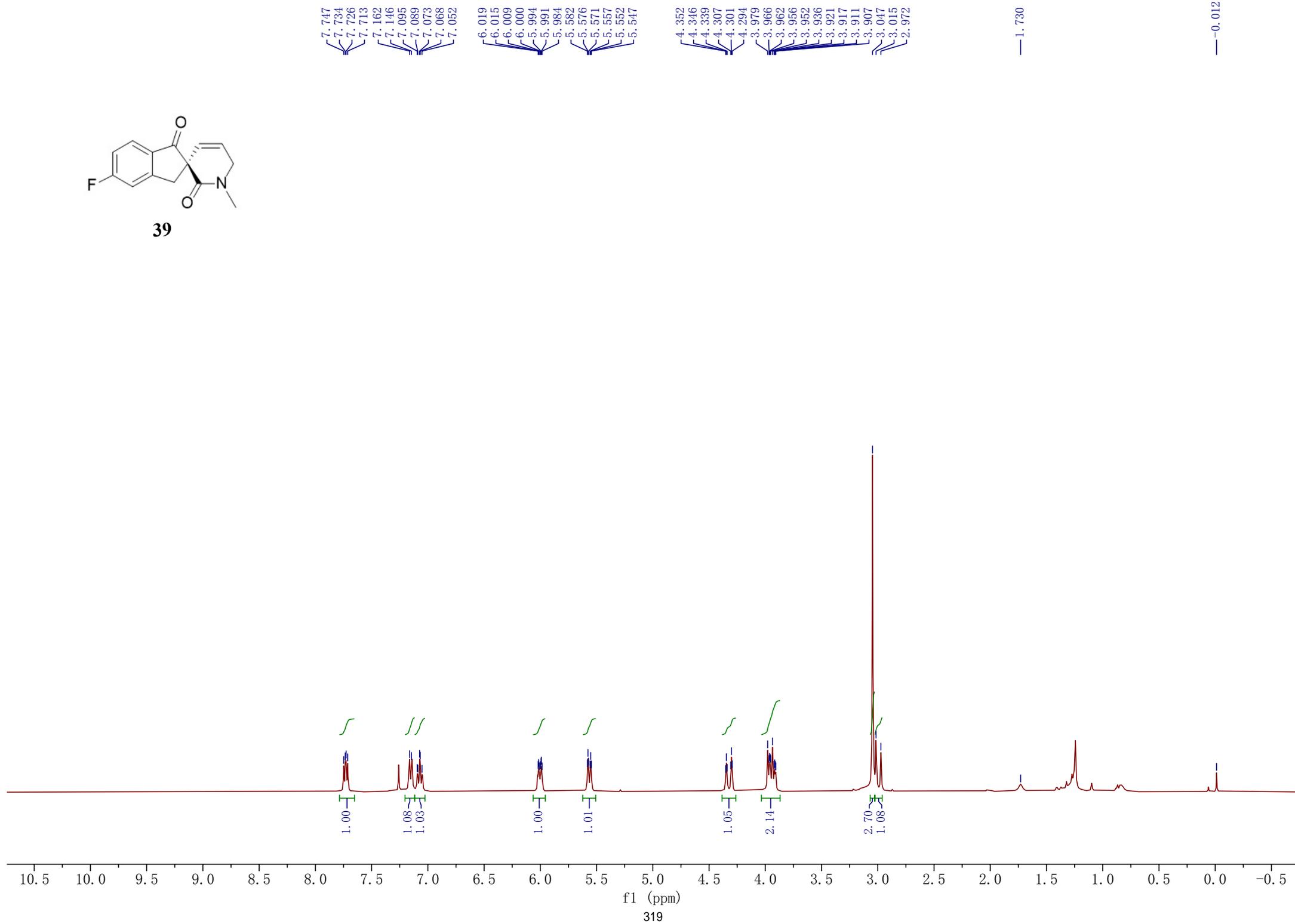
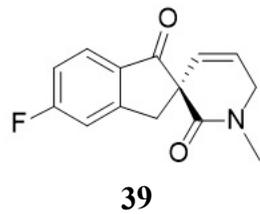
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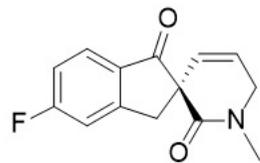




38







39

— 201.324

— 169.014
— 166.850
— 166.456

— 157.554
— 157.450

— 130.823
— 127.519
— 127.413
— 126.877
— 123.597

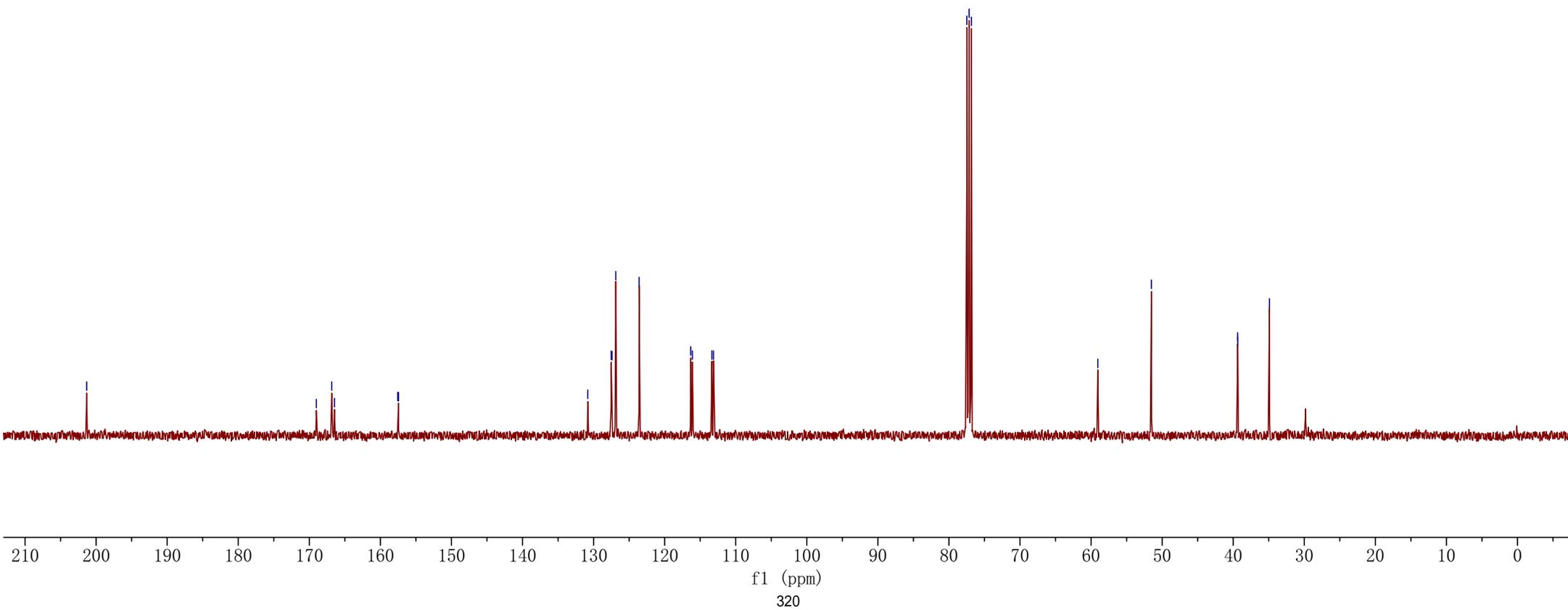
— 116.329
— 116.090
— 113.349
— 113.125

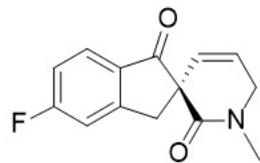
— 77.478
— 77.160
— 76.843

— 59.055

— 51.515

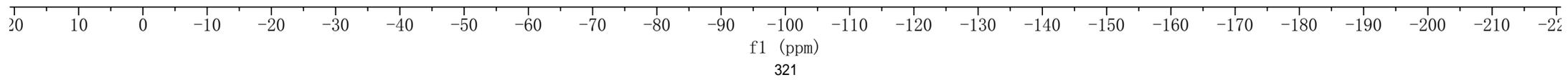
— 39.374
— 39.353
— 34.898

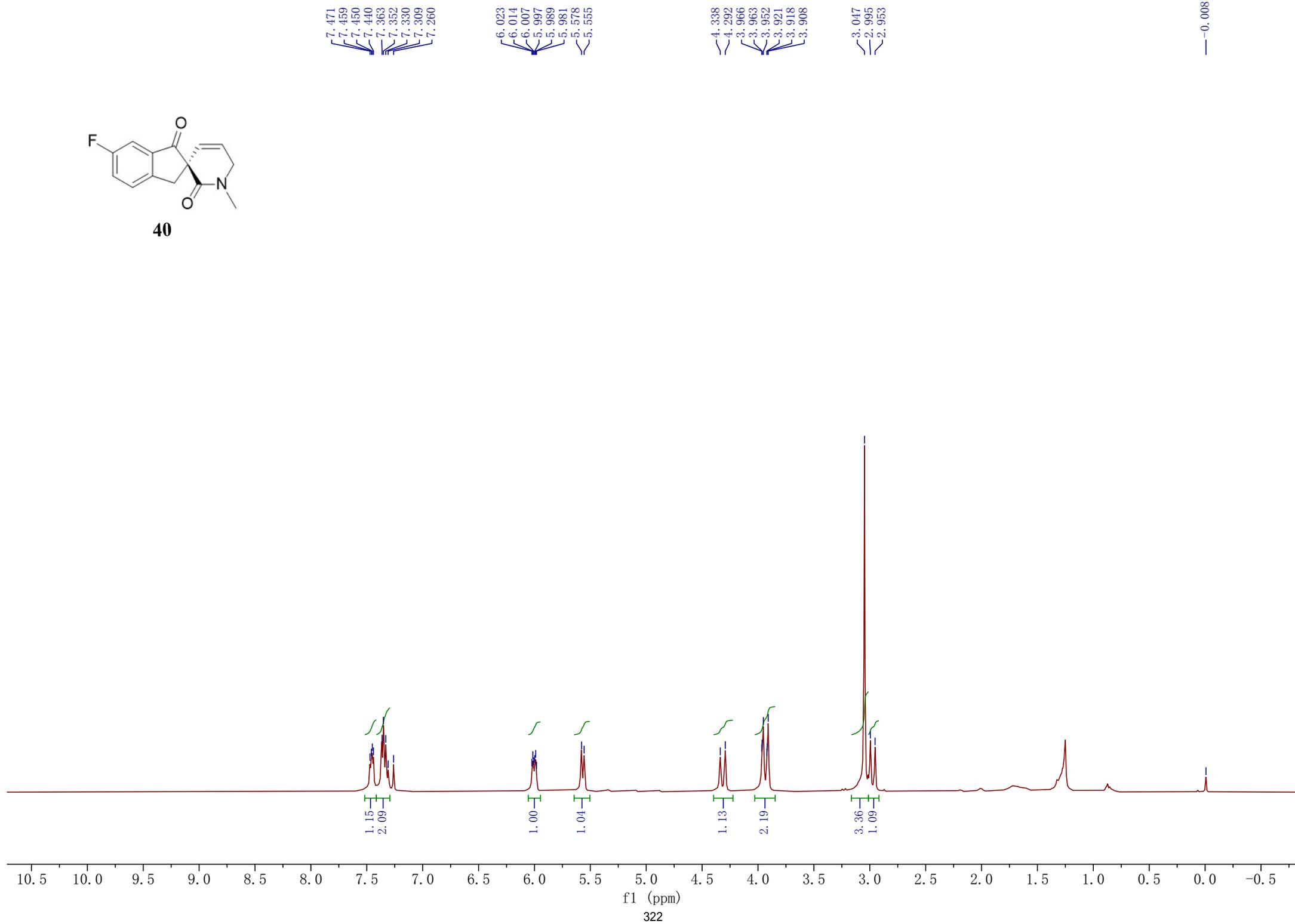
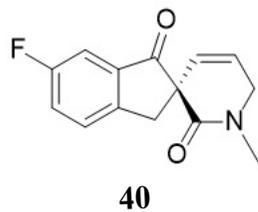


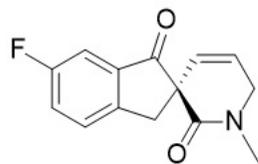


39

-101.569







40

— 202.365

— 166.792
— 163.803
— 161.335

— 149.989

— 136.228
— 136.153
— 127.934
— 127.855
— 126.877
— 123.590
— 123.399
— 123.162

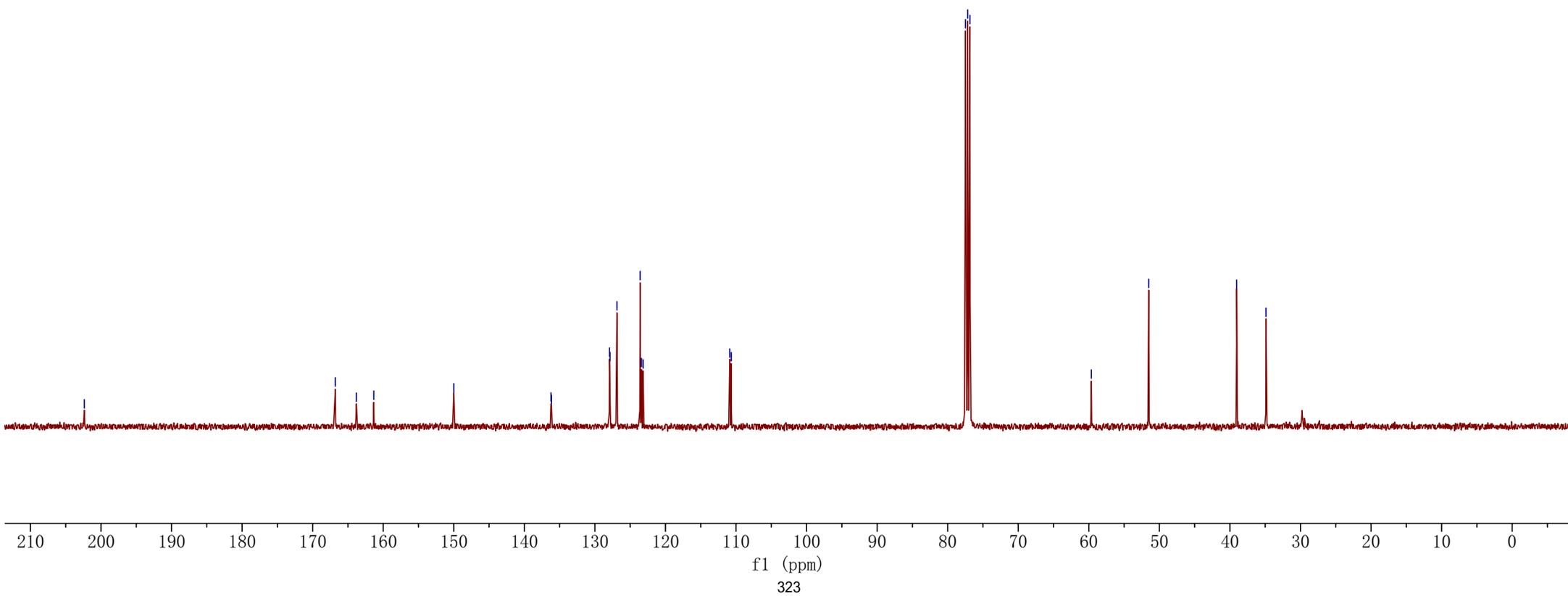
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— 110.668

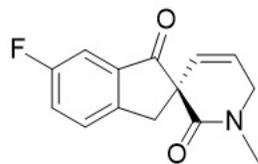
— 77.478
— 77.160
— 76.842

— 59.642

— 51.511

— 39.048
— 34.890





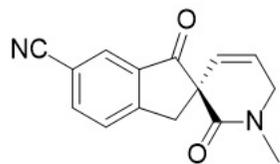
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-114.268

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f1 (ppm)

324



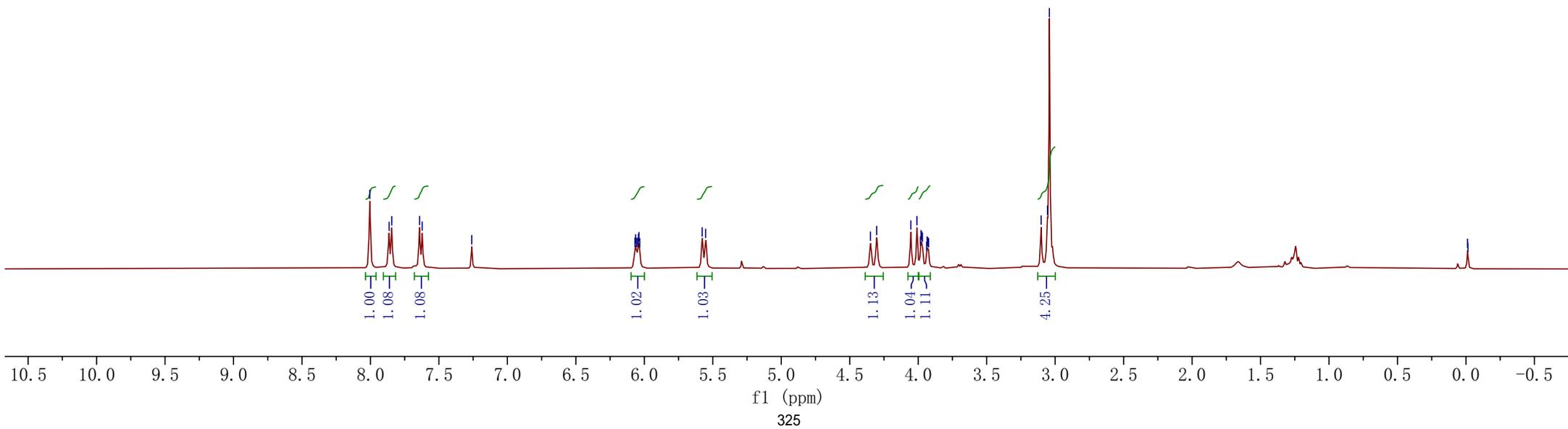
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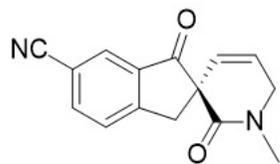
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7.864
7.844
7.641
7.622
7.260

6.069
6.064
6.058
6.049
6.044
6.039
6.033
5.578
5.552

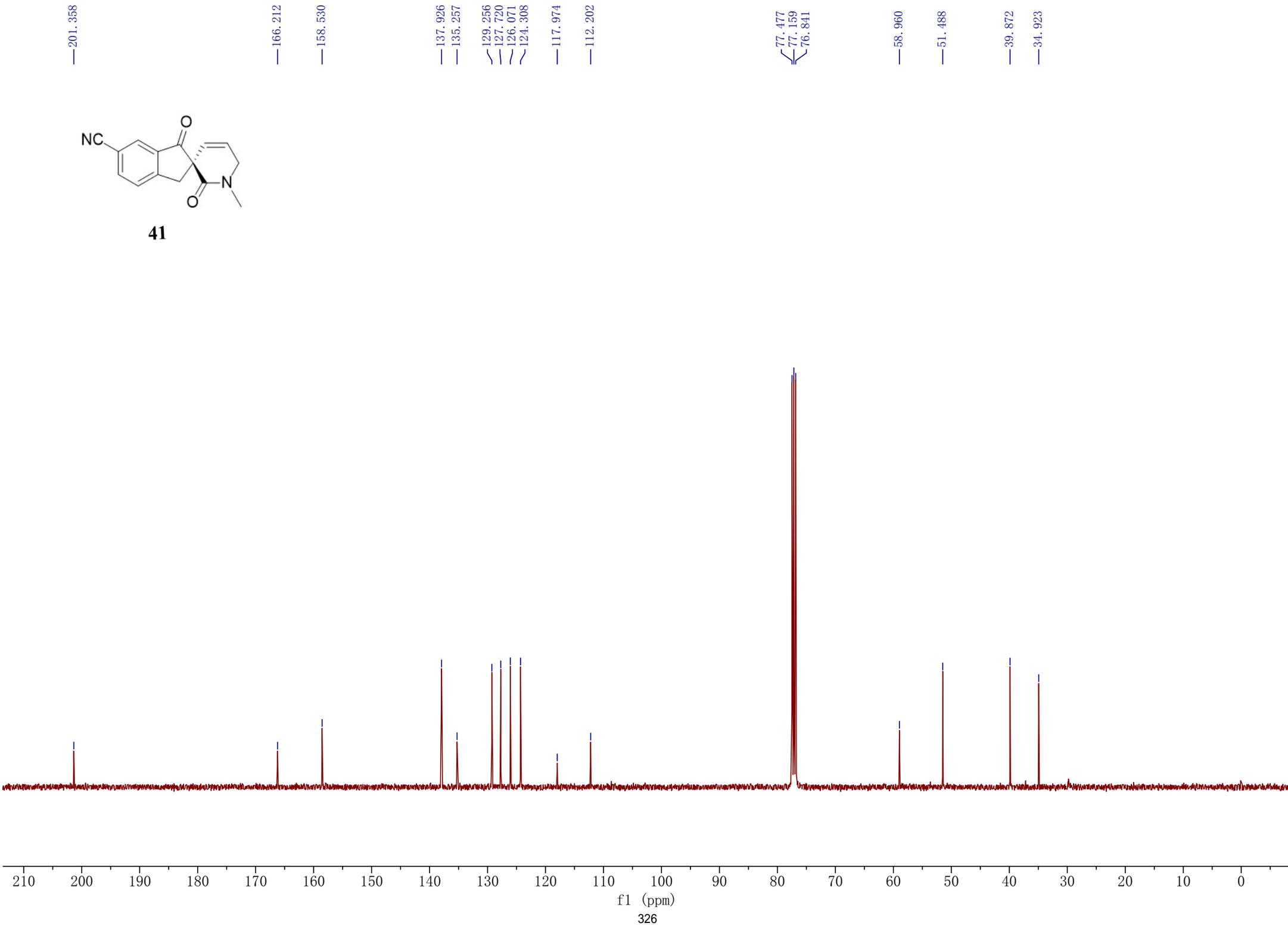
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4.303
4.054
4.009
3.984
3.980
3.974
3.969
3.939
3.935
3.929
3.924
3.102
3.056
3.042

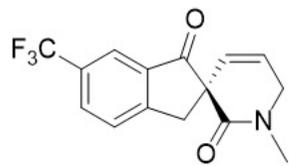
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-0.015





41





42

7.995
7.868
7.848
7.646
7.626
7.260

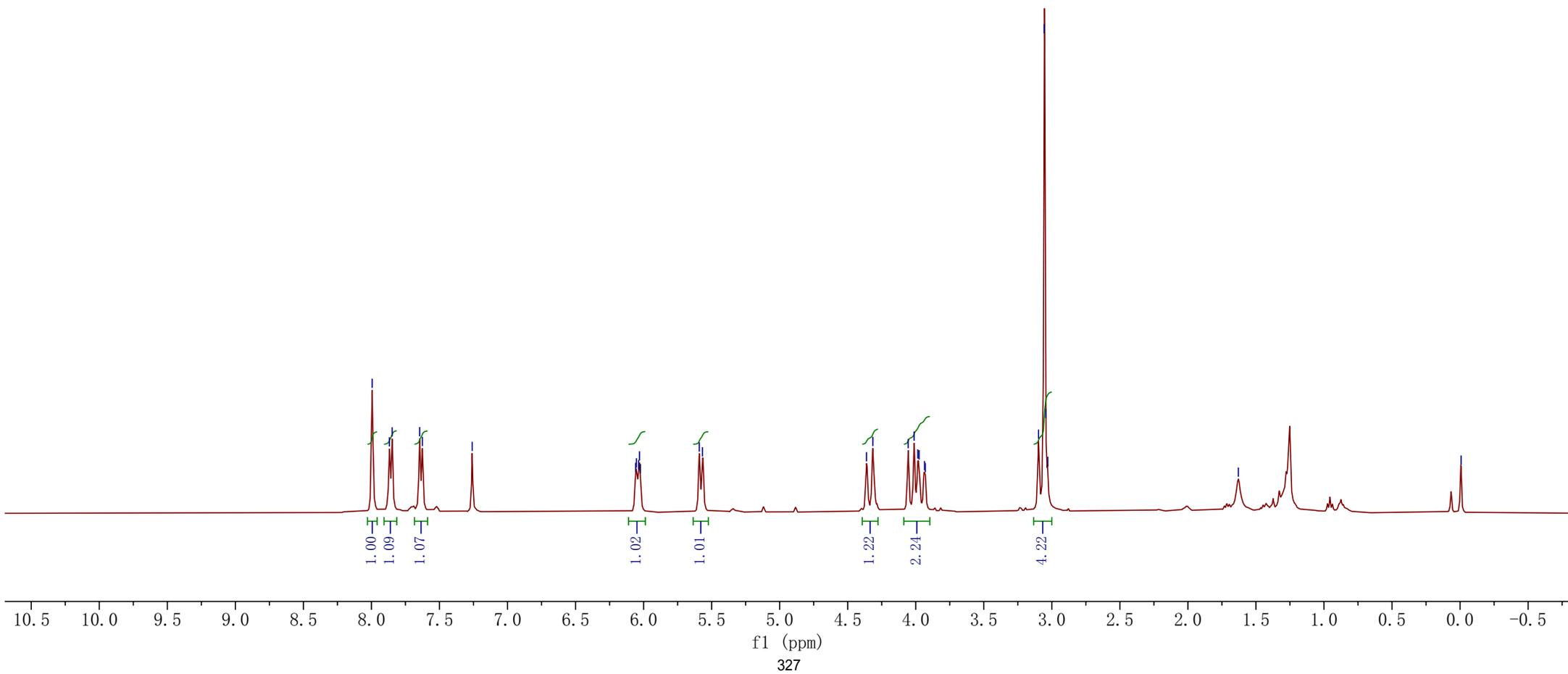
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6.053
6.037
6.030
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5.591
5.567

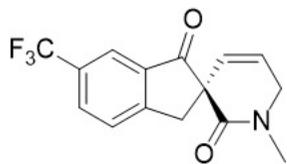
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4.315
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4.012
3.985
3.975
3.936
3.930

3.097
3.056
3.044
3.030

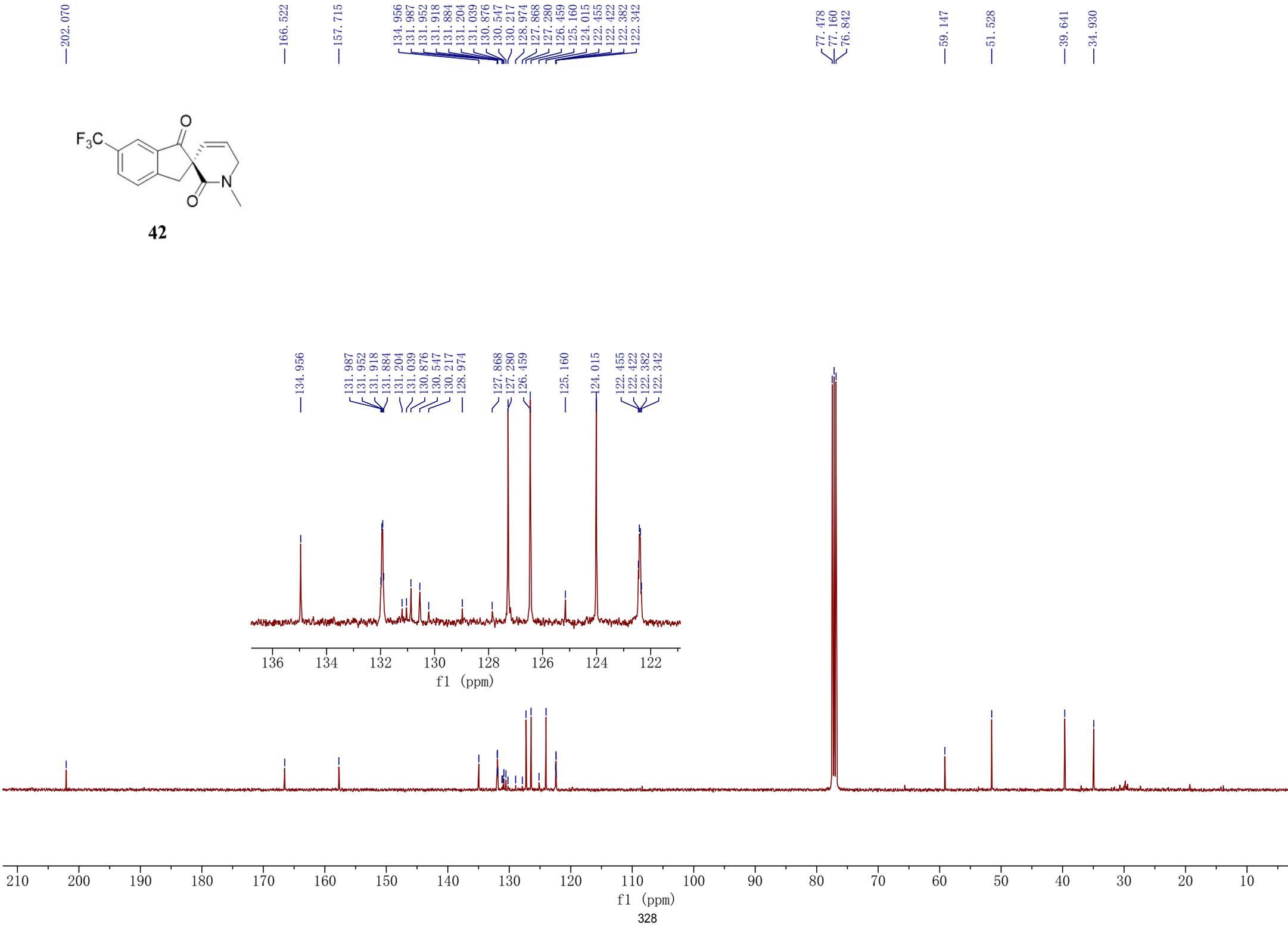
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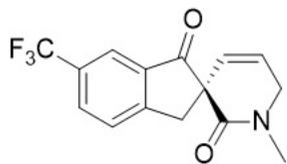
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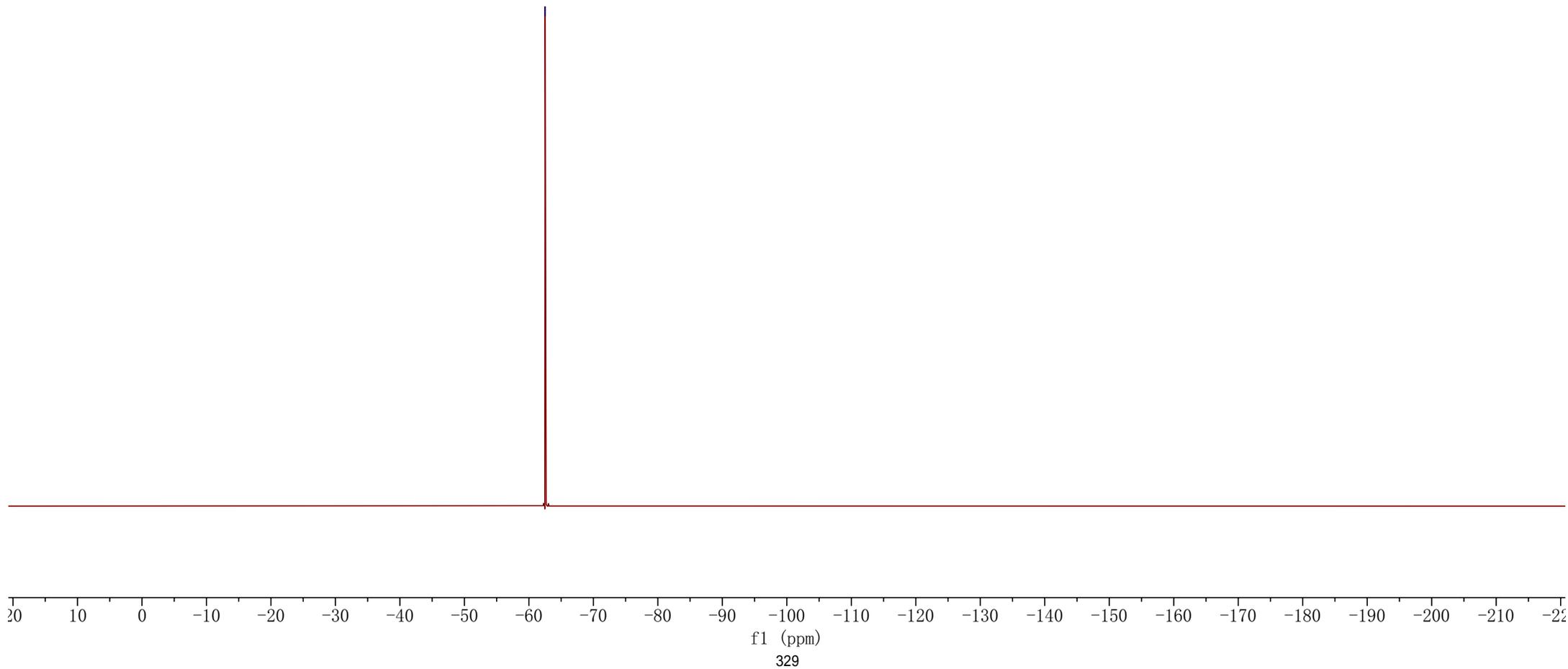
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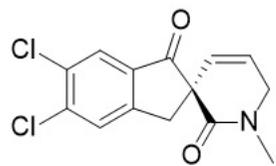




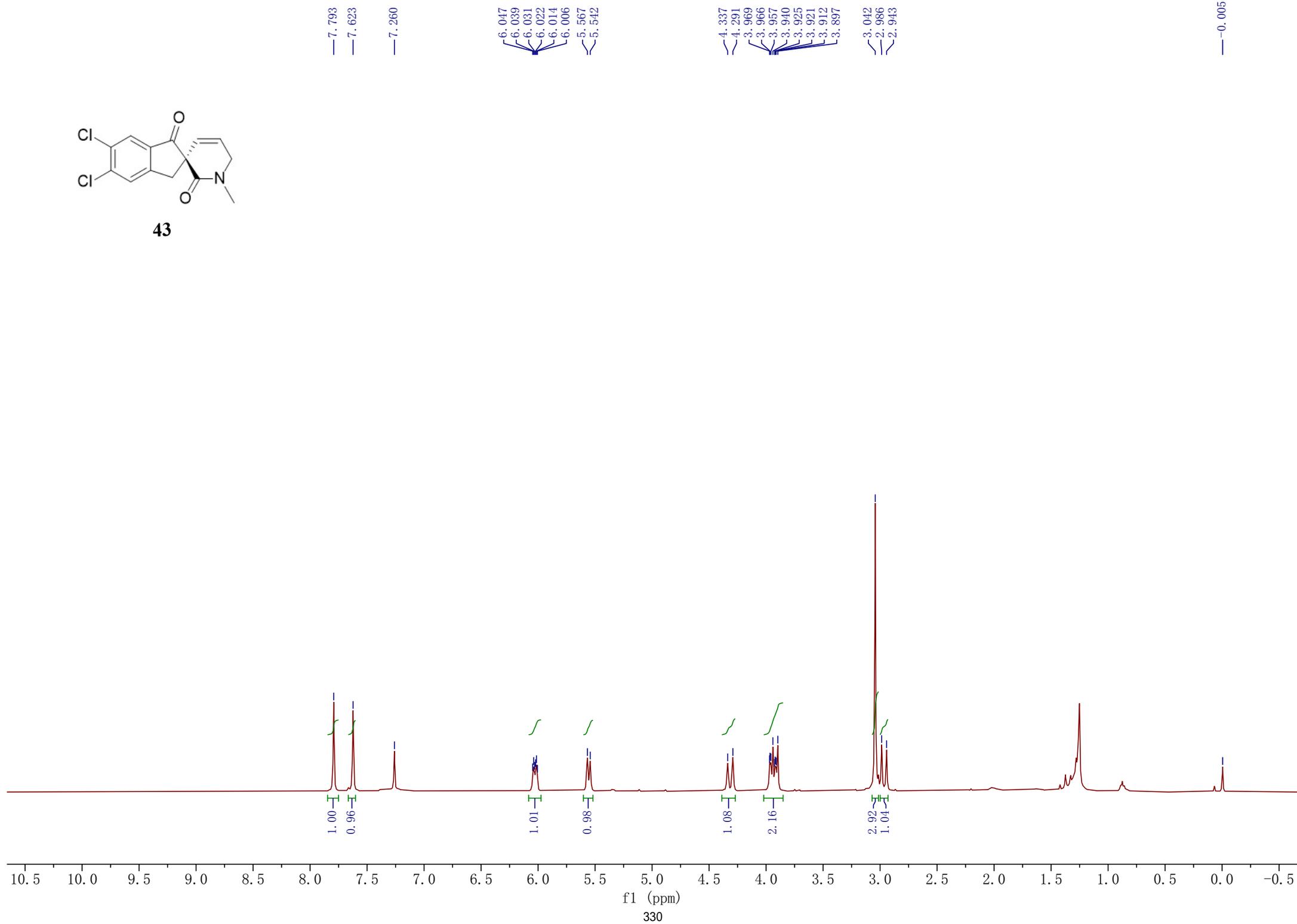
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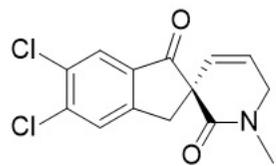
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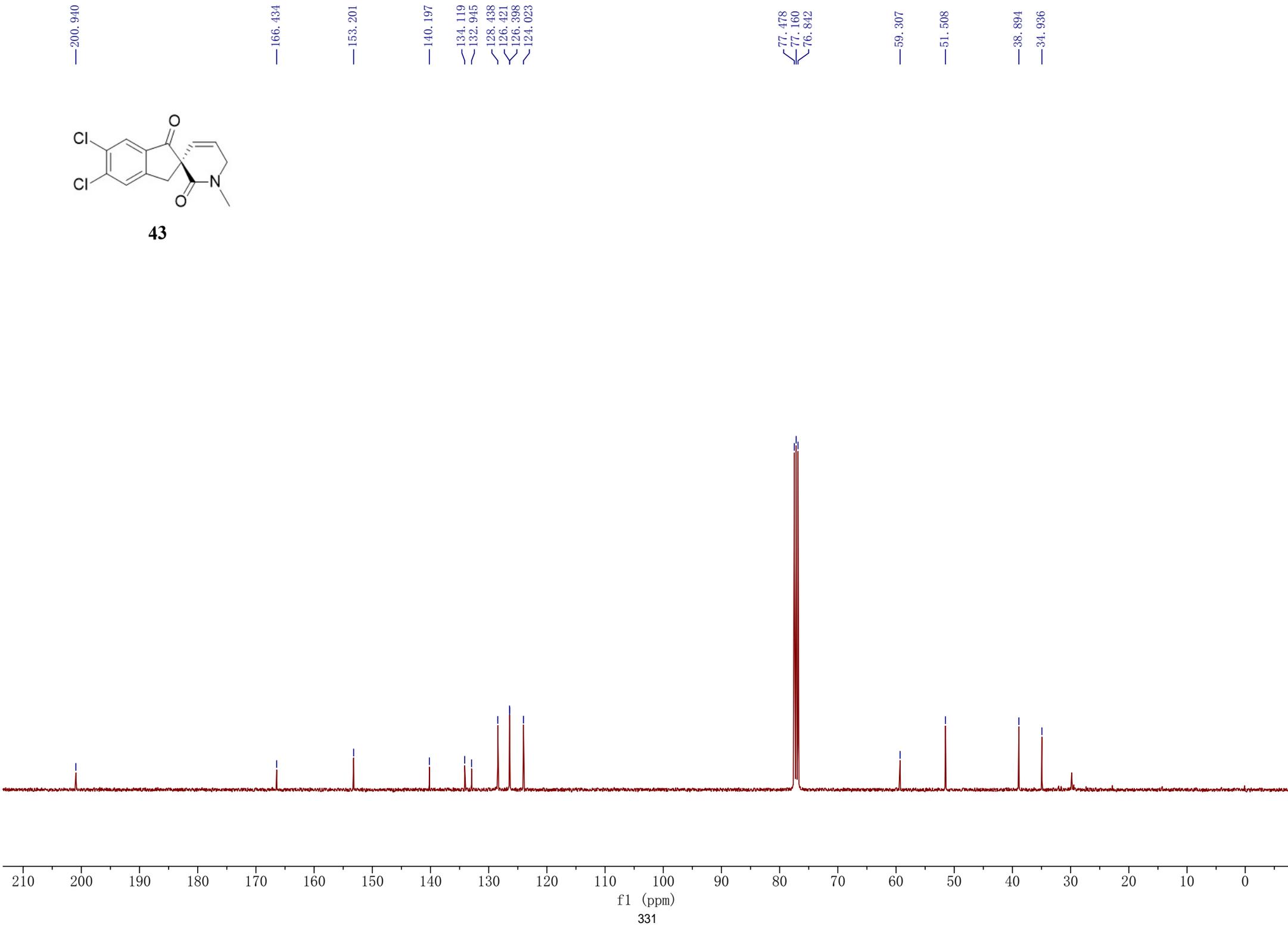


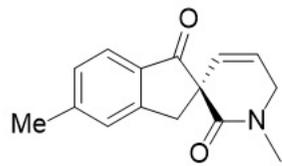
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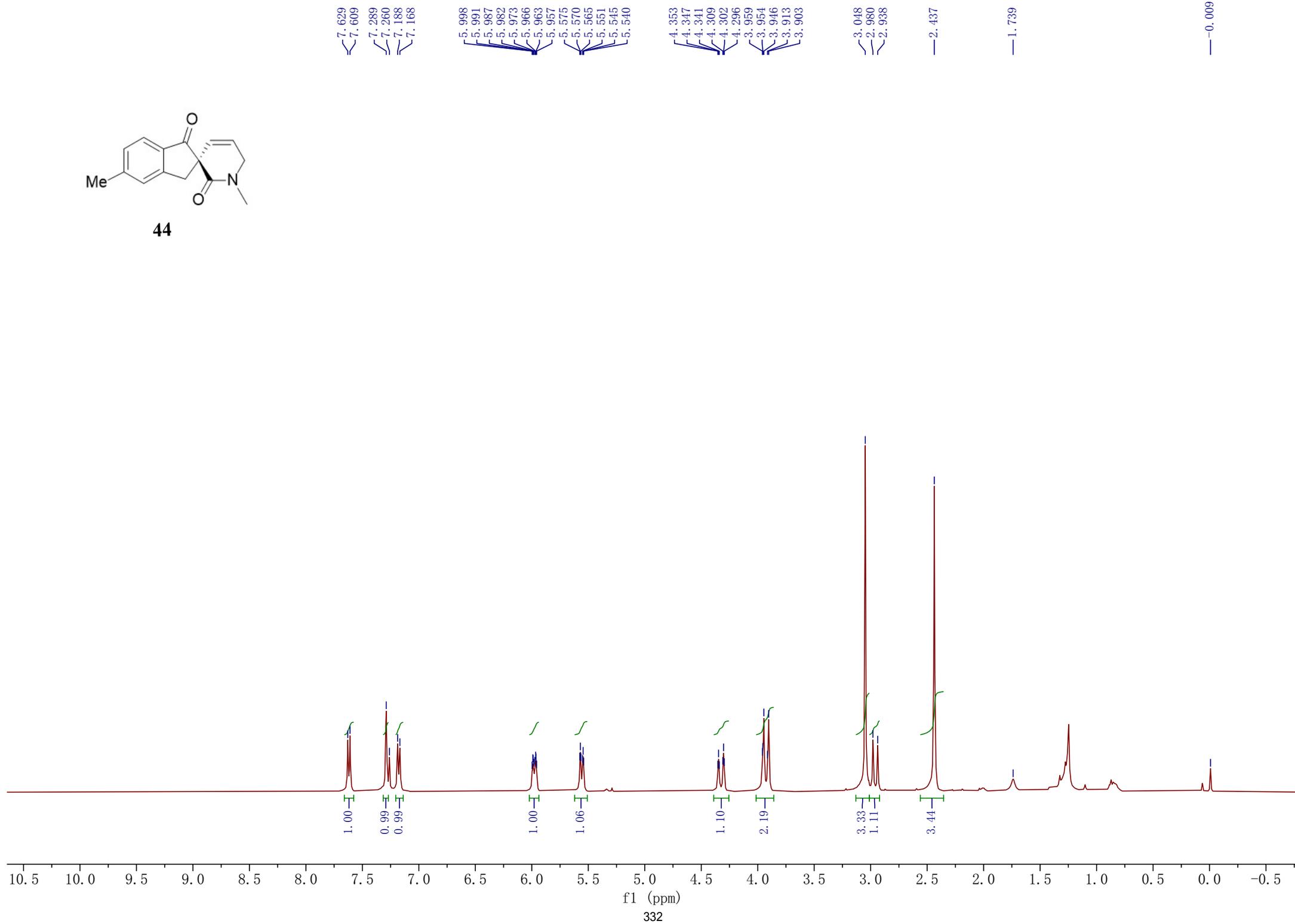


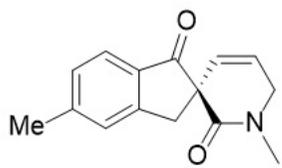
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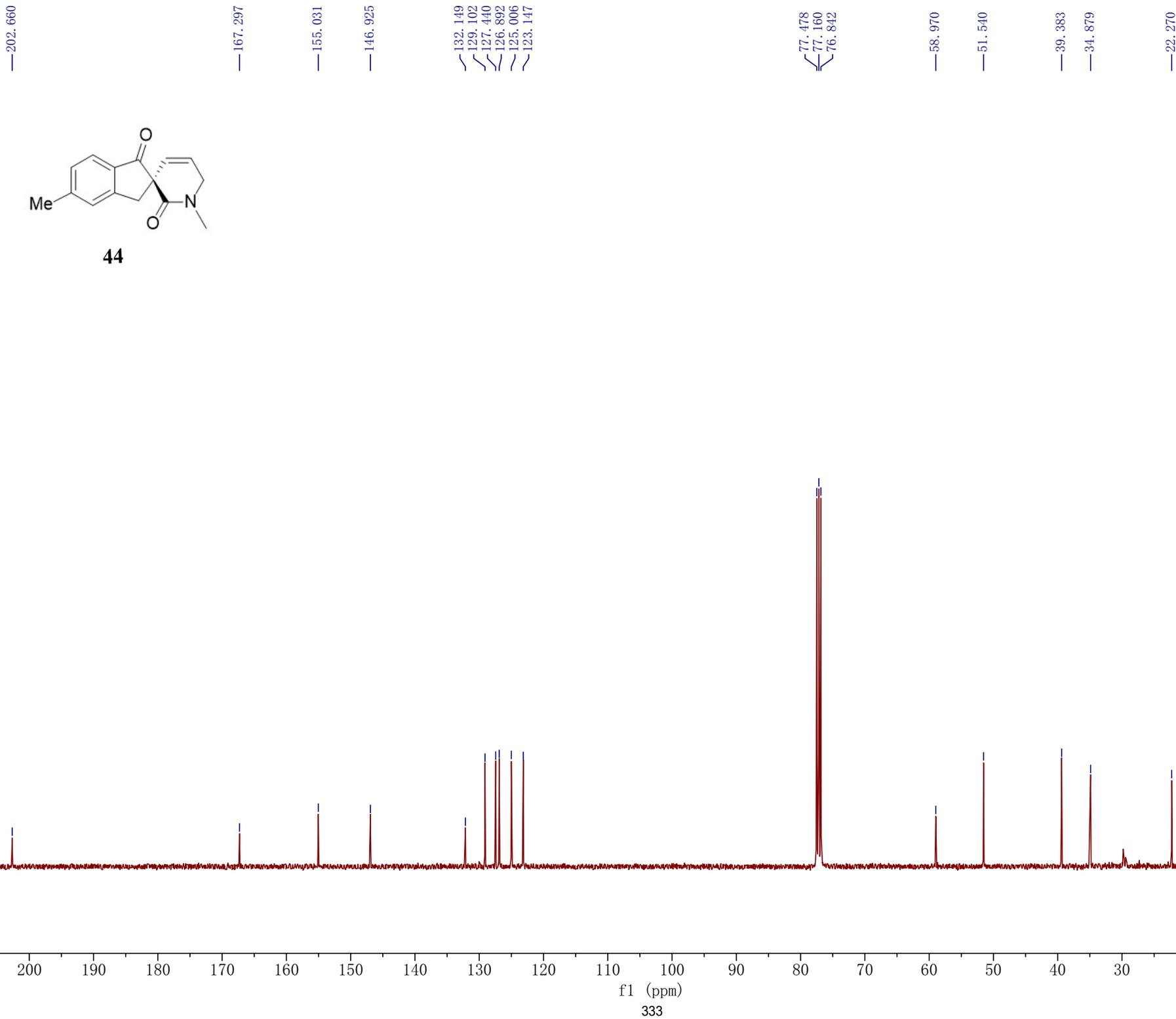


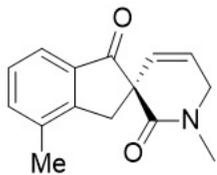
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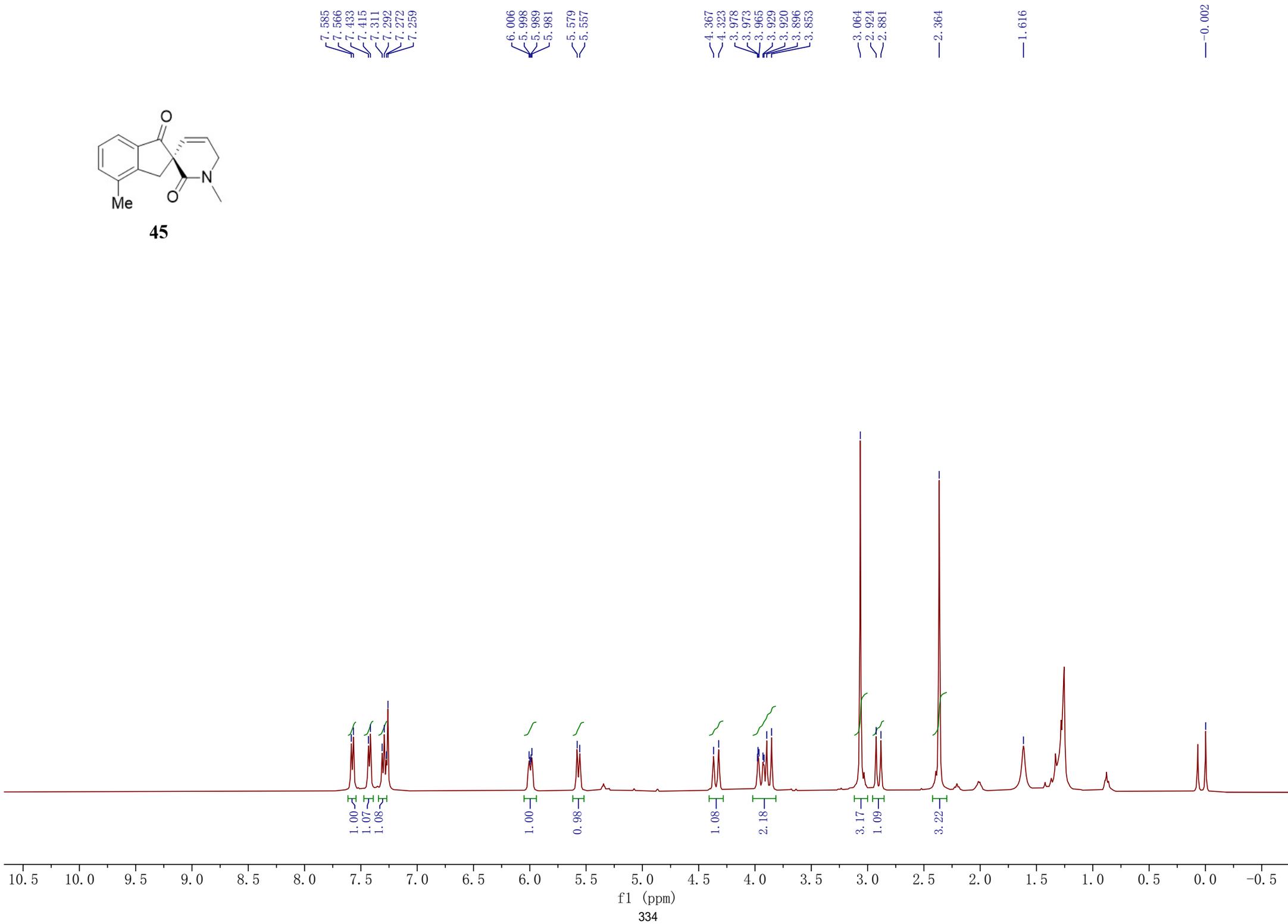


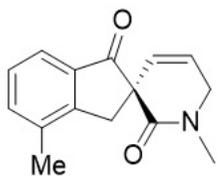
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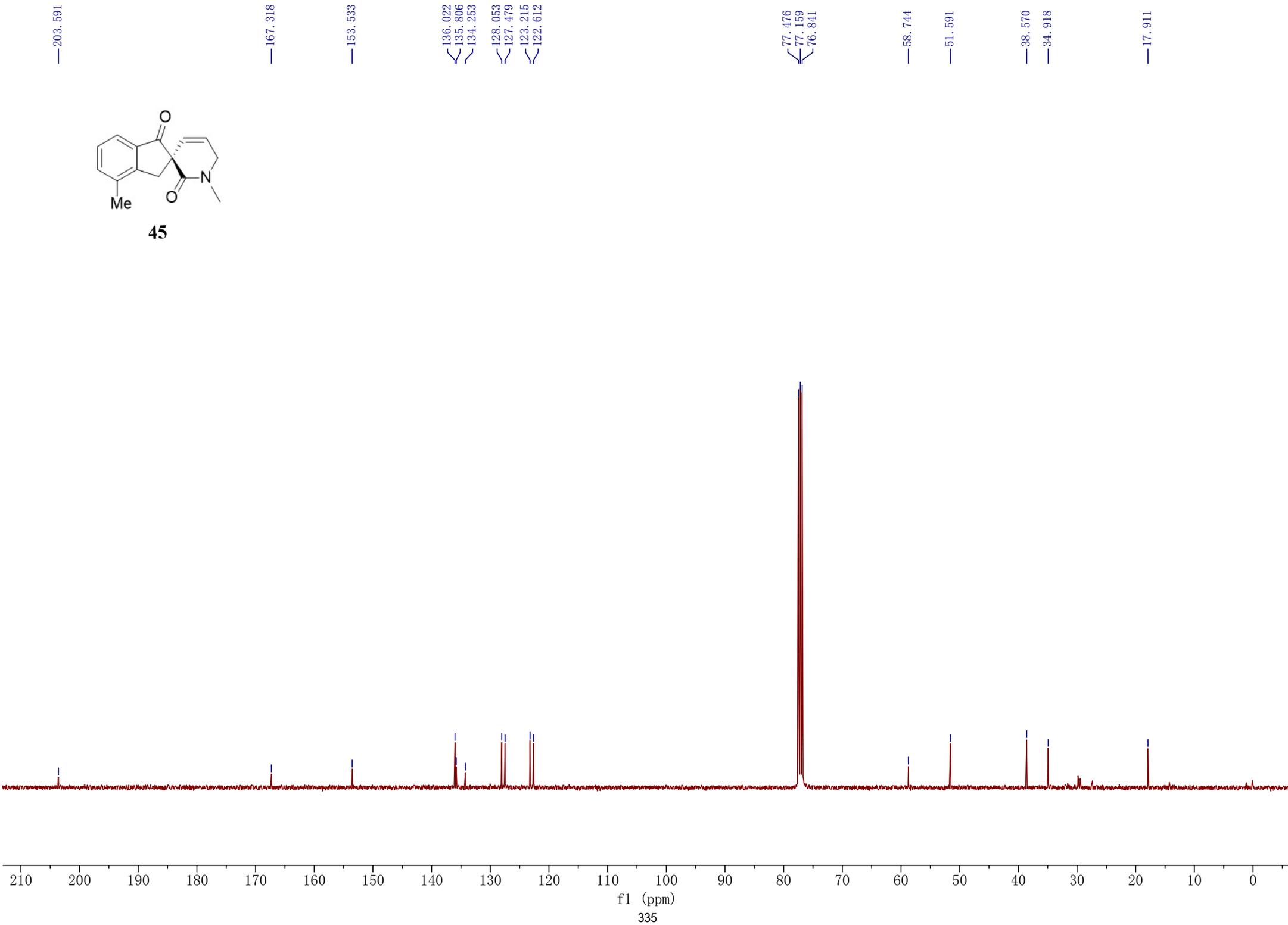


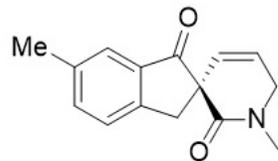
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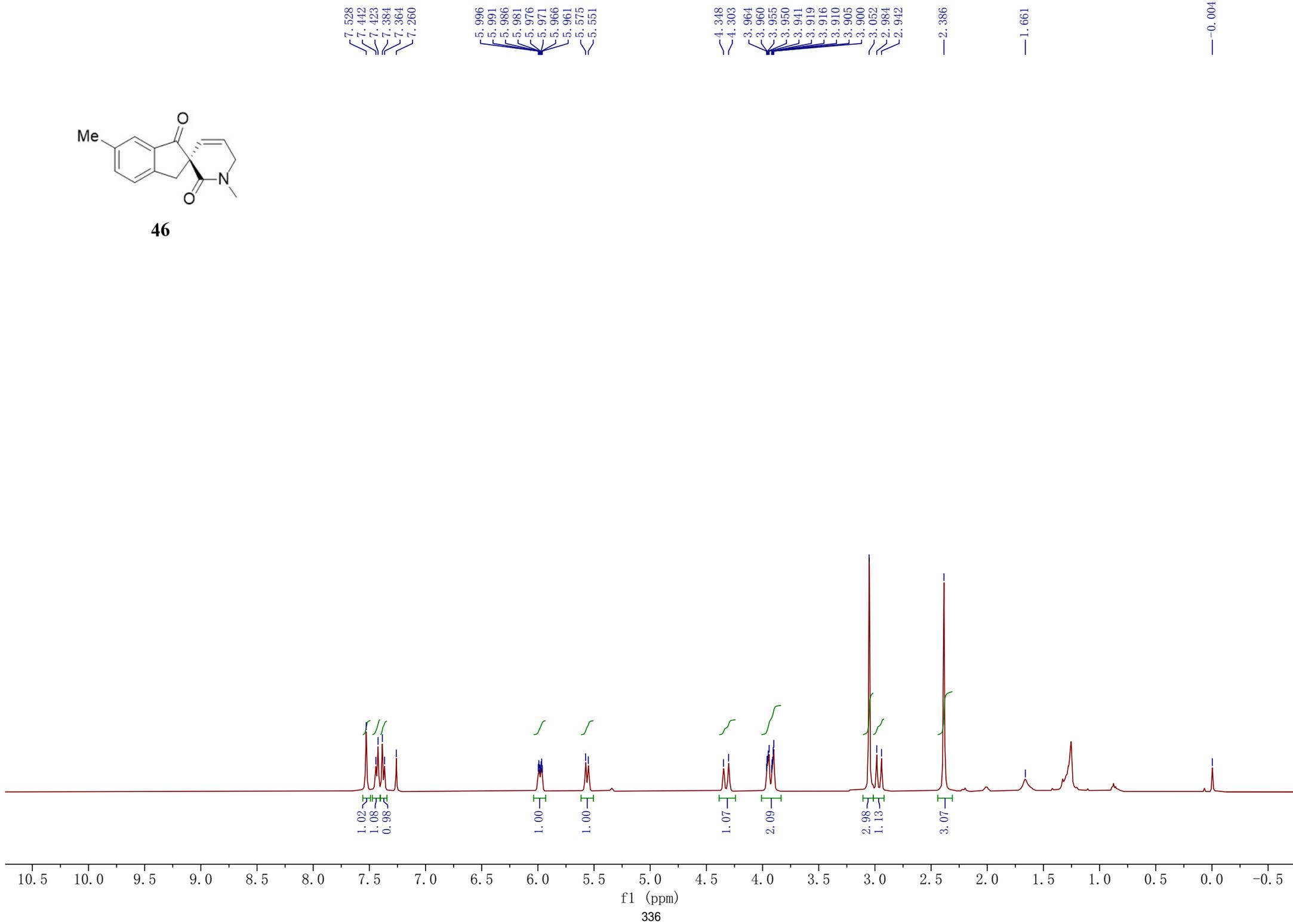


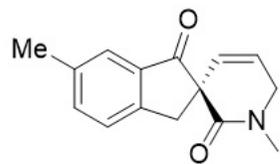
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46





46

—203.289

—167.270

—151.960

137.786
136.846
134.648

127.457
126.217
125.054
123.173

77.477
77.159
76.843

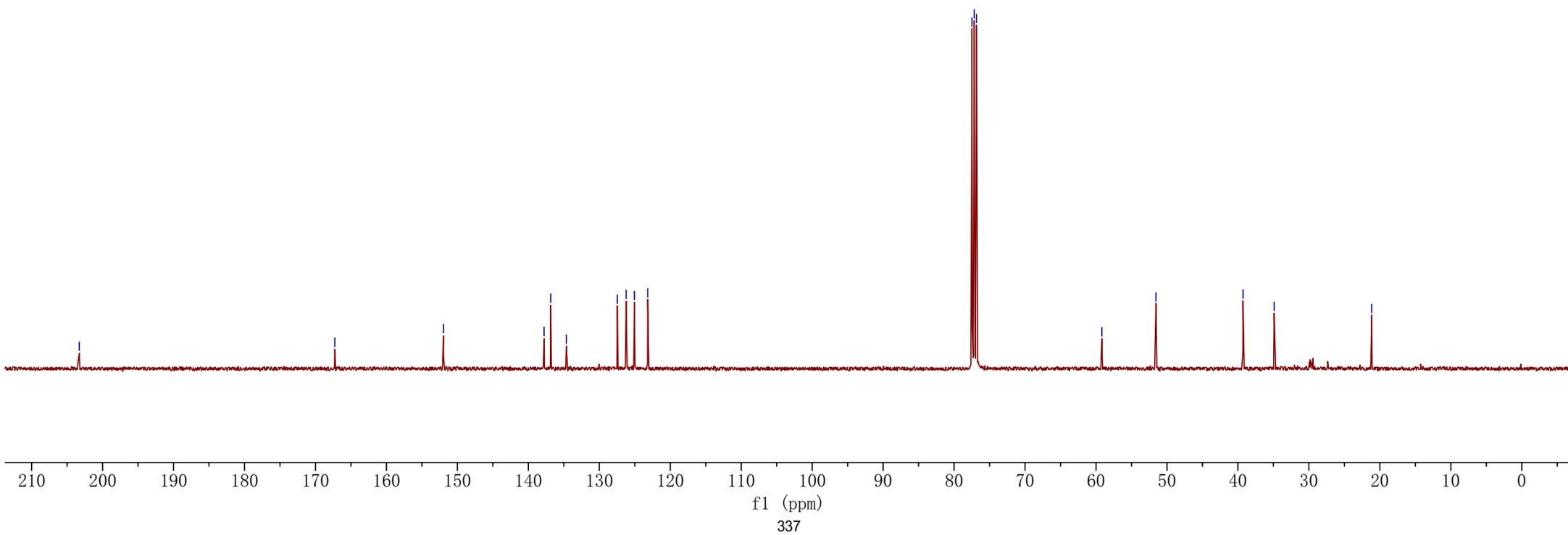
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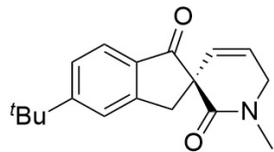
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—39.276

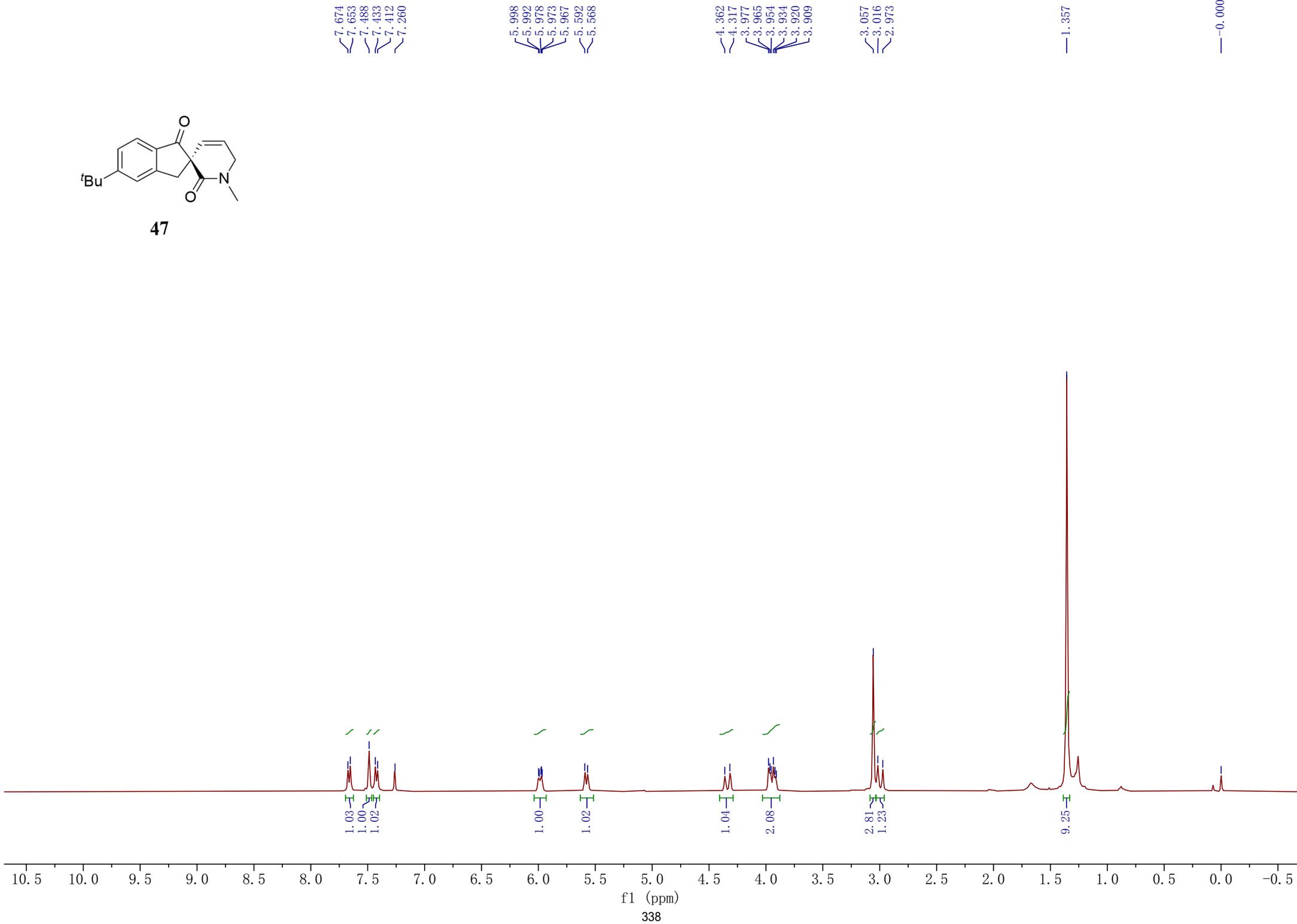
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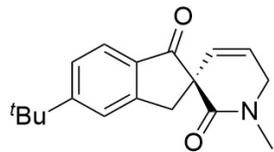
—21.149





47





47

— 202.755

— 167.384

— 159.895

— 154.868

— 132.083

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— 125.660

— 124.810

— 123.142

— 123.132

— 77.480

— 77.162

— 76.844

— 59.051

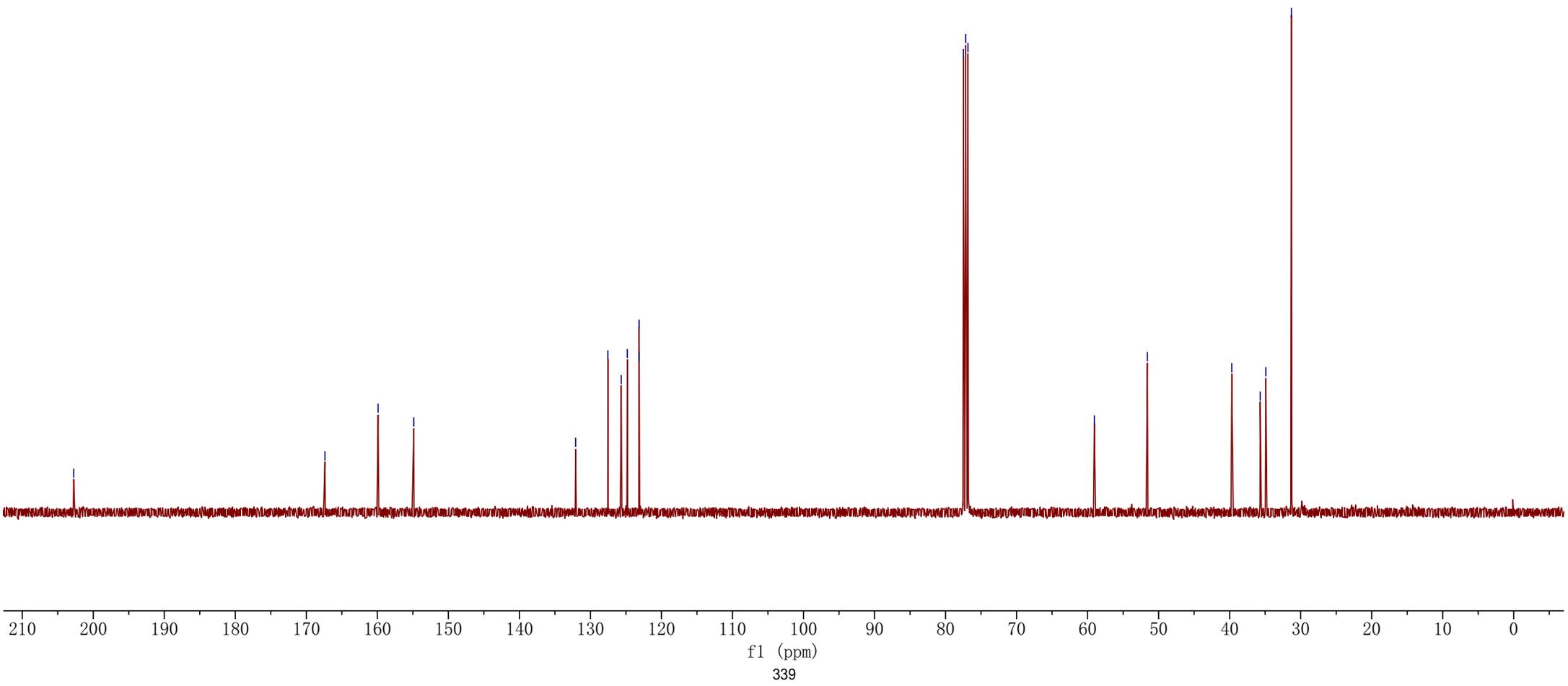
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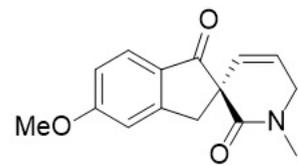
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— 35.692

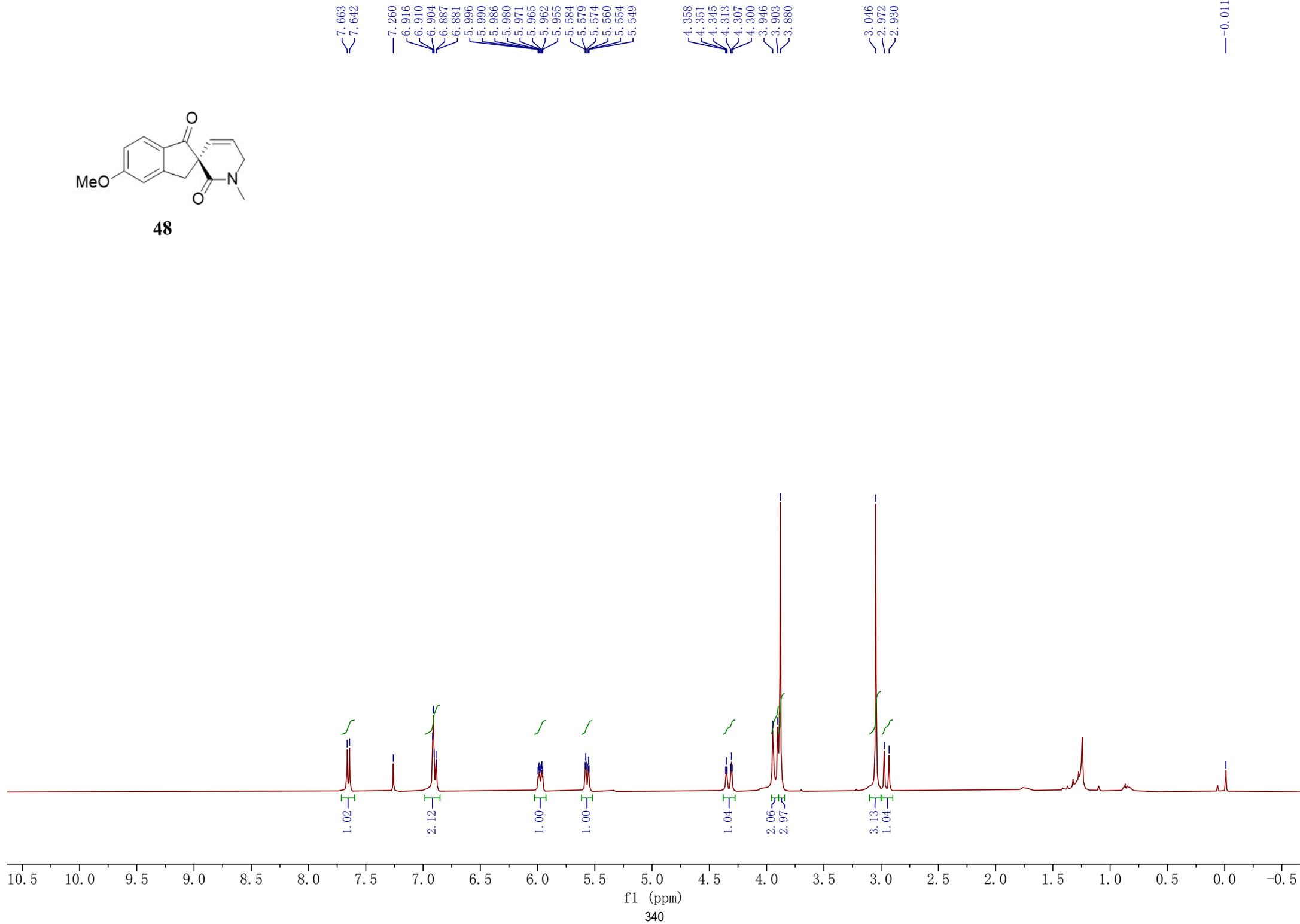
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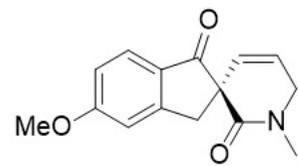
— 31.304



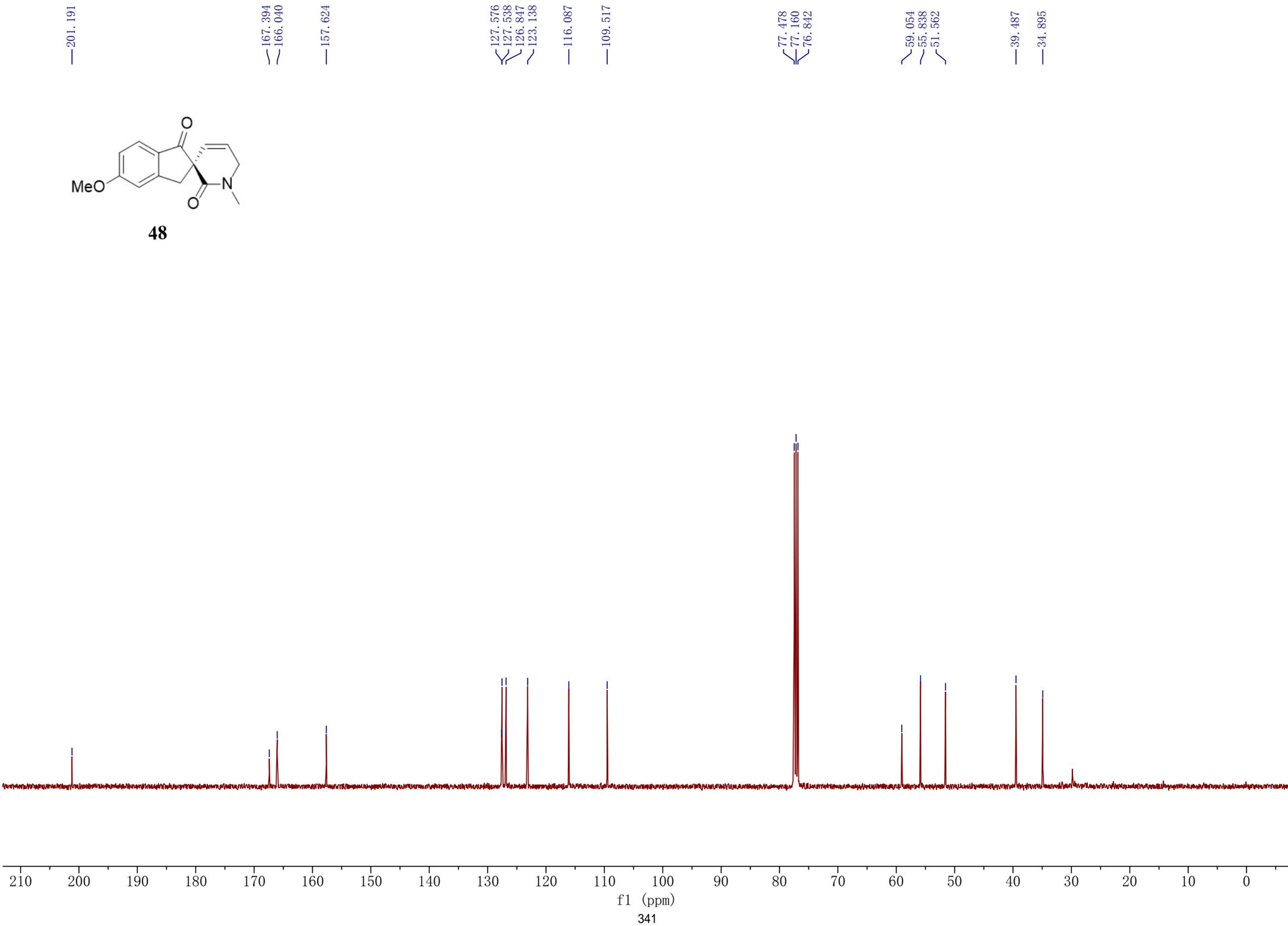


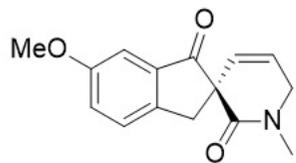
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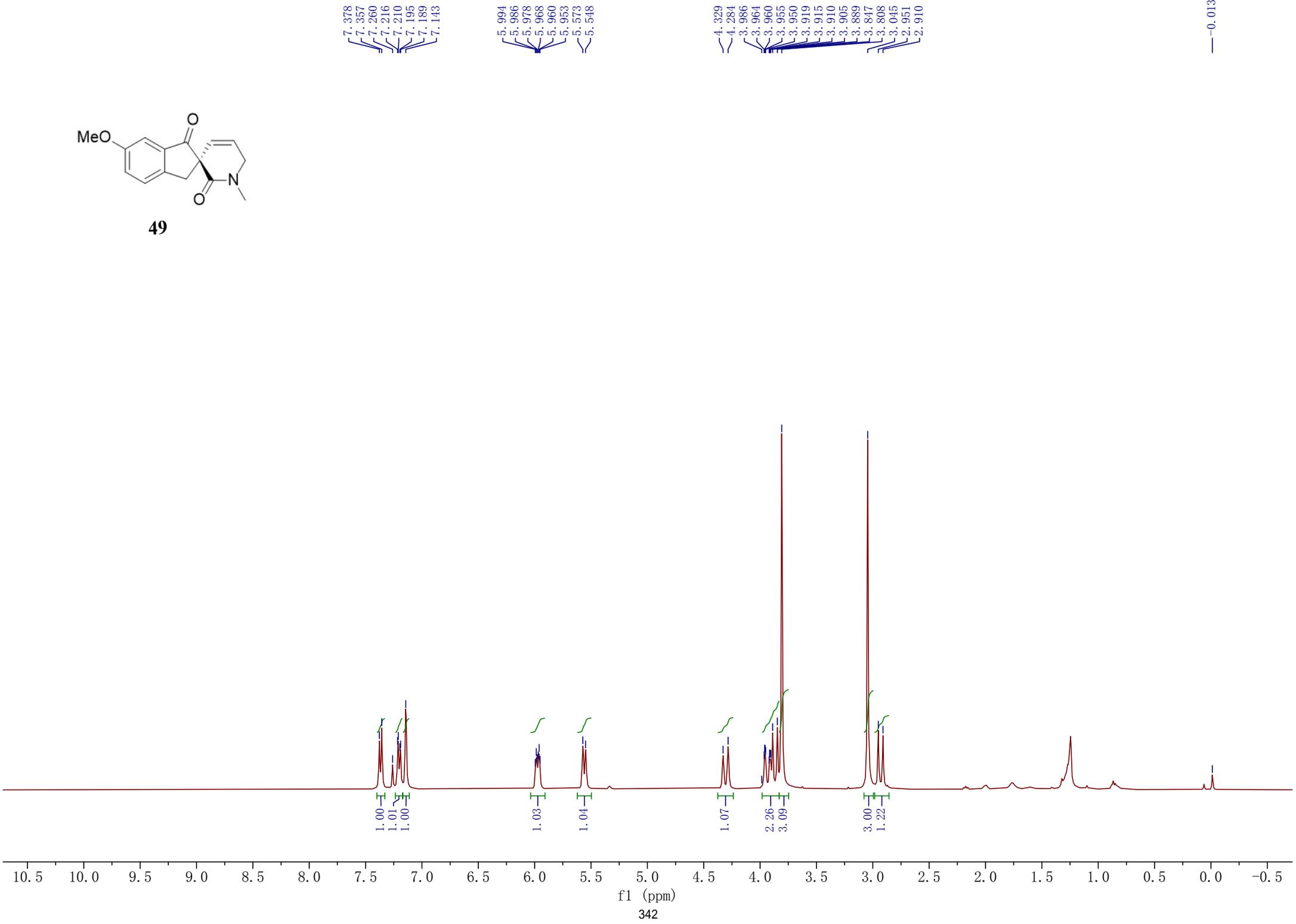


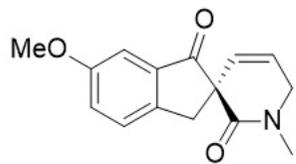
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49





49

—203.161

—167.187

—159.741

—147.479

—135.620

127.331

127.196

125.034

123.122

—106.134

77.479

77.161

76.843

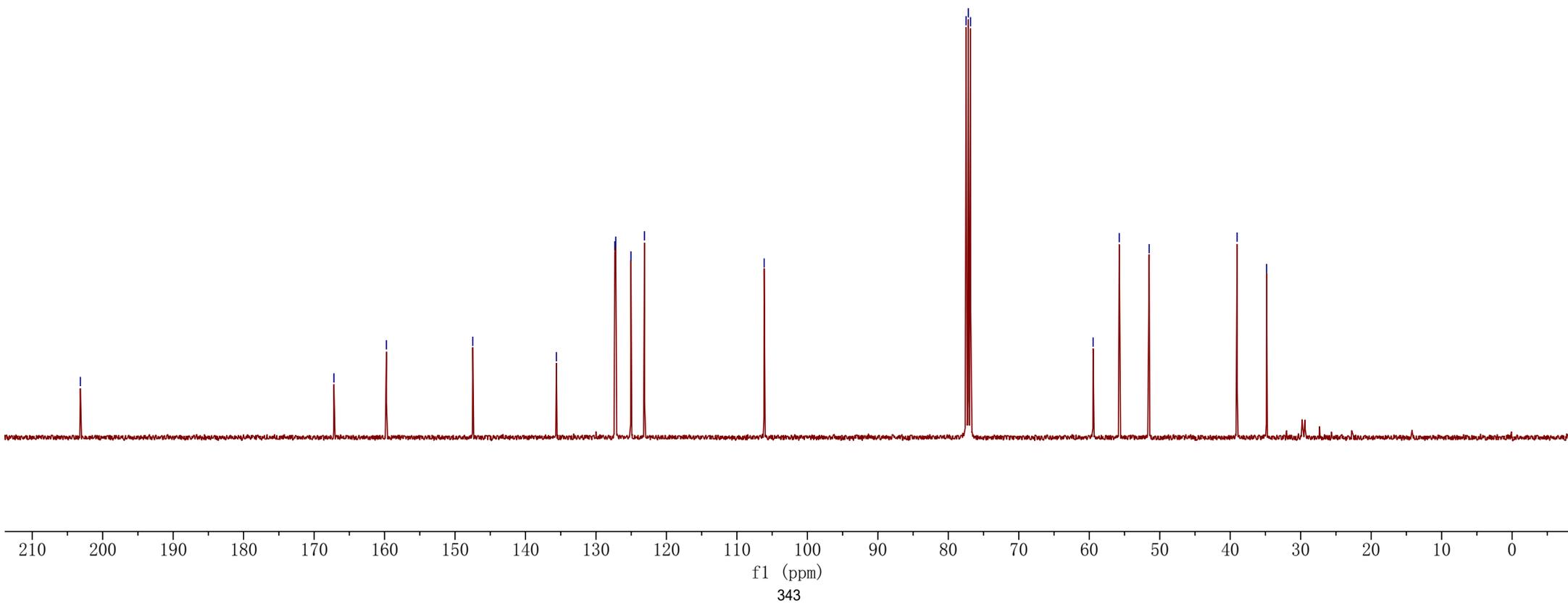
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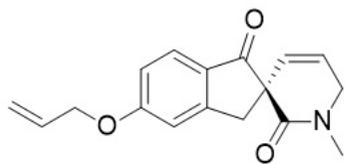
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51.501

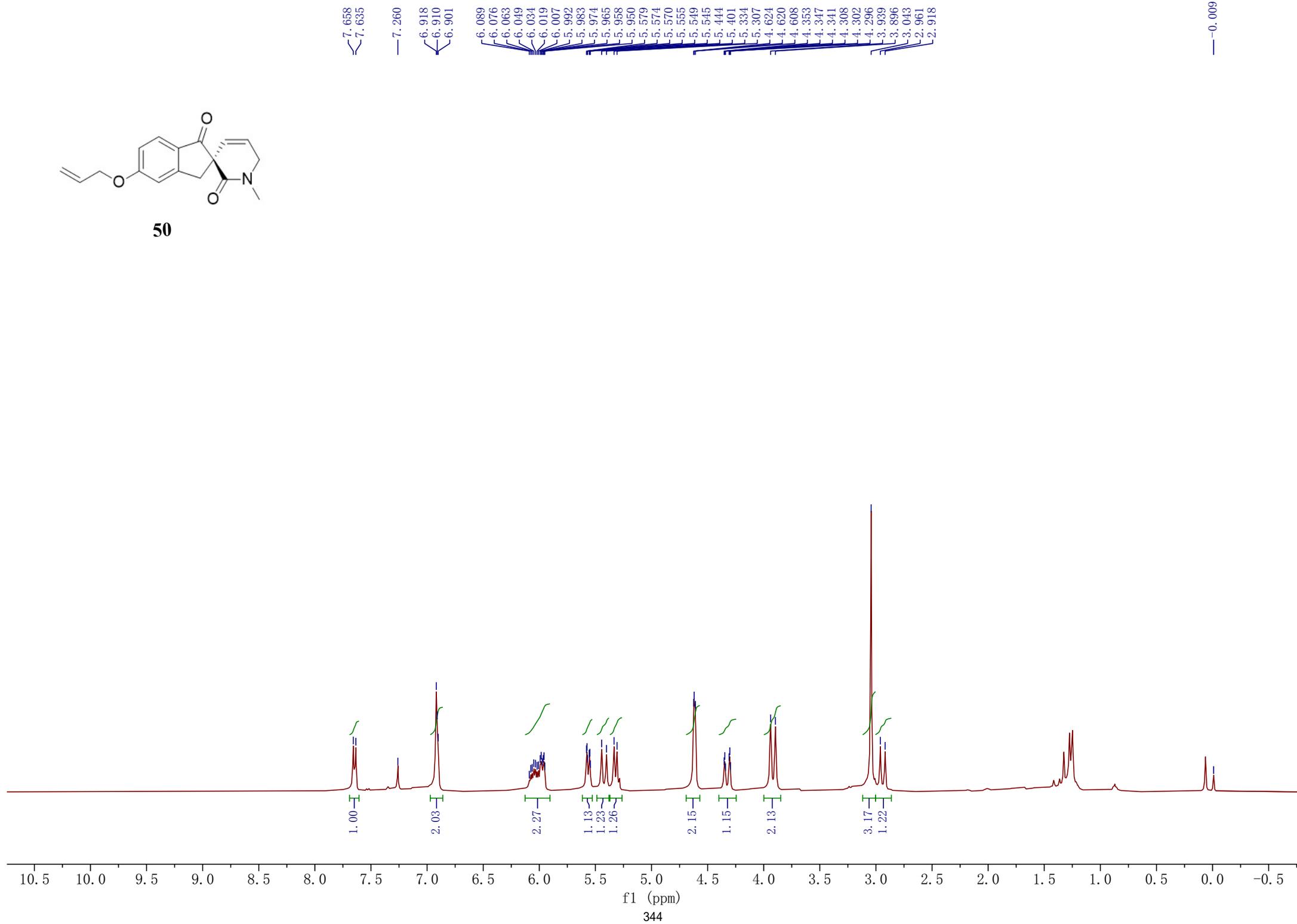
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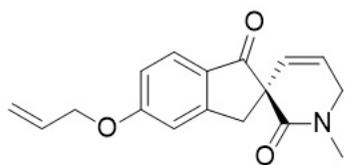
—34.838





50





50

— 201.126

— 167.387

— 165.021

— 157.495

— 132.413

— 127.683

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— 118.406

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— 110.441

— 77.478

— 77.160

— 76.842

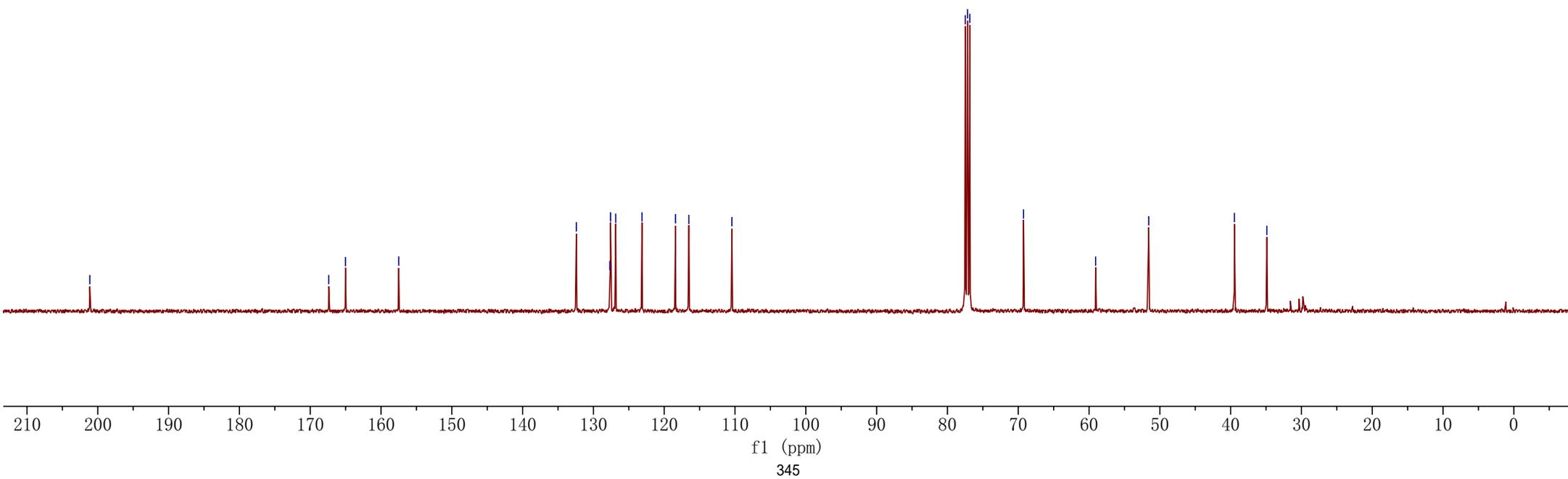
— 69.247

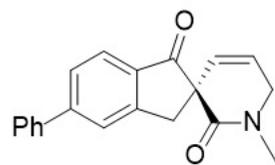
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— 51.567

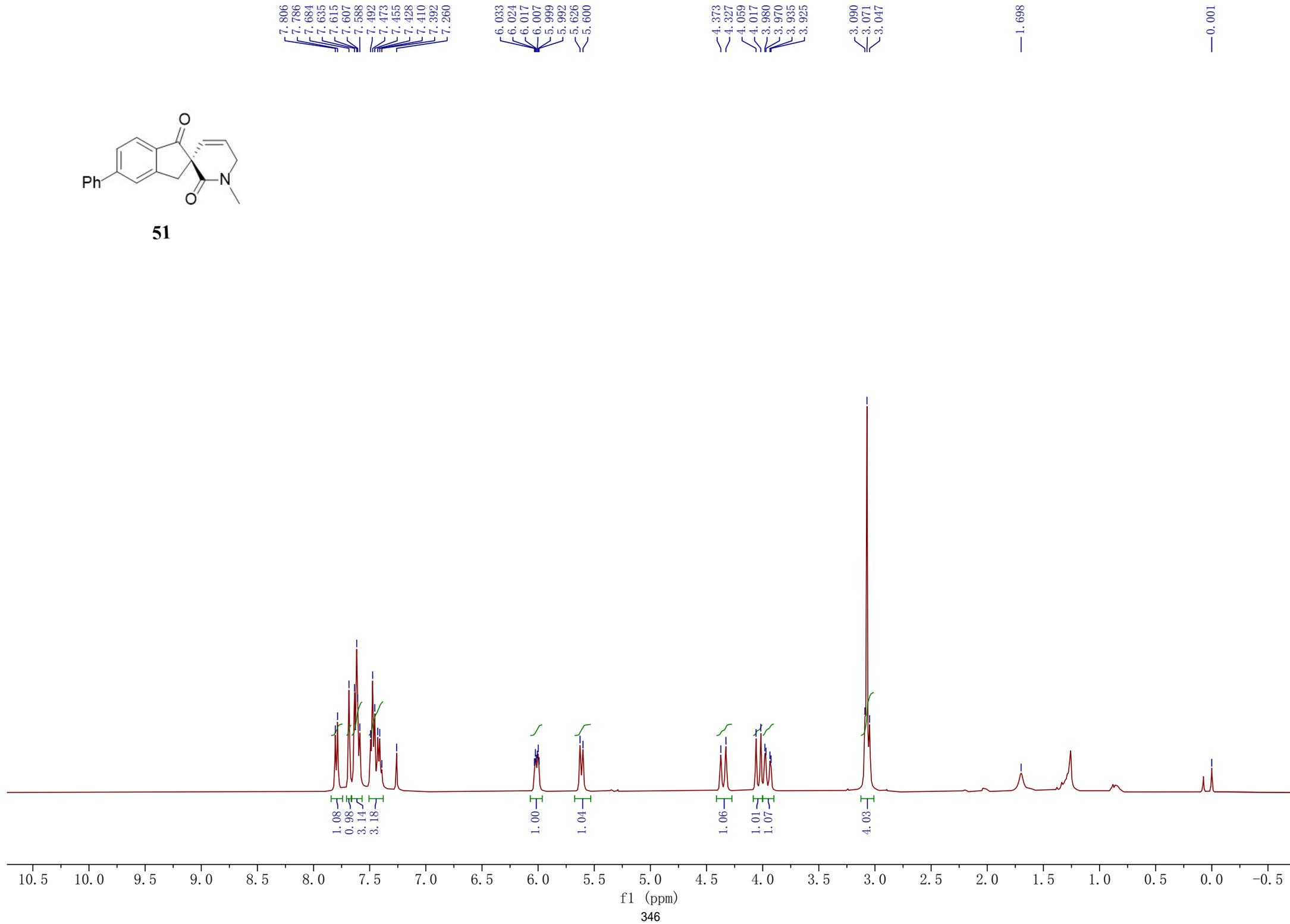
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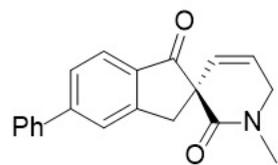
— 34.884





51



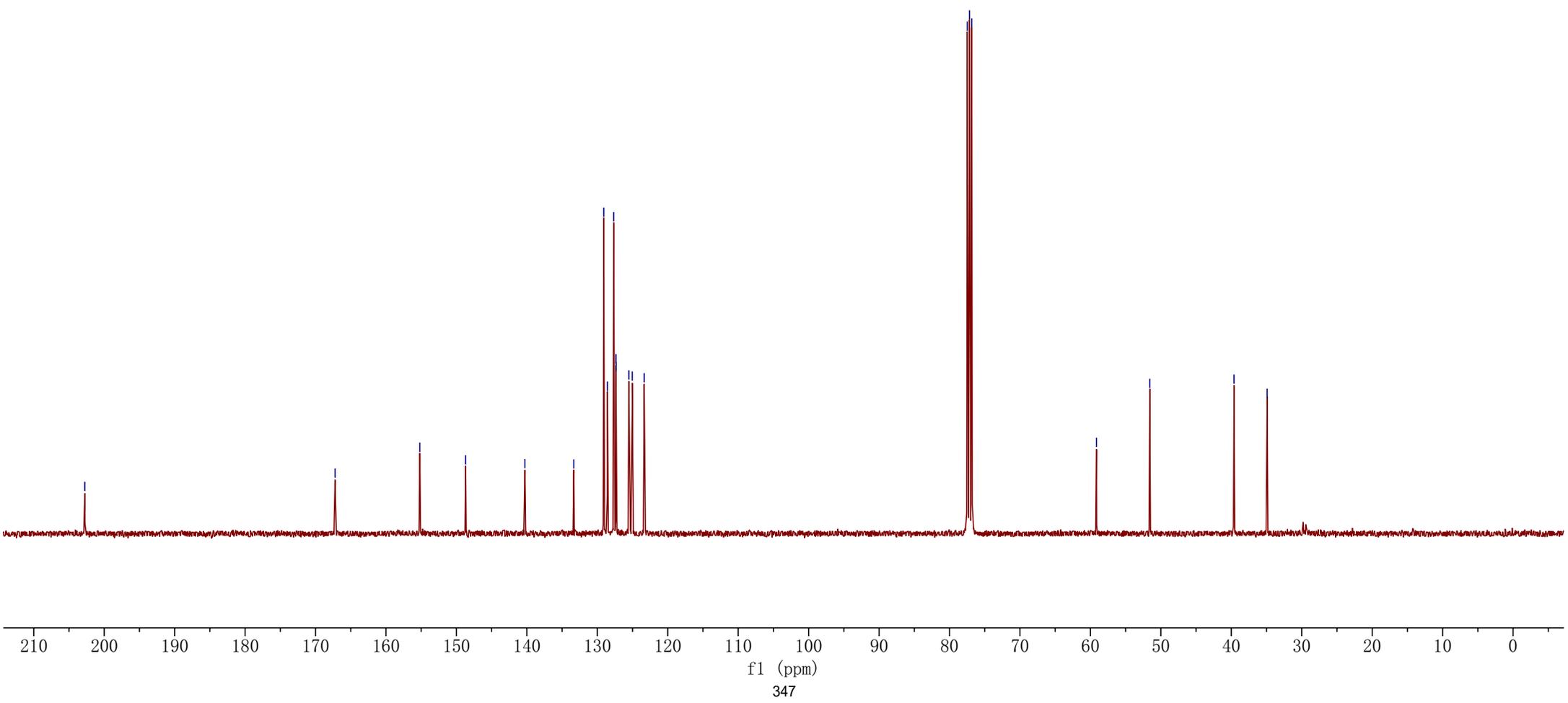


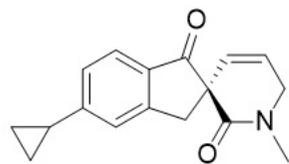
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—167.226
—155.195
—148.697
—140.279
133.338
129.084
128.557
127.675
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127.319
125.520
125.039
123.341

77.478
77.160
76.842

—59.143
—51.575
—39.614
—34.910





52

7.605
7.585
7.260
7.123
7.050
7.030

5.984
5.976
5.968
5.959
5.950
5.942
5.559
5.535

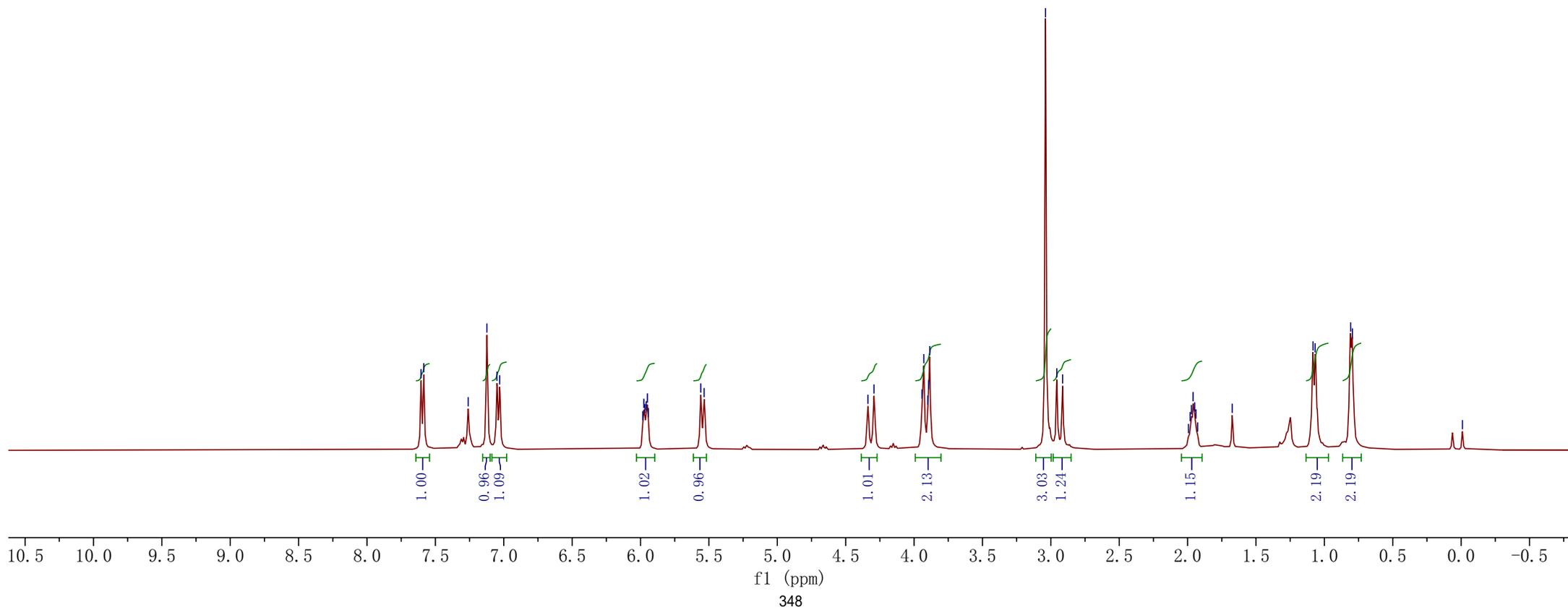
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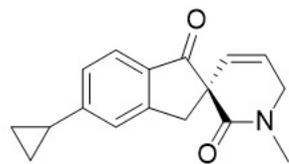
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1.972
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1.927
1.674

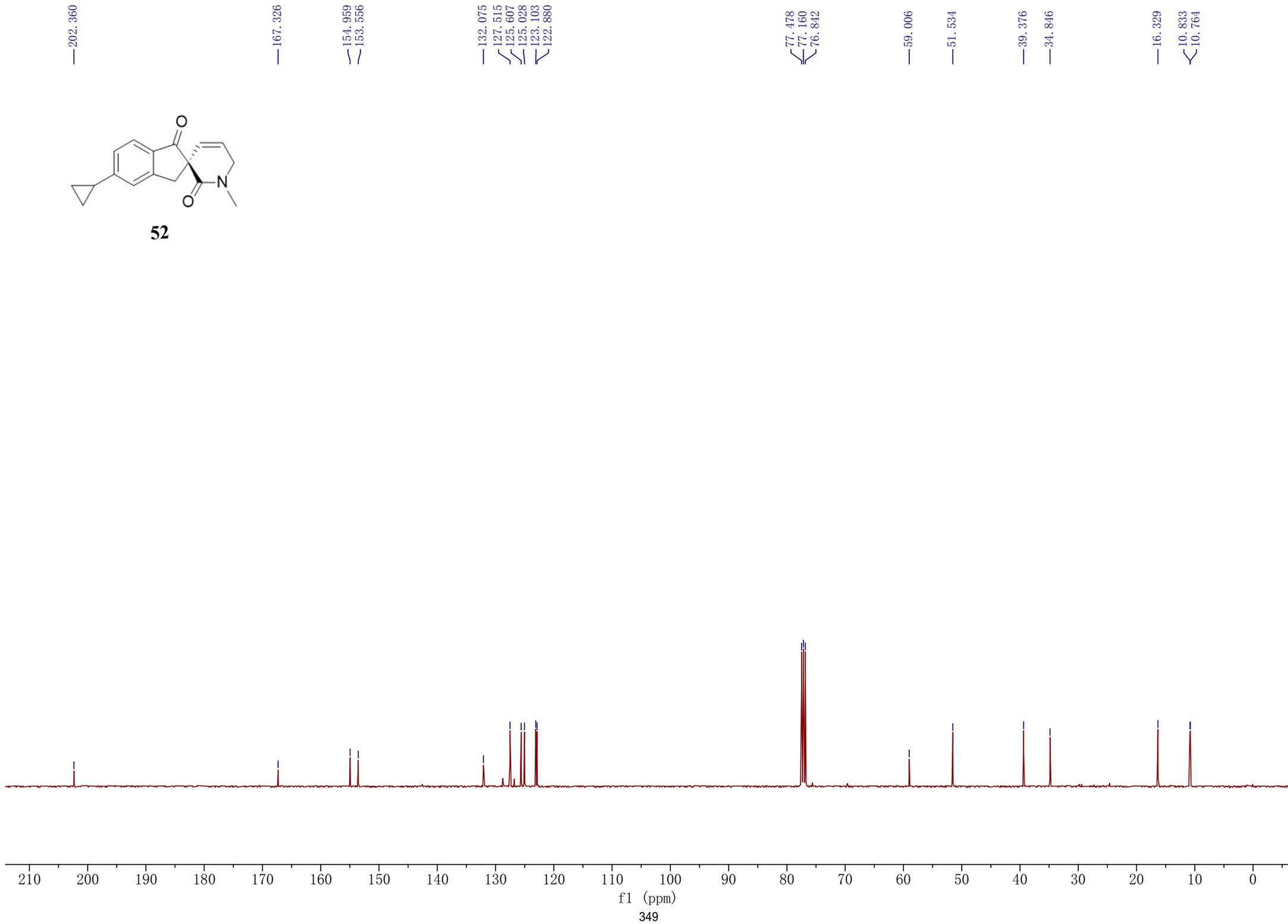
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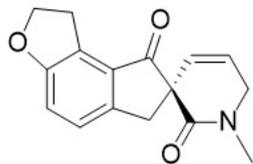
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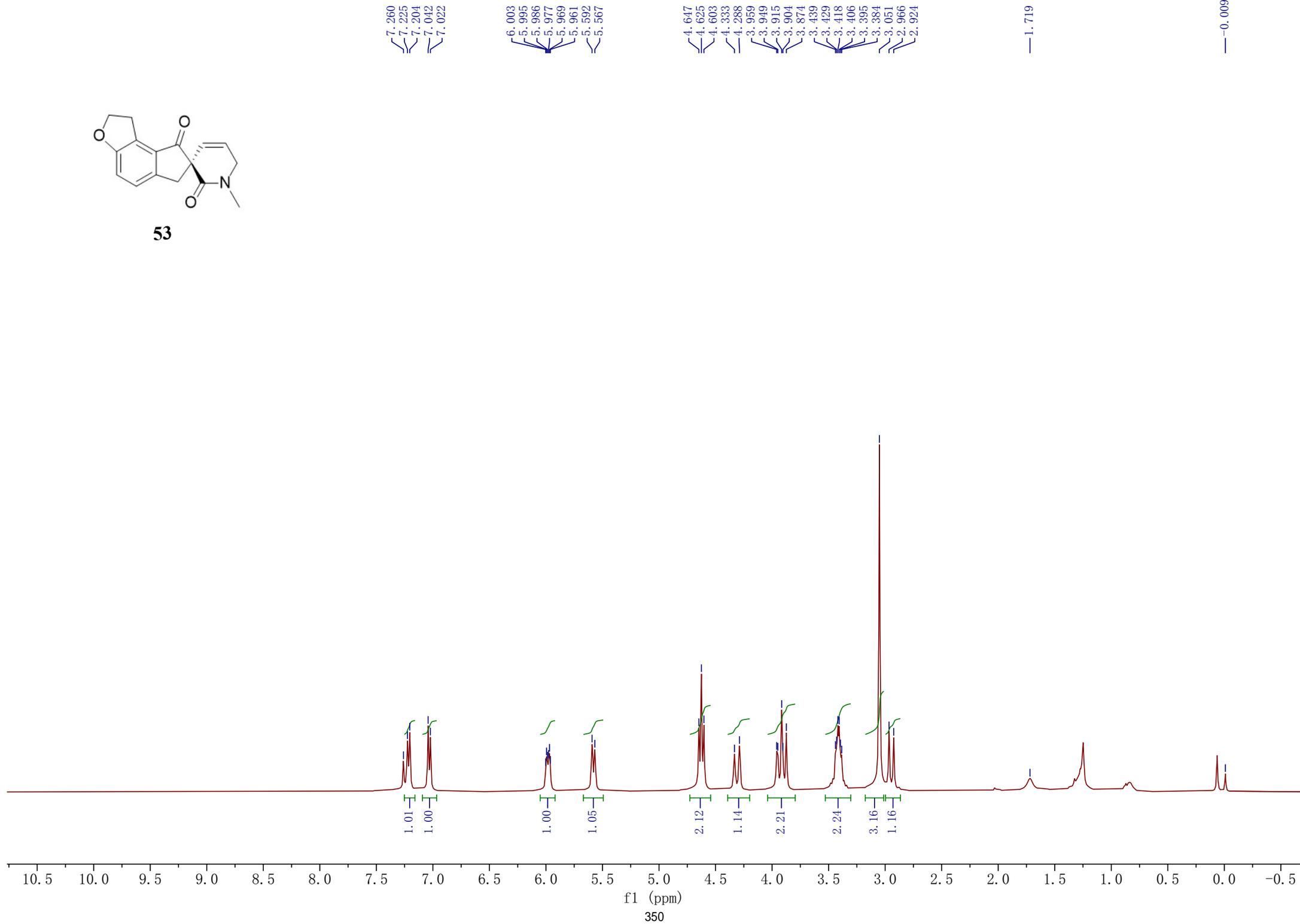


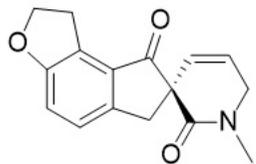
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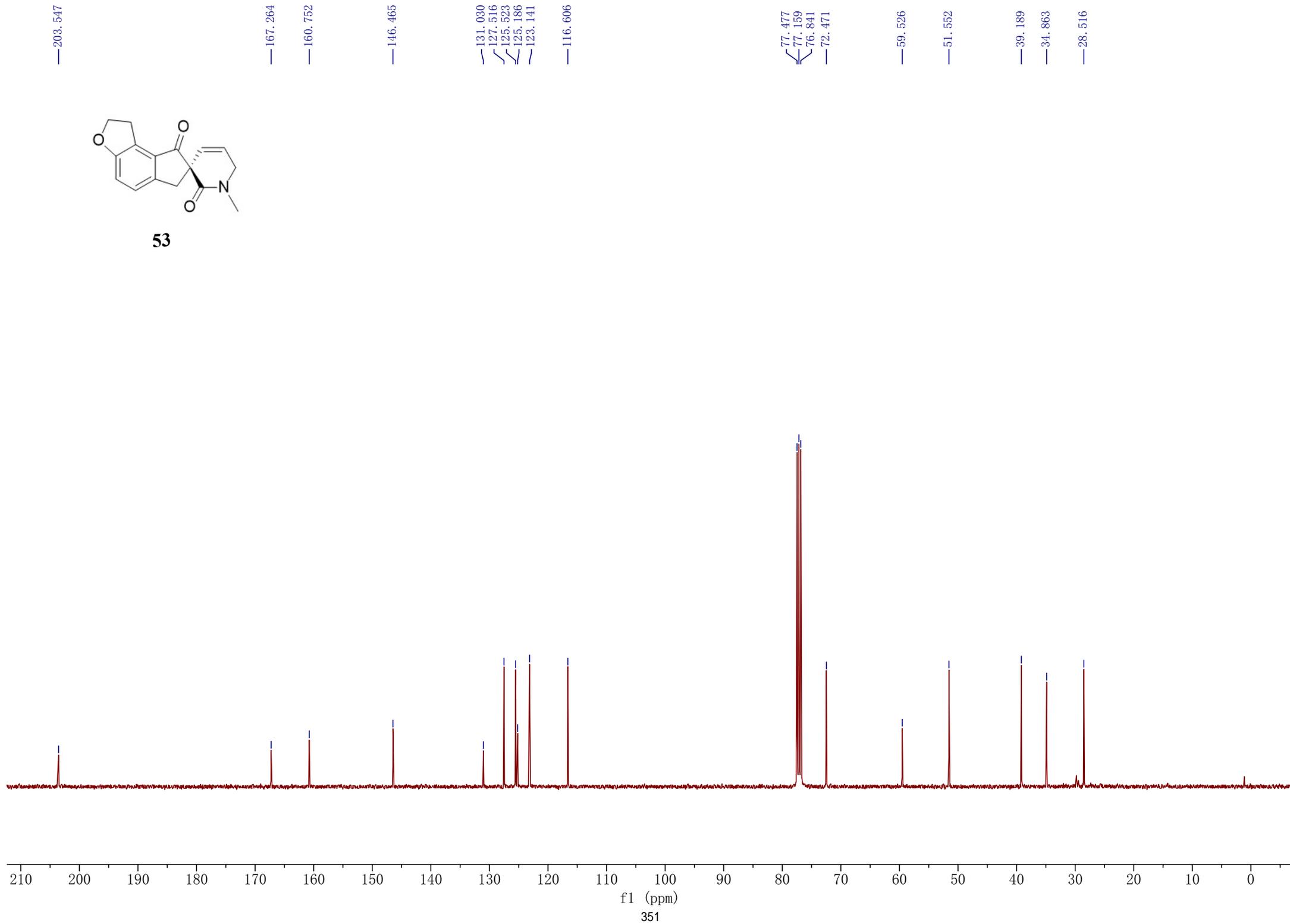


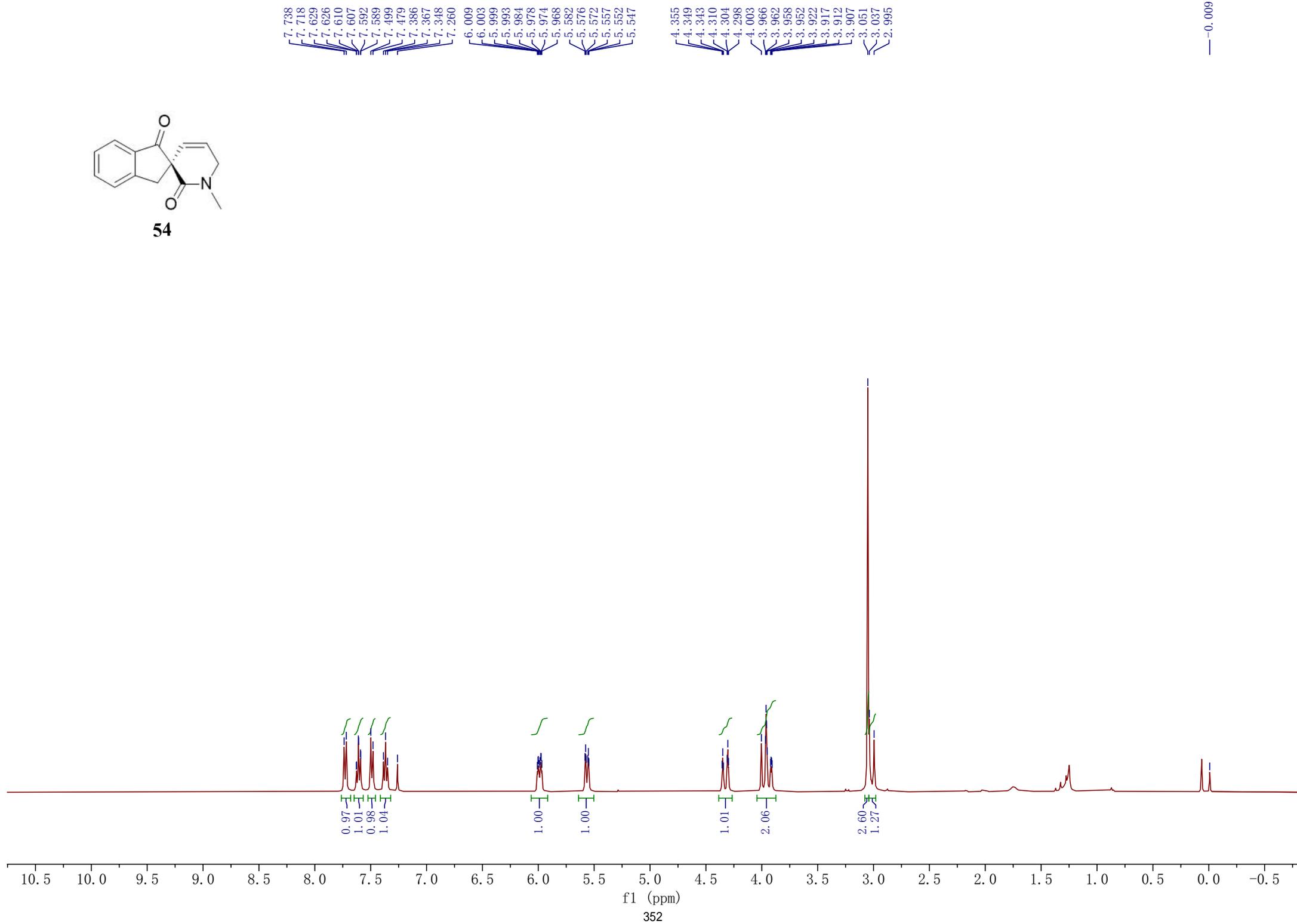
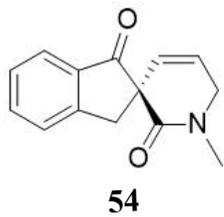
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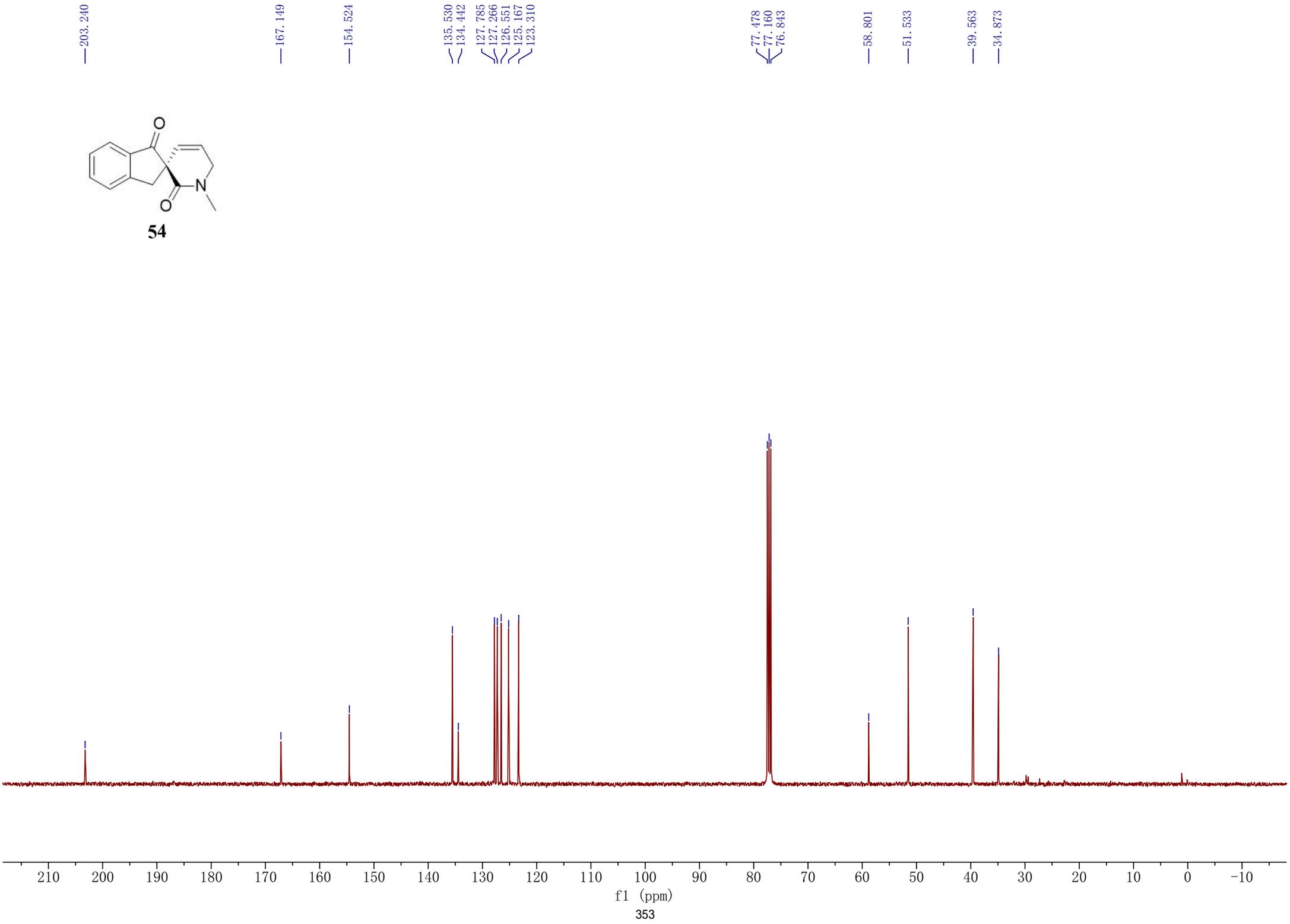
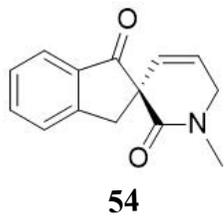


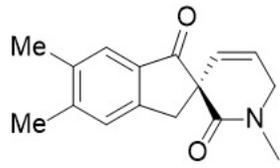


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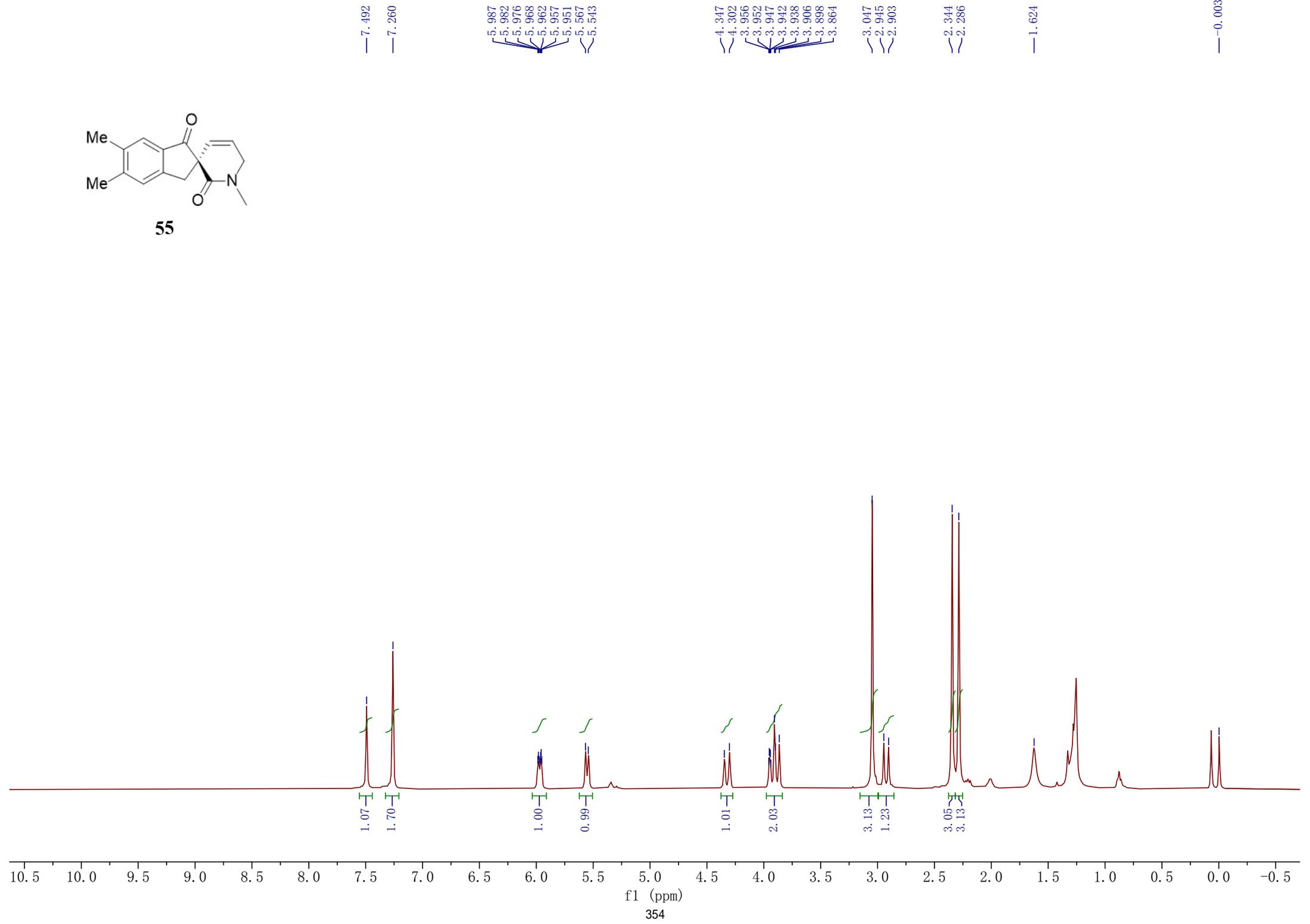


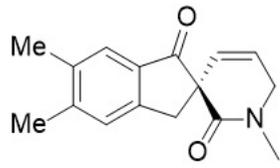




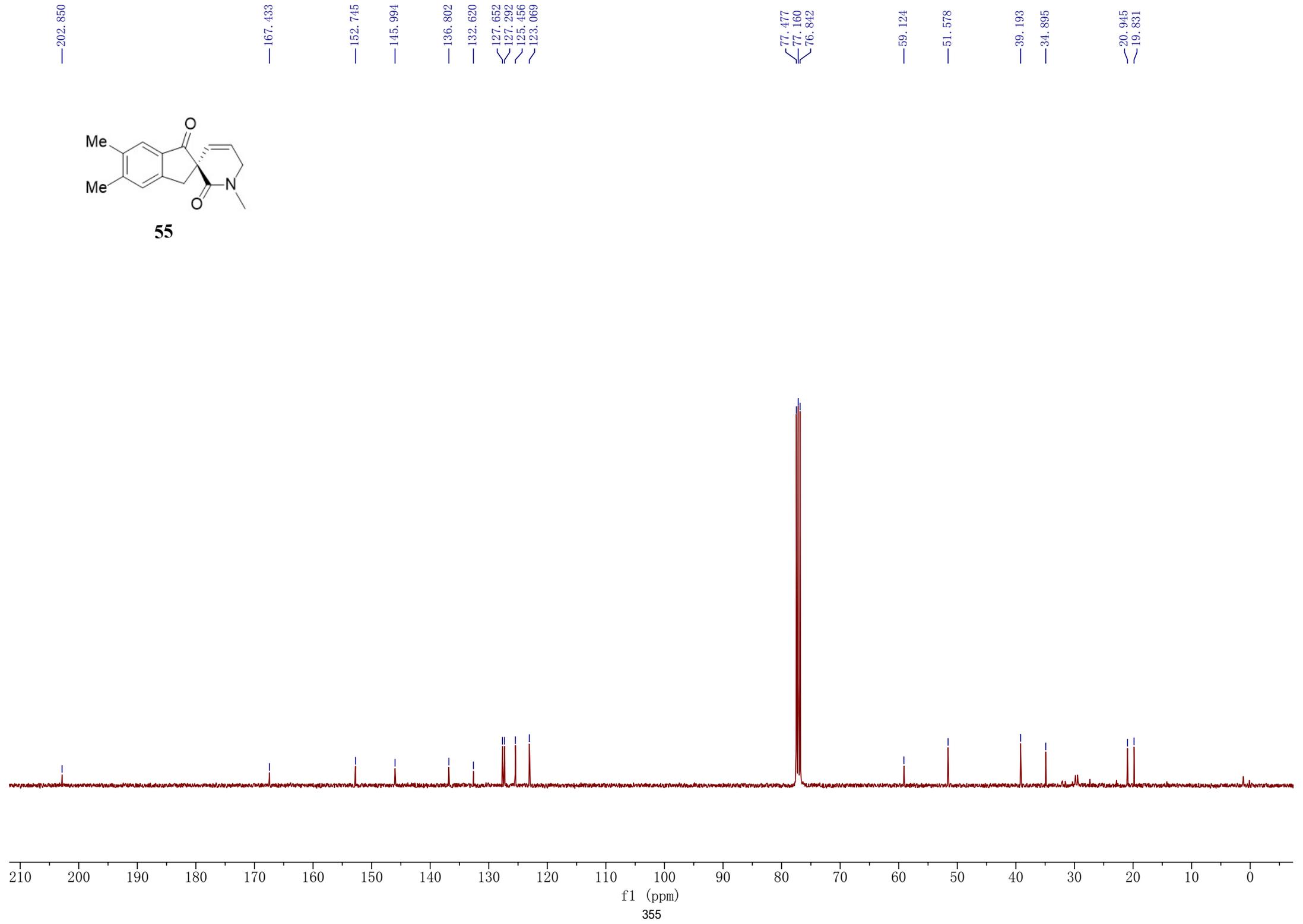


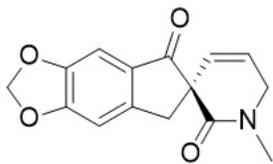
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55





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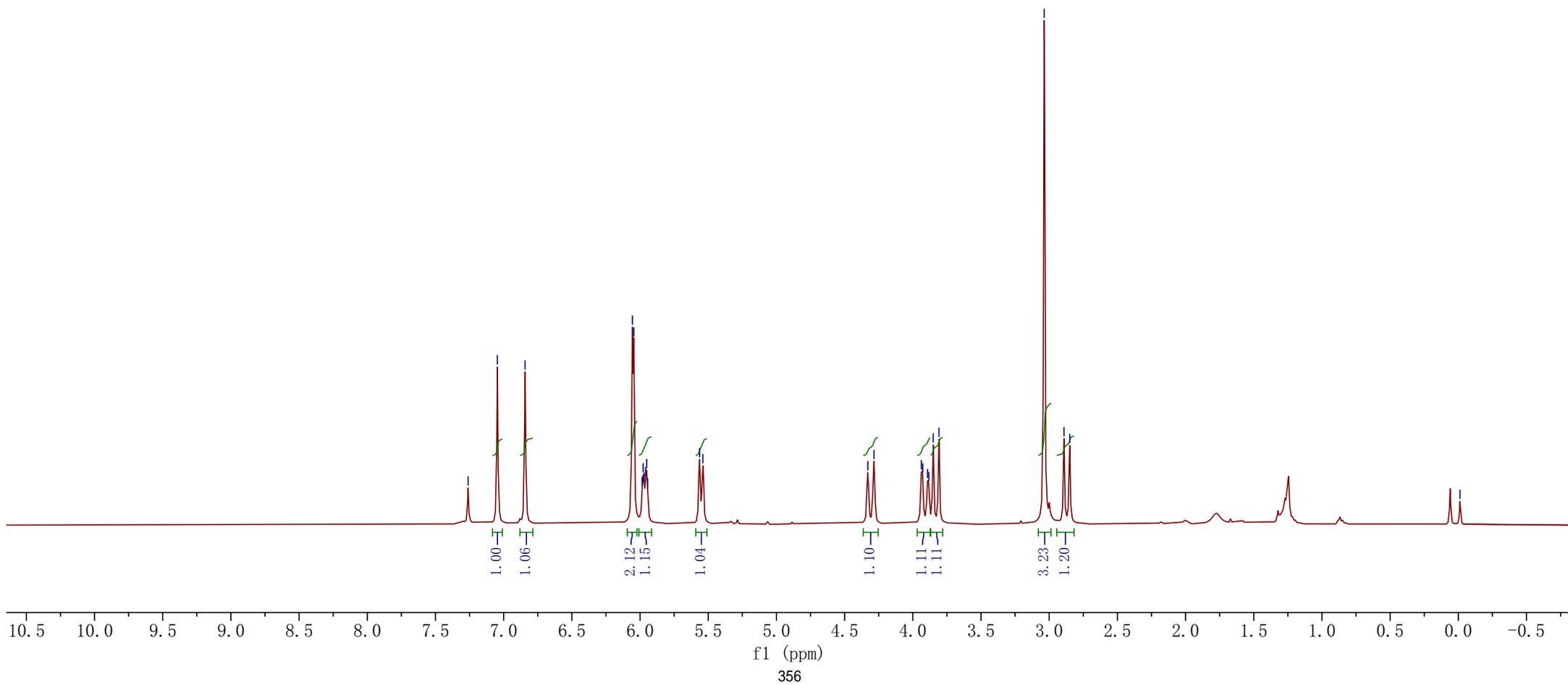
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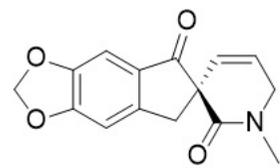
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6.045
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5.977
5.969
5.959
5.951
5.944
5.563
5.539

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3.851
3.808

3.036
2.892
2.849

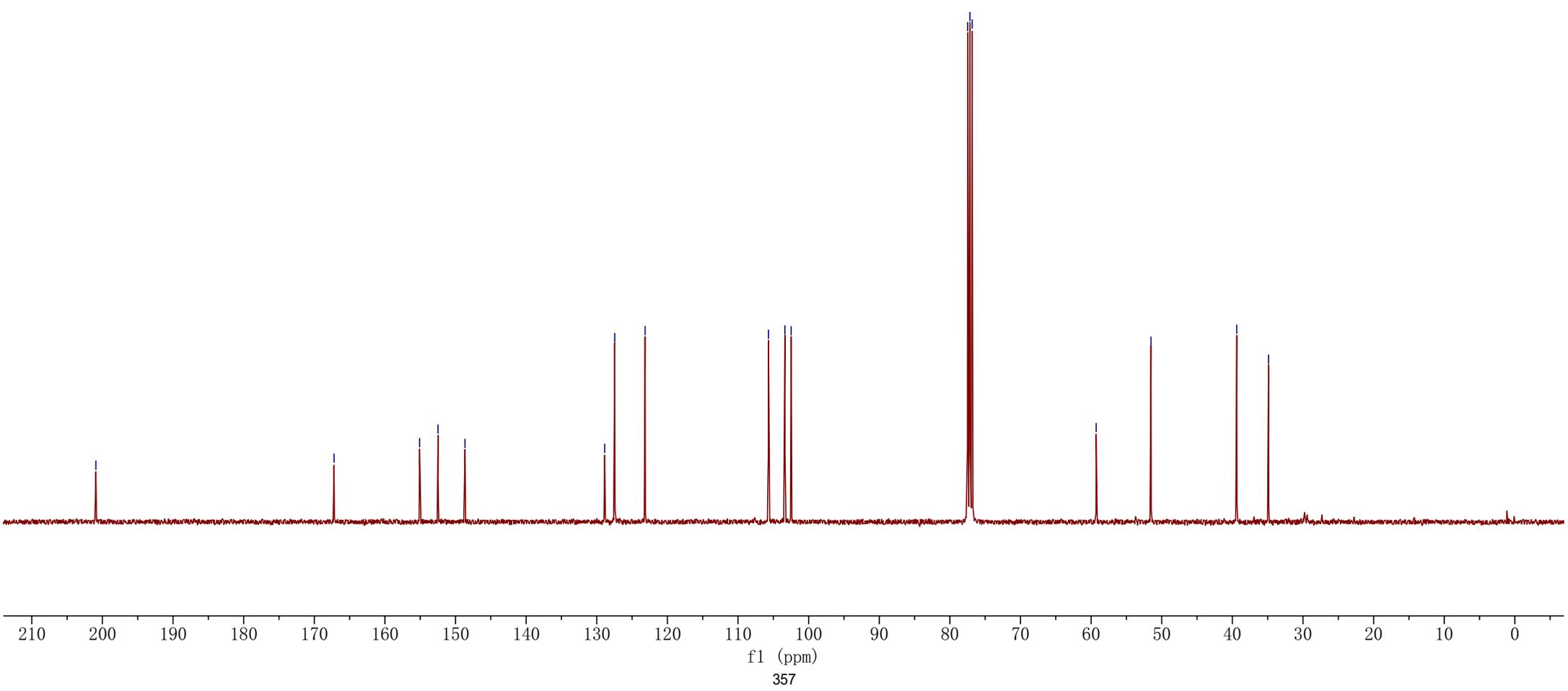
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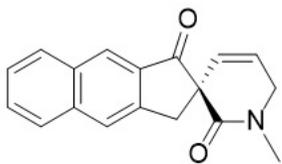




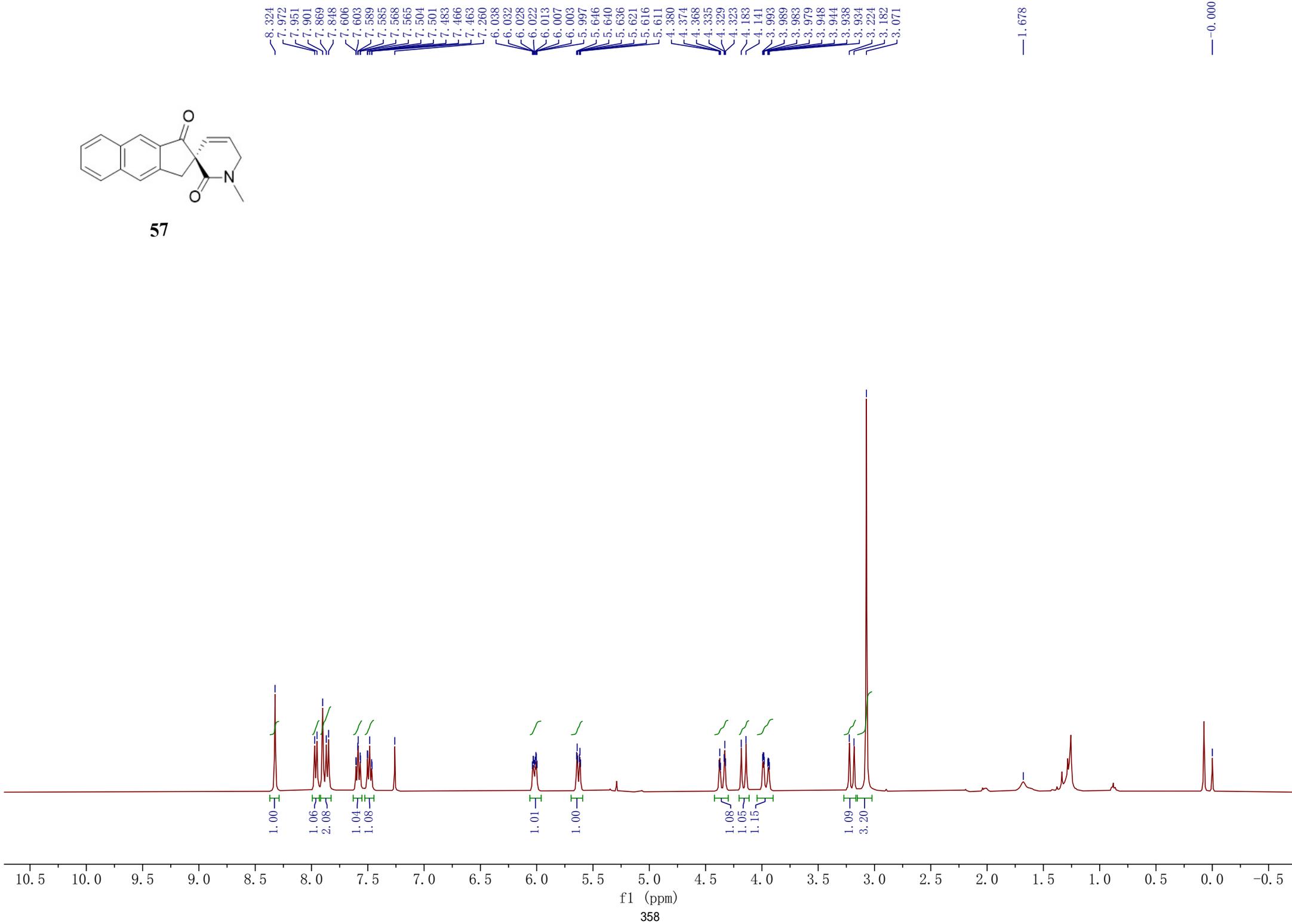
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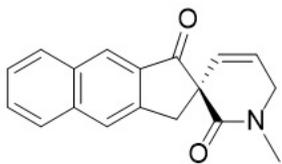
- 200.923
- 167.200
- 155.083
- 152.477
- 148.654
- 128.876
- 127.454
- 123.157
- 105.686
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- 102.473
- 77.478
- 77.160
- 76.842
- 59.285
- 51.523
- 39.378
- 34.872



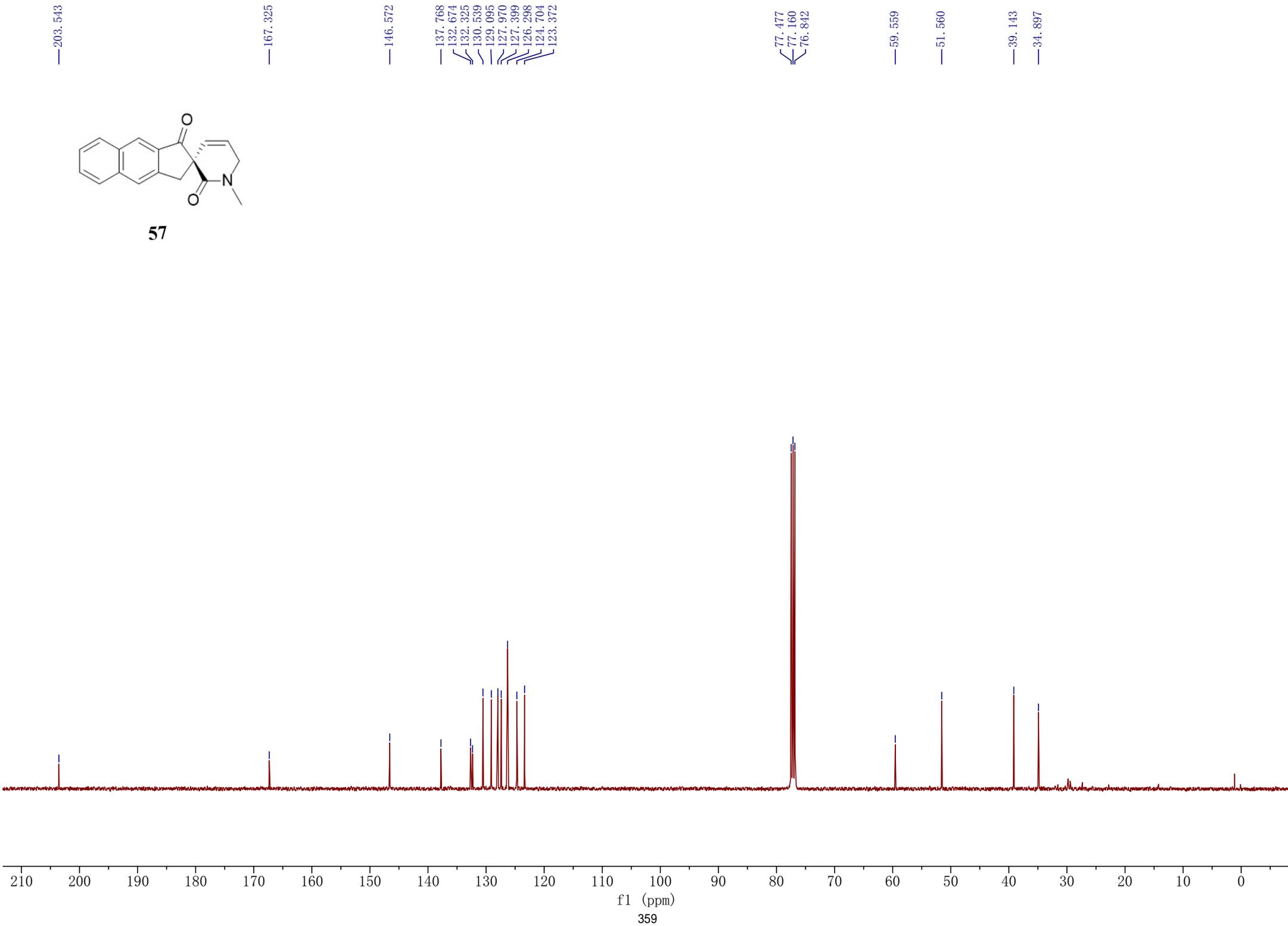


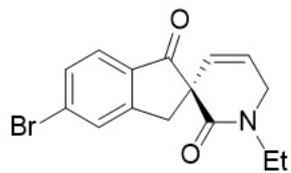
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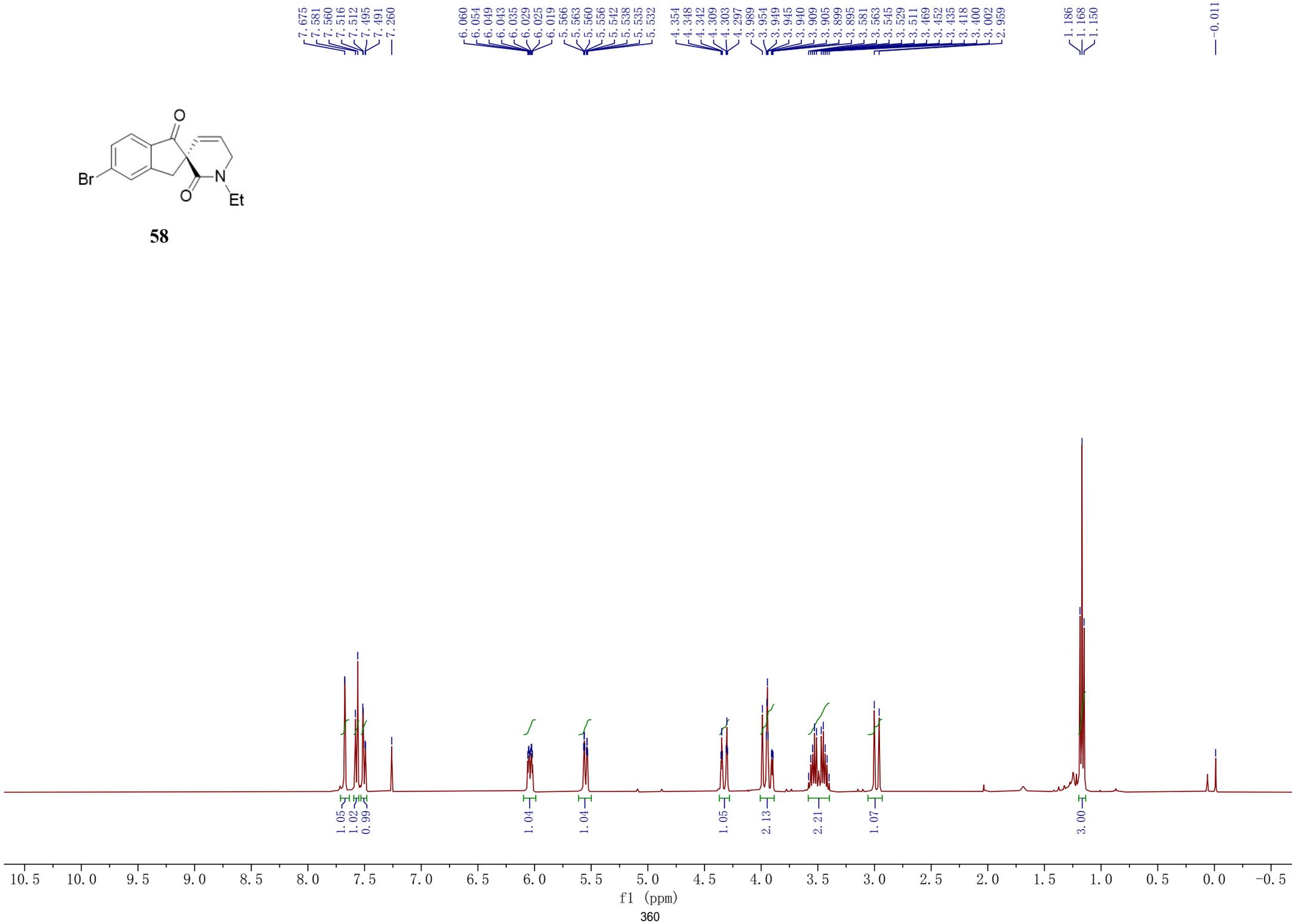


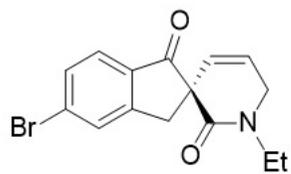
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58





58

—202.131

—166.133

—156.131

133.306
131.409
131.035
129.815
126.691
126.208
124.023

77.477
77.159
76.842

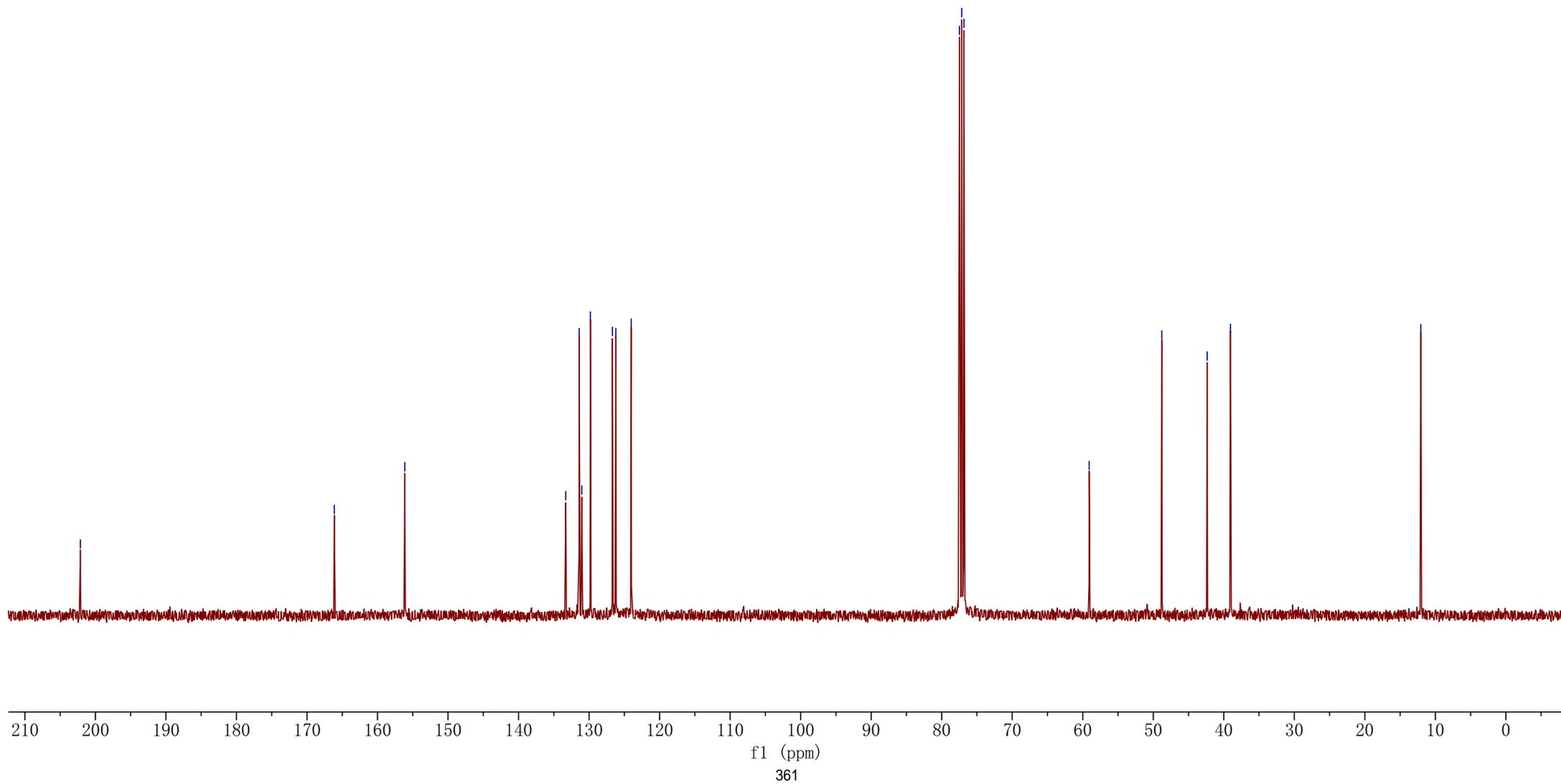
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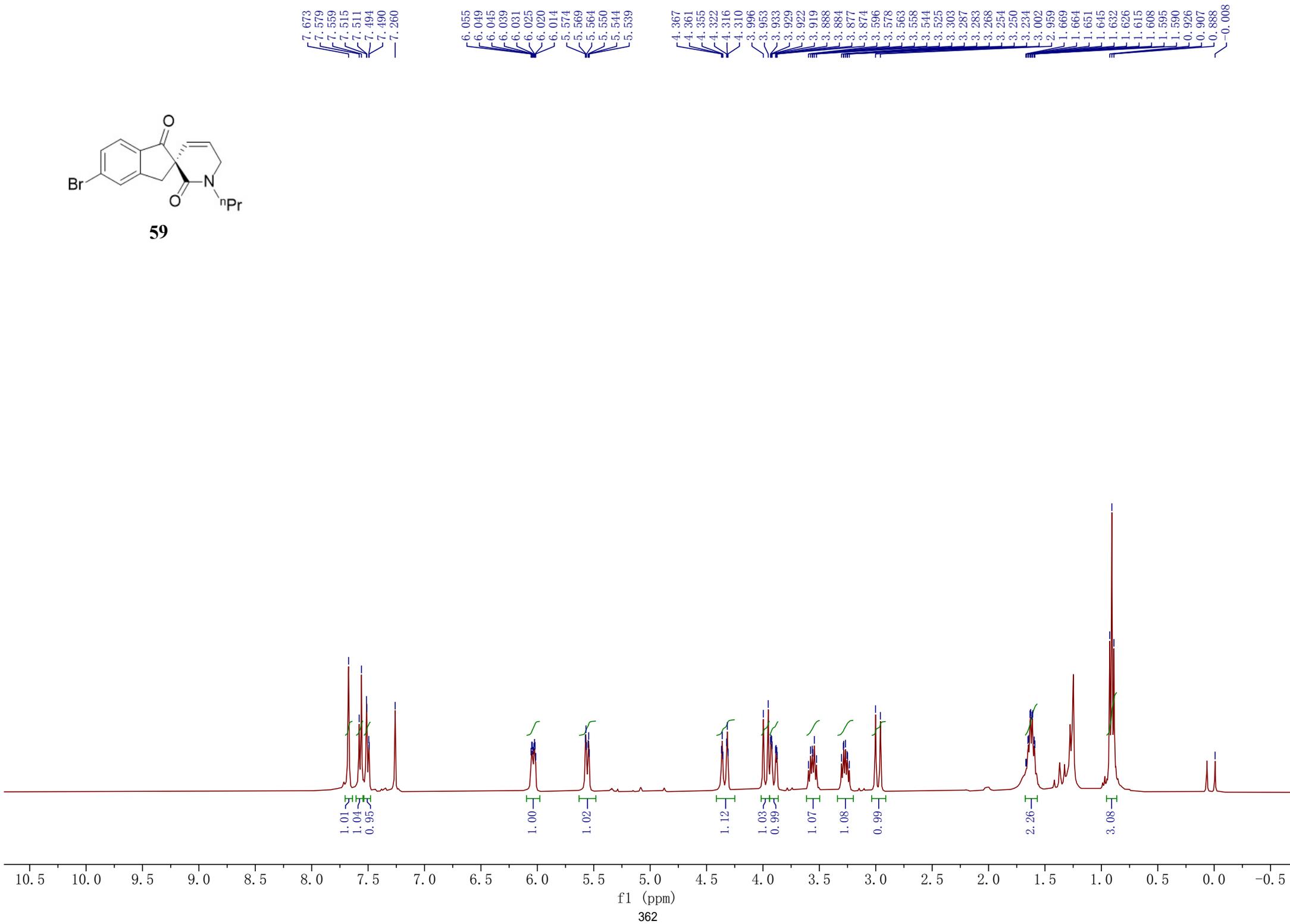
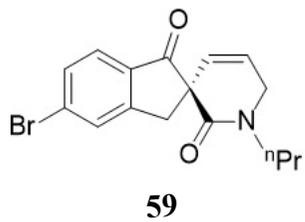
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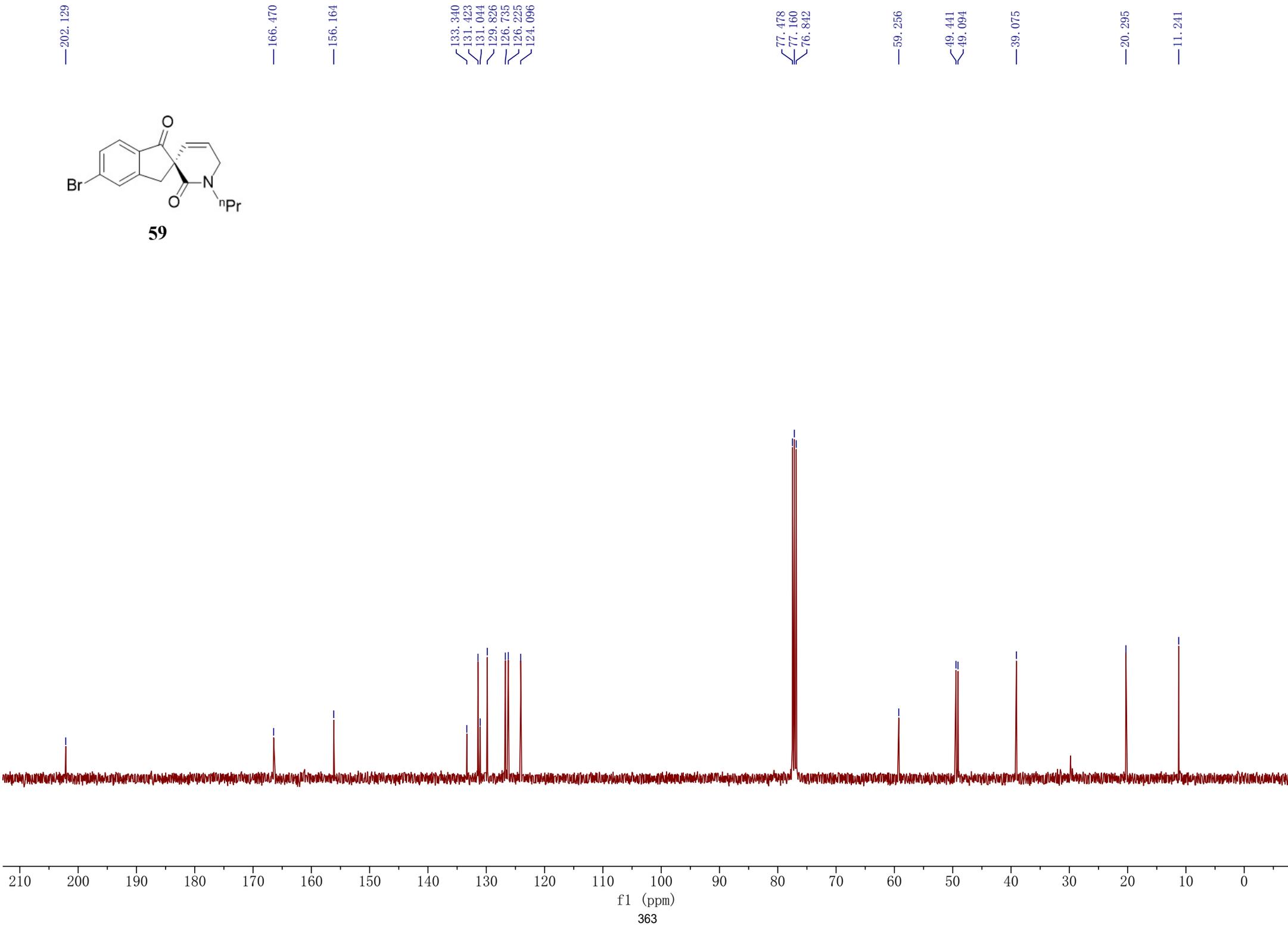
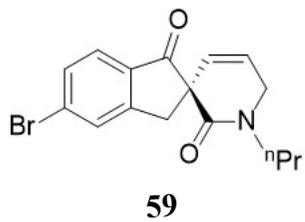
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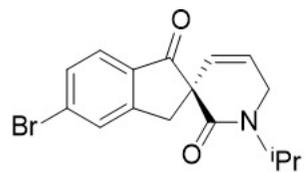
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—12.068

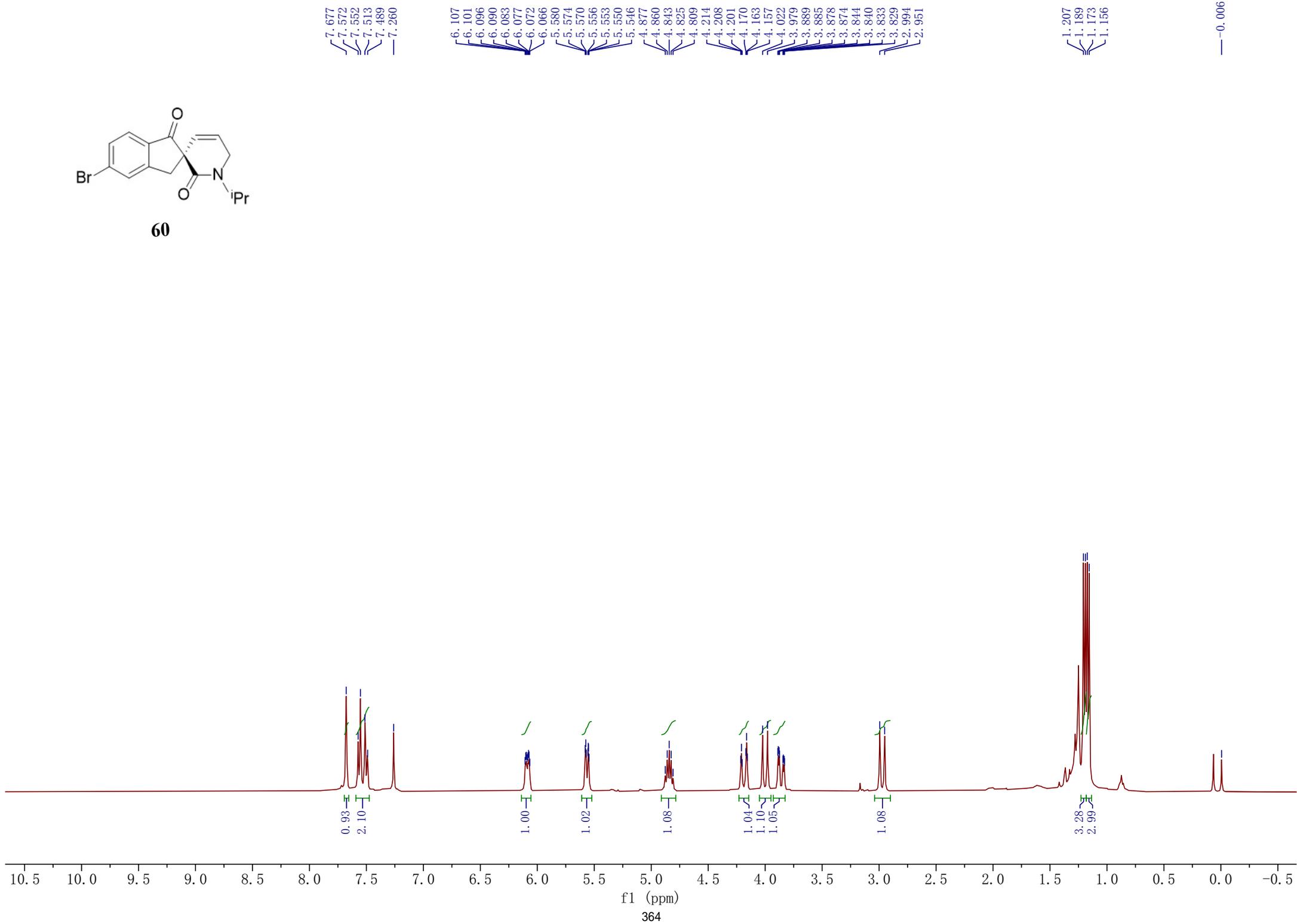


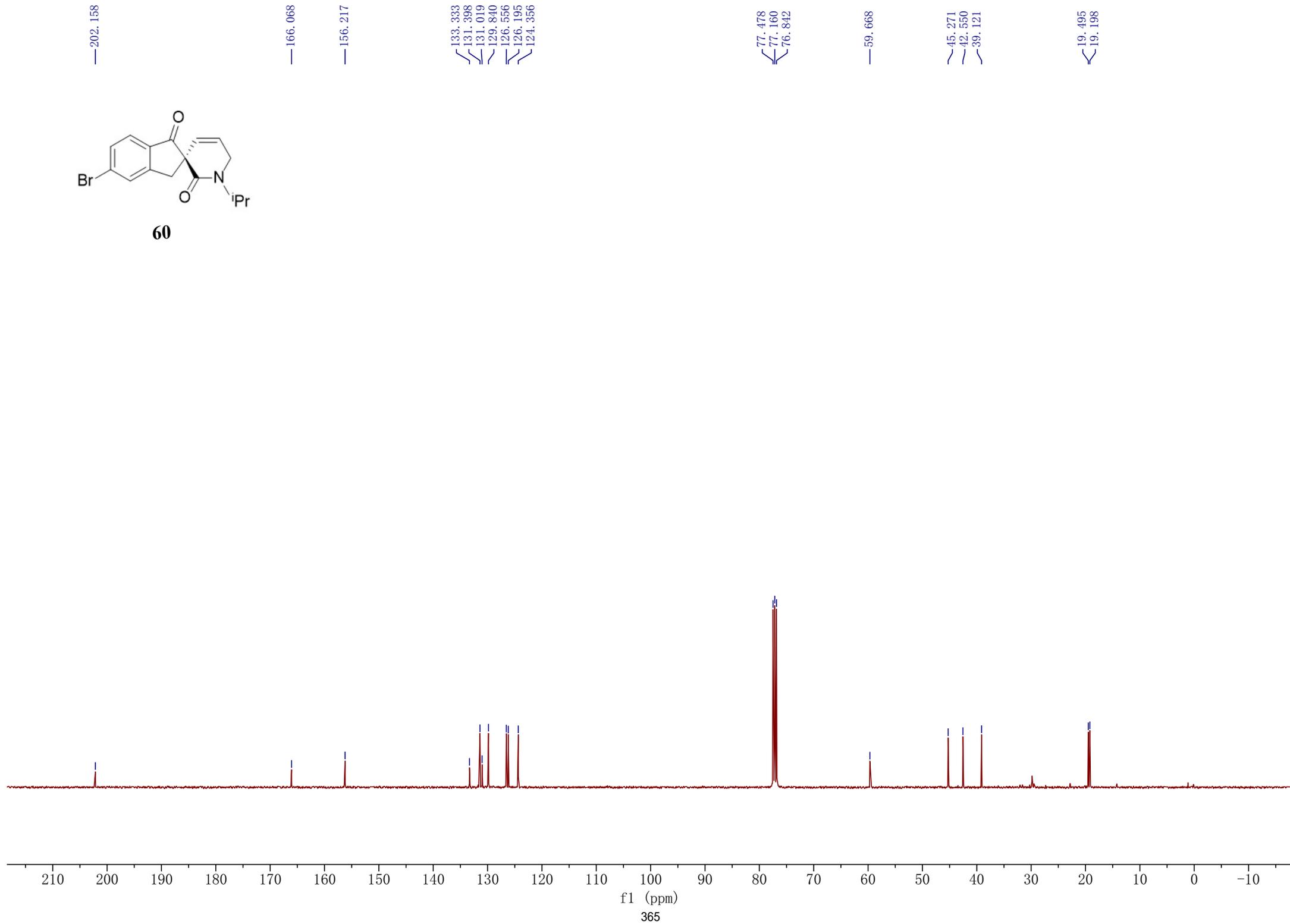
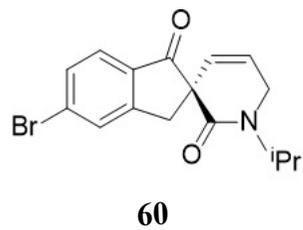


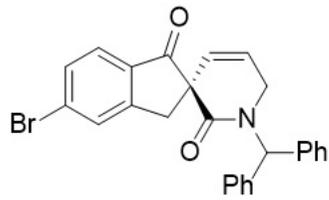




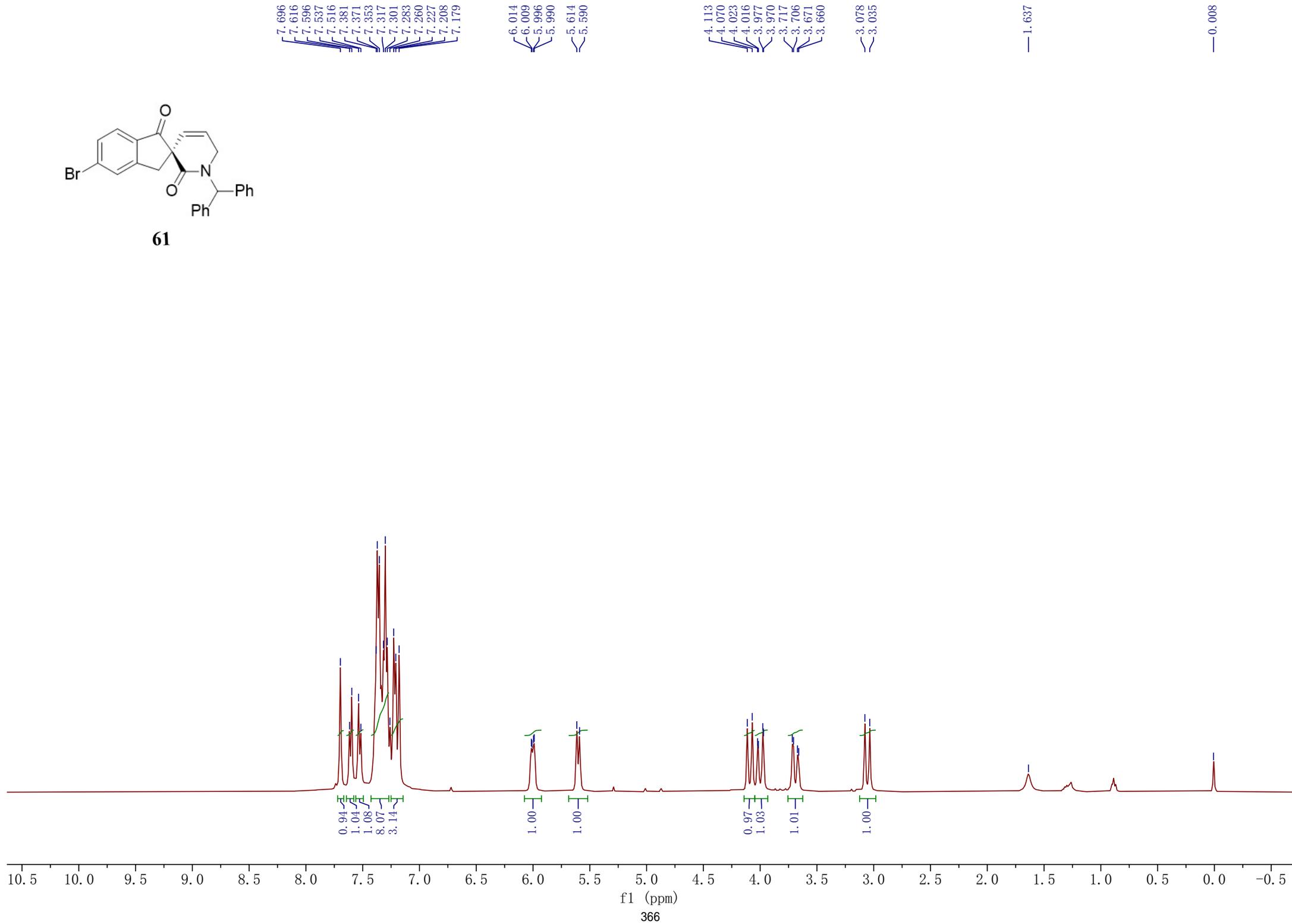
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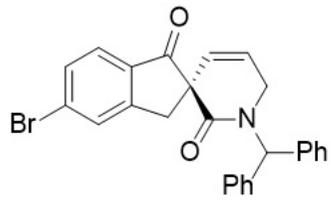




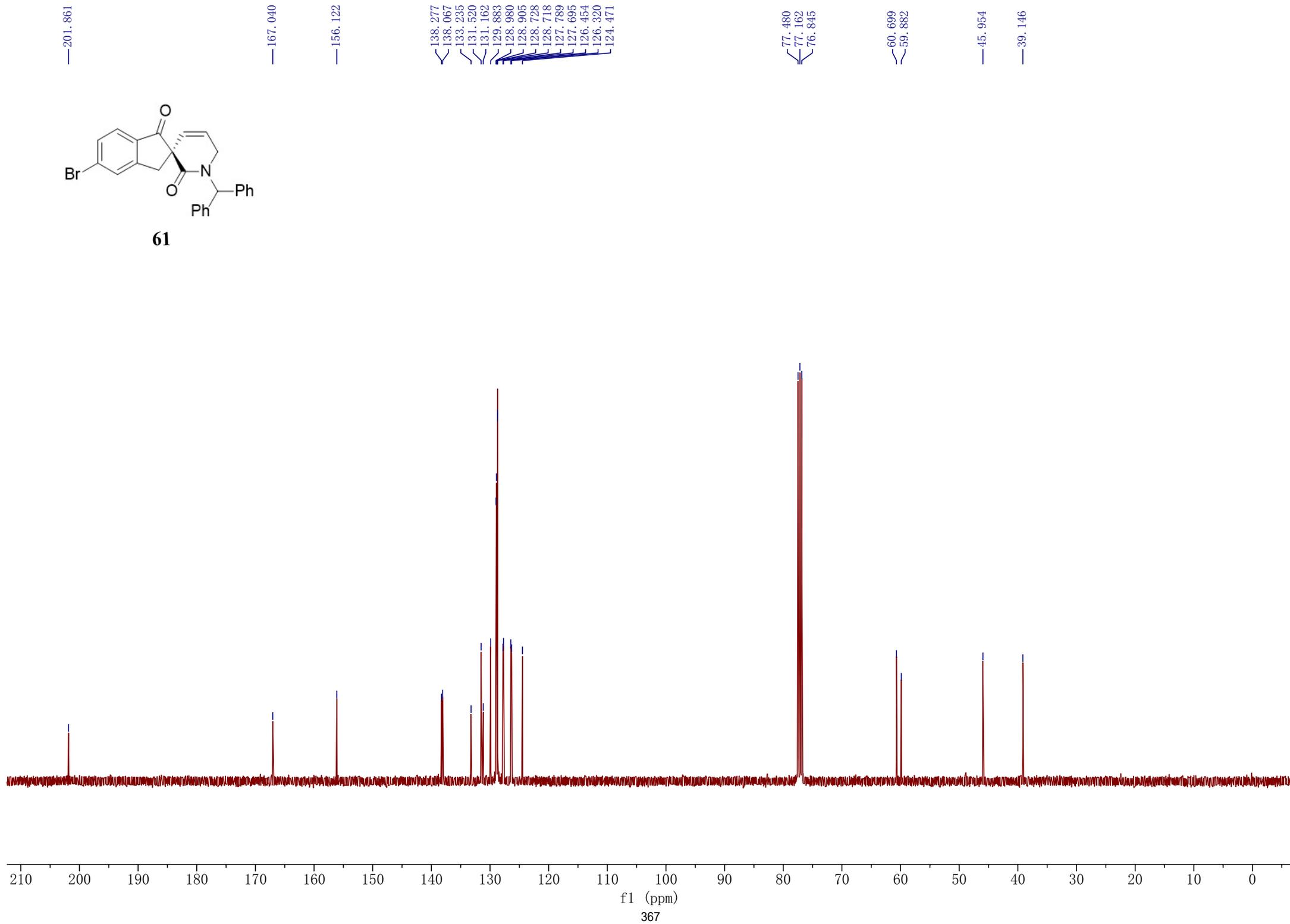


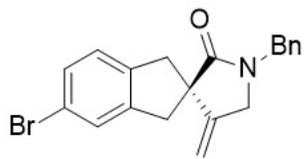
61





61





62

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7.314
7.279
7.260
7.237
7.221
7.051
7.031

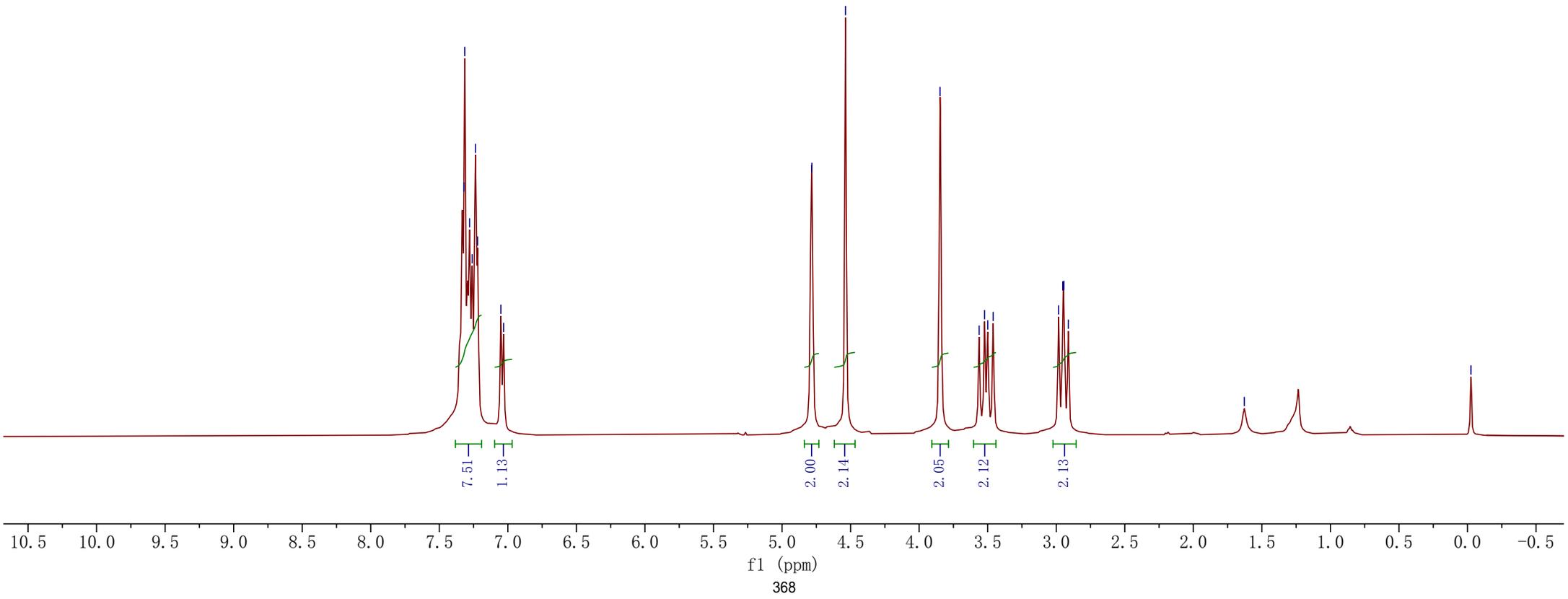
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4.537

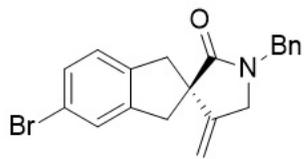
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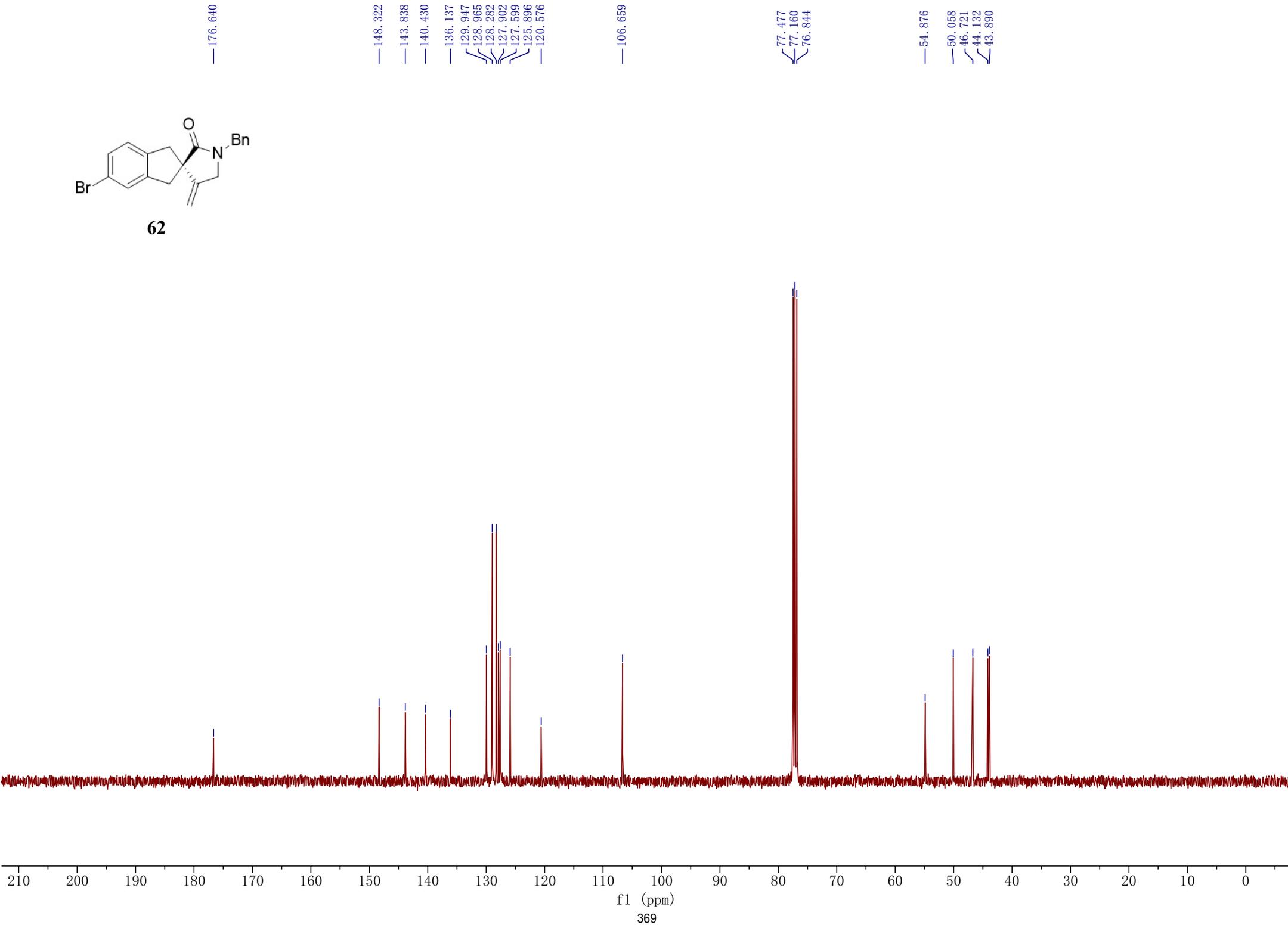
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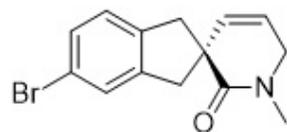
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62





63

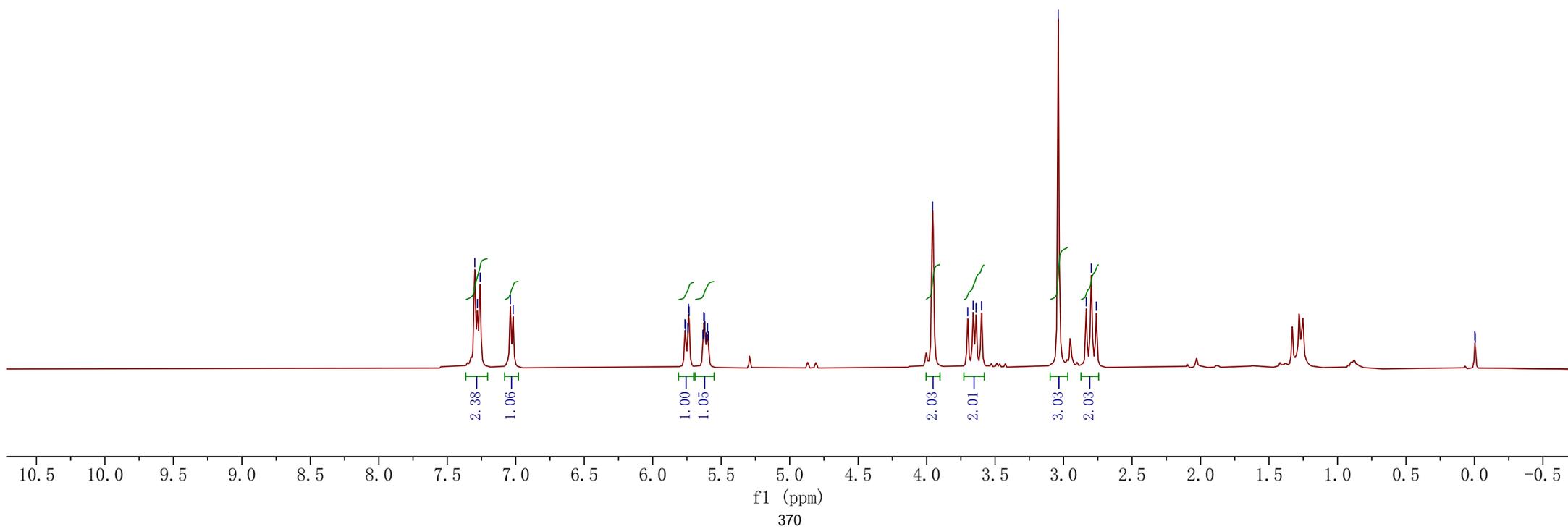
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7.260
7.039
7.019

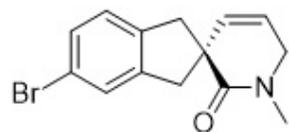
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5.744
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5.734
5.634
5.627
5.623
5.619
5.609
5.600
5.594

3.957
3.700
3.660
3.639
3.599

3.039
2.884
2.798
2.761

-0.002
-0.006





63

— 172.374

— 143.700

— 140.278

— 131.911

— 129.782

— 127.674

— 126.023

— 120.365

— 118.142

— 77.478

— 77.160

— 76.843

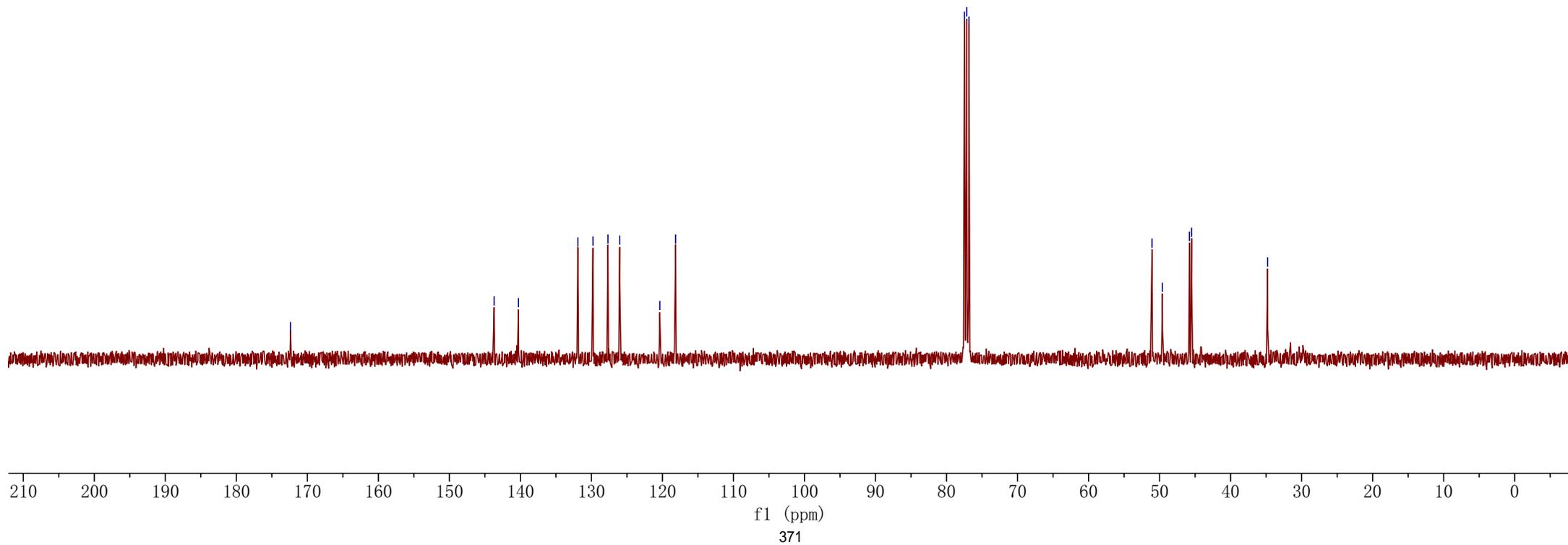
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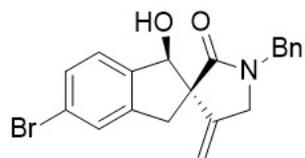
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— 45.801

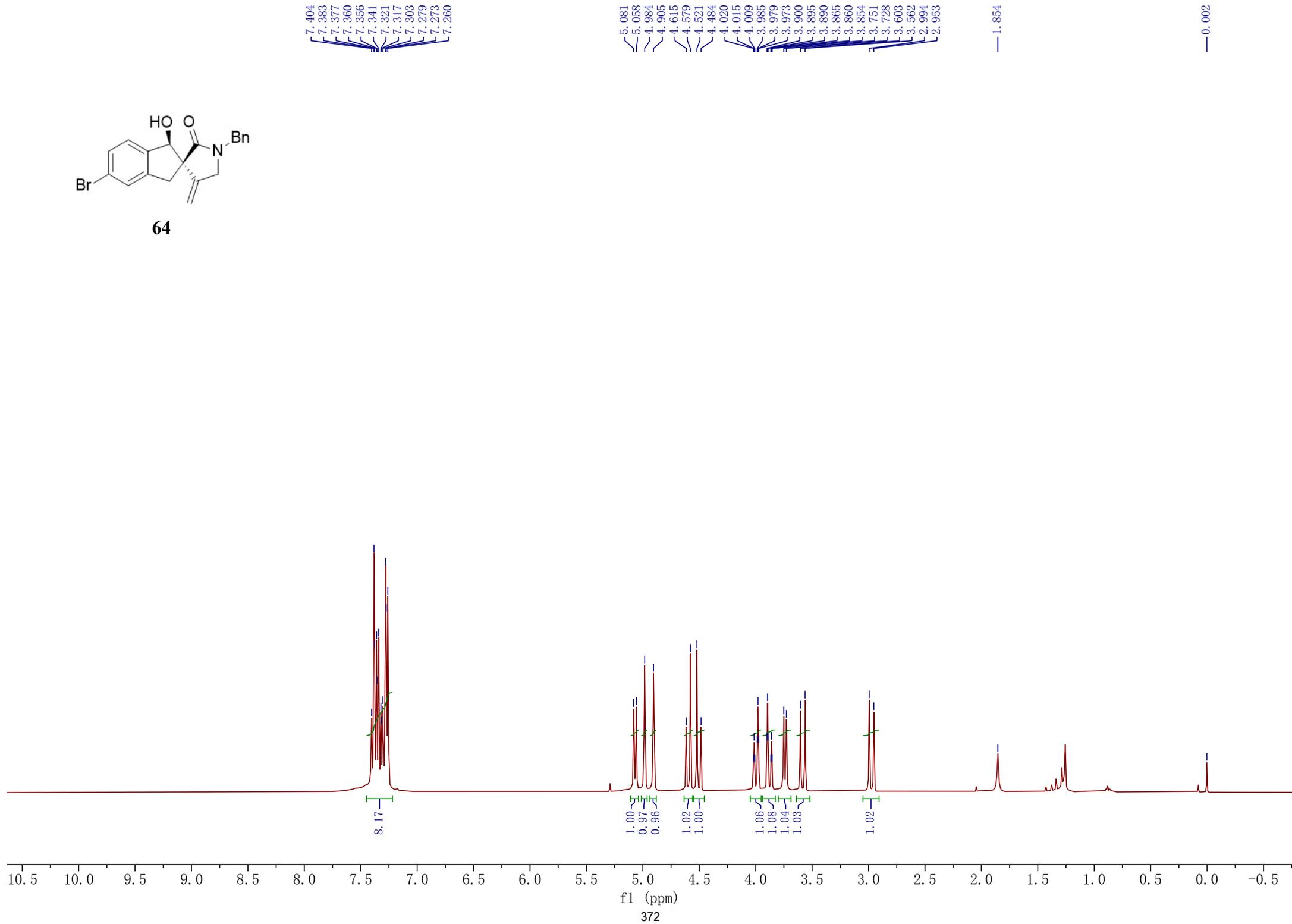
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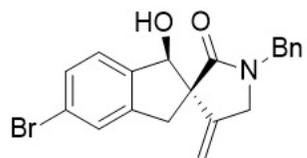
— 34.785





64





64

— 174.833

— 145.863
— 143.324
— 141.930

— 135.600
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— 128.966
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— 127.931
— 127.833
— 126.378
— 122.944

— 108.163

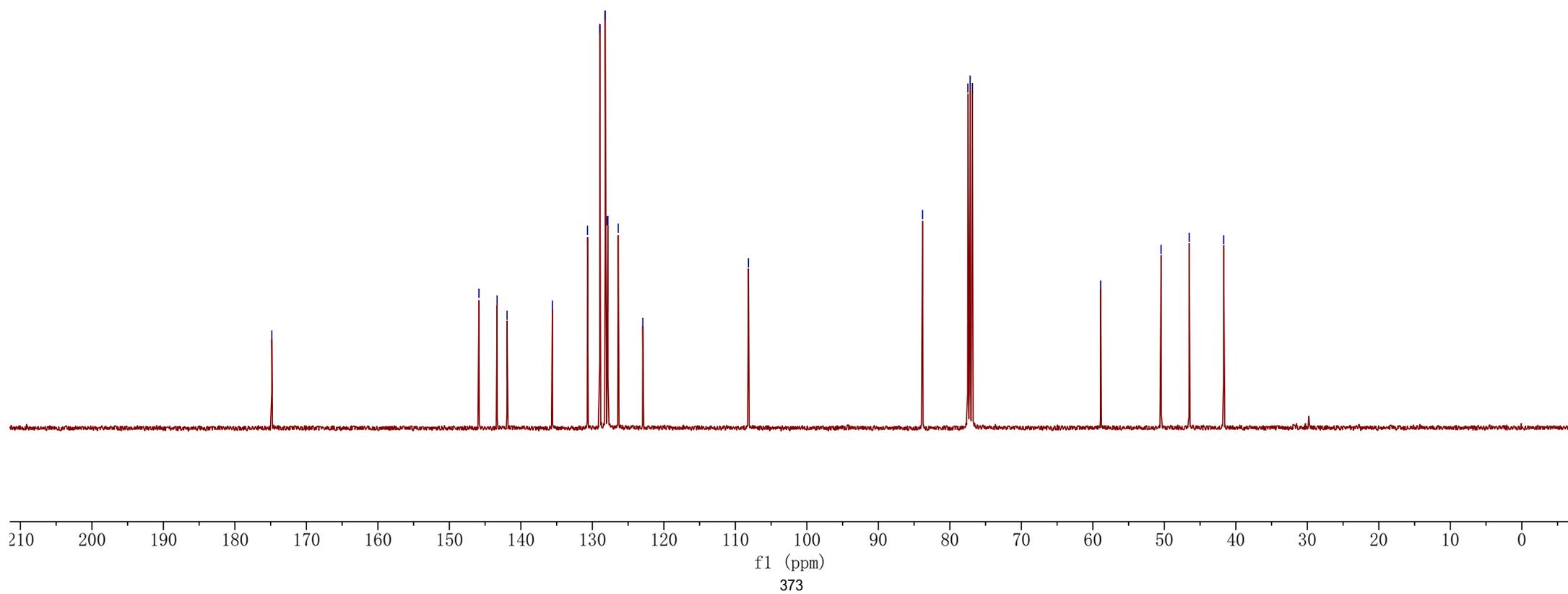
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— 77.478
— 77.160
— 76.842

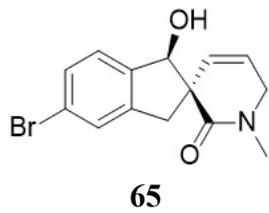
— 58.909

— 50.457

— 46.518

— 41.701





7.373
7.353
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5.649

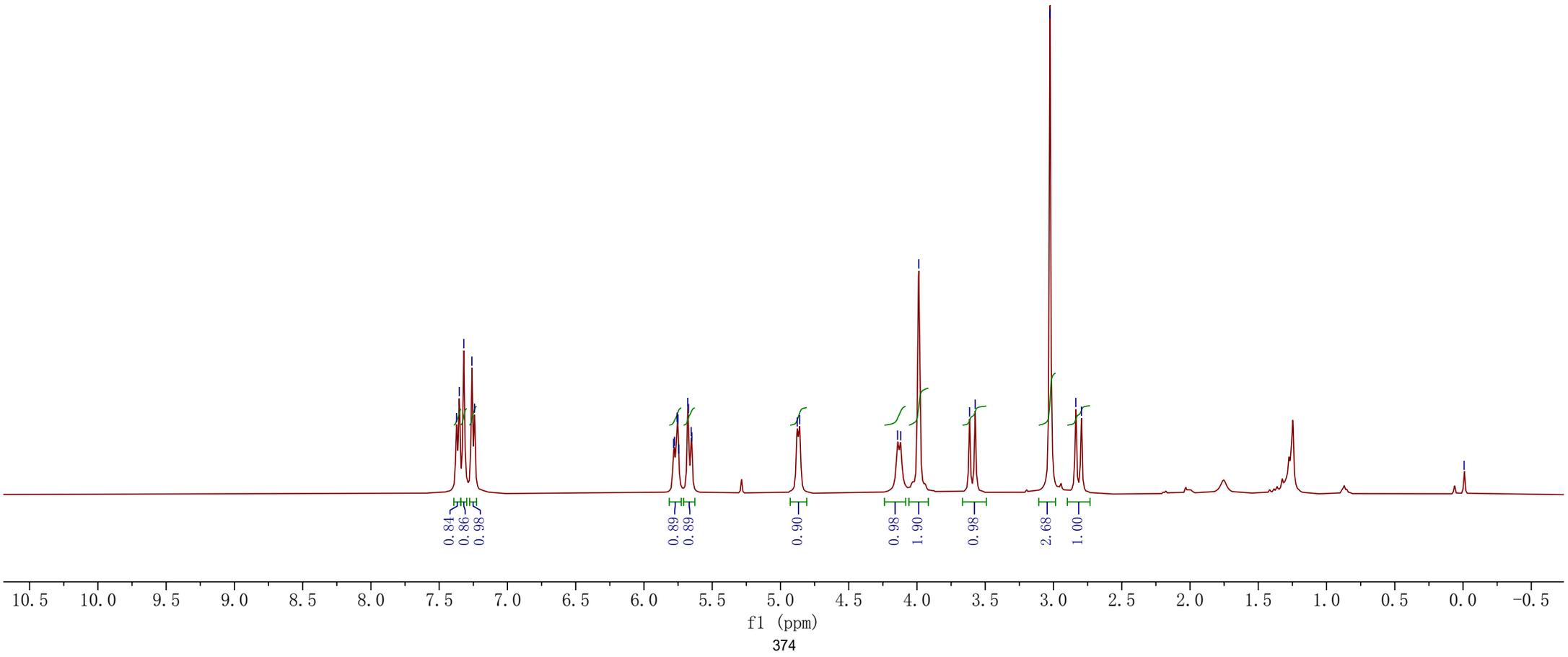
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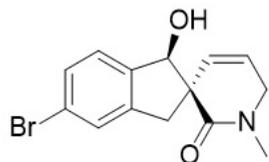
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3.615
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3.026
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-0.008





65

— 170.867

143.108
142.833

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120.189

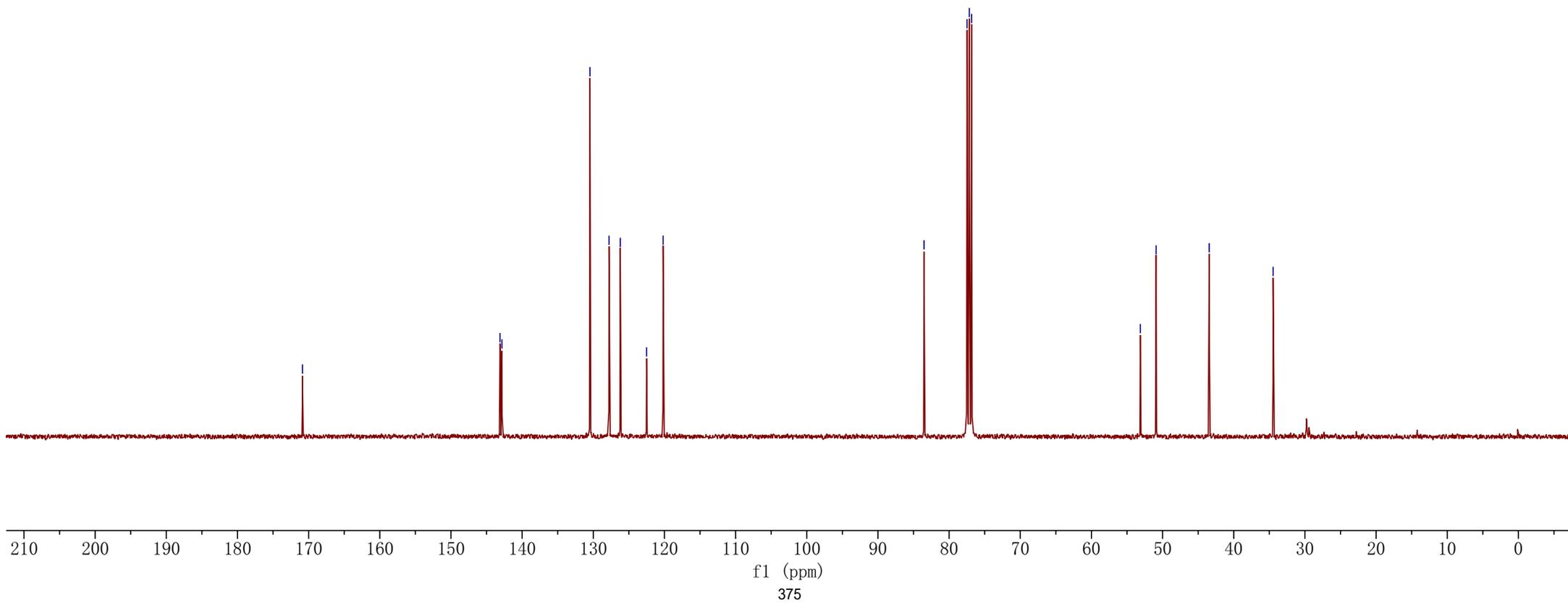
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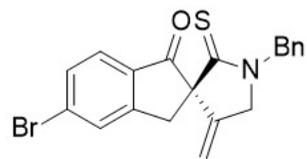
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— 53.129
— 50.909

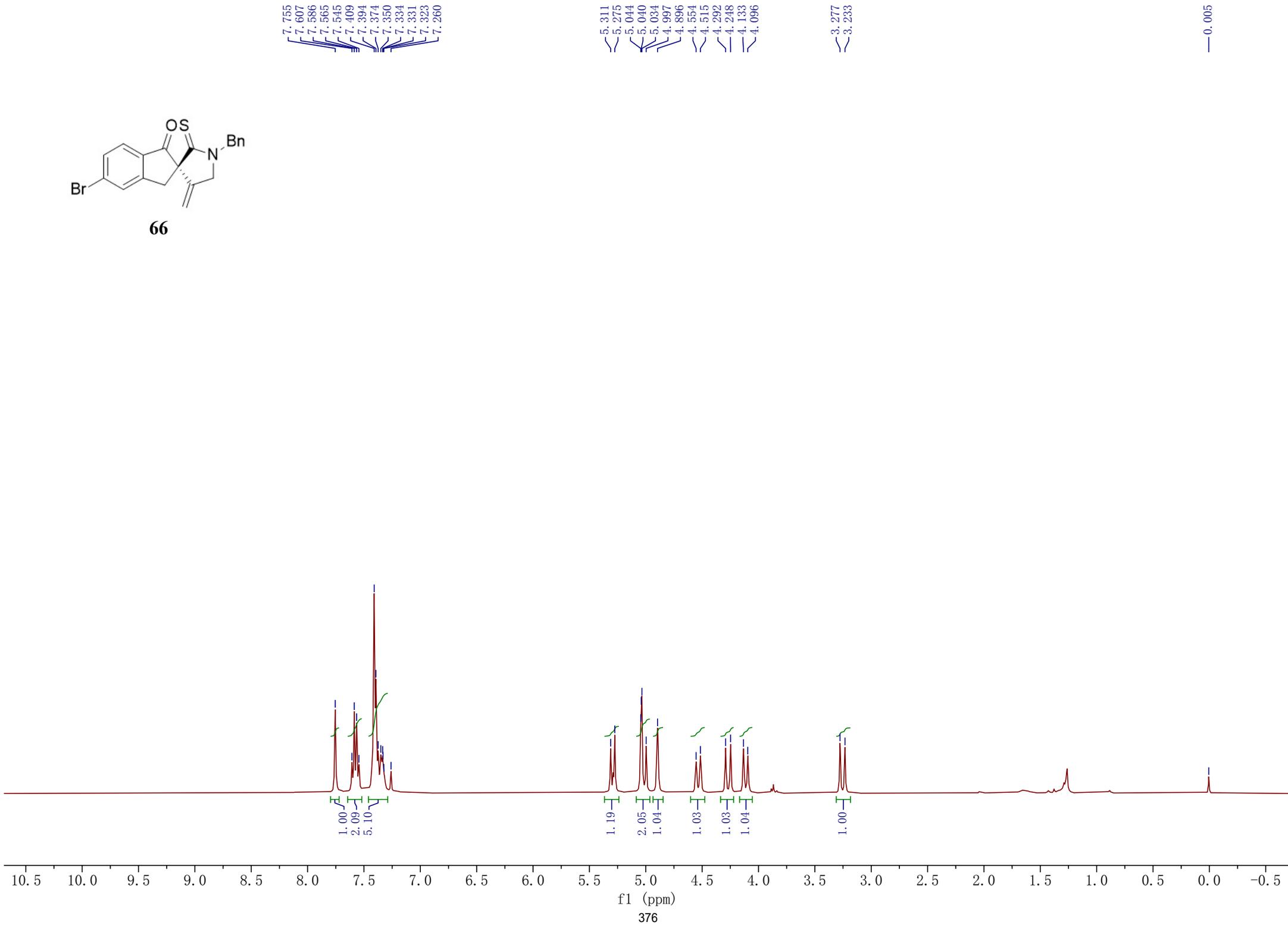
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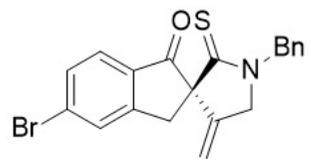
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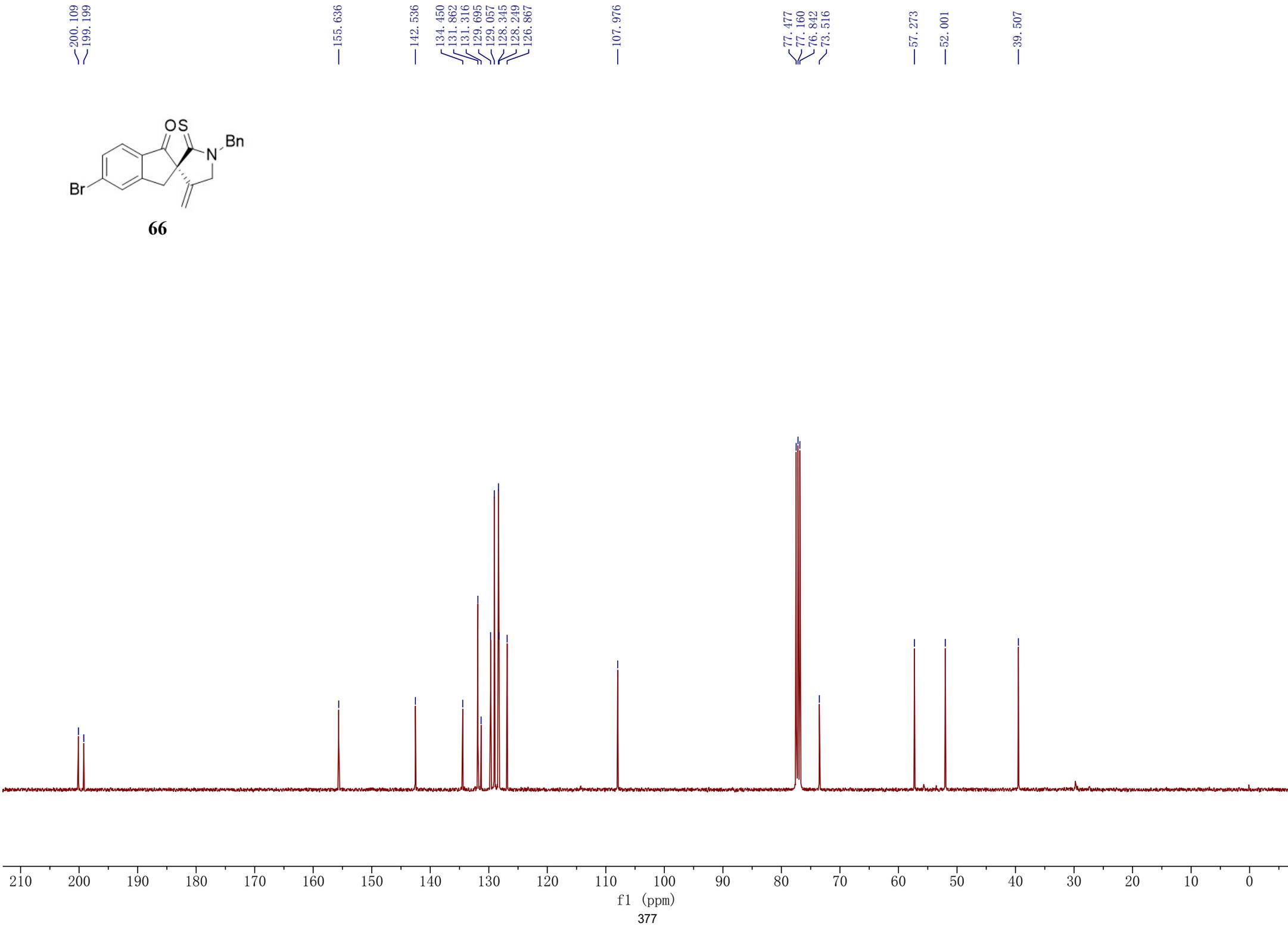


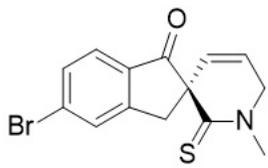
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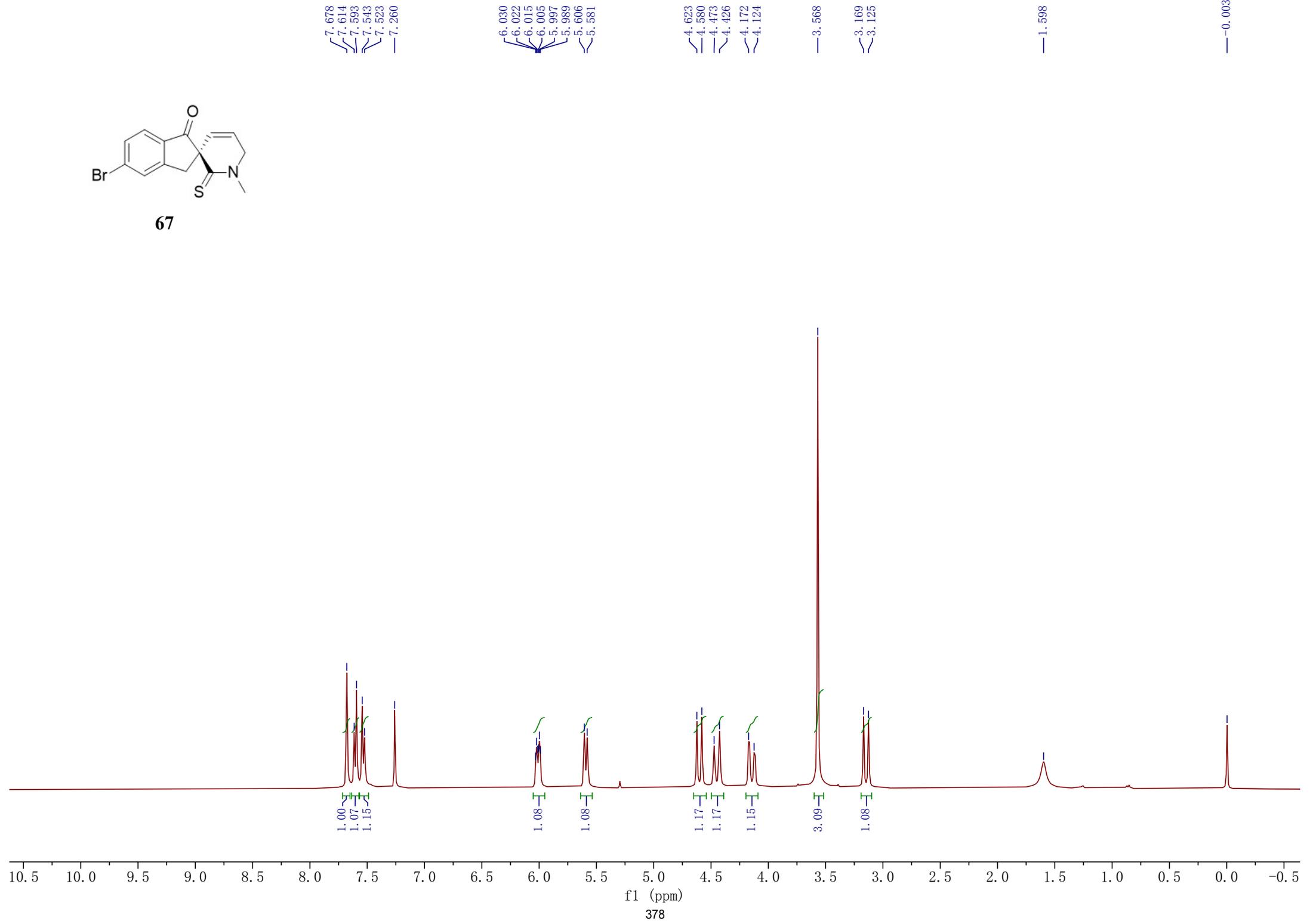


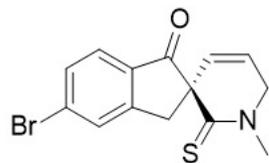
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67





67

