Supplementary Information

Radical-mediated 1,2-nitrogen migration from silicon to carbon through iron LMCT photochemistry

Yingying Yang,[1] Hao Jin,[1] Siyu Wang,[1] Dijie Li,[1] Yingcheng Wang,[1] Zhihui Shao,[1] Pengcheng Gao*[,2] and Yi Jin*[,1]

[1] Key Laboratory of Medicinal Chemistry for Natural Resource, Ministry of Education; Yunnan Provincial Center for Research & Development of Natural Products; School of Pharmacy, Yunnan University, Kunming, 650091, P. R. China.

[2] School of Pharmaceutical Science and Yunnan Key Laboratory of Pharmacology for Natural Products and College of Modern Biomedical Industry, Kunming Medical University, Kunming, Yunnan 650500, China

*Corresponding author. Email: pg459@scarletmail.rutgers.edu (P.G.); jinyi@ynu.edu.cn (Y.J.)

1 General information 2

1.1 Reagents and characterization 2

1.2 Photoreaction equipment 2

2 Experimental Procedures and Characterization Data 4

2.1 Optimization Studies 4

2.2 General Procedure and Product Characterization. 9

3 X-ray Structure and Data 54

4 Mechanism exploration 60

4.1 Radical capture experiment 60

4.2 UV-vis absorption spectra 63

4.3 Detection of putative intermediates 65

4.4 Deuterium-labelling experiment 69

4.5 Light on / off experiment 71

4.6 Control experiment 72

4.7 Crossover experiment 74

4.8 DFT calculations 76

5 NMR Spectra 76

6 References 189

1 General information

1.1 Reagents and characterization

All chemicals and reagents were used of commercial grade and were used without further purification. The reactions were monitored by thin-layer chromatography (TLC) using silica gel GF254. Column chromatography was performed with 200–300 mesh silica gel. Unless otherwise noted, yields refer to isolated products after purification. The intermediates and the products synthesized were fully characterized by spectroscopic data. The NMR spectra were recorded on Bruker DRX-400 (^{1}H: 400 MHz, ^{13}C: 100MHz) using $CDCl_3$ and DMSO-d^6 as solvents. The following abbreviations were used to explain the multiplicities: (s) = singlet, (d) = doublet, (t) = triplet, (q) = quartet, (sept) = septuplet, (dd) = double doublet, (dt) = double triplet, (dq) = double quartet, (ddd) = double-double doublet, (m) = multiplet; Chemical shifts (δ) are expressed in parts per million (ppm) and J values are given in hertz (Hz). IR spectra were recorded on an FT-IR Thermo Nicolet Avatar 360 using a KBr pellet. HRMS was performed on an Agilent LC/MSD TOF instrument. The melting points were measured by the XT-4A melting point apparatus without correction.

1.2 Photoreaction equipment

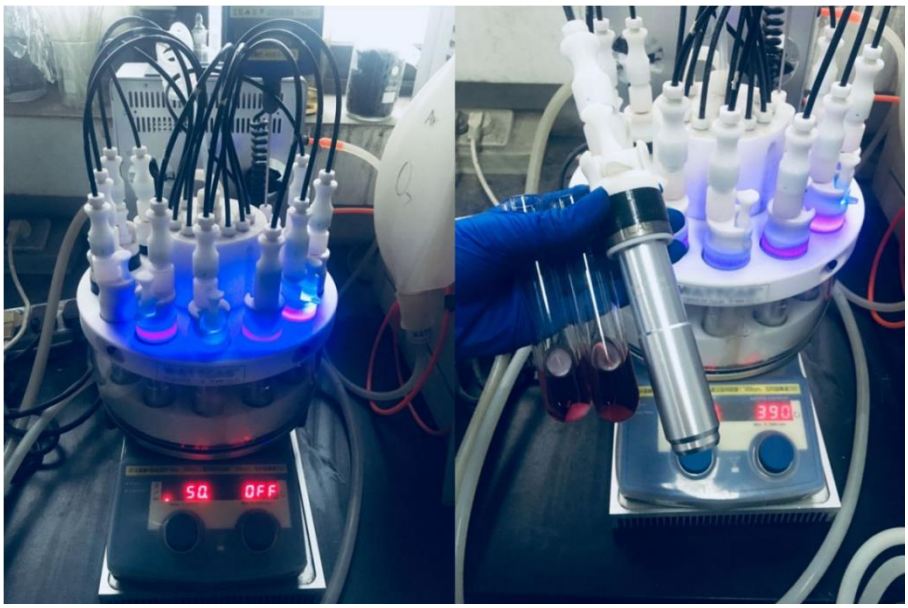


Fig. S1. Details for the photochemical reaction setup.

The light Source and the Material of the Irradiation Vessel

Manufacturer: Xi'an WATTECS experimental equipment Co. Ltd

Model: WP-TEC-1020SL

Broadband source: X = 395 nm (light power: 36 W).

Material of the irradiation vessel: borosilicate reaction tube (20 ml)

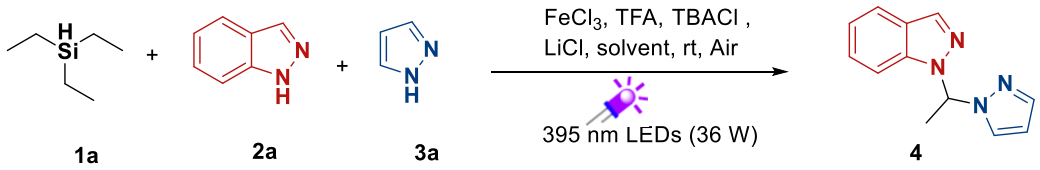
Distance from the light source to the irradiation vessel: 2.0 cm

Not use any filters

2 Experimental Procedures and Characterization Data

2.1 Optimization Studies

Table S1. Optimization of solvent.[a, b]

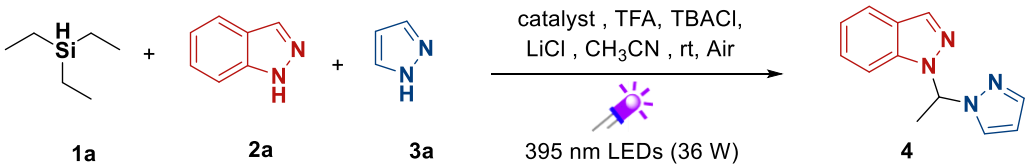


1a 2a 3a 4

Entry	Solvent	yield of 4 (%)
1	DCE	62
2	EtOAc	41
3	CH_3CN	80
4	Toluene	N.D.
5	DMSO	N.D.
6	DMF	N.D.
7	H_2O	N.D.
8	EtOH	N.D.
9	CH3CN: H_2O ((2:1))	N.D.

[a]Conditions: **1a** (4.0 equiv), **2a** (1.0 equiv), **3a** (2.0 equiv), $FeCl_3$ (30 mol %), TFA (2.0 equiv), TBACl (0.5 equiv), LiCl (2.0 equiv) in solvent (0.1 M), 395 nm LED (36 W) under air atmosphere at room temperature for 24 h. [b]Yields were determined by analysis of the crude ^1H NMR spectra using CH_2Br_2 as the internal standard. N.D. = not detected.

Table S2. Optimization of catalyst.[a, b]

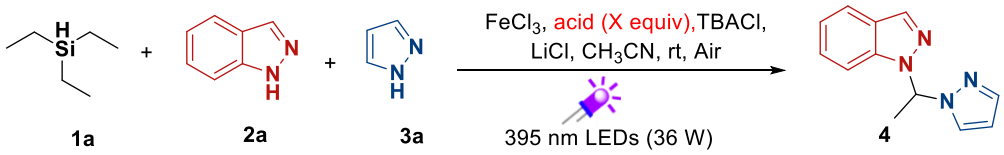


1a 2a 3a 4

Entry	catalyst	yield of 4 (%)
1	$FeCl_3$	80
2	$Fe(OTf)_3$	71
3	$FeCl_2$	73
4	$Fe(NO_3)_3\ 9H_2O$	36
5	$Fe(OTf)_2$	45
6	FeF_3	trace
7	Ferroceneas	trace
8	$Fe(acac)_3$	N.D.
9	$Fe(OAc)_2$	N.D.

[a]Conditions: **1a** (4.0 equiv), **2a** (1.0 equiv), **3a** (2.0 equiv), catalyst (30 mol %), TFA (2.0 equiv), TBACl (0.5 equiv), LiCl (2.0 equiv) in CH_3CN (0.1 M), 395 nm LED (36 W) under air atmosphere at room temperature for 24 h. [b]Yields were determined by analysis of the crude ^1H NMR spectra using CH_2Br_2 as the internal standard. N.D. = not detected.

Table S3. Optimization of acid.[a, b]

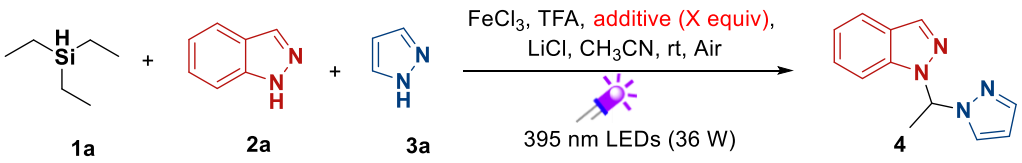


1a 2a 3a 4

Entry	acid (equiv)	yield of 4 (%)
1	TFA (2.0 equiv)	80
2	TFA (1.0 equiv)	65
3	TFA (3.0 equiv)	74
4	TFAA	72
5	CHF_2COOH	68
6	TfOH	59
7	HCl	79
8	AcOH	19
9	TFANa	10

[a]Conditions: **1a** (4.0 equiv), **2a** (1.0 equiv), **3a** (2.0 equiv), $FeCl_3$ (30 mol %), acid (X equiv), TBACl (0.5 equiv), LiCl (2.0 equiv) in CH_3CN (0.1 M), 395 nm LED (36 W) under air atmosphere at room temperature for 24 h. [b]Yields were determined by analysis of the crude ^1H NMR spectra using CH_2Br_2 as the internal standard. N.D. = not detected.

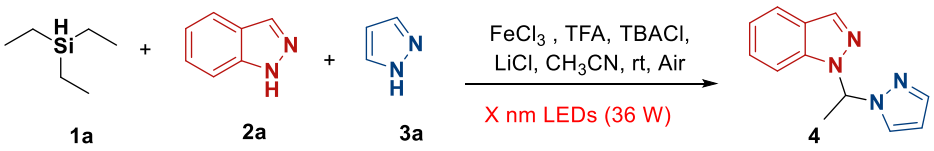
Table S4. Optimization of additive.[a,b]



Entry	additive (equiv)	yield of 4 (%)
1	TBACl (0.5 equiv)	80
2	TBACl (1 equiv)	71
3	TBACl (1.5 equiv)	65
4	TBAF	78
5	TBABr	61
6	$TBABF_4$	76
7	TBAI	58
8	$TBAPF_6$	57

[a]Conditions: **1a** (4.0 equiv), **2a** (1.0 equiv), **3a** (2.0 equiv), $FeCl_3$ (30 mol %), TFA (2.0 equiv), additive (X equiv), LiCl (2.0 equiv) in CH_3CN (0.1 M), 395 nm LED (36 W) under air atmosphere at room temperature for 24 h. [b]Yields were determined by analysis of the crude ^1H NMR spectra using CH_2Br_2 as the internal standard. N.D. = not detected.

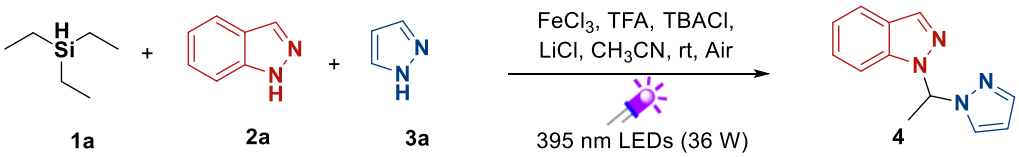
Table S5. Light wavelength evaluation.[a b]



Entry	Light wavelength	yield of 4 (%)
1	365nm	65
2	395nm	80
3	460nm	36

[a]Conditions: **1a** (4.0 equiv), **2a** (1.0 equiv), **3a** (2.0 equiv), $FeCl_3$ (30 mol %), TFA (2.0 equiv), TBACl (0.5 equiv), LiCl (2.0 equiv) in CH_3CN (0.1 M), X nm LED (36 W) under air atmosphere at room temperature for 24 h. [b]Yields were determined by analysis of the crude ^1H NMR spectra using CH_2Br_2 as the internal standard. N.D. = not detected.

Table S6. Optimization of loading of silane **1**.[a b]

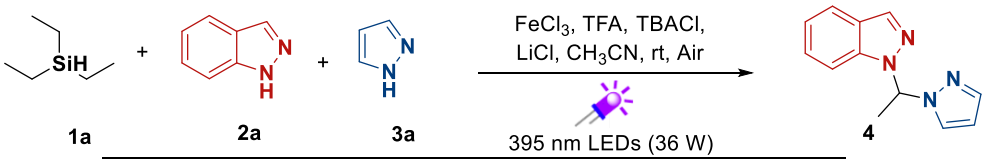


1a 2a 3a 4

Entry	1a (X equiv)	yield of 4 (%)
1	1	35
2	2	69
3	3	73
4	4	80
5	10	82

[a]Conditions: **1a** (X equiv), **2a** (1.0 equiv), **3a** (2.0 equiv), $FeCl_3$ (30 mol %), TFA (2.0 equiv), TBACl (0.5 equiv), LiCl (2.0 equiv) in CH_3CN (0.1 M), 395 nm LED (36 W) under air atmosphere at room temperature for 24 h. [b]Yields were determined by analysis of the crude ^1H NMR spectra using CH_2Br_2 as the internal standard. N.D. = not detected.

Table S7. Control experiment.[a b]

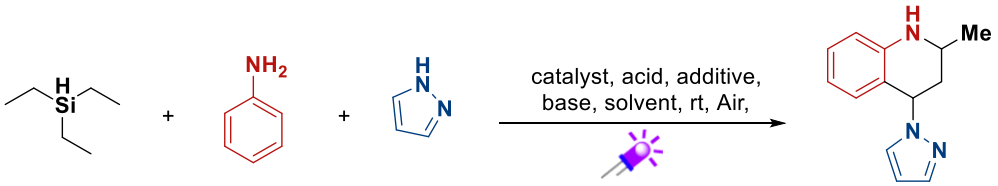


1a 2a 3a 4

Entry		yield of 4 (%)
1	no $FeCl_3$	N.D.
2	no TFA	trace
3	no TBACl	68
4	no LiCl	72
5	50 °C (in the dark)	N.D.

[a]Conditions: **1a** (4.0 equiv), **2a** (1.0 equiv), **3a** (2.0 equiv), $FeCl_3$ (30 mol %), TFA (2.0 equiv), TBACl (0.5 equiv), LiCl (2.0 equiv) in CH_3CN (0.1 M), 395 nm LED (36 W) under air atmosphere at room temperature for 24 h. [b]Yields were determined by analysis of the crude ^1H NMR spectra using CH_2Br_2 as the internal standard. N.D. = not detected.

Table S8. Control experiment.[a, b, c]

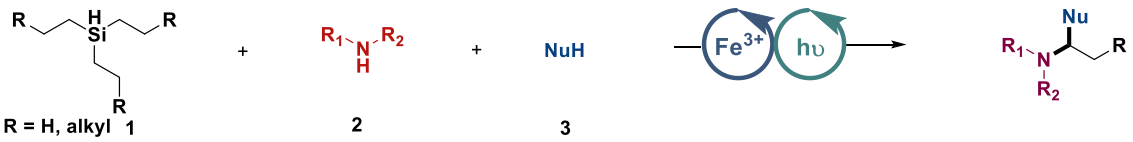


1a 3a 89

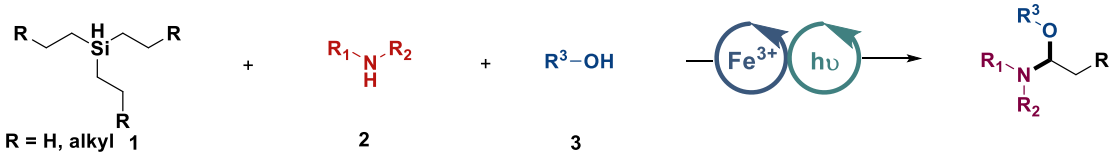
Entry	catalyst	acid	additive	solvent	yield of 89 (%)
1	$FeCl_3$	TFA	TBACl	CH_3CN	67
2	$FeCl_2$	TFA	TBACl	CH_3CN	71
3	$Fe(OTf)_3$	TFA	TBACl	CH_3CN	65
4	$Fe(OAc)_3$	TFA	TBACl	CH_3CN	N.D.
5	$FeCl_2$	TsOH	TBACl	CH_3CN	70
6	$FeCl_2$	CHF_2COOH	TBACl	CH_3CN	56
7	--	TFA	TBACl	CH_3CN	N.D.
8	$FeCl_2$	--	TBACl	CH_3CN	N.D.
9	$FeCl_2$	TFA	--	CH_3CN	48
[b]10	$FeCl_2$	TFA	TBACl	CH_3CN	59

[a]Conditions: **1a** (4.0 equiv), **aniline** (1.0 equiv), **3a** (2.0 equiv), **catalyst** (30 mol %), **acid** (2.0 equiv), TBACl (0.5 equiv), LiCl (2.0 equiv) in CH_3CN (0.1 M), 395 nm LED (36 W) under air atmosphere at room temperature for 24 h. [b]Conditions: conditions as in footnote, but without LiCl. [c]Yields were determined by analysis of the crude ^1H NMR spectra using CH_2Br_2 as the internal standard. N.D. = not detected.

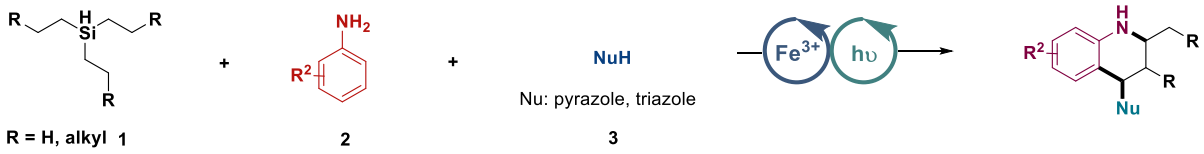
2.2 General Procedure and Product Characterization.



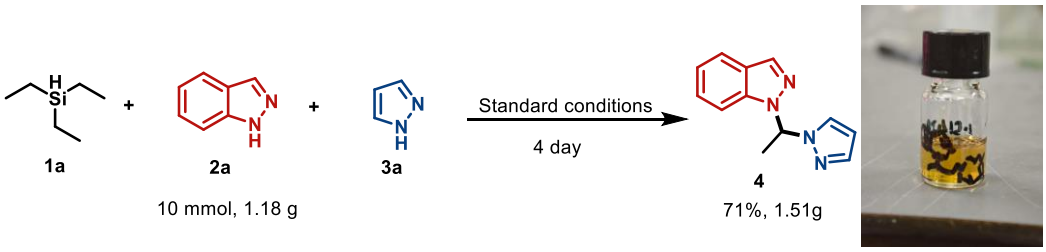
General Procedure 1: To a 20-mL borosilicate reaction tube under air were added silane 1 (0.80 mmol, 4.0 equiv.), substrate 2 (0.20 mmol, 1.0 equiv.), nucleophile 3 (0.40 mmol, 2.0 equiv.), $FeCl_3$ (9.7 mg, 0.060 mmol, 30 mol%), TBACl (0.10 mmol, 0.5 equiv.) and LiCl (0.40 mmol, 2.0 equiv.), followed by MeCN (2.0 mL, 0.10 M with respect to 2). TFA (0.40 mmol, 2.0 equiv.) was then added. The reaction mixture was irradiated with 395-nm LEDs (36 W) at room temperature for 24–36 h. After completion of the reaction, the mixture was quenched with saturated aqueous NaCl and extracted with EtOAc (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the desired product **4-32**, **40-83**, and **87-88**. The products were further identified by NMR spectroscopy and HRMS.



General Procedure 2: To a 20-mL borosilicate reaction tube under air were added silane **1** (0.80 mmol, 4.0 equiv.), substrate **2** (0.20 mmol, 1.0 equiv.), nucleophile **3** (0.40 mmol, 2.0 equiv.), $FeCl_3$ (9.7 mg, 0.060 mmol, 30 mol%), TBACl (0.10 mmol, 0.5 equiv.) and LiCl (0.40 mmol, 2.0 equiv.), followed by MeCN: DCE (1:1, 2.0 mL, 0.10 M with respect to 2). TFA (0.40 mmol, 2.0 equiv.) was then added. The reaction mixture was irradiated with 395-nm LEDs (36 W) at room temperature for 24–36 h. After completion of the reaction, the mixture was quenched with saturated aqueous NaCl and extracted with EtOAc (3 ×20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the desired product **33-39** and **84-85**. The products were further identified by NMR spectroscopy and HRMS.

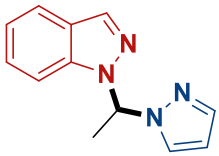


General Procedure 3: To a 20-mL borosilicate reaction tube under air were added silane **1** (0.8 mmol, 4.0 equiv.), substrate **2** (0.2 mmol, 1.0 equiv.), nucleophile **3** (0.4 mmol, 2.0 equiv.), FeCl2 (7.6 mg, 30 mol%), TBACl (0.1 mmol, 0.5 equiv.) and LiCl (0.4 mmol, 2.0 equiv.), followed by MeCN (2.0 mL, 0.1 M with respect to 2). TFA (0.4 mmol, 2.0 equiv.) was then added. The reaction mixture was irradiated with 395-nm LEDs (36 W) at room temperature for 24–36 h. After completion of the reaction, the mixture was quenched with saturated aqueous NaCl and extracted with EtOAc (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the desired produc **89-104**. The products were further identified by NMR spectroscopy and HRMS.



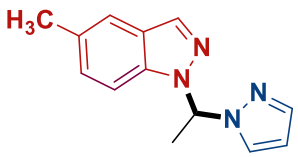
Scale-up protocol: Under air atmosphere, triethylsilane **1a** (4.65 g, 40 mmol), indazole **2a** (1.18 g, 10 mmol), pyrazole **3a** (1.36 g, 20 mmol), $FeCl_3$ (487 mg, 30 mol%), TBACl (1.39 g, 5 mmol), LiCl (848 mg, 20 mmol) in MeCN (50 mL, 0.2 M) were added to 250 mL reaction bottle. Finally, TFA was added (1.53 mL, 20 mmol). The mixture was stirred at 395 nm LEDs (36 W) and monitored by TLC. After stirring for 4 days, the reaction was quenched with saturated NaCl solution and extracted with EtOAc (3 × 200 mL). The organic layers were combined, dried over Na_2SO_4, filtered and evaporated under reduced pressure. The residues were purified by flash column chromatography (15:1) on silica gel to provide the products **4** (1.51g, 71%) as orange oil

1-(1-(1*H*-pyrazol-1-yl)ethyl)-1*H*-indazole (4).



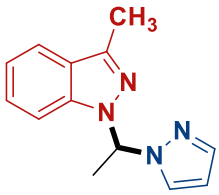
According to the **General Procedure 1**, the reaction afforded compound **4** in 82% yield (35 mg) as orange oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.98 (s, 1H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.45 (d, *J* = 2.5 Hz, 1H), 7.41 (d, *J* = 1.8 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.93 (q, *J* = 6.8 Hz, 1H), 6.15 (t, *J* = 2.1 Hz, 1H), 2.24 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 138.3, 138.1, 133.6, 126.0, 125.7, 123.6, 120.5, 120.1, 108.6, 105.6, 68.4, 18.8. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{12}H_{12}N_4Na^+$, 235.0954; found, 235.0960.

1-(1-(1*H*-pyrazol-1-yl)ethyl)-5-methyl-1*H*-indazole (5).



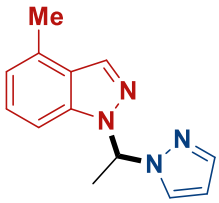
According to the **General Procedure 1**, the reaction afforded compound **5** in 86% yield (39 mg) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.87 (s, 1H), 7.46 – 7.33 (m, 4H), 7.12 (d, *J* = 7.0 Hz, 1H), 6.87 (q, *J* = 6.8 Hz, 1H), 6.11 (t, *J* = 2.2 Hz, 1H), 2.33 (s, 3H), 2.20 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 139.1, 138.0, 134.0, 131.1, 129.1, 126.7, 125.1, 120.1, 109.3, 106.6, 69.5, 21.3, 19.8. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{13}H_{14}N_4Na^+$, 249.1111; found, 249.1109.

1-(1-(1*H*-pyrazol-1-yl)ethyl)-3-methyl-1*H*-indazole (6).



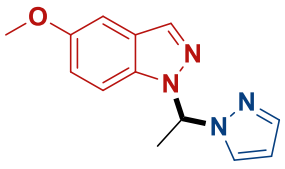
According to the **General Procedure 1**, the reaction afforded compound **6** in 84% yield (38 mg) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.51 (s, 1H), 7.46 – 7.40 (m, 2H), 7.38 (d, *J* = 1.8 Hz, 1H), 7.26 (t, *J* = 7.1 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.82 (q, *J* = 6.8 Hz, 1H), 6.10 (t, *J* = 2.1 Hz, 1H), 2.47 (s, 3H), 2.18 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 142.1, 139.1, 138.0, 125.9, 125.7, 123.2, 119.7, 119.3, 108.5, 105.4, 68.2, 18.8, 11.0. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{13}H_{14}N_4Na^+$, 249.1111; found, 249.1109.

1-(1-(1*H*-pyrazol-1-yl) ethyl)-4-methyl-1*H*-indazole (7).



According to the **General Procedure 1**, the reaction afforded compound **7** in 81% yield (37 mg) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.98 (s, 1H), 7.43 (d, *J* = 2.5 Hz, 1H), 7.39 (d, *J* = 1.8 Hz, 1H), 7.35 (s, 1H), 7.23 – 7.14 (m, 1H), 6.87 (m, 2H), 6.12 (t, *J* = 2.1 Hz, 1H), 2.48 (s, 3H), 2.22 (d, *J* = 6.8 Hz, 3H).**^{13}C NMR** (100 MHz, Chloroform-*d*) δ 138.2, 138.1, 132.4, 130.6, 126.2, 125.7, 124.0, 120.5, 106.0, 105.6, 68.4, 18.8, 17.5. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{13}H_{14}N_4Na^+$, 249.1111; found, 249.1109.

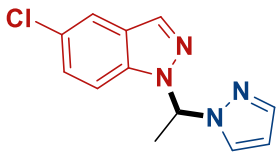
1-(1-(1*H*-pyrazol-1-yl)ethyl)-5-methoxy-1*H*-indazole (8).



According to the **General Procedure 1**, the reaction afforded compound **8** in 82% yield (40 mg) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.88 (s, 1H), 7.45 – 7.36 (m, 3H), 7.02 – 6.95 (m, 2H), 6.86 (q, *J* = 6.9 Hz, 1H), 6.14 (t, *J* = 2.2 Hz, 1H), 3.74 (s, 3H), 2.21 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 154.1, 138.1, 134.1, 132.8, 125.6, 124.0, 118.0, 109.6,

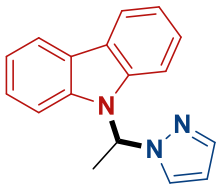
105.6, 99.3, 68.6, 54.6, 18.7. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{13}H_{14}N_4ONa^+$, 265.1060; found, 265.1059.

1-(1-(1*H*-pyrazol-1-yl)ethyl)-5-chloro-1*H*-indazole (9).



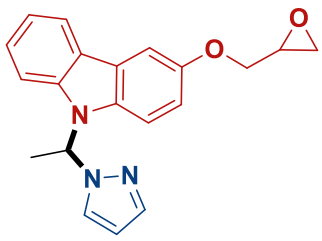
According to the **General Procedure 1**, the reaction afforded compound **9** in 36% yield (18 mg) as a colorless liquid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.94 (s, 1H), 7.59 – 7.52 (m, 2H), 7.49 (d, *J* = 2.4 Hz, 1H), 7.44 (d, *J* = 1.9 Hz, 1H), 7.06 (d, *J* = 8.6 Hz, 1H), 6.85 (q, *J* = 6.9 Hz, 1H), 6.18 (t, *J* = 2.2 Hz, 1H), 2.23 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 138.6, 138.4, 133.5, 132.5, 125.7, 122.2, 121.8, 120.9, 108.7, 105.8, 68.5, 18.7. **HRMS** (TOF-ESI$^+$): *m/z* [M+H]$^+$ calcd for $C_{12}H_{12}ClN_4^+$, 247.0745; found, 247.0746.

9-(1-(1*H*-pyrazol-1-yl)ethyl)-9*H*-carbazole (10).



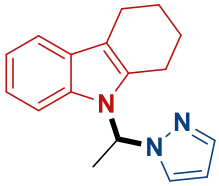
According to the **General Procedure 1**, the reaction afforded compound **10** in 69% yield (36 mg) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 7.7 Hz, 2H), 7.53 (s, 1H), 7.37 – 7.23 (m, 5H), 7.20 – 7.13 (m, 2H), 6.90 (q, *J* = 6.8 Hz, 1H), 6.16 (t, *J* = 2.1 Hz, 1H), 2.23 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 139.5, 139.0 128.5, 126.1, 123.9, 120.5, 120.1, 110.0, 106.9, 66.6, 18.1. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{17}H_{15}N_3Na^+$, 284.1158; found, 284.1154.

9-(1-(1*H*-pyrazol-1-yl)ethyl)-3-(oxiran-2-ylmethoxy)-9*H*-carbazole (11).



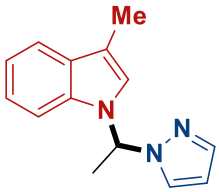
According to the **General Procedure 1**, the reaction afforded compound **11** in 52% yield (35 mg) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.16 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 1.8 Hz, 1H), 7.31 (m, 3H), 7.25 (t, *J* = 8.2 Hz, 1H), 7.21 – 7.17 (m, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.90 (q, *J* = 6.8 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 6.20 – 6.15 (m, 1H), 4.30 (m, 3H), 3.90 – 3.76 (m, 2H), 2.24 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 153.7, 139.6, 138.5, 137.2, 127.4, 125.9, 124.4, 122.0, 121.9, 119.4, 111.9, 108.6, 105.8, 102.5, 101.0, 68.9, 67.6, 65.6, 45.4, 17.0. **HRMS** (TOF-ESI^{+}): *m/z* [M+Na]$^{+}$ calcd for $C_{20}H_{19}N_3O_2Na^{+}$, 356.1369; found, 356.1365.

9-(1-(1*H*-pyrazol-1-yl)ethyl)-2,3,4,9-tetrahydro-1*H*-carbazole (12).



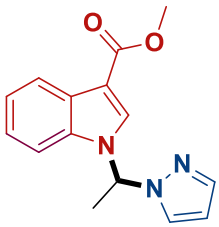
According to the **General Procedure 1**, the reaction afforded compound **12** in 56% yield (30 mg) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 1.7 Hz, 1H), 7.41 – 7.36 (m, 1H), 7.21 (d, *J* = 2.4 Hz, 1H), 7.18 – 7.15 (m, 1H), 7.03 – 7.00 (m, 2H), 6.55 (q, *J* = 6.9 Hz, 1H), 6.17 (t, *J* = 2.1 Hz, 1H), 2.79 – 2.68 (m, 1H), 2.63 (m, *J* = 5.1, 4.3, 3.0 Hz, 2H), 2.56 – 2.49 (m, 1H), 2.16 (d, *J* = 6.8 Hz, 3H), 1.86 (m, 2H), 1.78 (m, 2H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 138.3, 134.1, 133.6, 127.5, 127.0, 120.3, 118.6, 117.0, 110.6, 109.3, 105.3, 65.3, 22.3, 21.8, 21.8, 19.9, 18.2. **HRMS** (TOF-ESI^{+}): *m/z* [M+Na]$^{+}$ calcd for $C_{17}H_{19}N_3Na^{+}$, 288.1471; found, 288.1467.

1-(1-(1*H*-pyrazol-1-yl)ethyl)-3-methyl-1*H*-indole (13).



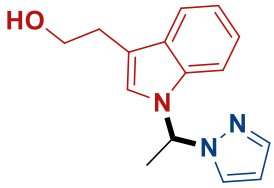
According to the **General Procedure 1**, the reaction afforded compound **13** in 57% yield (26 mg) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.51 – 7.43 (m, 2H), 7.28 (d, *J* = 8.2 Hz, 1H), 7.17 – 7.00 (m, 4H), 6.66 (q, *J* = 6.7 Hz, 1H), 6.11 (t, *J* = 2.1 Hz, 1H), 2.25 (s, 3H), 2.10 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 138.5, 135.1, 128.3, 125.9, 121.3, 120.0, 118.8, 118.2, 111.7, 108.3, 105.1, 65.7, 19.6, 8.7. **HRMS** (TOF-ESI^{+}): *m/z* [M+Na]$^{+}$ calcd for $C_{14}H_{15}N_3Na^{+}$, 248.1158; found, 248.1163.

methyl 1-(1-(1*H*-pyrazol-1-yl)ethyl)-1*H*-indole-3-carboxylate (14).



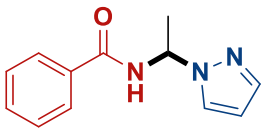
According to the **General Procedure 1**, the reaction afforded compound **14** in 52% yield (28 mg) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.54 (s, 1H), 7.47 (d, *J* = 9.9 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.21 – 7.14 (m, 2H), 7.08 (t, *J* = 7.1 Hz, 1H), 6.71 (q, *J* = 6.7 Hz, 1H), 6.12 (t, *J* = 2.1 Hz, 1H), 2.29 (s, 3H), 2.09 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 168.4, 139.6, 133.0, 131.2, 126.8, 123.4, 121.0, 120.6, 117.9, 112.7, 109.7, 106.5, 67.1, 21.1, 20.6. **HRMS** (TOF-ESI^{+}): *m/z* [M+Na]$^{+}$ calcd for $C_{15}H_{15}N_3O_2Na^{+}$, 292.1056; found, 292.1050.

2-(1-(1-(1*H*-pyrazol-1-yl)ethyl)-1*H*-indol-3-yl) ethan-1-ol (15).



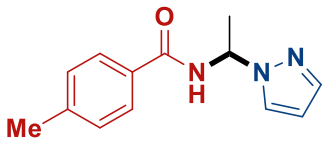
According to the **General Procedure 1**, the reaction afforded compound **15** in 51% yield (26 mg) as a brown solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.70 (s, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 1.8 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.23 – 7.19 (m, 2H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.66 (q, *J* = 6.8 Hz, 1H), 6.12 (t, *J* = 2.1 Hz, 1H), 3.85 (t, *J* = 6.4 Hz, 2H), 2.98 – 2.90 (t, *J* = 6.4 Hz, 2H), 2.09 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 138.6, 135.2, 127.5, 126.0, 121.6, 120.9, 119.2, 118.3, 112.4, 108.6, 105.2, 65.8, 61.4, 27.6, 19.6. **HRMS** (TOF-ESI$^+$): *m/z* [M+H]$^+$ calcd for $C_{15}H_{18}N_3O^+$, 256.1444; found, 256.1448.

***N*-(1-(1*H*-pyrazol-1-yl)ethyl) benzamide (16).**



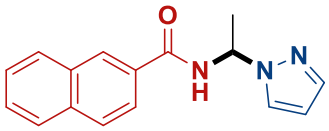
According to the **General Procedure 1**, the reaction afforded compound **16** in 51% yield (22 mg) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.71 – 7.61 (m, 3H), 7.52 – 7.36 (m, 3H), 7.30 (t, *J* = 7.6 Hz, 2H), 6.49 – 6.39 (m, 1H), 6.16 (s, 1H), 1.80 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 166.7, 134.0, 133.3, 132.0, 129.8, 128.6, 127.2, 105.3, 61.6, 20.7. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{12}H_{13}N_3ONa^+$, 238.0951; found, 238.0951.

***N*-(1-(1*H*-pyrazol-1-yl)ethyl)-4-methylbenzamide (17).**



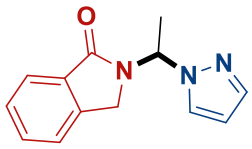
According to the **General Procedure 1**, the reaction afforded compound **17** in 49% yield (23 mg) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 2.4 Hz, 1H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 1.8 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.48 – 6.38 (m, 1H), 6.16 (t, *J* = 2.1 Hz, 1H), 2.30 (s, 3H), 1.80 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 165.55, 141.54, 138.93, 129.42, 128.63, 128.21, 126.16, 104.19, 60.51, 20.43, 19.82. **HRMS** (TOF-ESI$^+$): *m/z* [M+H]$^+$ calcd for $C_{13}H_{16}N_3O^+$, 230.1288; found, 230.1281.

***N*-(1-(1*H*-pyrazol-1-yl)ethyl)-2-naphthamide (18).**



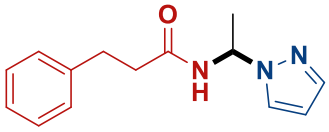
According to the **General Procedure 1**, the reaction afforded compound **18** in 48% yield (25 mg) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.23 (s, 1H), 7.81 – 7.77 (m, 3H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.68 (d, *J* = 2.4 Hz, 1H), 7.58 (s, 1H), 7.52 (s, 1H), 7.51 – 7.41 (m, 2H), 6.57 – 6.47 (m, 1H), 6.19 (t, *J* = 2.1 Hz, 1H), 1.86 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 165.8, 139.0, 133.9, 131.5, 129.5, 128.8, 128.0, 127.4, 126.9, 126.9, 126.7, 125.8, 122.6, 104.2, 60.7, 19.9. **HRMS** (TOF-ESI$^+$): *m/z* $[M+H]^+$ calcd for $C_{16}H_{16}N_3O^+$, 266.1288; found, 266.1291.

2-(1-(1*H*-pyrazol-1-yl)ethyl)isoindolin-1-one (19).



According to the **General Procedure 1**, the reaction afforded compound **19** in 52% yield (24 mg) as a colorless liquid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 7.6 Hz, 1H), 7.59 (dd, *J* = 2.3, 0.7 Hz, 1H), 7.51 – 7.43 (m, 2H), 7.41 – 7.32 (m, 2H), 6.68 (q, *J* = 6.9 Hz, 1H), 6.16 (t, *J* = 2.1 Hz, 1H), 4.51 (d, *J* = 16.8 Hz, 1H), 4.36 (d, *J* = 16.8 Hz, 1H), 1.93 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 167.2, 140.6, 138.7, 131.0, 130.9, 128.5, 127.1, 123.0, 122.0, 104.8, 61.0, 45.0, 16.9. **HRMS** (TOF-ESI$^+$): *m/z* $[M+H]^+$ calcd for $C_{13}H_{14}N_3O^+$, 228.1131; found, 228.1133.

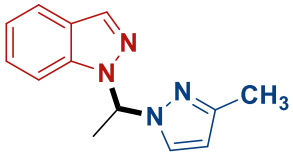
***N*-(1-(1*H*-pyrazol-1-yl)ethyl)-3-phenylpropanamide (20).**



According to the **General Procedure 1**, the reaction afforded compound **20** in 46% yield (22 mg) as a colorless liquid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 2.4 Hz, 1H), 7.41 (d, *J* = 1.8 Hz, 1H), 7.18 – 7.13 (m, 2H), 7.10 (d, *J* = 6.4 Hz, 2H), 7.02 (d, *J* = 7.2 Hz, 2H), 6.22 – 6.11

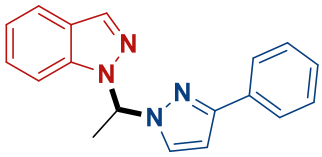
(m, 2H), 2.83 (t, *J* = 7.6 Hz, 2H), 2.36 (m, 2H), 1.56 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 171.8, 140.5, 139.8, 129.7, 128.5, 128.3, 126.3, 105.1, 61.0, 38.0, 31.3, 20.4. **HRMS** (TOF-ESI$^+$): *m/z* [M+H]$^+$ calcd for $C_{14}H_{18}N_3O^+$, 244.1444; found, 244.1448.

1-(1-(3-methyl-1*H*-pyrazol-1-yl)ethyl)-1*H*-indazole (21).



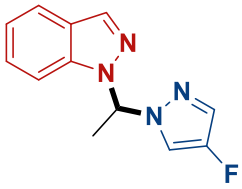
According to the **General Procedure 1**, the reaction afforded compound **21** in 72% yield (33 mg) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.05 (s, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.62 (d, *J* = 7.4 Hz, 1H), 7.43 – 7.35 (m, 2H), 7.19 – 7.14 (m, 1H), 6.90 (q, *J* = 6.8 Hz, 1H), 5.99 (t, *J* = 2.4 Hz, 1H), 2.26 (d, *J* = 6.8 Hz, 3H), 2.24 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 148.4, 139.3, 134.4, 127.4, 126.9, 124.6, 121.5, 121.1, 109.7, 106.5, 69.2, 20.1, 13.6. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na] $^+$ calcd for $C_{13}H_{14}N_4Na^+$, 249.1111; found, 249.1109

1-(1-(3-phenyl-1*H*-pyrazol-1-yl)ethyl)-1*H*-indazole (22).



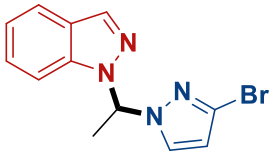
According to the **General Procedure 1**, the reaction afforded compound **22** in 83% yield (48 mg) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.96 (s, 1H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 9.2 Hz, 2H), 7.38 (d, *J* = 2.4 Hz, 1H), 7.32 – 7.22 (m, 3H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.09 – 7.01 (m, 1H), 6.91 (q, *J* = 6.8 Hz, 1H), 6.39 (t, *J* = 2.5 Hz, 1H), 2.21 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 150.0, 138.3, 133.5, 132.2, 127.5, 126.9, 126.7, 125.9, 124.6, 123.6, 120.5, 120.0, 108.8, 103.0, 68.7, 18.9. **HRMS** (TOF-ESI$^+$): *m/z* [M+H] $^+$ calcd for $C_{18}H_{17}N_4^+$, 289.1448; found, 289.1443.

1-(1-(4-fluoro-1H-pyrazol-1-yl)ethyl)-1H-indazole (23).



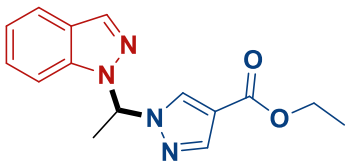
According to the **General Procedure 1**, the reaction afforded compound **23** in 86% yield (40 mg) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.99 (s, 1H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.51 (d, *J* = 8.5 Hz, 1H), 7.36 – 7.28 (m, 2H), 7.23 (d, *J* = 4.4 Hz, 1H), 7.16 – 7.06 (m, 1H), 6.77 (q, *J* = 6.2, 5.5 Hz, 1H), 2.19 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-d) δ 149.0 (d, J_{C-F} =246.42 Hz), 138.3, 133.8, 126.2, 125.4, 125.3, 123.6, 120.4 (d, J_{C-F} =55.5 Hz), 111.9(d, J_{C-F} =27.57 Hz), 108.5, 69.4, 18.6. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -174.89. **HRMS** (TOF-ESI^{+}): *m/z* $[M+H]^{+}$ calcd for $C_{12}H_{12}FN_4^{+}$, 231.1041; found, 231.1033.

1-(1-(3-bromo-1*H*-pyrazol-1-yl)ethyl)-1*H*-indazole (24).



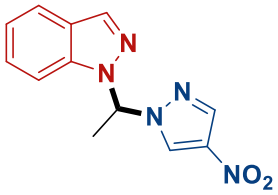
According to the **General Procedure 1**, the reaction afforded compound **24** in 77% yield (45 mg) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.99 (s, 1H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.51 (d, *J* = 8.5 Hz, 1H), 7.44 (s, 1H), 7.35 – 7.29 (m, 2H), 7.10 (t, *J* = 7.1 Hz, 1H), 6.83 (q, *J* = 6.8 Hz, 1H), 2.20 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 139.8, 139.3, 135.0, 127.3, 127.0, 124.7, 121.8, 121.3, 109.5, 94.5, 70.0, 19.8. **HRMS** (TOF-ESI^{+}): *m/z* $[M+Na]^{+}$ calcd for $C_{12}H_{11}BrN_4Na^{+}$, 313.0059; found, 313.0055.

ethyl-1-(1-(1*H*-indazol-1-yl)ethyl)-1*H*-pyrazole-4-carboxylate (25).



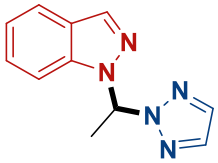
According to the **General Procedure 1**, the reaction afforded compound **25** in 89% yield (51 mg) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.00 (s, 1H), 7.91 (s, 1H), 7.79 (s, 1H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.51 (d, *J* = 8.5 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.10 (t, *J* = 6.9 Hz, 1H), 6.88 (q, *J* = 6.8 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.23 (d, *J* = 5.6 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 161.7, 139.7, 138.3, 134.2, 129.2, 126.3, 123.7, 120.8, 120.2, 115.1, 108.3, 68.6, 59.2, 18.8, 13.3. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{15}H_{16}N_4O_2Na^+$, 307.1165; found, 307.1170.

1-(1-(3-nitro-1*H*-pyrazol-1-yl)ethyl)-1*H*-indazole (26).



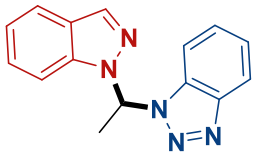
According to the **General Procedure 1**, the reaction afforded compound **26** in 85% yield (44 mg) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.09 (s, 1H), 8.05 (s, 1H), 7.95 (s, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.51 (d, *J* = 8.2 Hz, 1H), 7.42 – 7.33 (m, 1H), 7.22 – 7.12 (m, 1H), 6.88 (q, *J* = 6.8 Hz, 1H), 2.28 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 139.5, 136.0, 135.4, 127.7, 126.3, 124.8, 122.3, 121.5, 109.0, 70.4, 19.9. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{12}H_{11}N_5O_2Na^+$, 280.0805; found, 280.0803

1-(1-(1*H*-1,2,3-triazol-1-yl)ethyl)-1*H*-indazole (27).



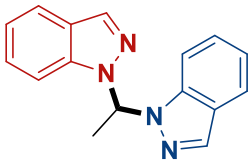
According to the **General Procedure 1**, the reaction afforded compound **27** in 65% yield (28 mg) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.01 (s, 1H), 7.66 – 7.62 (m, 2H), 7.52 (s, 2H), 7.38 – 7.31 (m, 1H), 7.16 (t, *J* = 6.8 Hz, 1H), 7.13 – 7.08 (q, 1H), 2.39 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 138.3, 133.9, 133.8, 126.0, 123.7, 120.6, 120.2, 108.6, 70.3, 17.8. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{11}H_{11}N_5Na^+$, 236.0907; found, 236.0912.

1-(1-(1*H*-indazol-1-yl)ethyl)-1*H*-benzo[d] [1,2,3] triazole (28).



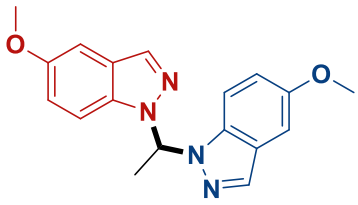
According to the **General Procedure 1**, the reaction afforded compound **28** in 81% yield (43 mg) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.02 (s, 1H), 7.90 (d, *J* = 9.4 Hz, 1H), 7.68 – 7.49 (m, 4H), 7.34 – 7.16 (m, 3H), 7.11 – 6.95 (q, 1H), 2.48 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 145.7, 138.0, 133.5, 130.2, 126.7, 126.3, 123.9, 123.3, 120.9, 120.2, 118.9, 110.0, 108.5, 67.7, 17.5. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{15}H_{13}N_5Na^+$, 286.1063; found, 286.1071.

1,1'-(ethane-1,1-diyl) bis(1*H*-indazole) (29).



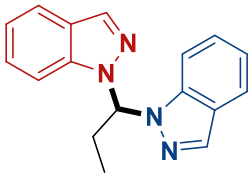
According to the **General Procedure 1**, the reaction afforded compound **29** in 89% yield (47 mg) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.97 (s, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.27 – 7.15 (m, 3H), 7.02 (t, *J* = 7.5 Hz, 2H), 2.37 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 138.7, 133.7, 126.8, 125.0, 121.4, 121.1, 110.2, 69.8, 18.6. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{16}H_{14}N_4Na^+$, 285.1111; found, 285.1106.

1,1'-(ethane-1,1-diyl) bis(5-methoxy-1*H*-indazole) (30).



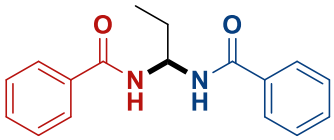
According to the **General Procedure 1**, the reaction afforded compound **30** in 84% yield (54 mg) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.86 (s, 2H), 7.33 (d, *J* = 9.1 Hz, 2H), 7.12 (q, *J* = 6.9 Hz, 1H), 6.92 (d, *J* = 2.3 Hz, 2H), 6.86 (dd, *J* = 9.1, 2.4 Hz, 2H), 3.71 (s, 6H), 2.33 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 153.9, 133.4, 131.9, 124.4, 117.8, 110.1, 99.2, 69.1, 54.6, 17.5. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{18}H_{18}N_4O_2Na^+$, 345.1322; found, 345.1330.

1,1'-(propane-1,1-diyl) bis(1*H*-indazole) (31).



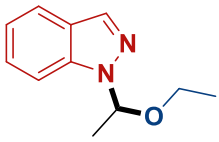
According to the **General Procedure 1**, the reaction afforded compound **31** in 85% yield (47 mg) as a white solid. Data consistent with those previously reported. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.97 (s, 2H), 7.60 (dd, *J* = 8.5, 5.7 Hz, 4H), 7.27 – 7.17 (m, 2H), 7.08 – 6.99 (m, 2H), 6.92 (t, *J* = 7.6 Hz, 1H), 2.95 (p, *J* = 7.5 Hz, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 139.0, 133.7, 126.7, 124.9, 121.3, 121.1, 110.2, 74.8, 25.6, 10.4. **HRMS** (TOF-ESI$^+$): *m/z* [M+H]$^+$ calcd for $C_{17}H_{17}N_4^+$, 277.1448; found, 277.1444.

***N, N'*-(propane-1,1-diyl) dibenzamide (32).**



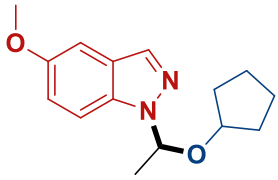
According to the **General Procedure 1**, the reaction afforded compound **32** in 41% yield (23 mg) as a white solid.[1] **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.56 (d, *J* = 7.7 Hz, 2H), 7.89 – 7.81 (m, 4H), 7.57 – 7.51 (m, 2H), 7.50 – 7.42 (m, 4H), 5.77 (p, *J* = 7.4 Hz, 1H), 1.84 (p, *J* = 7.3 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 166.2, 134.7, 131.9, 128.8, 127.8, 58.9, 27.7, 10.5.

1-(1-ethoxyethyl)-1*H*-indazole (33).



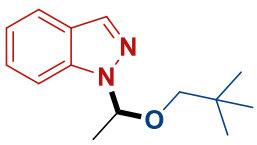
According to the **General Procedure 2**, the reaction afforded compound **33** in 76% yield (29 mg) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.92 (s, 1H), 7.64 (m, 2H), 7.36 – 7.25 (m, 1H), 7.14 – 7.02 (m, 1H), 5.82 (q, *J* = 6.1 Hz, 1H), 3.44 – 3.03 (m, 2H), 1.73 (d, 3H), 1.05 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 137.4, 132.4, 125.3, 123.9, 120.1, 120.0, 109.5, 85.7, 62.6, 19.8, 13.8. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{11}H_{14}N_2ONa^+$, 213.0998; found, 213.0995.

1-(1-(cyclopentyloxy)ethyl)-5-methoxy-1*H*-indazole (34).



According to the **General Procedure 2**, the reaction afforded compound **34** in 59% yield (31 mg) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.82 (s, 1H), 7.54 (d, *J* = 9.0 Hz, 1H), 7.05 – 6.92 (m, 2H), 5.81 (q, *J* = 6.1 Hz, 1H), 3.79 (s, 3H), 3.72 (p, *J* = 5.6, 5.1 Hz, 1H), 1.66 (d, *J* = 6.1 Hz, 4H), 1.54 (m, 5H), 1.33 – 1.29 (m, 2H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 153.7, 133.2, 131.4, 124.3, 117.4, 110.8, 99.1, 84.8, 77.9, 54.6, 31.6, 30.7, 22.5, 22.3, 20.4. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{15}H_{20}N_2O_2Na^+$, 283.1417; found, 283.1416.

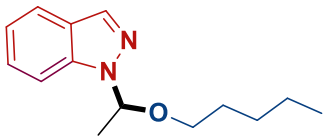
1-(1-(neopentyloxy)ethyl)-1*H*-indazole (35).



According to the **General Procedure 2**, the reaction afforded compound **35** in 43% yield (20 mg) as a colorless liquid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.91 (s, *J* = 0.9 Hz, 1H), 7.73 – 7.58 (m, 2H), 7.30 (m, 1H), 7.16 – 7.04 (m, 1H), 5.79 (q, *J* = 6.1 Hz, 1H), 3.00 (d, *J* = 8.7 Hz, 1H), 2.77

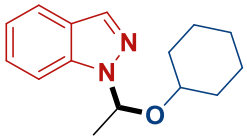
(d, *J* = 8.7 Hz, 1H), 1.71 (d, *J* = 6.1 Hz, 3H), 0.77 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 137.1, 132.0, 125.2, 124.0, 120.1, 119.9, 109.9, 87.1, 77.6, 30.7, 25.6, 19.6. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{14}H_{20}N_2ONa^+$, 255.1468; found, 255.1471.

1-(1-(pentyloxy)ethyl)-1*H*-indazole (36).



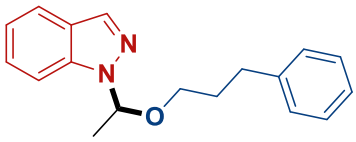
According to the **General Procedure 2**, the reaction afforded compound **36** in 43% yield (20 mg) as a colorless liquid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.92 (s, 1H), 7.65 (m, *J* = 15.1, 8.3 Hz, 2H), 7.34 – 7.26 (m, 1H), 7.14 – 7.04 (m, 1H), 5.81 (q, *J* = 6.1 Hz, 1H), 3.37 – 3.02 (m, 2H), 1.72 (d, *J* = 6.1 Hz, 3H), 1.43 (t, *J* = 7.3 Hz, 2H), 1.13 (m, 4H), 0.78 – 0.72 (t, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 137.4, 132.3, 125.3, 124.0, 120.1, 120.0, 109.6, 86.0, 67.3, 28.0, 27.1, 21.3, 19.8, 12.9. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{14}H_{20}N_2ONa^+$, 255.1468; found, 255.1473.

1-(1-(cyclohexyloxy)ethyl)-1H-indazole (37).



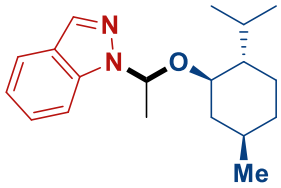
According to the **General Procedure 2**, the reaction afforded compound **37** in 53% yield (26 mg) as a colorless liquid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.90 (s, 1H), 7.72 – 7.65 (m, 2H), 7.34 – 7.26 (m, 1H), 7.10 (m, 1H), 5.98 (q, *J* = 6.1 Hz, 1H), 3.16 (m, *J* = 9.5, 4.7 Hz, 1H), 1.68 (d, *J* = 6.1 Hz, 3H), 1.55 – 1.45 (m, 1H), 1.37 (m, 2H), 1.21 – 1.03 (m, 4H), 1.00 – 0.87 (m, 2H), 0.81 (m, 1H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 137.2, 132.0, 125.1, 124.1, 120.1, 119.9, 110.1, 83.7, 73.9, 31.8, 30.2, 24.5, 23.0, 22.9, 20.3. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{15}H_{20}N_2ONa^+$, 267.1468; found, 267.1474.

1-(1-(3- phenylpropoxy)ethyl)-1*H*-indazole (38).



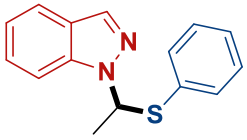
According to the **General Procedure 2**, the reaction afforded compound **38** in 50% yield (28 mg) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.92 (s, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.62 (d, *J* = 8.5 Hz, 1H), 7.33 – 7.28 (m, 1H), 7.12 (m, *J* = 7.4 Hz, 4H), 6.97 (d, *J* = 7.5 Hz, 2H), 5.85 – 5.77 (q, 1H), 3.38 – 3.29 (m, 1H), 3.18 – 3.09 (m, 1H), 2.51 (m, 7.6 Hz, 4H), 1.75 (d, *J* = 5.0 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 140.6, 137.5, 132.4, 127.4, 127.2, 125.4, 124.7, 124.0, 120.2, 120.0, 109.5, 85.9, 66.4, 31.2, 30.0, 19.7. **HRMS** (TOF-ESI^{+}): *m/z* [M+Na]$^{+}$ calcd for $C_{18}H_{20}N_2ONa^{+}$, 303.1468; found, 303.1462.

1-(1-(((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)ethyl)-1*H*-indazole (39).



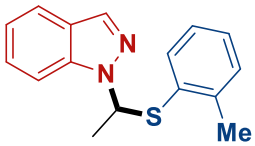
According to the General Procedure 2, the reaction afforded compound 39 in 61% yield (37 mg, dr = 5.2:1) as a colorless oil. 1H NMR (400 MHz, Chloroform-d) δ 7.91 (d, J = 7.6 Hz, 1H), 7.68 – 7.59 (m, 3H), 7.32 – 7.26 (m, 1H), 7.08 (t, J = 7.5 Hz, 1H), 6.01 (q, J = 6.2 Hz, 1H), 2.92 (m, J = 10.6, 4.2 Hz, 1H), 2.24 (d, J = 12.7 Hz, 1H), 1.92 (m, 1H), 1.77 (d, J = 6.2 Hz, 3H), 1.72 (d, J = 6.1 Hz, 1H), 1.51 (d, J = 13.2 Hz, 2H), 1.45 – 1.39 (m, 1H), 1.23 – 1.17 (m, 1H), 1.15 – 1.08 (m, 1H), 0.90 – 0.80 (m, 7H), 0.74 (d, J = 7.8 Hz, 1H), 0.64 (d, J = 7.0 Hz, 3H), 0.51 (d, J = 6.5 Hz, 1H), -0.36 (d, J = 6.9 Hz, 3H). 13C NMR (100 MHz, Chloroform-d) δ 137.4, 132.1, 132.0, 125.1, 124.1, 120.1, 120.0, 119.9, 119.9, 109.7, 81.9, 79.0, 74.4, 47.9, 46.8, 40.6, 38.7, 33.4, 33.2, 30.4, 30.3, 23.6, 22.1, 21.6, 21.3, 21.0, 20.2, 20.1, 20.1, 20.0, 15.4, 13.4. HRMS (TOF-ESI+): m/z [M+Na]+ calcd for C19H28N2ONa+, 323.2094; found, 323.2090.

1-(1-(phenylthio) ethyl)-1*H*-indazole (40).



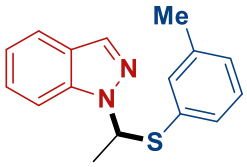
According to the **General Procedure 1**, the reaction afforded compound **40** in 80% yield (41 mg) as a colorless liquid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.99 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.29 – 7.21 (m, 2H), 7.16 (m, 1H), 7.10 – 7.04 (m, 5H), 6.01 (q, *J* = 6.9 Hz, 1H), 2.05 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 139.1, 134.5, 133.9, 132.3, 128.7, 128.5, 126.1, 124.5, 121.1, 120.9, 109.9, 63.2, 21.1. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{15}H_{14}N_2SNa^+$, 277.0770; found, 277.0777.

1-(1-(*o*-tolylthio)ethyl)-1*H*-indazole (41).



According to the **General Procedure 1**, the reaction afforded compound **41** in 82% yield (44 mg) as a colorless liquid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.91 (s, 1H), 7.57 (m, 1H), 7.14 – 6.90 (m, 6H), 6.83 (t, *J* = 6.8 Hz, 1H), 5.88 (q, *J* = 6.9 Hz, 1H), 2.06 (s, 3H), 2.00 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 140.6, 138.1, 134.5, 132.8, 130.9, 129.1, 127.7, 125.3, 124.9, 123.3, 119.9, 119.7, 108.6, 61.9, 20.2, 19.5. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{16}H_{16}N_2SNa^+$, 291.0926; found, 291.0930.

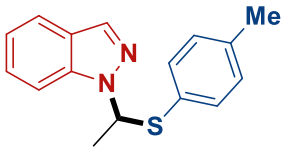
1-(1-(*m*-tolylthio)ethyl)-1*H*-indazole (42).



According to the **General Procedure 1**, the reaction afforded compound **42** in 78% yield (42 mg) as a colorless liquid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.93 (s, 1H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.19 – 7.13 (m, 2H), 7.01 (m, 1H), 6.92 – 6.85 (m, 3H), 6.71 (s, 1H), 5.90 (q, *J* = 6.9 Hz, 1H), 2.00

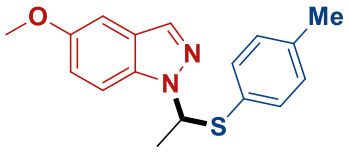
(s, 3H), 1.97 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 138.2, 137.5, 134.2, 132.9, 130.9, 130.3, 128.2, 127.5, 125.0, 123.3, 119.9, 119.8, 108.8, 62.0, 20.1, 19.9. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{16}H_{16}N_2SNa^+$, 291.0926; found, 291.0930.

1-(1-(*p*-tolylthio)ethyl)-1*H*-indazole (43).



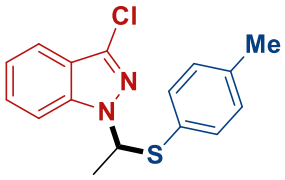
According to the **General Procedure 1**, the reaction afforded compound **43** in 82% yield (44 mg) as a colorless liquid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.90 (s, 1H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.23 – 7.16 (m, 2H), 7.07 – 6.99 (m, 1H), 6.90 (d, *J* = 8.1 Hz, 2H), 6.80 (d, *J* = 7.9 Hz, 2H), 5.87 (q, *J* = 6.9 Hz, 1H), 2.15 (s, 3H), 1.95 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 138.0, 137.7, 133.7, 132.7, 128.5, 127.5, 125.0, 123.4, 120.0, 119.7, 109.0, 62.3, 20.1, 20.0. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{16}H_{16}N_2SNa^+$, 291.0926; found, 291.0930.

5-methoxy-1-(1-(*p*-tolylthio)ethyl)-1*H*-indazole (44).



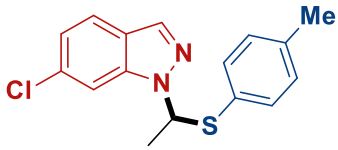
According to the **General Procedure 1**, the reaction afforded compound **44** in 63% yield (38 mg) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.79 (s, 1H), 7.12 (d, *J* = 9.0 Hz, 1H), 6.98 – 6.80 (m, 6H), 5.82 (q, *J* = 6.9 Hz, 1H), 3.76 (s, 3H), 2.16 (s, 3H), 1.94 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 153.5, 137.7, 133.8, 133.6, 131.9, 128.5, 127.5, 123.8, 117.1, 110.0, 99.1, 62.5, 54.6, 20.1, 20.0. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{17}H_{18}N_2OSNa^+$, 321.1032; found, 321.1032

3-chloro-1-(1-(*p*-tolylthio)ethyl)-1*H*-indazole (45).



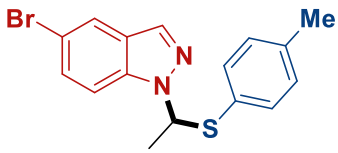
According to the **General Procedure 1**, the reaction afforded compound **45** in 74% yield (45 mg) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 8.1 Hz, 1H), 7.17 (t, *J* = 7.7 Hz, 1H), 7.09 – 7.01 (m, 2H), 6.92 (d, *J* = 8.1 Hz, 2H), 6.81 (d, *J* = 7.9 Hz, 2H), 5.77 (q, *J* = 6.9 Hz, 1H), 2.15 (s, 3H), 1.92 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 139.4, 138.0, 133.8, 132.7, 128.5, 127.2, 126.1, 120.4, 120.4, 118.6, 109.2, 62.7, 20.1, 19.9. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{16}H_{15}ClN_2SNa^+$, 325.0537; found, 325.0527.

6-chloro-1-(1-(*p*-tolylthio)ethyl)-1*H*-indazole (46).



According to the **General Procedure 1**, the reaction afforded compound **46** in 72% yield (43 mg) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.88 (s, 1H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.00 – 6.94 (m, 2H), 6.88 (d, *J* = 8.1 Hz, 2H), 6.80 (d, *J* = 8.5 Hz, 2H), 5.76 (q, *J* = 6.9 Hz, 1H), 2.16 (s, 3H), 1.96 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 138.6, 138.2, 134.0, 133.0, 131.4, 128.5, 127.2, 121.7, 120.7, 120.7, 108.7, 62.7, 20.1, 19.7. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{16}H_{15}ClN_2SNa^+$, 325.0537; found, 325.0527.

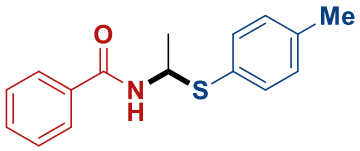
5-bromo-1-(1-(*p*-tolylthio)ethyl)-1*H*-indazole (47).



According to the **General Procedure 1**, the reaction afforded compound **47** in 68% yield (47 mg) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.82 (s, 1H), 7.73 (s, 1H), 7.22 (d, *J* = 8.9,

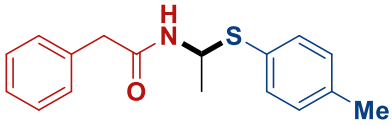
1.8 Hz, 1H), 7.06 (d, *J* = 8.9 Hz, 1H), 6.87 (d, *J* = 8.2 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 2H), 5.81 (q, *J* = 6.9 Hz, 1H), 2.16 (s, 3H), 1.94 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 138.0, 136.7, 133.7, 131.9, 128.5, 128.0, 127.2, 124.7, 122.4, 112.8, 110.4, 62.6, 20.1, 19.8. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{16}H_{15}BrN_2SNa^+$, 369.0032; found, 369.0027.

***N*-(1-(*p*-tolylthio)ethyl) benzamide (48)**.



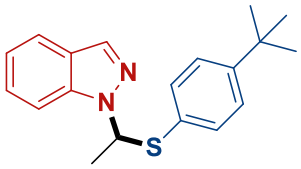
According to the **General Procedure 1**, the reaction afforded compound **48** in 59% yield (32 mg) as a colorless liquid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.60 – 7.50 (m, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.32 (m, 7.9 Hz, 4H), 7.02 (d, *J* = 7.8 Hz, 2H), 6.17 (d, *J* = 9.4 Hz, 1H), 5.66 – 5.51 (m, 1H), 2.23 (s, 3H), 1.51 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 166.2, 138.3, 134.1, 133.7, 131.7, 129.8, 128.6, 128.6, 126.8, 53.1, 22.3, 21.2. **HRMS** (TOF-ESI$^+$): *m/z* [M+H]$^+$ calcd for $C_{16}H_{18}NOS^+$, 272.1104; found, 272.1102.

2-phenyl-*N*-(1-(*p*-tolylthio)ethyl) acetamide (49).



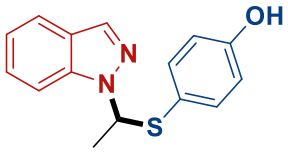
According to the **General Procedure 1**, the reaction afforded compound **49** in 55% yield (31 mg) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.29 – 7.20 (m, 3H), 7.11 (d, *J* = 8.1 Hz, 2H), 7.05 – 6.94 (m, 4H), 5.40 (m, 2H), 3.37 (s, 2H), 2.26 (s, 3H), 1.31 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 168.60, 137.20, 133.24, 132.82, 128.67, 128.43, 127.99, 127.28, 126.37, 51.53, 42.67, 20.91, 20.16. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{17}H_{19}NOSNa^+$, 308.1080; found, 308.1076.

1-(1-((4-(tert-butyl)phenyl)thio)ethyl)-1*H*-indazole (50).



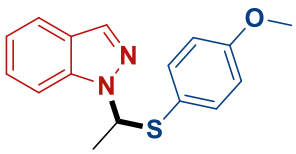
According to the **General Procedure 1**, the reaction afforded compound **50** in 72% yield (45 mg) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.94 (s, 1H), 7.57 (d, *J* = 8.1 Hz, 1H), 7.11 – 6.90 (m, 7H), 5.87 (q, *J* = 6.9 Hz, 1H), 1.98 (d, *J* = 6.9 Hz, 3H), 1.12 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 150.9, 138.4, 133.5, 133.0, 127.7, 124.9, 124.7, 123.1, 119.9, 119.6, 108.7, 62.1, 33.5, 30.1, 19.9. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{19}H_{22}N_2SNa^+$, 333.1396; found, 333.1393.

4-((1-(1*H*-indazol-1-yl)ethyl)thio) phenol (51).



According to the **General Procedure 1**, the reaction afforded compound **51** in 55% yield (30 mg) as a white solid. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.15 (s, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.52 (d, *J* = 8.5 Hz, 1H), 7.37 – 7.29 (m, 1H), 7.20 – 7.13 (m, 1H), 6.96 (d, *J* = 8.5 Hz, 2H), 6.58 (d, *J* = 8.5 Hz, 2H), 6.25 (q, *J* = 6.7 Hz, 1H), 1.95 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 158.6, 139.5, 137.1, 134.0, 126.2, 124.1, 121.2, 121.1, 120.3, 116.1, 110.7, 62.1, 21.1. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{15}H_{14}N_2OSNa^+$, 293.0719; found, 293.0722.

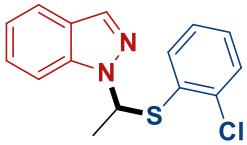
1-(1-((4-methoxyphenyl)thio)ethyl)-1*H*-indazole (52).



According to the **General Procedure 1**, the reaction afforded compound **52** in 77% yield (44 mg) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.91 (s, 1H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.19 – 7.10 (m, 2H), 7.02 (m, 1H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.50 (d, *J* = 8.7 Hz, 2H), 5.80 (q, *J* =

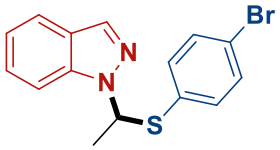
6.9 Hz, 1H), 3.62 (s, 3H), 1.95 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 159.3, 138.2, 135.9, 132.8, 125.0, 123.3, 121.5, 119.9, 119.7, 113.2, 108.9, 62.4, 54.2, 19.7. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{16}H_{16}N_2OSNa^+$, 307.0876; found, 307.0881.

1-(1-((2-chlorophenyl)thio)ethyl)-1H-indazole (53).



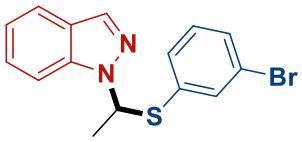
According to the **General Procedure 1**, the reaction afforded compound **53** in 64% yield (37 mg) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d* δ 7.91 (s, 1H), 7.55 (d, *J* = 8.1 Hz, 1H), 7.24 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.19 (d, *J* = 8.6 Hz, 1H), 7.16 – 7.10 (m, 1H), 7.04 – 6.93 (m, 3H), 6.76 (m, 1H), 6.13 (q, *J* = 6.9 Hz, 1H), 2.01 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 138.2, 137.1, 135.1, 133.2, 130.4, 128.8, 128.7, 125.9, 125.1, 123.3, 119.9, 119.8, 108.5, 60.3, 19.8. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{15}H_{13}ClN_2SNa^+$, 311.0380; found, 311.0377.

1-(1-((4-bromophenyl)thio)ethyl)-1*H*-indazole (54).



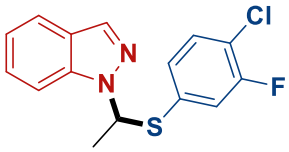
According to the **General Procedure 1**, the reaction afforded compound **54** in 84% yield (56 mg) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.90 (s, 1H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.25 – 7.16 (m, 2H), 7.15 – 7.02 (m, 3H), 6.85 (d, *J* = 8.4 Hz, 2H), 5.92 (q, *J* = 6.9 Hz, 1H), 1.96 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 137.9, 134.9, 133.0, 130.8, 130.2, 125.3, 123.5, 122.0, 120.1, 120.0, 108.8, 62.0, 19.9. **HRMS** (TOF-ESI$^+$): *m/z* [M+H]$^+$ calcd for $C_{15}H_{14}BrN_2S^+$, 333.0056; found, 333.0046.

1-(1-((3-bromophenyl)thio)ethyl)-1*H*-indazole (55).



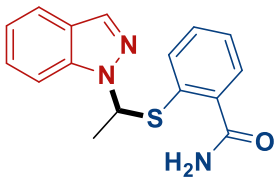
According to the **General Procedure 1**, the reaction afforded compound **55** in 86% yield (57 mg) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.92 (s, 1H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.18 (d, *J* = 2.1 Hz, 2H), 7.13 (t, *J* = 1.9 Hz, 1H), 7.03 (m, 2H), 6.91 (d, *J* = 7.9 Hz, 1H), 6.82 (t, *J* = 7.8 Hz, 1H), 5.94 (q, *J* = 6.9 Hz, 1H), 1.97 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 138.2, 135.8, 133.3, 133.1, 131.7, 130.4, 128.9, 125.3, 123.4, 121.2, 120.2, 120.0, 108.6, 61.9, 20.0. **HRMS** (TOF-ESI$^+$): *m/z* [M+H]$^+$ calcd for $C_{15}H_{14}BrN_2S^+$, 333.0056; found, 333.0046.

1-(1-((4-chloro-3-fluorophenyl)thio)ethyl)-1*H*-indazole (56).



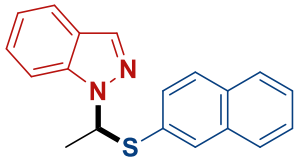
According to the **General Procedure 1**, the reaction afforded compound **56** in 67% yield (41 mg) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.92 (s, 1H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.19 (m, 2H), 7.10 – 7.01 (m, 1H), 6.97 (dd, *J* = 7.0, 2.2 Hz, 1H), 6.81 (m, 1H), 6.72 (t, *J* = 8.7 Hz, 1H), 5.89 (q, *J* = 6.9 Hz, 1H), 1.98 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 157.5(d, J_{C-F} =250.3 Hz), 138.1, 136.0, 134.0, 133.9, 133.2, 127.3(d, J_{C-F} =4.13 Hz), 125.3, 123.4, 120.2(d, J_{C-F} =10.87 Hz), 120.0 (d, J_{C-F} =18.00 Hz), 115.6 (d, J_{C-F} =21.26 Hz), 108.5, 62.1(d, J_{C-F} =1.5 Hz), 19.7. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{15}H_{12}ClFN_2SNa^+$, 329.0286; found, 329.0288.

2-((1-(1*H*-indazol-1-yl)ethyl)thio) benzamide (57).



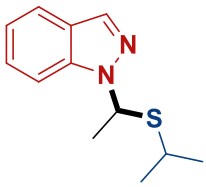
According to the **General Procedure 1**, the reaction afforded compound **57** in 50% yield (30 mg) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.94 (s, 1H), 7.52 (m, 2H), 7.19 (s, 1H), 7.17 – 7.12 (m, 1H), 7.09 (d, *J* = 5.0 Hz, 2H), 6.97 – 6.92 (m, 2H), 6.63 (s, 1H), 6.20 (q, *J* = 6.8 Hz, 1H), 5.92 (s, 1H), 1.99 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 169.2, 138.6, 138.5, 135.9, 133.5, 129.4, 128.5, 128.1, 127.9, 125.3, 122.8, 119.9, 119.82, 108.47, 62.23, 19.91. **HRMS** (TOF-ESI^{+}): *m/z* [M+Na]$^{+}$ calcd for $C_{16}H_{15}N_3OSNa^{+}$, 320.0828; found, 320.0824.

1-(1-(naphthalen-2-ylthio)ethyl)-1H-indazole (58).



According to the **General Procedure 1**, the reaction afforded compound **58** in 74% yield (45 mg) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.90 (s, 1H), 7.59 (m, 7.7 Hz, 2H), 7.51 – 7.42 (m, 3H), 7.31 (m, 1.7 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 1H), 7.11 – 7.03 (m, 2H), 6.96 (t, *J* = 7.0 Hz, 1H), 6.02 (q, *J* = 6.9 Hz, 1H), 2.00 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 138.0, 132.8, 132.8, 132.2, 131.7, 129.8, 128.6, 127.2, 126.5, 126.5, 125.5, 125.2, 125.0, 123.5, 120.0, 119.8, 108.9, 62.0, 20.2. **HRMS** (TOF-ESI^{+}): *m/z* [M+Na]$^{+}$ calcd for $C_{19}H_{16}N_2SNa^{+}$, 327.0926; found, 327.0923.

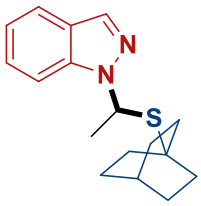
1-(1-(isopropylthio)ethyl)-1H-indazole (59).



According to the **General Procedure 1**, the reaction afforded compound **59** in 72% yield (32 mg) as a colorless liquid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.92 (s, *J* = 0.9 Hz, 1H), 7.65 (t, *J* = 7.9 Hz, 2H), 7.37 – 7.28 (m, 1H), 7.10 (t, *J* = 7.9 Hz, 1H), 5.91 (q, *J* = 7.0 Hz, 1H), 2.53 (m, 1H), 1.84 (d, *J* = 7.0 Hz, 3H), 1.20 (d, *J* = 6.6 Hz, 3H), 0.90 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz,

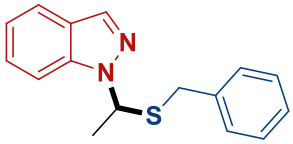
Chloroform-*d*) δ 137.1, 132.2, 125.1, 123.9, 120.3, 119.9, 109.6, 58.4, 33.7, 22.8, 21.8, 20.4. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{12}H_{16}N_2SNa^+$, 243.0926; found, 243.0929.

1-(1-(bicyclo[2.2.2]octan-1-ylthio)ethyl)-1*H*-indazole (60).



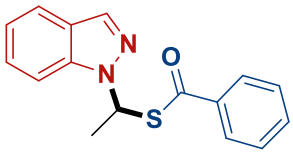
According to the **General Procedure 1**, the reaction afforded compound **60** in 49% yield (28 mg) as a colorless liquid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.67 (m, 2H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.06 (q, *J* = 7.1 Hz, 1H), 1.85 – 1.70 (m, 9H), 1.51 – 1.43 (m, 8H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 136.5, 131.6, 124.8, 124.2, 120.2, 119.7, 110.3, 56.0, 45.5, 42.0, 35.0, 28.6, 21.7. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{17}H_{22}N_2SNa^+$, 309.1396; found, 309.1396.

1-(1-(benzylthio)ethyl)-1*H*-indazole (61).



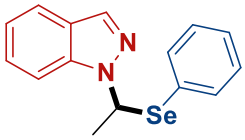
According to the **General Procedure 1**, the reaction afforded compound **61** in 46% yield (25 mg) as a colorless liquid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.96 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.45 (d, J = 8.5 Hz, 1H), 7.38 – 7.25 (m, 1H), 7.19 – 7.07 (m, 6H), 5.69 (q, *J* = 7.0 Hz, 1H), 3.52 – 3.27 (m, 2H), 1.82 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 137.4, 136.5, 132.6, 127.8, 127.4, 126.0, 125.1, 123.9, 120.3, 120.0, 109.5, 58.1, 34.1, 20.0. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{16}H_{16}N_2SNa^+$, 291.0926; found, 291.0923.

(1-(1*H*-indazol-1-yl)ethyl) benzothioate (62).



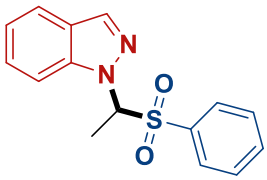
According to the **General Procedure 1**, the reaction afforded compound **62** in 32% yield (18 mg) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.02 (s, 1H), 7.86 – 7.81 (m, 2H), 7.66 (m, *J* = 11.7, 8.3 Hz, 2H), 7.51 – 7.45 (m, 1H), 7.40 – 7.32 (m, 3H), 7.14 – 7.07 (m, 1H), 6.78 (q, *J* = 7.0 Hz, 1H), 2.13 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 189.6, 138.1, 135.2, 134.1, 132.8, 127.7, 126.4, 125.8, 123.2, 120.4, 120.0, 109.0, 55.6, 21.3. **HRMS** (TOF-ESI$^+$): *m/z* [M+H]$^+$ calcd for $C_{16}H_{15}N_2OS^+$, 283.0900; found, 283.0897.

1-(1-(phenylselanyl)ethyl)-1*H*-indazole (63).



According to the **General Procedure 1**, the reaction afforded compound **63** in 78% yield (47 mg) as a colorless liquid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.95 (s, 1H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.21 (d, *J* = 6.7 Hz, 2H), 7.17 – 7.08 (m, 3H), 7.01 (m, 3H), 6.08 (q, *J* = 6.9 Hz, 1H), 2.11 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 138.1, 135.5, 133.1, 127.7, 127.5, 126.7, 125.0, 123.3, 120.0, 119.9, 108.8, 54.5, 21.1. **HRMS** (TOF-ESI$^+$): *m/z* [M+H]$^+$ calcd for $C_{15}H_{15}N_2Se^+$, 303.0395; found, 303.0400.

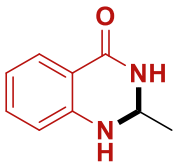
1-(1-(phenylsulfonyl)ethyl)-1*H*-indazole (64).



According to the **General Procedure 1**, the reaction afforded compound **64** in 28% yield (16 mg) as a colorless liquid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.91 (s, 1H), 7.60 (d, *J* = 8.0, 1.0 Hz, 1H), 7.23 – 6.94 (m, 8H), 5.94 (q, *J* = 6.9 Hz, 1H), 1.98 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz,

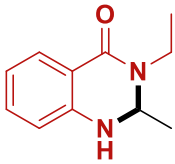
Chloroform-*d*) δ 138.04, 133.39, 132.83, 131.29, 127.69, 127.42, 125.04, 123.44, 120.02, 119.80, 108.88, 62.15, 20.09. **HRMS** (TOF-ESI$^+$): *m/z* [M+H]$^+$ calcd for $C_{15}H_{15}N_2O_2S^+$, 287.0849; found, 287.0852.

2-methyl-2,3-dihydroquinazolin-4(1*H*)-one (65).



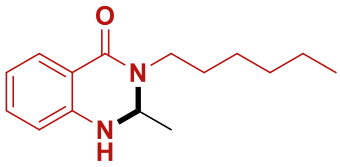
According to the **General Procedure 1**, the reaction afforded compound **65** in 77% yield (25 mg) as a white solid. Data consistent with those previously reported[2]. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.94 (s, 1H), 7.65 – 7.59 (m, 1H), 7.29 – 7.20 (m, 1H), 6.73 – 6.65 (m, 2H), 4.84 (q, *J* = 5.3, 4.8 Hz, 1H), 1.32 (d, *J* = 5.8 Hz, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 164.6, 149.2, 133.5, 127.9, 117.6, 115.6, 114.8, 61.3, 21.7.

3-ethyl-2-methyl-2,3-dihydroquinazolin-4(1H)-one (66).



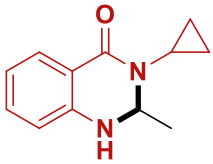
According to the **General Procedure 1**, the reaction afforded compound **66** in 76% yield (29 mg) as a colorless oil. Data consistent with those previously reported.[3] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 9.4 Hz, 1H), 7.17 (dd, *J* = 7.4, 6.3 Hz, 1H), 6.73 (t, *J* = 7.5 Hz, 1H), 6.56 (d, *J* = 9.1 Hz, 1H), 4.78 (q, *J* = 6.0 Hz, 1H), 4.03 (s, 1H), 3.90 (m, 1H), 3.01 (m, 1H), 1.34 (d, *J* = 6.0 Hz, 3H), 1.15 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 161.5, 144.6, 132.2, 127.3, 117.8, 115.2, 113.9, 64.2, 38.2, 19.6, 12.6.

3-hexyl-2-methyl-2,3-dihydroquinazolin-4(1*H*)-one (67).



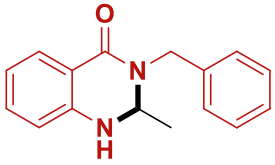
According to the **General Procedure 1**, the reaction afforded compound **67** in 57% yield (28 mg) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 7.8 Hz, 1H), 7.24 – 7.16 (m, 1H), 6.77 (t, *J* = 7.5 Hz, 1H), 6.56 (d, *J* = 7.0 Hz, 1H), 4.77 (q, *J* = 6.0 Hz, 1H), 4.02 – 3.87 (m, 1H), 2.84 (m, 1H), 1.56 (m, 2H), 1.35 (d, *J* = 6.0 Hz, 3H), 1.30 – 1.18 (m, 6H), 0.84 – 0.78 (m, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 161.4, 144.2, 132.1, 127.5, 118.1, 115.6, 113.8, 64.5, 43.4, 30.6, 27.3, 25.6, 21.6, 19.4, 13.0. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{15}H_{22}N_2ONa^+$, 269.1624; found, 269.1630.

3-cyclopropyl-2-methyl-2,3-dihydroquinazolin-4(1*H*)-one (68).



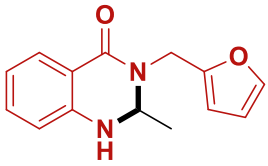
According to the **General Procedure 1**, the reaction afforded compound **68** in 49% yield (20 mg) as a white solid. Data consistent with those previously reported.[4] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 7.8, 1.6 Hz, 1H), 7.20 (dd, *J* = 15.3, 1.6 Hz, 1H), 6.75 (dd, *J* = 8.0, 7.0 Hz, 1H), 6.55 (d, *J* = 8.0 Hz, 1H), 4.80 (q, *J* = 6.0 Hz, 1H), 4.36 (s, 1H), 2.57 (m, J = 7.2, 3.9 Hz, 1H), 1.38 (d, *J* = 6.0 Hz, 3H), 1.10 – 0.99 (m, 1H), 0.83 – 0.77 (m, 1H), 0.73 – 0.63 (m, 1H), 0.58 – 0.47 (m, 1H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 163.6, 143.9, 132.5, 127.4, 117.9, 114.9, 113.9, 66.2, 26.3, 19.0, 8.8, 4.6.

3-benzyl-2-methyl-2,3-dihydroquinazolin-4(1*H*)-one (69).



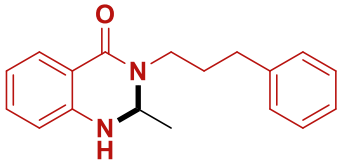
According to the **General Procedure 1**, the reaction afforded compound **69** in 57% yield (29 mg) as a white solid. Data consistent with those previously reported.[4] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 9.4 Hz, 1H), 7.32 – 7.17 (m, 7H), 6.85 – 6.77 (m, 1H), 6.56 (d, *J* = 7.0 Hz, 1H), 5.37 (d, *J* = 15.5 Hz, 1H), 4.77 – 4.66 (m, 1H), 4.03 (d, *J* = 15.4 Hz, 1H), 1.32 (d, *J* = 6.0 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 161.8, 144.3, 136.2, 132.4, 127.8, 127.7, 126.8, 126.5, 118.3, 115.2, 114.0, 63.7, 46.0, 18.9.

3-(furan-2-ylmethyl)-2-methyl-2,3-dihydroquinazolin-4(1*H*)-one (70).



According to the **General Procedure 1**, the reaction afforded compound **70** in 66% yield (32 mg) as a white solid. Data consistent with those previously reported.[4] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 7.8 Hz, 1H), 7.29 (s, 1H), 7.22 (d, *J* = 6.0 Hz, 1H), 6.78 (t, *J* = 7.6 Hz, 1H), 6.55 (d, *J* = 8.1 Hz, 1H), 6.32 – 6.22 (m, 2H), 5.07 (d, *J* = 15.7 Hz, 1H), 4.84 (m, 1H), 4.27 (d, *J* = 15.7 Hz, 1H), 1.32 (d, *J* = 6.0 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 161.6, 149.6, 144.3, 141.3, 132.4, 127.8, 118.2, 115.2, 114.0, 109.5, 107.6, 64.1, 39.1, 19.1.

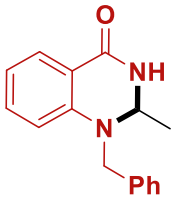
2-methyl-3-(3-phenylpropyl)-2,3-dihydroquinazolin-4(1*H*)-one (71).



According to the **General Procedure 1**, the reaction afforded compound **71** in 68% yield (38 mg) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 7.7, 1.6 Hz, 1H), 7.25 – 7.13 (m, 3H), 7.13 – 7.03 (m, 3H), 6.82 – 6.71 (m, 1H), 6.55 (d, *J* = 7.0 Hz, 1H), 4.70 (q, *J* = 6.0 Hz, 1H), 4.35 (s, 1H), 4.06 – 3.87 (m, 1H), 2.89 (m, 1H), 2.67 – 2.54 (m, 2H), 1.90 (m, 2H), 1.30 (d, *J* = 6.0 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 161.6, 144.3, 140.5, 132.2, 127.4, 127.4,

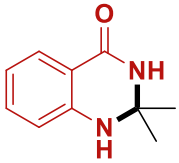
127.3, 124.9, 118.0, 115.4, 113.9, 64.7, 43.1, 32.1, 28.8, 19.4. **HRMS** (TOF-ESI$^+$): *m/z* [M+H]$^+$ calcd for $C_{18}H_{21}N_2O^+$, 281.1648; found, 281.1655.

1-benzyl-2-methyl-2,3-dihydroquinazolin-4(1*H*)-one (72).



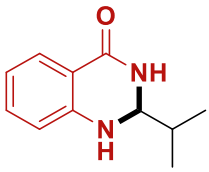
According to the **General Procedure 1**, the reaction afforded compound **72** in 45% yield (23 mg) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.89 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.29 (d, *J* = 4.4 Hz, 4H), 7.27 – 7.21 (m, 2H), 6.78 (t, *J* = 7.5 Hz, 1H), 6.60 (d, *J* = 8.4 Hz, 1H), 4.77 – 4.70 (m, 1H), 4.56 (d, *J* = 15.9 Hz, 1H), 4.22 (d, *J* = 15.9 Hz, 1H), 1.31 (d, *J* = 6.1 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 163.3, 145.7, 135.9, 133.1, 127.9, 127.7, 126.6, 126.1, 117.42, 115.53, 112.65, 64.82, 51.01, 18.67. **HRMS** (TOF-ESI$^+$): *m/z* [M+H]$^+$ calcd for $C_{16}H_{17}N_2O^+$, 253.1335; found, 253.1338.

2,2-dimethyl-2,3-dihydroquinazolin-4(1*H*)-one (73).



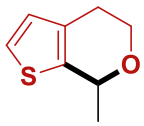
According to the **General Procedure 1**, the reaction afforded compound **73** in 80% yield (28 mg) as a white solid. Data consistent with those previously reported.[5] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 7.8 Hz, 1H), 7.23 (t, *J* = 7.7 Hz, 1H), 6.75 (t, *J* = 7.5 Hz, 1H), 6.55 (d, *J* = 8.1 Hz, 1H), 6.48 (s, 1H), 1.49 (s, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 163.3, 144.9, 132.9, 127.3, 117.8, 113.7, 113.7, 66.6, 28.7.

2-isopropyl-2,3-dihydroquinazolin-4(1*H*)-one (74).



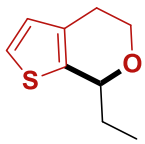
According to the **General Procedure 1**, the reaction afforded compound **74** in 63% yield (24 mg) as a white solid. Data consistent with those previously reported.[6] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 7.8 Hz, 1H), 7.28 – 7.14 (m, 1H), 6.76 (t, *J* = 7.5 Hz, 1H), 6.59 (d, *J* = 8.1 Hz, 1H), 6.37 (s, 1H), 4.63 (d, *J* = 4.8 Hz, 1H), 1.90 (m, 1H), 0.98 (m, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 164.4, 146.5, 132.9, 127.5, 118.0, 114.5, 113.5, 69.1, 31.8, 15.9, 15.9.

7-methyl-4,7-dihydro-5*H*-thieno[2,3-c]pyran (75).



According to the **General Procedure 1**, the reaction afforded compound **75** in 42% yield (13 mg) as a colorless liquid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.07 (d, *J* = 5.9 Hz, 1H), 6.74 (d, *J* = 5.0 Hz, 1H), 4.81 (d, *J* = 6.6 Hz, 1H), 4.14 (m, 1H), 3.71 (m, 1H), 2.86 – 2.77 (m, 1H), 2.55 – 2.48 (m, 1H), 1.45 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (100MHz, Chloroform-*d*) δ 137.6, 131.9, 126.1, 121.5, 70.3, 63.6, 25.2, 21.9. **HRMS** (TOF-ESI^{+}): *m/z* [M+H]$^{+}$ calcd for $C_8H_{11}OS^{+}$, 155.0525; found,155.0528.

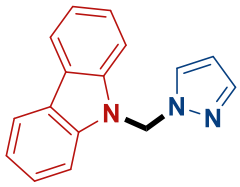
7-ethyl-4,7-dihydro-5*H*-thieno[2,3-c]pyran (76).



According to the **General Procedure 1**, the reaction afforded compound **76** in 56% yield (19 mg) as a colorless liquid. Data consistent with those previously reported.[7] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.07 (d, *J* = 5.0 Hz, 1H), 6.75 (d, *J* = 5.0 Hz, 1H), 4.64 (t, *J* = 7.0, 4.5 Hz, 1H), 4.14 (m, 1H), 3.68 (m, 1H), 2.80 (m, 1H), 2.57 – 2.45 (m, 1H), 1.84 (m, 1H), 1.71 (m, 1H), 0.98

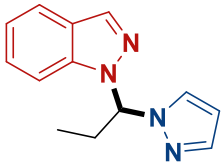
(t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 136.5, 132.4, 126.1, 121.5, 75.2, 63.4, 29.2, 25.3, 8.5.

9-((1H-pyrazol-1-yl)methyl)-9*H*-carbazole (77).



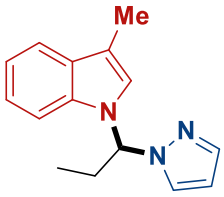
According to the **general procedure 1**, the reaction afforded compound **77** in 67% yield (33 mg) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 7.7 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.47 – 7.40 (m, 3H), 7.33 (d, *J* = 2.4 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 2H), 6.47 (s, 2H), 6.12 (d, *J* = 2.2 Hz, 1H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 138.8, 138.8, 127.3, 125.3, 122.6, 119.5, 119.4, 107.9, 105.9, 57.1. **HRMS** (TOF-ESI^{+}): *m/z* $[M+H]^{+}$ calcd for $C_{16}H_{14}N_3^{+}$, 248.1182; found, 248.1179.

1-(1-(1*H*-pyrazol-1-yl)propyl)-1*H*-indazole (78).



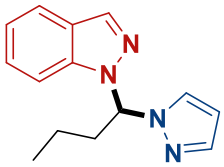
According to the **general procedure 1**, the reaction afforded compound **78** in 70% yield (32 mg) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.99 (s, 1H), 7.61 (m, 7.52 (s, 1H), 7.39 (s, 1H), 7.35 – 7.28 (m, 1H), 7.13 – 7.05 (m, 1H), 6.62 (t, *J* = 7.6 Hz, 1H), 6.15 (t, *J* = 2.1 Hz, 1H), 2.70 (m, 7.0 Hz, 2H), 0.88 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 139.8, 139.1, 134.8, 127.1, 127.0, 124.5, 121.5, 121.1, 109.6, 106.7, 74.6, 27.2, 10.1. **HRMS** (TOF-ESI^{+}): *m/z* $[M+Na]^{+}$ calcd for $C_{13}H_{14}N_4Na^{+}$, 249.1111; found, 249.1109.

1-(1-(1*H*-pyrazol-1-yl)propyl)-3-methyl-1*H*-indole (79).



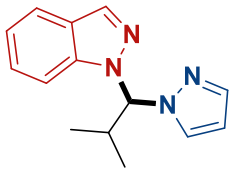
According to the **general procedure 1**, the reaction afforded compound **79** in 42% yield (20 mg) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.49 – 7.43 (m, 2H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.26 (d, *J* = 3.1 Hz, 1H), 7.17 – 7.11 (m, 2H), 7.08 – 7.03 (m, 1H), 6.33 (t, *J* = 7.5 Hz, 1H), 6.14 – 6.06 (m, 1H), 2.62 (m, 1H), 2.51 – 2.40 (m, 1H), 2.25 (s, 3H), 0.91 (d, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 138.5, 135.4, 128.2, 126.4, 121.2, 120.2, 118.7, 118.2, 111.7, 108.2, 104.9, 71.0, 26.6, 9.2, 8.7. **HRMS** (TOF-ESI^{+}): *m/z* [M+Na]$^{+}$ calcd for $C_{15}H_{17}N_3Na^{+}$, 262.1315; found, 262.1312.

1-(1-(1*H*-pyrazol-1-yl)butyl)-1*H*-indazole (80).



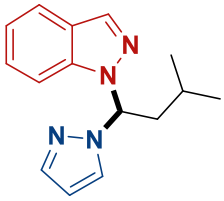
According to the **general procedure 1**, the reaction afforded compound **80** in 33% yield (16 mg) as a colorless liquid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.99 (s, 1H), 7.61 (m, 2H), 7.53 (d, *J* = 2.5 Hz, 1H), 7.39 (d, *J* = 1.8 Hz, 1H), 7.36 – 7.31 (m, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.72 (dd, *J* = 8.3, 6.9 Hz, 1H), 6.15 (t, *J* = 2.2 Hz, 1H), 2.75 (m, 1H), 2.58 (m, 1H), 1.27 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 139.7, 139.0, 134.7, 127.1, 127.0, 124.5, 121.5, 121.1, 109.6, 106.7, 73.0, 35.7, 18.8, 13.5. **HRMS** (TOF-ESI^{+}): *m/z* [M+H]$^{+}$ calcd for $C_{14}H_{17}N_4^{+}$, 241.1448; found, 241.1448.

1-(2-methyl-1-(1*H*-pyrazol-1-yl) propyl)-1*H*-indazole (81).



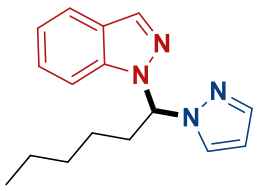
According to the **general procedure 1**, the reaction afforded compound **81** in 56% yield (27 mg) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.00 (s, 1H), 7.69 – 7.59 (m, 3H), 7.33 (m, 2H), 7.11 – 7.05 (m, 1H), 6.26 (d, *J* = 10.9 Hz, 1H), 6.17 (t, *J* = 2.2 Hz, 1H), 3.31 (m, 1H), 0.86 (d, *J* = 6.8 Hz, 3H), 0.81 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 139.0, 137.7, 133.8, 126.3, 126.0, 123.2, 120.4, 120.0, 108.4, 105.8, 78.0, 31.8, 18.0, 17.8. **HRMS** (TOF-ESI$^+$): *m/z* [M+H]$^+$ calcd for $C_{14}H_{17}N_4^+$, 241.1448; found, 241.1450.

1-(3-methyl-1-(1*H*-pyrazol-1-yl)butyl)-1*H*-indazole (82).



According to the **general procedure 1**, the reaction afforded compound **82** in 30% yield (15 mg) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.99 (s, 1H), 7.63 (dd, J = 8.9, 1.0 Hz, 2H), 7.55 (d, J = 2.5 Hz, 1H), 7.39 (d, J = 1.8 Hz, 1H), 7.37 – 7.32 (m, 1H), 7.13 – 7.07 (m, 1H), 6.82 (dd, J = 8.5, 6.9 Hz, 1H), 6.15 (t, J = 2.1 Hz, 1H), 2.77 – 2.67 (m, 1H), 2.50 – 2.41 (m, 1H), 1.43 – 1.37 (m, 1H), 0.90-0.94 (d, J = 10.6, 6.7 Hz, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 138.6, 137.9, 133.7, 126.1, 126.0, 123.4, 120.5, 120.1, 108.5, 105.6, 70.5, 41.2, 23.5, 21.5, 21.0. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{15}H_{18}N_4Na^+$, 277.1424; found, 277.1428.

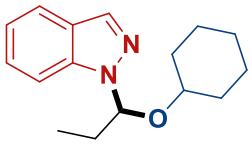
1-(1-(1*H*-pyrazol-1-yl)hexyl)-1*H*-indazole (83).



According to the **general procedure 1**, the reaction afforded compound **83** in 37% yield (20 mg) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.99 (s, 1H), 7.61 (m, 2H), 7.53 (d, *J* = 2.5 Hz, 1H), 7.39 (d, *J* = 1.8 Hz, 1H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.15 – 7.05 (m, 1H), 6.70 (t, *J* = 8.2, 7.0 Hz, 1H), 6.15 (t, *J* = 2.1 Hz, 1H), 2.83 – 2.54 (m, 2H), 1.27 – 1.21 (m, 6H), 0.77 (t, *J* = 7.1

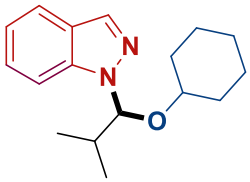
Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 138.7, 138.0, 133.7, 126.0, 125.9, 123.4, 120.5, 120.0, 108.5, 105.6, 72.2, 32.6, 30.1, 24.1, 21.3, 12.9. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{16}H_{20}N_4Na^+$, 291.1580; found, 291.1576.

1-(1-(cyclohexyloxy)propyl)-1H-indazole (84).



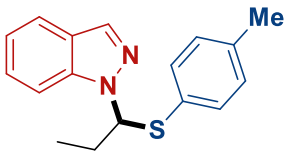
According to the **general procedure 2**, the reaction afforded compound **84** in 38% yield (20 mg) as a colorless liquid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.90 (s, 1H), 7.70 – 7.65 (m, 2H), 7.31 – 7.26 (m, 1H), 7.13 – 7.06 (m, 1H), 5.67 (t, *J* = 6.8 Hz, 1H), 3.18 (m, 1H), 2.07 (m, 2H), 1.96 – 1.88 (m, 1H), 1.65 (m, 1H), 1.50 (m, 1H), 1.40 – 1.28 (m, 4H), 1.12 (m, 2H), 0.99 (m, 1H), 0.93 – 0.86 (m, 1H), 0.76 (d, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 138.44, 132.96, 126.06, 125.12, 121.06, 120.89, 111.21, 90.10, 75.06, 32.84, 31.10, 28.34, 25.61, 23.96, 23.84, 9.62. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{16}H_{22}N_2ONa^+$, 281.1624; found, 281.1619.

1-(1-(cyclohexyloxy)-2-methylpropyl)-1*H*-indazole (85).



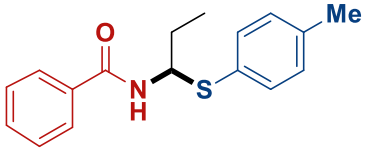
According to the **general procedure 2**, the reaction afforded compound **85** in 31% yield (17 mg) as a colorless liquid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.66 (m, 2H), 7.26 (t, *J* = 7.7 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 5.29 (d, *J* = 9.1 Hz, 1H), 3.17 (m, J = 8.7, 3.8 Hz, 1H), 2.45 (m, 1H), 1.90 – 1.83 (m, 1H), 1.81 – 1.72 (m, 2H), 1.65 (m, 1H), 1.55 – 1.45 (m, 1H), 1.34 (m, 3H), 1.15 (m, 2H), 1.09 (d, *J* = 6.6 Hz, 3H), 0.45 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 137.54, 131.67, 124.92, 124.02, 119.94, 119.80, 110.36, 93.24, 74.04, 32.31, 31.73, 29.78, 24.60, 22.75, 22.62, 18.42, 16.85. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{17}H_{24}N_2ONa^+$, 295.1781; found, 295.1780.

1-(1-(*p*-tolylthio)propyl)-1*H*-indazole (86).



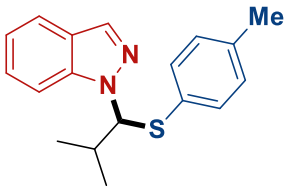
According to the **general procedure 1**, the reaction afforded compound **86** in 64% yield (36 mg) as a colorless liquid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.92 (s, 1H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.25 – 7.16 (m, 2H), 7.07 – 6.99 (m, 1H), 6.91 (d, *J* = 8.1 Hz, 2H), 6.81 (d, *J* = 7.9 Hz, 2H), 5.59 (dd, *J* = 9.3, 5.7 Hz, 1H), 2.44 (m, 1H), 2.28 (m, 1H), 2.15 (s, 3H), 0.85 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 138.5, 137.5, 133.4, 132.8, 128.5, 127.8, 125.0, 123.4, 120.0, 119.7, 108.9, 68.8, 27.2, 20.1, 10.5. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{17}H_{18}N_2SNa^+$, 305.1083; found, 305.1078.

***N*-(1-(*p*-tolylthio)propyl)benzamide (87).**



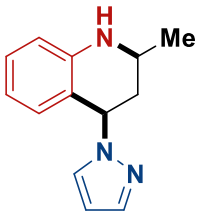
According to the **general procedure 1**, the reaction afforded compound **87** in 48% yield (27 mg) as a colorless liquid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 7.0 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.36 – 7.27 (m, 4H), 7.01 (d, *J* = 7.8 Hz, 2H), 6.11 (d, *J* = 9.6 Hz, 1H), 5.48 – 5.39 (m, 1H), 2.22 (s, 3H), 1.80 (m, 2H), 1.03 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 165.48, 137.05, 133.15, 132.44, 130.61, 128.79, 127.63, 127.56, 125.78, 57.84, 28.24, 20.10, 9.88. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{17}H_{19}NOSNa^+$, 308.1080; found, 308.1076.

1-(2-methyl-1-(*p*-tolylthio)propyl)-1*H*-indazole (88).



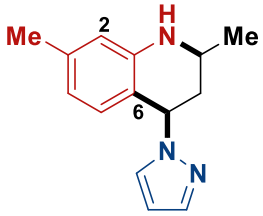
According to the **general procedure 1**, the reaction afforded compound **88** in 58% yield (34 mg) as a colorless liquid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.90 (s, 1H), 7.59 (d, *J* = 8.2 Hz, 1H), 7.22 – 7.13 (m, 2H), 7.06 – 6.99 (m, 1H), 6.89 (d, *J* = 8.5 Hz, 2H), 6.77 (d, *J* = 7.8 Hz, 2H), 5.35 (d, *J* = 9.8 Hz, 1H), 2.68 (m, 1H), 2.12 (s, 3H), 1.26 (d, *J* = 7.8 Hz, 3H), 0.68 (d, *J* = 6.7, 1.2 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 138.5, 137.2, 133.0, 132.5, 128.4, 128.3, 124.9, 123.2, 120.0, 119.6, 109.1, 74.7, 32.9, 20.1, 20.0, 18.9. **HRMS** (TOF-ESI$^+$): *m/z* [M+H]$^+$ calcd for $C_{18}H_{21}N_2S^+$, 297.1420; found, 297.1410.

2-methyl-4-(1*H*-pyrazol-1-yl)-1,2,3,4-tetrahydroquinoline (89).



According to the **general procedure 3**, the reaction afforded compound **89** in 71% yield (30 mg) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 1.8 Hz, 1H), 7.12 – 6.92 (m, 3H), 6.67 – 6.49 (m, 2H), 6.07 (t, *J* = 2.1 Hz, 1H), 5.48 – 5.33 (t, 1H), 3.90 (s, 1H), 3.09 (m, 1H), 2.37 (m, 1H), 1.78 (m, 1H), 1.12 (d, *J* = 6.2 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 144.4, 138.5, 130.2, 128.7, 128.1, 116.3, 115.1, 113.6, 103.4, 56.7, 41.1, 35.7, 20.8. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{13}H_{15}N_3Na^+$, 236.1158; found, 236.1154.

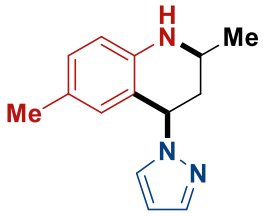
2,7-dimethyl-4-(1*H*-pyrazol-1-yl)-1,2,3,4-tetrahydroquinoline (90).



According to the **general procedure 3**, the reaction afforded compound **90** in 29% yield (13 mg) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.50 (s, 1H), 7.01 (d, *J* = 2.4 Hz, 1H), 6.89 (d, *J* = 7.7 Hz, 1H), 6.49 – 6.38 (m, 1H), 6.36 (s, 1H), 6.07 (d, *J* = 2.1 Hz, 1H), 5.41 – 5.33 (m, 1H), 3.07 (m, 1H), 2.35 (m, 1H), 2.19 (s, 3H), 1.76 (m, 1H), 1.11 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR**

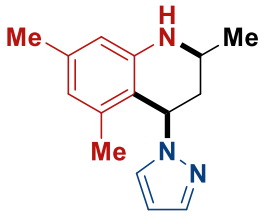
(100 MHz, Chloroform-*d*) δ 144.2, 138.7, 138.5, 130.0, 128.0, 117.6, 114.0, 112.4, 103.3, 56.5, 41.1, 35.9, 20.8, 20.3. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{14}H_{17}N_3Na^+$, 250.1315; found, 250.1314.

2,6-dimethyl-4-(1*H*-pyrazol-1-yl)-1,2,3,4-tetrahydroquinoline (91).



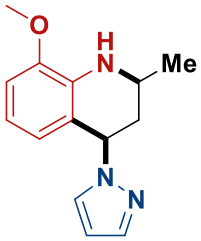
According to the **general procedure 3**, the reaction afforded compound **91** in 70% yield (32 mg) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 1.8 Hz, 1H), 7.00 (d, *J* = 2.3 Hz, 1H), 6.88 (m, *J* = 8.2, 2.1 Hz, 1H), 6.80 (s, 1H), 6.45 (d, *J* = 8.2 Hz, 1H), 6.07 (t, *J* = 2.1 Hz, 1H), 5.43 – 5.31 (m, 1H), 3.86 – 3.43 (m, 1H), 3.07 (m, 1H), 2.31 (m, 1H), 2.11 (s, 3H), 1.76 (m, 4.3 Hz, 1H), 1.09 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 142.1, 138.4, 130.3, 129.5, 128.1, 125.6, 115.1, 113.8, 103.3, 56.8, 41.2, 36.0, 20.8, 19.3. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{14}H_{17}N_3Na^+$, 250.1315; found, 250.1314.

2,5,7-trimethyl-4-(1*H*-pyrazol-1-yl)-1,2,3,4-tetrahydroquinoline (92).



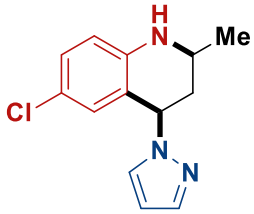
According to the **general procedure 3**, the reaction afforded compound **92** in 52% yield (25 mg) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 1.8 Hz, 1H), 6.97 (d, *J* = 2.3 Hz, 1H), 6.31 (s, 1H), 6.23 (s, 1H), 6.06 (t, *J* = 2.1 Hz, 1H), 5.48 (t, *J* = 4.2, 2.3 Hz, 1H), 3.81 (s, 1H), 3.02 (m, 1H), 2.32 (m, 1H), 2.16 (s, 3H), 1.86 (s, 3H), 1.77 – 1.66 (m, 1H), 1.10 (d, *J* = 6.2 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 144.5, 138.4, 138.3, 137.9, 127.7, 119.6, 112.0, 111.0, 103.3, 54.3, 40.6, 36.4, 20.8, 20.2, 17.3. **HRMS** (TOF-ESI$^+$): *m/z* [M+Na]$^+$ calcd for $C_{15}H_{19}N_3Na^+$, 264.1471; found, 264.1477.

8-methoxy-2-methyl-4-(1*H*-pyrazol-1-yl)-1,2,3,4-tetrahydroquinoline (93).



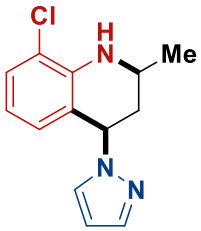
According to the **general procedure 3**, the reaction afforded compound **93** in 59% yield (29 mg) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 1.7 Hz, 1H), 6.99 (d, *J* = 2.3 Hz, 1H), 6.67 (t, *J* = 7.2 Hz, 2H), 6.57 (t, *J* = 7.8 Hz, 1H), 6.07 (t, *J* = 2.1 Hz, 1H), 5.49 – 5.40 (m, 1H), 4.35 (s, 1H), 3.81 (s, 3H), 3.09 (m, 1H), 2.37 (m, 1H), 1.79 (m, 1H), 1.17 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 145.2, 138.4, 134.7, 128.1, 121.8, 115.2, 114.9, 108.2, 103.3, 56.6, 54.4, 40.7, 35.8, 20.7. **HRMS** (TOF-ESI^{+}): *m/z* [M+H]$^{+}$ calcd for $C_{14}H_{18}N_3O^{+}$, 244.1444; found, 244.1444.

6-chloro-2-methyl-4-(1*H*-pyrazol-1-yl)-1,2,3,4-tetrahydroquinoline (94).



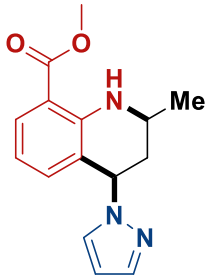
According to the **general procedure 3**, the reaction afforded compound **94** in 50% yield (25 mg) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 1.8 Hz, 1H), 7.06 – 6.99 (m, 2H), 6.97 (d, *J* = 2.5 Hz, 1H), 6.48 (d, *J* = 8.6 Hz, 1H), 6.12 (t, *J* = 2.1 Hz, 1H), 5.41 – 5.33 (m, 1H), 3.13 (m, 1H), 2.34 (m, 1H), 1.75 (m, 1H), 1.13 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 142.8, 138.7, 129.4, 128.7, 128.0, 120.7, 116.4, 114.9, 103.8, 56.3, 41.3, 35.4, 20.6. **HRMS** (TOF-ESI^{+}): *m/z* [M+H] $^{+}$ calcd for $C_{13}H_{15}ClN_3^{+}$, 248.0949; found, 248.0953.

8-chloro-2-methyl-4-(1*H*-pyrazol-1-yl)-1,2,3,4-tetrahydroquinoline (95).



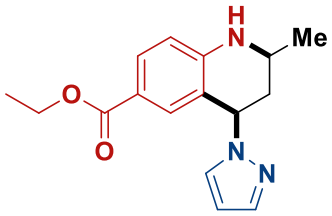
According to the **general procedure 3**, the reaction afforded compound **95** in 58% yield (29 mg) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 1.8 Hz, 1H), 7.19 (m, *J* = 7.9, 1.5 Hz, 2H), 7.00 – 6.91 (m, 2H), 6.54 (t, *J* = 7.7 Hz, 1H), 6.10 (t, *J* = 2.1 Hz, 1H), 5.48 – 5.40 (m, 1H), 4.44 (s, 1H), 3.21 – 3.07 (m, 1H), 2.42 (m, 1H), 1.78 (m, 1H), 1.21 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 140.4, 138.6, 128.6, 128.6, 128.0, 117.4, 116.4, 115.8, 103.7, 56.6, 41.2, 35.2, 20.63. **HRMS** (TOF-ESI^{+}): *m/z* [M+H] $^{+}$ calcd for $C_{13}H_{15}ClN_3^{+}$, 248.0949; found, 248.0953.

methyl 2-methyl-4-(1*H*-pyrazol-1-yl)-1,2,3,4-tetrahydroquinoline-8-carboxylate (96).



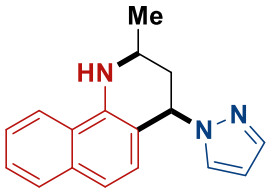
According to the **general procedure 3**, the reaction afforded compound **96** in 52% yield (28 mg) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 8.0, 1.7 Hz, 1H), 7.51 (d, *J* = 1.6 Hz, 1H), 7.16 (d, *J* = 7.3, 1.6 Hz, 1H), 6.97 (d, *J* = 2.3 Hz, 1H), 6.49 (t, *J* = 7.7 Hz, 1H), 6.09 (t, *J* = 2.1 Hz, 1H), 5.43 (t, *J* = 3.4 Hz, 1H), 3.80 (s, 3H), 3.13 (m, 1H), 2.43 (m, 1H), 1.72 (m, 1H), 1.21 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 167.8, 147.1, 138.7, 135.4, 131.6, 127.9, 116.0, 113.2, 108.5, 103.7, 57.0, 50.6, 40.6, 34.2, 20.6. **HRMS** (TOF-ESI^{+}): *m/z* [M+Na]$^{+}$ calcd for $C_{15}H_{17}N_3O_2Na^{+}$, 294.1213; found, 294.1208.

ethyl 2-methyl-4-(1*H*-pyrazol-1-yl)-1,2,3,4-tetrahydroquinoline-6-carboxylate (97).



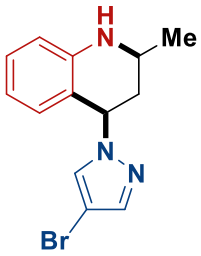
According to the **general procedure 3**, the reaction afforded compound **97** in 72% yield (41 mg) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 6.1, 2.0 Hz, 2H), 7.51 (d, *J* = 1.5 Hz, 1H), 6.98 (d, *J* = 2.4 Hz, 1H), 6.49 (d, *J* = 9.1 Hz, 1H), 6.09 (t, *J* = 2.1 Hz, 1H), 5.43 (t, *J* = 3.3 Hz, 1H), 4.42 (s, 1H), 4.29 – 4.10 (m, 2H), 3.15 (m, 1H), 2.43 (m, 1H), 1.74 (m, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.15 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 165.5, 147.9, 138.8, 132.4, 130.6, 128.0, 117.6, 113.9, 112.6, 103.7, 59.3, 56.4, 41.2, 35.1, 20.5, 13.4. **HRMS** (TOF-ESI^{+}): *m/z* [M+Na]$^{+}$ calcd for $C_{16}H_{19}N_3O_2Na^{+}$, 308.1369; found, 308.1372.

2-methyl-4-(1*H*-pyrazol-1-yl)-1,2,3,4-tetrahydrobenzo[*h*]quinoline (98).



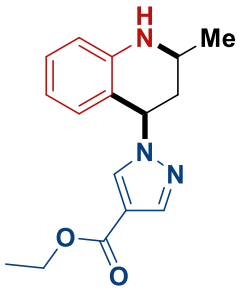
According to the **general procedure 3**, the reaction afforded compound **98** in 66% yield (35 mg) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.78 – 7.67 (m, 2H), 7.53 (d, *J* = 1.8 Hz, 1H), 7.46 – 7.37 (m, 2H), 7.15 – 7.06 (m, 2H), 7.00 (d, *J* = 2.3 Hz, 1H), 6.07 (t, *J* = 2.1 Hz, 1H), 5.56 (dd, *J* = 4.4, 2.3 Hz, 1H), 3.24 (m, 1H), 2.46 (m, 1H), 1.88 (m, 1H), 1.29 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 139.8, 138.6, 133.3, 128.3, 127.7, 127.5, 125.5, 124.2, 121.7, 118.9, 116.4, 108.9, 103.4, 57.2, 41.5, 35.6, 20.8. **HRMS** (TOF-ESI^{+}): *m/z* [M+H] $^{+}$calcd for $C_{17}H_{18}N_3^{+}$, 264.1495; found, 264.1493.

4-(4-bromo-1*H*-pyrazol-1-yl)-2-methyl-1,2,3,4-tetrahydroquinoline (99).



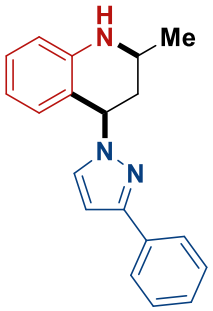
According to the **general procedure 3**, the reaction afforded compound **99** in 59% yield (34 mg) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.44 (s, 1H), 7.11 – 7.05 (m, 1H), 6.98 (d, *J* = 7.0 Hz, 2H), 6.61 (dd, *J* = 8.0, 6.9 Hz, 1H), 6.53 (d, *J* = 8.1 Hz, 1H), 5.35 (t, *J* = 3.4 Hz, 1H), 3.90 (s, 1H), 3.08 (m, 1H), 2.38 – 2.27 (m, 1H), 1.81 – 1.69 (m, 1H), 1.12 (d, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 144.4, 139.1, 130.2, 129.1, 128.3, 116. 5, 114.17, 113.7, 91.0, 57.7, 41.0, 35.4, 20.7. **HRMS** (TOF-ESI^{+}): *m/z* [M+H]$^{+}$ calcd for $C_{13}H_{15}BrN_3^{+}$, 292.0444; found, 292.0446.

ethyl 1-(2-methyl-1,2,3,4-tetrahydroquinolin-4-yl)-1*H*-pyrazole-4-carboxylate (100).



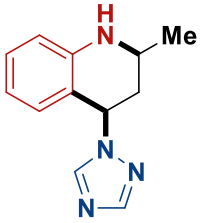
According to the **general procedure 3**, the reaction afforded compound **100** in 73% yield (42 mg) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.90 (s, 1H), 7.49 (s, 1H), 7.10 (t, *J* = 7.7 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.63 (t, *J* = 7.6 Hz, 1H), 6.56 (d, *J* = 8.2 Hz, 1H), 5.43 – 5.30 (m, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.06 (m, 1H), 2.37 (m, 1H), 1.80 (m, 1H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.16 – 1.04 (d, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 162.2, 144.3, 140.4, 131.7, 130.2, 129.2, 116.7, 113.9, 113.8, 113.1, 59.1, 57.5, 40.8, 35.1, 20.6, 13.4. **HRMS** (TOF-ESI^{+}): *m/z* [M+Na]$^{+}$ calcd for $C_{16}H_{19}N_3O_2Na^{+}$, 308.1369; found, 308.1372.

2-methyl-4-(3-phenyl-1*H*-pyrazol-1-yl)-1,2,3,4-tetrahydroquinoline (101).



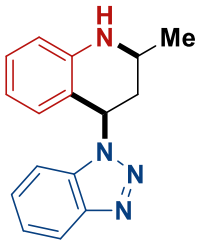
According to the **general procedure 3**, the reaction afforded compound **101** in 72% yield (42 mg) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 7.0 Hz, 2H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.08 (dd, *J* = 12.9, 6.6 Hz, 2H), 6.97 (d, *J* = 2.4 Hz, 1H), 6.62 (t, *J* = 7.4 Hz, 1H), 6.55 (d, *J* = 8.5 Hz, 1H), 6.37 (d, *J* = 2.4 Hz, 1H), 5.51 – 5.45 (m, 1H), 4.00 (s, 1H), 3.13 (m, 1H), 2.46 (m, 1H), 1.85 – 1.74 (m, 1H), 1.13 (d, *J* = 6.2 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 150.6, 144.4, 132.7, 130.3, 129.5, 128.8, 127.6, 126.5, 124.6, 116.4, 114.9, 113.6, 100.7, 57.0, 41.1, 35.7, 20.7. **HRMS** (TOF-ESI^{+}): *m/z* $[M+H]^{+}$ calcd for $C_{19}H_{20}N_3^{+}$, 290.1652; found, 290.1655.

2-methyl-4-(1*H*-1,2,4-triazol-1-yl)-1,2,3,4-tetrahydroquinoline (102).



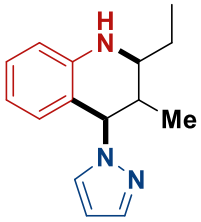
According to the **general procedure 3**, the reaction afforded compound **102** in 63% yield (27 mg) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.97 (s, 1H), 7.75 (s, 1H), 7.11 (t, *J* = 7.7 Hz, 1H), 7.00 (d, *J* = 7.7 Hz, 1H), 6.64 (t, *J* = 7.5 Hz, 1H), 6.56 (d, *J* = 8.2 Hz, 1H), 6.05 (s, 1H), 5.47 – 5.36 (m, 1H), 3.03 (m, 1H), 2.39 (m, 1H), 1.83 (m, 1H), 1.15 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 150.0, 144.3, 129.9, 129.6, 128.5, 116.7, 114.1, 112.6, 56.1, 40.7, 34.6, 20.5. **HRMS** (TOF-ESI^{+}): *m/z* $[M+Na]^{+}$ calcd for $C_{12}H_{14}N_4Na^{+}$, 237.1111; found, 237.1108.

4-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2-methyl-1,2,3,4-tetrahydroquinoline (103).



According to the **general procedure 3**, the reaction afforded compound **103** in 65% yield (34 mg) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 7.1 Hz, 1H), 7.25 – 7.14 (m, 2H), 7.14 – 7.07 (m, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 6.63 (d, *J* = 8.2 Hz, 1H), 6.56 (t, *J* = 6.9 Hz, 1H), 6.15 (dd, *J* = 4.9, 3.1 Hz, 1H), 4.12 (s, 1H), 3.39 – 3.27 (m, 1H), 2.33 (m, 1H), 2.05 (m, 1H), 1.13 (d, *J* = 6.2 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 145.2, 144.6, 132.0, 129.8, 129.1, 126.0, 122.6, 118.9, 116.7, 113.8, 113.7, 109.8, 55.4, 42.1, 36.8, 20.7. **HRMS** (TOF-ESI^{+}): *m/z* [M+Na]$^{+}$ calcd for $C_{16}H_{16}N_4Na^{+}$, 287.1267; found, 287.1273.

2-ethyl-3-methyl-4-(1*H*-pyrazol-1-yl)-1,2,3,4-tetrahydroquinoline (104).

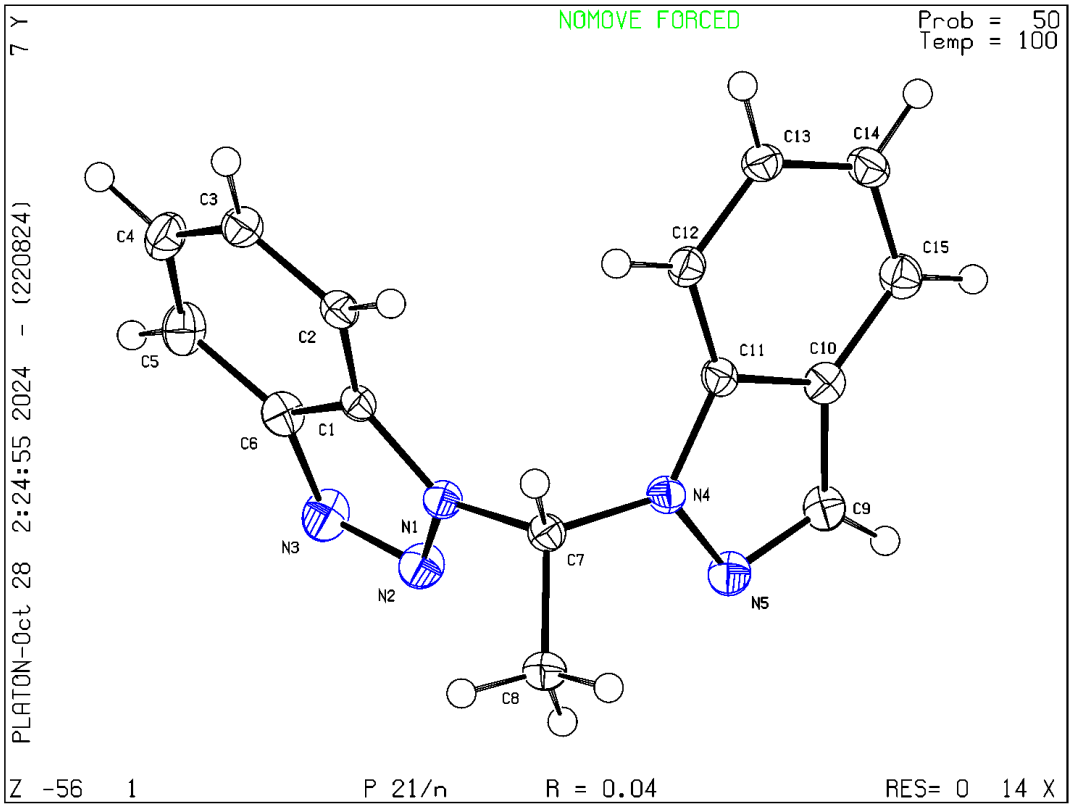


According to the general procedure 3, the reaction afforded compound 104 in 26% yield (13 mg, dr = 7:3) as a white solid. 1H NMR (400 MHz, Chloroform-d) δ 7.42 (d, J = 1.1 Hz, 1H), 7.10 – 6.96 (m, 2H), 6.91 (dd, J = 5.8, 1.9 Hz, 1H), 6.57 – 6.50 (m, 2H), 6.13 (t, J = 2.1 Hz, 1H), 5.30 (d, J = 4.5 Hz, 1H), 3.97 (s, 1H), 3.15 (m, 1H), 2.45 (m, 1H), 2.07 – 1.94 (m, 1H), 1.65 – 1.58 (m, 1H), 1.42 (m, 2H), 0.92 (t, 3H), 0.83 (m, 3H), 0.75 (d, J = 6.9 Hz, 3H). 13C NMR (100 MHz, Chloroform-d) δ 143.52, 138.44, 137.43, 130.97, 129.11, 128.56, 128.29, 128.07, 116.98, 116.26, 116.00, 113.25, 113.22, 103.80, 103.20, 63.40, 61.90, 51.47, 49.79, 34.99, 33.90, 24.81, 24.06, 12.79, 9.91, 9.28, 7.52. HRMS (TOF-ESI+): m/z [M+H]+ calcd for C15H20N3+, 242.1652; found, 242.1652.

3 X-ray Structure and Data

X-ray Structure and Data of 28

Crystallographic data for compound **28** (CCDC-2557203) has been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC (Email: deposit@ccdc.cam.ac.uk).



The ellipsoid contour percent probability level is 50% in the caption of the thermal ellipsoid plot.

Fig. S2. X-ray crystal structure of **28**

Table S9. Crystal data and structure refinement for **28**

Datablock: 1

Bond precision: C-C = 0.0020 A Wavelength=0.71073

Cell: a=9.5533(4) b=14.2913(6) c=10.2240(4)
alpha=90 beta=112.457(2) gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	1290.02(9)	1290.02(9)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C15 H13 N5	C15 H13 N5
Sum formula	C15 H13 N5	C15 H13 N5
Mr	263.30	263.30
Dx,g cm-3	1.356	1.356
Z	4	4
Mu (mm-1)	0.086	0.086
F000	552.0	552.0
F000'	552.16	
h,k,lmax	12,19,13	12,19,13
Nref	3205	3197
Tmin,Tmax	0.981,0.984	0.704,0.746
Tmin'	0.981	

Correction method= # Reported T Limits: Tmin=0.704 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.998 Theta(max)= 28.323

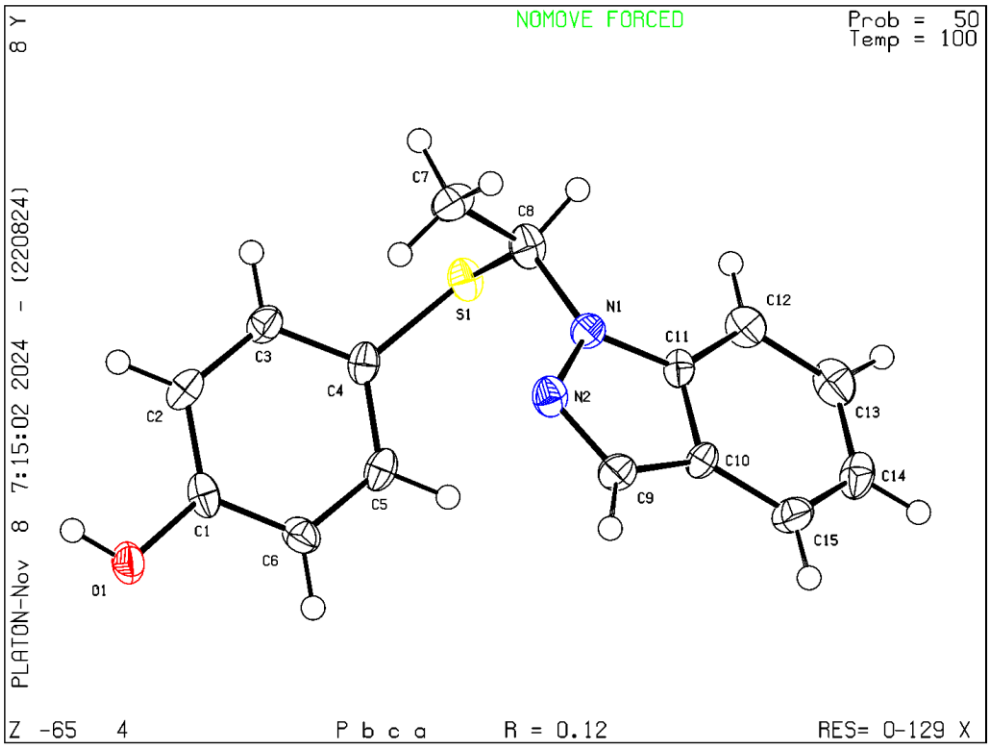
R(reflections)= 0.0430(2629) wR2(reflections)= 0.1032(3197)

S = 1.045 Npar= 182

Add compound **28** (25mg) to a 10mL sample bottle, add DCM (1mL), n-hexane (1mL) and toluene (0.25 mL), seal the bottle with a parafilm, poke 15 small holes on the parafilm, Place the sample bottle in a safe place to allow it to volatilize and separate out the single crystal. Take out the single crystal and send it to the relevant test center for single crystal diffraction test to obtain relevant data. Instrument model: Bruker Apex 2. At the temperature of 100 K, the Mo-Kα radiation monochromated by the graphite monochromator (λ = 0.71073 Å), use BRUKER SAINT restores the data and performs absorption correction on the diffraction data through the SADABS program. Using SHELXTL software, the crystal structure was solved by the direct method. The coordinates of all non-hydrogen atoms and their anisotropic thermal parameters are corrected by the full matrix least square method.

X-ray Structure and Data of 51

Crystallographic data for compound **51** (CCDC-2559619) has been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC (Email: deposit@ccdc.cam.ac.uk).



The ellipsoid contour percent probability level is 50% in the caption of the thermal ellipsoid plot.

Fig. S3. X-ray crystal structure of **51**

Table S10. Crystal data and structure refinement for **51**

Datablock: 4

Bond precision: C-C = 0.0081 A Wavelength=0.71073

Cell: a=17.629(2) b=7.8704(11) c=18.671(2)
alpha=90 beta=90 gamma=90

Temperature: 100 K

	Calculated	Reported
Volume	2590.6(5)	2590.6(6)
Space group	P b c a	P b c a
Hall group	-P 2ac 2ab	-P 2ac 2ab
Moiety formula	C15 H14 N2 O S	C15 H14 N2 O S
Sum formula	C15 H14 N2 O S	C15 H14 N2 O S
Mr	270.34	270.34
Dx,g cm-3	1.386	1.386
Z	8	8
Mu (mm-1)	0.242	0.242
F000	1136.0	1136.0
F000'	1137.38	
h,k,lmax	20,9,22	20,9,22
Nref	2285	2283
Tmin,Tmax	0.966,0.990	0.532,0.746
Tmin'	0.962	

Correction method= # Reported T Limits: Tmin=0.532 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.999 Theta(max)= 25.020

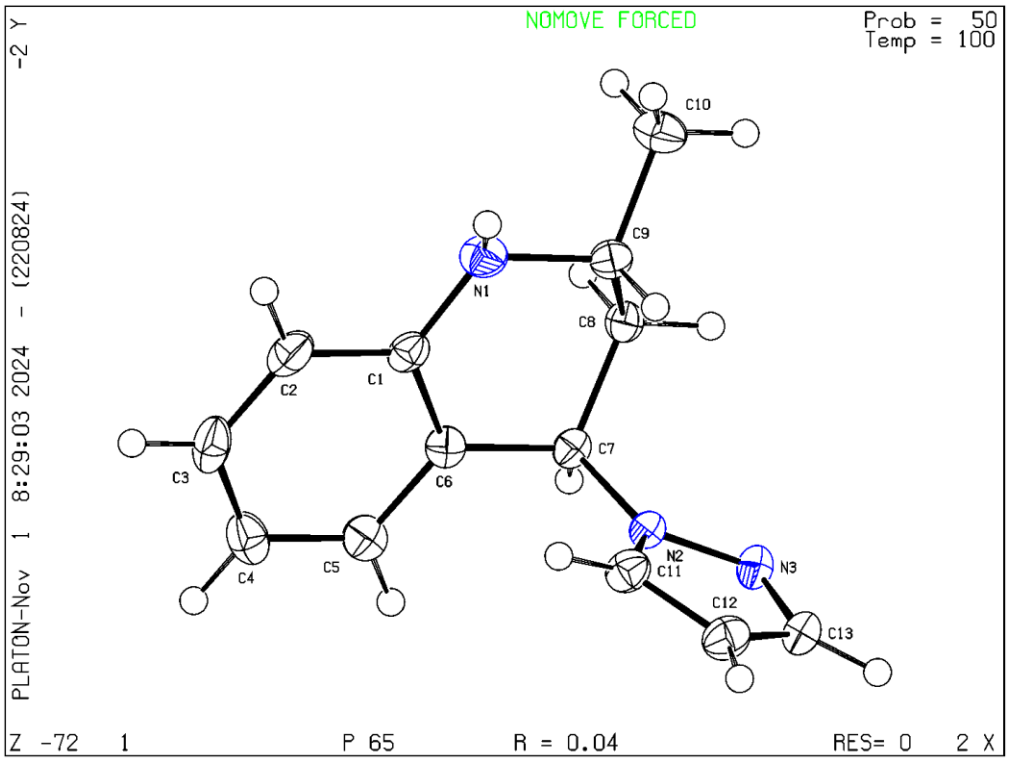
R(reflections)= 0.1202(1745) wR2(reflections)= 0.1762(2283)

S = 1.254 Npar= 174

Add compound **51** (25mg) to a 10 mL sample bottle, add DCM (1mL), n-hexane (1mL) and toluene (0.25 mL), seal the bottle with a parafilm, poke 15 small holes on the parafilm, Place the sample bottle in a safe place to allow it to volatilize and separate out the single crystal. Take out the single crystal and send it to the relevant test center for single crystal diffraction test to obtain relevant data. Instrument model： Bruker Apex 2. At the temperature of 100 K, the Mo-Kα radiation monochromated by the graphite monochromator (λ = 0.71073 Å), use BRUKER SAINT restores the data and performs absorption correction on the diffraction data through the SADABS program. Using SHELXTL software, the crystal structure was solved by the direct method. The coordinates of all non-hydrogen atoms and their anisotropic thermal parameters are corrected by the full matrix least square method.

X-ray Structure and Data of 89

Crystallographic data for compound **89** (CCDC-2559618) has been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC (Email: deposit@ccdc.cam.ac.uk).



The ellipsoid contour percent probability level is 50% in the caption of the thermal ellipsoid plot.

Fig. S4. X-ray crystal structure of **89**

Table S11. Crystal data and structure refinement for **89**

Datablock: 1

Bond precision: C-C = 0.0038 A Wavelength=0.71073

Cell: a=8.9208(7) b=8.9208(7) c=25.204(2)
alpha=90 beta=90 gamma=120
Temperature: 100 K

	Calculated	Reported
Volume	1737.0(3)	1737.0(3)
Space group	P 65	P 65
Hall group	P 65	P 65
Moiety formula	C13 H15 N3	C13 H15 N3
Sum formula	C13 H15 N3	C13 H15 N3
Mr	213.28	213.28
Dx,g cm-3	1.223	1.223
Z	6	6
Mu (mm-1)	0.075	0.075
F000	684.0	684.0
F000'	684.20	
h,k,lmax	11,11,33	11,11,33
Nref	2867[1465]	2836
Tmin,Tmax	0.976,0.979	0.687,0.746
Tmin'	0.976	

Correction method= # Reported T Limits: Tmin=0.687 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 1.94/0.99 Theta(max)= 28.289

R(reflections)= 0.0431(2326) wR2(reflections)= 0.0903(2836)

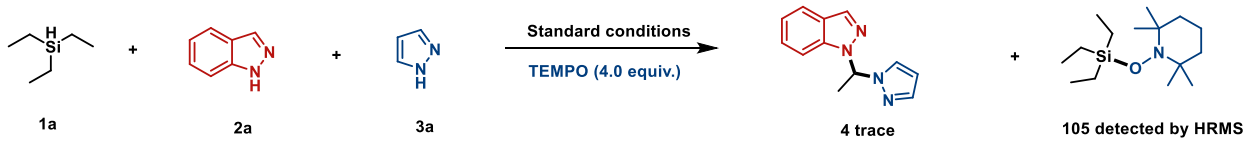
S = 1.085 Npar= 147

Add compound **89** (25mg) to a 10mL sample bottle, add DCM (1mL), n-hexane (1mL) and toluene (0.25 mL), seal the bottle with a parafilm, poke 15 small holes on the parafilm, Place the sample bottle in a safe place to allow it to volatilize and separate out the single crystal. Take out the single crystal and send it to the relevant test center for single crystal diffraction test to obtain relevant data. Instrument model： Bruker Apex 2. At the temperature of 100 K, the Mo-Kα radiation monochromated by the graphite monochromator (λ = 0.71073 Å), use BRUKER SAINT restores the data and performs absorption correction on the diffraction data through the SADABS program. Using SHELXTL software, the crystal structure was solved by the direct method. The coordinates of all non-hydrogen atoms and their anisotropic thermal parameters are corrected by the full matrix least square method.

4 Mechanism exploration

4.1 Radical capture experiment

TEMPO trapping experiment



We added the free radical scavenger 2,2,6,6-tetramethylpiperidoxyl (TEMPO) under standard conditions to investigate the reaction mechanism. The reaction steps are as follows: under air atmosphere, triethylsilane **1a** (0.8 mmol, 4.0 equiv), indazole **2a** (0.2 mmol, 1.0 equiv), pyrazol **3a** (0.4 mmol, 2.0 equiv), TEMPO (0.8 mmol, 4.0 equiv), $FeCl_3$ (30 mol%, 9.7 mg), TBACl (0.1mmol, 0.5 equiv), LiCl (0.4 mmol, 2.0 equiv) in MeCN (2.0 mL, 0.1 M) were added to 20 mL reaction tube, Finally, TFA was added (0.4 mmol, 2.0 equiv). The mixture was stirred at 395 nm light-emitting diodes (LEDs, 36 W) and monitored by TLC. After stirring for 10 h, the reaction was quenched with saturated NaCl solution and extracted with EtOAc (20 mL ×3). The organic layers were combined, dried over Na_2SO_4, filtered and evaporated under reduced pressure. The TEMPO adduct of triethylsilane **105** was detected by HRMS. **HRMS** (TOF-ESI$^+$): *m/z* $[M+H]^+$ calcd for $C_{15}H_{34}NOSi^+$, 272.2404; found, 272.2408.

MS Formula Results: + Scan (0.429 min) Sub (YYY02331-1.d)

m/z	Ion	Formula	Abundance
272.2408	M*+	C15 H34 N O Si	11768.7

Best	Formula (M)	Ion Formula	Score	Cross Score	Calc m/z	Diff (ppm)	Mass Match	Abund Match	Spacing Match
☑	C15 H34 N O Si	C15 H34 N O Si	85.95		272.2404	-1.51	98.66	97.8	46.31

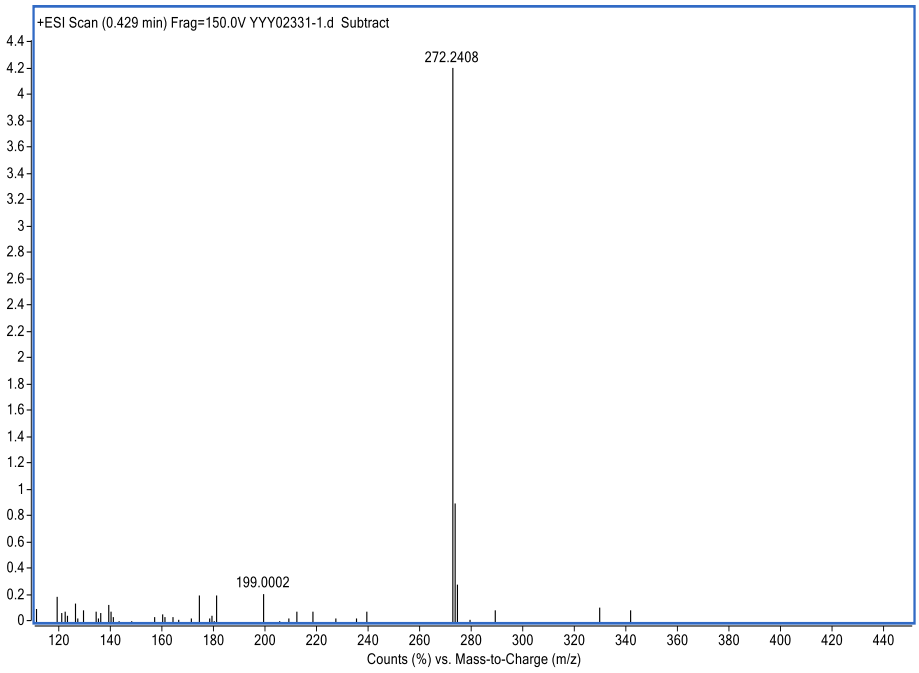
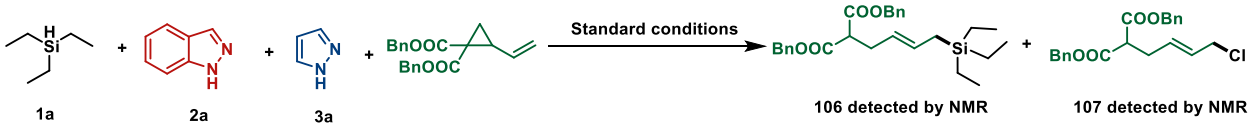


Fig. S5. HRMS detection of silyl–TEMPO adduct **105**

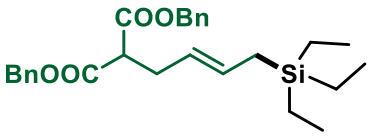
Radical clock experiments



A radical clock experiment was performed to probe the involvement of radical intermediates in the reaction. Under an air atmosphere, triethylsilane **1a** (0.8 mmol, 4.0 equiv.), indazole **2a** (0.2 mmol, 1.0 equiv.), pyrazole **3a** (0.4 mmol, 2.0 equiv.), the cyclopropyl-containing radical clock substrate (0.4 mmol, 2.0 equiv.), $FeCl_3$ (30 mol%, 9.7 mg), TBACl (0.1 mmol, 0.5 equiv.) and LiCl (0.4 mmol, 2.0 equiv.) were added to a 20-mL reaction tube containing MeCN (2.0 mL, 0.1 M). TFA (0.4 mmol, 2.0 equiv.) was then added, and the resulting mixture was irradiated with 395-nm LEDs (36 W) for 10 h. The reaction was subsequently quenched with saturated aqueous NaCl and extracted with EtOAc (3 × 20 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. Analysis of the crude reaction mixture by NMR spectroscopy revealed the formation of the ring-opened products **106** and **107**, consistent with the generation of a carbon-centred radical intermediate.

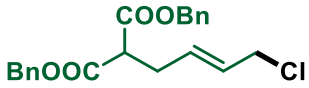
Spectroscopic Data of 106 and 107.

Dibenzyl (*E*)-2-(4-(triethylsilyl)but-2-en-1-yl)malonate. (106)



The reaction afforded compound **106** was purified by FC on silica gel as a colorless liquid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.30 – 7.20 (m, 10H), 5.43 (m, 1H), 5.14 – 5.04 (m, 5H), 3.39 (t, J = 7.6 Hz, 1H), 2.58 – 2.50 (m, 2H), 1.33 (d, J = 8.1 Hz, 2H), 0.83 (t, J = 7.9 Hz, 9H), 0.41 (q, J = 7.9 Hz, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 167.8, 134.4, 129.4, 127.5, 127.3, 127.1, 122.1, 66.0, 51.6, 31.1, 16.5, 6.3, 2.0. *m/z* $[M+H]^+$ calcd for $C_{27}H_{37}O_4Si^+$, 453.2456; found, 453.2459.

Dibenzyl (*E*)-2-(4-chlorobut-2-en-1-yl)malonate. (107)



The reaction afforded compound **107** was purified by FC on silica gel as a colorless liquid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.32 – 7.15 (m, 10H), 5.59 (m, 2H), 5.08 (s, 4H), 3.83 (d, J = 6.0 Hz, 2H), 3.46 (t, J = 7.5 Hz, 1H), 2.61 (t, J = 6.8 Hz, 2H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 167.3, 134.2, 129.3, 128.3, 127.6, 127.4, 127.3, 66.2, 50.4, 43.5, 30.2. *m/z* $[M+H]^+$ calcd for $C_{21}H_{22}ClO_4^+$, 373.1201; found, 373.1199.

NMR Spectroscopic Data of 106 and 107.

4.2 UV-vis absorption spectra

As shown in Figure **S6**, the UV-visible absorption sample was prepared in CH_3CN at a concentration of 4.0×10^{-4} mol L^{-1}. The spectra were acquired from 200 to 500 nm.

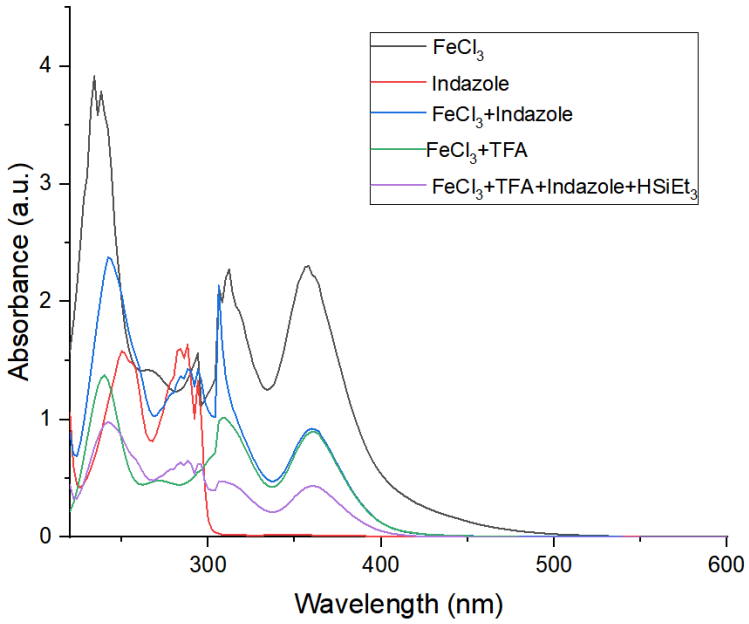


Fig. S6. UV-vis absorption spectra of $FeCl_3$

As shown in Figure **S7**, the UV-visible absorption sample was prepared in CH_3CN at a concentration of 4.0×10^{-4} mol L^{-1}. The spectra were acquired from 200 to 500 nm. The time-dependent UV/vis absorption spectra of $FeCl_3$/TFA system were recorded under irradiation at 395 nm.

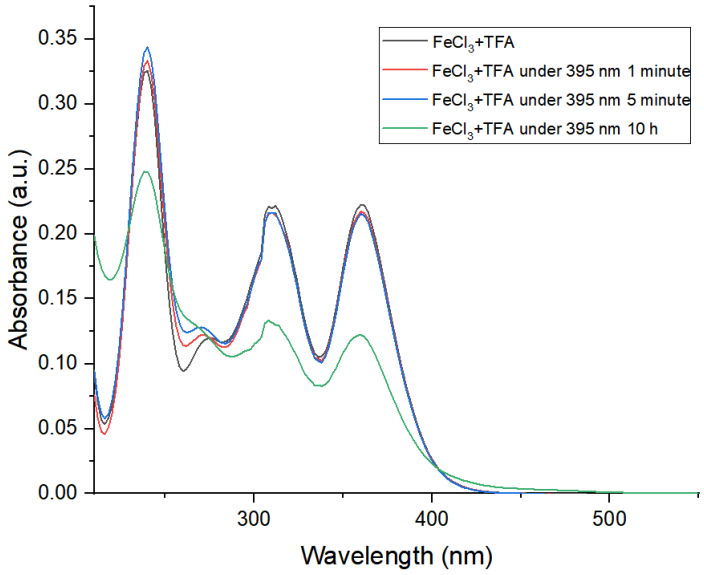


Fig. S7. UV-vis absorption spectra of $FeCl_3$/TFA at different time intervals

As shown in Figure **S8**, the UV-visible absorption sample was prepared in CH_3CN at a concentration of 4.0×10^{-4} mol L^{-1}. The spectra were acquired from 200 to 500 nm.

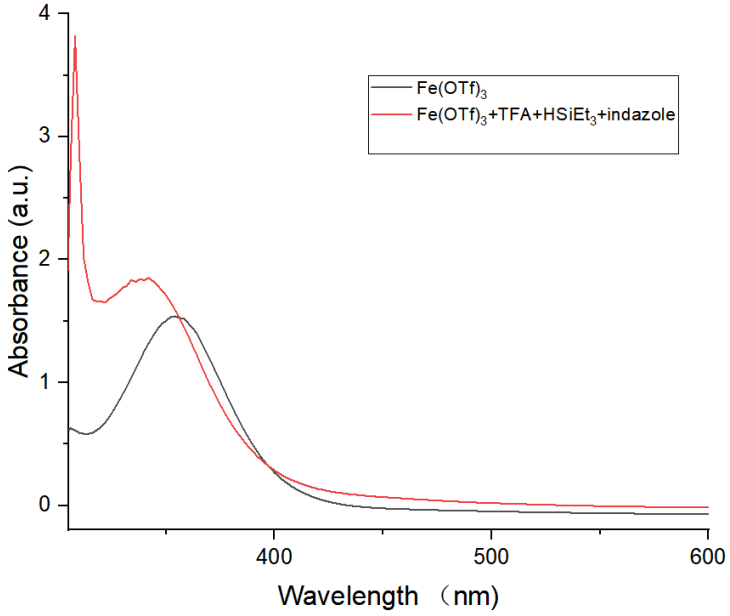


Fig. S8. UV-vis absorption spectra of $Fe(OTf)_3$

As shown in Figure **S9**, the UV-visible absorption sample was prepared in CH_3CN at a concentration of 4.0×10^{-4} mol L^{-1}. The spectra were acquired from 200 to 500 nm.

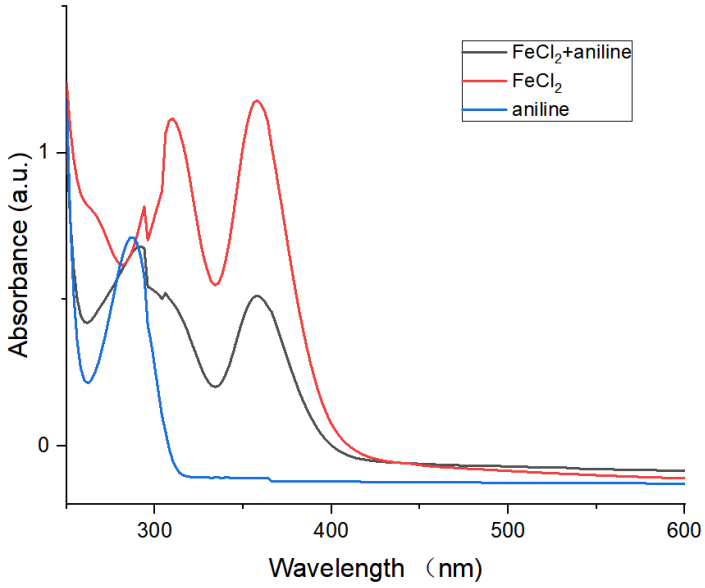
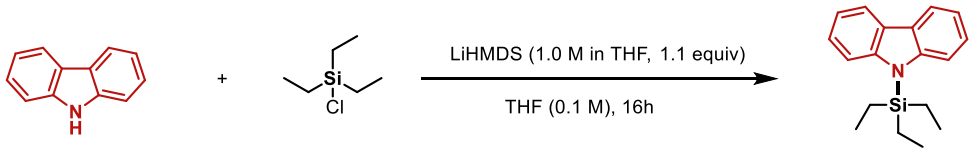


Fig. S9. UV-vis absorption spectra of $FeCl_2$

4.3 Detection of putative intermediates

Preparation of 9-(triethylsilyl)-9*H*-carbazole (108)[8]

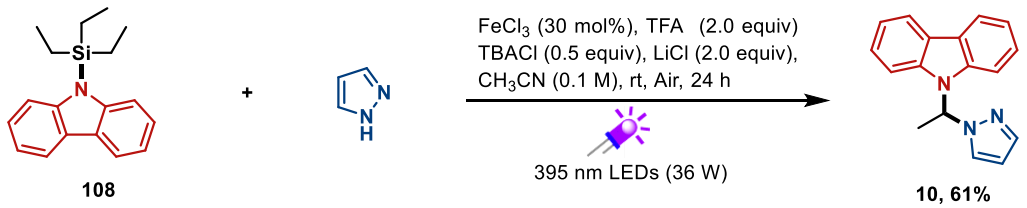


108

Lithium bis(trimethylsilyl)amide (LiHMDS, 1.0 M in THF, 1.1 equiv.) was added to a solution of 9H-carbazole (2.0 mmol, 1.0 equiv.) in THF (0.1 M), and the reaction mixture was stirred at room temperature for 15 min. Chlorotriethylsilane (1.2 equiv.) was then added, and the mixture was stirred for a further 16 h. Water was added, and the resulting mixture was extracted with EtOAc (3×). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography or recrystallization to afford 9-(triethylsilyl)-9*H*-carbazole (**108**) in 76% yield (427 mg). **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.05 (t, J = 7.0 Hz, 2H), 7.61 (t, J = 8.1 Hz, 2H),

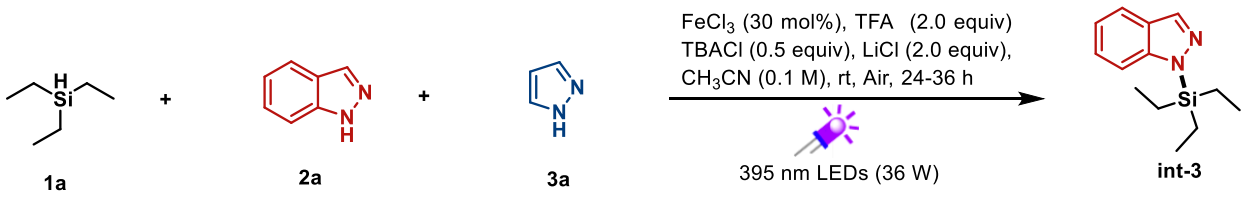
7.35 (td, J = 8.9, 7.9, 6.4 Hz, 2H), 7.26 – 7.17 (m, 2H), 1.22 (t, J = 7.7 Hz, 6H), 0.98 (t, J = 7.9 Hz, 9H).

Reaction of intermediate 108 under the standard conditions



To evaluate the competence of 108 as a reaction intermediate, 9-(triethylsilyl)-9H-carbazole (108, 1.0 equiv.) and pyrazole (2.0 equiv.) were subjected to the standard reaction conditions in the presence of $FeCl_3$ (30 mol%), TFA (2.0 equiv.), TBACl (0.5 equiv.) and LiCl (2.0 equiv.) in MeCN (0.1 M) under air. The reaction mixture was irradiated with 395-nm LEDs (36 W) at room temperature for 24 h, affording the desired product **10** in 61% yield.

In situ HR-MS detection (int-3)



Under an air atmosphere, triethylsilane **1a** (4.0 equiv.), indazole **2a** (1.0 equiv.), pyrazole **3a** (2.0 equiv.), $FeCl_3$ (30 mol%), TBACl (0.5 equiv.) and LiCl (2.0 equiv.) were added to MeCN (0.1 M), followed by TFA (2.0 equiv.). The reaction mixture was irradiated with 395-nm LEDs (36 W) at room temperature. Analysis of the reaction mixture by HRMS showed a signal attributable to intermediate **int-3**: HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{13}H_{21}N_2Si^+$, 233.1469; found, 233.1461.

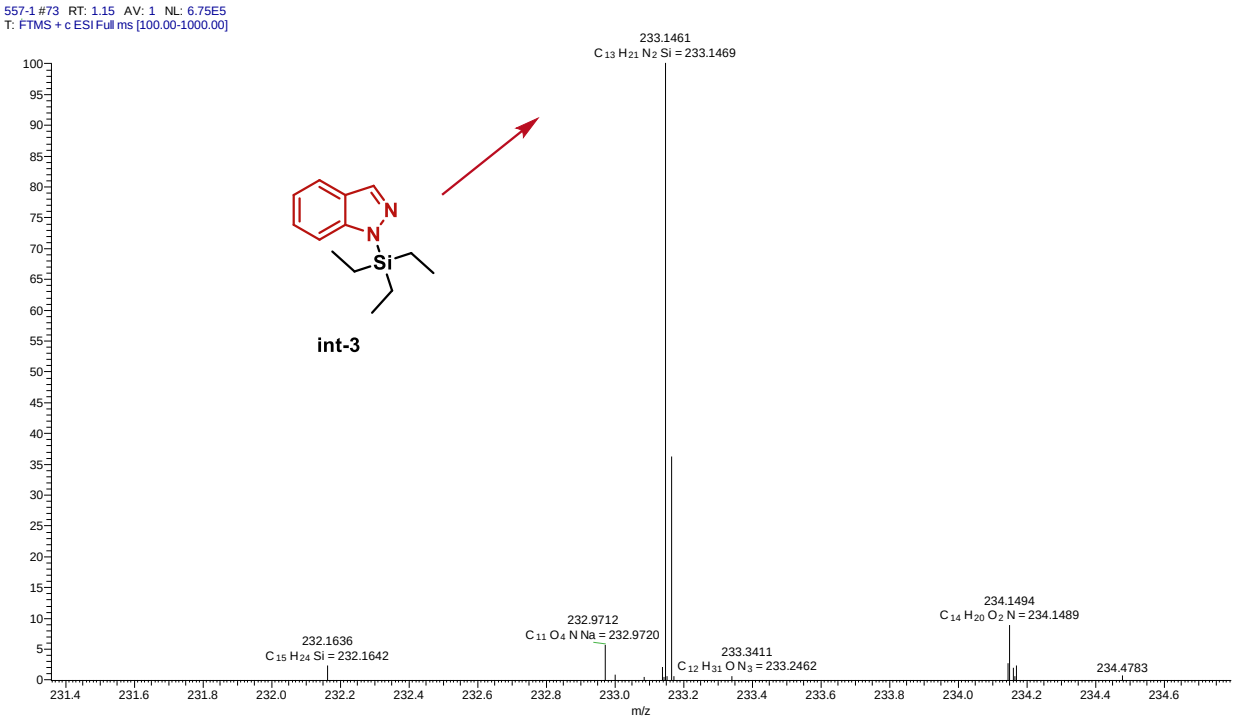
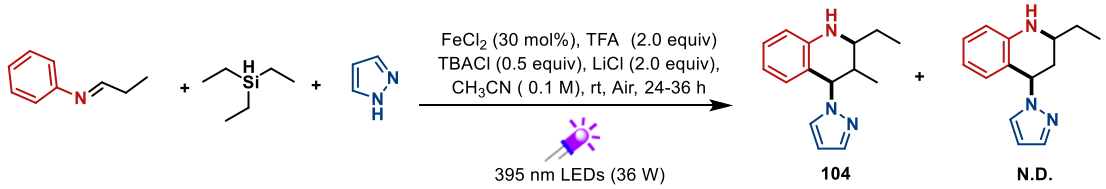


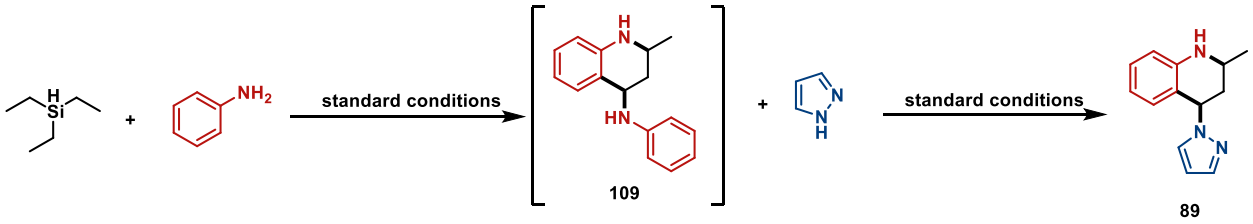
Fig. S10. HRMS detection of the putative N-silylated intermediate int-3.

Conversion of the imine intermediate under the standard conditions



To probe the possible involvement of the imine intermediate, the independently synthesized imine was subjected to the standard reaction conditions in the presence of pyrazole (1.0 equiv.) and triethylsilane (4.0 equiv.). Under $FeCl_2$ (30 mol%), TFA (2.0 equiv.), TBACl (0.5 equiv.) and LiCl (2.0 equiv.) in MeCN (0.1 M) under air, irradiation with 395-nm LEDs (36 W) at room temperature for 24–36 h afforded the desired product **104** in 37% yield. Notably, formation of **104** was also observed in the absence of triethylsilane, indicating that silane is not required for the conversion of the imine to the final product. Together, these results establish the imine as a chemically competent intermediate and are consistent with its involvement in the reaction pathway.

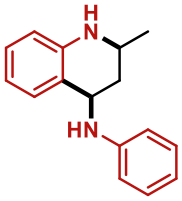
Verification of intermediate 109



Conditions: Triethylsilane (4.0 equiv), aniline (2.0 equiv), FeCl2 (30 mol%), TFA (2.0 equiv), TBACl (0.5 equiv), LiCl (2.0 equiv.), CH3CN (0.1 M).

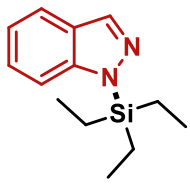
To evaluate the possible involvement of **109** as a reaction intermediate, triethylsilane and aniline were subjected to the standard reaction conditions. After 20 h, compound **109** was obtained in 65% yield and isolated. The isolated **109** was then subjected to the standard reaction conditions in the presence of pyrazole, affording the desired product **89** with 71% yield. These results demonstrate that **109** is a competent intermediate and support its involvement in the reaction pathway.

2-methyl-*N*-phenyl-1,2,3,4-tetrahydroquinolin-4-amine (109)



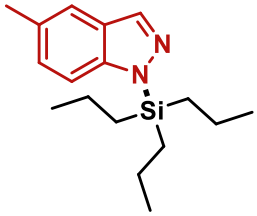
The reaction afforded compound **109** was purified by FC on silica gel as a colorless liquid. Data consistent with those previously reported.[9] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.17 – 7.10 (m, 3H), 7.04 – 6.97 (m, 1H), 6.68 – 6.57 (m, 4H), 6.49 (d, *J* = 8.2 Hz, 1H), 4.48 (t, *J* = 4.0, 2.3 Hz, 1H), 3.82 (s, 1H), 3.43 – 3.33 (m, 1H), 2.12 (m, 1H), 1.53 – 1.44 (m, 1H), 1.15 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 145.4, 144.0, 129.8, 128.4, 127.6, 120.2, 116.4, 116.1, 113.5, 111.6, 47.9, 41.4, 34.1, 21.0.

1-(triethylsilyl)-1H-indazole （110）



Same procedure was used for preparation of compound108. The crude product was purified by flash column chromatography or recrystallization to afford 1-(triethylsilyl)-1H-indazole (**110**) in 57% yield (132 mg). 1H NMR (400 MHz, Chloroform-d) δ 8.09 (s, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.33 – 7.29 (m, 1H), 7.19 – 7.14 (m, 1H), 1.32 – 1.23 (m, 6H), 1.14 (t, J = 7.7 Hz, 9H). 13C NMR (151 MHz, Chloroform-d) δ 135.48, 133.50, 123.98, 122.88, 121.67, 120.98, 115.33, 12.32, 7.10.

5-methyl-1-(tripropylsilyl)-1H-indazole （111）



Same procedure was used for preparation of compound108. The crude product was purified by flash column chromatography or recrystallization to afford 5-methyl-1-(tripropylsilyl)-1H-indazole (**111**) in 43% yield (123 mg). 1H NMR (400 MHz, Chloroform-d) δ8.04 (s, 1H), 7.53 (d, J = 9.0 Hz, 1H), 7.38 (s, 1H), 7.11 (d, J = 9.0 Hz, 1H), 2.39 (s, 3H), 1.67 (q, J = 7.1 Hz, 6H), 1.30 (t, J = 7.0 Hz, 6H), 1.03 (t, J = 7.2 Hz, 9H). 13C NMR (151 MHz, Chloroform-d) δ 135.48, 133.50, 132.10, 125.34, 122.88, 115.33, 111.95, 21.30, 18.42, 17.66, 12.32.

4.4 Deuterium-labelling experiment



Deuterated triethylsilane **1-d** (1.0 equiv.), indazole **2a** (1.0 equiv.) and pyrazole **3a** (2.0 equiv.) were subjected to the standard reaction conditions using $FeCl_3$ (30 mol%), TFA (2.0 equiv.), and TBACl (0.5 equiv.) and LiCl (2.0 equiv.) in CH_3CN (0.1 M) for 36 h. Deuterium-labelled products

29’ and 4’ were formed in 25% and <10% yield, respectively. These results indicate that the alkyl fragment incorporated into the products is derived from the silane.

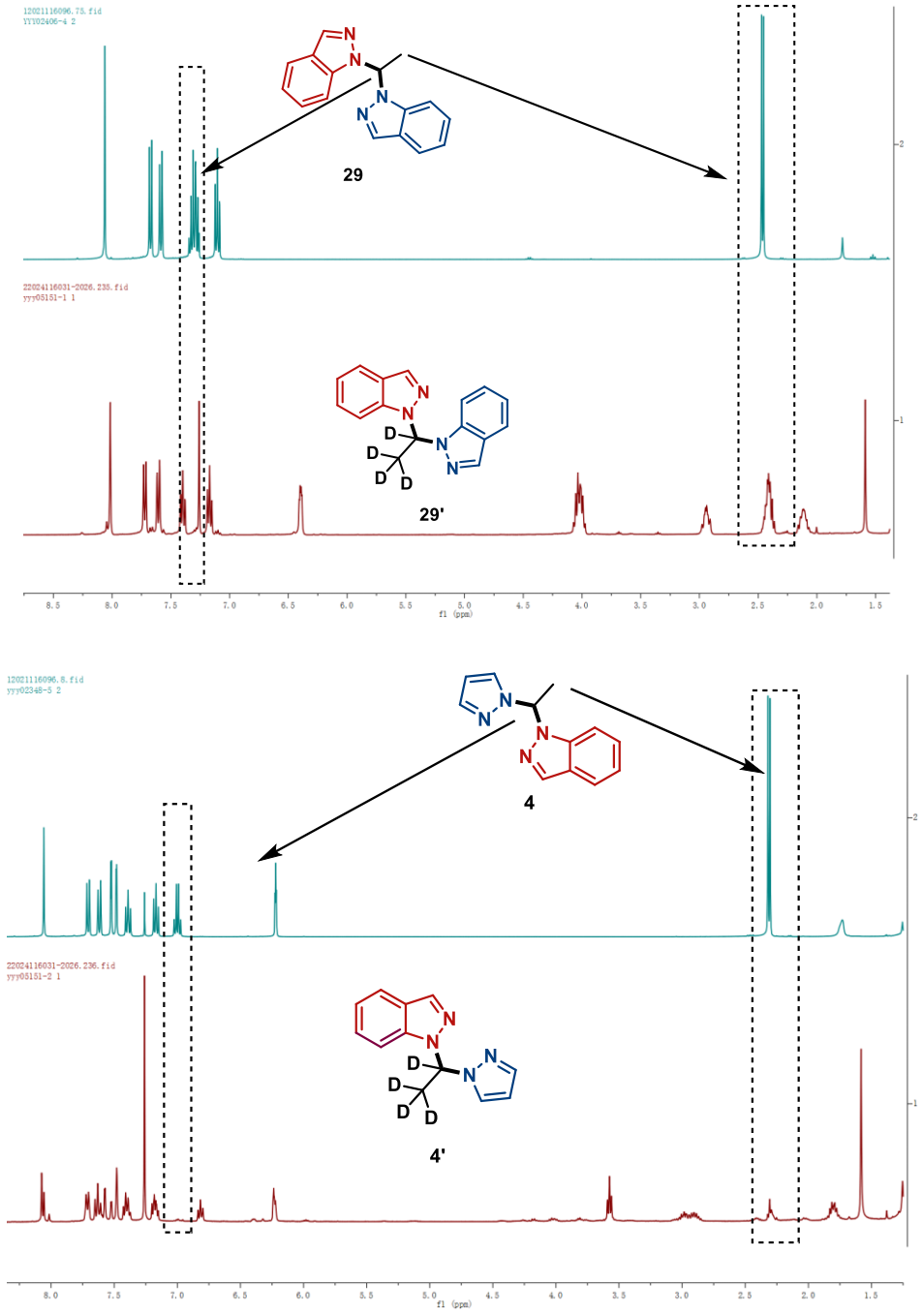
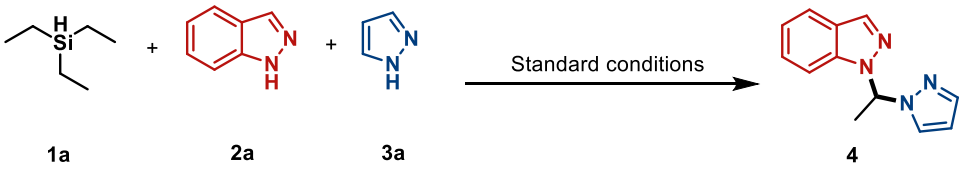


Fig. S11. Deuterium-labelling experiment

4.5 Light on / off experiment



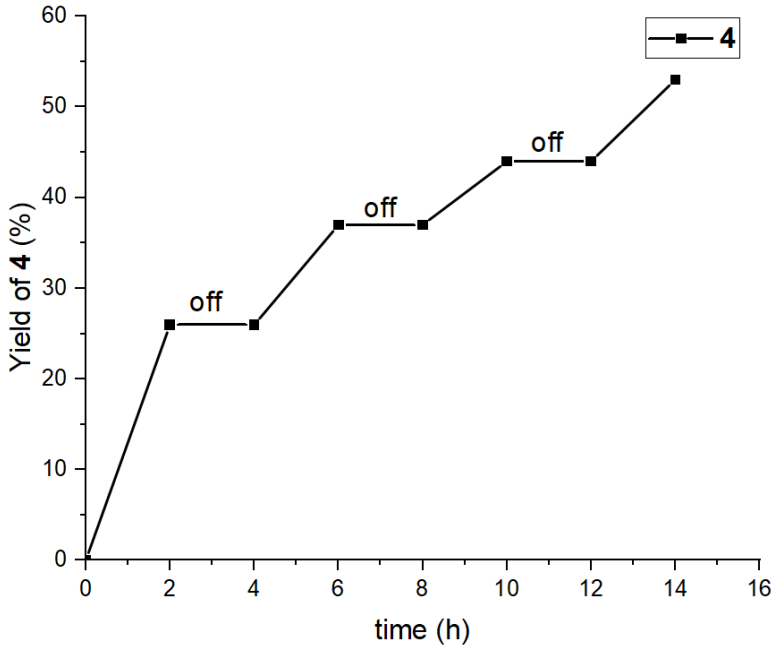
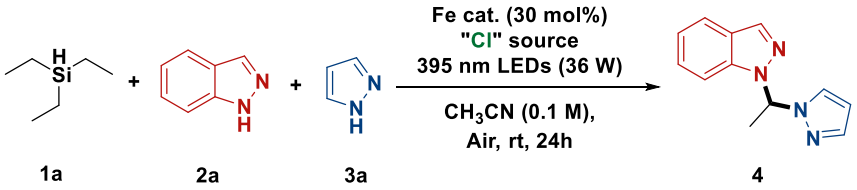


Fig. S12. Switching light experiment[a, b]

[a]Conditions: **1a** (4.0 equiv), **2a** (1.0 equiv), **3a** (2.0 equiv) $FeCl_3$ (30 mol%), TFA (2.0 equiv), TBACl (0.5 equiv), LiCl (2.0 equiv), CH_3CN (0.1 M). [b]Yields were determined by analysis of the crude ^1H NMR spectra using CH_2Br_2 as the internal standard.

4.6 Control experiment

Table S12. Dependence on Fe(III) and chloride.[a,b]

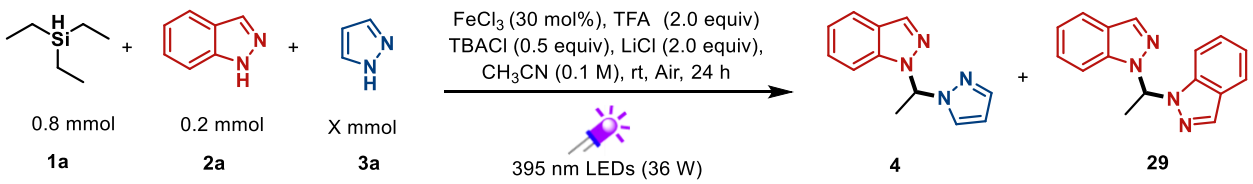


entry	Fe cat.	"Cl" source	yield of 4 (%) [a, b]
1	$FeCl_3$	—	68
2	$Fe(OTf)_3$	LiCl (2 eq.)	65
3	$Fe(OTf)_3$	—	trace

[a]Conditions: **1a** (4.0 equiv), **2a** (1.0 equiv), **3a** (2.0 equiv) Fe cat (30 mol%), TFA (2.0 equiv), $TBABF_4$ (0.5 equiv), CH_3CN (0.1 M), 24 h. [b]Yields were determined by analysis of the crude ^1H NMR spectra using CH_2Br_2 as the internal standard.

Control experiments revealed a pronounced dependence of the reaction on the simultaneous presence of Fe(III) and chloride. $FeCl_3$ promoted the formation of **4** in 68% yield in the absence of an additional chloride source (entry 1), whereas $Fe(OTf)_3$ afforded only trace product under otherwise comparable conditions (entry 3). Supplementation of the $Fe(OTf)_3$ system with LiCl (2.0 equiv.) restored productive reactivity, furnishing **4** in 65% yield (entry 2). Thus, the triflate-ligated Fe(III) precursor alone is largely ineffective, whereas reintroduction of chloride recovers a level of reactivity comparable to that obtained with $FeCl_3$. These observations support a critical role for chloride in the photoinduced iron-mediated activation process and are consistent with the generation of photoactive Fe(III)–chloride species capable of undergoing Fe–Cl ligand-to-metal charge transfer.

Effect of pyrazole loading on the formation of 4 and 96.[a,b]



aConditions: **1a** (4.0 equiv), **2a** (1.0 equiv, 0.2 mmol), **3a** (**X** equiv) $FeCl_3$ (30 mol%), TFA (2.0 equiv), TBACl (0.5 equiv), LiCl (2.0 equiv), CH_3CN (0.1 M), 24 h. [b]Yields were determined by analysis of the crude ^1H NMR spectra using CH_2Br_2 as the internal standard.

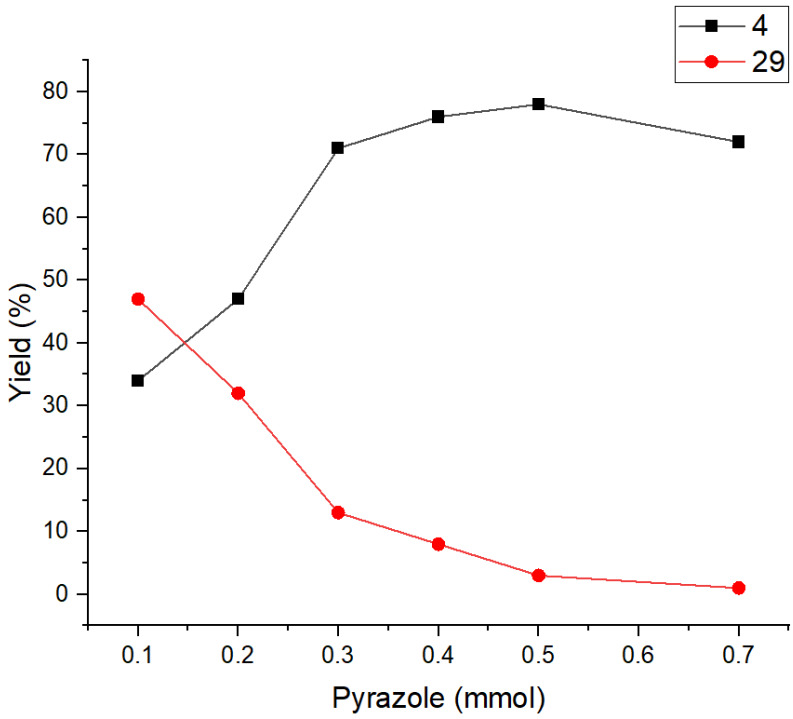


Fig. S13. Effect of pyrazole loading on the formation of **4** and **96**

4.7 Crossover experiment

To probe whether the Si-to-C nitrogen translocation occurs intramolecularly within a discrete N-silylated intermediate, two independently prepared N-silylated precursors carrying orthogonal nitrogen and carbon-fragment labels were examined. Precursor A (**110**) was N-triethylsilyl indazole (N-tag: indazole; C-tag: Et), whereas precursor B (**111**) was N-tri-n-propylsilyl 5-methylindazole (N-tag: 5-Me-indazole; C-tag: n-Pr). An equimolar mixture of A and B (total N-silylated substrate = 1.0 equiv.) was subjected to the standard photochemical conditions with pyrazole (2.0 equiv.), $FeCl_3$ (30 mol%), TFA (2.0 equiv.), TBACl (0.5 equiv.) and LiCl (2.0 equiv.) in MeCN (0.1 M) under air and irradiated with 395-nm LEDs (36 W) at room temperature for 24 h.

The crude reaction mixture was analysed by LC-HRMS. Signals corresponding to the two matched products AA (indazole + Et; the same connectivity as compound 4) and BB (5-Me-indazole + n-Pr) were detected. In contrast, no signal attributable to the crossover products AB (indazole + n-Pr; the same connectivity as compound 78) or BA (5-Me-indazole + Et; the same connectivity as compound 5) was detected under the same analysis conditions. The calculated sodium-adduct exact masses used for targeted assessment are summarized in Table S13. Notably, AB and BA are constitutional isomers and therefore share the same elemental composition and calculated exact mass. The exclusive observation of matched products is consistent with retention of the original N-silyl/carbon-fragment pairing and strongly supports an intramolecular Si-to-C 1,2-nitrogen migration rather than an intermolecular exchange/recombination pathway.

Table S13. Qualitative LC-HRMS outcome of the crossover experiment.

Outcome	N-tag	C-tag	Assignment	calcd m/z $[M+Na]^+$	LC-HRMS outcome
AA	indazole	Et	matched; compound 4 connectivity	235.0954	detected
BB	5-Me-indazole	n-Pr	matched	263.1267	detected
AB	indazole	n-Pr	crossover; compound 78 connectivity	249.1111	not detected

BA	5-Me-indazole	Et	crossover; compound 5 connectivity	249.1111	not detected

[a] Detected/not detected refers to the presence or absence of signals assignable to the expected products under the LC-HRMS analysis conditions. The m/z values shown are calculated sodium-adduct exact masses.

4.8 DFT calculations

Computational methods. Geometry optimizations and harmonic vibrational-frequency calculations were performed for open-shell doublets at the UωB97X-D/def2-SVP level with SMD solvation for acetonitrile. Minima were required to have no imaginary frequencies, whereas TS-mig was required to have exactly one imaginary frequency associated with the nitrogen-transfer coordinate. Final single-point energies were evaluated at UωB97X-D/def2-TZVPP/SMD(MeCN), and Gibbs free-energy differences are reported relative to int-4 ($\Delta G = 0.0$ kcal mol^{-1}).

Transition-state validation and IRC. The direct intramolecular int-4→int-6 Si-to-C nitrogen-migration coordinate proceeds through the three-membered Si–C–N transition state TS-mig. TS-mig is a first-order saddle point with one imaginary frequency at −425 cm^{-1}. The corresponding normal mode shows synchronous C–N bond formation and Si–N bond cleavage. In the optimized transition state, the Si–N, N–C and Si–C distances are 2.13, 1.91 and 1.92 Å, respectively. IRC calculations connect int-4, TS-mig and int-6, supporting the assigned migration coordinate.

Table S14. Relative Gibbs free energies and spin-density evolution along the direct Si-to-C nitrogen-migration coordinate.

Species	ΔG / kcal mol^{-1}	ρ(C)	ρ(Si)	ρ(N)	Radical character
int-4	0.0	0.85	0.05	—	predominantly carbon-centred
TS-mig	+14.2	0.34	0.37	0.18	delocalized
int-6	−8.7	0.04	0.83	—	predominantly silicon-centred

Table S15. Structural descriptors for TS-mig.

Species	Imaginary frequency / cm^{-1}	Si–N / Å	N–C / Å	Si–C / Å
TS-mig	−425	2.13	1.91	1.92

Energetic comparison of migration and competing pathways. The calculated Gibbs free-energy barrier for the intramolecular migration is 14.2 kcal mol^{-1} relative to int-4, and formation of int-6 is exergonic by 8.7 kcal mol^{-1}. Representative competing pathways are substantially higher in energy, including N–Si bond homolysis (27.6 kcal mol^{-1}), direct C–Si bond cleavage (24.7 kcal mol^{-1}), and an intermolecular nitrogen-transfer model (25.1 kcal mol^{-1}).

Table S16. Relative free-energy requirements for the migration and representative competing pathways.

Pathway	Calculated energy / kcal mol^{-1}	Reference
Intramolecular Si-to-C 1,2-N migration via TS-mig	14.2	relative to int-4
N–Si bond homolysis	27.6	relative to int-4
Direct C–Si bond cleavage	24.7	relative to int-4
Intermolecular nitrogen-transfer model	25.1	relative to int-4

Table S17. Connectivity and electronic reorganization along the migration coordinate.

Feature	Result
IRC connectivity	int-4 ↔ TS-mig ↔ int-6
Bond reorganization at TS-mig	synchronous C–N bond formation and Si–N bond cleavage
Spin-density evolution	carbon-centred int-4 → delocalized TS-mig → silicon-centred int-6

Energetic interpretation. The direct three-centre Si–C–N migration is both kinetically accessible and thermodynamically favourable at the reported level of theory. The substantially higher energies calculated for N–Si homolysis, direct C–Si cleavage and intermolecular nitrogen transfer further support the intramolecular 1,2-nitrogen-migration pathway. The simultaneous bond reorganization and accompanying shift of spin density from carbon to silicon are consistent with formation of int-6 through TS-mig.

Cartesian coordinates of reported stationary points (Å). Atom numbering is retained from the mechanistic model; all structures have charge 0 and multiplicity 2.

int-4

1	C	2.87401600	-3.40737800	0.85899800
2	C	1.64526200	-3.42320300	0.15334800
3	C	0.92196700	-2.26706200	-0.07889600
4	C	1.45881700	-1.06255000	0.41821900
5	C	2.68087200	-1.03420300	1.12576000
6	C	3.39955100	-2.22567700	1.34879900
7	N	0.99138600	0.22612100	0.35765400
8	N	1.84908400	1.06089200	0.99789200
9	C	2.85070900	0.34641200	1.45494000
10	Si	-0.57496500	0.83050000	-0.32912800
11	C	-0.43234500	2.69914800	-0.32926700
12	C	-0.73304400	0.12776600	-2.03152700
13	C	-1.93265200	0.20880100	0.80569200
14	C	-1.70587300	3.39197300	-0.82216700
15	C	-1.80046800	0.71165200	2.24552700
16	C	-1.80998600	-0.77116700	-2.53567900
17	H	3.40814100	-4.34716400	1.01676000
18	H	1.25950100	-4.37614000	-0.21705200
19	H	-0.02425000	-2.29339000	-0.62293900

20	H	4.34559600	-2.21320000	1.89491200
21	H	3.66569100	0.81935900	2.00327700
22	H	-0.18030900	3.02992500	0.69180600
23	H	0.42993600	2.97925700	-0.95855700
24	H	0.03013000	0.40724300	-2.77243200
25	H	-2.90696800	0.50703400	0.37985700
26	H	-1.92081400	-0.89507300	0.78245100
27	H	-1.59026000	4.48718500	-0.82993700
28	H	-1.96727300	3.08208300	-1.84726100
29	H	-2.57031000	3.15957500	-0.17939000
30	H	-2.58117300	0.28785000	2.89657600
31	H	-0.82534600	0.43879500	2.68061500
32	H	-1.88668600	1.80861600	2.30049800
33	H	-2.38981400	-0.28102300	-3.34102300
34	H	-2.52042100	-1.07886800	-1.75391300
35	H	-1.38759700	-1.68573900	-2.99159600

TS-mig

1	C	1.89299400	-2.53098300	2.10636600
2	C	0.91903700	-3.02209000	1.19670200
3	C	0.65456900	-2.37936400	0.00215100
4	C	1.37972900	-1.20115100	-0.28282900
5	C	2.35863000	-0.70512200	0.61970900
6	C	2.61839600	-1.38665700	1.82846000
7	N	1.31972800	-0.36744900	-1.36367200
8	N	2.17703200	0.64860100	-1.17523100
9	C	2.82544300	0.47336700	-0.03065000
10	Si	-1.11554200	0.95724800	-0.74930900
11	C	-0.41281400	2.59099000	-0.20686700
12	C	-0.61322800	0.24397700	-2.29088700
13	C	-2.03056500	-0.03599800	0.53383900
14	C	-1.43207300	3.55886700	0.40460600
15	C	-1.37015200	-0.00235400	1.91907300
16	C	-1.13125700	-1.01670800	-2.90521300
17	H	2.07106500	-3.07460100	3.03759300
18	H	0.36901400	-3.93204300	1.45055900
19	H	-0.09318200	-2.76362500	-0.69463000
20	H	3.37275500	-1.01881300	2.52902500
21	H	3.58804500	1.18067100	0.29879100
22	H	0.37380300	2.34912600	0.53209100
23	H	0.10876900	3.04514800	-1.06418100
24	H	-0.07364800	0.91420100	-2.97003600
25	H	-3.06202400	0.35356700	0.59947700
26	H	-2.11995300	-1.06951200	0.16098400
27	H	-0.93128700	4.46828600	0.76972700
28	H	-2.18931500	3.86931500	-0.33158500
29	H	-1.96264100	3.10971200	1.25887200
30	H	-1.93727700	-0.62256600	2.62979300
31	H	-0.33833000	-0.38531300	1.89224800
32	H	-1.33648500	1.01979800	2.32667600
33	H	-1.87483500	-0.76989300	-3.68231800
34	H	-1.61600800	-1.68188600	-2.17603200
35	H	-0.31828900	-1.56839700	-3.40048800

int-6

1	C	3.50265000	-2.31135400	1.60022400

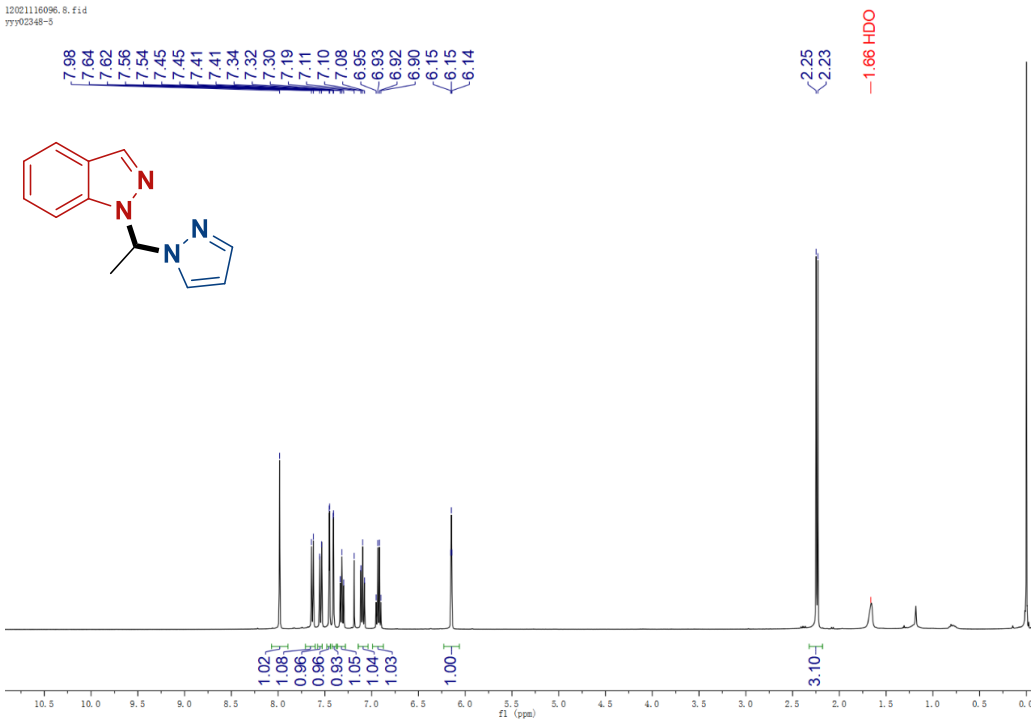
2	C	2.12472900	-2.64421200	1.64257100
3	C	1.20667900	-2.06461200	0.78660500
4	C	1.70019000	-1.11777100	-0.13424500
5	C	3.07048200	-0.77041900	-0.18423900
6	C	3.98498300	-1.38258600	0.69748000
7	N	1.07269000	-0.36331500	-1.08292900
8	N	1.94424000	0.43398600	-1.72422800
9	C	3.13799100	0.21407500	-1.21437900
10	Si	-1.37365500	0.36235100	0.08654600
11	C	-0.31264500	1.70460900	0.90028700
12	C	-0.34806600	-0.30772800	-1.40434900
13	C	-3.01229200	1.01326300	-0.60643400
14	C	-1.02425300	2.62266000	1.89465000
15	C	-4.13992300	1.26789700	0.39646800
16	C	-0.85179200	-1.59990600	-2.04322400
17	H	4.18820000	-2.80041300	2.29598600
18	H	1.78013300	-3.38207400	2.37107600
19	H	0.14876100	-2.33114700	0.82441500
20	H	5.04594800	-1.12428600	0.66717000
21	H	4.00768200	0.75617500	-1.58481000
22	H	0.54812800	1.21133700	1.38451600
23	H	0.11711300	2.29858800	0.07072900
24	H	-0.41954100	0.50186400	-2.15067800
25	H	-2.76662400	1.94484700	-1.15189100
26	H	-3.35003300	0.29706100	-1.37561400
27	H	-0.32586400	3.35373500	2.33254100
28	H	-1.83348200	3.19335300	1.41267400
29	H	-1.47004000	2.05596700	2.72781700
30	H	-5.03723100	1.66430700	-0.10525600
31	H	-4.43481200	0.34163200	0.91469700
32	H	-3.84815800	1.99560200	1.16917800
33	H	-1.90050700	-1.48321500	-2.35567300
34	H	-0.80346900	-2.45161200	-1.34820500
35	H	-0.25810700	-1.85030600	-2.93665900

int-6 IRC rotamer

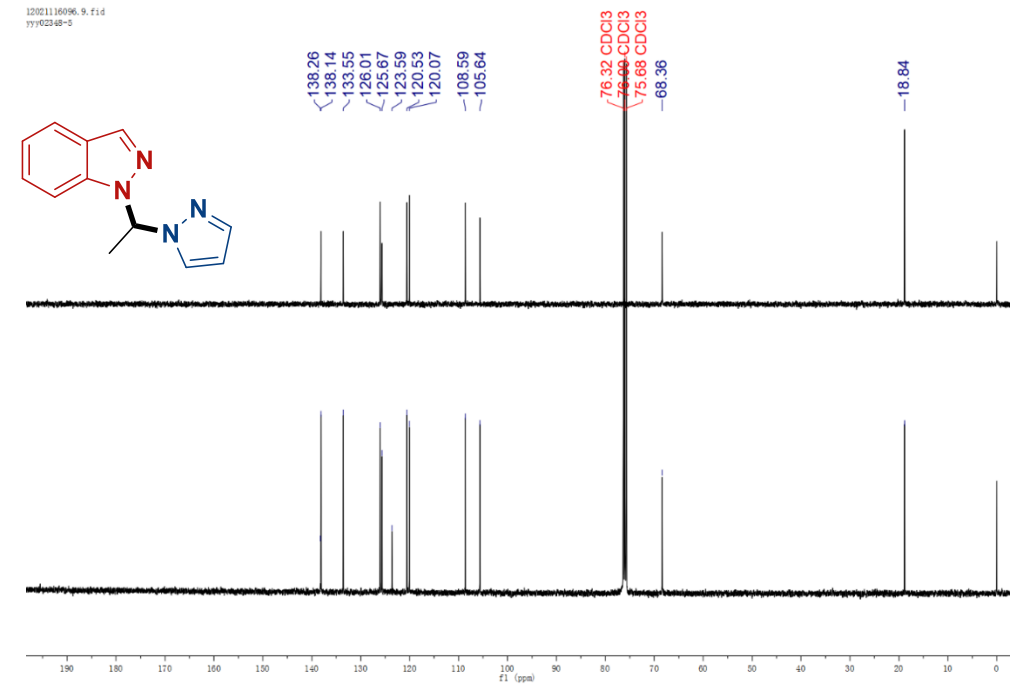
1	C	1.86336500	-2.74066500	1.93988300
2	C	0.61423500	-2.98340900	1.31453700
3	C	0.11311800	-2.15288800	0.33075100
4	C	0.89742500	-1.03823800	-0.03593700
5	C	2.14295200	-0.78226800	0.58720200
6	C	2.63170200	-1.64886600	1.58661100
7	N	0.70495800	-0.03044600	-0.94136000
8	N	1.73098400	0.83857400	-0.92288700
9	C	2.60042500	0.41791700	-0.02952300
10	Si	-1.80054900	1.24100600	-0.83228000
11	C	-1.02124100	2.84427500	-0.19864100
12	C	-0.44529700	0.26721700	-1.80090400
13	C	-2.56425000	0.24000600	0.58804000
14	C	-1.99150300	3.82592700	0.46227100
15	C	-1.82388300	0.33838200	1.92833900
16	C	-0.94109000	-0.94462500	-2.58533000
17	H	2.21476700	-3.42858500	2.71218700
18	H	0.02778700	-3.85269000	1.62186300
19	H	-0.85612700	-2.35183600	-0.12396700
20	H	3.59259300	-1.45447600	2.06858000

21	H	3.52275500	0.96958800	0.15057500
22	H	-0.23047900	2.54752900	0.51649400
23	H	-0.49319800	3.32984800	-1.03715500
24	H	-0.03967700	0.99357700	-2.52154300
25	H	-3.60671400	0.57781900	0.72144000
26	H	-2.63839900	-0.81099300	0.25898000
27	H	-1.46234900	4.70381500	0.86638500
28	H	-2.74231800	4.19606700	-0.25392900
29	H	-2.53894600	3.36157100	1.29834500
30	H	-2.29985600	-0.30003800	2.69040400
31	H	-0.77224900	0.02366300	1.84919400
32	H	-1.82878100	1.36911400	2.31542500
33	H	-1.59876100	-0.60004600	-3.39706400
34	H	-1.52383900	-1.65016500	-1.97610400
35	H	-0.10006600	-1.49270700	-3.03905600

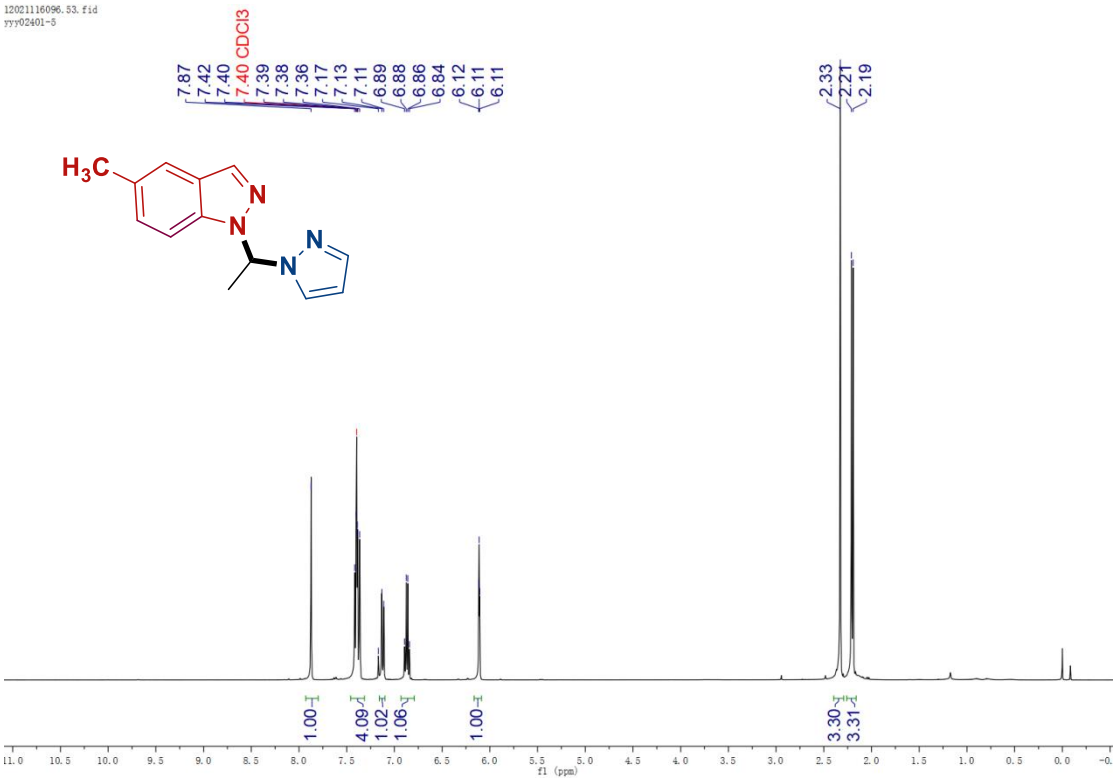
5 NMR Spectra



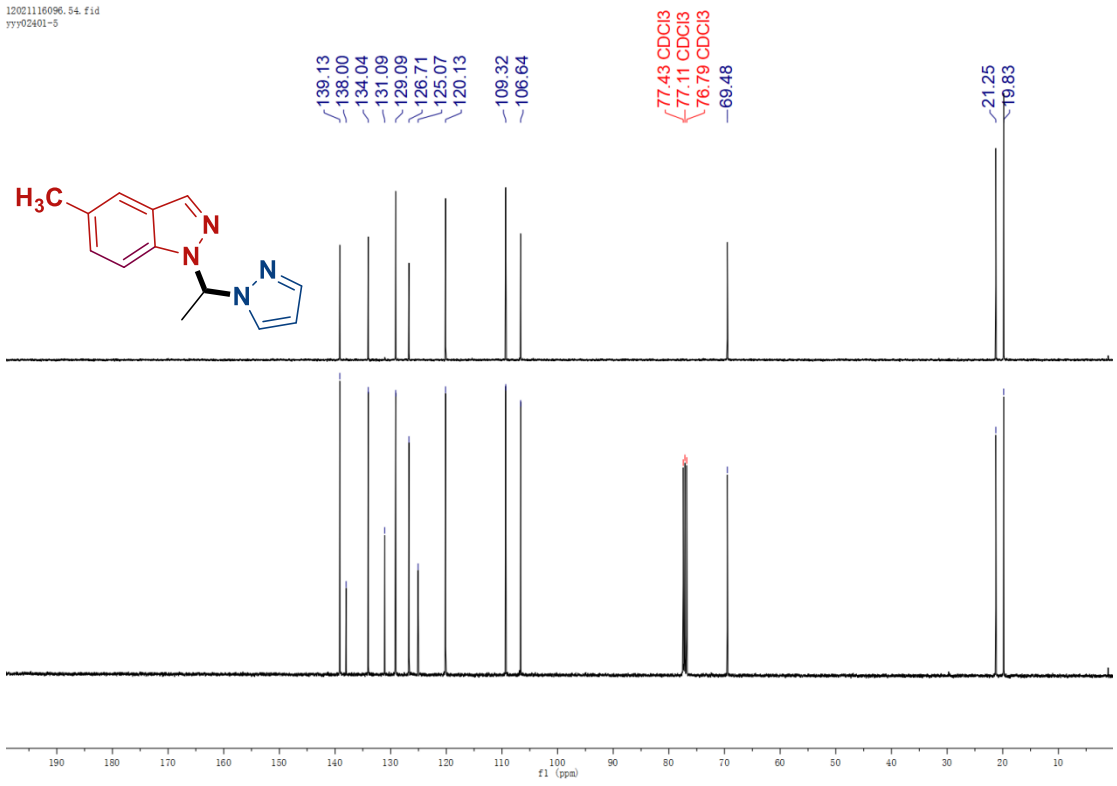
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 4**



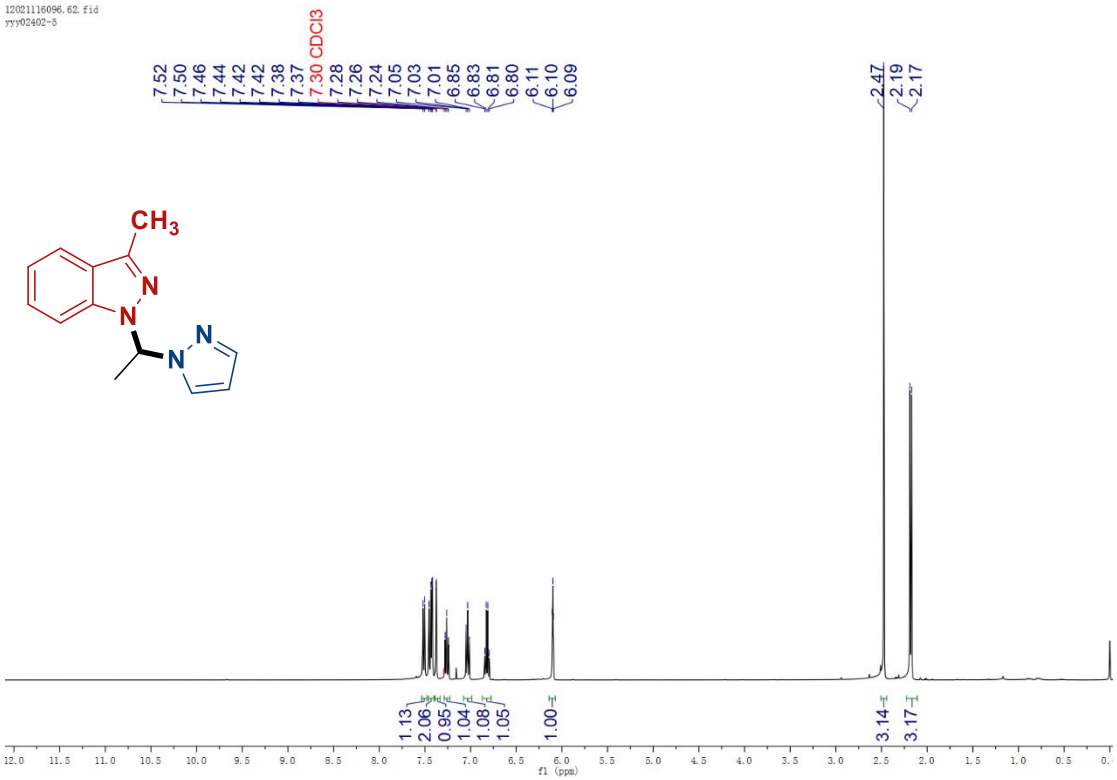
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 4**



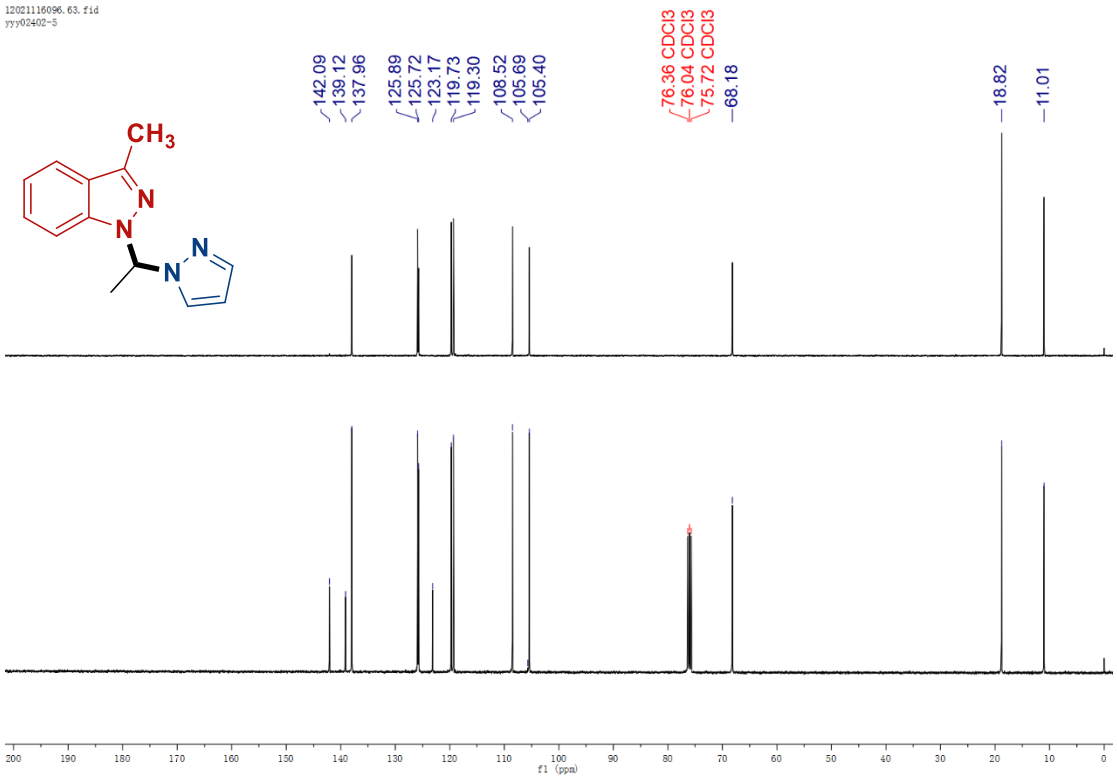
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 5**



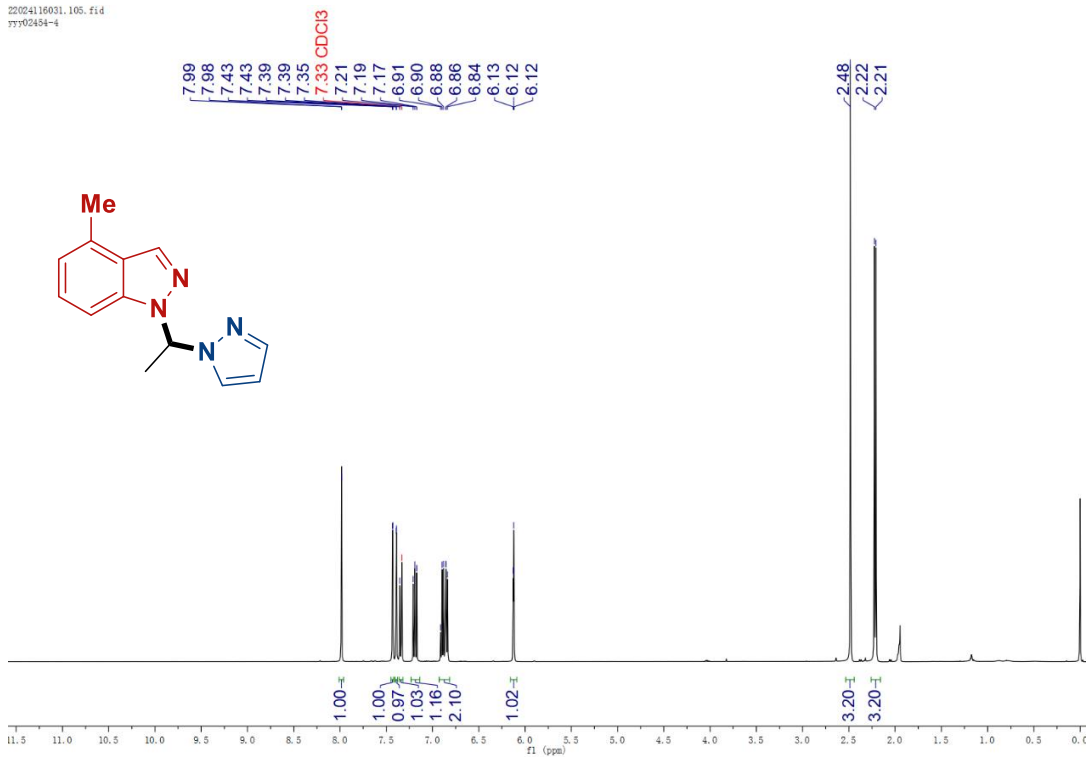
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 5**



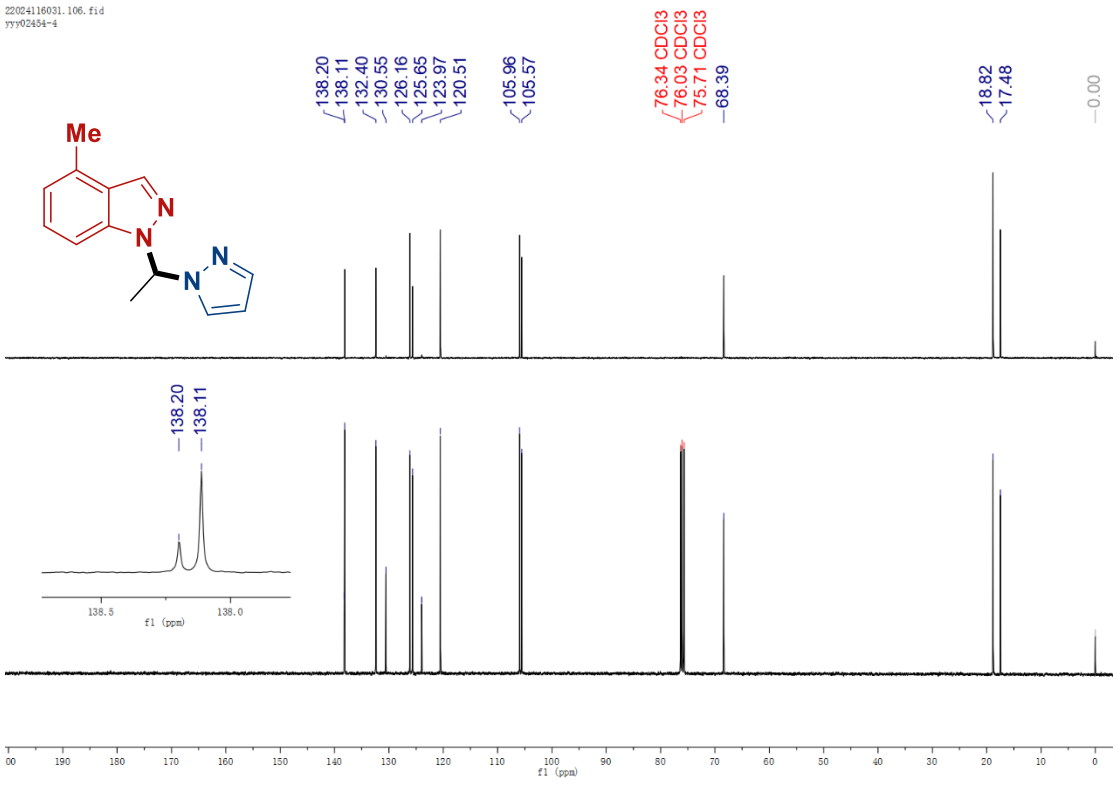
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 6**



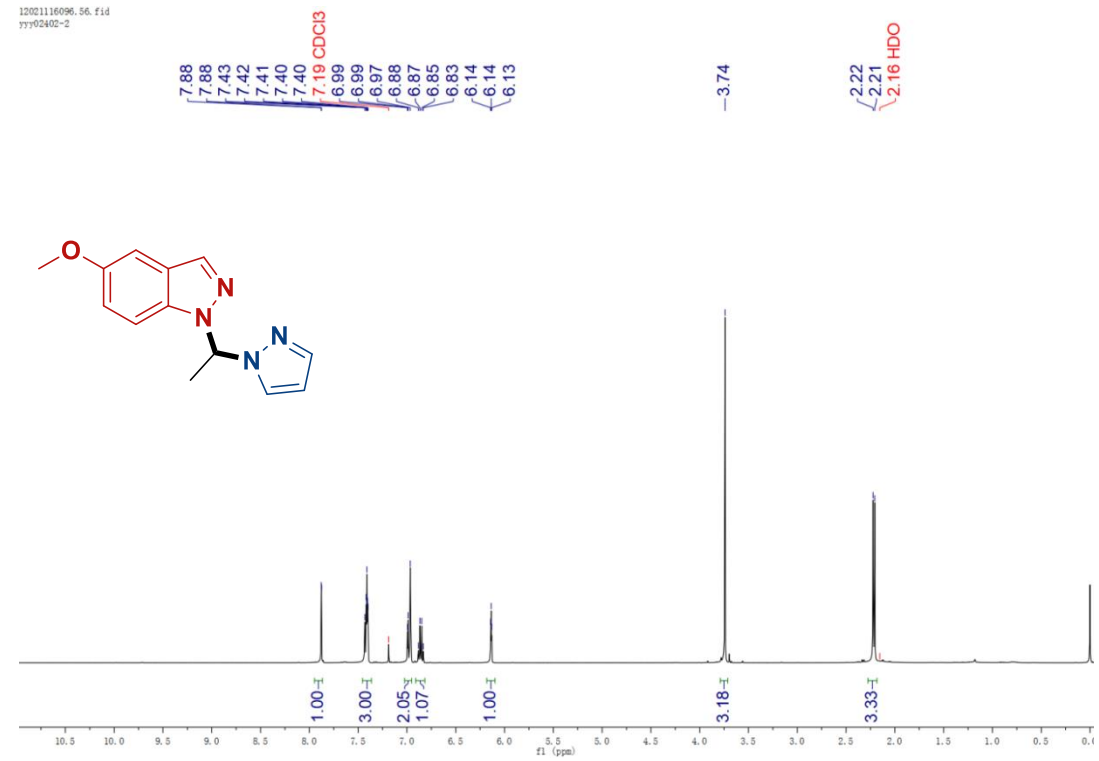
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 6**



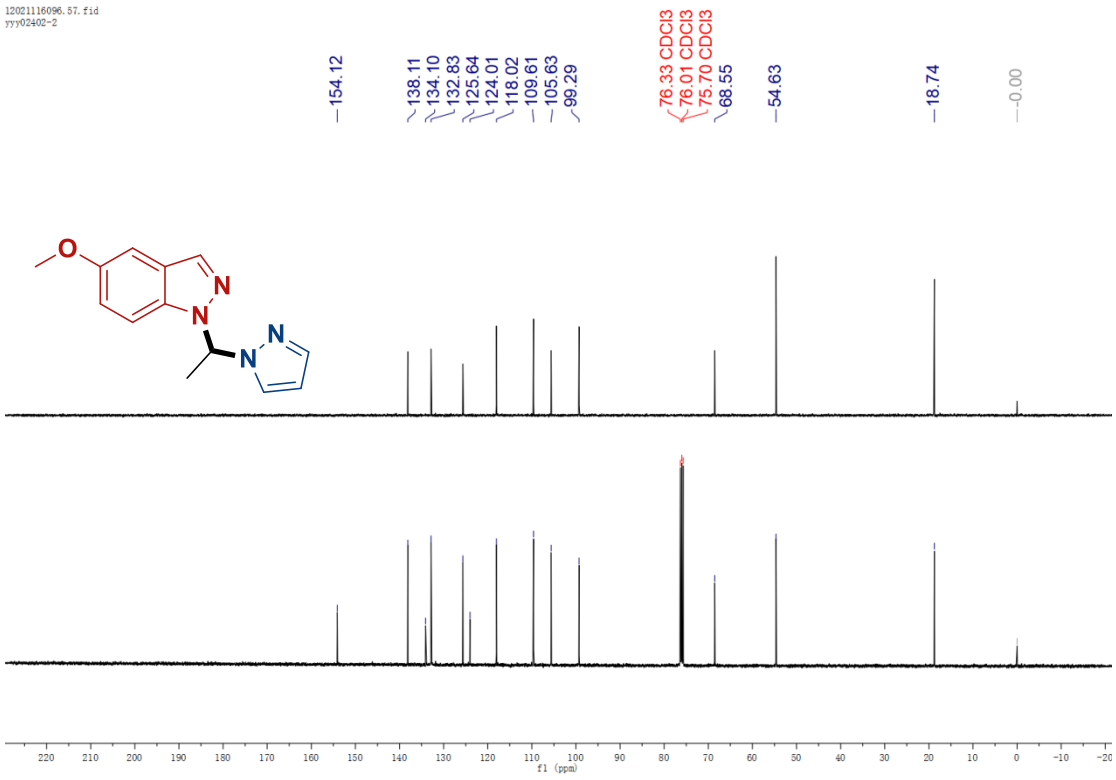
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 7**



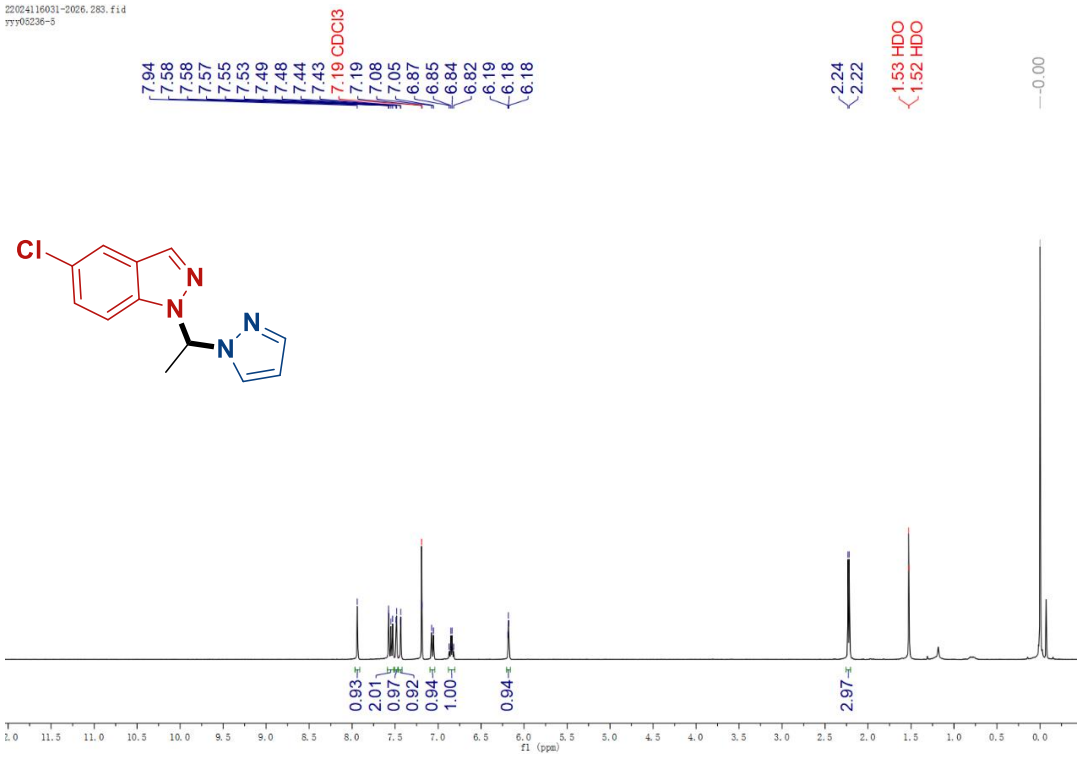
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 7**



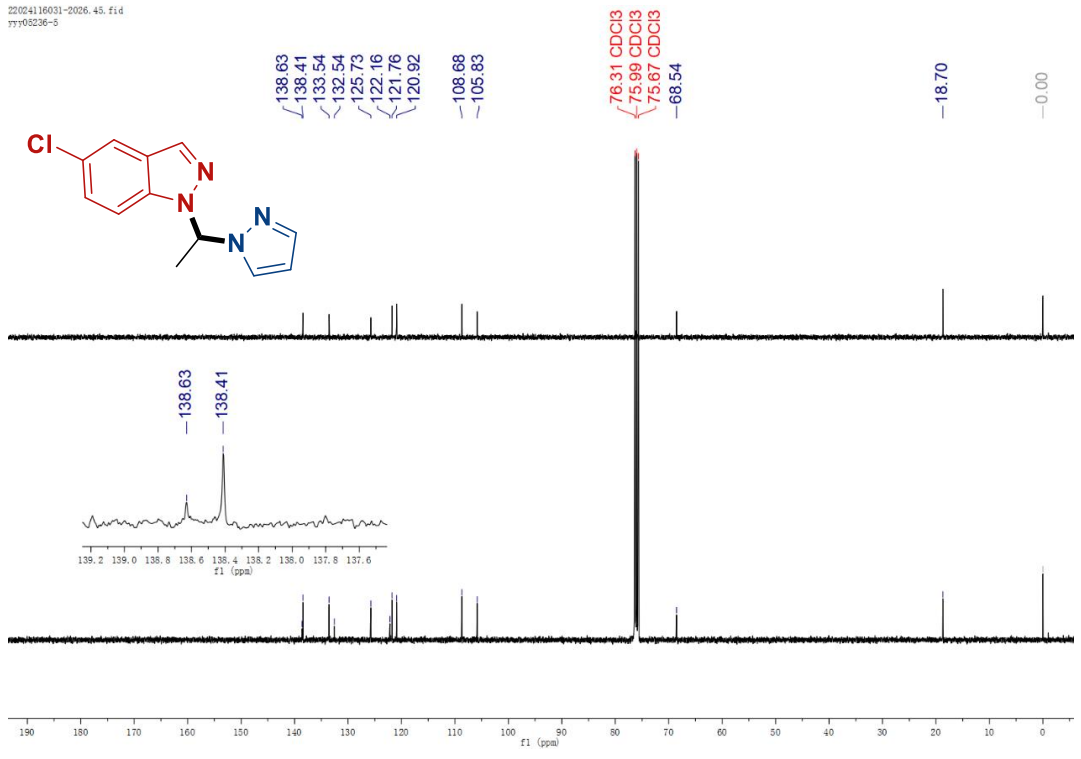
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 8**



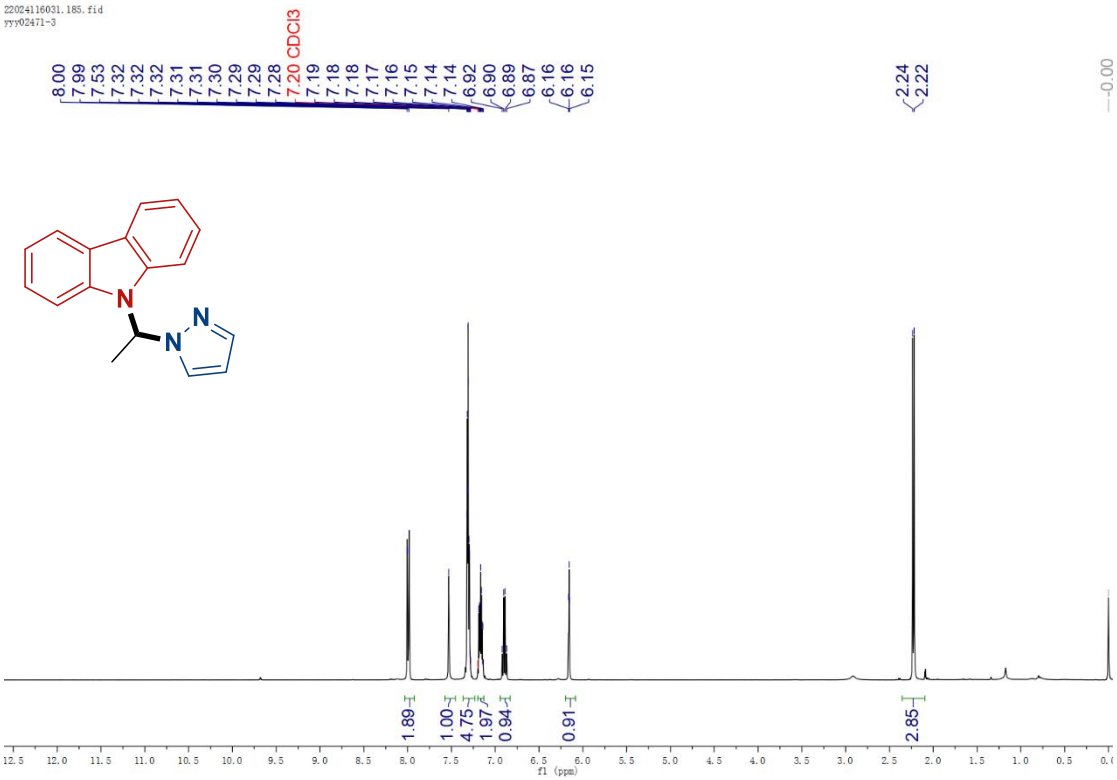
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 8**



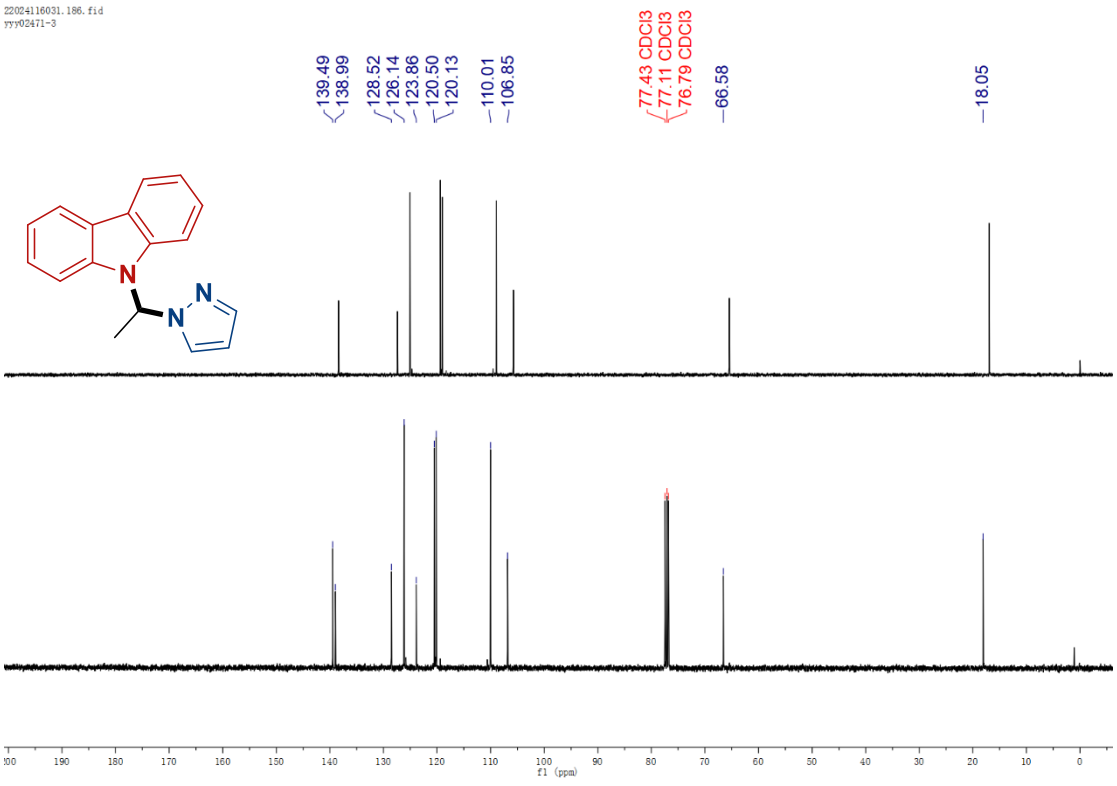
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 9**



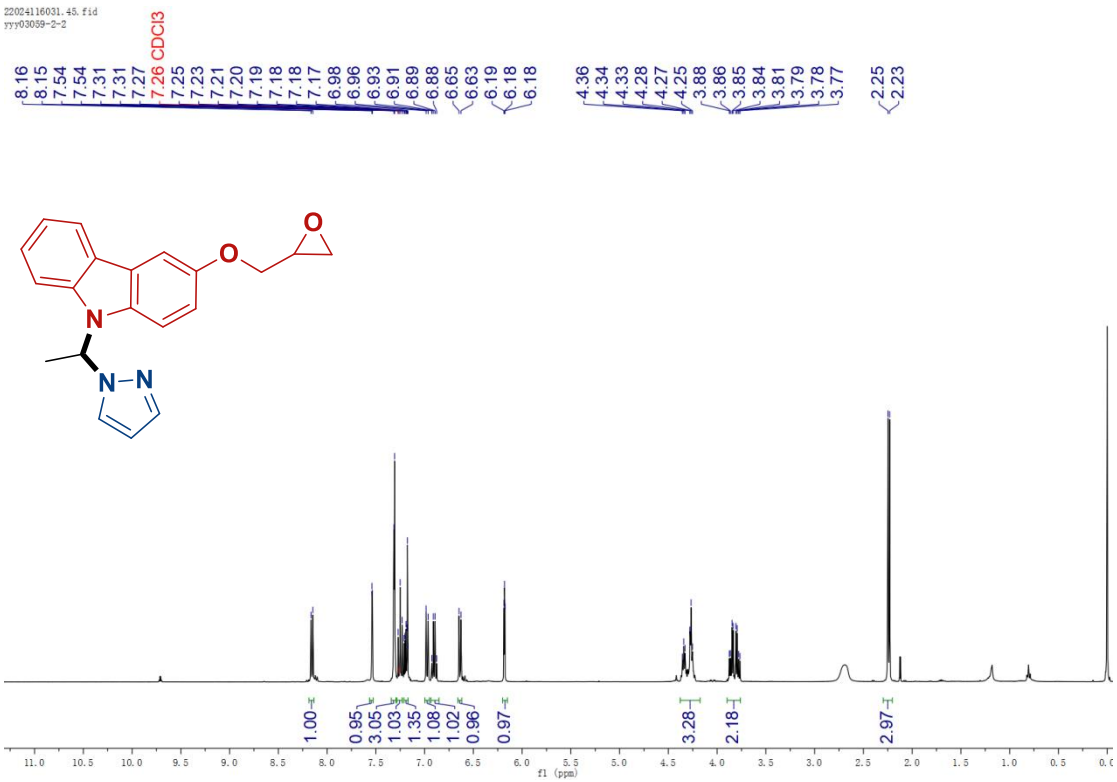
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 9**



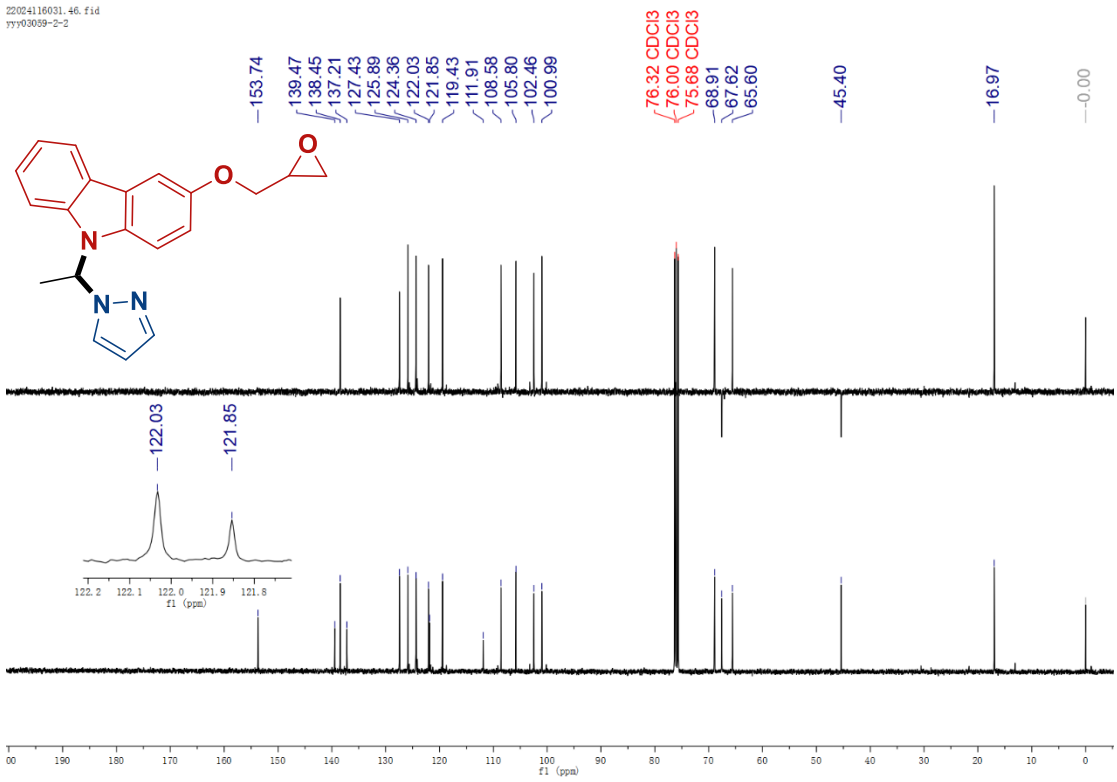
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 10**



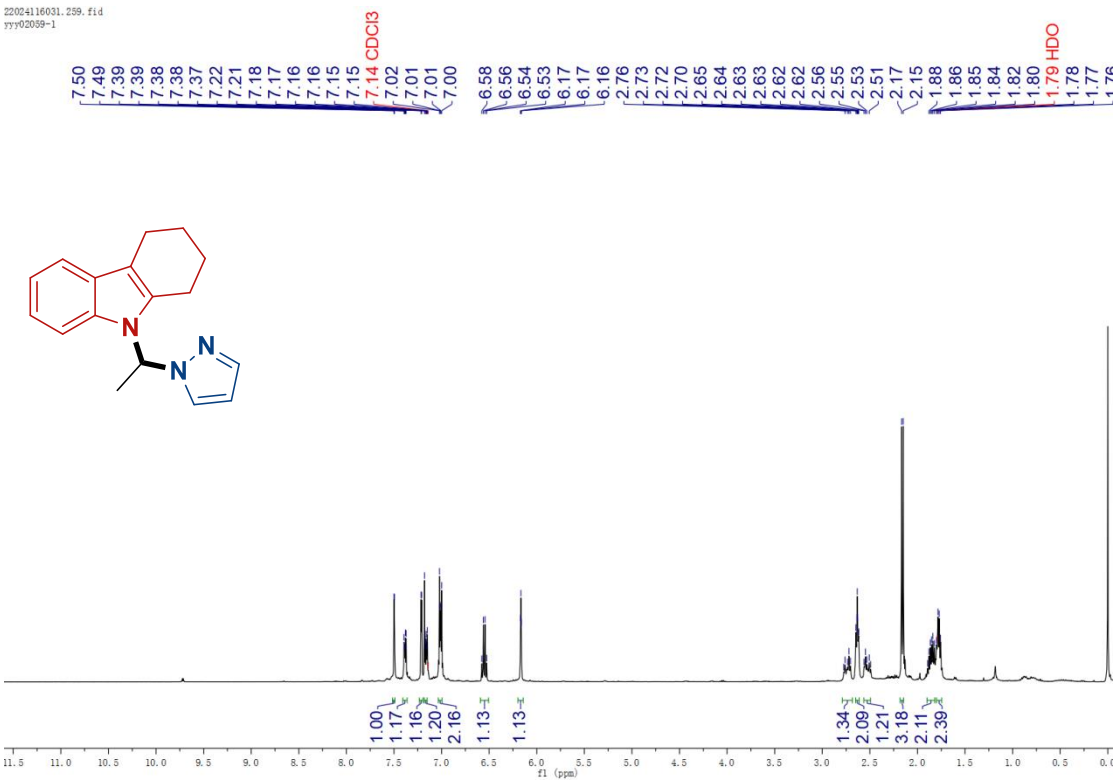
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 10**



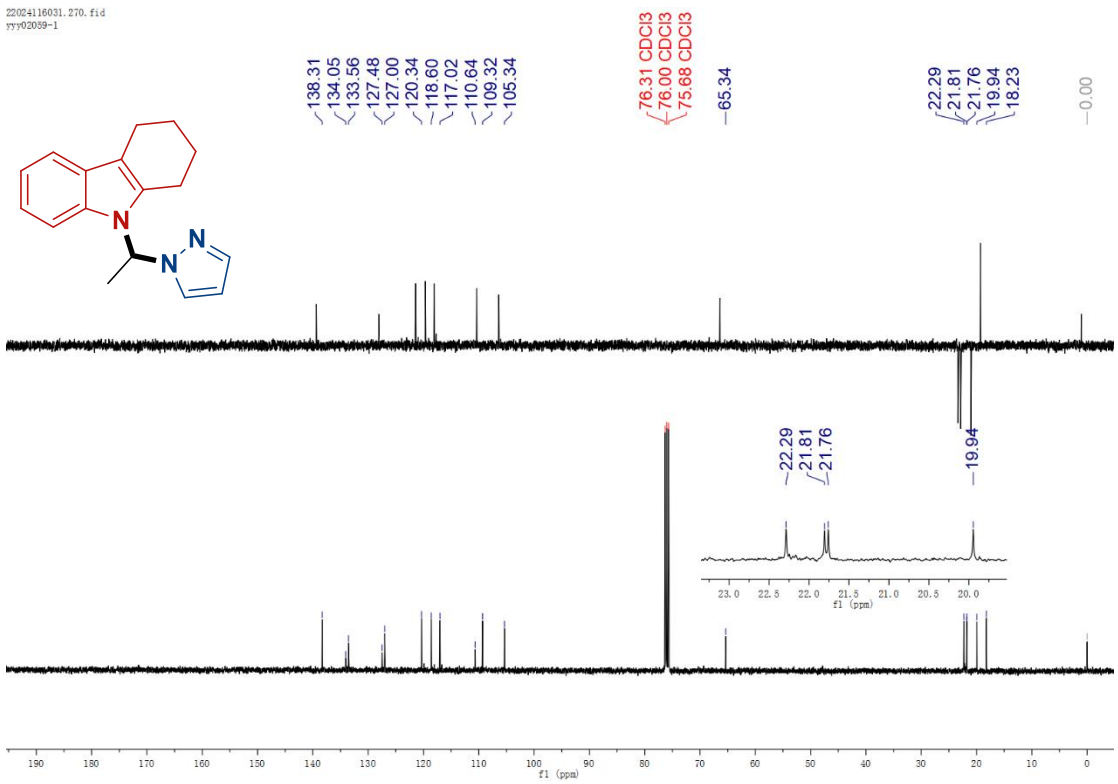
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 11**



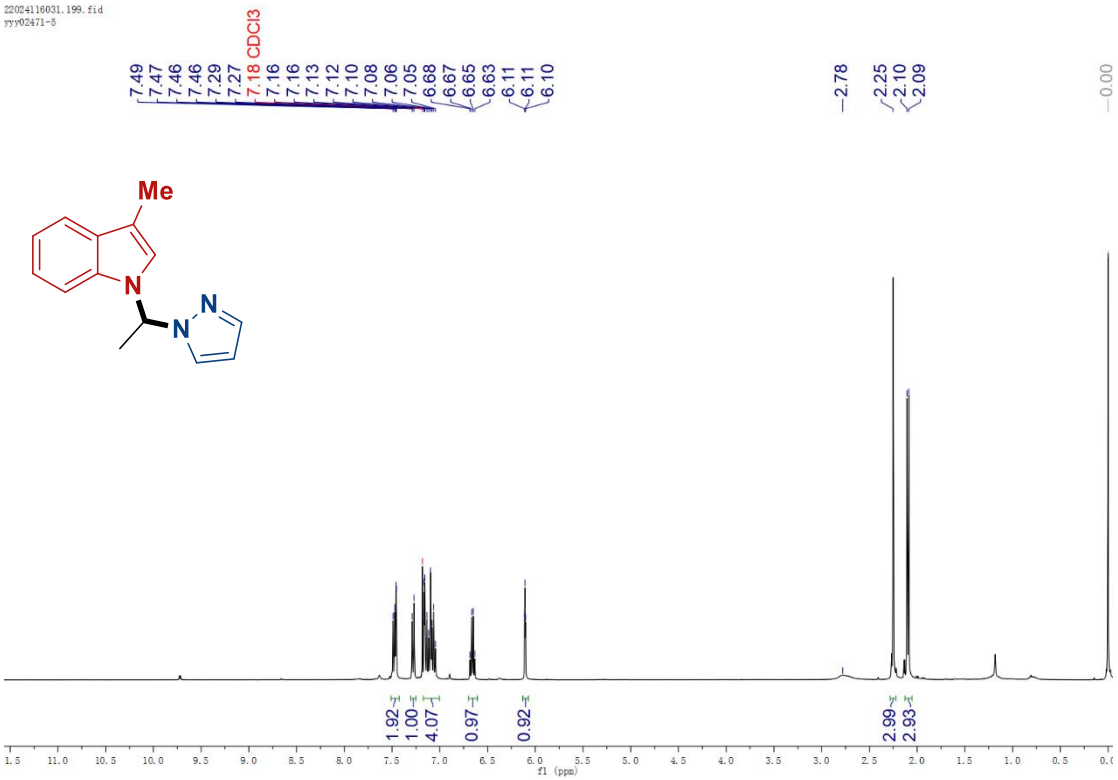
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 11**



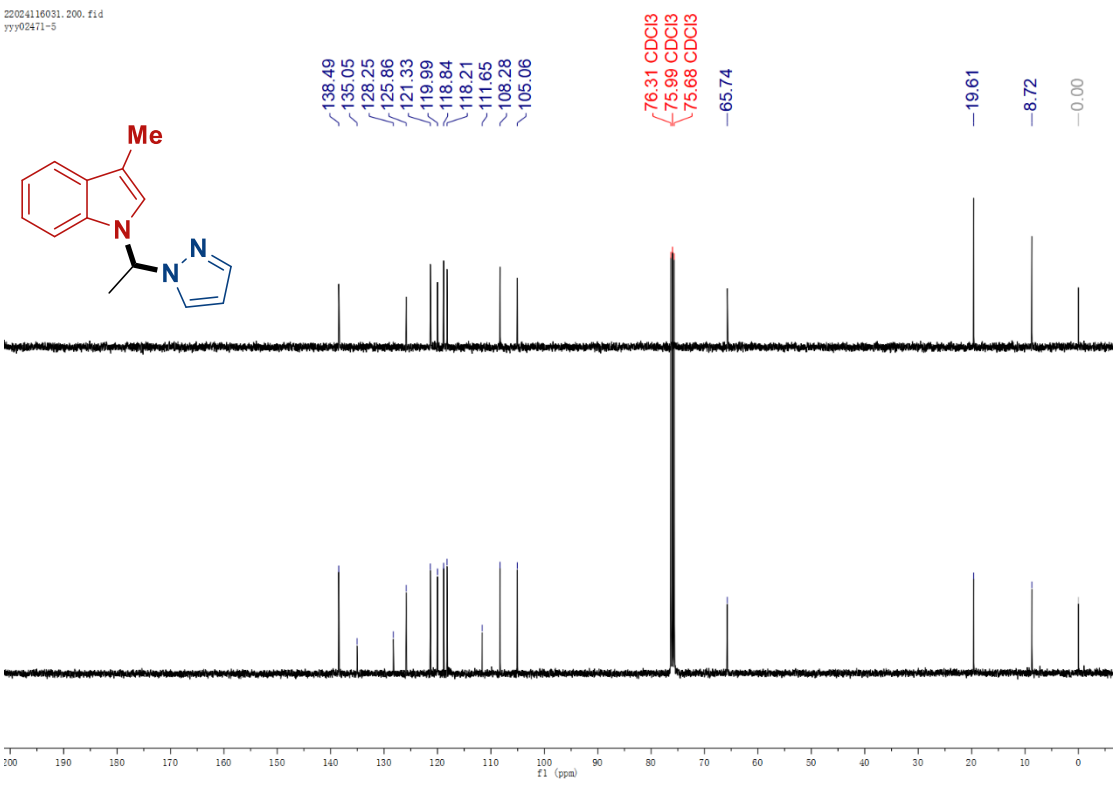
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 12**



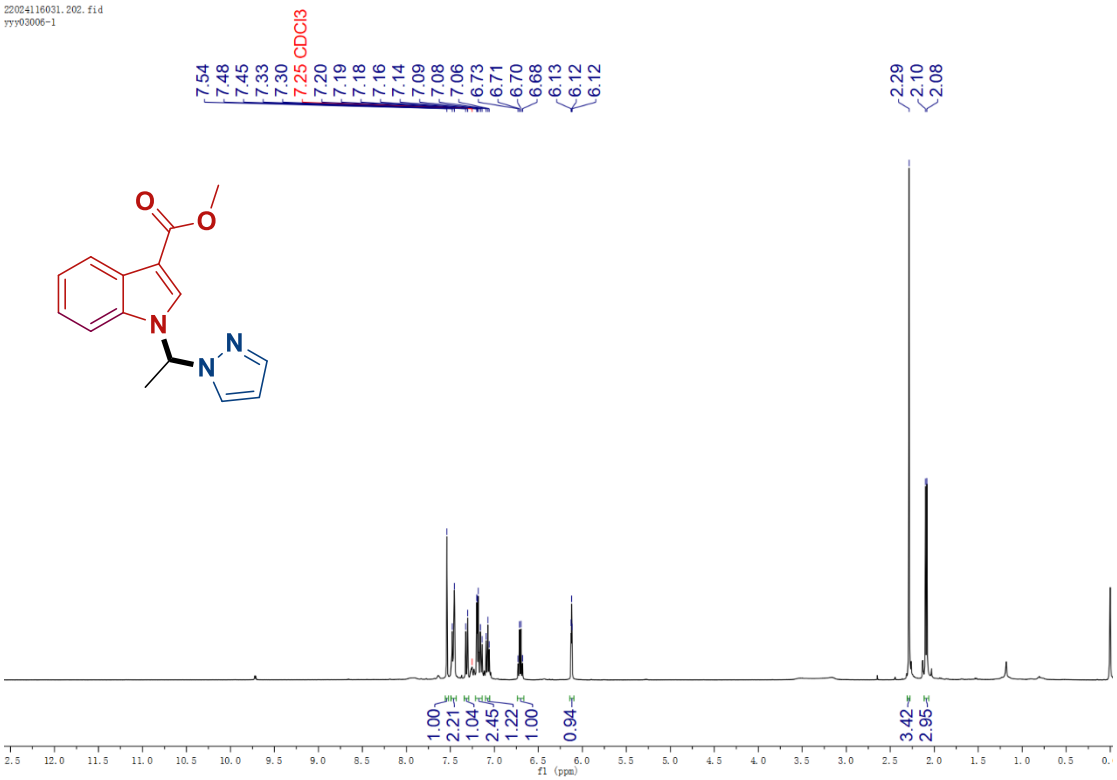
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 12**



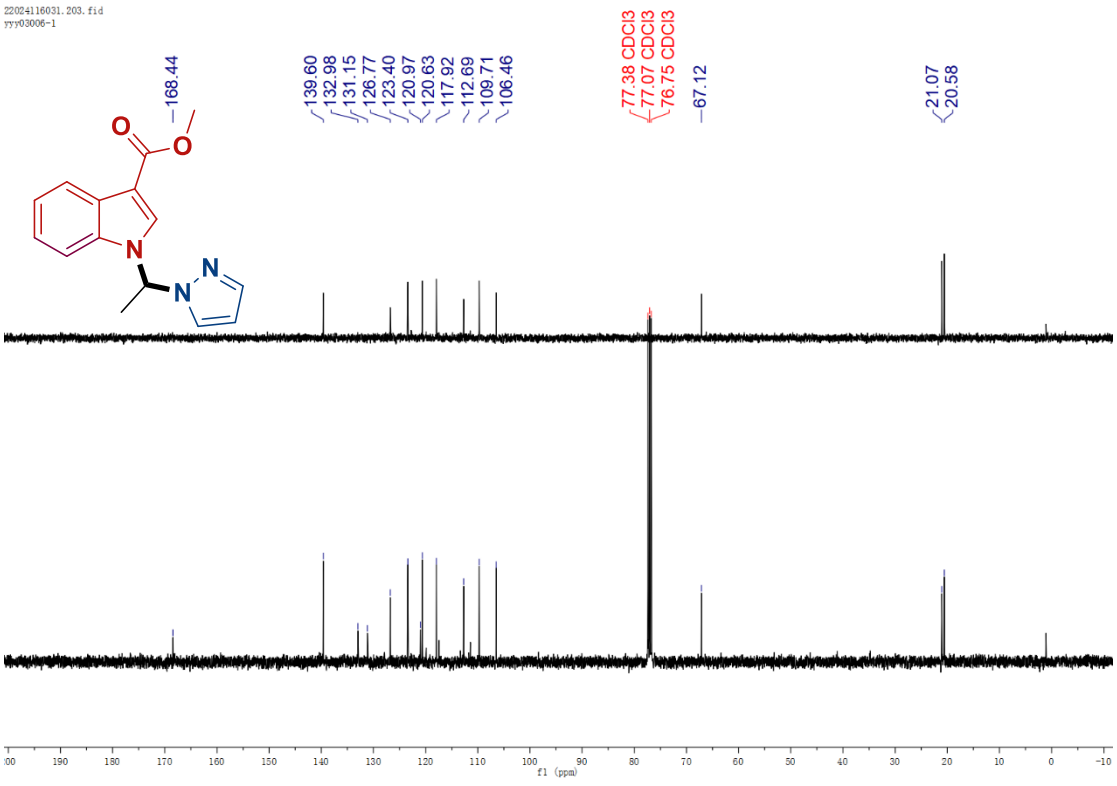
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 13**



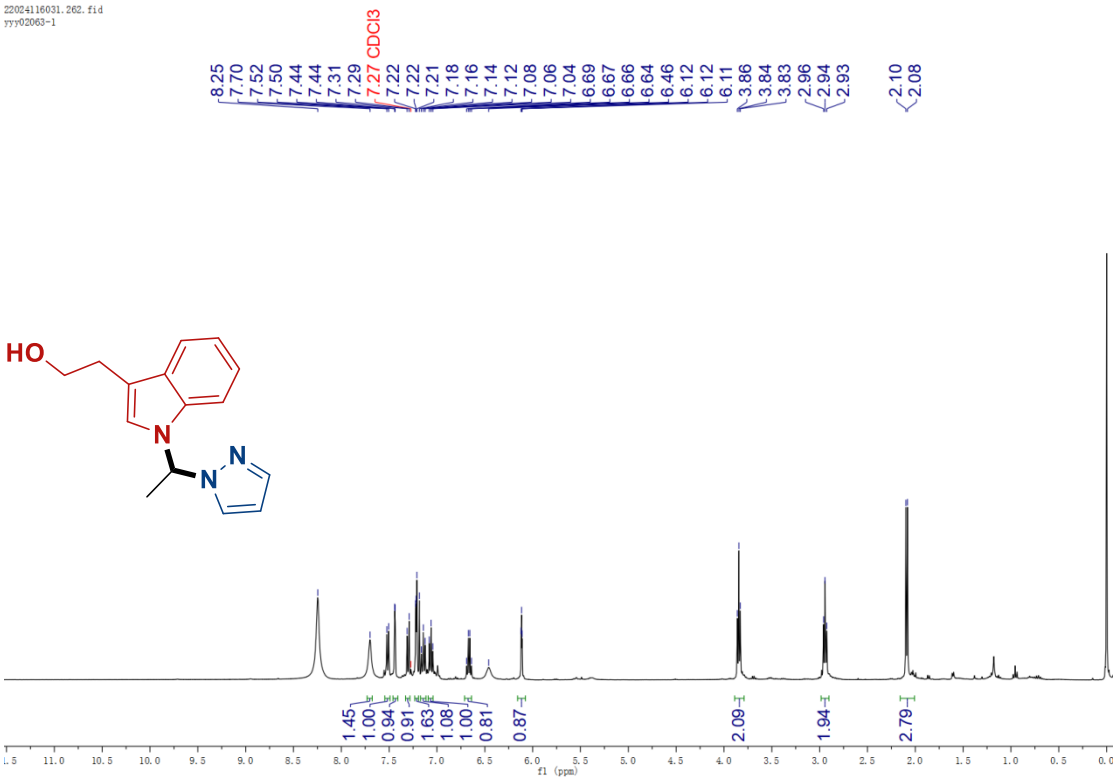
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 13**



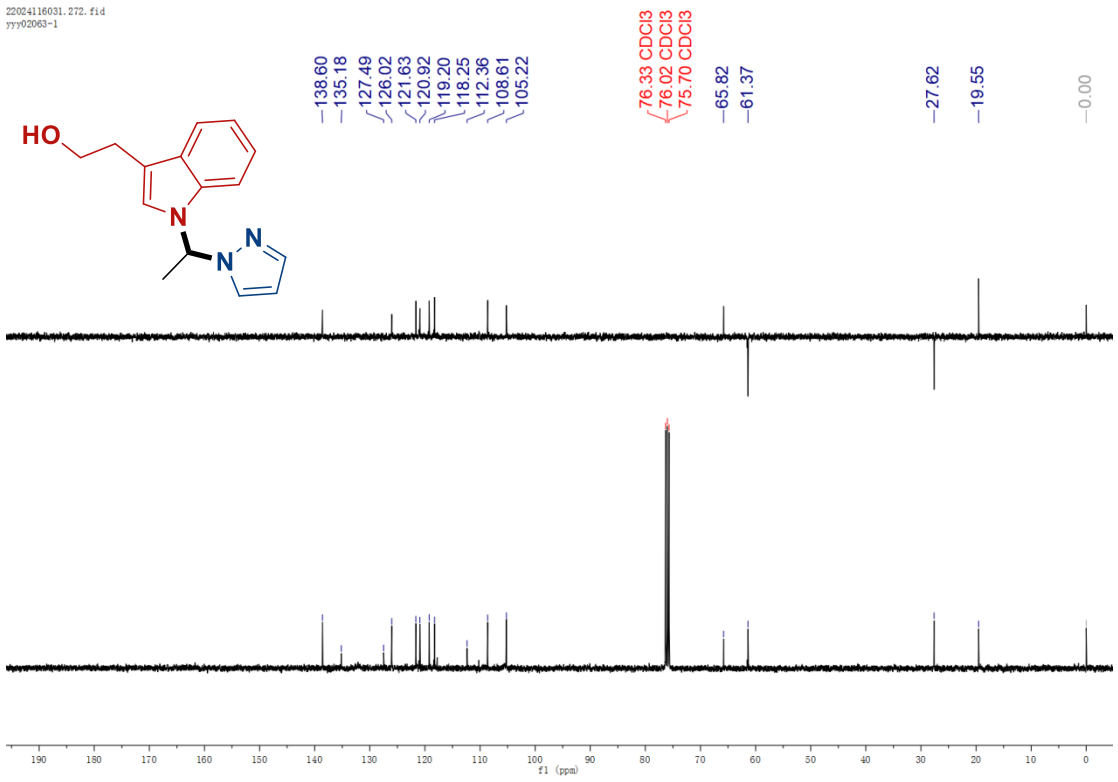
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 14**



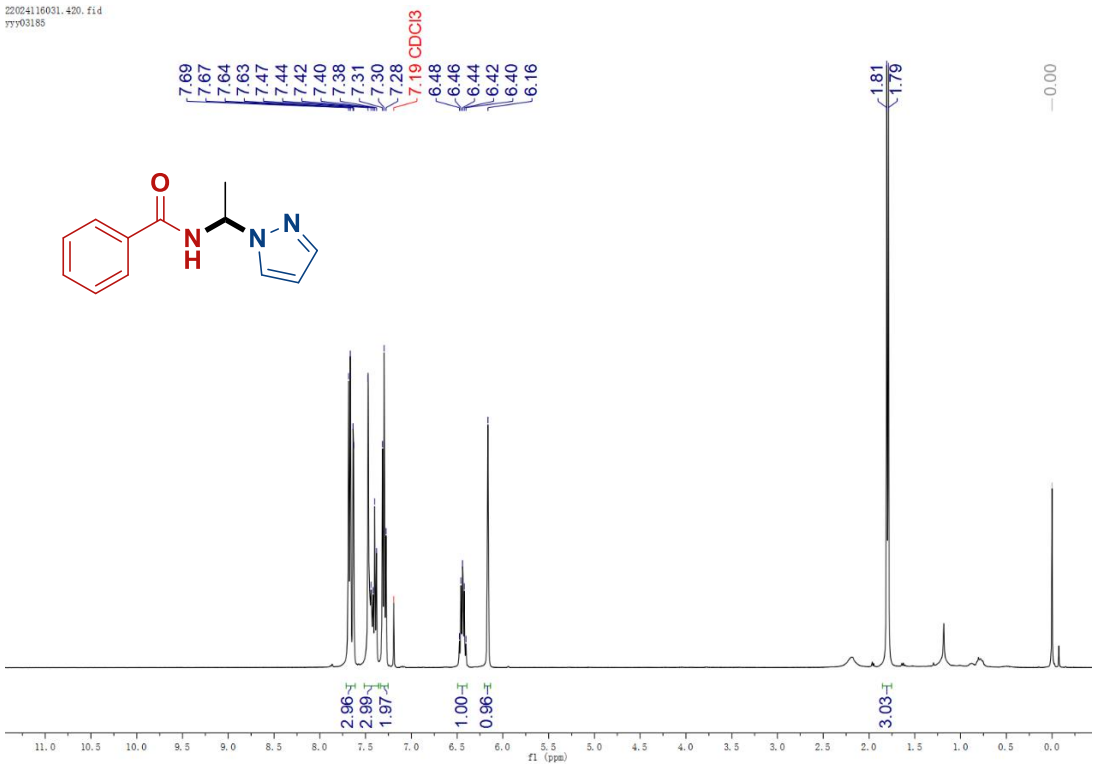
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 14**



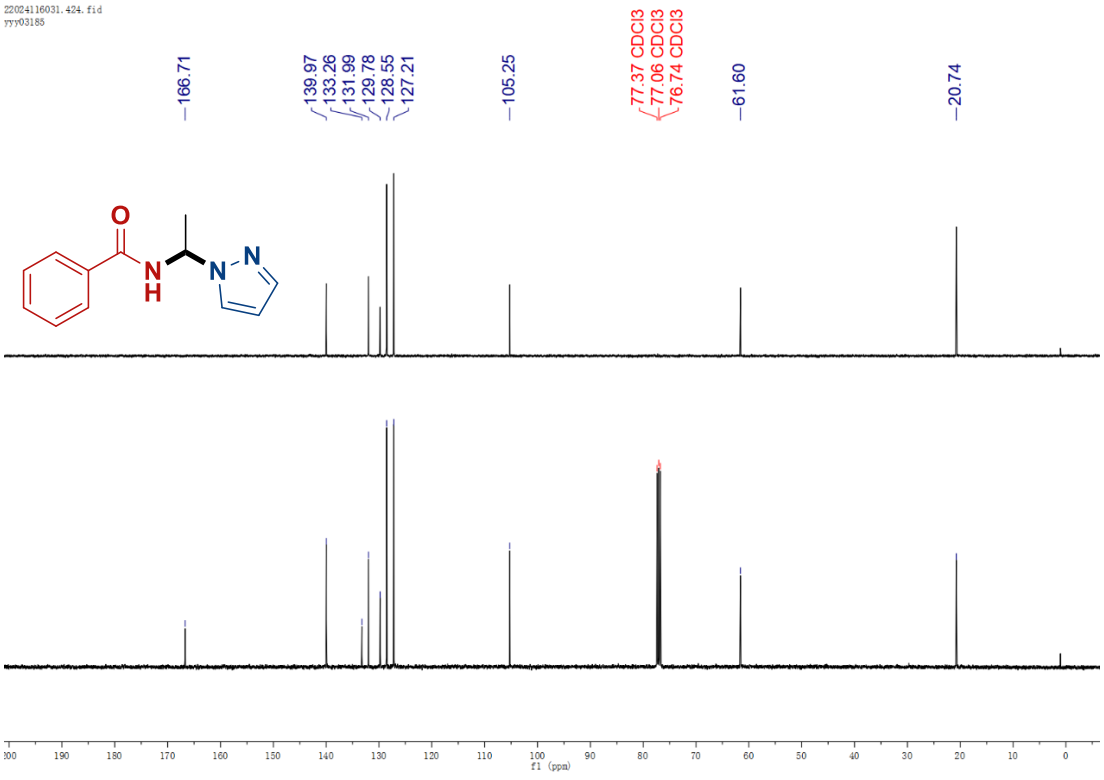
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 15**



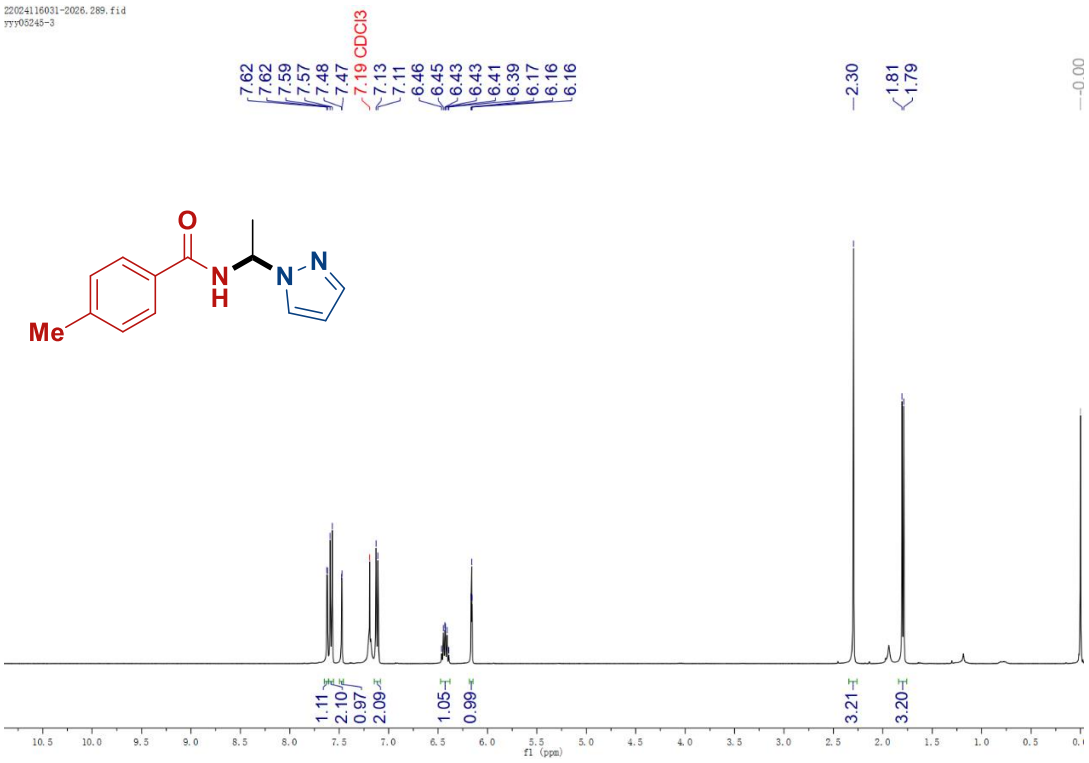
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 15**



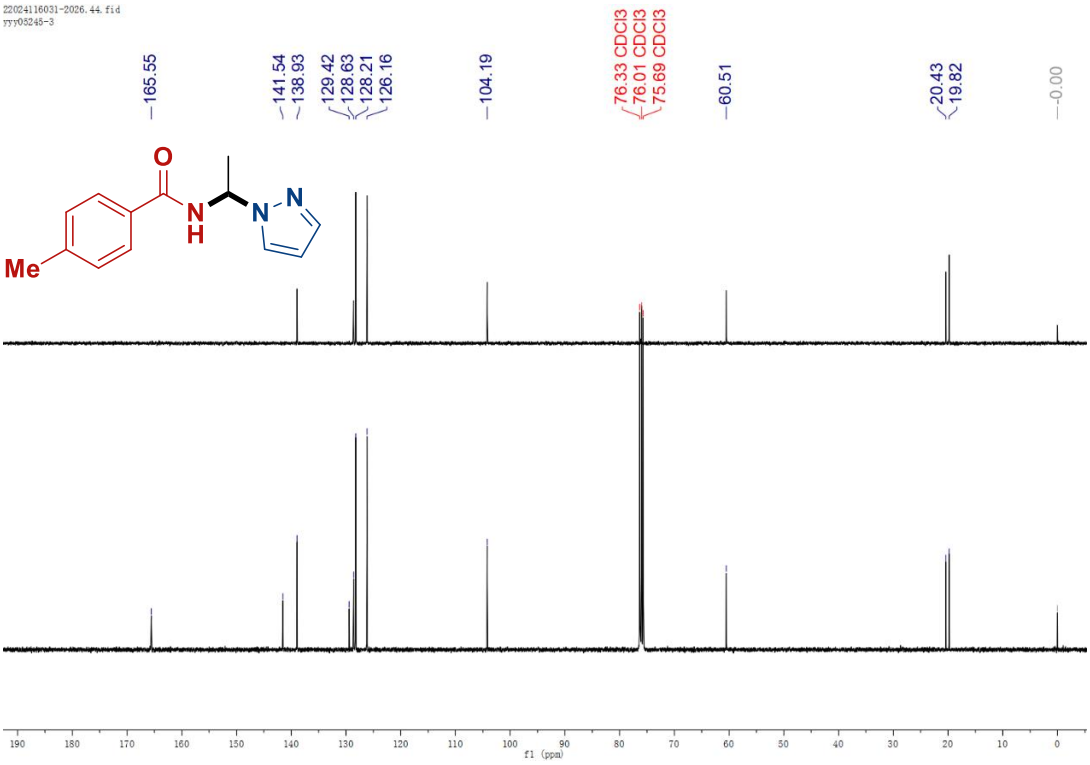
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 16**



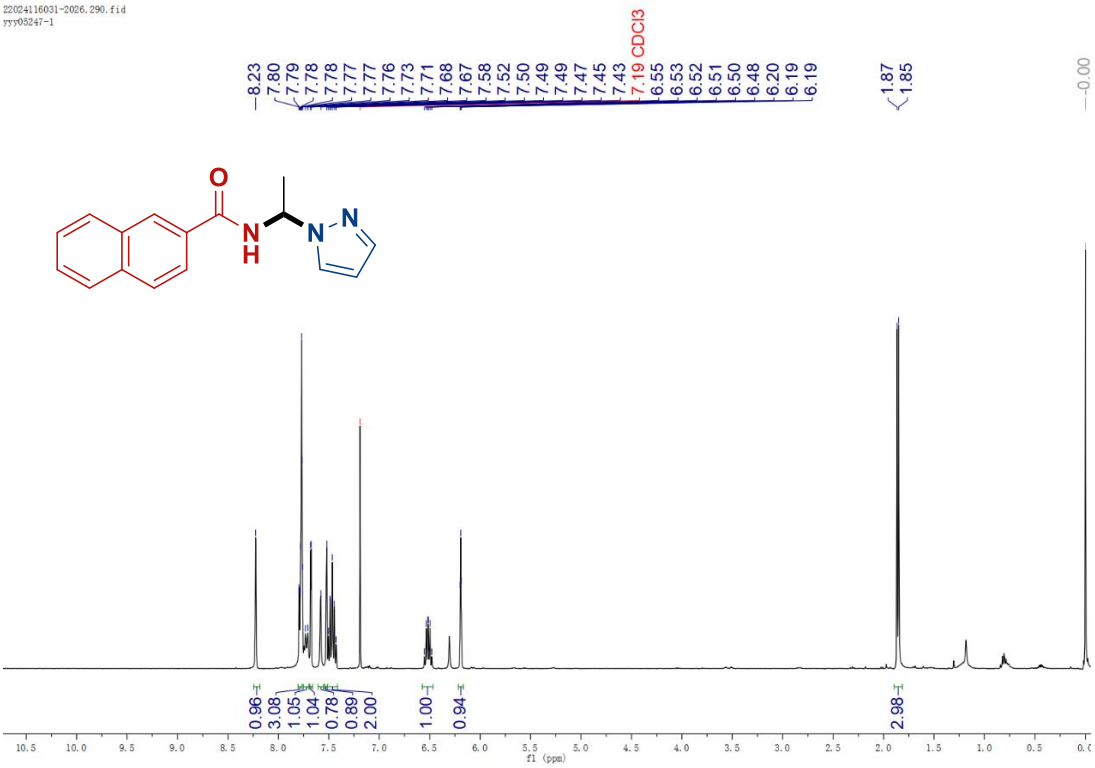
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 16**



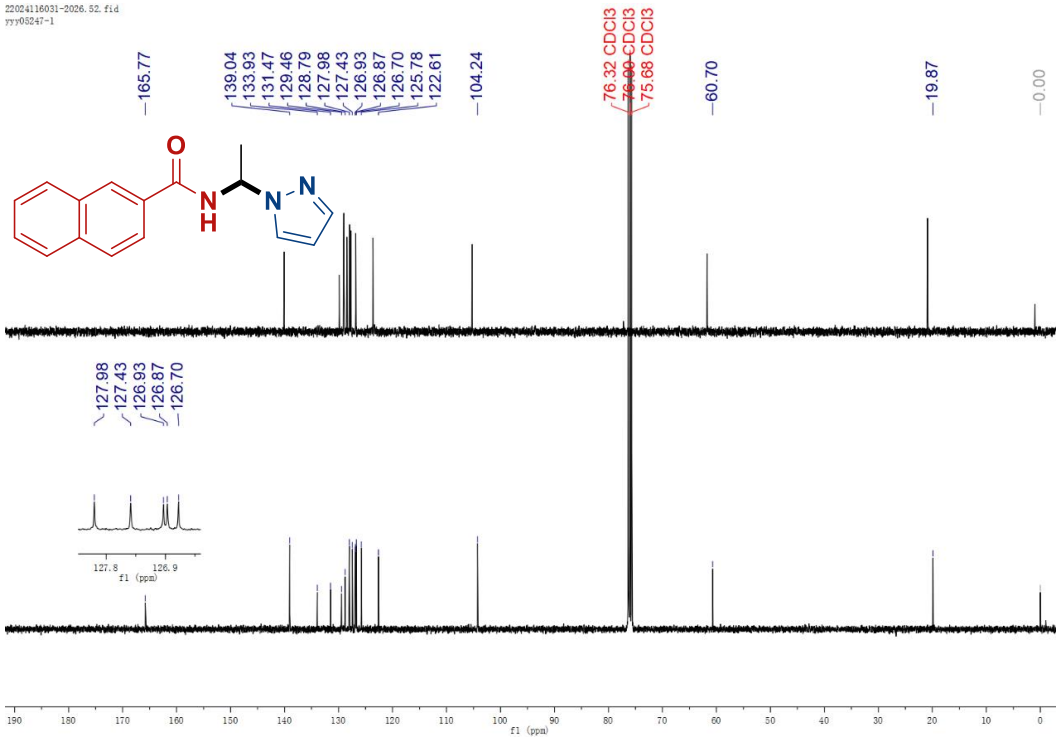
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 17**



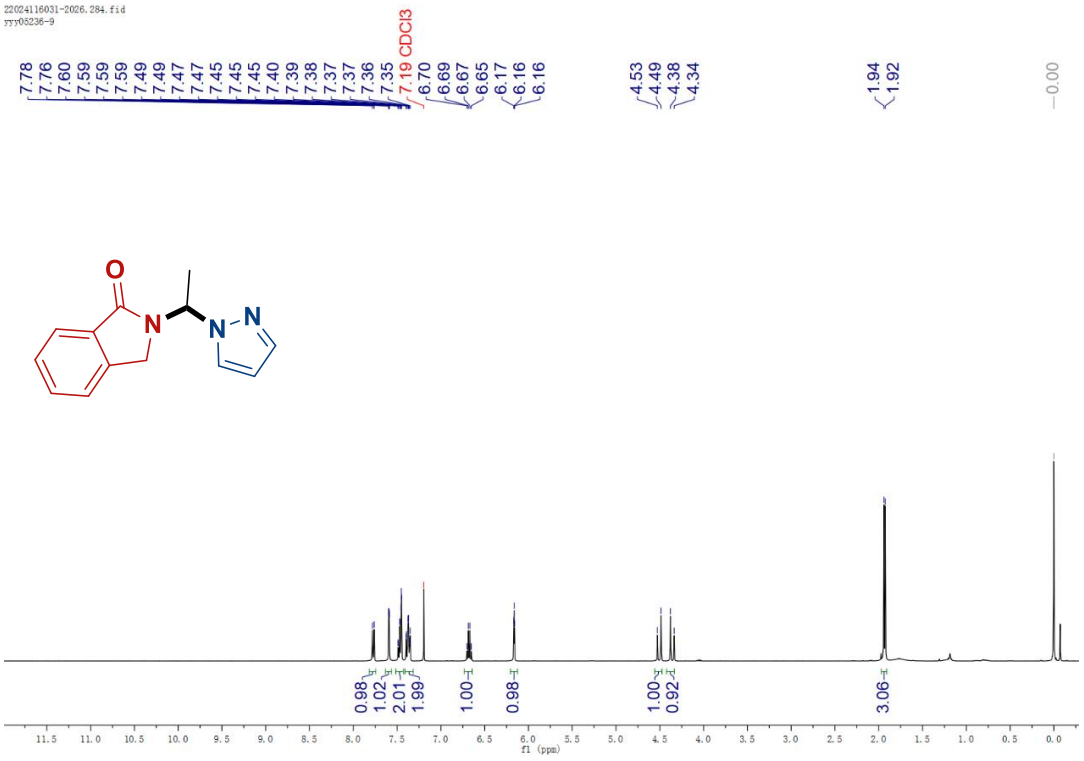
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 17**



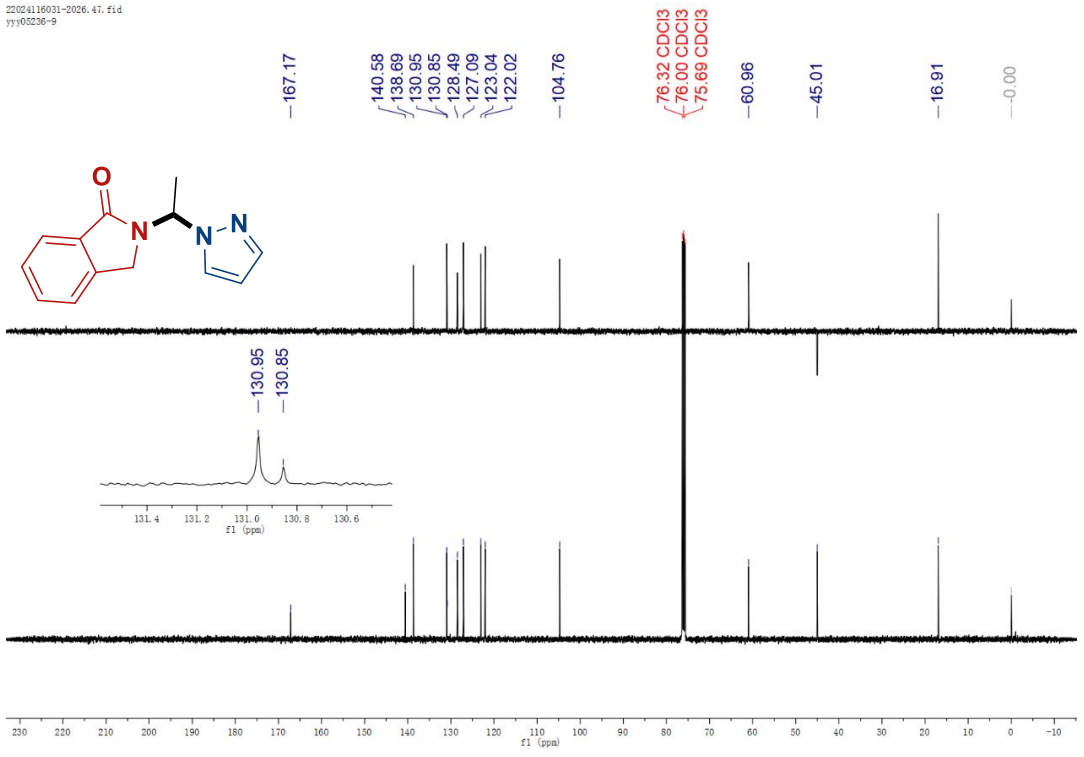
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 18**



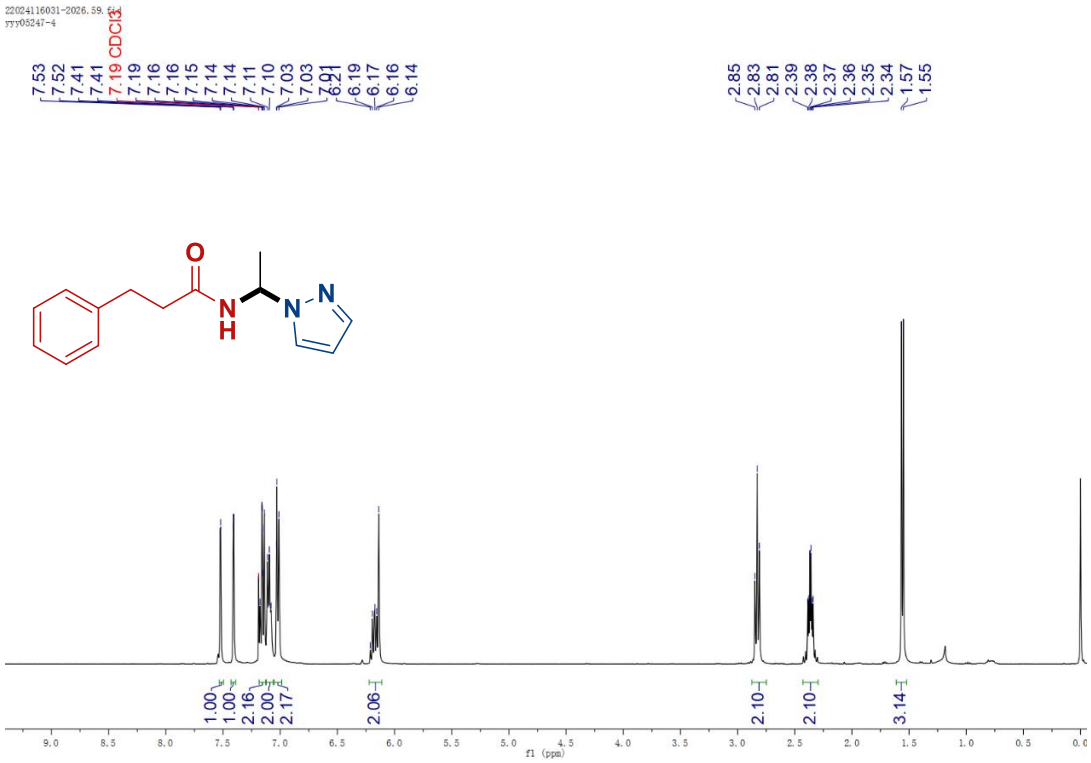
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 18**



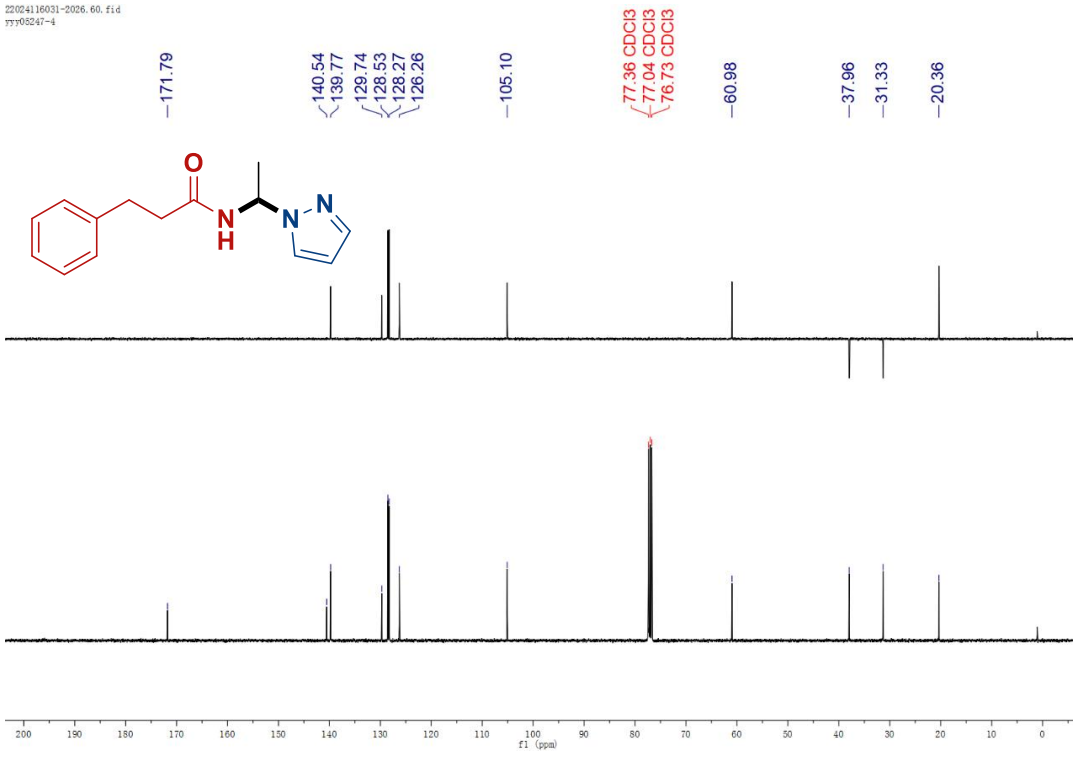
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 19**



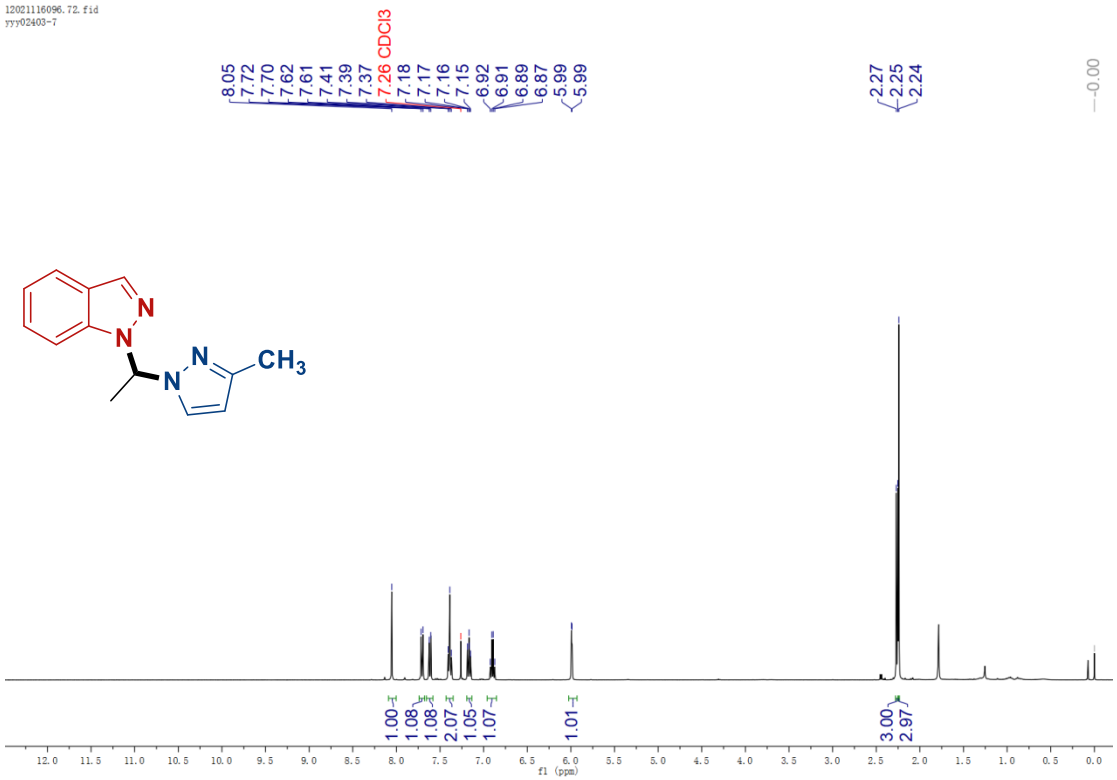
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 19**



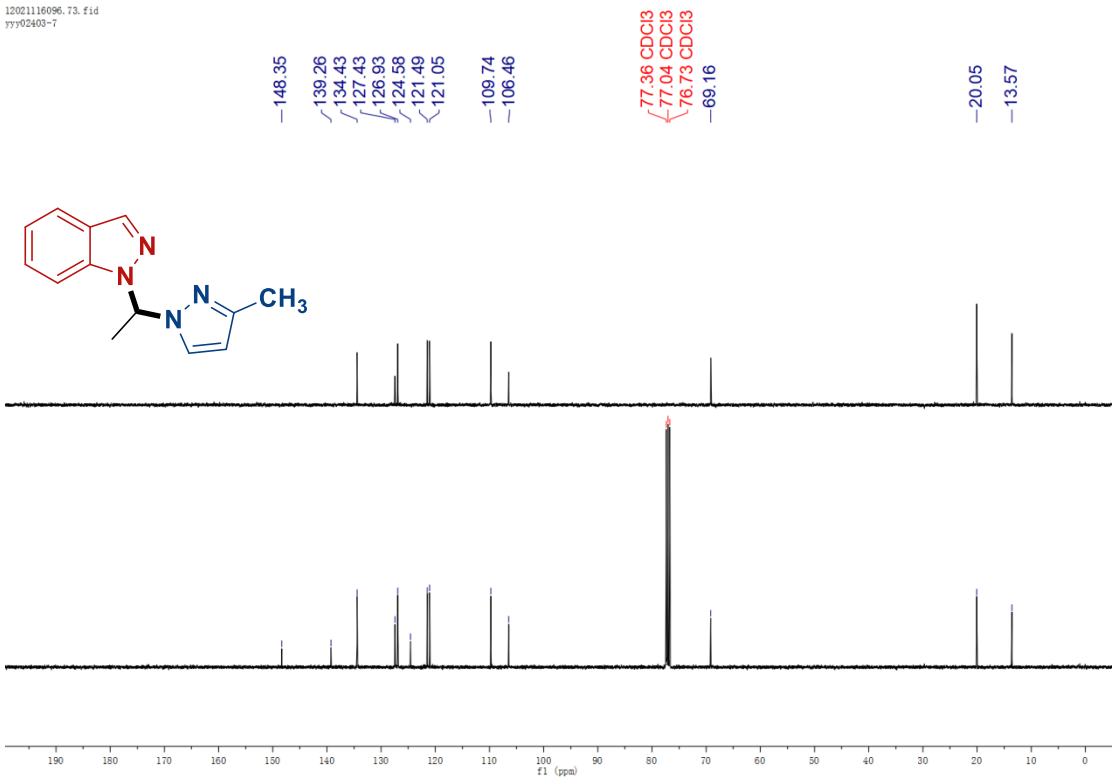
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 20**



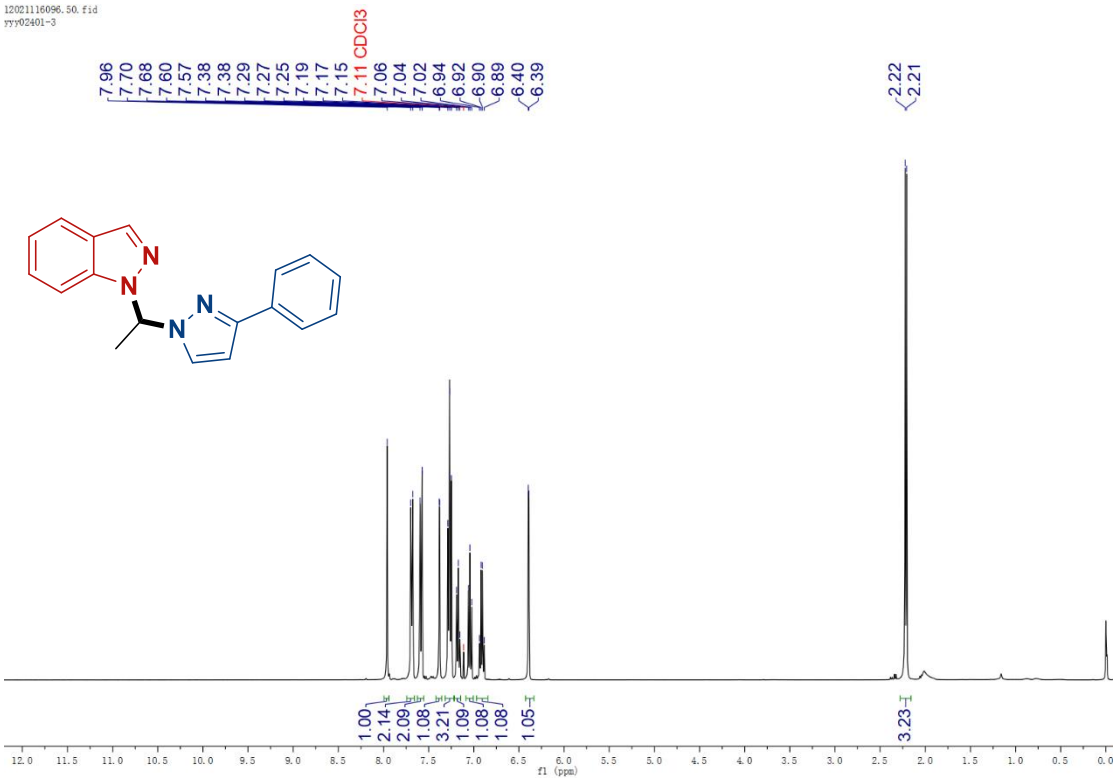
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 20**



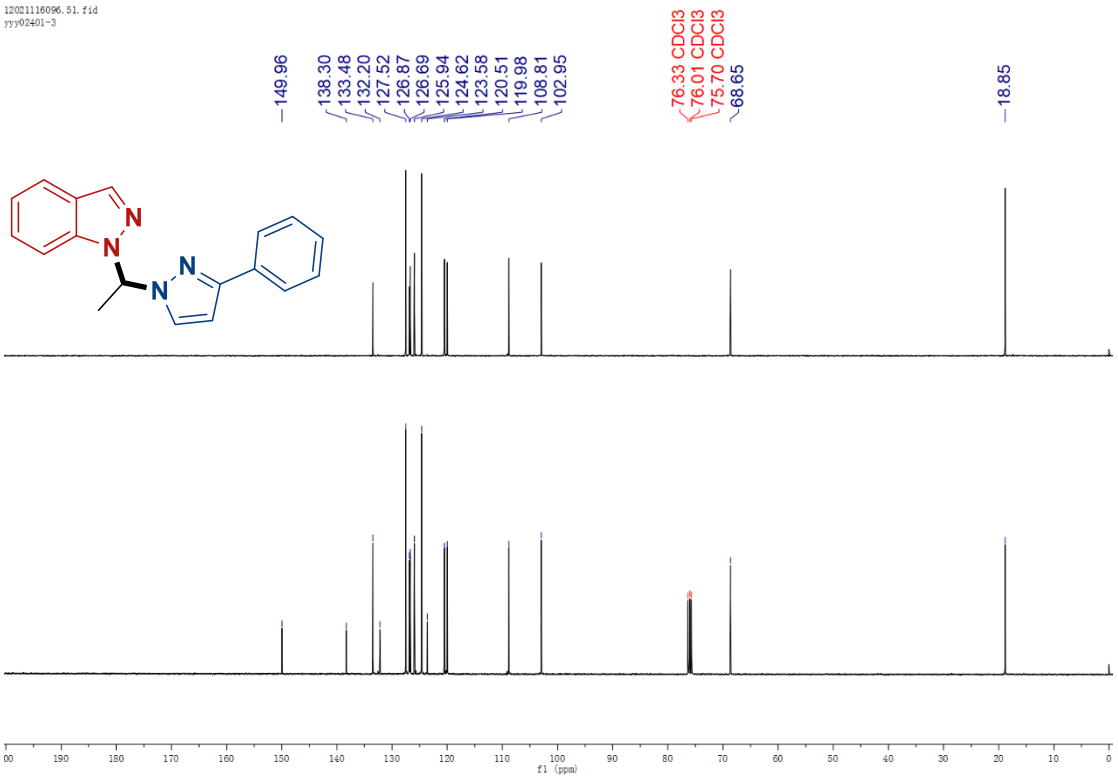
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 21**



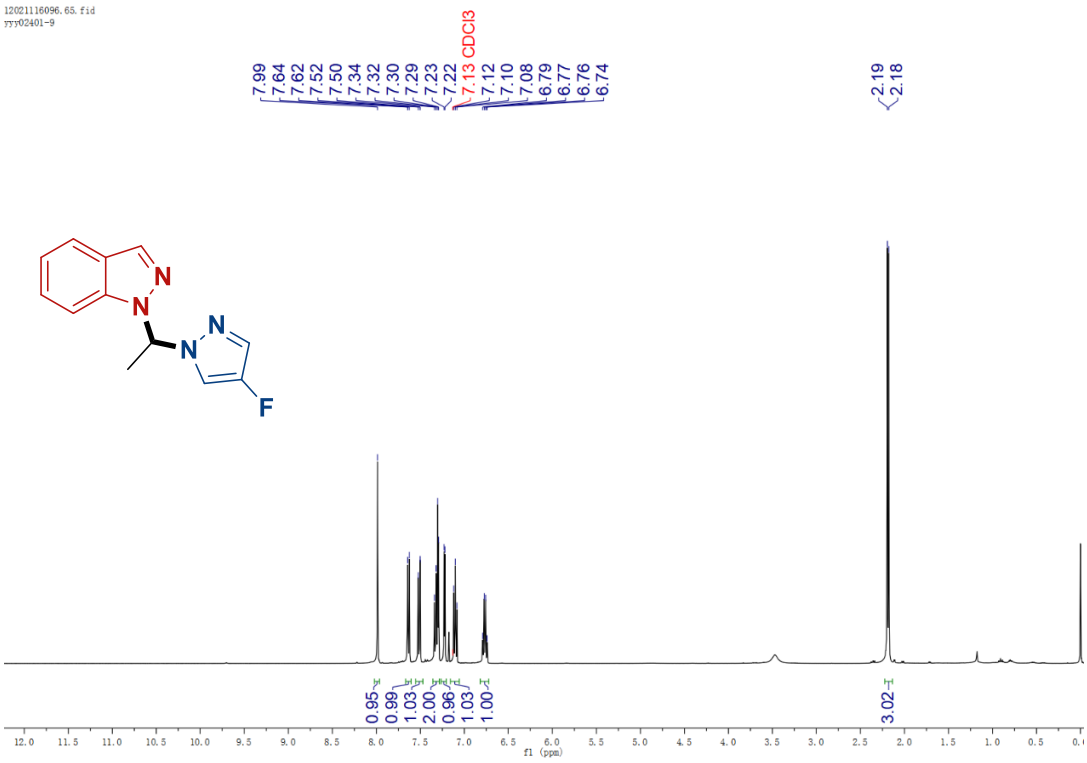
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 21**



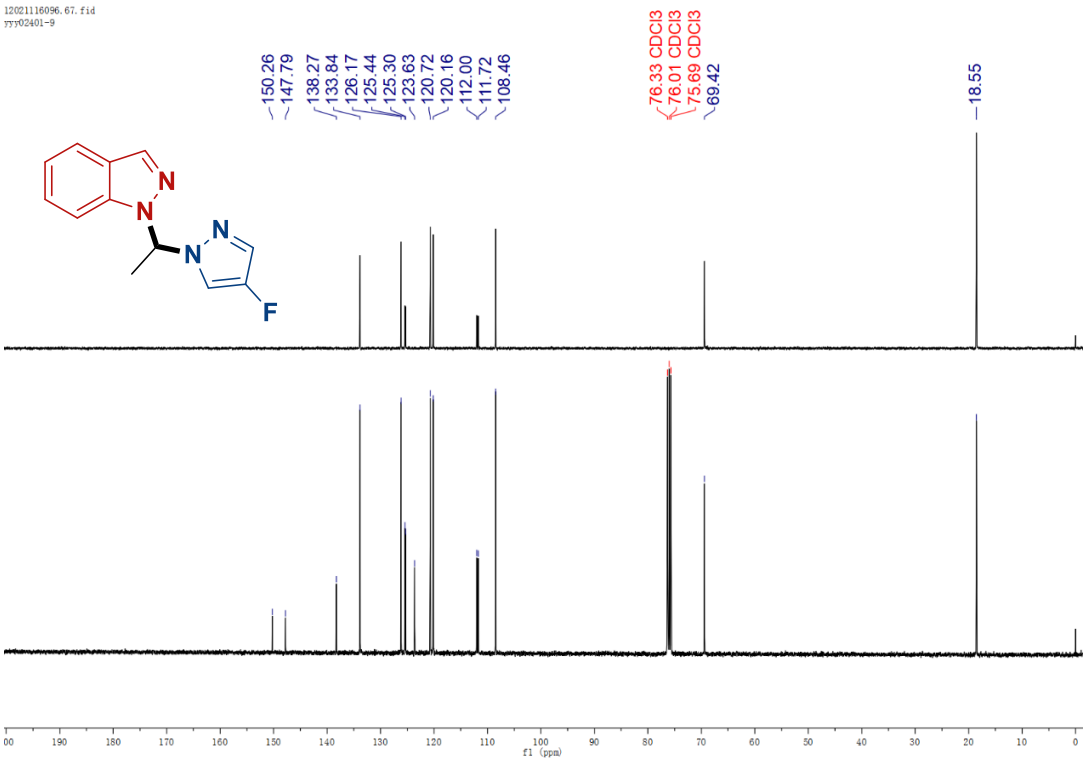
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 22**



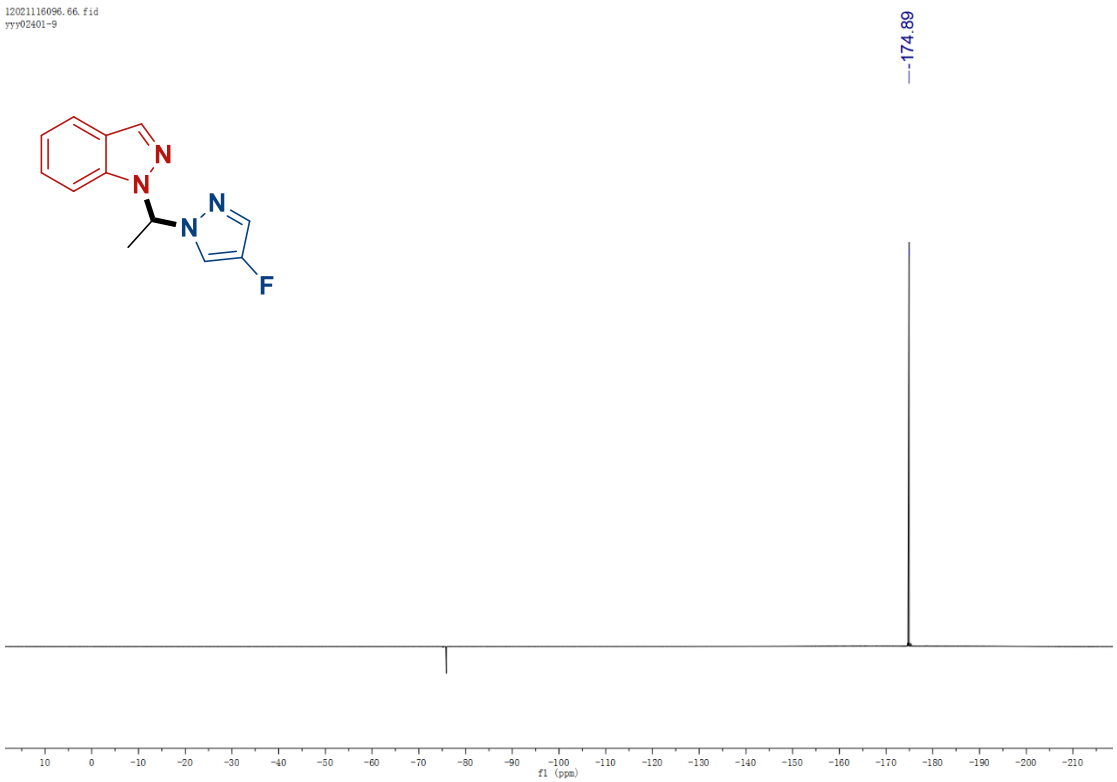
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 22**



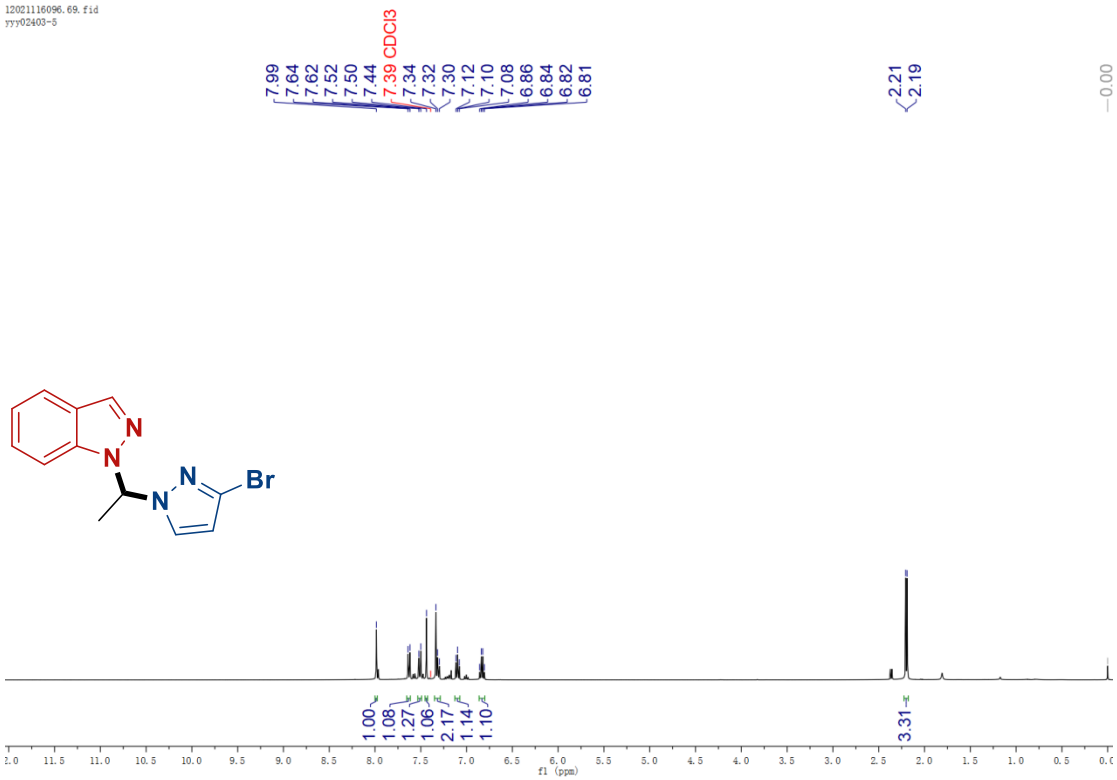
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 23**



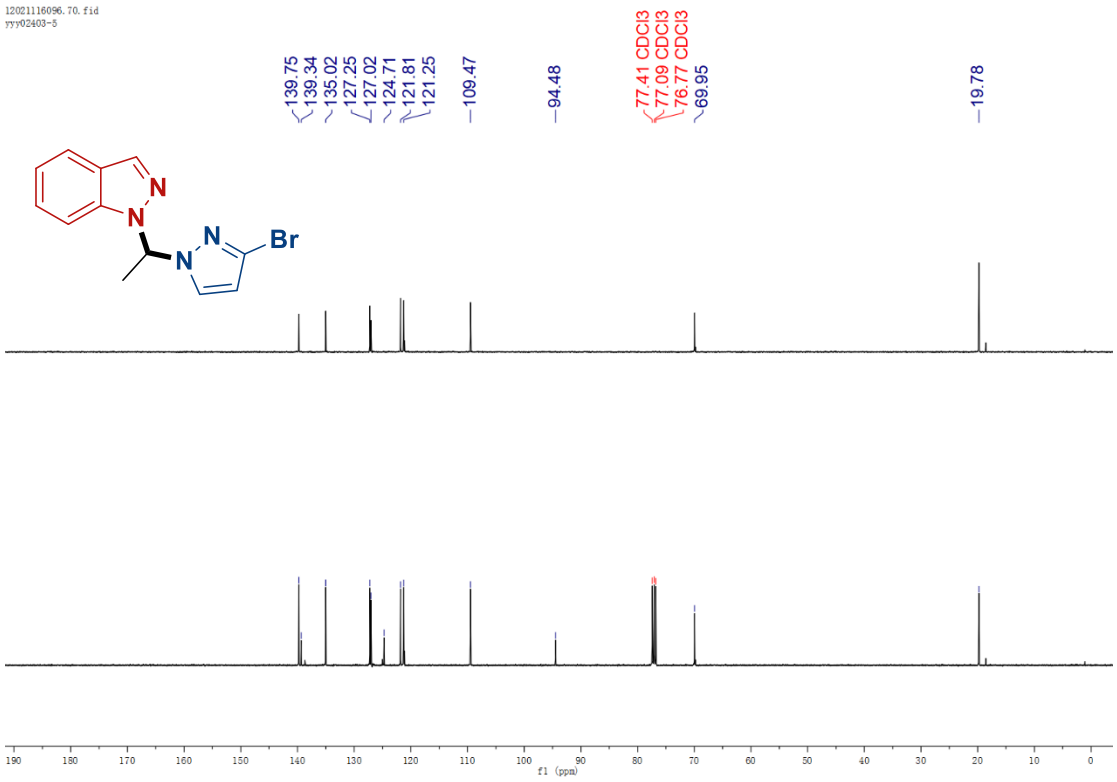
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 23**



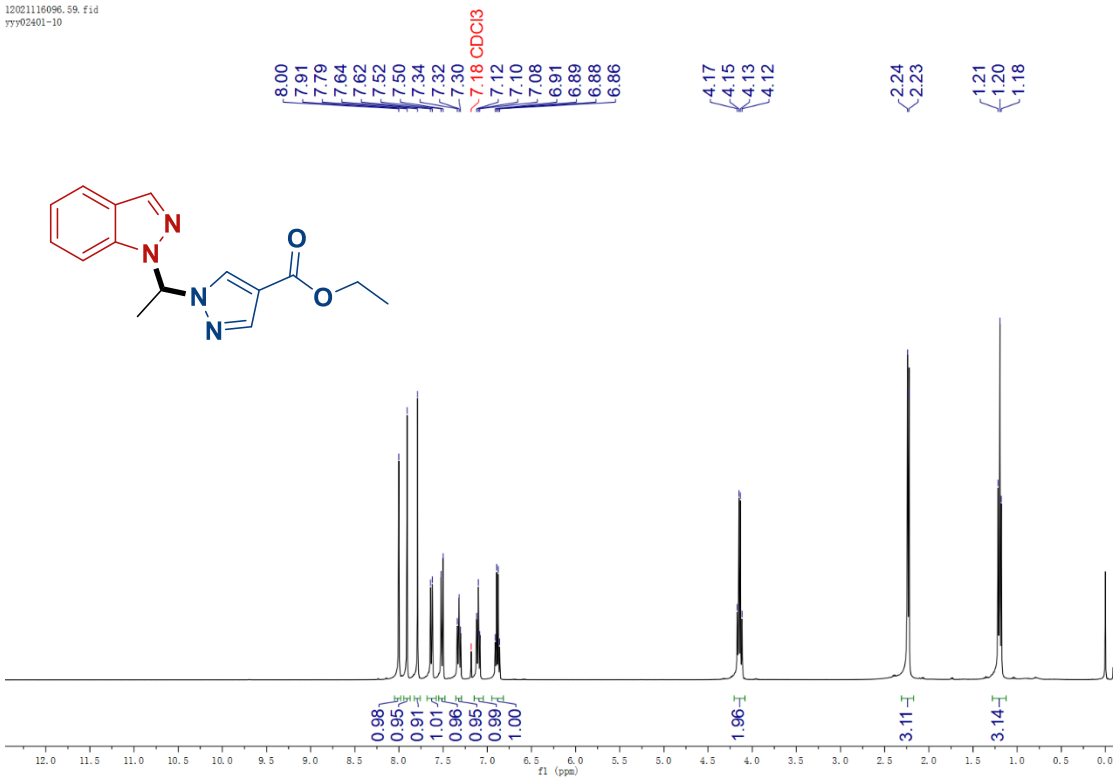
19^{F} NMR (376 MHz, Chloroform-*d*) **Spectrum of 23**



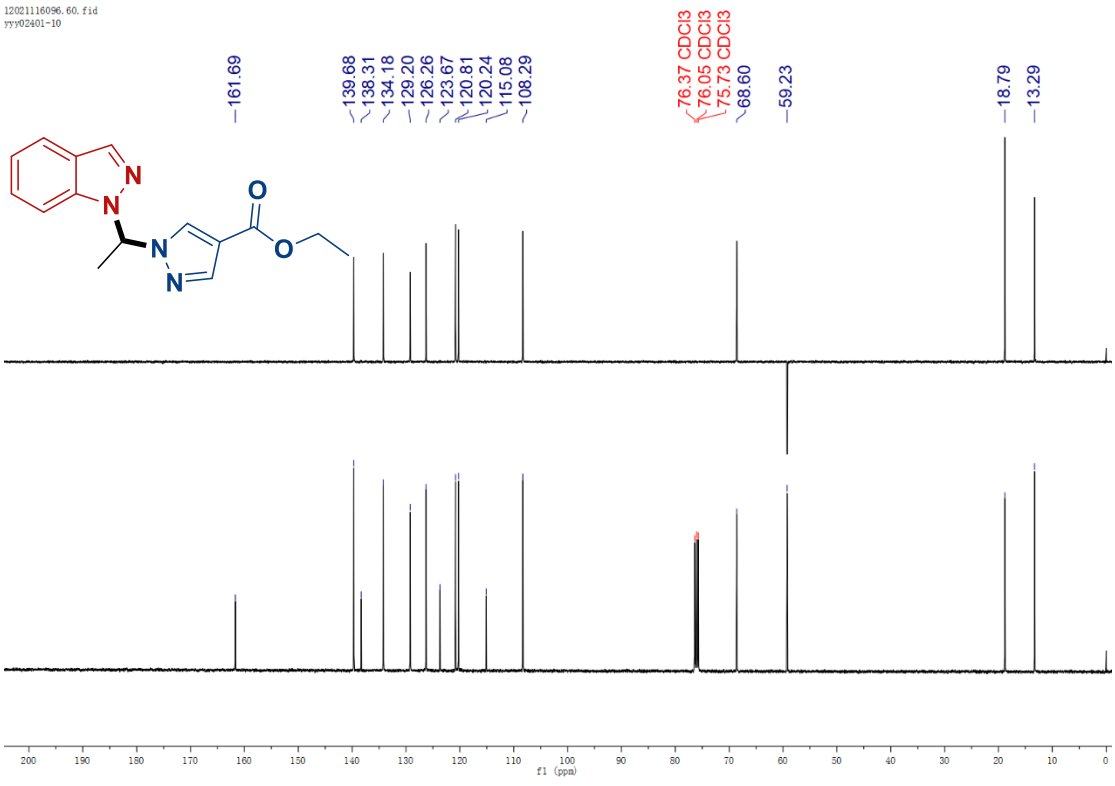
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 24**



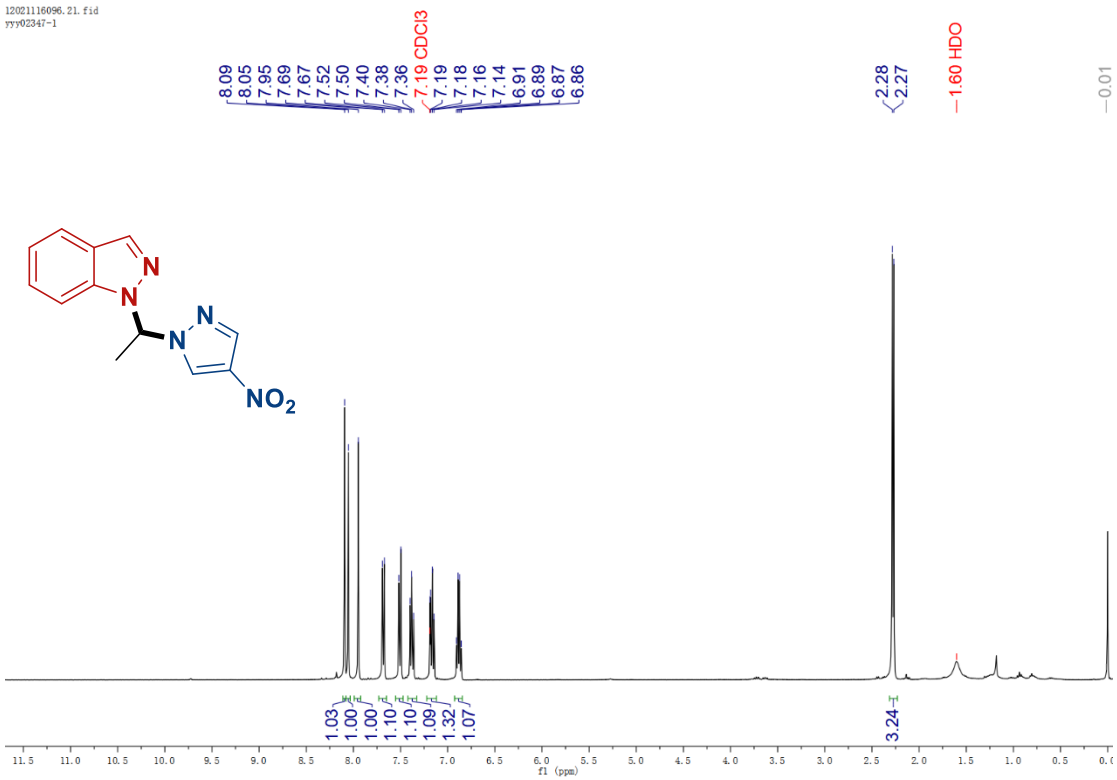
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 24**



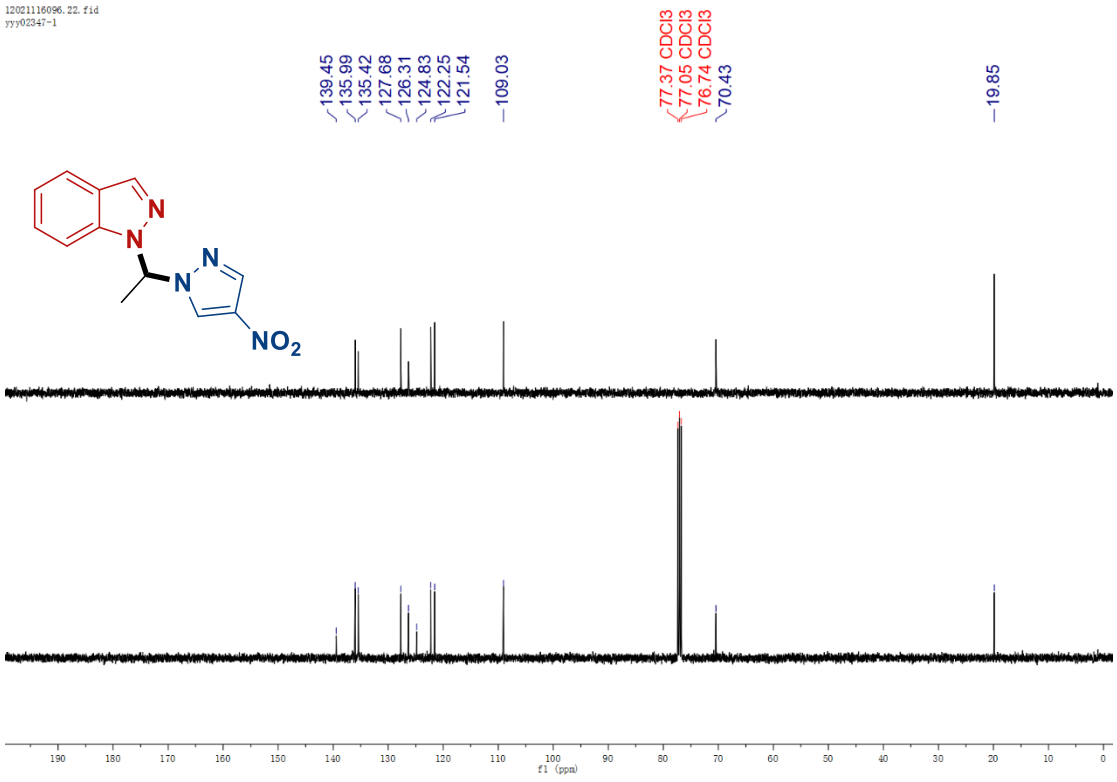
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 25**



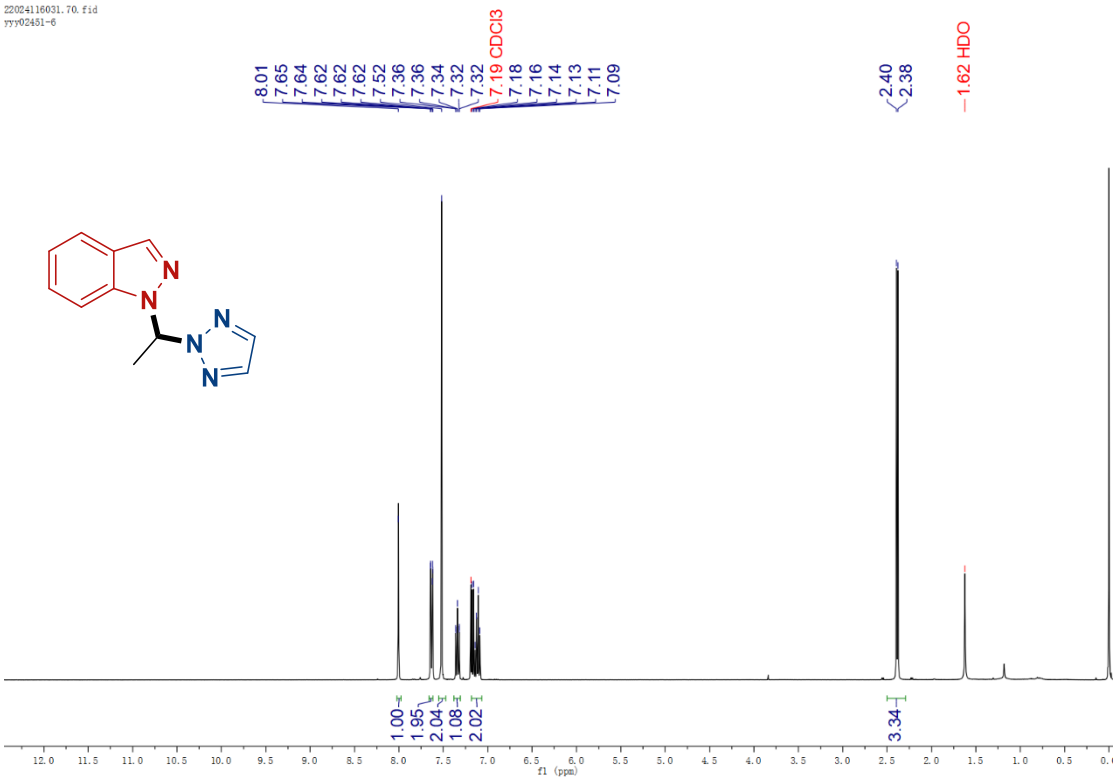
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 25**



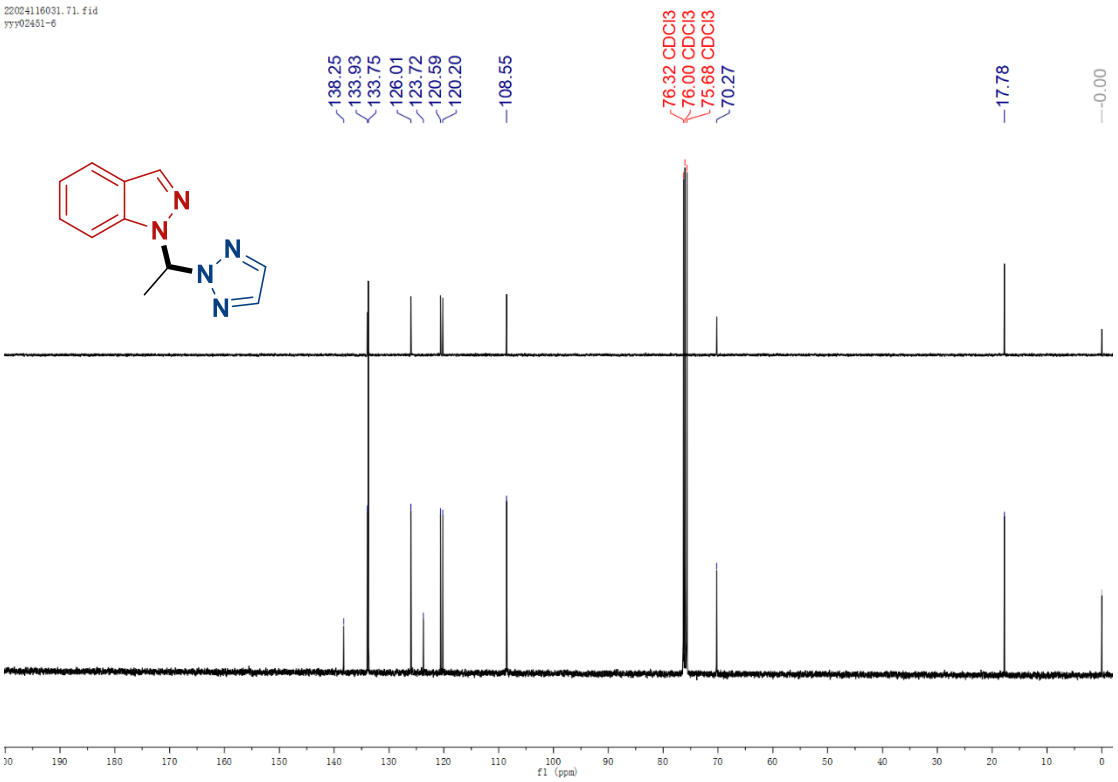
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 26**



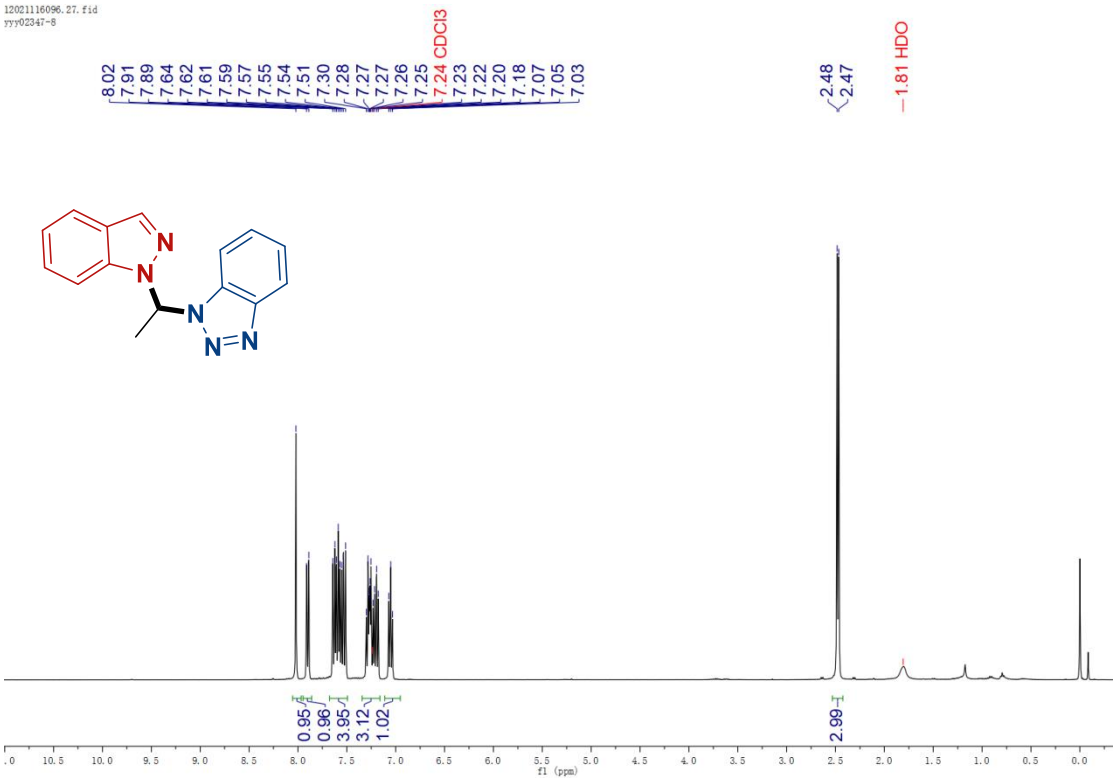
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 26**



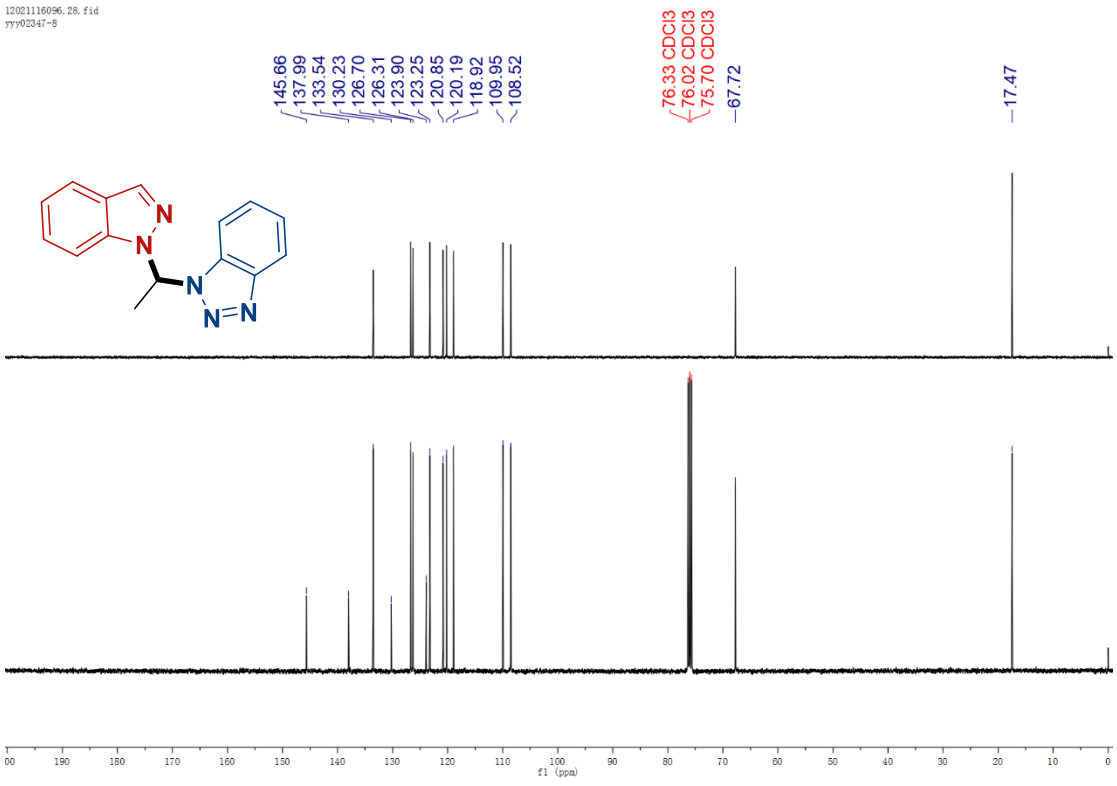
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 27**



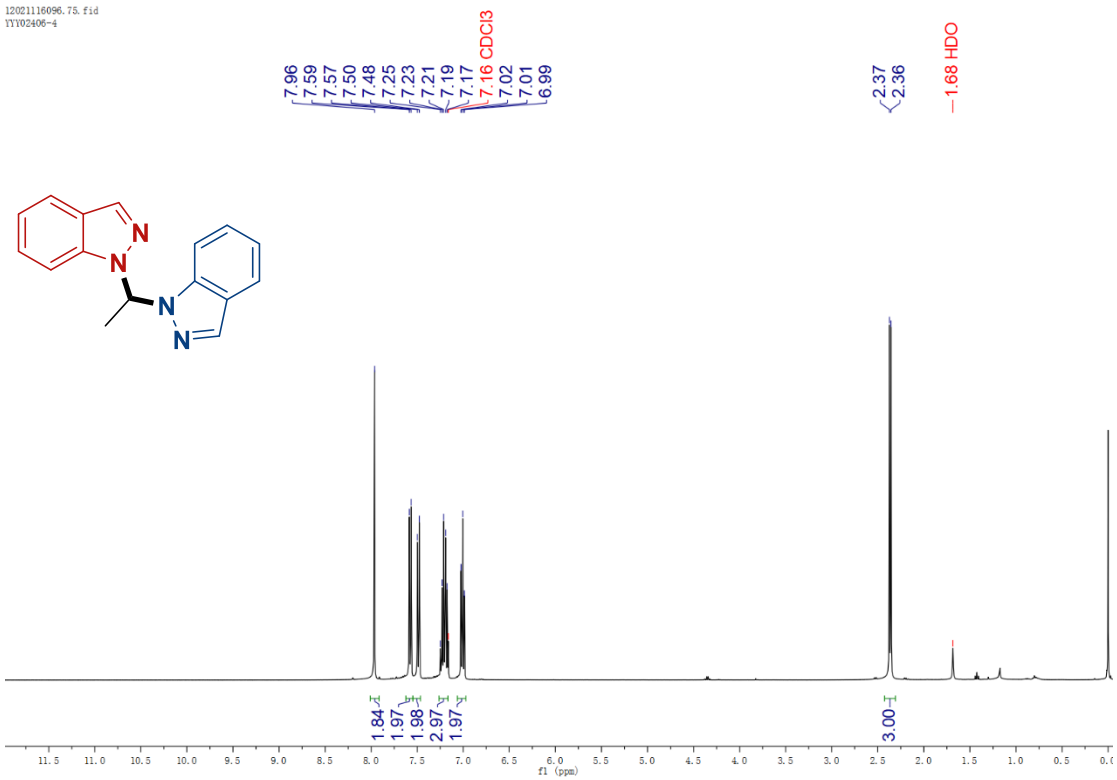
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 27**



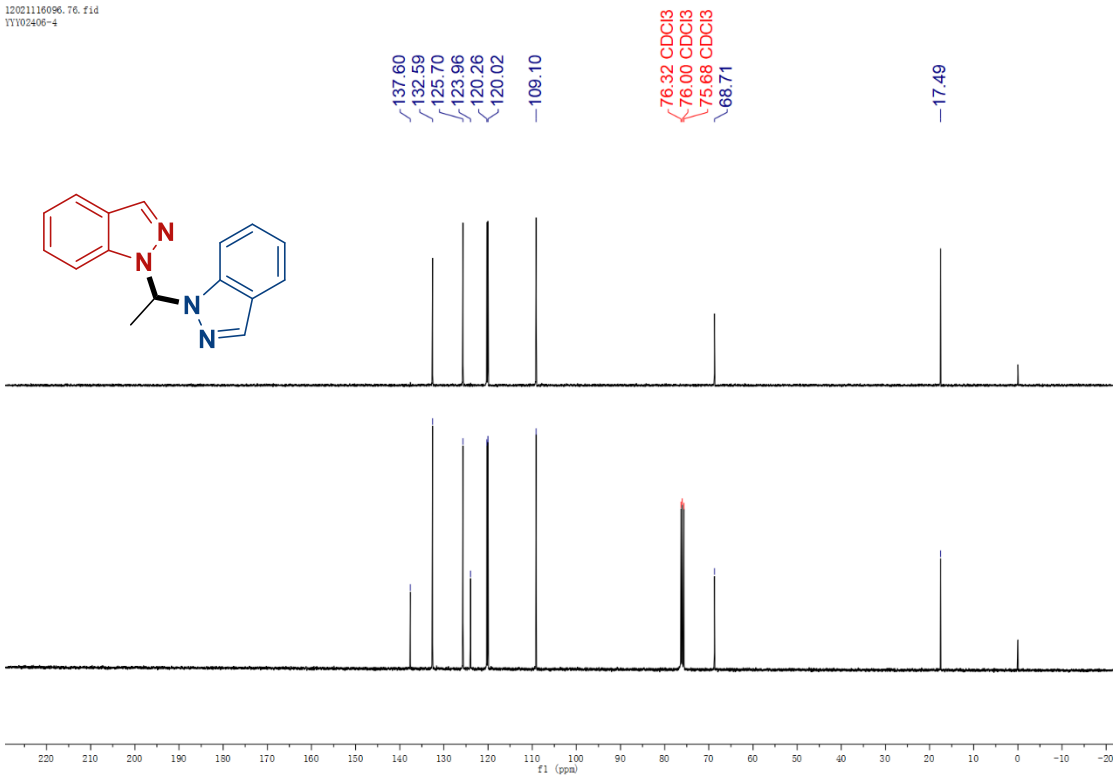
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 28**



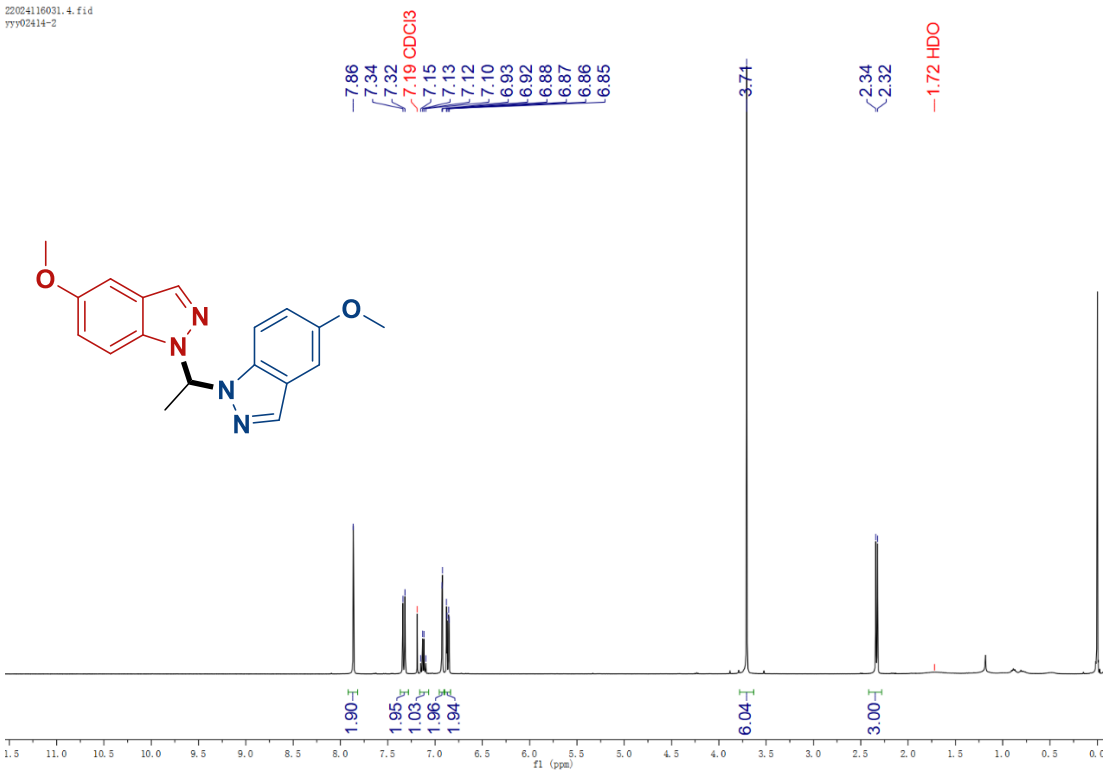
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 28**



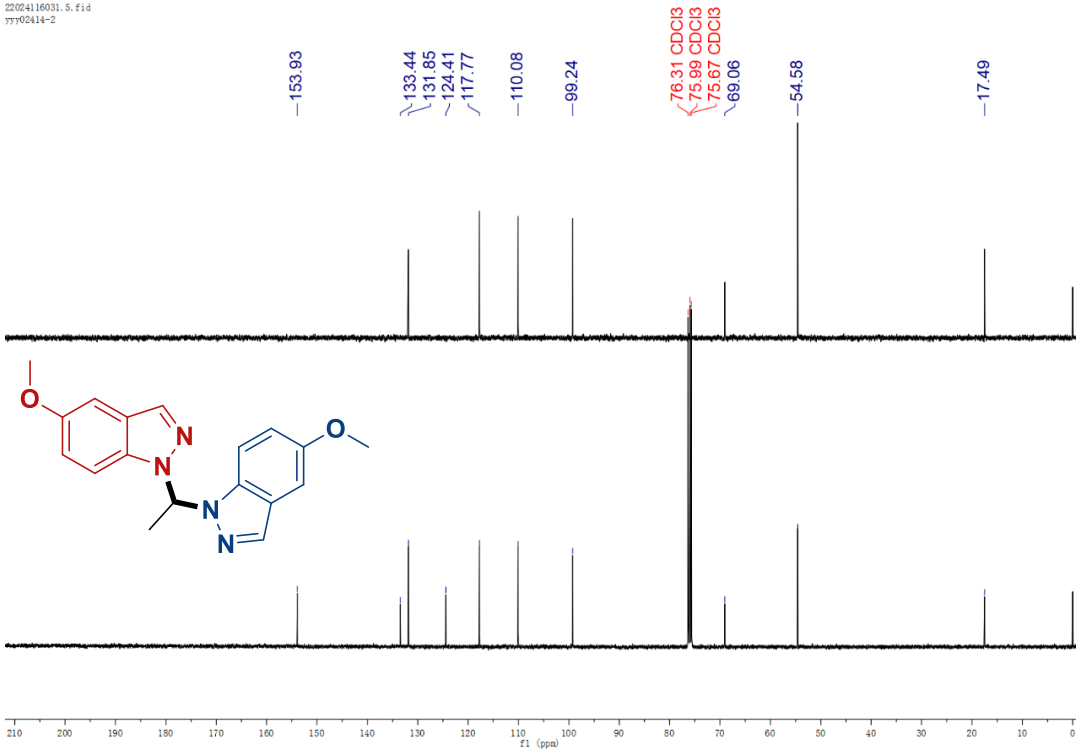
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 29**



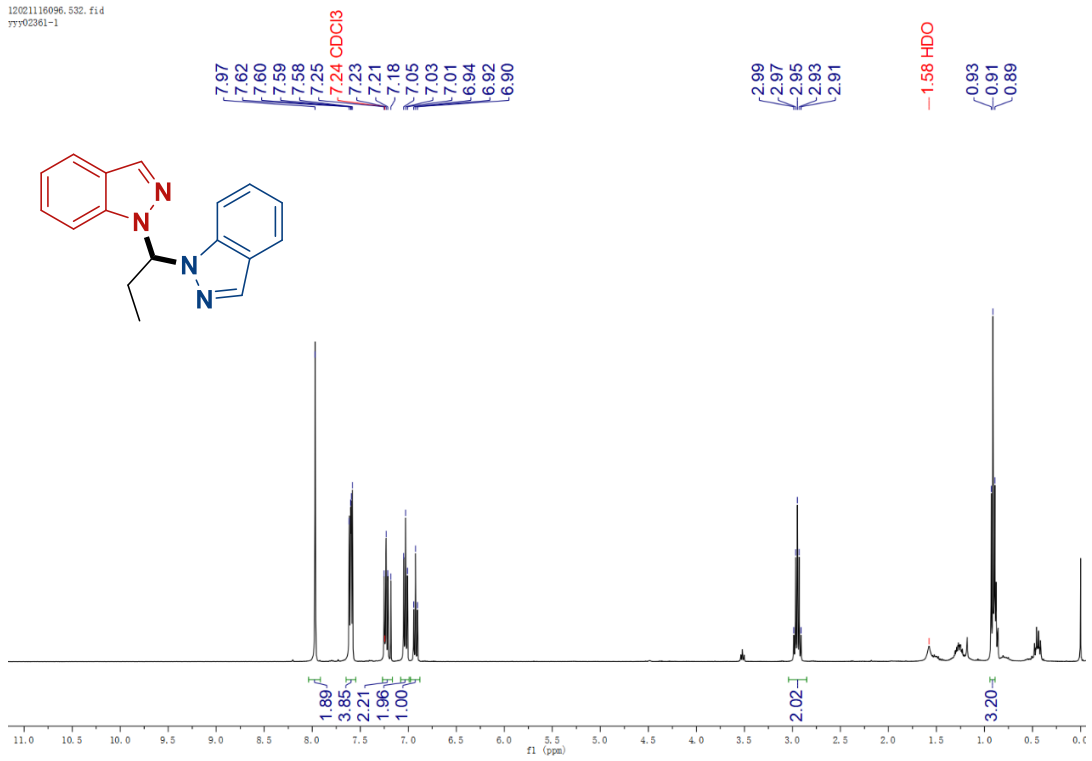
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 29**



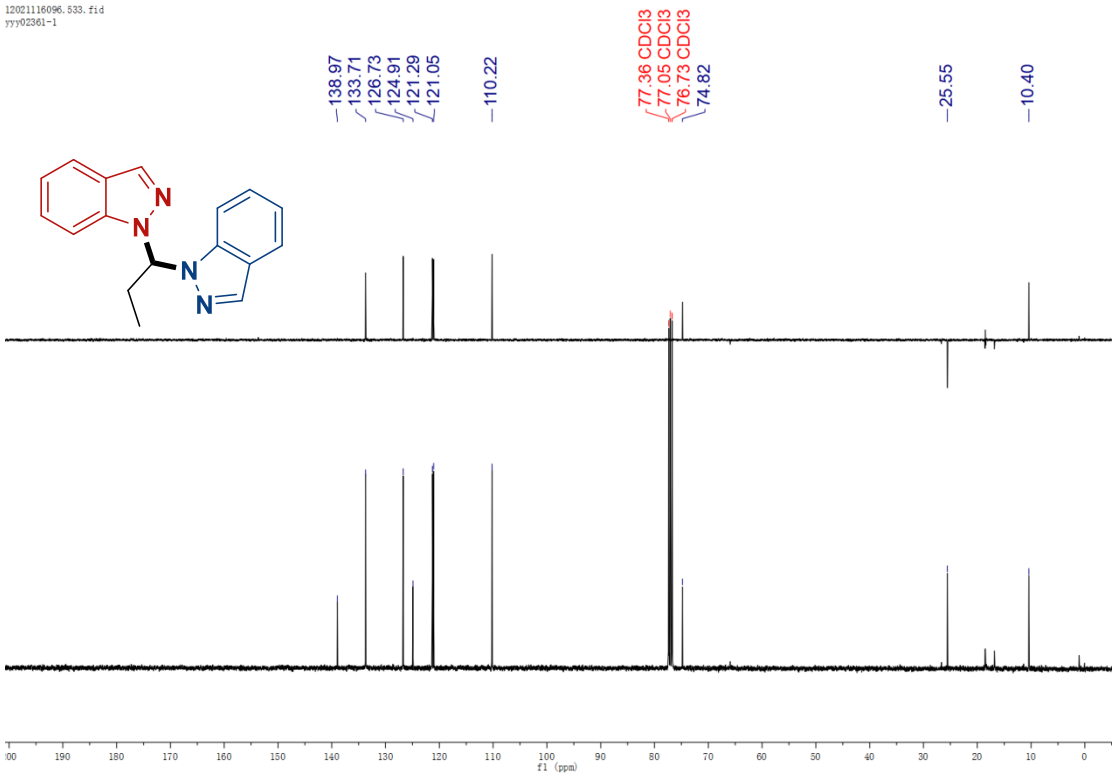
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 30**



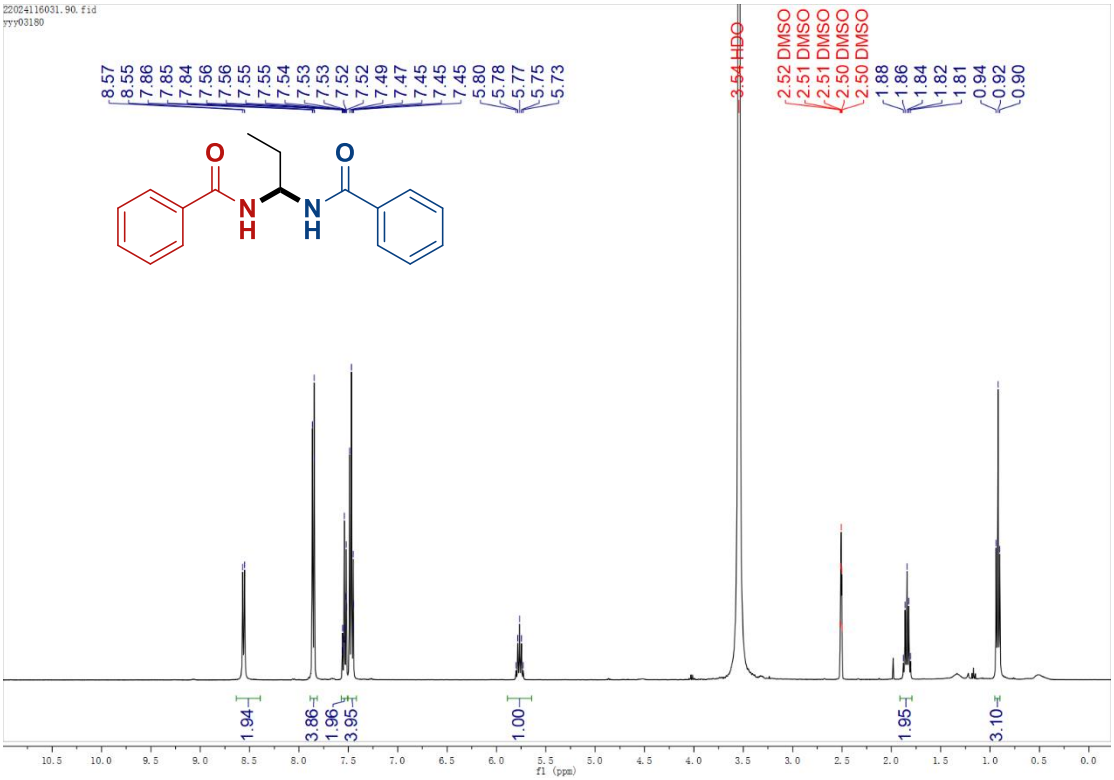
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 30**



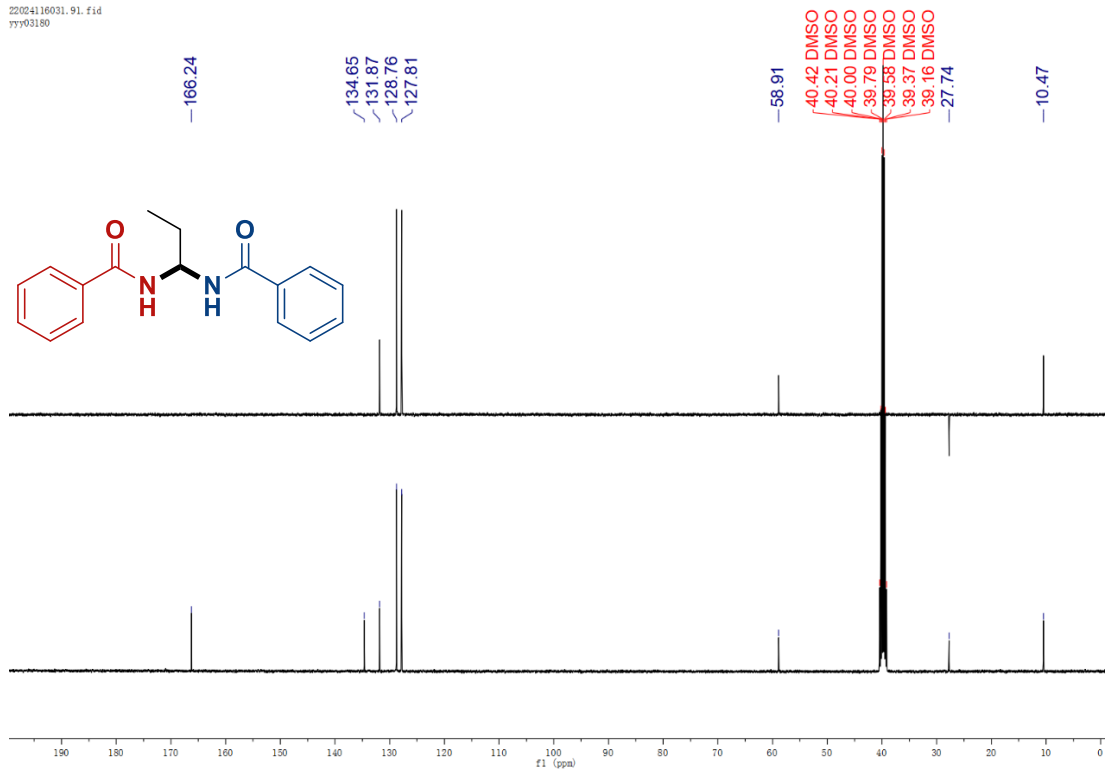
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 31**



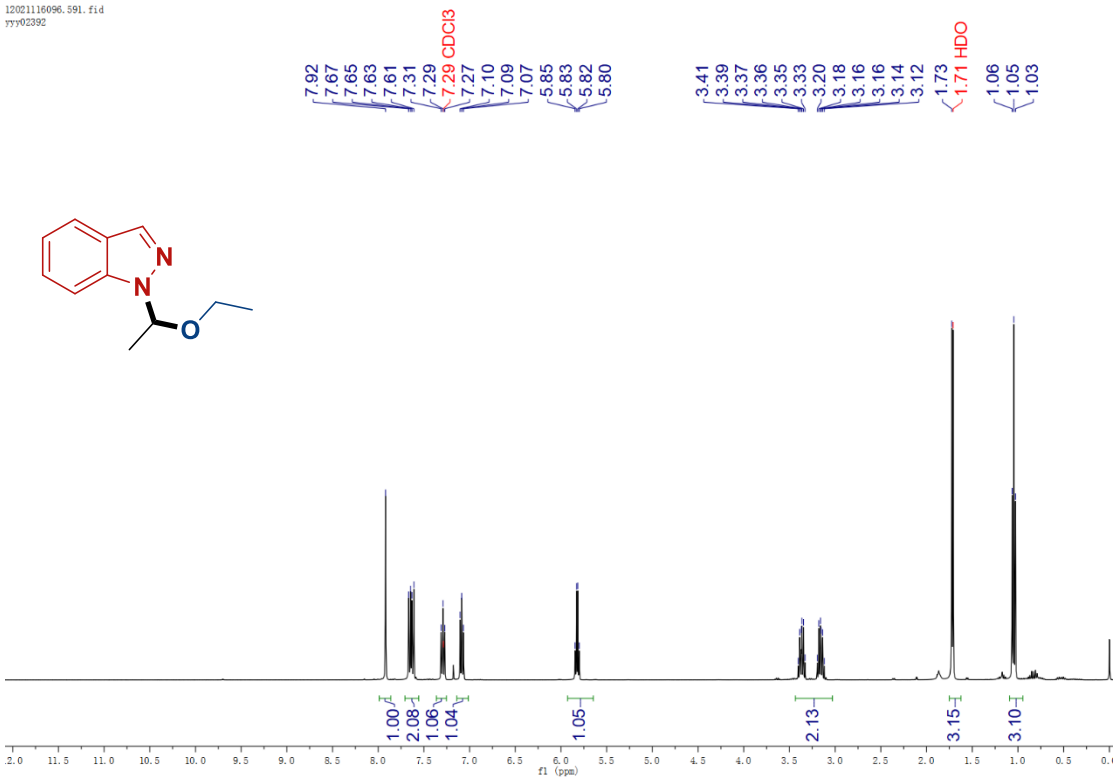
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 31**



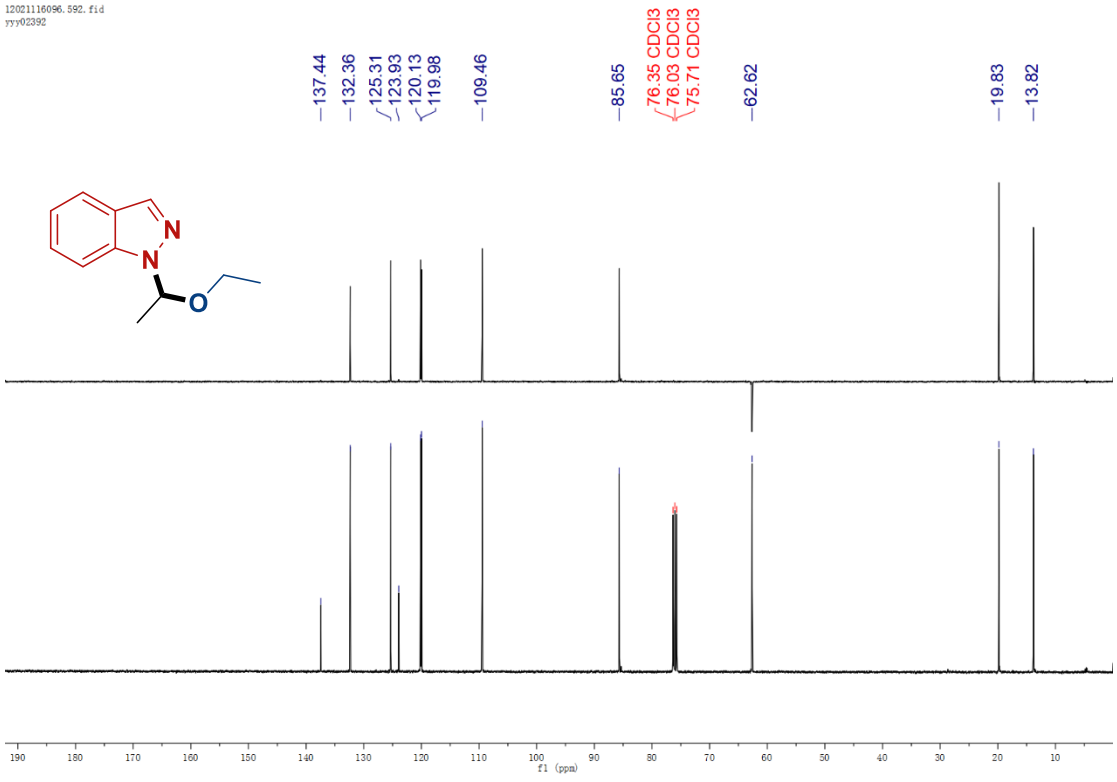
^{1}H-NMR (400 MHz, DMSO-d_6) **Spectrum of 32**



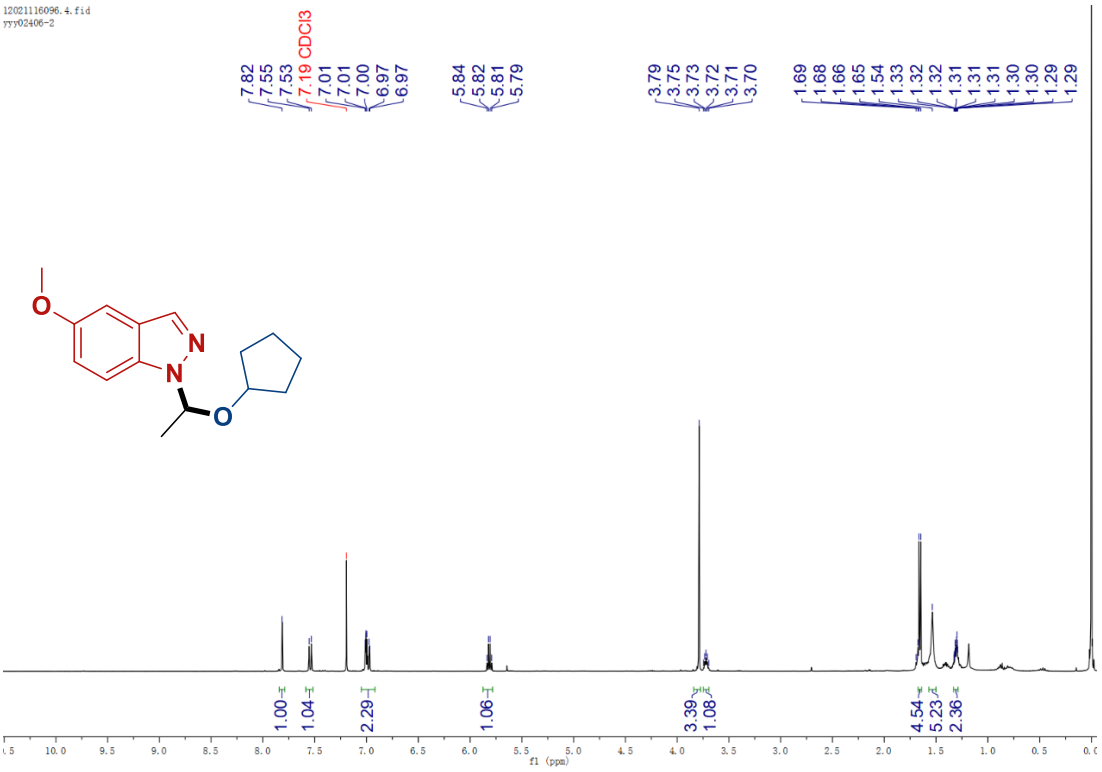
^{13}C-NMR (100 MHz, DMSO-d_6) **Spectrum of 32**



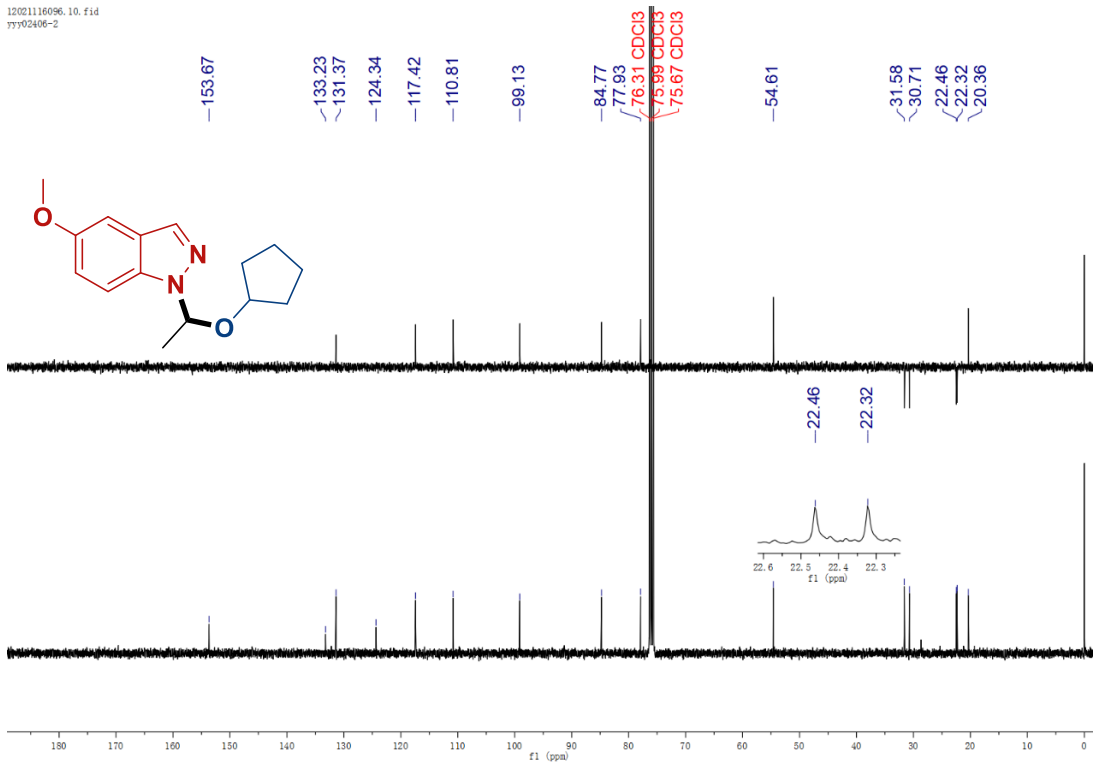
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 33**



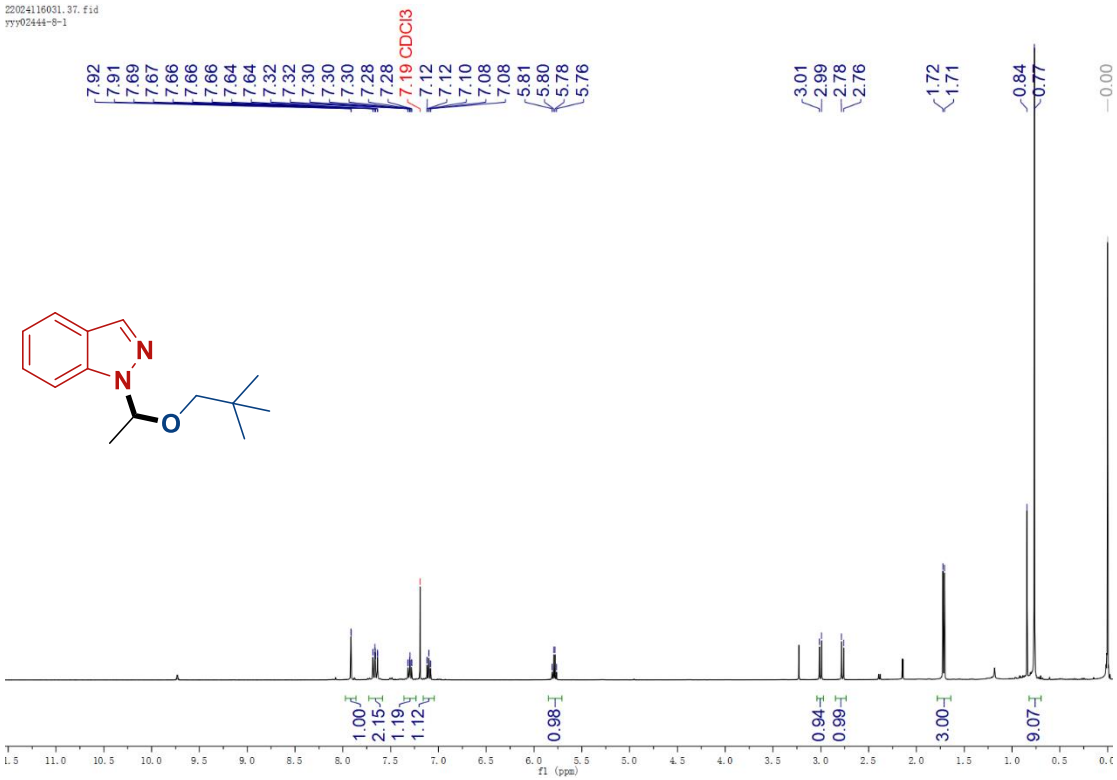
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 33**



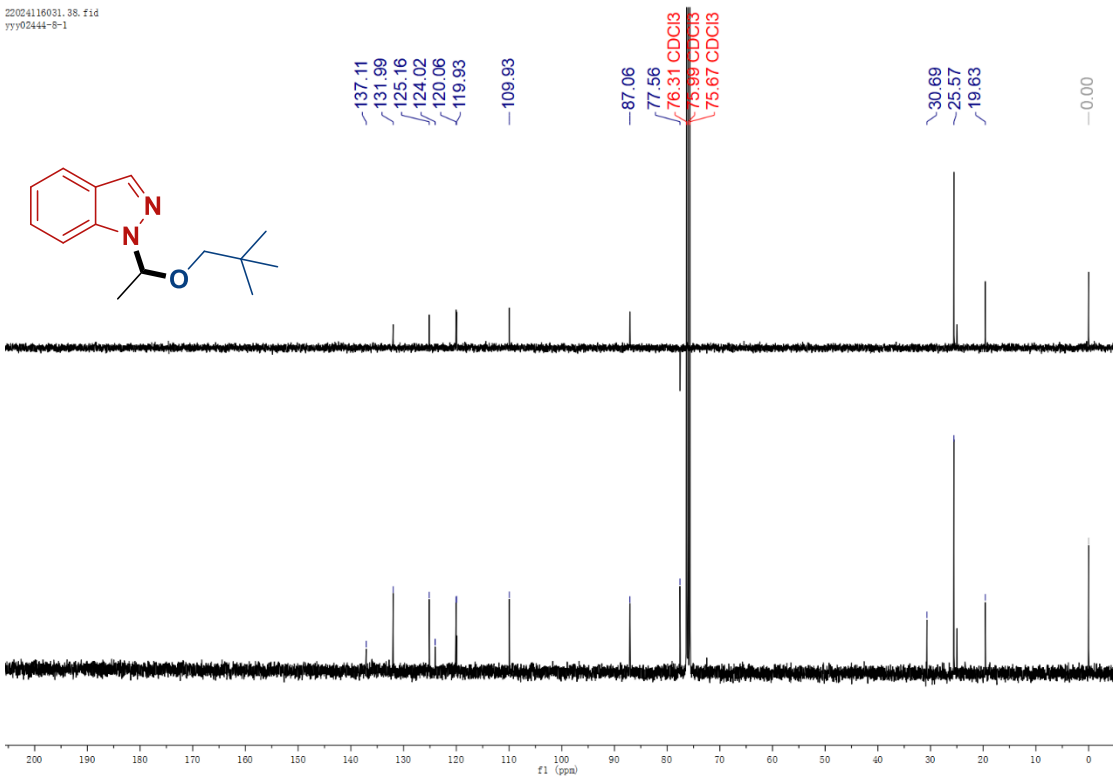
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 34**



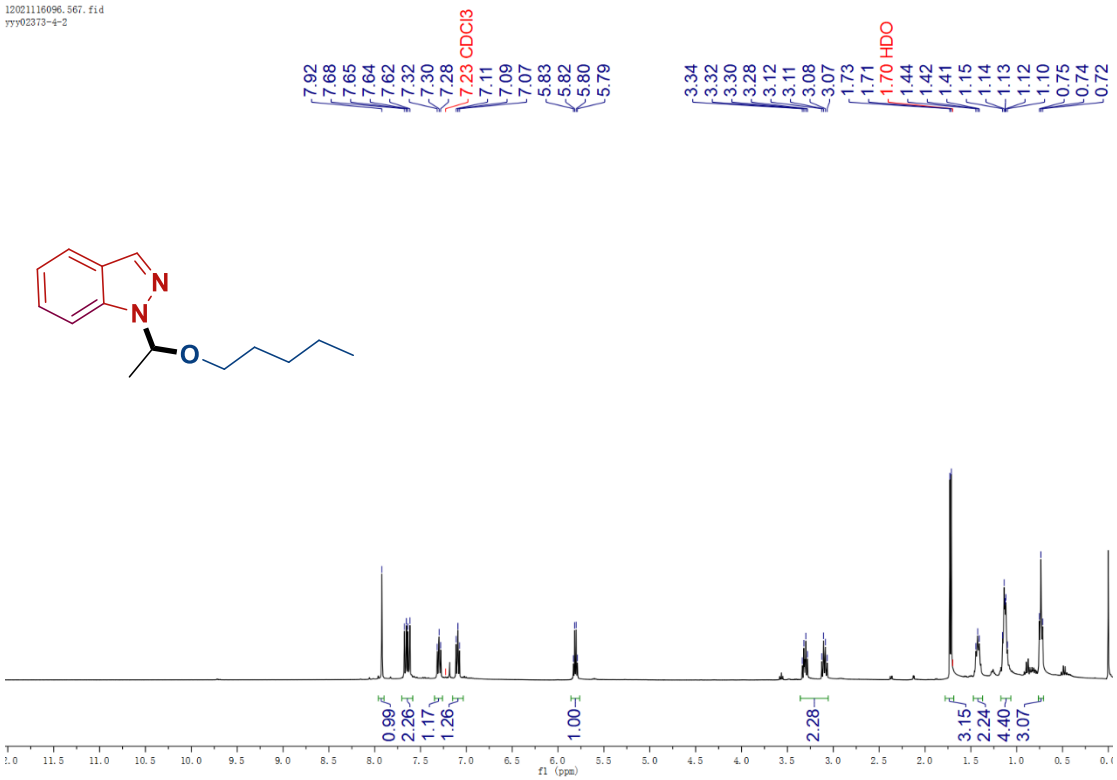
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 34**



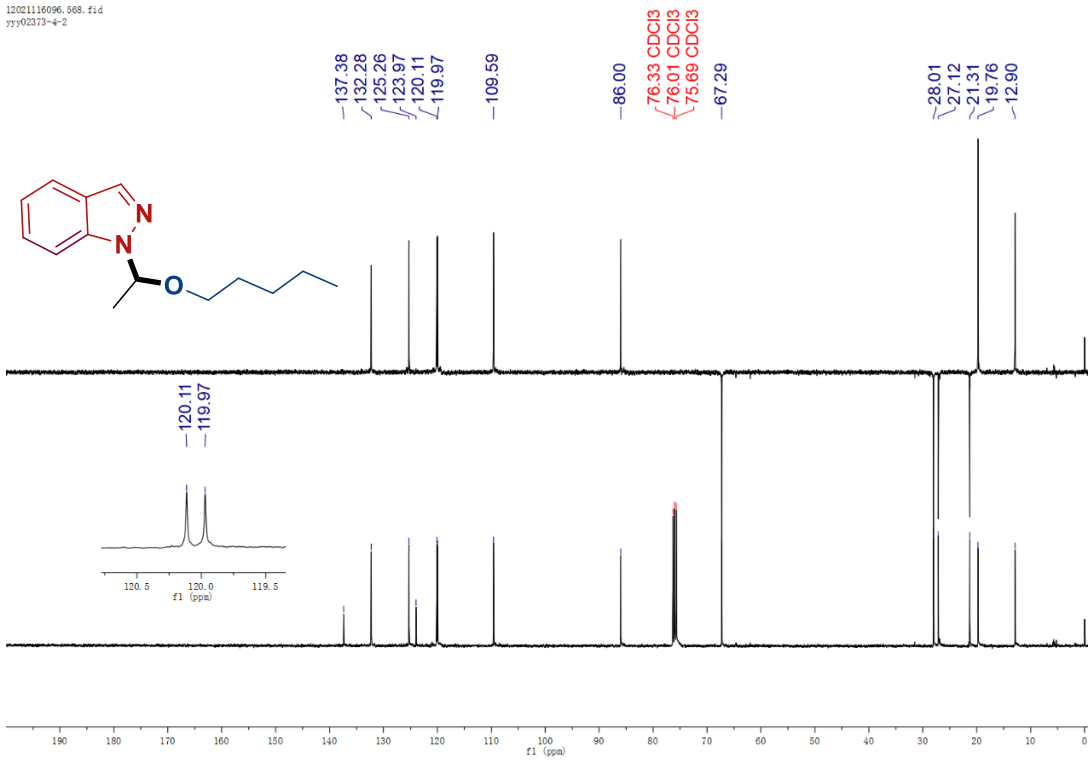
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 35**



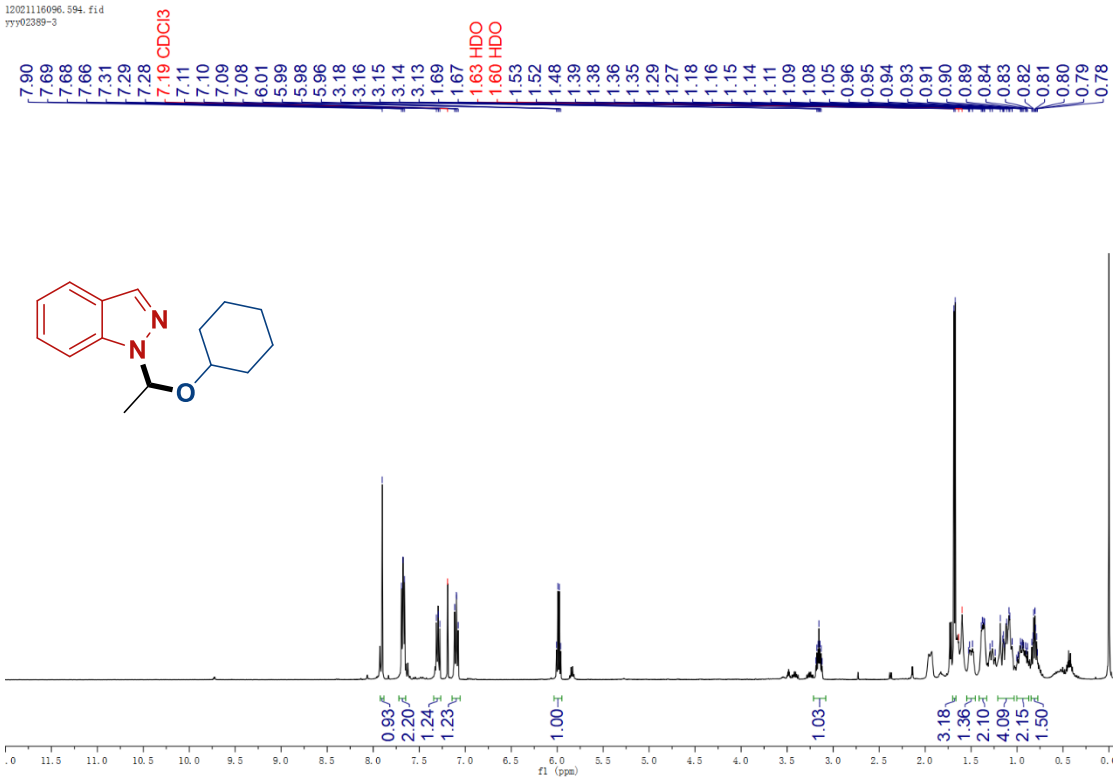
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 35**



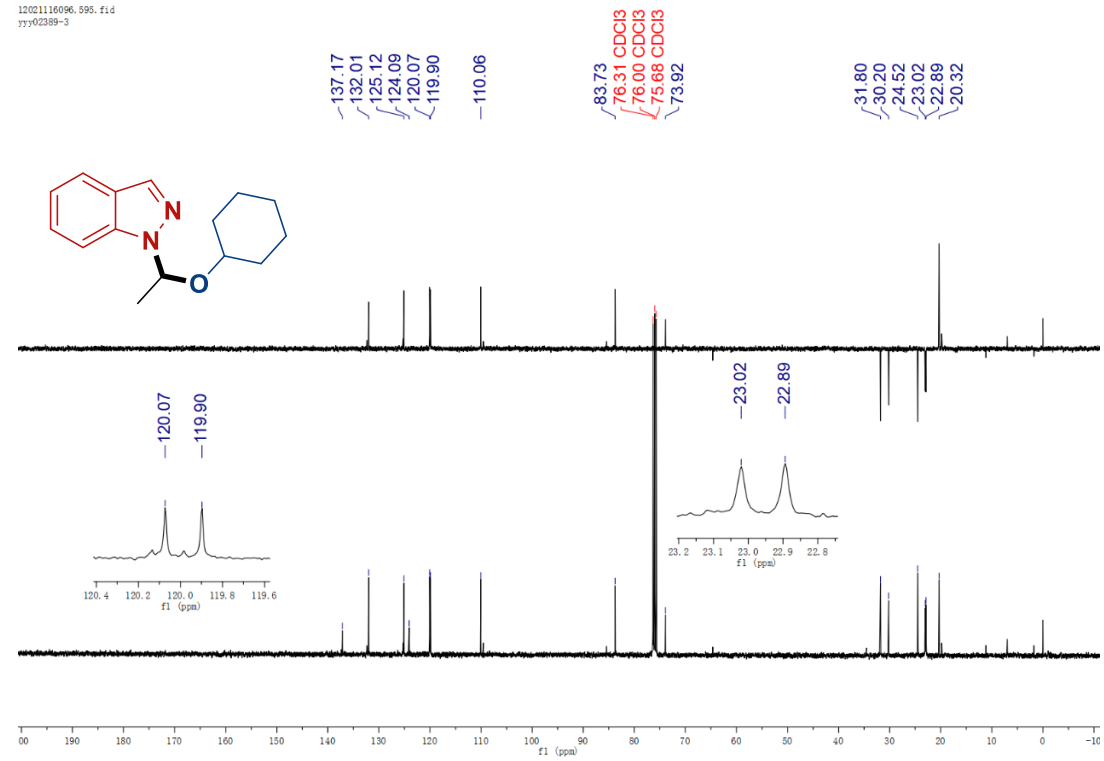
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 36**



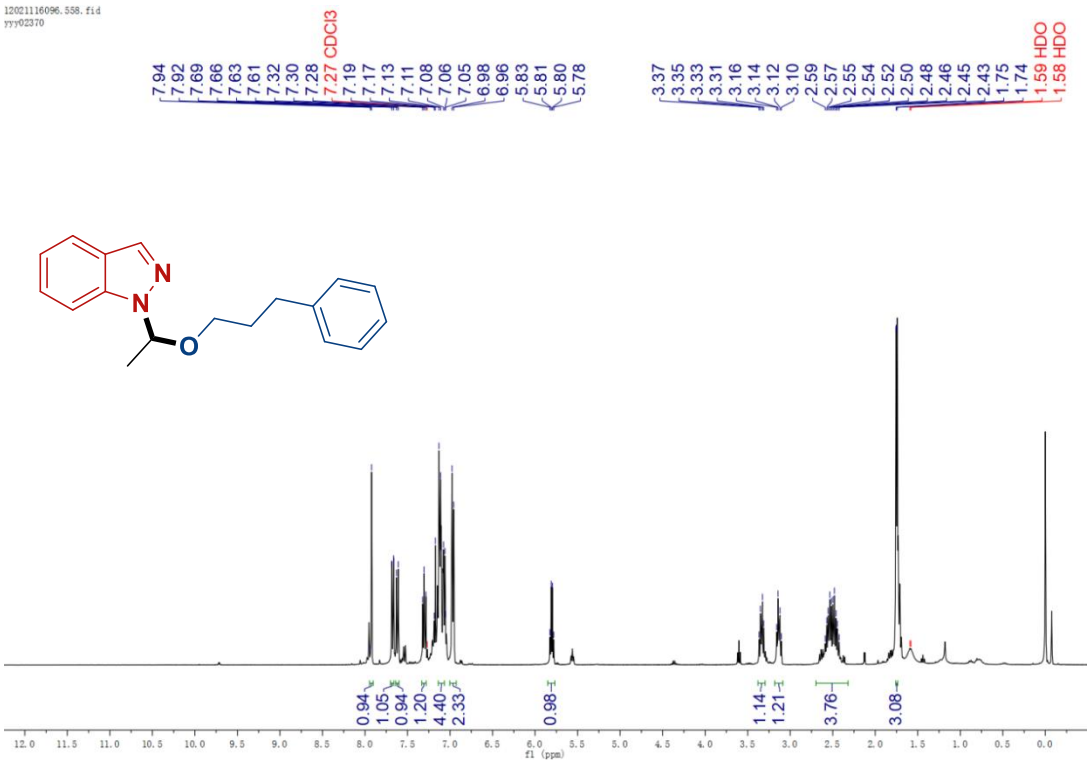
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 36**



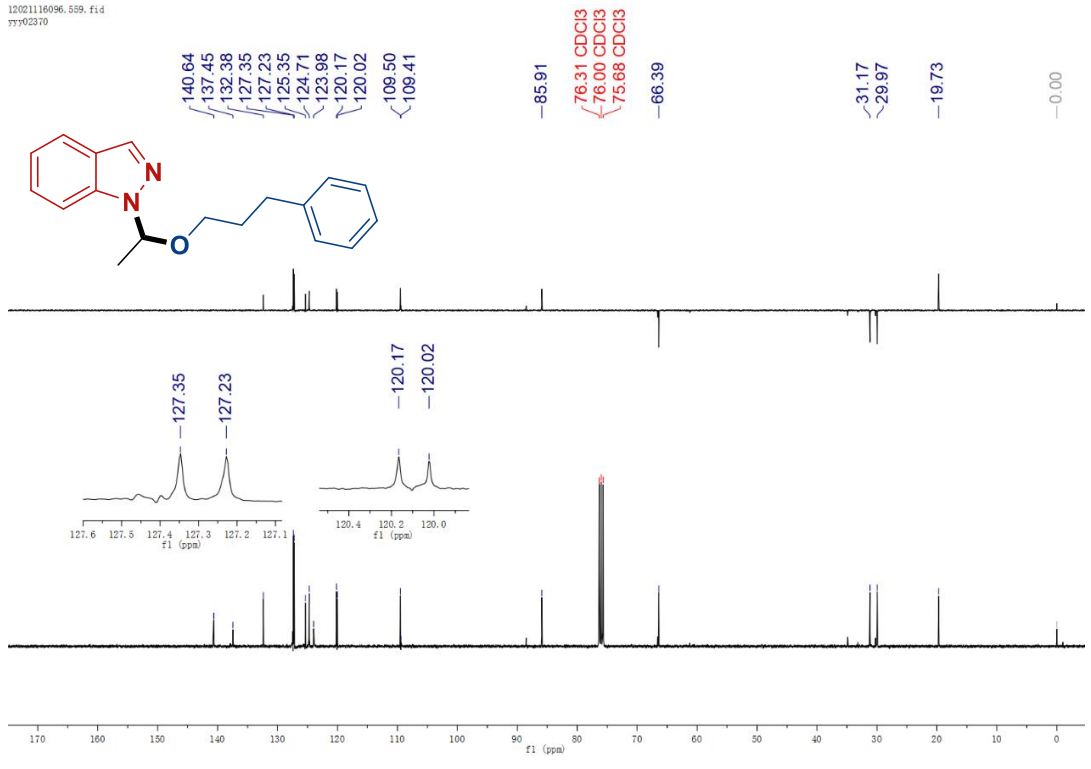
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 37**



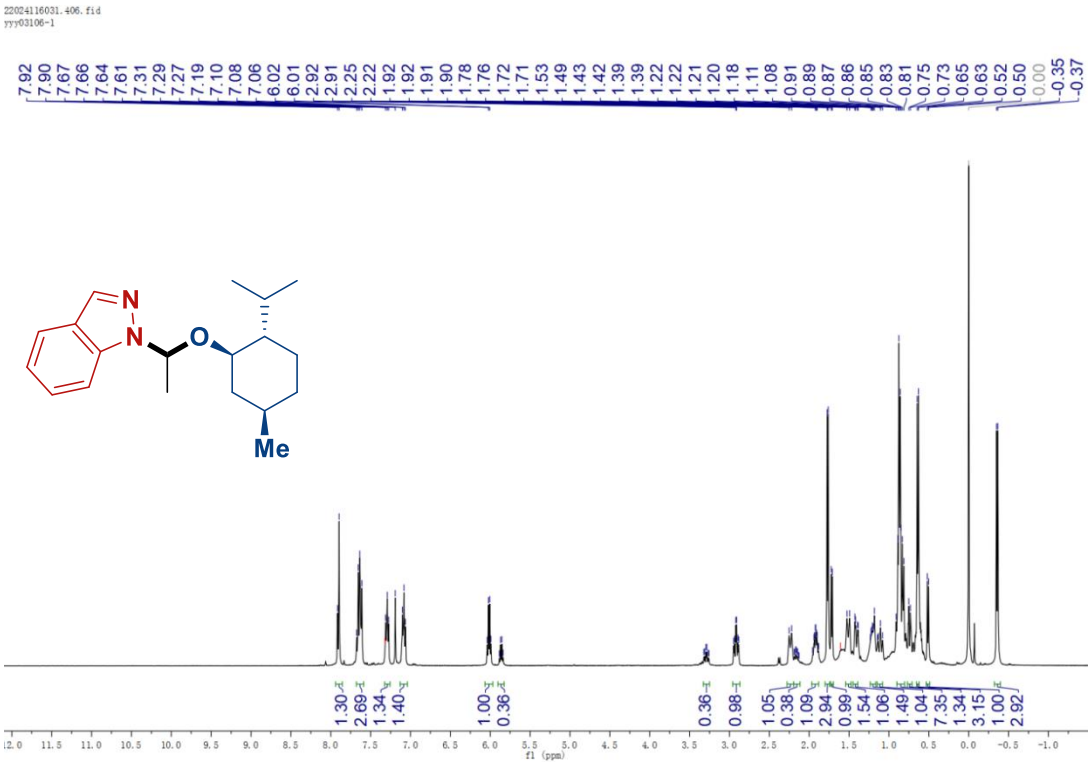
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 37**



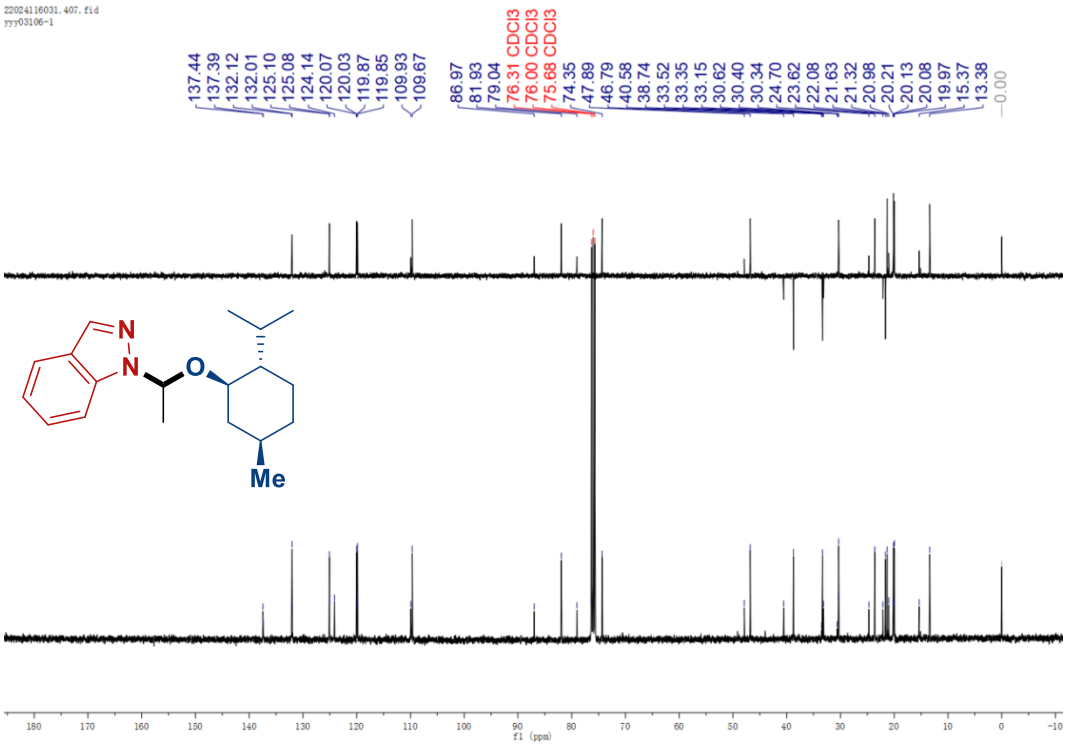
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 38**



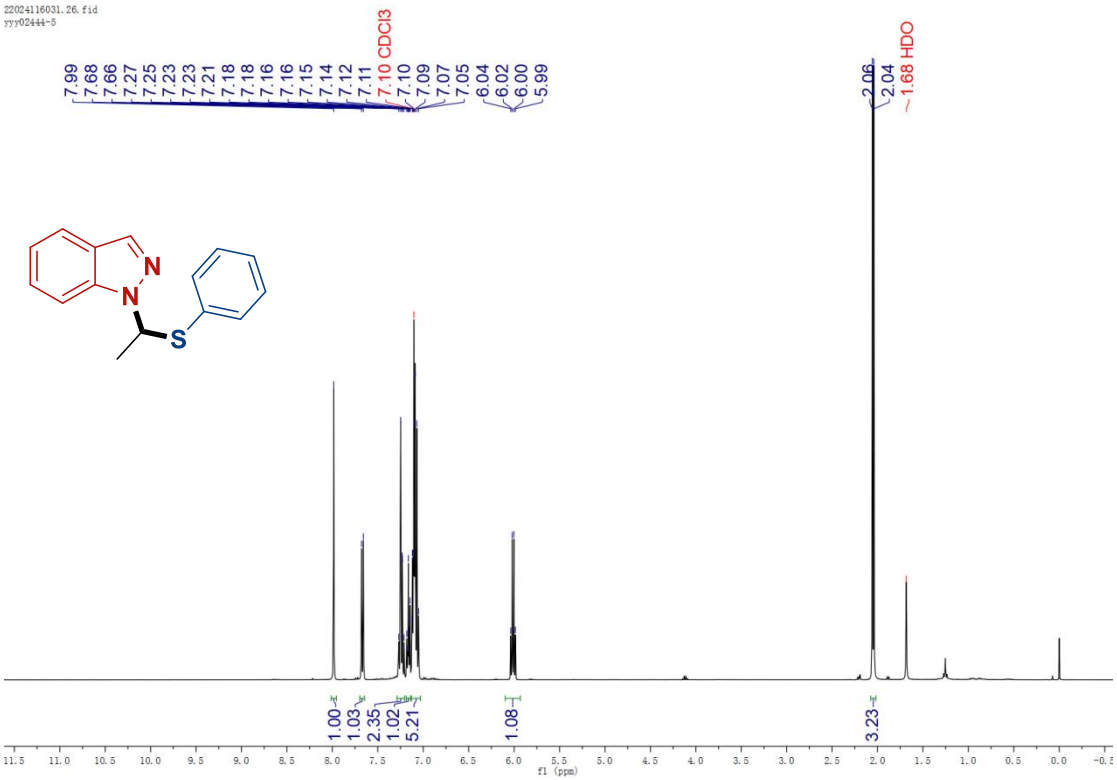
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 38**



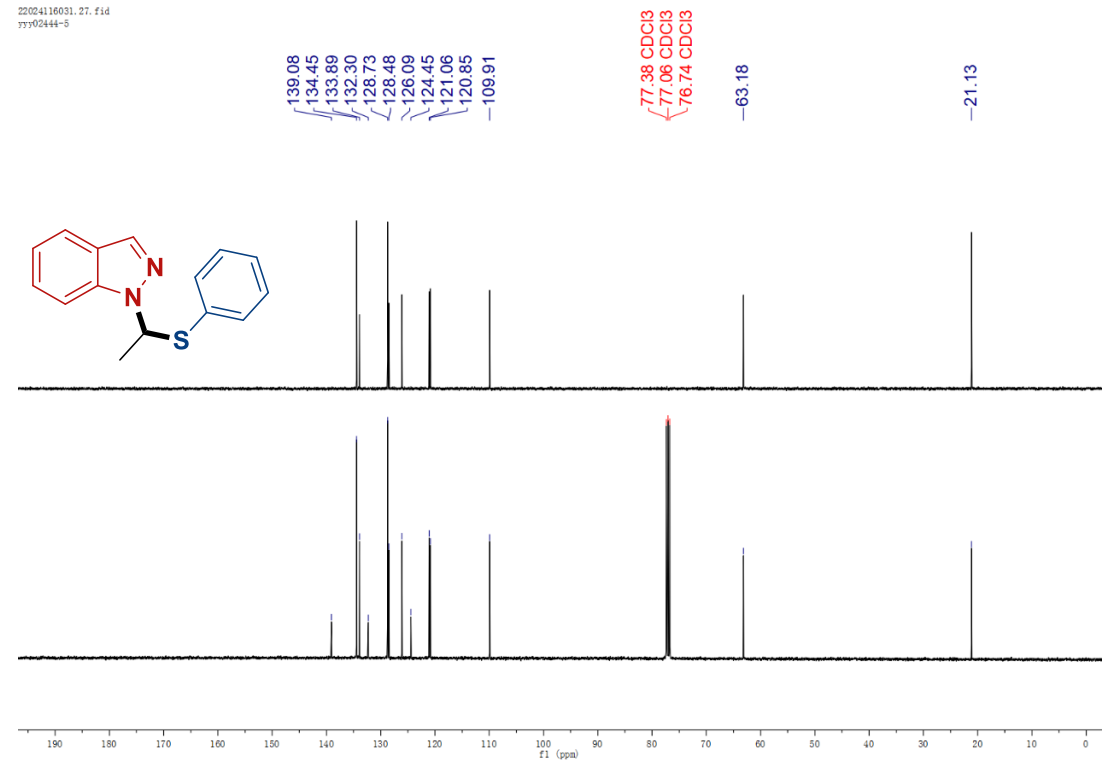
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 39**



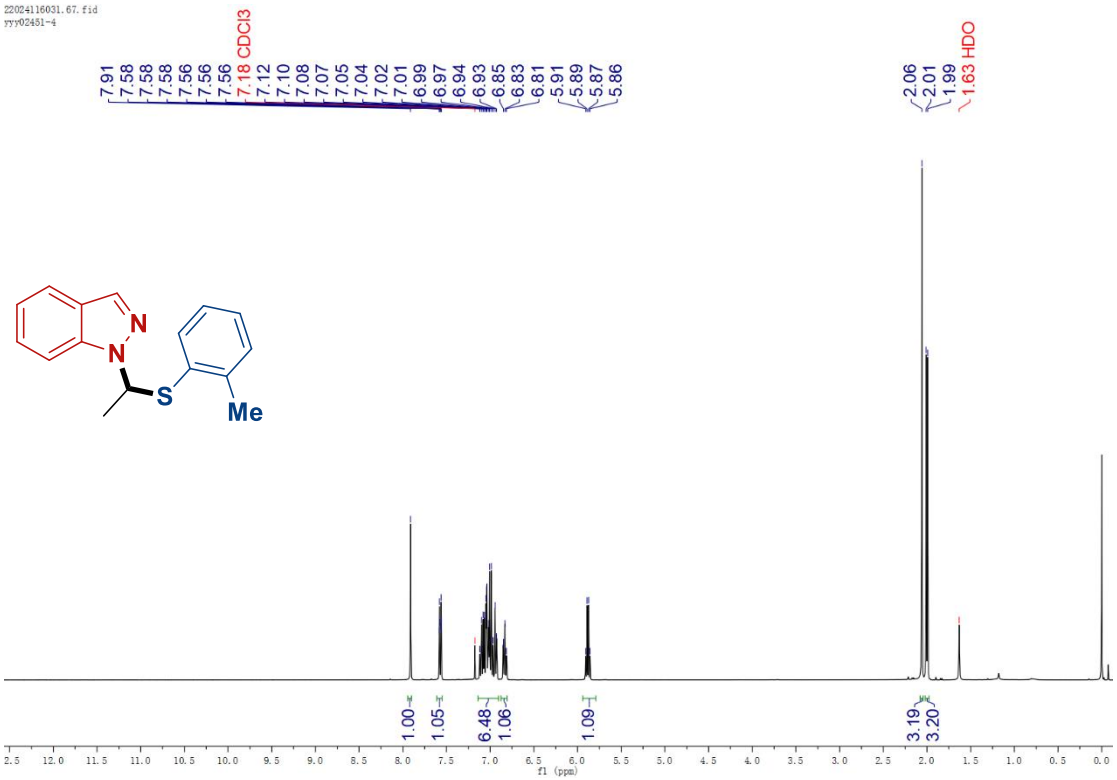
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 39**



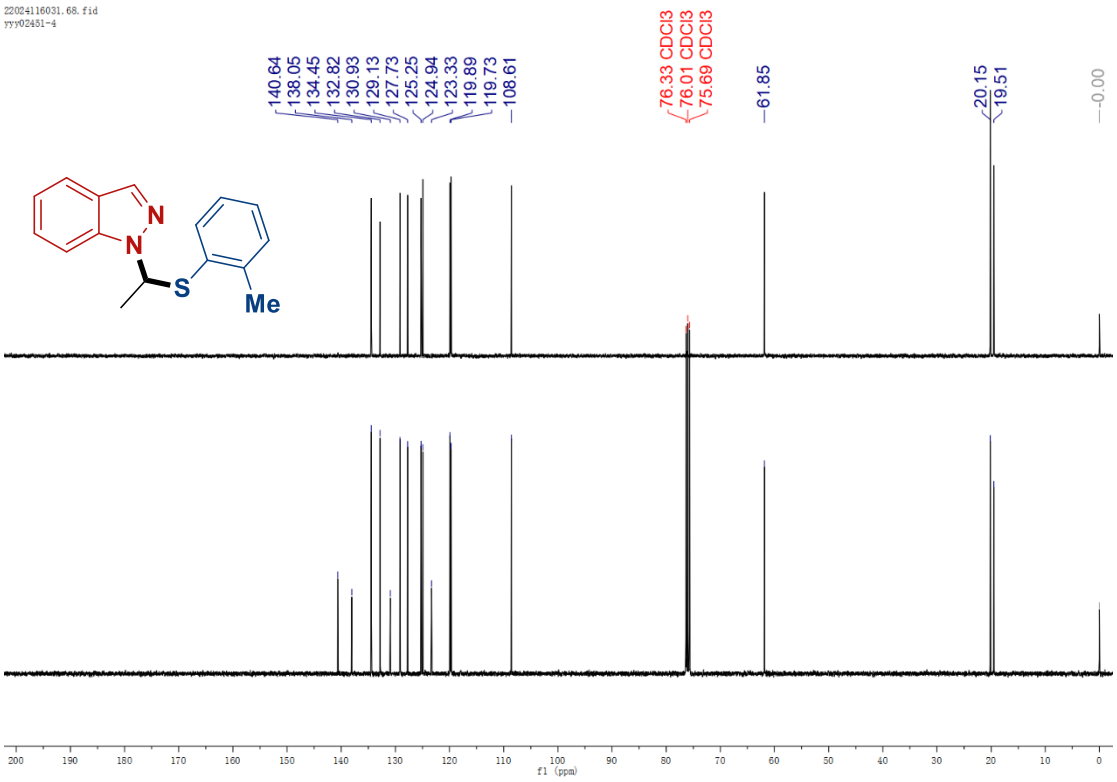
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 40**



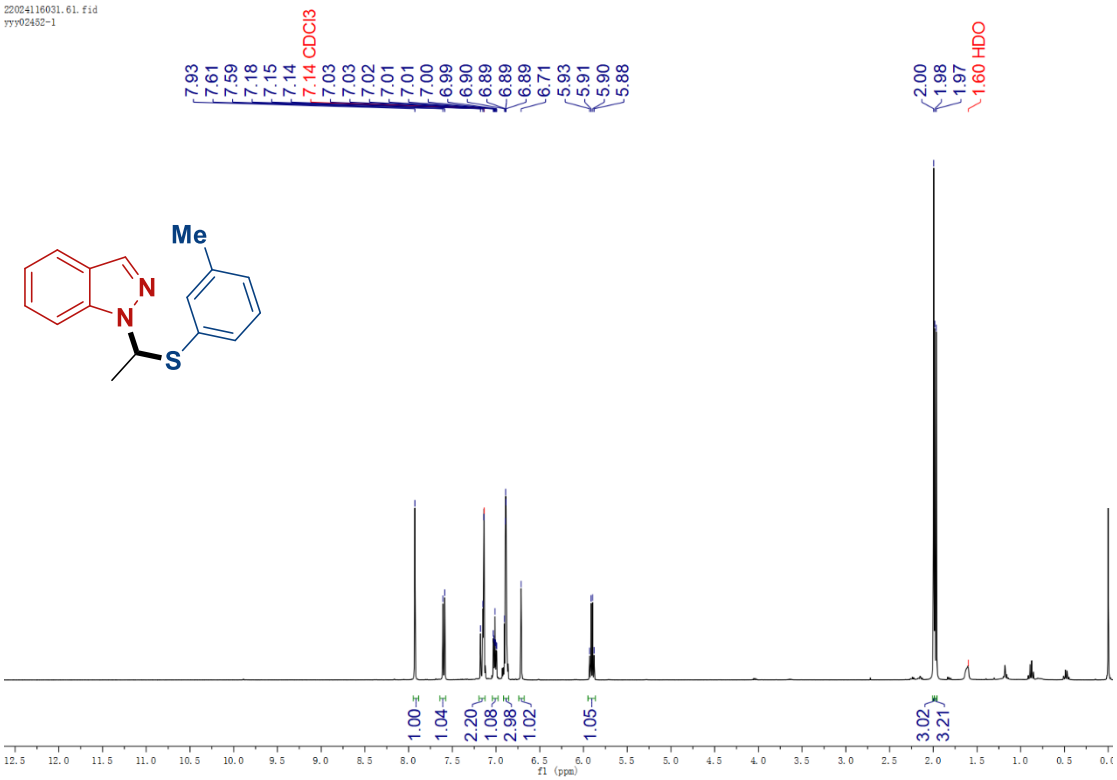
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 40**



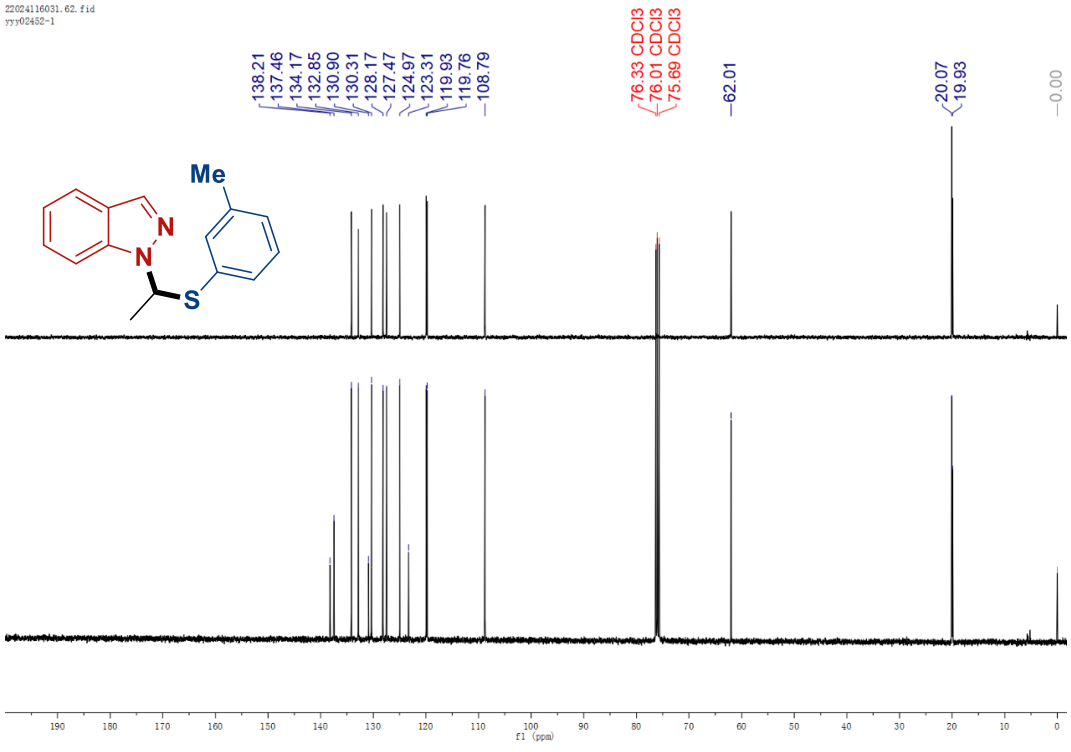
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 41**



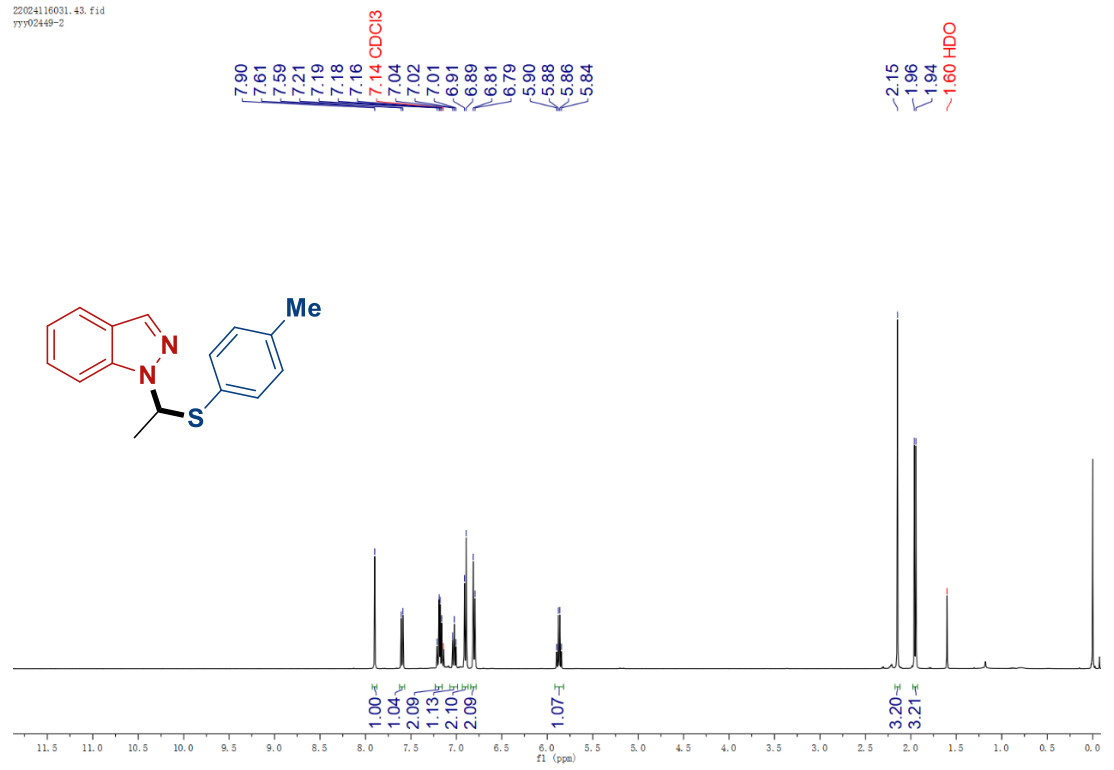
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 41**



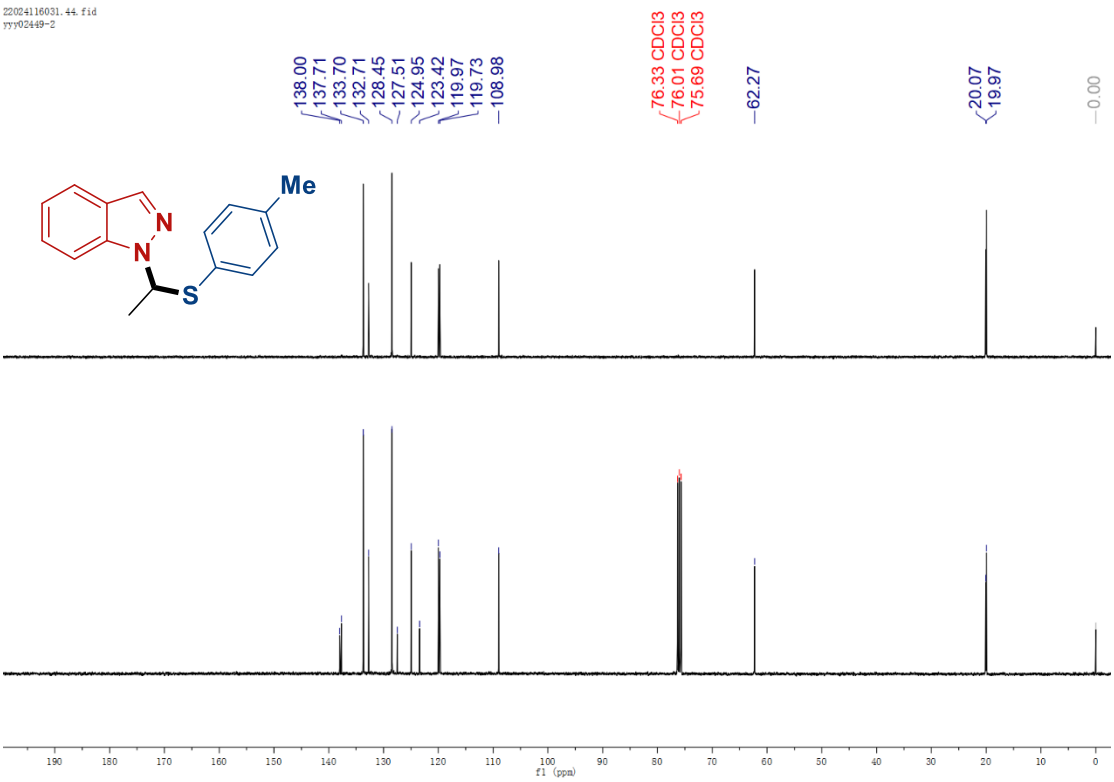
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 42**



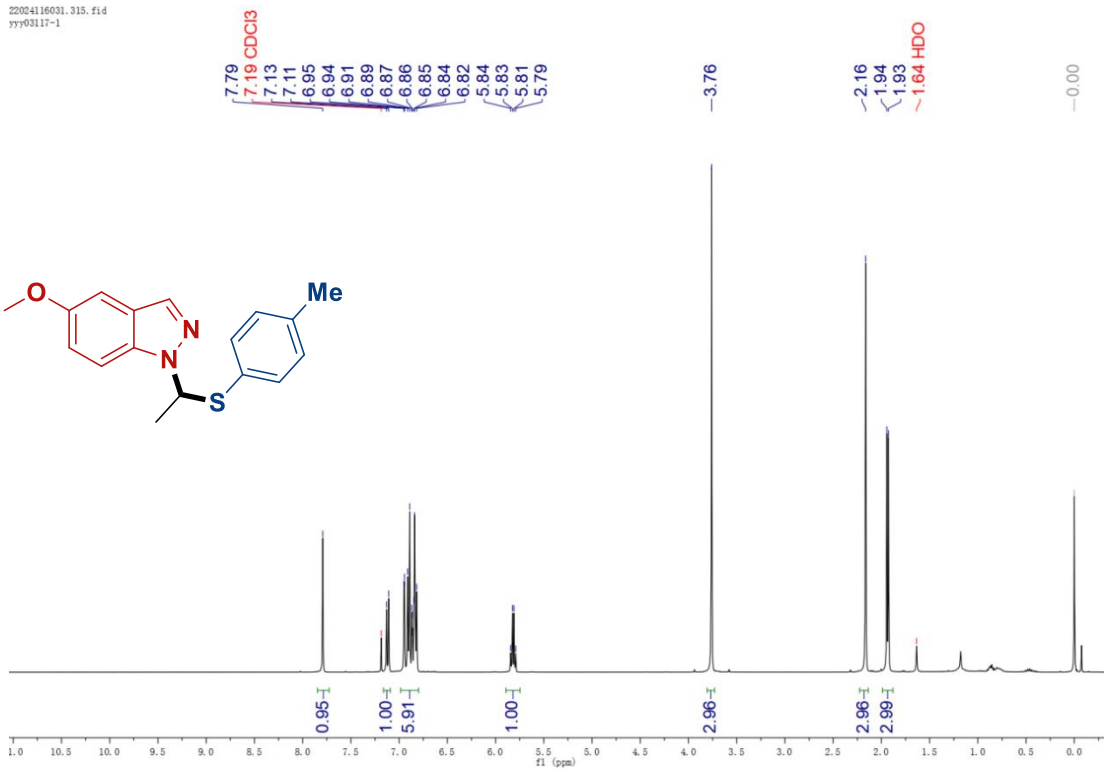
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 42**



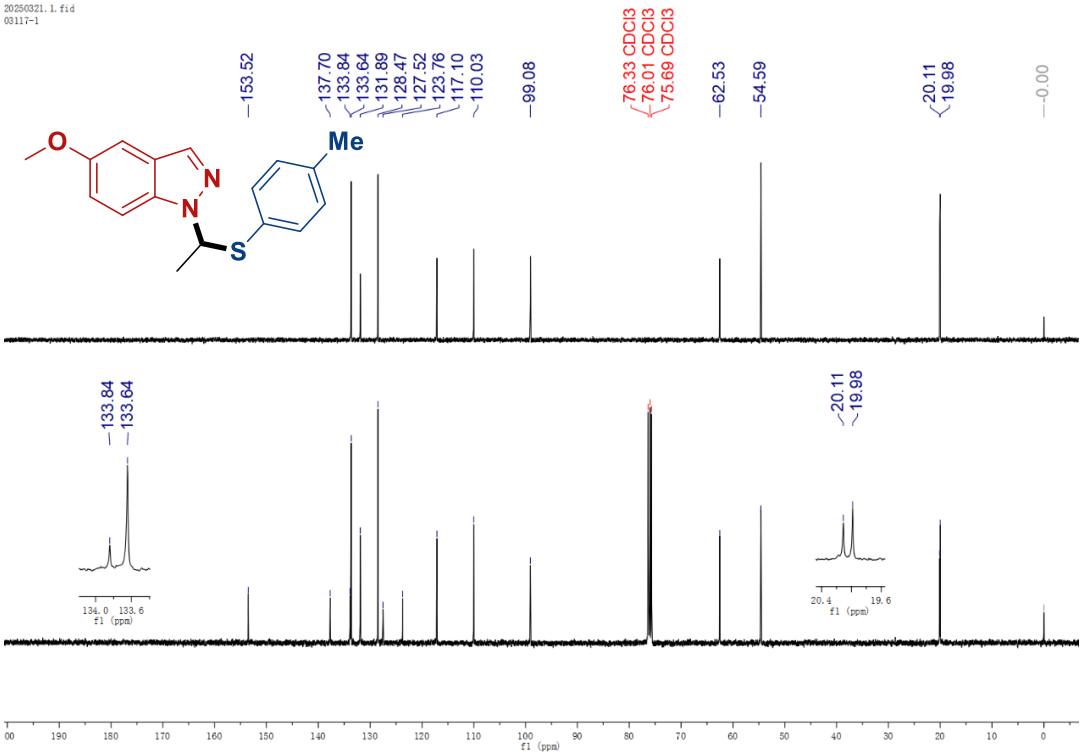
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 43**



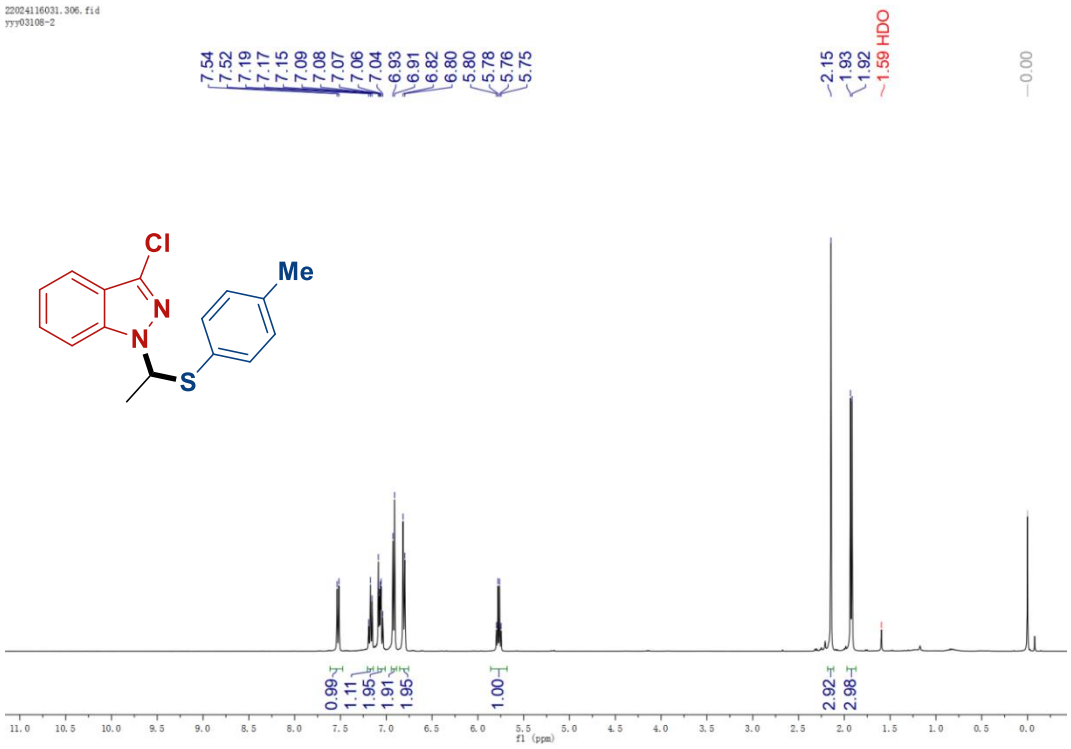
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 43**



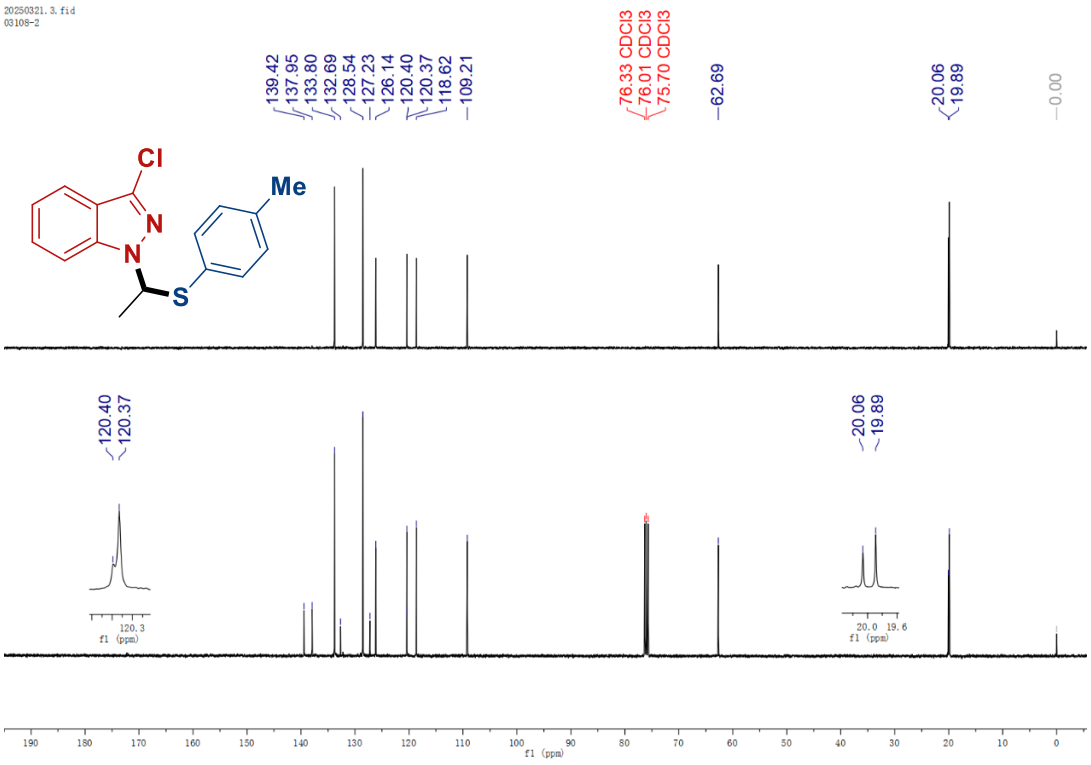
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 44**



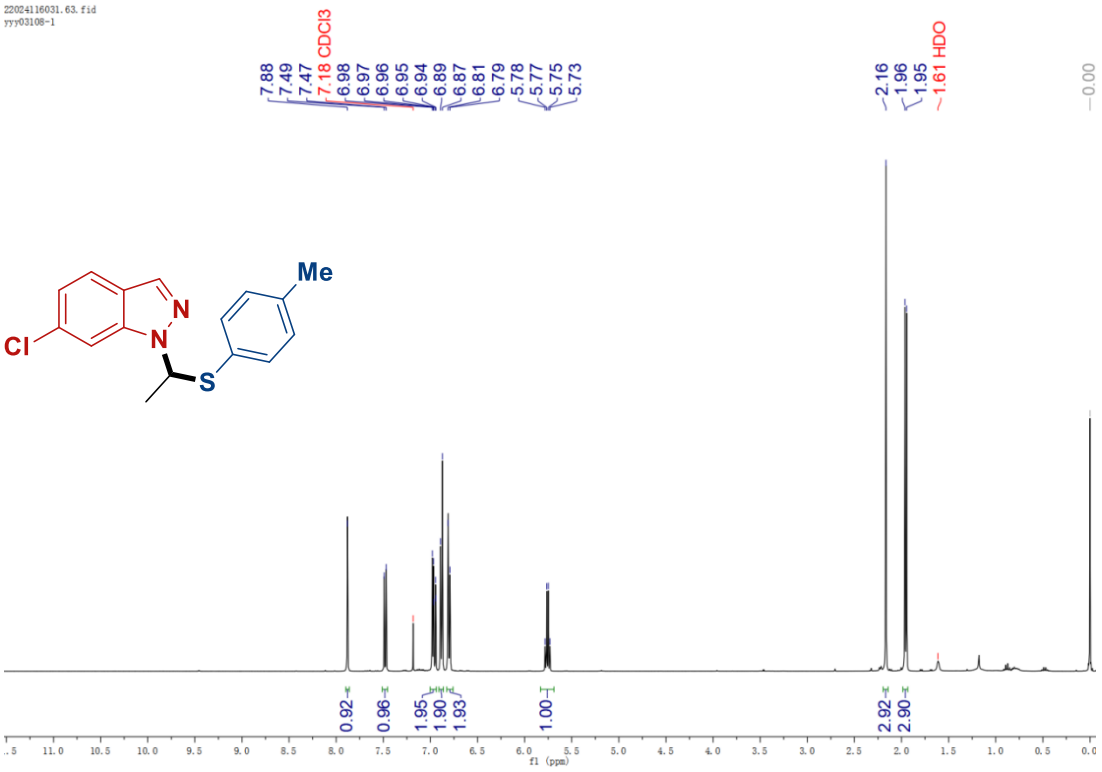
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 44**



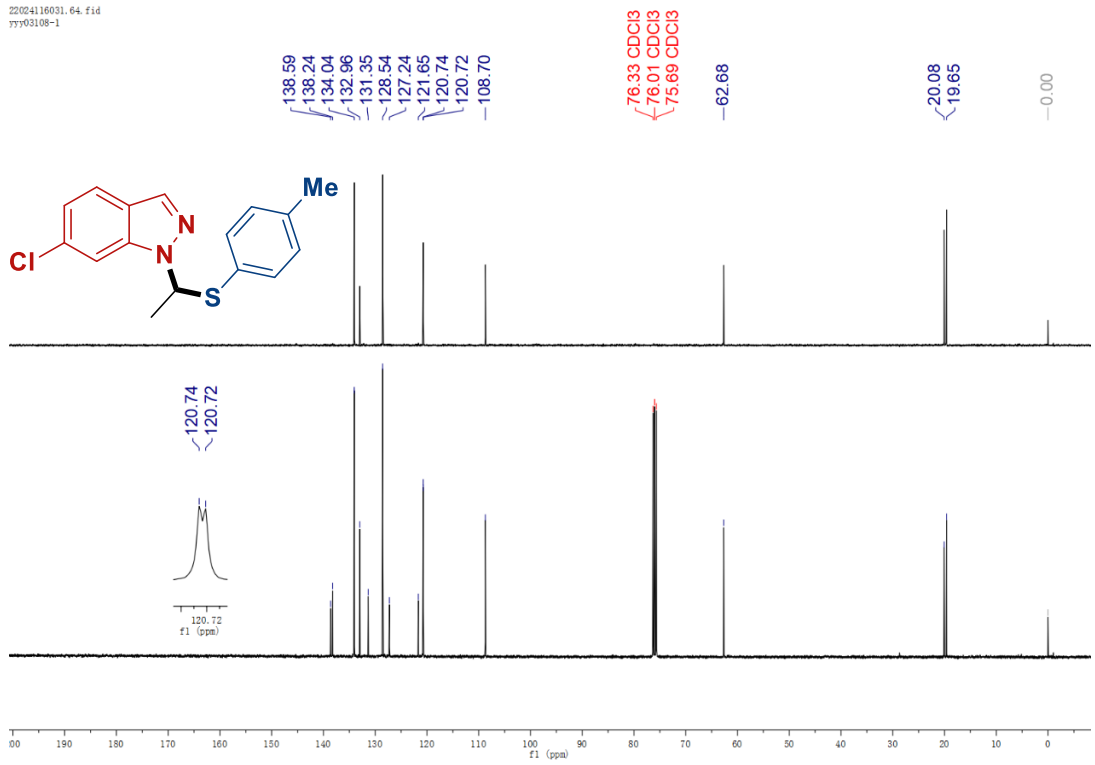
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 45**



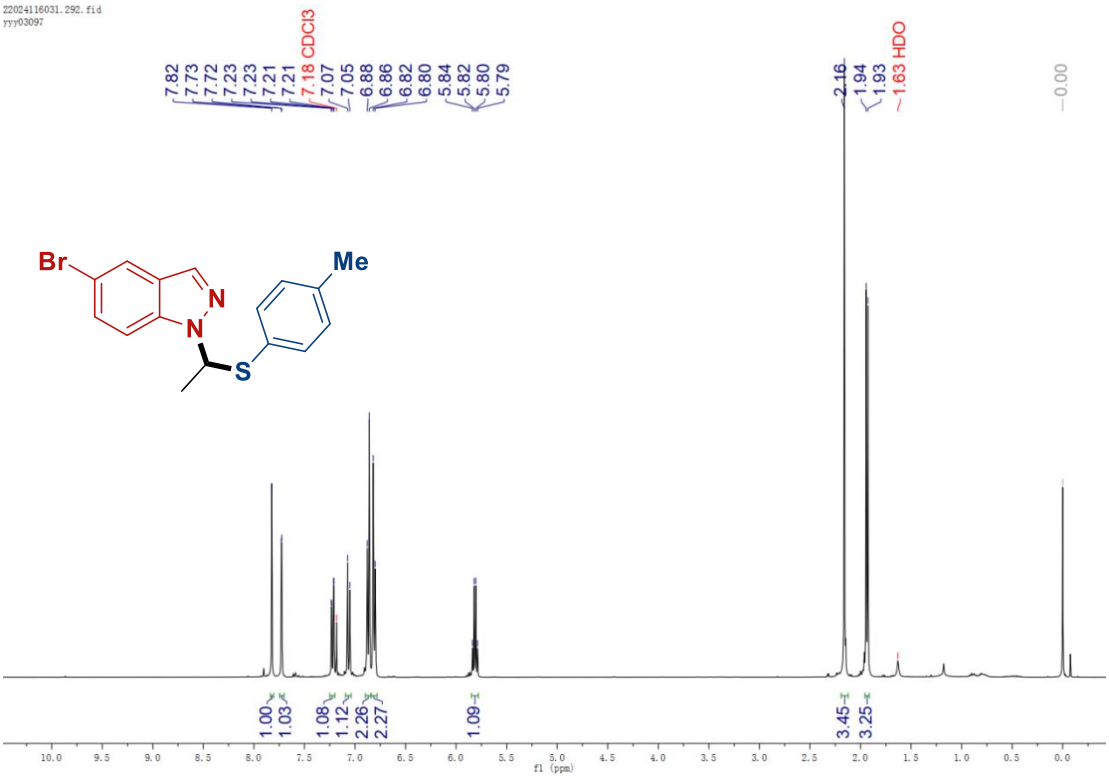
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 45**



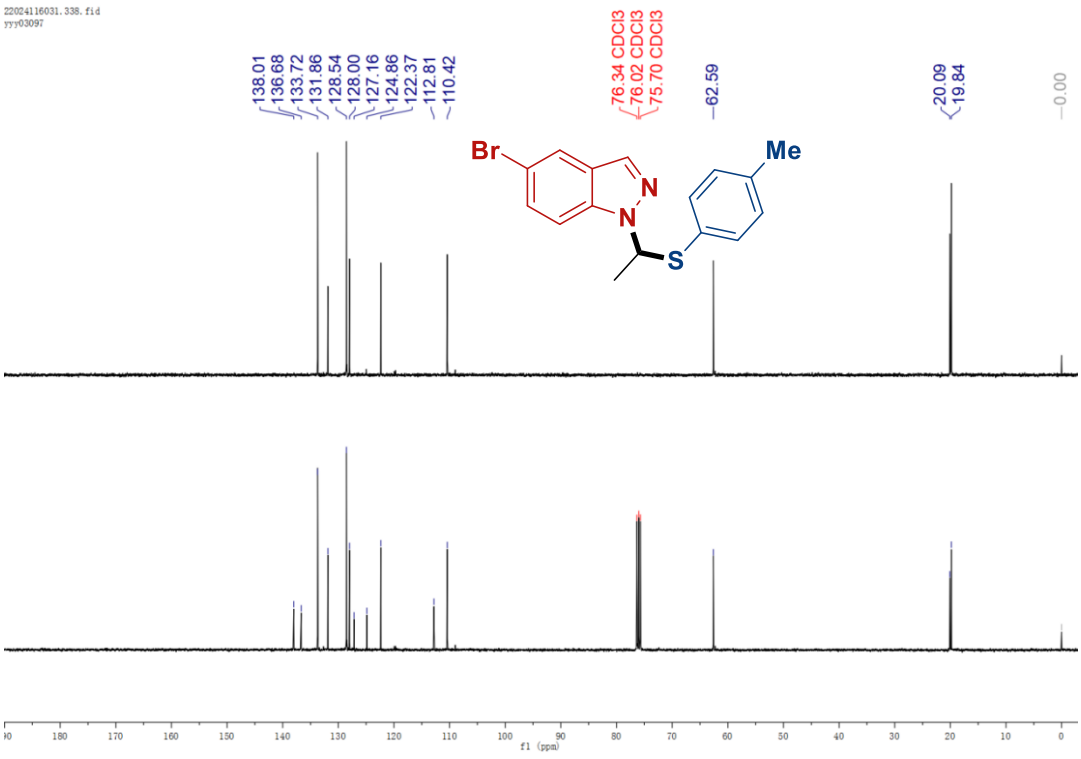
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 46**



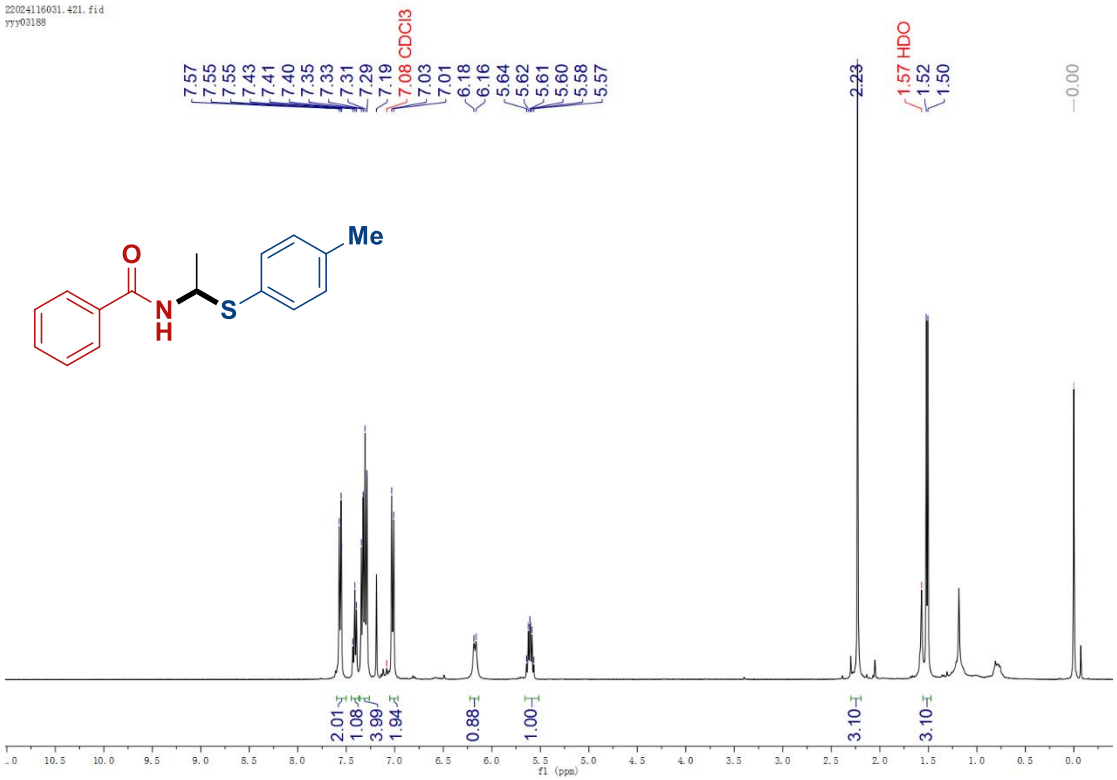
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 46**



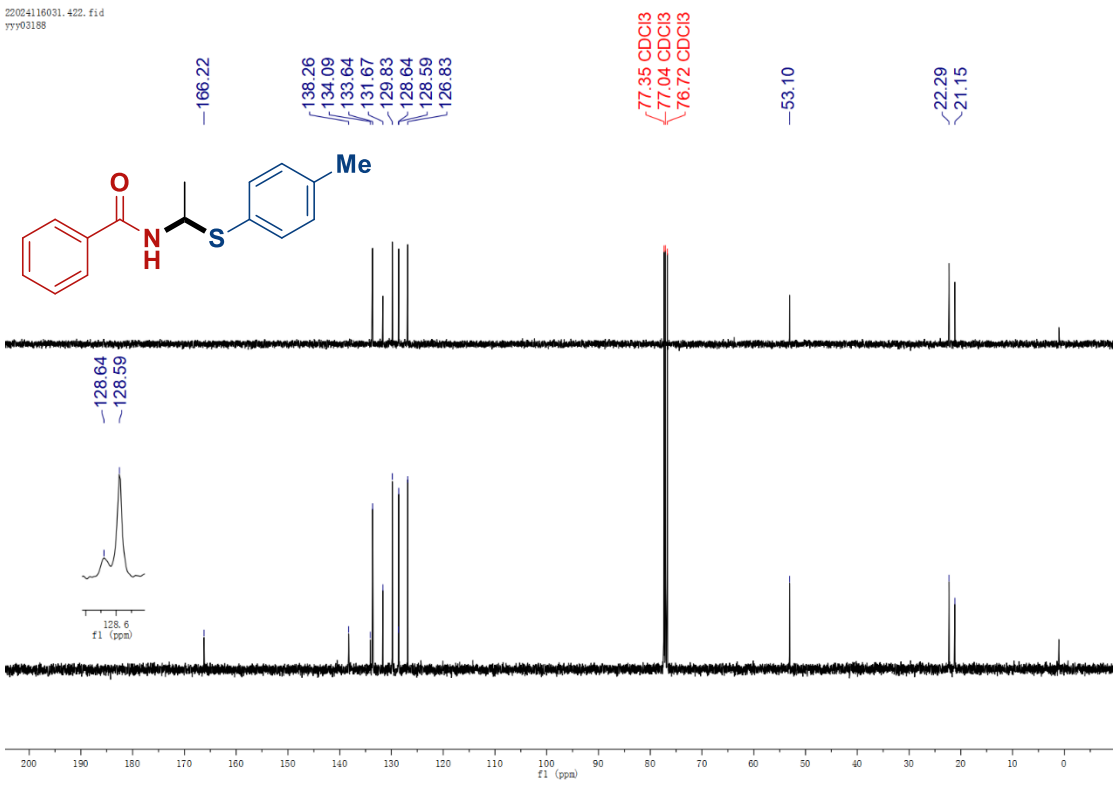
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 47**



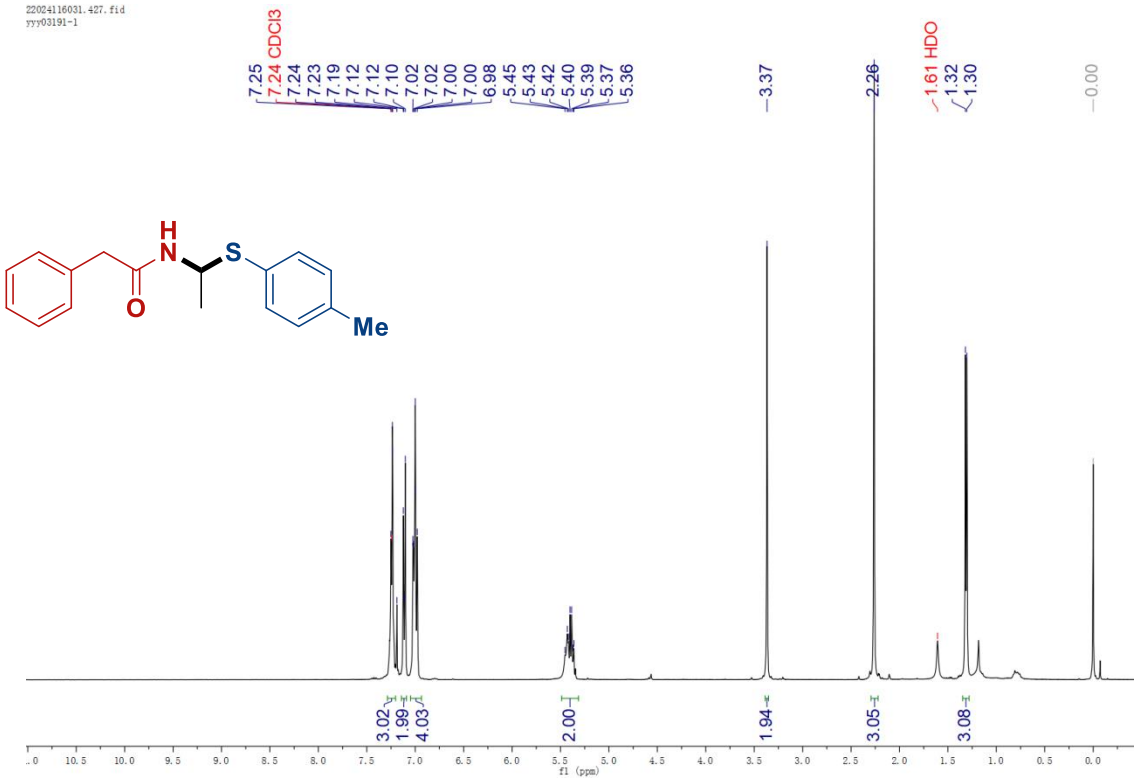
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 47**



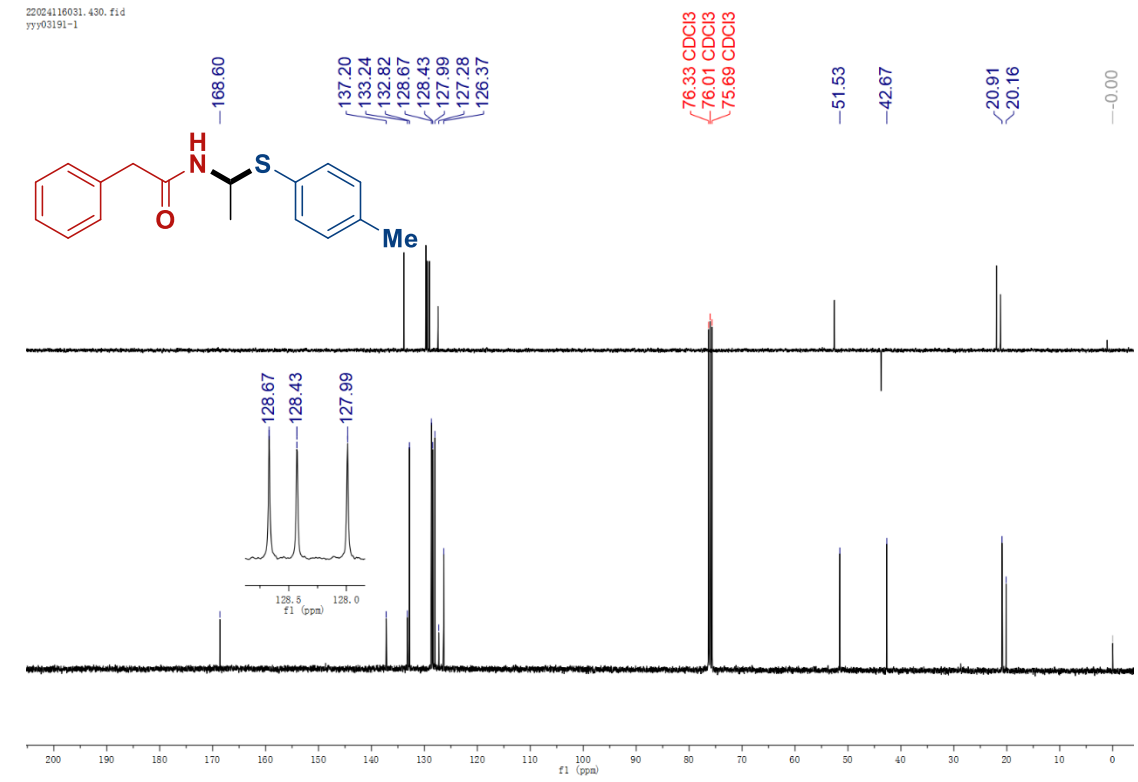
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 48**



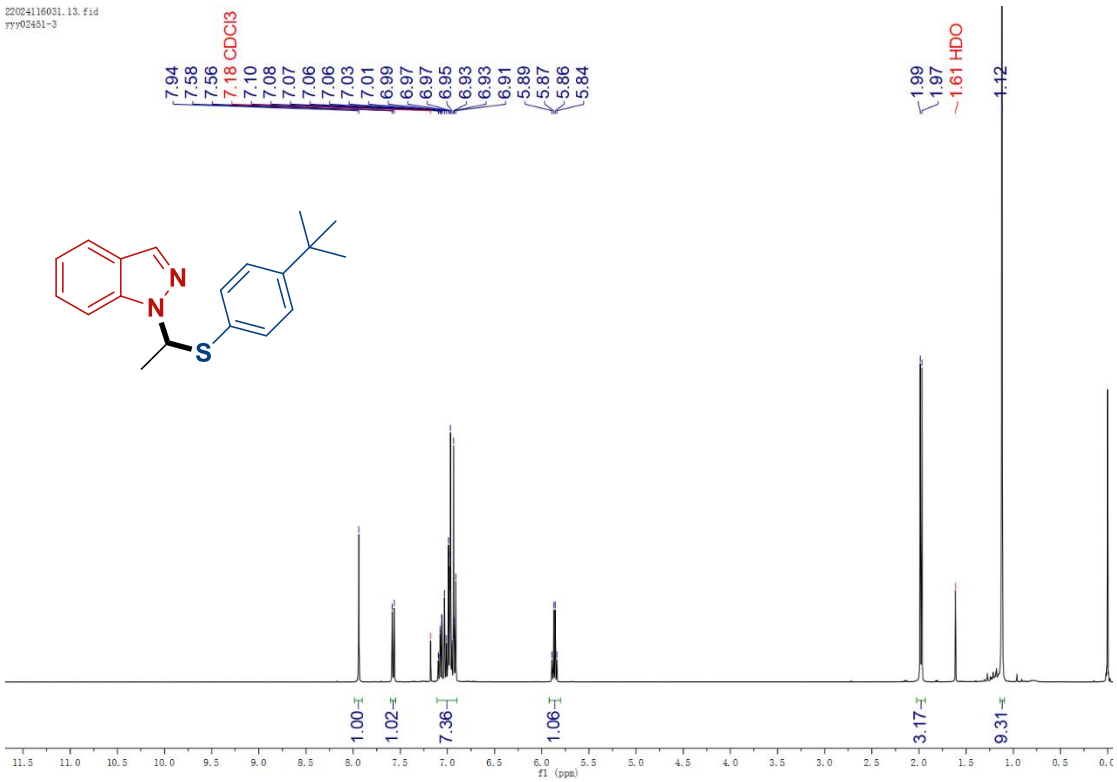
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 48**



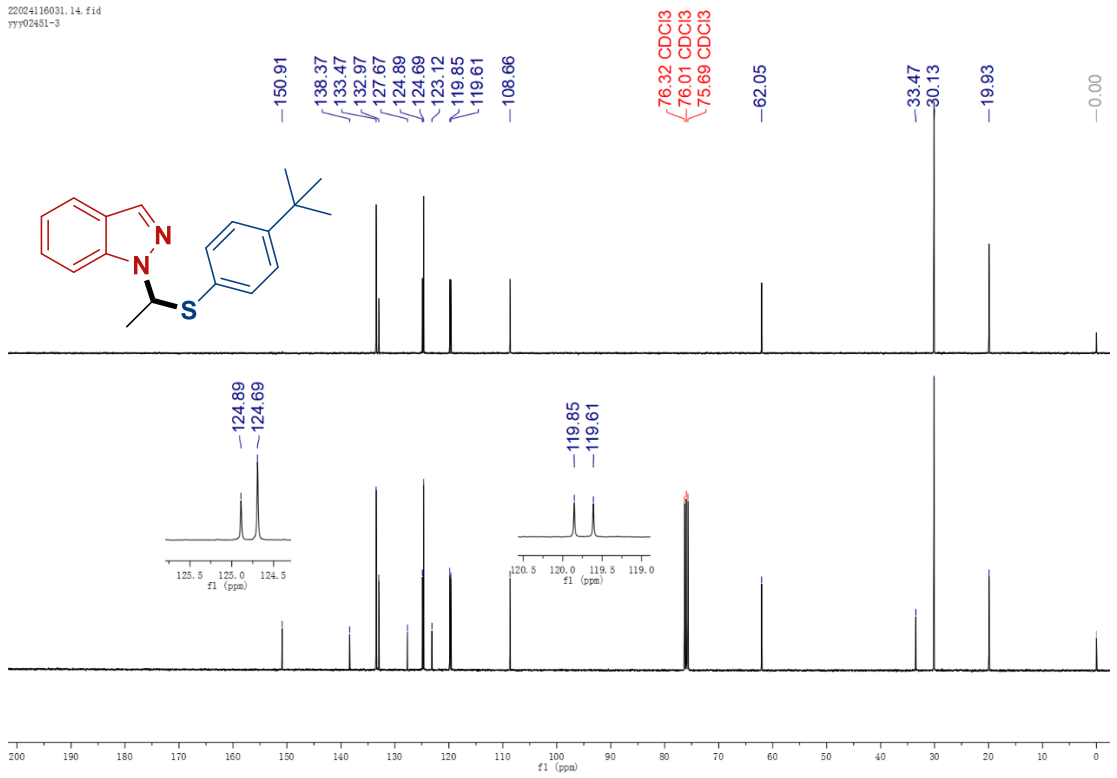
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 49**



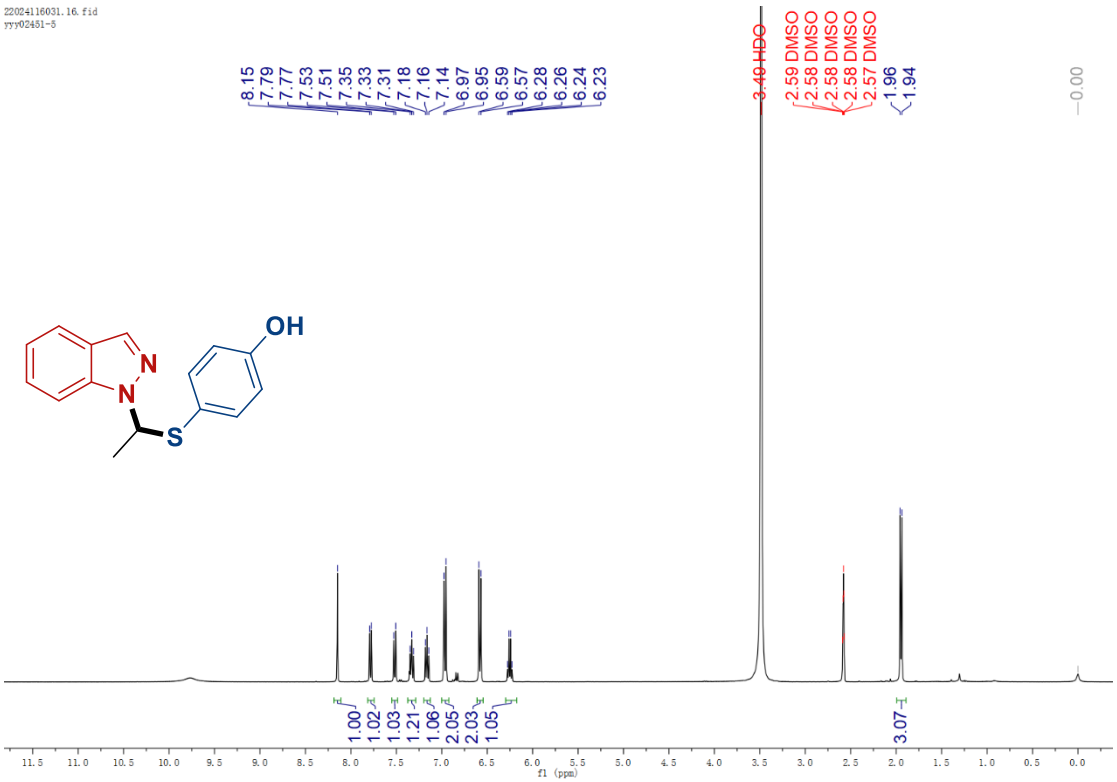
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 49**



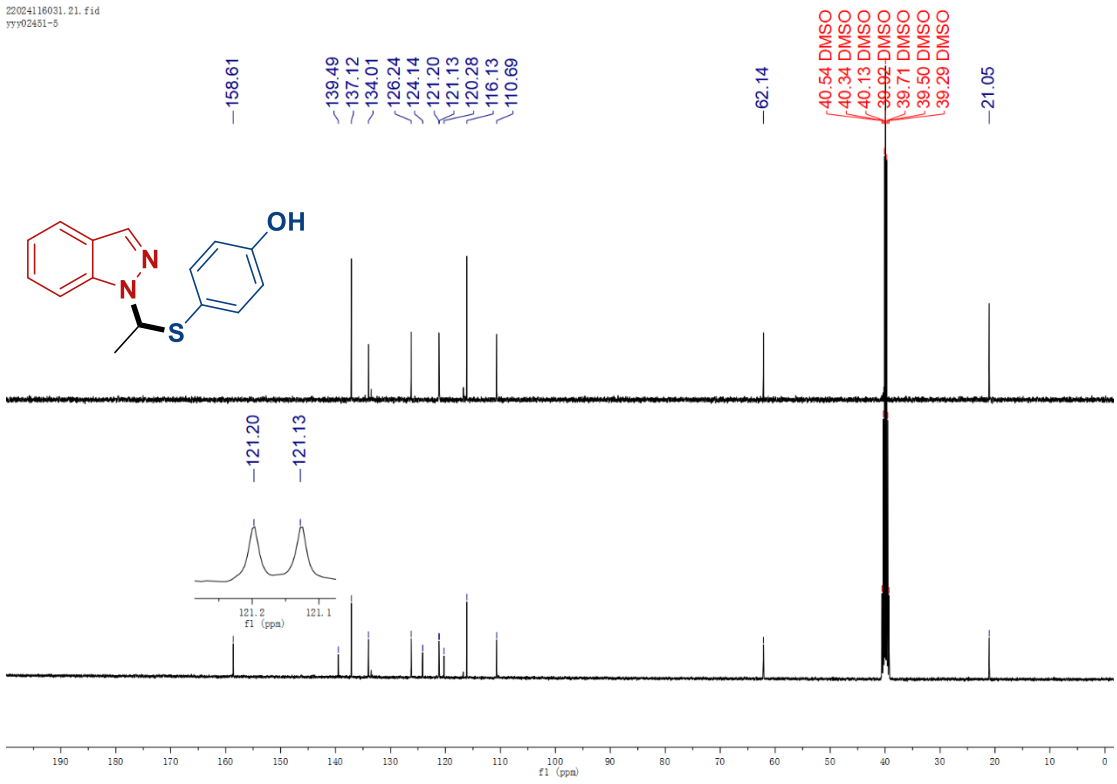
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 50**



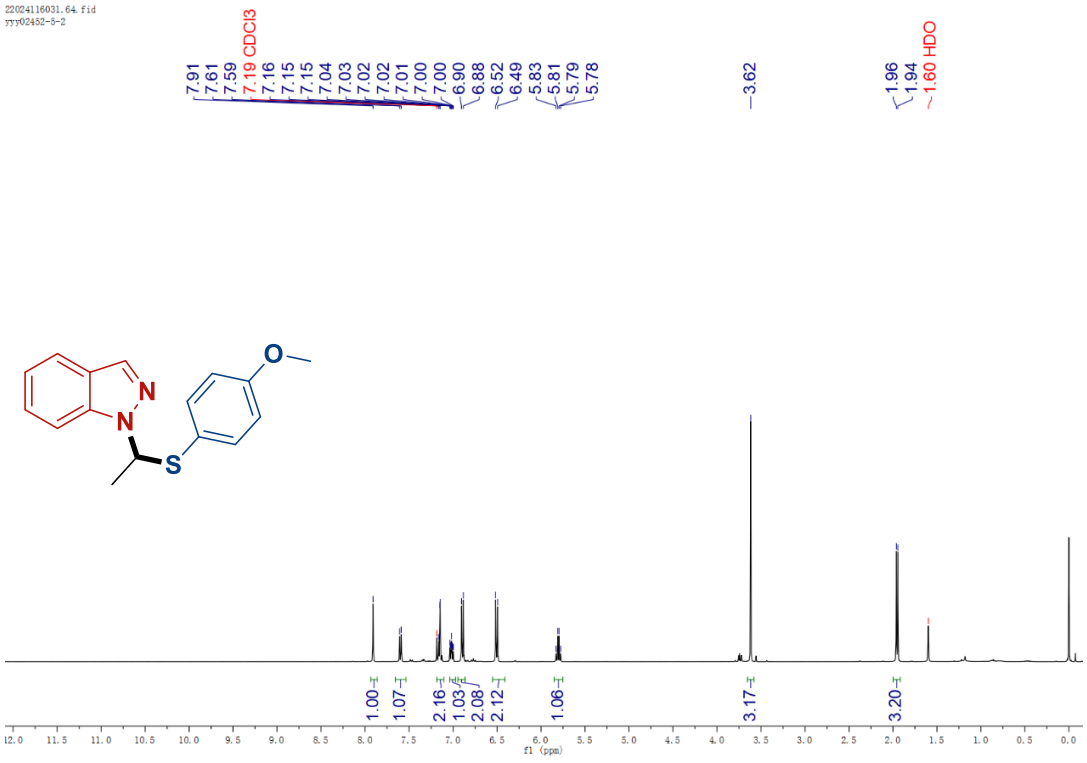
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 50**



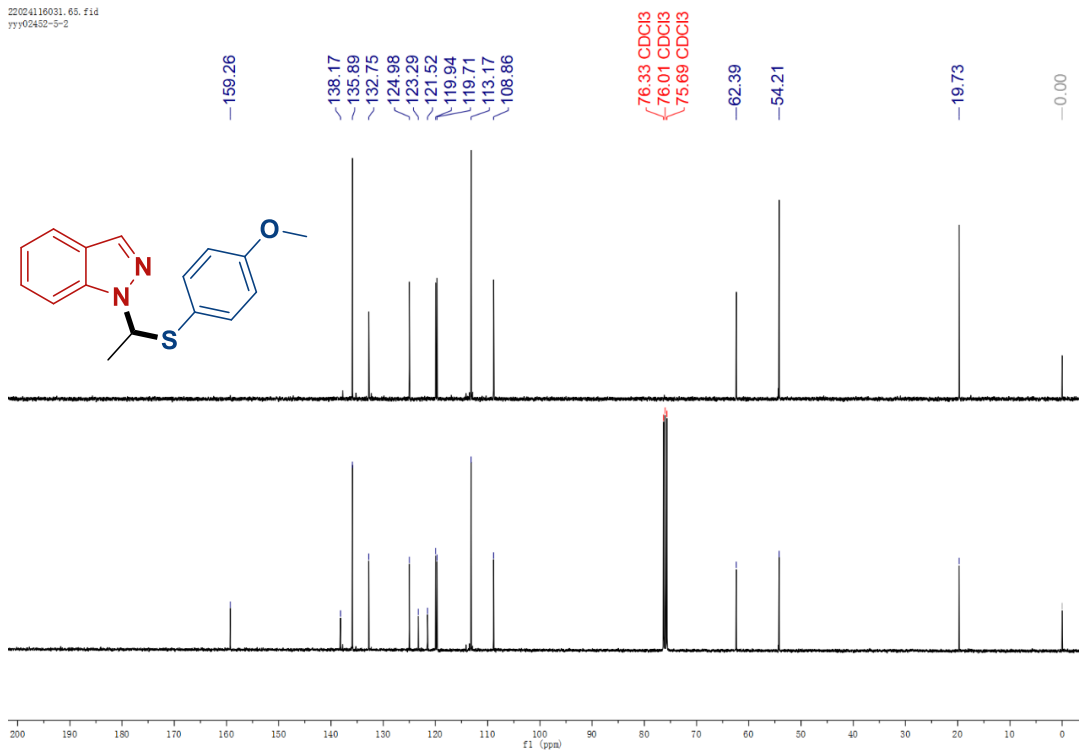
^{1}H-NMR (400 MHz, DMSO-d_6) **Spectrum of 51**



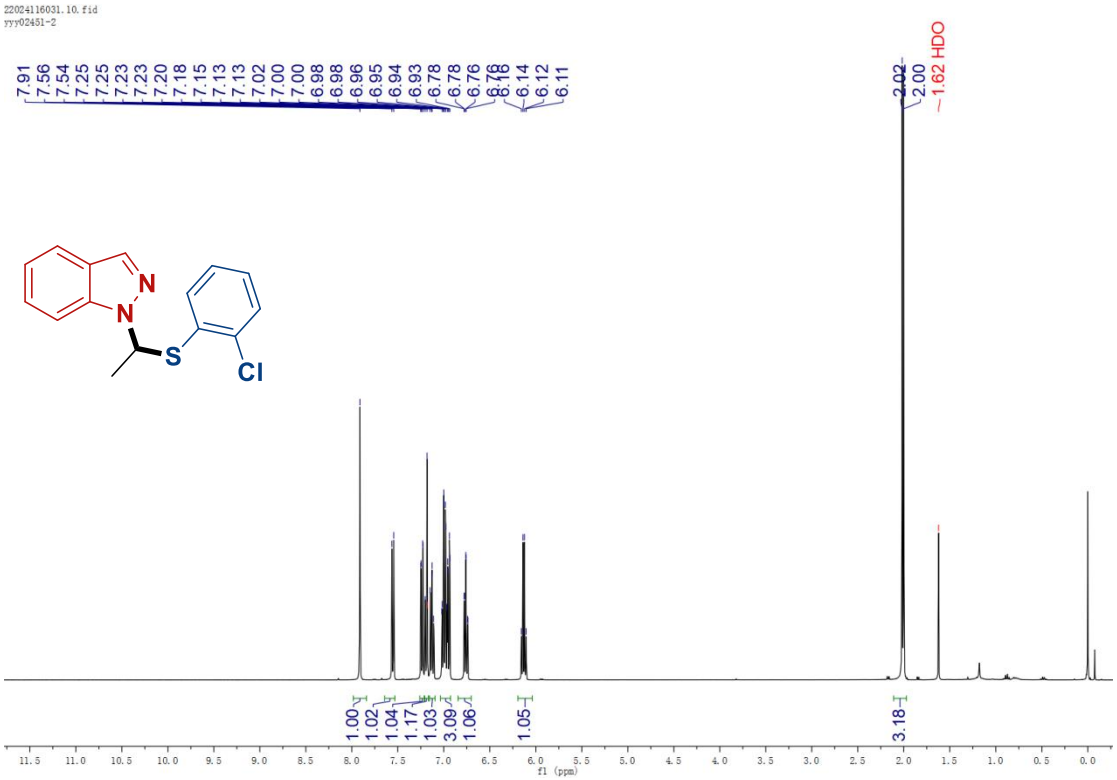
^{13}C-NMR (100 MHz, DMSO-d_6) **Spectrum of 51**



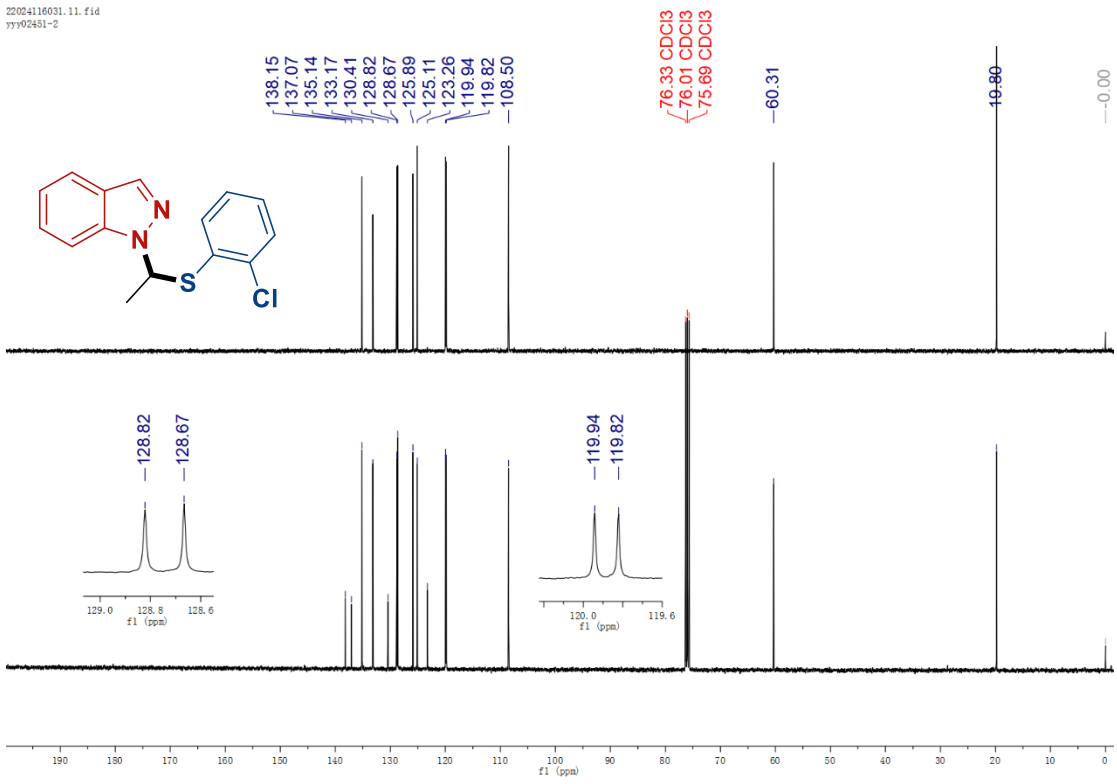
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 52**



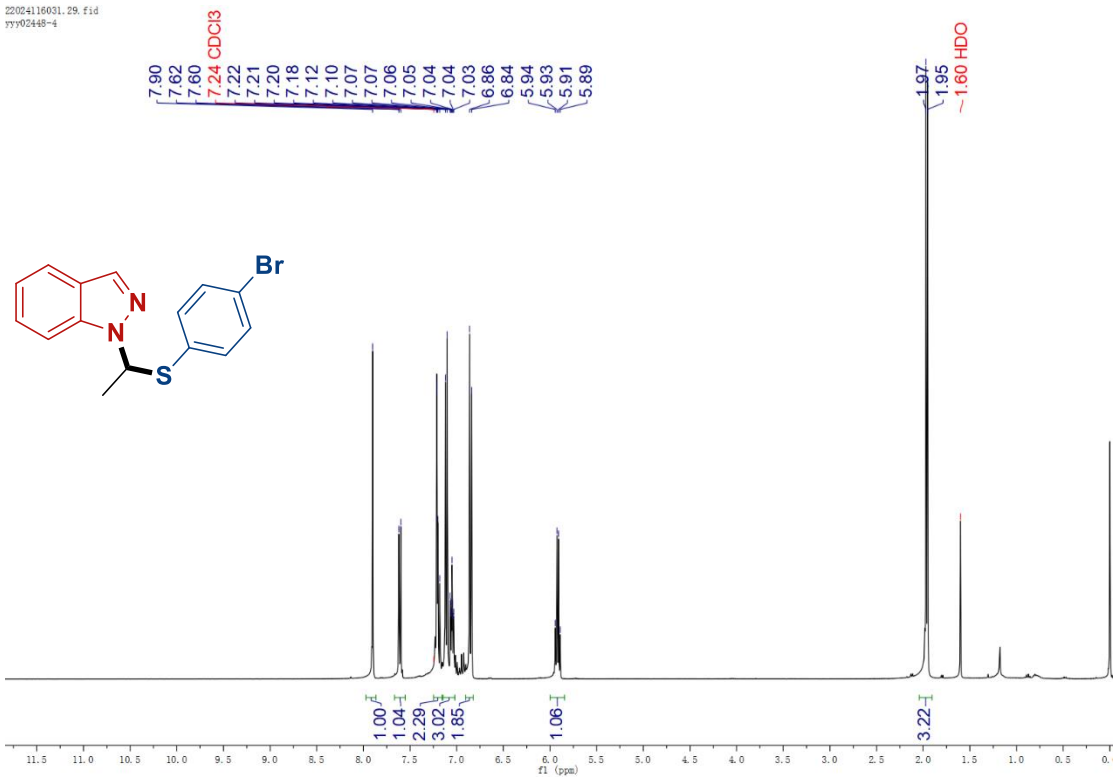
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 52**



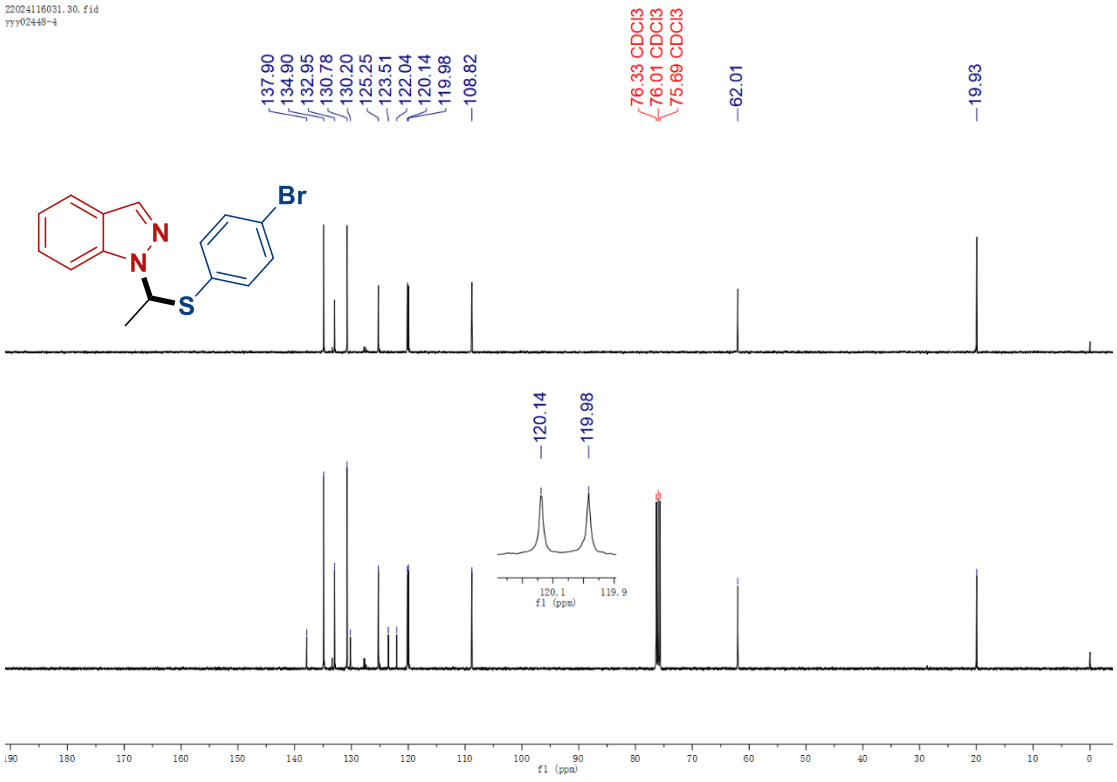
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 53**



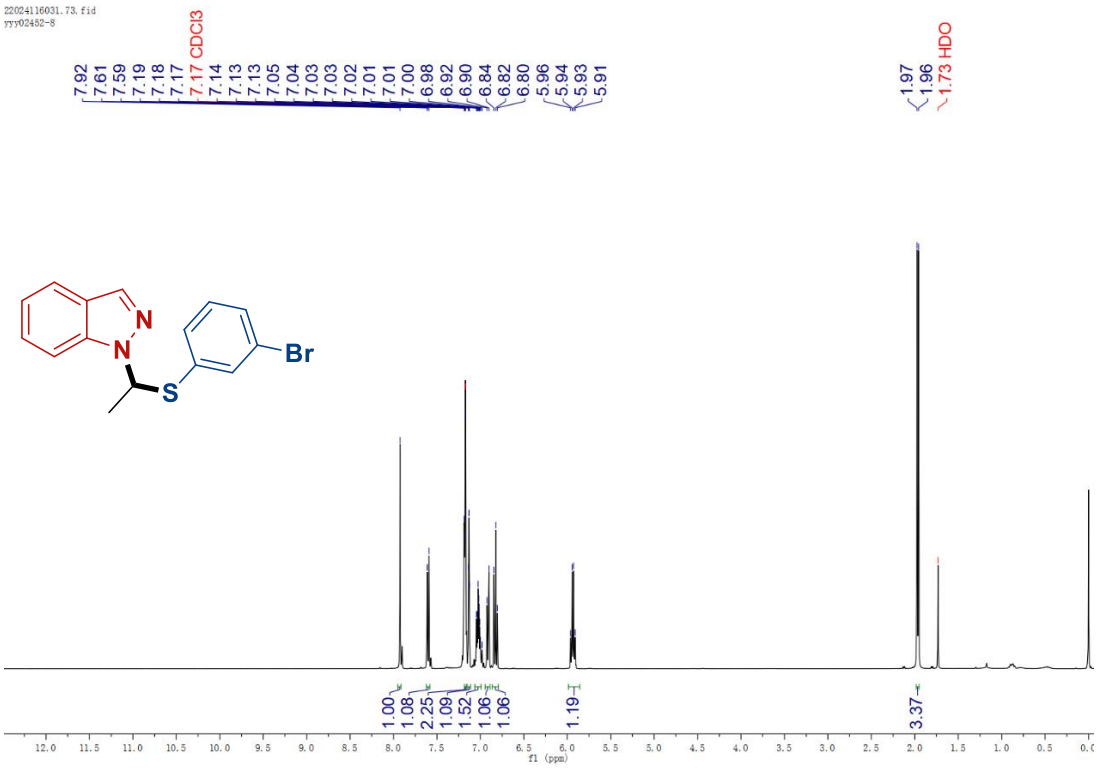
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 53**



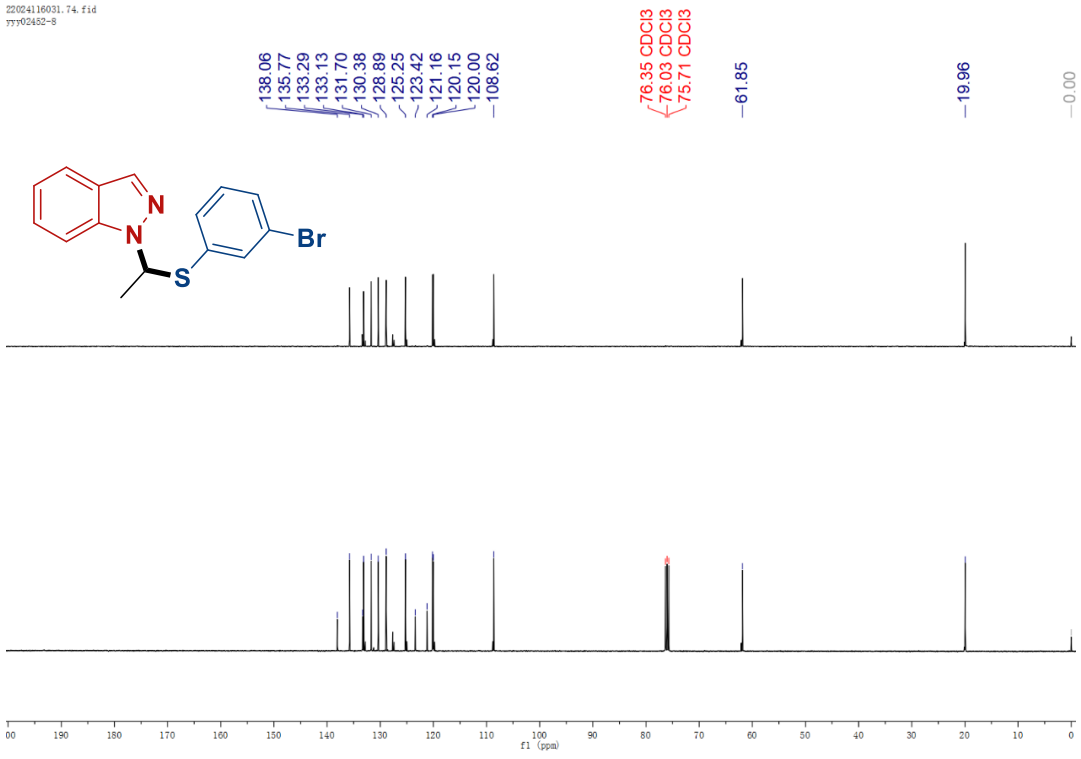
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 54**



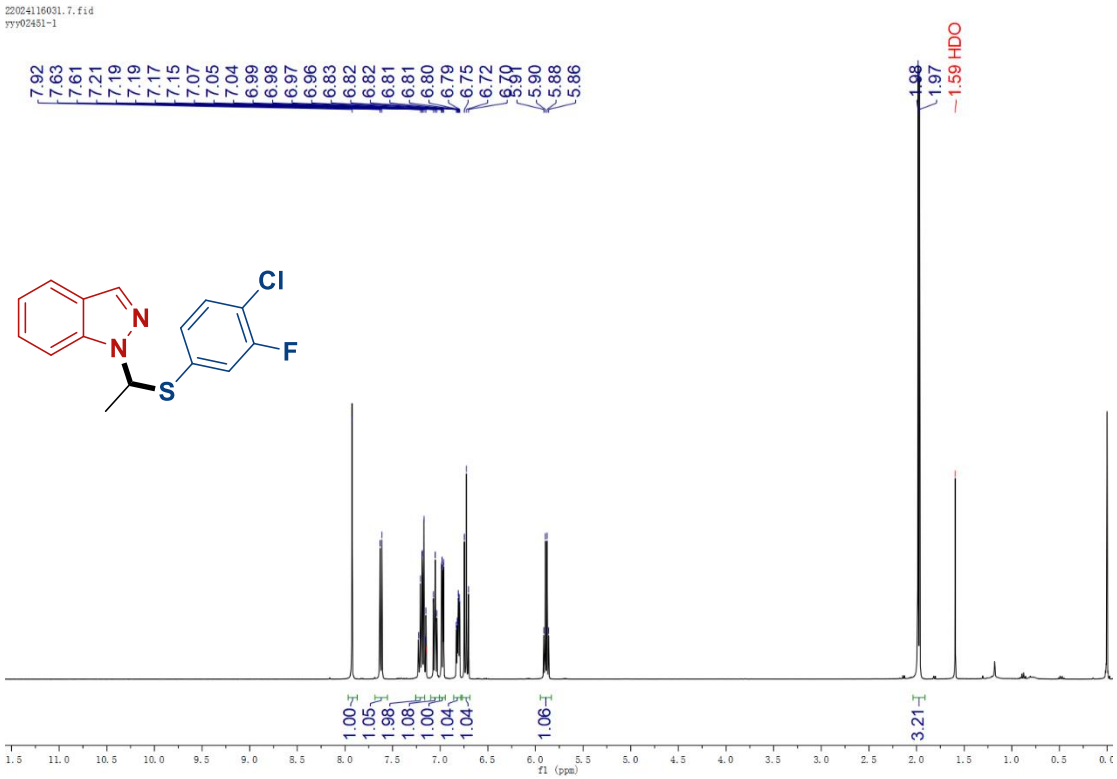
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 54**



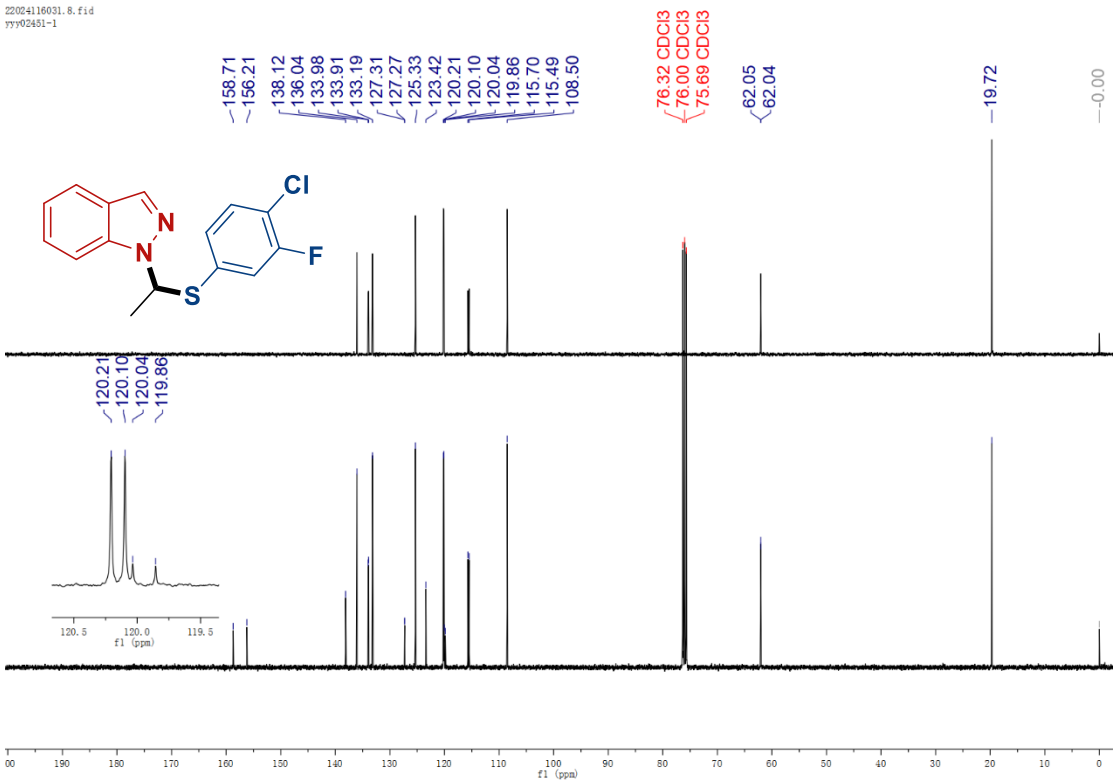
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 55**



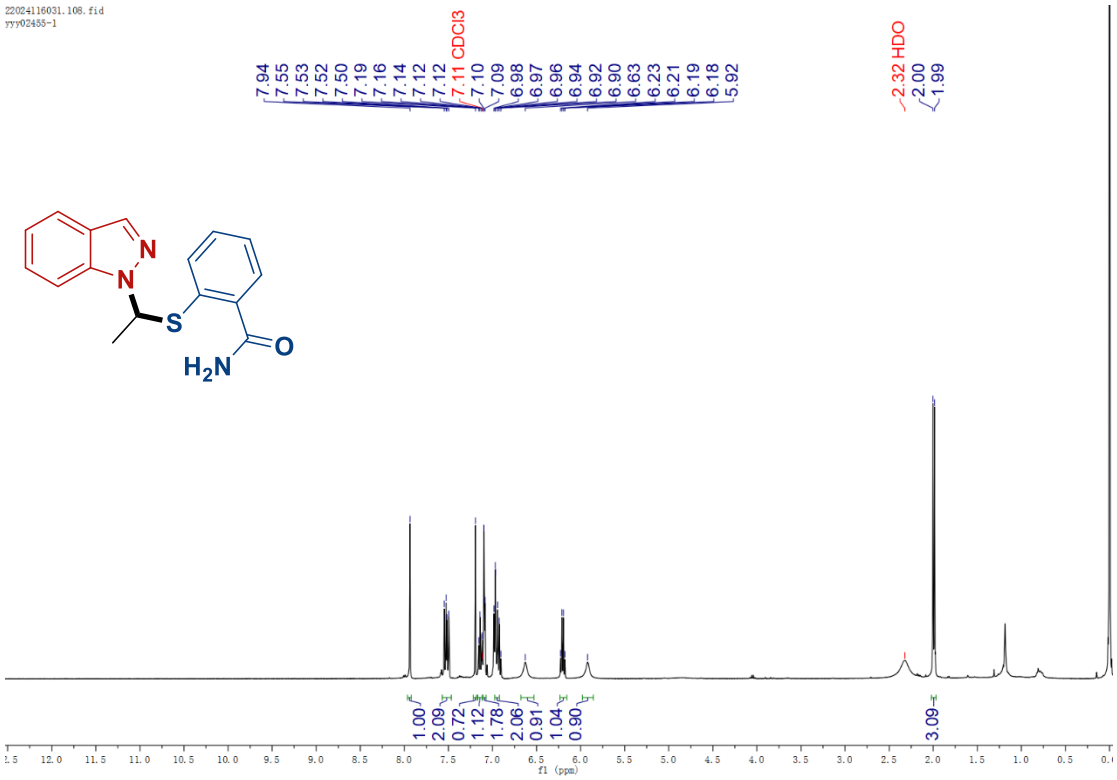
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 55**



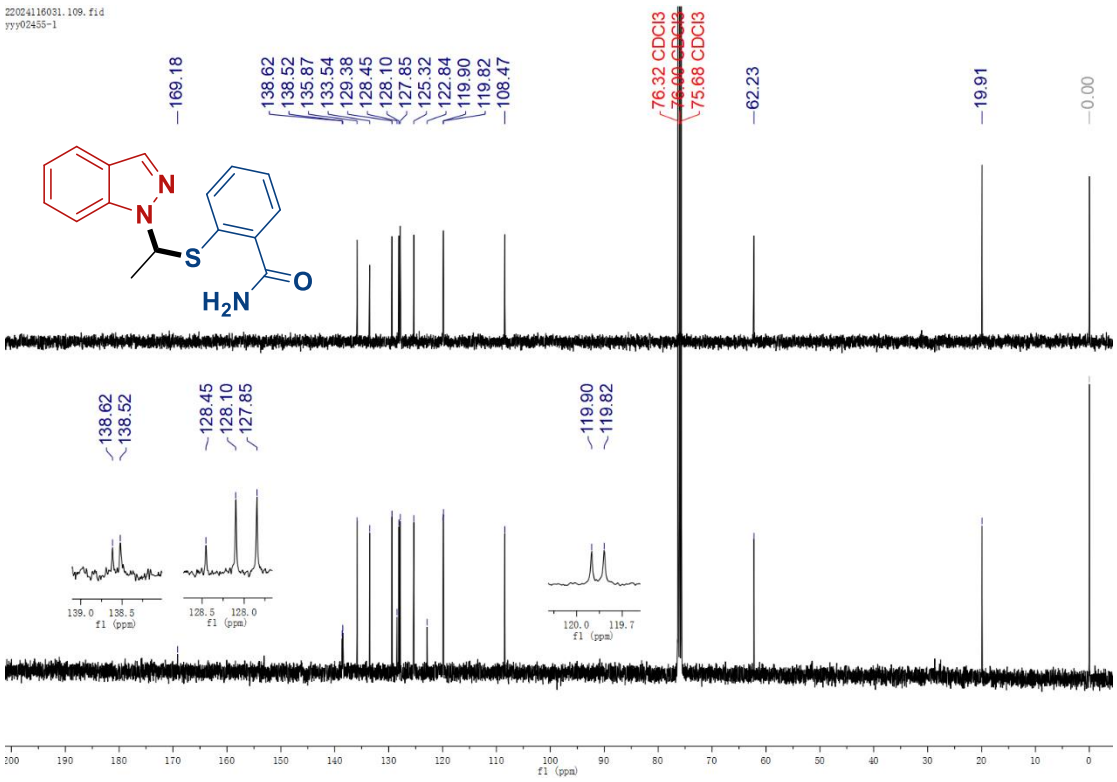
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 56**



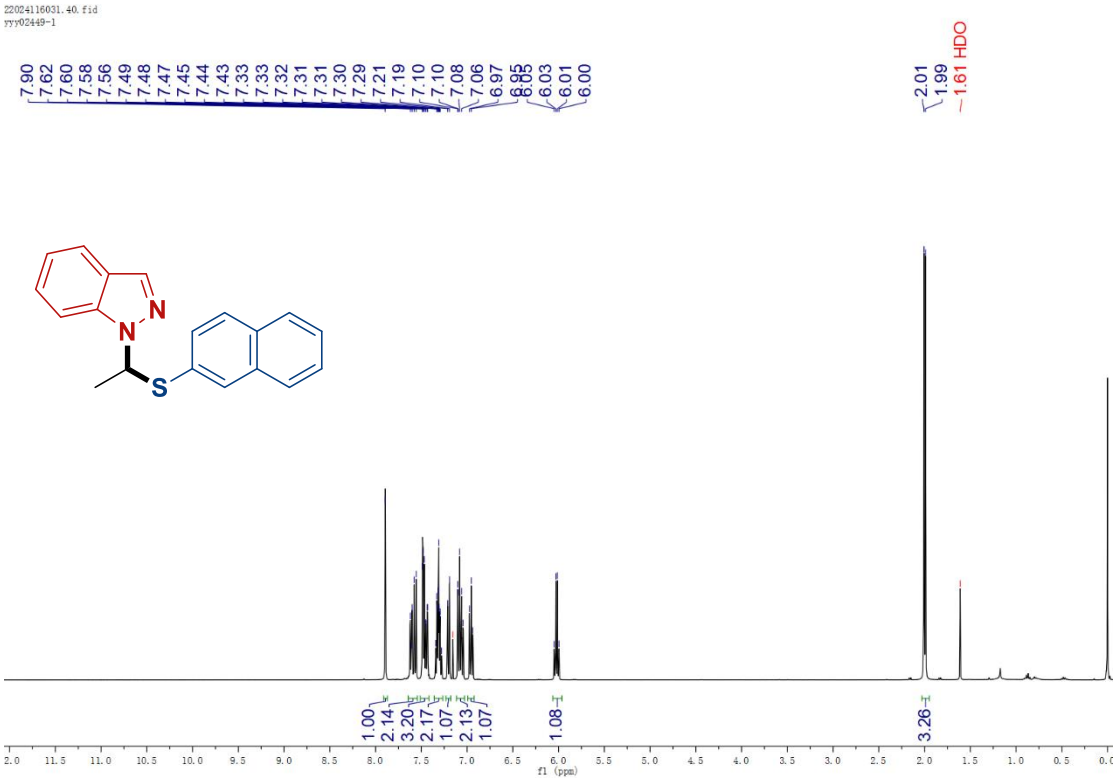
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 56**



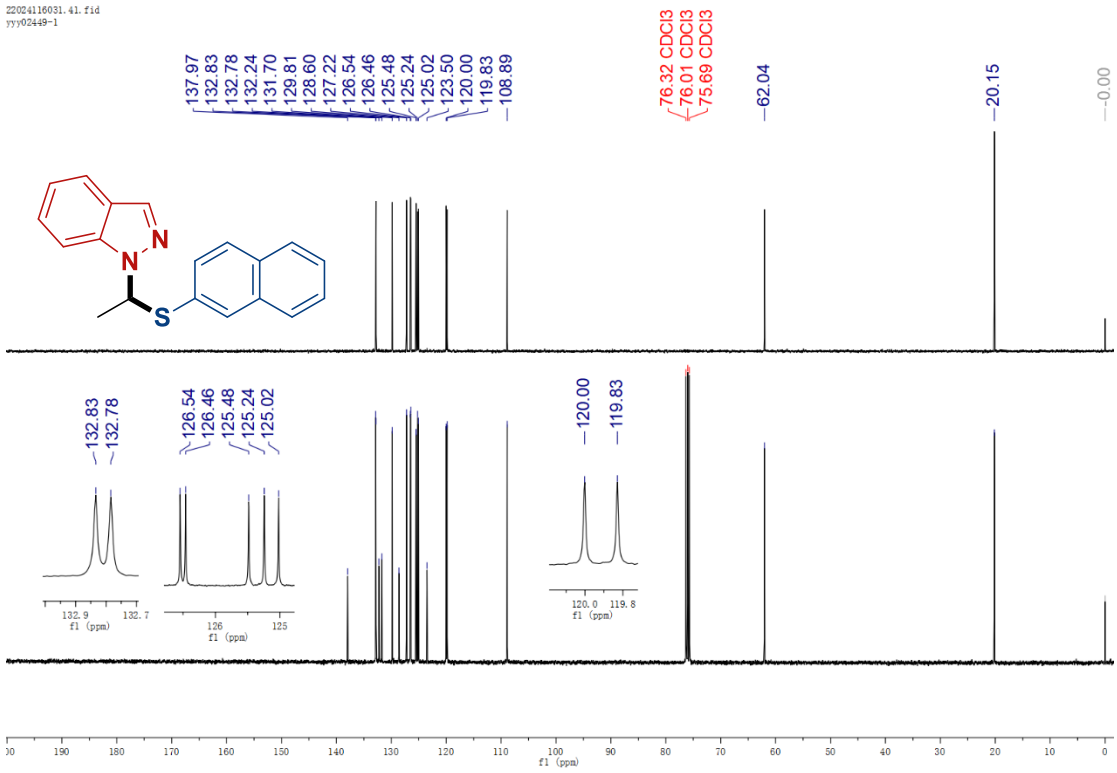
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 57**



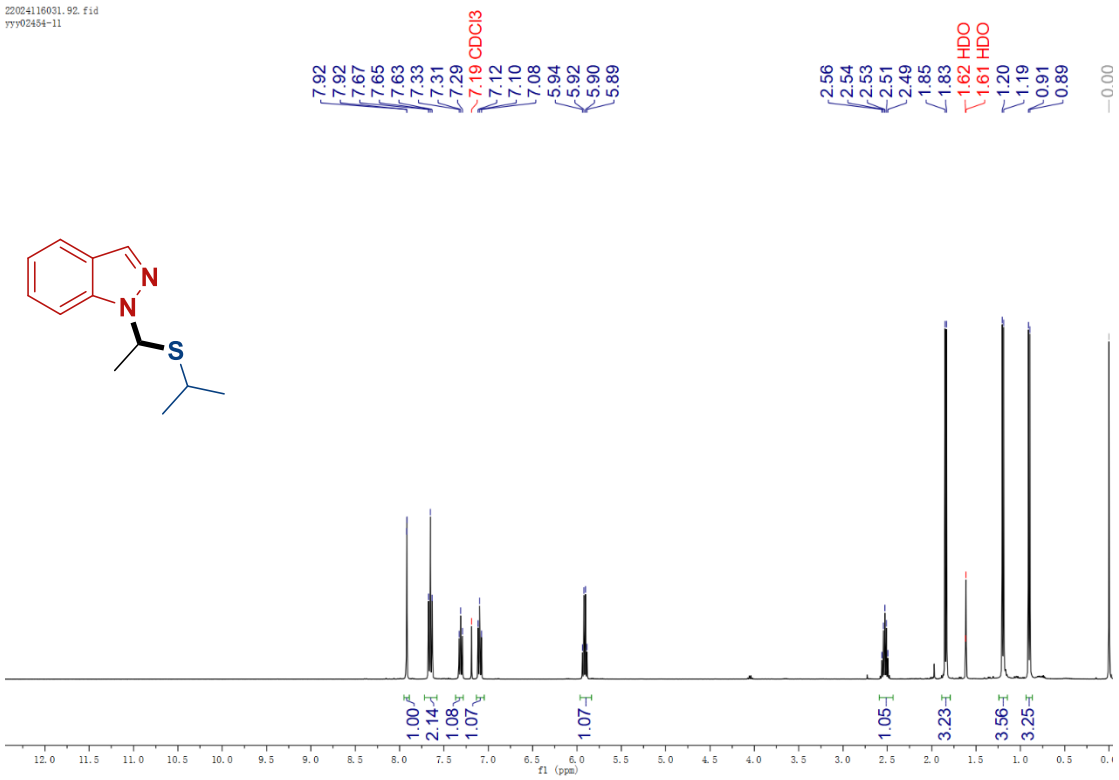
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 57**



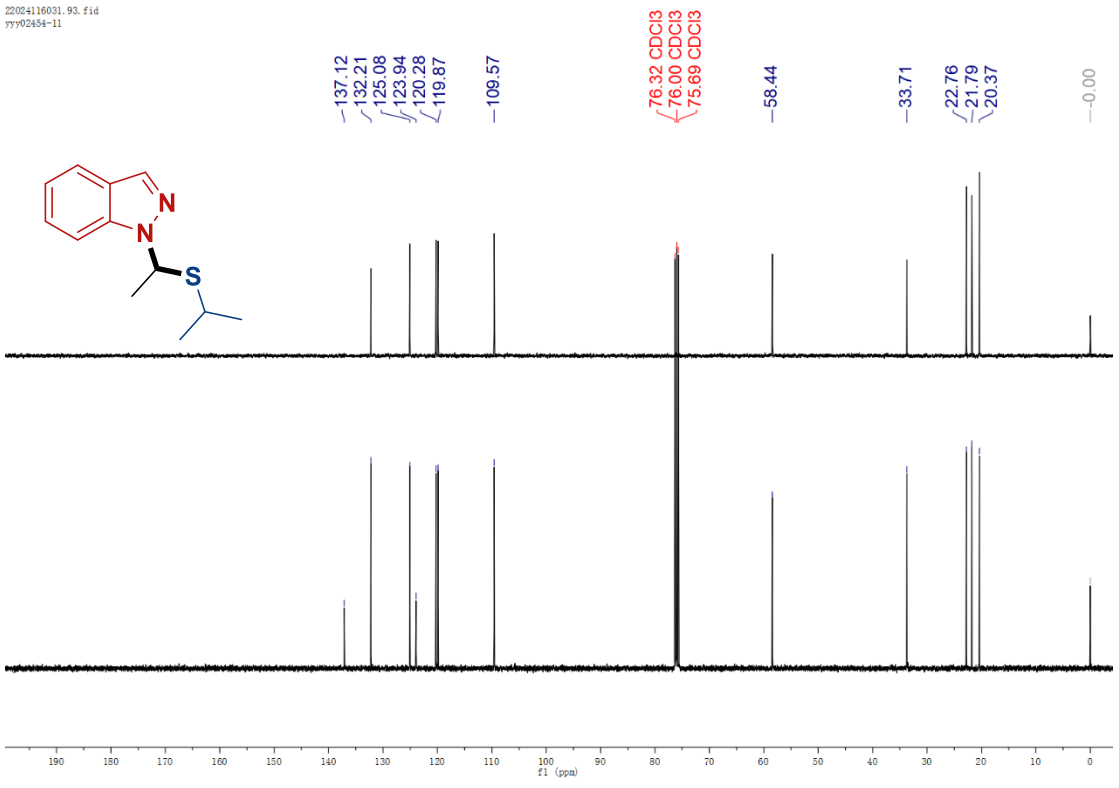
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 58**



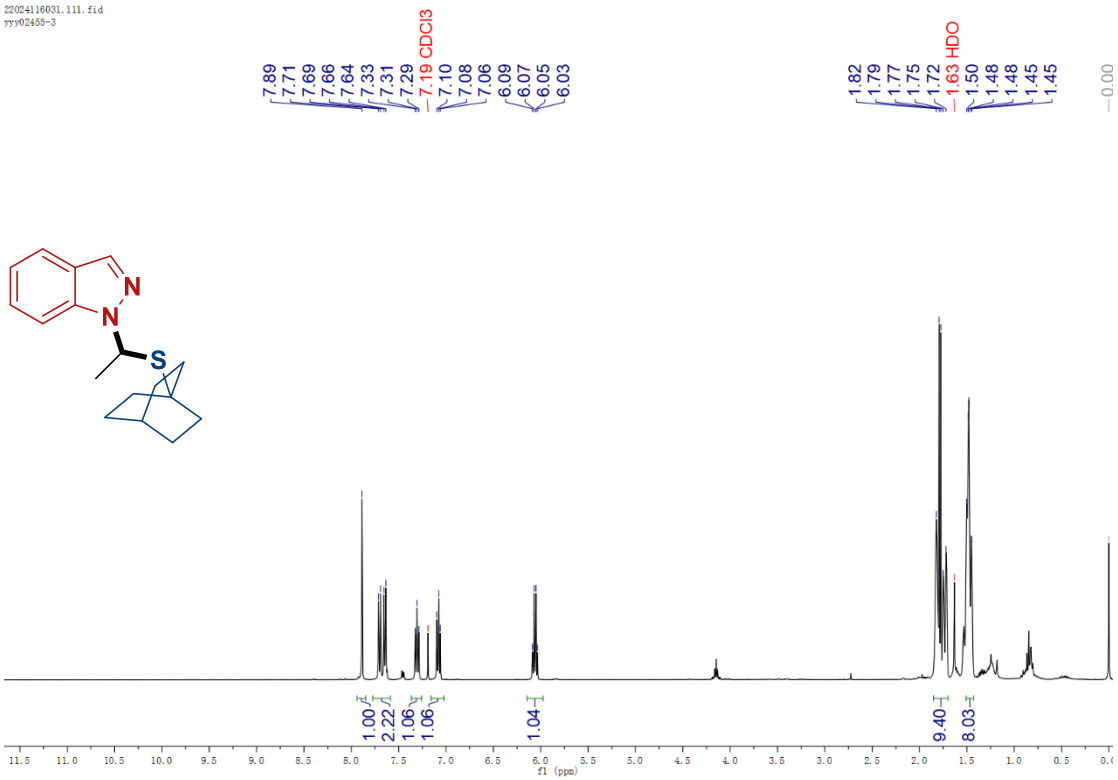
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 58**



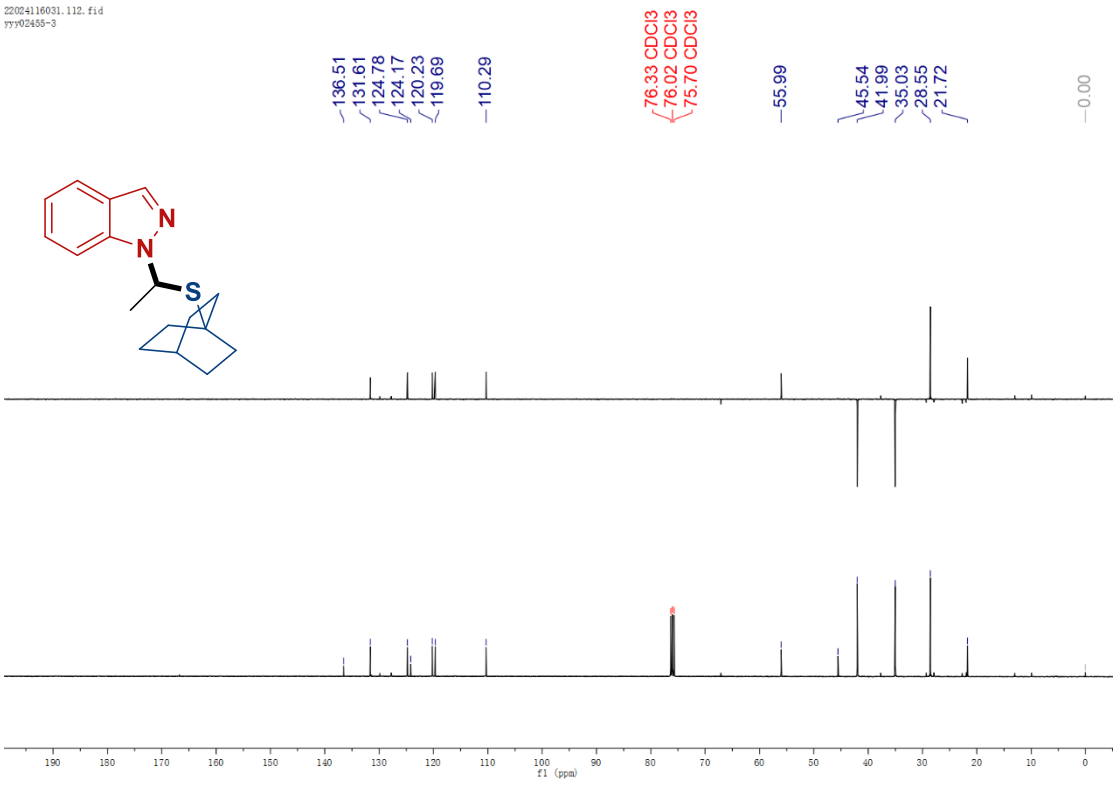
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 59**



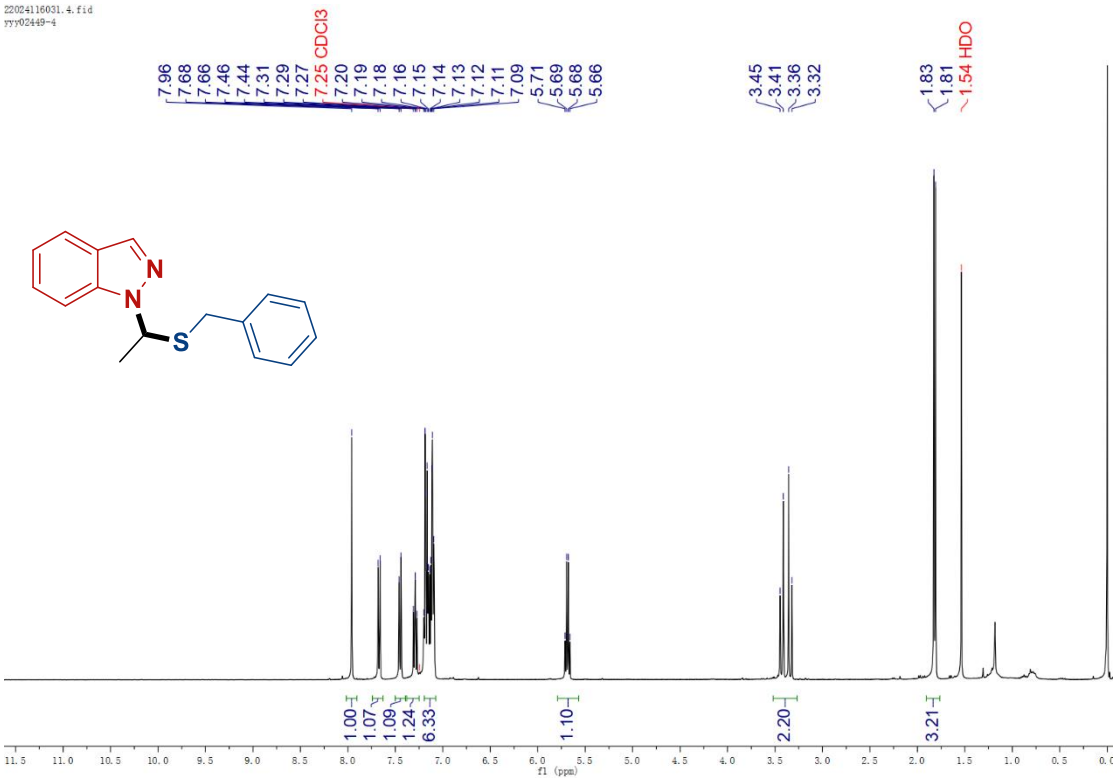
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 59**



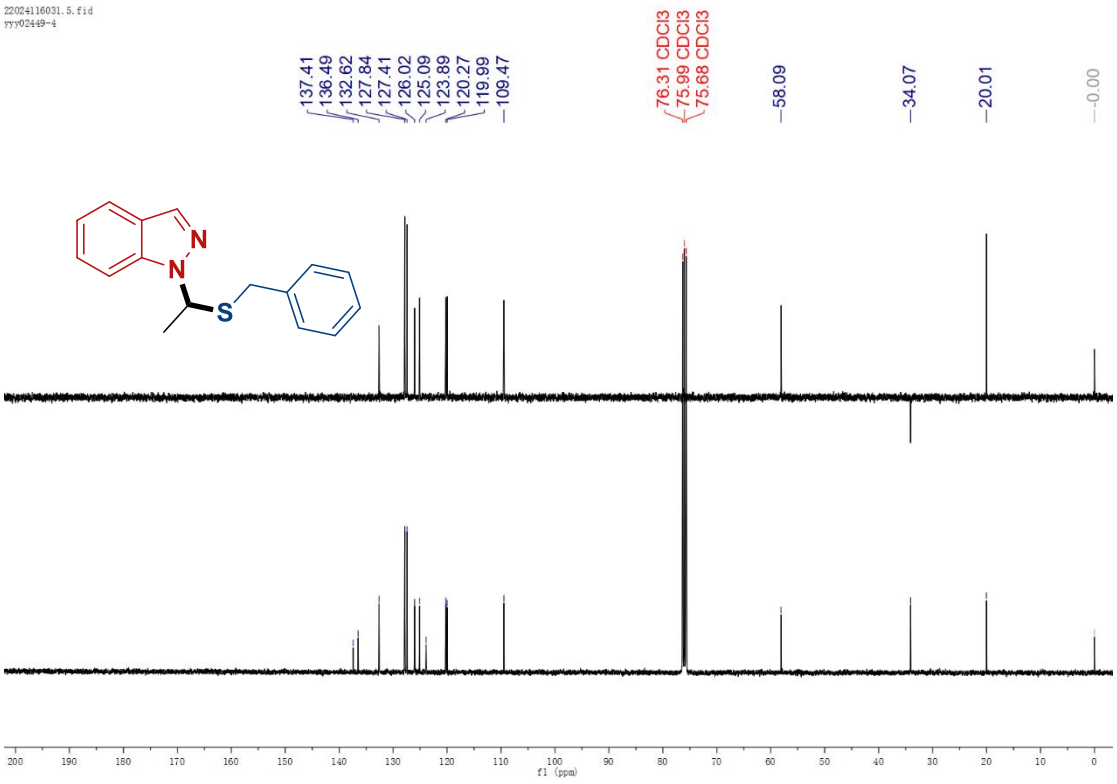
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 60**



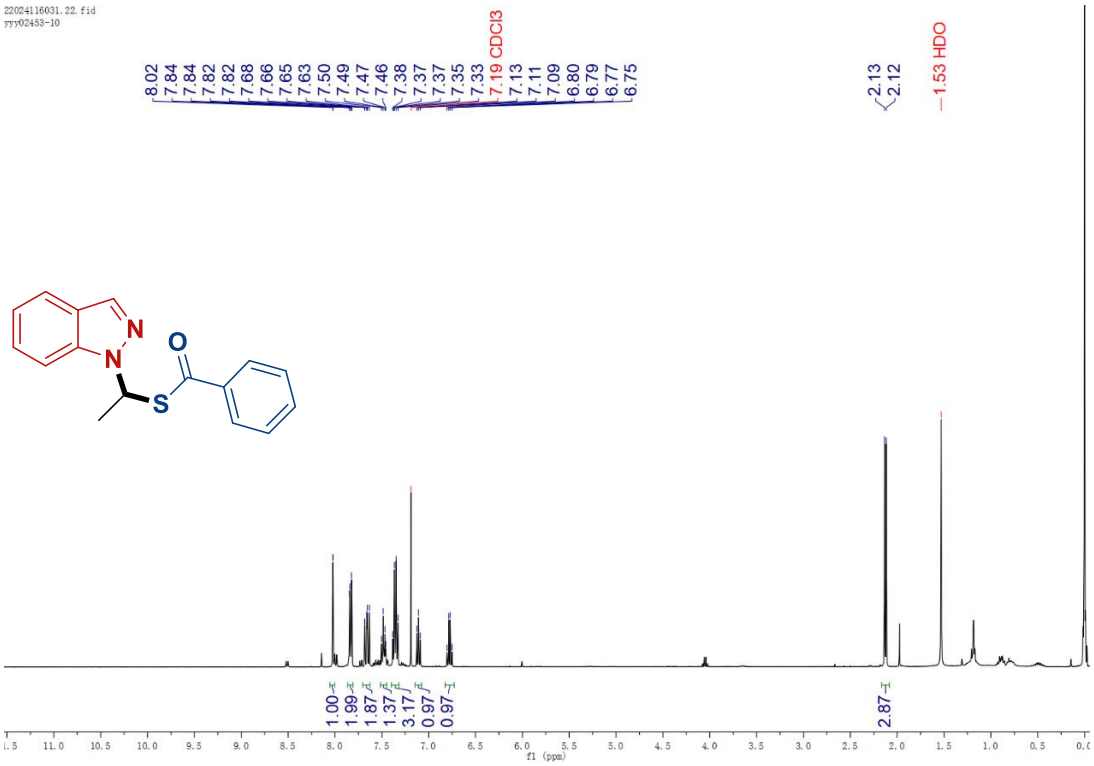
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 60**



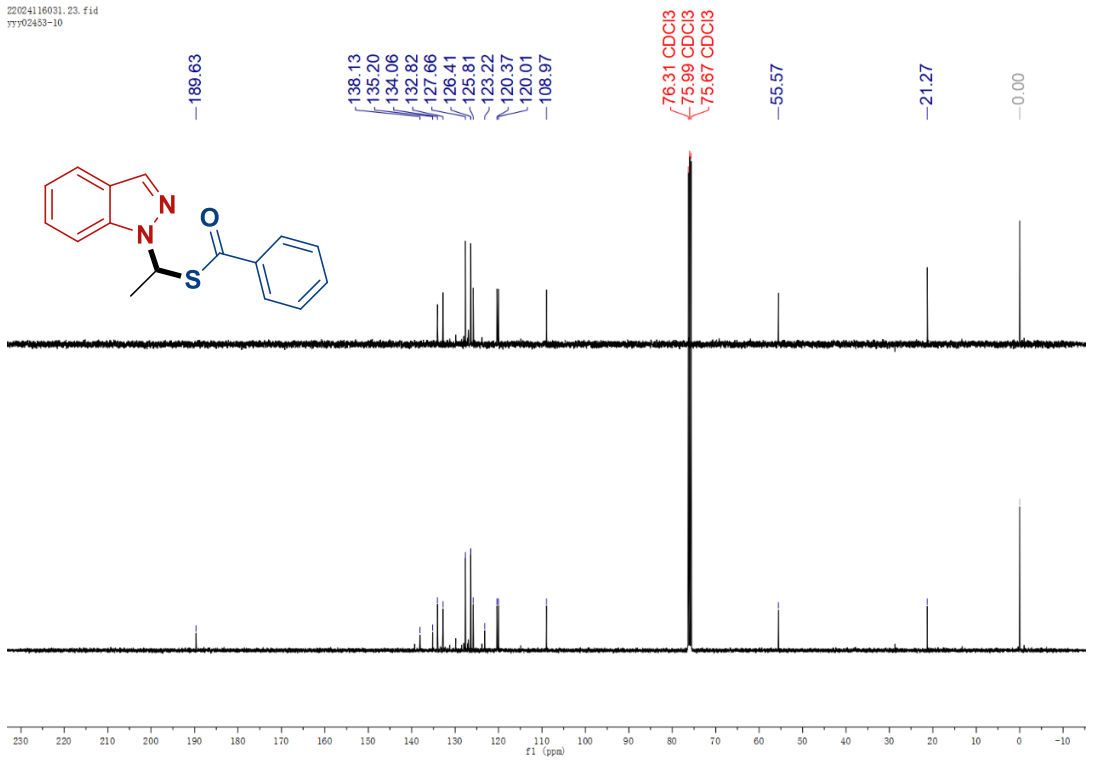
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 61**



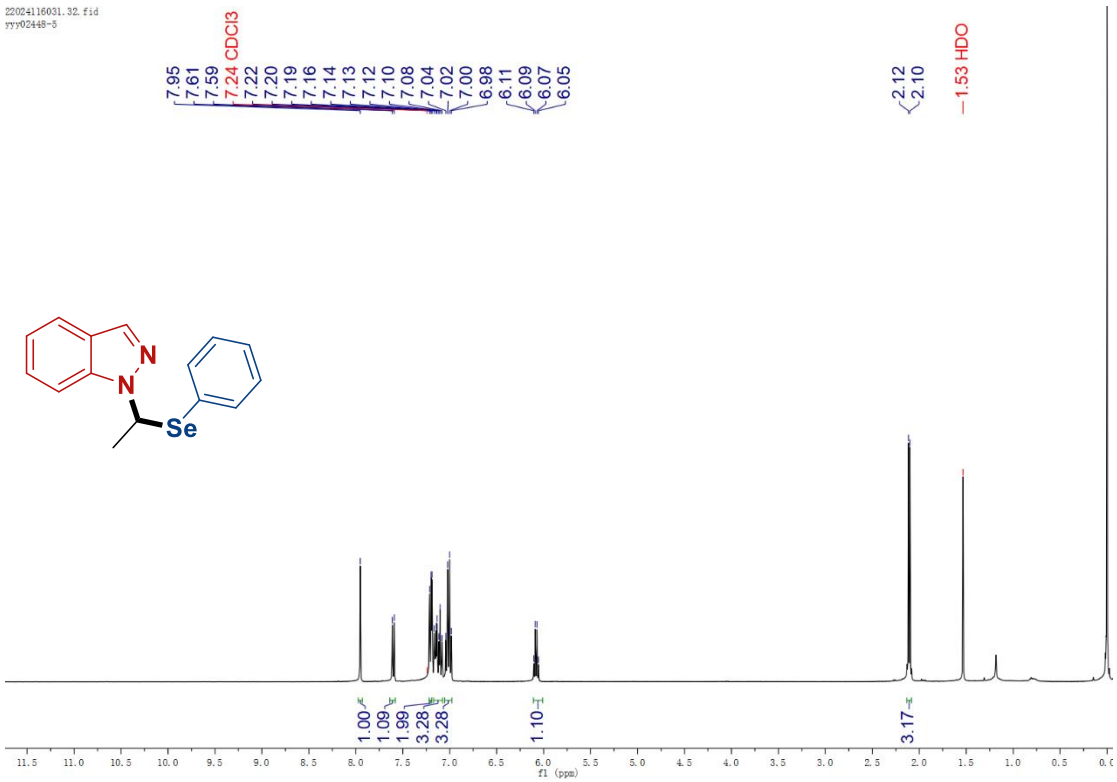
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 61**



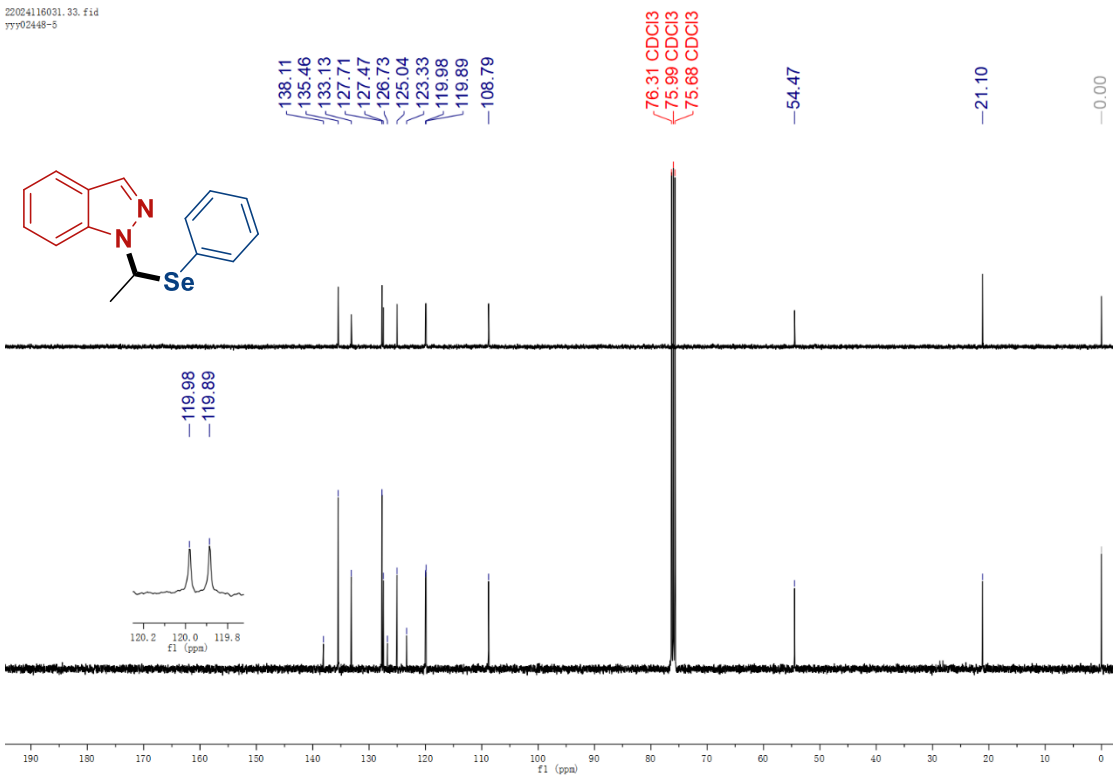
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 62**



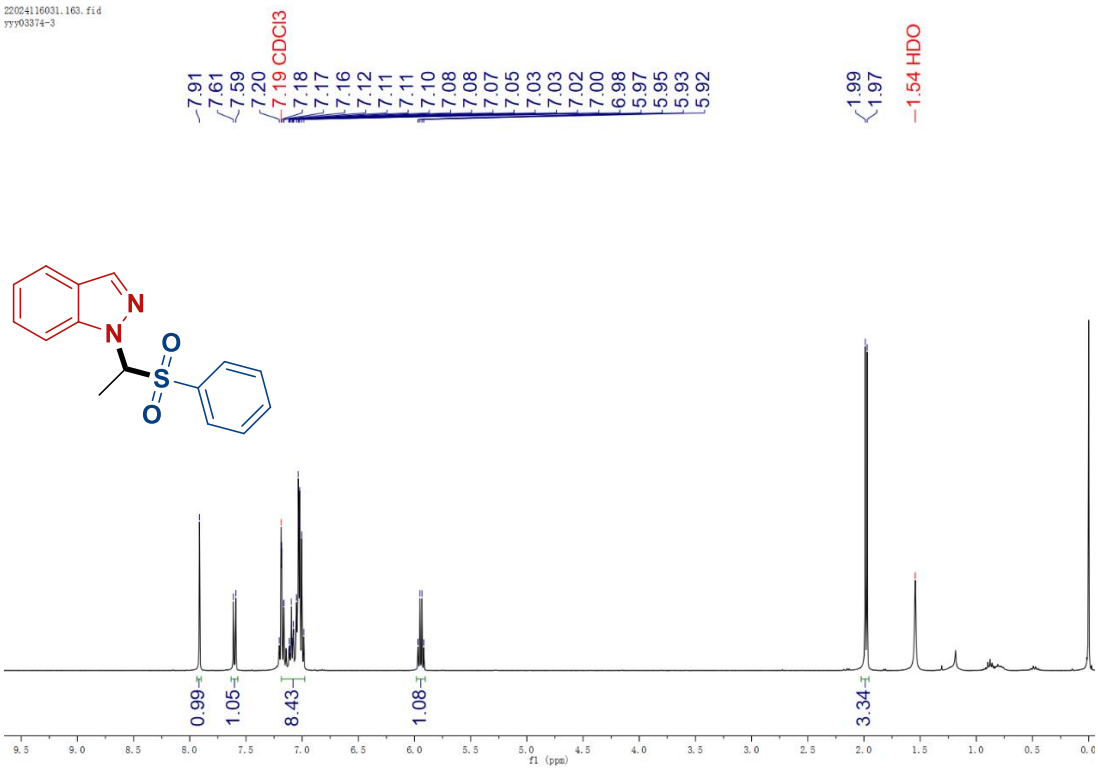
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 62**



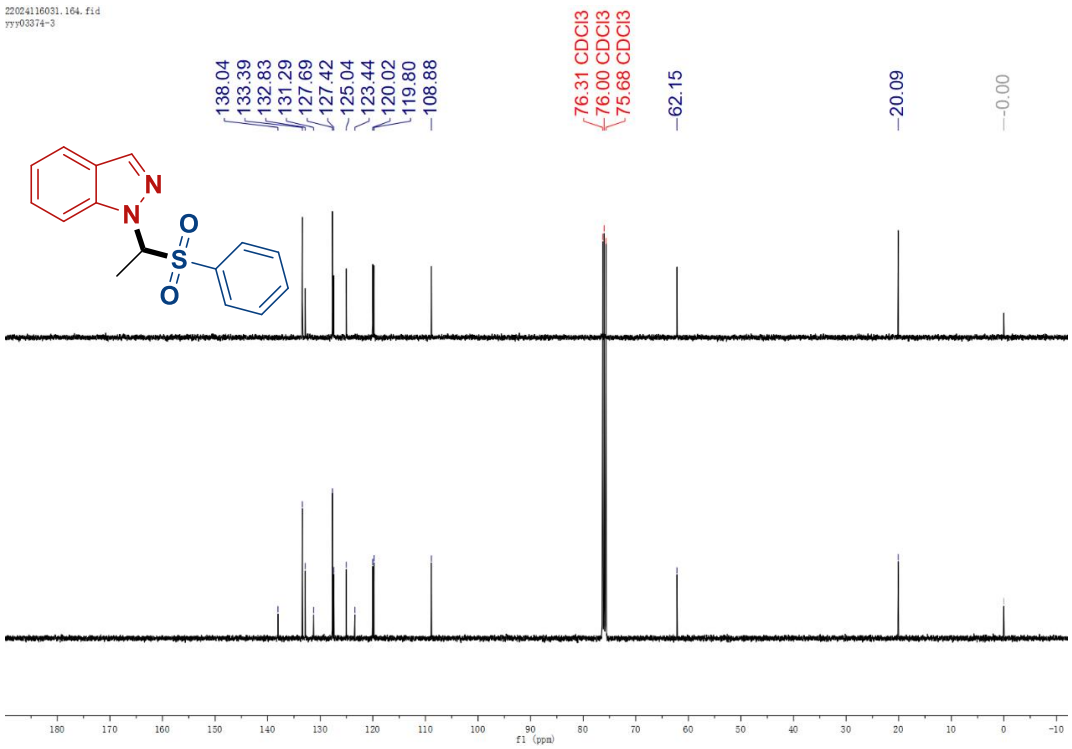
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 63**



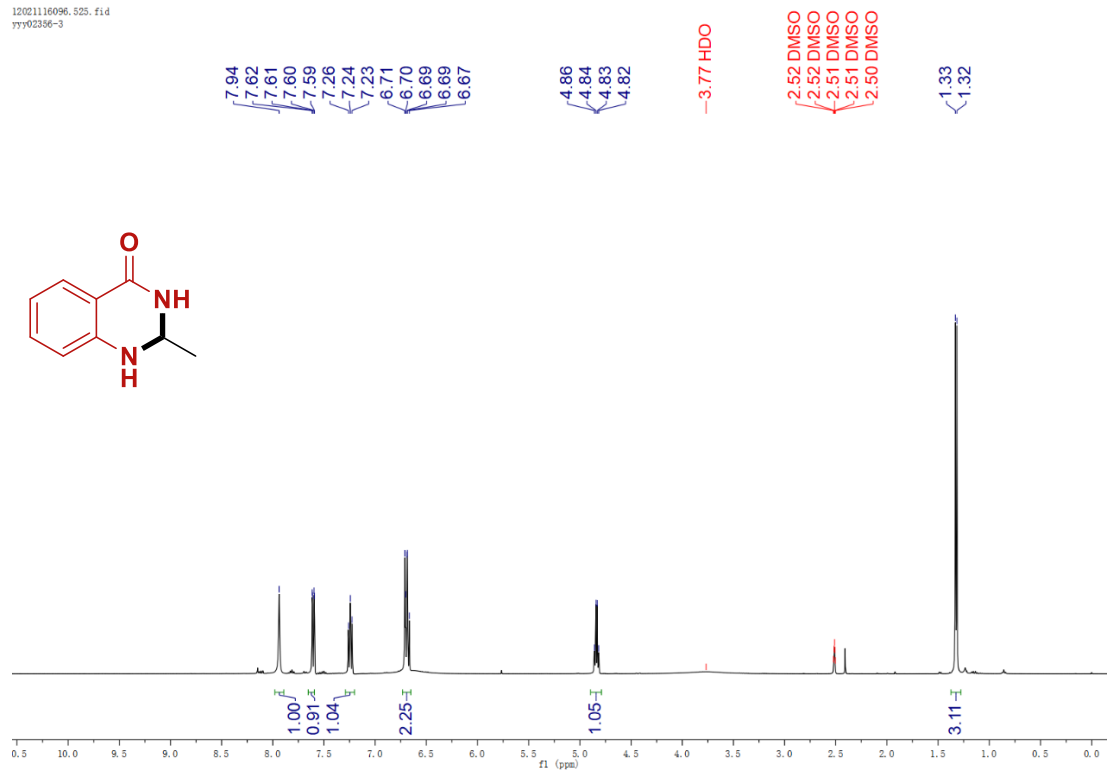
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 63**



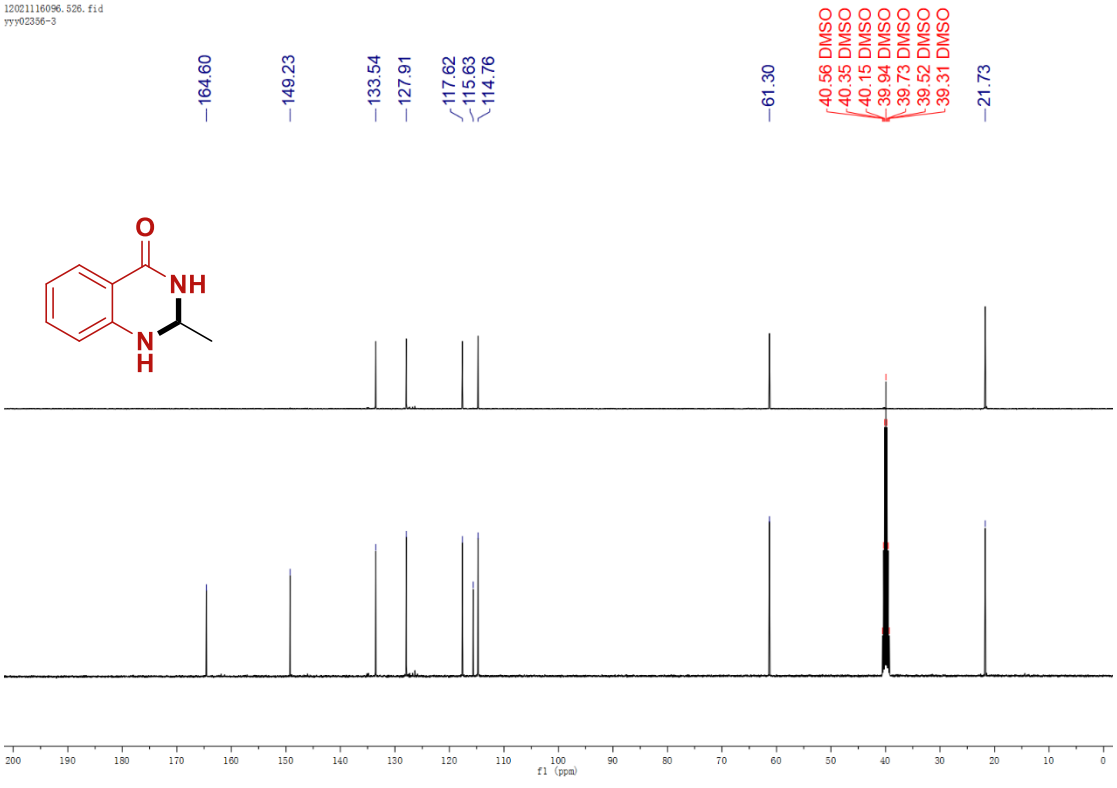
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 64**



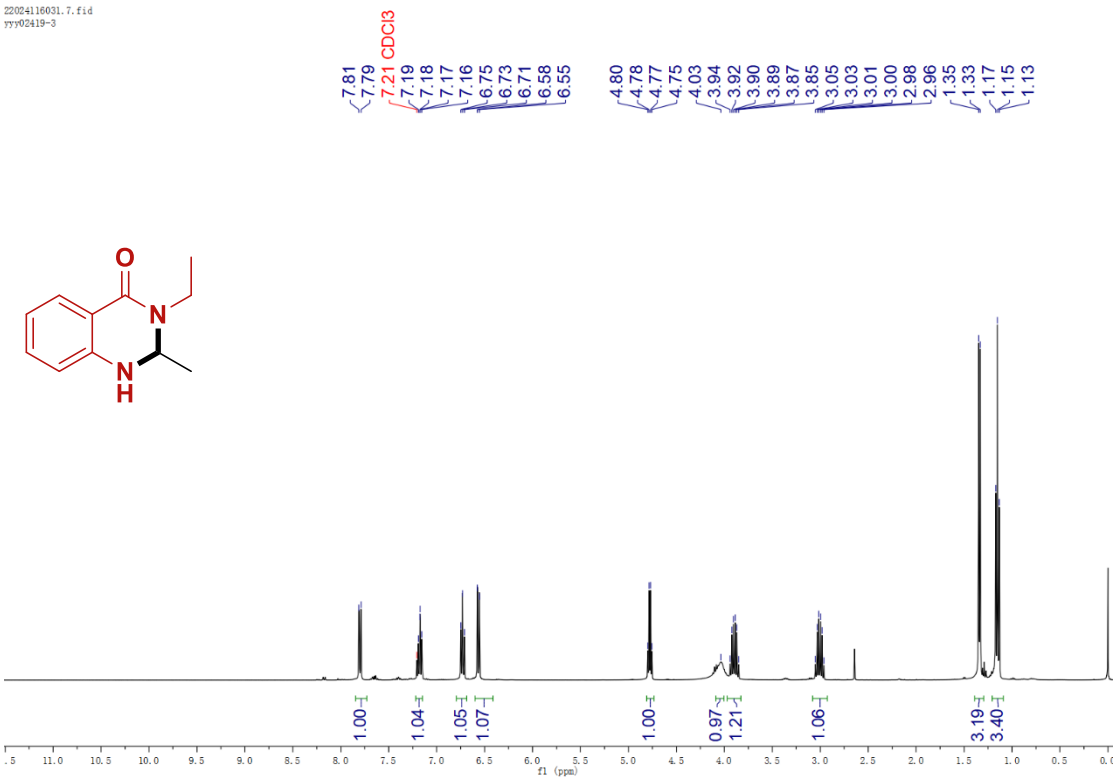
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 64**



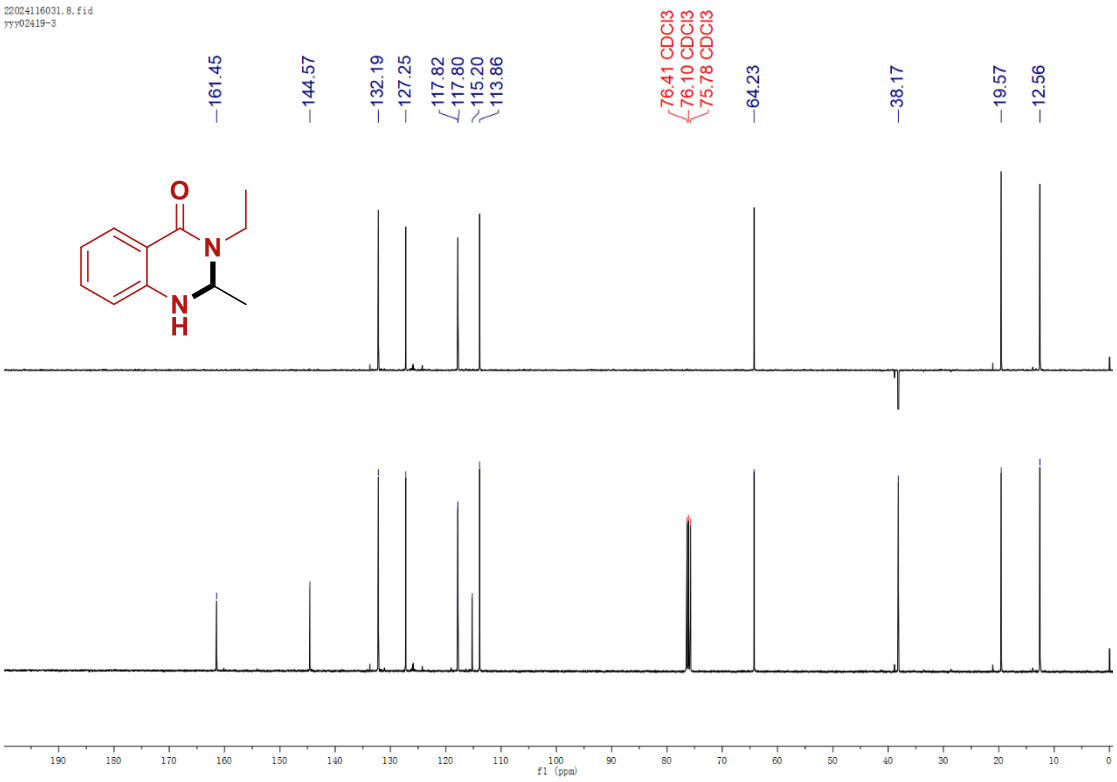
^{1}H-NMR (400 MHz, DMSO-d_6) **Spectrum of 65**



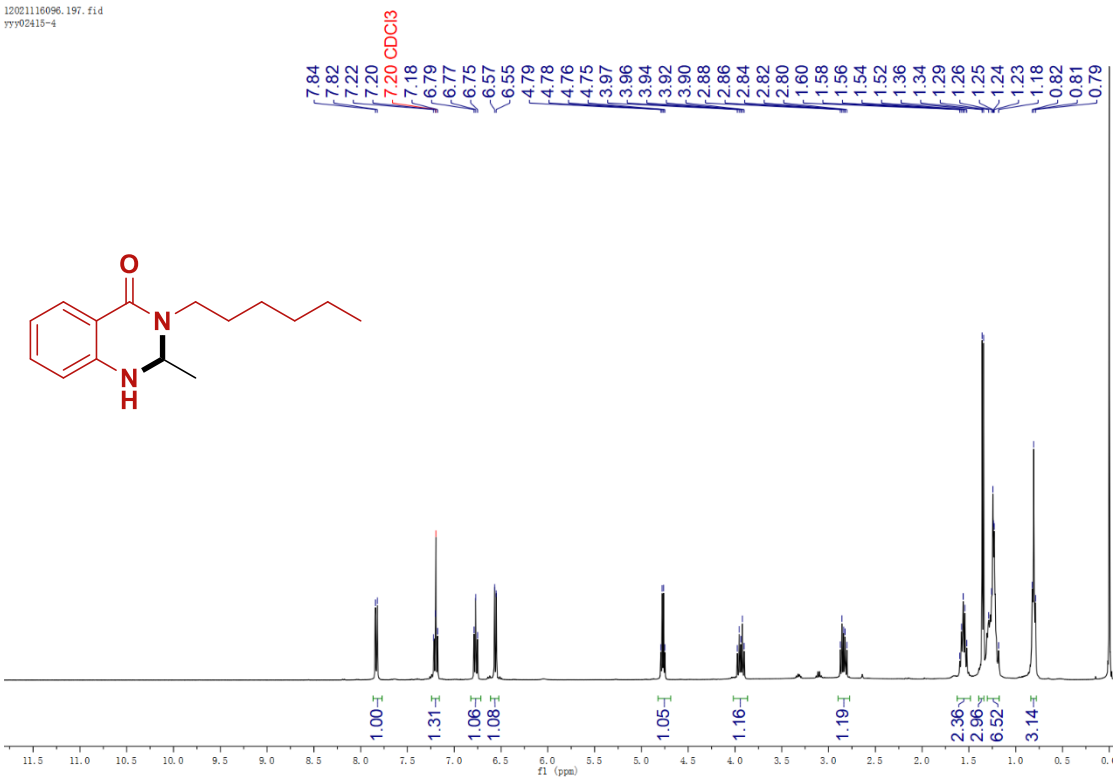
^{13}C-NMR (100 MHz, DMSO-d_6) **Spectrum of 65**



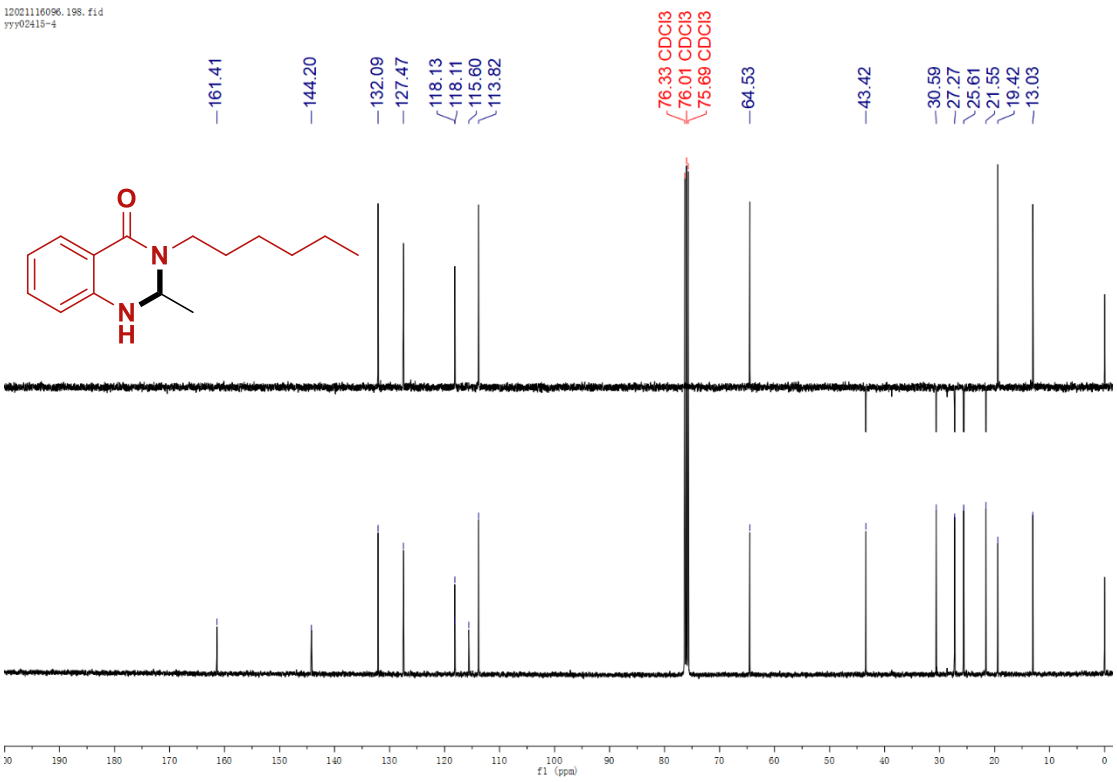
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 66**



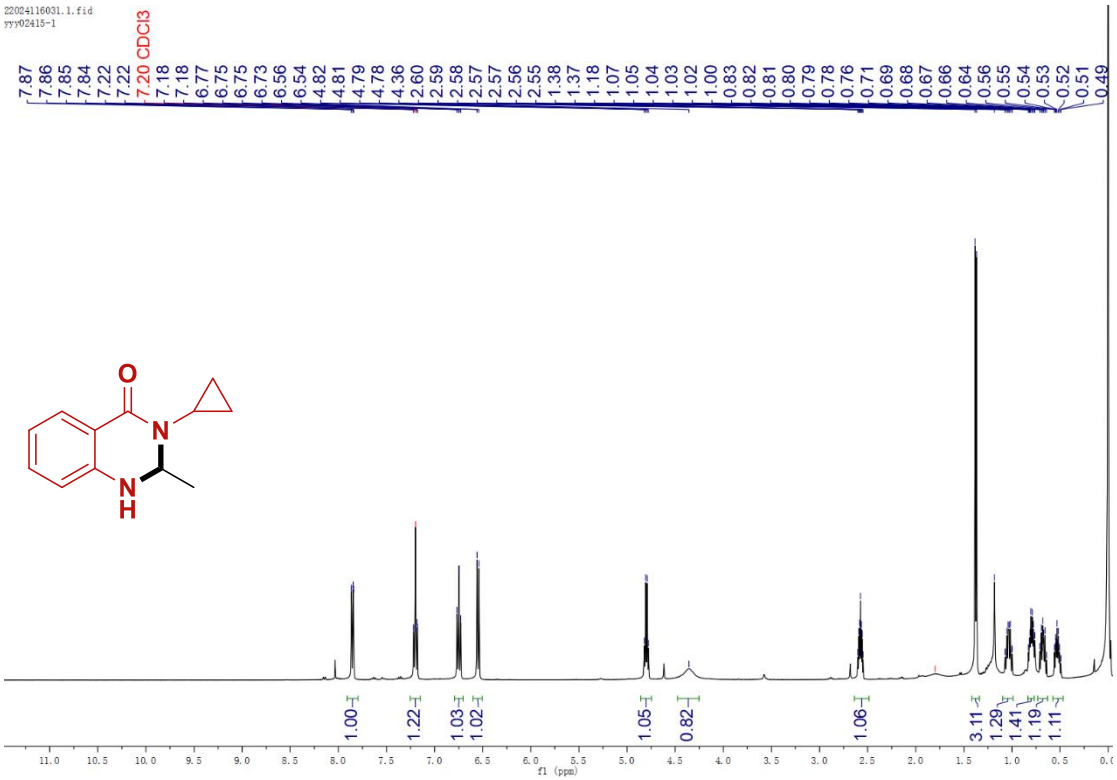
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 66**



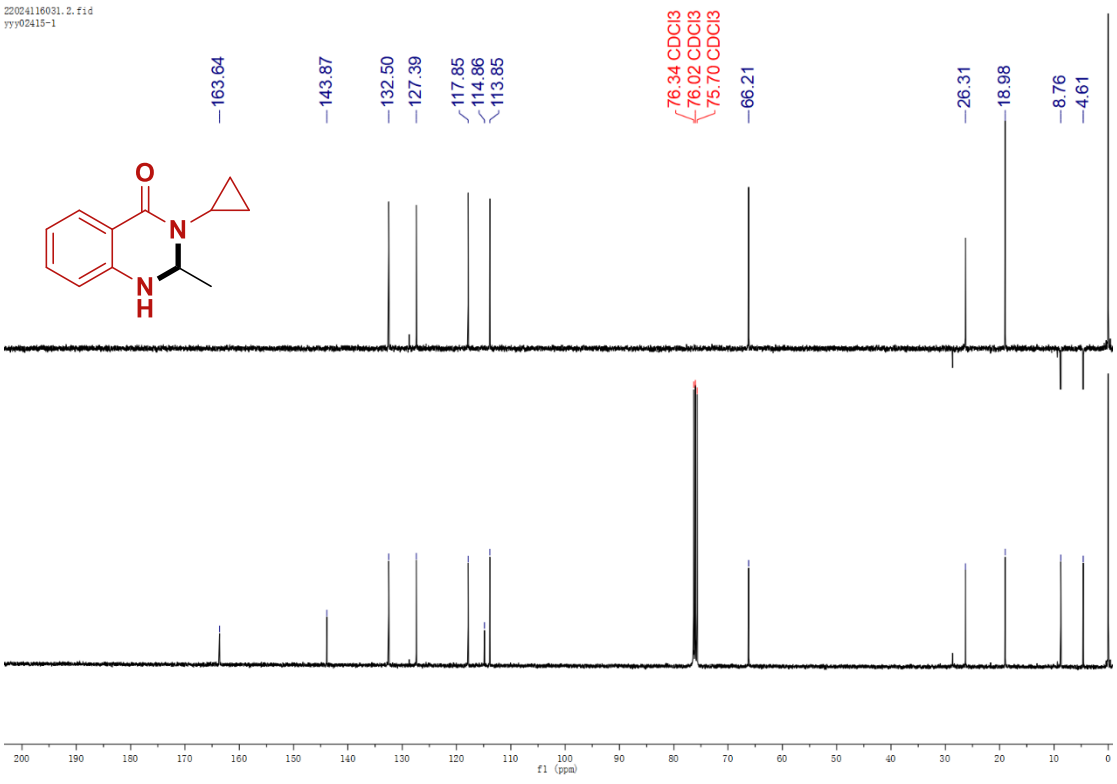
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 67**



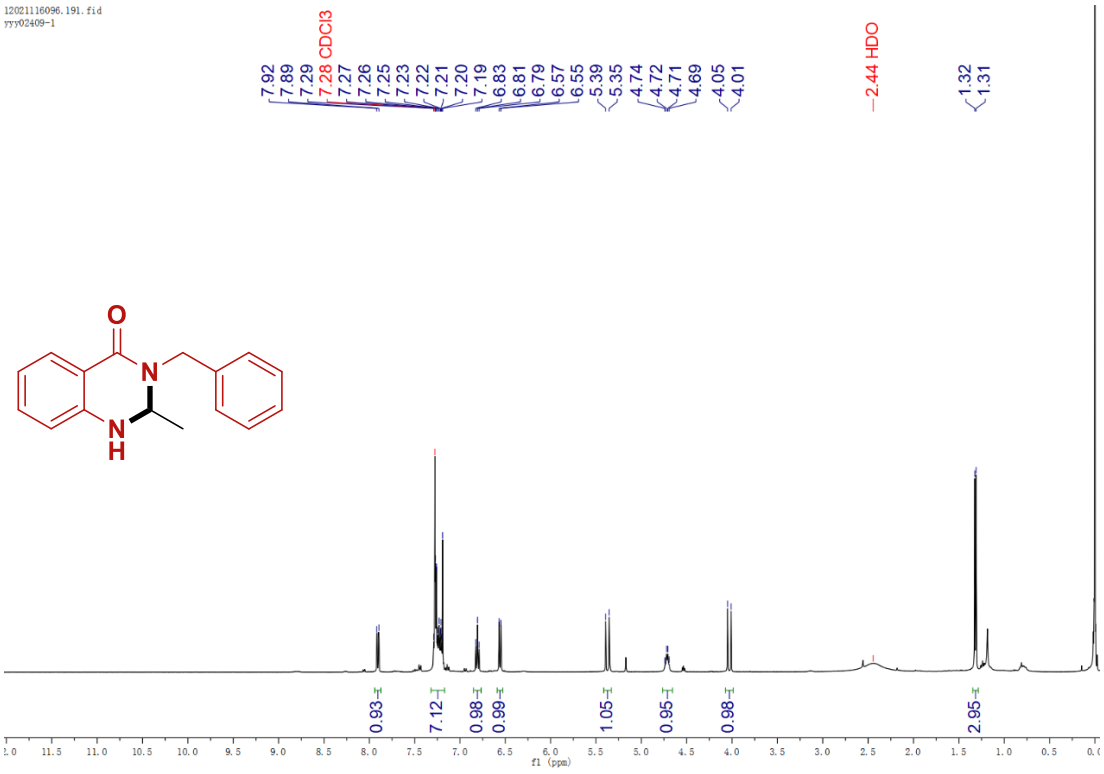
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 67**



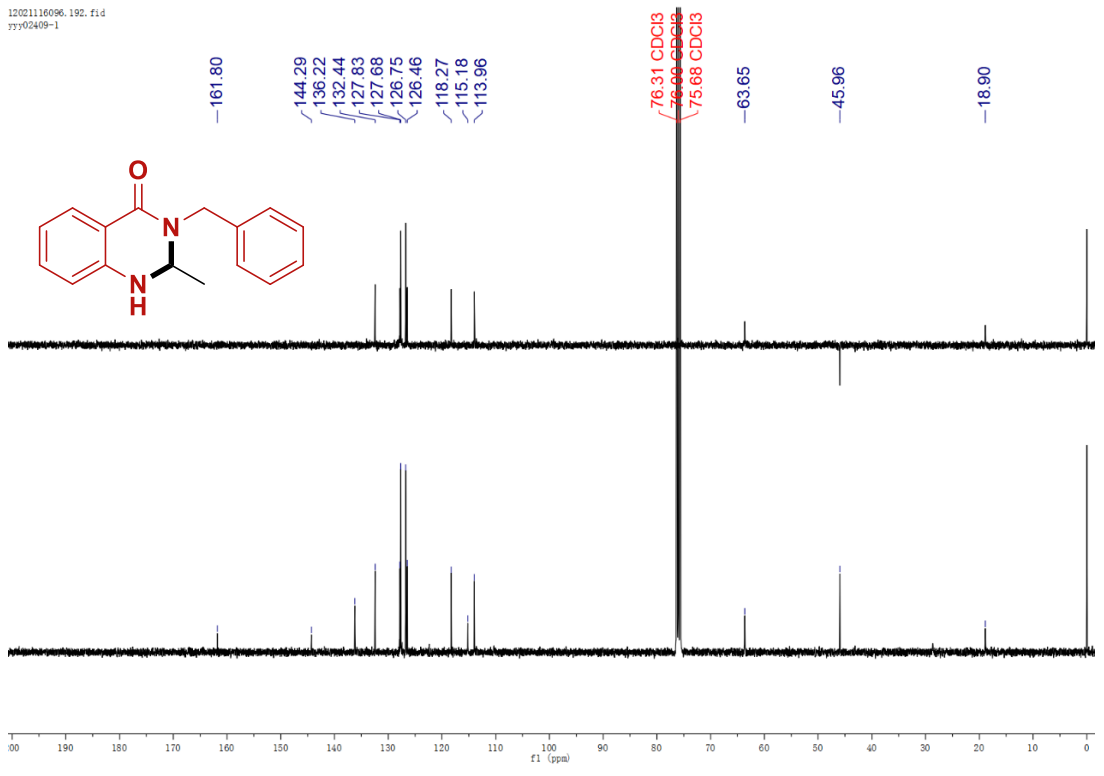
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 68**



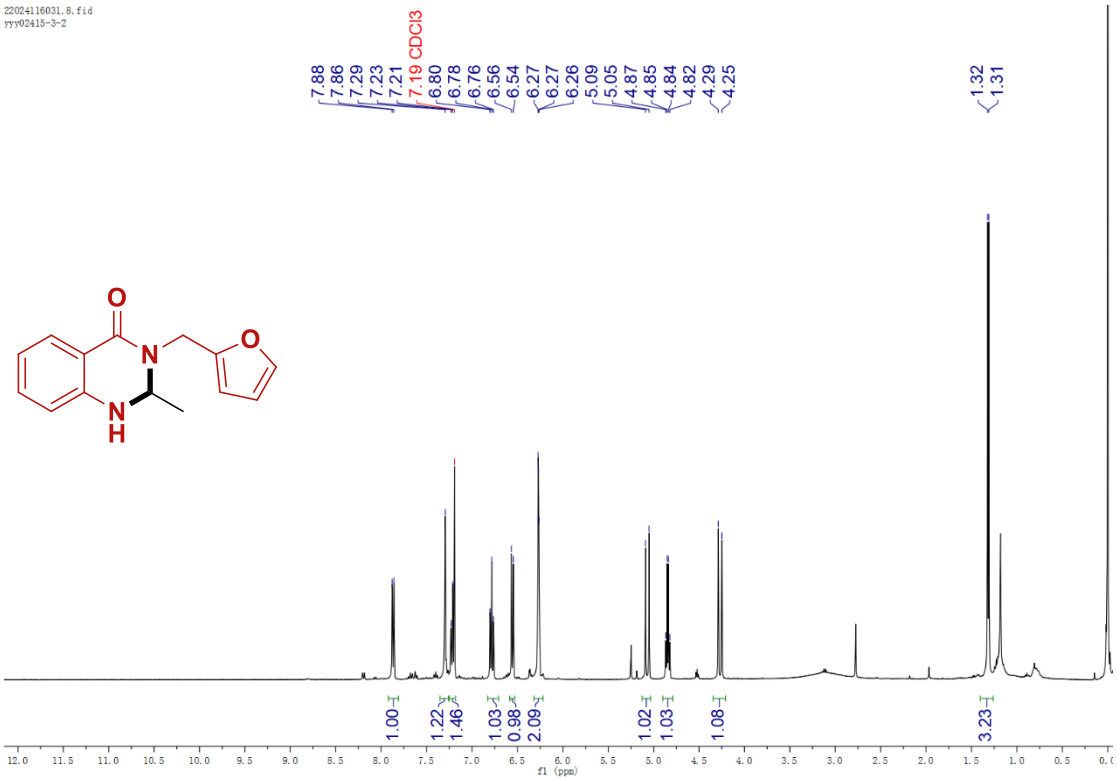
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 68**



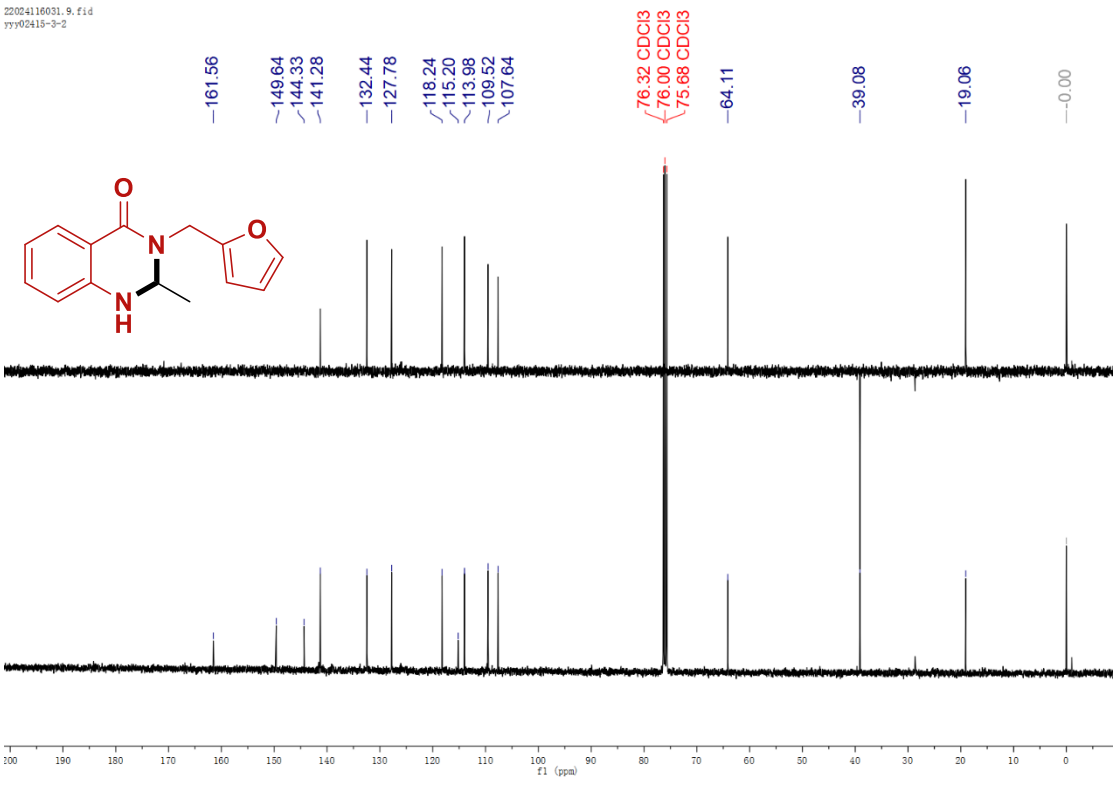
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 69**



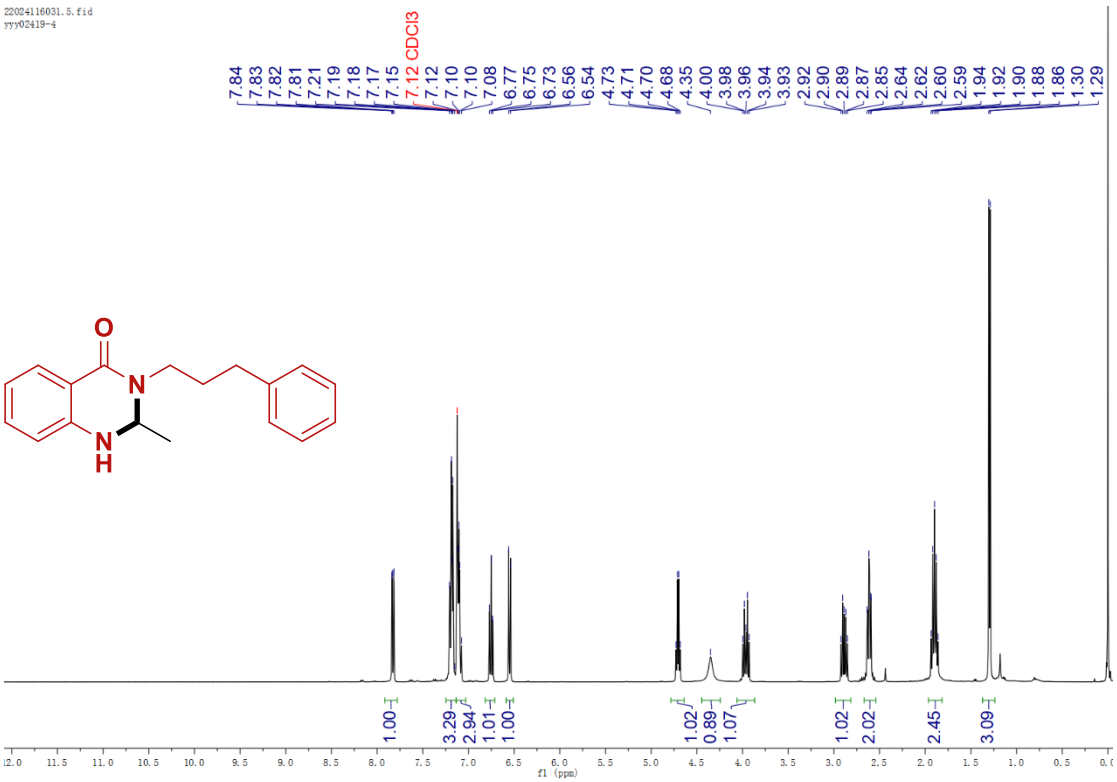
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 69**



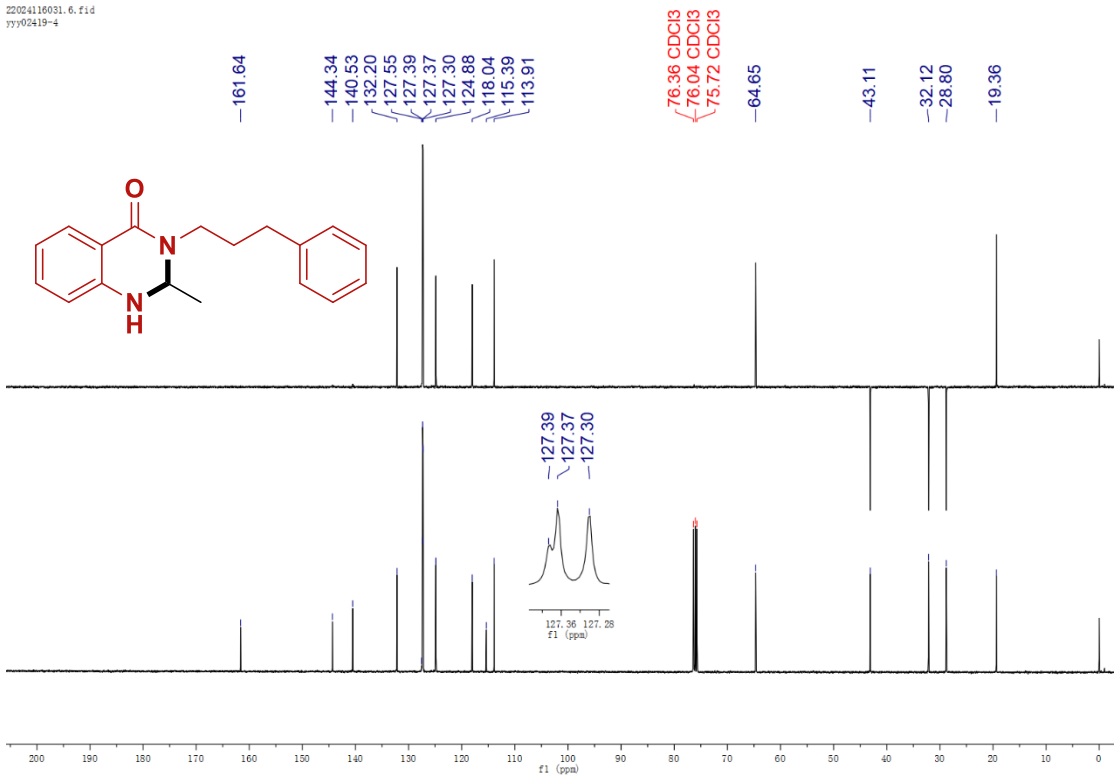
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 70**



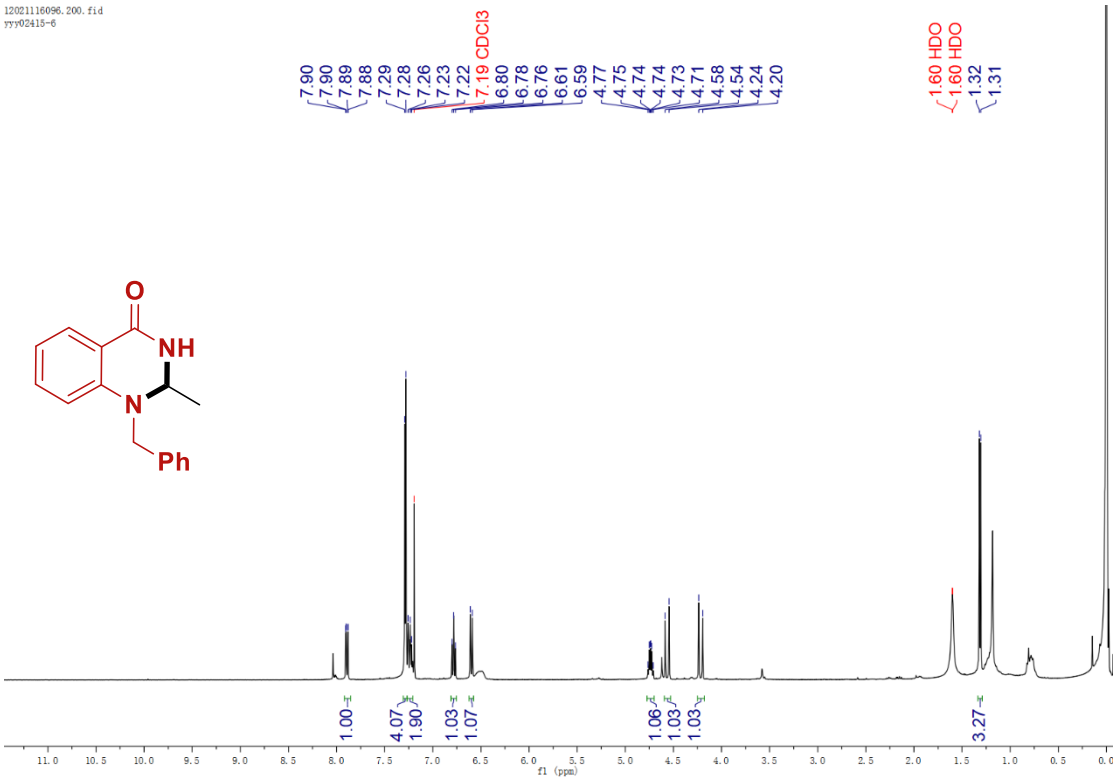
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 70**



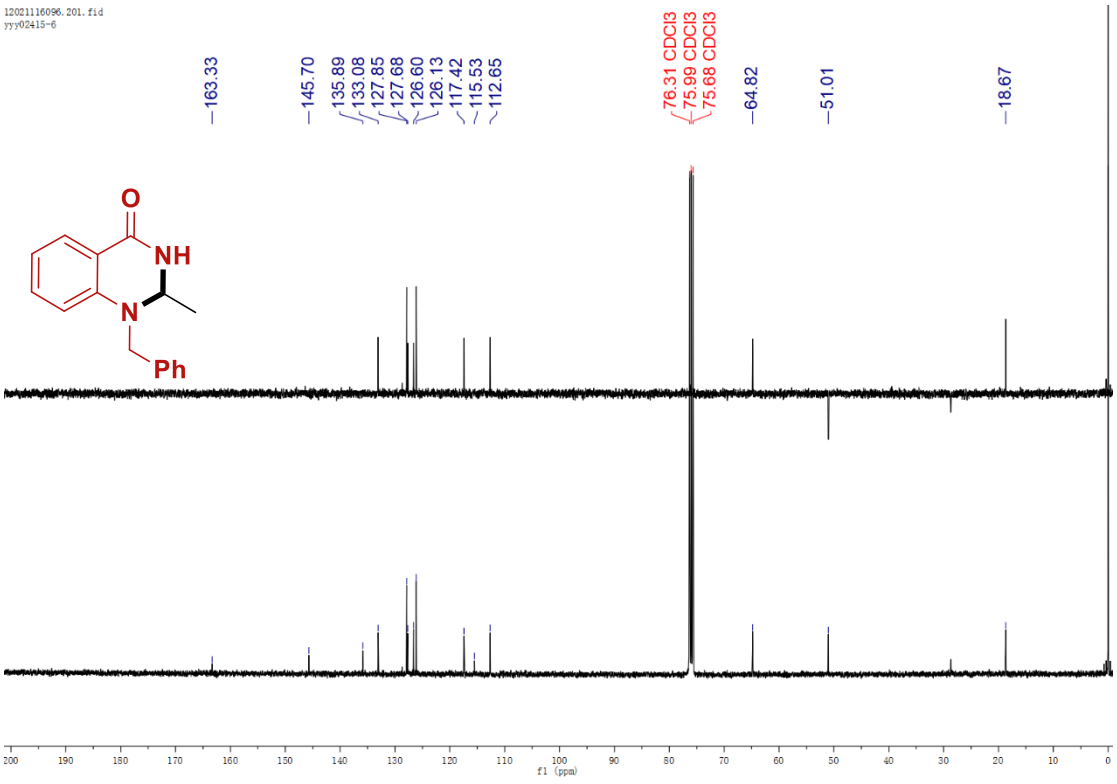
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 71**



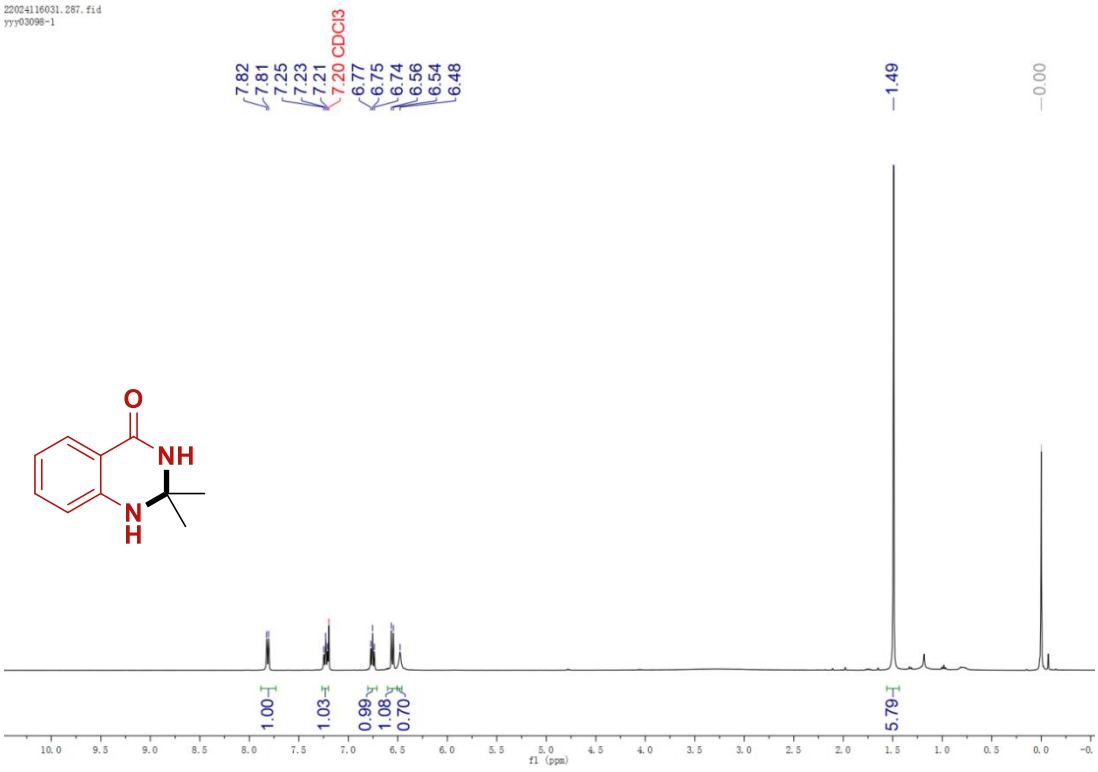
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 71**



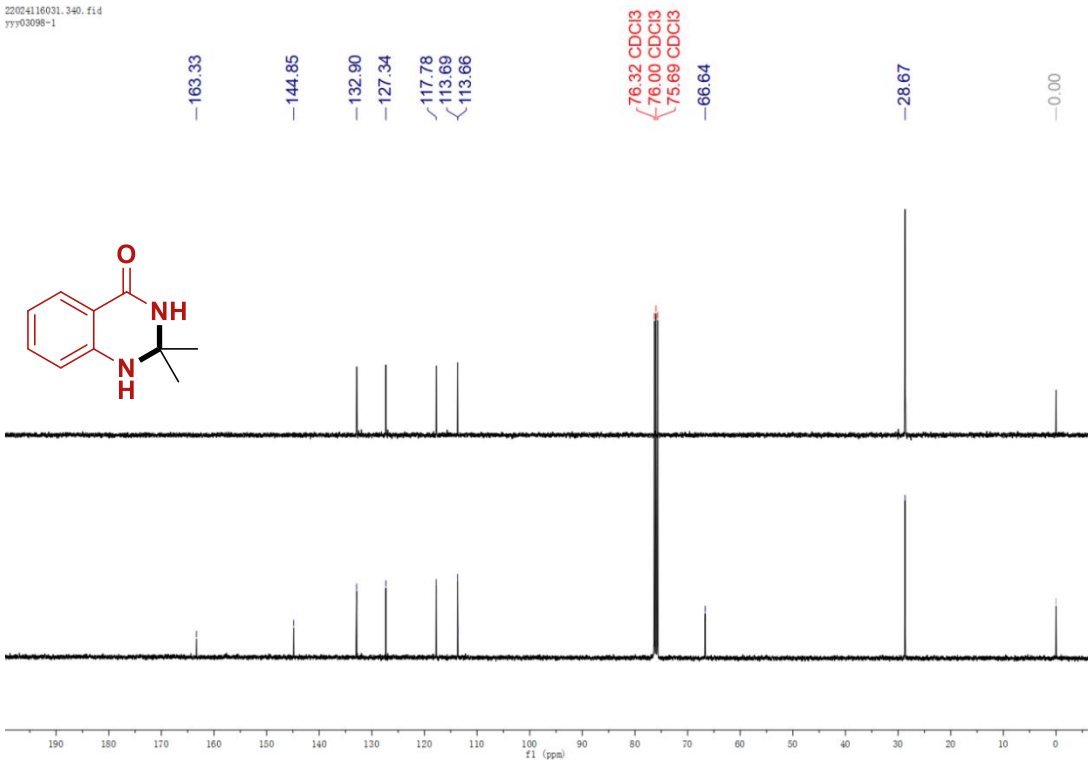
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 72**



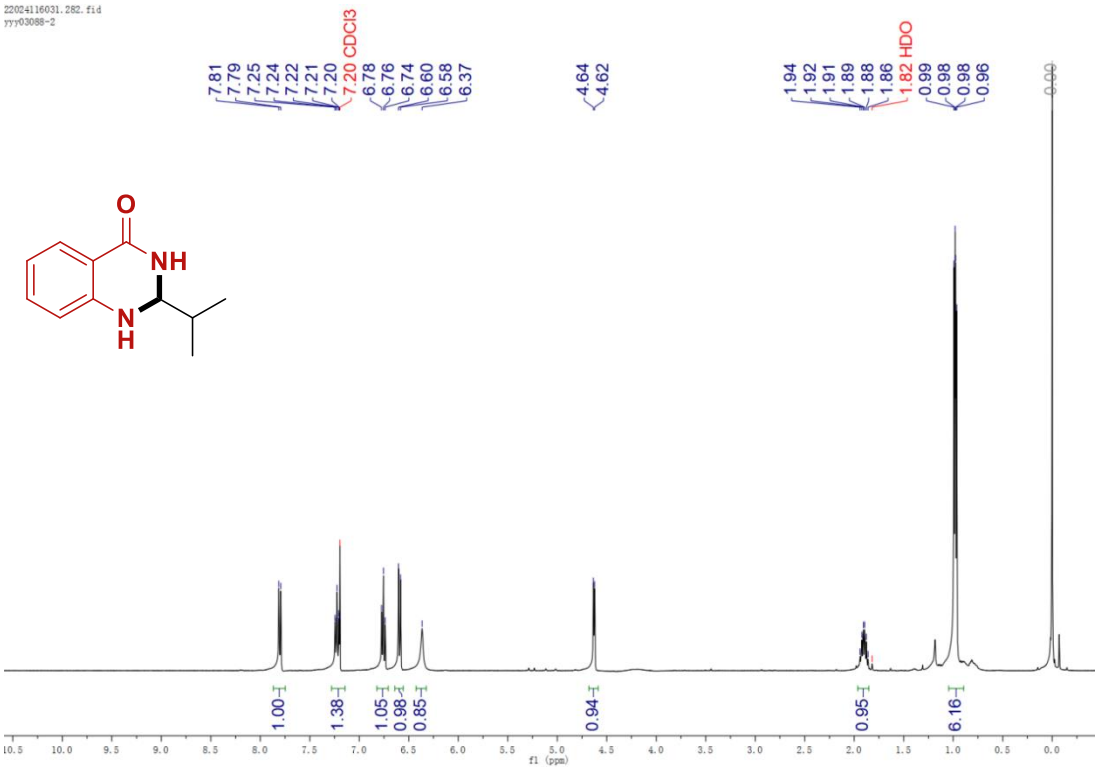
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 72**



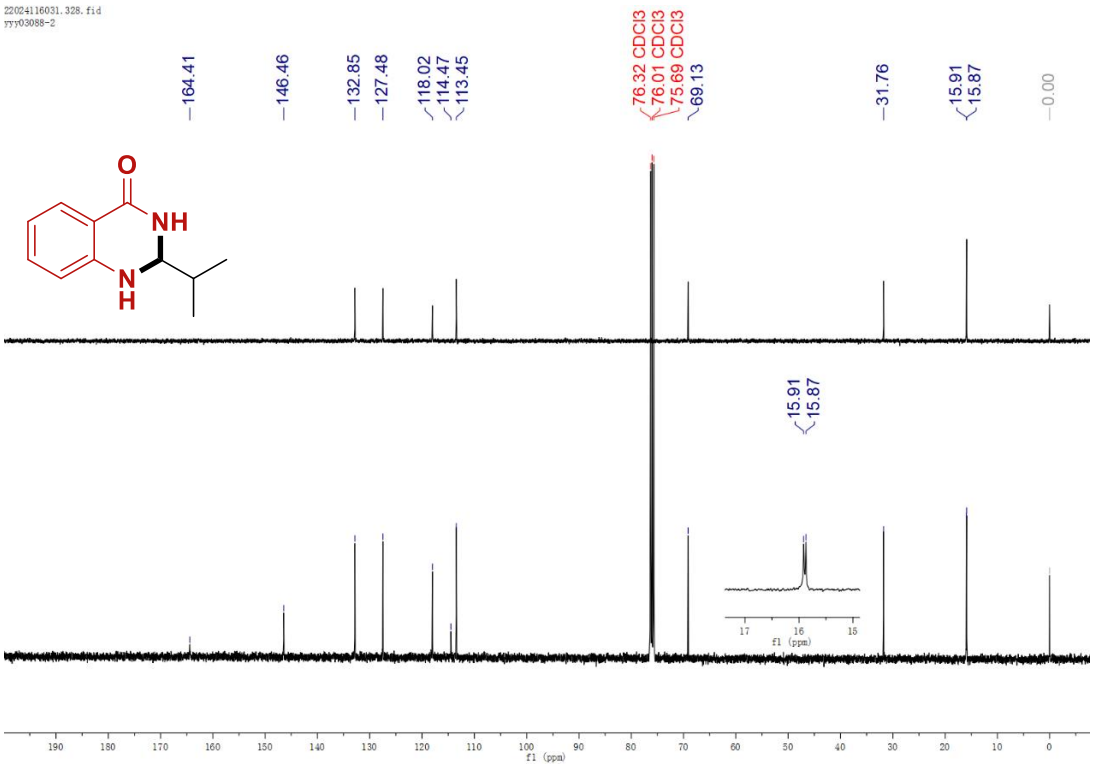
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 73**



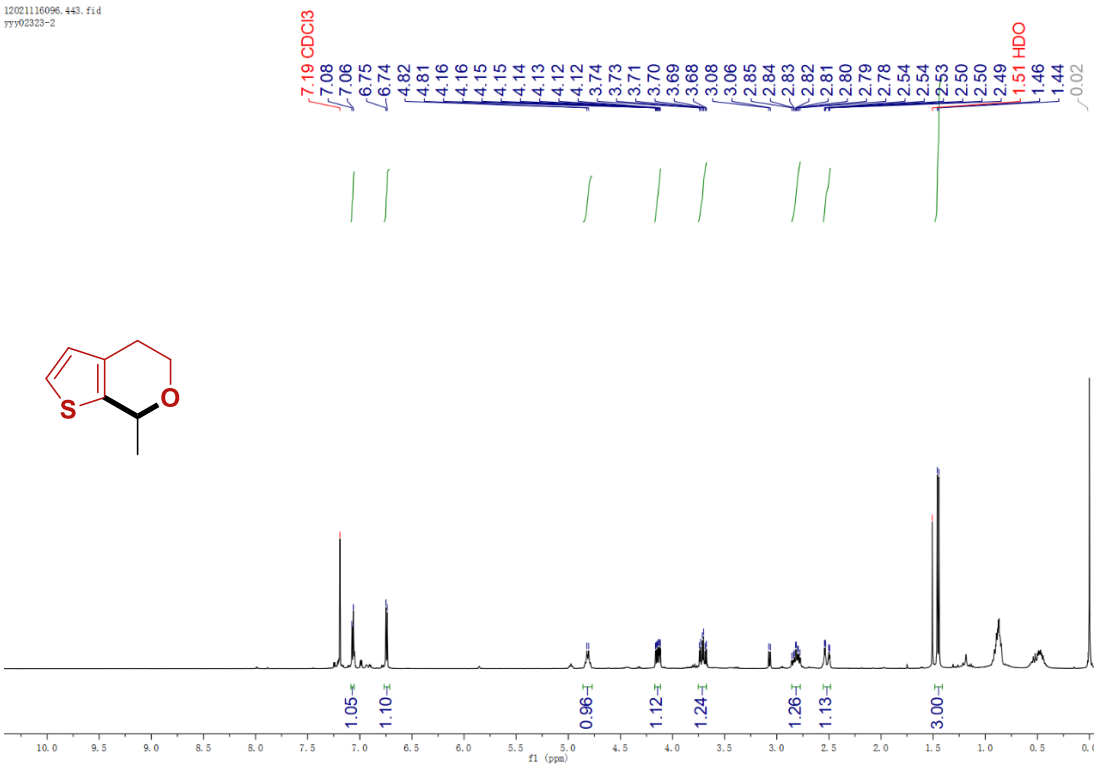
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 73**



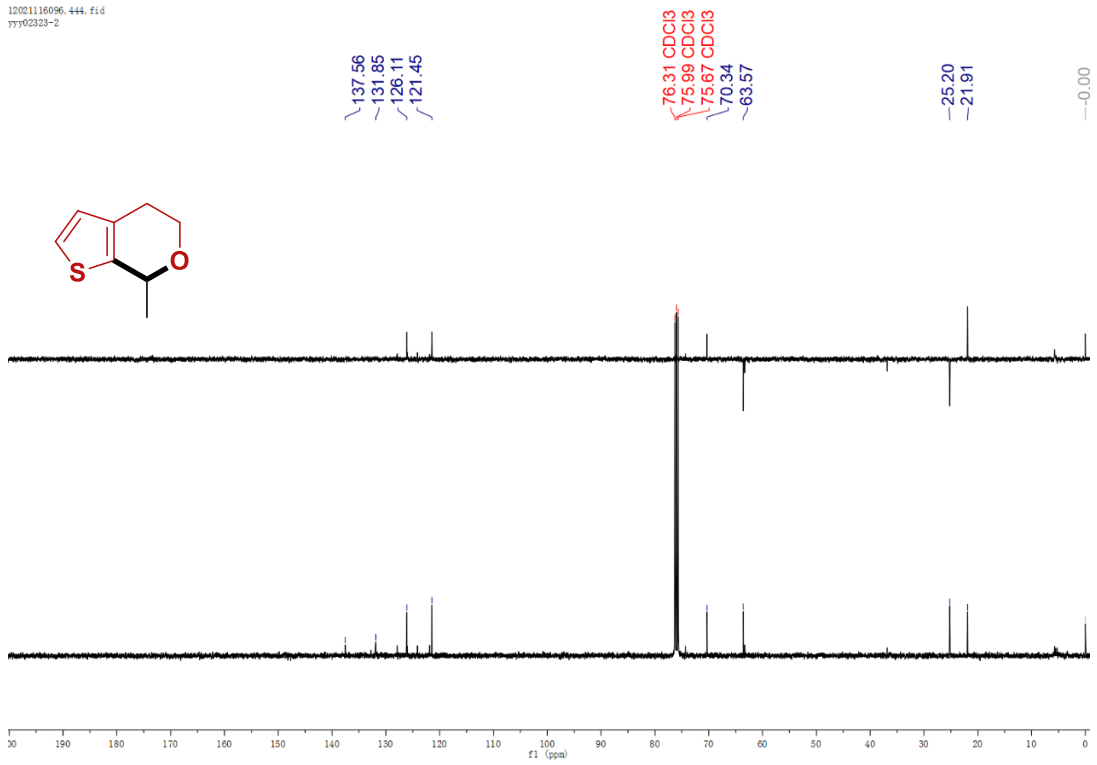
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 74**



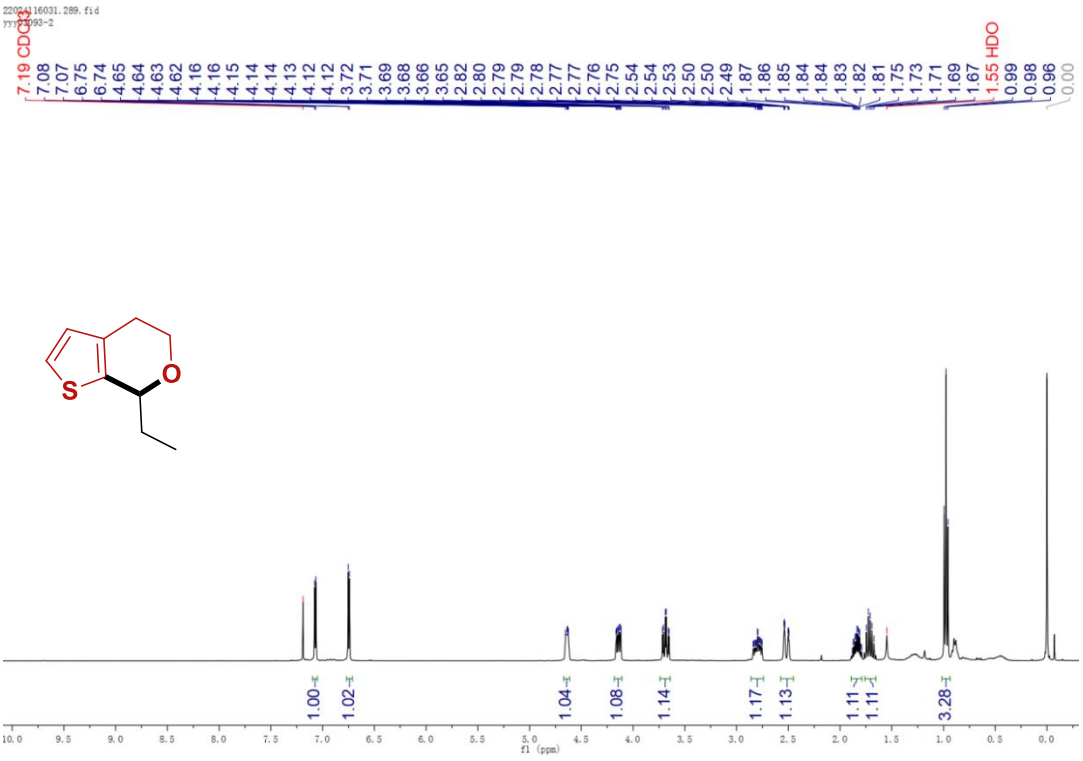
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 74**



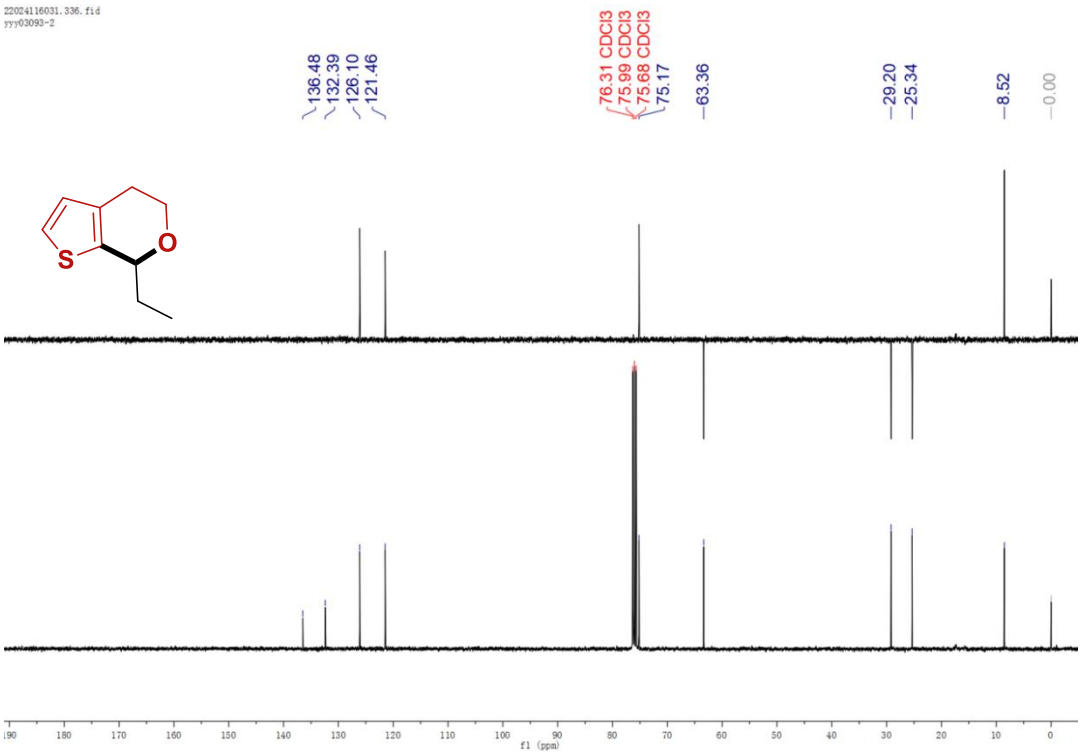
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 75**



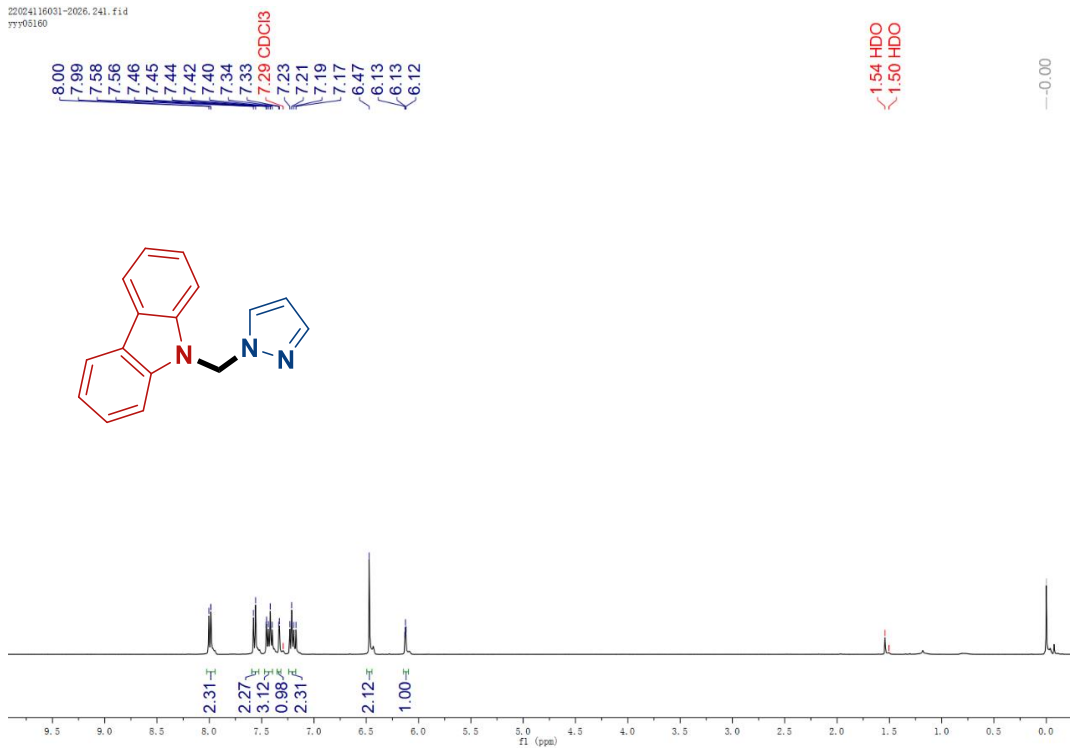
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 75**



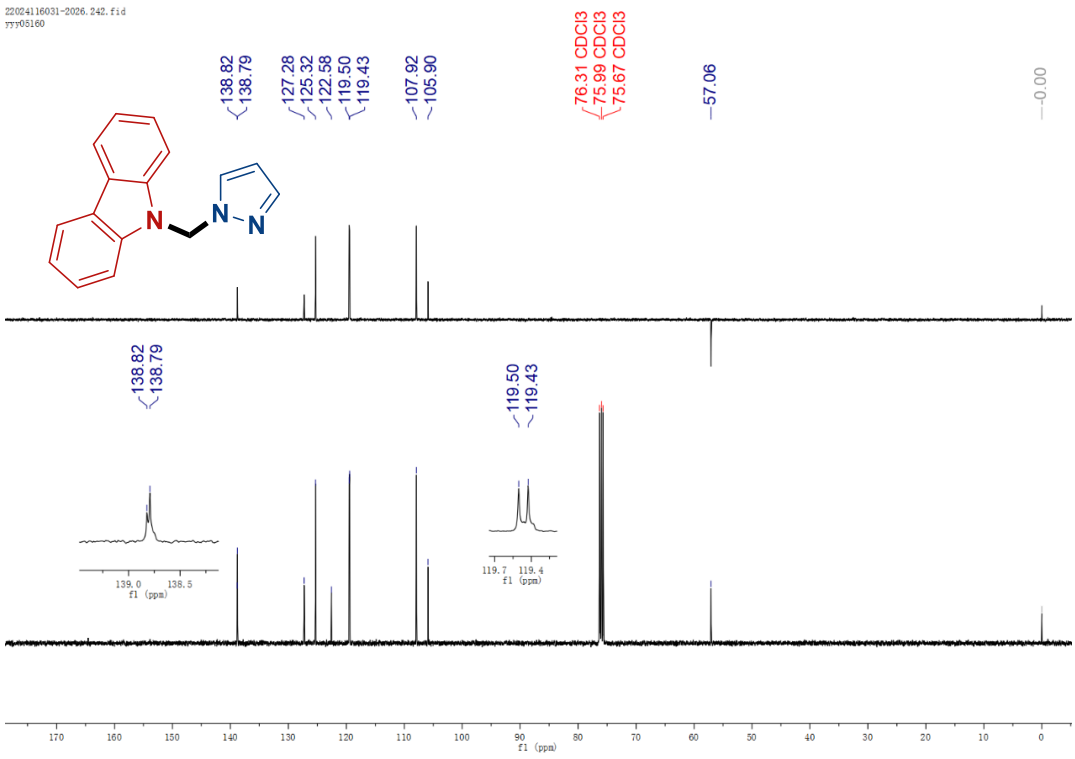
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 76**



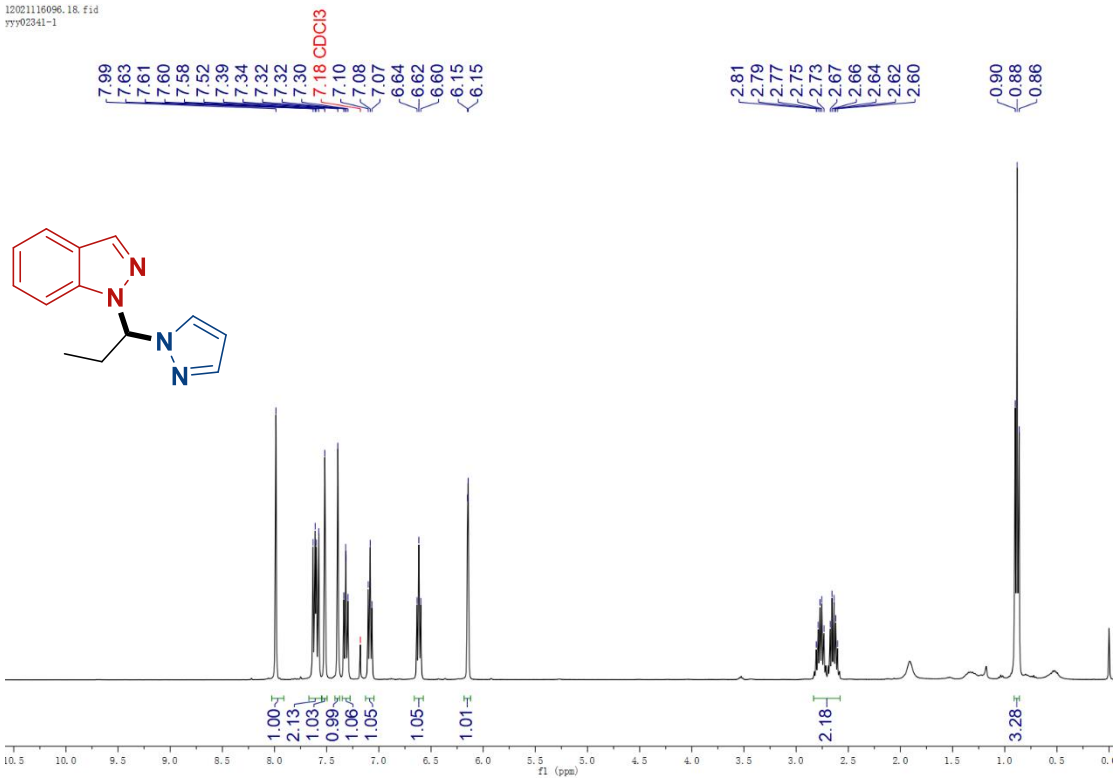
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 76**



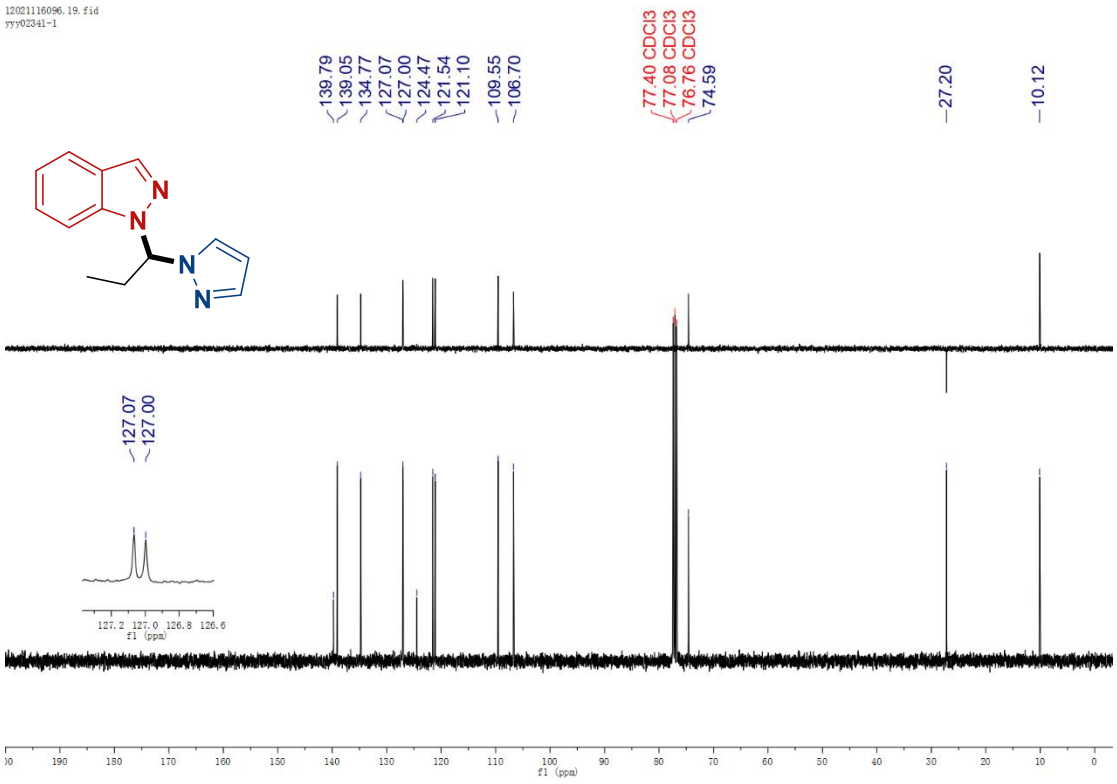
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 77**



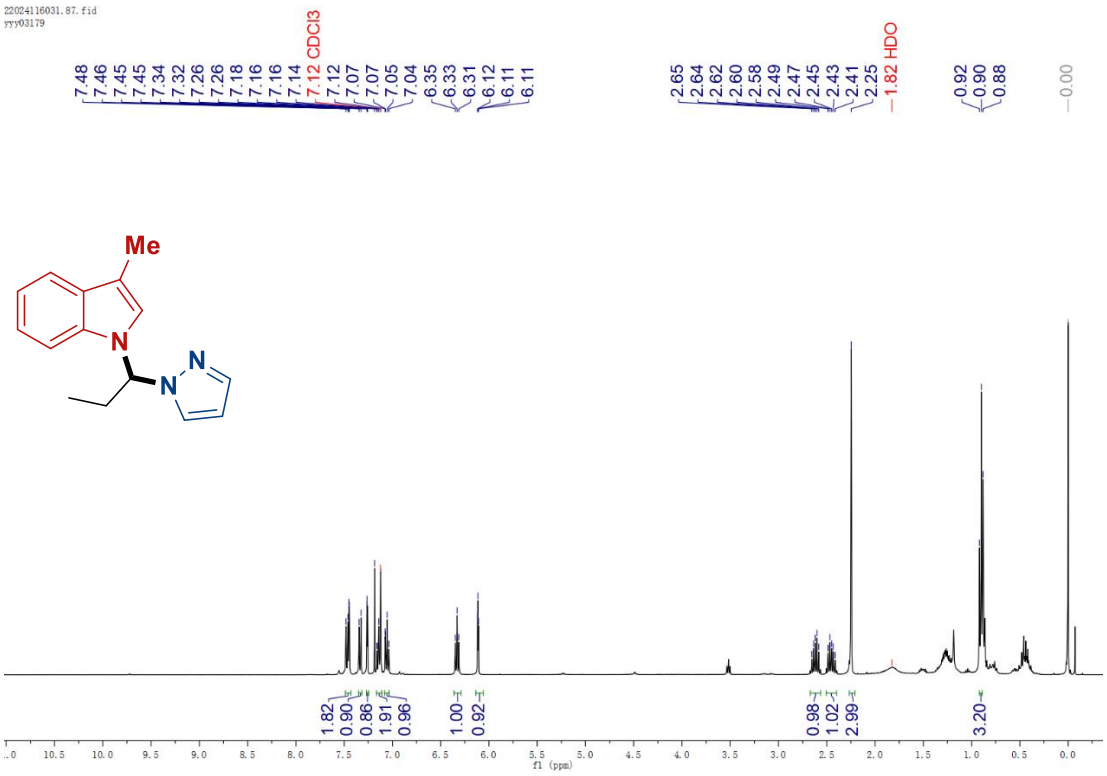
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 77**



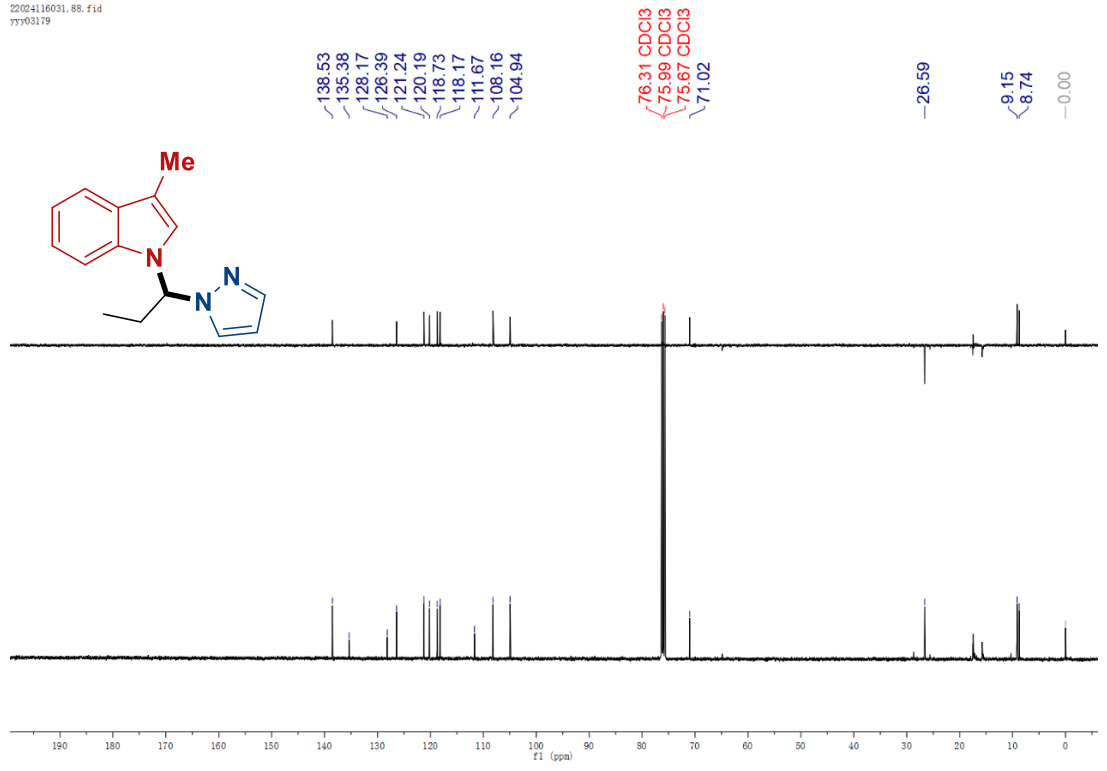
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 78**



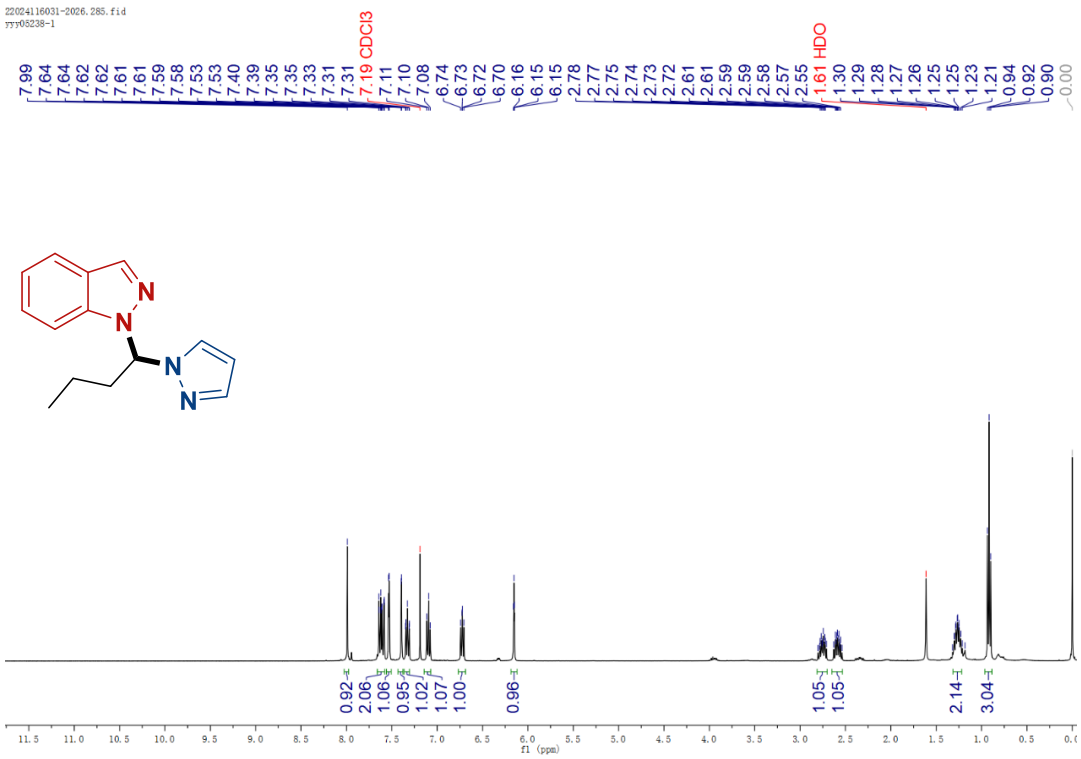
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 78**



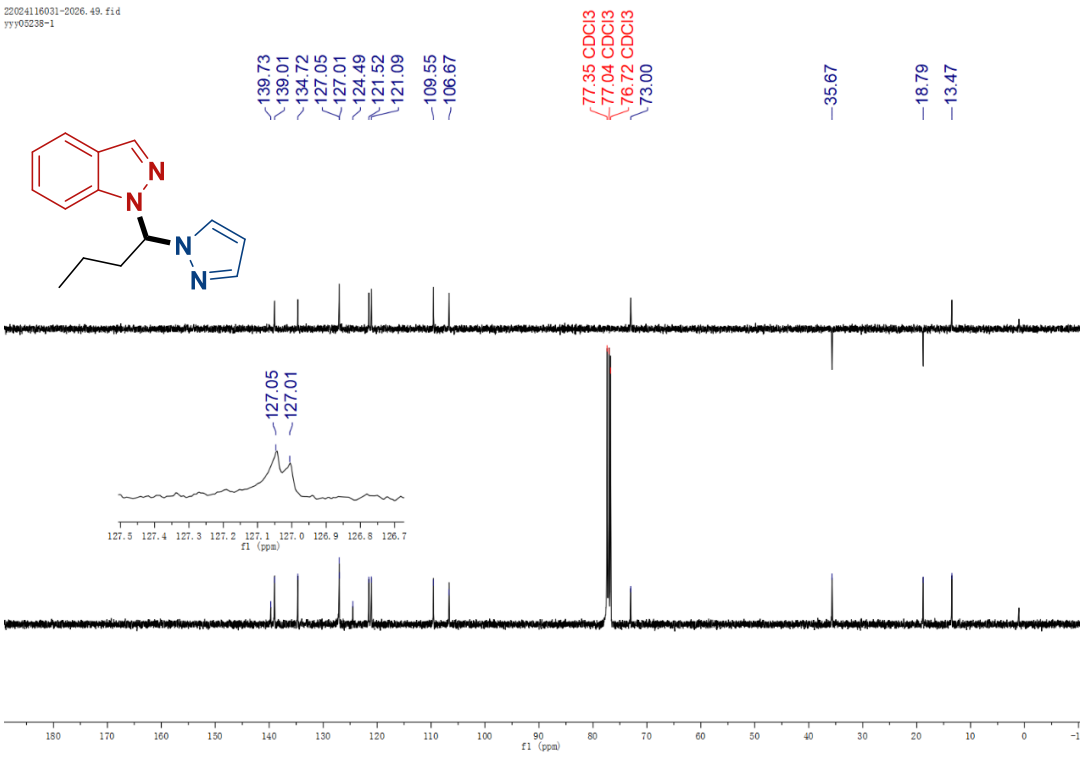
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 79**



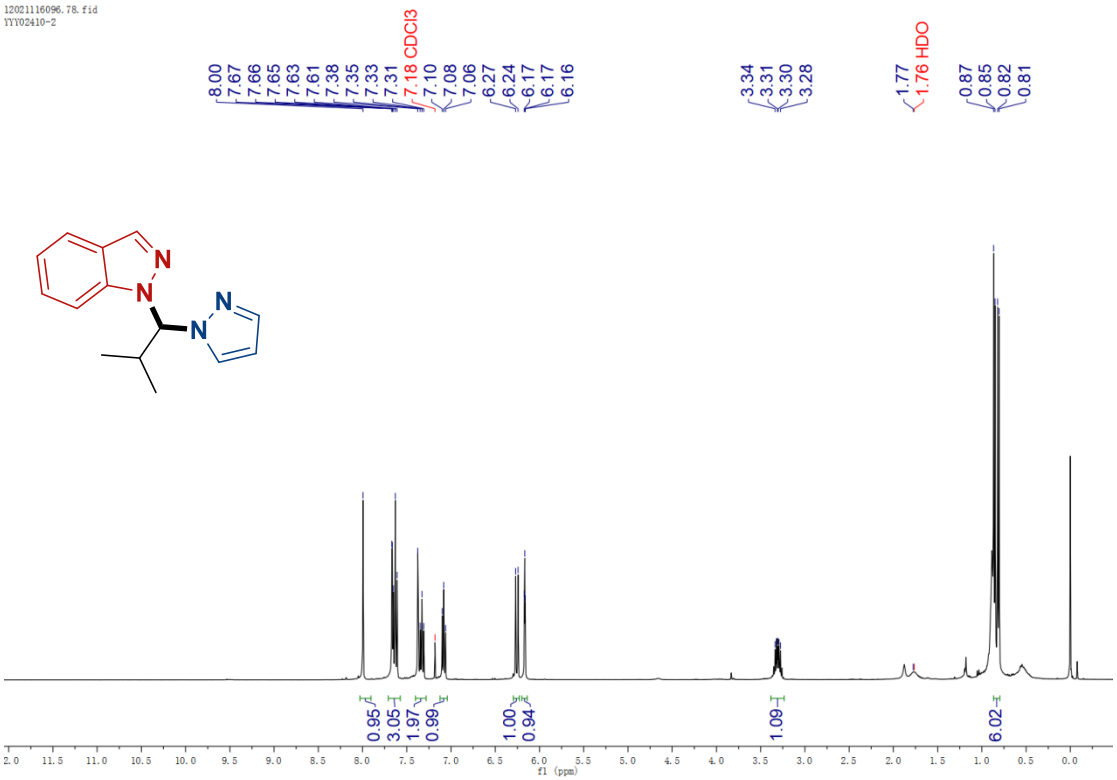
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 79**



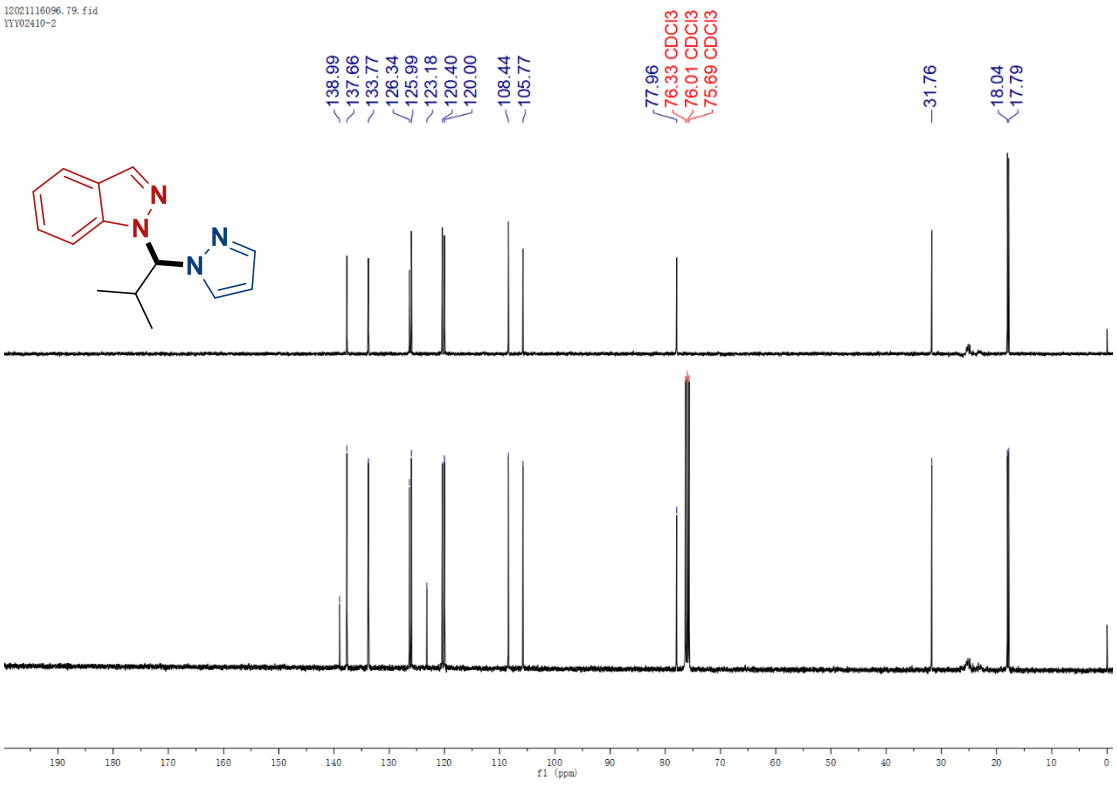
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 80**



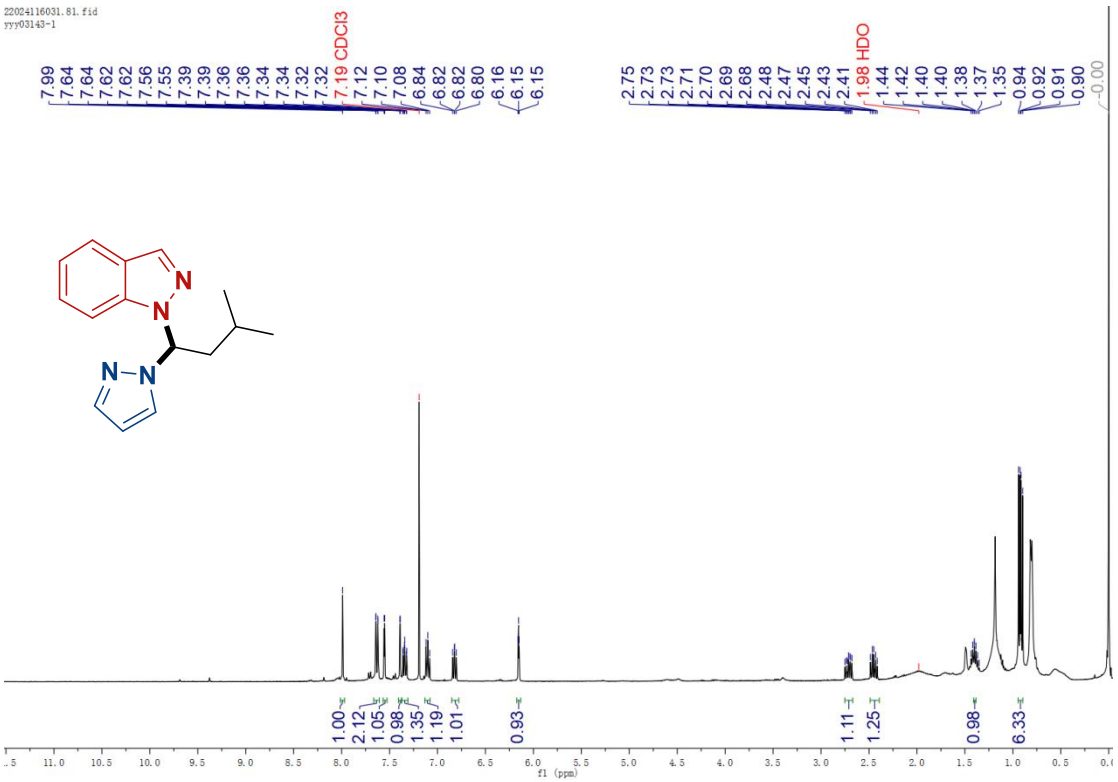
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 80**



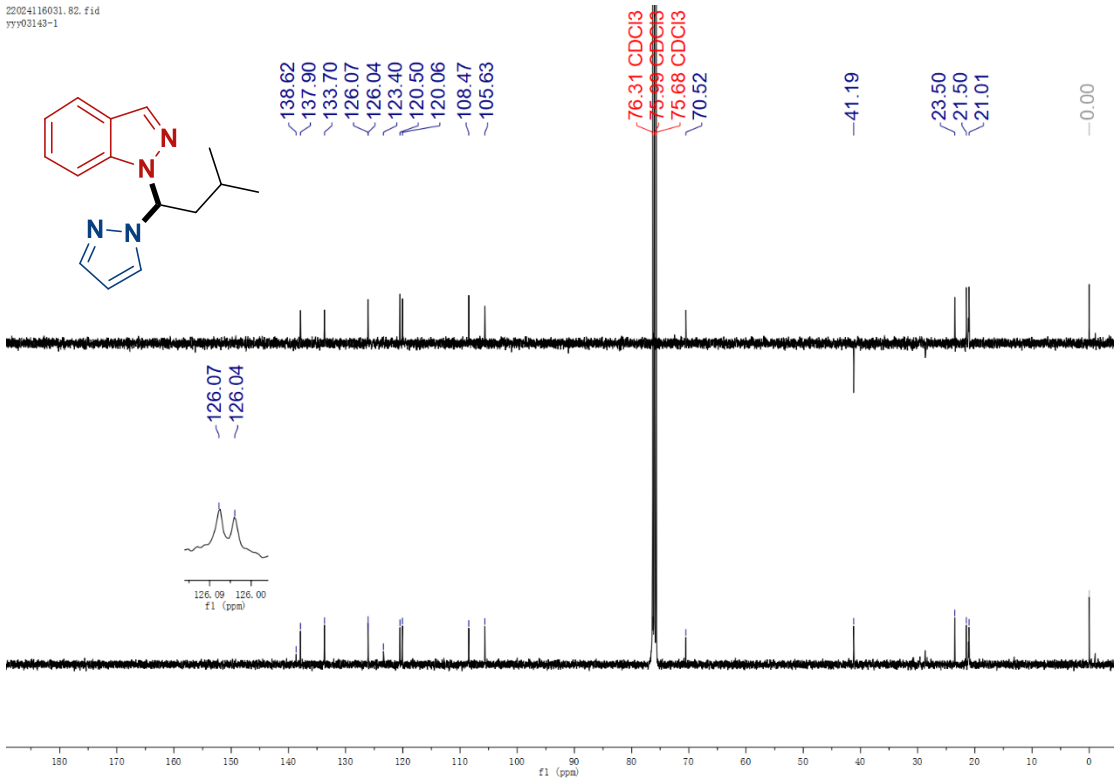
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 81**



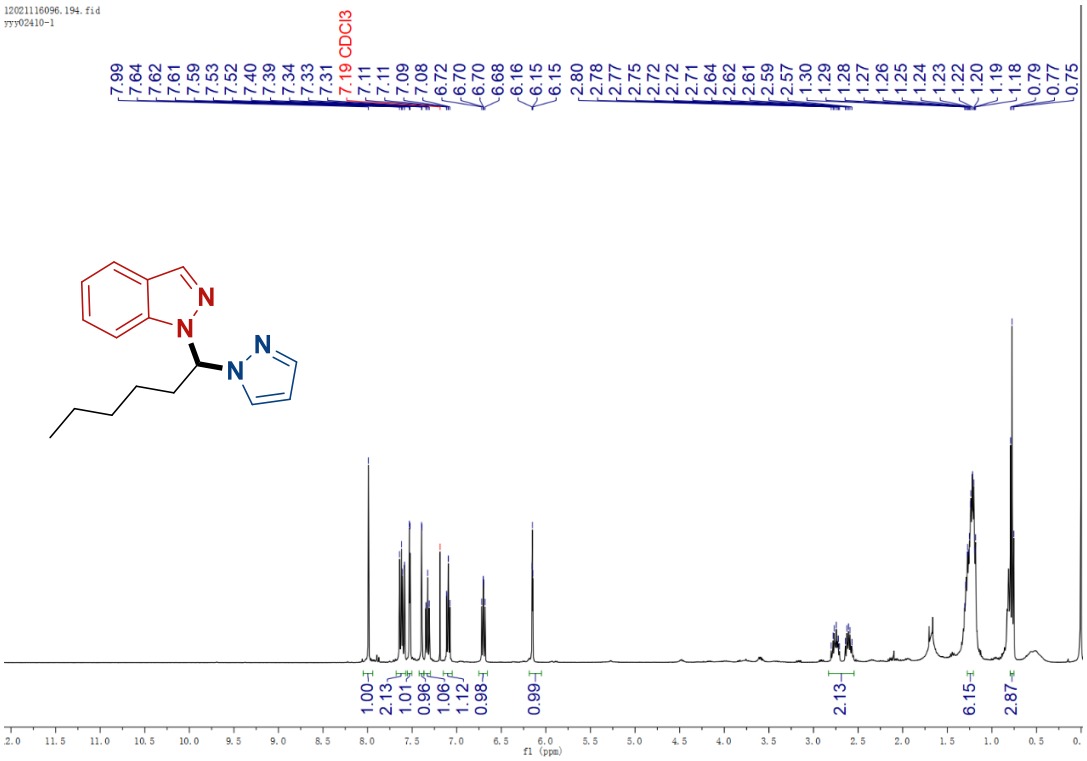
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 81**



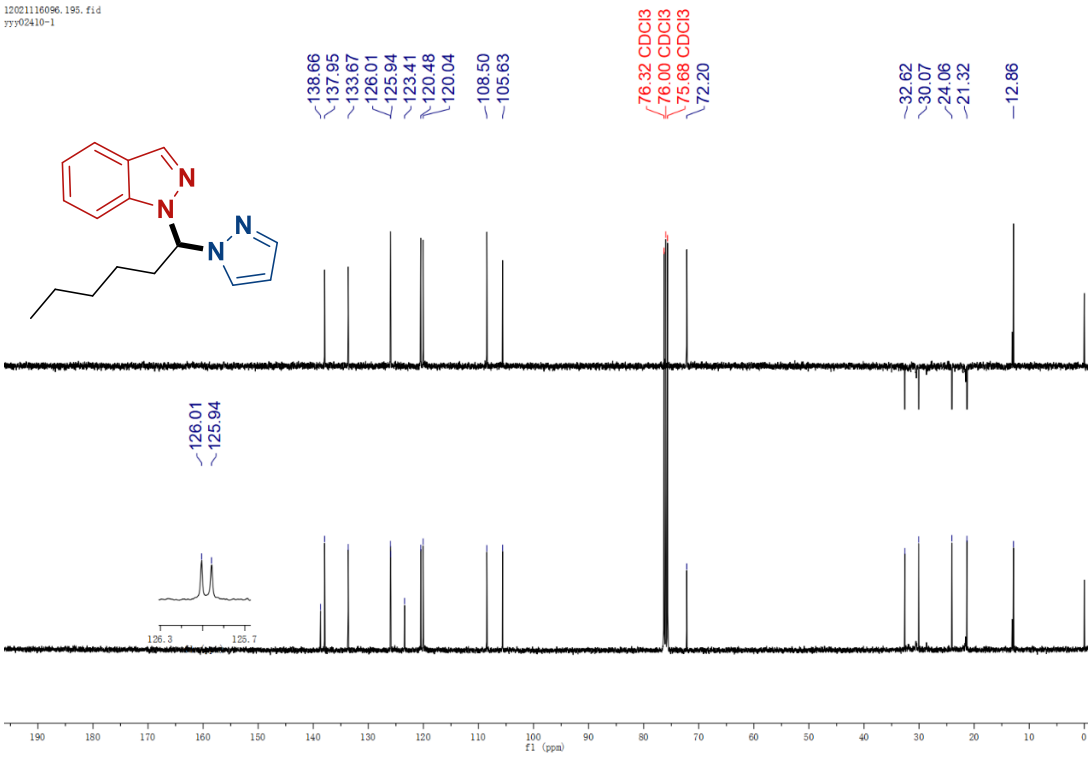
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 82**



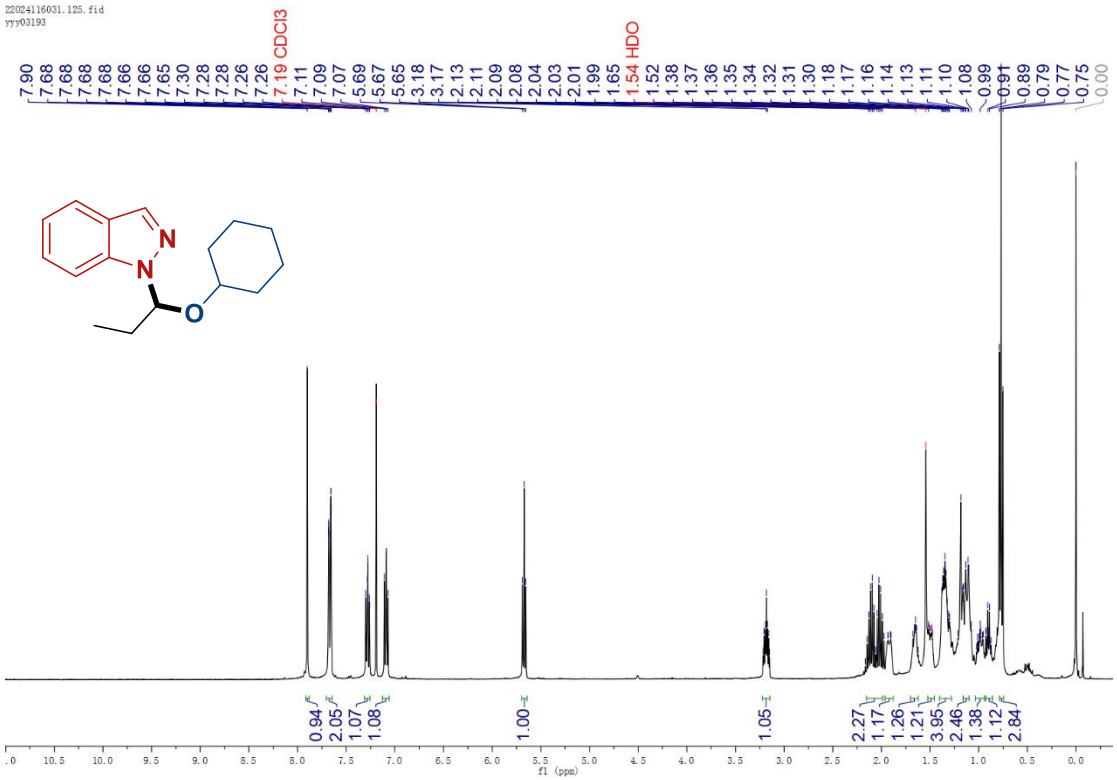
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 82**



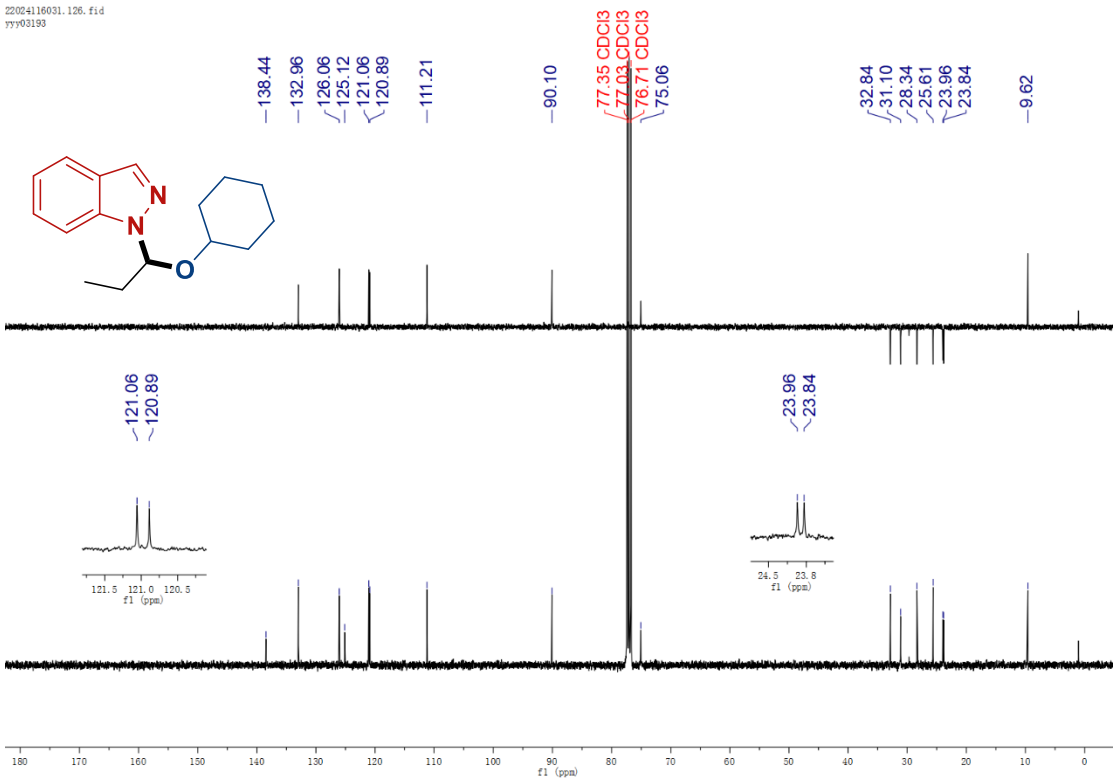
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 83**



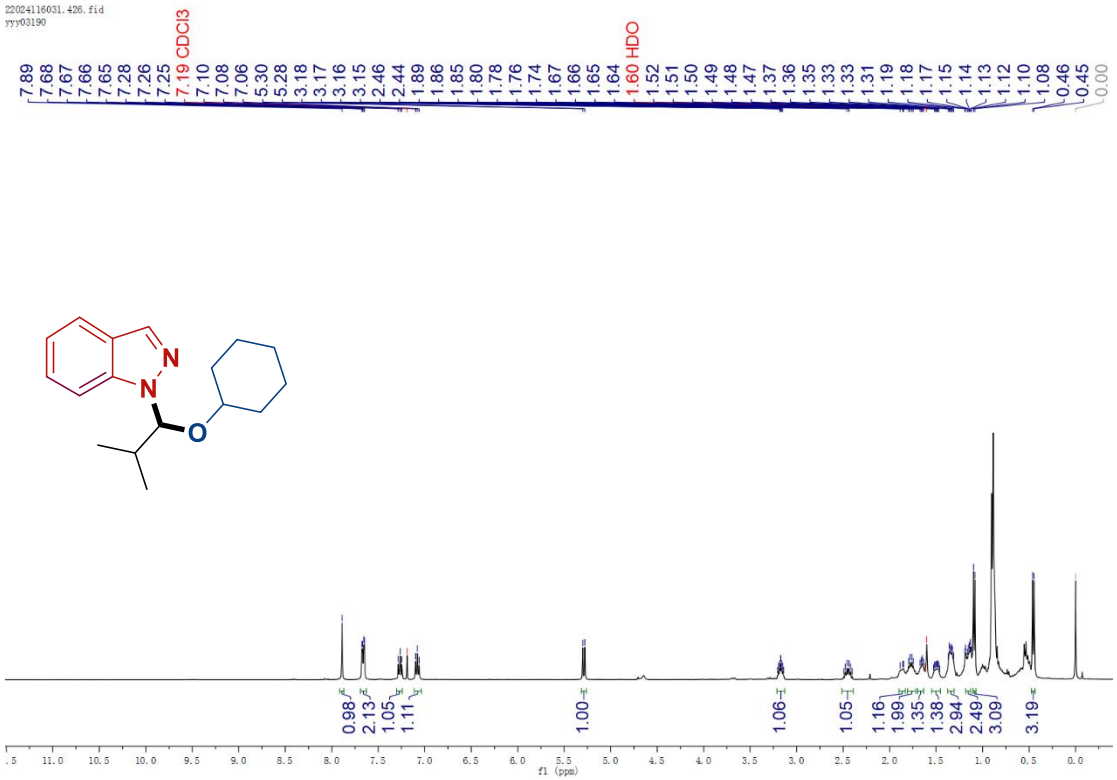
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 83**



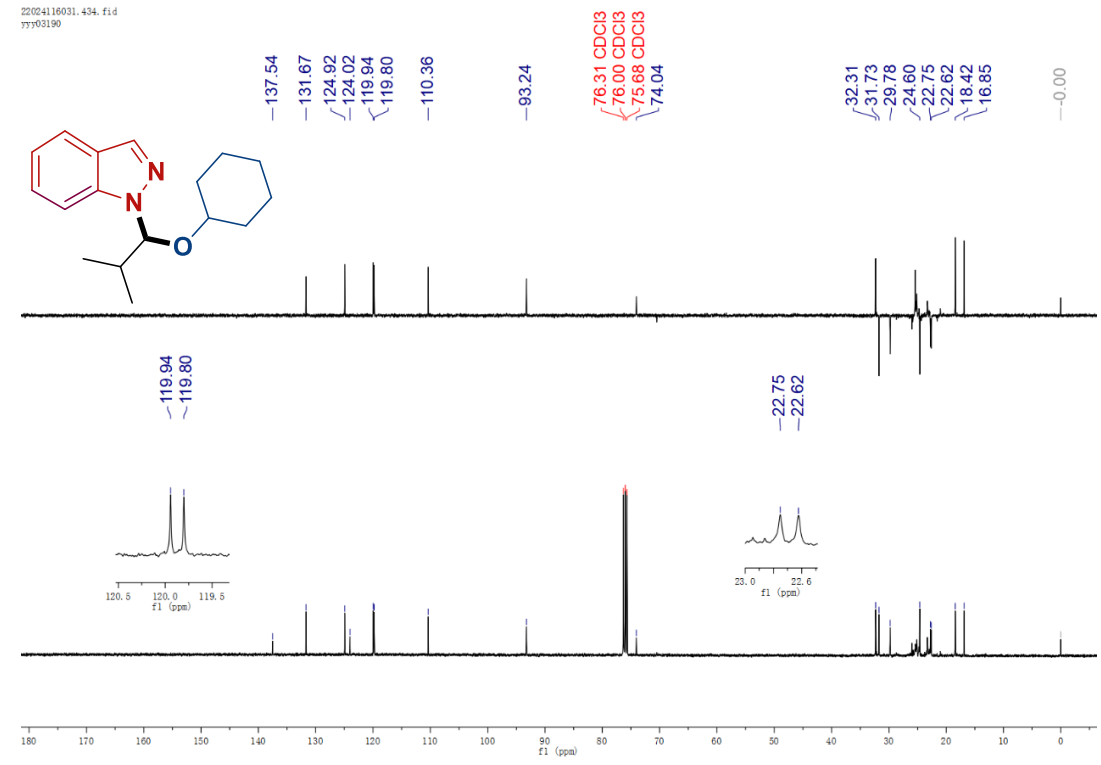
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 84**



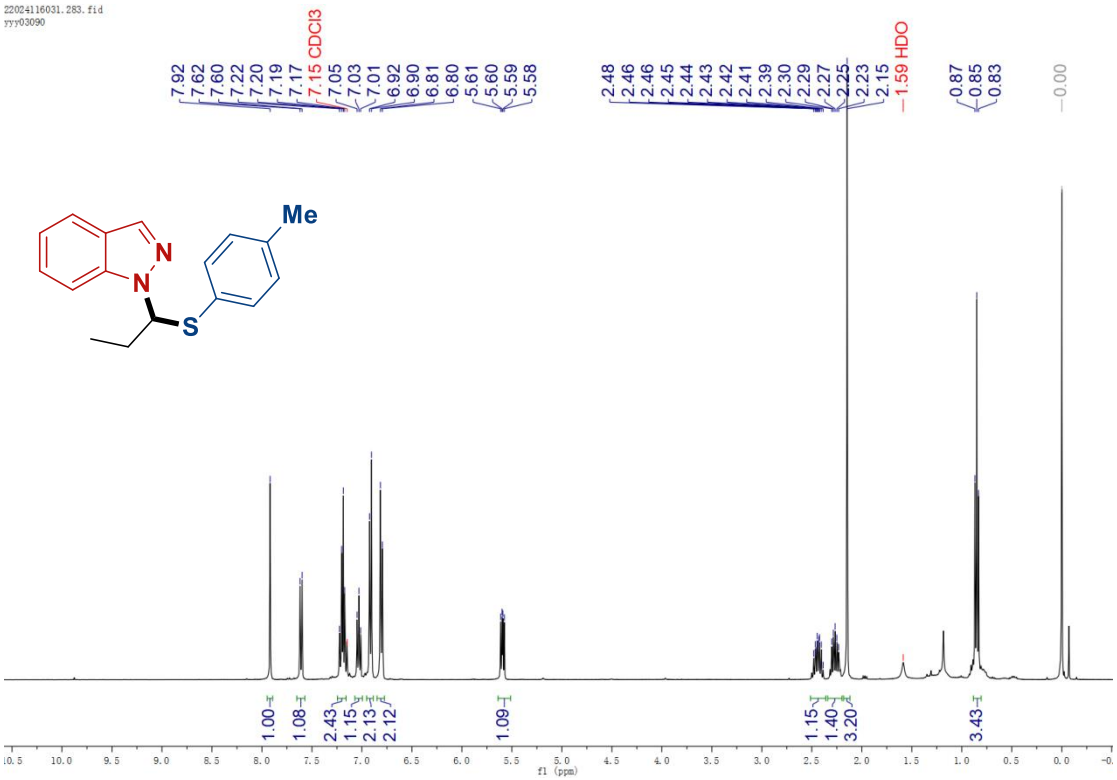
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 84**



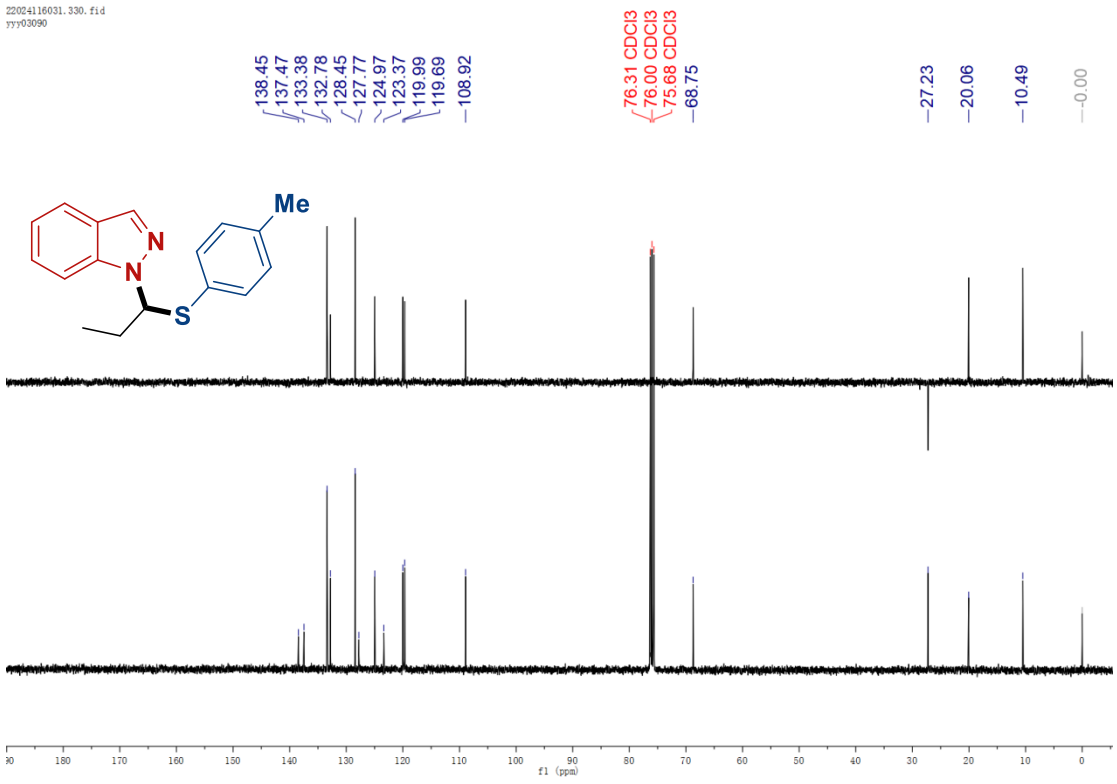
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 85**



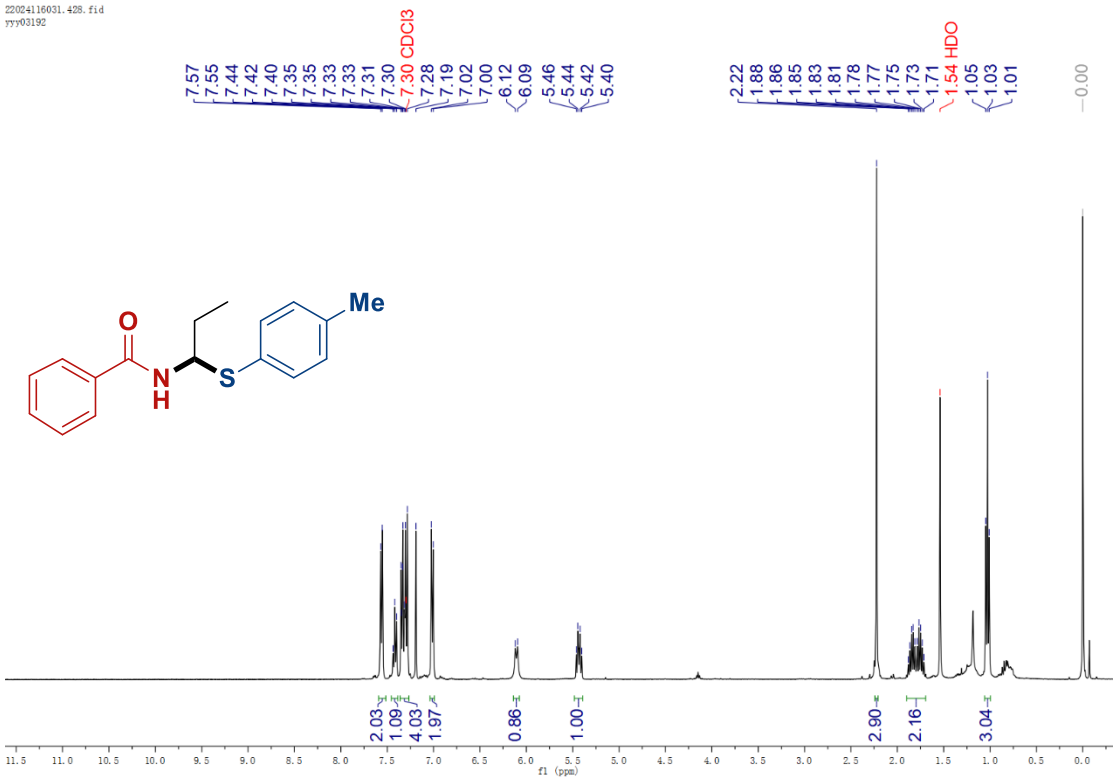
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 85**



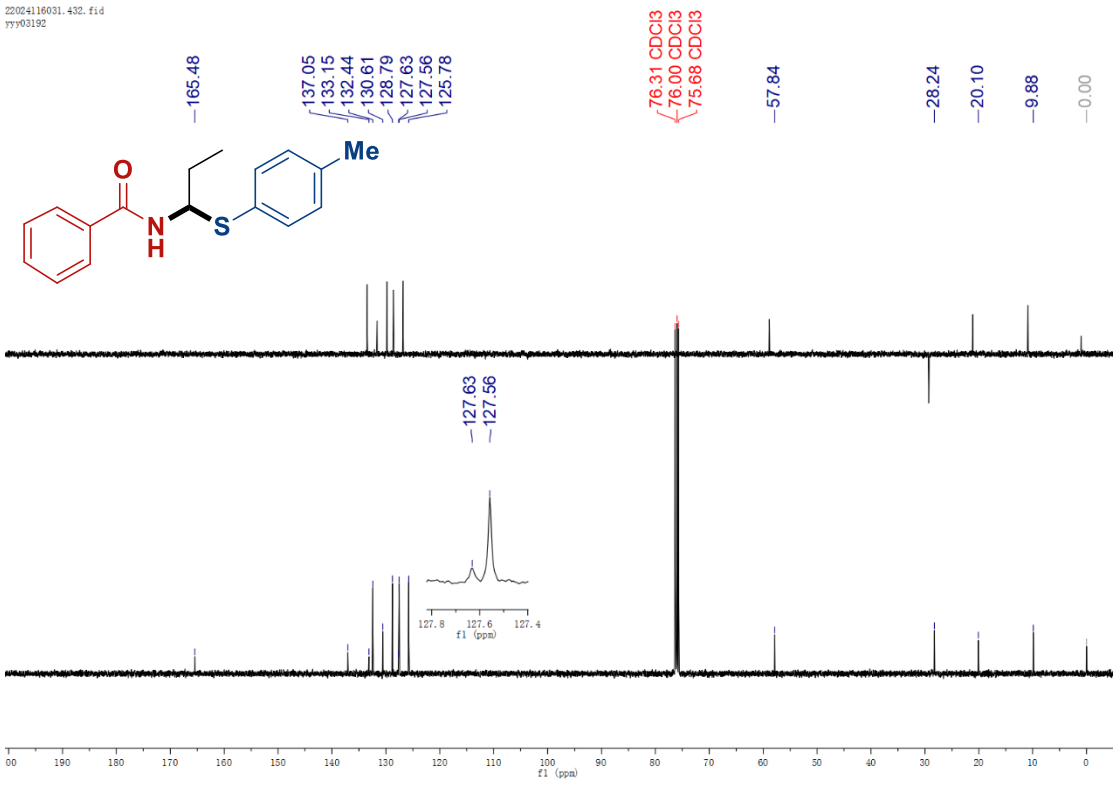
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 86**



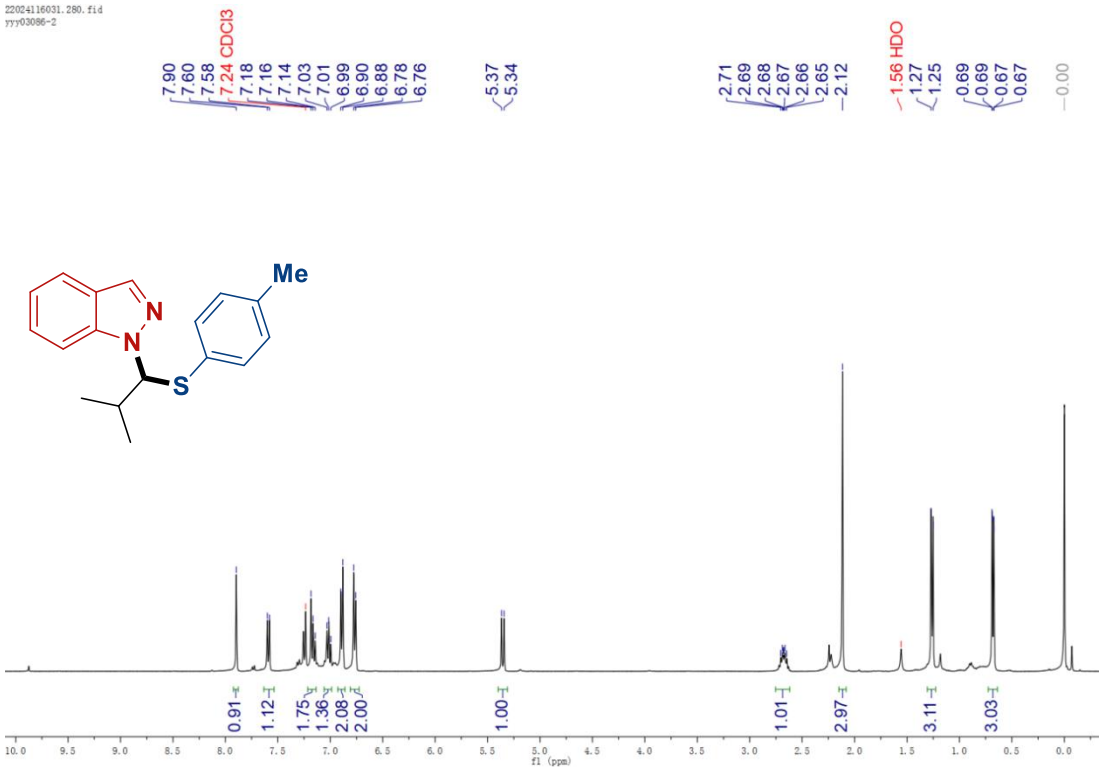
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 86**



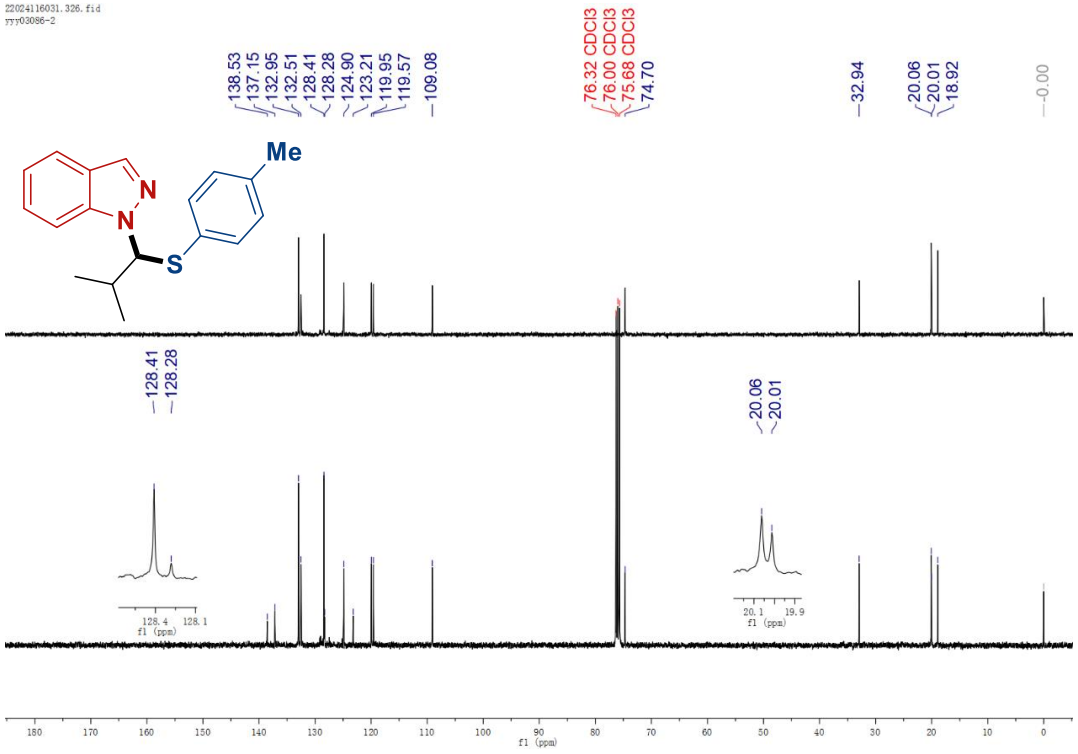
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 87**



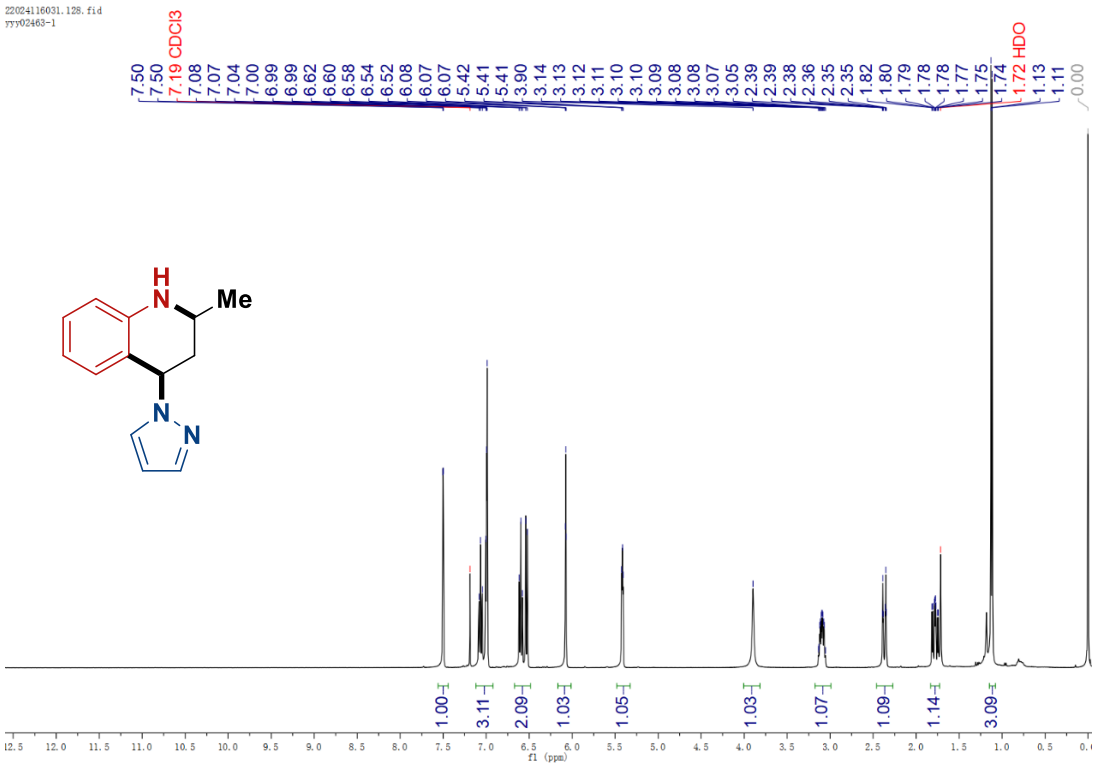
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 87**



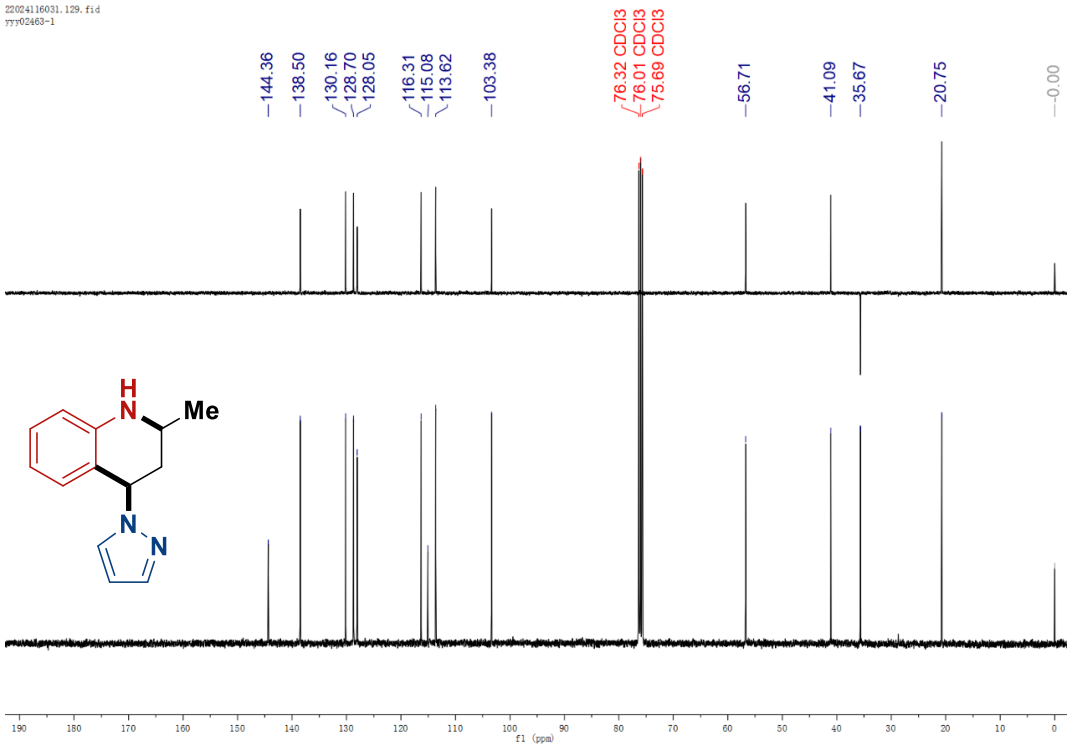
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 88**



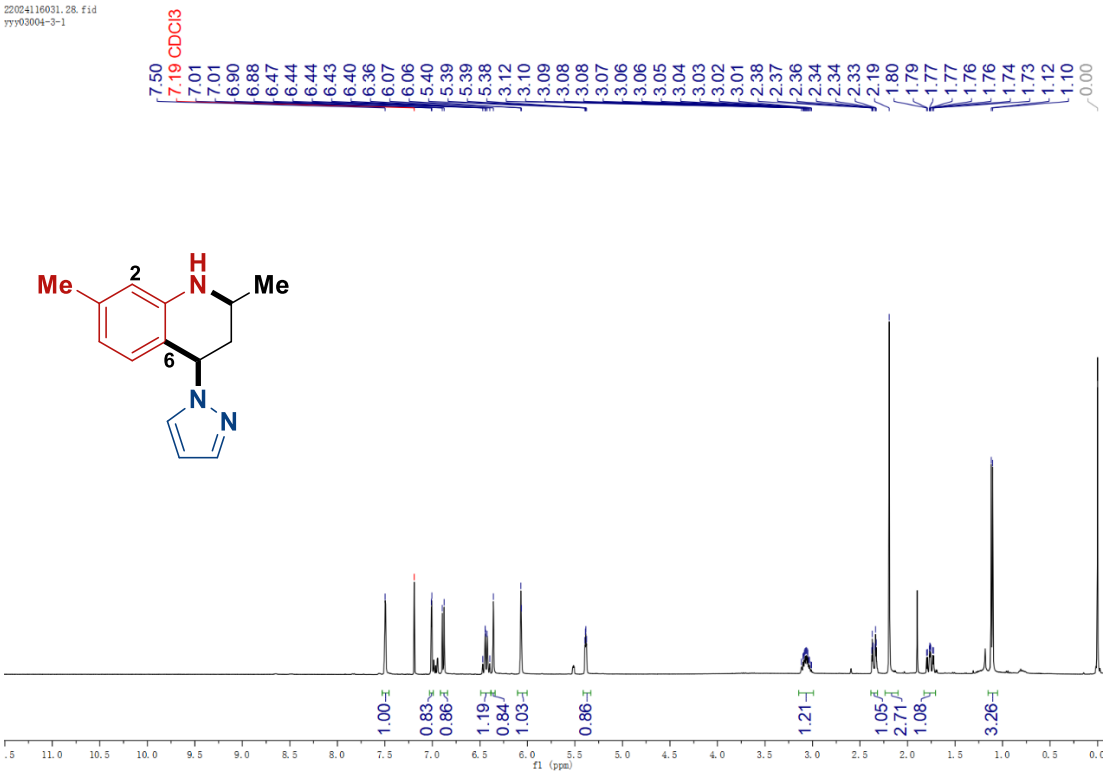
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 88**



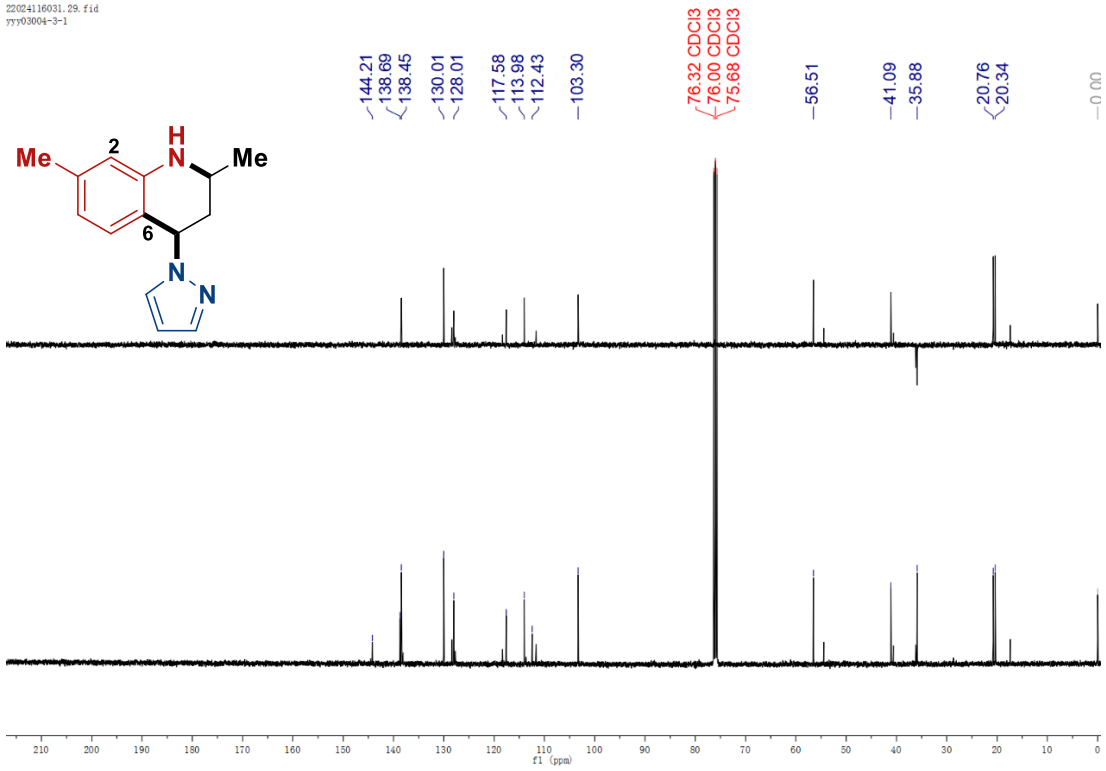
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 89**



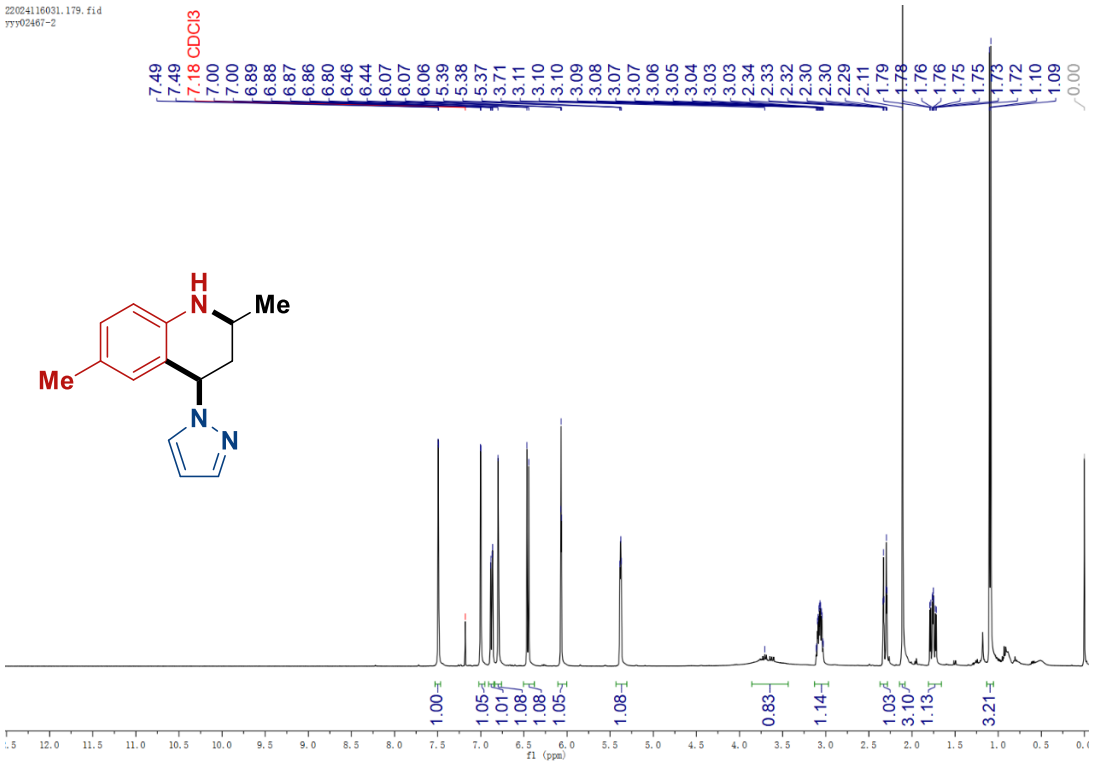
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 89**



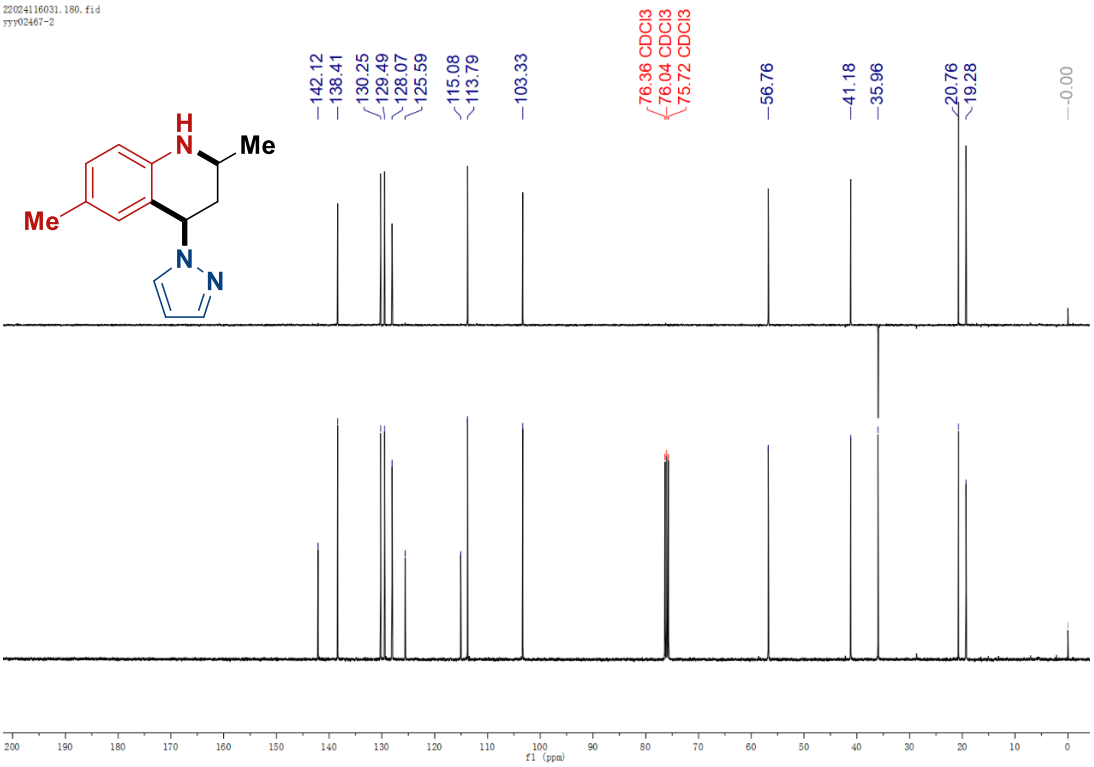
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 90**



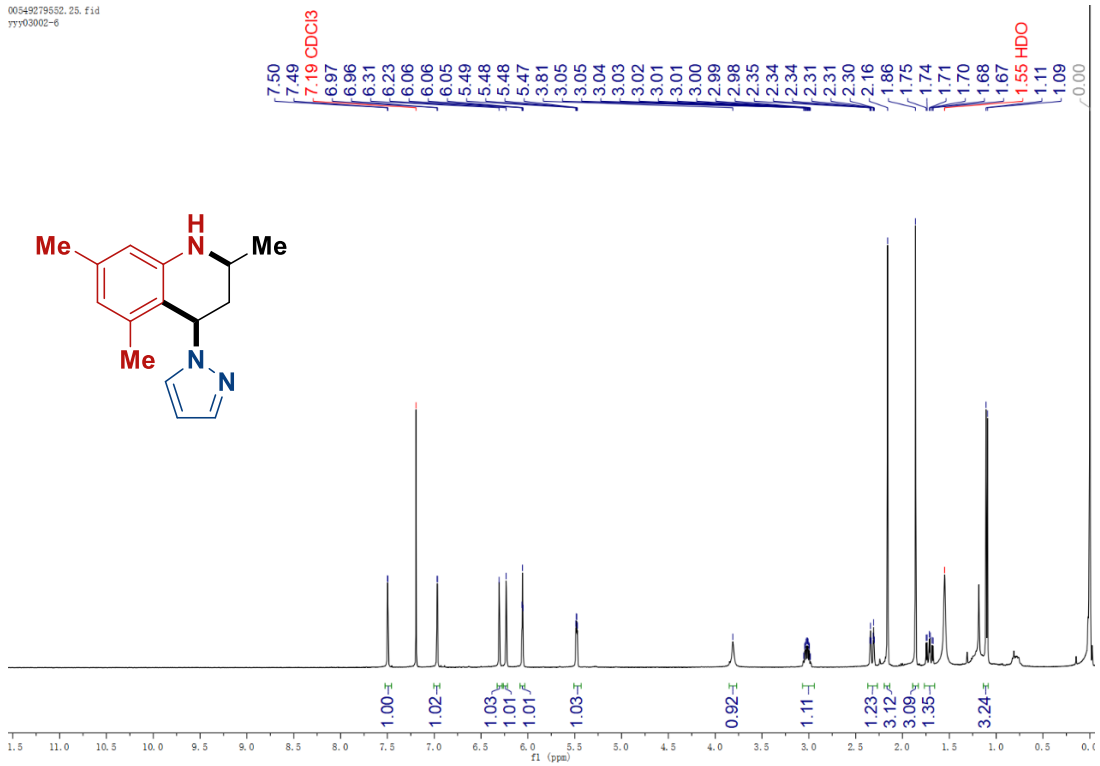
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 90**



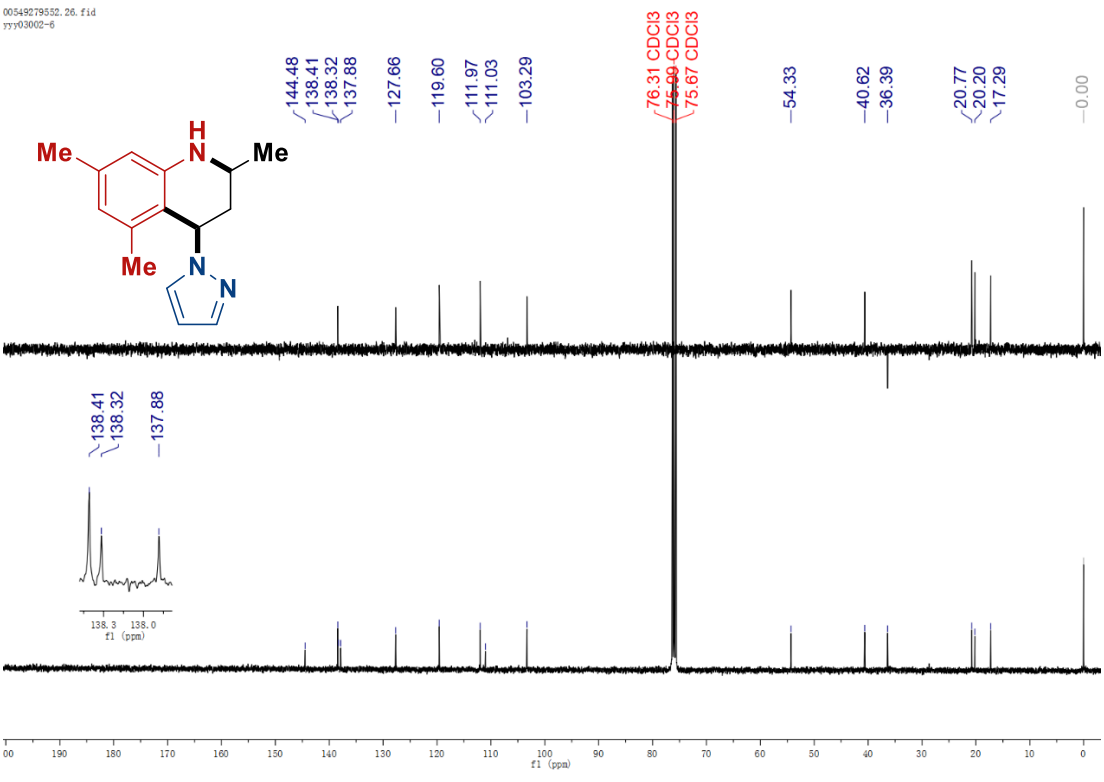
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 91**



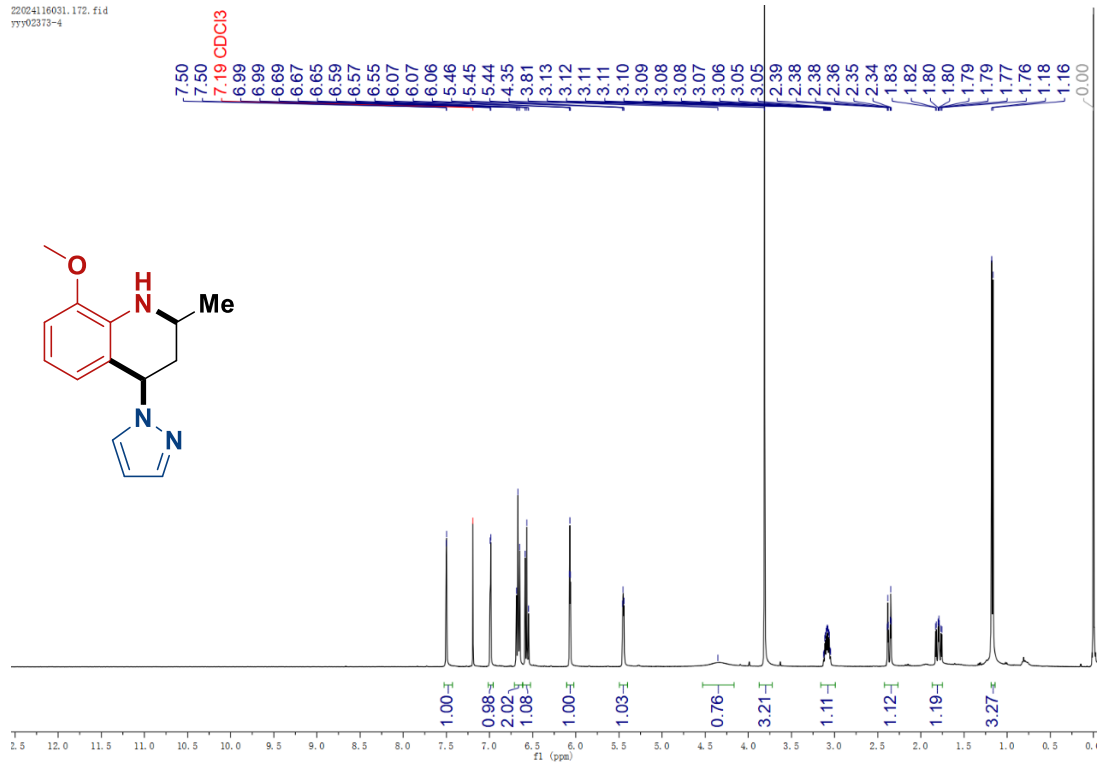
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 91**



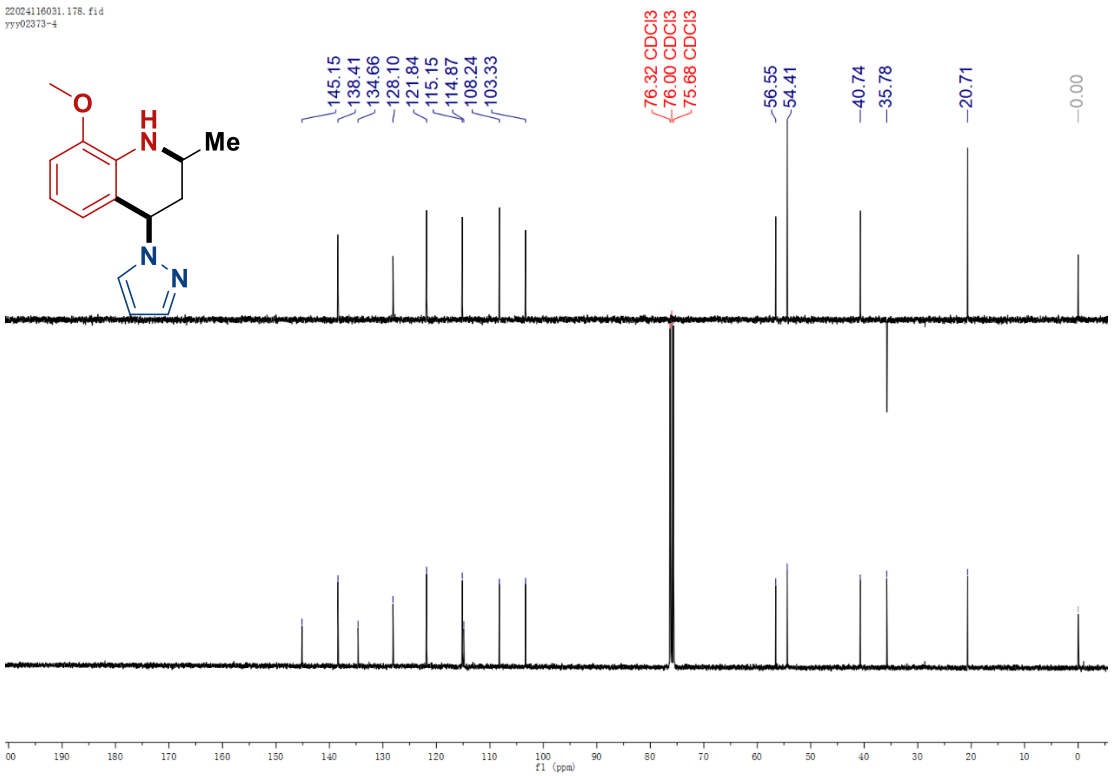
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 92**



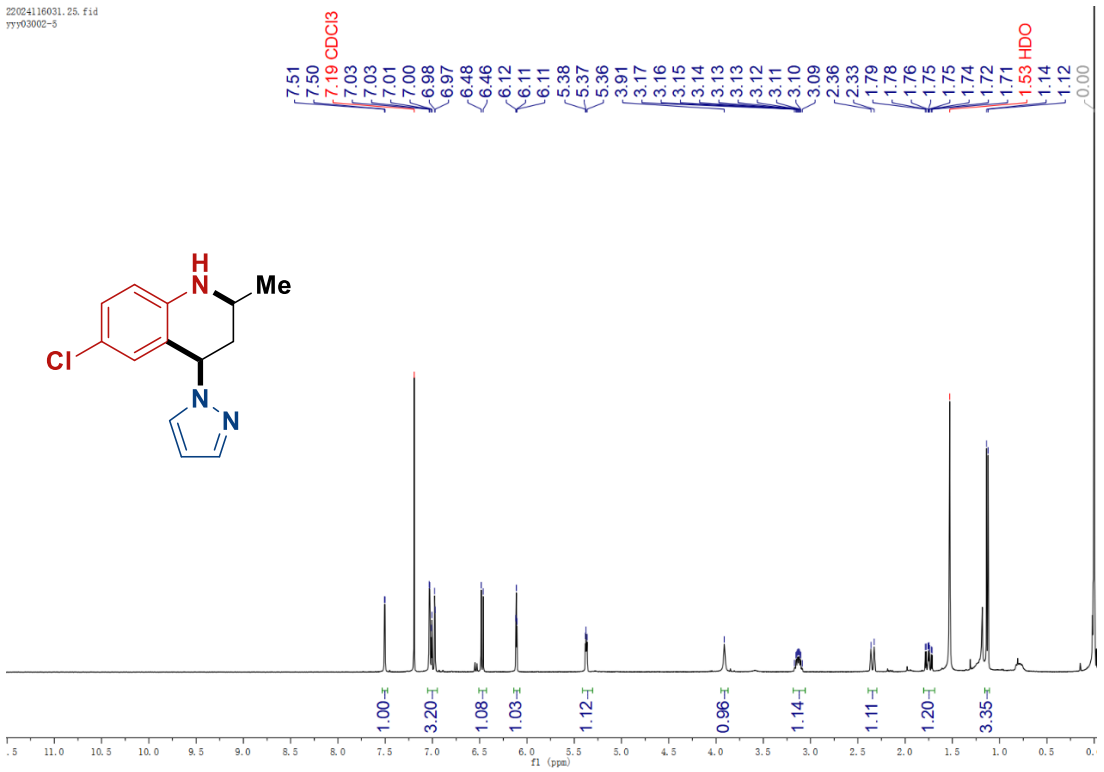
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 92**



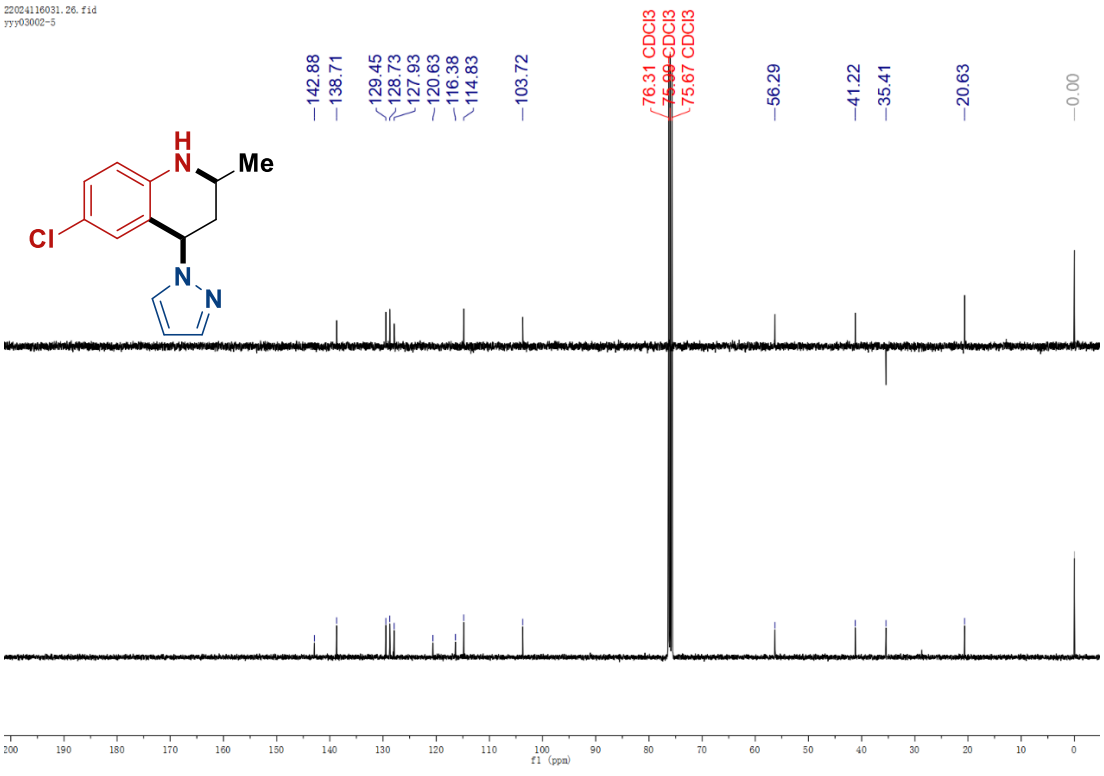
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 93**



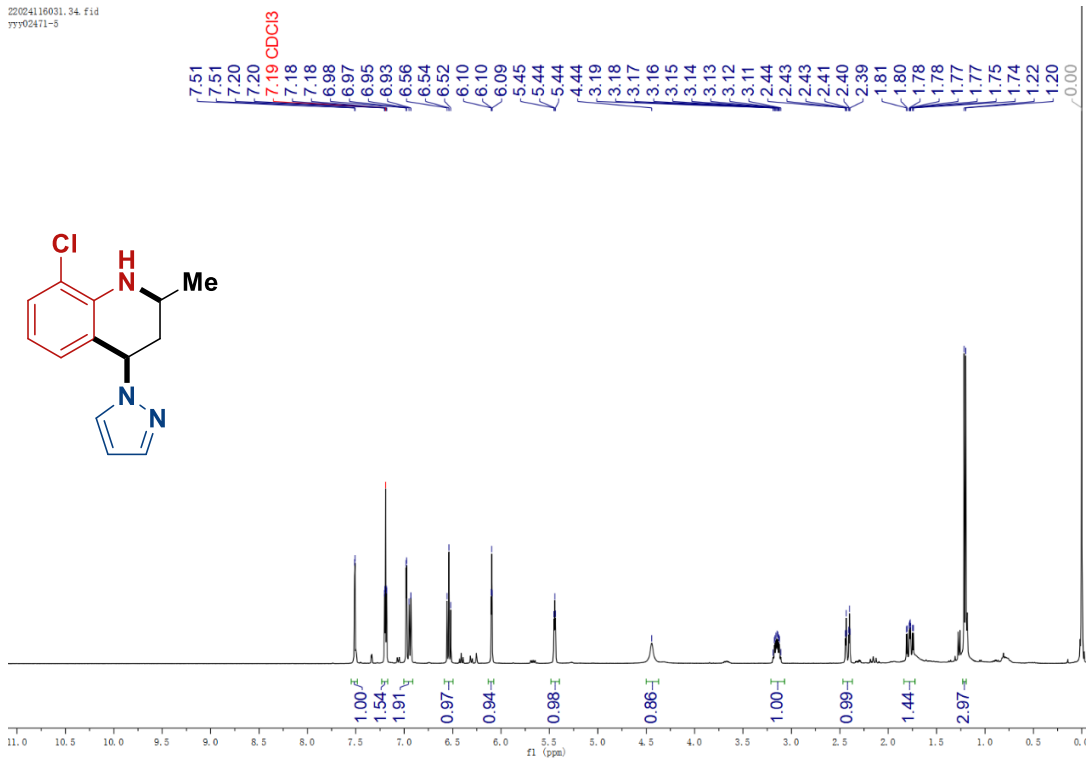
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 93**



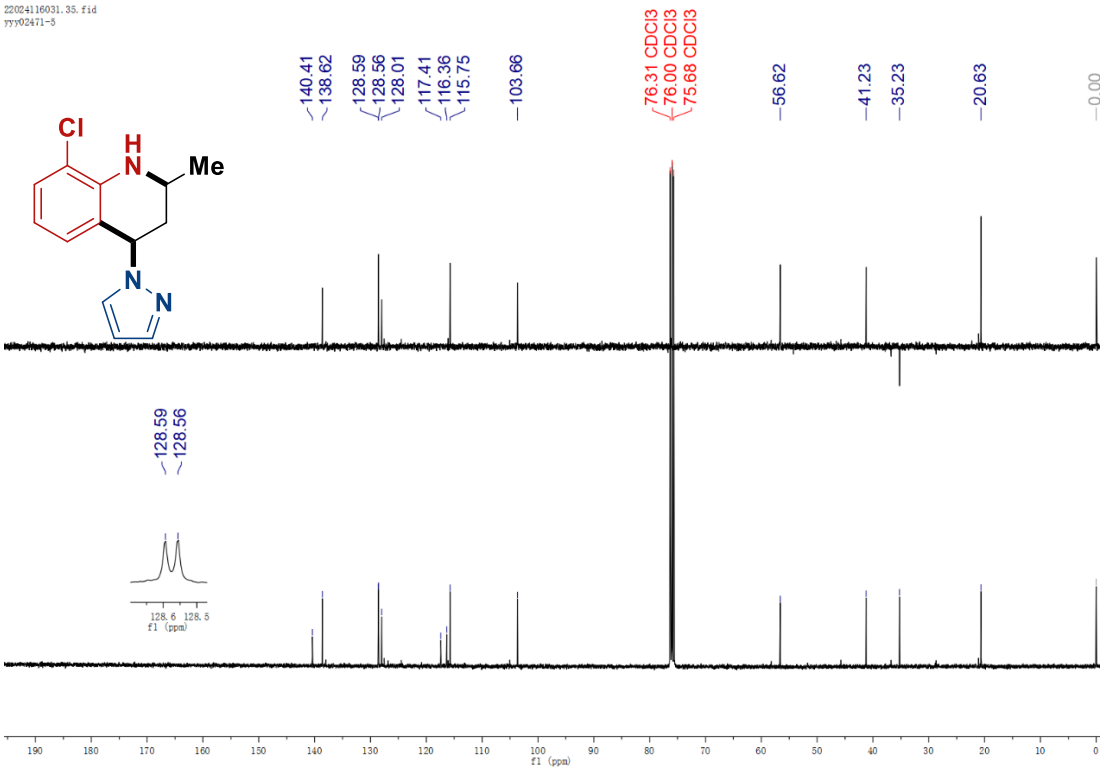
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 94**



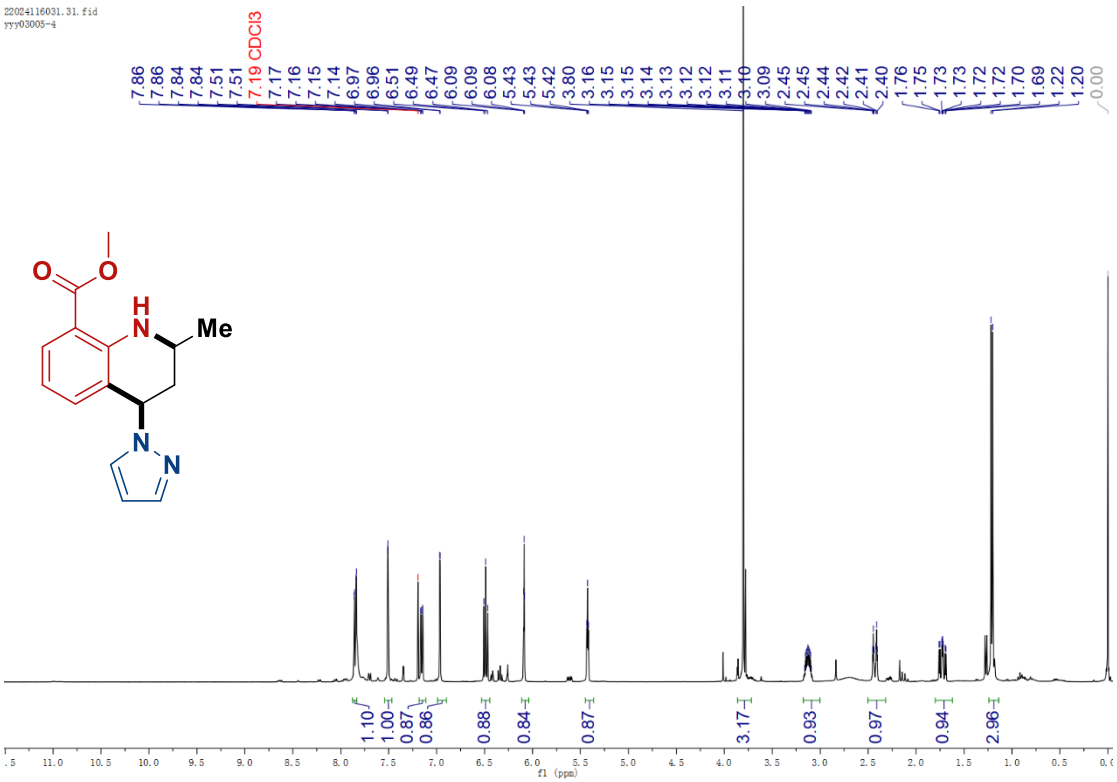
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 94**



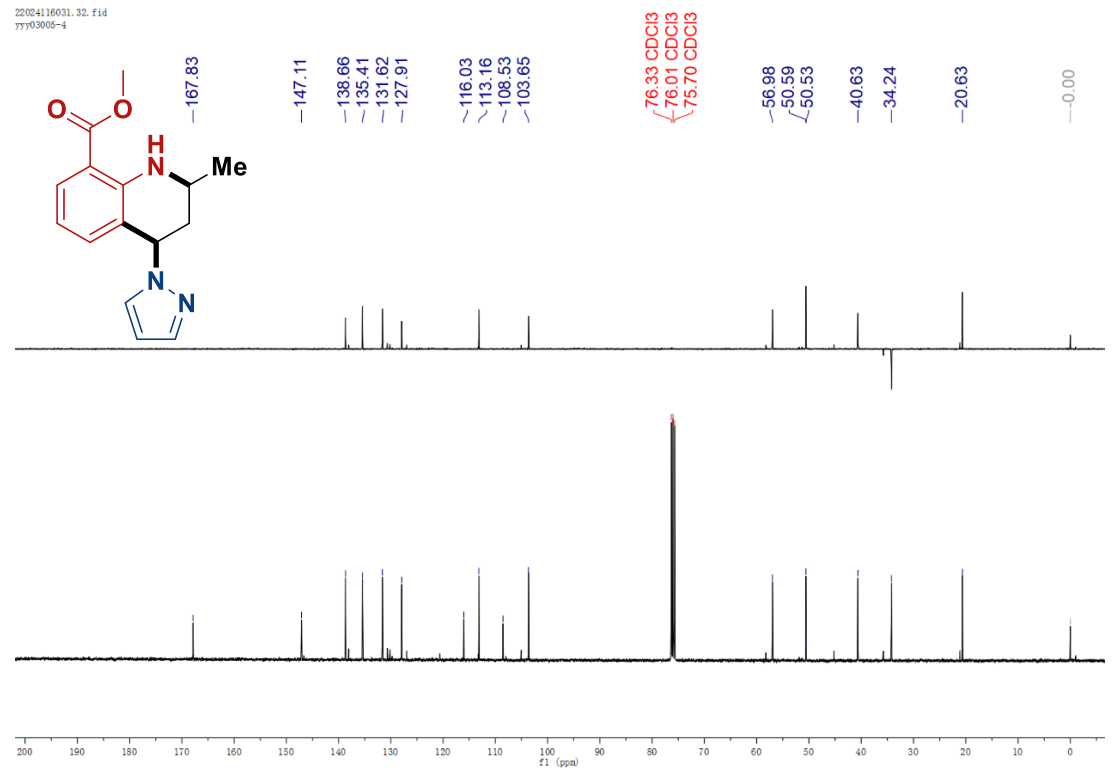
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 95**



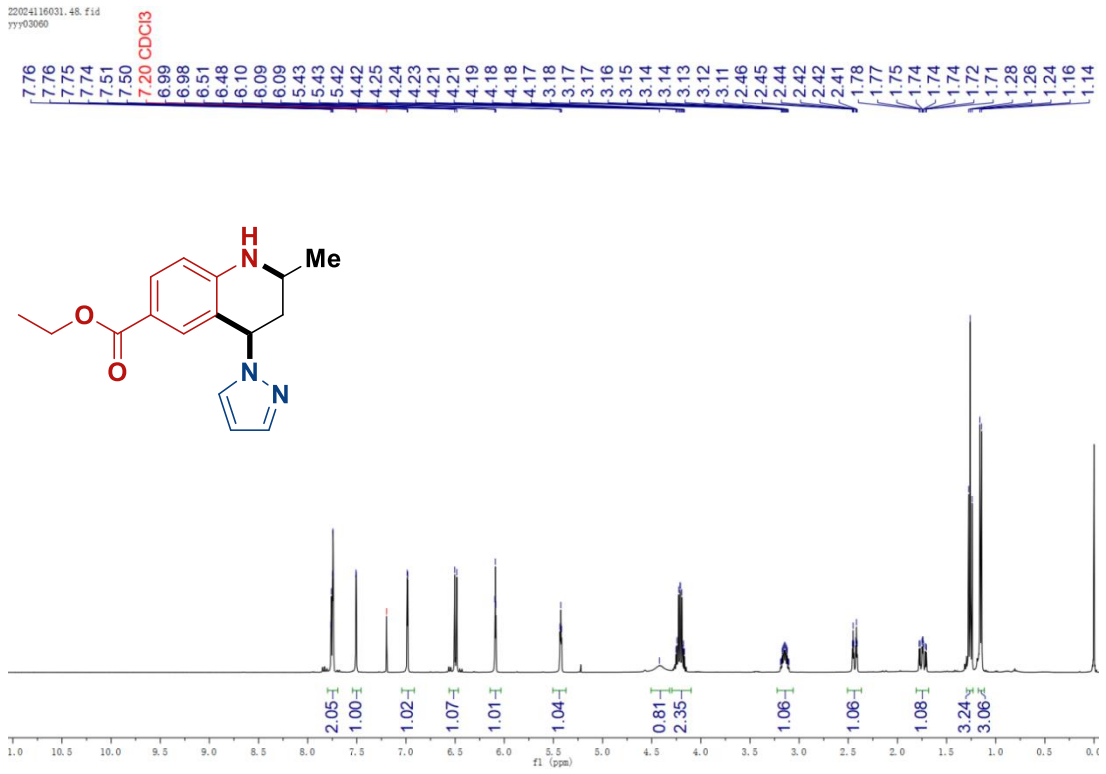
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 95**



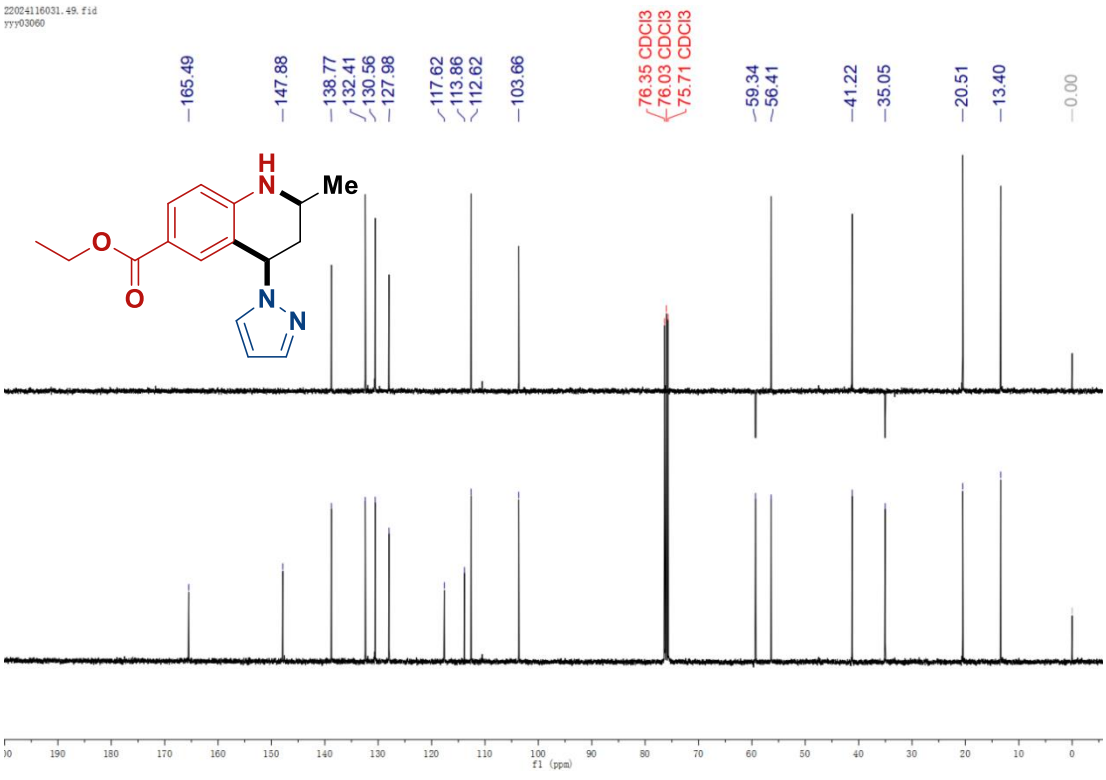
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 96**



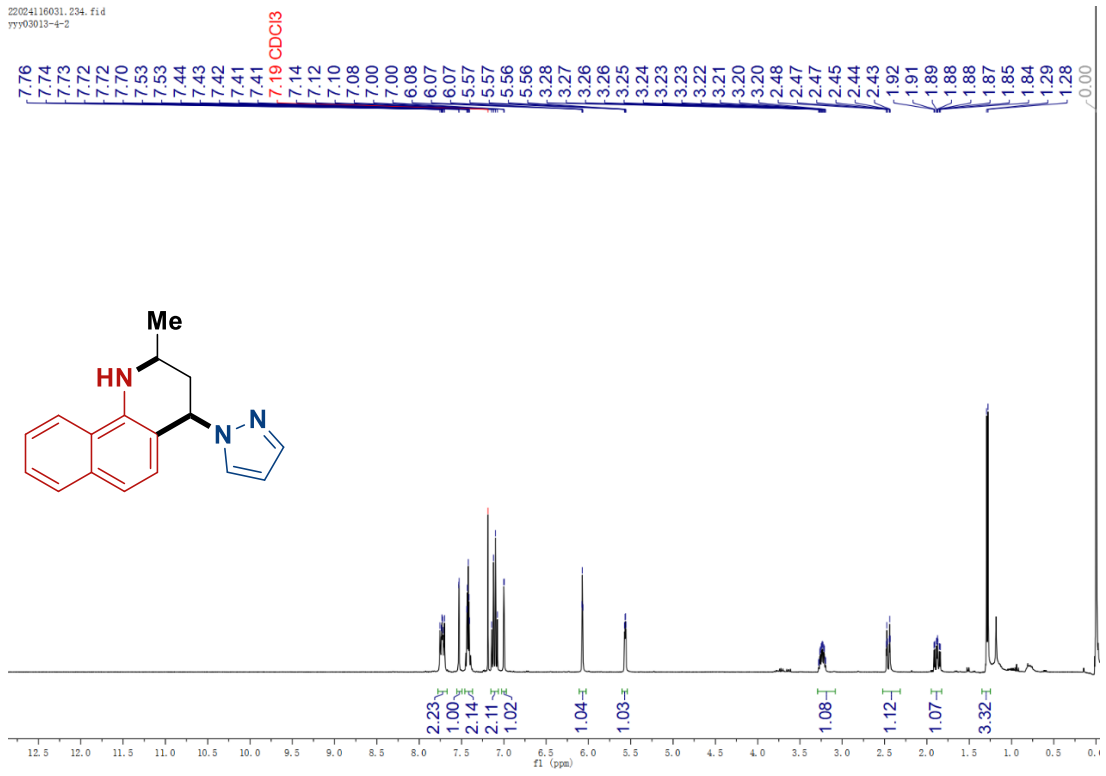
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 96**



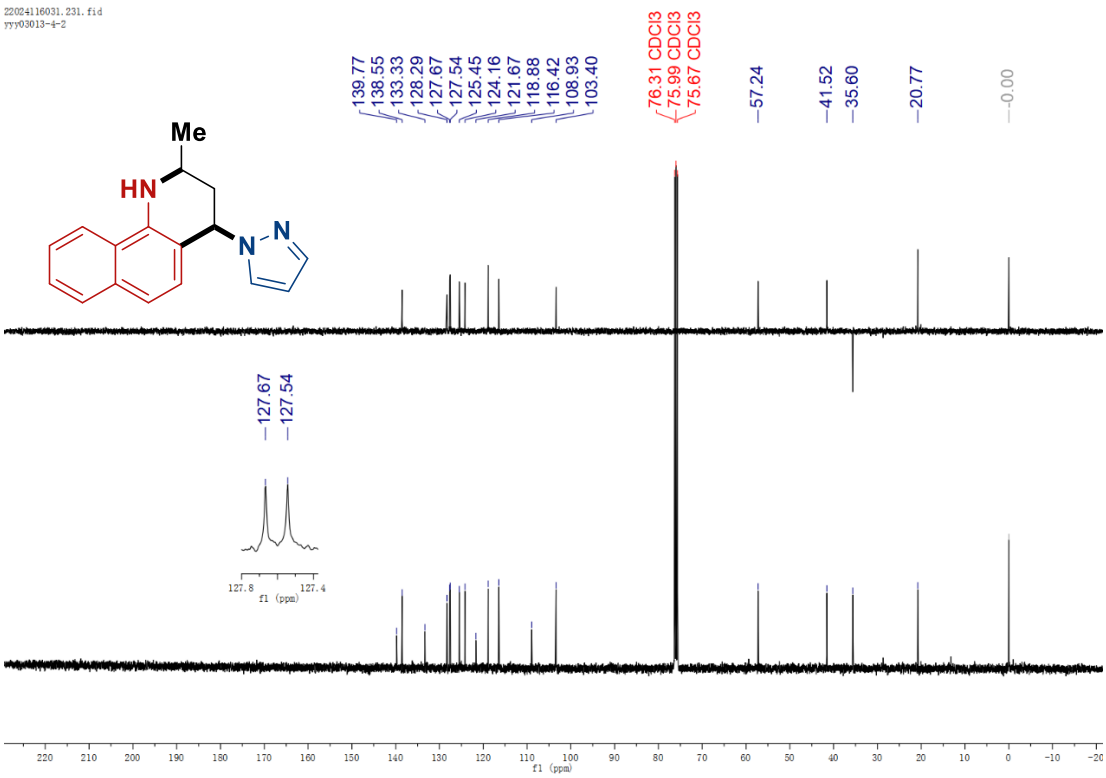
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 97**



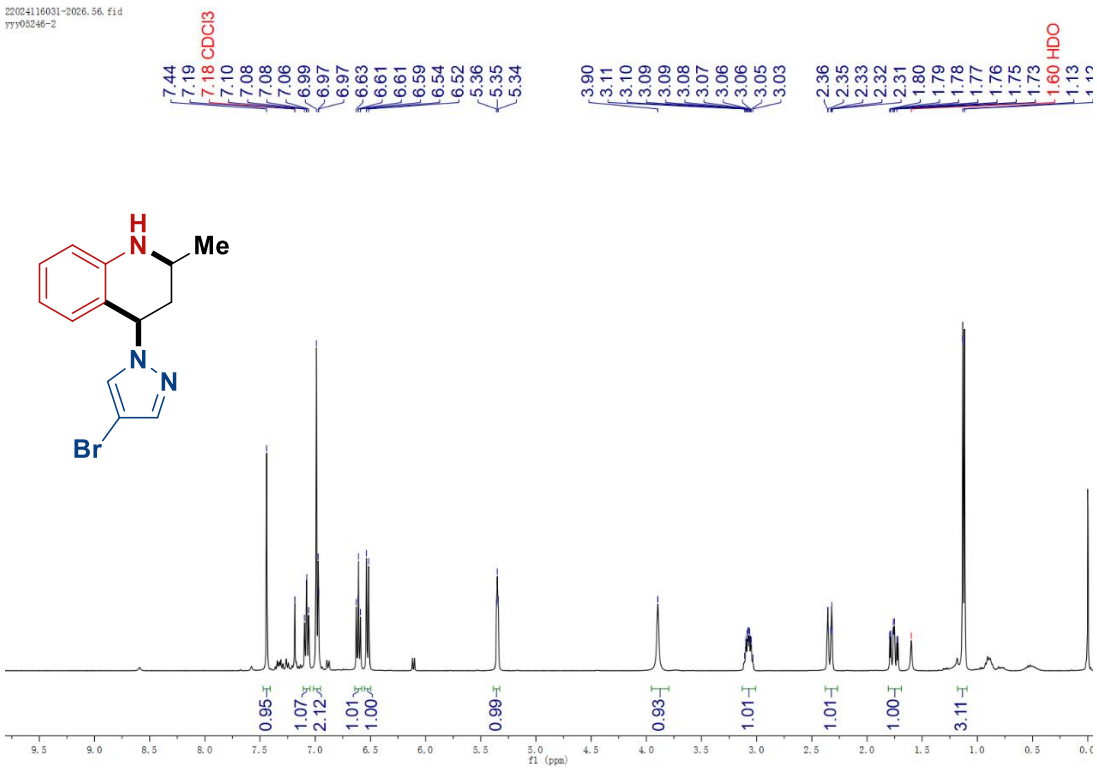
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 97**



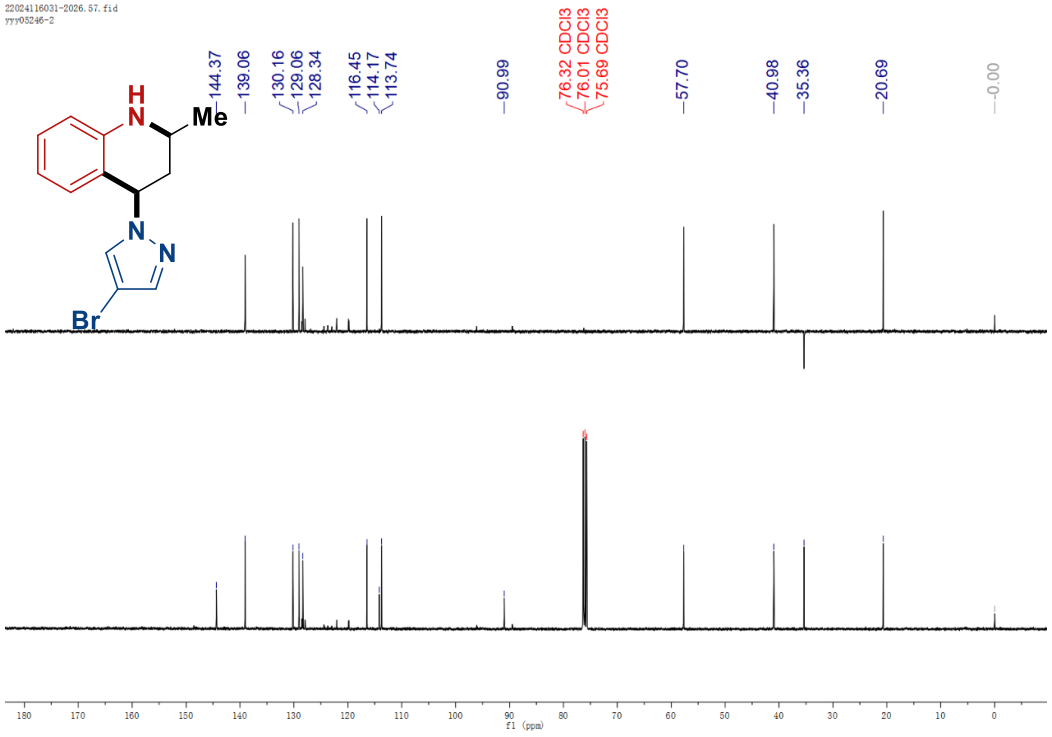
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 98**



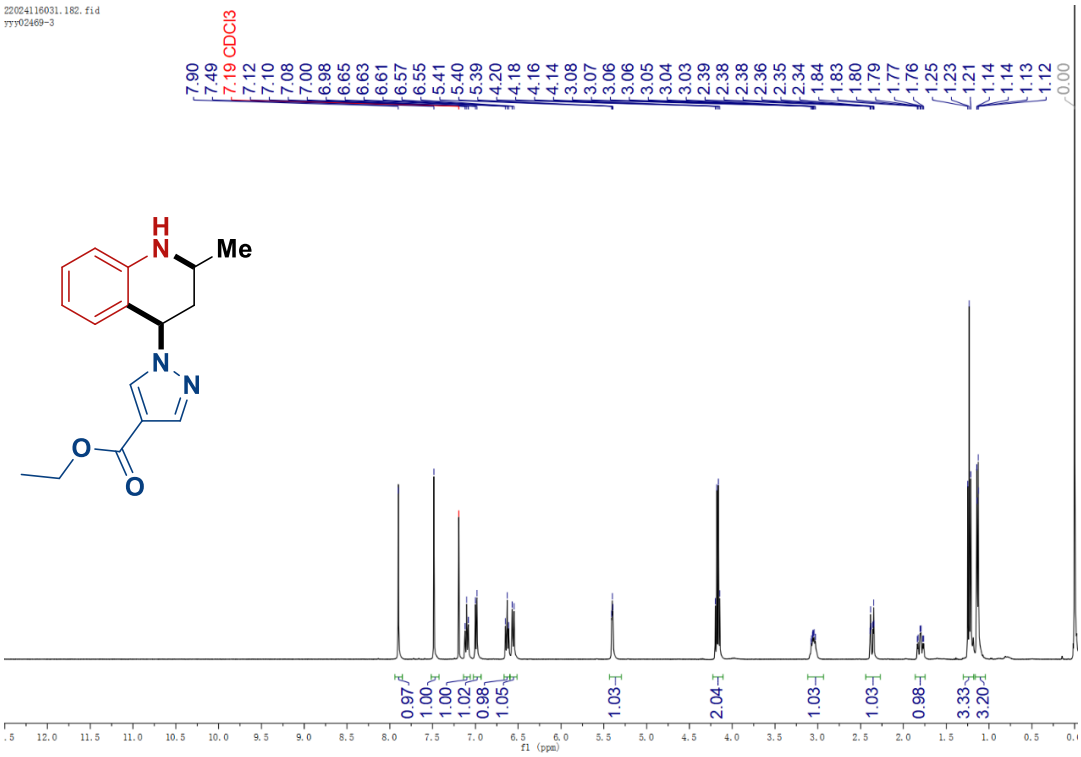
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 98**



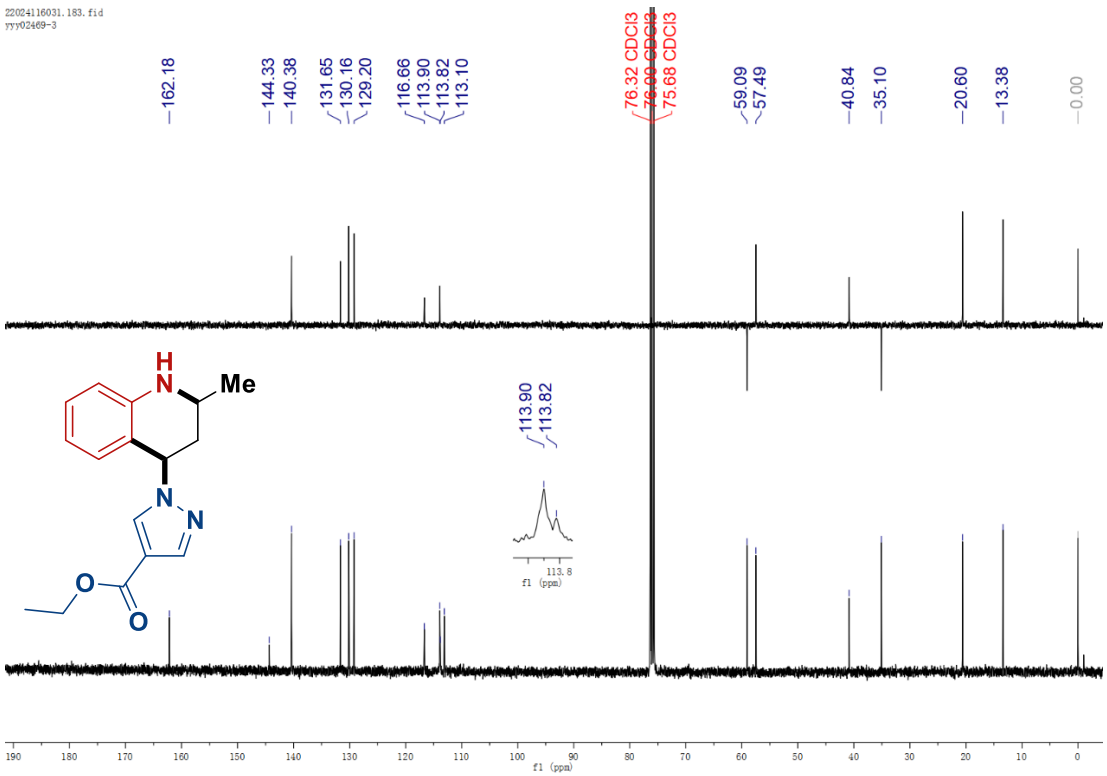
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 99**



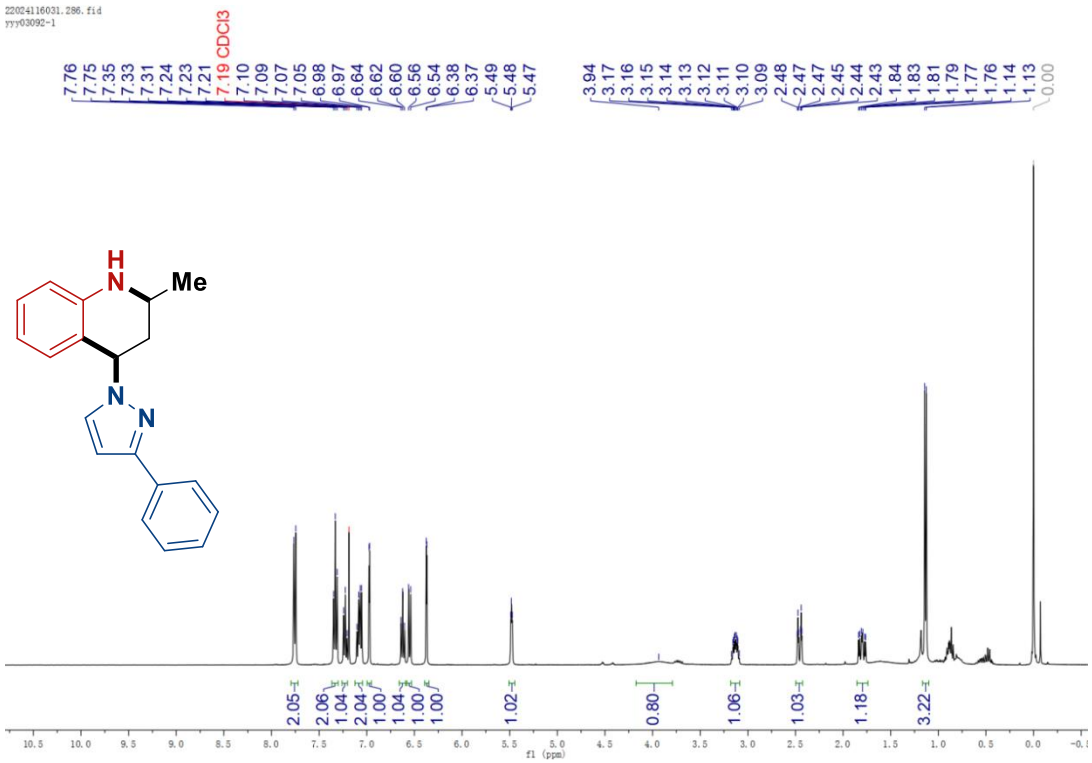
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 99**



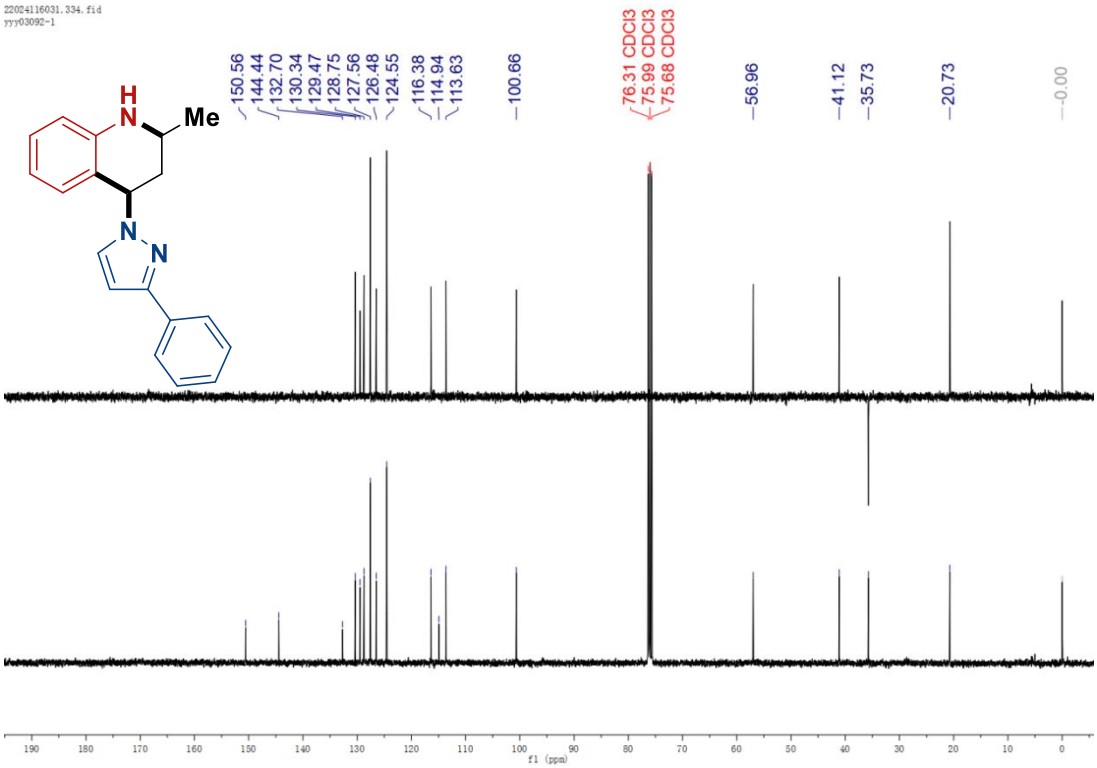
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 100**



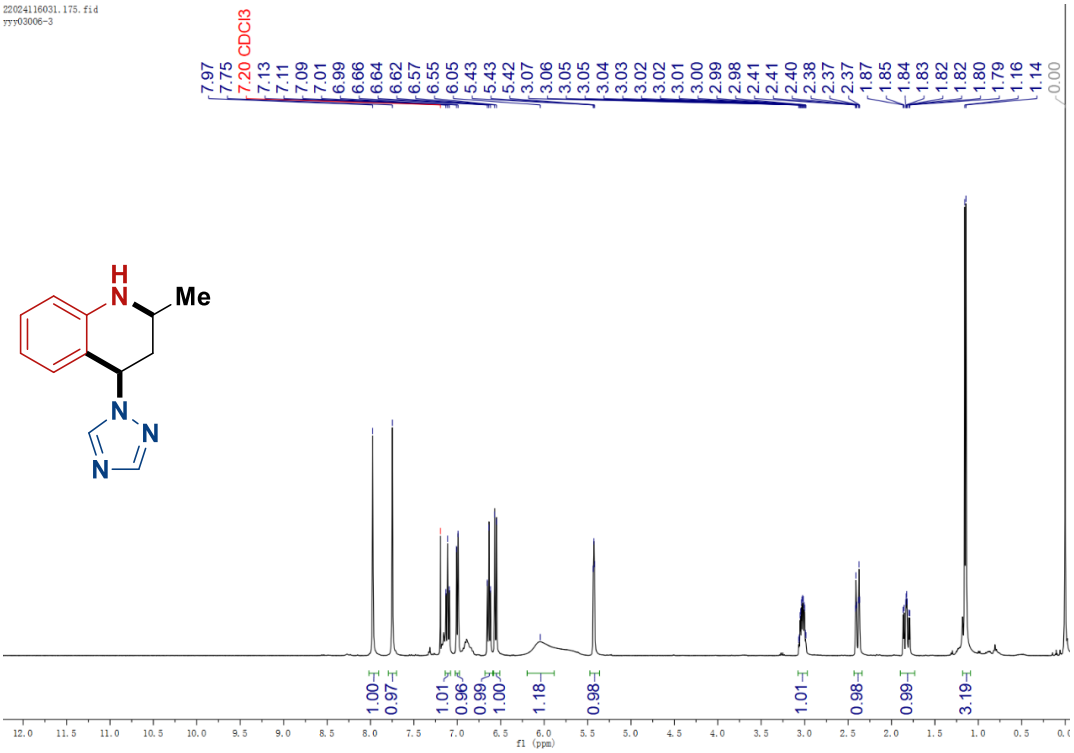
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 100**



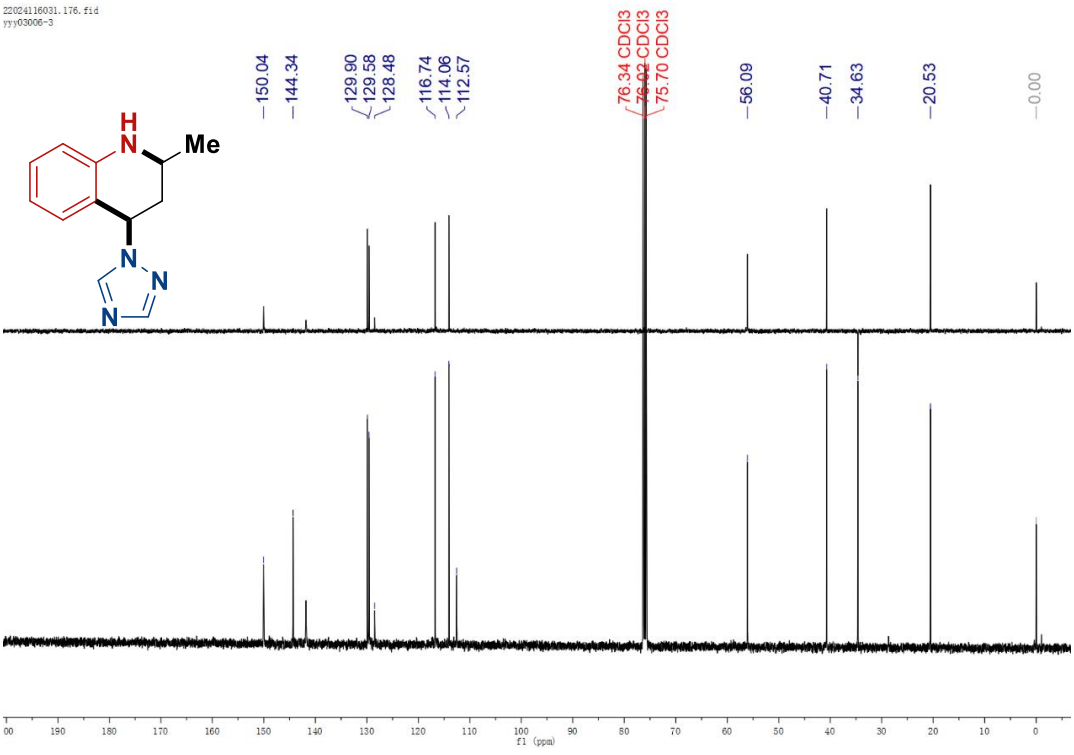
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 101**



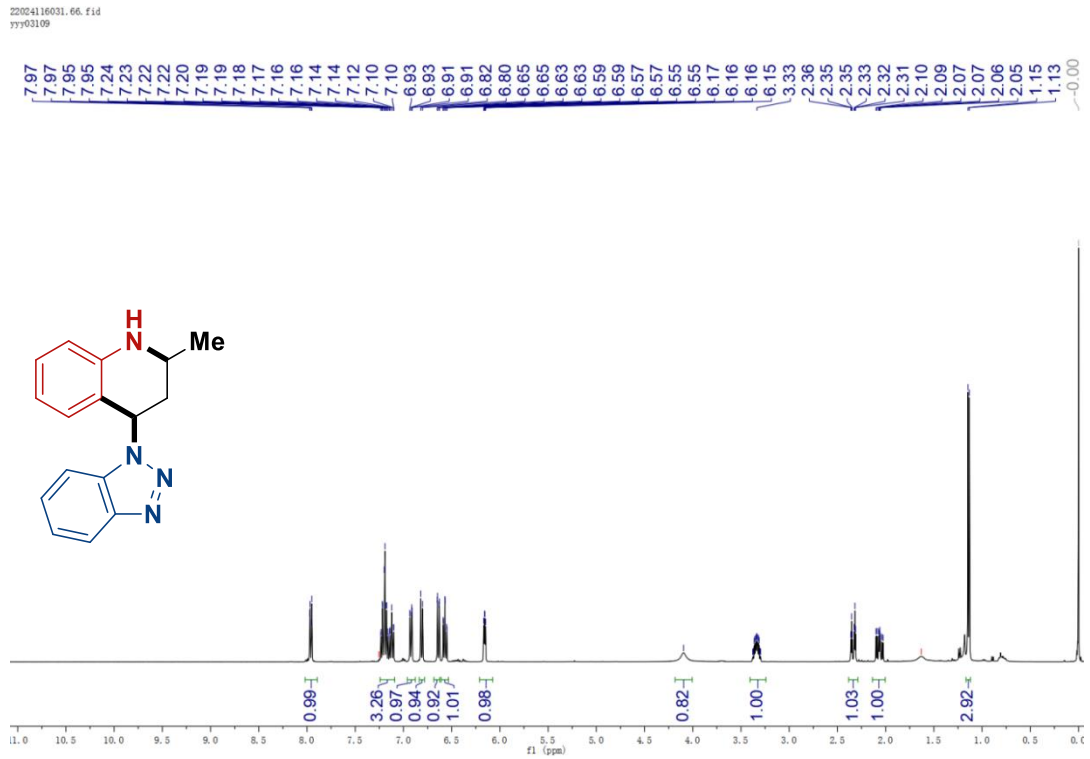
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 101**



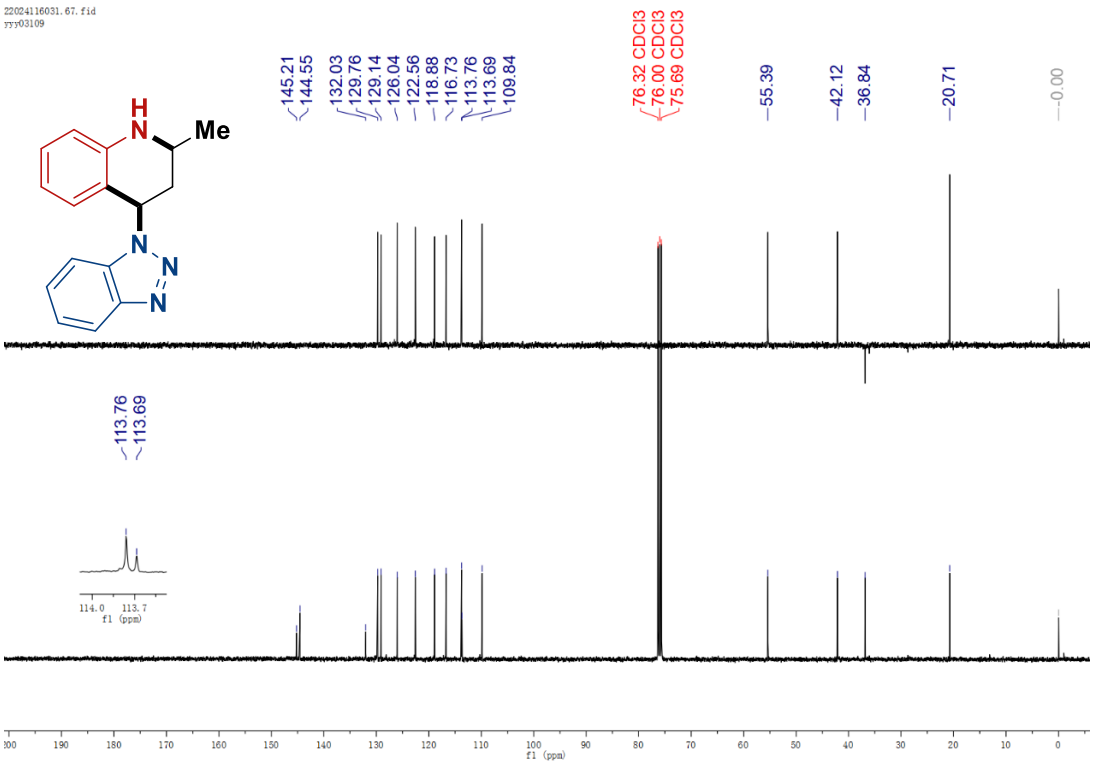
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 102**



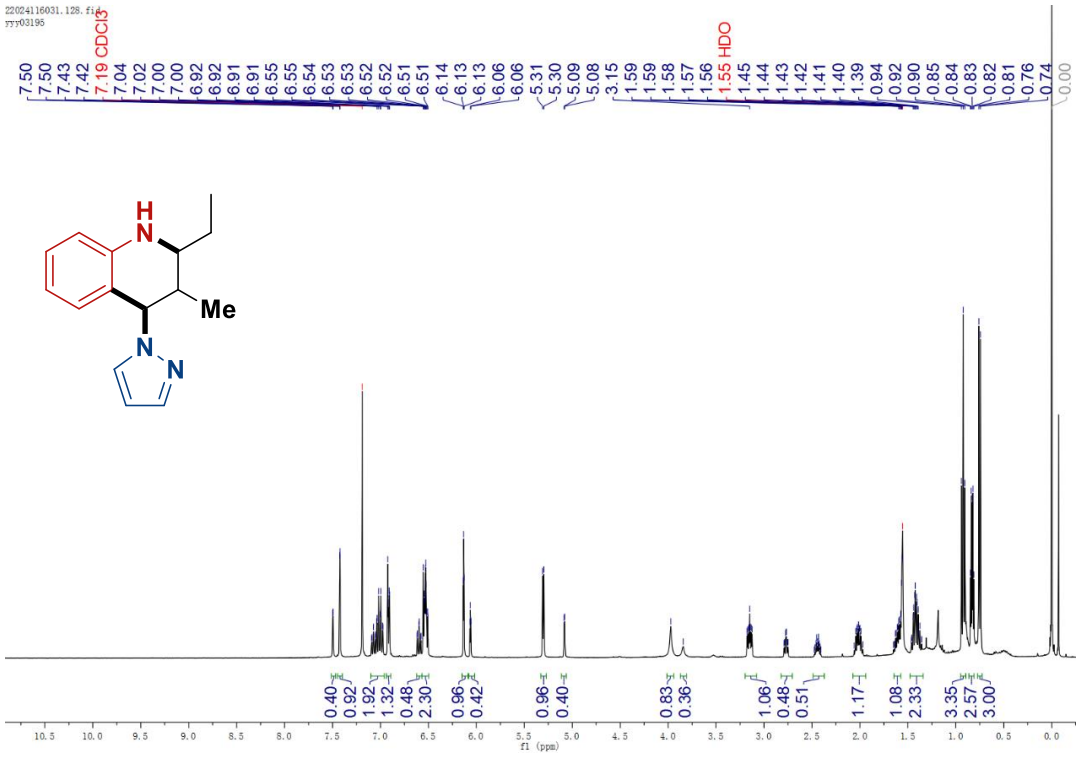
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 102**



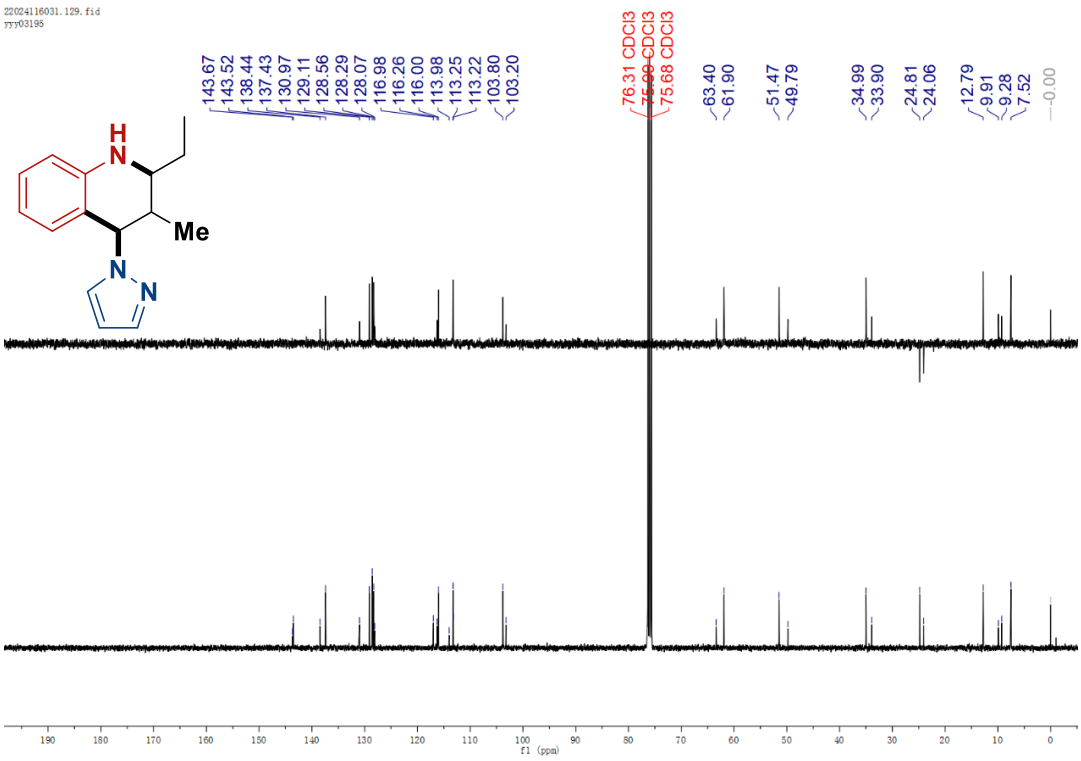
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 103**



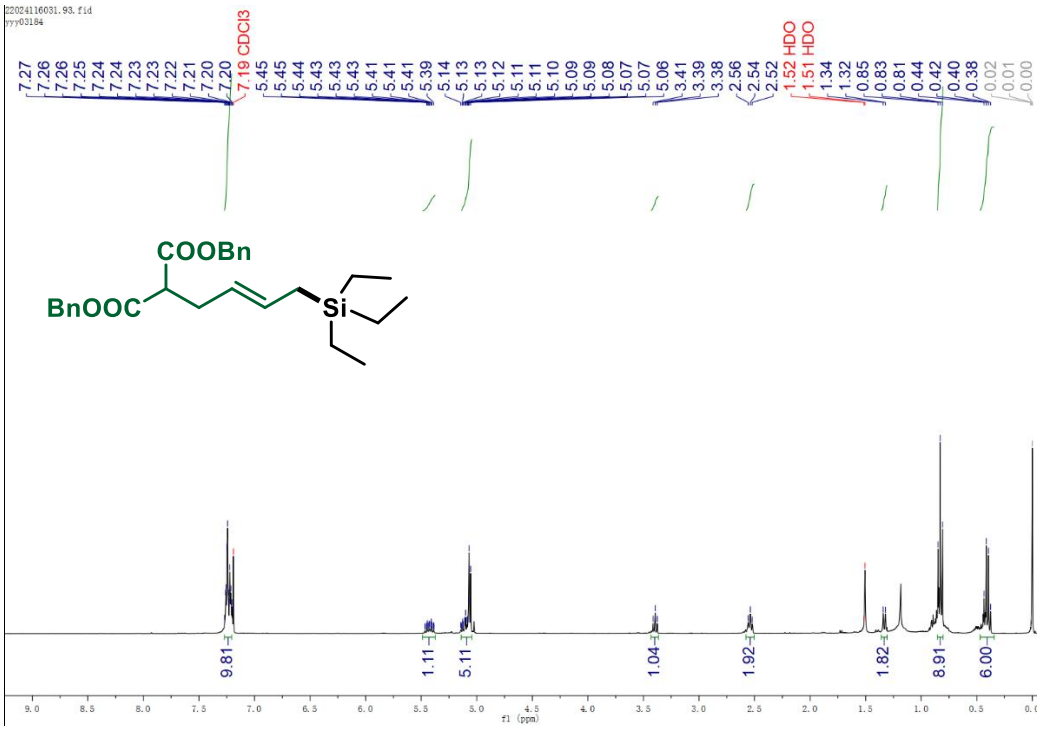
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 103**



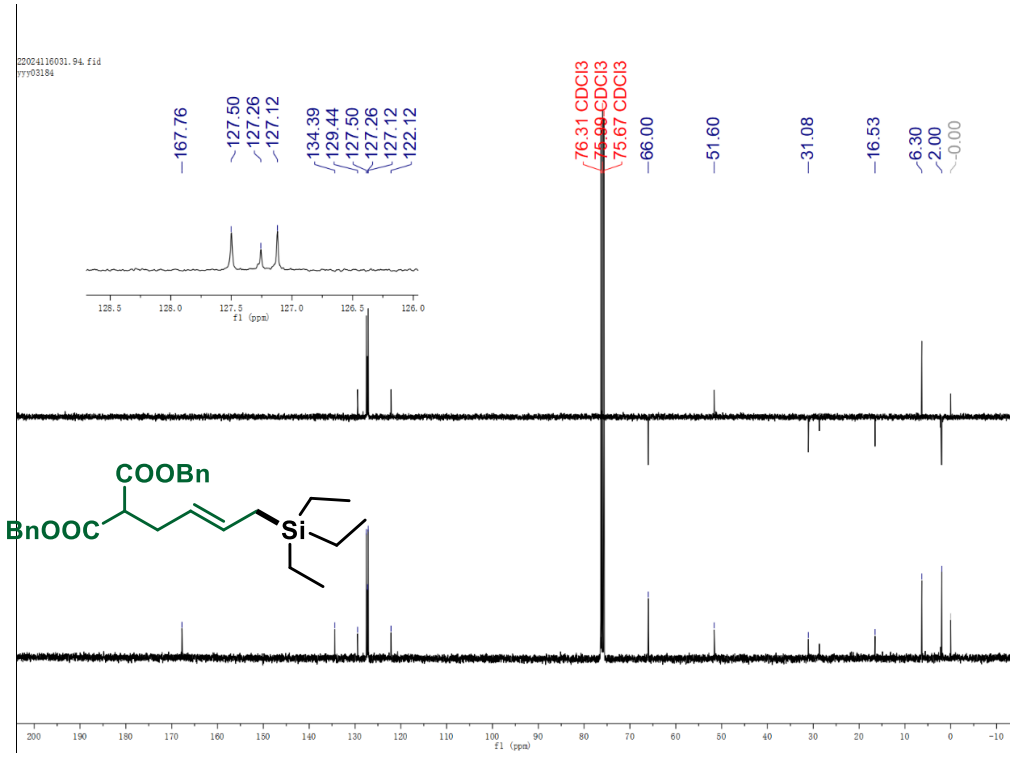
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 104**



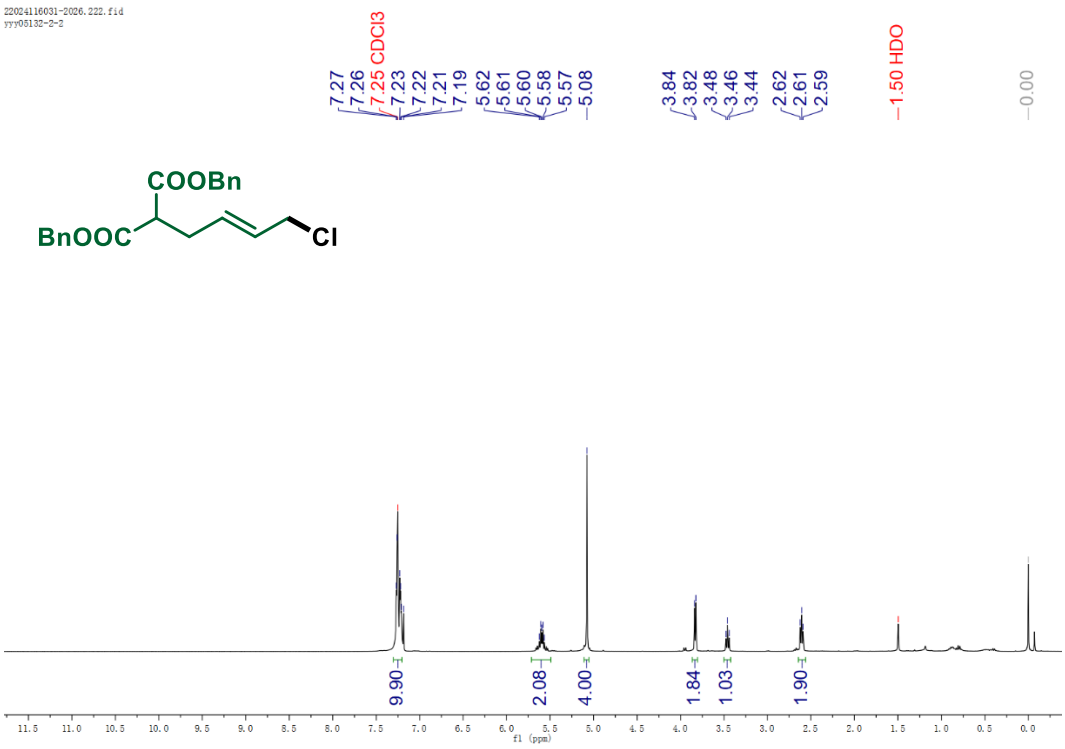
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 104**



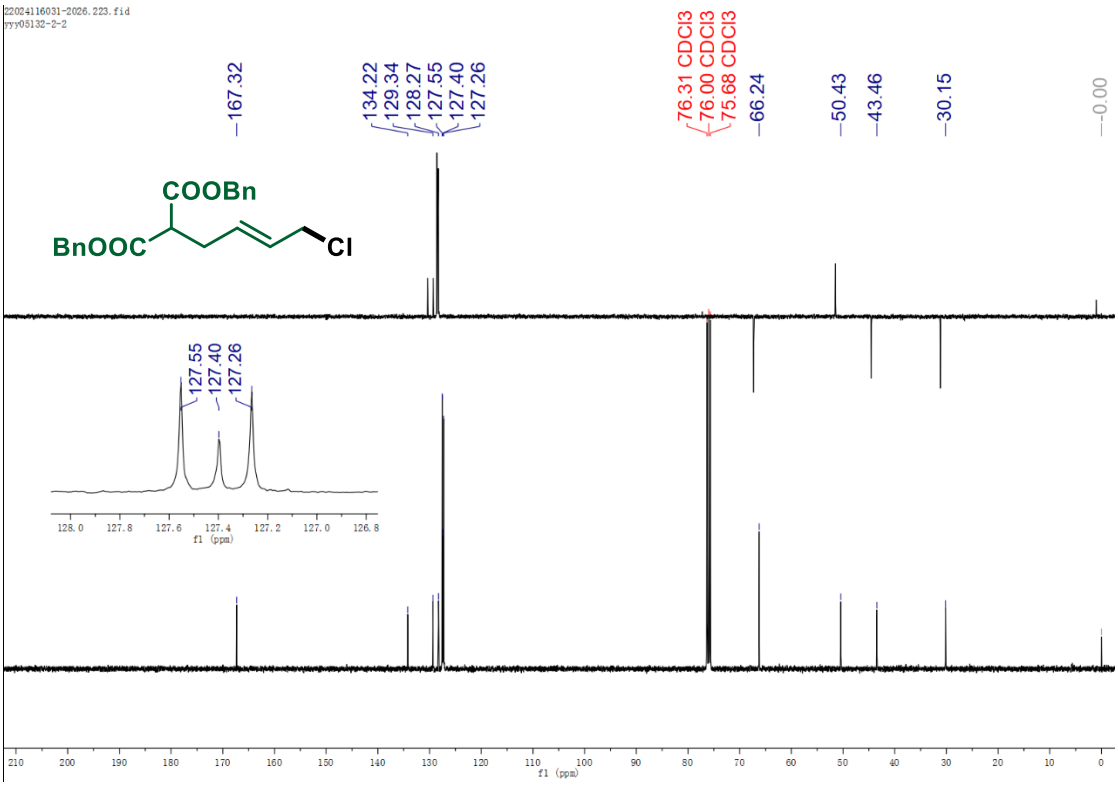
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 106**



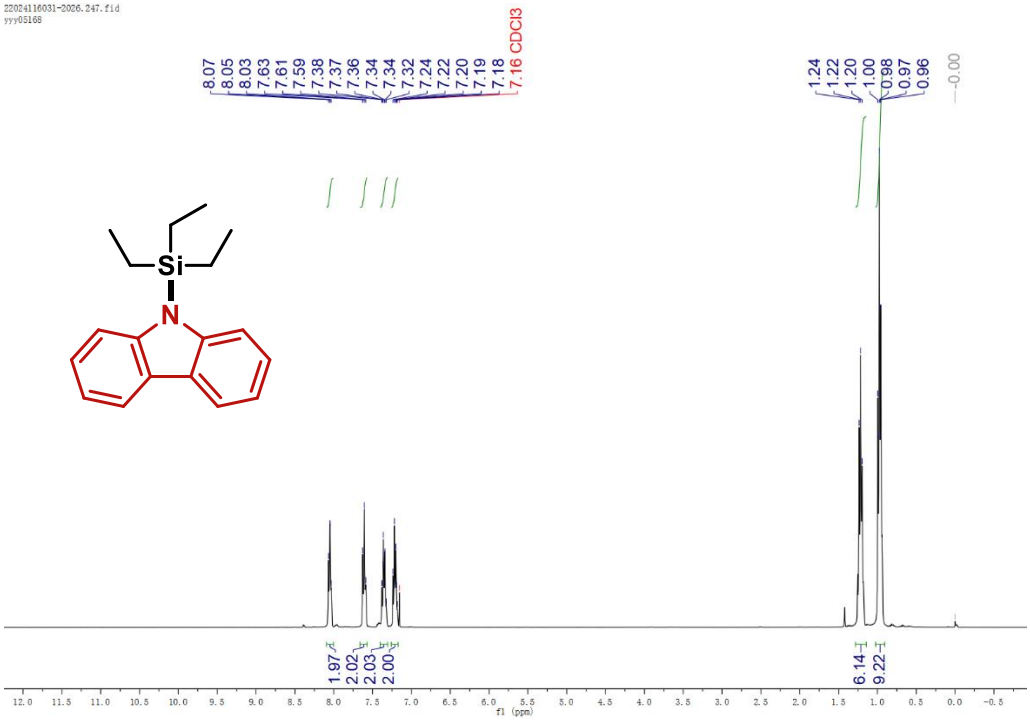
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 106**



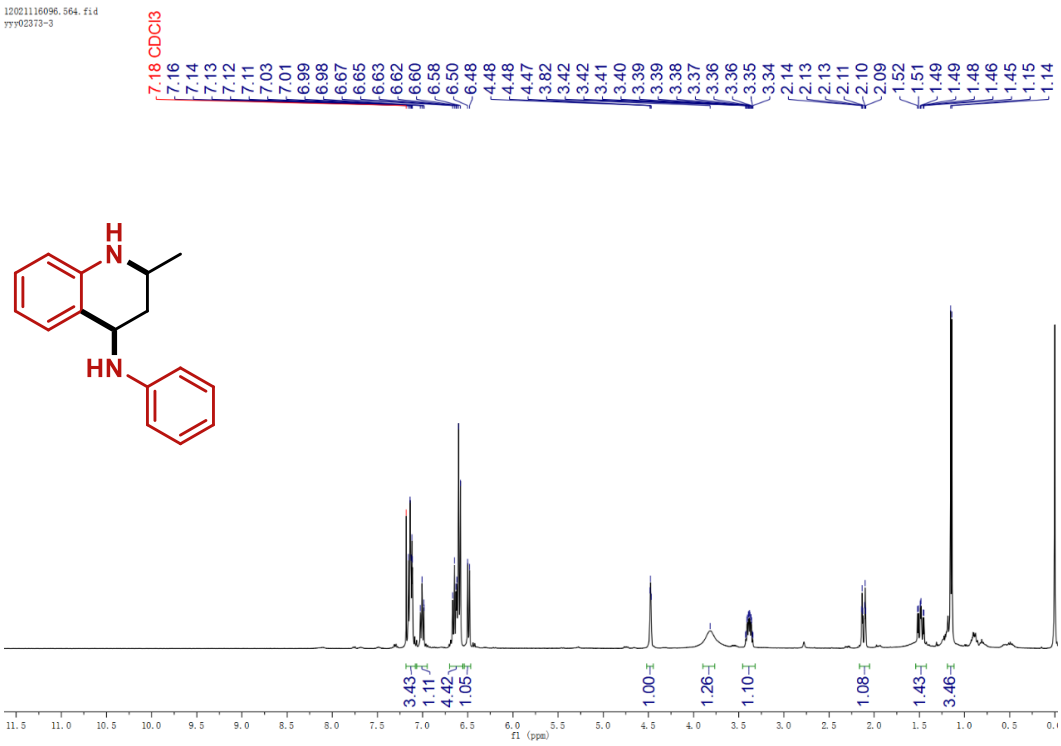
[1]H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 107**



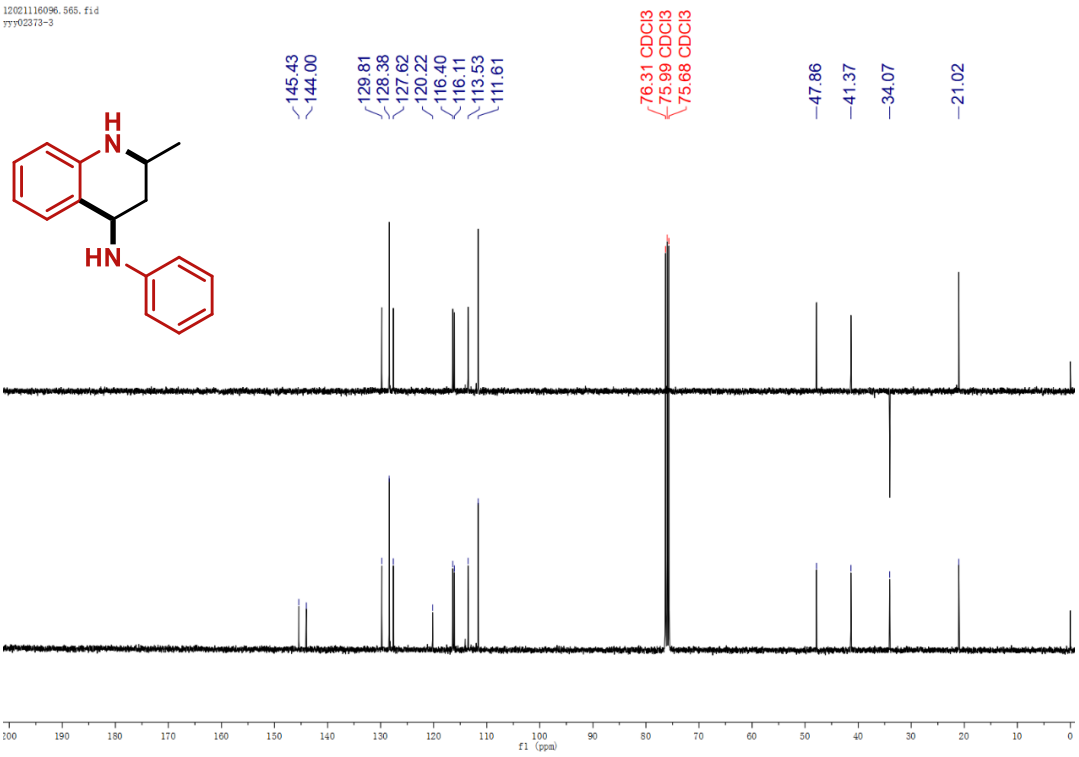
[13]C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 107**



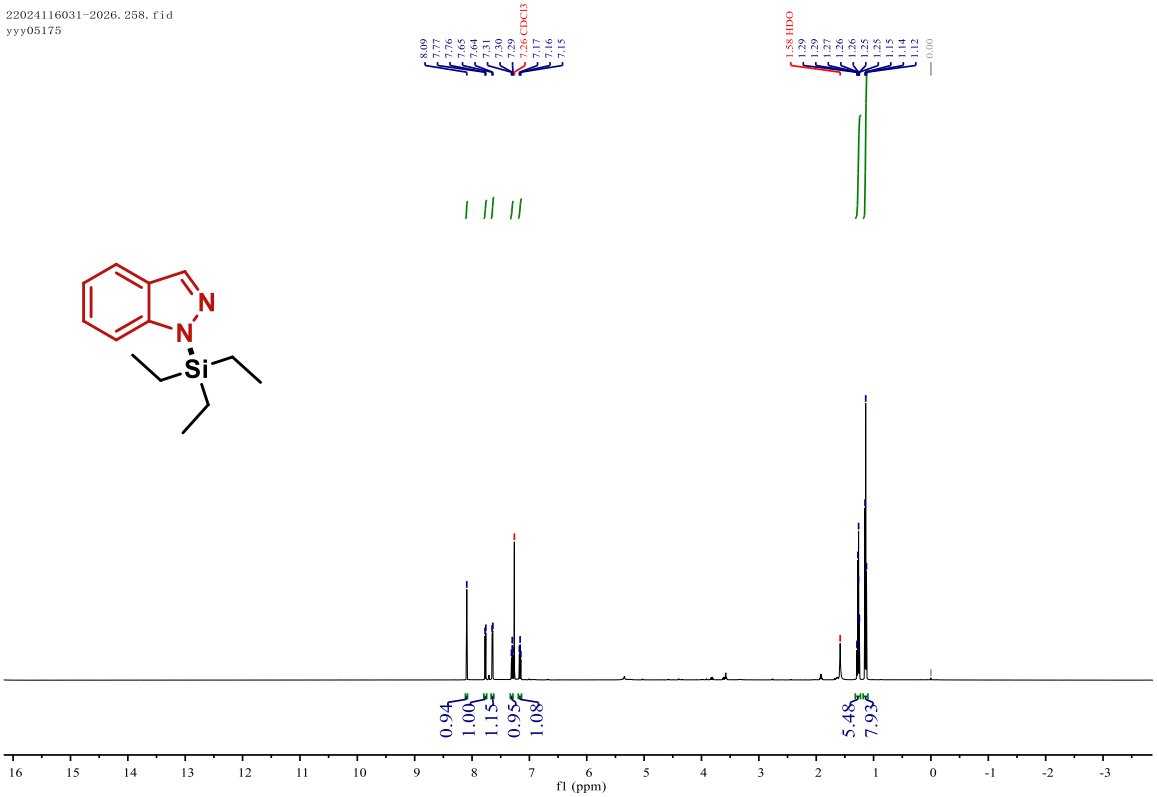
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 108**



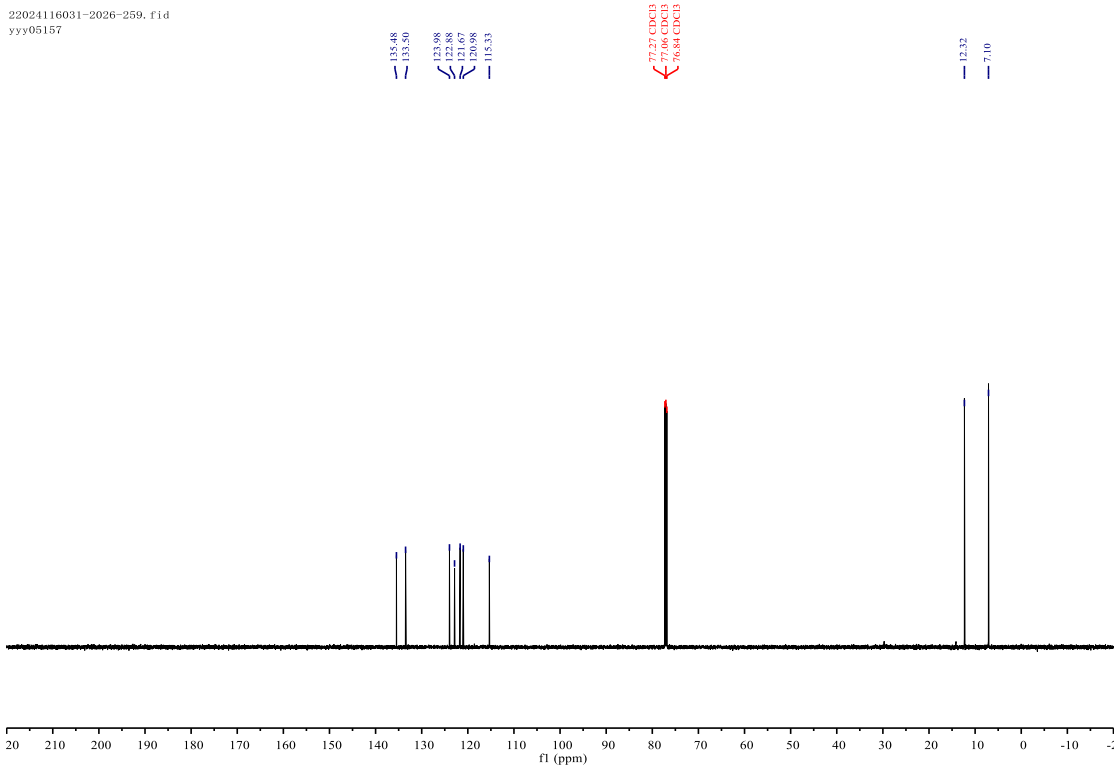
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 109**



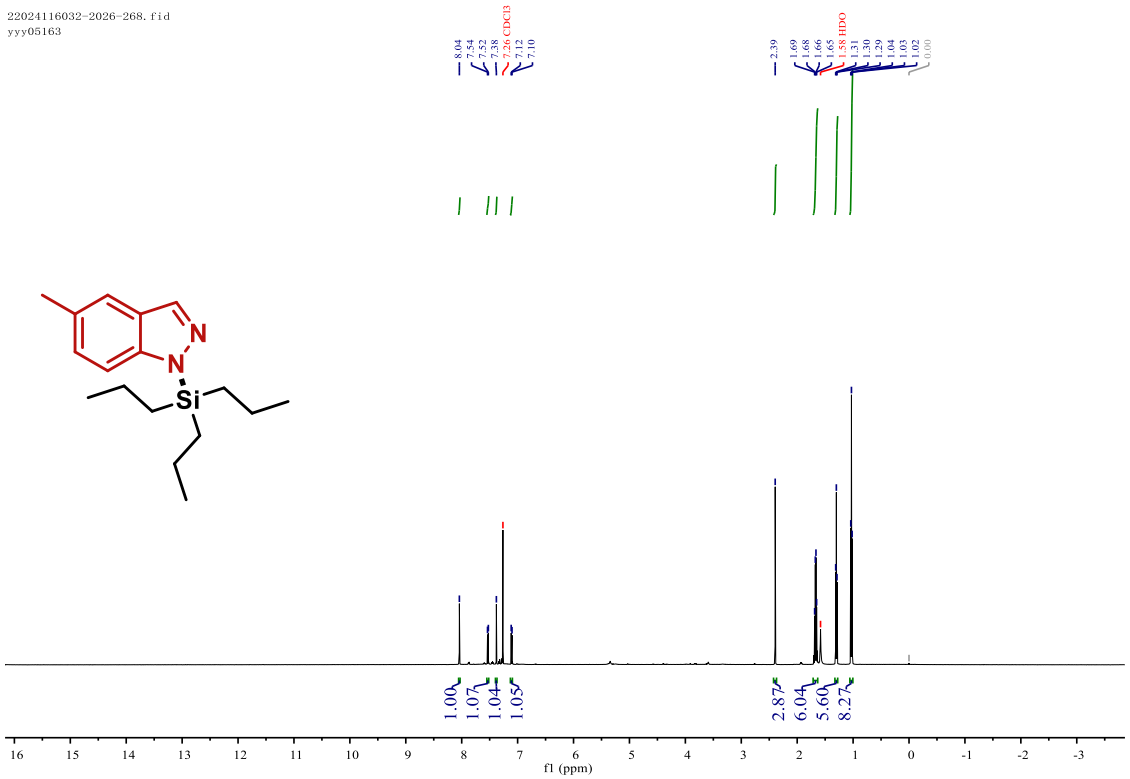
^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 109**



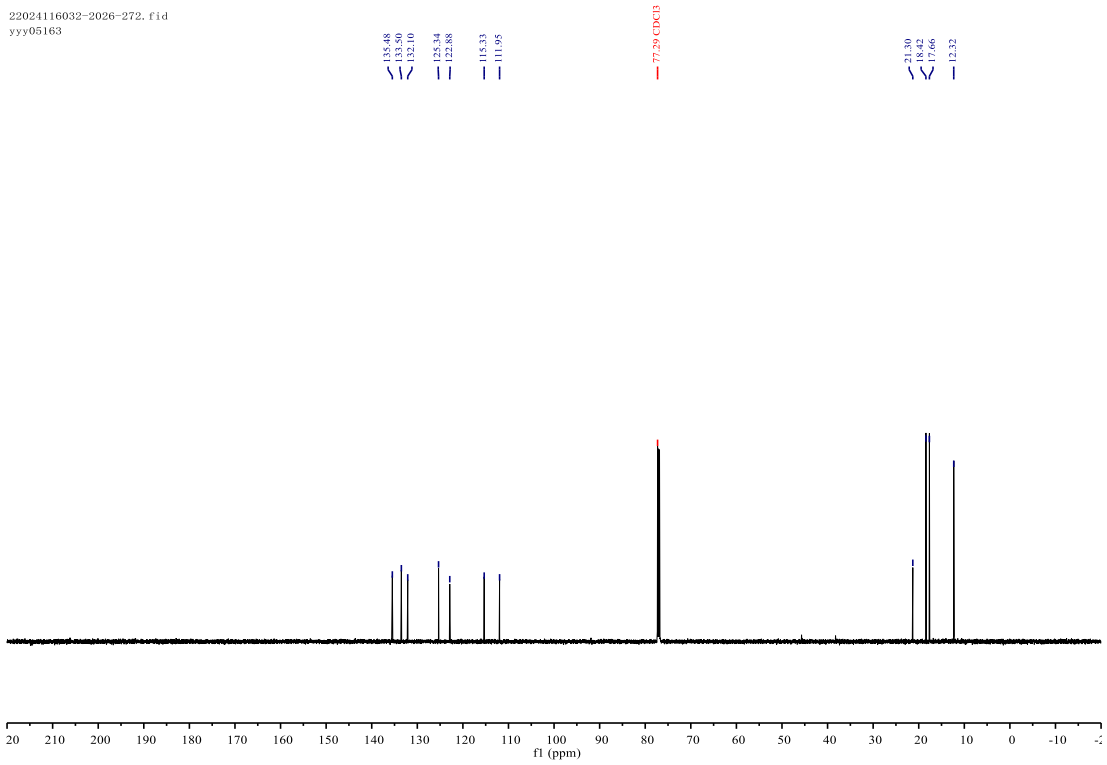
^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 110**



^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 110**



^{1}H-NMR (400 MHz, Chloroform-*d*) **Spectrum of 111**



^{13}C-NMR (100 MHz, Chloroform-*d*) **Spectrum of 111**

6 References

1. Tajbakhsh, M., Hosseinzadeh, R., Alinezhad, H. & Rezaee, P. Efficient Synthesis of Symmetrical Bisamides from Aldehydes and Amides Catalyzed by Silica-Bonded S-Sulfonic Acid Nanoparticles. *Synth. Commun.* **43**, 2370-2379 (2013).
2. Chen, X. *et al.* Metal-free aerobic oxidative C-N bond cleavage of tertiary amines for the synthesis of N-heterocycles with high atom efficiency. *Org. Biomol. Chem.* **12**, 3802-3807 (2014).
3. Liu, Y., Wei, J. & Che, C.-M. Fe(F20TPP)Cl catalyzed intramolecular C-N bond formation for alkaloid synthesis using aryl azides as nitrogen source. *Chem. Commun.* **46**, 6926-6928 (2010).
4. Sriramoju, V., Kurva, S. & Madabhushi, S. Oxone-mediated annulation of 2-aminobenzamides and 1,2-diaminobenzenes with sec-amines via imine-N-oxides: new syntheses of 2,3-dihydroquinazolin-4(1H)-ones and 1H-benzimidazoles. *New J. Chem.* **42**, 3188-3191 (2018).
5. Das, S. *et al.* The Remarkable Cooperative Effect of a Bronsted-Acidic Ionic Liquid in the Cyclization of 2-Aminobenzamides with Ketones. *Eur. J. Org. Chem.* **2017**, 4955-4962 (2017).
6. Norouzi, M., Ghorbani-Choghamarani, A. & Nikoorazm, M. Heterogeneous Cu(II)/L-His@Fe_3O_4 nanocatalyst: a novel, efficient and magnetically-recoverable catalyst for organic transformations in green solvents. *RSC Adv.* **6**, 92387-92401 (2016).
7. Ascic, E. *et al.* Synthesis of Oxacyclic Scaffolds via Dual Ruthenium Hydride/Bronsted Acid-Catalyzed Isomerization/Cyclization of Allylic Ethers. *Chem. Eur. J.* **20**, 3297-3300 (2014).
8. Pocock, I. A. *et al.* Direct formation of 4,5-disubstituted carbazoles via regioselective dilithiation. *Chem. Commun.* **57**, 7252-7255 (2021).
9. Shao, T. *et al.* Sequential Photoredox Catalysis for Cascade Aerobic Decarboxylative Povarov and Oxidative Dehydrogenation Reactions of N-Aryl α-Amino Acids. *Adv. Synth. Catal.* **360**, 1754-1760 (2018).