Supporting Information

Versatile, tunable method for $NaNO_2$/HX (Cl or Br)–mediated radical dihalogenation or nitration of olefins

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Content

1. Reagents

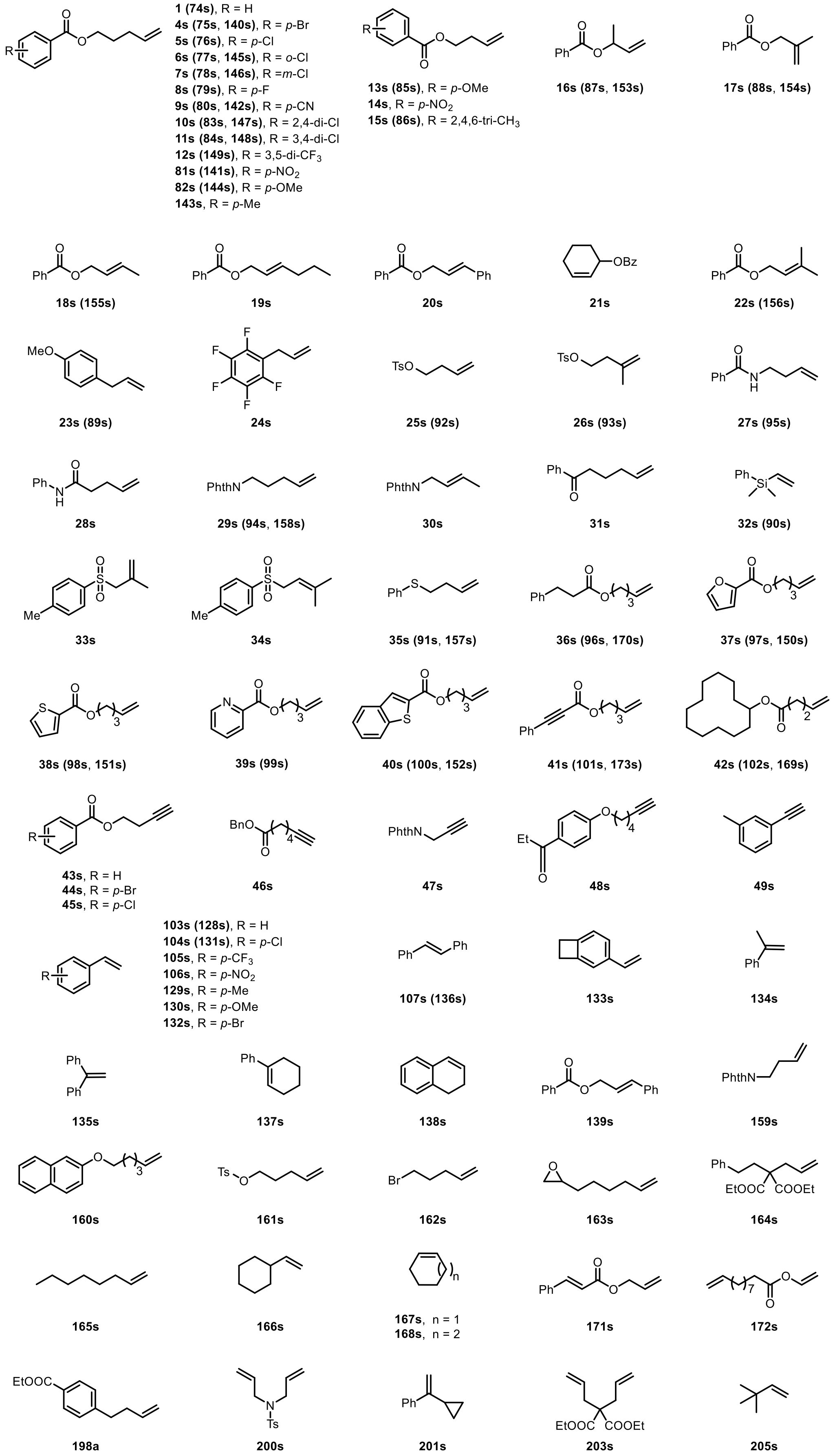
All commercial materials were used as received unless otherwise noted. Superdry solvents and deuterated solvents were purchased from *J&K* Chemical. Starting materials were synthesized according to reported procedures. Aqueous HCl (37% in water, GENERAL-REAGENT Titan), aqueous HBr (40% in water, GENERAL-REAGENT Titan), and $NaNO_2$ (99.99%, Adamas-beta) were used in the chloridation, dibromination and nitration of olefins. TLC were performed on silica gel Huanghai HSGF254 plates and visualization of the developed chromatogram was performed by fluorescence quenching (λ_{max} = 254 nm). Flash chromatography was performed using silica gel (200-300 mesh) purchased from Qingdao Haiyang Chemical Co., China.

2. Instruments

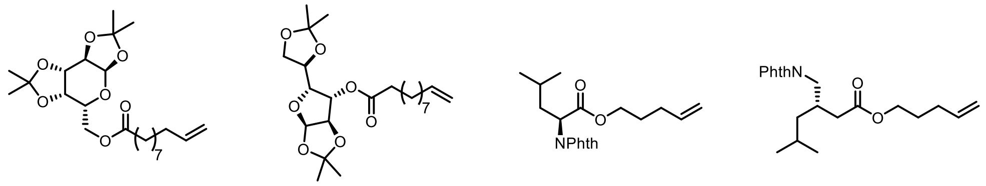
NMR spectra were recorded on Bruker AVANCE AV 500 instruments and all NMR experiments were reported in units, parts per million (ppm), using residual solvent peaks as internal reference. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, td = triplet of doublets, br = broad singlet, m = multiplet. High resolution ESI mass experiments were operated on a Waters LCT Premier instrument. All reactions were carried out in a 4 mL glass vial (Thermo SCIENTIFIC National B7999-2, made from superior quality 33 expansion borosilicate clear glass), sealed with a PTEF cap on bench top if necessay.

Lights: PHILIPS TORNADO 24W CFL, Cnlight 220V/24W UV (254nm), Cnlight 220V/24W UV (365nm), Cnlight LED lights 24 W (red LED, yellow LED, green LED, blue LED, purple LED, white LED) were used in the screening conditions of dichlorination and dibromination of olefins. Cnlight blue LED 24 W was used in the dichlorination and dibromination of olefins.

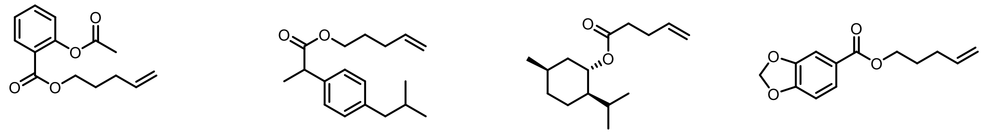
3. Synthesis of substrates



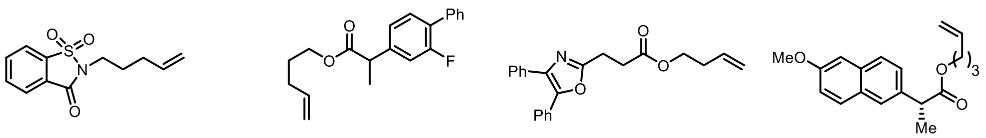
Scheme S1. Alkenes and alkynes substrates used in this study



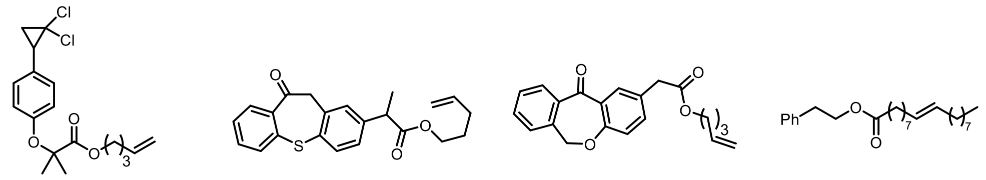
D-Galactopyranose derivative **50s (108s, 183s)** | D-Glucofuranose derivative **51s (109s, 182s)** | L-Leucine derivative **52s (110s, 184s)** | Pregabalin derivative **53s (111s, 194s)**



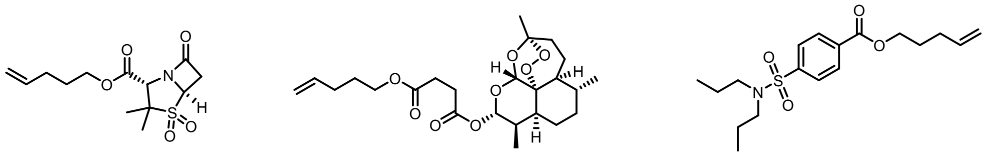
Aspirin derivative **54s (112s, 186s)** | Ibuprofen derivative **55s (113s, 187s)** | Isomenthol derivative **56s** | Piperonylic acid derivative **57s (115s, 190s)**



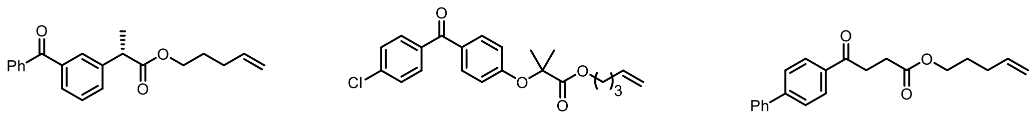
Saccharin derivative **58s (114s)** | Fluorobiprofen derivative **59s (117s)** | Oxaprozin derivative **60s (118s)** | Naproxen derivative **61s (191s)**



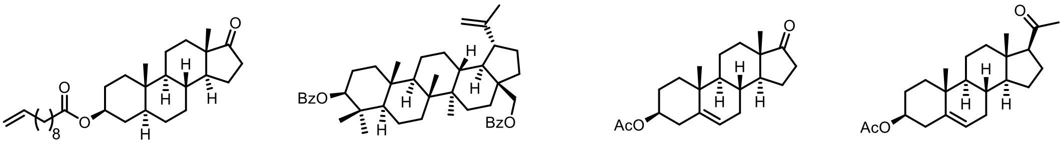
Ciprofibrate derivative **62s (116s, 185s)** | Zaltoprofen derivative **63s (196s)** | Isoxepac derivative **64s (119s, 195s)** | Oleic acid derivative **65s (121s)**



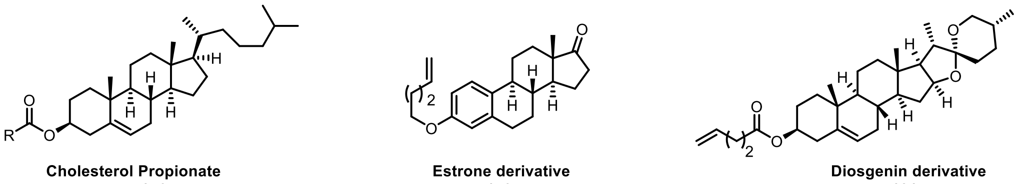
Salbactam acid derivative **66s (120s, 188s)** | Artesunate derivative **67s (126s, 197s)** | Probenecid derivative **68s (122s, 189s)**



Ketoprofen derivative **69s (123s, 193s)** | Fenofibric acid derivative **70s (124s, 192s)** | Fenbufen derivative **71s (125s)**



Epiandrosterone derivative **72s (127s, 180s)** | Betulin derivative **73s (178s)** | Dehydroepiandrosterone **174s** | Pregnenolone **175s**

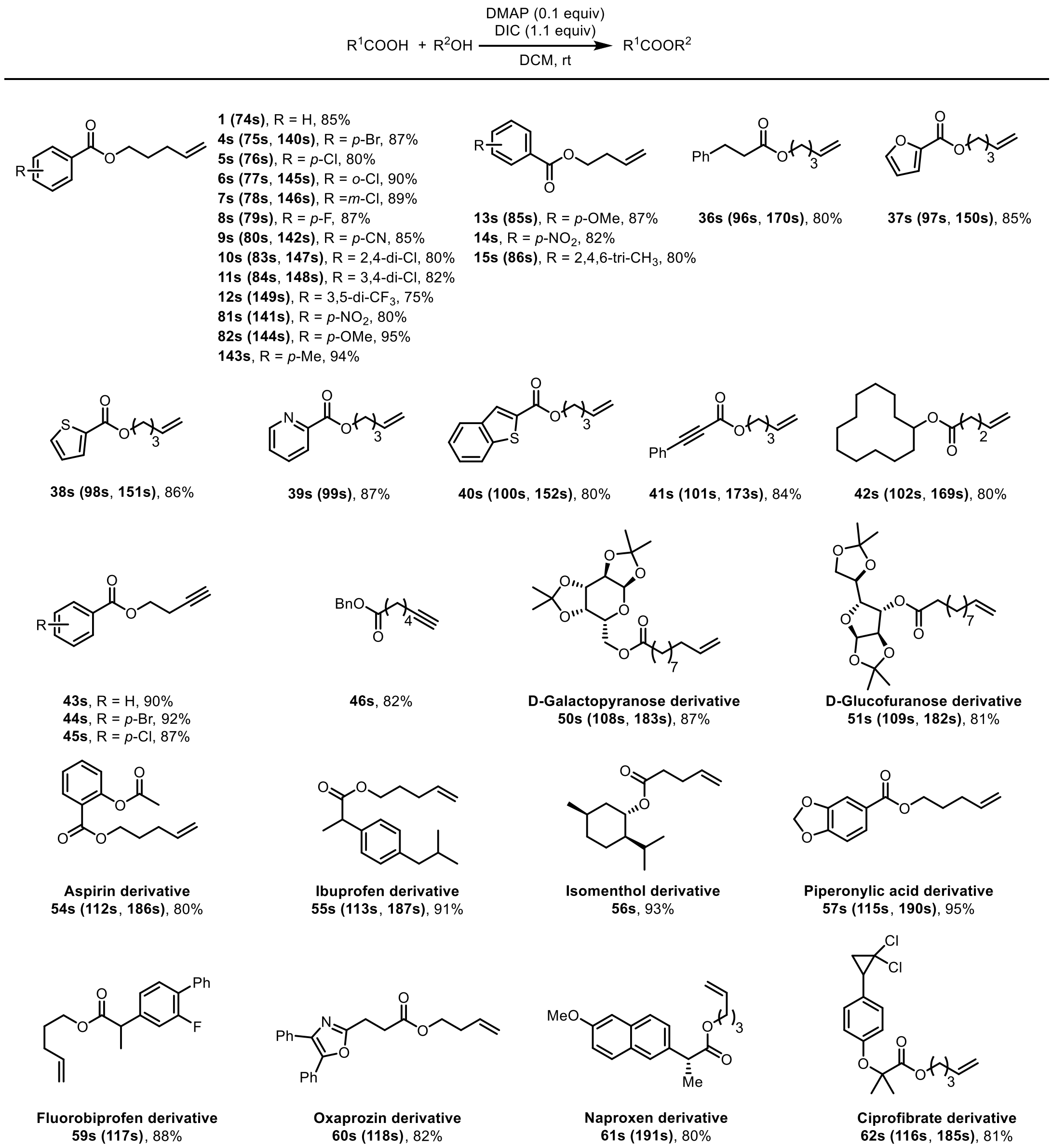


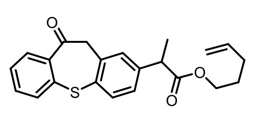
Cholesterol Propionate R = Et, **176s**; R = Ph, **177s** | Estrone derivative **179s** | Diosgenin derivative **181s**

Scheme S2. Natural products and drug derivatives substrates used in this study

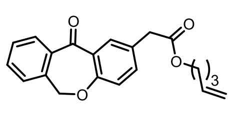
Compounds **23s**, **24s**, **32s** , **49s, 103s to 107s, 129s, 130s, 132s to 135s, 137s, 138s, 162s, 163s, 165s to 168s, 171s, 172s, 198a, 203s, 205s** were commercial available and used as received. Other compounds for this study were known compounds and were synthesized following the reported procedures.

3.1 Synthesis of compounds 1, 4s to 15s, 36s to 46s, 50s, 51s, 54s to 57s, 59s to 72s, 81s, 82s, 143s, 174s to 177s, 181s

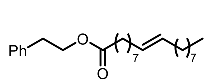




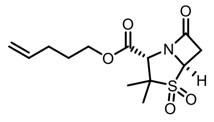
Zaltoprofen derivative
63s (196s), 80%



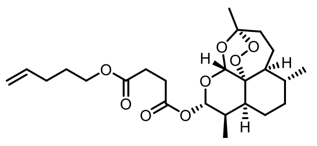
Isoxepac derivative
64s (119s, 195s), 87%



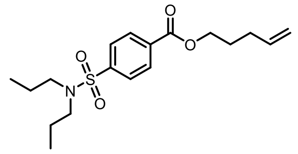
Oleic acid derivative
65s (121s), 85%



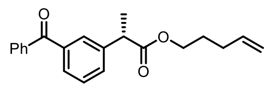
Salbactam acid derivative
66s (120s, 188s), 81%



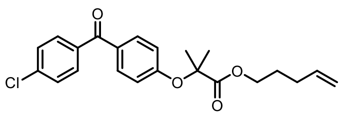
Artesunate derivative
67s (126s, 197s), 78%



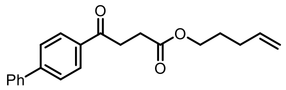
Probenecid derivative
68s (122s, 189s), 86%



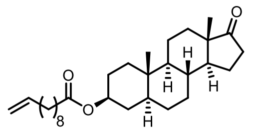
Ketoprofen derivative
69s (123s, 193s), 88%



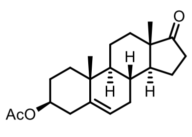
Fenofibric acid derivative
70s (124s, 192s), 80%



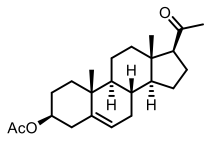
Fenbufen derivative
71s (125s), 81%



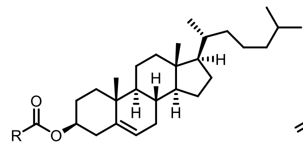
Epiandrosterone derivative
72s (127s, 180s), 78%



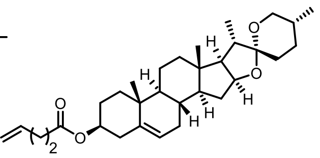
Dehydroepiandrosterone
174s, 80%



Pregnenolone
175s, 85%



Cholesterol Propionate
R = Et, **176s**, 82%
R = Ph, **177s**, 84%

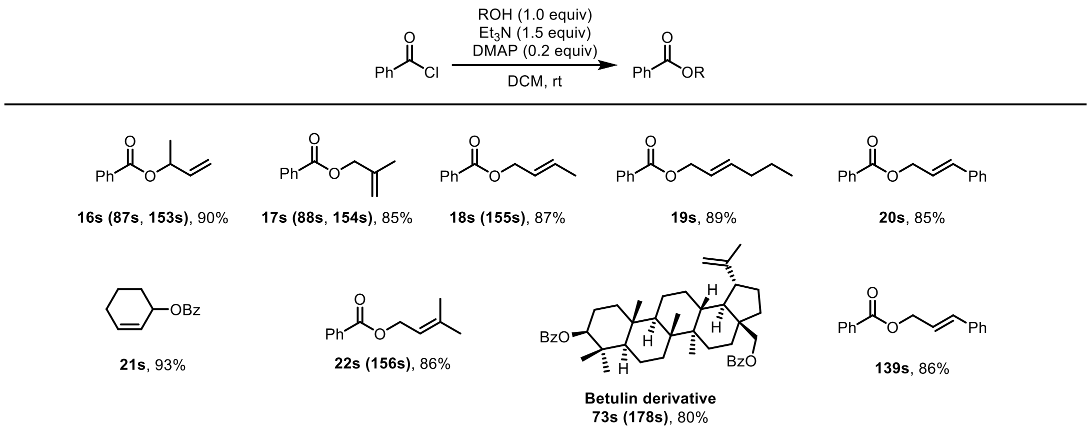


Diosgenin derivative
181s, 80%

Scheme S3. Synthesis of compounds 1, 4s to 15s, 36s to 46s, 50s, 51s, 54s to 57s, 59s to 72s, 81s, 82s, 143s, 174s to 177s, 181s

To a solution of acid (10.0 mmol, 1.0 equiv) in DCM (50.0 mL) was added *N, N'*-diisopropylcarbodiimide (DIC) (11.0 mmol, 1.1 equiv), 4-dimethylaminopyridine (DMAP) (1.0 mmol, 0.1 equiv) and alcohol (10.0 mmol, 1.0 equiv). Stir the reaction mixture for 24 h. The reaction mixture was poured into H_2O (75.0 mL) and extracted with CH_2Cl_2 (3 x 50 mL). The combined organic phase was washed with 100.0 mL of aq. KOH (0.2 M) and water. The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography to afford compounds **1, 4s to 15s, 36s to 46s, 50s, 51s, 54s to 57s, 59s to 72s, 81s, 82s, 143s, 174s to 177s, 181s**.[1]

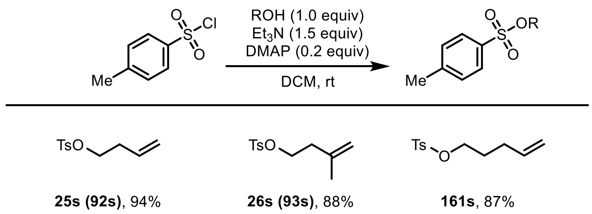
3.2 Synthesis of compounds 16s to 22s, 73s, 139s



Scheme S4. Synthesis of compounds 16s to 22s, 73s, 139s

To a solution of alcohol (10.0 mmol, 1.0 equiv), 4-dimethylaminopyridine (DMAP) (2.0 mmol, 0.2 equiv) and Et_3N (15.0 mmol, 1.5 equiv) in DCM (50.0 mL) was added benzoyl chloride (12.0 mmol, 1.2 equiv) at 0 °C. Stir the reaction mixture for 6 h. The reaction mixture was poured into H_2O (75.0 mL) and extracted with CH_2Cl_2 (3 x 50 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (eluted with Petroleum ether/EtOAc (v/v 100:1)) to afford compounds **16s to 22s, 73s, 139s**.[2,3]

3.3 Synthesis of compounds 25s, 26s, 161s

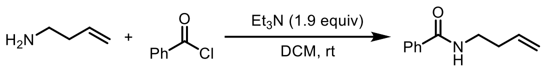


Scheme S5. Synthesis of compounds 25s, 26s, 161s

To a solution of alcohol (10.0 mmol, 1.0 equiv), 4-dimethylaminopyridine (DMAP) (2.0 mmol, 0.2 equiv) and Et_3N (15.0 mmol, 1.5 equiv) in DCM (50.0 mL) was added *p*-toluenesulfonyl chloride (12.0 mmol, 1.2 equiv) at 0 °C. Stir the reaction mixture for 6 h. The reaction mixture was poured into H_2O (75.0 mL) and extracted with CH_2Cl_2

(3 x 50 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (eluted with Petroleum ether/EtOAc (v/v 20:1)) to afford compounds **25s, 26s, 161s**.[4]

3.4 Synthesis of compound 27s

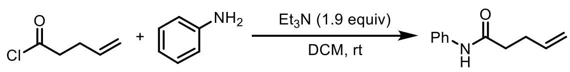


27s (95s), 80%

Scheme S6. Synthesis of compound 27s

To a solution of but-3-en-1-amine (0.9 mmol, 0.9 equiv) and Et_3N (1.9 mmol, 1.9 equiv) in DCM (5.0 mL) was added benzoyl chloride (1.0 mmol, 1.0 equiv) at 0 °C. Stir the reaction mixture for 24 h. The reaction mixture was poured into H_2O (10.0 mL) and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phase was washed with 10.0 mL of aq. KOH (0.2 M) and water. The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (eluted with hexane/acetone (v/v 5:1)) to afford compound **27s** in 80% yield (0.126 g).[5]

3.5 Synthesis of compound 28s

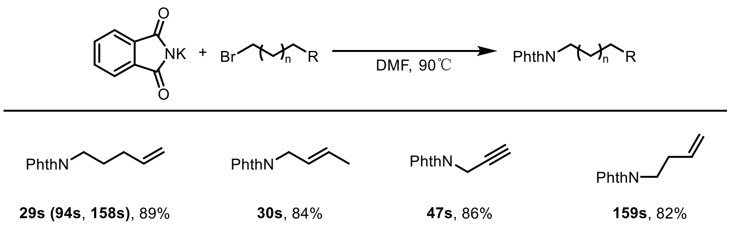


28s, 74%

Scheme S7. Synthesis of compound **28s**

To a solution of aniline (0.9 mmol, 0.9 equiv) and Et_3N (1.9 mmol, 1.9 equiv) in DCM (5.0 mL) was added 4-pentenoyl chloride (1.0 mmol, 1.0 equiv) at 0 °C. Stir the reaction mixture for 24 h. The reaction mixture was poured into H_2O (10.0 mL) and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phase was washed with 10.0 mL of aq. KOH (0.2 M) and water. The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (eluted with hexane/acetone (v/v 5:1)) to afford compound **28s** in 74% yield (0.116 g). [5]

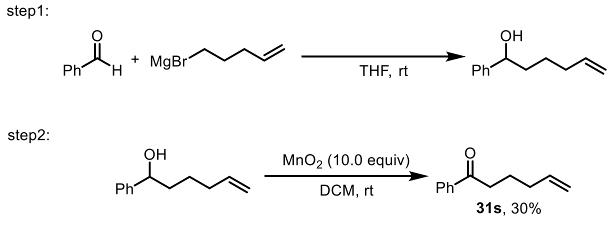
3.6 Synthesis of compounds 29s, 30s, 47s, 159s



Scheme S8. Synthesis of compounds **29s, 30s, 47s, 159s**

To a solution of alkyl bromide (19.6 mmol, 1.0 equiv) in DMF (23.0 mL) was added potassium phthalimide (21.6 mmol, 1.1 equiv). The reaction mixture was heated to 90 °C for 16 h. After been cooled to room temperature, the reaction mixture was poured into H_2O (100.0 mL) and extracted with CH_2Cl_2 (3 x 50 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (eluted with Petroleum ether/EtOAc (v/v 5:1)) to afford compounds **29s, 30s, 47s, 159s**.[6]

3.7 Synthesis of compound 31s

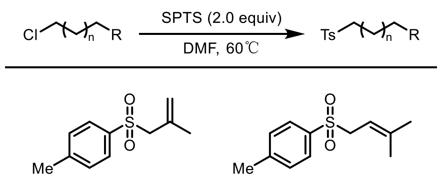


Scheme S9. Synthesis of compound **31s**

To a solution of benzaldehyde (10.0 mmol, 1.0 equiv) in THF (30.0 mL) was added at 0 ℃ pent-4-en-1-ylmagnesium bromide (0.5 M in THF, 15.0 mmol, 1.5 equiv). Stir the reaction mixture for 2 h, saturated ammonium chloride (25.0 mL) was added at 0 ℃ and the reaction was extracted with EtOAc (3 x 25 mL). The organic phase was washed with brine (1 x 40 mL), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (eluted with Petroleum ether/EtOAc (v/v 50:1)) to afford α-4-penten-1-yl Benzenemethanol in 55% yield (0.98 g).

To a solution of α-4-penten-1-yl Benzenemethanol (5.6 mmol, 1.0 equiv) in DCM (120.0 mL) was added MnO_2 (56.0 mmol, 10.0 equiv). The reaction was allowed to stir overnight at room temperature. The resulting slurry was filtered through celite, and the celite was washed with Et_2O. Solvent was removed in vacuo to afford compound **31s** in 30% yield (0.29 g).[7]

3.8 Synthesis of compounds 33s and 34s



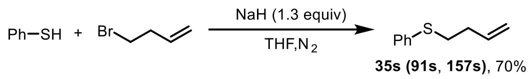
33s, 78% **34s**, 74%

Scheme S10. Synthesis of compounds **33s** and **34s**

To a solution of chlorinated hydrocarbons (28.0 mmol, 1.0 equiv) in DMF (40.0 mL) was added sodium *p*-toluene sulfinate (SPTS) (56.0 mmol, 2.0 equiv). The reaction mixture was heated to 60 °C for 3 h. After been cooled to room temperature, the reaction mixture was poured into H_2O (75.0 mL) and extracted with CH_2Cl_2 (3 x 50 mL). The combined organic phase was washed with 100.0 mL of aq. KOH (0.2 M) and water. The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo.

The resulting residue was purified by silica gel column chromatography (eluted with Petroleum ether/EtOAc (v/v 20:1)) to afford compounds **33s** and **34s**.[8]

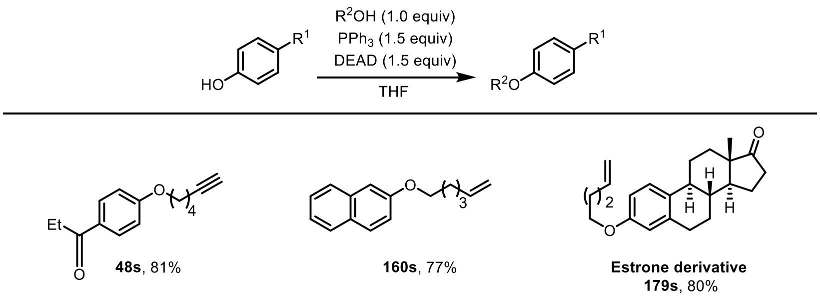
3.9 Synthesis of compound 35s



Scheme S11. Synthesis of compound 35s

To a solution of benzenethiol (15.0 mmol, 1.0 equiv) in THF (70.0 mL), NaH (19.5 mmol, 1.3 equiv) was added portionwise at 0 °C under N_2. The resulting mixture was stirred for 15 minutes at 0 °C, followed by addition of 4-bromo-1-butene (18.0 mmol, 1.2 equiv). Stir the reaction mixture for 24 h at room temperature. The reaction was quenched by slow addition of MeOH (25.0 mL) and then H_2O (25.0 mL). The reaction was extracted with EtOAc (3 x 25 mL). The organic phase was washed with brine (1 x 40 mL), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (eluted with Petroleum ether/EtOAc (v/v 50:1)) to afford compound **35s** in 70% yield (1.72 g).[9]

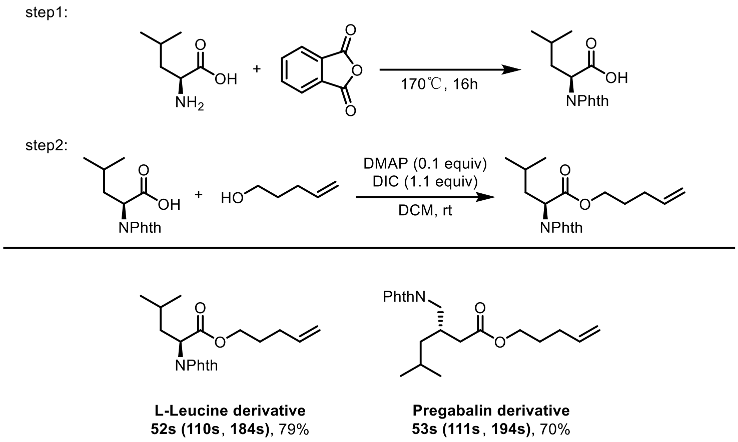
3.10 Synthesis of compounds 48s, 160s, 179s



Scheme S12. Synthesis of compounds 48s, 160s, 179s

To a solution of phenols (28.6 mmol, 1.2 equiv), alcohol (23.8 mmol, 1.0 equiv) in THF(100.0 mL) was added PPh_3(35.7 mmol, 1.5 equiv) at room temperature. Then diethyl azodicarboxylate (DEAD) (35.7 mmol, 1.5 equiv) was added slowly at 0 °C. Stir the reaction mixture for 24 h at room temperature. The reaction mixture was poured into H_2O (100.0 mL) and extracted with EtOAc (3 x 50 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (eluted with Petroleum ether/EtOAc (v/v 100:1)) to afford compounds **48s, 160s, 179s**.[10]

3.11 Synthesis of compounds 52s and 53s

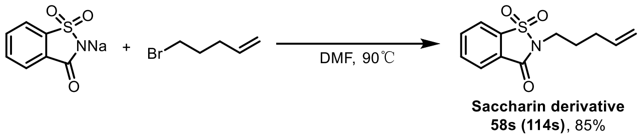


Scheme S13. Synthesis of compounds 52s and 53s

L-Leucine (27.0 mmol, 1.0 equiv) was added to phthalic anhydride (27.0 mmol, 1.0 equiv) at room temperature. The mixture was heated to 170 °C for 6 h. After been cooled to room temperature, the reaction mixture was poured into H_2O (50.0 mL) and extracted with CH_2Cl_2 (3 x 50 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo to afford corresponding acid. To a solution of acid (10.0 mmol, 1.0 equiv) in DCM (50.0 mL) was added *N, N'*-diisopropylcarbodiimide (DIC) (11.0 mmol, 1.1 equiv), 4-dimethylaminopyridine (DMAP) (1.0 mmol, 0.1 equiv) and 4-penten-1-ol (10.0 mmol, 1.0 equiv). Stir the reaction mixture for 24 h. The reaction mixture was poured into H_2O (100.0 mL) and extracted with CH_2Cl_2 (3 x 50 mL). The combined organic phase was washed with 100.0 mL of aq. KOH (0.2 M) and water. The organic phase was dried over anhydrous

Na_2SO_4, filtered and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (eluted with Petroleum ether/EtOAc (v/v 10:1)) to afford compound **52s** in 79% yield (2.6 g). According to the same method above can be obtained **53s** in 70% yield (2.50g).[1, 11]

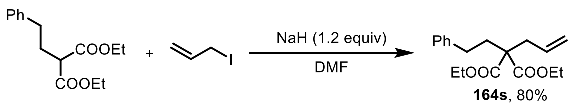
3.12 Synthesis of compound 58s



Scheme S14. Synthesis of compound 58s

To a solution of 5-bromopentene (19.6 mmol, 1.0 equiv) in DMF (23.0 mL) was added sodium saccharine (21.6 mmol, 1.1 equiv). The reaction mixture was heated to 90 °C for 16 h. After been cooled to room temperature, the reaction mixture was poured into H_2O (100.0 mL) and extracted with CH_2Cl_2 (3 x 50 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (eluted with Petroleum ether/EtOAc (v/v 5:1)) to afford compound **58s** in 85% yield (4.20 g).[6]

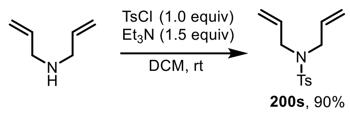
3.13 Synthesis of compound 164s



Scheme S15. Synthesis of compound 164s

To a solution of 1,3-diethyl 2-(2 phenylethyl)propanedioate (5.0 mmol, 1.0 equiv) in DMF (5.0 mL), NaH (6.0 mmol, 1.2 equiv) was added portionwise at 0 °C. The resulting mixture was stirred for 30 minutes at 0 °C, followed by addition of 3-iodo-1-propene (7.5mmol, 1.5 equiv). The mixture was warmed to 22 °C and allowed to stir at that temperature for 3 h. The reaction was quenched with saturated aq. NH_4Cl (40.0 mL) and extracted with EtOAc (3 × 40 mL). The organic phase was washed with brine (1 x 40 mL), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (eluted with hexane /EtOAc (v/v 20:1)) to afford compound **164s** in 80% yield (1.21g).[12]

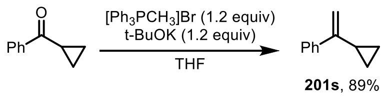
3.14 Synthesis of compound 200s



Scheme S16. Synthesis of compound 200s

To a solution of diallylamine (10.0 mmol, 1.0 equiv) and Et_3N (15.0 mmol, 1.5 equiv) in DCM (50.0 mL) was added *p*-toluenesulfonyl chloride (10.0 mmol, 1.0 equiv) at 0 °C. Stir the reaction mixture for 6 h. The reaction mixture was poured into H_2O (100.0 mL) and extracted with CH_2Cl_2 (3 x 50 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (eluted with Petroleum ether/EtOAc (v/v 5:1)) to afford compound **200s** in 90% yield (0.90g).[13]

3.15 Synthesis of compound 201s

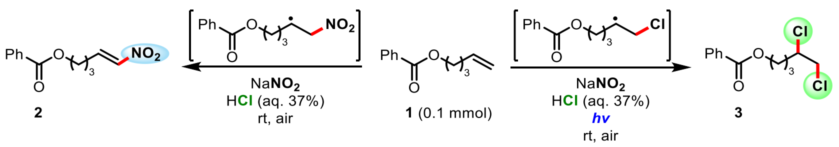


Scheme S17. Synthesis of compound 201s

To a solution of methyltriphenylphosphonium bromide (6.0 mmol, 1.2 equiv) in THF (13.0 mL), *t*-BuOK (6.0 mmol, 1.2 equiv) was added dropwise at 0 °C under N_2. The resulting mixture was stirred for 1 h at 0 °C, followed by addition of cyclopropyl phenyl ketone (5.0 mmol, 1.0 equiv). Stir the reaction mixture for 3 h at room temperature. The reaction mixture was poured into H_2O (100.0 mL) and extracted with EtOAc (3 x 50 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (eluted with Petroleum ether/EtOAc (v/v 100:1)) to afford compound **201s** in 89% yield (0.64 g).[14]

4. Reaction optimization for dichlorination and nitration of olefin 1

All screening reactions were carried out at a 0.1 mmol scale in a 4 mL glass vial (Thermo Scientific, National B7999-2) sealed with PTEF cap and stirred on bench top. A 24 W LED light was positioned 5 cm aside from the reaction vials if necessary.
Olefin 1 (0.1 mmol, 1.0 equiv) and $NaNO_2$ were first dispersed in specific solvent and stirred for 1 min at room temperature. Specified acid was then added and the resulting mixture was vigorously stirred at room temperature (30 ºC) with or without light irradiation for several hours. After removal of the solvent *in vacuo*, the resulting residue was dissolved in 1 mL of $CDCl_3$ along with $Cl_2CHCHCl_2$ (20 μL) as an internal standard for ^{1}H-NMR analysis. The composition of reaction mixture was analyzed based on the olefins hydrogen peak at 7.03 ppm (d, J = 13.4 Hz, 1H) for compound **2**, and chlorinated hydrocarbon α-hydrogen peak 3.67 ppm (dd, J = 11.3, 7.8 Hz, 1H) for compound **3**.



Entry	reagents (equiv), light, time (h)	solvent (mL)	**2** %	**3** %
1	$NaNO_2$ (2.5), HCOOH (3.0), 2 h	DCM (1.0)	31	0
2	$NaNO_2$ (2.5), CH_3COOH (3.0), 2 h	DCM (1.0)	<5	0

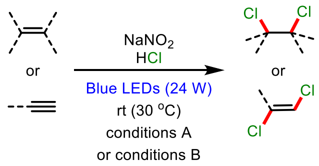
3	$NaNO_2$ (2.5), CF_3COOH (3.0), 2 h	DCM (1.0)	10	0
4	$NaNO_2$ (2.5), H_2SO_4 (3.0), 2 h	DCM (1.0)	<5	0
5	$NaNO_2$ (2.5), HCl (25 *u*L), 2 h	DCM (1.0)	96 (89[b])	<5
6	$NaNO_2$ (2.5), HCl (25 *u*L), 2 h	No solvent	97 (89[b])	<5
7	$NaNO_2$ (1.0), HCl (25 *u*L), 2 h	DCM (1.0)	82	<5
8	$NaNO_2$ (1.0), HCl (40 *u*L), 2 h	DCM (1.0)	43	7
9	$NaNO_2$ (1.0), HCl (50 *u*L), 2 h	DCM (1.0)	32	18
10	$NaNO_2$ (1.0), HCl (50 *u*L), 2 h, in darkness	DCM (1.0)	40	10
11	$NaNO_2$ (1.0), HCl (50 *u*L), Blue LEDs (24 W), 6 h	DCM (1.0)	11 (5[b])	88 (69[b])
12	$NaNO_2$ (1.0), HCl (50 *u*L), Blue LEDs (24 W), 6 h	DCM (0.5)	23	55
13	$NaNO_2$ (1.0), HCl (50 *u*L), Blue LEDs (24 W), 6 h	DCM (1.5)	10	74
14	$NaNO_2$ (1.0), HCl (50 *u*L), Blue LEDs (24 W), 6 h	DCM (2.0)	10	72
15	$NaNO_2$ (1.0), HCl (50 *u*L), Blue LEDs (24 W), 6 h	$CHCl_3$ (1.0)	8	50
16	$NaNO_2$ (1.0), HCl (50 *u*L), Blue LEDs (24 W), 6 h	DCE (1.0)	7	45
17	$NaNO_2$ (1.0), HCl (50 *u*L), Blue LEDs (24 W), 6 h	TCE (1.0)	13	63
18	$NaNO_2$ (1.0), HCl (50 *u*L), Blue LEDs (24 W), 6 h	CH_3CN (1.0)	<5	10
19	$NaNO_2$ (1.0), HCl (50 *u*L), Blue LEDs (24 W), 6 h	Ph-Cl (1.0)	<5	65

20	$NaNO_2$ (1.0), HCl (50 *u*L), Blue LEDs (24 W), 6 h	CH_2Br_2 (1.0)	8	43
21	$NaNO_2$ (1.0), HCl (50 *u*L), Blue LEDs (24 W), 6 h	H_2O (1.0)	<5	<5
22	$NaNO_2$ (1.0), HCl (25 *u*L), Blue LEDs (24 W), 6 h	DCM (1.0)	14	36
23	$NaNO_2$ (1.0), HCl (40 *u*L), Blue LEDs (24 W), 6 h	DCM (1.0)	10	71
24	$NaNO_2$ (0.3), HCl (50 *u*L), Blue LEDs (24 W), 6 h	DCM (1.0)	<5	<5
25	$NaNO_2$ (0.5), HCl (50 *u*L), Blue LEDs (24 W), 6 h	DCM (1.0)	<5	12
26	$NaNO_2$ (0.8), HCl (50 *u*L), Blue LEDs (24 W), 6 h	DCM (1.0)	10	72
27	$NaNO_2$ (1.0), HCl (50 *u*L), White CFL (24 W), 6 h	DCM (1.0)	7	54
28	$NaNO_2$ (1.0), HCl (50 *u*L), UV (365 nm) (24 W), 6 h	DCM (1.0)	8	57
29	$NaNO_2$ (1.0), HCl (50 *u*L), UV (254 nm) (24 W), 6 h	DCM (1.0)	6	50
30	$NaNO_2$ (1.0), HCl (50 *u*L), Green LEDs (24 W), 6 h	DCM (1.0)	8	58
31	$NaNO_2$ (1.0), HCl (50 *u*L), Red LEDs (24 W), 6 h	DCM (1.0)	<5	23
32	HCl (50 *u*L), Blue LEDs (24 W), 6 h	DCM (1.0)	0	0

a) All screening reactions were carried out on a 0.1 mmol scale at 30 °C and yields are based on ^{1}H-NMR analysis. HCl (aq. 37% in water). b) Isolated yield.

Table S1. Reaction optimization for the dichlorination and nitration of olefin **1**

5. General procedures and substrate scope of dichlorination reactions

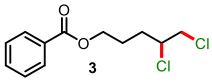


Scheme S18. General procedures and substrate scope of dichlorination reactions

General conditions A: Substrate alkenes or alkynes (0.2 mmol, 1.0 equiv), $NaNO_2$ (0.2 mmol, 1.0 equiv) and HCl (100 *u*L, aq. 37% in water) were dispersed in CH_2Cl_2 (2.0 mL) in a 4 mL glass vial at room temperature. The reaction vial was sealed with a PTEF cap and the reaction mixture vigorously stirred at 30 °C under the 24 W blue LEDs irradiation for 12 h (It is worth noting that 24 W blue LEDs was positioned 5 cm aside from the reaction vials.). Then, the reaction mixture was extracted with CH_2Cl_2 (3 × 2 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by chromatography on silica gel to afford the desired dichlorination products.

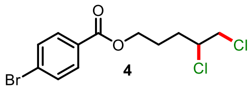
General conditions B: Substrate alkenes or alkynes (0.2 mmol, 1.0 equiv), $NaNO_2$ (0.2 mmol, 1.0 equiv) and HCl (100 *u*L, aq. 37% in water) were dispersed in PhCl (2.0 mL) in a 4 mL glass vial at room temperature. The reaction vial was sealed with a PTEF cap and the reaction mixture vigorously stirred at 30 °C under the 24 W blue LEDs irradiation for 12 h (It is worth noting that 24 W blue LEDs was positioned 5 cm aside from the reaction vials.). Then, the reaction mixture was extracted with CH_2Cl_2 (3 × 2 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by chromatography on silica gel to afford the desired dichlorination products.

5.1 Visible-light-induced vicinal dichlorination of alkenes



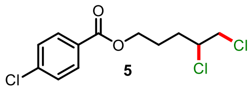
3

Compound **3** was isolated in 69% yield following the general conditions A (crude ^{1}H NMR yield: 88%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.3 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 4.38 (td, *J* = 6.3, 2.9 Hz, 2H), 4.15 – 4.06 (m, 1H), 3.81 (dd, *J* = 11.3, 5.0 Hz, 1H), 3.67 (dd, *J* = 11.3, 7.8 Hz, 1H), 2.24 – 2.17 (m, 1H), 2.12 – 2.04 (m, 1H), 1.97 – 1.83 (m, 2H).[15]



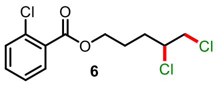
4

Compound **4** was isolated in 70% yield following the general conditions A. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.5 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 4.37 (td, *J* = 6.3, 2.4 Hz, 2H), 4.14 – 4.07 (m, 1H), 3.81 (dd, *J* = 11.3, 4.9 Hz, 1H), 3.66 (dd, *J* = 11.3, 7.9 Hz, 1H), 2.23 – 2.17 (m, 1H), 2.12 – 2.03 (m, 1H), 1.97 – 1.82 (m, 2H).[15]



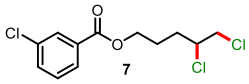
5

Compound **5** was isolated in 70% yield following the general conditions A. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 2H), 4.37 (td, *J* = 5.9, 2.0 Hz, 2H), 4.15 – 4.07 (m, 1H), 3.80 (dd, *J* = 11.3, 4.7 Hz, 1H), 3.66 (dd, *J* = 11.0, 8.1 Hz, 1H), 2.24 – 2.16 (m, 1H), 2.12 – 2.01 (m, 1H), 1.98 – 1.82 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.78, 139.61, 131.09, 128.90, 128.70, 64.41, 60.47, 48.02, 31.81, 25.36. **HRMS** Calcd for $C_{12}H_{13}Cl_3NaO_2$ [M+Na$^+$]: 316.9873; Found: 316.9874.



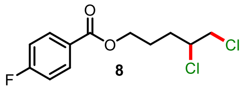
6

Compound **6** was isolated in 71% yield following the general conditions A. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.7 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 4.43 – 4.35 (m, 2H), 4.14 – 4.07 (m, 1H), 3.80 (dd, *J* = 11.3, 5.0 Hz, 1H), 3.66 (dd, *J* = 11.3, 7.8 Hz, 1H), 2.26 – 2.20 (m, 1H), 2.12 – 2.04 (m, 1H), 1.97 – 1.84 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.90, 133.75, 132.71, 131.52, 131.21, 130.31, 126.75, 64.75, 60.55, 48.09, 31.91, 25.35. **HRMS** Calcd for $C_{12}H_{14}Cl_3O_2$ [M+H$^+$]: 295.0054; Found: 295.0054.



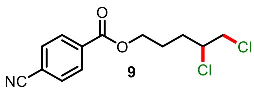
7

Compound **7** was isolated in 72% yield following the general conditions A. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 7.9 Hz, 1H), 4.43 – 4.34 (m, 2H), 4.13 – 4.08 (m, 1H), 3.81 (dd, *J* = 11.3, 4.9 Hz, 1H), 3.67 (dd, *J* = 11.3, 7.9 Hz, 1H), 2.24 – 2.17 (m, 1H), 2.11 – 2.04 (m, 1H), 1.97 – 1.82 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.43, 134.70, 133.18, 132.00, 129.87, 129.78, 127.82, 64.57, 60.46, 48.02, 31.78, 25.36. **HRMS** Calcd for $C_{12}H_{13}Cl_3NaO_2$ [M+Na$^+$]: 316.9873; Found: 316.9874.



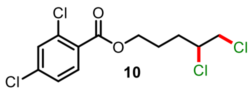
8

Compound **8** was isolated in 73% yield following the general conditions A. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 8.4, 5.6 Hz, 2H), 7.11 (t, *J* = 8.5 Hz, 2H), 4.40 – 4.32 (m, 2H), 4.14 – 4.05 (m, 1H), 3.81 (dd, *J* = 11.3, 4.9 Hz, 1H), 3.66 (dd, *J* = 11.3, 7.9 Hz, 1H), 2.24 – 2.16 (m, 1H), 2.12 – 2.04 (m, 1H), 1.96 – 1.83 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.94 (d, *J* = 254.0 Hz), 165.69 (s), 132.25 (d, *J* = 9.3 Hz), 126.52 (d, *J* = 3.0 Hz), 115.71 (d, *J* = 22.0 Hz), 64.31, 60.50, 48.04, 31.85, 25.40. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -105.54 - -105.62 (m, 1F). **HRMS** Calcd for $C_{12}H_{13}Cl_2FNaO_2$ [M+Na$^+$]: 301.0169; Found: 301.0169.



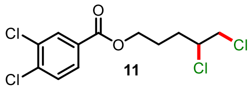
9

Compound **9** was isolated in 70% yield following the general conditions A. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 4.45 - 4.38 (m, 2H), 4.13 - 4.07 (m, 1H), 3.81 (dd, *J* = 11.3, 4.9 Hz, 1H), 3.66 (dd, *J* = 11.3, 8.1 Hz, 1H), 2.24 - 2.17 (m, 1H), 2.13 - 2.05 (m, 1H), 1.98 - 1.83 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.99, 134.05, 132.39, 130.20, 118.05, 116.62, 64.99, 60.33, 47.94, 31.73, 25.28. **HRMS** Calcd for $C_{13}H_{13}Cl_2NNaO_2$ [M+Na$^+$]: 308.0216; Found: 308.0209.



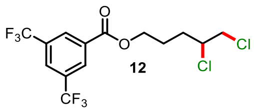
10

Compound **10** was isolated in 71% yield following the general conditions A. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4 Hz, 1H), 7.47 (s, 1H), 7.31 (d, *J* = 8.3 Hz, 1H), 4.42 – 4.34 (m, 2H), 4.12 – 4.06 (m, 1H), 3.80 (dd, *J* = 11.3, 4.9 Hz, 1H), 3.65 (dd, *J* = 11.2, 8.0 Hz, 1H), 2.25 – 2.18 (m, 1H), 2.11 – 2.03 (m, 1H), 1.96 – 1.82 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.96, 138.53, 134.97, 132.66, 131.17, 128.46, 127.20, 64.96, 60.45, 48.01, 31.85, 25.28. **HRMS** Calcd for $C_{12}H_{12}Cl_4NaO_2$ [M+Na$^+$]: 350.9484; Found: 350.9483.



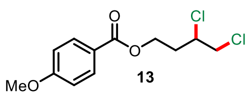
11

Compound **11** was isolated in 72% yield following the general conditions A. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.52 (d, *J* = 8.3 Hz, 1H), 4.38 (t, *J* = 6.2 Hz, 2H), 4.13 – 4.08 (m, 1H), 3.81 (dd, *J* = 11.3, 4.9 Hz, 1H), 3.66 (dd, *J* = 11.3, 8.0 Hz, 1H), 2.23 – 2.15 (m, 1H), 2.11 – 2.04 (m, 1H), 1.96 – 1.82 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.75, 137.80, 133.11, 131.63, 130.70, 130.08, 128.75, 64.76, 60.38, 47.96, 31.72, 25.31. **HRMS** Calcd for $C_{12}H_{12}Cl_4NaO_2$ [M+Na$^+$]: 350.9484; Found: 350.9475.



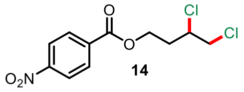
12

Compound **12** was isolated in 70% yield following the general conditions A. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.48 (s, 2H), 8.07 (s, 1H), 4.46 (t, *J* = 6.5 Hz, 2H), 4.15 – 4.08 (m, 1H), 3.82 (dd, *J* = 11.3, 4.8 Hz, 1H), 3.67 (dd, *J* = 11.3, 8.2 Hz, 1H), 2.27 – 2.19 (m, 1H), 2.17 – 2.09 (m, 1H), 2.01 – 1.93 (m, 1H), 1.91 – 1.83 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.99, 132.42, 132.39 (q, *J* = 34.1 Hz), 129.87 (d, *J* = 3.3 Hz), 126.69 – 126.45 (m), 124.07, 121.90, 65.37, 60.23, 47.85, 31.59, 25.25. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -63.01 (s, 6F). **HRMS** Calcd for $C_{14}H_{12}Cl_2F_6NaO_2$ [M+Na$^+$]: 419.0011; Found: 419.0001.

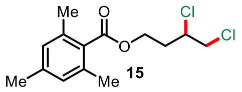


13

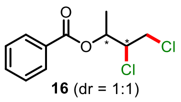
Compound **13** was isolated in 60% yield following the general conditions A. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.9 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 4.57 – 4.52 (m, 1H), 4.49 – 4.43 (m, 1H), 4.29 – 4.24 (m, 1H), 3.88 – 3.83 (m, 4H), 3.74 (dd, *J* = 11.4, 7.5 Hz, 1H), 2.55 – 2.47 (m, 1H), 2.17 – 2.09 (m, 1H).[16]



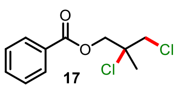
Compound **14** was isolated in 67% yield following the general conditions A. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.9 Hz, 2H), 8.21 (d, *J* = 8.9 Hz, 2H), 4.67 – 4.60 (m, 1H), 4.60 – 4.53 (m, 1H), 4.29 – 4.21 (m, 1H), 3.87 (dd, *J* = 11.4, 4.8 Hz, 1H), 3.73 (dd, *J* = 11.4, 8.0 Hz, 1H), 2.62 – 2.53 (m, 1H), 2.22 – 2.13 (m, 1H).[16]



Compound **15** was isolated in 38% yield following the general conditions A. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.86 (s, 2H), 4.59 – 4.54 (m, 1H), 4.51 – 4.45 (m, 1H), 4.26 – 4.20 (m, 1H), 3.82 (dd, *J* = 11.4, 4.2 Hz, 1H), 3.69 (dd, *J* = 11.1, 8.0 Hz, 1H), 2.55 – 2.48 (m, 1H), 2.30 (s, 3H), 2.29 (s, 6H), 2.09 – 2.02 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.03, 139.66, 135.27, 130.77, 128.60, 61.29, 57.48, 48.30, 34.45, 21.27, 19.97. **HRMS** Calcd for $C_{14}H_{18}Cl_2NaO_2$ [M+Na$^+$]: 311.0576; Found: 311.0576.

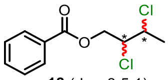


Compound **16** was isolated in 58% yield following the general conditions A (the recovery of starting material is 30%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.06 (t, *J* = 7.5 Hz, 2H), 7.67 – 7.56 (m, 1H), 7.55 – 7.38 (m, 2H), 5.73 – 5.59 (m, 0.46H), 5.58 – 5.45 (m, 0.40H), 4.36 (dd, *J* = 11.6, 6.0 Hz, 0.42H), 4.18 (dd, *J* = 9.7, 4.0 Hz, 0.43H), 3.97 – 3.66 (m, 2H), 1.51 (d, *J* = 6.3 Hz, 1.49H), 1.48 (d, *J* = 6.3 Hz, 1.49H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.50, 165.47, 133.49, 133.47, 129.89, 129.86, 128.64, 128.62, 70.50, 68.92, 63.38, 62.72, 44.98, 44.62, 17.52, 15.40. **HRMS** Calcd for $C_{11}H_{12}Cl_2NaO_2$ [M+Na$^+$]: 269.0107; Found: 269.0107.



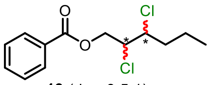
Compound **17** was isolated in 41% yield following the general conditions A (the recovery of starting material is 47%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.1 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 4.55 (d, *J* = 1.9 Hz, 2H), 3.97

(d, J = 11.4 Hz, 1H), 3.79 (d, J = 11.4 Hz, 1H), 1.75 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.80, 133.55, 129.87, 129.61, 128.68, 68.32, 67.65, 50.00, 25.25. **HRMS** Calcd for $C_{11}H_{12}Cl_2NaO_2$ [M+Na$^+$]: 269.0107; Found: 269.0107.



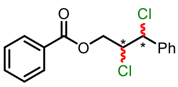
18 (dr = 3.5:1)

Compound **18** was isolated in 60% yield following the general conditions B (the recovery of starting material is 30%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.07 (d, J = 7.7 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 4.79 – 4.71 (m, 1H), 4.68 – 4.62 (m, 1H), 4.48 – 4.21 (m, 2H), 1.72 (d, J = 6.3 Hz, 2H), 1.67 (d, J = 6.7 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.98, 133.49, 129.85, 129.56, 128.61, 65.70, 65.47, 63.09, 62.06, 56.84, 56.68, 22.24, 21.83. **HRMS** Calcd for $C_{11}H_{12}Cl_2NaO_2$ [M+Na$^+$]: 269.0107; Found: 269.0107.



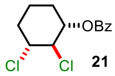
19 (dr = 3.5:1)

Compound **19** was isolated in 51% yield following the general conditions B (the recovery of starting material is 38%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.07 (d, J = 7.6 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.8 Hz, 2H), 4.82 – 4.75 (m, 1H), 4.69 – 4.62 (m, 1H), 4.46 – 4.37 (m, 0.22H), 4.34 – 4.29 (m, 0.77H), 4.28 – 4.22 (m, 0.23H), 4.21 – 4.16 (m, 0.78H), 2.11 – 2.03 (m, 1H), 1.92 – 1.82 (m, 1H), 1.75 – 1.63 (m, 1H), 1.54 – 1.42 (m, 1H), 0.98 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.09, 133.54, 133.48, 129.88, 129.73, 129.66, 129.55, 128.63, 128.44, 65.86, 65.73, 62.20, 61.81, 61.74, 61.16, 37.24, 36.91, 19.96, 19.25, 13.79, 13.57. **HRMS** Calcd for $C_{13}H_{16}Cl_2NaO_2$ [M+Na$^+$]: 297.0420; Found: 297.0421.



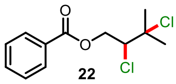
20 (dr = 3.0:1)

Compound **20** was isolated in 35% yield following the general conditions B (the recovery of starting material is 43%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.08 (d, J = 7.5 Hz, 1.48H), 8.04 (d, J = 7.5 Hz, 0.50H), 7.61 (t, J = 7.4 Hz, 1H), 7.48 (dd, J = 13.9, 7.2 Hz, 4H), 7.43 – 7.35 (m, 3H), 5.29 (d, J = 4.9 Hz, 0.27H), 5.16 (d, J = 8.5 Hz, 0.77H), 4.85 – 4.75 (m, 1.59H), 4.68 – 4.55 (m, 1.36H), 4.39 (d, J = 26.3 Hz, 0.33H).[17]



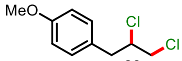
21

Compound **21** was isolated in 52% yield following the general conditions B (the recovery of starting material is 37%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 5.15 – 5.07 (m, 1H), 4.08 – 3.94 (m, 2H), 2.43 – 2.34 (m, 1H), 2.31 – 2.19 (m, 1H), 1.97 – 1.86 (m, 1H), 1.86 – 1.73 (m, 1H), 1.60 – 1.47 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.65, 133.38, 129.93, 128.57, 75.53, 66.65, 62.07, 35.77, 30.67, 21.28. **HRMS** Calcd for $C_{13}H_{14}Cl_2NaO_2$ [$M+Na^+$]: 295.0263; Found: 295.0256.



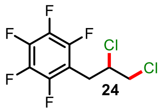
22

Compound **22** was isolated in 46% yield following the general conditions B (the recovery of starting material is 30%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.1 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 5.00 (dd, *J* = 11.9, 3.1 Hz, 1H), 4.57 (dd, *J* = 11.9, 8.4 Hz, 1H), 4.35 (dd, *J* = 8.4, 3.1 Hz, 1H), 1.81 (s, 3H), 1.73 (s, 3H).[17]



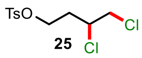
23

Compound **23** was isolated in 57% yield following the general conditions A. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 4.25 - 4.19 (m, 1H), 3.80 (s, 3H), 3.71 (dd, *J* = 11.4, 4.8 Hz, 1H), 3.64 (dd, *J* = 11.4, 6.9 Hz, 1H), 3.23 (dd, *J* = 14.4, 5.8 Hz, 1H), 3.02 (dd, *J* = 14.4, 7.1 Hz, 1H).[18]



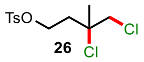
24

Compound **24** was isolated in 36% yield following the general conditions A. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.30 – 4.23 (m, 1H), 3.86 (dd, *J* = 11.5, 4.7 Hz, 1H), 3.73 (dd, *J* = 11.5, 7.7 Hz, 1H), 3.43 (d, *J* = 14.4 Hz, 1H), 3.13 (dd, *J* = 14.4, 9.8 Hz, 1H).[16]

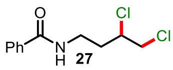


25

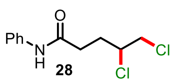
Compound **25** was isolated in 76% yield following the general conditions A. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 4.27 – 4.19 (m, 2H), 4.18 – 4.12 (m, 1H), 3.75 (dd, *J* = 11.6, 4.8 Hz, 1H), 3.64 (dd, *J* = 11.6, 7.1 Hz, 1H), 2.45 (s, 3H), 2.44 – 2.36 (m, 1H), 1.98 – 1.90 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.23, 132.70, 130.09, 128.05, 66.65, 56.58, 48.15, 34.68, 21.78. **HRMS** Calcd for $C_{11}H_{14}Cl_2NaO_3S$ [M+Na$^+$]: 318.9933; Found: 318.9927.



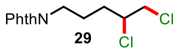
Compound **26** was isolated in 55% yield following the general conditions A (the recovery of starting material is 28%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 2H), 4.26 (t, *J* = 6.6 Hz, 2H), 3.71 – 3.59 (m, 2H), 2.45 (s, 3H), 2.34 – 2.15 (m, 2H), 1.62 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.18, 132.93, 130.08, 128.05, 68.77, 66.61, 52.94, 39.29, 28.39, 21.78. **HRMS** Calcd for $C_{12}H_{16}Cl_2NaO_3S$ [M+Na$^+$]: 333.0089; Found: 333.0092.



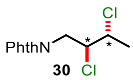
Compound **27** was isolated in 60% yield following the general conditions A. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.2 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 6.44 (br, 1H), 4.19 – 4.12 (m, 1H), 3.83 (dd, *J* = 11.5, 5.1 Hz, 1H), 3.76 – 3.68 (m, 2H), 3.66 – 3.58 (m, 1H), 2.50 – 2.41 (m, 1H), 2.02 – 1.93 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.88, 134.35, 131.80, 128.79, 127.00, 59.07, 48.37, 37.39, 35.03. **HRMS** Calcd for $C_{11}H_{13}Cl_2NNaO$ [M+Na$^+$]: 268.0266; Found: 268.0268.



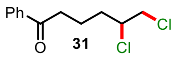
Compound **28** was isolated in 58% yield following the general conditions A. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.9 Hz, 2H), 7.33 (t, *J* = 7.9 Hz, 2H), 7.23 (br, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 4.25 - 4.17 (m, 1H), 3.81 (dd, *J* = 11.5, 5.1 Hz, 1H), 3.71 (dd, *J* = 11.5, 7.0 Hz, 1H), 2.68 - 2.50 (m, 3H), 2.08 - 1.99 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.72, 137.73, 129.20, 124.64, 119.99, 60.59, 48.44, 33.74, 30.87. **HRMS** Calcd for $C_{11}H_{13}Cl_2NNaO$ [M+Na$^+$]: 268.0266; Found: 268.0267.



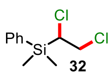
Compound **29** was isolated in 75% yield following the general conditions A. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 – 7.82 (m, 2H), 7.74 – 7.69 (m, 2H), 4.12 – 4.06 (m, 1H), 3.77 – 3.70 (m, 3H), 3.65 – 3.60 (m, 1H), 2.09 – 1.95 (m, 2H), 1.88 – 1.73 (m, 2H).[19]



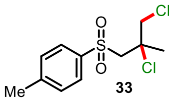
Compound **30** was isolated in 44% yield following the general conditions A (the recovery of starting material is 49%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 – 7.86 (m, 2H), 7.78 – 7.73 (m, 2H), 4.50 – 4.45 (m, 1H), 4.22 – 4.07 (m, 3H), 1.72 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.30, 168.02, 134.43, 131.90, 123.74, 62.94, 60.54, 58.07, 41.97. **HRMS** Calcd for $C_{12}H_{11}Cl_2NNaO_2$ [$M+Na^+$]: 294.0059; Found: 294.0060.



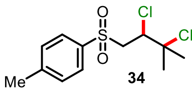
Compound **31** was isolated in 57% yield following the general conditions A (the recovery of starting material is 30%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 6.9 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 4.13 – 4.06 (m, 1H), 3.79 (dd, *J* = 11.4, 5.1 Hz, 1H), 3.68 (dd, *J* = 11.4, 7.4 Hz, 1H), 3.11 – 2.98 (m, 2H), 2.16 – 2.08 (m, 1H), 2.08 – 1.99 (m, 1H), 1.95 – 1.86 (m, 1H), 1.86 – 1.77 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 199.50, 136.99, 133.27, 128.79, 128.15, 60.99, 48.26, 37.77, 34.70, 20.67. **HRMS** Calcd for $C_{12}H_{14}\ {}^{37}Cl^{35}ClNaO$ [$M+Na^+$]: 269.0284; Found: 269.0274.



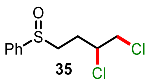
Compound **32** was isolated in 67% yield following the general conditions B. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.0 Hz, 2H), 7.46 – 7.38 (m, 3H), 3.86 (d, *J* = 11.5 Hz, 1H), 3.70 – 3.60 (m, 2H), 0.50 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 134.35, 134.16, 130.29, 128.32, 51.22, 48.65, -4.13, -5.30. **HRMS** Calcd for $C_{10}H_{14}Cl_2KSi$ [$M+K^+$]: 270.9873; Found: 270.9872.



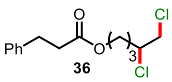
Compound **33** was isolated in 35% yield following the general conditions B (the recovery of starting material is 40%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.8 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 4.11 – 4.00 (m, 2H), 3.81 (d, *J* = 14.5 Hz, 1H), 3.60 (d, *J* = 14.6 Hz, 1H), 2.45 (s, 3H), 1.93 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.41, 137.66, 130.18, 128.08, 66.43, 63.59, 52.86, 28.59, 21.81. **HRMS** Calcd for $C_{11}H_{14}Cl_2NaO_2S$ [M+Na$^+$]: 302.9984; Found: 302.9982.



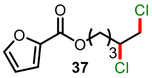
Compound **34** was isolated in 33% yield following the general conditions B (the recovery of starting material is 43%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.9 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 4.35 (d, *J* = 9.5 Hz, 1H), 3.99 (d, *J* = 15.1 Hz, 1H), 3.52 (dd, *J* = 15.1, 9.6 Hz, 1H), 2.45 (s, 3H), 1.70 (s, 3H), 1.55 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.35, 136.39, 130.09, 128.55, 70.44, 61.81, 60.87, 31.16, 26.88, 21.84. **HRMS** Calcd for $C_{12}H_{16}Cl_2NaO_2S$ [M+Na$^+$]: 317.0140; Found: 317.0147.



Compound **35** was isolated in 60% yield following the general conditions A. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.8 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 4.30 – 4.23 (m, 1H), 3.78 (dd, *J* = 11.4, 4.9 Hz, 1H), 3.65 (dd, *J* = 11.4, 7.5 Hz, 1H), 3.23 – 3.16 (m, 1H), 3.05 – 2.99 (m, 1H), 2.32 – 2.24 (m, 1H), 2.07 – 1.99 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 135.42, 129.98, 129.21, 126.65, 59.47, 48.11, 34.72, 30.51. **HRMS** Calcd for $C_{10}H_{13}Cl_2OS$ [M+H$^+$]: 251.0059; Found: 251.0059.

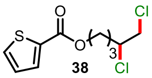


Compound **36** was isolated in 77% yield following the general conditions A. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.20 (d, *J* = 7.7 Hz, 3H), 4.16 – 4.07 (m, 2H), 4.05 – 3.99 (m, 1H), 3.75 (dd, *J* = 11.3, 5.0 Hz, 1H), 3.62 (dd, *J* = 11.3, 7.7 Hz, 1H), 2.96 (t, *J* = 7.7 Hz, 2H), 2.65 (t, *J* = 7.7 Hz, 2H), 2.06 – 1.98 (m, 1H), 1.93 – 1.83 (m, 1H), 1.78 – 1.66 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.98, 140.54, 128.64, 128.41, 126.43, 63.64, 60.59, 48.12, 35.95, 31.75, 31.09, 25.32. **HRMS** Calcd for $C_{14}H_{18}Cl_2NaO_2$ [M+Na$^+$]: 311.0576; Found: 311.0575.



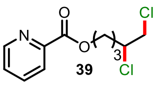
37

Compound **37** was isolated in 65% yield following the general conditions A. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 0.9 Hz, 1H), 7.18 (d, *J* = 3.5 Hz, 1H), 6.51 (dd, *J* = 3.5, 1.7 Hz, 1H), 4.39 – 4.32 (m, 2H), 4.13 – 4.07 (m, 1H), 3.79 (dd, *J* = 11.4, 5.0 Hz, 1H), 3.66 (dd, *J* = 11.4, 7.7 Hz, 1H), 2.21 – 2.14 (m, 1H), 2.09 – 2.02 (m, 1H), 1.94 – 1.79 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.76, 146.53, 144.67, 118.16, 111.99, 64.10, 60.53, 48.11, 31.78, 25.42. **HRMS** Calcd for $C_{10}H_{12}Cl_2NaO_3$ [M+Na$^+$]: 273.0056; Found: 273.0057.



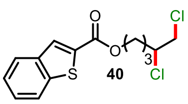
38

Compound **38** was isolated in 67% yield following the general conditions A. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 3.6 Hz, 1H), 7.56 (d, *J* = 4.9 Hz, 1H), 7.11 (t, 1H), 4.39 – 4.32 (m, 2H), 4.14 – 4.09 (m, 1H), 3.80 (dd, *J* = 11.3, 5.0 Hz, 1H), 3.66 (dd, 1H), 2.23 – 2.15 (m, 1H), 2.09 – 2.02 (m, 1H), 1.95 – 1.81 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.29, 133.79, 133.63, 132.60, 127.93, 64.31, 60.55, 48.11, 31.85, 25.42. **HRMS** Calcd for $C_{10}H_{12}Cl_2NaO_2S$ [M+Na$^+$]: 288.9827; Found: 288.9829.



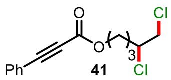
39

Compound **39** was isolated in 66% yield following the general conditions A. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.77 (d, *J* = 4.6 Hz, 1H), 8.13 (d, *J* = 7.8 Hz, 1H), 7.85 (t, *J* = 7.7 Hz, 1H), 7.49 (dd, *J* = 6.8, 4.8 Hz, 1H), 4.52 – 4.43 (m, 2H), 4.16 – 4.09 (m, 1H), 3.79 (dd, *J* = 11.4, 5.0 Hz, 1H), 3.67 (dd, *J* = 11.4, 7.6 Hz, 1H), 2.25 – 2.08 (m, 2H), 2.03 – 1.93 (m, 1H), 1.91 – 1.82 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.29, 150.09, 148.12, 137.19, 127.11, 125.31, 65.12, 60.59, 48.16, 31.81, 25.47. **HRMS** Calcd for $C_{11}H_{13}Cl_2NNaO_2$ [M+Na$^+$]: 284.0216; Found: 284.0213.

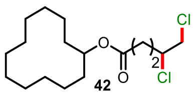


40

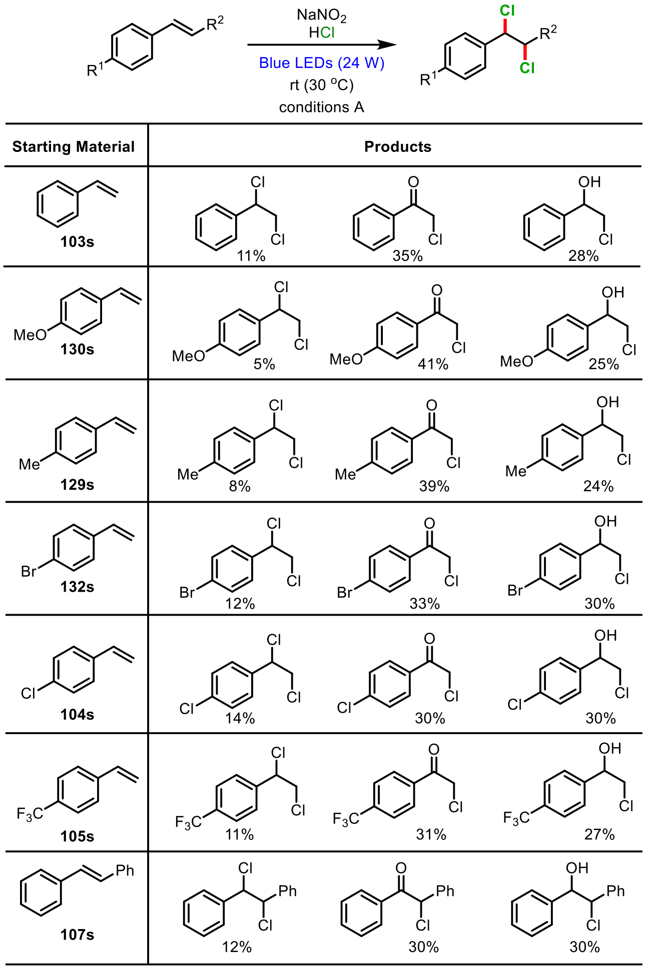
Compound **40** was isolated in 76% yield following the general conditions A. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.59 (d, *J* = 8.2 Hz, 1H), 8.39 (s, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 4.48 - 4.38 (m, 2H), 4.18 - 4.10 (m, 1H), 3.82 (dd, *J* = 11.3, 4.9 Hz, 1H), 3.68 (dd, *J* = 11.3, 7.9 Hz, 1H), 2.29 - 2.20 (m, 1H), 2.16 - 2.06 (m, 1H), 2.02 - 1.86 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.81, 140.18, 136.85, 136.79, 127.18, 125.60, 125.20, 124.82, 122.67, 63.85, 60.53, 48.05, 31.93, 25.45. **HRMS** Calcd for $C_{14}H_{14}Cl_2NaO_2S$ [M+Na$^+$]: 338.9984; Found: 338.9983.



Compound **41** was isolated in 70% yield following the general conditions A. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 4.33 – 4.25 (m, 2H), 4.12 – 4.06 (m, 1H), 3.80 (dd, *J* = 11.3, 5.0 Hz, 1H), 3.67 (dd, *J* = 11.3, 7.7 Hz, 1H), 2.21 – 2.14 (m, 1H), 2.08 – 2.00 (m, 1H), 1.91 – 1.79 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.16, 133.16, 130.86, 128.73, 119.67, 86.76, 80.60, 65.25, 60.55, 48.13, 31.77, 25.30. **HRMS** Calcd for $C_{14}H_{14}Cl_2NaO_2$ [M+Na$^+$]: 307.0263; Found: 307.0263.

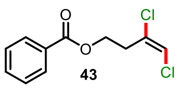


Compound **42** was isolated in 71% yield following the general conditions B. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.09 – 4.99 (m, 1H), 4.18 – 4.10 (m, 1H), 3.78 (dd, *J* = 11.4, 5.0 Hz, 1H), 3.65 (dd, *J* = 11.4, 7.5 Hz, 1H), 2.60 – 2.45 (m, 2H), 2.41 – 2.34 (m, 1H), 2.00 – 1.91 (m, 1H), 1.75 – 1.66 (m, 2H), 1.53 – 1.46 (m, 2H), 1.42 – 1.29 (m, 18H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.26, 72.81, 60.22, 48.21, 31.05, 30.56, 29.23, 24.19, 23.96, 23.50, 23.33, 21.06. **HRMS** Calcd for $C_{17}H_{30}Cl_2NaO_2$ [M+Na$^+$]: 359.1515; Found: 359.1515.

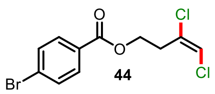


Scheme S19. Visible-light-induced vicinal dichlorination of active alkenes

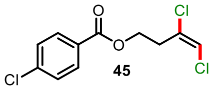
5.2 Visible-light-induced vicinal dichlorination of alkynes



Compound **43** was isolated in 40% yield following the general conditions A (the recovery of starting material is 42%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.05 (d, J = 7.1 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.8 Hz, 2H), 6.31 (s, 1H), 4.54 (t, J = 6.2 Hz, 2H), 3.01 (t, J = 6.2 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.51, 133.20, 132.25, 130.05, 129.82, 128.51, 116.53, 61.08, 33.22. **HRMS** Calcd for $C_{11}H_{11}Cl_2O_2$ [M+H$^+$]: 245.0131; Found: 245.0131.

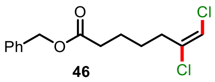


Compound **44** was isolated in 46% yield following the general conditions A (the recovery of starting material is 37%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 6.30 (s, 1H), 4.53 (t, *J* = 6.2 Hz, 2H), 3.00 (t, *J* = 6.2 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.77, 132.14, 131.90, 131.34, 128.94, 128.38, 116.61, 61.31, 33.20. **HRMS** Calcd for $C_{11}H_9BrCl_2NaO_2$ [M+Na$^+$]: 344.9055; Found: 344.9049.



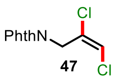
45

Compound **45** was isolated in 43% yield following the general conditions A (the recovery of starting material is 42%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 6.31 (s, 1H), 4.53 (t, *J* = 6.2 Hz, 2H), 3.00 (t, *J* = 6.2 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.64, 139.70, 132.15, 131.21, 128.90, 128.49, 116.60, 61.29, 33.20. **HRMS** Calcd for $C_{11}H_9Cl_3NaO_2$ [M+Na$^+$]: 300.9560; Found: 300.9553.



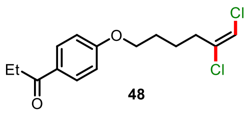
46

Compound **46** was isolated in 48% yield following the general conditions B (the recovery of starting material is 34%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 5H), 6.15 (s, 1H), 5.12 (s, 2H), 2.53 (t, *J* = 7.1 Hz, 2H), 2.40 (t, *J* = 7.3 Hz, 2H), 1.74 – 1.66 (m, 2H), 1.65 – 1.60 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.28, 136.13, 135.93, 128.70, 128.35, 128.33, 114.21, 66.35, 34.06, 32.90, 25.91, 23.89. **HRMS** Calcd for $C_{14}H_{16}Cl_2NaO_2$ [M+Na$^+$]: 309.0420; Found: 309.0418.

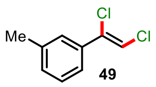


47

Compound **47** was isolated in 41% yield following the general conditions B (the recovery of starting material is 34%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 – 7.86 (m, 2H), 7.77 – 7.72 (m, 2H), 6.38 (s, 1H), 4.71 (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.46, 134.39, 131.94, 129.72, 123.73, 117.74, 38.41. **HRMS** Calcd for $C_{11}H_7Cl_2NNaO_2$ [M+Na$^+$]: 277.9746; Found: 277.9739.

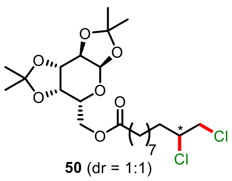


Compound **48** was isolated in 41% yield following the general conditions B (the recovery of starting material is 42%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.18 (s, 1H), 4.04 (t, *J* = 6.0 Hz, 2H), 2.95 (q, *J* = 7.3 Hz, 2H), 2.61 (t, *J* = 7.0 Hz, 2H), 1.88 – 1.75 (m, 4H), 1.21 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 199.64, 162.87, 135.97, 130.36, 130.10, 114.35, 114.26, 67.74, 32.84, 31.55, 28.02, 23.03, 8.61. **HRMS** Calcd for $C_{15}H_{18}Cl_2NaO_2$ [M+Na$^+$]: 323.0576; Found: 323.0583.



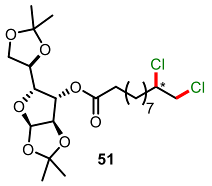
Compound **49** was isolated in 14% yield following the general conditions A. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 11.7 Hz, 2H), 7.28 (s, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 6.67 (s, 1H), 2.37 (s, 3H).[20]

5.3 Visible-light-induced vicinal dichlorination of natural products and drug derivatives



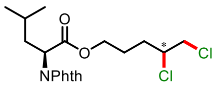
Alkene (**50s**) (0.2 mmol, 1.0 equiv), $NaNO_2$ (0.2 mmol, 1.0 equiv) and HCl (100 *u*L, aq. 37% in water) were dispersed in PhCl (2.0 mL) in a 4 mL glass vial at room temperature. The reaction vial was sealed with a PTEF cap and the reaction mixture vigorously stirred at 30 °C under the 24 W blue LEDs irradiation for 0.5 h (It is worth noting that 24 W blue LEDs was positioned 5 cm aside from the reaction vials.). Then, the reaction mixture was extracted with CH_2Cl_2 (3 × 2 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by chromatography on silica gel to afford the desired dichlorination products. Compound **50** was isolated in 55% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.54 (d, *J* =

5.0 Hz, 1H), 4.61 (dd, J = 7.9, 2.3 Hz, 1H), 4.31 (dd, J = 11.7, 4.6 Hz, 2H), 4.23 (dd, J = 7.9, 1.2 Hz, 1H), 4.16 (dd, J = 11.5, 7.8 Hz, 1H), 4.06 – 3.99 (m, 2H), 3.76 (dd, J = 11.3, 5.2 Hz, 1H), 3.65 (dd, J = 11.3, 7.4 Hz, 1H), 2.33 (t, J = 7.5 Hz, 2H), 2.02 – 1.93 (m, 1H), 1.75 – 1.65 (m, 1H), 1.65 – 1.52 (m, 5H), 1.50 (s, 3H), 1.45 (s, 3H), 1.43 – 1.37 (m, 1H), 1.33 (d, J = 3.8 Hz, 6H), 1.31 – 1.26 (m, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.88, 109.78, 108.89, 96.46, 71.24, 70.85, 70.61, 66.19, 63.39, 61.36, 48.40, 35.17, 34.33, 29.32, 29.28, 29.16, 29.05, 26.17, 26.10, 25.92, 25.12, 25.07, 24.64. **HRMS** Calcd for $C_{23}H_{38}Cl_2NaO_7$ [M+Na$^+$]: 519.1887; Found: 519.1888.



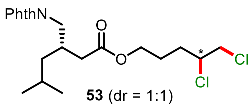
51

Alkene (**51s**) (0.2 mmol, 1.0 equiv), $NaNO_2$ (0.2 mmol, 1.0 equiv) and HCl (100 *u*L, aq. 37% in water) were dispersed in PhCl (2.0 mL) in a 4 mL glass vial at room temperature. The reaction vial was sealed with a PTEF cap and the reaction mixture vigorously stirred at 30 °C under the 24 W blue LEDs irradiation for 0.5 h (It is worth noting that 24 W blue LEDs was positioned 5 cm aside from the reaction vials.). Then, the reaction mixture was extracted with CH_2Cl_2 (3 × 2 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by chromatography on silica gel to afford the desired dichlorination products. Compound **51** was isolated in 60% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.87 (d, J = 3.6 Hz, 1H), 5.27 (s, 1H), 4.47 (d, J = 3.6 Hz, 1H), 4.21 (t, J = 3.4 Hz, 2H), 4.12 – 4.07 (m, 1H), 4.06 – 3.98 (m, 2H), 3.76 (dd, J = 11.3, 5.1 Hz, 1H), 3.65 (dd, J = 11.3, 7.5 Hz, 1H), 2.34 (td, J = 7.5, 3.0 Hz, 2H), 2.02 – 1.94 (m, 1H), 1.75 – 1.68 (m, 1H), 1.67 – 1.60 (m, 2H), 1.52 (s, 3H), 1.41 (m, 4H), 1.38 – 1.26 (m, 15H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.47, 112.45, 109.47, 105.22, 83.56, 80.04, 76.01, 72.60, 67.45, 61.32, 48.37, 35.15, 34.39, 29.33, 29.25, 29.13, 29.05, 26.98, 26.90, 26.37, 25.90, 25.44, 24.99. **HRMS** Calcd for $C_{23}H_{38}Cl_2NaO_7$ [M+Na$^+$]: 519.1887; Found: 519.1885.



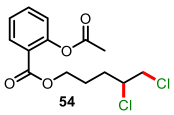
52 (dr = 1:1)

Compound **52** was isolated in 68% yield following the general conditions A. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.89 – 7.84 (m, 2H), 7.77 – 7.72 (m, 2H), 4.94 (dd, *J* = 11.5, 4.3 Hz, 1H), 4.25 – 4.11 (m, 2H), 4.01 – 3.93 (m, 1H), 3.72 – 3.66 (m, 1H), 3.55 (dd, *J* = 11.2, 7.8 Hz, 1H), 2.36 – 2.28 (m, 1H), 2.02 – 1.93 (m, 2H), 1.91 – 1.84 (m, 1H), 1.77 – 1.65 (m, 2H), 1.54 – 1.45 (m, 1H), 0.95 (d, *J* = 6.5 Hz, 3H), 0.92 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.87, 167.88, 134.35, 131.92, 123.68, 64.86, 60.36, 50.80, 48.03, 47.99, 37.44, 31.54, 25.21, 25.09, 25.06, 23.29, 21.18. **HRMS** Calcd for $C_{19}H_{23}Cl_2NNaO_4$ [M+Na$^+$]: 422.0896; Found: 422.0895.



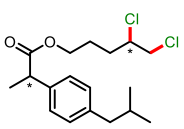
53 (dr = 1:1)

Compound **53** was isolated in 48% yield following the general conditions B. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 – 7.81 (m, 2H), 7.74 – 7.68 (m, 2H), 4.12 – 3.89 (m, 3H), 3.77 (dd, *J* = 11.3, 5.0 Hz, 1H), 3.73 – 3.57 (m, 3H), 2.50 – 2.40 (m, 1H), 2.35 – 2.24 (m, 2H), 2.10 – 2.01 (m, 1H), 1.90 – 1.81 (m, 1H), 1.77 – 1.65 (m, 3H), 1.25 – 1.17 (m, 2H), 0.95 (d, *J* = 6.5 Hz, 3H), 0.89 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.54, 168.70, 134.09, 132.14, 123.36, 63.57, 63.56, 60.67, 48.20, 42.06, 41.91, 37.73, 32.83, 31.81, 25.43, 25.28, 22.80, 22.71, 18.56. **HRMS** Calcd for $C_{21}H_{27}Cl_2NNaO_4$ [M+Na$^+$]: 450.1209; Found: 450.1208.



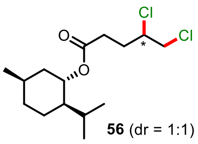
54

Compound **54** was isolated in 64% yield following the general conditions A. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 8.1 Hz, 1H), 4.37 – 4.27 (m, 2H), 4.14 – 4.09 (m, 1H), 3.79 (dd, *J* = 11.3, 5.0 Hz, 1H), 3.66 (dd, *J* = 11.3, 7.7 Hz, 1H), 2.35 (s, 3H), 2.19 – 2.12 (m, 1H), 2.05 – 2.03 (m, 1H), 1.93 – 1.80 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.77, 164.45, 150.84, 134.05, 131.73, 126.15, 123.94, 123.29, 64.26, 60.57, 48.11, 31.77, 25.39, 21.18. **HRMS** Calcd for $C_{14}H_{16}Cl_2NaO_4$ [M+Na$^+$]: 341.0318; Found: 341.0318.



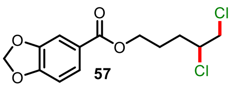
55 (dr = 1:1)

Compound **55** was isolated in 53% yield following the general conditions A. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.20 (d, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 7.8 Hz, 2H), 4.17 – 4.06 (m, 2H), 3.98 – 3.92 (m, 1H), 3.69 (dd, 2H), 3.54 (dd, *J* = 11.2, 7.6 Hz, 1H), 2.44 (d, *J* = 7.2 Hz, 2H), 1.98 – 1.81 (m, 3H), 1.75 – 1.62 (m, 2H), 1.49 (d, *J* = 7.1 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.81, 140.75, 137.82, 129.49, 127.28, 63.81, 63.71, 60.55, 60.53, 48.12, 45.30, 45.16, 31.72, 31.63, 30.33, 25.24, 25.23, 22.53, 18.45, 18.43. **HRMS** Calcd for $C_{18}H_{26}Cl_2NaO_2$ [M+Na$^+$]: 367.1202; Found: 367.1201.



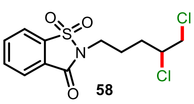
56 (dr = 1:1)

Compound **56** was isolated in 61% yield following the general conditions B. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.09 – 5.02 (m, 1H), 4.20 – 4.09 (m, 1H), 3.79 (dd, *J* = 11.4, 5.0 Hz, 1H), 3.66 (dd, *J* = 11.4, 7.5 Hz, 1H), 2.62 – 2.47 (m, 2H), 2.43 – 2.33 (m, 1H), 2.01 – 1.92 (m, 1H), 1.91 – 1.82 (m, 1H), 1.77 – 1.68 (m, 1H), 1.63 – 1.53 (m, 2H), 1.52 – 1.42 (m, 3H), 1.36 – 1.27 (m, 1H), 1.26 – 1.16 (m, 1H), 0.93 (t, *J* = 6.4 Hz, 6H), 0.84 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.96, 72.30, 60.24, 60.22, 48.18, 45.84, 45.79, 35.91, 31.12, 30.56, 30.54, 30.04, 30.03, 27.69, 27.67, 26.44, 26.41, 21.01, 21.00, 20.94, 20.63, 20.60, 19.17, 19.15. **HRMS** Calcd for $C_{15}H_{26}Cl_2NaO_2$ [M+Na$^+$]: 331.1202; Found: 331.1203.



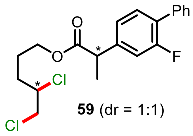
57

Compound **57** was isolated in 53% yield following the general conditions B. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.1 Hz, 1H), 7.46 (s, 1H), 6.84 (d, *J* = 8.2 Hz, 1H), 6.04 (s, 2H), 4.38 – 4.30 (m, 2H), 4.16 – 4.07 (m, 1H), 3.80 (dd, *J* = 11.3, 4.9 Hz, 1H), 3.67 (dd, *J* = 11.3, 7.8 Hz, 1H), 2.24 – 2.15 (m, 1H), 2.10 – 2.02 (m, 1H), 1.95 – 1.82 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.00, 151.81, 147.89, 125.49, 124.29, 109.62, 108.15, 101.95, 64.10, 60.58, 48.10, 31.91, 25.46. **HRMS** Calcd for $C_{13}H_{14}Cl_2NaO_4$ [M+Na$^+$]: 327.0161; Found: 327.0162.



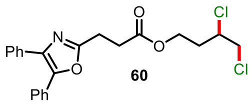
58

Compound **58** was isolated in 65% yield following the general conditions A. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.3 Hz, 1H), 7.93 (d, *J* = 7.5 Hz, 1H), 7.91 – 7.82 (m, 2H), 4.14 – 4.08 (m, 1H), 3.84 (t, *J* = 6.6 Hz, 2H), 3.77 (dd, *J* = 11.4, 5.1 Hz, 1H), 3.66 (dd, *J* = 11.3, 7.5 Hz, 1H), 2.20 – 2.11 (m, 2H), 2.04 – 1.95 (m, 1H), 1.90 – 1.81 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.18, 137.78, 134.98, 134.54, 127.41, 125.38, 121.12, 60.28, 48.17, 38.66, 32.31, 25.14. **HRMS** Calcd for $C_{12}H_{13}Cl_2NNaO_3S$ [M+Na$^+$]: 343.9885; Found: 343.9885.



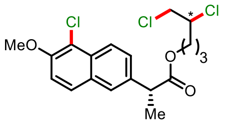
59 (dr = 1:1)

Compound **59** was isolated in 60% yield following the general conditions B. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 6.8 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.43 – 7.35 (m, 2H), 7.15 (dd, *J* = 14.3, 9.8 Hz, 2H), 4.24 – 4.09 (m, 2H), 4.04 – 3.95 (m, 1H), 3.82 – 3.69 (m, 2H), 3.57 (dd, *J* = 11.4, 7.8 Hz, 1H), 2.07 – 1.97 (m, 1H), 1.96 – 1.87 (m, 1H), 1.82 – 1.73 (m, 1H), 1.73 – 1.64 (m, 1H), 1.55 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.99, 160.79, 158.81, 141.88, 141.82, 135.55, 130.98, 130.95, 129.07, 129.04, 128.58, 127.81, 123.68, 123.65, 115.45, 115.26, 64.14, 64.07, 60.40, 60.38, 47.99, 45.15, 31.68, 31.60, 25.18, 18.31. **HRMS** Calcd for $C_{20}H_{21}Cl_2FNaO_2$ [M+Na$^+$]: 405.0795; Found: 405.0796.



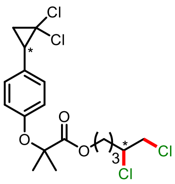
60

Compound **60** was isolated in 60% yield following the general conditions B. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.3 Hz, 2H), 7.57 (d, *J* = 7.3 Hz, 2H), 7.40 – 7.30 (m, 6H), 4.42 – 4.36 (m, 1H), 4.34 – 4.26 (m, 1H), 4.19 – 4.12 (m, 1H), 3.71 (dd, *J* = 11.4, 4.8 Hz, 1H), 3.59 (dd, *J* = 11.4, 7.3 Hz, 1H), 3.19 (t, *J* = 7.3 Hz, 2H), 2.94 (t, *J* = 7.3 Hz, 2H), 2.41 – 2.31 (m, 1H), 2.07 – 1.96 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.90, 161.73, 145.63, 135.28, 132.55, 129.08, 128.80, 128.70, 128.64, 128.23, 128.03, 126.63, 61.29, 57.44, 48.28, 34.31, 31.17, 23.63. **HRMS** Calcd for $C_{22}H_{21}Cl_2NNaO_3$ [M+Na$^+$]: 440.0791; Found: 440.0787.



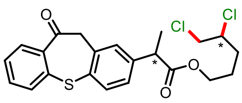
61 (dr = 1:1)

Compound **61** was isolated in 61% yield following the general conditions B. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.8 Hz, 1H), 7.75 (d, *J* = 9.0 Hz, 1H), 7.70 (s, 1H), 7.52 (d, *J* = 8.8 Hz, 1H), 7.30 (d, *J* = 9.0 Hz, 1H), 4.19 – 4.07 (m, 2H), 4.03 (s, 3H), 3.94 – 3.84 (m, 2H), 3.61 (dd, *J* = 10.9, 4.5 Hz, 1H), 3.49 – 3.42 (m, 1H), 1.95 – 1.81 (m, 2H), 1.76 – 1.65 (m, 1H), 1.63 – 1.55 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.43, 152.71, 136.56, 131.23, 129.64, 127.96, 127.95, 127.57, 127.55, 126.33, 126.30, 124.21, 124.20, 117.00, 114.19, 64.07, 63.97, 60.46, 57.15, 48.00, 45.47, 31.69, 31.60, 25.25, 25.23, 18.32. **HRMS** Calcd for $C_{19}H_{21}Cl_3NaO_3$ [M+Na$^+$]: 425.0448; Found: 425.0448.



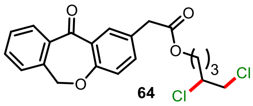
62 (dr = 1:1)

Compound **62** was isolated in 57% yield following the general conditions A. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.7 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 4.24 – 4.15 (m, 2H), 3.98 – 3.91 (m, 1H), 3.67 (dd, *J* = 11.3, 5.1 Hz, 1H), 3.52 (dd, *J* = 11.3, 7.6 Hz, 1H), 2.82 (dd, *J* = 10.5, 8.5 Hz, 1H), 1.97 – 1.84 (m, 3H), 1.79 – 1.63 (m, 3H), 1.61 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.33, 155.11, 129.82, 128.20, 118.36, 79.22, 64.63, 61.01, 60.47, 48.08, 34.93, 31.61, 25.99, 25.59, 25.57, 25.17. **HRMS** Calcd for $C_{18}H_{22}Cl_4NaO_3$ [M+Na$^+$]: 449.0215; Found: 449.0216.



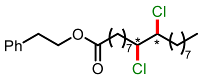
63 (dr = 1:1)

Compound **63** was isolated in 56% yield following the general conditions B. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.38 (s, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 4.36 (s, 2H), 4.15 – 4.05 (m, 2H), 3.95 – 3.89 (m, 1H), 3.74 – 3.70 (m, 1H), 3.65 (dd, *J* = 11.3, 5.0 Hz, 1H), 3.51 (dd, *J* = 11.2, 7.8 Hz, 1H), 1.95 – 1.80 (m, 2H), 1.73 – 1.65 (m, 1H), 1.64 – 1.58 (m, 1H), 1.48 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 191.44, 173.92, 142.77, 140.32, 138.12, 136.27, 133.45, 132.67, 131.66, 130.99, 128.75, 127.00, 126.46, 64.15, 64.08, 60.44, 51.19, 48.02, 45.34, 31.67, 31.60, 25.18, 18.37. **HRMS** Calcd for $C_{22}H_{22}Cl_2NaO_3S$ [M+Na$^+$]: 459.0559; Found: 459.0560.



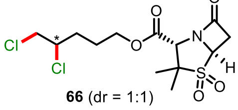
64

Compound **64** was isolated in 50% yield following the general conditions A. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.42 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.36 (d, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 5.18 (s, 2H), 4.21 – 4.11 (m, 2H), 4.04 – 3.99 (m, 1H), 3.74 (dd, *J* = 11.3, 5.0 Hz, 1H), 3.66 – 3.59 (m, 3H), 2.08 – 2.01 (m, 1H), 1.97 – 1.89 (m, 1H), 1.81 – 1.69 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 190.91, 171.42, 160.60, 140.51, 136.41, 135.65, 132.91, 132.52, 129.59, 129.38, 127.93, 127.85, 125.27, 121.22, 73.74, 64.15, 60.54, 48.11, 40.40, 31.73, 25.24. **HRMS** Calcd for $C_{21}H_{20}Cl_2NaO_4$ [M+Na$^+$]: 429.0631; Found: 429.0630.



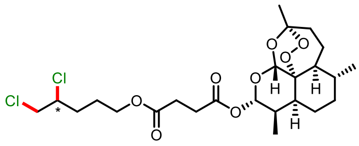
65 (dr = 1:1)

Compound **65** was isolated in 41% yield following the general conditions B. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 7.26 – 7.20 (m, 3H), 4.29 (t, *J* = 7.0 Hz, 2H), 4.00 (dd, *J* = 30.5, 6.9 Hz, 2H), 2.94 (t, *J* = 7.0 Hz, 2H), 2.28 (t, *J* = 7.5 Hz, 2H), 1.99 – 1.87 (m, 2H), 1.84 – 1.73 (m, 2H), 1.65 – 1.50 (m, 4H), 1.29 (s, 18H), 0.89 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.85, 138.00, 129.03, 128.60, 126.66, 66.27, 66.21, 65.74, 65.69, 64.85, 35.28, 34.89, 34.80, 34.55, 34.52, 34.41, 31.98, 29.54, 29.53, 29.35, 29.19, 29.17, 29.10, 28.95, 26.86, 26.79, 26.23, 26.15, 24.99, 22.80, 14.25. **HRMS** Calcd for $C_{26}H_{43}Cl_2O_2$ [M+H$^+$]: 457.2635; Found: 457.2634.



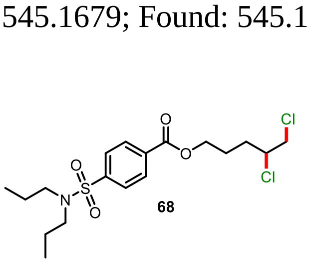
66 (dr = 1:1)

Compound **66** was isolated in 66% yield following the general conditions B. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.62 (t, 1H), 4.40 (s, 1H), 4.27 (t, *J* = 5.4 Hz, 2H), 4.10 – 4.03 (m, 1H), 3.81 (dd, *J* = 11.3, 4.5 Hz, 1H), 3.64 (dd, *J* = 11.3, 8.3 Hz, 1H), 3.48 (dd, *J* = 8.4, 3.0 Hz, 2H), 2.18 – 2.10 (m, 1H), 2.05 – 1.96 (m, 1H), 1.89 – 1.75 (m, 2H), 1.62 (s, 3H), 1.43 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.83, 167.08, 65.69, 63.43, 62.84, 61.26, 60.15, 60.02, 47.83, 47.76, 38.51, 31.63, 31.53, 25.15, 25.08, 20.57, 20.55, 18.81. **HRMS** Calcd for $C_{13}H_{19}Cl_2NNaO_5S$ [M+Na$^+$]: 394.0253; Found: 394.0253.



67 (dr = 1:1)

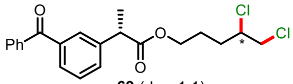
Alkene (**67s**) (0.2 mmol, 1.0 equiv), $NaNO_2$ (0.2 mmol, 1.0 equiv) and HCl (100 *u*L, aq. 37% in water) were dispersed in PhCl (2.0 mL) in a 4 mL glass vial at room temperature. The reaction vial was sealed with a PTEF cap and the reaction mixture vigorously stirred at 30 °C under the 24 W blue LEDs irradiation for 0.5 h (It is worth noting that 24 W blue LEDs was positioned 5 cm aside from the reaction vials.). Then, the reaction mixture was extracted with CH_2Cl_2 (3 × 2 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by chromatography on silica gel to afford the desired dichlorination products. Compound **67** was isolated in 51% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.79 (d, *J* = 9.8 Hz, 1H), 5.43 (s, 1H), 4.21 – 4.10 (m, 2H), 4.10 – 4.02 (m, 1H), 3.78 (dd, *J* = 11.3, 3.7 Hz, 1H), 3.66 (dd, *J* = 11.3, 7.6 Hz, 1H), 2.76 – 2.70 (m, 2H), 2.70 – 2.52 (m, 3H), 2.37 (td, *J* = 14.0, 3.9 Hz, 1H), 2.11 – 2.01 (m, 2H), 1.96 – 1.86 (m, 2H), 1.82 – 1.69 (m, 4H), 1.43 (s, 3H), 1.37 – 1.25 (m, 5H), 1.05 – 0.98 (m, 1H), 0.96 (d, *J* = 6.0 Hz, 3H), 0.85 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.22, 172.20, 171.30, 171.28, 104.62, 92.35, 91.66, 80.26, 63.96, 63.90, 60.68, 60.54, 58.63, 51.71, 48.24, 45.38, 37.42, 36.36, 34.23, 31.95, 31.78, 31.74, 29.35, 29.02, 26.10, 25.31, 24.73, 22.15, 21.20, 20.35, 18.58, 14.35, 12.20. **HRMS** Calcd for $C_{24}H_{36}Cl_2NaO_8$ [M+Na$^+$]: 545.1679; Found: 545.1685.



68

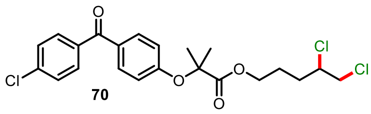
Compound **68** was isolated in 43% yield following the general conditions A. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.3 Hz, 2H), 7.88 (d, *J* = 8.3 Hz, 2H), 4.41 (t, *J* = 5.8 Hz, 2H), 4.16 – 4.08 (m, 1H), 3.82 (dd, *J* = 11.3, 4.8 Hz, 1H), 3.67 (dd, *J* = 11.2, 8.1

Hz, 1H), 3.10 (t, 4H), 2.25 – 2.18 (m, 1H), 2.14 – 2.06 (m, 1H), 1.97 – 1.85 (m, 2H), 1.57 – 1.51 (m, 4H), 0.87 (t, *J* = 7.4 Hz, 6H).[15]



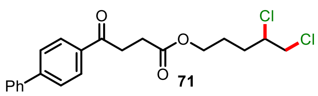
69 (dr = 1:1)

Compound **69** was isolated in 52% yield following the general conditions A. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.3 Hz, 2H), 7.76 (s, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.44 (t, *J* = 7.7 Hz, 1H), 4.17 – 4.09 (m, 2H), 3.99 – 3.93 (m, 1H), 3.83 – 3.77 (m, 1H), 3.71 (dd, *J* = 11.3, 4.9 Hz, 1H), 3.57 (dd, *J* = 11.3, 7.7 Hz, 1H), 2.01 – 1.94 (m, 1H), 1.92 – 1.84 (m, 1H), 1.77 – 1.64 (m, 2H), 1.54 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 196.58, 196.57, 174.09, 140.93, 138.07, 138.06, 137.61, 137.59, 132.66, 132.65, 131.61, 130.18, 129.28, 129.22, 128.69, 128.45, 128.44, 64.12, 64.07, 60.47, 60.46, 48.05, 45.55, 31.67, 31.62, 25.22, 18.45. **HRMS** Calcd for $C_{21}H_{23}Cl_2O_3$ [M+H$^+$]: 393.1019; Found: 393.1020.



70

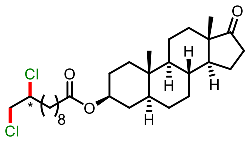
Compound **70** was isolated in 54% yield following the general conditions A. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.7 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.3 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 4.21 (t, *J* = 5.5 Hz, 2H), 3.96 – 3.90 (m, 1H), 3.68 (dd, *J* = 11.3, 4.9 Hz, 1H), 3.51 (dd, *J* = 11.3, 7.9 Hz, 1H), 1.96 – 1.83 (m, 2H), 1.77 – 1.70 (m, 1H), 1.68 (s, 6H), 1.63 – 1.57 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 194.25, 173.78, 159.76, 138.52, 136.44, 132.20, 131.28, 130.52, 128.68, 117.19, 79.51, 64.90, 60.29, 47.95, 31.55, 25.59, 25.16. **HRMS** Calcd for $C_{22}H_{23}Cl_3NaO_4$ [M+Na$^+$]: 479.0554; Found: 479.0555.



71

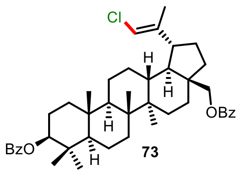
Compound **71** was isolated in 70% yield following the general conditions B. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 1H), 4.23 – 4.12 (m, 2H), 4.11 – 4.01 (m, 1H), 3.77 (dd, *J* = 11.4, 5.1 Hz, 1H), 3.65 (dd, *J* = 11.4, 7.5 Hz, 1H), 3.36 (t, *J*

= 6.5 Hz, 2H), 2.80 (t, *J* = 6.5 Hz, 2H), 2.16 – 2.05 (m, 1H), 2.03 – 1.90 (m, 1H), 1.85 – 1.73 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 197.77, 172.99, 146.09, 139.96, 135.34, 129.10, 128.77, 128.40, 127.42, 127.41, 63.85, 60.67, 48.22, 33.52, 31.78, 28.41, 25.34. **HRMS** Calcd for $C_{21}H_{23}Cl_2O_3$ [M+H$^+$]: 393.1019; Found: 393.1020.



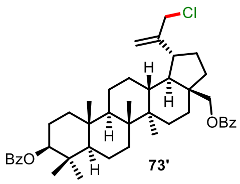
72 (dr = 1:1)

Compound **72** was isolated in 55% yield following the general conditions B. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.73 – 4.65 (m, 1H), 4.06 – 3.99 (m, 1H), 3.75 (dd, *J* = 11.3, 5.2 Hz, 1H), 3.64 (dd, *J* = 11.3, 7.4 Hz, 1H), 2.43 (dd, *J* = 19.3, 8.8 Hz, 1H), 2.25 (t, *J* = 7.5 Hz, 2H), 2.07 (dd, *J* = 19.0, 9.4 Hz, 1H), 2.01 – 1.89 (m, 2H), 1.84 – 1.68 (m, 5H), 1.64 – 1.56 (m, 5H), 1.55 – 1.47 (m, 3H), 1.39 – 1.21 (m, 16H), 1.07 – 0.94 (m, 2H), 0.85 (d, *J* = 2.5 Hz, 6H), 0.71 (td, *J* = 11.4, 3.8 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 221.38, 173.54, 73.37, 61.36, 54.48, 51.53, 48.39, 47.93, 44.82, 36.87, 36.00, 35.82, 35.20, 35.17, 34.86, 34.15, 31.68, 30.97, 29.32, 29.25, 29.18, 29.03, 28.44, 27.61, 25.91, 25.17, 21.93,20.62, 13.97, 12.37. **HRMS** Calcd for $C_{30}H_{48}Cl_2NaO_3$ [M+Na$^+$]: 549.2873; Found: 549.2875.



73

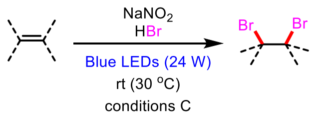
Compound **73** was isolated in 30% yield following the general conditions B. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.09 – 8.02 (m, 4H), 7.59 – 7.52 (m, 2H), 7.48 – 7.42 (m, 4H), 5.84 (s, 0.5H), 5.67 (s, 0.4H), 4.76 – 4.69 (m, 1H), 4.58 (d, *J* = 11.1 Hz, 0.4H), 4.51 (d, *J* = 11.1 Hz, 0.6H), 4.18 – 4.05 (m, 1H), 3.39 – 3.21 (m, 0.4H), 2.66 – 2.56 (m, 0.6H), 2.04 – 1.92 (m, 3H), 1.86 – 1.67 (m, 10H), 1.55 (m, 1H), 1.51 – 1.39 (m, 5H), 1.34 (t, *J* = 13.6 Hz, 3H), 1.23 – 1.17 (m, 1H), 1.09 (d, *J* = 10.8 Hz, 6H), 1.00 (s, 6H), 0.94 – 0.85 (m, 7H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.04, 166.41, 142.86, 142.22, 133.10, 133.04, 132.84, 131.10, 130.55, 130.48, 129.71, 129.68, 129.65, 128.54, 128.51, 128.44, 111.95, 110.90, 81.69, 81.65, 63.52, 63.27, 55.60, 55.56, 50.44, 50.29, 49.01, 48.94, 47.15, 46.96, 46.70, 42.93, 41.05, 40.22, 38.54, 38.34, 37.62, 37.51, 37.28, 37.25, 35.26, 34.83, 34.26, 34.22, 30.29, 30.09, 28.83, 28.25, 27.52, 27.25, 27.17, 25.05, 24.87, 23.89, 21.03, 20.94, 18.32, 17.46, 16.93, 16.31, 16.29, 16.25, 16.19, 14.88, 14.85, 13.44. **HRMS** Calcd for $C_{44}H_{57}ClNaO_4$ [M+Na$^+$]: 707.3838; Found: 707.3840.



73'

Compound **73'** was isolated in 24% yield following the general conditions B. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.05 (t, J = 8.4 Hz, 4H), 7.61 – 7.51 (m, 2H), 7.49 – 7.38 (m, 4H), 5.13 (s, 1H), 5.06 (s, 1H), 4.76 – 4.67 (m, 1H), 4.61 – 4.48 (m, 1H), 4.21 – 4.03 (m, 3H), 2.68 – 2.45 (m, 1H), 2.34 – 2.19 (m, 1H), 2.04 – 1.92 (m, 2H), 1.87 – 1.68 (m, 6H), 1.58 – 1.52 (m, 1H), 1.52 – 1.37 (m, 6H), 1.36 – 1.23 (m, 6H), 1.20 – 1.12 (m, 2H), 1.09 (s, 3H), 1.04 (s, 3H), 1.00 (s, 3H), 0.92 (s, 3H), 0.91 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.05, 166.43, 150.51, 133.07, 132.84, 131.11, 130.52, 129.70, 129.66, 128.54, 128.45, 112.76, 81.68, 63.20, 60.53, 55.58, 50.40, 50.23, 48.58, 46.91, 42.90, 41.13, 38.55, 38.35, 37.71, 37.27, 34.62, 34.31, 32.26, 30.19, 28.26, 27.26, 27.16, 23.89, 21.12, 18.33, 16.94, 16.33, 16.26, 14.95. **HRMS** Calcd for $C_{44}H_{57}ClNaO_4$ [M+Na$^+$]: 707.3838; Found: 707.3822.

6. General procedures and substrate scope of dibromination reactions

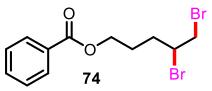


Scheme S20. General procedures and substrate scope of dibromination reactions

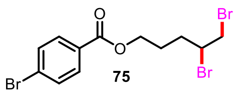
General conditions C: Substrate alkenes (0.2 mmol, 1.0 equiv), $NaNO_2$ (0.2 mmol, 1.0 equiv) and HBr (100 uL, aq. 40% in water) were dispersed in CH_2Cl_2 (2.0 mL) in a 4 mL glass vial at room temperature. The reaction vial was sealed with a PTEF cap and the reaction mixture vigorously stirred at 30 °C under the 24 W blue LEDs irradiation for 12 h (It is worth noting that 24 W blue LEDs was positioned 5 cm aside from the reaction vials.). Then, the reaction mixture was extracted with CH_2Cl_2 (3 × 2 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated.

The residue was purified by chromatography on silica gel to afford the desired dibromination products.

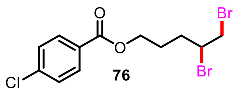
6.1 Visible-light-induced vicinal dibromination of alkenes



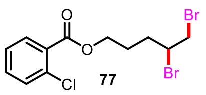
Compound **74** was isolated in 79% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 6.9 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 4.38 (t, *J* = 6.1 Hz, 2H), 4.27 – 4.20 (m, 1H), 3.88 (dd, *J* = 10.3, 4.3 Hz, 1H), 3.65 (t, *J* = 10.1 Hz, 1H), 2.42 – 2.34 (m, 1H), 2.15 – 2.05 (m, 1H), 2.00 – 1.89 (m, 2H).[21]



Compound **75** was isolated in 77% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.3 Hz, 2H), 7.59 (d, *J* = 8.3 Hz, 2H), 4.37 (t, *J* = 6.0 Hz, 2H), 4.26 – 4.19 (m, 1H), 3.88 (dd, *J* = 10.3, 4.2 Hz, 1H), 3.64 (t, *J* = 10.2 Hz, 1H), 2.41 – 2.31 (m, 1H), 2.14 – 2.05 (m, 1H), 1.99 – 1.87 (m, 2H).[22]

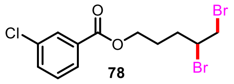


Compound **76** was isolated in 70% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 4.37 (t, *J* = 6.0 Hz, 2H), 4.26 – 4.20 (m, 1H), 3.88 (dd, *J* = 10.3, 4.3 Hz, 1H), 3.64 (t, *J* = 10.2 Hz, 1H), 2.40 – 2.31 (m, 1H), 2.17 – 2.04 (m, 1H), 1.99 – 1.85 (m, 2H).[22]



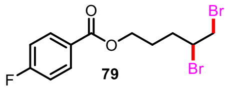
Compound **77** was isolated in 61% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.7 Hz, 1H), 7.50 – 7.39 (m, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 4.39 (t, *J* = 5.8 Hz, 2H), 4.25 – 4.19 (m, 1H), 3.87 (dd, *J* = 10.3, 4.3 Hz, 1H), 3.63 (t, *J* = 10.1 Hz, 1H), 2.42 – 2.36 (m, 1H), 2.13 – 2.04 (m, 1H), 1.99 – 1.85 (m, 2H). **^{13}C**

NMR (126 MHz, $CDCl_3$) δ 165.87, 133.77, 132.71, 131.56, 131.21, 130.24, 126.73, 64.61, 52.08, 36.04, 32.96, 26.33. **HRMS** Calcd for $C_{12}H_{13}Br_2ClNaO_2$ [M+Na$^+$]: 404.8863; Found: 404.8864.



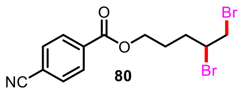
78

Compound **78** was isolated in 62% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.53 (d, *J* = 7.0 Hz, 1H), 7.38 (t, *J* = 7.9 Hz, 1H), 4.38 (t, *J* = 6.2 Hz, 2H), 4.25 – 4.19 (m, 1H), 3.88 (dd, *J* = 10.3, 4.3 Hz, 1H), 3.64 (t, *J* = 10.2 Hz, 1H), 2.40 – 2.31 (m, 1H), 2.13 – 2.04 (m, 1H), 1.98 – 1.88 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.43, 134.73, 133.17, 132.05, 129.87, 129.82, 127.84, 64.40, 51.91, 35.96, 32.83, 26.32. **HRMS** Calcd for $C_{12}H_{13}Br_2{}^{37}ClNaO_2$ [M+Na$^+$]: 406.8833; Found: 406.8836.



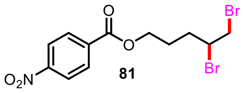
79

Compound **79** was isolated in 63% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 8.7, 5.6 Hz, 2H), 7.11 (t, *J* = 8.6 Hz, 2H), 4.37 (t, *J* = 6.1 Hz, 2H), 4.26 – 4.20 (m, 1H), 3.88 (dd, *J* = 10.3, 4.3 Hz, 1H), 3.64 (t, *J* = 10.2 Hz, 1H), 2.41 – 2.31 (m, 1H), 2.12 – 2.05 (m, 1H), 1.99 – 1.88 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.94, 165.68, 164.92, 132.30, 132.22, 126.53, 126.51, 115.78, 115.61, 64.13, 51.98, 36.00, 32.87, 26.35. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -105.57– -105.61. (m, 1F) **HRMS** Calcd for $C_{12}H_{13}Br_2FNaO_2$ [M+Na$^+$]: 388.9159; Found: 388.9142.



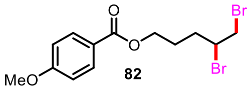
80

Compound **80** was isolated in 66% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.1 Hz, 2H), 7.75 (d, *J* = 8.1 Hz, 2H), 4.41 (t, *J* = 6.0 Hz, 2H), 4.26 – 4.18 (m, 1H), 3.88 (dd, *J* = 10.3, 4.3 Hz, 1H), 3.63 (t, *J* = 10.2 Hz, 1H), 2.42 – 2.31 (m, 1H), 2.16 – 2.07 (m, 1H), 2.01 – 1.86 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.96, 134.03, 132.39, 130.21, 118.06, 116.59, 64.79, 51.75, 35.89, 32.72, 26.19. **HRMS** Calcd for $C_{13}H_{13}Br_2NNaO_2$ [M+Na$^+$]: 395.9205; Found: 395.9207.



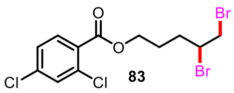
81

Compound **81** was isolated in 76% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.8 Hz, 2H), 8.21 (d, *J* = 8.8 Hz, 2H), 4.43 (t, *J* = 6.1 Hz, 2H), 4.26 – 4.19 (m, 1H), 3.89 (dd, *J* = 10.3, 4.3 Hz, 1H), 3.64 (t, *J* = 10.3 Hz, 1H), 2.41 – 2.32 (m, 1H), 2.18 – 2.06 (m, 1H), 2.02 – 1.89 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.72, 150.71, 135.61, 130.84, 123.72, 64.94, 51.73, 35.88, 32.73, 26.20. **HRMS** Calcd for $C_{12}H_{13}Br_2NNaO_4$ [M+Na$^+$]: 415.9104; Found: 415.9115.



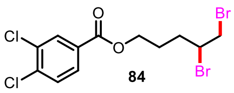
82

Compound **82** was isolated in 70% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 4.34 (t, *J* = 6.0 Hz, 2H), 4.27 – 4.18 (m, 1H), 3.88 (dd, *J* = 10.4, 4.4 Hz, 1H), 3.86 (s, 3H), 3.64 (t, *J* = 10.1 Hz, 1H), 2.42 – 2.29 (m, 1H), 2.17 – 2.02 (m, 1H), 1.99 – 1.83 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.37, 163.51, 131.72, 122.67, 113.76, 63.66, 55.55, 52.15, 36.08, 32.92, 26.39. **HRMS** Calcd for $C_{13}H_{16}{}^{81}Br{}^{79}BrNaO_3$ [M+Na$^+$]: 402.9338; Found: 402.9337.



83

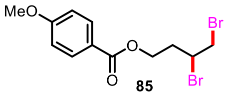
Compound **83** was isolated in 70% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.4 Hz, 1H), 7.47 (s, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 4.39 (t, *J* = 5.7 Hz, 2H), 4.24 – 4.18 (m, 1H), 3.88 (dd, *J* = 10.3, 4.3 Hz, 1H), 3.63 (t, *J* = 10.2 Hz, 1H), 2.42 – 2.32 (m, 1H), 2.12 – 2.03 (m, 1H), 1.99 – 1.87 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.94, 138.53, 135.01, 132.71, 131.17, 128.42, 127.19, 64.81, 51.95, 35.97, 32.91, 26.27. **HRMS** Calcd for $C_{12}H_{12}Br_2Cl_2NaO_2$ [M+Na$^+$]: 438.8473; Found: 438.8454.



84

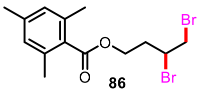
Compound **84** was isolated in 70% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.86 (d, *J* = 8.3 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 4.38 (t, *J* = 6.2 Hz, 2H), 4.25 – 4.19 (m, 1H), 3.88 (dd, *J* = 10.3, 4.3 Hz, 1H), 3.64 (t, *J*

= 10.2 Hz, 1H), 2.39 – 2.32 (m, 1H), 2.13 – 2.05 (m, 1H), 1.98 – 1.88 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.77, 137.81, 133.11, 131.66, 130.71, 130.08, 128.77, 64.59, 51.81, 35.91, 32.73, 26.24. **HRMS** Calcd for $C_{12}H_{13}Br_2Cl_2O_2$ [M+H$^+$]: 416.8654; Found: 416.8656.



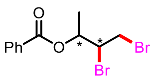
85

Compound **85** was isolated in 57% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 4.60 – 4.53 (m, 1H), 4.48 – 4.42 (m, 1H), 4.39 – 4.30 (m, 1H), 3.92 (dd, J = 10.4, 4.3 Hz, 1H), 3.86 (s, 3H), 3.71 (t, J = 10.0 Hz, 1H), 2.72 – 2.65 (m, 1H), 2.23 – 2.15 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.20, 163.65, 131.80, 122.43, 113.84, 62.19, 55.59, 48.80, 36.30, 35.54. **HRMS** Calcd for $C_{12}H_{14}Br_2NaO_3$ [M+Na$^+$]: 386.9202; Found: 386.9196.



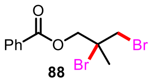
86

Compound **86** was isolated in 35% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.87 (s, 2H), 4.65 – 4.57 (m, 1H), 4.51 – 4.42 (m, 1H), 4.38 – 4.27 (m, 1H), 3.90 (dd, J = 10.4, 4.3 Hz, 1H), 3.66 (t, J = 10.1 Hz, 1H), 2.76 – 2.65 (m, 1H), 2.30 (s, 6H), 2.29 (s, 3H), 2.12 – 2.03 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.99, 139.66, 135.32, 130.72, 128.59, 62.37, 48.72, 36.24, 35.51, 21.27, 20.05. **HRMS** Calcd for $C_{14}H_{18}Br_2NaO_2$ [M+Na$^+$]: 398.9566; Found: 398.9567.



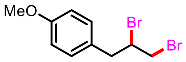
87 (dr = 1:1)

Compound **87** was isolated in 45% yield following the general conditions C (the recovery of starting material is 31%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.07 (t, J = 8.1 Hz, 2H), 7.63 – 7.55 (m, 1H), 7.51 – 7.43 (m, 2H), 5.61 – 5.56 (m, 0.52H), 5.55 – 5.50 (m,0.44H), 4.62 – 4.45 (m, 0.41H), 4.41 – 4.20 (m, 0.49H), 3.86 – 3.64 (m, 2H), 1.52 (d, J = 6.2 Hz, 1.51H), 1.47 (d, J = 6.3 Hz, 1.51H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.43, 165.38, 133.49, 133.45, 129.93, 129.91, 129.84, 129.75, 128.65, 128.61, 70.42, 68.72, 55.38, 54.58, 32.20, 31.91, 19.24, 15.49. **HRMS** Calcd for $C_{11}H_{13}Br_2O_2$ [M+H$^+$]: 334.9277; Found: 334.9277.



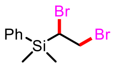
88

Compound **88** was isolated in 30% yield following the general conditions C (the recovery of starting material is 50%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 6.9 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.9 Hz, 2H), 4.65 – 4.54 (m, 2H), 4.09 (d, *J* = 10.5 Hz, 1H), 3.86 (d, *J* = 10.4 Hz, 1H), 1.95 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.72, 133.54, 129.91, 128.69, 69.65, 61.57, 39.37, 27.21. **HRMS** Calcd for $C_{11}H_{13}{}^{81}Br^{79}BrO_2$ [M+H$^+$]: 336.9257; Found: 336.9271.



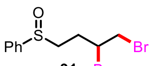
89

Compound **89** was isolated in 17% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.2 Hz, 2H), 6.88 (d, *J* = 8.2 Hz, 2H), 4.39 – 4.28 (m, 1H), 3.84 – 3.78 (m, 4H), 3.61 (t, *J* = 9.7 Hz, 1H), 3.42 (dd, *J* = 14.7, 4.9 Hz, 1H), 3.11 (dd, *J* = 14.7, 7.5 Hz, 1H).[23]



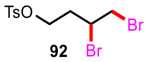
90

Compound **90** was isolated in 67% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.4 Hz, 2H), 7.47 – 7.38 (m, 3H), 3.93 – 3.84 (m, 1H), 3.66 – 3.58 (m, 2H), 0.53 (d, *J* = 3.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 134.50, 134.17, 130.26, 128.30, 42.57, 36.98, -3.23, -4.65. **HRMS** Calcd for $C_{10}H_{15}Br_2Si$ [M+H$^+$]: 320.9304; Found: 320.9313.



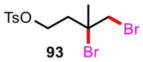
91

Compound **91** was isolated in 62% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 4.42 – 4.34 (m, 1H), 3.86 (dd, *J* = 10.4, 4.3 Hz, 1H), 3.62 (t, *J* = 10.1 Hz, 1H), 3.26 – 3.18 (m, 1H), 3.06 – 2.97 (m, 1H), 2.49 – 2.40 (m, 1H), 2.12 – 2.03 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 135.34, 130.05, 129.18, 126.64, 51.04, 35.98, 35.72, 31.58. **HRMS** Calcd for $C_{10}H_{13}{}^{81}Br^{79}BrOS$ [M+H$^+$]: 340.9028; Found: 340.9028.



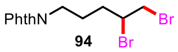
92

Compound **92** was isolated in 50% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 4.29 – 4.24 (m, 1H), 4.23 – 4.17 (m, 2H), 3.82 (dd, *J* = 10.5, 4.3 Hz, 1H), 3.58 (t, 1H), 2.61 – 2.53 (m, 1H), 2.45 (s, 3H), 2.01 – 1.93 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.22, 132.75, 130.10, 128.11, 67.70, 47.65, 36.05, 35.80, 21.80. **HRMS** Calcd for $C_{11}H_{14}Br_2NaO_3S$ [M+Na$^+$]:406.8923; Found: 406.8924.



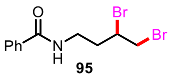
93

Compound **93** was isolated in 43% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.9 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 4.29 (t, *J* = 6.8 Hz, 2H), 3.77 (s, 2H), 2.46 (s, 3H), 2.30 (t, *J* = 6.7 Hz, 2H), 1.83 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.18, 132.97, 130.09, 128.11, 67.91, 63.51, 42.57, 40.78, 30.80, 21.81. **HRMS** Calcd for $C_{12}H_{16}{}^{81}Br^{79}BrNaO_3S$ [M+Na$^+$]: 422.9059; Found: 422.9057.



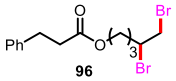
94

Compound **94** was isolated in 66% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 – 7.81 (m, 2H), 7.79 – 7.69 (m, 2H), 4.28 – 4.16 (m, 1H), 3.85 – 3.79 (m, 1H), 3.73 (t, 2H), 3.59 (t, *J* = 10.0 Hz, 1H), 2.28 – 2.17 (m, 1H), 2.06 – 1.97 (m, 1H), 1.90 – 1.78 (m, 2H).[24]



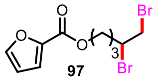
95

Compound **95** was isolated in 60% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 6.50 (br, 1H), 4.28 – 4.19 (m, 1H), 3.88 (dd, *J* = 10.5, 4.5 Hz, 1H), 3.78 – 3.70 (m, 1H), 3.67 (t, *J* = 9.9 Hz, 1H), 3.64 – 3.56 (m, 1H), 2.65 – 2.56 (m, 1H), 2.10 – 2.00 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.87, 134.38, 131.76, 128.76, 127.03, 50.17, 38.35, 36.38, 36.19. **HRMS** Calcd for $C_{11}H_{14}Br_2NO$ [M+H$^+$]: 333.9437; Found: 333.9442.



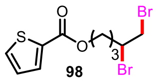
96

Compound **96** was isolated in 55% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.23 – 7.19 (m, 3H), 4.17 – 4.09 (m, 3H), 3.84 (dd, *J* = 10.3, 4.4 Hz, 1H), 3.60 (t, *J* = 10.1 Hz, 1H), 2.96 (t, *J* = 7.8 Hz, 2H), 2.65 (t, *J* = 7.8 Hz, 2H), 2.25 – 2.16 (m, 1H), 1.95 – 1.87 (m, 1H), 1.83 – 1.70 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.96, 140.55, 128.64, 128.40, 126.42, 63.49, 52.13, 36.09, 35.96, 32.79, 31.09, 26.29. **HRMS** Calcd for $C_{14}H_{18}Br_2NaO_2$ [M+Na$^+$]: 398.9566; Found: 398.9566.



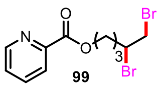
97

Compound **97** was isolated in 69% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 1.6 Hz, 1H), 7.18 (d, *J* = 3.5 Hz, 1H), 6.53 – 6.50 (m, 1H), 4.35 (t, *J* = 6.0 Hz, 2H), 4.25 – 4.18 (m, 1H), 3.87 (dd, *J* = 10.3, 4.3 Hz, 1H), 3.63 (t, *J* = 10.1 Hz, 1H), 2.37 – 2.30 (m, 1H), 2.10 – 2.03 (m, 1H), 1.94 – 1.87 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.74, 146.52, 144.66, 118.14, 111.97, 63.94, 52.03, 36.06, 32.81, 26.37. **HRMS** Calcd for $C_{10}H_{12}Br_2NaO_3$ [M+Na$^+$]: 360.9045; Found: 360.9050.



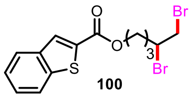
98

Compound **98** was isolated in 67% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 3.8, 1.3 Hz, 1H), 7.56 (dd, *J* = 4.9, 1.3 Hz, 1H), 7.10 (dd, *J* = 5.0, 3.7 Hz, 1H), 4.37 – 4.33 (m, 2H), 4.26 – 4.20 (m, 1H), 3.87 (dd, *J* = 10.3, 4.4 Hz, 1H), 3.64 (t, *J* = 10.1 Hz, 1H), 2.39 – 2.31 (m, 1H), 2.09 – 2.03 (m, 1H), 1.97 – 1.88 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.26, 133.76, 133.62, 132.60, 127.91, 64.14, 52.05, 36.05, 32.85, 26.35. **HRMS** Calcd for $C_{10}H_{12}Br_2NaO_2S$ [M+Na$^+$]: 376.8817; Found: 376.8816.



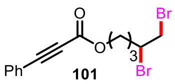
99

Compound **99** was isolated in 80% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.74 (d, *J* = 4.7 Hz, 1H), 8.10 (d, *J* = 7.9 Hz, 1H), 7.83 (t, *J* = 7.7 Hz, 1H), 7.46 (dd, *J* = 7.6, 4.7 Hz, 1H), 4.45 (t, *J* = 6.3 Hz, 2H), 4.25 – 4.17 (m, 1H), 3.84 (dd, J = 10.3, 4.3 Hz, 1H), 3.61 (t, J = 10.0 Hz, 1H), 2.38 – 2.27 (m, 1H), 2.17 – 2.04 (m, 1H), 1.98 – 1.87 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.15, 150.00, 148.00, 137.11, 127.03, 125.24, 64.87, 52.02, 36.08, 32.74, 26.34. **HRMS** Calcd for $C_{11}H_{14}Br_2NO_2$ [M+H$^+$]: 349.9386; Found: 349.9394.



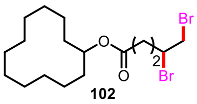
100

Compound **100** was isolated in 76% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.59 (d, J = 8.1 Hz, 1H), 8.40 (s, 1H), 7.88 (d, J = 8.1 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 7.41 (t, J = 7.5 Hz, 1H), 4.43 (t, J = 5.8 Hz, 2H), 4.29 – 4.23 (m, 1H), 3.90 (dd, J = 10.3, 4.3 Hz, 1H), 3.66 (t, J = 10.2 Hz, 1H), 2.46 – 2.36 (m, 1H), 2.16 – 2.09 (m, 1H), 2.03 – 1.92 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.80, 140.17, 136.87, 136.78, 127.19, 125.60, 125.17, 124.84, 122.65, 63.69, 52.03, 36.00, 32.97, 26.38. **HRMS** Calcd for $C_{14}H_{14}Br_2NaO_2S$ [M+Na$^+$]: 426.8973; Found: 426.8975.



101

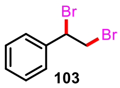
Compound **101** was isolated in 50% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60 (d, J = 6.8 Hz, 2H), 7.46 (t, J = 7.5 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 4.29 (t, J = 5.9 Hz, 2H), 4.24 – 4.17 (m, 1H), 3.88 (dd, J = 10.4, 4.4 Hz, 1H), 3.64 (t, J = 10.1 Hz, 1H), 2.36 – 2.28 (m, 1H), 2.10 – 1.99 (m, 1H), 1.96 – 1.82 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.16, 133.17, 130.85, 128.73, 119.69, 86.76, 80.61, 65.12, 52.02, 36.06, 32.82, 26.29. **HRMS** Calcd for $C_{14}H_{14}Br_2NaO_2$ [M+Na$^+$]: 394.9253; Found: 394.9249.



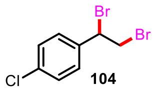
102

Compound **102** was isolated in 39% yield following the general conditions C (the recovery of starting material is 42%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.07 – 4.99 (m, 1H), 4.28 – 4.21 (m, 1H), 3.87 (dd, J = 10.5, 4.3 Hz, 1H), 3.62 (t, J = 10.0 Hz, 1H), 2.61 – 2.44 (m, 3H), 2.07 – 1.95 (m, 1H), 1.75 – 1.67 (m, 2H), 1.53 – 1.46 (m, 2H), 1.41 – 1.29 (m, 18H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.13, 72.88, 51.84, 36.11, 32.26, 31.72, 29.25, 24.23, 24.00, 23.52, 23.51, 23.35, 21.08. **HRMS** Calcd for

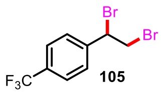
$C_{17}H_{30}Br_2NaO_2$ [M+Na$^+$]: 447.0505; Found: 447.0501.



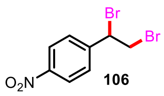
Compound **103** was isolated in 49% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 – 7.33 (m, 5H), 5.15 (dd, *J* = 10.7, 5.4 Hz, 1H), 4.12 – 4.01 (m, 2H).[25]



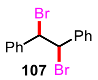
Compound **104** was isolated in 57% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 4H), 5.11 (dd, *J* = 11.1, 5.0 Hz, 1H), 4.07 (dd, *J* = 10.3, 5.1 Hz, 1H), 3.97 (t, *J* = 10.7 Hz, 1H).[25]



Compound **105** was isolated in 57% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.1 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 5.15 (dd, *J* = 11.1, 5.0 Hz, 1H), 4.09 (dd, *J* = 10.4, 5.0 Hz, 1H), 4.00 (t, *J* = 10.8 Hz, 1H).[26]

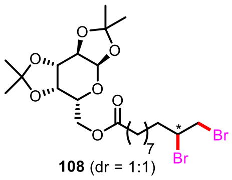


Compound **106** was isolated in 67% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.8 Hz, 2H), 7.58 (d, *J* = 8.8 Hz, 2H), 5.17 (dd, *J* = 11.3, 4.9 Hz, 1H), 4.09 (dd, *J* = 10.5, 4.9 Hz, 1H), 3.98 (t, *J* = 10.9 Hz, 1H).[27]



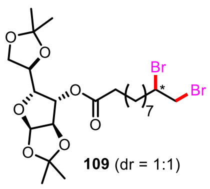
Compound **107** was isolated in 27% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.18 (m, 10H), 5.48 (s, 2H).[28]

6.2 Visible-light-induced vicinal dibromination of natural products and drug derivatives



108 (dr = 1:1)

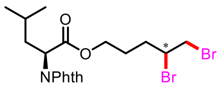
Alkene (**50s**) (0.2 mmol, 1.0 equiv), $NaNO_2$ (0.2 mmol, 1.0 equiv) and HBr (100 *u*L, aq. 40% in water) were dispersed in CH_2Cl_2 (2.0 mL) in a 4 mL glass vial at room temperature. The reaction vial was sealed with a PTEF cap and the reaction mixture vigorously stirred at 30 °C under the 24 W blue LEDs irradiation for 0.5 h (It is worth noting that 24 W blue LEDs was positioned 5 cm aside from the reaction vials.). Then, the reaction mixture was extracted with CH_2Cl_2 (3 × 2 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by chromatography on silica gel to afford the desired dibromination products. Compound **108** was isolated in 67% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.51 (d, J = 5.0 Hz, 1H), 4.59 (d, J = 5.4 Hz, 1H), 4.29 (dd, J = 11.5, 3.8 Hz, 2H), 4.21 (d, J = 6.1 Hz, 1H), 4.18 – 4.11 (m, 2H), 4.02 – 3.97 (m, 1H), 3.82 (dd, J = 10.2, 4.4 Hz, 1H), 3.60 (t, J = 10.0 Hz, 1H), 2.31 (t, J = 7.5 Hz, 2H), 2.15 – 2.06 (m, 1H), 1.81 – 1.71 (m, 1H), 1.62 – 1.57 (m, 2H), 1.56 – 1.51 (m, 1H), 1.48 (s, 3H), 1.43 (s, 3H), 1.41 – 1.36 (m, 1H), 1.31 (d, J = 3.8 Hz, 6H), 1.30 – 1.19 (m, 8H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.81, 109.71, 108.83, 96.40, 71.18, 70.79, 70.54, 66.12, 63.33, 53.20, 36.45, 36.09, 34.27, 29.25, 29.24, 29.11, 28.83, 26.81, 26.13, 26.06, 25.09, 25.03, 24.59. **HRMS** Calcd for $C_{23}H_{39}Br_2O_7$ [M+H$^+$]: 585.1057; Found: 585.1059.



109 (dr = 1:1)

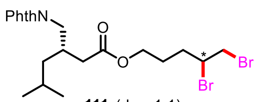
Alkene (**51s**) (0.2 mmol, 1.0 equiv), $NaNO_2$ (0.2 mmol, 1.0 equiv) and HBr (100 *u*L, aq. 40% in water) were dispersed in CH_2Cl_2 (2.0 mL) in a 4 mL glass vial at room temperature. The reaction vial was sealed with a PTEF cap and the reaction mixture vigorously stirred at 30 °C under the 24 W blue LEDs irradiation for 0.5 h (It is worth noting that 24 W blue LEDs was positioned 5 cm aside from the reaction vials.). Then, the reaction mixture was extracted with CH_2Cl_2 (3 × 2 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by chromatography on silica gel to afford the desired dibromination products.

Compound **109** was isolated in 70% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.86 (d, *J* = 3.7 Hz, 1H), 5.25 (s, 1H), 4.46 (d, *J* = 3.7 Hz, 1H), 4.23 – 4.18 (m, 2H), 4.18 – 4.11 (m, 1H), 4.10 – 4.05 (m, 1H), 4.03 – 3.98 (m, 1H), 3.84 (dd, *J* = 10.2, 4.4 Hz, 1H), 3.61 (t, *J* = 10.0 Hz, 1H), 2.33 (td, *J* = 7.4, 3.1 Hz, 2H), 2.16 – 2.07 (m, 1H), 1.81 – 1.72 (m, 1H), 1.65 – 1.58 (m, 2H), 1.58 – 1.53 (m, 1H), 1.51 (s, 3H), 1.43 – 1.37 (m, 4H), 1.35 – 1.25 (m, 14H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.46, 112.41, 109.44, 105.19, 83.53, 80.00, 75.97, 72.57, 67.42, 53.18, 36.44, 36.09, 34.36, 29.28, 29.23, 29.10, 28.85, 26.96, 26.87, 26.82, 26.35, 25.42, 24.96. **HRMS** Calcd for $C_{23}H_{38}Br_2NaO_7$ [M+Na$^+$]: 607.0876; Found: 607.0886.



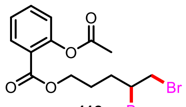
110 (dr = 1:1)

Compound **110** was isolated in 60% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.73 (dd, *J* = 5.5, 3.1 Hz, 2H), 4.94 (dd, *J* = 11.5, 4.4 Hz, 1H), 4.24 – 4.12 (m, 2H), 4.12 – 4.03 (m, 1H), 3.79 – 3.74 (m, 1H), 3.51 (t, *J* = 9.1 Hz, 1H), 2.36 – 2.28 (m, 1H), 2.19 – 2.10 (m, 1H), 2.00 – 1.93 (m, 1H), 1.91 – 1.83 (m, 1H), 1.79 – 1.67 (m, 2H), 1.55 – 1.43 (m, 1H), 0.94 (d, *J* = 6.6 Hz, 3H), 0.92 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.82, 167.82, 134.31, 131.89, 123.67, 64.72, 51.88, 51.84, 50.75, 37.40, 35.94, 35.91, 32.59, 25.98, 25.16, 23.28, 21.15. **HRMS** Calcd for $C_{19}H_{24}Br_2NO_4$ [M+H$^+$]: 488.0067; Found: 488.0071.



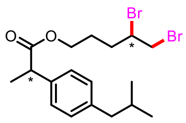
111 (dr = 1:1)

Compound **111** was isolated in 63% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.71 (dd, *J* = 5.5, 3.1 Hz, 2H), 4.19 – 4.07 (m, 1H), 4.04 – 3.89 (m, 2H), 3.84 (dd, *J* = 10.3, 4.4 Hz, 1H), 3.69 (dd, *J* = 13.9, 5.6 Hz, 1H), 3.64 – 3.57 (m, 2H), 2.50 – 2.41 (m, 1H), 2.35 – 2.26 (m, 2H), 2.25 – 2.16 (m, 1H), 1.91 – 1.65 (m, 4H), 1.24 – 1.18 (m, 2H), 0.94 (d, *J* = 6.5 Hz, 3H), 0.88 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.54, 168.68, 134.08, 132.09, 123.36, 63.42, 63.39, 58.52, 52.22, 52.22, 42.01, 41.86, 37.70, 36.18, 32.81, 32.80, 26.22, 25.39, 22.81, 22.69. **HRMS** Calcd for $C_{21}H_{28}Br_2NO_4$ [M+H$^+$]: 516.0380; Found: 516.0382.



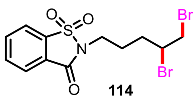
112

Compound **112** was isolated in 61% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.9 Hz, 1H), 7.56 (t, *J* = 6.9 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 4.32 (t, *J* = 5.3 Hz, 2H), 4.26 – 4.17 (m, 1H), 3.87 (dd, *J* = 10.4, 4.4 Hz, 1H), 3.64 (t, *J* = 10.1 Hz, 1H), 2.36 (s, 3H), 2.35 – 2.27 (m, 1H), 2.12 – 2.01 (m, 1H), 1.97 – 1.83 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.80, 164.45, 150.90, 134.09, 131.79, 126.19, 123.98, 123.30, 64.15, 52.11, 36.11, 32.85, 26.39, 21.24. **HRMS** Calcd for $C_{14}H_{16}Br_2NaO_4$ [M+Na$^+$]: 428.9308; Found: 428.9308.



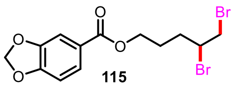
113 (dr = 1:1)

Compound **113** was isolated in 43% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.20 (d, *J* = 7.7 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 4.17 – 4.05 (m, 3H), 3.78 (dd, *J* = 10.3, 4.4 Hz, 1H), 3.74 – 3.66 (m, 1H), 3.53 (t, *J* = 10.0 Hz, 1H), 2.45 (d, *J* = 7.2 Hz, 2H), 2.16 – 2.08 (m, 1H), 1.93 – 1.79 (m, 2H), 1.77 – 1.66 (m, 2H), 1.50 (d, *J* = 7.1 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.80, 174.79, 140.71, 140.71, 137.80, 129.50, 129.50, 127.30, 63.69, 63.61, 52.16, 52.14, 45.30, 45.17, 36.11, 32.80, 32.72, 30.32, 26.23, 26.22, 22.54, 18.47. **HRMS** Calcd for $C_{18}H_{26}Br_2NaO_2$ [M+Na$^+$]: 455.0192; Found: 455.0194.



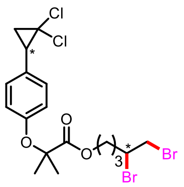
114

Compound **114** was isolated in 63% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.4 Hz, 1H), 7.93 (d, *J* = 7.5 Hz, 1H), 7.87 (t, *J* = 7.3 Hz, 1H), 7.84 (t, *J* = 7.4 Hz, 1H), 4.24 – 4.18 (m, 1H), 3.89 – 3.80 (m, 3H), 3.62 (t, *J* = 10.0 Hz, 1H), 2.34 – 2.26 (m, 1H), 2.22 – 2.13 (m, 1H), 2.04 – 1.87 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.13, 137.74, 134.95, 134.52, 127.39, 125.35, 121.11, 51.68, 38.51, 36.12, 33.36, 26.13. **HRMS** Calcd for $C_{12}H_{13}Br_2NNaO_3S$ [M+Na$^+$]: 431.8875; Found: 431.8875.



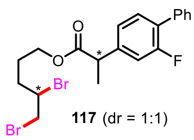
115

Compound **115** was isolated in 63% yield following the general conditions C. ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.2 Hz, 1H), 7.46 (s, 1H), 6.83 (d, *J* = 8.1 Hz, 1H), 6.03 (s, 2H), 4.33 (t, *J* = 6.1 Hz, 2H), 4.25 – 4.19 (m, 1H), 3.87 (dd, *J* = 10.3, 4.3 Hz, 1H), 3.64 (t, *J* = 10.2 Hz, 1H), 2.39 – 2.28 (m, 1H), 2.11 – 1.99 (m, 1H), 1.96 – 1.85 (m, 2H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 165.98, 151.79, 147.87, 125.49, 124.27, 109.62, 108.13, 101.95, 63.92, 52.10, 36.06, 32.90, 26.38. **HRMS** Calcd for $C_{13}H_{14}Br_2NaO_4$ [M+Na$^+$]: 414.9151; Found: 414.9153.



116 (dr = 1:1)

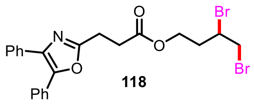
Compound **116** was isolated in 68% yield following the general conditions C. ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.1 Hz, 2H), 6.79 (d, *J* = 8.2 Hz, 2H), 4.18 (t, *J* = 6.0 Hz, 2H), 4.13 – 4.03 (m, 1H), 3.76 (dd, *J* = 10.3, 4.4 Hz, 1H), 3.50 (t, *J* = 10.0 Hz, 1H), 2.85 – 2.79 (m, 1H), 2.11 – 2.03 (m, 1H), 1.96 – 1.84 (m, 2H), 1.79 – 1.66 (m, 3H), 1.60 (s, 6H).^{13}**C NMR** (126 MHz, $CDCl_3$) δ 174.18, 155.01, 129.75, 128.10, 118.38, 79.14, 64.40, 60.96, 51.99, 36.04, 34.85, 32.61, 26.11, 25.90, 25.52. **HRMS** Calcd for $C_{18}H_{22}{}^{81}Br^{79}BrCl_2NaO_3$ [M+Na$^+$]: 538.9185; Found: 538.9185.



117 (dr = 1:1)

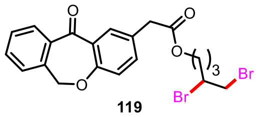
Compound **117** was isolated in 74% yield following the general conditions C. ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.6 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.43 – 7.34 (m, 2H), 7.16 (dd, *J* = 14.4, 9.8 Hz, 2H), 4.23 – 4.14 (m, 2H), 4.14 – 4.07 (m, 1H), 3.81 (dd, *J* = 10.2, 4.3 Hz, 1H), 3.77 (t, *J* = 7.2 Hz, 1H), 3.55 (t, *J* = 10.2 Hz, 1H), 2.18 (t, *J* = 9.9 Hz, 1H), 1.98 – 1.87 (m, 1H), 1.82 – 1.72 (m, 2H), 1.56 (d, *J* = 7.2 Hz, 3H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 173.99, 160.80, 158.82, 141.86, 141.80, 135.57, 130.99, 130.96, 129.08, 129.06, 128.58, 127.80, 123.70, 123.68, 115.48, 115.29, 64.03, 63.95, 51.98, 51.95, 45.17, 35.98, 35.96, 32.78, 32.69, 26.18, 18.34. ^{19}**F NMR** (471 MHz, $CDCl_3$) δ -117.48(q, J = 9.4 Hz). **HRMS** Calcd for $C_{20}H_{21}{}^{81}Br^{79}BrFNaO_2$ [M+Na$^+$]: 494.9765;

Found: 494.9766.



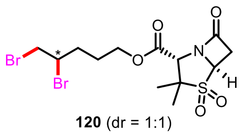
118

Compound **118** was isolated in 68% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.64 (d, J = 7.5 Hz, 2H), 7.58 (d, J = 7.5 Hz, 2H), 7.39 – 7.29 (m, 6H), 4.43 – 4.36 (m, 1H), 4.35 – 4.27 (m, 1H), 4.27 – 4.21 (m, 1H), 3.77 (dd, J = 10.5, 4.3 Hz, 1H), 3.57 (t, J = 10.0 Hz, 1H), 3.20 (t, J = 7.4 Hz, 2H), 2.94 (t, J = 7.4 Hz, 2H), 2.58 – 2.49 (m, 1H), 2.08 – 2.00 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.77, 161.65, 145.51, 135.17, 132.46, 128.98, 128.71, 128.61, 128.54, 128.13, 127.94, 126.54, 62.21, 48.55, 36.27, 35.25, 31.05, 23.52. **HRMS** Calcd for $C_{22}H_{22}{}^{81}Br^{79}BrNO_3$ [M+H$^+$]: 507.9941; Found: 507.9949.



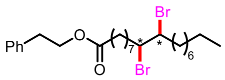
119

Compound **119** was isolated in 67% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.87 (d, J = 7.7 Hz, 1H), 7.54 (t, J = 7.4 Hz, 1H), 7.46 (d, J = 7.6 Hz, 1H), 7.44 – 7.40 (m, 1H), 7.34 (d, J = 7.4 Hz, 1H), 7.02 (d, J = 8.3 Hz, 1H), 5.16 (s, 2H), 4.21 – 4.08 (m, 3H), 3.81 (dd, J = 10.3, 4.3 Hz, 1H), 3.64 (s, 2H), 3.57 (t, J = 10.0 Hz, 1H), 2.26 – 2.13 (m, 1H), 1.96 – 1.87 (m, 1H), 1.85 – 1.71 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 190.83, 171.34, 160.53, 140.47, 136.38, 135.59, 132.84, 132.50, 129.55, 129.31, 127.88, 127.80, 125.22, 121.17, 73.67, 63.96, 52.08, 40.35, 36.09, 32.74, 26.16. **HRMS** Calcd for $C_{21}H_{21}Br_2O_4$ [M+H$^+$]: 494.9801; Found: 494.9806.



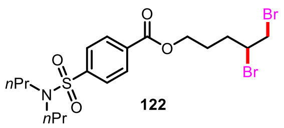
120 (dr = 1:1)

Alkene (**66s**) (0.2 mmol, 1.0 equiv), $NaNO_2$ (0.2 mmol, 1.0 equiv) and HBr (100 *u*L, aq. 40% in water) were dispersed in PhCl (2.0 mL) in a 4 mL glass vial at room temperature. The reaction vial was sealed with a PTEF cap and the reaction mixture vigorously stirred at 30 °C under the 24 W blue LEDs irradiation for 0.5 h (It is worth noting that 24 W blue LEDs was positioned 5 cm aside from the reaction vials.). Then, the reaction mixture was extracted with CH_2Cl_2 (3 × 2 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by chromatography on silica gel to afford the desired dibromination products. Compound **120** was isolated in 26% yield (the recovery of starting material is 60%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.64 – 4.61 (m, 1H), 4.40 (s, 1H), 4.28 (t, J = 6.0 Hz, 2H), 4.21 – 4.14 (m, 1H), 3.89 (dd, J = 10.3, 4.2 Hz, 1H), 3.62 (t, J = 10.4 Hz, 1H), 3.48 (dd, J = 8.2, 3.2 Hz, 2H), 2.35 – 2.27 (m, 1H), 2.04 – 1.97 (m, 1H), 1.92 – 1.82 (m, 2H), 1.63 (s, 3H), 1.44 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.81, 167.08, 65.56, 65.54, 63.43, 62.84, 62.83, 61.26, 51.50, 51.37, 38.51, 35.77, 35.72, 32.72, 32.61, 26.14, 26.06, 20.60, 20.59, 18.84. **HRMS** Calcd for $C_{13}H_{19}{}^{81}Br^{79}Br\ NNaO_5S$ [M+Na$^+$]: 483.9223; Found: 483.9224.



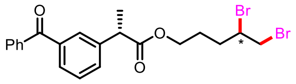
121 (dr = 1:1)

Compound **121** was isolated in 61% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31 (t, J = 7.4 Hz, 2H), 7.27 – 7.20 (m, 3H), 4.29 (t, J = 7.1 Hz, 2H), 4.25 – 4.19 (m, 2H), 2.94 (t, J = 7.0 Hz, 2H), 2.29 (t, J = 7.5 Hz, 2H), 2.12 – 2.00 (m, 2H), 1.90 – 1.78 (m, 2H), 1.64 – 1.53 (m, 4H), 1.42 – 1.26 (m, 18H), 0.89 (t, J = 6.7 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.77, 137.96, 128.98, 128.56, 126.62, 64.79, 59.87, 59.80, 35.25, 34.97, 34.94, 34.36, 31.93, 29.47, 29.31, 29.11, 29.06, 28.93, 28.71, 27.92, 27.84, 24.95, 22.76, 14.22. **HRMS** Calcd for $C_{26}H_{42}Br_2NaO_2$ [M+Na$^+$]: 567.1444; Found: 567.1445.



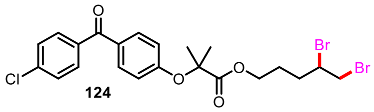
122

Compound **122** was isolated in 60% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.15 (d, J = 8.5 Hz, 2H), 7.87 (d, J = 8.5 Hz, 2H), 4.41 (t, J = 6.1 Hz, 2H), 4.28 – 4.18 (m, 1H), 3.88 (dd, J = 10.3, 4.3 Hz, 1H), 3.64 (t, J = 10.2 Hz, 1H), 3.12 – 3.07 (m, 4H), 2.40 – 2.33 (m, 1H), 2.15 – 2.04 (m, 1H), 1.99 – 1.89 (m, 2H), 1.58 – 1.50 (m, 4H), 0.86 (t, J = 7.4 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.26, 144.44, 133.49, 130.32, 127.13, 64.62, 51.83, 50.02, 35.94, 32.77, 26.23, 22.03, 11.26. **HRMS** Calcd for $C_{18}H_{28}Br_2NO_4S$ [M+H$^+$]: 512.0100; Found: 512.0108.



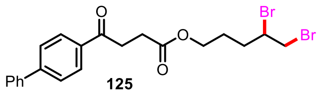
123 (dr = 1:1)

Compound **123** was isolated in 64% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.7 Hz, 2H), 7.76 (s, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.44 (t, *J* = 7.7 Hz, 1H), 4.15 – 4.06 (m, 3H), 3.87 – 3.75 (m, 2H), 3.54 (t, *J* = 10.1 Hz, 1H), 2.24 – 2.06 (m, 1H), 1.97 – 1.82 (m, 1H), 1.80 – 1.65 (m, 2H), 1.54 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 196.50, 174.03, 140.88, 138.02, 137.57, 132.60, 131.61, 130.16, 129.27, 129.18, 128.68, 128.41, 63.94, 63.89, 52.00, 45.51, 36.04, 32.71, 32.65, 26.16, 18.44. **HRMS** Calcd for $C_{21}H_{23}Br_2O_3$ [M+H$^+$]: 481.0008; Found: 481.0011.



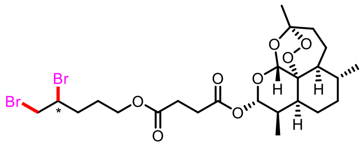
124

Compound **124** was isolated in 67% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.8 Hz, 2H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 4.20 (t, *J* = 6.1 Hz, 2H), 4.09 – 4.01 (m, 1H), 3.77 (dd, *J* = 10.4, 4.3 Hz, 1H), 3.49 (t, *J* = 10.2 Hz, 1H), 2.16 – 2.02 (m, 1H), 1.96 – 1.85 (m, 1H), 1.79 – 1.70 (m, 1H), 1.68 (s, 6H), 1.67 – 1.58 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 194.17, 173.70, 159.71, 138.44, 136.40, 132.17, 131.25, 130.46, 128.63, 117.21, 79.46, 64.72, 51.79, 35.94, 32.61, 26.13, 25.56. **HRMS** Calcd for $C_{22}H_{24}Br_2ClO_4$ [M+H$^+$]: 544.9724; Found: 544.9734.



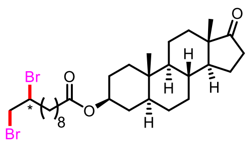
125

Compound **125** was isolated in 62% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 6.8 Hz, 2H), 7.69 (d, *J* = 7.9 Hz, 2H), 7.63 (d, *J* = 7.5 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 4.22 – 4.10 (m, 3H), 3.85 (dd, *J* = 10.6, 4.4 Hz, 1H), 3.61 (t, *J* = 10.0 Hz, 1H), 3.35 (t, *J* = 6.5 Hz, 2H), 2.80 (t, *J* = 6.5 Hz, 2H), 2.32 – 2.21 (m, 1H), 2.01 – 1.91 (m, 1H), 1.90 – 1.72 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 197.72, 172.95, 146.04, 139.93, 135.32, 129.08, 128.76, 128.38, 127.39, 63.70, 52.23, 36.19, 33.51, 32.83, 28.41, 26.29. **HRMS** Calcd for $C_{21}H_{23}Br_2O_3$ [M+H$^+$]: 481.0008; Found: 481.0013.



126 (dr = 1:1)

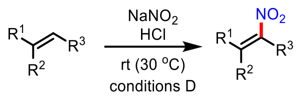
Alkene (**67s**) (0.2 mmol, 1.0 equiv), $NaNO_2$ (0.2 mmol, 1.0 equiv) and HBr (100 *u*L, aq. 40% in water) were dispersed in PhCl (2.0 mL) in a 4 mL glass vial at room temperature. The reaction vial was sealed with a PTEF cap and the reaction mixture vigorously stirred at 30 °C under the 24 W blue LEDs irradiation for 0.5 h (It is worth noting that 24 W blue LEDs was positioned 5 cm aside from the reaction vials.). Then, the reaction mixture was extracted with CH_2Cl_2 (3 × 2 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by chromatography on silica gel to afford the desired dibromination products. Compound **126** was isolated in 61% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.79 (d, *J* = 9.8 Hz, 1H), 5.43 (s, 1H), 4.23 – 4.08 (m, 3H), 3.86 (dd, *J* = 10.4, 4.5 Hz, 1H), 3.63 (t, *J* = 10.0 Hz, 1H), 2.75 – 2.71 (m, 2H), 2.70 – 2.66 (m, 1H), 2.65 – 2.59 (m, 1H), 2.59 – 2.52 (m, 1H), 2.37 (td, *J* = 14.0, 4.0 Hz, 1H), 2.28 – 2.21 (m, 1H), 2.05 – 2.00 (m, 1H), 1.98 – 1.84 (m, 3H), 1.81 – 1.75 (m, 2H), 1.73 – 1.69 (m, 1H), 1.63 – 1.58 (m, 1H), 1.50 – 1.44 (m, 1H), 1.43 (s, 3H), 1.39 – 1.35 (m, 1H), 1.34 – 1.28 (m, 2H), 1.05 – 0.98 (m, 1H), 0.96 (d, *J* = 6.1 Hz, 3H), 0.85 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.19, 172.18, 171.25, 104.60, 92.33, 91.64, 80.25, 63.80, 63.77, 52.23, 51.70, 45.37, 37.40, 36.35, 36.21, 36.20, 34.22, 32.83, 32.79, 31.94, 29.34, 29.02, 26.29, 26.27, 26.09, 24.71, 22.14, 20.34, 12.20. **HRMS** Calcd for $C_{24}H_{36}Br_2NaO_8$ [M+Na$^+$]: 633.0669; Found: 633.0674.



127 (dr = 1:1)

Compound **127** was isolated in 70% yield following the general conditions C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.71 – 4.64 (m, 1H), 4.18 – 4.10 (m, 1H), 3.82 (dd, *J* = 10.2, 4.4 Hz, 1H), 3.60 (t, *J* = 10.0 Hz, 1H), 2.40 (dd, *J* = 19.3, 8.9 Hz, 1H), 2.23 (t, *J* = 7.5 Hz, 2H), 2.13 – 2.05 (m, 1H), 2.05 – 1.97 (m, 1H), 1.94 – 1.87 (m, 1H), 1.82 – 1.69 (m, 5H), 1.68 – 1.54 (m, 5H), 1.53 – 1.45 (m, 3H), 1.35 – 1.20 (m, 16H), 1.05 – 0.94 (m, 2H), 0.83 (s, 6H), 0.73 – 0.66 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 221.30, 173.51, 73.35, 54.47, 53.22, 51.52, 47.91, 44.82, 36.87, 36.47, 36.15, 35.97, 35.80, 35.19, 34.84, 34.14, 31.68, 30.95, 29.28, 29.23, 29.16, 28.84, 28.43, 27.60, 26.83, 25.16, 21.91, 20.60, 13.95, 12.36. **HRMS** Calcd for $C_{30}H_{48}Br_2NaO_3$ [M+Na$^+$]: 637.1862; Found: 637.1869.

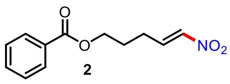
7. General procedures and substrate scope of nitration reactions



Scheme S21. General procedures and substrate scope of nitration reactions

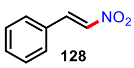
General conditions D: Substrate alkenes (0.2 mmol, 1.0 equiv), $NaNO_2$ (0.5 mmol, 2.5 equiv) and HCl (50 *u*L, aq. 37% in water) were dispersed in CH_2Cl_2 (2.0 mL) in a 4 mL glass vial at room temperature. The reaction vial was sealed with a PTEF cap and the reaction mixture vigorously stirred at 30 °C for 2 h. Then, the reaction mixture was extracted with CH_2Cl_2 (3 × 2 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by chromatography on silica gel to afford the desired nitration products.

7.1 Nitration of alkenes



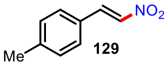
2

Compound **2** was isolated in 89% yield following the general conditions D (crude ^{1}H NMR yield: 96%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.3 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.39 – 7.28 (m, 1H), 7.03 (d, *J* = 13.4 Hz, 1H), 4.39 (t, *J* = 6.2 Hz, 2H), 2.47 (q, *J* = 7.4 Hz, 2H), 2.08 – 1.92 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.55, 141.37, 140.19, 133.32, 129.99, 129.68, 128.60, 63.76, 27.22, 25.52. **HRMS** Calcd for $C_{12}H_{14}NO_4$ [M+H$^+$]: 236.0917; Found: 236.0911.



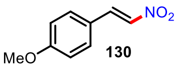
128

Compound **128** was isolated in 77% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 13.7 Hz, 1H), 7.59 (d, *J* = 13.7 Hz, 1H), 7.57 – 7.54 (m, 2H), 7.53 – 7.48 (m, 1H), 7.48 – 7.43 (m, 2H).[29]



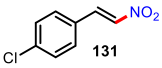
129

Compound **129** was isolated in 75% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 13.6 Hz, 1H), 7.56 (d, *J* = 13.6 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.26 (t, *J* = 3.9 Hz, 2H), 2.41 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.22, 139.26, 136.48, 130.29, 129.32, 127.47, 21.79.[29]



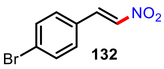
130

Compound **130** was isolated in 73% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 13.6 Hz, 1H), 7.55 – 7.48 (m, 3H), 6.96 (d, *J* = 8.6 Hz, 2H), 3.87 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.09, 139.16, 135.20, 131.30, 122.71, 115.08, 55.68.[29]



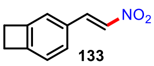
131

Compound **131** was isolated in 80% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 13.7 Hz, 1H), 7.56 (d, *J* = 13.7 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.43, 137.77, 137.56, 130.37, 129.87, 128.67.[29]



132

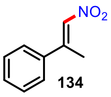
Compound **132** was isolated in 81% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 13.7 Hz, 1H), 7.62 – 7.55 (m, 3H), 7.43 – 7.40 (m, 2H).[29]



133

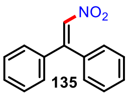
Compound **133** was isolated in 88% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 (d, J = 13.6 Hz, 1H), 7.55 (d, J = 13.6 Hz, 1H), 7.38 (d, J = 7.5 Hz, 1H), 7.24 (s, 1H), 7.13 (d, J = 7.6 Hz, 1H), 3.23 (s, 4H). **^{13}C NMR** (126 MHz,

$CDCl_3$) δ 151.48, 147.22, 140.61, 136.09, 129.42, 128.91, 123.69, 122.44, 30.13, 29.52.[29]



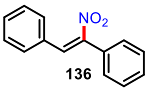
134

Compound **134** was isolated in 75% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48 – 7.41 (m, 5H), 7.31 (d, J = 1.3 Hz, 1H), 2.65 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.05, 138.47, 136.51, 130.50, 129.18, 126.98, 18.73.[30]



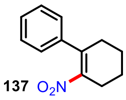
135

Compound **135** was isolated in 75% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.47 – 7.43 (m, 5H), 7.39 (t, J = 7.7 Hz, 2H), 7.29 (d, J = 7.9 Hz, 2H), 7.23 (dd, J = 7.0, 1.5 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.61, 137.22, 135.66, 134.52, 131.03, 129.45, 129.04, 129.01, 128.93, 128.63.[29]



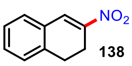
136

Compound **136** was isolated in 70% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.53 – 7.46 (m, 3H), 7.37 – 7.30 (m, 3H), 7.23 (t, J = 7.7 Hz, 2H), 7.10 (d, J = 7.7 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.86, 134.89, 131.39, 131.24, 130.87, 130.72, 130.19, 129.35, 128.85.[31]



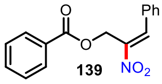
137

Compound **137** was isolated in 75% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 3H), 7.19 – 7.12 (m, 2H), 2.75 – 2.67 (m, 2H), 2.52 – 2.46 (m, 2H), 1.91 – 1.84 (m, 2H), 1.81 – 1.76 (m, 2H).[32]



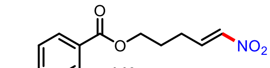
138

Compound **138** was isolated in 78% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.38 – 7.30 (m, 2H), 7.28 (d, J = 7.4 Hz, 1H), 7.23 (d, J = 7.3 Hz, 1H), 3.06 (t, J = 8.0 Hz, 2H), 2.99 (t, 2H).[33]



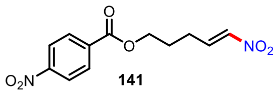
139

Compound **139** was isolated in 77% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.10 – 8.03 (m, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.54 – 7.51 (m, 2H), 7.50 – 7.46 (m, 5H), 5.47 (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.02, 145.42, 140.30, 133.58, 131.45, 131.10, 130.21, 129.95, 129.45, 129.38, 128.64, 58.47. **HRMS** Calcd for $C_{16}H_{13}NNaO_4$ [M+Na$^+$]: 306.0737; Found: 306.0733.[34]



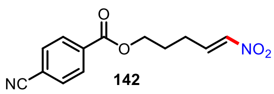
140

Compound **140** was isolated in 89% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 – 7.85 (m, 2H), 7.61 – 7.55 (m, 2H), 7.37 – 7.27 (m, 1H), 7.03 (d, J = 13.4 Hz, 1H), 4.37 (t, J = 6.2 Hz, 2H), 2.49 – 2.40 (m, 2H), 2.05 – 1.97 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.81, 141.21, 140.21, 131.95, 131.18, 128.87, 128.46, 64.05, 27.15, 25.47. **HRMS** Calcd for $C_{12}H_{12}BrNNaO_4$ [M+Na$^+$]: 335.9842; Found: 335.9830.



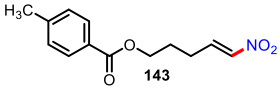
141

Compound **141** was isolated in 85% yield following the general conditions D**.** **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.30 – 8.26 (m, 2H), 8.21 – 8.17 (m, 2H), 7.36 – 7.27 (m, 1H), 7.04 (d, J = 13.4 Hz, 1H), 4.43 (t, J = 6.2 Hz, 2H), 2.47 (q, J = 7.0 Hz, 2H), 2.07 – 2.02 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.61, 150.78, 140.96, 140.27, 135.33, 130.79, 123.71, 64.74, 27.08, 25.39. **HRMS** Calcd for $C_{12}H_{12}N_2NaO_6$ [M+Na$^+$]: 303.0588; Found: 303.0580.



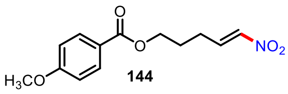
142

Compound **142** was isolated in 80% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.11 (d, J = 8.5 Hz, 2H), 7.74 (d, J = 8.5 Hz, 2H), 7.37 – 7.27 (m, 1H), 7.03 (dt, J = 13.4, 1.4 Hz, 1H), 4.41 (t, J = 6.2 Hz, 2H), 2.46 (m, J = 7.5, 1.4 Hz, 2H), 2.09 – 1.95 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.86, 141.04, 140.22, 133.73, 132.40, 130.15, 117.95, 116.70, 64.59, 27.04, 25.38. **HRMS** Calcd for $C_{13}H_{12}N_2NaO_4$ [M+Na$^+$]: 283.0689; Found: 283.0693.



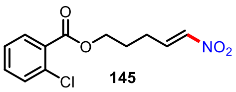
143

Compound **143** was isolated in 75% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.39 – 7.28 (m, 1H), 7.24 (d, *J* = 7.9 Hz, 2H), 7.03 (d, *J* = 13.4 Hz, 1H), 4.36 (t, *J* = 6.1 Hz, 2H), 2.45 (q, *J* = 7.4 Hz, 2H), 2.41 (s, 3H), 2.08 – 1.95(m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.60, 144.02, 141.44, 140.14, 129.68, 129.29, 127.24, 63.57, 27.22, 25.52, 21.78. **HRMS** Calcd for $C_{13}H_{15}NNaO_4$ [M+Na$^+$]: 272.0893; Found: 272.0894.



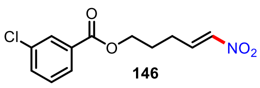
144

Compound **144** was isolated in 75% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.8 Hz, 2H), 7.37 – 7.25 (m, 1H), 7.01 (d, *J* = 13.4 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 4.33 (t, *J* = 6.2 Hz, 2H), 3.84 (s, 3H), 2.43 (q, *J* = 7.1 Hz, 2H), 2.01 – 1.94 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.19, 163.58, 141.50, 140.05, 131.63, 122.32, 113.76, 63.42, 55.51, 27.18, 25.48. **HRMS** Calcd for $C_{13}H_{15}NNaO_5$ [M+Na$^+$]: 288.0842; Found: 288.0844.



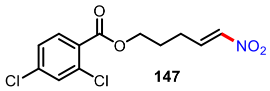
145

Compound **145** was isolated in 90% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81 – 7.77 (m, 1H), 7.46 – 7.40 (m, 2H), 7.34 – 7.26 (m, 2H), 7.02 (d, *J* = 13.4 Hz, 1H), 4.39 (t, *J* = 6.1 Hz, 2H), 2.47 (q, *J* = 7.4 Hz, 2H), 2.06 – 1.96 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.79, 141.17, 140.26, 133.69, 132.86, 131.49, 131.26, 130.07, 126.82, 64.29, 27.07, 25.44. **HRMS** Calcd for $C_{12}H_{12}ClNNaO_4$ [M+Na$^+$]: 292.0347; Found: 292.0348.



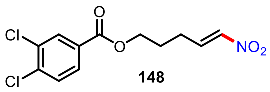
146

Compound **146** was isolated in 90% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.39 (t, J = 7.9 Hz, 1H), 7.35 – 7.27 (m, 1H), 7.03 (d, J = 13.4 Hz, 1H), 4.38 (t, J = 6.2 Hz, 2H), 2.46 (q, J = 7.4 Hz, 2H), 2.12 – 1.93 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.32, 141.13, 140.24, 134.76, 133.33, 131.73, 129.93, 129.73, 127.81, 64.16, 27.14, 25.42. **HRMS** Calcd for $C_{12}H_{12}ClNNaO_4$ [M+Na$^+$]: 292.0347; Found: 292.0348.



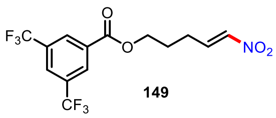
147

Compound **147** was isolated in 89% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.79 (d, J = 8.4 Hz, 1H), 7.48 (d, J = 1.9 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.03 (d, J = 13.4 Hz, 1H), 4.39 (t, J = 6.2 Hz, 2H), 2.46 (q, J = 7.5 Hz, 2H), 2.04 – 1.98 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.86, 141.06, 140.29, 138.74, 134.94, 132.65, 131.24, 128.21, 127.28, 64.51, 27.05, 25.44. **HRMS** Calcd for $C_{12}H_{11}Cl_2NNaO_4$ [M+Na$^+$]: 325.9957; Found: 325.9958.



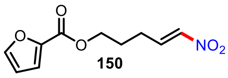
148

Compound **148** was isolated in 89% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.09 (d, J = 1.9 Hz, 1H), 7.84 (dd, J = 8.4, 1.9 Hz, 1H), 7.54 (d, J = 8.4 Hz, 1H), 7.36 – 7.28 (m, 1H), 7.03 (d, J = 13.4 Hz, 1H), 4.39 (t, J = 6.2 Hz, 2H), 2.45 (qd, J = 7.5, 1.3 Hz, 2H), 2.08 – 1.97 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.71, 141.01, 140.29, 138.05, 133.24, 131.62, 130.80, 129.81, 128.75, 64.40, 27.14, 25.43. **HRMS** Calcd for $C_{12}H_{11}Cl_2NNaO_4$ [M+Na$^+$]: 325.9957; Found: 325.9948.



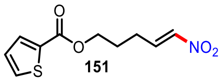
149

Compound **149** was isolated in 88% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.46 (s, 2H), 8.08 (s, 1H), 7.38 – 7.27 (m, 1H), 7.04 (d, J = 13.4 Hz, 1H), 4.47 (t, J = 6.4 Hz, 2H), 2.47 (qd, J = 7.6, 1.4 Hz, 2H), 2.12 – 2.02 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.93, 140.74, 140.35, 132.44 (q, J = 34.1 Hz), 132.17, 129.82 (d, J = 3.1 Hz), 126.82 – 126.59 (m), 124.02, 121.85, 64.96, 27.05, 25.27. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -63.01 (s, 6F). **HRMS** Calcd for $C_{14}H_{11}F_6NNaO_4$ [M+Na$^+$]: 394.0484; Found: 394.0486.



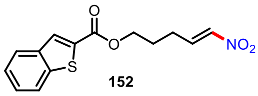
150

Compound **150** was isolated in 80% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 0.7 Hz, 1H), 7.31 – 7.21 (m, 1H), 7.13 (d, *J* = 3.5 Hz, 1H), 6.98 (d, *J* = 13.4 Hz, 1H), 6.52 – 6.44 (m, 1H), 4.30 (t, *J* = 6.2 Hz, 2H), 2.43 – 2.34 (m, 2H), 1.99 – 1.87 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.46, 146.55, 144.31, 141.36, 140.01, 118.20, 111.96, 63.61, 26.95, 25.28.[33]



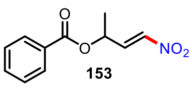
151

Compound **151** was isolated in 79% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.57 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.38 – 7.27 (m, 1H), 7.14 – 7.08 (m, 1H), 7.03 (d, *J* = 13.4 Hz, 1H), 4.35 (t, *J* = 6.2 Hz, 2H), 2.44 (qd, *J* = 7.5, 1.3 Hz, 2H), 2.05 – 1.93 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.14, 141.30, 140.20, 133.77, 133.41, 132.79, 128.00, 63.87, 27.15, 25.44. **HRMS** Calcd for $C_{10}H_{11}NNaO_5$ [M+Na^+]: 264.0301; Found: 264.0299.



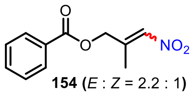
152

Compound **152** was isolated in 76% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 8.1 Hz, 1H), 8.38 (s, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.37 – 7.29 (m, 1H), 7.04 (d, *J* = 13.4 Hz, 1H), 4.42 (t, *J* = 6.2 Hz, 2H), 2.47 (q, *J* = 7.4 Hz, 2H), 2.12 – 1.93 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.60, 141.29, 140.18, 140.13, 136.92, 136.71, 126.83, 125.62, 125.24, 124.65, 122.68, 63.40, 27.23, 25.48. **HRMS** Calcd for $C_{14}H_{13}NNaO_4S$ [M+Na^+]: 314.0457; Found: 314.0456.



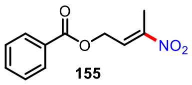
153

Compound **153** was isolated in 73% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.10 – 8.03 (m, 2H), 7.66 – 7.58 (m, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.31 (dd, *J* = 13.4, 4.7 Hz, 1H), 7.17 (dd, *J* = 13.4, 1.6 Hz, 1H), 5.91 – 5.83 (m, 1H), 1.58 (d, *J* = 1.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.31, 140.40, 139.84, 133.78, 129.84, 129.38, 128.75, 66.83, 19.86. **HRMS** Calcd for $C_{11}H_{11}NNaO_4$ [M+Na$^+$]: 244.0580; Found: 244.0581.



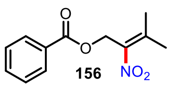
154 (*E* : *Z* = 2.2 : 1)

Compound **154** was isolated in 70% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 8.4, 1.1 Hz, 1.35H), 8.07 (dd, *J* = 8.3, 1.1 Hz, 0.73H), 7.66 – 7.61 (m, 1H), 7.60 (s, 1H), 7.52 – 7.45 (m, 2H), 5.19 (s, 0.62H), 4.93 (s, 1.38H), 1.98 (d, *J* = 1.2 Hz, 1.98H), 1.91 (d, *J* = 1.3 Hz, 0.92H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.01, 162.76, 138.35, 136.65, 134.16, 130.18, 130.16, 128.87, 128.83, 112.46, 111.13, 79.63, 74.53, 16.71, 13.12. **HRMS** Calcd for $C_{11}H_{11}NNaO_4$ [M+Na$^+$]: 244.0580; Found: 244.0581.



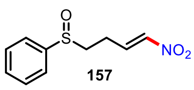
155

Compound **155** was isolated in 70% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.9 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.24 (t, *J* = 13.7, 7.2 Hz, 1H), 5.03 (d, *J* = 6.5 Hz, 2H), 2.30 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.16, 149.82, 133.65, 129.85, 129.27, 129.13, 128.67, 60.15, 13.23. **HRMS** Calcd for $C_{11}H_{11}NNaO_4$ [M+Na$^+$]: 244.0580; Found: 244.0580.



156

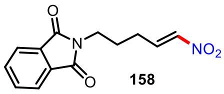
Compound **156** was isolated in 60% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 – 7.98 (m, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 5.31 (s, 2H), 2.10 (s, 3H), 2.09 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.17, 144.11, 143.82, 133.51, 129.91, 129.43, 128.58, 60.01, 22.26, 21.94. **HRMS** Calcd for $C_{12}H_{13}NNaO_4$ [M+Na$^+$]: 258.0737; Found: 258.0737.



157

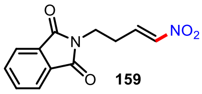
Compound **157** was isolated in 76% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.22 (m, 2H), 6.99 (d, *J* = 13.4 Hz, 1H), 3.07 (t, *J* = 7.0 Hz, 2H), 2.57 (qd, *J* = 7.2, 1.4 Hz, 2H). **^{13}C**

NMR (126 MHz, $CDCl_3$) δ 140.68, 139.80, 134.76, 130.63, 129.36, 127.17, 32.32, 28.32. **HRMS** Calcd for $C_{10}H_{11}NNaO_3S$ [$M+Na^+$]: 248.0352; Found: 248.0342.



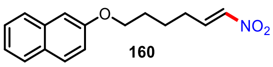
158

Compound **158** was isolated in 83% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.87 – 7.82 (m, 2H), 7.75 – 7.69 (m, 2H), 7.28 – 7.20 (m, 1H), 7.03 (d, *J* = 13.4 Hz, 1H), 3.74 (t, *J* = 6.8 Hz, 2H), 2.34 (q, *J* = 7.4 Hz, 2H), 1.98 – 1.87 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.43, 140.92, 140.29, 134.28, 132.01, 123.47, 37.09, 26.85, 25.92.[35]



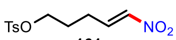
159

Compound **159** was isolated in 85% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.87 – 7.81 (m, 2H), 7.76 – 7.70 (m, 2H), 7.22 (dd, *J* = 14.1, 6.8 Hz, 1H), 7.02 (d, *J* = 13.5 Hz, 1H), 3.89 (t, *J* = 6.9 Hz, 2H), 2.69 (q, *J* = 7.0 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.09, 141.11, 138.02, 134.39, 131.89, 123.62, 35.92, 27.81.[33]



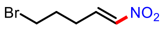
160

Compound **160** was isolated in 80% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 – 7.72 (m, 3H), 7.51 – 7.44 (m, 1H), 7.41 – 7.34 (m, 1H), 7.33 – 7.23 (m, 1H), 7.21 – 7.11 (m, 2H), 7.01 (d, *J* = 13.4 Hz, 1H), 4.08 (t, *J* = 6.1 Hz, 2H), 2.39 – 2.27 (m, 2H), 1.93 – 1.82 (m, 2H), 1.79 – 1.66 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.88, 142.18, 139.87, 134.64, 129.51, 129.06, 127.73, 126.77, 126.48, 123.72, 118.89, 106.68, 67.25, 28.69, 28.17, 24.55.[29]



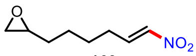
161

Compound **161** was isolated in 75% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.13 – 7.05 (m, 1H), 6.84 (d, *J* = 13.4 Hz, 1H), 4.03 (t, *J* = 5.9 Hz, 2H), 2.43 (s, 3H), 2.32 (q, *J* = 7.3 Hz, 2H), 1.91 – 1.79 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.27, 140.39, 140.28, 132.68, 130.02, 127.81, 68.79, 26.96, 24.40, 21.60.[29]



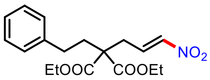
162

Compound **162** was isolated in 80% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29 – 7.19 (m, 1H), 7.03 (dt, *J* = 13.4, 1.4 Hz, 1H), 3.43 (t, *J* = 6.3 Hz, 2H), 2.51 – 2.44 (m, 2H), 2.12 – 2.02 (m, 2H).[36]



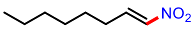
163

Compound **163** was isolated in 65% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 1H), 7.00 – 6.92 (m, 1H), 2.93 – 2.82 (m, 1H), 2.77 – 2.67 (m, 1H), 2.47 – 2.39 (m, 1H), 2.32 – 2.21 (m, 2H), 1.67 – 1.53 (m, 4H), 1.51 – 1.45 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.27, 139.87, 52.04, 47.00, 32.16, 28.41, 27.62, 25.69.[33]



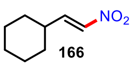
164

Compound **164** was isolated in 83% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.24 – 7.19 (m, 2H), 7.16 (d, *J* = 7.1 Hz, 2H), 6.97 (d, *J* = 13.4 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 4H), 2.86 (dd, *J* = 8.1, 1.2 Hz, 2H), 2.61 – 2.52 (m, 2H), 2.25 – 2.16 (m, 2H), 1.27 (t, *J* = 4.9 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.15, 141.62, 140.65, 137.24, 128.74, 128.46, 126.54, 62.08, 57.28, 35.57, 32.33, 30.82, 30.34, 29.84, 14.23. **HRMS** Calcd for $C_{18}H_{23}NNaO_6$ [M+Na$^+$]: 372.1418; Found: 372.1403.



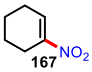
165

Compound **165** was isolated in 80% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 1H), 6.98 (d, *J* = 13.4 Hz, 1H), 2.27 (qd, *J* = 7.5, 1.3 Hz, 2H), 1.55 – 1.47 (m, 2H), 1.39 – 1.28 (m, 6H), 0.89 (t, *J* = 6.8 Hz, 3H).[37]



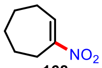
166

Compound **166** was isolated in 77% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 13.5, 7.2 Hz, 1H), 6.93 (dd, *J* = 13.5, 1.3 Hz, 1H), 2.31 – 2.20 (m, 1H), 1.83 – 1.76 (m, 4H), 1.73 – 1.67 (m, 1H), 1.37 – 1.30 (m, 2H), 1.23 – 1.16 (m, 3H).[38]



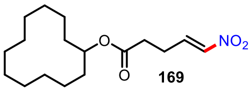
167

Compound **167** was isolated in 75% yield following the general conditions D**.** **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32 (m, 1H), 2.58 (m, 2H), 2.38 – 2.29 (m, 2H), 1.83 – 1.73 (m, 2H), 1.67 – 1.59 (m, 2H).[29]



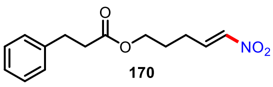
168

Compound **168** was isolated in 78% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 (t, *J* = 6.7 Hz, 1H), 2.89 – 2.84 (m, 2H), 2.38 – 2.34 (m, 2H), 1.81 – 1.77 (m, 2H), 1.69 – 1.64 (m, 4H).[39]



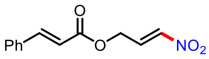
169

Compound **169** was isolated in 82% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30 – 7.21 (m, 1H), 7.01 (d, *J* = 13.4 Hz, 1H), 5.07 – 4.99 (m, 1H), 2.61 – 2.56 (m, 2H), 2.50 (t, *J* = 7.0 Hz, 2H), 1.74 – 1.66 (m, 2H), 1.51 – 1.45 (m, 2H), 1.42 – 1.28 (m, 18H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.31, 140.57, 140.42, 73.26, 32.46, 29.24, 24.13, 23.91, 23.48, 23.31, 21.05. **HRMS** Calcd for $C_{17}H_{29}NNaO_4$ [M+Na$^+$]: 334.1989; Found: 334.1989.



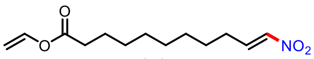
170

Compound **170** was isolated in 89% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.25 – 7.16 (m, 4H), 6.95 (d, *J* = 13.4 Hz, 1H), 4.11 (t, *J* = 6.2 Hz, 2H), 2.95 (t, *J* = 7.7 Hz, 2H), 2.65 (t, *J* = 7.7 Hz, 2H), 2.24 (qd, *J* = 7.5, 1.4 Hz, 2H), 1.88 – 1.75 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.86, 141.31, 140.40, 140.10, 128.66, 128.41, 126.49, 63.16, 35.86, 31.07, 27.02, 25.23. **HRMS** Calcd for $C_{14}H_{16}NO_4$ [M-H$^+$]: 262.1085; Found: 262.1093.



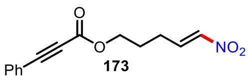
171

Compound **171** was isolated in 76% yield following the general conditions D**.** ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 16.0 Hz, 1H), 7.56 (dd, *J* = 6.6, 2.7 Hz, 2H), 7.46 – 7.38 (m, 3H), 7.34 (dt, *J* = 13.4, 4.3 Hz, 1H), 7.20 (dt, *J* = 13.4, 1.8 Hz, 1H), 6.48 (d, *J* = 16.0 Hz, 1H), 4.99 (dd, *J* = 4.2, 2.0 Hz, 2H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 165.89, 146.79, 140.28, 135.81, 134.00, 130.98, 129.14, 128.40, 116.45, 59.57.[33]



172

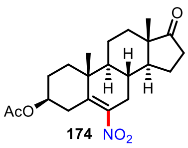
Compound **172** was isolated in 78% yield following the general conditions D. ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.29 – 7.21 (m, 2H), 6.96 (d, *J* = 13.4 Hz, 1H), 4.85 (dd, *J* = 14.0, 1.4 Hz, 1H), 4.54 (dd, *J* = 6.3, 1.4 Hz, 1H), 2.36 (t, *J* = 7.5 Hz, 2H), 2.24 (q, *J* = 7.4 Hz, 2H), 1.65 – 1.60 (m, 2H), 1.52 – 1.46 (m, 2H), 1.32 – 1.28 (m, 8H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 170.85, 142.78, 141.23, 139.65, 97.53, 33.91, 29.05, 29.03, 28.96, 28.46, 27.73, 24.56. **HRMS** Calcd for $C_{13}H_{21}NNaO_4$ [M+Na$^+$]: 278.1363; Found: 278.1364.



173

Compound **173** was isolated in 79% yield following the general conditions D. ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.2 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 1 H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.33 – 7.25 (m, 1H), 7.03 (d, *J* = 13.4 Hz, 1H), 4.28 (t, *J* = 6.2 Hz, 2H), 2.49 – 2.37 (m, 2H), 2.05 – 1.88 (m, 2H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 153.96, 141.02, 140.27, 133.14, 130.94, 128.74, 119.47, 87.05, 80.35, 64.67, 26.85, 25.23. **HRMS** Calcd for $C_{14}H_{13}NNaO_4$ [M+Na$^+$]: 282.0737; Found: 282.0740.

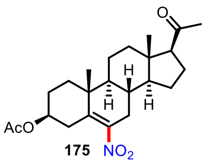
7.2 Nitration of natural products and drug derivatives



174

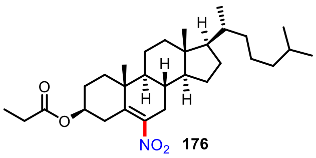
Compound **174** was isolated in 68% yield following the general conditions D. ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 4.73 – 4.57 (m, 1H), 2.82 (dd, *J* = 14.2, 4.4 Hz, 1H), 2.67 – 2.59

(m, 1H), 2.49 (dd, J = 19.4, 8.9 Hz, 1H), 2.34 – 2.20 (m, 2H), 2.16 – 2.09 (m, 1H), 2.03 (s, 3H), 2.01 – 1.96 (m, 2H), 1.92 – 1.80 (m, 2H), 1.77 – 1.70 (m, 1H), 1.66 – 1.55 (m, 3H), 1.54 – 1.46 (m, 1H), 1.42 – 1.28 (m, 3H), 1.17 (s, 3H), 1.11 (td, J = 11.7, 4.5 Hz, 1H), 0.89 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 219.76, 170.21, 146.07, 138.03, 71.86, 51.30, 49.20, 47.50, 38.13, 36.28, 35.81, 32.44, 31.37, 31.29, 31.24, 27.07, 21.91, 21.35, 20.45, 19.93, 13.66.[40]



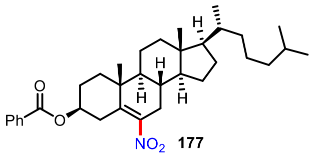
175

Compound **175** was isolated in 69% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.74 – 4.54 (m, 1H), 2.78 (dd, J = 14.0, 3.1 Hz, 1H), 2.61 – 2.45 (m, 2H), 2.29 – 2.15 (m, 3H), 2.13 (s, 3H), 2.03 (s, 3H), 1.77 – 1.56 (m, 8H), 1.47 (d, J = 8.9 Hz, 2H), 1.36 – 1.25 (m, 3H), 1.14 (s, 3H), 1.05 – 0.98 (m, 1H), 0.64 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 209.12, 170.25, 146.47, 137.65, 71.97, 63.39, 56.25, 48.94, 43.90, 38.47, 37.98, 36.33, 33.28, 31.64, 31.26, 29.84, 27.10, 24.46, 23.03, 21.36, 21.08, 19.88, 13.31. **HRMS** Calcd for $C_{23}H_{33}NNaO_5$ [M+Na$^+$]: 426.2251; Found: 426.2243.



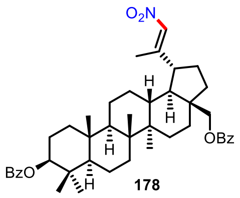
176

Compound **176** was isolated in 65% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.71 – 4.57 (m, 1H), 2.76 (dd, J = 14.2, 3.4 Hz, 1H), 2.51 – 2.42 (m, 1H), 2.29 (q, J = 7.5 Hz, 2H), 2.24 – 2.19 (m, 1H), 2.18 – 2.12 (m, 1H), 2.04 (t, J = 6.4 Hz, 1H), 2.00 – 1.92 (m, 2H), 1.91 – 1.82 (m, 1H), 1.65 – 1.43 (m, 7H), 1.38 – 1.18 (m, 8H), 1.13 – 1.09 (m, 9H), 1.04 – 0.97 (m, 2H), 0.91 (d, J = 6.5 Hz, 3H), 0.86 (dd, J = 6.6, 2.1 Hz, 6H), 0.68 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.63, 146.80, 137.53, 71.87, 56.17, 56.09, 49.04, 42.43, 39.60, 39.43, 37.94, 36.28, 36.23, 35.85, 33.44, 31.72, 31.28, 28.22, 28.13, 27.87, 27.14, 24.25, 23.95, 22.94, 22.68, 21.08, 19.86, 18.81, 11.93, 9.18. **HRMS** Calcd for $C_{30}H_{49}NNaO_4$ [M+Na$^+$]: 510.3554; Found: 510.3557.



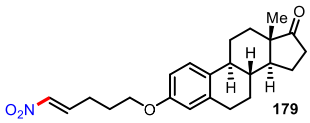
177

Compound **177** was isolated in 66% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.9 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 4.95 – 4.83 (m, 1H), 2.92 (dd, *J* = 14.2, 3.2 Hz, 1H), 2.54 – 2.44 (m, 1H), 2.44 – 2.34 (m, 1H), 2.25 – 2.16 (m, 1H), 2.11 (d, *J* = 12.5 Hz, 1H), 2.07 – 1.98 (m, 2H), 1.91 – 1.82 (m, 1H), 1.74 (d, *J* = 14.3 Hz, 1H), 1.68 – 1.55 (m, 3H), 1.54 – 1.44 (m, 2H), 1.39 – 1.23 (m, 6H), 1.18 (s, 3H), 1.16 – 1.05 (m, 7H), 1.02 – 0.97 (m, 1H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.87 (dd, *J* = 6.6, 2.2 Hz, 6H), 0.69 (d, *J* = 3.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.74, 146.95, 137.45, 133.08, 130.42, 129.71, 128.44, 72.71, 56.17, 56.10, 49.06, 42.45, 39.60, 39.43, 38.01, 36.32, 36.24, 35.85, 33.47, 31.74, 31.36, 28.23, 28.13, 27.23, 24.26, 23.95, 22.95, 22.69, 21.10, 19.92, 18.82, 11.94. **HRMS** Calcd for $C_{34}H_{49}NNaO_4$ [M+Na$^+$]: 558.3554; Found: 558.3556.



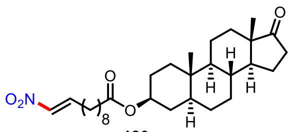
178

Compound **178** was isolated in 70% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (t, *J* = 6.8 Hz, 4H), 7.57 – 7.52 (m, 2H), 7.46 – 7.41 (m, 4H), 7.03 (s, 1H), 4.71 (dd, *J* = 11.1, 4.6 Hz, 1H), 4.55 – 4.47 (m, 1H), 4.12 – 4.08 (m, 1H), 2.65 – 2.49 (m, 1H), 2.22 (s, 3H), 2.15 – 2.04 (m, 2H), 1.81 – 1.68 (m, 7H), 1.49 – 1.31 (m, 11H), 1.27 – 1.22 (m, 4H), 1.06 (s, 3H), 1.00 (s, 3H), 0.99 (s, 3H), 0.91 (s, 3H), 0.89 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.92, 166.63, 166.08, 157.64, 135.14, 133.03, 132.66, 130.88, 130.10, 129.48, 128.41, 128.26, 81.29, 62.71, 60.26, 55.31, 53.48, 49.98, 47.29, 47.02, 42.76, 40.81, 38.29, 38.11, 37.02, 35.05, 33.99, 29.86, 28.05, 26.87, 25.75, 23.67, 20.95, 20.65, 18.10, 16.74, 16.06, 15.93, 14.60, 14.16. **HRMS** Calcd for $C_{44}H_{57}NNaO_6$ [M+Na$^+$]: 718.4078; Found: 718.4079.



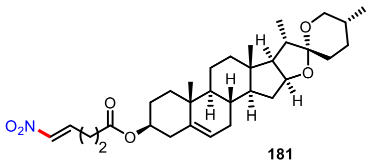
179

Compound **179** was isolated in 75% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 1H), 7.20 (d, J = 8.6 Hz, 1H), 7.01 (d, J = 13.4 Hz, 1H), 6.69 (dd, J = 8.5, 2.5 Hz, 1H), 6.63 (s, 1H), 3.99 (t, J = 5.8 Hz, 2H), 2.94 – 2.86 (m, 2H), 2.54 – 2.46 (m, 3H), 2.42 – 2.37 (m, 1H), 2.28 – 2.22 (m, 1H), 2.18 – 2.10 (m, 1H), 2.02 – 1.96 (m, 3H), 1.66 – 1.41 (m, 8H), 0.91 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 221.03, 156.71, 141.95, 140.04, 138.03, 132.59, 126.56, 114.66, 112.17, 66.49, 50.55, 48.14, 44.12, 38.49, 36.01, 31.72, 29.79, 27.72, 26.66, 26.06, 25.52, 21.72, 13.99. **HRMS** Calcd for $C_{23}H_{29}NNaO_4$ [M+Na$^+$]: 406.1989; Found: 406.1983.



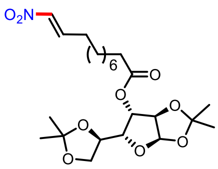
180

Compound **180** was isolated in 76% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 1H), 6.97 (d, *J* = 13.4 Hz, 1H), 4.72 – 4.64 (m, 1H), 2.46 – 2.38 (m, 1H), 2.25 (t, *J* = 7.3 Hz, 4H), 2.10 – 2.01 (m, 1H), 1.95 – 1.88 (m, 1H), 1.85 – 1.70 (m, 5H), 1.68 – 1.56 (m, 6H), 1.53 – 1.45 (m, 5H), 1.33 – 1.28 (m, 11H), 1.10 – 0.92 (m, 3H), 0.85 (s, 3H), 0.84 (s, 3H), 0.71 (td, *J* = 11.4, 3.8 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 221.36, 173.43, 142.85, 139.66, 73.32, 54.38, 51.43, 47.87, 44.73, 36.79, 35.94, 35.74, 35.11, 34.74, 34.08, 31.60, 30.89, 29.13, 29.09, 29.08, 28.52, 28.37, 27.77, 27.54, 25.06, 21.86, 20.55, 13.91, 12.31. **HRMS** Calcd for $C_{30}H_{47}NNaO_5$ [M+Na$^+$]: 524.3346; Found: 524.3350.



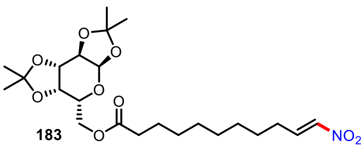
181

Compound **181** was isolated in 62% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.27 – 7.21 (m, 1H), 7.00 (d, *J* = 13.5 Hz, 1H), 5.36 (d, *J* = 4.3 Hz, 1H), 4.64 – 4.57 (m, 1H), 4.41 – 4.36 (m, 1H), 3.47 – 3.42 (m, 1H), 3.35 (t, *J* = 10.9 Hz, 1H), 2.61 – 2.53 (m, 2H), 2.49 (t, *J* = 7.0 Hz, 2H), 2.29 (d, *J* = 7.7 Hz, 2H), 2.00 – 1.93 (m, 2H), 1.86 – 1.81 (m, 3H), 1.77 – 1.70 (m, 2H), 1.66 – 1.49 (m, 6H), 1.46 – 1.38 (m, 2H), 1.30 – 1.21 (m, 3H), 1.20 – 1.04 (m, 4H), 1.01 (s, 3H), 0.95 (d, *J* = 7.0 Hz, 3H), 0.78 – 0.75 (m, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.94, 140.45, 140.40, 139.45, 122.71, 109.32, 80.85, 74.70, 66.90, 62.17, 56.50, 49.99, 41.68, 40.33, 39.78, 38.13, 36.97, 36.79, 32.37, 32.11, 31.91, 31.47, 30.37, 29.78, 28.89, 27.81, 23.78, 20.89, 19.39, 17.23, 16.36, 14.61. **HRMS** Calcd for $C_{32}H_{47}NNaO_6$ [M+Na$^+$]: 564.3296; Found: 564.3294.



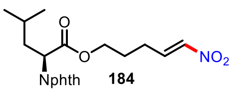
182

Compound **182** was isolated in 61% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 1H), 6.97 (d, *J* = 13.4 Hz, 1H), 5.86 (d, *J* = 3.6 Hz, 1H), 5.28 – 5.25 (m, 1H), 4.47 (d, *J* = 3.7 Hz, 1H), 4.20 (t, *J* = 3.4 Hz, 2H), 4.09 – 4.06 (m, 1H), 4.03 – 3.99 (m, 1H), 2.34 (td, *J* = 7.5, 3.3 Hz, 2H), 2.29 – 2.22 (m, 2H), 1.66 – 1.58 (m, 4H), 1.51 (s, 3H), 1.51 – 1.47 (m, 2H), 1.40 (s, 3H), 1.31 – 1.29 (m, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.42, 142.78, 139.74, 112.44, 109.44, 105.19, 83.53, 80.00, 76.01, 72.58, 67.42, 34.33, 29.19, 29.16, 29.09, 28.55, 27.83, 26.95, 26.88, 26.35, 25.43, 24.93. **HRMS** Calcd for $C_{23}H_{37}NNaO_9$ [M+Na$^+$]: 494.2361; Found: 494.2367.



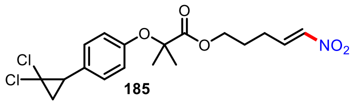
183

Compound **183** was isolated in 64% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.27 – 7.19 (m, 1H), 6.95 (d, *J* = 13.4 Hz, 1H), 5.50 (d, *J* = 4.9 Hz, 1H), 4.58 (dd, *J* = 7.9, 2.1 Hz, 1H), 4.32 – 4.24 (m, 2H), 4.20 (d, *J* = 7.9 Hz, 1H), 4.16 – 4.09 (m, 1H), 4.01 – 3.95 (m, 1H), 2.30 (t, *J* = 7.5 Hz, 2H), 2.23 (q, *J* = 7.3 Hz, 2H), 1.63 – 1.53 (m, 2H), 1.52 – 1.43 (m, 5H), 1.41 (s, 3H), 1.33 – 1.21 (m, 14H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.70, 142.78, 139.63, 109.65, 108.76, 96.34, 71.13, 70.73, 70.49, 66.07, 63.31, 34.17, 29.10, 29.06, 29.00, 28.46, 27.74, 26.05, 26.00, 25.01, 24.92, 24.52. **HRMS** Calcd for $C_{23}H_{37}NNaO_9$ [M+Na$^+$]: 494.2361; Found: 494.2357.



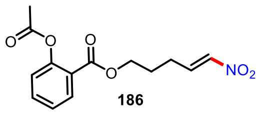
184

Compound **184** was isolated in 80% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84 – 7.81 (m, 2H), 7.73 – 7.71 (m, 2H), 7.21 – 7.09 (m, 1H), 6.90 (d, J = 13.4 Hz, 1H), 4.90 (dd, J = 11.5, 4.2 Hz, 1H), 4.22 – 4.16 (m, 1H), 4.14 – 4.08 (m, 1H), 2.31 – 2.21 (m, 3H), 1.94 – 1.87 (m, 1H), 1.82 – 1.75 (m, 2H), 1.48 – 1.42 (m, 1H), 0.91 (d, J = 6.5 Hz, 3H), 0.88 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.71, 167.76, 140.98, 140.17, 134.41, 131.74, 123.58, 64.32, 50.66, 37.34, 26.83, 25.06, 24.92, 23.20, 21.03. **HRMS** Calcd for $C_{19}H_{22}N_2NaO_6$ [M+Na$^+$]: 397.1370; Found: 397.1373.



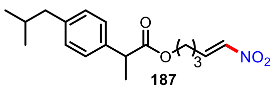
185

Compound **185** was isolated in 90% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.16 – 7.07 (m, 3H), 6.82 (d, J = 13.4 Hz, 1H), 6.78 (d, J = 8.7 Hz, 2H), 4.17 (t, J = 6.1 Hz, 2H), 2.82 (dd, J = 10.6, 8.5 Hz, 1H), 2.16 – 2.06 (m, 2H), 1.99 – 1.89 (m, 1H), 1.83 – 1.74 (m, 3H), 1.62 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.26, 155.15, 140.98, 140.16, 129.85, 128.22, 117.99, 79.14, 64.06, 61.01, 34.86, 26.76, 25.92, 25.57, 25.53, 24.95. **HRMS** Calcd for $C_{18}H_{21}Cl_2NNaO_5$ [M+Na$^+$]: 424.0689; Found: 424.0689.



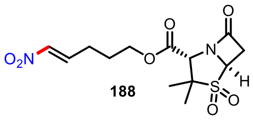
186

Compound **186** was isolated in 90% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.96 (d, J = 7.8 Hz, 1H), 7.56 (t, J = 7.7 Hz, 1H), 7.34 – 7.22 (m, 2H), 7.10 (d, J = 8.0 Hz, 1H), 7.01 (d, J = 13.4 Hz, 1H), 4.30 (t, J = 6.2 Hz, 2H), 2.39 (q, J = 7.3 Hz, 2H), 2.33 (s, 3H), 1.99 – 1.88 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.65, 164.23, 150.75, 141.17, 140.15, 134.11, 131.49, 126.08, 123.86, 123.01, 63.70, 26.95, 25.13, 21.03. **HRMS** Calcd for $C_{14}H_{15}NNaO_6$ [M+Na$^+$]: 316.0792; Found: 316.0789.



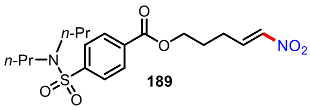
187

Compound **187** was isolated in 88% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.19 (d, J = 8.0 Hz, 2H), 7.17 – 7.12 (m, 1H), 7.10 (d, J = 7.9 Hz, 2H), 6.81 (d, J = 13.4 Hz, 1H), 4.17 – 4.09 (m, 1H), 4.09 – 4.02 (m, 1H), 3.69 (q, J = 7.1 Hz, 1H), 2.45 (d, J = 7.2 Hz, 2H), 2.15 (q, J = 7.4 Hz, 2H), 1.90 – 1.72 (m, 3H), 1.48 (d, J = 7.2 Hz, 3H), 0.88 (d, J = 6.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.63, 141.19, 140.82, 140.07, 137.75, 129.48, 127.18, 63.13, 45.20, 45.06, 30.26, 26.88, 24.94, 22.42, 18.24. **HRMS** Calcd for $C_{18}H_{25}NNaO_4$ [M+Na$^+$]: 342.1676; Found: 342.1674.



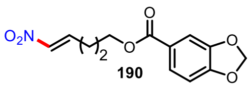
188

Compound **188** was isolated in 74% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29 – 7.18 (m, 1H), 7.00 (d, J = 13.4 Hz, 1H), 4.61 (d, J = 2.6 Hz, 1H), 4.35 (s, 1H), 4.30 – 4.13 (m, 2H), 3.49 (dd, J = 16.3, 4.0 Hz, 1H), 3.40 (d, J = 16.3 Hz, 1H), 2.36 (q, J = 7.1 Hz, 2H), 1.97 – 1.85 (m, 2H), 1.56 (s, 3H), 1.37 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.03, 166.92, 140.73, 140.27, 65.22, 63.20, 62.71, 61.16, 38.36, 26.69, 25.08, 20.28, 18.57. **HRMS** Calcd for $C_{13}H_{18}N_2NaO_7S$ [M+Na$^+$]: 369.0727; Found: 369.0726.



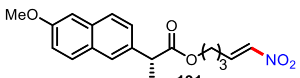
189

Compound **189** was isolated in 70% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.13 (d, J = 8.4 Hz, 2H), 7.87 (d, J = 8.3 Hz, 2H), 7.35 – 7.27 (m, 1H), 7.03 (d, J = 13.4 Hz, 1H), 4.41 (t, J = 6.2 Hz, 2H), 3.17 – 3.00 (m, 4H), 2.54 – 2.38 (m, 2H), 2.11 – 1.96 (m, 2H), 1.58 – 1.49 (m, 4H), 0.86 (t, J = 7.4 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.19, 144.62, 141.10, 140.23, 133.22, 130.30, 127.19, 64.42, 50.05, 27.11, 25.44, 22.04, 11.26. **HRMS** Calcd for $C_{18}H_{26}KN_2O_6S$ [M+K$^+$]: 437.1143; Found: 437.1134.



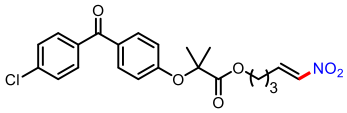
190

Compound **190** was isolated in 70% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60 (d, J = 8.2 Hz, 1H), 7.40 (s, 1H), 7.35 – 7.24 (m, 1H), 7.01 (dd, J = 13.4, 0.9 Hz, 1H), 6.81 (dd, J = 8.2, 1.4 Hz, 1H), 6.01 (s, 2H), 4.31 (t, J = 6.0 Hz, 2H), 2.42 (q, J = 7.4 Hz, 2H), 2.09 – 1.86 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.70, 151.76, 147.77, 141.43, 139.99, 125.31, 123.80, 109.33, 107.99, 101.90, 63.59, 27.03, 25.36. **HRMS** Calcd for $C_{13}H_{13}NNaO_6$ [M+Na$^+$]: 302.0635; Found: 302.0629.



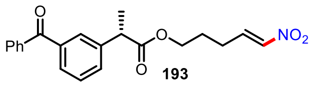
191

Compound **191** was isolated in 71% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 8.6, 3.9 Hz, 2H), 7.66 (s, 1H), 7.39 (d, *J* = 8.5 Hz, 1H), 7.18 – 7.06 (m, 3H), 6.70 (d, *J* = 13.4 Hz, 1H), 4.15 – 4.10 (m, 1H), 4.09 – 4.04 (m, 1H), 3.91 (s, 3H), 3.85 (q, *J* = 7.1 Hz, 1H), 2.12 – 2.04 (m, 2H), 1.79 – 1.68 (m, 2H), 1.58 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.50, 157.74, 141.20, 139.86, 135.56, 133.72, 129.22, 128.87, 127.25, 126.07, 125.95, 119.20, 105.56, 63.26, 55.31, 45.42, 26.78, 24.91, 18.23. **HRMS** Calcd for $C_{19}H_{21}NNaO_5$ [M+Na$^+$]: 366.1312; Found: 366.1311.



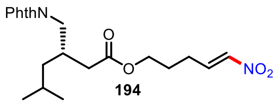
192

Compound **192** was isolated in 82% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.7 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.17 – 7.07 (m, 1H), 6.86 – 6.82 (m, 3H), 4.18 (t, *J* = 6.1 Hz, 2H), 2.15 (q, *J* = 7.4 Hz, 2H), 1.83 – 1.77 (m, 2H), 1.67 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 194.13, 173.68, 159.67, 140.81, 140.12, 138.51, 136.30, 132.15, 131.21, 130.52, 128.64, 117.05, 79.43, 64.35, 26.71, 25.50, 24.96. **HRMS** Calcd for $C_{22}H_{22}ClNNaO_6$ [M+Na$^+$]: 454.1028; Found: 454.1028.



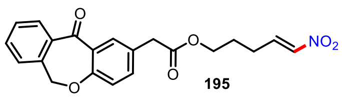
193

Compound **193** was isolated in 72% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81 – 7.73 (m, 3H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.52 (d, *J* = 7.5 Hz, 1H), 7.50 – 7.40 (m, 3H), 7.21 – 7.11 (m, 1H), 6.88 (d, *J* = 13.4 Hz, 1H), 4.10 (t, *J* = 5.8 Hz, 2H), 3.80 (q, *J* = 7.1 Hz, 1H), 2.22 (q, *J* = 7.4 Hz, 2H), 1.89 – 1.70 (m, 2H), 1.53 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 196.43, 173.90, 141.10, 140.84, 140.07, 138.02, 137.43, 132.64, 131.47, 130.07, 129.19, 129.07, 128.62, 128.39, 63.55, 45.41, 26.83, 25.02, 18.33. **HRMS** Calcd for $C_{21}H_{21}NNaO_5$ [M+Na$^+$]: 390.1312; Found: 390.1311.



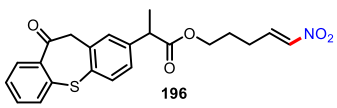
194

Compound **194** was isolated in 48% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.85 – 7.79 (m, 2H), 7.73 – 7.68 (m, 2H), 7.28 – 7.19 (m, 1H), 7.02 (d, *J* = 13.4 Hz, 1H), 4.00 (t, *J* = 6.0 Hz, 2H), 3.69 (dd, *J* = 13.7, 4.9 Hz, 1H), 3.61 (dd, *J* = 13.7, 8.1 Hz, 1H), 2.47 – 2.41 (m, 1H), 2.37 – 2.28 (m, 3H), 1.85 – 1.76 (m, 2H), 1.72 (dd, *J* = 13.2, 6.6 Hz, 1H), 1.27 – 1.14 (m, 3H), 0.94 (d, *J* = 6.5 Hz, 3H), 0.88 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.42, 168.70, 141.36, 140.16, 134.11, 132.05, 123.31, 63.07, 41.96, 41.83, 37.54, 32.73, 26.95, 25.36, 25.22, 22.70, 22.67. **HRMS** Calcd for $C_{21}H_{26}N_2NaO_6$ [M+Na$^+$]: 425.1683; Found: 425.1684.



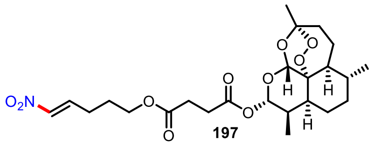
195

Compound **195** was isolated in 69% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 2.3 Hz, 1H), 7.90 – 7.82 (m, 1H), 7.56 (td, *J* = 7.4, 1.3 Hz, 1H), 7.47 (td, *J* = 7.6, 1.2 Hz, 1H), 7.43 – 7.39 (m, 1H), 7.36 (d, *J* = 7.4 Hz, 1H), 7.27 – 7.19 (m, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.97 (d, *J* = 13.4 Hz, 1H), 5.19 (s, 2H), 4.15 (t, *J* = 6.2 Hz, 2H), 3.64 (s, 2H), 2.33 (qd, *J* = 7.5, 1.5 Hz, 2H), 1.96 – 1.79 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 190.94, 171.39, 140.56, 137.47, 136.41, 135.71, 132.97, 132.56, 132.30, 129.64, 129.44, 127.99, 127.82, 125.36, 121.29, 118.06, 73.82, 63.62, 40.40, 27.17, 26.50. **HRMS** Calcd for $C_{21}H_{19}NNaO_6$ [M+Na$^+$]: 404.1105; Found: 404.1105.



196

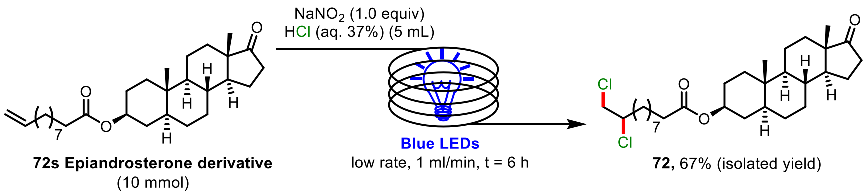
Compound **196** was isolated in 76% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.9 Hz, 1H), 7.60 (t, *J* = 8.5 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.37 (s, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.18 – 7.08 (m, 2H), 6.82 (d, *J* = 13.4 Hz, 1H), 4.35 (s, 2H), 4.15 – 4.01 (m, 2H), 3.71 (q, *J* = 7.1 Hz, 1H), 2.13 (q, *J* = 7.5 Hz, 2H), 1.81 – 1.71 (m, 2H), 1.48 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 191.36, 173.79, 142.62, 141.19, 140.19, 139.98, 138.11, 136.05, 133.49, 132.71, 131.68, 131.54, 130.94, 128.61, 126.99, 126.30, 63.62, 51.04, 45.21, 26.78, 25.05, 18.27. **HRMS** Calcd for $C_{22}H_{21}NNaO_5S$ [M+Na$^+$]: 434.1033; Found: 434.1033.



Compound **197** was isolated in 64% yield following the general conditions D. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31 – 7.21 (m, 1H), 7.03 (d, *J* = 13.4 Hz, 1H), 5.77 (d, *J* = 9.8 Hz, 1H), 5.43 (s, 1H), 4.21 – 4.14 (m, 1H), 4.14 – 4.07 (m, 1H), 2.72 (t, *J* = 6.6 Hz, 2H), 2.67 – 2.56 (m, 2H), 2.40 – 2.31 (m, 2H), 2.03 (m, 2H), 1.92 – 1.81 (m, 3H), 1.80 – 1.65 (m, 3H), 1.61 (dt, *J* = 13.7, 4.2 Hz, 1H), 1.52 – 1.44 (m, 1H), 1.41 (s, 3H), 1.37 – 1.22 (m, 4H), 0.95 (d, *J* = 6.0 Hz, 3H), 0.84 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.11, 171.28, 141.32, 140.29, 104.58, 92.37, 91.62, 80.24, 63.39, 51.68, 45.34, 37.37, 36.32, 34.19, 31.91, 29.29, 28.98, 27.00, 26.04, 25.17, 24.68, 22.09, 20.33, 12.16. **HRMS** Calcd for $C_{24}H_{35}NNaO_{10}$ [M+Na$^+$]: 520.2153; Found: 520.2156.

8. Synthetic applications

8.1 Gram-scale continuous flow dichlorination reaction of epiandrosterone



Scheme S22. Gram-scale continuous flow dichlorination reaction of epiandrosterone

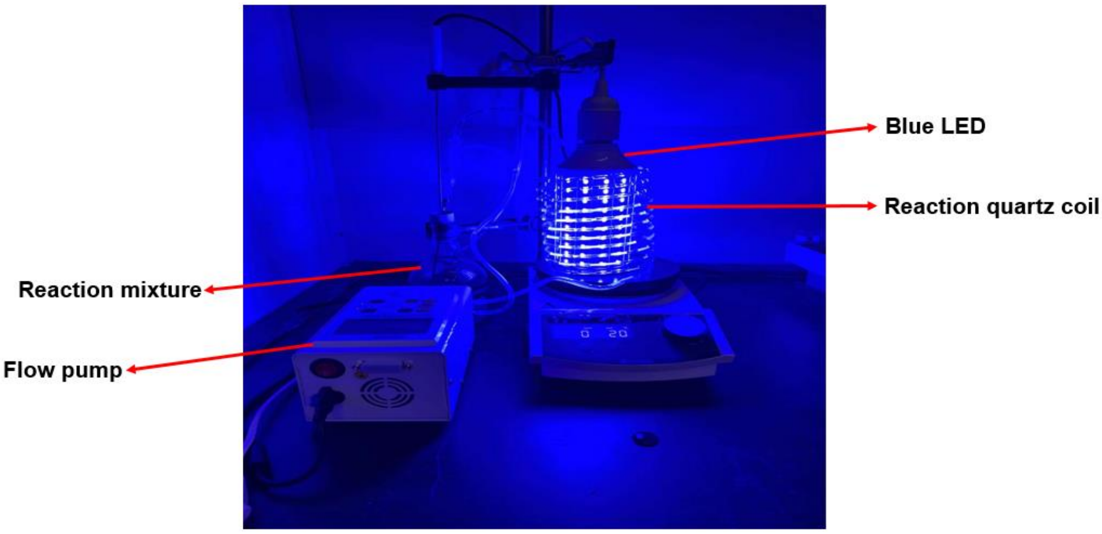
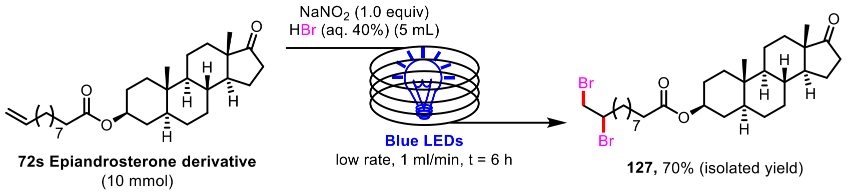


Figure S1. Gram-scale continuous flow dichlorination reaction of epiandrosterone

Substrate Epiandrosterone derivative **72s** (10.0 mmol, 1.0 equiv) and $NaNO_2$ (10.0 mmol, 1.0 equiv) were dispersed in CH_2Cl_2 (100.0 mL) in a 250 mL round bottom flask. Then HCl (5 mL, aq. 37% in water) was added at 0 ºC. As shown in Figure S1, a flow pump was employed to pump the reaction mixture, and then attached to the flow apparatus was placed into a platform equipped with a 24 W blue LEDs and quartz reaction coil (The reaction coil is made of quartz, O.D. = 2 mm, I.D. = 1 mm). The flow apparatus itself was set up with flow rate = 1 mL/min. The flow reaction mixture irradiated with blue LEDs at room temperature (30 ºC) for 6 h until the reaction was complete (monitored by TLC). The reaction mixture was concentrated under reduced pressure, and then the resulting crude product was purified by column chromatography (eluent: *n*-hexane/AcOEt) to provide the dichlorination product **72** in 67% isolated yield (3.50 g).

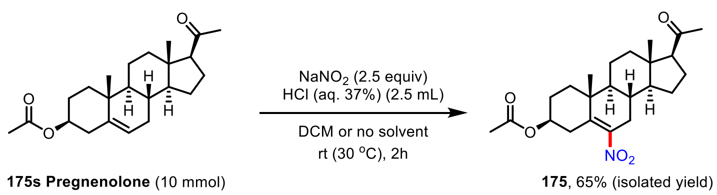
8.2 Gram-scale continuous flow dibromination reaction of epiandrosterone



Scheme S23. Gram-scale continuous flow dibromination reaction of epiandrosterone

Substrate Epiandrosterone derivative **72s** (10.0 mmol, 1.0 equiv) and $NaNO_2$ (10.0 mmol, 1.0 equiv) were dispersed in CH_2Cl_2 (100.0 mL) in a 250 mL round bottom flask. Then HBr (5 mL, aq. 40% in water) was added at 0 °C. As shown in Figure S1, a flow pump was employed to pump the reaction mixture, and then attached to the flow apparatus was placed into a platform equipped with a 24 W blue LEDs and quartz reaction coil (The reaction coil is made of quartz, O.D. = 2 mm, I.D. = 1 mm). The flow apparatus itself was set up with flow rate = 1 mL/min. The flow reaction mixture irradiated with blue LEDs at room temperature (30 °C) for 6 h until the reaction was complete (monitored by TLC). The reaction mixture was concentrated under reduced pressure, and then the resulting crude product was purified by column chromatography (eluent: *n*-hexane/AcOEt) to provide the dibromination product **127** in 70% isolated yield (4.27 g).

8.3 Gram-scale nitration of pregnenolone



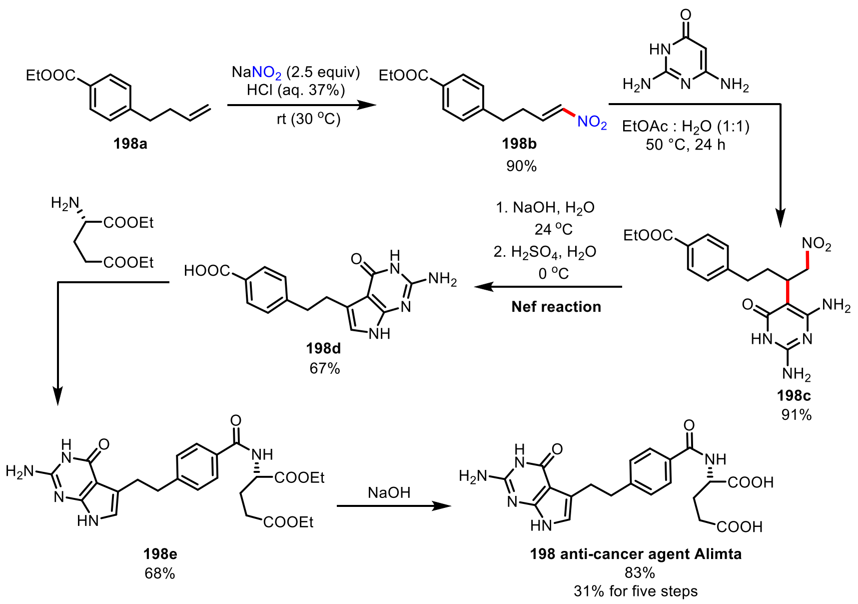
Scheme S24. Gram-scale nitration of pregnenolone

Substrate pregnenolone **175s** (10 mmol, 1.0 equiv) and $NaNO_2$ (25 mmol, 2.5 equiv) were dispersed in CH_2Cl_2 (100.0 mL) in a 250 mL round bottom flask. Then HCl (2.5

mL, aq. 37% in water) was added at 0 °C. The reaction mixture vigorously stirred at room temperature (30 °C) for 2 h. Then, the reaction mixture was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by chromatography on silica gel to afford the desired nitration product in 65% isolated yield (2.62 g).

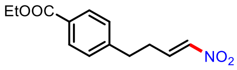
Note: The gram-scale nitration reaction of pregnenolone **175s** can be carried out without solvent DCM to give the desired nitration product in 63% isolated yield (2.54 g).

8.4 Synthetic applications of olefin nitration reaction in the synthesis of anti-cancer agent Alimta



Scheme S25. Synthetic applications of olefin nitration reaction in the synthesis of anti-cancer agent Alimta

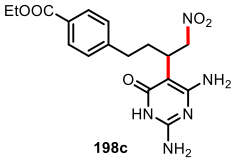
4-(Nitrobut-3-enyl)benzene (**198b**): Substrate alkene **198a** (1.0 mmol, 1.0 equiv), $NaNO_2$ (2.5 mmol, 2.5 equiv) and HCl (250 *u*L, aq. 37% in water) were dispersed in CH_2Cl_2 (20.0 mL) in a 100 mL round bottom flask. The reaction mixture vigorously stirred at 30 ℃ for 2 h. Then, the reaction mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by chromatography on silica gel to afford the desired nitration product **198b** 224.2 mg (90%).



198b

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.9 Hz, 2H), 7.32 – 7.14 (m, 3H), 6.95 (d, *J* = 13.4 Hz, 1H), 4.37 (q, *J* = 7.0 Hz, 2H), 2.89 (t, *J* = 7.5 Hz, 2H), 2.61 (q, *J* = 7.4 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H).[41, 42]

4-[3-(2,4-Diamino-6-oxo-1,6-dihydropyrimidin-5-yl)-4-nitrobutyl]benzoic acid ethyl ester (**198c**): The mixture of (0.57 mmol, 1.0 equiv) of **198b** and (0.57 mmol, 1.0 equiv) of 2,6-diamino-3*H*-pyrimidin-4-one in 2 mL of water and 2 mL of ethyl acetate was stirred at 50 °C for 24 h. The solid slowly disappeared. The reaction mixture was poured into 10 mL of ethyl acetate, washed with water (2 × 4 mL), dried with Na_2SO_4, and then concentrated. The residue was purified by column chromatorgaphy (silica gel/ethyl acetate:methanol) 8:1) to afford product **198c** 195 mg (91%).

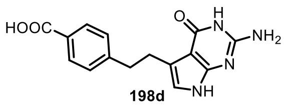


198c

^{1}H NMR (500 MHz, DMSO) δ 10.59 (br, 1H), 7.82 (d, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 7.8 Hz, 2H), 6.50 (br, 2H), 5.87 (br, 2H), 5.06 – 4.92 (m, 1H), 4.76 (dd, *J* = 11.7, 6.2 Hz, 1H), 4.27 (q, *J* = 6.9 Hz, 2H), 3.39 (m, 1H), 2.70 – 2.58 (m, 1H), 2.57 – 2.50 (m, 1H), 2.23 – 2.06 (m, 1H), 1.73 – 1.64 (m, 1H), 1.28 (t, *J* = 7.0 Hz, 3H) .[41, 42]

4-[2-(2-Amino-4-oxo-4,7-dihydro-3*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl)ethyl]benzoic acid (198d): To a mixture of (6.0 mmol, 6.0 equiv) of NaOH in 3.0 mL of water was added (1.0 mmol, 1.0 equiv) of **198c** at room temperature. The mixture was stirred at room temperature for 2 h and then was slowly added to (10.0 mmol, 10.0 equiv) of

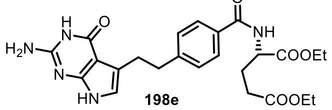
H_2SO_4 in 4.0 mL of water at 0 °C. After 3 h, aqueous sodium hydroxide (2.0 N) was added to adjust the pH to 7. The mixture was stirred at room temperature for another 1 h. Acetic acid (0.5 mL) was added and the precipitated solid was collected by filtration, washed with water followed by ethyl acetate, and dried under vacuum to give 0.20 g (67%) of product as a light green solid that is used without further purification for the next reaction.



198d

^{1}H NMR (500 MHz, DMSO) δ 10.61 (s, 1H), 10.16 (s, 1H), 7.82 (d, *J* = 7.5 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 6.30 (s, 1H), 6.01 (s, 2H), 3.00 – 2.93 (m, 2H), 2.87 – 2.80 (m, 2H).[41, 42]

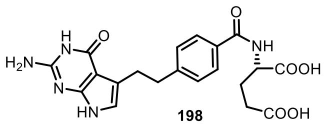
***N*-{4-(2-Amino-4-oxo-4,7-dihydro-3*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl)ethyl]benzoyl}-L-glutamic acid diethyl ester (198e):** To a suspension of 185 mg (0.5 mmol, 1.0 equiv) of **198d** in 15 mL of dry DMF were added (0.6 mmol, 1.2 equiv) of 4-methylmorpholine and 130 mg (0.6 mmol, 1.2 equiv) of 2-chloro-4,6-dimethoxy-1,3,5-triazine. The resulting mixture was stirred at room temperature for 2 h, and 0.08 mL of 4-methylmorpholine and 221 mg (0.75 mmol, 1.5 equiv) of diethyl L-glutamate hydrochloride were added. The reaction mixture was stirred for another 4 h at room temperature. Solvent was evaporated under vacuum and the residue was purified by column chromatography (silica gel/ CH_2Cl_2:MeOH) 9:1) to give 164 mg (68%) of product as an off-white solid.



198e

^{1}H NMR (500 MHz, DMSO) δ 10.98 (s, 1H), 10.56 (s, 1H), 8.64 (d, *J* = 7.0 Hz, 1H), 7.76 (d, *J* = 7.4 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 6.38 (s, 1H), 6.27 (s, 2H), 5.31 (s, 1H), 4.41 (s, 1H), 4.09 (q, *J* = 6.3 Hz, 2H), 4.03 (q, *J* = 6.8 Hz, 2H), 2.96 (t, *J* = 7.7 Hz, 2H), 2.83 (t, J = 7.4 Hz, 2H), 2.42 (t, J = 6.6 Hz, 2H), 2.11 – 2.05 (m, 1H), 1.99 – 1.96 (m, 1H), 1.20 – 1.11 (m, 6H).[41, 42]

***N*-{4-[2-(2-Amino-4-oxo-4,7-dihydro-3*H*-pyrrolo[2,3-*d*]-pyrimidin-5-yl)ethyl]benzoyl}-L-glutamic acid (Alimta,198):** To a solution of 100 mg of **198e** in 3.0 mL of THF was added 1.0 mL of 1 N aqueous NaOH at room temperature. The resulting mixture was stirred for 4 h. Solvent was evaporated under reduced pressure and the mixture was acidified by addition of acetic acid. The precipitate was collected, washed with water (3 × 10 mL) and EtOAc (3 × 10 mL), and dried under vacuum to afford 73 mg (83%) of **198** as an off-white solid.

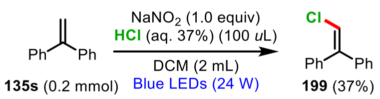


^{1}H NMR (500 MHz, D_2O) δ 8.45 (s, 1H), 7.69 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 7.9 Hz, 2H), 6.35 (s, 1H), 4.36 – 4.27 (m, 1H), 3.00 (m, 4H), 2.31 (t, J = 7.8 Hz, 2H), 2.21 – 2.13 (m, 1H), 2.06 – 1.98 (m, 1H). **^{13}C NMR** (126 MHz, D_2O) δ 182.33, 179.03, 171.09, 170.24, 168.30, 152.17, 147.15, 130.88, 128.88, 127.12, 116.99, 114.65, 99.93, 55.99, 35.74, 34.30, 28.44, 27.28.[41, 42]

9. Mechanistic studies

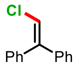
9.1 Mechanistic studies of dichlorination of olefins

Radical scavenger experiment: Compound **135s** was examined for the dichlorination reaction in order to prove that chlorine radical was produced under our dichlorination standard conditions.



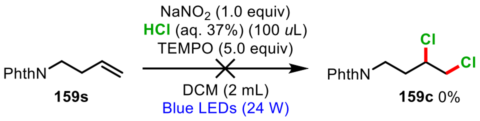
Scheme S26. Radical scavenger experiment

Radical scavenger 1,1-Diphenylethylene (0.2 mmol, 1.0 equiv), $NaNO_2$ (0.2 mmol, 1.0 equiv) and HCl (100 *u*L, aq. 37% in water) were dispersed in CH_2Cl_2 (2.0 mL) in a 4 mL glass vial at room temperature. The reaction vial was sealed with a PTEF cap and the reaction mixture vigorously stirred at 30 ℃ under the 24 W blue LEDs irradiation for 6 h. Then, the reaction mixture was extracted with CH_2Cl_2 (3 × 2 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by chromatography on silica gel to afford the 2-chloro-1,1-diphenylethylene 16 mg (37%).



199

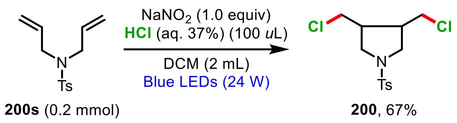
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 2H), 7.37 – 7.30 (m, 6H), 7.24 – 7.20 (m, 2H), 6.60 (s, 1H).[43]



Scheme S27. Radical scavenger experiment

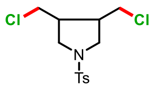
Alkene **159s** (0.2 mmol, 1.0 equiv), radical scavenger TEMPO (1.0 mmol, 5.0 equiv), $NaNO_2$ (0.2 mmol, 1.0 equiv) and HCl (100 *u*L, aq. 37% in water) were dispersed in CH_2Cl_2 (2.0 mL) in a 4 mL glass vial at room temperature. The reaction vial was sealed with a PTEF cap and the reaction mixture vigorously stirred at 30 ℃ under the 24 W blue LEDs irradiation for 6 h. Then, the reaction mixture was extracted with CH_2Cl_2 (3 × 2 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated. The dichlorination product **159c** was completely inhibited.

Radical clock experiment： Compounds **200s** and **201s** were examined for the dichlorination reaction in order to prove that chlorine radical was produced under our dichlorination standard conditions and carbon radical intermediate was involved in this dichlorination process.



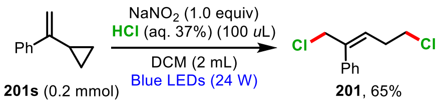
Scheme S28. Radical clock experiment of *N*-tosyldiallyamine

N-tosyldiallyamine (0.2 mmol, 1.0 equiv), $NaNO_2$ (0.2 mmol, 1.0 equiv) and HCl (100 *u*L, aq. 37% in water) were dispersed in CH_2Cl_2 (2.0 mL) in a 4 mL glass vial at room temperature. The reaction vial was sealed with a PTEF cap and the reaction mixture vigorously stirred at 30 ℃ under the 24 W blue LEDs irradiation for 12 h. Then, the reaction mixture was extracted with CH_2Cl_2 (3 × 2 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by chromatography on silica gel to afford the cyclization-derived pyrrolidine 43 mg (67%).



200

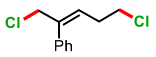
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (t, *J* = 8.8 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 3.54 – 3.37 (m, 5H), 3.31 – 3.24 (m, 2H), 3.12 (dd, *J* = 10.3, 6.1 Hz, 1H), 2.66 – 2.58 (m, 1H), 2.44 (s, 3H), 2.42 – 2.34 (m, 1H).[17]



Scheme S29. Radical clock experiment of (1-cyclopropylvinyl)benzene

Cyclopropane-containing alkene (1-cyclopropylvinyl)benzene (0.2 mmol, 1.0 equiv), $NaNO_2$ (0.2 mmol, 1.0 equiv) and HCl (100 *u*L, aq. 37% in water) were dispersed in

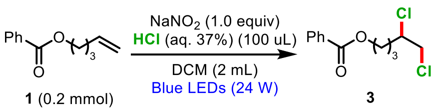
CH_2Cl_2 (2.0 mL) in a 4 mL glass vial at room temperature. The reaction vial was sealed with a PTEF cap and the reaction mixture vigorously stirred at 30 ℃ under the 24 W blue LEDs irradiation for 12 h. Then, the reaction mixture was extracted with CH_2Cl_2 (3 × 2 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by chromatography on silica gel to afford the ring-opening product 28 mg (65%).



201

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, J = 7.6 Hz, 2H), 7.37 (t, J = 7.4 Hz, 2H), 7.34 – 7.28 (m, 1H), 6.01 (t, J = 7.4 Hz, 1H), 4.48 (s, 2H), 3.68 (t, J = 6.7 Hz, 2H), 2.81 (q, J = 6.9 Hz, 2H).[44]

Light/dark experiment of dichlorination of olefin 1:



Scheme S30. Light/dark experiment of dichlorination of **1**

Six vials were equipped with a stir bar and charged with **1** (0.2 mmol, 1.0 equiv), $NaNO_2$ (0.2 mmol, 1.0 equiv) and HCl (100 uL, aq. 37% in water) were dispersed in CH_2Cl_2 (2.0 mL) in a 4 mL glass vial at room temperature. The reaction vial was sealed with a PTEF cap and the reactions was alternatively irradiated with a Blue LEDs (24 W) and kept in the dark in 1 h intervals. After each interval, one vial was take out, the solvent was removed under reduced pressure, and the yield was determined by ^{1}H NMR based on a $Cl_2CHCHCl_2$ as an internal standard. These results indicated that continuous irradiation with light was essential for promoting the reaction.

Vial	Time (h)/condition						Yield (%)[a]
1	0-1/hv						17

2	0-1/hv	1-2/dark					21
3	0-1/hv	1-2/dark	2-3/hv				30
4	0-1/hv	1-2/dark	2-3/hv	3-4/dark			40
5	0-1/hv	1-2/dark	2-3/hv	3-4/dark	4-5/hv		44
6	0-1/hv	1-2/dark	2-3/hv	3-4/dark	4-5/hv	5-6/hv	56

a) NMR yield, average of three experiments.

Table S2. Yields of Light/Dark experiment.

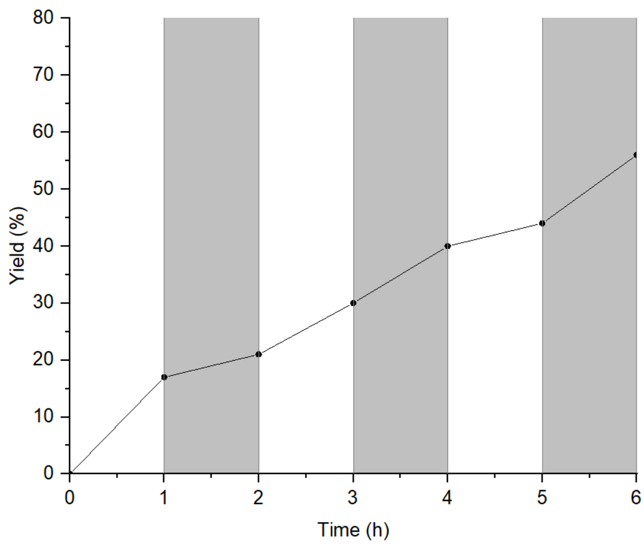


Figure S2. Light/dark experiment of dichlorination of **1**

UV-vis experiment: Ultraviolet–visible absorption experiments were performed using a Unicosh UV-4800 UV-visible spectrophotometer. Six samples were prepared, H_2O (2.0 mL); H_2O (2.0 mL) and mixtures of HCl (aq. 37% in water, 5 µL); H_2O (2.0 mL) and mixtures of $NaNO_2$ (0.1 mmol); H_2O (2.0 mL) and mixtures of $NaNO_2$ (0.1 mmol), HCl (aq. 37% in water, 5 µL); H_2O (2.0 mL) and mixtures of $NaNO_2$ (0.1 mmol), HCl (aq. 37% in water, 10 µL) and H_2O (2.0 mL) and mixtures of $NaNO_2$ (0.1 mmol), HCl (aq. 37% in water, 60 µL), a series of aliquots was transferred into the 2.0 mL quartz tube under an air atmosphere and measured directly.

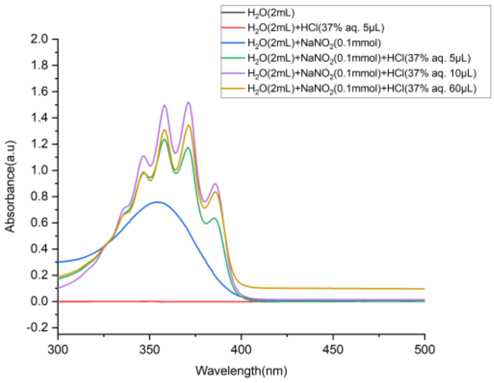
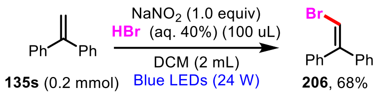


Figure S3. Ultraviolet–visible absorption spectrum

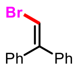
9.2 Mechanistic studies of dibromination of olefins

Radical scavenger experiment： Compound **135s** was examined for the dibromination reaction in order to prove that bromine radical was produced under our dibromination standard conditions.



Scheme S31. Radical scavenger experiment

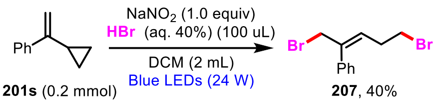
Radical scavenger 1,1-Diphenylethylene (0.2 mmol, 1.0 equiv), $NaNO_2$ (0.2 mmol, 1.0 equiv) and HBr (100 *u*L, aq. 40% in water) were dispersed in CH_2Cl_2 (2.0 mL) in a 4 mL glass vial at room temperature. The reaction vial was sealed with a PTEF cap and the reaction mixture vigorously stirred at 30 ℃ under the 24 W blue LEDs irradiation for 6 h. Then, the reaction mixture was extracted with CH_2Cl_2 (3 × 2 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by chromatography on silica gel to afford the 2-Bromo-1,1-diphenylethylene 35 mg (68%).



206

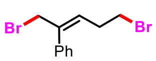
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.38 (m, 3H), 7.35 – 7.30 (m, 5H), 7.25 – 7.22 (m, 2H), 6.80 (s, 1H).[45]

Radical clock experiment： Compound **201s** was examined for the dibromination reaction in order to prove that bromine radical was produced under our dibromination standard conditions and carbon radical intermediate was involved in this dibromination process.



Scheme S32. Radical clock experiment of (1-cyclopropylvinyl)benzene

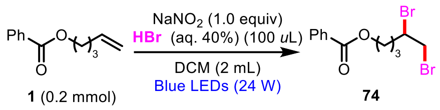
Cyclopropane-containing alkene (1-cyclopropylvinyl)benzene (0.2 mmol, 1.0 equiv), $NaNO_2$ (0.2 mmol, 1.0 equiv) and HBr (100 *u*L, aq. 40% in water) were dispersed in CH_2Cl_2 (2.0 mL) in a 4 mL glass vial at room temperature. The reaction vial was sealed with a PTEF cap and the reaction mixture vigorously stirred at 30 ℃ under the 24 W blue LEDs irradiation for 12 h. Then, the reaction mixture was extracted with CH_2Cl_2 (3 × 2 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by chromatography on silica gel to afford the ring-opening product 24 mg (40%).



207

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, J = 7.6 Hz, 2H), 7.37 (t, J = 7.4 Hz, 2H), 7.34 – 7.29 (m, 1H), 5.97 (t, J = 7.3 Hz, 1H), 4.36 (s, 2H), 3.54 (t, J = 6.9 Hz, 2H), 2.90 (q, J = 7.0 Hz, 2H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.05, 138.91, 130.76, 128.70, 128.02, 126.20, 32.11, 31.32, 28.78. **HRMS** Calcd for $C_{11}H_{12}Br_2K$ [M+K$^+$]: 340.8937; Found: 340.8947.

Light/dark experiment of dibromination of olefin 1:



Scheme S33. Light/dark experiment of dibromination of **1**

Five vials were equipped with a stir bar and charged with **1** (0.2 mmol, 1.0 equiv), $NaNO_2$ (0.2 mmol, 1.0 equiv) and HBr (100 *u*L, aq. 40% in water) were dispersed in CH_2Cl_2 (2.0 mL) in a 4 mL glass vial at room temperature. The reaction vial was sealed with a PTEF cap and the reactions was alternatively irradiated with a Blue LEDs (24 W) and kept in the dark in 1 h intervals. After each interval, one vial was take out, the solvent was removed under reduced pressure, and the yield was determined by ^{1}H NMR based on a $Cl_2CHCHCl_2$ as an internal standard. These results indicated that continuous irradiation with light was essential for promoting the reaction.

Vial	Time (h)/condition					Yield (%)[a]
1	0-1/hv					37
2	0-1/hv	1-2/dark				39
3	0-1/hv	1-2/dark	2-3/hv			50
4	0-1/hv	1-2/dark	2-3/hv	3-4/dark		55
5	0-1/hv	1-2/dark	2-3/hv	3-4/dark	4-5/hv	67

a) NMR yield, average of three experiments.

Table S3. Yields of Light/Dark experiment.

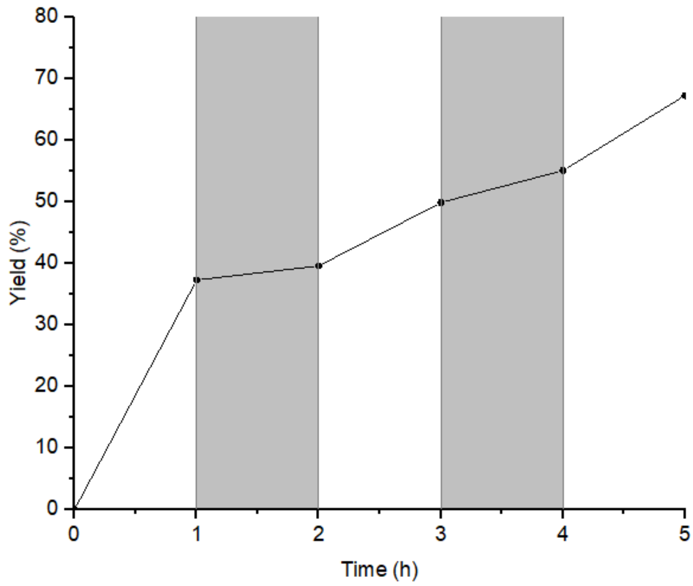
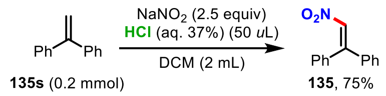


Figure S4. Light/dark experiment of dibromination of **1**

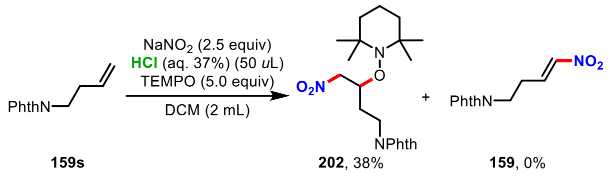
9.3 Mechanistic studies of nitration of olefins

Radical scavenger experiment: Compound **135s** was examined for the nitration reaction in order to prove that nitrogen dioxide radical was produced under our nitration standard conditions.



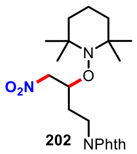
Scheme S34. Radical scavenger experiment

Radical scavenger 1,1-Diphenylethylene (0.2 mmol, 1.0 equiv), $NaNO_2$ (0.5 mmol, 2.5 equiv) and HCl (50 *u*L, aq. 37% in water) were dispersed in CH_2Cl_2 (2.0 mL) in a 4 mL glass vial at room temperature. The reaction vial was sealed with a PTEF cap and the reaction mixture vigorously stirred at 30 ℃ for 2 h. Then, the reaction mixture was extracted with CH_2Cl_2 (3 × 2 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by chromatography on silica gel to afford the nitration product 34 mg (75%).



Scheme S35. Radical scavenger experiment

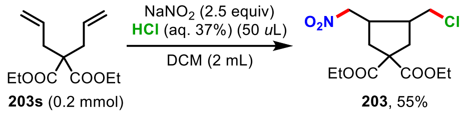
Alkene **159s** (0.2 mmol, 1.0 equiv), radical scavenger TEMPO (1.0 mmol, 5.0 equiv), $NaNO_2$ (0.5 mmol, 2.5 equiv) and HCl (50 *u*L, aq. 37% in water) were dispersed in CH_2Cl_2 (2.0 mL) in a 4 mL glass vial at room temperature. The reaction vial was sealed with a PTEF cap and the reaction mixture vigorously stirred at 30 ℃ for 2 h. Then, the reaction mixture was extracted with CH_2Cl_2 (3 × 2 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by chromatography on silica gel to afford the corresponding product of radical trapping the product 31 mg (38%) and formation of nitration product **159** was completely inhibited.



202

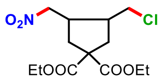
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 – 7.81 (m, 2H), 7.74 – 7.68 (m, 2H), 4.26 – 3.84 (m, 3H), 2.81 (m, 2H), 1.64 (t, J = 12.0 Hz, 4H), 1.55 – 1.47 (m, 2H), 1.44 – 1.33 (m, 2H), 1.12 (s, 6H), 1.03 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.96, 134.04, 132.04, 123.33, 60.07, 39.00, 33.76, 31.96, 31.02, 29.71, 20.50, 16.92.[33]

Radical clock experiment： Compounds **203s** and **201s** were examined for the nitration reaction in order to prove that nitrogen dioxide radical was produced under our nitration standard conditions and carbon radical intermediate was involved in this nitration process.



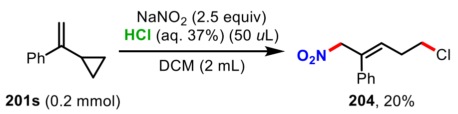
Scheme S36. Radical clock experiment of Diethyl 2,2-diallylmalonate

Diethyl 2,2-diallylmalonate (0.2 mmol, 1.0 equiv), $NaNO_2$ (0.5 mmol, 2.5 equiv) and HCl (50 *u*L, aq. 37% in water) were dispersed in CH_2Cl_2 (2.0 mL) in a 4 mL glass vial at room temperature. The reaction vial was sealed with a PTEF cap and the reaction mixture vigorously stirred at 30 ℃ for 2 h. Then, the reaction mixture was extracted with CH_2Cl_2 (3 × 2 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by chromatography on silica gel to afford the cyclization product 35 mg (55%).



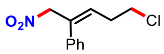
203

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.53 (dd, *J* = 13.0, 6.4 Hz, 1H), 4.33 (dd, *J* = 12.9, 9.3 Hz, 1H), 4.14 – 4.08 (m, 4H), 3.55 – 3.33 (m, 2H), 3.00 – 2.85 (m, 1H), 2.63 – 2.55 (m, 1H), 2.51 – 2.36 (m, 2H), 2.18 – 2.07 (m, 2H), 1.16 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.62, 171.44, 77.42, 77.16, 76.91, 75.12, 61.88, 61.82, 58.23, 43.79, 42.94, 39.49, 36.99, 36.78, 13.84. **HRMS** Calcd for $C_{13}H_{20}ClNNaO_6$ [M+Na$^+$]: 344.0871; Found: 344.0871.



Scheme S37. Radical clock experiment of (1-cyclopropylvinyl)benzene

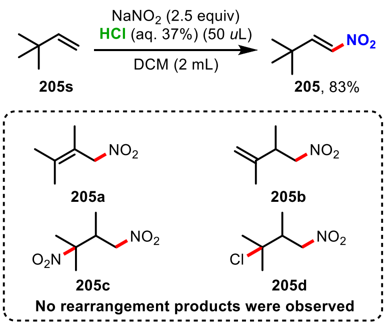
Cyclopropane-containing alkene (1-cyclopropylvinyl)benzene (0.2 mmol, 1.0 equiv), $NaNO_2$ (0.5 mmol, 2.5 equiv) and HCl (50 *u*L, aq. 37% in water) were dispersed in CH_2Cl_2 (2.0 mL) in a 4 mL glass vial at room temperature. The reaction vial was sealed with a PTEF cap and the reaction mixture vigorously stirred at 30 ℃ for 2 h. Then, the reaction mixture was extracted with CH_2Cl_2 (3 × 2 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by chromatography on silica gel to afford the ring-opening product 9 mg (20%).



204

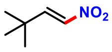
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.31 (m, 5H), 6.26 (t, *J* = 7.4 Hz, 1H), 5.42 (s, 2H), 3.69 (t, *J* = 6.5 Hz, 2H), 2.83 (q, *J* = 6.8 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.29, 134.22, 132.59, 128.95, 128.41, 126.27, 74.74, 43.40, 32.32. **HRMS** Calcd for $C_{11}H_{12}ClNNaO_2$ [$M+Na^+$]: 248.0449; Found: 248.0445.

Carbonradical vs carbocation experiment： Compound **205s** was examined for the nitration reaction in order to prove that carbocation intermediate was not involved in this nitration process.



Scheme S38. Carbonradical vs carbocation experiment

Alkene 3,3-dimethylbut-1-ene (0.2 mmol, 1.0 equiv), $NaNO_2$ (0.5 mmol, 2.5 equiv) and HCl (50 *u*L, aq. 37% in water) were dispersed in CH_2Cl_2 (2.0 mL) in a 4 mL glass vial at room temperature. The reaction vial was sealed with a PTEF cap and the reaction mixture vigorously stirred at 30 ℃ for 2 h. Then, the reaction mixture was extracted with CH_2Cl_2 (3 × 2 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by chromatography on silica gel to afford nitration product 21.4 mg (83%). There is no rearrangement products.



205

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (d, J = 13.5 Hz, 1H), 6.88 (d, J = 13.6 Hz, 1H), 1.15 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 152.10, 137.27, 32.81, 28.55.[46]

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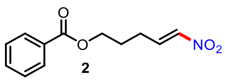
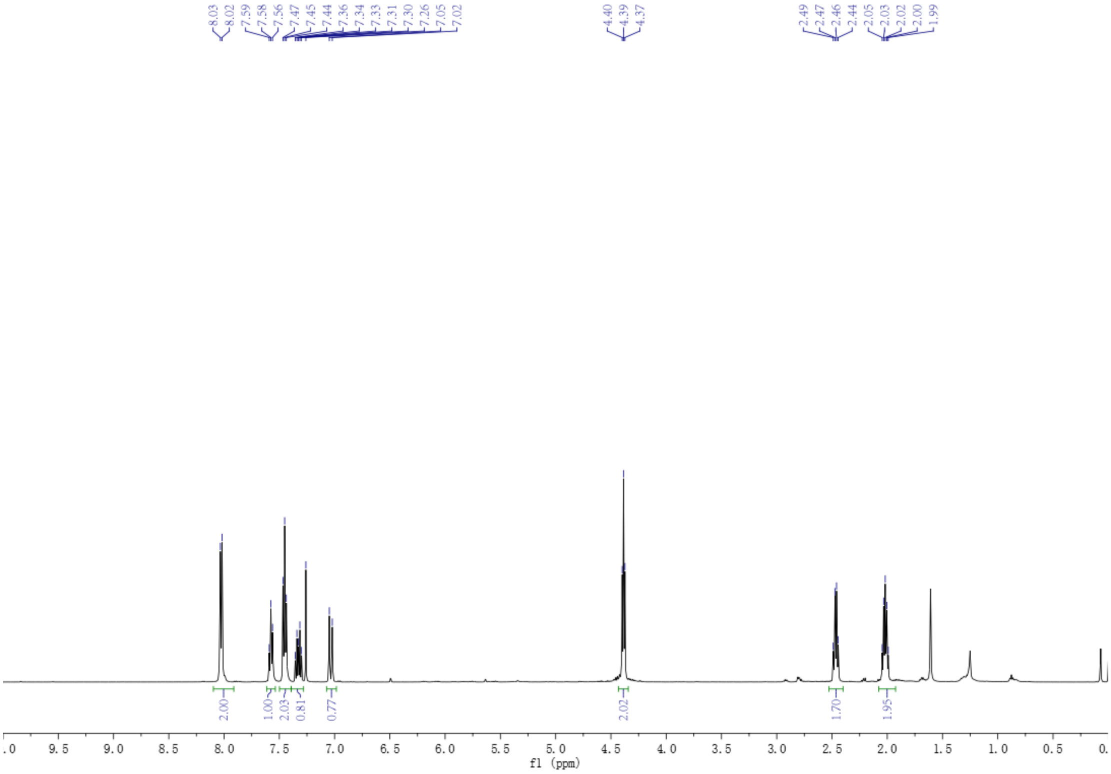
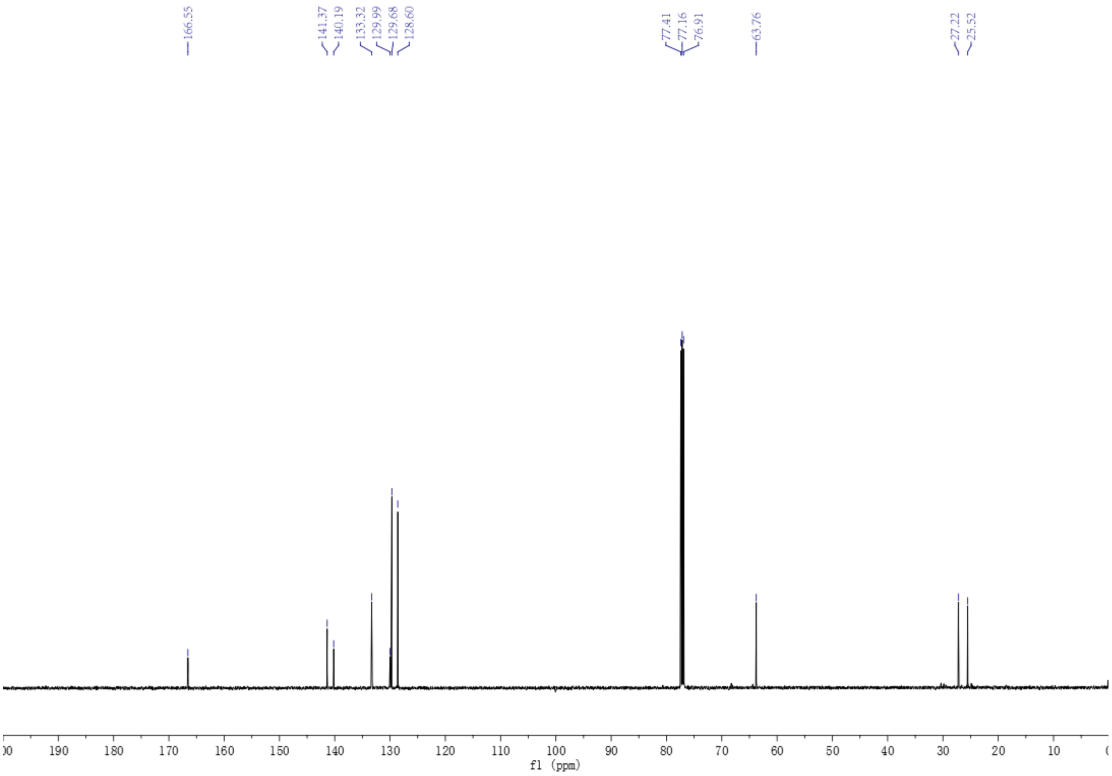
11. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra





^{1}H NMR of compound **2**（500 MHz, $CDCl_3$）



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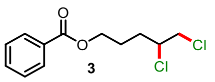

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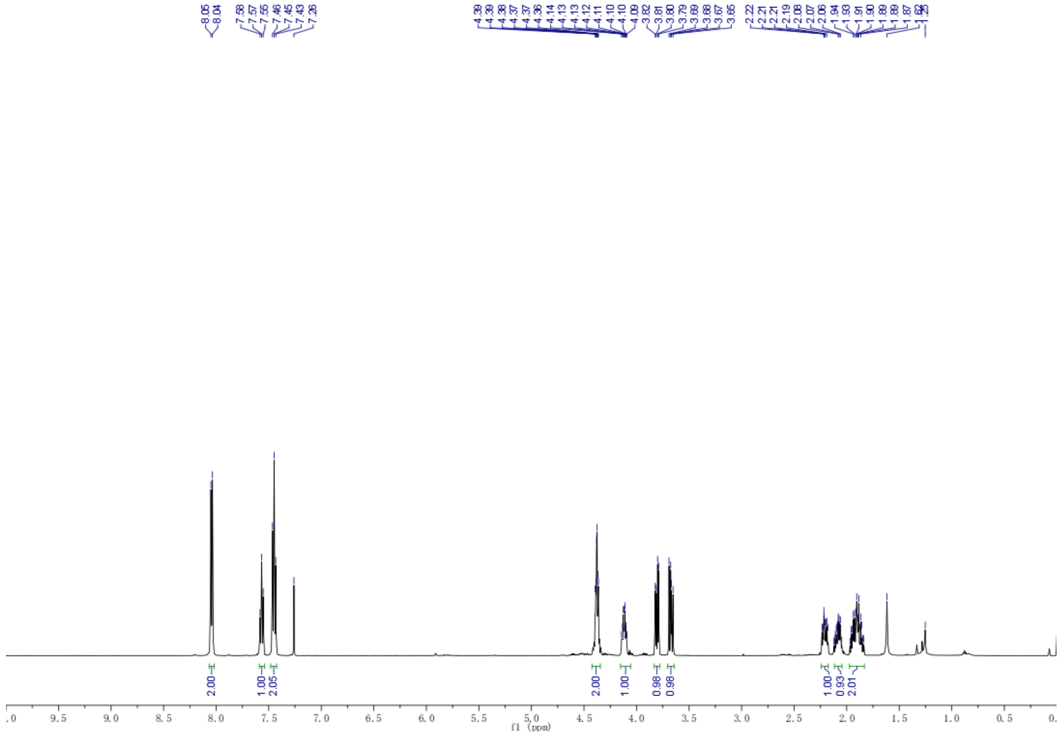

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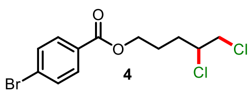

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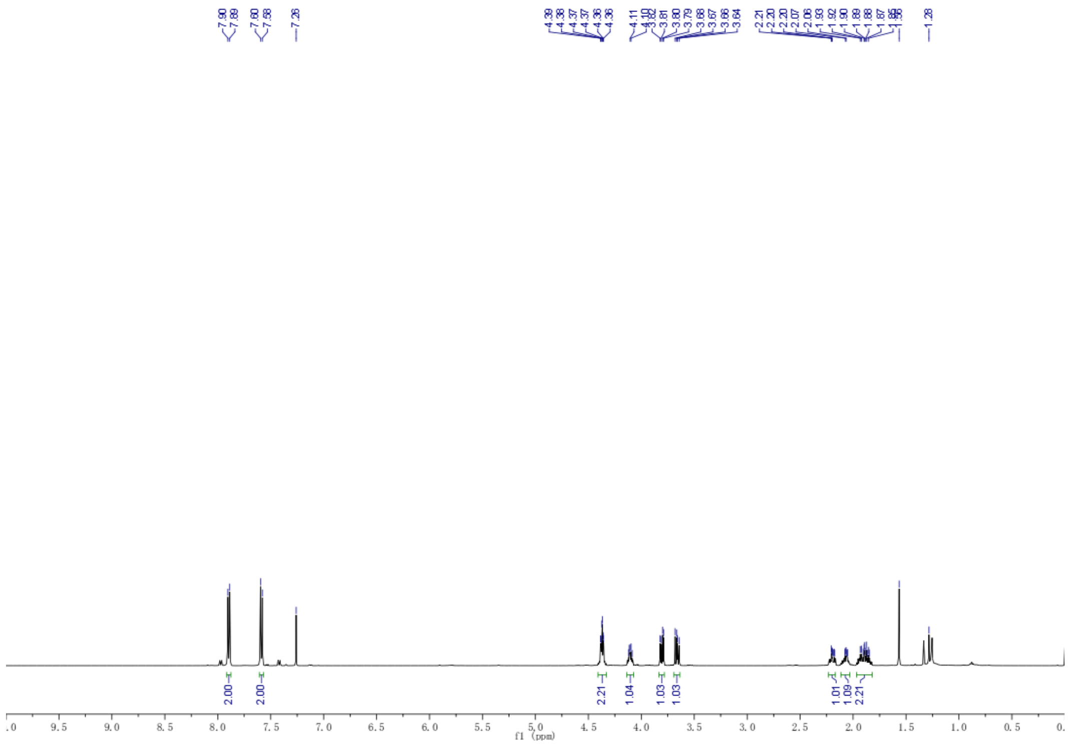
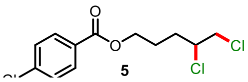
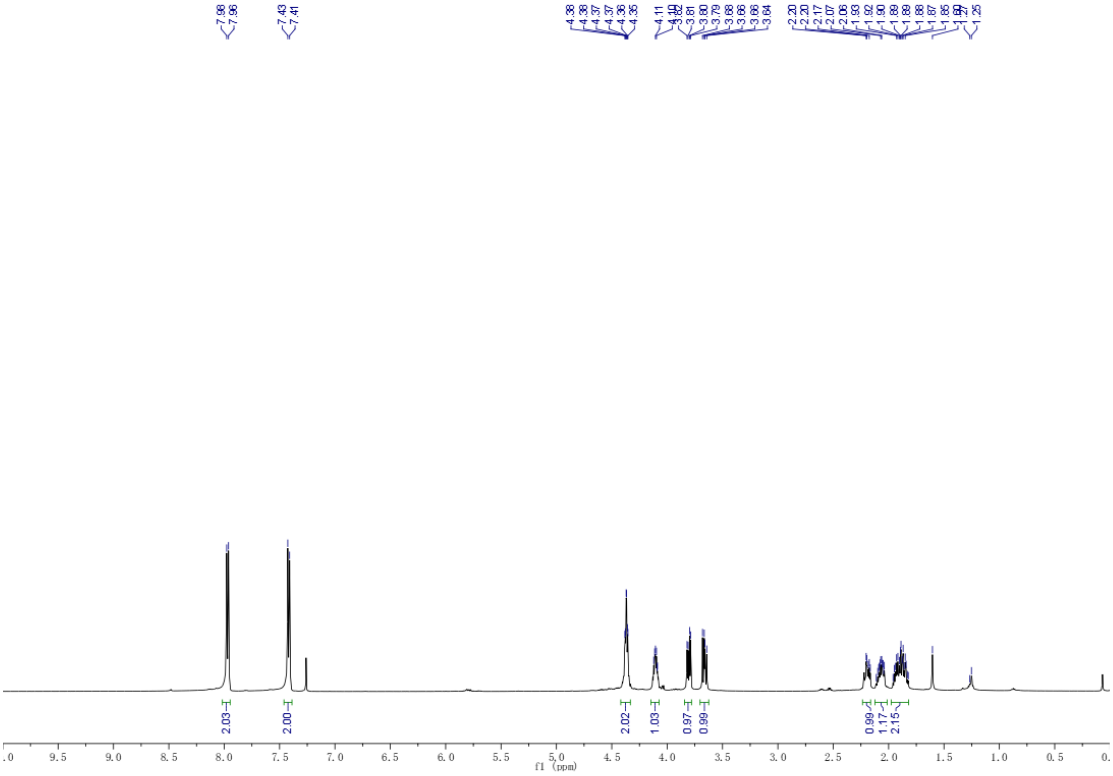


^{1}H NMR of compound **4**（500 MHz, $CDCl_3$）





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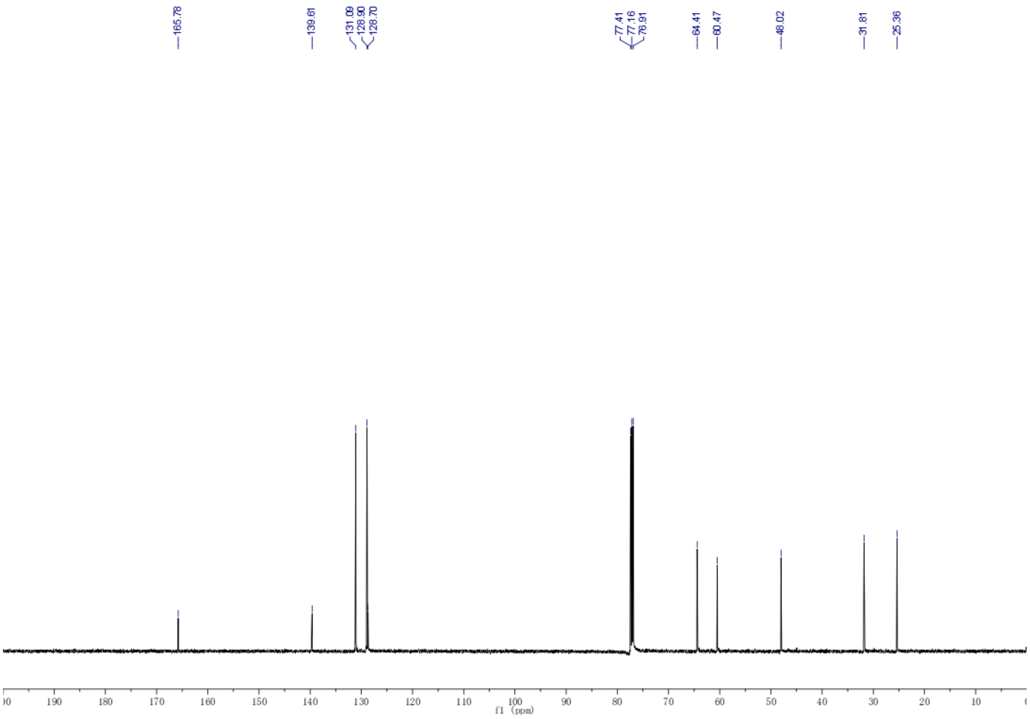
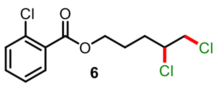


[13]C NMR of compound **5**（126 MHz, $CDCl_3$）



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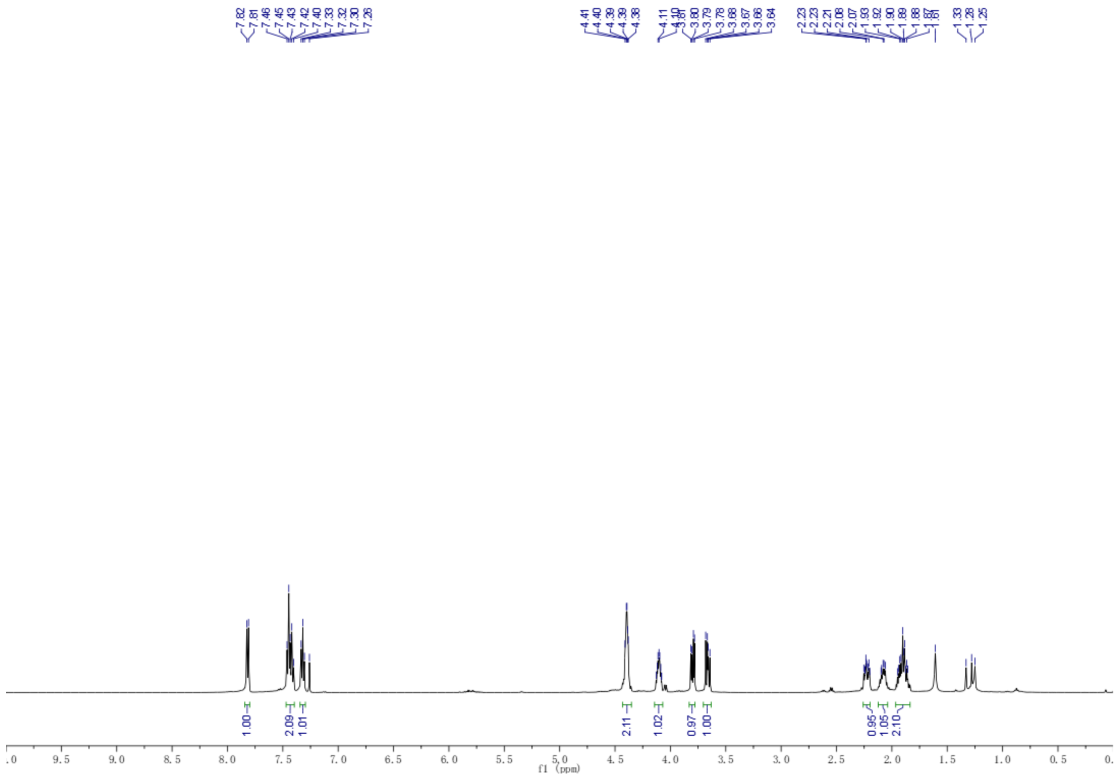

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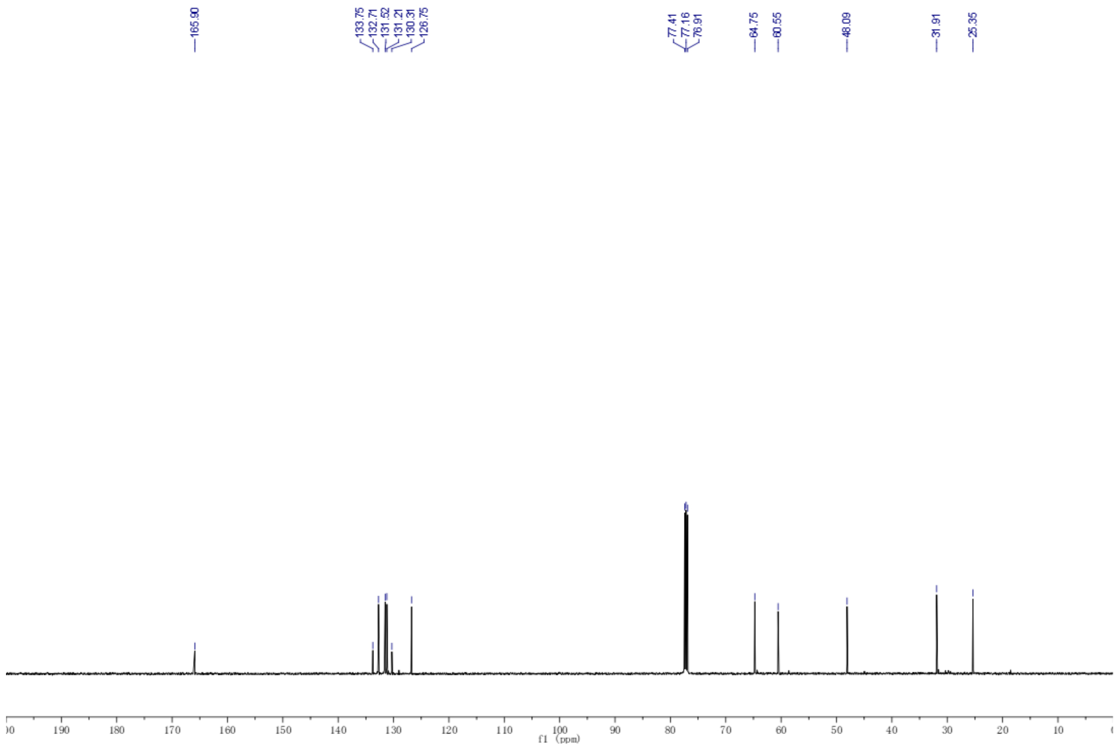

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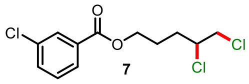

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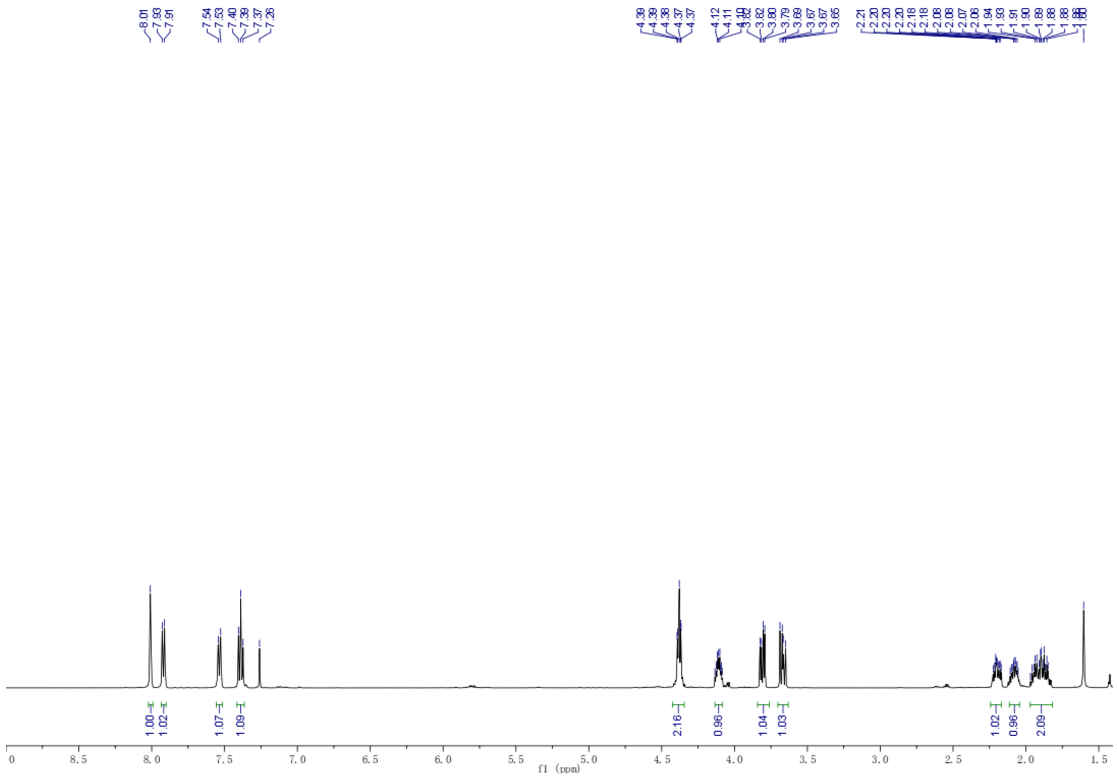

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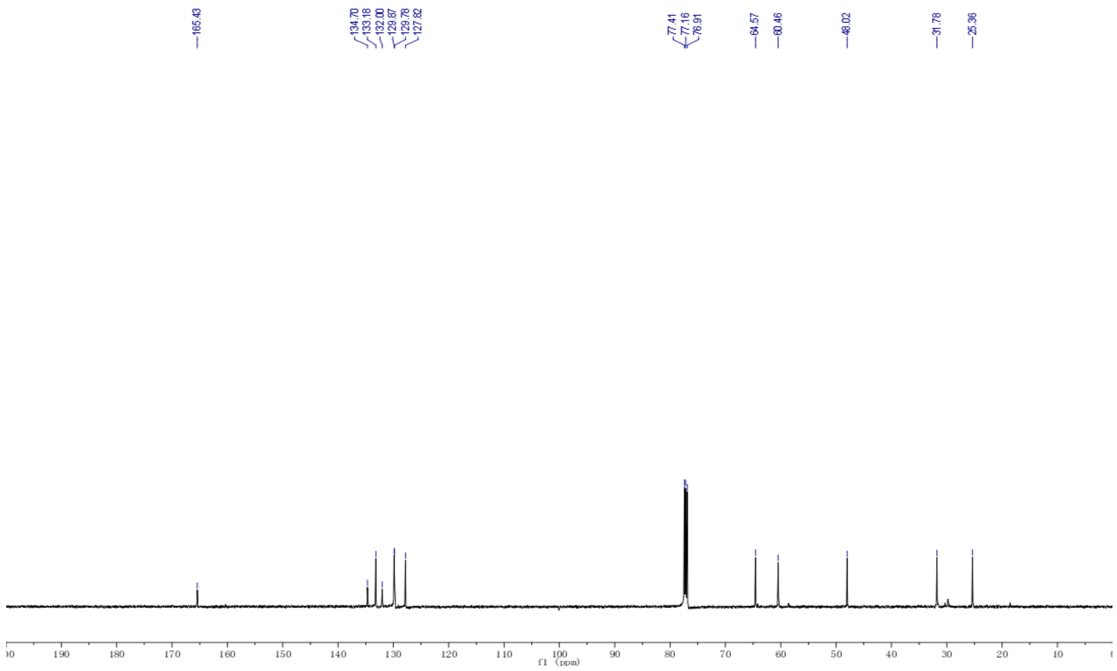
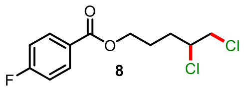


[13]C NMR of compound **7**（126 MHz, $CDCl_3$）



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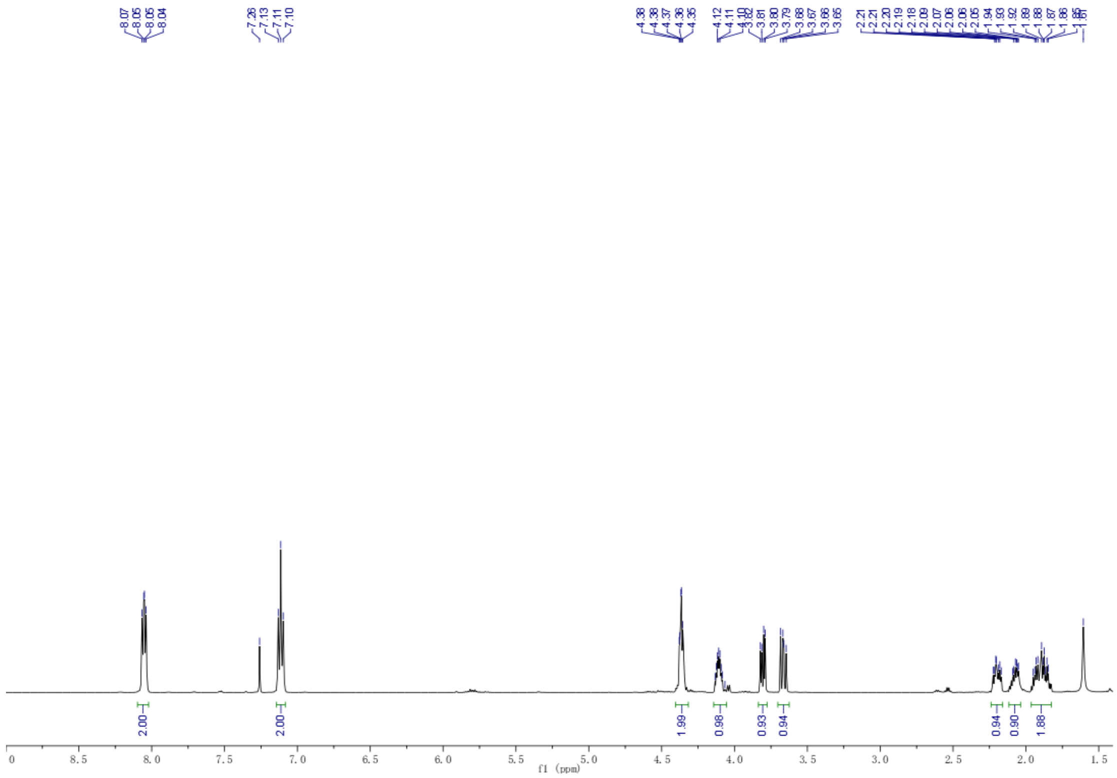
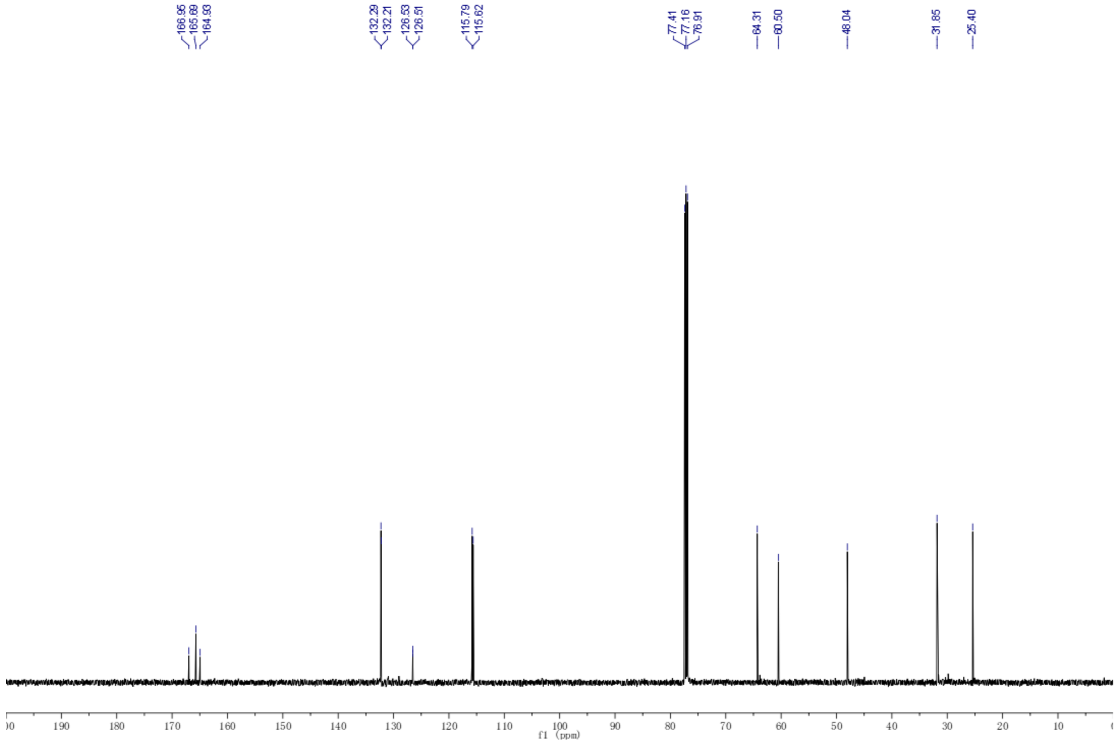
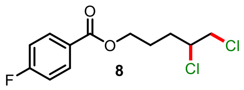


[1]H NMR of compound **8**（500 MHz, $CDCl_3$）



[13]C NMR of compound **8**（126 MHz, $CDCl_3$）



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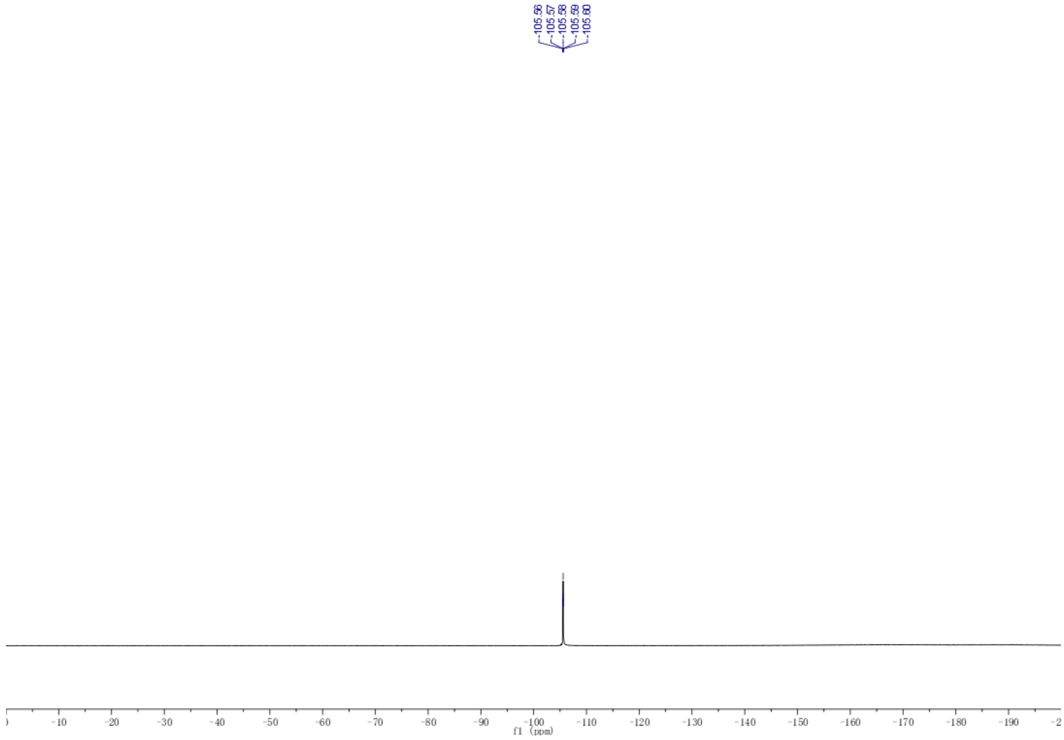
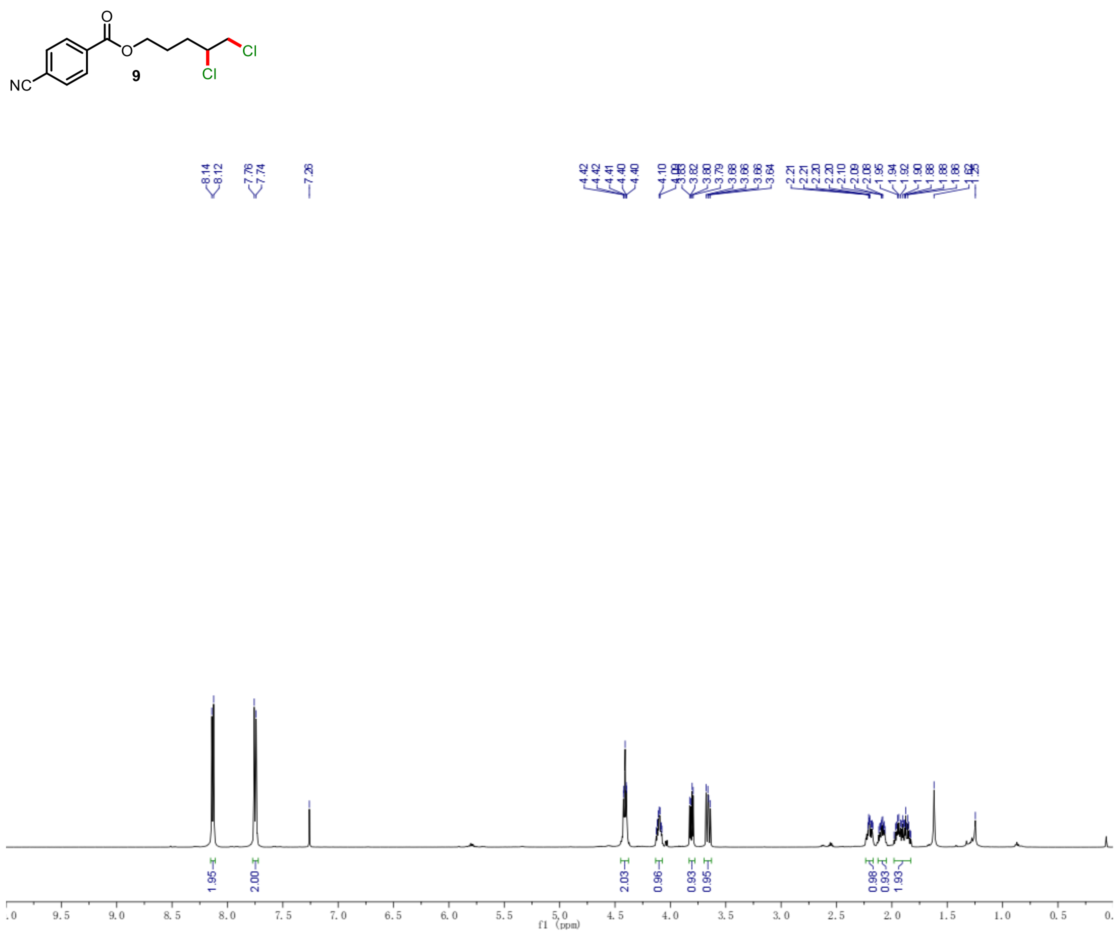
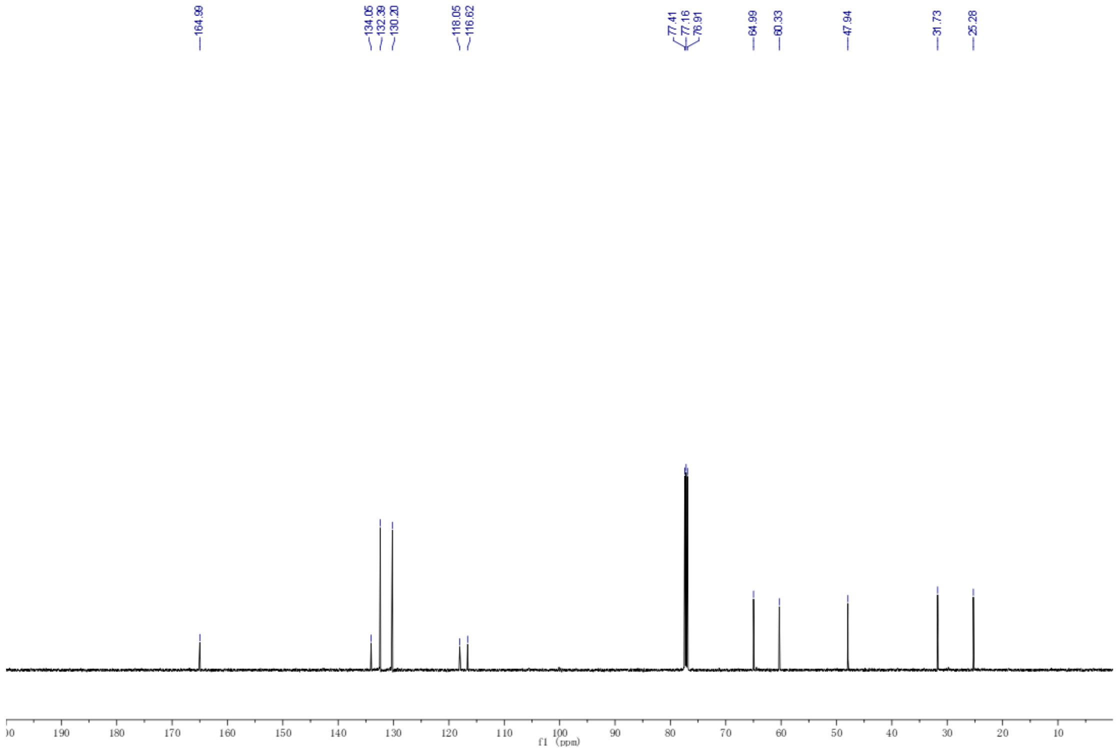


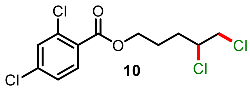
^{19}F NMR of compound **8**（471 MHz, $CDCl_3$）



^{1}H NMR of compound **9**（500 MHz, $CDCl_3$）



^{13}C NMR of compound **9**（126 MHz, $CDCl_3$）



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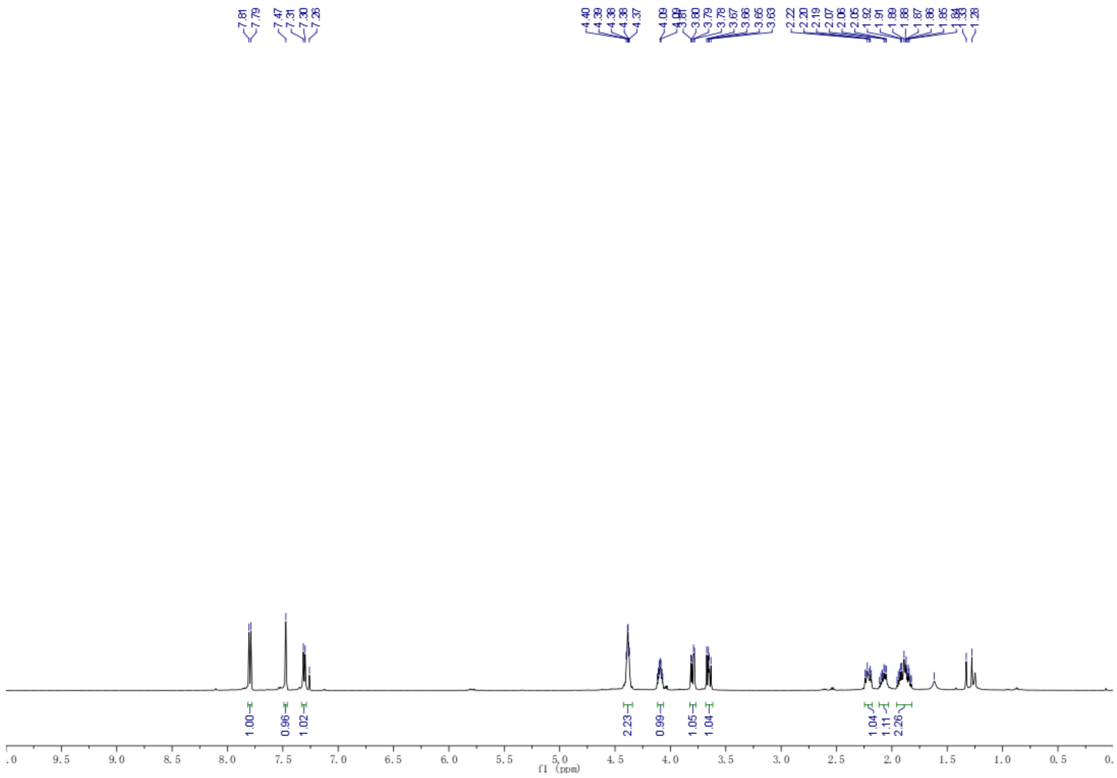
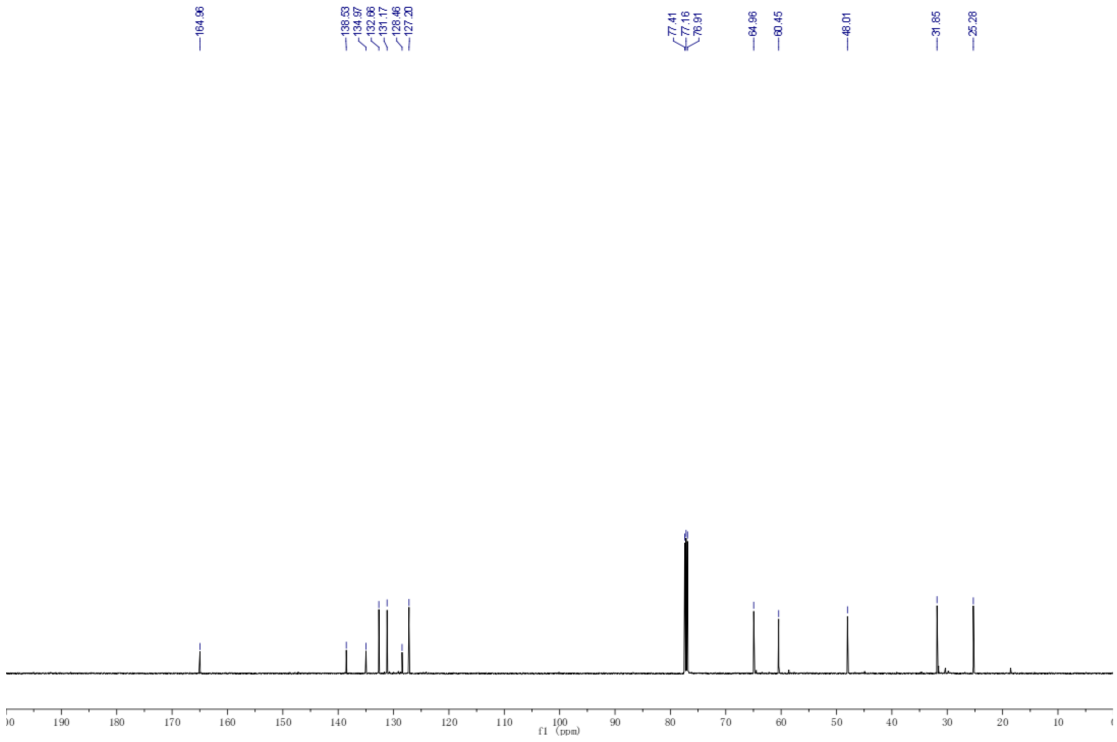
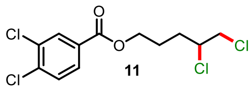
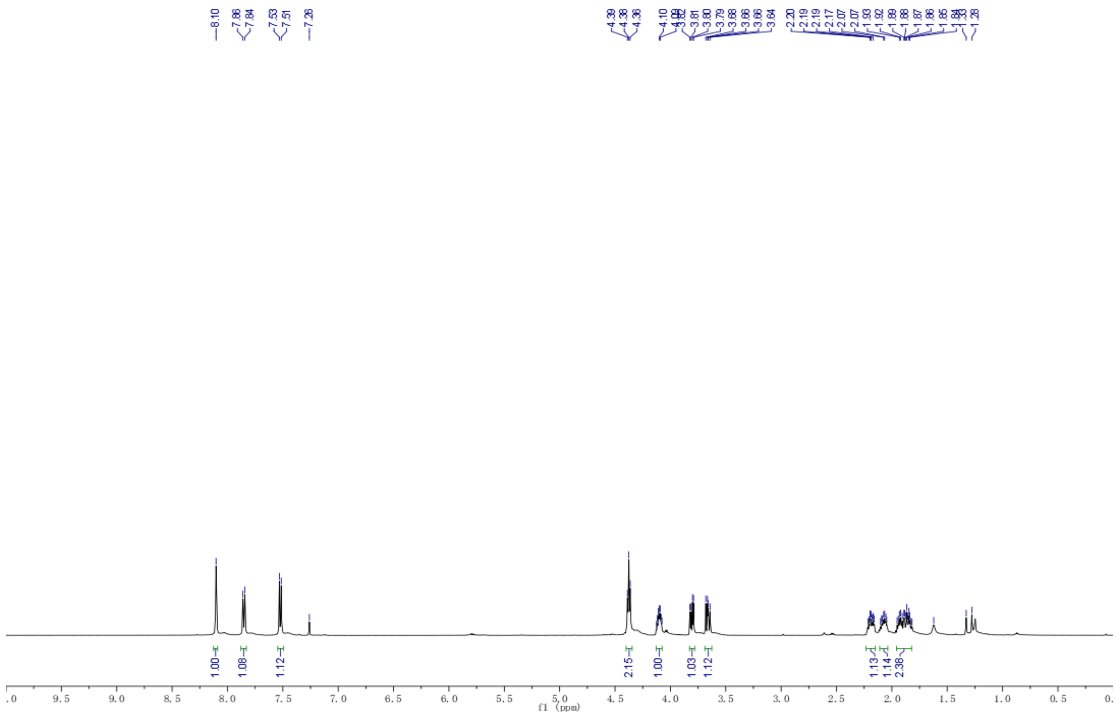


[1]H NMR of compound **10**（500 MHz, $CDCl_3$）

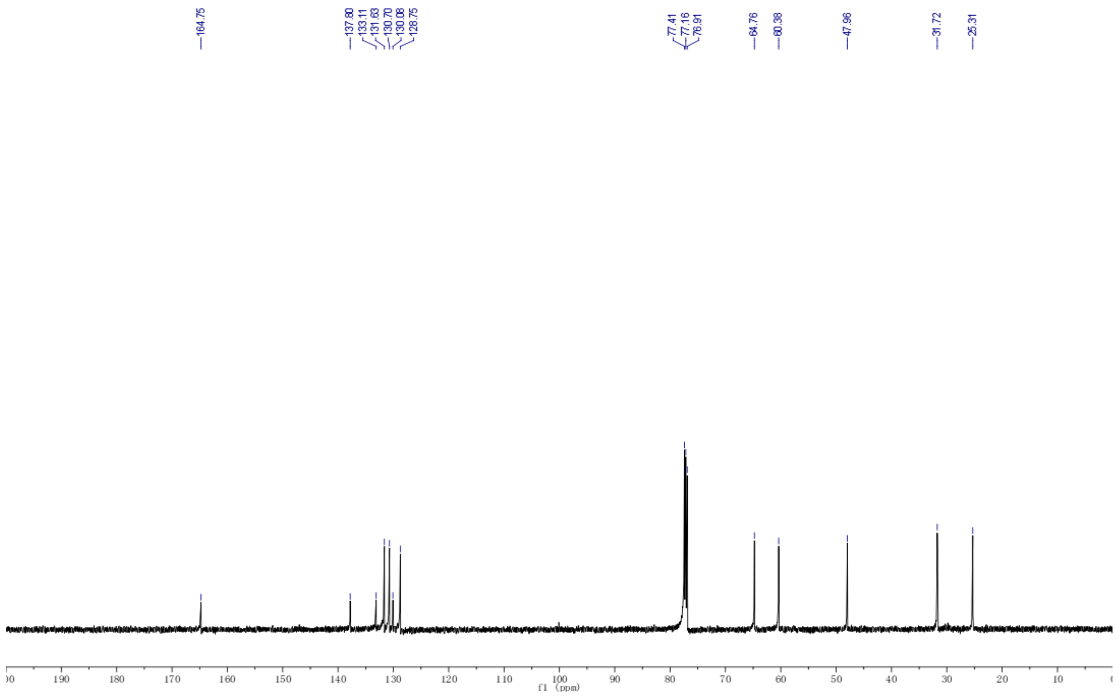


[13]C NMR of compound **10**（126 MHz, $CDCl_3$）

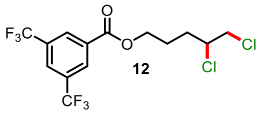


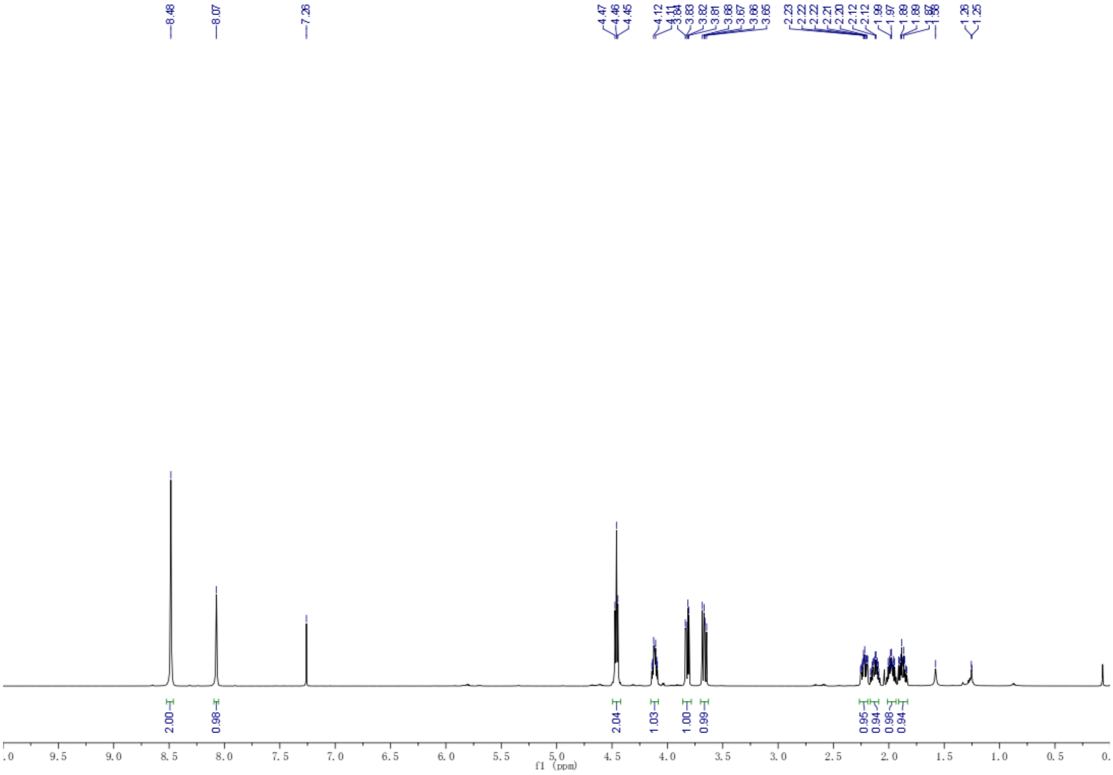


[1]H NMR of compound **11**（500 MHz, $CDCl_3$）

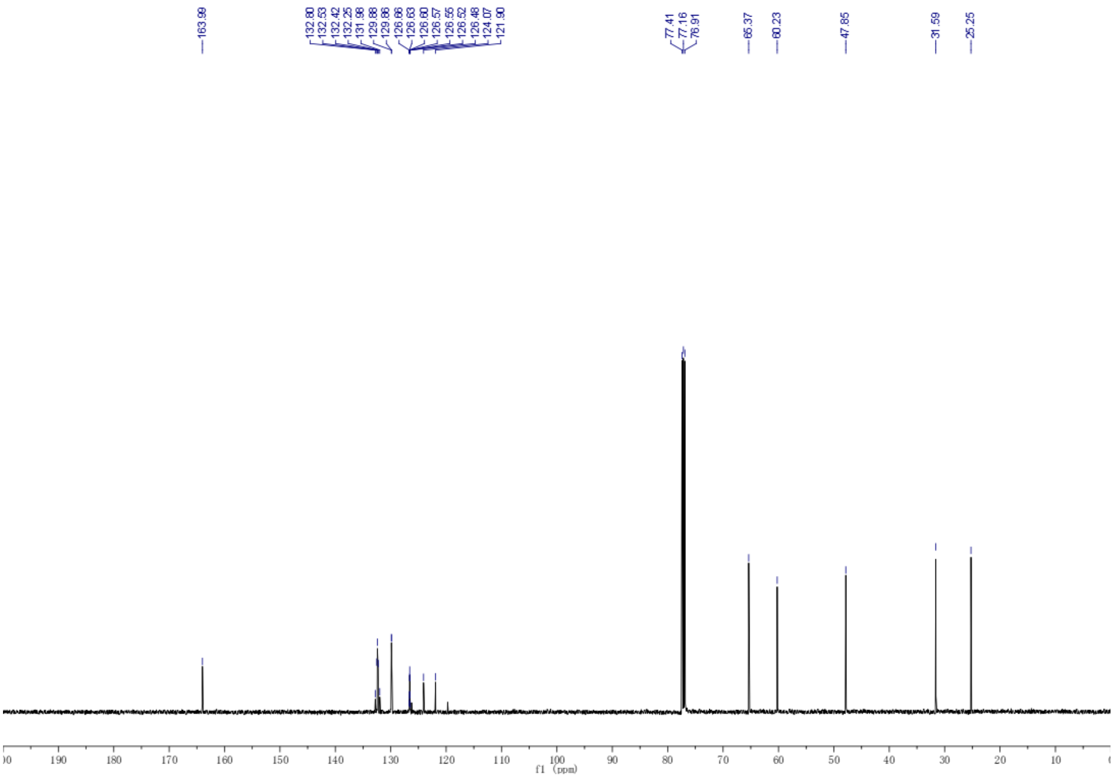


[13]C NMR of compound **11**（126 MHz, $CDCl_3$）

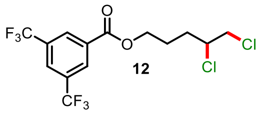


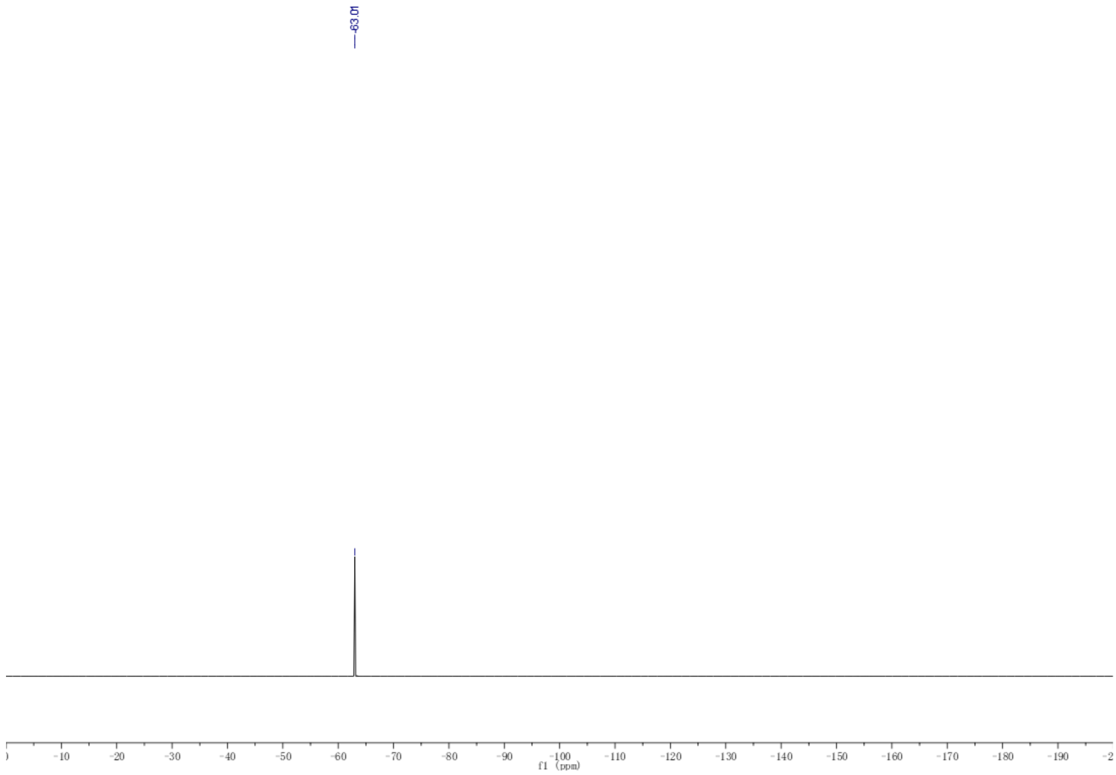


^{1}H NMR of compound **12**（500 MHz, $CDCl_3$）

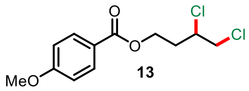


^{13}C NMR of compound **12**（126 MHz, $CDCl_3$）

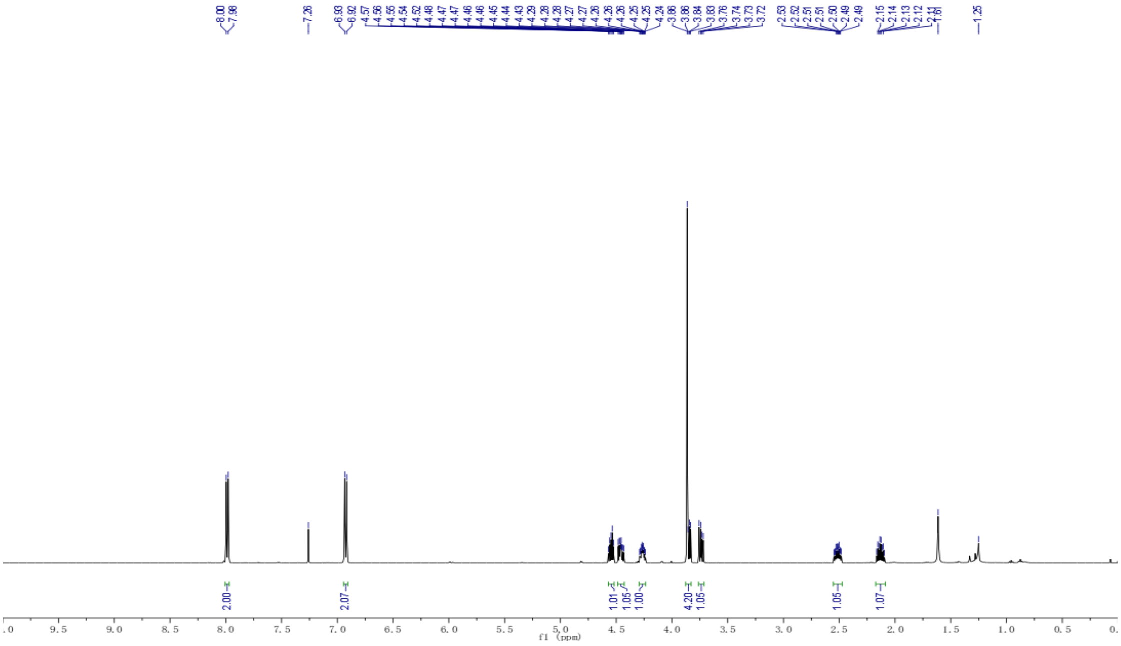




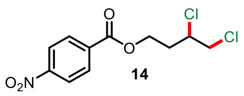
^{19}F NMR of compound **12**（471 MHz, $CDCl_3$）



13



[1]H NMR of compound **13**（500 MHz, $CDCl_3$）



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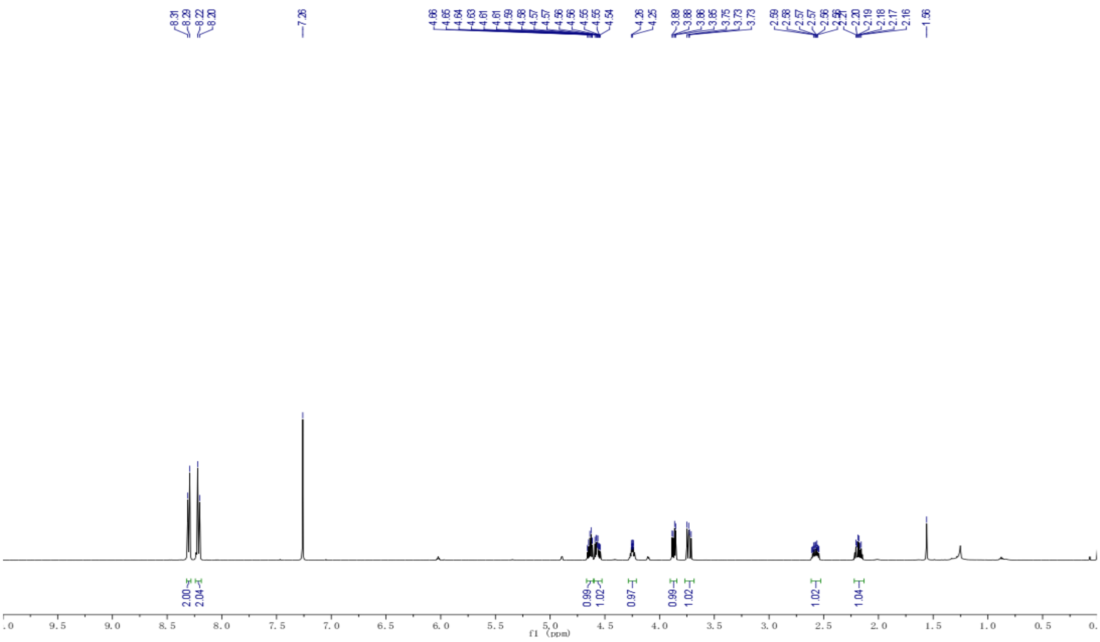
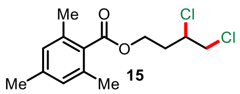


[1]H NMR of compound **14**（500 MHz, $CDCl_3$）



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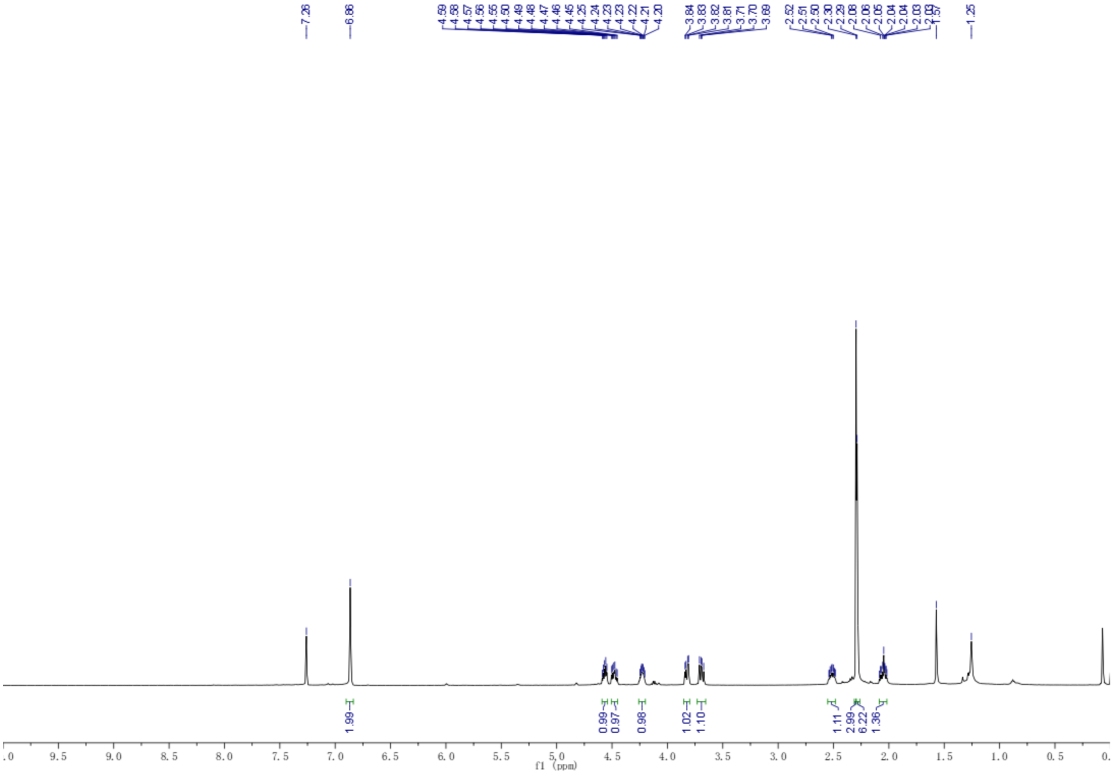
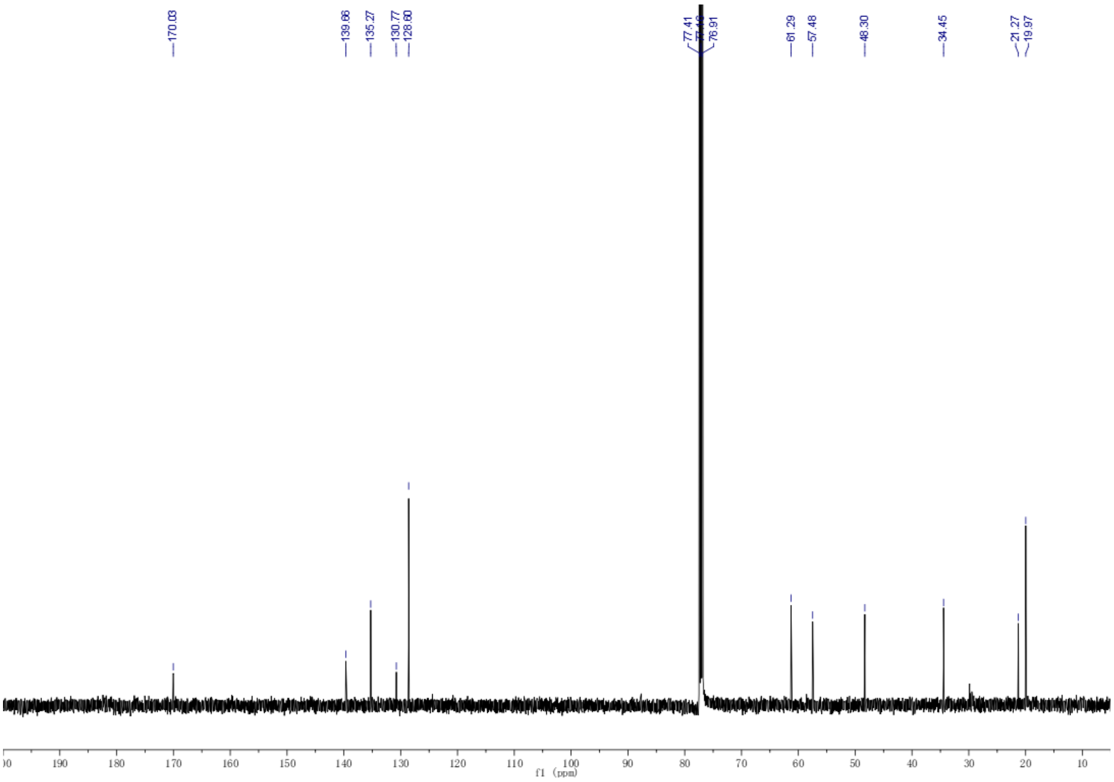
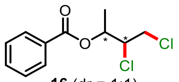


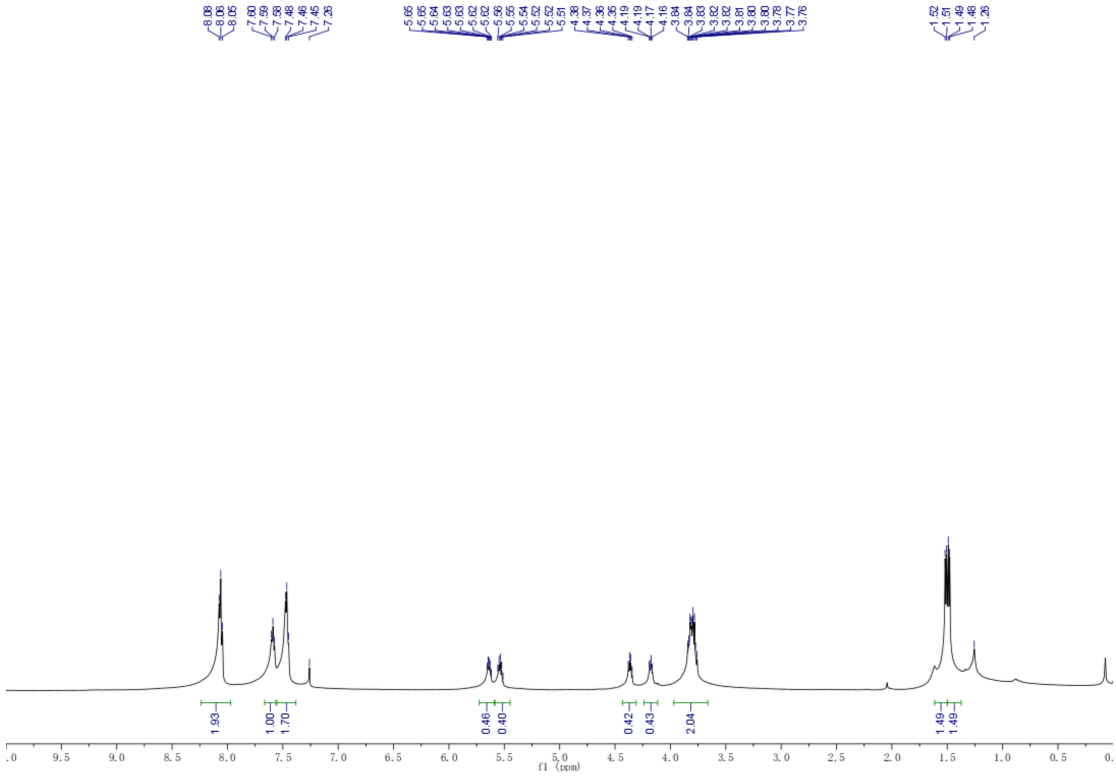
^{1}H NMR of compound **15**（500 MHz, $CDCl_3$）



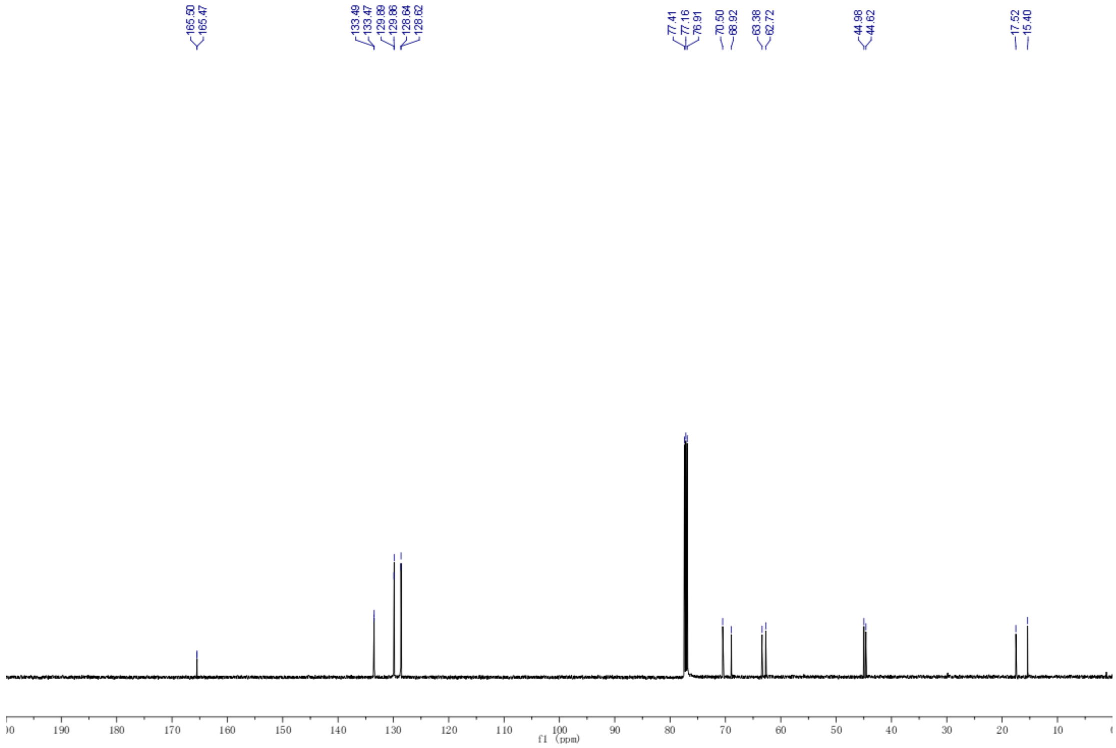
^{13}C NMR of compound **15**（126 MHz, $CDCl_3$）



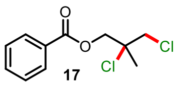
16 (dr = 1:1)

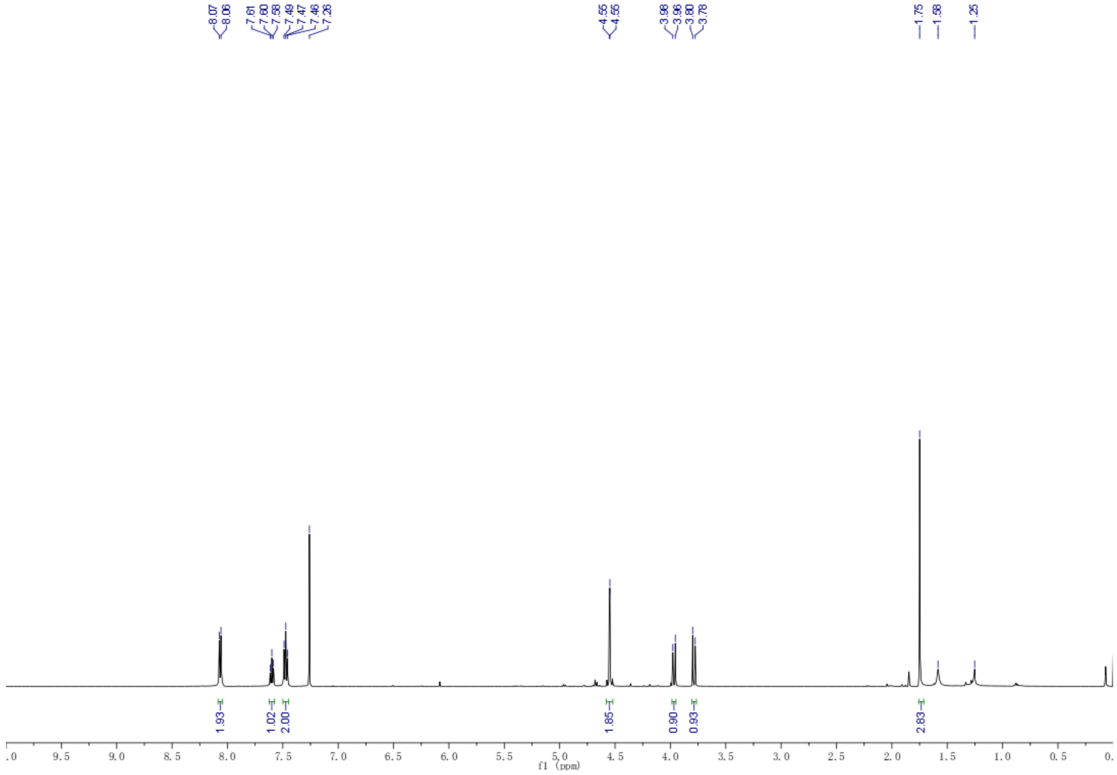


[1]H NMR of compound **16**（500 MHz, $CDCl_3$）

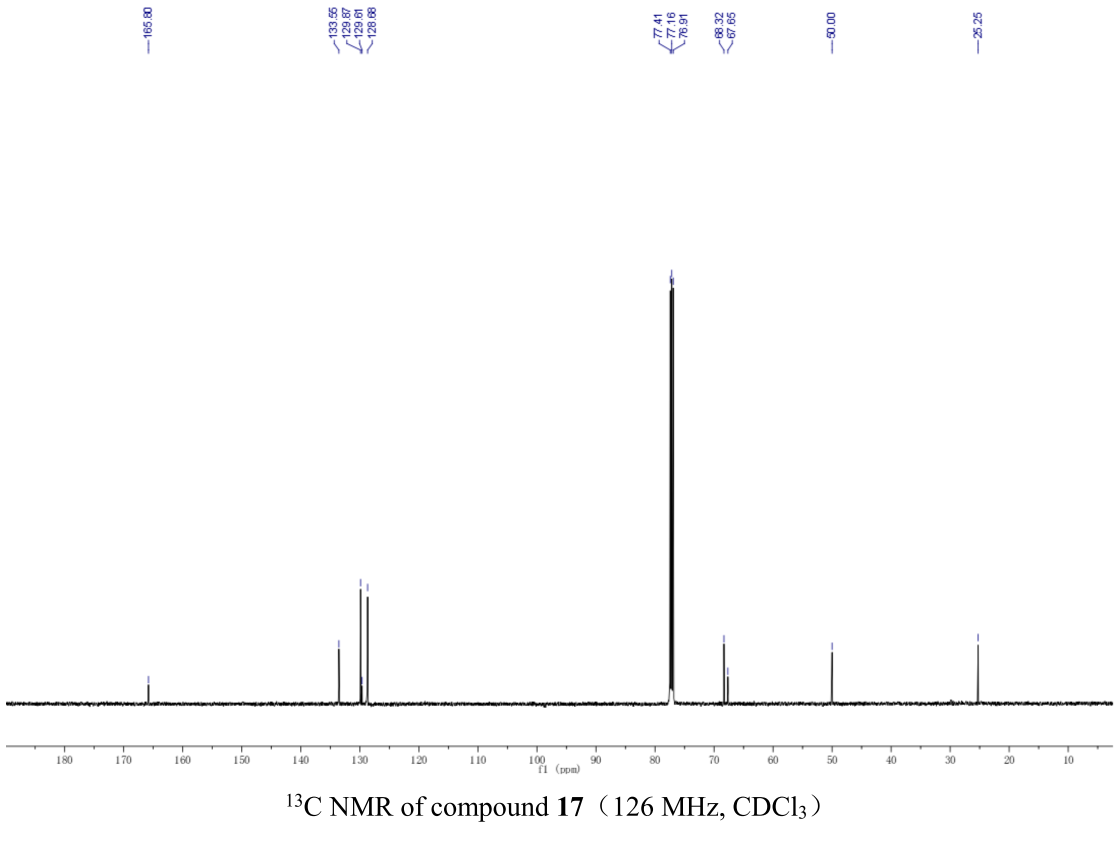


[13]C NMR of compound **16**（126 MHz, $CDCl_3$）

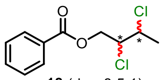




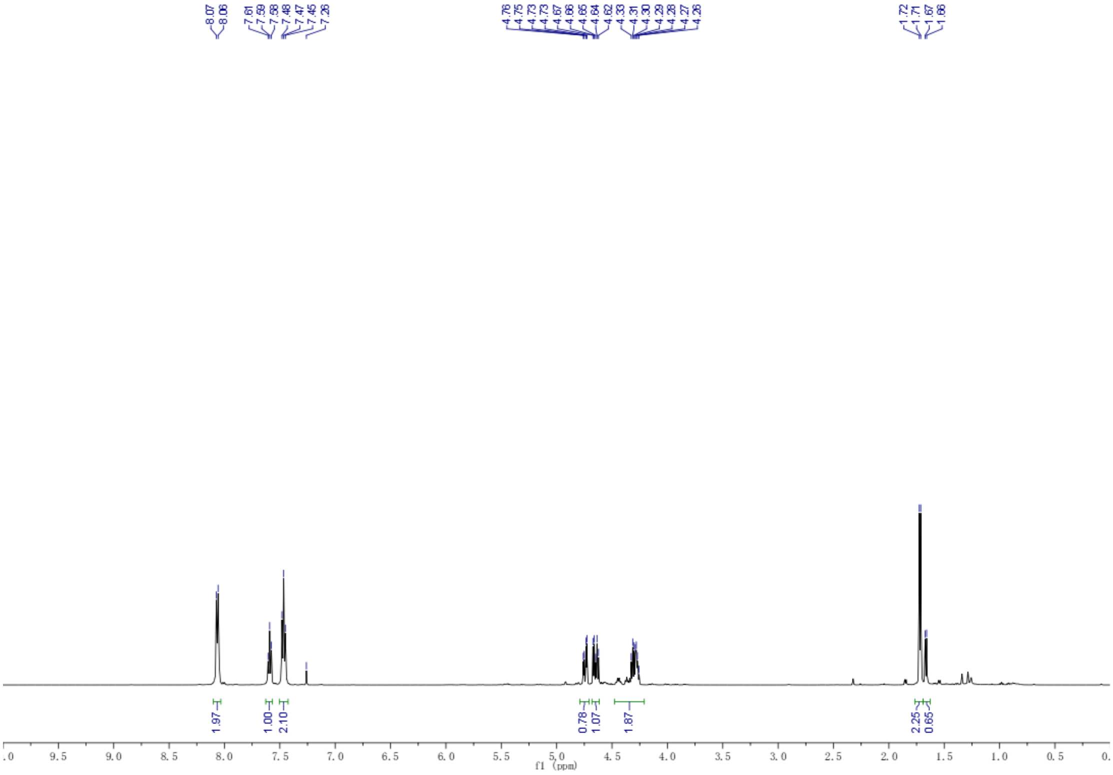
[1]H NMR of compound **17**（500 MHz, $CDCl_3$）



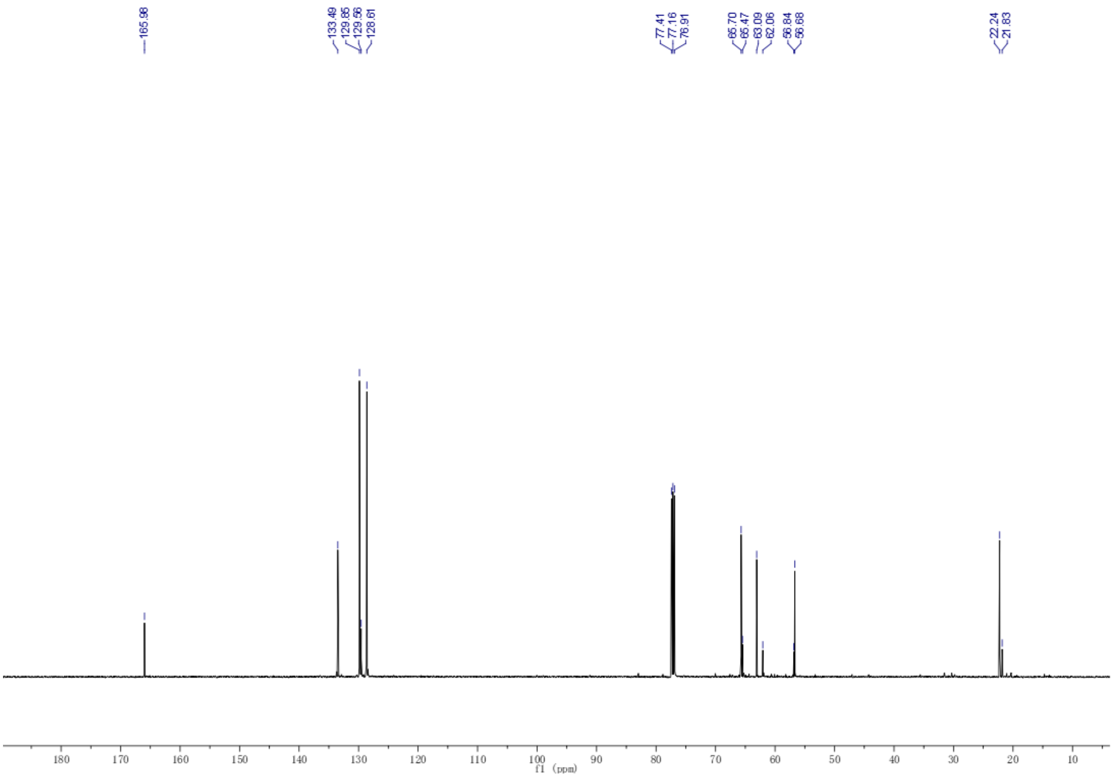
[13]C NMR of compound **17**（126 MHz, $CDCl_3$）



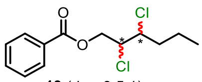
18 (dr = 3.5:1)



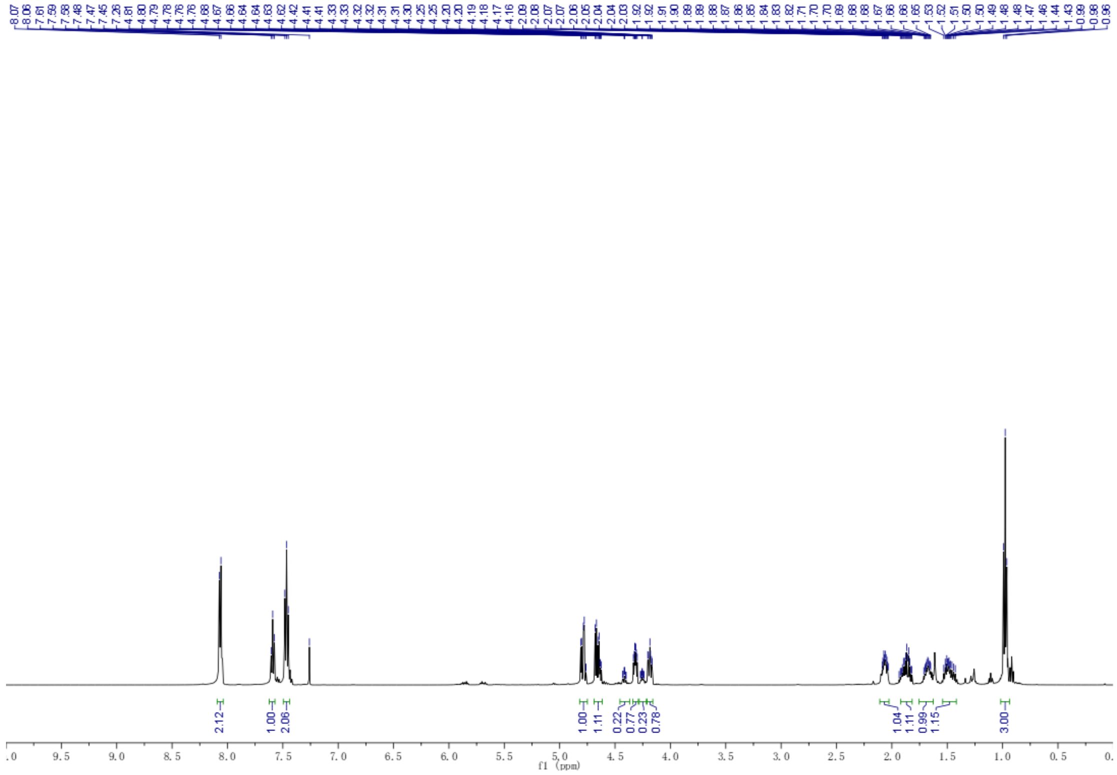
^{1}H NMR of compound **18**（500 MHz, $CDCl_3$）



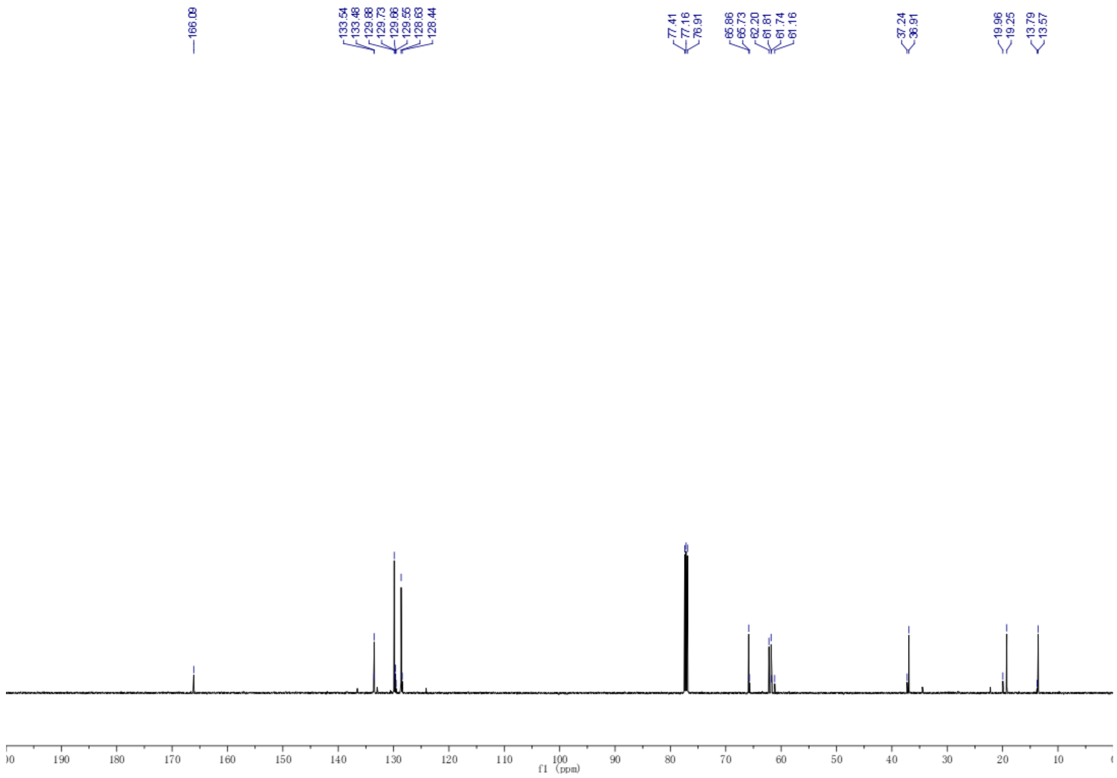
^{13}C NMR of compound **18**（126 MHz, $CDCl_3$）



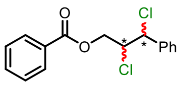
19 (dr = 3.5:1)



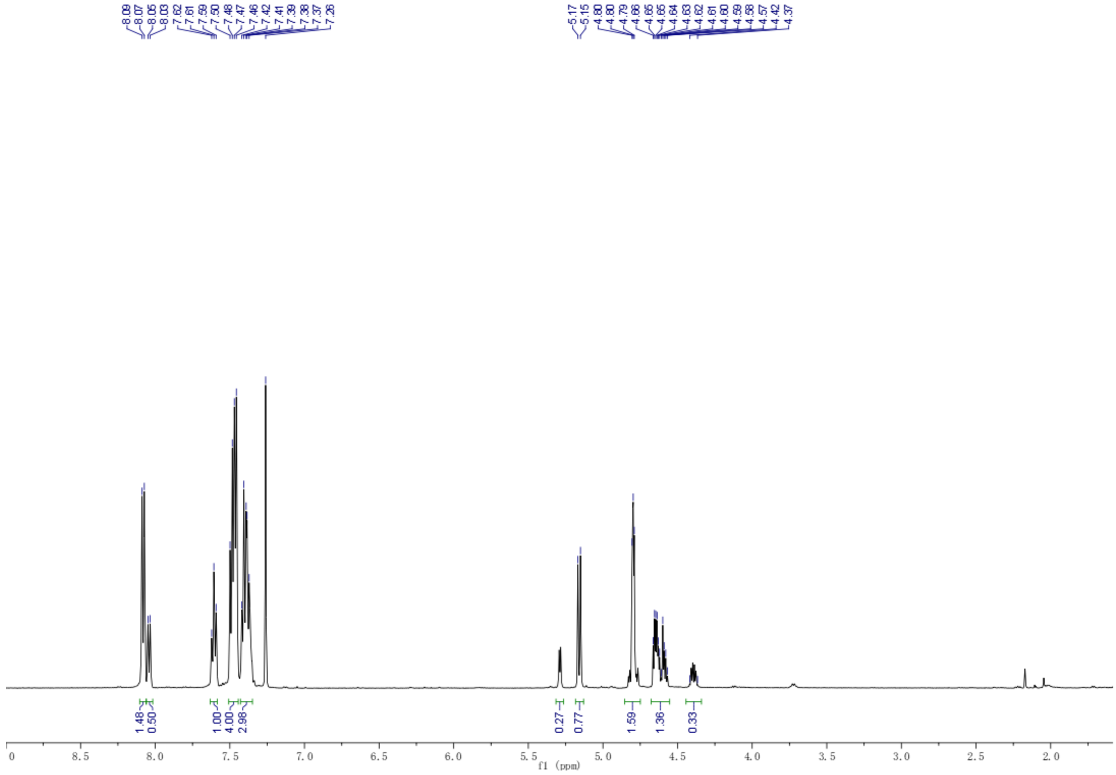
[1]H NMR of compound **19**（500 MHz, $CDCl_3$）



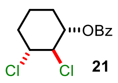
[13]C NMR of compound **19**（126 MHz, $CDCl_3$）



20 (dr = 3.0:1)



[1]H NMR of compound **20**（500 MHz, $CDCl_3$）



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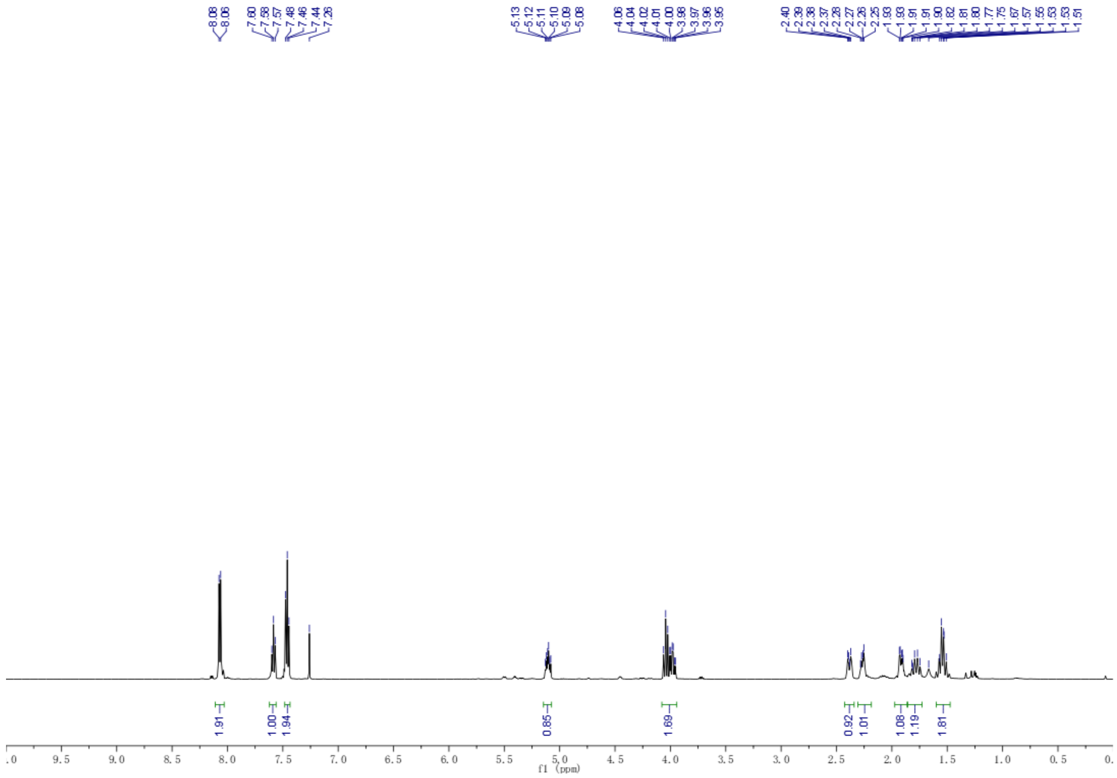
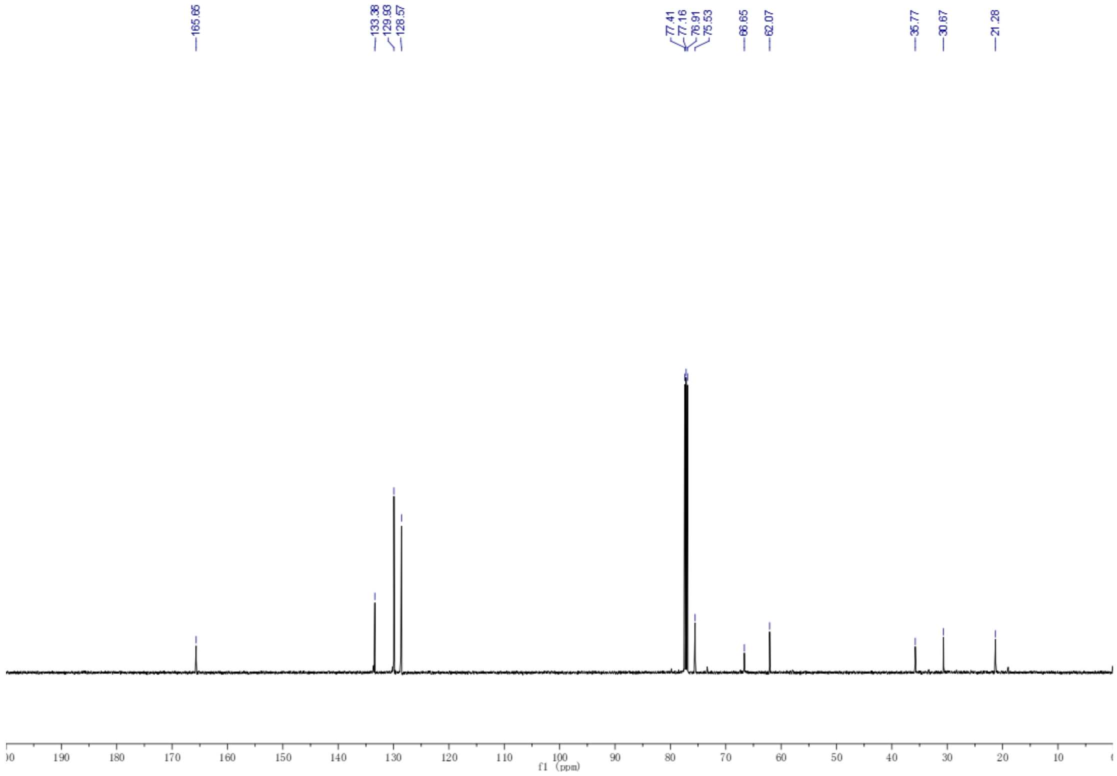
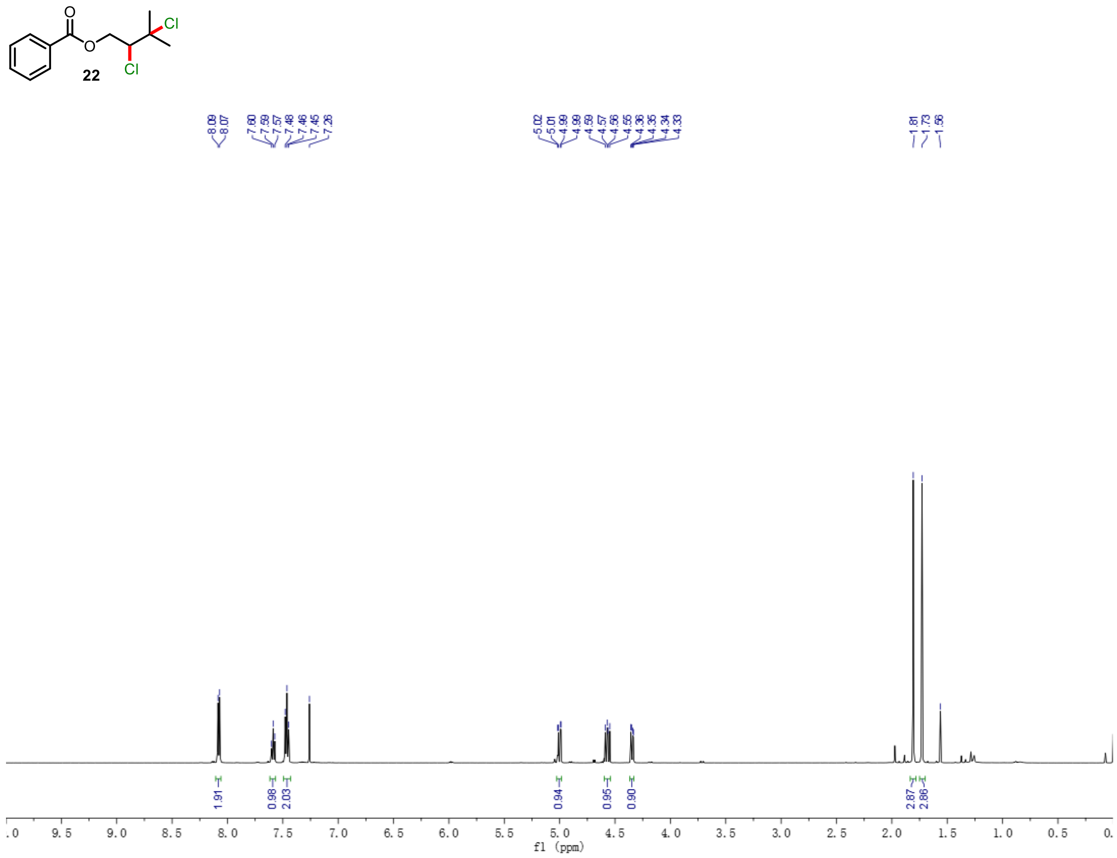


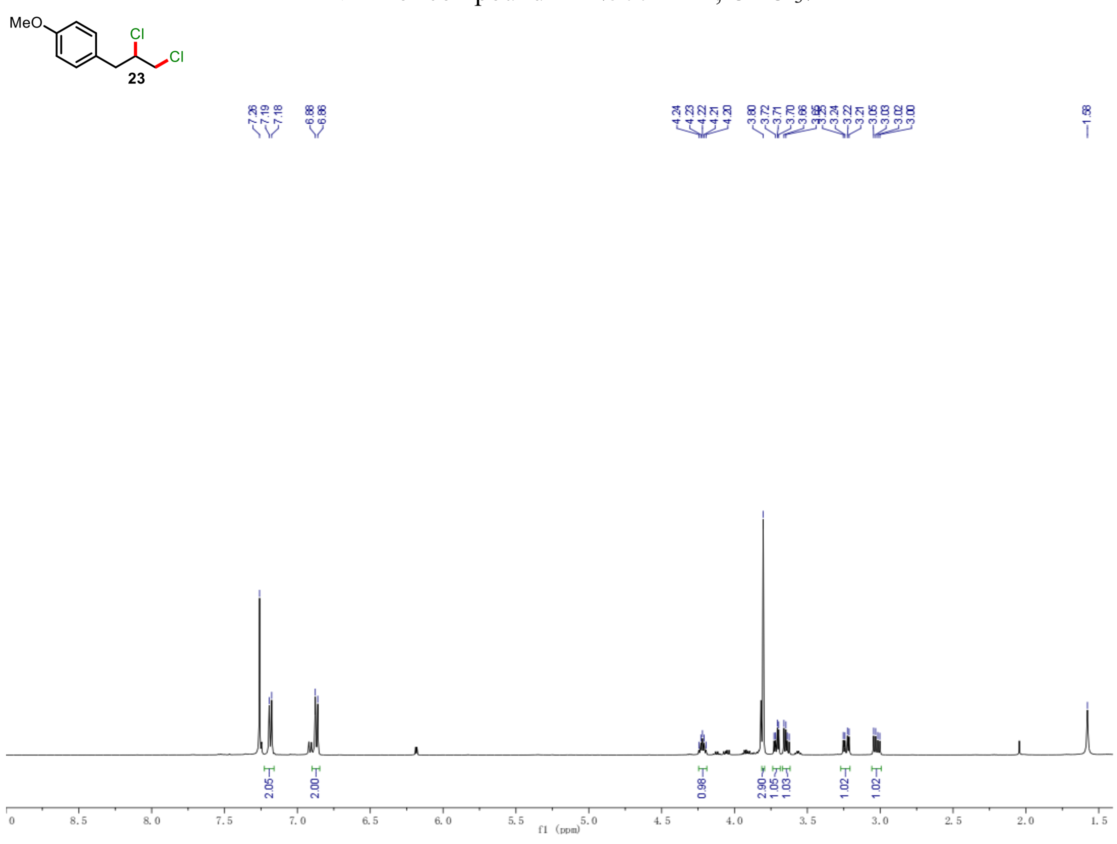
[1]H NMR of compound **21**（500 MHz, $CDCl_3$）



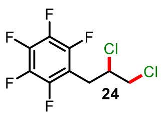
[13]C NMR of compound **21**（126 MHz, $CDCl_3$）

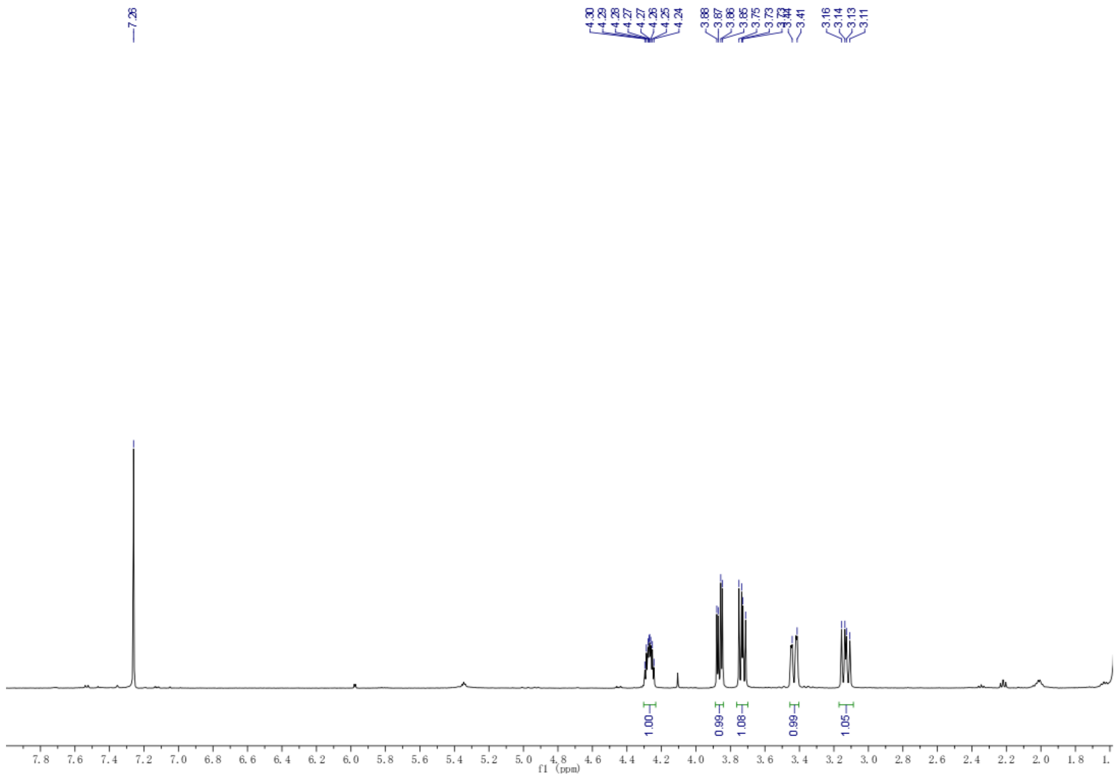


^{1}H NMR of compound **22**（500 MHz, $CDCl_3$）

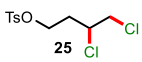


^{1}H NMR of compound **23**（500 MHz, $CDCl_3$）





^{1}H NMR of compound **24**（500 MHz, $CDCl_3$）



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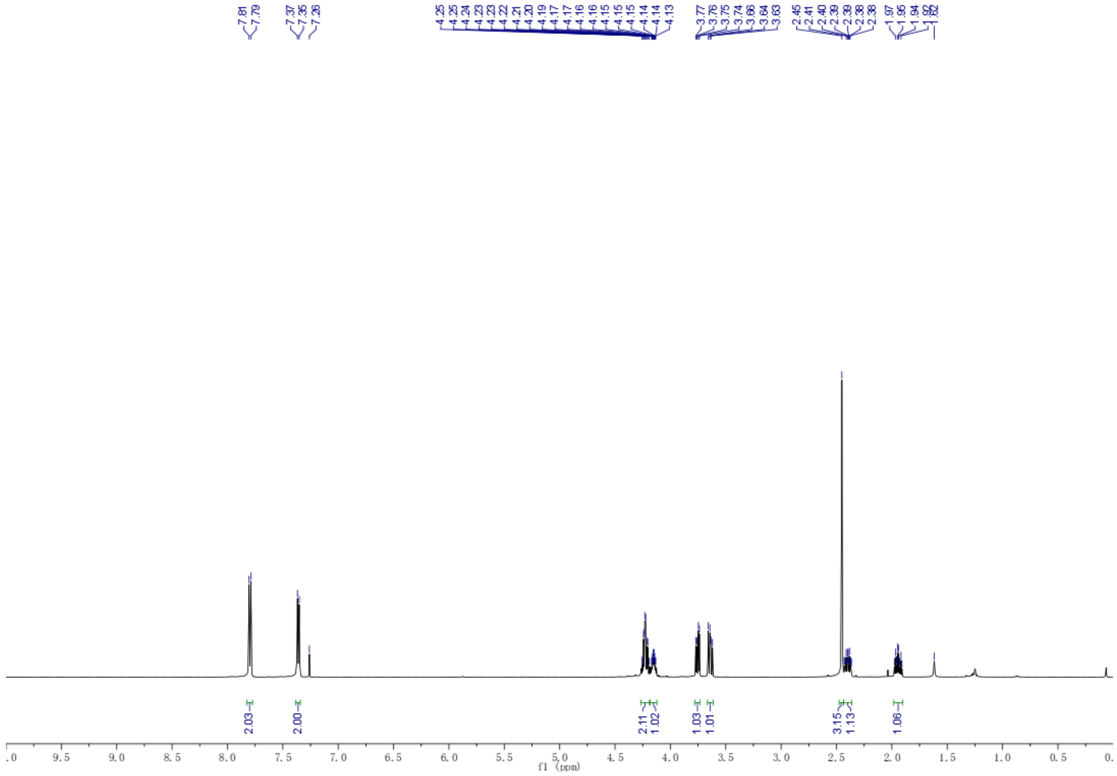
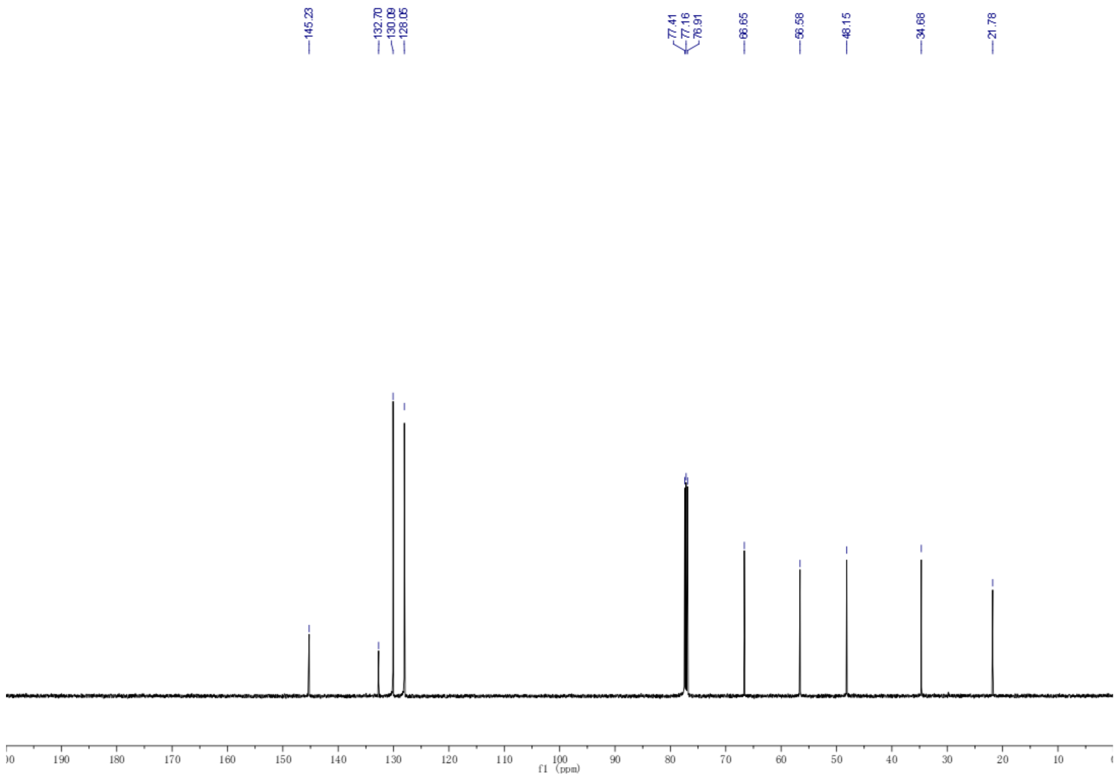
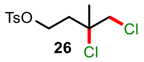


[1]H NMR of compound **25**（500 MHz, $CDCl_3$）



[13]C NMR of compound **25**（126 MHz, $CDCl_3$）



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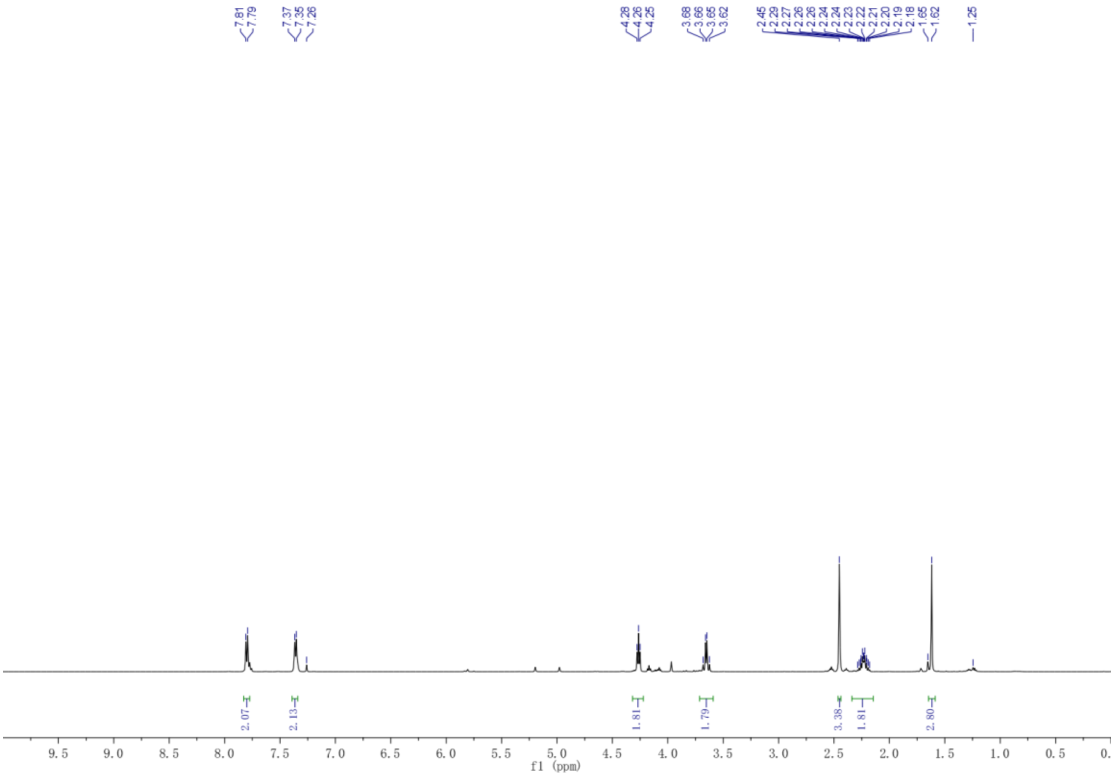
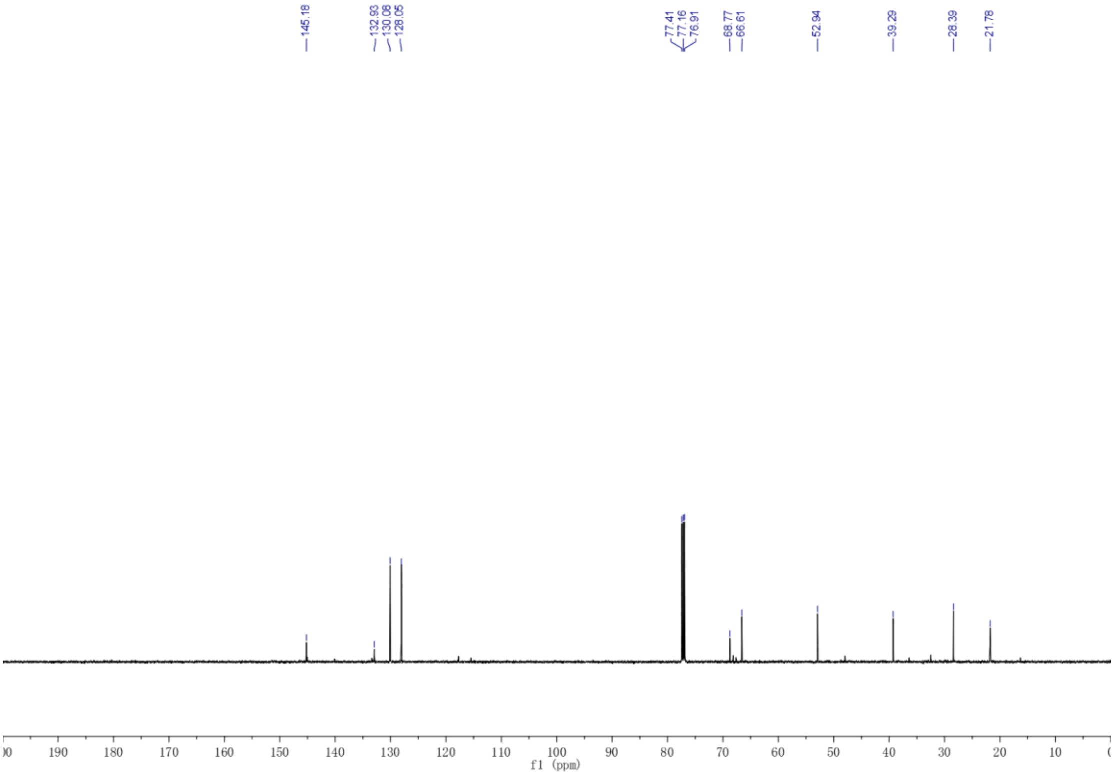
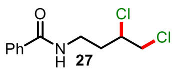


^{1}H NMR of compound **26**（500 MHz, $CDCl_3$）



^{13}C NMR of compound **26**（126 MHz, $CDCl_3$）



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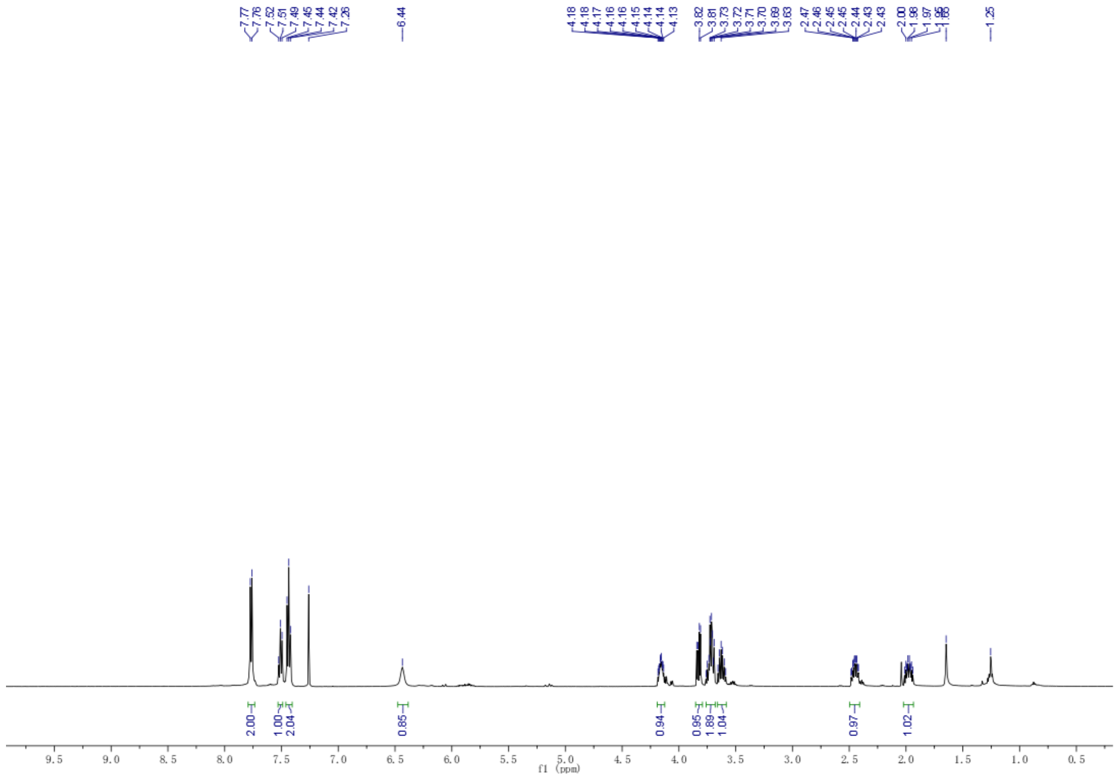
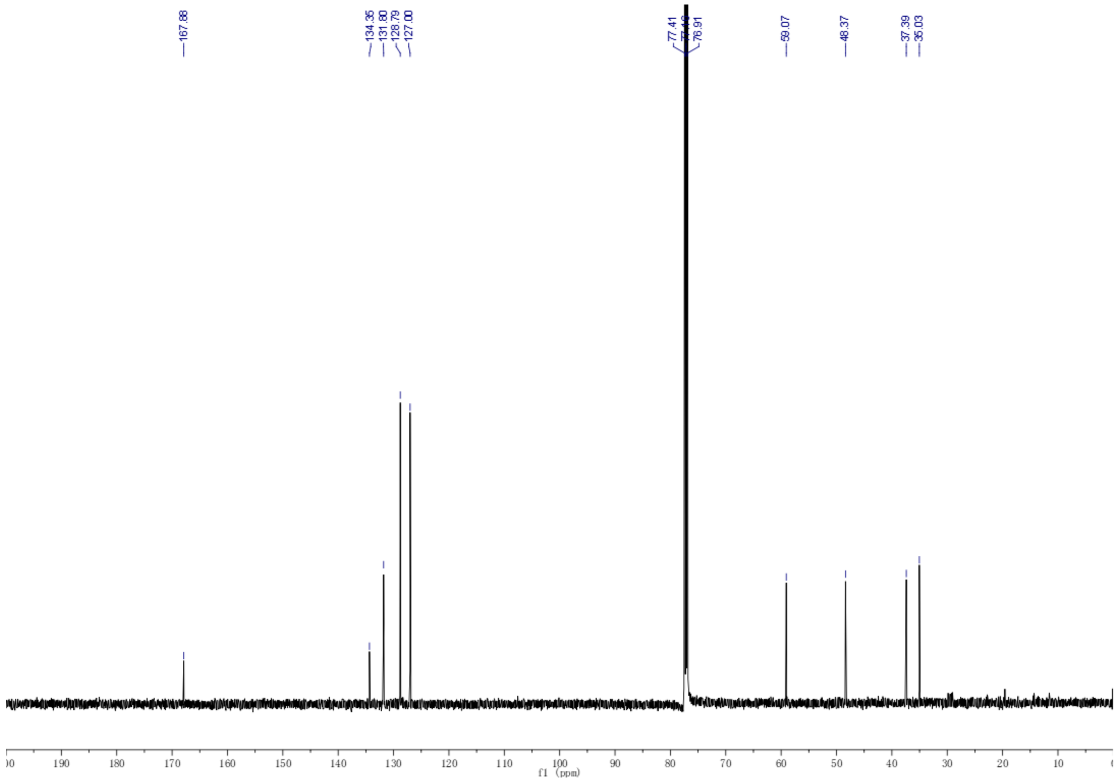
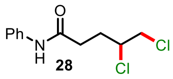
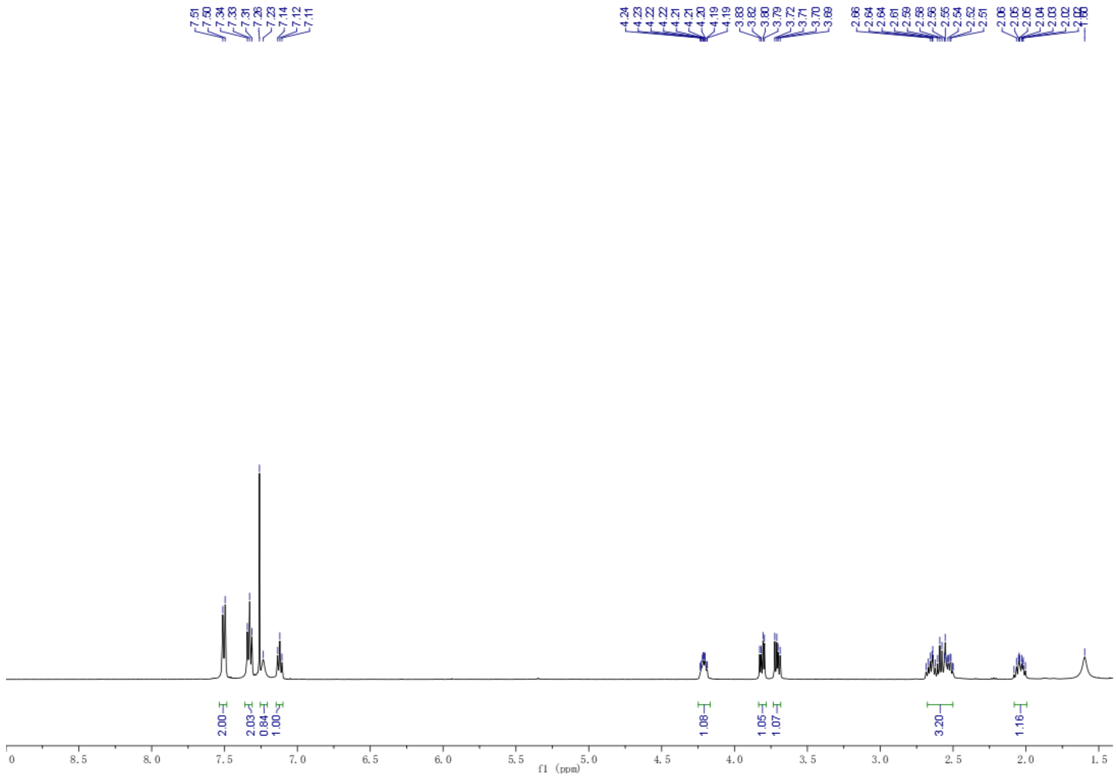


^{1}H NMR of compound **27**（500 MHz, $CDCl_3$）

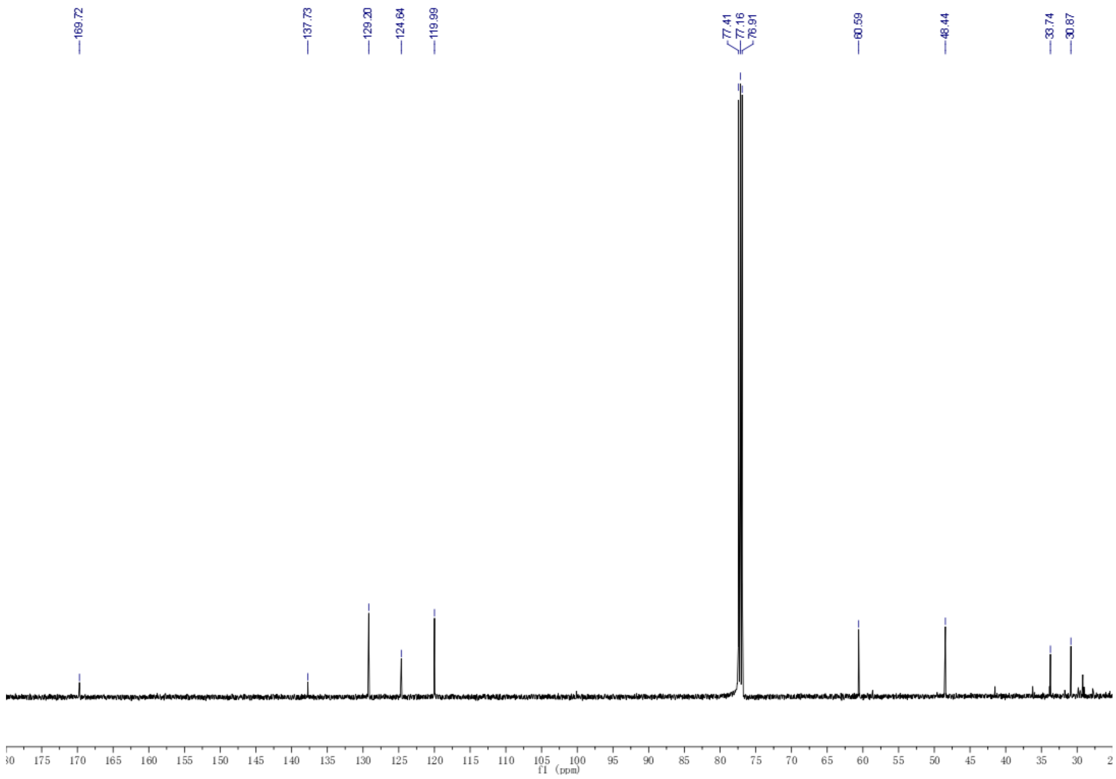


^{13}C NMR of compound **27**（126 MHz, $CDCl_3$）

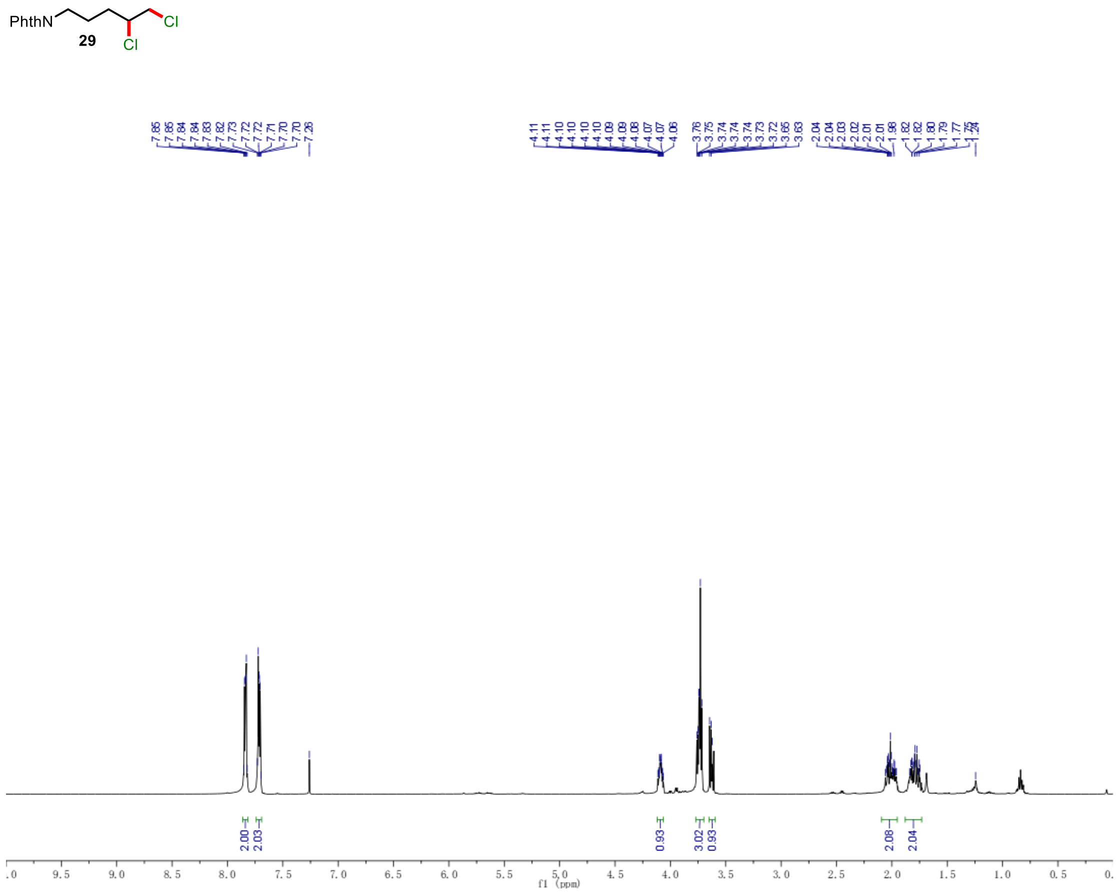




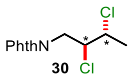
^{1}H NMR of compound **28**（500 MHz, $CDCl_3$）



^{13}C NMR of compound **28**（126 MHz, $CDCl_3$）



[1]H NMR of compound **29**（500 MHz, $CDCl_3$）



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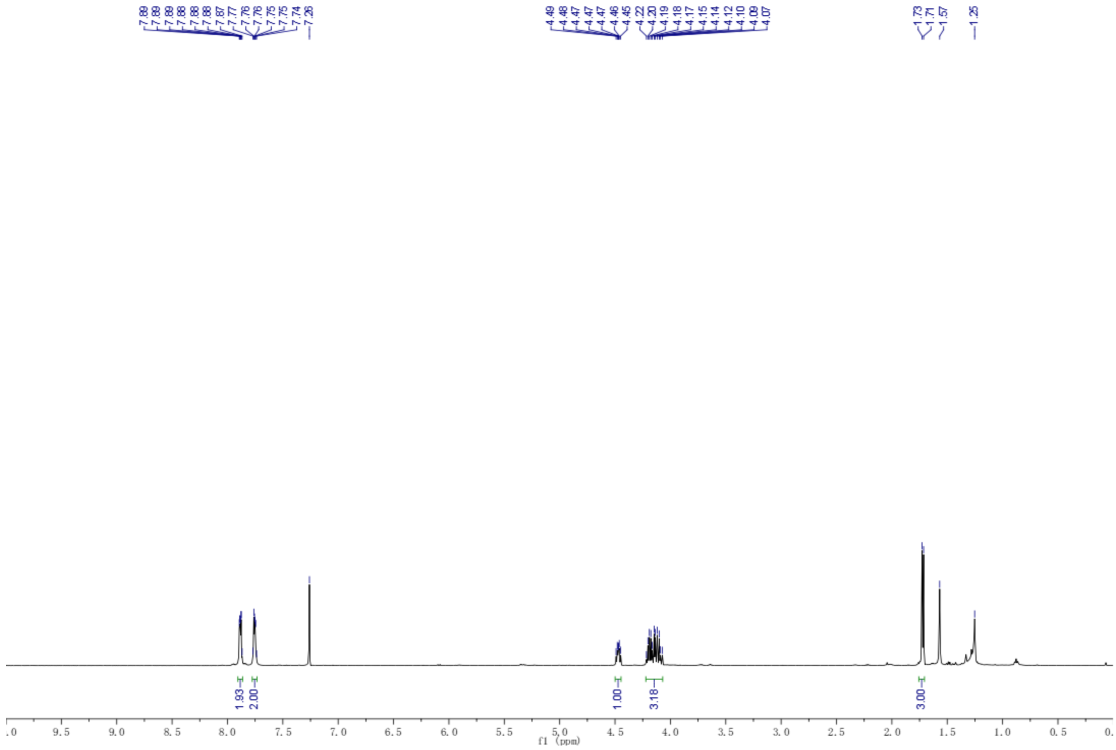
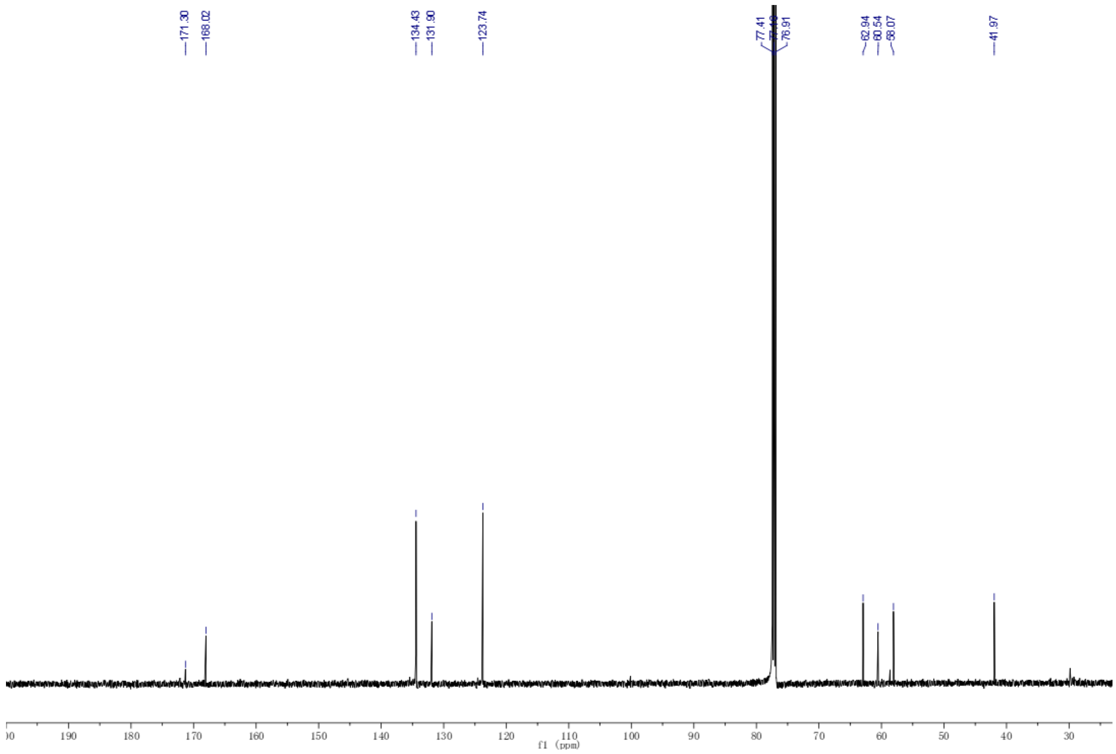
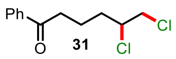
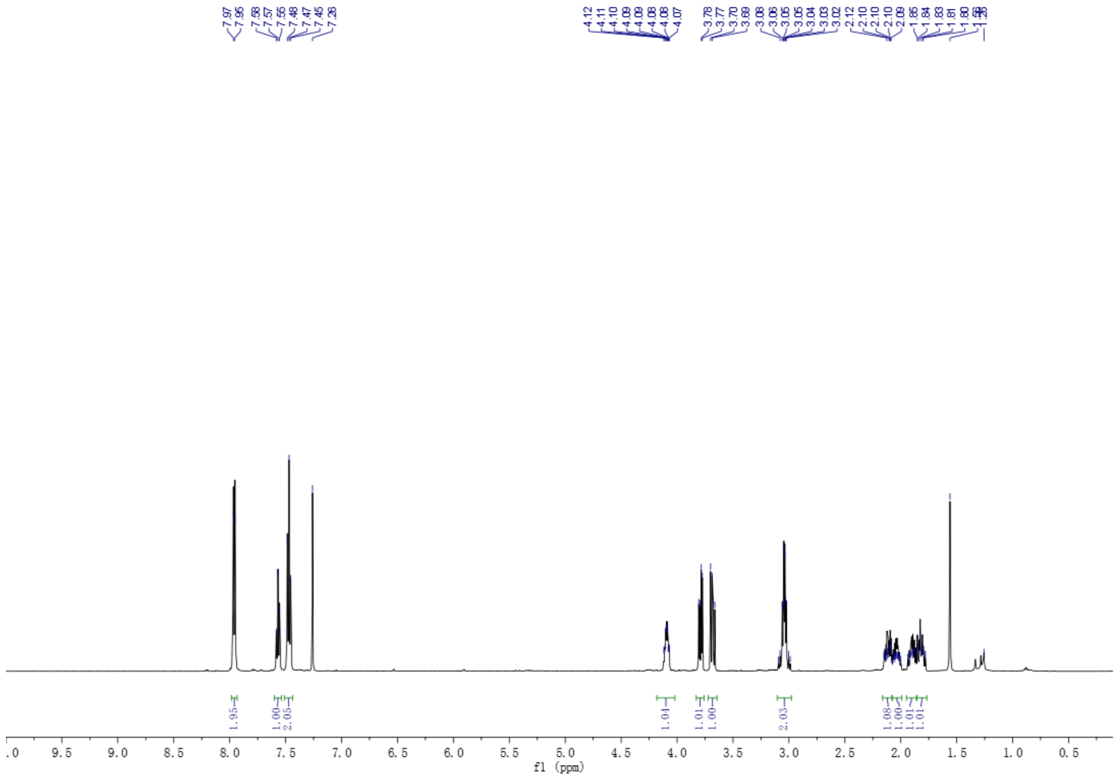


[1]H NMR of compound **30**（500 MHz, $CDCl_3$）

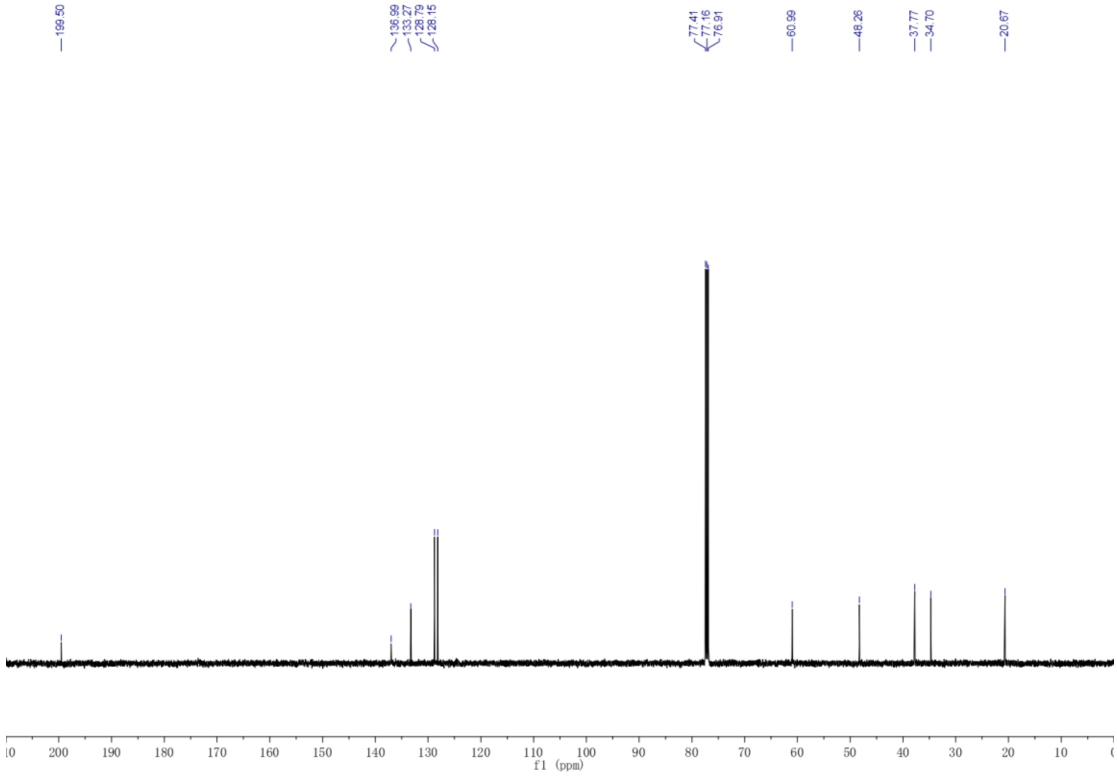


[13]C NMR of compound **30**（126 MHz, $CDCl_3$）

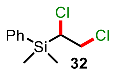


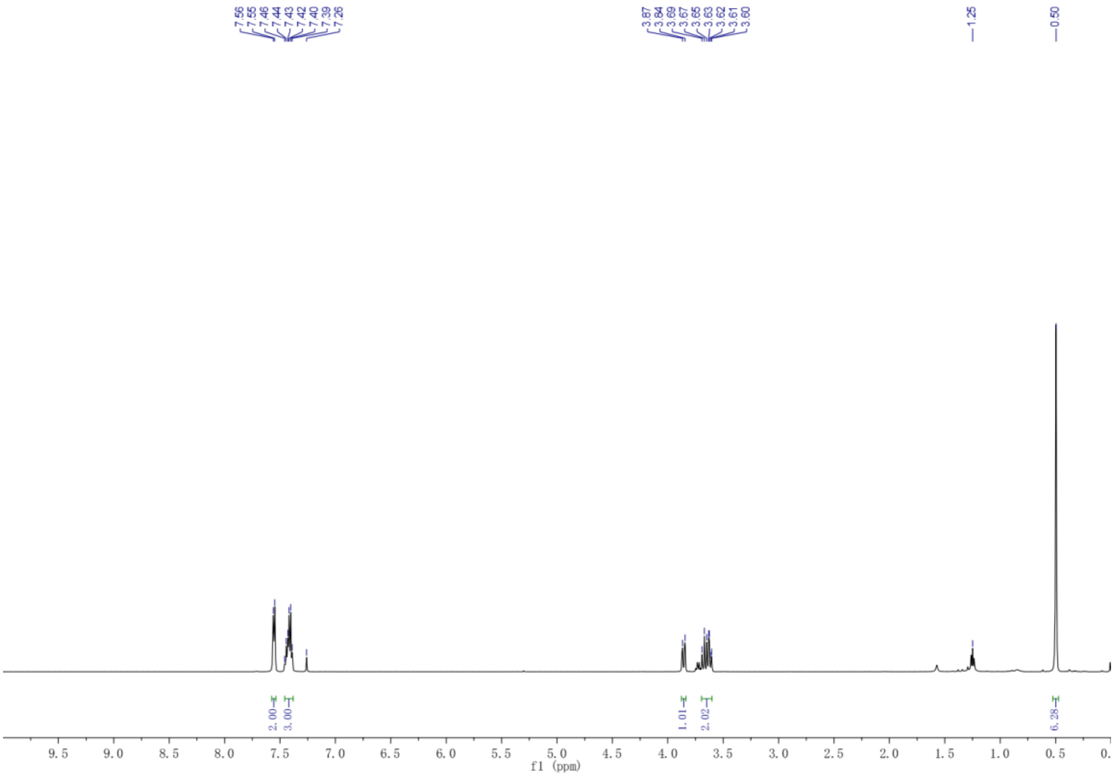


^{1}H NMR of compound **31**（500 MHz, $CDCl_3$）

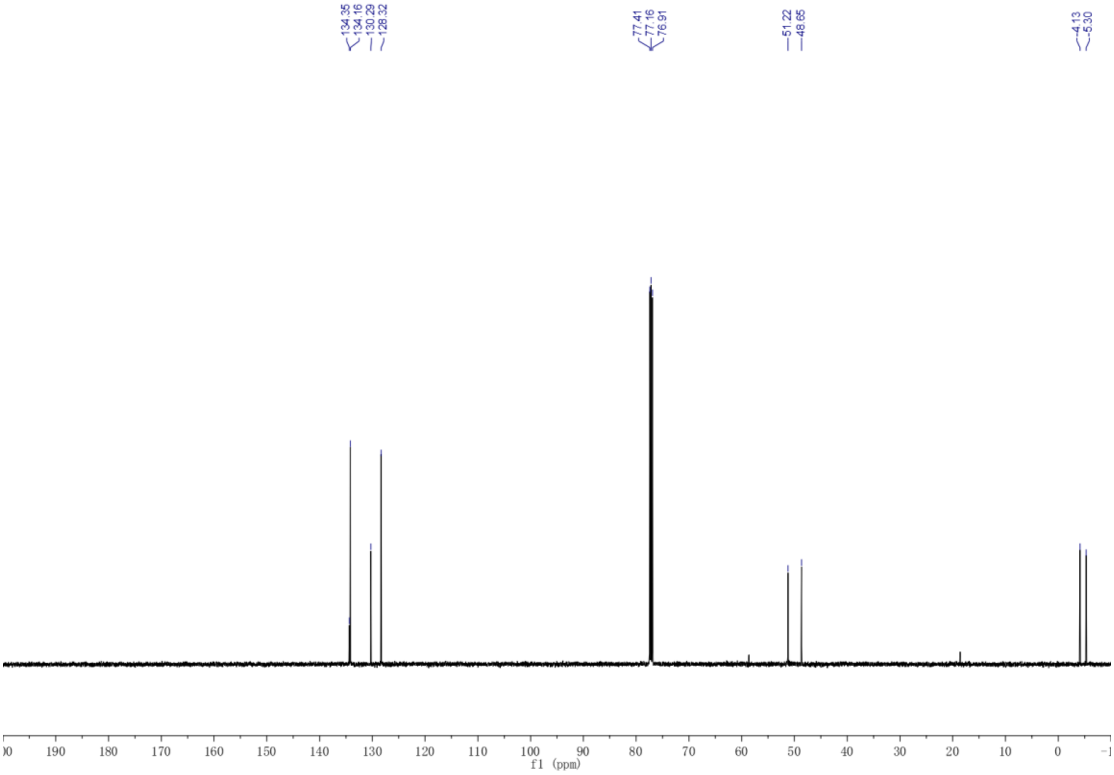


^{13}C NMR of compound **31**（126 MHz, $CDCl_3$）

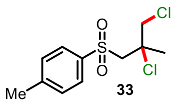




[1]H NMR of compound **32**（500 MHz, $CDCl_3$）



[13]C NMR of compound **32**（126 MHz, $CDCl_3$）



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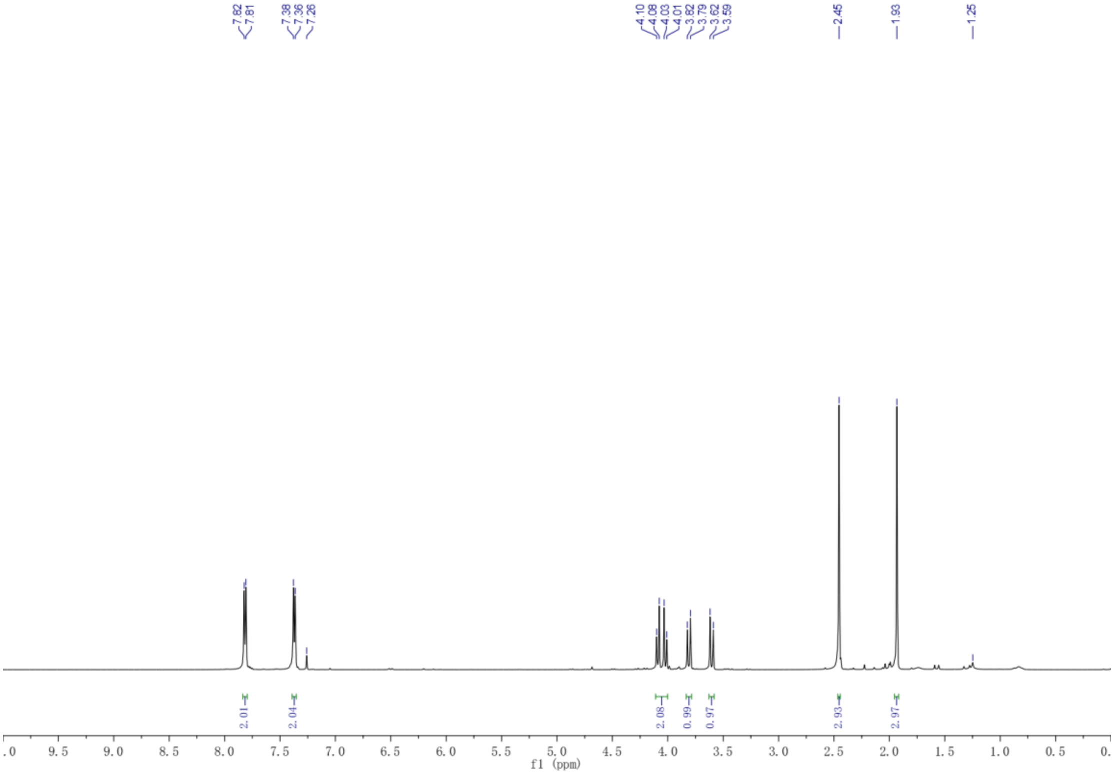
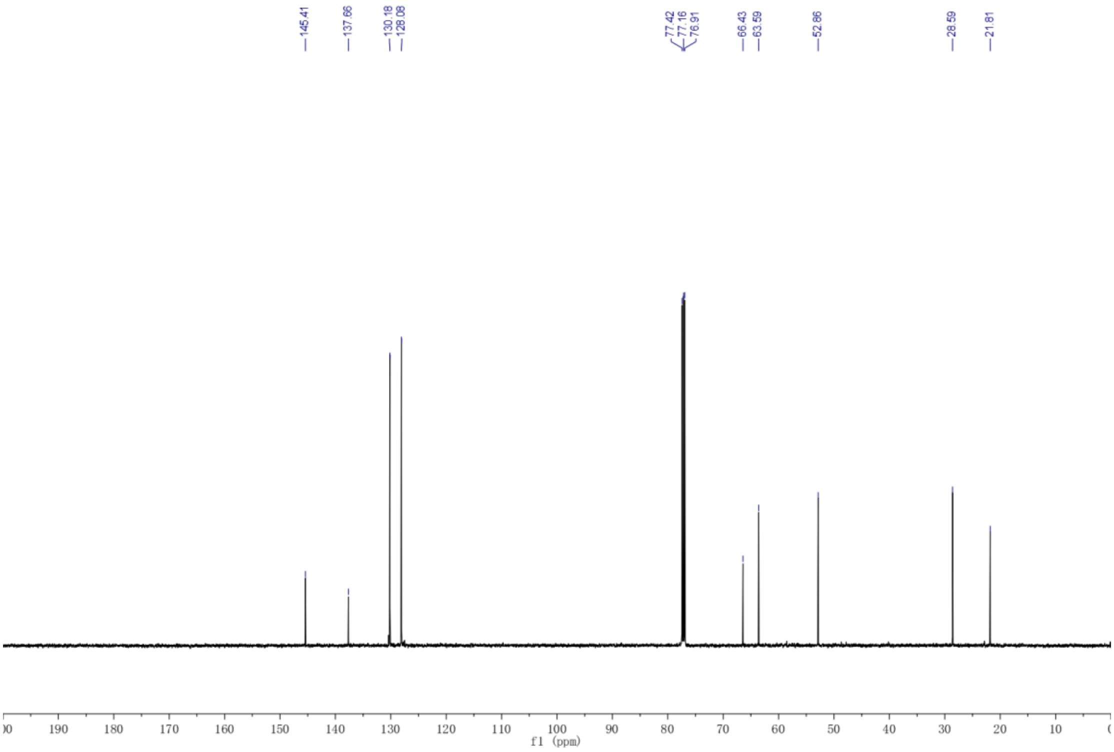
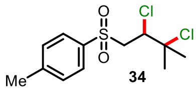


[1]H NMR of compound **33** (500 MHz, $CDCl_3$)



[13]C NMR of compound **33** (126 MHz, $CDCl_3$)



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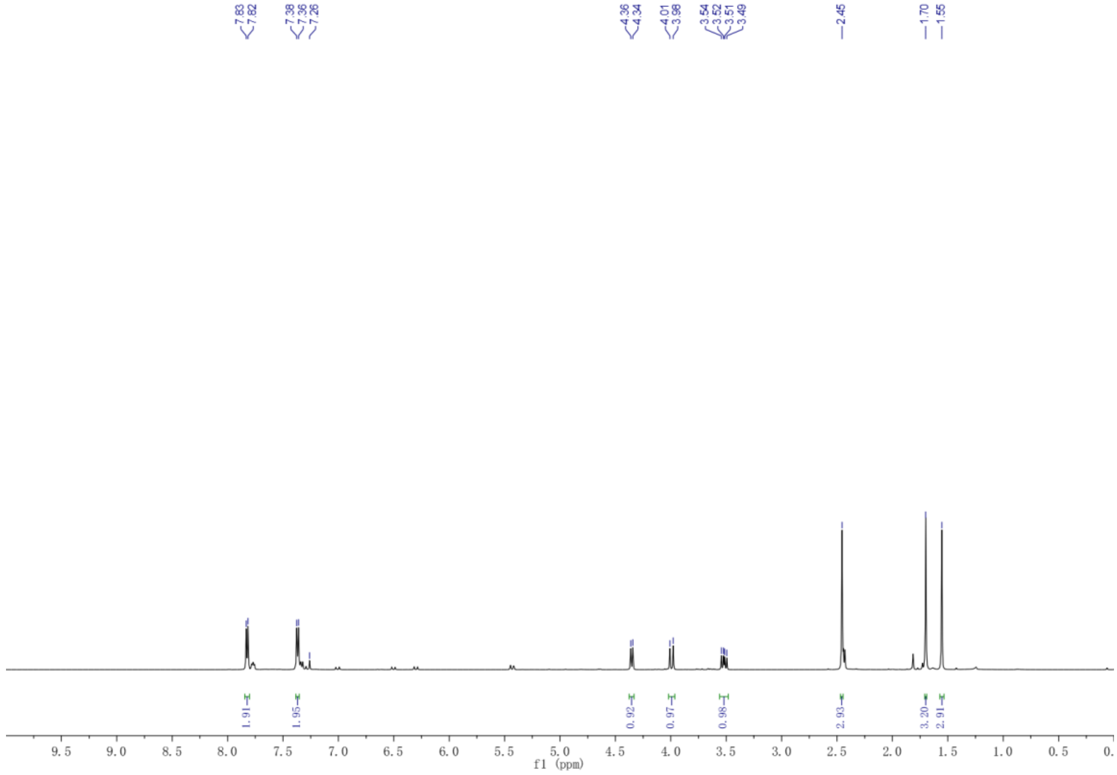
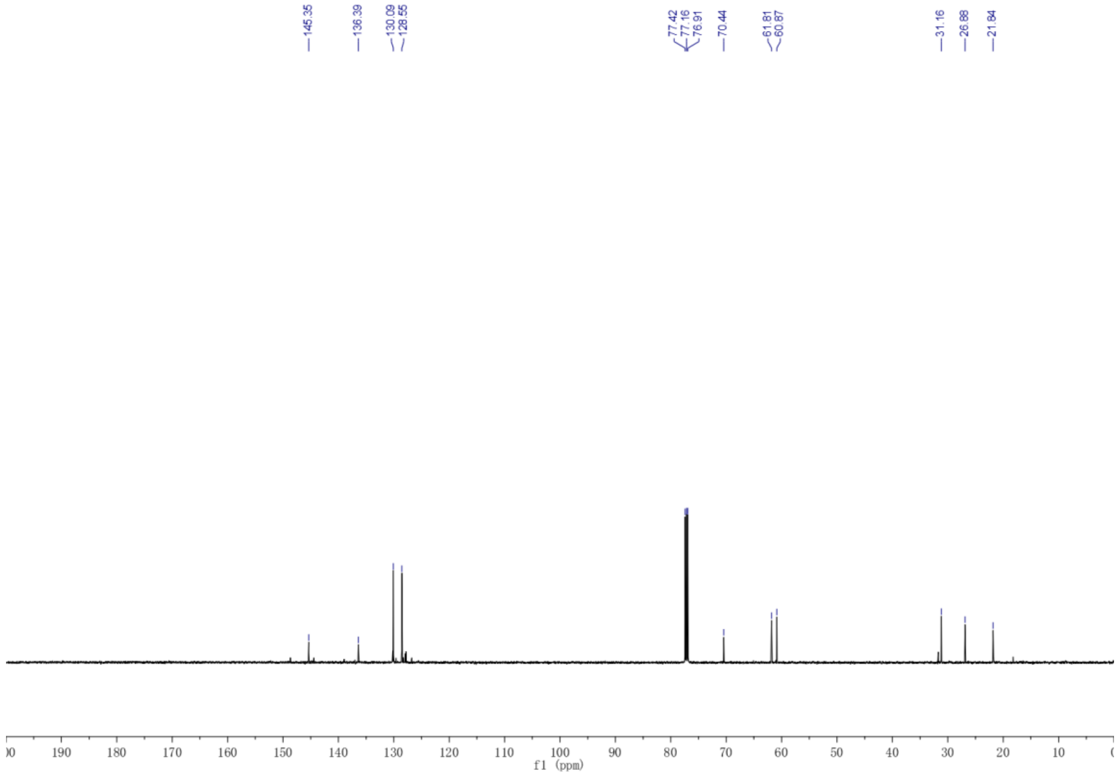
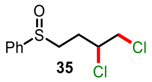


[1]H NMR of compound **34**（500 MHz, $CDCl_3$）



[13]C NMR of compound **34**（126 MHz, $CDCl_3$）



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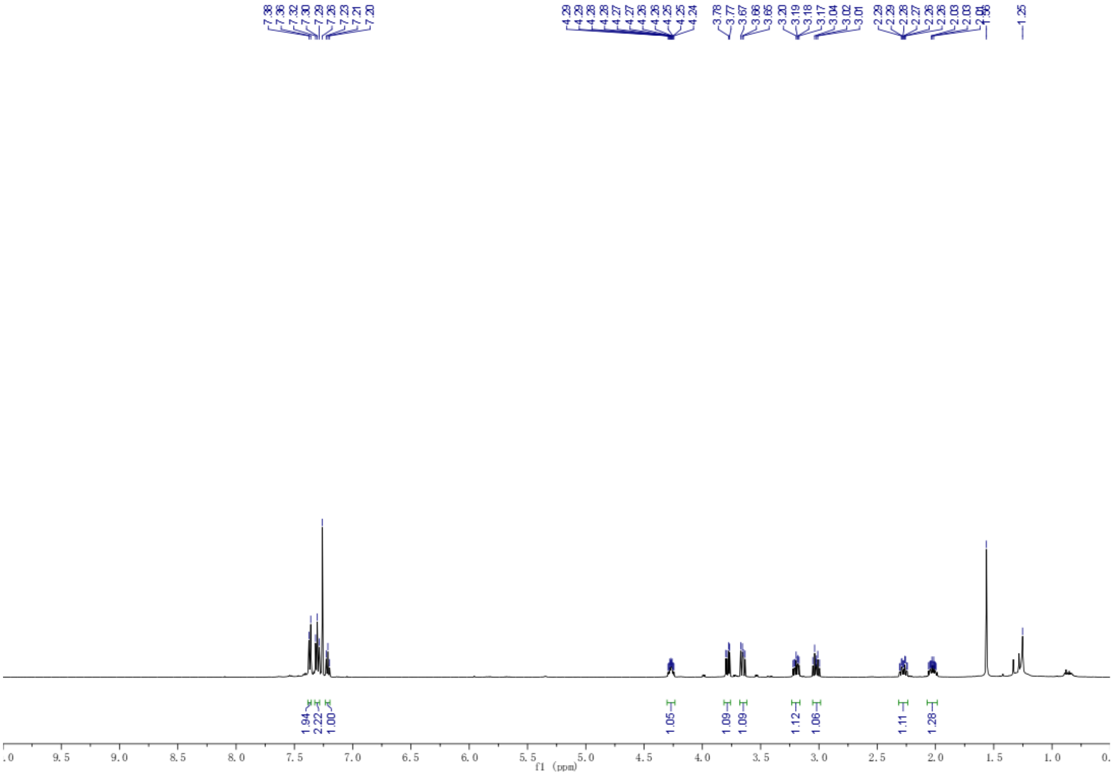
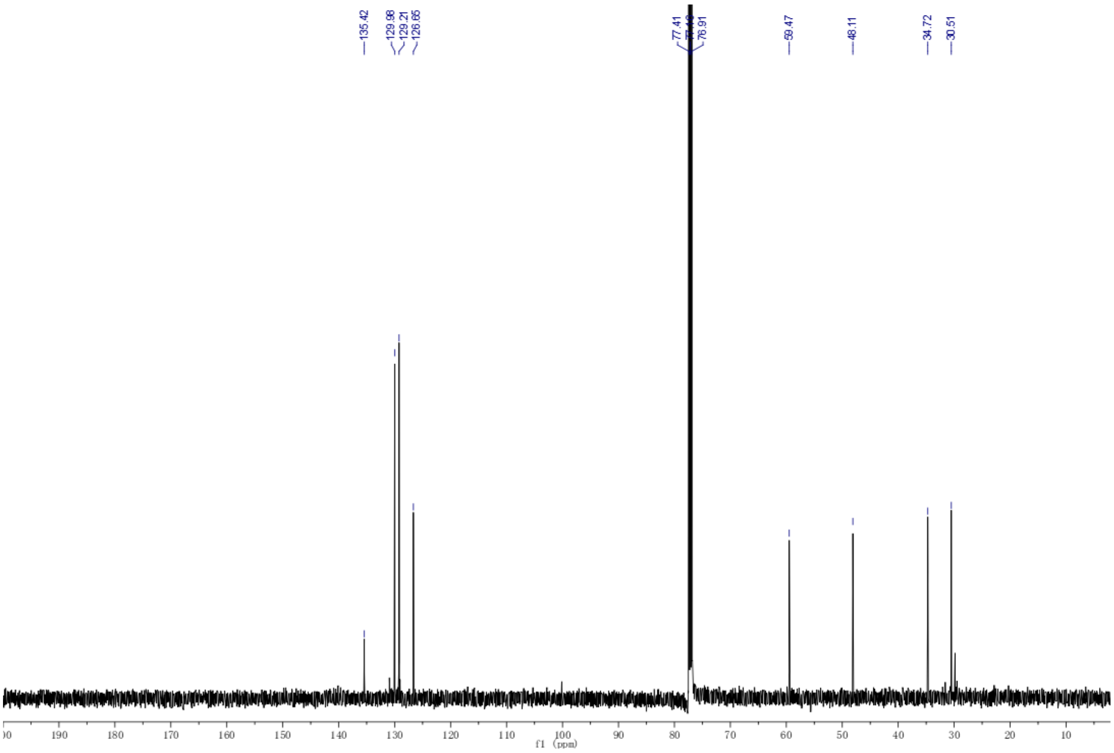
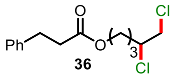
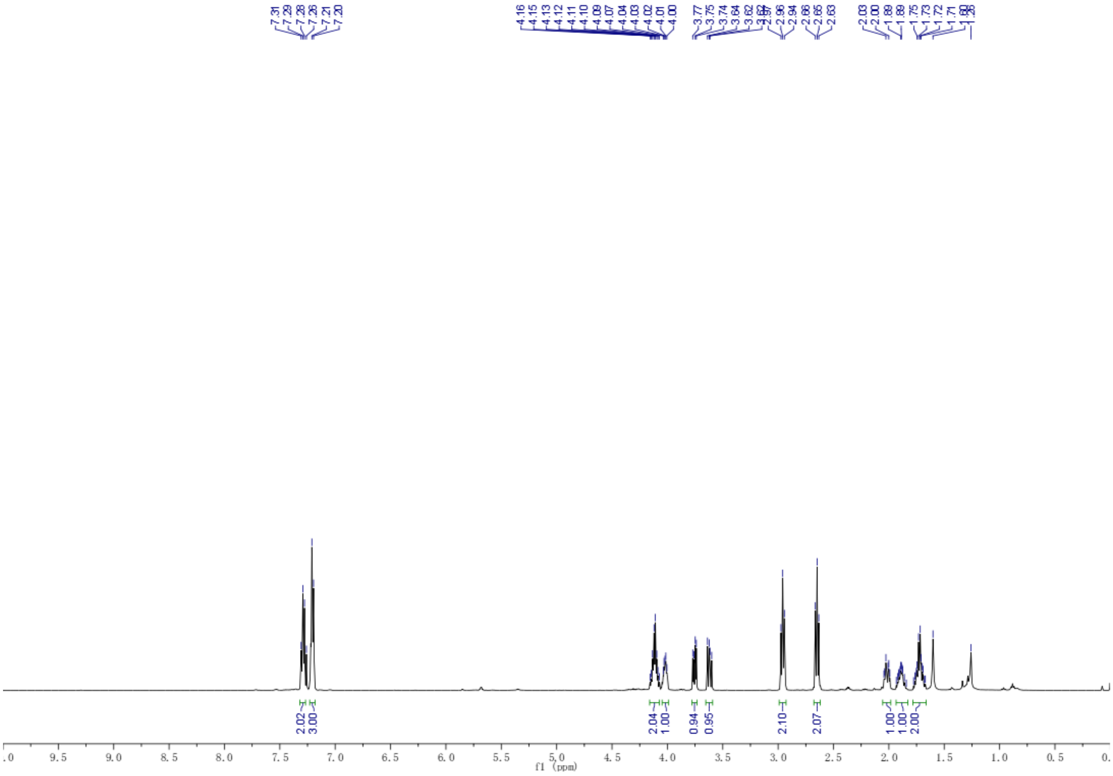


[1]H NMR of compound **35**（500 MHz, $CDCl_3$）

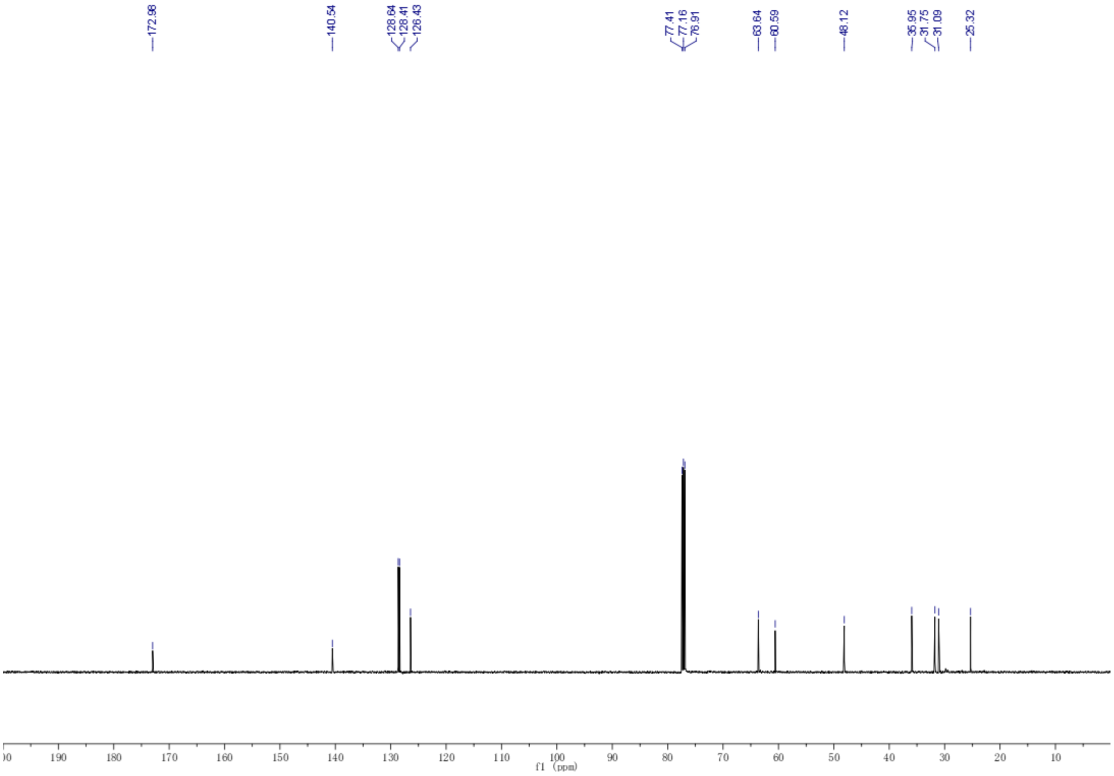


[13]C NMR of compound **35**（126 MHz, $CDCl_3$）

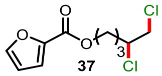




[1]H NMR of compound **36**（500 MHz, $CDCl_3$）



[13]C NMR of compound **36**（126 MHz, $CDCl_3$）



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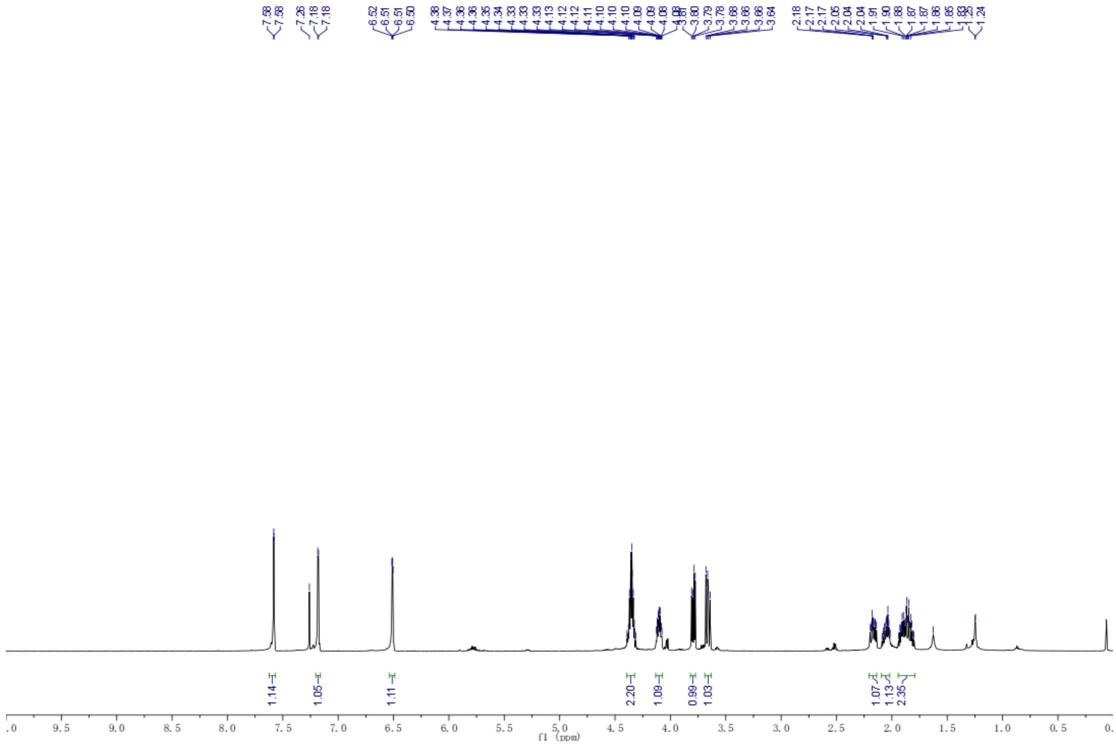
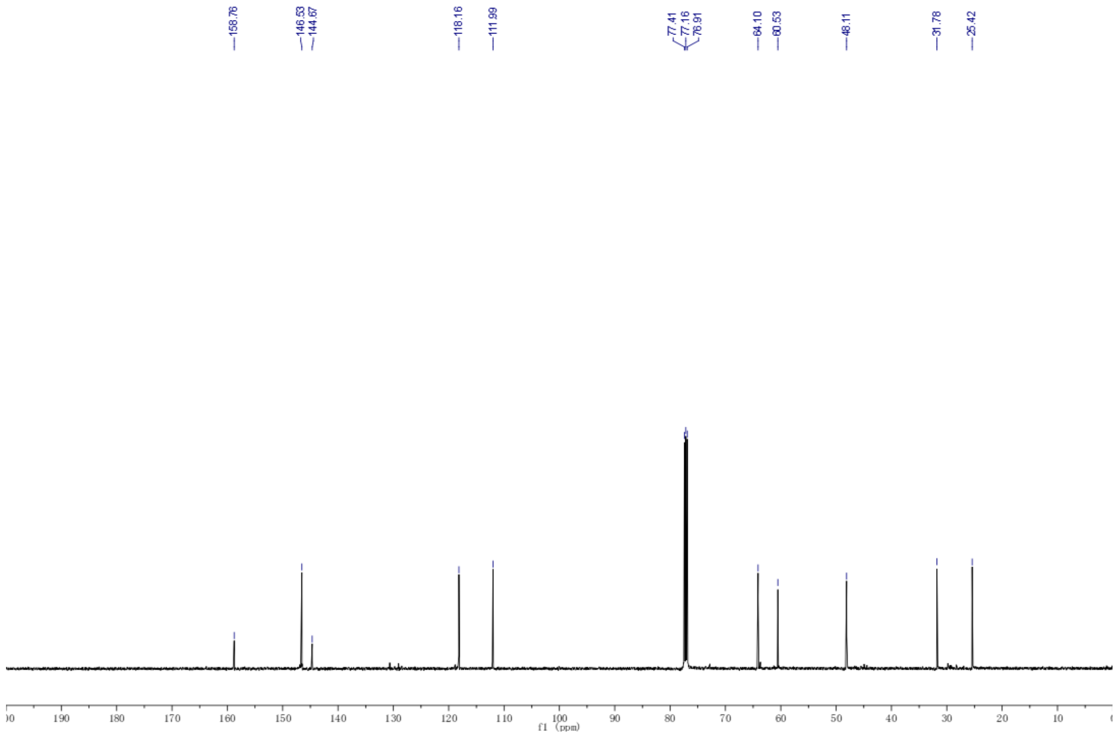
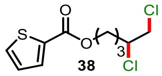


[1]H NMR of compound **37**（500 MHz, $CDCl_3$）



[13]C NMR of compound **37**（126 MHz, $CDCl_3$）



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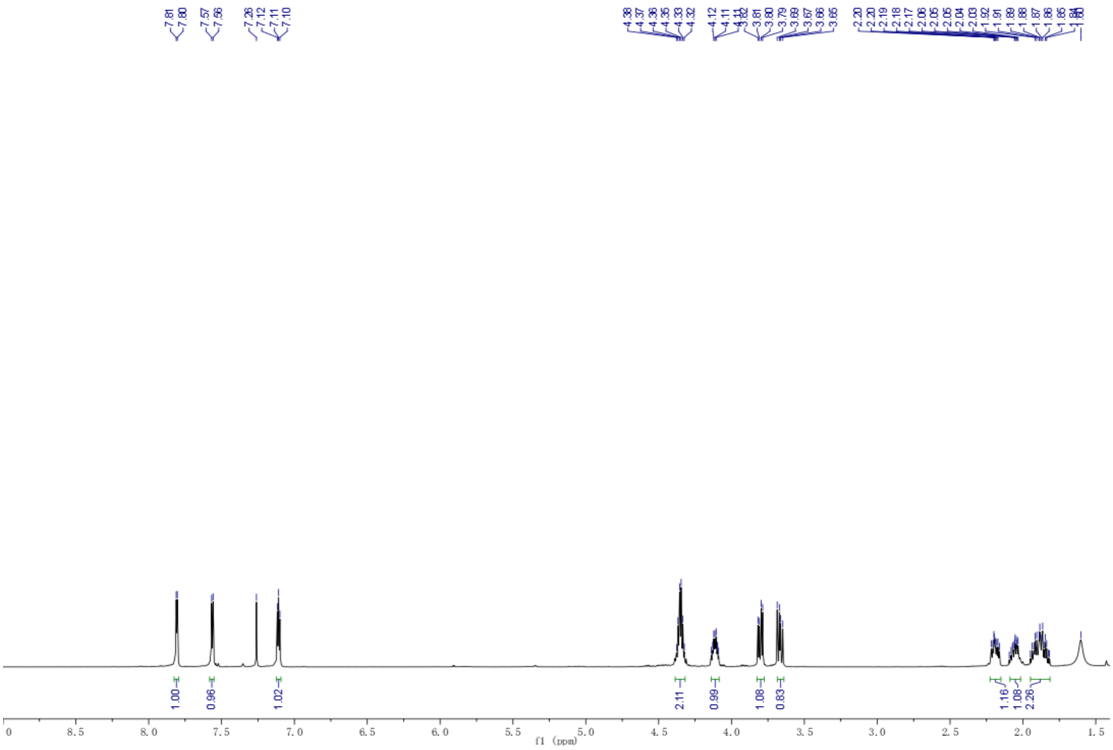
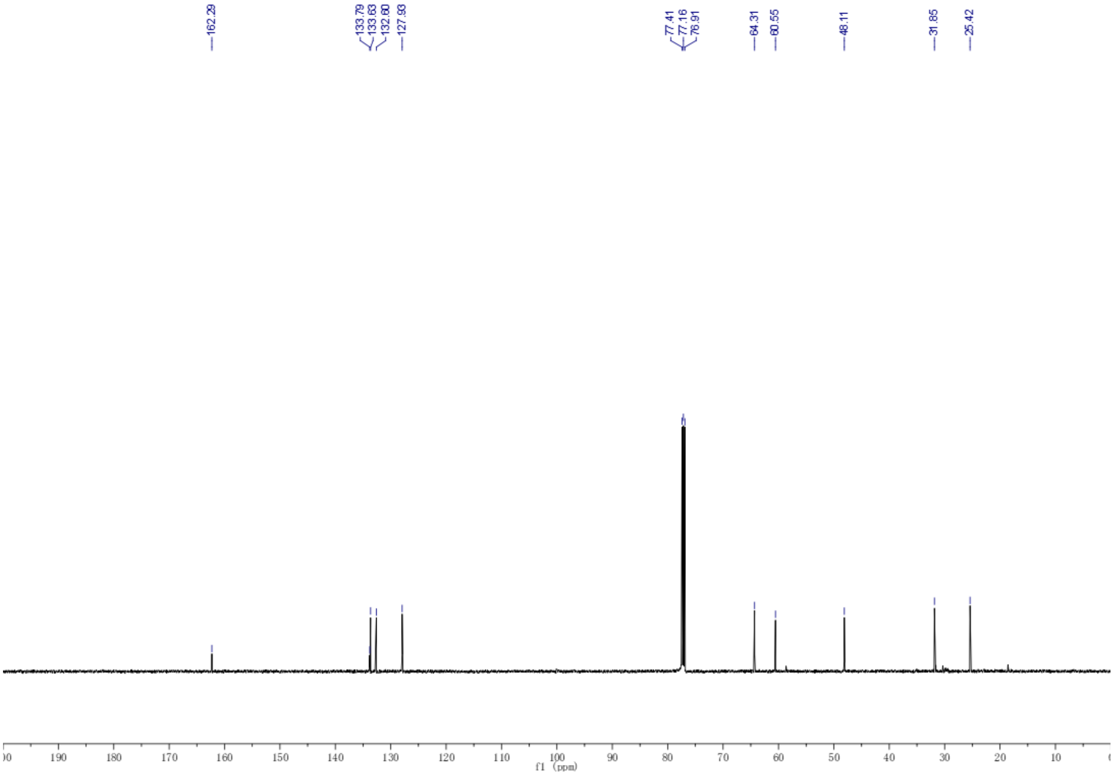
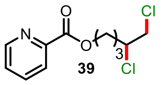


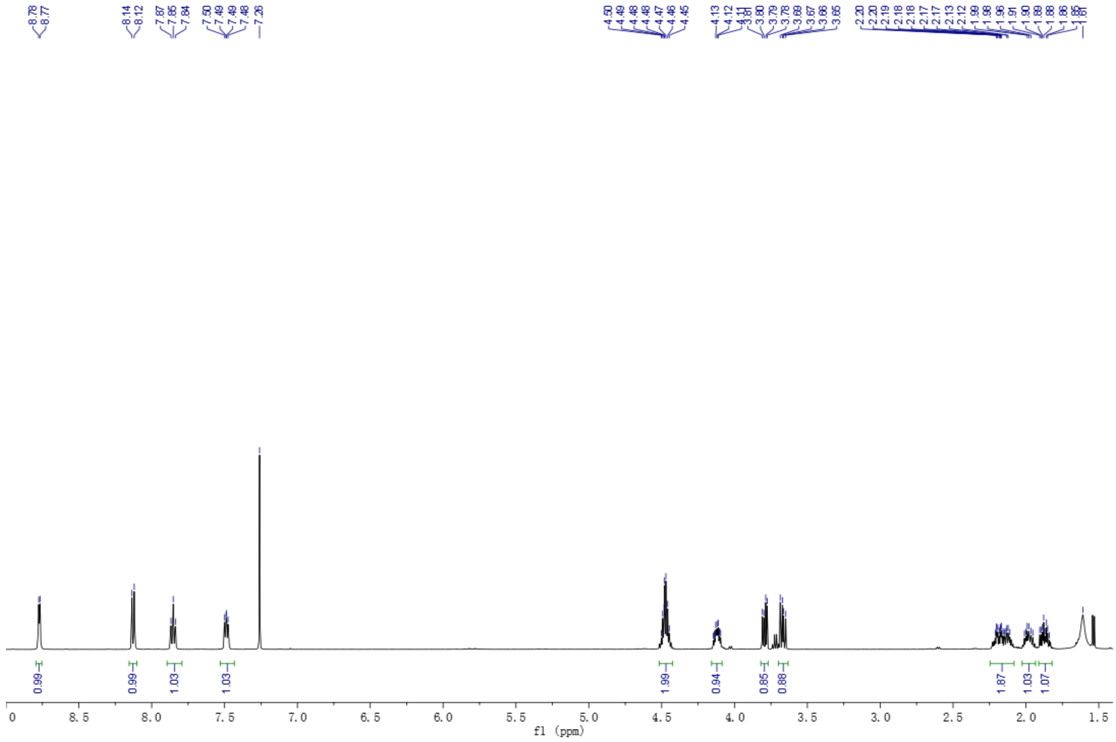
^{1}H NMR of compound **38**（500 MHz, $CDCl_3$）



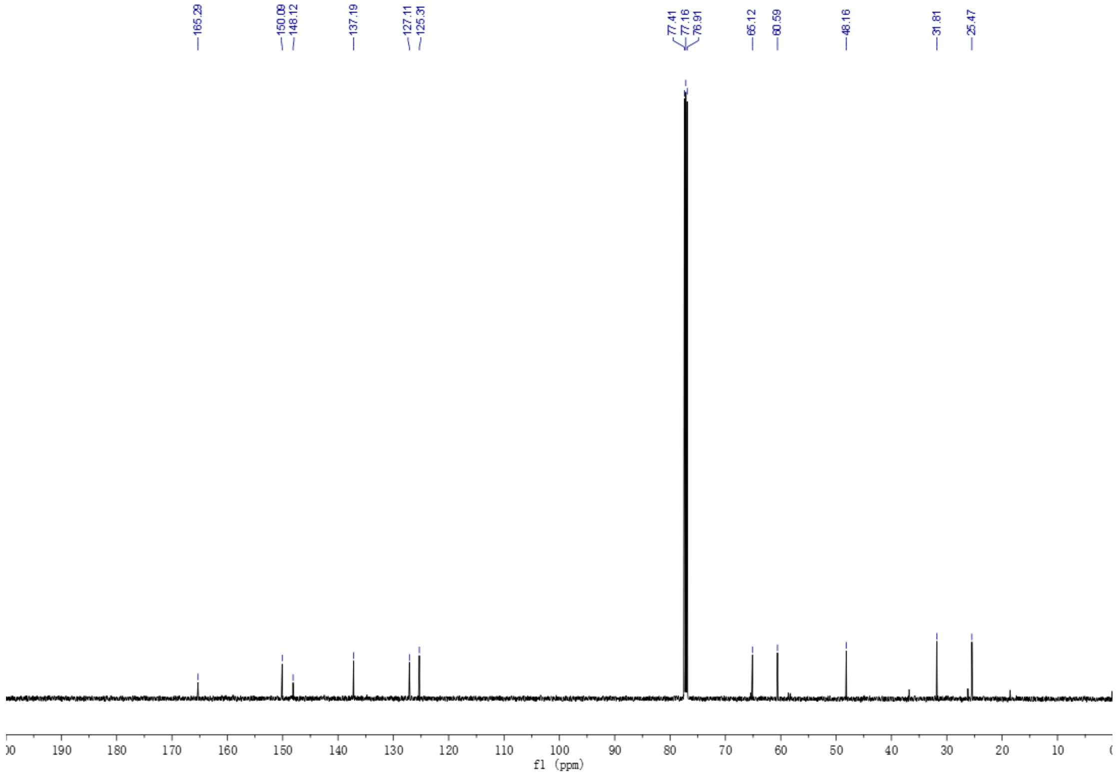
^{13}C NMR of compound **38**（126 MHz, $CDCl_3$）



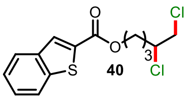
39

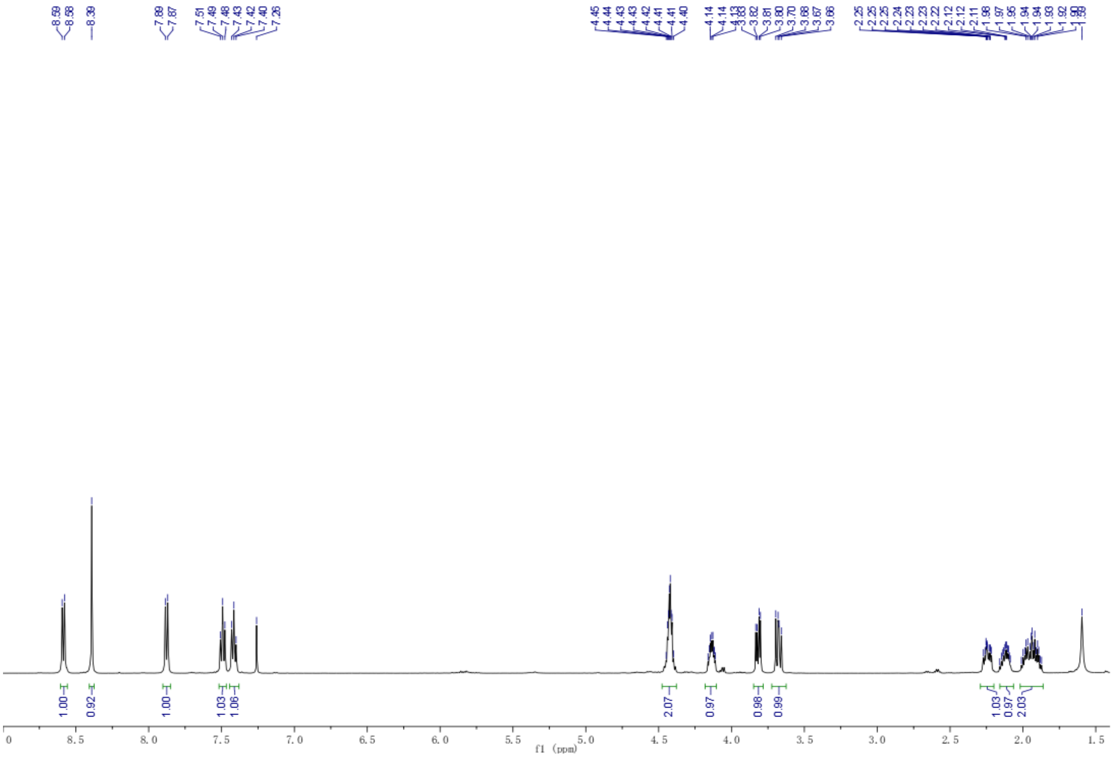


^{1}H NMR of compound **39**（500 MHz, $CDCl_3$）

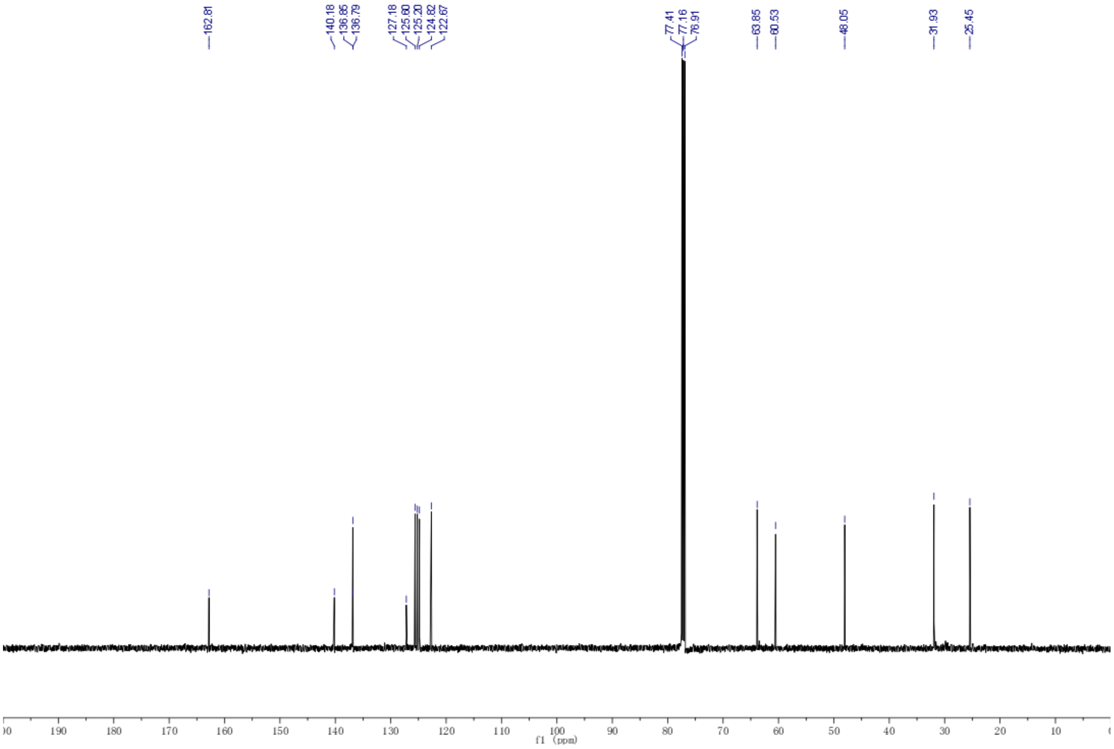


^{13}C NMR of compound **39**（126 MHz, $CDCl_3$）

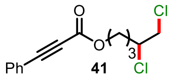


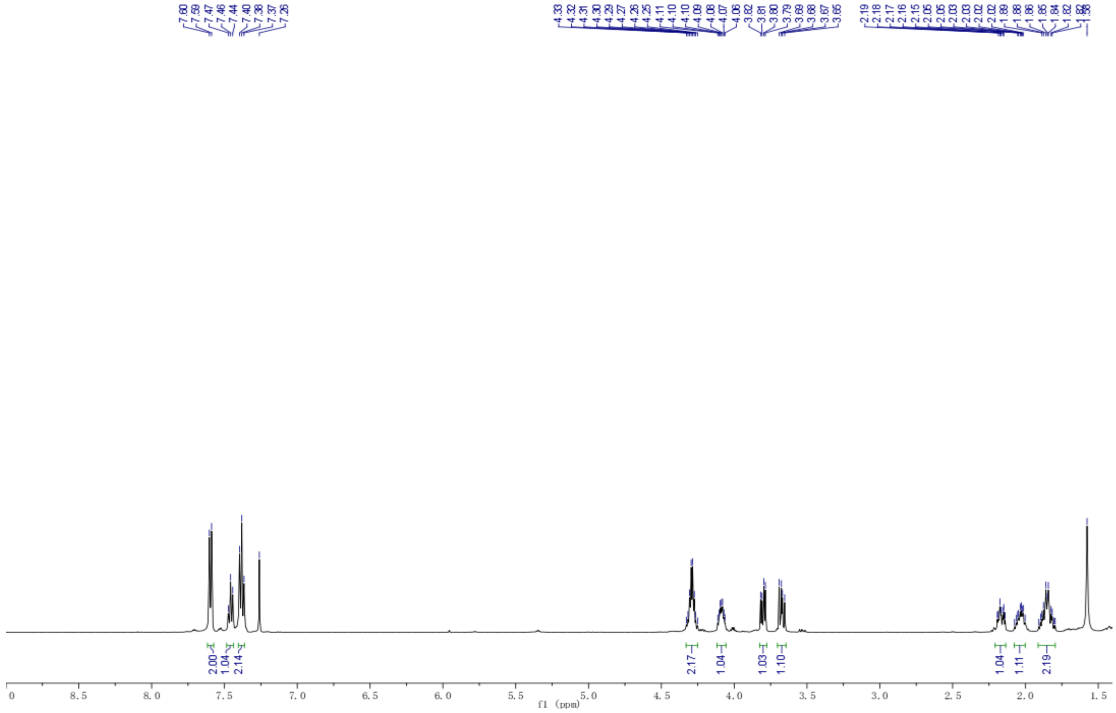


^{1}H NMR of compound **40**（500 MHz, $CDCl_3$）

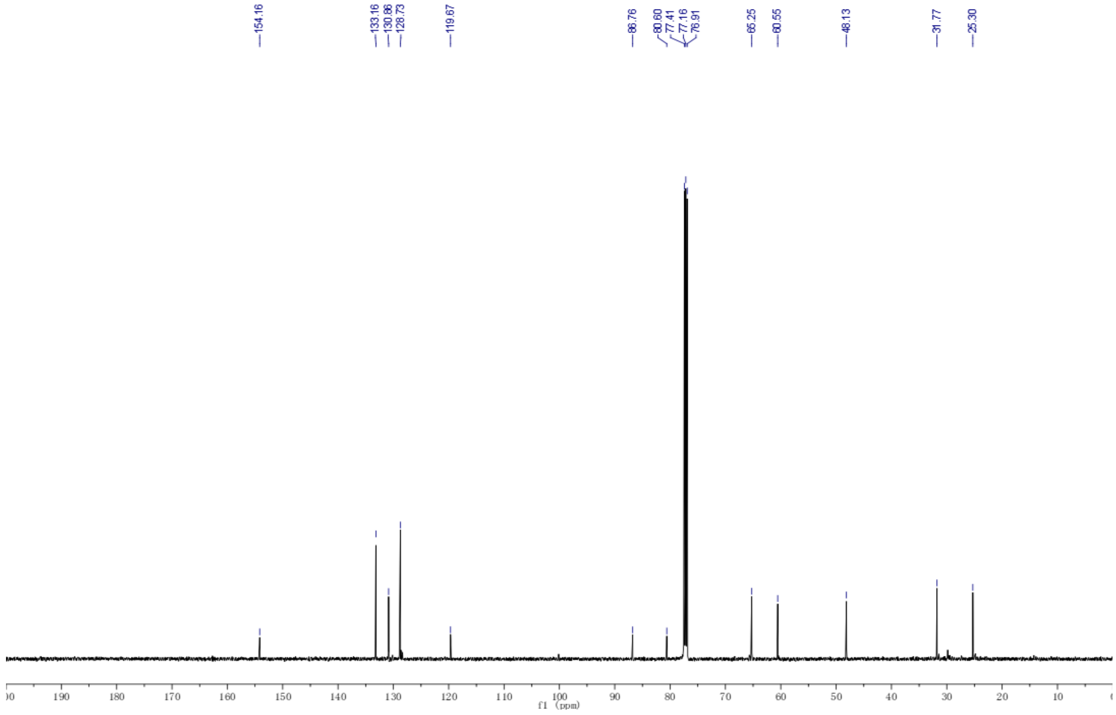


^{13}C NMR of compound **40**（126 MHz, $CDCl_3$）

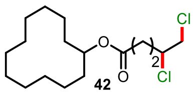


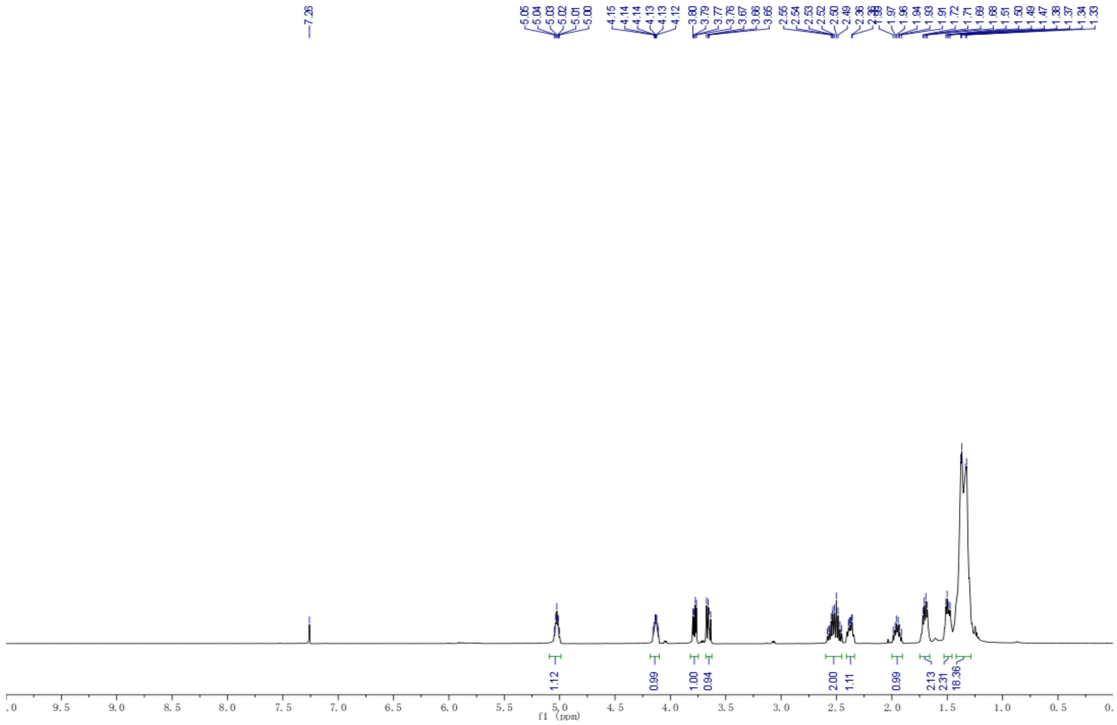


^{1}H NMR of compound **41**（500 MHz, $CDCl_3$）

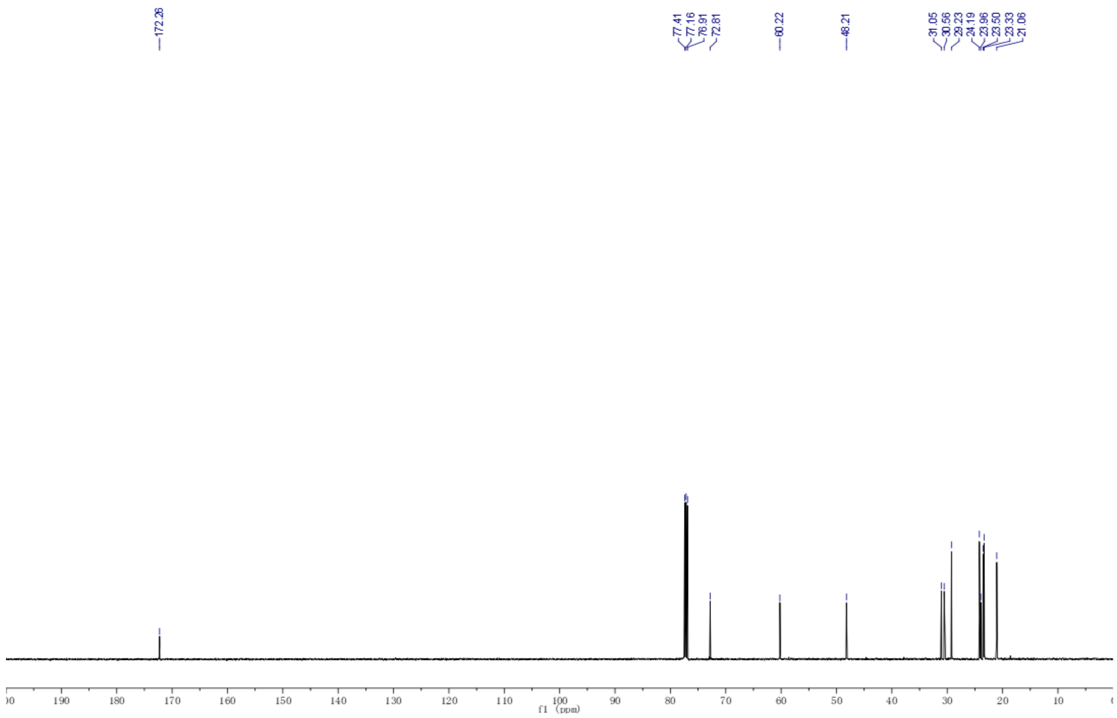


^{13}C NMR of compound **41**（126 MHz, $CDCl_3$）

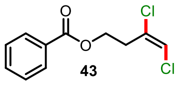




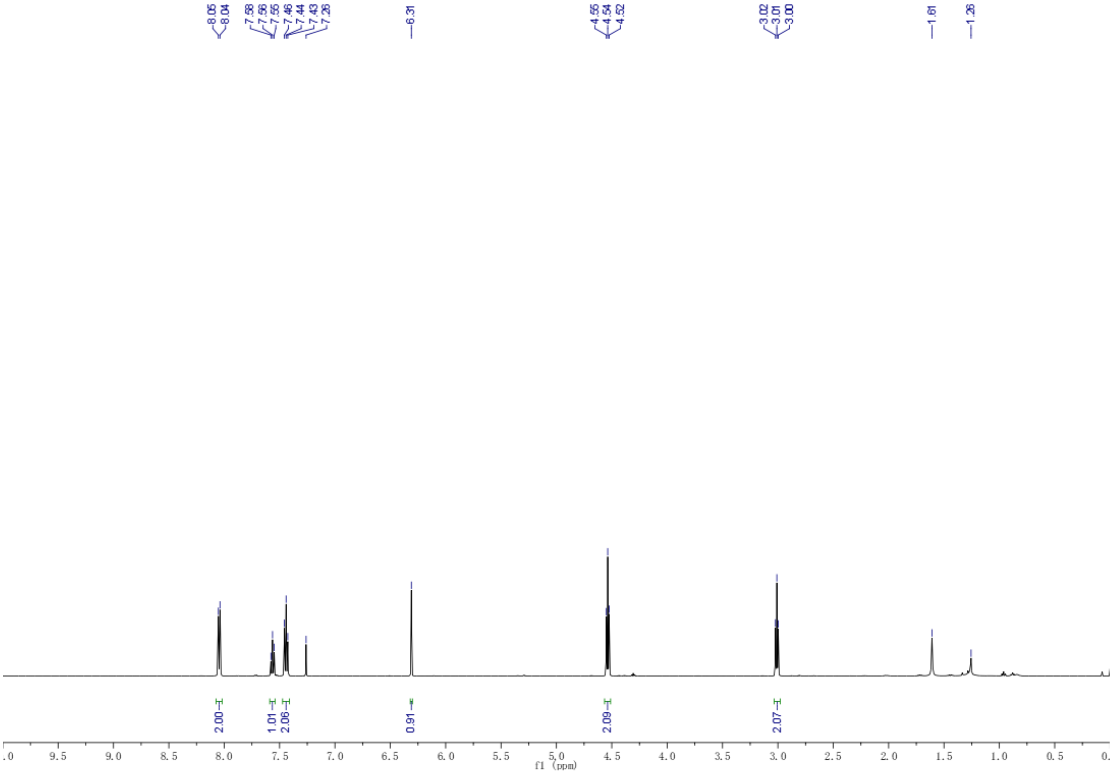
^{1}H NMR of compound **42**（500 MHz, $CDCl_3$）



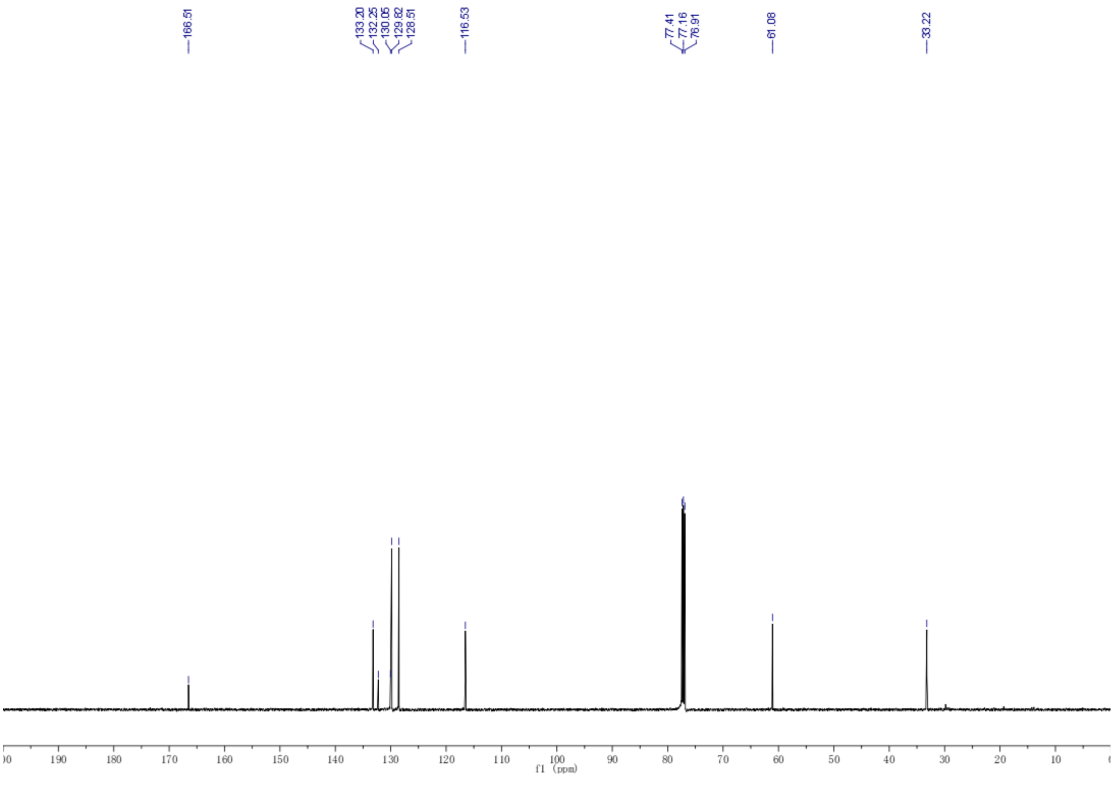
^{13}C NMR of compound **42**（126 MHz, $CDCl_3$）



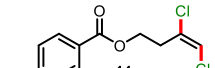
43



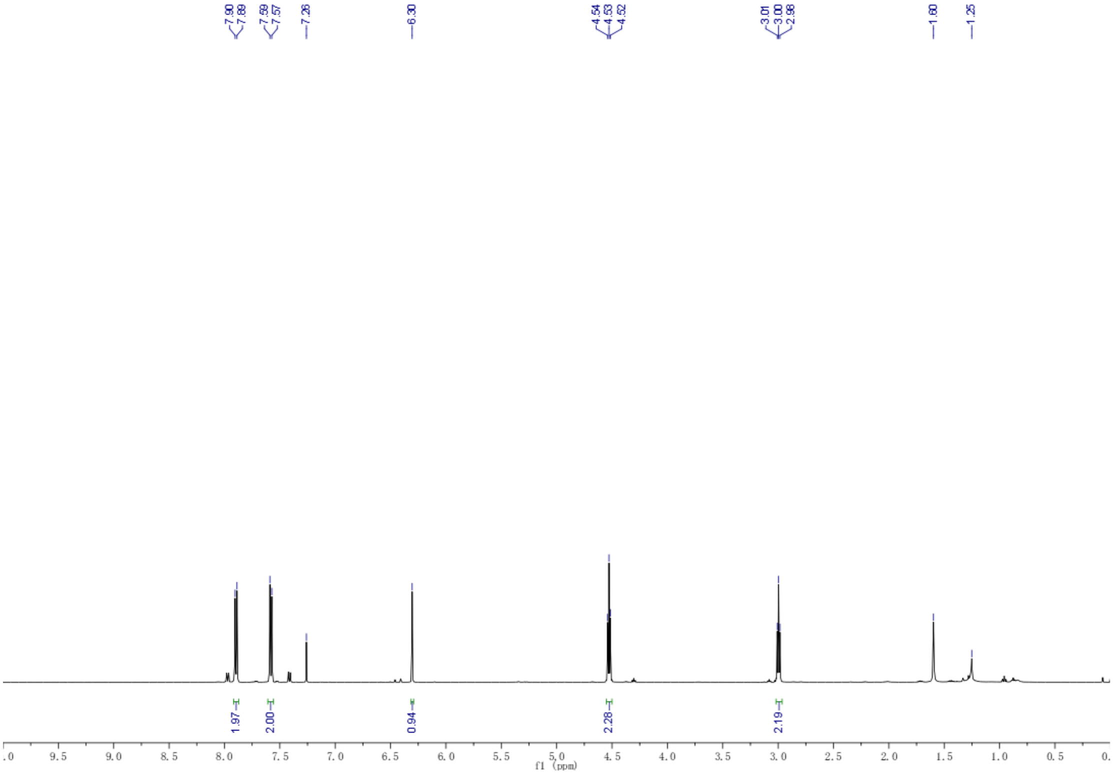
^{1}H NMR of compound **43**（500 MHz, $CDCl_3$）



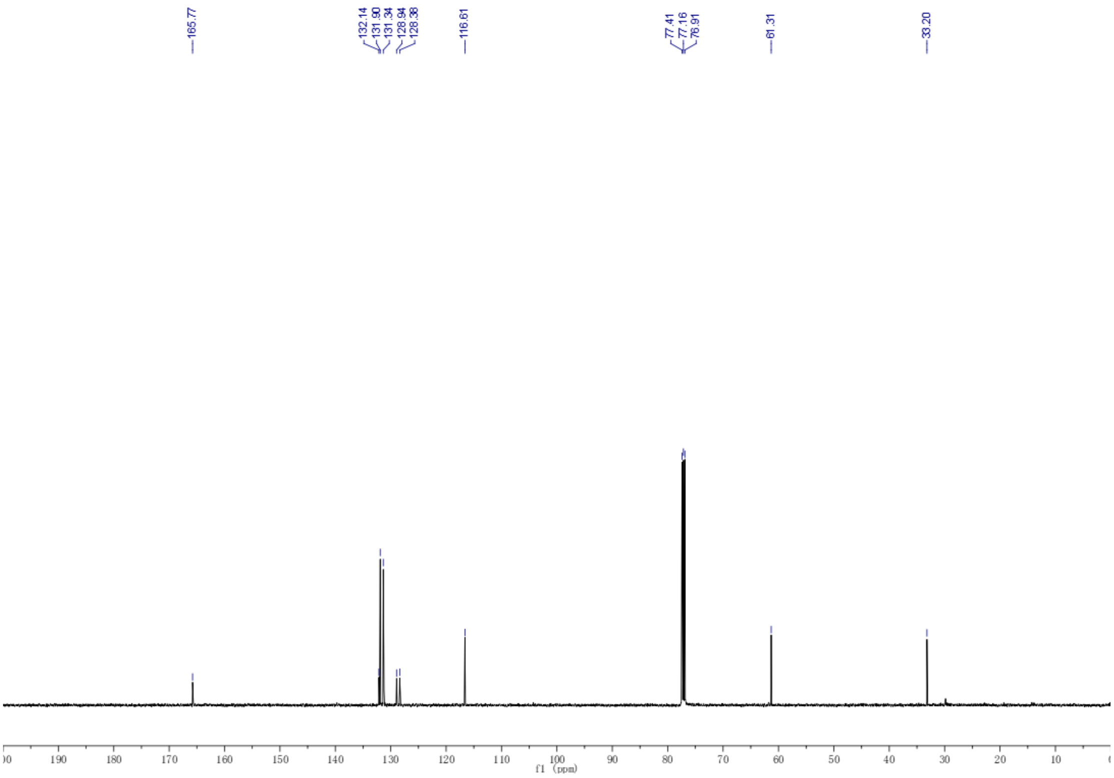
^{13}C NMR of compound **43**（126 MHz, $CDCl_3$）



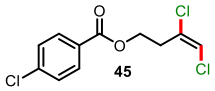
44



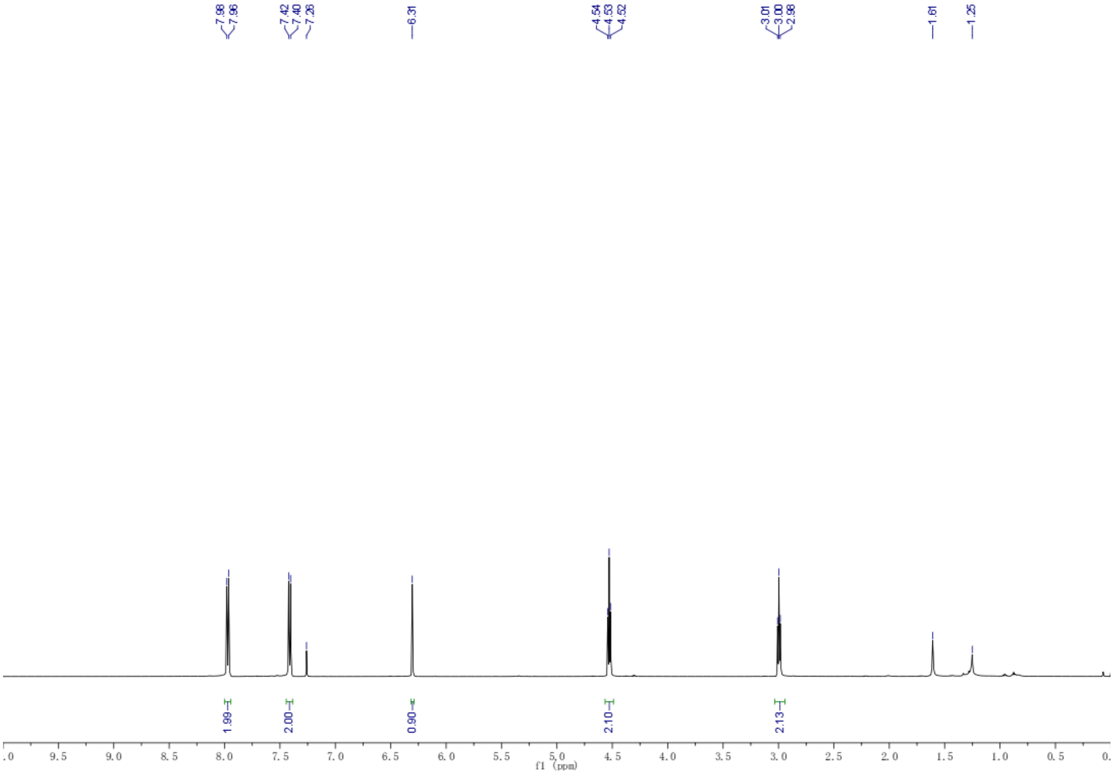
^{1}H NMR of compound **44**（500 MHz, $CDCl_3$）



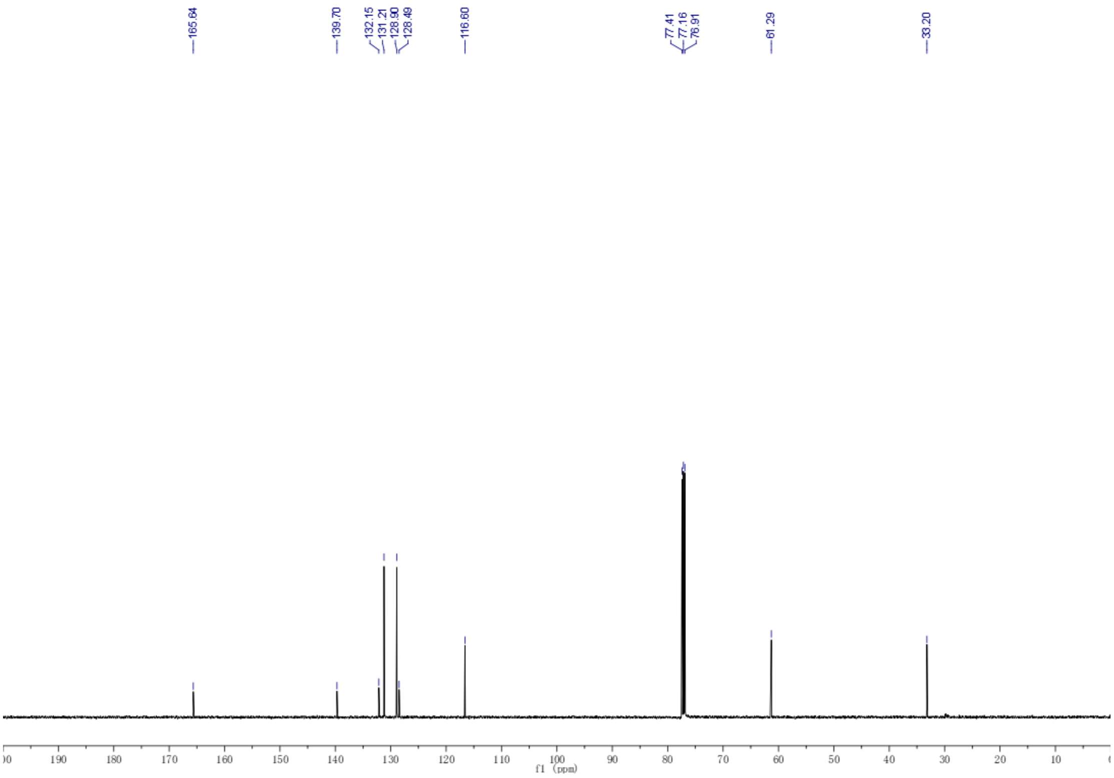
^{13}C NMR of compound **44**（126 MHz, $CDCl_3$）



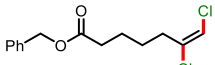
45



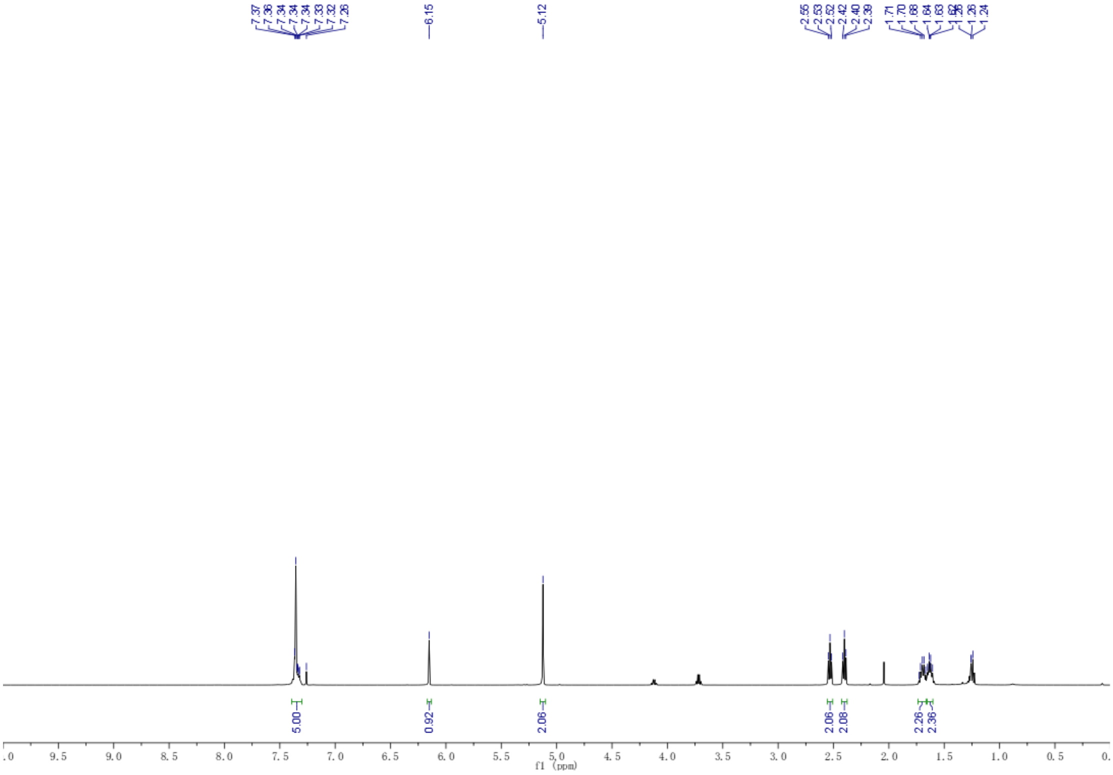
[1]H NMR of compound **45**（500 MHz, $CDCl_3$）



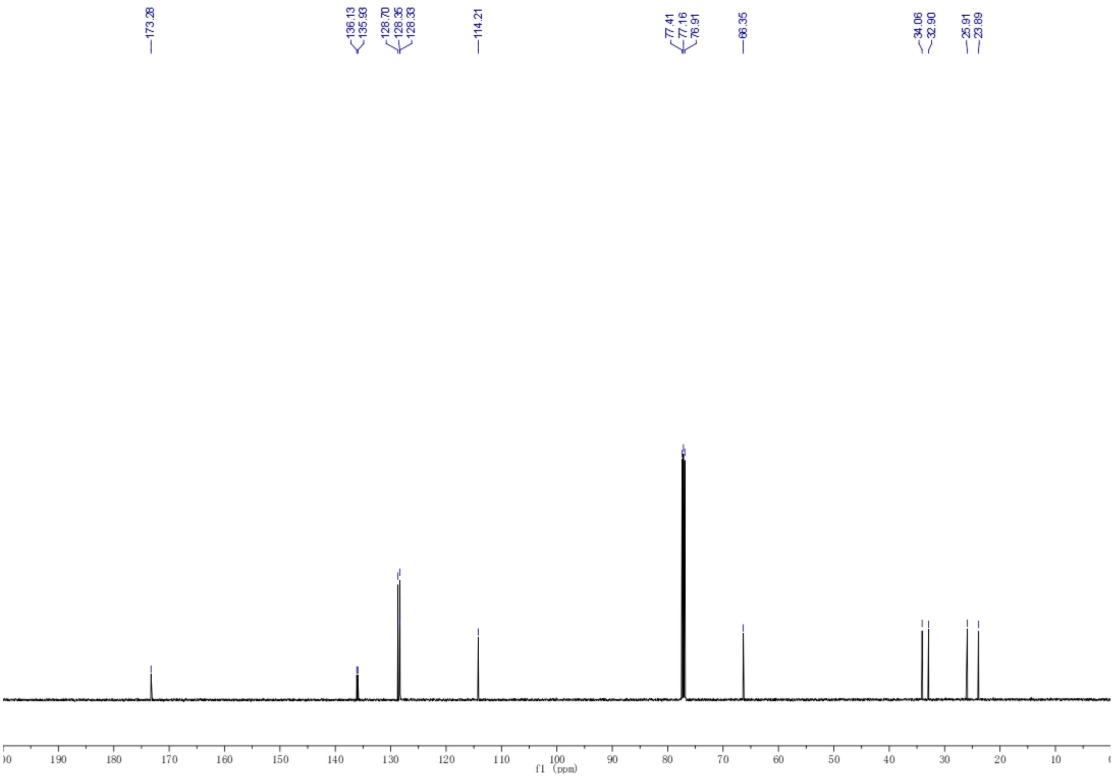
[13]C NMR of compound **45**（126 MHz, $CDCl_3$）



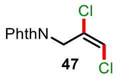
46



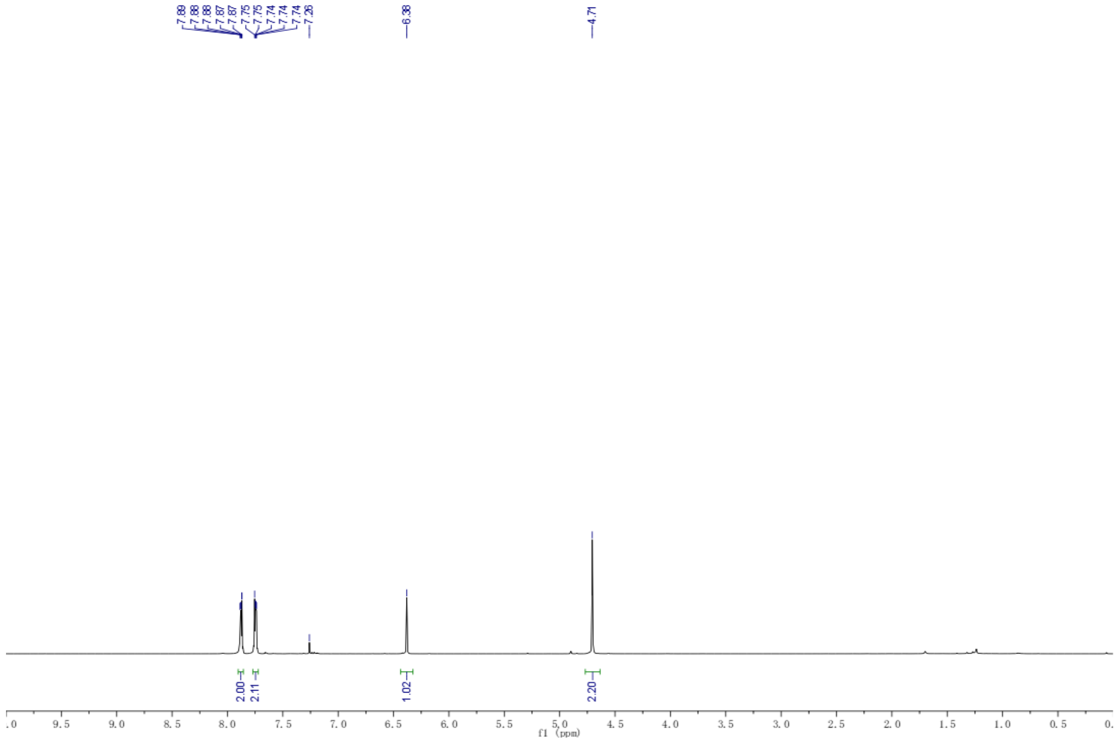
^{1}H NMR of compound **46**（500 MHz, $CDCl_3$）



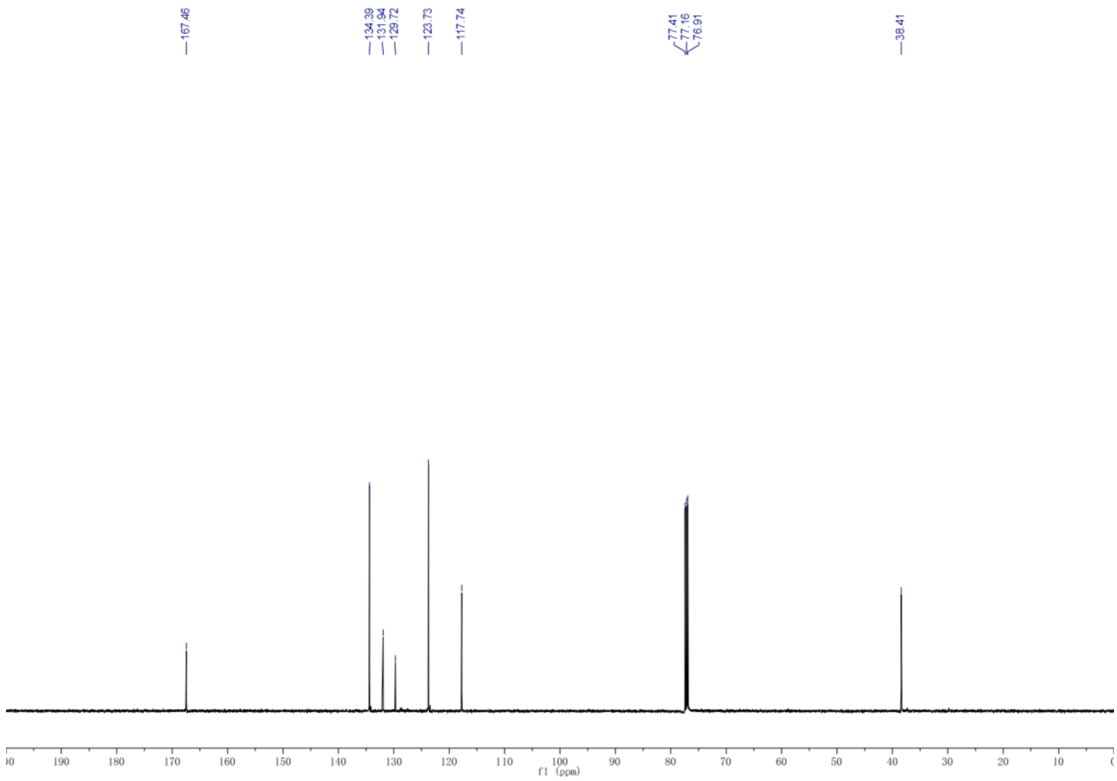
^{13}C NMR of compound **46**（126 MHz, $CDCl_3$）



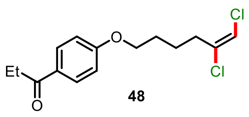
47

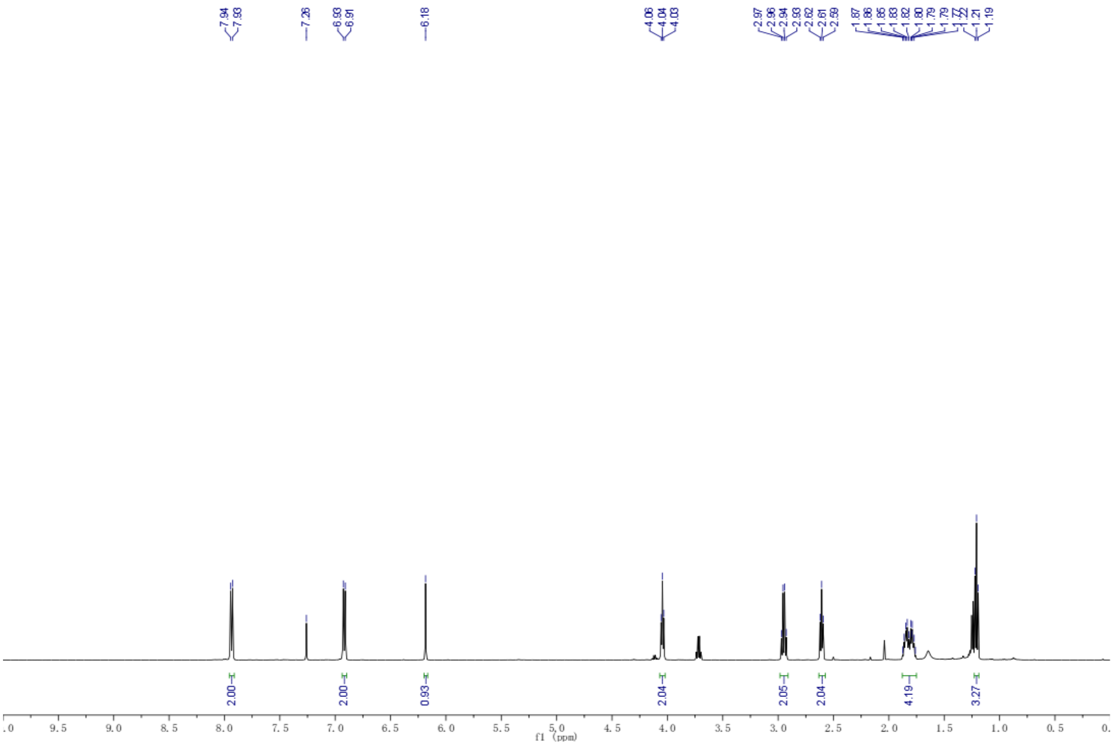


^{1}H NMR of compound **47**（500 MHz, $CDCl_3$）

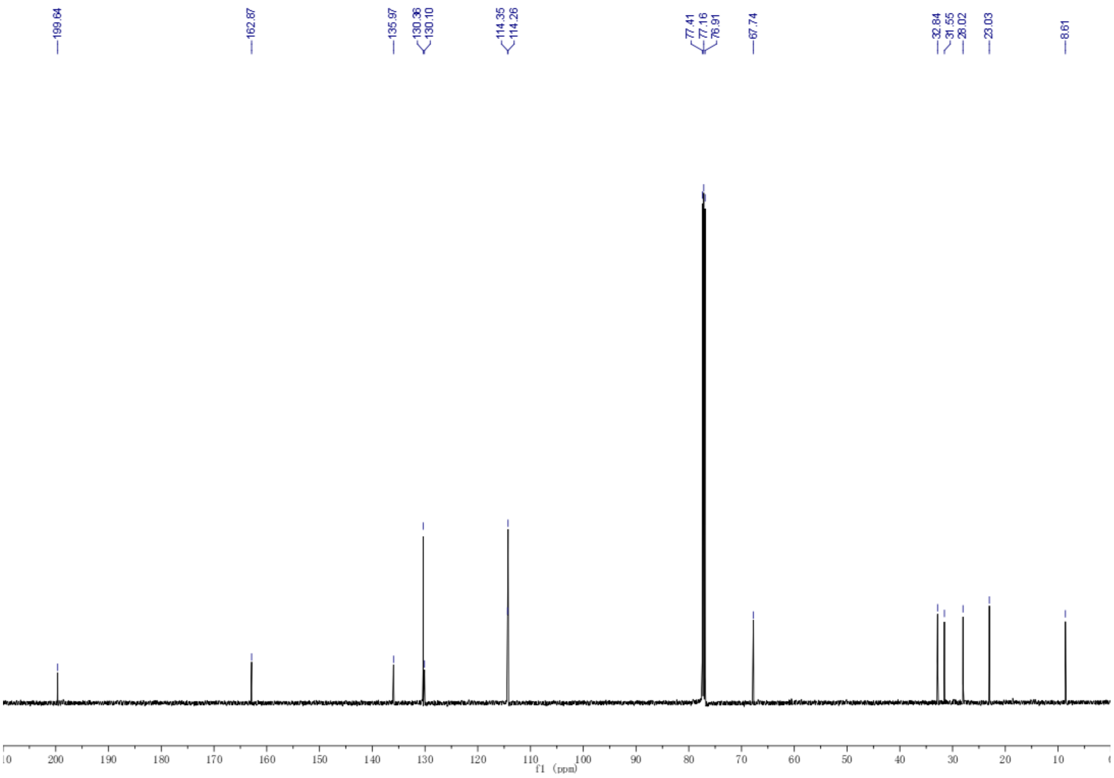


^{13}C NMR of compound **47**（126 MHz, $CDCl_3$）

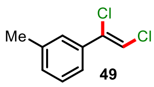


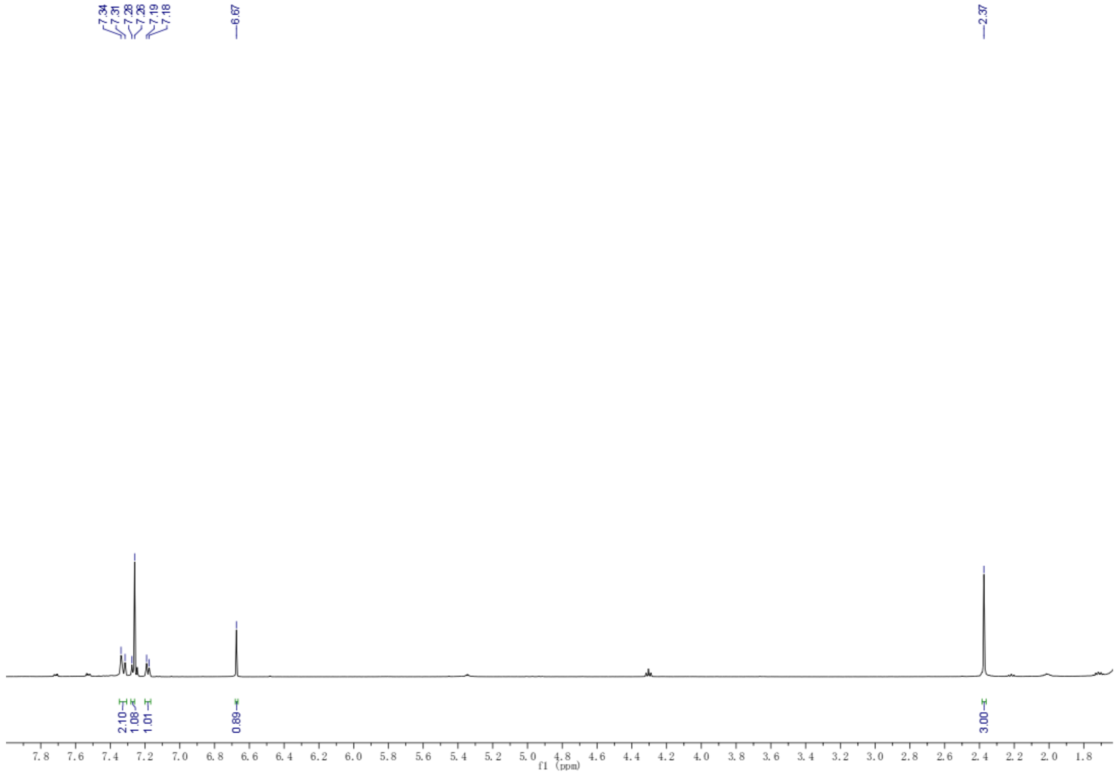


^{1}H NMR of compound **48**（500 MHz, $CDCl_3$）

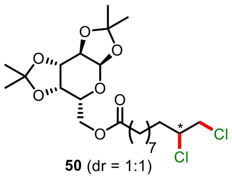


^{13}C NMR of compound **48**（126 MHz, $CDCl_3$）

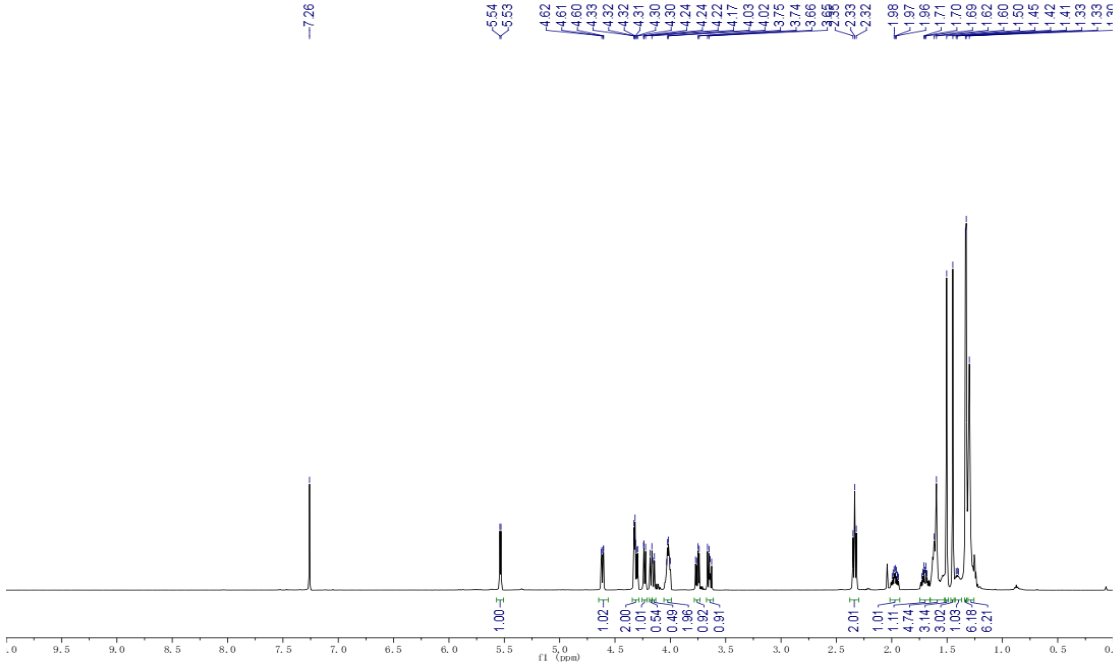




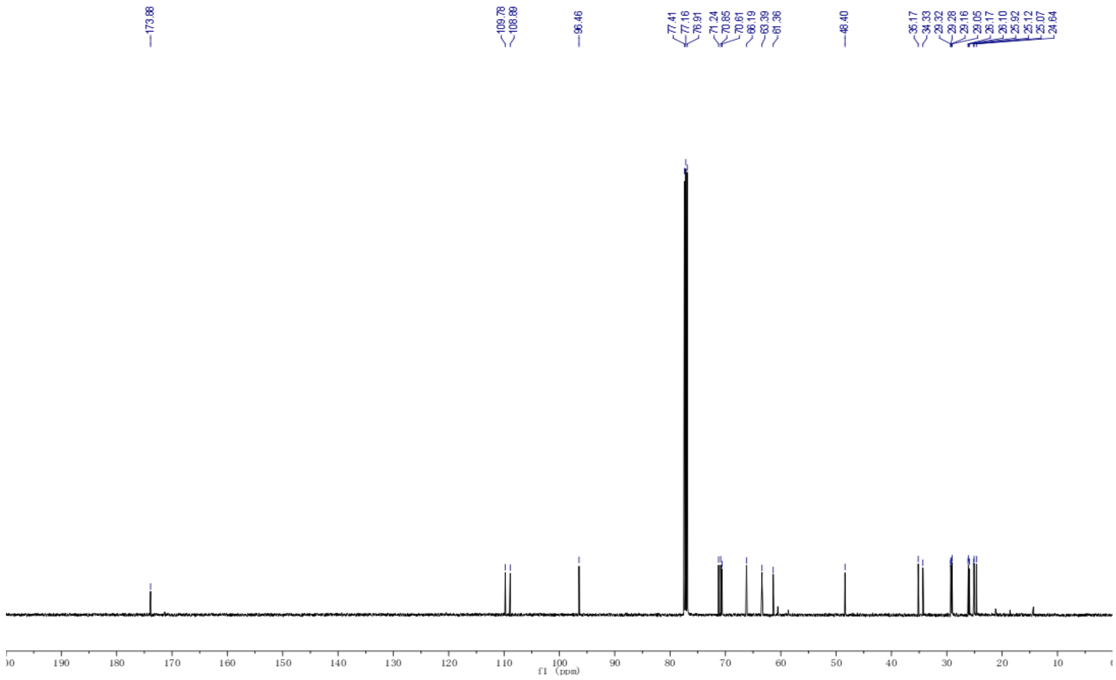
^{1}H NMR of compound **49**（500 MHz, $CDCl_3$）



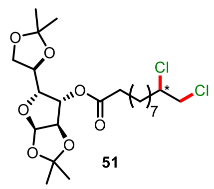
50 (dr = 1:1)



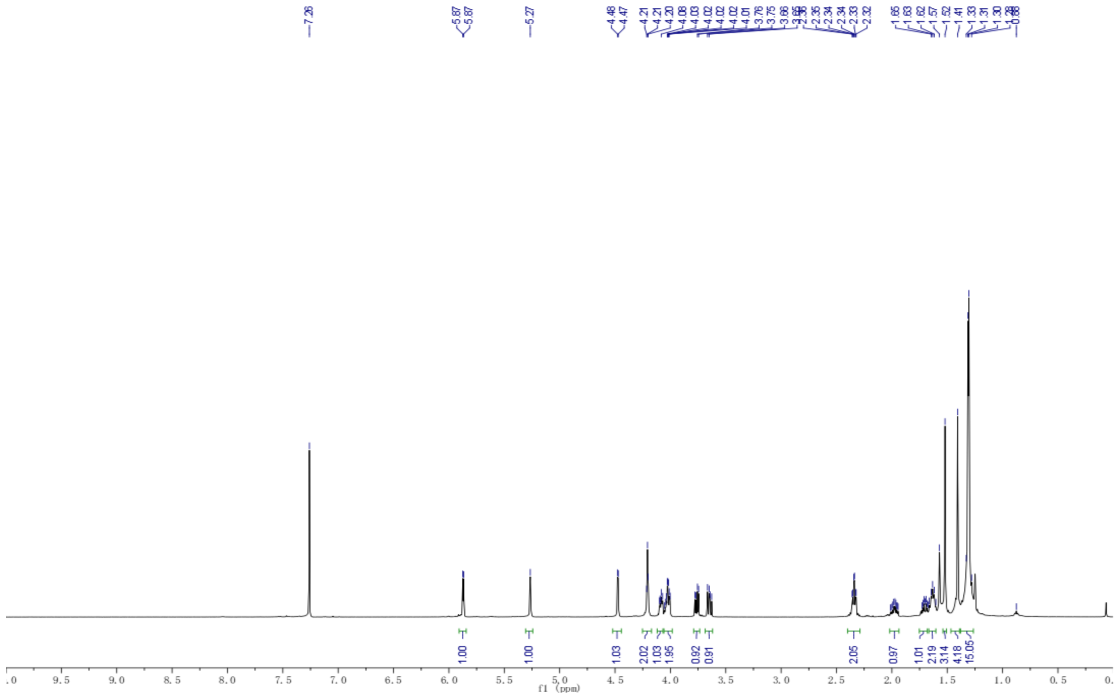
[1]H NMR of compound **50**（500 MHz, $CDCl_3$）



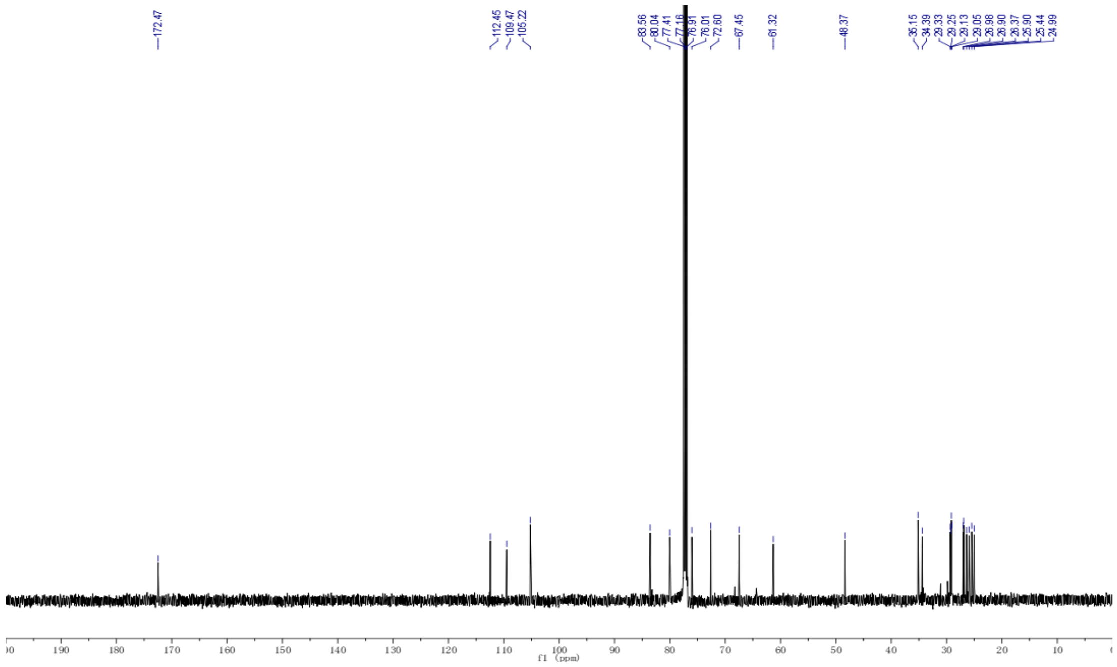
[13]C NMR of compound **50**（126 MHz, $CDCl_3$）



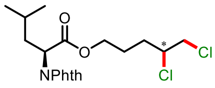
51



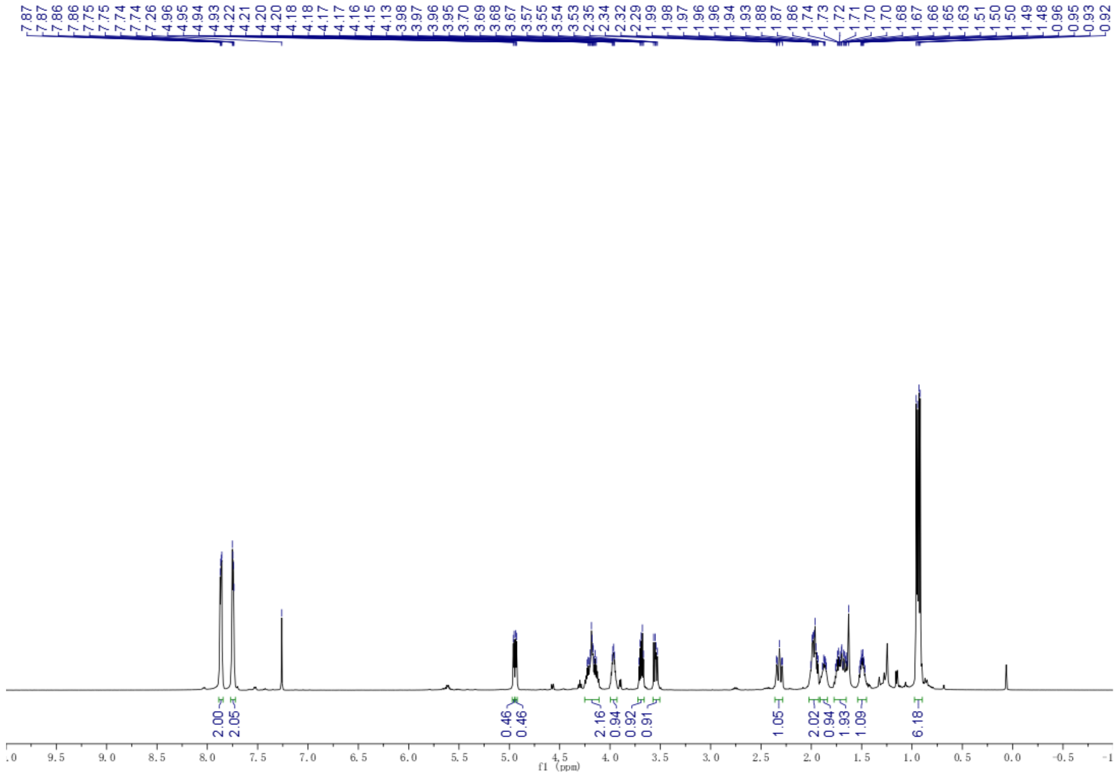
[1]H NMR of compound **51**（500 MHz, $CDCl_3$）



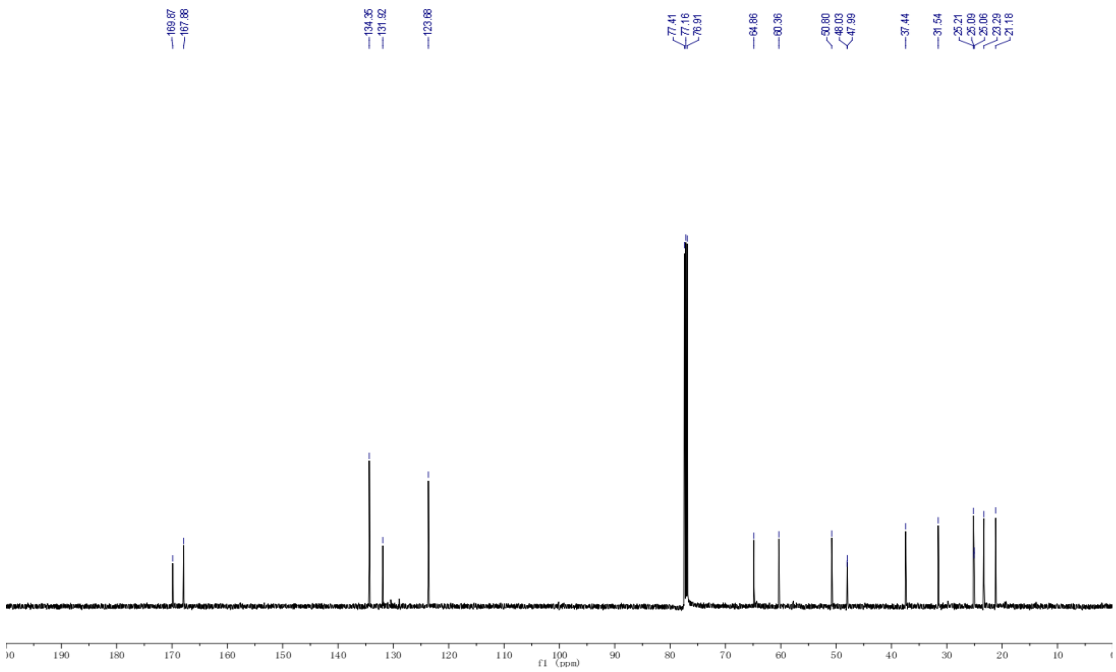
[13]C NMR of compound **51**（126 MHz, $CDCl_3$）



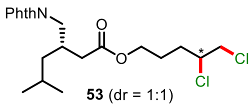
52 (dr = 1:1)



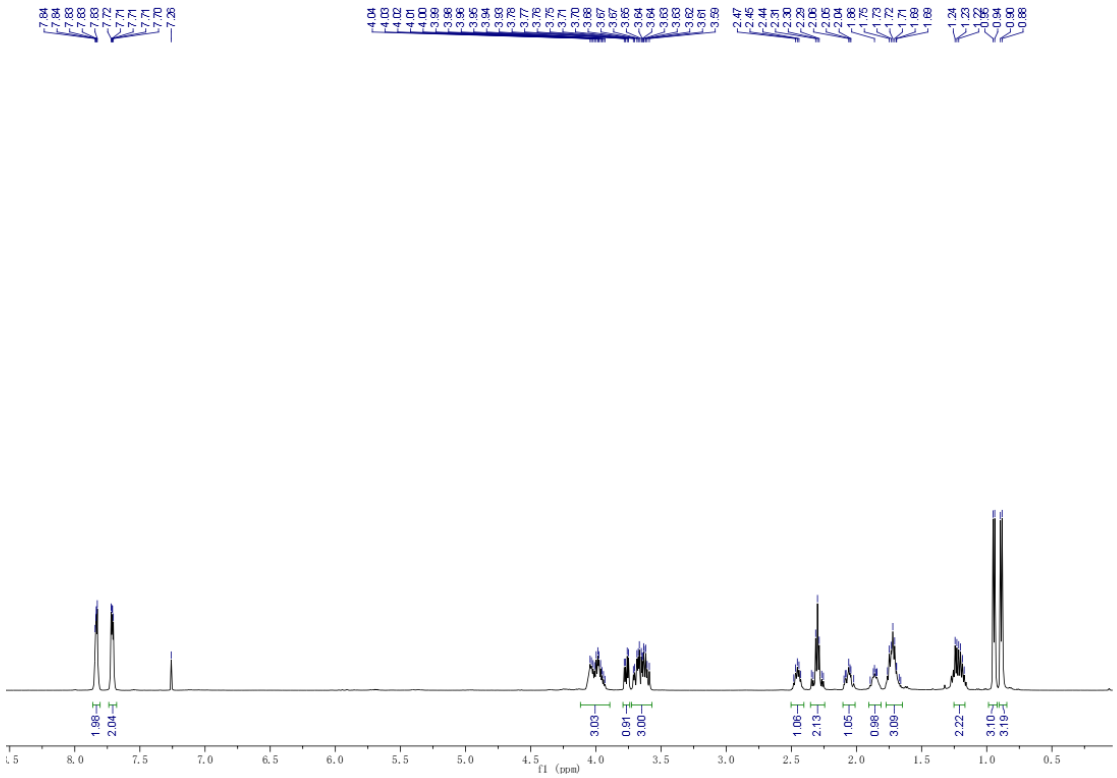
^{1}H NMR of compound **52**（500 MHz, $CDCl_3$）



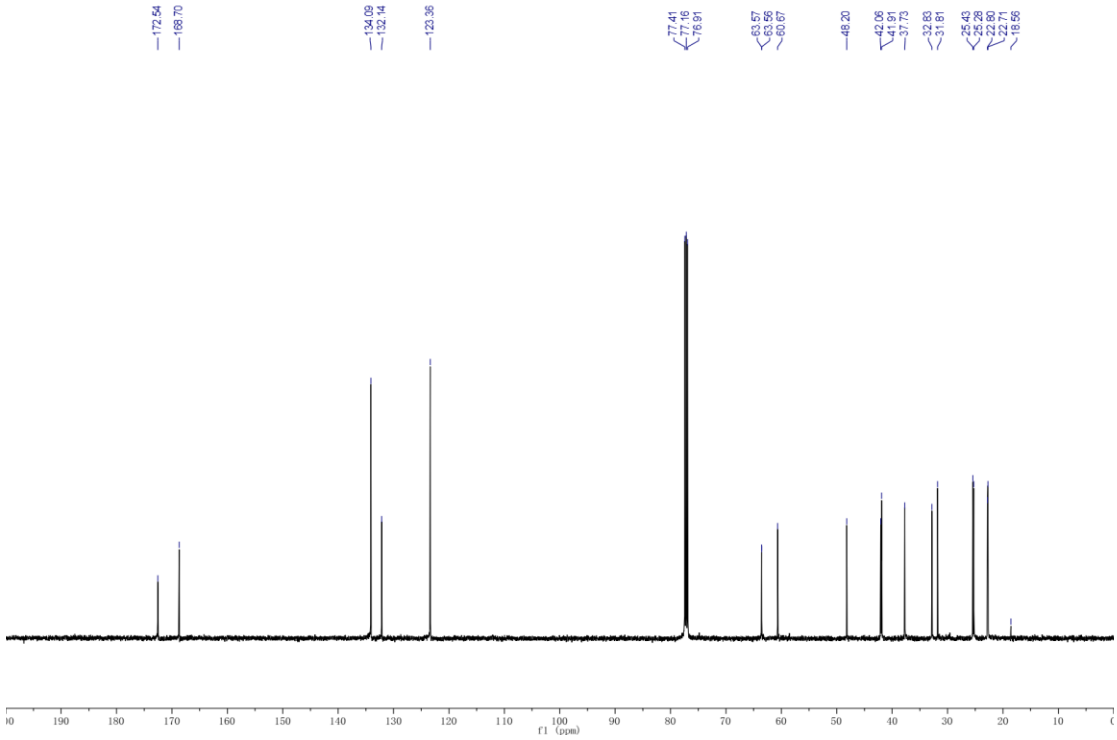
^{13}C NMR of compound **52**（126 MHz, $CDCl_3$）



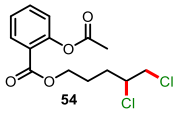
53 (dr = 1:1)



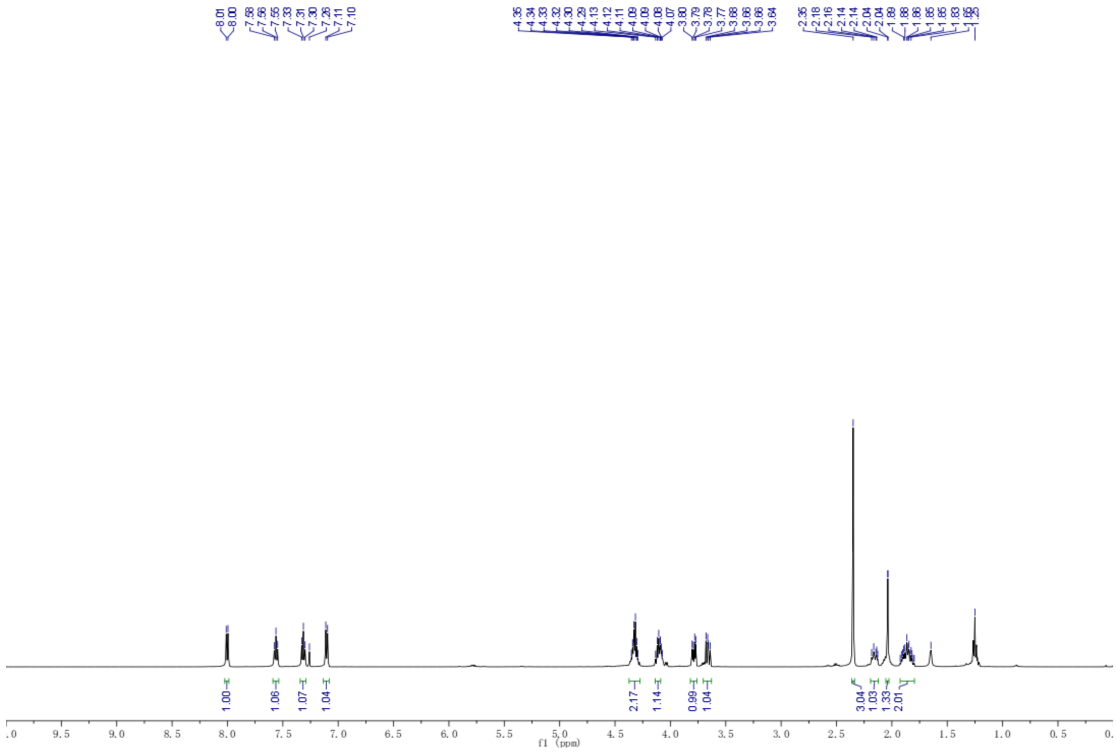
[1]H NMR of compound **53**（500 MHz, $CDCl_3$）



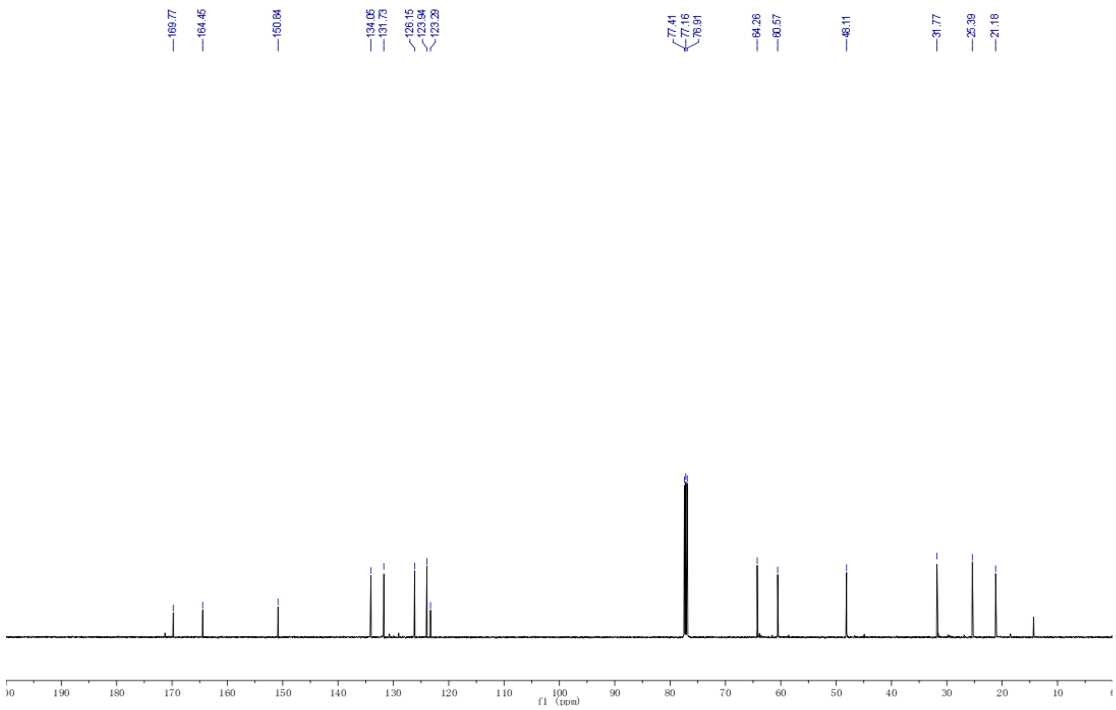
[13]C NMR of compound **53**（126 MHz, $CDCl_3$）



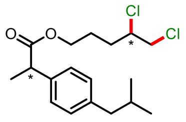
54



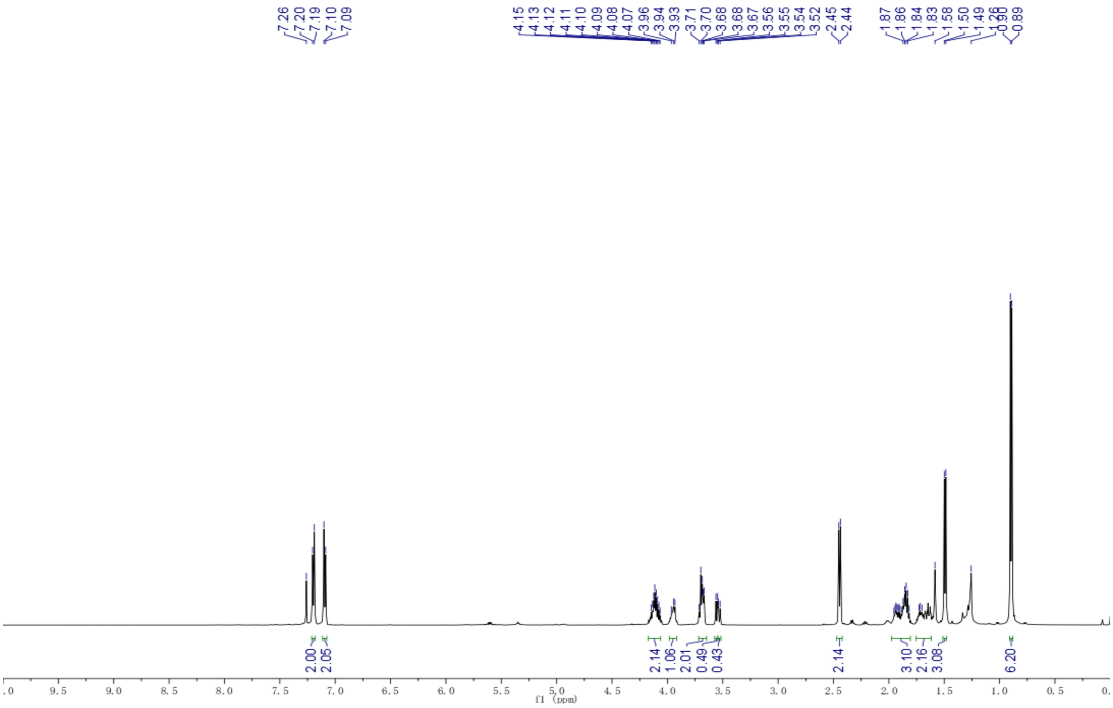
[1]H NMR of compound **54**（500 MHz, $CDCl_3$）



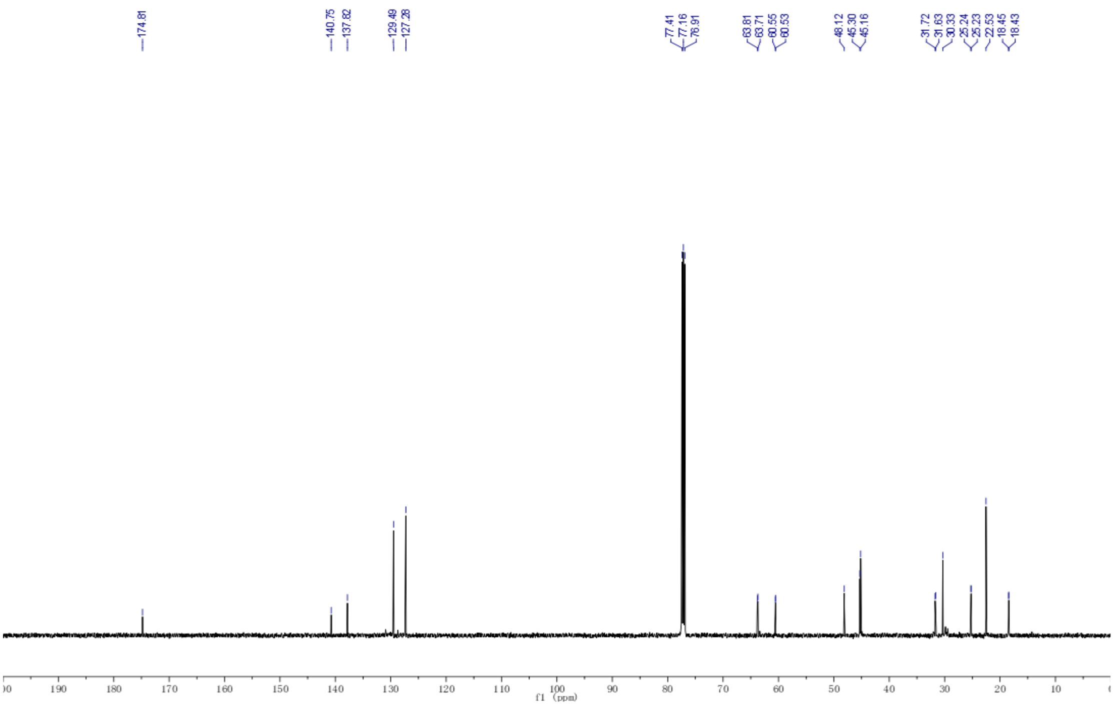
[13]C NMR of compound **54**（126 MHz, $CDCl_3$）



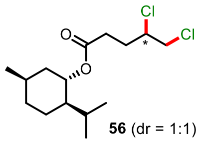
55 (dr = 1:1)



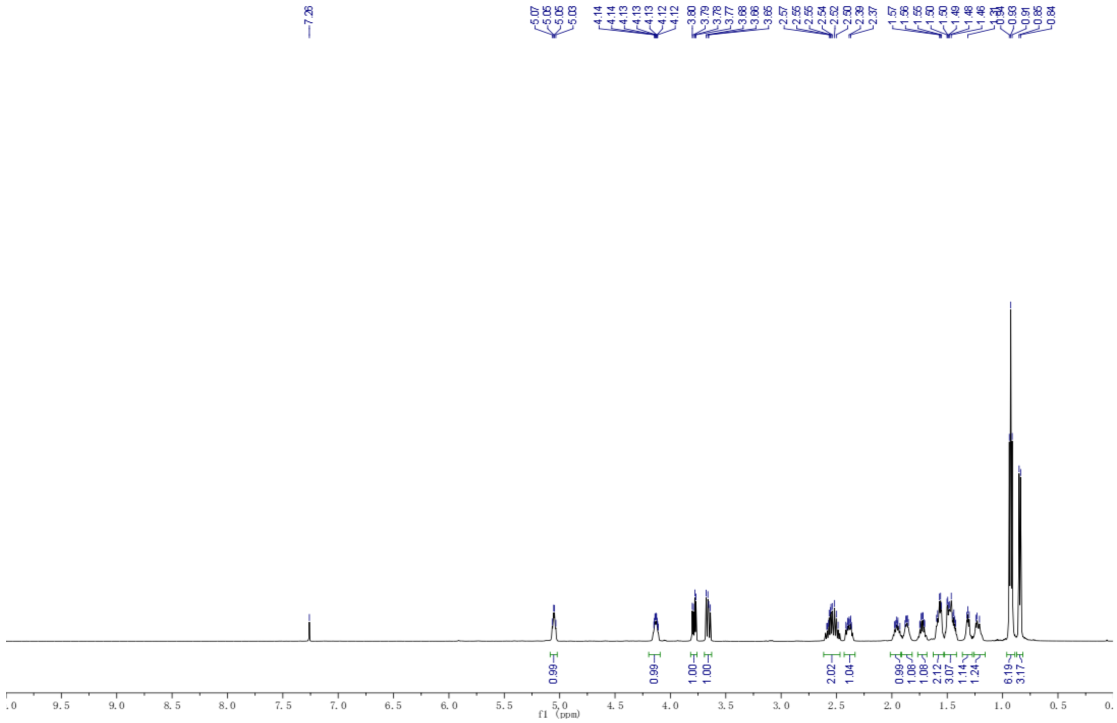
[1]H NMR of compound **55**（500 MHz, $CDCl_3$）



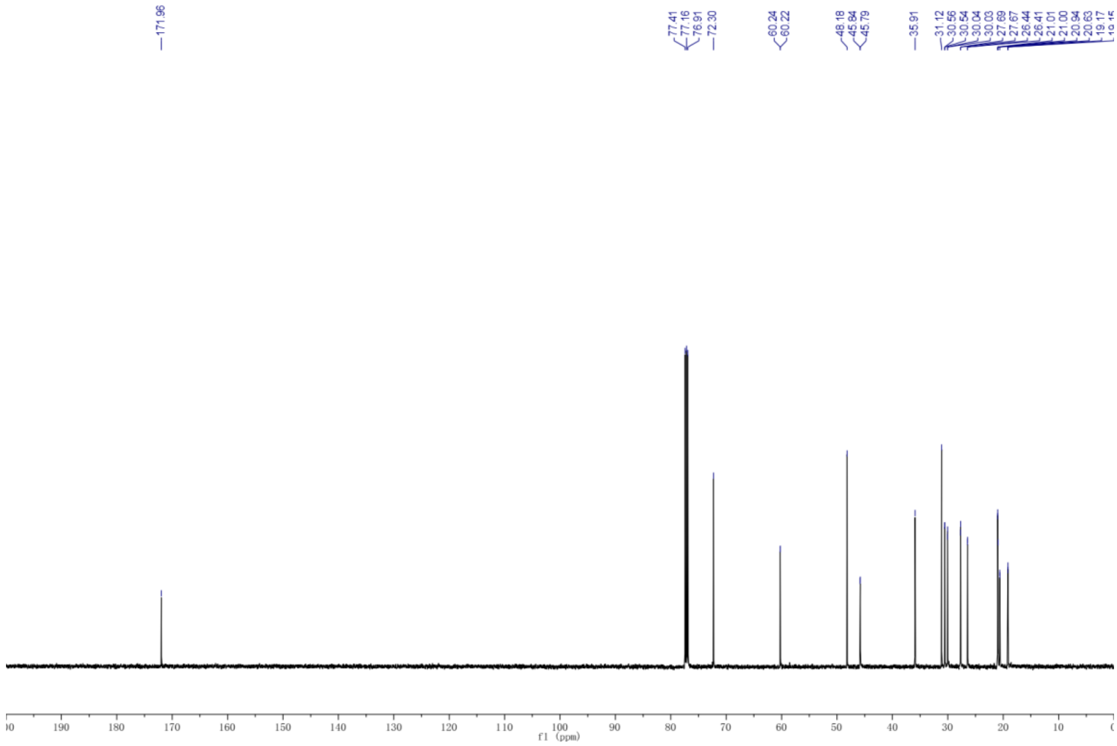
[13]C NMR of compound **55**（126 MHz, $CDCl_3$）



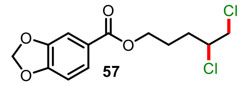
56 (dr = 1:1)

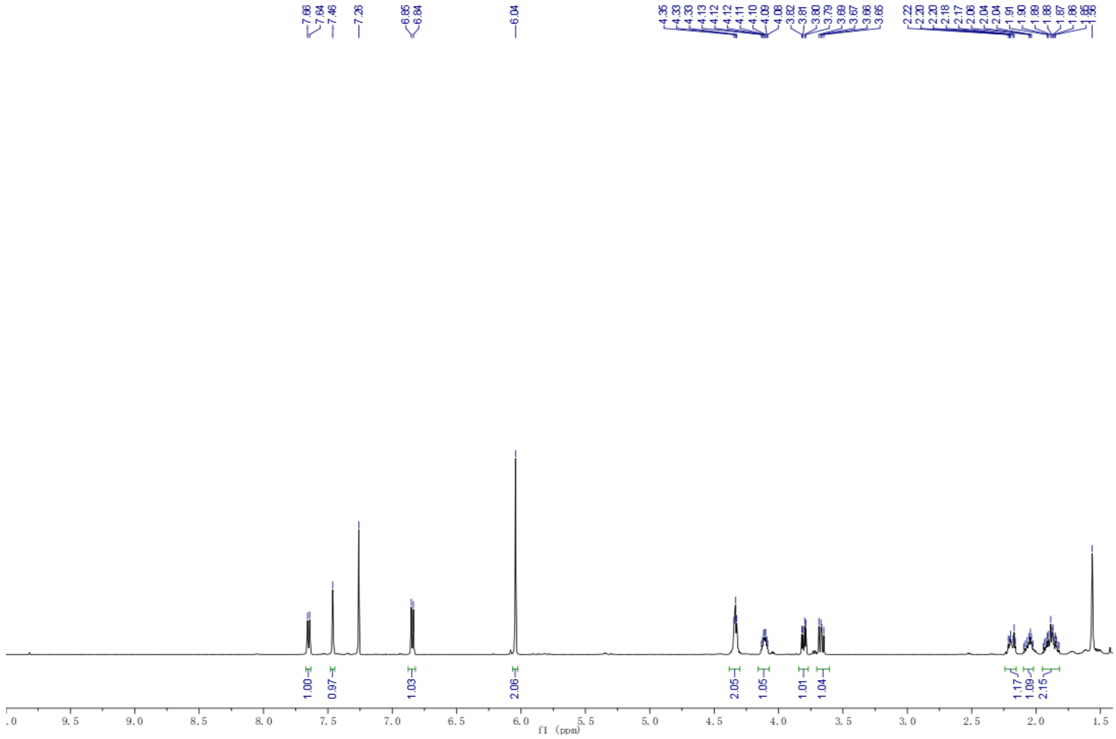


^{1}H NMR of compound **56**（500 MHz, $CDCl_3$）

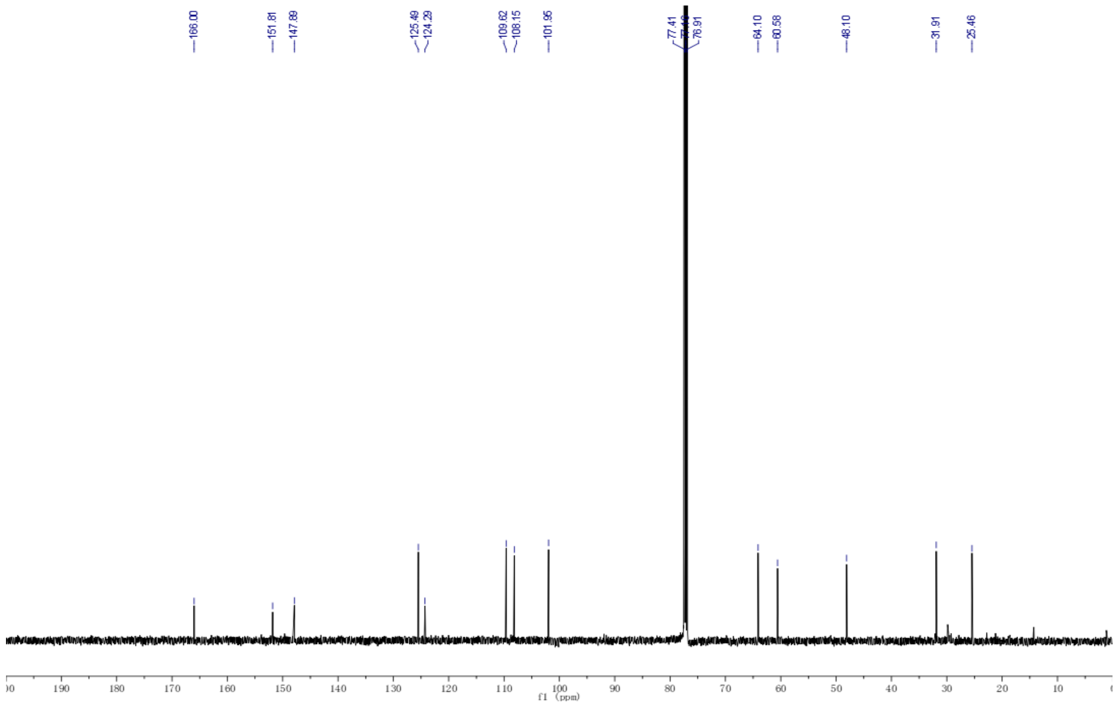


^{13}C NMR of compound **56**（126 MHz, $CDCl_3$）

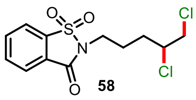




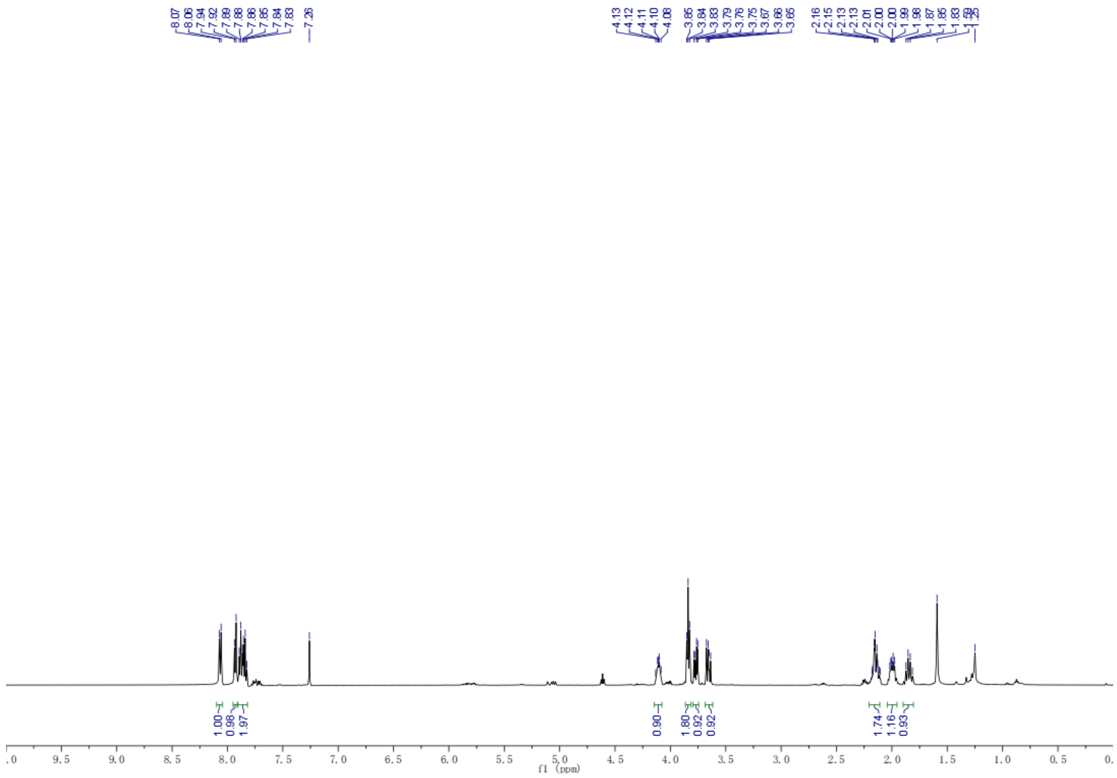
^{1}H NMR of compound **57**（500 MHz, $CDCl_3$）



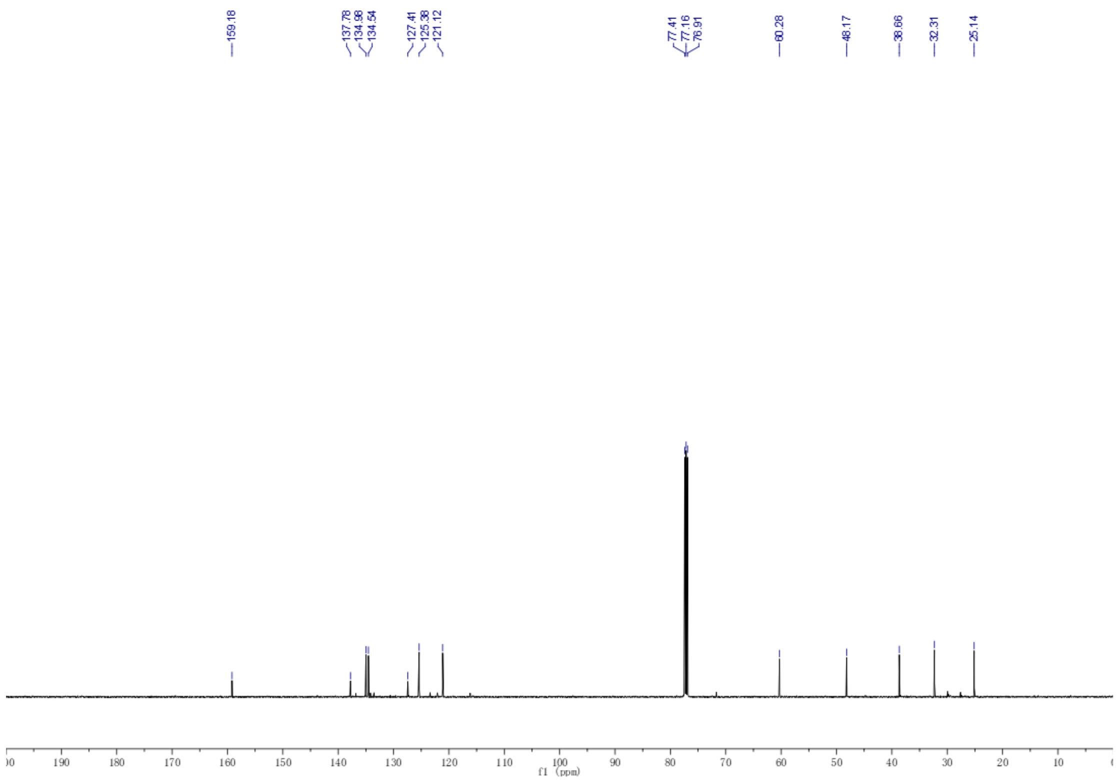
^{13}C NMR of compound **57**（126 MHz, $CDCl_3$）



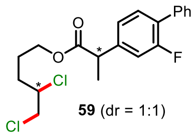
58



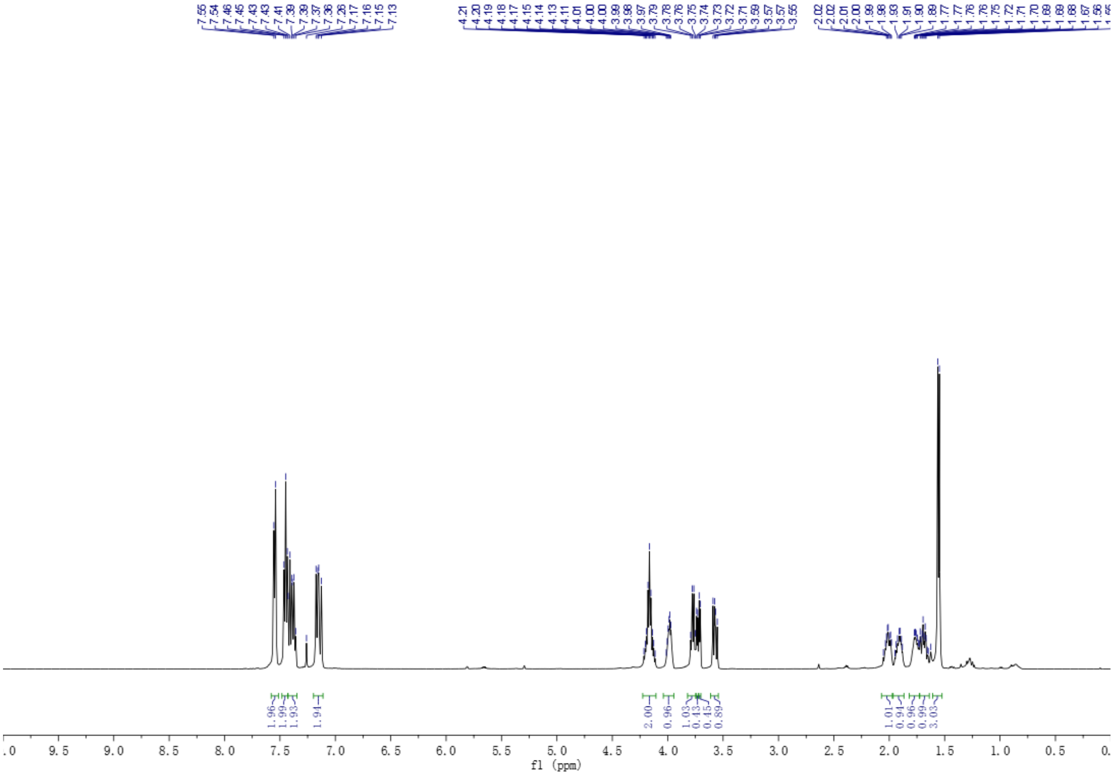
^{1}H NMR of compound **58**（500 MHz, $CDCl_3$）



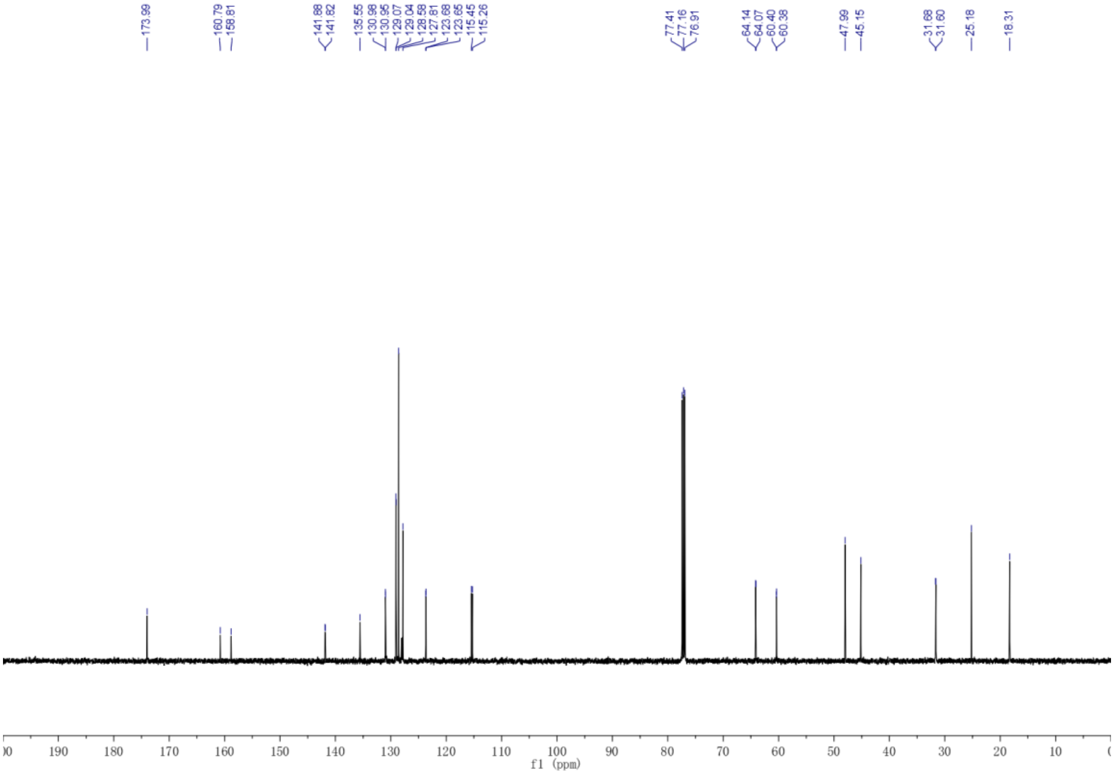
^{13}C NMR of compound **58**（126 MHz, $CDCl_3$）



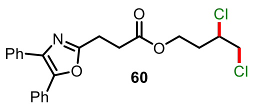
59 (dr = 1:1)

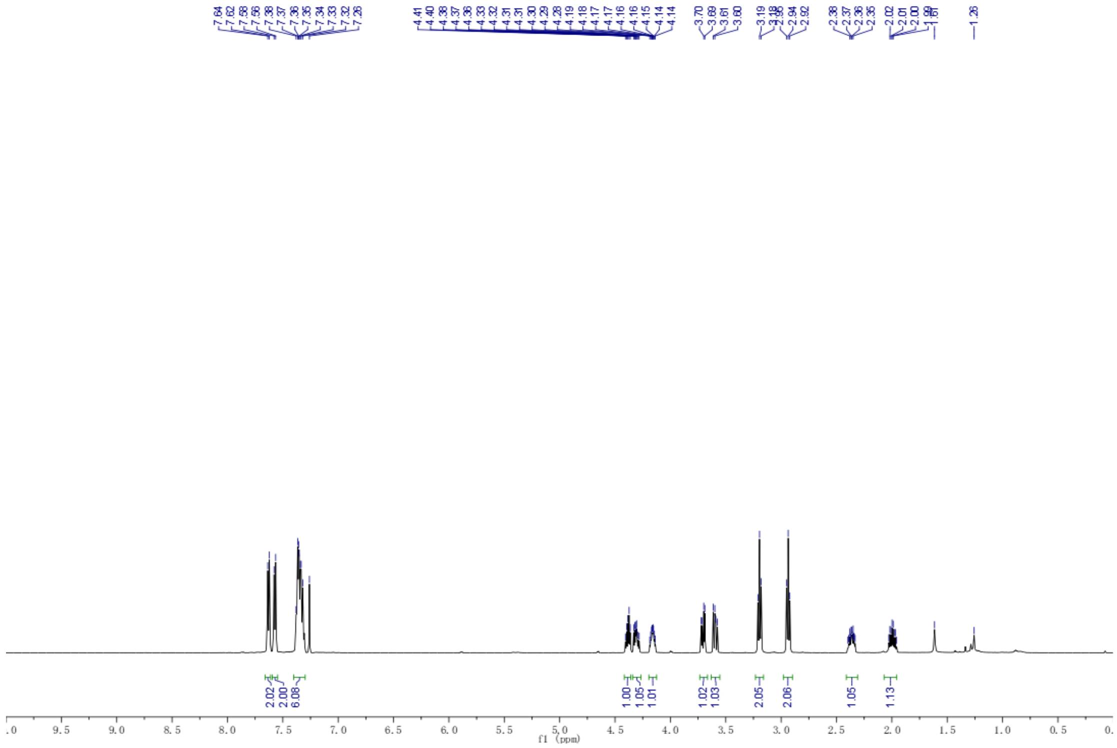


^{1}H NMR of compound **59**（500 MHz, $CDCl_3$）

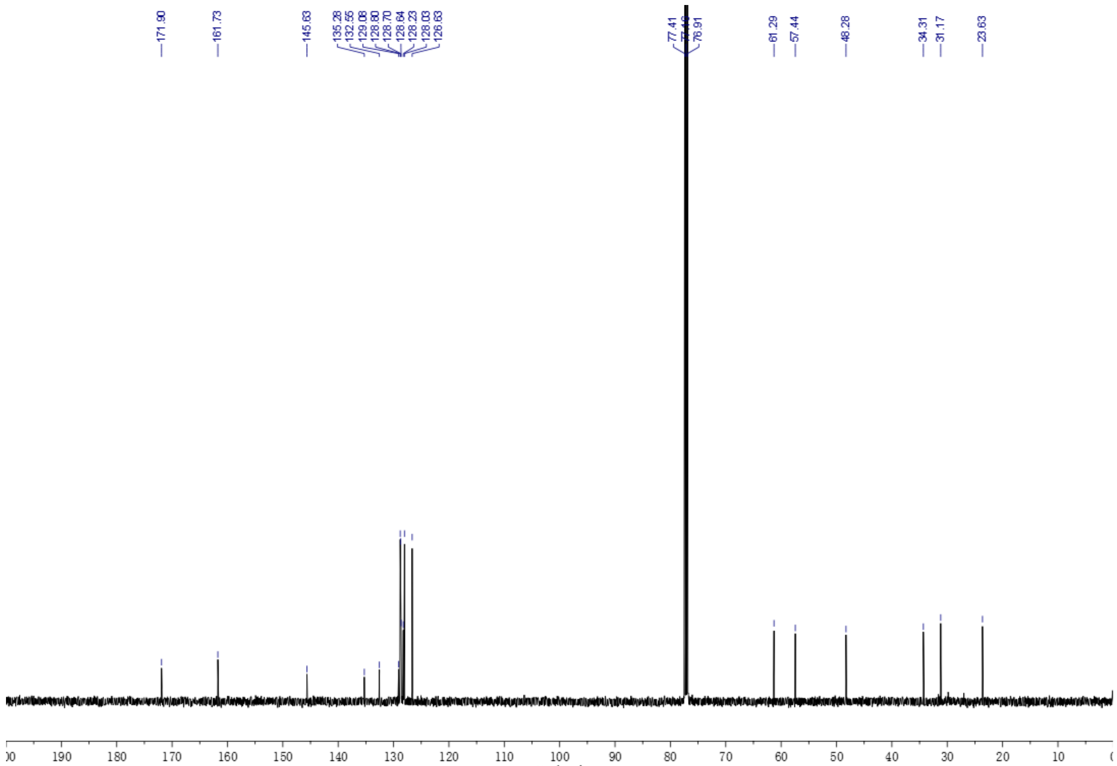


^{13}C NMR of compound **59**（126 MHz, $CDCl_3$）

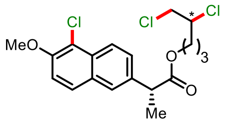




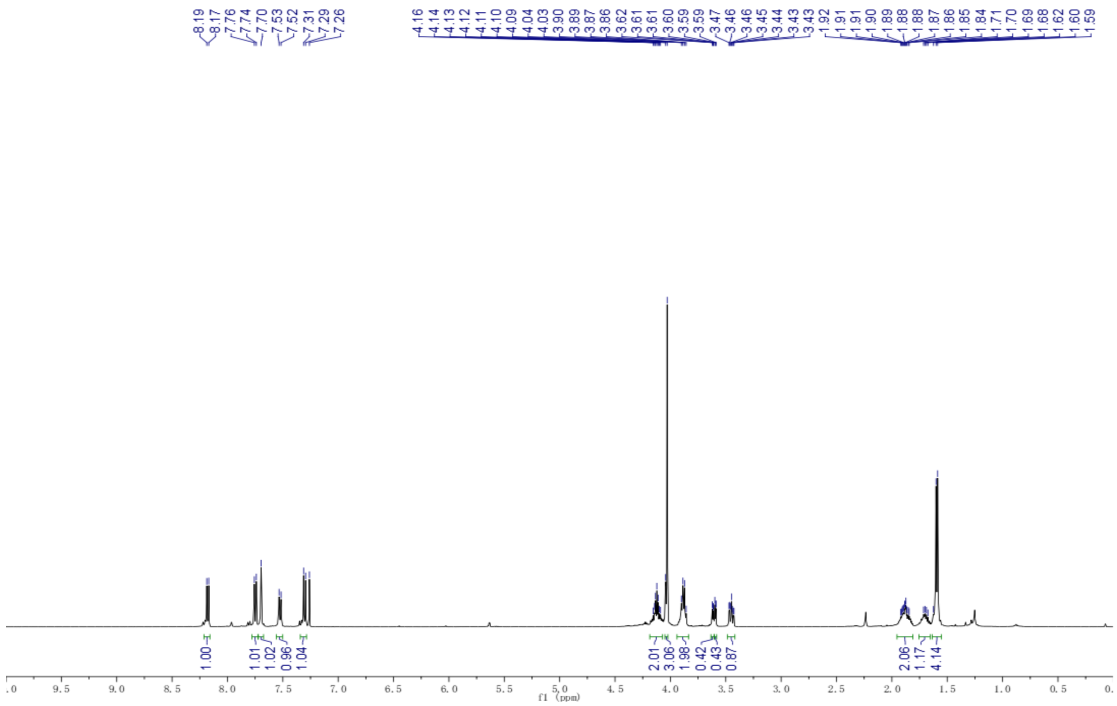
[1]H NMR of compound **60**（500 MHz, $CDCl_3$）



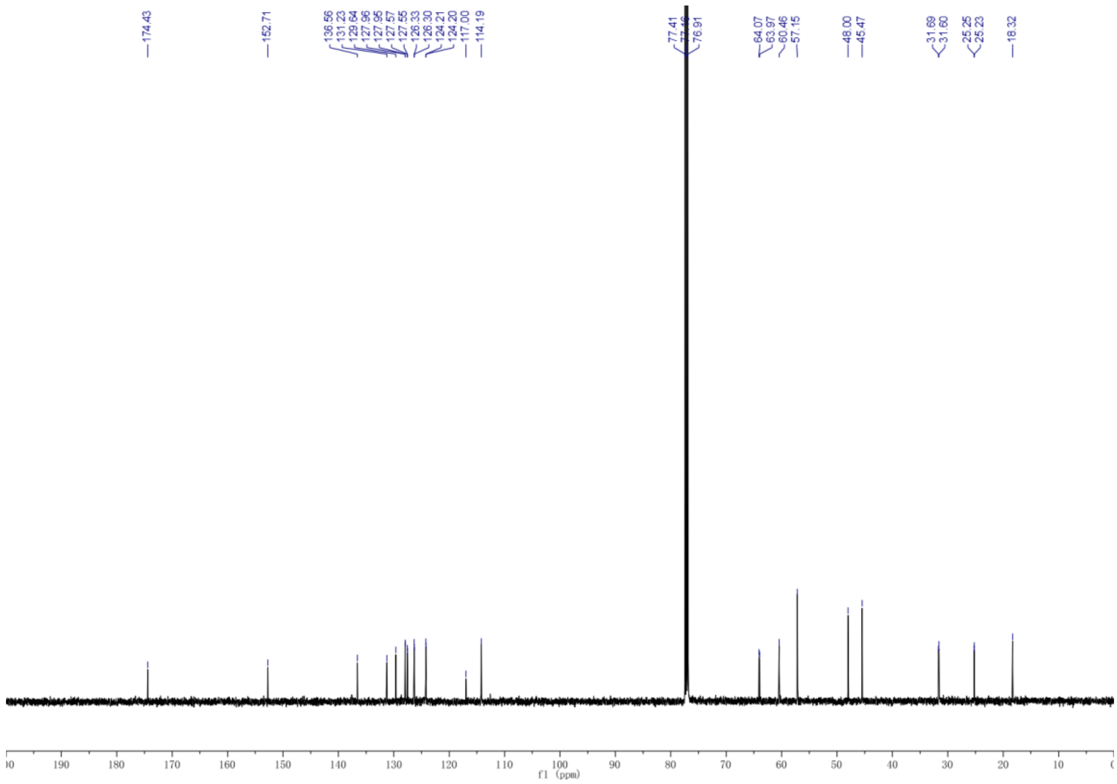
[13]C NMR of compound **60**（126 MHz, $CDCl_3$）



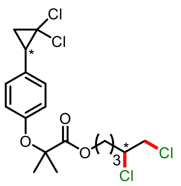
61 (dr = 1:1)



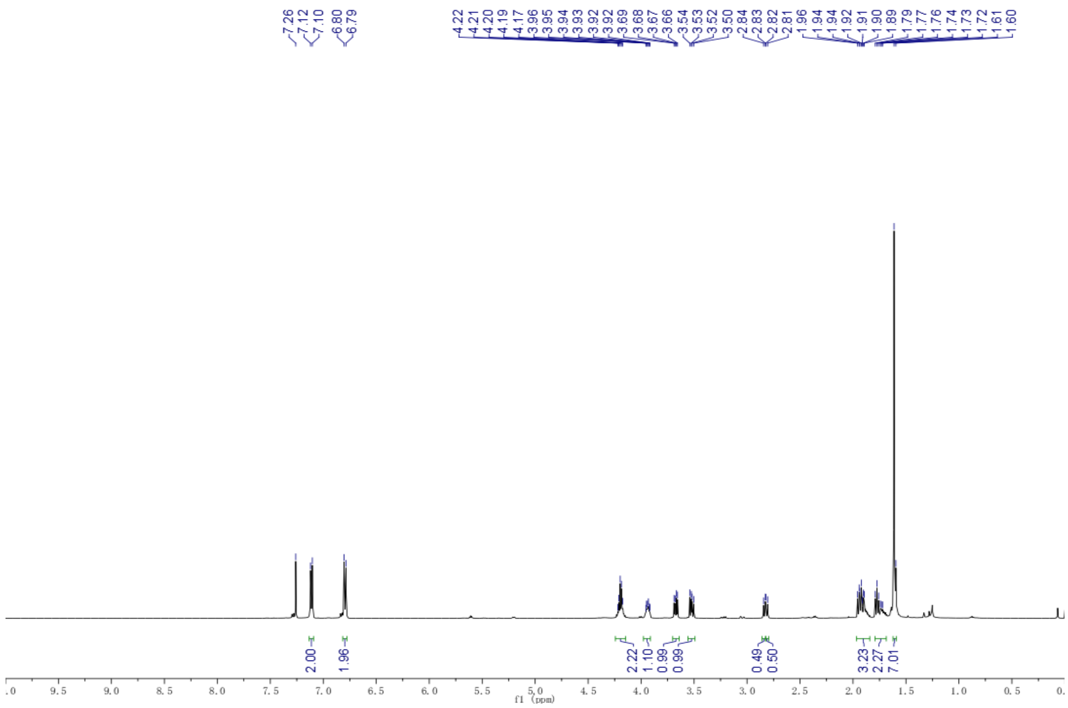
[1]H NMR of compound **61**（500 MHz, $CDCl_3$）



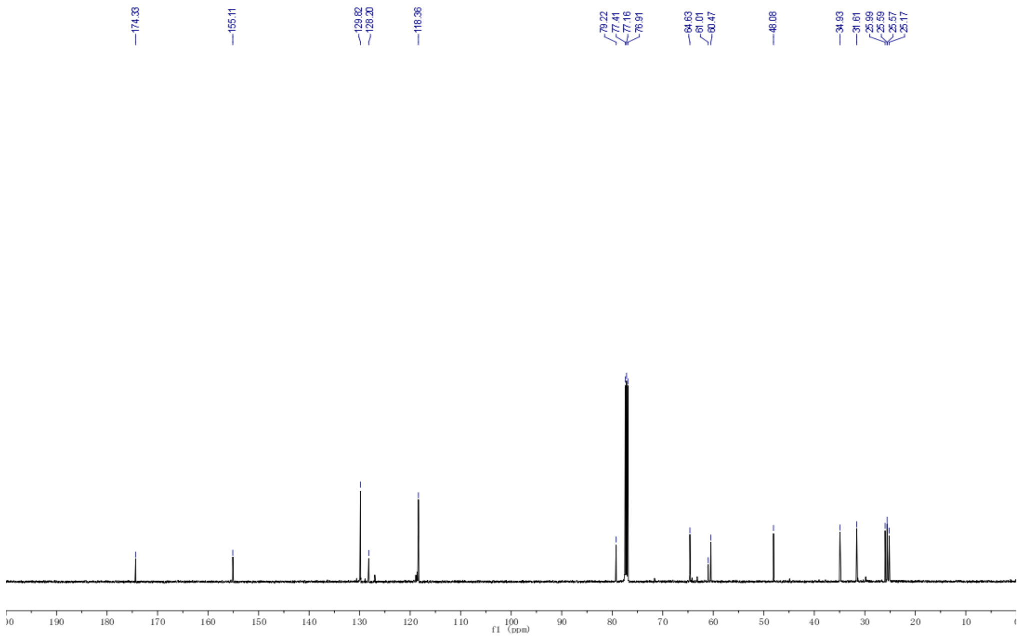
[13]C NMR of compound **61**（126 MHz, $CDCl_3$）



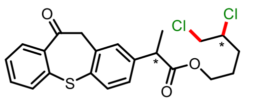
62 (dr = 1:1)



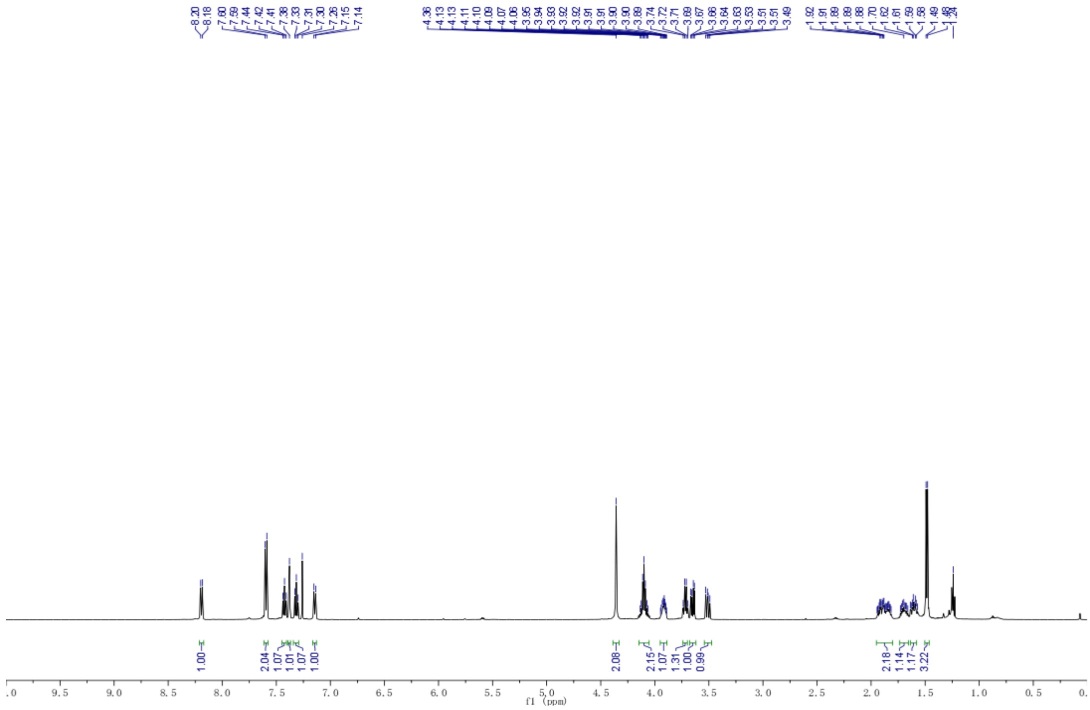
^{1}H NMR of compound **62**（500 MHz, $CDCl_3$）



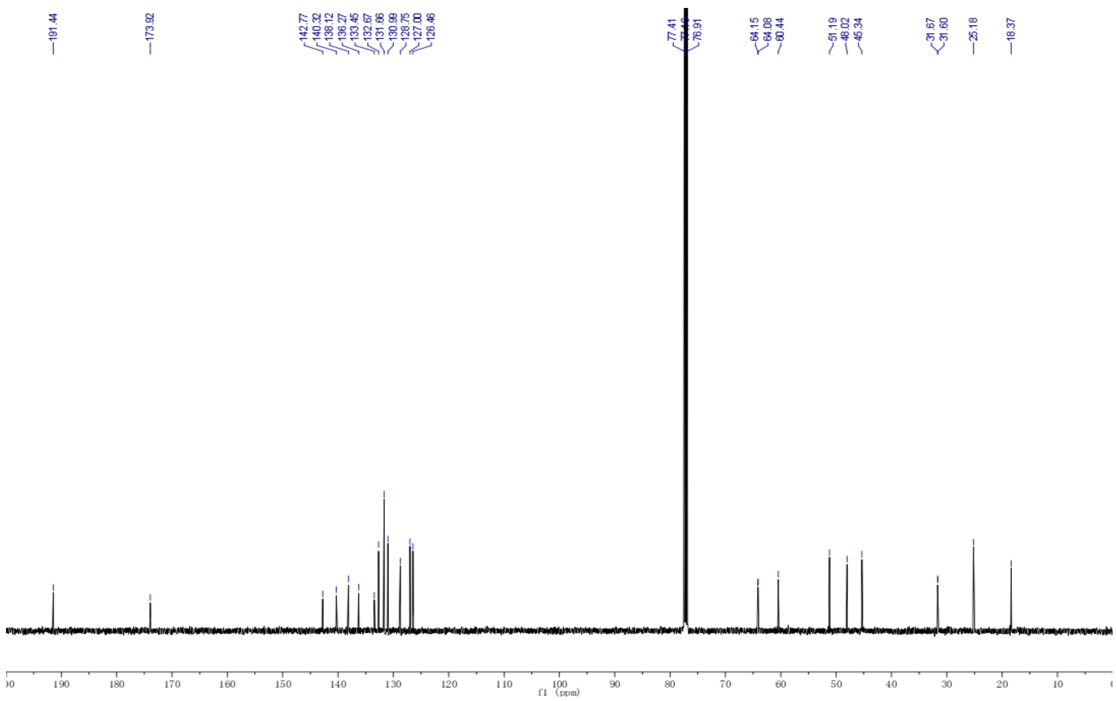
^{13}C NMR of compound **62**（126 MHz, $CDCl_3$）



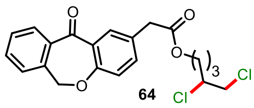
63 (dr = 1:1)



^{1}H NMR of compound **63**（500 MHz, $CDCl_3$）



^{13}C NMR of compound **63**（126 MHz, $CDCl_3$）



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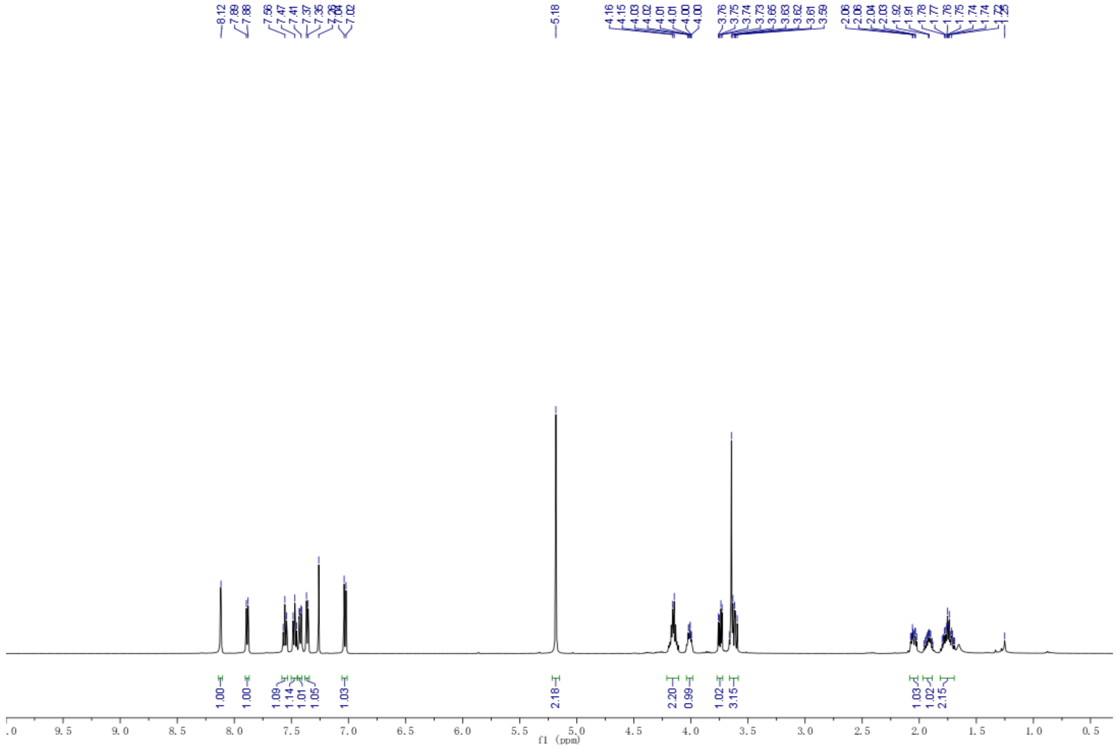
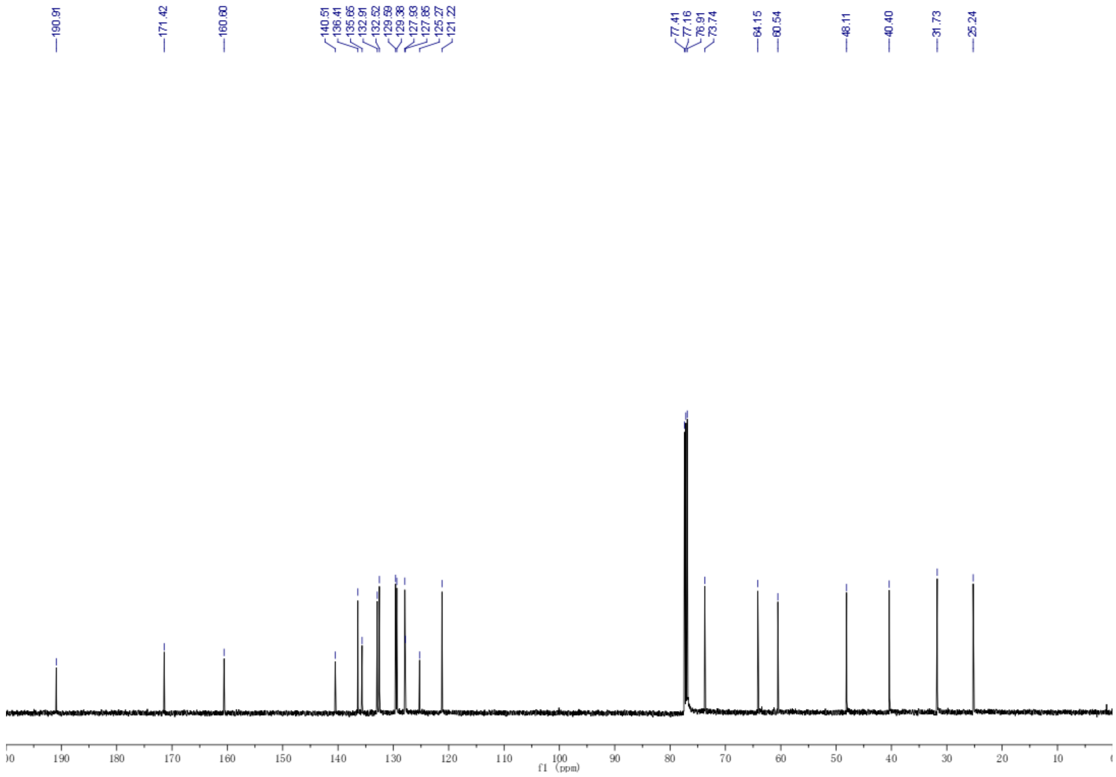
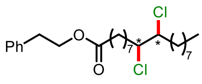


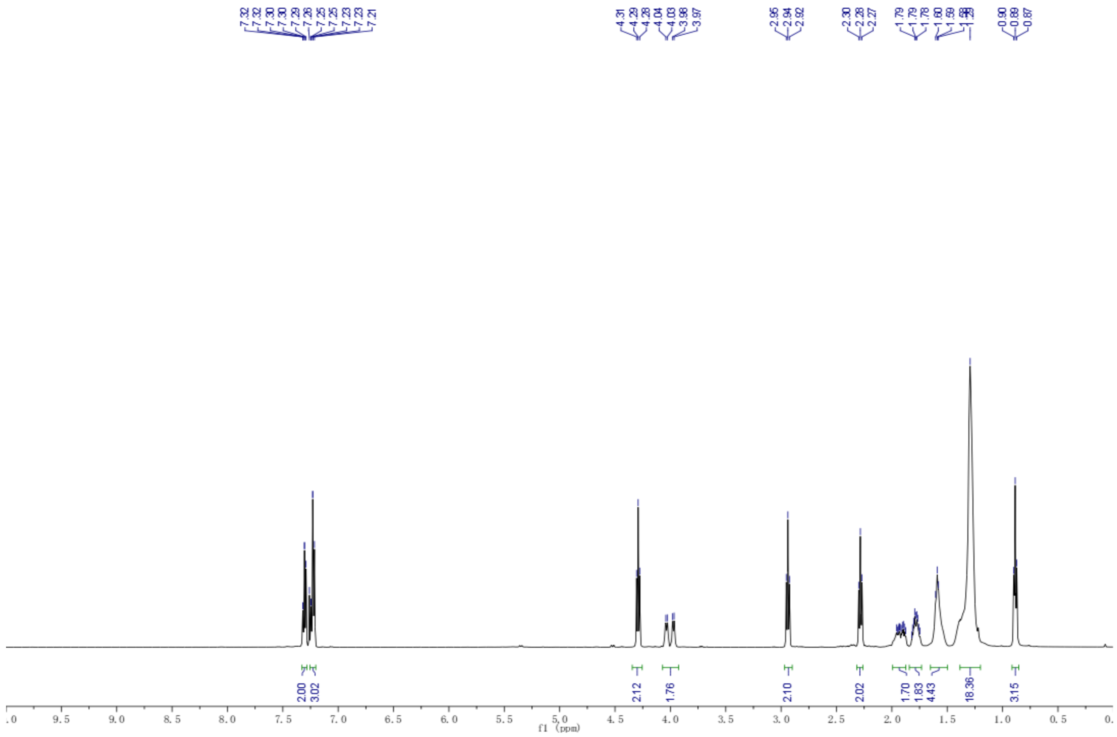
[1]H NMR of compound **64**（500 MHz, $CDCl_3$）



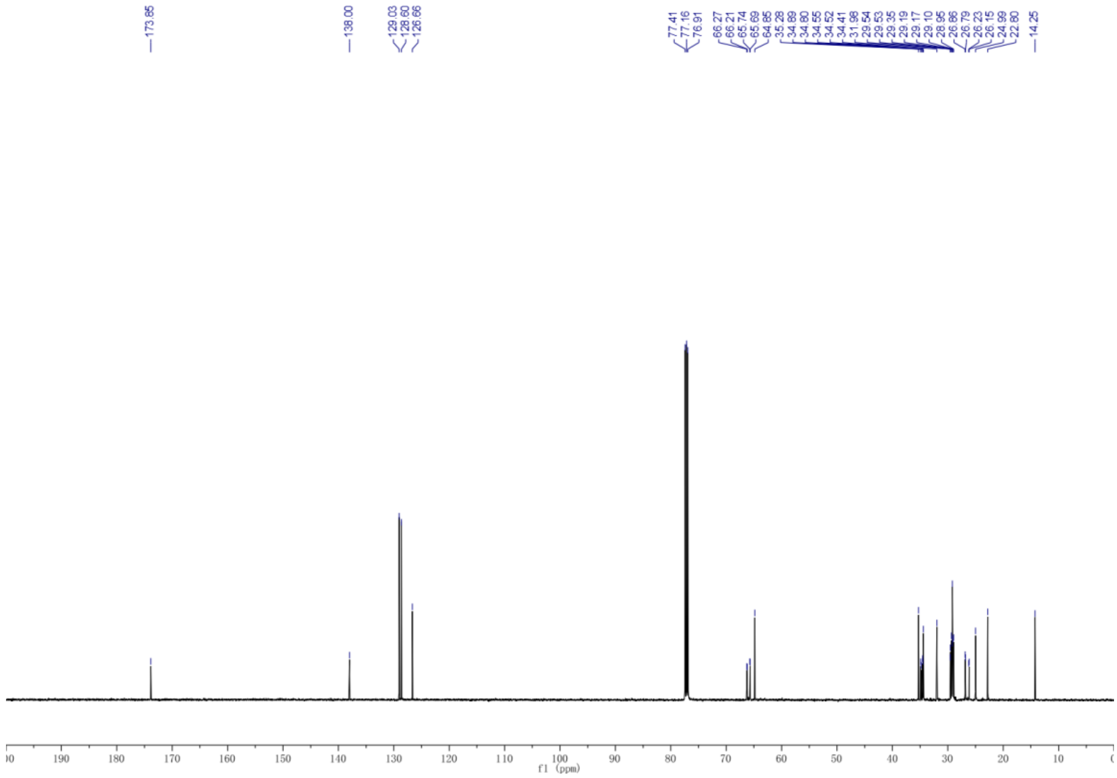
[13]C NMR of compound **64**（126 MHz, $CDCl_3$）



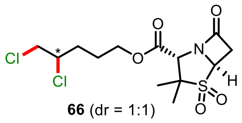
65 (dr = 1:1)



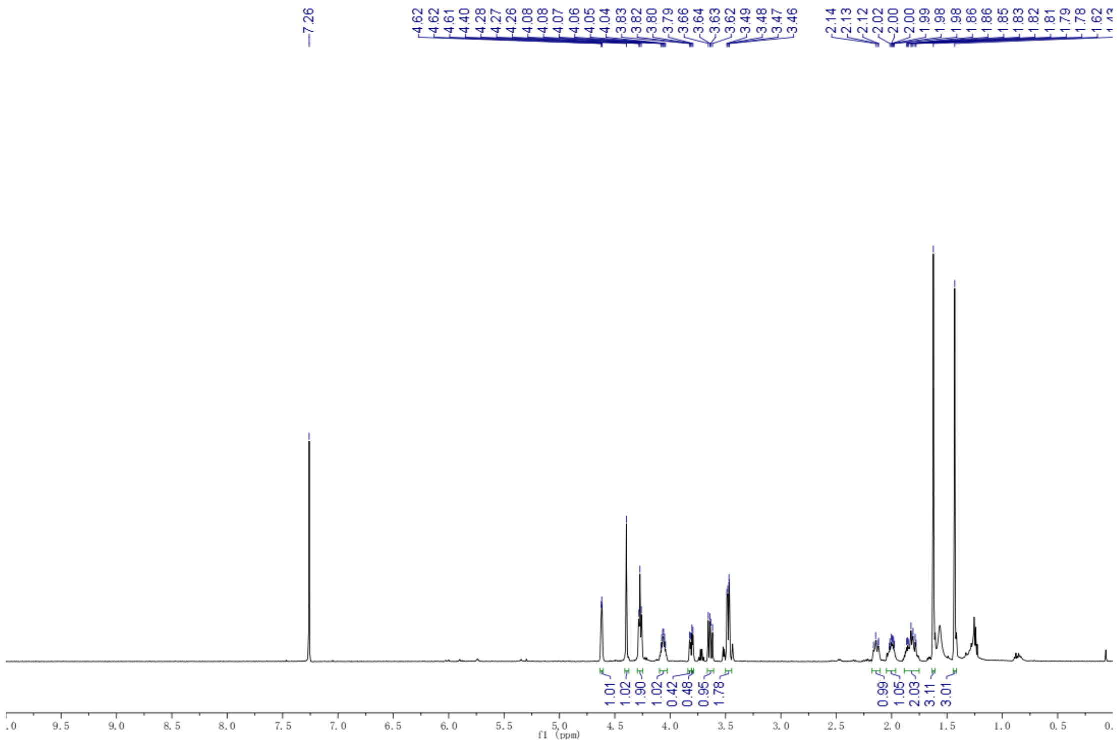
[1]H NMR of compound **65**（500 MHz, $CDCl_3$）



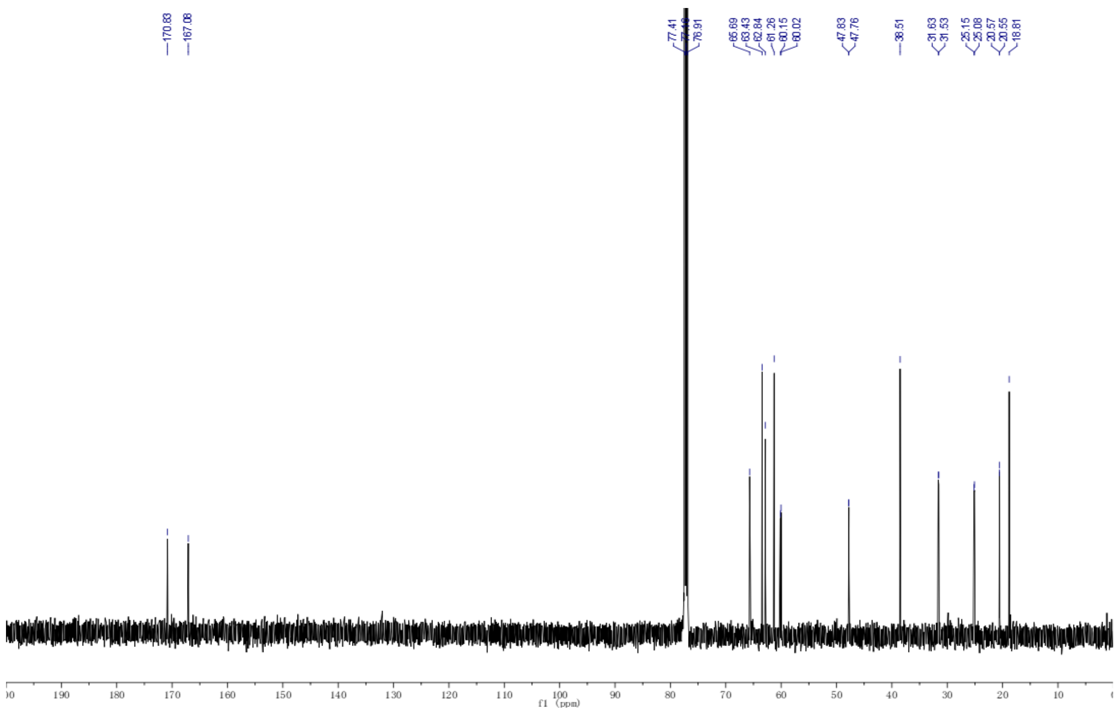
[13]C NMR of compound **65**（126 MHz, $CDCl_3$）



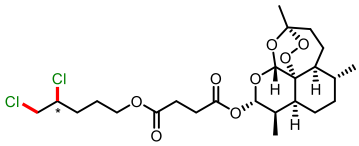
66 (dr = 1:1)



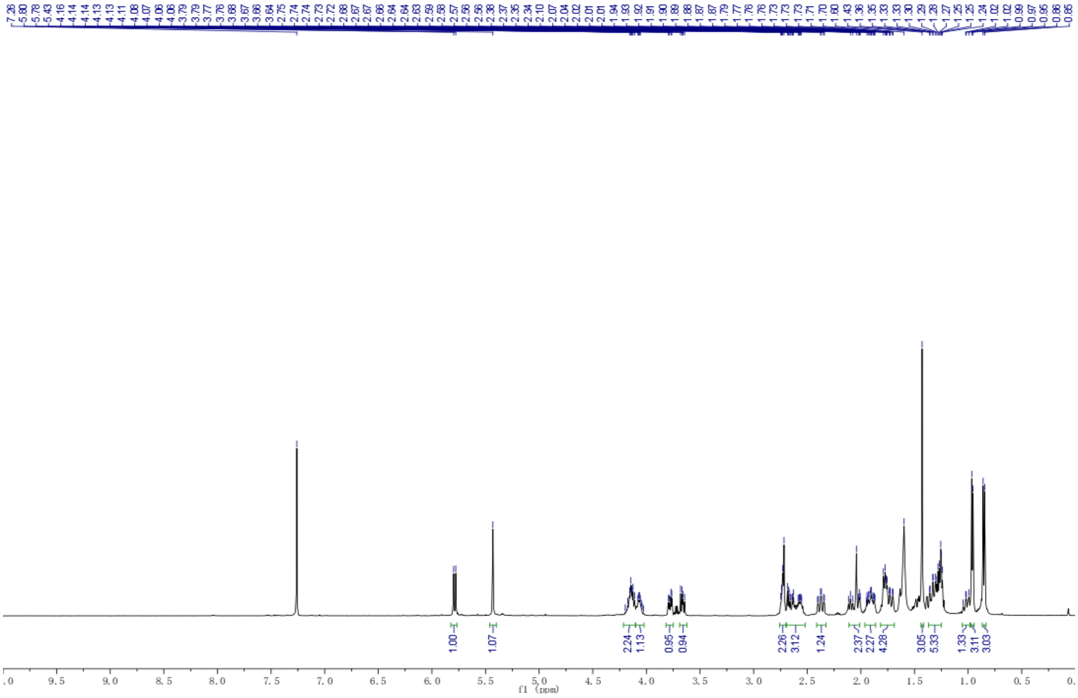
[1]H NMR of compound **66**（500 MHz, $CDCl_3$）



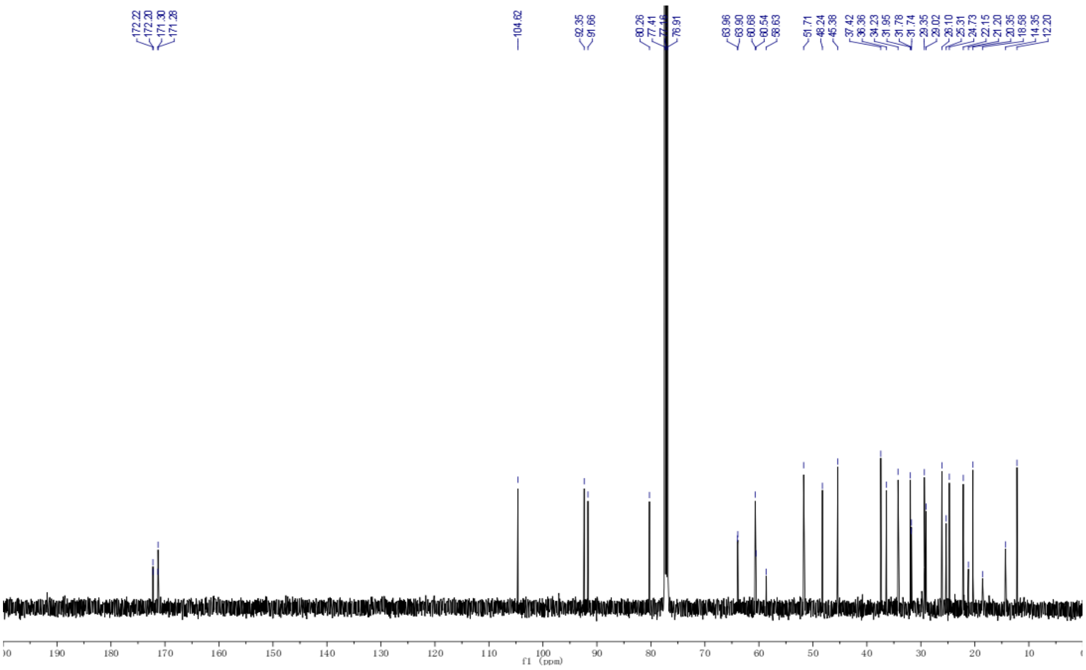
[13]C NMR of compound **66**（126 MHz, $CDCl_3$）



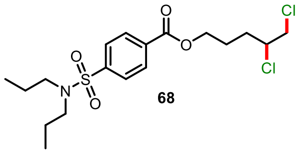
67 (dr = 1:1)



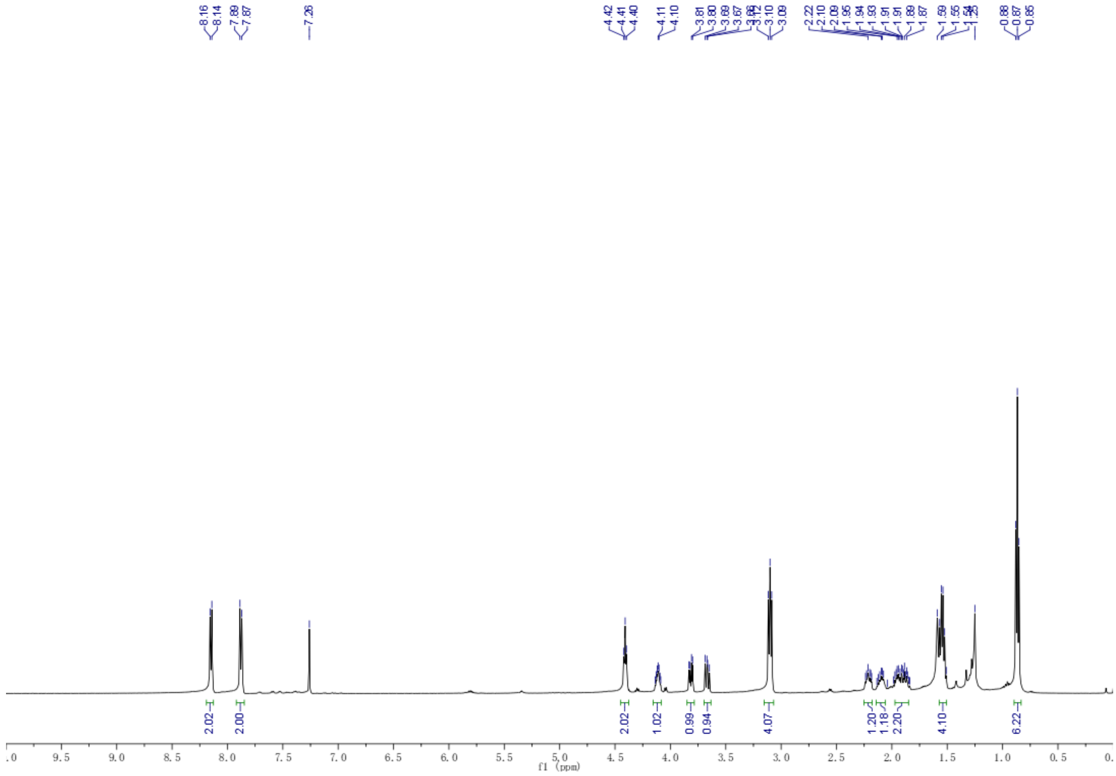
^{1}H NMR of compound **67**（500 MHz, $CDCl_3$）



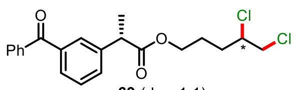
^{13}C NMR of compound **67**（126 MHz, $CDCl_3$）



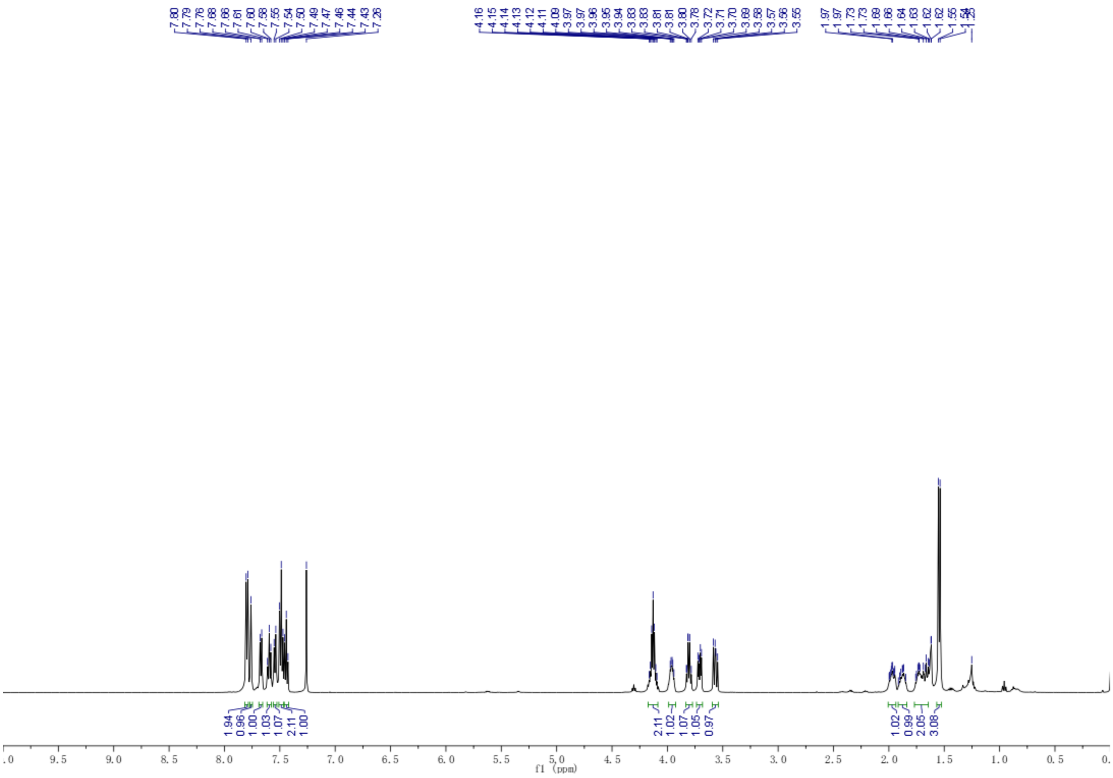
68



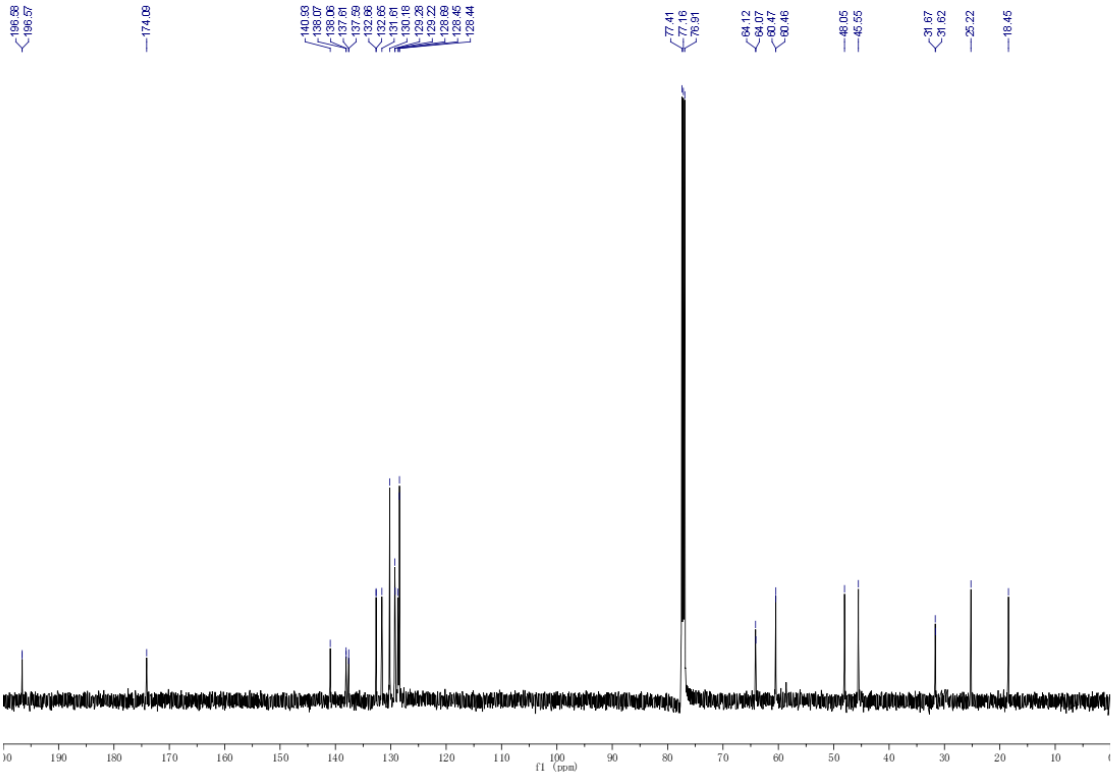
^{1}H NMR of compound **68**（500 MHz, $CDCl_3$）



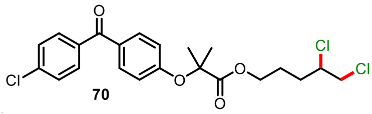
69 (dr = 1:1)

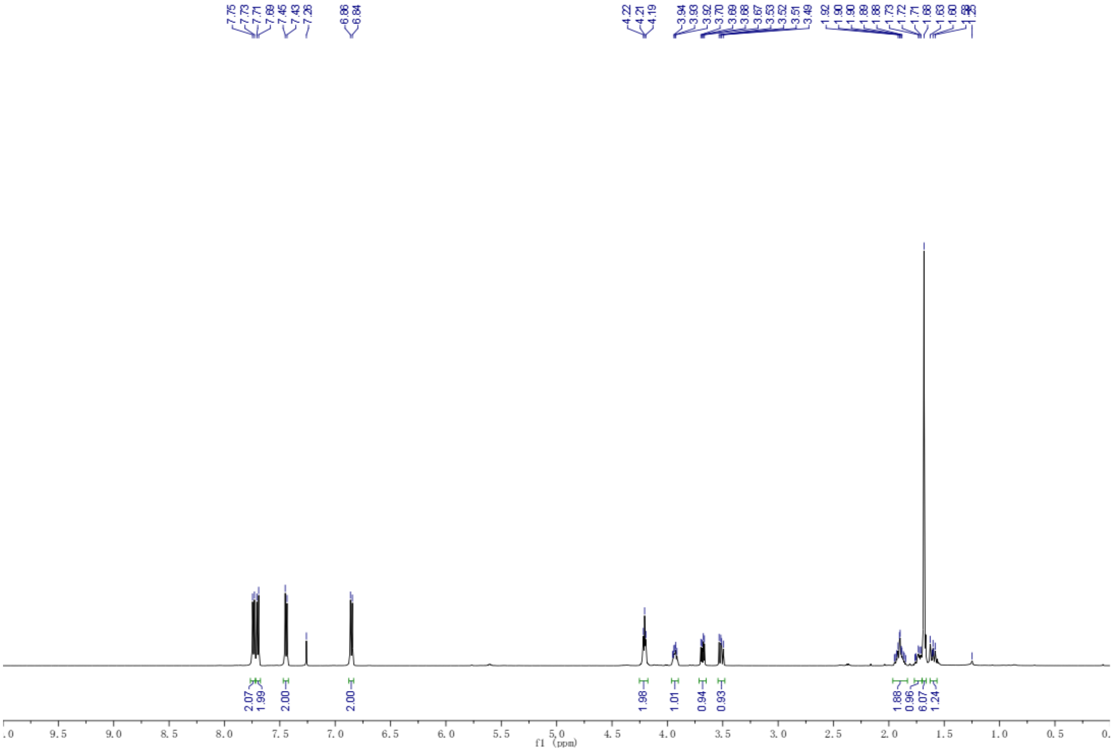


^{1}H NMR of compound **69**（500 MHz, $CDCl_3$）

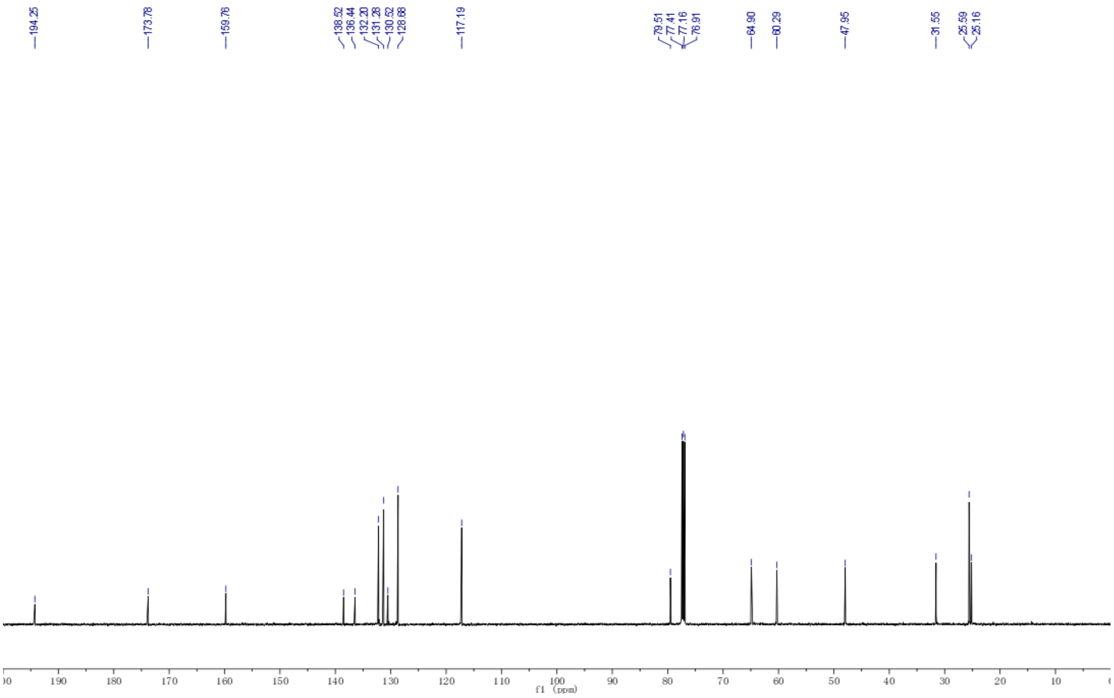


^{13}C NMR of compound **69**（126 MHz, $CDCl_3$）

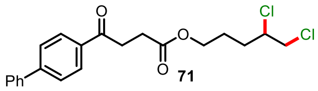




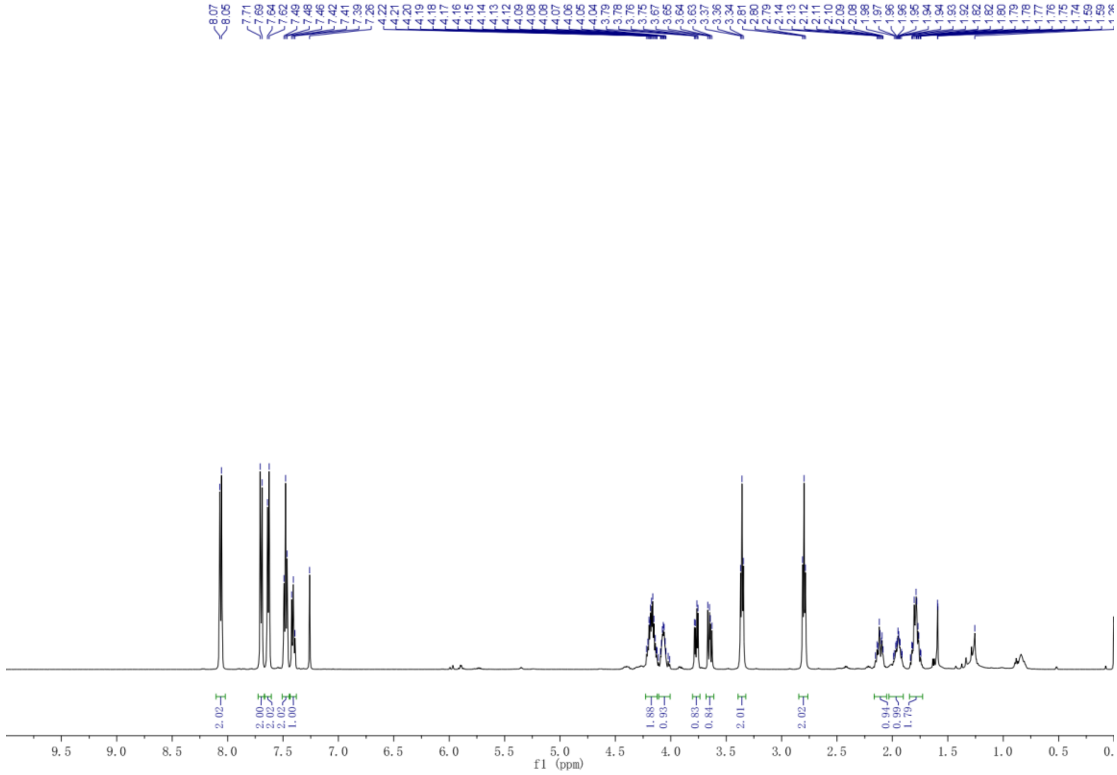
[1]H NMR of compound **70**（500 MHz, $CDCl_3$）



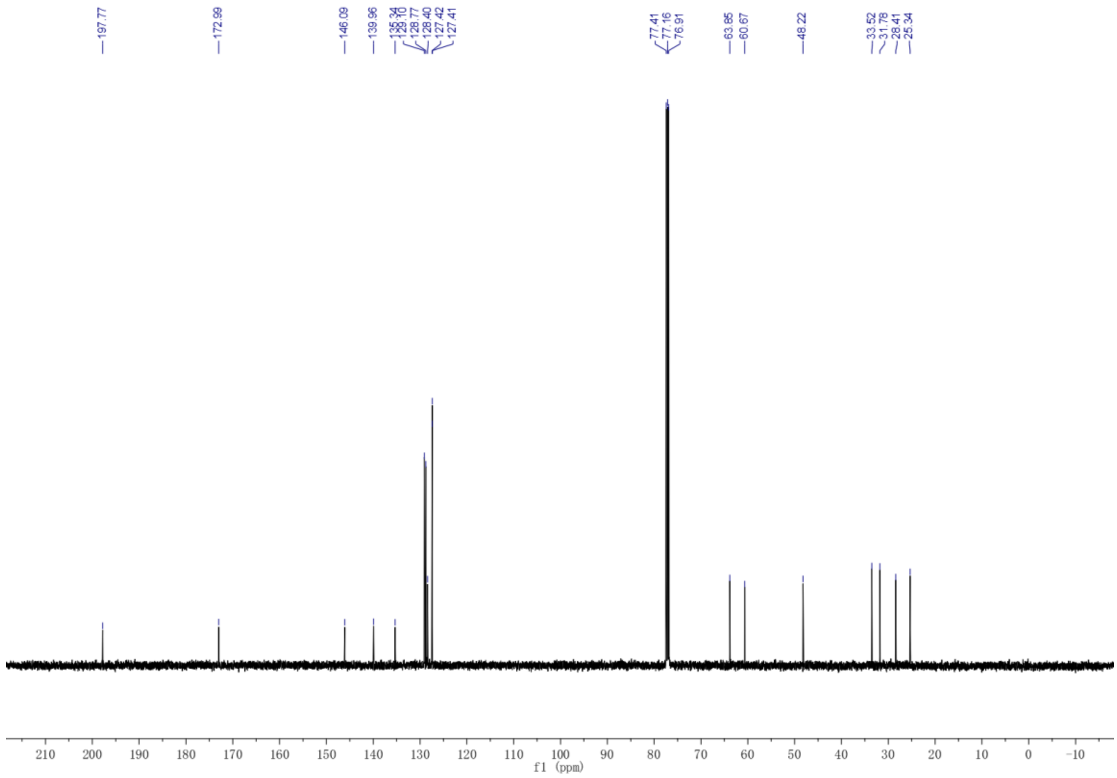
[13]C NMR of compound **70**（126 MHz, $CDCl_3$）



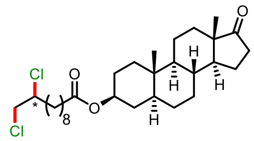
71



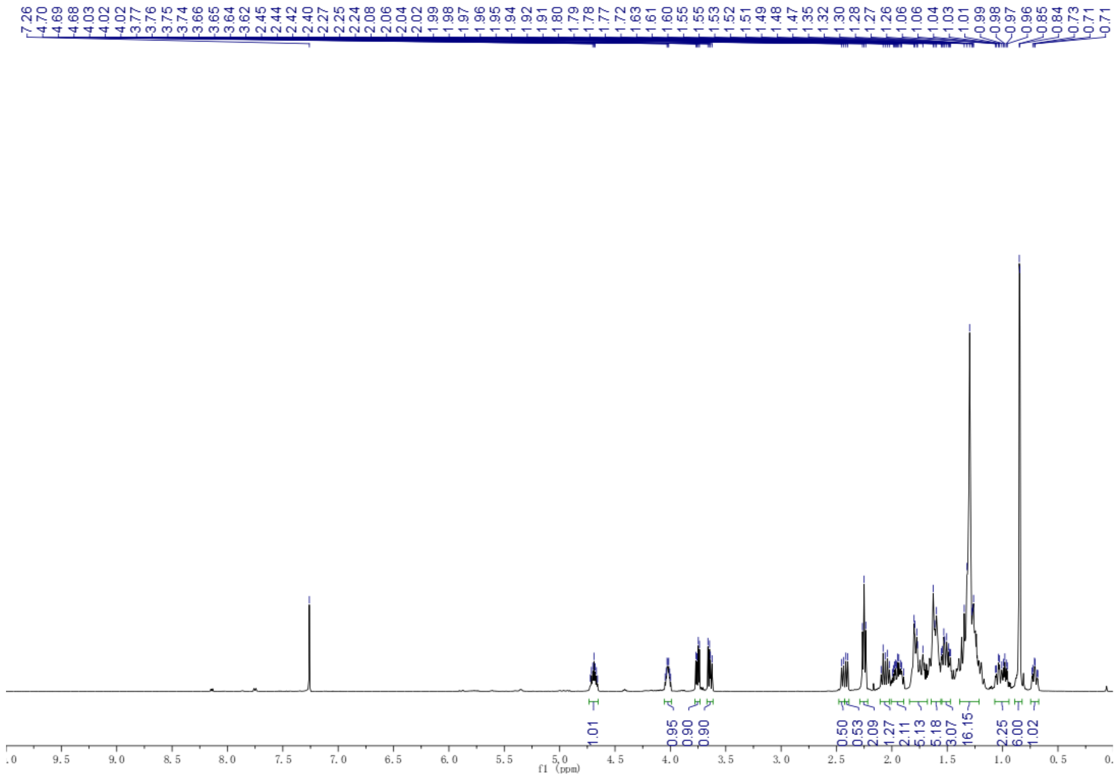
^{1}H NMR of compound **71**（500 MHz, $CDCl_3$）



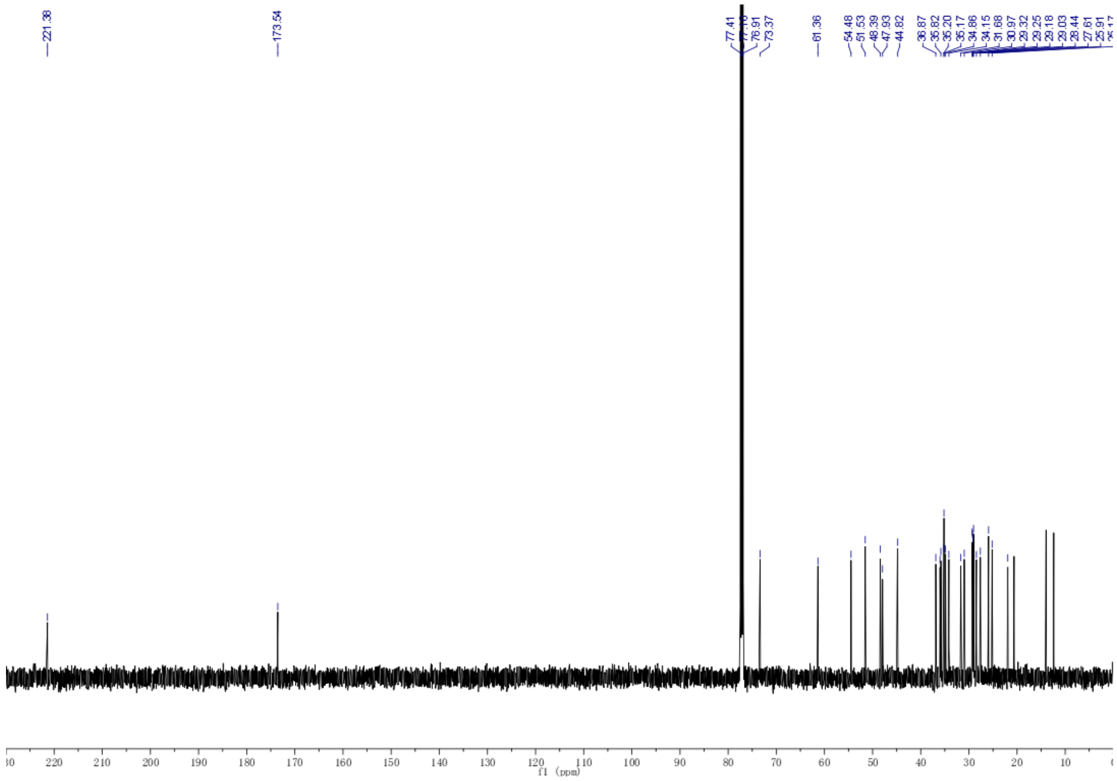
^{13}C NMR of compound **71**（126 MHz, $CDCl_3$）



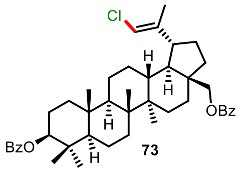
72 (dr = 1:1)



^{1}H NMR of compound **72**（500 MHz, $CDCl_3$）



^{13}C NMR of compound **72**（126 MHz, $CDCl_3$）



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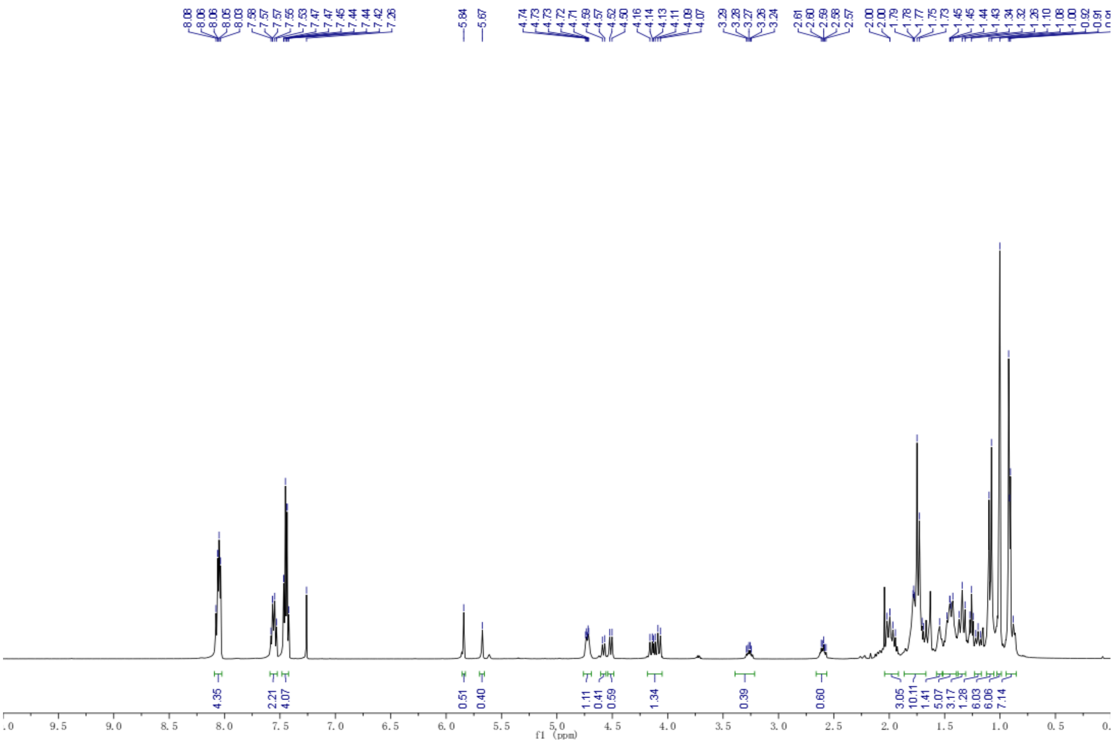
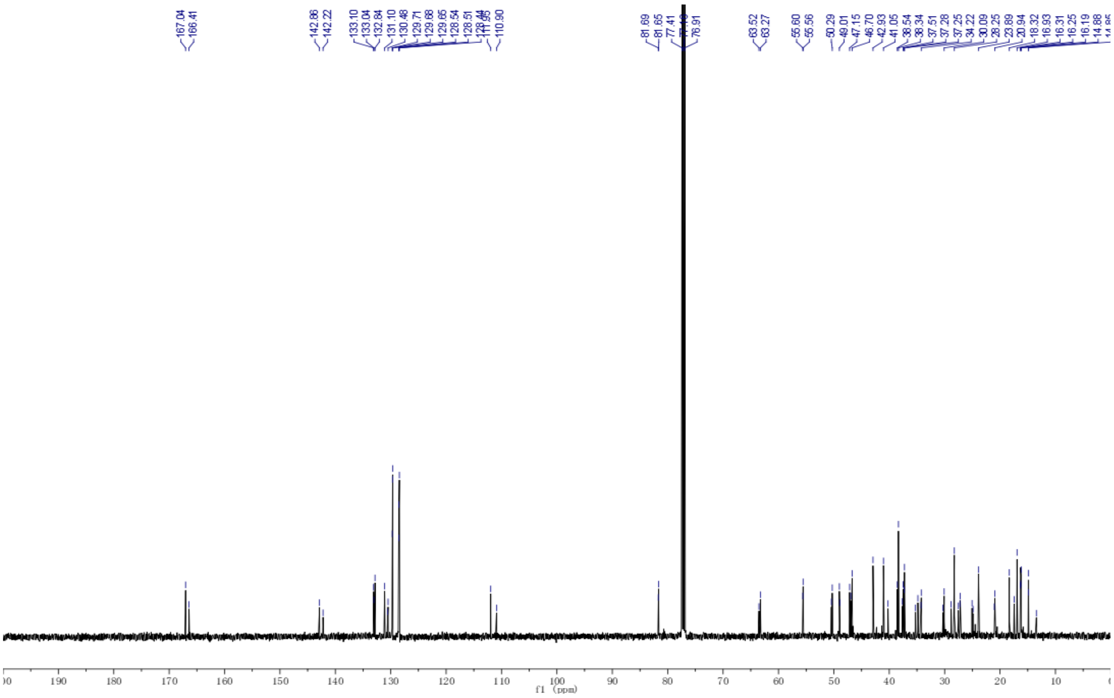
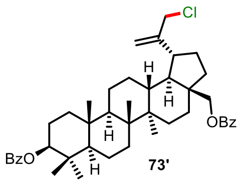
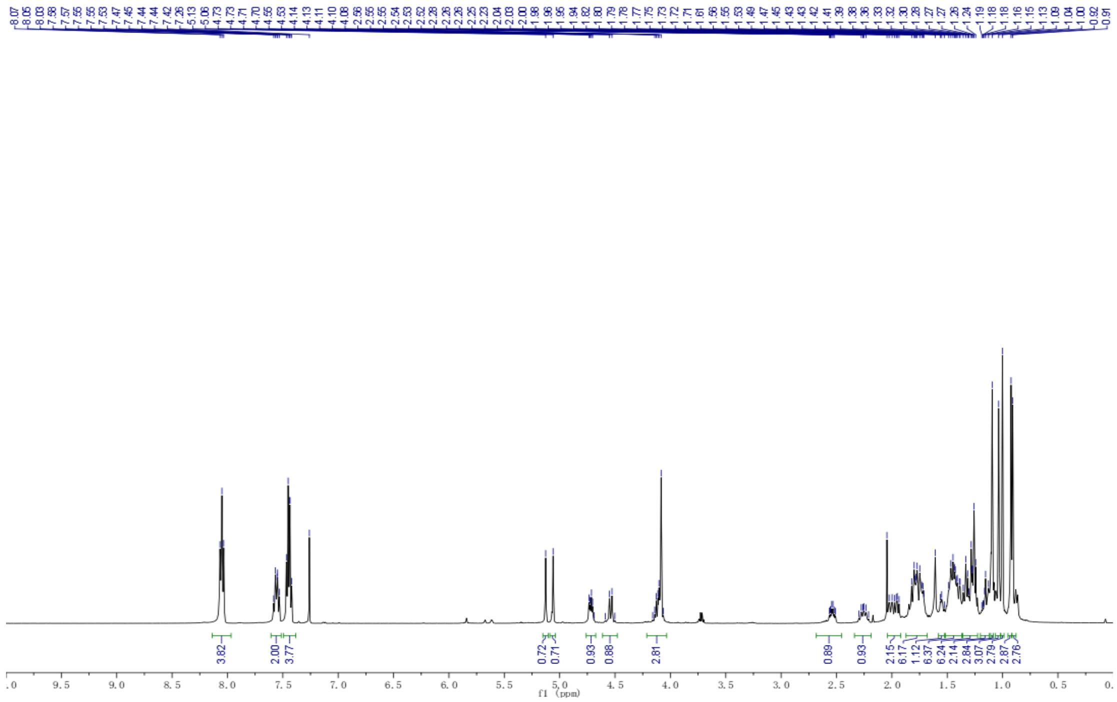


^{1}H NMR of compound **73**（500 MHz, $CDCl_3$）

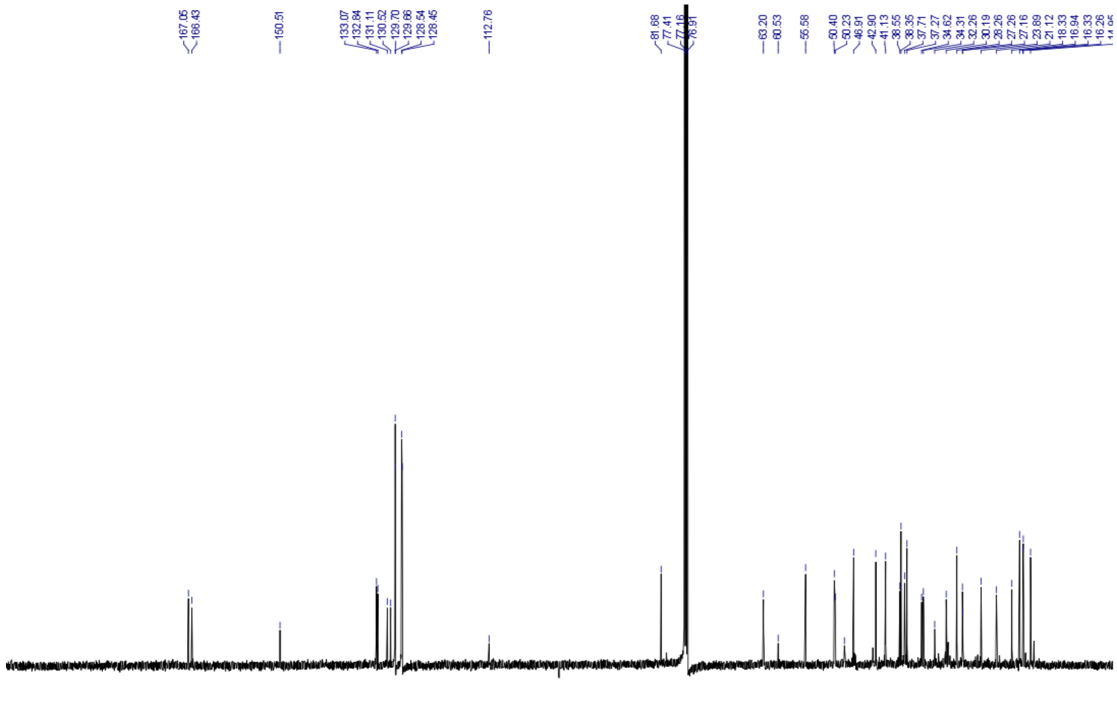


^{13}C NMR of compound **73**（126 MHz, $CDCl_3$）

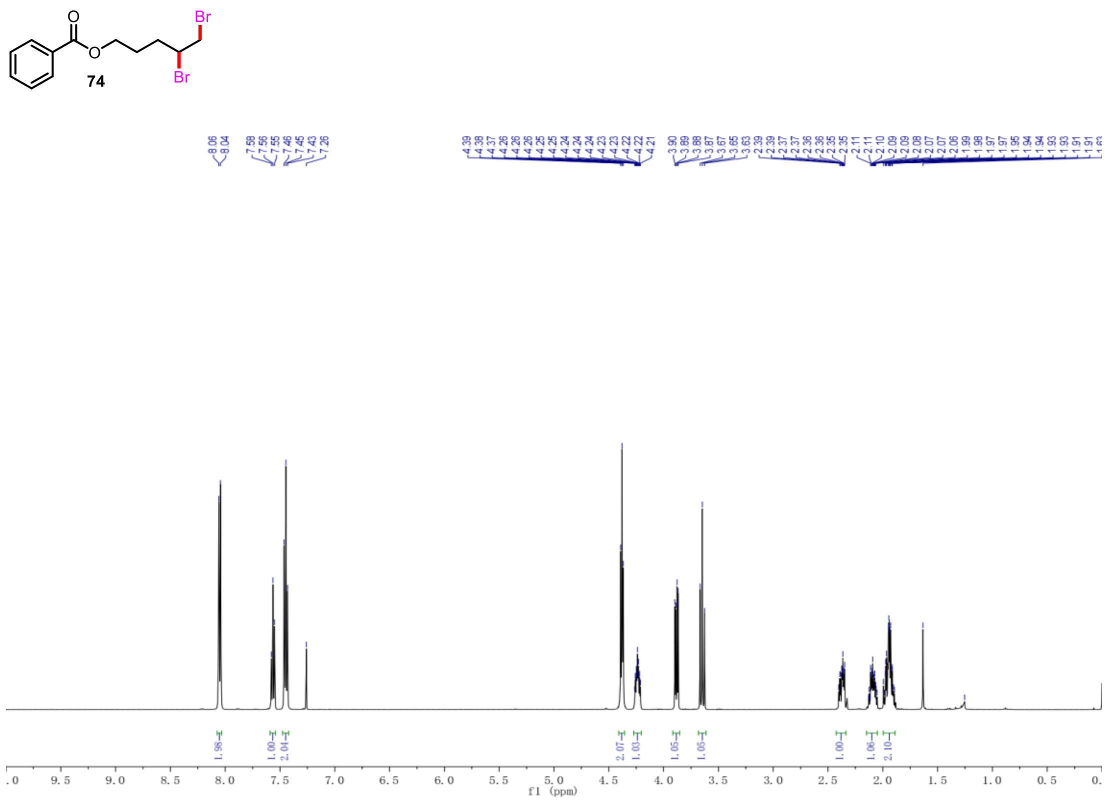




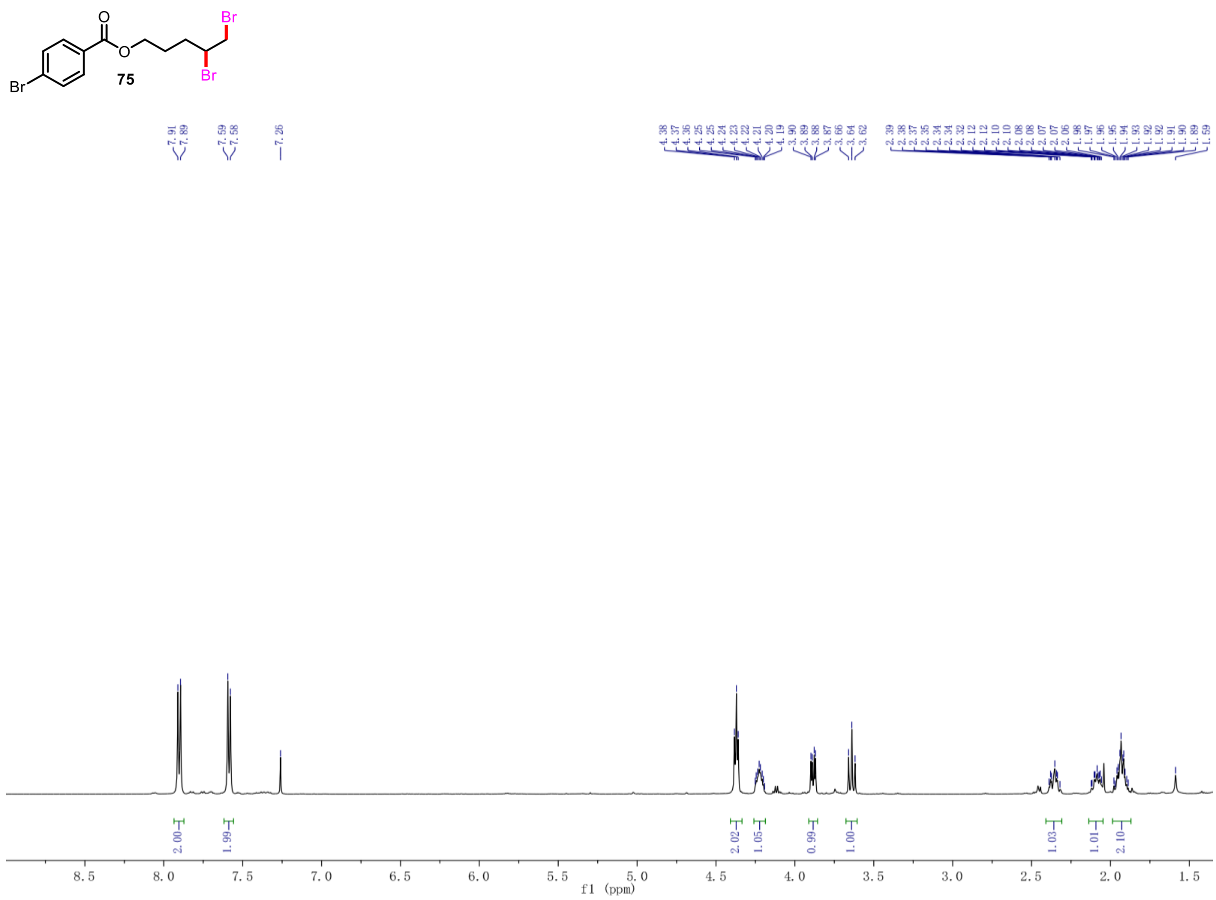
[1]H NMR of compound **73’**（500 MHz, $CDCl_3$）



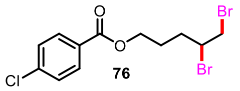
[13]C NMR of compound **73’**（126 MHz, $CDCl_3$）



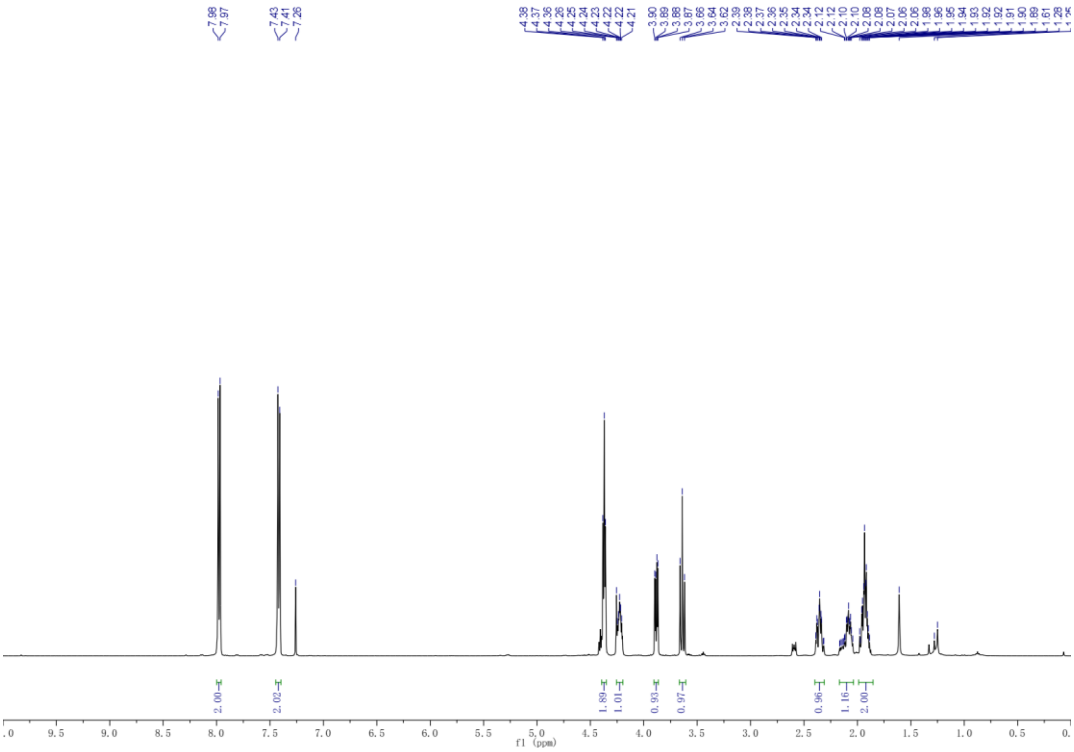
^{1}H NMR of compound **74**（500 MHz, $CDCl_3$）



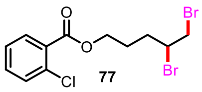
^{1}H NMR of compound **75**（500 MHz, $CDCl_3$）



76



^{1}H NMR of compound **76**（500 MHz, $CDCl_3$）



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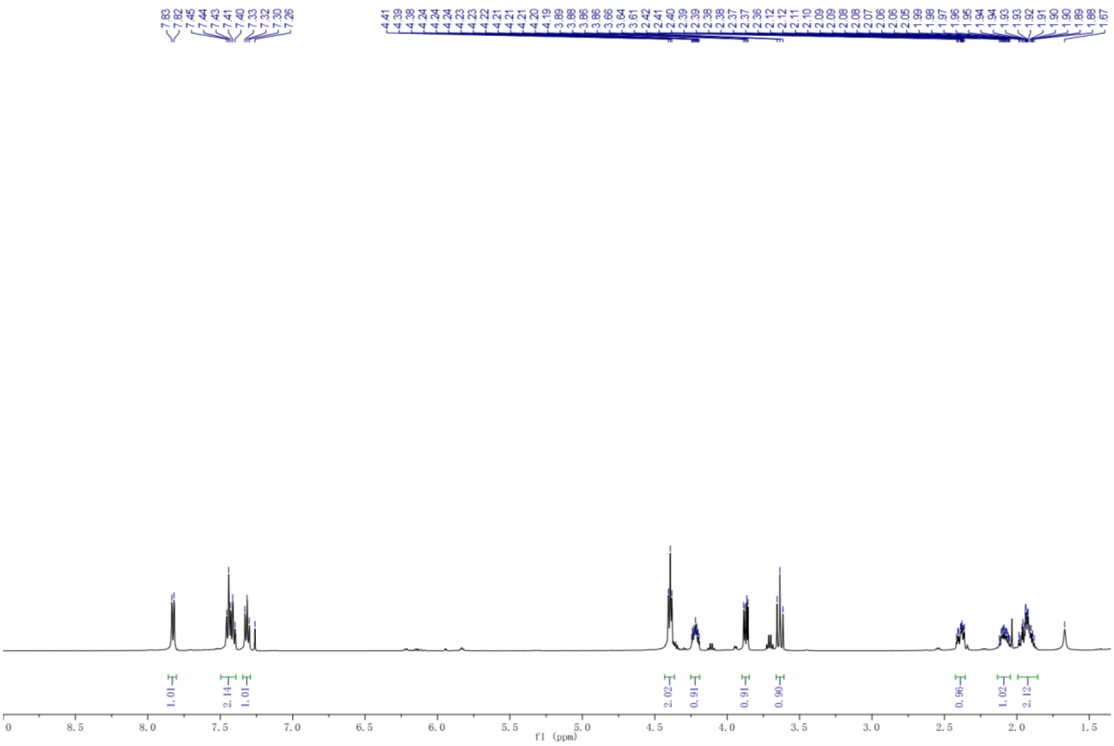
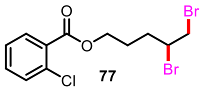
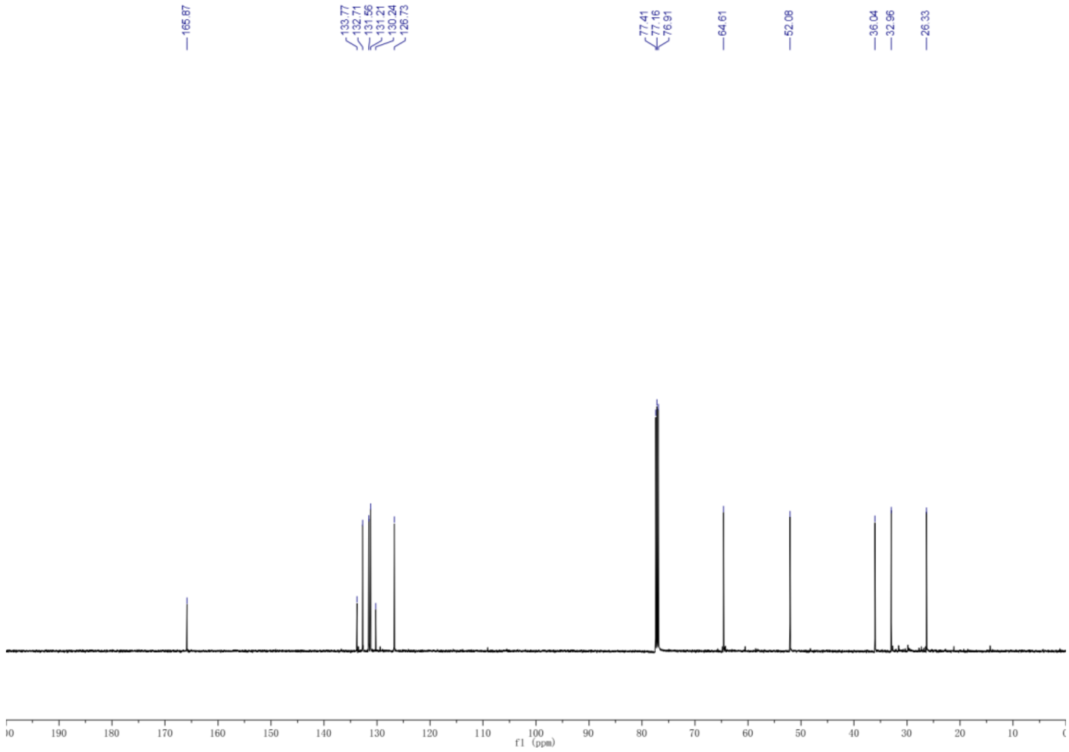
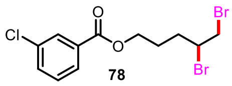


^{1}H NMR of compound **77**（500 MHz, $CDCl_3$）

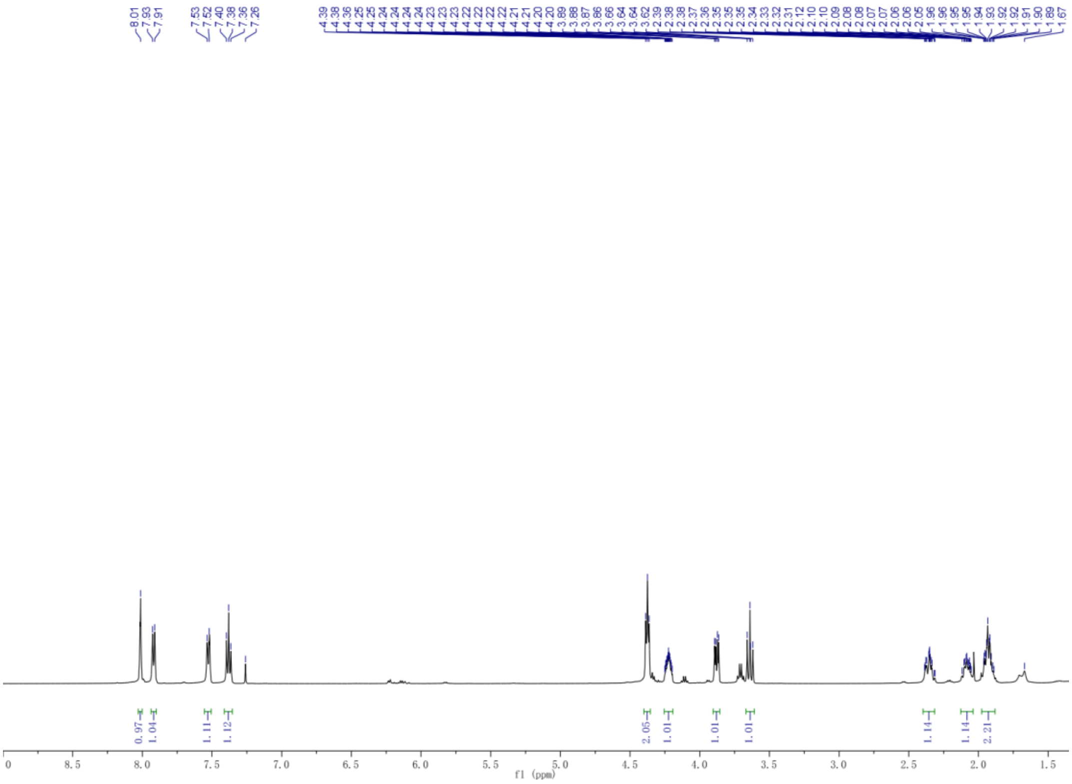




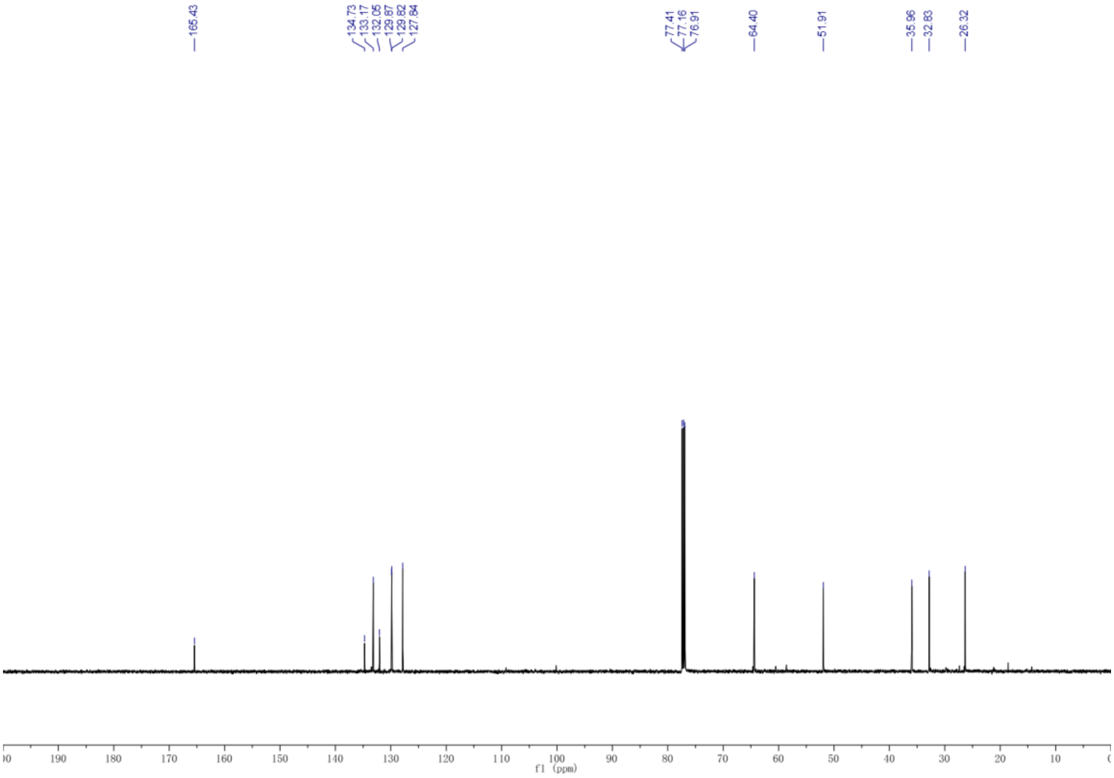
^{13}C NMR of compound **77**（126 MHz, $CDCl_3$）



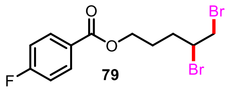
78



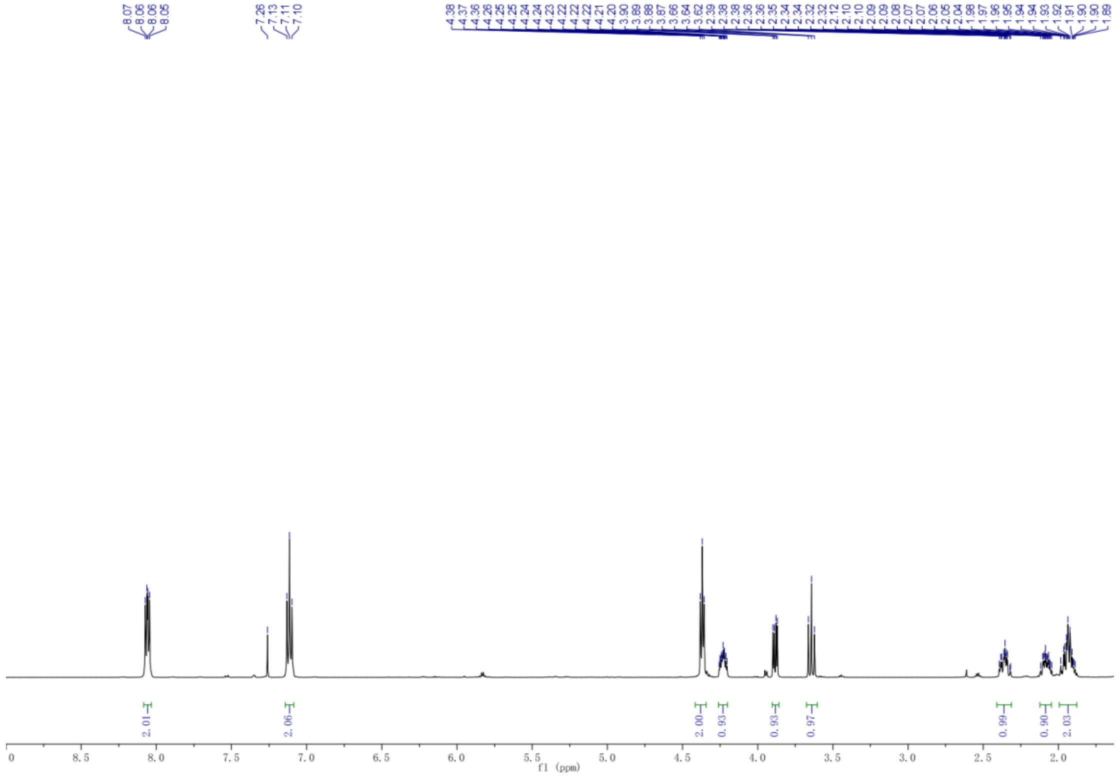
^{1}H NMR of compound **78**（500 MHz, $CDCl_3$）



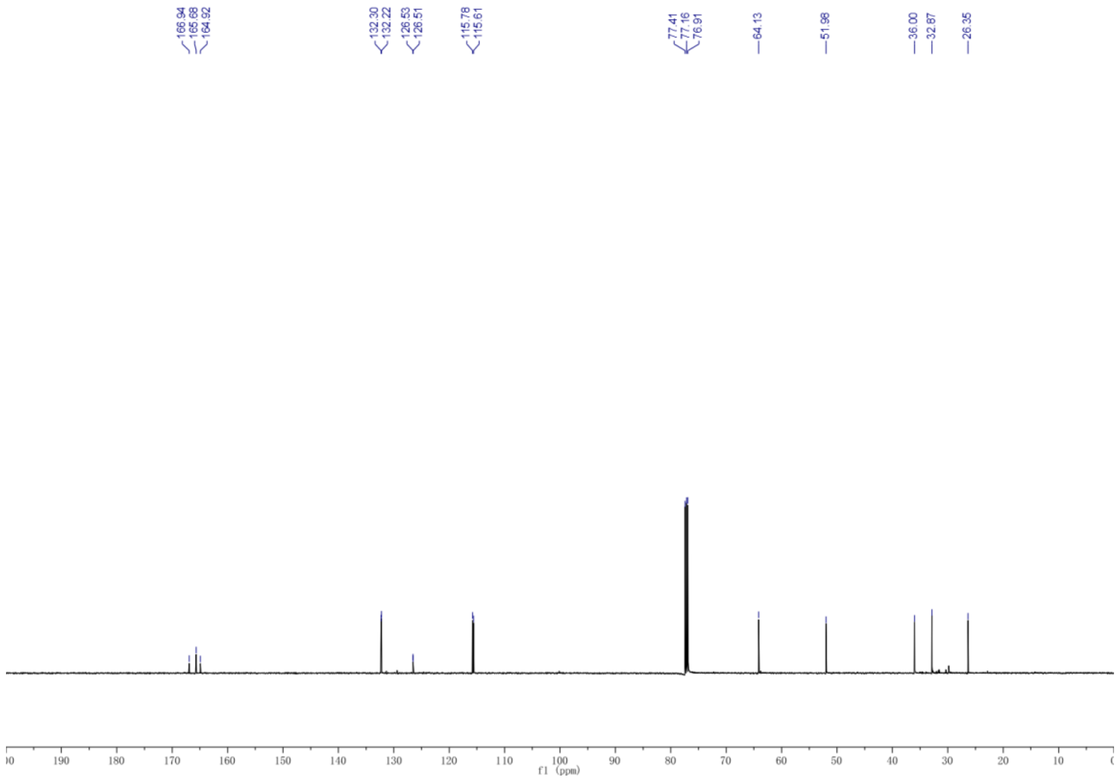
^{13}C NMR of compound **78**（126 MHz, $CDCl_3$）



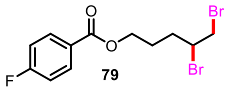
79

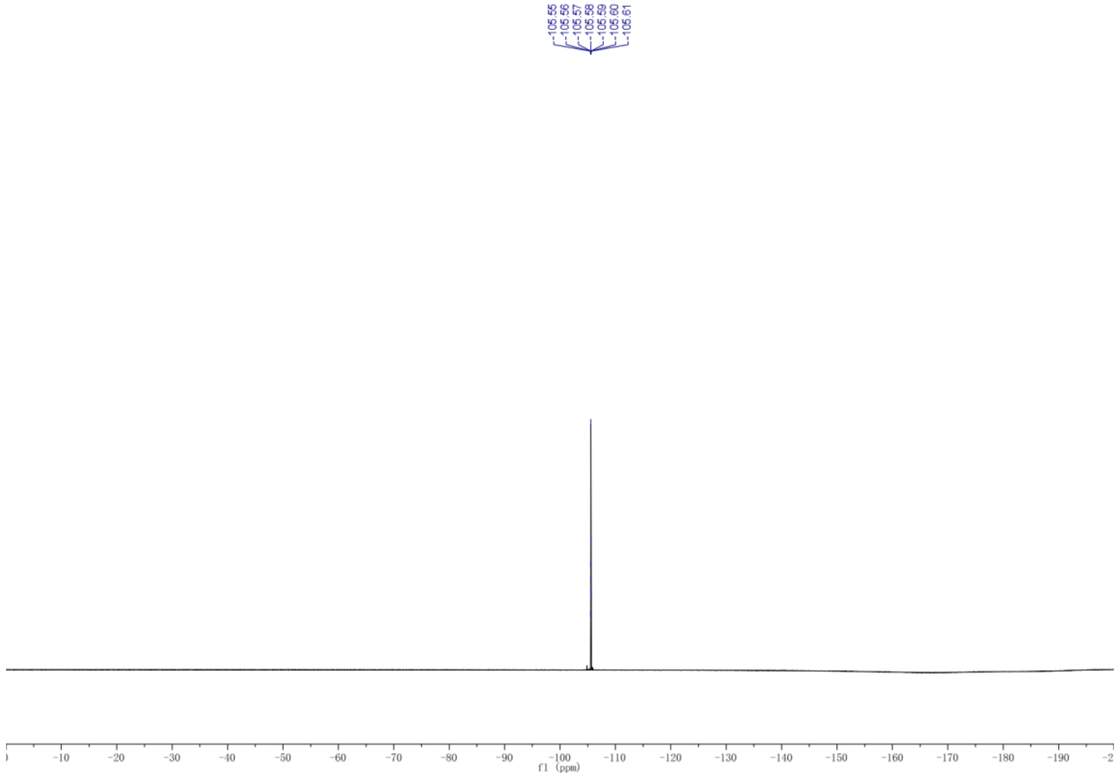


[1]H NMR of compound **79**（500 MHz, $CDCl_3$）

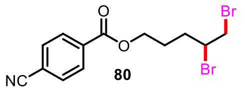


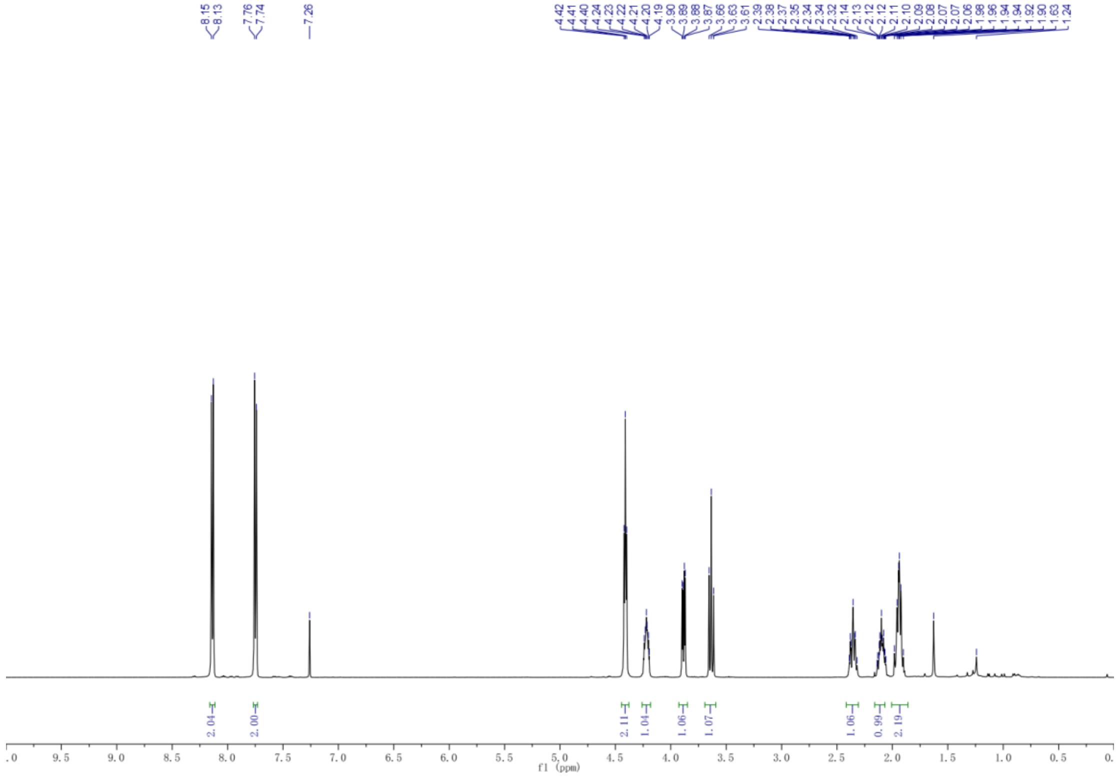
[13]C NMR of compound **79**（126 MHz, $CDCl_3$）



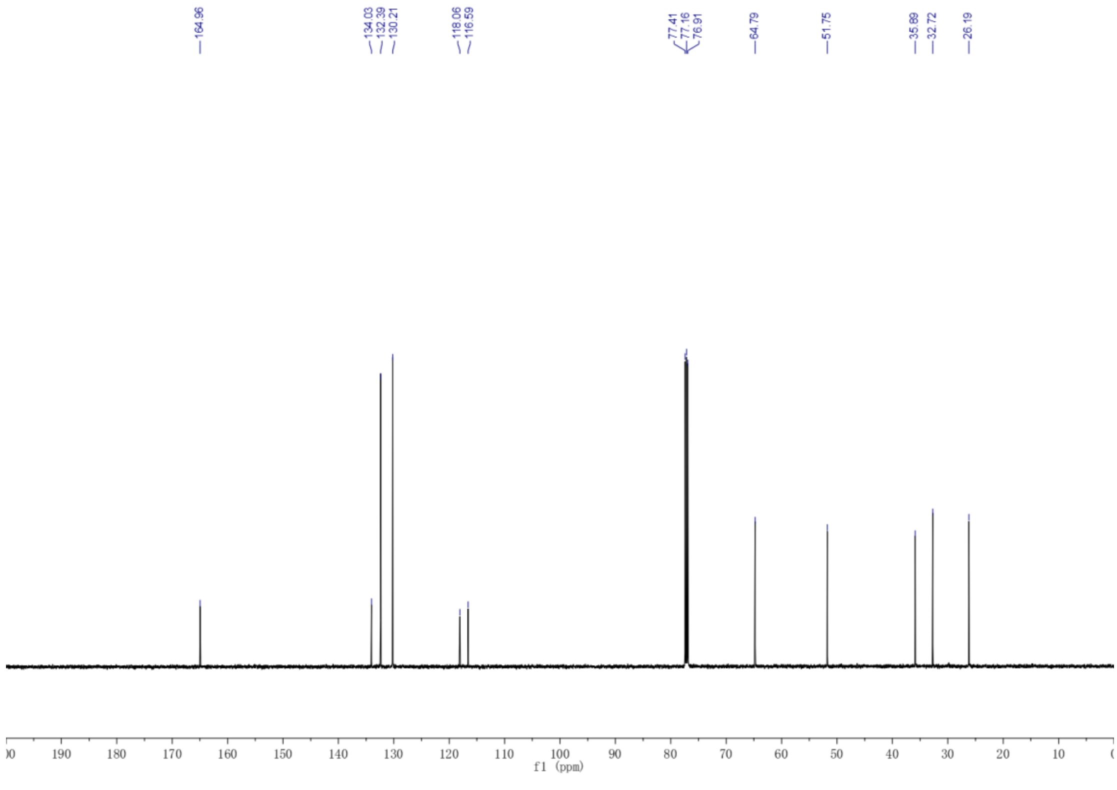


^{19}F NMR of compound **79**（471 MHz, $CDCl_3$）

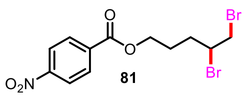




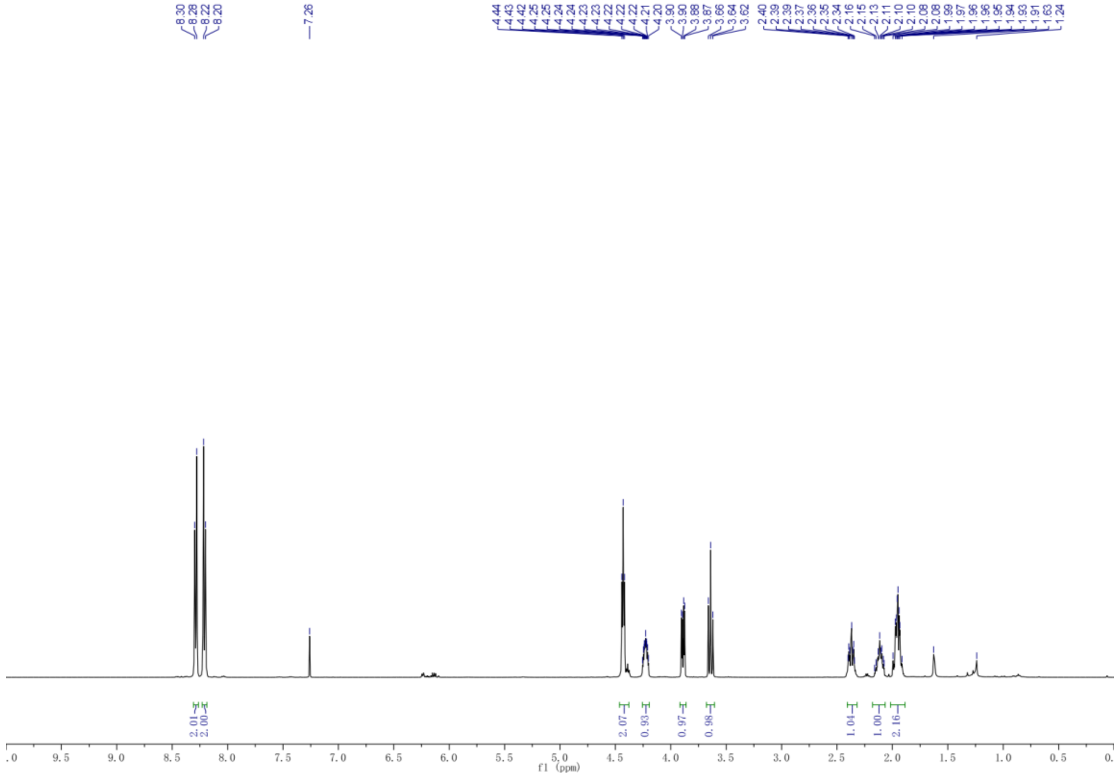
^{1}H NMR of compound **80**（500 MHz, $CDCl_3$）



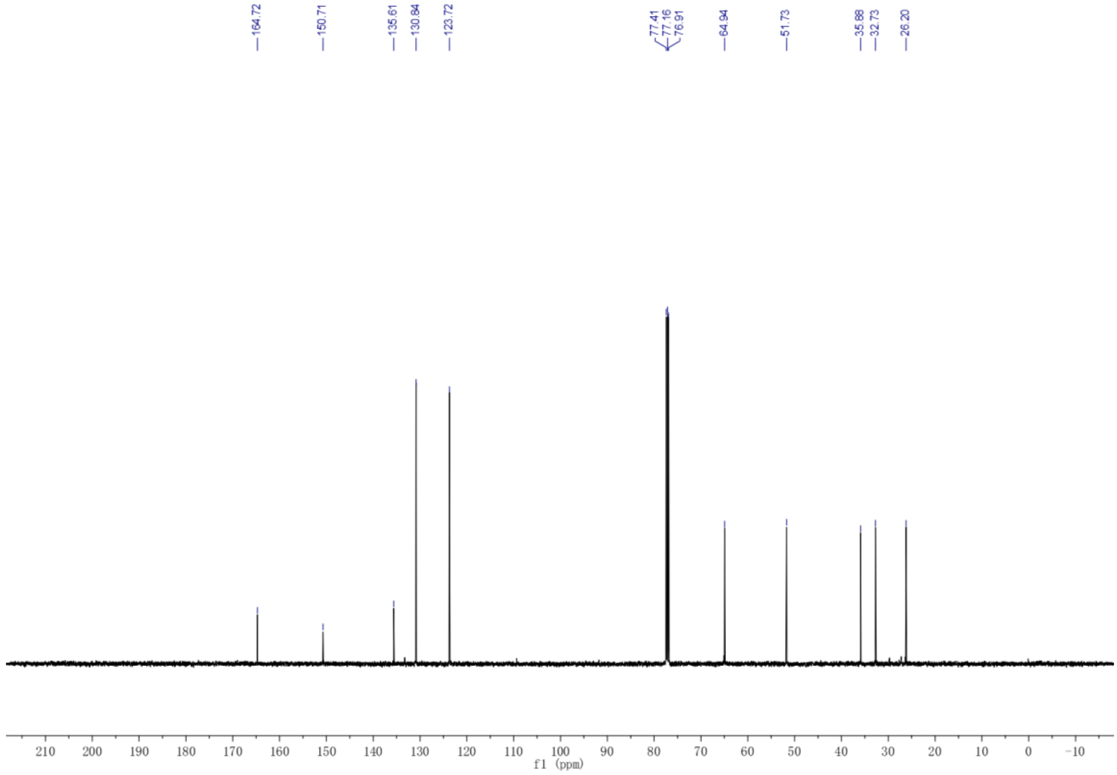
^{13}C NMR of compound **80**（126 MHz, $CDCl_3$）



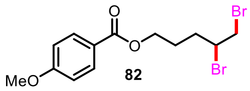
81

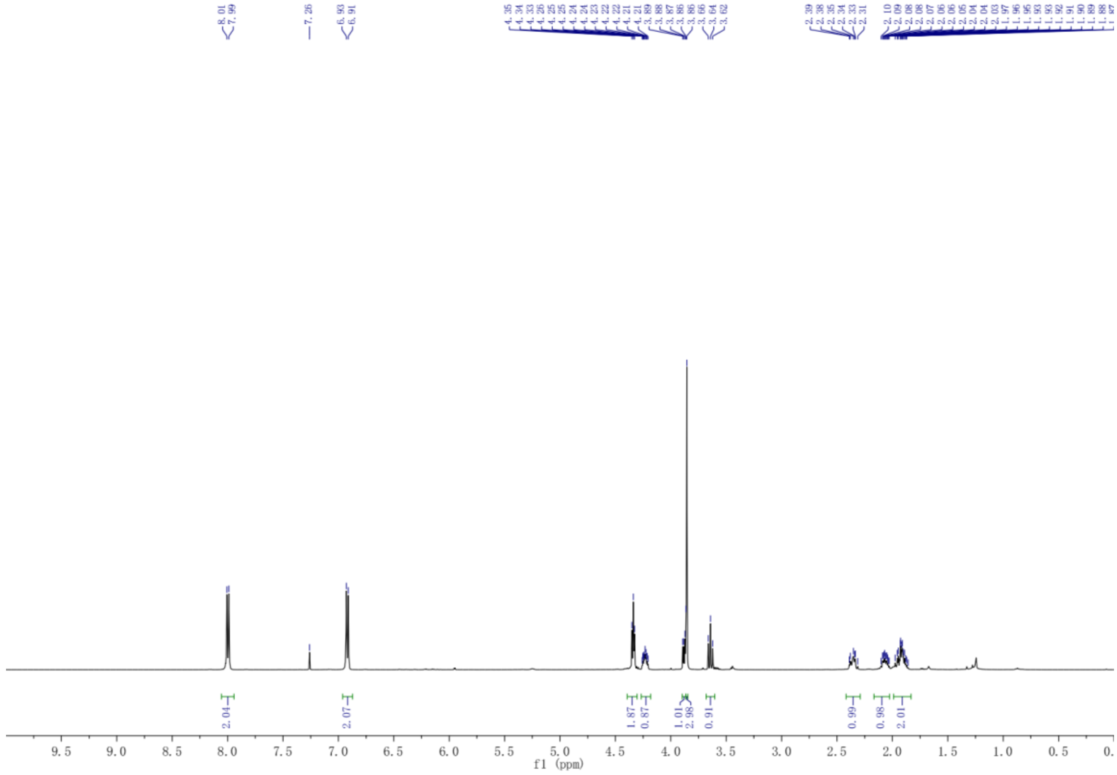


^{1}H NMR of compound **81**（500 MHz, $CDCl_3$）

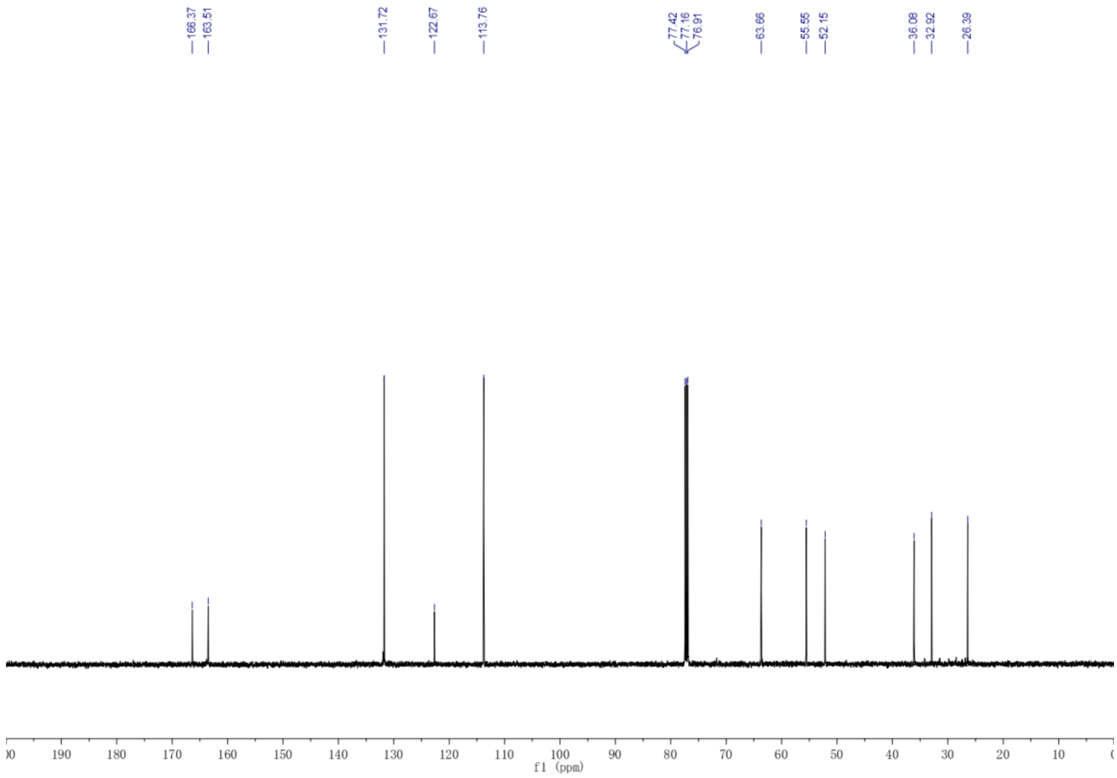


^{13}C NMR of compound **81**（126 MHz, $CDCl_3$）

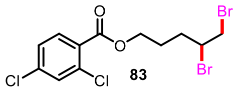




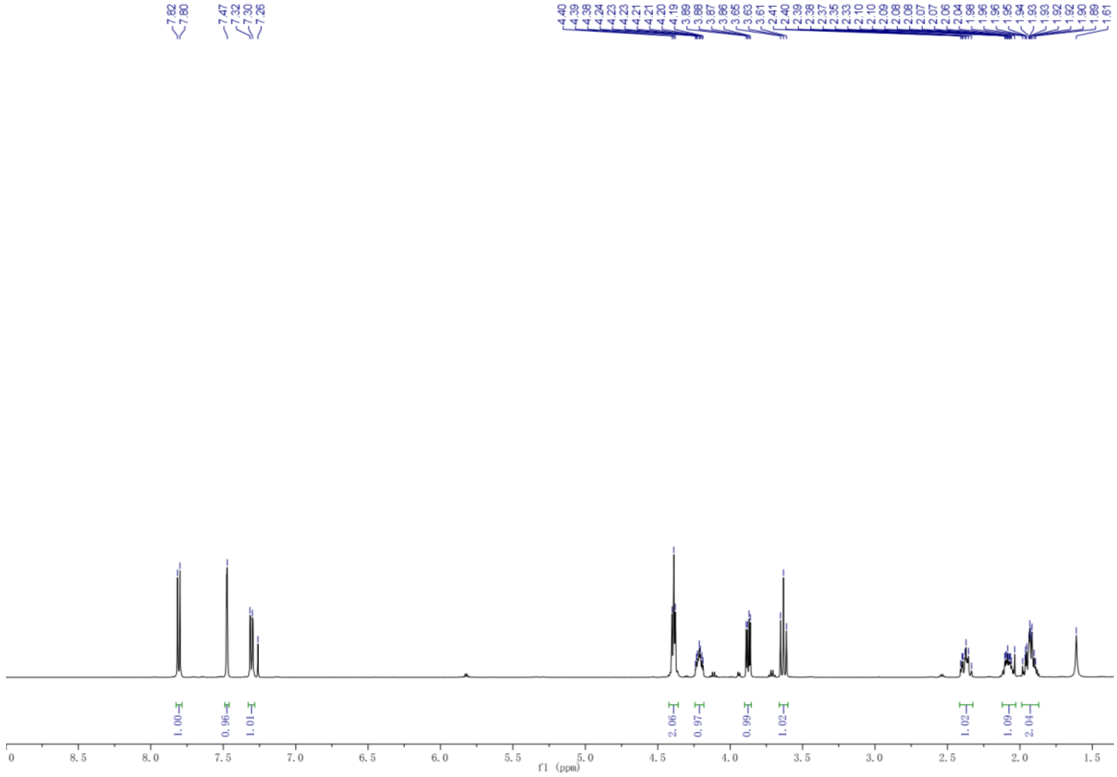
^{1}H NMR of compound **82**（500 MHz, CDCl$_3$）



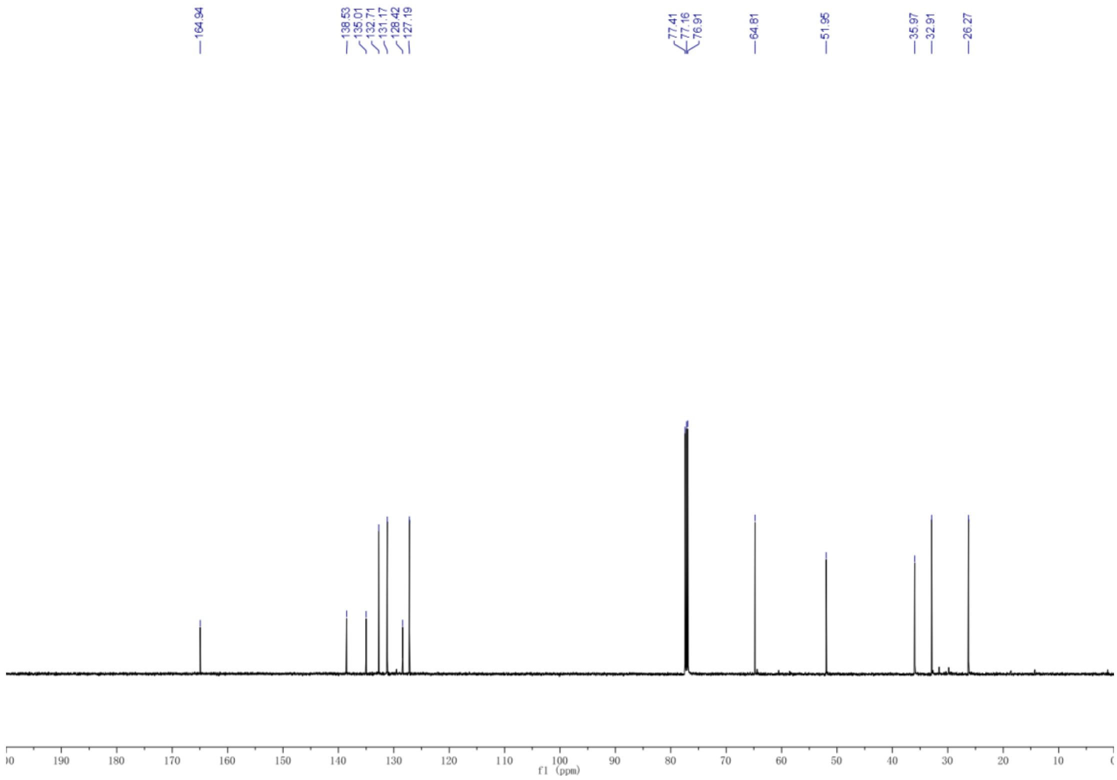
^{13}C NMR of compound **82**（126 MHz, CDCl$_3$）



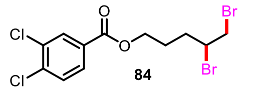
83



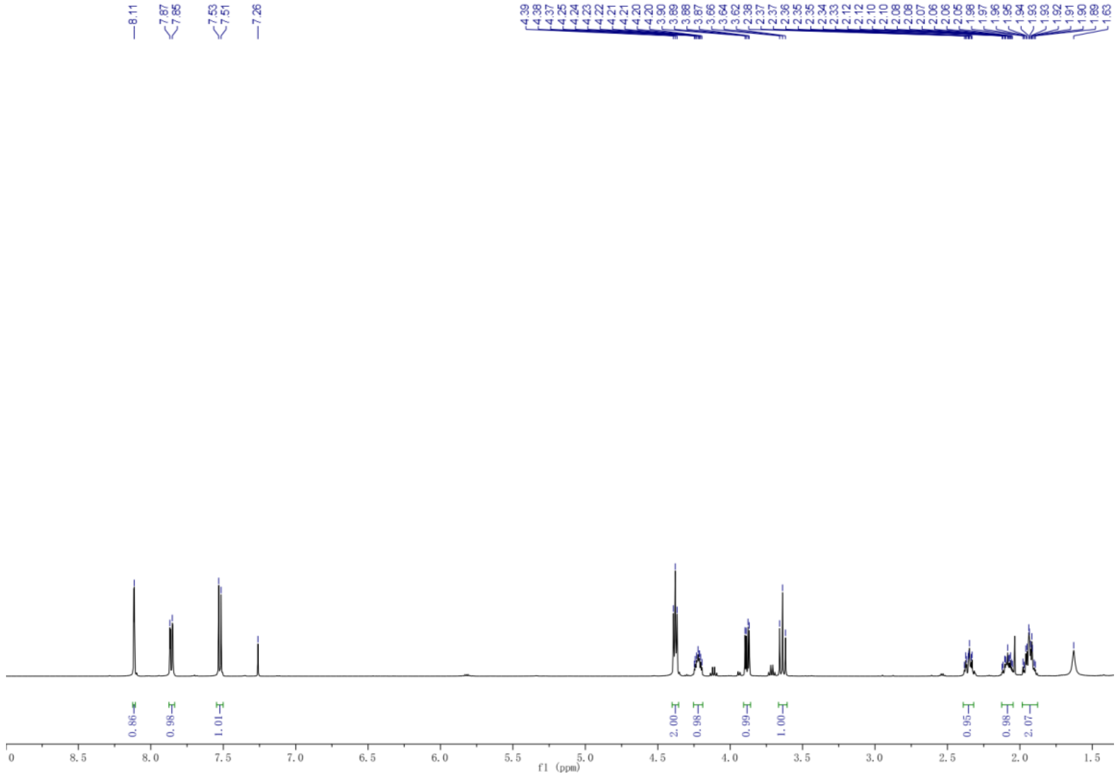
[1]H NMR of compound **83**（500 MHz, $CDCl_3$）



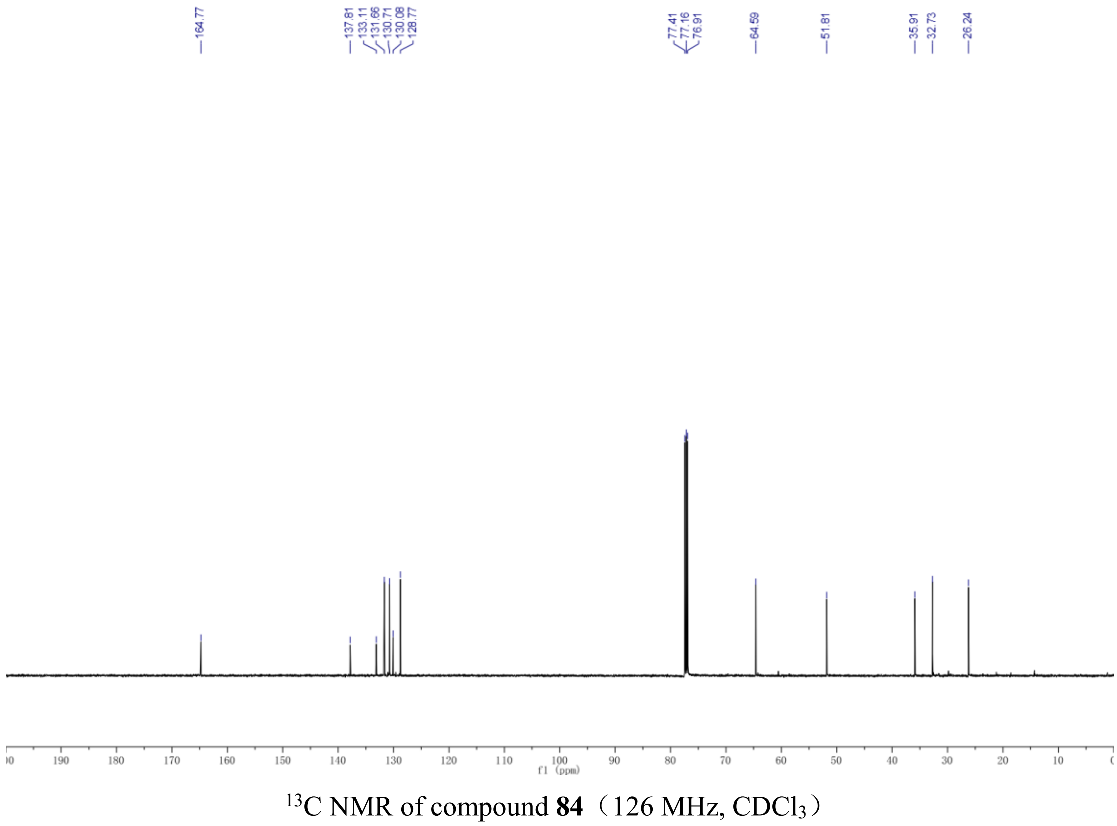
[13]C NMR of compound **83**（126 MHz, $CDCl_3$）



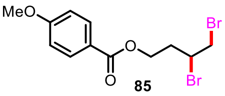
84



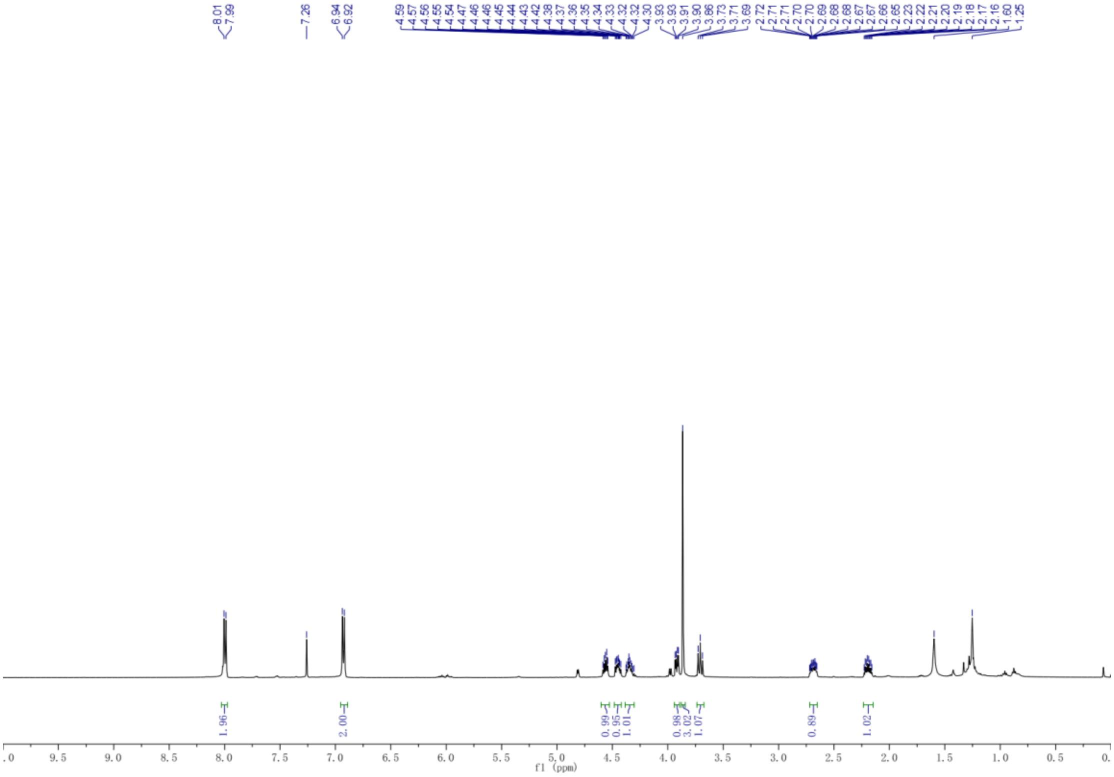
^{1}H NMR of compound **84**（500 MHz, $CDCl_3$）



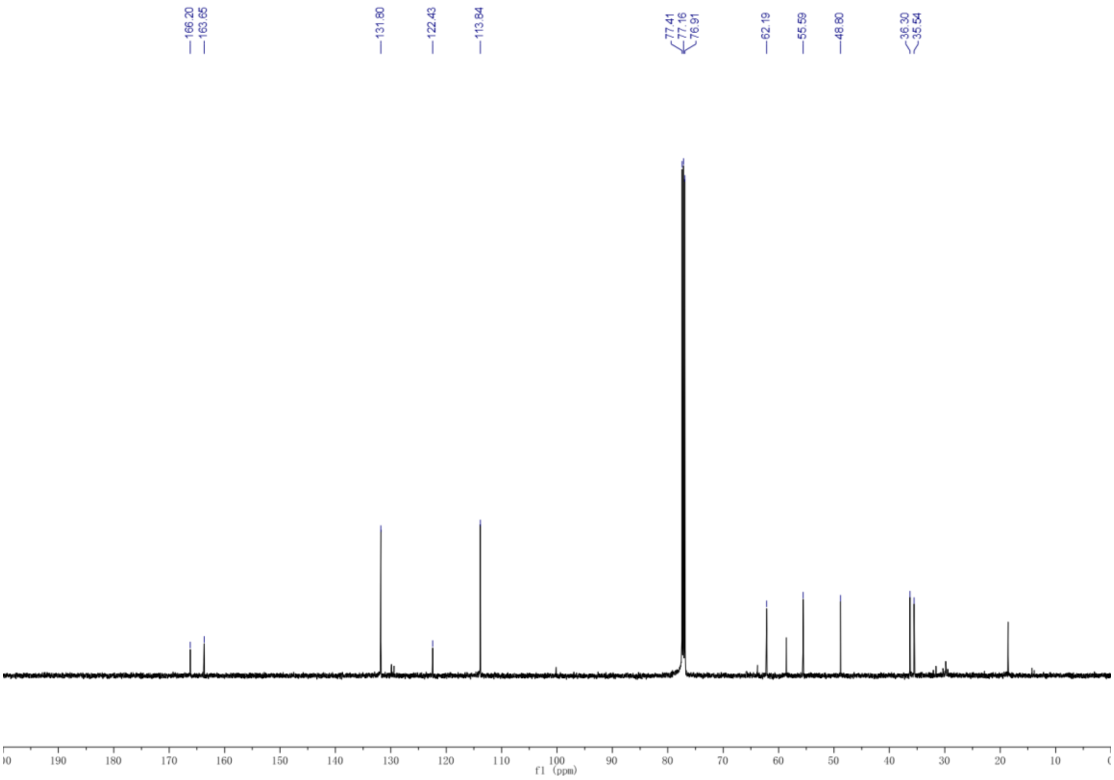
^{13}C NMR of compound **84**（126 MHz, $CDCl_3$）



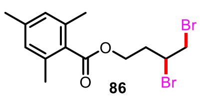
85

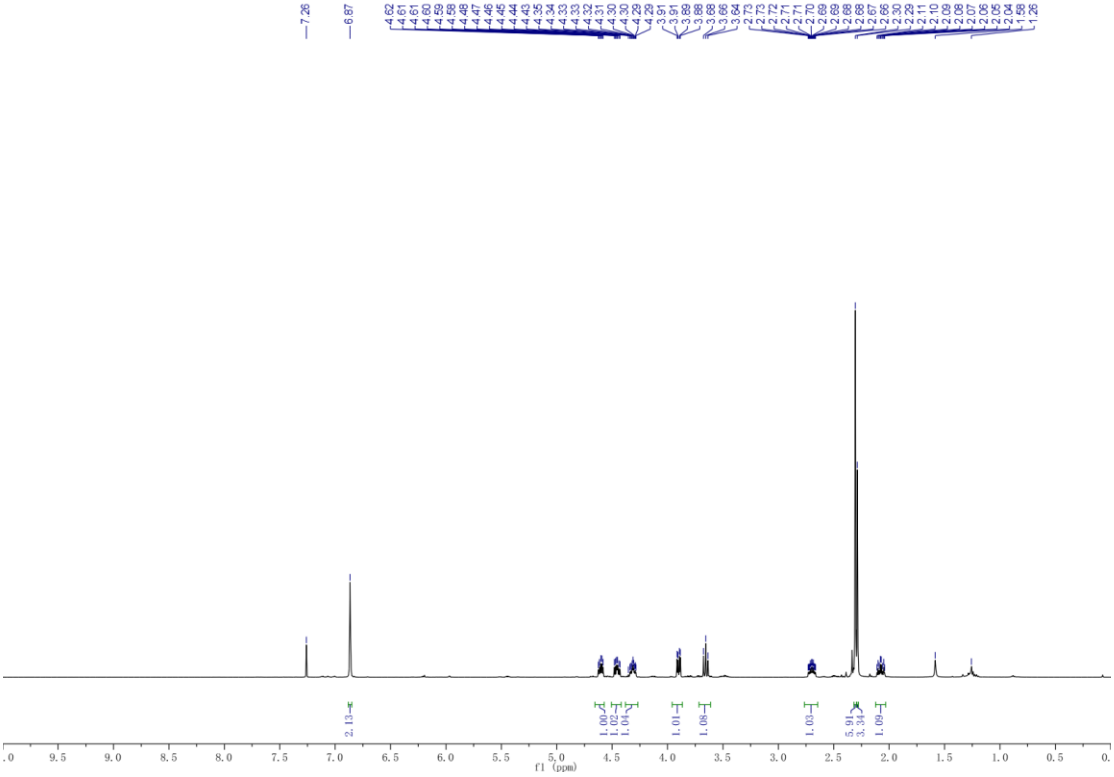


^{1}H NMR of compound **85**（500 MHz, $CDCl_3$）

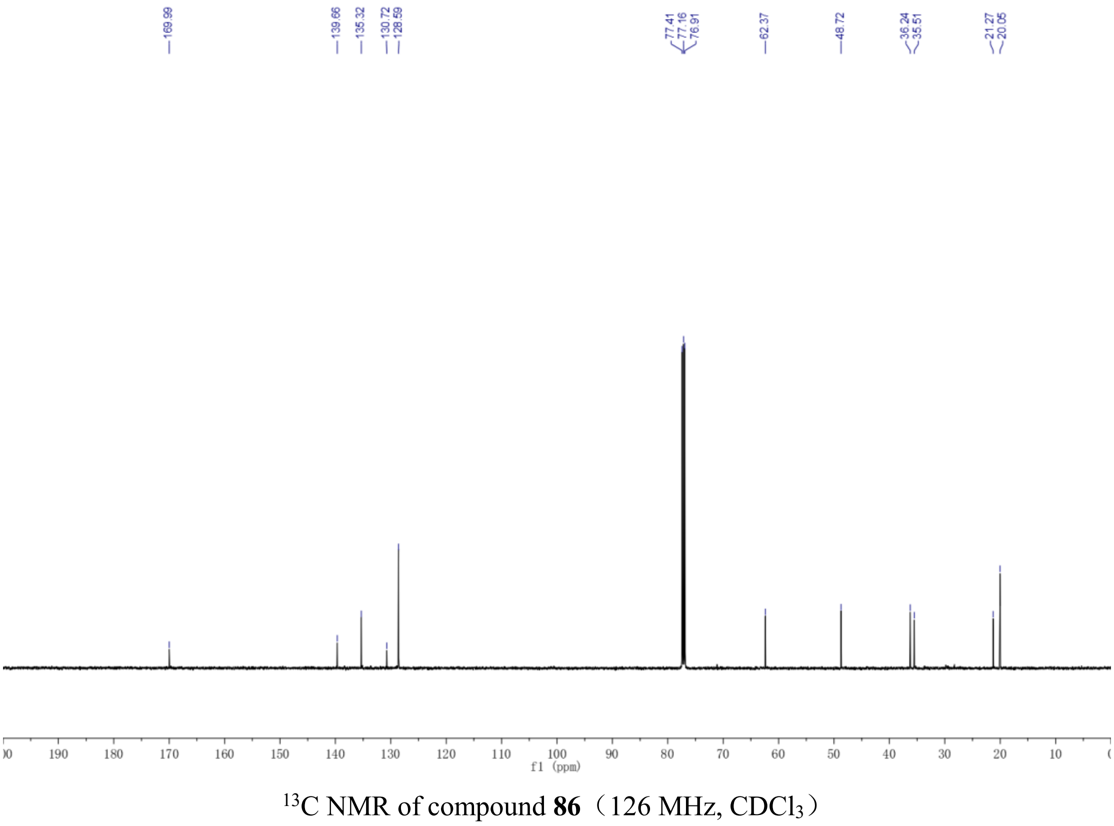


^{13}C NMR of compound **85**（126 MHz, $CDCl_3$）

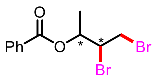




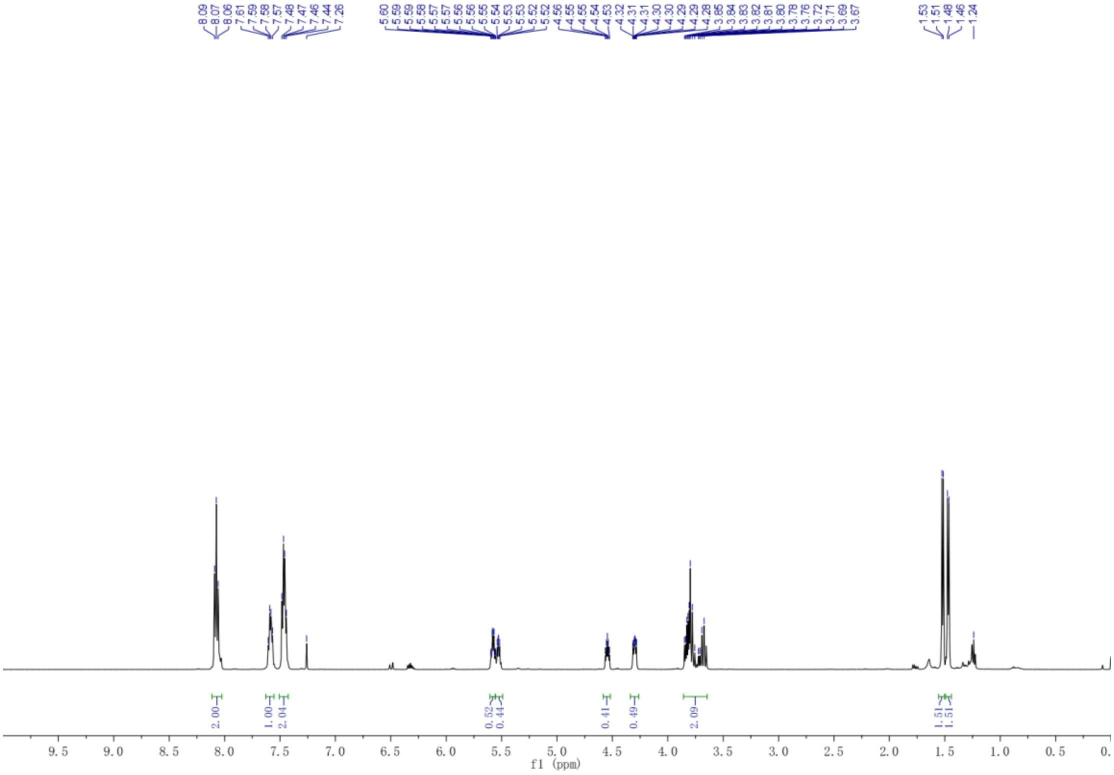
[1]H NMR of compound **86**（500 MHz, $CDCl_3$）



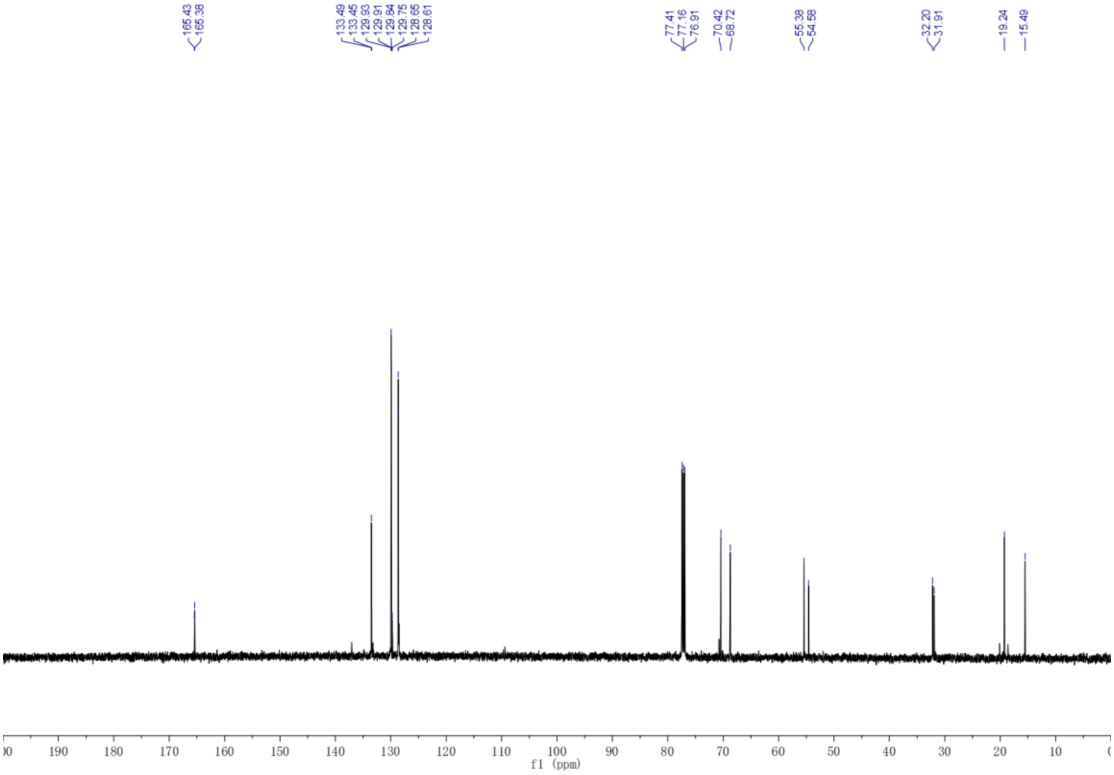
[13]C NMR of compound **86**（126 MHz, $CDCl_3$）



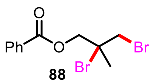
87 (dr = 1:1)

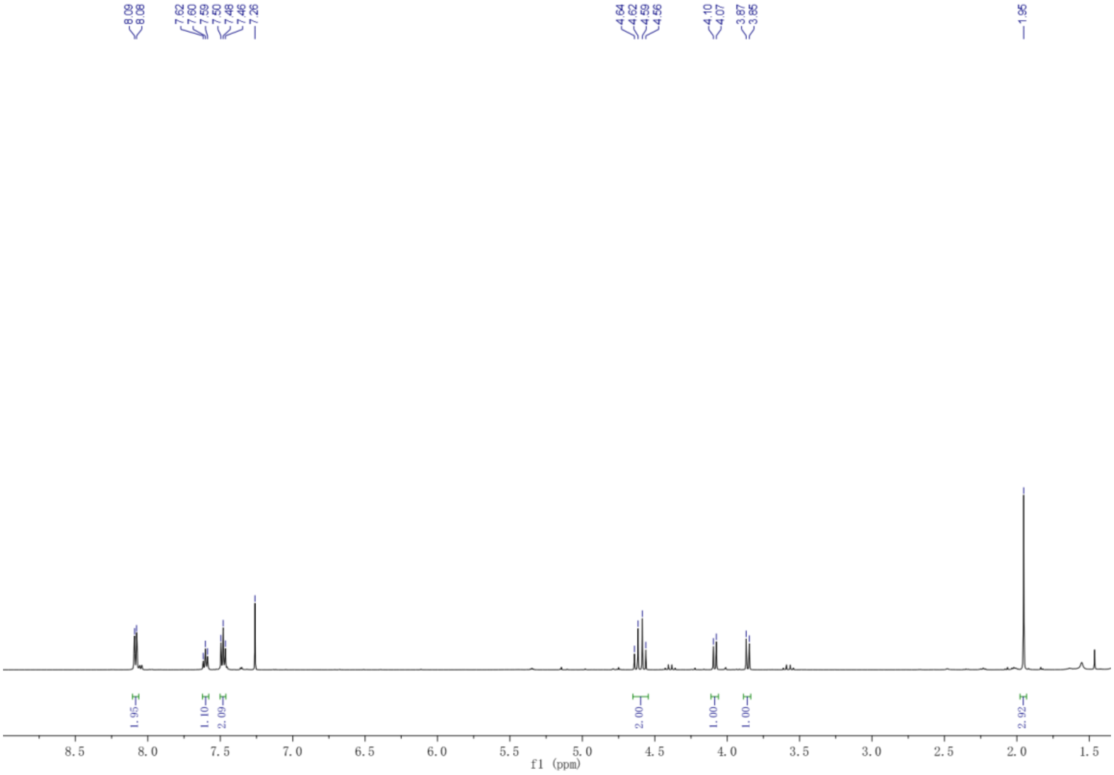


^{1}H NMR of compound **87**（500 MHz, $CDCl_3$）

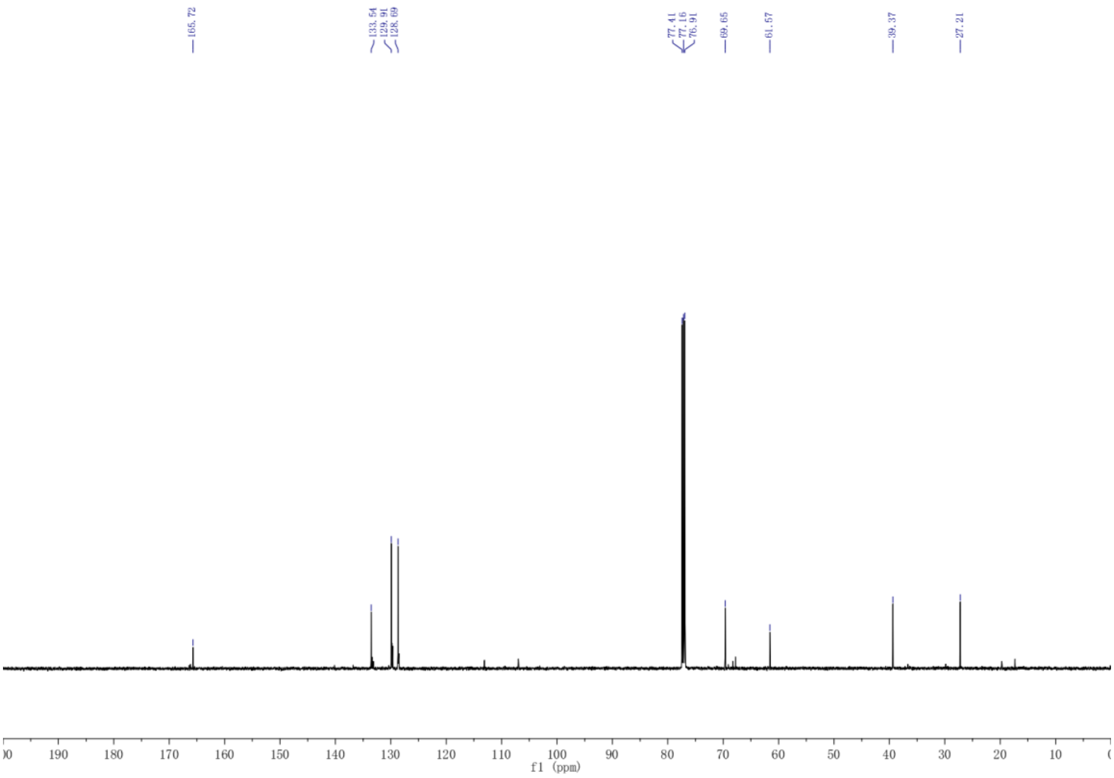


^{13}C NMR of compound **87**（126 MHz, $CDCl_3$）

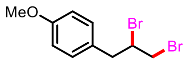


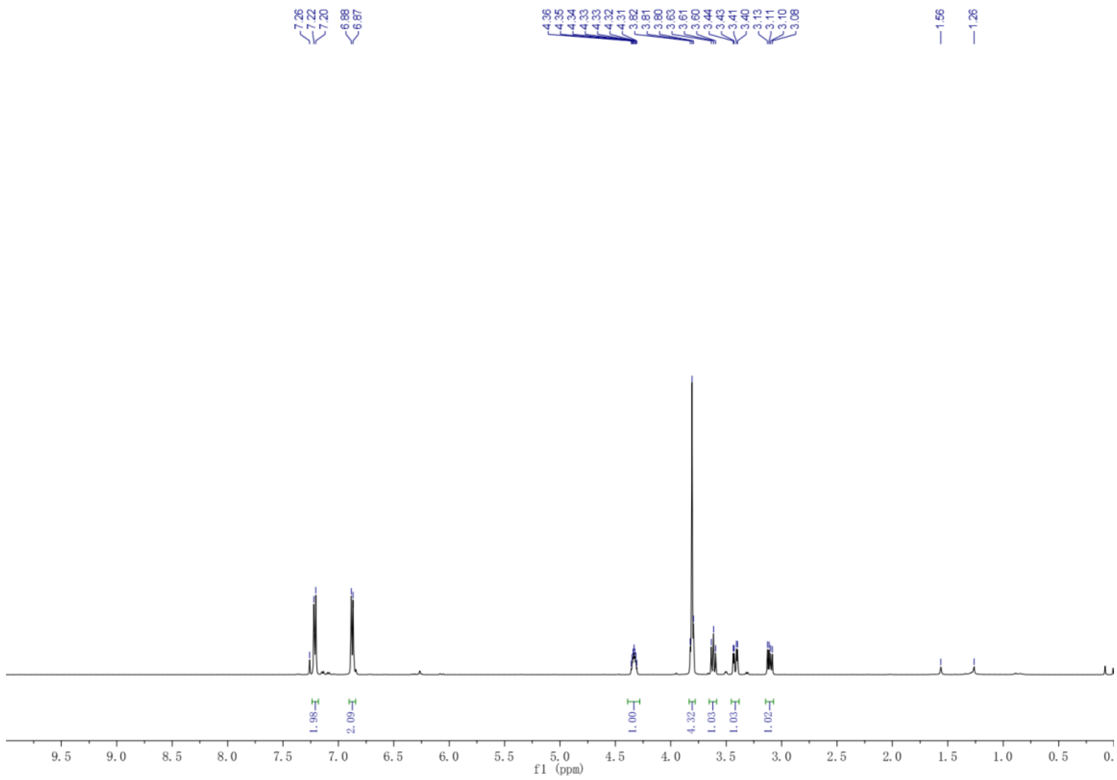


[1]H NMR of compound **88**（500 MHz, $CDCl_3$）

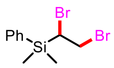


[13]C NMR of compound **88**（126 MHz, $CDCl_3$）

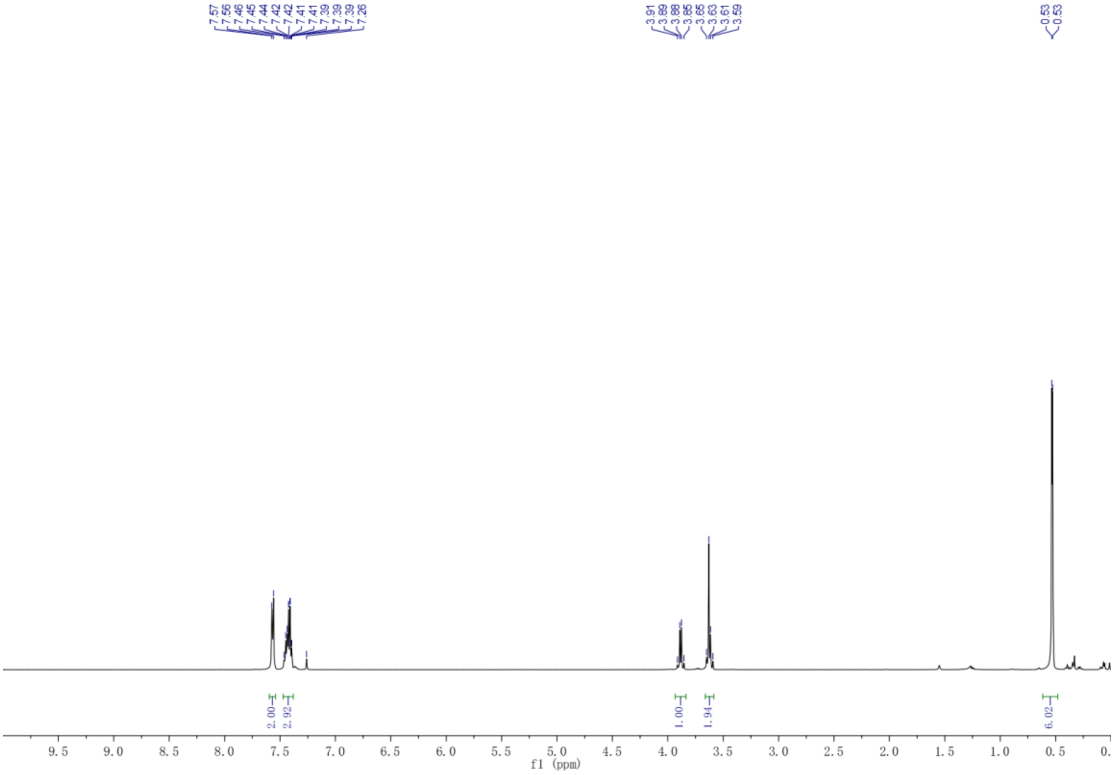




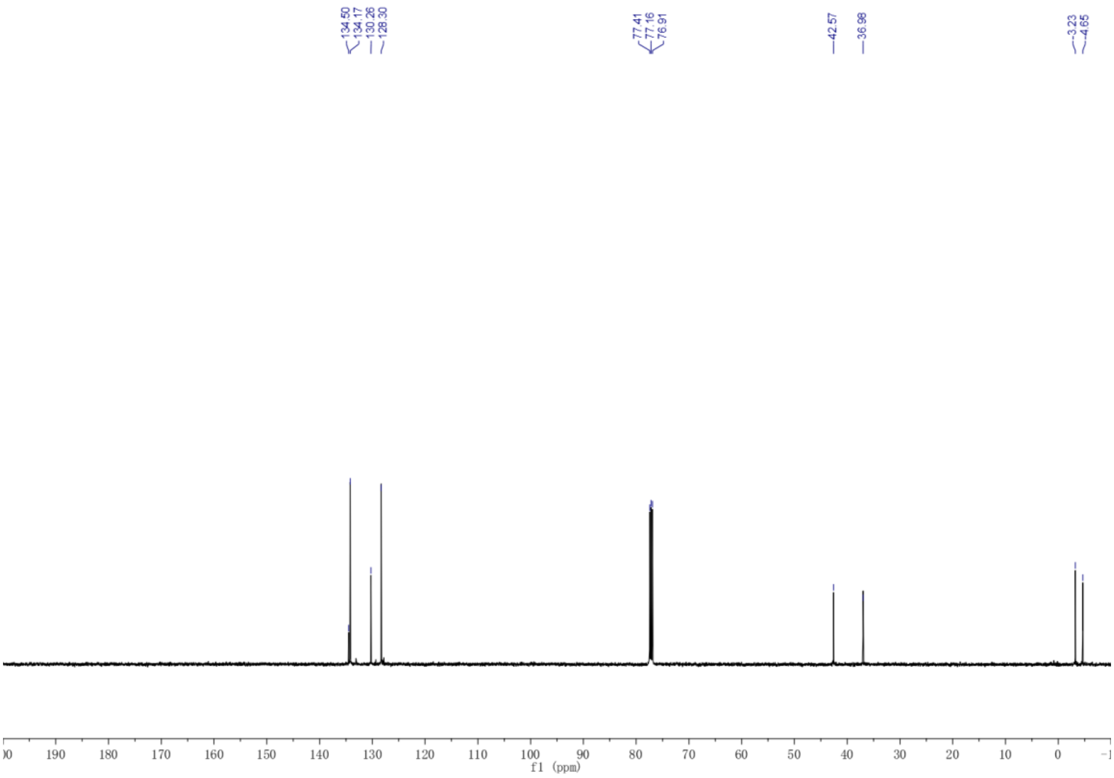
^{1}H NMR of compound **89**（500 MHz, $CDCl_3$）



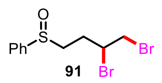
90

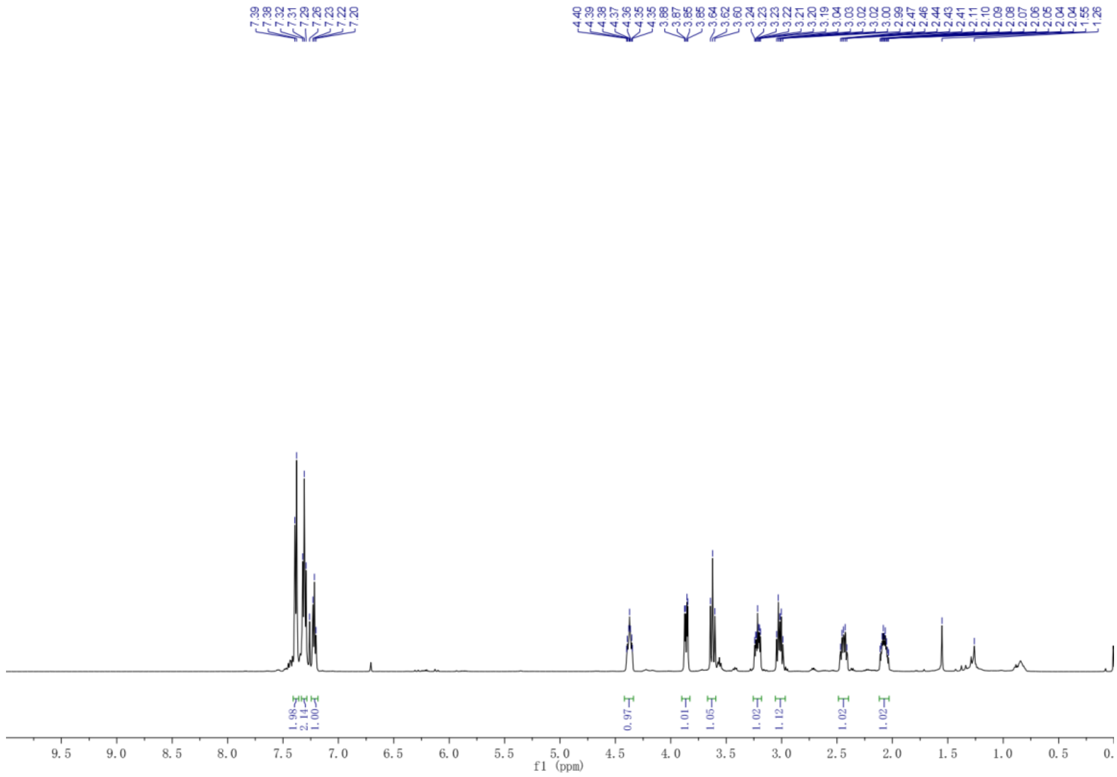


[1]H NMR of compound **90**（500 MHz, $CDCl_3$）

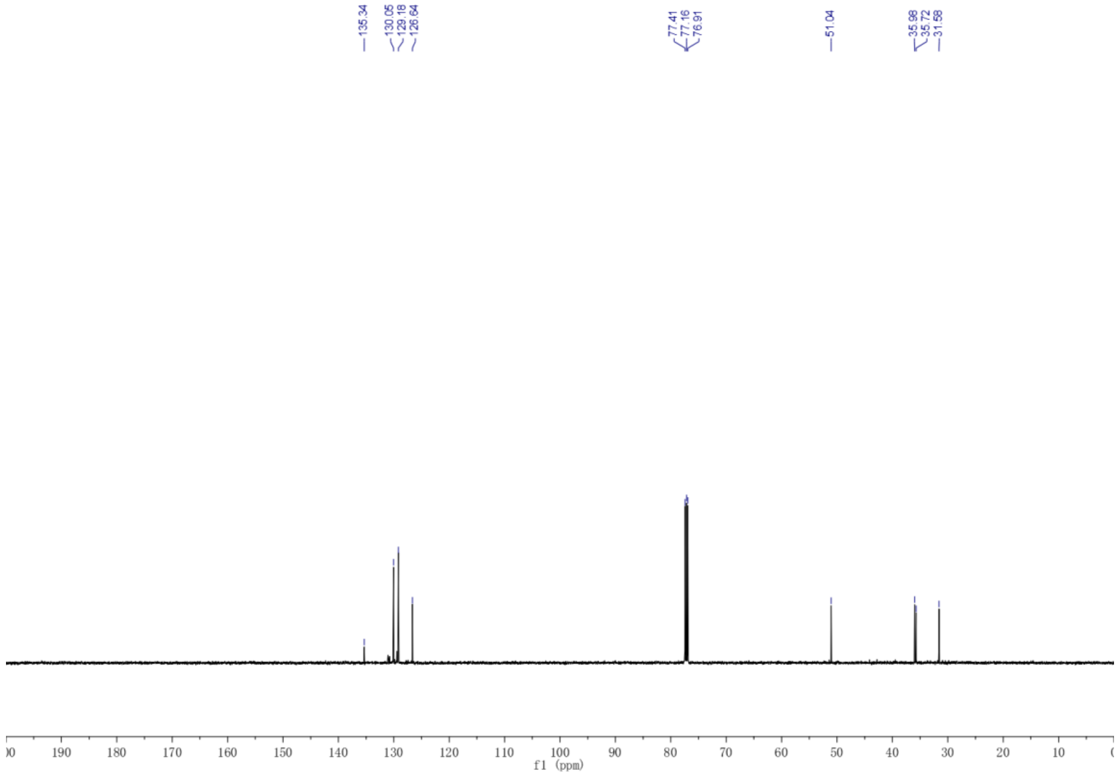


[13]C NMR of compound **90**（126 MHz, $CDCl_3$）

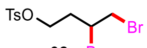




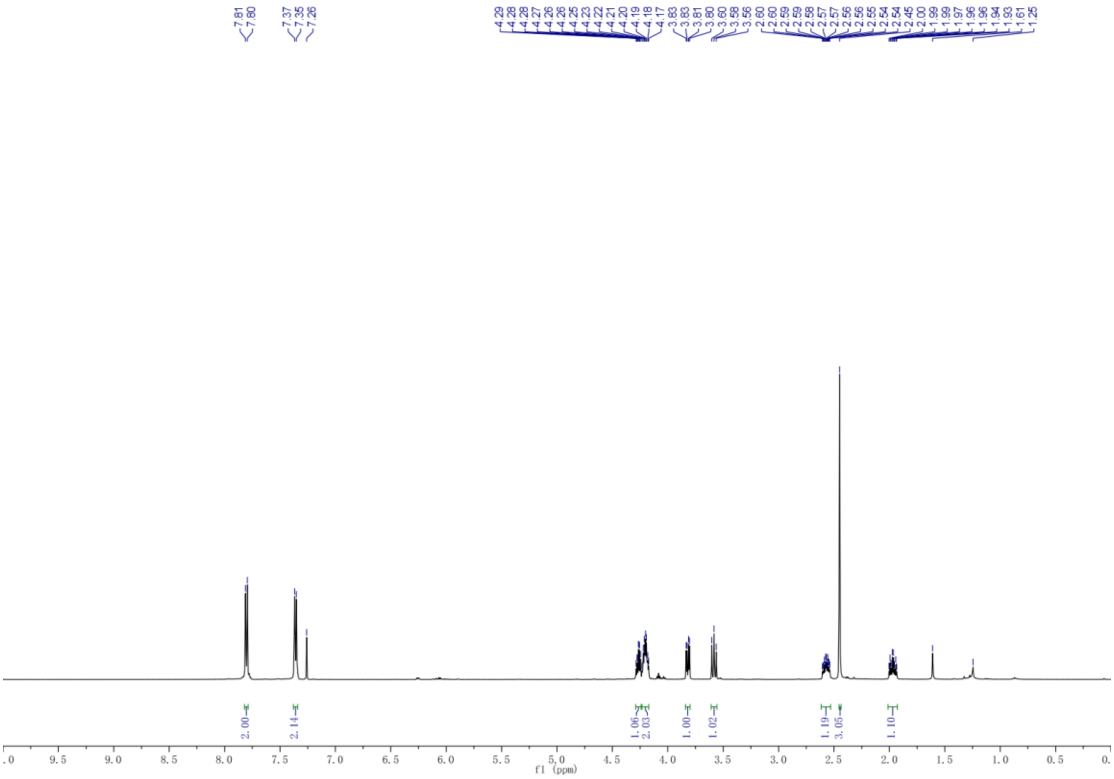
[1]H NMR of compound **91**（500 MHz, $CDCl_3$）



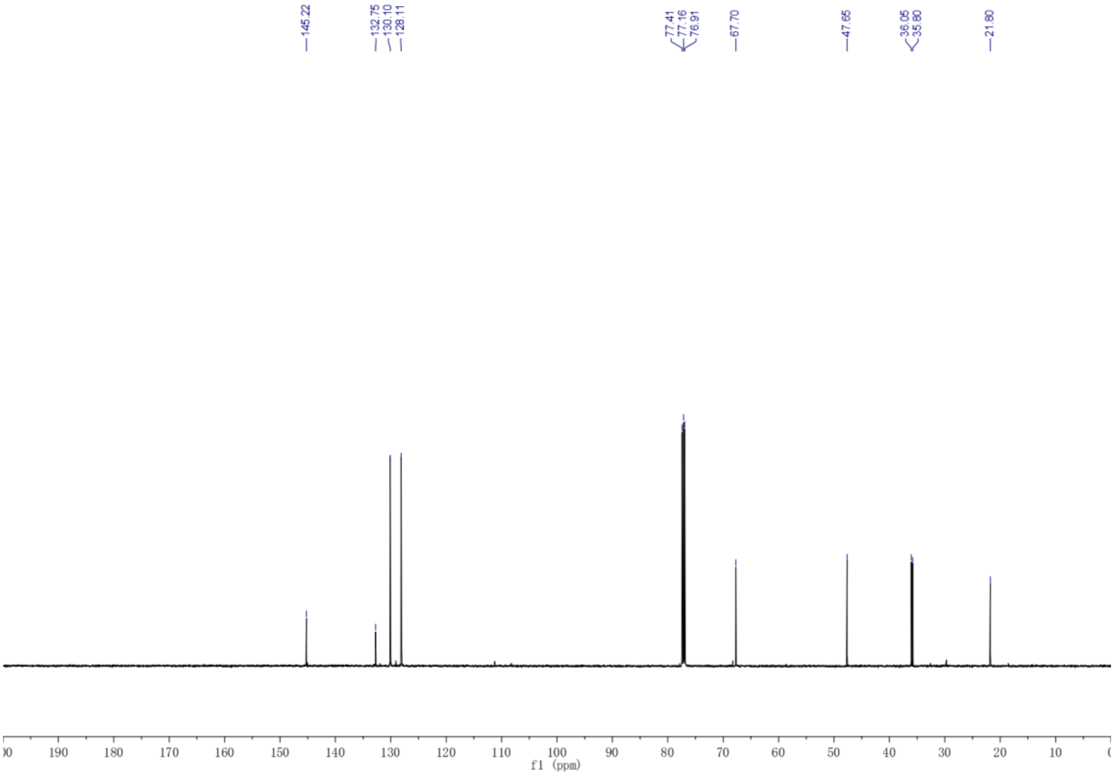
[13]C NMR of compound **91**（126 MHz, $CDCl_3$）



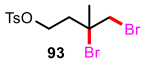
92



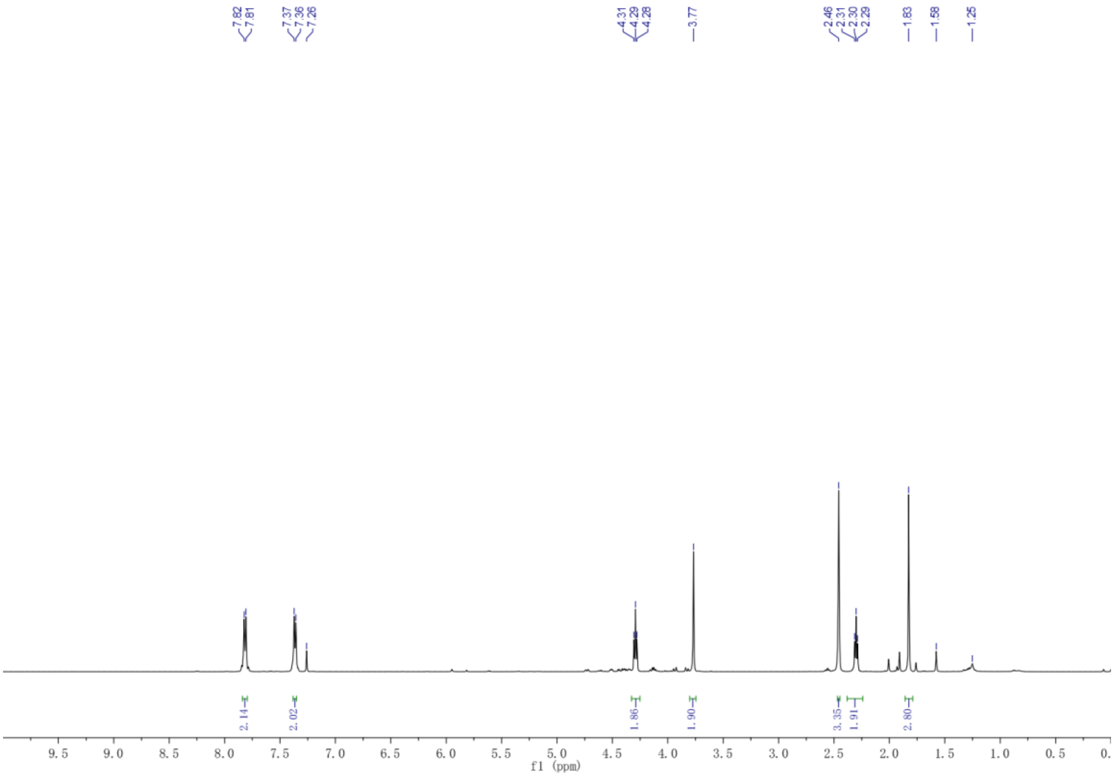
^{1}H NMR of compound **92**（500 MHz, $CDCl_3$）



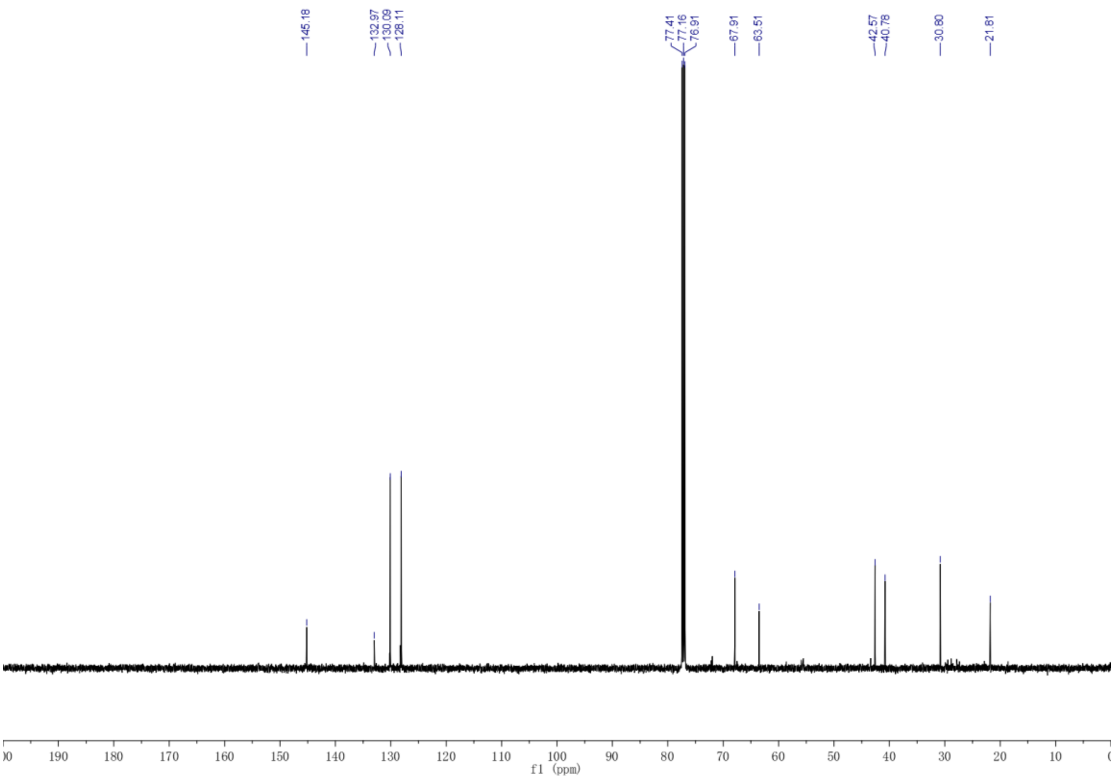
^{13}C NMR of compound **92**（126 MHz, $CDCl_3$）



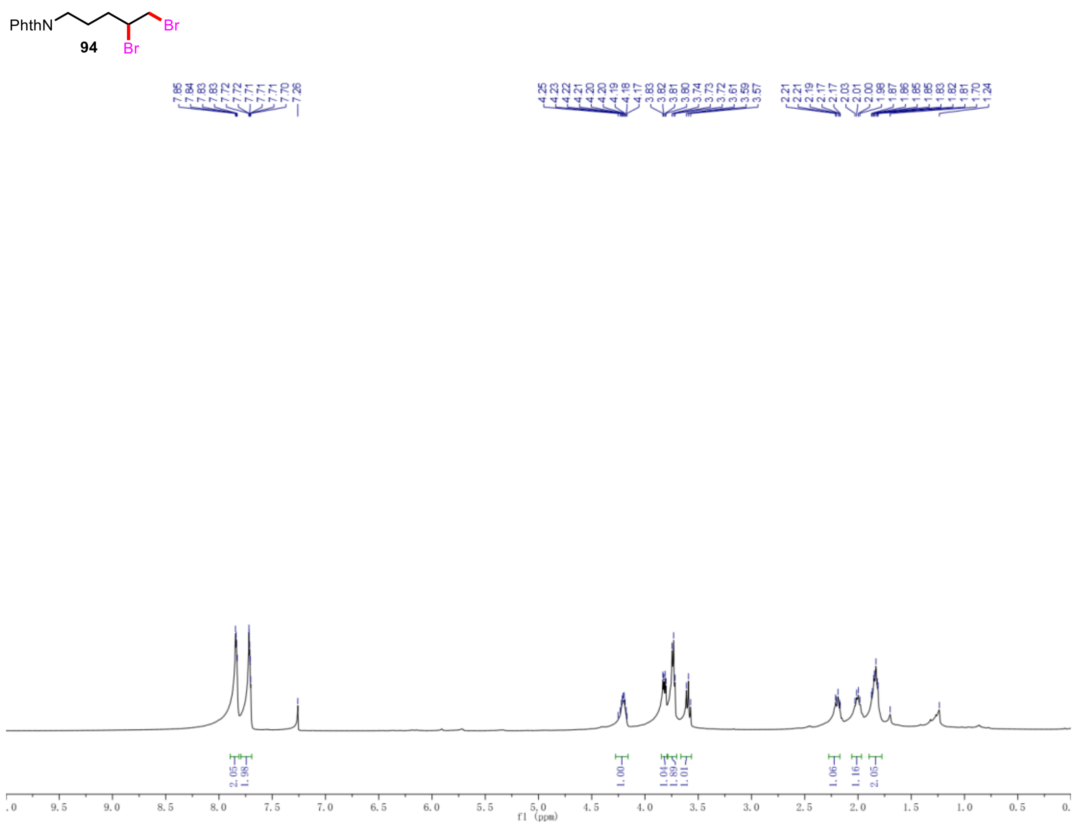
93



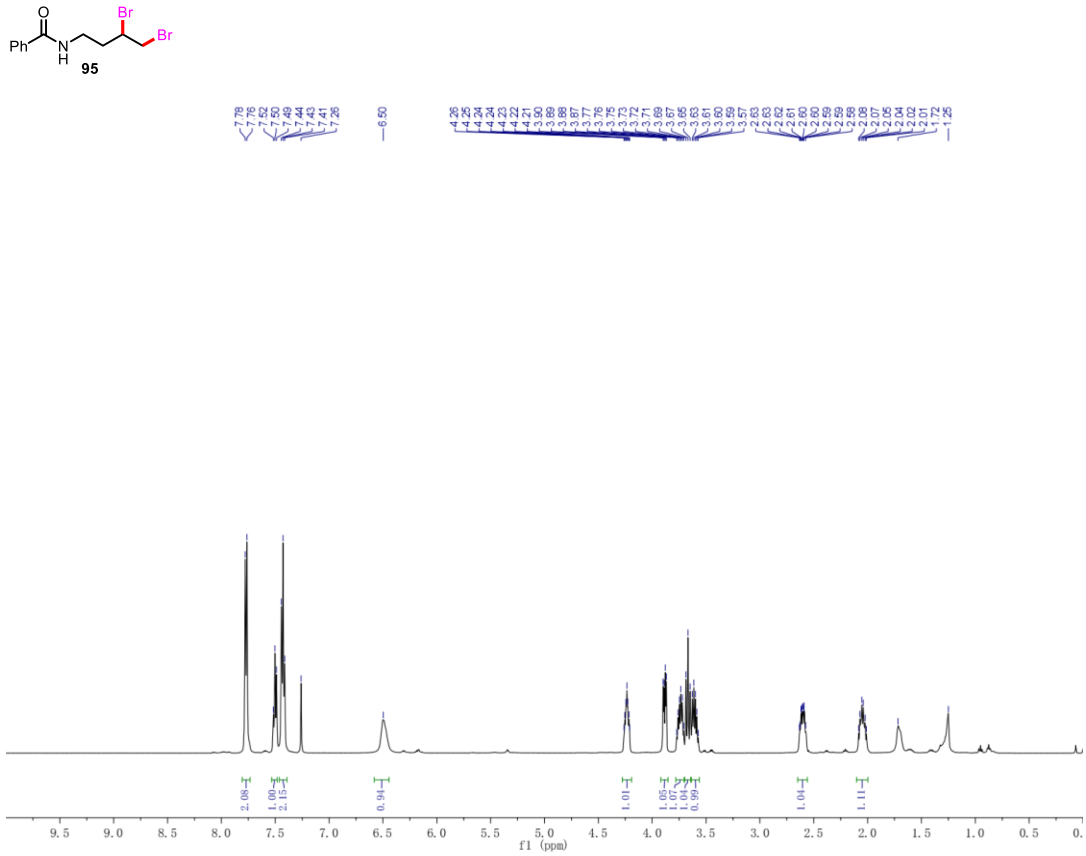
[1]H NMR of compound **93**（500 MHz, $CDCl_3$）



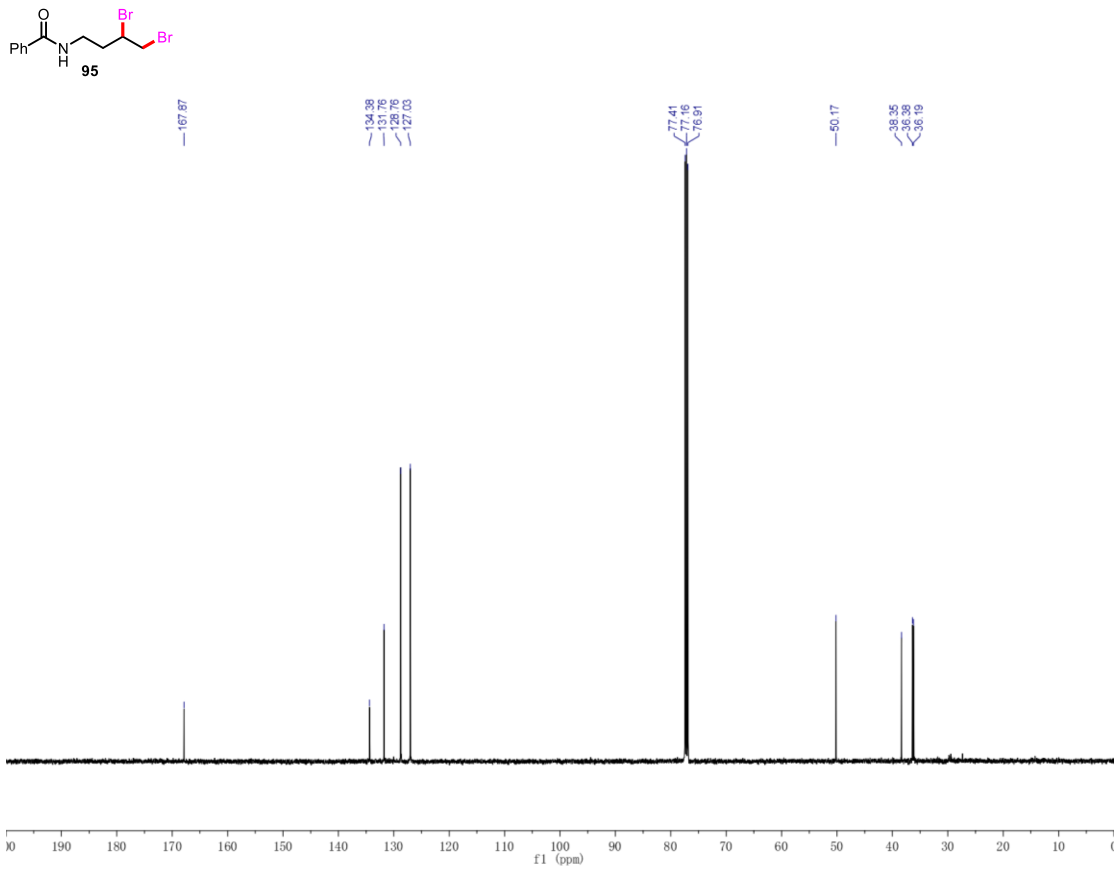
[13]C NMR of compound **93**（126 MHz, $CDCl_3$）



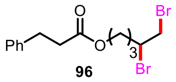
^{1}H NMR of compound **94**（500 MHz, $CDCl_3$）

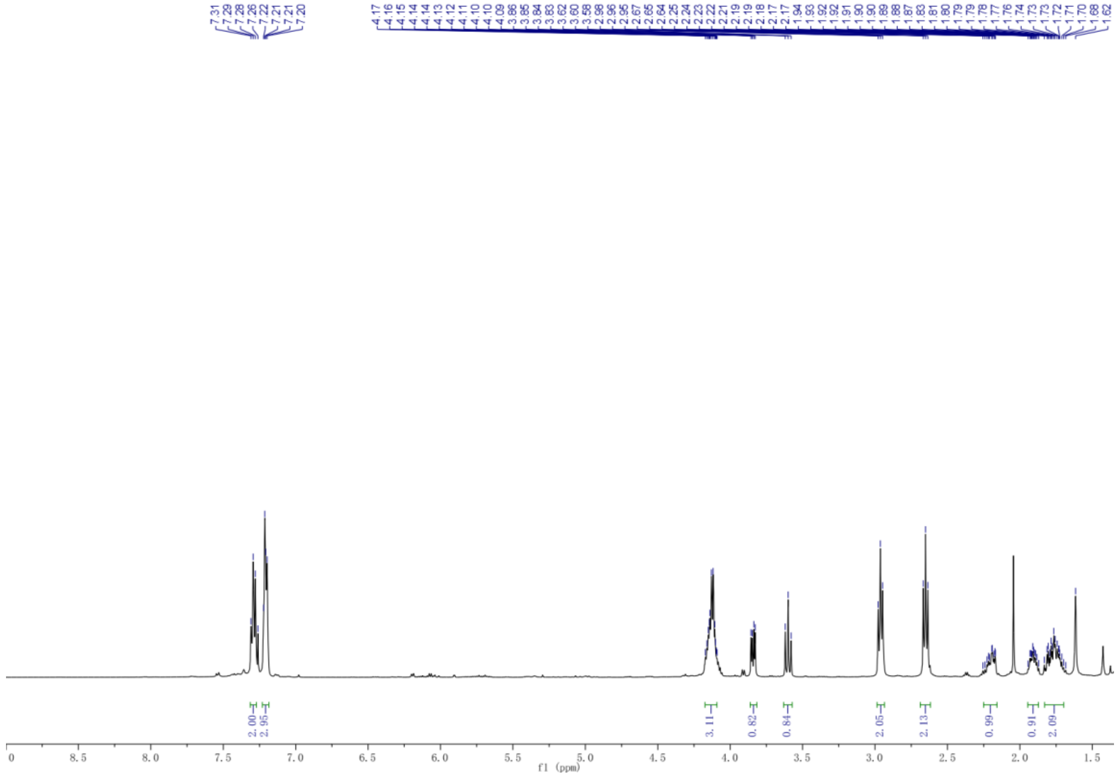


^{1}H NMR of compound **95**（500 MHz, $CDCl_3$）

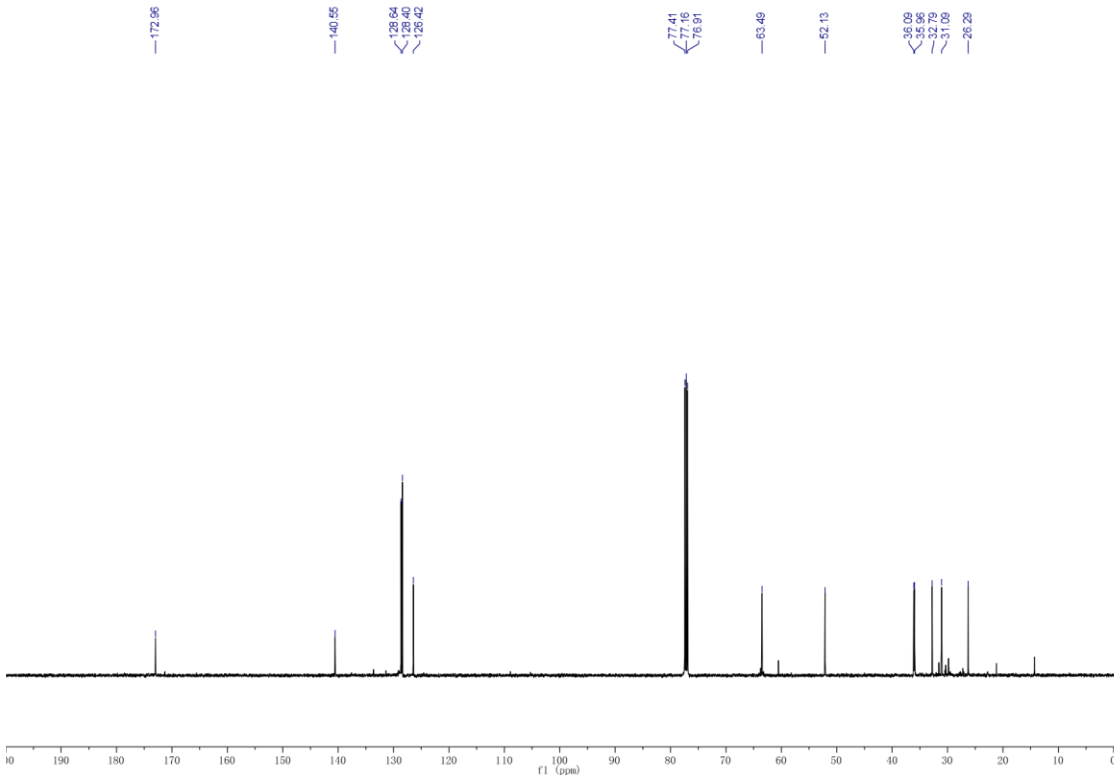


^{13}C NMR of compound **95**（126 MHz, $CDCl_3$）

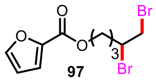


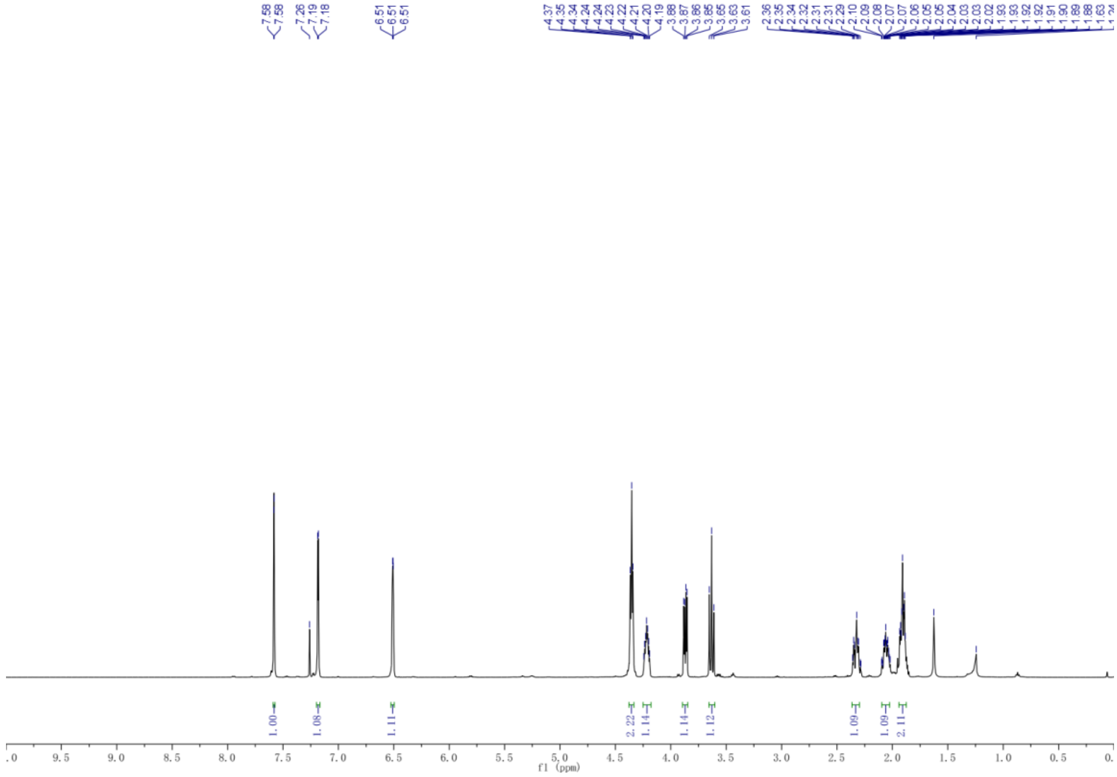


^{1}H NMR of compound **96**（500 MHz, $CDCl_3$）

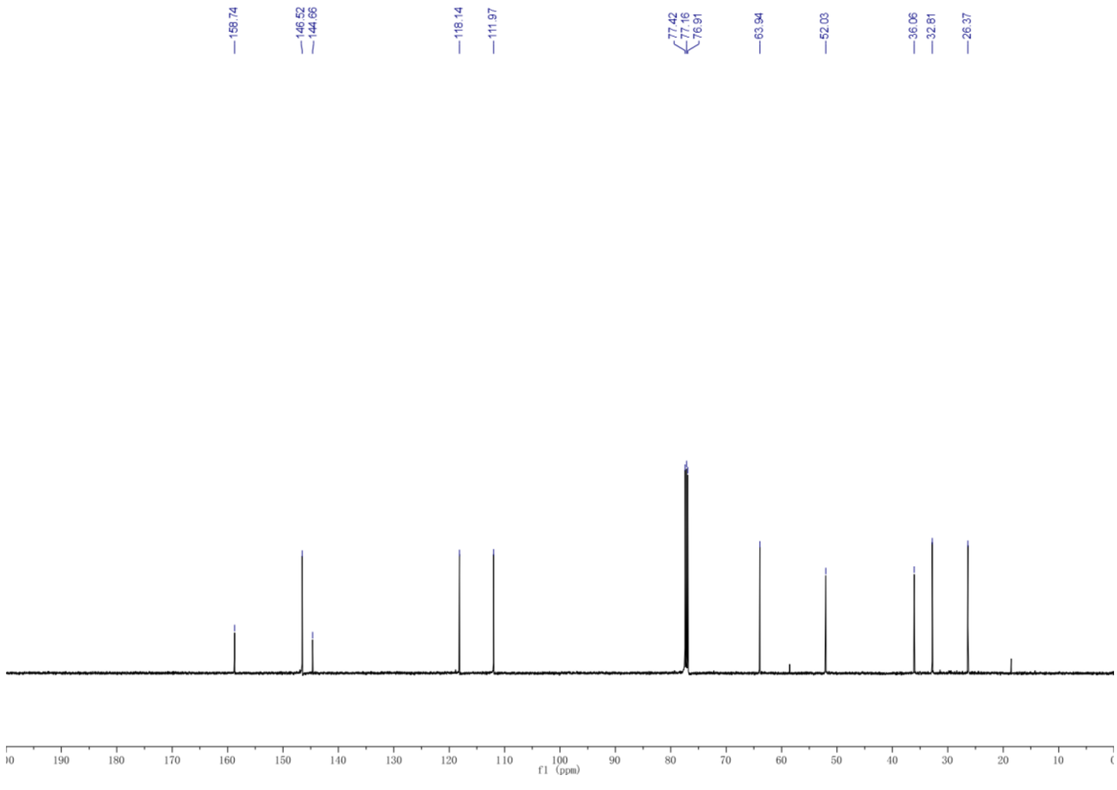


^{13}C NMR of compound **96**（126 MHz, $CDCl_3$）

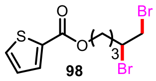


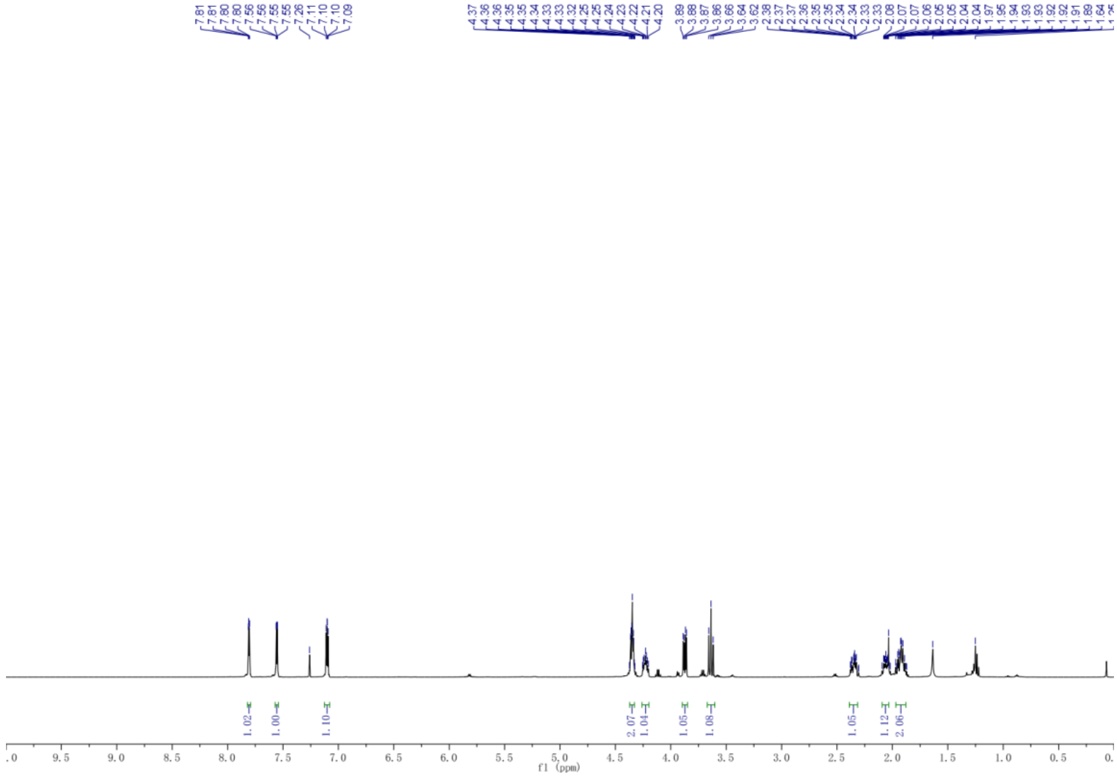


[1]H NMR of compound **97**（500 MHz, $CDCl_3$）

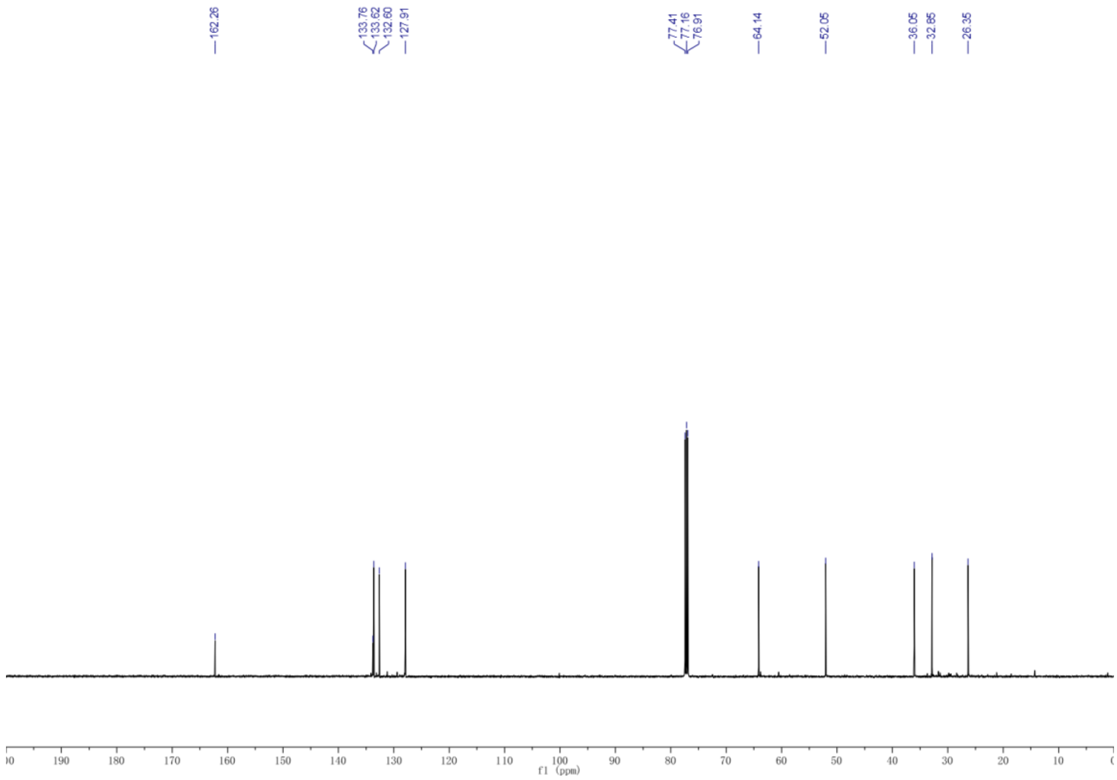


[13]C NMR of compound **97**（126 MHz, $CDCl_3$）

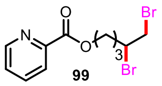


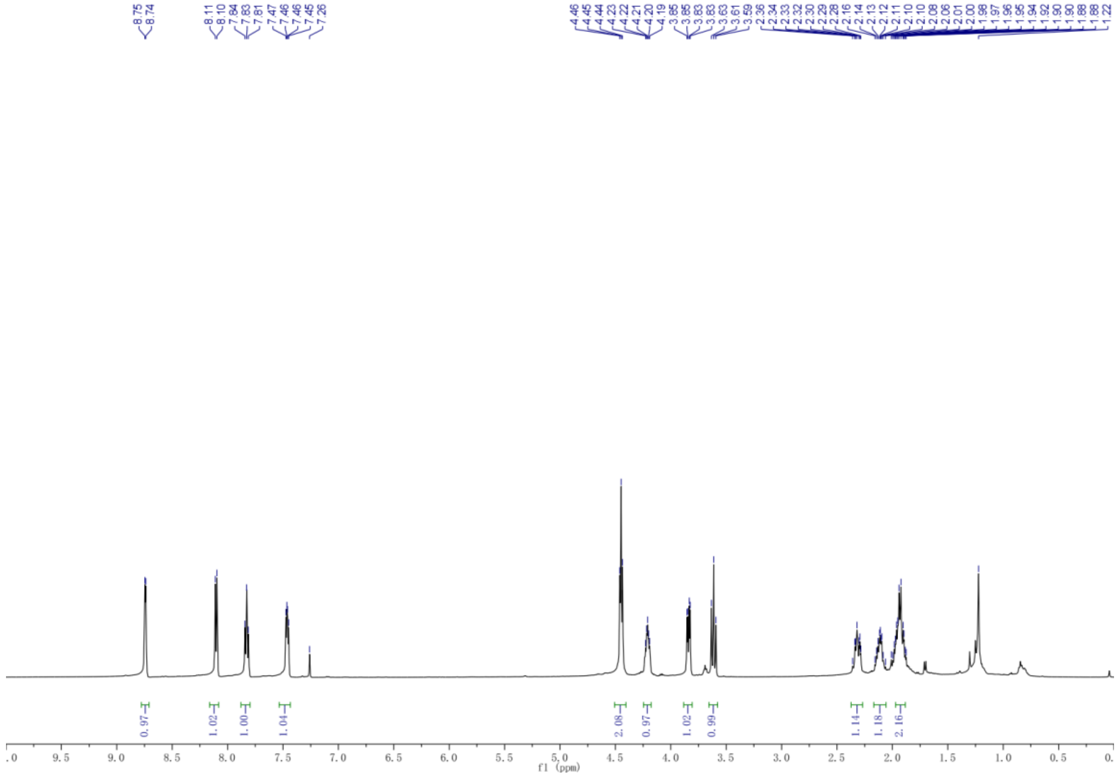


^{1}H NMR of compound **98**（500 MHz, $CDCl_3$）

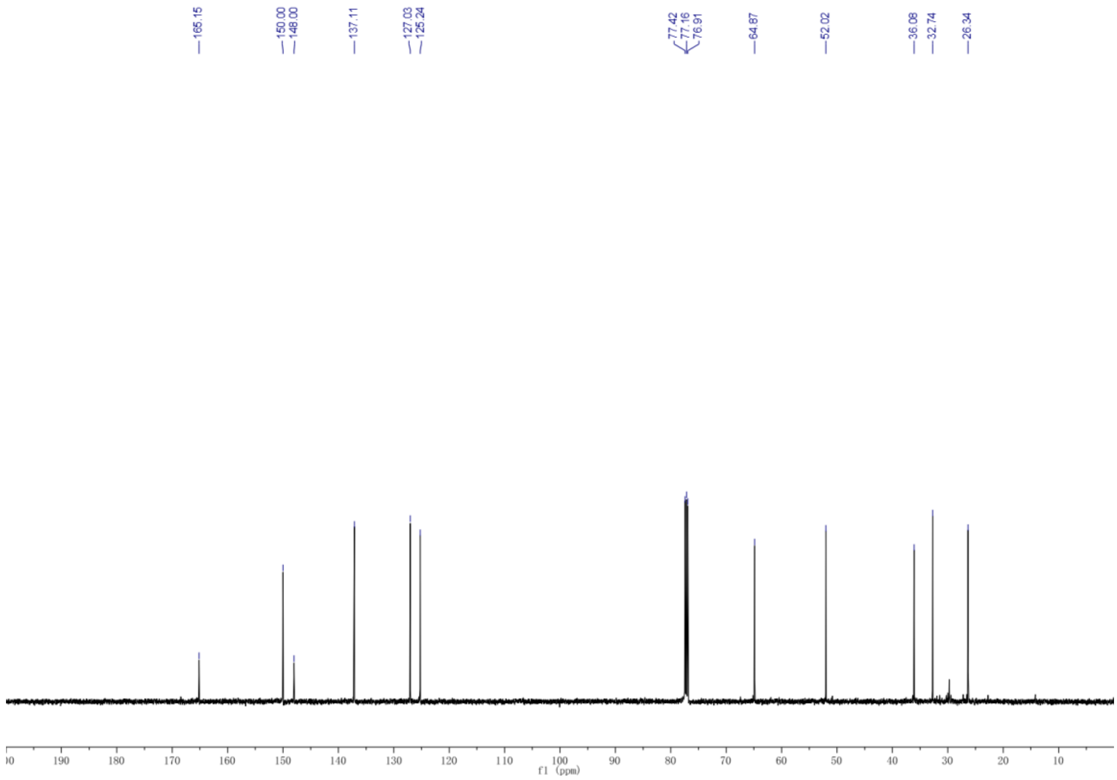


^{13}C NMR of compound **98**（126 MHz, $CDCl_3$）

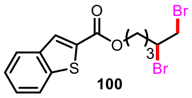




^{1}H NMR of compound **99**（500 MHz, $CDCl_3$）



^{13}C NMR of compound **99**（126 MHz, $CDCl_3$）



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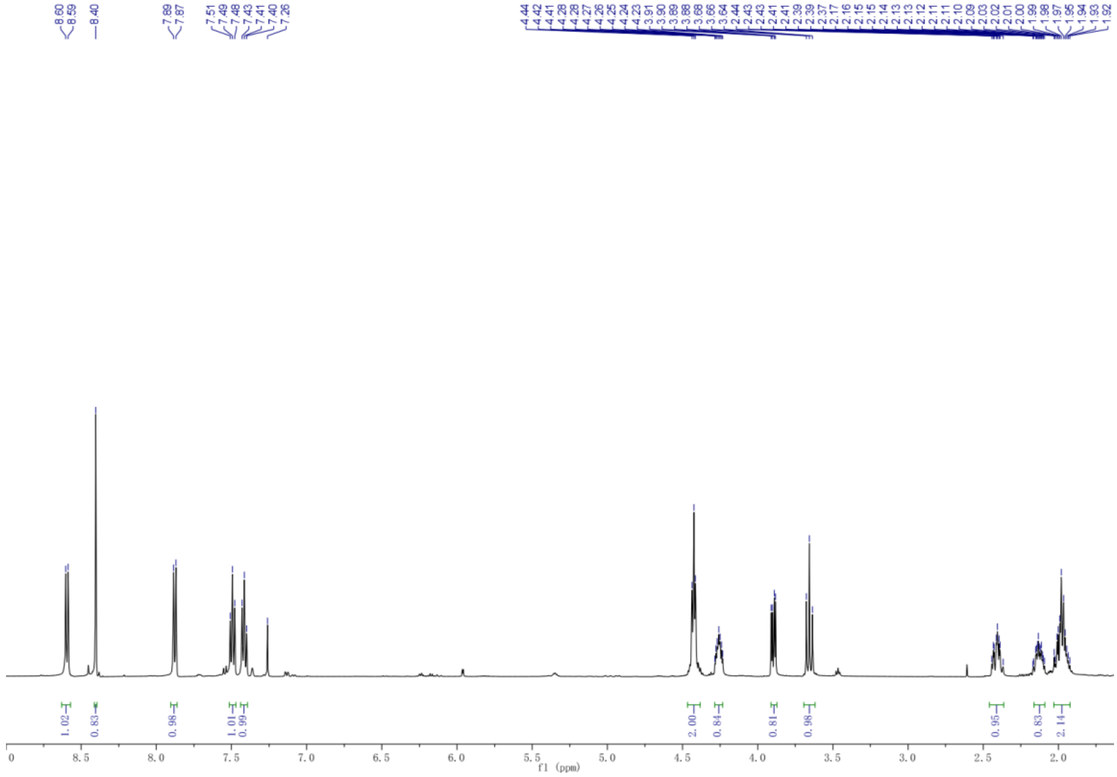
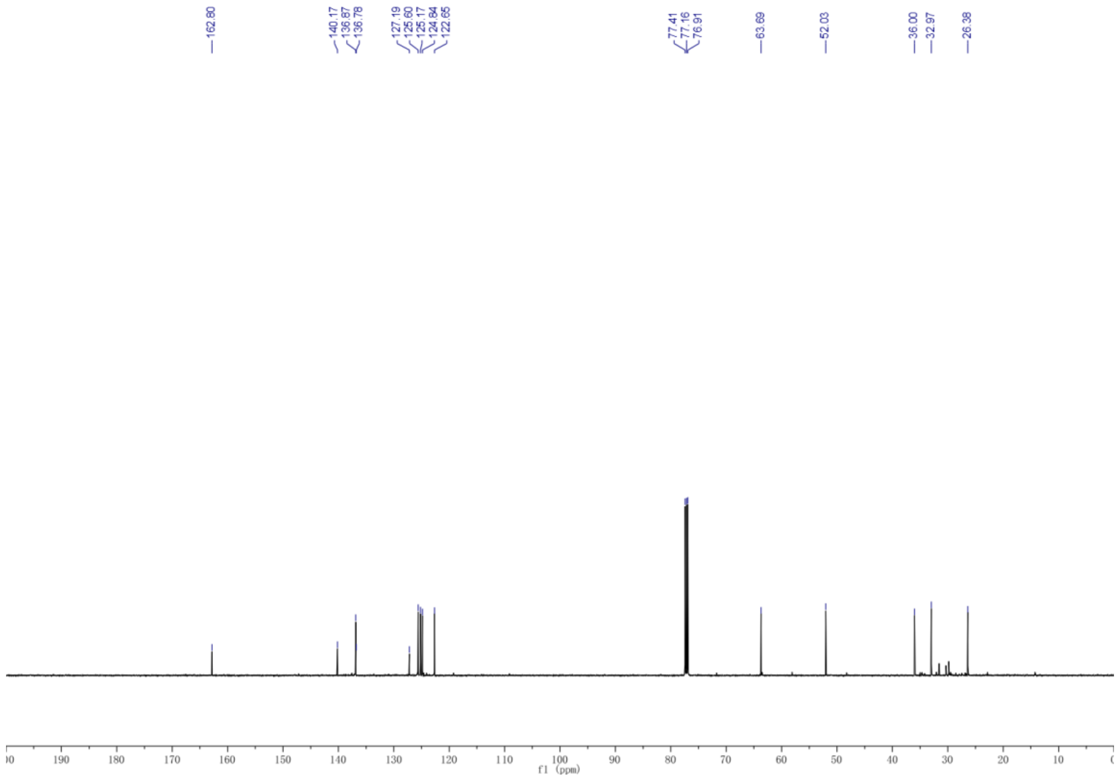
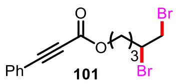


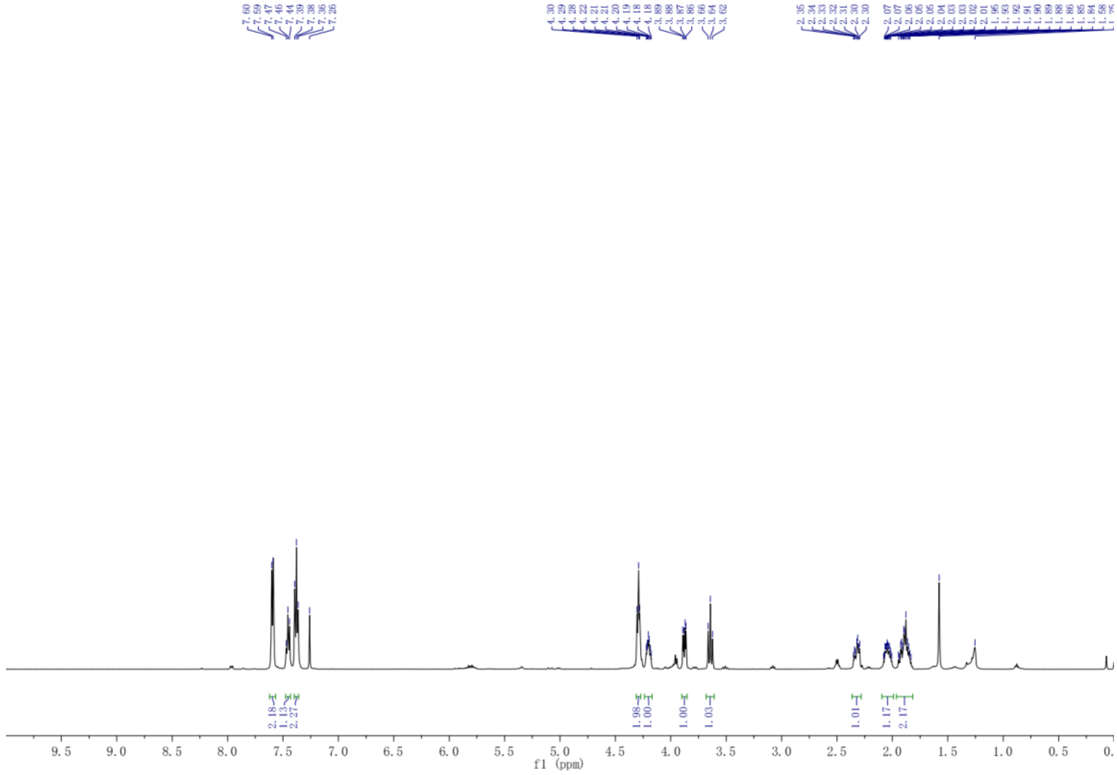
^{1}H NMR of compound **100**（500 MHz, $CDCl_3$）



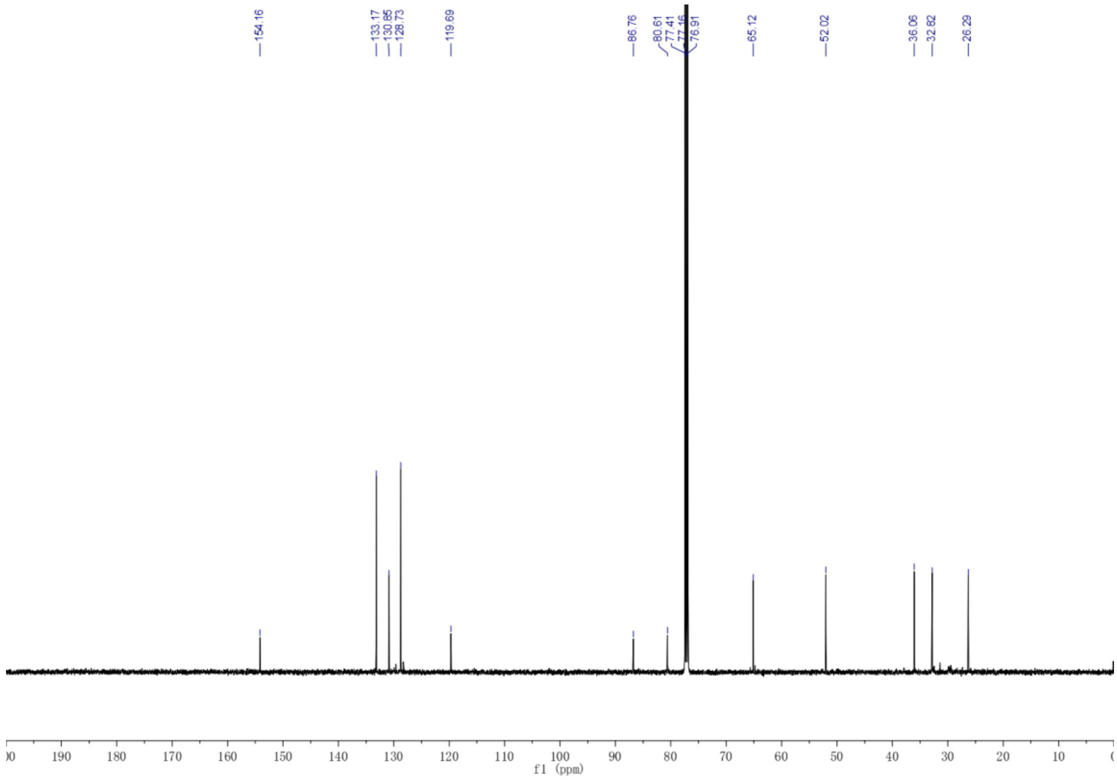
^{13}C NMR of compound **100**（126 MHz, $CDCl_3$）



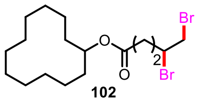
101



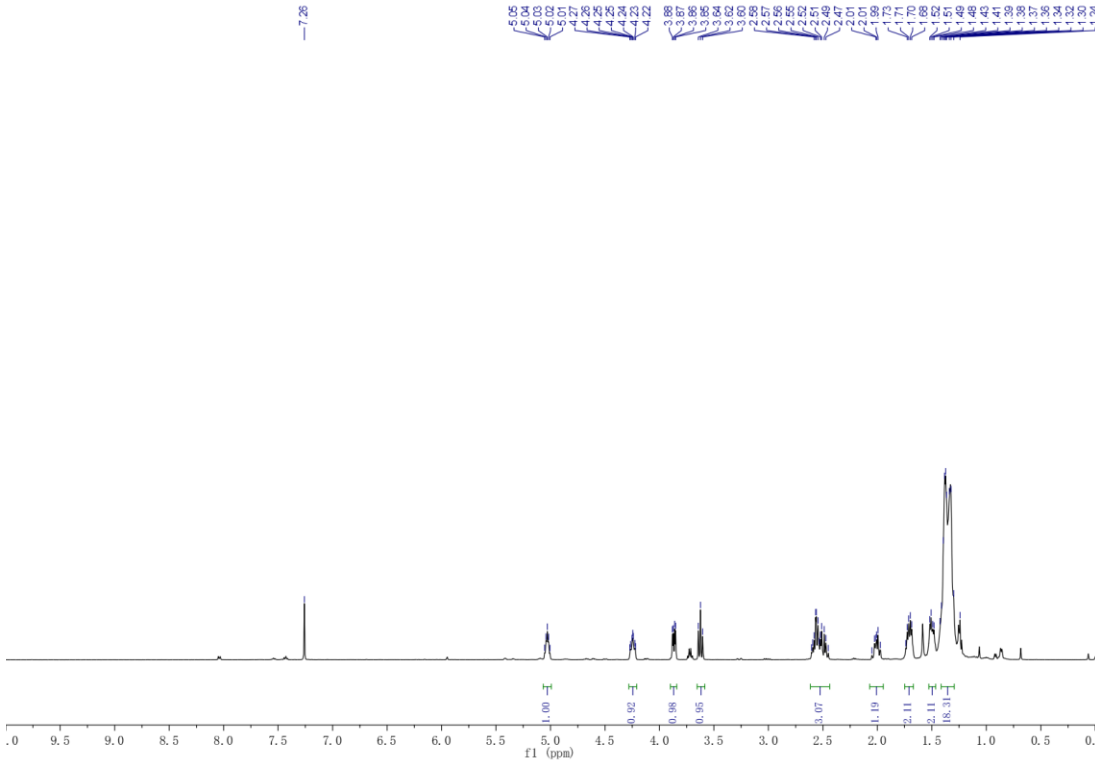
^{1}H NMR of compound **101**（500 MHz, $CDCl_3$）



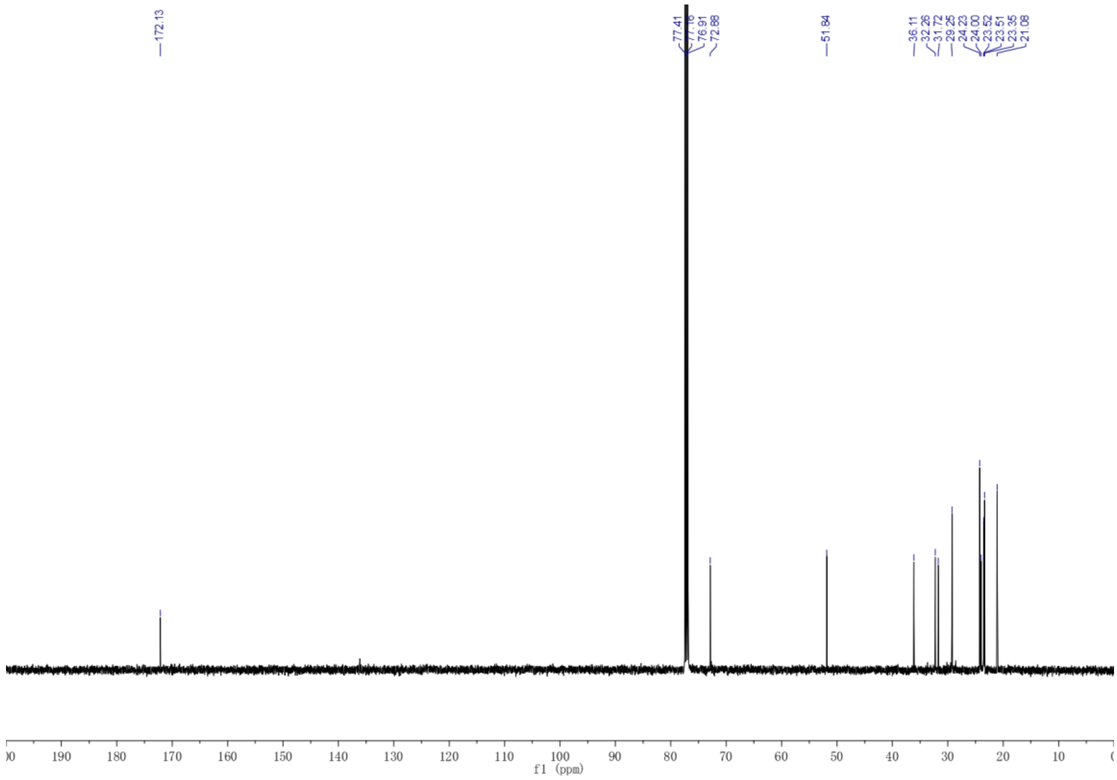
^{13}C NMR of compound **101**（126 MHz, $CDCl_3$）



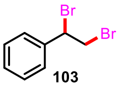
102



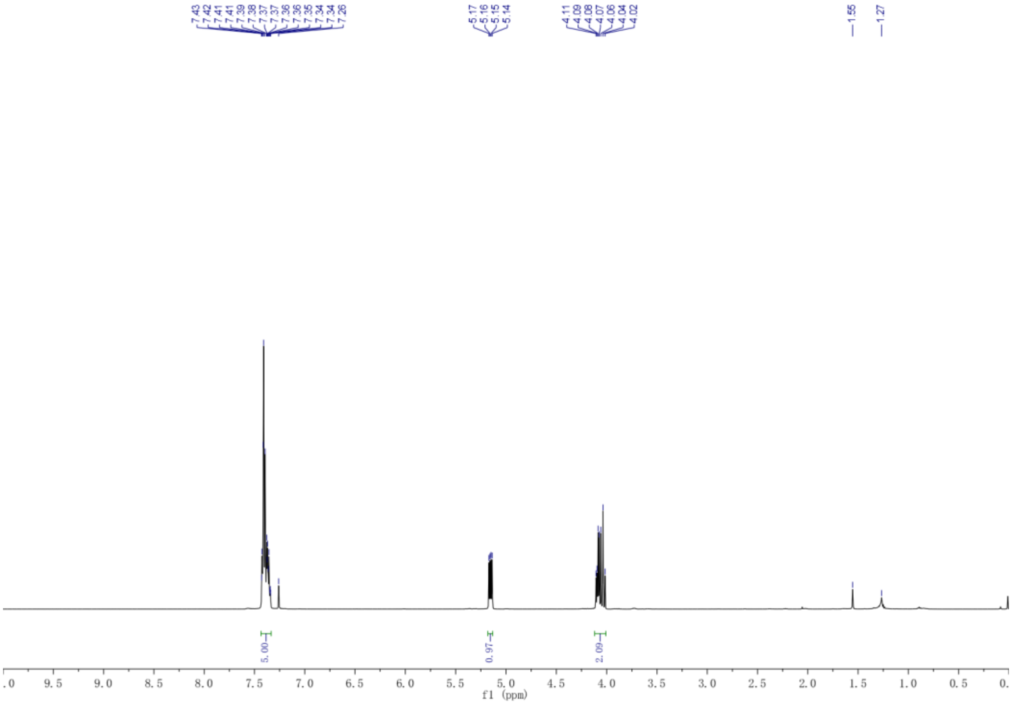
[1]H NMR of compound **102**（500 MHz, $CDCl_3$）



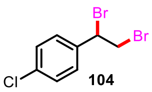
[13]C NMR of compound **102**（126 MHz, $CDCl_3$）



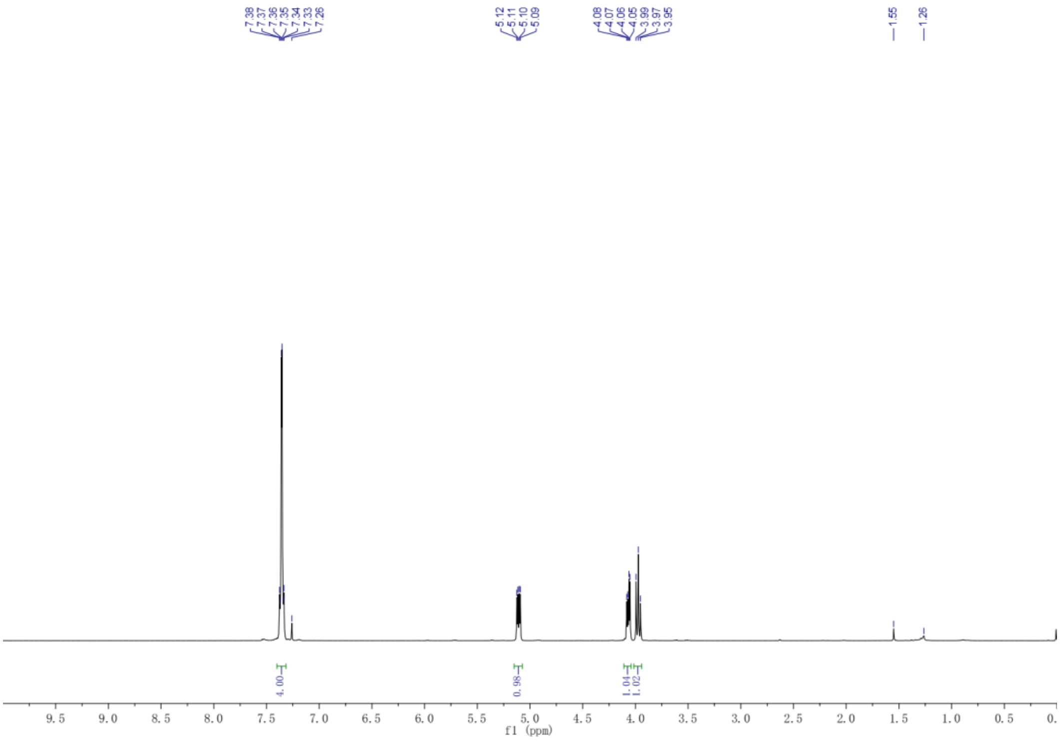
103



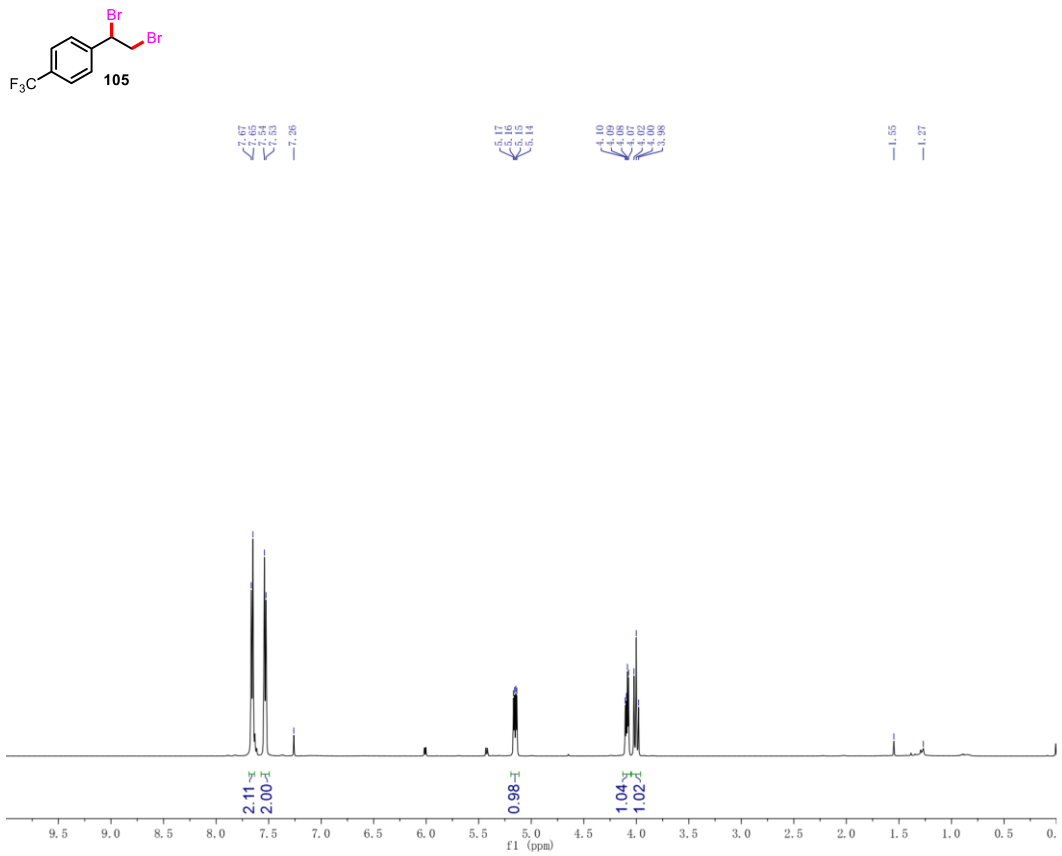
^{1}H NMR of compound **103**（500 MHz, $CDCl_3$）



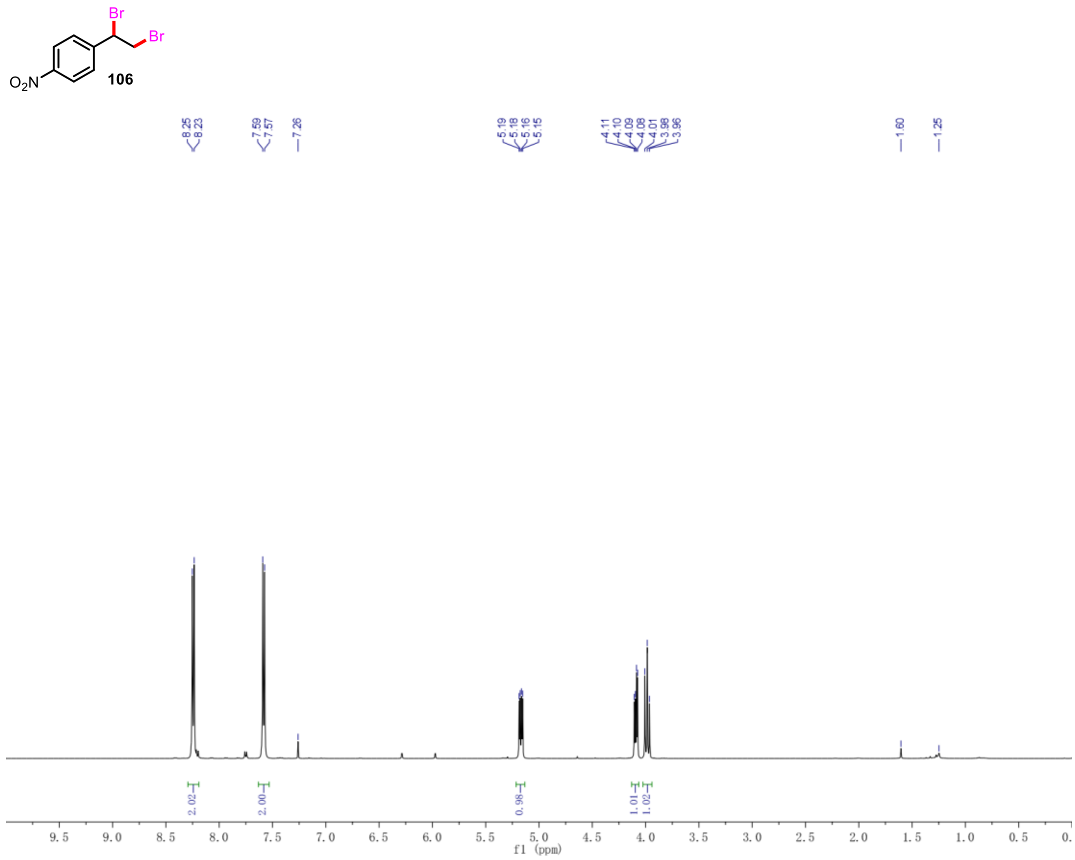
104



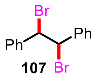
^{1}H NMR of compound **104**（500 MHz, $CDCl_3$）



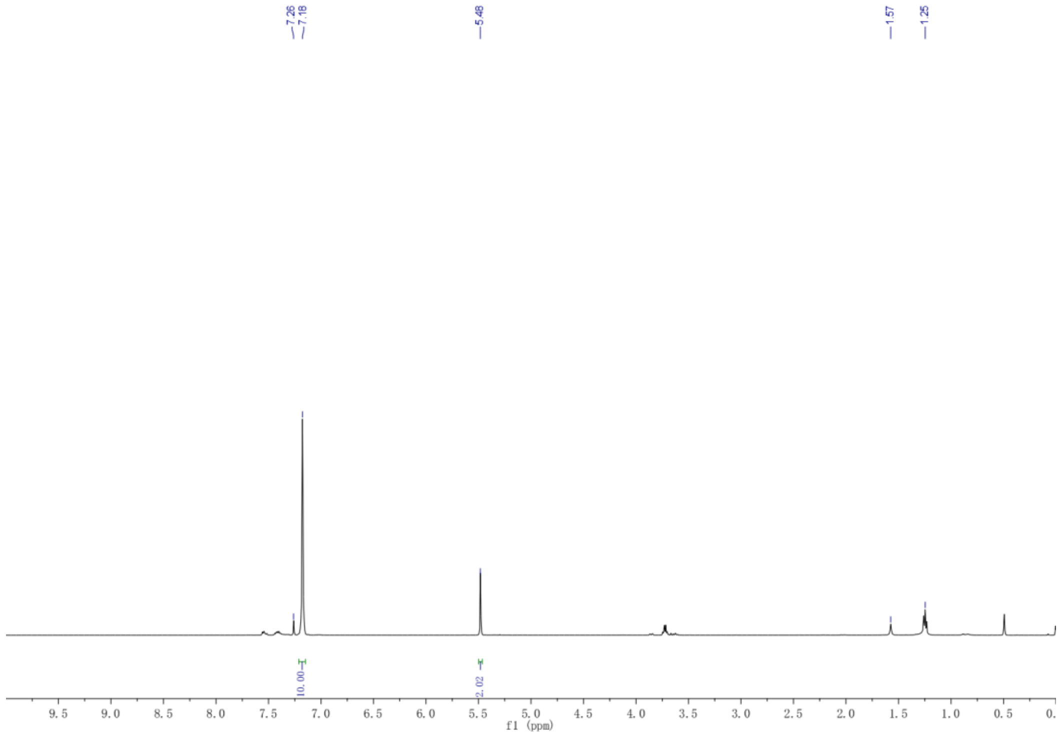
^{1}H NMR of compound **105**（500 MHz, $CDCl_3$）



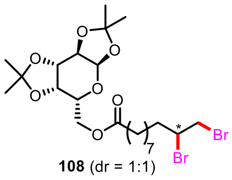
^{1}H NMR of compound **106**（500 MHz, $CDCl_3$）



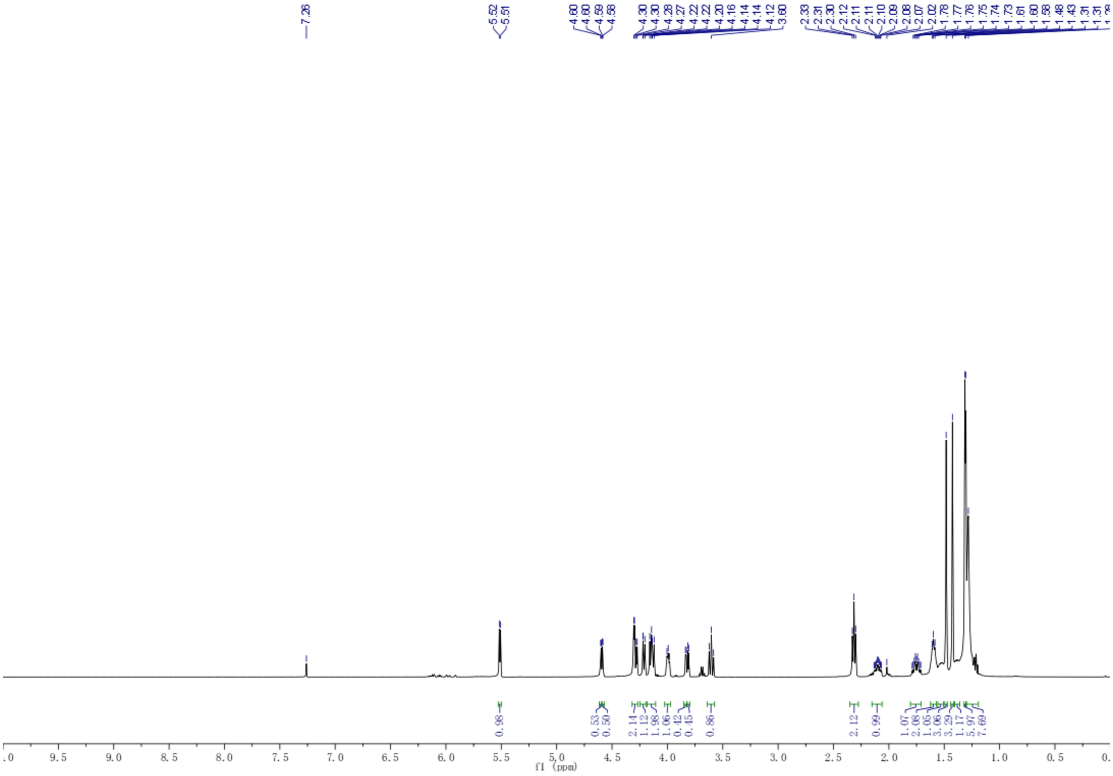
107



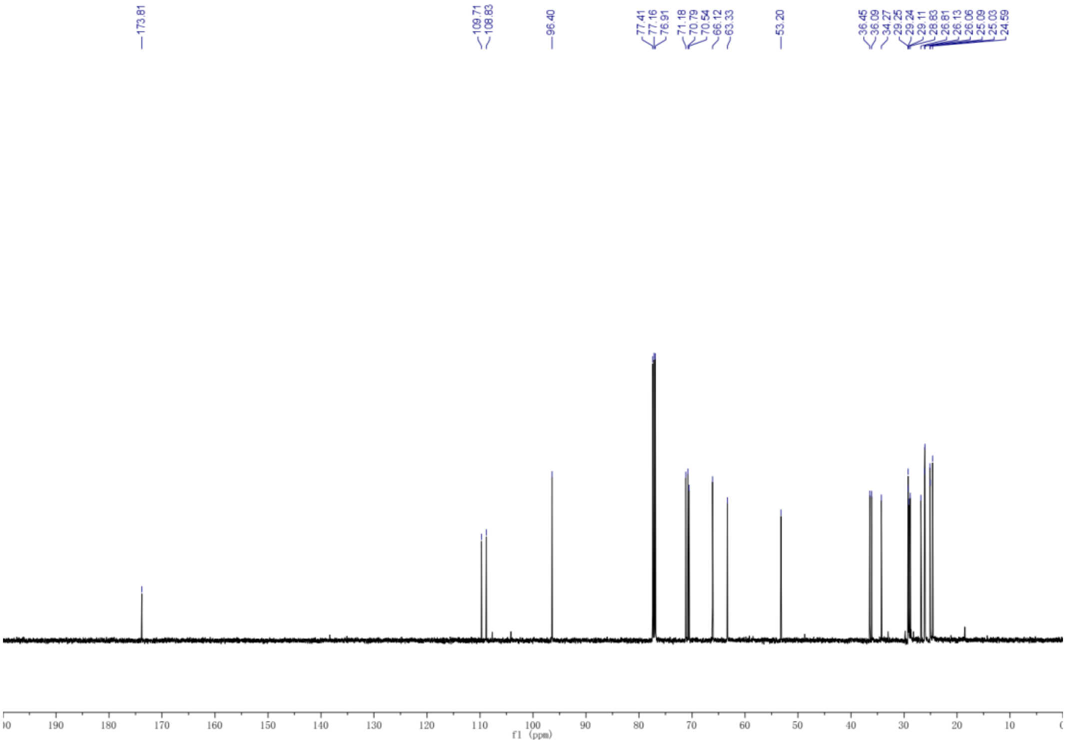
[1]H NMR of compound **107**（500 MHz, $CDCl_3$）



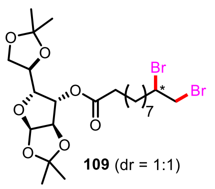
108 (dr = 1:1)



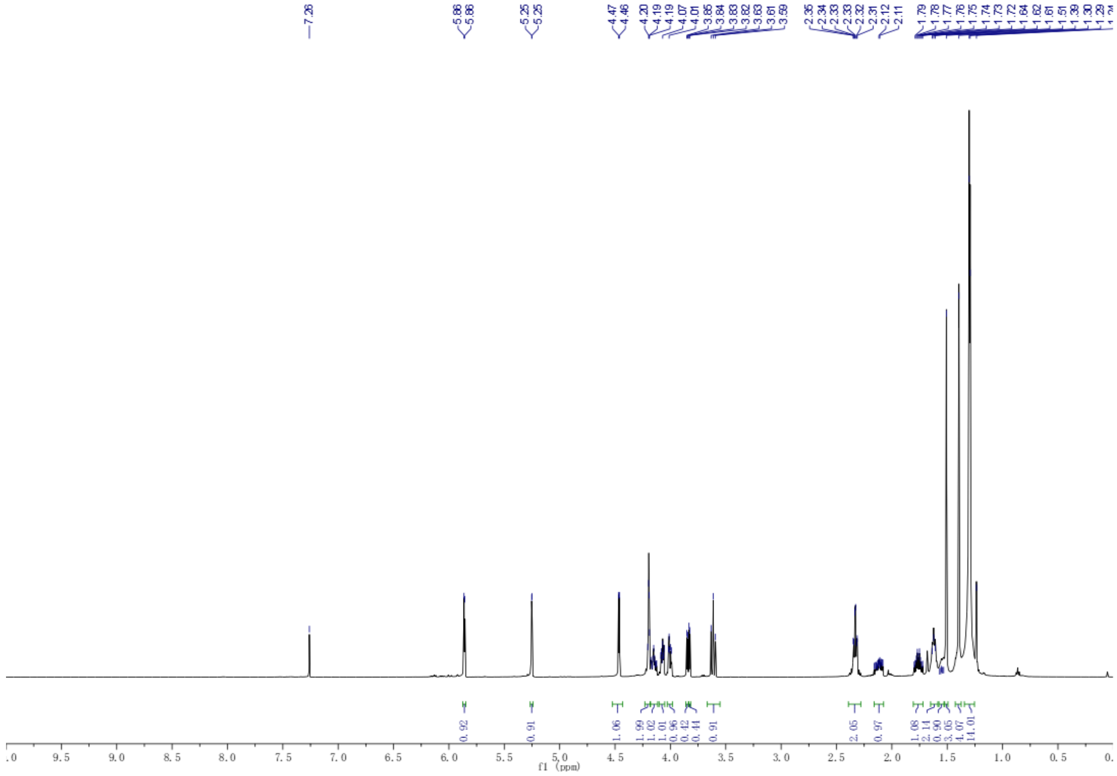
[1]H NMR of compound **108**（500 MHz, $CDCl_3$）



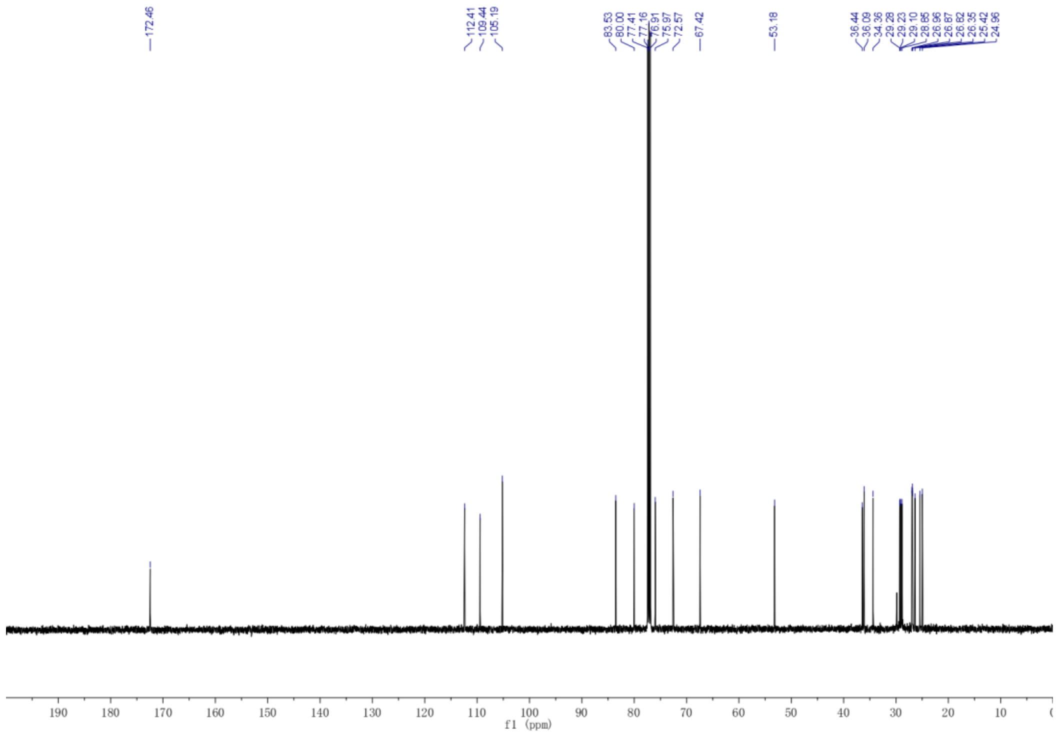
[13]C NMR of compound **108**（126 MHz, $CDCl_3$）



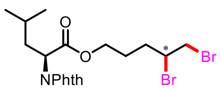
109 (dr = 1:1)



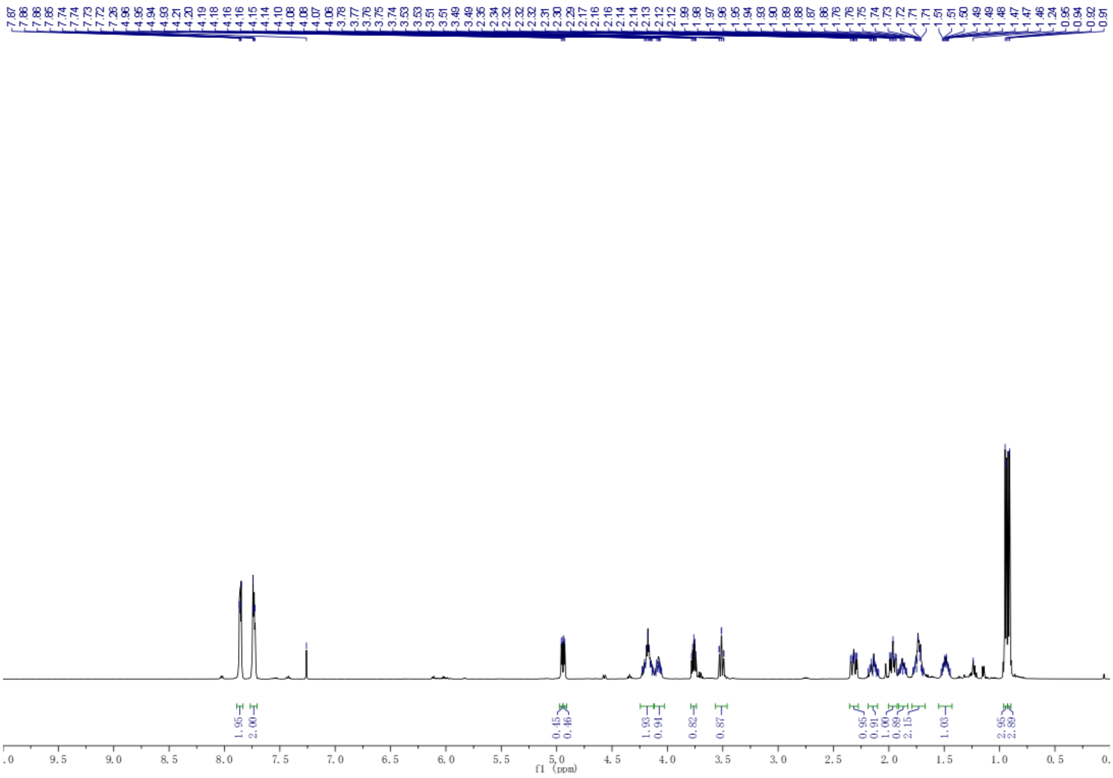
[1]H NMR of compound **109**（500 MHz, $CDCl_3$）



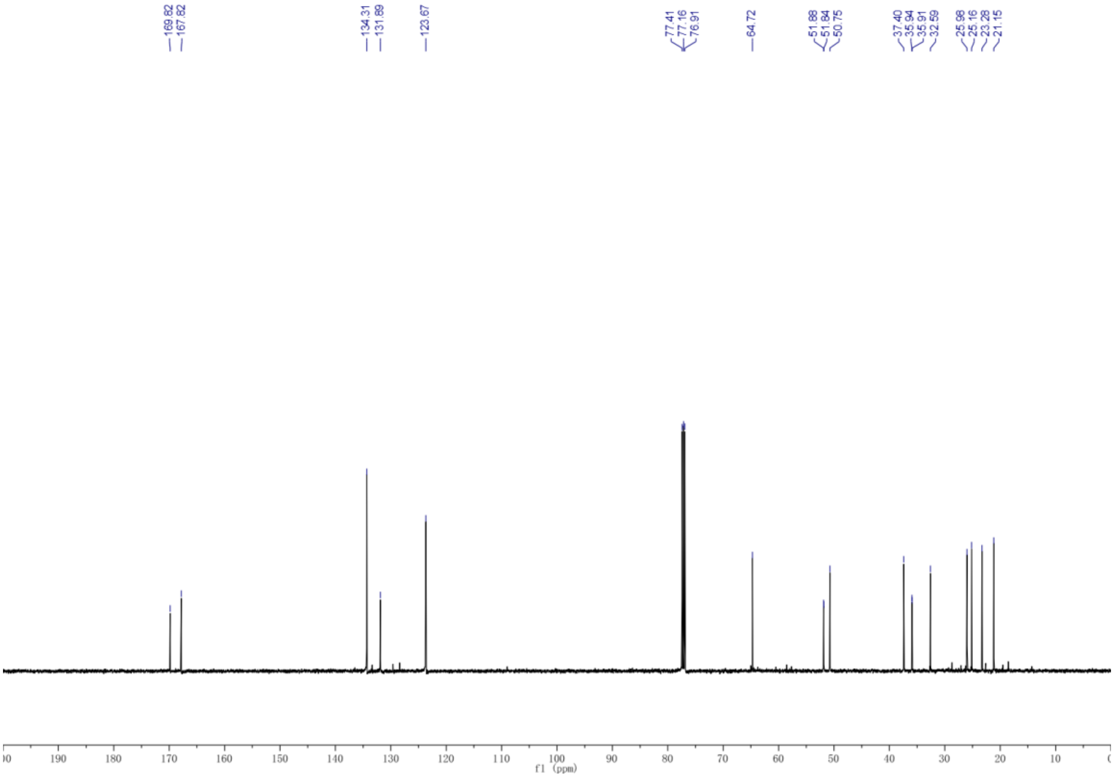
[13]C NMR of compound **109**（126 MHz, $CDCl_3$）



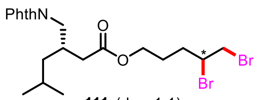
110 (dr = 1:1)



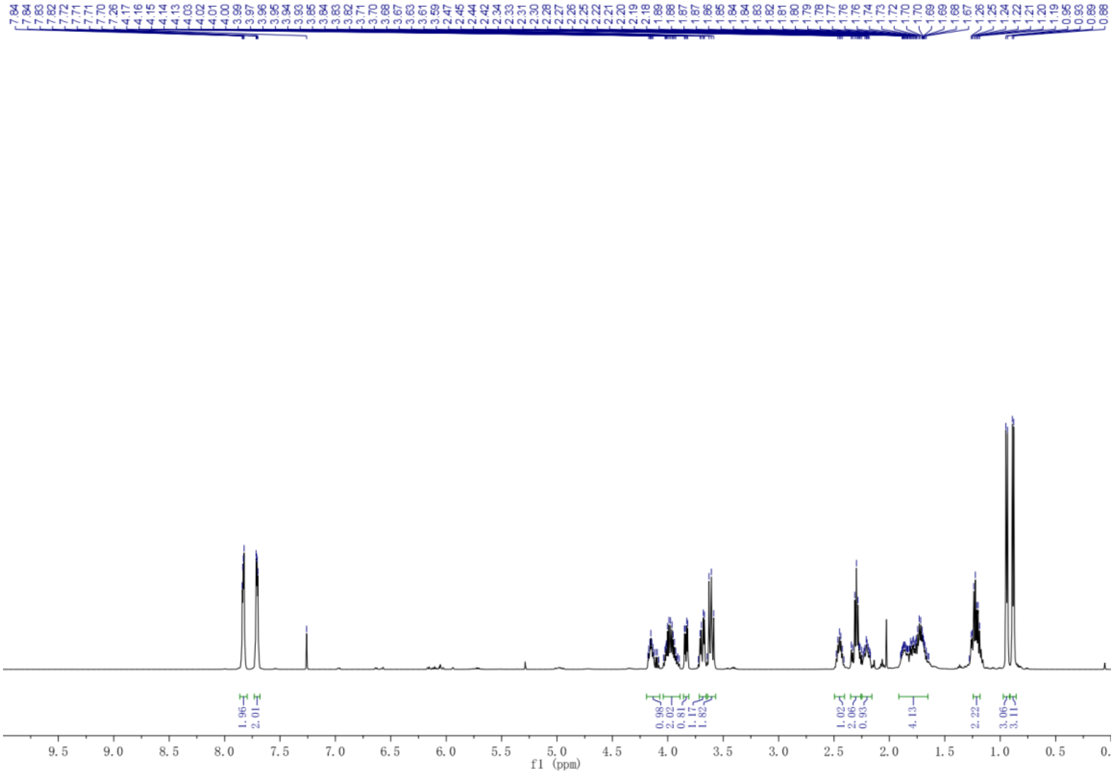
[1]H NMR of compound **110**（500 MHz, $CDCl_3$）



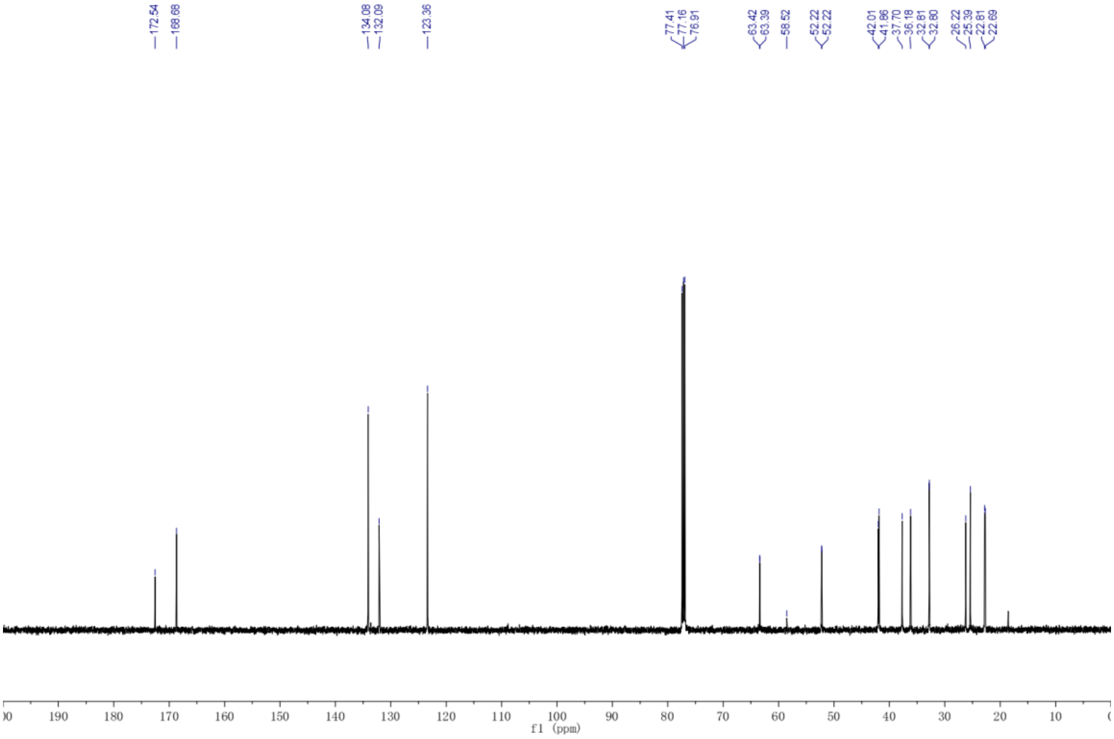
[13]C NMR of compound **110**（126 MHz, $CDCl_3$）



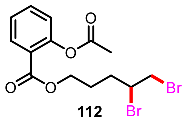
111 (dr = 1:1)



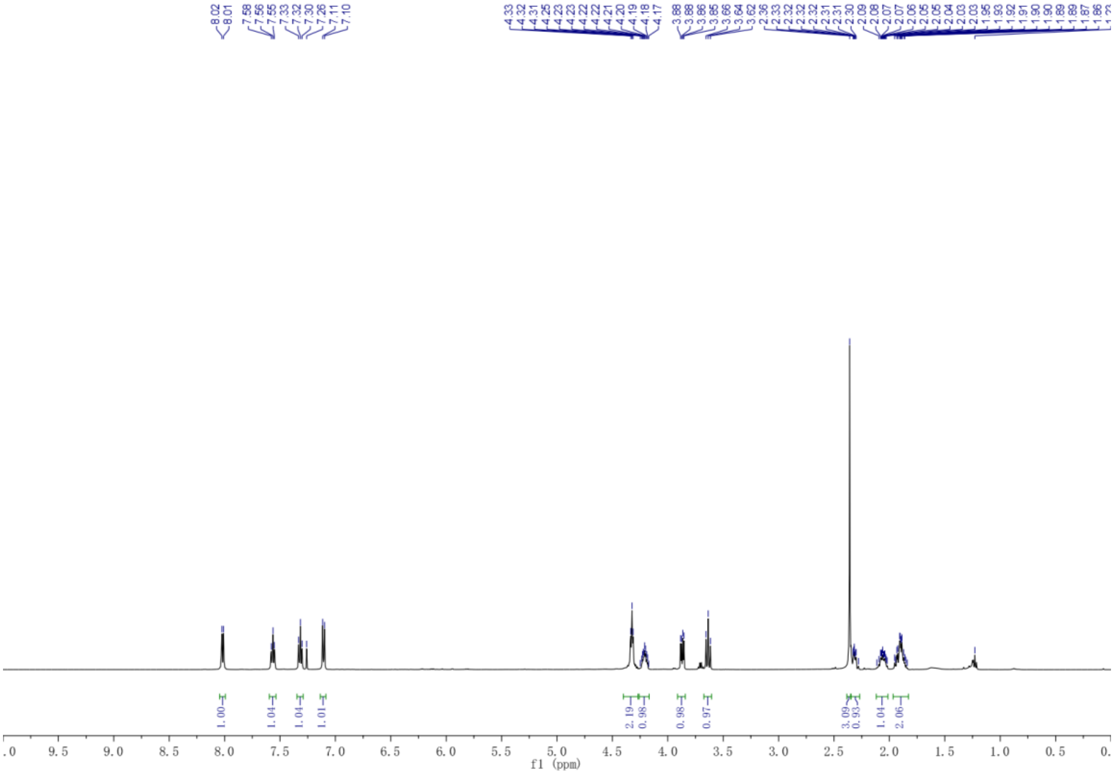
[1]H NMR of compound **111**（500 MHz, $CDCl_3$）



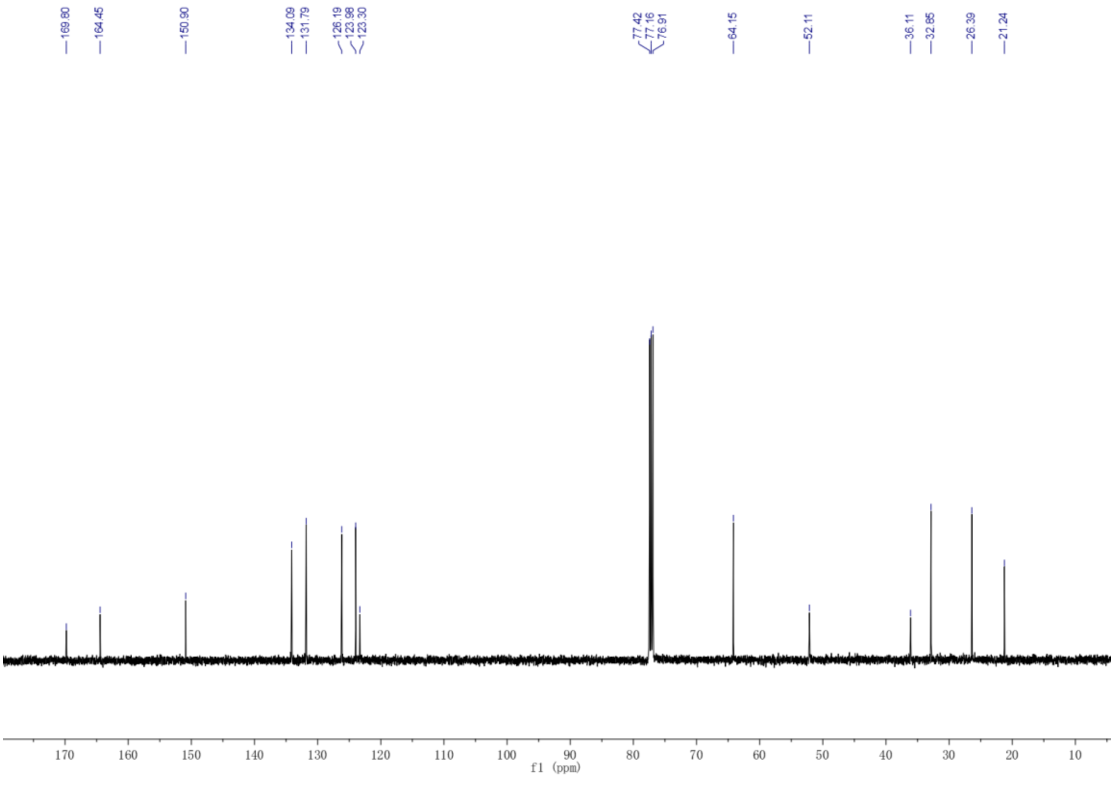
[13]C NMR of compound **111**（126 MHz, $CDCl_3$）



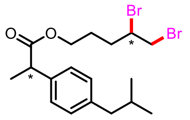
112



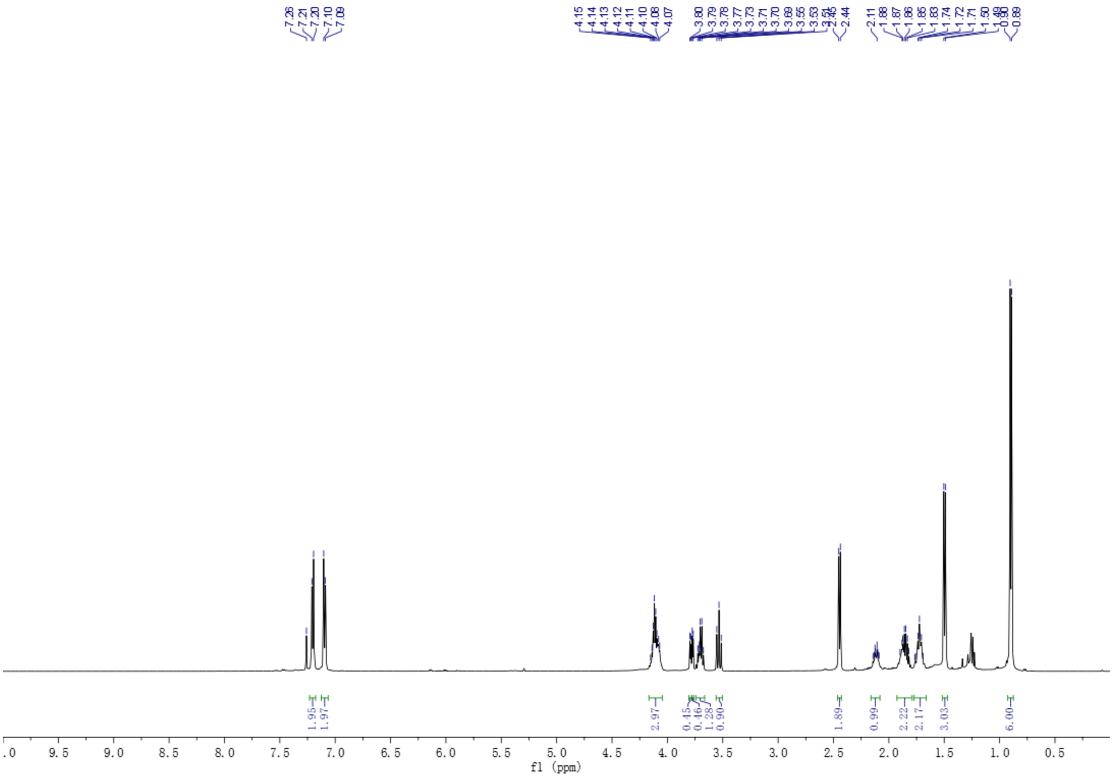
[1]H NMR of compound **112**（500 MHz, $CDCl_3$）



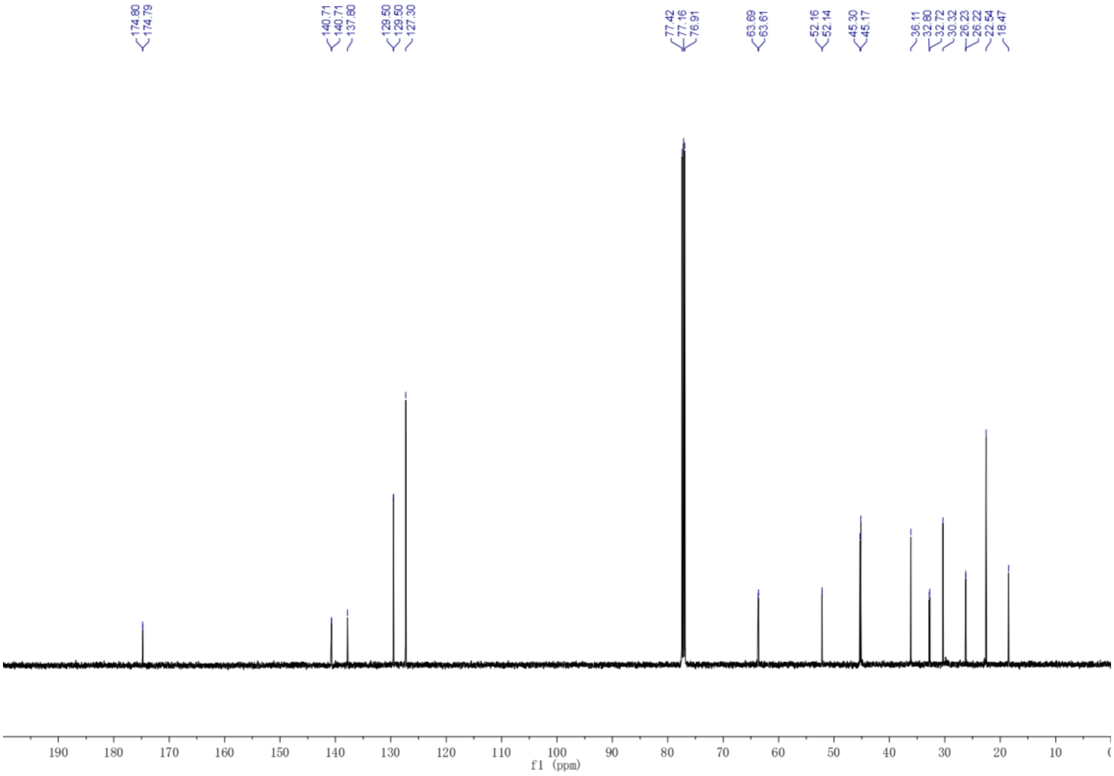
[13]C NMR of compound **112**（126 MHz, $CDCl_3$）



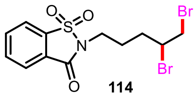
113 (dr = 1:1)



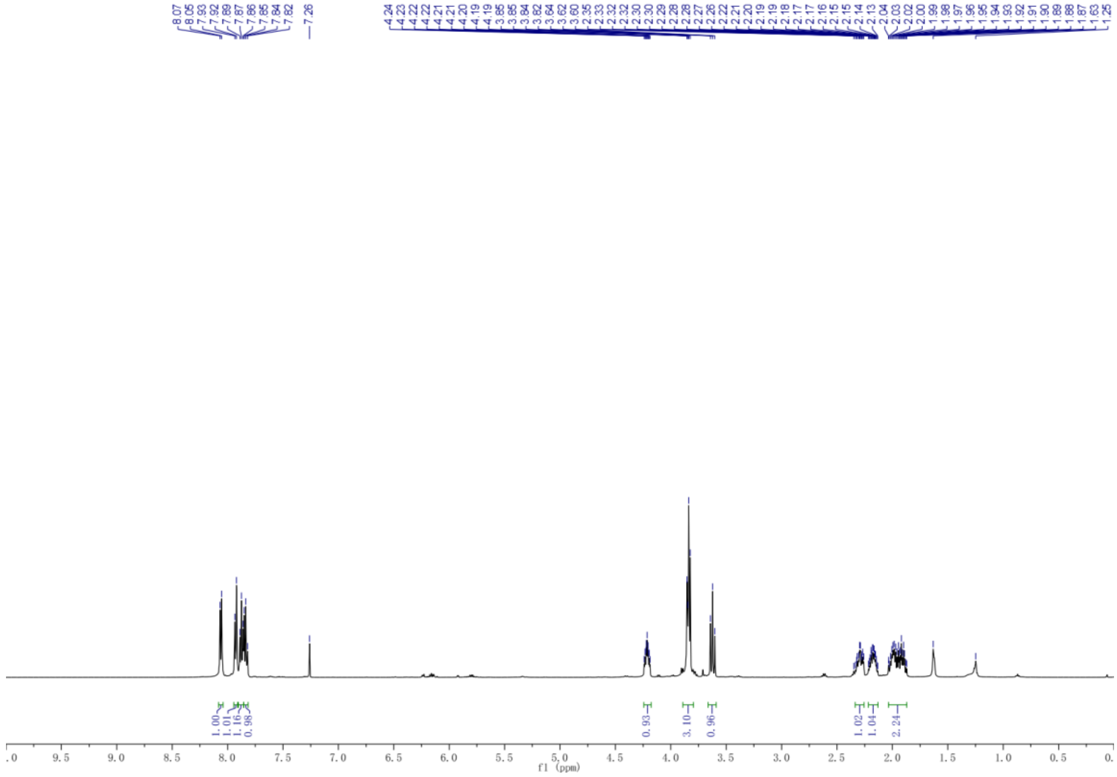
^{1}H NMR of compound **113**（500 MHz, $CDCl_3$）



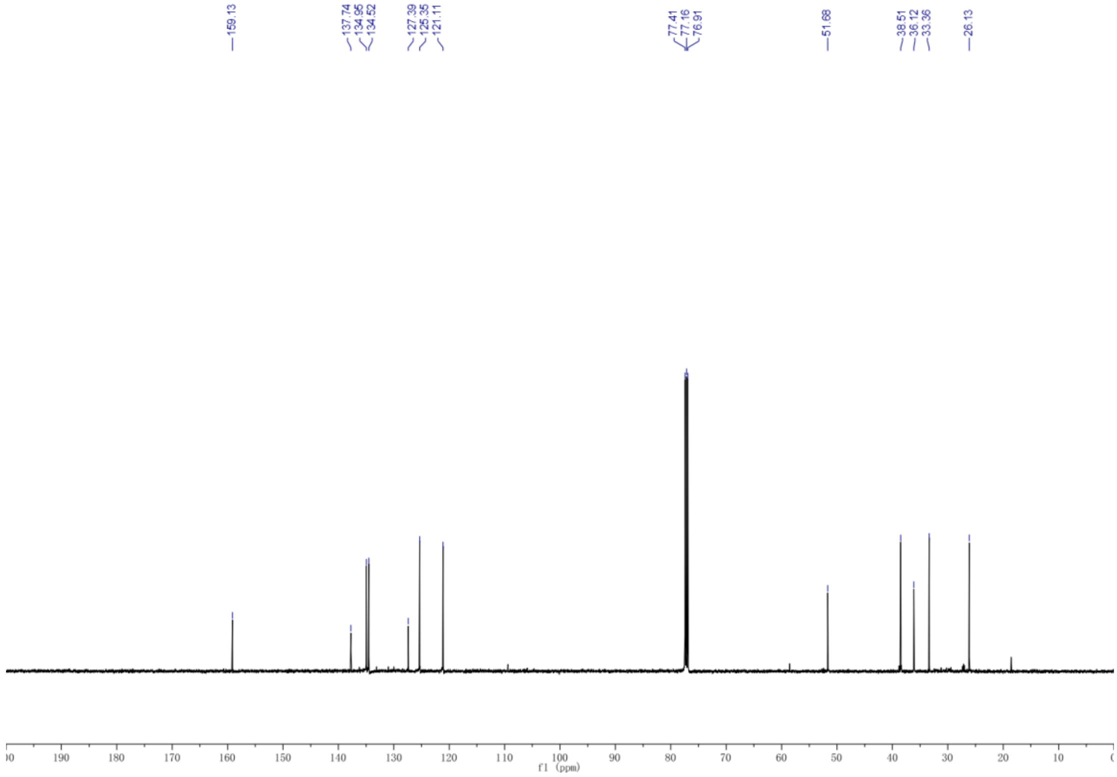
^{13}C NMR of compound **113**（126 MHz, $CDCl_3$）



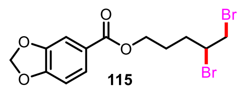
114



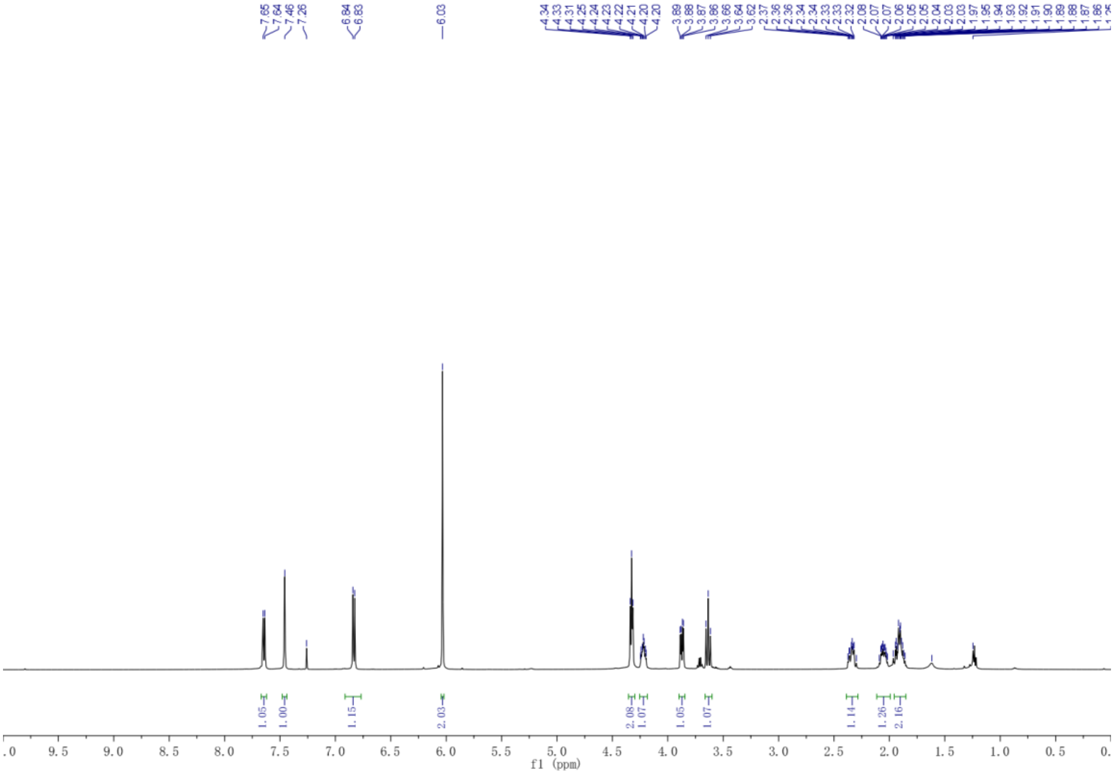
[1]H NMR of compound **114**（500 MHz, $CDCl_3$）



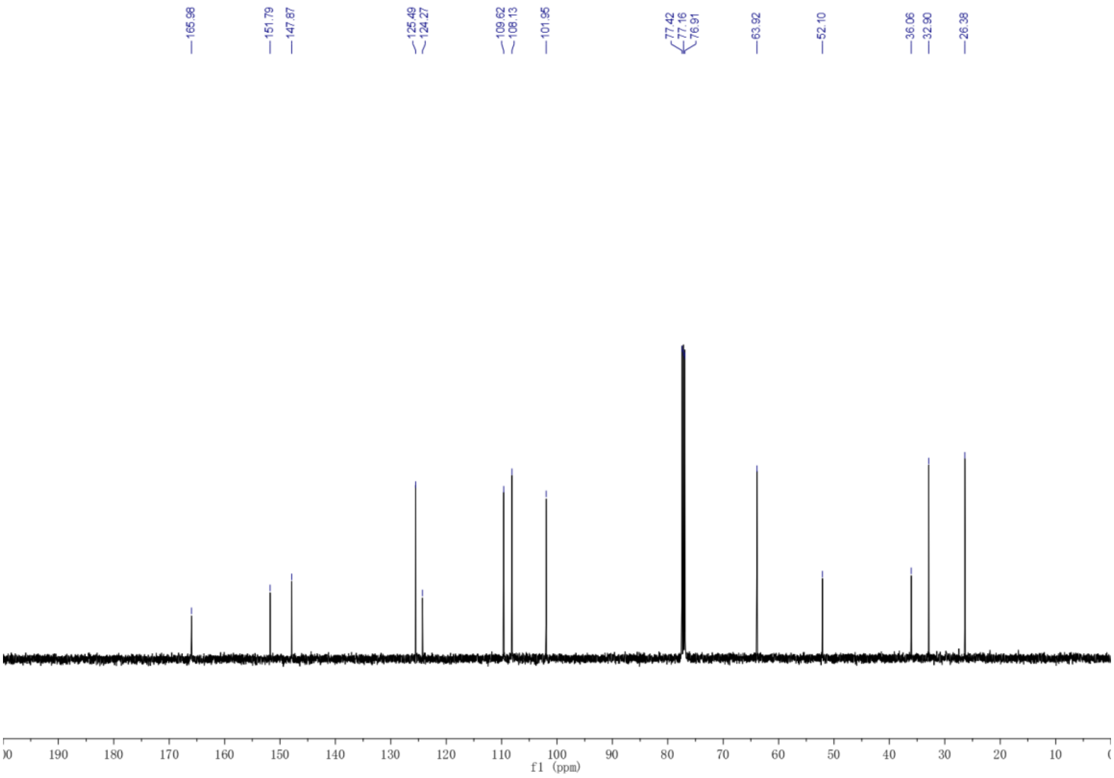
[13]C NMR of compound **114**（126 MHz, $CDCl_3$）



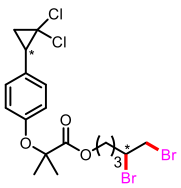
115



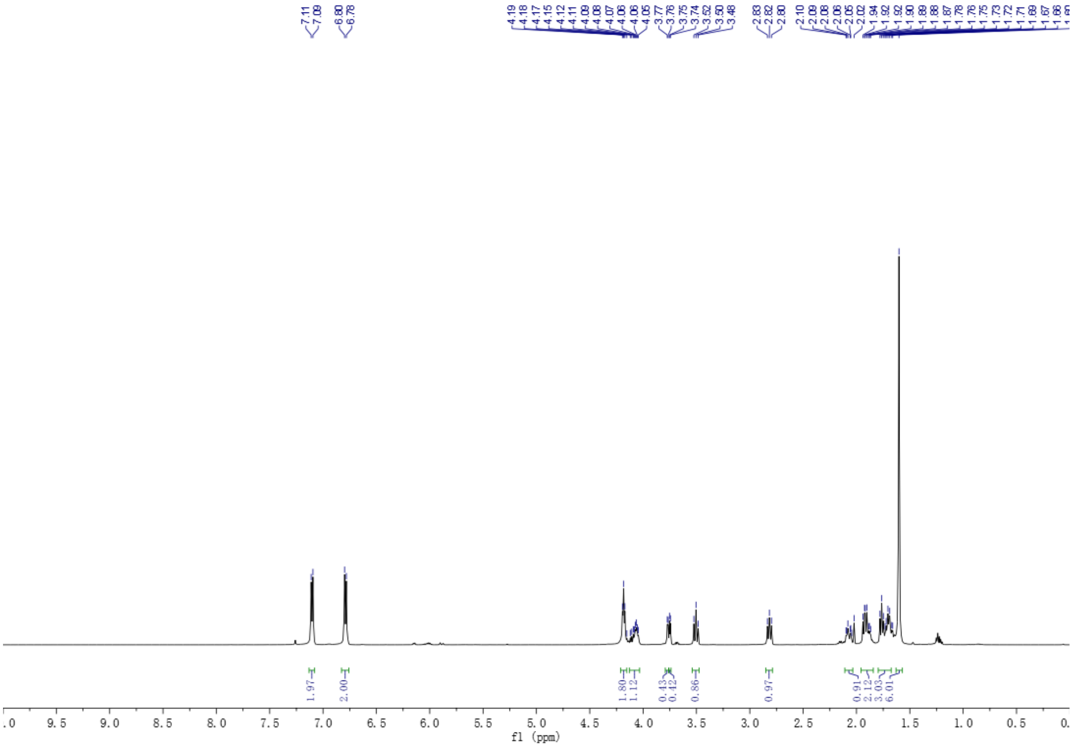
^{1}H NMR of compound **115**（500 MHz, $CDCl_3$）



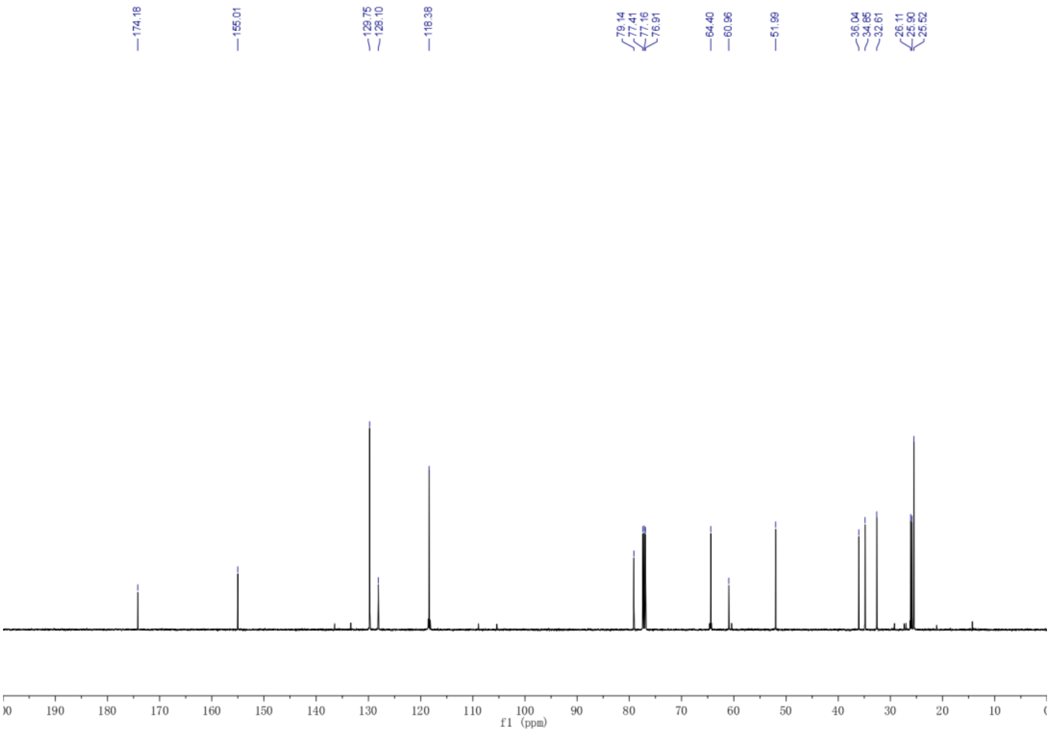
^{13}C NMR of compound **115**（126 MHz, $CDCl_3$）



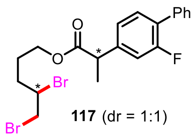
116 (dr = 1:1)



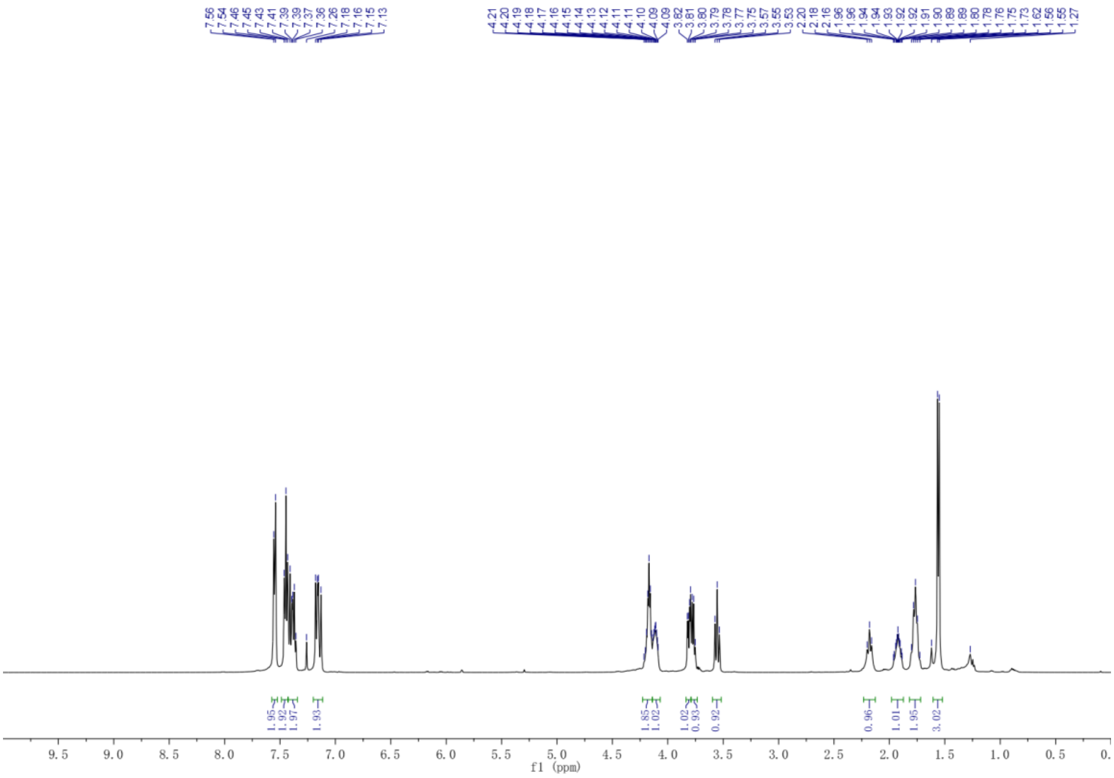
[1]H NMR of compound **116**（500 MHz, $CDCl_3$）



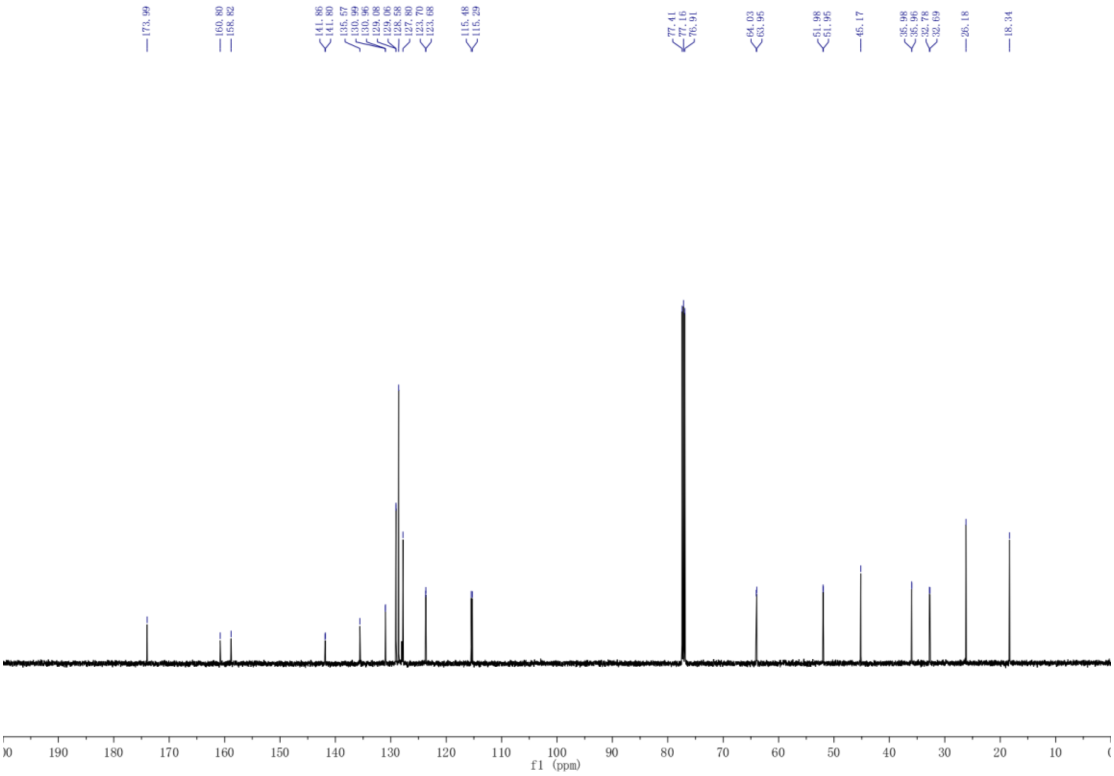
[13]C NMR of compound **116**（126 MHz, $CDCl_3$）



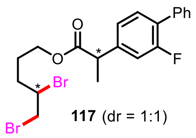
117 (dr = 1:1)



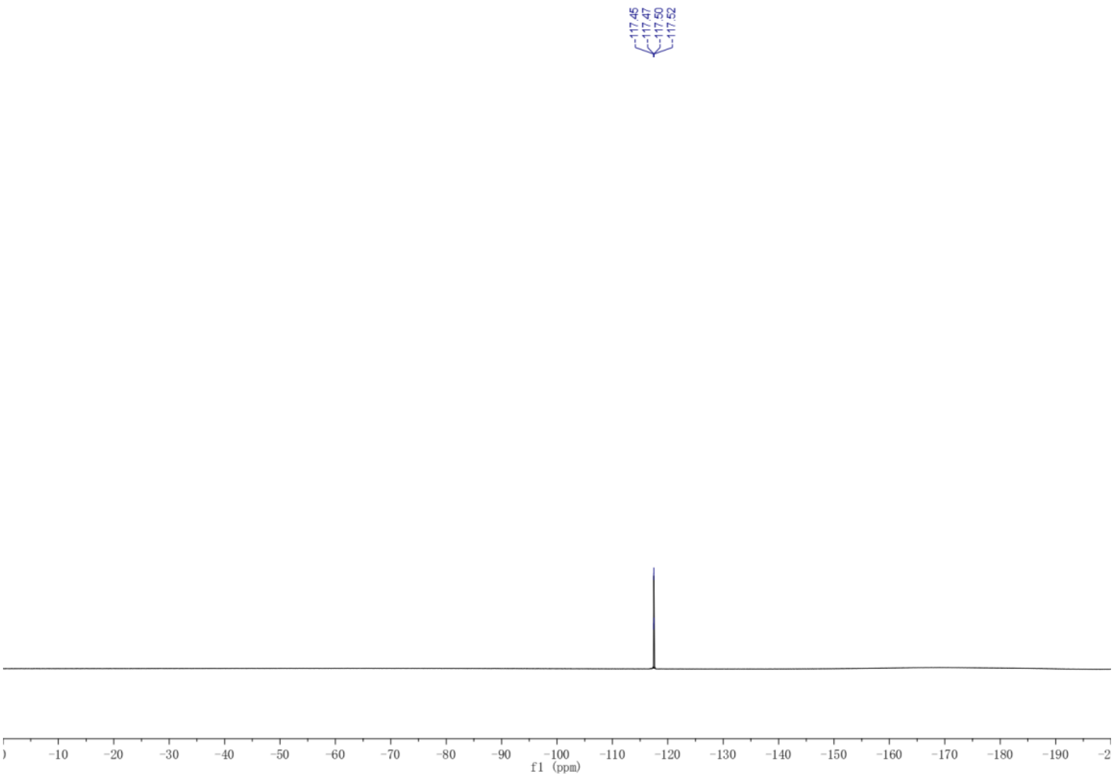
[1]H NMR of compound **117**（500 MHz, $CDCl_3$）



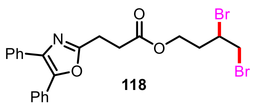
[13]C NMR of compound **117**（126 MHz, $CDCl_3$）



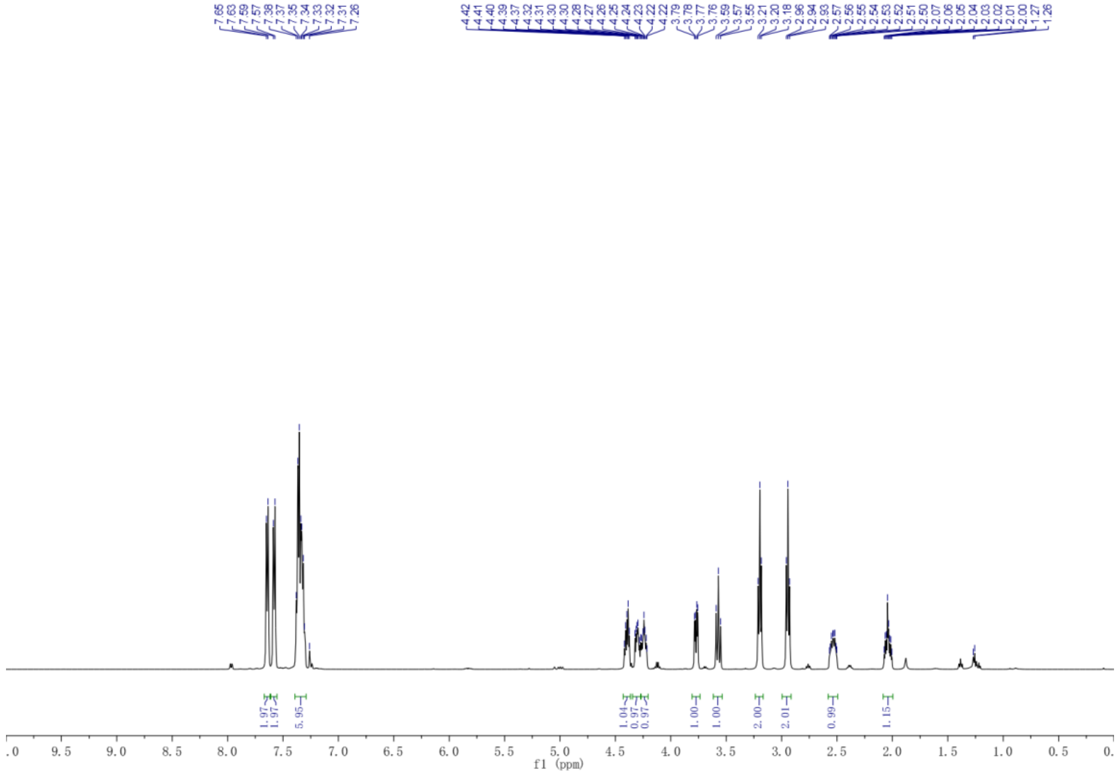
117 (dr = 1:1)



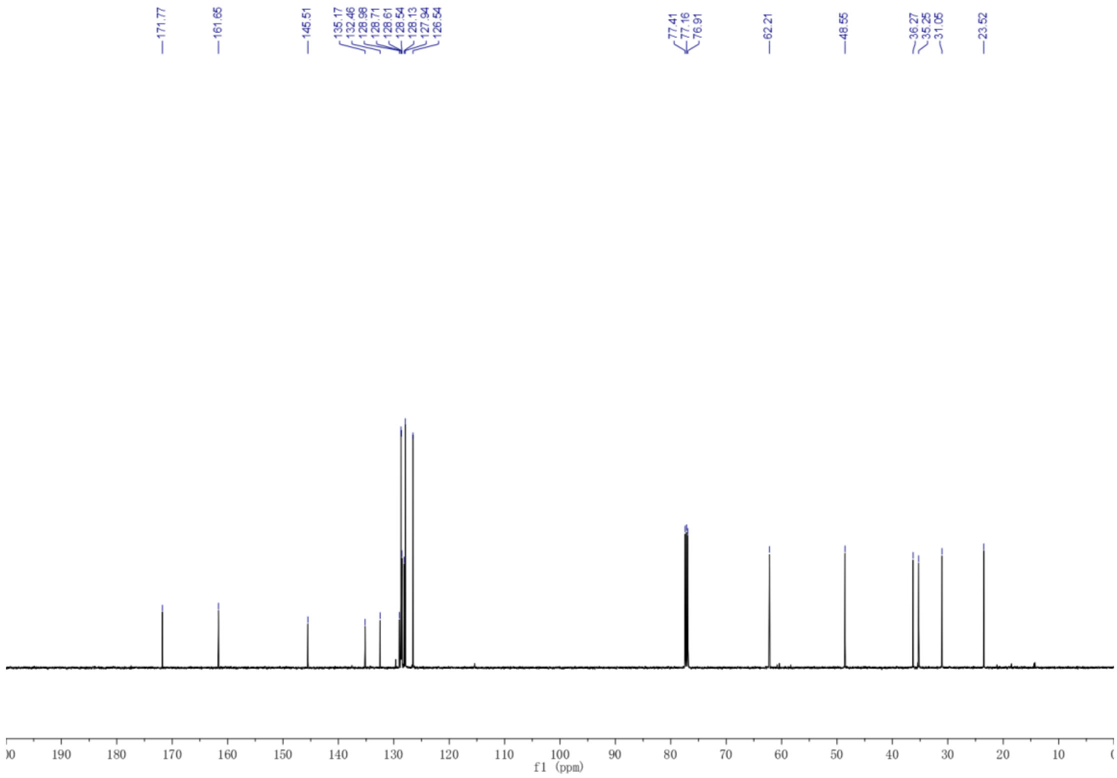
^{19}F NMR of compound **117**（471 MHz, $CDCl_3$）



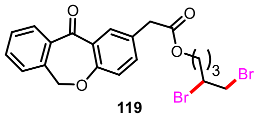
118



[1]H NMR of compound **118**（500 MHz, $CDCl_3$）



[13]C NMR of compound **118**（126 MHz, $CDCl_3$）



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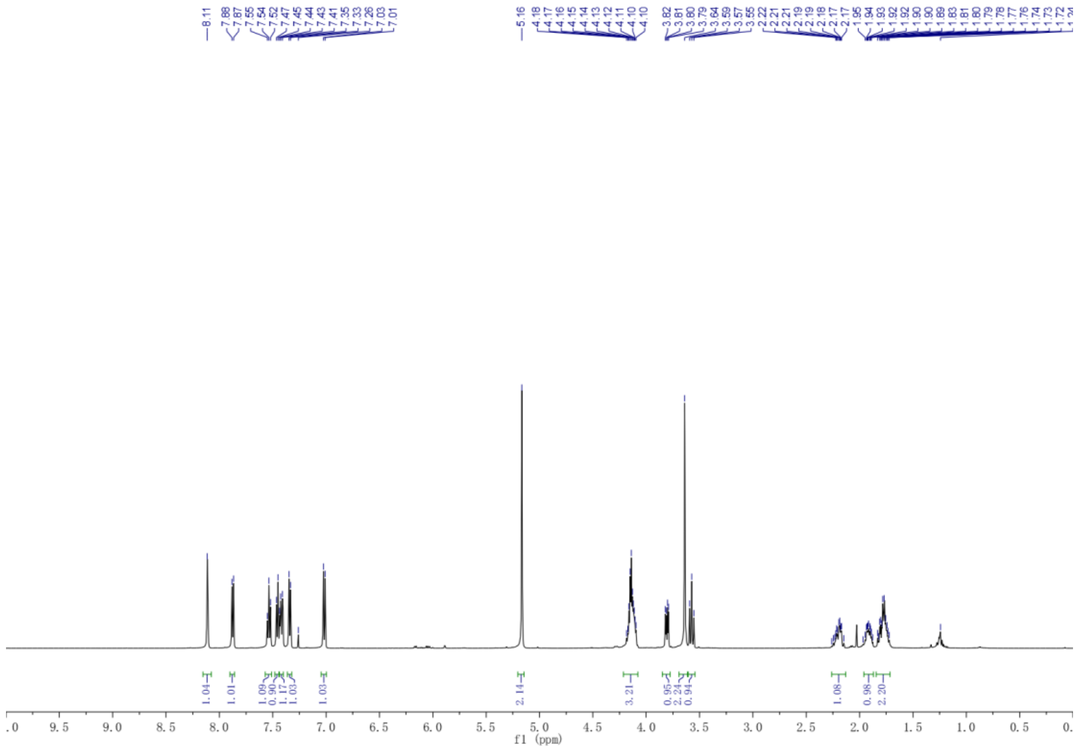
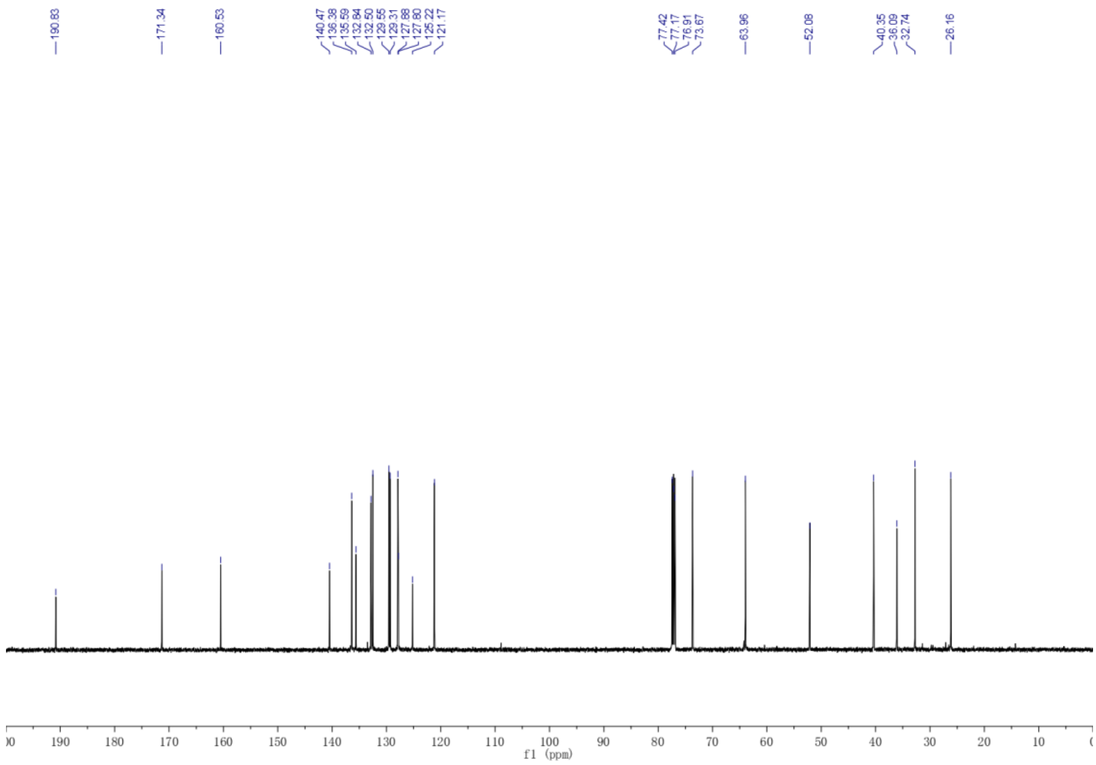
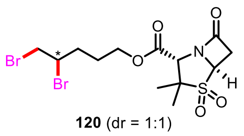


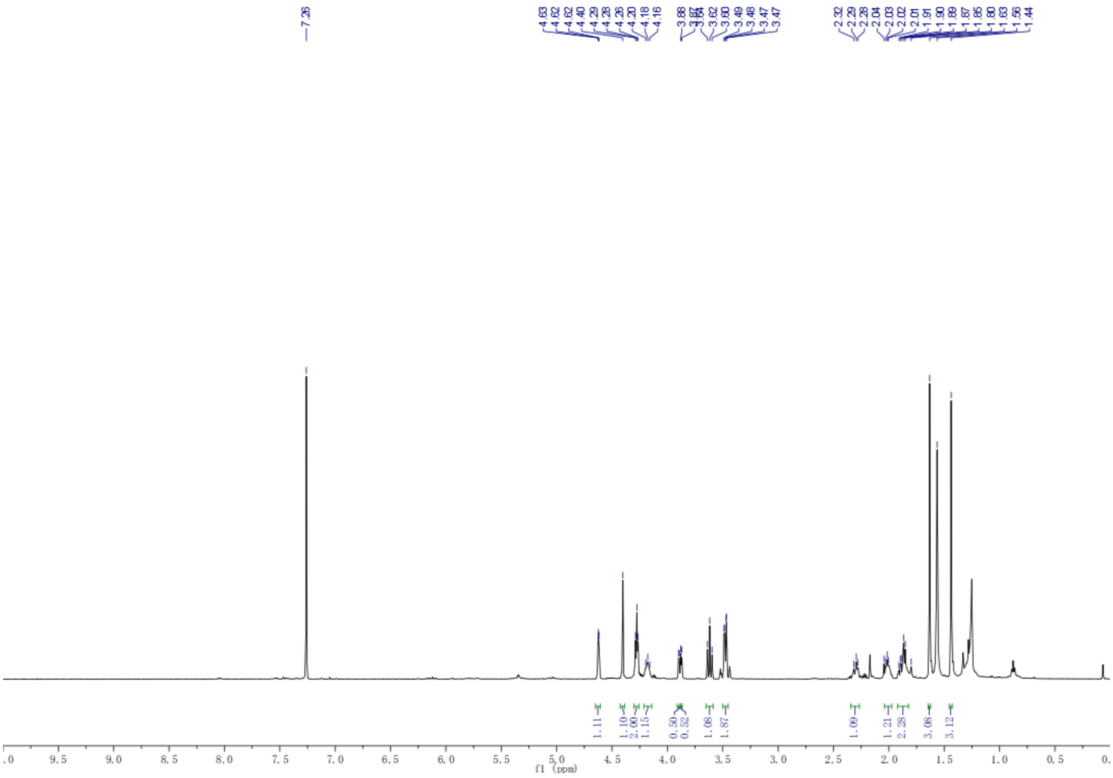
^{1}H NMR of compound **119**（500 MHz, $CDCl_3$）



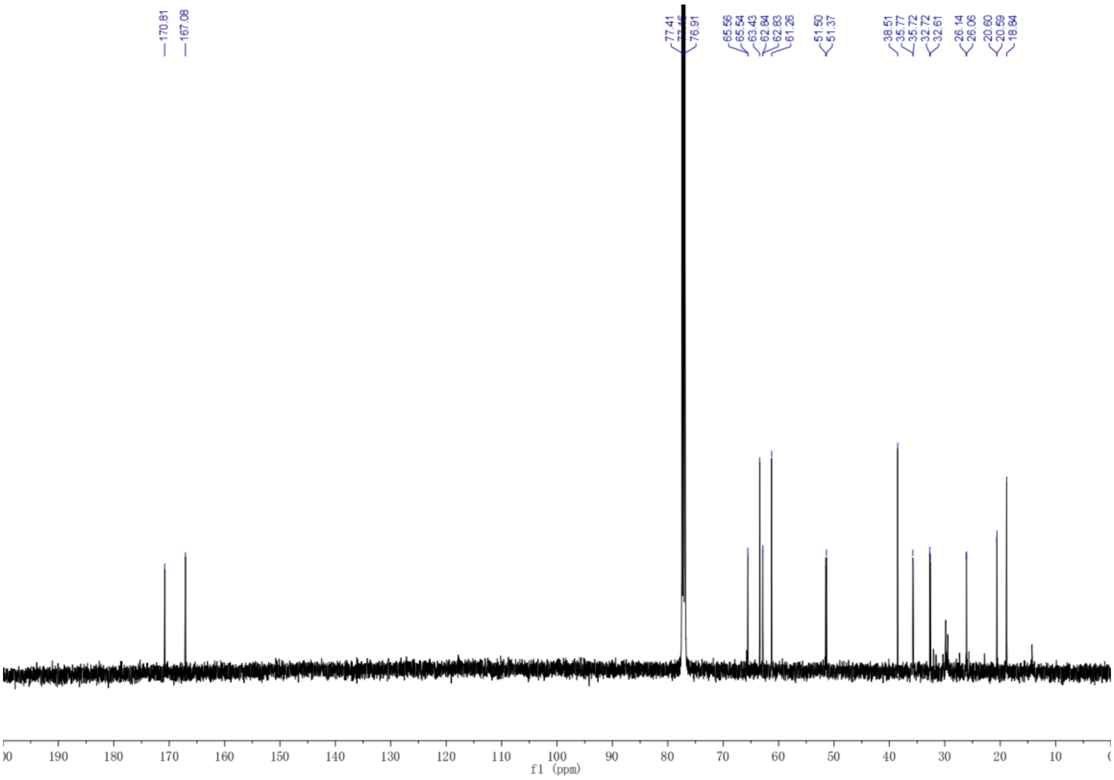
^{13}C NMR of compound **119**（126 MHz, $CDCl_3$）



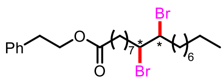
120 (dr = 1:1)



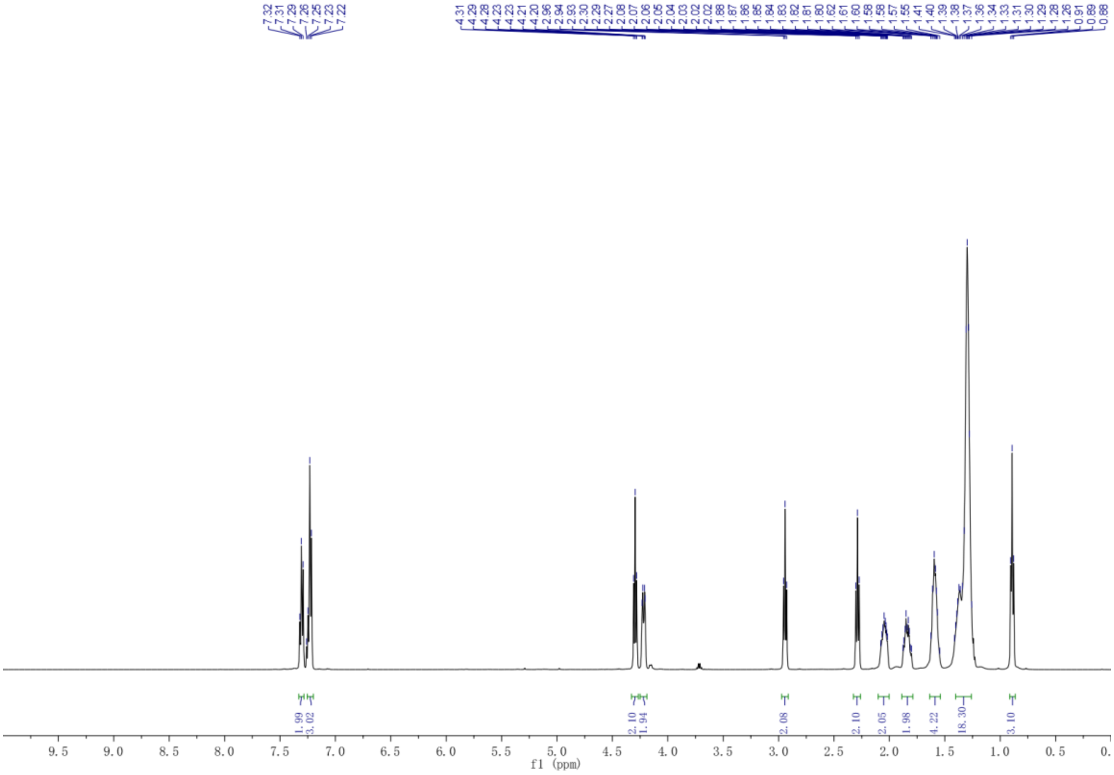
^{1}H NMR of compound **120**（500 MHz, CDCl$_3$）



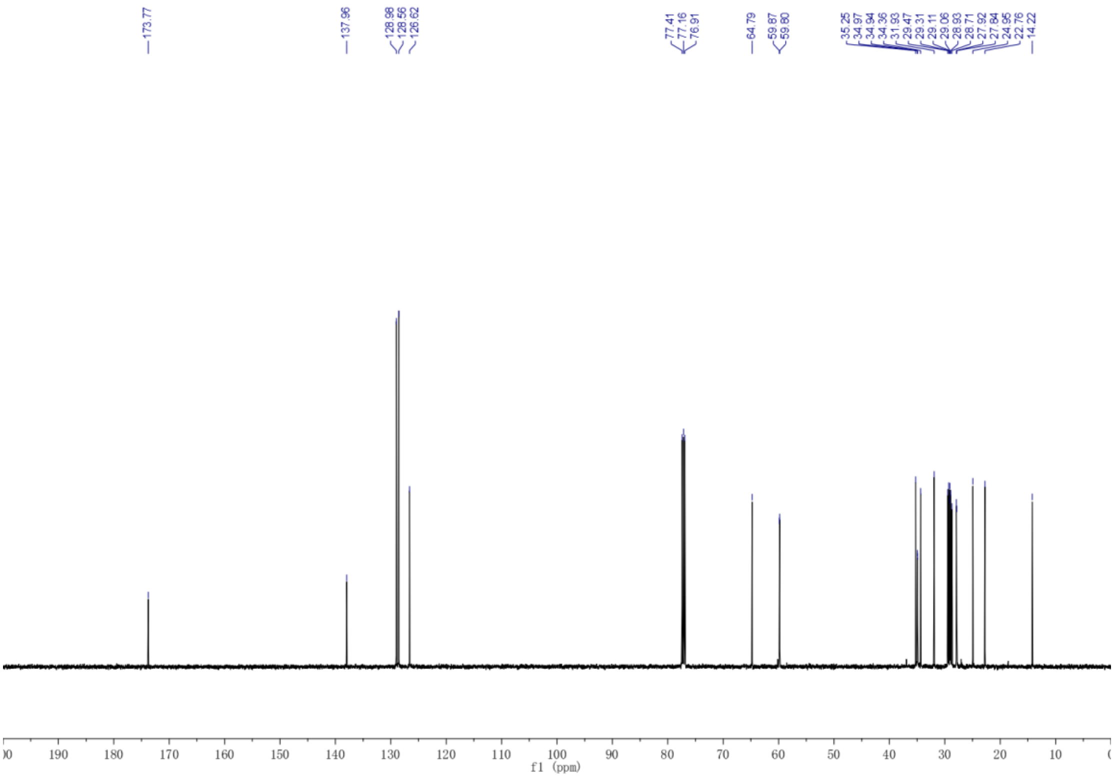
^{13}C NMR of compound **120**（126 MHz, CDCl$_3$）



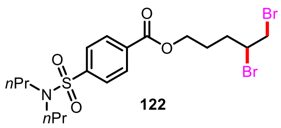
121 (dr = 1:1)

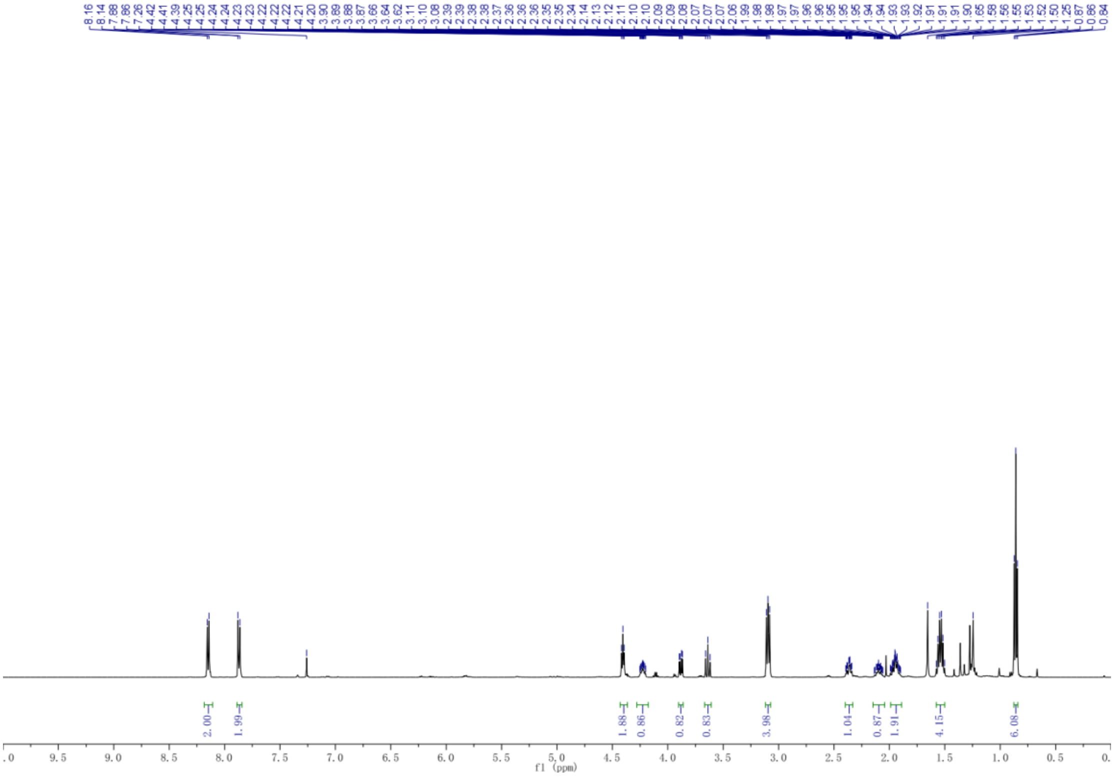


[1]H NMR of compound **121**（500 MHz, $CDCl_3$）

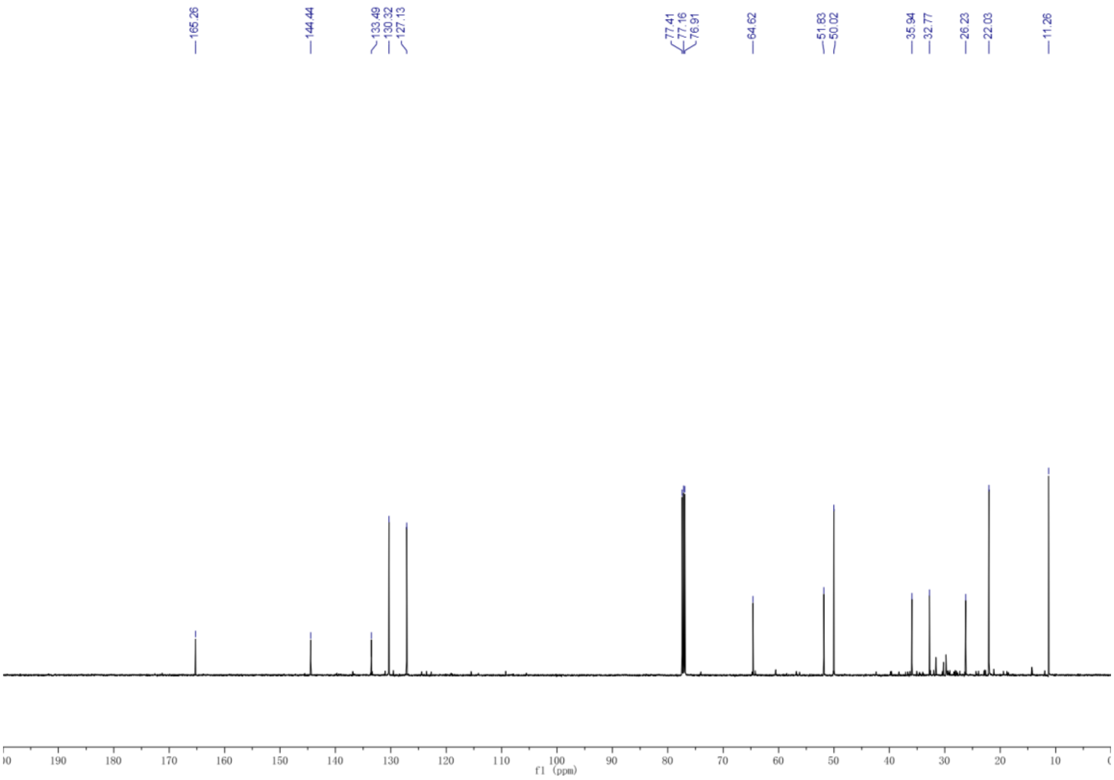


[13]C NMR of compound **121**（126 MHz, $CDCl_3$）

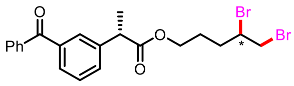




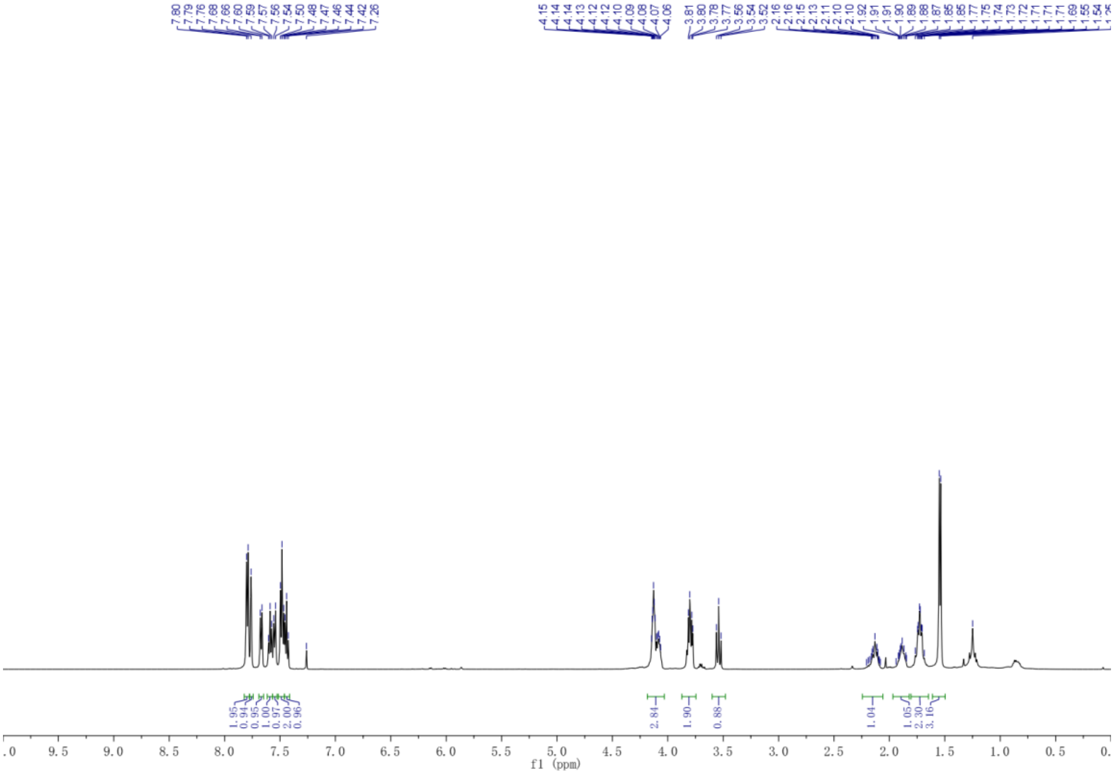
^{1}H NMR of compound **122**（500 MHz, $CDCl_3$）



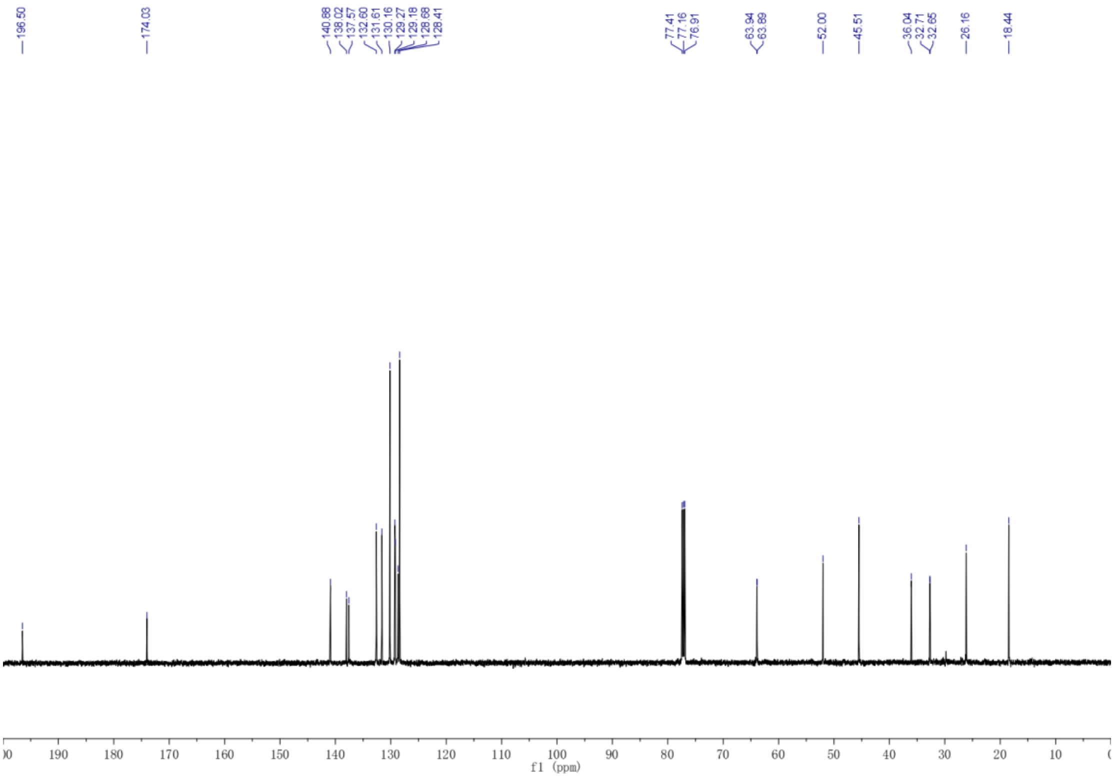
^{13}C NMR of compound **122**（126 MHz, $CDCl_3$）



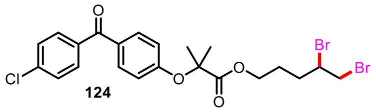
123 (dr = 1:1)



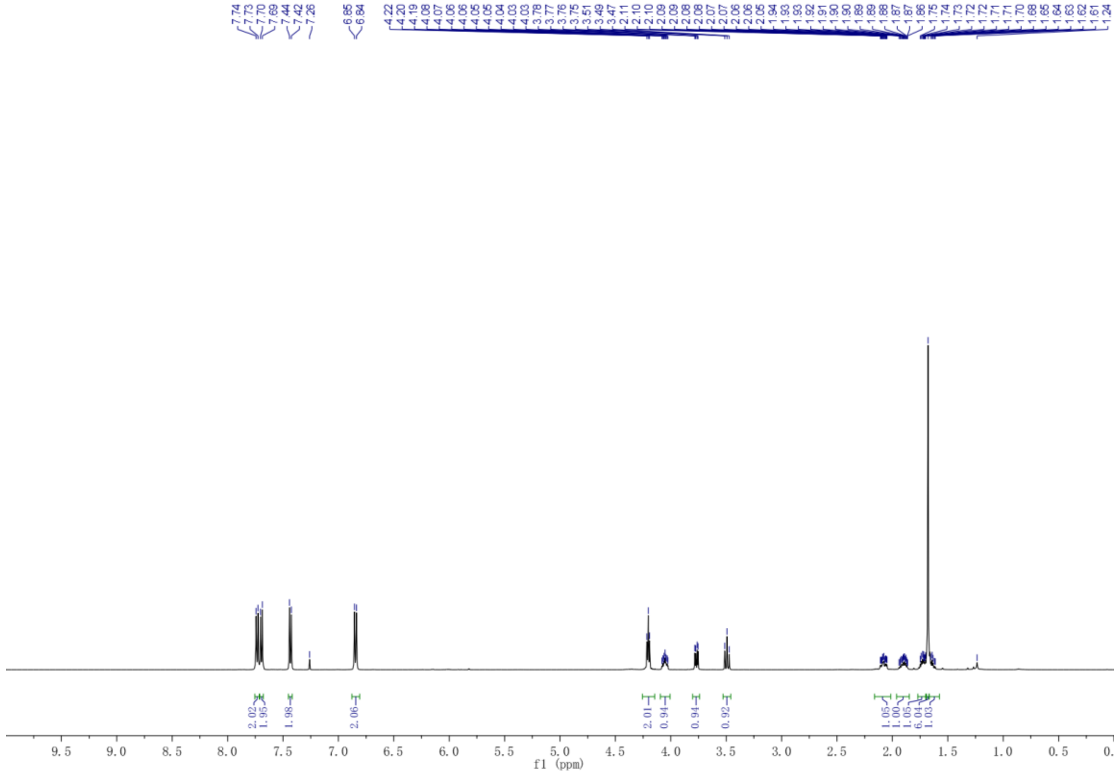
^{1}H NMR of compound **123**（500 MHz, CDCl$_3$）



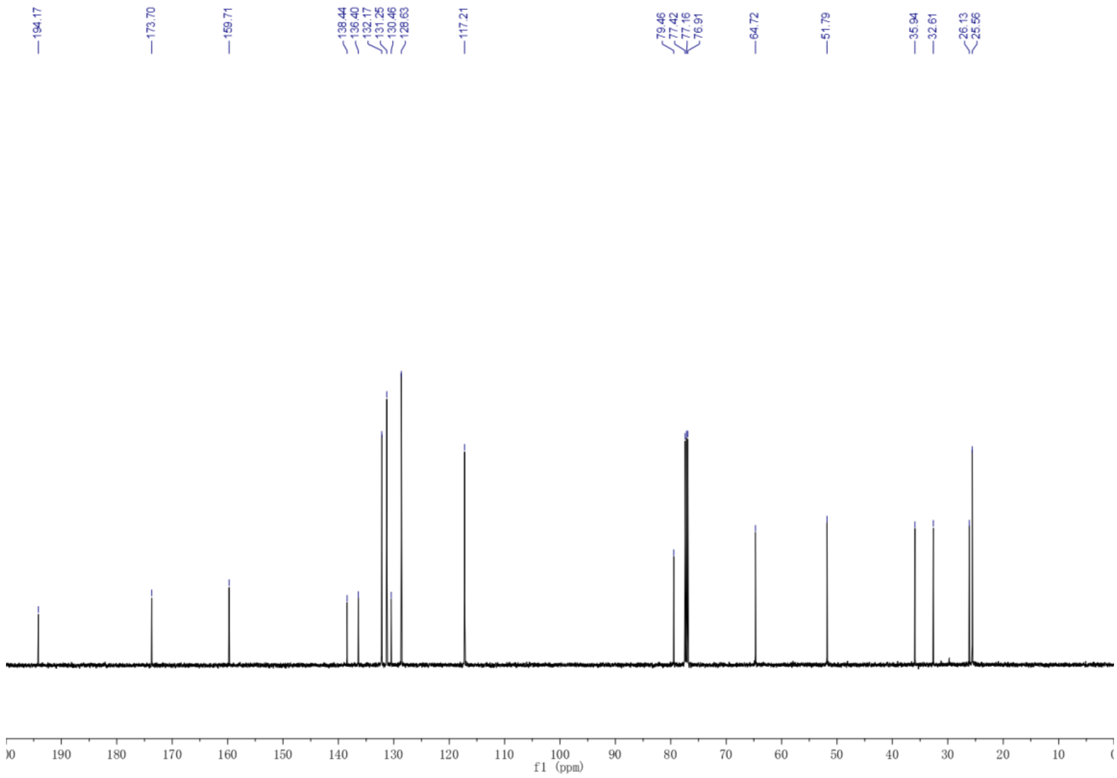
^{13}C NMR of compound **123**（126 MHz, CDCl$_3$）



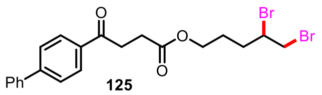
124



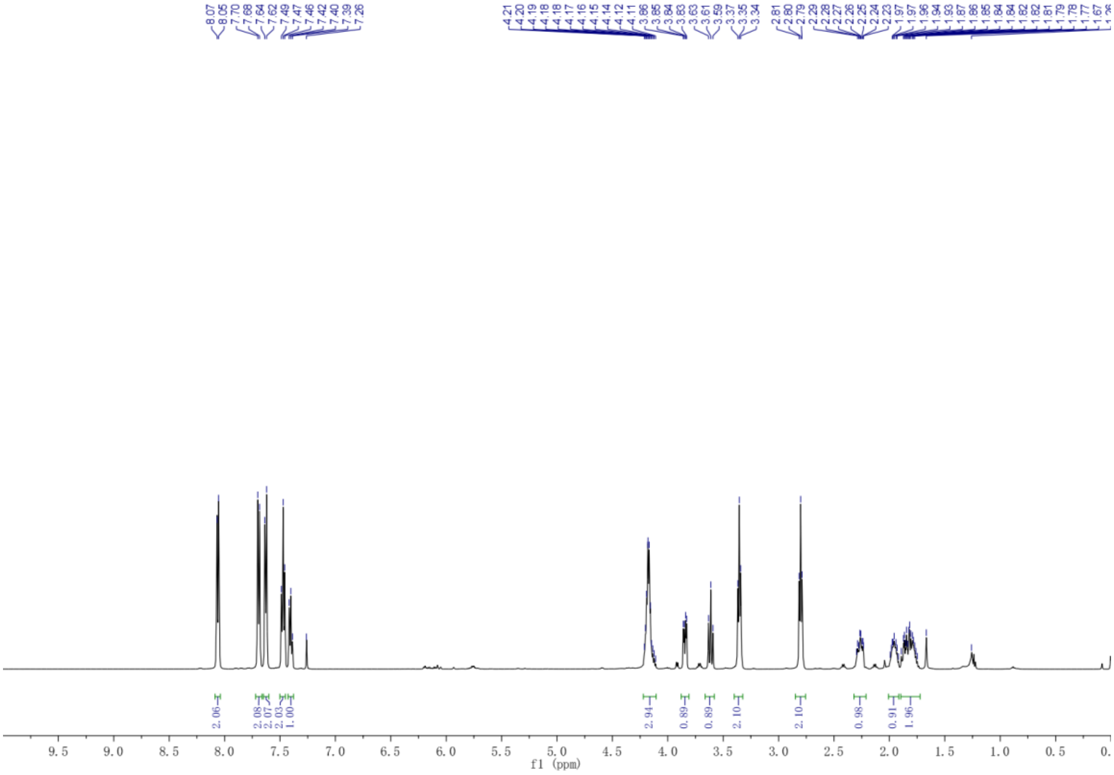
^{1}H NMR of compound **124**（500 MHz, $CDCl_3$）



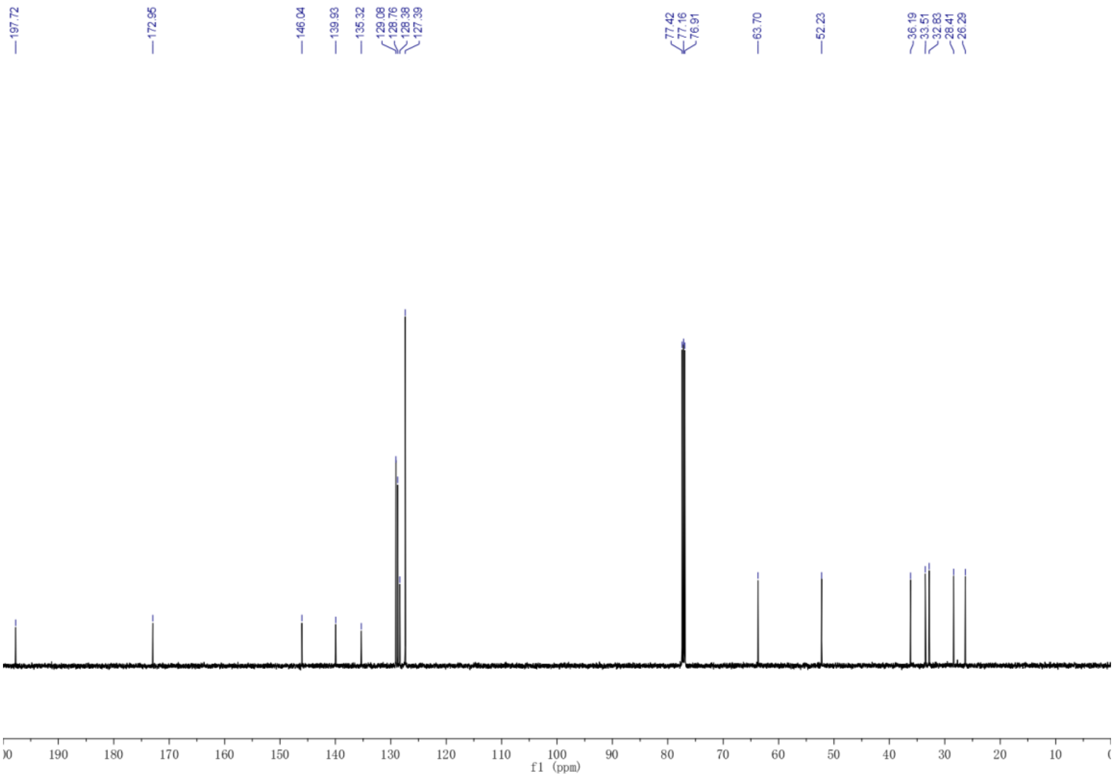
^{13}C NMR of compound **124**（126 MHz, $CDCl_3$）



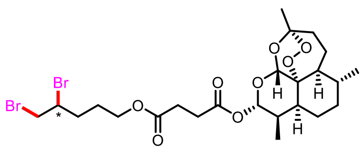
125



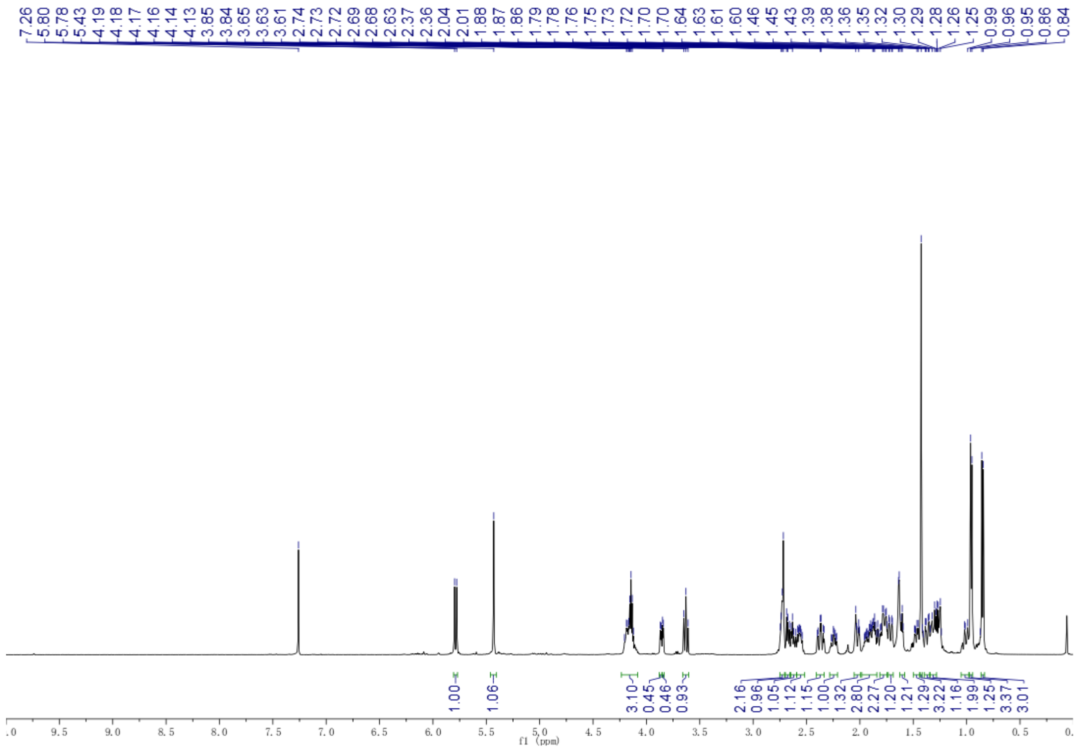
^{1}H NMR of compound **125**（500 MHz, $CDCl_3$）



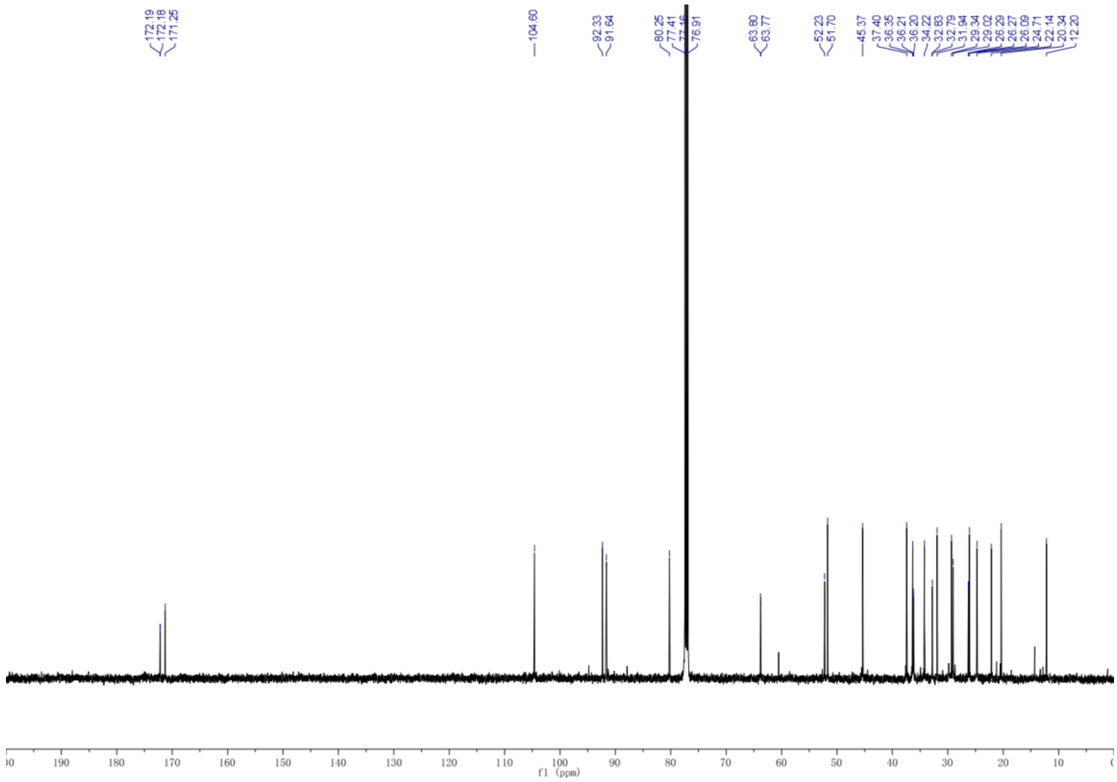
^{13}C NMR of compound **125**（126 MHz, $CDCl_3$）



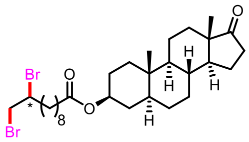
126 (dr = 1:1)



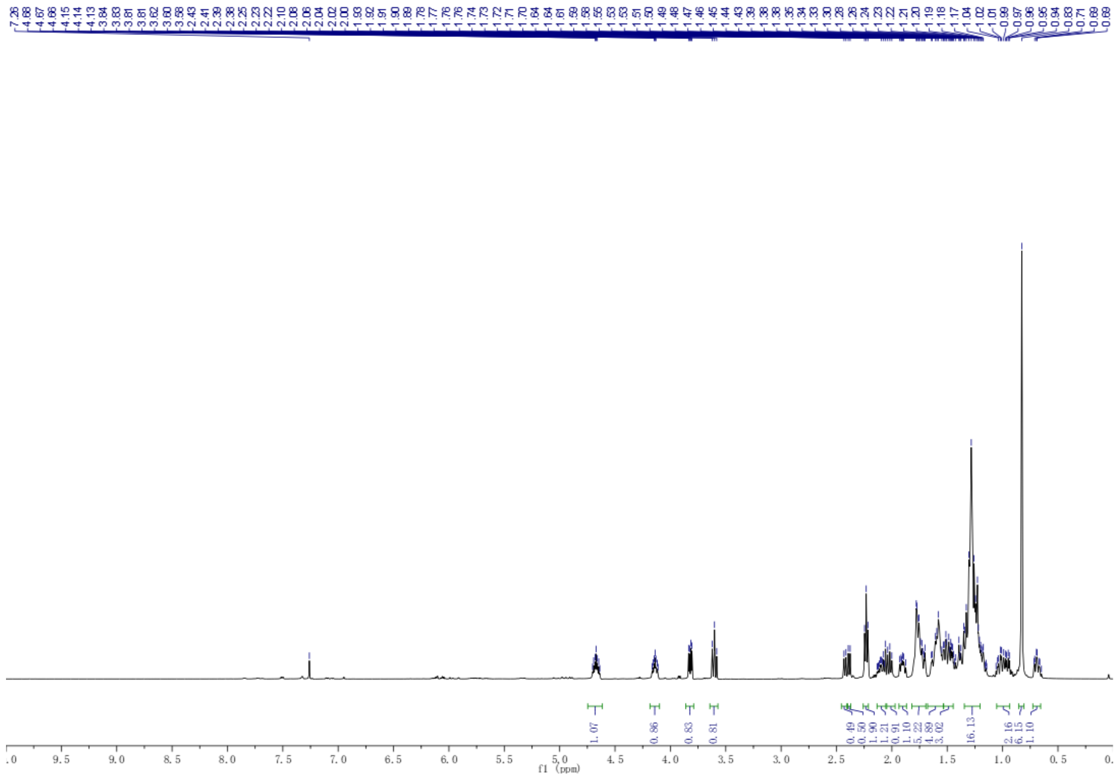
^{1}H NMR of compound **126**（500 MHz, CDCl$_3$）



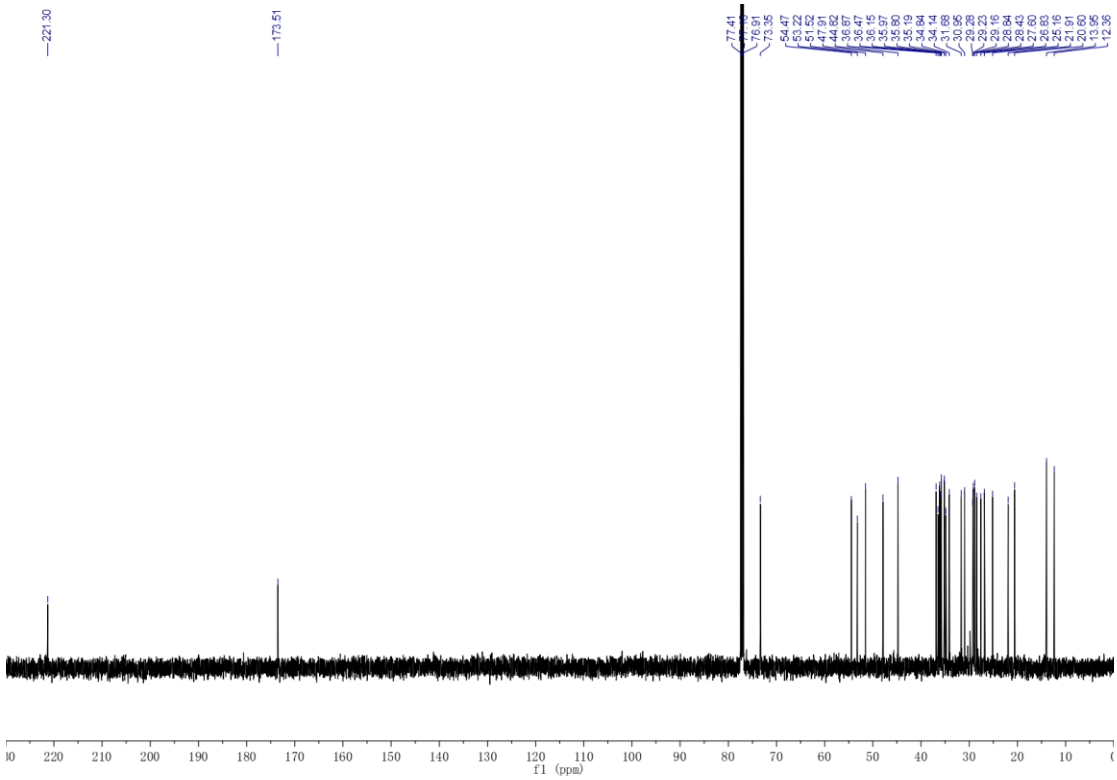
^{13}C NMR of compound **126**（126 MHz, CDCl$_3$）



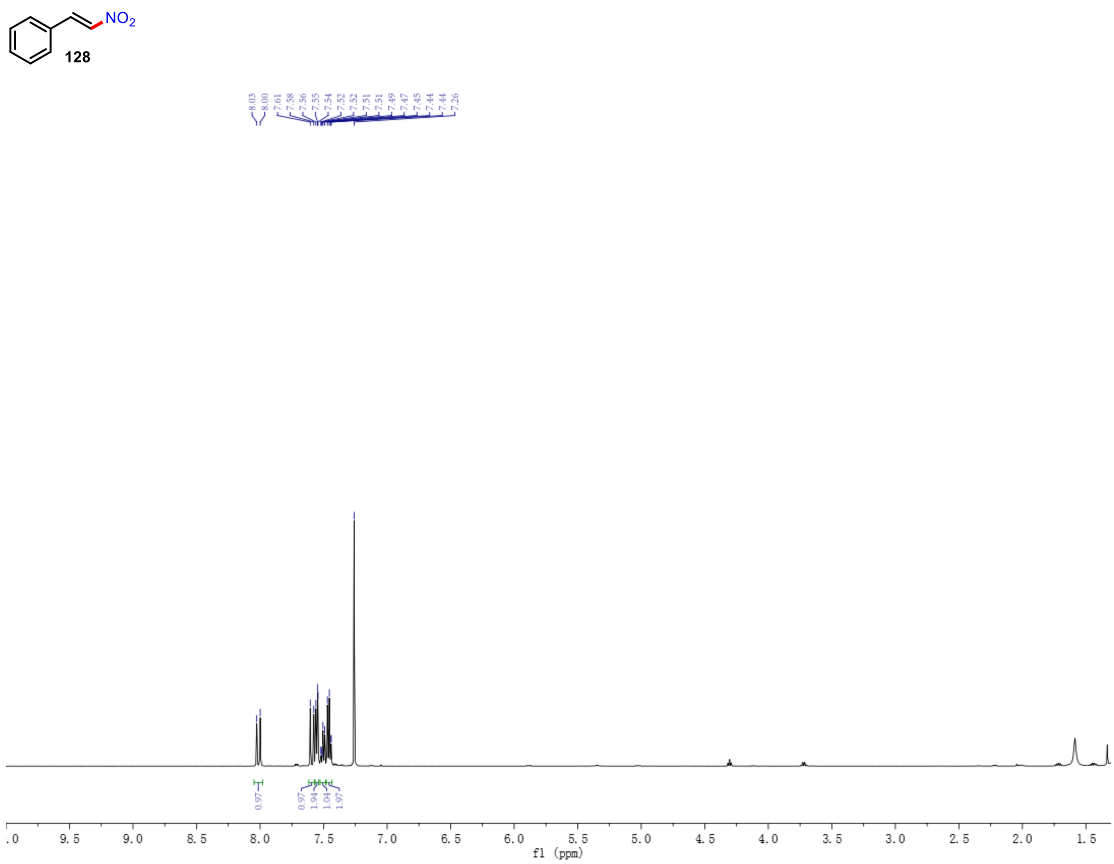
127 (dr = 1:1)



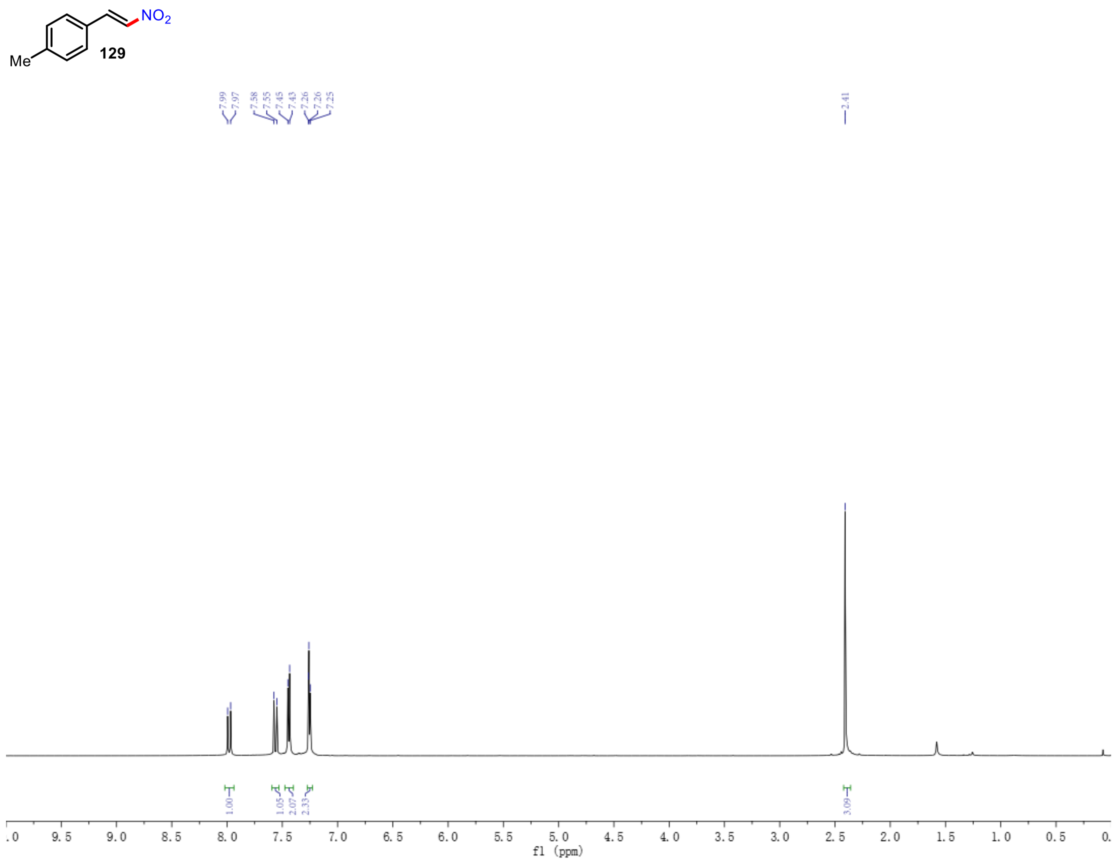
[1]H NMR of compound **127**（500 MHz, $CDCl_3$）



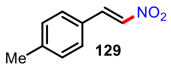
[13]C NMR of compound **127**（126 MHz, $CDCl_3$）



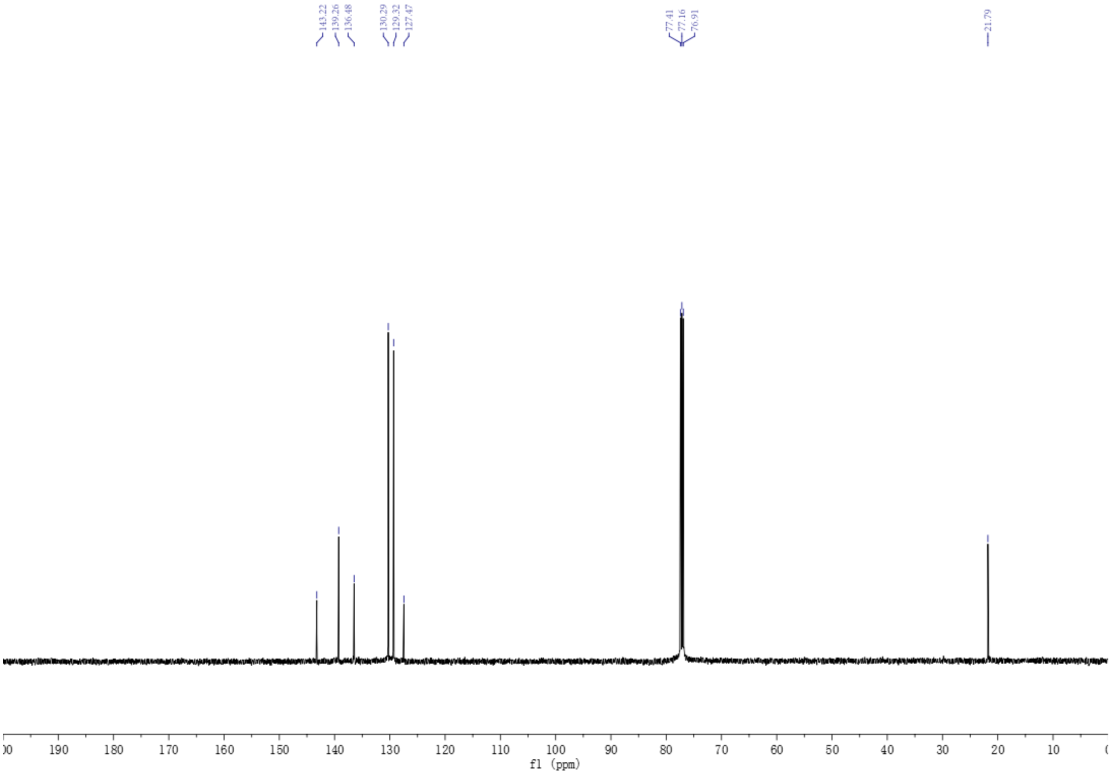
^{1}H NMR of compound **128**（500 MHz, $CDCl_3$）



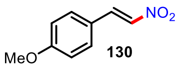
^{1}H NMR of compound **129**（500 MHz, $CDCl_3$）



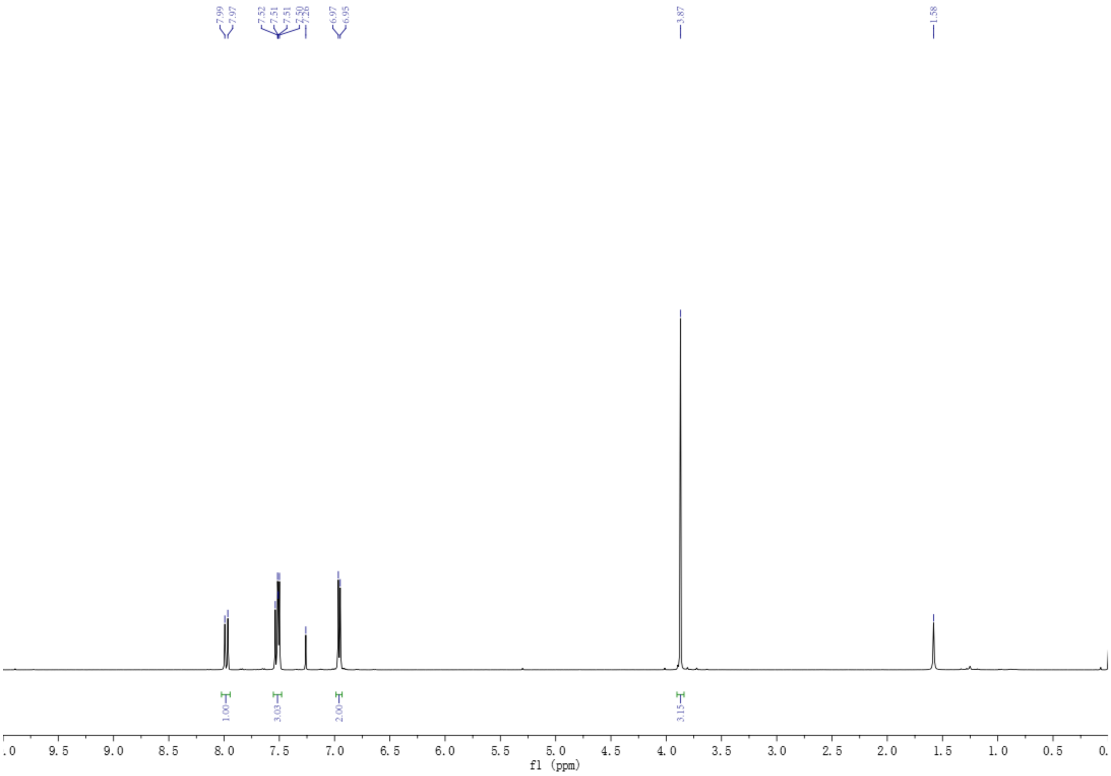
129



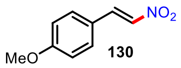
^{13}C NMR of compound **129**（126 MHz, $CDCl_3$）



130



^{1}H NMR of compound **130**（500 MHz, $CDCl_3$）



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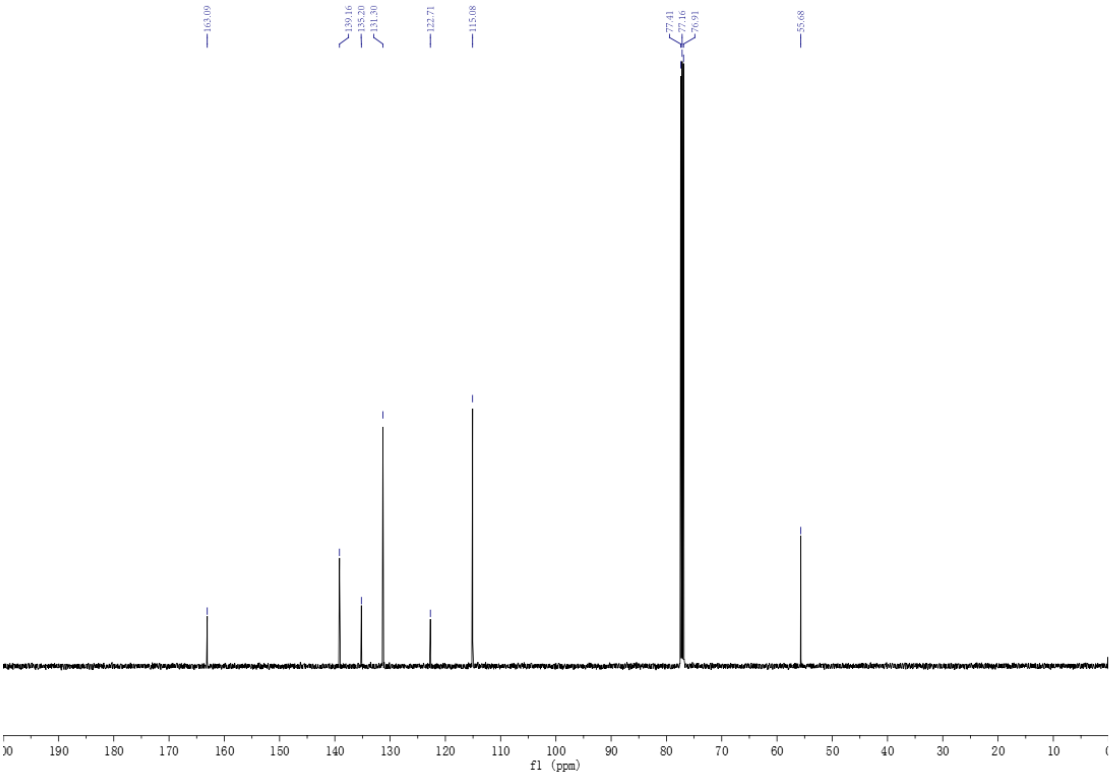
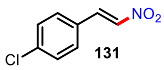


^{13}C NMR of compound **130**（126 MHz, $CDCl_3$）



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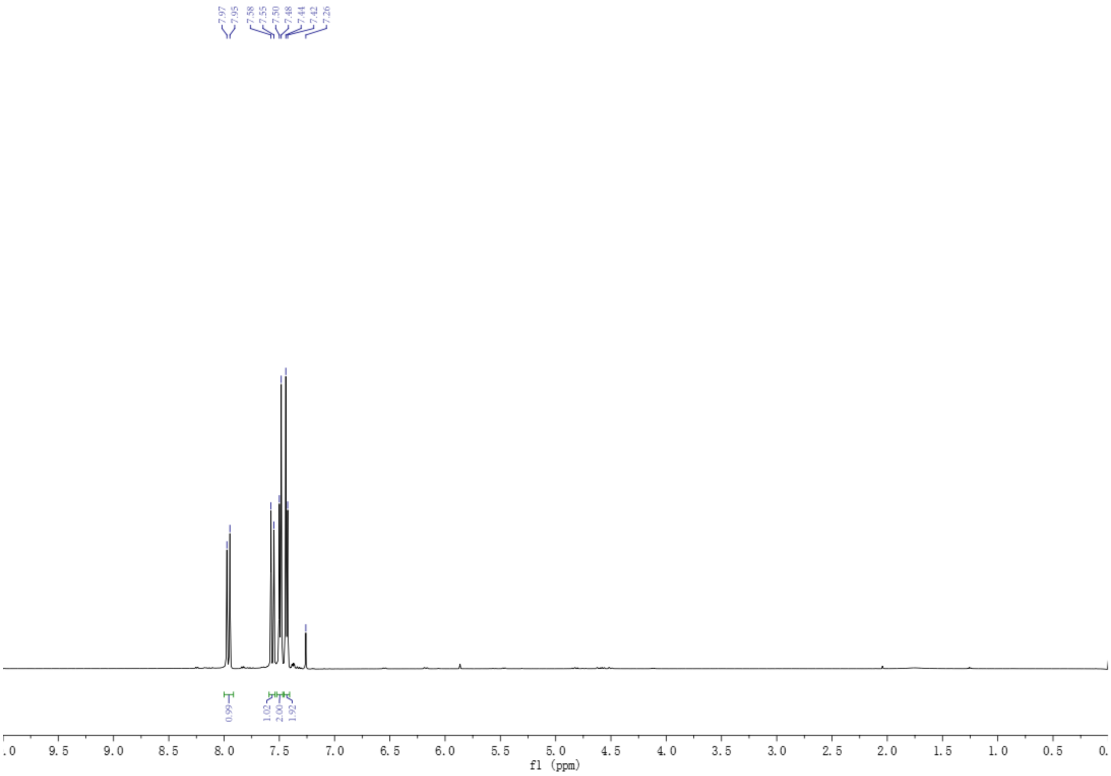
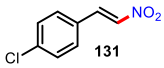
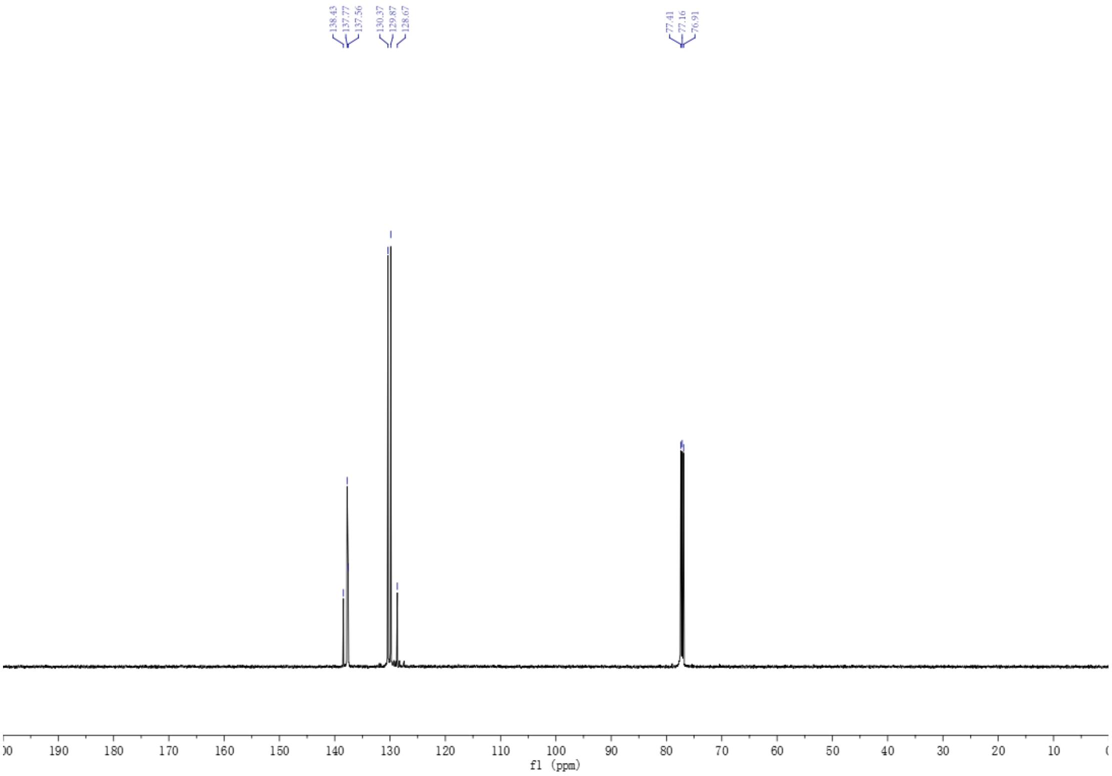


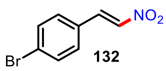
^{1}H NMR of compound **131**（500 MHz, $CDCl_3$）



131



^{13}C NMR of compound **131**（126 MHz, $CDCl_3$）



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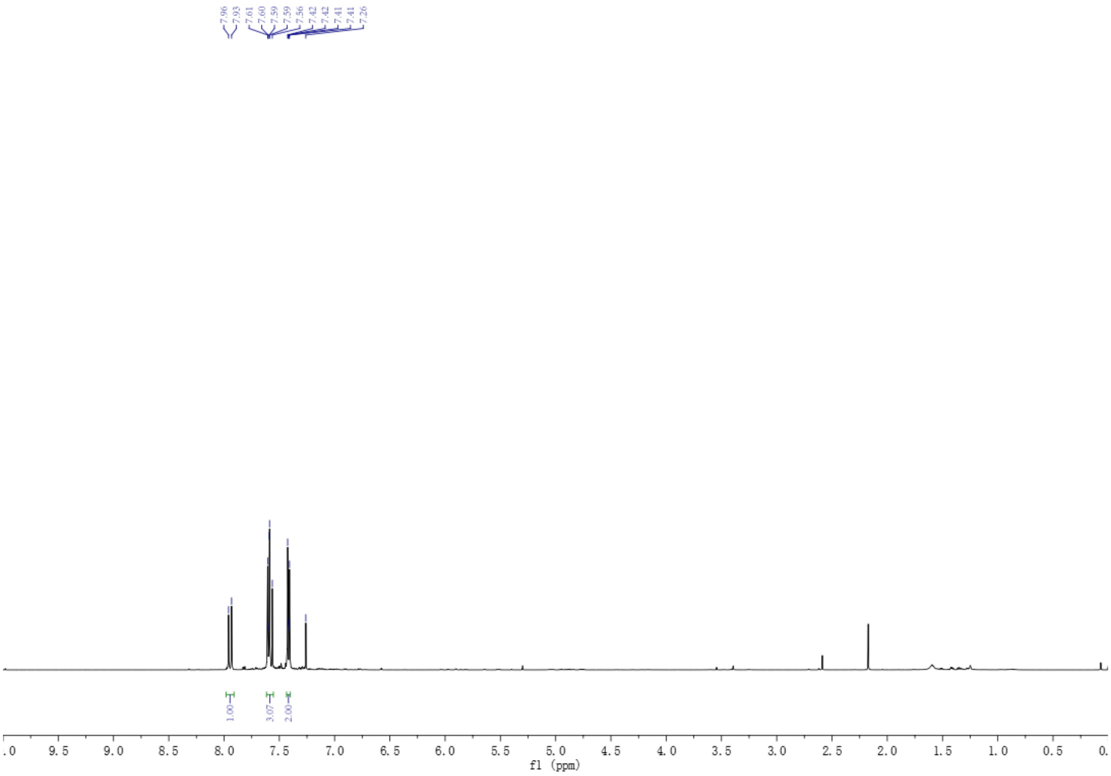
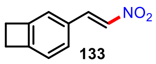


^{1}H NMR of compound **132**（500 MHz, $CDCl_3$）



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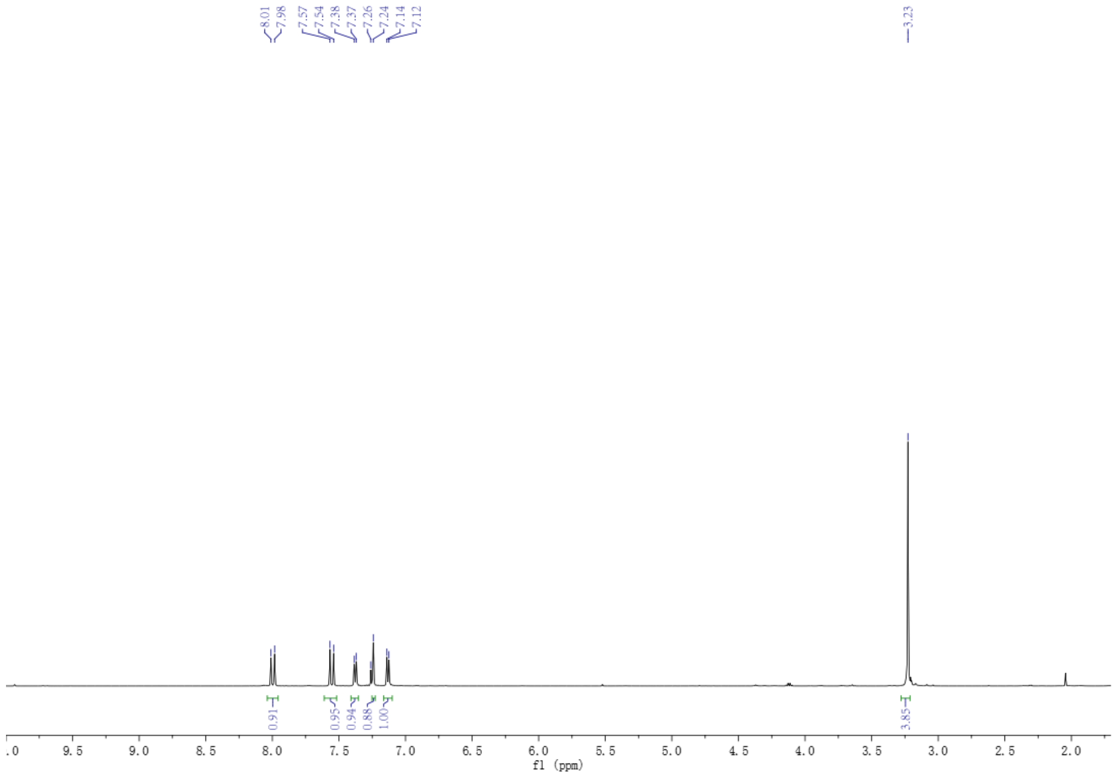
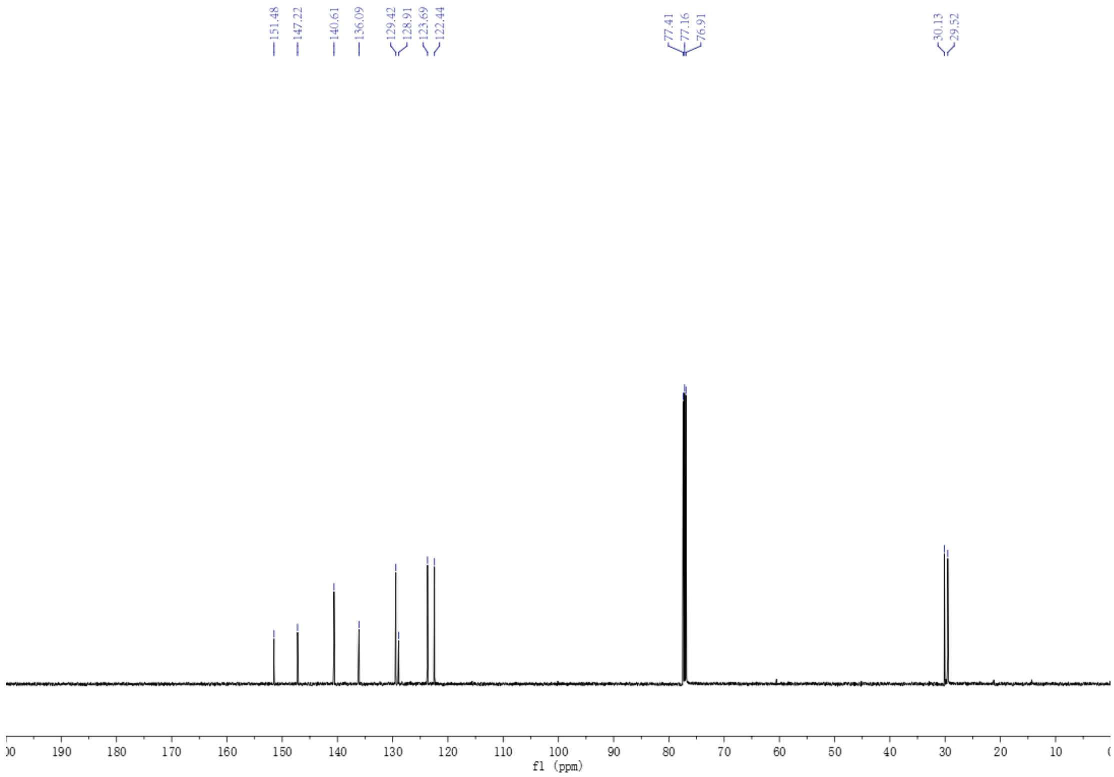
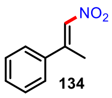


^{1}H NMR of compound **133**（500 MHz, $CDCl_3$）



^{13}C NMR of compound **133**（126 MHz, $CDCl_3$）



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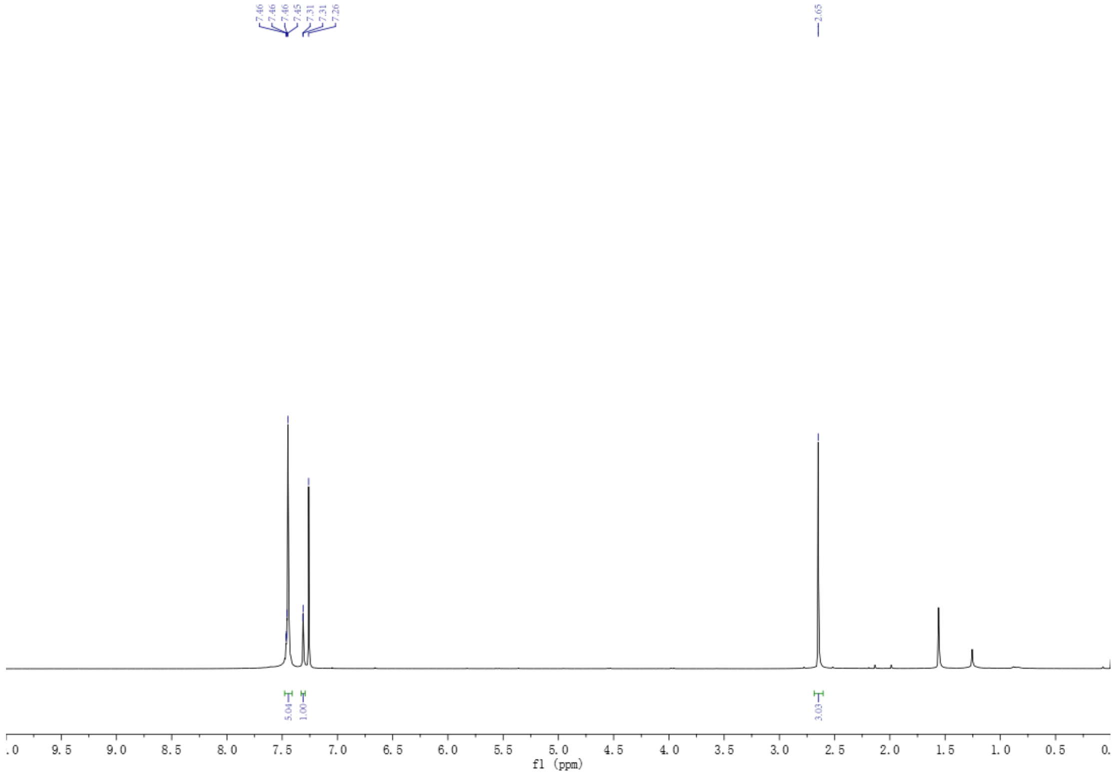
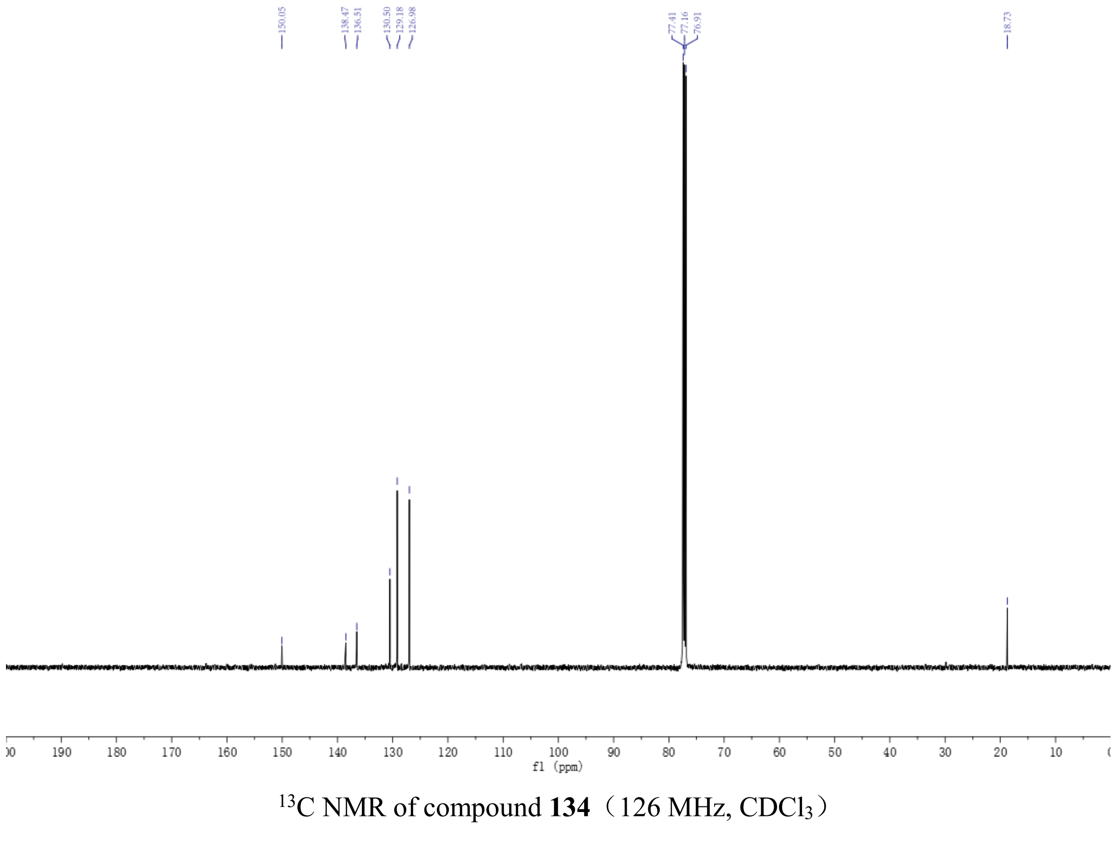
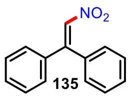
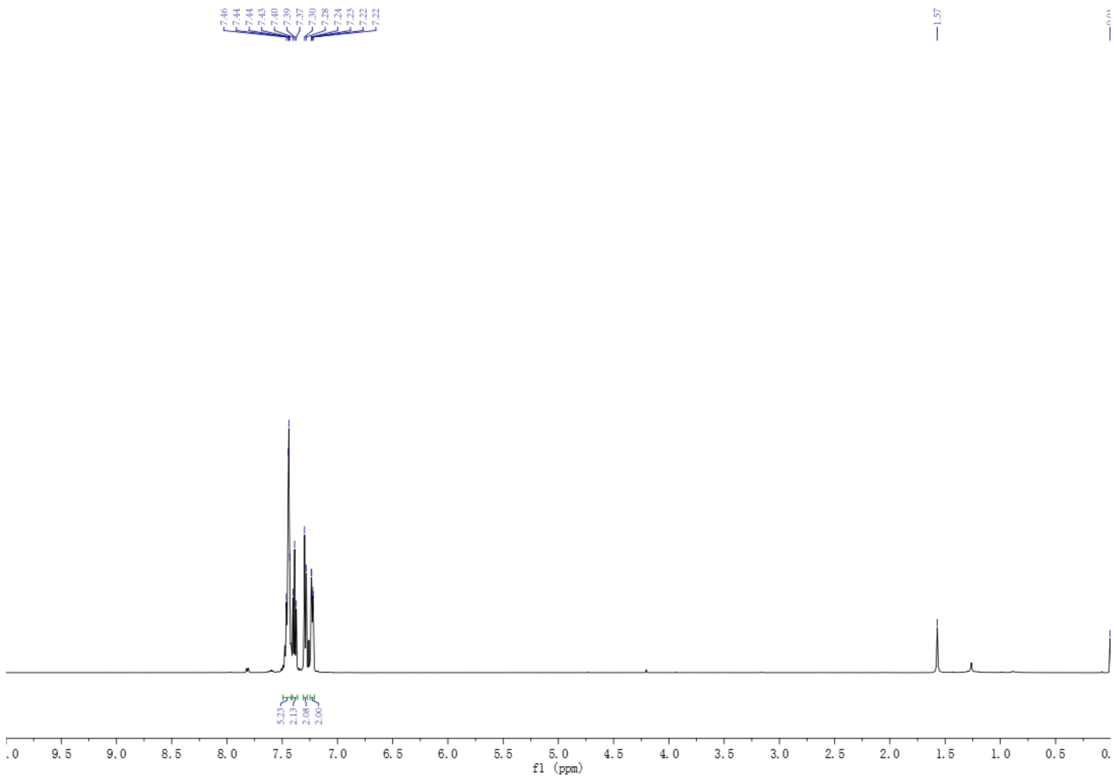


[1]H NMR of compound **134**（500 MHz, $CDCl_3$）

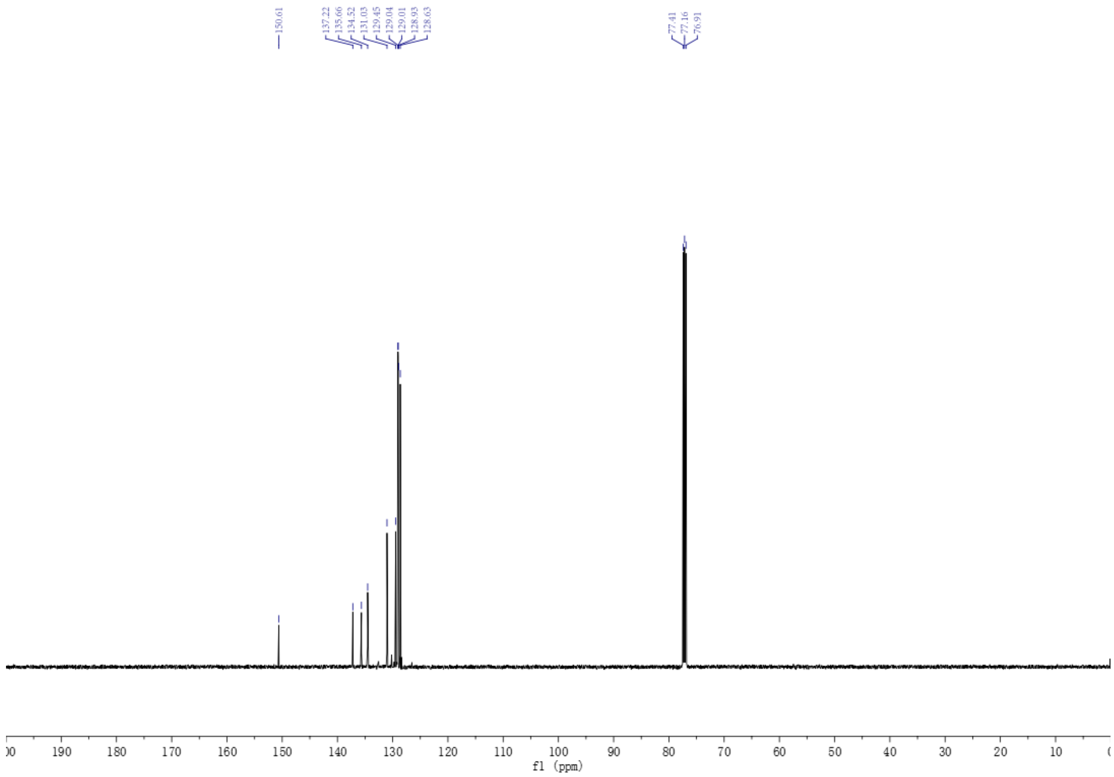


[13]C NMR of compound **134**（126 MHz, $CDCl_3$）

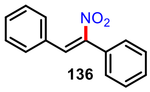


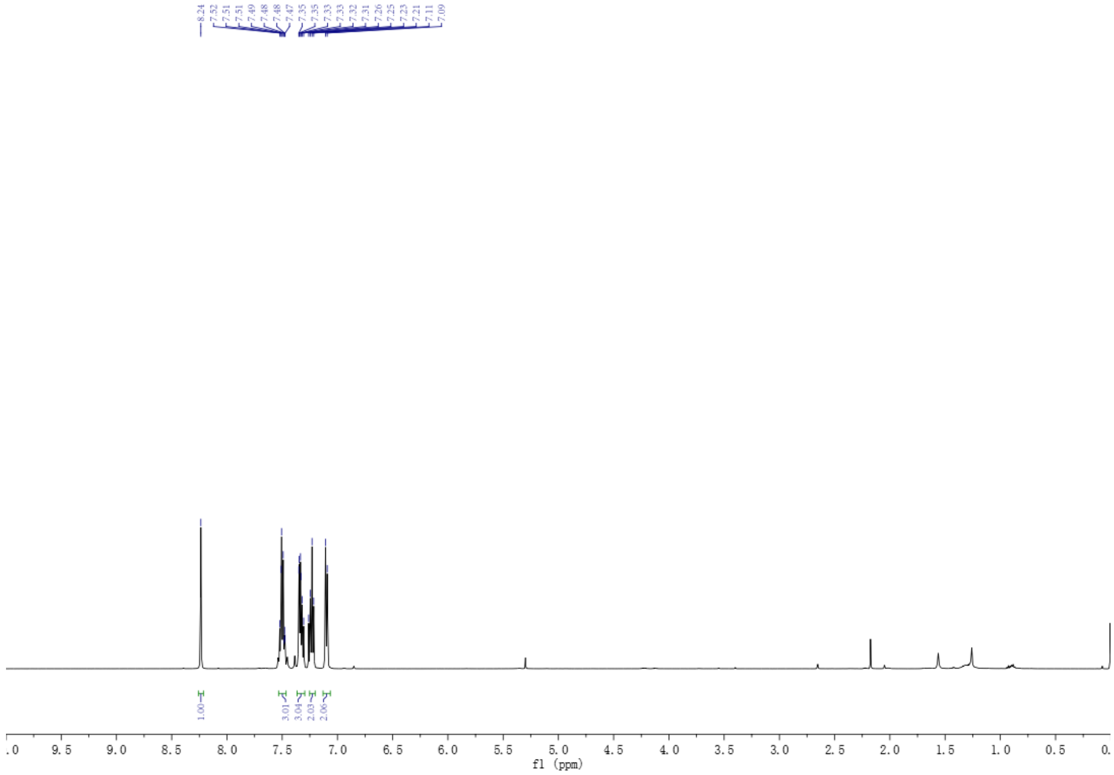


^{1}H NMR of compound **135**（500 MHz, $CDCl_3$）

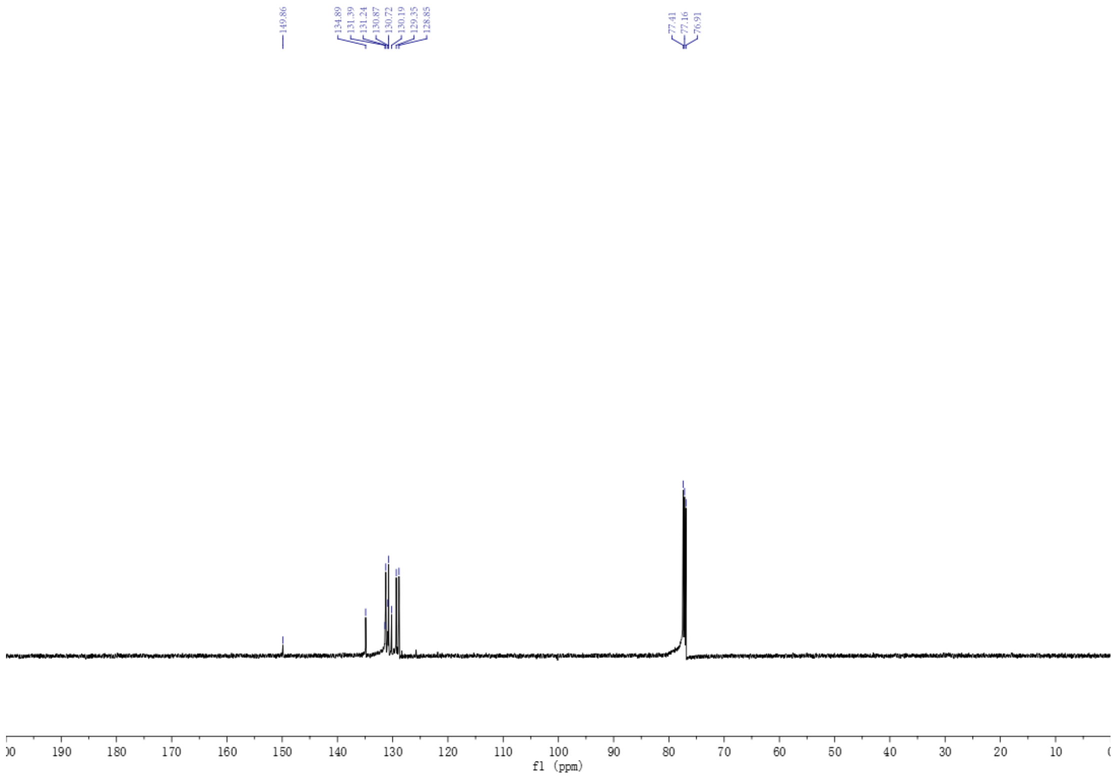


^{13}C NMR of compound **135**（126 MHz, $CDCl_3$）

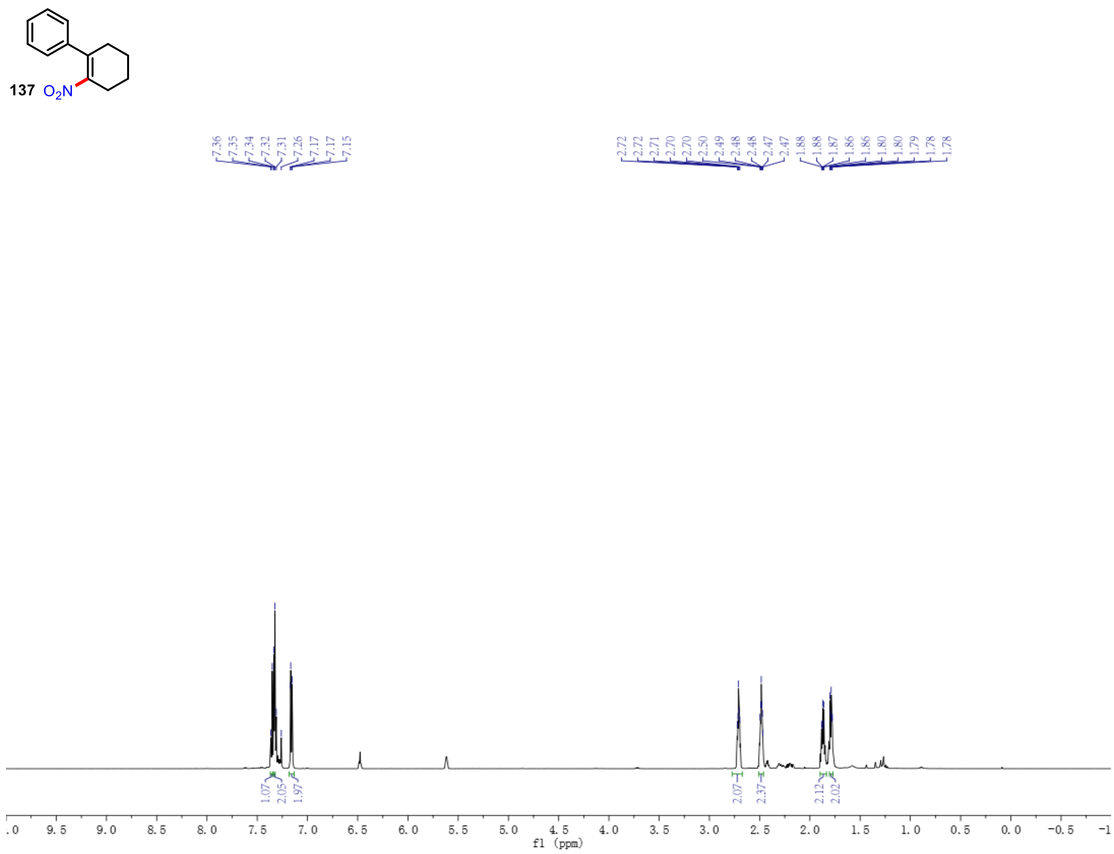




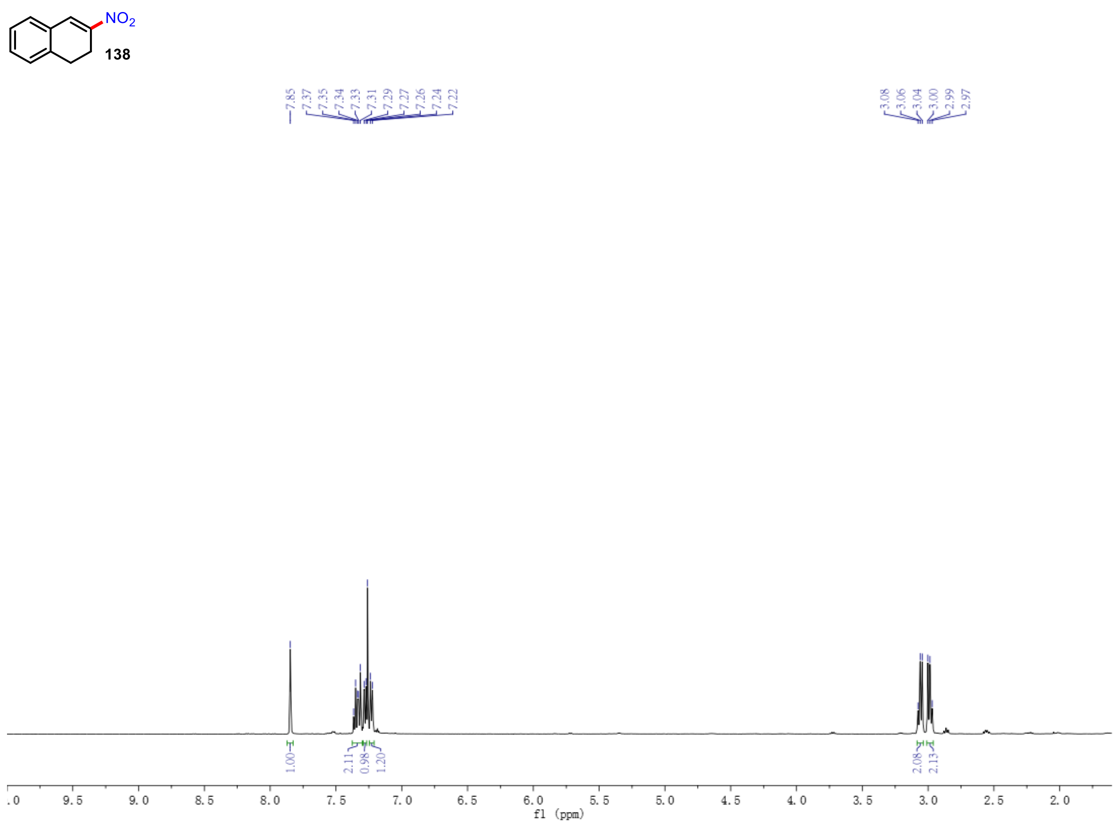
^{1}H NMR of compound **136**（500 MHz, $CDCl_3$）



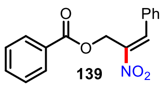
^{13}C NMR of compound **136**（126 MHz, $CDCl_3$）



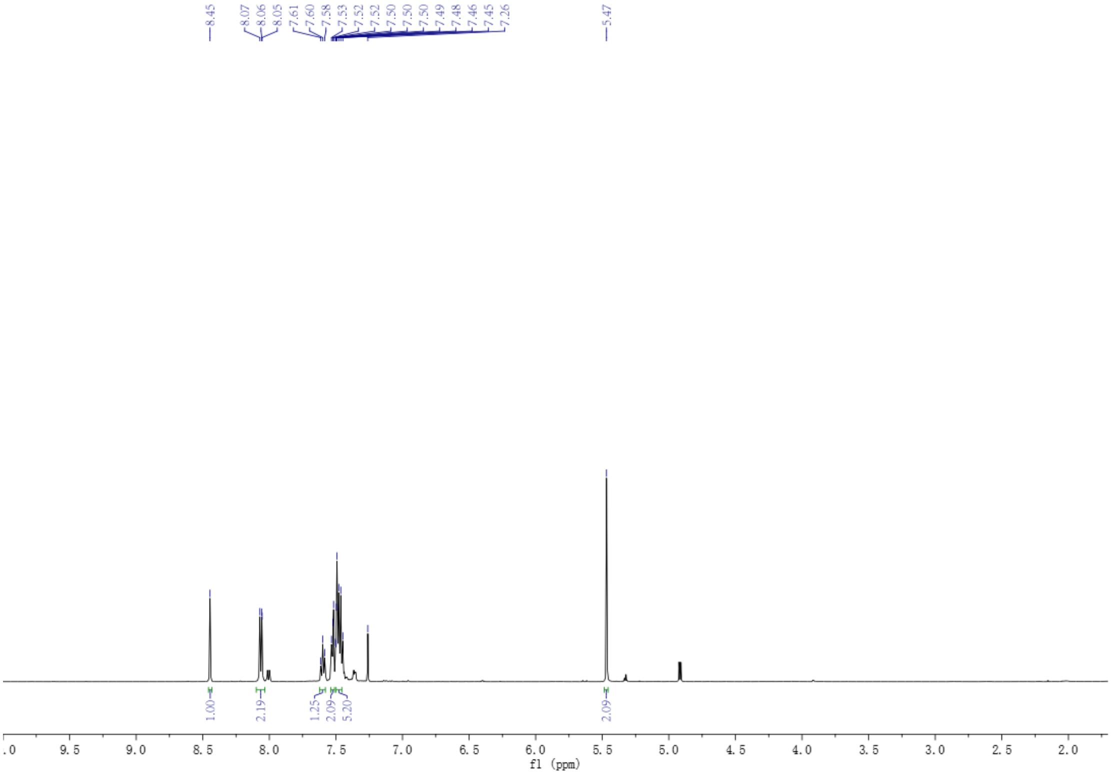
^{1}H NMR of compound **137**（500 MHz, $CDCl_3$）



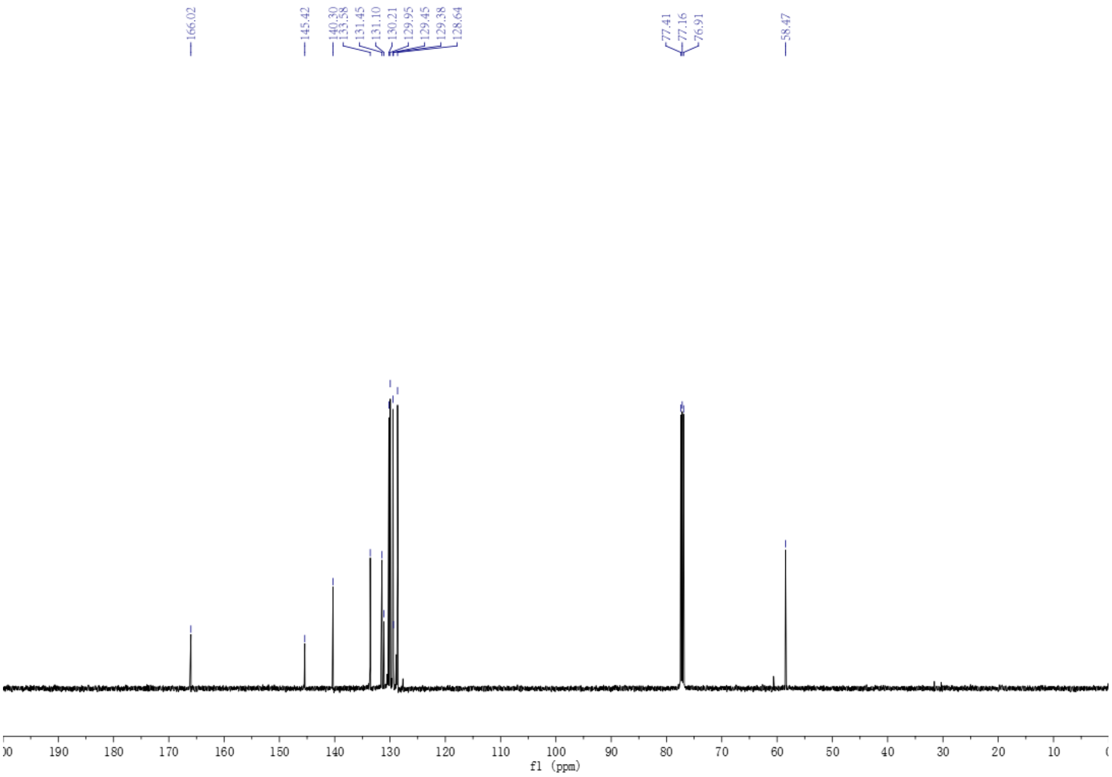
^{1}H NMR of compound **138**（500 MHz, $CDCl_3$）



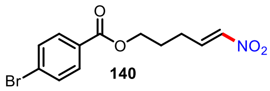
139



[1]H NMR of compound **139**（500 MHz, $CDCl_3$）



[13]C NMR of compound **139**（126 MHz, $CDCl_3$）



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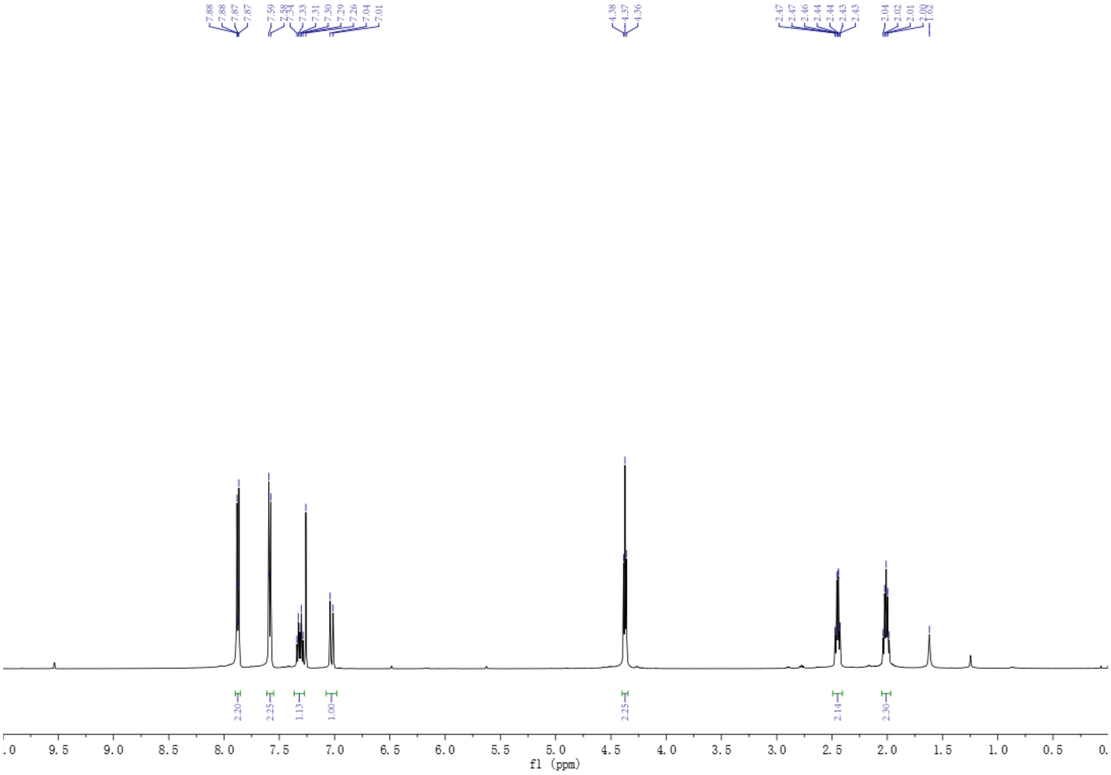
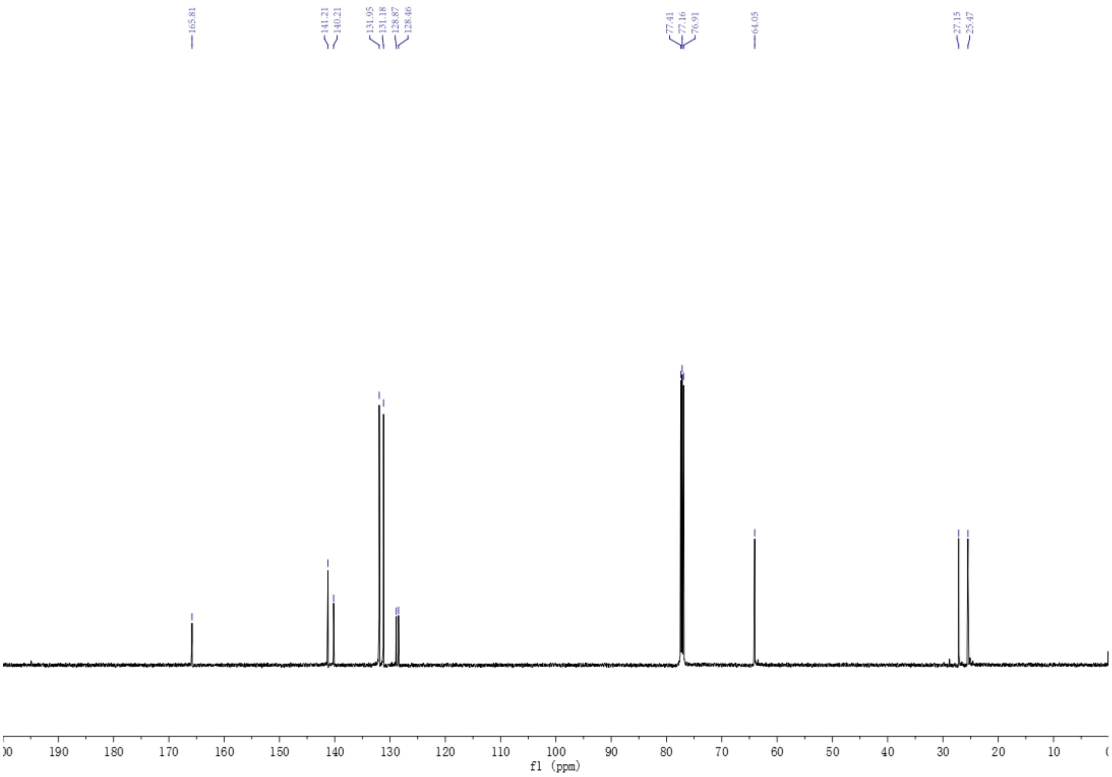
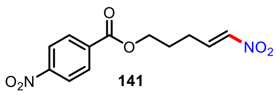


^{1}H NMR of compound **140**（500 MHz, $CDCl_3$）



^{13}C NMR of compound **140**（126 MHz, $CDCl_3$）



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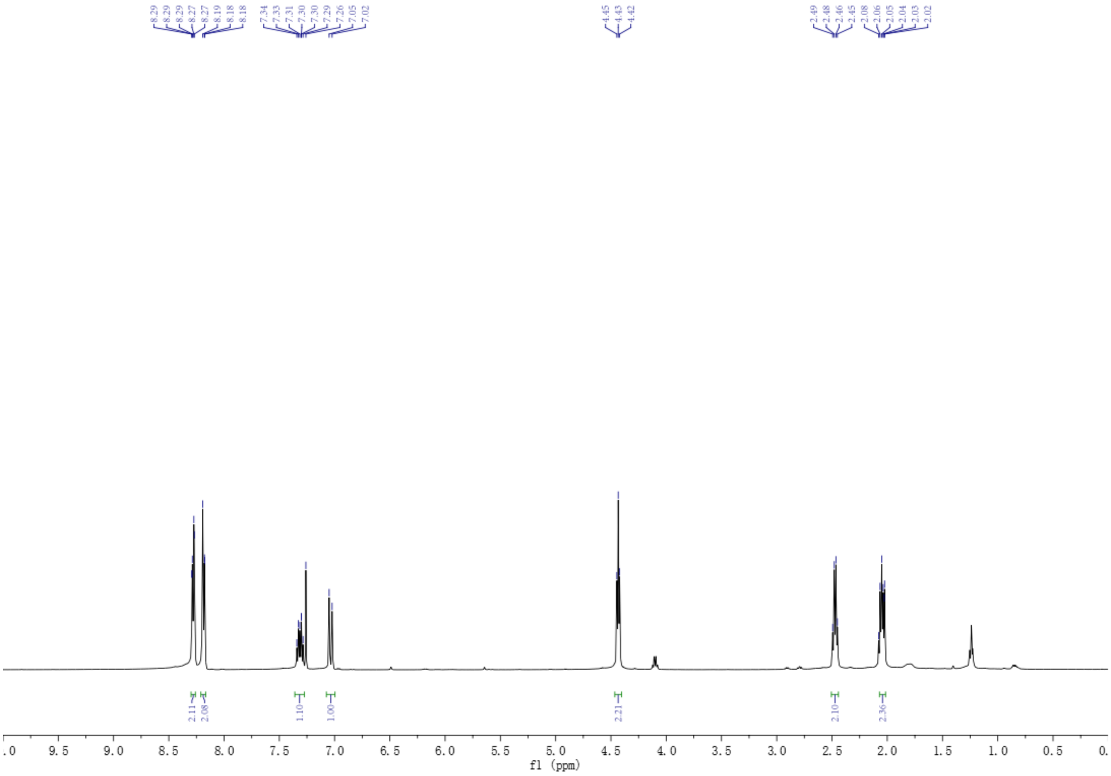
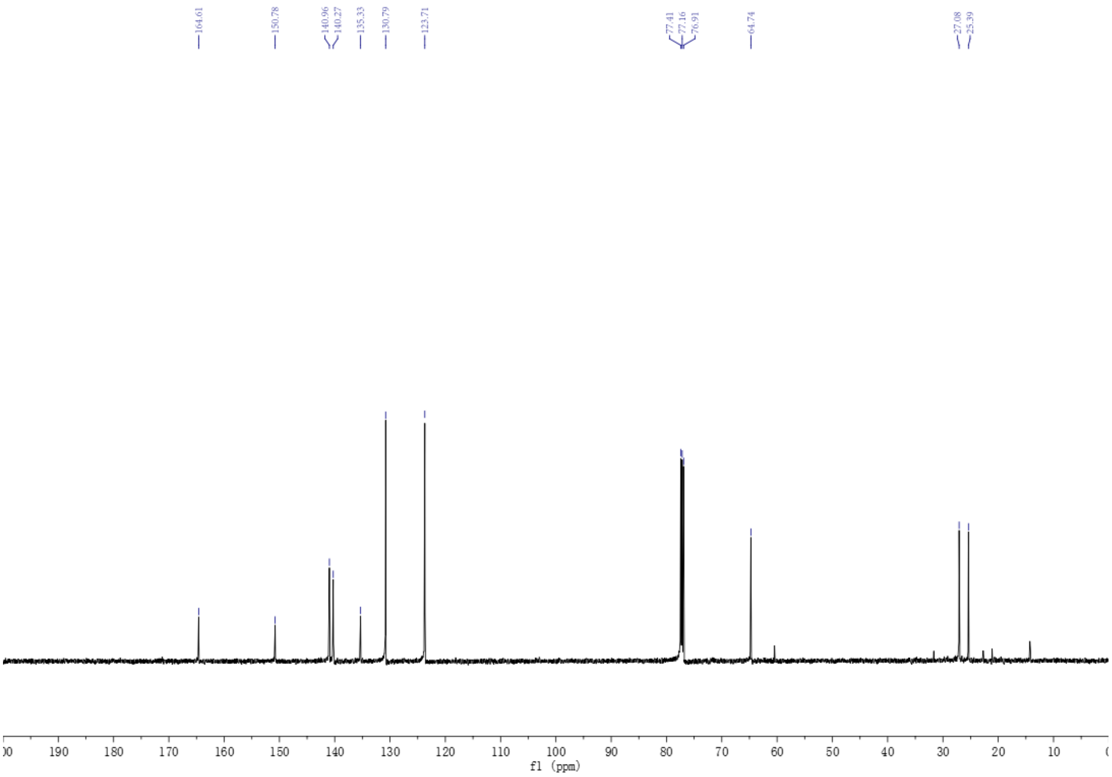
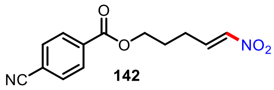


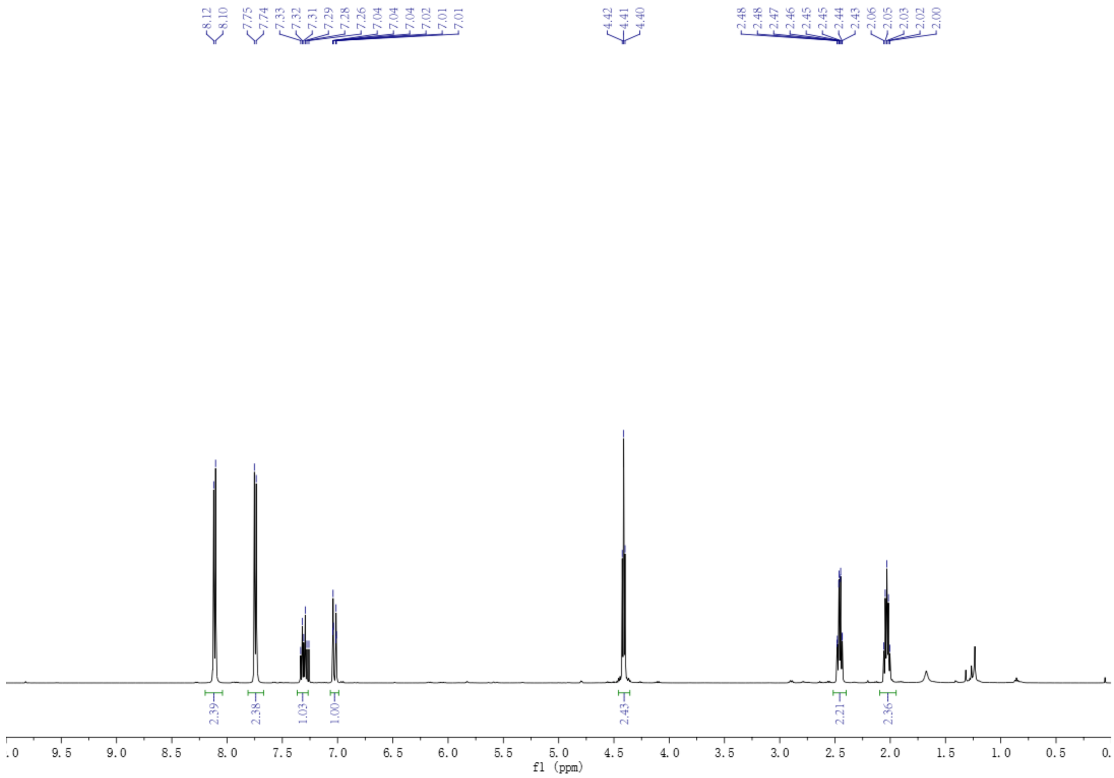
^{1}H NMR of compound **141**（500 MHz, $CDCl_3$）



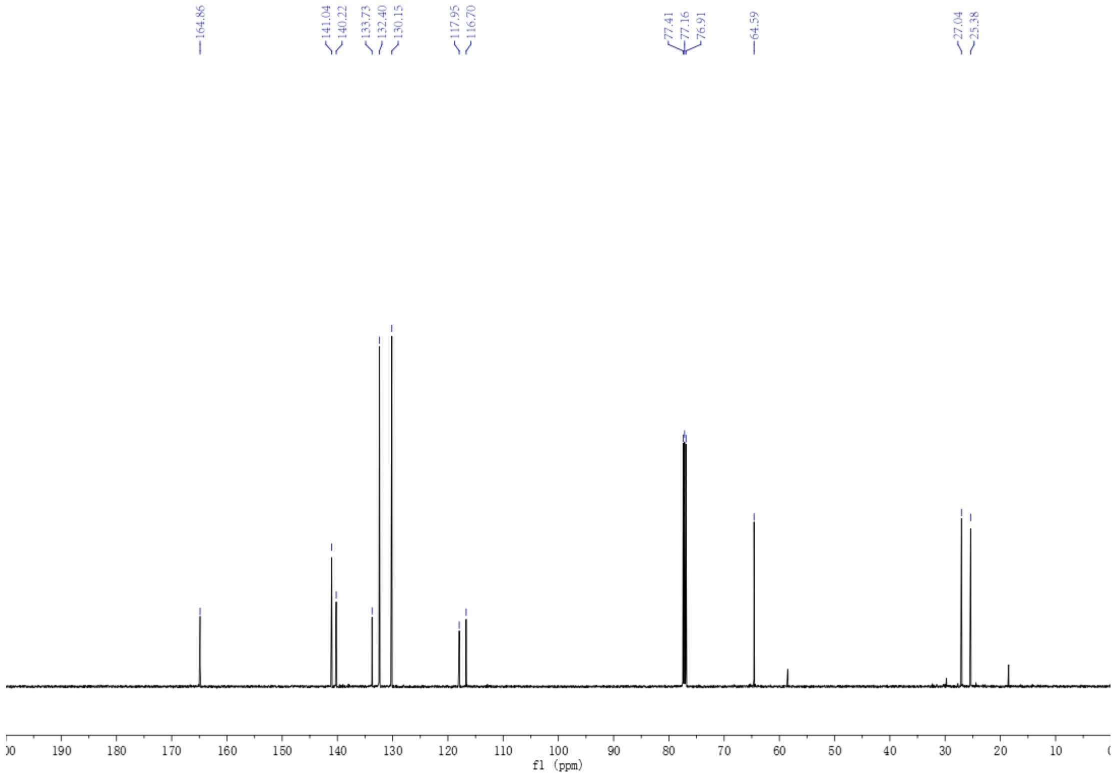
^{13}C NMR of compound **141**（126 MHz, $CDCl_3$）



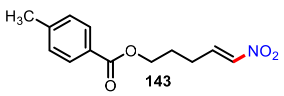
142



[1]H NMR of compound **142**（500 MHz, $CDCl_3$）



[13]C NMR of compound **142**（126 MHz, $CDCl_3$）



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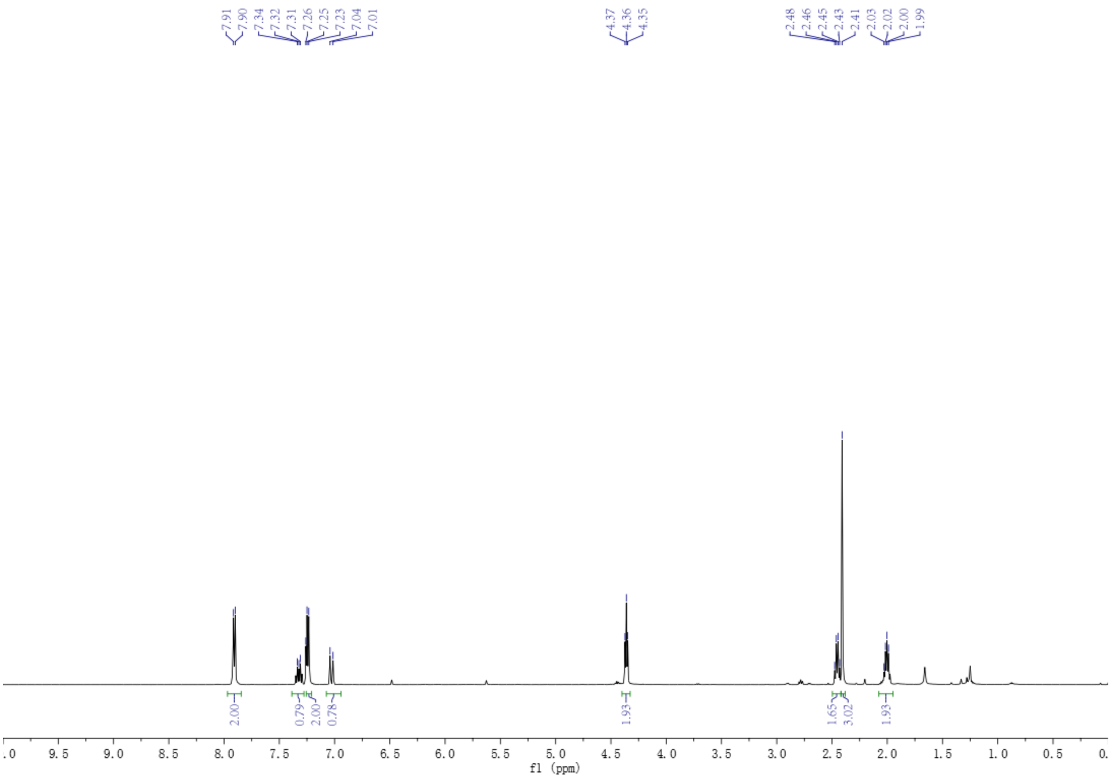
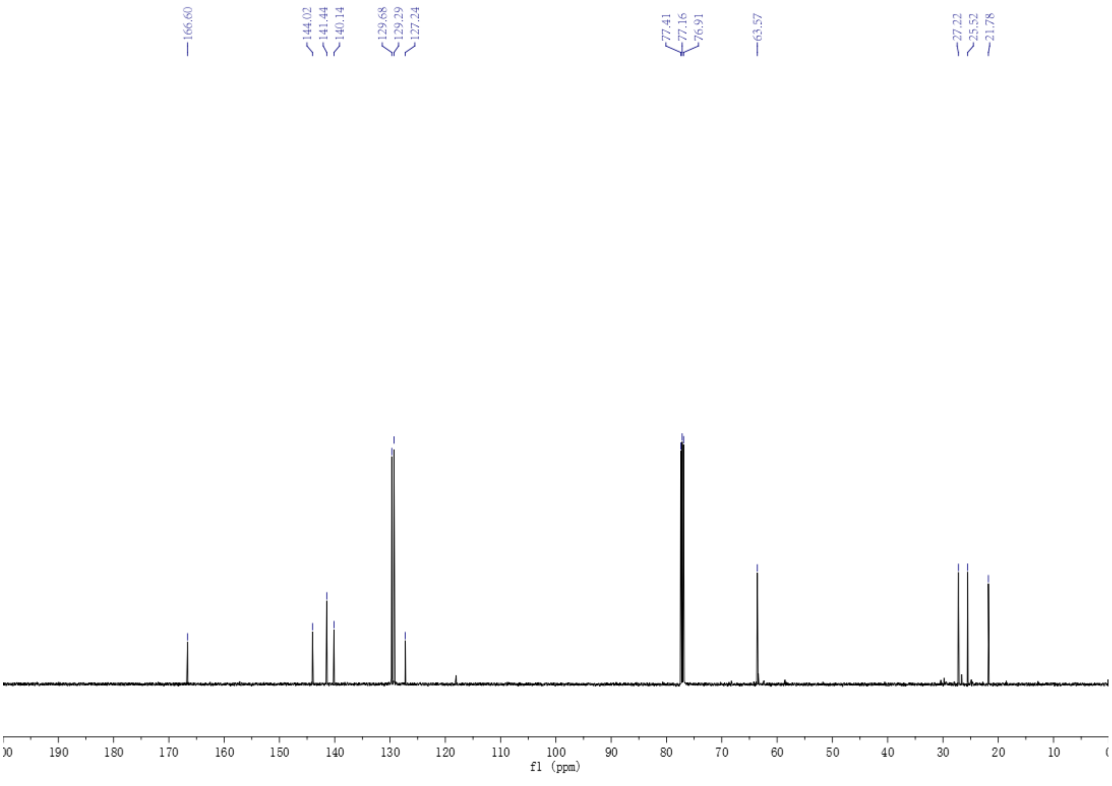
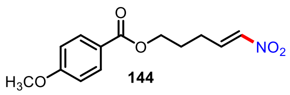


^{1}H NMR of compound **143**（500 MHz, $CDCl_3$）



^{13}C NMR of compound **143**（126 MHz, $CDCl_3$）



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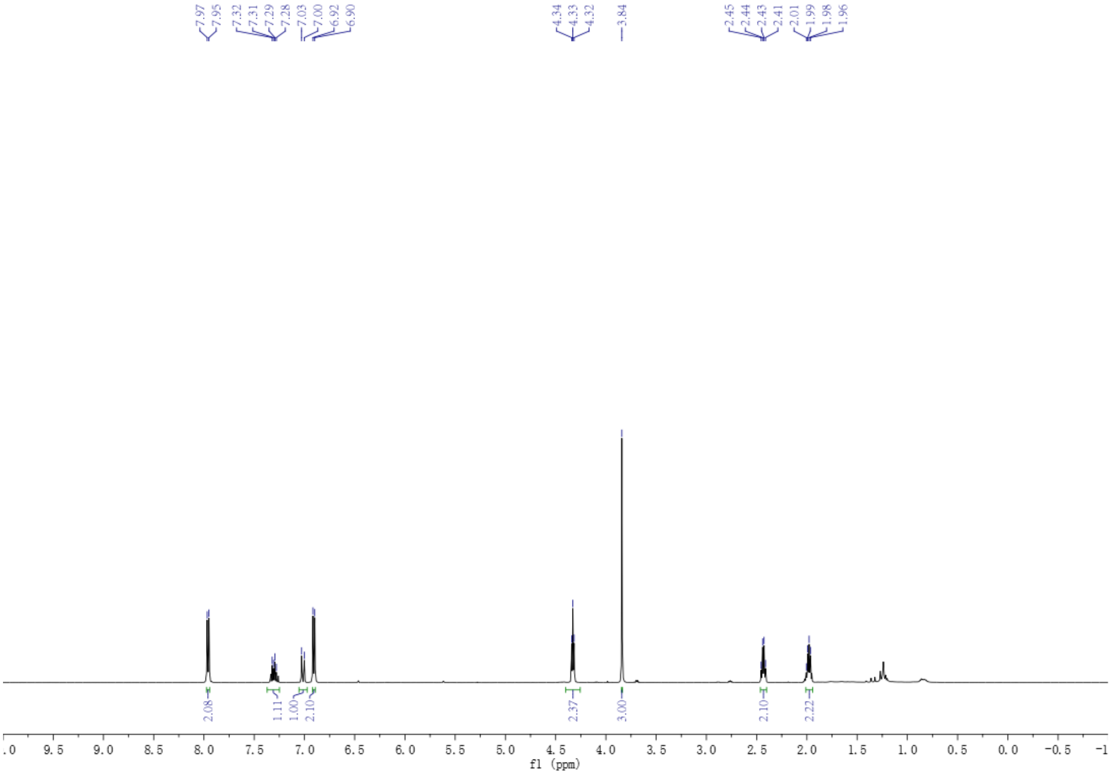
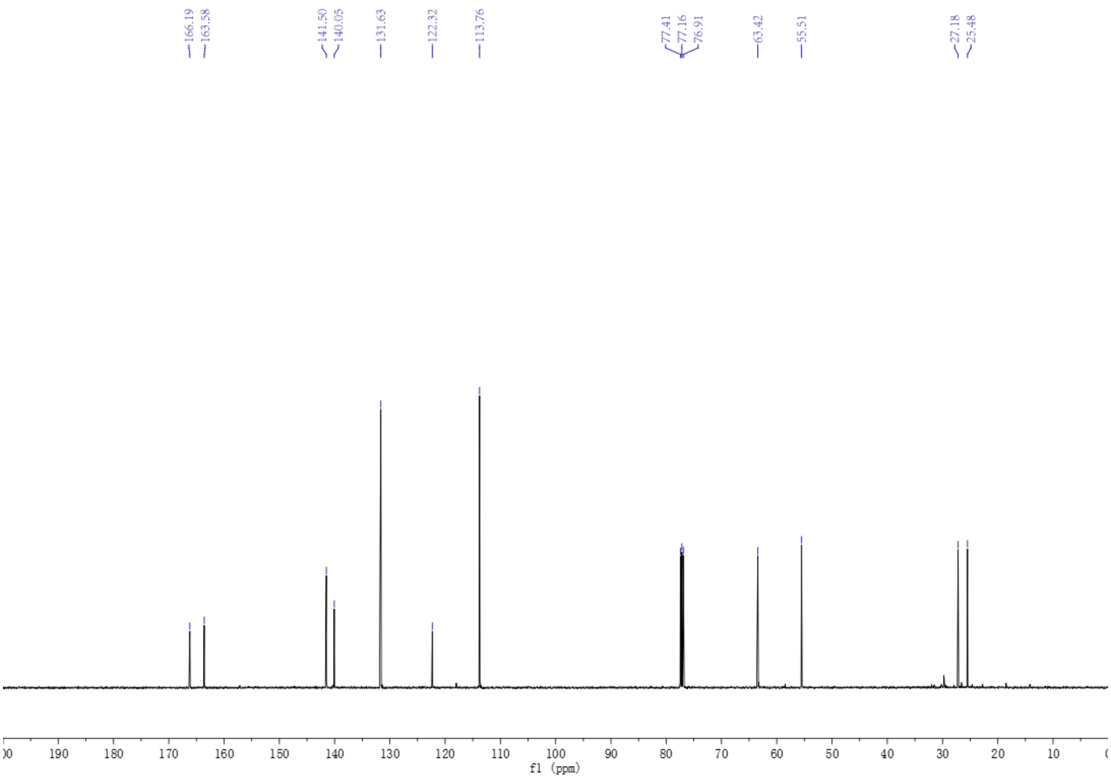
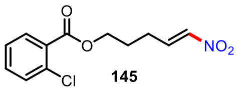


^{1}H NMR of compound **144**（500 MHz, $CDCl_3$）



^{13}C NMR of compound **144**（126 MHz, $CDCl_3$）



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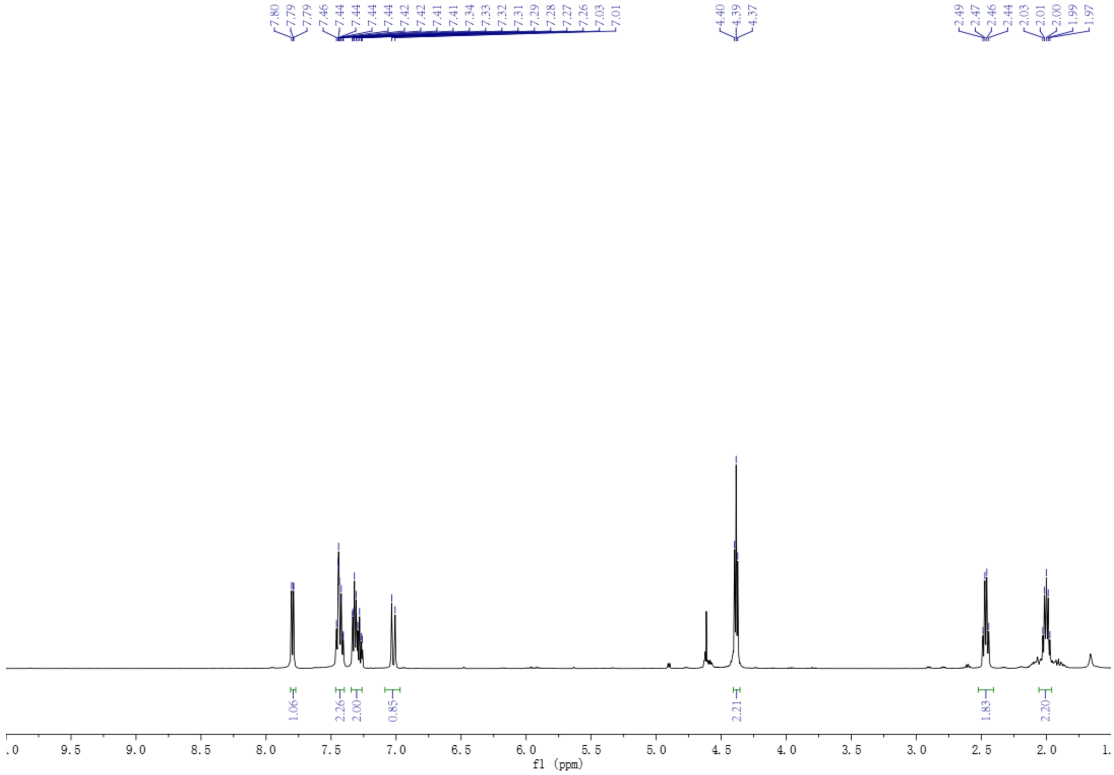
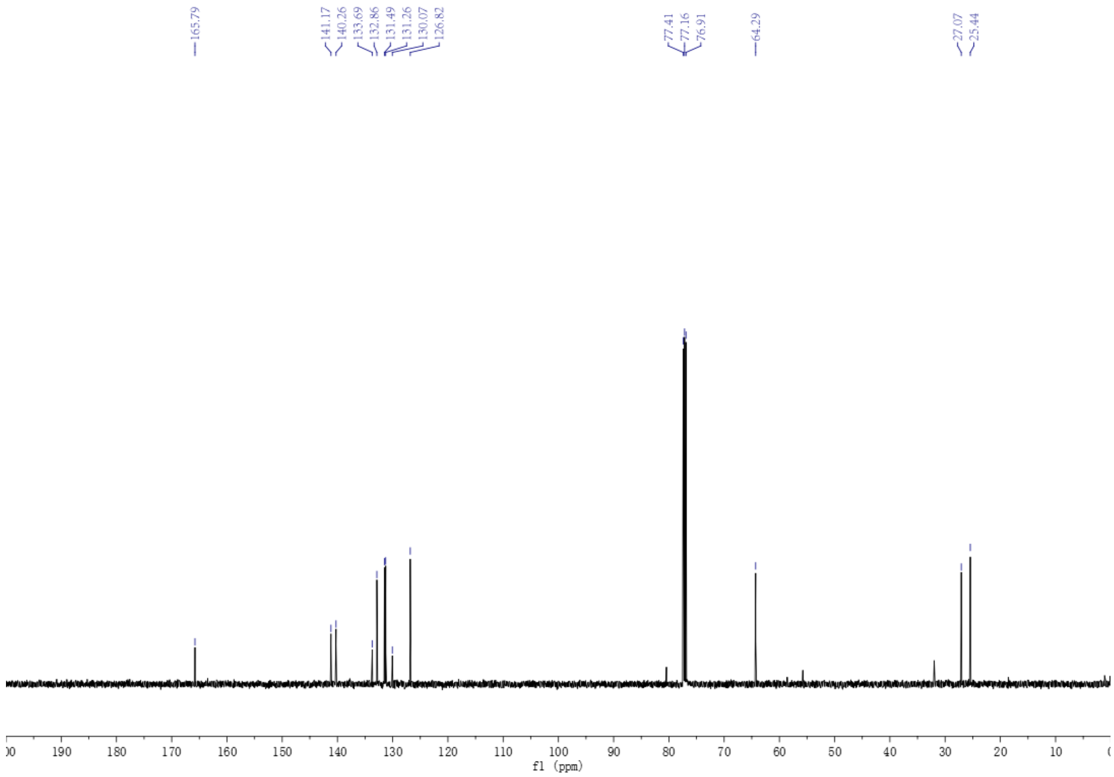
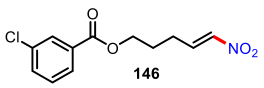


^{1}H NMR of compound **145**（500 MHz, $CDCl_3$）



^{13}C NMR of compound **145**（126 MHz, $CDCl_3$）



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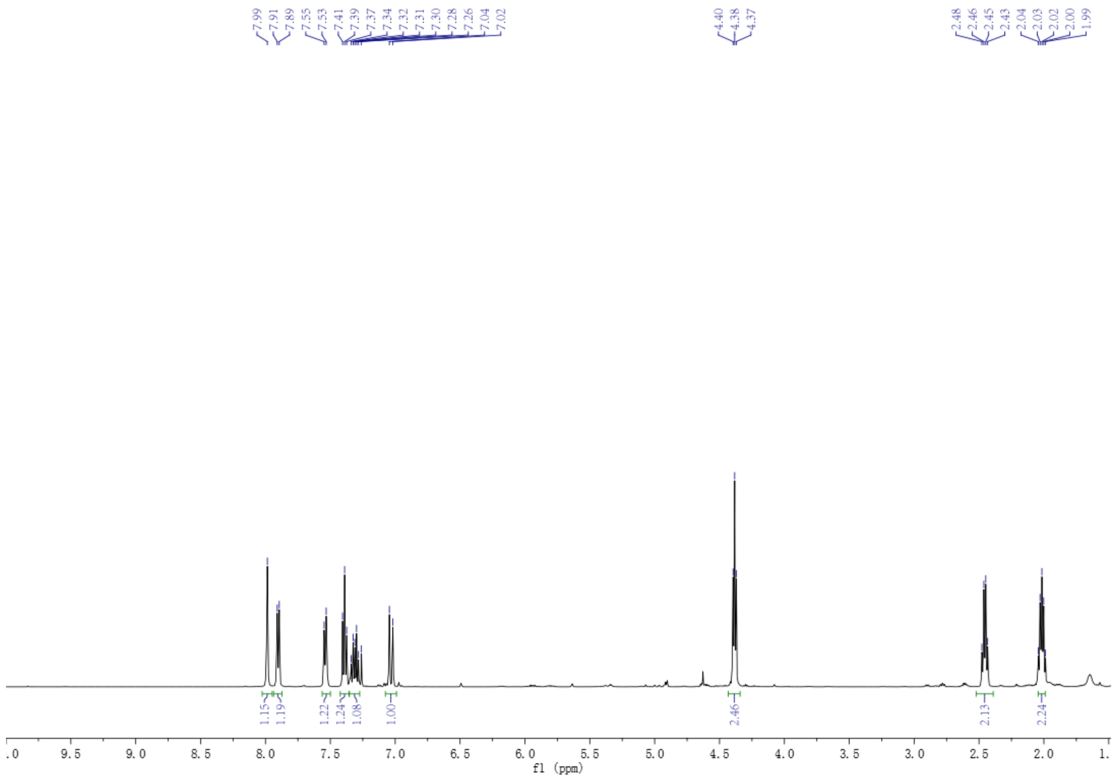
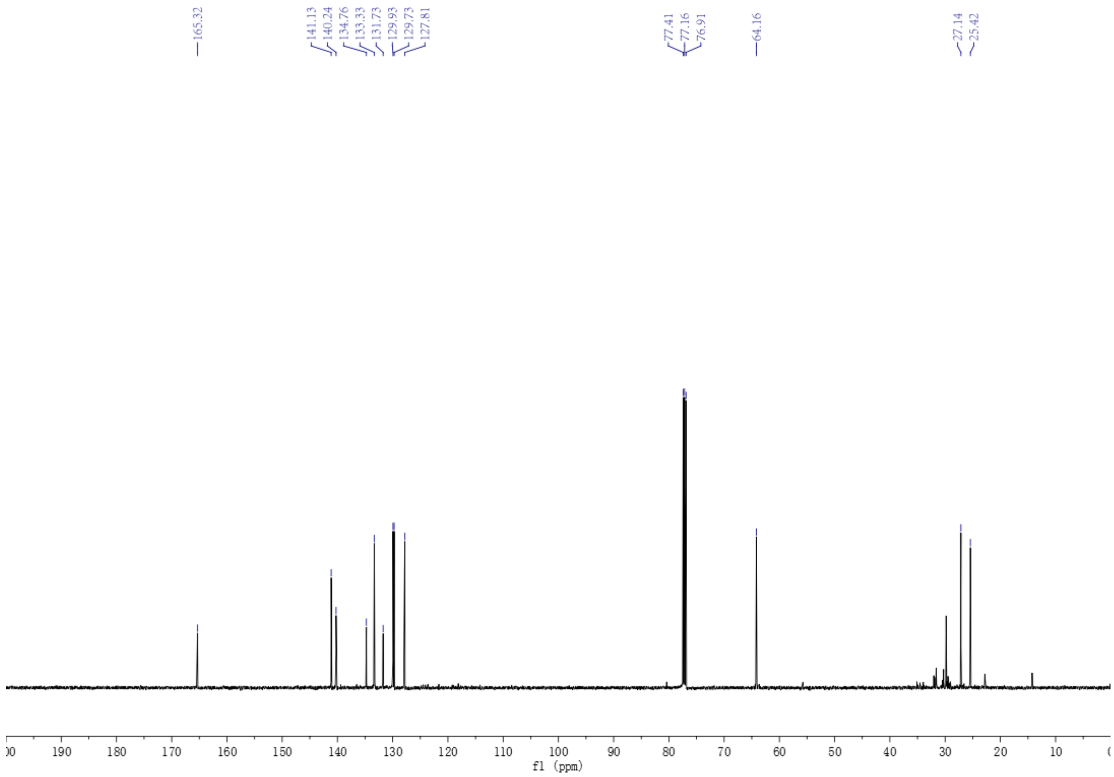
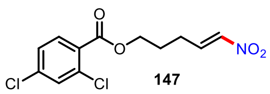


[1]H NMR of compound **146**（500 MHz, $CDCl_3$）



[13]C NMR of compound **146**（126 MHz, $CDCl_3$）



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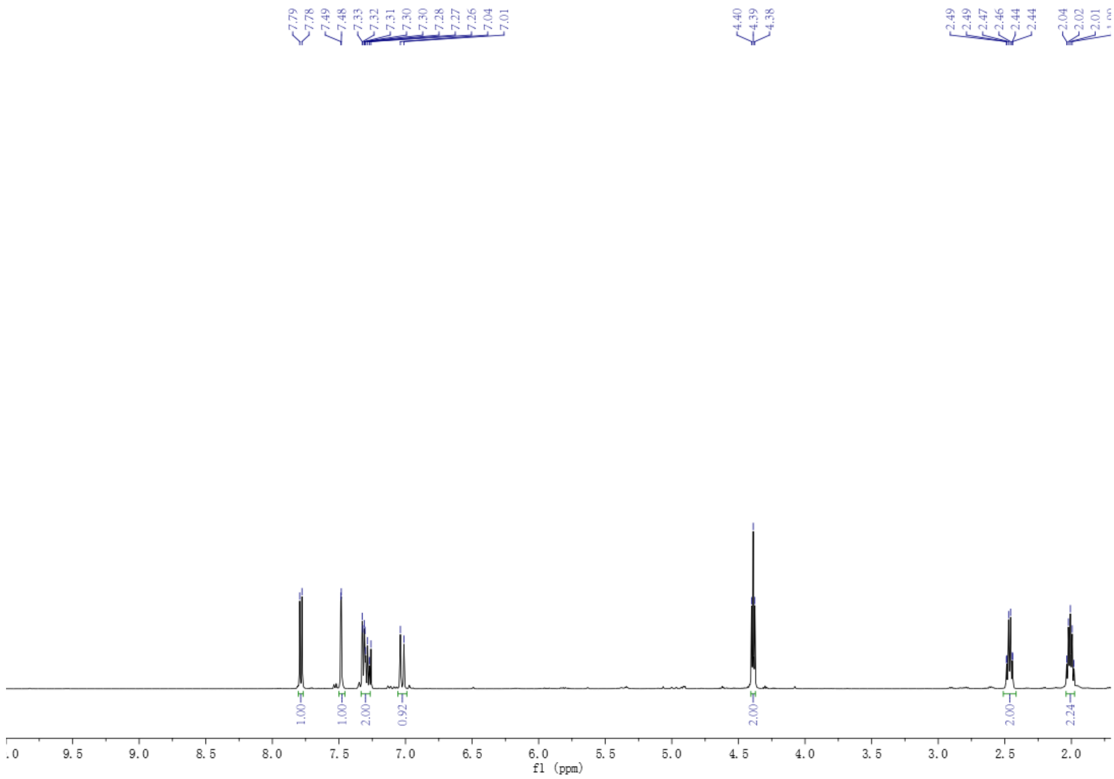
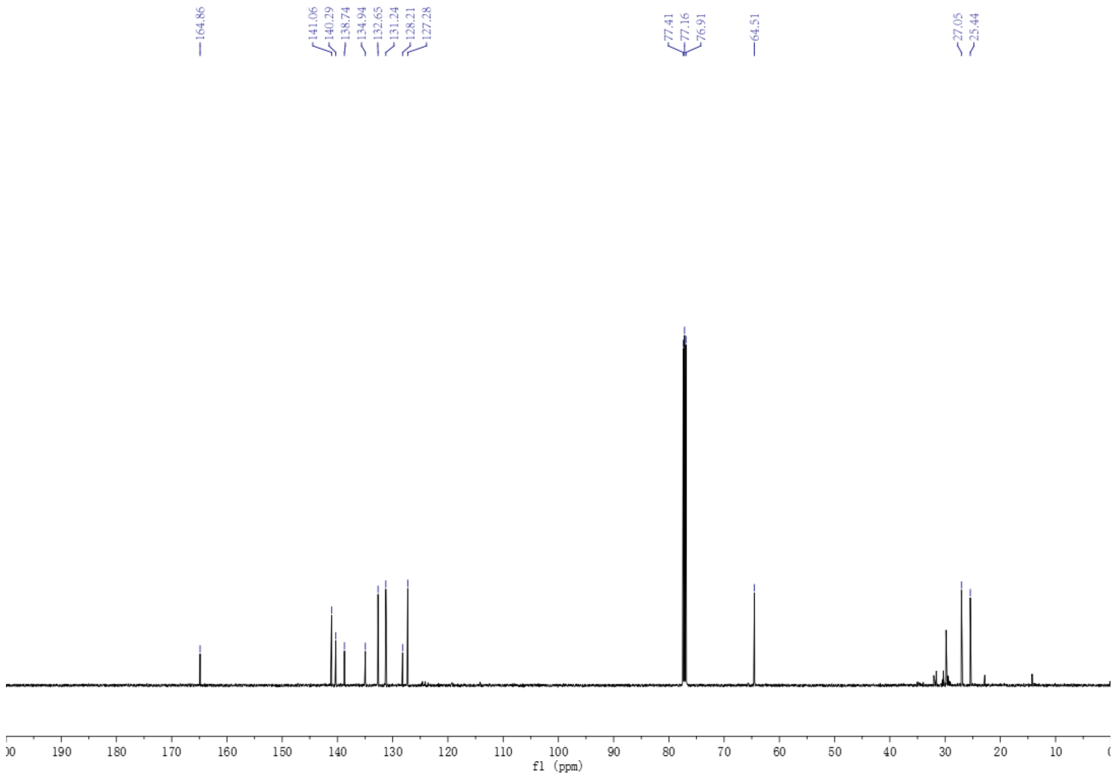
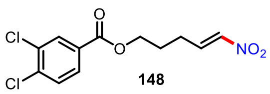
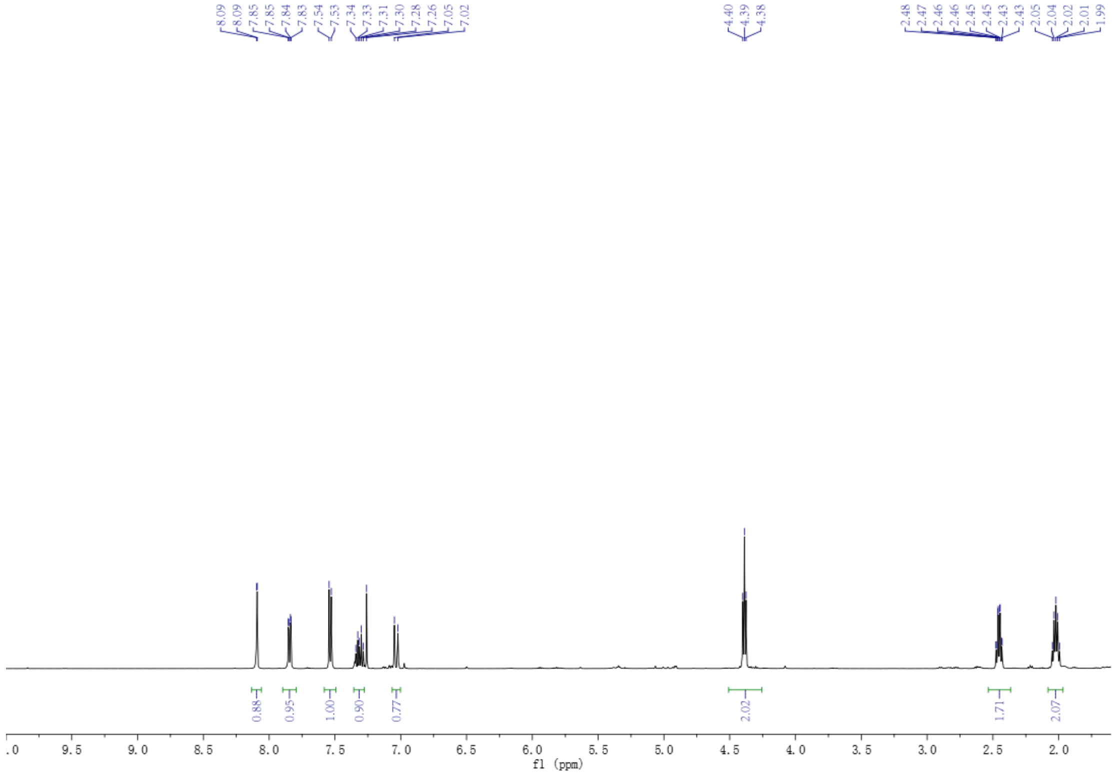


^{1}H NMR of compound **147**（500 MHz, $CDCl_3$）

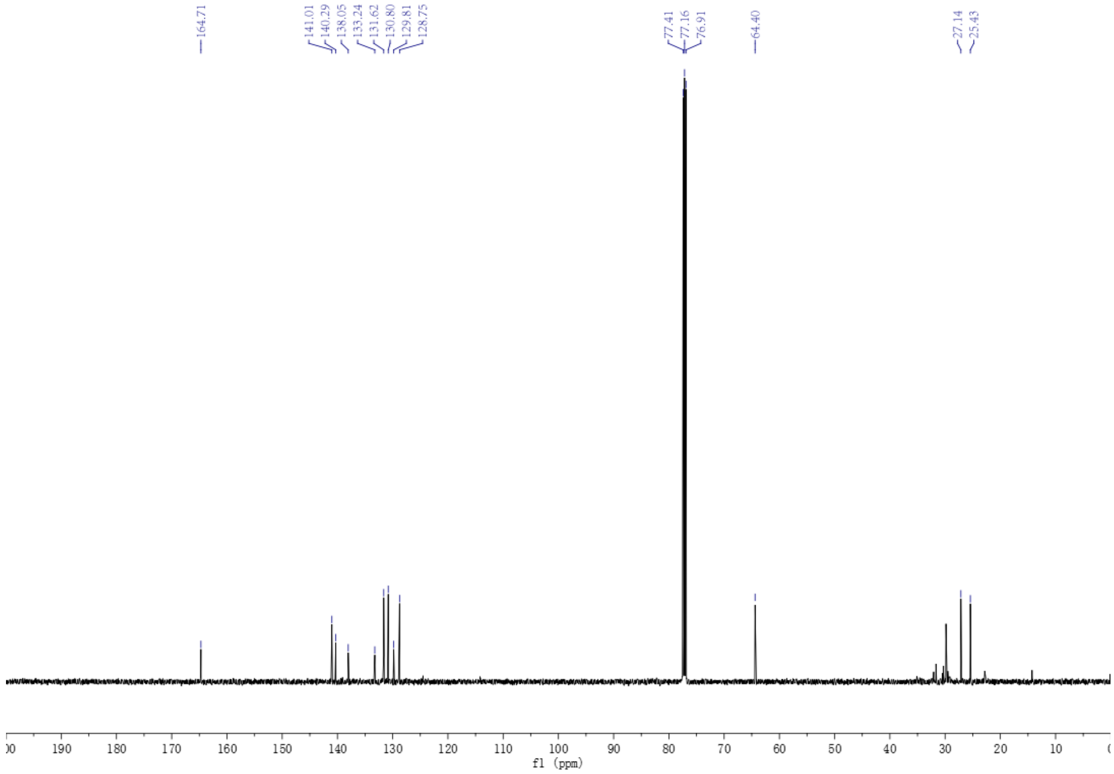


^{13}C NMR of compound **147**（126 MHz, $CDCl_3$）

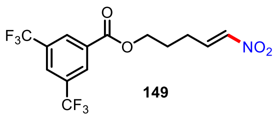




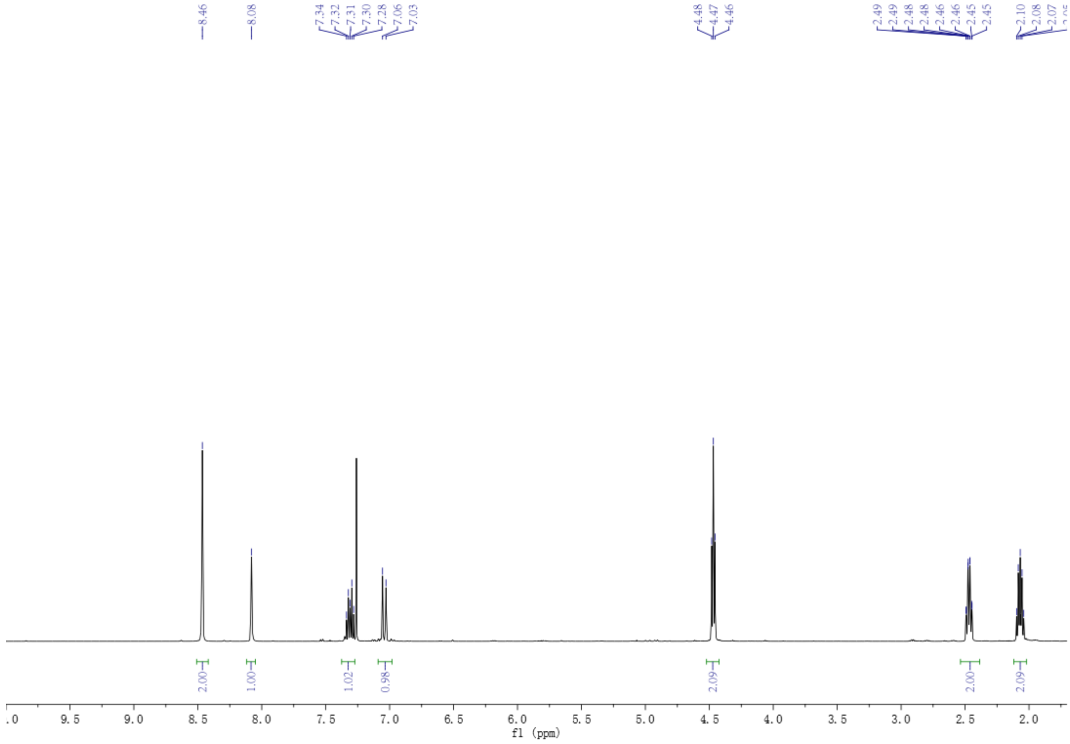
^{1}H NMR of compound **148**（500 MHz, $CDCl_3$）



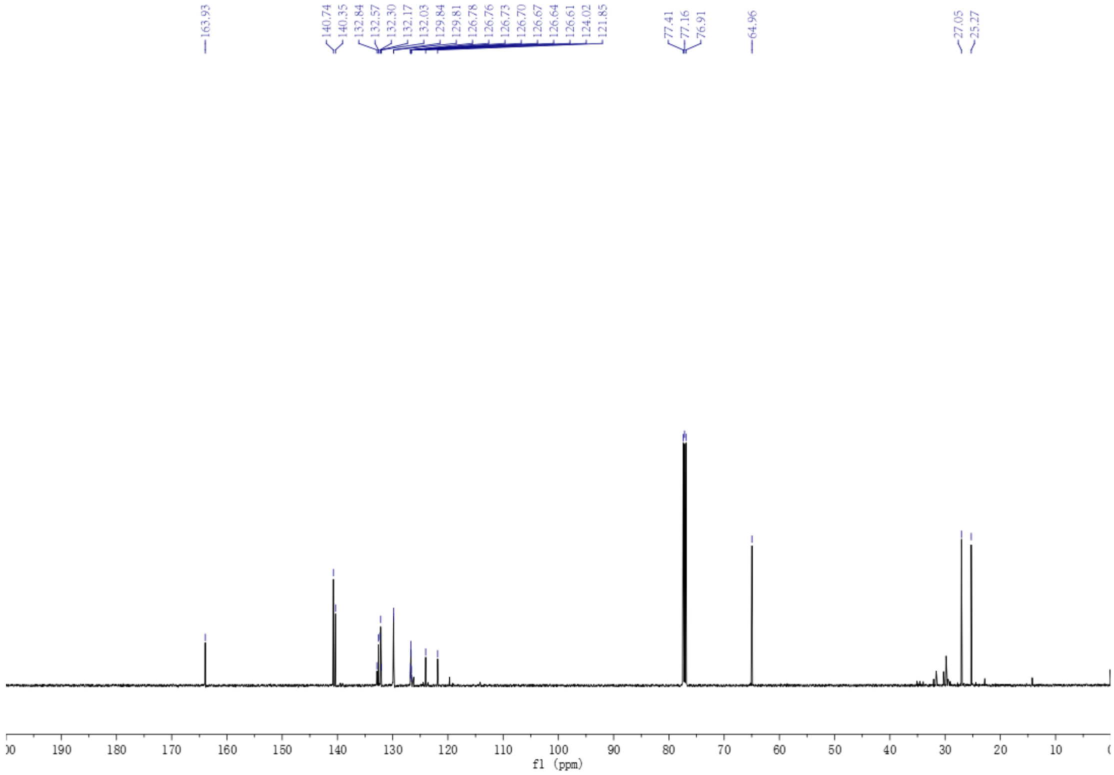
^{13}C NMR of compound **148**（126 MHz, $CDCl_3$）



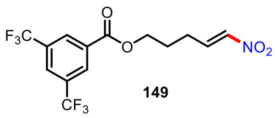
149



^{1}H NMR of compound **149**（500 MHz, $CDCl_3$）



^{13}C NMR of compound **149**（126 MHz, $CDCl_3$）



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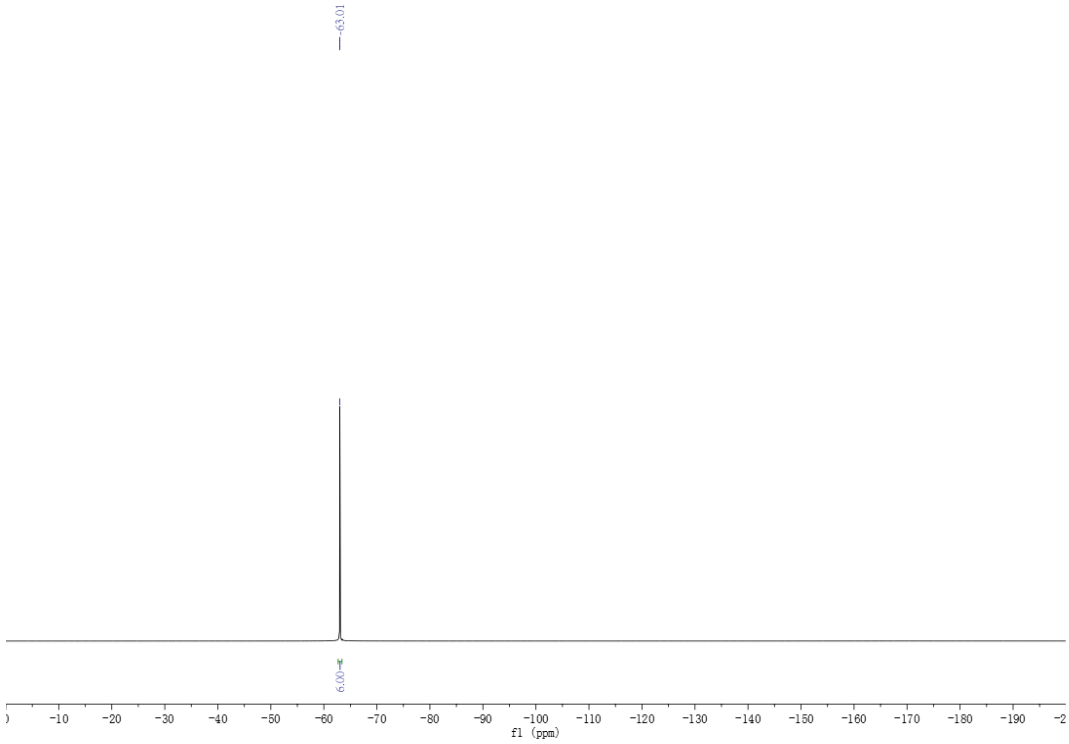
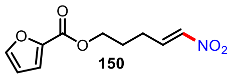
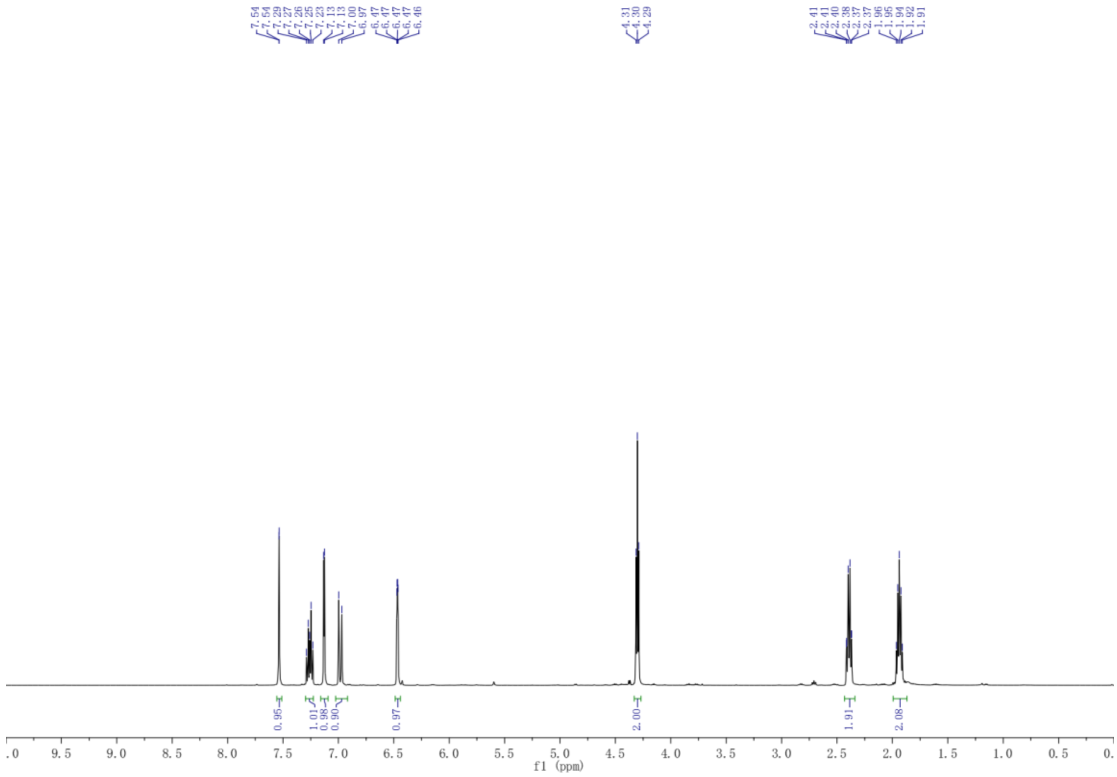
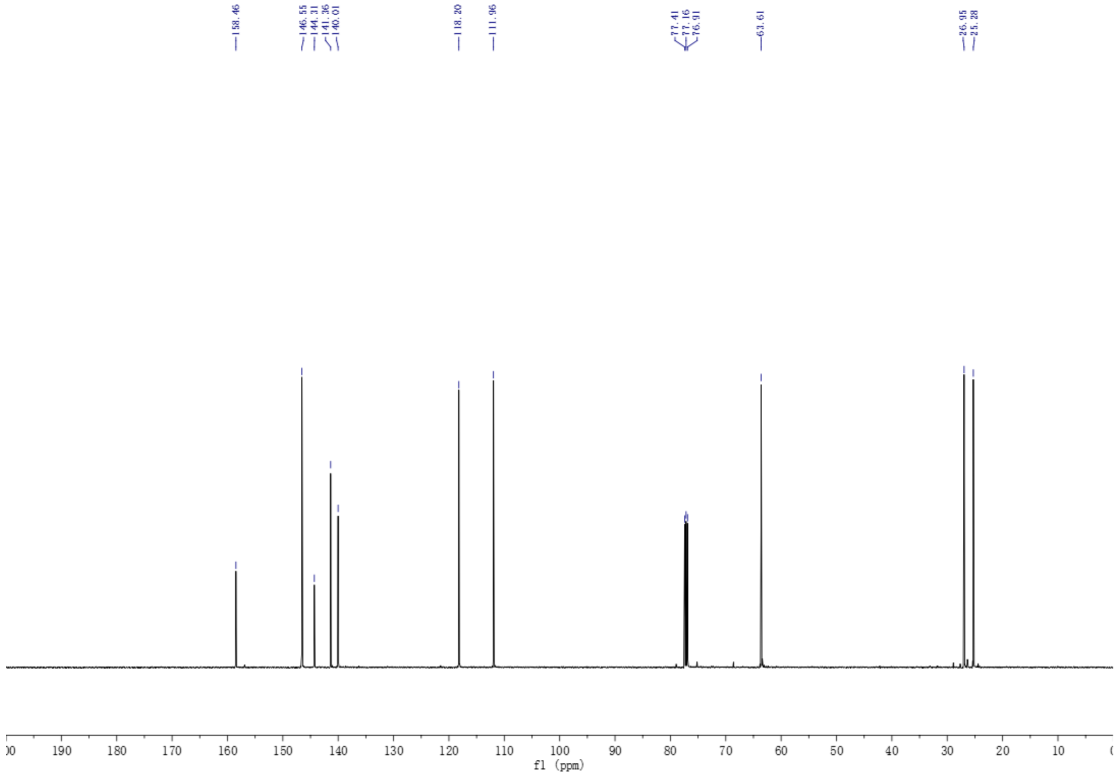


^{19}F NMR of compound **149**（471 MHz, $CDCl_3$）

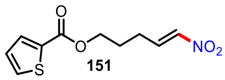




^{1}H NMR of compound **150**（500 MHz, $CDCl_3$）



^{13}C NMR of compound **150**（126 MHz, $CDCl_3$）



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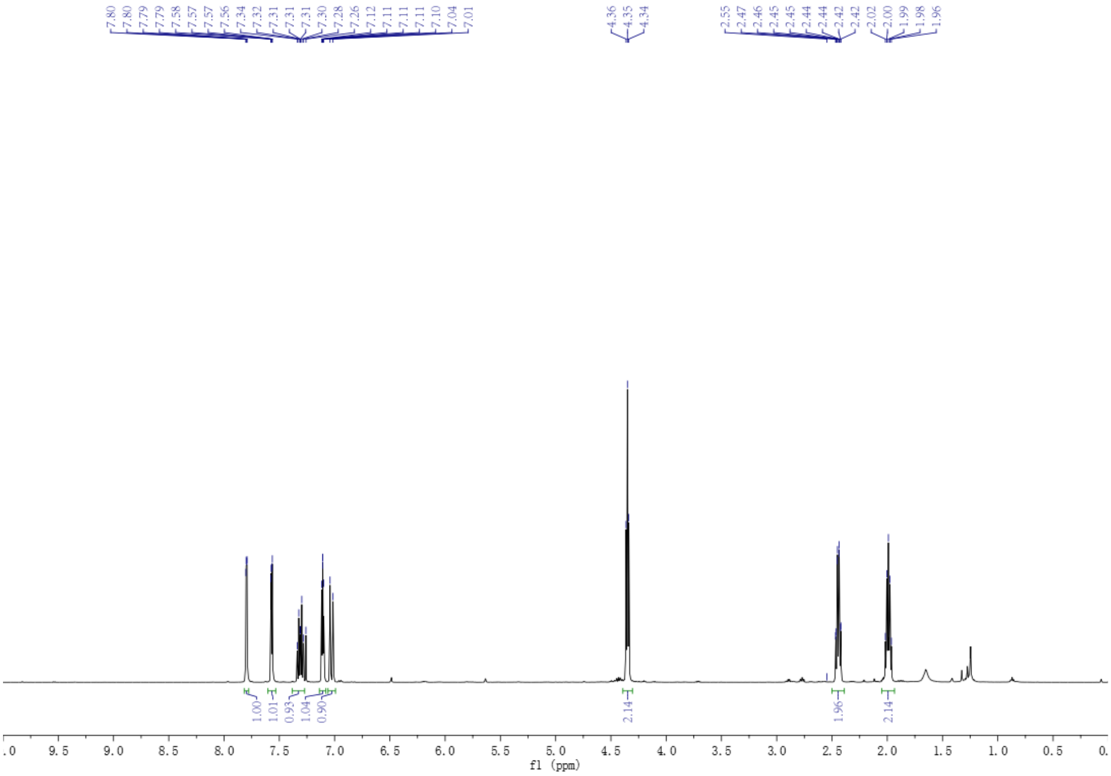
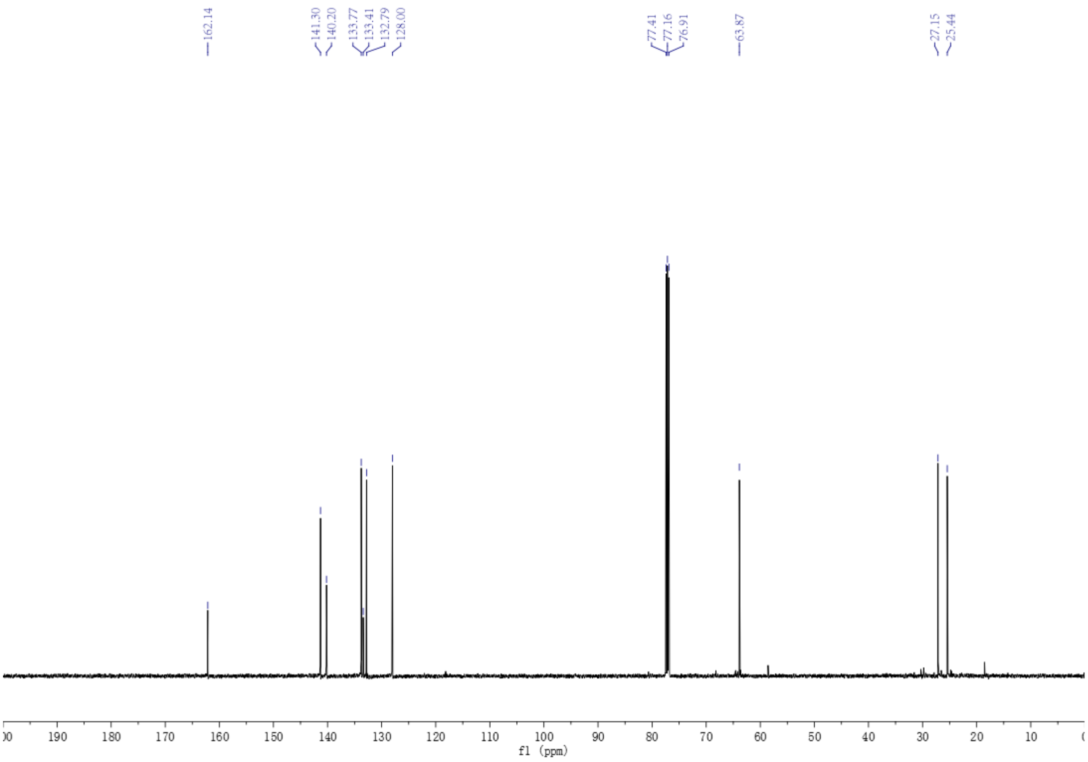
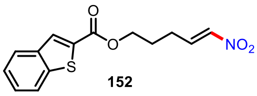


^{1}H NMR of compound **151**（500 MHz, $CDCl_3$）



^{13}C NMR of compound **151**（126 MHz, $CDCl_3$）



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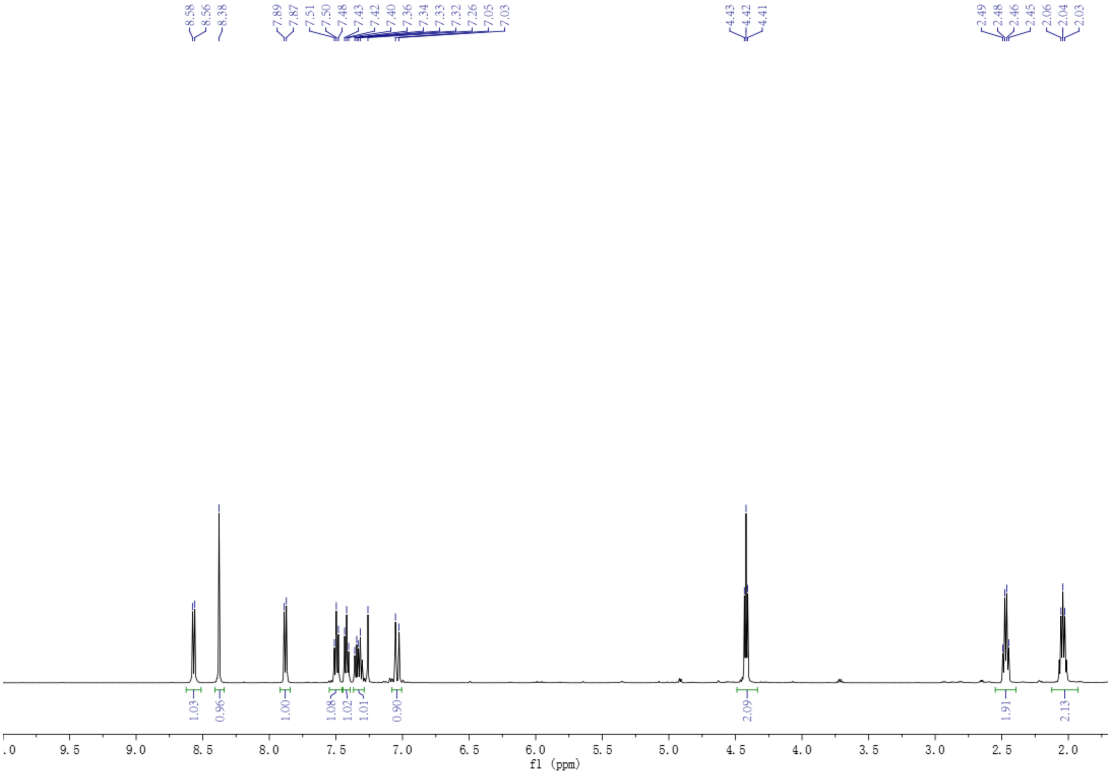
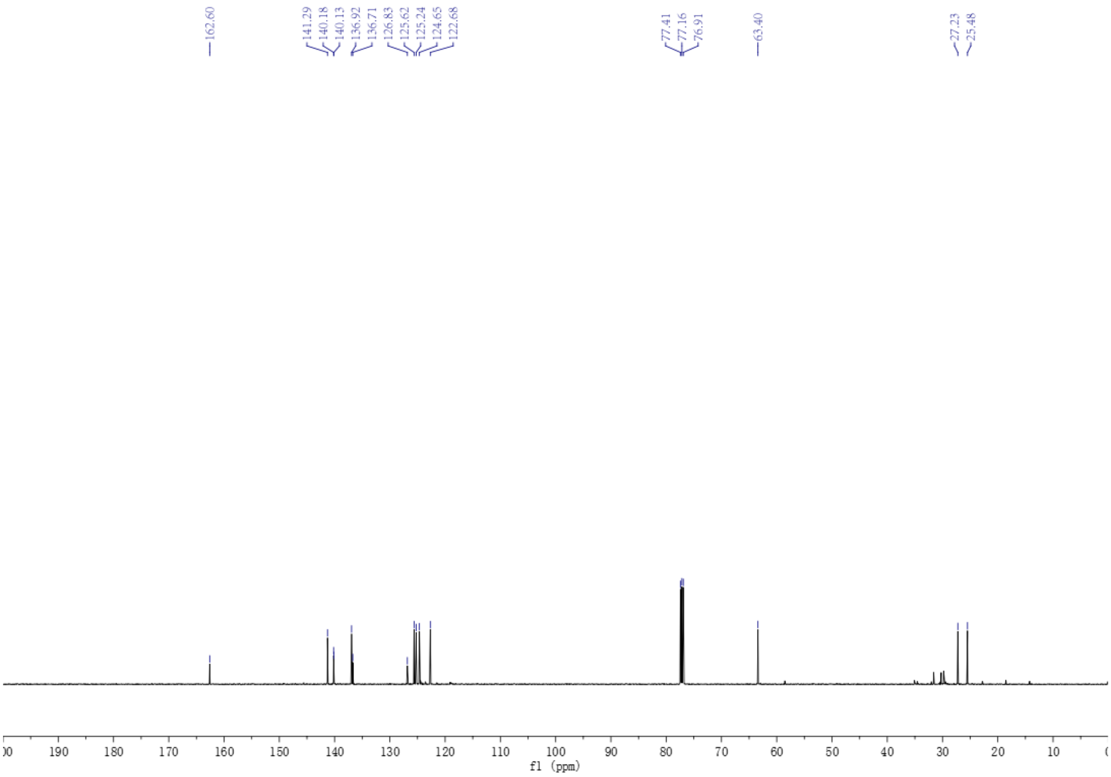
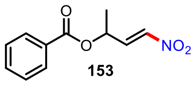


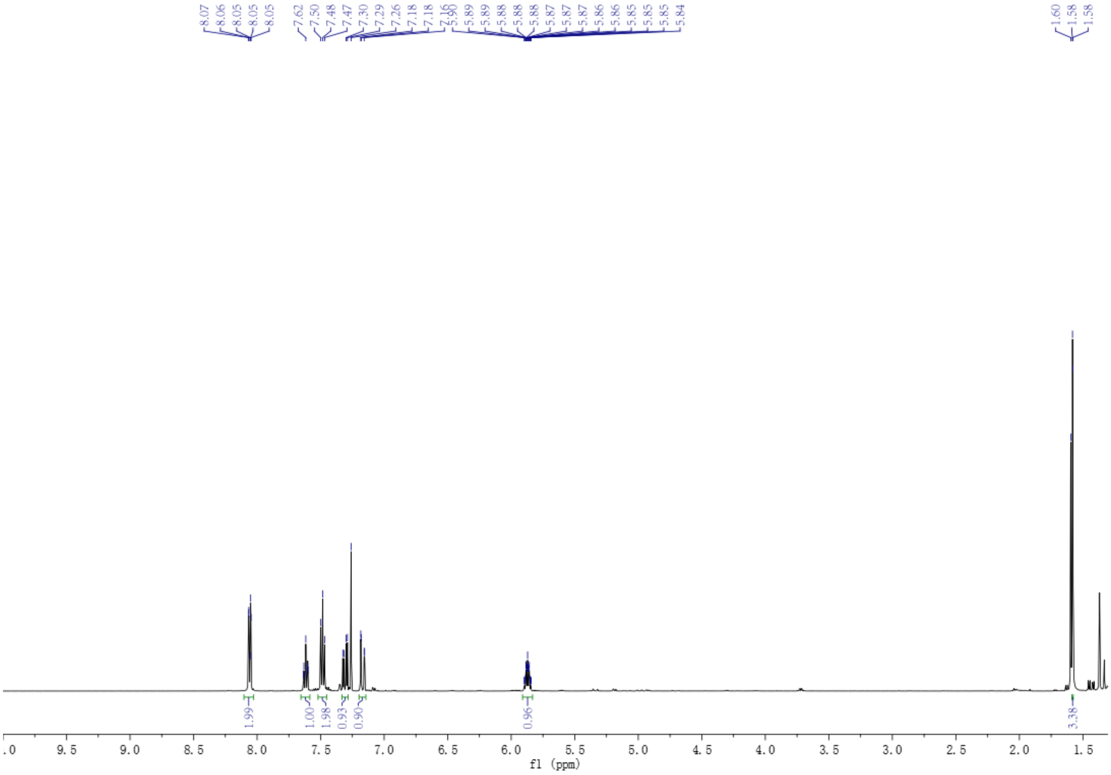
^{1}H NMR of compound **152**（500 MHz, $CDCl_3$）



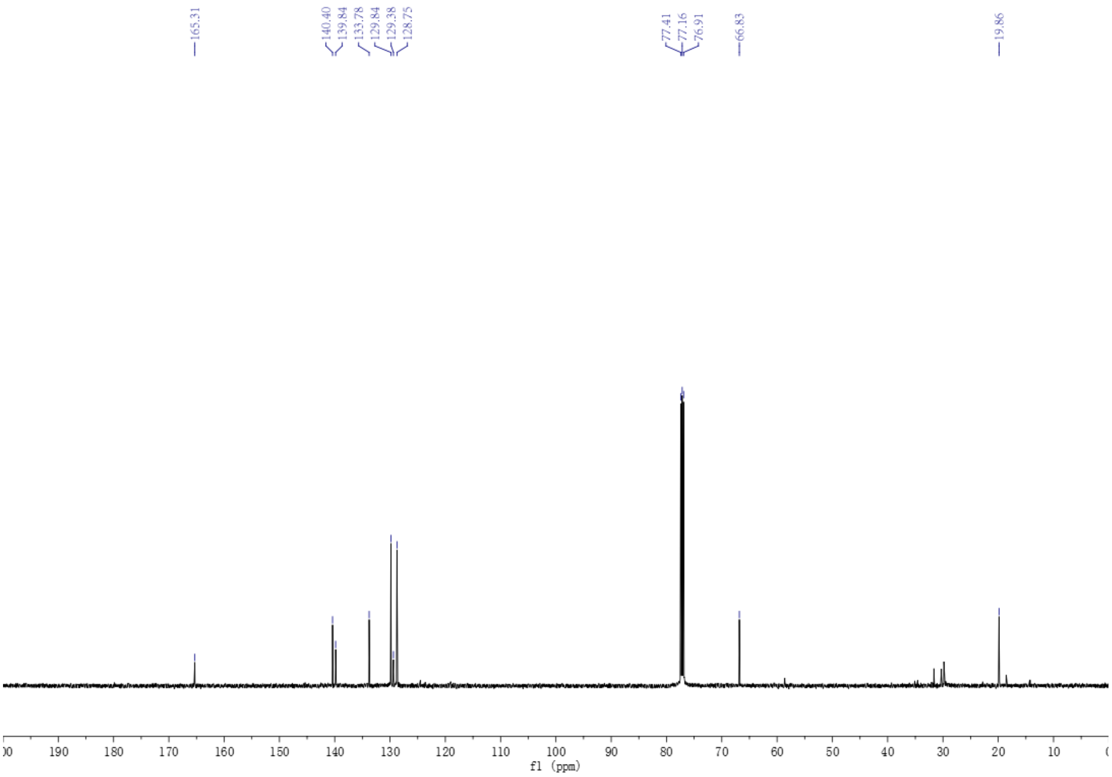
^{13}C NMR of compound **152**（126 MHz, $CDCl_3$）



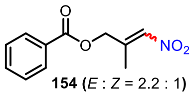
153



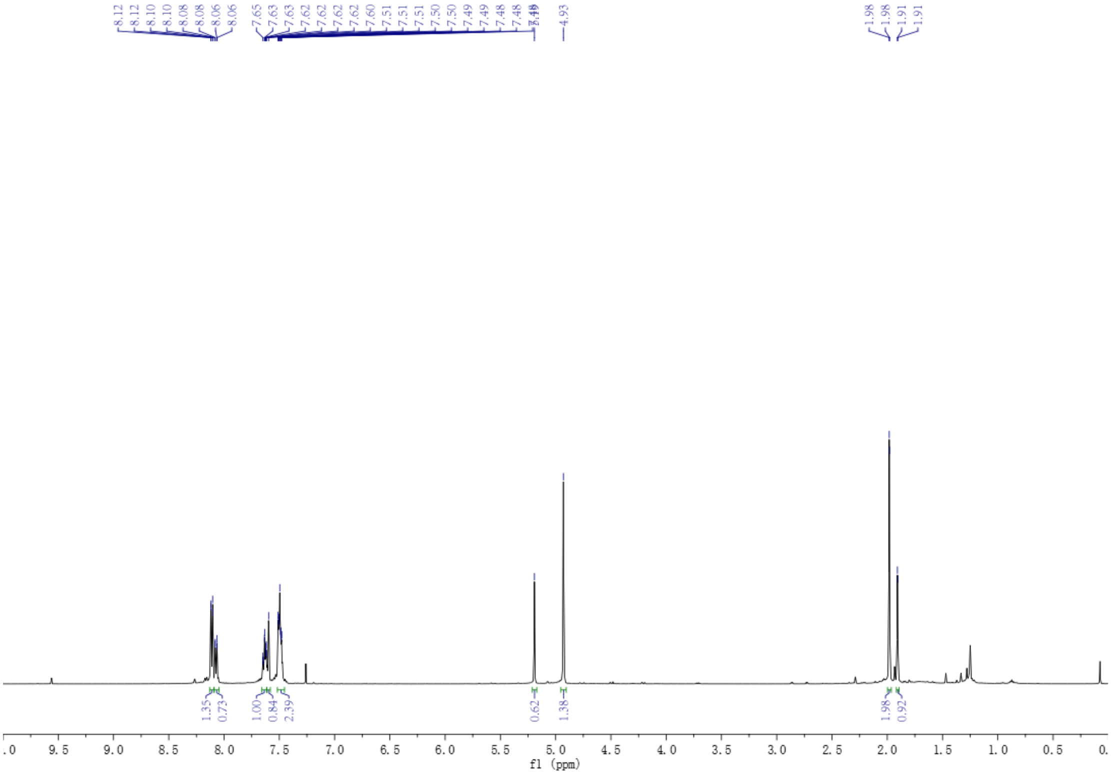
[1]H NMR of compound **153**（500 MHz, $CDCl_3$）



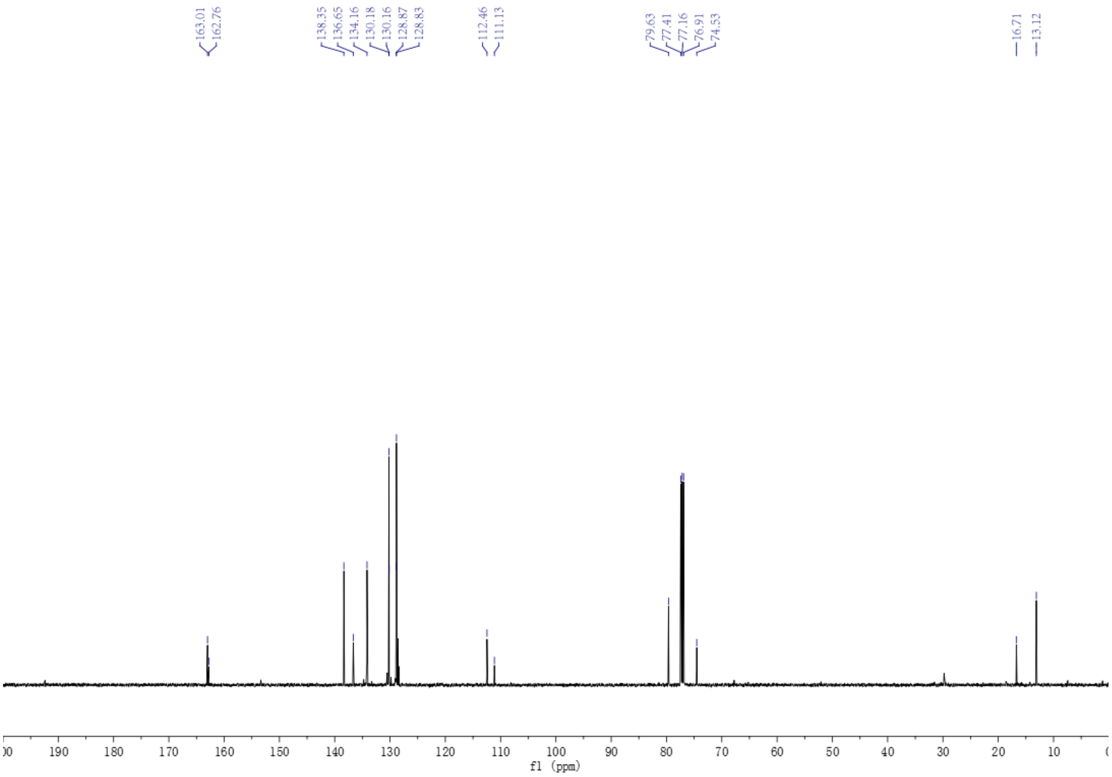
[13]C NMR of compound **153**（126 MHz, $CDCl_3$）



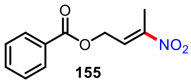
154 (*E* : *Z* = 2.2 : 1)



^{1}H NMR of compound **154**（500 MHz, $CDCl_3$）



^{13}C NMR of compound **154**（126 MHz, $CDCl_3$）



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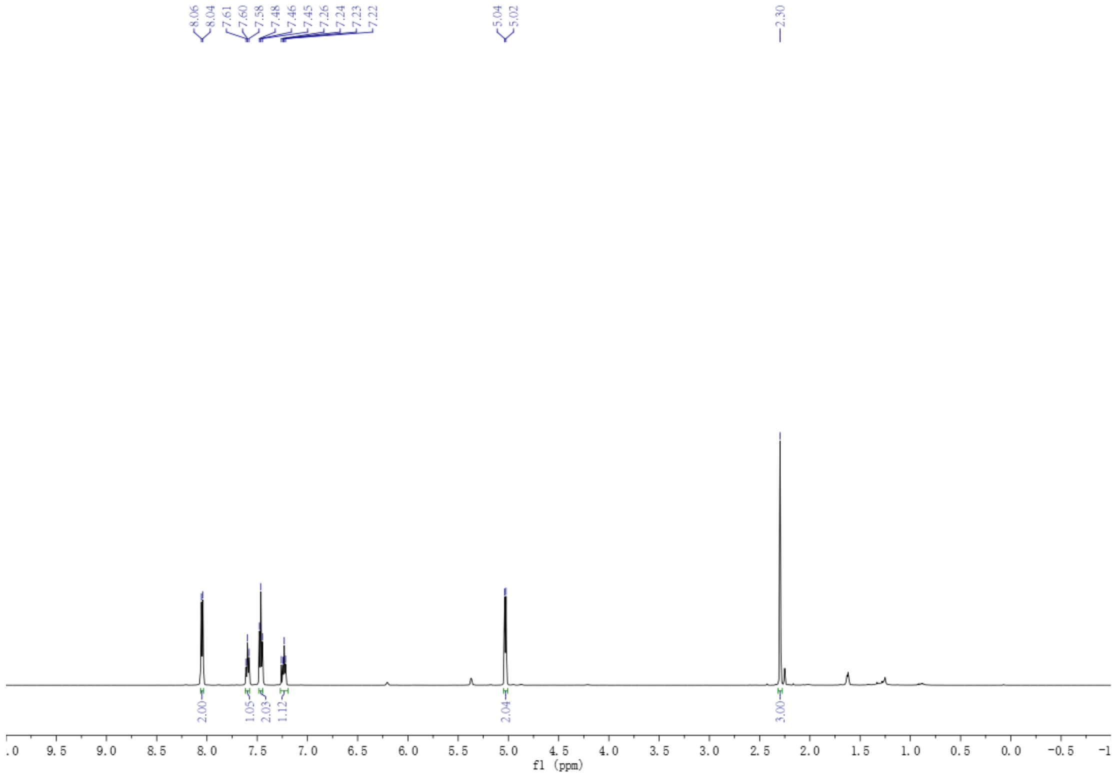
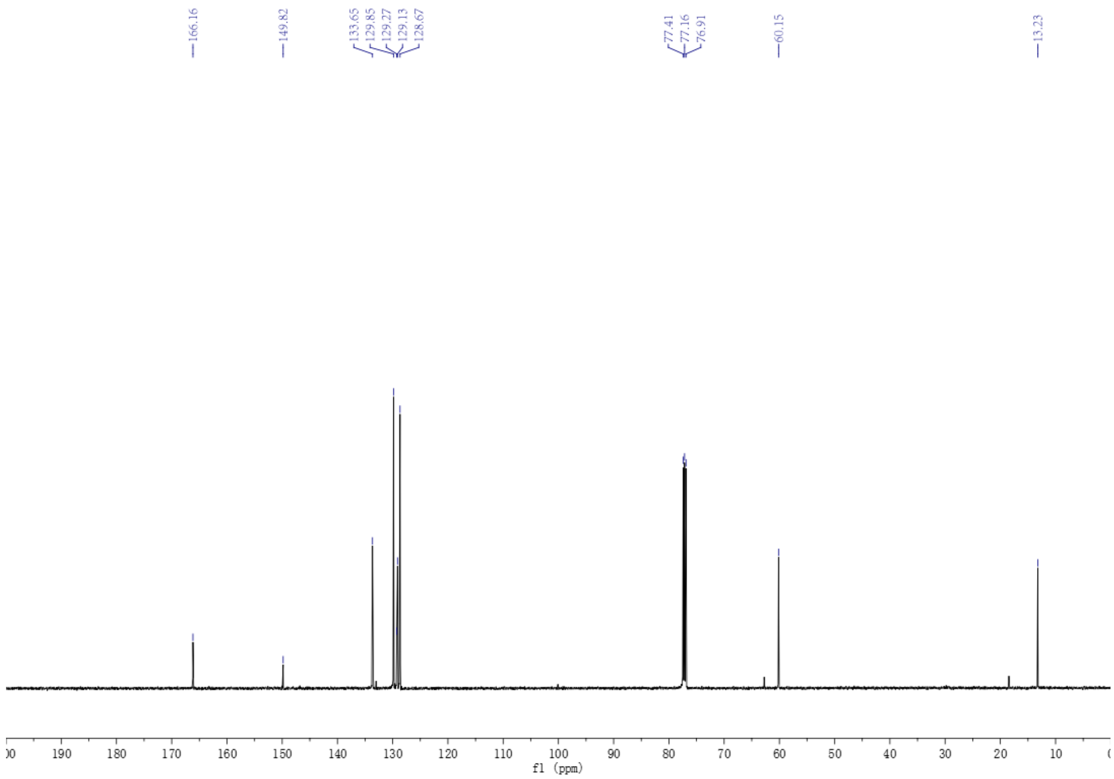
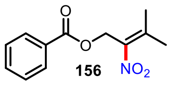


^{1}H NMR of compound **155**（500 MHz, $CDCl_3$）



^{13}C NMR of compound **155**（126 MHz, $CDCl_3$）



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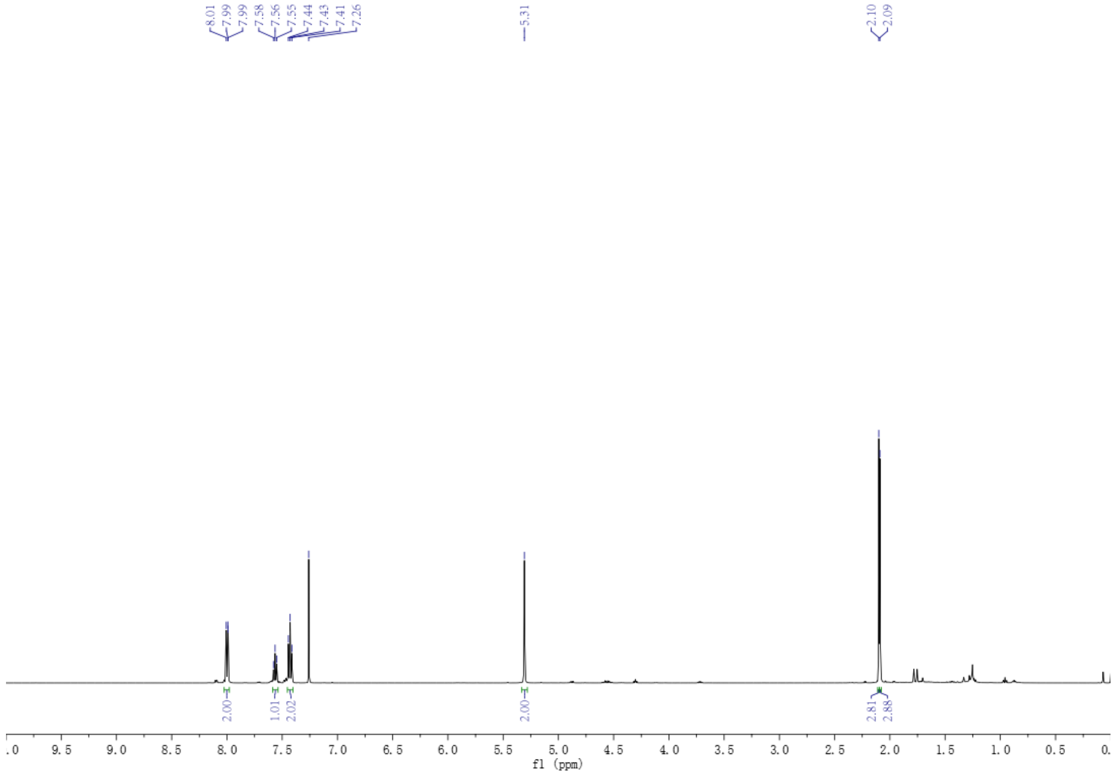
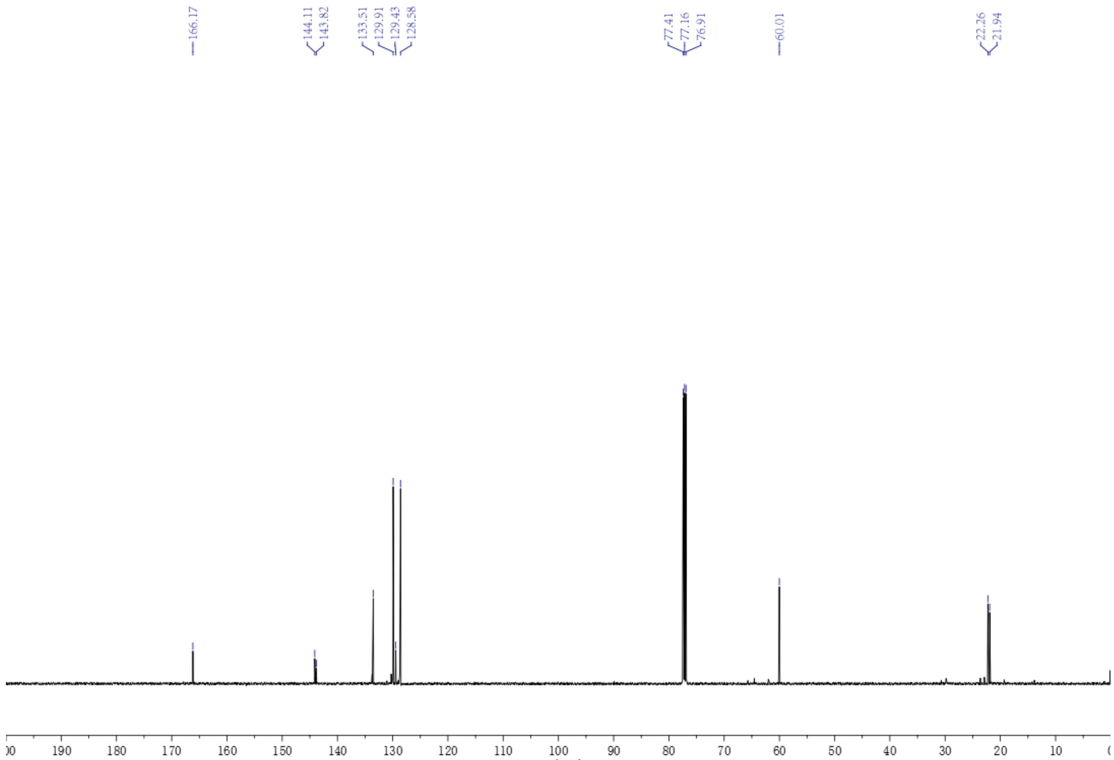
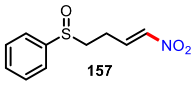


[1]H NMR of compound **156**（500 MHz, $CDCl_3$）



[13]C NMR of compound **156**（126 MHz, $CDCl_3$）



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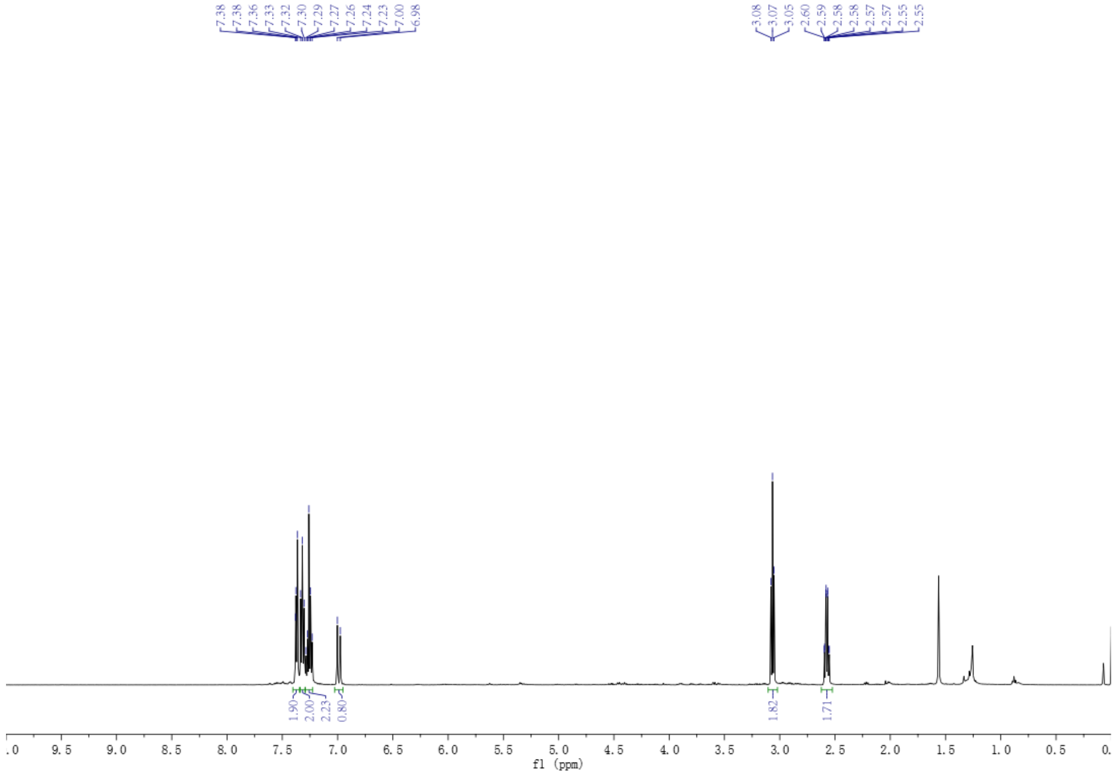
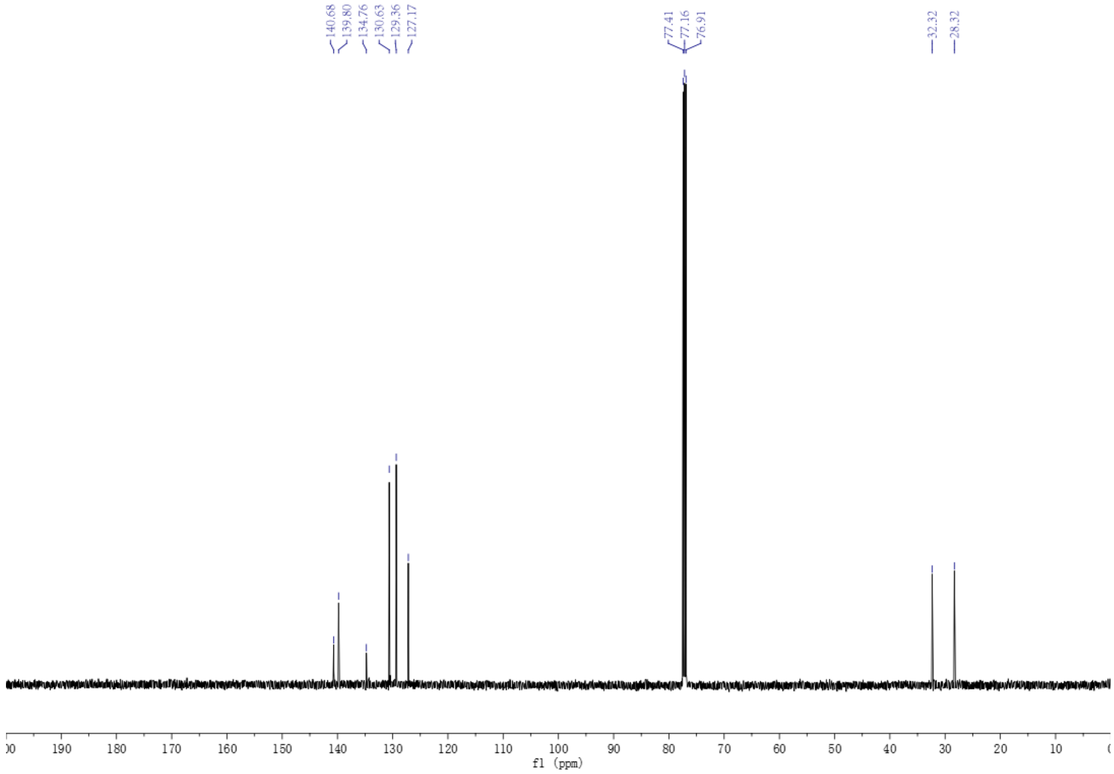
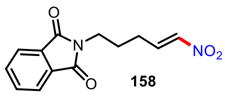
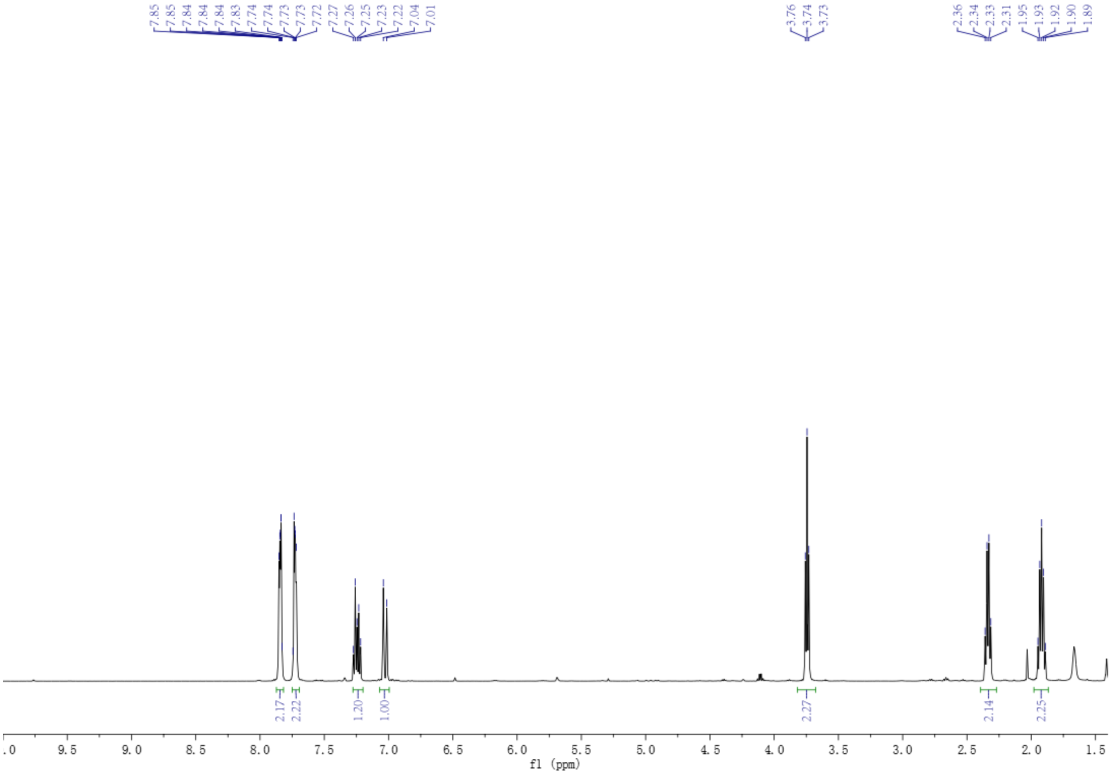


[1]H NMR of compound **157**（500 MHz, CDCl3）

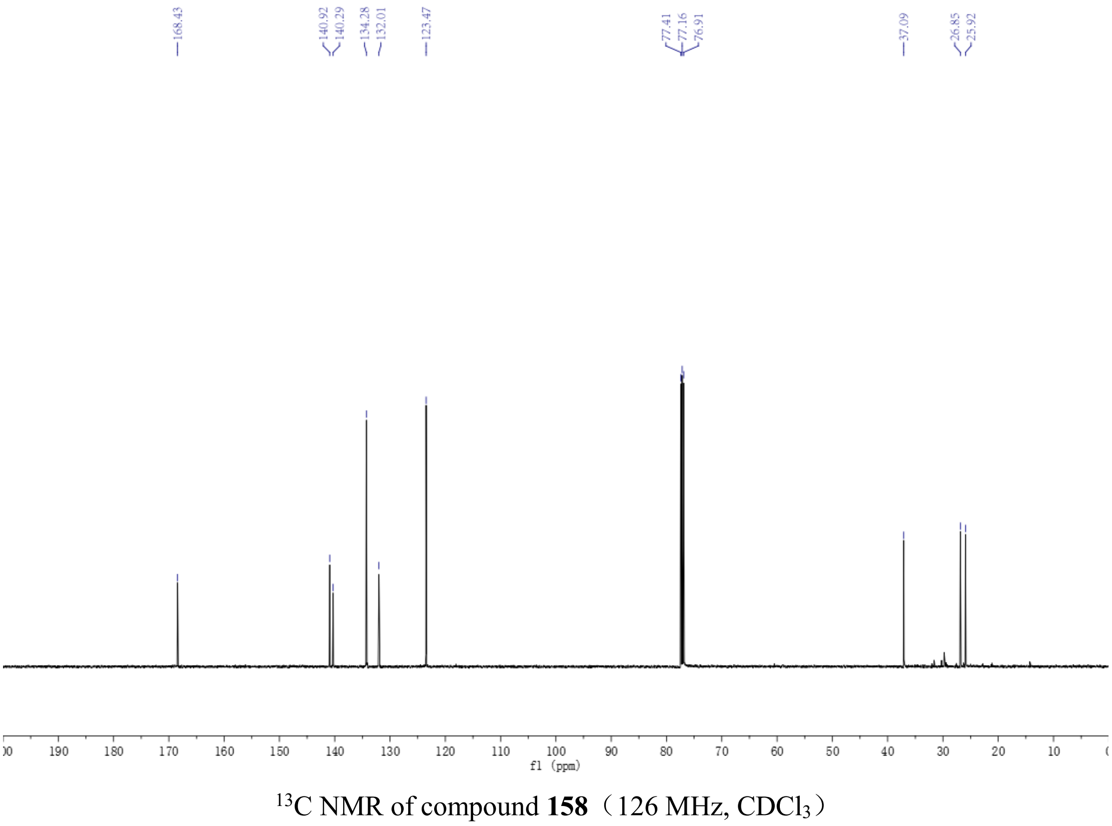


[13]C NMR of compound **157**（126 MHz, CDCl3）

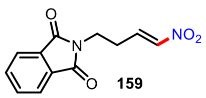




^{1}H NMR of compound **158**（500 MHz, $CDCl_3$）



^{13}C NMR of compound **158**（126 MHz, $CDCl_3$）



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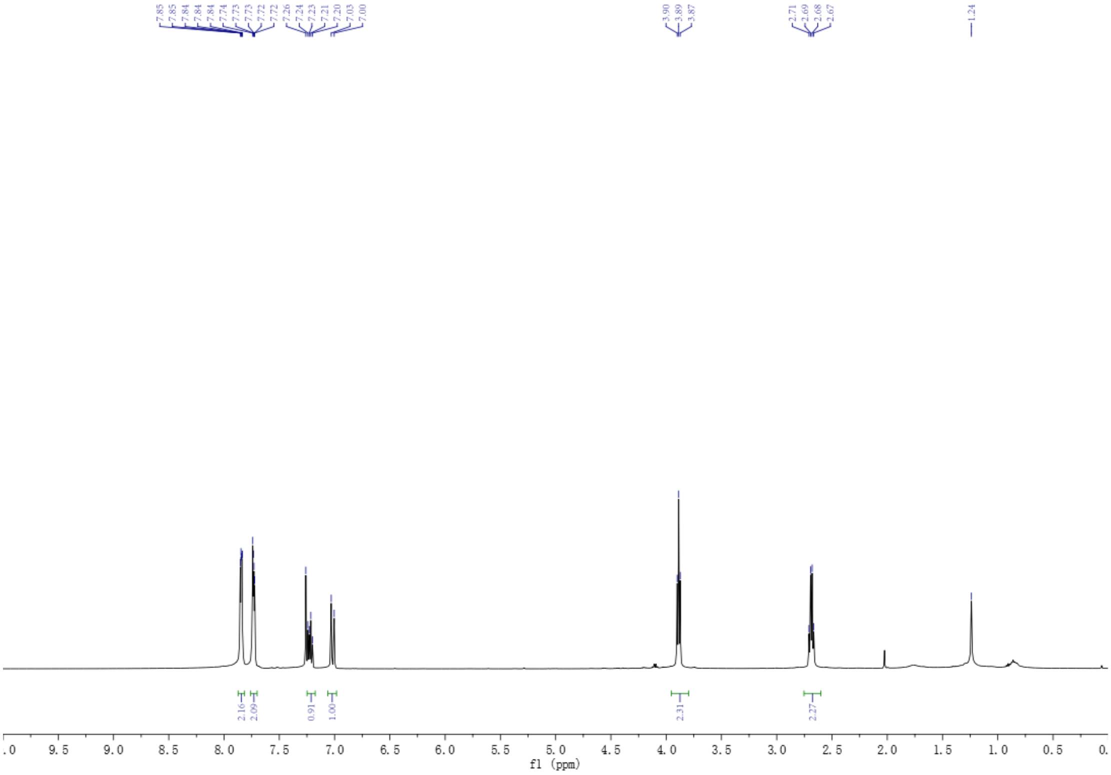
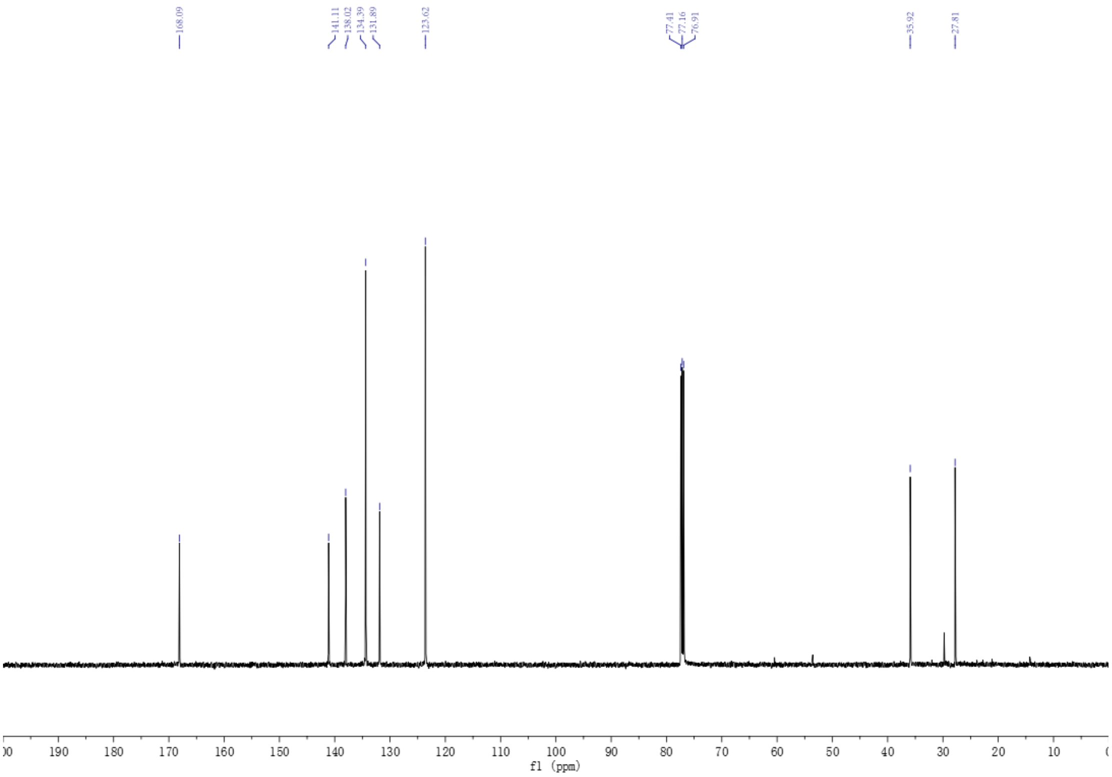
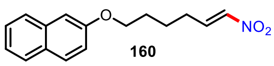


[1]H NMR of compound **159**（500 MHz, $CDCl_3$）



[13]C NMR of compound **159**（126 MHz, $CDCl_3$）



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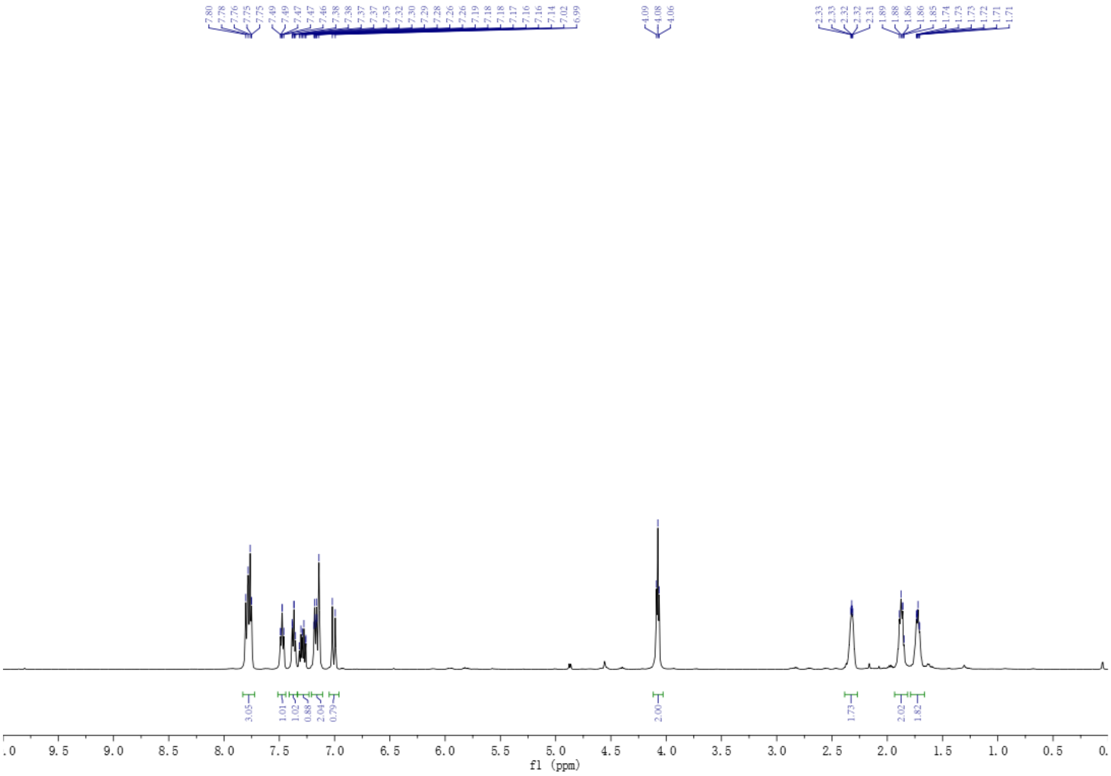
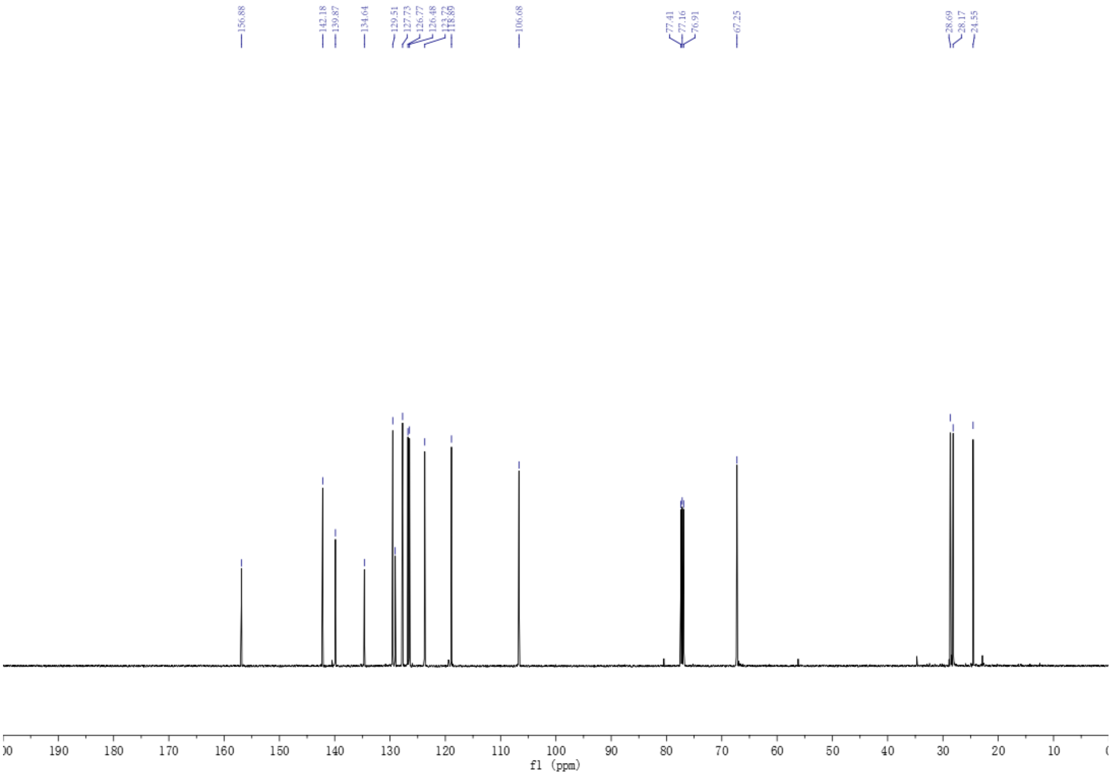
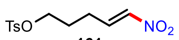


[1]H NMR of compound **160**（500 MHz, $CDCl_3$）



[13]C NMR of compound **160**（126 MHz, $CDCl_3$）



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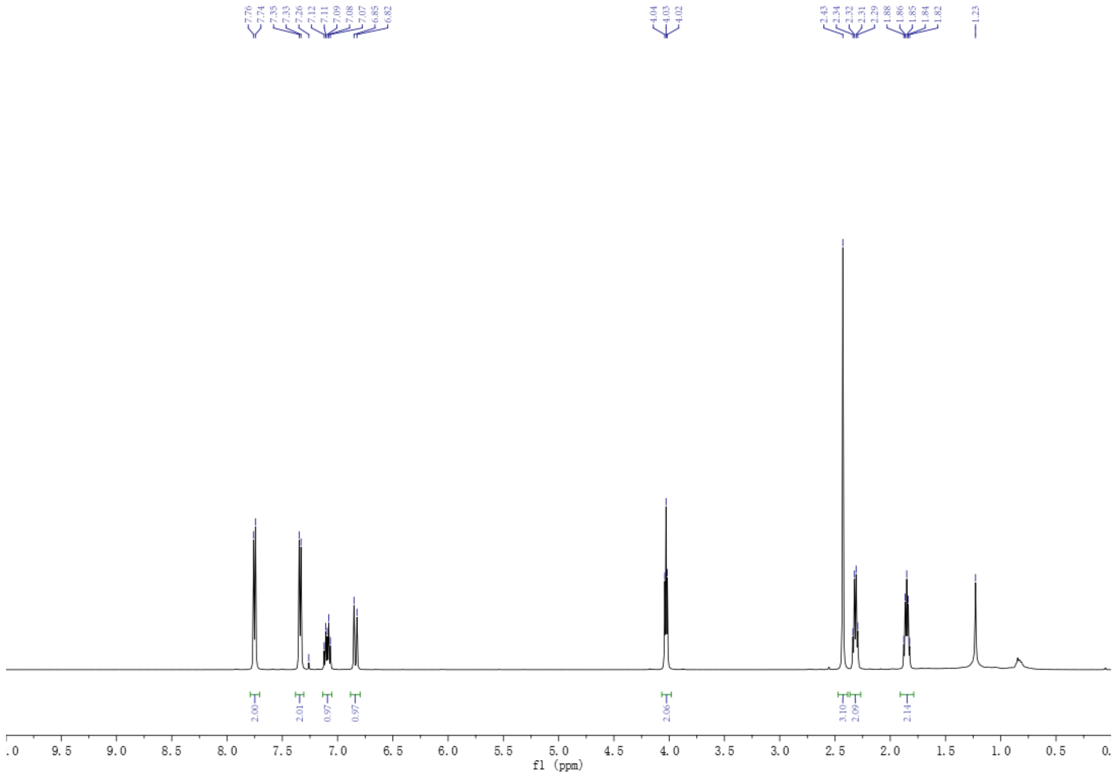
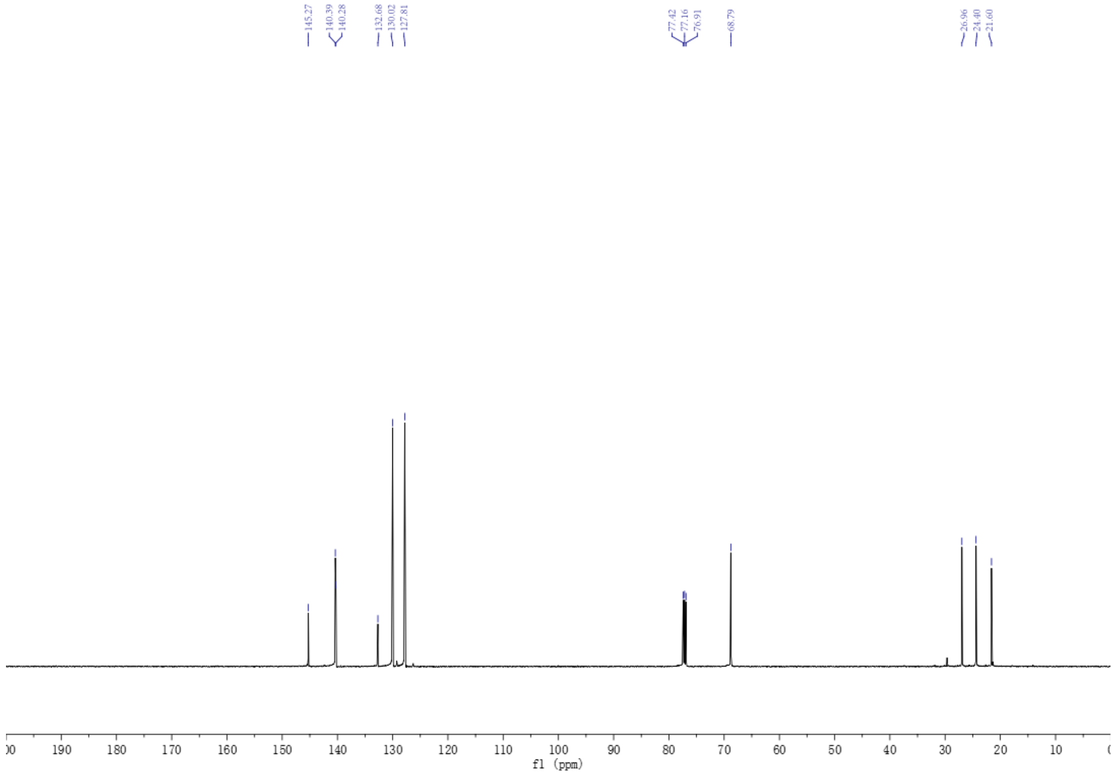
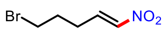


[1]H NMR of compound **161**（500 MHz, $CDCl_3$）



[13]C NMR of compound **161**（126 MHz, $CDCl_3$）



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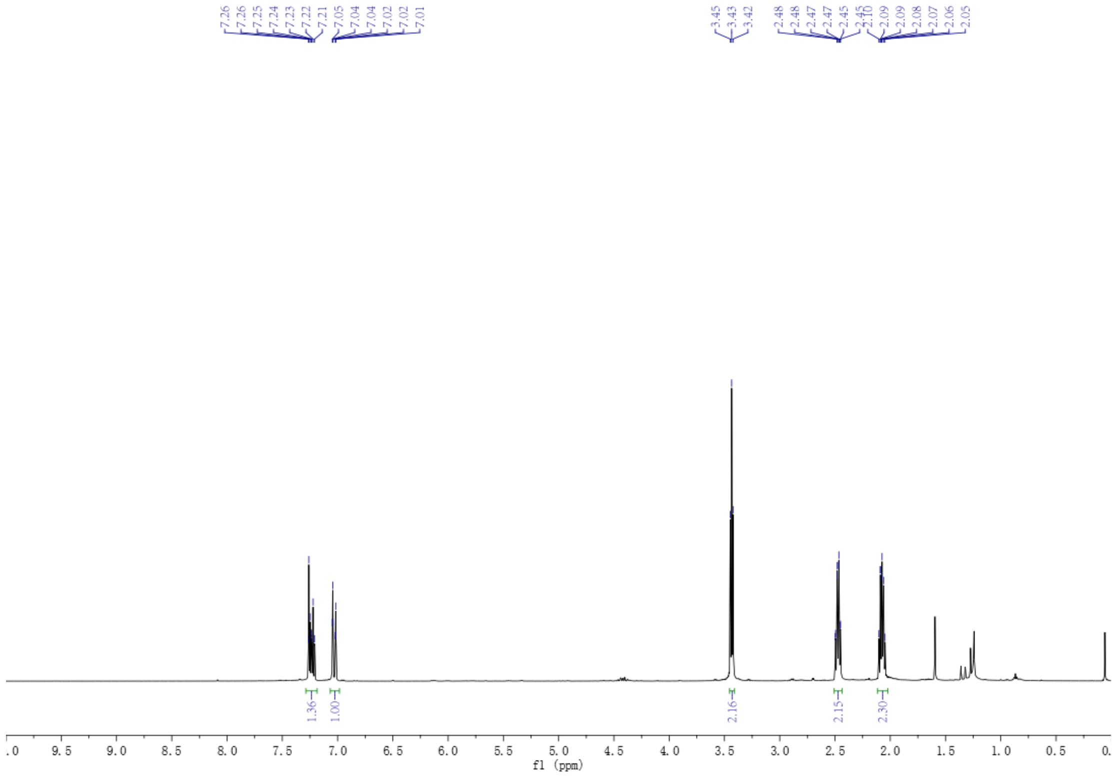
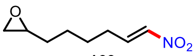


^{1}H NMR of compound **162**（500 MHz, $CDCl_3$）



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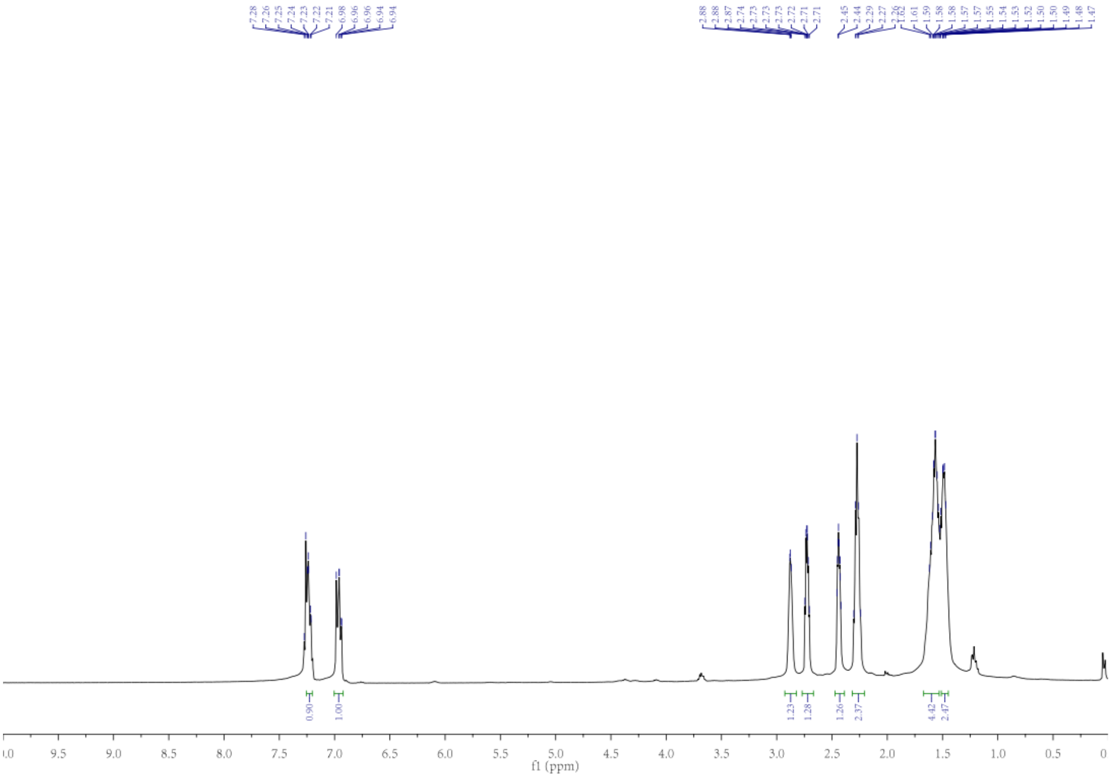
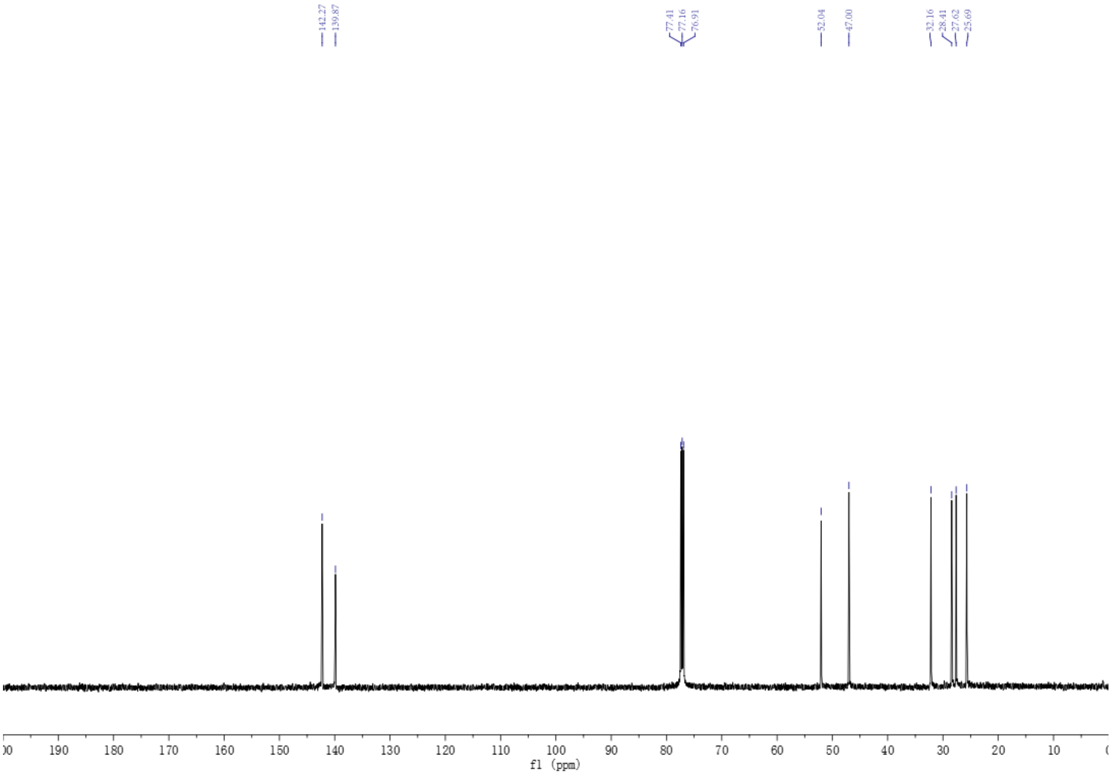
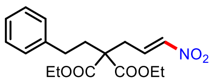


^{1}H NMR of compound **163**（500 MHz, $CDCl_3$）



^{13}C NMR of compound **163**（126 MHz, $CDCl_3$）



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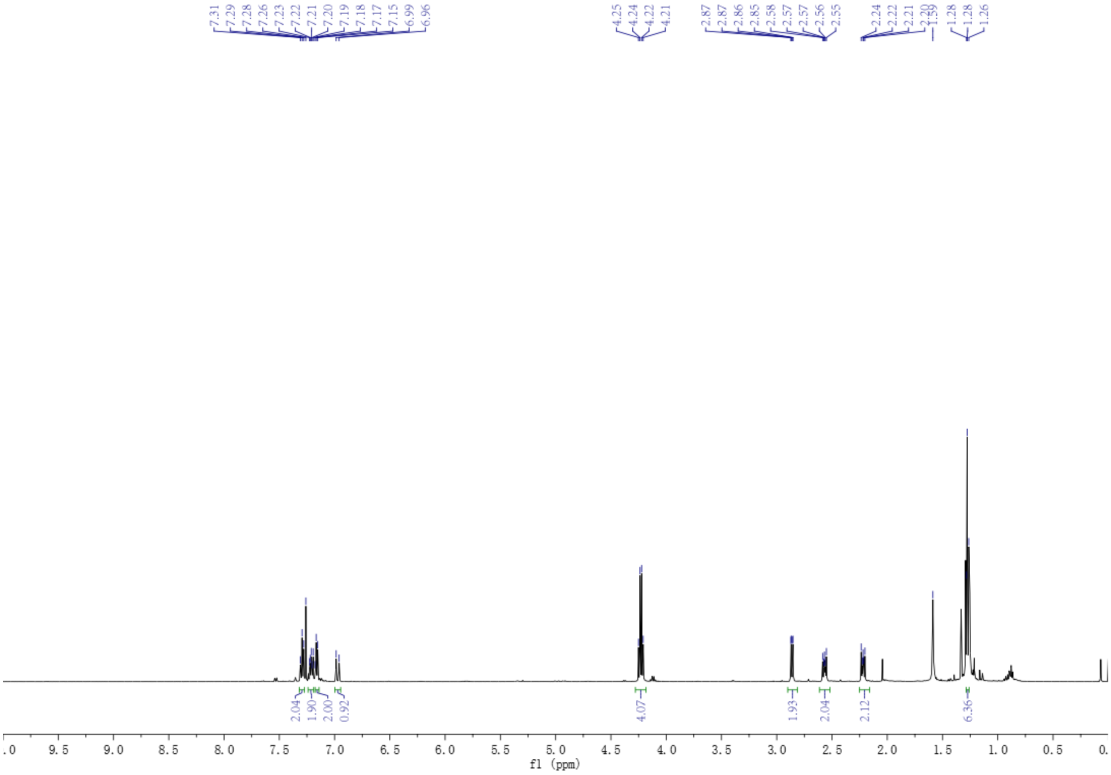
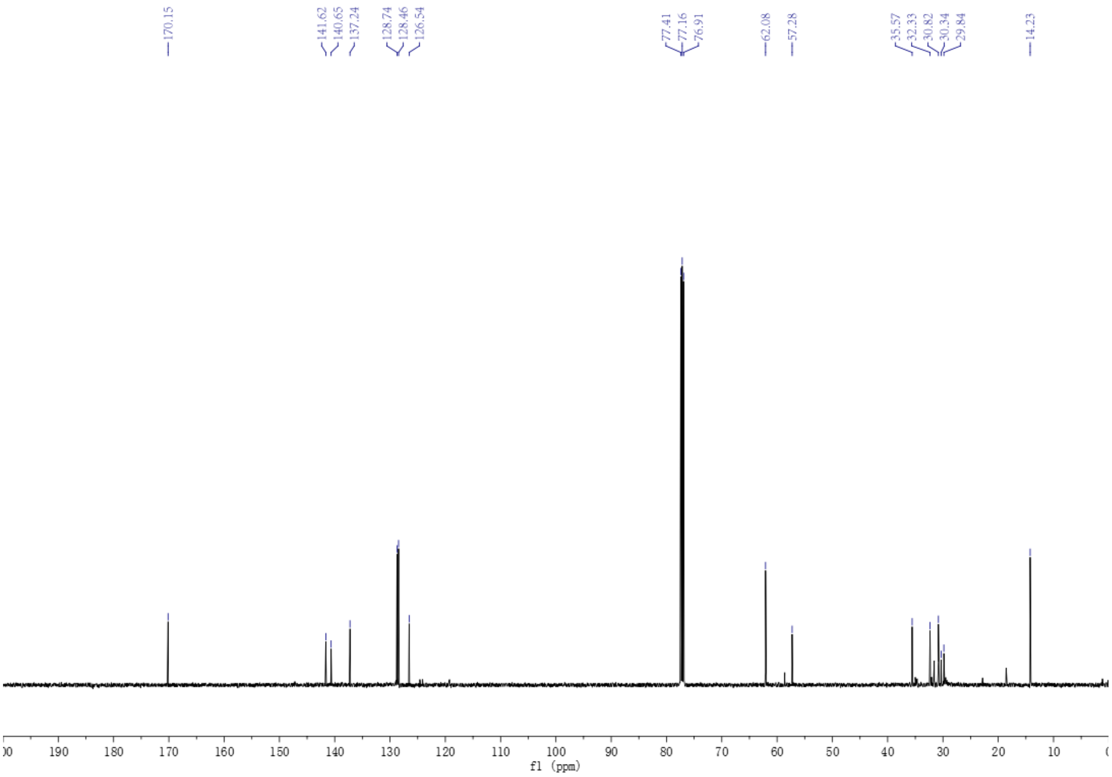
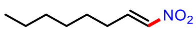


[1]H NMR of compound **164**（500 MHz, $CDCl_3$）



[13]C NMR of compound **164**（126 MHz, $CDCl_3$）



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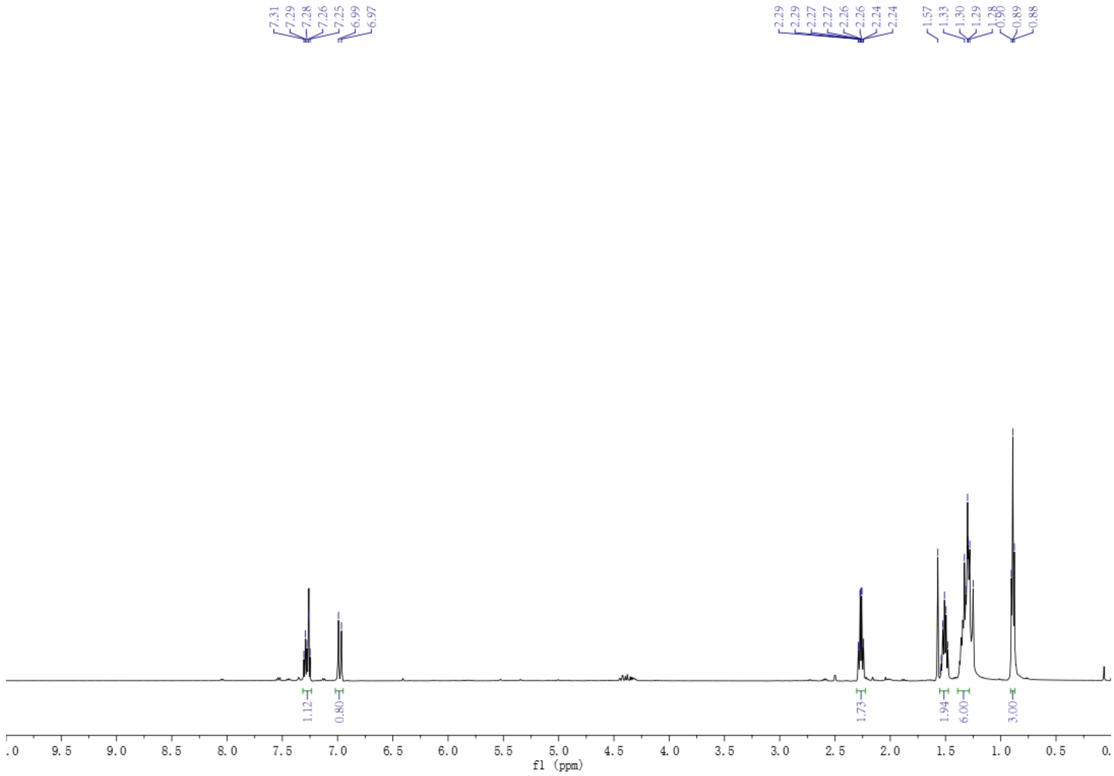

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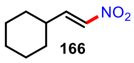

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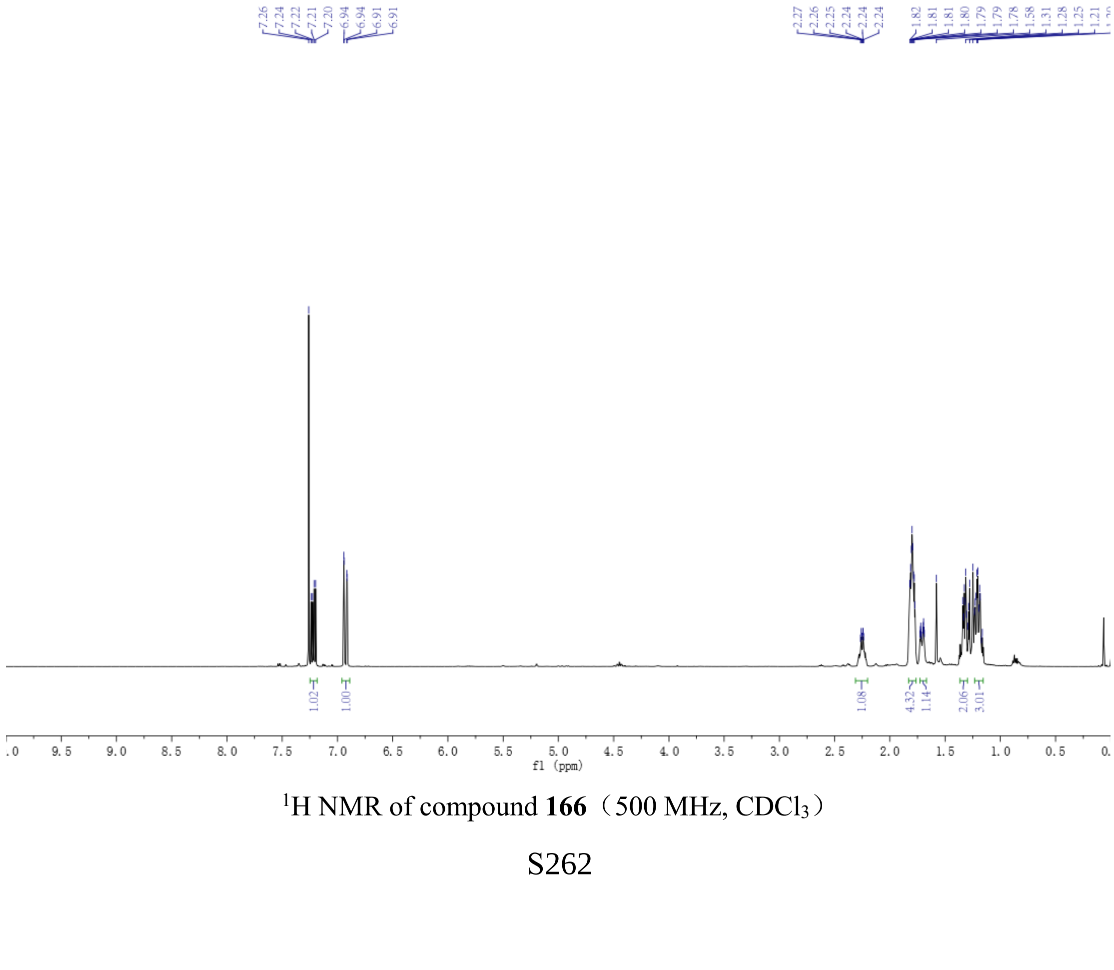
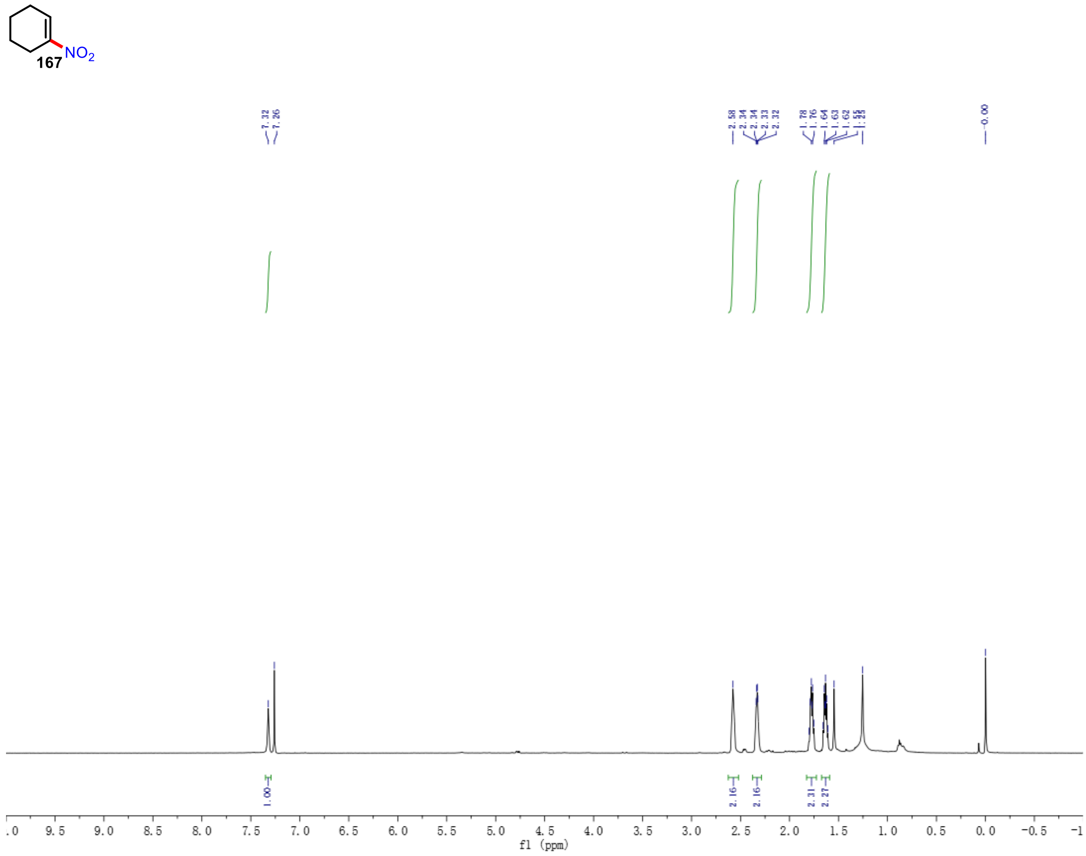
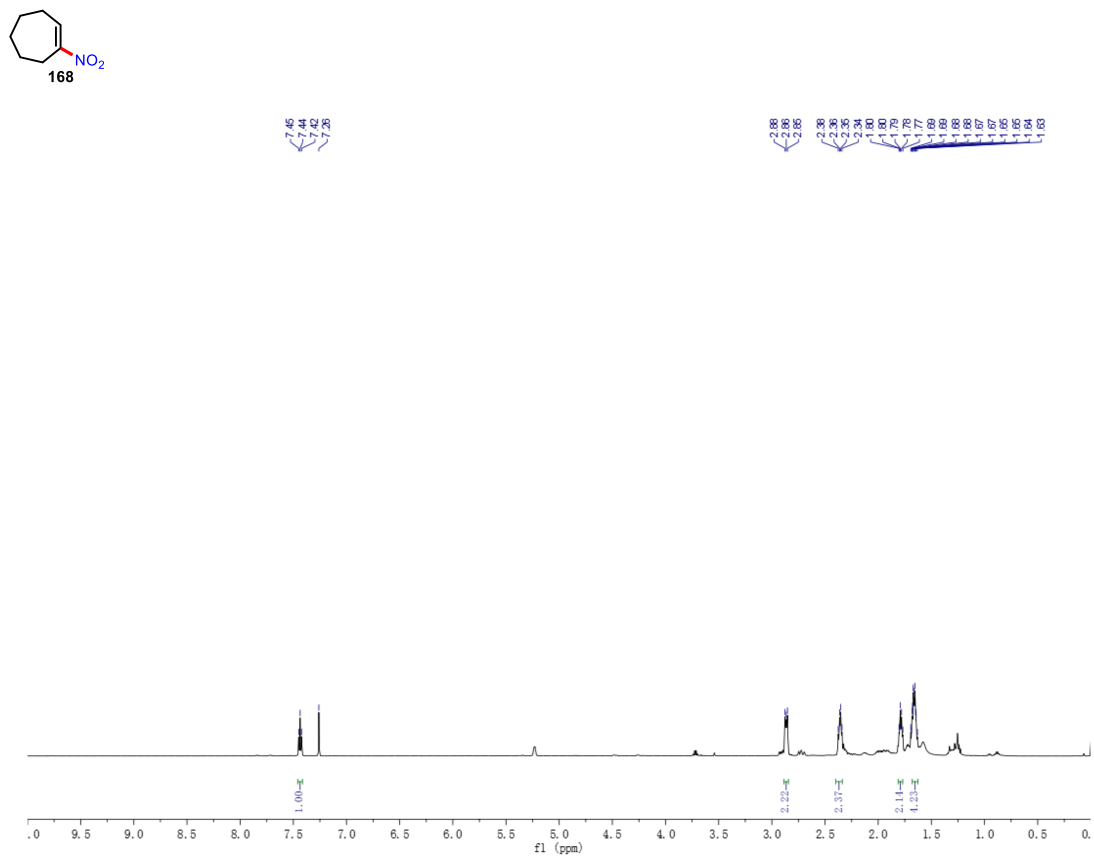


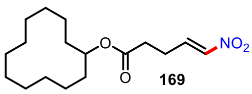
[1]H NMR of compound **166**（500 MHz, $CDCl_3$）



[1]H NMR of compound **167**（500 MHz, $CDCl_3$）



[1]H NMR of compound **168**（500 MHz, $CDCl_3$）



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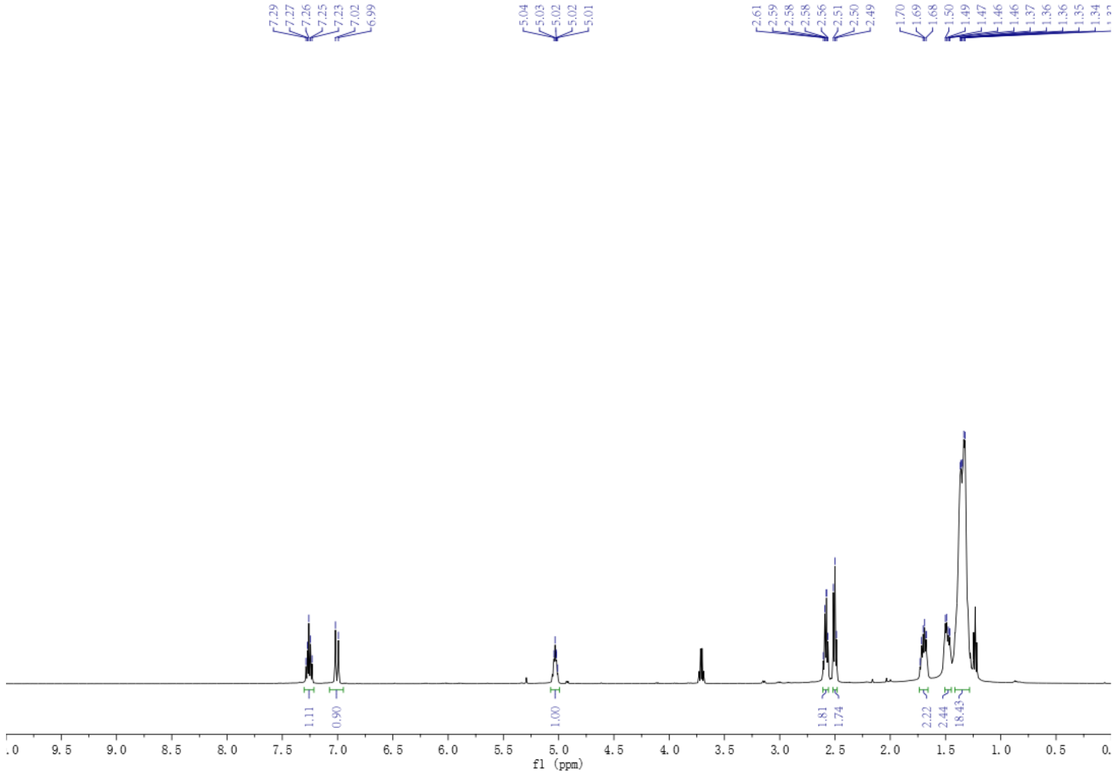
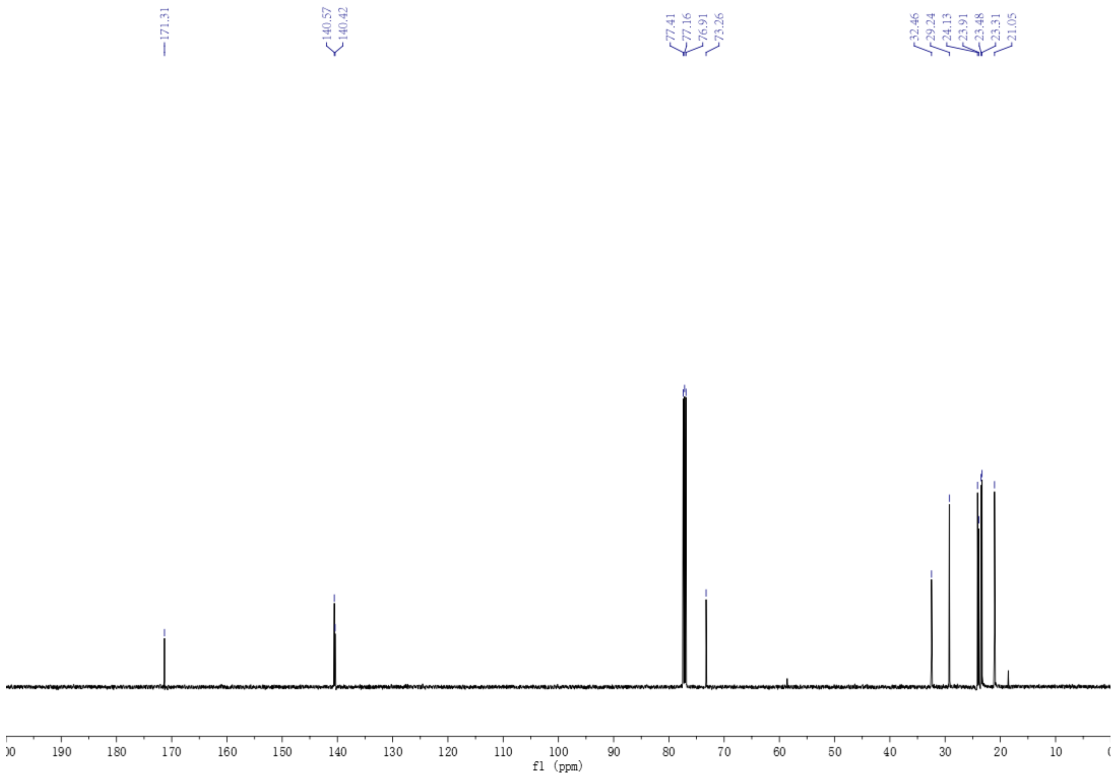
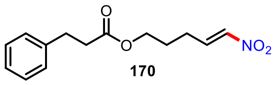


[1]H NMR of compound **169**（500 MHz, $CDCl_3$）



[13]C NMR of compound **169**（126 MHz, $CDCl_3$）



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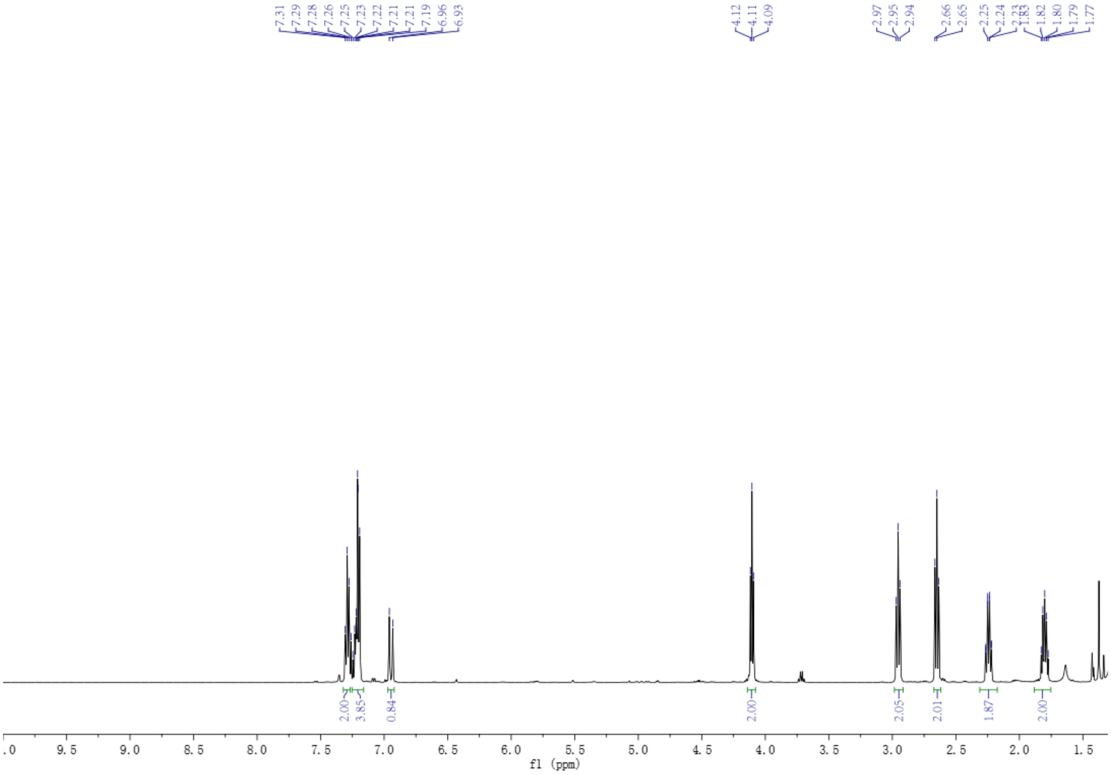

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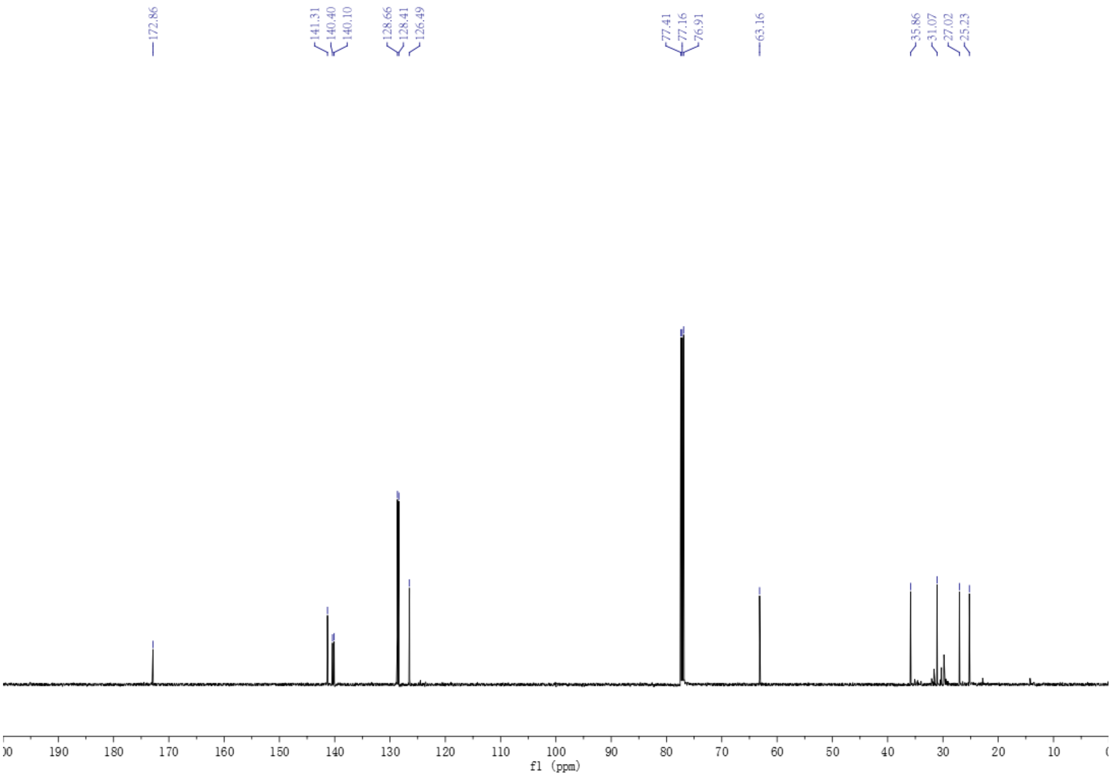
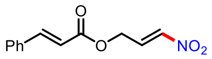


[13]C NMR of compound **170**（126 MHz, $CDCl_3$）



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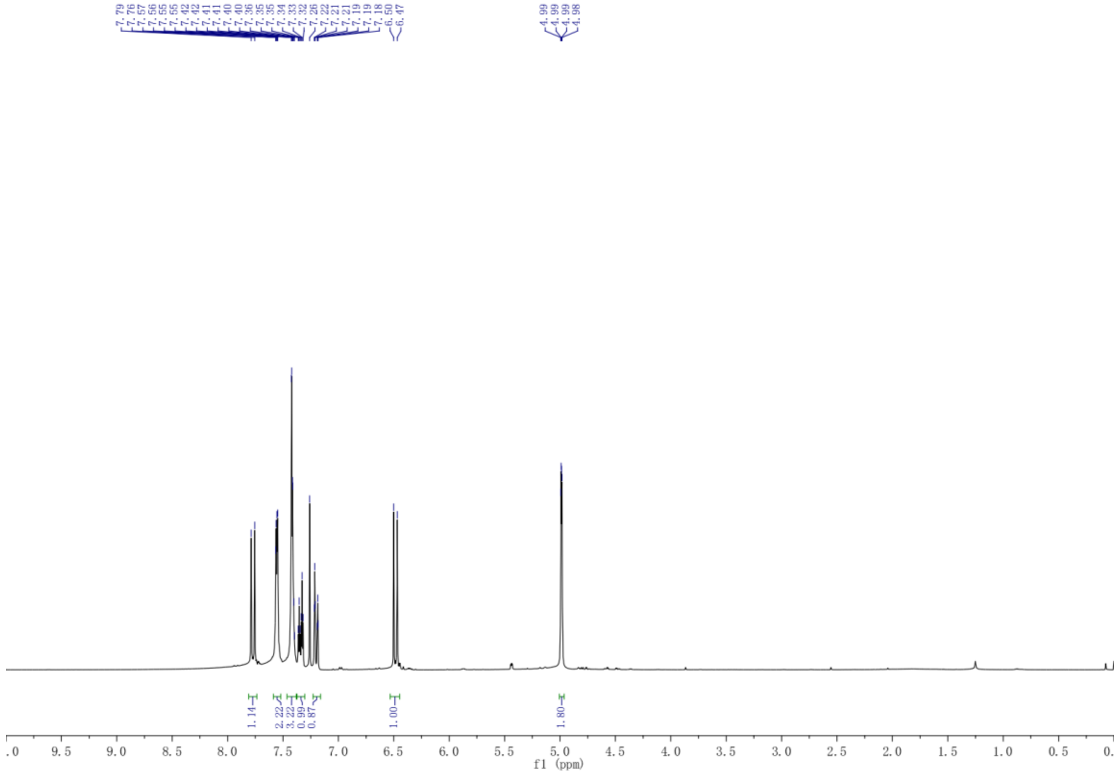
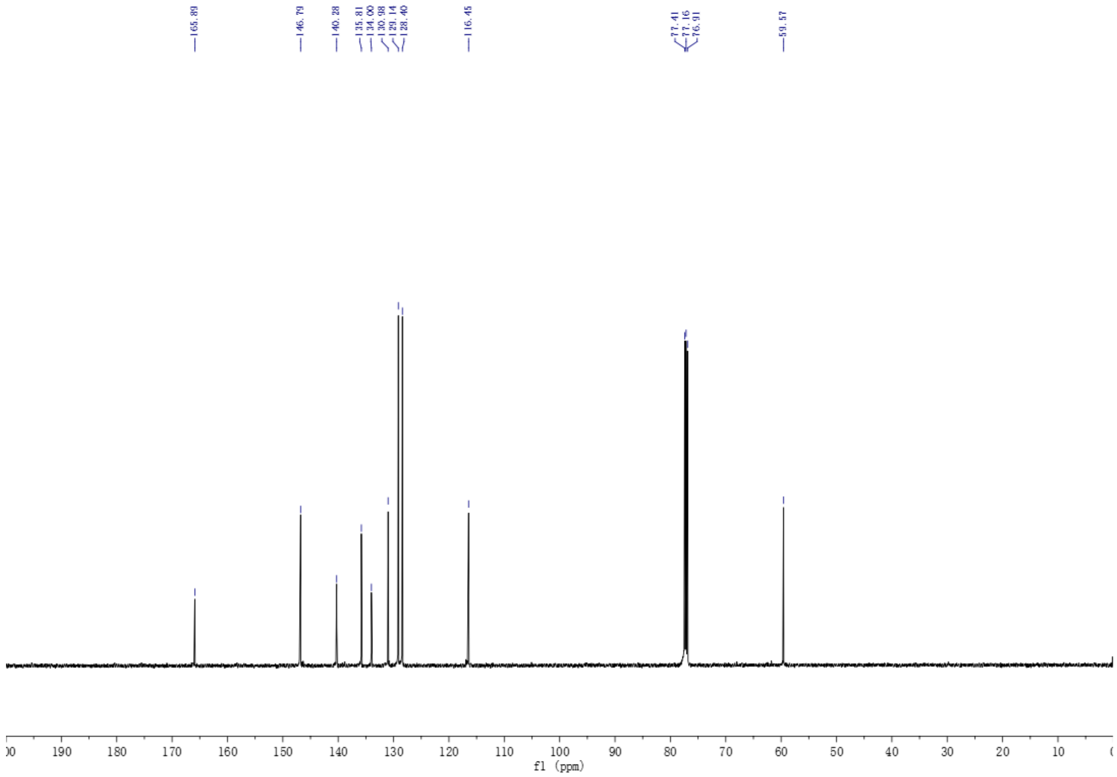
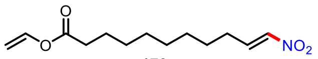


[1]H NMR of compound **171**（500 MHz, $CDCl_3$）



[13]C NMR of compound **171**（126 MHz, $CDCl_3$）



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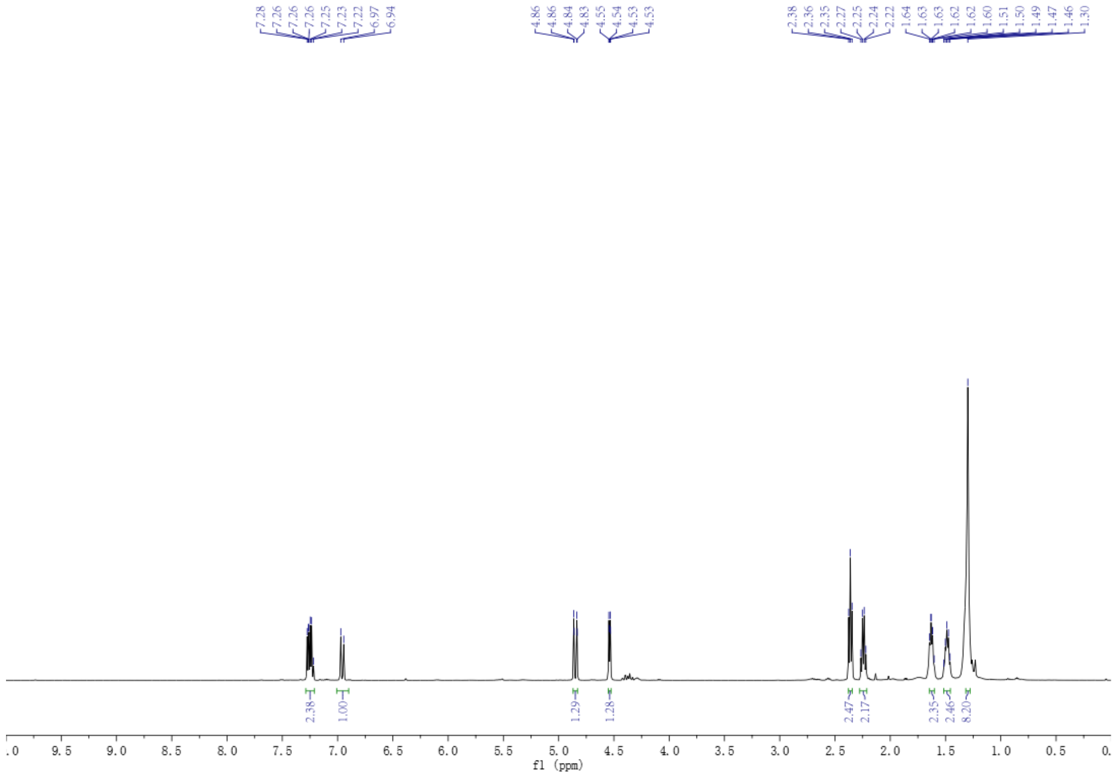
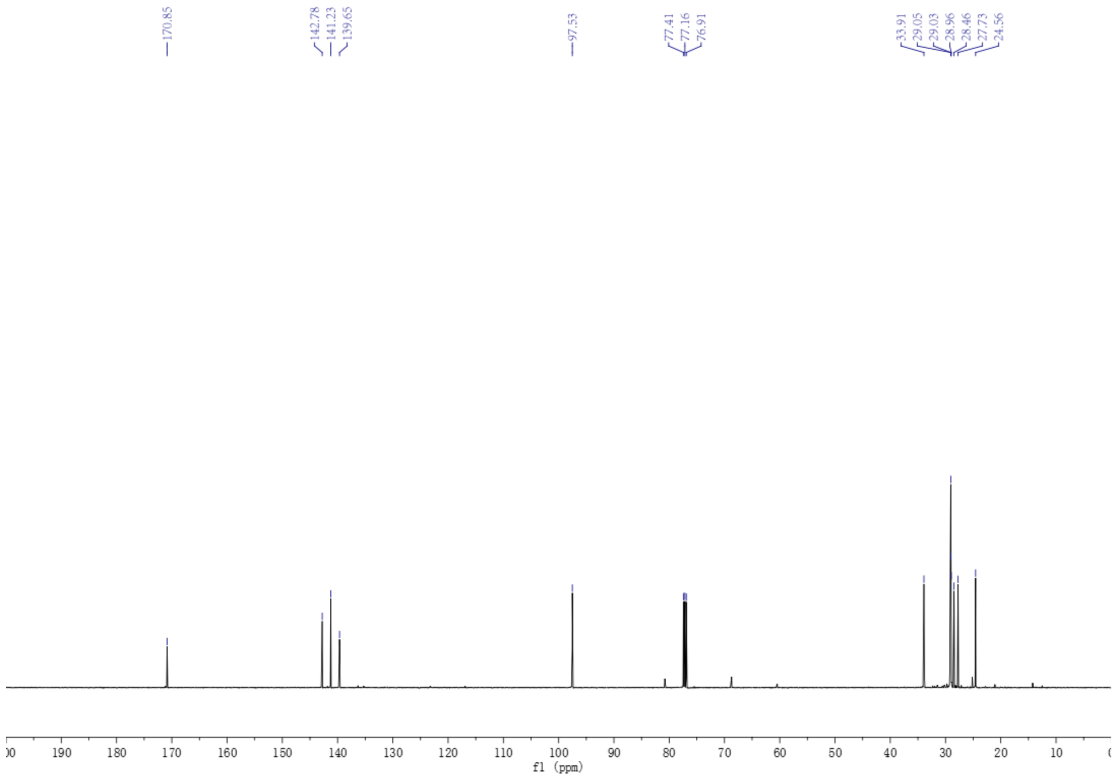
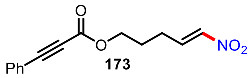
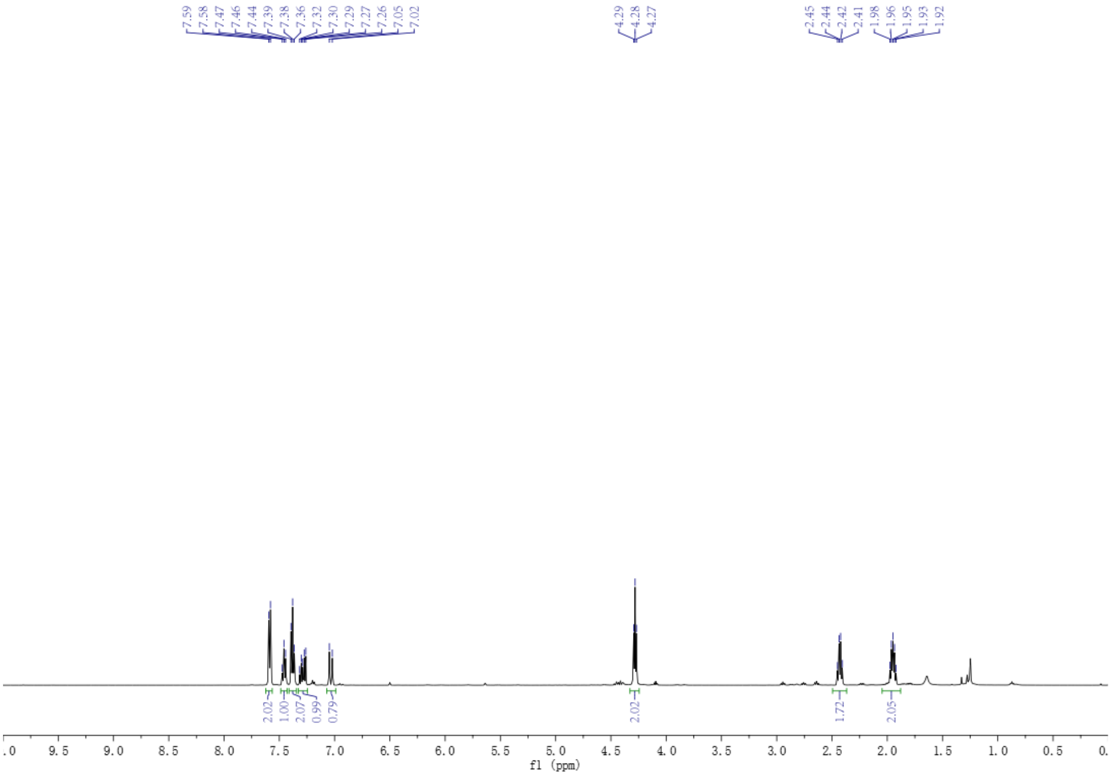


[1]H NMR of compound **172**（500 MHz, $CDCl_3$）

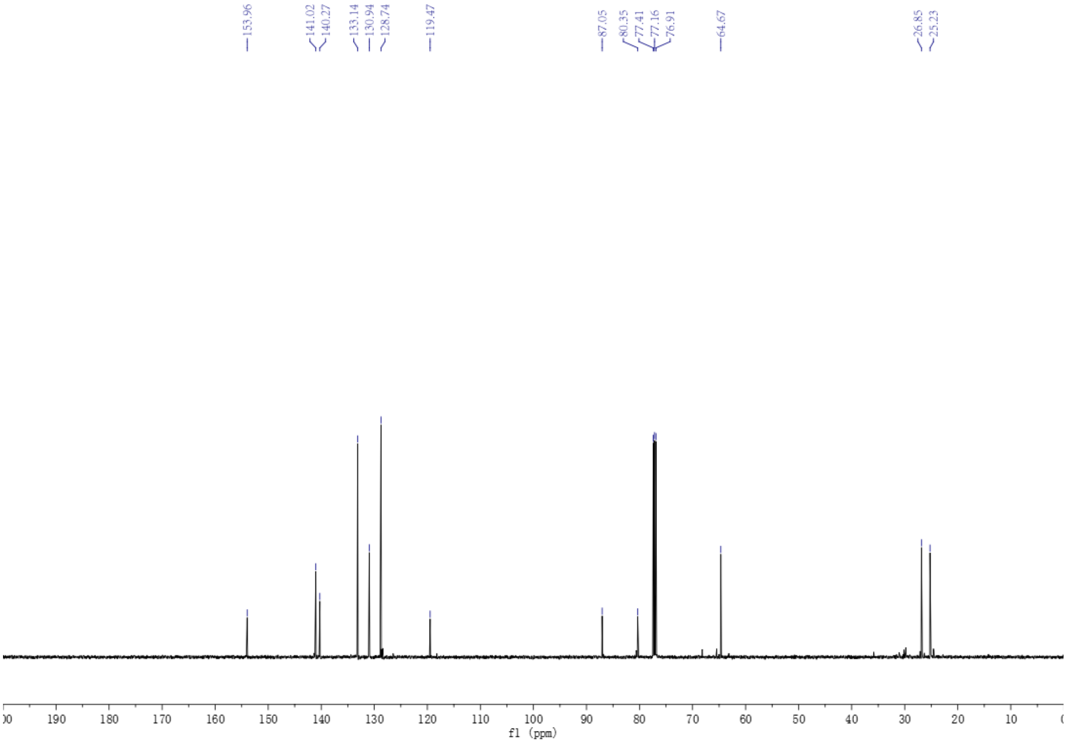


[13]C NMR of compound **172**（126 MHz, $CDCl_3$）

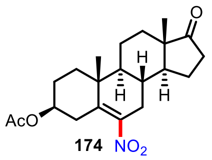


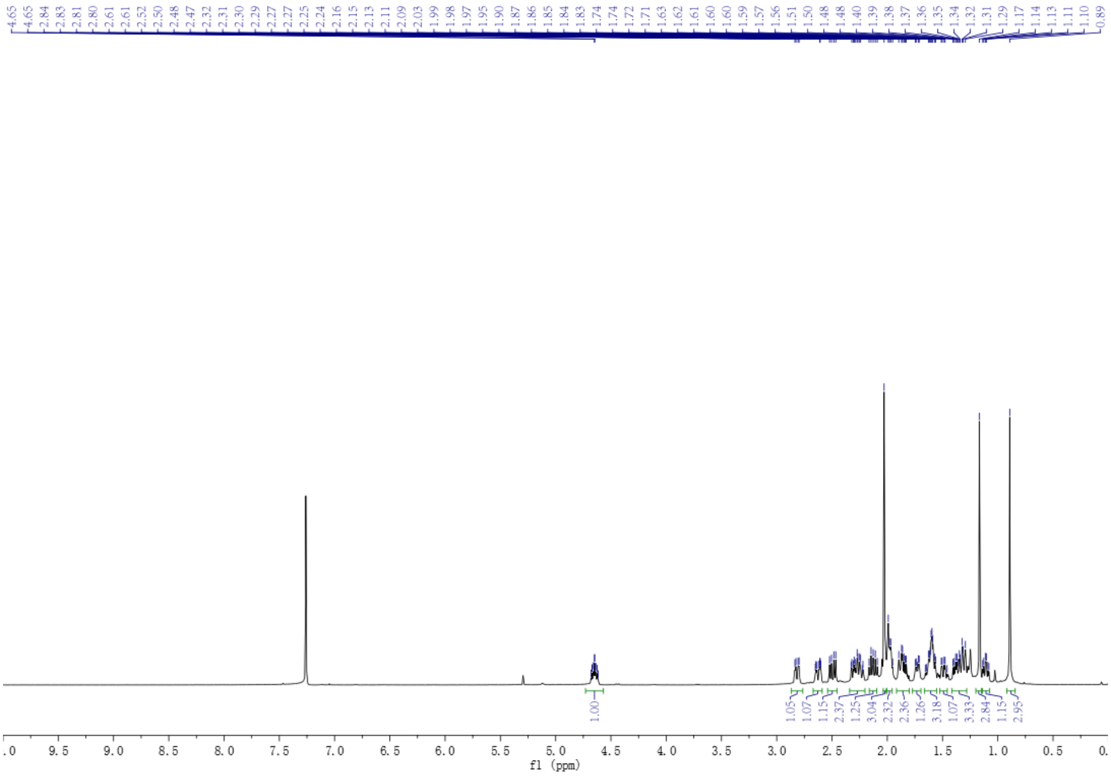


[1]H NMR of compound **173**（500 MHz, $CDCl_3$）

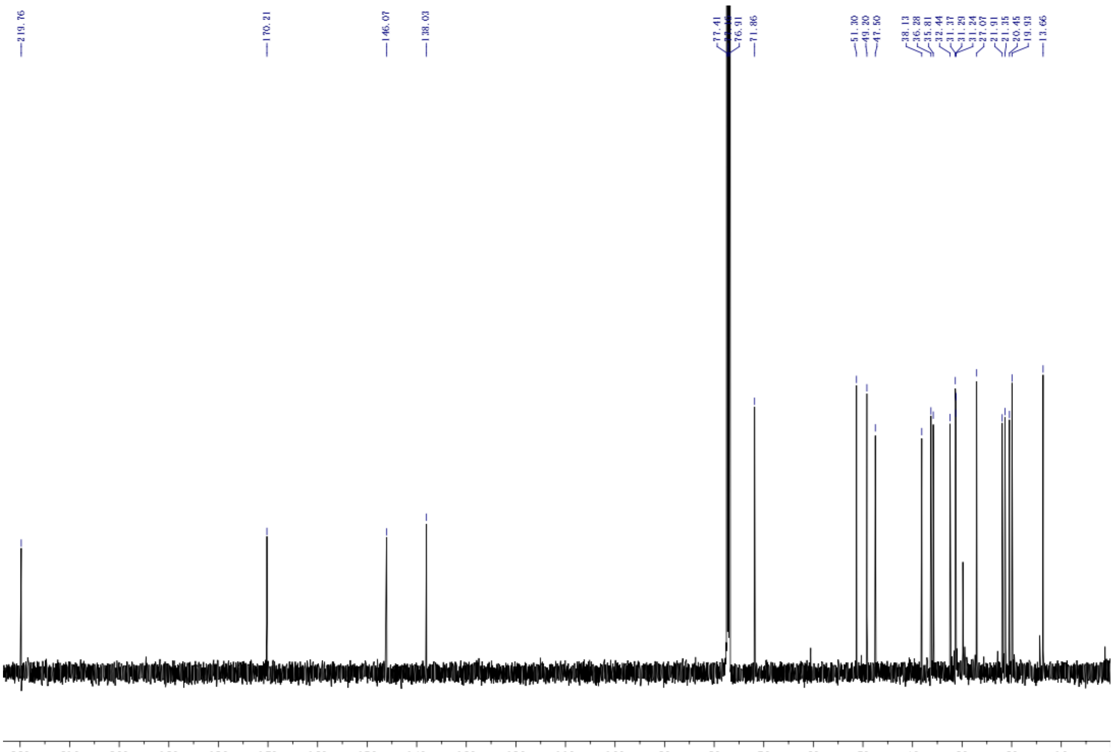


[13]C NMR of compound **173**（126 MHz, $CDCl_3$）

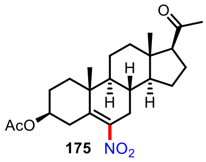


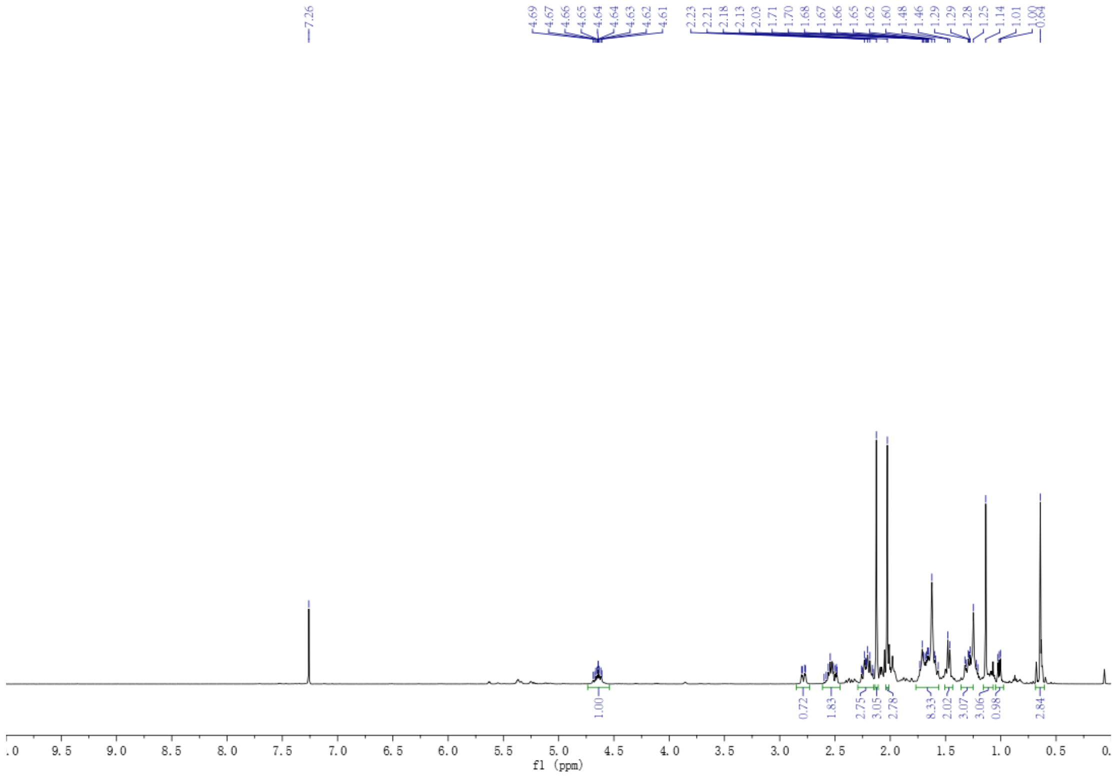


^{1}H NMR of compound **174**（500 MHz, $CDCl_3$）

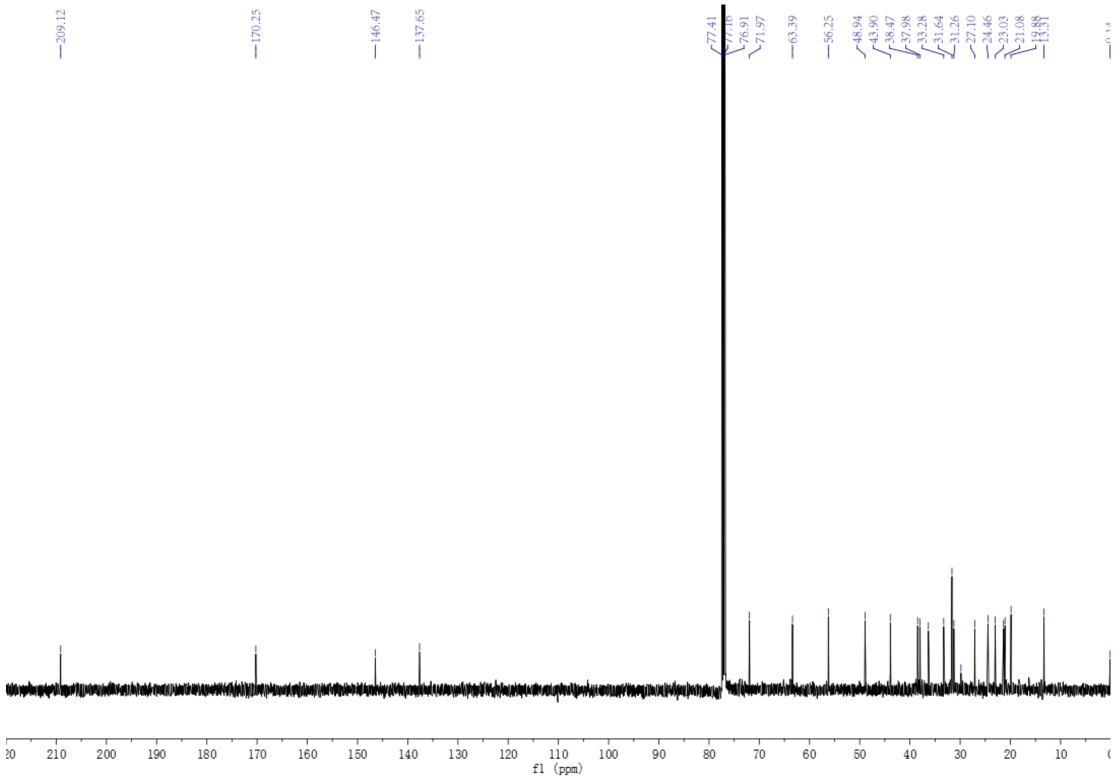


^{13}C NMR of compound **174**（126 MHz, $CDCl_3$）

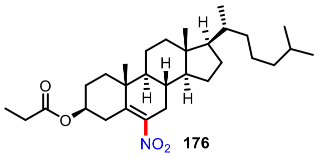




[1]H NMR of compound **175**（500 MHz, $CDCl_3$）



[13]C NMR of compound **175**（126 MHz, $CDCl_3$）



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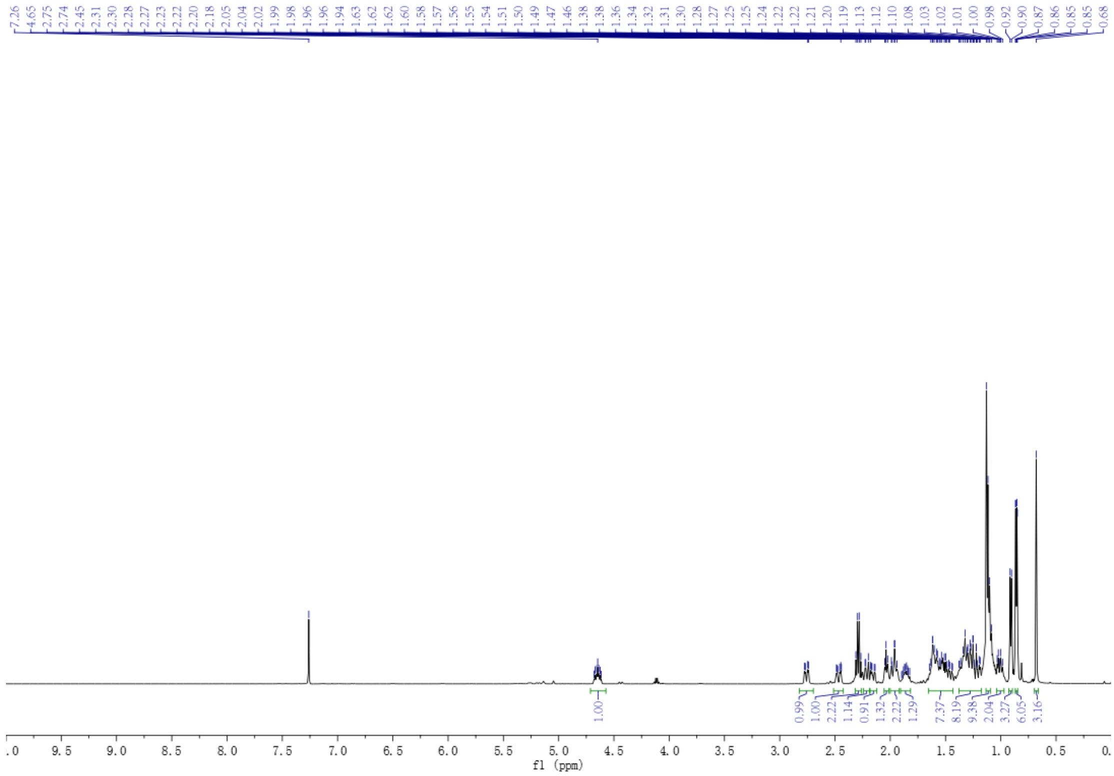
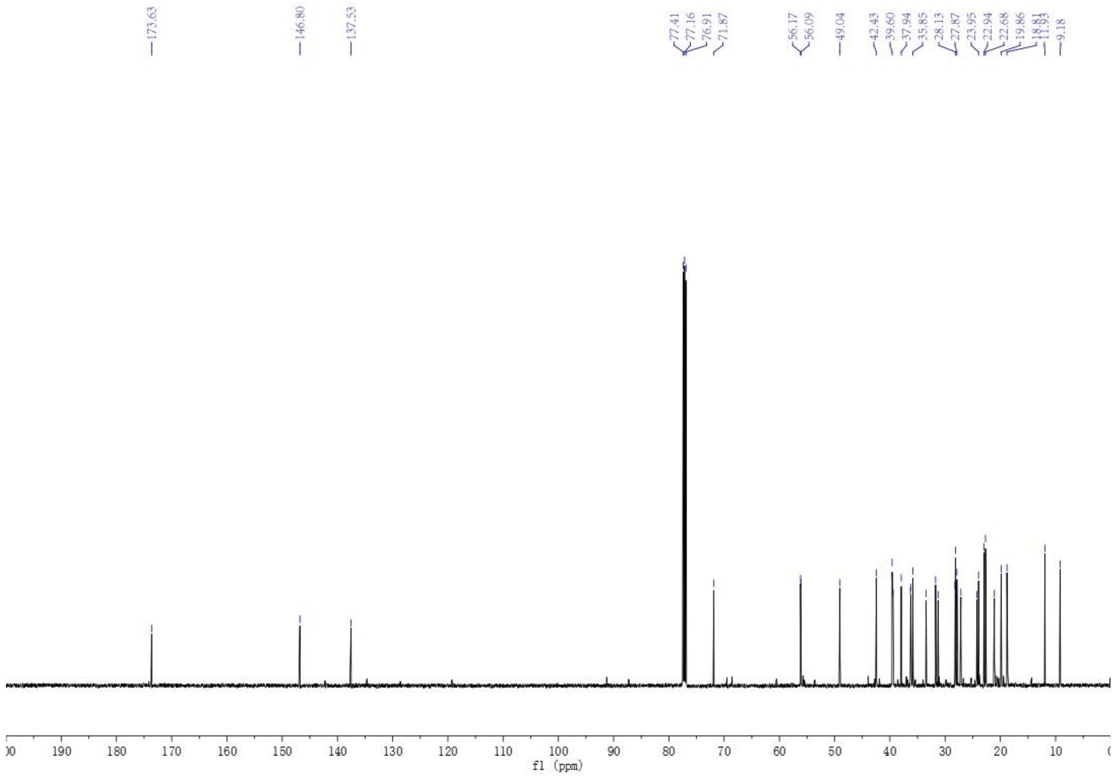
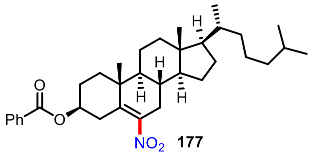
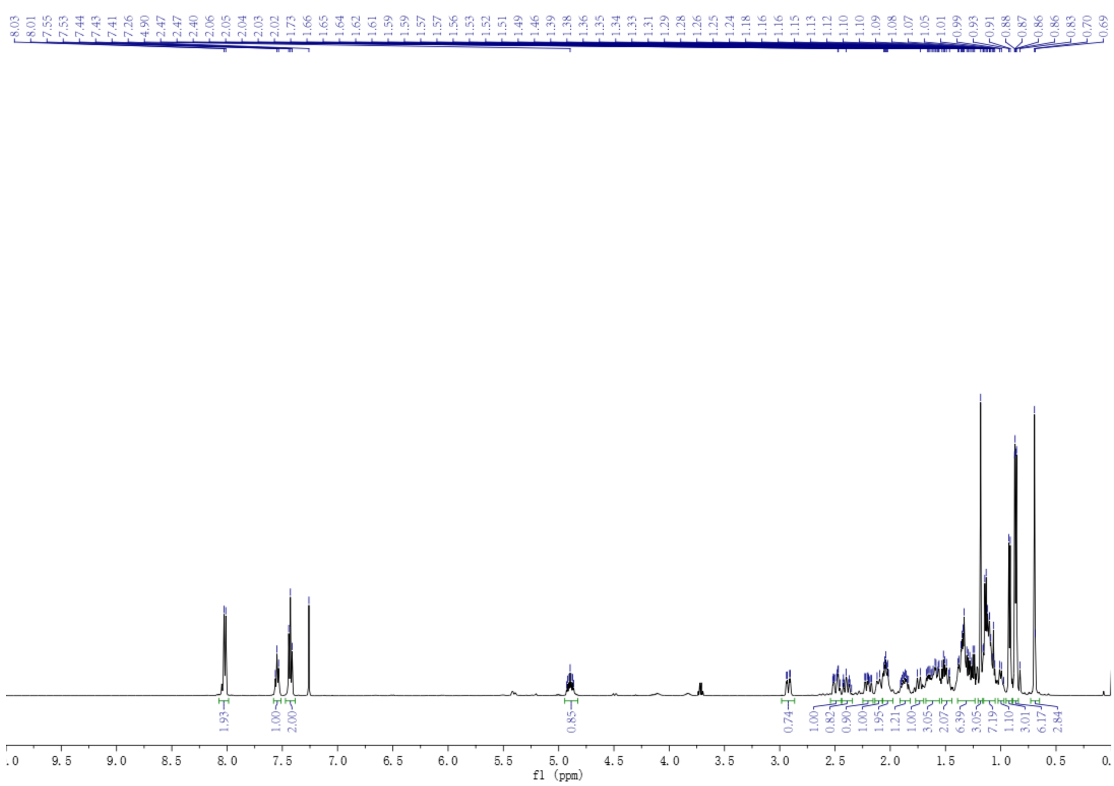


^{1}H NMR of compound **176**（500 MHz, $CDCl_3$）

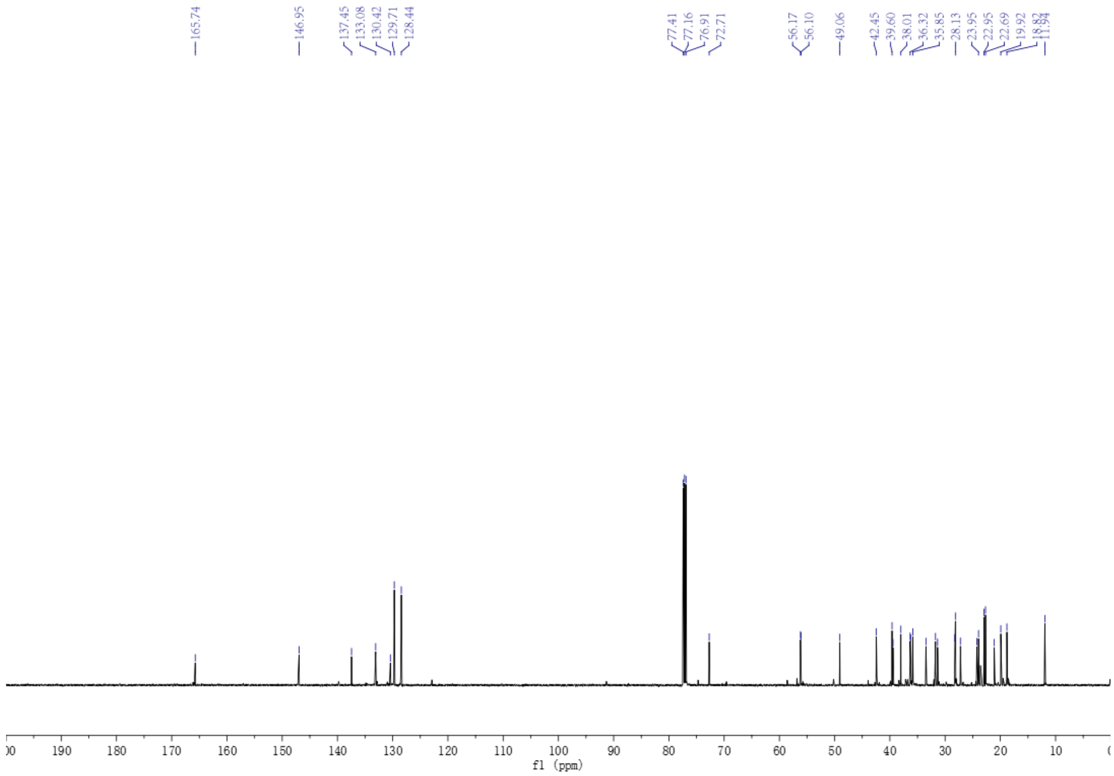


^{13}C NMR of compound **176**（126 MHz, $CDCl_3$）

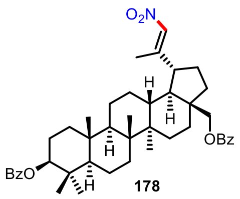




^{1}H NMR of compound **177**（500 MHz, $CDCl_3$）



^{13}C NMR of compound **177**（126 MHz, $CDCl_3$）



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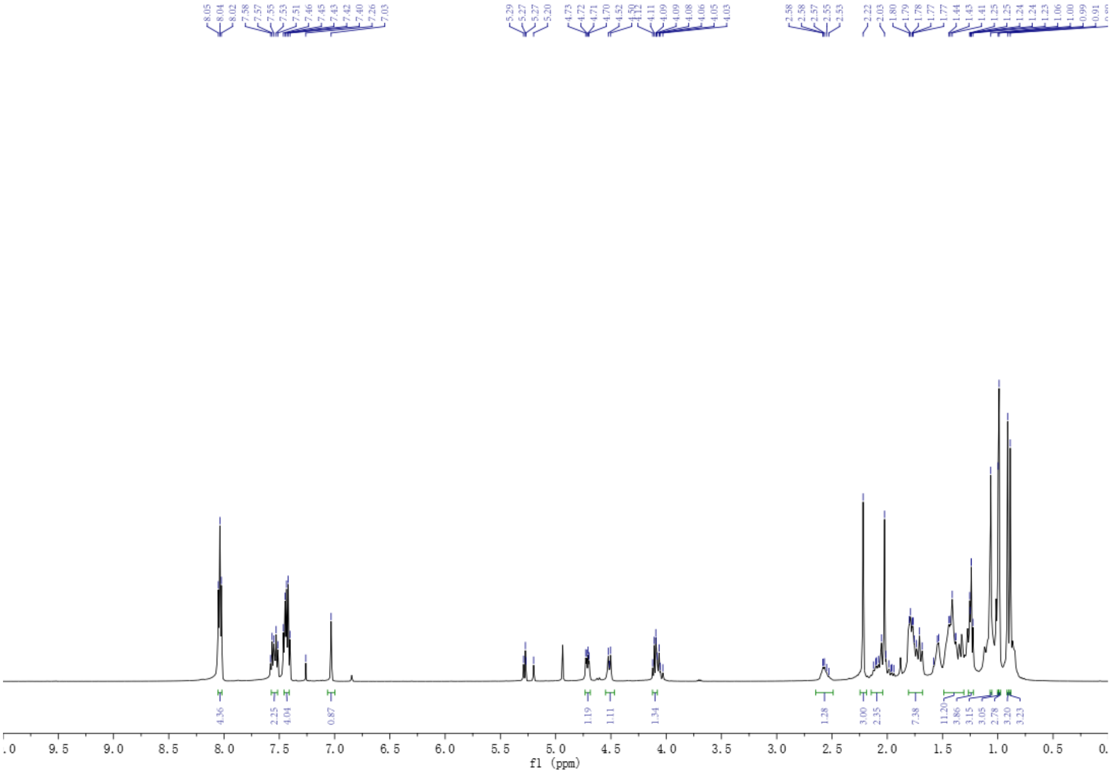

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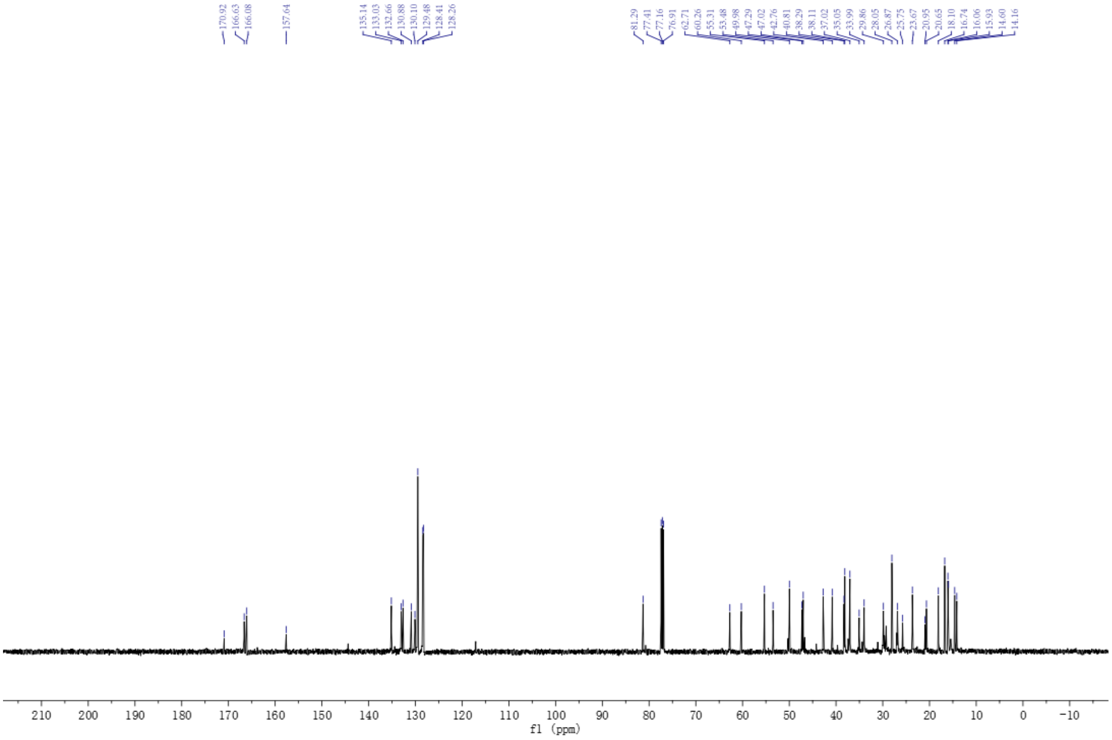
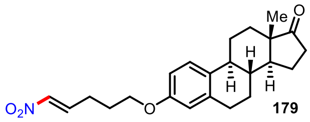


^{13}C NMR of compound **178**（126 MHz, $CDCl_3$）



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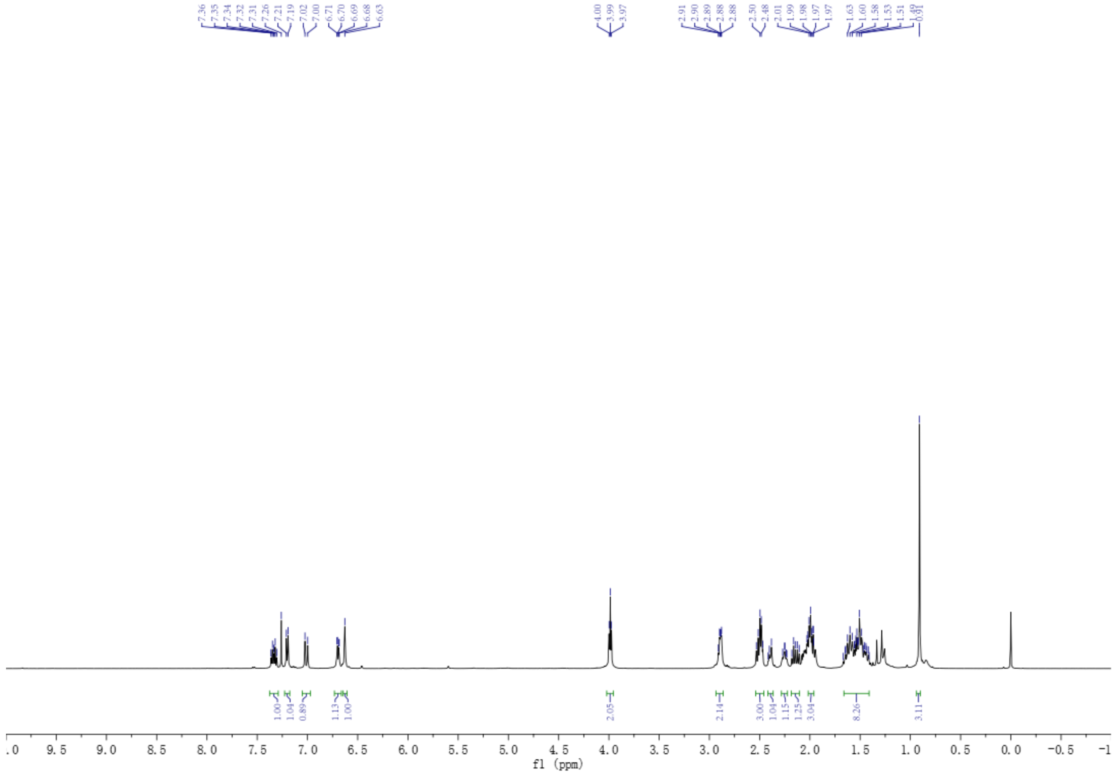
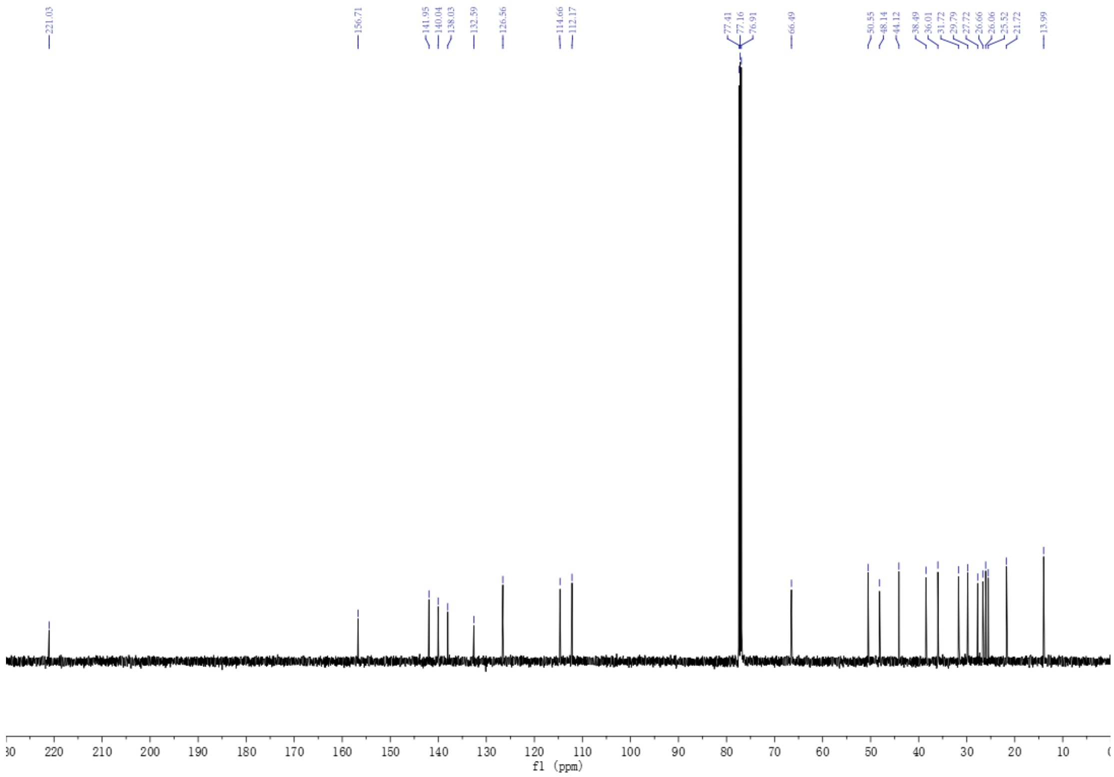
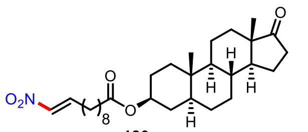


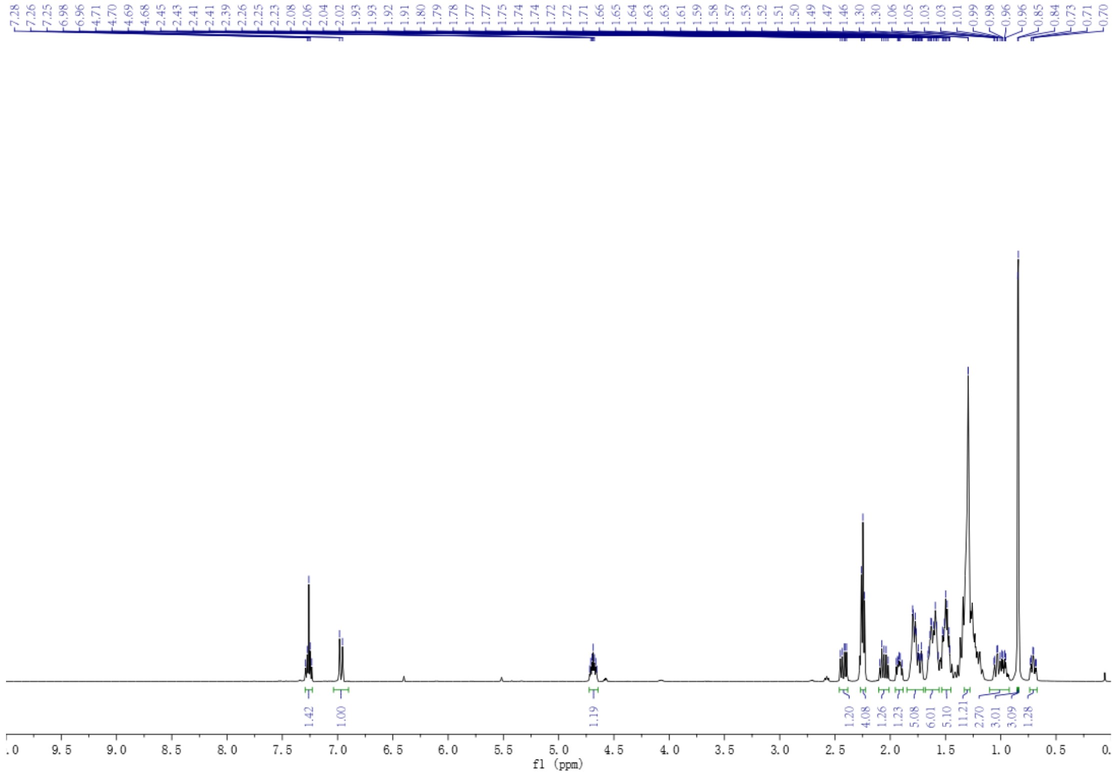
^{1}H NMR of compound **179**（500 MHz, $CDCl_3$）



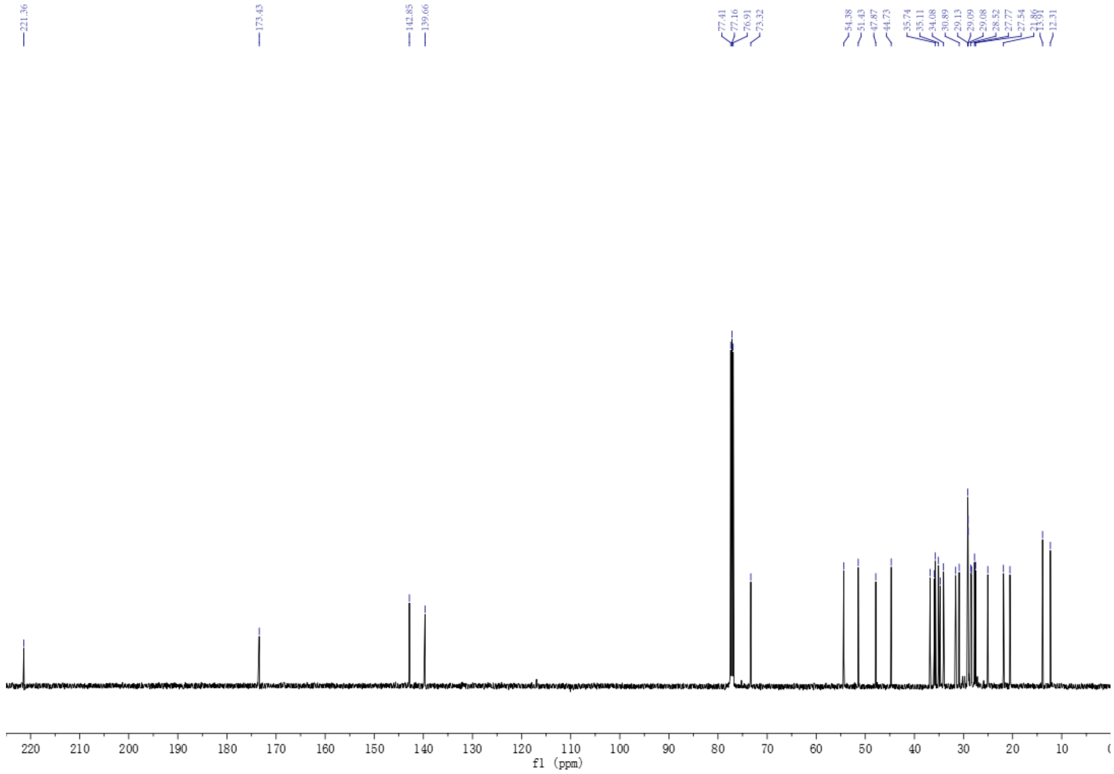
^{13}C NMR of compound **179**（126 MHz, $CDCl_3$）



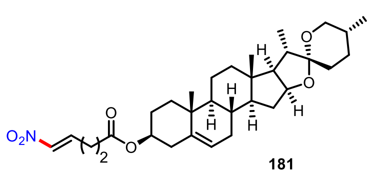
180



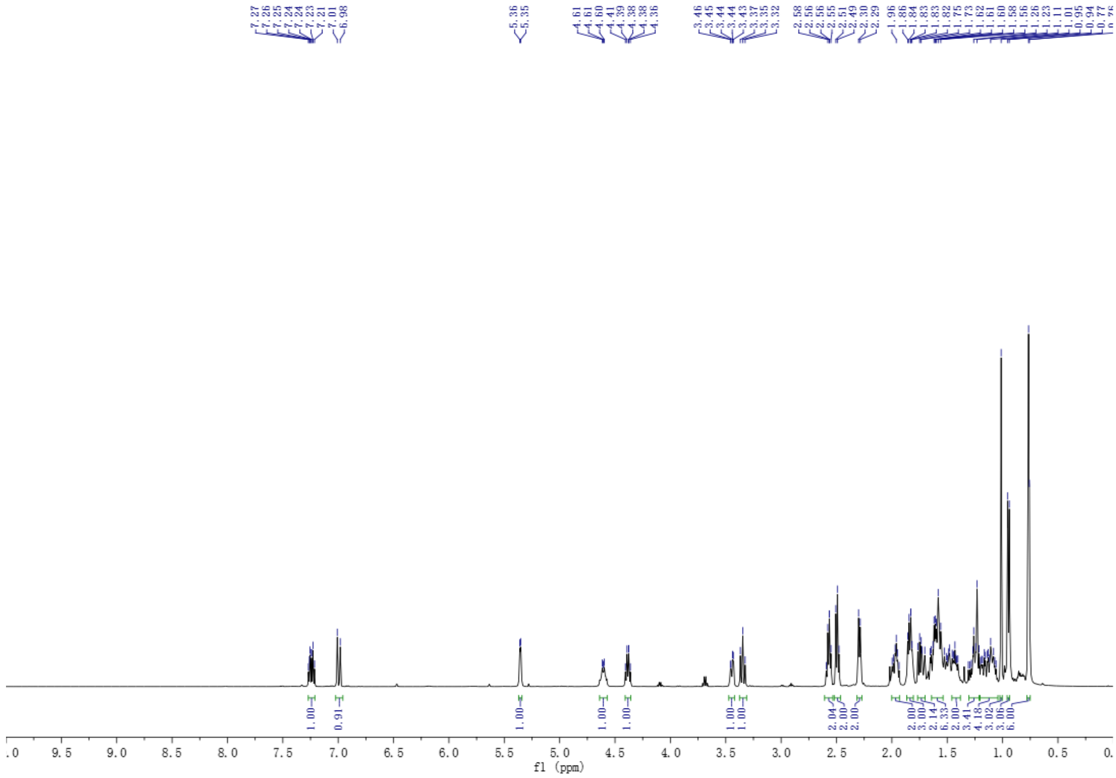
[1]H NMR of compound **180**（500 MHz, $CDCl_3$）



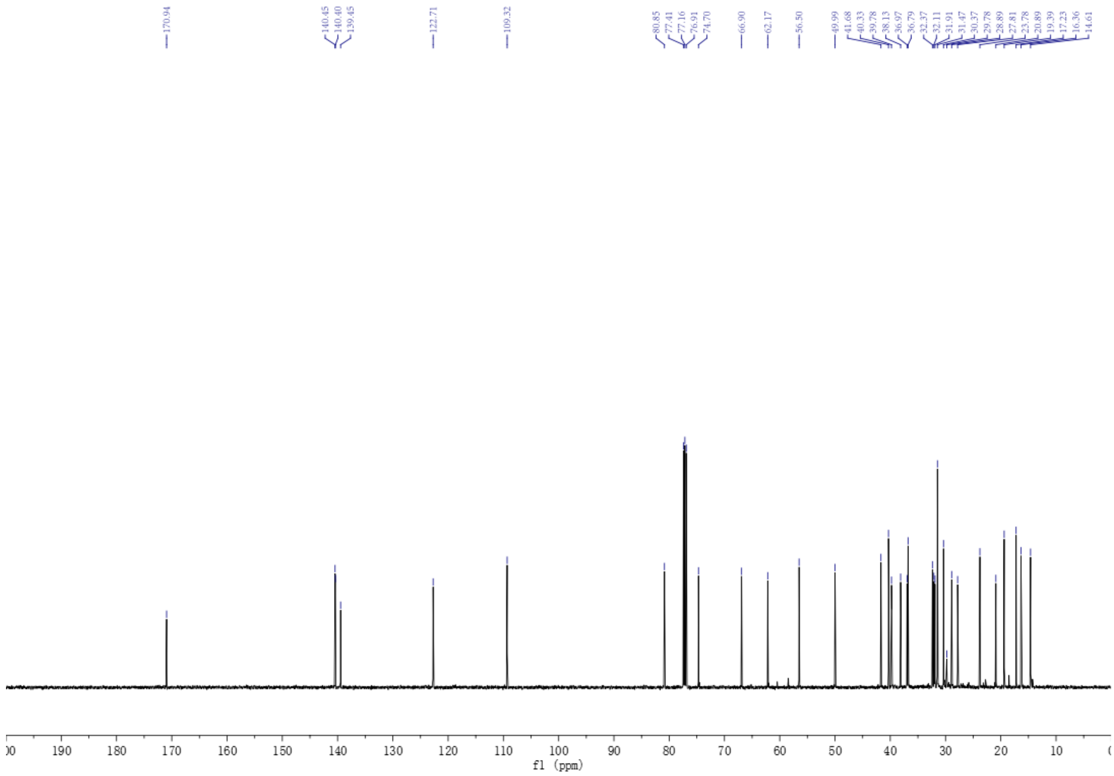
[13]C NMR of compound **180**（126 MHz, $CDCl_3$）



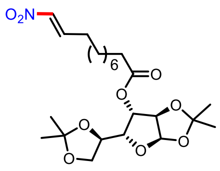
181



^{1}H NMR of compound **181**（500 MHz, $CDCl_3$）



^{13}C NMR of compound **181**（126 MHz, $CDCl_3$）



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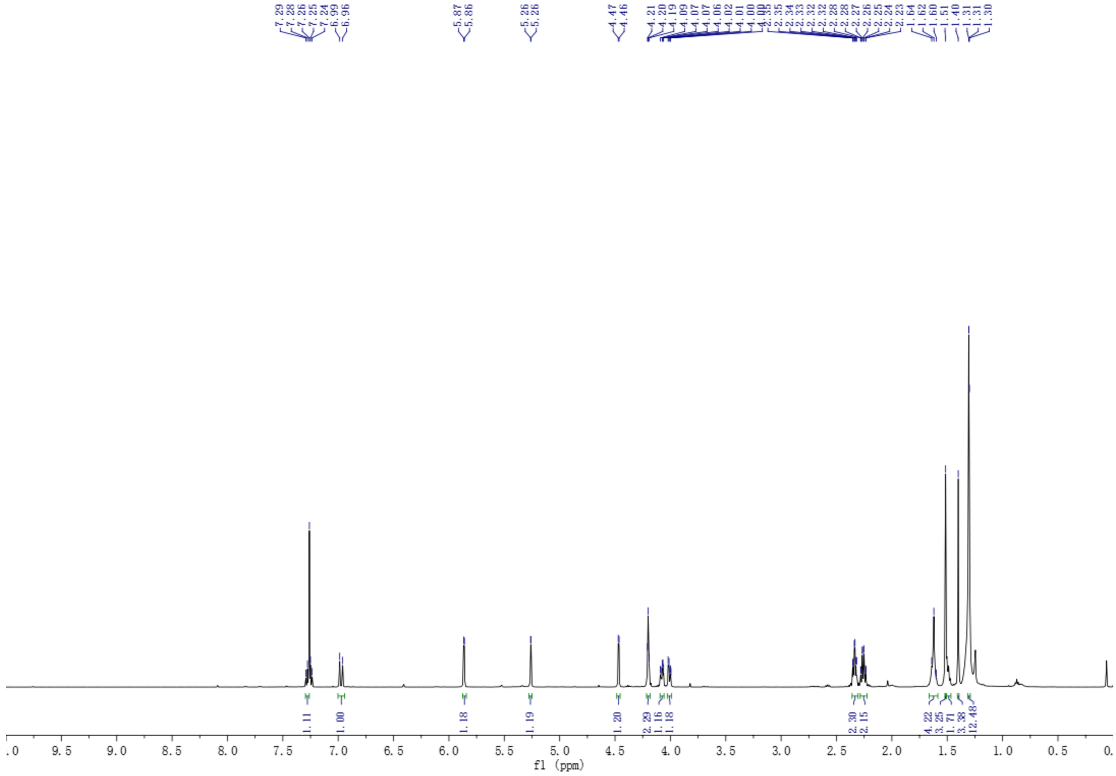
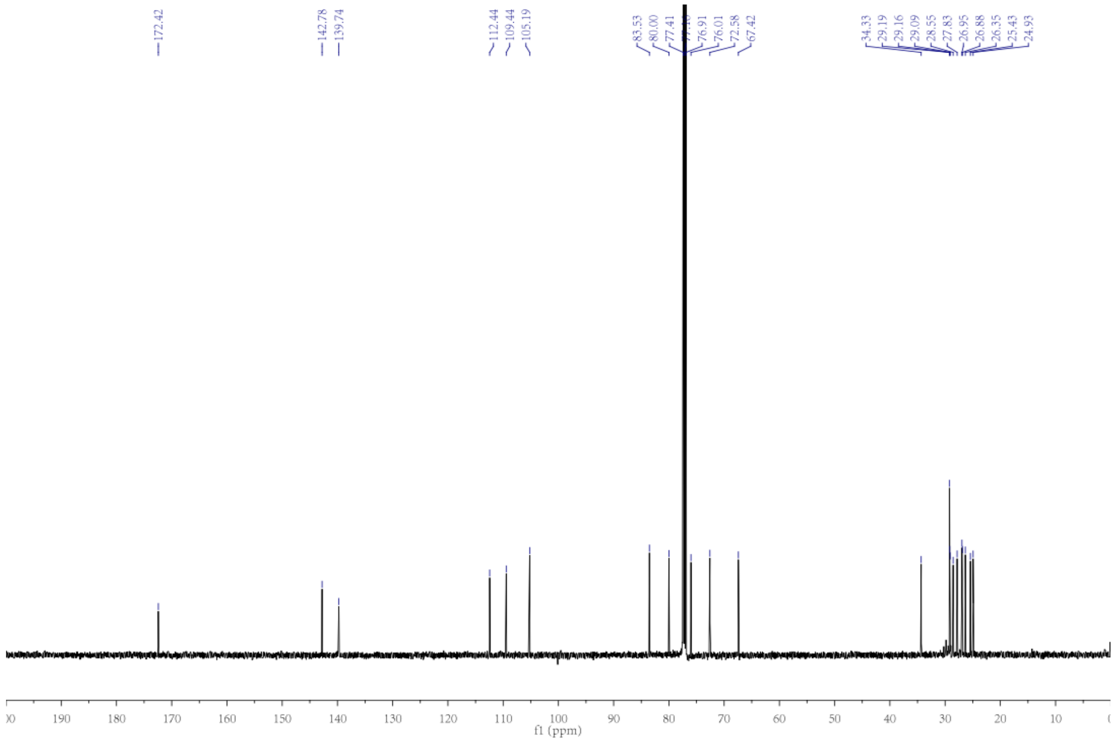
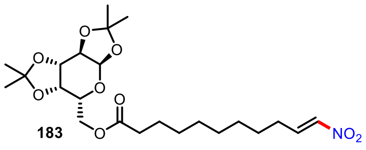
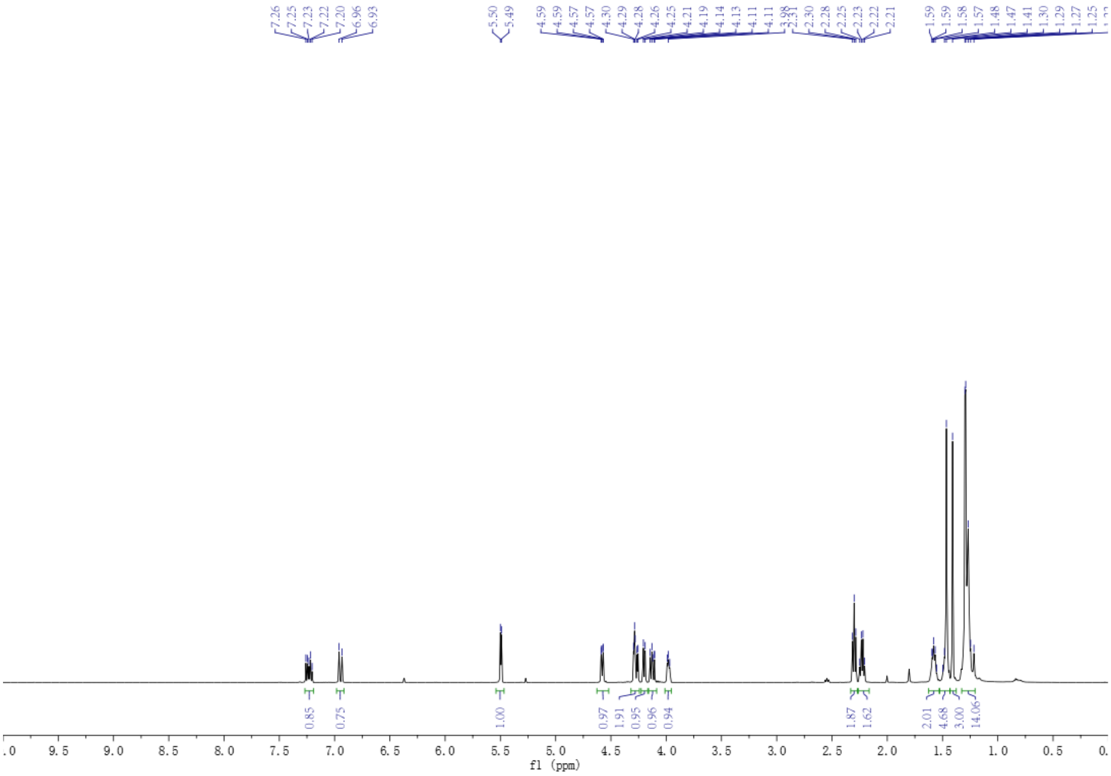


[1]H NMR of compound **182**（500 MHz, $CDCl_3$）

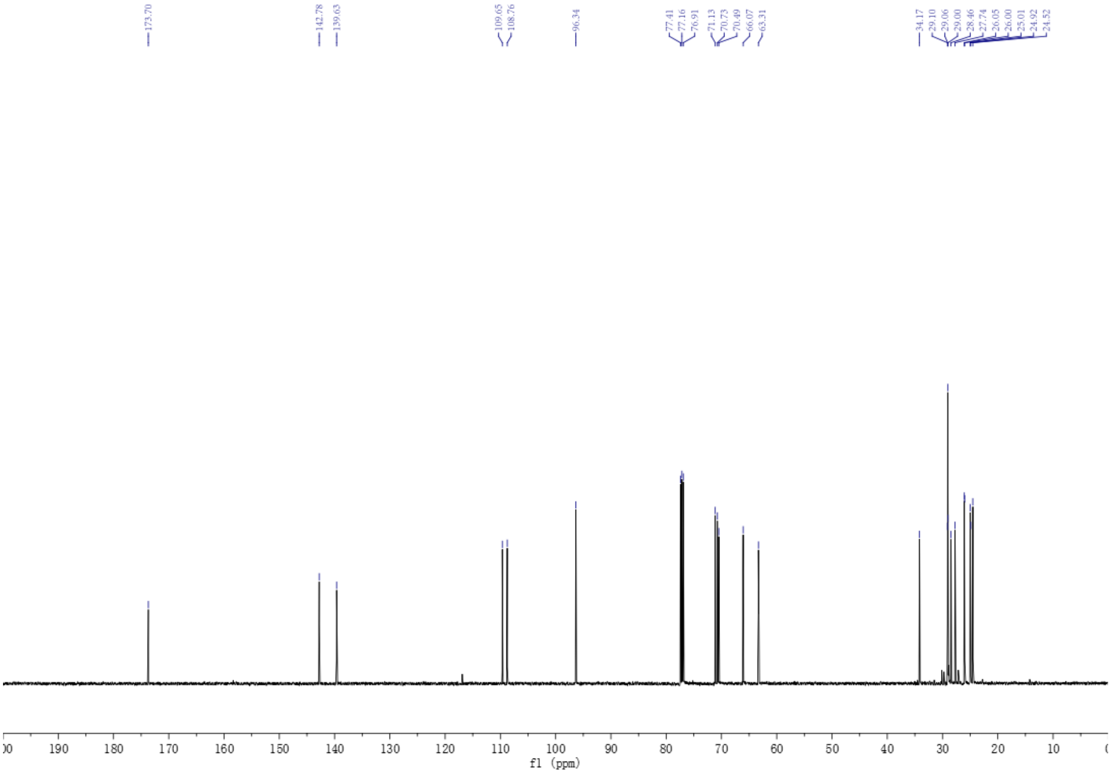


[13]C NMR of compound **182**（126 MHz, $CDCl_3$）

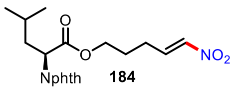




^{1}H NMR of compound **183**（500 MHz, $CDCl_3$）



^{13}C NMR of compound **183**（126 MHz, $CDCl_3$）



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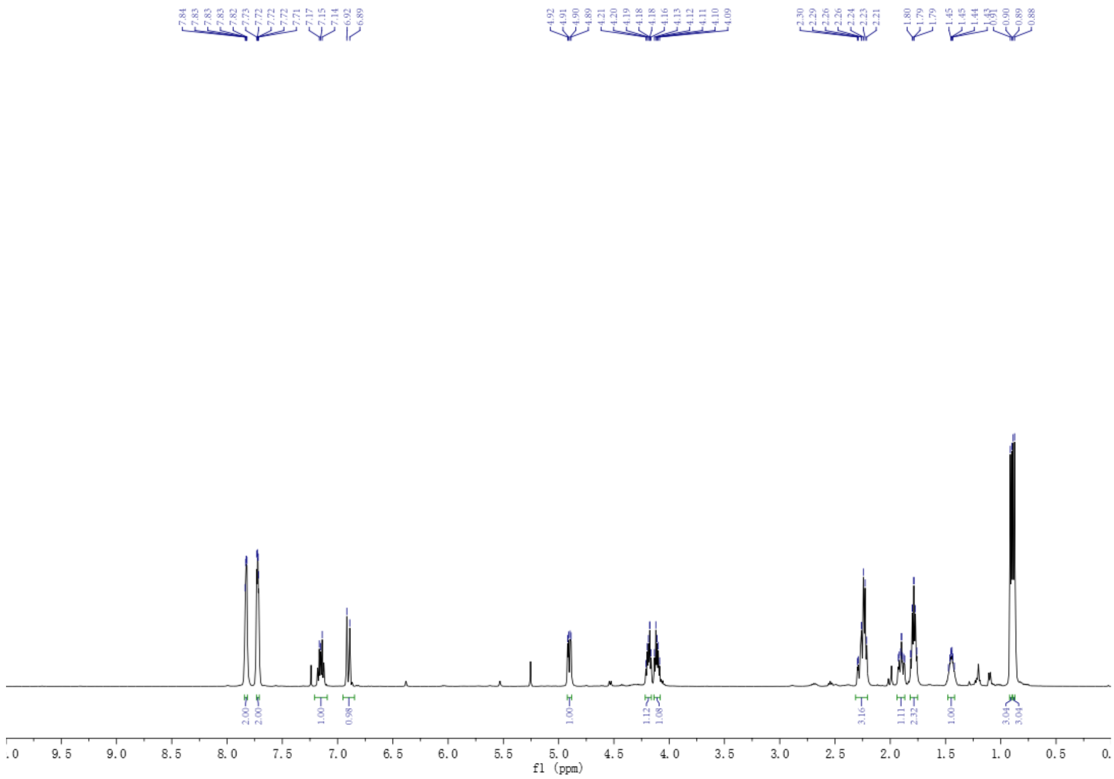
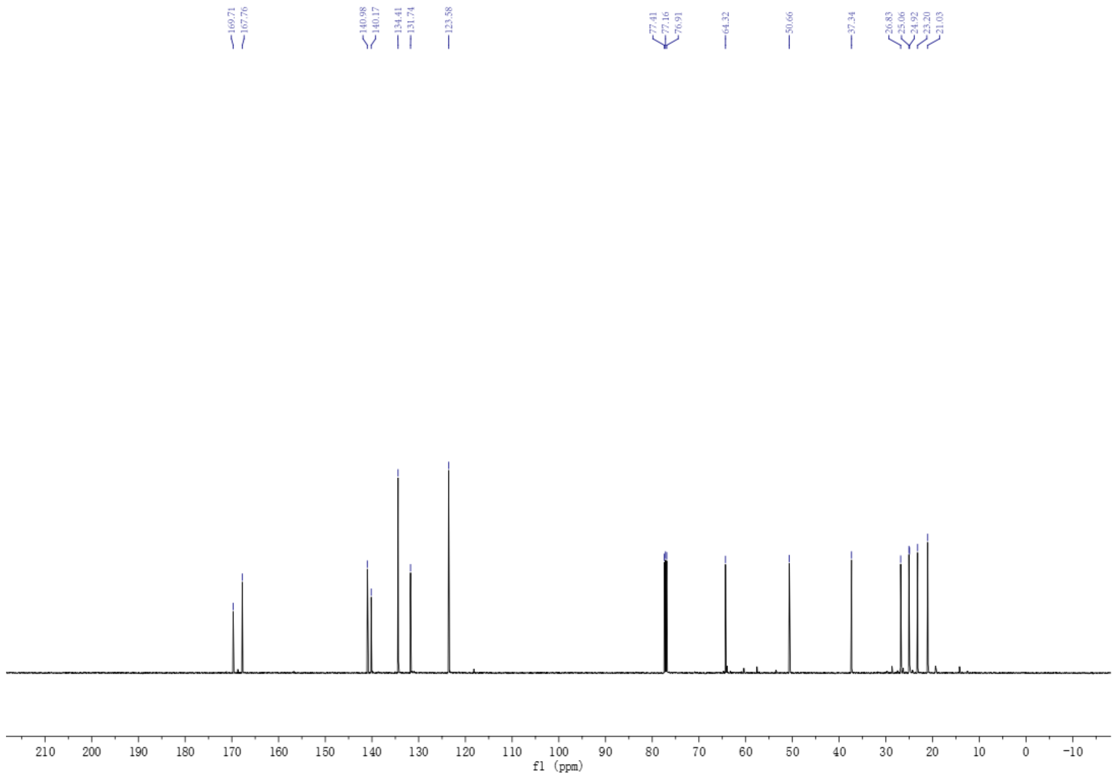
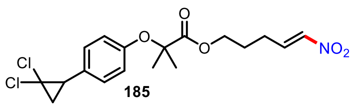


[1]H NMR of compound **184**（500 MHz, $CDCl_3$）



[13]C NMR of compound **184**（126 MHz, $CDCl_3$）



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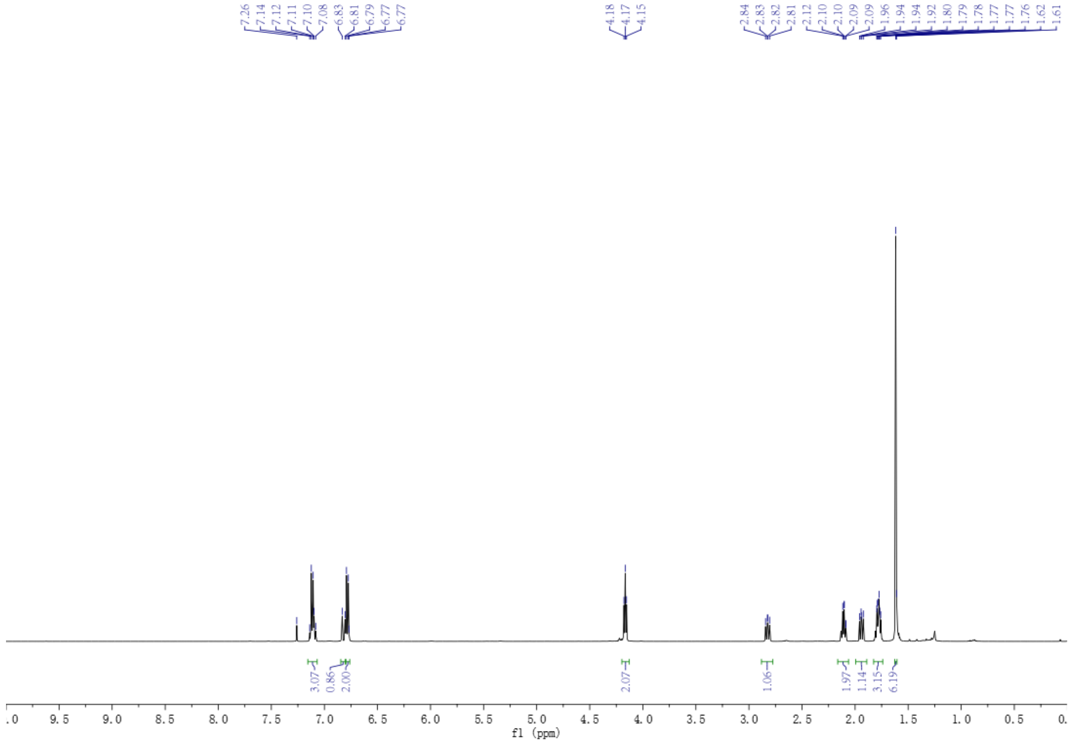
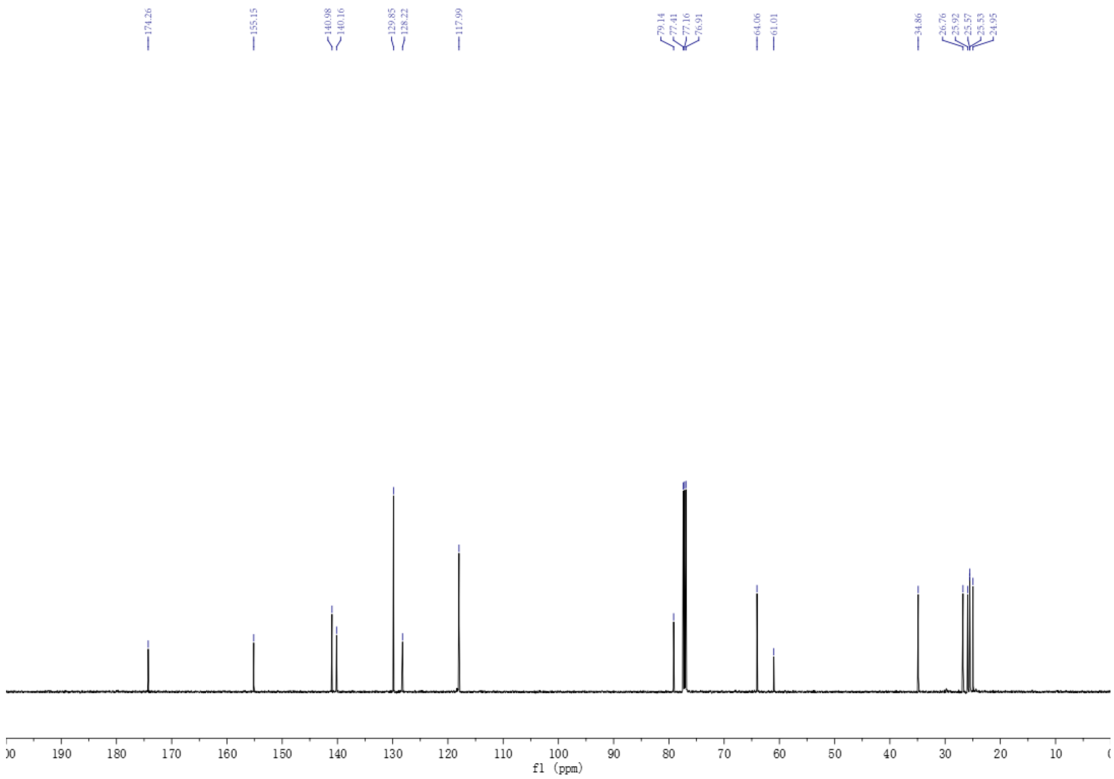
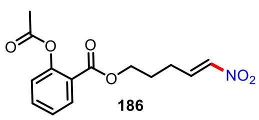
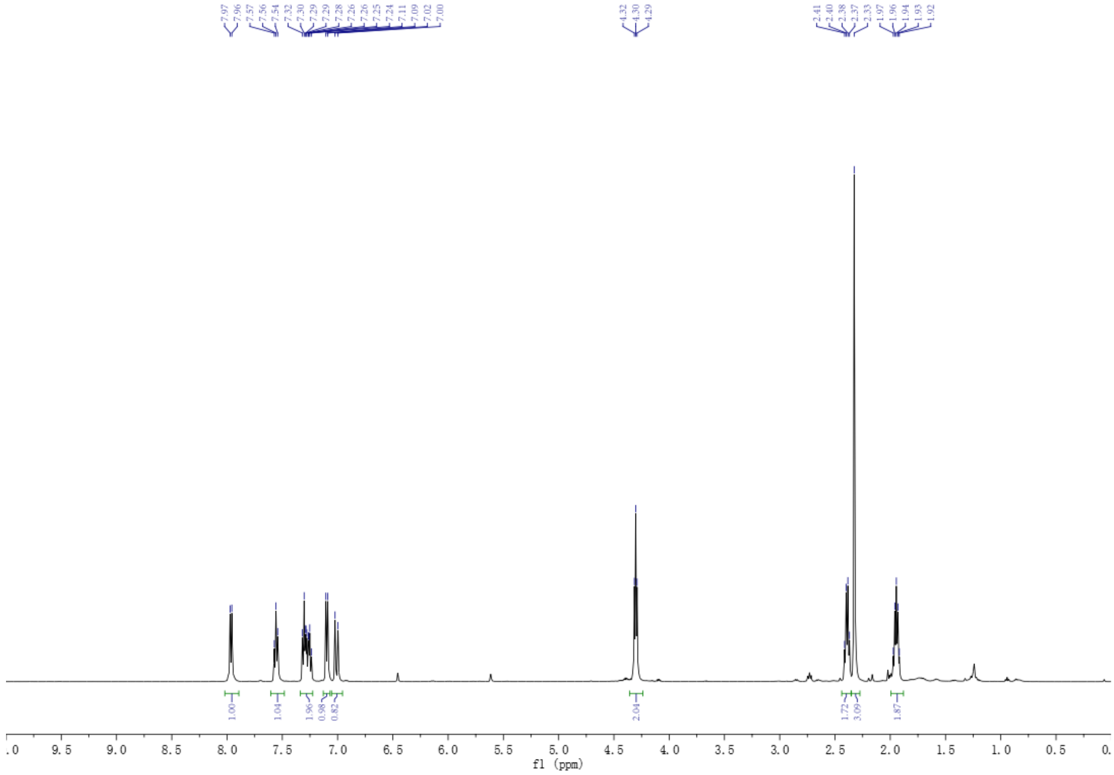


[1]H NMR of compound **185**（500 MHz, $CDCl_3$）

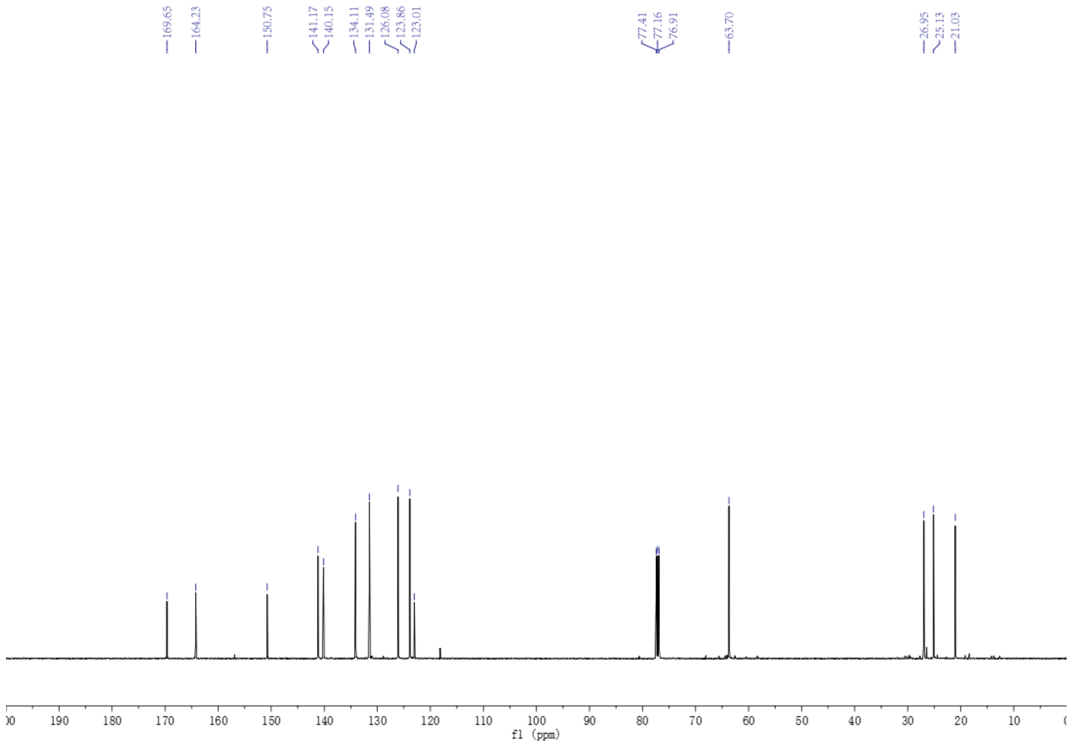


[13]C NMR of compound **185**（126 MHz, $CDCl_3$）

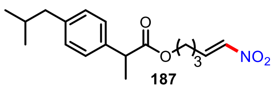




^{1}H NMR of compound **186**（500 MHz, $CDCl_3$）



^{13}C NMR of compound **186**（126 MHz, $CDCl_3$）



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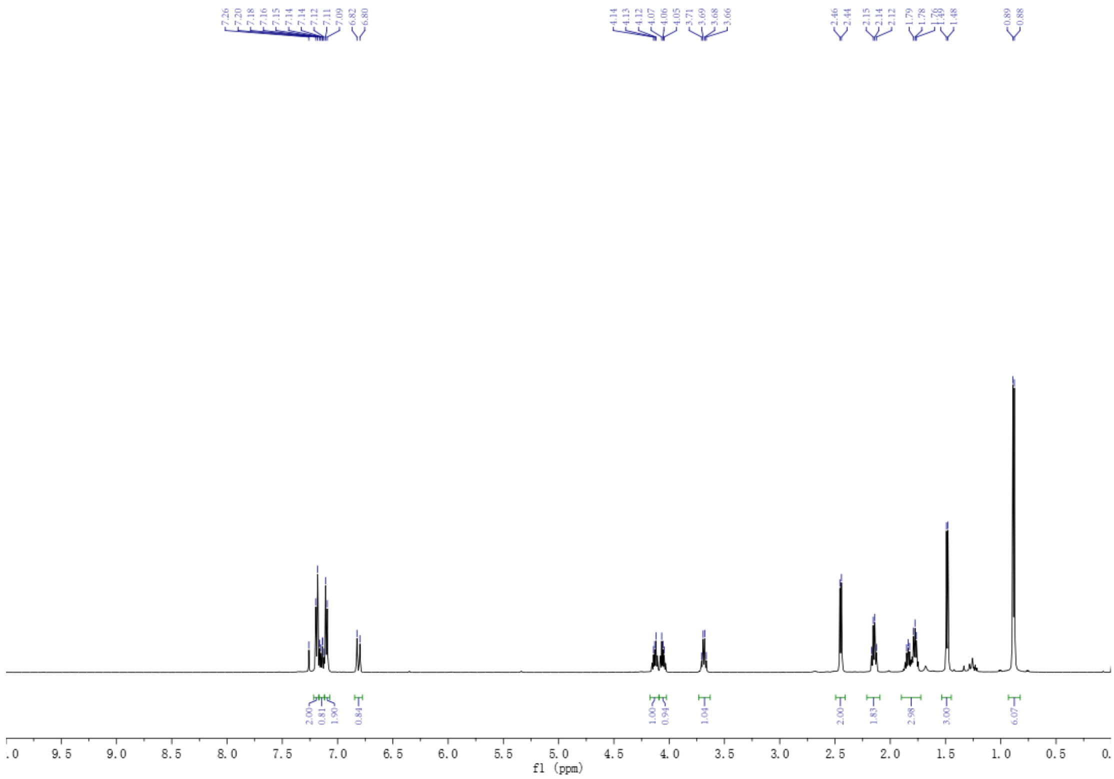
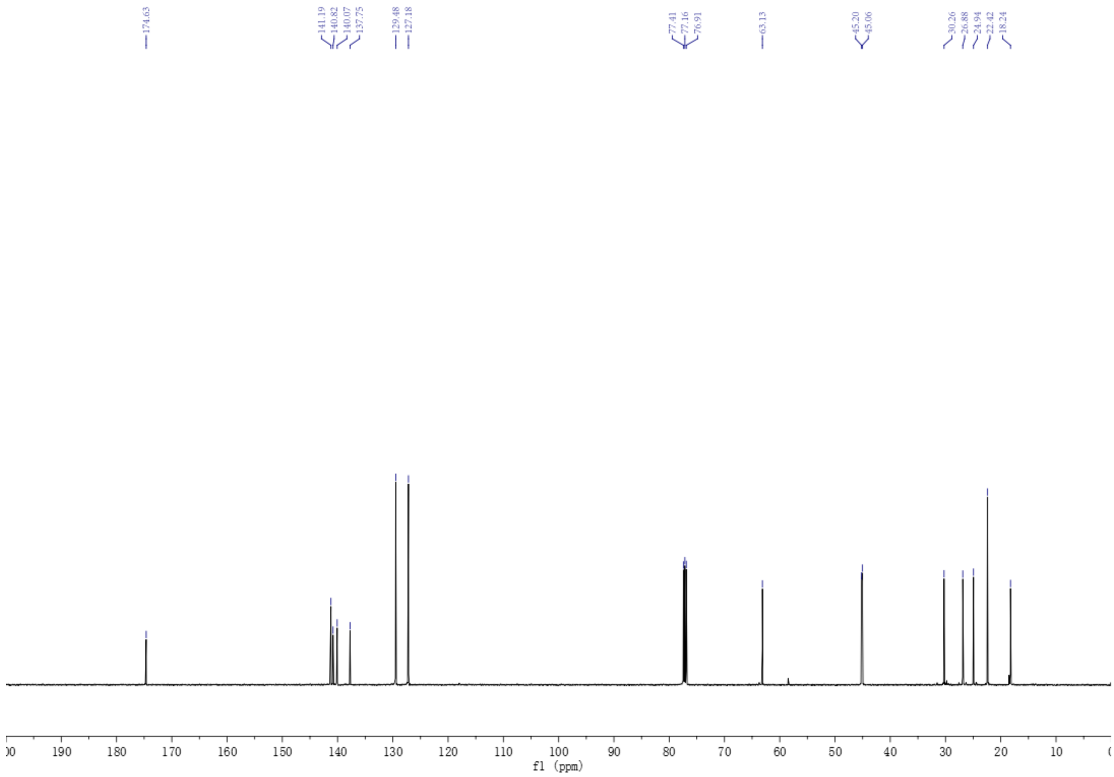
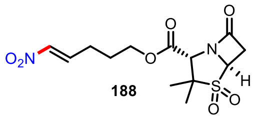


^{1}H NMR of compound **187**（500 MHz, $CDCl_3$）



^{13}C NMR of compound **187**（126 MHz, $CDCl_3$）



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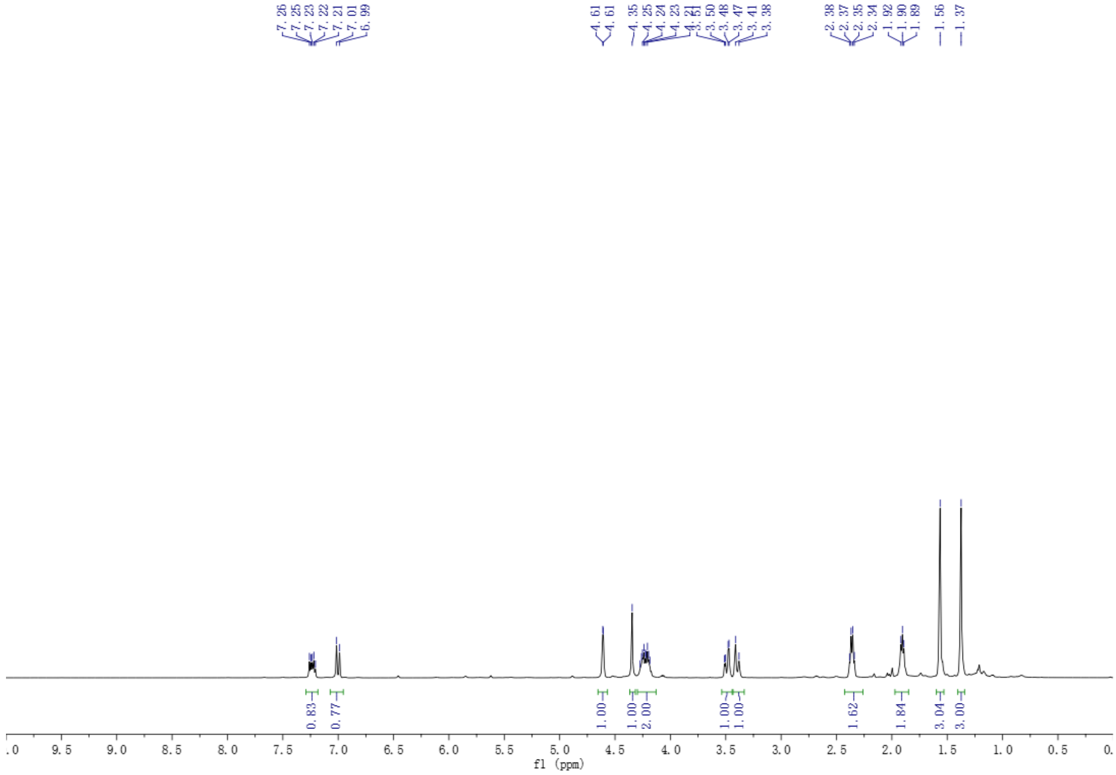
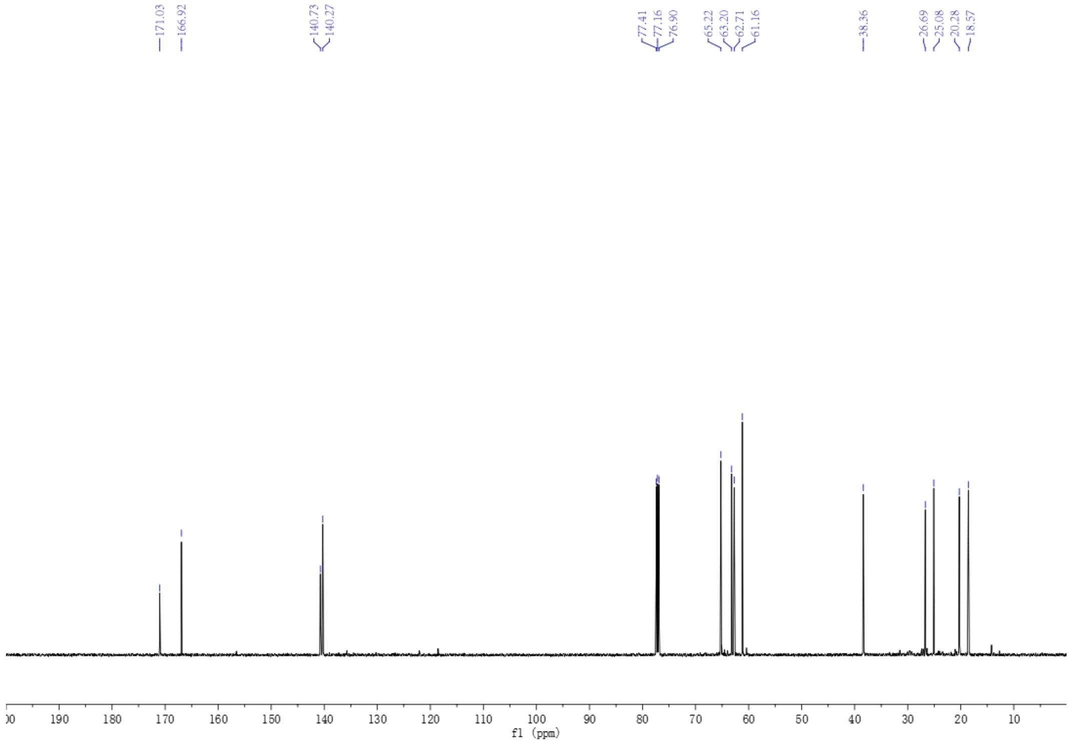
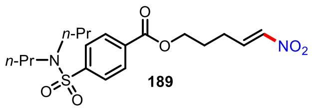


[1]H NMR of compound **188**（500 MHz, $CDCl_3$）



[13]C NMR of compound **188**（126 MHz, $CDCl_3$）



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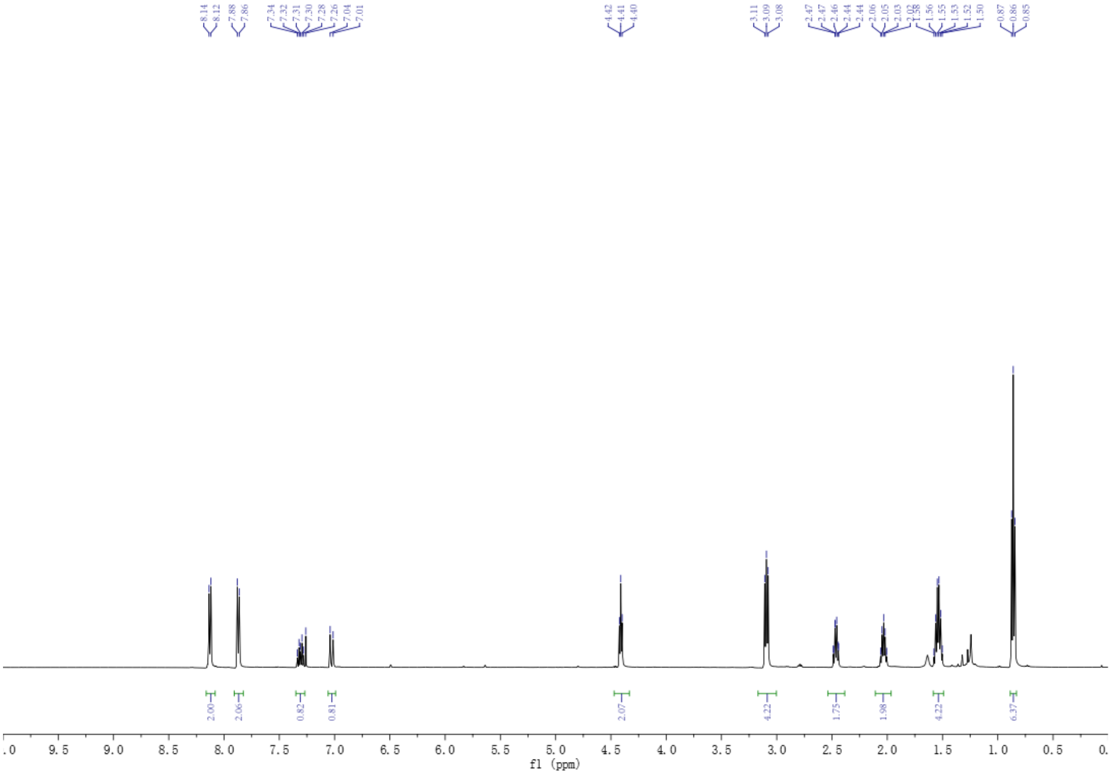
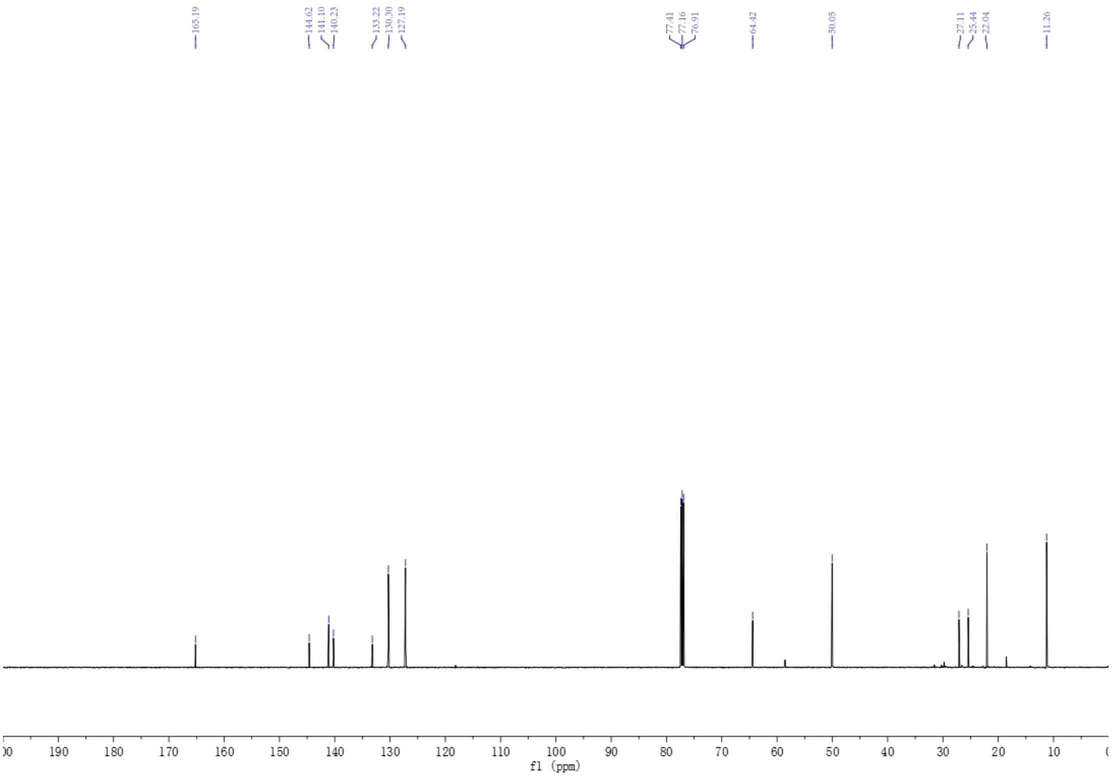
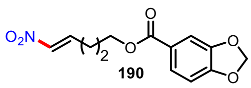
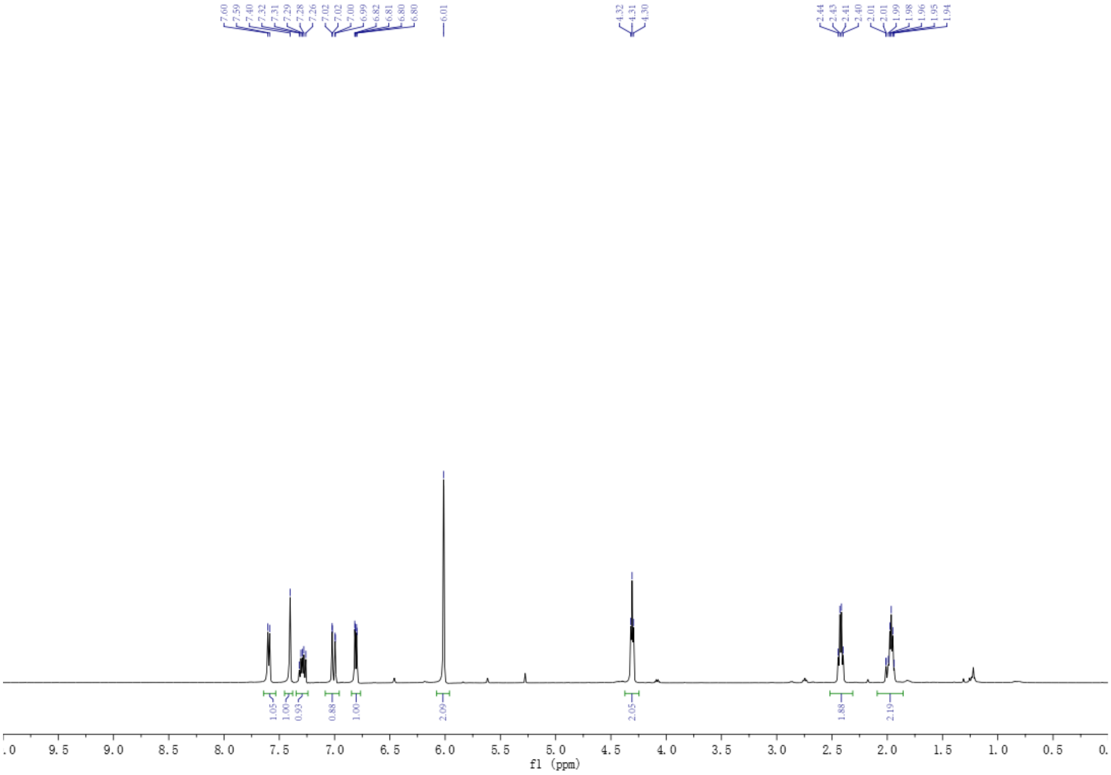


^{1}H NMR of compound **189**（500 MHz, $CDCl_3$）

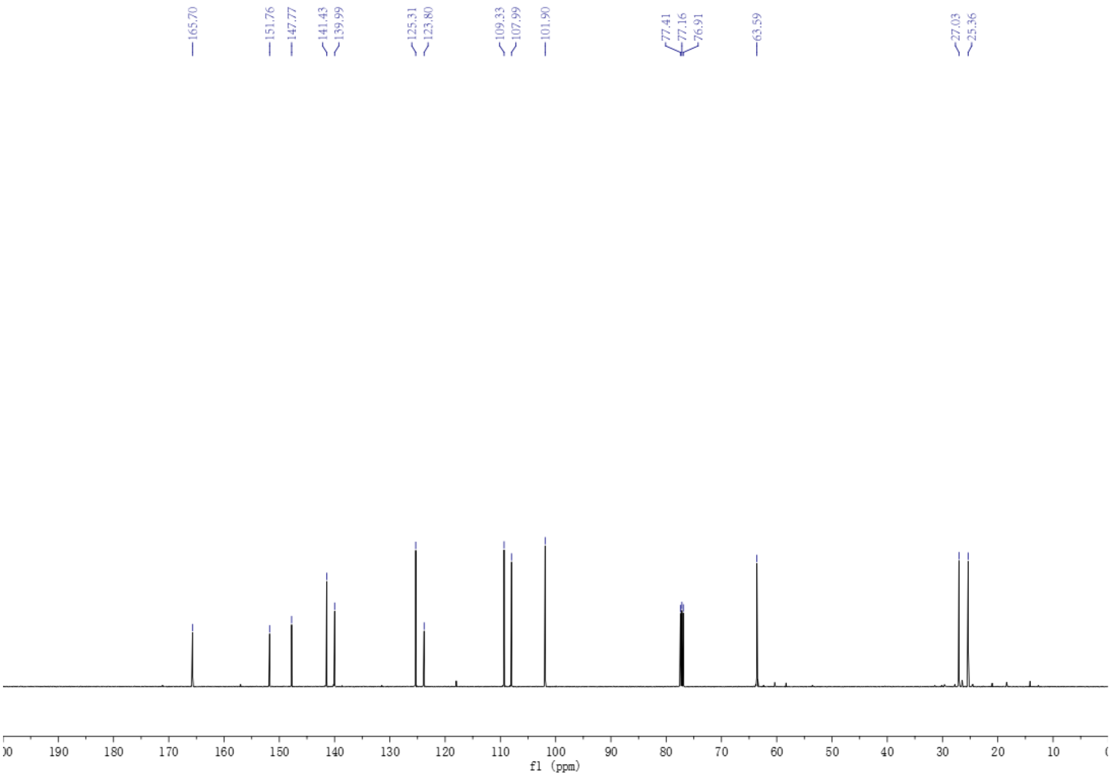


^{13}C NMR of compound **189**（126 MHz, $CDCl_3$）

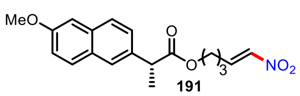


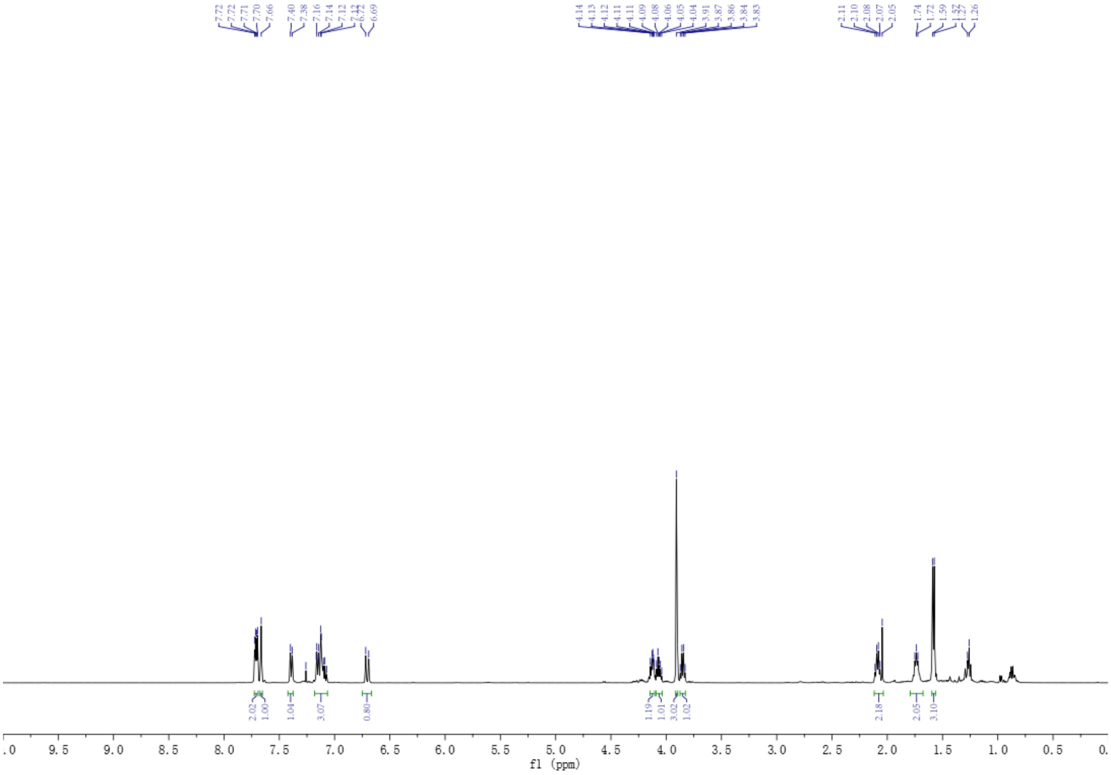


^{1}H NMR of compound **190**（500 MHz, $CDCl_3$）

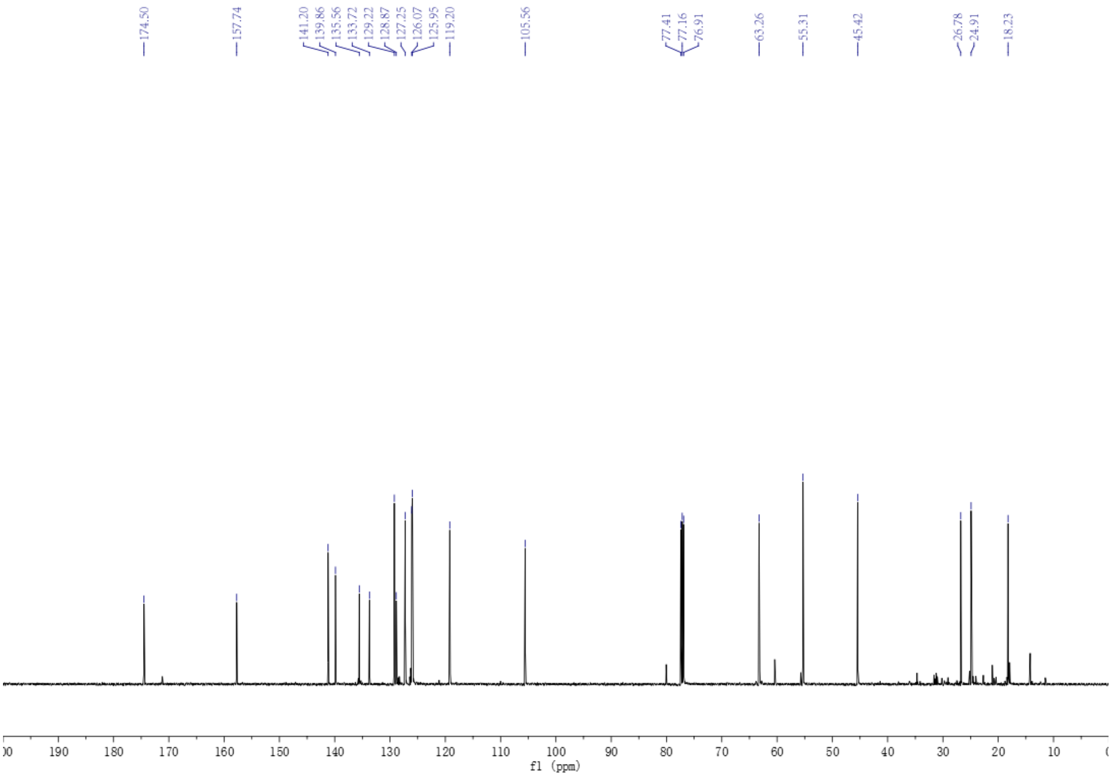


^{13}C NMR of compound **190**（126 MHz, $CDCl_3$）

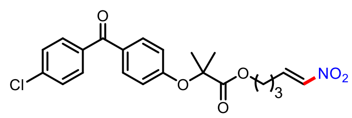




^{1}H NMR of compound **191**（500 MHz, CDCl$_3$）



^{13}C NMR of compound **191**（126 MHz, CDCl$_3$）



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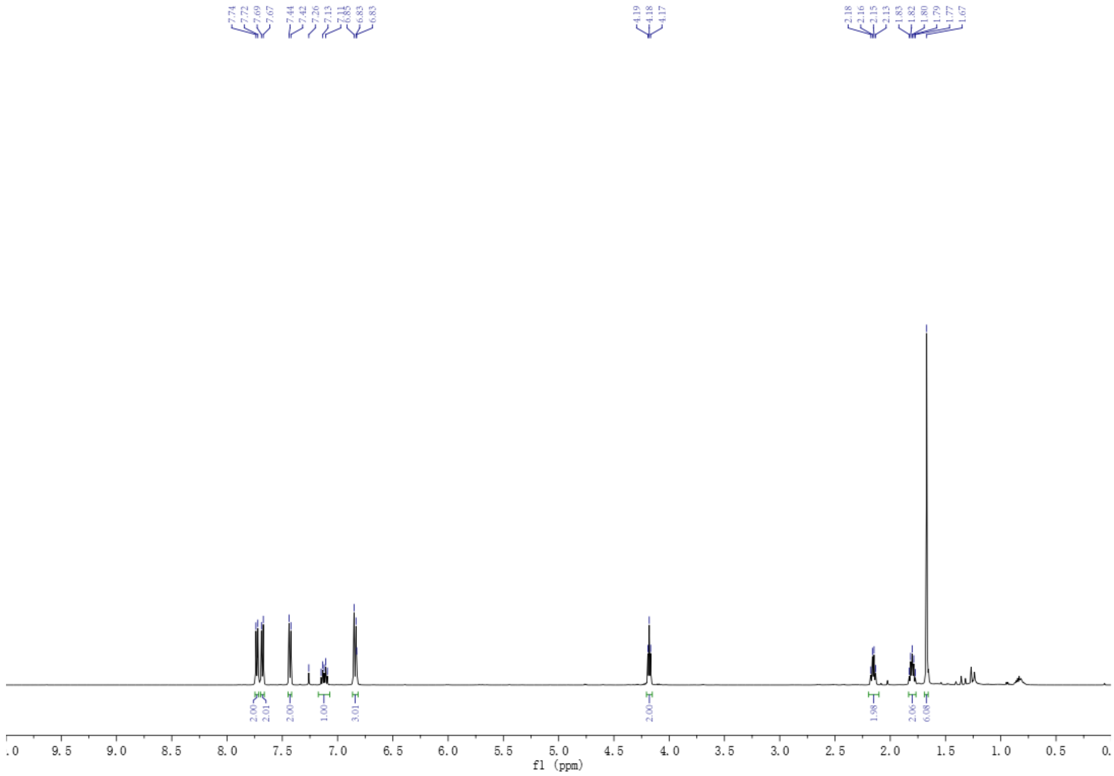
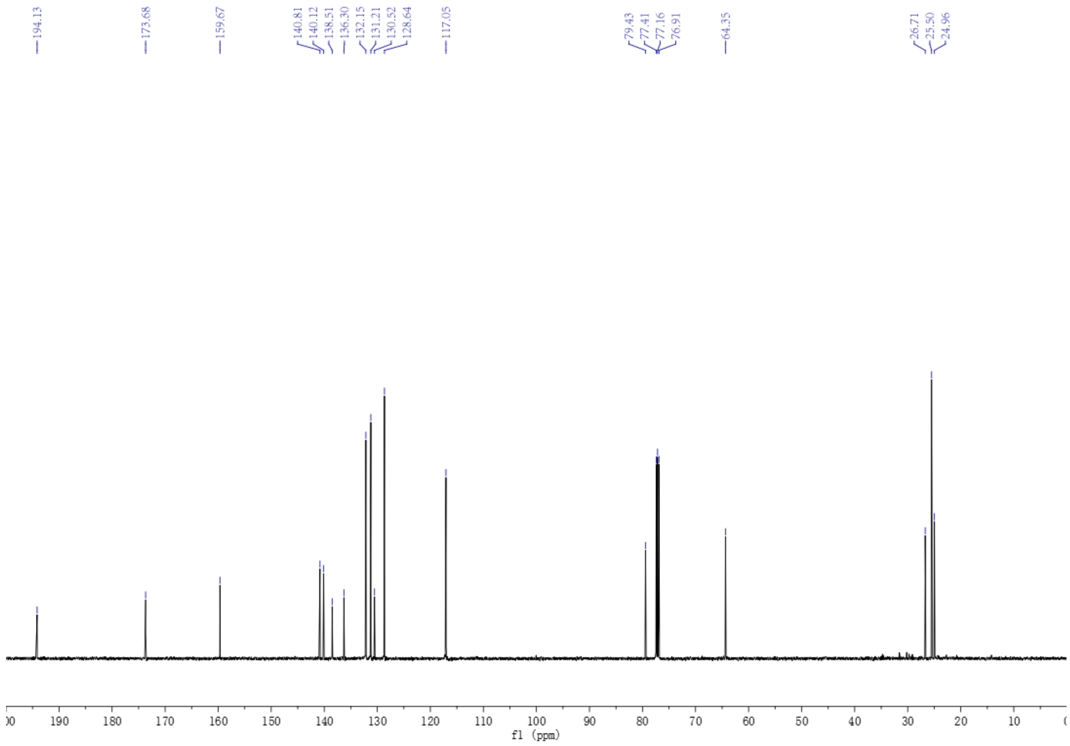
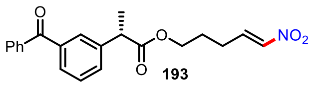


^{1}H NMR of compound **192**（500 MHz, $CDCl_3$）



^{13}C NMR of compound **192**（126 MHz, $CDCl_3$）



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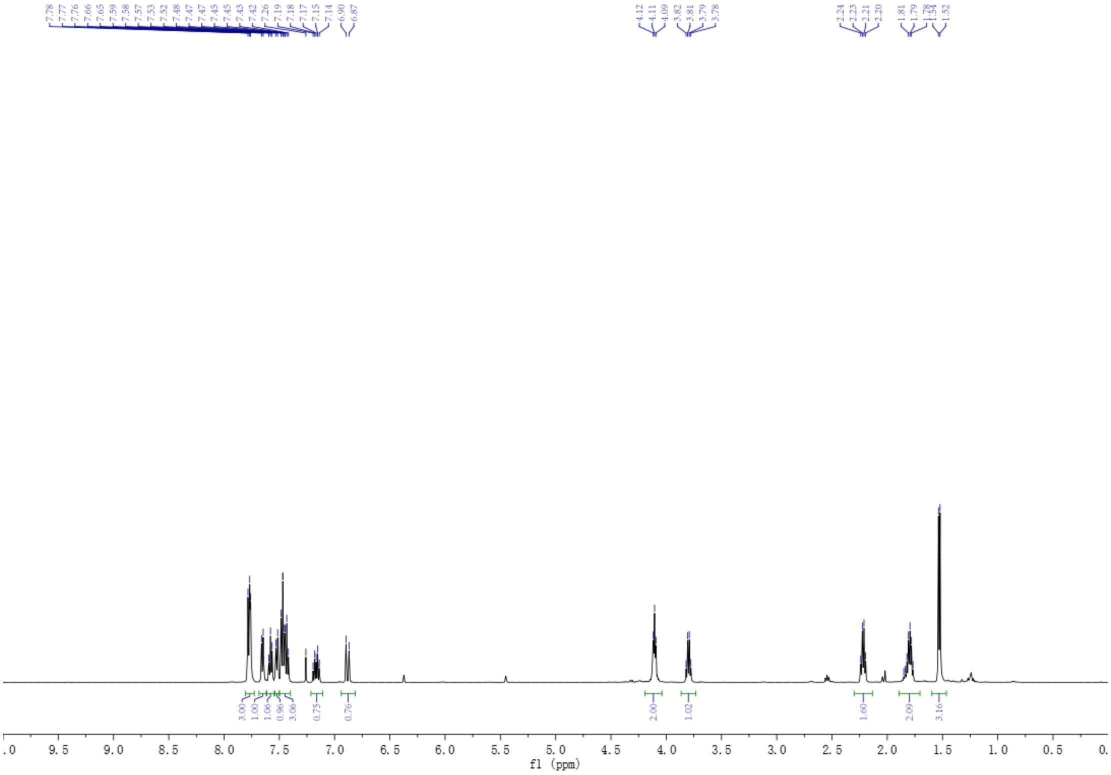
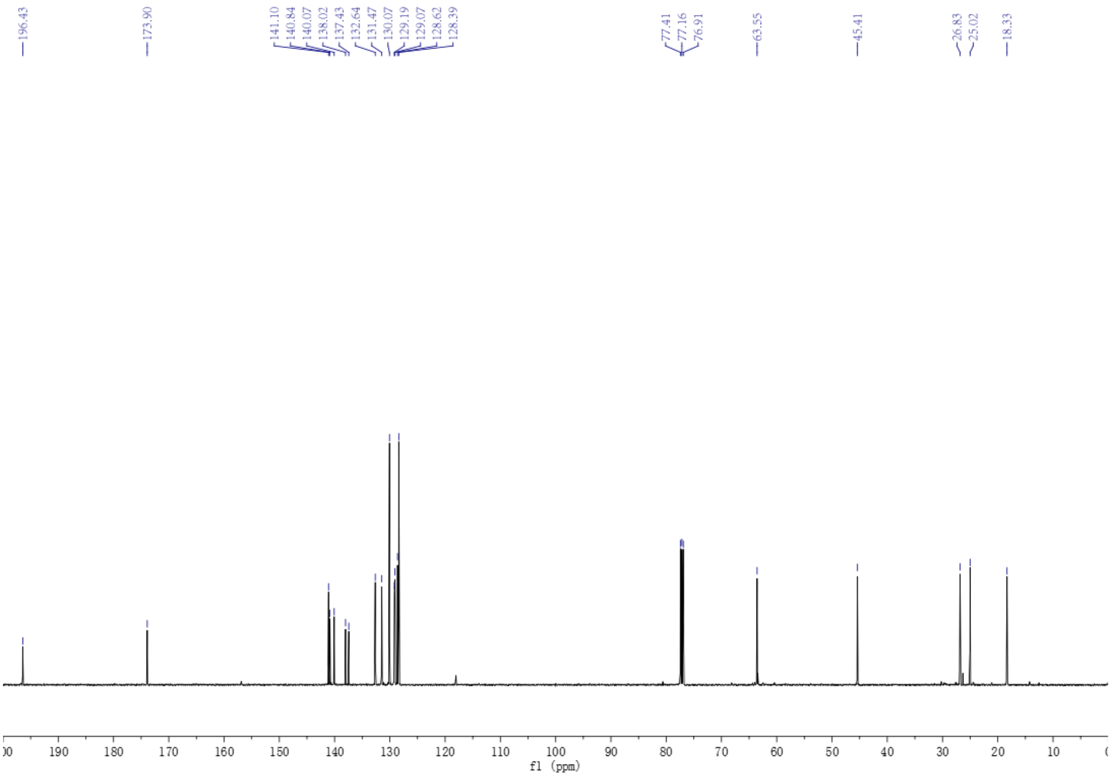
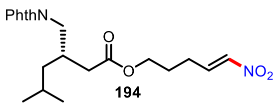


^{1}H NMR of compound **193**（500 MHz, $CDCl_3$）



^{13}C NMR of compound **193**（126 MHz, $CDCl_3$）



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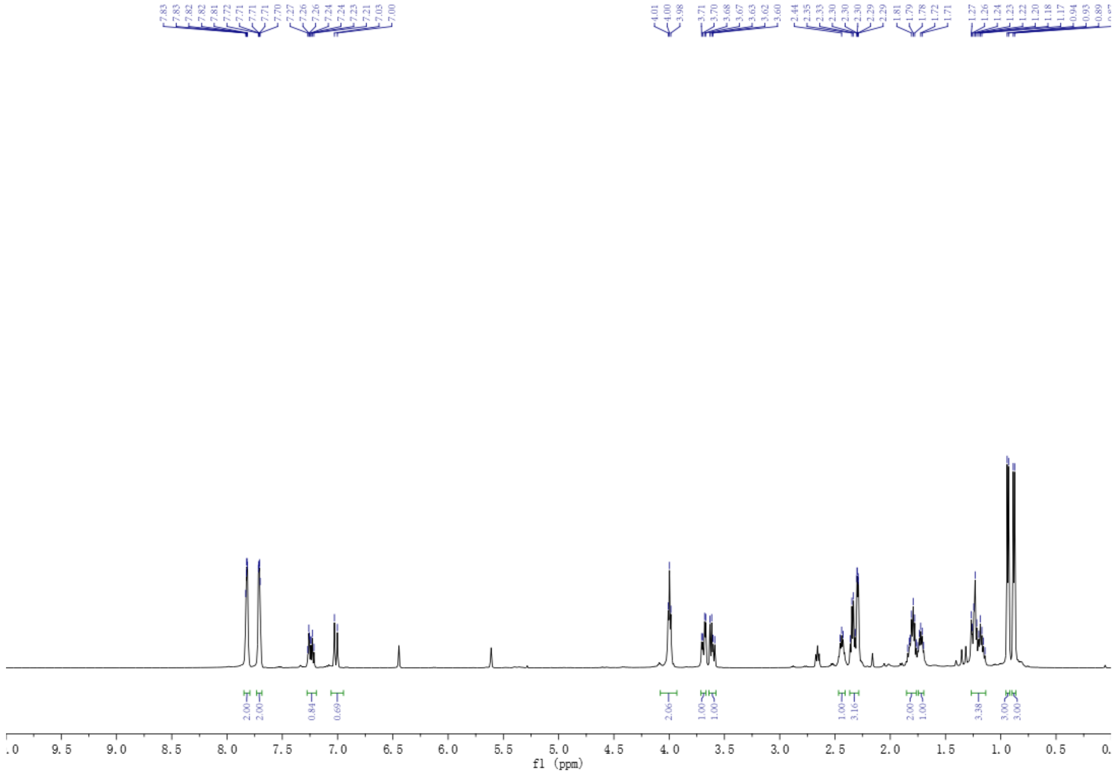
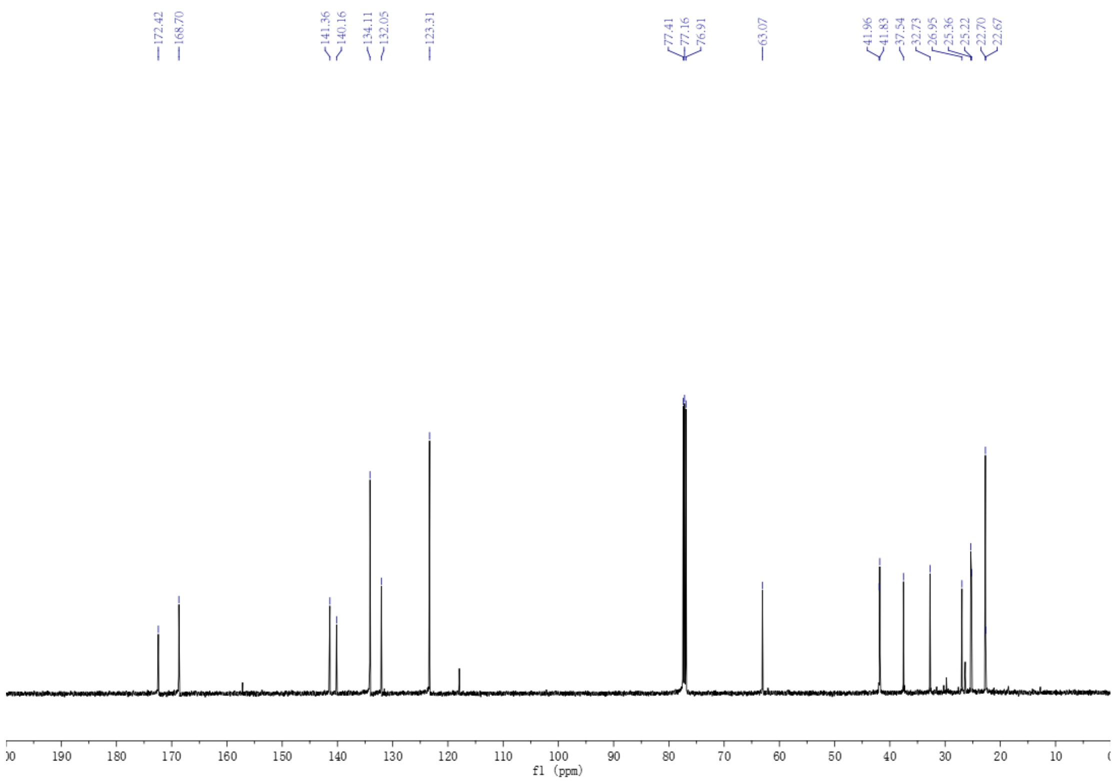
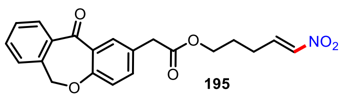


[1]H NMR of compound **194**（500 MHz, $CDCl_3$）



[13]C NMR of compound **194**（126 MHz, $CDCl_3$）



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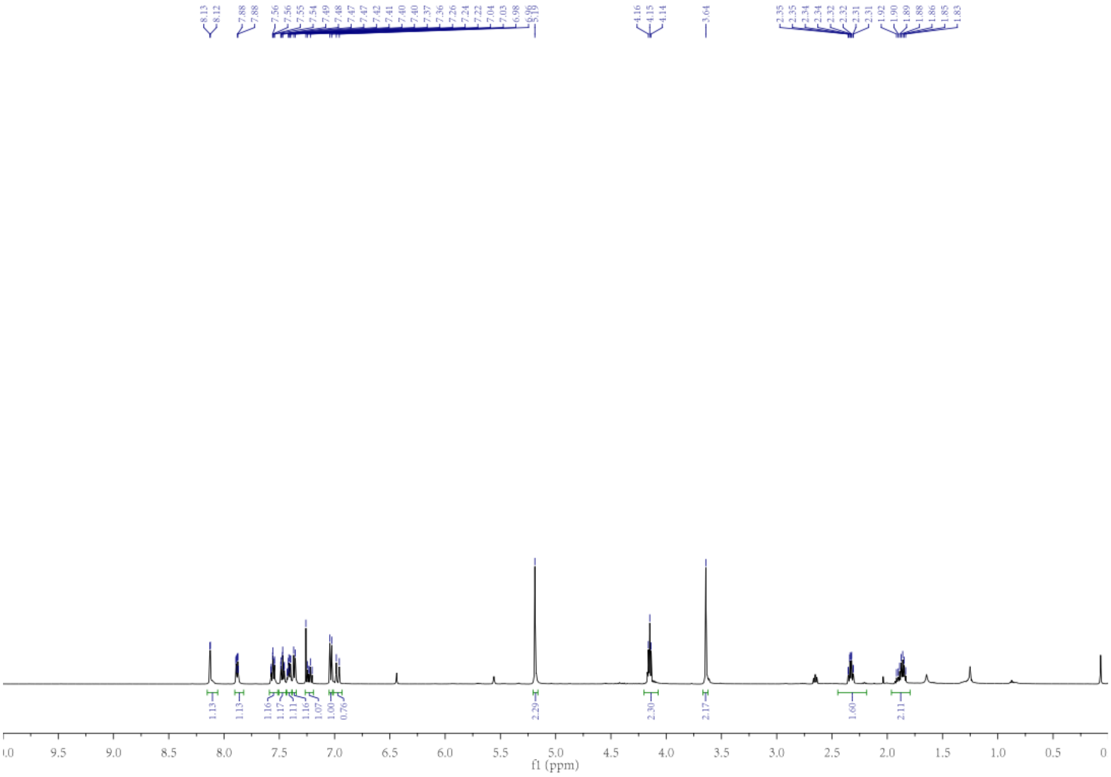
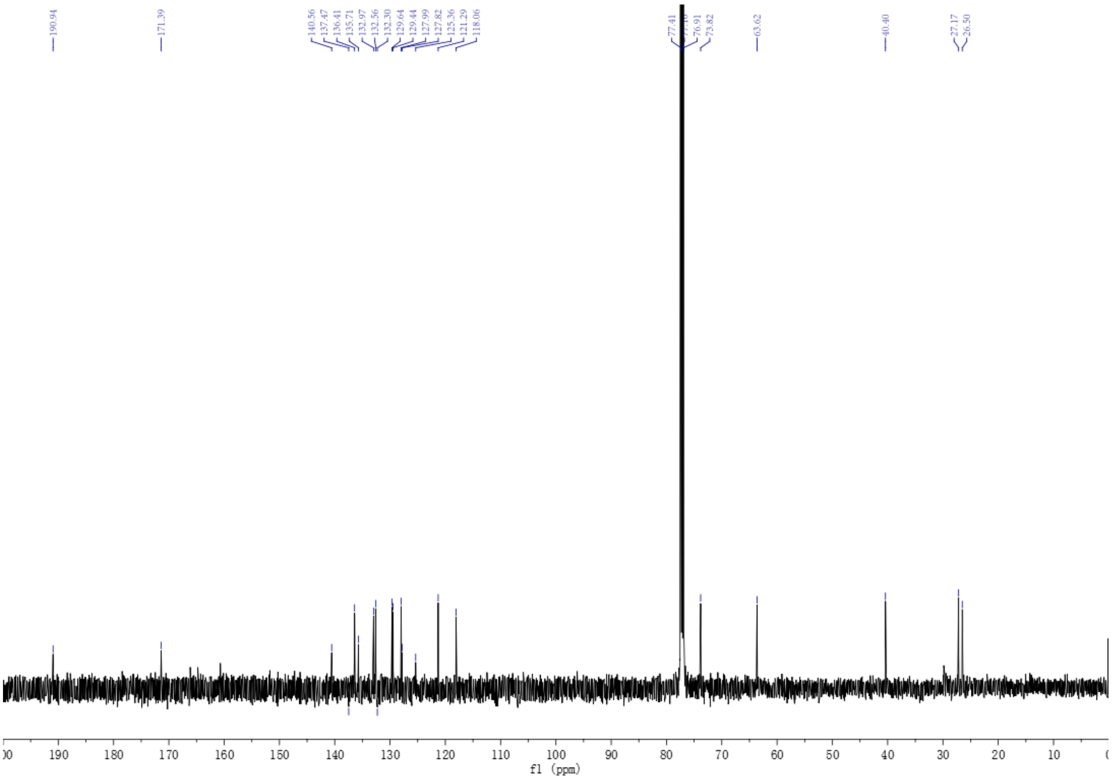
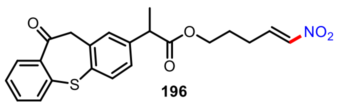


[1]H NMR of compound **195**（500 MHz, $CDCl_3$）



[13]C NMR of compound **195**（126 MHz, $CDCl_3$）



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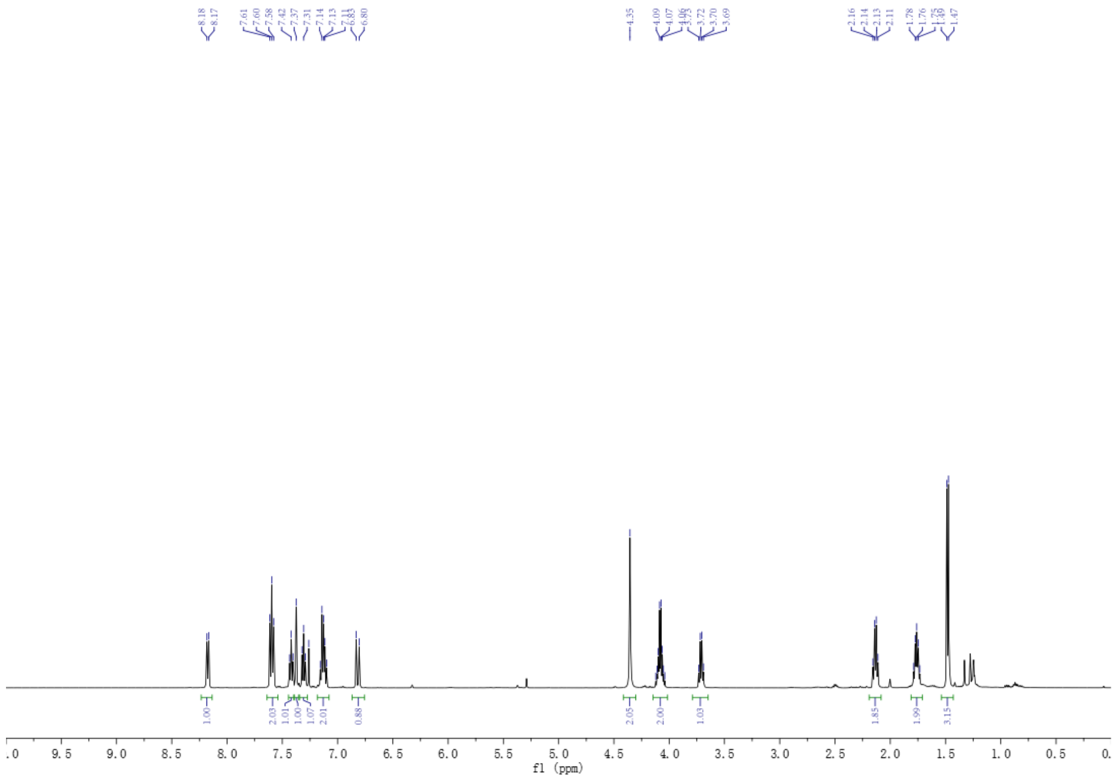
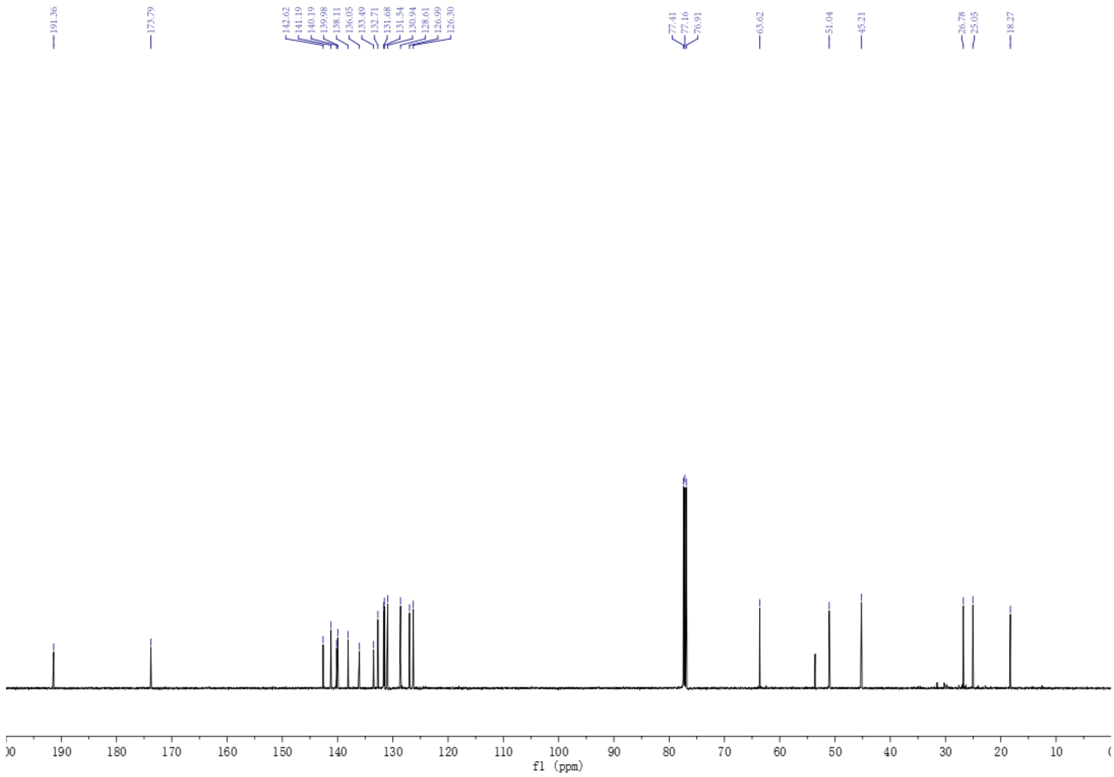
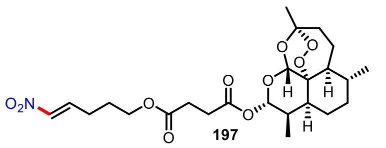
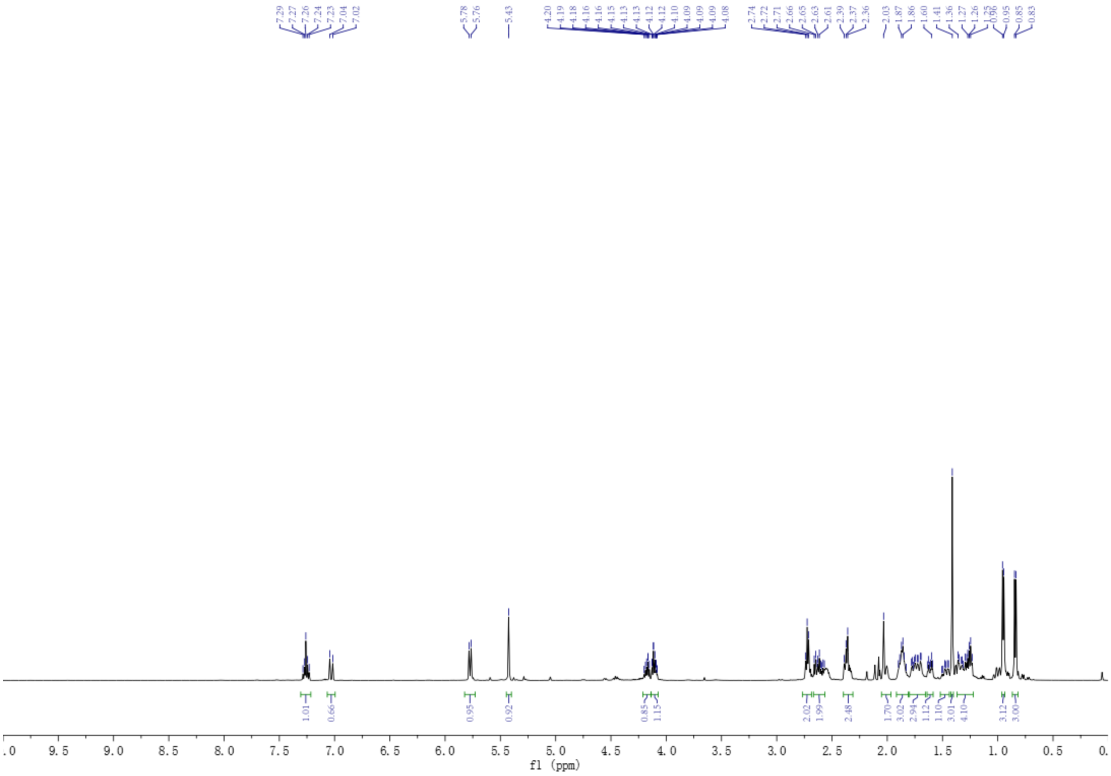


[1]H NMR of compound **196** (500 MHz, $CDCl_3$)

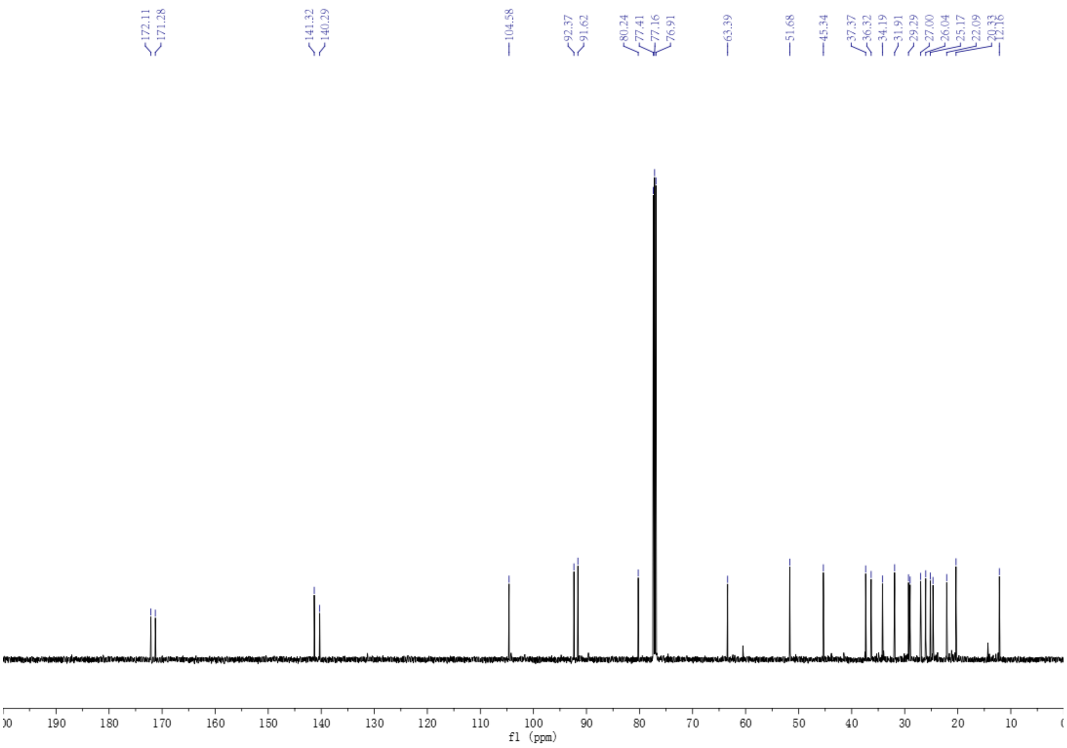


[13]C NMR of compound **196** (126 MHz, $CDCl_3$)

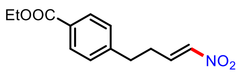




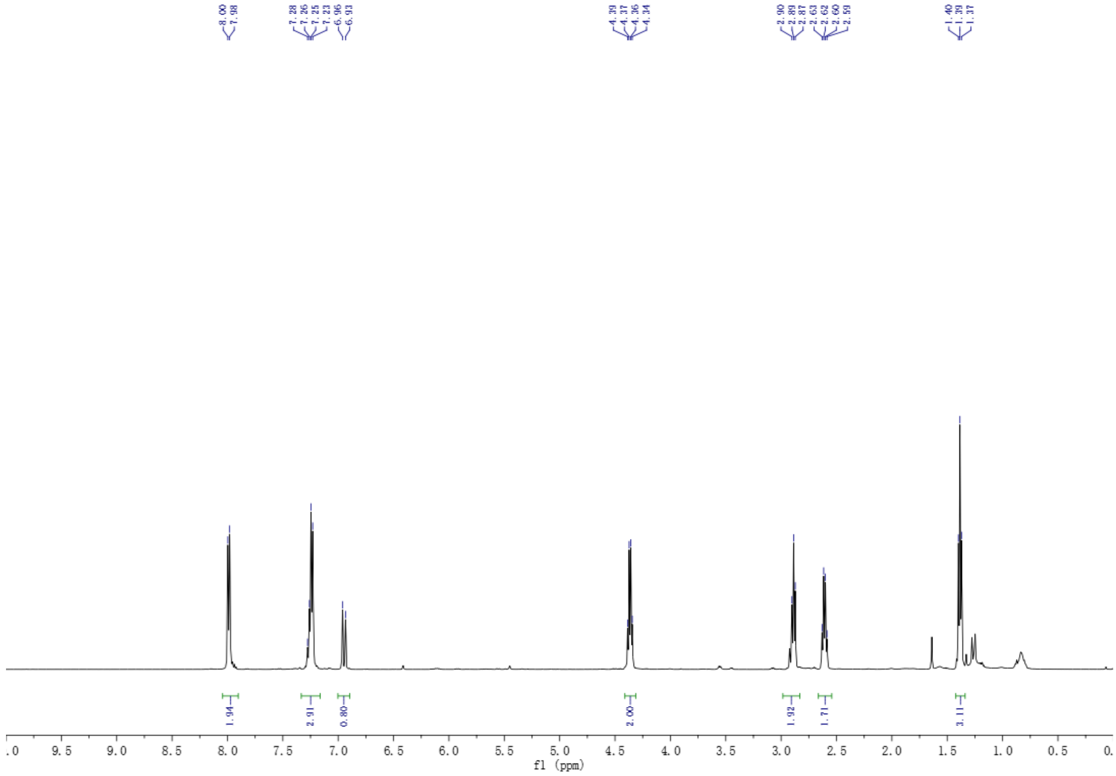
[1]H NMR of compound **197**（500 MHz, $CDCl_3$）



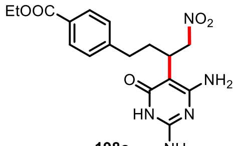
[13]C NMR of compound **197**（126 MHz, $CDCl_3$）



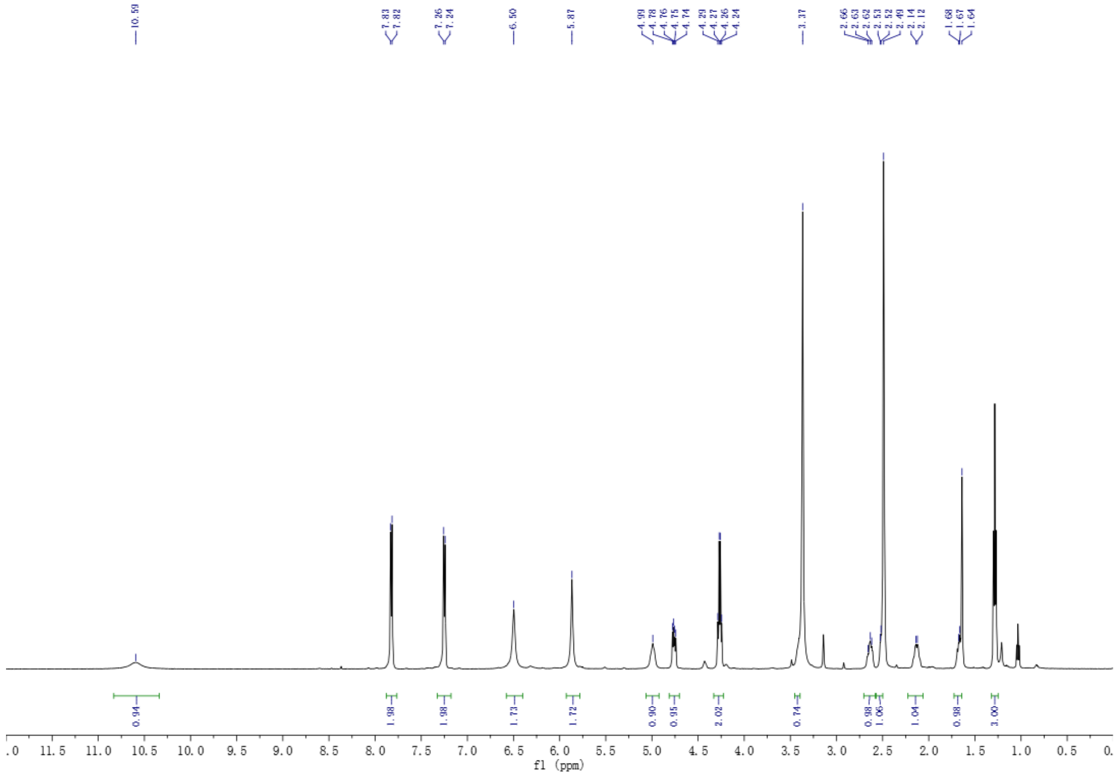
198b



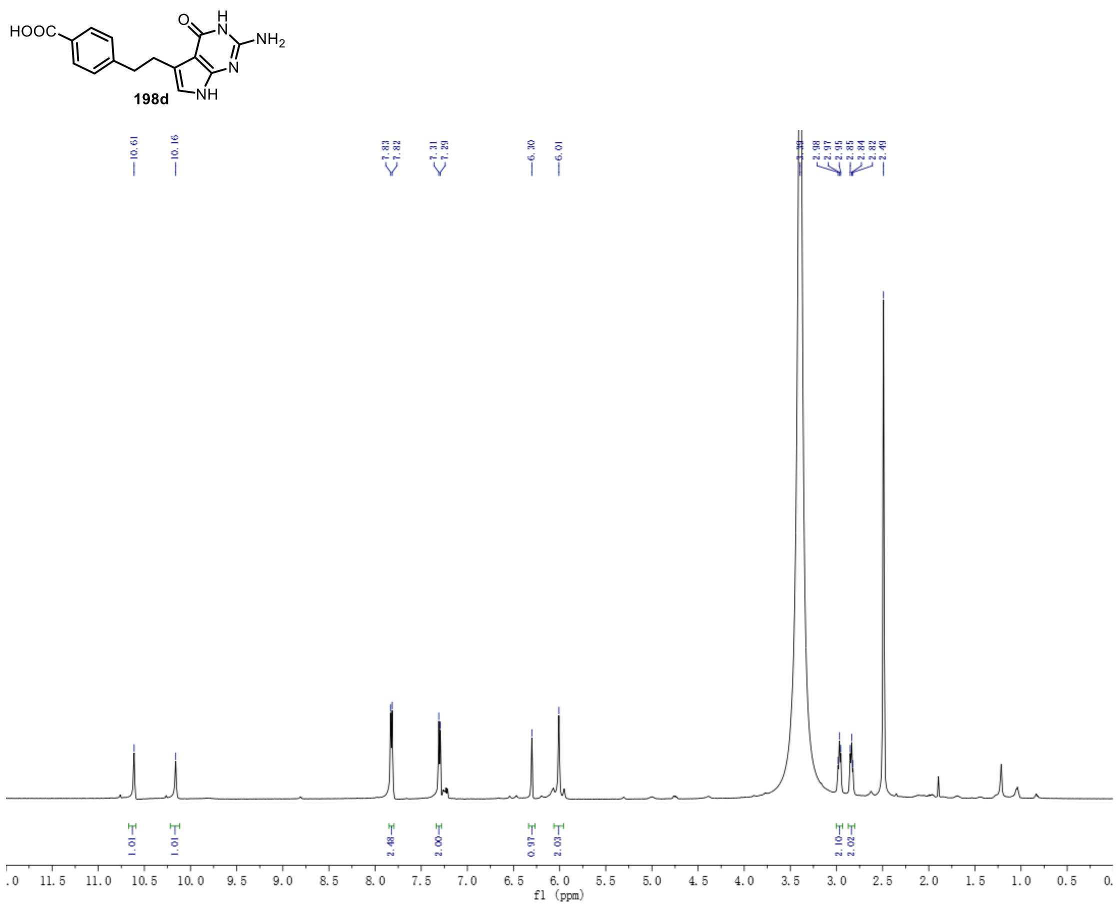
[1]H NMR of compound **198b**（500 MHz, $CDCl_3$）



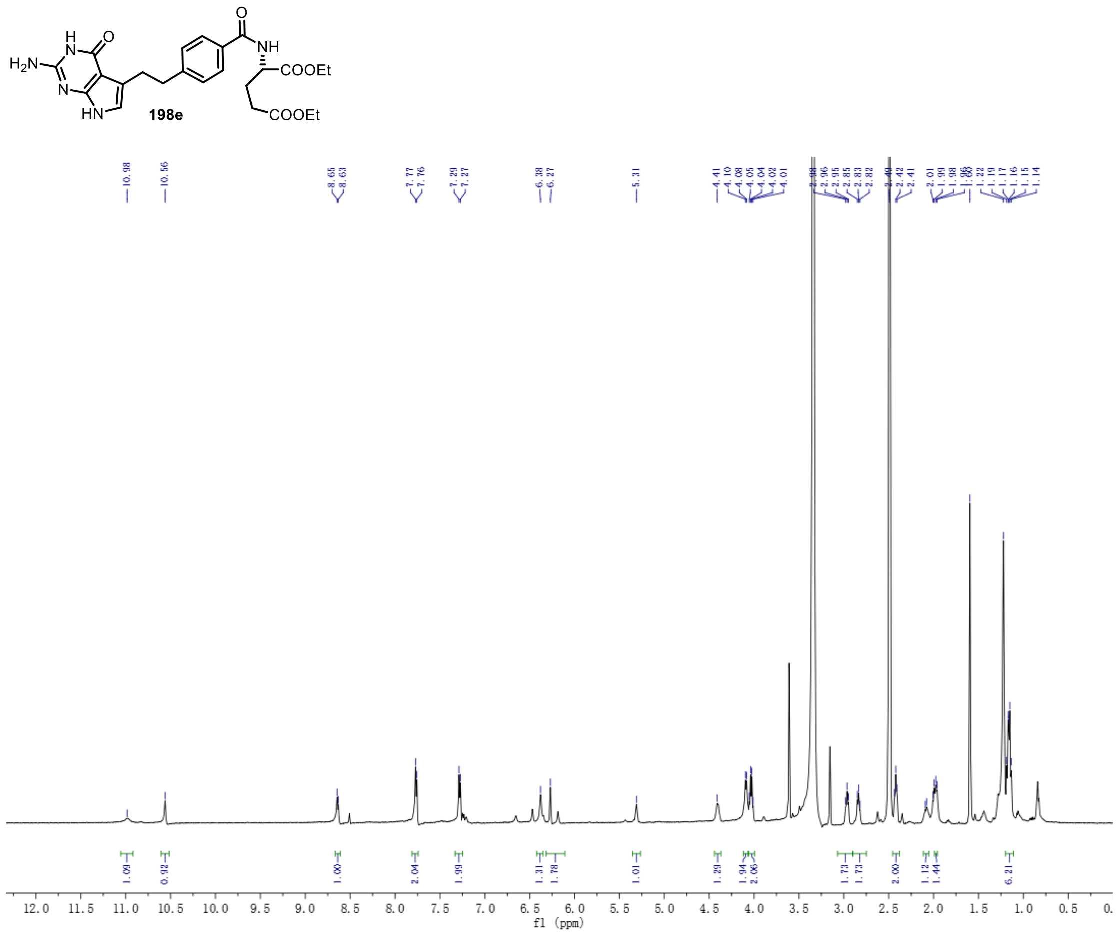
198c



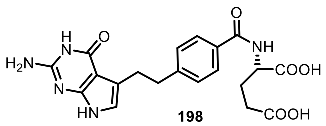
[1]H NMR of compound **198c**（500 MHz, DMSO）



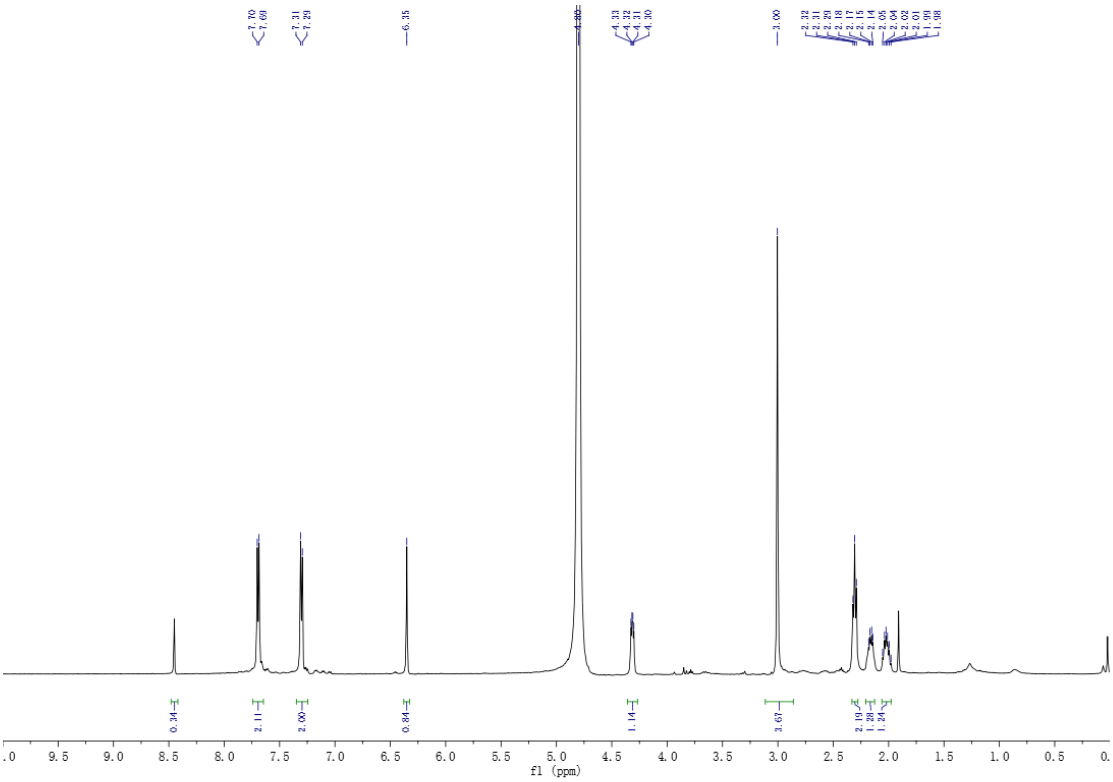
[1]H NMR of compound **198d**（500 MHz, DMSO）



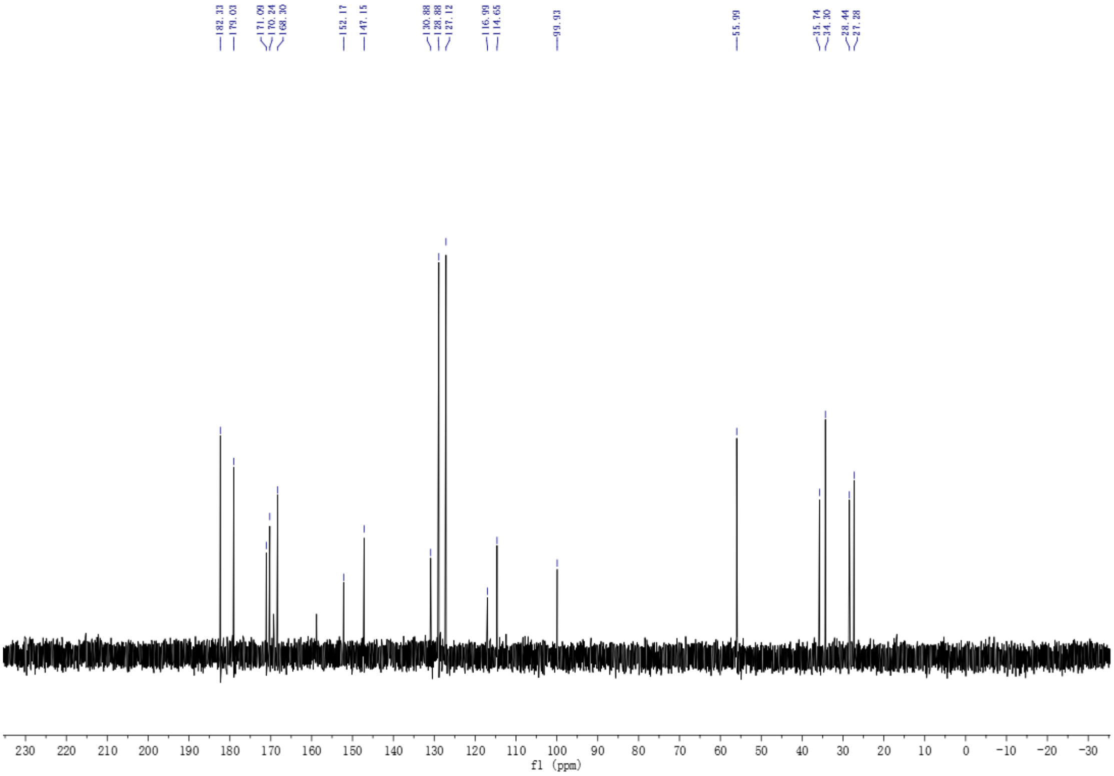
^{1}H NMR of compound **198e**（500 MHz, DMSO）



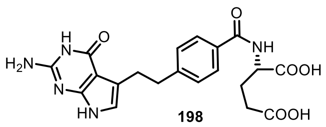
198

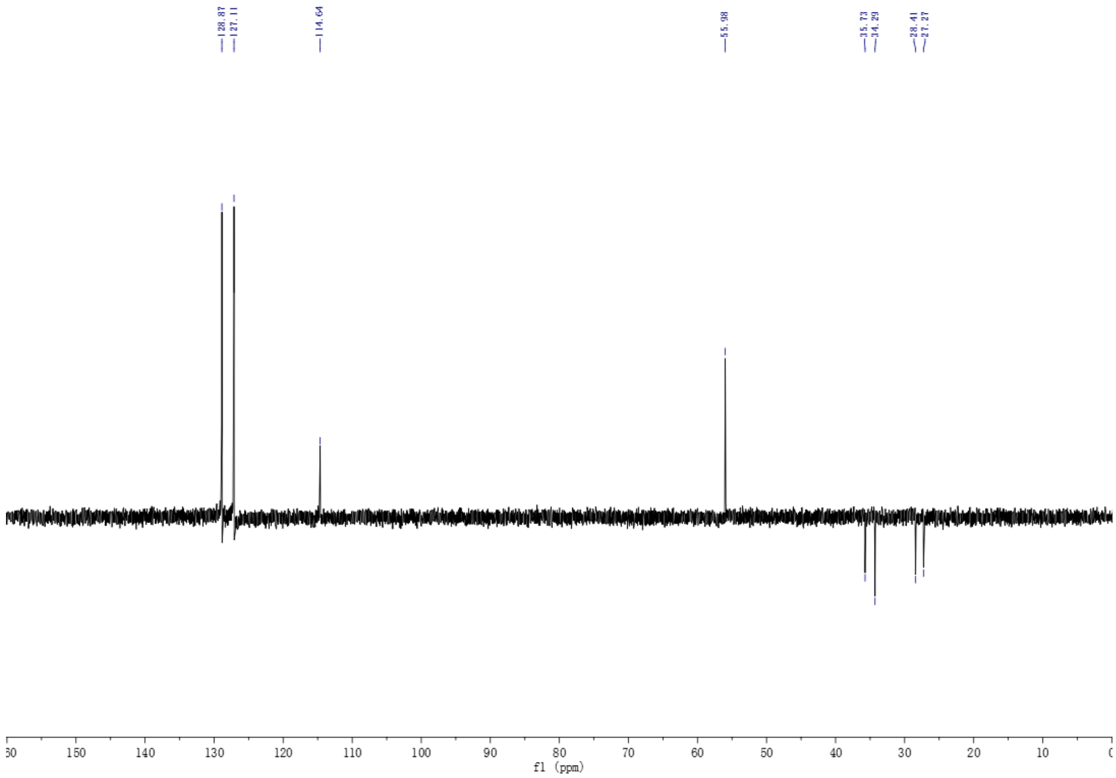


^{1}H NMR of compound **198**（500 MHz, D_2O）

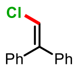


^{13}C NMR of compound **198**（126 MHz, D_2O）

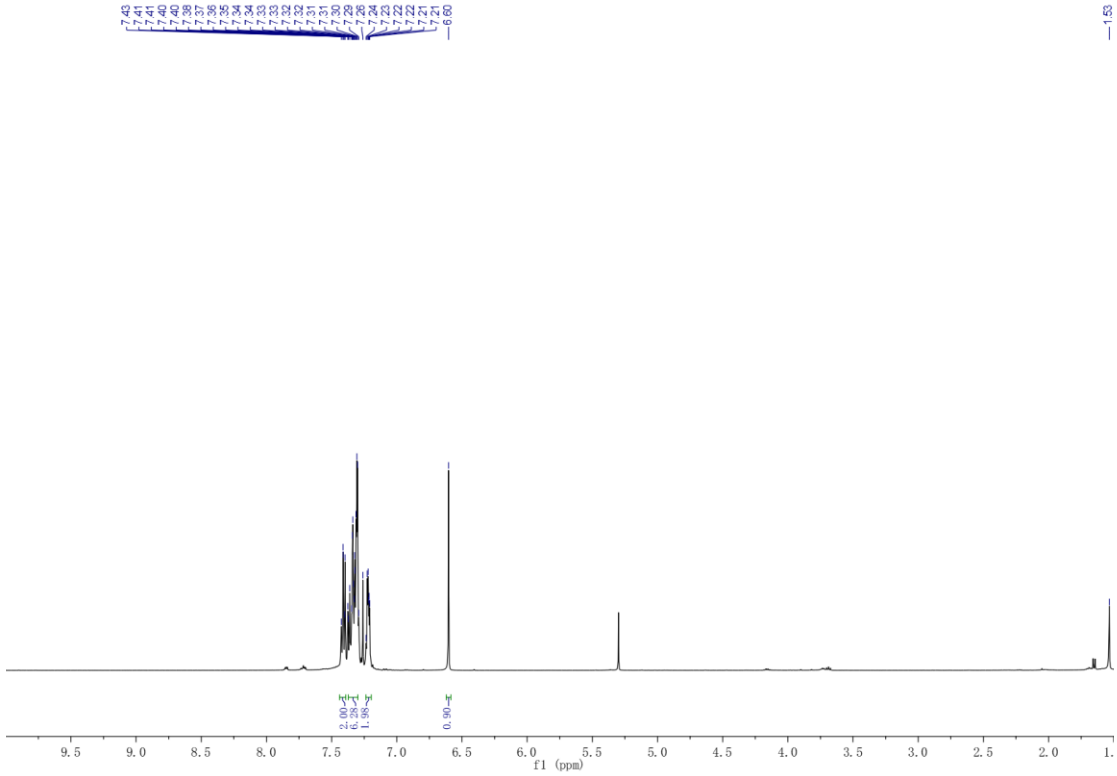




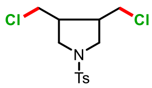
[13]C NMR of compound **198**（126 MHz, D_2O）



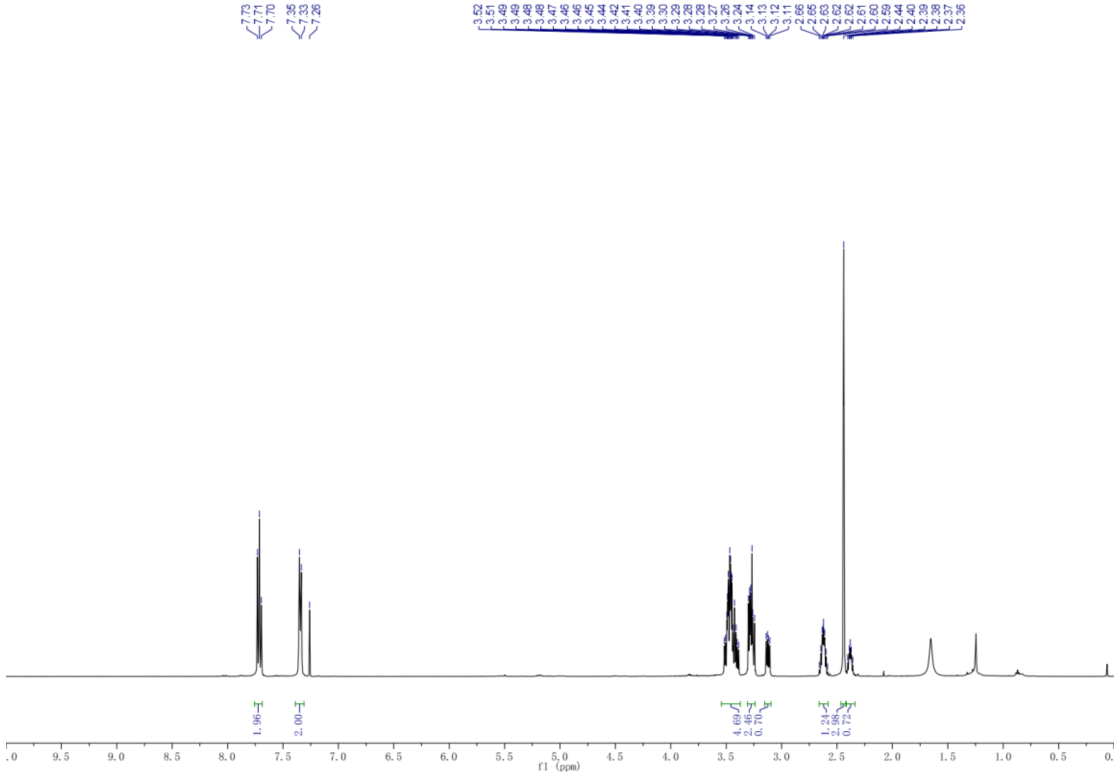
199



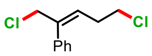
[1]H NMR of compound **199**（500 MHz, $CDCl_3$）



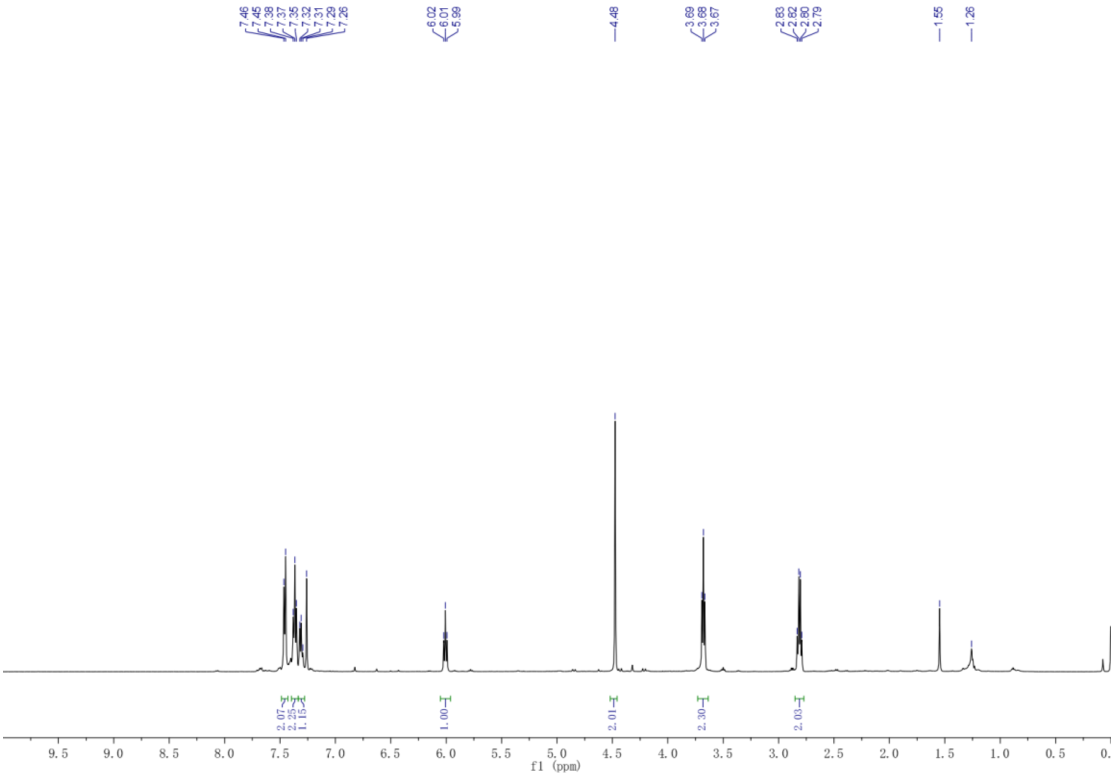
200



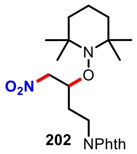
[1]H NMR of compound **200**（500 MHz, $CDCl_3$）



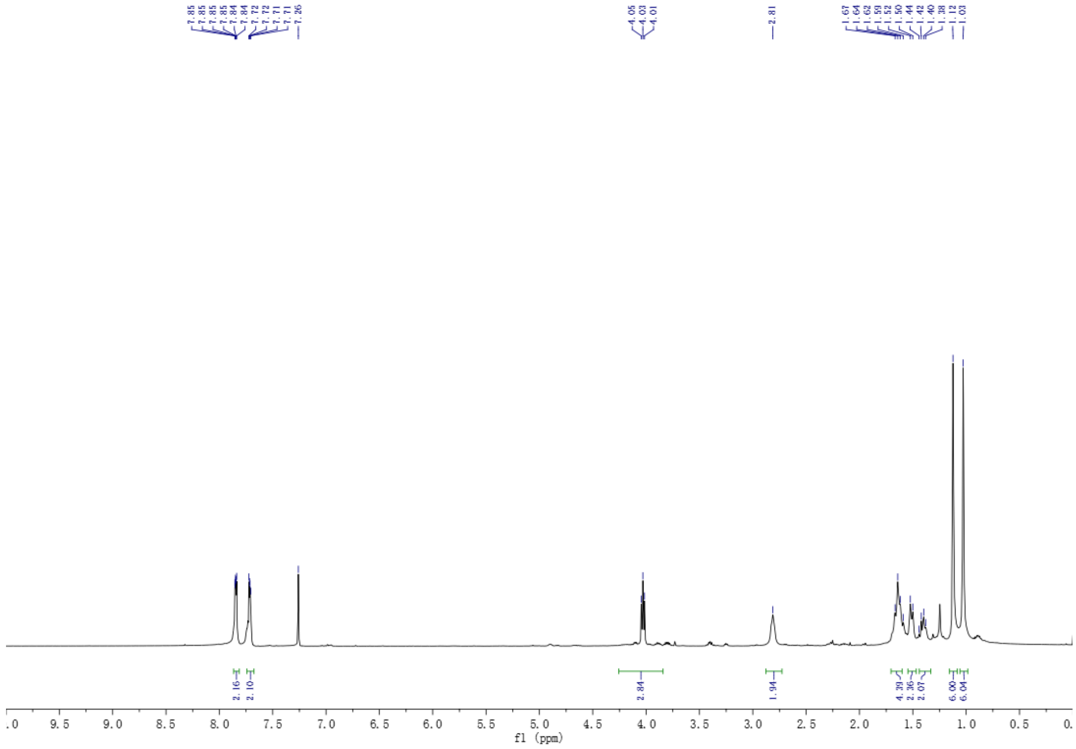
201



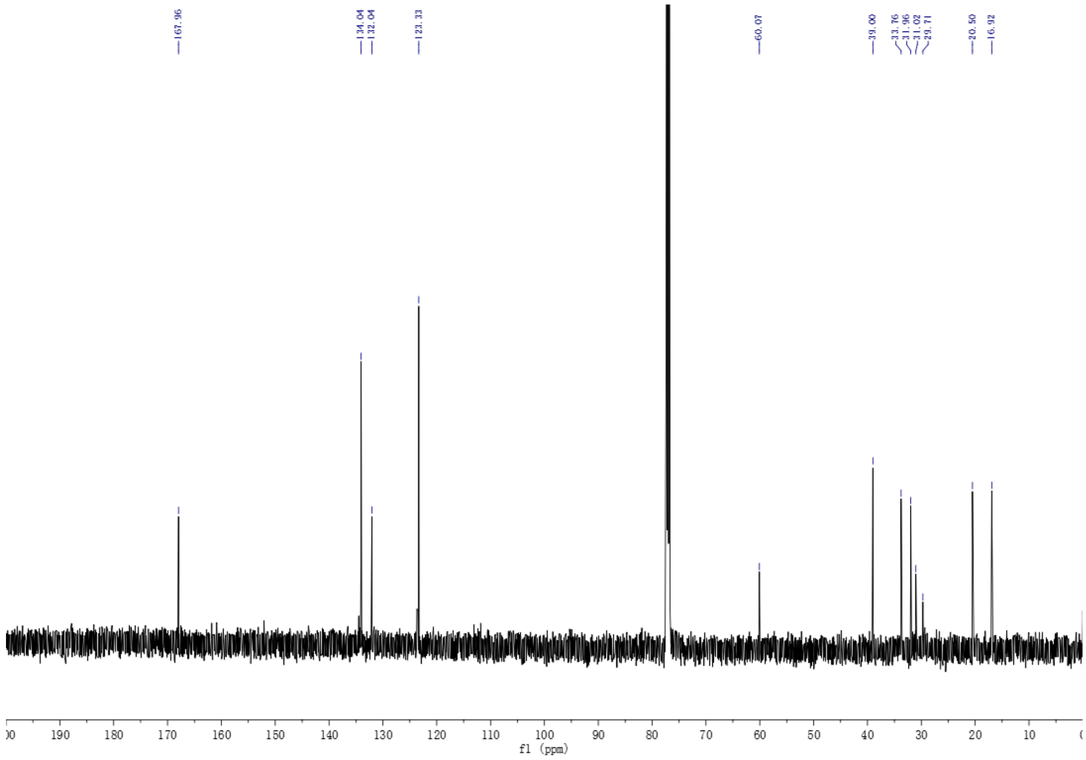
[1]H NMR of compound **201**（500 MHz, $CDCl_3$）



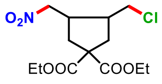
202



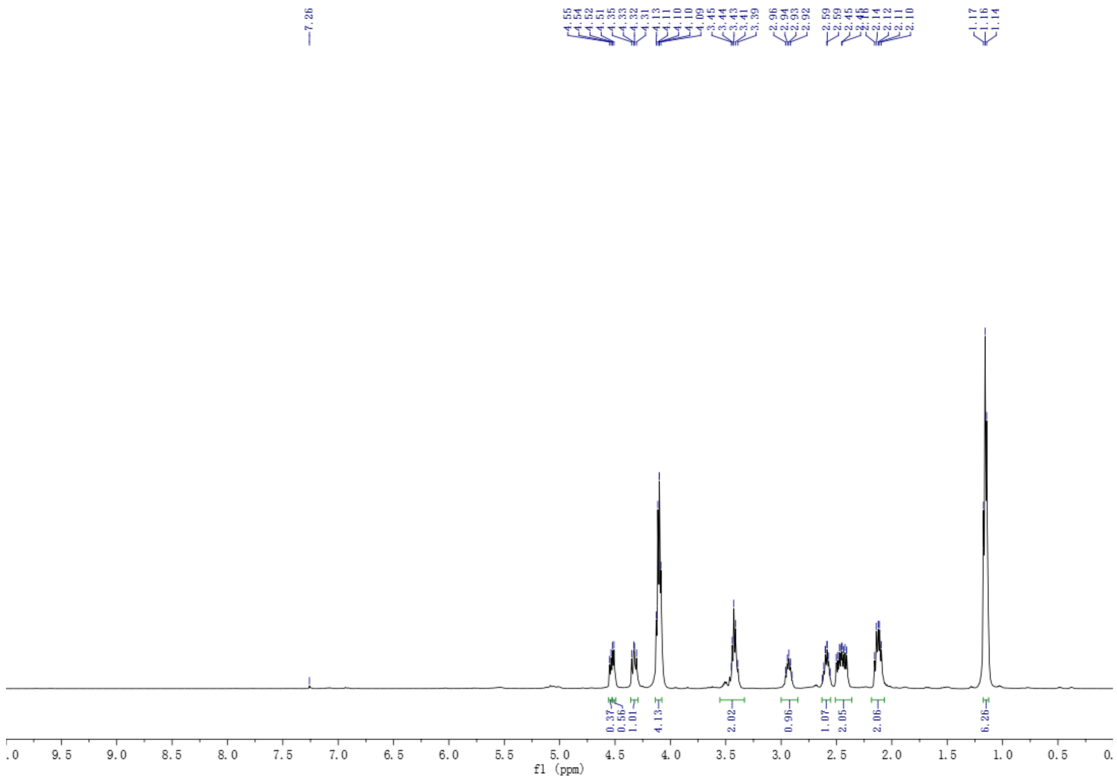
^{1}H NMR of compound **202**（500 MHz, $CDCl_3$）



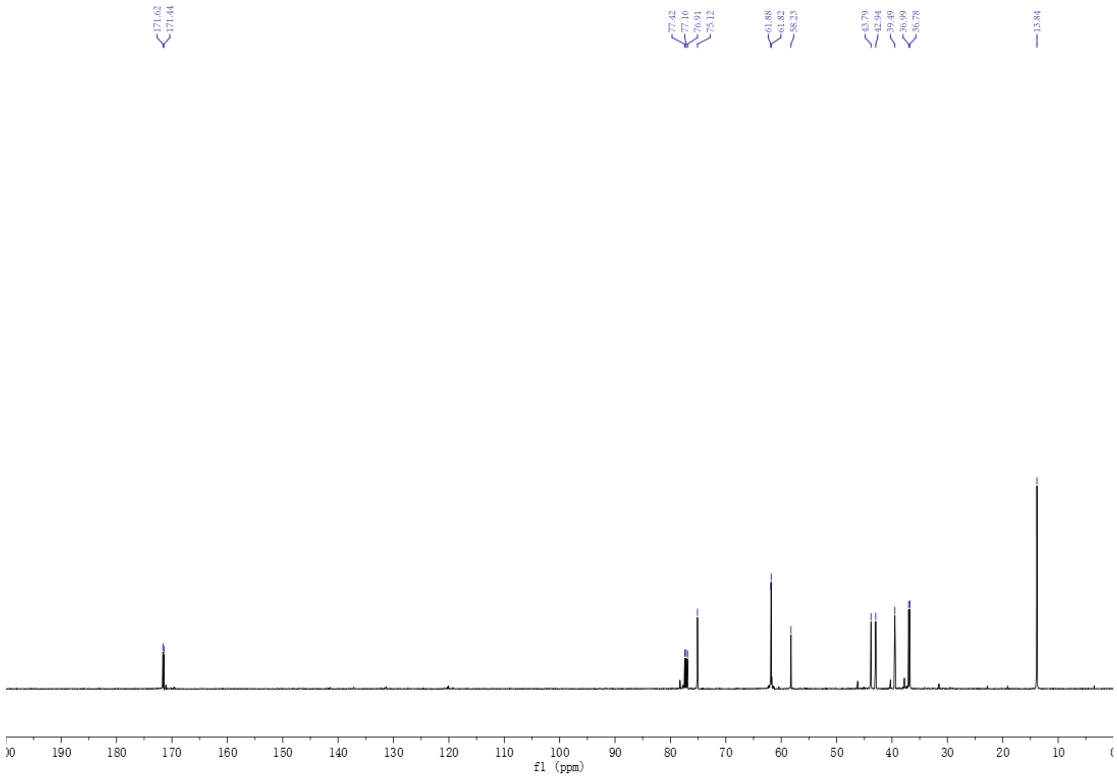
^{13}C NMR of compound **202**（126 MHz, $CDCl_3$）



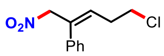
203



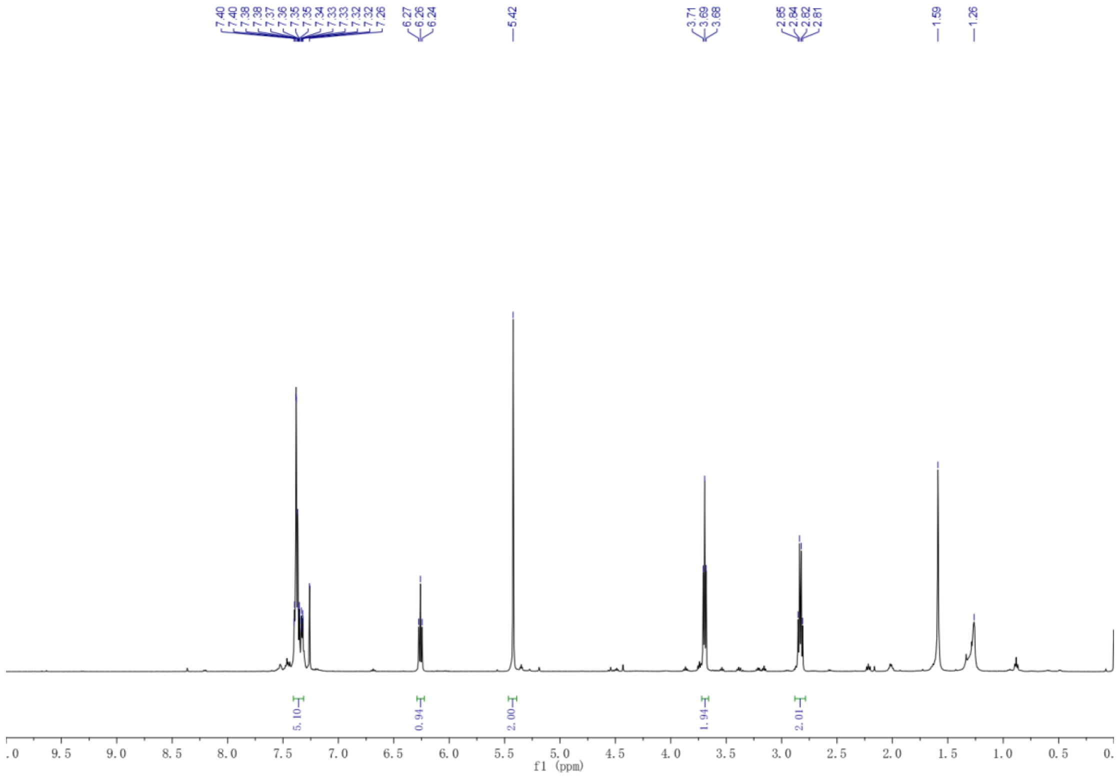
[1]H NMR of compound **203**（500 MHz, $CDCl_3$）



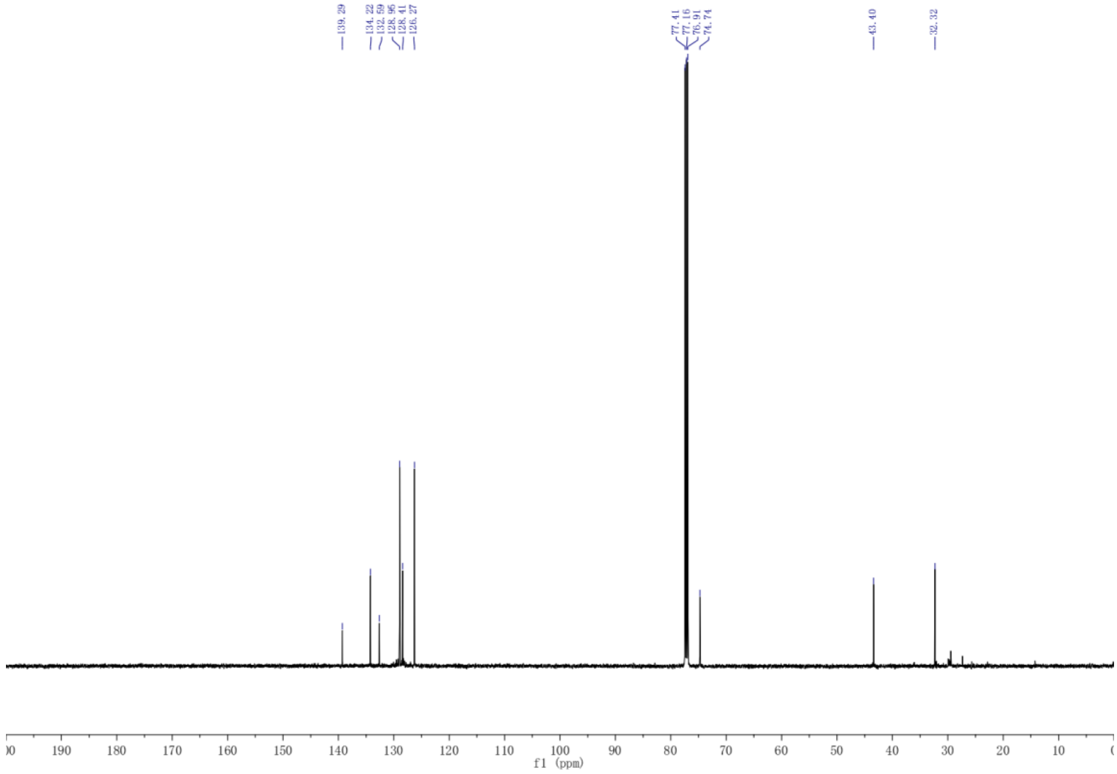
[13]C NMR of compound **203**（126 MHz, $CDCl_3$）



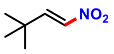
204



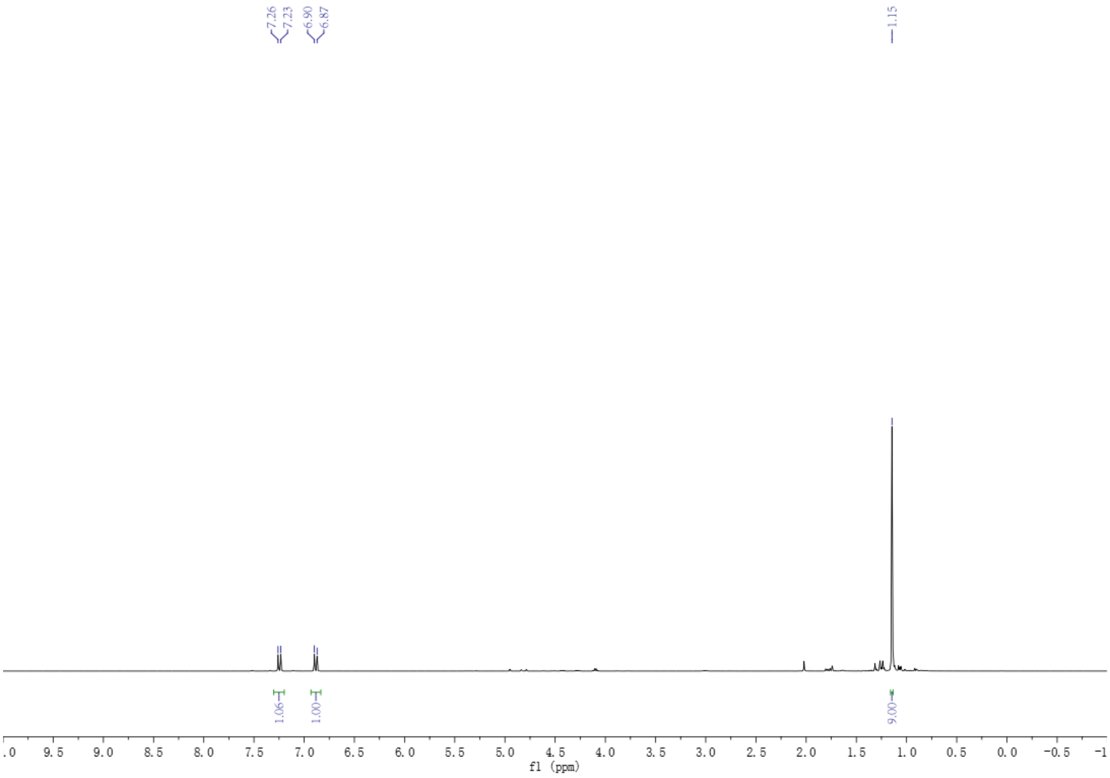
^{1}H NMR of compound **204**（500 MHz, CDCl$_3$）



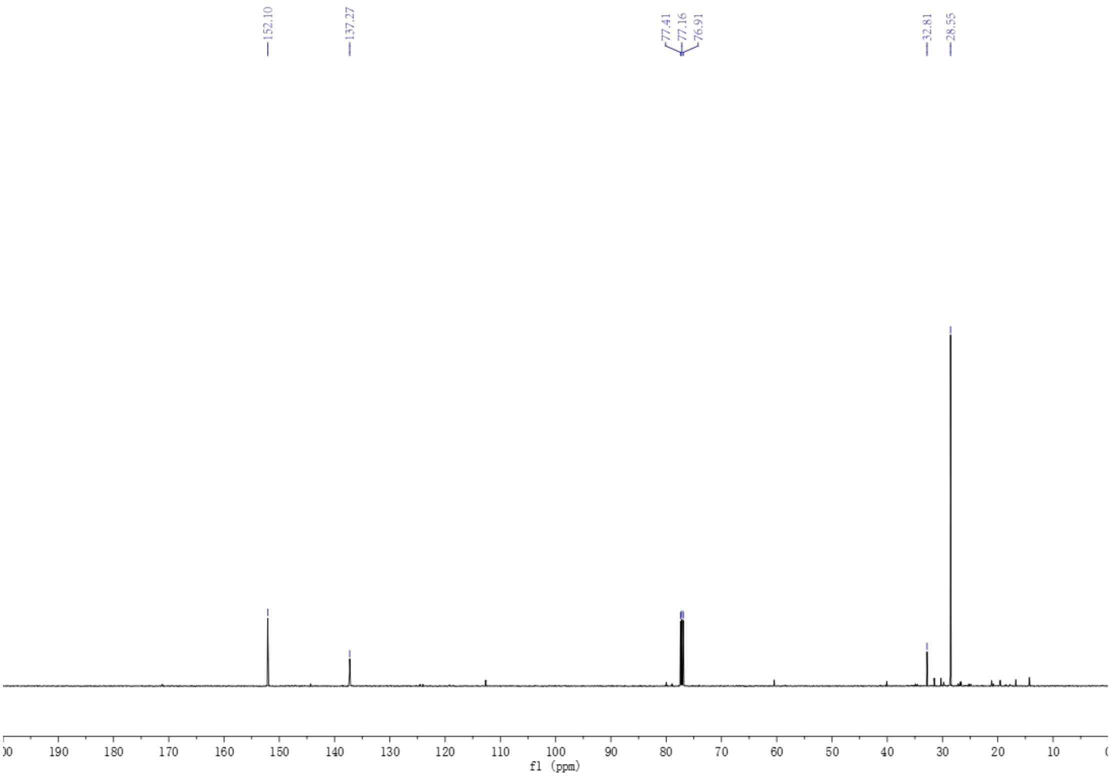
^{13}C NMR of compound **204**（126 MHz, CDCl$_3$）



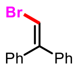
205



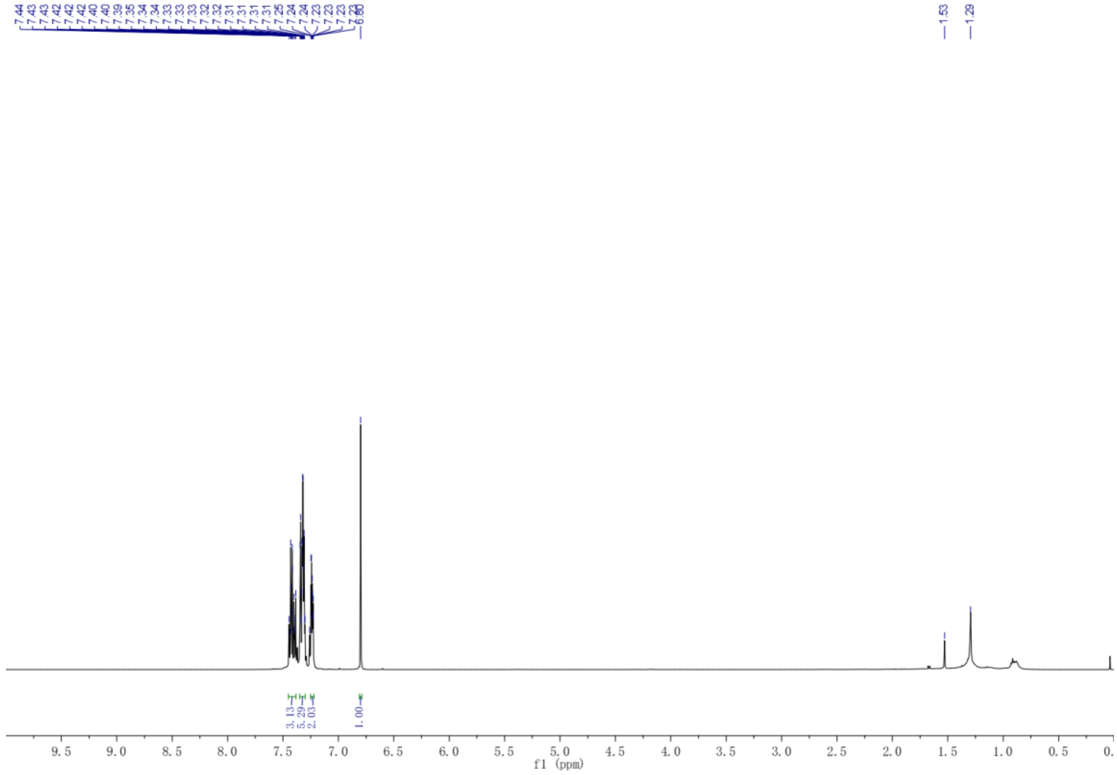
^{1}H NMR of compound **205**（500 MHz, $CDCl_3$）



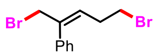
^{13}C NMR of compound **205**（126 MHz, $CDCl_3$）



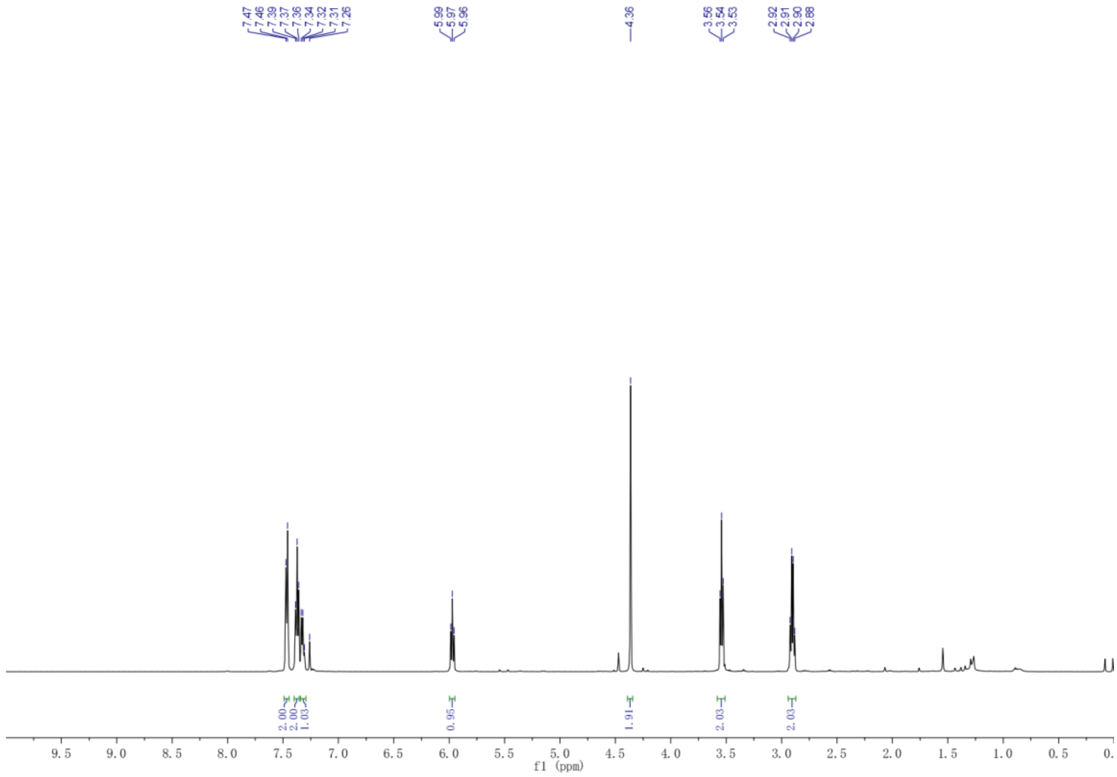
206



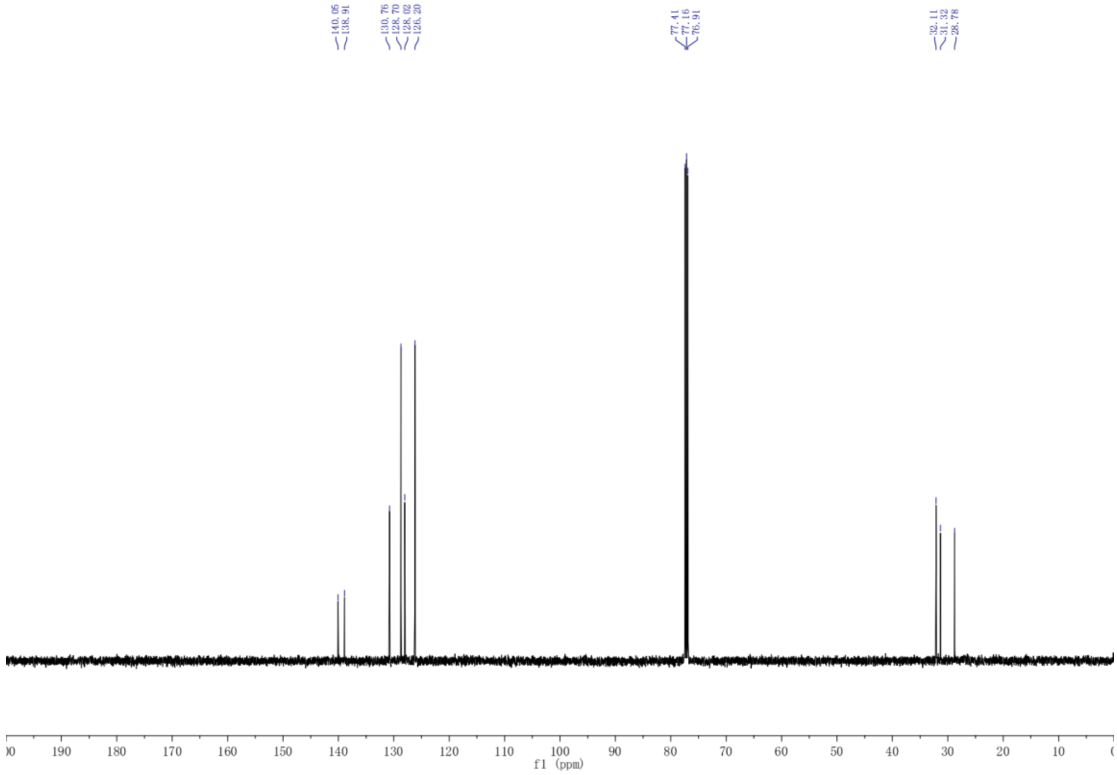
[1]H NMR of compound **206**（500 MHz, $CDCl_3$）



207



^{1}H NMR of compound **207**（500 MHz, $CDCl_3$）



^{13}C NMR of compound **207** （126 MHz, $CDCl_3$）