# Supporting Information

## A Facile and Versatile Electro-Reductive System for Hydrodefunctionalization under Ambient Conditions

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# 1. General and experimental details

## 1.1 General information:

All commercially available reagents were directly used as received without further purification. All organic solvents applied in the reactions were pre-dried by distillation over appropriate drying reagents unless otherwise noted. The electrochemical reactions were performed on a DJS-292B potentiostat (made in China) in constant current mode. All yields of products refer to the isolated yields after chromatography.

$^{1}$H NMR (400, 500 or 600 MHz), $^{13}$C NMR (101, 126 or 151 MHz) and $^{19}$F NMR (376 MHz) spectra were recorded on a Bruker AV-400 spectrometer in $CDCl_3$ or DMSO-$d_6$. For $^{1}$H NMR, $CDCl_3$ ($\delta$ = 7.26 ppm), DMSO-$d_6$ ($\delta$ = 2.50 ppm) or tetramethylsilane (TMS, $\delta$ = 0 ppm) serves as the internal standard; for $^{13}$C NMR, $CDCl_3$ ($\delta$ = 77.16 ppm) or DMSO-$d_6$ ($\delta$ = 39.52 ppm) serves as the internal standard. Data are reported as follows: chemical shift (in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, hept = heptet, m = multiplet, br = broad), coupling constant (in Hz), and integration.

GC analysis was performed on a 7890B/Agilent, while GC-MS analysis was performed on a 7890A-5975C/Agilent. HR-MS spectra were recorded on a Bruker Esquire LC mass spectrometer using electrospray ionization.

## 1.2 Substrates preparation

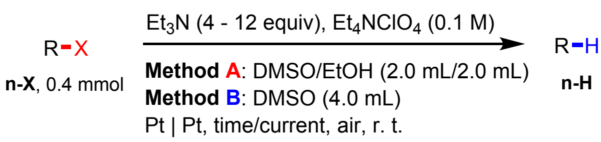
1.2.1 Substrates directly obtained from commercial sources:

| Substrate | CAS No. | Substrate | CAS No. | Substrate | CAS No. |
|---|---|---|---|---|---|
| **1-Br** | 573-17-1 | **17-Br** | 86499-96-9 | **6-Cl** | 54453-93-9 |
| **2-Br** | 1714-29-0 | **18-Br** | 4876-10-2 | **37-Cl** | 90-99-3 |
| **3-Br** | 92-66-0 | **20-Br** | 2675-79-8 | **39-Cl** | 202409-33-4 |
| **4-Br** | 1607-57-4 | **21-Br** | 86-76-0 | **46-Boc** | 75400-67-8 |
| **5-Br** | 29488-24-2 | **22-Br** | 1564-64-3 | **46-Me** | 603-76-9 |
| **6-Br** | 89978-52-9 | **3-I** | 1591-31-7 | **60-CN** | 40817-08-1 |
| **7-Br** | 83664-33-9 | **25-I** | 132034-89-0 | **61-CN** | 3029-30-9 |
| **8-Br** | 63996-36-1 | **26-I** | 502161-03-7 | **64-Azo** | 112809-51-5 |
| **15-Br** | 1940-57-4 | **27-I** | 211029-67-3 | **65-Azo** | 120511-73-1 |
| **16-Br** | 35081-45-9 | **3-Cl** | 2051-62-9 | **66-Azo** | 23593-75-1 |
| | | | | **3-Br-I** | 105946-82-5 |

1.2.2 Substrates acquired after brief synthesis (generally in 5.0 mmol scale):

| Substrate(s)/Data *ref.* | Method description |
| --- | --- |
| **9-Br**[1] | as described in *ref.* [1] |
| **10-Br**,[2] **24-I**,[3] **35-Cl**, **38-Cl**, **42-F**[4] | acyl chloride (1.0 eq.)/amine (1.05 eq.)/TEA (1.2 eq.)/EtOAc/0 °C – r. t./1 – 4 h |
| **11-Br**,[5] **11-I**,[5] **11-Cl**,[5] **40-F**,[5] **59-CN**[6] | sulfonyl or acyl chloride (1.0 eq.)/dimethyl amine (aq., 5 eq.)/THF/0 °C – r. t./1 h |
| **12-Br**, **13-Br**, **14-Br**, **28-I**,[7] **55-Bz**[8] | acid (1.0 eq.)/alcohol (1.0 eq.)/DCC (1.0 eq.)/ DMAP (0.1 eq.)/DCM/r. t./overnight |
| **19-Br**,[9] **19-I**,[10] **19-Cl**,[11] **36-Cl** | phenol (1.0 eq.)/bromide (1.2 eq.)/$K_2CO_3$ (2.0 eq.)/MeCN/r. t. or 60 °C/4 h |
| **23-Br**[12] | as described in *ref.* [12] |
| **29-I** | as described in *ref.* [13] |
| **30-I**[14] | as described in *ref.* [14] |
| **31-I**[15] | as described in *ref.* [15] |
| **32-I**[16] | as described in *ref.* [16] |
| **33-I**[17] | as described in *ref.* [17] |
| **34-I**[18] | as described in *ref.* [18] |
| **41-F**,[19] **43-F**,[20] **8-CN**[21] | (hetero)aryl bromide (1.0 eq.)/boronic acid (1.5 eq.)/$K_2CO_3$ (2.0 eq.)/$Pd(OAc)_2$ (5.0 mol%)/ /EtOH:$H_2O$ = 3:1/80 °C/overnight |
| **44-Ts**,[22] **45-Ts**,[23] **48-Ts**,[23] **49-Ts** | amine (1.0 eq.)/TsCl (1.1 eq.)/TEA (1.5 eq.)/DCM/ 0 °C – r. t./1 – 4 h |
| **46-Ts**,[23] **46-Ns**,[23] **46-Bz**,[24] **46-Bn**,[24] **47-Ts**[25] | indole (1.0 eq.)/sulfonyl, acyl chloride or benzylic bromide (1.2 eq.)/KOH (3.0 eq.)/$Bu_4NHSO_4$ (10 mol%)/DCM/ 0 °C – r. t./10 min – 3 h |
| **50-Ts**[26] | as described in *ref.* [26] |
| **51-Ts** | amine (1.0 eq.)/TsCl (2.2 eq.)/ TEA (3.0 eq.)/ DMAP (0.1 eq.)/DCM/0 °C – r. t./24 h |
| **52-Ts**,[27] **53-Ts**,[27] **54-Ts**, **55-Ts**,[28] **56-Ts**,[29] **57-Ts**[30] | phenol or alcohol (1.0 eq.)/TsCl (1.1 eq.)/TEA (1.5 eq.)/DMAP (0.1 eq.)/DCM/r. t./overnight |
| **53-Tf**[31] | as described in *ref.* [31] |
| **58-Ts-Bz**[32] | as described in *ref.* [32] |
| **62-CN**,[33] **63-CN**[34] | as described in *ref.* [35] |

## 1.3 General procedure for the electrochemical reduction (0.4 mmol scale)



To a 25 mL three-necked flask was added the substrate **n-X** (0.4 mmol) and electrolyte $Et_4NClO_4$ (91.9 mg, 0.4 mmol), followed by 4.0 mL solvent (**Method A**: DMSO:EtOH = 1:1 / **Method B**: DMSO) and $Et_3N$ (0.22 – 0.67 mL, 1.6 – 4.8 mmol, depending on the specific current and reaction time, see **Table S1** for their relationship). Subsequently, the flask was equipped with two platinum plate electrodes (10×10×0.2 mm), the distance between which was approximately 2 cm. To minimize the evaporation of the alcohol co-solvent and $Et_3N$, the system was closed with a septum with a needle through it (see **Fig. S1**, it is worth noting that reactions conducted in open flask also provided identical results). The constant current (8, 16 or 24 mA) electrolysis was then performed at room temperature under air atmosphere with vigorous stirring for the indicated time as monitored by TLC or GC-MS analysis (for the 16 mA electrolysis, the voltage was generally around 10 V). Upon completion, the reaction mixture was poured into brine and extracted with EtOAc for three times. The combined organic layer was dried over anhydrous $Na_2SO_4$, and the solvent was then removed under reduced pressure. The resulting mixture was purified by column chromatography on silica gel (eluted with EtOAc/PE) to afford the desired product **n-H**.

**Table S1.** Relationship among the applied current, reaction time and amount of $Et_3N$.

| Entry | Constant current | Reaction time | Amount of $Et_3N$ |
|---|---|---|---|
| 1 | 16 mA | $t \leq 12$ h | 4 equiv, 0.22 mL |
| 2 | | 12 h < $t \leq 24$ h | 8 equiv, 0.44 mL |
| 3 | 8 mA | $t \leq 24$ h | 4 equiv, 0.22 mL |
| 4 | 24 mA | $t \leq 8$ h | 4 equiv, 0.22 mL |
| 5 | | 8 h < $t \leq 16$ h | 8 equiv, 0.44 mL |
| 6 | | 16 h < $t \leq 24$ h | 12 equiv, 0.67 mL |

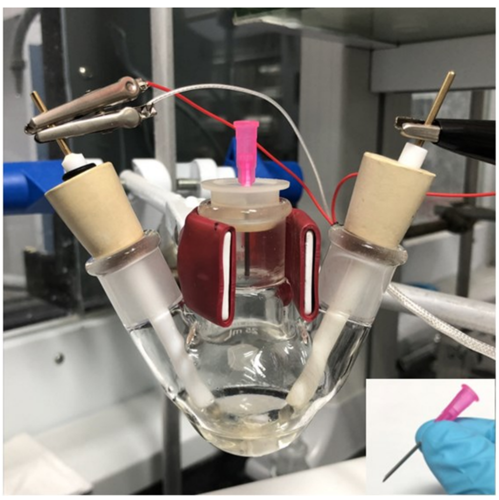
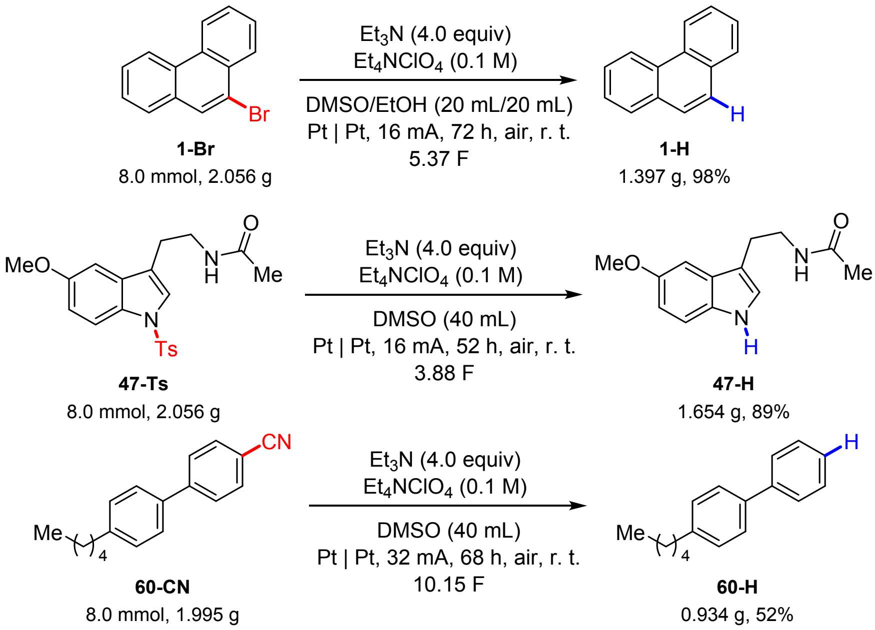


**Fig. S1** Setup for the 0.4 mmol scale reactions

## 1.4 Procedure for the gram-scale reactions (8.0 mmol scale)




To a 50 mL three-necked flask was added substrate **n-X** (8.0 mmol) and electrolyte $Et_4NClO_4$ (0.919 g, 4.0 mmol), followed by the reaction solvent (40 mL, 0.2 M for the substrate; DMSO:EtOH = 1:1 or DMSO) and $Et_3N$ (4.44 mL, 32 mmol). Subsequently, the flask was equipped with two platinum plate electrodes (10×10×0.2 mm), the distance between which was approximately 3 cm. To minimize the evaporation of the alcohol co-solvent and $Et_3N$, the system was closed with a needle-through-septum (see Fig. S2). The constant current (16 or 32 mA) electrolysis was then performed at room temperature under air atmosphere with vigorous stirring for the indicated time (monitored by TLC or GC-MS analysis). Upon completion, the reaction mixture was poured into brine and extracted with EtOAc for three times. The combined organic layer was dried over anhydrous $Na_2SO_4$, and the solvent was then removed under reduced pressure. The resulting mixture was purified by column chromatography on silica gel (eluted with EtOAc/PE) to afford the desired product **n-H**.

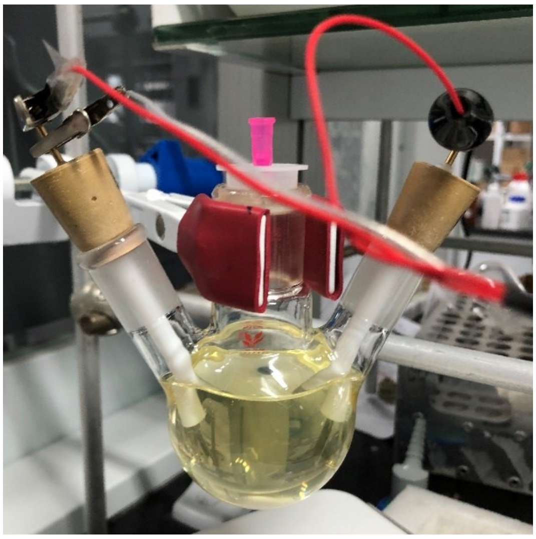
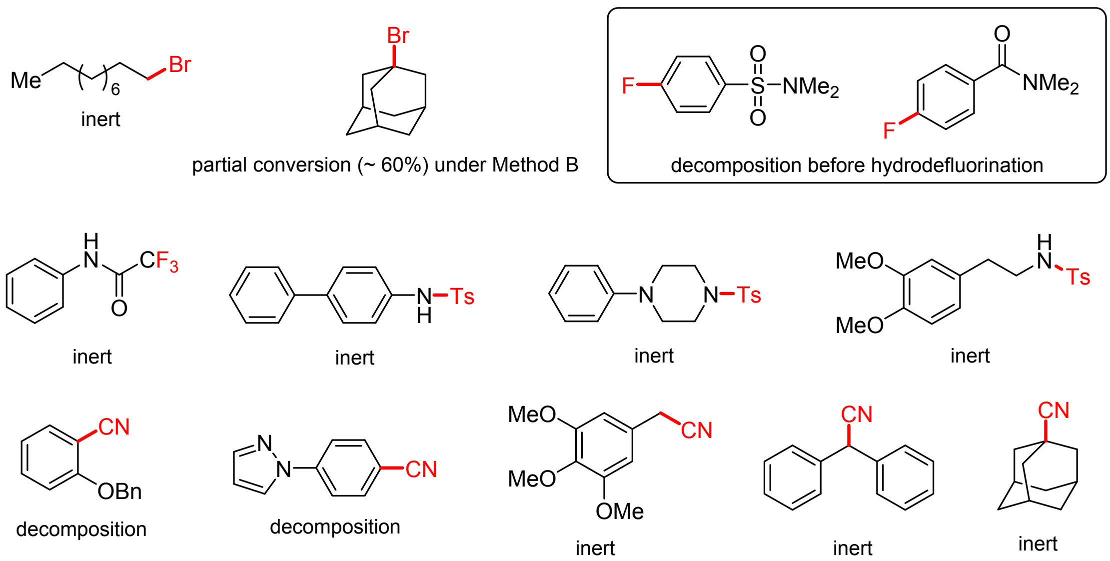


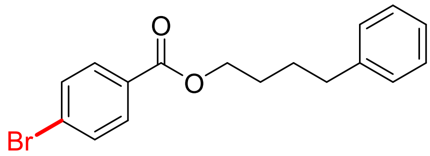
**Fig. S2** Setup for 8.0 mmol scale reaction

## 1.5 Some inert, partially converted or decomposed substrates



## 2. Characterization data

### 2.1 Characterization data for the unreported substrate




4-phenylbutyl 4-bromobenzoate (**12-Br**)

Colorless oil, obtained from the condensation of 4-bromobenzoic acid (CAS: 586-76-5) and 4-phenylbutan-1-ol (CAS: 3360-41-6).

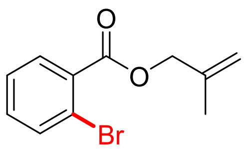
$^1$H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, $J$ = 8.3 Hz, 2H), 7.58 (d, $J$ = 8.3 Hz, 2H), 7.29 (t, $J$ = 7.6 Hz, 2H), 7.23 – 7.17 (m, 3H), 4.33 (t, $J$ = 6.1 Hz, 2H), 2.69 (t, $J$ = 7.1 Hz, 2H), 1.85 – 1.74 (m, 4H).

$^{13}$C NMR (151 MHz, $CDCl_3$) δ 166.06, 142.08, 131.82, 131.23, 129.42, 128.54, 128.52, 128.10, 126.03, 65.26, 35.59, 28.39, 27.92.

IR (KBr, cm$^{-1}$): 3026, 2948, 2855, 1725, 1580, 1395, 1270, 1124, 1013, 850, 758, 699.

GC-MS (EI): 334.1, 332.0, 185.0, 183.0, 132.1, 104.1, 91.1.

HRMS (ESI) calcd for $C_{17}H_{17}BrNaO_2^+$ m/z $[M+Na]^+$: 355.0304, found 355.0301.




2-methylallyl 2-bromobenzoate (**13-Br**)

Colorless oil, obtained from the condensation of 2-bromobenzoic acid (CAS: 88-65-3) and methallyl alcohol (CAS: 513-42-8).

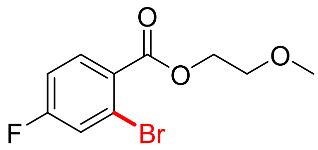
$^1$H NMR (600 MHz, $CDCl_3$) δ 7.85 – 7.80 (m, 1H), 7.70 – 7.65 (m, 1H), 7.41 – 7.31 m, 2H), 5.11 (s, 1H), 5.00 (s, 1H), 4.76 (s, 2H), 1.86 (s, 3H).

$^{13}$C NMR (151 MHz, $CDCl_3$) δ 166.02, 139.69, 134.55, 132.75, 132.28, 131.53, 127.32, 121.88, 113.91, 69.08, 19.89.

IR (KBr, cm$^{-1}$): 2981, 2898, 1732, 1650, 1455, 1299, 1251, 1048, 879, 745.

GC-MS (EI): 256.0, 254.0, 185.0, 183.0, 157.0, 155.0, 104.0, 76.1, 50.1.

HRMS (ESI) calcd for $C_{11}H_{12}BrO_2^+$ m/z $[M+H]^+$: 255.0015, found 255.0017.



2-methoxyethyl 2-bromo-4-fluorobenzoate (**14-Br**)

Colorless oil, obtained from the condensation of 2-bromo-4-fluorobenzoic acid (CAS: 1006-41-3) and 2-methoxyethanol (CAS: 109-86-4).

$^1$H NMR (600 MHz, $CDCl_3$) δ 7.90 (ddd, *J* = 8.7, 6.0, 1.1 Hz, 1H), 7.40 (ddd, *J* = 8.2, 2.6, 1.1 Hz, 1H), 7.07 (tdd, *J* = 8.7, 2.6, 1.1 Hz, 1H), 4.52 – 4.43 (m, 2H), 3.77 – 3.69 (m, 2H), 3.42 (s, 3H).

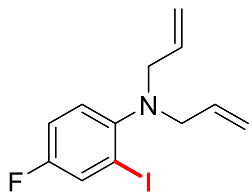
$^{13}$C NMR (151 MHz, $CDCl_3$) δ 165.19, 164.00 (d, *J* = 257.3 Hz), 133.67 (d, *J* = 9.4 Hz), 127.99 (d, *J* = 3.4 Hz), 123.37 (d, *J* = 9.9 Hz), 122.01 (d, *J* = 24.7 Hz), 114.65 (d, *J* = 21.4 Hz), 70.41, 64.71, 59.18.

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -105.71.

IR (KBr, cm$^{-1}$): 2982, 2930, 2895, 2820, 1735, 1595, 1490, 1288, 1253, 1117, 1041, 869, 770, 608.

GC-MS (EI): 220.0, 218.0, 203.0, 201.0, 175.0, 173.0, 122.1, 94.1, 58.1.

HRMS (ESI) calcd for $C_{10}H_{11}BrFO_3^+$ m/z [M+H]$^+$: 276.9870, found 276.9866.



N,N-diallyl-4-fluoro-2-iodoaniline (**29-I**)

Light yellow oil, obtained from the reaction between 4-fluoro-2-iodoaniline (CAS: 61272-76-2) and allyl bromide (CAS: 106-95-6).

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.57 (ddd, *J* = 7.9, 2.9, 1.2 Hz, 1H), 7.04 – 6.93 (m, 2H), 5.90 – 5.72 (m, 2H), 5.20 – 5.05 (m, 4H), 3.56 (dd, *J* = 6.3, 1.5 Hz, 4H).

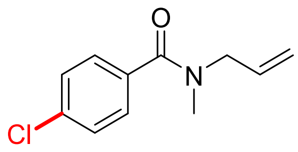
$^{13}$C NMR (151 MHz, $CDCl_3$) δ 158.91 (d, *J* = 247.8 Hz), 148.08 (d, *J* = 3.0 Hz), 134.76, 126.42 (d, *J* = 24.1 Hz), 124.56 (d, *J* = 8.3 Hz), 118.07, 115.33 (d, *J* = 21.5 Hz), 100.70 (d, *J* = 8.2 Hz), 56.74.

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -117.57.

IR (KBr, cm$^{-1}$): 3076, 3012, 2977, 2925, 2815, 1592, 1575, 1480, 1267, 1191, 990, 865, 813, 748.

GC-MS (EI): 317.0, 290.0, 248.0, 221.0, 190.2, 176.1, 148.1.

HRMS (ESI) calcd for $C_{12}H_{14}FIN^+$ m/z $[M+H]^+$: 318.0149, found 318.0149.




N-allyl-4-chloro-N-methylbenzamide (**35-Cl**)

Colorless oil, obtained from the condensation of 4-chlorobenzoyl chloride (CAS: 122-01-0) and N-allylmethylamine (CAS: 627-37-2).

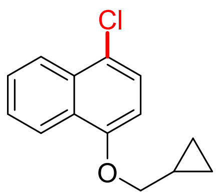
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.31 (m, 4H), 5.95 – 5.64 (m, 1H), 5.30 – 5.13 (m, 2H), 4.20 – 3.72 (m, 2H), 3.10 – 2.79 (m, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 171.15, 170.30, 135.77, 134.65, 132.86, 132.53, 128.72, 128.26, 118.01, 117.67, 53.99, 50.17, 37.01, 33.29.

IR (KBr, $cm^{-1}$): 3081, 2978, 2925, 1631, 1400, 1262, 1090, 1022, 840, 758.

GC-MS (EI): 211.1, 209.1, 196.0, 194.0, 141.0, 139.0, 111.0, 75.0.

HRMS (ESI) calcd for $C_{11}H_{13}ClNO^+$ m/z $[M+H]^+$: 210.0680, found 210.0682.




1-chloro-4-(cyclopropylmethoxy)naphthalene (**36-Cl**)

Colorless oil, obtained from the reaction between 4-chloro-1-naphthol (CAS: 604-44-4) and cyclopropylmethyl bromide (CAS: 7051-34-5).

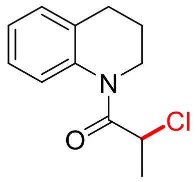
$^1$H NMR (400 MHz, $CDCl_3$) δ 8.40 (dd, $J$ = 8.4, 1.4 Hz, 1H), 8.27 – 8.19 (m, 1H), 7.63 (ddd, $J$ = 8.4, 6.8, 1.4 Hz, 1H), 7.56 (ddd, $J$ = 8.2, 6.8, 1.3 Hz, 1H), 7.44 (d, $J$ = 8.2 Hz, 1H), 6.67 (d, $J$ = 8.2 Hz, 1H), 3.97 (d, $J$ = 6.7 Hz, 2H), 1.49 – 1.34 (m, 1H), 0.75 – 0.68 (m, 2H), 0.50 – 0.42 (m, 2H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 154.11, 131.44, 127.54, 126.94, 125.93, 125.90, 124.27, 123.10, 122.78, 104.96, 73.12, 10.34, 3.30.

IR (KBr, $cm^{-1}$): 3080, 3008, 2919, 2870, 1507, 1458, 1380, 1262, 1240, 1079, 805, 762, 660.

GC-MS (EI): 234.1, 232.1, 180.0, 178.0, 151.0, 149.0, 115.0, 55.1.

HRMS (ESI) calcd for $C_{14}H_{14}ClO^+$ m/z $[M+H]^+$: 233.0728, found 233.0735.



(S)-2-chloro-1-(3,4-dihydroquinolin-1(2H)-yl)propan-1-one (**38-Cl**)

Colorless oil, obtained from the condensation of 1,2,3,4-tetrahydroquinoline (CAS: 635-46-1) and 2-chloropropionyl chloride (CAS: 7623-09-8).

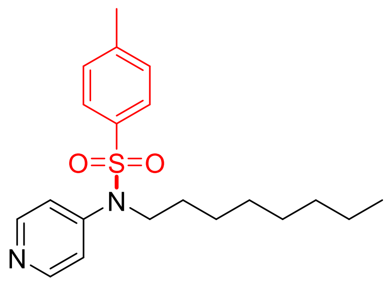
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.04 (m, 4H), 4.89 (q, *J* = 6.5 Hz, 1H), 3.94 (dt, *J* = 13.2, 6.7 Hz, 1H), 3.70 (dt, *J* = 13.0, 6.6 Hz, 1H), 2.87 – 2.58 (m, 2H), 2.16 – 1.87 (m, 2H), 1.66 (d, *J* = 6.5 Hz, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 169.58, 138.57, 134.55, 128.84, 126.72, 126.33, 123.82, 50.64, 43.41, 26.62, 23.99, 21.80.

IR (KBr, $cm^{-1}$): 2951, 2879, 2850, 1670, 1489, 1395, 1201, 1069, 767, 655.

GC-MS (EI): 225.2, 223.2, 188.2, 160.2, 132.2, 117.1, 77.1.

HRMS (ESI) calcd for $C_{12}H_{15}ClNO^{+}$ m/z $[M+H]^{+}$: 224.0837, found 224.0835.



4-methyl-N-octyl-N-(pyridin-4-yl)benzenesulfonamide (**49-Ts**)

Light yellow oil, obtained from the condensation of N-octylpyridin-4-amine (CAS: 64690-19-3) and *p*-toluenesulfonyl chloride (CAS: 98-59-9).

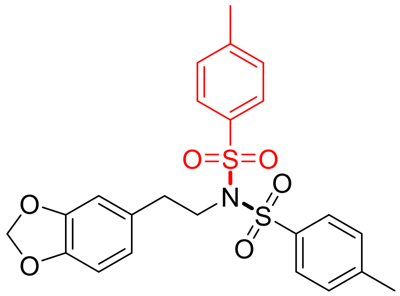
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.55 – 8.46 (m, 2H), 7.47 – 7.41 (m, 2H), 7.25 – 7.20 (m, 2H), 7.10 – 7.04 (m, 2H), 3.58 (t, *J* = 7.2 Hz, 2H), 2.39 (s, 3H), 1.50 – 1.39 (m, 2H), 1.32 – 1.14 (m, 10H), 0.84 (t, *J* = 6.8 Hz, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 150.77, 147.28, 144.09, 134.98, 129.75, 127.50, 121.09, 49.02, 31.77, 29.17, 29.05, 28.06, 26.47, 22.68, 21.63, 14.15.

IR (KBr, $cm^{-1}$): 3025, 2955, 2928, 2857, 1581, 1496, 1356, 1170, 1089, 995, 902, 726, 658, 575, 549.

GC-MS (EI): 360.2, 296.1, 261.1, 205.2, 155.0, 107.1, 91.1, 78.0, 65.0.

HRMS (ESI) calcd for $C_{20}H_{29}N_2O_2S^+$ m/z $[M+H]^+$: 361.1944, found 361.1949.



N-(2-(benzo[d][1,3]dioxol-5-yl)ethyl)-4-methyl-N-tosylbenzenesulfonamide (**51-Ts**)

Light yellow solid, obtained from the condensation of 3,4-methylenedioxyphenethylamine (CAS: 1484-85-1) and *p*-toluenesulfonyl chloride (CAS: 98-59-9).

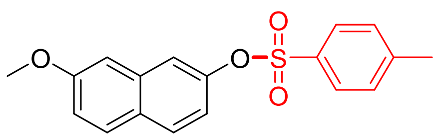
$^1$H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.84 (m, 4H), 7.40 – 7.29 (m, 4H), 6.76 – 6.59 (m, 3H), 5.93 (s, 2H), 3.83 – 3.73 (m, 2H), 2.94 – 2.83 (m, 2H), 2.45 (s, 6H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 148.01, 146.65, 145.19, 137.25, 131.53, 129.95, 128.45, 122.14, 109.52, 108.68, 101.19, 50.76, 36.59, 21.92.

IR (KBr, $cm^{-1}$): 2970, 2922, 2875, 2841, 1542, 1509, 1375, 1249, 1165, 1086, 856, 810, 741, 667, 551.

GC-MS (EI): 473.1, 338.0, 155.0, 148.1, 135.0, 91.1, 77.0, 65.0.

HRMS (ESI) calcd for $C_{23}H_{23}NNaO_6S_2^+$ m/z $[M+Na]^+$: 496.0859, found 496.0866.



7-methoxynaphthalen-2-yl 4-methylbenzenesulfonate (**54-Ts**)

Colorless crystal, obtained from the condensation of 7-methoxy-2-naphthol (CAS: 5060-82-2) and *p*-toluenesulfonyl chloride (CAS: 98-59-9).

$^{1}H$ NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.71 (m, 2H), 7.69 (d, $J$ = 9.0 Hz, 1H), 7.64 (d, $J$ = 8.9 Hz, 1H), 7.42 (d, $J$ = 2.4 Hz, 1H), 7.29 (d, $J$ = 7.8 Hz, 2H), 7.13 (dd, $J$ = 8.9, 2.5 Hz, 1H), 7.03 (d, $J$ = 2.5 Hz, 1H), 6.90 (dd, $J$ = 8.9, 2.4 Hz, 1H), 3.90 (s, 3H), 2.44 (s, 3H).

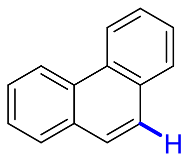
$^{13}C$ NMR (101 MHz, $CDCl_3$) δ 158.51, 148.00, 145.43, 135.05, 132.66, 129.88, 129.50, 129.34, 128.67, 127.48, 119.45, 119.05, 118.69, 105.90, 55.49, 21.84.

IR (KBr, $cm^{-1}$): 2962, 1630, 1518, 1470, 1372, 1252, 1176, 1129, 1095, 886, 851, 738.

GC-MS (EI): 328.0, 281.0, 236.1, 207.0, 173.0, 145.1, 102.0, 91.1.

HRMS (ESI) calcd for $C_{18}H_{17}O_4S^+$ m/z $[M+H]^+$: 329.0842, found 329.0843.

## 2.2 Characterization data for the products




phenanthrene (**1-H**) [36]

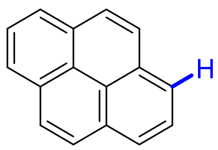
White solid.

68.4 mg, 96% yield (from 0.4 mmol **1-Br**, 16 $mA/cm^2$, 12 h, 4.0 equiv $Et_3N$, DMSO/EtOH)

1.397 g, 98% yield (from 8.0 mmol **1-Br**, 16 $mA/cm^2$, 72 h, 4.0 equiv $Et_3N$, DMSO/EtOH)

$^{1}H$ NMR (600 MHz, $CDCl_3$) δ 8.79 – 8.69 (m, 2H), 8.00 – 7.90 (m, 2H), 7.83 – 7.76 (m, 2H), 7.75 – 7.61 (m, 4H).

$^{13}C$ NMR (151 MHz, $CDCl_3$) δ 132.16, 130.42, 128.70, 127.05, 126.69, 122.79.



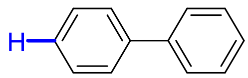

pyrene (**2-H**) [36]

Light yellow solid.

74.4 mg, 92% yield (from 0.4 mmol **2-Br**, 16 $mA/cm^2$, 12 h, 4.0 equiv $Et_3N$, DMSO/EtOH)

$^{1}H$ NMR (400 MHz, $CDCl_3$) δ 8.20 (d, $J$ = 7.6 Hz, 4H), 8.09 (s, 4H), 8.05 – 7.99 (m, 2H).

$^{13}C$ NMR (101 MHz, $CDCl_3$) δ 131.30, 127.53, 125.99, 125.08, 124.83.




1,1'-biphenyl (**3-H**) [37]

White solid.

50.6 mg, 82% yield (from 0.4 mmol **3-Br**, 24 mA/cm$^2$, 24 h, 12.0 equiv $Et_3N$, DMSO/EtOH)

53.7 mg, 87% yield (from 0.4 mmol **3-Br**, 16 mA/cm$^2$, 4 h, 4.0 equiv $Et_3N$, DMSO)

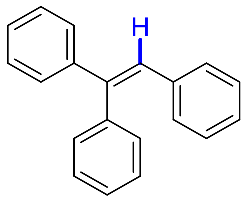
56.7 mg, 92% yield (from 0.4 mmol **3-I**, 16 mA/cm$^2$, 12 h, 4.0 equiv $Et_3N$, DMSO/EtOH)

54.9 mg, 89% yield (from 0.4 mmol **3-I**, 16 mA/cm$^2$, 4 h, 4.0 equiv $Et_3N$, DMSO)

56.1 mg, 91% yield (from 0.4 mmol **3-Cl**, 16 mA/cm$^2$, 8 h, 4.0 equiv $Et_3N$, DMSO)

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.61 (m, 4H), 7.52 – 7.44 (m, 4H), 7.43 – 7.35 (m, 2H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 141.40, 128.89, 127.39, 127.31.



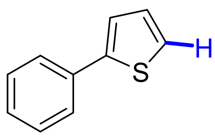

ethene-1,1,2-triyltribenzene (**4-H**) [38]

White solid.

100.4 mg, 98% yield (from 0.4 mmol **4-Br**, 16 mA/cm$^2$, 18 h, 8.0 equiv $Et_3N$, DMSO/EtOH)

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.23 (m, 8H), 7.23 – 7.17 (m, 2H), 7.16 – 7.06 (m, 3H), 7.05 – 6.99 (m, 2H), 6.96 (s, 1H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 143.59, 142.76, 140.53, 137.54, 130.54, 129.70, 128.77, 128.35, 128.32, 128.11, 127.76, 127.65, 127.55, 126.89.



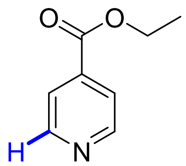

2-phenylthiophene (**5-H**) [37]

White solid.

57.7 mg, 90% yield (from 0.4 mmol **5-Br**, 24 mA/cm$^2$, 18 h, 12.0 equiv $Et_3N$, DMSO/EtOH)

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 2H), 7.42 – 7.36 (m, 2H), 7.34 – 7.26 (m, 3H), 7.09 (dd, $J$ = 5.1, 3.6 Hz, 1H).

$^{13}$C NMR (151 MHz, $CDCl_3$) δ 144.56, 134.53, 129.02, 128.14, 127.60, 126.09, 124.94, 123.21.



ethyl isonicotinate (**6-H**) [39]

Light yellow oil.

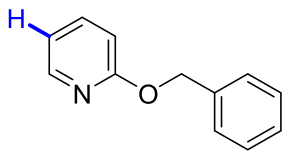
43.5 mg, 72% yield (from 0.4 mmol **6-Br**, 8 mA/cm$^2$, 8 h, 4.0 equiv $Et_3N$, DMSO/EtOH)

21.2 mg, 35% yield (from 0.4 mmol **6-Br**, 8 mA/cm$^2$, 4 h, 4.0 equiv $Et_3N$, DMSO)

35.7 mg, 59% yield (from 0.4 mmol **6-Cl**, 8 mA/cm$^2$, 12 h, 4.0 equiv $Et_3N$, DMSO/EtOH)

$^1$H NMR (600 MHz, $CDCl_3$) δ 8.75 (d, $J$ = 5.0 Hz, 2H), 7.88 – 7.76 (m, 2H), 4.39 (q, $J$ = 7.1 Hz, 2H), 1.38 (t, $J$ = 7.1 Hz, 3H).

$^{13}$C NMR (151 MHz, $CDCl_3$) δ 165.19, 150.65, 137.69, 122.92, 61.90, 14.28.



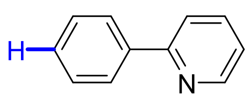
2-(benzyloxy)pyridine (**7-H**) [40]

Colorless oil.

68.1 mg, 92% yield (from 0.4 mmol **7-Br**, 16 mA/cm$^2$, 20 h, 8.0 equiv $Et_3N$, DMSO/EtOH)

$^1$H NMR (400 MHz, $CDCl_3$) δ 8.19 (ddd, $J$ = 5.0, 2.1, 0.9 Hz, 1H), 7.59 (ddd, $J$ = 8.4, 7.1, 2.0 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.42 – 7.36 (m, 2H), 7.35 – 7.29 (m, 1H), 6.89 (ddd, $J$ = 7.1, 5.1, 1.0 Hz, 1H), 6.82 (dt, $J$ = 8.4, 1.0 Hz, 1H), 5.39 (s, 2H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 163.76, 146.97, 138.76, 137.49, 128.60, 128.09, 127.95, 117.05, 111.47, 67.65.



2-phenylpyridine (**8-H**) [37]

Colorless oil.

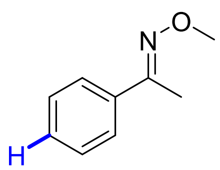
57.7 mg, 93% yield (from 0.4 mmol **8-Br**, 16 mA/cm$^2$, 12 h, 4.0 equiv $Et_3N$, DMSO/EtOH)

55.3 mg, 89% yield (from 0.4 mmol **8-CN**, 8 mA/cm$^2$, 12 h, 4.0 equiv $Et_3N$, DMSO/EtOH)

56.5 mg, 91% yield (from 0.4 mmol **8-CN**, 8 mA/cm$^2$, 3 h, 4.0 equiv $Et_3N$, DMSO)

$^1$H NMR (600 MHz, $CDCl_3$) δ 8.70 (d, *J* = 4.7 Hz, 1H), 8.00 (d, *J* = 7.6 Hz, 2H), 7.78 – 7.69 (m, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.23 (t, *J* = 5.6 Hz, 1H).

$^{13}$C NMR (151 MHz, $CDCl_3$) δ 157.58, 149.80, 139.52, 136.85, 129.06, 128.86, 127.02, 122.21, 120.68.



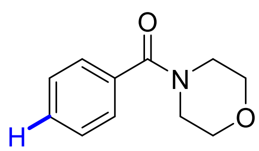

(E)-1-phenylethan-1-one O-methyl oxime (**9-H**) [1]

Colorless oil.

48.4 mg, 81% yield (from 0.4 mmol **9-Br**, 16 mA/cm$^2$, 20 h, 8.0 equiv $Et_3N$, DMSO/EtOH)

$^1$H NMR (600 MHz, $CDCl_3$) δ 7.69 – 7.62 (m, 2H), 7.41 – 7.35 (m, 3H), 4.01 (s, 3H), 2.24 (s, 3H).

$^{13}$C NMR (151 MHz, $CDCl_3$) δ 154.80, 136.76, 129.15, 128.53, 126.16, 62.04, 12.79.




morpholino(phenyl)methanone (**10-H**) [41]

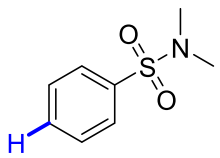
Colorless oil.

65.0 mg, 85% yield (from 0.4 mmol **10-Br**, 24 mA/cm$^2$, 24 h, 12.0 equiv $Et_3N$, DMSO/EtOH)

61.2 mg, 80% yield (from 0.4 mmol **10-Br**, 16 mA/cm$^2$, 8 h, 4.0 equiv $Et_3N$, DMSO)

$^1$H NMR (600 MHz, $CDCl_3$) δ 7.50 – 7.34 (m, 5H), 3.89 – 3.57 (m, 6H), 3.55 – 3.32 (m, 2H).

$^{13}$C NMR (151 MHz, $CDCl_3$) δ 170.46, 135.34, 129.92, 128.60, 127.12, 66.92, 48.25, 42.58.




N,N-dimethylbenzenesulfonamide (**11-H**) [5]

White solid.

63.7 mg, 86% yield (from 0.4 mmol **11-Br**, 16 mA/cm$^2$, 24 h, 8.0 equiv $Et_3N$, DMSO/EtOH)

14.1 mg, 19% yield (from 0.4 mmol **11-Br**, 16 mA/cm$^2$, 8 h, 4.0 equiv $Et_3N$, DMSO)

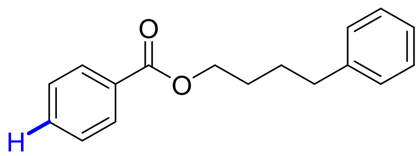
65.9 mg, 89% yield (from 0.4 mmol **11-I**, 16 mA/cm$^2$, 8 h, 4.0 equiv $Et_3N$, DMSO/EtOH)

25.9 mg, 35% yield (from 0.4 mmol **11-I**, 16 mA/cm$^2$, 4 h, 4.0 equiv $Et_3N$, DMSO)

62.2 mg, 84% yield (from 0.4 mmol **11-Cl**, 24 mA/cm$^2$, 20 h, 12.0 equiv $Et_3N$, DMSO/EtOH)

$^1$H NMR (600 MHz, $CDCl_3$) δ 7.80 – 7.74 (m, 2H), 7.62 – 7.58 (m, 1H), 7.57 – 7.51 (m, 2H), 2.69 (s, 6H).

$^{13}$C NMR (151 MHz, $CDCl_3$) δ 135.47, 132.82, 129.12, 127.81, 38.04.



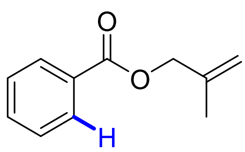

4-phenylbutyl benzoate (**12-H**) [42]

Colorless oil.

80.4 mg, 79% yield (from 0.4 mmol **12-Br**, 16 mA/cm$^2$, 12 h, 4.0 equiv $Et_3N$, DMSO/EtOH)

$^1$H NMR (600 MHz, $CDCl_3$) δ 8.05 (d, $J$ = 7.7 Hz, 2H), 7.59 – 7.54 (m, 1H), 7.48 – 7.42 (m, 2H), 7.33 – 7.28 (m, 2H), 7.24 – 7.17 (m, 3H), 4.35 (t, $J$ = 5.6 Hz, 2H), 2.70 (t, $J$ = 6.9 Hz, 2H), 1.88 – 1.75 (m, 4H).

$^{13}$C NMR (151 MHz, $CDCl_3$) δ 166.79, 142.16, 132.98, 130.54, 129.67, 128.55, 128.50, 128.47, 125.99, 64.97, 35.62, 28.46, 27.96.



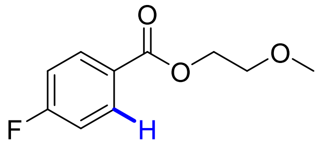

2-methylallyl benzoate (**13-H**) [43]

Colorless oil.

49.3 mg, 70% yield (from 0.4 mmol **13-Br**, 16 mA/cm$^2$, 12 h, 4.0 equiv $Et_3N$, DMSO/EtOH)

$^1$H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.03 (m, 2H), 7.60 – 7.53 (m, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 5.08 (s, 1H), 4.99 (s, 1H), 4.75 (s, 2H), 1.84 (s, 3H).

$^{13}$C NMR (151 MHz, $CDCl_3$) δ 166.41, 140.14, 133.14, 130.32, 129.77, 128.53, 113.09, 68.28, 19.74.



2-methoxyethyl 4-fluorobenzoate (**14-H**)

Colorless oil.

57.9 mg, 73% yield (from 0.4 mmol **14-Br**, 16 mA/cm$^2$, 12 h, 4.0 equiv $Et_3N$, DMSO/EtOH)

$^1$H NMR (600 MHz, $CDCl_3$) δ 8.14 – 8.04 (m, 2H), 7.16 – 7.05 (m, 2H), 4.51 – 4.42 (m, 2H), 3.77 – 3.68 (m, 2H), 3.42 (s, 3H).

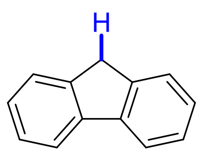
$^{13}$C NMR (151 MHz, $CDCl_3$) δ 165.93 (d, *J* = 253.7 Hz), 165.77, 132.40 (d, *J* = 9.3 Hz), 126.42 (d, *J* = 2.9 Hz), 115.62 (d, *J* = 21.9 Hz). 70.66, 64.28, 59.20.

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -105.67.

IR (KBr, cm$^{-1}$): 2980, 2931, 2895, 2825, 1734, 1598, 1482, 1265, 1117, 1040, 845, 771, 650.

GC-MS (EI): 168.1, 140.0, 123.1, 95.1, 75.1, 58.1.

HRMS (ESI) calcd for $C_{10}H_{12}FO_3^+$ m/z $[M+H]^+$: 199.0765, found: 199.0761.



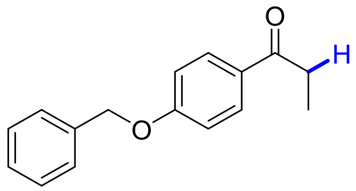
9H-fluorene (**15-H**) [44]

White solid.

63.2 mg, 95% yield (from 0.4 mmol **15-Br**, 8 mA/cm$^2$, 4 h, 4.0 equiv $Et_3N$, DMSO/EtOH)

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.83 (dt, *J* = 7.7, 1.0 Hz, 2H), 7.58 (dt, *J* = 7.4, 1.1 Hz, 2H), 7.45 – 7.38 (m, 2H), 7.38 – 7.30 (m, 2H), 3.93 (s, 2H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 143.35, 141.85, 126.85, 126.83, 125.15, 120.00, 37.04.




1-(4-(benzyloxy)phenyl)propan-1-one (**16-H**) [45]

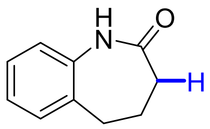
White solid.

83.6 mg, 87% yield (from 0.4 mmol **16-Br**, 8 mA/cm$^2$, 4 h, 4.0 equiv $Et_3N$, DMSO/EtOH)

69.2 mg, 72% yield (from 0.4 mmol **16-Br**, 8 mA/cm$^2$, 3 h, 4.0 equiv $Et_3N$, DMSO)

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.92 (m, 2H), 7.49 – 7.30 (m, 5H), 7.04 – 6.97 (m, 2H), 5.13 (s, 2H), 2.95 (q, *J* = 7.3 Hz, 2H), 1.22 (t, *J* = 7.3 Hz, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 199.58, 162.59, 136.39, 130.39, 130.36, 128.82, 128.35, 127.59, 114.67, 70.25, 31.54, 8.56.



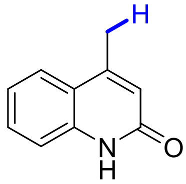

1,3,4,5-tetrahydro-2H-benzo[b]azepin-2-one (**17-H**) [46]

White solid.

62.5 mg, 97% yield (from 0.4 mmol **17-Br**, 8 mA/cm$^2$, 12 h, 4.0 equiv $Et_3N$, DMSO/EtOH)

$^1$H NMR (600 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.25 – 7.20 (m, 2H), 7.13 (td, *J* = 7.5, 1.3 Hz, 1H), 7.00 (dd, *J* = 7.8, 1.3 Hz, 1H), 2.80 (t, *J* = 7.3 Hz, 2H), 2.36 (t, *J* = 7.3 Hz, 2H), 2.24 (p, *J* = 7.3 Hz, 2H).

$^{13}$C NMR (151 MHz, $CDCl_3$) δ 175.52, 137.99, 134.43, 129.97, 127.59, 125.79, 121.95, 32.88, 30.45, 28.64.



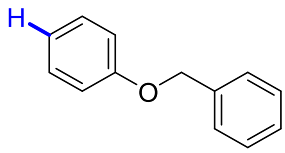

4-methylquinolin-2(1H)-one (**18-H**) [47]

White solid.

60.5 mg, 95% yield (from 0.4 mmol **18-Br**, 8 mA/cm$^2$, 4 h, 4.0 equiv $Et_3N$, DMSO/EtOH)

$^1$H NMR (600 MHz, $CDCl_3$) δ 12.65 (br, 1H), 7.71 – 7.66 (m, 1H), 7.53 – 7.44 (m, 2H), 7.26 – 7.21 (m, 1H), 6.60 (s, 1H), 2.52 (s, 3H).

$^{13}$C NMR (151 MHz, $CDCl_3$) δ 164.62, 149.38, 138.44, 130.59, 124.48, 122.58, 120.66, 120.61, 116.80, 19.28.




(benzyloxy)benzene (**19-H**) [9]

White solid.

63.4 mg, 86% yield (from 0.4 mmol **19-Br**, 16 mA/cm$^2$, 6 h, 4.0 equiv $Et_3N$, DMSO)

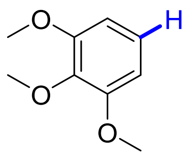
65.6 mg, 89% yield (from 0.4 mmol **19-I**, 16 mA/cm$^2$, 18 h, 8.0 equiv $Et_3N$, DMSO/EtOH)

62.6 mg, 85% yield (from 0.4 mmol **19-I**, 16 mA/cm$^2$, 4 h, 4.0 equiv $Et_3N$, DMSO)

59.7 mg, 81% yield (from 0.4 mmol **19-Cl**, 16 mA/cm$^2$, 8 h, 4.0 equiv $Et_3N$, DMSO)

$^1$H NMR (600 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 2H), 7.45 – 7.40 (m, 2H), 7.39 – 7.30 (m, 3H), 7.07 – 6.96 (m, 3H), 5.10 (s, 2H).

$^{13}$C NMR (151 MHz, $CDCl_3$) δ 158.90, 137.18, 129.61, 128.71, 128.06, 127.61, 121.05, 114.95, 70.00.



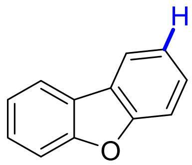

1,2,3-trimethoxybenzene (**20-H**) [36]

Colorless solid.

60.6 mg, 90% yield (from 0.4 mmol **20-Br**, 16 mA/cm$^2$, 6 h, 4.0 equiv $Et_3N$, DMSO)

$^1$H NMR (400 MHz, $CDCl_3$) δ 6.98 (t, $J$ = 8.4 Hz, 1H), 6.58 (d, $J$ = 8.4 Hz, 2H), 3.86 (s, 6H), 3.85 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 153.64, 138.23, 123.75, 105.32, 60.92, 56.16.



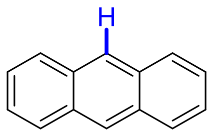
dibenzo[b,d]furan (**21-H**) [44]

White solid.

63.2 mg, 94% yield (from 0.4 mmol **21-Br**, 16 mA/cm$^2$, 4 h, 4.0 equiv $Et_3N$, DMSO)

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.98 (dt, *J* = 7.6, 1.0 Hz, 2H), 7.61 (dt, *J* = 8.2, 0.9 Hz, 2H), 7.49 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 2H), 7.37 (td, *J* = 7.5, 1.0 Hz, 2H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 156.30, 127.25, 124.34, 122.80, 120.77, 111.79.



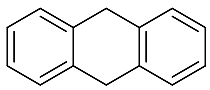
anthracene (**22-H**) [36]

Light yellow solid.

41.3 mg, 58% yield (from 0.4 mmol **22-Br**, 8 mA/cm$^2$, 10 h, 4.0 equiv $Et_3N$, DMSO/EtOH)

$^1$H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 2H), 8.06 – 7.99 (m, 4H), 7.52 – 7.44 (m, 4H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 131.82, 128.30, 126.35, 125.47.



9,10-dihydroanthracene (**22-H'**) [44]

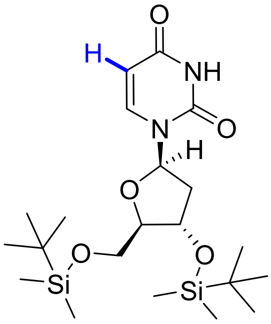
White solid.

14.4 mg, 20% yield (from 0.4 mmol **22-Br**, 8 mA/cm$^2$, 10 h, 4.0 equiv $Et_3N$, DMSO/EtOH)

46.9 mg, 65% yield (from 0.4 mmol **22-Br**, 8 mA/cm$^2$, 4 h, 4.0 equiv $Et_3N$, DMSO)

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 4H), 7.25 – 7.18 (m, 4H), 3.97 (s, 4H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 136.76, 127.46, 126.16, 36.24.




1-((2R,4S,5R)-4-((tert-butyldimethylsilyl)oxy)-5-(((tert-butyldimethylsilyl)oxy)methyl)tetrahydrofuran-2-yl)pyrimidine-2,4(1H,3H)-dione (**23-H**)

Light yellow solid.

102.3 mg, 56% yield (from 0.4 mmol **23-Br**, 16 mA/cm$^2$, 24 h, 8.0 equiv $Et_3N$, DMSO/EtOH)

63.9 mg, 35% yield (from 0.4 mmol **23-Br**, 16 mA/cm$^2$, 12 h, 4.0 equiv $Et_3N$, DMSO)

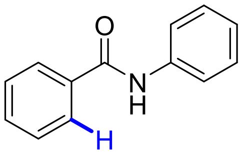
$^1$H NMR (600 MHz, $CDCl_3$) δ 9.38 (br, 1H), 7.89 (dt, *J* = 8.2, 1.4 Hz, 1H), 6.28 (t, *J* = 6.2 Hz, 1H), 5.68 (d, *J* = 8.1 Hz, 1H), 4.47 – 4.34 (m, 1H), 3.93 – 3.85 (m, 2H), 3.77 – 3.72 (m, 1H), 2.31 (dt, *J* = 12.8, 5.3 Hz, 1H), 2.05 (dt, *J* = 12.9, 6.2 Hz, 1H), 0.90 (s, 9H), 0.87 (s, 9H), 0.09 (s, 6H), 0.06 (s, 6H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 163.41, 150.32, 140.35, 102.28, 87.89, 85.32, 71.29, 62.53, 41.98, 26.00, 25.85, 18.48, 18.11, -4.49, -4.74, -5.38, -5.45.

IR (KBr, cm$^{-1}$): 2958, 2928, 2857, 1701, 1470, 1389, 1254, 1120, 839, 775.

GC-MS (EI): 399.1, 369.2, 355.1, 287.1, 267.1, 155.1, 89.0, 73.0, 59.0.

HRMS (ESI) calcd for $C_{21}H_{40}N_2NaO_5Si_2^+$ m/z [M+Na]$^+$: 479.2368, found 479.2366.




N-phenylbenzamide (**24-H**, **58-Bz**) [44]

White solid.

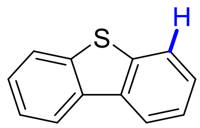
71.0 mg, 90% yield (from 0.4 mmol **24-I**, 16 mA/cm$^2$, 18 h, 8.0 equiv $Et_3N$, DMSO/EtOH)

61.5 mg, 78% yield (from 0.4 mmol **24-I**, 16 mA/cm$^2$, 5 h, 4.0 equiv $Et_3N$, DMSO)

63.1 mg, 80% yield (from 0.4 mmol **58-Ts-Bz**, 16 mA/cm$^2$, 4 h, 4.0 equiv $Et_3N$, DMSO)

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.79 (m, 3H), 7.69 – 7.62 (m, 2H), 7.58 – 7.51 (m, 1H), 7.51 – 7.43 (m, 2H), 7.40 – 7.33 (m, 2H), 7.19 – 7.12 (m, 1H).

$^{13}C$ NMR (101 MHz, $CDCl_3$) δ 165.92, 138.09, 135.17, 131.97, 129.23, 128.92, 127.17, 124.72, 120.39.



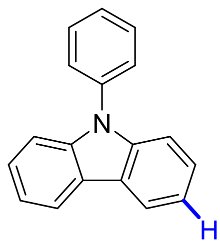
dibenzo[b,d]thiophene (**25-H**) [48]

White solid.

70.7 mg, 96% yield (from 0.4 mmol **25-I**, 16 mA/cm$^2$, 12 h, 4.0 equiv $Et_3N$, DMSO/EtOH)

$^1H$ NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.13 (m, 2H), 7.92 – 7.82 (m, 2H), 7.52 – 7.42 (m, 4H).

$^{13}C$ NMR (151 MHz, $CDCl_3$) δ 139.53, 135.65, 126.82, 124.47, 122.93, 121.70.



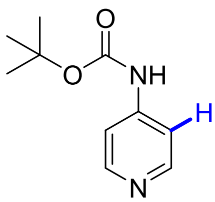
9-phenyl-9H-carbazole (**26-H**) [49]

Light yellow solid.

75.9 mg, 78% yield (from 0.4 mmol **26-I**, 24 mA/cm$^2$, 20 h, 12.0 equiv $Et_3N$, DMSO/EtOH)

$^1H$ NMR (600 MHz, $CDCl_3$) δ 8.19 (d, $J$ = 7.8 Hz, 2H), 7.67 – 7.57 (m, 4H), 7.51 – 7.47 (m, 1H), 7.47 – 7.40 (m, 4H), 7.36 – 7.29 (m, 2H).

$^{13}C$ NMR (151 MHz, $CDCl_3$) δ 141.00, 137.82, 129.99, 127.57, 127.26, 126.04, 123.45, 120.43, 120.02, 109.89.



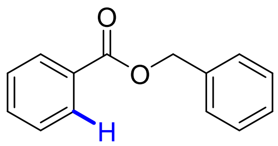
tert-butyl pyridin-4-ylcarbamate (**27-H**) [50]

White solid.

66.8 mg, 86% yield (from 0.4 mmol **27-I**, 16 mA/cm$^2$, 10 h, 4.0 equiv $Et_3N$, DMSO/EtOH)

$^{1}H$ NMR (600 MHz, $CDCl_3$) δ 8.47 – 8.35 (m, 2H), 8.06 (br, 1H), 7.42 – 7.31 (m, 2H), 1.48 (s, 9H).

$^{13}C$ NMR (151 MHz, $CDCl_3$) δ 152.46, 150.20, 146.50, 112.57, 81.45, 28.31.



benzyl benzoate (**28-H**) [9]

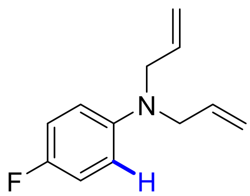
Colorless oil.

64.5 mg, 76% yield (from 0.4 mmol **28-I**, 16 mA/cm$^2$, 12 h, 4.0 equiv $Et_3N$, DMSO/EtOH)

28.9 mg, 34% yield (from 0.4 mmol **28-I**, 16 mA/cm$^2$, 4 h, 4.0 equiv $Et_3N$, DMSO)

$^{1}H$ NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.06 (m, 2H), 7.60 – 7.53 (m, 1H), 7.49 – 7.32 (m, 7H), 5.38 (s, 2H).

$^{13}C$ NMR (101 MHz, $CDCl_3$) δ 166.56, 136.22, 133.15, 130.30, 129.84, 128.73, 128.50, 128.37, 128.29, 66.80.



N,N-diallyl-4-fluoroaniline (**29-H**) [51]

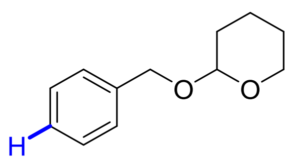
Colorless oil.

47.4 mg, 62% yield (from 0.4 mmol **29-I**, 16 mA/cm$^2$, 18 h, 8.0 equiv $Et_3N$, DMSO/EtOH)

$^{1}H$ NMR (400 MHz, $CDCl_3$) δ 6.97 – 6.83 (m, 2H), 6.69 – 6.56 (m, 2H), 5.94 – 5.74 (m, 2H), 5.26 – 5.08 (m, 4H), 3.97 – 3.80 (m, 4H).

$^{13}C$ NMR (151 MHz, $CDCl_3$) δ 145.48, 134.12, 116.29, 115.58, 115.43, 113.65, 53.52.

$^{19}F$ NMR (376 MHz, $CDCl_3$) δ -129.54.



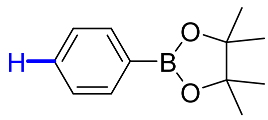
2-(benzyloxy)tetrahydro-2H-pyran (**30-H**) [52]

Colorless oil.

65.4 mg, 85% yield (from 0.4 mmol **30-I**, 16 mA/cm$^2$, 20 h, 8.0 equiv $Et_3N$, DMSO/EtOH)

$^1$H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.33 (m, 4H), 7.31 – 7.27 (m, 1H), 4.80 (dd, *J* = 12.0, 1.8 Hz, 1H), 4.75 – 4.69 (m, 1H), 4.51 (dd, *J* = 12.1, 1.9 Hz, 1H), 3.99 – 3.89 (m, 1H), 3.60 – 3.52 (m, 1H), 1.93 – 1.83 (m, 1H), 1.79 – 1.71 (m, 1H), 1.70 – 1.50 (m, 4H).

$^{13}$C NMR (151 MHz, $CDCl_3$) δ 138.41, 128.49, 127.94, 127.63, 97.84, 68.93, 62.24, 30.69, 25.61, 19.48.



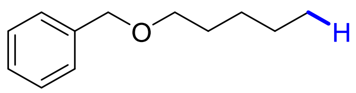
4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (**31-H**) [53]

Colorless oil.

64.5 mg, 79% yield (from 0.4 mmol **31-I**, 16 mA/cm$^2$, 12 h, 4.0 equiv $Et_3N$, DMSO)

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.79 (m, 2H), 7.50 – 7.43 (m, 1H), 7.41 – 7.34 (m, 2H), 1.36 (s, 12H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 134.88, 131.39, 127.84, 83.91, 25.01.



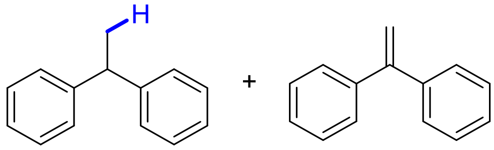
((pentyloxy)methyl)benzene (**32-H**) [54]

Colorless oil.

40.7 mg, 57% yield (from 0.4 mmol **32-I**, 16 mA/cm$^2$, 24 h, 8.0 equiv $Et_3N$, DMSO/EtOH)

$^1$H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 4H), 7.30 – 7.26 (m, 1H), 4.51 (s, 2H), 3.51 – 3.44 (m, 2H), 1.67 – 1.59 (m, 2H), 1.39 – 1.29 (m, 4H), 0.90 (t, *J* = 6.8 Hz, 3H).

$^{13}$C NMR (151 MHz, $CDCl_3$) δ 138.85, 128.48, 127.76, 127.60, 72.99, 70.67, 29.61, 28.51, 22.69, 14.20.



ethane-1,1-diyldibenzene (**33-H**) [55] + ethene-1,1-diyldibenzene (**33-H'**) [55]

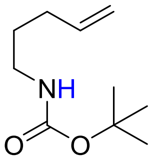
Colorless oil, inseparable mixture.

51.4 mg in total (0.45 : 1 by $^1$H NMR), 23% and 48% respective yield (from 0.4 mmol **33-I**, 16 mA/cm$^2$, 16 h, 8.0 equiv $Et_3N$, DMSO/EtOH)

45.7 mg in total (3.92 : 1 by $^1$H NMR), 50% and 13% respective yield (from 0.4 mmol **33-I**, 16 mA/cm$^2$, 3 h, 4.0 equiv $Et_3N$, DMSO)

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.03 (m, 14.5H), 5.46 (s, 2H), 4.20 – 4.10 (m, 0.45H), 1.67 – 1.62 (m, 1.35H) (**Method A**).

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.12 (m, 49.2H), 5.46 (s, 2H), 4.15 (q, *J* = 7.3 Hz, 3.92H), 1.64 (d, *J* = 7.2 Hz, 11.76H) (**Method B**).



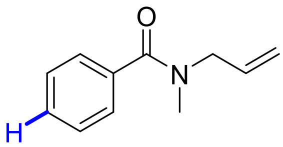

tert-butyl pent-4-en-1-ylcarbamate (**34-H**) [56]

Colorless oil.

40.0 mg, 54% yield (from 0.4 mmol **34-I**, 24 mA/cm$^2$, 18 h, 12.0 equiv $Et_3N$, DMSO/EtOH)

$^1$H NMR (600 MHz, $CDCl_3$) δ 5.84 – 5.73 (m, 1H), 5.02 (dt, *J* = 17.0, 1.8 Hz, 1H), 4.96 (d, *J* = 10.2 Hz, 1H), 4.55 (s, 1H), 3.12 (q, *J* = 6.8 Hz, 2H), 2.07 (q, *J* = 7.2 Hz, 2H), 1.60 – 1.52 (m, 2H), 1.43 (s, 9H).

$^{13}$C NMR (151 MHz, $CDCl_3$) δ 156.07, 137.98, 115.21, 79.18, 40.19, 31.11, 29.33, 28.54.



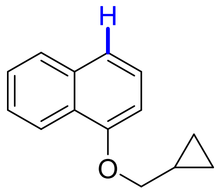

N-allyl-N-methylbenzamide (**35-H**)[41]

Colorless oil.

36.5 mg, 52% yield (from 0.4 mmol **35-Cl**, 16 mA/cm$^2$, 12 h, 4.0 equiv $Et_3N$, DMSO)

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.32 (m, 5H), 6.01 – 5.62 (m, 1H), 5.32 – 5.12 (m, 2H), 4.25 – 3.75 (m, 2H), 3.15 – 2.79 (m, 3H).

$^{13}C$ NMR (101 MHz, $CDCl_3$) δ 172.29, 136.40, 133.18, 132.83, 129.71, 128.48, 127.13, 126.74, 117.62, 54.09, 50.09, 37.07, 33.14.



1-(cyclopropylmethoxy)naphthalene (**36-H**)

Colorless oil.

11.9 mg, 15% yield (from 0.4 mmol **36-Cl**, 16 mA/cm$^2$, 12 h, 4.0 equiv $Et_3N$, DMSO/EtOH)

67.4 mg, 85% yield (from 0.4 mmol **36-Cl**, 16 mA/cm$^2$, 6 h, 4.0 equiv $Et_3N$, DMSO)

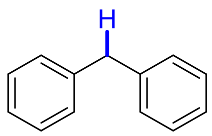
$^1H$ NMR (400 MHz, $CDCl_3$) δ 8.42 – 8.32 (m, 1H), 7.85 – 7.77 (m, 1H), 7.54 – 7.46 (m, 2H), 7.46 – 7.41 (m, 1H), 7.40 – 7.34 (m, 1H), 6.83 – 6.76 (m, 1H), 4.01 (d, $J$ = 6.7 Hz, 2H), 1.42 (dddd, $J$ = 13.1, 8.0, 6.7, 2.6 Hz, 1H), 0.75 – 0.67 (m, 2H), 0.50 – 0.42 (m, 2H).

$^{13}C$ NMR (101 MHz, $CDCl_3$) δ 155.00, 134.66, 127.54, 126.47, 126.01, 125.97, 125.20, 122.36, 120.22, 104.99, 72.89, 10.47, 3.28.

IR (KBr, cm$^{-1}$): 3075, 3000, 2921, 2869, 1510, 1457, 1396, 1269, 1235, 1096, 795, 770.

GC-MS (EI): 198.1, 181.0, 144.0, 127.1, 115.1, 89.0, 55.1.

HRMS (ESI) calcd for $C_{14}H_{15}O^+$ m/z $[M+H]^+$: 199.1117, found 199.1119.



diphenylmethane (**37-H**) [57]

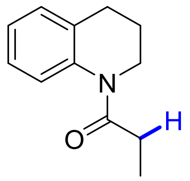
Colorless oil.

59.9 mg, 89% yield (from 0.4 mmol **37-Cl**, 16 mA/cm$^2$, 12 h, 4.0 equiv $Et_3N$, DMSO/EtOH)

61.9 mg, 92% yield (from 0.4 mmol **37-Cl**, 16 mA/cm$^2$, 3 h, 4.0 equiv $Et_3N$, DMSO)

$^1H$ NMR (600 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 4H), 7.25 – 7.18 (m, 6H), 4.00 (s, 2H).

$^{13}C$ NMR (151 MHz, $CDCl_3$) δ 141.25, 129.07, 128.59, 126.20, 42.07.



1-(3,4-dihydroquinolin-1(2H)-yl)propan-1-one (**38-H**)

Colorless oil.

74.2 mg, 98% yield (from 0.4 mmol **38-Cl**, 16 mA/cm$^2$, 18 h, 8.0 equiv $Et_3N$, DMSO/EtOH)

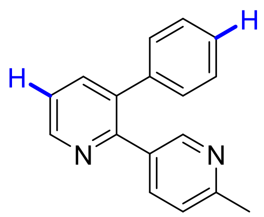
$^1$H NMR (600 MHz, $CDCl_3$) δ 7.38 – 6.95 (m, 4H), 3.78 (t, $J$ = 6.6 Hz, 2H), 2.71 (t, $J$ = 6.7 Hz, 2H), 2.51 (q, $J$ = 7.4 Hz, 2H), 1.95 (p, $J$ = 6.7 Hz, 2H), 1.15 (t, $J$ = 7.4 Hz, 3H).

$^{13}$C NMR (151 MHz, $CDCl_3$) δ 173.83, 139.31, 128.55, 126.12, 125.22, 124.72, 43.10, 27.99, 26.94, 24.23, 10.22.

IR (KBr, cm$^{-1}$): 2978, 2933, 2875, 2845, 1656, 1490, 1384, 1292, 1200, 1062, 769.

GC-MS (EI): 189.2, 160.2, 133.1, 117.1, 77.1, 57.1.

HRMS (ESI) calcd for $C_{12}H_{16}NO^+$ m/z $[M+H]^+$: 190.1226, found 190.1227.



6'-methyl-3-phenyl-2,3'-bipyridine (**39-H**)

Yellow oil.

41.4 mg, 42% yield (from 0.4 mmol **39-Cl**, 16 mA/cm$^2$, 7 h, 4.0 equiv $Et_3N$, DMSO)

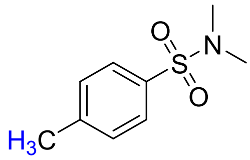
$^1$H NMR (400 MHz, $CDCl_3$) δ 8.70 (dd, $J$ = 4.8, 1.7 Hz, 1H), 8.48 – 8.44 (m, 1H), 7.73 (dd, $J$ = 7.7, 1.7 Hz, 1H), 7.58 (dd, $J$ = 8.0, 2.4 Hz, 1H), 7.35 (dd, $J$ = 7.7, 4.8 Hz, 1H), 7.32 – 7.26 (m, 3H), 7.20 – 7.15 (m, 2H), 7.03 (d, $J$ = 8.0 Hz, 1H), 2.52 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 157.59, 154.29, 150.15, 148.75, 139.42, 138.73, 137.52, 136.54, 133.05, 129.59, 128.72, 127.71, 122.56, 122.45, 24.28.

IR (KBr, cm$^{-1}$): 2954, 2856, 1599, 1499, 1424, 1375, 1015, 782, 701.

GC-MS (EI): 246.1, 229.1, 203.9, 176.0, 122.8, 101.8, 74.9.

HRMS (ESI) calcd for $C_{17}H_{15}N_2^+$ m/z $[M+H]^+$: 247.1230, found 247.1232.



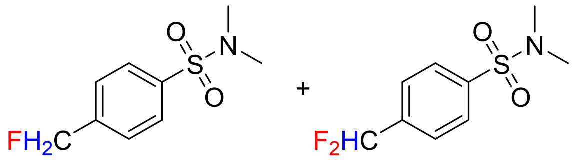
N,N,4-trimethylbenzenesulfonamide (**40-H**) [5]

White solid.

43.8 mg, 55% yield (from 0.4 mmol **40-F**, 16 mA/cm$^2$, 12 h, 4.0 equiv $Et_3N$, DMSO/EtOH)

$^1$H NMR (600 MHz, $CDCl_3$) δ 7.71 – 7.60 (m, 2H), 7.38 – 7.29 (m, 2H), 2.67 (s, 6H), 2.42 (s, 3H).

$^{13}$C NMR (151 MHz, $CDCl_3$) δ 143.59, 132.41, 129.72, 127.87, 38.05, 21.61.



4-(fluoromethyl)-N,N-dimethylbenzenesulfonamide (**40-H'**) +

4-(difluoromethyl)-N,N-dimethylbenzenesulfonamide (**40-H''**)

White solid, inseparable mixture.

30.9 mg in total (4 : 1 by $^1$H NMR), 28% and 7% respective yield (from 0.4 mmol **40-F**, 16 mA/cm$^2$, 12 h, 4.0 equiv $Et_3N$, DMSO/EtOH)

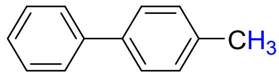
$^1$H NMR (600 MHz, $CDCl_3$) δ 7.87 (d, $J$ = 8.0 Hz, 0.5H), 7.80 (d, $J$ = 7.9 Hz, 2H), 7.69 (d, $J$ = 8.0 Hz, 0.5H), 7.53 (d, $J$ = 7.9 Hz, 2H), 6.72 (t, $J$ = 55.9 Hz, 0.25H), 5.47 (d, $J$ = 47.0 Hz, 2H), 2.72 (s, 1.5H), 2.71 (s, 6H).

$^{13}$C NMR (151 MHz, $CDCl_3$) δ 141.32 (d, $J$ = 17.6 Hz), 138.32 (d, $J$ = 62.5 Hz), 135.68 (d, $J$ = 2.6 Hz), 128.24, 128.16, 127.23 (d, $J$ = 6.8 Hz), 126.53 (t, $J$ = 6.0 Hz), 113.66 (t, $J$ = 240.4 Hz), 83.40 (d, $J$ = 169.5 Hz), 38.03.

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -112.55, -213.91.

GC-MS (EI): 217.1, 199.0, 173.0, 153.0, 142.1, 109.1, 91.0, 83.0, 63.0 (**40-H'**); 235.1, 191.0, 170.1, 152.0, 127.1, 107.0, 101.0, 77.1 (**40-H''**).

HRMS (ESI) calcd for $C_9H_{12}FNNaO_2S^+$ and $C_9H_{11}F_2NNaO_2S^+$ m/z $[M+Na]^+$: 240.0465 and 258.0371, found 240.0463 and 258.0368.




4-methyl-1,1'-biphenyl (**41-H**) [37]

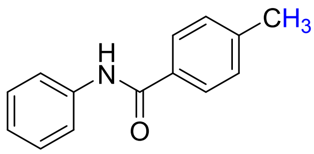
White solid.

6.7 mg, 10% yield (from 0.4 mmol **41-F**, 16 mA/cm$^2$, 12 h, 4.0 equiv $Et_3N$, DMSO/EtOH)

59.9 mg, 89% yield (from 0.4 mmol **41-F**, 16 mA/cm$^2$, 6 h, 4.0 equiv $Et_3N$, DMSO)

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 2H), 7.55 – 7.50 (m, 2H), 7.48 – 7.41 (m, 2H), 7.38 – 7.32 (m, 1H), 7.30 – 7.24 (m, 2H), 2.42 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 141.33, 138.52, 137.15, 129.62, 128.85, 127.14, 127.12, 21.22.




4-methyl-N-phenylbenzamide (**42-H**) [4]

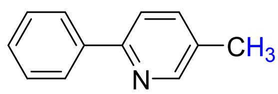
White solid.

62.5 mg, 74% yield (from 0.4 mmol **42-F**, 16 mA/cm$^2$, 18 h, 8.0 equiv $Et_3N$, DMSO/EtOH)

56.6 mg, 67% yield (from 0.4 mmol **42-F**, 16 mA/cm$^2$, 5 h, 4.0 equiv $Et_3N$, DMSO)

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.79 – 7.74 (m, 2H), 7.68 – 7.59 (m, 2H), 7.40 – 7.33 (m, 2H), 7.28 (d, $J$ = 7.9 Hz, 2H), 7.18 – 7.10 (m, 1H), 2.42 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 165.83, 142.53, 138.16, 132.23, 129.58, 129.22, 127.16, 124.58, 120.30, 21.63.



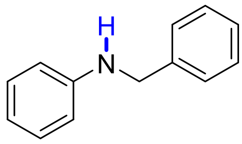

5-methyl-2-phenylpyridine (**43-H**) [20]

Colorless oil.

48.1 mg, 71% yield (from 0.4 mmol **43-F**, 16 mA/cm$^2$, 18 h, 8.0 equiv $Et_3N$, DMSO/EtOH)

$^1$H NMR (600 MHz, $CDCl_3$) δ 8.55 – 8.50 (m, 1H), 8.01 – 7.93 (m, 2H), 7.63 (d, $J$ = 8.0 Hz, 1H), 7.58 – 7.54 (m, 1H), 7.46 (t, $J$ = 7.6 Hz, 2H), 7.42 – 7.37 (m, 1H), 2.37 (s, 3H).

$^{13}$C NMR (151 MHz, $CDCl_3$) δ 154.94, 150.21, 139.55, 137.44, 131.73, 128.83, 128.71, 126.82, 120.19, 18.30.



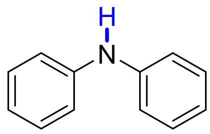
N-benzylaniline (**44-H**) [9]

White solid.

61.6 mg, 84% yield (from 0.4 mmol **44-Ts**, 8 mA/cm$^2$, 10 h, 4.0 equiv $Et_3N$, DMSO)

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.31 (m, 4H), 7.30 – 7.23 (m, 1H), 7.21 – 7.13 (m, 2H), 6.71 (t, $J$ = 7.3 Hz, 1H), 6.67 – 6.60 (m, 2H), 4.33 (s, 2H), 4.02 (s, 1H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 148.30, 139.57, 129.40, 128.77, 127.65, 127.36, 117.71, 112.99, 48.47.



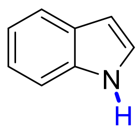
Diphenylamine (**45-H**) [23]

White solid.

50.8 mg, 75% yield (from 0.4 mmol **45-Ts**, 8 mA/cm$^2$, 10 h, 4.0 equiv $Et_3N$, DMSO)

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 4H), 7.14 – 7.07 (m, 4H), 7.02 – 6.92 (m, 2H), 5.72 (s, 1H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 143.24, 129.46, 121.11, 117.93.



1H-indole (**46-H**) [36]

Light yellow solid.

43.6 mg, 93% yield (from 0.4 mmol **46-Ts**, 8 mA/cm$^2$, 9 h, 4.0 equiv $Et_3N$, DMSO)

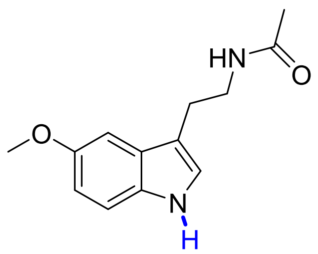
28.1 mg, 60% yield (from 0.4 mmol **46-Ns**, 8 mA/cm$^2$, 6 h, 4.0 equiv $Et_3N$, DMSO)

45.0 mg, 96% yield (from 0.4 mmol **46-Bz**, 8 mA/cm$^2$, 7 h, 4.0 equiv $Et_3N$, DMSO)

17.8 mg, 38% yield (from 0.4 mmol **46-Boc**, 16 mA/cm$^2$, 11 h, 4.0 equiv $Et_3N$, DMSO)

$^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.69 – 7.60 (m, 1H), 7.40 – 7.33 (m, 1H), 7.22 – 7.15 (m, 2H), 7.15 – 7.08 (m, 1H), 6.58 – 6.51 (m, 1H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 135.89, 127.96, 124.26, 122.10, 120.85, 119.93, 111.15, 102.71,.



N-(2-(5-methoxy-1H-indol-3-yl)ethyl)acetamide (**47-H**) [58]

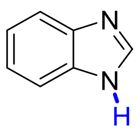
Light yellow solid.

85.5 mg, 92% yield (from 0.4 mmol **47-Ts**, 8 mA/cm$^2$, 10 h, 4.0 equiv $Et_3N$, DMSO)

1.654 g, 89% yield (from 8.0 mmol **47-Ts**, 16 mA/cm$^2$, 52 h, 4.0 equiv $Et_3N$, DMSO)

$^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.29 – 7.21 (m, 1H), 7.05 – 6.96 (m, 2H), 6.90 – 6.82 (m, 1H), 5.67 (s, 1H), 3.85 (s, 3H), 3.58 (q, $J$ = 6.5 Hz, 2H), 2.93 (t, $J$ = 6.8 Hz, 2H), 1.92 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.35, 154.15, 131.71, 127.85, 122.98, 112.68, 112.50, 112.17, 100.59, 56.07, 39.90, 25.38, 23.48.



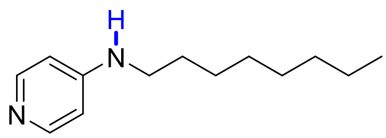
1H-benzo[d]imidazole (**48-H**) [23]

Light yellow solid.

42.5 mg, 90% yield (from 0.4 mmol **48-Ts**, 8 mA/cm$^2$, 8 h, 4.0 equiv $Et_3N$, DMSO)

$^{1}$H NMR (400 MHz, DMSO-$d_6$) δ 12.49 (br, 1H), 8.22 (s, 1H), 7.65 – 7.55 (m, 2H), 7.23 – 7.13 (m, 2H).

$^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 141.86, 138.13, 121.68, 115.32.



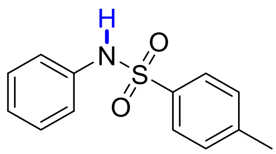
N-octylpyridin-4-amine (**49-H**) [59]

Light yellow solid.

65.2 mg, 79% yield (from 0.4 mmol **49-Ts**, 8 mA/cm$^2$, 9 h, 4.0 equiv $Et_3N$, DMSO)

$^1$H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.09 (m, 2H), 6.44 – 6.35 (m, 2H), 4.34 (s, 1H), 3.10 (td, *J* = 7.2, 5.4 Hz, 2H), 1.59 (p, *J* = 7.2 Hz, 2H), 1.41 – 1.19 (m, 10H), 0.92 – 0.82 (m, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 153.61, 149.98, 107.51, 42.73, 31.87, 29.39, 29.30, 29.21, 27.11, 22.72, 14.17.



4-methyl-N-phenylbenzenesulfonamide (**50-H**, **58-Ts**) [60]

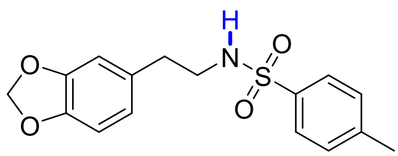
Light yellow solid.

84.1 mg, 85% yield (from 0.4 mmol **50-Ts**, 8 mA/cm$^2$, 16 h, 4.0 equiv $Et_3N$, DMSO)

7.9 mg, 8% yield (from 0.4 mmol **58-Ts-Bz**, 16 mA/cm$^2$, 4 h, 4.0 equiv $Et_3N$, DMSO)

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.64 (m, 2H), 7.25 – 7.19 (m, 4H), 7.16 (s, 1H), 7.11 – 7.05 (m, 3H), 2.36 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 144.00, 136.71, 136.10, 129.77, 129.39, 127.39, 125.31, 121.53, 21.64.



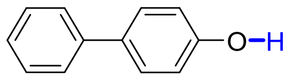
N-(2-(benzo[d][1,3]dioxol-5-yl)ethyl)-4-methylbenzenesulfonamide (**51-H**) [61]

White solid.

115.0 mg, 90% yield (from 0.4 mmol **51-Ts**, 16 mA/cm$^2$, 9 h, 4.0 equiv $Et_3N$, DMSO)

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.66 (m, 2H), 7.32 – 7.26 (m, 2H), 6.72 – 6.66 (m, 1H), 6.55 – 6.48 (m, 2H), 5.91 (s, 2H), 4.48 (t, *J* = 6.3 Hz, 1H), 3.15 (q, *J* = 6.7 Hz, 2H), 2.66 (t, *J* = 6.9 Hz, 2H), 2.42 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 148.00, 146.53, 143.57, 136.98, 131.44, 129.82, 127.21, 121.86, 109.09, 108.55, 101.09, 44.46, 35.59, 21.64.



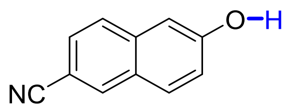

[1,1'-biphenyl]-4-ol (**52-H**) [62]

White solid.

59.9 mg, 85% yield (from 0.4 mmol **52-Ts**, 16 mA/cm$^2$, 6 h, 4.0 equiv $Et_3N$, DMSO)

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.52 (m, 2H), 7.52 – 7.46 (m, 2H), 7.45 – 7.38 (m, 2H), 7.34 – 7.28 (m, 1H), 6.95 – 6.88 (m, 2H), 5.02 (s, 1H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 155.16, 140.83, 134.07, 128.78, 128.45, 126.78, 126.76, 115.71.




6-hydroxy-2-naphthonitrile (**53-H**) [63]

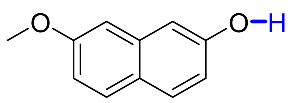
Light grey solid.

63.6 mg, 94% yield (from 0.4 mmol **53-Ts**, 8 mA/cm$^2$, 6 h, 4.0 equiv $Et_3N$, DMSO)

61.6 mg, 91% yield (from 0.4 mmol **53-Tf**, 8 mA/cm$^2$, 9 h, 4.0 equiv $Et_3N$, DMSO)

$^1$H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.13 (m, 1H), 7.81 (d, $J$ = 8.8 Hz, 1H), 7.74 (d, $J$ = 8.5 Hz, 1H), 7.55 (dd, $J$ = 8.5, 1.7 Hz, 1H), 7.25 – 7.17 (m, 2H), 5.44 (s, 1H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 156.24, 136.50, 134.19, 130.77, 127.82, 127.67, 127.26, 119.83, 119.67, 109.96, 106.90.



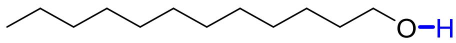

7-methoxynaphthalen-2-ol (**54-H**) [64]

Light yellow solid.

30.0 mg, 43% yield (from 0.4 mmol **54-Ts**, 16 mA/cm$^2$, 10 h, 4.0 equiv $Et_3N$, DMSO)

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.62 (m, 2H), 7.08 – 7.04 (m, 1H), 7.02 – 6.92 (m, 3H), 5.34 (s, 1H), 3.90 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 158.39, 154.16, 136.11, 129.71, 129.42, 124.50, 116.39, 115.35, 108.95, 104.83, 55.41.



dodecan-1-ol (**55-H**) [65]

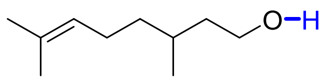
Colorless oil.

71.5 mg, 96% yield (from 0.4 mmol **55-Ts**, 16 mA/cm$^2$, 6 h, 4.0 equiv $Et_3N$, DMSO)

61.9 mg, 83% yield (from 0.4 mmol **55-Bz**, 16 mA/cm$^2$, 6 h, 4.0 equiv $Et_3N$, DMSO)

$^1$H NMR (400 MHz, $CDCl_3$) δ 3.63 (t, $J$ = 6.6 Hz, 2H), 1.67 (br, 1H), 1.60 – 1.50 (m, 2H), 1.38 – 1.19 (m, 18H), 0.90 – 0.84 (m, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 63.24, 32.95, 32.06, 29.80, 29.78, 29.75, 29.58, 29.49, 25.88, 22.83, 14.25.



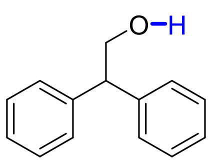
3,7-dimethyloct-6-en-1-ol (**56-H**) [66]

Colorless oil.

54.4 mg, 87% yield (from 0.4 mmol **56-Ts**, 8 mA/cm$^2$, 10 h, 4.0 equiv $Et_3N$, DMSO)

$^1$H NMR (400 MHz, $CDCl_3$) δ 5.15 – 5.02 (m, 1H), 3.74 – 3.59 (m, 2H), 2.07 – 1.88 (m, 2H), 1.70 – 1.65 (m, 3H), 1.64 – 1.50 (m, 5H), 1.46 – 1.28 (m, 3H), 1.23 – 1.11 (m, 1H), 0.90 (d, $J$ = 6.6 Hz, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 131.40, 124.83, 61.31, 40.02, 37.34, 29.29, 25.84, 25.58, 19.64, 17.77.



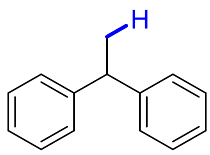
2,2-diphenylethan-1-ol (**57-H**) [65]

Colorless oil.

9.5 mg, 12% yield (from 0.4 mmol **57-Ts**, 16 mA/cm$^2$, 4 h, 4.0 equiv $Et_3N$, DMSO)

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.17 (m, 10H), 4.22 – 4.17 (m, 1H), 4.16 – 4.10 (m, 2H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 141.52, 128.82, 128.43, 126.92, 66.23, 53.75.



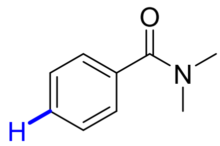
ethane-1,1-diyldibenzene (**57-H'**) [55]

Colorless oil.

48.8 mg, 67% yield (from 0.4 mmol **57-Ts**, 16 mA/cm$^2$, 4 h, 4.0 equiv $Et_3N$, DMSO)

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.15 (m, 10H), 4.15 (q, $J$ = 7.2 Hz, 1H), 1.64 (d, $J$ = 7.2 Hz, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 146.51, 128.49, 127.77, 126.15, 44.92, 22.00.



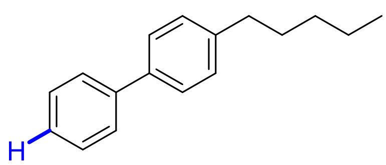
N,N-dimethylbenzamide (**59-H**) [66]

Colorless oil.

41.8 mg, 70% yield (from 0.4 mmol **59-CN**, 8 mA/cm$^2$, 6 h, 4.0 equiv $Et_3N$, DMSO)

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.31 (m, 5H), 3.09 (s, 3H), 2.95 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 171.71, 136.35, 129.55, 128.38, 127.06, 39.61, 35.37.



4-pentyl-1,1'-biphenyl (**60-H**) [67]

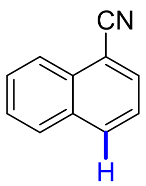
Colorless oil.

55.6 mg, 62% yield (from 0.4 mmol **60-CN**, 16 mA/cm$^2$, 8 h, 4.0 equiv $Et_3N$, DMSO)

0.934 g, 52% yield (from 8.0 mmol **60-CN**, 32 mA/cm$^2$, 8 h, 4.0 equiv $Et_3N$, DMSO)

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.56 (m, 2H), 7.53 – 7.48 (m, 2H), 7.45 – 7.39 (m, 2H), 7.35 – 7.29 (m, 1H), 7.27 – 7.23 (m, 2H), 2.67 – 2.62 (m, 2H), 1.70 – 1.61 (m, 2H), 1.39 – 1.32 (m, 4H), 0.94 – 0.87 (m, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 142.26, 141.35, 138.69, 128.96, 128.91, 128.83, 127.13, 127.08, 35.73, 31.72, 31.33, 22.71, 14.18.



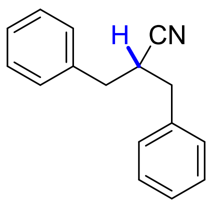
1-naphthonitrile (**61-H**) [68]

White solid.

33.1 mg, 54% yield (from 0.4 mmol **61-CN**, 8 mA/cm$^2$, 6 h, 4.0 equiv $Et_3N$, DMSO)

$^1$H NMR (400 MHz, $CDCl_3$) δ 8.26 – 8.19 (m, 1H), 8.10 – 8.04 (m, 1H), 7.95 – 7.87 (m, 2H), 7.72 – 7.65 (m, 1H), 7.64 – 7.58 (m, 1H), 7.55 – 7.46 (m, 1H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 133.37, 133.00, 132.71, 132.42, 128.75, 128.68, 127.63, 125.21, 125.01, 117.91, 110.25.



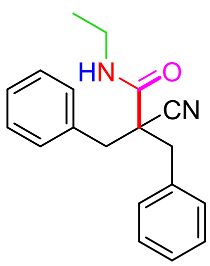
2-benzyl-3-phenylpropanenitrile (**62-H**) [34]

White solid.

17.7 mg, 20% yield (from 0.4 mmol **62-CN**, 8 mA/cm$^2$, 5 h, 4.0 equiv $Et_3N$, DMSO)

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 4H), 7.31 – 7.20 (m, 6H), 3.07 – 2.98 (m, 1H), 2.93 (s, 2H), 2.91 (s, 2H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 136.91, 129.17, 128.93, 127.46, 121.42, 38.11, 36.04.



2-benzyl-2-cyano-N-ethyl-3-phenylpropanamide (**62-H'**)

Colorless oil.

84.2 mg, 72% yield (from 0.4 mmol **62-CN**, 8 mA/cm$^2$, 12 h, 4.0 equiv $Et_3N$, DMSO/EtOH)

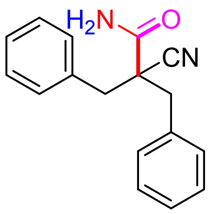
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 11H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.30 (d, *J* = 13.5 Hz, 2H), 3.09 (d, *J* = 13.5 Hz, 2H), 1.42 (t, *J* = 7.2 Hz, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 164.81, 134.51, 130.00, 128.68, 127.95, 119.44, 63.00, 55.90, 42.85, 14.32.

IR (KBr, cm$^{-1}$): 3070, 3031, 2980, 2929, 1740, 1496, 1457, 1228, 1085, 750, 702.

GC-MS (EI): 292.0, 263.1, 246.2, 201.1, 173.1, 91.1, 77.0, 65.0.

HRMS (ESI) calcd for $C_{19}H_{21}N_2O^+$ m/z $[M+H]^+$: 293.1648, found 293.1649.




2-benzyl-2-cyano-3-phenylpropanamide (**62-H''**) [69]

White solid.

10.6 mg, 10% yield (from 0.4 mmol **62-CN**, 8 mA/cm$^2$, 12 h, 4.0 equiv $Et_3N$, DMSO/EtOH)

82.5 mg, 78% yield (from 0.4 mmol **62-CN**, 8 mA/cm$^2$, 5 h, 4.0 equiv $Et_3N$, DMSO)

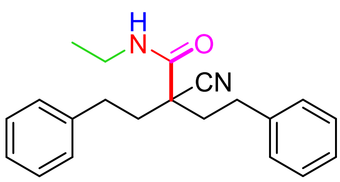
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 10H), 5.75 (s, 1H), 5.55 (s, 1H), 3.38 (d, *J* = 13.4 Hz, 2H), 3.03 (d, *J* = 13.3 Hz, 2H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 168.63, 134.43, 130.25, 128.71, 127.94, 120.26, 53.45, 42.94.

IR (KBr, cm$^{-1}$): 3478, 3352, 3081, 3028, 2923, 1695, 1601, 1497, 1455, 1372, 1250, 769, 702, 599.

GC-MS (EI): 264.1, 218.1, 191.0, 173.1, 156.0, 115.1, 91.1, 65.1.

HRMS (ESI) calcd for $C_{17}H_{16}N_2NaO^+$ m/z $[M+Na]^+$: 287.1155, found 287.1154.



2-cyano-N-ethyl-2-phenethyl-4-phenylbutanamide (**63-H'-Et**)

Light yellow oil.

108.9 mg, 85% yield (from 0.4 mmol **63-CN**, 8 mA/cm$^2$, 6 h, 4.0 equiv $Et_3N$, DMSO/EtOH)

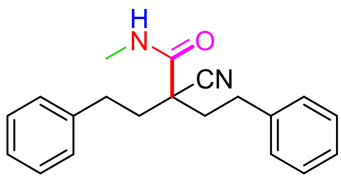
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.87 (br, 1H), 7.34 – 7.28 (m, 4H), 7.25 – 7.15 (m, 6H), 4.24 (q, $J$ = 7.1 Hz, 2H), 2.86 (td, $J$ = 12.8, 5.1 Hz, 2H), 2.63 (td, $J$ = 12.8, 5.0 Hz, 2H), 2.20 (td, $J$ = 12.9, 5.0 Hz, 2H), 2.08 (td, $J$ = 12.9, 5.1 Hz, 2H), 1.36 (t, $J$ = 7.1 Hz, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.01, 140.02, 128.75, 128.48, 126.61, 119.95, 63.17, 52.11, 38.94, 31.91, 14.24.

IR (KBr, cm$^{-1}$): 3331, 3062, 2978, 2930, 2815, 1652, 1500, 1460, 1305, 1102, 856, 751, 699.

GC-MS (EI): 283.0, 274.1, 246.0, 169.1, 158.1, 120.1, 91.1, 77.0.

HRMS (ESI) calcd for $C_{21}H_{25}N_2O^+$ m/z $[M+H]^+$: 321.1961, found 321.1957.




2-cyano-N-methyl-2-phenethyl-4-phenylbutanamide (**63-H'-Me**)

Light yellow oil.

116.4 mg, 95% yield (from 0.4 mmol **63-CN**, 16 mA/cm$^2$, 12 h, 4.0 equiv $Et_3N$, DMSO/MeOH)

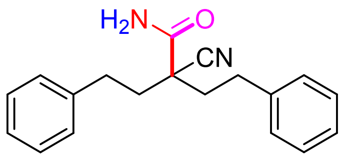
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.90 (br, 1H), 7.33 – 7.25 (m, 4H), 7.23 – 7.11 (m, 6H), 3.76 (s, 3H), 2.84 (td, $J$ = 12.8, 5.1 Hz, 2H), 2.60 (td, $J$ = 12.8, 5.1 Hz, 2H), 2.17 (td, $J$ = 12.9, 12.3, 5.2 Hz, 2H), 2.12 – 2.00 (m, 2H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.53, 139.84, 128.63, 128.39, 126.51, 119.83, 54.45, 51.84, 38.84, 31.79.

IR (KBr, cm$^{-1}$): 3330, 3062, 3027, 2942, 2861, 1653, 1497, 1455, 1300, 1101, 1081, 754, 698.

GC-MS (EI): 274.1, 246.0, 202.1, 169.1, 158.1, 111.1, 91.1, 77.1, 65.1.

HRMS (ESI) calcd for $C_{20}H_{22}N_2NaO^+$ m/z $[M+Na]^+$: 329.1624, found 329.1621.



2-cyano-2-phenethyl-4-phenylbutanamide (**63-H''**)

White solid.

107.6 mg, 92% yield (from 0.4 mmol **63-CN**, 8 mA/cm$^2$, 5 h, 4.0 equiv $Et_3N$, DMSO)

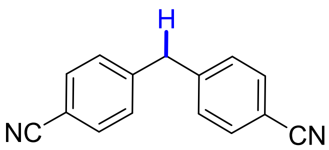
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 4H), 7.23 – 7.15 (m, 6H), 6.50 (s, 1H), 6.44 (s, 1H), 2.86 (td, $J$ = 12.8, 4.8 Hz, 2H), 2.73 (td, $J$ = 12.8, 4.9 Hz, 2H), 2.28 (ddd, $J$ = 13.6, 12.4, 5.0 Hz, 2H), 2.03 (ddd, $J$ = 13.5, 12.4, 4.8 Hz, 2H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 169.66, 139.86, 128.74, 128.59, 128.52, 126.63, 120.92, 49.50, 39.20, 31.88.

IR (KBr, cm$^{-1}$): 3390, 3180, 3069, 3025, 2927, 2862, 1751, 1695, 1544, 1455, 1246, 1044, 759, 696.

GC-MS (EI): 293.1, 188.1, 156.1, 128.0, 117.1, 104.1, 91.1, 77.0.

HRMS (ESI) calcd for $C_{19}H_{20}N_2NaO^+$ m/z $[M+Na]^+$: 315.1468, found 315.1469.



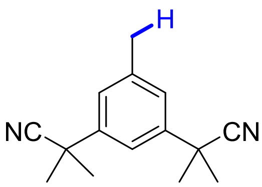
4,4'-methylenedibenzonitrile (**64-H**) [70]

White solid.

48.0 mg, 55% yield (from 0.4 mmol **64-Azo**, 16 mA/cm$^2$, 6 h, 4.0 equiv $Et_3N$, DMSO)

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.56 (m, 4H), 7.31 – 7.23 (m, 4H), 4.10 (s, 2H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 144.93, 132.68, 129.81, 118.77, 110.85, 41.98.



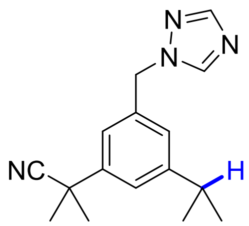
2,2'-(5-methyl-1,3-phenylene)bis(2-methylpropanenitrile) (**65-H**) [71]

White solid.

42.5 mg, 47% yield (from 0.4 mmol **65-Azo**, 16 mA/cm$^2$, 9 h, 4.0 equiv $Et_3N$, DMSO)

$^{1}H$ NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.31 (m, 1H), 7.25 – 7.23 (m, 2H), 2.40 (s, 3H), 1.73 (s, 12H).

$^{13}C$ NMR (126 MHz, $CDCl_3$) δ 142.35, 139.68, 125.61, 124.43, 118.75, 37.32, 29.25, 21.70.




2-(3-((1H-1,2,4-triazol-1-yl)methyl)-5-isopropylphenyl)-2-methylpropanenitrile (**65-H'**)

Brown oil.

27.9 mg, 26% yield (from 0.4 mmol **65-Azo**, 16 mA/$cm^2$, 9 h, 4.0 equiv $Et_3N$, DMSO)

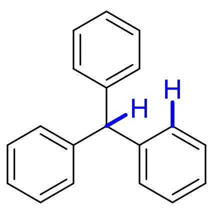
$^{1}H$ NMR (500 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.96 (s, 1H), 7.29 (s, 1H), 7.15 (s, 1H), 7.03 (s, 1H), 5.33 (s, 2H), 2.90 (hept, $J$ = 7.0 Hz, 1H), 1.68 (s, 6H), 1.22 (s, 3H), 1.21 (s, 3H).

$^{13}C$ NMR (126 MHz, $CDCl_3$) δ 152.26, 150.93, 143.22, 142.48, 135.51, 125.56, 124.37, 123.83, 122.20, 53.56, 37.22, 34.24, 29.21, 23.92.

IR (KBr, $cm^{-1}$): 3121, 2965, 2929, 2872, 1605, 1506, 1470, 1369, 1275, 1207, 1139, 1024, 878, 708, 677, 652.

GC-MS (EI): 268.1, 253.1, 241.2, 199.1, 184.1, 156.0, 128.0, 115.0, 91.0.

HRMS (ESI) calcd for $C_{16}H_{21}N_4^+$ m/z $[M+H]^+$: 269.1761, found 269.1764.




triphenylmethane (**66-H**) [72]

White crystal.

79.2 mg, 81% yield (from 0.4 mmol **66-Azo**, 16 mA/$cm^2$, 24 h, 8.0 equiv $Et_3N$, DMSO)

$^{1}H$ NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 6H), 7.23 – 7.16 (m, 3H), 7.14 – 7.08 (m, 6H), 5.54 (s, 1H).

$^{13}C$ NMR (101 MHz, $CDCl_3$) δ 144.07, 129.62, 128.45, 126.45, 57.03.

## 3. Observations, mechanistic studies and other experiments

### 3.1 Results and observations using graphite rod as the cathode

During the condition optimization of **1-Br** (**Method A**), it was found that a graphite rod cathode, either in combination with a Pt or a graphite (C) anode, would degrade after the electrolysis, and the desired reduction product **1-H** could only be afforded in trace amount, along with various overreduction products. The GC-MS analysis results of a typical reaction using Pt | Pt (Fig. S3) and the reaction with C | C electrodes (Fig. S4) are presented below. The retention time of the desired product **1-H** (molecular weight = 178) is around 10.6 min under our GC method.

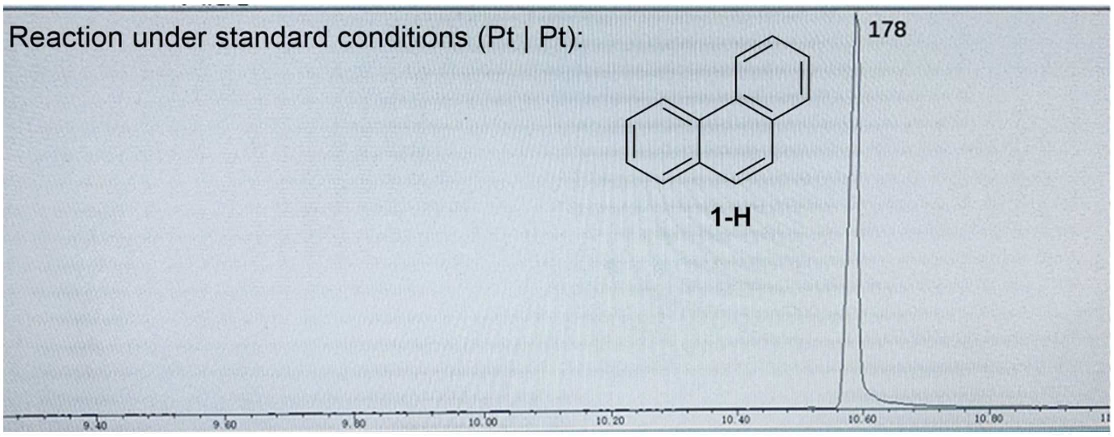



**Fig. S3** Result of GC-MS analysis on a typical reaction system

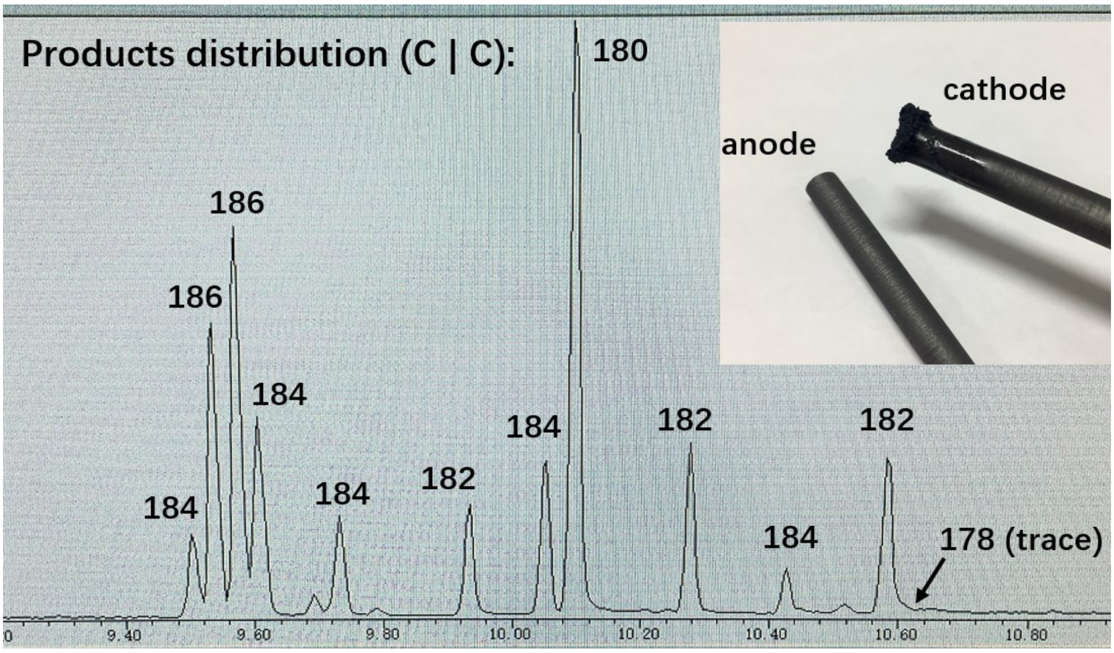
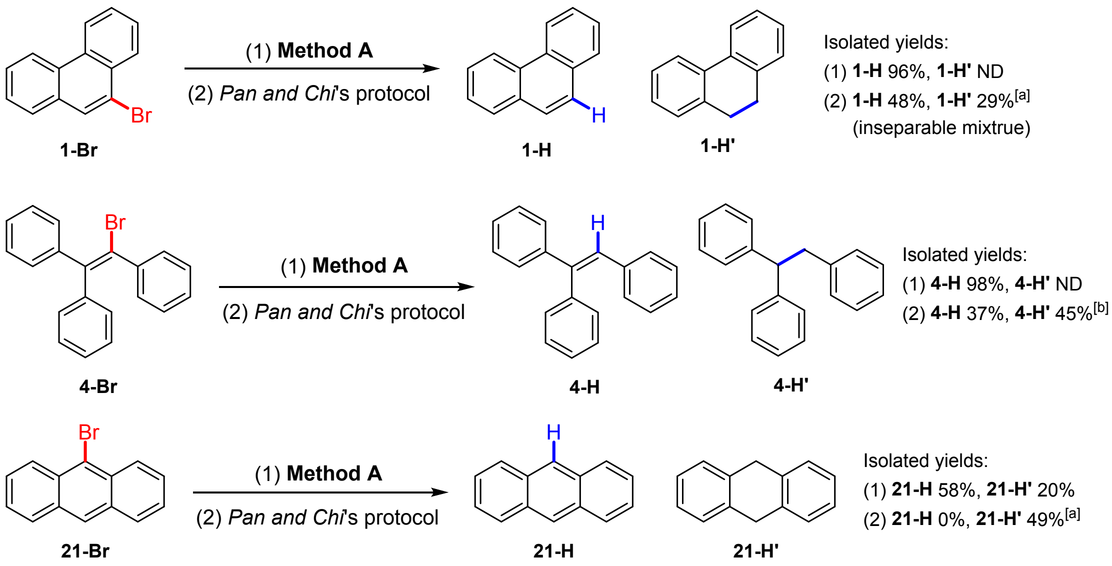


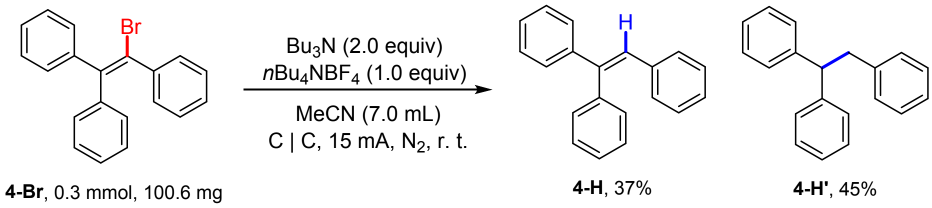

**Fig. S4** Result of GC-MS analysis on a reaction system with graphite electrodes

## 3.2 Comparison of this protocol (Method A) with Pan and Chi's protocol[44]



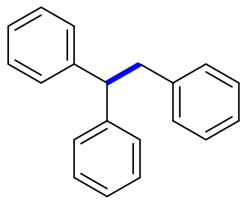

**Scheme S1** Comparison employing certain substrates. [a] Yields as reported in the literature; [b] results produced in our laboratory.

Hydrodebromination of **4-Br** using Pan and Chi's protocol[44]:




To a 25 mL three-necked flask was added the substrate **4-Br** (100.6 mg, 0.3 mmol) and electrolyte *n*$Bu_4NBF_4$ (98.8 mg, 0.3 mmol). Then the flask was equipped with two graphite rod electrodes ($\Phi$ = 6 mm) and flushed with nitrogen, followed by the sequential addition of MeCN (7.0 mL) and tributylamine ($Bu_3N$, 0.14 mL, 0.6 mmol, 2.0 equiv) via syringe. After piercing the septum with a nitrogen-filled balloon to sustain nitrogen atmosphere, the electrolysis was initiated at a constant current of 15 mA at room temperature. The system was electrolyzed for 2.5 h until trace amount of **4-Br** was left as monitored by TLC. Then the reaction mixture was concentrated under reduced pressure and purified by column chromatography on silica gel (eluted with PE) to afford **4-H** as a white solid (28.5 mg, 37%) and **4-H'** as a colorless oil (34.9 mg, 45%).

Characterization data of **4-H'**:



ethane-1,1,2-triyltribenzene (**4-H'**) [73]

Colorless oil, 34.9 mg, 45%.

$^1$H NMR (600 MHz, $CDCl_3$) δ 7.23 (t, *J* = 7.5 Hz, 4H), 7.19 (d, *J* = 7.5 Hz, 4H), 7.17 – 7.12 (m, 4H), 7.11 (d, *J* = 7.1 Hz, 1H), 6.99 (d, *J* = 7.4 Hz, 2H), 4.22 (t, *J* = 7.8 Hz, 1H), 3.35 (d, *J* = 7.8 Hz, 2H).

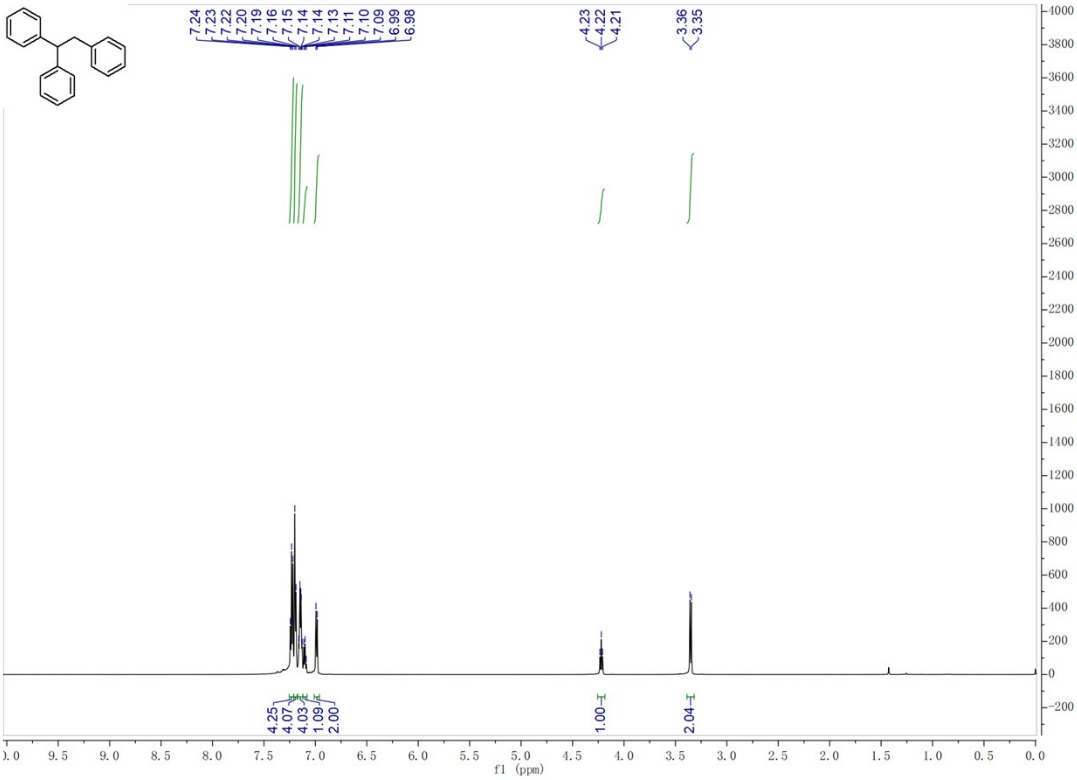
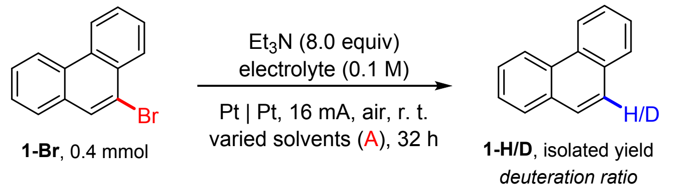


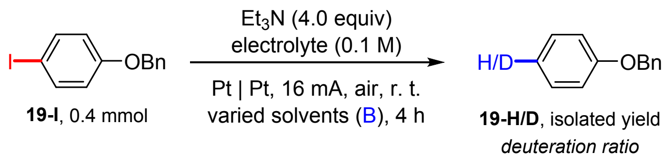
**Fig. S5** NMR spectra of **4-H'** obtained using Pan and Chi's protocol

## 3.3 Deuterium labelling experiments

Deuterium labelling experiments were conducted with **1-Br** and **19-I** under the conditions of **Method A** and **Method B**, respectively (Scheme S2, methanol was used instead of ethanol for availability reason of the *d*-labelled alternatives in **Method A**). The *d*-labelled solvents were purchased from commercial sources and used without further purification: DMSO-$d_6$ (99.8% D), MeOD (99.0% D), MeOH-$d_4$ (99.8% D). And the $^{1}$H NMR spectra of the obtained reduction products **1-H/D** and **19-H/D** are listed as follow (Fig. S5 and S6).

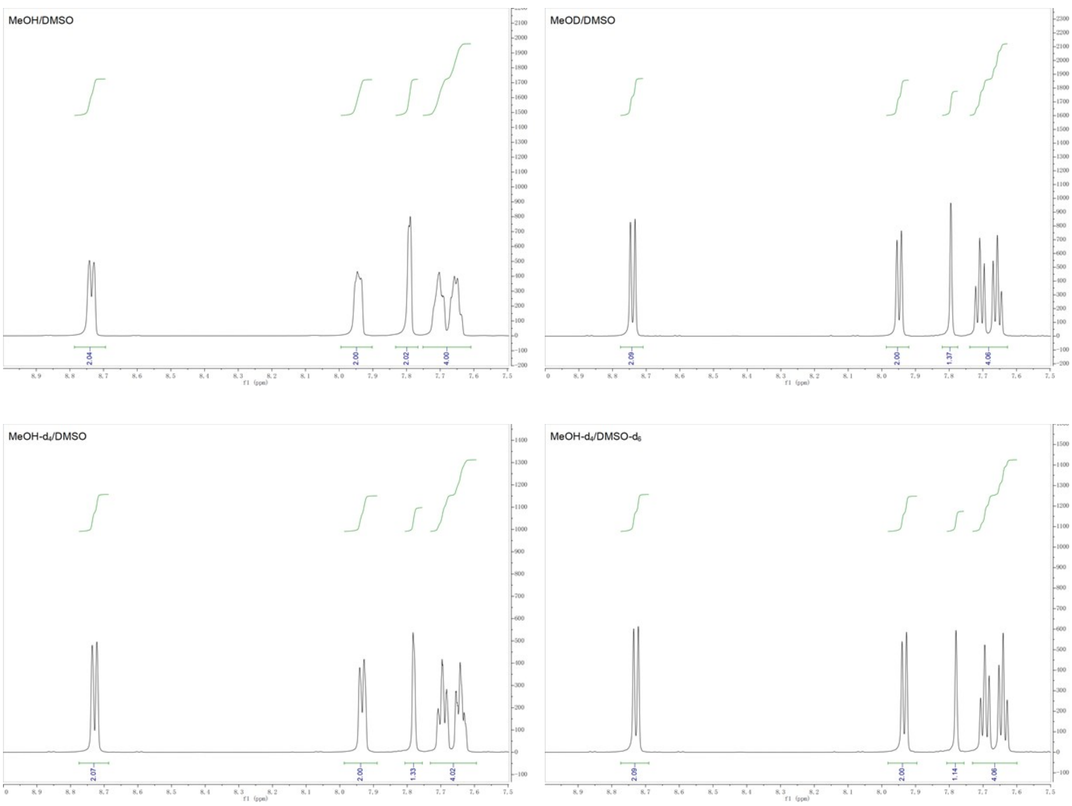



| Entry | Electrolyte/Solvent | Yield of **1-H/D** | D ratio |
|---|---|---|---|
| 1 | $Et_4NClO_4$, DMSO/MeOH = 1:1 | 90% | 0% |
| 2 | $Et_4NClO_4$, DMSO/MeOD = 1:1 | 96% | 63% |
| 3 | $Et_4NClO_4$, DMSO/MeOH-$d_4$ = 1:1 | 95% | 67% |
| 4 | $Et_4NClO_4$, DMSO-$d_6$/MeOH-$d_4$ = 1:1 | 91% | 86% |
| 5 | $LiClO_4$, DMSO-$d_6$/MeOH-$d_4$ = 1:1 | 95% | 86% |




| Entry | Electrolyte/Solvent | Yield of **19-H/D** | D ratio |
|---|---|---|---|
| 6 | $Et_4NClO_4$, DMSO | 85% | 0% |
| 7 | $Et_4NClO_4$, DMSO-$d_6$ | 87% | 80% |
| 8 | $LiClO_4$, DMSO-$d_6$ | low conv. | N/A |

**Scheme S2** Results of deuterium labelling experiments with varied electrolytes/solvents.



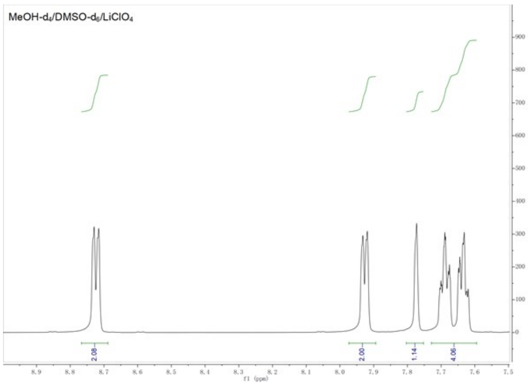



**Fig. S6** $^{1}$H NMR spectra of the products in deuterium labelling experiments (on **1-Br** with **Method A**)

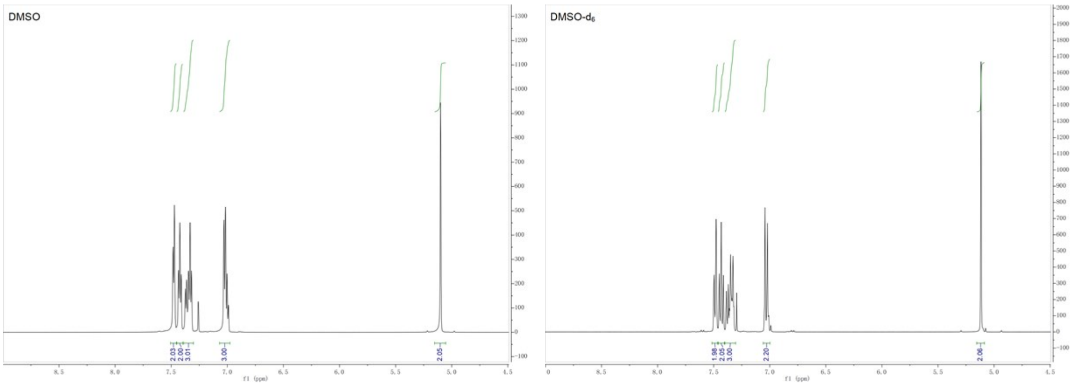



**Fig. S7** $^{1}$H NMR spectra of the products in deuterium labelling experiments (on **19-I** with **Method B**)

## 3.4 Cyclic voltammetry studies

The cyclic voltammogram of $Et_3N$ in DMSO/EtOH was collected with a CHI 760E Potentiostat. The sample was prepared with 0.1 mmol of target molecule, dissolved in 10 mL of 0.1 M $Et_4NClO_4$ in solvent (DMSO or DMSO/EtOH of 1:1 volume ratio). The measurement employed a glassy carbon working electrode, a platinum plate counter electrode and a SCE reference electrode. The scan rate applied was 0.1 V/s. Maximum current ($C_p$) of each compound was obtained using Origin, and the potential ($E_{p/2}$) was determined at half of this value ($C_{p/2}$).

(1) The CV plots of model substrate **1-Br**:

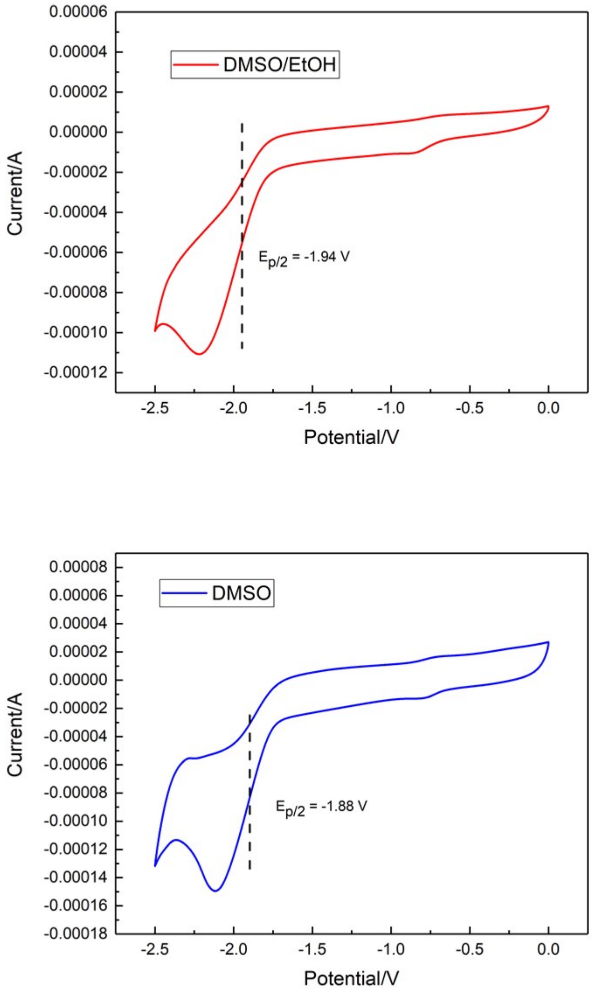
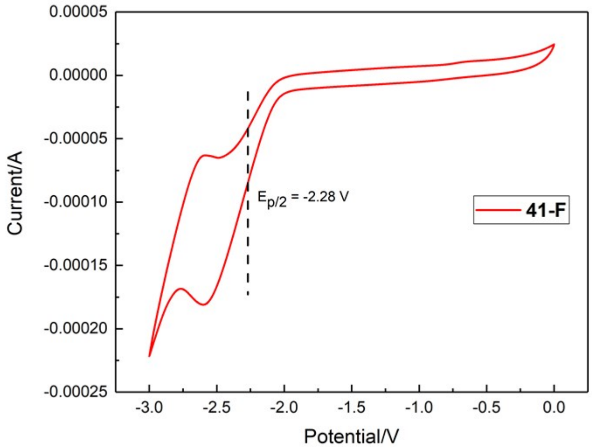



**Fig. S8** CV plot of **1-Br** in 0.1 M $Et_4NClO_4$ DMSO solution

The CV plots of model substrate **1-Br** were recorded in both DMSO/EtOH and DMSO (Fig. S8), and the $E_{p/2}$ values were determined as -1.94 V and -1.88 V, respectively. The value in DMSO/EtOH (for **Method A**) is a bit higher than that in DMSO (for **Method B**), but does not present very significant discrepancy.

(2) CV plots of typical reduction substrates with fewer reports in organic electrosynthesis (**41-F** and **60-CN**):



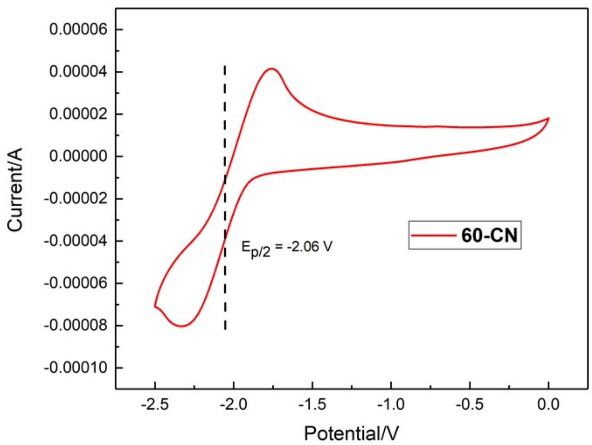




**Fig. S9** CV plots of **41-F** and **60-CN** in 0.1 M $Et_4NClO_4$ DMSO solution

The $E_{p/2}$ values of **41-F** and **60-CN** were determined as -2.28 V and -2.06 V in DMSO, respectively (Fig. S9).

(3) CV plots of substrates employed in competitive reduction (**3-Br** and **3-I**):

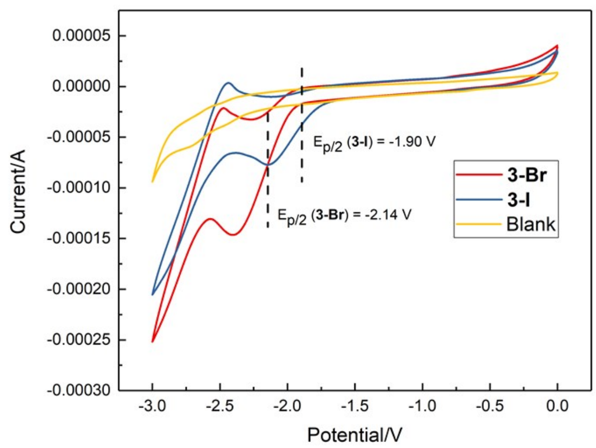



**Fig. S10** CV plots of **3-Br** and **3-I** in 0.1 M $Et_4NClO_4$ DMSO solution

The $E_{p/2}$ values of **3-Br** and **3-I** were determined as -2.14 V and -1.90 V in DMSO, respectively (Fig. S10).

(4) CV plot of additive $Et_3N$:

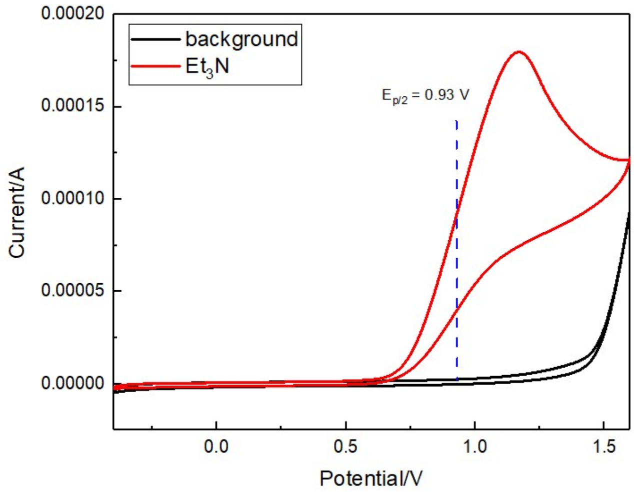


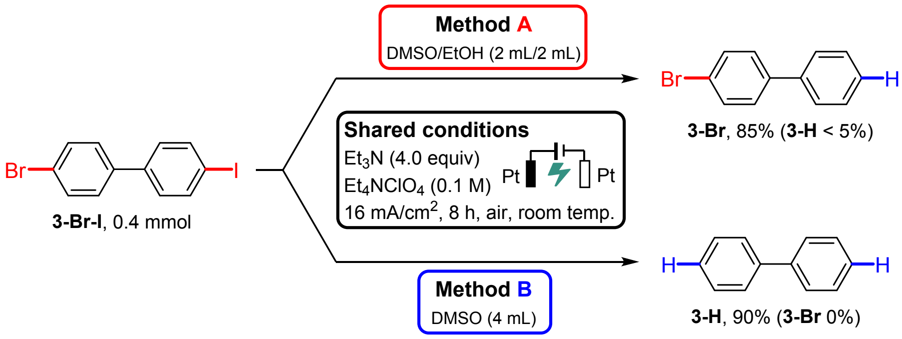

**Fig. S11** CV plot of $Et_3N$ in 0.1 M $Et_4NClO_4$ DMSO/EtOH solution

The CV plot in Fig. S11 shows that $Et_3N$ has an obvious oxidation peak at +1.17 V, and the $E_{p/2}$ value is determined as +0.93 V (vs SCE), which should be the predominant sacrificial reductant in this system compared with another possible reductant DMSO (the "background" line).

## 3.5 Competitive reductions using Method A and B

(1) Reactions of **3-Br-I**

Two parallel reactions of substrate **3-Br-I** were conducted under identical conditions (0.1 M $Et_4NClO_4$, 4.0 equiv of $Et_3N$, 16 mA/cm$^2$, 8 h), except for the different reaction solvents applied (4.0 mL 1:1 DMSO/EtOH for **Method A**; 4.0 mL DMSO for **Method B**). The deiodination-selective product **3-Br** was isolated in 85% yield with **Method A**, while non-selective reduction product **3-H** was afforded in 90% yield with **Method B**.




During the two reactions, the ratios of GC peak area of **3-Br-I**, **3-Br** and **3-H** were monitored and documented every 2 h (Table S2 and S3). And on the basis of these data, two line graphs were drawn (Fig. S12 and S13).

**Table S2** GC ratios of **3-Br-I**, **3-Br** and **3-H** (**Method A**):

| Entry | Reaction time | Ratio of **3-Br-I** | Ratio of **3-Br** | Ratio of **3-H** |
|---|---|---|---|---|
| 1 | 0 h | 1.00 | 0 | 0 |
| 2 | 2 h | 0.64 | 0.36 | < 0.01 |
| 3 | 4 h | 0.35 | 0.65 | < 0.01 |
| 4 | 6 h | 0.16 | 0.83 | 0.01 |
| 5 | 8 h | 0.02 | 0.92 | 0.06 |

**Table S3** GC ratios of **3-Br-I**, **3-Br** and **3-H** (**Method B**):

| Entry | Reaction time | Ratio of **3-Br-I** | Ratio of **3-Br** | Ratio of **3-H** |
|---|---|---|---|---|
| 1 | 0 h | 1.00 | 0 | 0 |
| 2 | 2 h | 0.74 | < 0.01 | 0.26 |
| 3 | 4 h | 0.48 | < 0.01 | 0.52 |
| 4 | 6 h | 0.20 | < 0.01 | 0.80 |
| 5 | 8 h | < 0.01 | < 0.01 | > 0.99 |

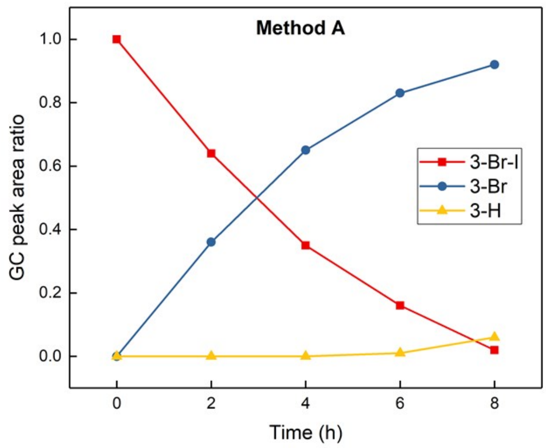



**Fig. S12** Ratio variation of **3-Br-I**, **3-Br** and **3-H** over time under the conditions of **Method A**

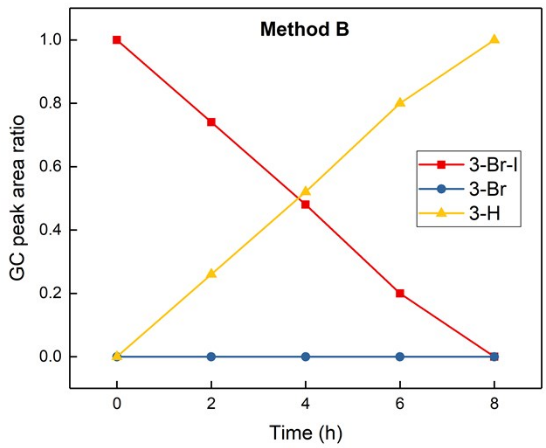



**Fig. S13** Ratio variation of **3-Br-I**, **3-Br** and **3-H** over time under the conditions of **Method B**

(2) Competitive reductions of **3-Br** and **3-I**

Two parallel reactions of substrates **3-Br** and **3-I** (0.2 mmol each) were conducted under identical conditions (0.1 M $Et_4NClO_4$, 4.0 equiv of $Et_3N$, 16 mA/cm$^2$), except for the different reaction solvents applied (4.0 mL 1:1 DMSO/EtOH for **Method A**; 4.0 mL DMSO for **Method B**). The ratios of GC peak area of **3-Br**, **3-I** and **3-H** were monitored and documented before electrolysis and at the indicated time (Table S4 and S5).

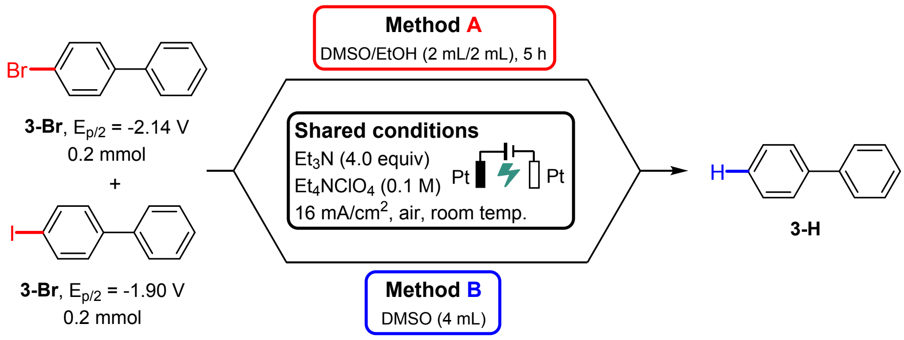



**Table S4** GC ratios of **3-Br**, **3-I** and **3-H** (**Method A**):

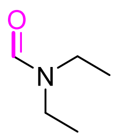
| Entry | Reaction time | Ratio of **3-Br** | Ratio of **3-I** | Ratio of **3-H** |
|---|---|---|---|---|
| 1 | 0 h | 0.54 | 0.46 | 0 |
| 2 | 5 h | 0.53 | < 0.01 | 0.47 |

**Table S5** GC ratios of **3-Br**, **3-I** and **3-H** (**Method B**):

| Entry | Reaction time | Ratio of **3-Br** | Ratio of **3-I** | Ratio of **3-H** |
|---|---|---|---|---|
| 1 | 0 h | 0.52 | 0.48 | 0 |
| 2 | 1 h | 0.36 | 0.33 | 0.31 |
| 3 | 4 h | < 0.01 | < 0.01 | > 0.99 |

## 3.6 Detection and characterization of some by-products

Possible by-products detected by GC-MS:




N,N-diethylformamide (by-product **a** in the proposed mechanism) Mw = 101

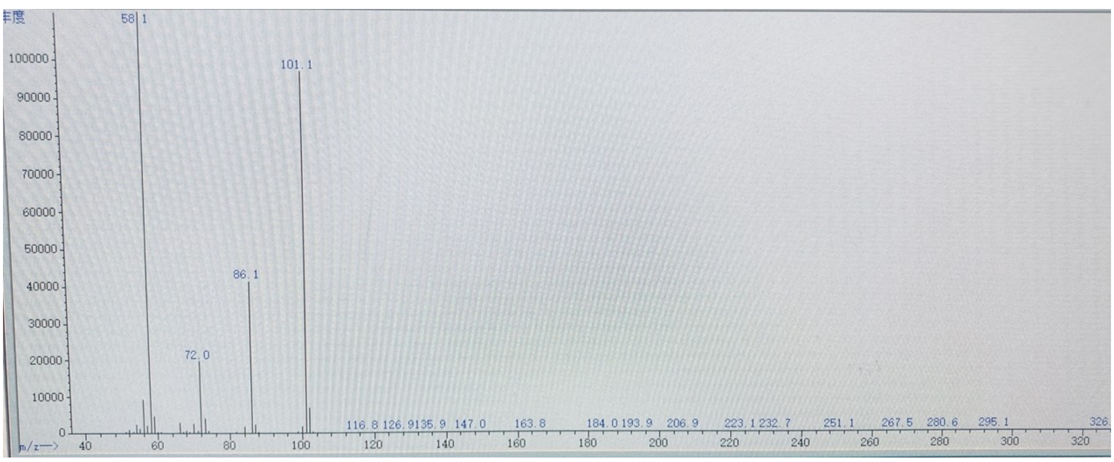
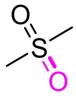



**Fig. S14** MS spectrum of possible by-product **a**



(methylsulfonyl)methane (by-product **b** in the proposed mechanism) Mw = 94

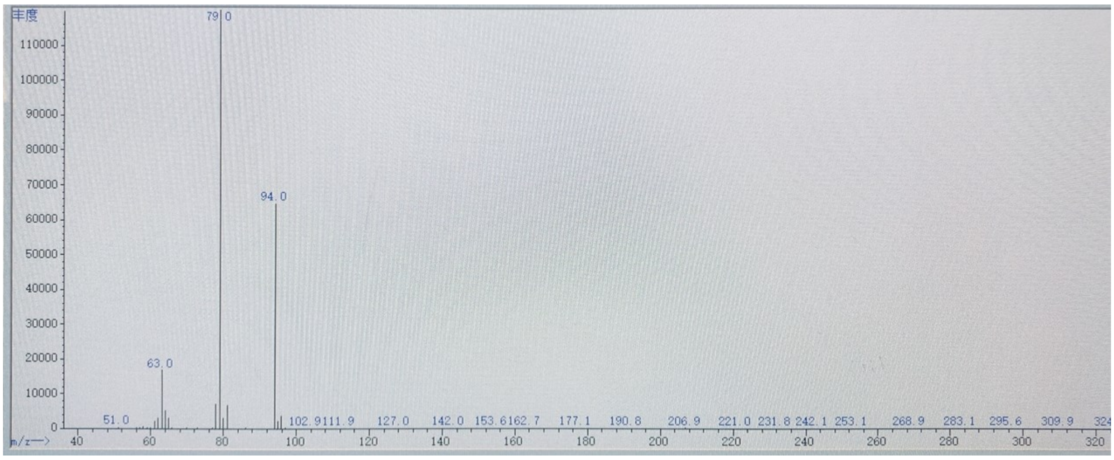
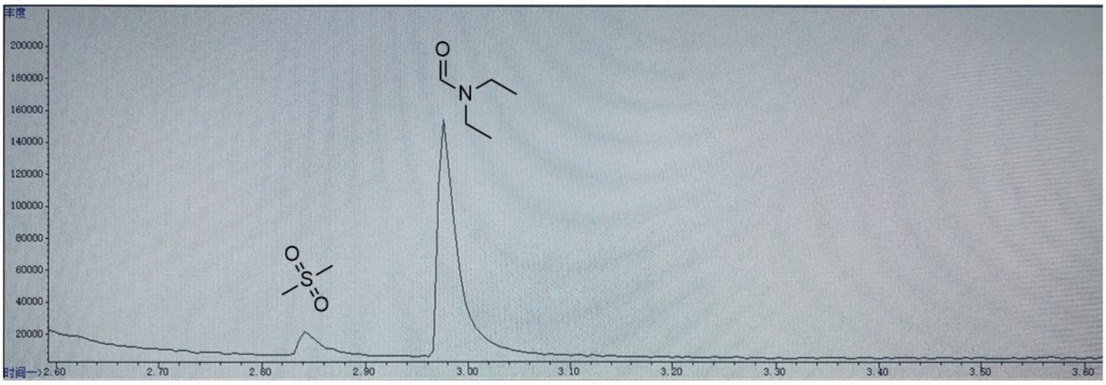
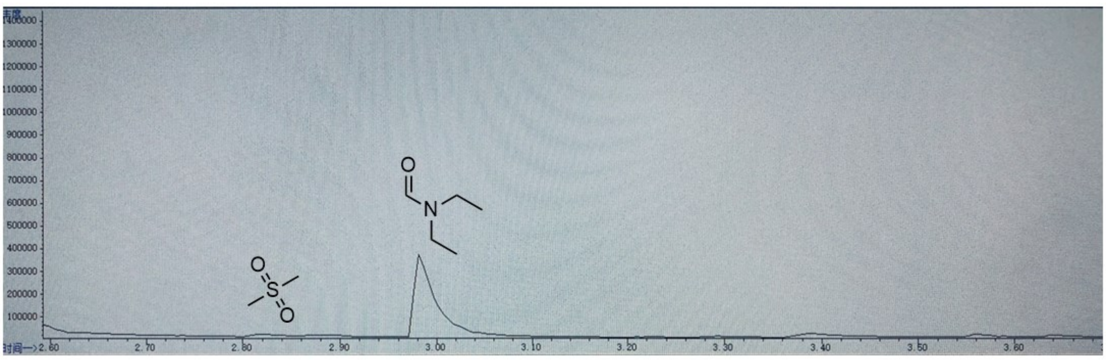
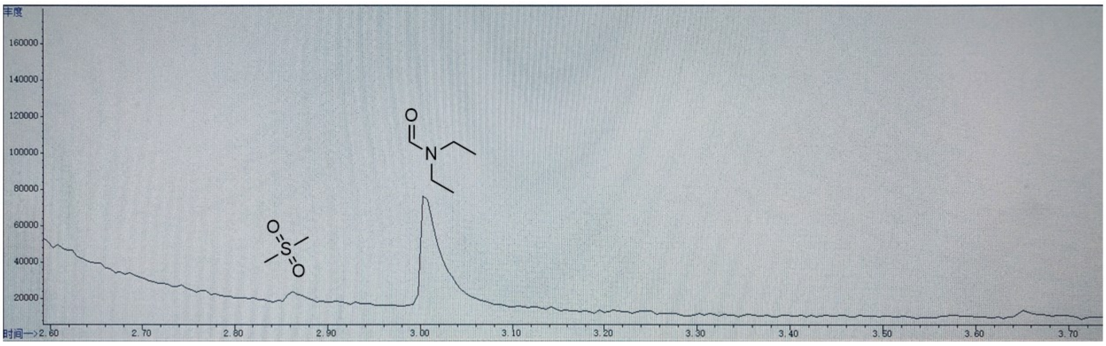


**Fig. S15** MS spectrum of possible by-product **b**

GC images containing by-products **a** and **b** in some typical reaction systems after electrolysis:







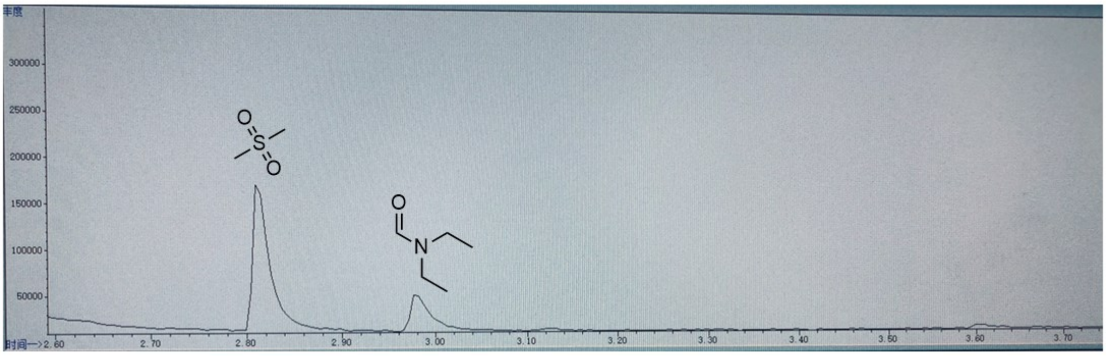
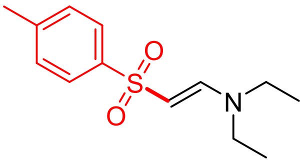


**Fig. S16** GC images containing **a** and **b** in some systems after electrolysis

The dehydrogenative cross-coupling product **Ts-NEt$_3$** (by-product **c** in the proposed mechanism) could be observed in every desulfonylation reaction and isolated in 5% ~ 15% yield from the reactions of **44-Ts**, **48-Ts**, **52-Ts** and **55-Ts**.

Characterization data of **Ts-NEt$_3$**:



(E)-N,N-diethyl-2-tosylethen-1-amine (**Ts-NEt$_3$**) [74]:

Brown oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.78 – 7.73 (m, 2H), 7.32 (d, $J$ = 12.7 Hz, 1H), 7.27 – 7.23 (m, 2H), 4.91 (d, $J$ = 12.7 Hz, 1H), 3.36 – 3.02 (m, 4H), 2.42 (s, 3H), 1.23 – 1.04 (m, 6H).

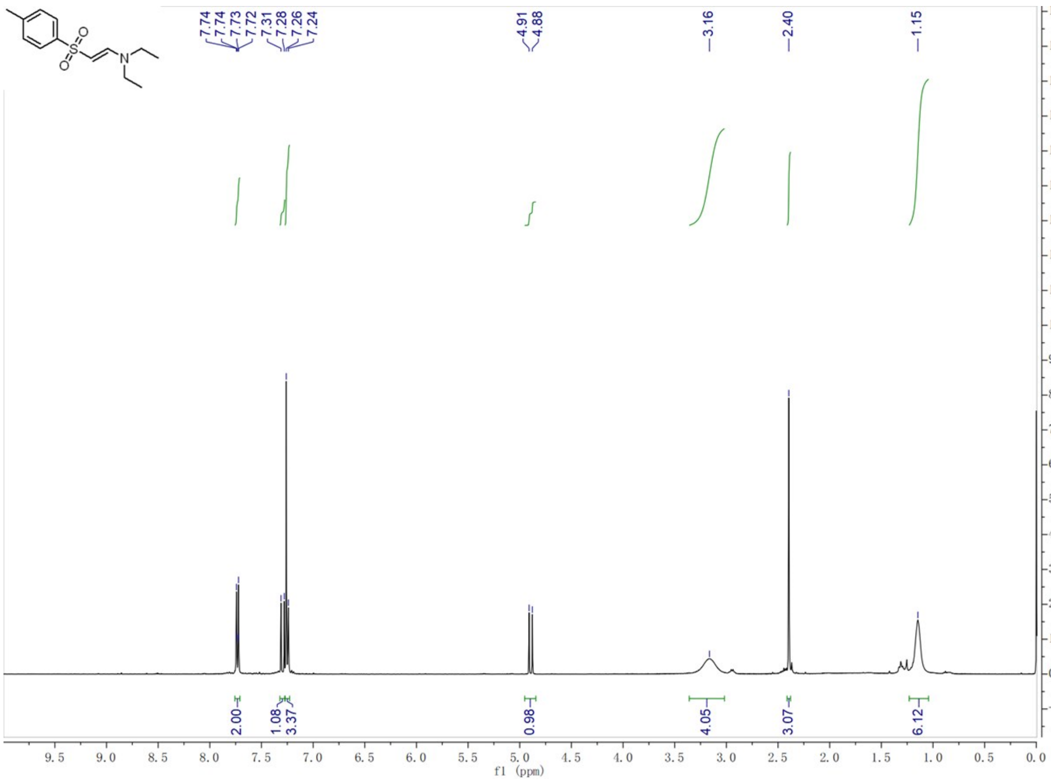


**Fig. S17** $^{1}$H-NMR spectrum of **Ts-NEt$_3$** (by-product **c**)

## 3.7 Calculation of the current efficiencies (CEs)

The current efficiencies (CEs) were calculated as follows[75]:

$$CE(\%) = (n_{prod} \times F \times n / C) \times 100\%$$

$$= (0.4 \times 10^{-3}\ [mol] \times yield \times 96485\ [C/mol] \times 2) / (I\ [A] \times t\ [s]) \times 100\%$$

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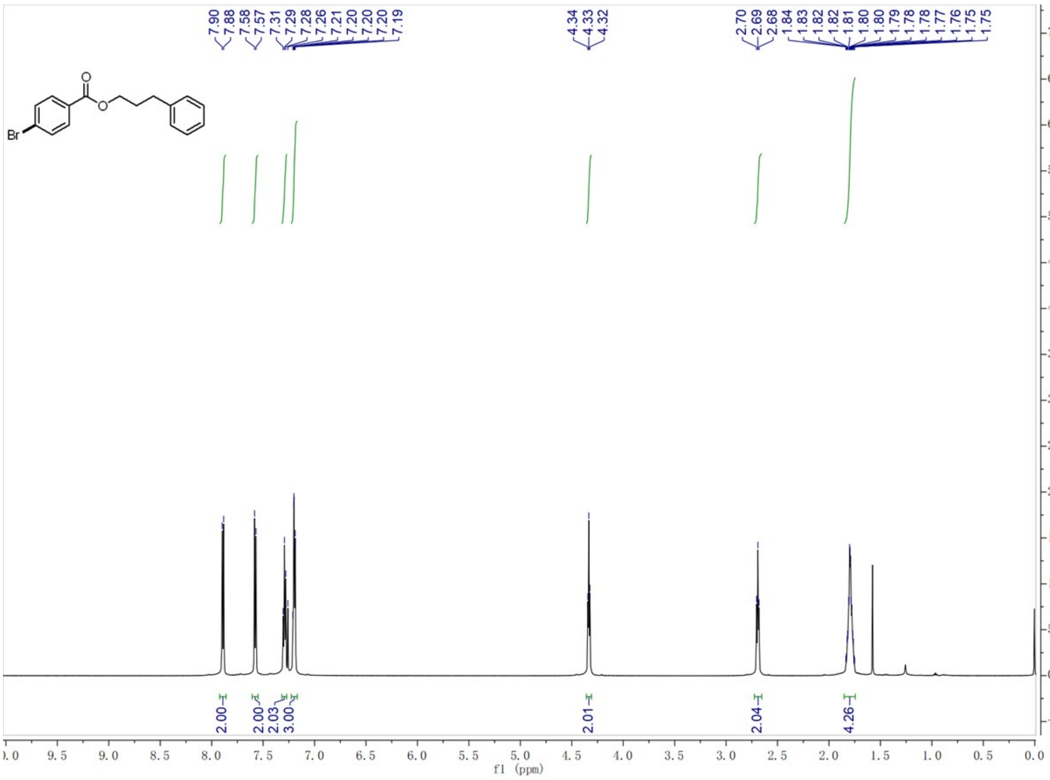
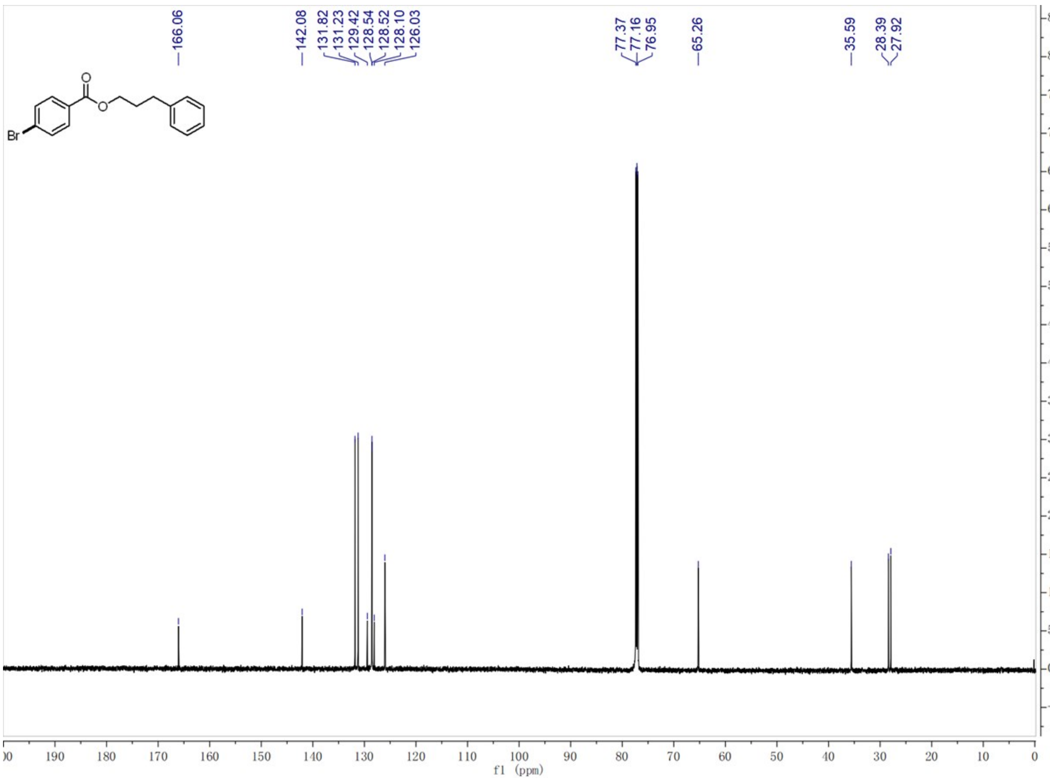
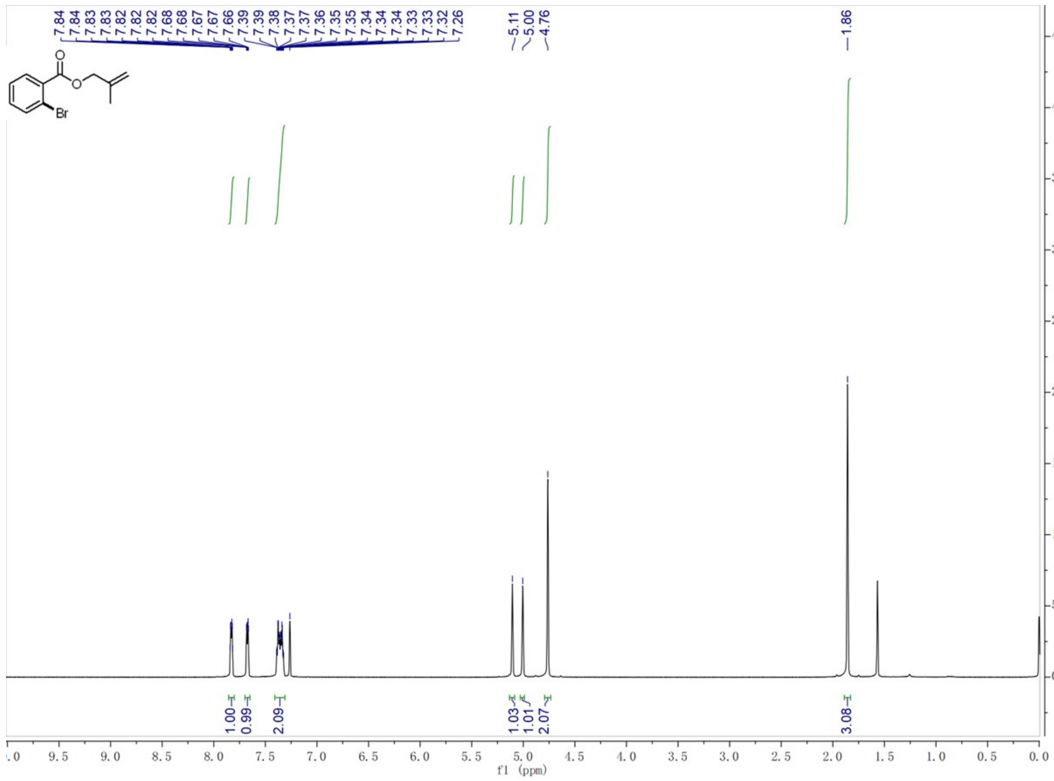
# 5. NMR spectra

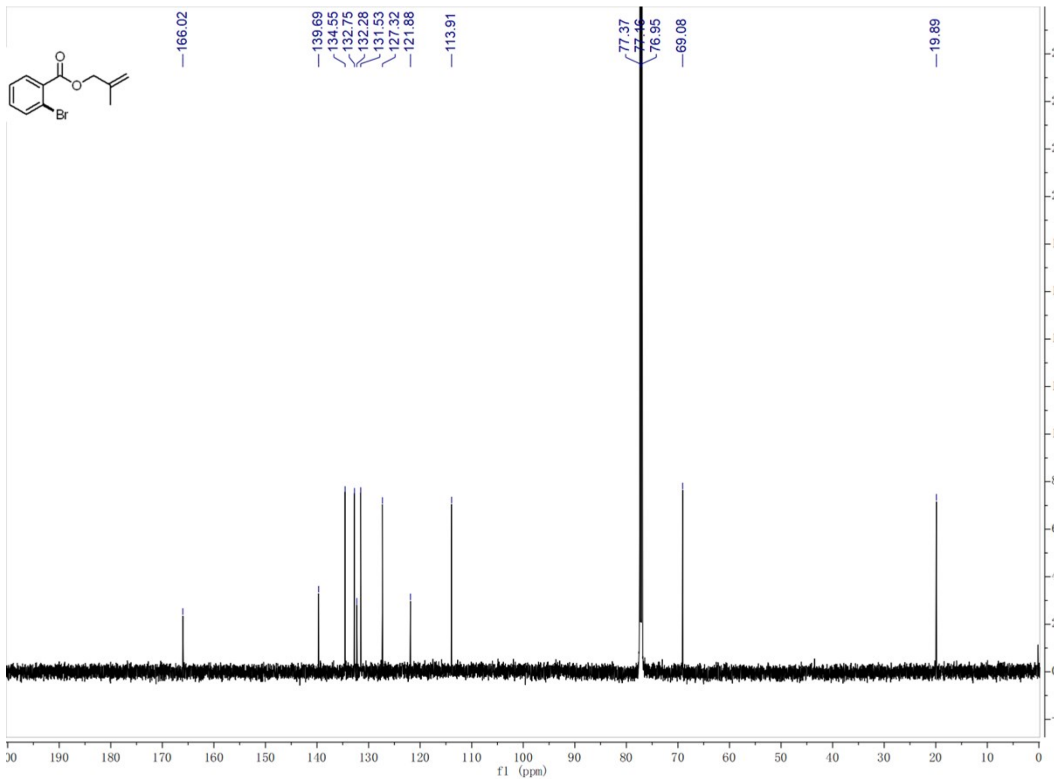
**12-Br** $^{1}$H NMR and $^{13}$C NMR



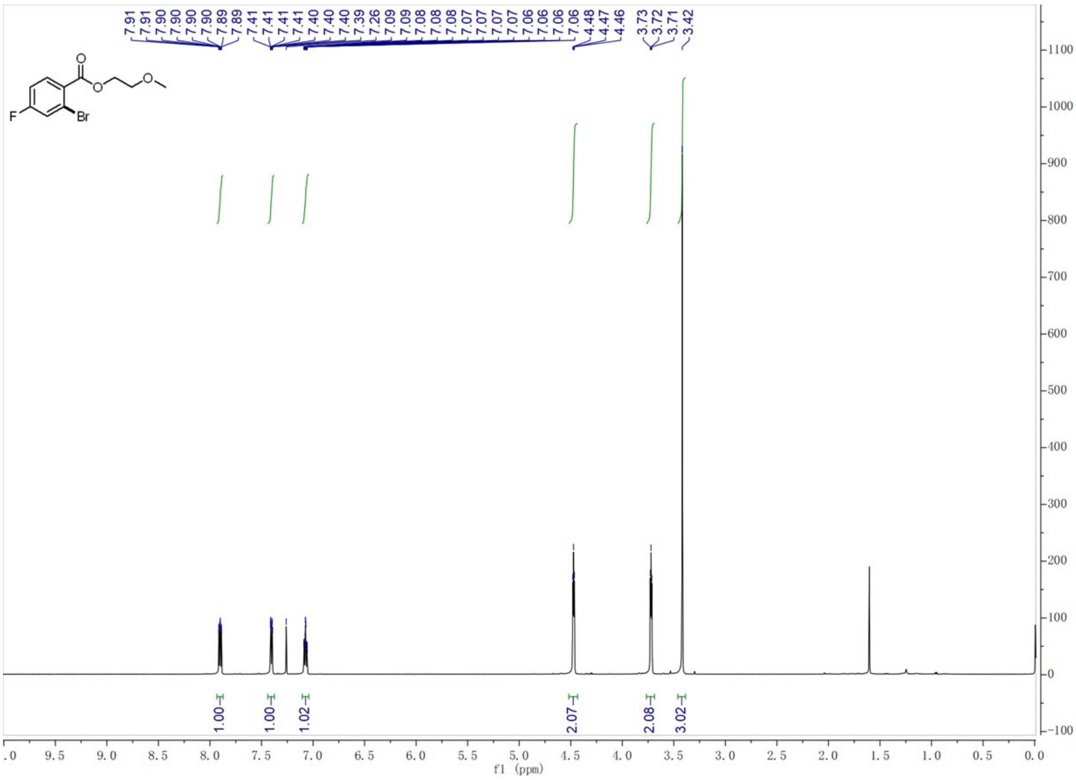


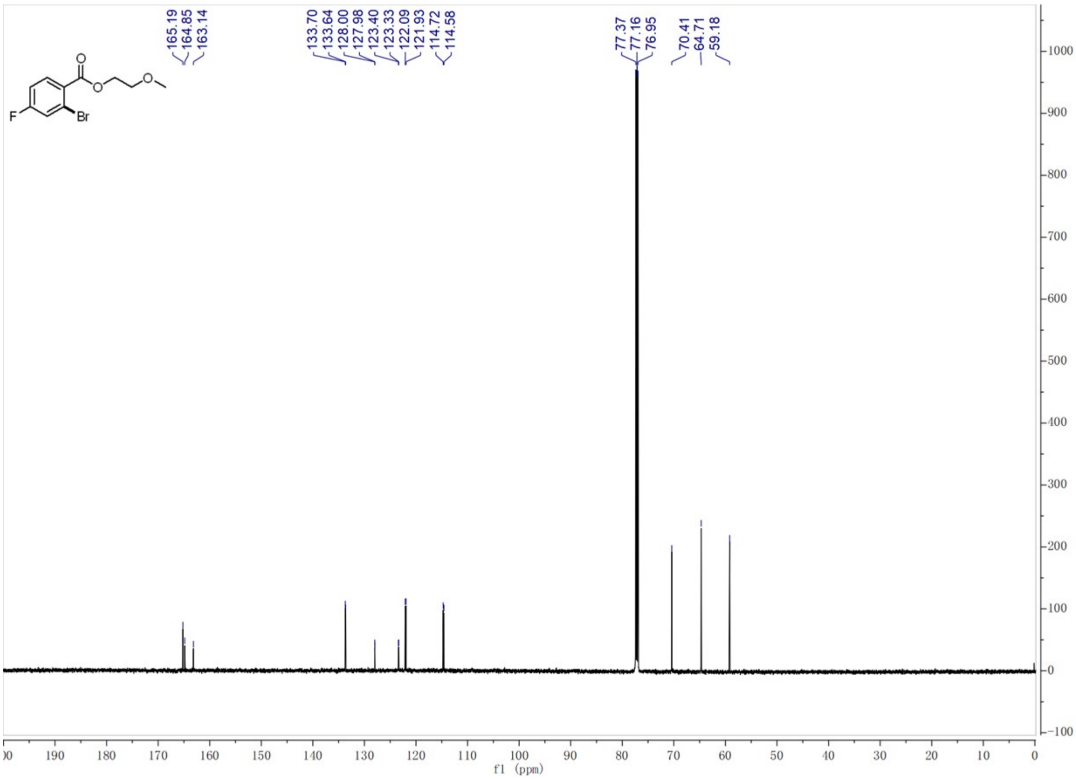
**13-Br** $^{1}H$ NMR and $^{13}C$ NMR

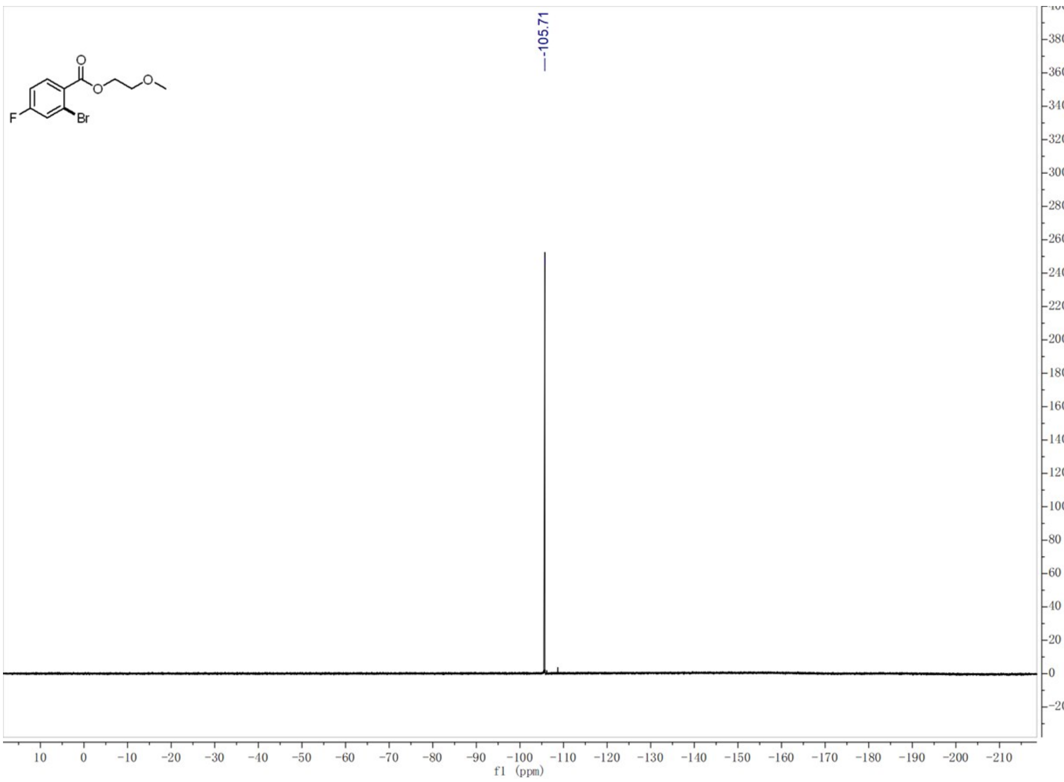




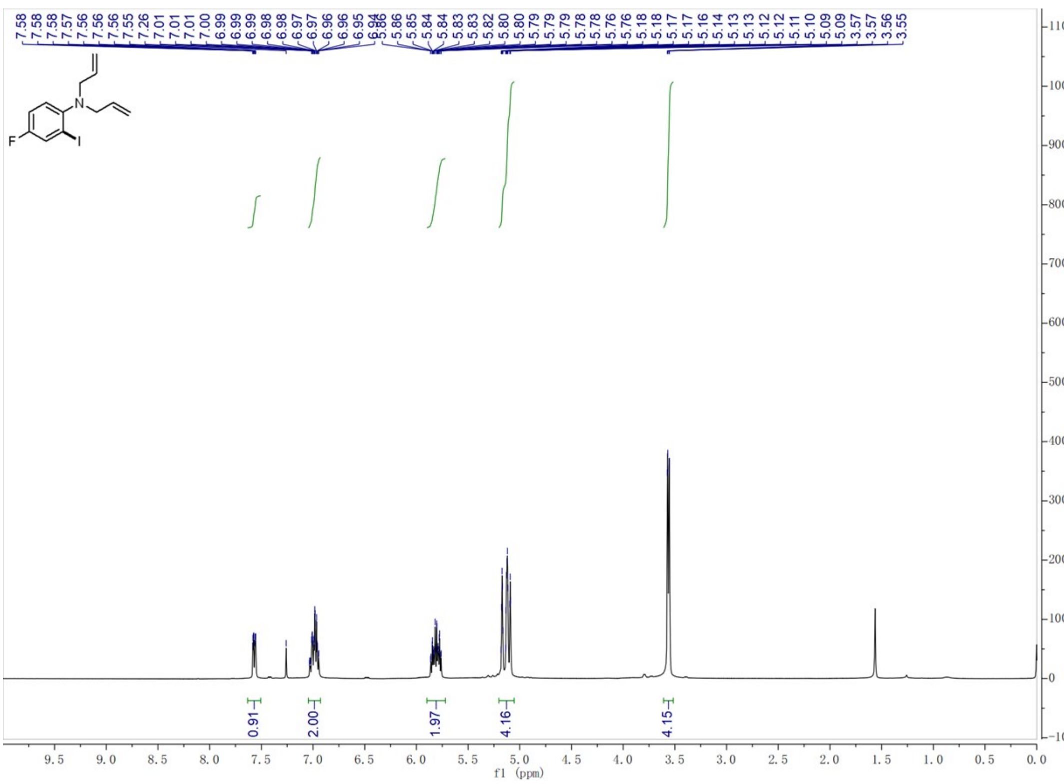
**14-Br** $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR

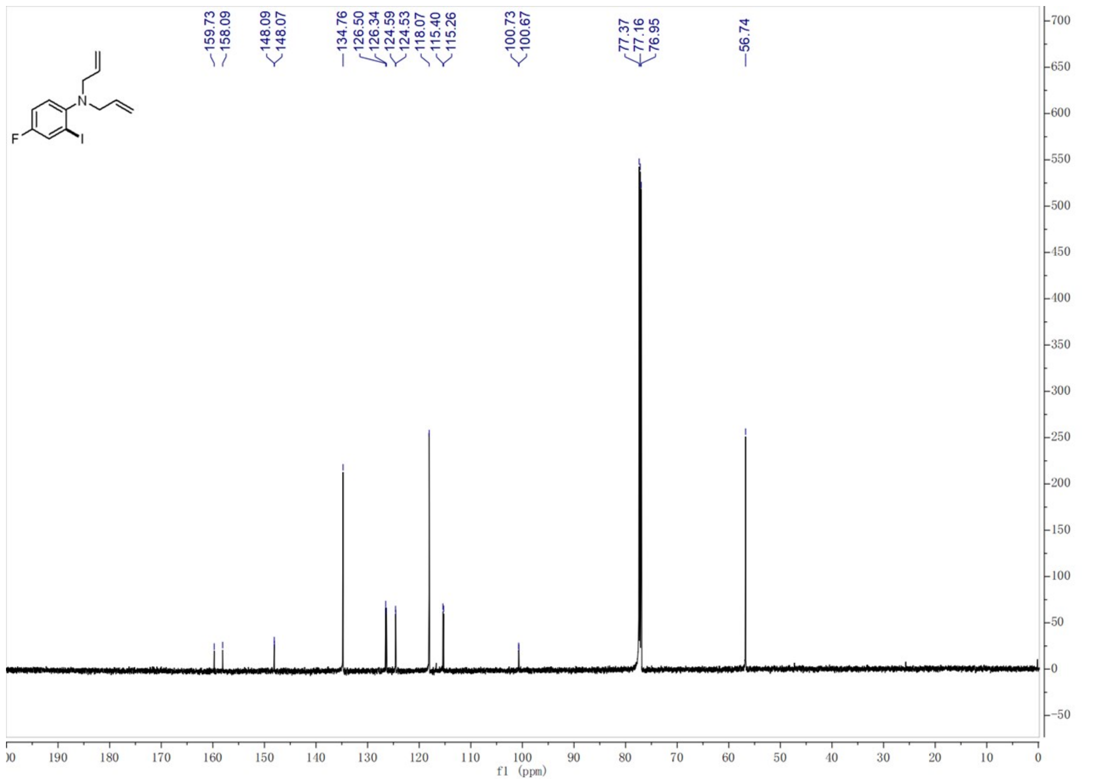


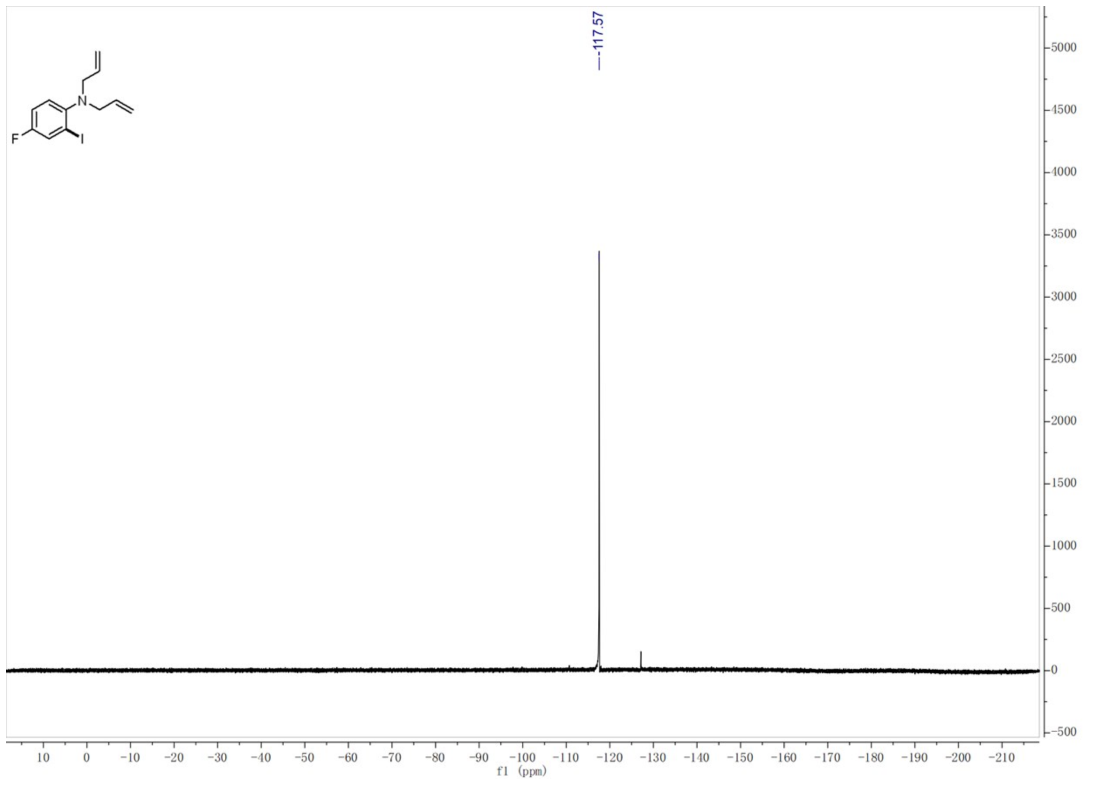




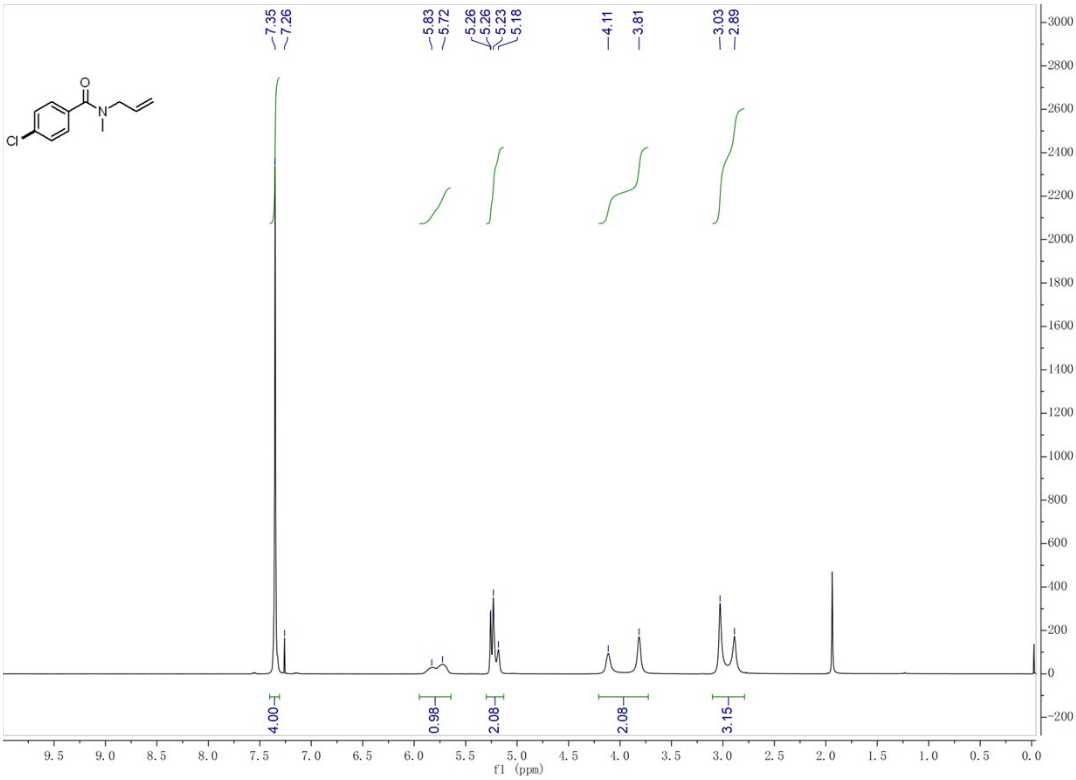
**29-I** [1]H NMR, [13]C NMR and [19]F NMR

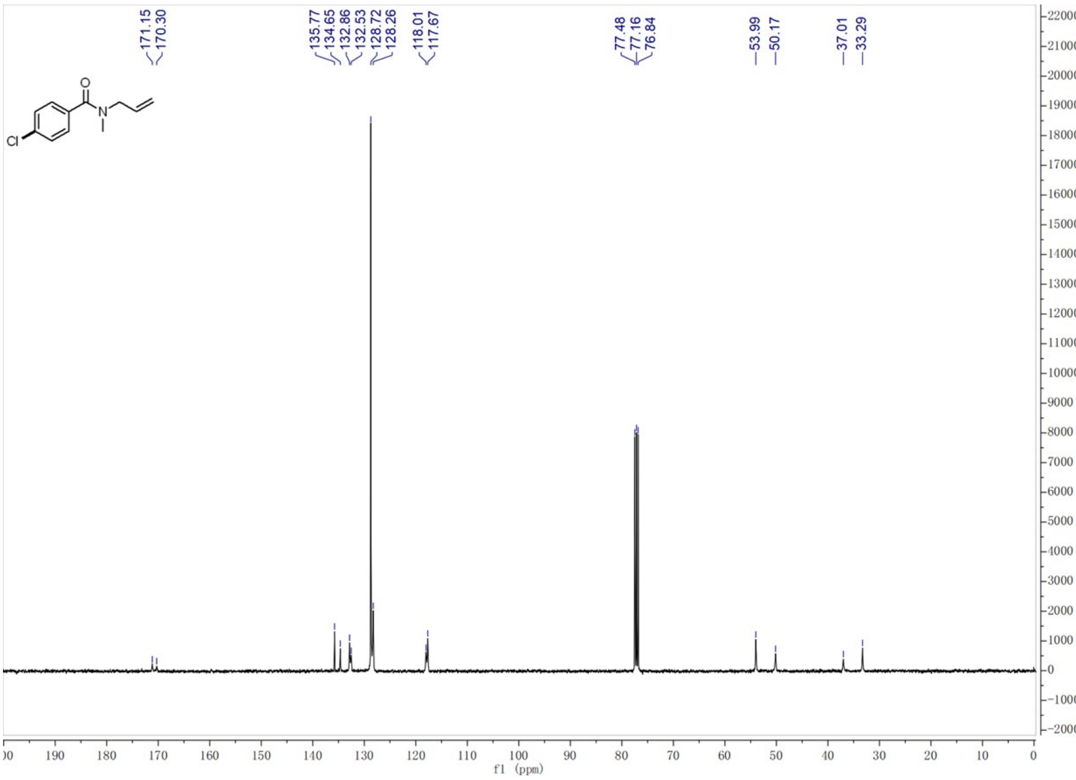



159.73
158.09
148.09
148.07
134.76
126.50
126.34
124.59
124.53
118.07
115.40
115.26
100.73
100.67
77.37
77.16
76.95
56.74
F
N
I
f1 (ppm)

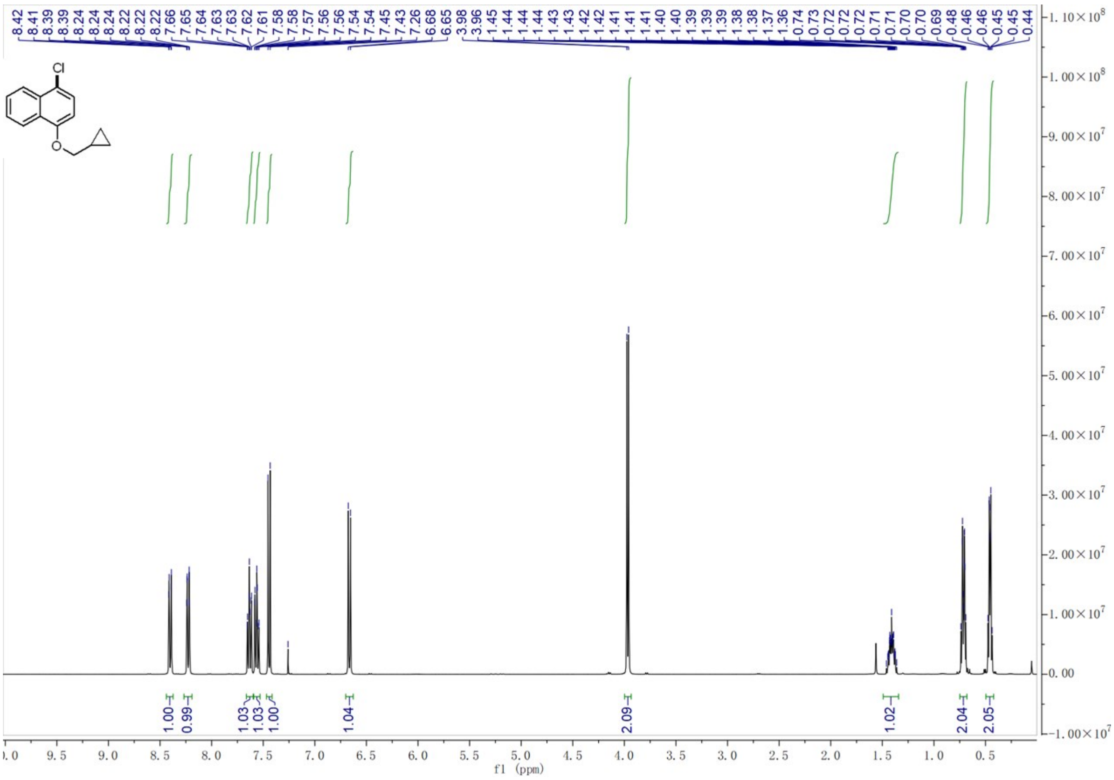

-117.57
F
N
I
f1 (ppm)

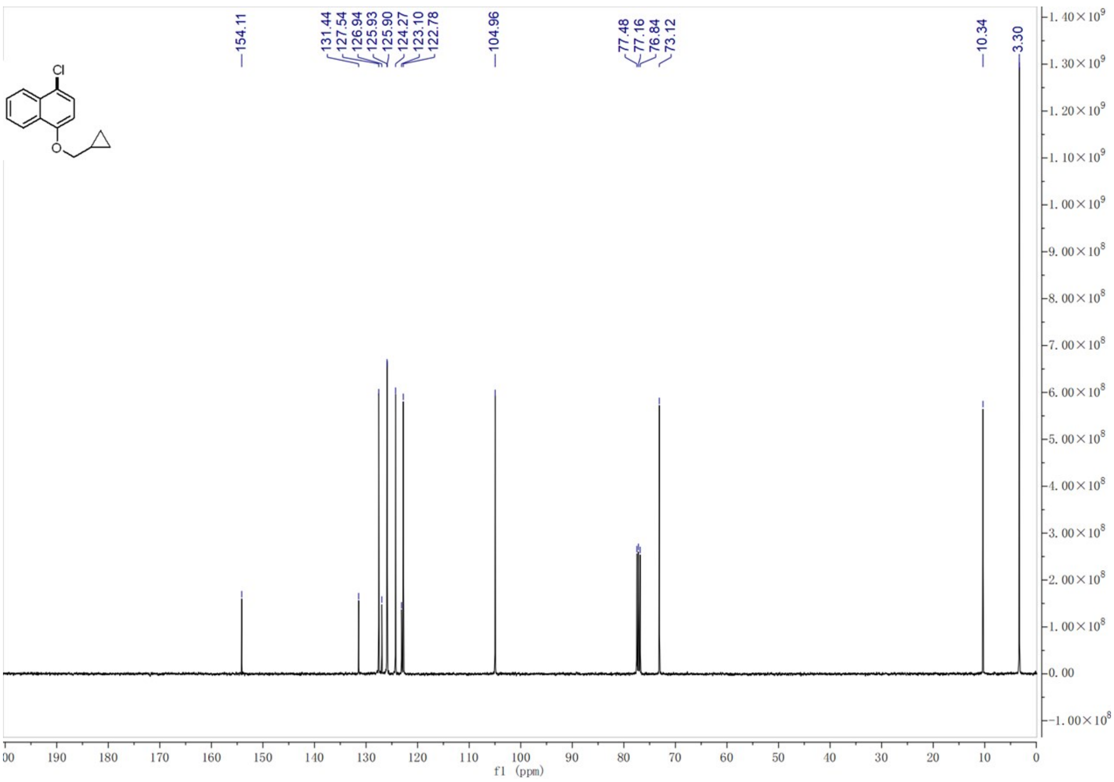
**35-Cl** $^{1}$H NMR and $^{13}$C NMR



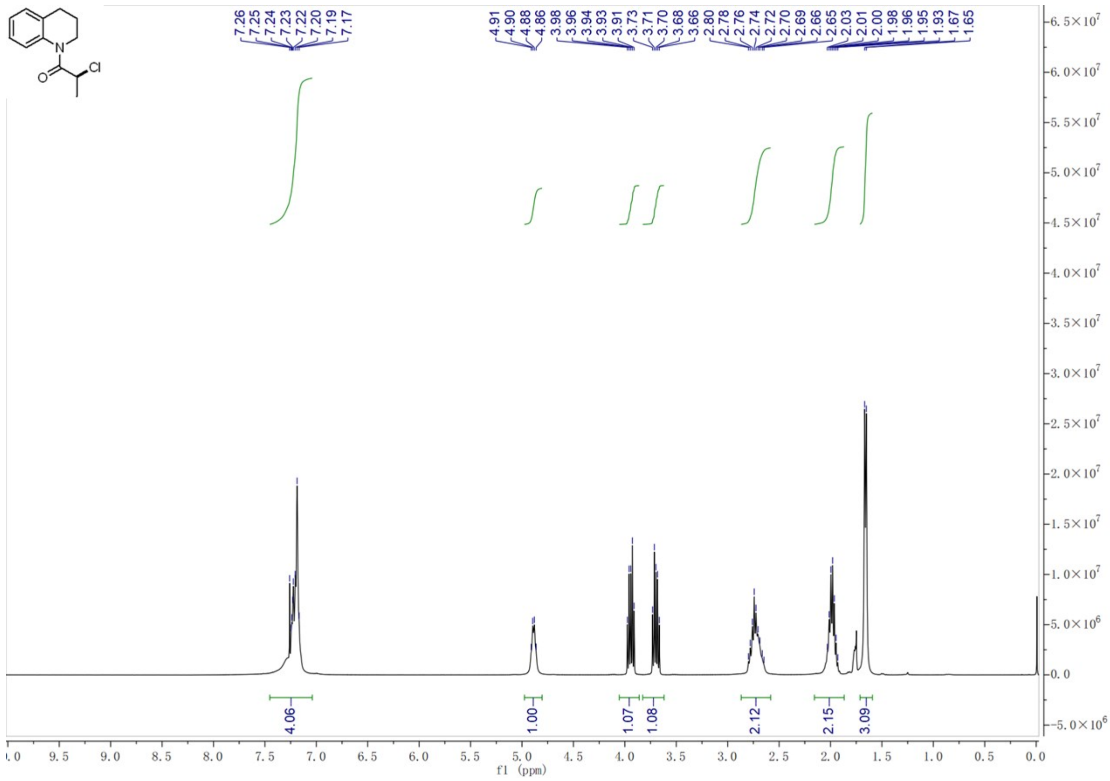



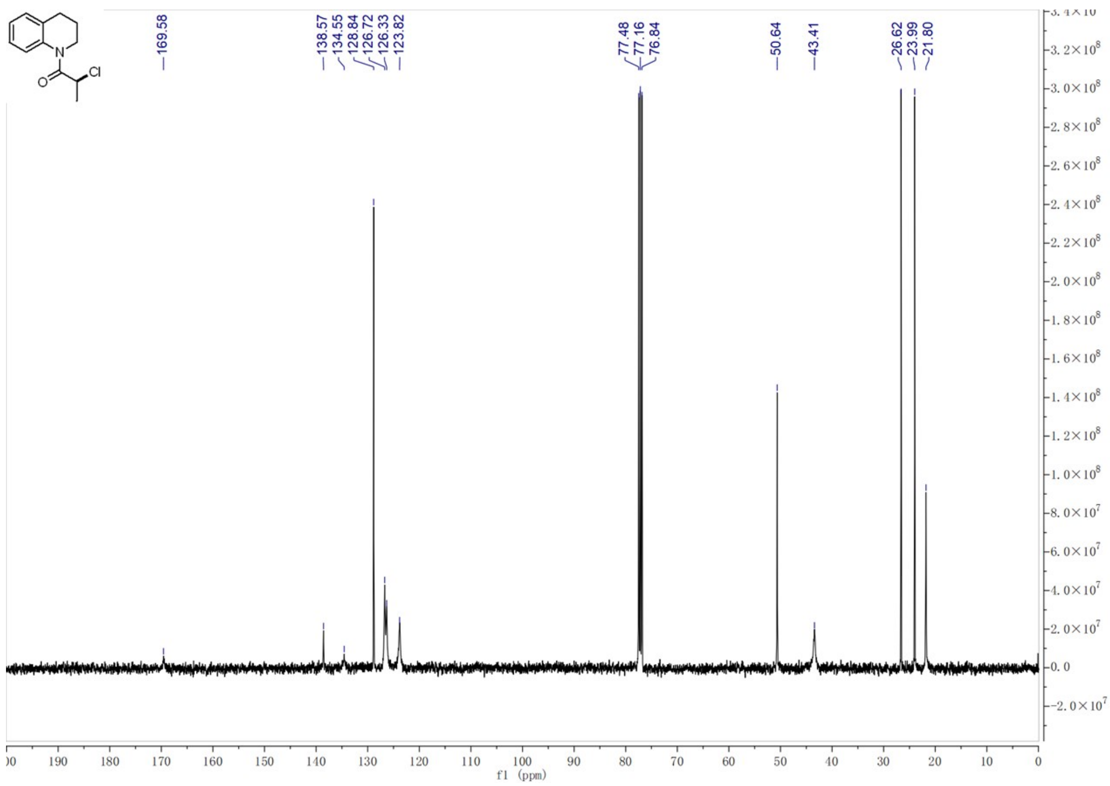
**36-Cl** $^{1}$H NMR and $^{13}$C NMR



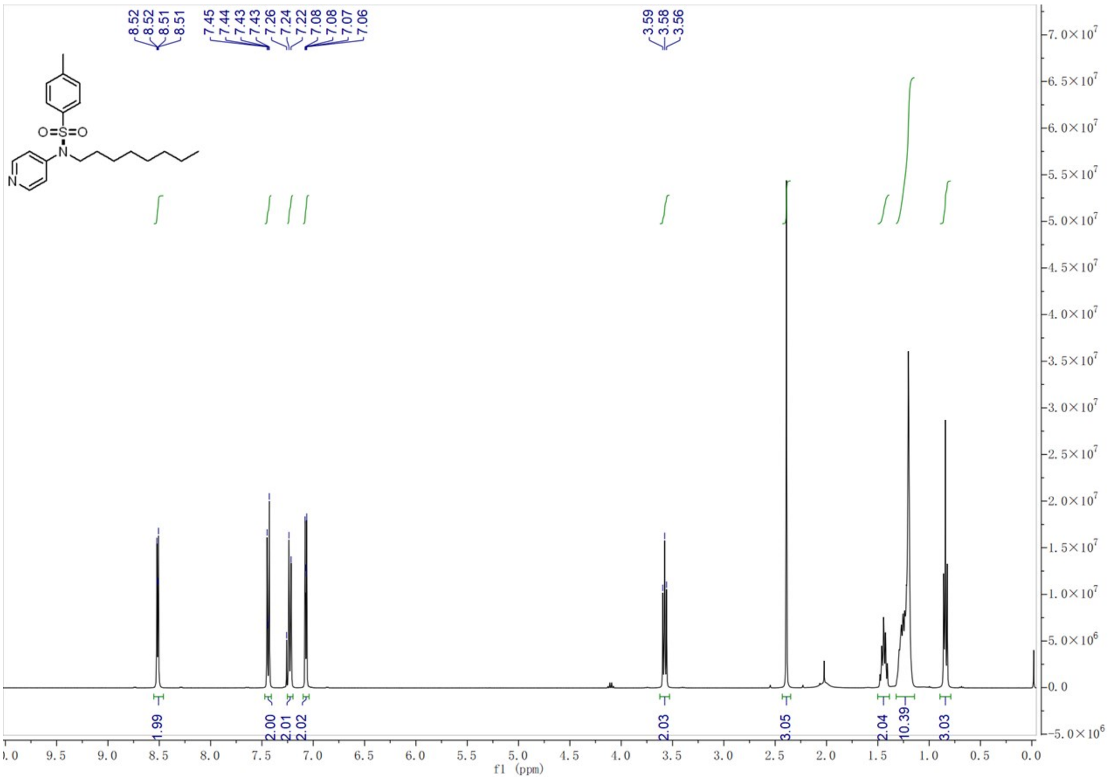


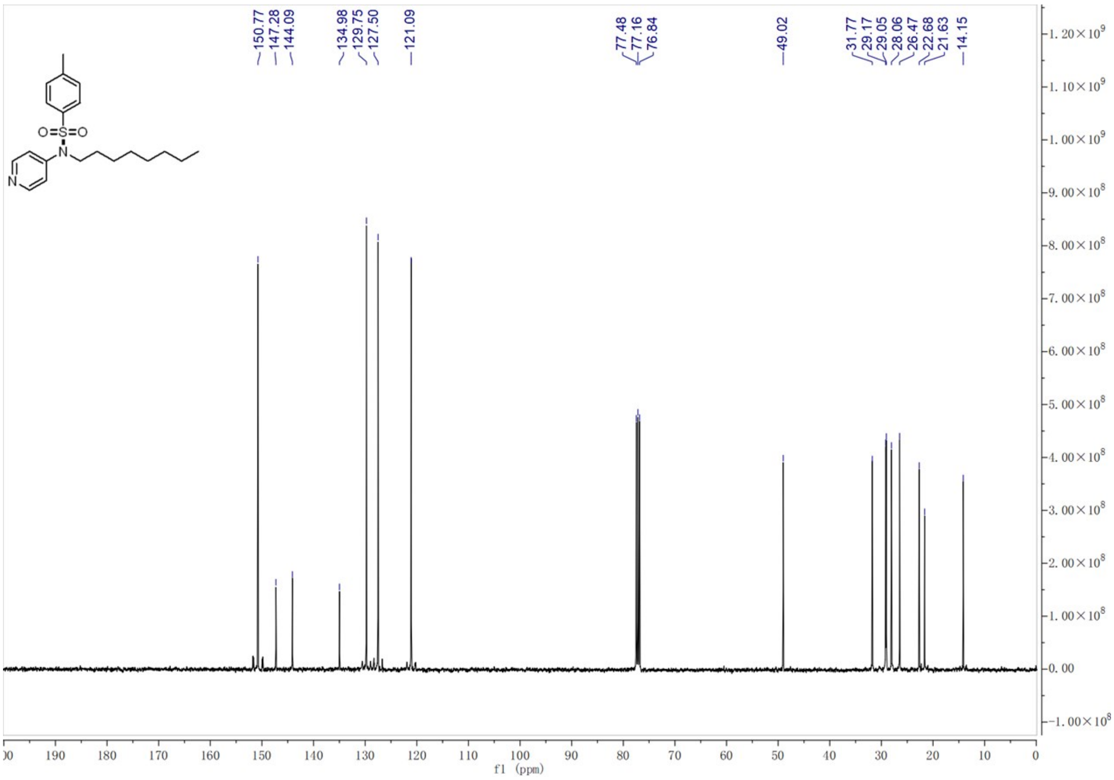
**38-Cl** $^{1}H$ NMR and $^{13}C$ NMR



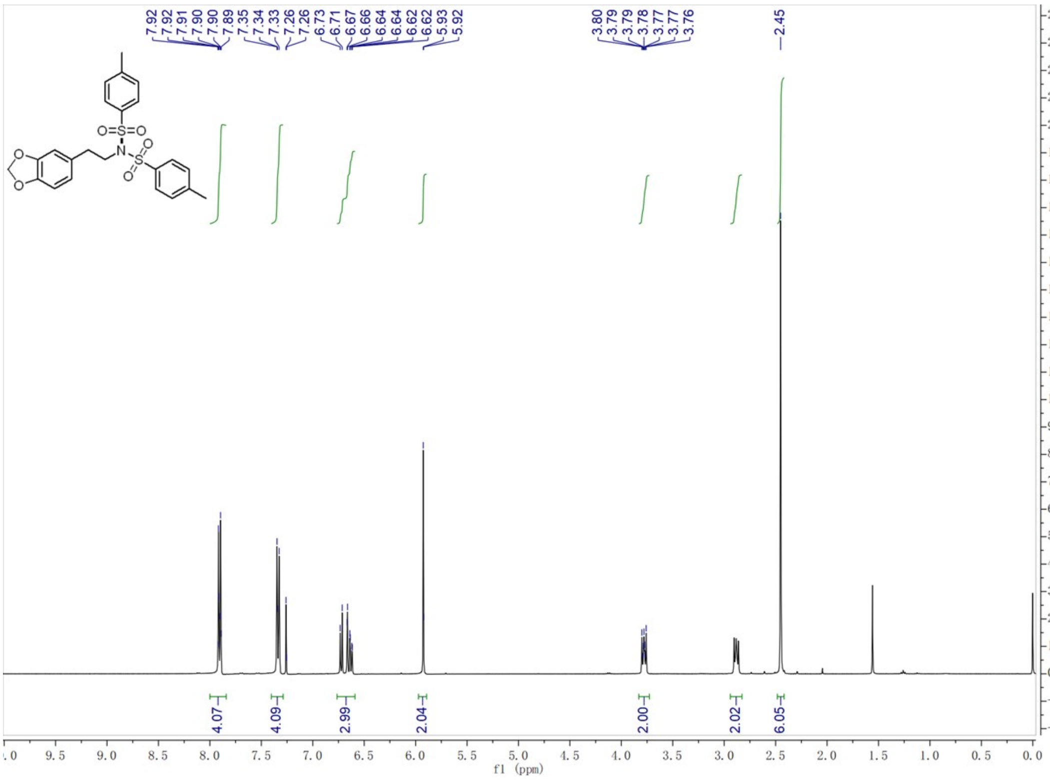


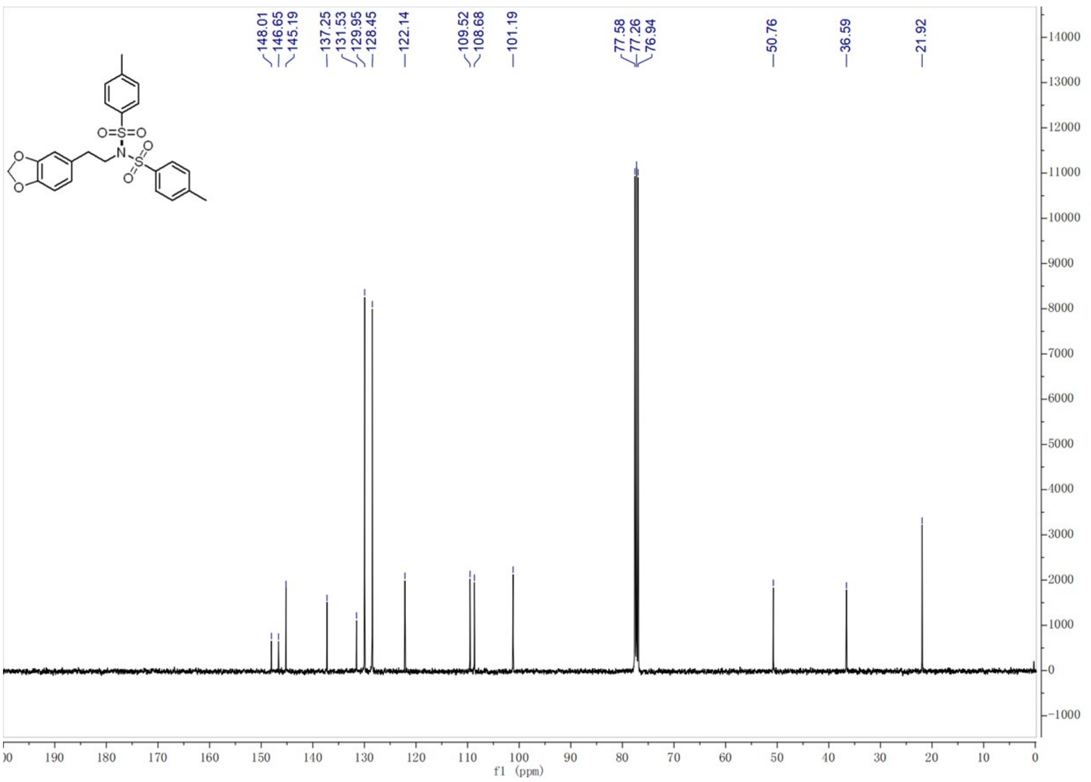
**49-Ts** $^{1}H$ NMR and $^{13}C$ NMR



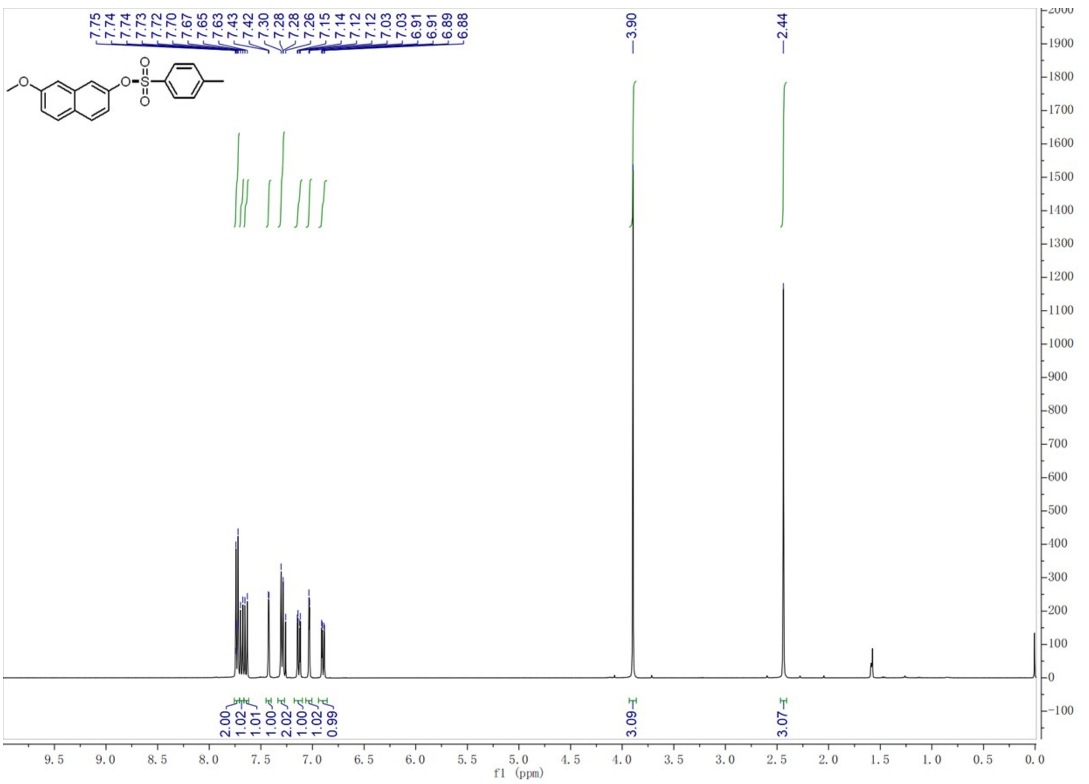



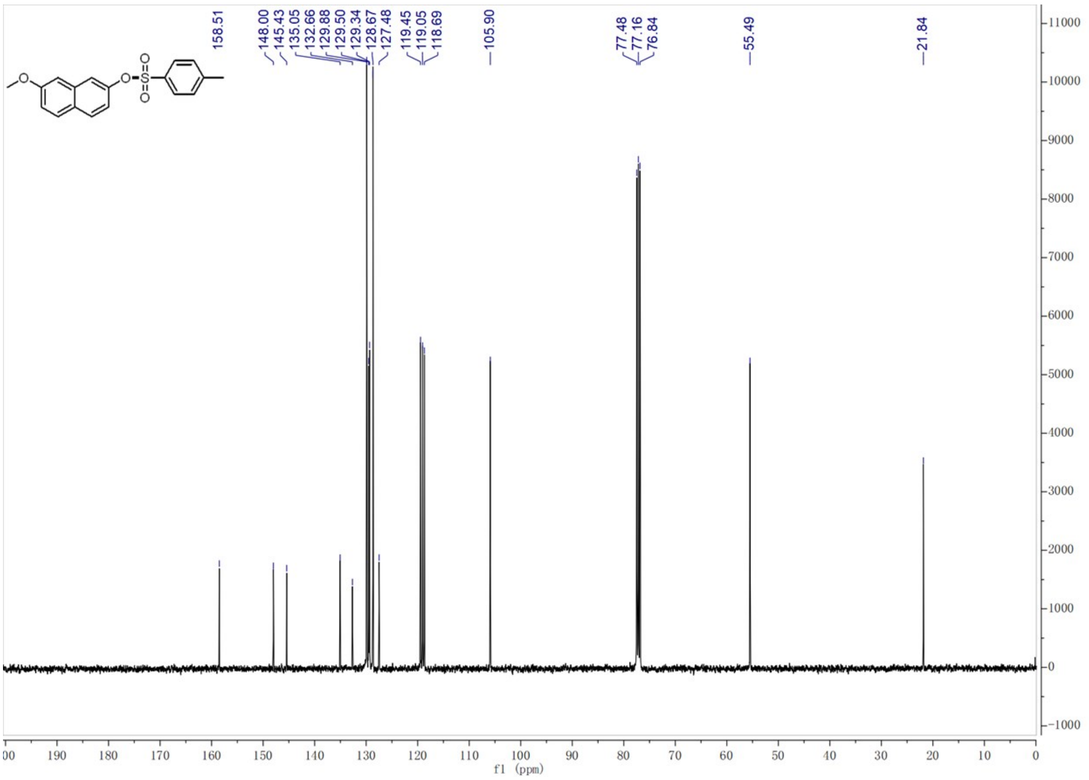
**51-Ts** $^1$H NMR and $^{13}$C NMR



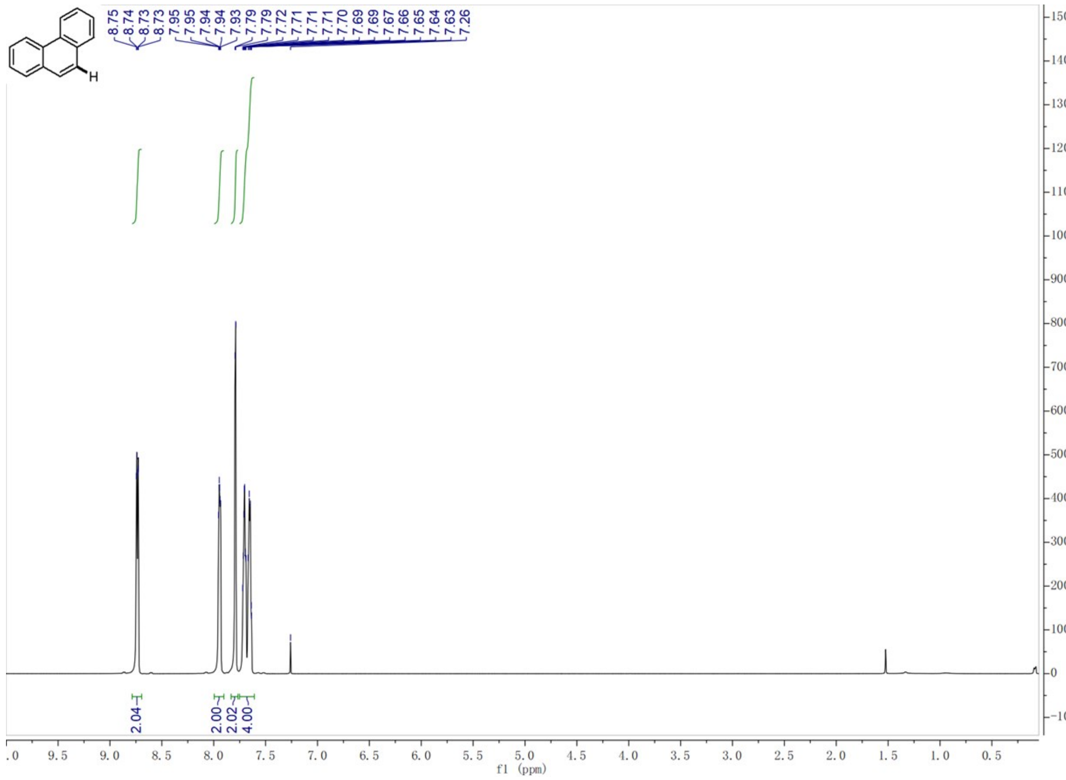



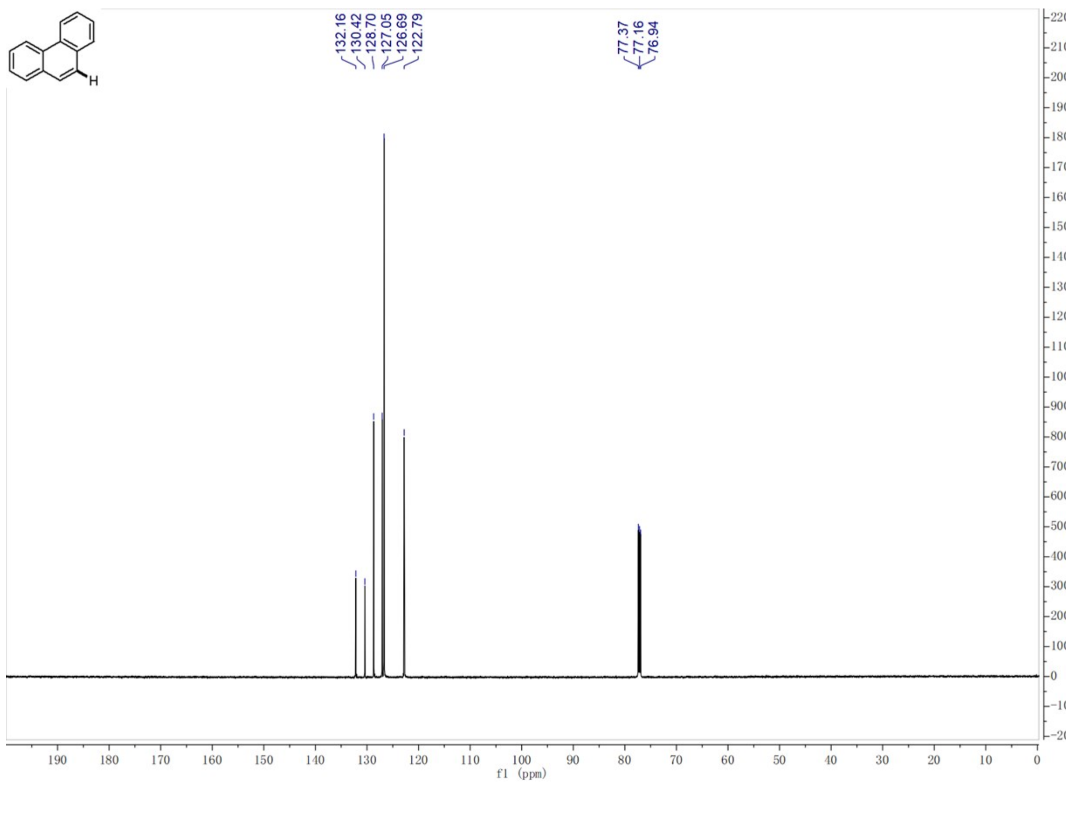
**54-Ts** $^{1}$H NMR and $^{13}$C NMR



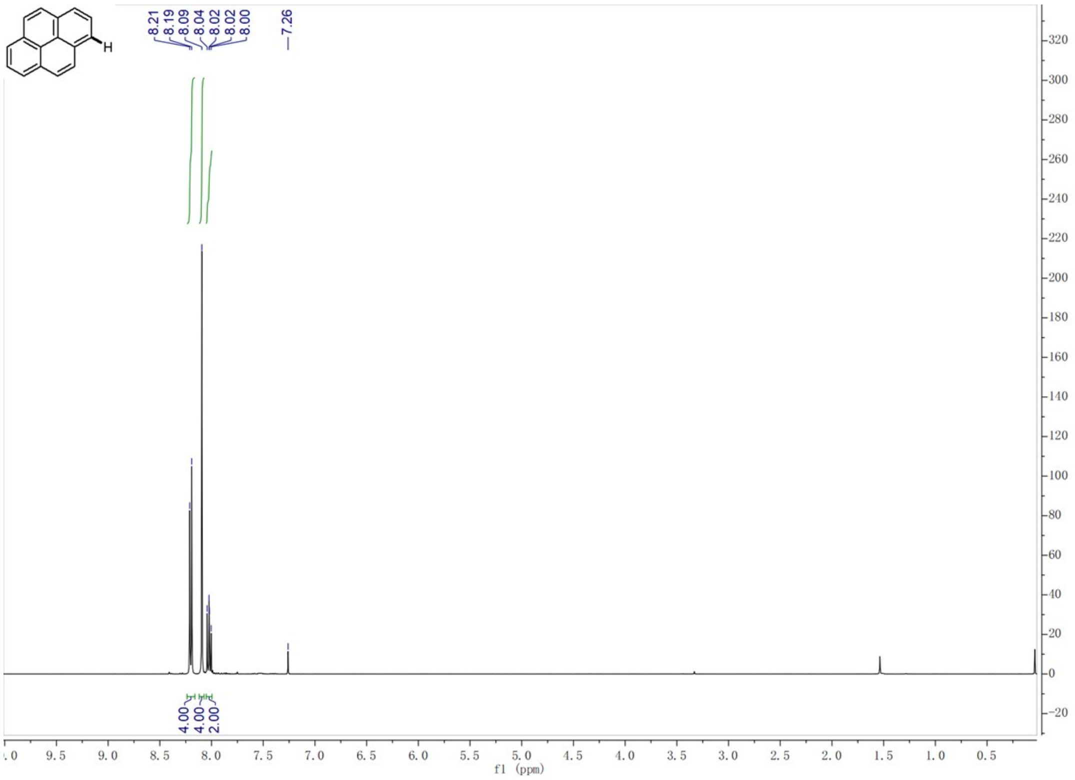



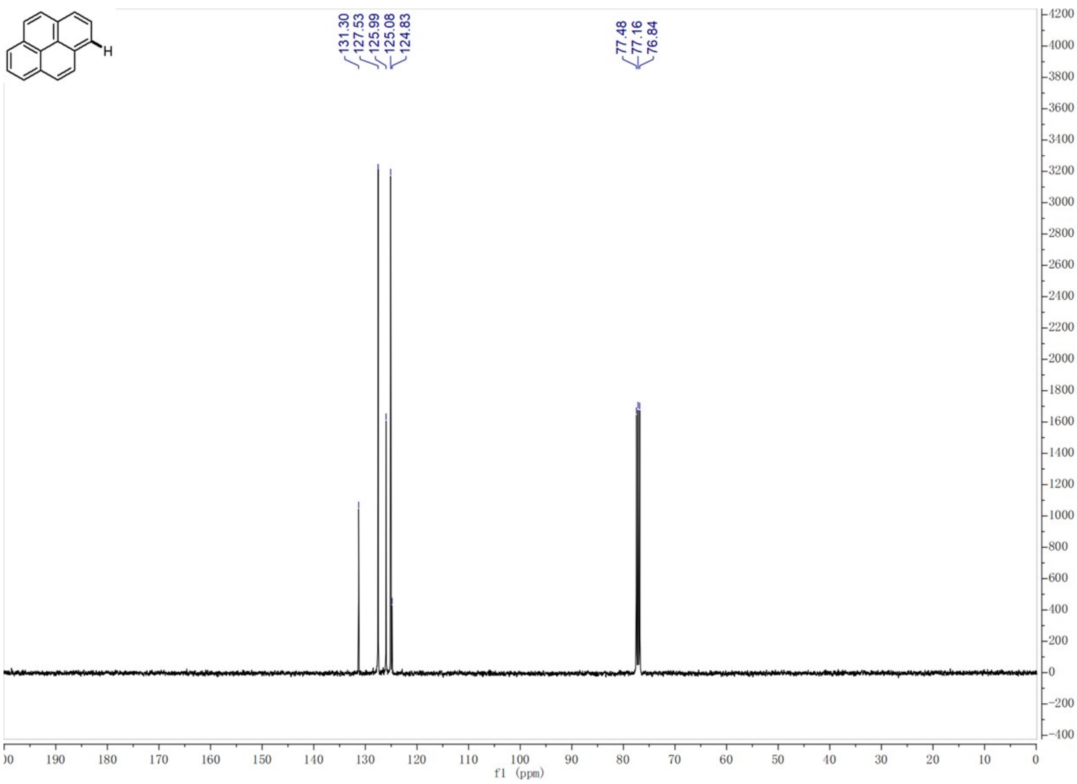
**1-H** $^{1}H$ NMR and $^{13}C$ NMR



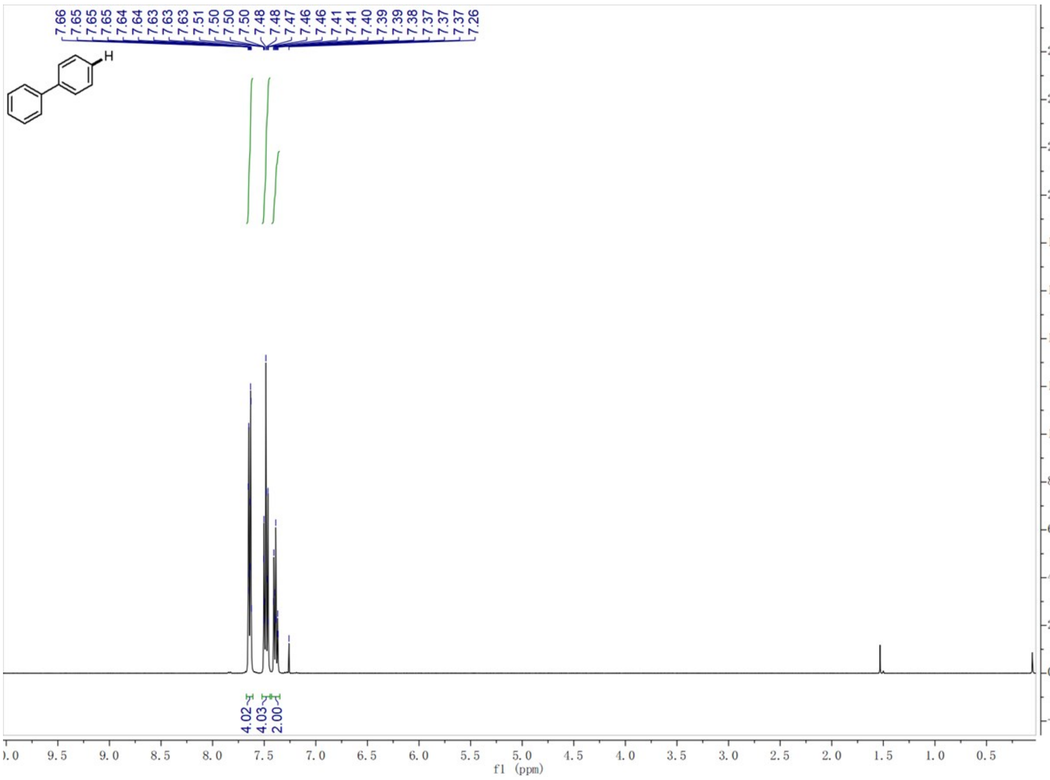



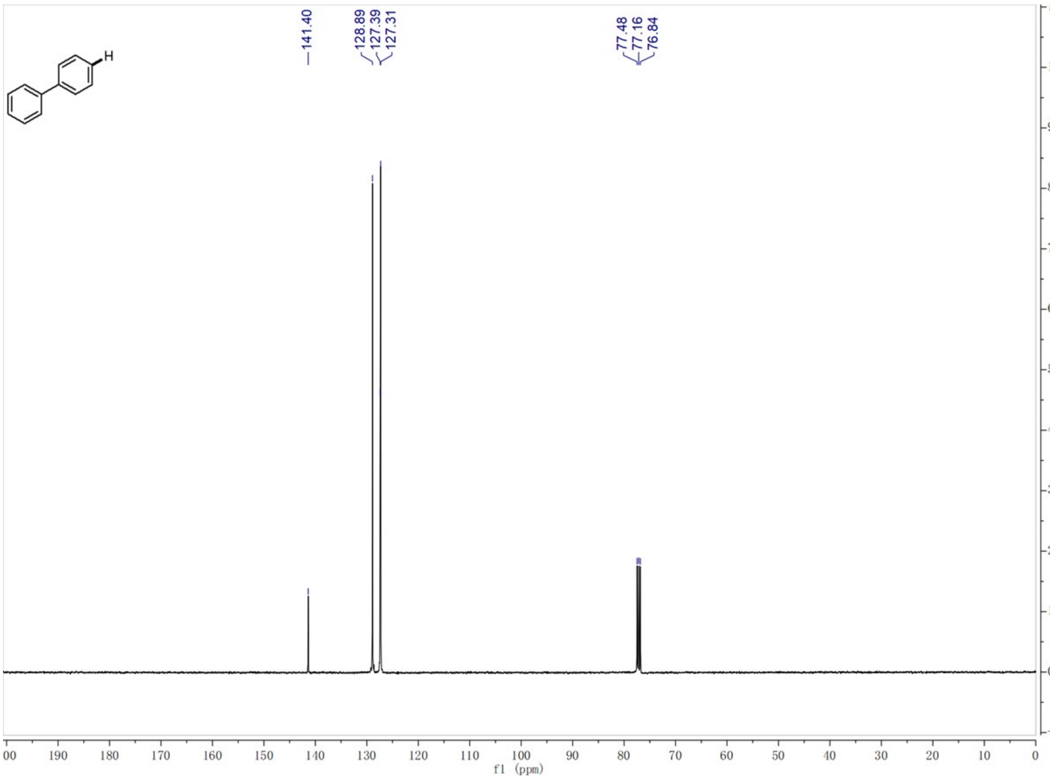
**2-H** $^{1}$H NMR and $^{13}$C NMR



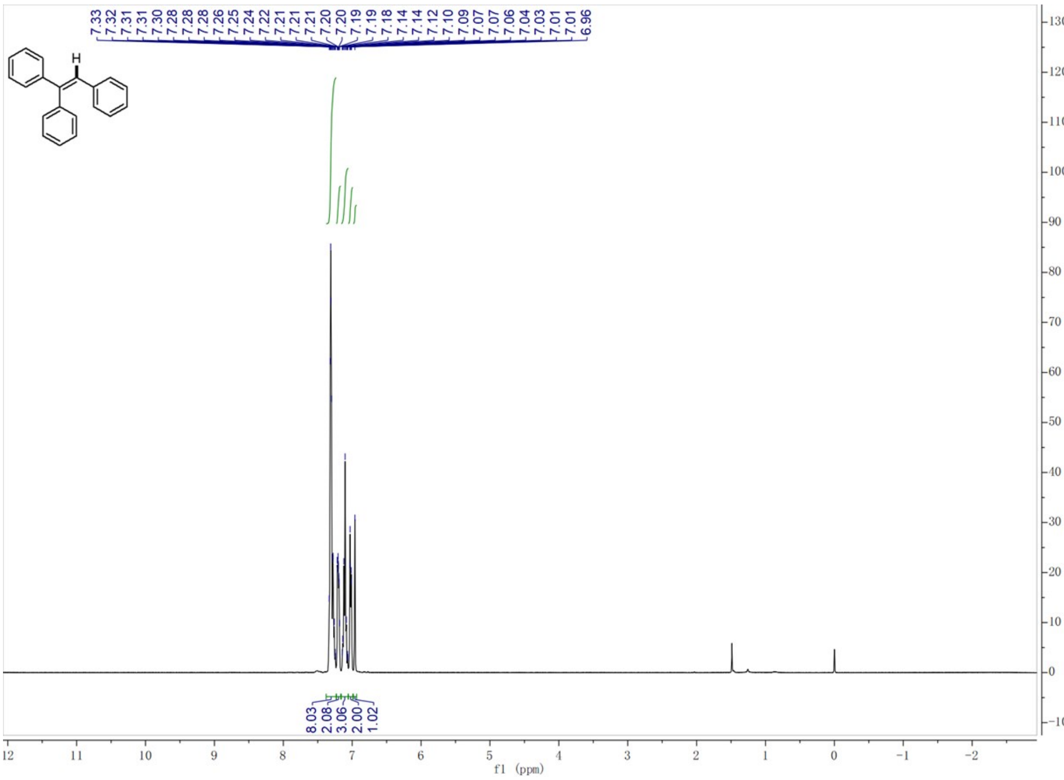



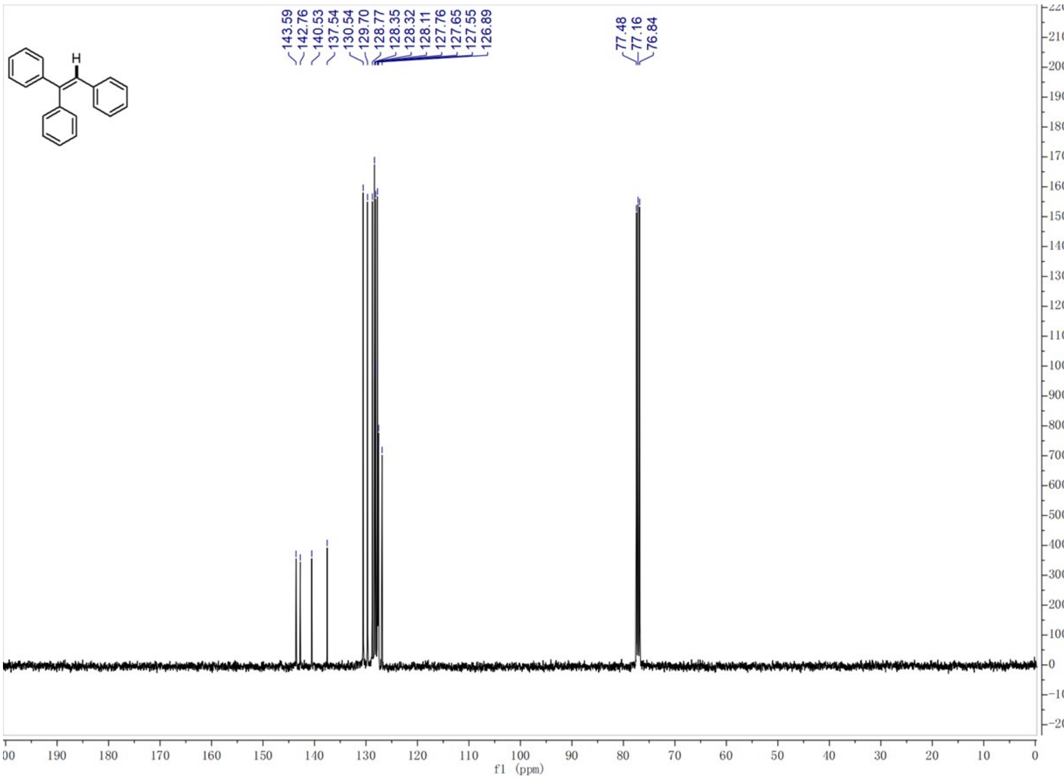
**3-H** $^{1}$H NMR and $^{13}$C NMR



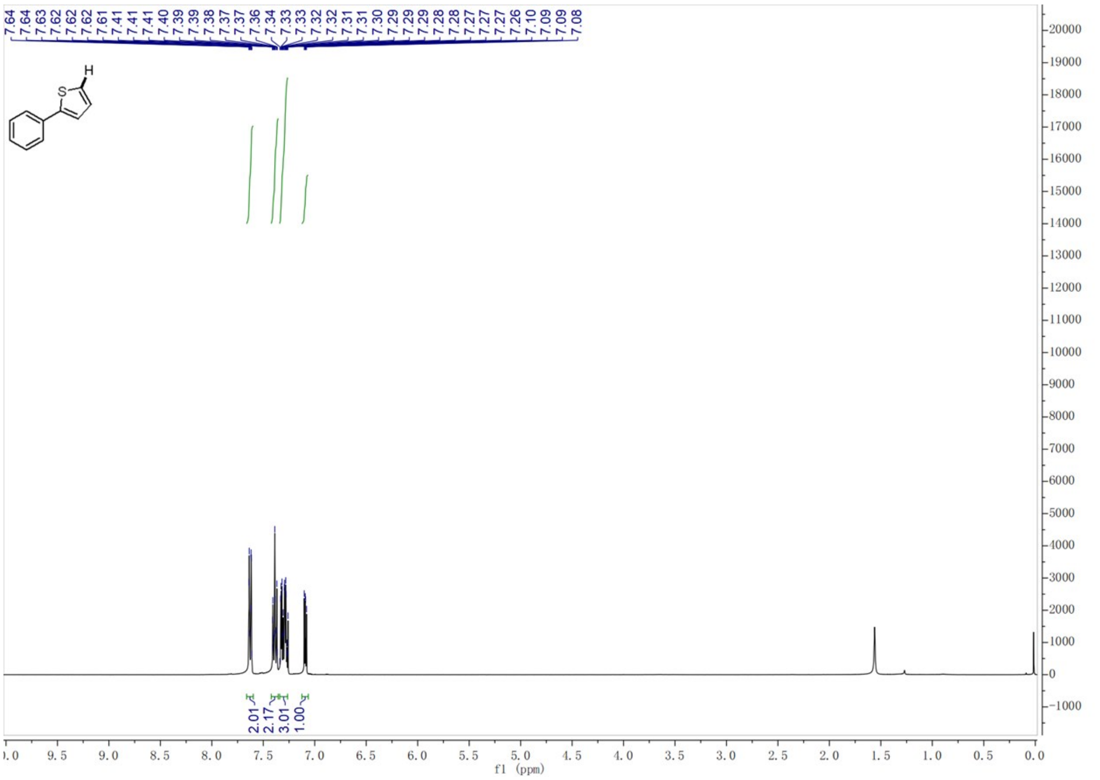


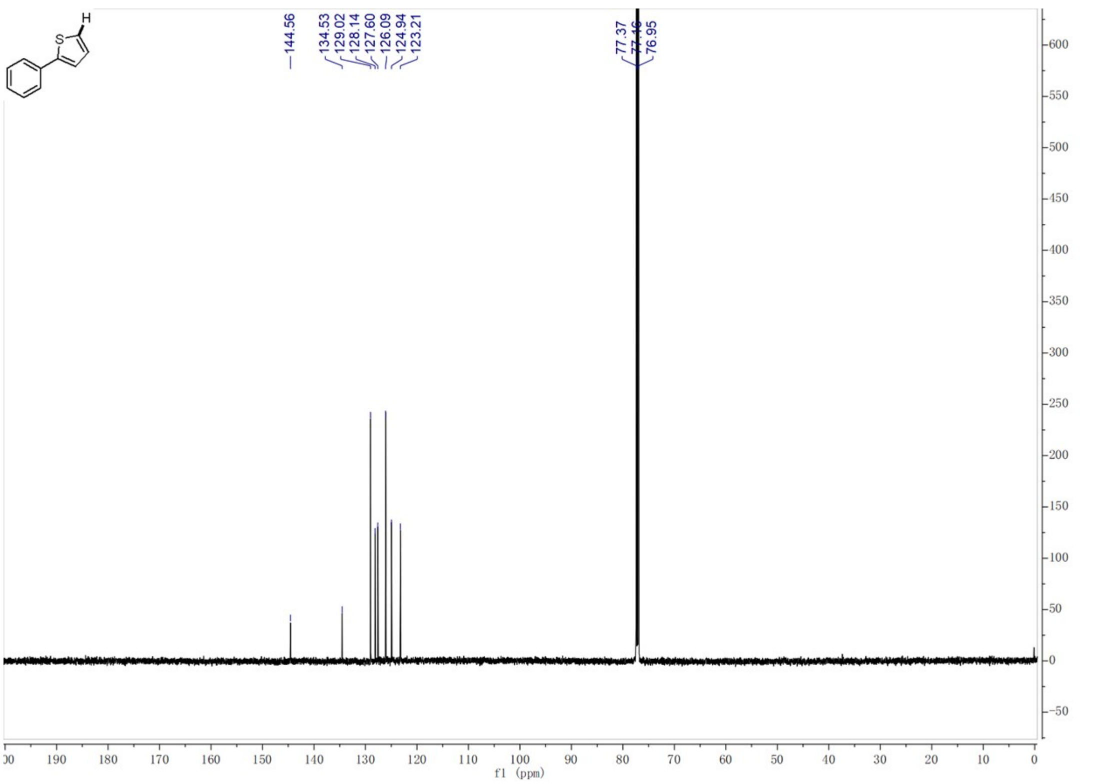
**4-H** $^{1}$H NMR and $^{13}$C NMR



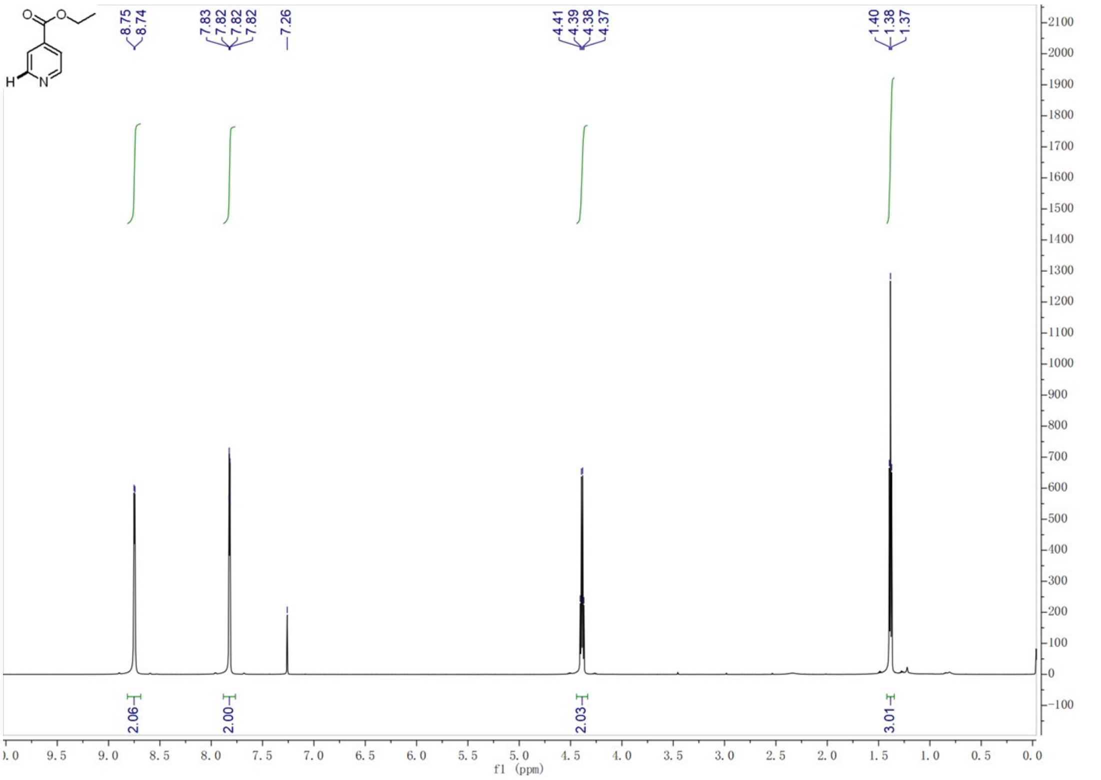



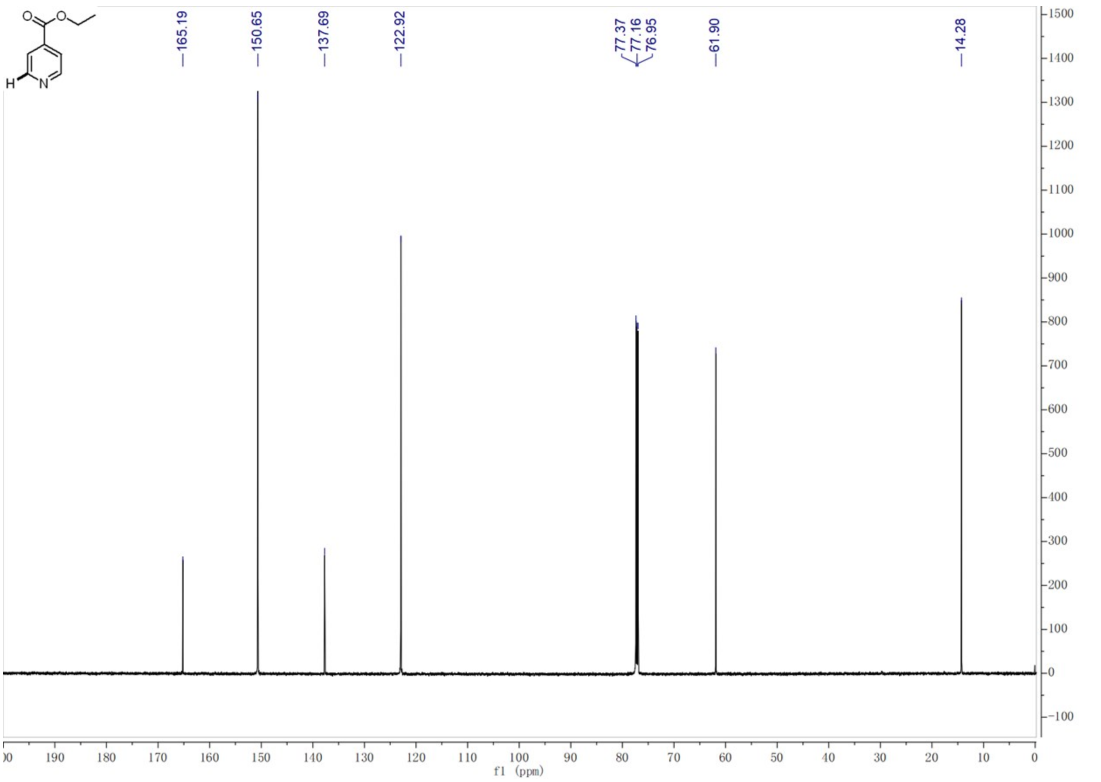
**5-H** $^{1}$H NMR and $^{13}$C NMR



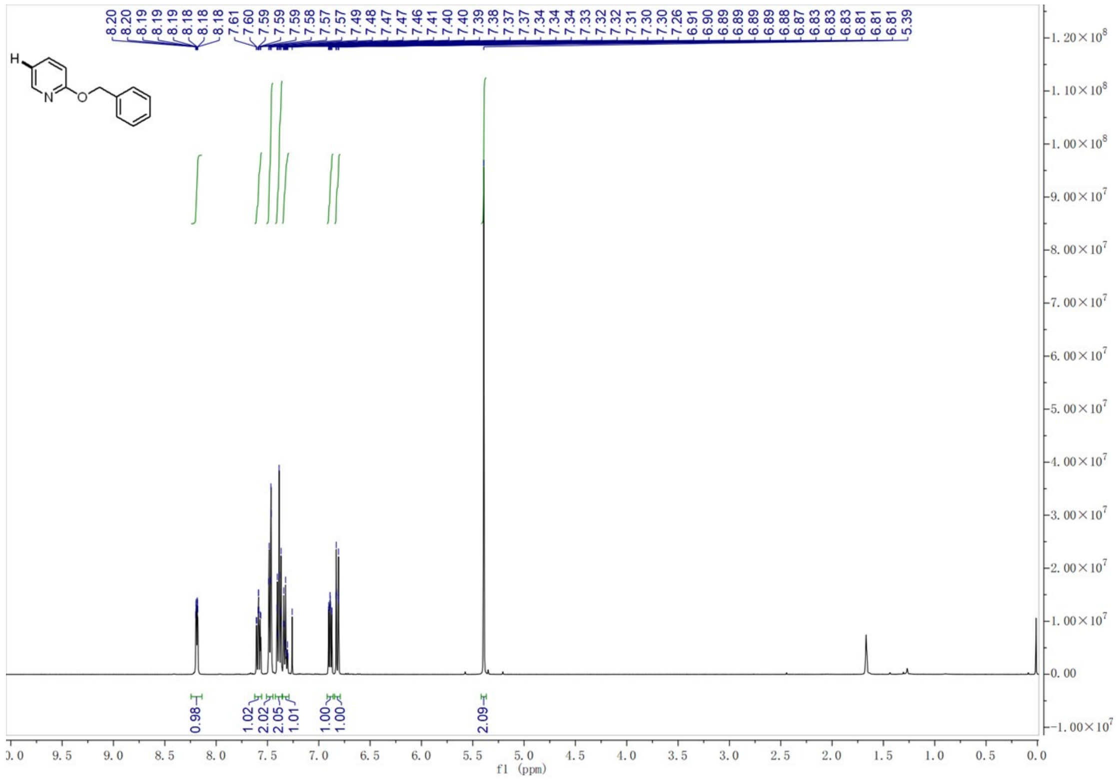



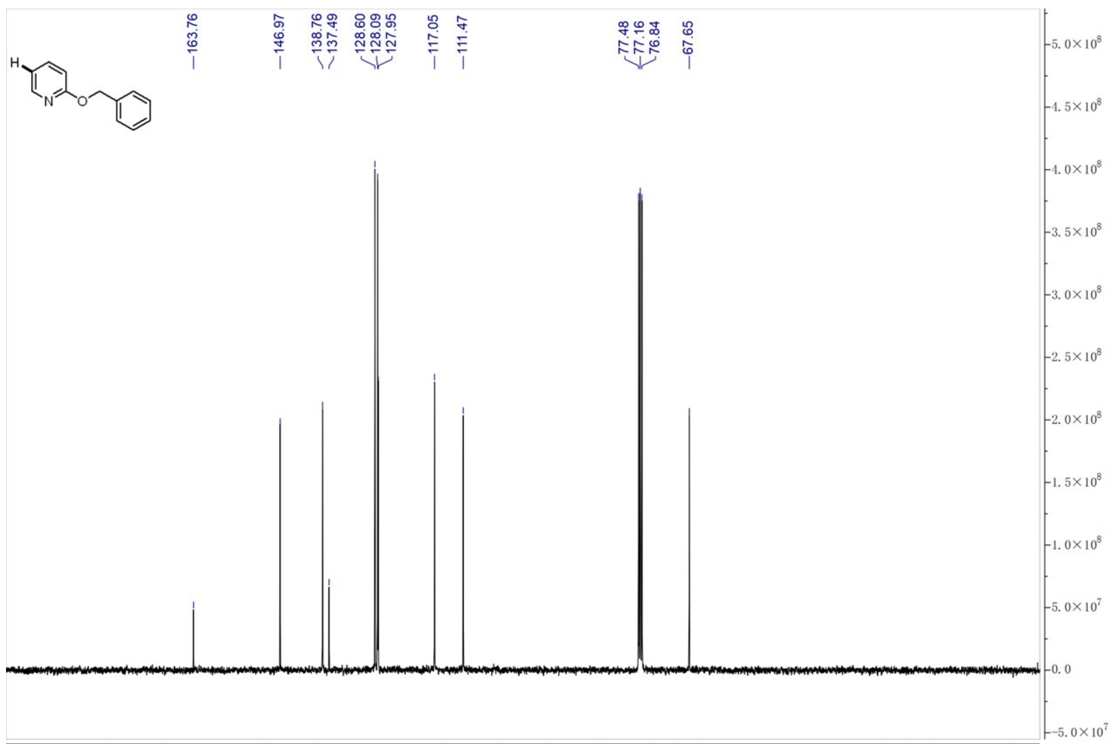
**6-H** $^{1}$H NMR and $^{13}$C NMR



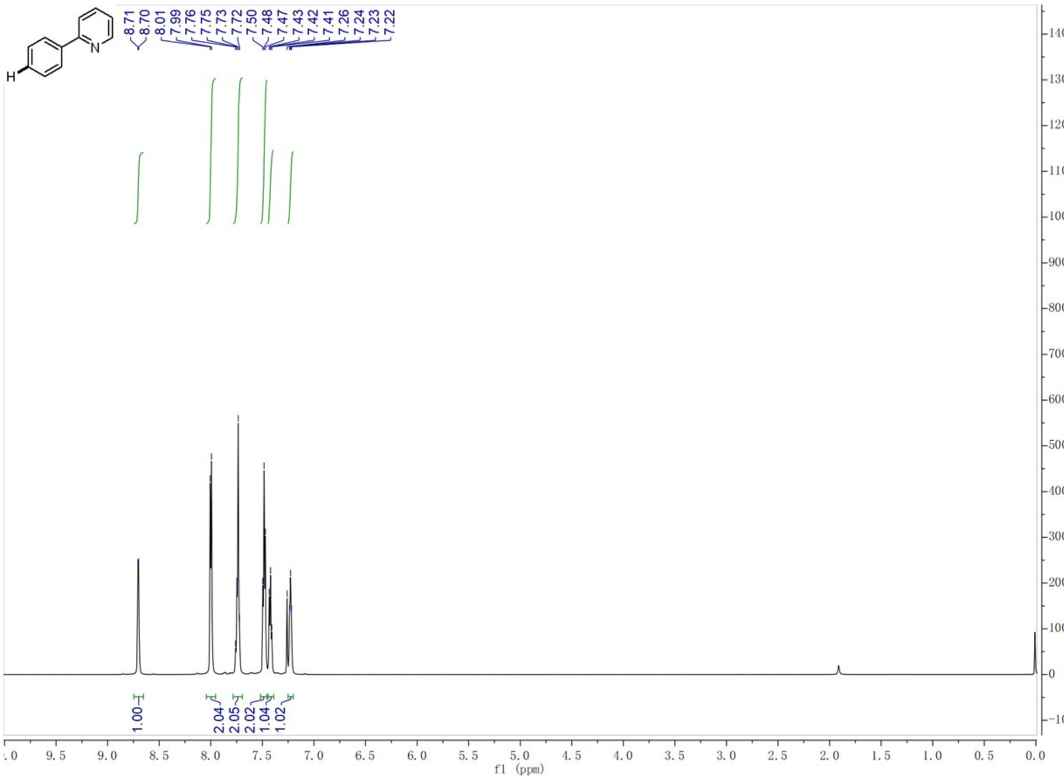


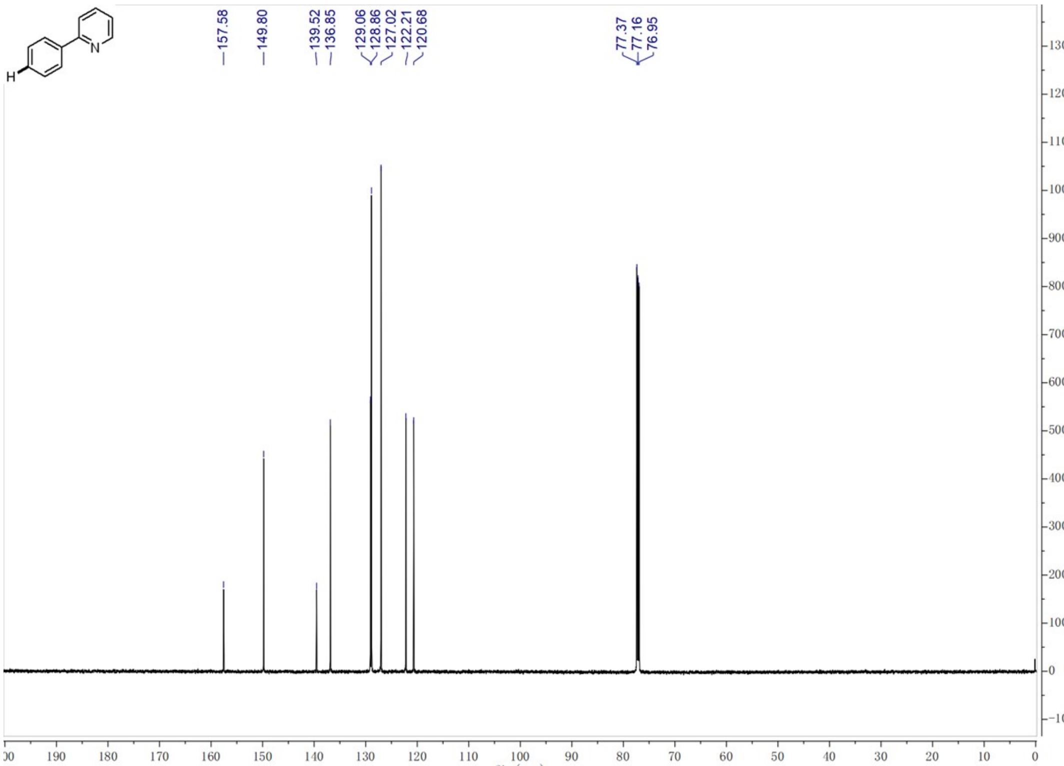
**7-H** $^{1}H$ NMR and $^{13}C$ NMR



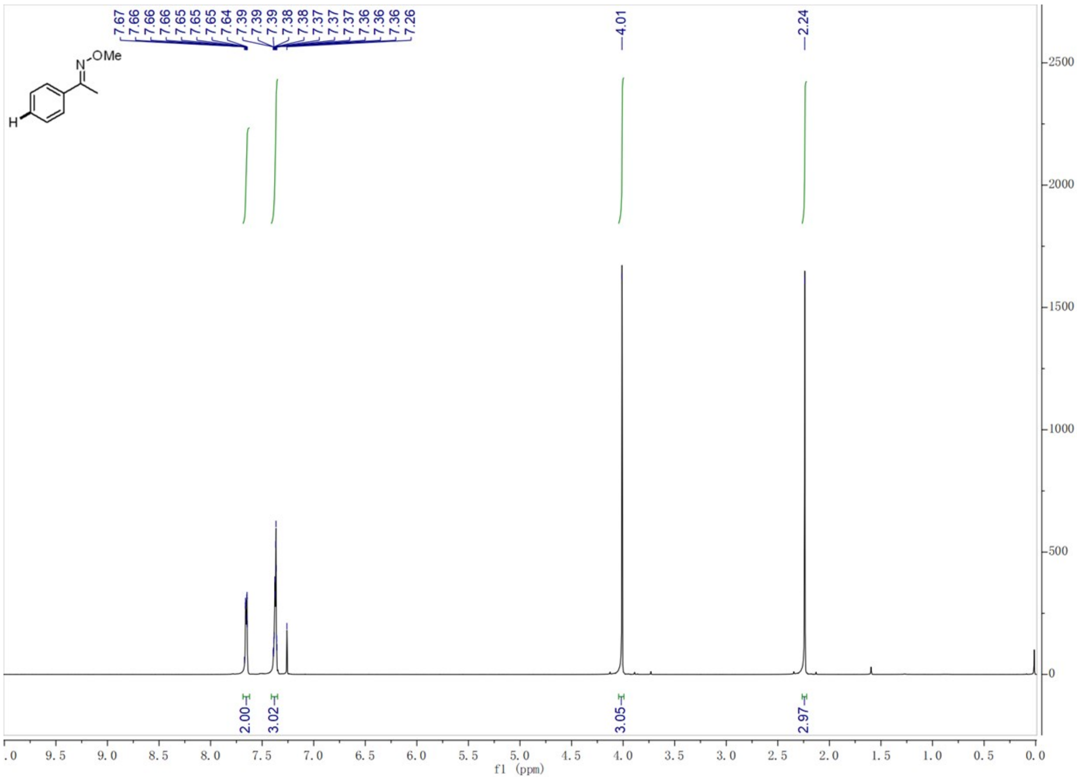


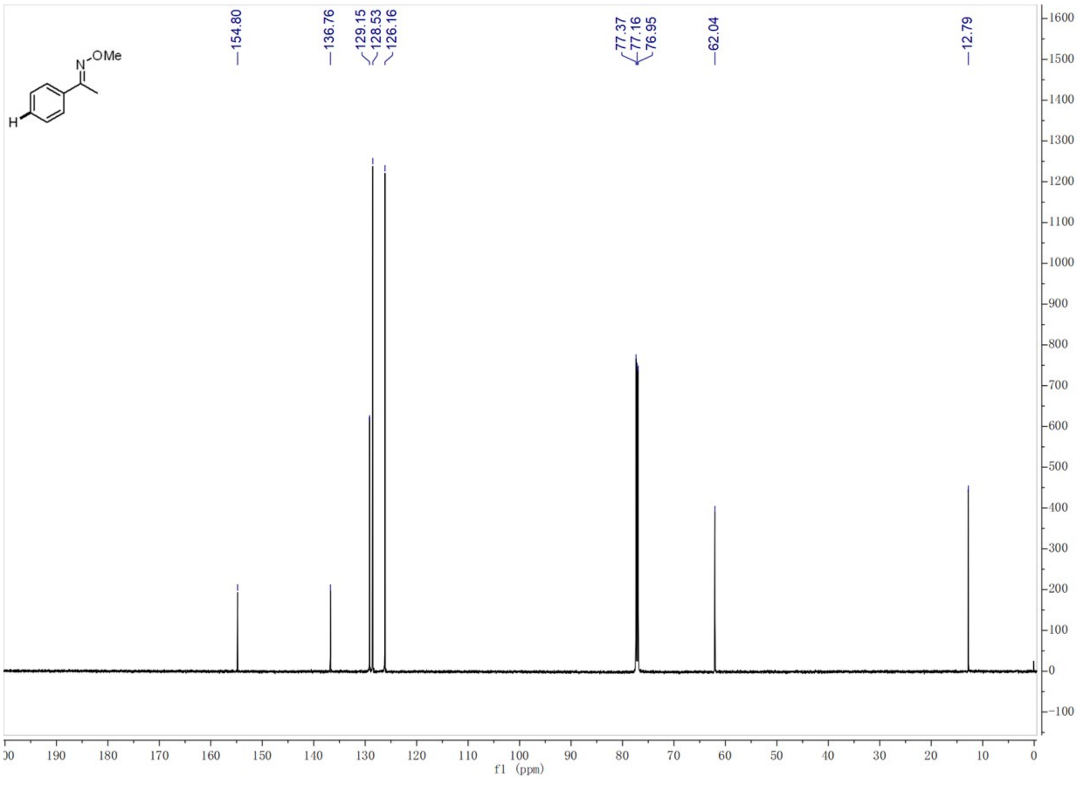
**8-H** $^1$H NMR and $^{13}$C NMR



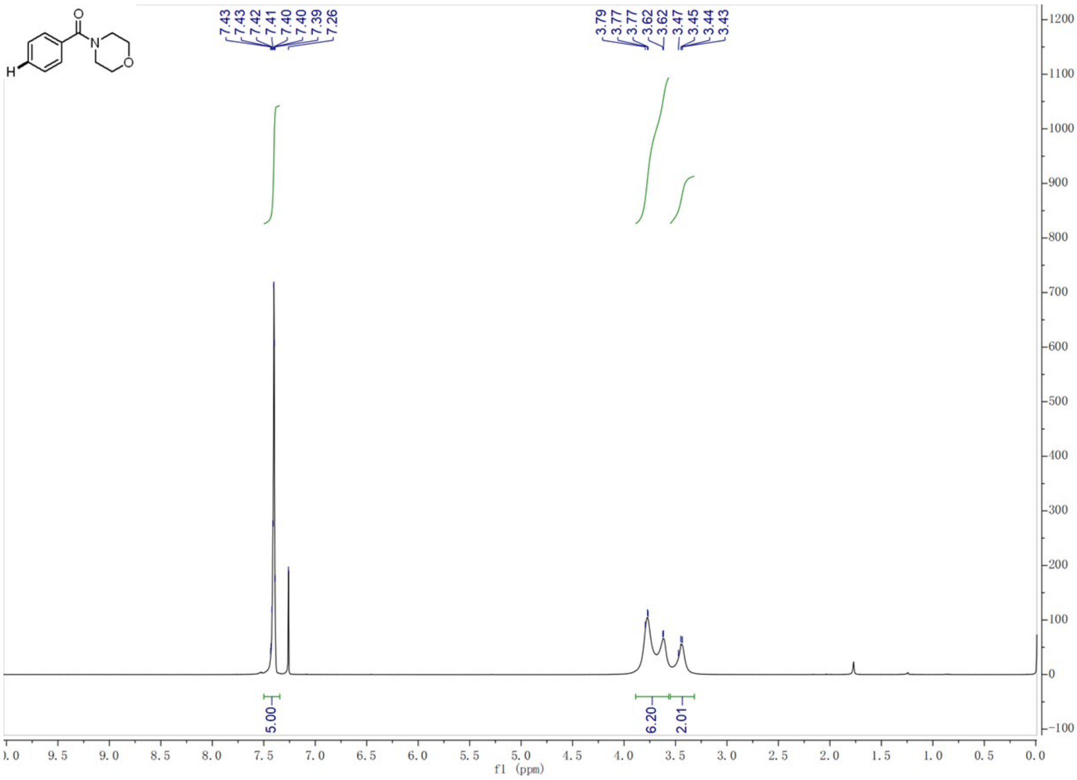



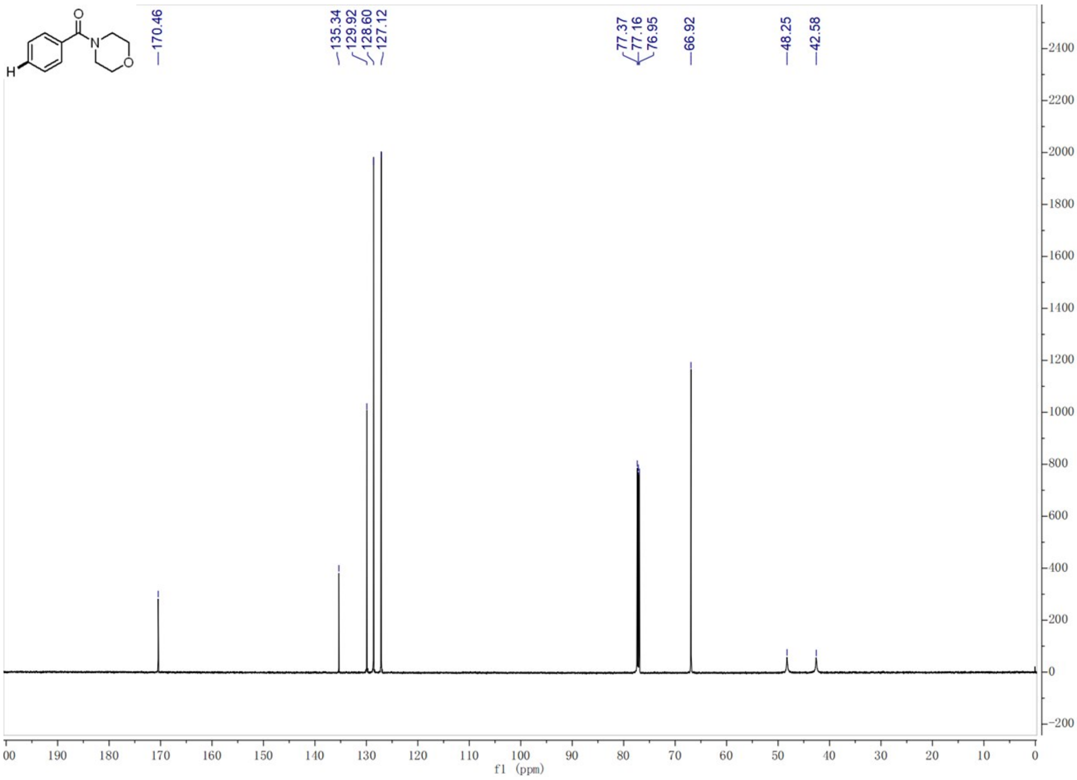
**9-H** $^{1}$H NMR and $^{13}$C NMR



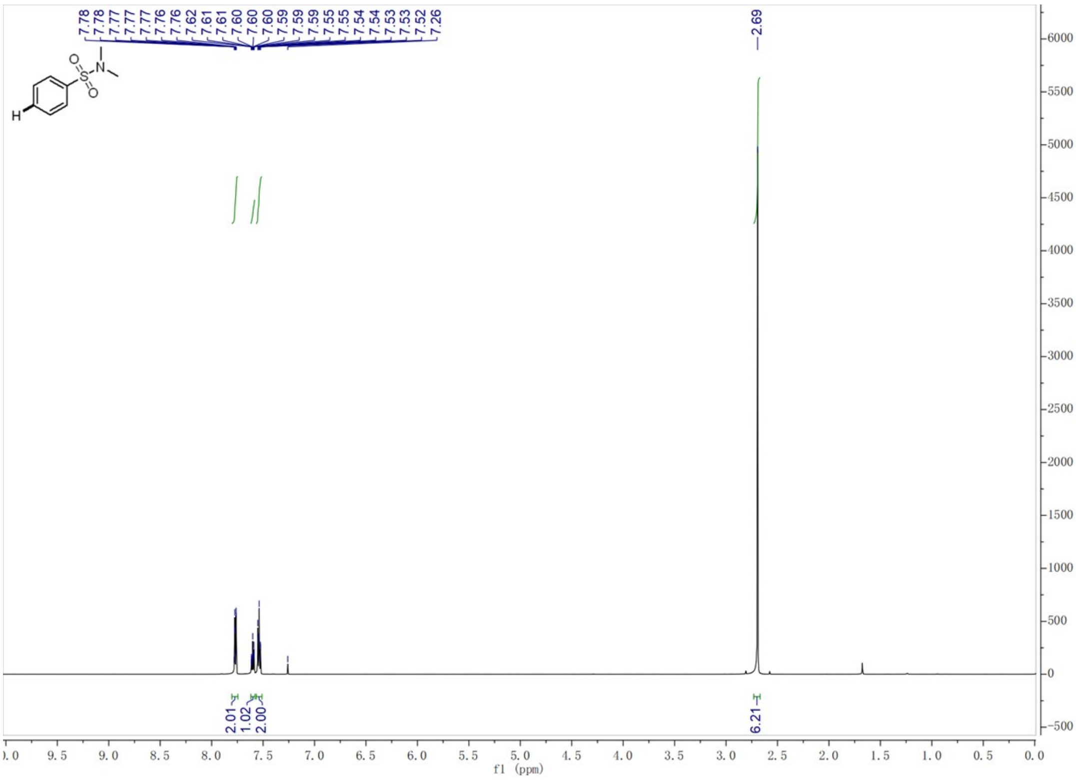


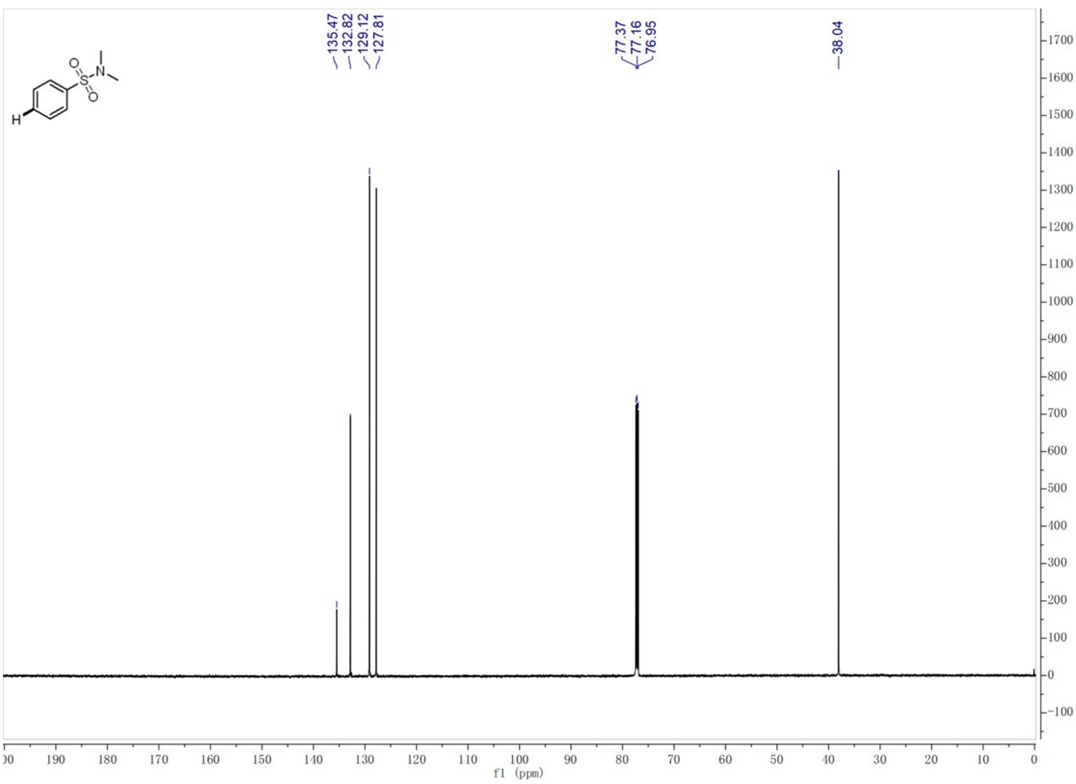
**10-H** $^{1}$H NMR and $^{13}$C NMR



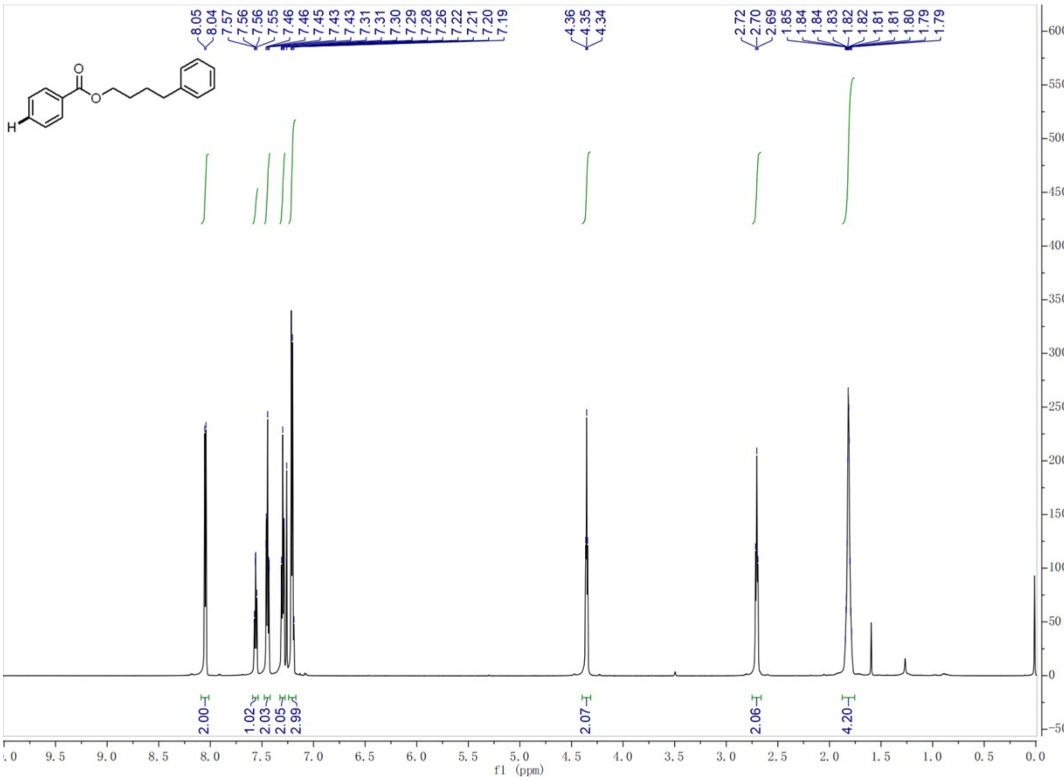


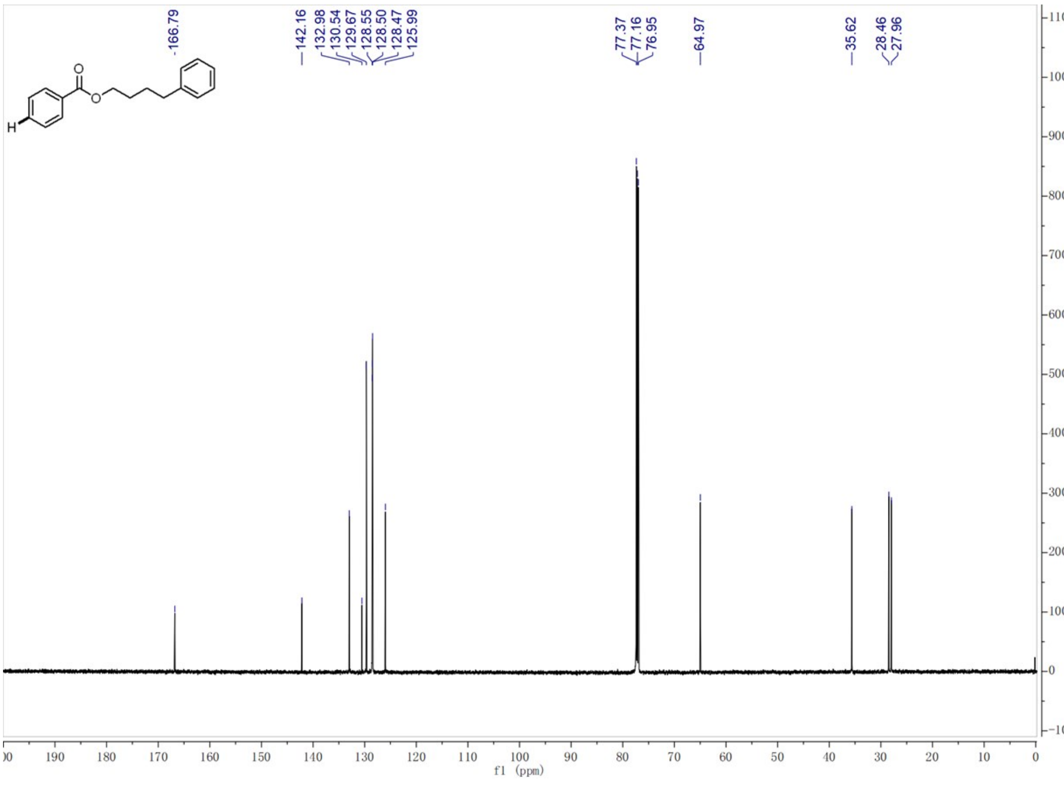
**11-H** $^1$H NMR and $^{13}$C NMR



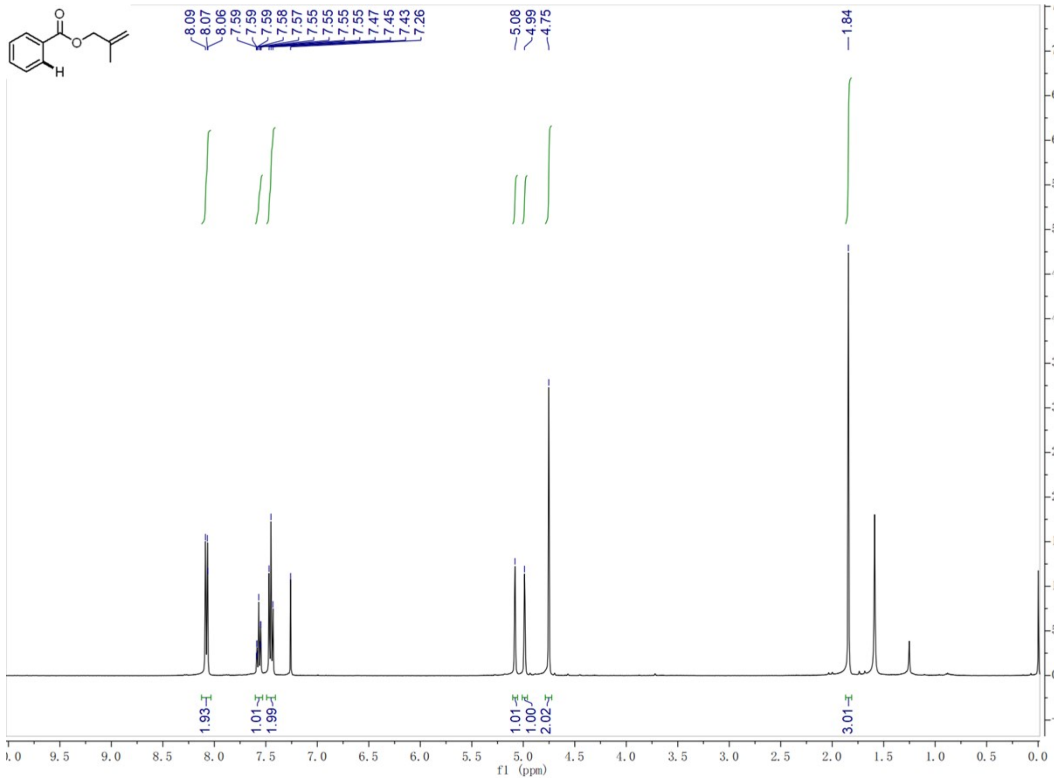



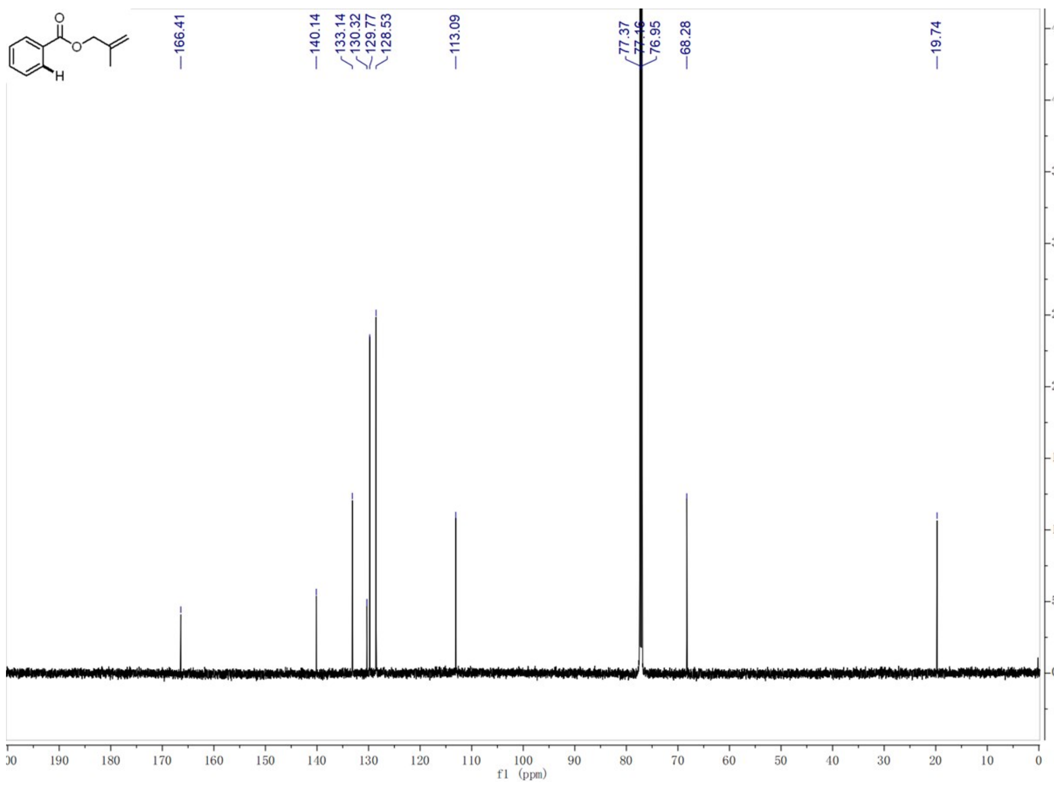
**12-H** $^1$H NMR and $^{13}$C NMR



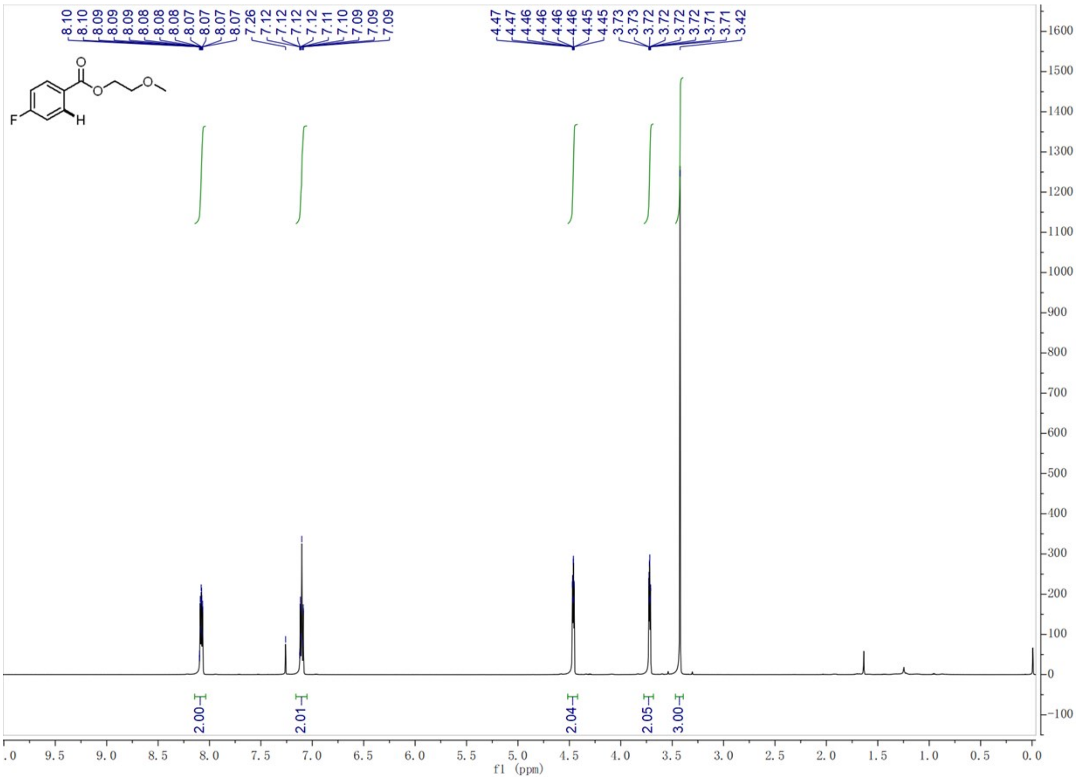


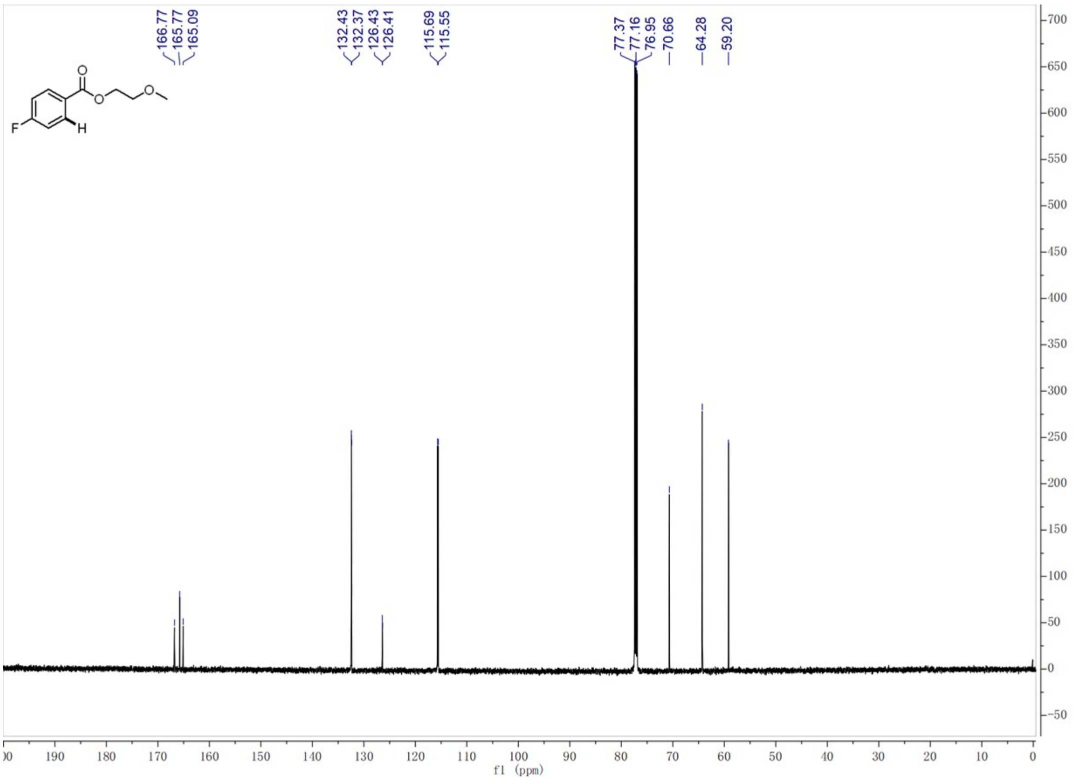
**13-H** $^{1}$H NMR and $^{13}$C NMR

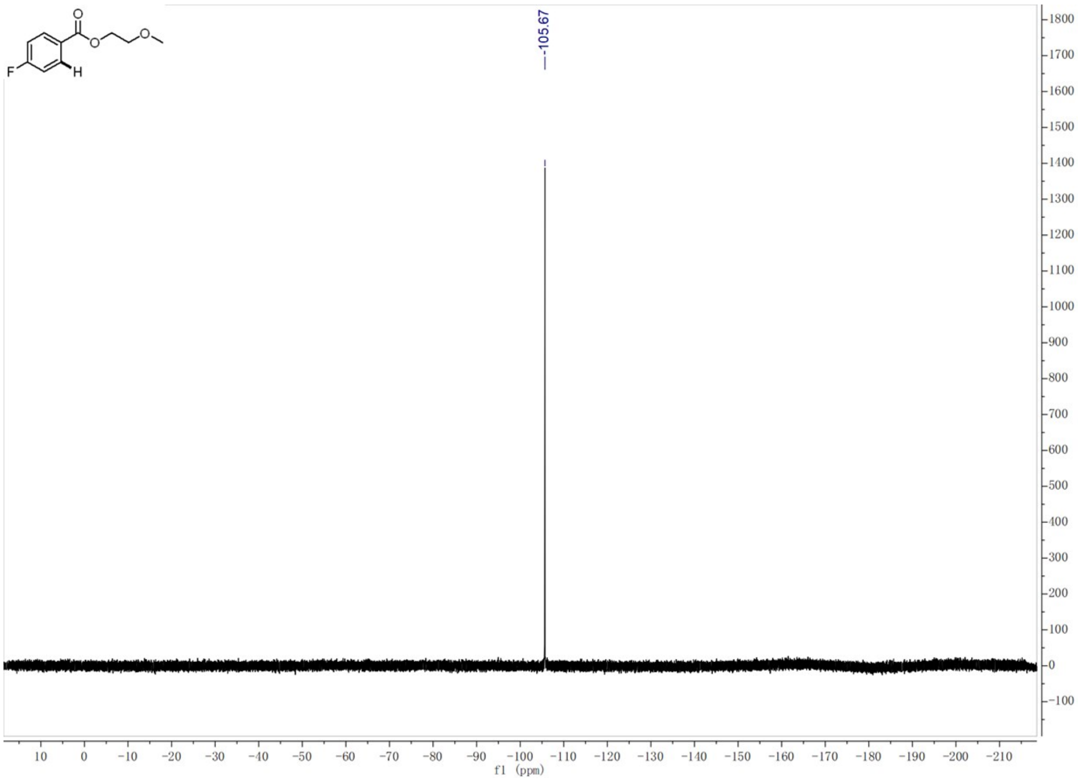


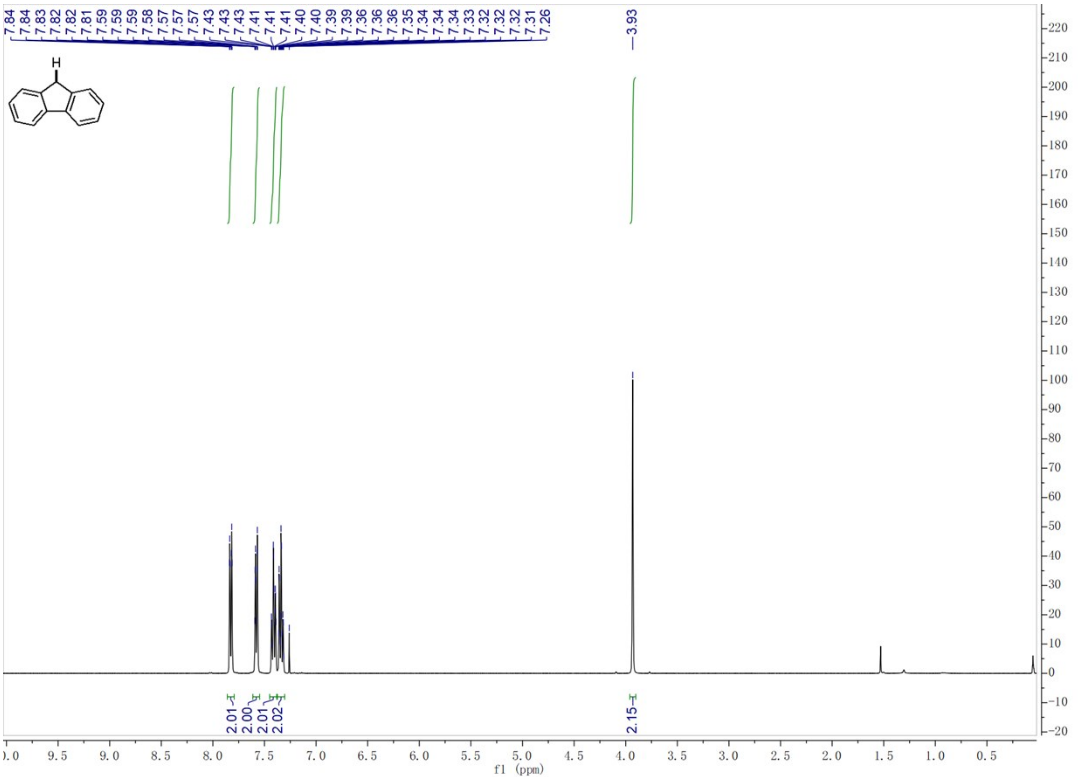
**14-H** $^{1}$H NMR, $^{13}$C NMR and $^{19}$F NMR

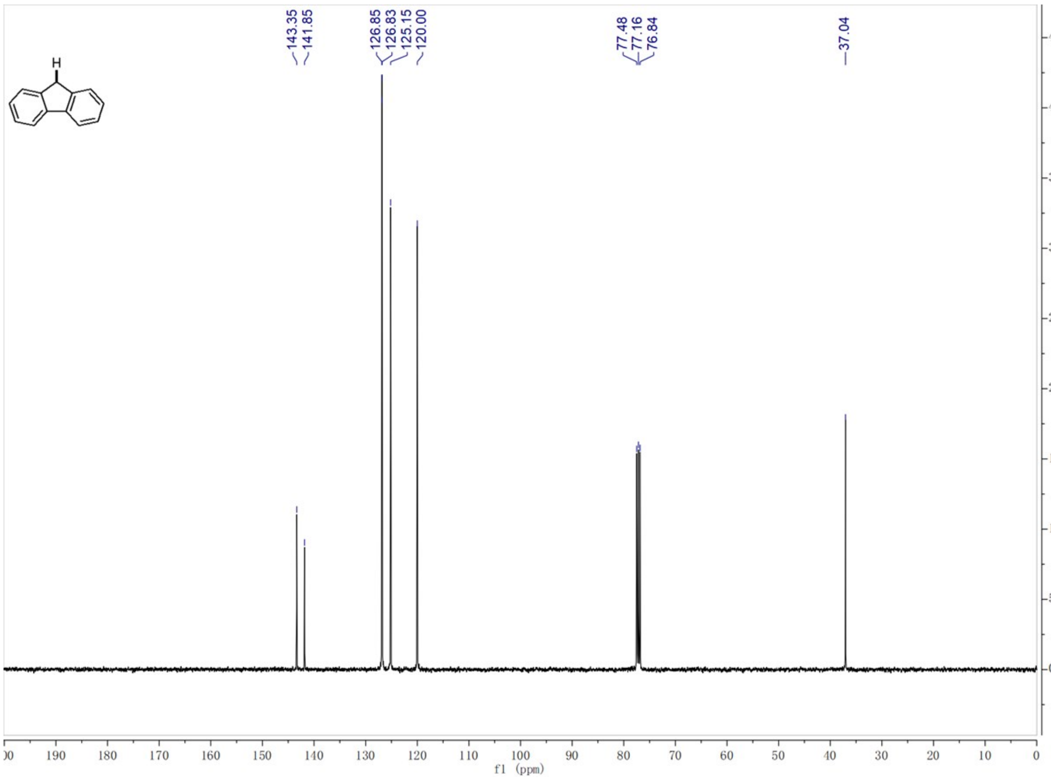


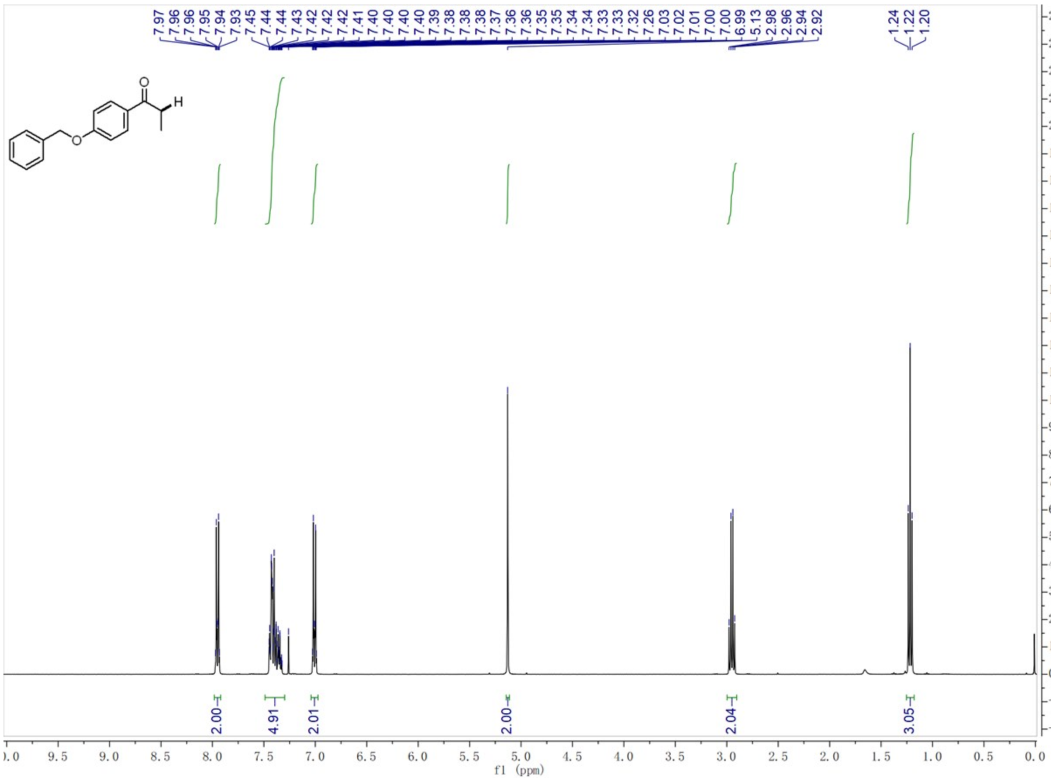


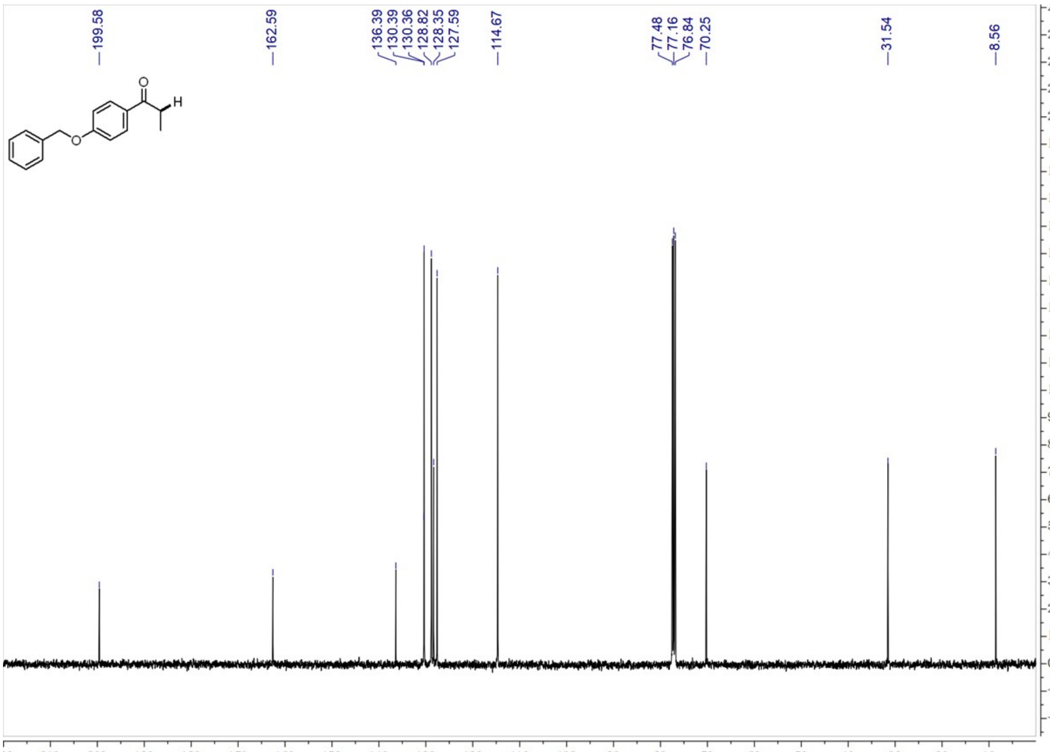

**15-H** $^{1}$H NMR and $^{13}$C NMR



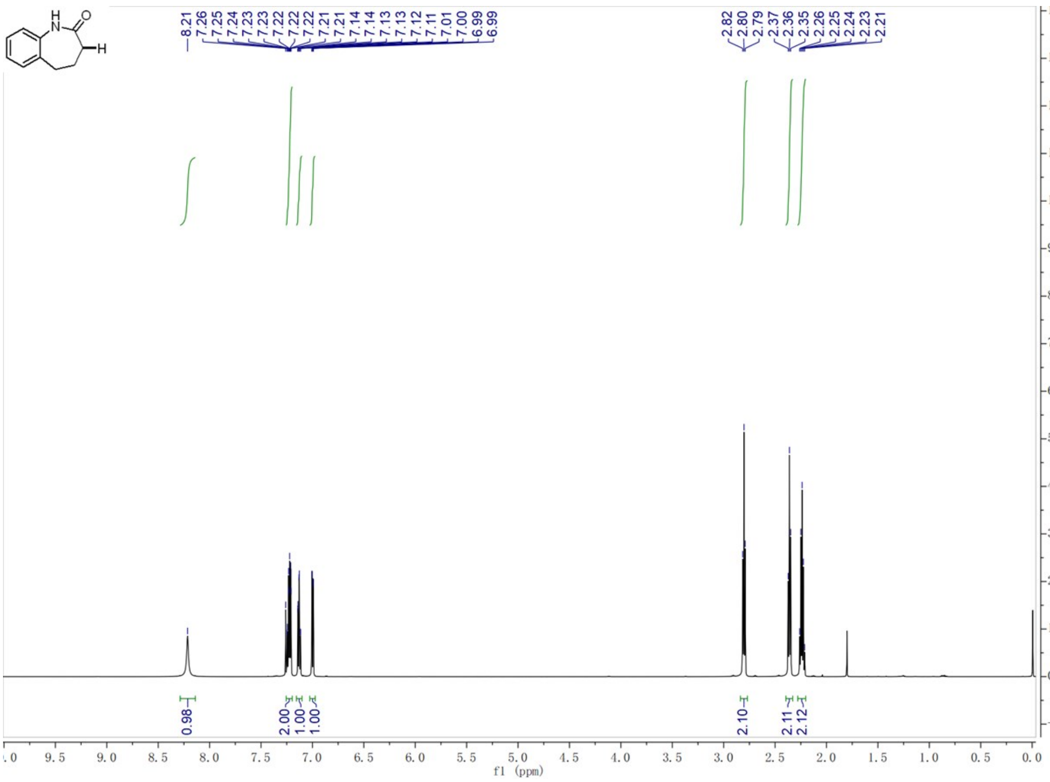


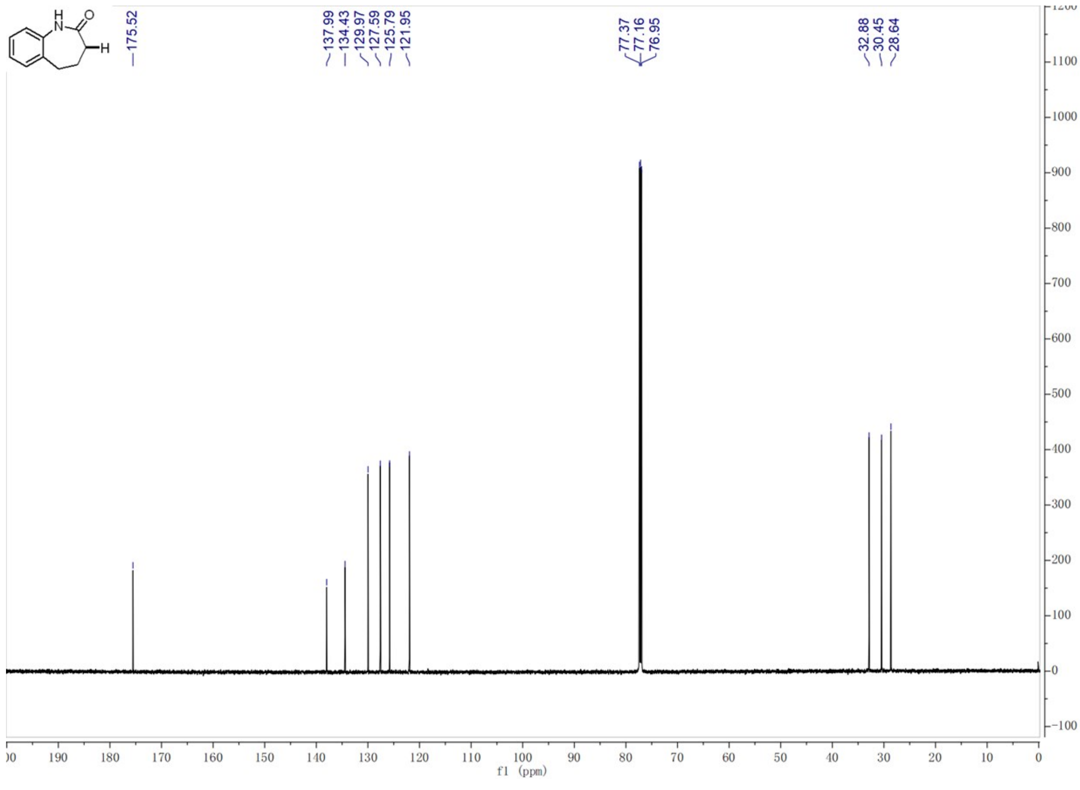
**16-H** $^{1}$H NMR and $^{13}$C NMR



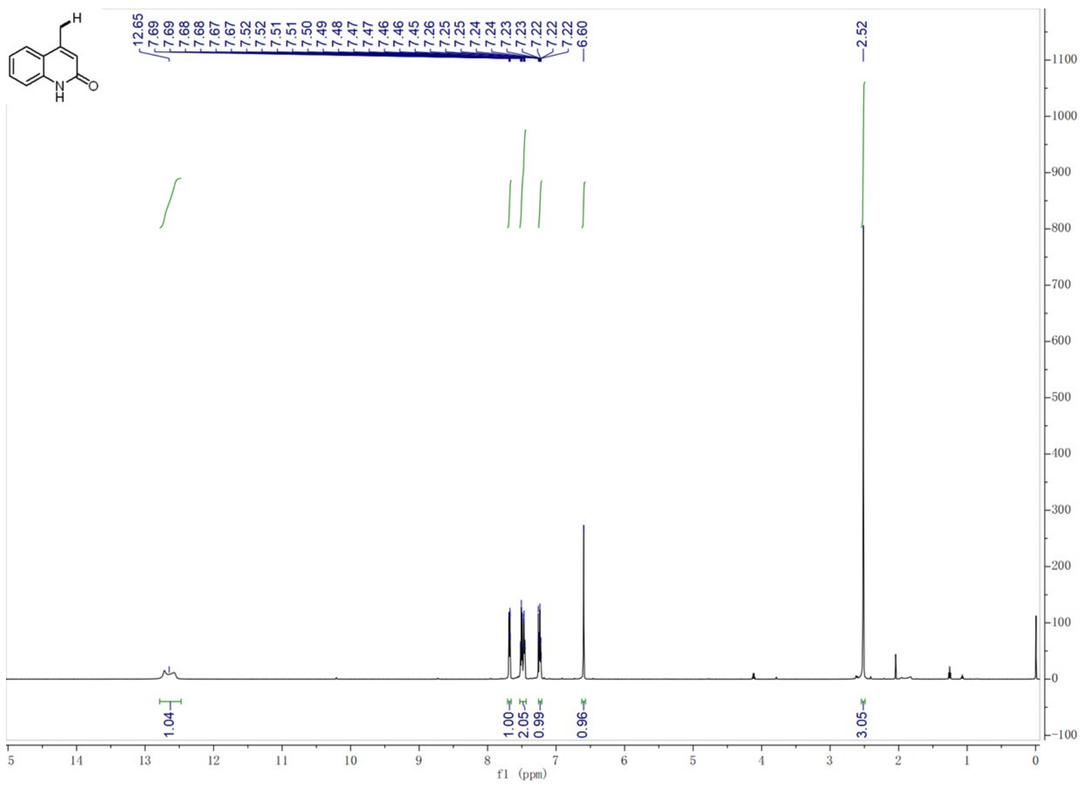


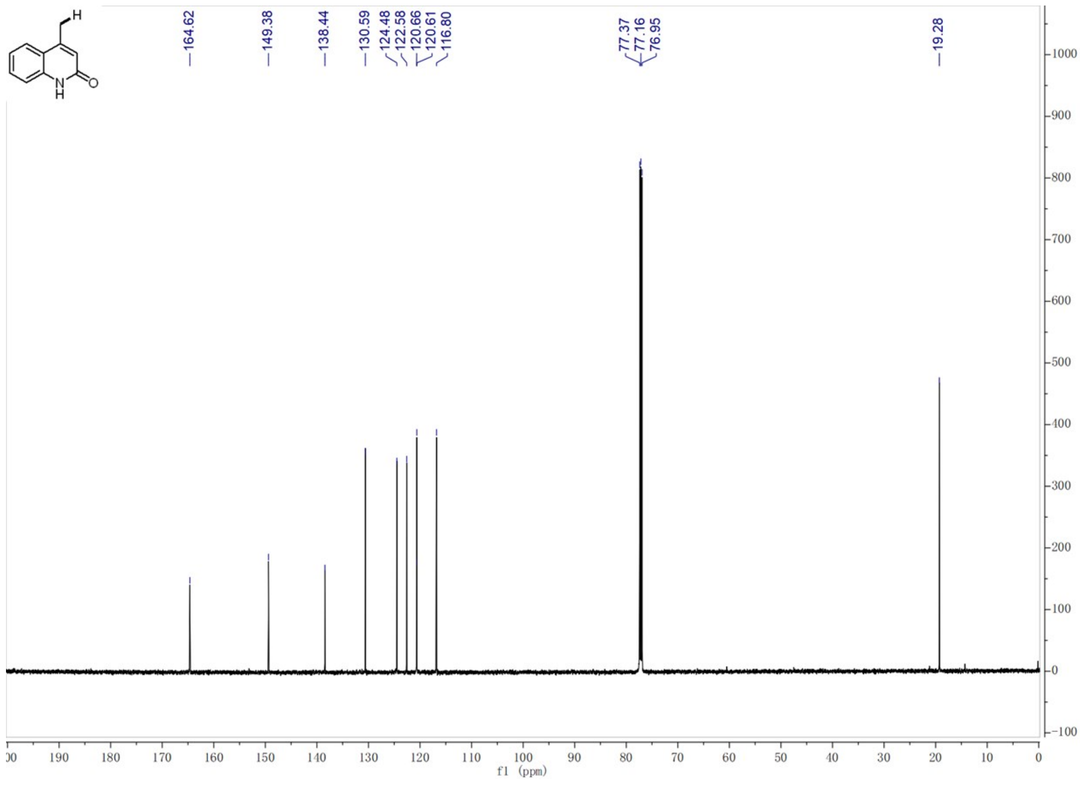

**17-H** $^{1}$H NMR and $^{13}$C NMR



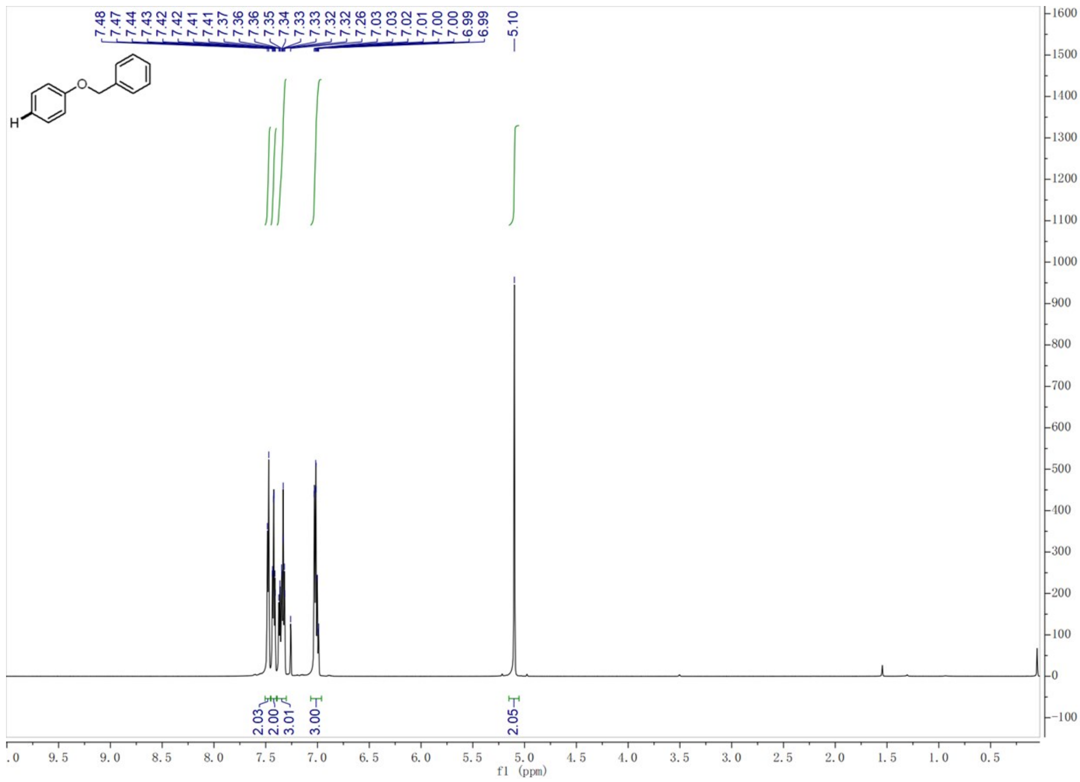


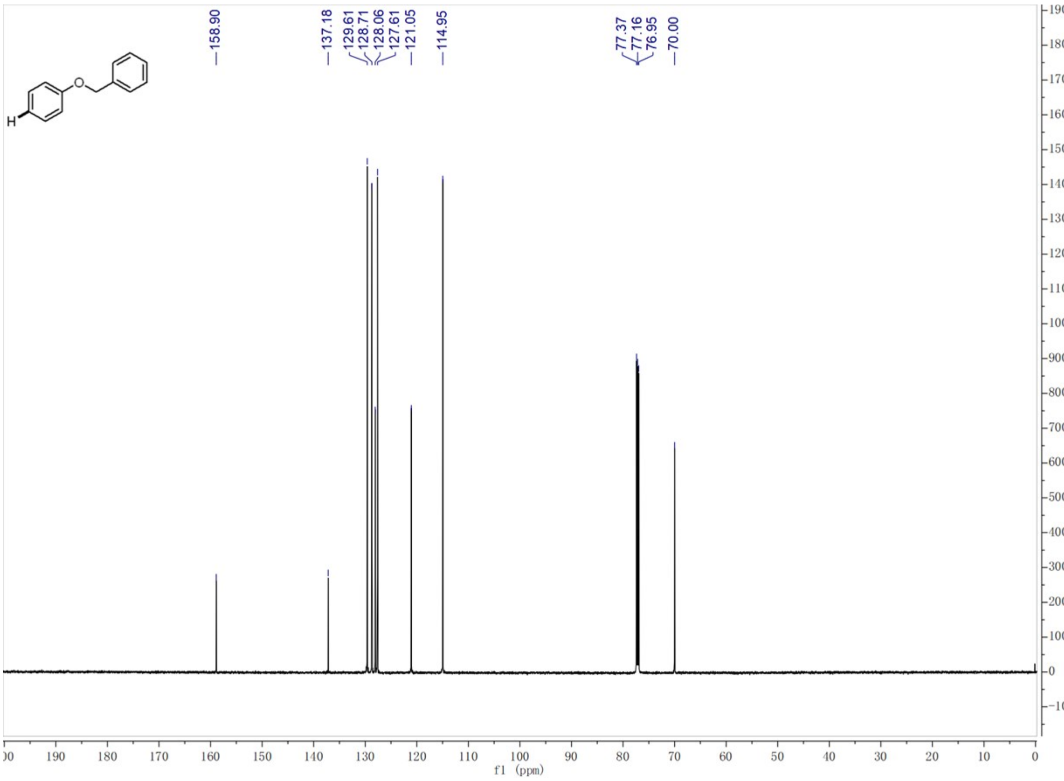
**18-H** $^{1}$H NMR and $^{13}$C NMR



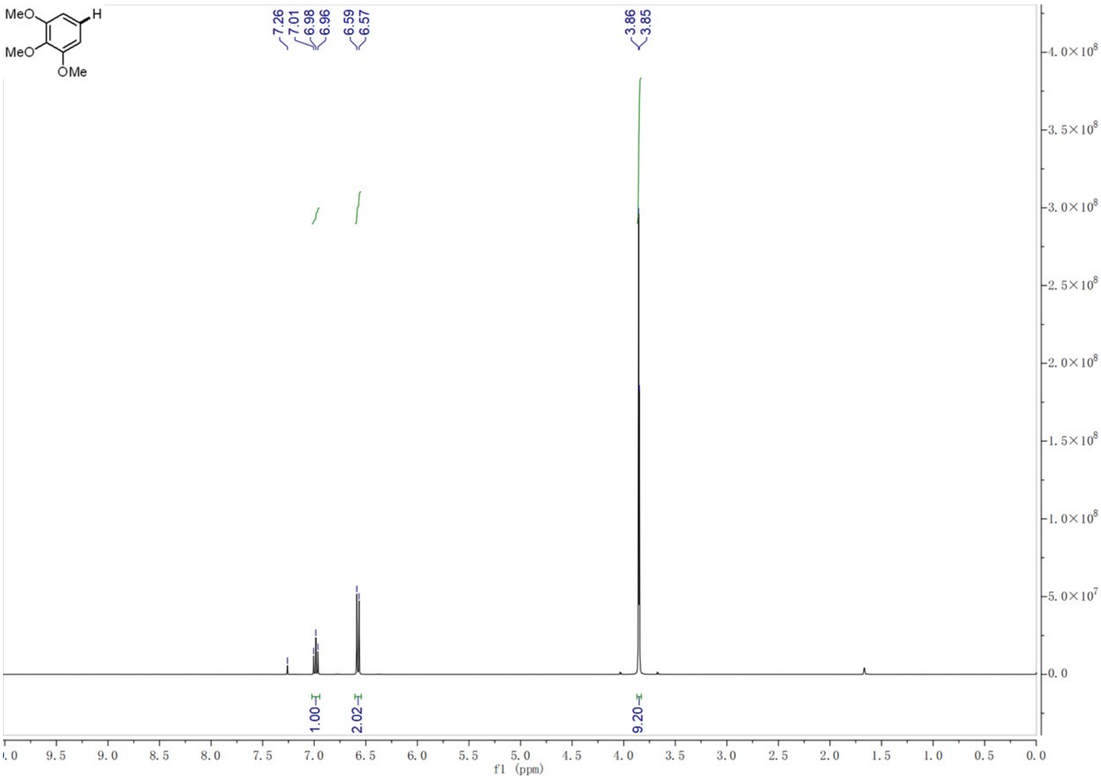


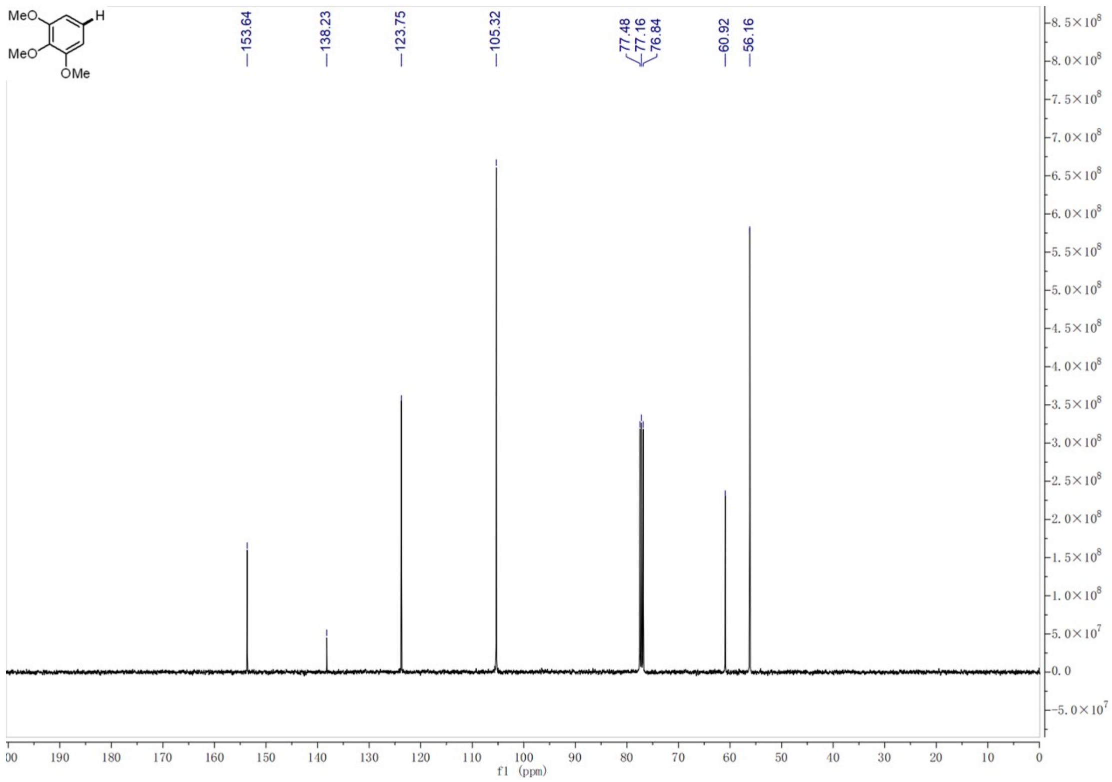
**19-H** $^{1}$H NMR and $^{13}$C NMR



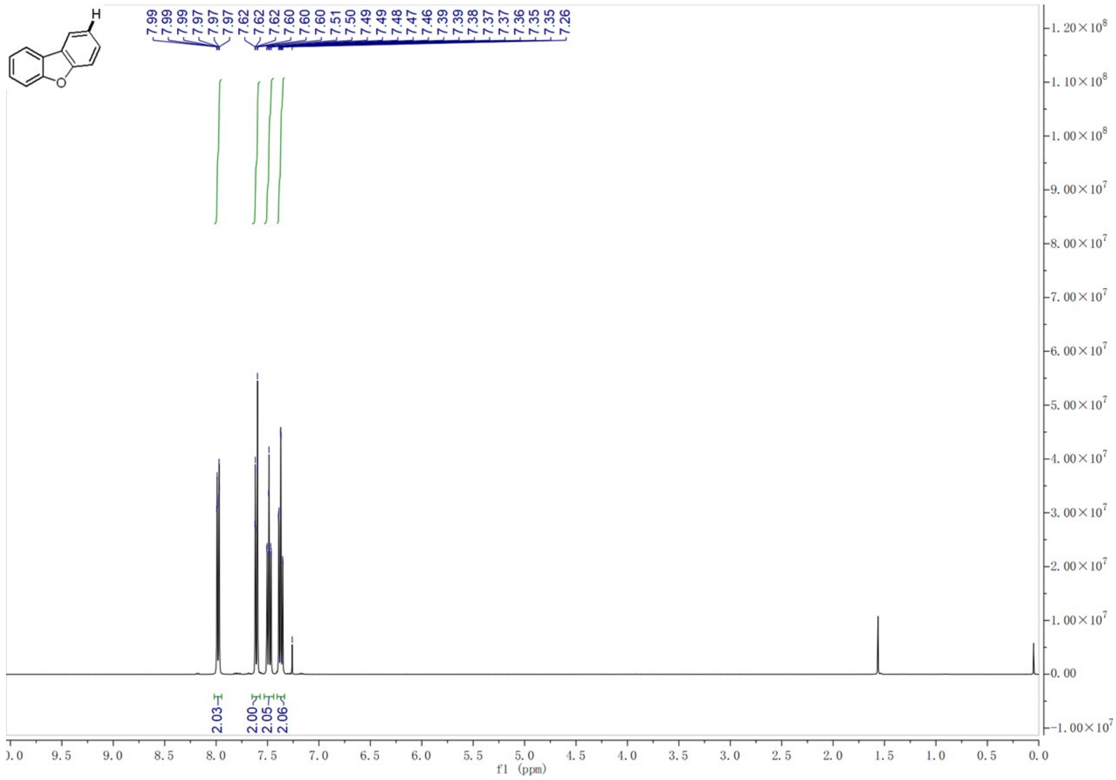


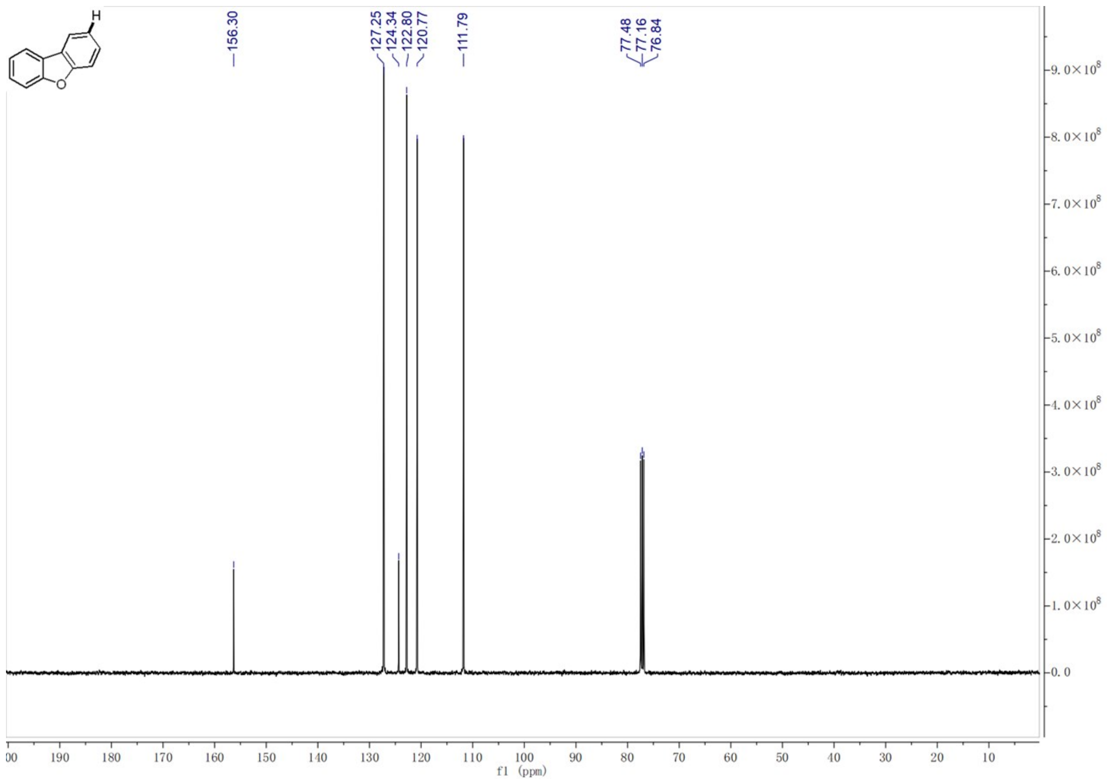

**20-H** $^{1}$H NMR and $^{13}$C NMR



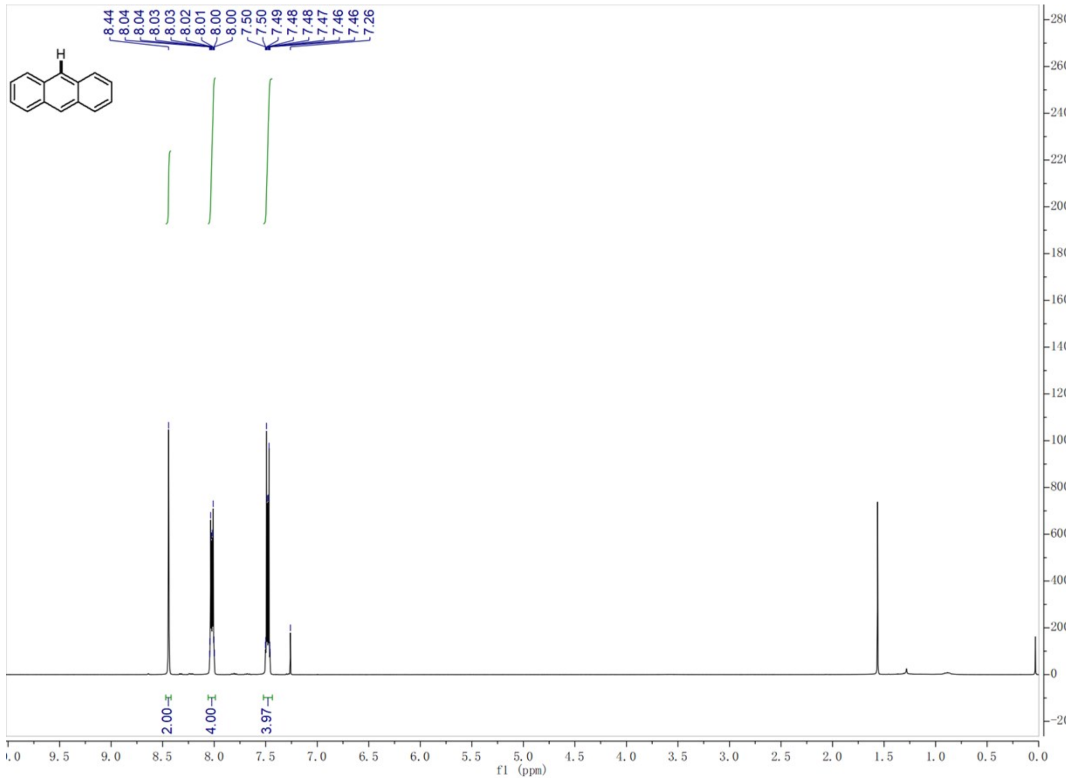


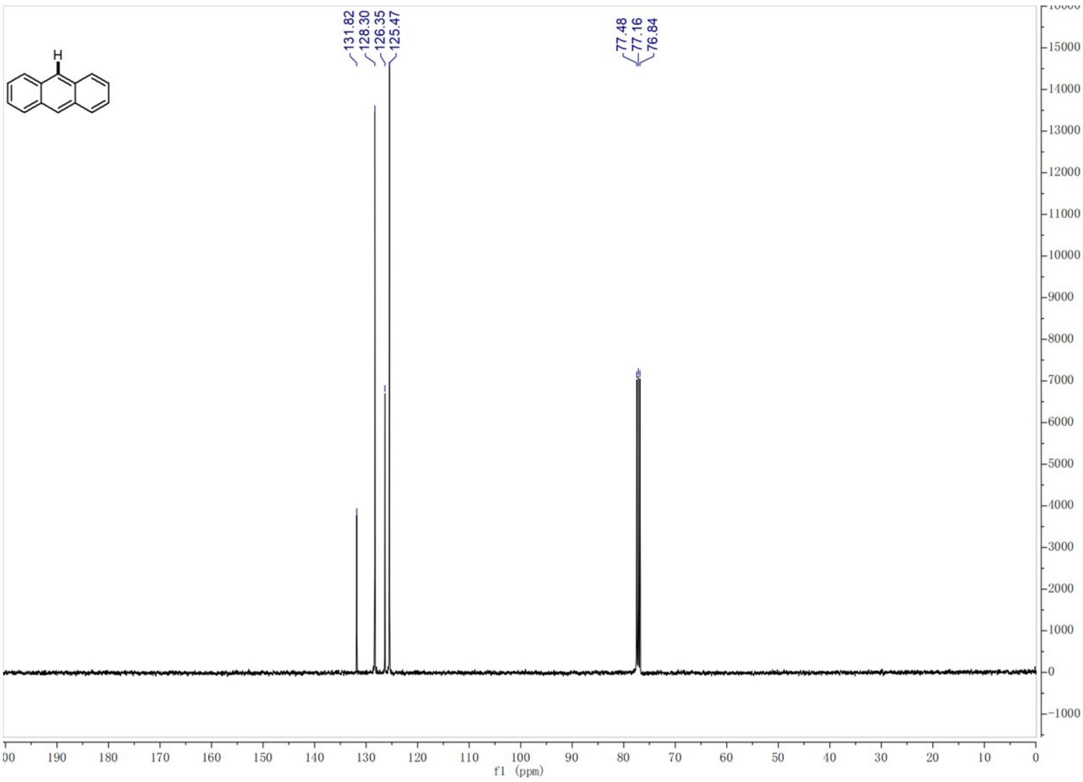
**21-H** $^{1}$H NMR and $^{13}$C NMR



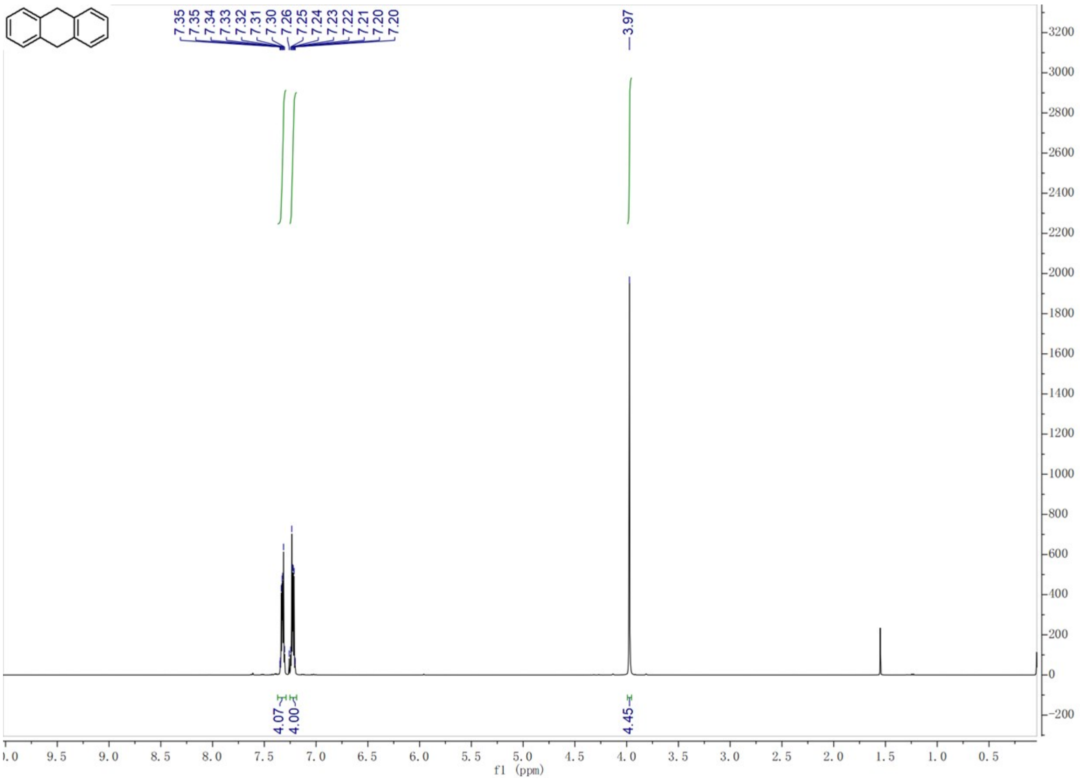


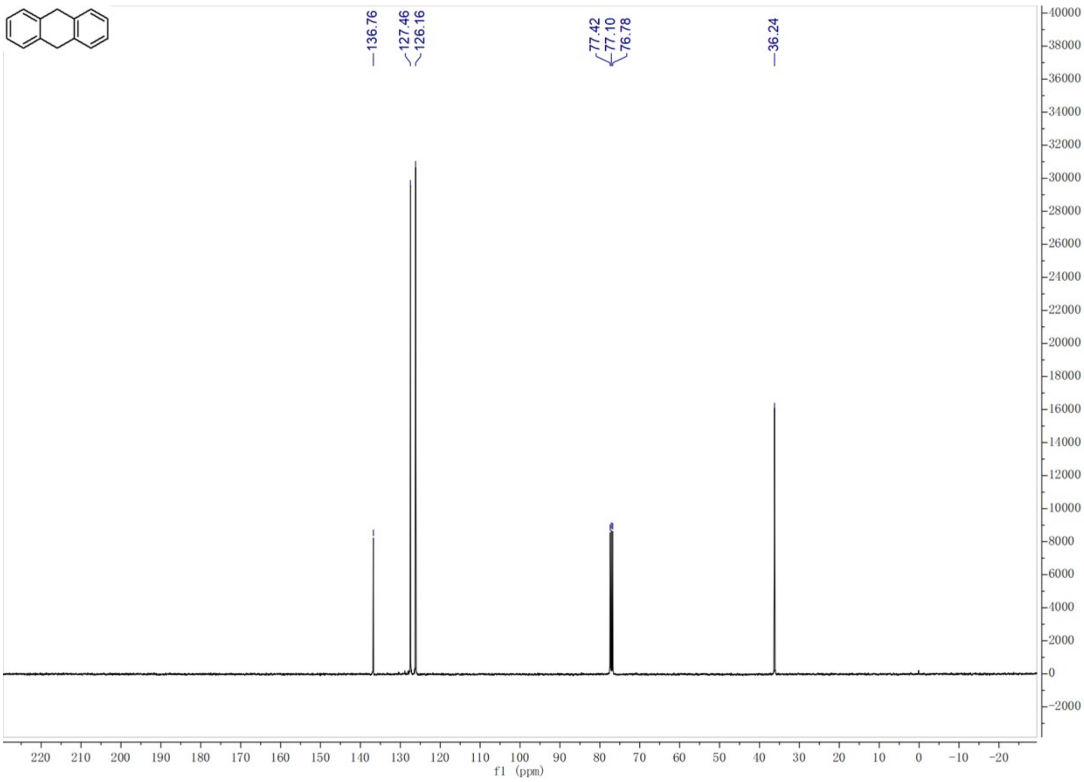

**22-H** $^{1}H$ NMR and $^{13}C$ NMR



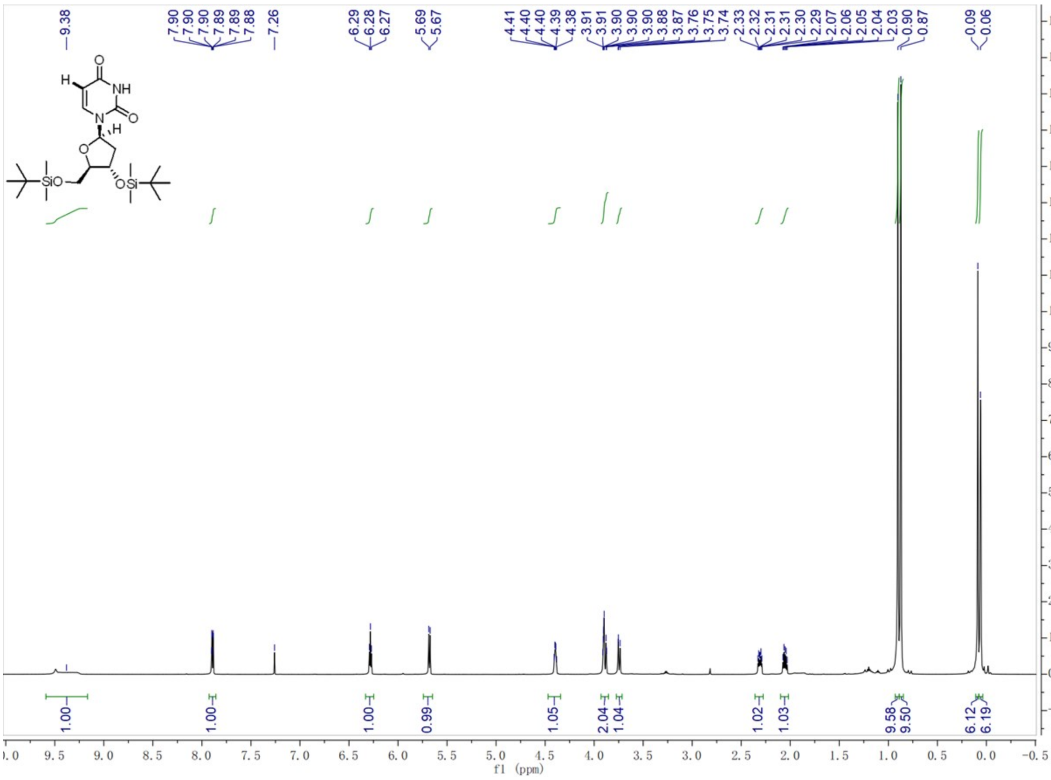


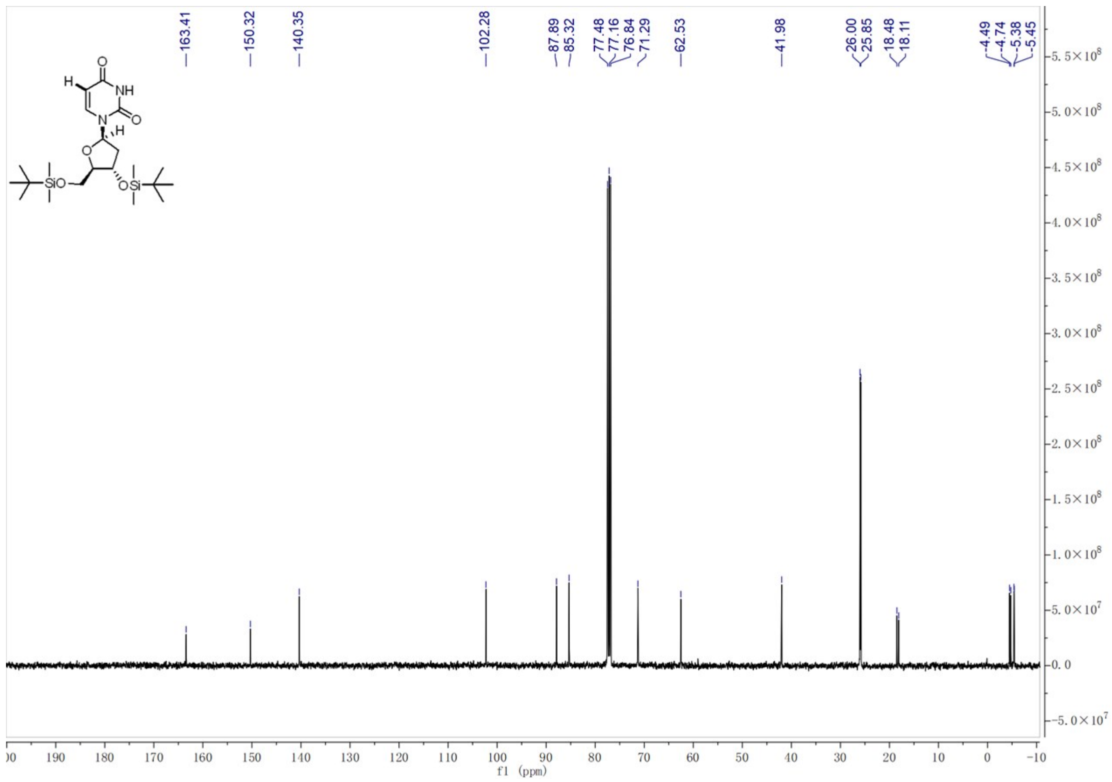
**22-H'** [1]H NMR and [13]C NMR



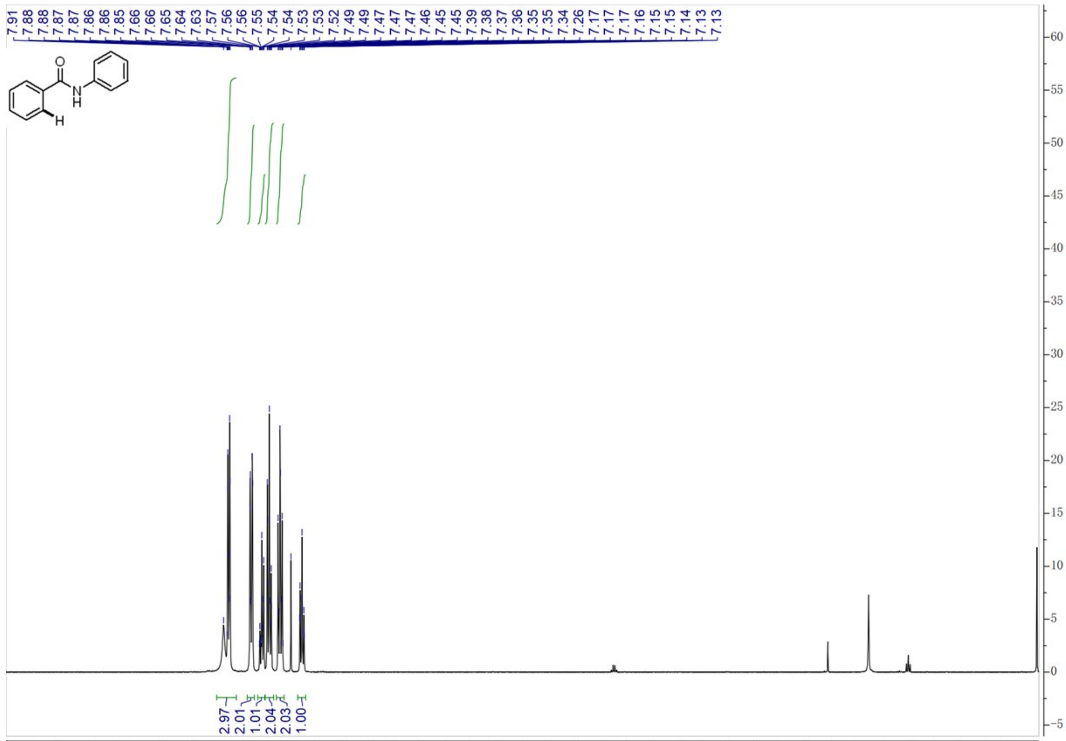


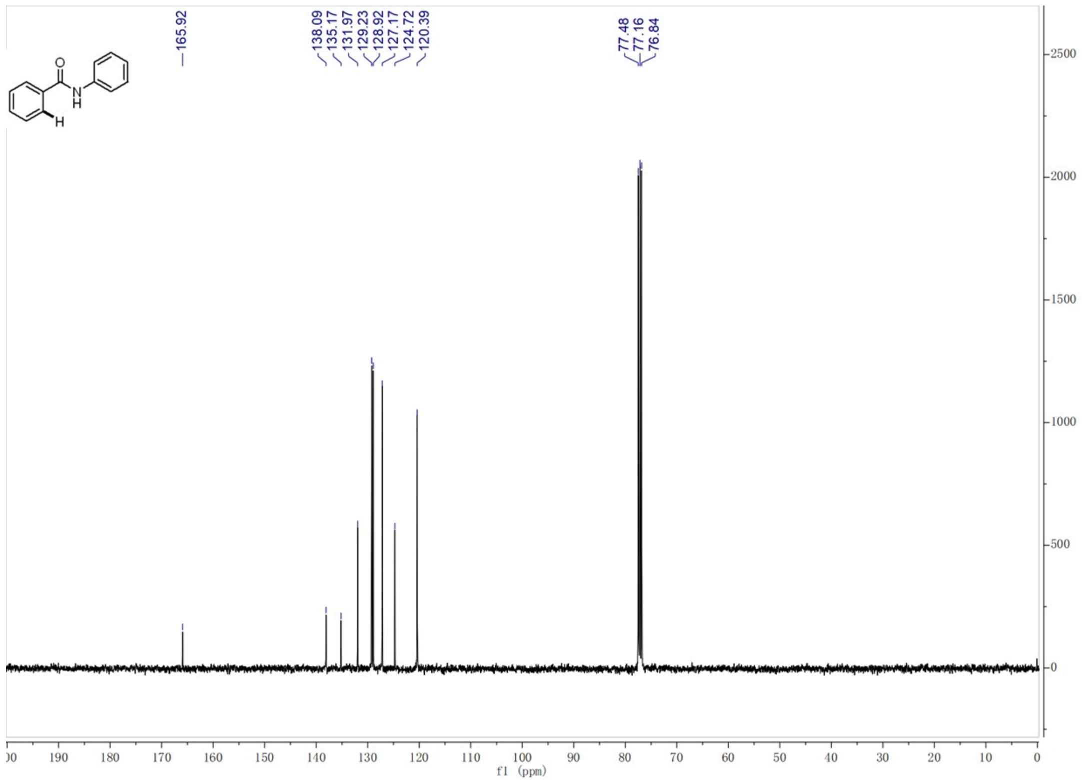
**23-H** $^{1}$H NMR and $^{13}$C NMR



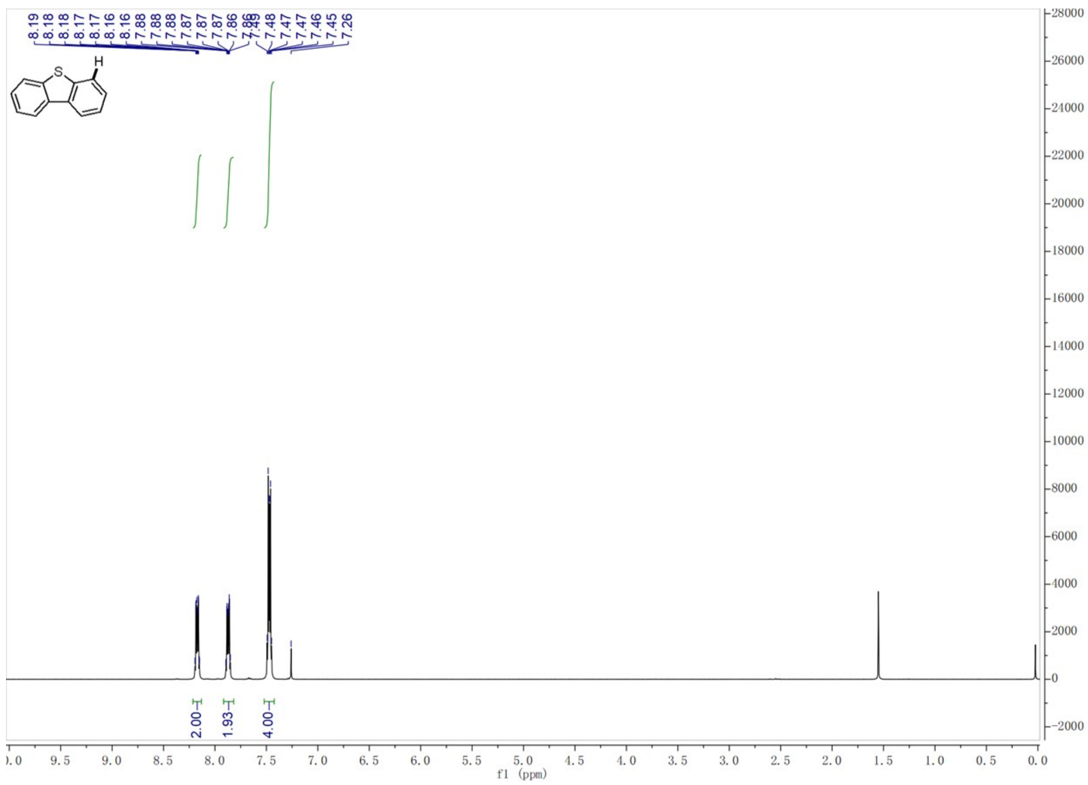


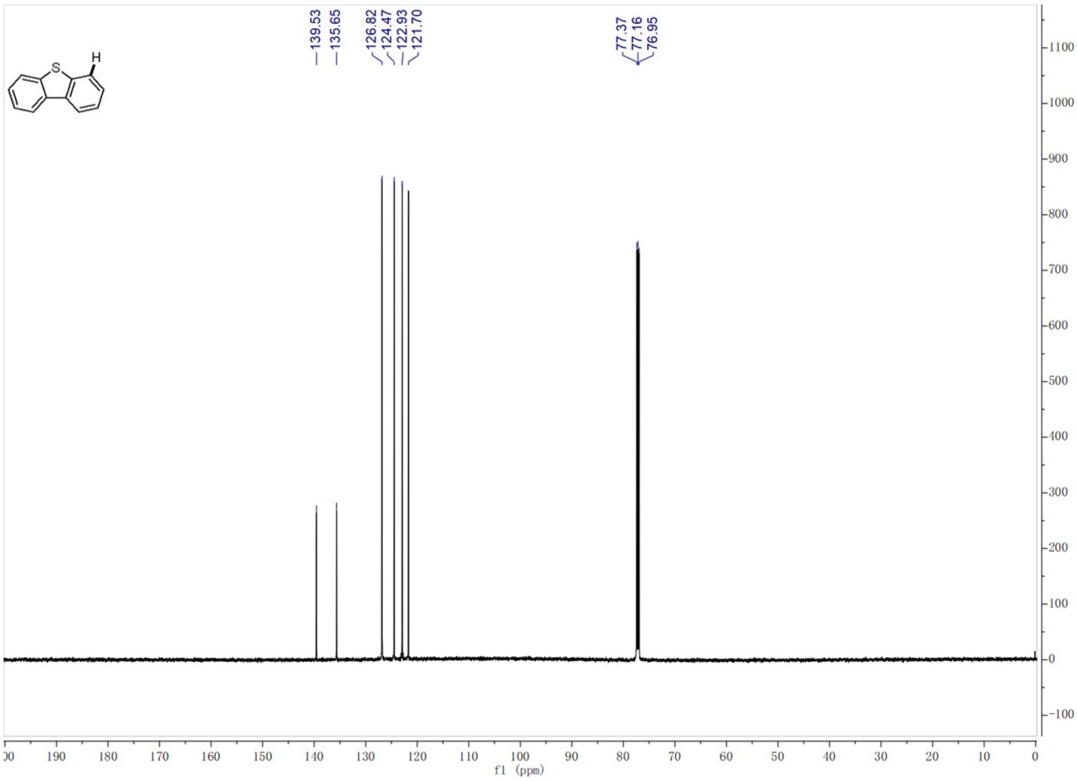
**24-H** (**58-Bz**) $^{1}$H NMR and $^{13}$C NMR



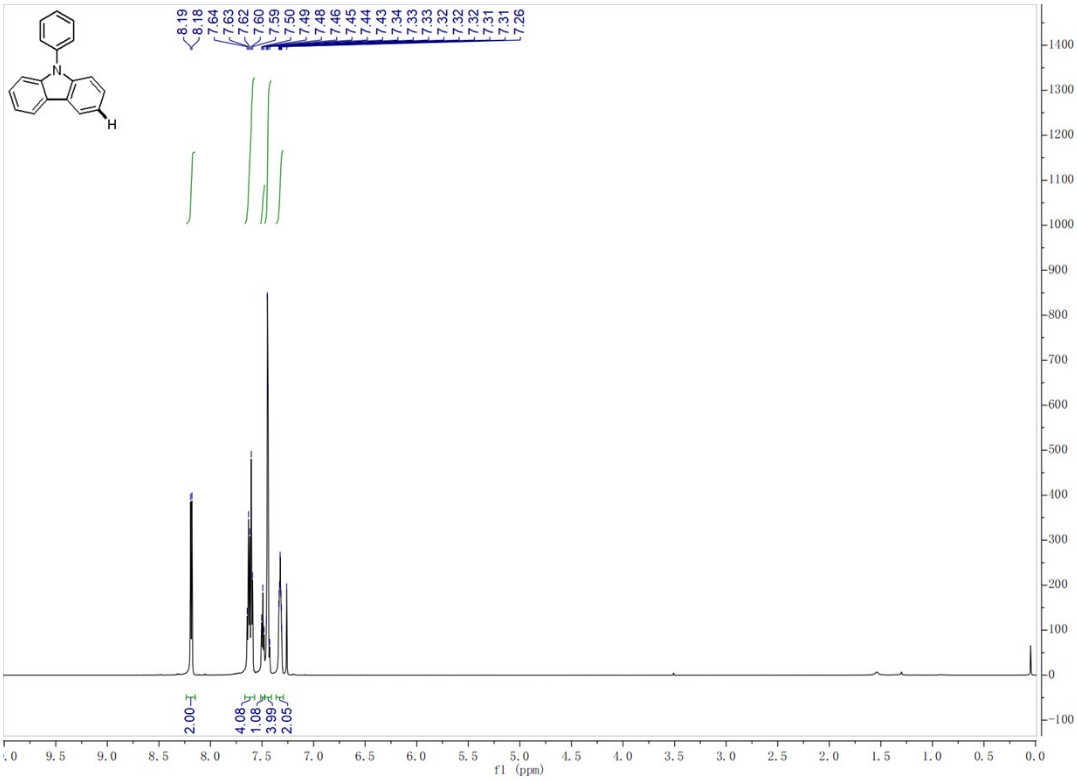


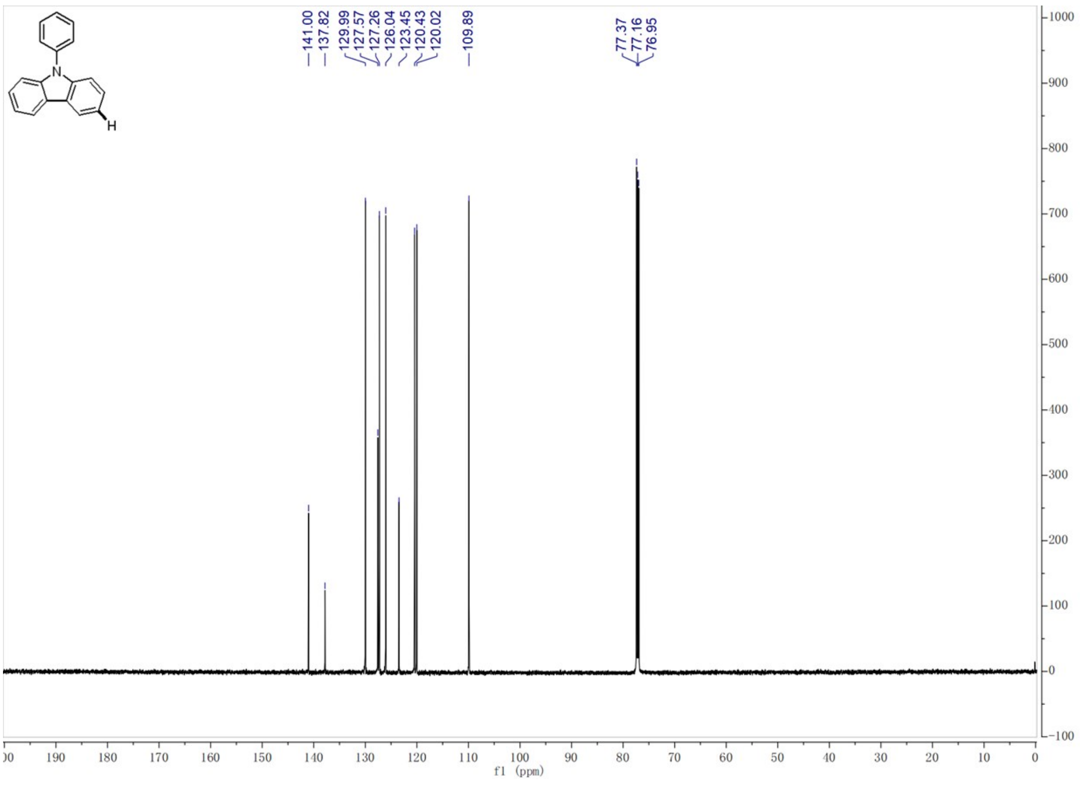

**25-H** $^{1}H$ NMR and $^{13}C$ NMR



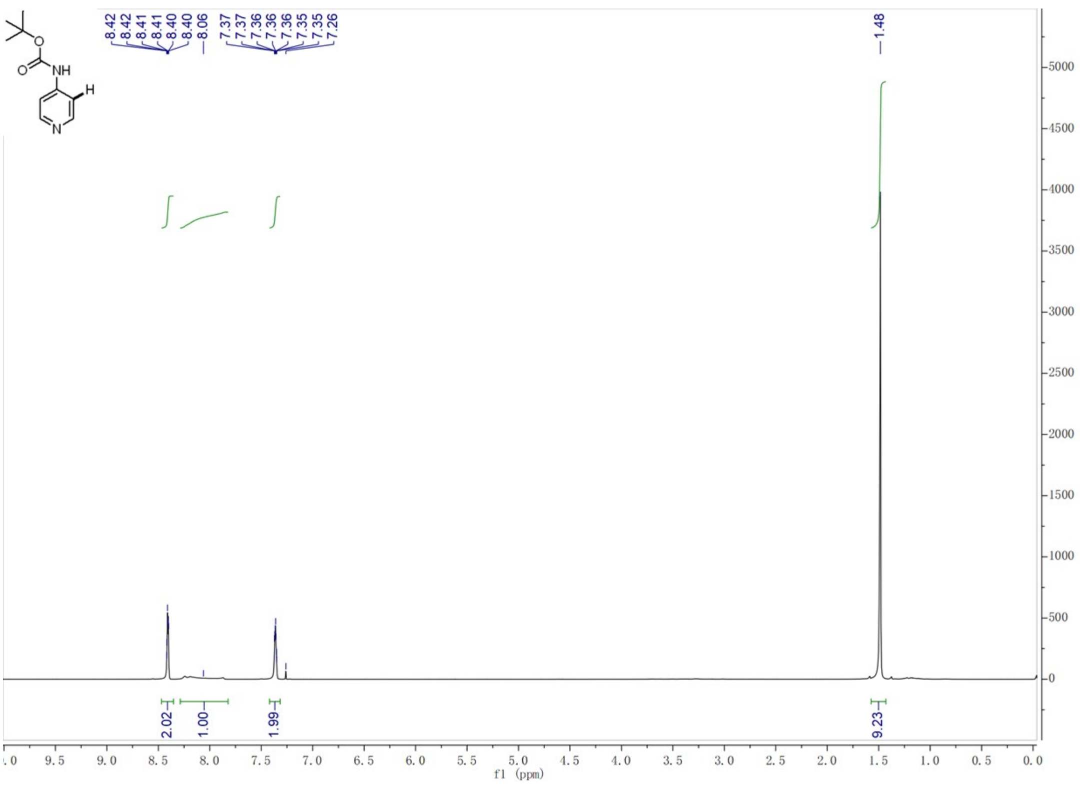


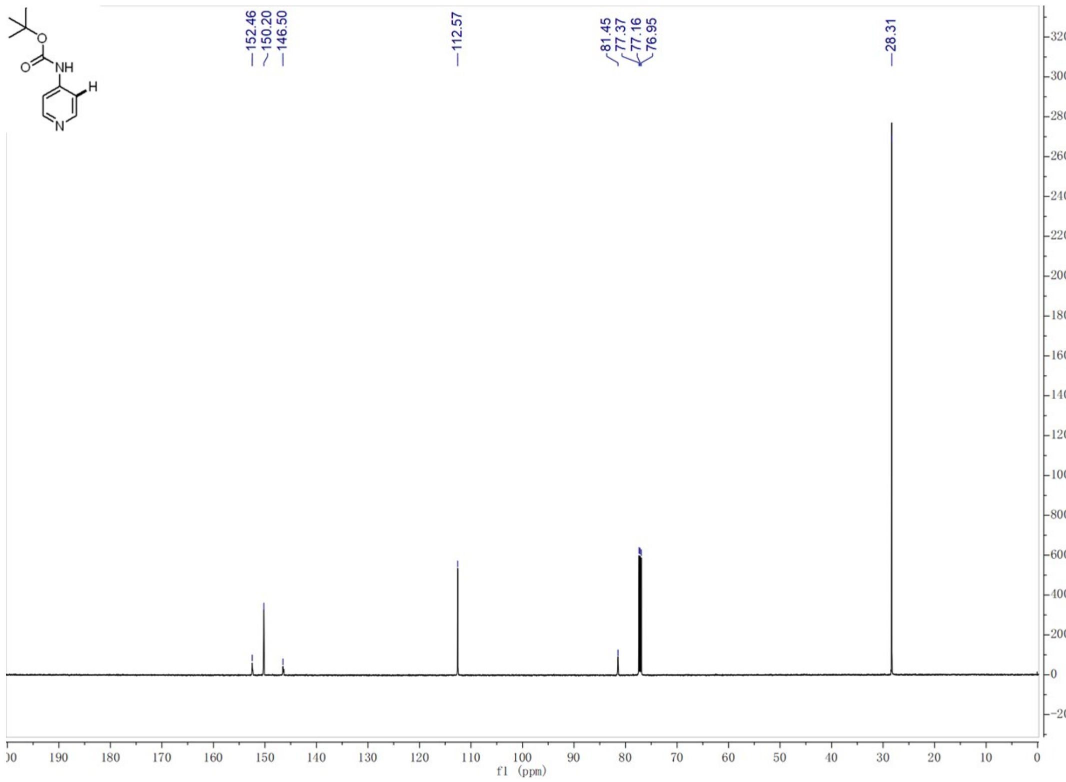

**26-H** $^{1}$H NMR and $^{13}$C NMR



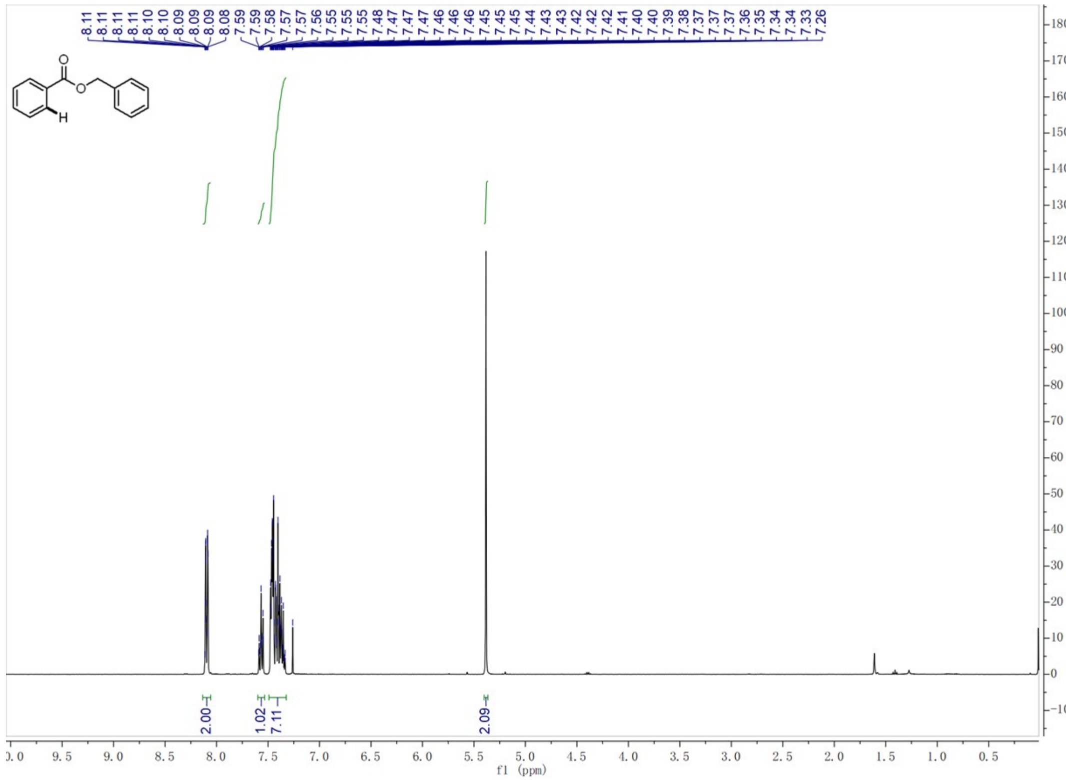


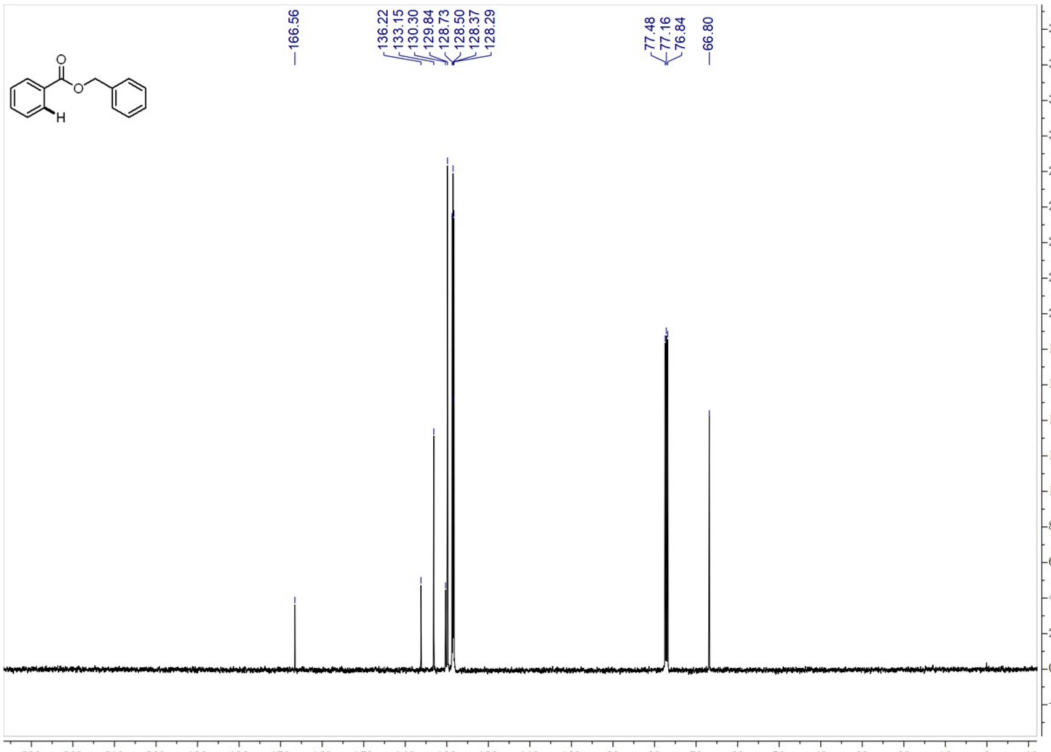

**27-H** $^1$H NMR and $^{13}$C NMR



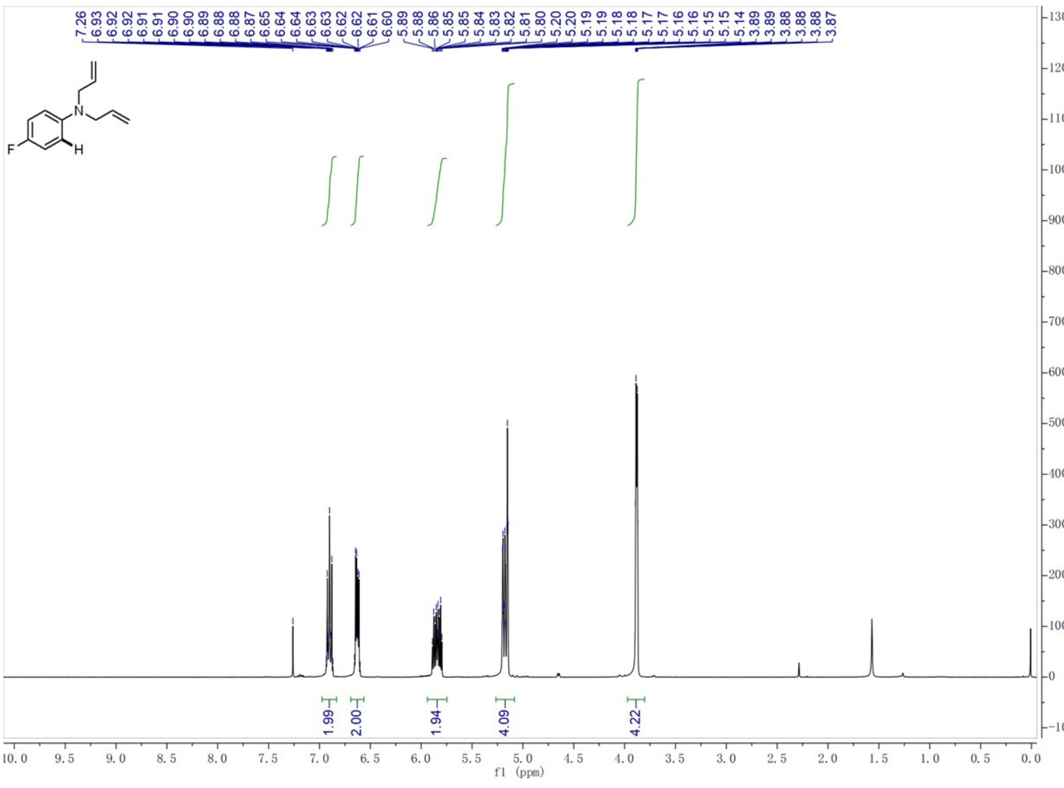


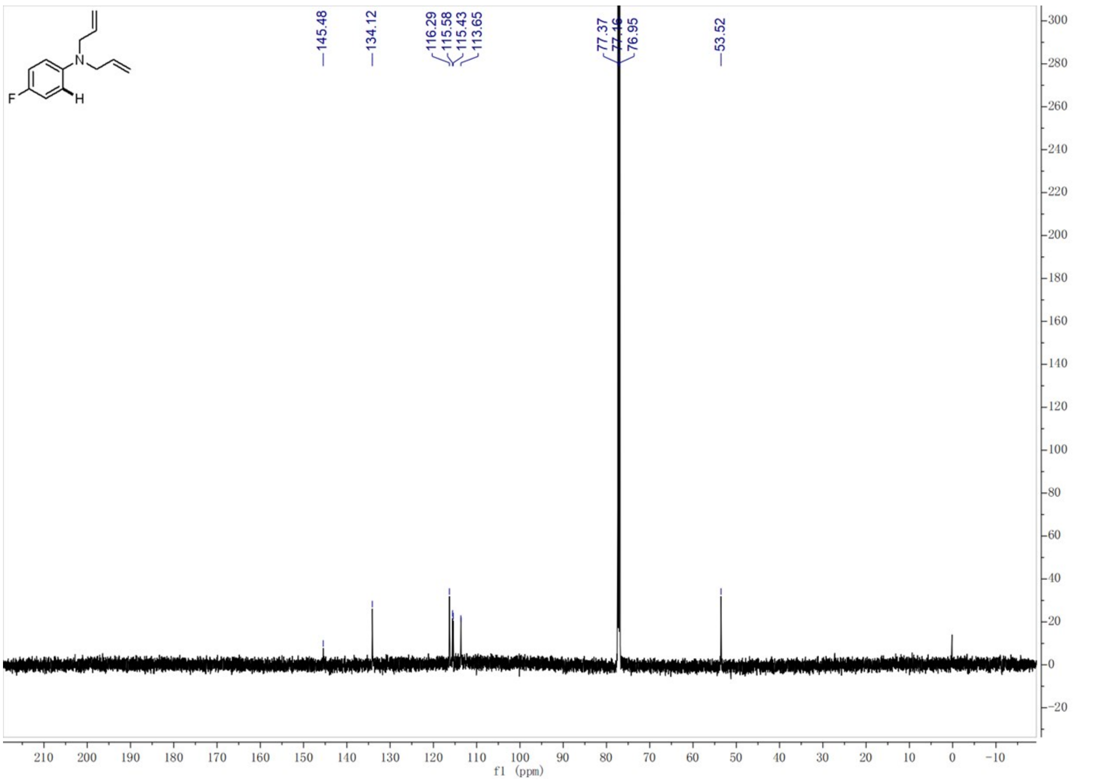

**28-H** $^{1}$H NMR and $^{13}$C NMR



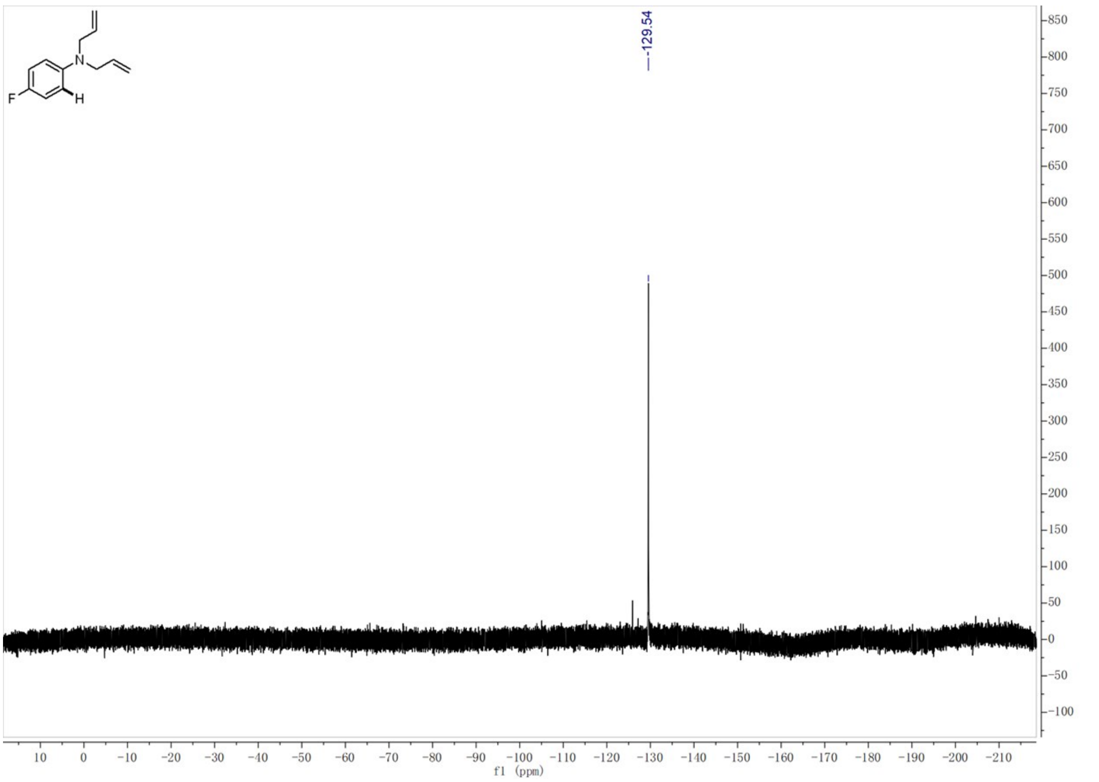



**29-H** $^{1}$H NMR, $^{13}$C NMR and $^{19}$F NMR



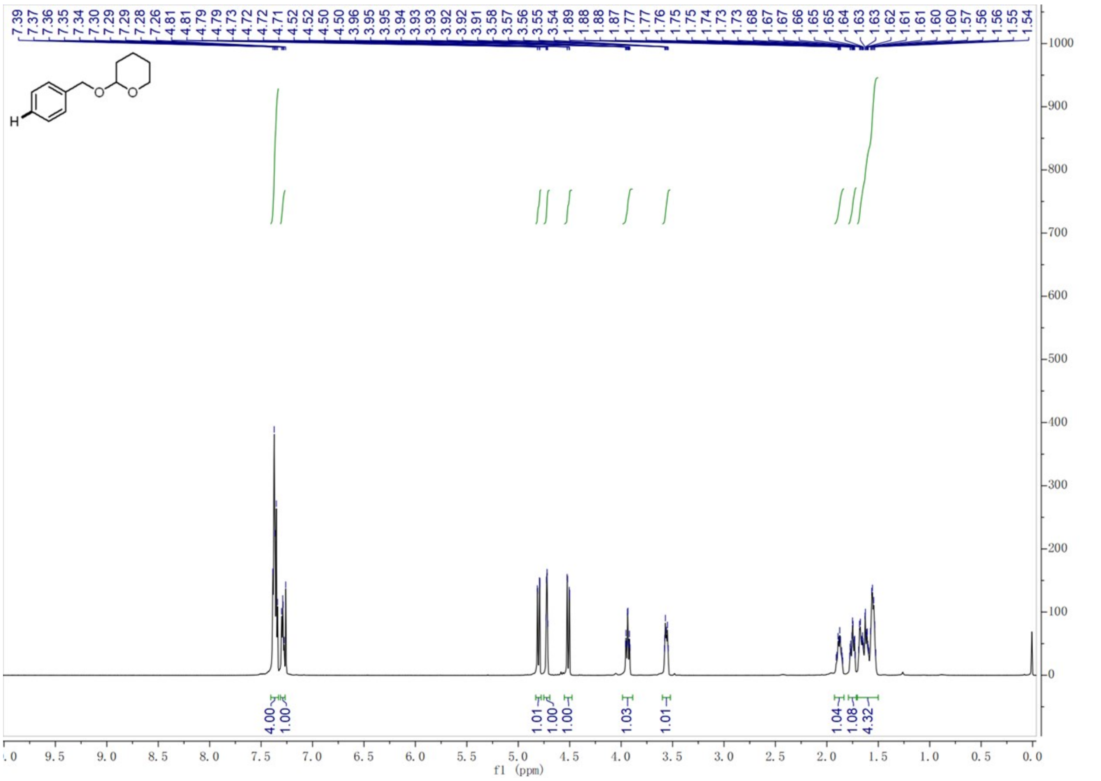


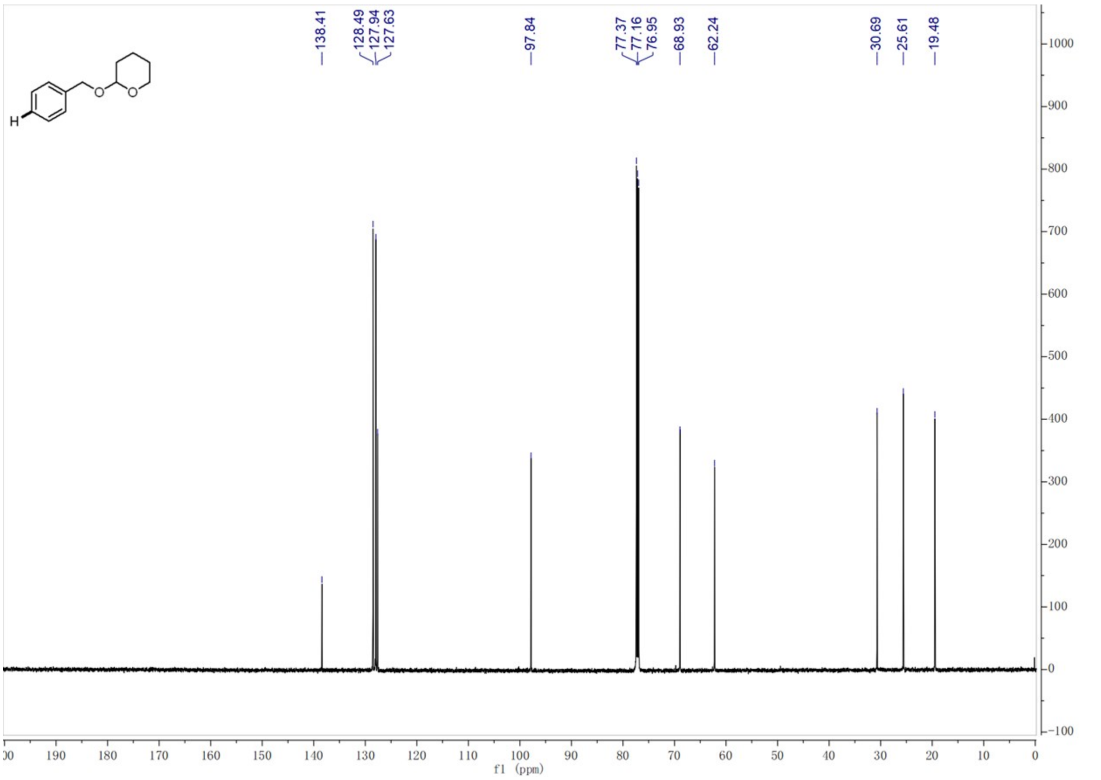
145.48
134.12
116.29
115.58
115.43
113.65
77.37
77.16
76.95
53.52
F
N
H
f1 (ppm)

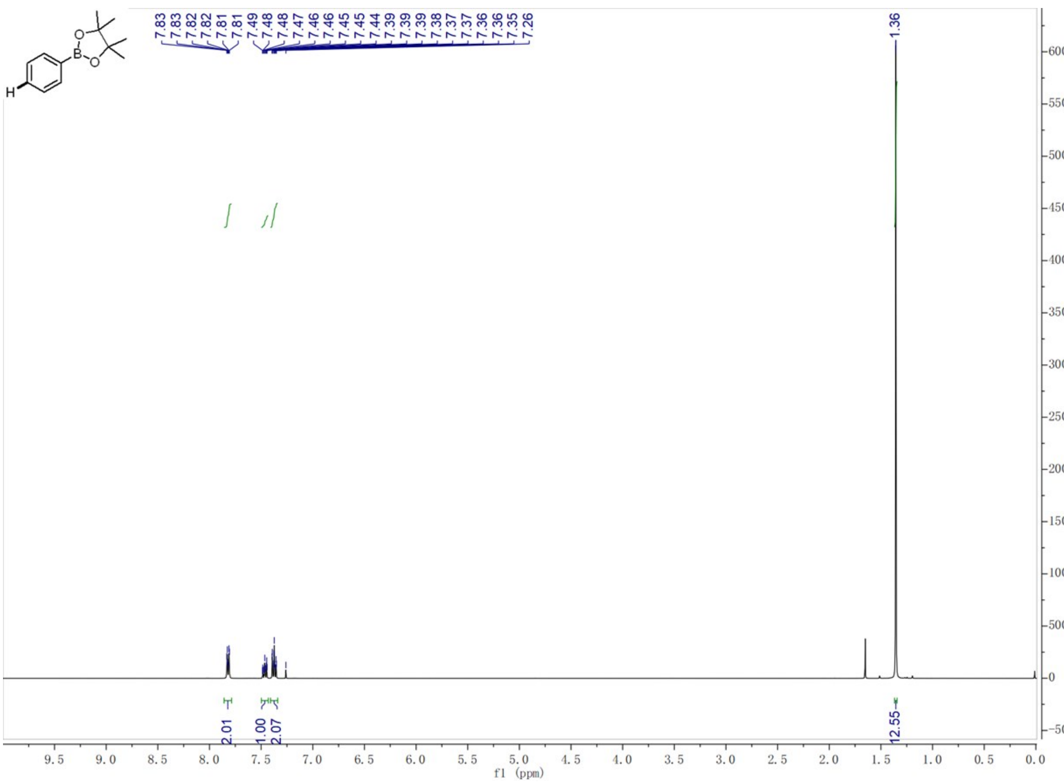
-129.54
F
N
H
f1 (ppm)

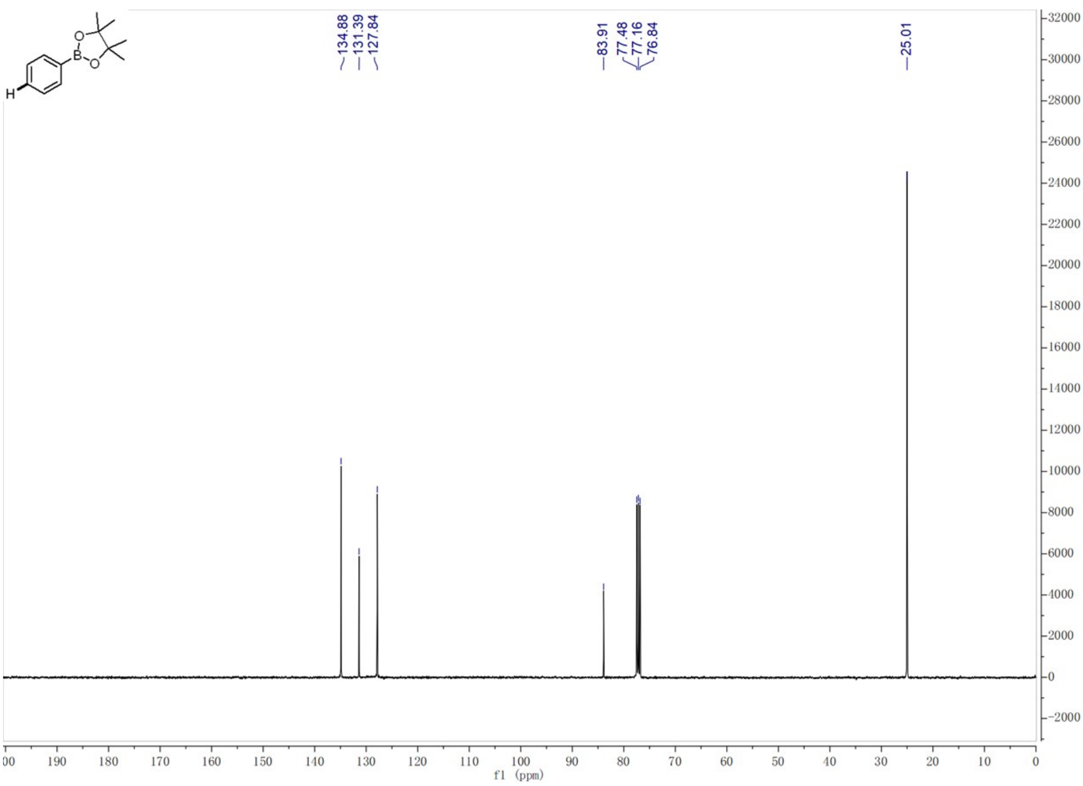
**30-H** $^{1}$H NMR and $^{13}$C NMR



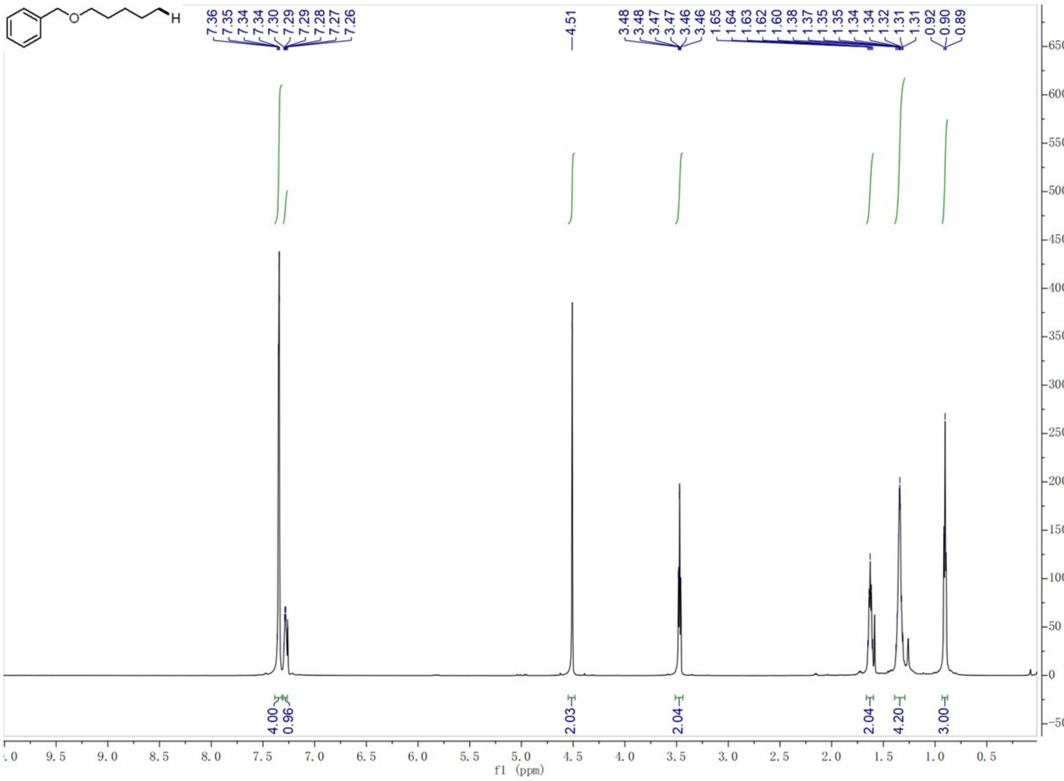


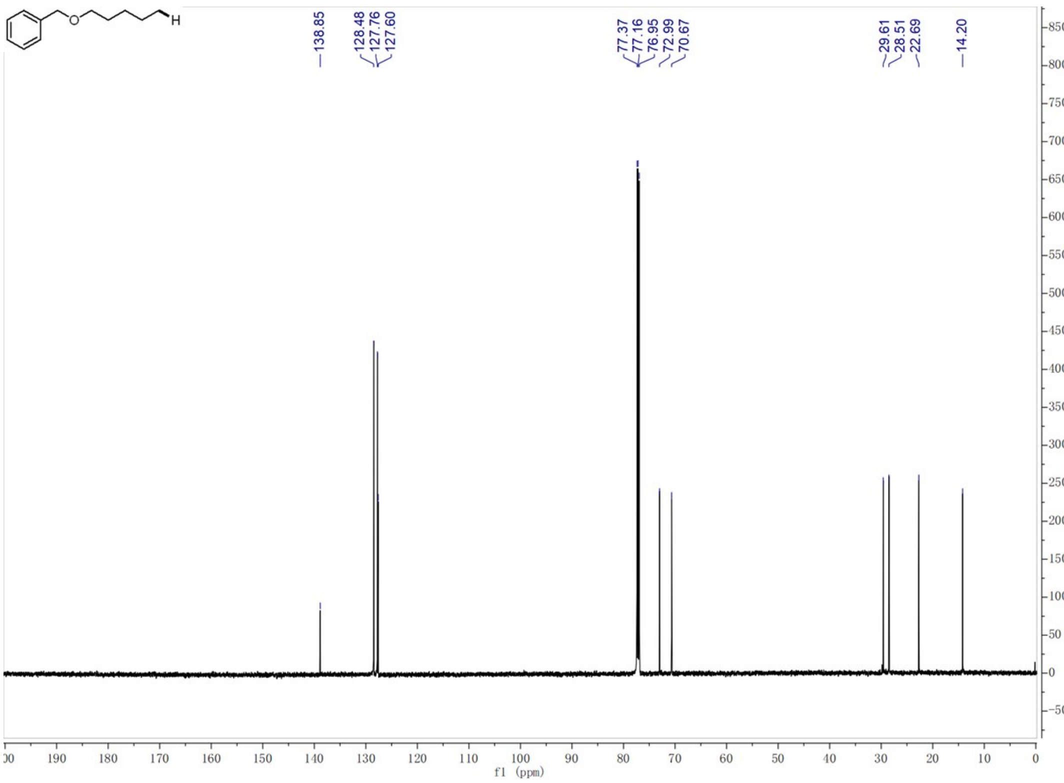
**31-H** $^{1}$H NMR and $^{13}$C NMR



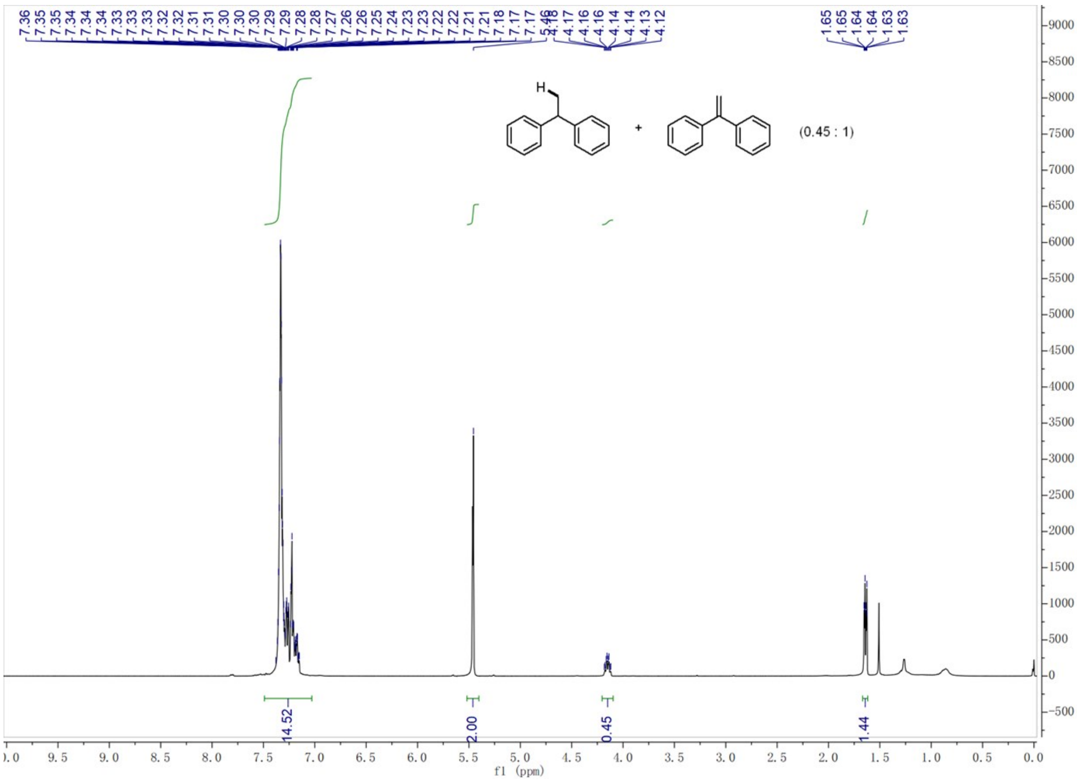



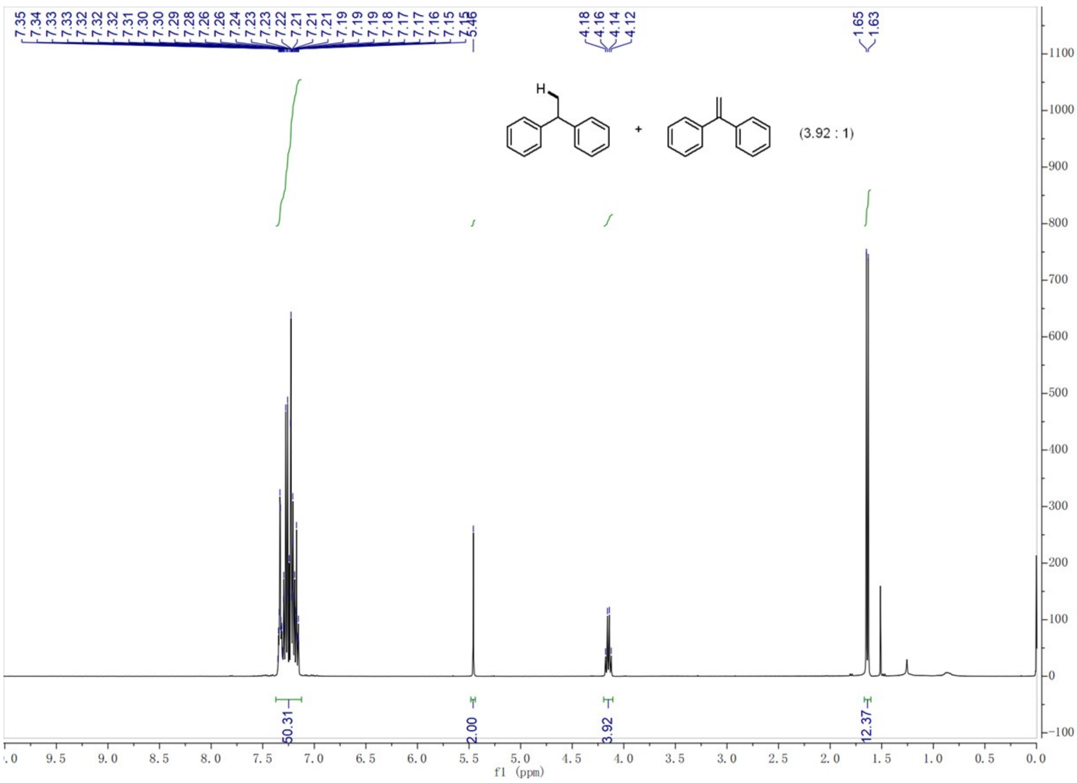
**32-H** $^{1}$H NMR and $^{13}$C NMR



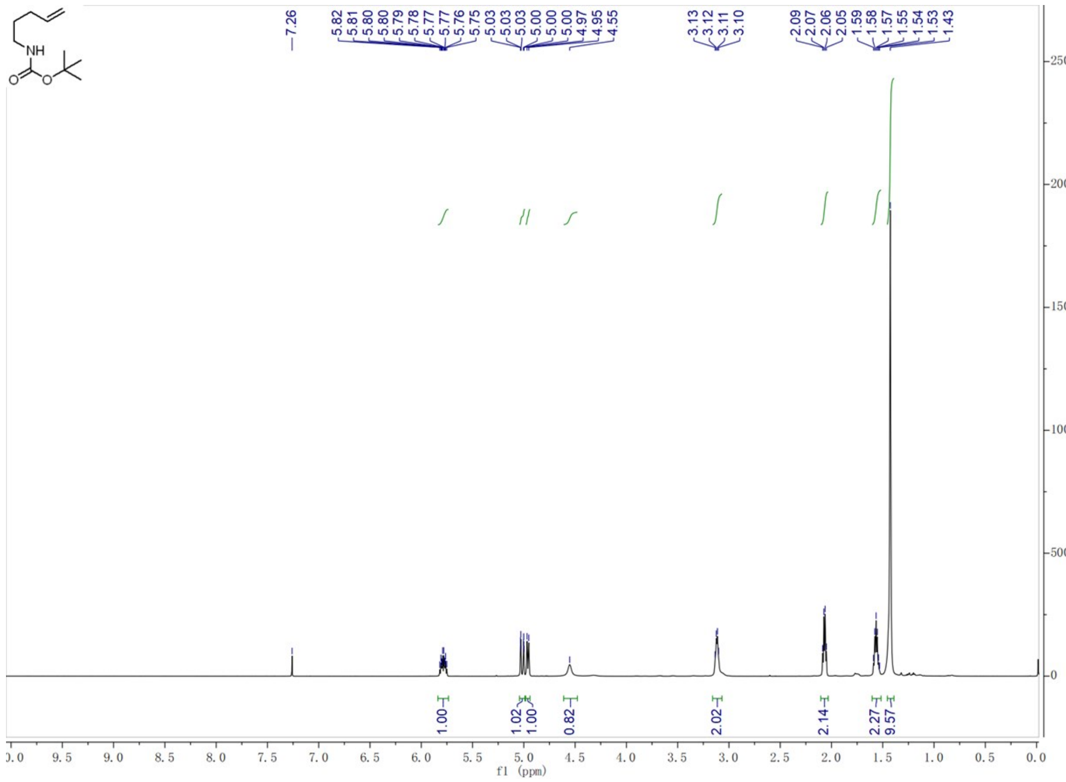


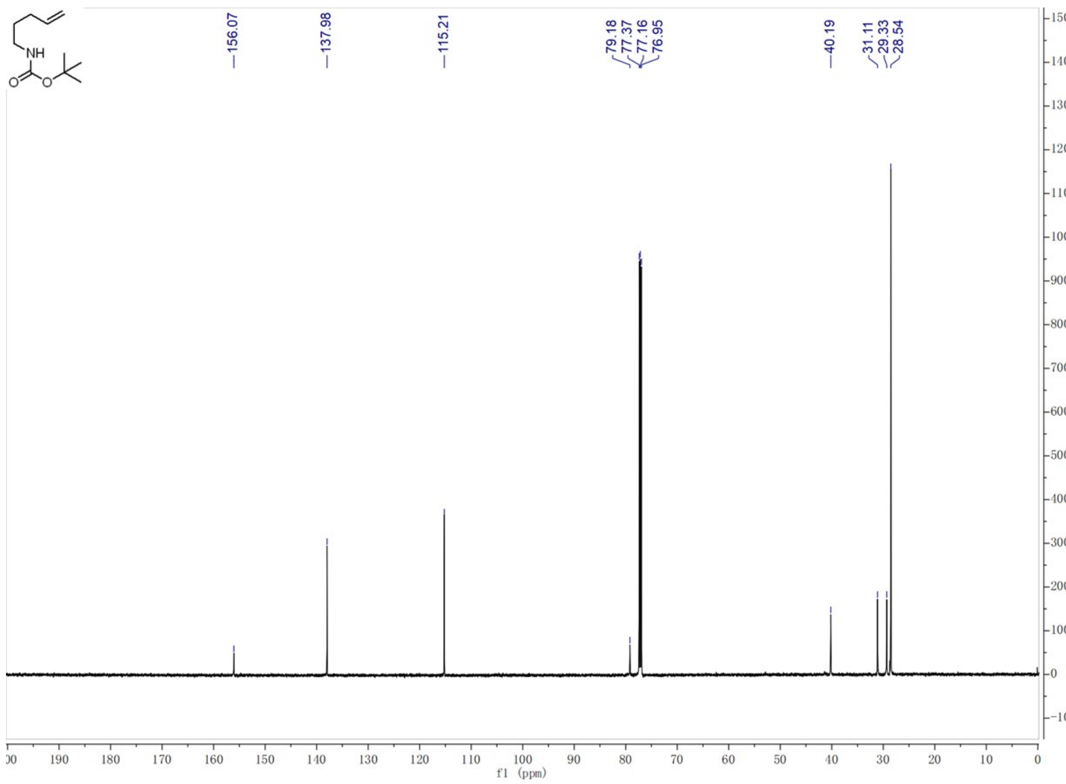
**33-H+33-H'** mixture $^{1}$H NMR (by **Method A** and **Method B**, respectively)



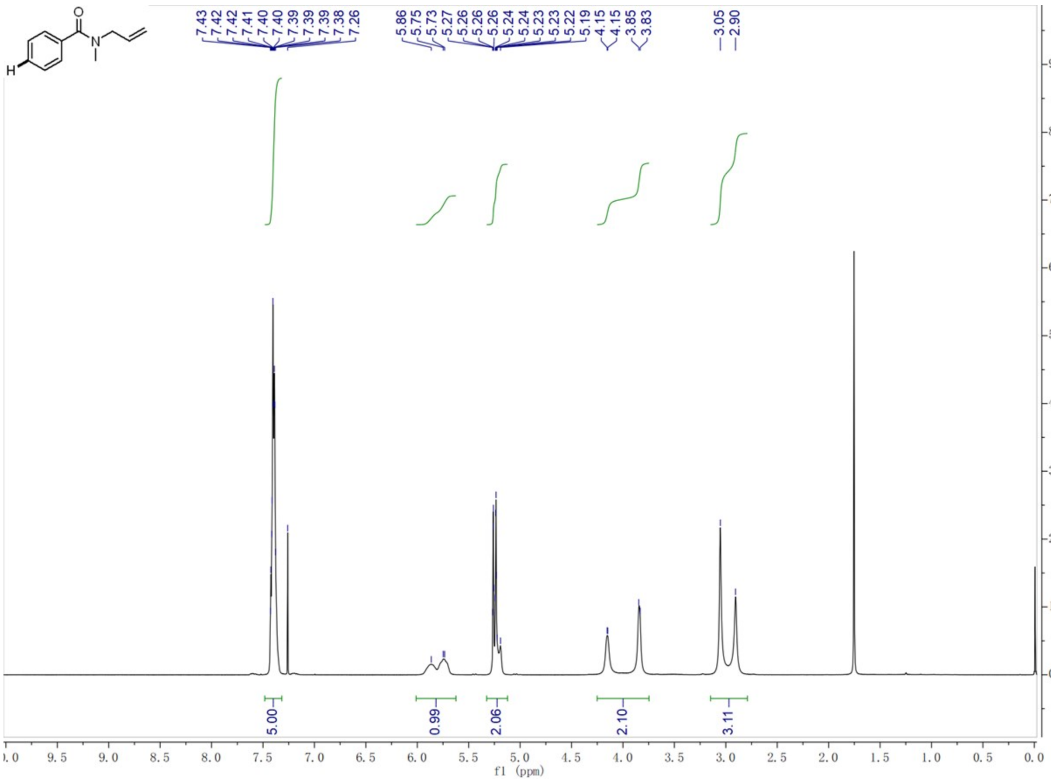


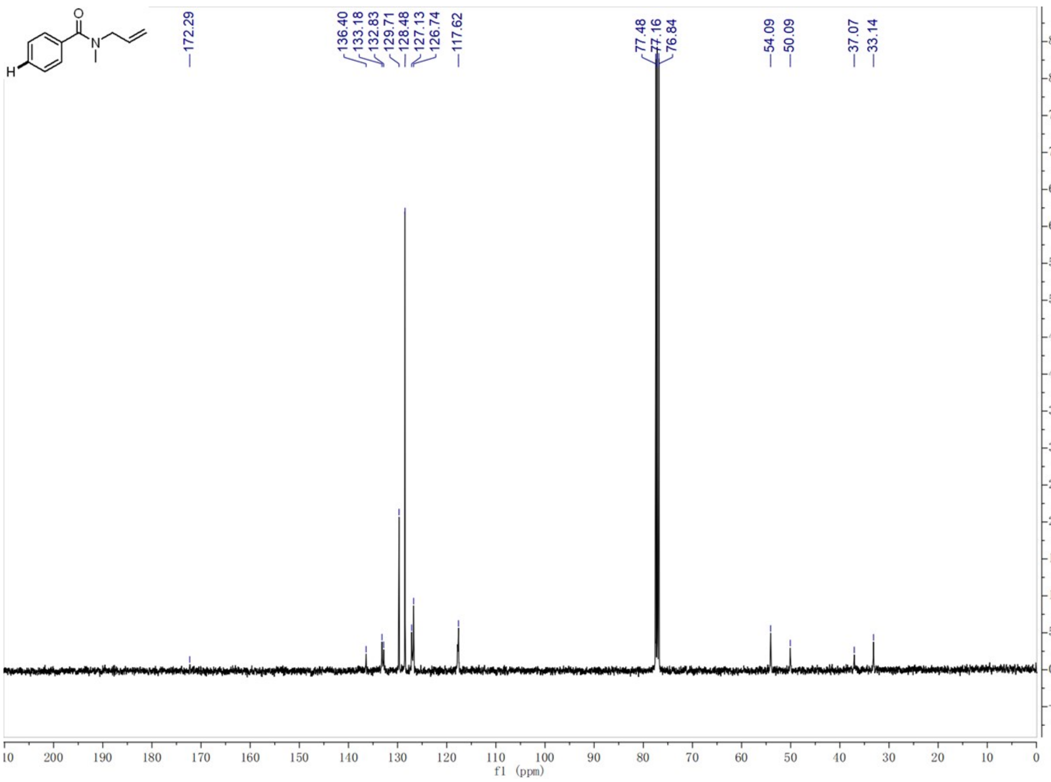
**34-H** $^1$H NMR and $^{13}$C NMR



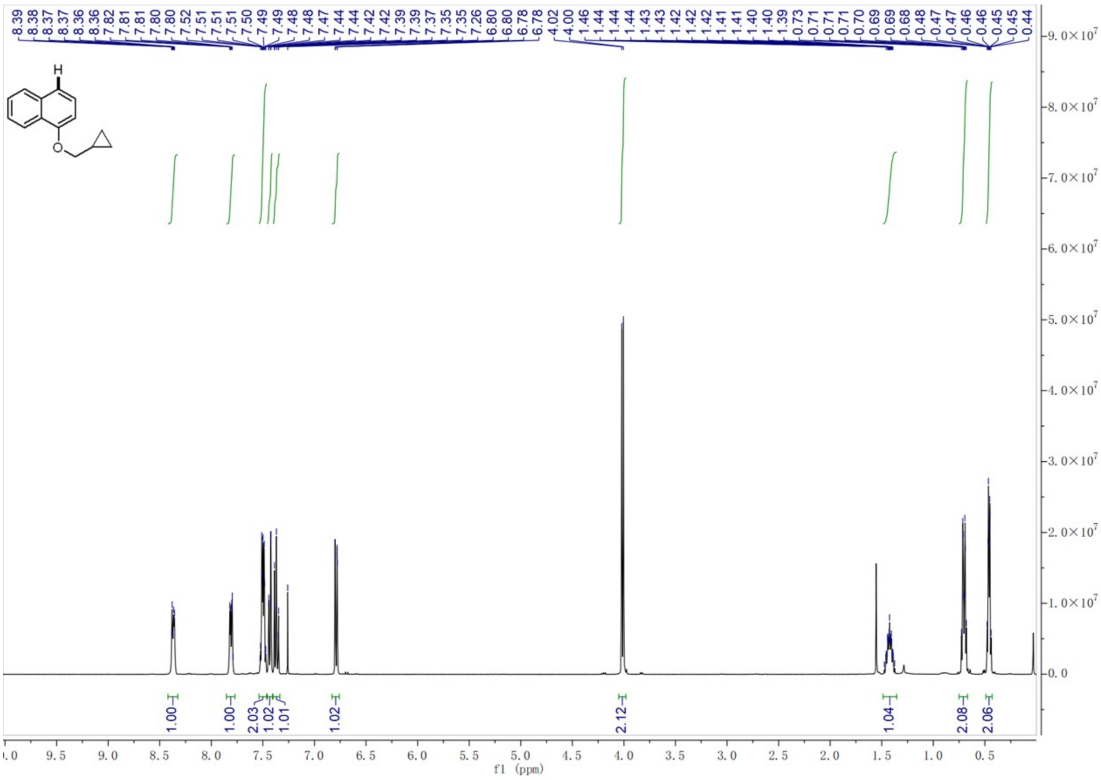


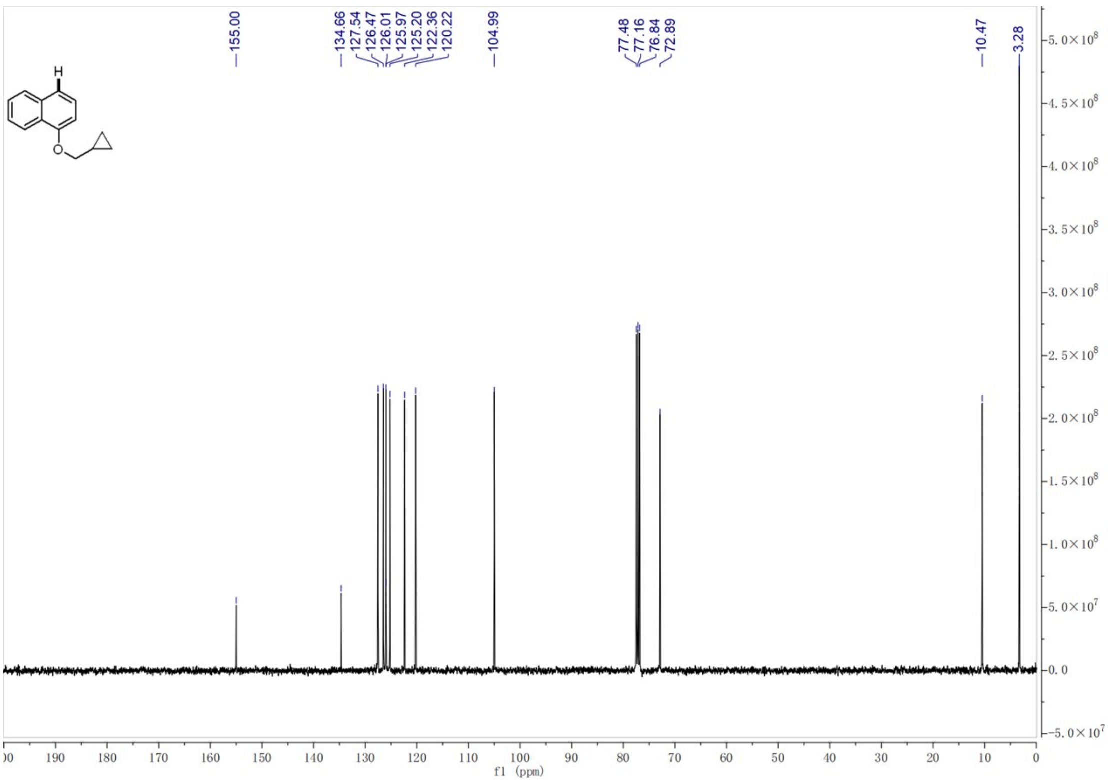
**35-H** $^{1}$H NMR and $^{13}$C NMR



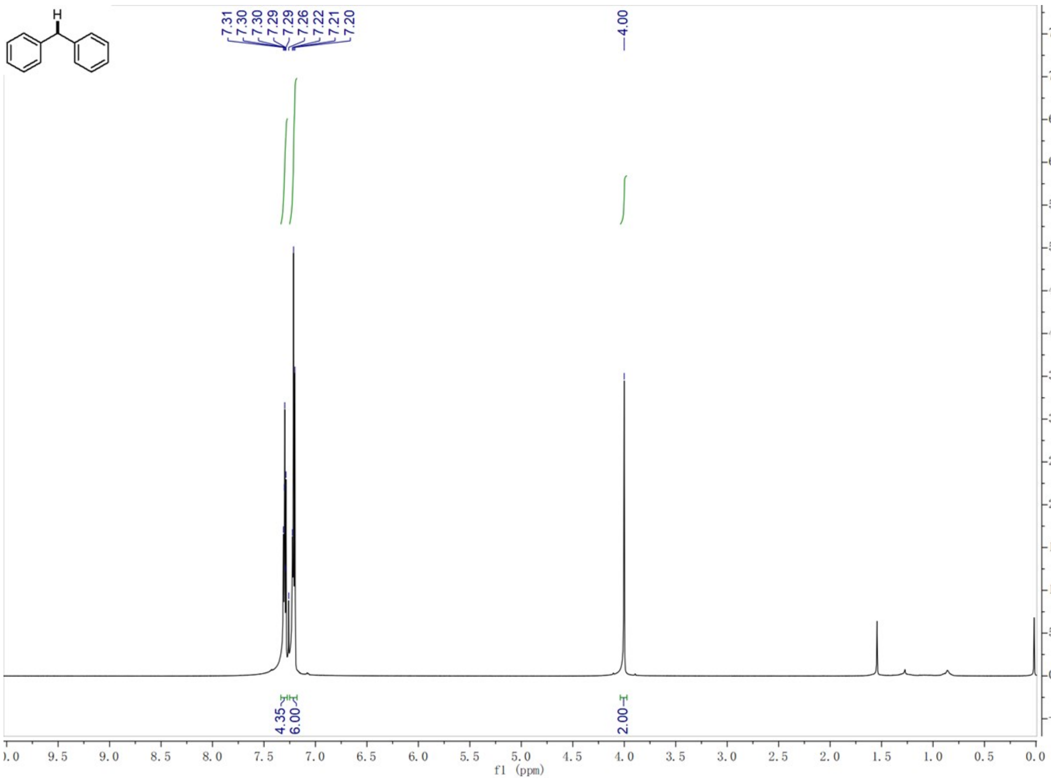


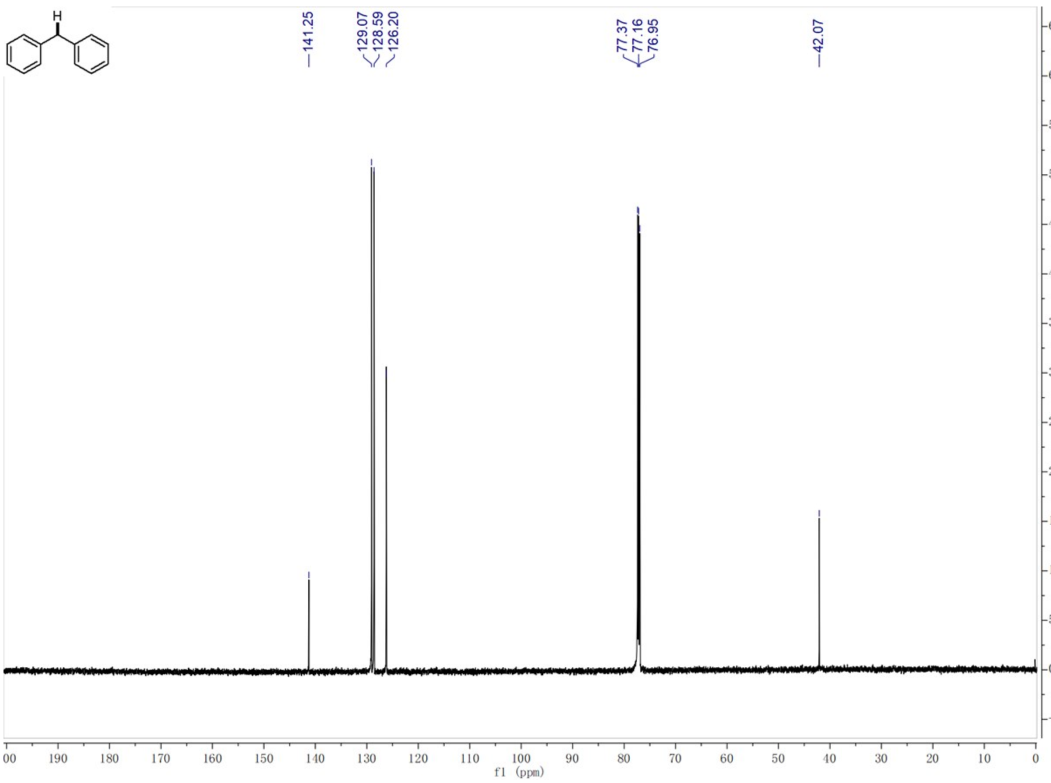
**36-H** $^{1}H$ NMR and $^{13}C$ NMR



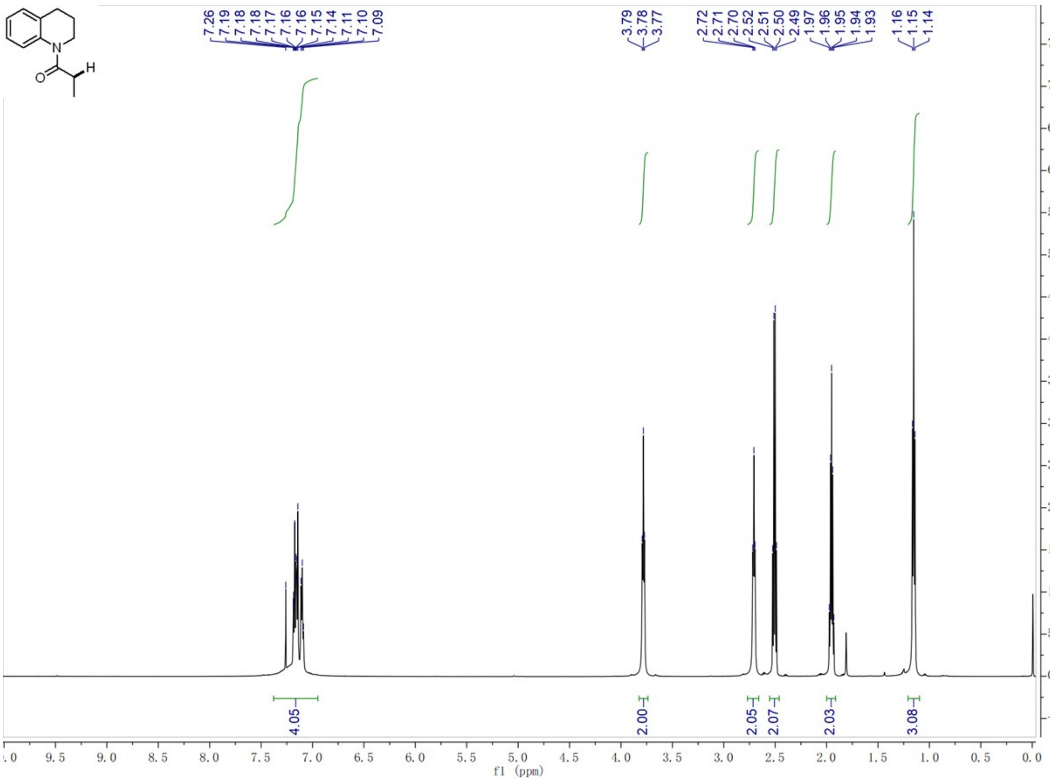


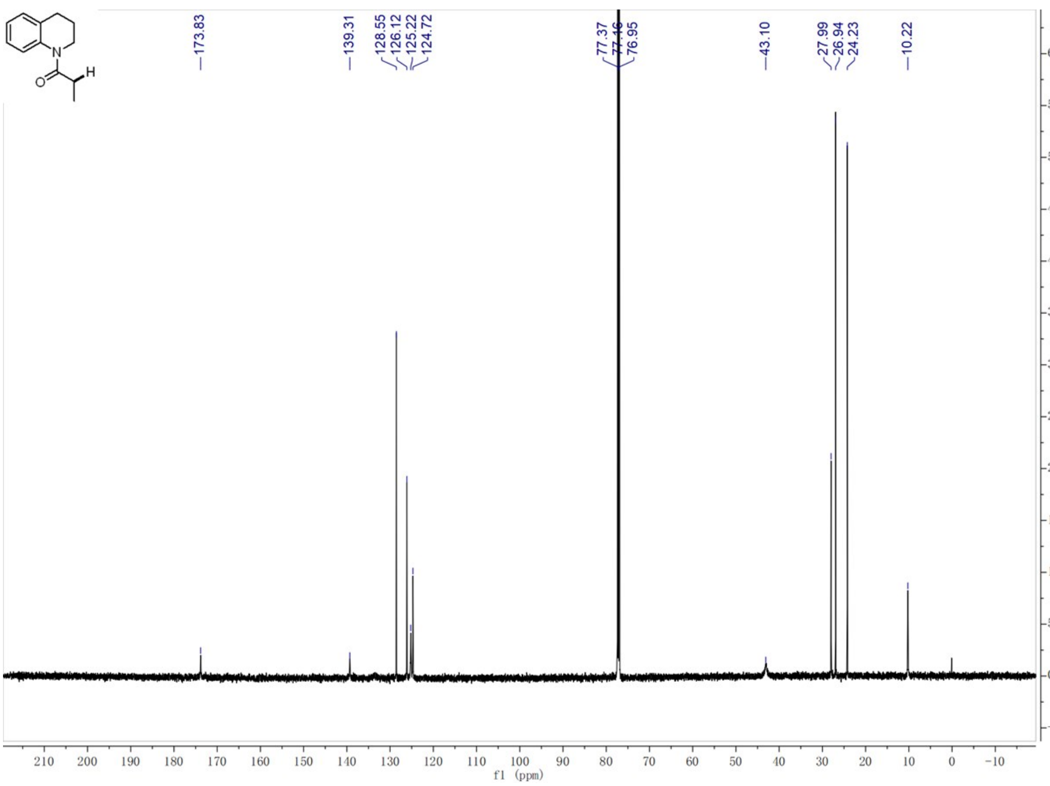
**37-H** $^1$H NMR and $^{13}$C NMR



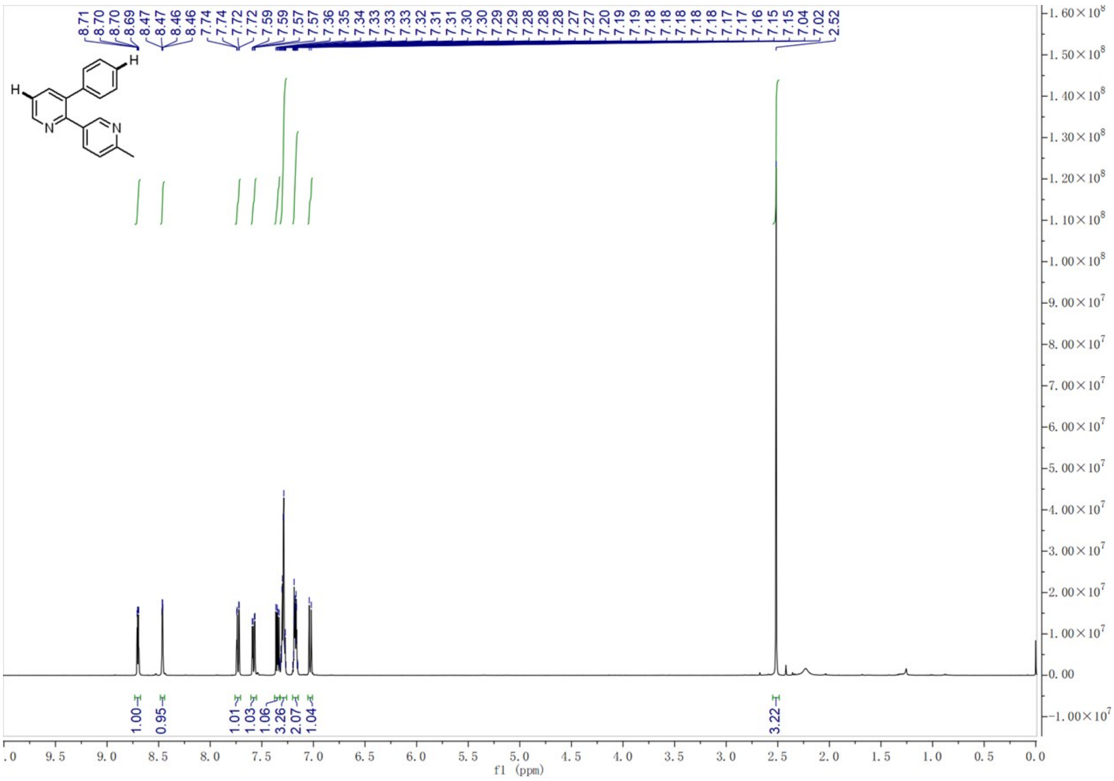



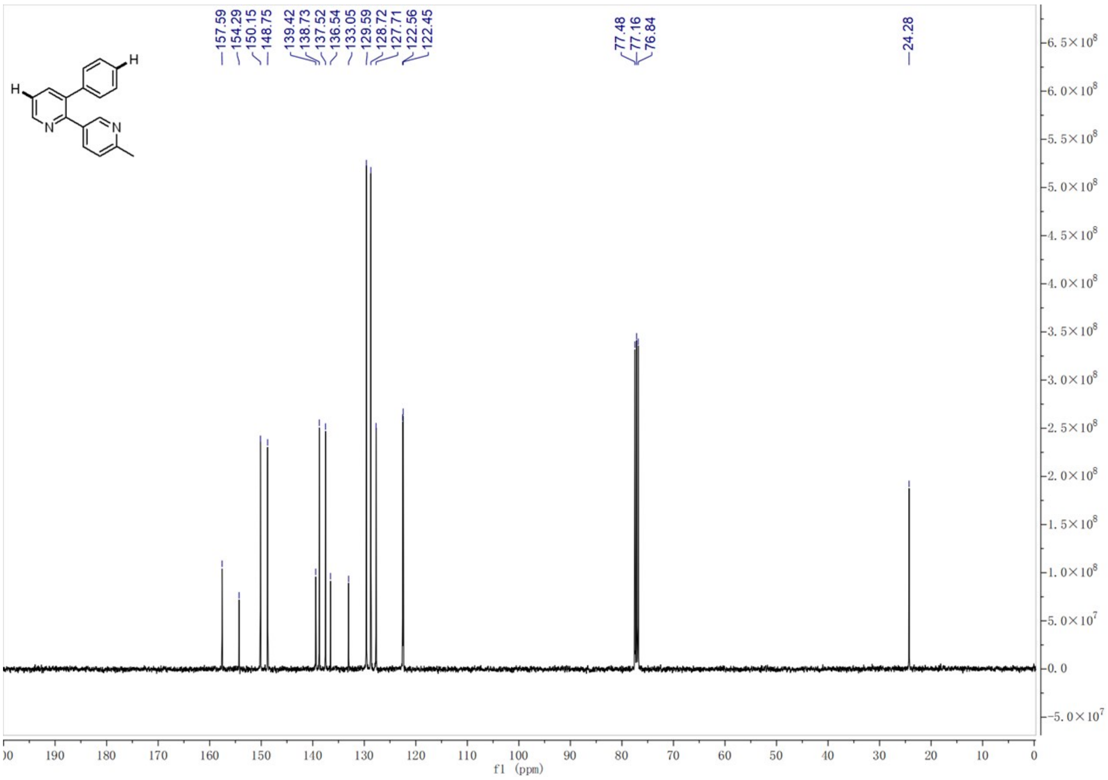
**38-H** $^{1}$H NMR and $^{13}$C NMR



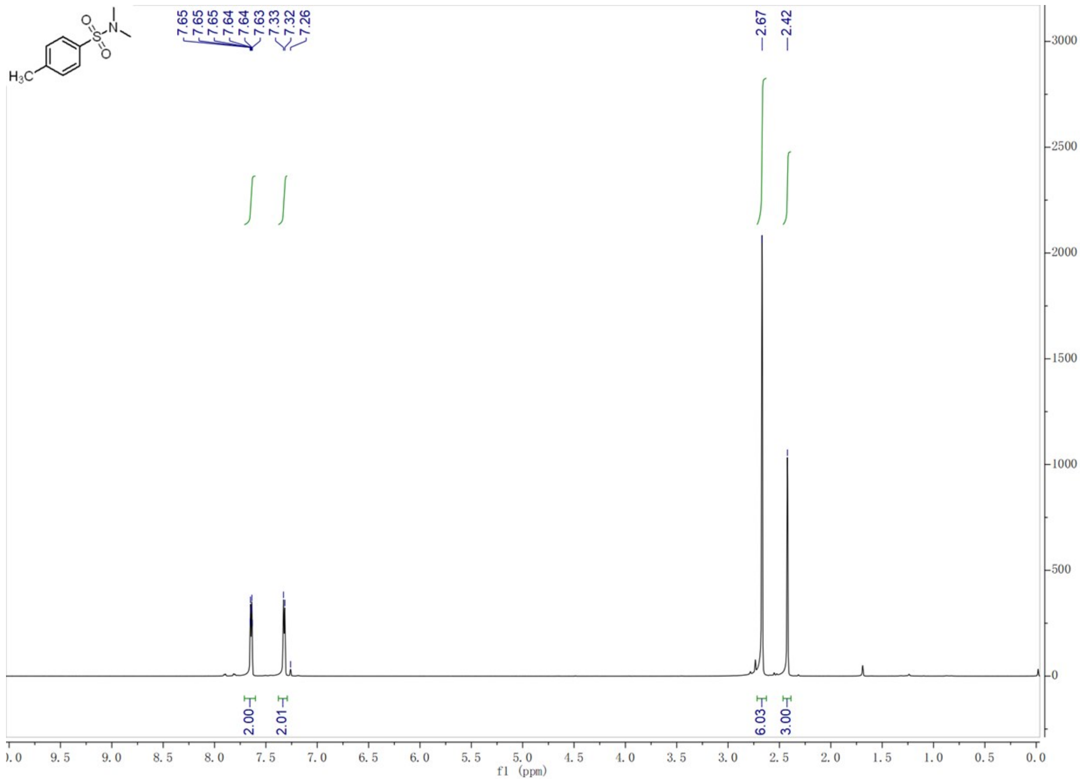



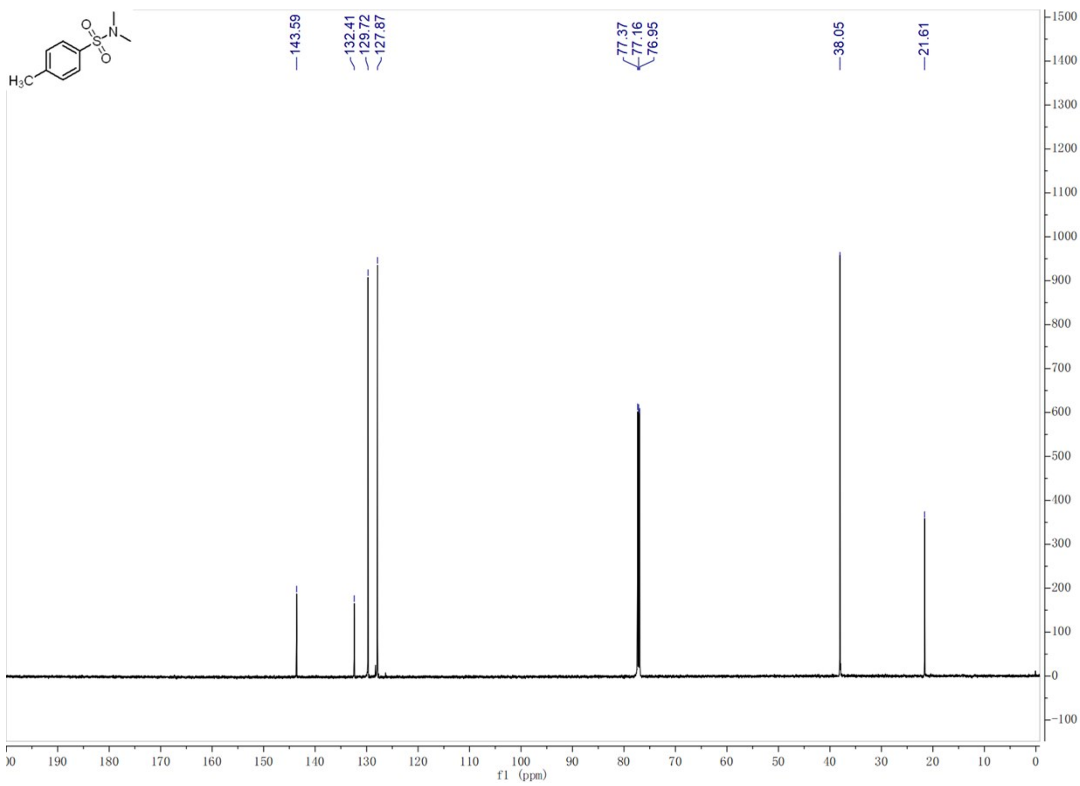
**39-H** $^{1}$H NMR and $^{13}$C NMR



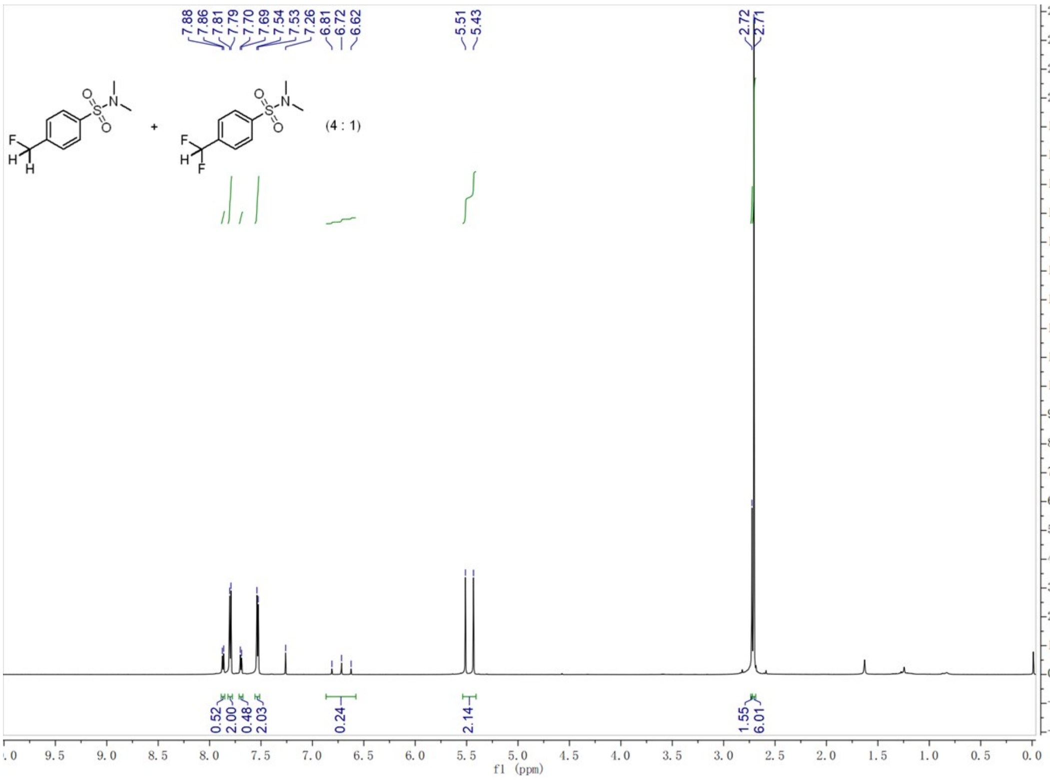



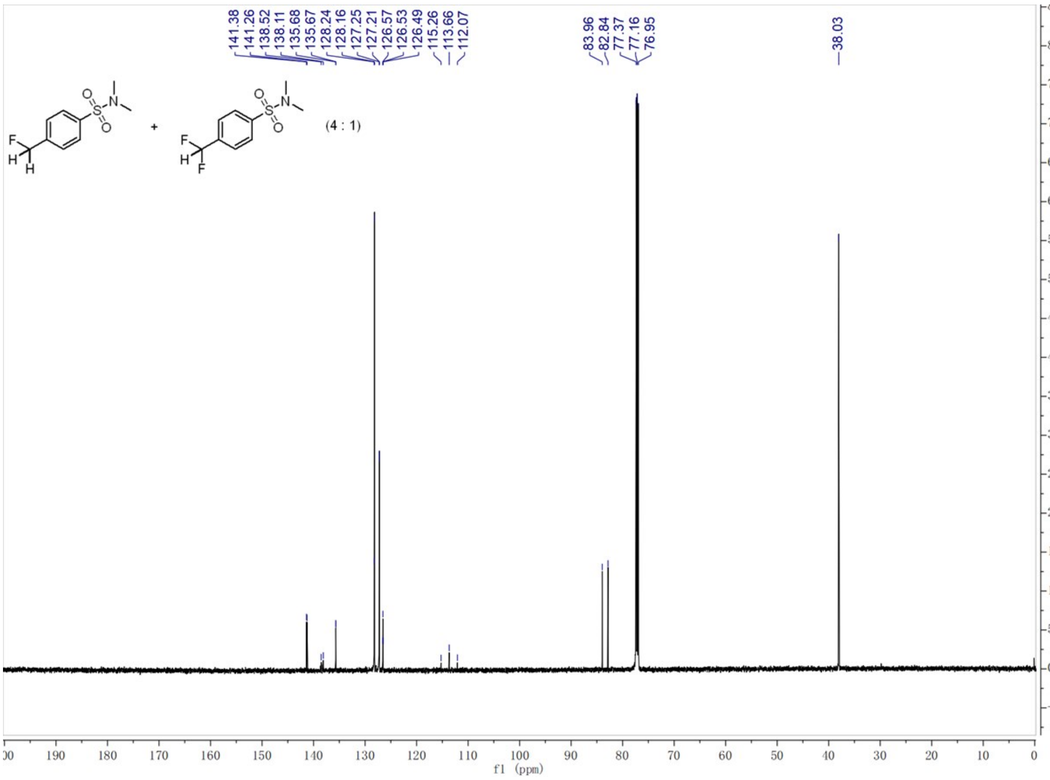
**40-H** $^{1}$H NMR and $^{13}$C NMR

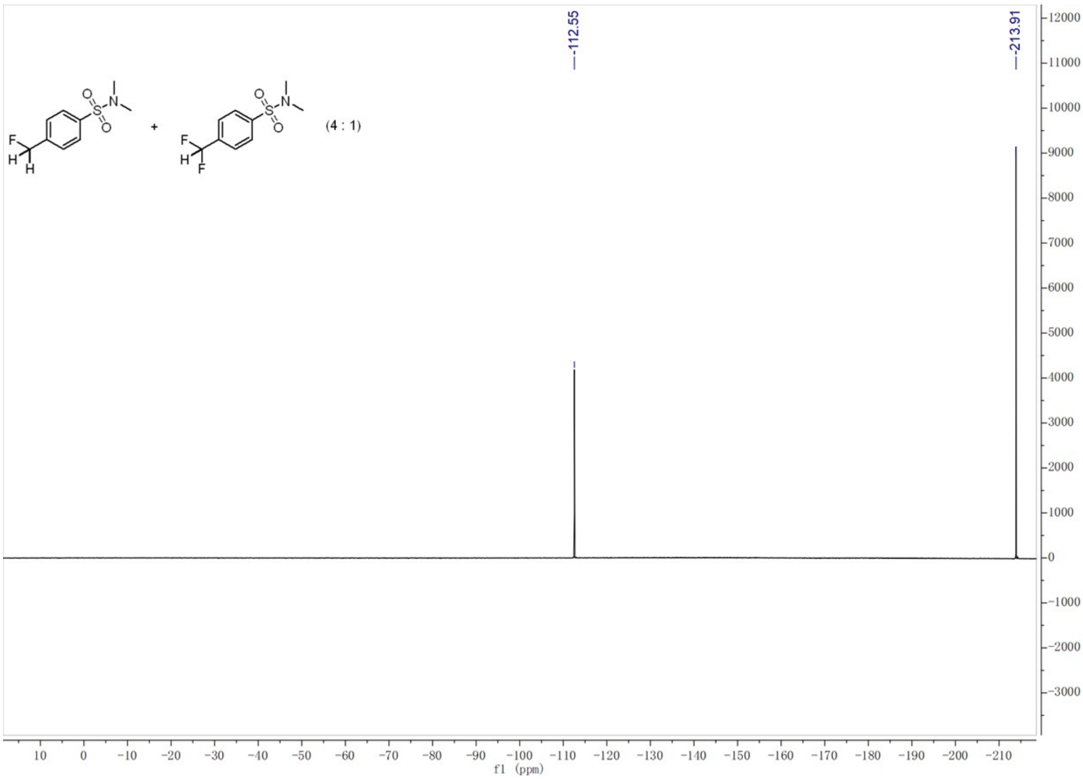




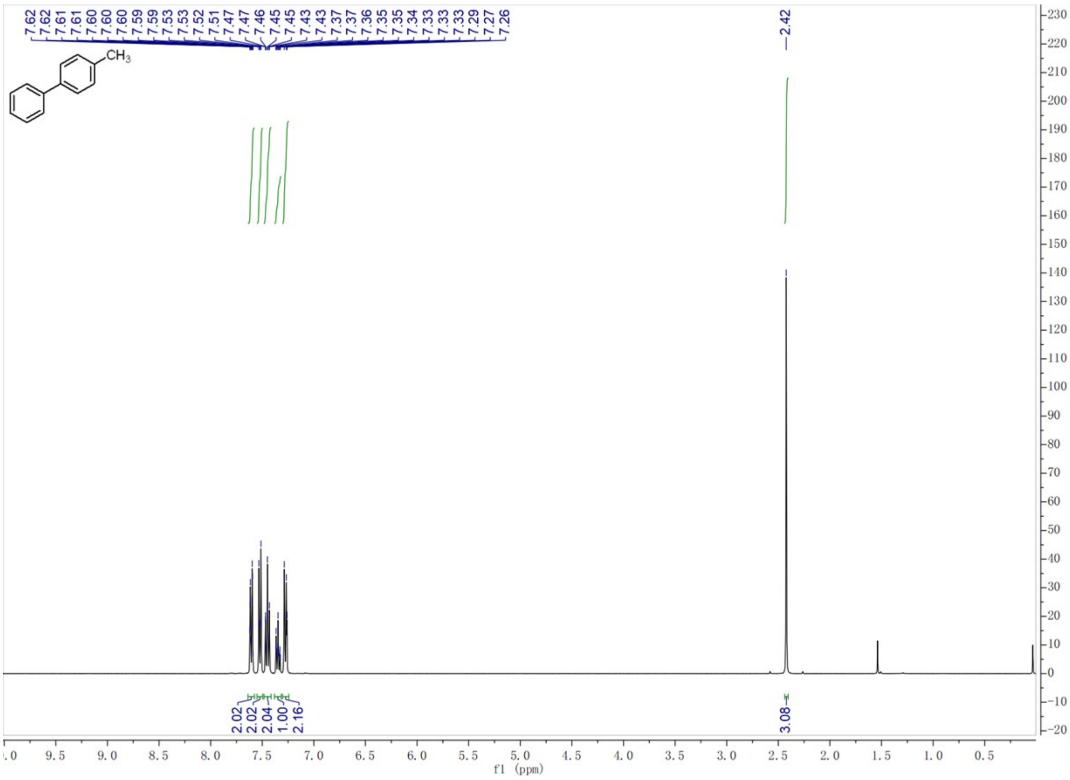
**40-H'+40-H''** $^{1}$H NMR, $^{13}$C NMR and $^{19}$F NMR

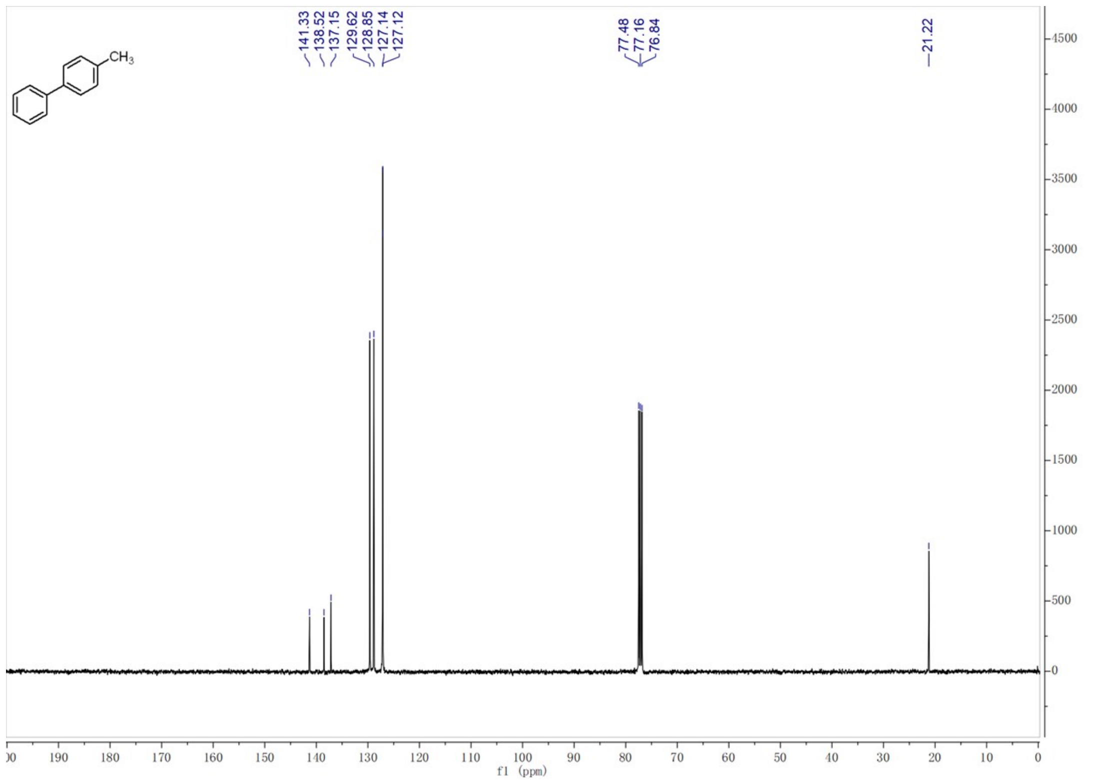




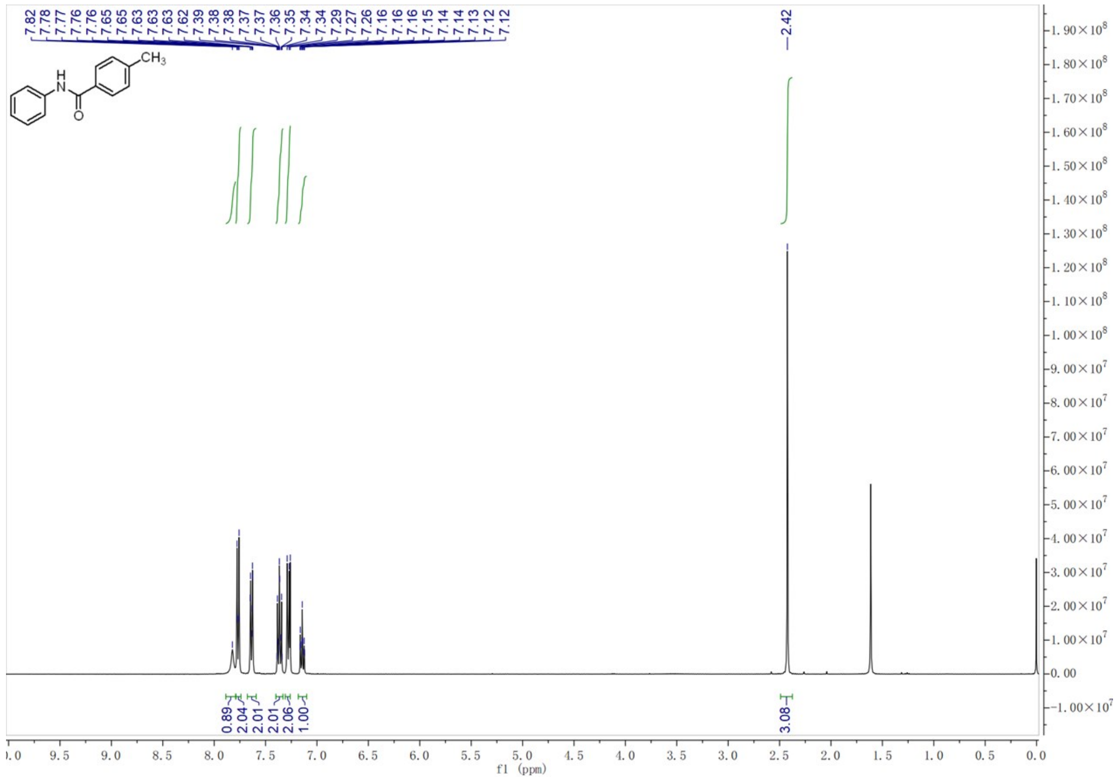


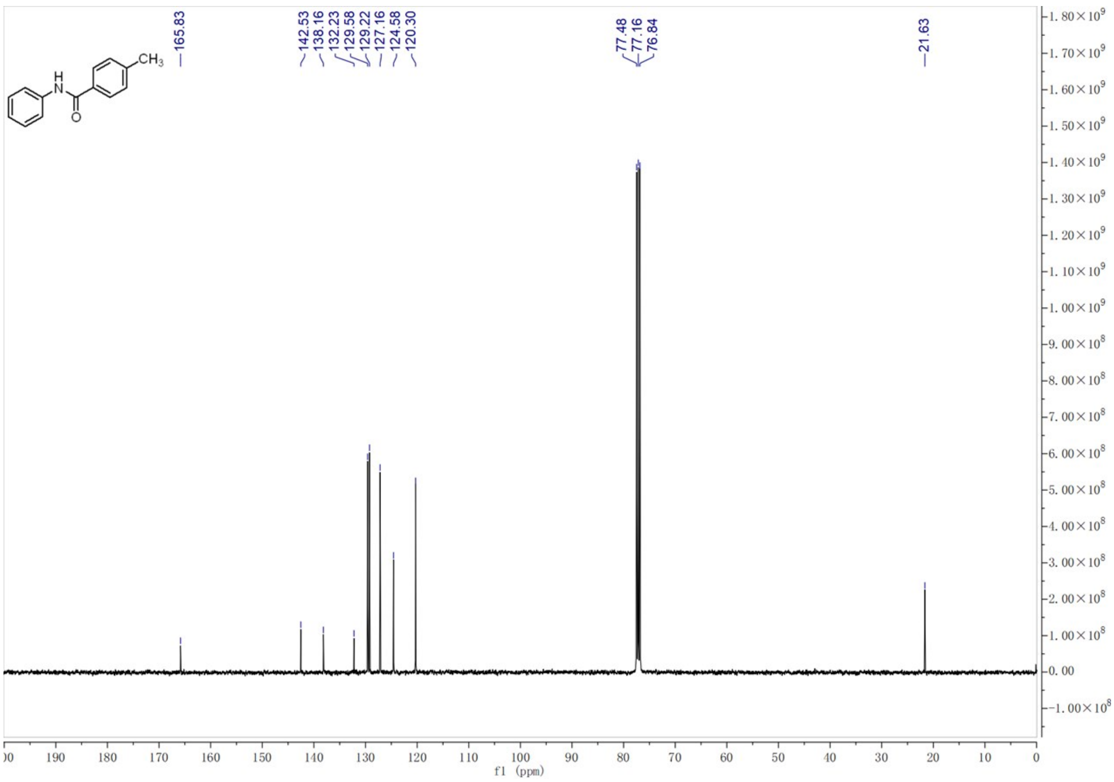

**41-H** $^{1}$H NMR and $^{13}$C NMR



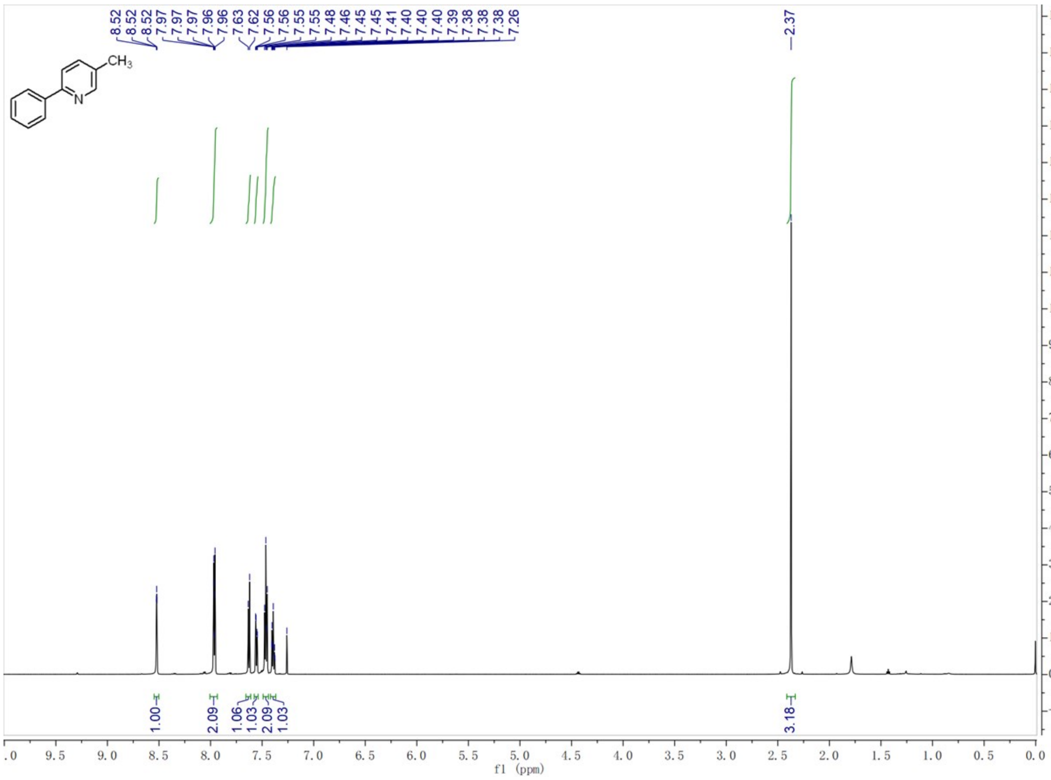


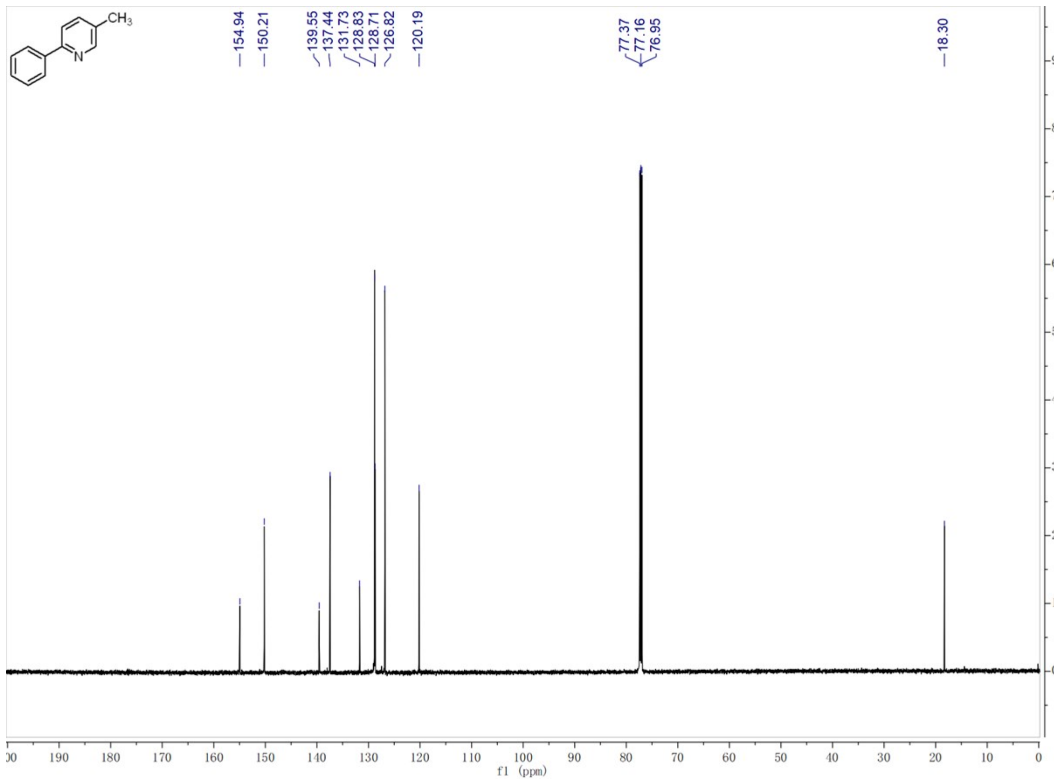

**42-H** [1]H NMR and [13]C NMR



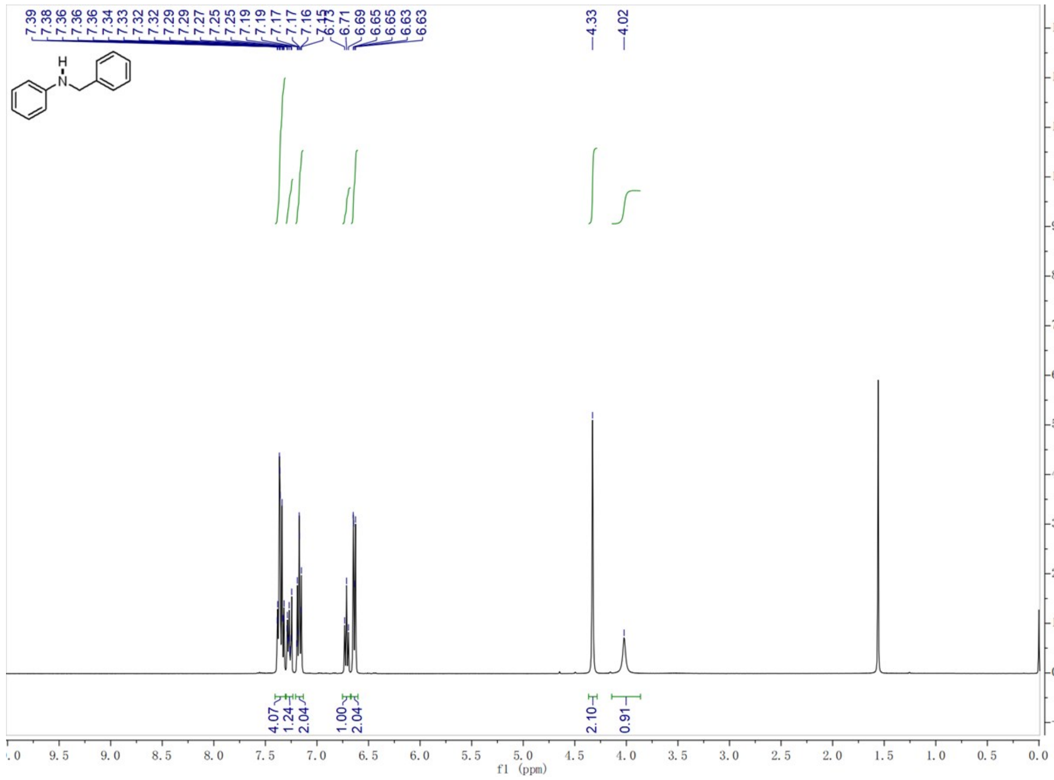


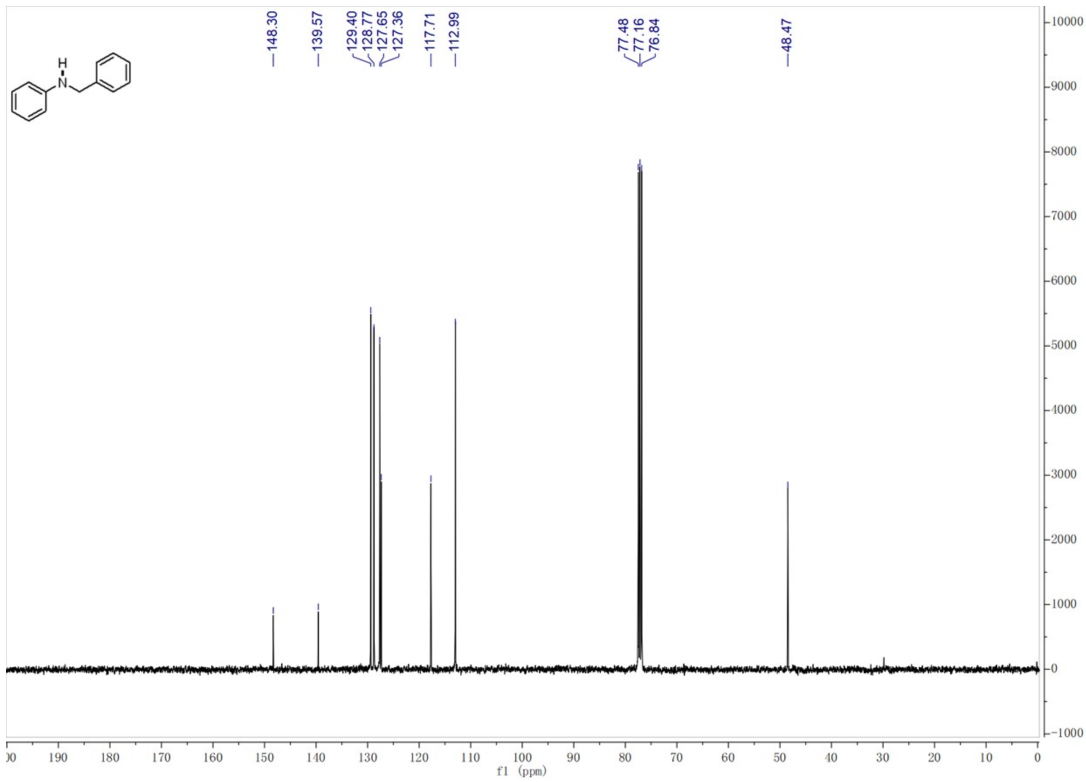

**43-H** $^1$H NMR and $^{13}$C NMR



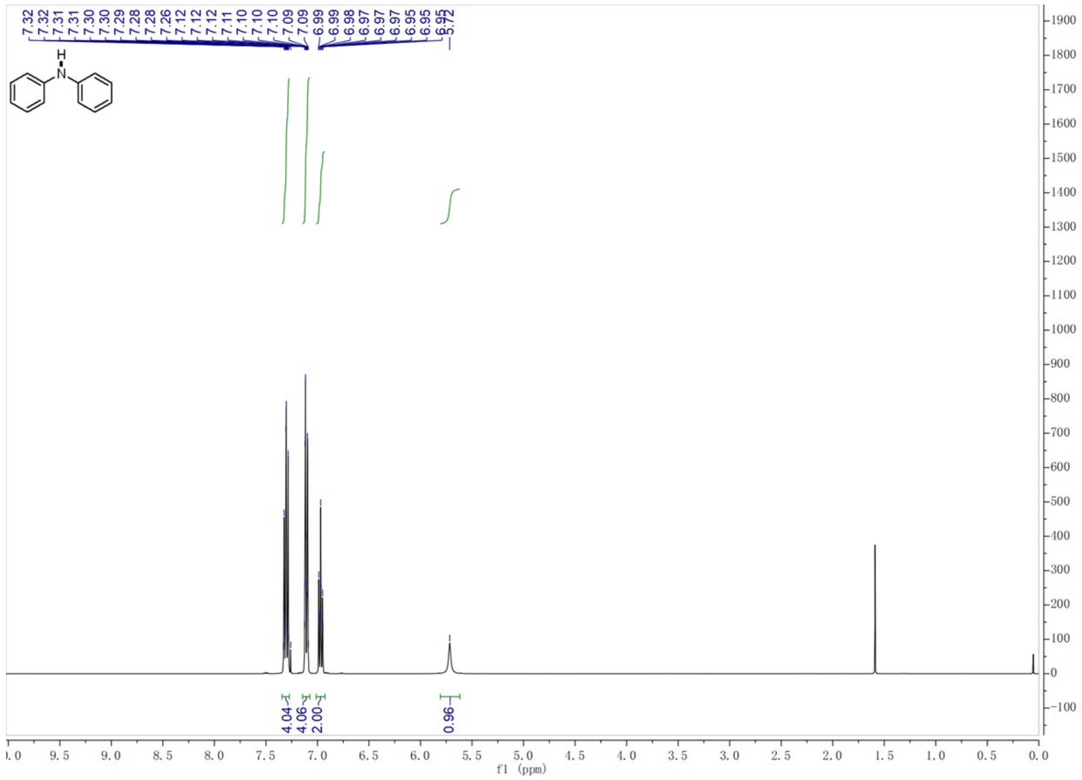


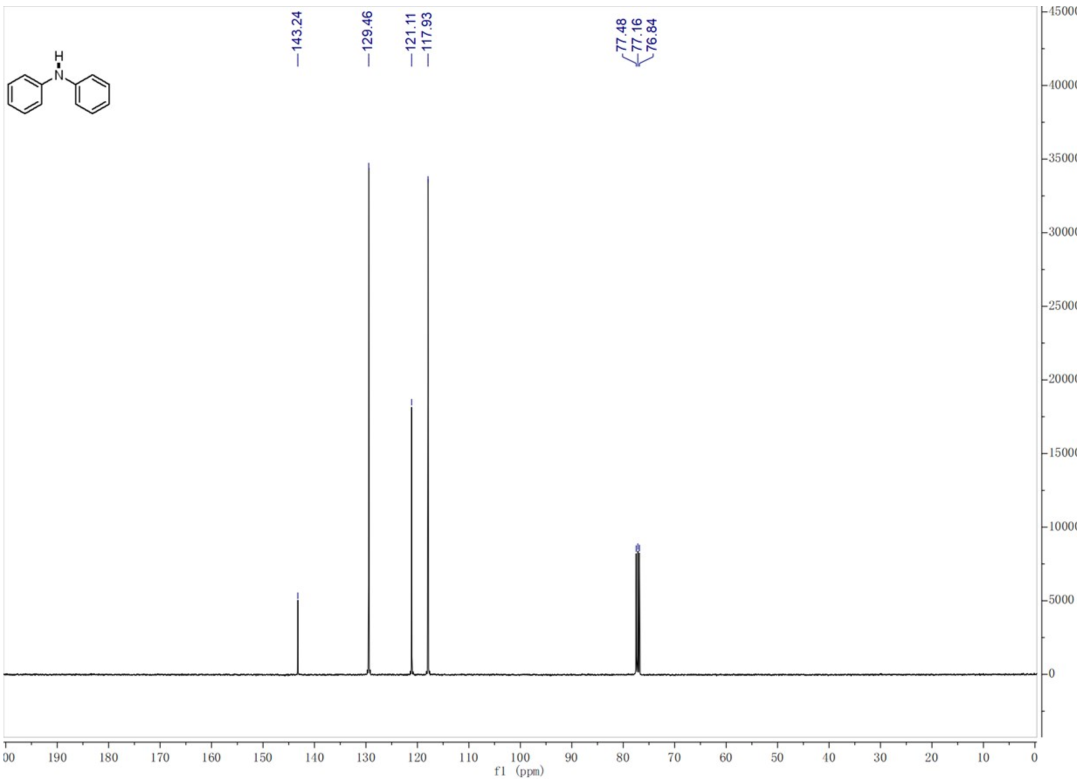
**44-H** $^1$H NMR and $^{13}$C NMR



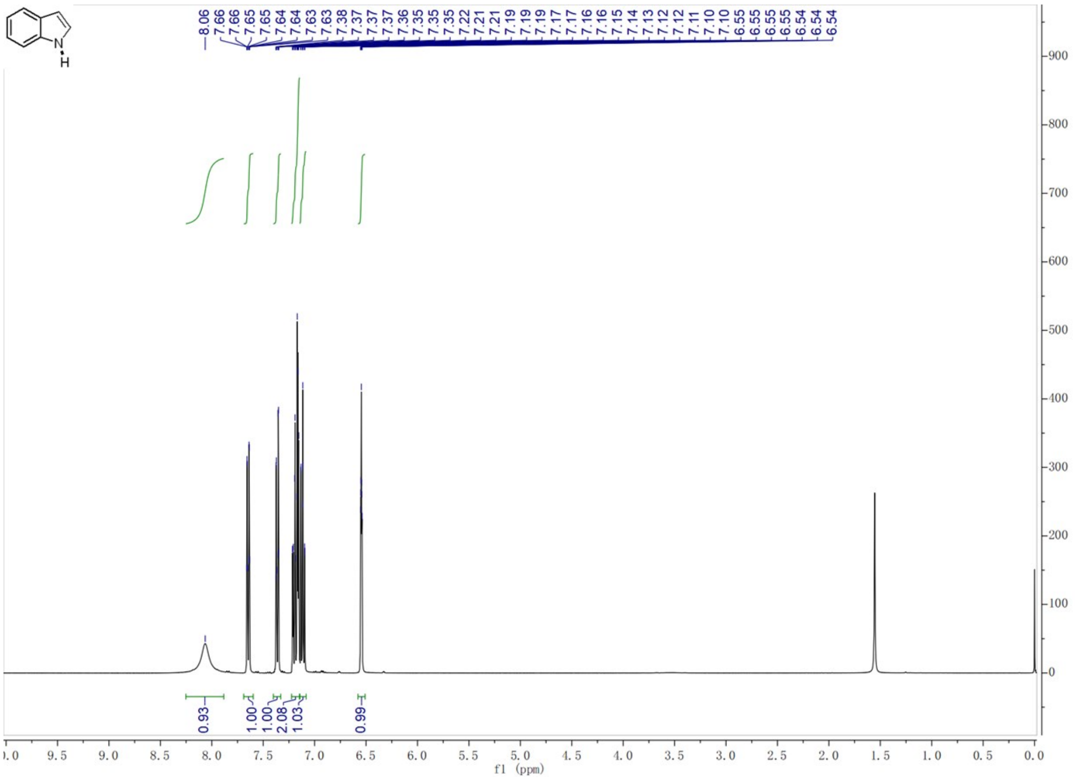


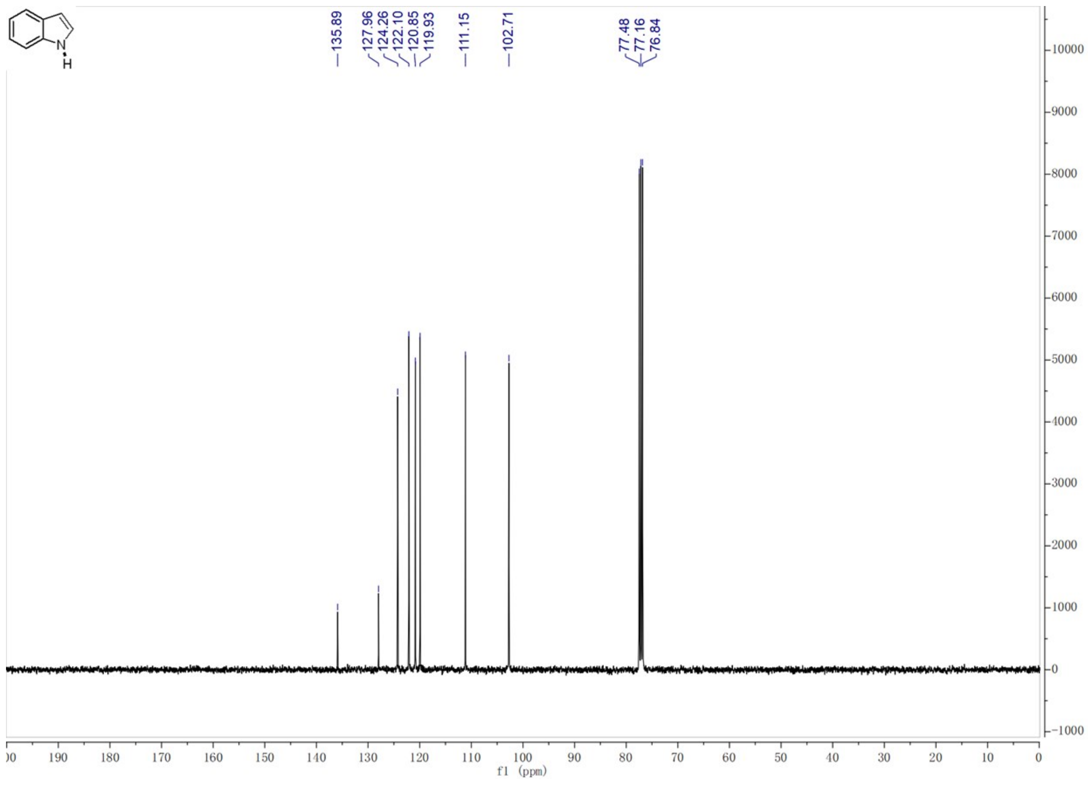

**45-H** $^{1}$H NMR and $^{13}$C NMR



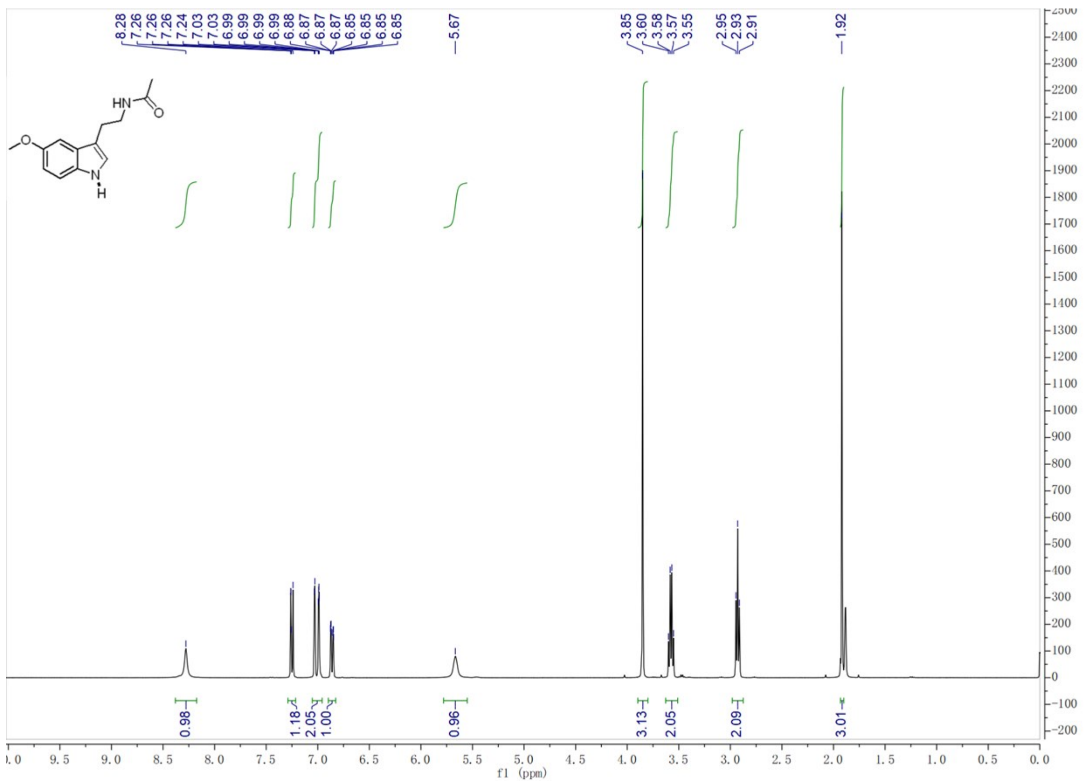


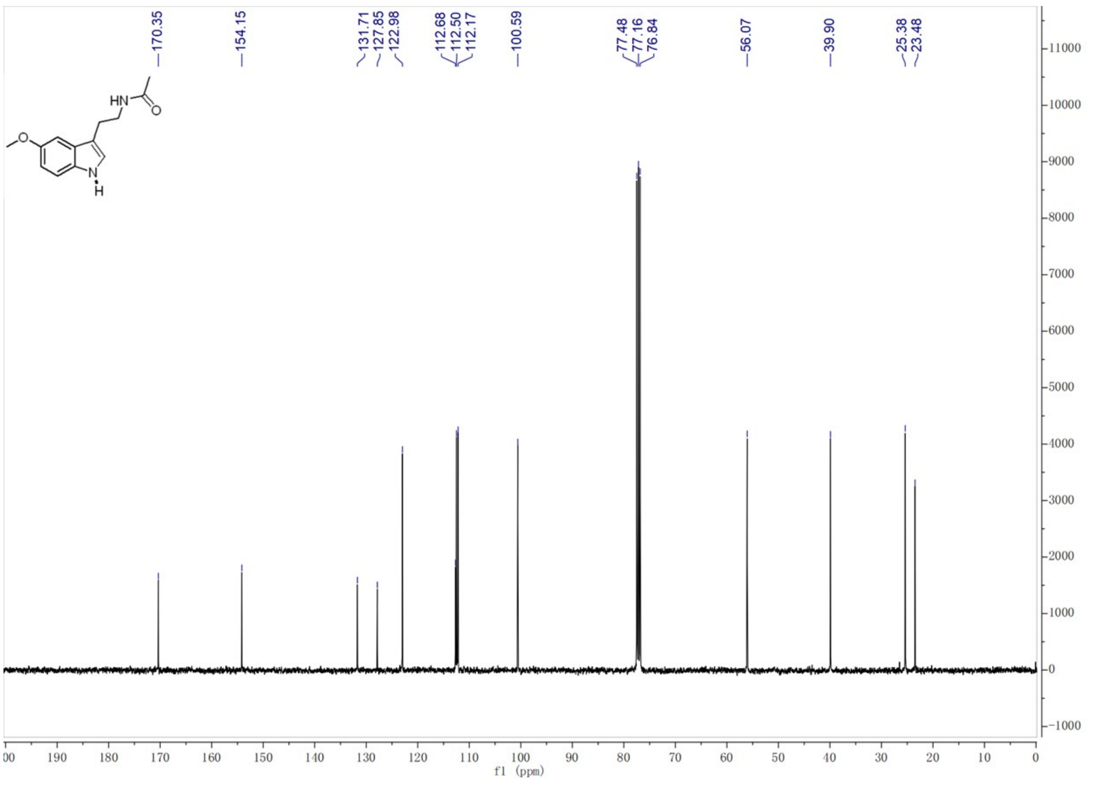

**46-H** $^{1}$H NMR and $^{13}$C NMR



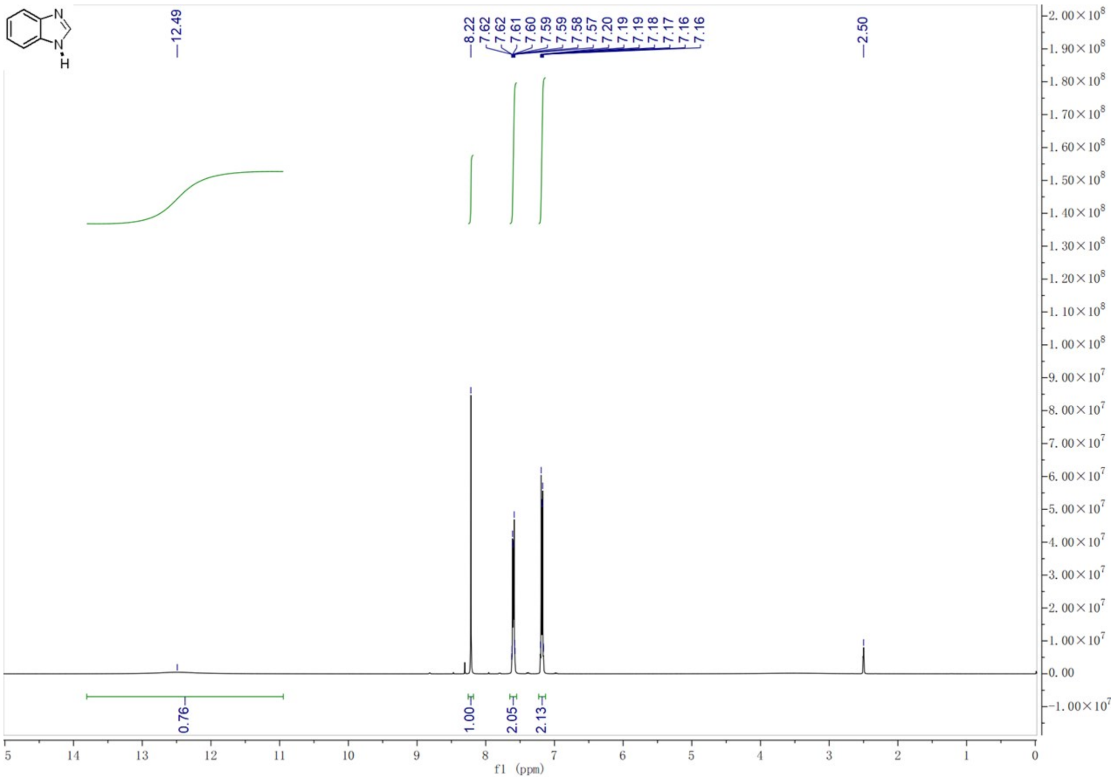


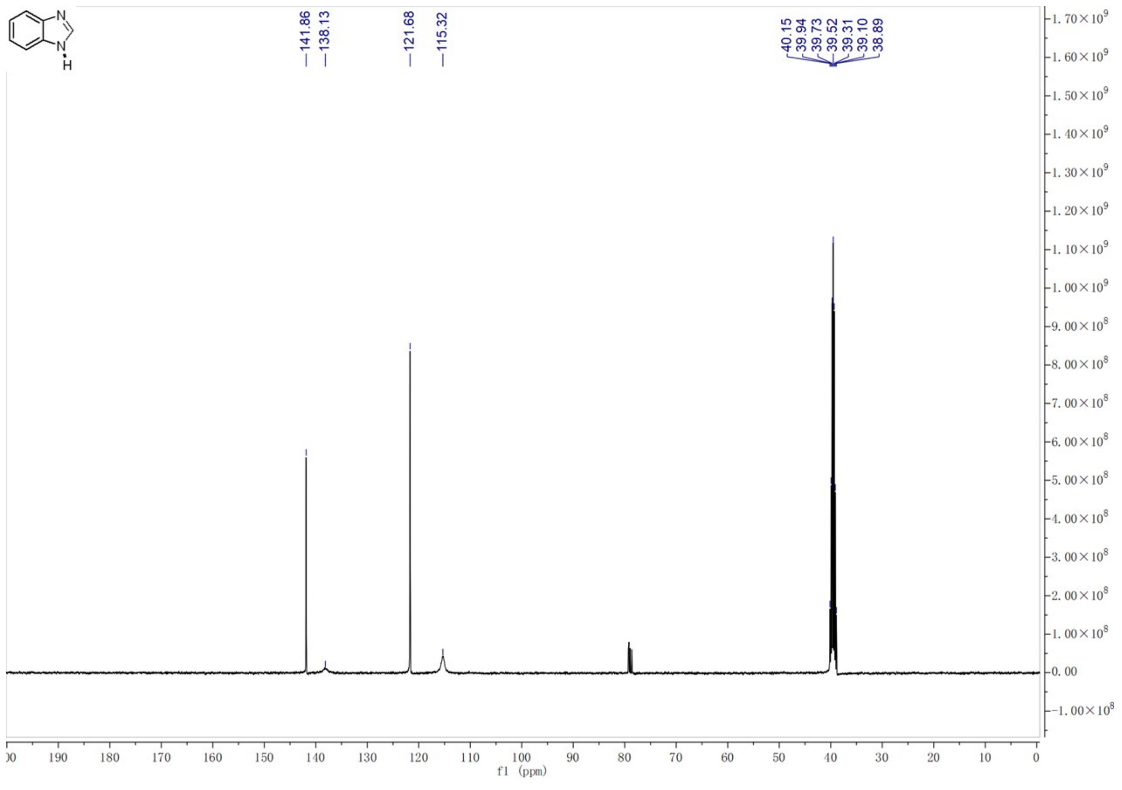
**47-H** $^{1}H$ NMR and $^{13}C$ NMR



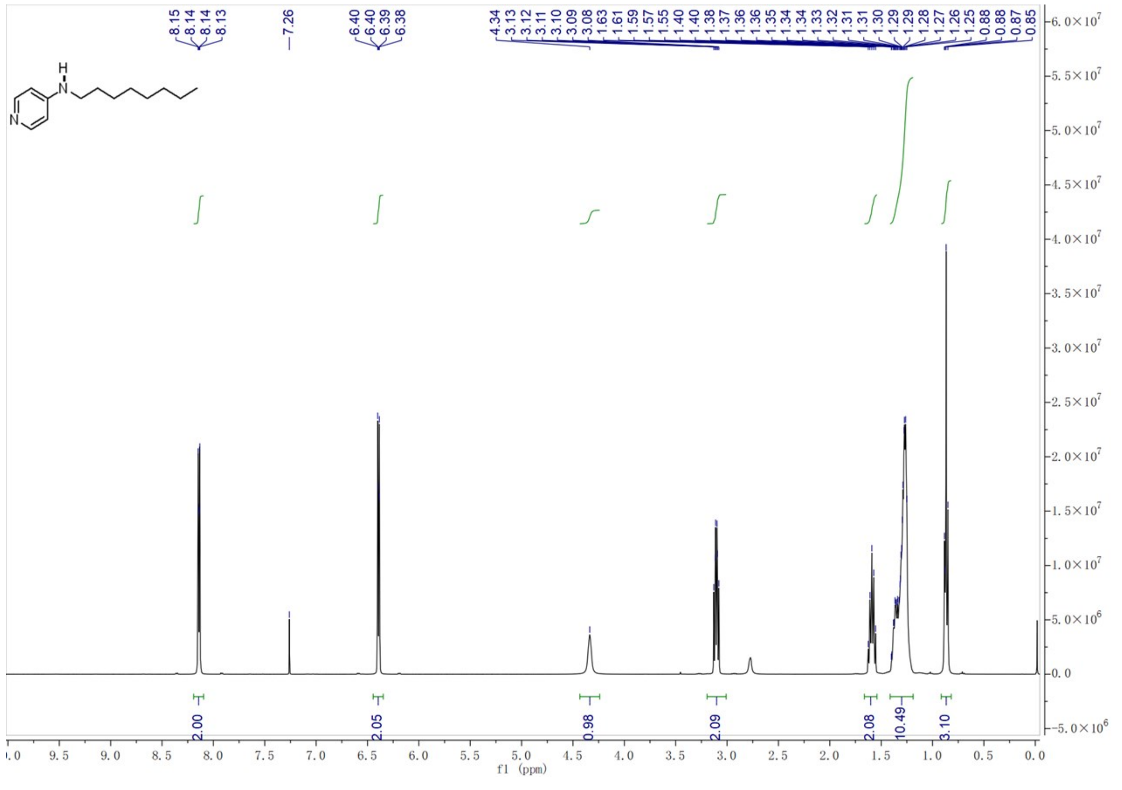


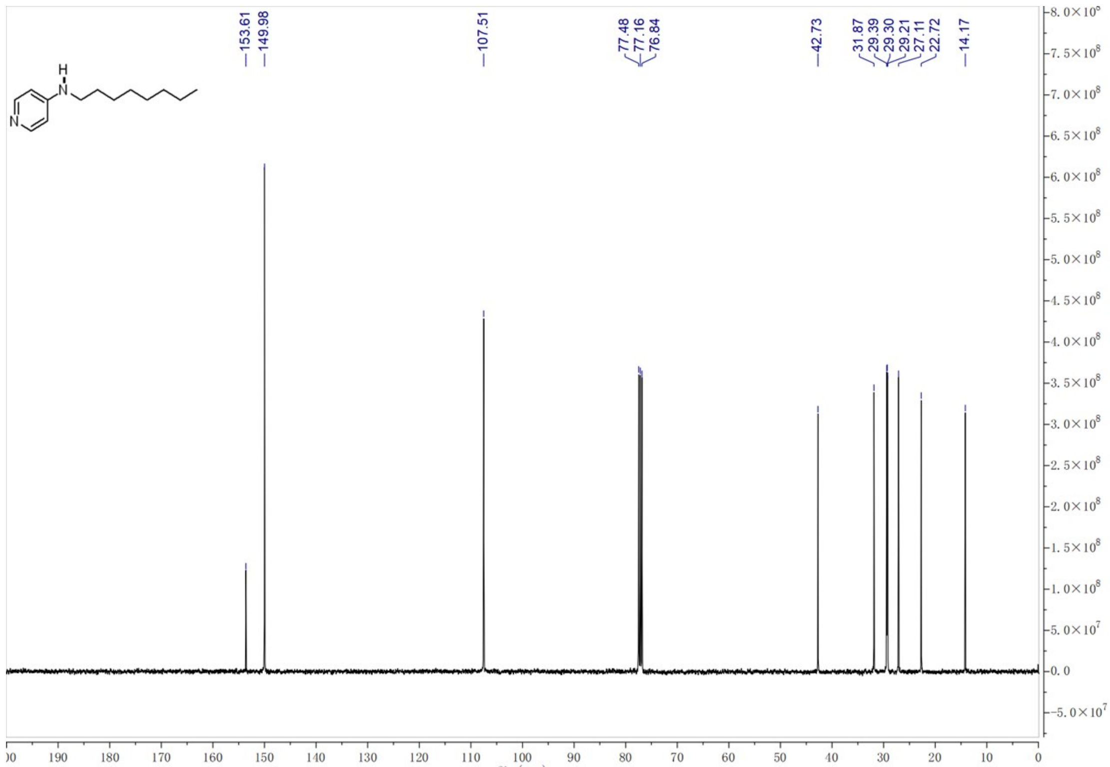

**48-H** $^{1}$H NMR and $^{13}$C NMR



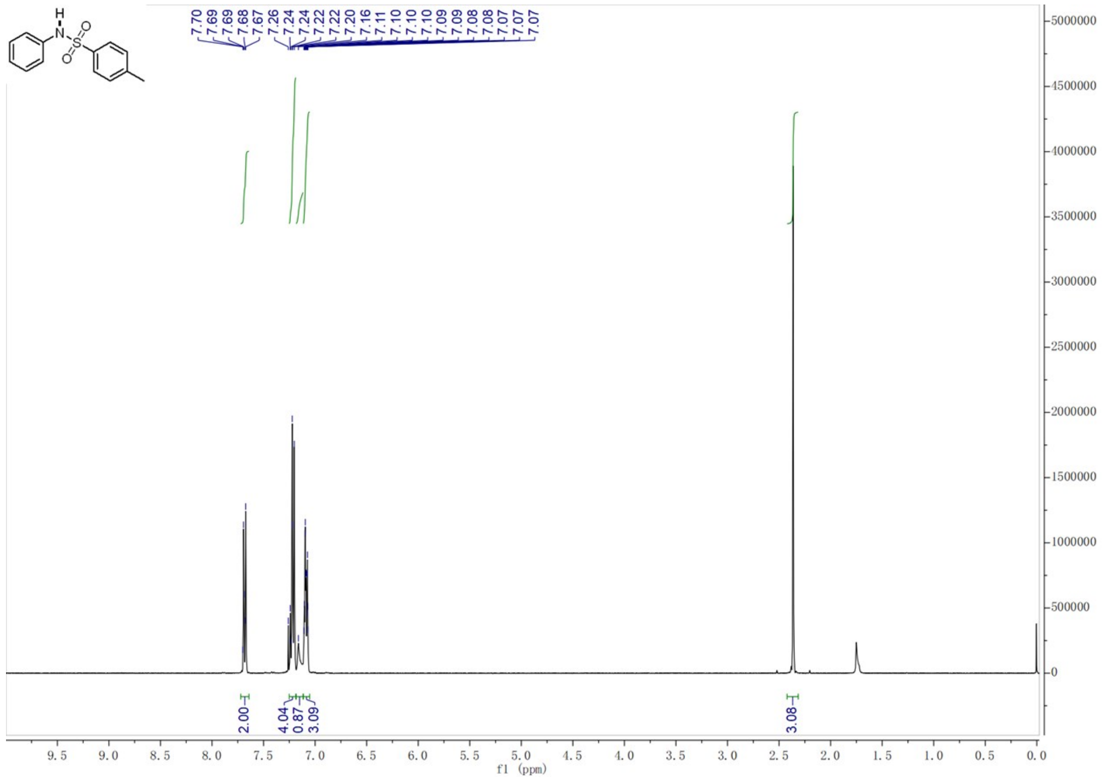


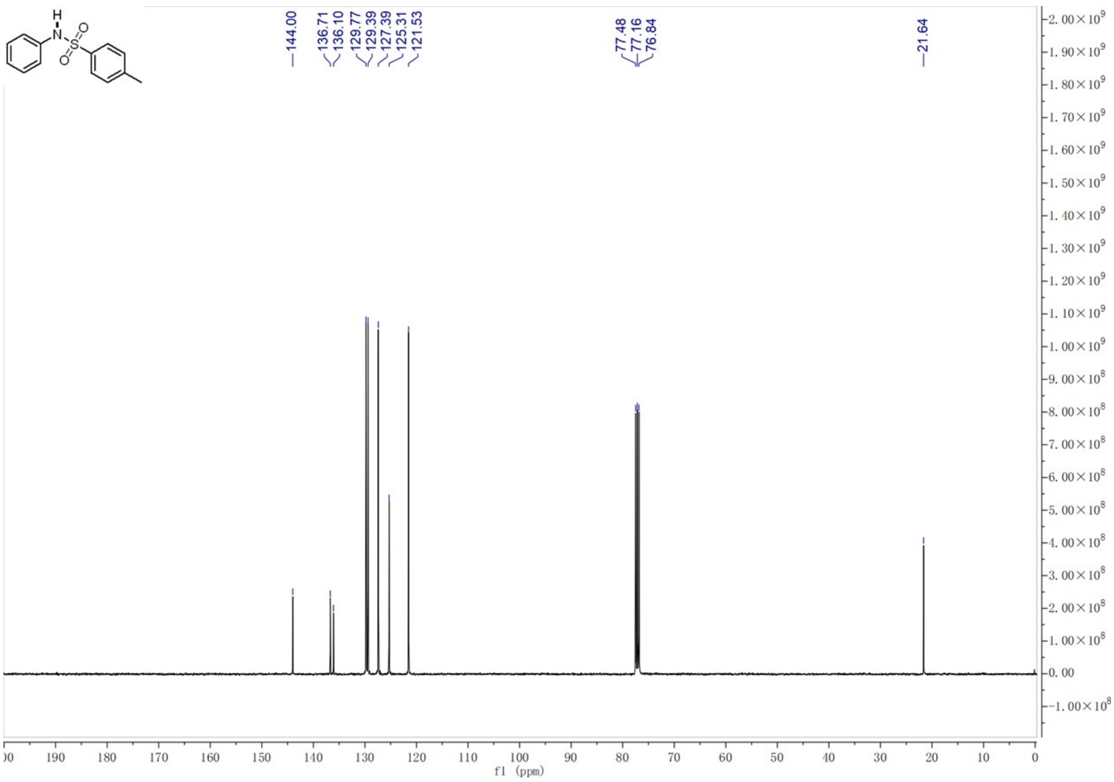
**49-H** $^{1}$H NMR and $^{13}$C NMR



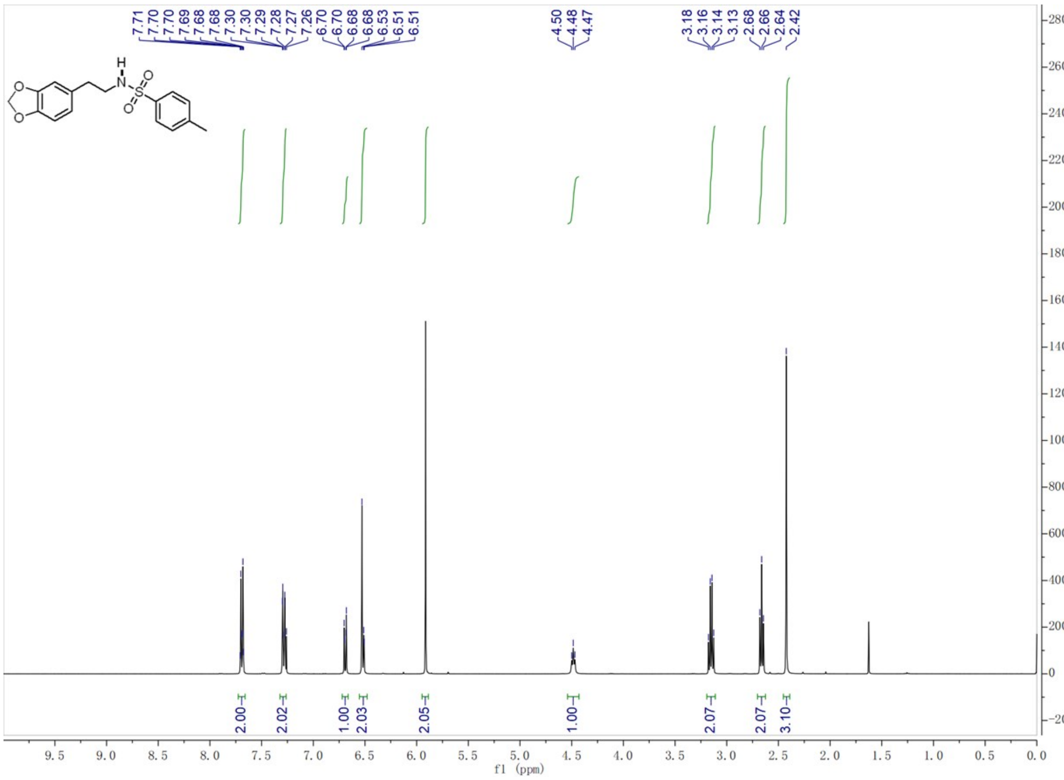


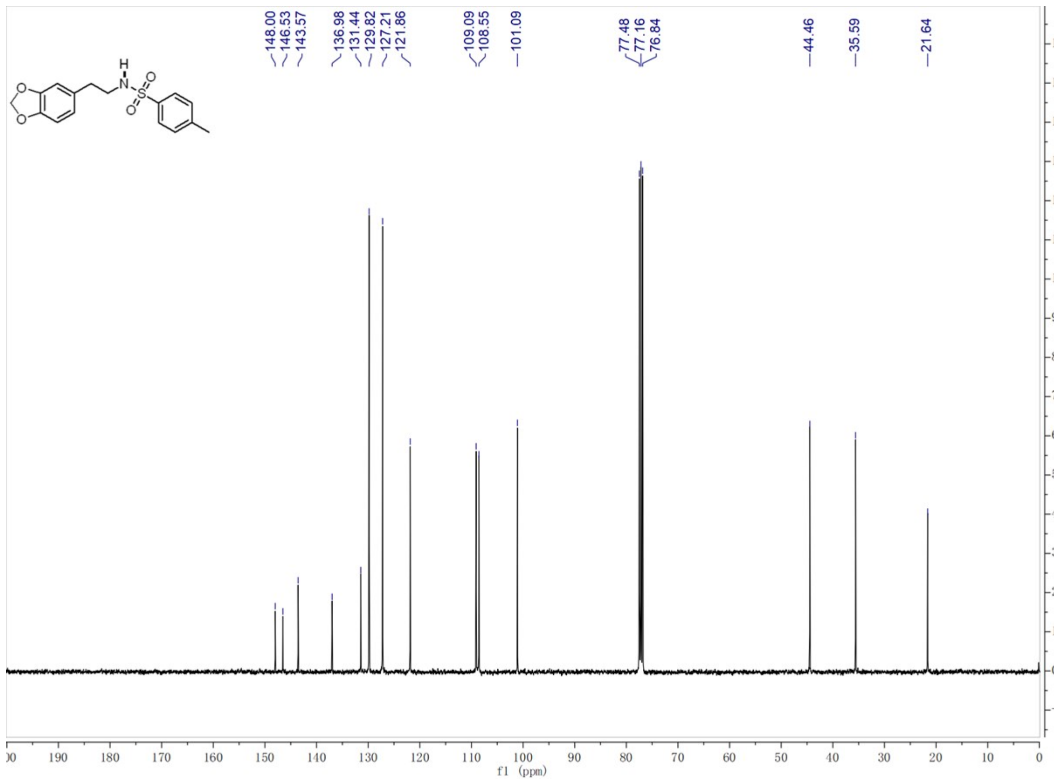

**50-H** (**58-Ts**) $^{1}$H NMR and $^{13}$C NMR



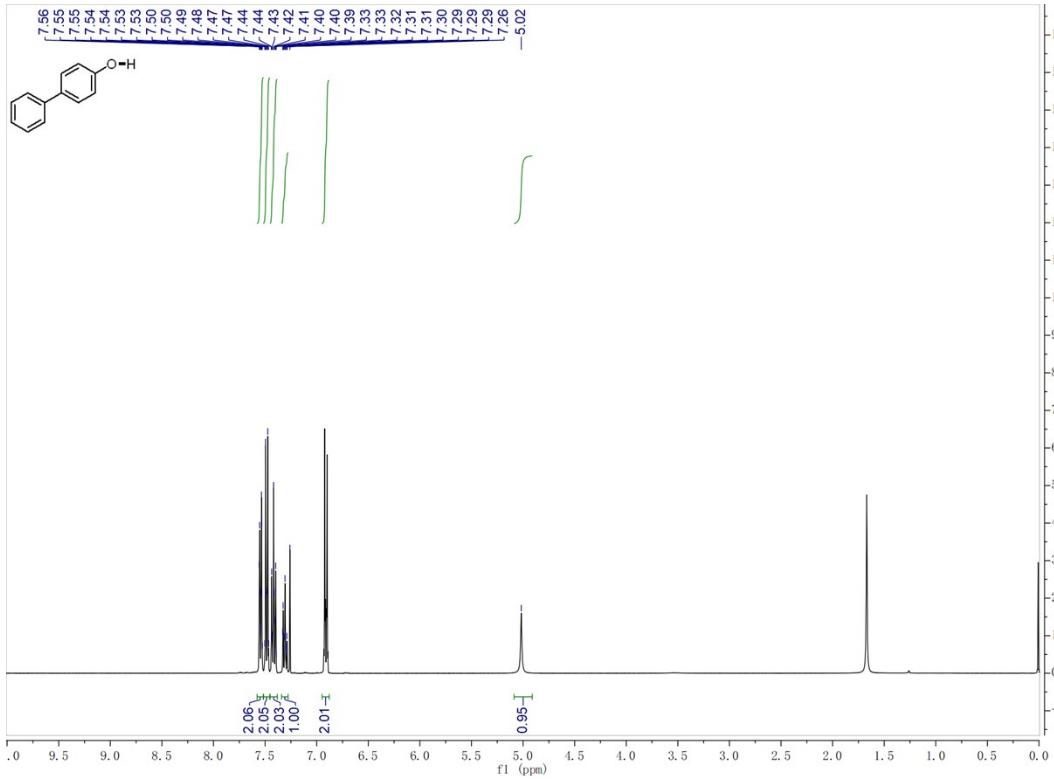


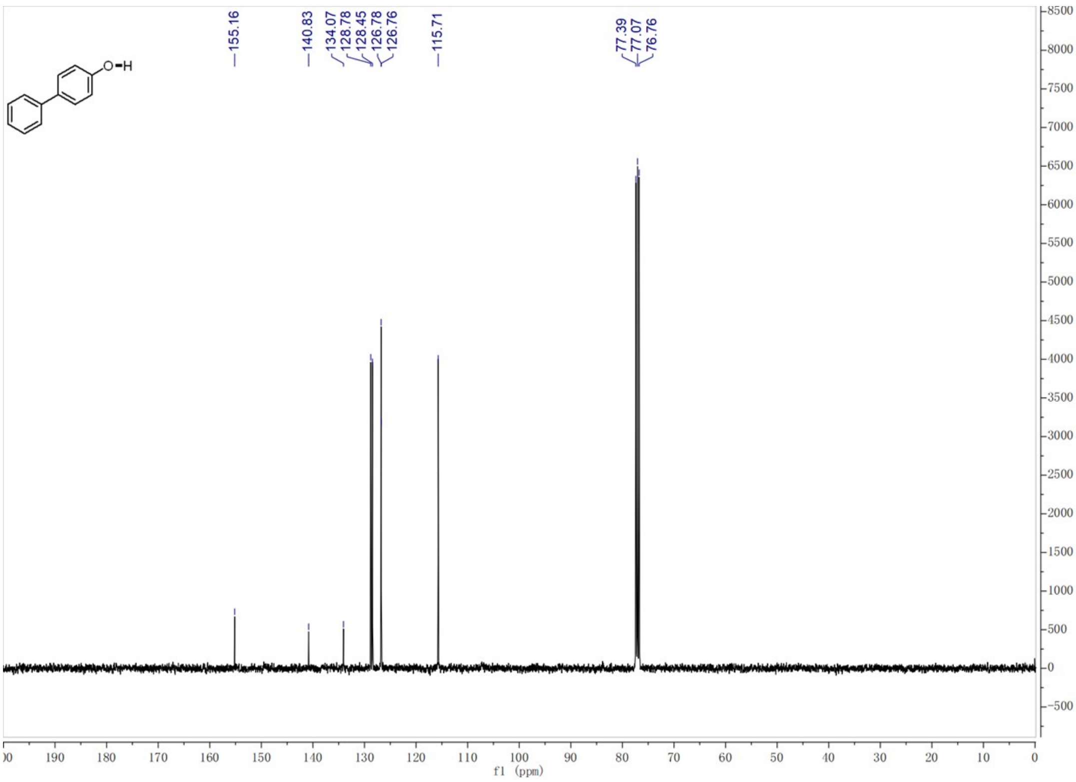

**51-H** $^{1}$H NMR and $^{13}$C NMR



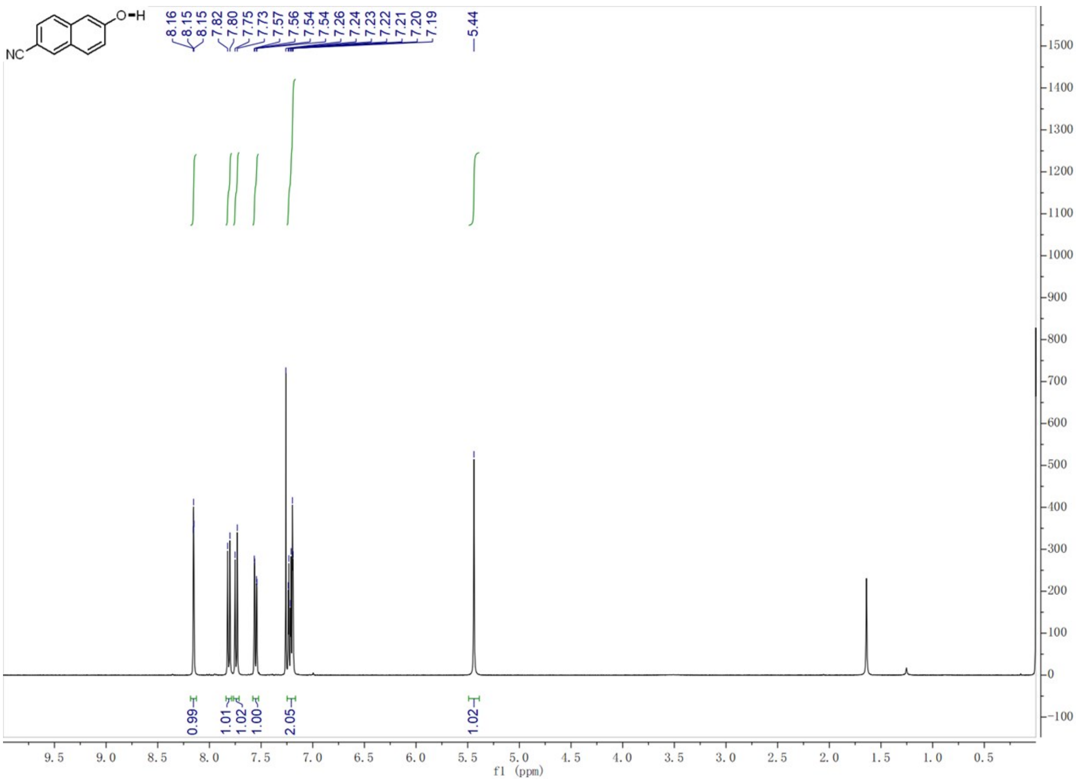


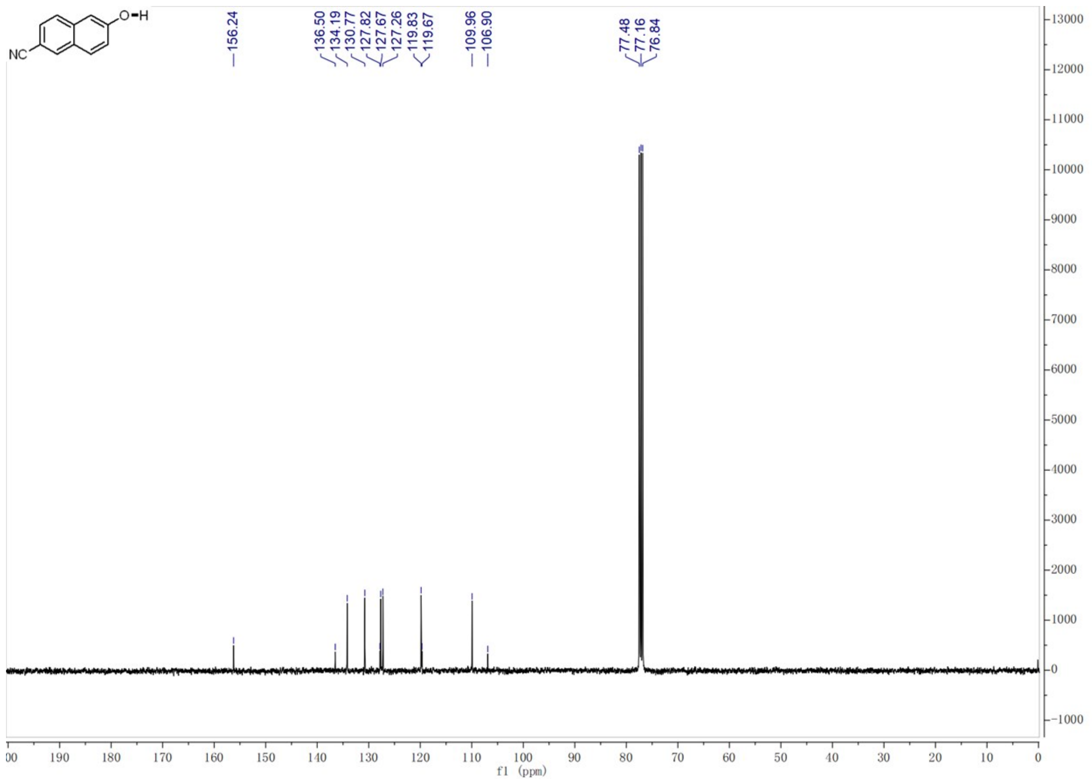
**52-H** $^{1}$H NMR and $^{13}$C NMR



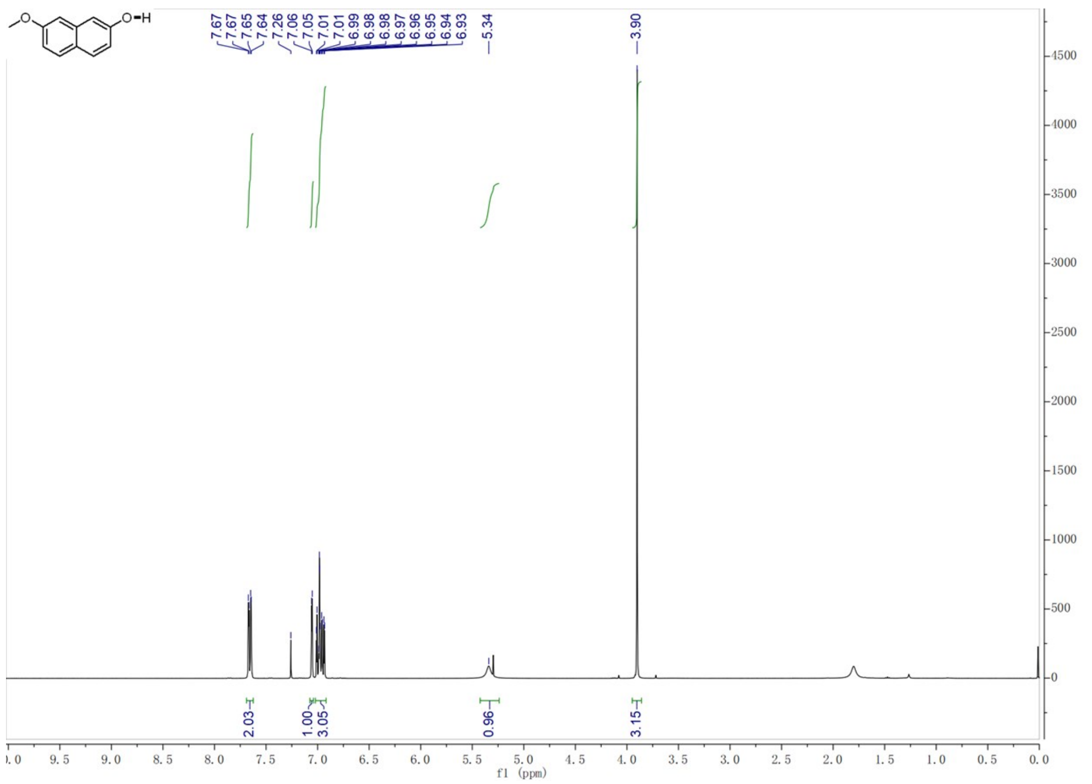


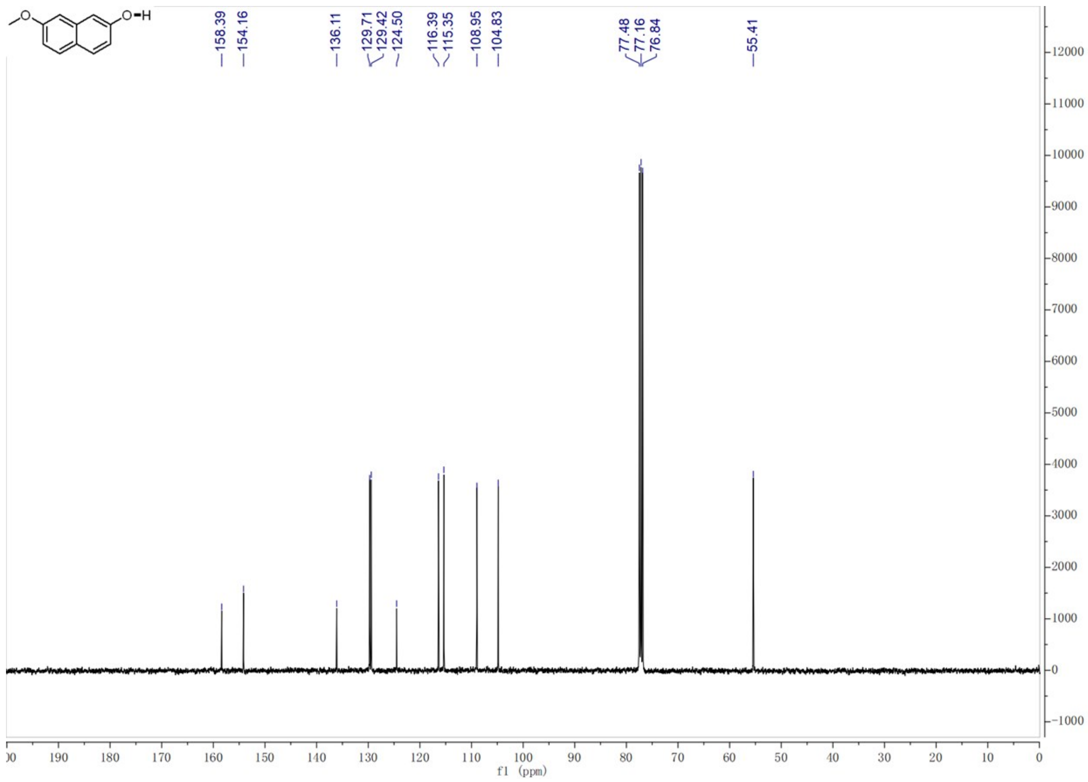

**53-H** $^{1}$H NMR and $^{13}$C NMR



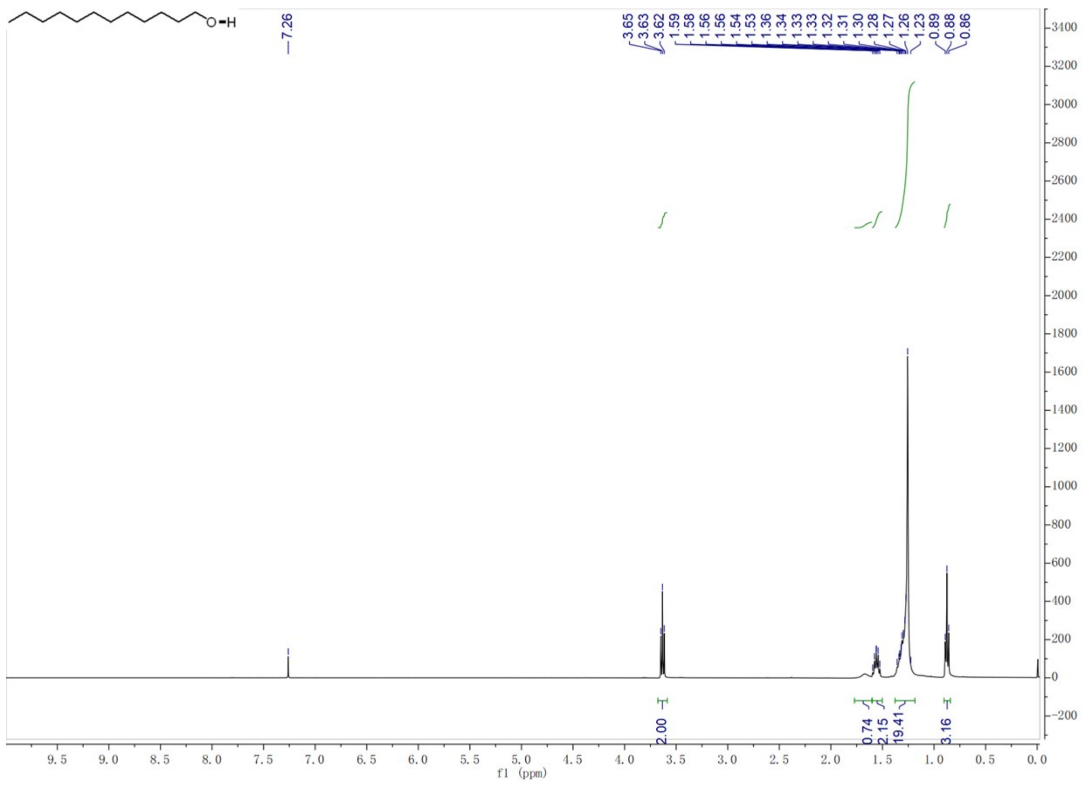


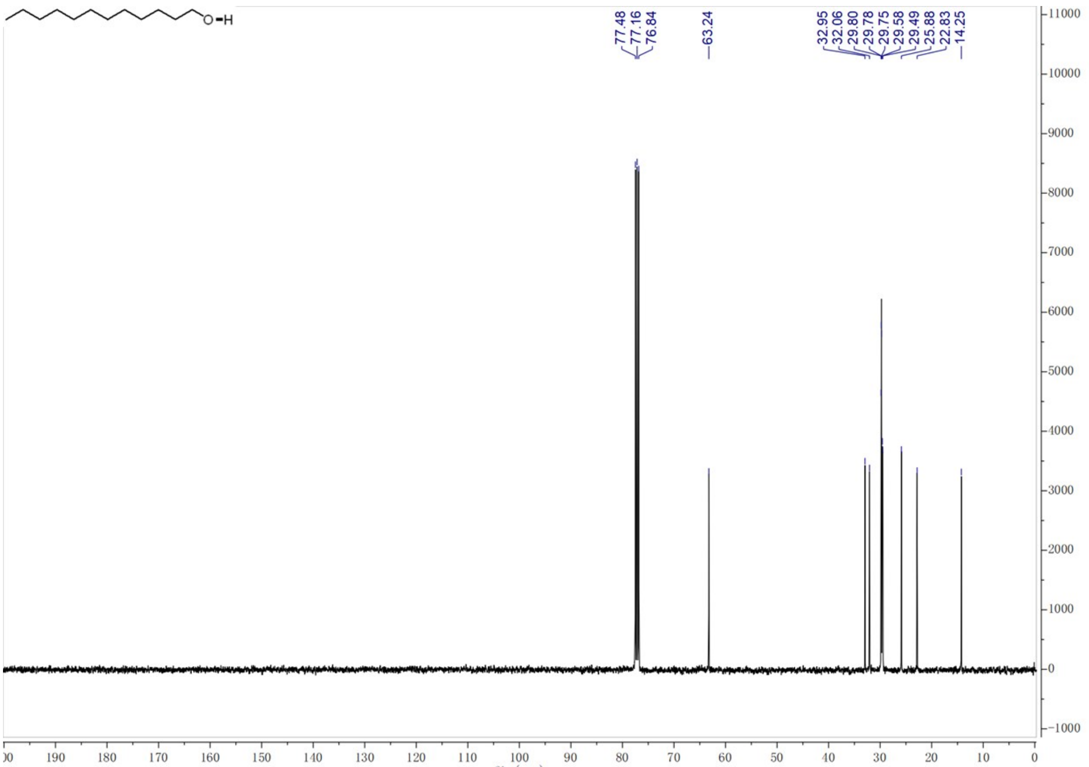

**54-H** $^1$H NMR and $^{13}$C NMR



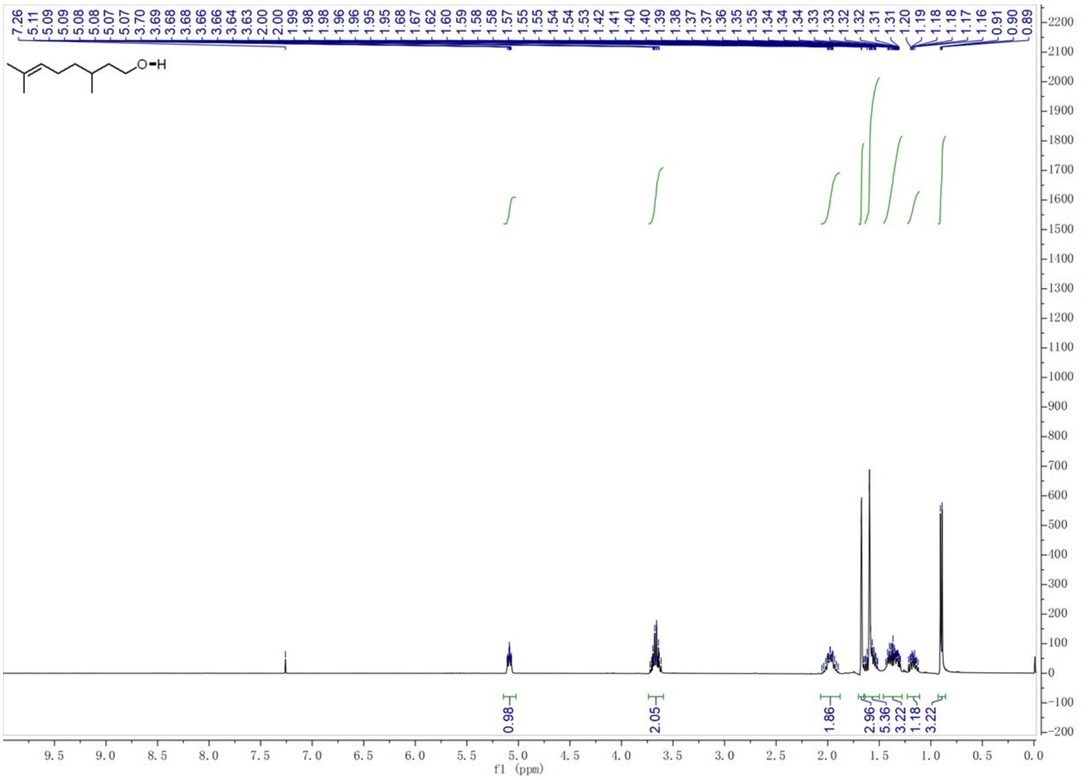


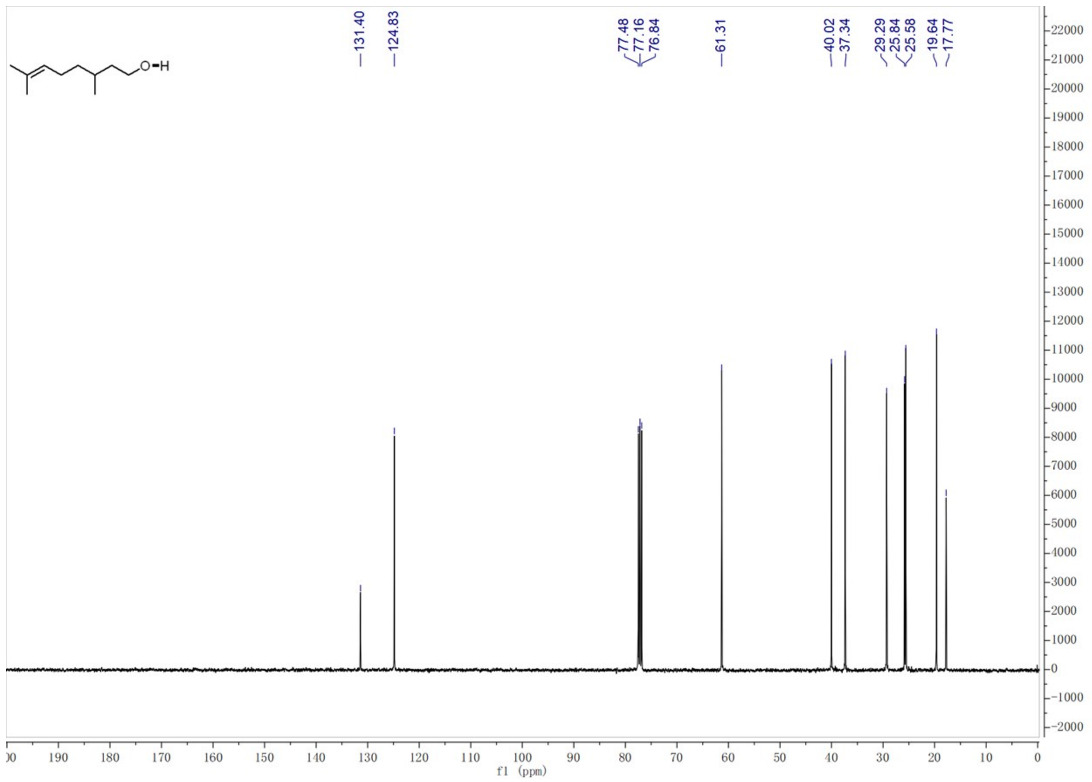
**55-H** $^{1}$H NMR and $^{13}$C NMR



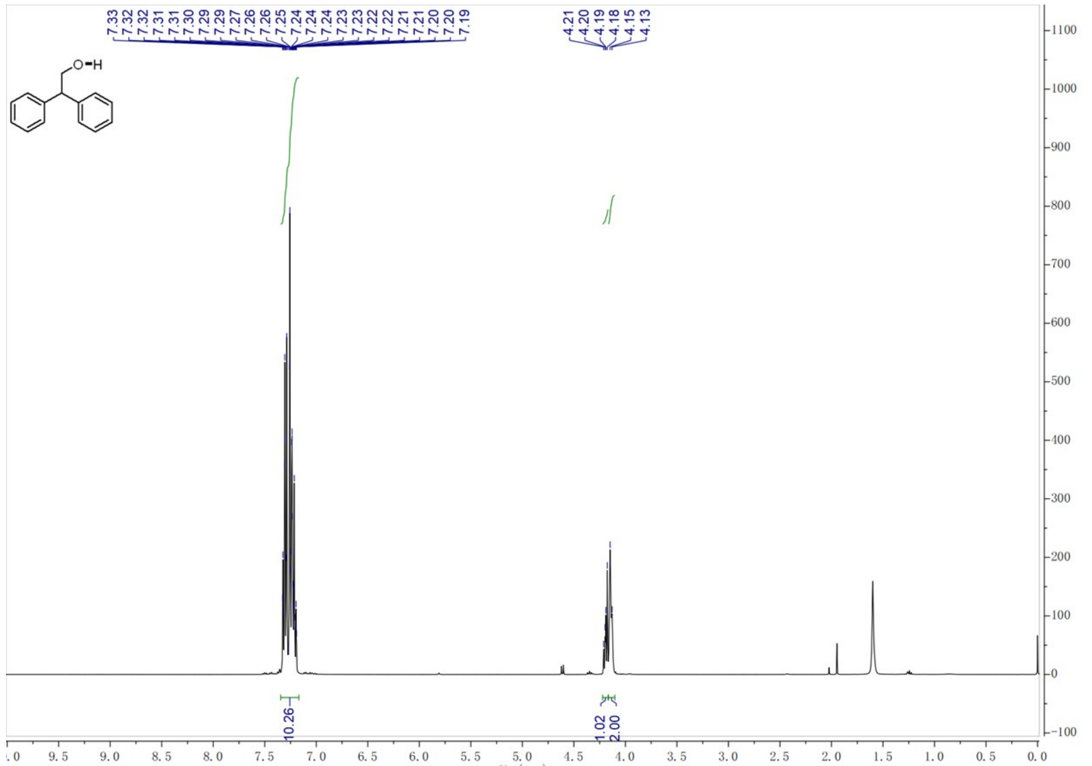


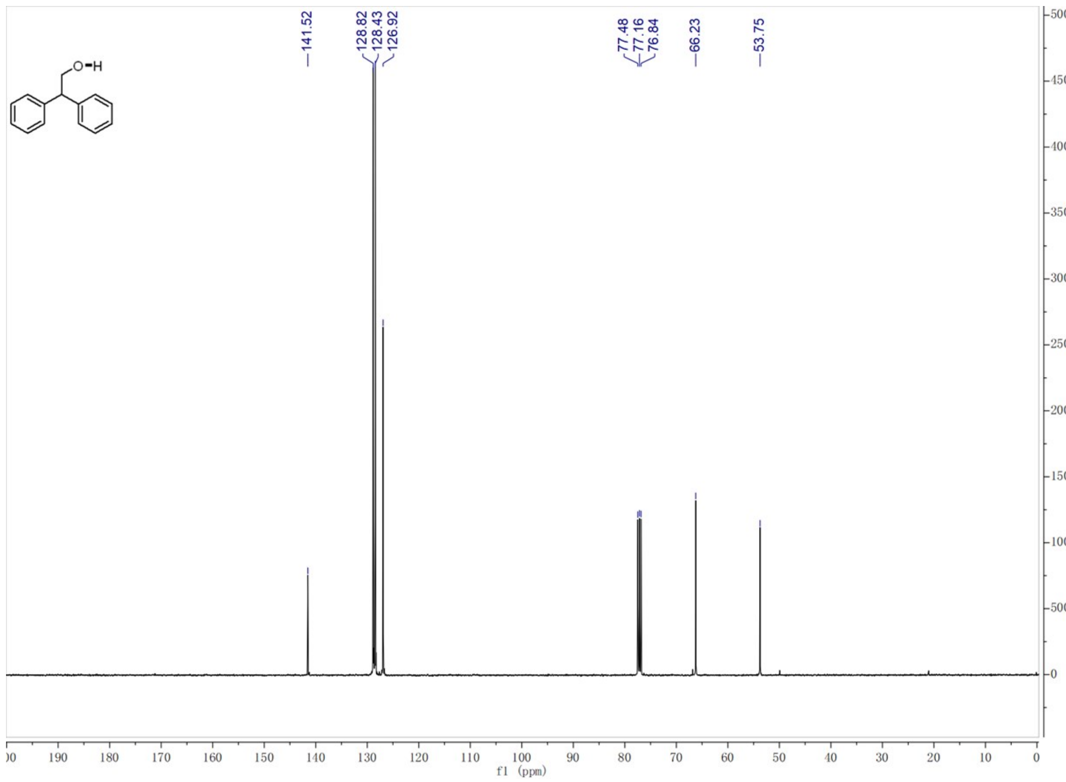

**56-H** $^1$H NMR and $^{13}$C NMR



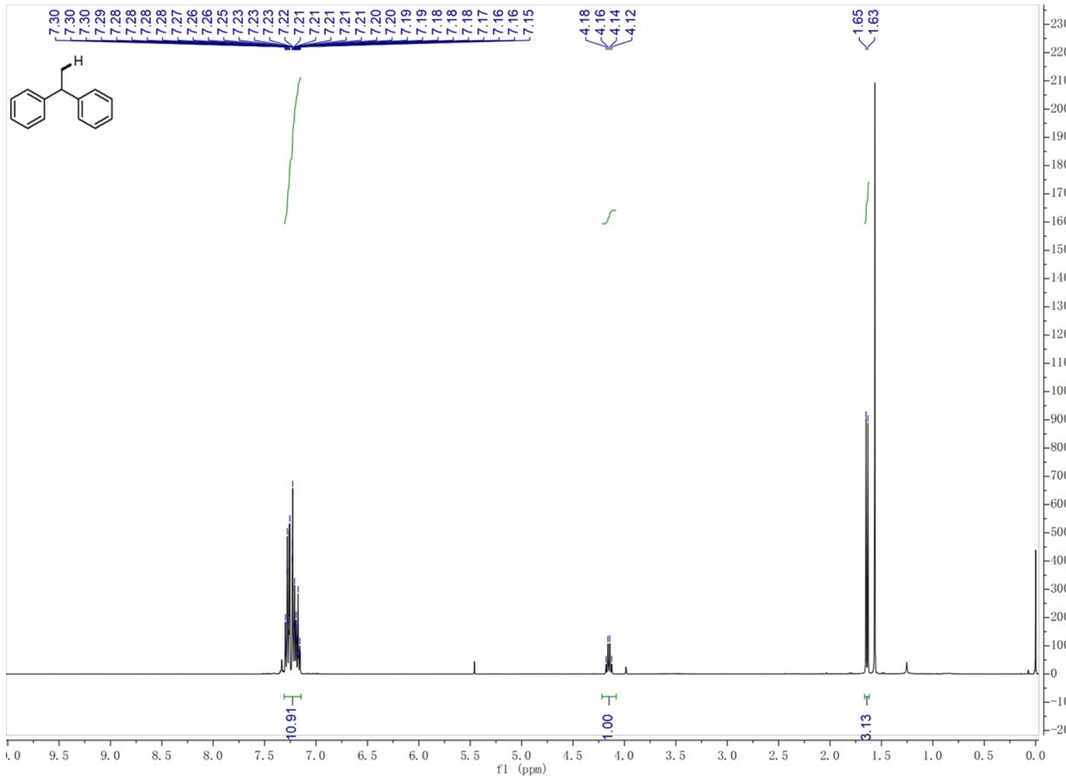


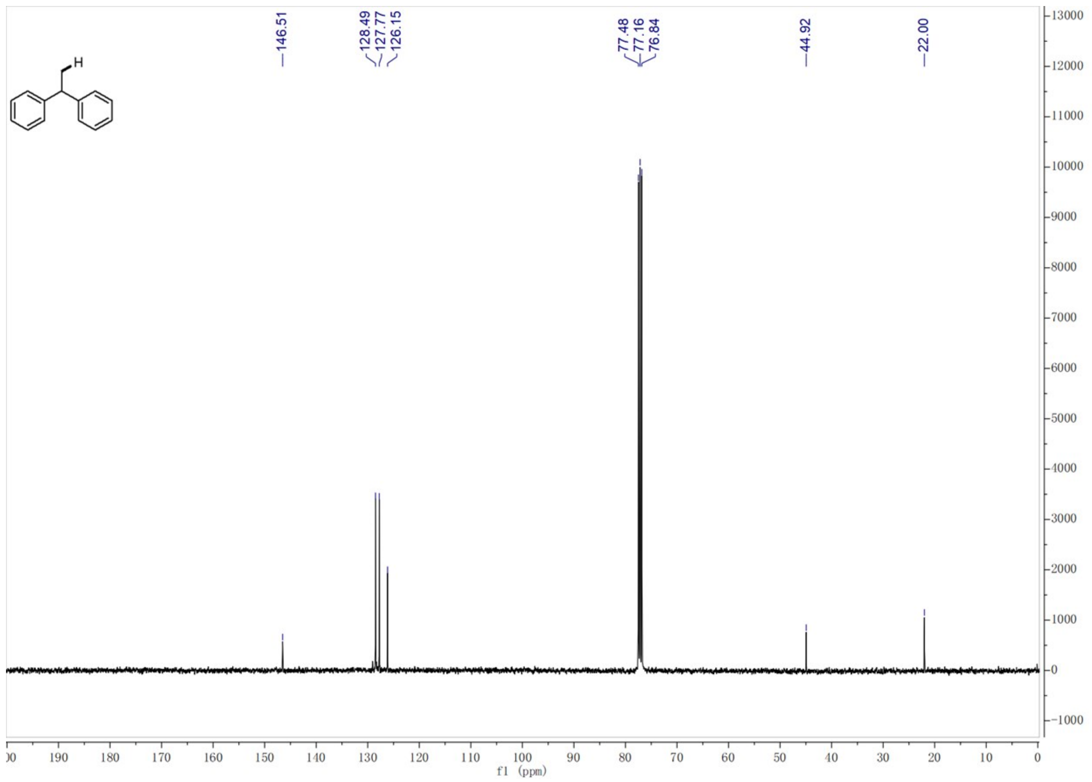
**57-H** $^{1}$H NMR and $^{13}$C NMR



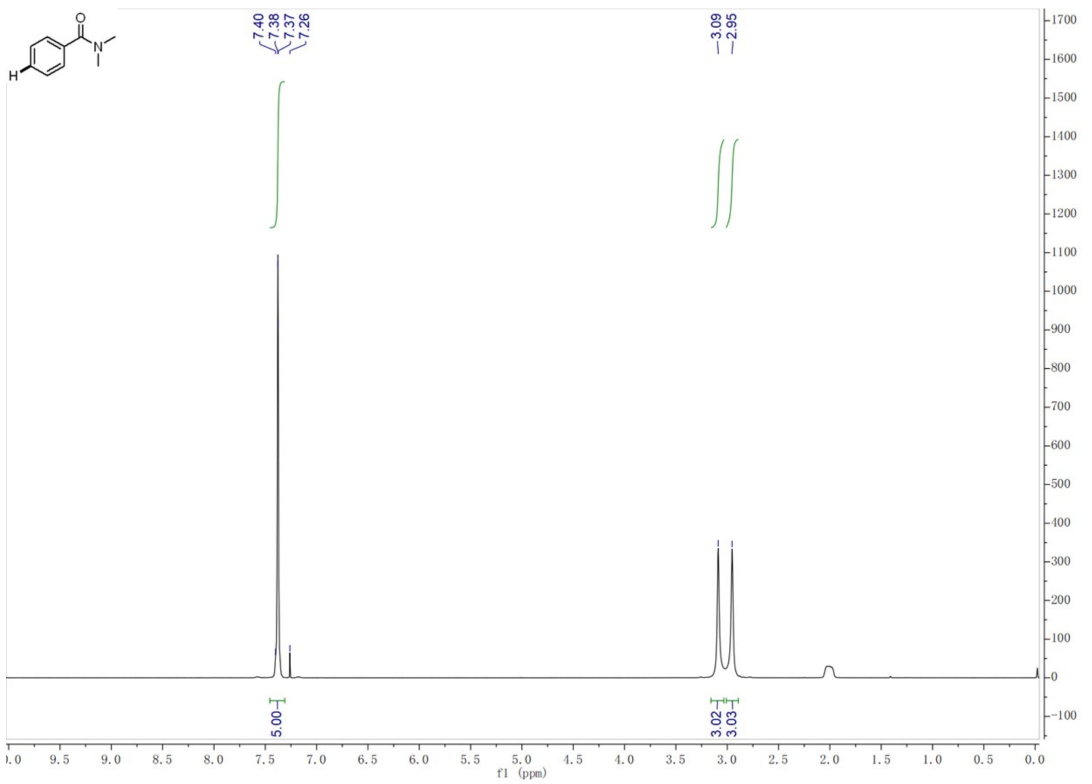


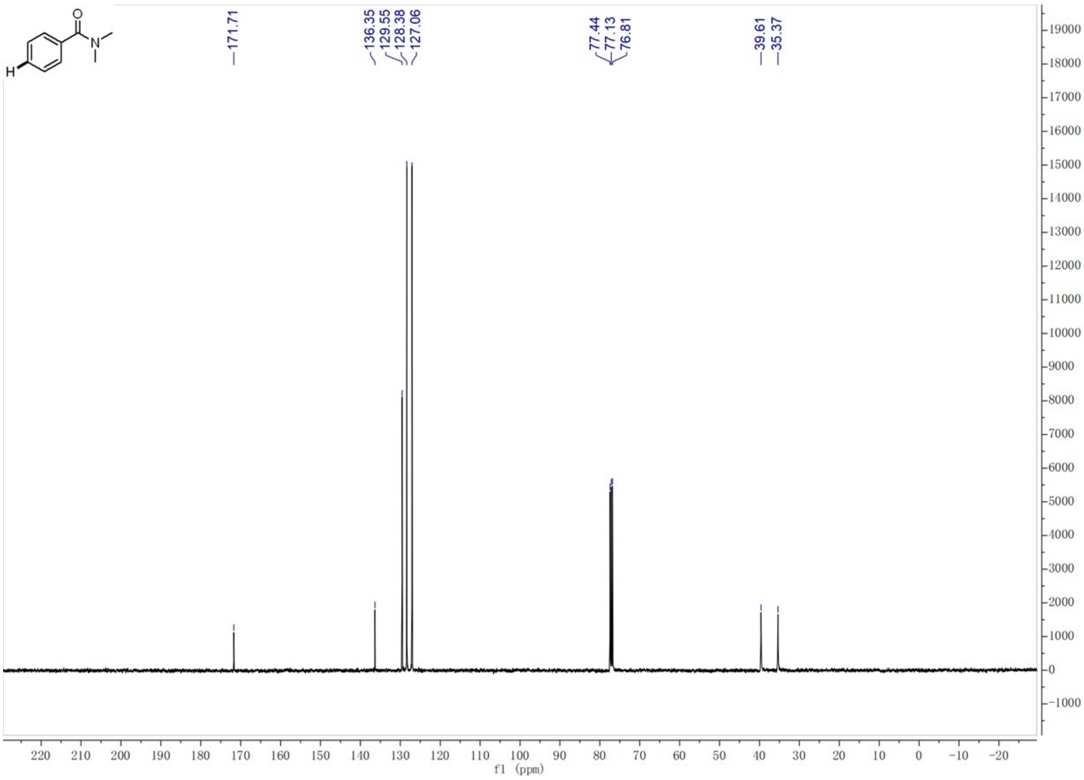
**57-H'** $^1$H NMR and $^{13}$C NMR



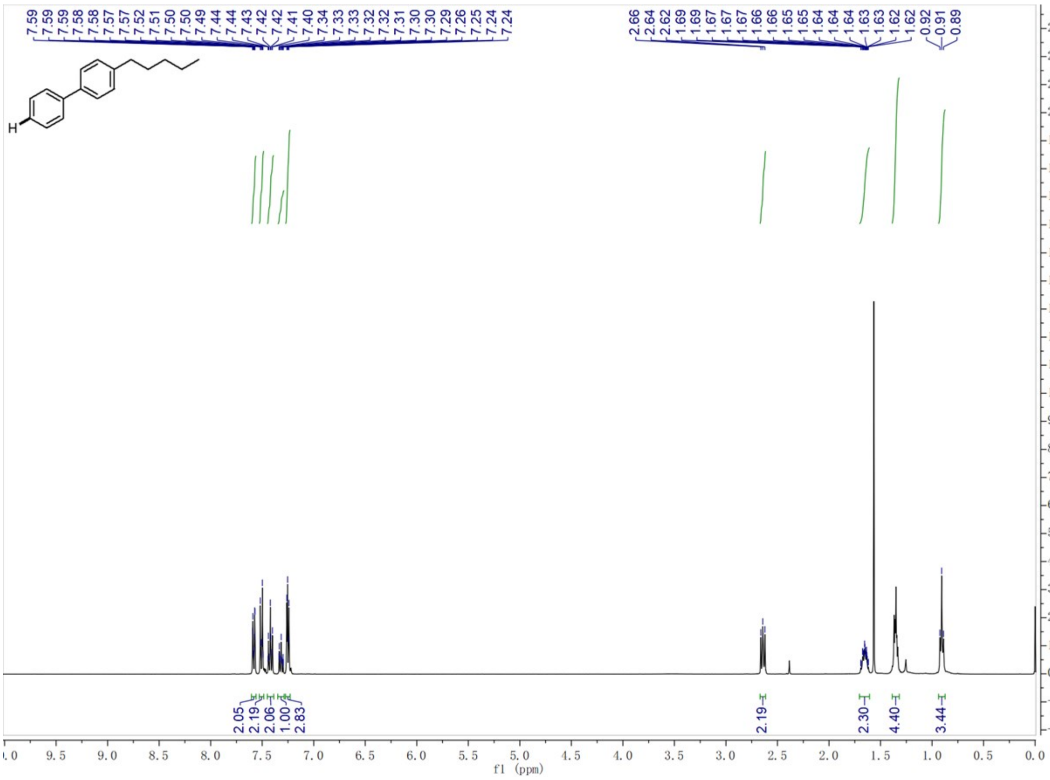


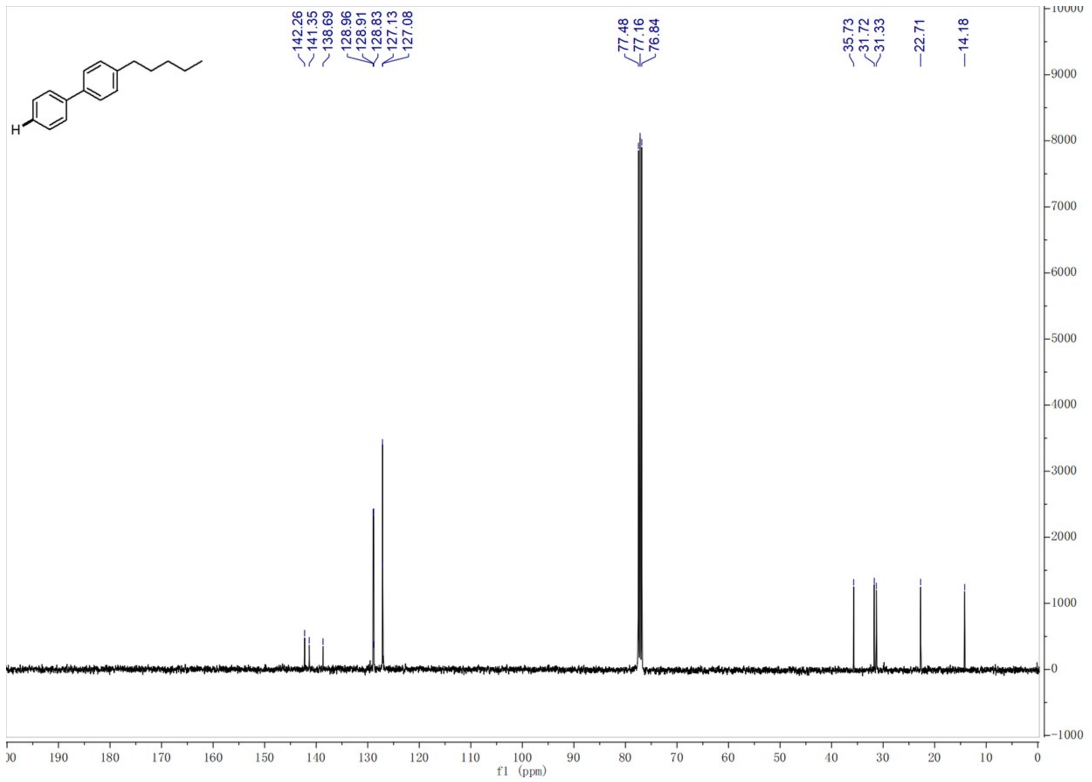

**59-H** $^1$H NMR and $^{13}$C NMR



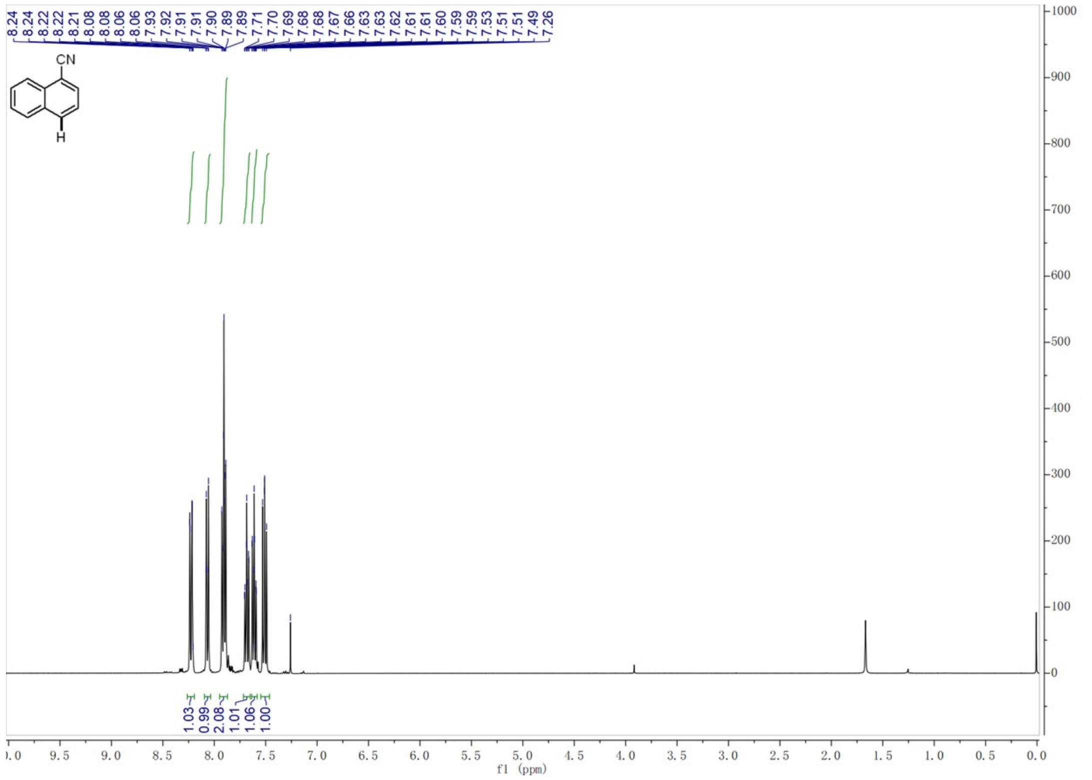


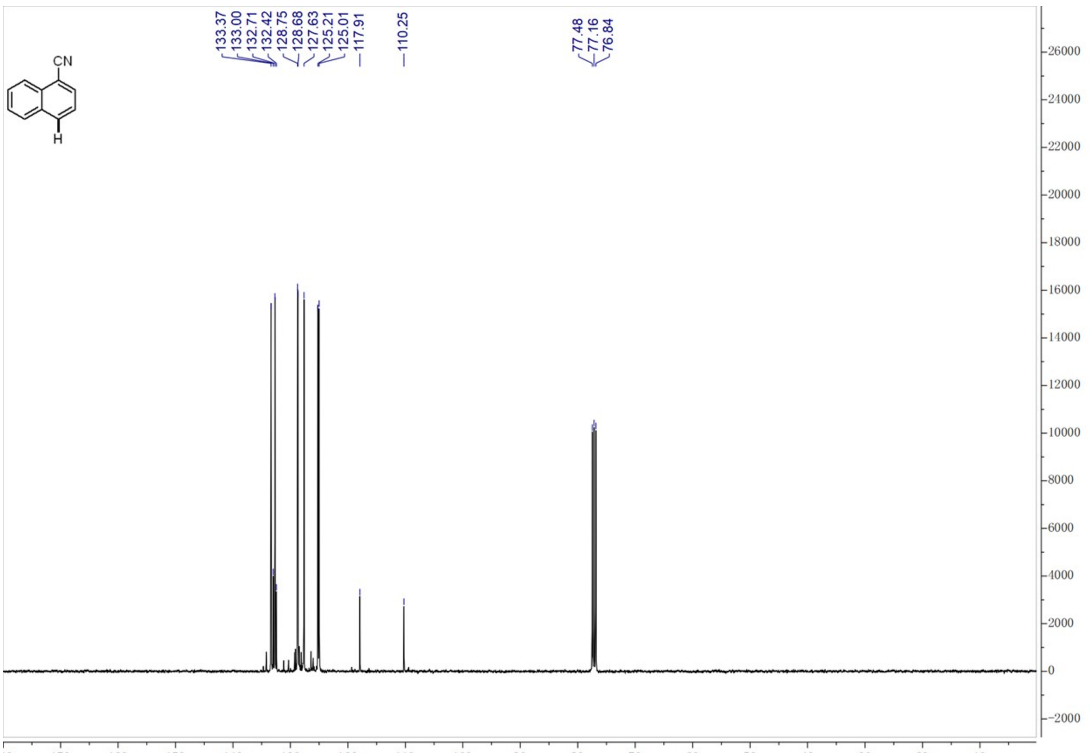

**60-H** $^{1}$H NMR and $^{13}$C NMR



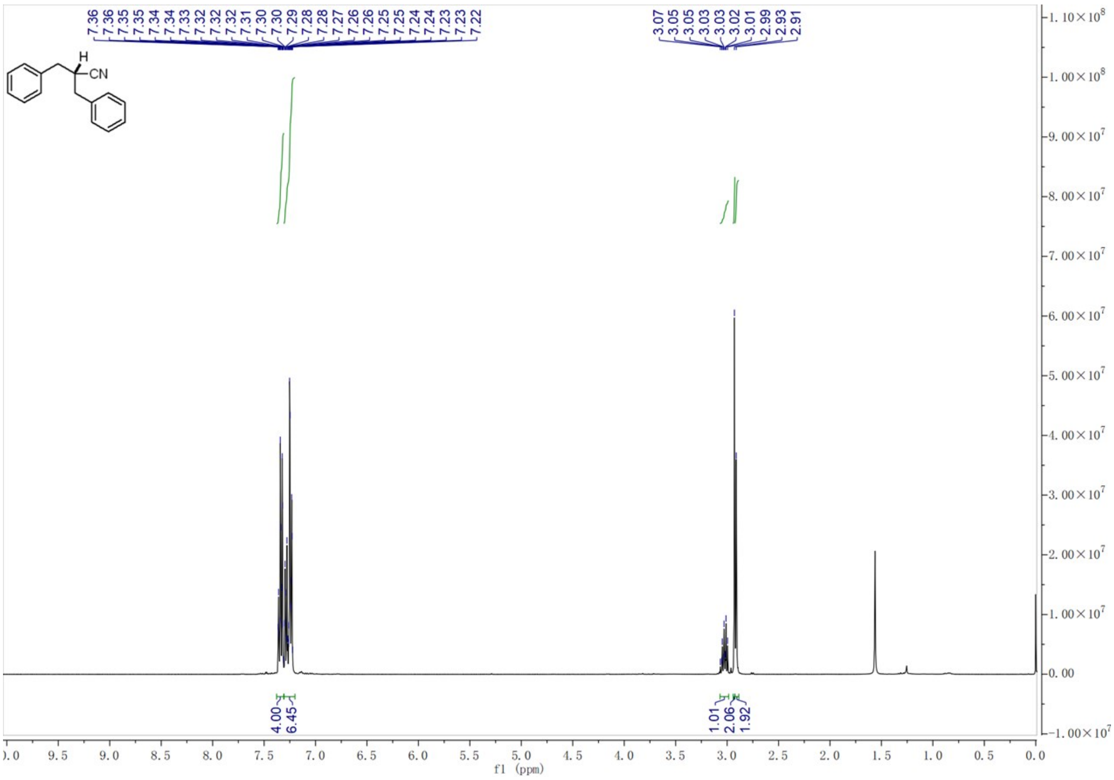


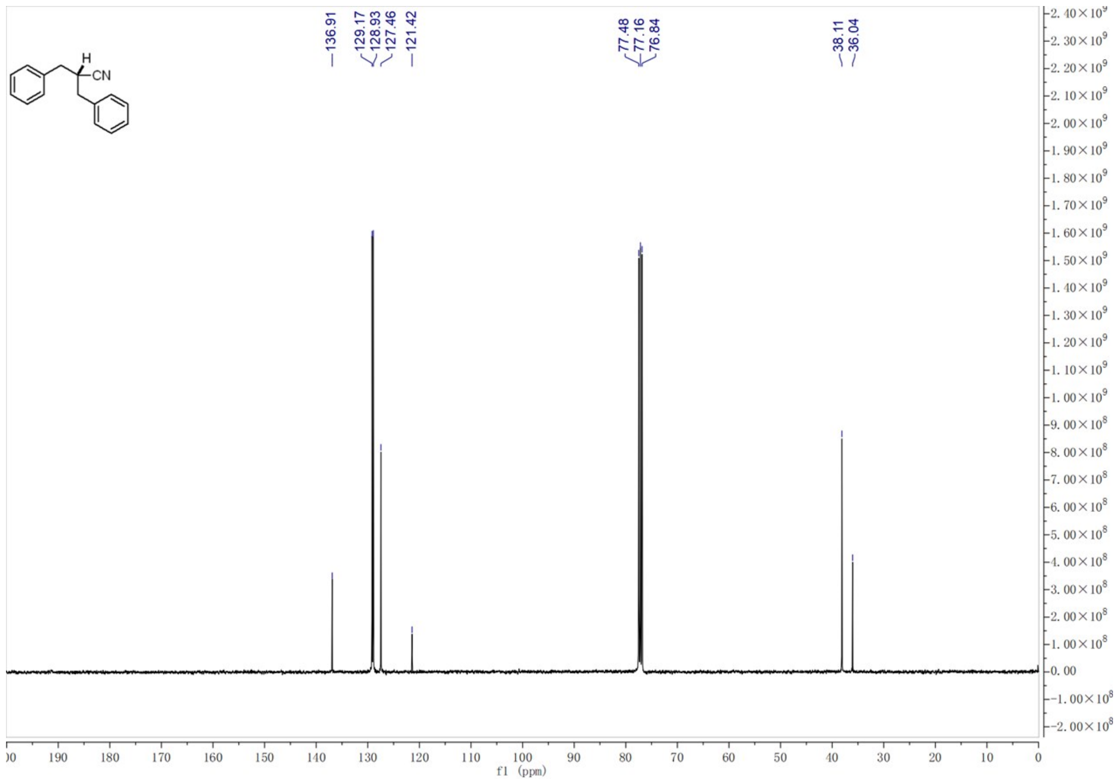
**61-H** $^1$H NMR and $^{13}$C NMR



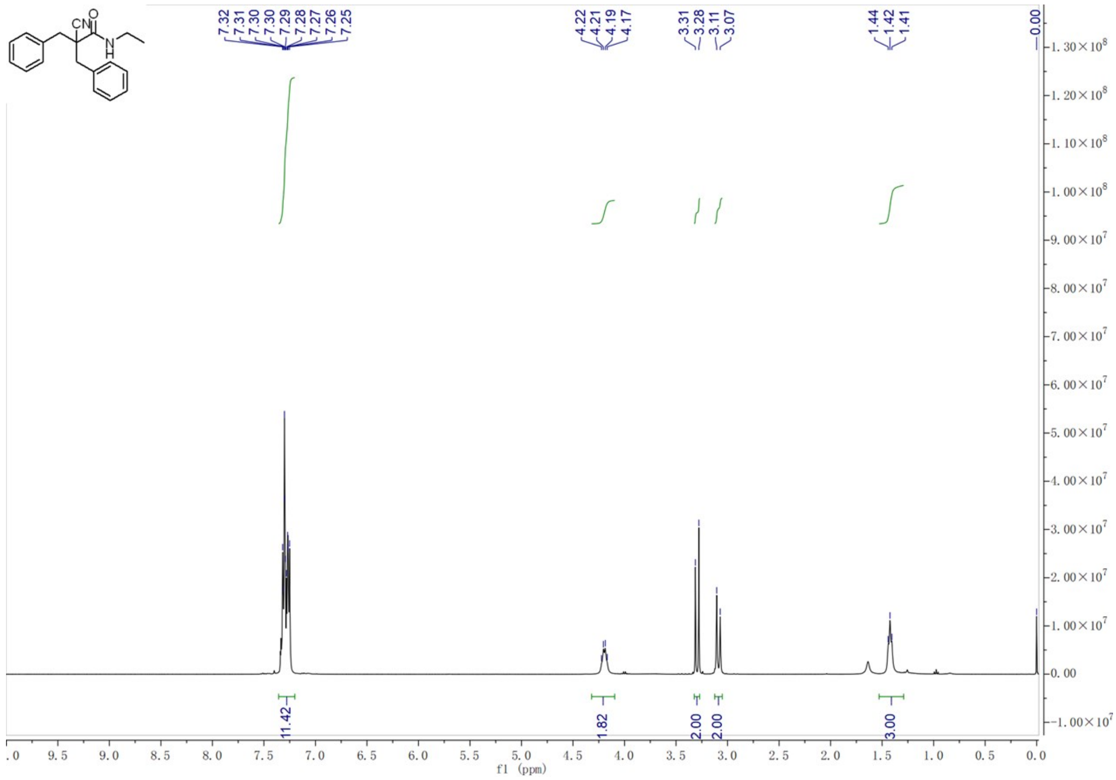


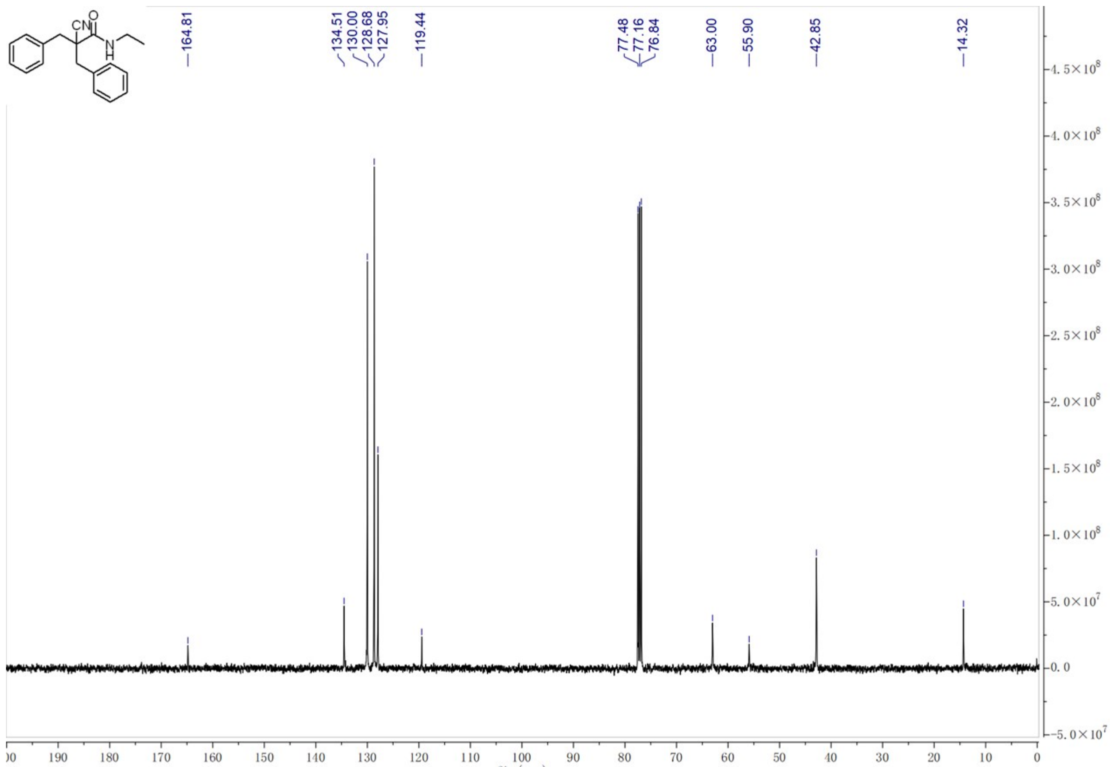

**62-H** $^1$H NMR and $^{13}$C NMR



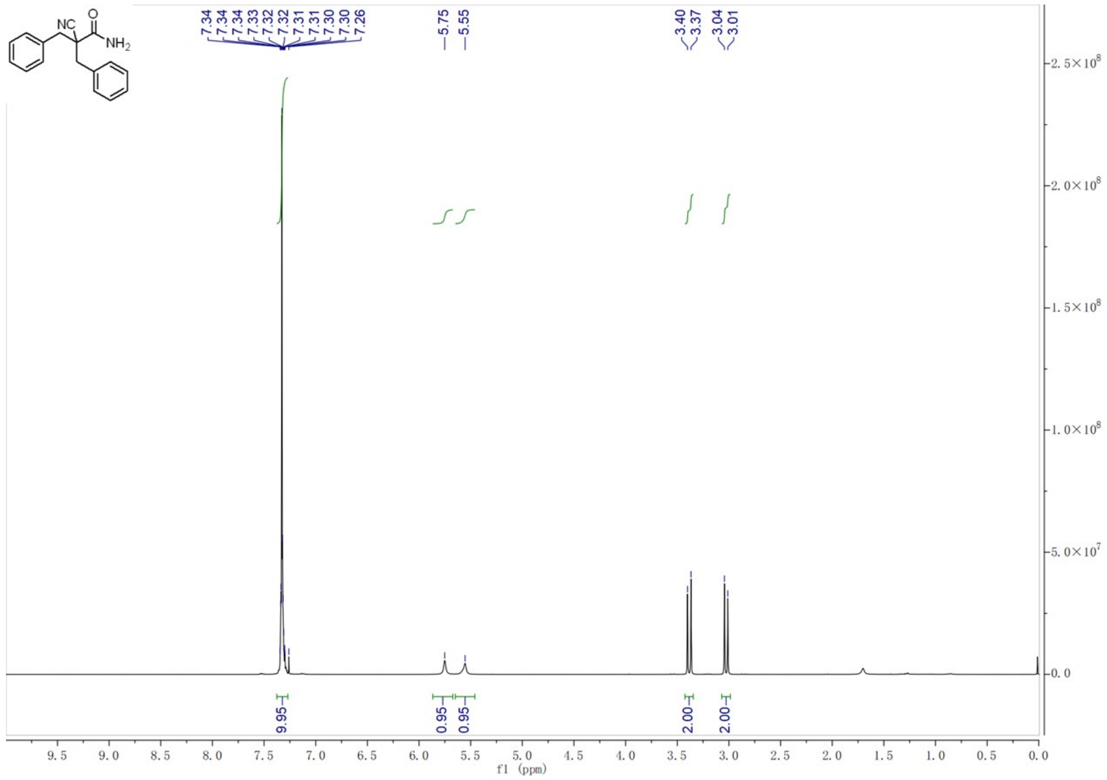


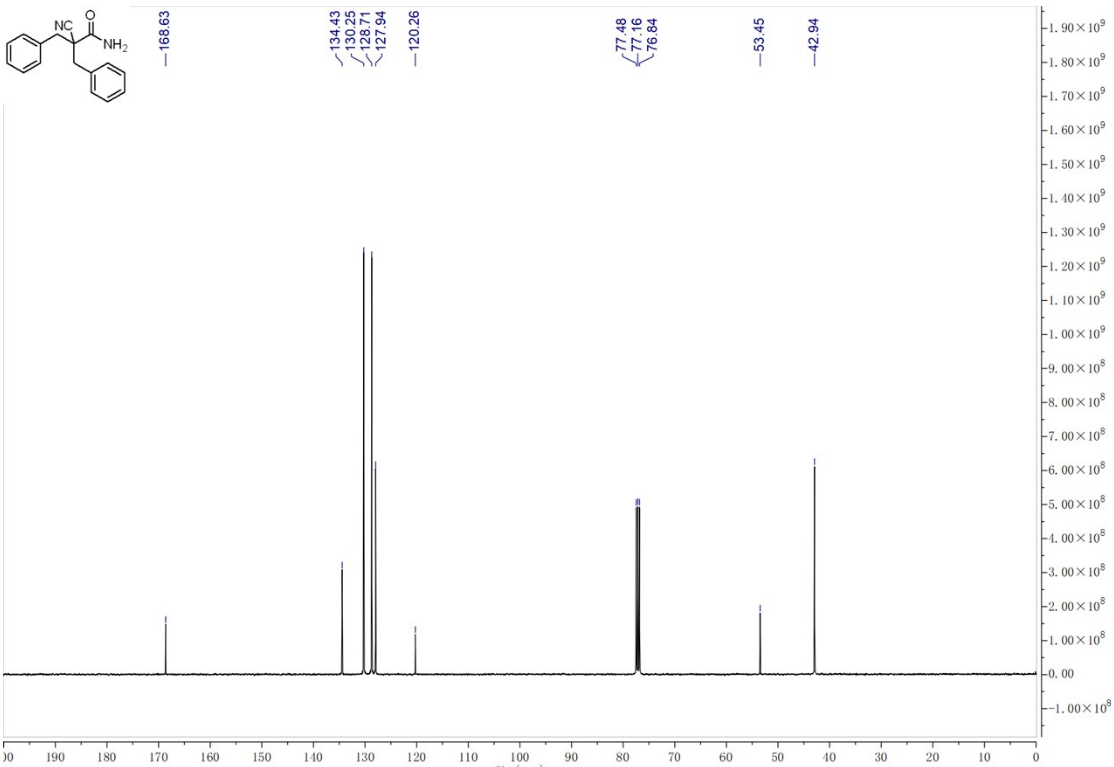
**62-H'** $^{1}H$ NMR and $^{13}C$ NMR



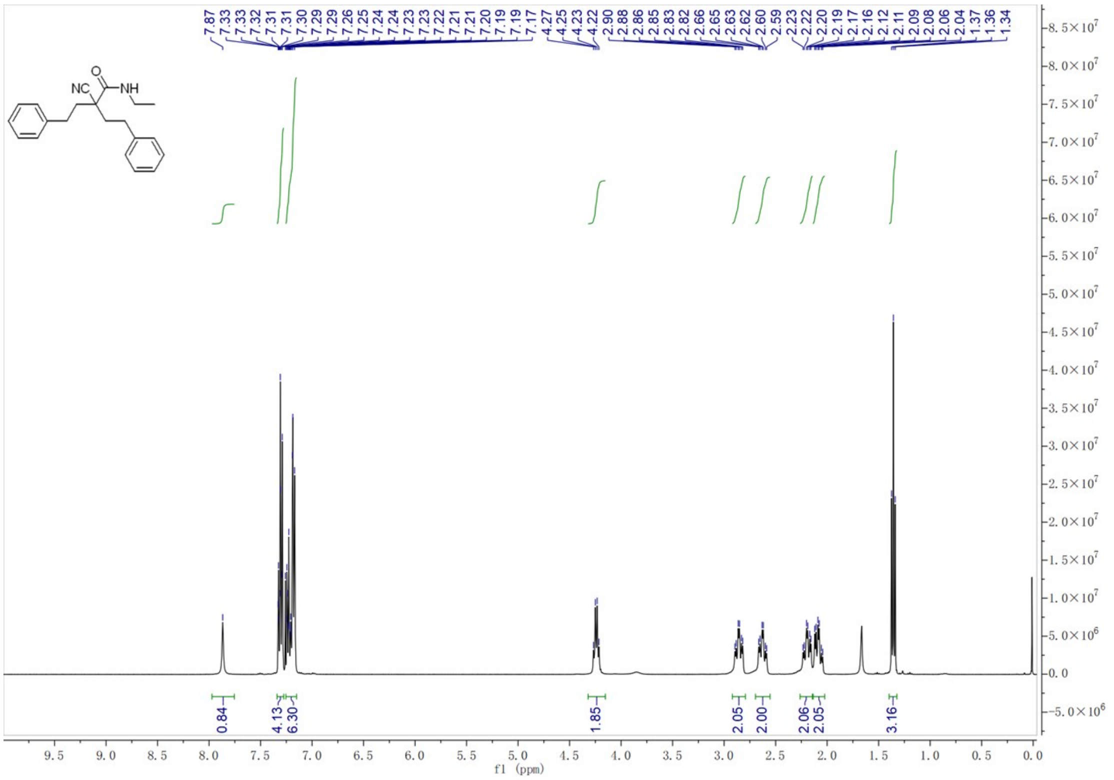


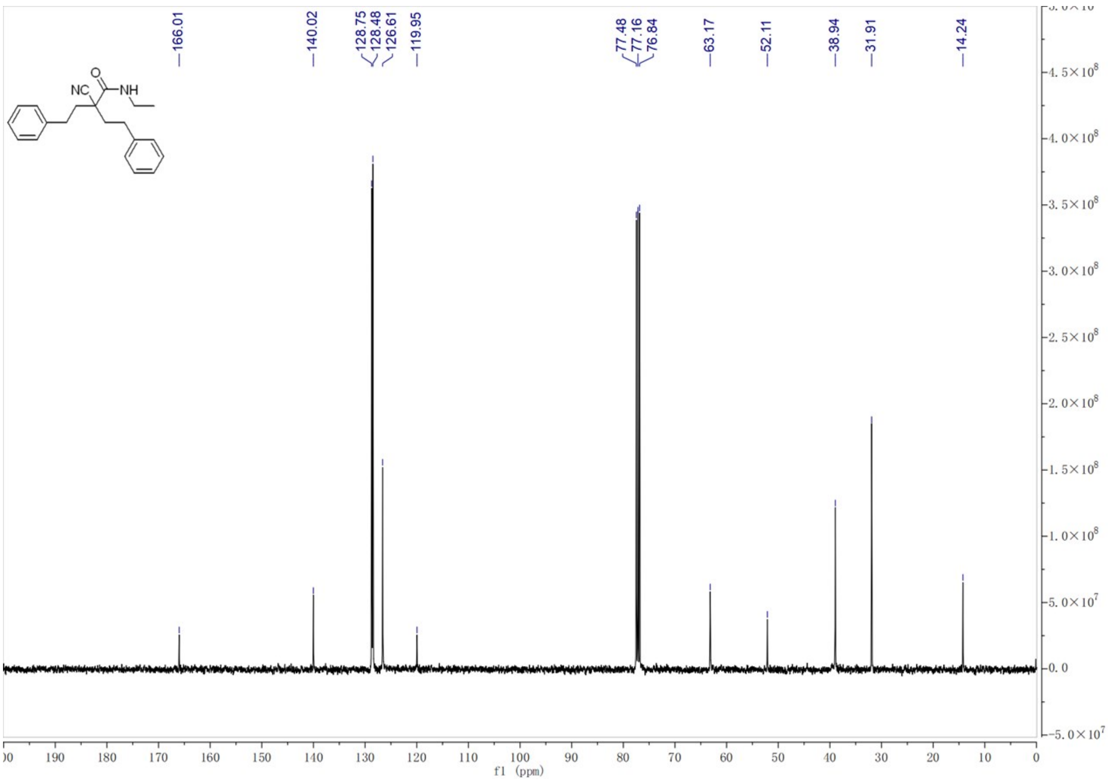
**62-H''** $^{1}$H NMR and $^{13}$C NMR



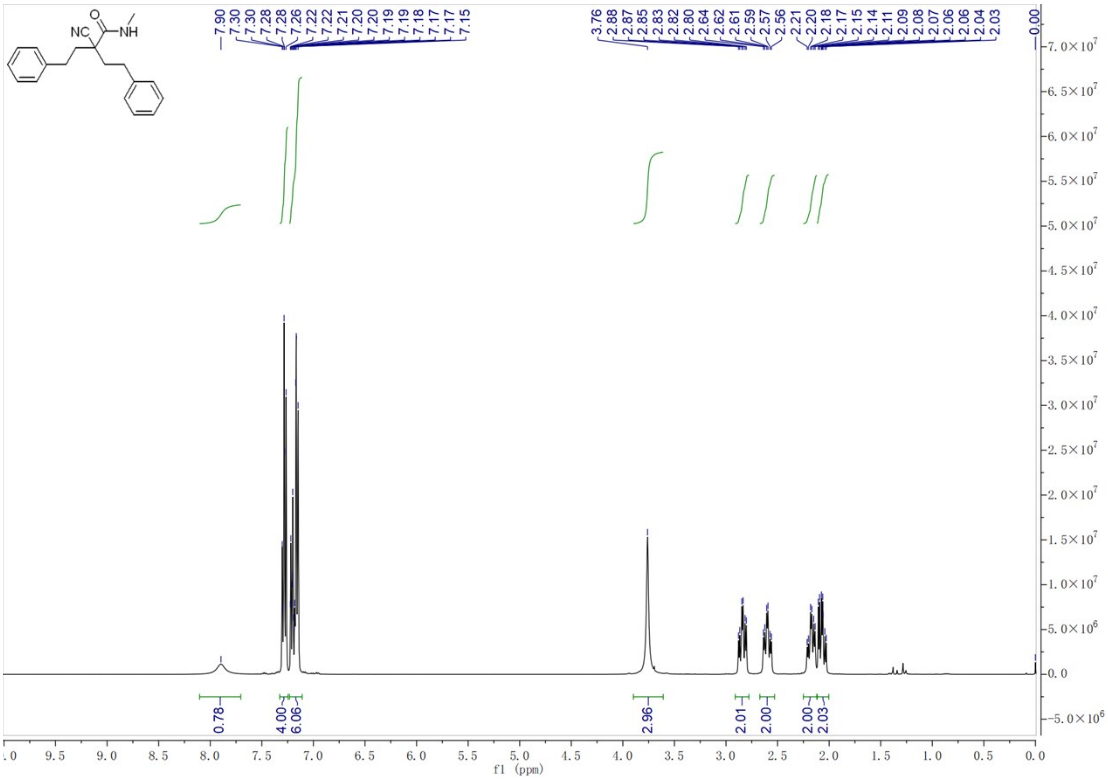


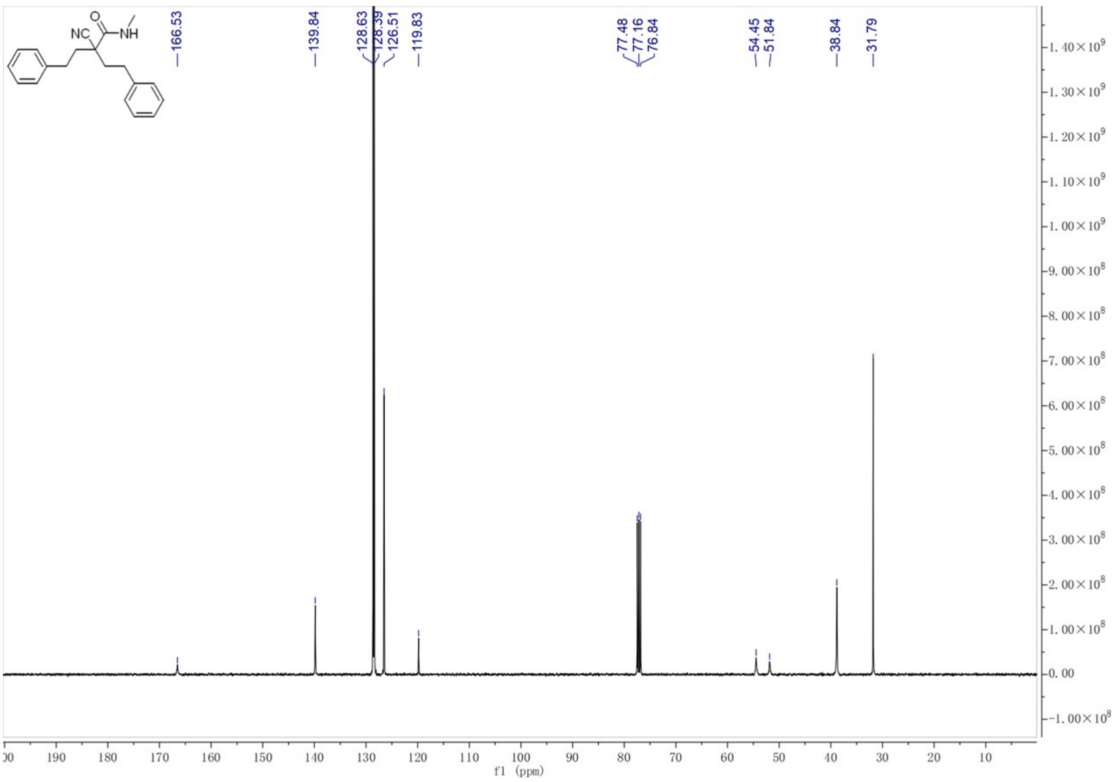

**63-H'-Et** $^{1}$H NMR and $^{13}$C NMR



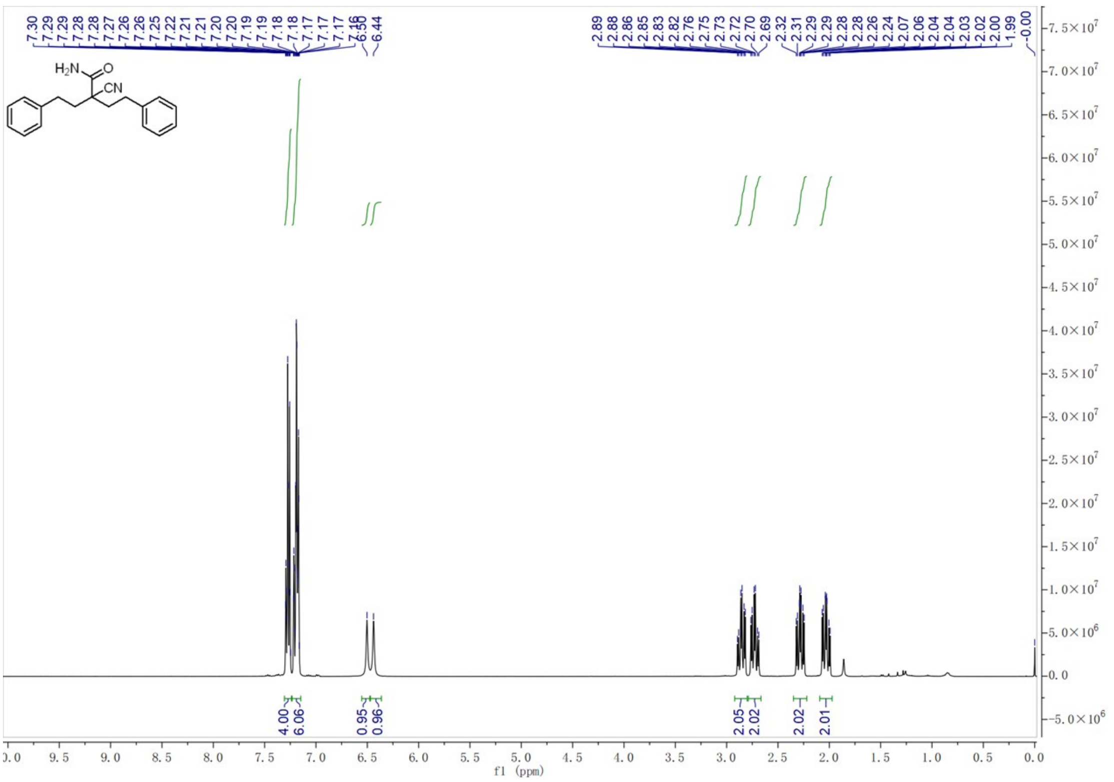


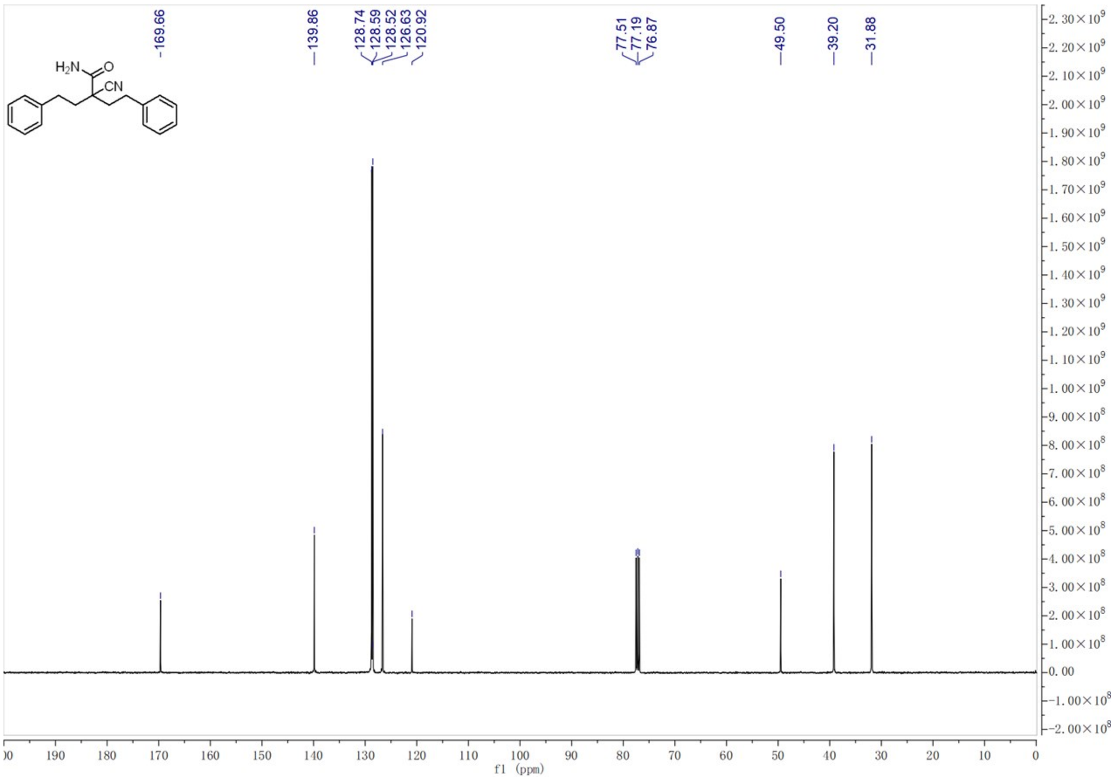
**63-H'-Me** ¹H NMR and ¹³C NMR



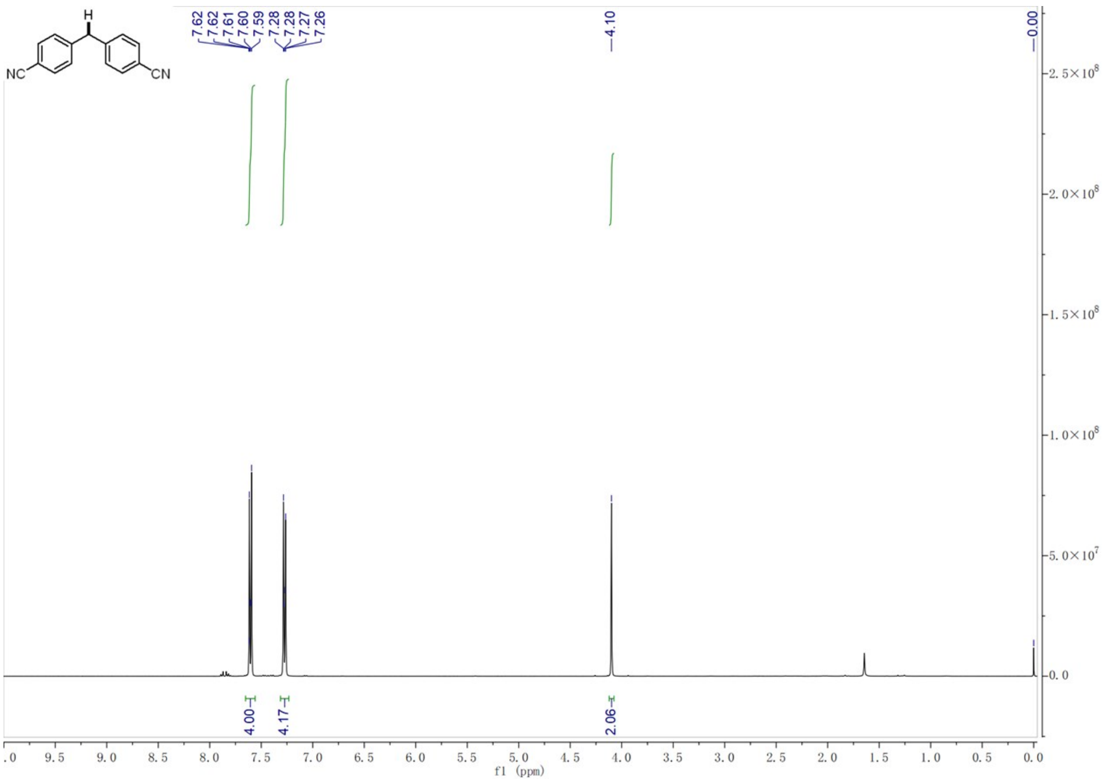


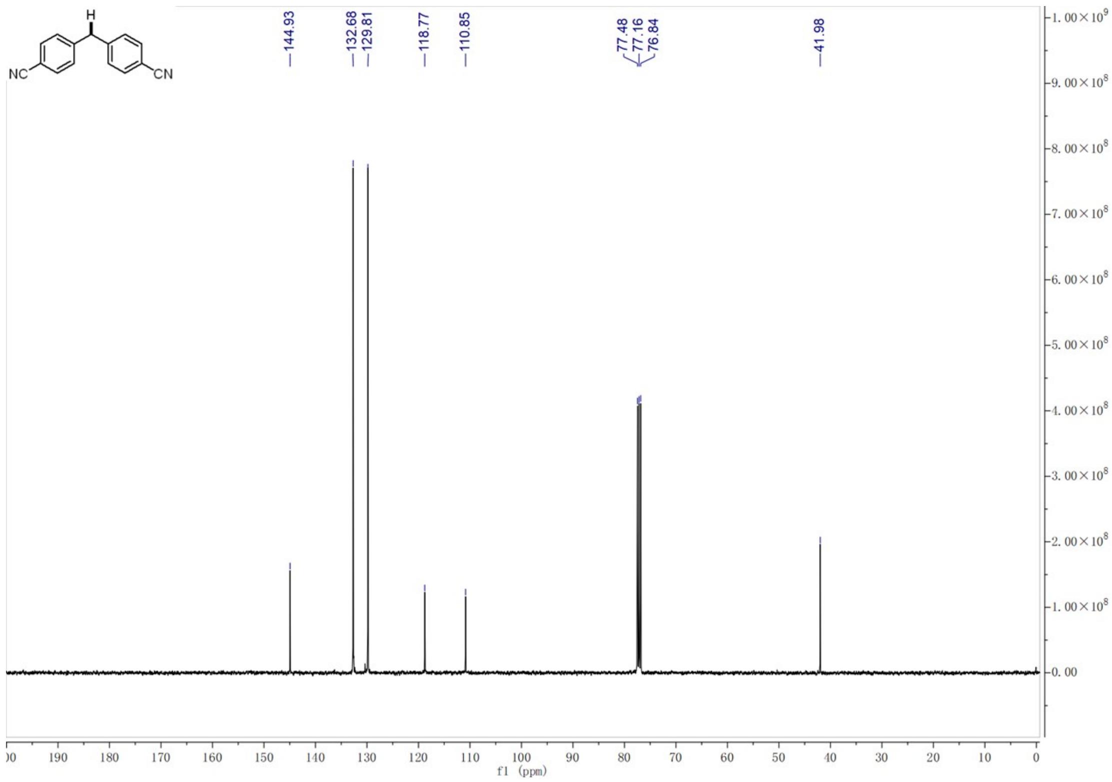
**63-H''** $^{1}$H NMR and $^{13}$C NMR



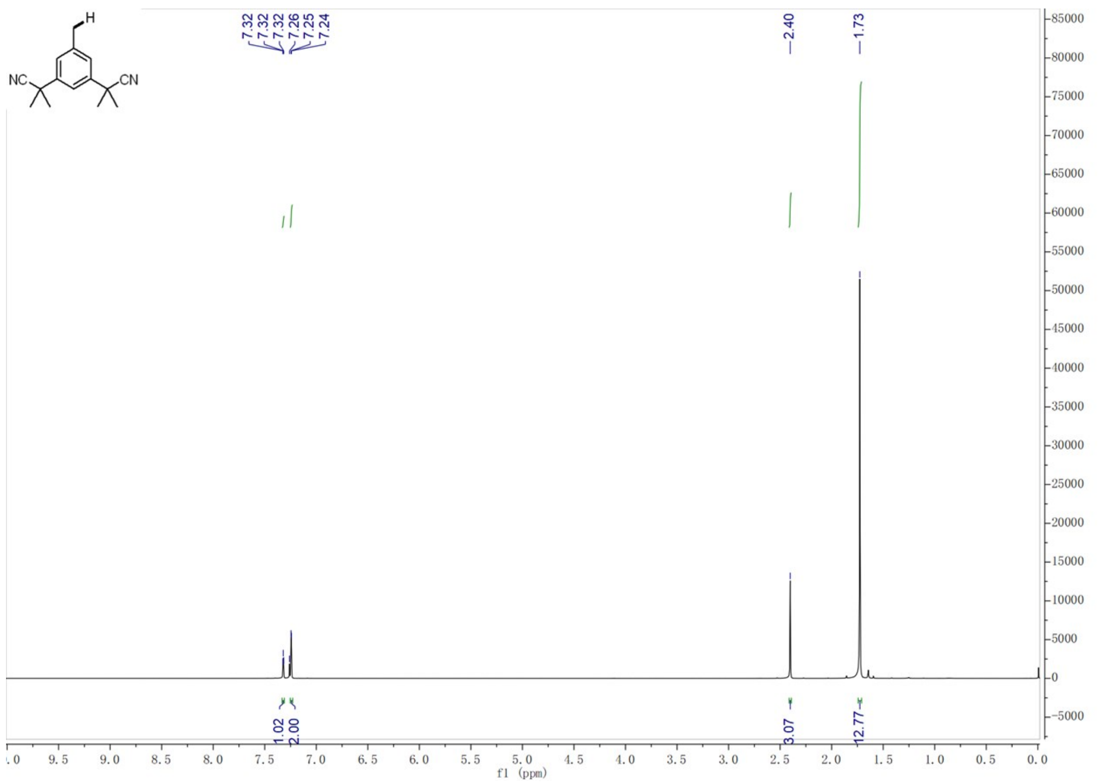


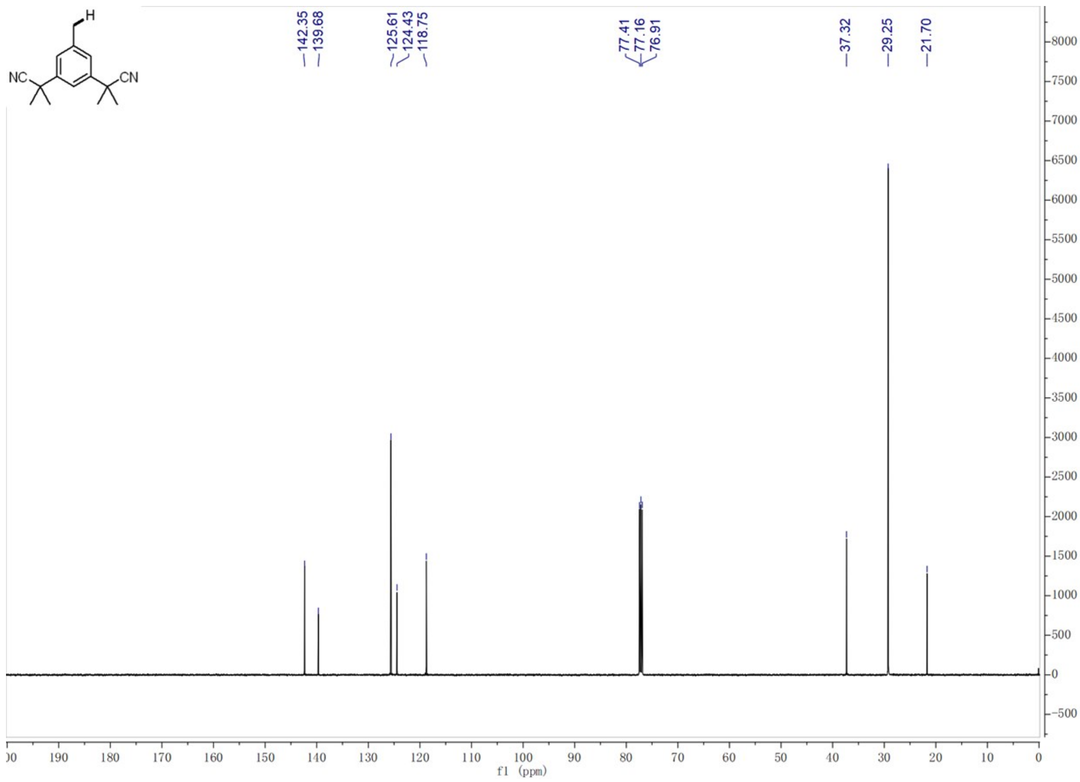
**64-H** $^{1}$H NMR and $^{13}$C NMR



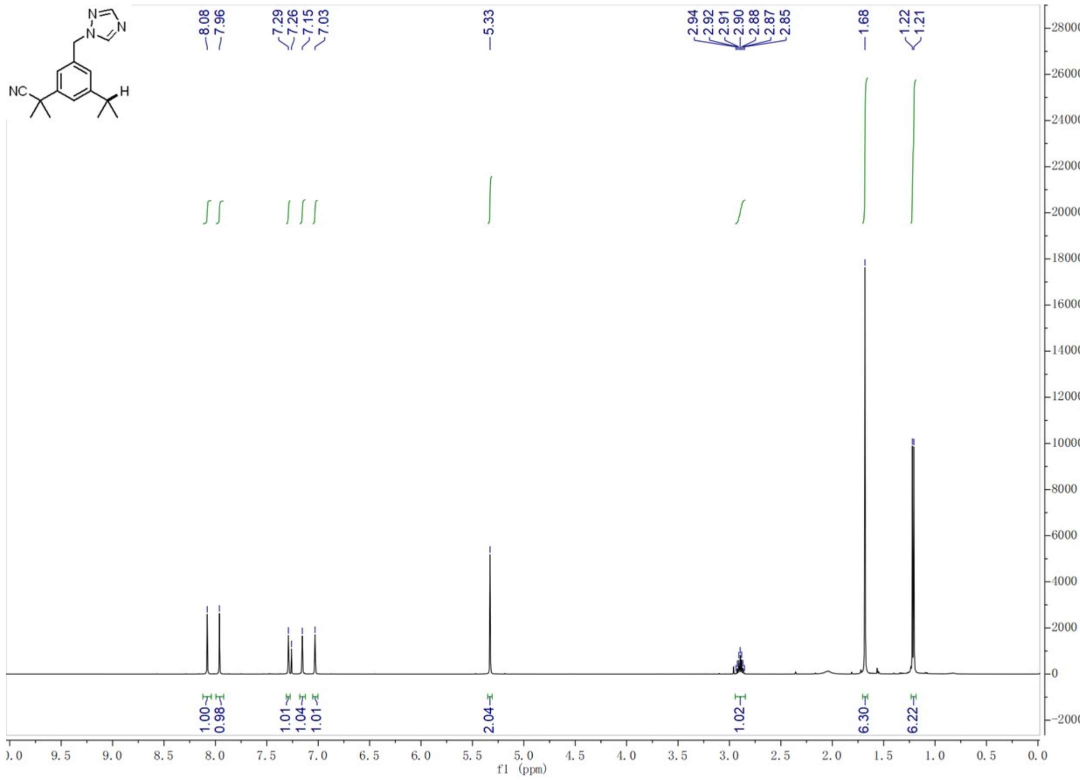


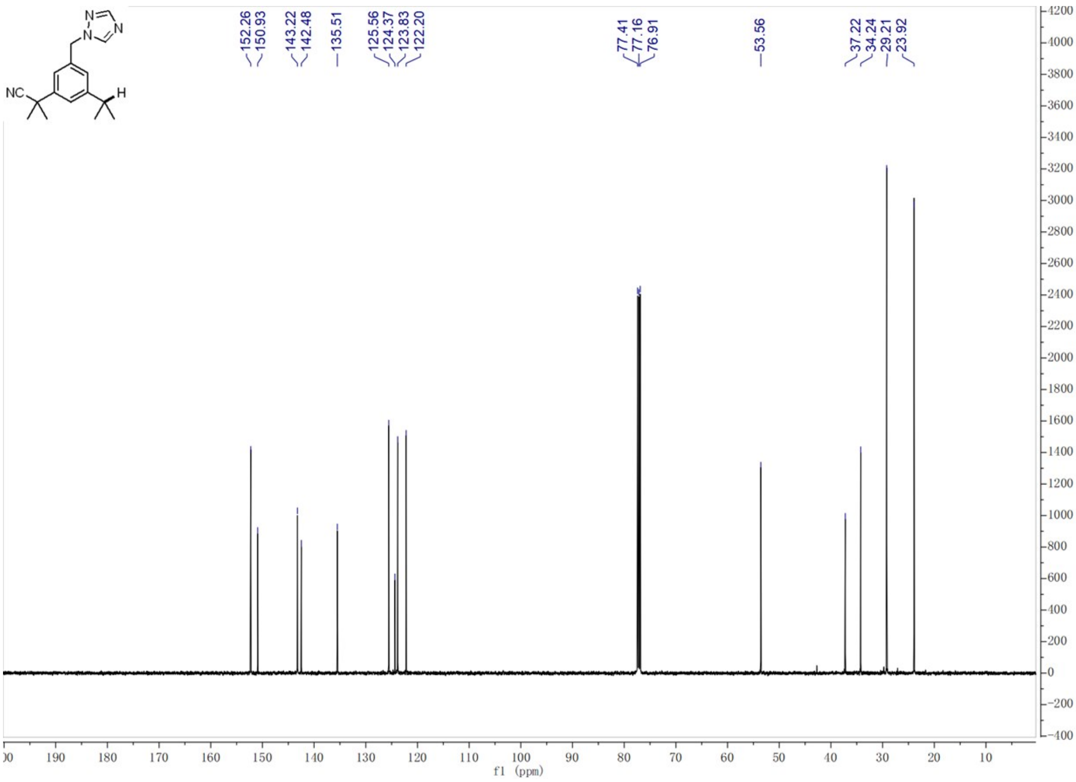
**65-H** $^1$H NMR and $^{13}$C NMR



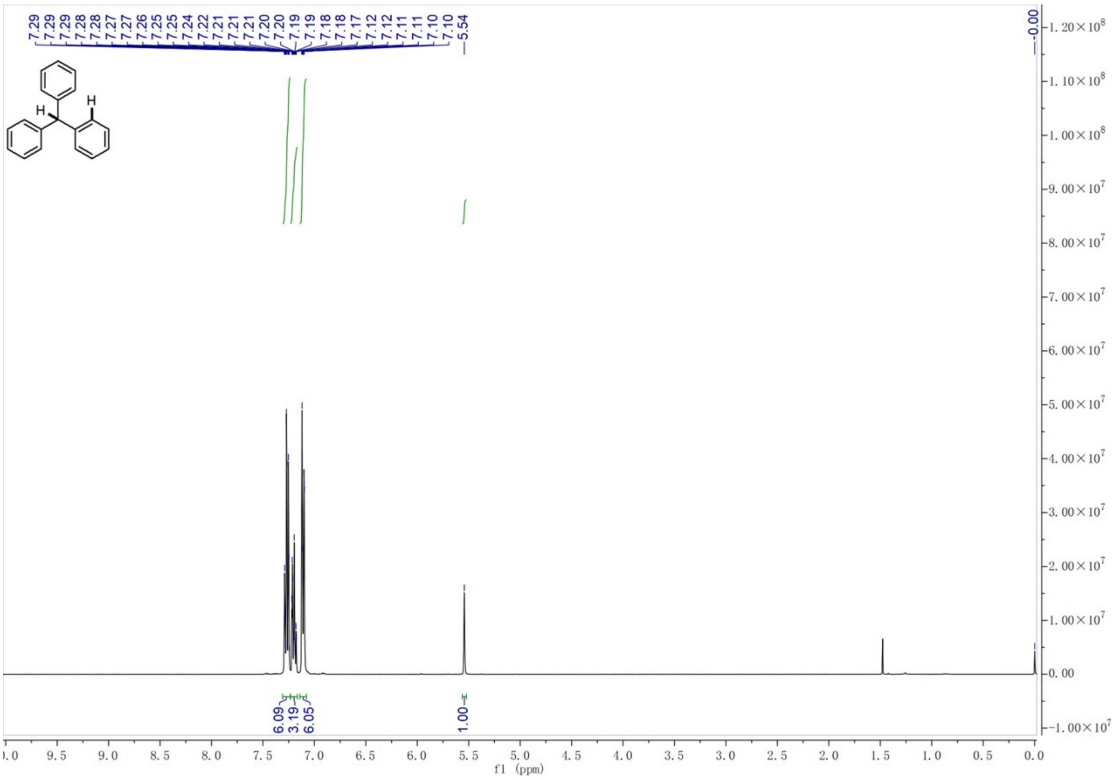


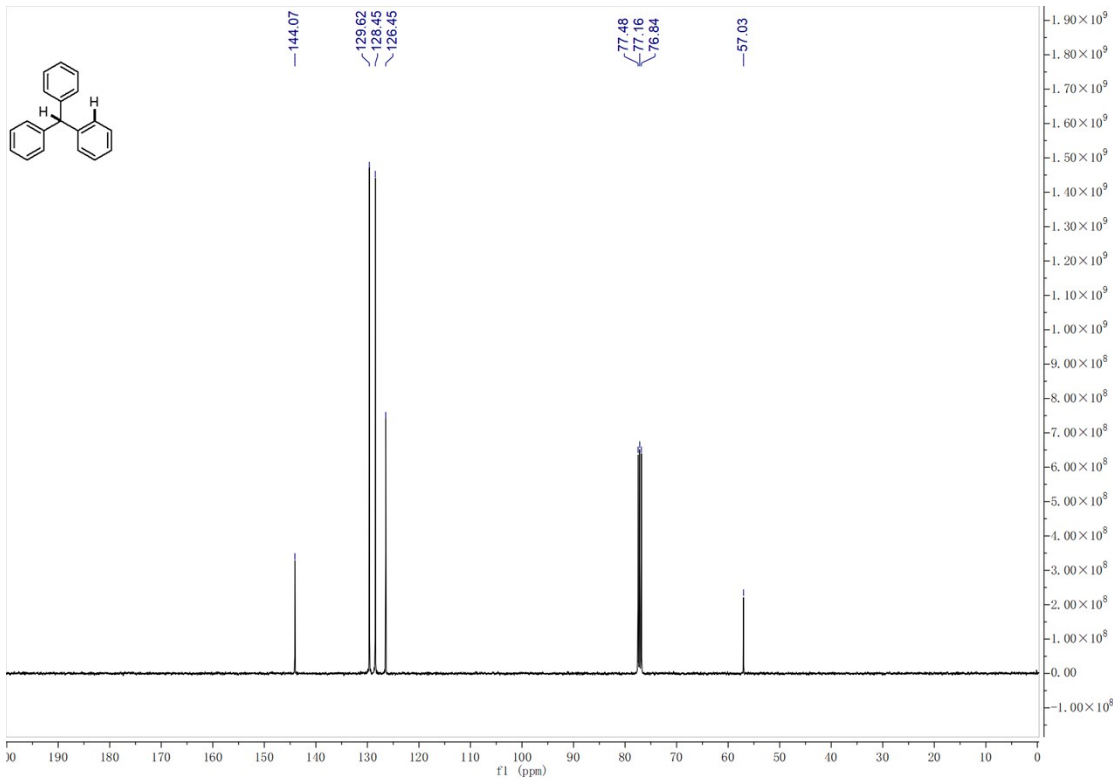
**65-H’** $^{1}H$ NMR and $^{13}C$ NMR






**66-H** $^{1}H$ NMR and $^{13}C$ NMR




144.07
129.62
128.45
126.45
77.48
77.16
76.84
57.03
H
H
f1 (ppm)