Electronic Supplementary Information (ESI)

Ruthenium(II) Complexes with *N*-Heterocyclic Carbene - Phosphine Ligands for the *N*-Alkylation of Amines with Alcohols

Ming Huang,*[,a,b] Yinwu Li,[b] Xiao-Bing Lan,[b] Jiahao Liu,[b] Cunyuan Zhao,[b] Yan Liu,*[,c] and Zhuofeng Ke*[,b]

[a]Clinical Pharmacy of The First Affiliated Hospital, School of Clinical Pharmacy, Guangdong Pharmaceutical University, Guangzhou 510006, P. R. China.
[b]School of Materials Science & Engineering, PCFM Lab, School of Chemistry, Sun Yat-sen University, Guangzhou 510275, P. R. China. E-mail: kezhf3@mail.sysu.edu.cn.
[c]School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, P. R. China. E-mail: yanliu@gdut.edu.cn

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I General Information

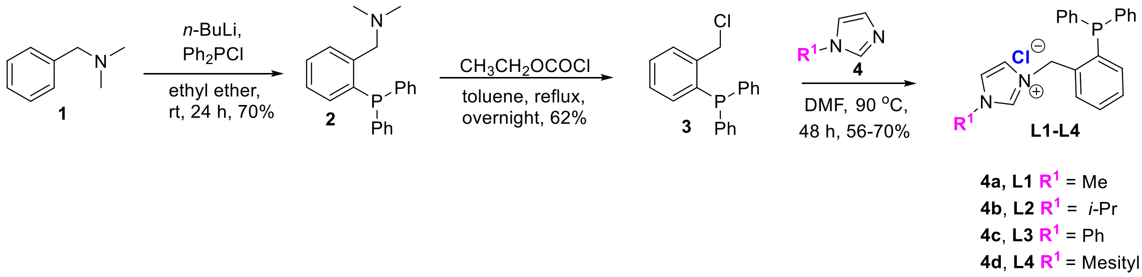
General considerations. Unless otherwise stated, all manipulations were carried out under dry argon using conventional Schlenk and glove box techniques. Non-halogenated solvents were dried over sodium benzophenone ketyl and halogenated solvents over CaH_2. The ligands **L1**-**L10** were prepared according to the literature procedure. All other reagents were purchased from commercial sources and used without further purification.

NMR spectra were recorded using a Bruker 400 MHz spectrometer, and chemical shifts are reported relative to TMS for ^{1}H and ^{13}C. ESI-MS spectra were taken on a Shimadzu LCMS-2010 instrument. GC analyses were recorded in a Shimadzu GC-2014C device equipped with a Wondacap 1 column. High resolution mass spectrometric (HRMS) data were obtained using an LTQ Orbitrap Elite instrument, using a sample concentration of approximately 1 ppm.

II Preparation of the ligands and the Ru complexes

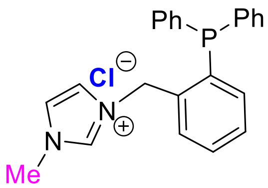
General Method for the Preparation of phosphine-functionalized imidazolium Salts L1-L4.[1]

To a solution of *o*-(diphenylphosphino)benzyl chloride (**3**, 1.02 mmol) in DMF (2 mL) was slowly added the imidazoles (1 mmol), and the resulting mixture was stirred at 90 °C for 48 h. After cooling to room temperature, the solvent was removed under vacuum and the crude product was recrystallized from dichloromethane/acetic ether (1: 5).



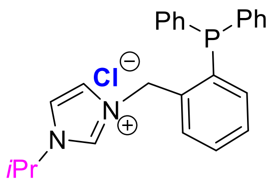
Scheme S1. Synthesis of the Imidazolium Salts L1-L4

3-(2-(Diphenylphosphino)benzyl)-1-methyl-1*H*-imidazol-3-ium chloride (L1).



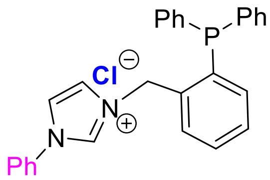
White solid, 76% yield (300 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.92 (s, 1H), 7.54 – 7.50 (m, 1H), 7.47 – 7.43 (m, 2H), 7.37 (d, J = 8.9 Hz, 2H), 7.34 – 7.28 (m, 6H), 7.02 (t, J = 6.7 Hz, 4H), 6.89 – 6.78 (m, 1H), 5.57 (s, 2H), 3.52 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 138.0, 137.8, 136.9, 136.5, 136.4, 134.8, 134.7, 134.2, 133.4, 133.2, 131.1, 131.0, 130.1, 129.7, 129.3, 128.9, 128.8, 123.6, 122.1, 51.0 (d, J = 22.1 Hz), 35.6; ^{31}P NMR (162 MHz, DMSO-d_6) δ -18.90 (s); HRMS (ESI, m/z): calcd for $C_{23}H_{22}N_2P$ [M − Cl]$^+$ 357.15151, found 357.15099.

3-(2-(Diphenylphosphino)benzyl)-1-isopropyl-1*H*-imidazol-3-ium chloride (L2).



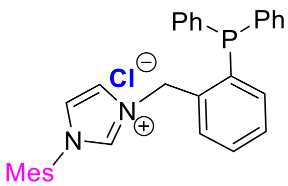
White solid, 80% yield (336 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.16 (s, 1H), 7.73 (s, 1H), 7.58 (s, 1H), 7.55 – 7.54 (m, 2H), 7.48 – 7.45 (m, 1H), 7.40 – 7.38 (m, 6H), 7.12 (t, *J* = 6.7 Hz, 4H), 6.95 – 6.94 (m, 2H), 5.64 (s, 2H), 4.44 (hept, *J* = 6.6 Hz, 1H), 1.32 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 138.2, 137.9, 136.3, 136.2, 135.2, 135.0, 134.9, 134.3, 133.3, 133.1, 130.8, 130.7, 130.2, 129.7, 129.3, 128.9, 128.9, 122.5, 120.5, 52.1, 51.0 (d, *J* = 23.2 Hz), 22.2; ^{31}P NMR (162 MHz, DMSO-d_6) δ -19.18 (s); HRMS (ESI, m/z): calcd for $C_{25}H_{26}N_2P$ [M − Cl]$^+$ 385.18281, found 385.18221.

3-(2-(Diphenylphosphino)benzyl)-1-phenyl-1*H*-imidazol-3-ium chloride (L3).[1]



White solid, 86% yield (390 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.91 (s, 1H), 8.17 (s, 1H), 7.78 (s, 1H), 7.73 – 7.66 (m, 1H), 7.66 – 7.59 (m, 4H), 7.56 (t, *J* = 7.1 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.33 (m, 6H), 7.18 – 7.04 (m, 4H), 6.95 – 6.92 (m, 1H), 5.78 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 137.7, 137.4, 136.4, 136.2, 135.6, 134.8, 134.7, 134.3, 134.1, 133.3, 133.1, 131.1, 131.0, 130.1, 129.9, 129.7, 129.6, 129.2, 128.8, 128.8, 123.1, 121.6, 121.1, 51.4 (d, *J* = 22.9 Hz); ^{31}P NMR (162 MHz, DMSO-d_6) δ -18.92 (s); HRMS (ESI, m/z): calcd for $C_{28}H_{24}N_2P$ [M − Cl]$^+$ 419.16716, found 419.16639.

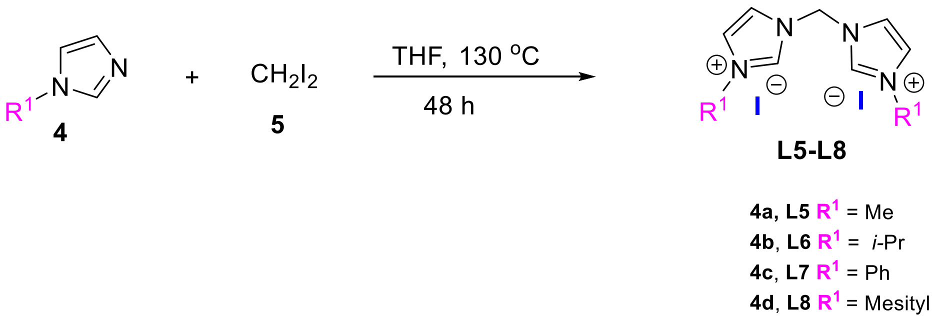
3-(2-(Diphenylphosphino)benzyl)-1-mesityl-1*H*-imidazol-3-ium chloride (L4).[1]



White solid, 74% yield (370 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.84 (s, 1H), 7.97 (d, *J* = 6.9 Hz, 2H), 7.58 – 7.49 (m, 2H), 7.42 (m, 7H), 7.24 – 7.21 (m, 4H), 7.12 (s, 2H), 7.00 – 6.97 (m, 1H), 5.79 (s, 2H), 2.31 (s, 3H), 1.97 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 140.1, 138.2, 138.2, 137.9, 136.2, 136.1, 135.0, 134.9, 134.2, 134.1, 133.4, 133.2, 131.1, 130.2, 130.0, 130.0, 129.6, 129.3, 129.2, 129.0, 129.0, 124.1, 123.1, 51.1 (d, *J* = 24.2 Hz), 20.6, 16.9; ^{31}P NMR (162 MHz, DMSO-d_6) δ -18.67 (s); HRMS (ESI, m/z): calcd for $C_{31}H_{30}N_2P$ [M − Cl]$^+$ 461.21411, found 461.21352.

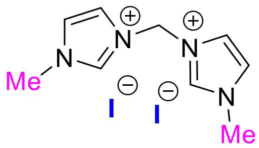
General Method for the Preparation of bis-NHC ligands L5-L8.[2]

To a solution of imidazole **4** (20 mmol) in 5 mL of THF in a sealed tube (15 mL) was added diiodomethane (10 mmol). The mixture is stirred at 130 °C for 48 hours, and the solid which precipitates is filtered and washed repeatedly with an excess amount of THF and CH_2Cl_2. The white solid was dried in vacuo, and **L5-L8** were obtained.



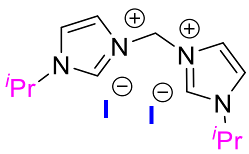
Scheme S2. Synthesis of the bis-NHC ligands L5-L8

Synthesis of 3, 3'-methylenebis(1-methyl-1*H*-imidazol-3-ium) iodide (L5)



Following the general method using 1-methylimidazole (20 mmol) and diiodomethane (10 mmol) in 5 mL of THF, gave **L5** as a white solid. Yield: 3.7 g (85%). ^{1}H NMR (400 MHz, DMSO-*d*$_6$) *δ* 9.40 (s, 2H), 7.99 (t, *J* = 1.7 Hz, 2H), 7.81 (t, *J* = 1.6 Hz, 2H), 6.67 (s, 2H), 3.90 (s, 6H); ^{13}C NMR (100 MHz, DMSO-*d*$_6$) *δ* 137.96, 124.31, 121.83, 58.06, 36.37; MS (ESI) $[(M-2I)]^{2+}$ 88.95.

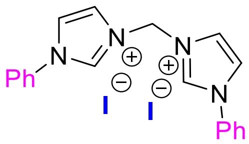
Synthesis of 3,3'-methylenebis(1-isopropyl-1H-imidazol-3-ium) iodide (L6)



Following the general method using 1-isopropylimidazole (20 mmol) and diiodomethane (10 mmol) in 5 mL of THF, gave **L6** as a white solid. Yield: 3.9 g (80%). ^{1}H NMR (400 MHz, DMSO-*d*$_6$) *δ* 9.53 (s, 2H), 8.05 (d, *J* = 1.3 Hz, 4H), 6.61 (s, 2H), 4.71 (hept, *J* = 6.5 Hz, 2H), 1.50

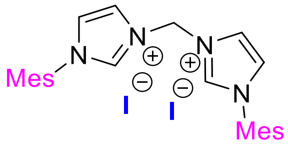
(d, J = 6.7 Hz, 12H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 136.44, 122.34, 121.33, 58.21, 52.81, 22.05; MS (ESI) [(M-2I)]$^{2+}$ 116.95.

Synthesis of 3,3'-methylenebis(1-phenyl-1H-imidazol-3-ium) iodide (L7)



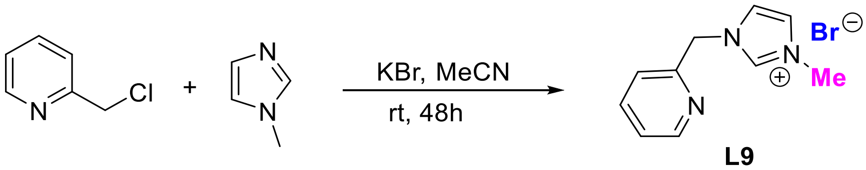
Following the general method using 1-phenyllimidazole (20 mmol) and diiodomethane (10 mmol) in 5 mL of THF, gave **L7** as a white solid. Yield: 4.17 g (75%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.11 (s, 2H), 8.45 (s, 2H), 8.30 (s, 2H), 7.82 (d, J = 7.9 Hz, 4H), 7.72 (t, J = 7.7 Hz, 4H), 7.65 (t, J = 7.3 Hz, 2H), 6.85 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 137.25, 134.41, 130.31, 130.27, 123.02, 122.04, 121.81, 58.82; MS (ESI) [(M-2I)]$^{2+}$ 150.95.

Synthesis of 3,3'-methylenebis(1-mesityl-1H-imidazol-3-ium) iodide (L8)



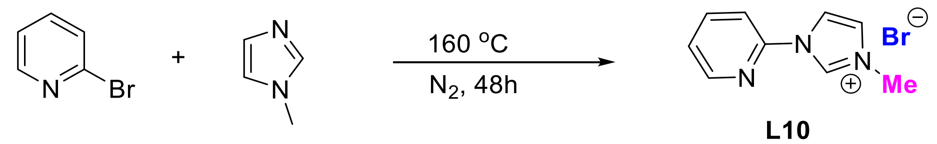
Following the general method using 1-mesitylimidazole (20 mmol) and diiodomethane (10 mmol) in 5 mL of THF, gave **L5** as a white solid. Yield: 3.84 g (60%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.82 (s, 2H), 8.38 (t, J = 1.6 Hz, 2H), 8.11 (t, J = 1.6 Hz, 2H), 7.18 (s, 4H), 6.89 (s, 2H), 2.34 (s, 6H), 2.05 (s, 12H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 140.56, 139.01, 134.16, 130.78, 129.31, 124.83, 122.79, 59.27, 20.59, 17.00; MS (ESI) [(M-2I)]$^{2+}$ 192.95.

Synthesis of 3-methyl-1-(pyridin-2-ylmethyl)-1*H*-imidazol-3-ium bromide (L9)[3]



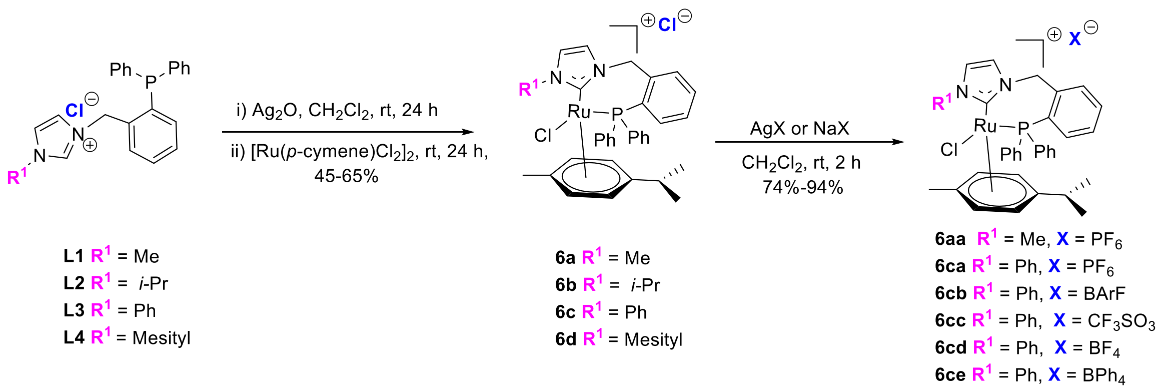
To an anhydrous MeCN solution (70 mL) of 2.54 g (20.0 mmol) of 2-chloromethylpyridine (obtained by neutralization with Na_2CO_3 of the corresponding hydrochloride), 3.57 g (30.0 mmol) of KBr and 1.9 mL (21.6 mmol) of 1-methylimidazole were added under inert atmosphere (Ar). The red-orange mixture was stirred for 48 h and the solvent reduced to 3–4 mL under vacuum. An equivalent volume of CH_2Cl_2 (70 mL) was then added and the resulting suspension was filtered on a Celite filter. The clear solution was evaporated to dryness and the reddish sticky residue was re-dissolved in CH_2Cl_2 (15 mL) and precipitated with diethyl ether (40 mL). 4.04 g (yield 80%) of red hygroscopic solid **L4** was obtained. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.34 (s, 1H), 8.55 (d, J = 4.8 Hz, 1H), 7.89 (td, J = 7.7, 1.7 Hz, 1H), 7.81 (s, 1H), 7.76 (s, 1H), 7.51 (d, J = 7.8 Hz, 1H), 7.40 (dd, J = 7.5, 4.9 Hz, 1H), 5.60 (s, 2H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 153.61, 149.53, 137.47, 137.25, 123.61, 123.04, 122.51, 52.90, 35.84; MS (ESI) [M-Br]$^+$ 173.80.

Synthesis of 3-methyl-1-(pyridin-2-yl)-1*H*-imidazol-3-ium bromide (L10)[4]



A mixture of 2-bromopyridine (3.16 g, 20.0 mmol) and 1-methylimidazole (1.64 g, 20.0 mmol) was kept neat at 160 °C for 48 h. After cooling, the formed oily mixture was purified by column chromatography over silica gel (CH_2Cl_2/MeOH = 20 :1), yielding 2.39 g (20.0 mmol, 50%) of the desired product as a brownish hygroscopic solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.23 (s, 1H), 8.45 (d, J = 3.7 Hz, 1H), 8.35 (d, J = 8.2 Hz, 1H), 8.28 (s, 1H), 7.99 – 7.95 (m, 1H), 7.82 (s, 1H), 7.42 – 7.39 (m, 1H), 4.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.12, 145.97, 140.59, 135.79, 125.19, 124.33, 118.88, 114.80, 37.39; MS (ESI) [M-Br]$^+$ 160.19.

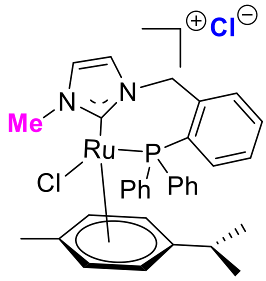
General Method for the Preparation of Ruthenium Complexes 6a−d.[5]



Scheme S3. Synthesis of the Ru complexes

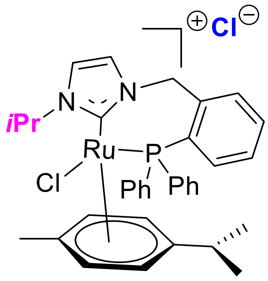
A suspension of the appropriate imidazolium salts (**L1−L4**, 0.1 mmol) and silver oxide (0.5 equiv.) in CH_2Cl_2 was stirred at room temperature in the dark for 24 h. The mixture was then filtered through a pad of celite into a solution of [(*p*-cymene)$RuCl_2$)]$_2$ (0.5 equiv.) in CH_2Cl_2 and stirred at room temperature for 24 h. Then the organic solvent was removed by evaporation and the crude product was purified by column chromatography (CH_2Cl_2: MeOH = 20:1).

Complex 6a.



Yellow solid, 54% yield (36 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.02 (s, 1H), 7.90 – 7.88 (m, 1H), 7.58 – 7.40 (m, 12H), 7.26 (t, J = 7.5 Hz, 1H), 6.75 (t, J = 8.9 Hz, 1H), 6.38 (d, J = 6.4 Hz, 1H), 6.33 (d, J = 5.4 Hz, 1H), 5.99 (d, J = 6.4 Hz, 1H), 5.50 (d, J = 14.2 Hz, 1H), 5.33 (d, J = 14.1 Hz, 1H), 5.27 (s, 1H), 3.92 (s, 3H), 2.20 (s, 3H), 2.04 – 1.97 (m, 1H), 0.84 (d, J = 6.8 Hz, 3H), 0.62 (d, J = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.4 (d, J = 19.3 Hz), 141.2 (d, J = 11.6 Hz), 137.6, 137.1, 136.5 (d, J = 10.0 Hz), 133.3, 132.6, 132.3 (d, J = 9.1 Hz), 132.1, 131.6, 130.8, 130.4, 129.9 (d, J = 7.3 Hz), 129.0, 128.9, 128.8, 128.4, 127.9, 127.8 (d, J = 10.0 Hz), 126.3, 122.3, 107.7, 105.8, 94.5, 94.4, 91.7, 88.6, 52.1 (d, J = 10.3 Hz), 38.7, 29.9, 22.7, 20.0, 17.6; ^{31}P NMR (162 MHz, DMSO-d_6) δ 25.66 (s); HRMS (ESI, m/z): calcd for $C_{33}H_{35}ClN_2PRu$ $[M - Cl]^+$ 627.12644, found 627.12602; Anal. Calcd for: $C_{33}H_{35}Cl_2N_2PRu{\bullet}0.6CH_2Cl_2$: C, 56.56; H 5.11; N 3.93, Found: C, 56.27; H, 5.42; N, 3.87.

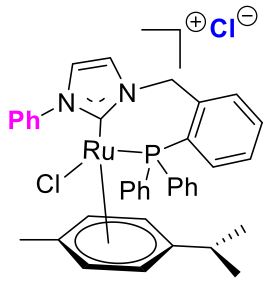
Complex 6b.



Yellow solid, 60% yield (41 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.07 (s, 1H), 7.91 (s, 1H), 7.85 – 7.79 (m, 1H), 7.80 – 7.72 (m, 2H), 7.67 (s, 3H), 7.49 (t, J = 7.3 Hz, 1H), 7.30 (t, J = 7.5 Hz, 1H), 7.17 (t, J = 7.1 Hz, 1H), 7.05 (d, J = 7.5 Hz, 3H), 6.52 – 6.42 (m, 2H), 5.87 (d, J = 5.6 Hz, 1H), 5.77 (d, J = 6.6 Hz, 1H), 5.60 (d, J = 14.8 Hz, 1H), 5.39 – 5.34 (m, 3H), 5.31 – 5.21 (m, 1H), 2.45 – 2.38 (m, 1H), 1.90 (s, 3H), 1.50 (d, J = 6.5 Hz, 3H), 1.22 (d, J = 6.1 Hz, 3H), 1.01 (d, J =

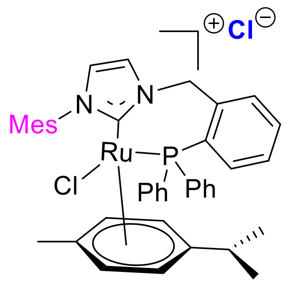
6.6 Hz, 3H), 0.91 (d, J = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.7 (d, J = 27.3 Hz), 140.3 (d, J = 12.4 Hz), 137.4, 137.0, 135.6, 135.0, 134.5, 132.4 (d, J = 8.9 Hz), 131.8 (d, J = 8.8 Hz), 131.4, 130.7, 130.7, 129.1, 128.9, 128.9, 128.8, 128.5, 127.6 (d, J = 10.3 Hz), 124.4, 121.5, 113.6, 103.5, 98.1 (d, J = 4.4 Hz), 92.7 (d, J = 5.3 Hz), 88.1 (d, J = 3.3 Hz), 86.3, 85.5, 52.4 (d, J = 7.2 Hz), 51.9, 29.9, 23.8, 23.7, 22.0, 21.5, 17.2; ^{31}P NMR (162 MHz, DMSO-d_6) δ 23.74 (s); HRMS (ESI, m/z): calcd for $C_{35}H_{39}ClN_2PRu$ $[M - Cl]^+$ 655.15774, found 655.15755; Anal. Calcd for: $C_{35}H_{39}Cl_2N_2PRu{\bullet}0.75CH_2Cl_2$: C, 56.92; H 5.41; N 3.71; Found: C, 56.63; H, 5.70; N, 3.78.

Complex 6c.



Yellow solid, 65% yield (47 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.12 (s, 1H), 7.85 (s, 1H), 7.70 – 7.65 (m, 3H), 7.60 – 7.51 (m, 9H), 7.43 – 7.32 (m, 4H), 7.08 (t, J = 8.6 Hz, 2H), 6.98 (t, J = 8.6 Hz, 1H), 5.72 (d, J = 6.1 Hz, 1H), 5.62 – 5.56 (m, 2H), 5.50 – 5.46 (m, 2H), 4.70 (d, J = 5.9 Hz, 1H), 2.24 – 2.19 (m, 1H), 1.87 (s, 3H), 0.85 (d, J = 6.4 Hz, 3H), 0.77 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.0 (d, J = 22.2 Hz), 140.4, 139.7 (d, J = 12.5 Hz), 137.1, 136.7, 134.3, 134.2, 133.8, 133.3, 132.8 (d, J = 8.9 Hz), 131.6, 130.6, 130.5, 130.4, 130.2 (d, J = 2.1 Hz), 129.5, 129.1, 129.0, 128.8 (d, J = 9.0 Hz), 128.6, 128.2, 128.0, 127.9, 127.8, 126.1, 125.3, 122.9, 108.9, 106.7, 93.6 (d, J = 7.1 Hz), 93.0, 93.0, 89.2, 52.6 (d, J = 9.6 Hz), 30.0, 22.2, 21.5, 17.5; ^{31}P NMR (162 MHz, DMSO-d_6) δ 23.99 (s); HRMS (ESI, m/z): calcd for $C_{38}H_{37}ClN_2PRu$ $[M - Cl]^+$ 689.14209, found 689.14183; Anal. Calcd for:$C_{38}H_{37}Cl_2N_2PRu{\bullet}0.9CH_2Cl_2$: C, 58.32; H 4.88; N 3.50, Found: C, 58.08; H, 4.79; N, 3.80.

Complex 6d.

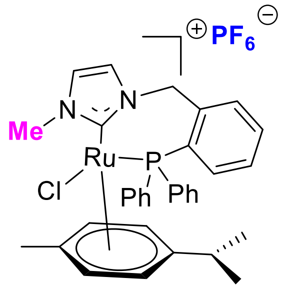


Yellow solid, 74% yield (57 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.13 (s, 1H), 7.85 – 7.81 (m, 3H), 7.73 – 7.67 (m, 3H), 7.61 (t, J = 7.4 Hz, 1H), 7.46 (s, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.20 – 7.05 (m, 4H), 6.99 (s, 1H), 6.79 (s, 1H), 6.51 – 6.46 (m, 2H), 5.85 – 5.69(m, 2H), 5.40 – 5.33 (m, 2H), 5.19 (s, 1H), 4.42 (s, 1H), 2.24 (m, 4H), 1.97 (s, 3H), 1.85 (s, 3H), 1.71 (s, 3H), 0.98 (d, J = 7.0 Hz, 3H), 0.52 (d, J = 6.4 Hz, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 171.5 (d, J = 25.7 Hz), 139.8 (d, J = 12.6 Hz), 137.9, 137.1, 136.8, 136.6, 136.5, 135.3, 135.1, 135.0, 132.6, 132.5, 131.7, 131.5, 131.4, 131.0, 130.7, 129.0 (d, J = 4.5 Hz), 128.8, 128.7, 128.6, 128.5, 128.2 (d, J = 4.5 Hz), 128.1, 128.0, 127.8, 127.7 (d, J = 10.6 Hz), 126.0, 124.0, 91.2, 89.1, 53.7 (d, J = 5.0 Hz), 30.4, 23.1, 20.4, 19.7, 19.1, 17.5, 17.4; ^{31}P NMR (162 MHz, DMSO-d_6) δ 23.34 (s); HRMS (ESI, m/z): calcd for $C_{41}H_{43}ClN_2PRu$ $[M - Cl]^+$ 731.18904, found 731.18879; Anal. Calcd for $C_{41}H_{43}Cl_2N_2PRu$•2.5CH_2Cl_2: C, 53.36; H 4.94; N 2.86, Found: C, 53.47; H, 4.68; N, 2.87.

General Method for the Preparation of Ruthenium Complexes 6ca−ce.[6]

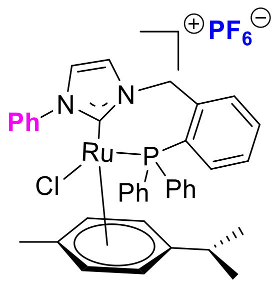
To a solution of NaX (0.1 mmol; X = BArF, BPh_4; for complex **6cb** and **6ce**, respectively) or appropriate AgX (0.20 mmol; X = PF_6, OTf and BF_4 for complex **6ca**, **6cc** and **6cd**, respectively) in CH_2Cl_2 (2 mL) was added the complex **6a** or **6c** (0.1 mmol)and the resulting mixture was stirred at rt for 2h. Then the products **6aa** and **6ca−ce** were obtained directly by silica gel column chromatography (CH_2Cl_2 : MeOH = 100 : 1 for **6aa**; CH_2Cl_2 : *n*-Hexane = 2 : 1 for **6cb**; CH_2Cl_2 : MeOH = 40 : 1 for **6cc** and **6cd**; CH_2Cl_2 : *n*-Hexane = 5 : 1 for **6ce**).

Complex 6aa. [7]



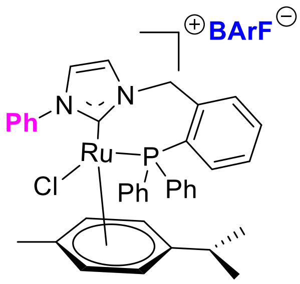
Yellow solid, 94% yield (73 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.78 (s, 1H), 7.74 – 7.71 (m, 1H), 7.55 – 7.49 (m, 9H), 7.44 – 7.36 (m, 4H), 7.29 (t, J = 7.5 Hz, 1H), 6.77 (t, J = 8.8 Hz, 1H), 6.31 (t, J = 6.8 Hz, 2H), 5.98 (d, J = 6.3 Hz, 1H), 5.42 – 5.29 (m, 2H), 3.92 (s, 3H), 2.20 (s, 3H), 2.05 – 1.99 (m, 1H), 0.85 (d, J = 6.8 Hz, 3H), 0.65 (d, J = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.76, 165.57, 141.07, 140.95, 137.51, 137.08, 136.39, 136.29, 133.43, 132.62, 132.35, 132.26, 132.10, 131.63, 131.34, 131.24, 130.75, 130.39, 129.74, 129.66, 129.07, 129.00, 128.94, 128.84, 128.40, 127.98, 127.87, 127.77, 126.37, 122.08, 107.57, 106.20, 94.57, 94.48, 94.29, 94.23, 91.71, 88.62, 52.46 (d, J = 9.1 Hz), 38.68, 29.95, 22.64, 20.13, 17.54; ^{31}P NMR (162 MHz, DMSO-d_6) δ 25.55, -144.18 (sept, ^{2}J(P, F) = 712 Hz, PF_6); HRMS (ESI, m/z): calcd for $C_{33}H_{35}ClN_2PRu$ [M −PF_6]$^+$ 627.12644, found 627.12602.

Complex 6ca.



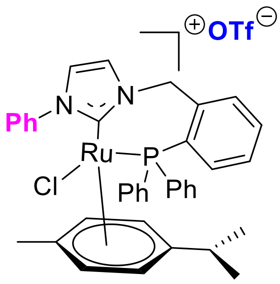
Yellow solid, 92% yield (62 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.02 (s, 1H), 7.80 – 7.77 (m, 1H), 7.70 – 7.68 (m, 3H), 7.60 – 7.51 (m, 9H), 7.45 – 7.33 (m, 4H), 7.10 – 7.05 (m, 2H), 7.00 (t, J = 8.7 Hz, 1H), 5.72 (d, J = 6.4 Hz, 1H), 5.63 (d, J = 14.5 Hz, 1H), 5.55 (d, J = 5.6 Hz, 1H), 5.50 (s, 1H), 5.40 (d, J = 14.5 Hz, 1H), 4.71 (d, J = 6.3 Hz, 1H), 2.25 – 2.18 (m, 1H), 1.87 (s, 3H), 0.85 (d, J = 6.7 Hz, 3H), 0.78 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.1 (d, J = 22.2 Hz), 140.4, 139.6 (d, J = 12.5 Hz), 137.1, 136.6, 134.3, 134.2, 133.8, 133.3, 132.80 (d, J = 8.9 Hz), 131.6, 130.6, 130.4, 130.3, 130.2, 129.5, 129.1, 129.0, 128.9 (d, J = 9.0 Hz), 128.5, 128.1, 127.8, 127.7, 109.1, 106.7, 93.6 (d, J = 7.1 Hz), 93.0, 93.0, 89.2, 52.8 (d, J = 9.6 Hz), 30.0, 22.3, 21.4, 17.4; ^{31}P NMR (162 MHz, DMSO-d_6) δ 23.96, -144.19, (sept, ^{2}J(P, F) = 712 Hz, PF_6); HRMS (ESI, m/z): calcd for $C_{38}H_{37}ClN_2PRu$ [M – PF_6]$^+$ 689.14209, found 689.14183; Anal. Calcd for $C_{38}H_{37}ClF_6N_2P_2Ru$: C, 54.71; H 4.47; N 3.36, Found: C, 54.37; H, 4.27; N, 3.19.

Complex 6cb.



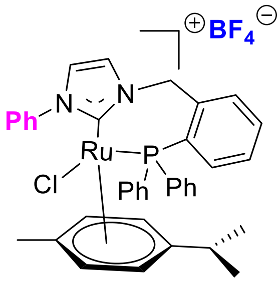
Yellow solid, 78% yield (108 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.03 (s, 1H), 7.83 – 7.76 (m, 1H), 7.72 – 7.64 (m, 7H), 7.61 – 7.55 (m, 13H), 7.54 – 7.50 (m, 4H), 7.40 – 7.35 (m, 4H), 7.12 – 7.03 (m, 2H), 6.99 (t, J = 8.7 Hz, 1H), 5.71 (d, J = 6.4 Hz, 1H), 5.62 (d, J = 14.4 Hz, 1H), 5.55 (d, J = 5.6 Hz, 1H), 5.49 (s, 1H), 5.40 (d, J = 14.5 Hz, 1H), 4.70 (d, J = 6.2 Hz, 1H), 2.22 – 2.19 (m, 1H), 1.86 (s, 3H), 0.81 (d, J = 4.0 Hz, 3H), 0.76 (d, J = 4.0 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.2 (d, J = 20.0 Hz), 161.7, 161.2, 160.7, 160.2, 140.5, 139.7 (d, J = 12.4 Hz), 137.1, 136.7, 134.4 – 134.1 (m), 133.8, 133.3, 132.9, 132.8, 131.7, 130.6, 130.4, 130.2, 129.5, 129.1, 128.9, 128.8, 128.7 – 128.6 (m), 128.4 – 128.3 (m), 128.1, 128.1, 127.9, 127.8, 125.4, 122.8, 122.7, 120.0, 117.6, 108.9, 106.8, 93.6 (d, J = 7.1 Hz), 93.1, 93.0, 89.2, 52.8 (d, J = 10.0 Hz), 30.0, 22.3, 21.5, 17.5; ^{31}P NMR (162 MHz, DMSO-d_6) δ 23.95 (s); HRMS (ESI, m/z): calcd for $C_{38}H_{37}ClN_2PRu$ [M − BArF]$^+$, 689.14209, found 689.14183.

Complex 6cc.



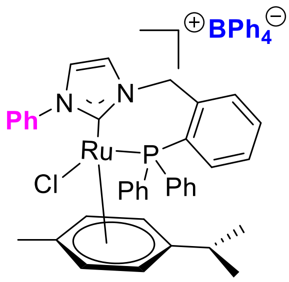
Yellow solid, 94% yield (85 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.02 (s, 1H), 7.81 – 7.78 (m, 1H), 7.71 – 7.68 (m, 3H), 7.62 – 7.50 (m, 9H), 7.42 – 7.30 (m, 4H), 7.10 – 7.05 (m, 2H), 6.99 (t, J = 8.7 Hz, 1H), 5.72 (d, J = 6.4 Hz, 1H), 5.63 (d, J = 14.4 Hz, 1H), 5.55 (d, J = 5.7 Hz, 1H), 5.50 (s, 1H), 5.40 (d, J = 14.5 Hz, 1H), 4.70 (d, J = 6.3 Hz, 1H), 2.24-2.18 (m, 1H), 1.87 (s, 3H), 0.85 (d, J = 6.7 Hz, 3H), 0.77 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.1 (d, J = 22.2 Hz), 140.4, 139.7 (d, J = 12.5 Hz), 137.1, 136.7, 134.4, 134.3, 133.8, 133.3, 132.8 (d, J = 8.9 Hz), 131.7, 130.7, 130.4, 130.3, 130.2, 129.5, 129.1, 129.1, 128.8 (d, J = 9.0 Hz), 128.6, 128.3, 128.1, 127.9, 127.8, 126.1, 122.8, 108.9, 106.8, 93.7 (d, J = 7.1 Hz), 93.1, 93.0, 89.3, 52.8 (d, J = 9.6 Hz), 30.0, 22.3, 21.5, 17.5; ^{31}P NMR (162 MHz, DMSO-d_6) δ 23.97; HRMS (ESI, m/z): calcd for $C_{38}H_{37}ClN_2PRu$ [M − CF_3SO_3]$^+$ 689.14209, found 689.14183.

Complex 6cd.



Yellow solid, 90% yield (75 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.03 (s, 1H), 7.81 – 7.78 (m, 1H), 7.72 – 7.67 (m, 3H), 7.60 – 7.50 (m, 9H), 7.41 – 7.33 (m, 4H), 7.10 – 7.05 (m, 2H), 6.99 (t, *J* = 8.7 Hz, 1H), 5.73 (d, *J* = 6.4 Hz, 1H), 5.63 (d, *J* = 14.5 Hz, 1H), 5.56 (s, 1H), 5.50 (s, 1H), 5.41 (d, *J* = 14.5 Hz, 1H), 4.71 (d, *J* = 6.2 Hz, 1H), 2.24 – 2.18 (m, 1H), 1.87 (s, 3H), 0.85 (d, *J* = 6.8 Hz, 3H), 0.77 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.1(d, *J* = 22.2 Hz), 140.4, 139.7 (d, *J* = 12.5 Hz), 137.1, 136.7, 134.4, 134.3, 133.8, 133.3, 132.8 (d, *J* = 8.1 Hz), 131.7, 130.7, 130.4, 130.3, 130.2, 129.5, 129.1, 129.1, 128.9 (d, *J* = 9.1 Hz), 128.6, 128.3, 128.1, 127.9, 127.8, 126.1, 125.5, 122.8, 108.9, 106.7, 93.7 (d, *J* = 7.1 Hz), 93.1, 93.0, 89.2, 52.8 (d, *J* = 10.1 Hz), 30.0, 22.3, 21.5, 17.5; ^{31}P NMR (162 MHz, DMSO-d_6) δ 23.97; HRMS (ESI, m/z): calcd for $C_{38}H_{37}ClN_2PRu$ [M – BF_4]$^+$ 689.14209, found 689.14183.

Complex 6ce.



Yellow solid, 89% yield (95 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.01 (s, 1H), 7.81 – 7.78 (m, 1H), 7.71 – 7.67 (m, 3H), 7.60 – 7.50 (m, 9H), 7.41 – 7.32 (m, 4H), 7.20 (s, 8H), 7.10 – 7.05 (m, 2H), 7.00 (t, *J* = 8.7 Hz, 1H), 6.93 (t, *J* = 7.2 Hz, 8H), 6.81 – 6.78 (m, 4H), 5.70 (d, *J* = 6.4 Hz, 1H), 5.63 (d, *J* = 14.4 Hz, 1H), 5.52 (d, *J* = 5.5 Hz, 1H), 5.47 (s, 1H), 5.39 (d, *J* = 8.0 Hz, 1H), 4.70 (d, *J* = 6.3 Hz, 1H), 2.24 – 2.18 (m, 1H), 1.85 (s, 3H), 0.85 (d, *J* = 6.7 Hz, 3H), 0.77 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.1 (d, *J* = 22.2 Hz), 164.1, 163.6, 163.1, 162.6, 140.4, 139.6 (d, J = 12.1 Hz), 137.1, 136.7, 135.6, 134.5, 134.4, 134.3, 133.8, 133.3, 132.8 (d, J = 9.1 Hz), 131.6, 130.6, 130.4 (d, J = 8.1 Hz), 130.2, 129.5, 129.1, 129.0, 128.9 (d, J = 5.1 Hz), 128.8, 128.6, 128.3, 128.1, 127.9, 127.8, 127.5, 127.4, 126.7, 125.35-125.26 (m), 122.7, 121.5, 108.9, 106.7, 93.7 (d, J = 7.1 Hz), 93.0, 93.0, 89.2, 52.8 (d, J = 10.1 Hz), 30.0, 22.3, 21.5, 17.5; ^{31}P NMR (162 MHz, DMSO-d_6) δ 23.97; HRMS (ESI, m/z): calcd for $C_{38}H_{37}ClN_2PRu$ [M – BPh_4]$^+$ 689.14209, found 689.14183.

III Single Crystal X-Ray Diffraction of 6d, 6aa and 6ca.

Table S1a. Crystal data and structure refinement for 6d

Identification code	CCDC 1830666
Empirical formula	$C_{41}H_{43}Cl_2N_2PRu$
Formula weight	766.71
Temperature/K	282.72(10)
Crystal system	triclinic
Space group	P-1
a/Å	10.0105(3)
b/Å	11.3092(4)
c/Å	19.0850(7)
α/°	85.671(3)
β/°	78.534(3)
γ/°	67.010(3)
Volume/Å^3	1949.31(12)
Z	2
ρ_{calc}g/cm^3	1.306
μ/mm^{-1}	5.122
F(000)	792.0
Crystal size/mm^3	0.17 × 0.12 × 0.1
Radiation	CuKα (λ = 1.54184)
Theta range for data	8.494 to 134.18
Index ranges	-11 ≤ h ≤ 11, -11 ≤ k ≤ 13, -22 ≤ l ≤ 22
Reflections collected	22685
Independent reflections	6911 [R_{int} = 0.0344, R_{sigma} = 0.0305]
Data/restraints/parameters	6911/0/430
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ	R_1 = 0.0301, wR_2 = 0.0737
Final R indexes [all data]	R_1 = 0.0336, wR_2 = 0.0759
Largest diff. peak/hole / e	1.54/-0.62

Table S1b. Crystal data and structure refinement for 6aa.

Identification code	CCDC 1911586
Empirical formula	$C_{33}H_{35}ClN_2P_2F_6Ru$
Formula weight	771.52
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	C2/c
a/Å	12.9079(2)
b/Å	14.7545(2)
c/Å	35.0697(4)
α/°	90
β/°	95.0420(10)
γ/°	90
Volume/Å^3	6653.17(16)
Z	62
ρ_{calc}g/cm^3	3.304
μ/mm^{-1}	37.631
F(000)	6138.0
Crystal size/mm^3	0.4 × 0.2 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.122 to 148.718
Index ranges	-15 ≤ h ≤ 15, -17 ≤ k ≤ 18, -23 ≤ l ≤ 43
Reflections collected	13757
Independent reflections	6569 [R_{int} = 0.0406, R_{sigma} = 0.0476]
Data/restraints/parameters	6569/0/380
Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0416, wR_2 = 0.1100
Final R indexes [all data]	R_1 = 0.0442, wR_2 = 0.1124
Largest diff. peak/hole / e Å^{-3}	1.00/-1.18

Table S1c. Crystal data and structure refinement for 6ca.

Identification code	CCDC 1912108
Empirical formula	$C_{39}H_{38}Cl_1F_6N_2P_2Ru_1$
Formula weight	855.52
Temperature/K	150.00(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	10.44120(10)
b/Å	11.3932(2)
c/Å	29.2341(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3477.65(8)
Z	39
ρ_{calc}g/cm^3	1.593
μ/mm^{-1}	5.783
F(000)	1696.0
Crystal size/mm^3	0.4 × 0.2 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.33 to 148.408
Index ranges	$-12 \leq h \leq 11$, $-14 \leq k \leq 13$, $-23 \leq l \leq 36$
Reflections collected	14160
Independent reflections	6846 [R_{int} = 0.0386, R_{sigma} = 0.0507]
Data/restraints/parameters	6846/0/455
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0315, wR_2 = 0.0823
Final R indexes [all data]	R_1 = 0.0329, wR_2 = 0.0836
Largest diff. peak/hole / e Å^{-3}	0.51/-0.57
Flack parameter	0.505(10)

IV Synthesis of *N*-alkylated amines via alkylation of amines with alcohols

1, GC analysis method for the condition optimization.

GC analysis method:

Injector: Mode: Split; temp.: 330 °C; Gas: N_2 Pressure: 1.34 bar; Split ratio: 39:1; Split flow: 67.6 mL/min.

Column: Wondacap 1 column Capillary column (30 m x 0.25 mm); Nominal film thickness: 0.250 μm; Temperature program: Initial temperature 100 °C, heat to 120 °C with 5 °C/min, then heat to 200 °C with 50 °C/min, hold for 5 min.

Initial Flow: 1.62 mL/min; Average velocity: 39.4 cm/sec, Pressure: 1.34 bar. Detector (FID): Temp.: 330 °C; Hydrogen flow: 40.0 mL/min; Air flow: 400.0 mL/min.

Preparation of GC sample:

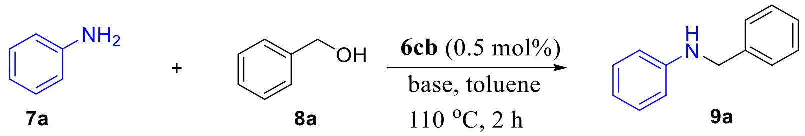
Dilute the crude reaction mixture with 5 mL of EtOAc, filtered through syringe filter and collected in GC vials for analysis.

Retention times: Benzaldehyde: 2.79 min; Aniline: 2.87 min; Benzyl alcohol: 3.33 min; *N*-1-diphenylmethanimine: 8.66 min; *N*, *N*-benzylphenylamine: 9.05 min.

2, Effects of Bases on *N*-Alkylation of Aniline with Benzyl Alcohol Catalyzed by 6cb.

The effect of the base was investigated in the presence of complex **6cb**. It was found that the KO^{t}Bu is an effective base to give the high yield. However, changing KO^{t}Bu to other bases resulted in decreased product yields, and the weak bases such as K_2CO_3 and Na_2CO_3 even are ineffective (Table S2, entries 6-10). In addition, nearly 75 mol% KO^{t}Bu is needed to obtain sufficient yields (Table S2, entries 1-5).

Table S2. Effects of Bases on *N*-Alkylation of Aniline with Benzyl Alcohol Catalyzed by 6cb[a, b]



entry[a]	base	base loading (mol%)	yield[b] (%)
1	none	-	6
2	KO^{t}Bu	100	97

3	KO^{t}Bu	200	90
4	KO^{t}Bu	75	95
5	KO^{t}Bu	50	54
6	KOH	100	40
7	NaO^{t}Bu	100	12
8	NaOH	100	8
9	K_2CO_3	100	-
10	Na_2CO_3	100	-

[a]*N*-alkylation reaction conditions: 1.0 mmol **7a**, 1.0 mmol **8a**, 0.5 mol% **6cb**, x mmol base, 2.0 mL toluene, 110 °C, 2 h. [b]GC yields.

3, General Method for the *N*-alkylation of Amines with Alcohols.

To a 15 mL reaction tube in a glovebox, was added complex **6cb** (0.25 mol%) and KO^{t}Bu (75 mol%), alcohols (0.5 mmol), amine (0.5 mmol) at room temperature. Then the tube was closed and removed from the glovebox. The reaction mixture was stirred at 70 °C for 12 h. After cooled to rt, the reaction mixture was filtered and dried under vacuum. The product was purified by column chromatography over silica-gel (300-400 mesh) with appropriate mixture of petroleum ether and ethyl acetate (80: 1).

***N*-benzylaniline (9a).[8]** Colorless oil, 95% yield (86 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 4H), 7.32 – 7.28 (m, 1H), 7.20 (t, J = 7.5 Hz, 2H), 6.75 (t, J = 7.3 Hz, 1H), 6.67 (d, J = 7.8 Hz, 2H), 4.35 (s, 2H), 4.04 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 139.6, 129.4, 128.7, 127.6, 127.3, 117.7, 113.0, 48.4; MS (ESI) $[M+H]^+$ 183.65.

***N*-(4-methylbenzyl)aniline (9b).[8]** Colorless oil, 94% yield (92 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, J = 8.1 Hz, 2H), 7.19 – 7.15 (m, 4H), 6.71 (t, J = 7.3 Hz, 1H), 6.64 (d, J = 8.0 Hz, 2H), 4.28 (s, 2H), 3.98 (s, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 137.0, 136.5, 129.4, 129.4, 127.6, 117.6, 113.0, 48.2, 21.2; MS (ESI) $[M+H]^+$ 197.65.

***N*-(4-methoxybenzyl)aniline (9c).[8]** Colorless oil, 92% yield (97 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 8.4 Hz, 2H), 7.20 (t, J = 7.8 Hz, 2H), 6.91 (d, J = 8.5 Hz, 2H), 6.74 (t, J = 7.3 Hz, 1H), 6.65 (d, J = 7.7 Hz, 2H), 4.28 (s, 2H), 3.97 (s, 1H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 148.3, 131.5, 129.4, 128.9, 117.6, 114.1, 112.9, 55.4, 47.9; MS (ESI) $[M+H]^+$ 213.60.

***N*-(4-(methylthio)benzyl)aniline (9d).[8]** Colorless oil, 75% yield (86 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.21 (m, 4H), 7.16 (t, J = 7.9 Hz, 2H), 6.71 (t, J = 7.3 Hz, 1H), 6.61 (d, J = 7.7

Hz, 2H), 4.27 (s, 2H), 3.99 (s, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 137.3, 136.5, 129.4, 128.1, 127.1, 117.7, 113.0, 48.0, 16.2; MS (ESI) $[M+H]^+$ 230.90.

***N*-(4-chlorobenzyl)aniline (9e).**[8] Colourless oil, 85% yield (92 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 4H), 7.18 (t, J = 7.4 Hz, 2H), 6.74 (t, J = 7.2 Hz, 1H), 6.62 (d, J = 7.9 Hz, 2H), 4.32 (s, 2H), 4.06 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 138.1, 133.0, 129.4, 128.9, 128.8, 117.9, 113.0, 47.7; MS (ESI) $[M+H]^+$ 217.50.

***N*-(4-bromobenzyl)aniline (9f).**[8] Colourless oil, 55% yield (72 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.1 Hz, 2H), 7.28 (s, 2H), 7.19 (t, J = 7.6 Hz, 2H), 6.75 (t, J = 7.1 Hz, 1H), 6.63 (d, J = 8.2 Hz, 2H), 4.32 (s, 2H), 4.07 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 138.7, 131.8, 129.4, 129.2, 121.0, 117.9, 113.0, 47.8; MS (ESI) $[M+H]^+$ 263.30.

***N*-(3-chlorobenzyl)aniline (9g).**[9] Colourless oil, 84% yield (91 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.28 – 7.25 (m, 3H), 7.21 – 7.17 (m, 2H), 6.75 (t, J = 6.9 Hz, 1H), 6.64 – 6.61 (m, 2H), 4.33 (s, 2H), 4.09 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 141.9, 134.6, 130.0, 129.4, 127.5, 127.5, 125.5, 118.0, 113.0, 47.9; MS (ESI) $[M+H]^+$ 218.56.

***N*-(3-methylbenzyl)aniline (9h).**[10] Colourless oil, 90% yield (89 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.14 (m, 5H), 7.08 (d, J = 7.4 Hz, 1H), 6.70 (t, J = 7.3 Hz, 1H), 6.62 (d, J = 7.8 Hz, 2H), 4.26 (s, 2H), 3.95 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 139.5, 138.4, 129.4, 128.6, 128.4, 128.1, 124.7, 117.6, 113.0, 48.5, 21.6; MS (ESI) $[M+H]^+$ 198.68.

***N*-(3-(trifluoromethyl)benzyl)aniline (9i).**[11] Colourless oil, 80% yield (100 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.58 – 7.53 (m, 2H), 7.46 (t, J = 7.7 Hz, 1H), 7.21 – 7.16 (m, 2H), 6.75 (t, J = 7.3 Hz, 1H), 6.63 (d, J = 7.7 Hz, 2H), 4.41 (s, 2H), 4.14 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 140.8, 130.8, 129.5, 129.2, 124.2, 124.2, 124.2, 124.2, 118.1, 113.1, 48.0; MS (ESI) $[M+Na]^+$ 274.03.

***N*-(2-methylbenzyl)aniline (9j).**[12] Colourless oil, 86% yield (85 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 6.8 Hz, 1H), 7.21 – 7.14 (m, 5H), 6.71 (t, J = 7.3 Hz, 1H), 6.62 (d, J = 7.8 Hz, 2H), 4.25 (s, 2H), 3.83 (s, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 137.1, 136.4, 130.5, 129.4, 128.4, 127.5, 126.3, 117.6, 112.8, 46.5, 19.0; MS (ESI) $[M+H]^+$ 198.62.

***N*-(naphthalen-2-ylmethyl)aniline (9k).**[13] Colorless oil, 80% yield (93 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.81 (m, 4H), 7.52 – 7.48 (m, 3H), 7.20 (t, J = 7.6 Hz, 2H), 6.75 (t, J = 7.4 Hz, 1H), 6.70 (d, J = 8.1 Hz, 2H), 4.51 (s, 2H), 4.15 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 137.1, 133.6, 132.9, 129.4, 128.5, 127.9, 127.8, 126.3, 126.0, 125.9, 117.8, 113.1, 48.6; MS (ESI) $[M+H]^+$ 233.65.

***N*-(benzo[d][1,3]dioxol-5-ylmethyl)aniline (9l).**[13] Colorless oil, 85% yield (96 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.17 (m, 2H), 6.88 – 6.83 (m, 2H), 6.78 (d, J = 7.9 Hz, 1H), 6.73 (t, J = 7.3 Hz, 1H), 6.65 – 6.63 (m, 2H), 5.95 (s, 2H), 4.24 (s, 2H), 3.99 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 148.0, 146.8, 133.5, 129.4, 120.7, 117.7, 113.0, 108.4, 108.2, 101.1, 48.3. MS (ESI) $[M+H]^+$ 227.87.

***N*-(pyridin-2-ylmethyl)aniline (9m).**[14] Yellow solid, 42% yield (38 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, J = 4.5 Hz, 1H), 7.64 (t, J = 7.5 Hz, 1H), 7.34 (d, J = 7.7 Hz, 1H), 7.18 (t, J = 7.2 Hz, 3H), 6.77 – 6.59 (m, 3H), 4.76 (s, 1H), 4.47 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 149.3, 148.0, 136.7, 129.4, 122.2, 121.7, 117.7, 113.2, 49.4; MS (ESI) $[M+H]^+$ 184.65.

***N*-isobutylaniline (9n).**[15] Colourless oil, 66% yield (49 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.17 (m, 2H), 6.73 – 6.69 (m, 1H), 6.64 – 6.62 (m, 2H), 3.72 (s, 1H), 2.96 (d, J = 6.8 Hz, 2H), 1.95 – 1.89 (m, 1H), 1.02 (d, J = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 129.3, 117.1, 112.8, 51.9, 28.1, 20.6; MS (ESI) $[M+H]^+$ 149.70.

***N*-(3-phenylpropyl)aniline (9o).**[16] Yellow oil, 83% yield (87 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.31 (m, 2H), 7.25 – 7.18 (m, 5H), 6.74 – 6.70 (m, 1H), 6.62 – 6.59 (m, 2H), 3.62 (s, 1H), 3.18 (t, J = 6.9 Hz, 2H), 2.76 (t, J = 7.6 Hz, 2H), 2.02 – 1.94 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 141.8, 129.3, 128.6, 128.5, 126.1, 117.3, 112.9, 43.5, 33.5, 31.2; MS (ESI) $[M+H]^+$ 211.60.

***N*-butylaniline (9p).**[17] Yellow oil, 88% yield (66 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.15 (m, 2H), 6.71 (t, J = 7.3 Hz, 1H), 6.66 – 6.59 (m, 2H), 3.60 (s, 1H), 3.13 (t, J = 7.1 Hz, 2H), 1.69 – 1.53 (m, 2H), 1.50 – 1.43 (m, 2H), 0.98 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 129.3, 117.2, 112.8, 43.8, 31.8, 20.4, 14.0; MS (ESI) $[M+H]^+$ 150.47.

***N*-hexylaniline (9q).**[17] Yellow oil, 78% yield (69 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.17 (m, 2H), 6.71 (t, J = 7.3 Hz, 1H), 6.63 – 6.61 (m, 2H), 3.60 (s, 1H), 3.12 (t, J = 7.1 Hz, 2H), 1.67 – 1.60 (m, 2H), 1.46 – 1.31 (m, 6H), 0.94 – 0.91 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 129.3, 117.2, 112.8, 44.1, 31.8, 29.7, 27.0, 22.8, 14.2; MS (ESI) $[M+H]^+$ 178.51.

***N*-(furan-2-ylmethyl)aniline (9r).**[18] Colorless oil, 65% yield (56 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.21 (t, J = 7.6 Hz, 2H), 6.76 (t, J = 7.2 Hz, 1H), 6.69 (d, J = 8.1 Hz, 2H), 6.33 (s, 1H), 6.24 (s, 1H), 4.33 (s, 2H), 4.04 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.87, 147.75, 142.04, 129.36, 118.16, 113.29, 110.46, 107.10, 41.58; MS (ESI) $[M+H]^+$173.70.

***N*-(thiophen-2-ylmethyl)aniline (9s).**[18] Colorless oil, 78% yield (74 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.20 (m, 3H), 7.05 (d, *J* = 3.3 Hz, 1H), 7.00 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.79 (t, *J* = 7.3 Hz, 1H), 6.71 (d, *J* = 7.7 Hz, 2H), 4.54 (s, 2H), 4.05 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.70, 143.05, 129.37, 126.95, 125.11, 124.67, 118.18, 113.27, 43.50; MS (ESI) $[M+H]^+$ 189.60.

***N*-benzyl-4-methylaniline (10a).**[19] Yellow oil, 83% yield (81 mg). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.42 – 7.35 (m, 4H), 7.32 – 7.28 (m, 1H), 7.02 (d, *J* = 7.8 Hz, 2H), 6.61 – 6.58 (m, 2H), 4.34 (s, 2H), 3.92 (s, 1H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 146.0, 139.8, 129.9, 128.7, 127.6, 127.3, 126.9, 113.1, 48.8, 20.5; MS (ESI) $[M+H]^+$ 197.65.

***N*-benzyl-4-methoxyaniline (10b).**[19] Brown solid, 92% yield (97 mg). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.43 – 7.37 (m, 4H), 7.33 – 7.30 (m, 1H), 6.85 – 6.81 (d, *J* = 8.7 Hz, 2H), 6.66 – 6.62 (m, 2H), 4.32 (s, 2H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 152.2, 142.5, 139.8, 128.7, 127.6, 127.2, 115.0, 114.2, 55.9, 49.3; MS (ESI) $[M+H]^+$ 213.60.

***N*-benzyl-4-chloroaniline (10c).**[8] Colourless oil, 87% yield (94 mg). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.36 (d, *J* = 3.9 Hz, 4H), 7.32 – 7.28 (m, 1H), 7.15 – 7.11 (m, 2H), 6.58 – 6.54 (m, 2H), 4.31 (s, 2H), 4.07 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 146.8, 139.1, 129.2, 128.8, 127.5, 127.5, 122.2, 114.0, 48.5; MS (ESI) $[M+H]^+$ 217.60.

***N*-benzyl-4-bromoaniline (10d).**[8] Colourless oil, 81% yield (106 mg). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.36 (d, *J* = 4.1 Hz, 4H), 7.32 – 7.28 (m, 1H), 7.25 (d, *J* = 8.9 Hz, 2H), 6.51 (d, *J* = 8.5 Hz, 2H), 4.31 (s, 2H), 4.08 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 147.2, 139.0, 132.1, 128.8, 127.5, 114.5, 109.2, 48.4; MS (ESI) $[M+H]^+$ 263.40.

***N*-benzyl-3-methylaniline (10e).**[20] Colourless oil, 86% yield, 85 mg). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.41 – 7.34 (m, 4H), 7.31 – 7.27 (m, 1H), 7.08 (t, *J* = 7.7 Hz, 1H), 6.57 (d, *J* = 7.5 Hz, 1H), 6.48 (dd, *J* = 11.7, 3.7 Hz, 2H), 4.34 (s, 2H), 3.98 (s, 1H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 148.4, 139.7, 139.2, 129.3, 128.8, 127.7, 127.3, 118.7, 113.8, 110.1, 48.5, 21.8; MS (ESI) $[M+H]^+$ 198.65.

***N*-benzyl-3-bromoaniline (10f).**[21] Colourless oil, 81% yield (106 mg). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.36 – 7.35 (m, 4H), 7.33 – 7.27 (m, 1H), 7.01 (t, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 7.9 Hz, 1H), 6.78 (t, *J* = 2.0 Hz, 1H), 6.53 (dd, *J* = 8.1, 1.9 Hz, 1H), 4.31 (s, 2H), 4.11 (s, 1H); ^{13}C NMR

(100 MHz, $CDCl_3$) δ 149.5, 138.8, 130.6, 128.9, 127.6, 127.6, 123.4, 120.5, 115.5, 111.6, 48.2; MS (ESI) $[M+H]^+$ 263.40.

***N*-benzyl-2-bromoaniline (10g).**[22] Colourless oil, 54% yield (71 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.8, 1H), 7.38 – 7.35 (m, 4H), 7.32 – 7.28 (m, 1H), 7.14 (t, *J* = 7.7, 1H), 6.63 – 6.57 (m, 2H), 4.78 (s, 1H), 4.42 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 138.8, 132.5, 128.8, 128.6, 127.4, 127.3, 118.1, 111.7, 109.8, 48.1; MS (ESI) $[M+H]^+$ 263.40.

***N*-benzyl-[1,1'-biphenyl]-2-amine (10h).**[17] Colourless oil, 83% yield (107 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.46 (m, 4H), 7.42 – 7.34 (m, 5H), 7.32 – 7.27 (m, 1H), 7.27 – 7.20 (m, 1H), 7.17 (dd, *J* = 7.4, 1.4 Hz, 1H), 6.83 (t, *J* = 7.4 Hz, 1H), 6.72 (d, *J* = 8.2 Hz, 1H), 4.44 (s, 1H), 4.38 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 139.6, 130.4, 129.5, 129.0, 128.8, 128.7, 127.8, 127.4, 127.2, 117.3, 110.9, 48.2; MS (ESI) $[M+H]^+$ 259.95.

***N*-benzyl-2,3-dihydrobenzo[b][1,4]dioxin-6-amine (10i).** [17] Colourless oil, 85% yield (102 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.31 (m, 4H), 7.30 – 7.24 (m, 1H), 6.71 (d, *J* = 8.4 Hz, 1H), 6.22 – 6.16 (m, 2H), 4.26 (s, 2H), 4.24 – 4.20 (m, 2H), 4.20 – 4.15 (m, 2H), 3.77 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 143.4, 139.7, 135.9, 128.7, 127.7, 127.3, 117.8, 106.9, 101.7, 64.9, 64.3, 49.2; MS (ESI) $[M+H]^+$ 241.87.

***N*-benzylnaphthalen-2-amine (10j).**[19] White solid, 92% yield (107 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.60 (m, 3H), 7.45 – 7.43 (m, 2H), 7.40 – 7.36 (m, 3H), 7.35 – 7.30 (m, 1H), 7.24 – 7.20 m, 1H), 6.93 (dd, *J* = 8.7 Hz, *J* = 2.4 Hz, 1H), 6.86 (d, *J* = 2.3 Hz, 1H), 4.45 (s, 2H), 4.20 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 139.3, 135.3, 129.1, 128.8, 127.8, 127.7, 127.5, 126.5, 126.1, 122.2, 118.0, 104.8, 48.5; MS (ESI) $[M+H]^+$ 233.60.

***N*-benzylpyridin-2-amine (10k).**[14] White solid, 83% yield (76 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 4.6 Hz, 1H), 7.44 – 7.30 (m, 5H), 7.29 (s, 1H), 6.63 – 6.56 (m, 1H), 6.38 (d, *J* = 8.4 Hz, 1H), 4.85 (s, 1H), 4.51 (d, *J* = 5.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 148.3, 139.3, 137.6, 128.7, 127.5, 127.3, 113.3, 106.9, 46.4; MS (ESI) $[M+H]^+$ 184.60.

***N*-benzylpyridin-3-amine (10l).**[17] White solid, 86% yield (79 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.95 (d, *J* = 4.2 Hz, 1H), 7.35 (d, *J* = 4.4 Hz, 4H), 7.30 – 7.25 (m, 1H), 7.05 (dd, *J* = 8.2, 4.5 Hz, 1H), 6.87 – 6.84 (m, 1H), 4.33 (d, *J* = 4.6 Hz, 2H), 4.22 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 138.9, 138.6, 136.2, 128.8, 127.5, 127.5, 123.8, 118.6, 47.9; MS (ESI) $[M+H]^+$ 184.60.

Dibenzylamine (10m).[23] Colorless oil, 51% yield (100 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 4H), 7.27 – 7.23 (m, 1H), 3.80 (s, 2H), 1.70 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.41, 128.52, 128.28, 127.07, 53.30; MS (ESI) $[M+H]^+$ 198.19.

***N*-benzylhexan-1-amine (10n).**[24] Colorless oil, 43% yield (82 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.30 (m, 4H), 7.26 – 7.23 (m, 1H), 3.78 (s, 2H), 2.62 (t, J = 7.2 Hz, 2H), 1.56 – 1.51 (m, 2H), 1.34 – 1.26 (m, 7H), 0.88 (t, J = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.67, 128.46, 128.20, 126.94, 54.21, 49.65, 31.90, 30.19, 27.16, 22.74, 14.15; MS (ESI) $[M+H]^+$ 192.26.

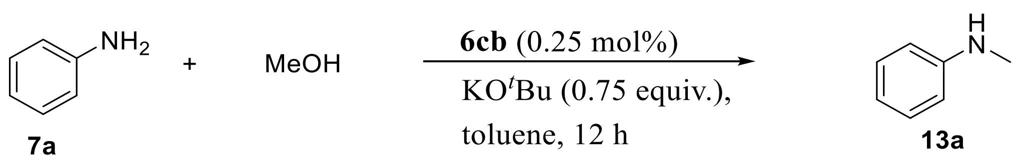
***N*-benzyl-2-(*p*-tolyl)ethan-1-amine (10o).**[25] Colorless oil, 45% yield (101 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.21 (m, 5H), 7.09 (s, 4H), 3.79 (s, 2H), 2.88 (t, J = 6.6 Hz, 2H), 2.79 (t, J = 6.8 Hz, 2H), 2.31 (s, 3H), 1.51 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.49, 137.05, 135.72, 129.27, 128.72, 128.49, 128.21, 127.00, 54.02, 50.81, 36.04, 21.14; MS (ESI) $[M+H]^+$ 226.27.

4, *N*-methylation of anilines with methanol catalyzed by 6cb

4.1 The condition optimization

Firstly, we conducted the methylation at 70 °C (the optimal conditions for *N*-alkylation of amines with alcohols). However, there is no reaction (entry 1) and increasing the amount of the MeOH did not improve the conversion (entry 2). To our delight, at 110 °C, in the presence of excess MeOH (25 equiv.), the yield is up to 84% (entry 8). Increasing the catalyst loading to 0.5 mol% (entry 11), the yield could be increased to 93%. We also have studied the *N*-methylation of aniline with MeOH under neat conditions (entries 12-15). When the amount of methanol is 10 equiv. (entry 14), the GC yield of **13a** is up to 100%. Finally, the optimal conditions selected to probe the substrate scope of the reaction were **6cb** (0.5 mol%), KO^{t}Bu (75 mol%), neat, 110 °C and 12 h (entry 15).

Table S3 Optimization of the Reaction Conditions[a, b]

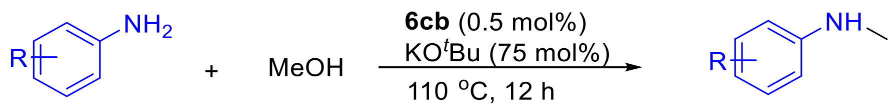


Entry	MeOH (μL)	Temperature	Yield(%)

		(°C)	
1	40 (2 equiv.)	70	trace
2	500 (25 equiv.)	70	3
3	40 (2 equiv.)	90	trace
6	500 (25 equiv.)	90	8
7	40 (2 equiv.)	110	17
8	500 (25 equiv.)	110	84
9	250 (12.5 equiv.)	110	63
10	1000 (50 equiv.)	110	66
11[c]	500 (25 equiv.)	110	93
12[c, d]	50 (2.5 equiv.)	110	65
13 [c, d]	100 (5 equiv.)	110	80
14 [c, d]	200 (10 equiv.)	110	100
15 [c, d]	500 (25 equiv.)	110	100

[a] General reaction conditions: 0.5 mmol **7a**, x µL MeOH, 75 mol% KO^{t}Bu, **6cb** (0.25 mol%), 1 mL toluene, 12 h, N_2. [b] GC yields. [c]**6cb** (0.5 mol%). [d] without toluene.

3.2 General method for the *N*-methylation of anilines with methanol.



To a 15 mL sealing tube in a glovebox, was added amine (0.5 mmol), MeOH (200 µL), **6cb** (0.5 mol%) and KO^{t}Bu (75 mol%). Then the tube was closed with a screw-top cap and removed from the glovebox. The reaction mixture was stirred for 12 h at 110 °C. After cooled to rt, the mixture was diluted with ethyl acetate and filtered through a short pad of silica (2 cm in a Pasteur pipette). The silica was washed with ethyl acetate. The filtrate was evaporated and the crude residue was purified by column chromatography (SiO_2, petroleum ether : ethyl acetate = 80 : 1).

4-methoxy-*N*-methylaniline (11b).[17] Yellow oil, 92 % yield (63 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.75 – 6.69 (m, 2H), 6.51 – 6.46 (m, 2H), 5.14 (s, 1H), 3.63 (s, 3H), 2.62 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 150.6, 144.3, 114.6, 112.6, 55.3, 30.5; MS (ESI) [M+H]$^+$ 138.34.

4-ethyl-*N*-methylaniline (**11c**).[17] Yellow oil, 88% yield (59 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, J = 8.5 Hz, 2H), 6.59 (d, J = 8.5 Hz, 2H), 2.84 (s, 3H), 2.57 (q, J = 7.6 Hz, 2H), 1.22 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 133.3, 128.6, 112.7, 31.2, 28.1, 16.1; MS (ESI) $[M+H]^+$ 136.36.

4-ethoxy-*N*-methylaniline (11d).[17] Yellow oil, 89% yield (67 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 – 6.77 (m, 2H), 6.61 – 6.56 (m, 2H), 3.97 (q, J = 7.0 Hz, 2H), 2.81 (s, 3H), 1.38 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 143.8, 115.9, 113.7, 64.3, 31.7, 15.2; MS (ESI) $[M+H]^+$ 152.36.

4-(tert-butyl)-*N*-methylaniline (**11e**).[17] Yellow oil, 90% yield (73 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.20 (m, 2H), 6.60 – 6.55 (m, 2H), 2.81 (s, 3H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 140.2, 126.1, 112.3, 34.0, 31.7, 31.1; MS (ESI) $[M+H]^+$ 164.40.

4-chloro-*N*-methylaniline (11f).[17] Yellow oil, 86% yield (61 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.10 (m, 2H), 6.55 – 6.50 (m, 2H), 3.71 (s, 1H), 2.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 129.1, 121.9, 113.6, 31.0; MS (ESI) $[M+H]^+$ 142.22.

4-bromo-*N*-methylaniline (11g).[17] Yellow oil, 90% yield (83 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.22 (m, 2H), 6.49 – 6.44 (m, 2H), 3.71 (s, 1H), 2.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 132.0, 114.0, 108.9, 30.8; MS (ESI) $[M+H]^+$ 186.25.

3-bromo-*N*-methylaniline (11h).[26] Yellow oil, 76% yield (70 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (t, J = 8.0 Hz, 1H), 6.83 – 6.81 (m, 1H), 6.74 (t, J = 2.0 Hz, 1H), 6.53 – 6.50 (m, 1H), 3.77 (s, 1H), 2.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 130.5, 123.4, 120.0, 114.9, 111.3, 30.6; MS (ESI) $[M+H]^+$ 186.25.

2-iodo-*N*-methylaniline (**11i**).[17] Yellow oil, 40% yield (47 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (dd, J = 7.8, 1.5 Hz, 1H), 7.25 – 7.21 (m, 1H), 6.56 (dd, J = 8.1, 1.3 Hz, 1H), 6.44 (td, J = 7.6, 1.4 Hz, 1H), 4.19 (s, 1H), 2.88 (d, J = 4.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 139.0, 129.6, 118.6, 110.2, 85.2, 31.1; MS (ESI) $[M+H]^+$ 234.11.

2-ethyl-*N*-methylaniline (**11j**).[17] Yellow oil, 76% yield (51 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (td, J = 7.9, 1.4 Hz, 1H), 7.10 (d, J = 7.3 Hz, 1H), 6.78 – 6.71 (m, 1H), 6.66 (d, J = 8.0 Hz, 1H), 3.69 (s, 1H), 2.92 (s, 3H), 2.51 (q, J = 7.5 Hz, 2H), 1.28 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8, 127.8, 127.6, 127.2, 117.1, 109.6, 31.0, 23.9, 13.0; MS (ESI) $[M+H]^+$ 135.85.

***N*-methylnaphthalen-2-amine (11k).**[27] Yellow oil, 90% yield (70 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.63 (m, 3H), 7.40 – 7.35 (m, 1H), 7.23 – 7.19 (m, 1H), 6.89 (dd, J = 8.7, 2.4 Hz, 1H), 6.81 (d, J = 2.2 Hz, 1H), 3.86 (s, 1H), 2.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 135.4, 128.9, 127.8, 127.6, 126.4, 126.0, 122.0, 118.0, 103.9, 30.9; MS (ESI) $[M+H]^+$ 157.85.

***N*-methyl-9*H*-fluoren-2-amine (11l).**[17] Yellow oil, 72% yield (70 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, J = 16.7, 7.9 Hz, 2H), 7.49 (d, J = 7.4 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H), 7.20 (t, J = 7.4 Hz, 1H), 6.82 (s, 1H), 6.65 (dd, J = 8.2, 1.9 Hz, 1H), 3.84 (s, 2H), 2.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 145.3, 142.5, 142.3, 131.9, 126.7, 124.9, 124.8, 120.7, 118.5, 111.7, 108.8, 37.1, 31.1; MS (ESI) $[M+H]^+$ 195.82.

***N*-methyl-3-(trifluoromethyl)aniline (11m).**[28] Yellow oil, 90% yield (79 mg).; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (t, J = 7.8 Hz, 1H), 6.93 (d, J = 7.6 Hz, 1H), 6.78 (s, 1H), 6.73 (d, J = 8.2 Hz, 1H), 3.90 (s, 1H), 2.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.53, 131.66 (q, J = 31.6 Hz), 129.66, 124.57 (q, J = 272.2 Hz), 115.59, 113.67 (q, J = 16.0 Hz), 108.45 (q, J = 16.0 Hz), 30.61; MS (ESI) $[M+H]^+$ 176.29.

***N*-methylbenzo[d][1,3]dioxol-5-amine (11n).**[26] Yellow oil, 92% yield (69 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.68 (d, J = 8.3 Hz, 1H), 6.25 (d, J = 2.1 Hz, 1H), 6.05 (dd, J = 8.3, 2.1 Hz, 1H), 5.85 (s, 2H), 3.51 (s, 1H), 2.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 145.4, 139.6, 108.7, 103.9, 100.6, 95.7, 31.7; MS (ESI) $[M+H]^+$ 151.84.

***N*-methylpyridin-3-amine (11o).**[17] Yellow oil, 94% yield (51 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.96 (d, J = 4.1 Hz, 1H), 7.10 (dd, J = 8.2, 4.5 Hz, 1H), 6.90 – 6.84 (m, 1H), 3.78 (s, 1H), 2.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 138.7, 135.8, 123.8, 118.2, 30.4; MS (ESI) $[M+H]^+$ 109.10.

5. General method for the *N*-alkylation of diamines.

Following the general method for the *N*-alkylation of amines with alcohols by using, 3-benzenediamine (216 mg, 2 mmol) and benzyl alcohol (52 μL, 0.5 mmol) for 12 h at 110 °C. After the reaction, the mixture was cooled to room temperature and the intermediate **12** was isolated by column chromatography. In the case of the complexes **13a-d**, 0.5 mmol intermediate **12** and alcohols were used.

***N*^{1}-(4-methoxybenzyl)benzene-1,3-diamine (12).**[8] Yellow oil, 83% yield (94 mg). ^{1}H NMR (400

MHz, $CDCl_3$) δ 7.28 (d, J = 8.4 Hz, 2H), 6.96 (t, J = 7.9 Hz, 1H), 6.88 (d, J = 8.4 Hz, 2H), 6.09 (d, J = 7.8 Hz, 2H), 5.98 (s, 1H), 4.22 (s, 2H), 3.80 (s, 3H), 3.59 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 149.5, 147.6, 131.7, 130.2, 128.9, 114.1, 105.1, 104.1, 99.6, 55.4, 47.8; MS (ESI) $[M+H]^+$ 228.65.

***N*[1]-benzyl-*N*[3]-(4-methoxybenzyl)benzene-1,3-diamine (13a).** [8] Yellow oil, 88% yield (139 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.37-7.31 (m, 4H), 7.28-7.25 (m, 3H), 6.98 (t, J = 8.0 Hz, 1H), 6.87 (d, J = 8.4 Hz, 2H), 6.06 (d, J = 7.9 Hz, 2H), 5.93 (s, 1H), 4.29 (s, 2H), 4.20 (s, 2H), 3.89 (s, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 148.9, 148.3, 139.3, 130.8, 130.2, 129.2, 128.7, 127.8, 127.3, 114.1, 104.3, 98.5, 55.4, 48.7, 48.5; MS (ESI) $[M+H]^+$ 318.50.

***N*[1]-(4-methoxybenzyl)-*N*[3]-(4-methylbenzyl)benzene-1,3-diamine (13b).** Yellow oil, 84% yield (139 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, J = 8.4 Hz, 4H), 7.19 (d, J = 7.6 Hz, 2H), 7.03 (t, J = 8.0 Hz, 1H), 6.92 (d, J = 8.3 Hz, 2H), 6.10 (d, J = 8.9 Hz, 2H), 5.96 (s, 1H), 4.28 (s, 2H), 4.24 (s, 2H), 3.90 (s, 2H), 3.84 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 149.5, 149.5, 136.8, 136.7, 131.8, 130.1, 129.3, 128.9, 127.6, 114.0, 103.1, 103.1, 97.3, 55.3, 48.2, 47.9, 21.2; MS (ESI) $[M+H]^+$ 332.50; Anal. Calcd for: $C_{22}H_{24}N_2O$: C, 79.48; H, 7.28; N, 8.43; Found: C, 79.51; H, 7.31; N, 8.41.

***N*[1]-(4-chlorobenzyl)-*N*[3]-(4-methoxybenzyl)benzene-1,3-diamine (13c).** Yellow oil, 75% yield (132 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.22 (m, 6H), 6.99 (t, J = 7.9 Hz, 1H), 6.88 (d, J = 8.4 Hz, 2H), 6.06 (dd, J = 16.8, 7.9 Hz, 2H), 5.88 (s, 1H), 4.26 (s, 2H), 4.20 (s, 2H), 3.93 (s, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 149.5, 149.2, 138.4, 132.8, 131.7, 130.1, 128.9, 128.8, 114.1, 103.4, 103.1, 97.3, 55.4, 47.9, 47.7; MS (ESI) $[M+H]^+$ 352.50; Anal. Calcd for: $C_{21}H_{21}ClN_2O$: C, 71.48; H, 6.00; N, 7.94; Found: C, 71.44; H, 6.02; N, 7.91.

***N*[1]-isobutyl-*N*[3]-(4-methoxybenzyl)benzene-1,3-diamine (13d).** Yellow oil, 65% yield (92 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 8.2 Hz, 2H), 7.00 (t, J = 7.9 Hz, 1H), 6.90 (d, J = 8.2 Hz, 2H), 6.04 (d, J = 7.9 Hz, 2H), 5.91 (s, 1H), 4.25 (s, 2H), 3.82 (s, 3H), 3.75 (s, 1H), 2.90 (d, J = 6.7 Hz, 2H), 1.91-1.84 (m, 1H), 0.98 (d, J = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 149.8, 149.5, 131.8, 130.0, 128.9, 114.1, 103.0, 102.6, 97.1, 55.4, 51.9, 48.0, 28.1, 20.6; MS (ESI) $[M+H]^+$ 284.55; Anal. Calcd for: $C_{18}H_{24}N_2O$: C, 76.02; H, 8.51; N, 9.85; Found: C, 76.05; H, 8.48; N, 9.81.

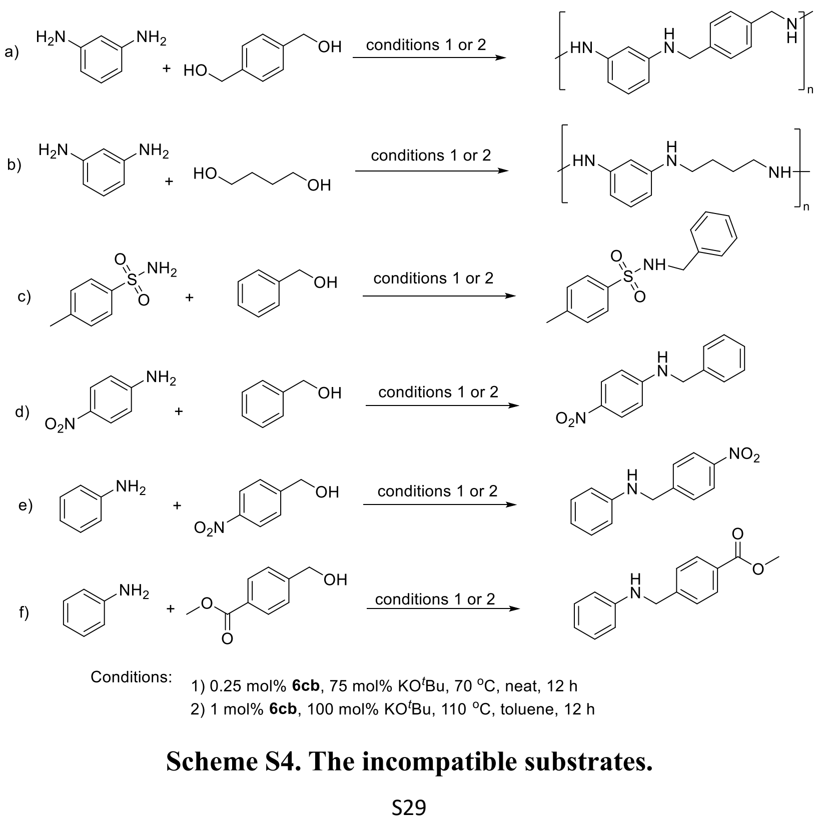
6. Gram-scale synthesis.

To a 25 mL round bottom flask in a glovebox, was added complex **6cb** (0.25 mol%), KO^{t}Bu (75 mol%), alcohols (10.0 mmol), and 2-aminopyridine (10.0 mmol) at room temperature. Then the tube was closed and removed from the glovebox. The reaction mixture was stirred at 70 °C for 12 h. After being cooled to rt, the reaction mixture diluted with CH_2Cl_2, washed with water, and dried with Na_2SO_4. The product was purified by column chromatography over silica-gel (300-400 mesh) with appropriate mixture of petroleum ether and ethyl acetate (4: 1).

***N*-(4-methoxybenzyl)pyridin-2-amine (10q).**[29] Colorless solid, 85% yield (1.8 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 4.1 Hz, 1H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.1 Hz, 2H), 6.58 (t, *J* = 4.2 Hz, 1H), 6.36 (d, *J* = 8.2 Hz, 1H), 4.90 (s, 1H), 4.42 (d, *J* = 4.7 Hz, 2H), 3.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.95, 158.75, 148.28, 137.56, 131.25, 128.80, 114.13, 113.17, 106.89, 55.40, 45.93; MS (ESI) $[M+H]^+$ 215.03.

***N*-(4-chlorobenzyl)pyridin-2-amine (10r).**[29] Colorless solid, 91% yield (1.98 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 3.9 Hz, 1H), 7.39 (t, *J* = 7.1 Hz, 1H), 7.29 (s, 4H), 6.59 (t, *J* = 7.1 Hz, 1H), 6.34 (d, *J* = 8.3 Hz, 1H), 5.02 (s, 1H), 4.48 (d, *J* = 5.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.53, 148.31, 137.94, 137.64, 132.99, 128.83, 128.77, 113.48, 107.00, 45.66; MS (ESI) $[M+H]^+$ 218.80.

7. The incompatible substrates.



Scheme S4. The incompatible substrates.

V Mechanism Details

5.1, The intermolecular competition reactions

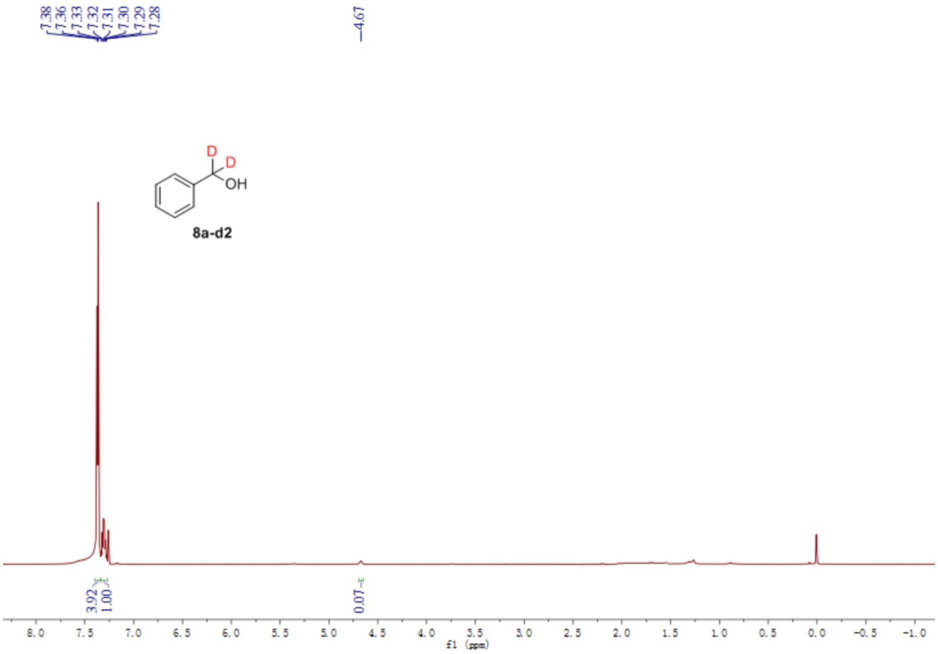


Figure S1. The ^{1}H NMR spectra of **8a-d2** in $CDCl_3$.

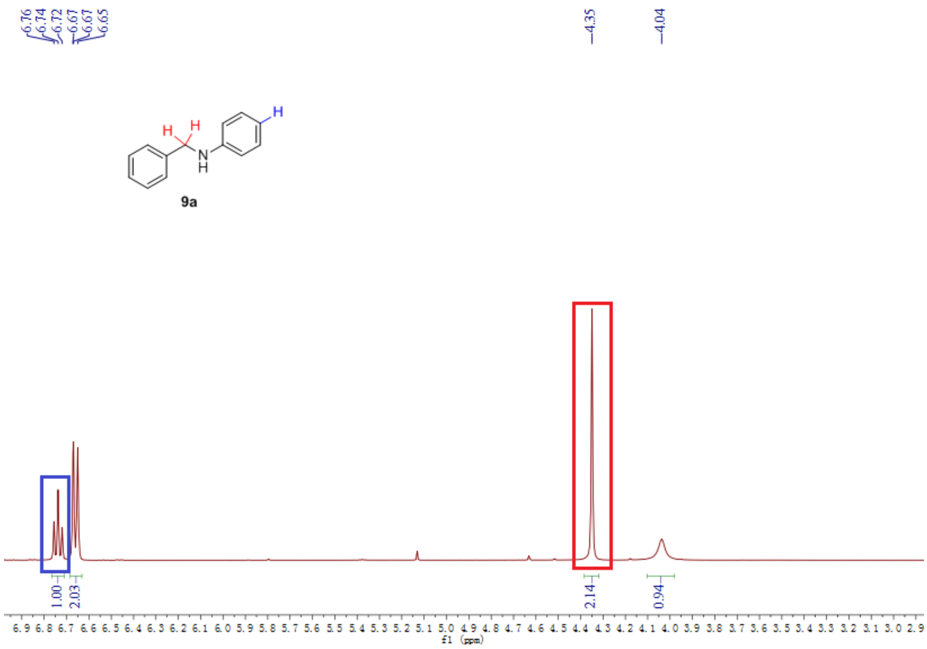


Figure S2. The ^{1}H NMR ($CDCl_3$) spectra of **9a** in the range of 3-7 ppm.

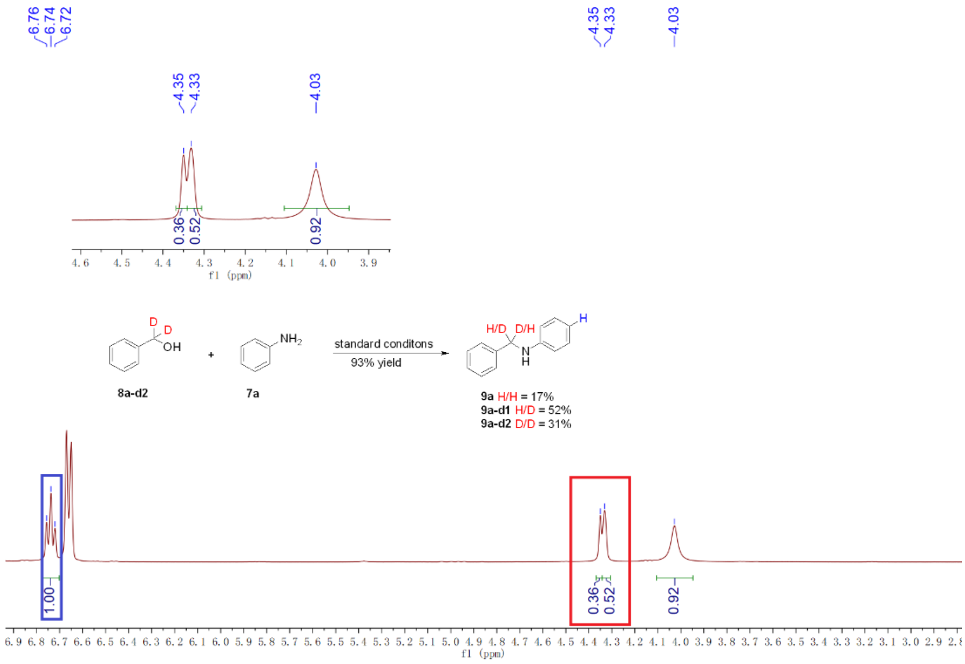


Figure S3. The ^{1}H NMR ($CDCl_3$) spectra of the products of the reaction of **8a-d2** with **7a** in the range of 3-7 ppm.

Table S4 Conversion was Calculated by ^{1}H NMR Integration Ratio.

	9a+9a-d1	**9a**	**9a-d1**	**9a-d2**
Signal δ	6.74 [*para*-H, (1H)]	4.35 [benzyl-H, (2H)]	4.33 [benzyl-H, (1H)]	
Integral Value	1.00	0.36/2.14 = 0.17	0.52	
Calculated ratio		17%	52%	31%

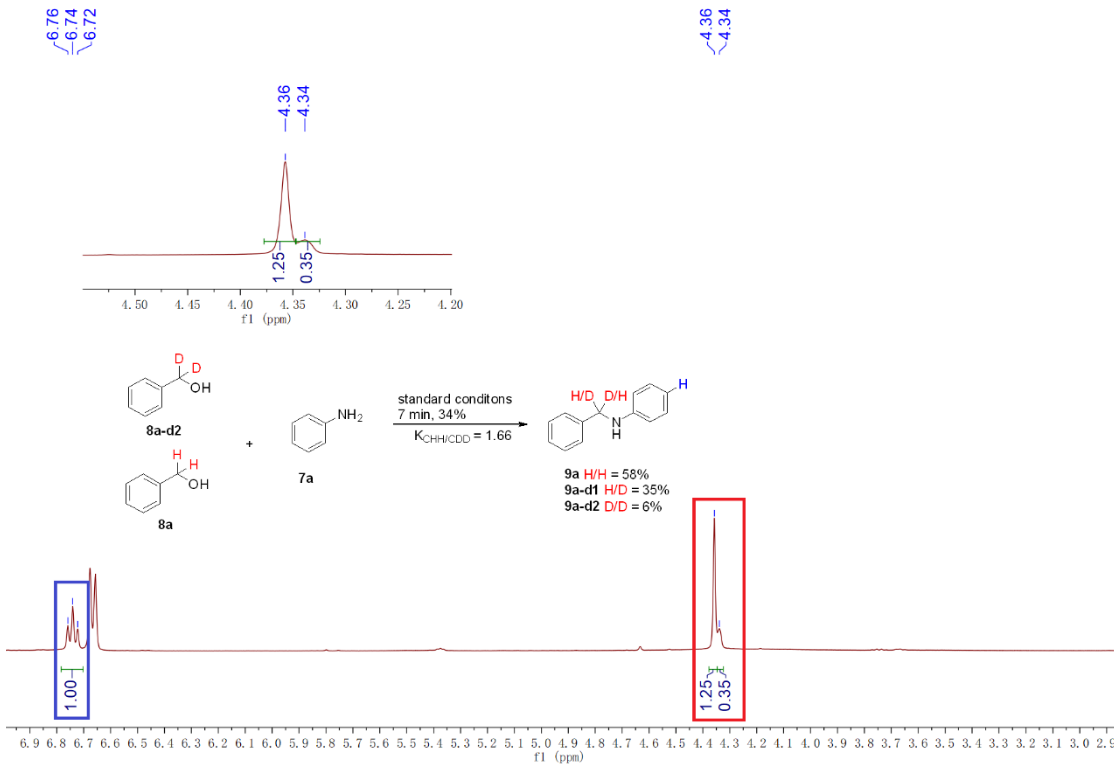


Figure S4. The ^{1}H NMR ($CDCl_3$) spectra of the products of intermolecular competition reactions in the range of 3-7 ppm.

Table S5 Conversion was Calculated by ^{1}H NMR Integration Ratio.

	9a+9a-d1	**9a**	**9a-d1**	**9a-d2**
Signal δ	6.74 [*para*-H, (1H)]	4.36 [benzyl-H, (2H)]	4.34 [benzyl-H, (2H)]	
Integral Value	1.00	1.25/2.14 = 0.58	0.35	
Calculated ratio		58%	35%	6%
KIE		k_{CHH}/k_{CDH} = 1.66		

5.2, The parallel reactions

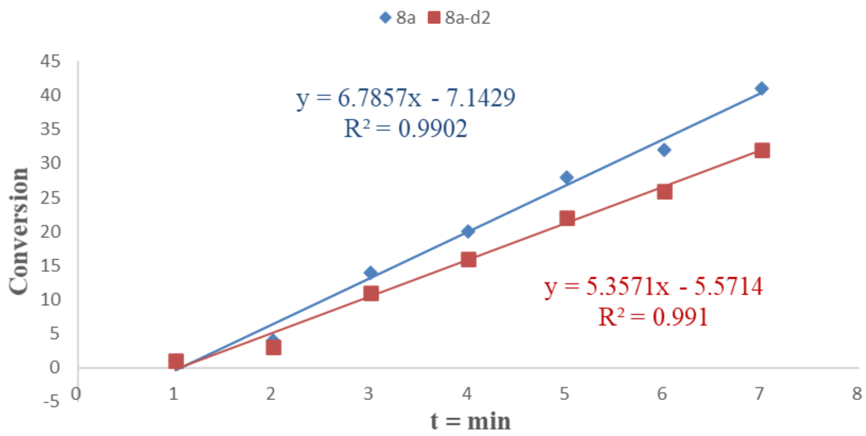


Figure S5. The plot of initial rates for KIE measurements.

5.3 Detection of hydrogen gas

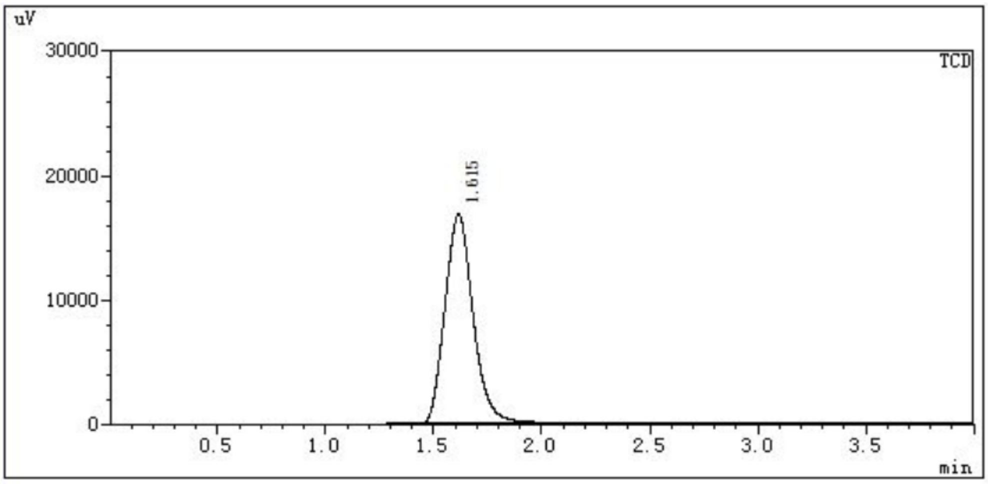


Figure S6. Detection of hydrogen gas by GC. GC parameters: injection temperature = 200 °C, column temperature = 60 °C, detector temperature = 150 °C. 5 Å molecular sieves column was used, and the carrier gas was N_2. The retention time for H_2 is 1.615 min.

5.4, NMR experiments for the mechanistic studies.

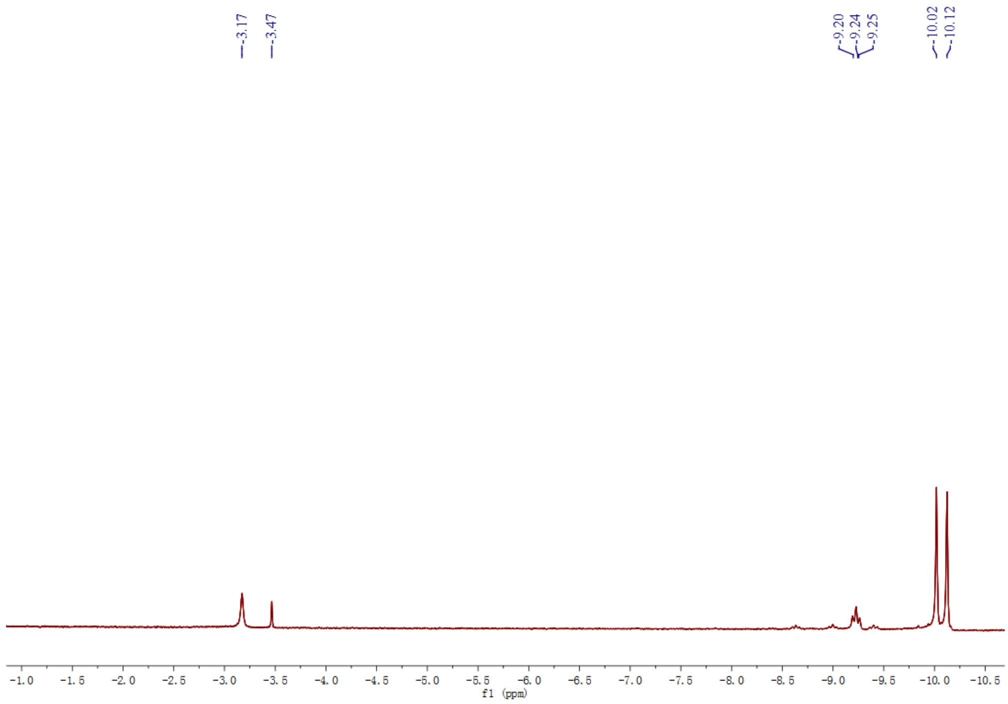


Figure S7. ^{1}H NMR (400 MHz, toluene-d_8) spectrum of reaction mixtures for amination at 0 min of hydride region.

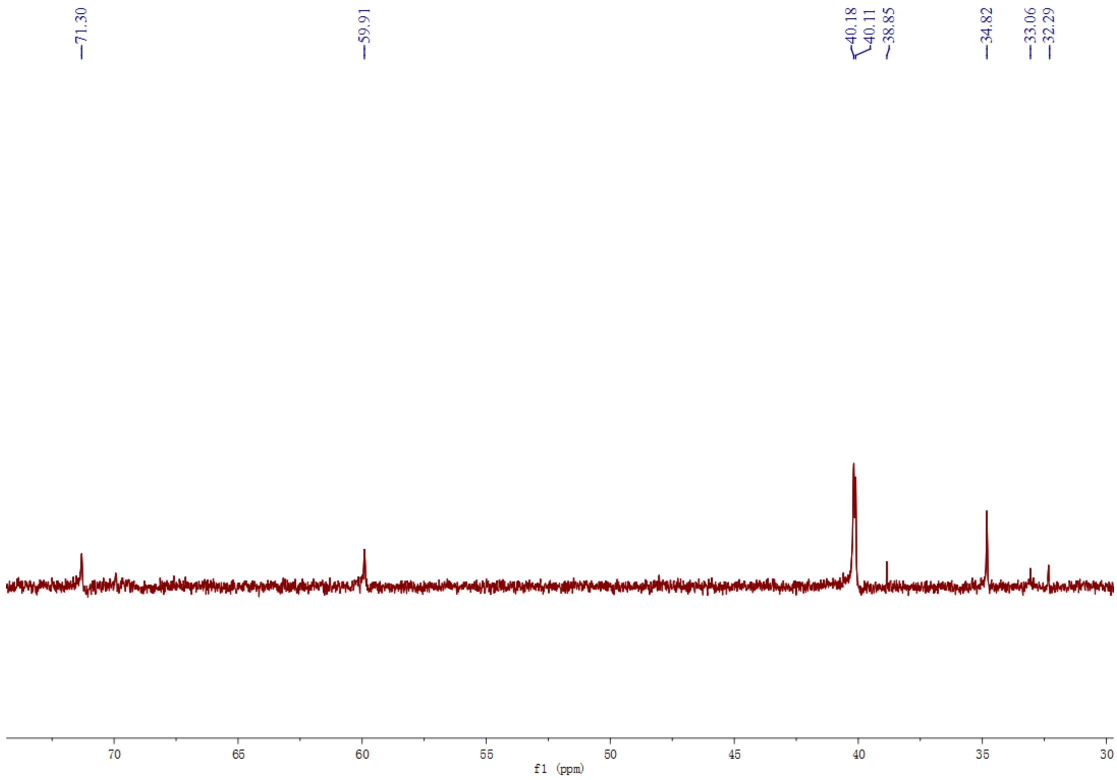


Figure S8. ^{31}P NMR (400 MHz, toluene-d_8) spectrum of reaction mixtures for amination at 0 min.

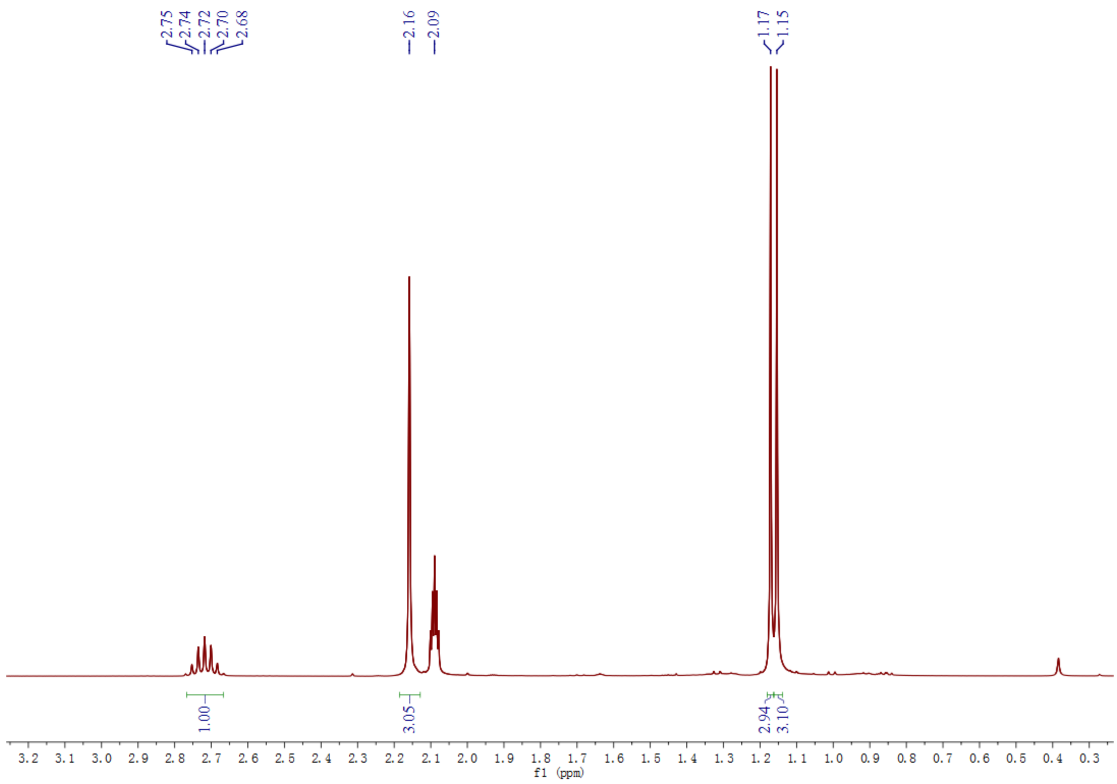


Figure S9. ^{1}H NMR (400 MHz, toluene-d_8) spectrum of *p*-cymene in the range of 0-3 ppm.

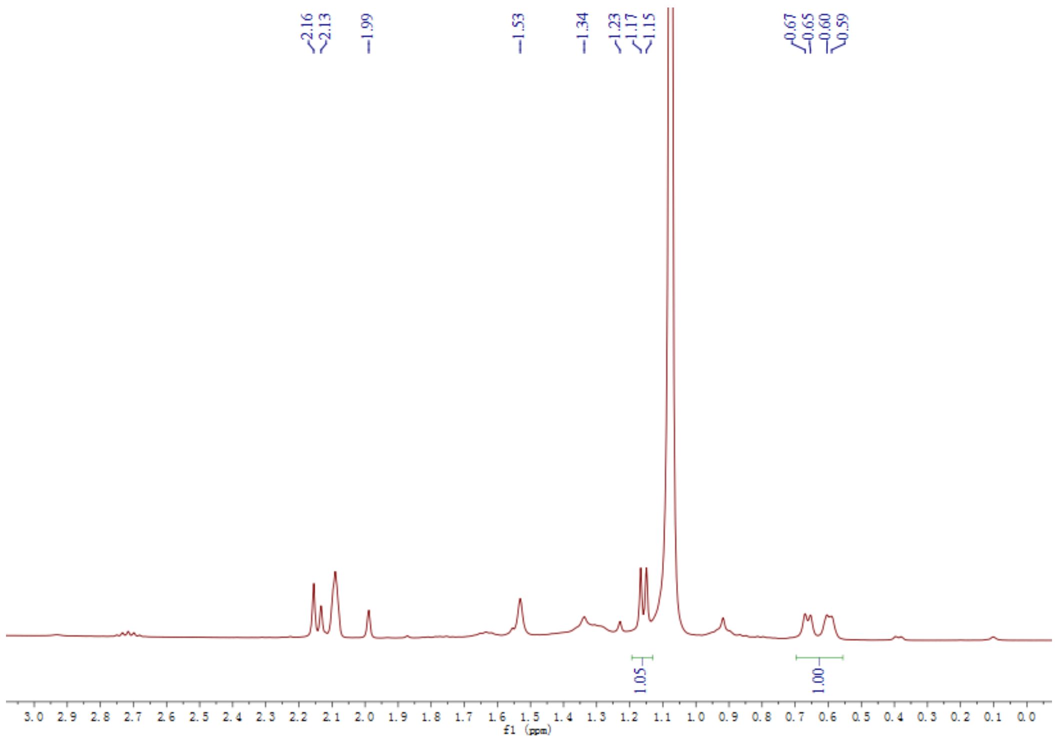


Figure S10. ^{1}H NMR (400 MHz, toluene-d_8) spectrum of reaction mixtures for amination in the range of 0-3 ppm at 0 min.

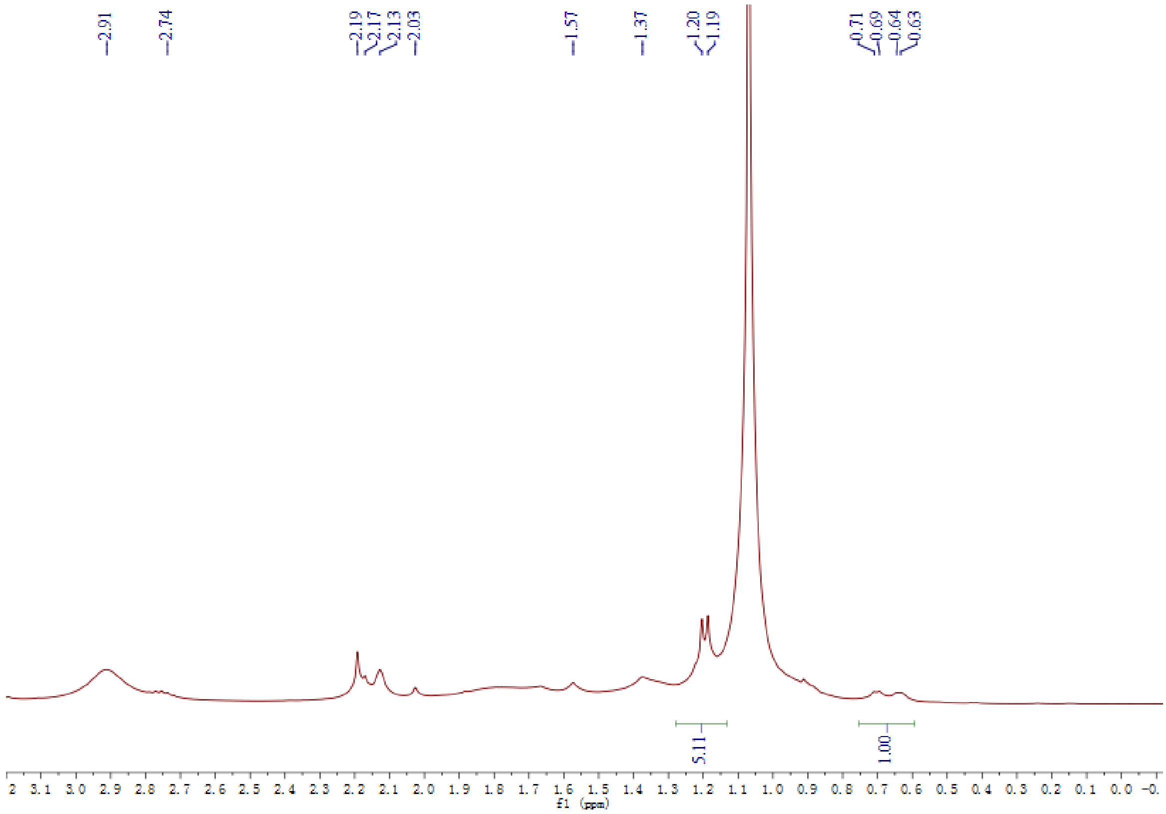


Figure S11. ^{1}H NMR (400 MHz, toluene-d_8) spectrum of reaction mixtures for amination in the range of 0-3 ppm after 1 h of heating at 110 °C.

5.5, Computational Section

Computational Details

All the structures were optimized by the density functional theory (DFT)[30] at the M06-L[31-33] functional with basis sets I (BSI, lanl2dz[34] for metal atom and 6-31G (d, p) for nonmetal atoms) in the gas phase. Frequency analysis calculations for optimized structures were performed to characterize the structures to be minima (no imaginary frequency) or transition states (one imaginary frequency). IRC calculations were taken to confirm the connection between two minima for a transition state. Based on M06-L/BSI optimized geometries, the energy results were further refined by calculating the single point energy at the M06-L/BSII (SMD[35], toluene) level of theory (BSII designates SDD[36] for metal atom and 6-311++G**[37] for nonmetal atoms). All the calculations were performed with the Gaussian 09 program.[38] The 3D optimized structures were displayed by CYLview visualization program.[39]

The Cartesian Coordinates (xyz) for All Optimized Structures.

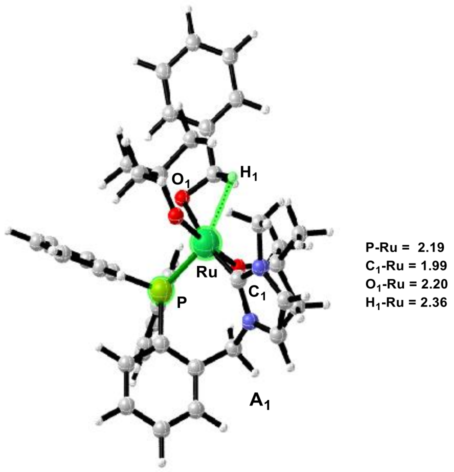
A_1

Imaginary frequencies: 0

Thermal correction to Enthalpy = 0.802948

Thermal correction to Gibbs Free Energy = 0.678419

Total free energy in solution: -with all non electrostatic terms (a.u.) = -2247.602658



44 -0.284048 -0.537112 -0.390882
15 1.306219 0.762928 0.361933
7 0.551753 -2.101095 -2.871474
7 2.103700 -2.147659 -1.384454
6 0.870822 -1.577760 -1.633225
6 3.053668 0.691726 -0.265847
6 3.819364 1.839417 -0.508833
1 3.370751 2.819029 -0.374953
6 1.531269 -2.955981 -3.342342
1 1.438423 -3.464957 -4.289715
6 0.515037 3.345560 1.212166
1 0.435008 2.916271 2.208156
6 0.926933 2.542577 0.146785
6 3.674161 -0.564967 -0.415824
6 0.321521 5.246427 -0.264155
1 0.091604 6.297707 -0.422876
6 2.851937 0.871656 2.770220
1 3.699364 1.173903 2.157926
6 0.716632 4.446945 -1.336685
1 0.781855 4.869083 -2.337265
6 0.993020 3.099038 -1.140041
1 1.247024 2.460600 -1.981586
6 2.896047 -1.829662 -0.204019
1 3.573278 -2.672445 -0.024484
1 2.184660 -1.775786 0.634429
6 5.011350 -0.638049 -0.809039
1 5.469231 -1.620677 -0.920776
6 2.520189 -2.967972 -2.415394
1 3.471324 -3.478602 -2.392468
6 0.205612 4.688515 1.005693
1 -0.116699 5.301730 1.844024
6 3.014608 0.749488 4.148598
1 3.983169 0.956602 4.599344
6 5.153747 1.754066 -0.898820
1 5.721732 2.664705 -1.074929
6 1.611616 0.607384 2.176003
6 0.534263 0.206450 2.978983
1 -0.422665 -0.004739 2.498181
6 5.757087 0.510256 -1.051155
1 6.800033 0.434833 -1.349994
6 1.938826 0.363573 4.944378
1 2.065618 0.267511 6.021133
6 0.703997 0.097658 4.356916
1 -0.136780 -0.212155 4.974025
6 -0.704952 -1.828530 -3.532011
1 -1.486808 -2.524460 -3.196936
1 -0.983977 -0.801108 -3.264966
1 -0.579150 -1.930829 -4.613456
6 -1.999409 1.514244 -2.242755
8 -0.815803 0.805005 -2.017445
6 -2.676513 -0.774072 0.800892
8 -1.799831 0.235831 1.002605
6 -0.111575 -3.327527 1.244279
8 0.168229 -1.968777 1.192222
1 -2.511917 -1.288251 -0.205101
6 -1.761006 2.332648 -3.522286
1 -1.497297 1.669431 -4.355614
1 -2.646436 2.916031 -3.810939
1 -0.927205 3.026533 -3.365486
6 -2.366254 2.477192 -1.105996
1 -3.352354 2.933602 -1.272882
1 -2.377394 1.929335 -0.161399

1 -1.633414 3.284951 -1.027476
6 -3.190658 0.573027 -2.499131
1 -3.024596 -0.027567 -3.402687
1 -3.329725 -0.113086 -1.659900
1 -4.133646 1.120734 -2.632462
6 -1.013338 -3.837229 0.109220
1 -1.215655 -4.912402 0.211225
1 -1.975447 -3.315045 0.104518
1 -0.533498 -3.678587 -0.863877
6 1.182637 -4.170856 1.214006
1 1.893286 -3.784796 1.954228
1 0.990252 -5.227885 1.444899
1 1.655353 -4.132145 0.226252
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1 -0.159662 -3.238931 3.406138
1 -1.746097 -3.046799 2.651692
1 -1.009864 -4.665528 2.759668
6 -4.139415 -0.373095 0.818179
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6 -4.517566 0.895309 1.256427
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1 -4.844690 -2.261397 0.070383
6 -5.860422 1.264215 1.287444
1 -3.727127 1.578485 1.555564
6 -6.845706 0.369294 0.877493
1 -7.238496 -1.608521 0.113272
1 -6.140250 2.259626 1.628008
1 -7.893982 0.659861 0.893337
1 -2.554598 -1.623895 1.513893

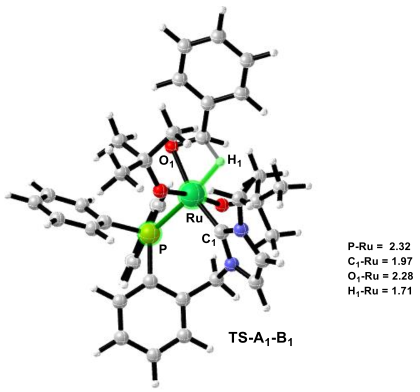
TS-A1-B1

Imaginary frequencies: -461.09

Thermal correction to Enthalpy = 0.798994

Thermal correction to Gibbs Free Energy = 0.679121

Total free energy in solution: -with all non electrostatic terms (a.u.) = -2247.585604



44 -0.563439 -0.355320 -0.175527
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7 1.181195 -2.164495 -1.873806
6 0.047039 -1.385812 -1.740439
6 3.022274 0.259522 -0.762673
6 3.954616 1.252030 -1.087659
1 3.797762 2.266292 -0.731255
6 0.049880 -2.531995 -3.720466
1 -0.340927 -2.852480 -4.674175
6 1.508936 3.062636 1.619418
1 1.544785 2.494730 2.546178
6 1.524273 2.389245 0.395095
6 3.259376 -1.054598 -1.214148
6 1.409218 5.191327 0.483483
1 1.370835 6.277820 0.517487
6 3.559482 0.114537 2.248956
1 4.280092 0.414256 1.490224
6 1.407351 4.527825 -0.742012
1 1.352620 5.094795 -1.669049
6 1.438088 3.137910 -0.788987
1 1.376092 2.618981 -1.741629
6 2.283244 -2.158608 -0.918156
1 2.783313 -3.131108 -0.992616
1 1.818650 -2.092863 0.078077
6 4.400452 -1.331067 -1.969611
1 4.568511 -2.353717 -2.307448
6 1.197306 -2.852261 -3.074202
1 2.017424 -3.497184 -3.351644
6 1.443043 4.453892 1.663514
1 1.428698 4.961476 2.625547
6 4.006204 -0.227377 3.523009
1 5.069820 -0.196479 3.750561
6 5.087661 0.964150 -1.844639

1 5.796868 1.755869 -2.075758
6 2.194957 0.079597 1.938456
6 1.278402 -0.307149 2.926324
1 0.220414 -0.346783 2.676312
6 5.315026 -0.333509 -2.289931
1 6.199301 -0.569252 -2.877382
6 3.090682 -0.606729 4.501916
1 3.437935 -0.876753 5.497522
6 1.731356 -0.640695 4.200686
1 1.012649 -0.939880 4.960746
6 -1.904205 -1.037454 -3.214791
1 -2.710173 -1.534480 -2.658491
1 -1.844211 0.006417 -2.892991
1 -2.093998 -1.116217 -4.288902
6 -1.913497 2.321400 -1.497393
8 -0.902846 1.365224 -1.535437
6 -2.435553 -0.461525 1.218740
8 -1.632283 0.427434 1.683252
6 -0.468122 -3.378300 1.133575
8 0.007846 -2.076580 1.083757
1 -2.177125 -0.873879 -0.406555
6 -1.599260 3.339177 -2.608277
1 -1.523425 2.823634 -3.573435
1 -2.375892 4.112890 -2.690084
1 -0.642647 3.833973 -2.411494
6 -1.966546 3.063777 -0.153432
1 -2.834474 3.736184 -0.084959
1 -2.006961 2.340878 0.664211
1 -1.062963 3.665779 -0.014065
6 -3.302191 1.727087 -1.814532
1 -3.371136 1.453034 -2.875257
1 -3.477108 0.823000 -1.226783
1 -4.119341 2.430838 -1.605582
6 -1.577076 -3.706224 0.120267
1 -1.873934 -4.762301 0.186568
1 -2.469152 -3.094943 0.287292
1 -1.230319 -3.509882 -0.900143
6 0.683554 -4.373646 0.872248
1 1.548170 -4.107658 1.491768
1 0.398545 -5.409744 1.102721
1 0.989195 -4.342169 -0.179954
6 -0.989558 -3.646038 2.560583
1 -0.193564 -3.422824 3.279787
1 -1.833660 -2.986889 2.792543
1 -1.314500 -4.685942 2.710973
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6 -4.756790 -1.036624 0.425200
6 -4.386841 1.098760 1.471975
6 -6.102812 -0.733755 0.268826
1 -4.355911 -1.982200 0.059871
6 -5.736540 1.404406 1.318438
1 -3.696356 1.798742 1.933206
6 -6.597700 0.493803 0.712174
1 -6.770518 -1.450478 -0.204683
1 -6.117395 2.361162 1.669534
1 -7.650715 0.735767 0.585262
1 -2.290727 -1.505923 1.541672

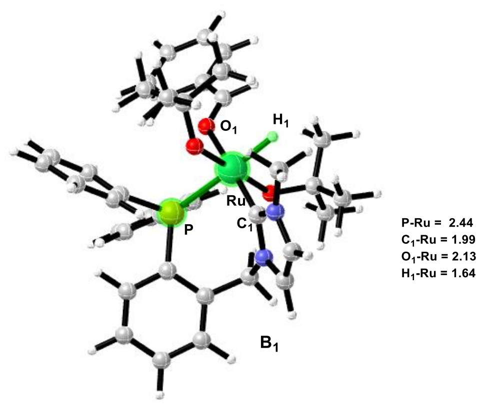
B1

Imaginary frequencies: 0

Thermal correction to Enthalpy = 0.799978

Thermal correction to Gibbs Free Energy = 0.678009

Total free energy in solution: -with all non electrostatic terms (a.u.) = -2247.608664



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7 -3.007396 -1.246778 -1.048091
6 -2.272359 -1.557372 0.075564
6 -2.057754 1.838268 -1.128719
6 -2.456222 3.172213 -0.968586
1 -1.886146 3.816538 -0.302601
6 -4.400528 -2.374286 0.219160

1 -5.226563 -2.895149 0.678766
6 0.701673 3.131394 1.395191
1 1.552878 3.139875 0.718057
6 -0.410157 2.334631 1.104330
6 -2.818507 1.011179 -1.981284
6 -0.349149 3.926731 3.420971
1 -0.328608 4.549384 4.312416
6 0.914218 3.130206 -1.786346
1 0.291792 3.872851 -1.288526
6 -1.446043 3.105098 3.162728
1 -2.280288 3.073725 3.860384
6 -1.467158 2.300806 2.030160
1 -2.303788 1.629718 1.853060
6 -2.499071 -0.449456 -2.160085
1 -2.981660 -0.824054 -3.071680
1 -1.425125 -0.682899 -2.227179
6 -3.928333 1.544485 -2.643046
1 -4.505553 0.892512 -3.298857
6 -4.300560 -1.729293 -0.968035
1 -5.023055 -1.564121 -1.752745
6 0.730809 3.923467 2.542917
1 1.602073 4.542185 2.746374
6 1.886309 3.539941 -2.692655
1 2.023929 4.599375 -2.899922
6 -3.563838 3.689538 -1.632738
1 -3.843238 4.731046 -1.489342
6 0.733995 1.771157 -1.494203
6 1.522797 0.822120 -2.157100
1 1.345673 -0.239314 -1.963731
6 -4.305323 2.872664 -2.480278
1 -5.171486 3.265049 -3.008396
6 2.680422 2.590561 -3.336241
1 3.443408 2.909698 -4.043535
6 2.487331 1.237848 -3.074881
1 3.101128 0.492631 -3.577290
6 -2.826479 -2.875261 2.105547
1 -2.312937 -3.829456 1.939094
1 -2.151265 -2.186627 2.625299
1 -3.741038 -3.044352 2.681516
6 -0.065125 -0.747168 3.519769
8 -0.886946 -0.569116 2.406512
6 2.749243 -1.367466 0.507193
8 1.714320 -0.664396 0.564226
6 0.208161 -3.092763 -2.052563
8 0.090698 -1.785958 -1.595043
1 -0.150886 -2.709865 0.934956
6 -0.965083 -0.595201 4.756141
1 -1.723422 -1.387794 4.779736
1 -0.395933 -0.638763 5.694775
1 -1.485678 0.368058 4.711171
6 1.027126 0.332666 3.579841
1 1.717545 0.165258 4.418856
1 1.606545 0.334635 2.652769
1 0.579248 1.323929 3.699854
6 0.605985 -2.126847 3.567244
1 -0.142184 -2.923311 3.483371
1 1.297304 -2.246387 2.727950
1 1.161742 -2.267843 4.505137
6 -1.045355 -3.930296 -1.759265
1 -0.961873 -4.947068 -2.167504
1 -1.194265 -3.996912 -0.676275
1 -1.934355 -3.458851 -2.195342
6 0.401021 -3.002708 -3.574610
1 1.288723 -2.401326 -3.802672
1 0.521929 -3.989532 -4.041648
1 -0.462709 -2.507073 -4.033688
6 1.421745 -3.803876 -1.440190
1 2.334958 -3.229516 -1.643140
1 1.289652 -3.865572 -0.354619
1 1.554925 -4.819988 -1.837767
1 2.682311 -2.458646 0.655124
6 4.049984 -0.805737 0.241741
6 5.184401 -1.637836 0.159781
6 4.217308 0.582755 0.043898
6 6.436864 -1.105587 -0.105602
1 5.057794 -2.710305 0.302879
6 5.470612 1.105661 -0.224185
1 3.336449 1.218606 0.095297
6 6.590381 0.270006 -0.299133
1 7.302462 -1.762074 -0.165732
1 5.583472 2.176563 -0.381037
1 7.572238 0.687071 -0.509483

A_2

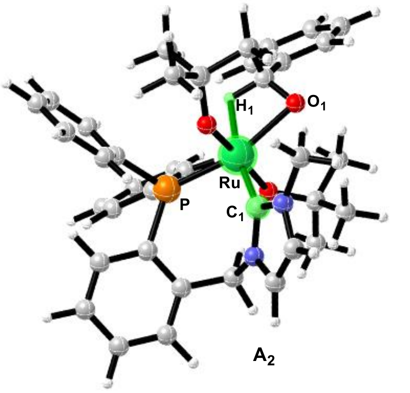
Imaginary frequencies: 0

Thermal correction to Enthalpy = 0.80405

Thermal correction to Gibbs Free Energy =

0.684281

Total free energy in solution: -with all non electrostatic terms (a.u.) = -2247.603837



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6 -0.558150 -2.091631 -0.973228
6 -2.848034 0.594145 -0.995575
6 -4.072614 1.111942 -0.552131
1 -4.131730 1.566652 0.433611
6 -1.326107 -4.106774 -1.702549
1 -1.441742 -5.179638 -1.693854
6 -1.743882 2.203110 2.415816
1 -1.083225 2.968026 2.014651
6 -2.026575 1.063960 1.657510
6 -2.807193 -0.010252 -2.267786
6 -3.155949 1.408557 4.206002
1 -3.599678 1.544474 5.189655
6 -1.682066 3.511704 -0.547768
1 -2.733155 3.327851 -0.332163
6 -3.425074 0.256501 3.468220
1 -4.070587 -0.515977 3.880903
6 -2.846987 0.071784 2.216796
1 -3.021904 -0.846742 1.663005
6 -1.550968 -0.666683 -2.759914
1 -1.619051 -0.863260 -3.836807
1 -0.634464 -0.078978 -2.571657
6 -3.961120 -0.055569 -3.053192
1 -3.905476 -0.526813 -4.034394
6 -1.822201 -3.163604 -2.540448
1 -2.460165 -3.241509 -3.407555
6 -2.300042 2.373326 3.683060
1 -2.068279 3.267708 4.257095
6 -1.263790 4.801043 -0.860628
1 -1.988234 5.612290 -0.894204
6 -5.217819 1.060593 -1.342768
1 -6.149994 1.478314 -0.969382
6 -0.765845 2.452758 -0.489094
6 0.581029 2.711632 -0.768867
1 1.278731 1.875804 -0.809779
6 -5.163732 0.479867 -2.604961
1 -6.050748 0.437964 -3.232675
6 0.082053 5.051760 -1.127134
1 0.410109 6.059891 -1.372669
6 0.997380 4.005025 -1.084347
1 2.048678 4.184706 -1.304253
6 0.233798 -4.107648 0.255613
1 1.066806 -3.451769 0.520780
1 -0.355021 -4.283207 1.158798
1 0.609815 -5.053739 -0.149442
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8 -0.514941 -1.735660 1.777142
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8 1.209303 0.107357 -1.795091
6 -1.130518 -2.609978 3.866869
1 -1.347198 -3.573257 3.389142
1 -0.827952 -2.802721 4.906003
1 -2.053424 -2.021596 3.878277
6 0.203738 -0.516197 3.759516
1 0.695314 -0.624842 4.736495
1 0.828794 0.130256 3.136016
1 -0.745359 0.005990 3.916085
6 1.239496 -2.743091 3.156615
1 0.990643 -3.793988 2.959986
1 1.972091 -2.443891 2.403127
1 1.698936 -2.703912 4.154295
6 1.912489 -1.977687 -2.881985
1 2.656257 -2.390389 -3.577631
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6 3.552284 -0.214480 -2.307777
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1 4.255753 -0.500861 -3.103228
8 2.432665 -1.515383 0.467406
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6 3.833514 0.452002 0.894401
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6 5.069277 -0.181134 0.738835
6 4.938162 2.594208 0.618708
1 2.822154 2.344181 0.951431
6 6.223795 0.561735 0.519946
1 5.096801 -1.268310 0.759371
6 6.163427 1.954022 0.455714
1 4.876007 3.679370 0.562149
1 7.177807 0.054508 0.389104.
1 7.065867 2.533726 0.274070
1 2.567559 -0.539960 2.282515
1 1.729870 0.393482 1.052502

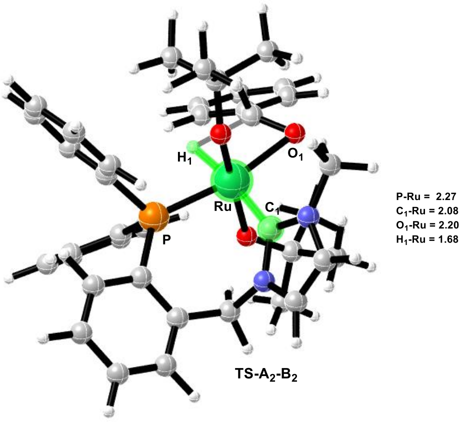
TS-A_2-B_2

Imaginary frequencies: -405.26

Thermal correction to Enthalpy = 0.79893

Thermal correction to Gibbs Free Energy = 0.67992

Total free energy in solution: -with all non electrostatic terms (a.u.) = -2247.585393



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6 -0.458378 -2.243036 -0.883792
6 -2.724785 0.518935 -1.066381
6 -3.952771 1.081464 -0.688295
1 -4.026556 1.616307 0.254784
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1 -1.459525 -5.334014 -1.399432
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6 -1.956503 1.194817 1.559129
6 -2.673067 -0.185430 -2.286648
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1 -3.643911 1.908200 4.995133
6 -1.621579 3.501321 -0.751708
1 -2.653380 3.334401 -0.447905
6 -3.446574 0.525683 3.351503
1 -4.132922 -0.203314 3.776688
6 -2.828370 0.259229 2.134724
1 -3.018095 -0.678092 1.618358
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1 -0.497168 -0.305104 -2.544388
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1 -2.419994 -3.471255 -3.229481
6 -2.257083 2.613391 3.503067
1 -2.016704 3.527835 4.040837
6 -1.232308 4.764720 -1.183983
1 -1.960815 5.571961 -1.224148
6 -5.087034 0.978028 -1.488007
1 -6.019398 1.433249 -1.161780
6 -0.697177 2.450534 -0.680821
6 0.626394 2.685154 -1.070830
1 1.322804 1.846019 -1.088826
6 -5.021053 0.299170 -2.699419
1 -5.898401 0.215975 -3.336629
6 0.090786 4.994161 -1.561171
1 0.396746 5.982258 -1.899665
6 1.011715 3.952911 -1.506929
1 2.045269 4.116896 -1.807705

6 0.211627 -4.176802 0.514907
1 -0.442314 -4.317808 1.379279
1 0.621362 -5.138803 0.187827
1 1.016213 -3.497524 0.803193
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8 -0.494093 -1.637718 1.862318
6 2.194841 -0.623144 -2.684359
8 1.316537 -0.002988 -1.798113
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1 -0.826226 0.181347 3.971769
1 0.598694 -0.424469 4.830645
6 1.125172 -2.634002 3.405422
1 0.845753 -3.681130 3.232512
1 1.931304 -2.405562 2.705730
1 1.511155 -2.570467 4.432592
6 1.979615 -2.138617 -2.822055
1 2.730149 -2.584296 -3.489705
1 2.066552 -2.612324 -1.838526
1 0.990729 -2.371117 -3.233852
6 1.965662 0.038786 -4.054498
1 2.117050 1.121206 -3.971042
1 2.647964 -0.348936 -4.823714
1 0.937032 -0.127716 -4.396399
6 3.655796 -0.402425 -2.278633
1 3.833298 0.657447 -2.058851
1 3.867083 -0.976334 -1.375153
1 4.355859 -0.718235 -3.066001
8 2.450749 -1.687140 0.579023
6 2.420807 -0.520698 1.183208
6 3.522235 0.470404 0.918093
6 3.342384 1.854615 0.966740
6 4.820550 -0.022412 0.745893
6 4.419920 2.722196 0.809975
1 2.335843 2.249571 1.097094
6 5.900525 0.839097 0.592452
1 4.957365 -1.100689 0.710060
6 5.704466 2.218598 0.616777
1 4.250945 3.797360 0.825932
1 6.899562 0.433423 0.445528
1 6.545374 2.896142 0.484305
1 2.201212 -0.543383 2.265886
1 1.099311 0.635994 0.930410

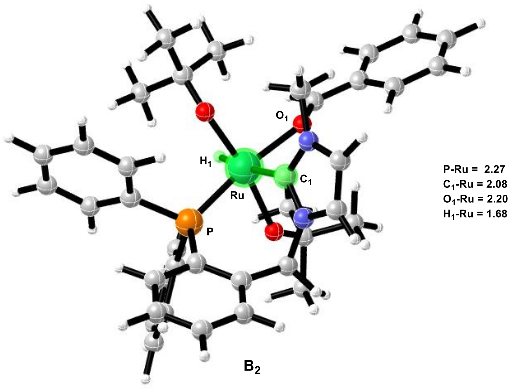
B_2

Imaginary frequencies: 0

Thermal correction to Enthalpy = 0.799571

Thermal correction to Gibbs Free Energy = 0.675999

Total free energy in solution: -with all non electrostatic terms (a.u.) = -2247.594564



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15 -1.834637 -0.054158 -0.154812
7 1.512980 0.505795 2.741073
7 0.244684 -1.210809 2.607590
6 0.676763 -0.143939 1.869651
6 -2.719289 -0.719433 1.363143
6 -4.037585 -0.306894 1.615597
1 -4.508376 0.397149 0.934741
6 1.595493 -0.141909 3.961323
1 2.219408 0.219669 4.765048
6 -3.661572 1.722324 -1.457391
1 -3.791104 0.959359 -2.222037
6 -2.813452 1.482571 -0.374763
6 -2.140573 -1.650871 2.253099
6 -4.195177 3.912703 -0.588333
1 -4.732236 4.855141 -0.671402
6 -3.610008 -2.029918 -1.266798

1 -4.101256 -2.086804 -0.298418
6 -3.347355 3.681509 0.494718
1 -3.213081 4.447766 1.255095
6 -2.650351 2.483627 0.595461
1 -1.954346 2.318048 1.412494
6 -0.736081 -2.159839 2.088624
1 -0.613531 -3.093525 2.650130
1 -0.461787 -2.333380 1.030773
6 -2.886535 -2.112275 3.343604
1 -2.419832 -2.827651 4.020819
6 0.780119 -1.224056 3.881204
1 0.541286 -1.991991 4.602329
6 -4.344427 2.934103 -1.566834
1 -5.000321 3.107863 -2.417227
6 -4.071021 -2.829821 -2.313017
1 -4.914227 -3.497478 -2.147935
6 -4.768775 -0.780119 2.699830
1 -5.789980 -0.438444 2.853013
6 -2.520603 -1.174823 -1.452997
6 -1.898010 -1.140540 -2.707288
1 -1.023459 -0.499312 -2.821249
6 -4.189186 -1.689952 3.576845
1 -4.744901 -2.068800 4.431714
6 -3.456484 -2.776611 -3.559512
1 -3.816264 -3.402094 -4.373943
6 -2.369109 -1.924855 -3.753419
1 -1.869320 -1.888436 -4.719395
6 2.222995 1.726618 2.413161
1 3.267107 1.518670 2.155999
1 1.706952 2.178135 1.557061
1 2.190214 2.405517 3.271822
6 0.504384 3.326040 -0.739653
8 0.207181 2.305719 0.166421
6 1.128678 -2.740769 -1.270056
8 0.251511 -1.896089 -0.602195
6 0.424643 4.636718 0.056210
1 1.166389 4.638703 0.864143
1 0.603647 5.516476 -0.576564
1 -0.569009 4.732004 0.508143
6 -0.496477 3.386482 -1.901977
1 -0.184265 4.115836 -2.662208
1 -0.558228 2.397087 -2.367975
1 -1.493401 3.671119 -1.551543
6 1.910585 3.178491 -1.332890
1 2.657745 3.053551 -0.539694
1 1.932962 2.288568 -1.967792
1 2.190096 4.050321 -1.940635
6 2.332366 -3.066219 -0.370904
1 3.037101 -3.763276 -0.845859
1 2.871320 -2.151724 -0.109475
1 1.979961 -3.521240 0.563635
6 0.355901 -4.037900 -1.556799
1 -0.522813 -3.818008 -2.173524
1 0.971966 -4.785181 -2.075868
1 0.002610 -4.478878 -0.616688
6 1.614782 -2.158685 -2.600651
1 0.764298 -1.995392 -3.271700
1 2.090051 -1.187814 -2.442097
1 2.327364 -2.828096 -3.101860
8 2.530953 0.251892 -0.123307
1 0.458703 0.496765 -1.879195
6 3.464344 0.374132 -0.956521
6 4.840659 0.147707 -0.606629
6 5.862485 0.360035 -1.556395
6 5.209616 -0.292457 0.685986
6 7.192436 0.151259 -1.228555
1 5.585800 0.693924 -2.555400
6 6.540370 -0.500805 1.003379
1 4.418176 -0.476376 1.409682
6 7.545031 -0.279008 0.053922
1 7.965616 0.321880 -1.974824
1 6.808117 -0.844638 2.000708
1 8.588499 -0.444545 0.309878
1 3.243828 0.655284 -2.000137

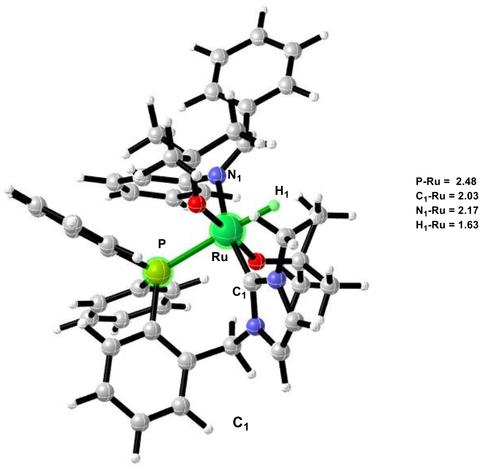
C_1

Imaginary frequencies: 0

Thermal correction to Enthalpy = 0.898504

Thermal correction to Gibbs Free Energy = 0.767178

Total free energy in solution: -with all non electrostatic terms (a.u.) = -2458.798279



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6 -1.416509 -2.425694 -0.332829
6 -3.261876 0.512732 -0.195034
6 -4.265875 1.185608 0.513509
1 -3.993515 1.795042 1.371338
6 -2.671186 -4.329706 -0.473726
1 -2.969511 -5.333701 -0.213428
6 -1.189811 2.764604 2.242489
1 -0.777614 3.439365 1.497725
6 -1.609758 1.486242 1.857711
6 -3.645707 -0.264443 -1.306174
6 -1.821372 2.336797 4.533755
1 -1.908459 2.666074 5.566777
6 -0.659922 2.044523 -2.170177
1 -0.142217 1.096544 -2.341707
6 -2.236273 1.058200 4.165652
1 -2.641744 0.381099 4.914477
6 -2.113646 0.625794 2.849413
1 -2.387580 -0.389905 2.580393
6 -2.645097 -1.099897 -2.052752
1 -3.046072 -1.391554 -3.031309
1 -1.664574 -0.629356 -2.215267
6 -4.992006 -0.335120 -1.672727
1 -5.264887 -0.942258 -2.535917
6 -3.153155 -3.464401 -1.399135
1 -3.967421 -3.550623 -2.102578
6 -1.286287 3.184998 3.568194
1 -0.952900 4.184510 3.840238
6 -0.661987 3.044369 -3.143282
1 -0.132021 2.875476 -4.079737
6 -5.604753 1.103957 0.142134
1 -6.356266 1.643809 0.714162
6 -1.334121 2.239735 -0.958852
6 -2.026974 3.442575 -0.757337
1 -2.601560 3.587898 0.155803
6 -5.974800 0.345077 -0.962874
1 -7.016675 0.281622 -1.268110
6 -1.319208 4.248676 -2.918767
1 -1.310228 5.030428 -3.675909
6 -2.003942 4.445904 -1.719207
1 -2.536519 5.378270 -1.541396
6 -0.796634 -4.287519 1.184344
1 0.107819 -4.714823 0.736166
1 -0.511504 -3.482535 1.869786
1 -1.363214 -5.071016 1.696585
6 0.645714 -1.555707 3.218610
8 -0.270510 -1.476034 2.176957
6 3.167095 -0.732647 0.214591
6 0.940476 -1.722187 -2.997239
8 0.355975 -0.862098 -2.078571
1 1.034588 -2.509090 0.022230
6 -0.144585 -1.973773 4.470794
1 -0.646242 -2.932978 4.294005
1 0.499852 -2.080531 5.354184
1 -0.913360 -1.227125 4.693672
6 1.319805 -0.202389 3.504180
1 1.938545 -0.239372 4.411717
1 1.967348 0.083305 2.670743
1 0.560854 0.578079 3.639221
6 1.746584 -2.604989 2.984782
1 1.323813 -3.615593 2.942478
1 2.246341 -2.419509 2.031344
1 2.498097 -2.592457 3.785975
6 0.168866 -3.043941 -3.138293
1 0.627801 -3.711098 -3.881050
1 0.151243 -3.561035 -2.171766
1 -0.868065 -2.859756 -3.442449
6 0.914403 -0.980865 -4.344205
1 1.468704 -0.037671 -4.257358
1 1.353885 -1.567652 -5.162250
1 -0.119957 -0.731053 -4.611784
6 2.395123 -2.073619 -2.650451
1 3.008127 -1.170002 -2.553847

1 2.419609 -2.599901 -1.690711
1 2.854258 -2.714812 -3.416087
1 3.073181 -1.814452 0.297607
7 2.013303 -0.106310 0.192129
6 2.021449 1.264996 -0.158213
6 1.620936 2.247507 0.750716
6 2.448294 1.646253 -1.437607
6 1.679907 3.591454 0.391608
1 1.281244 1.945603 1.737571
6 2.493828 2.988697 -1.788347
1 2.723630 0.866938 -2.142111
6 2.121441 3.972655 -0.873395
1 1.376791 4.347167 1.114616
1 2.812943 3.269139 -2.790192
1 2.153813 5.023094 -1.150835
6 4.533668 -0.250105 0.149939
6 5.523880 -1.218674 -0.132856
6 4.977596 1.069442 0.403024
6 6.869123 -0.892142 -0.194711
1 5.202239 -2.242259 -0.319051
6 6.327006 1.386034 0.350888
1 4.263670 1.844125 0.659638
6 7.285155 0.418799 0.043178
1 7.600231 -1.663621 -0.426955
1 6.637080 2.408127 0.557905
1 8.339140 0.681021 -0.001439

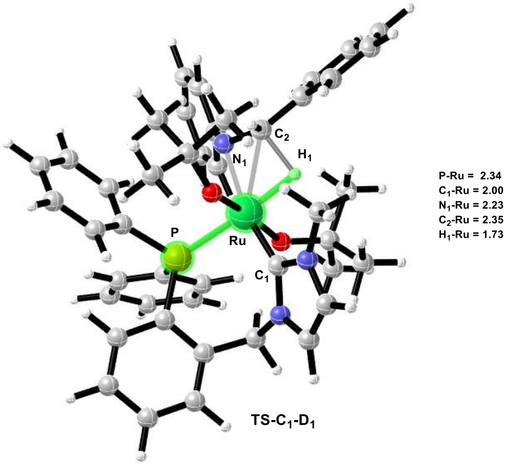
TS-C$_1$-D$_1$

Imaginary frequencies: -510.62

Thermal correction to Enthalpy = 0.897149

Thermal correction to Gibbs Free Energy = 0.767396

Total free energy in solution: -with all non electrostatic terms (a.u.) = -2458.764758



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7 1.441289 -2.797984 1.428715
6 0.369079 -2.493140 0.621709
6 3.329210 -0.511889 0.051404
6 4.464165 -0.195860 -0.705300
1 4.393347 0.560696 -1.481634
6 0.579408 -4.750236 0.929313
1 0.316928 -5.789986 0.807082
6 1.159064 2.376356 -1.992665
1 0.657000 2.857182 -1.154723
6 1.810650 1.148502 -1.799257
6 3.468220 -1.444061 1.099669
6 1.782343 2.377071 -4.325420
1 1.775749 2.854064 -5.302777
6 1.808360 1.864038 2.264392
1 1.091061 1.124325 2.619983
6 2.399363 1.141338 -4.152847
1 2.864898 0.638633 -4.997788
6 2.397269 0.524095 -2.904399
1 2.846632 -0.458369 -2.788288
6 2.314557 -1.790577 2.004804
1 2.695632 -2.189318 2.952753
1 1.668748 -0.933795 2.239385
6 4.703755 -2.058413 1.317962
1 4.792398 -2.775999 2.133596
6 1.587505 -4.160440 1.616208
1 2.391241 -4.576277 2.204932
6 1.146320 2.983655 -3.242765
1 0.631404 3.933156 -3.368894

6 2.262015 2.888862 3.092921
1 1.926563 2.924407 4.128023
6 5.689107 -0.815844 -0.479437
1 6.549159 -0.548403 -1.088957
6 2.209009 1.802322 0.924477
6 3.092912 2.780310 0.446497
1 3.430528 2.747519 -0.586943
6 5.811593 -1.762254 0.531902
1 6.764144 -2.252211 0.718940
6 3.123911 3.864960 2.603108
1 3.471833 4.668550 3.249001
6 3.538693 3.805538 1.274218
1 4.214961 4.560518 0.878703
6 -1.349564 -3.931407 -0.442154
1 -1.345169 -3.160933 -1.220515
1 -1.331819 -4.928765 -0.891505
1 -2.239908 -3.835895 0.193466
6 -0.667864 -1.499959 -3.312045
8 -0.190783 -1.651346 -2.020155
6 -2.509639 -0.122103 -0.704698
6 -1.187087 -0.539706 3.182001
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1 -1.999180 -1.266378 0.263786
6 0.415841 -2.045138 -4.266816
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1 0.088732 -2.049895 -5.316912
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6 -0.992132 -0.056218 -3.731875
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1 0.384375 -0.114728 4.625292
6 -2.646050 -0.130124 2.966394
1 -2.697988 0.932393 2.702343
1 -3.084832 -0.706349 2.146753
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1 -2.382376 -0.761471 -1.580105
7 -1.666125 0.933545 -0.682154
6 -1.898264 2.208014 -0.198169
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6 -1.201827 2.706655 0.919089
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1 -3.236119 2.734213 -1.803837
6 -1.292154 4.048435 1.271950
1 -0.628949 1.991667 1.504205
6 -2.088413 4.930570 0.541459
1 -3.422950 5.115109 -1.143263
1 -0.729999 4.402940 2.135507
1 -2.153459 5.980136 0.818412
6 -3.935670 -0.162957 -0.245792
6 -4.683212 -1.284683 -0.632392
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6 -6.017957 -1.424904 -0.276328
1 -4.185349 -2.061734 -1.212393
6 -5.915324 0.689201 0.864341
1 -4.019941 1.693768 0.846961
6 -6.643815 -0.430559 0.474379
1 -6.571854 -2.308825 -0.584398
1 -6.391195 1.467974 1.455792
1 -7.689891 -0.530738 0.755048

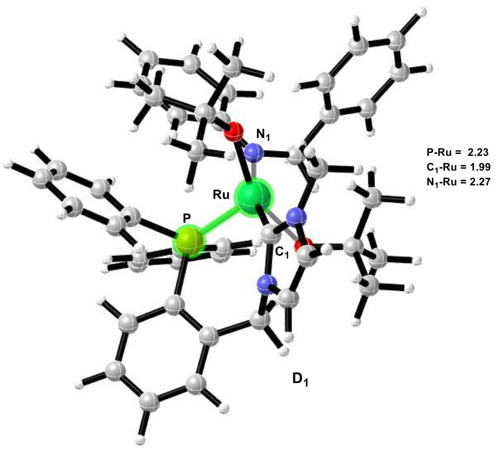
D_1

Imaginary frequencies: 0

Thermal correction to Enthalpy = 0.903924

Thermal correction to Gibbs Free Energy = 0.775035

Total free energy in solution: -with all non electrostatic terms (a.u.) = -2458.805108



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6 -3.236130 -0.378893 -0.927818
6 -4.351933 0.448433 -1.122654
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6 -1.160077 -4.184974 2.112559
1 -1.022088 -4.930279 2.880740
6 -2.074152 3.019645 0.627942
1 -1.410626 3.431262 -0.125617
6 -2.316231 1.641831 0.668856
6 -3.409021 -1.760532 -1.086585
6 -3.457046 3.361429 2.582200
1 -3.890563 4.026751 3.325032
6 -2.026075 2.447491 -2.463778
1 -2.827816 2.828462 -1.837366
6 -3.708178 1.991227 2.634330
1 -4.338502 1.577853 3.418398
6 -3.146791 1.146402 1.684878
1 -3.355987 0.078351 1.727024
6 -2.252839 -2.690210 -0.935073
1 -2.514075 -3.675865 -1.336485
1 -1.362626 -2.327380 -1.477598
6 -4.665312 -2.274497 -1.426555
1 -4.771693 -3.352774 -1.542502
6 -2.089724 -4.071137 1.137150
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1 -2.428492 4.935212 1.528953
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1 -6.435154 0.607424 -1.619345
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6 0.480722 -4.259714 -1.449544
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1 1.098669 -5.153082 -1.610047
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6 1.962225 -3.043066 -3.024779

1 1.186867 -3.040838 -3.798797
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6 5.187866 -0.295983 -1.624763
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6 6.407432 -0.639784 -1.048319
1 5.085762 -0.273687 -2.710541
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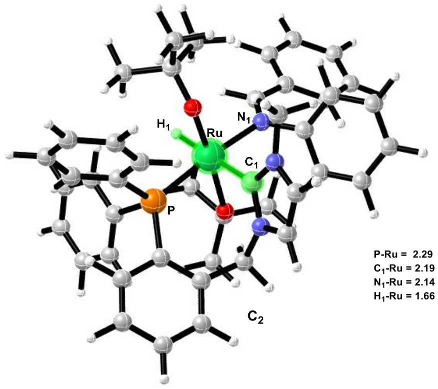
C_2

Imaginary frequencies: 0

Thermal correction to Enthalpy = 0.898124

Thermal correction to Gibbs Free Energy = 0.764997

Total free energy in solution: -with all non electrostatic terms (a.u.) = -2458.792656



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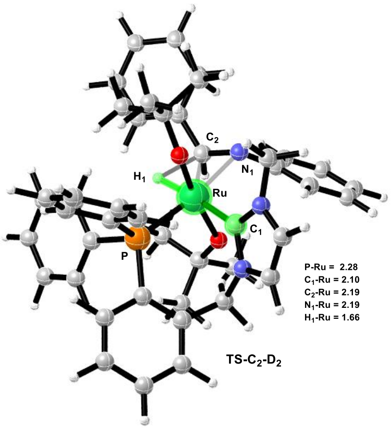
TS-C_2-D_2

Imaginary frequencies: -433.77

Thermal correction to Enthalpy = 0.896632

Thermal correction to Gibbs Free Energy = 0.768244

Total free energy in solution: -with all non electrostatic terms (a.u.) = -2458.784276



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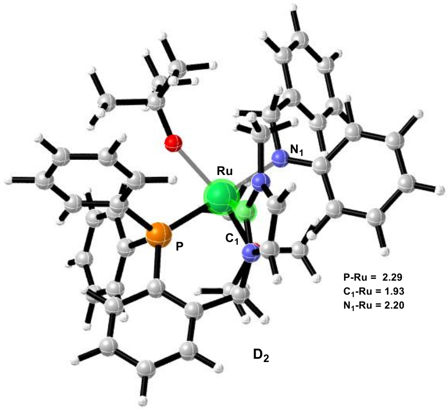
D2

Imaginary frequencies: 0

Thermal correction to Enthalpy = 0.902347

Thermal correction to Gibbs Free Energy = 0.769959

Total free energy in solution: -with all non electrostatic terms (a.u.) = -2458.81506



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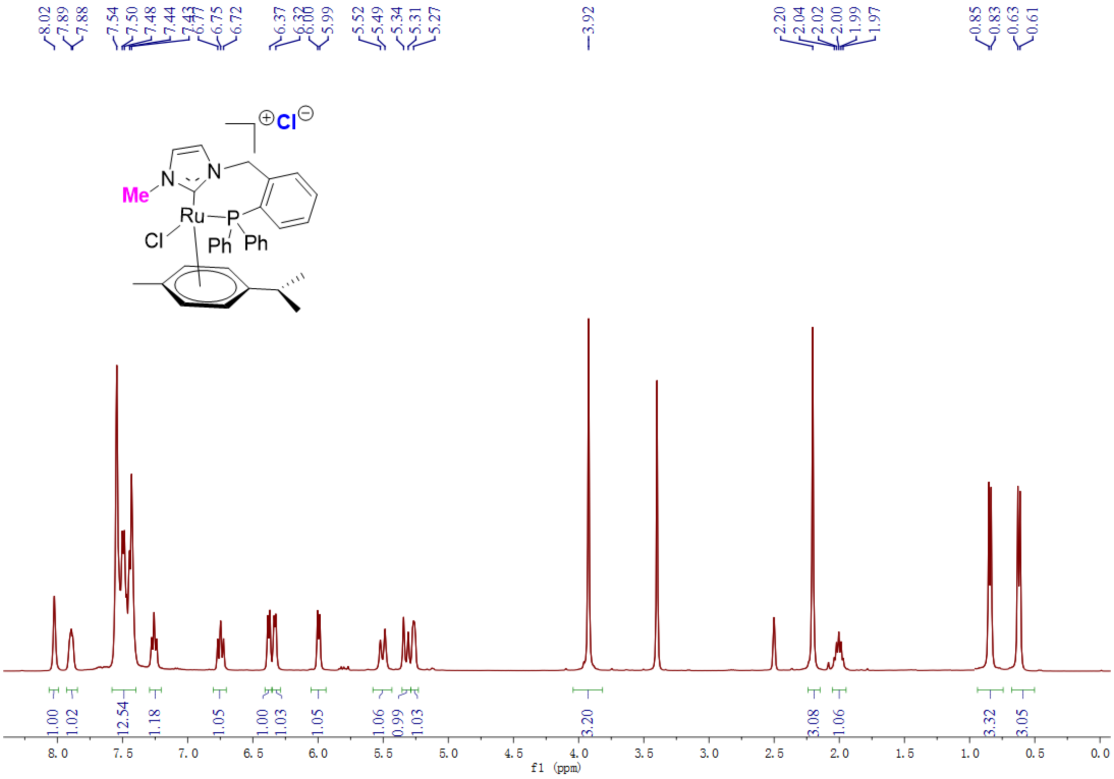
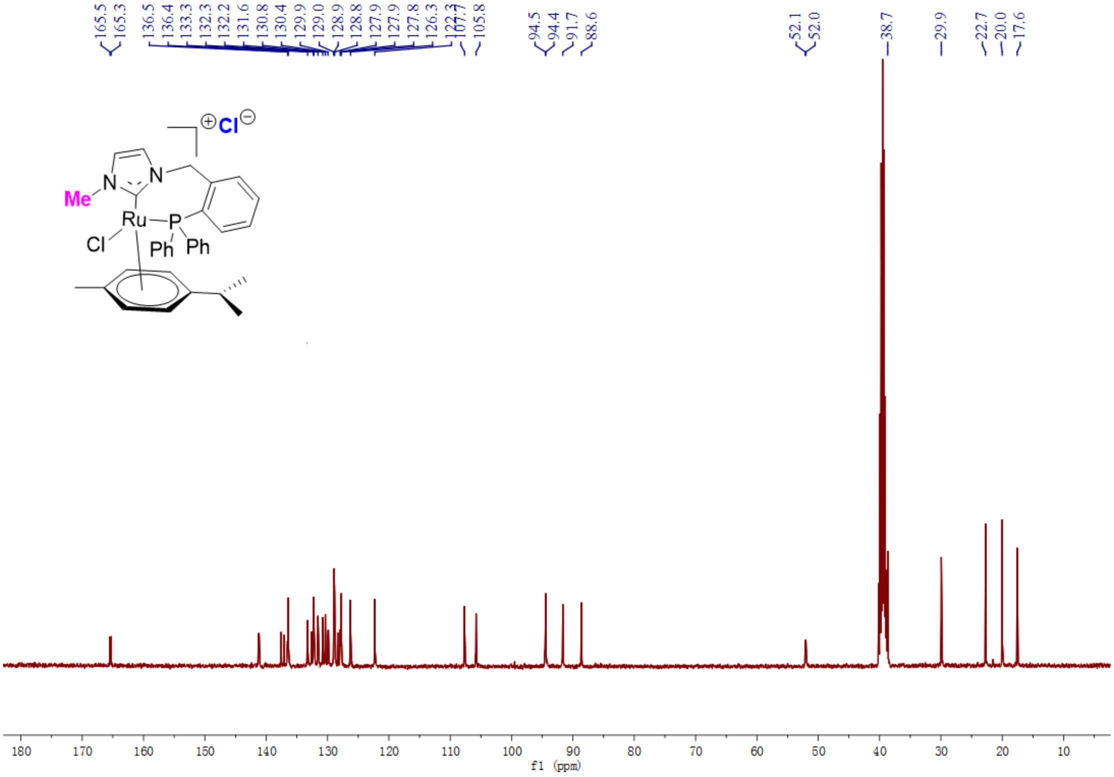
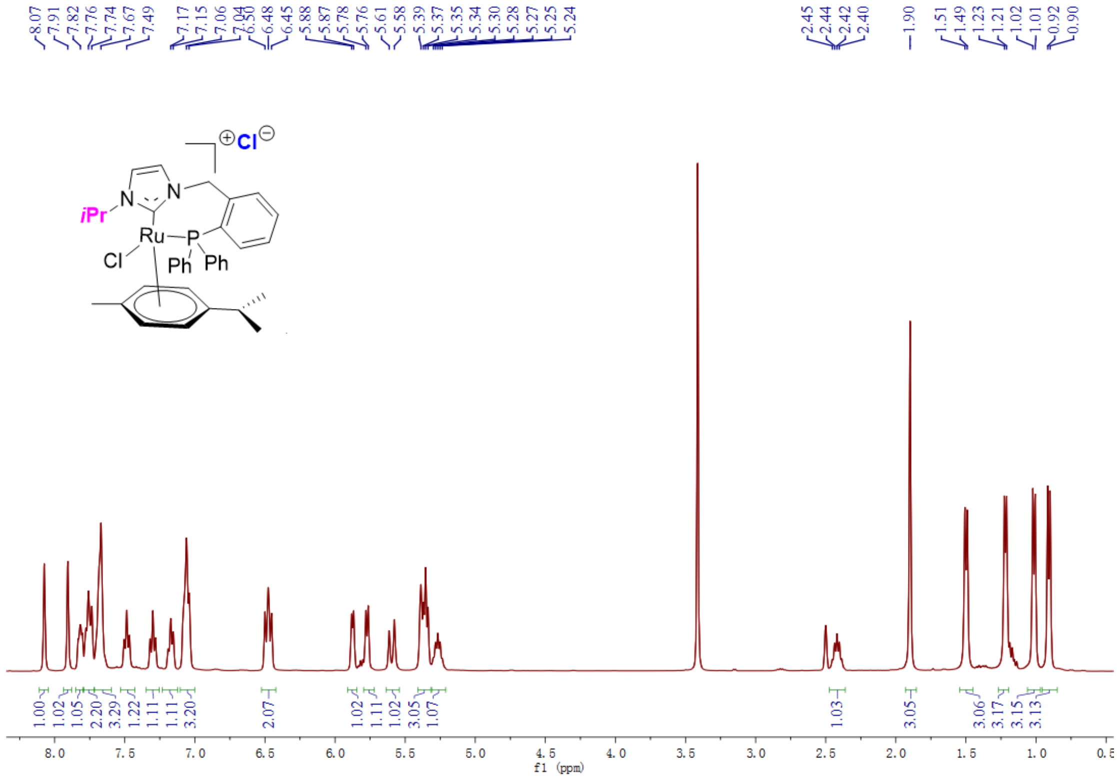
V Spectroscopic Data (NMR Spectrum)



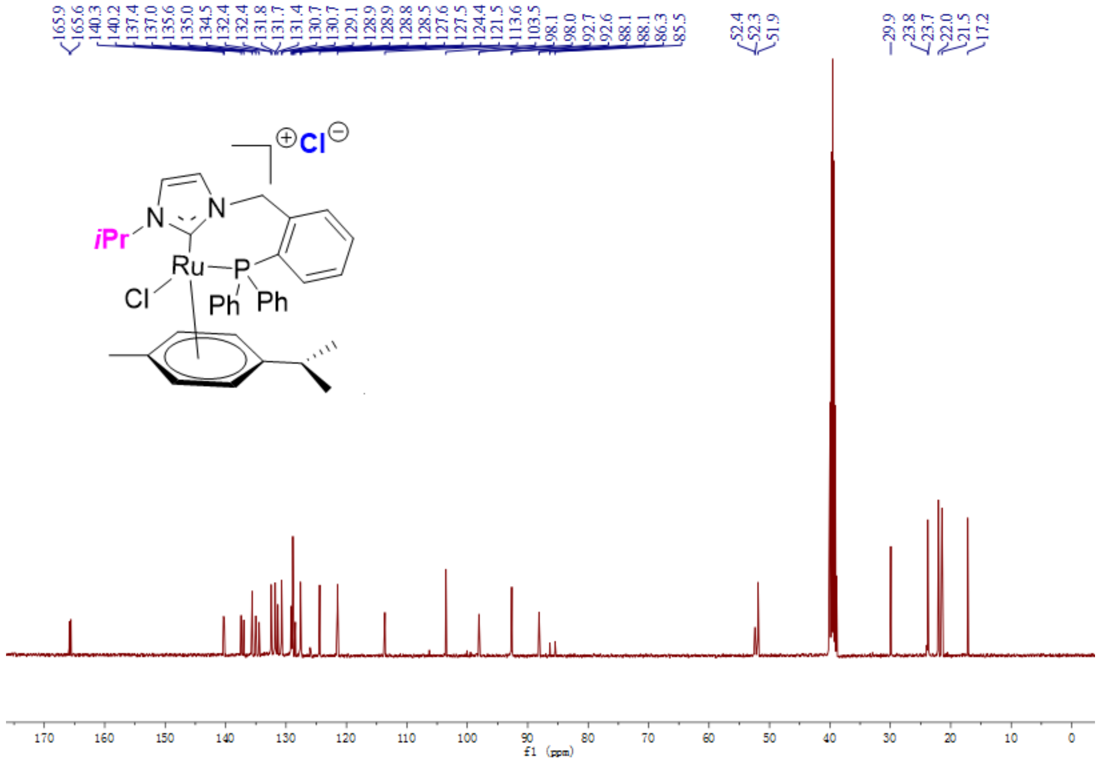
[1]H NMR (400 MHz, DMSO-d_6) spectrum of **6a**



[13]C NMR (100 MHz, DMSO-d_6) spectrum of **6a**



^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **6b**



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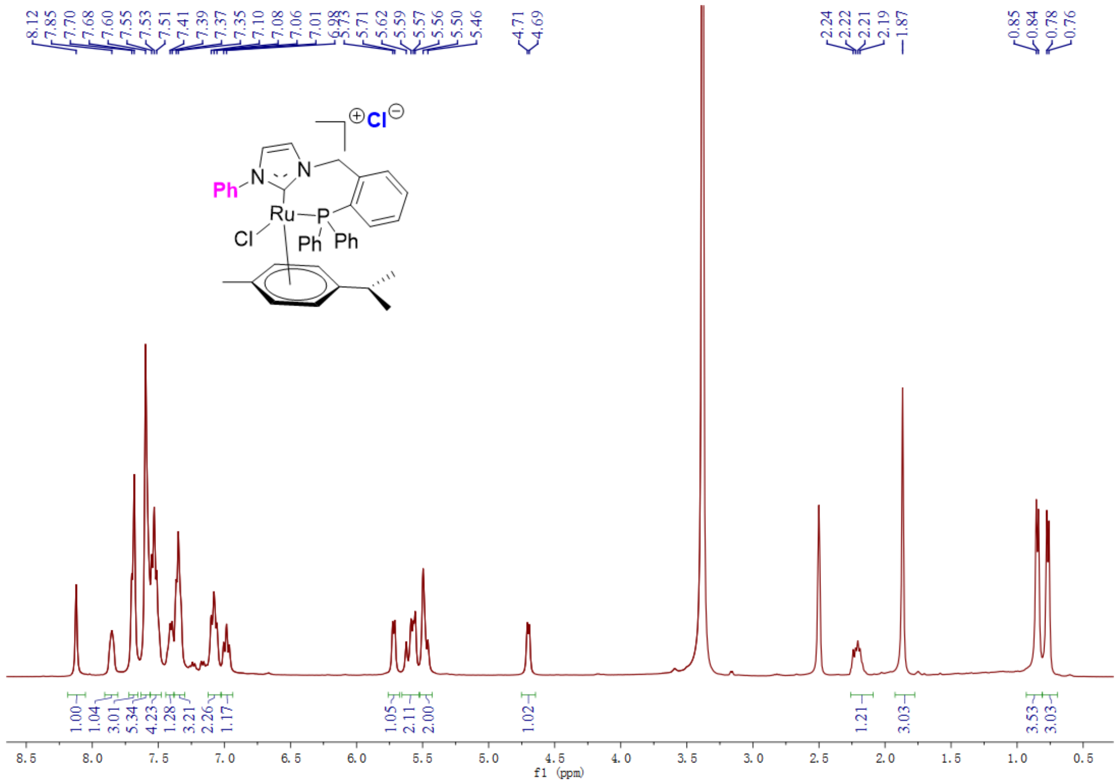

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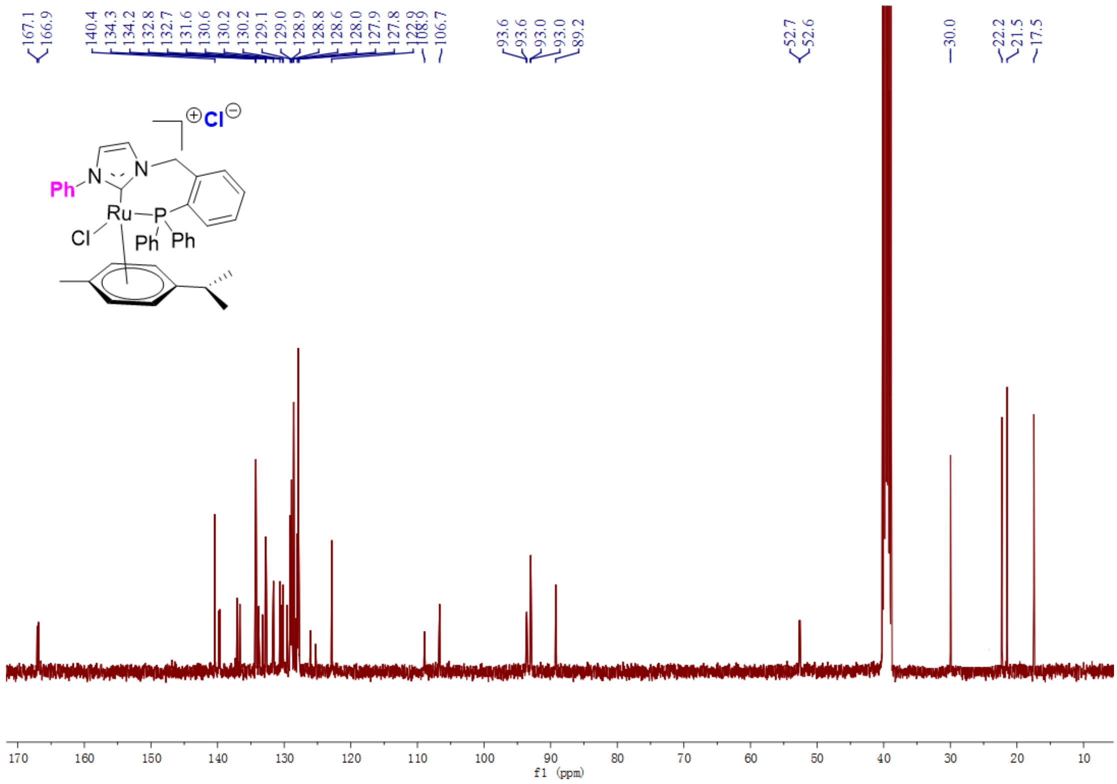

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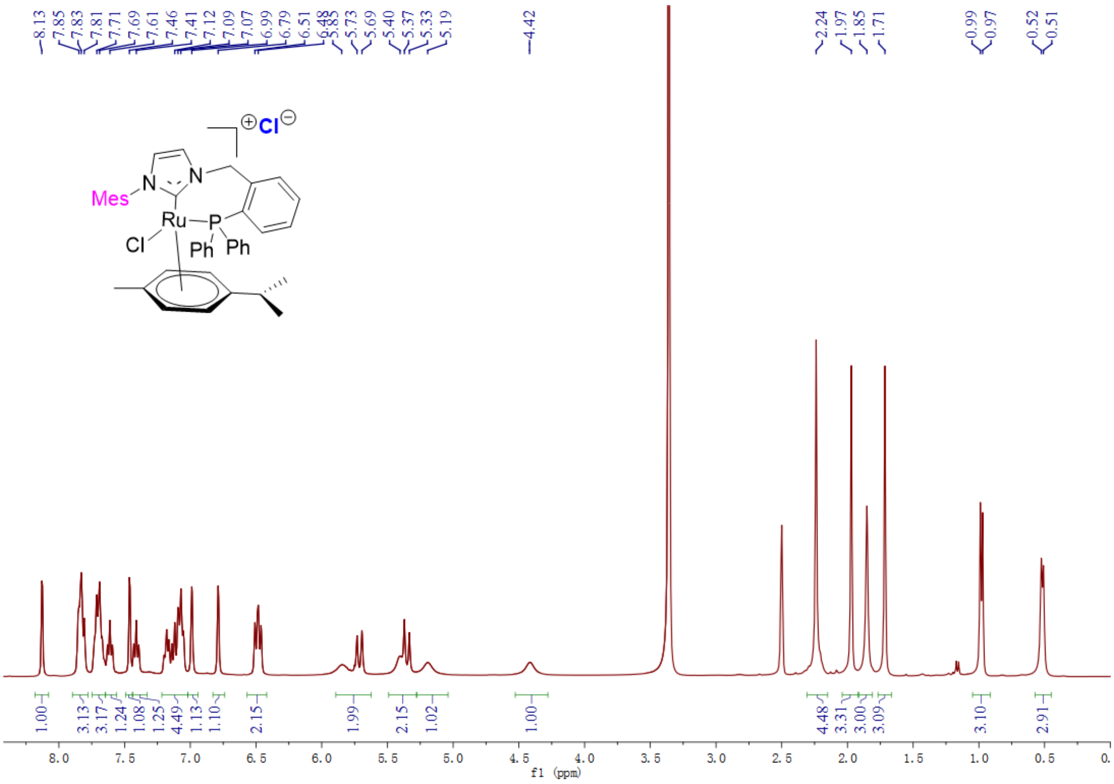

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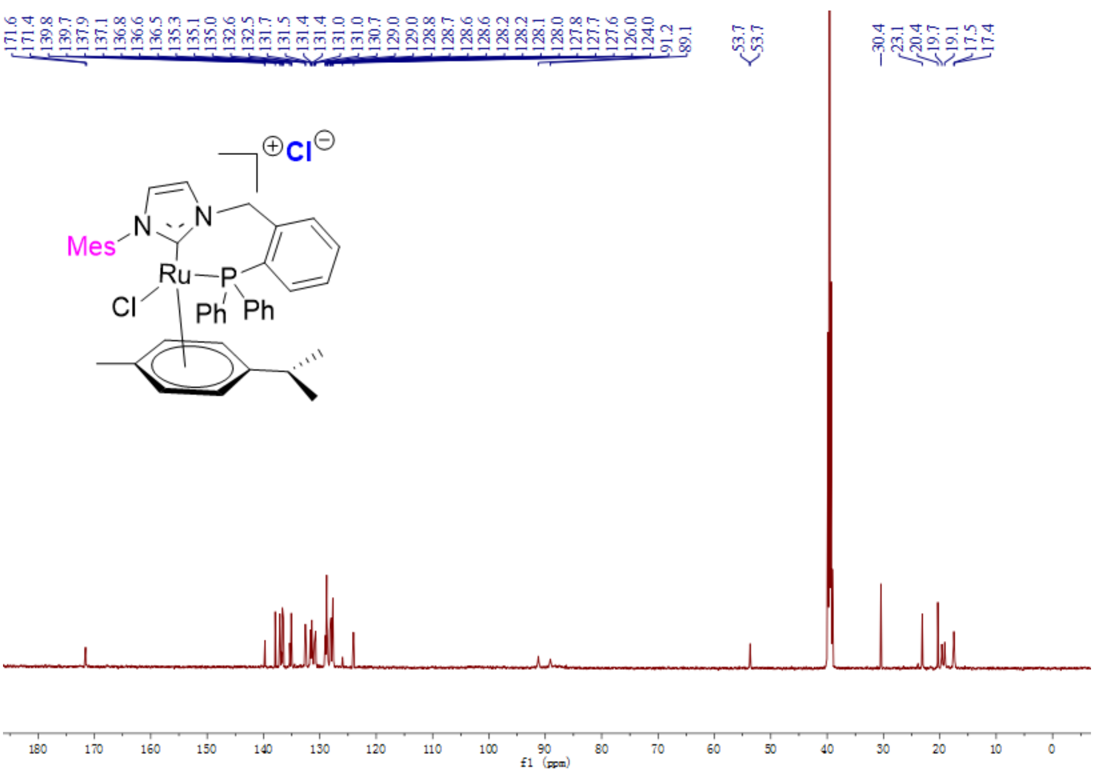
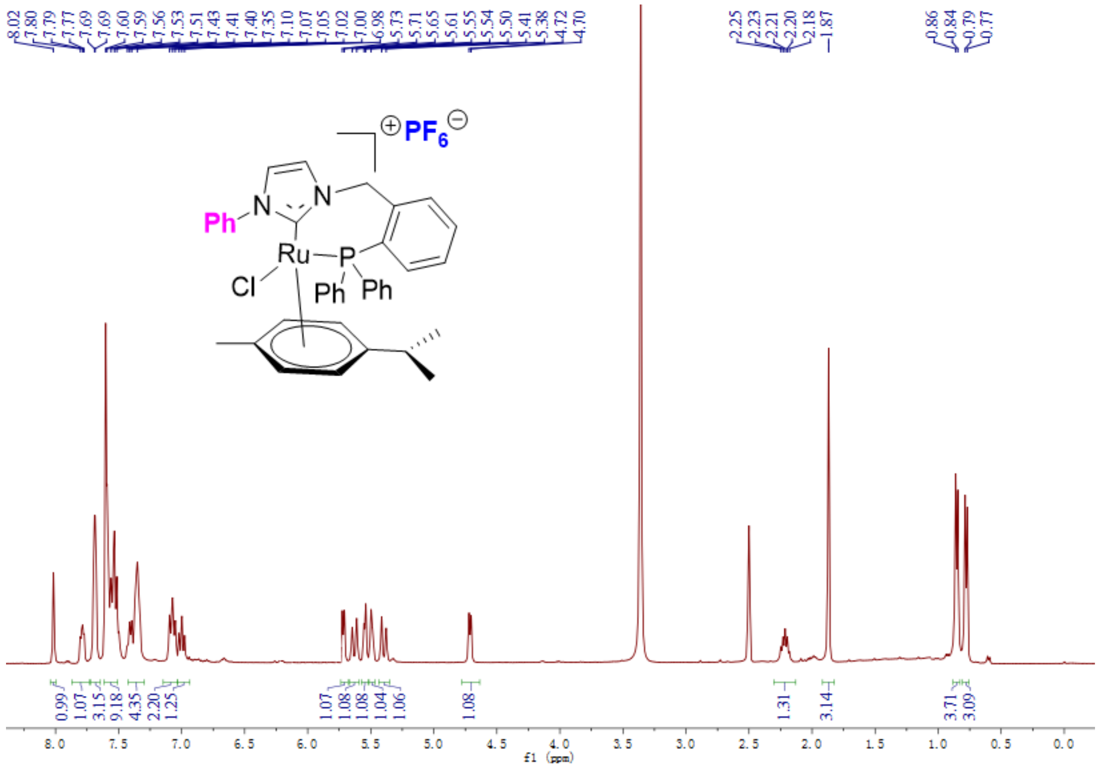


^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **6d**



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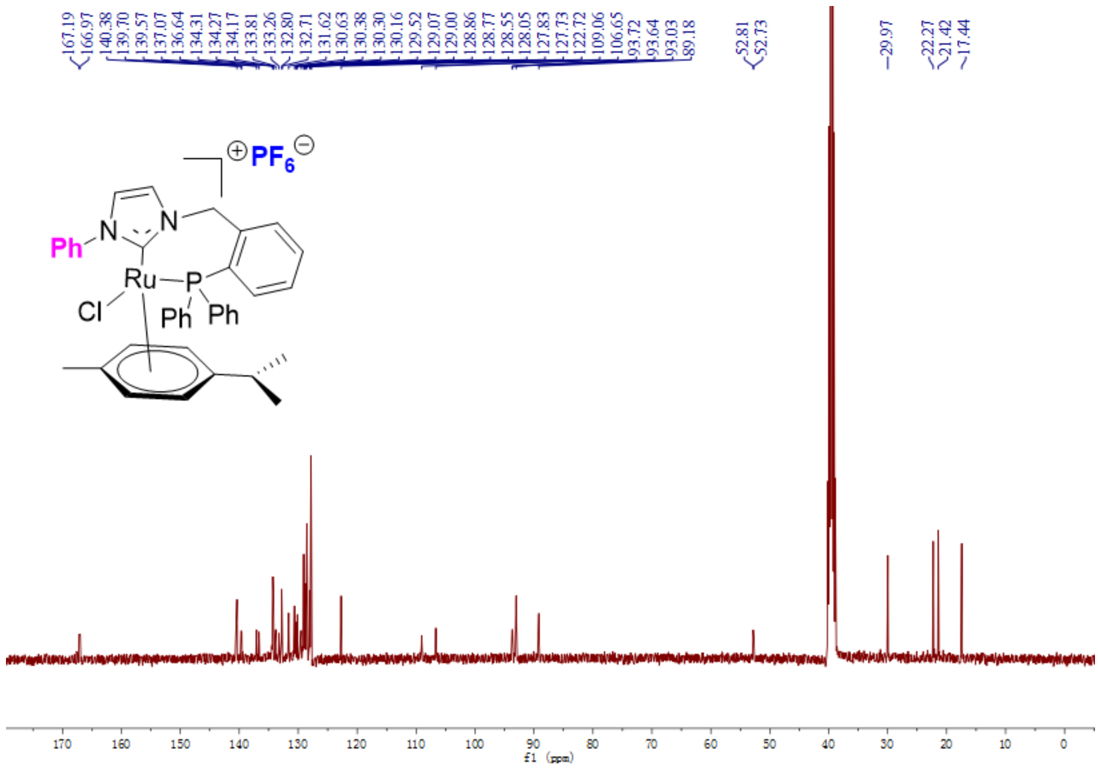

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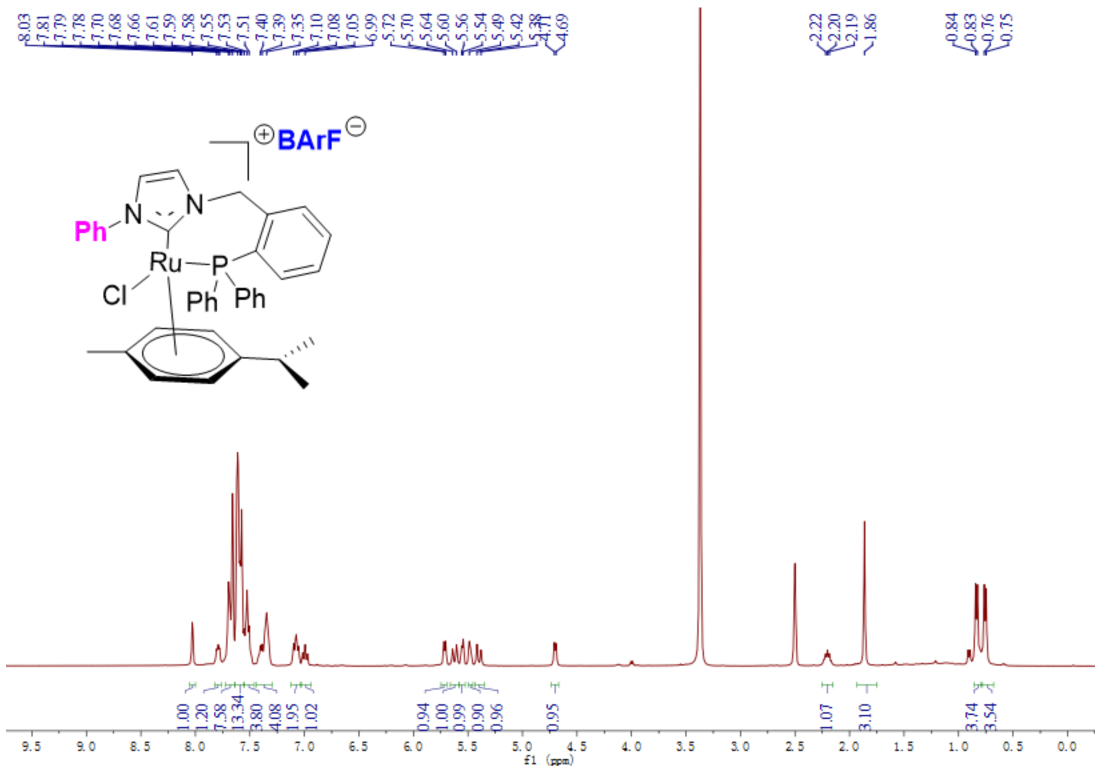

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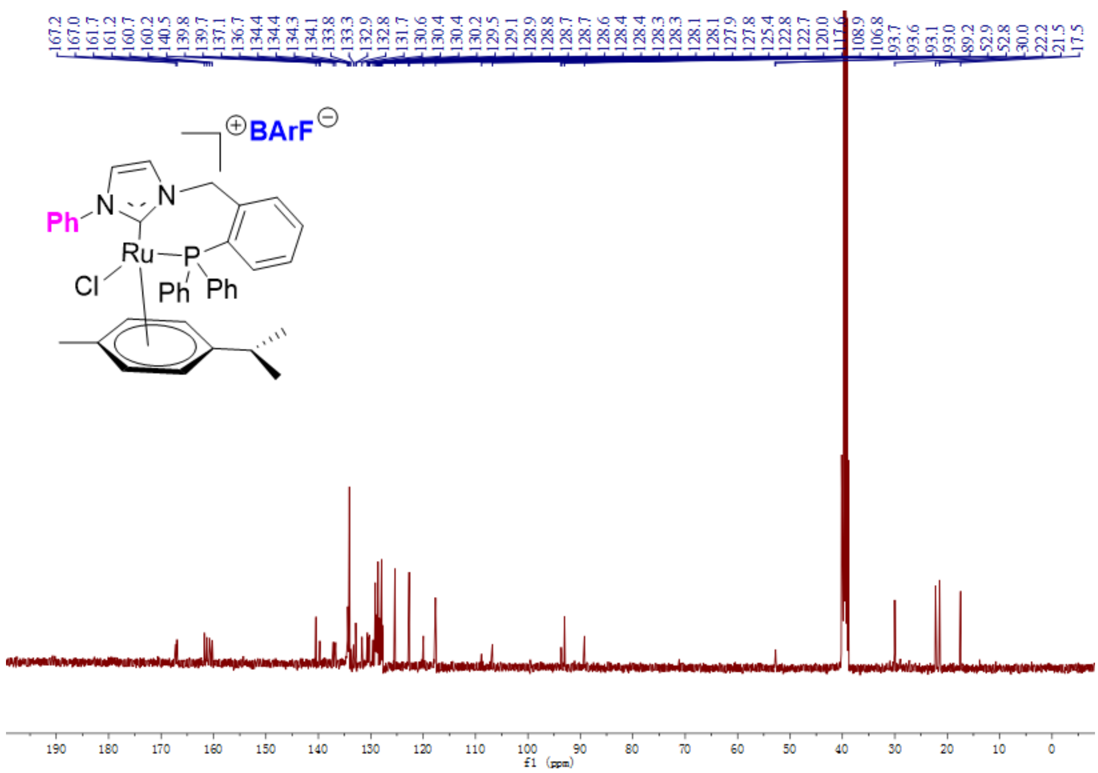

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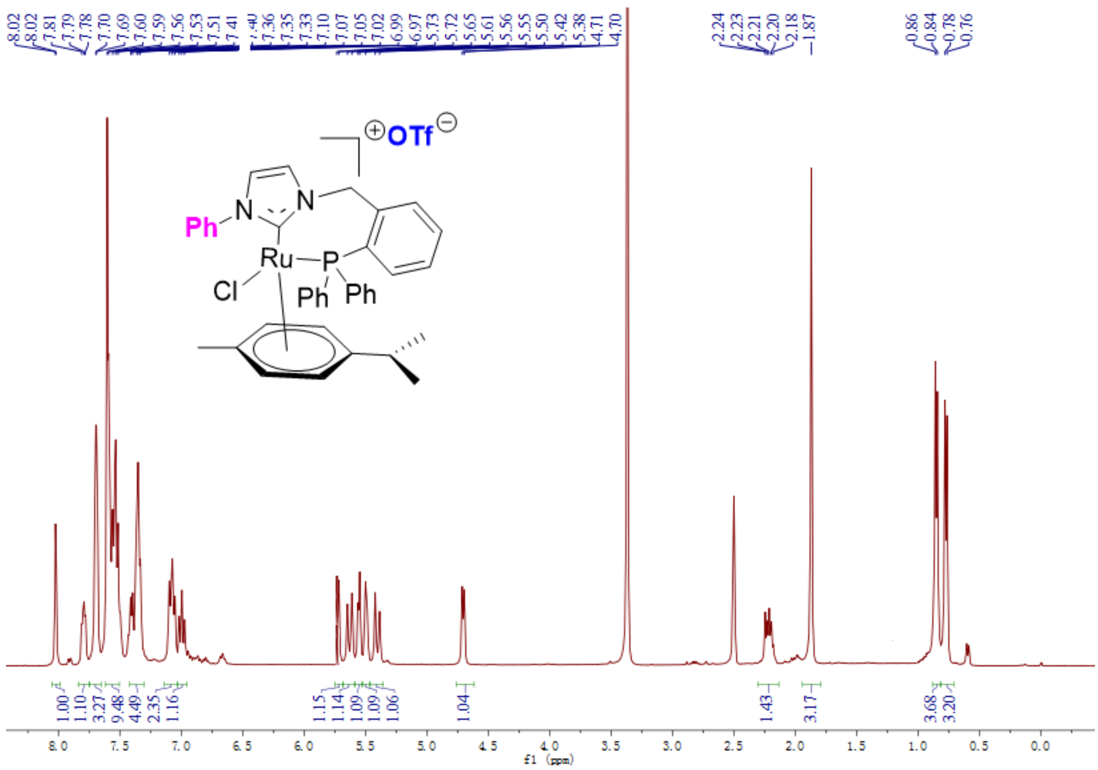

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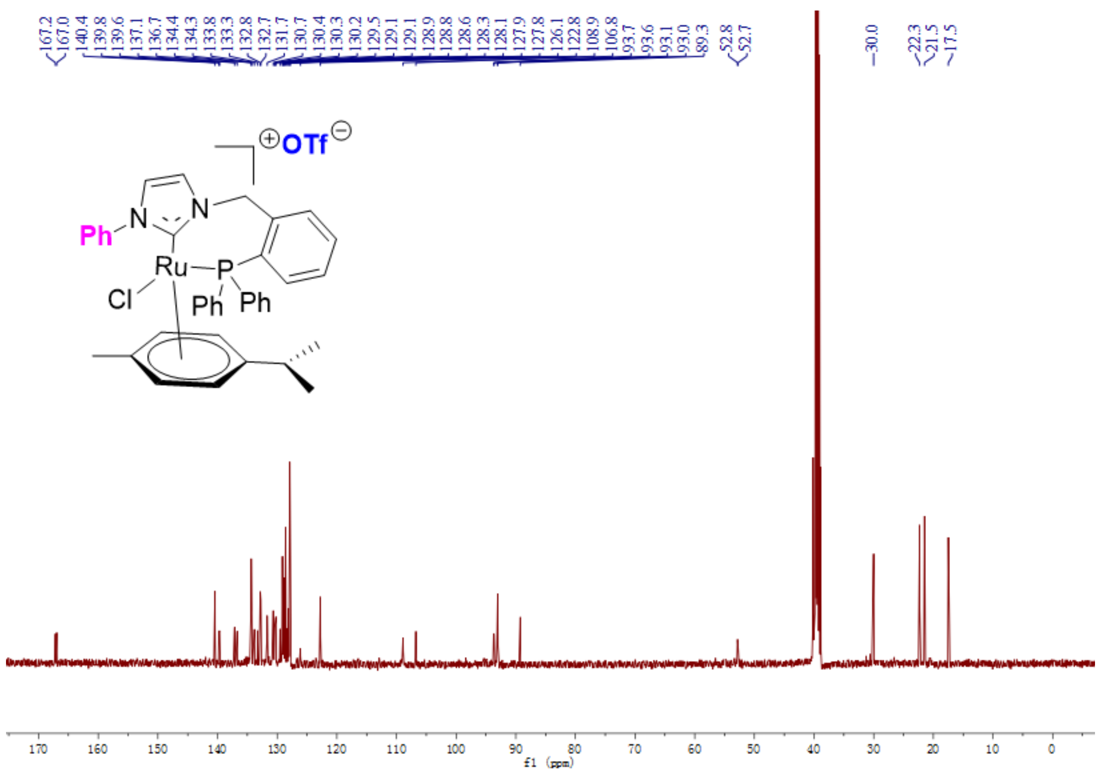

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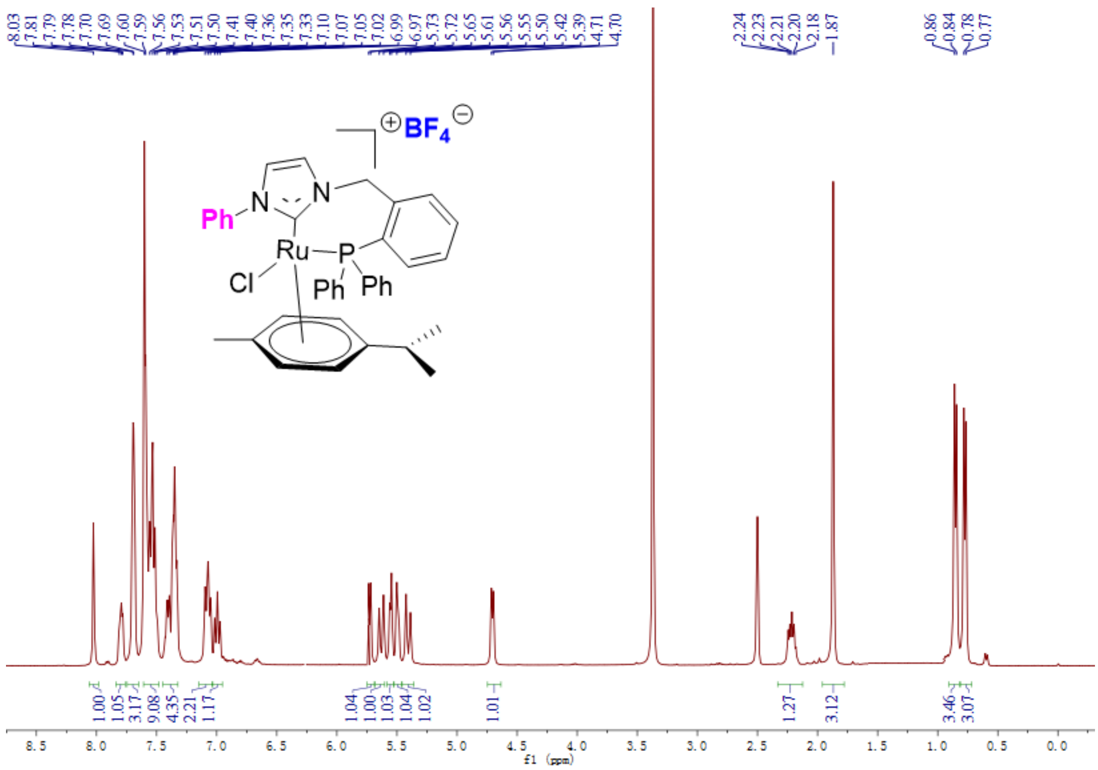

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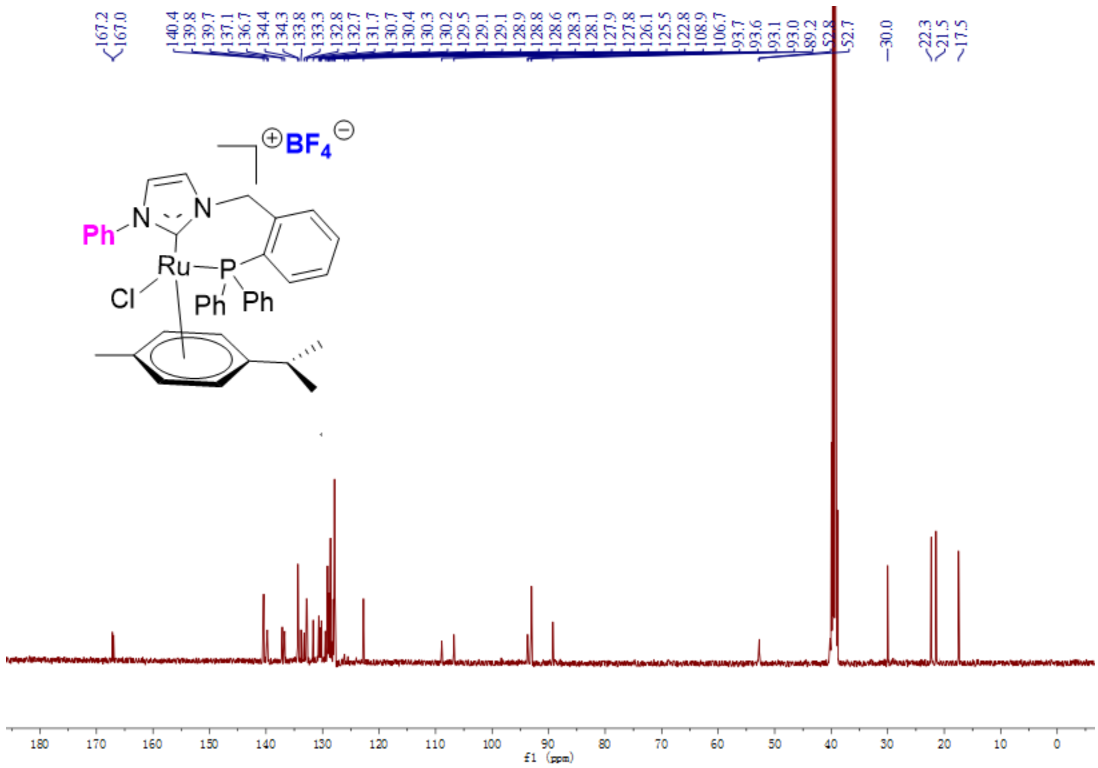

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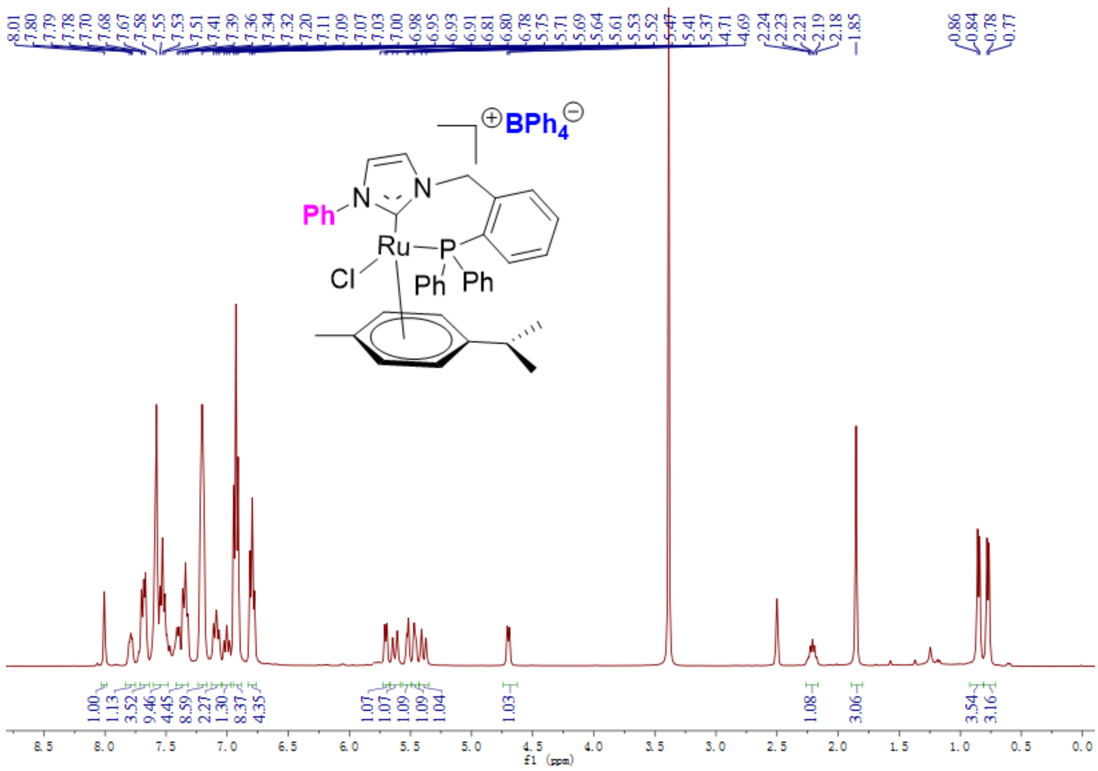

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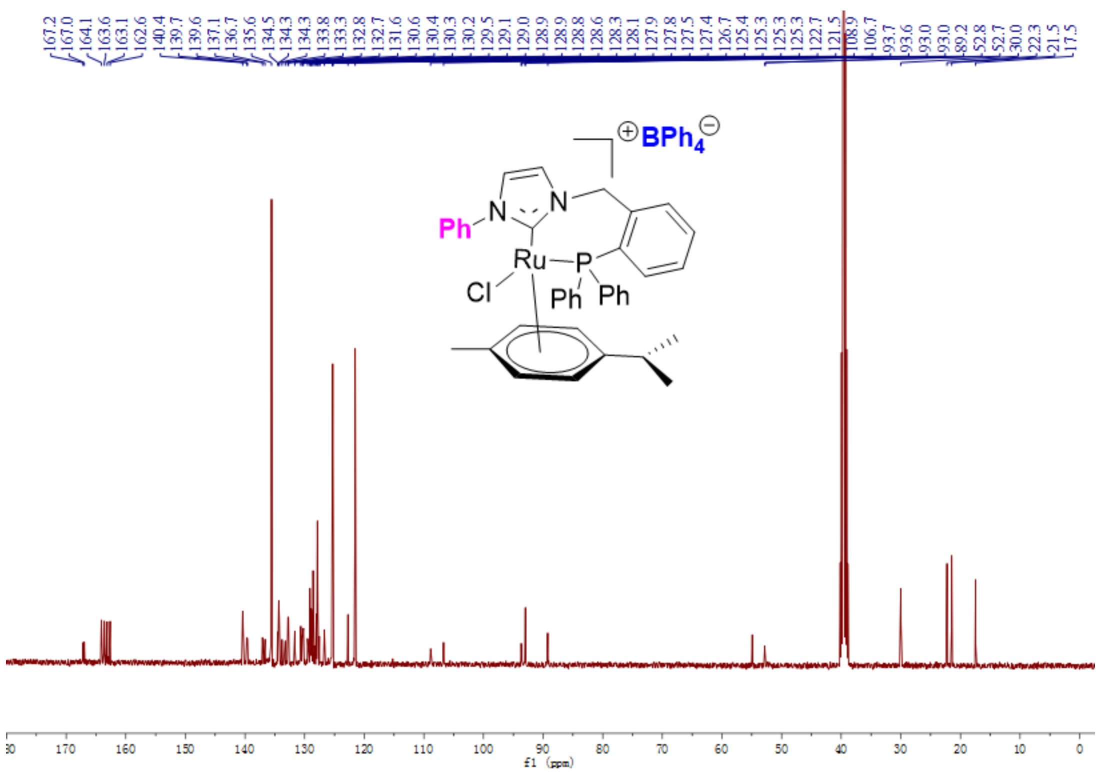
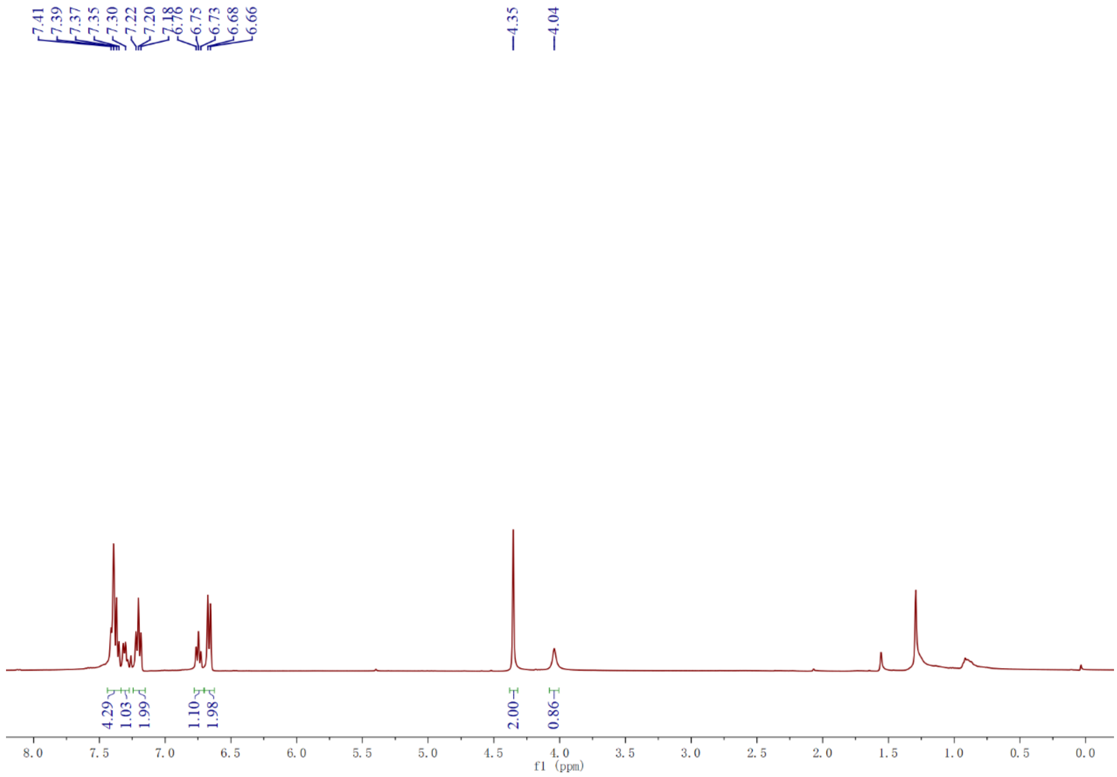
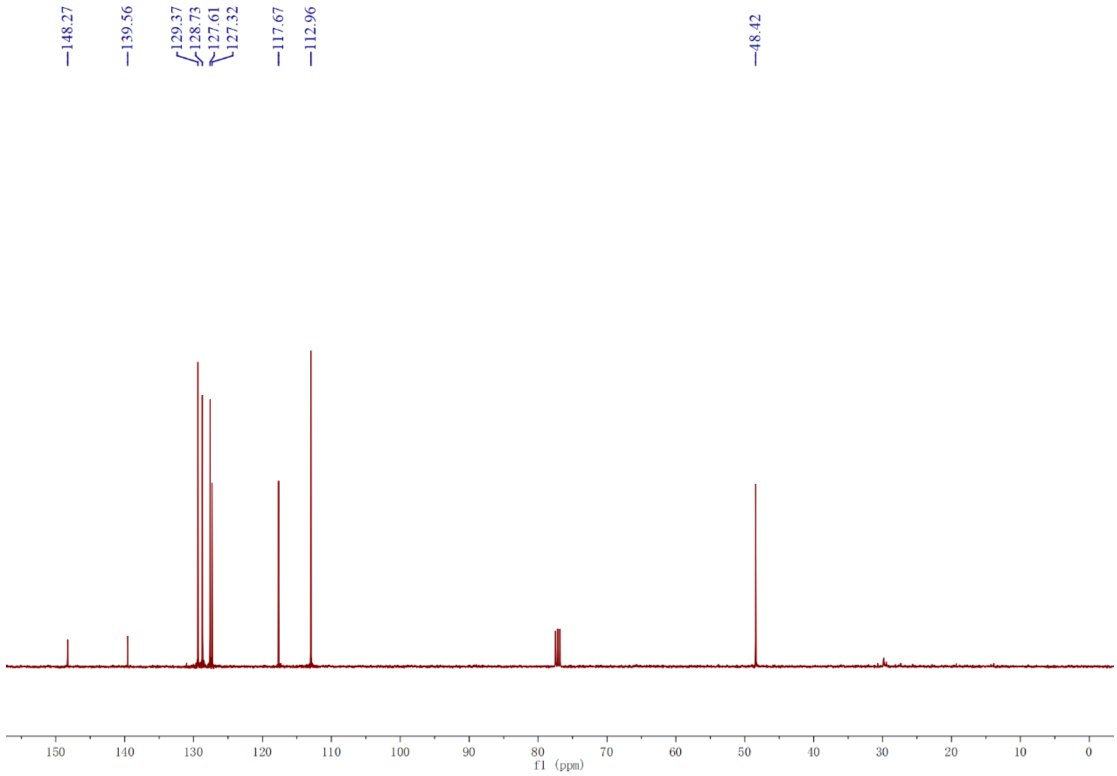


^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **6ce**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **9a**



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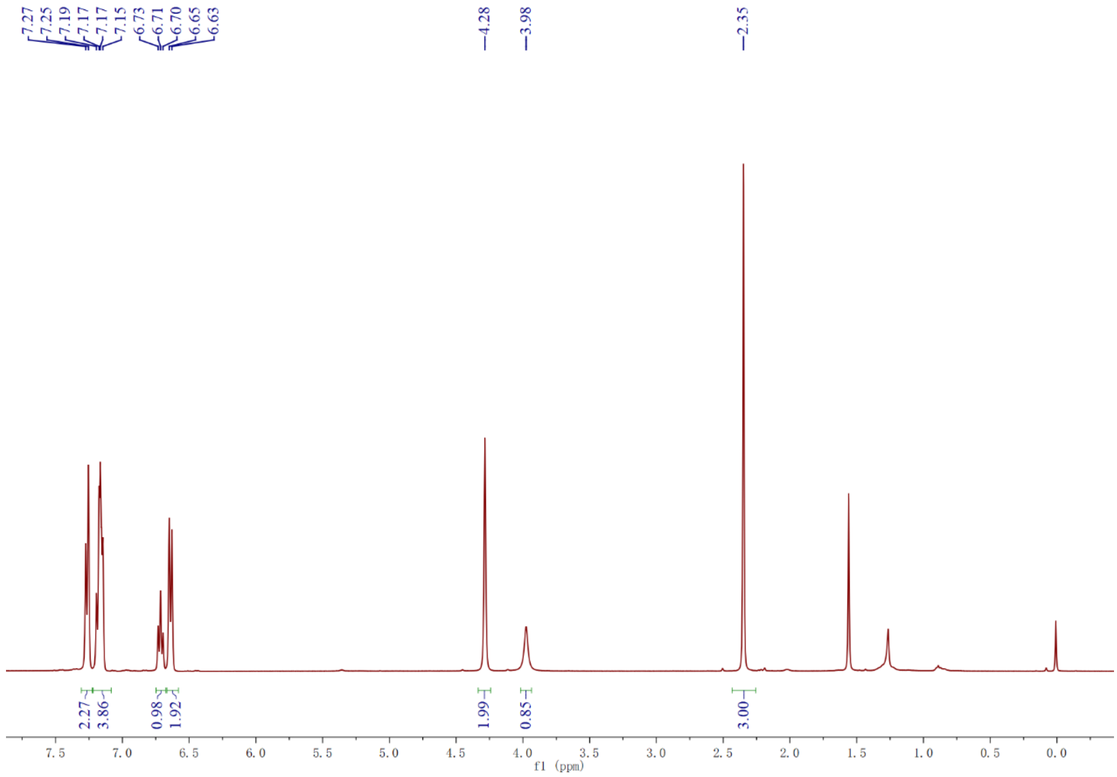

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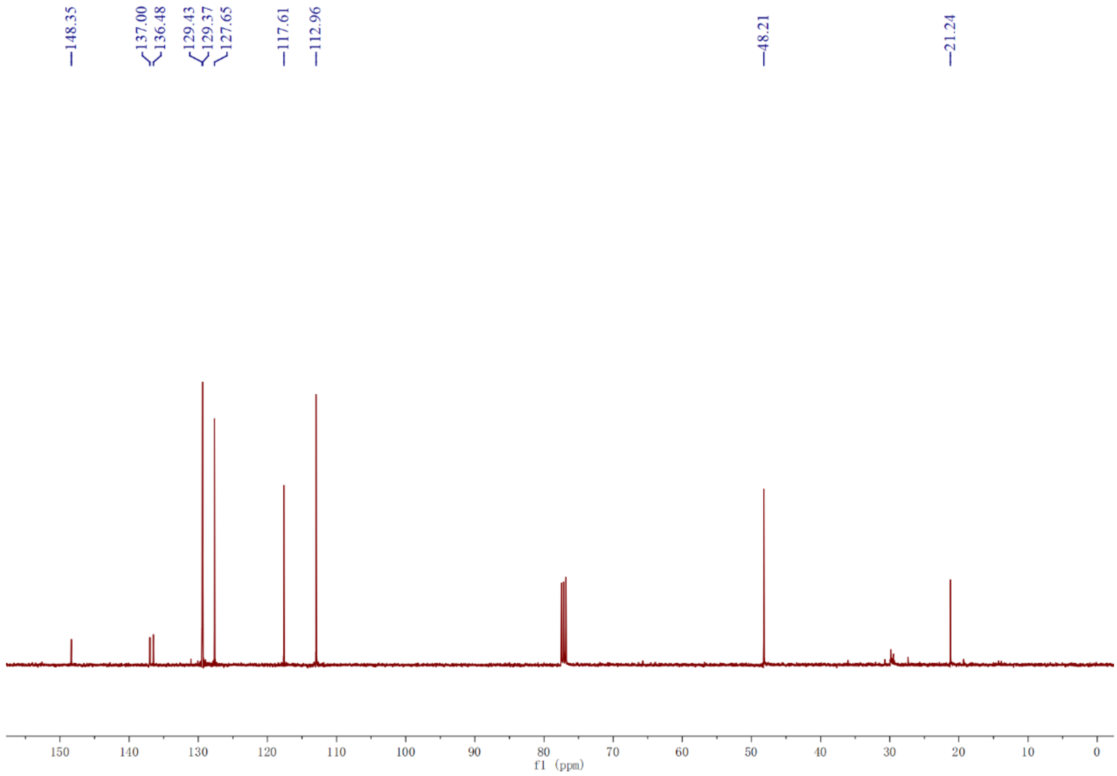

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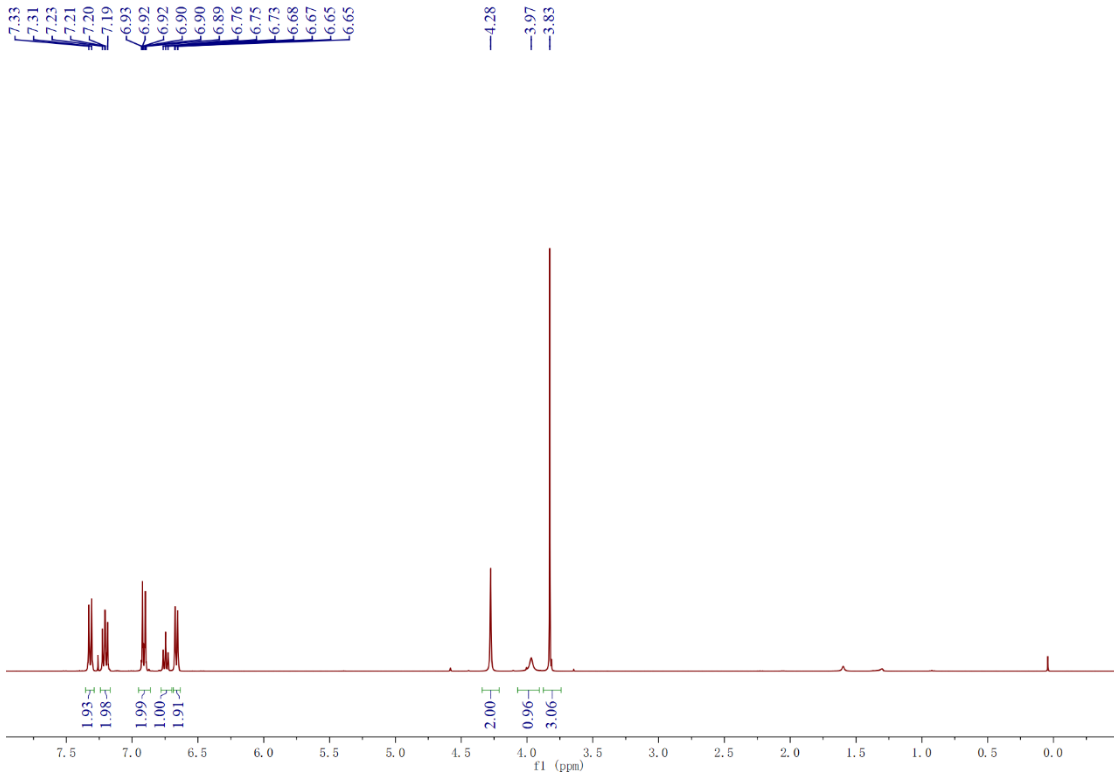

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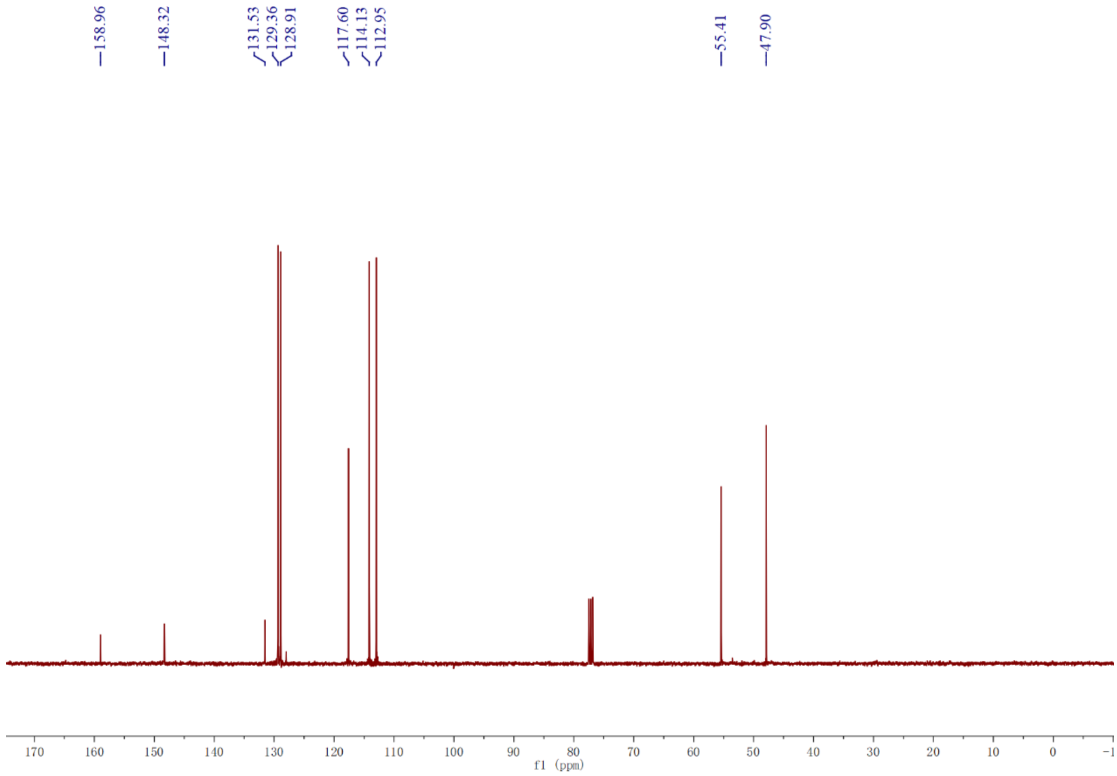

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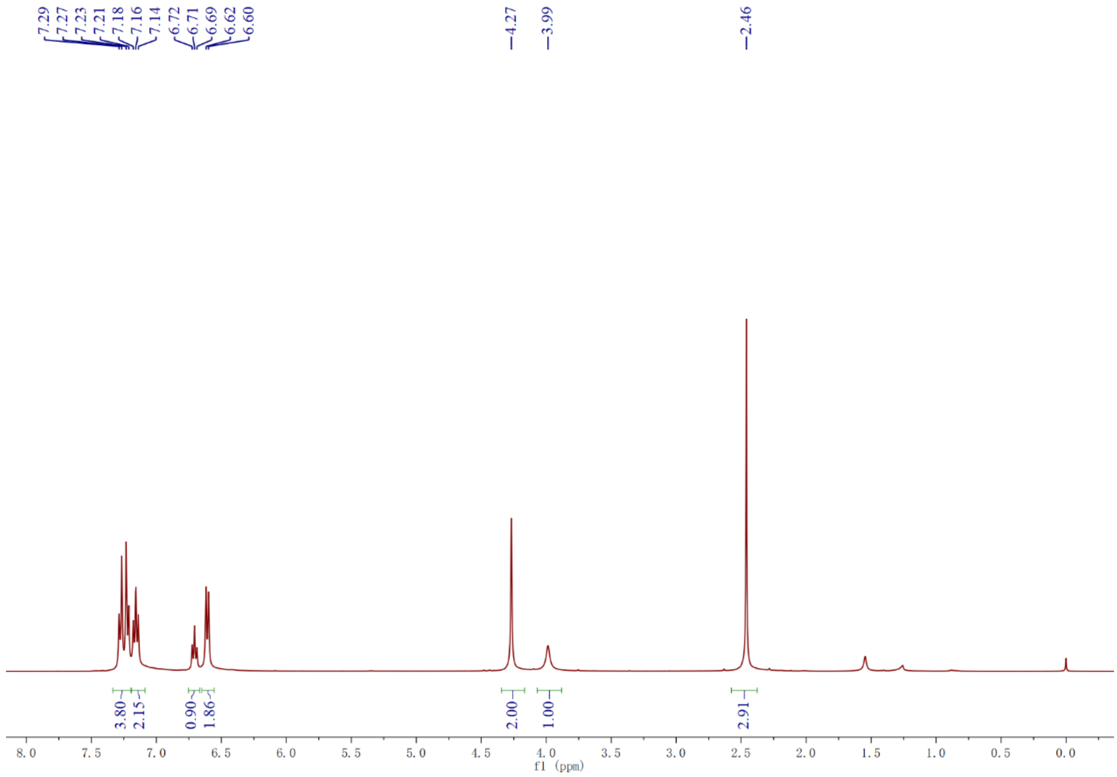

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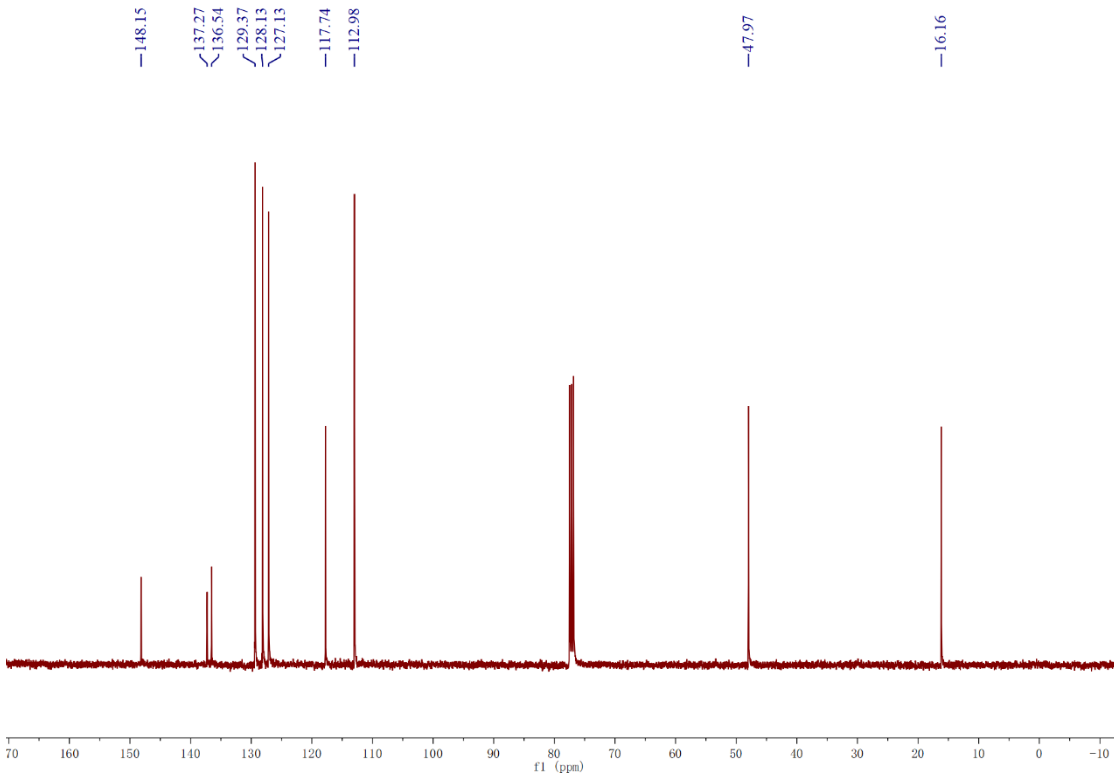

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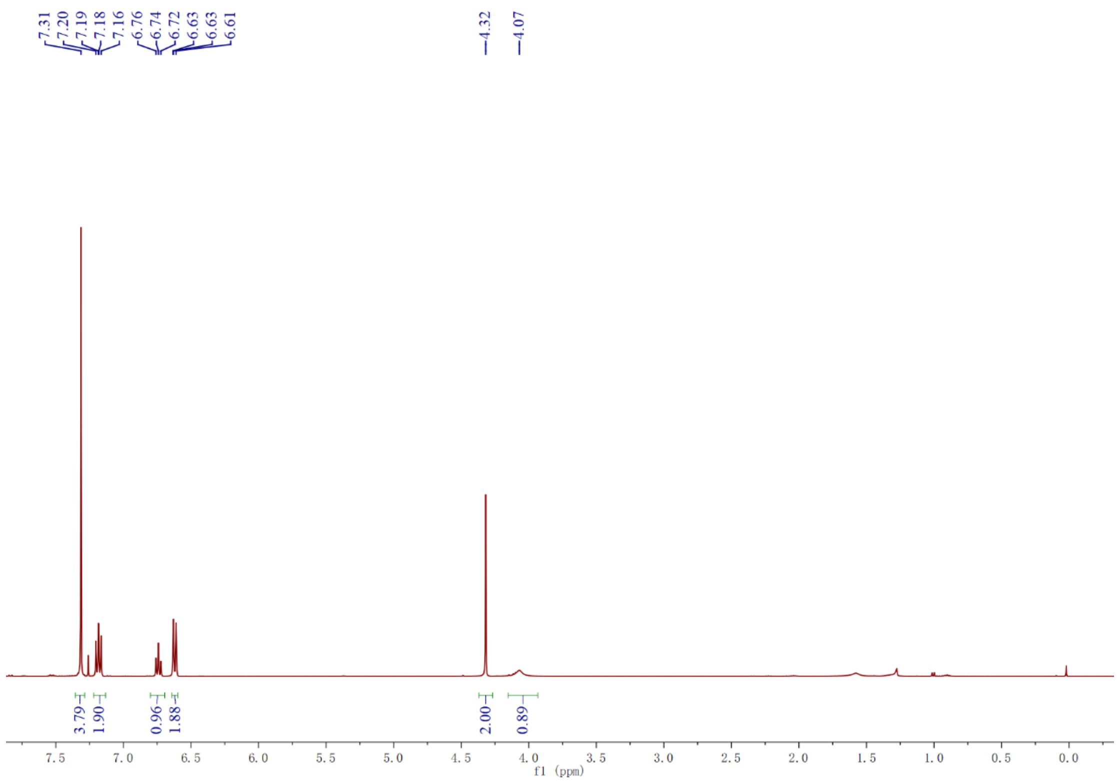

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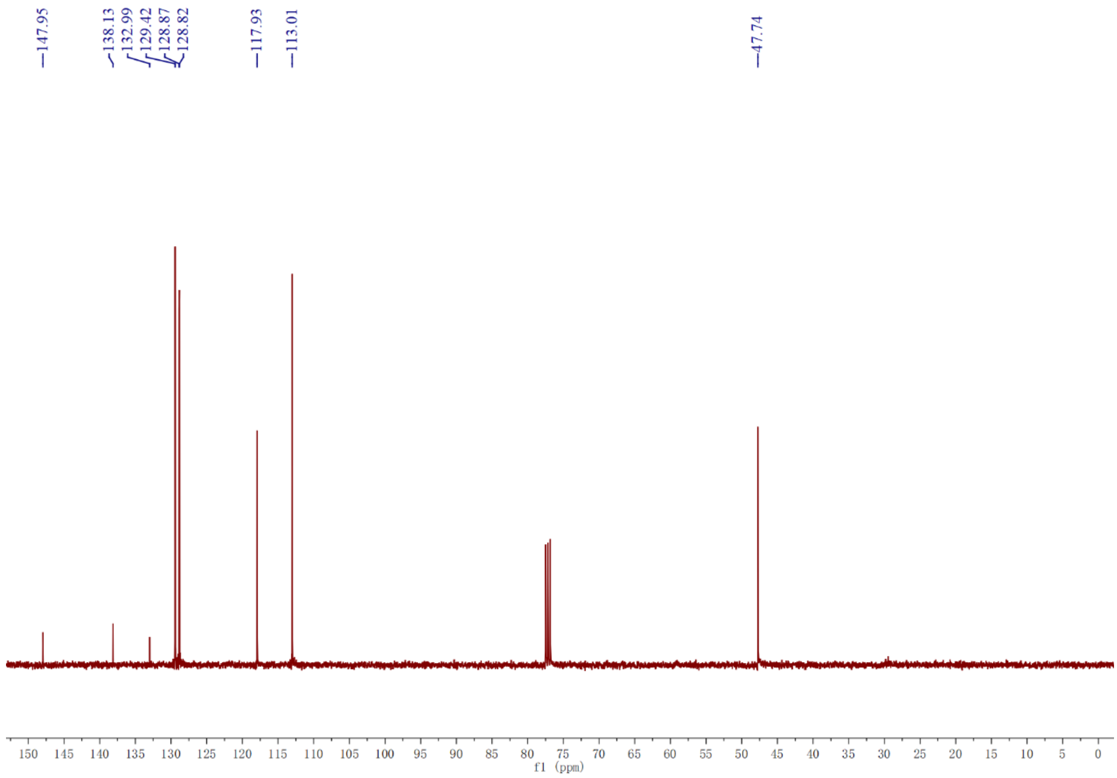

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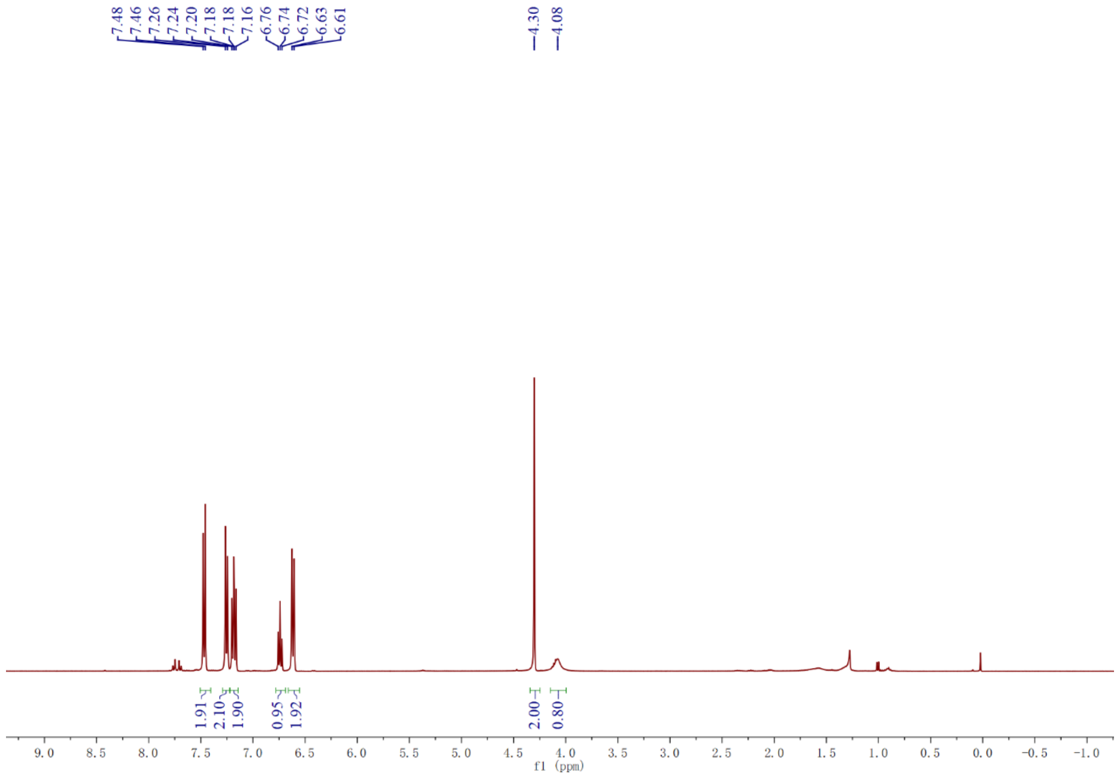

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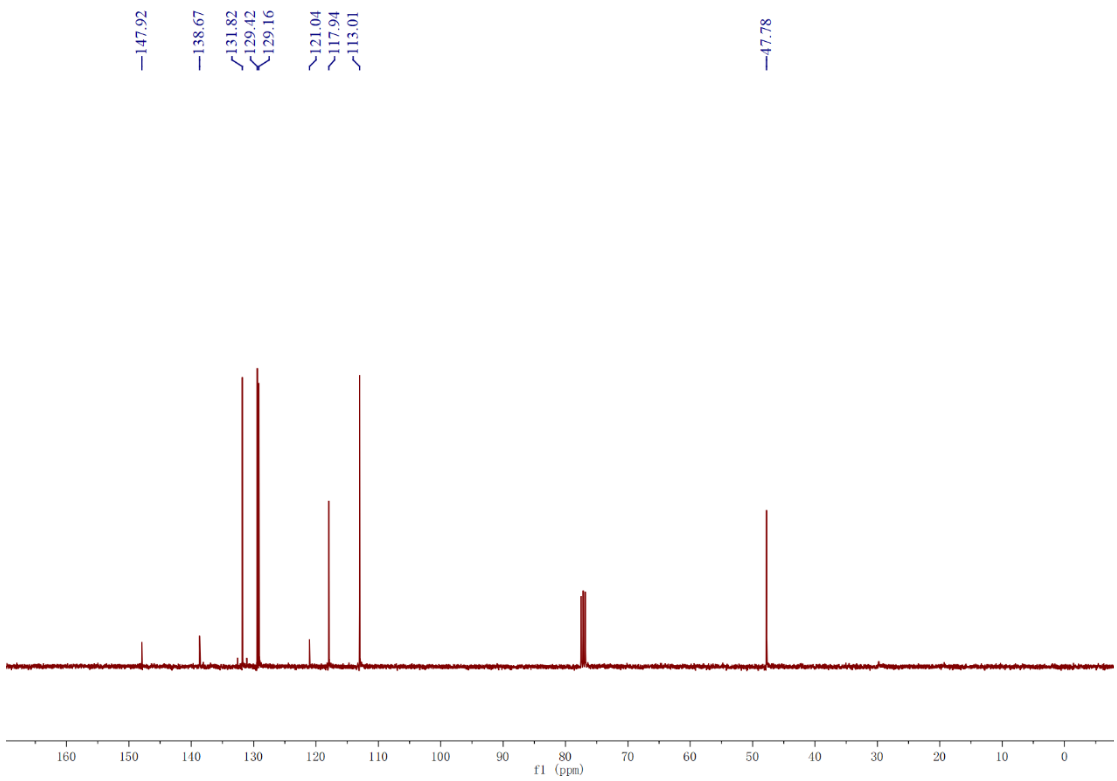
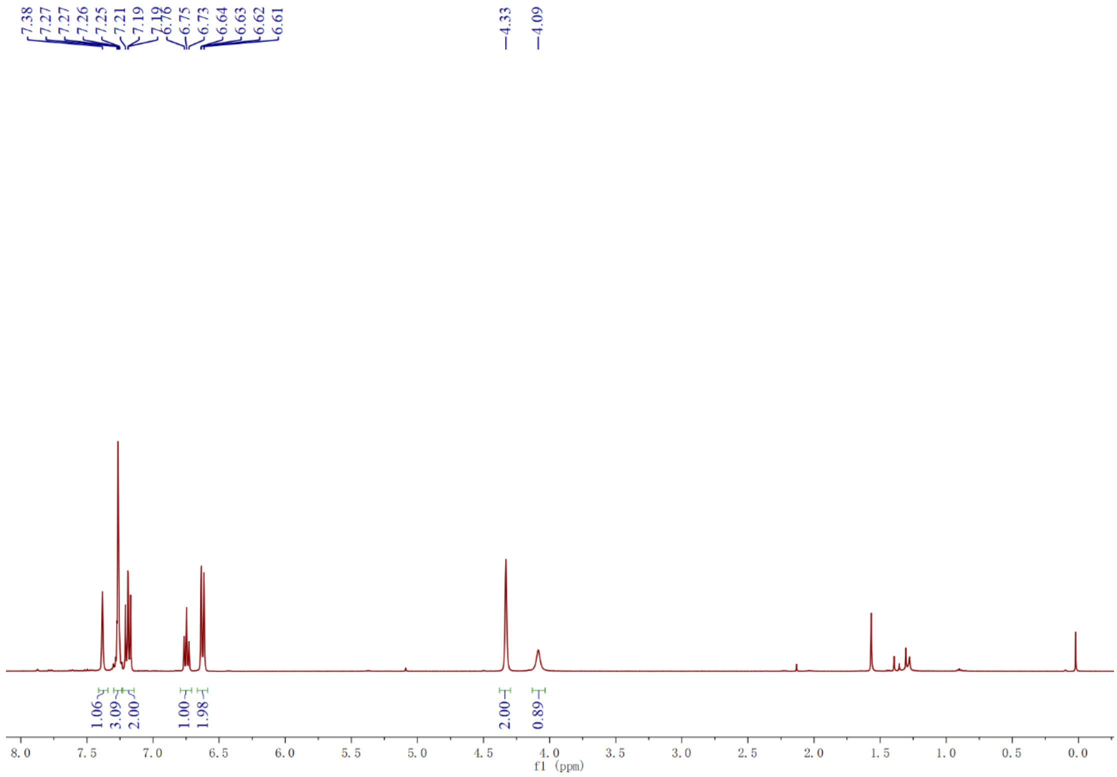


[13]C NMR (100 MHz, $CDCl_3$) spectrum of **9f**



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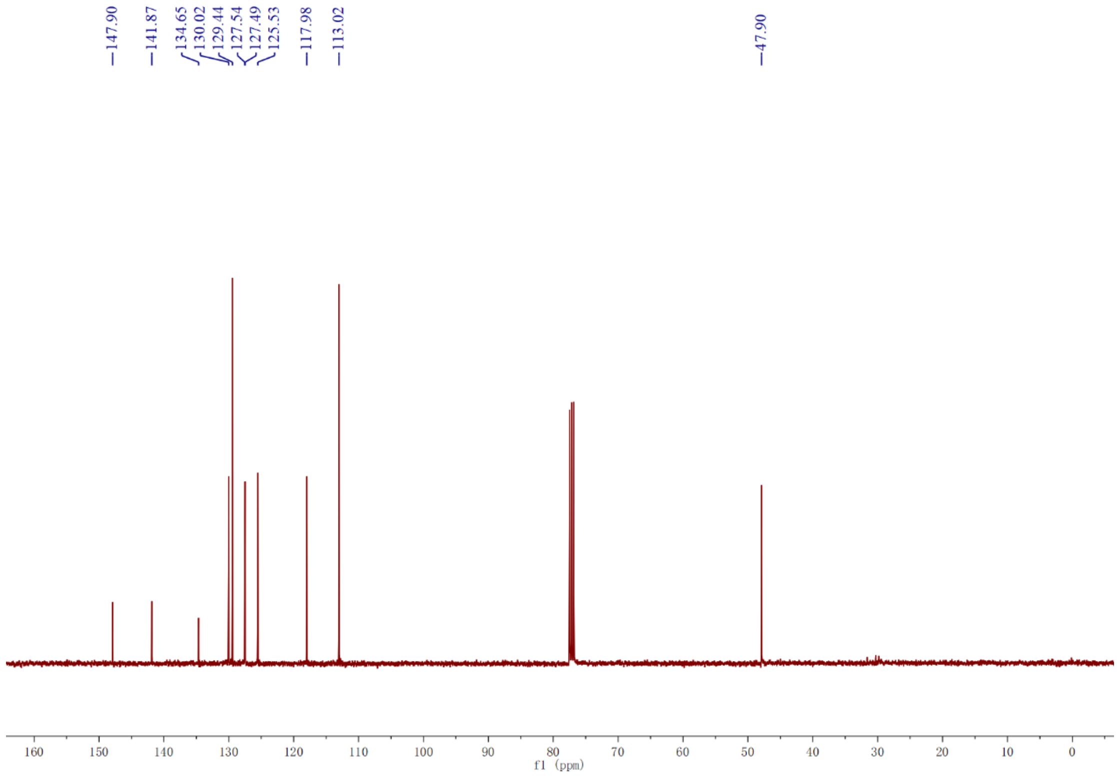

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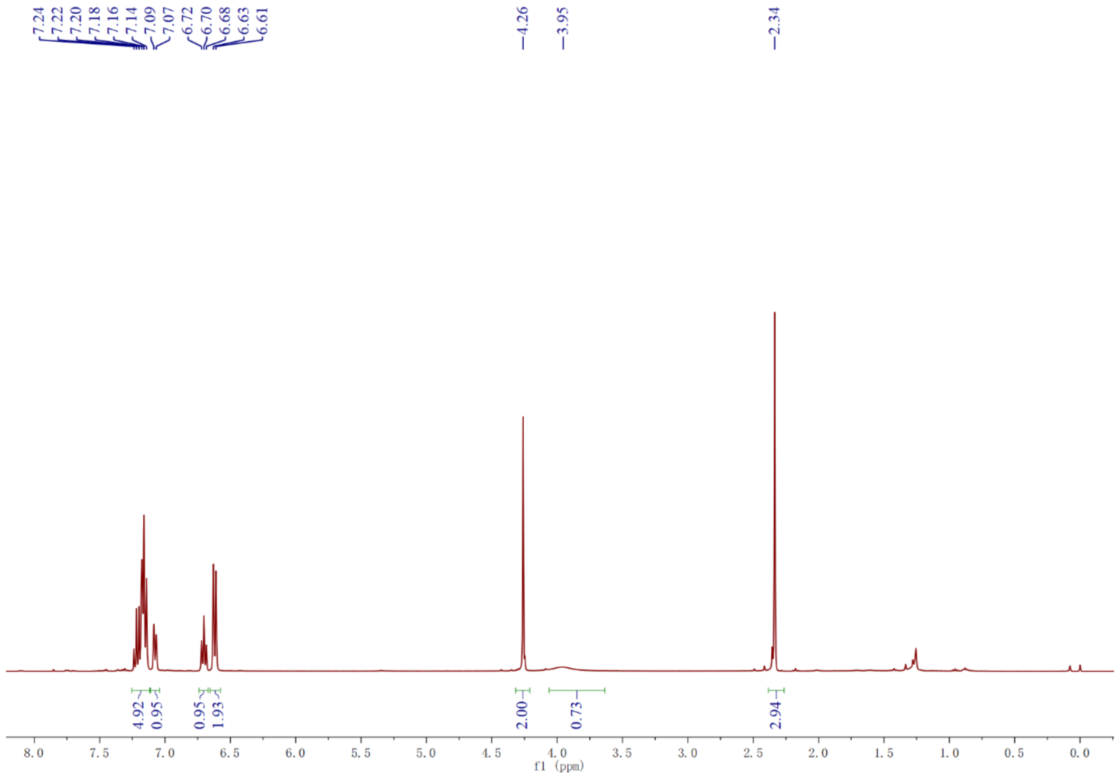

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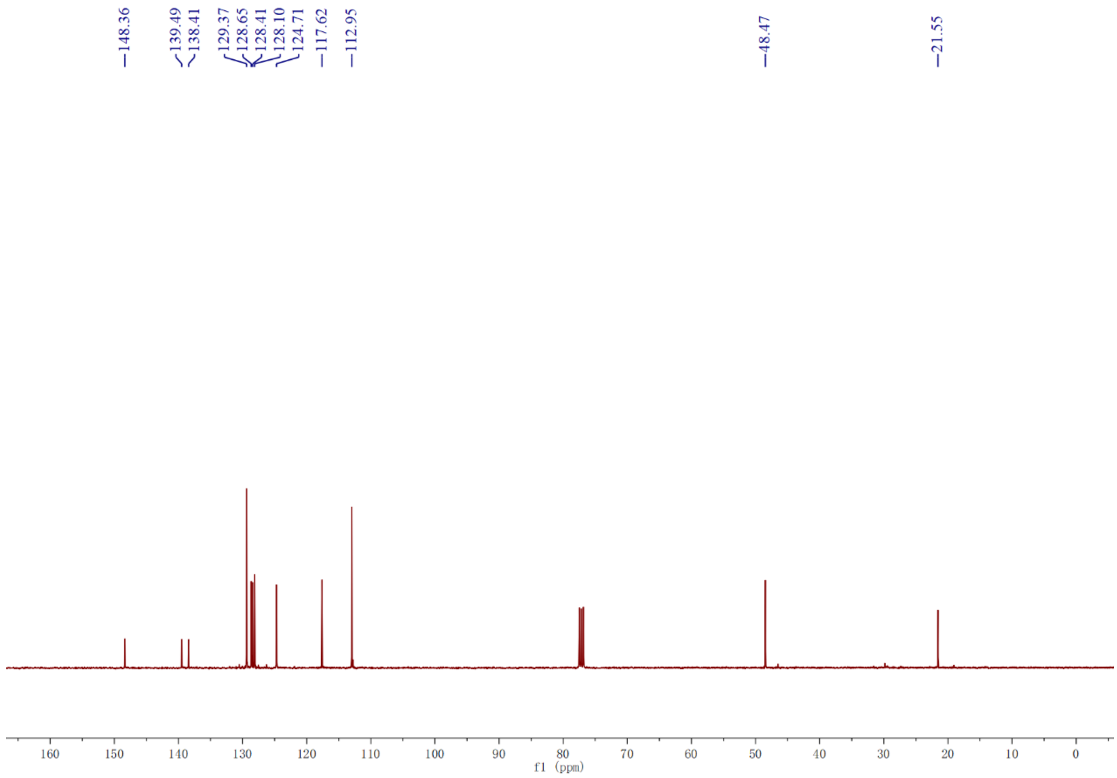

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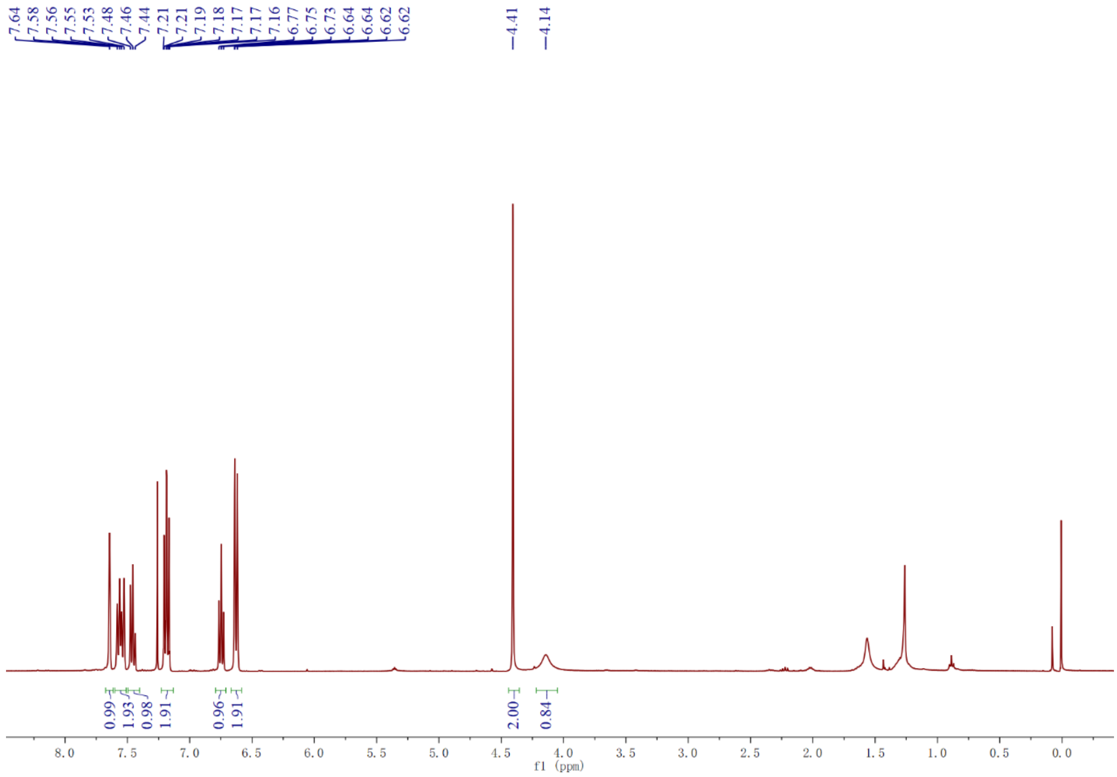

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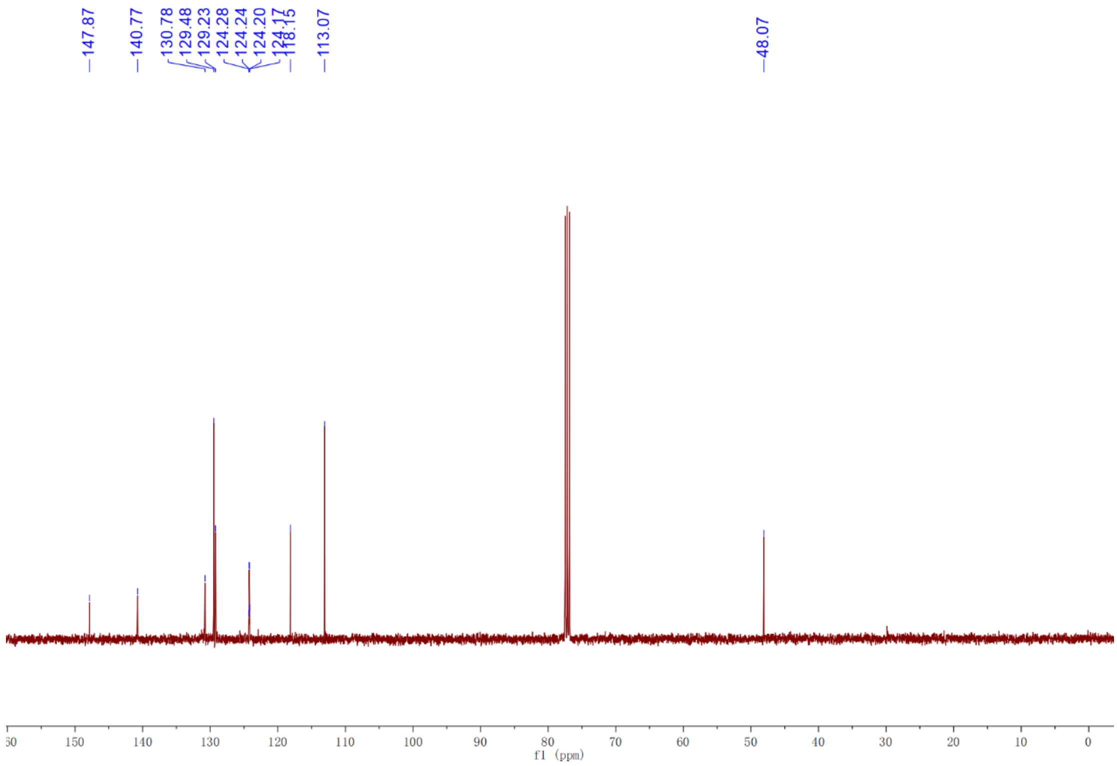

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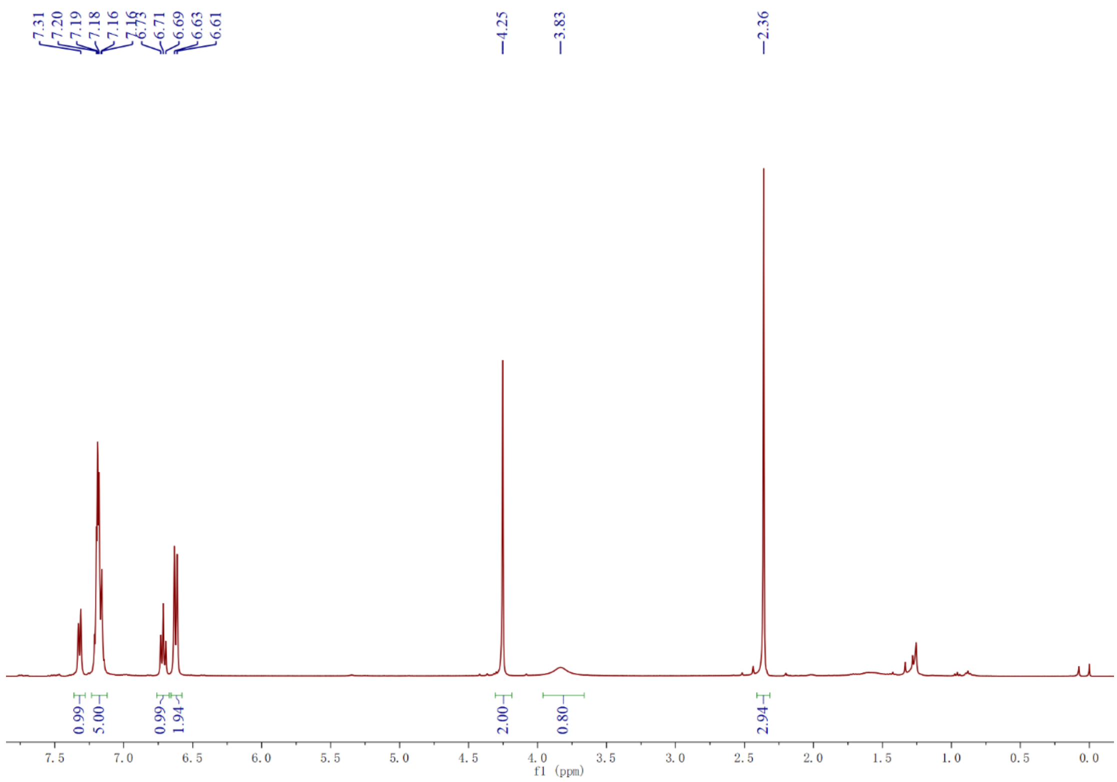

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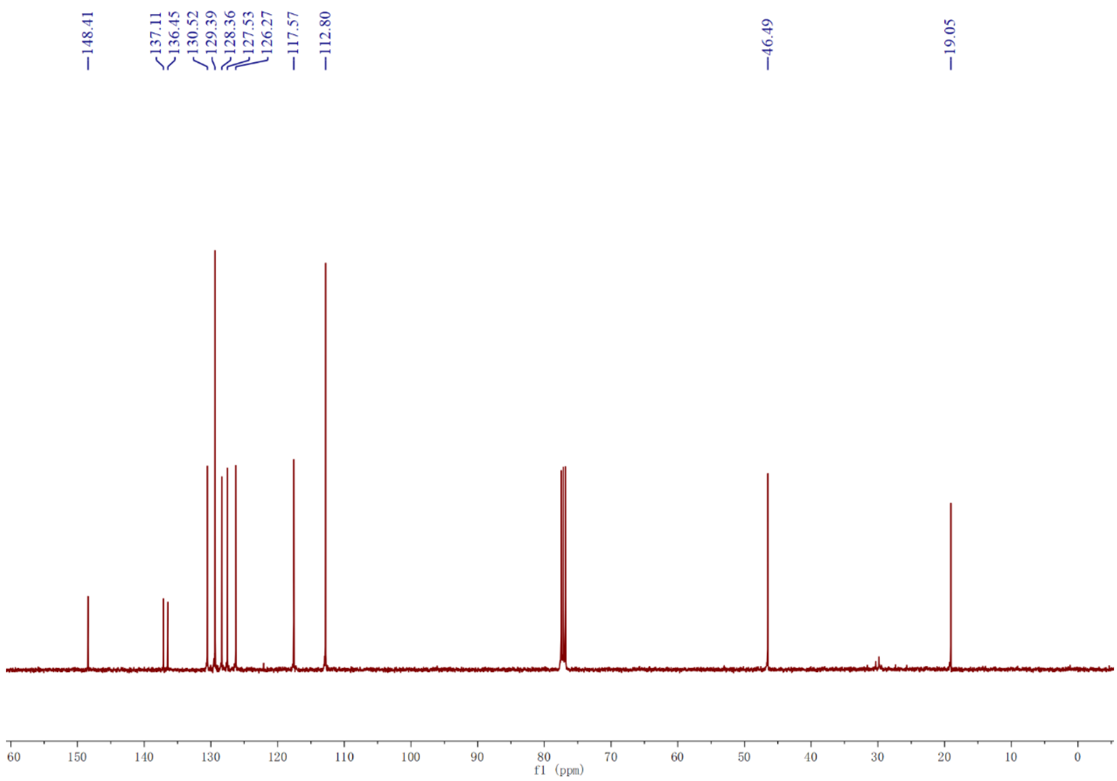

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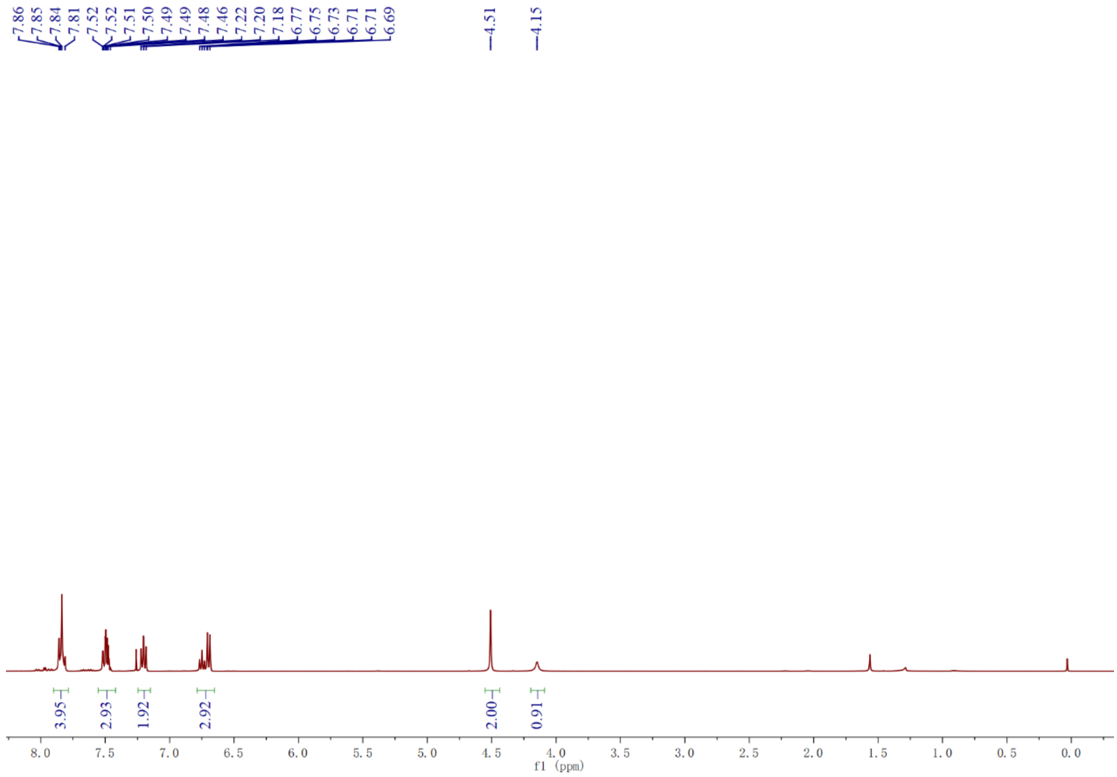

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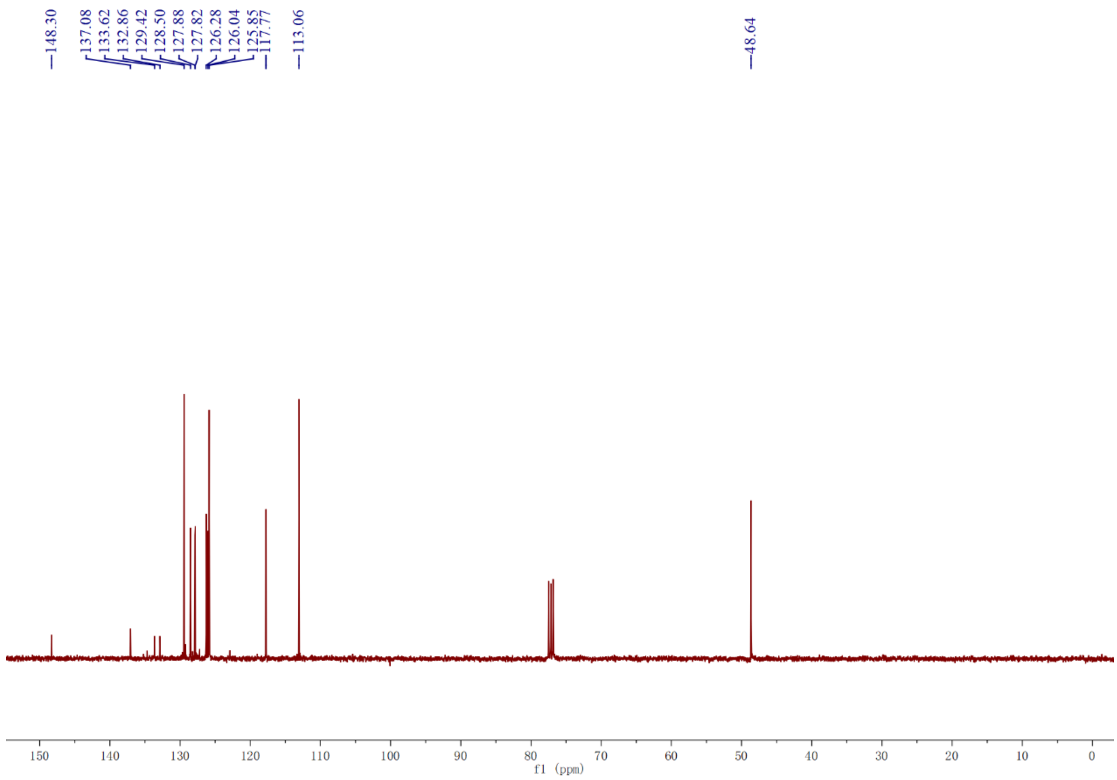

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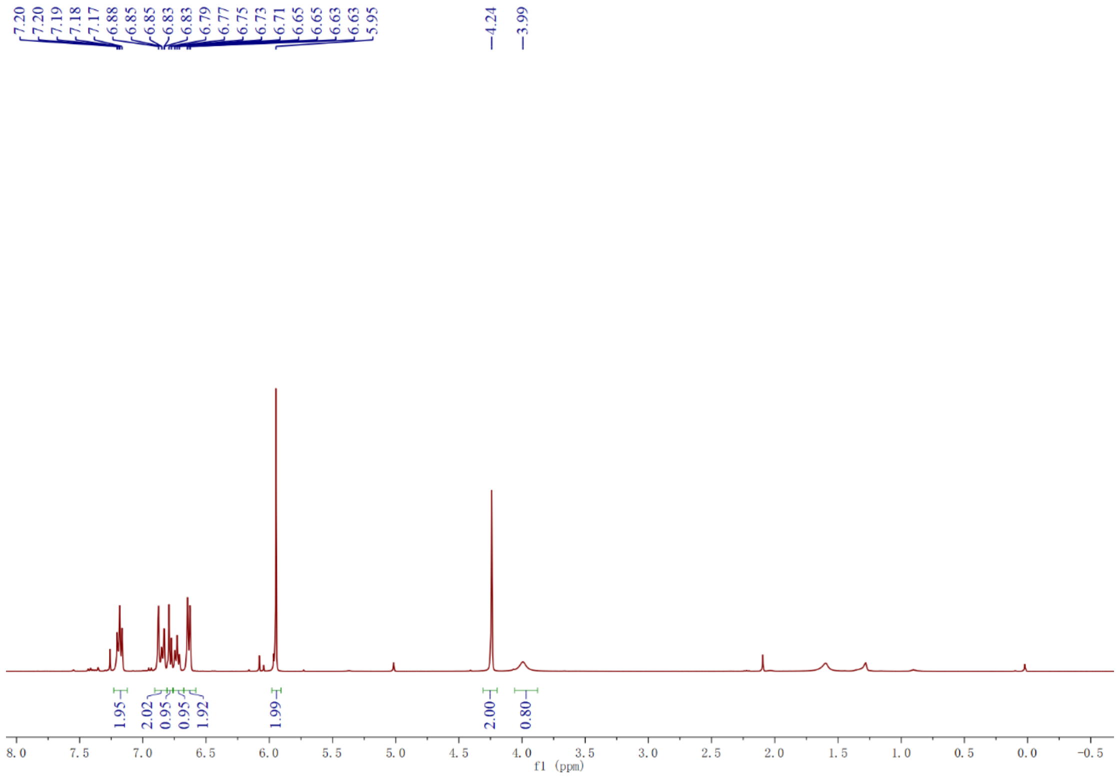

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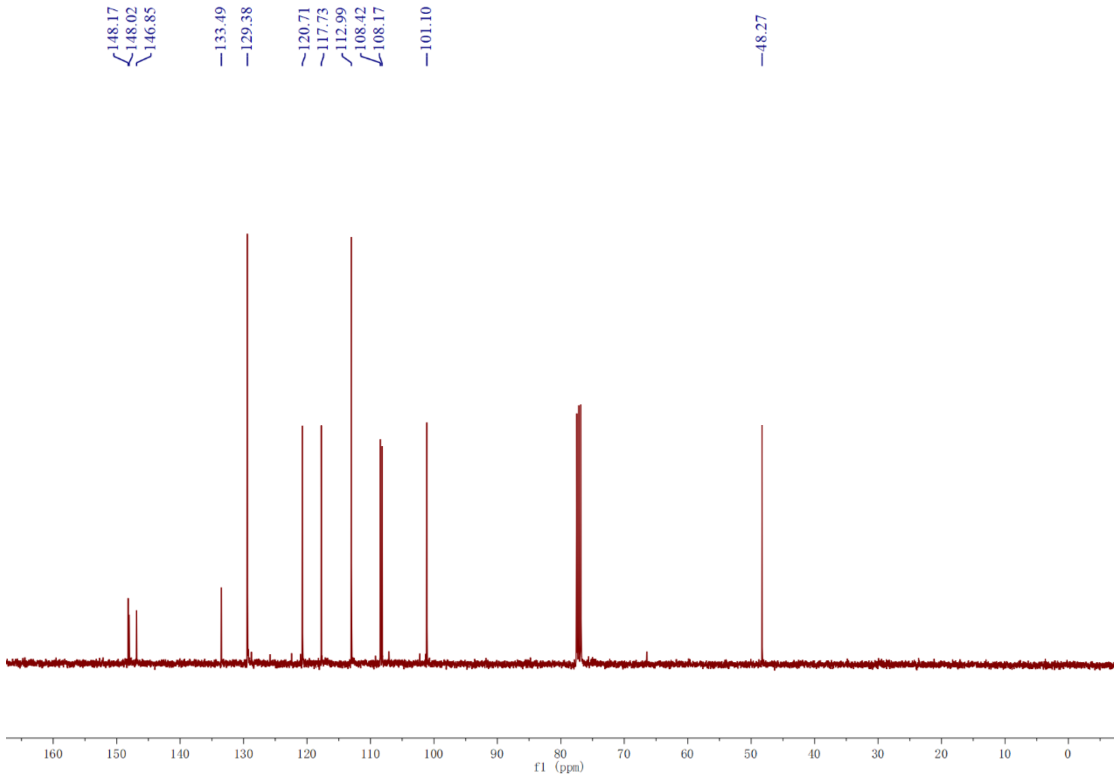

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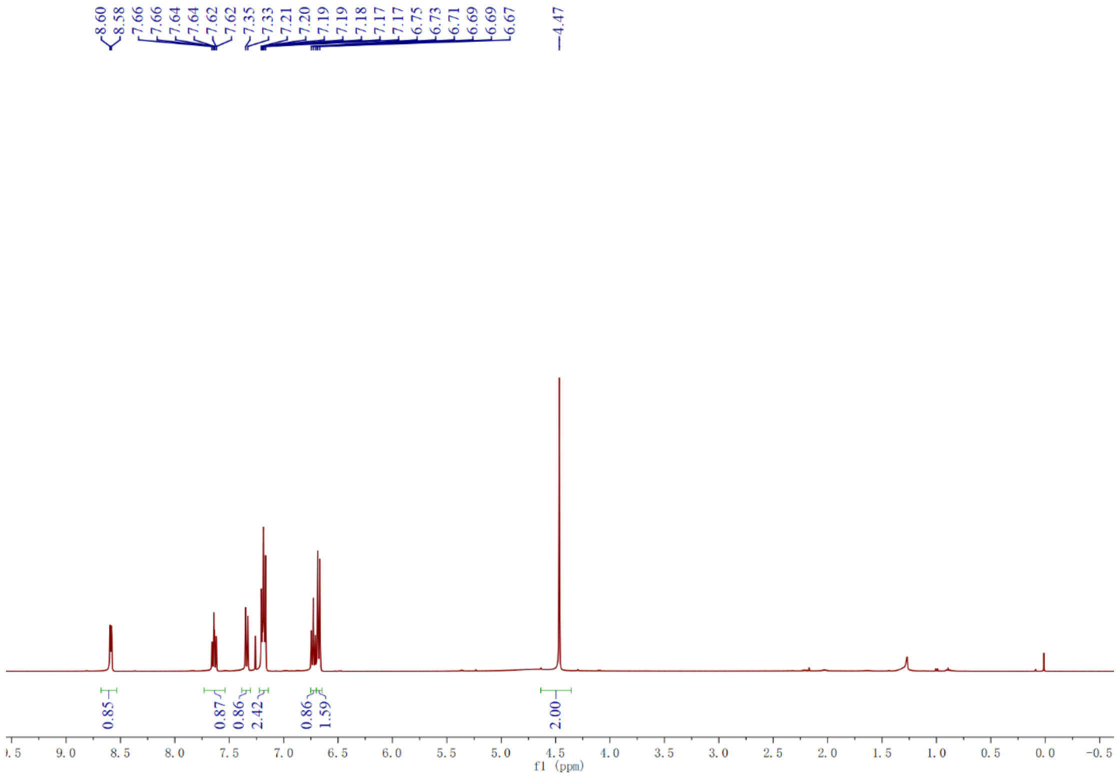

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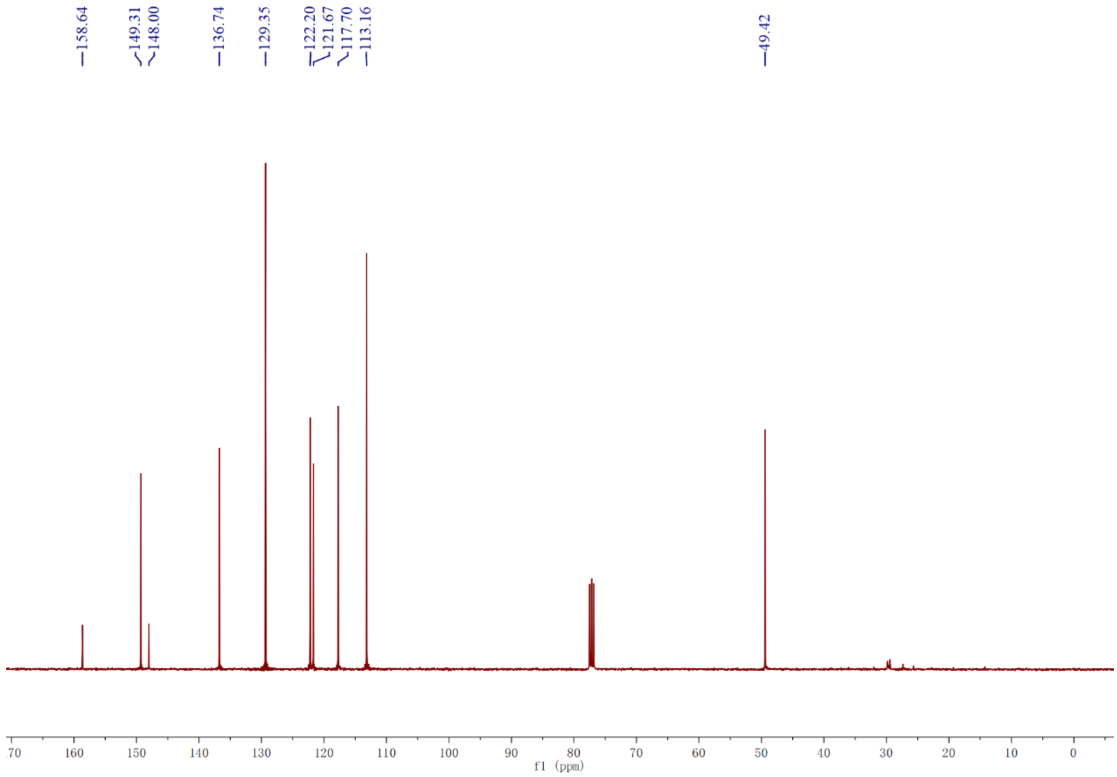

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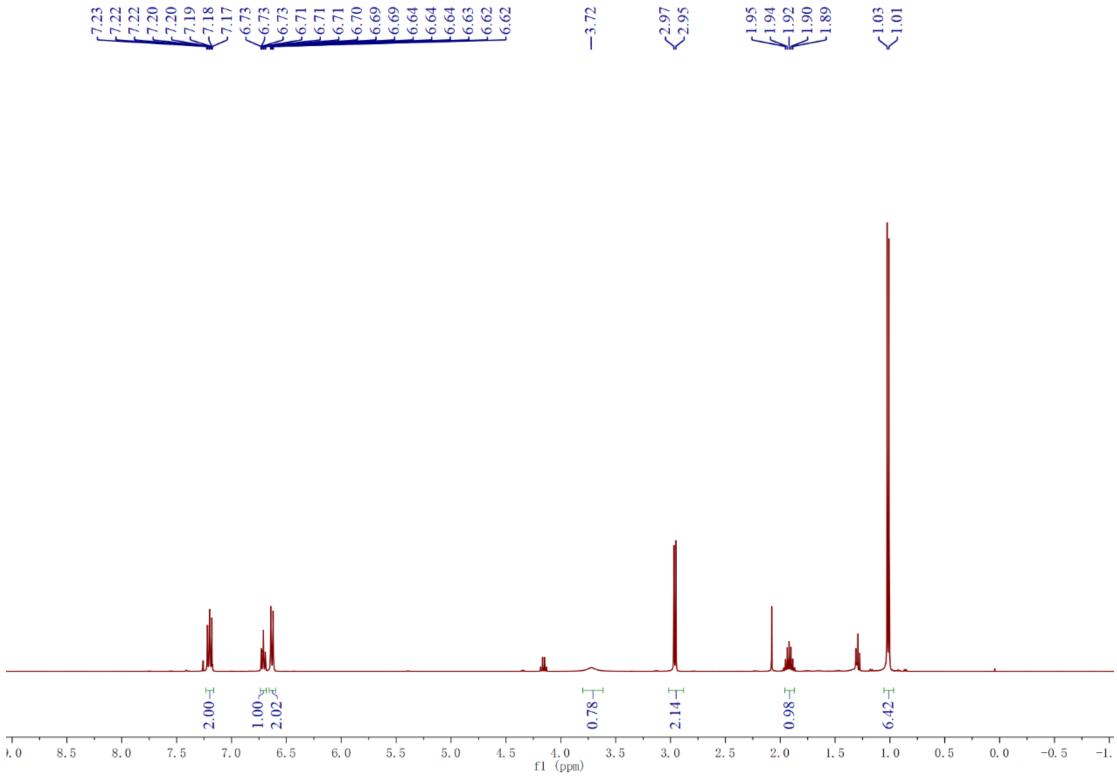

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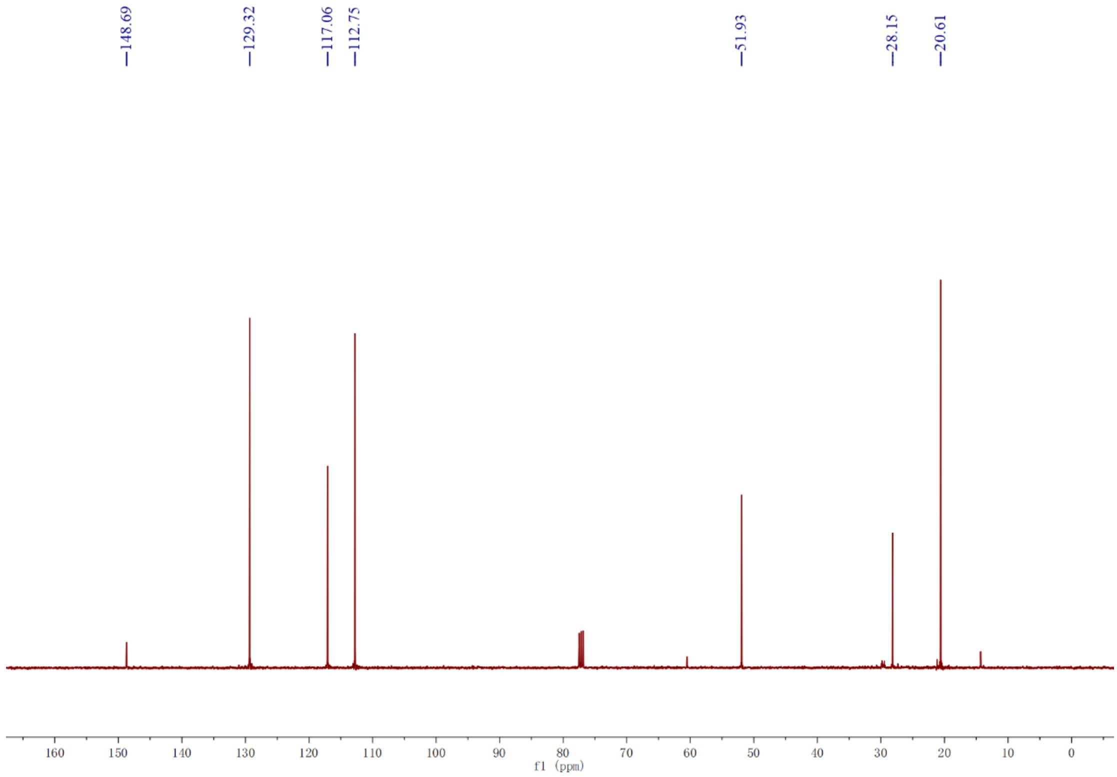

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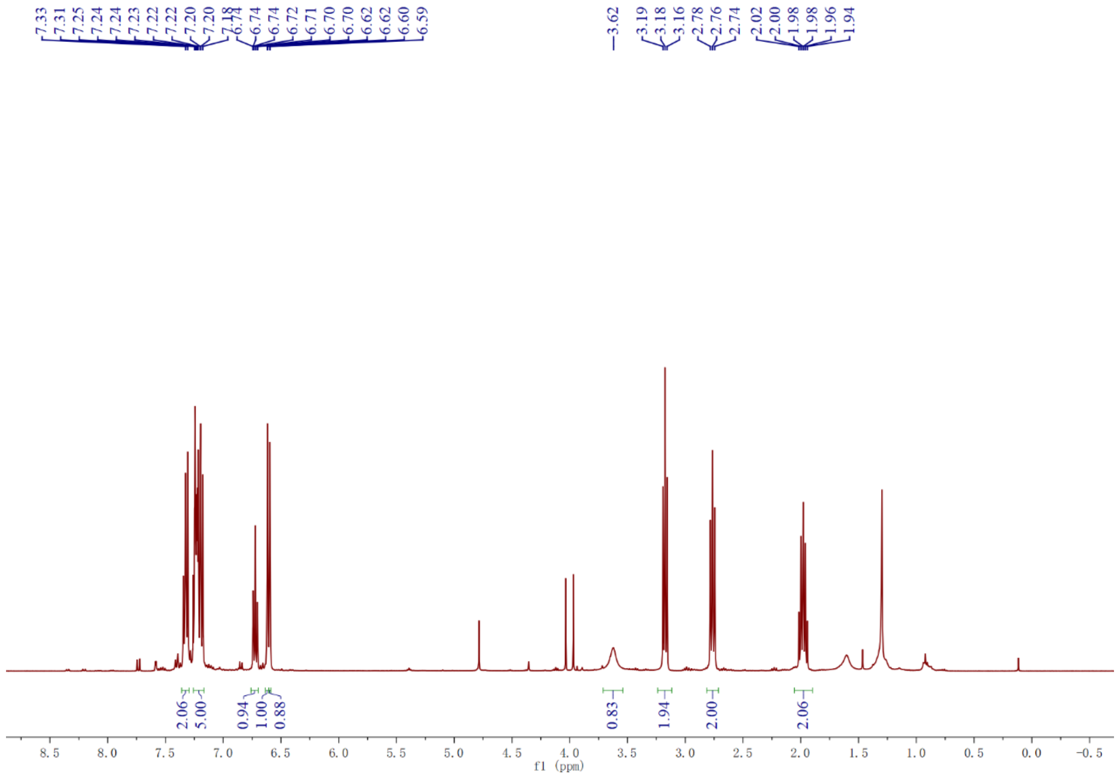

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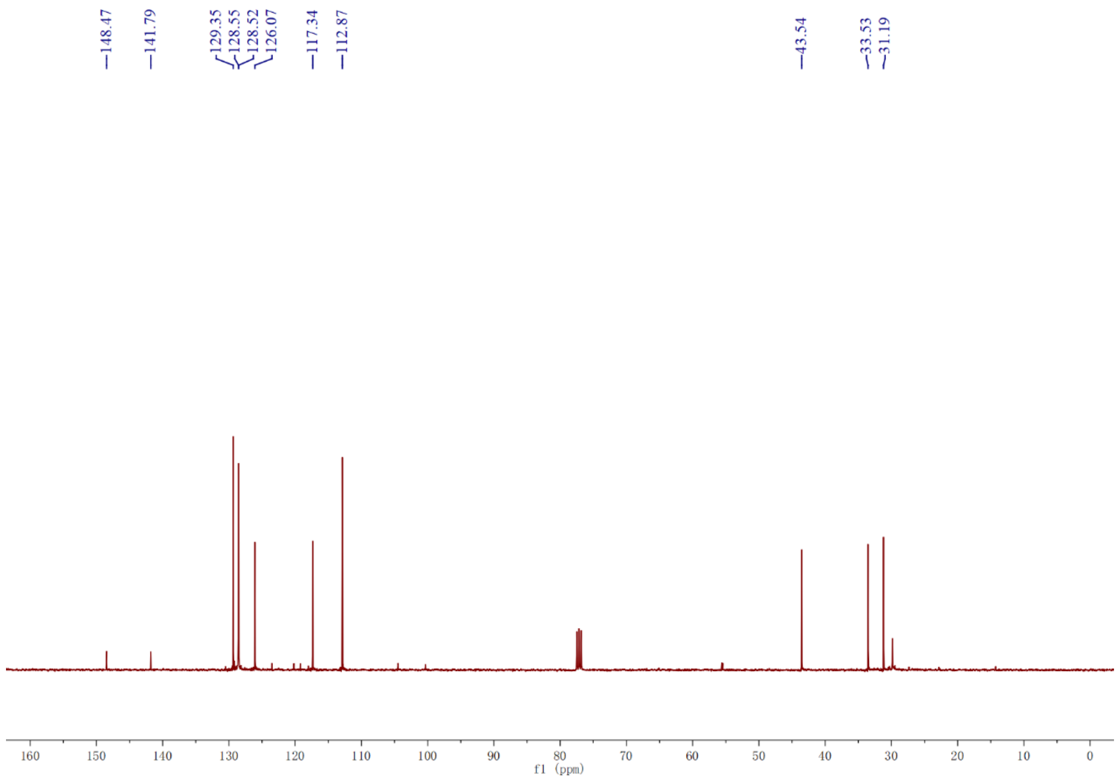

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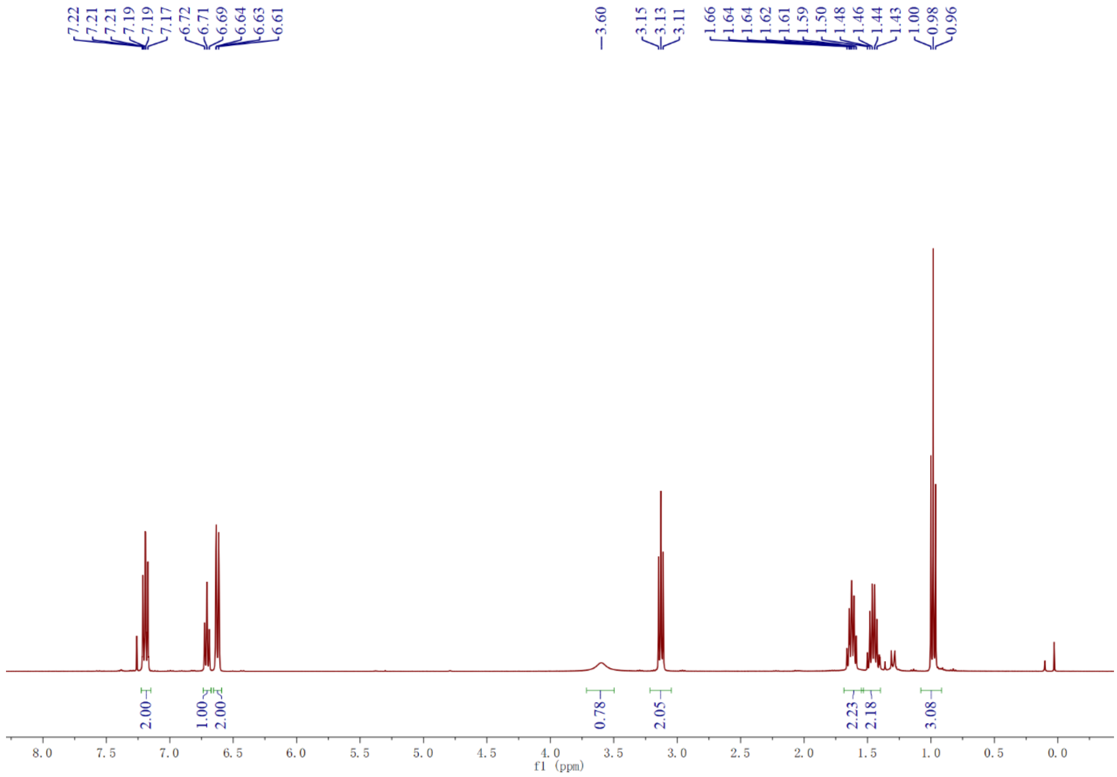

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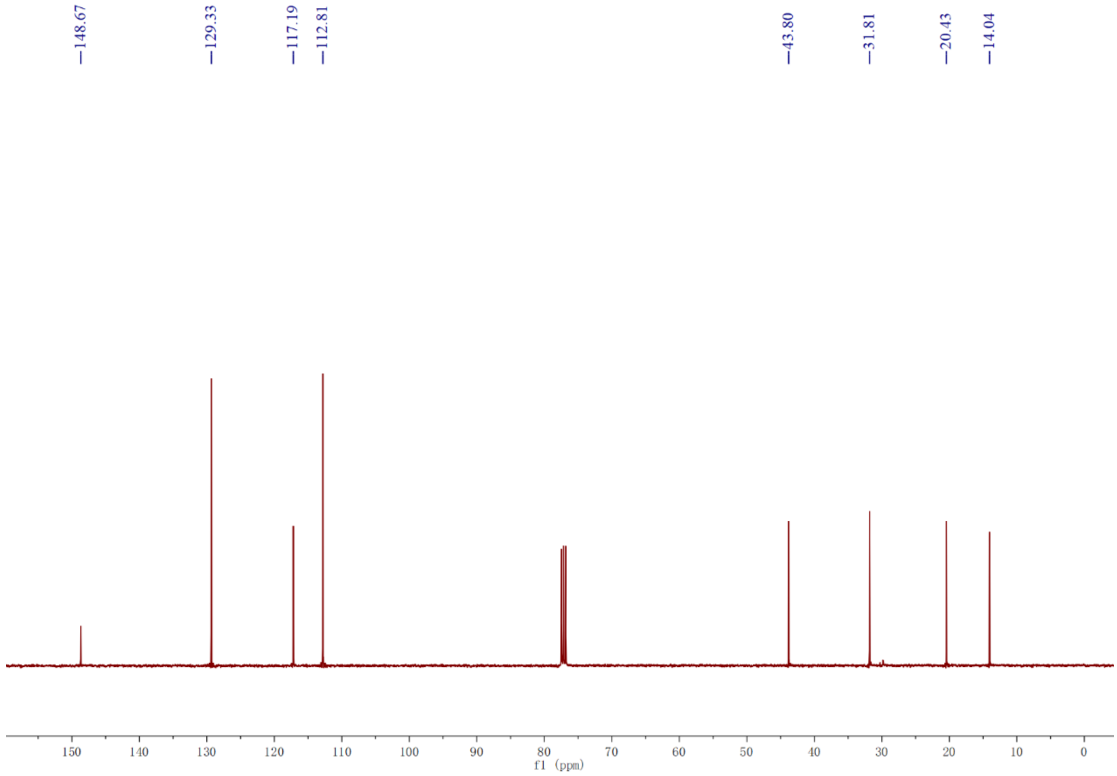
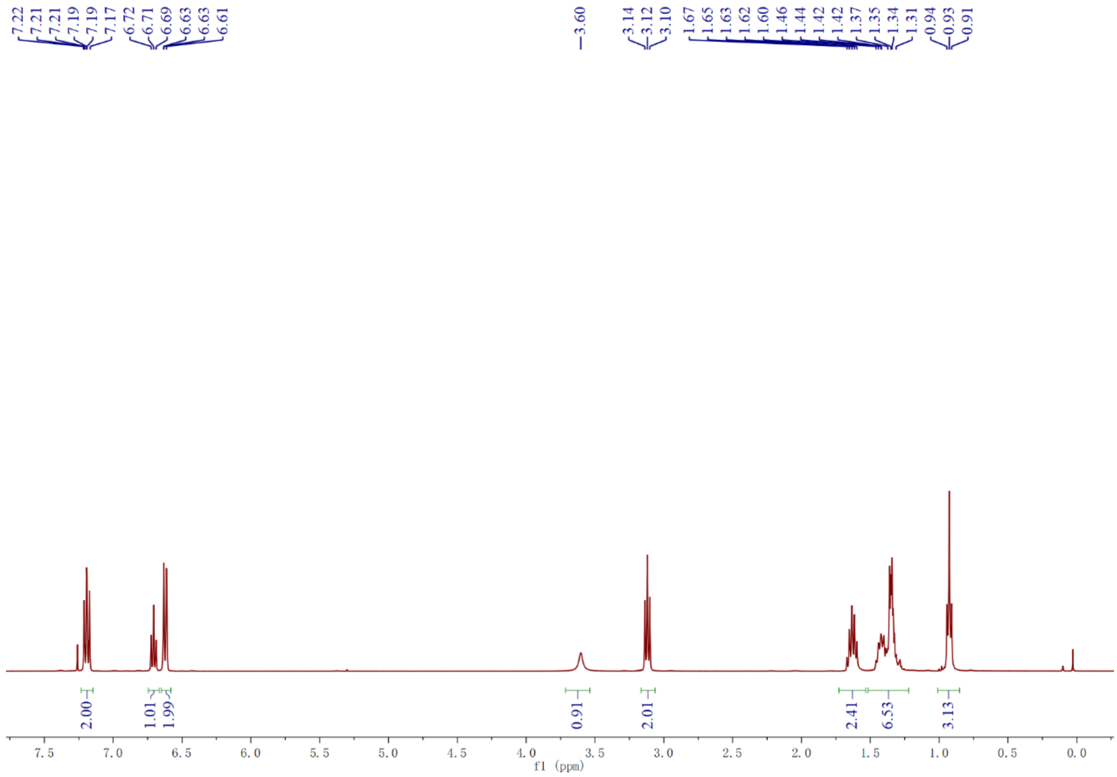
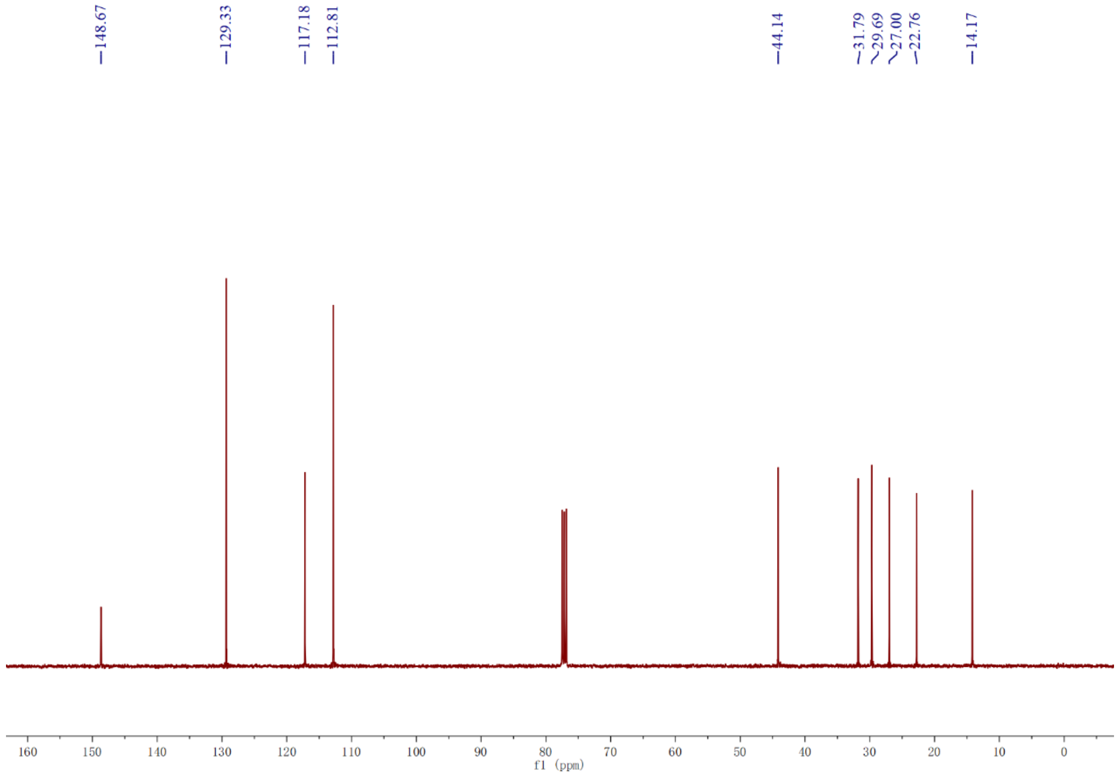


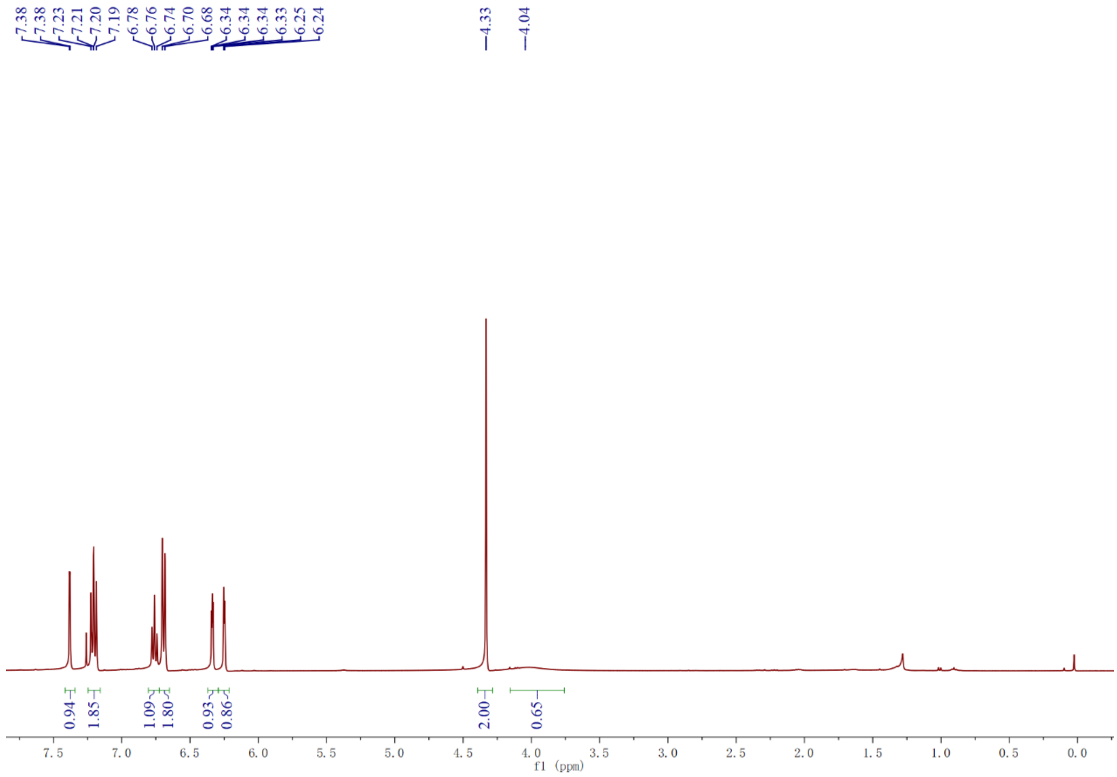
[13]C NMR (100 MHz, $CDCl_3$) spectrum of **9p**



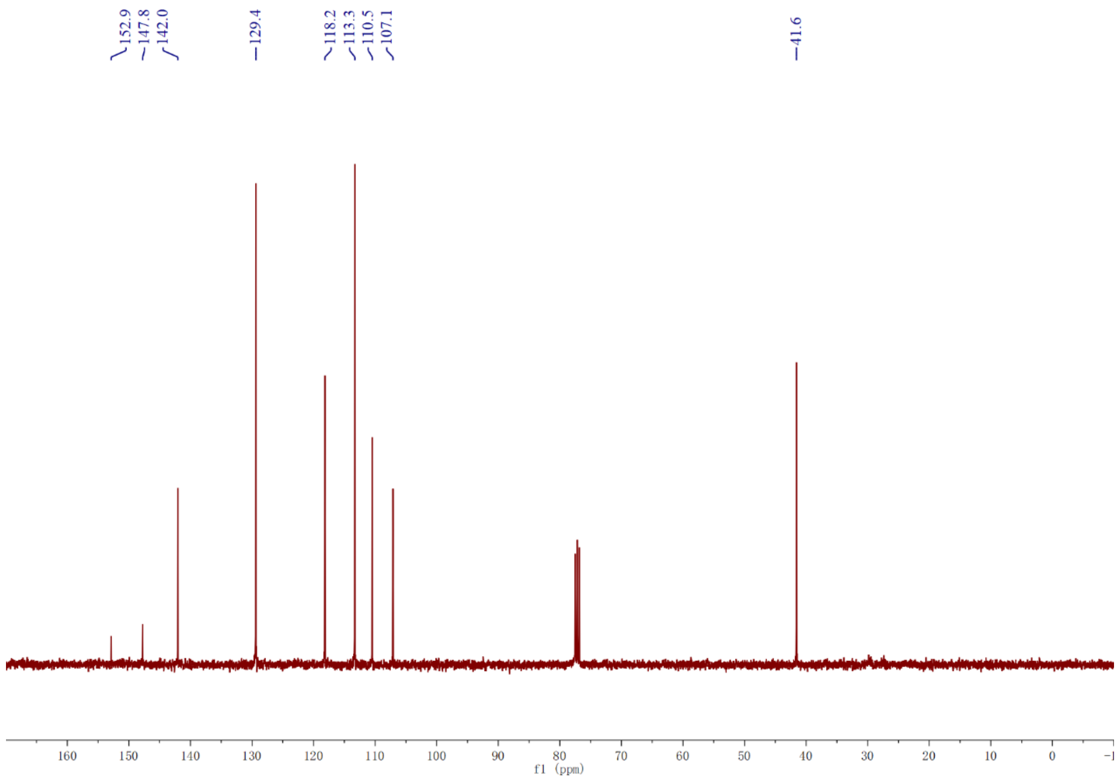
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **9q**



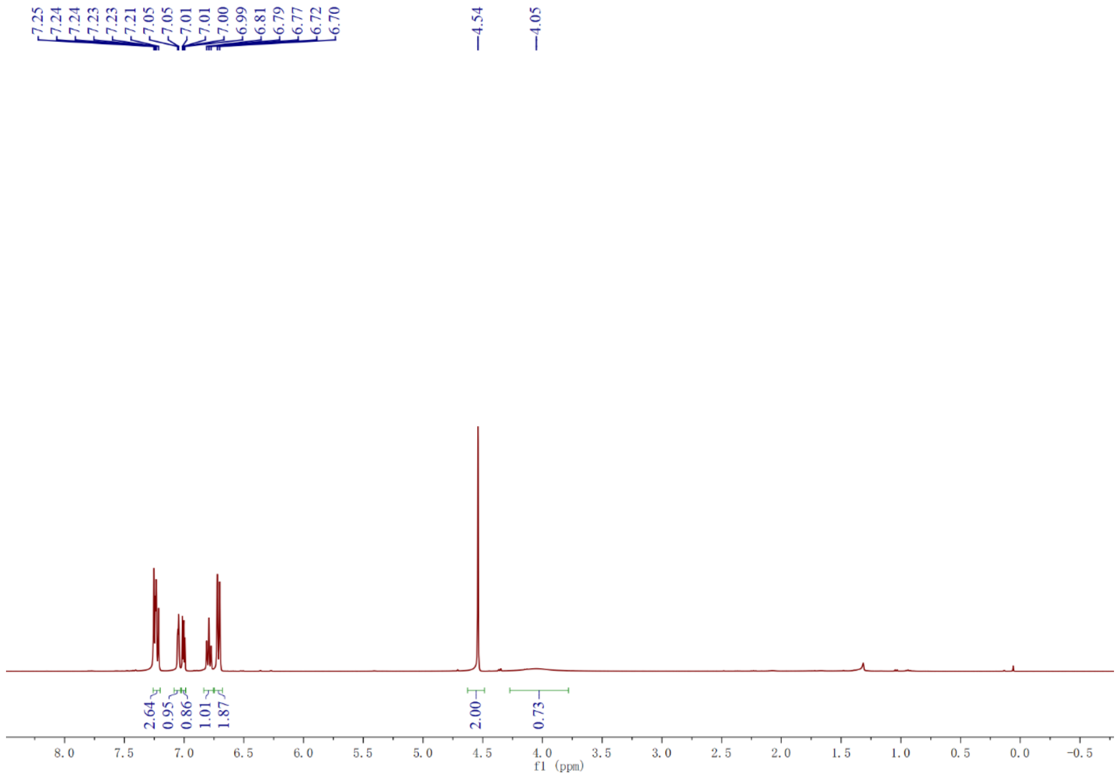
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **9q**



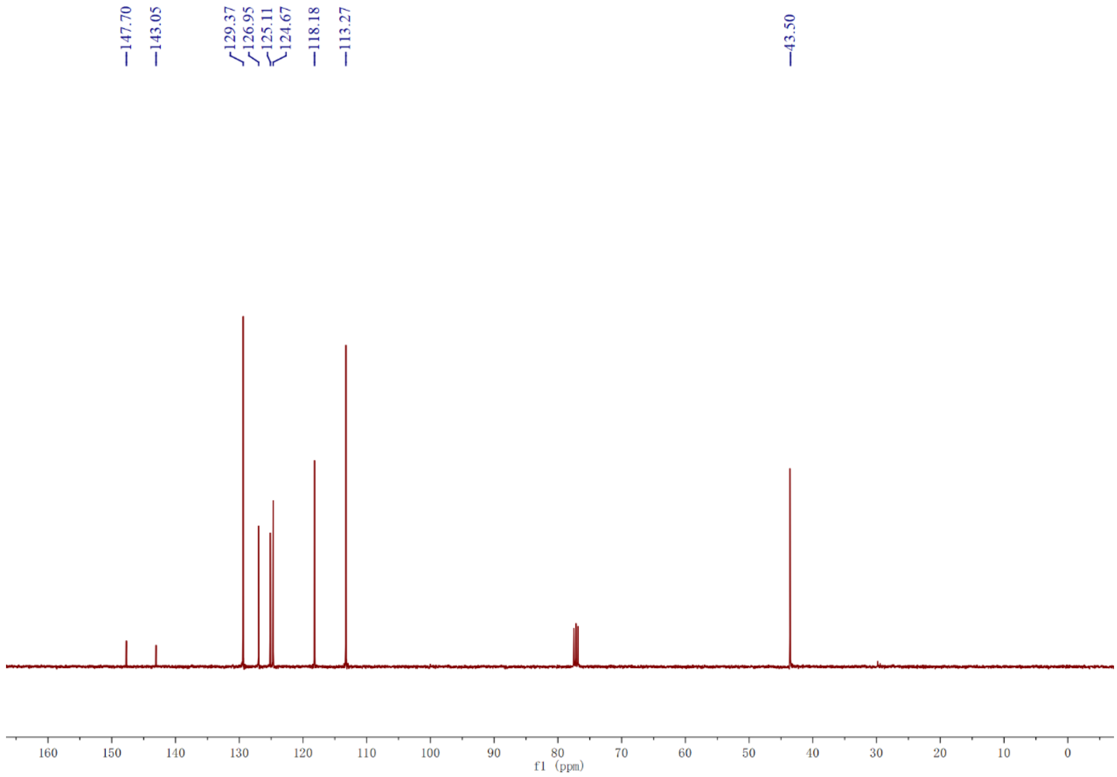
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **9r**



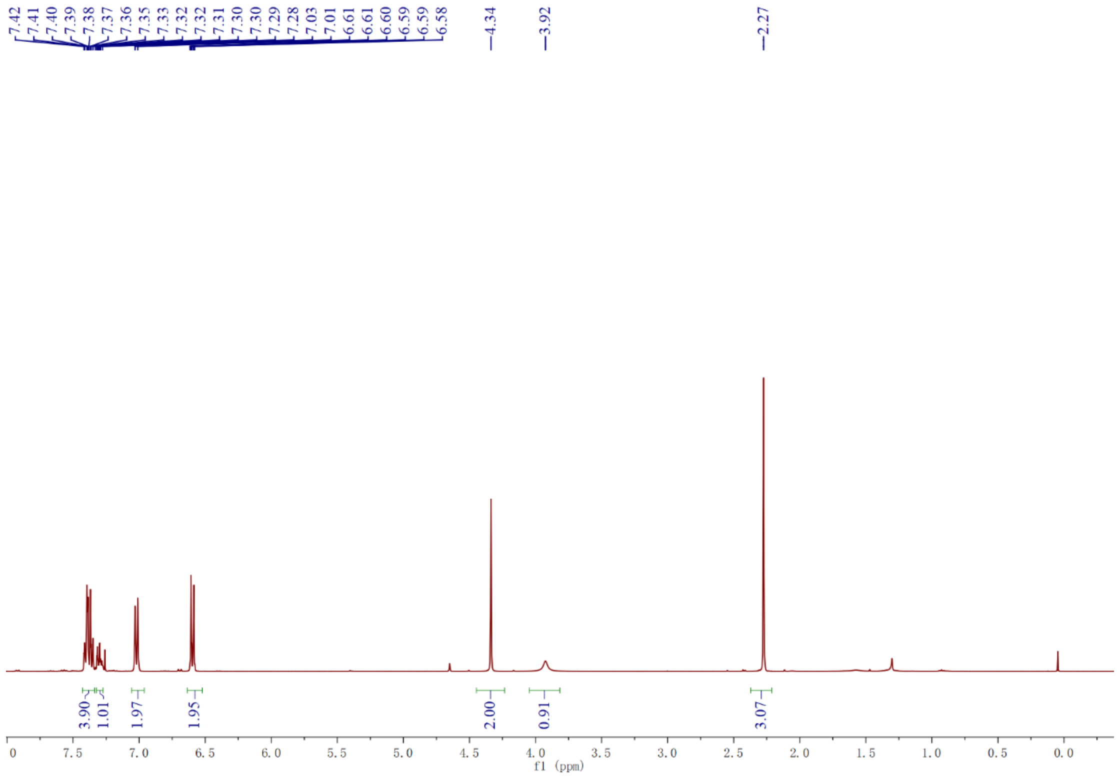
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **9r**



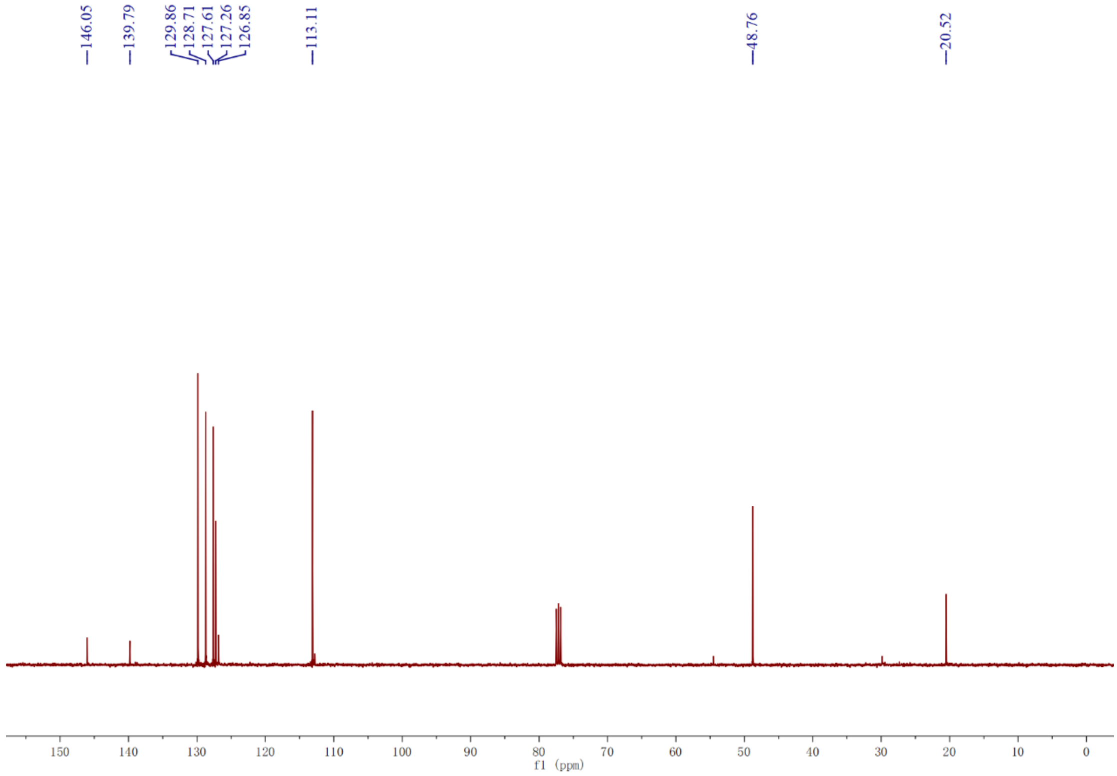
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **9s**



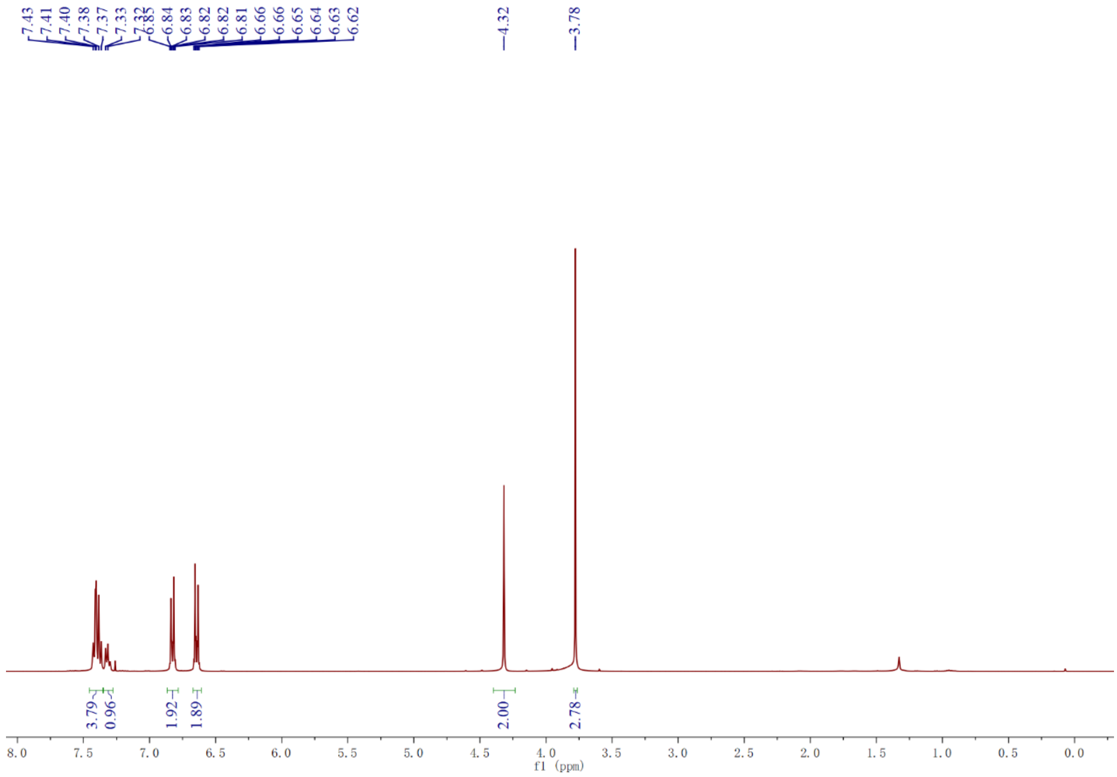
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **9s**



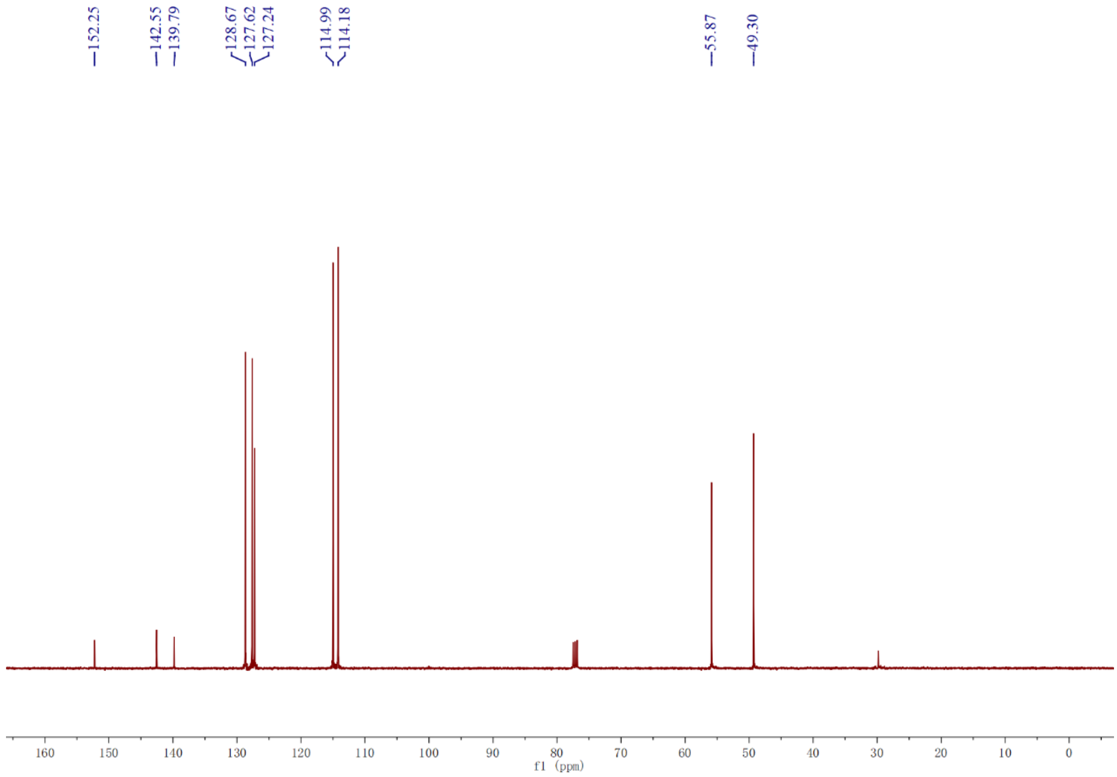
[1]H NMR (400 MHz, $CDCl_3$) spectrum of **10a**



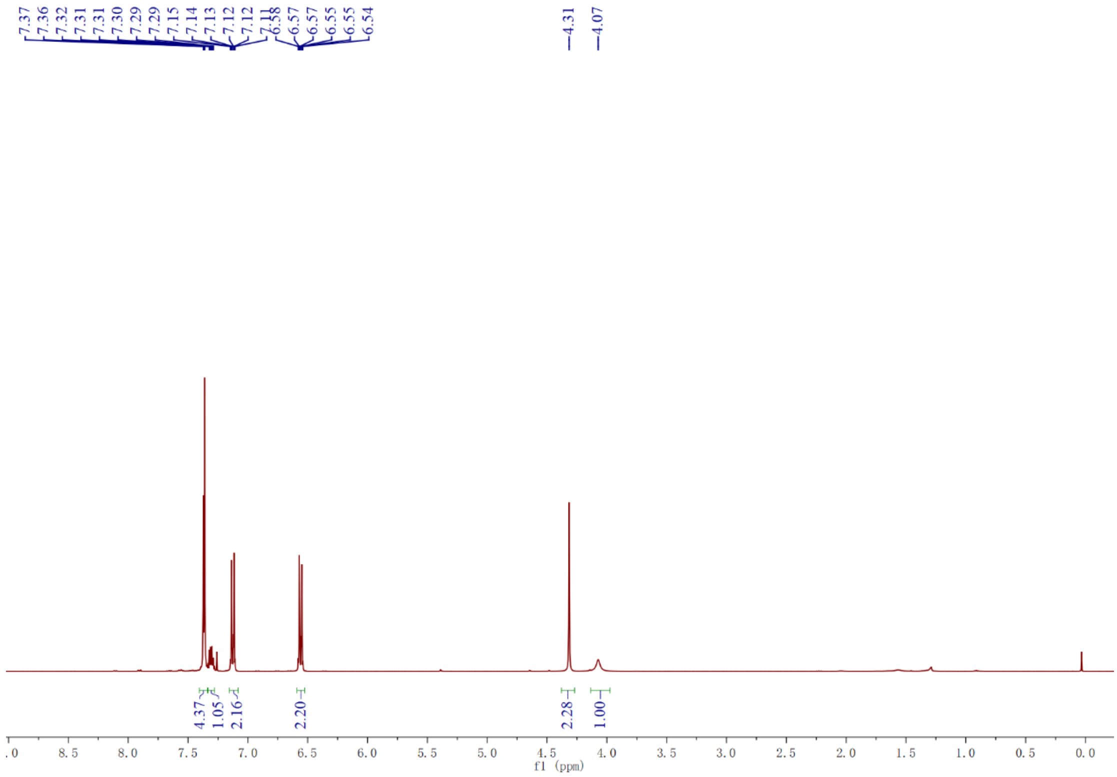
[13]C NMR (100 MHz, $CDCl_3$) spectrum of **10a**



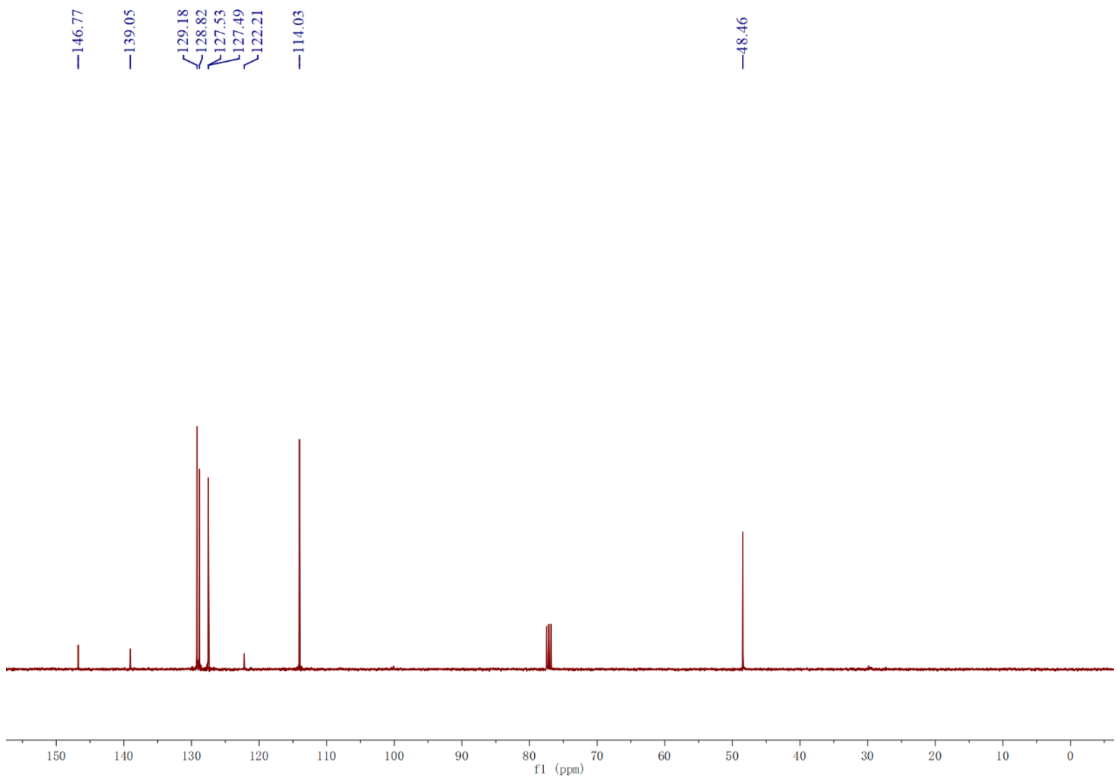
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **10b**



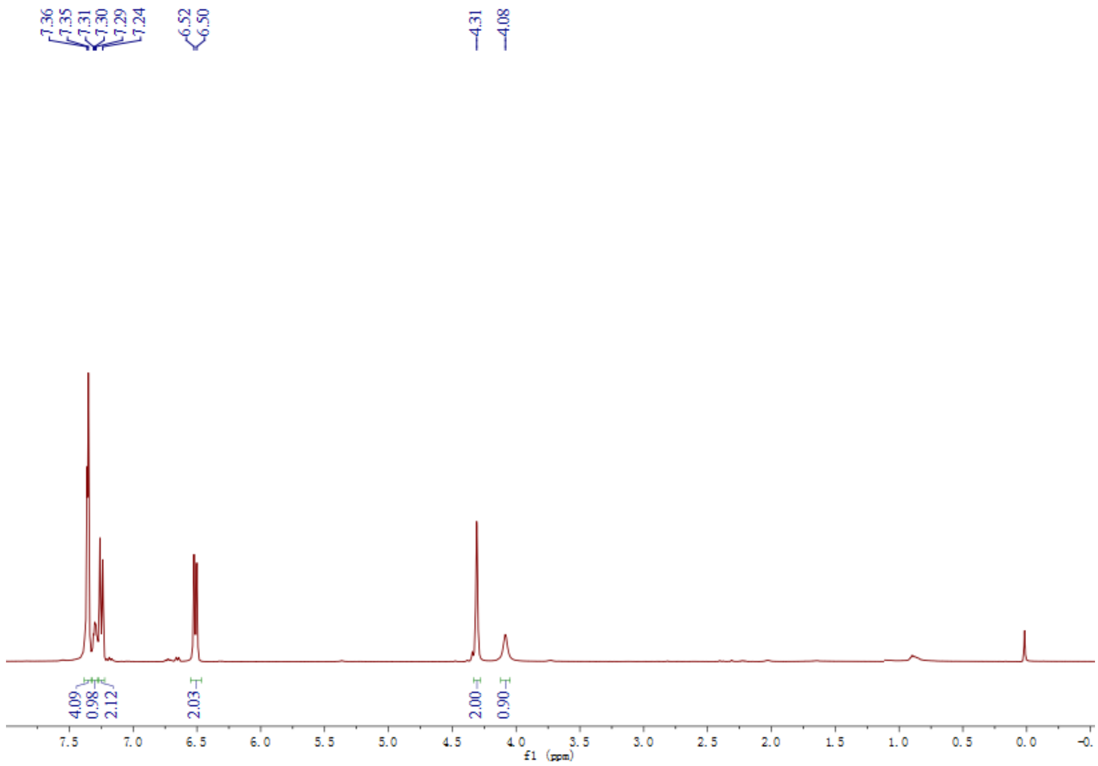
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **10b**



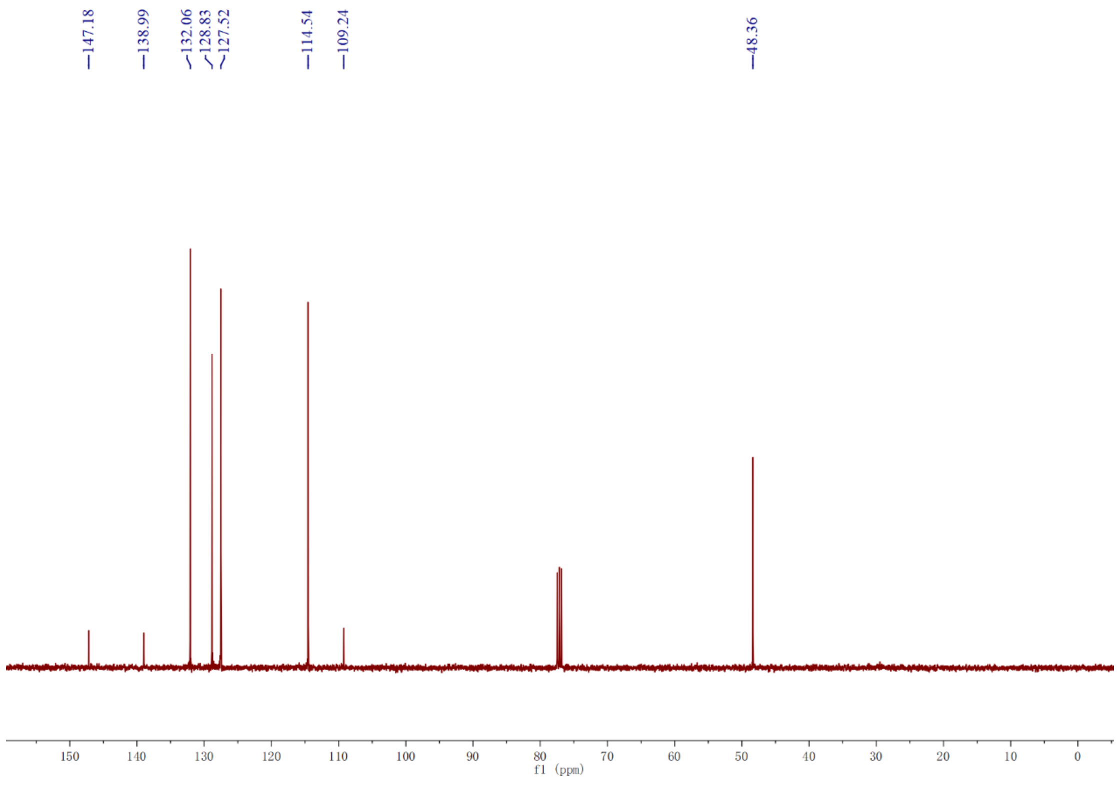
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **10c**



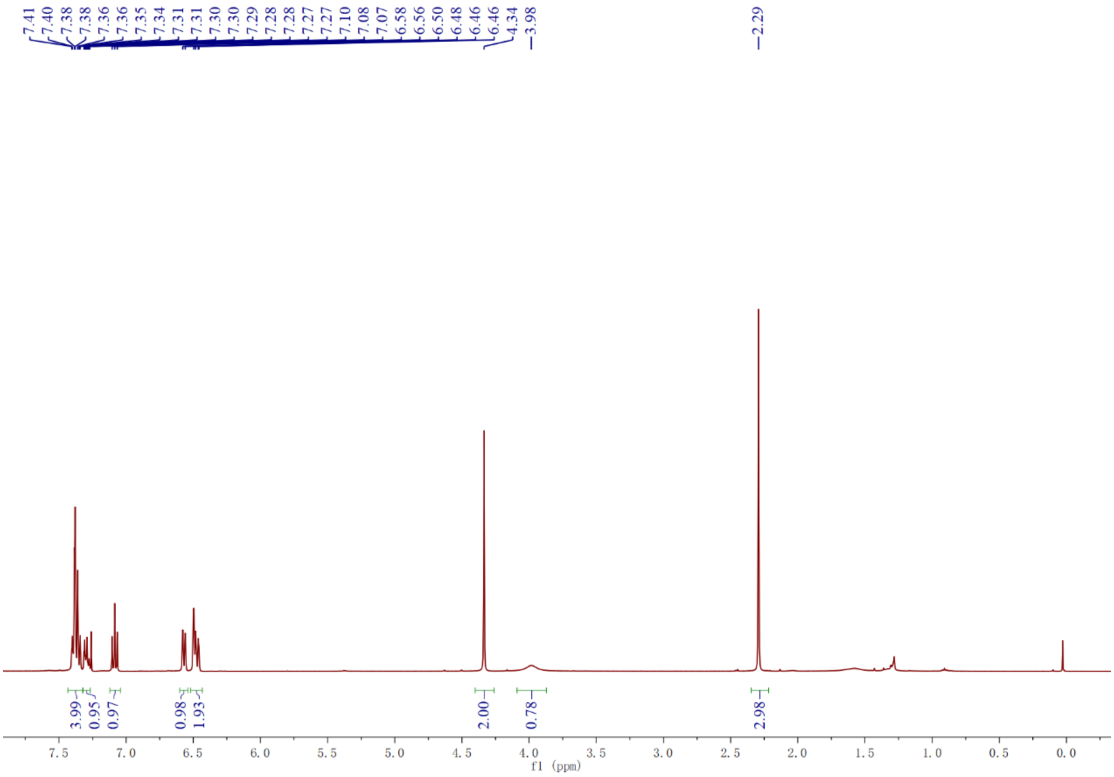
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **10c**



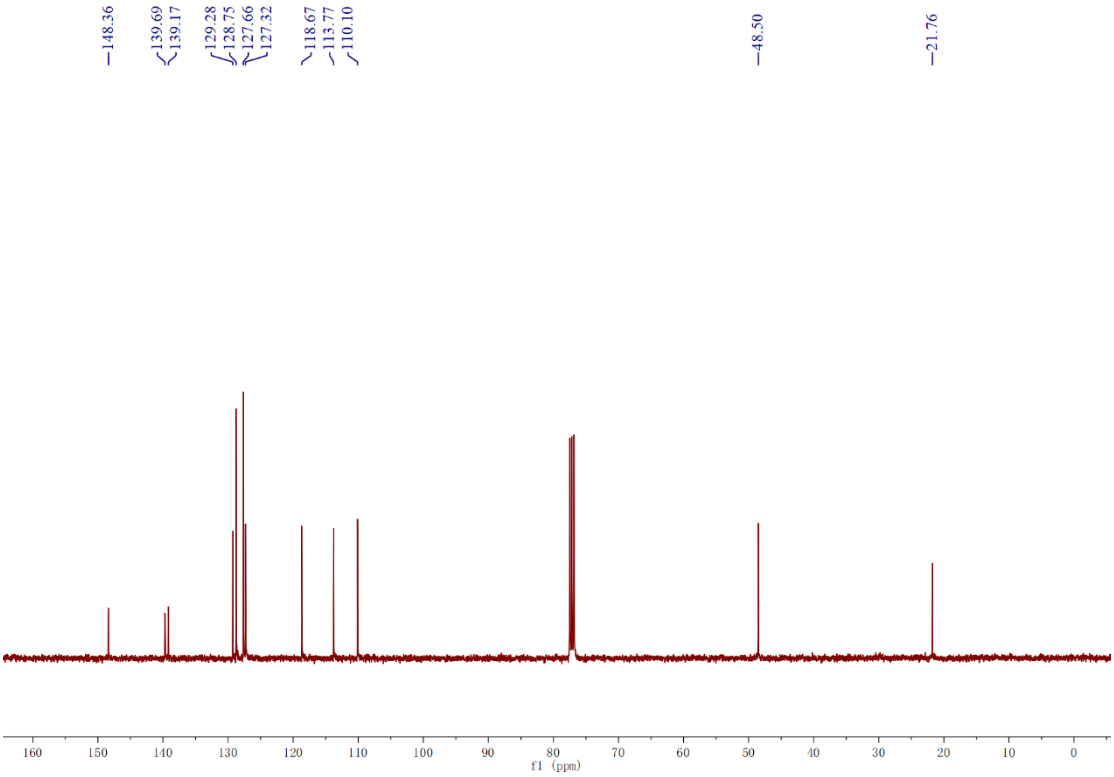
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **10d**



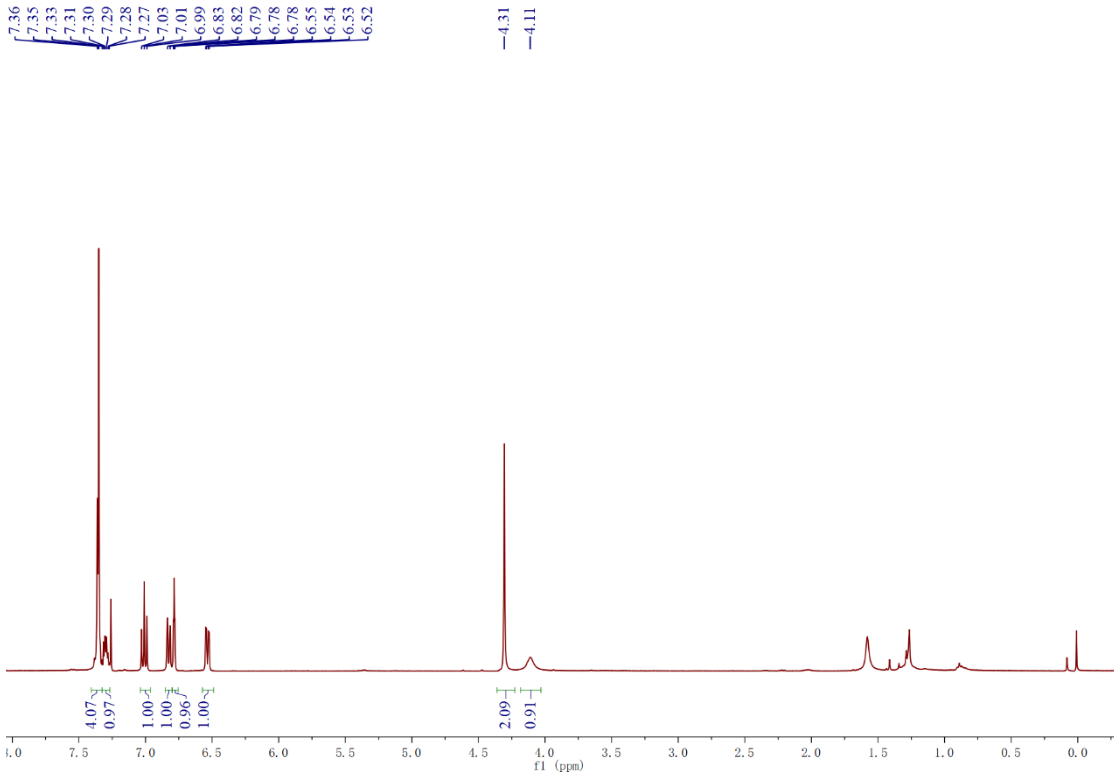
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **10d**



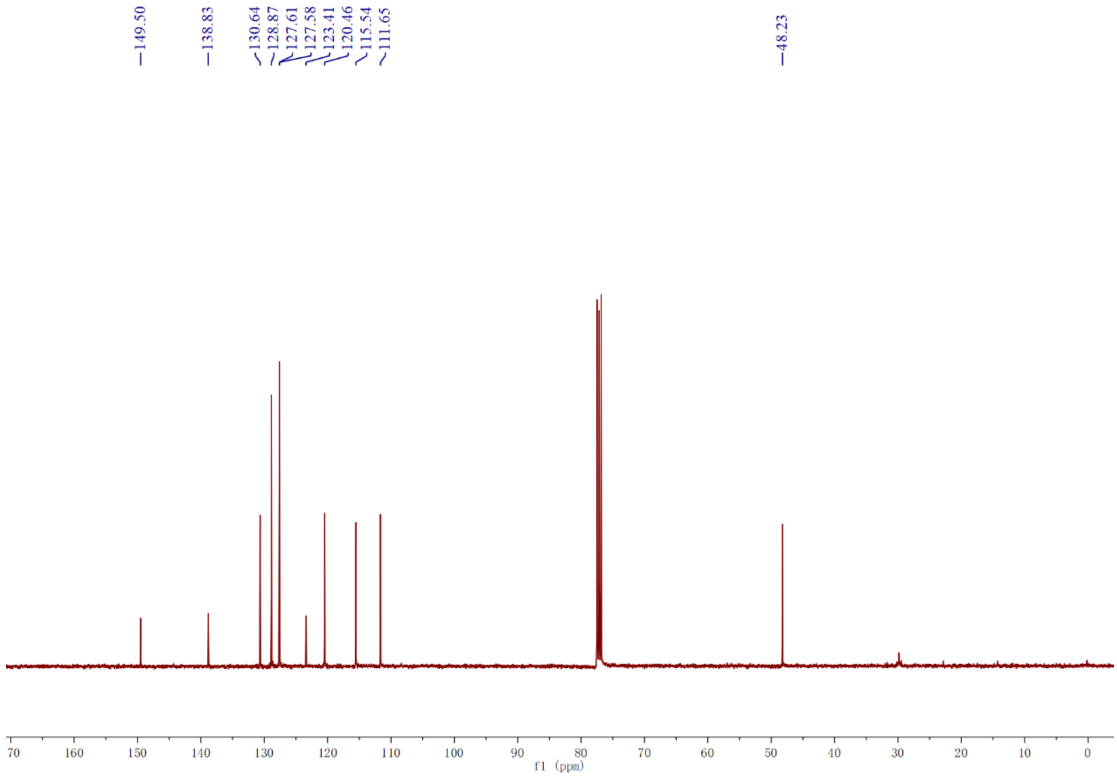
^{1}H NMR (400 MHz, CDCl$_3$) spectrum of **10e**



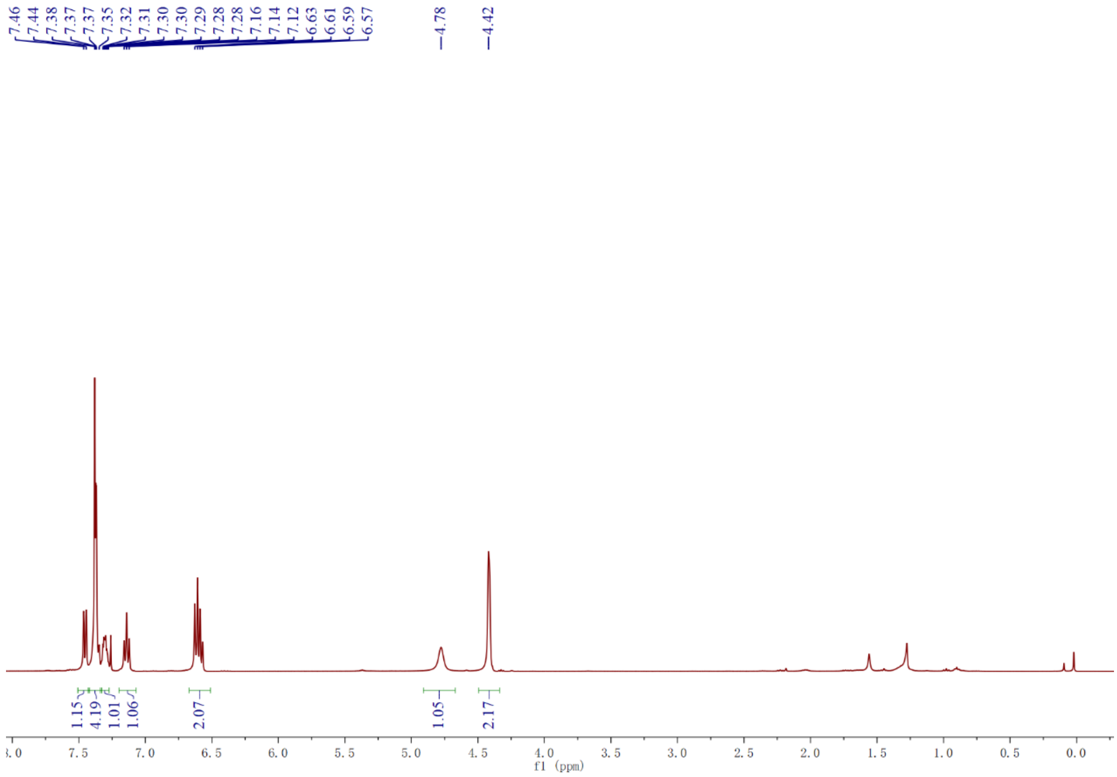
^{13}C NMR (100 MHz, CDCl$_3$) spectrum of **10e**



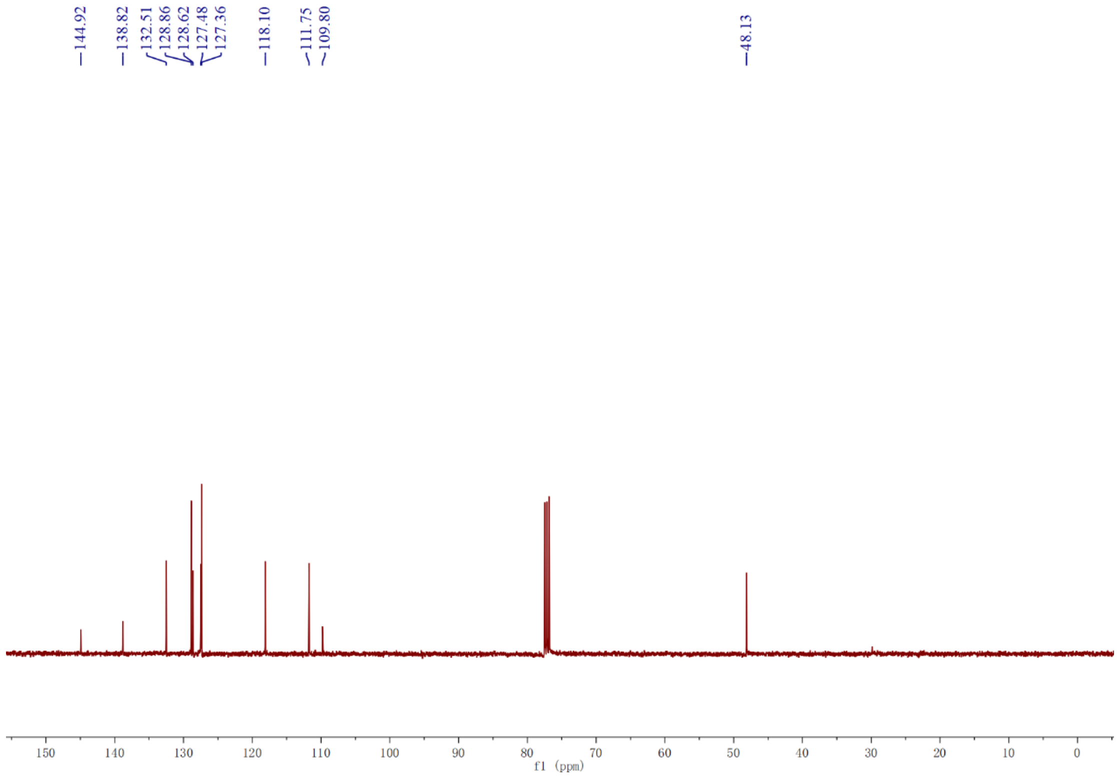
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **10f**



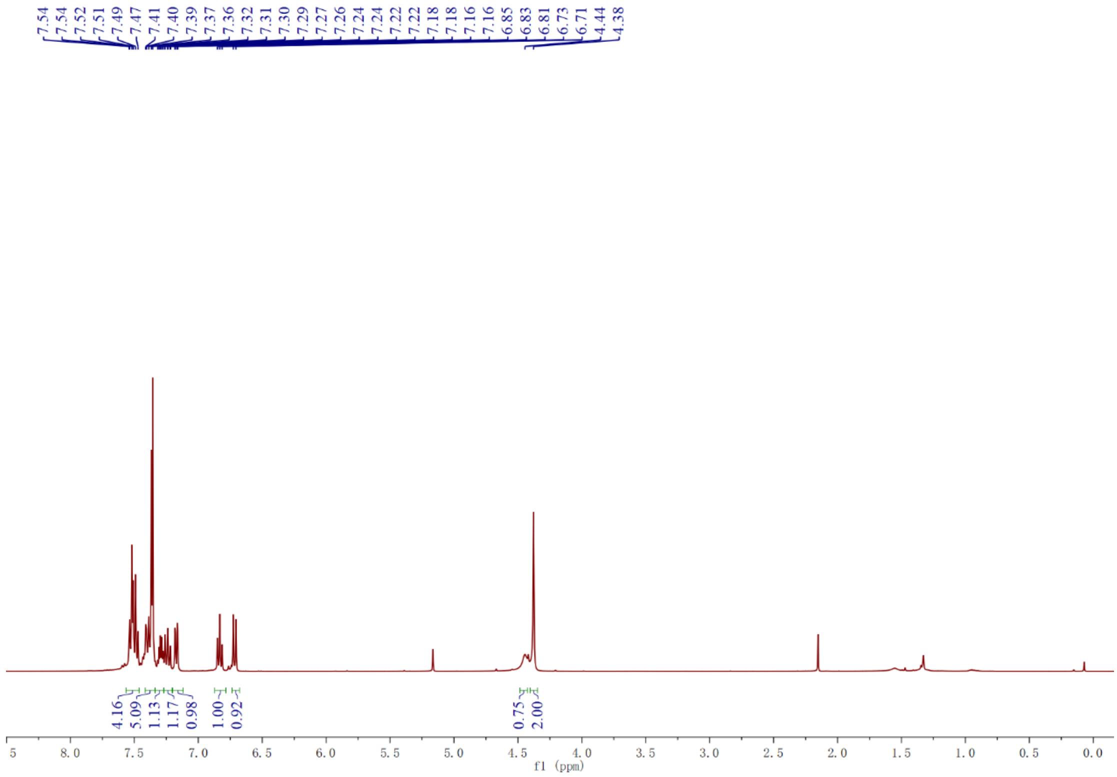
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **10f**



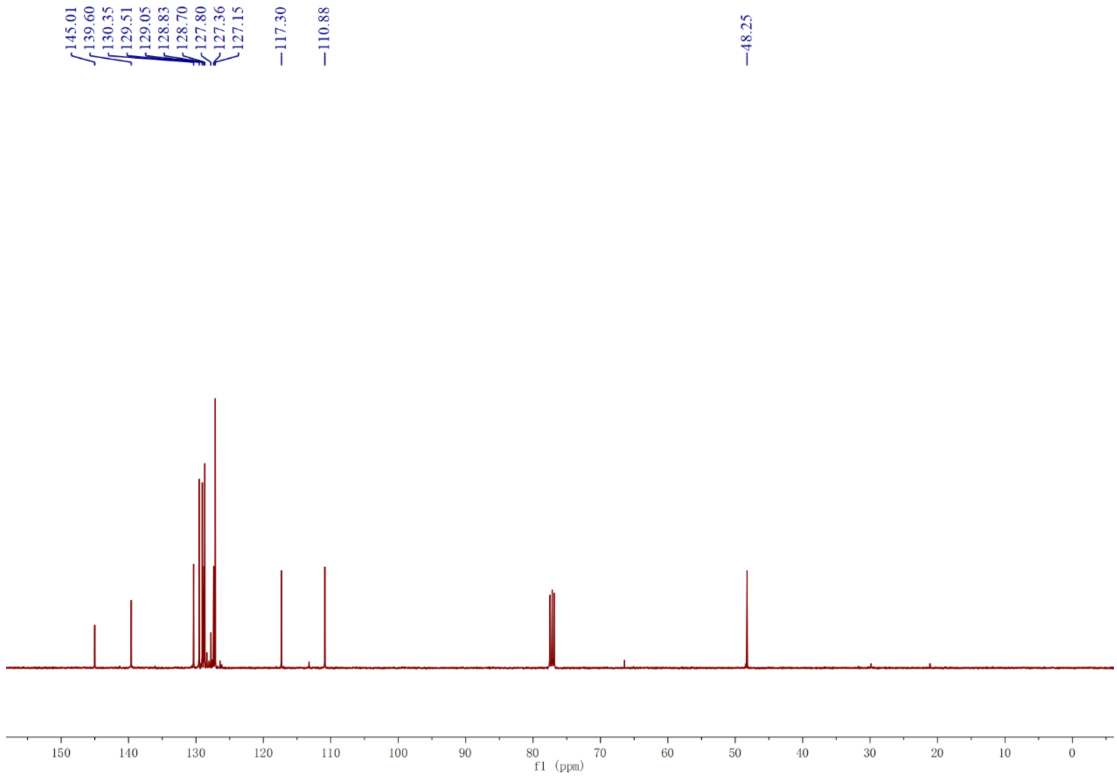
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **10g**



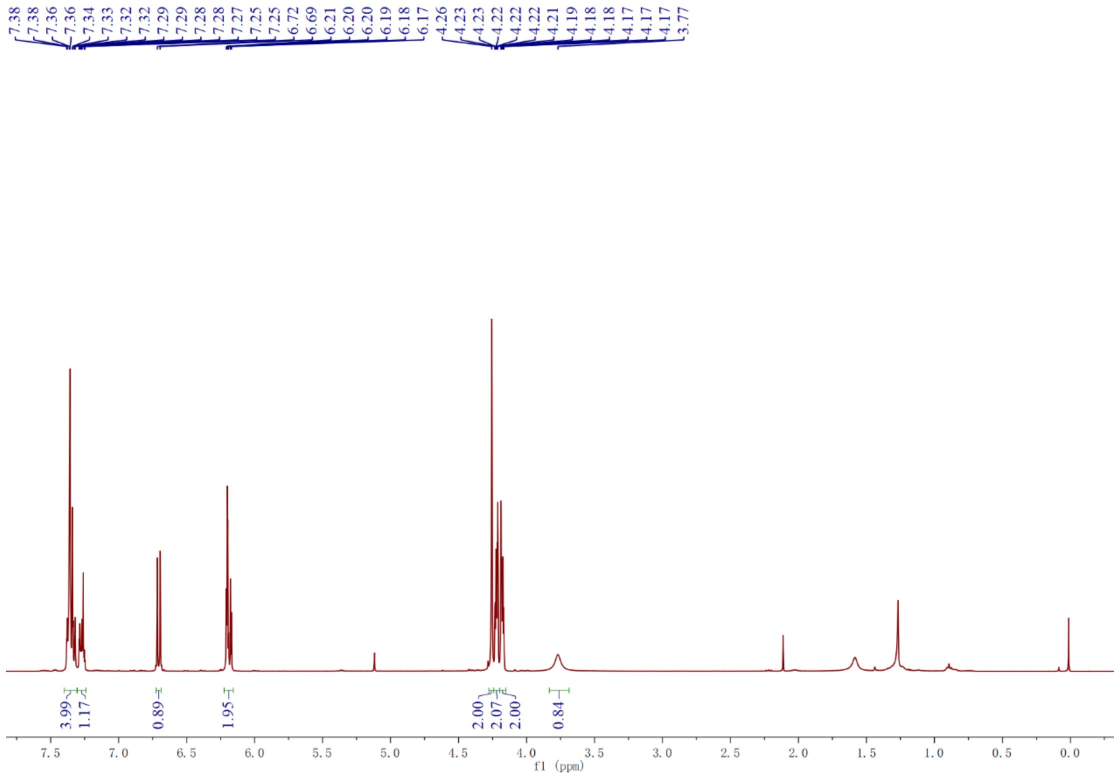
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **10g**



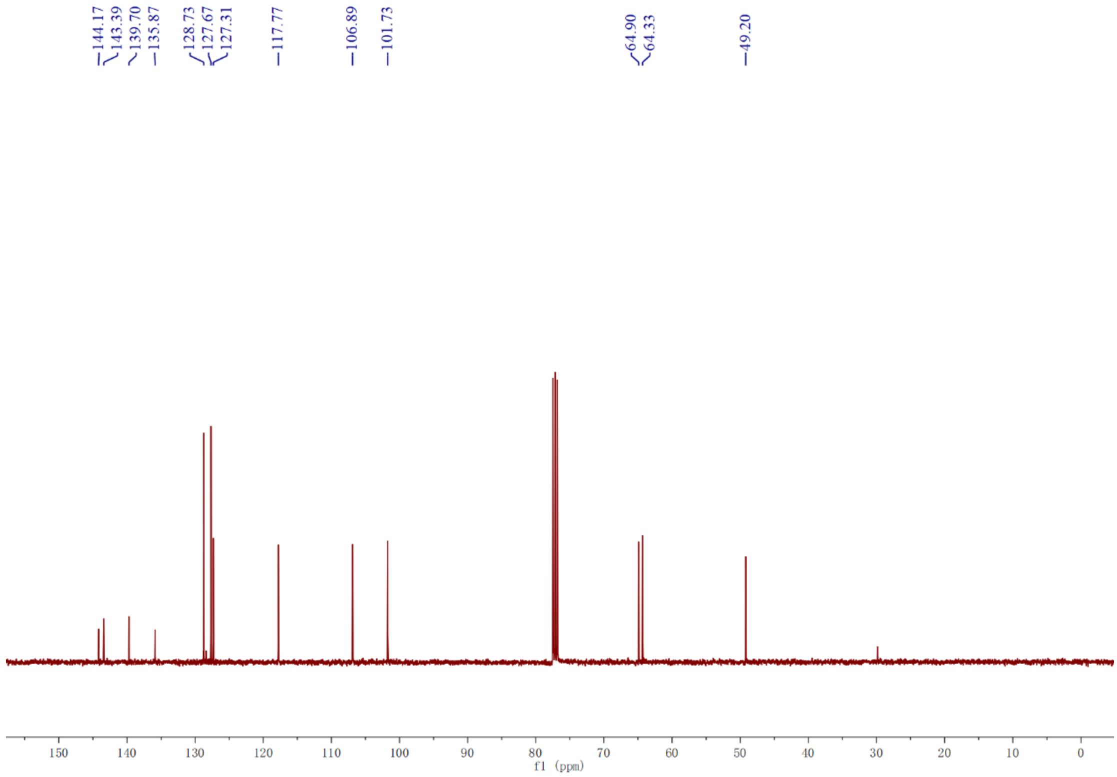
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **10h**



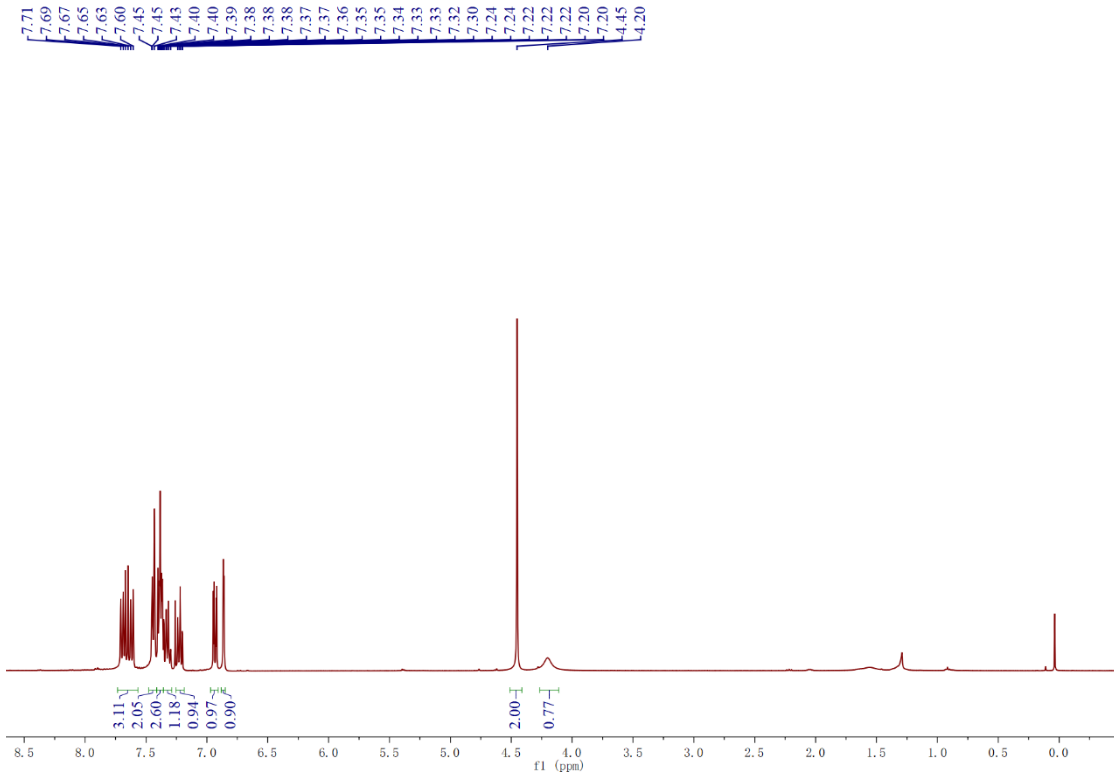
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **10h**



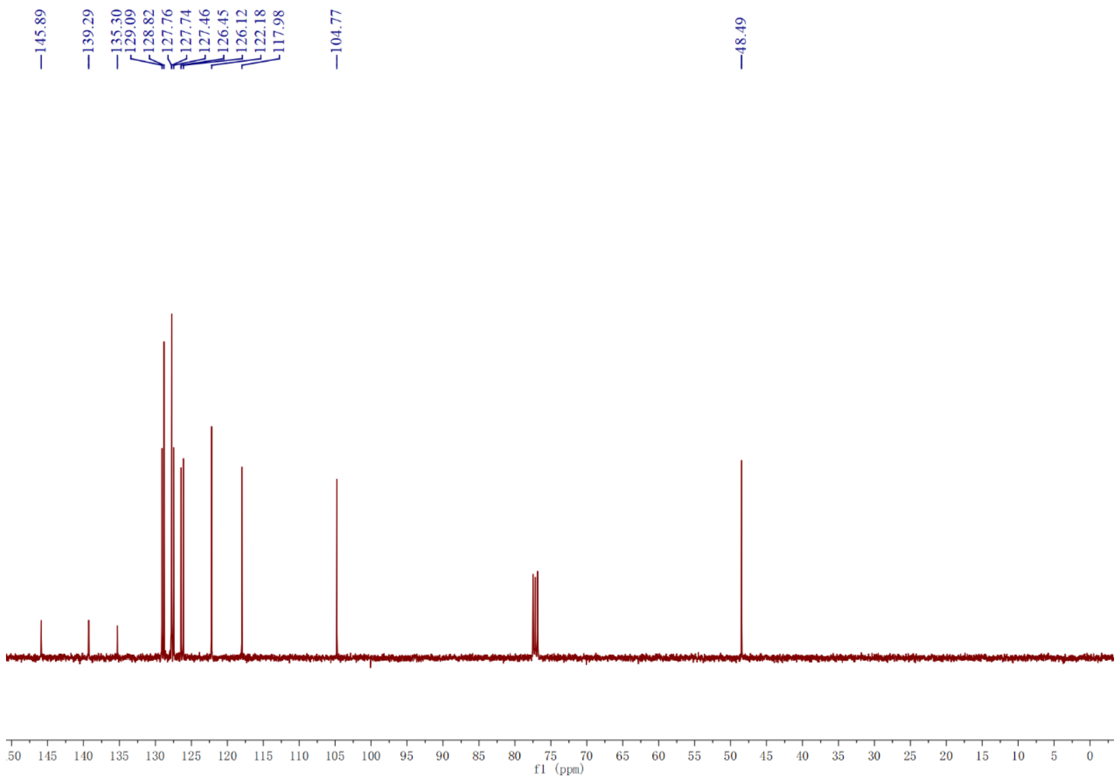
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **10i**



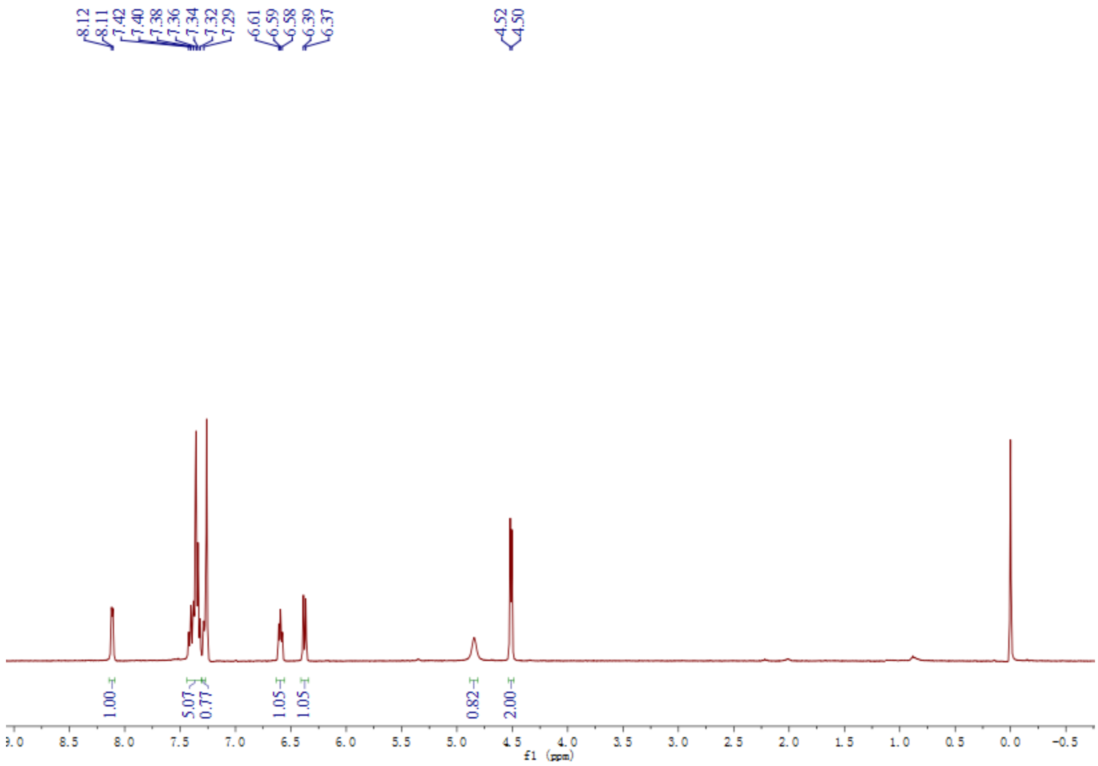
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **10i**



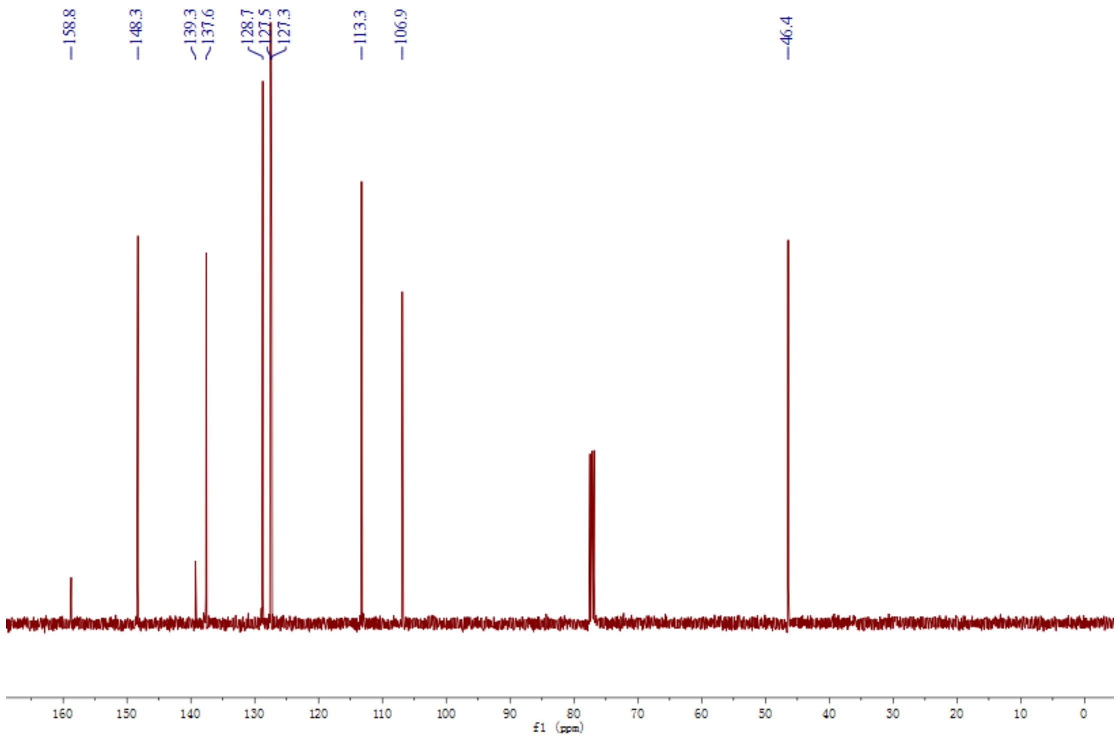
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **10j**



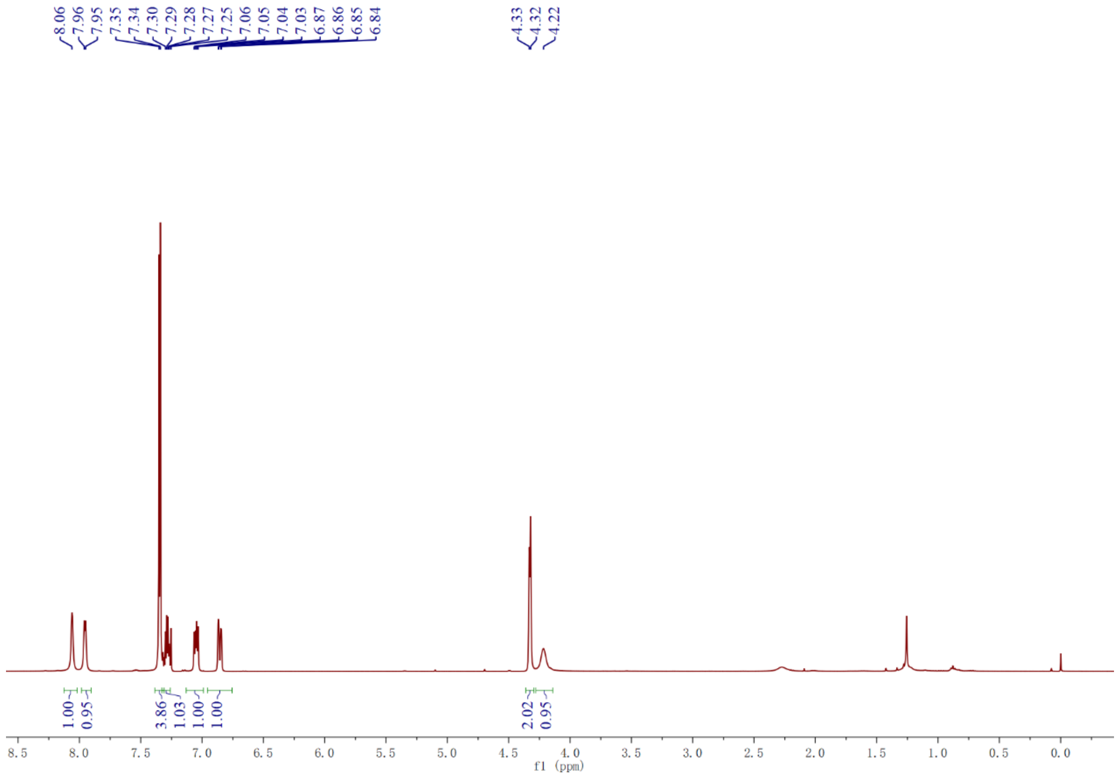
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **10j**



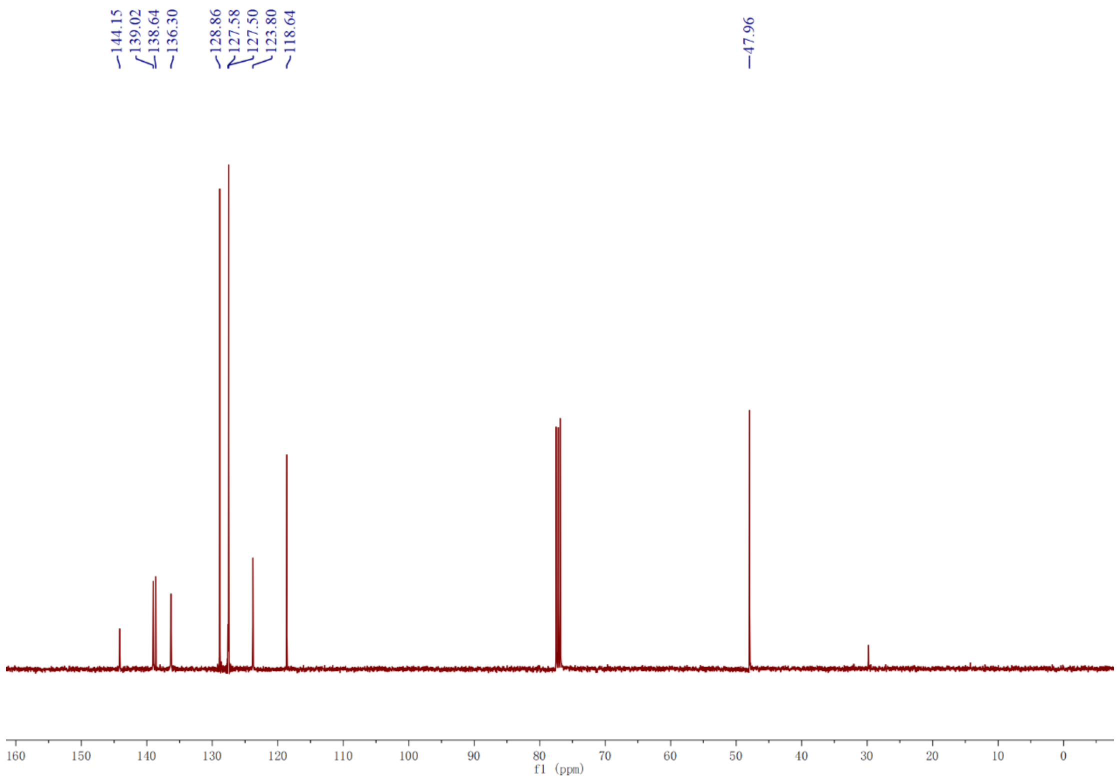
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **10k**



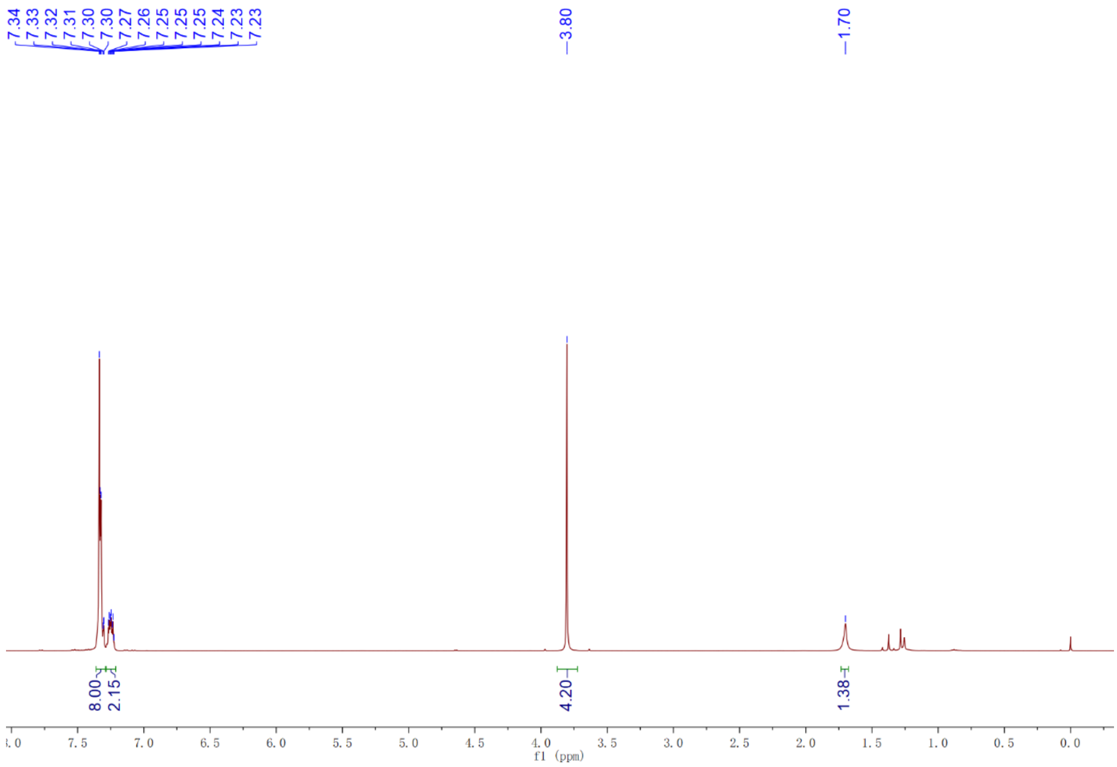
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **10k**



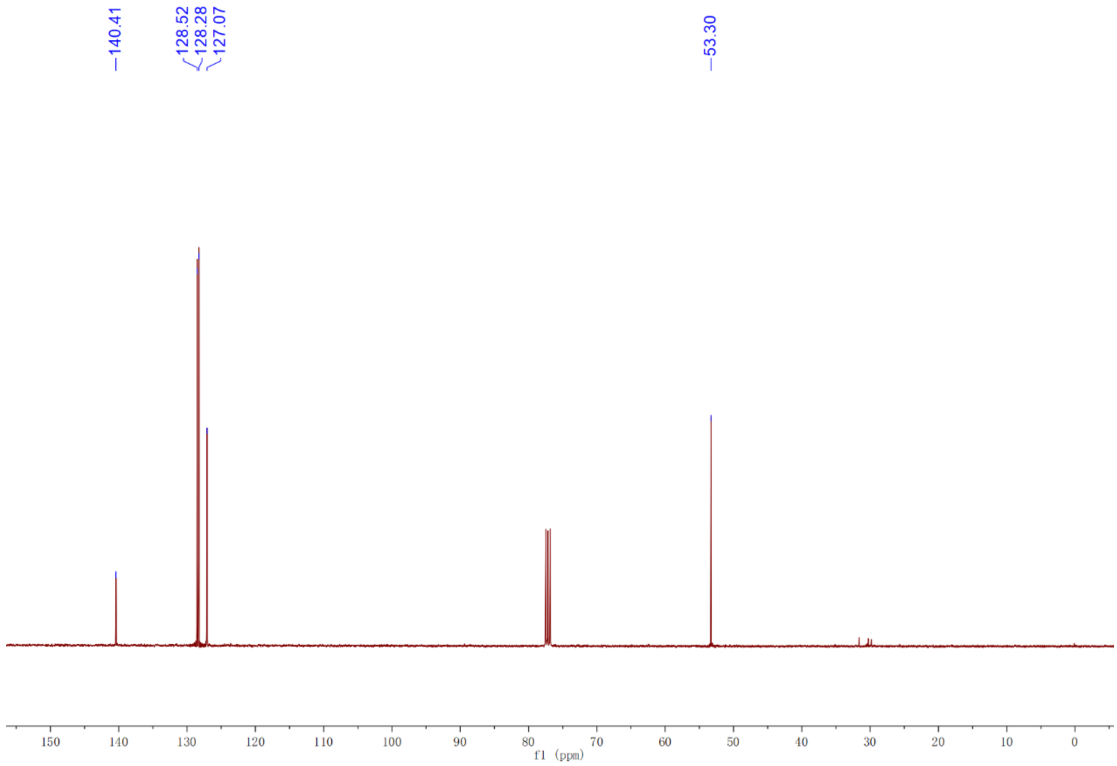
^{1}H NMR (400 MHz, CDCl$_3$) spectrum of **10l**



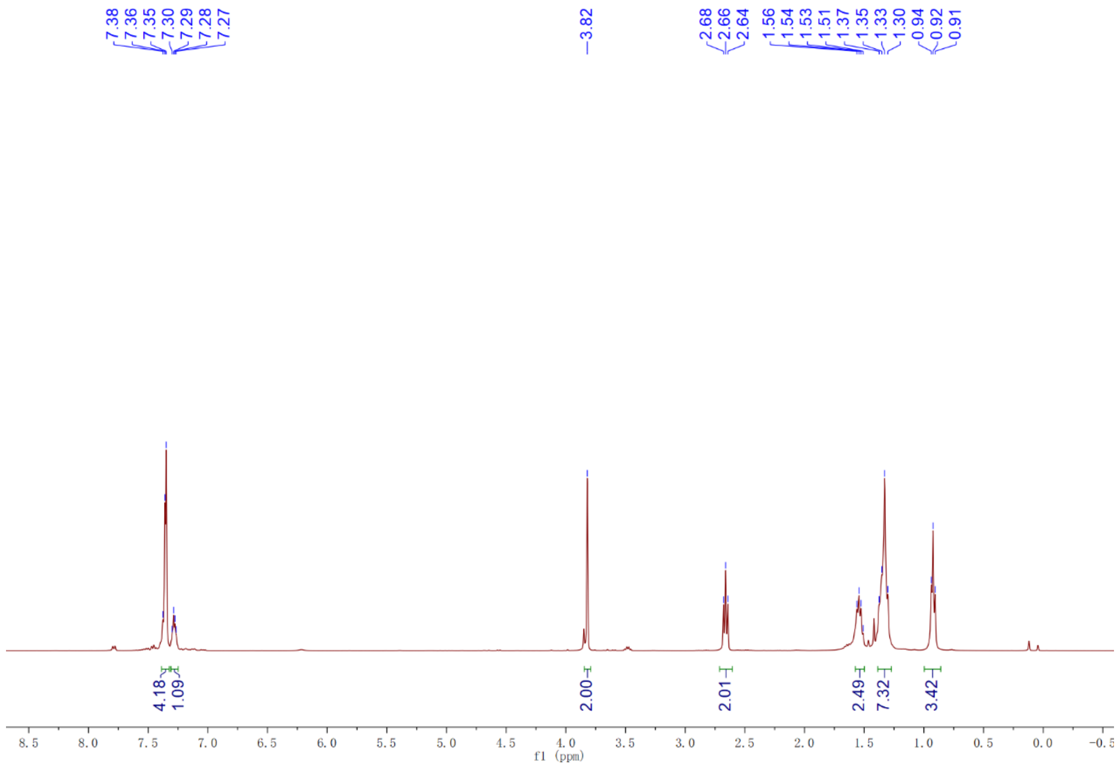
^{13}C NMR (100 MHz, CDCl$_3$) spectrum of **10l**



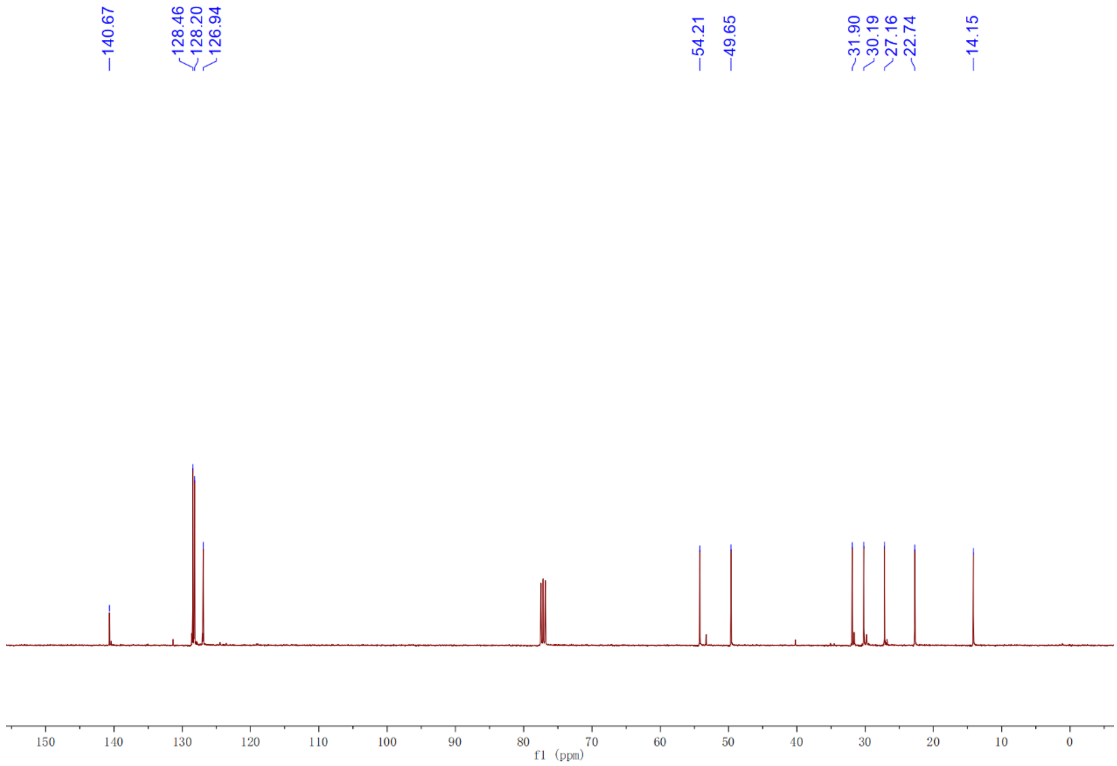
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **10m**



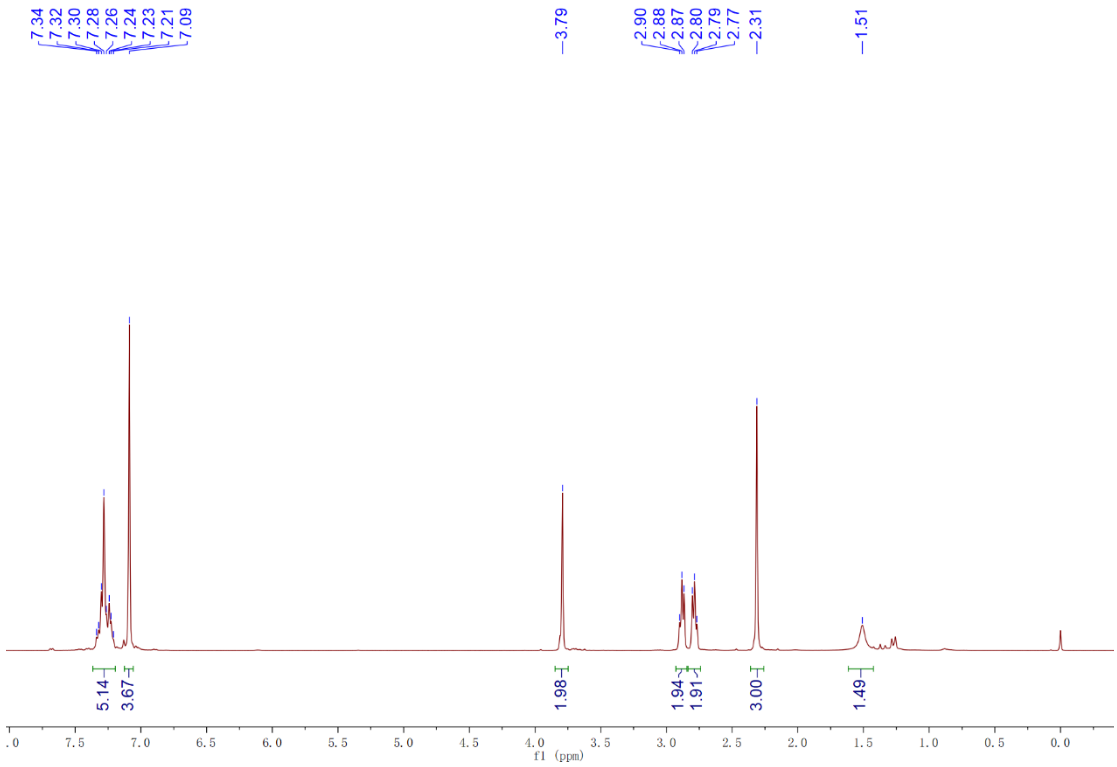
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **10m**



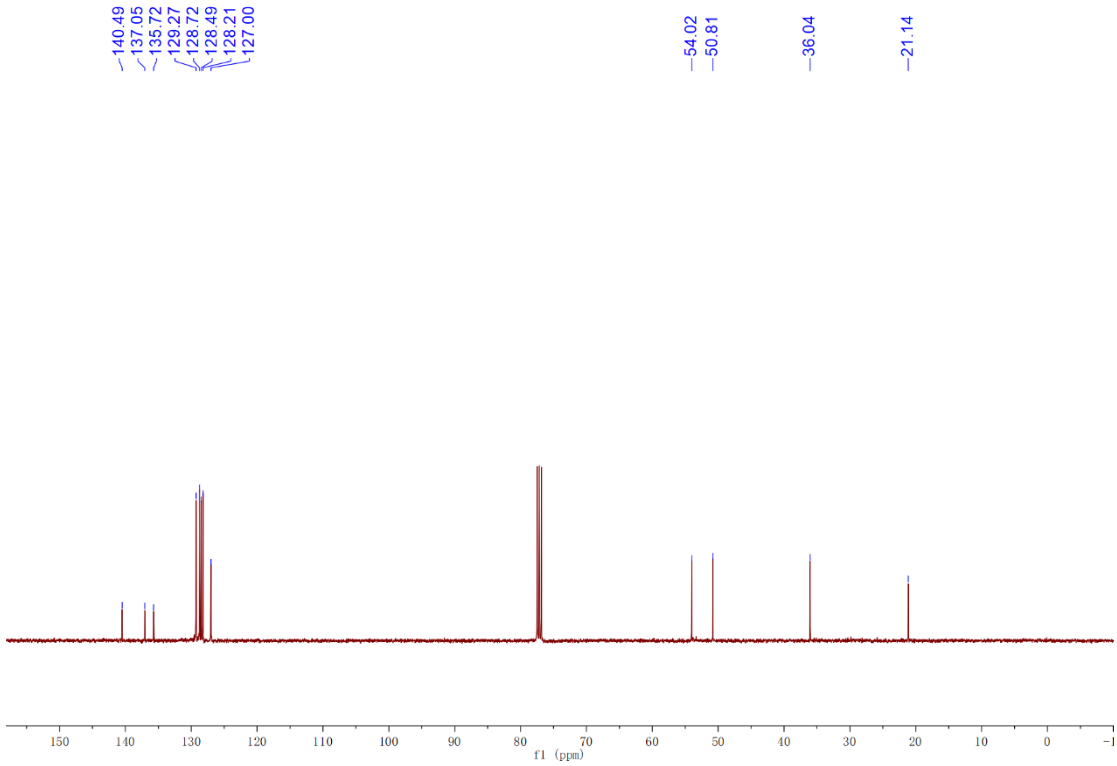
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **10n**



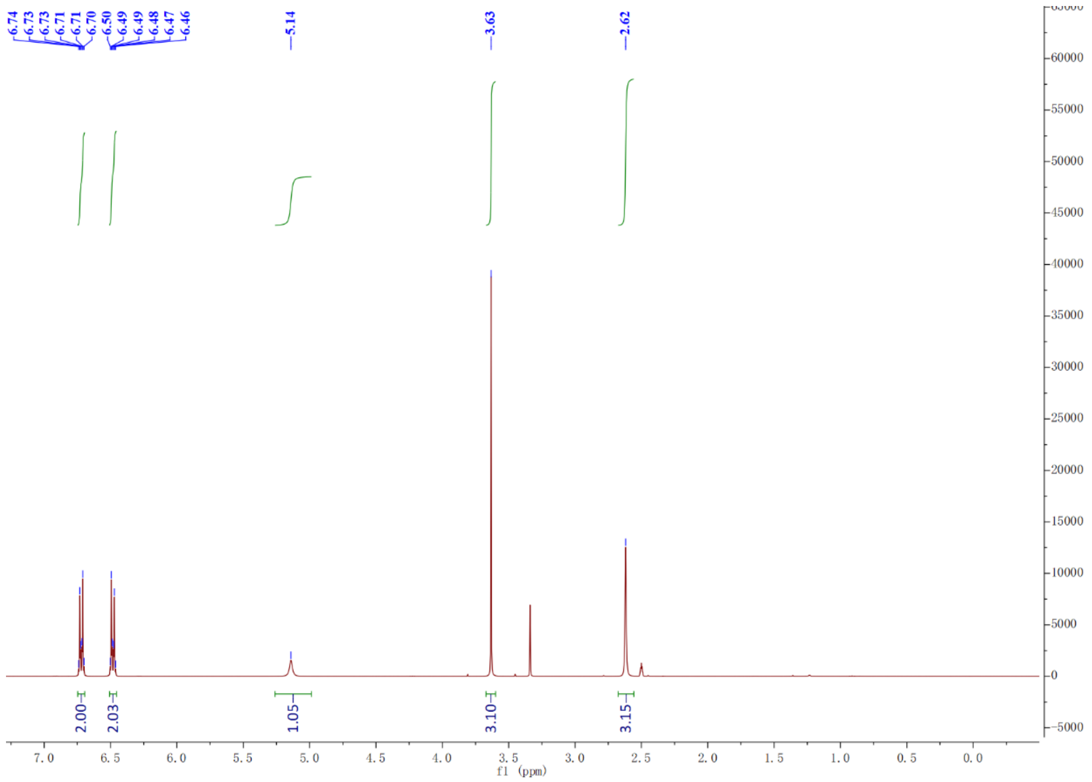
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **10n**



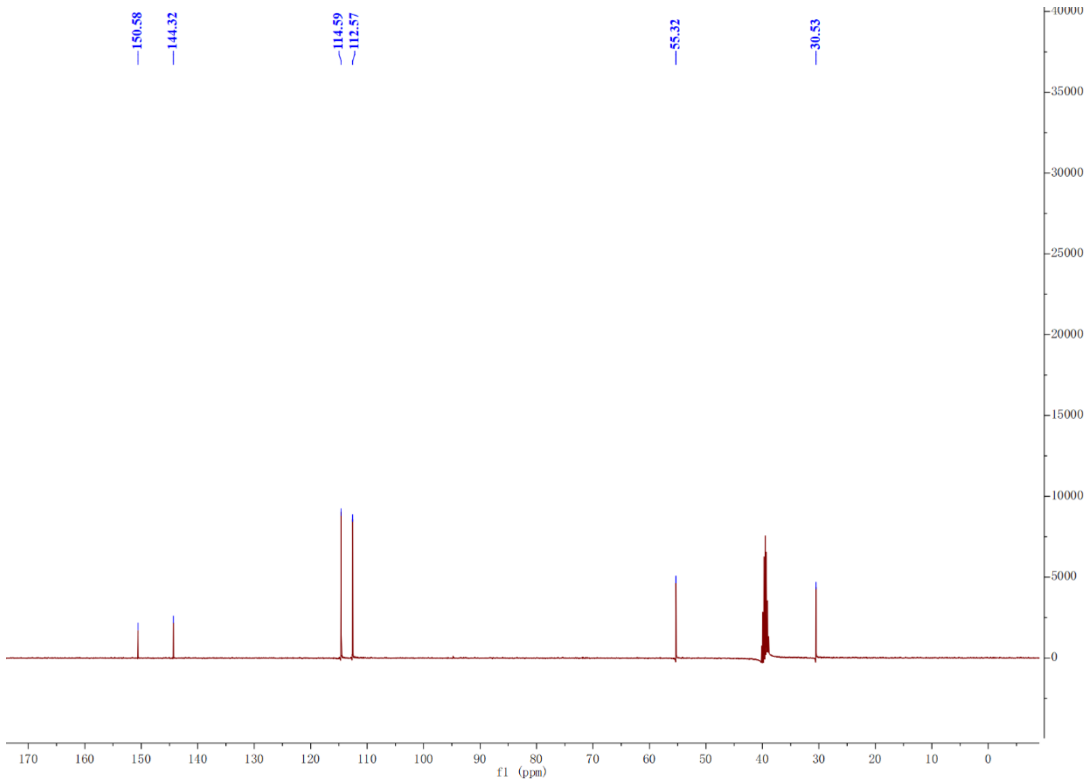
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **10o**



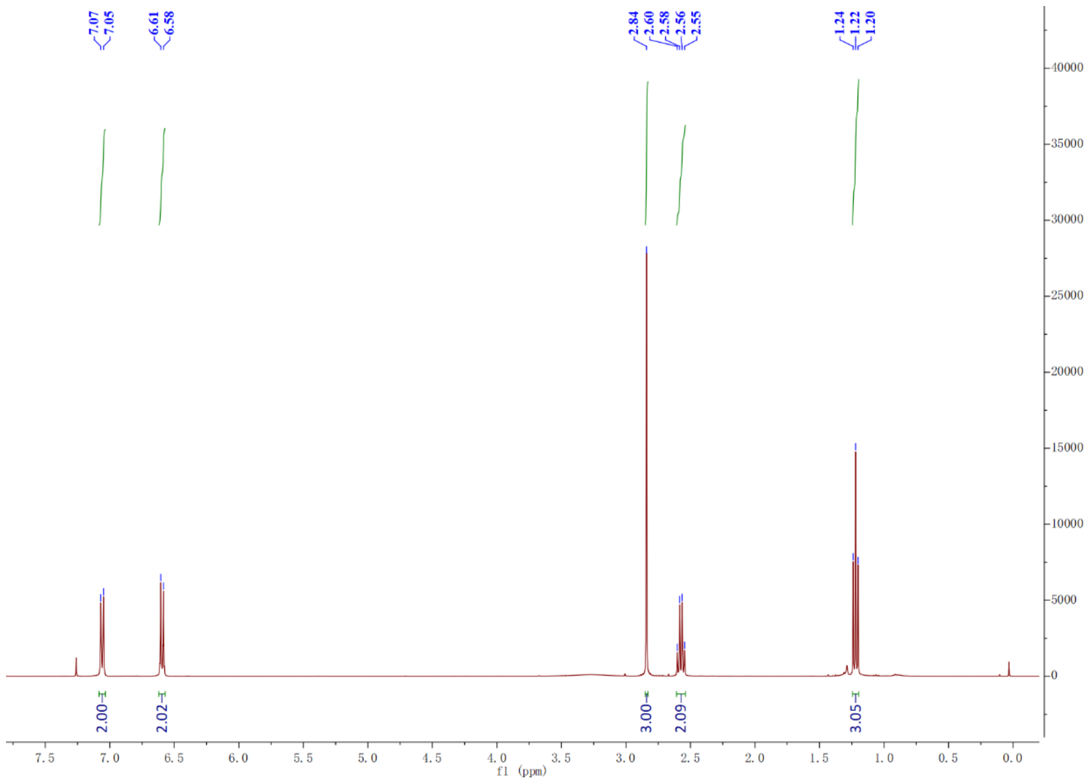
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **10o**



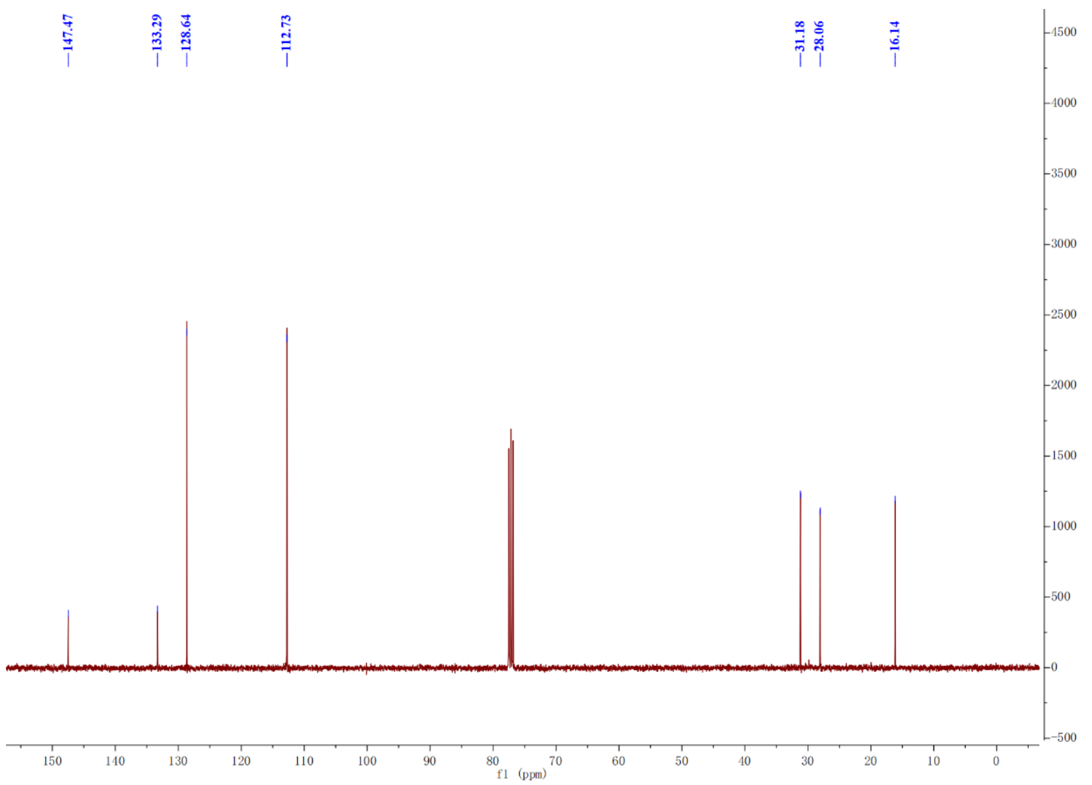
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **11b**



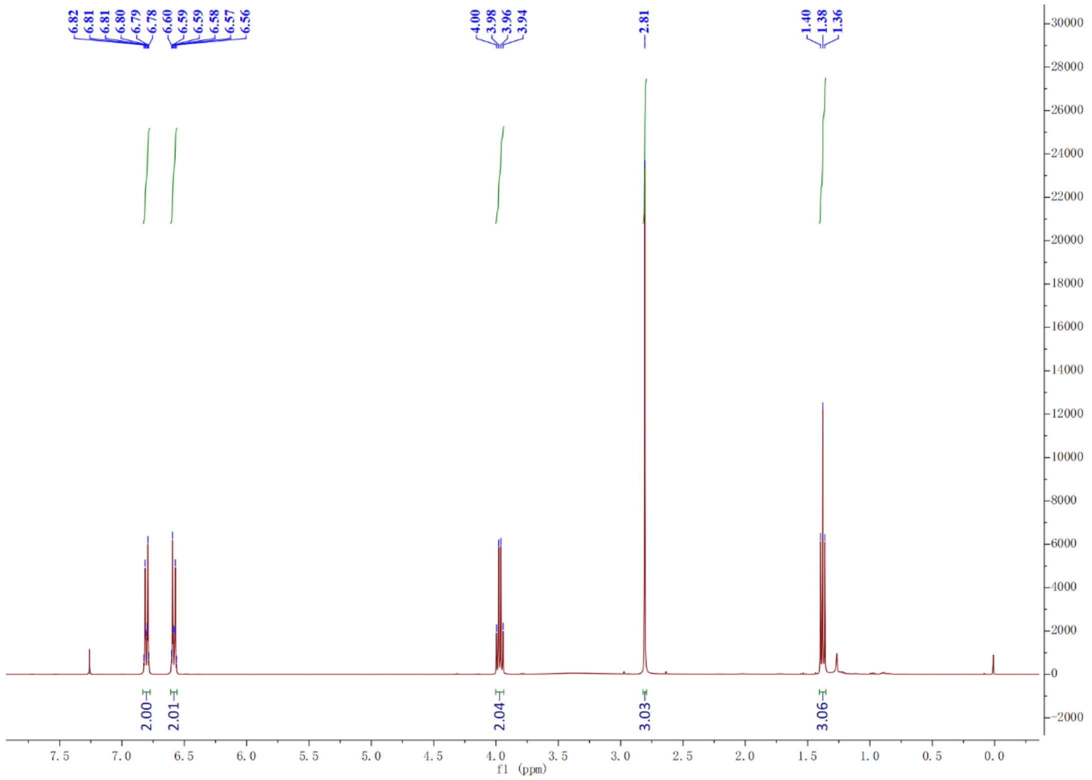
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **11b**



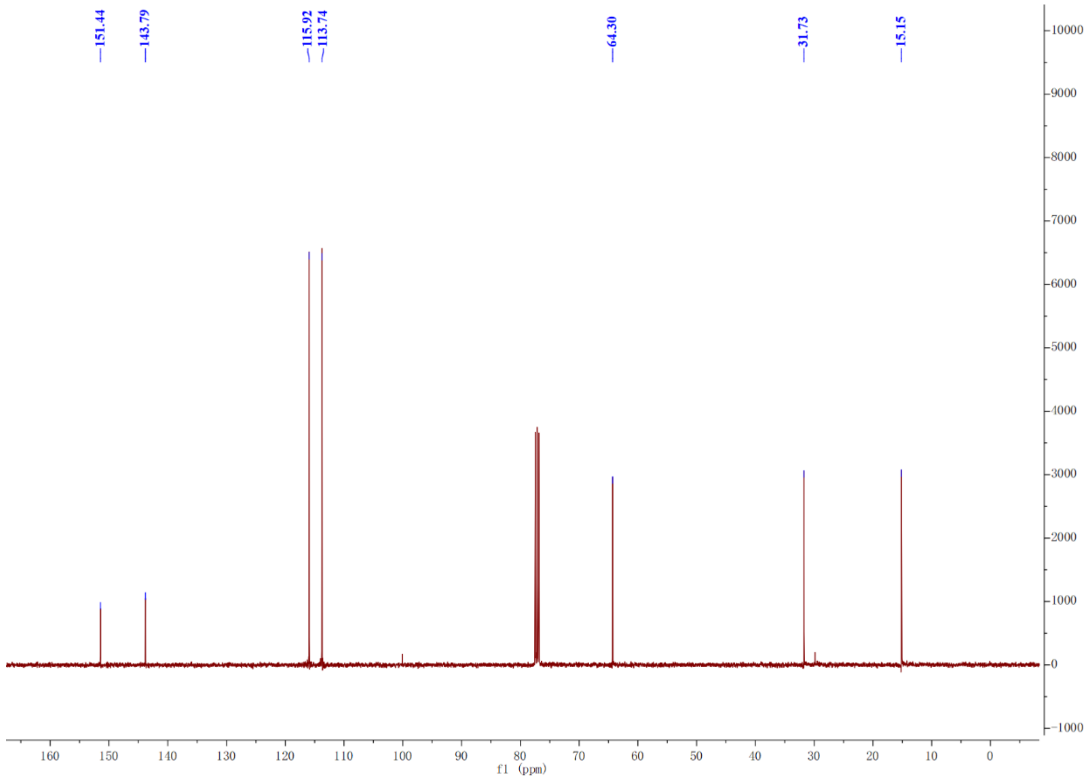
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **11c**



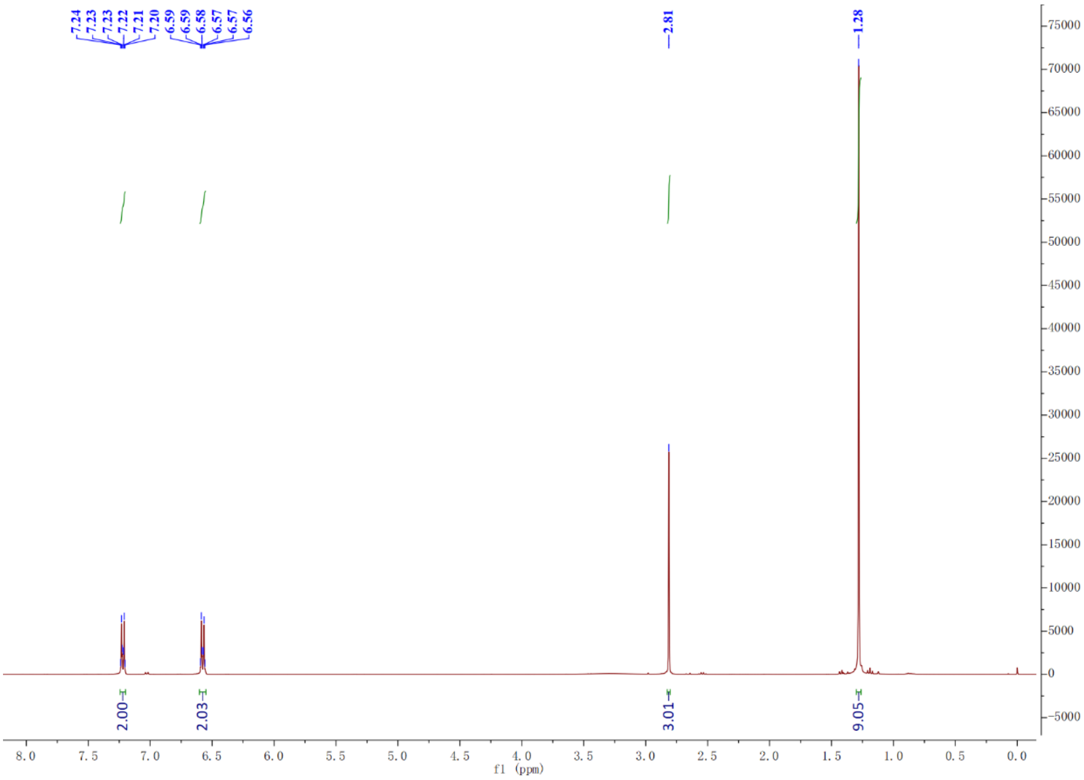
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **11c**



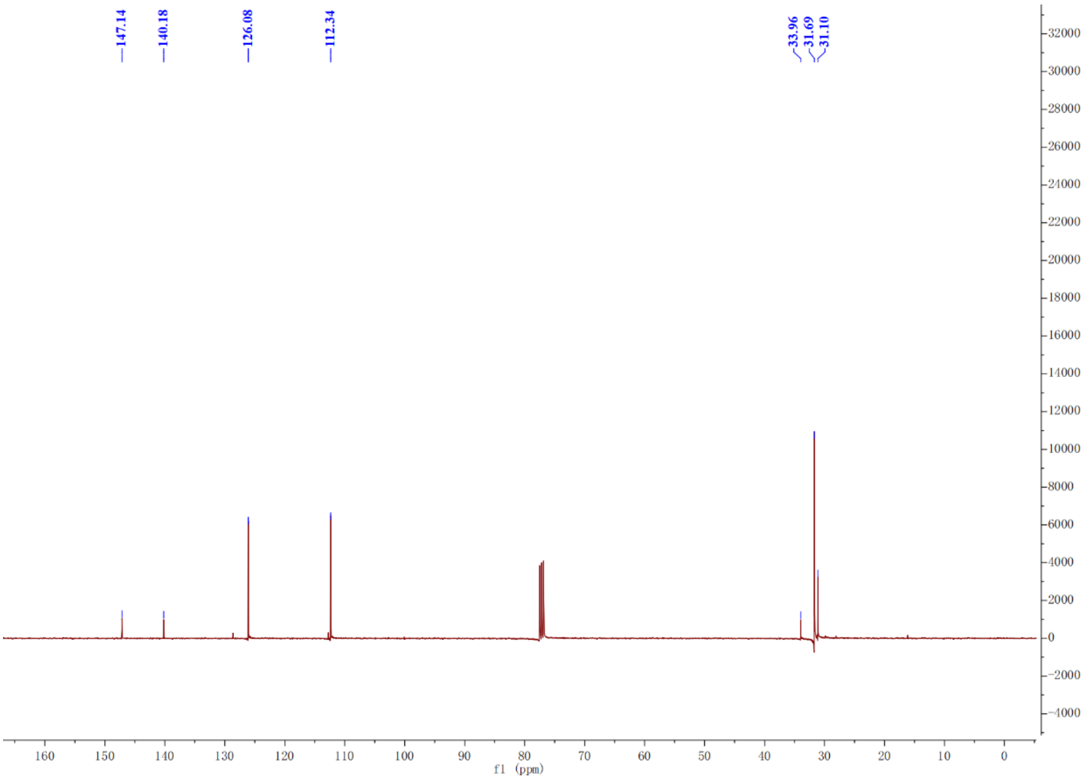
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **11d**



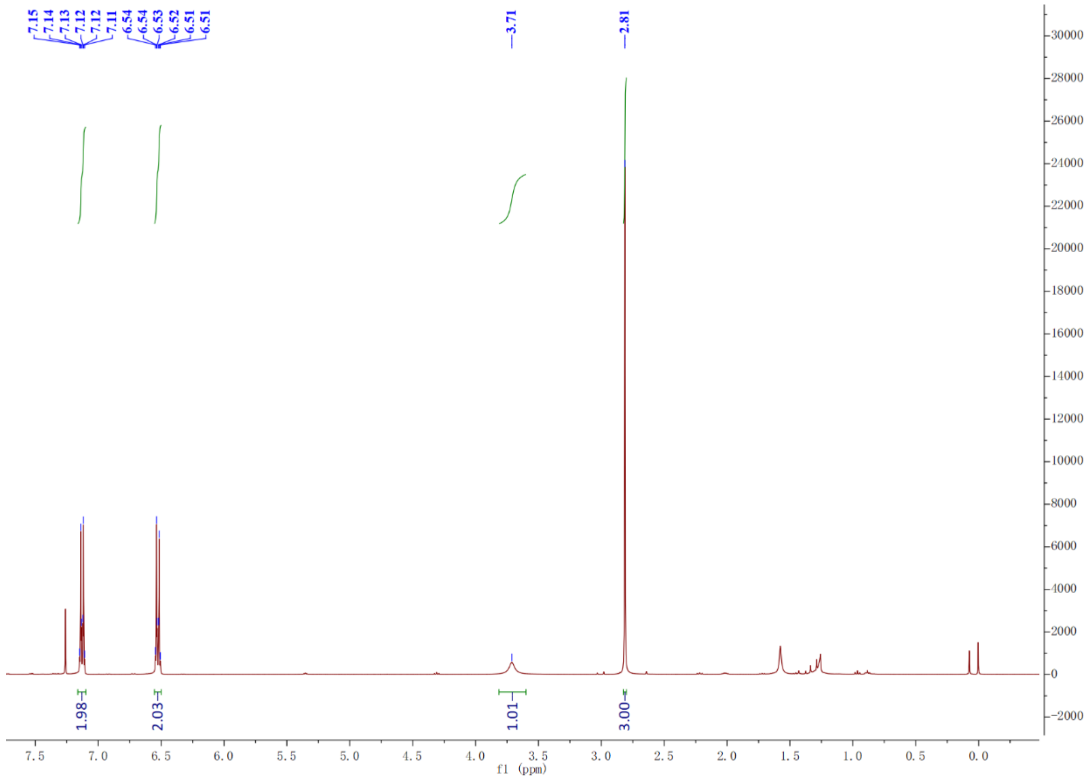
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **11d**



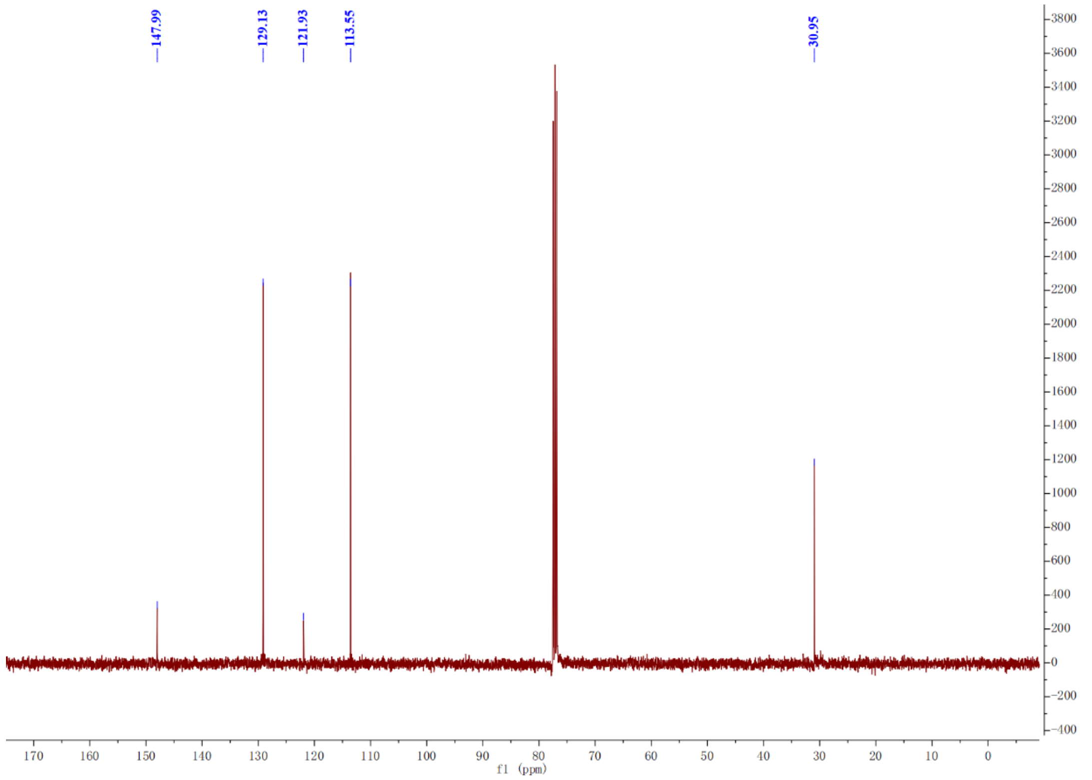
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **11e**



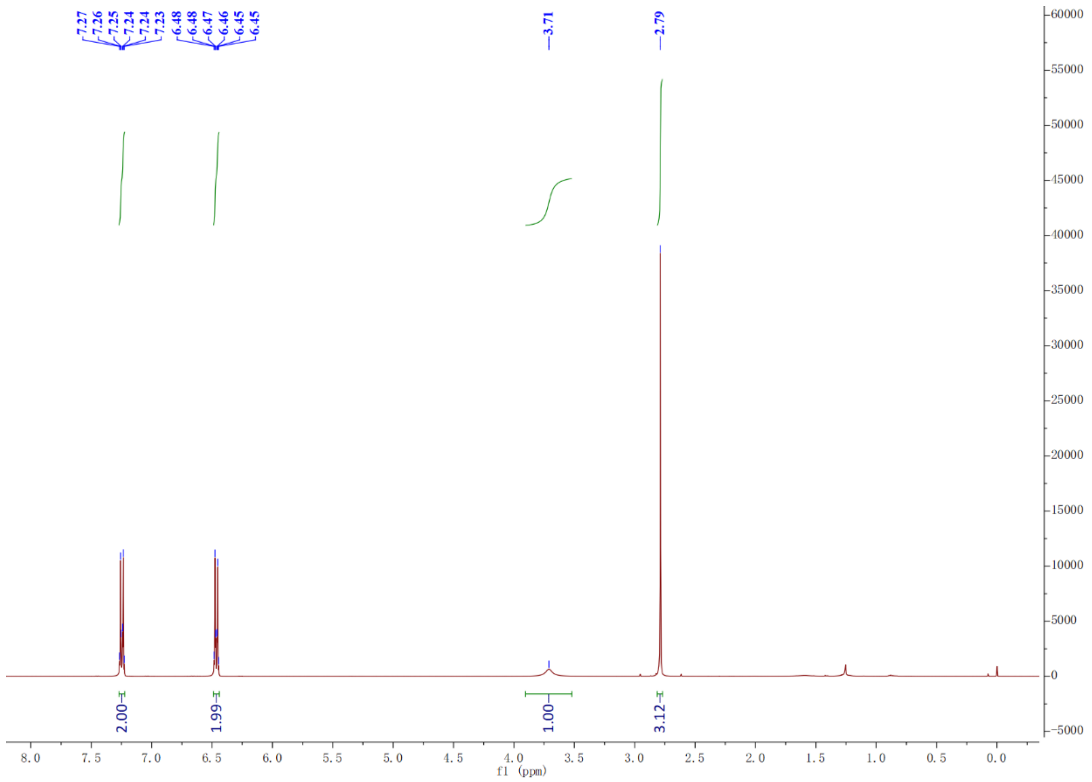
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **11e**



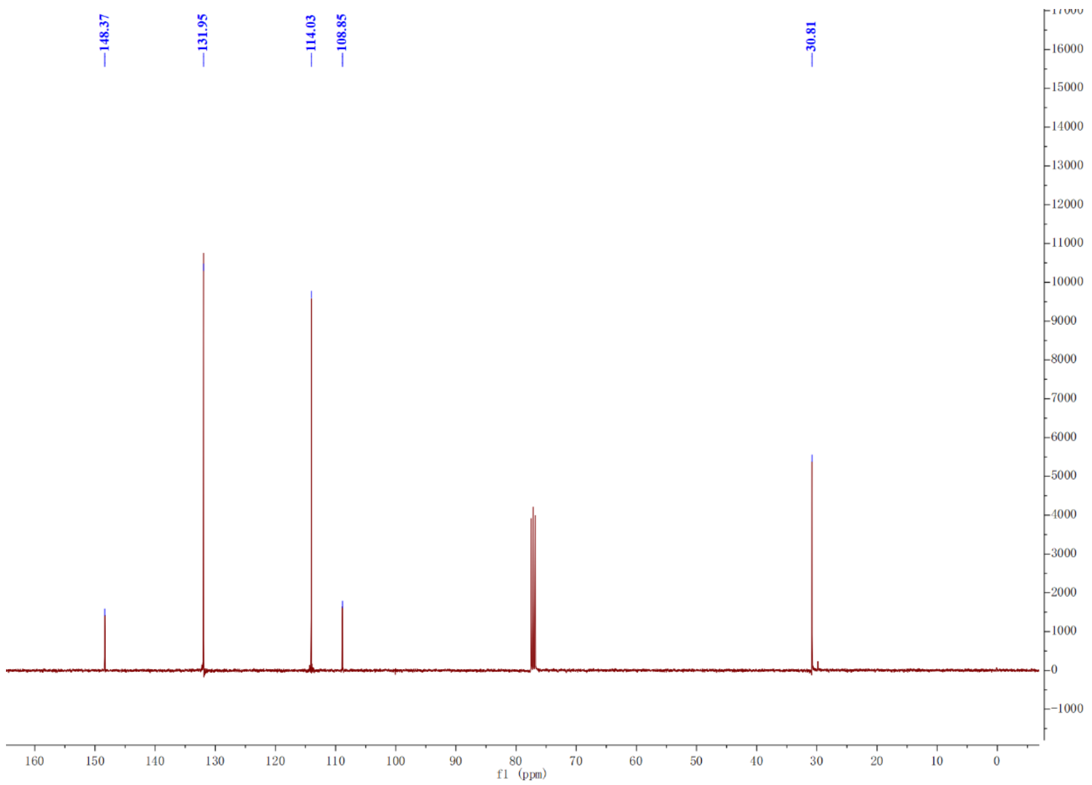
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **11f**



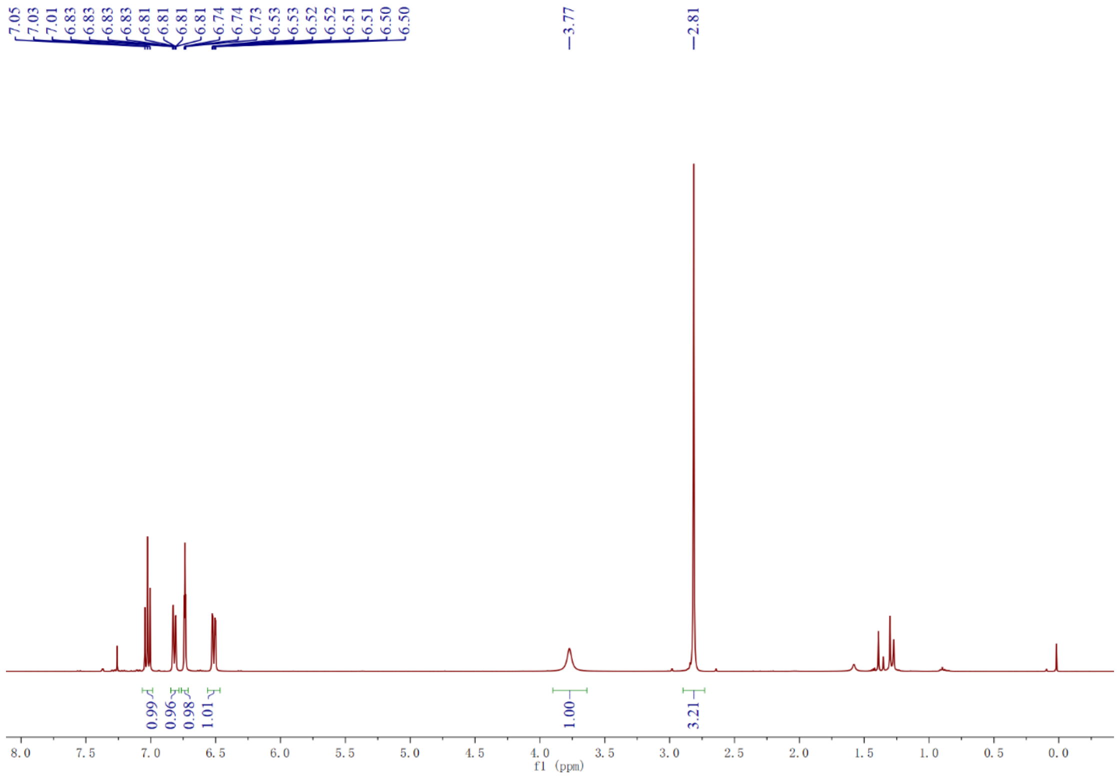
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **11f**



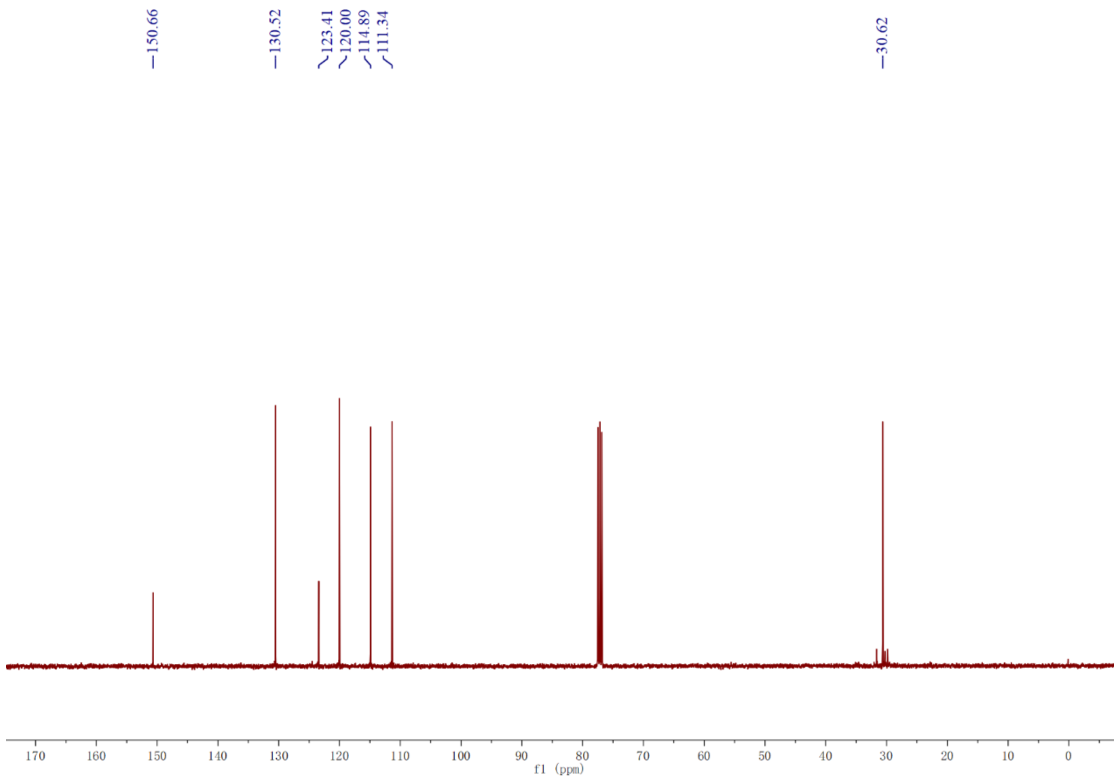
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **11g**



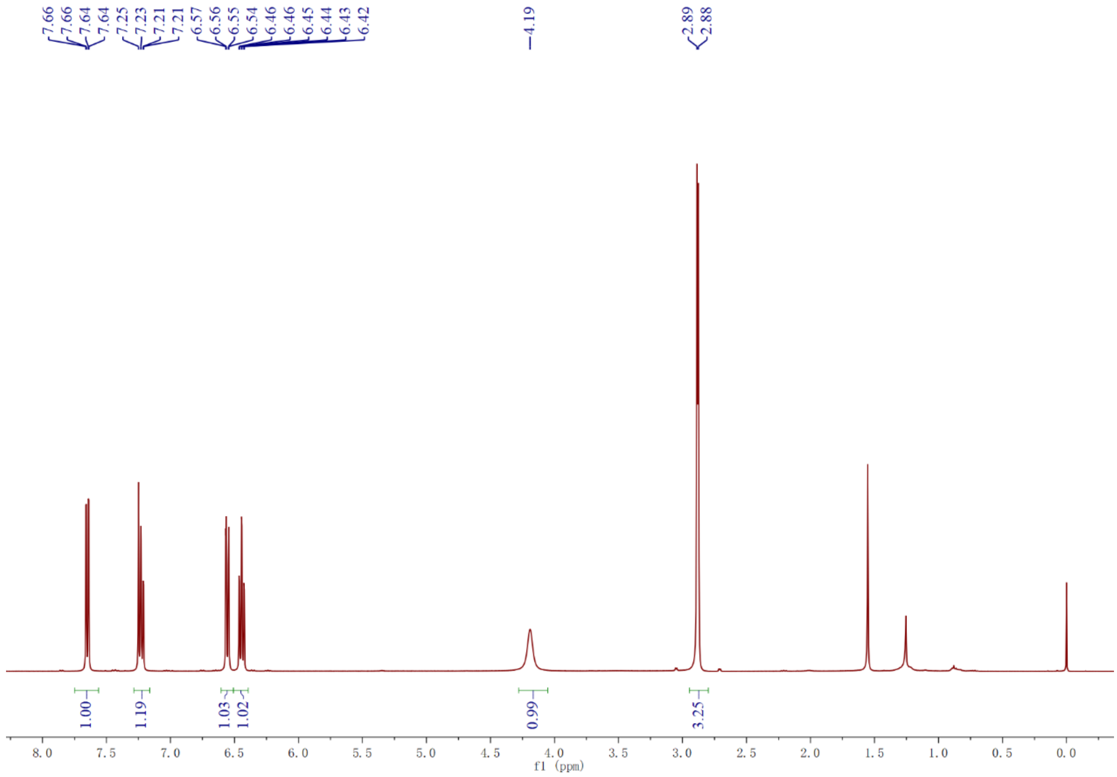
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **11g**



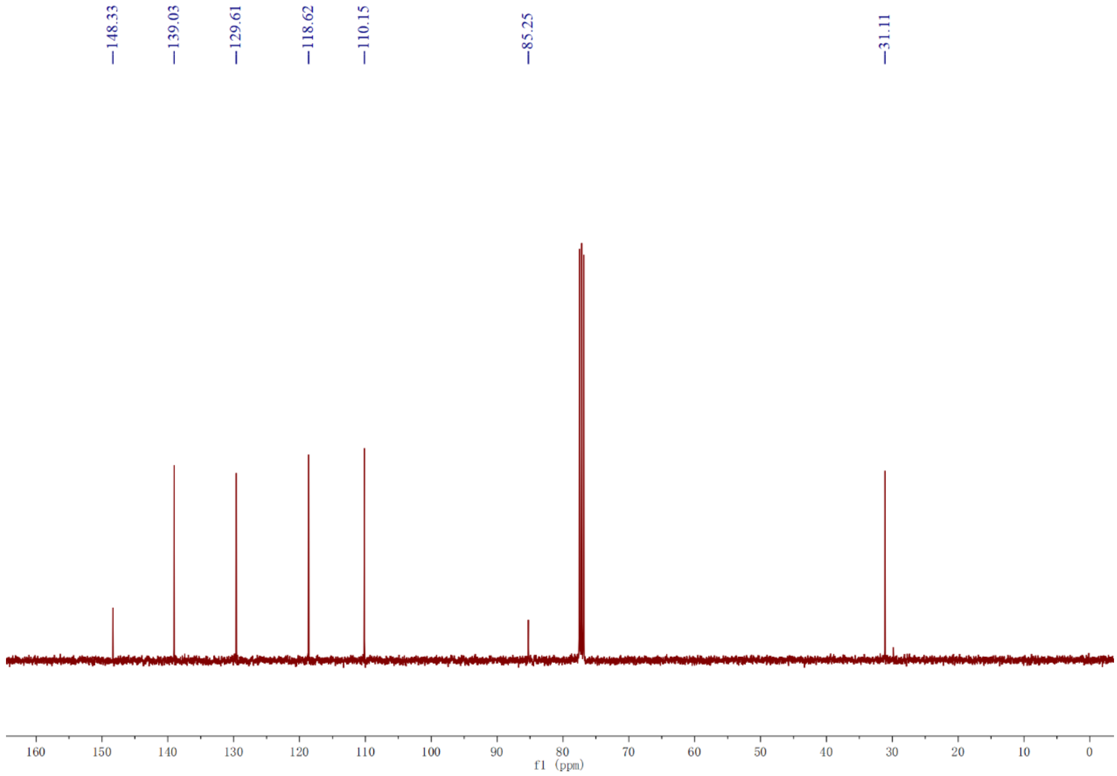
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **11h**



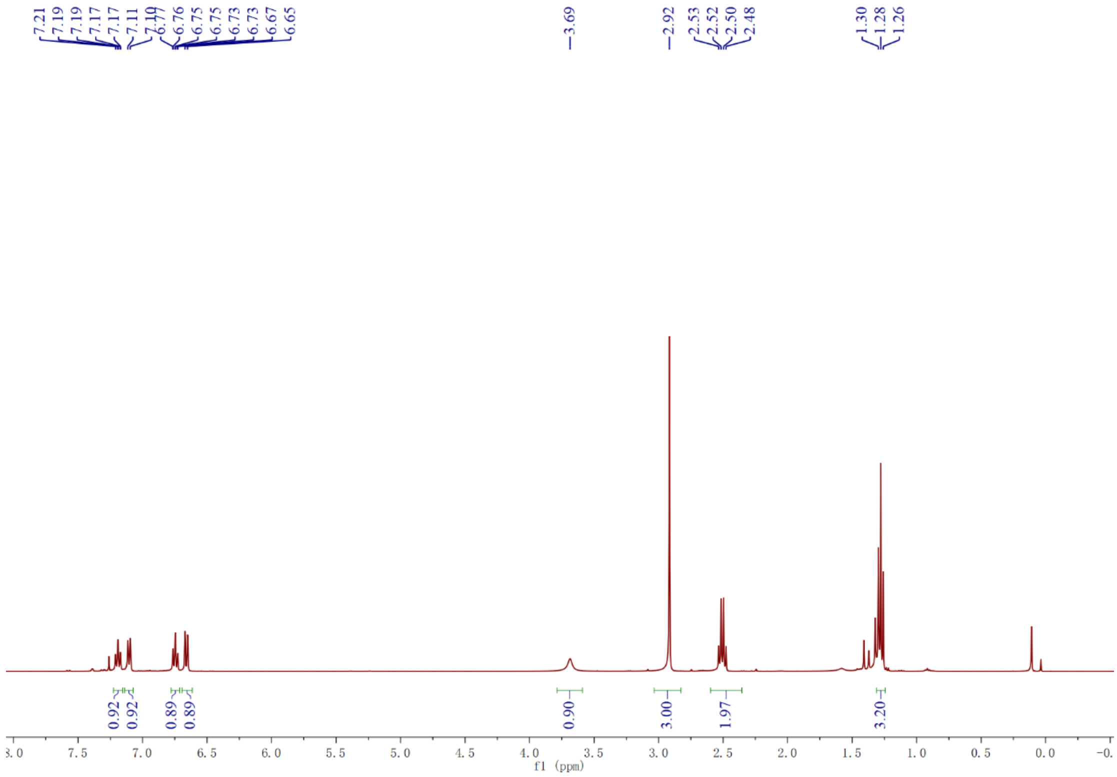
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **11h**



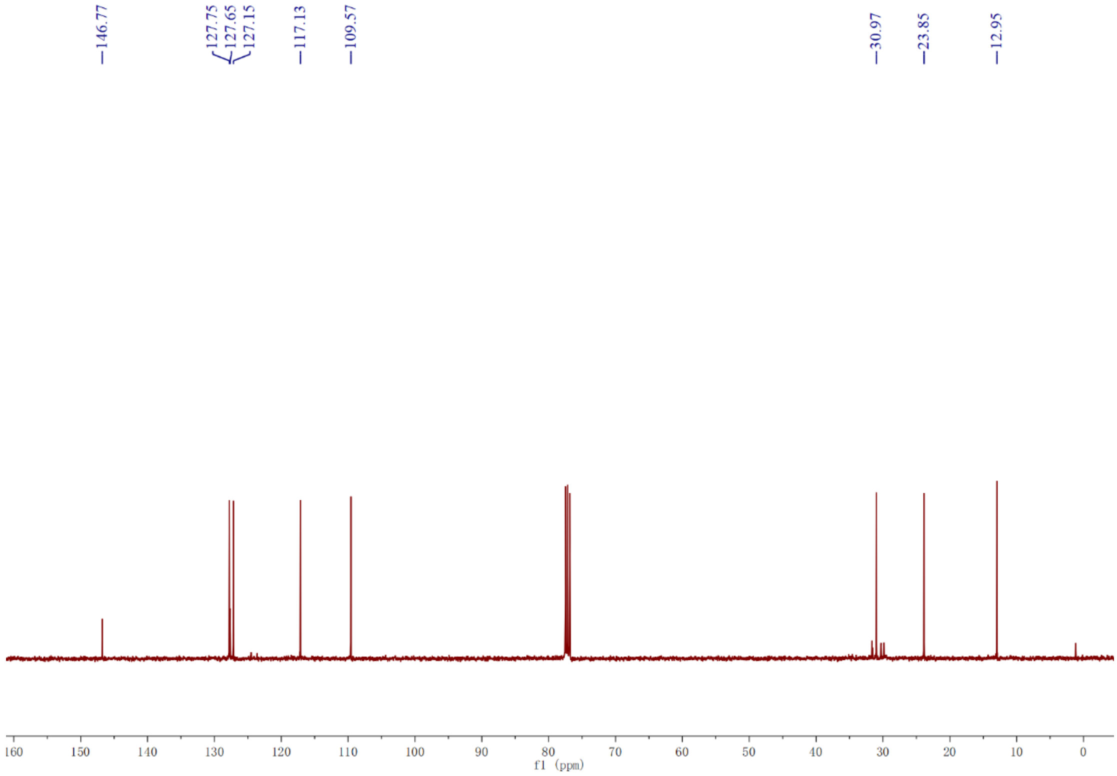
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **11i**



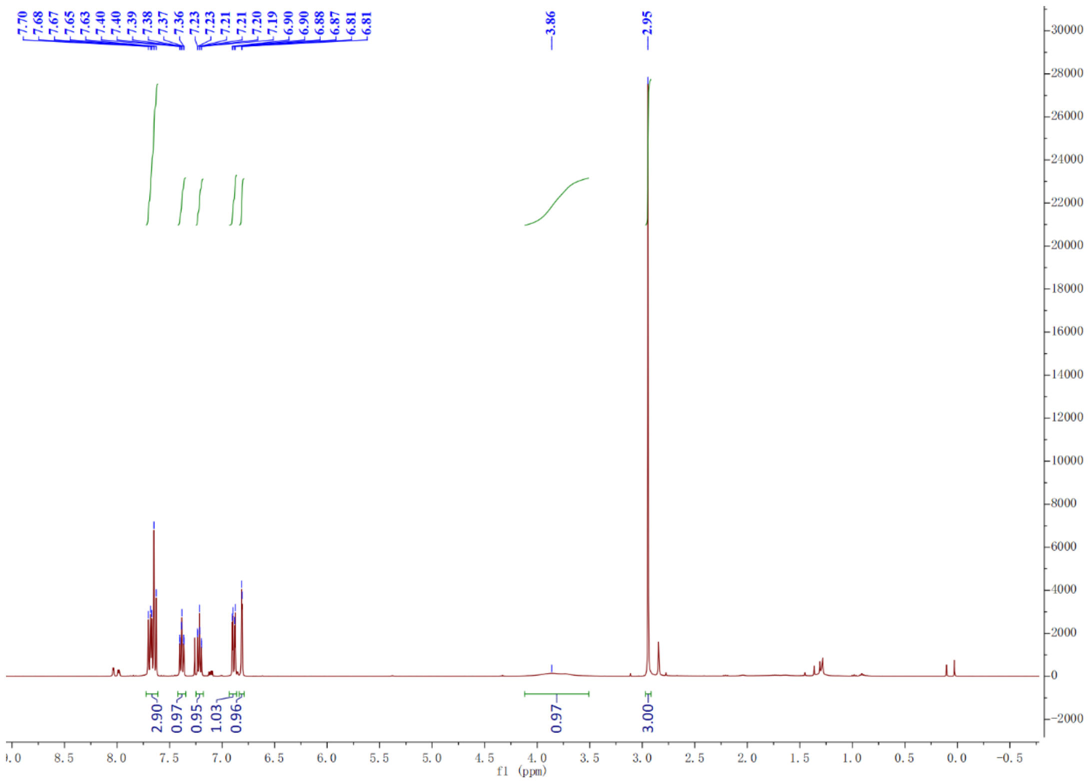
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **11i**



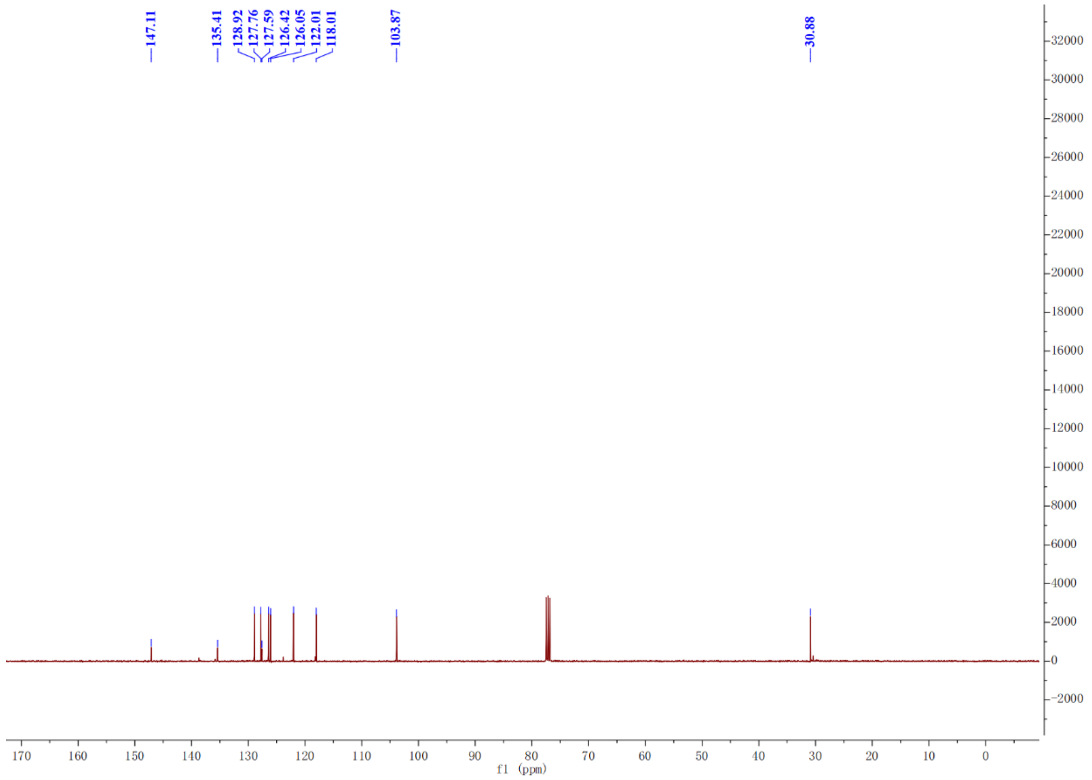
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **11j**



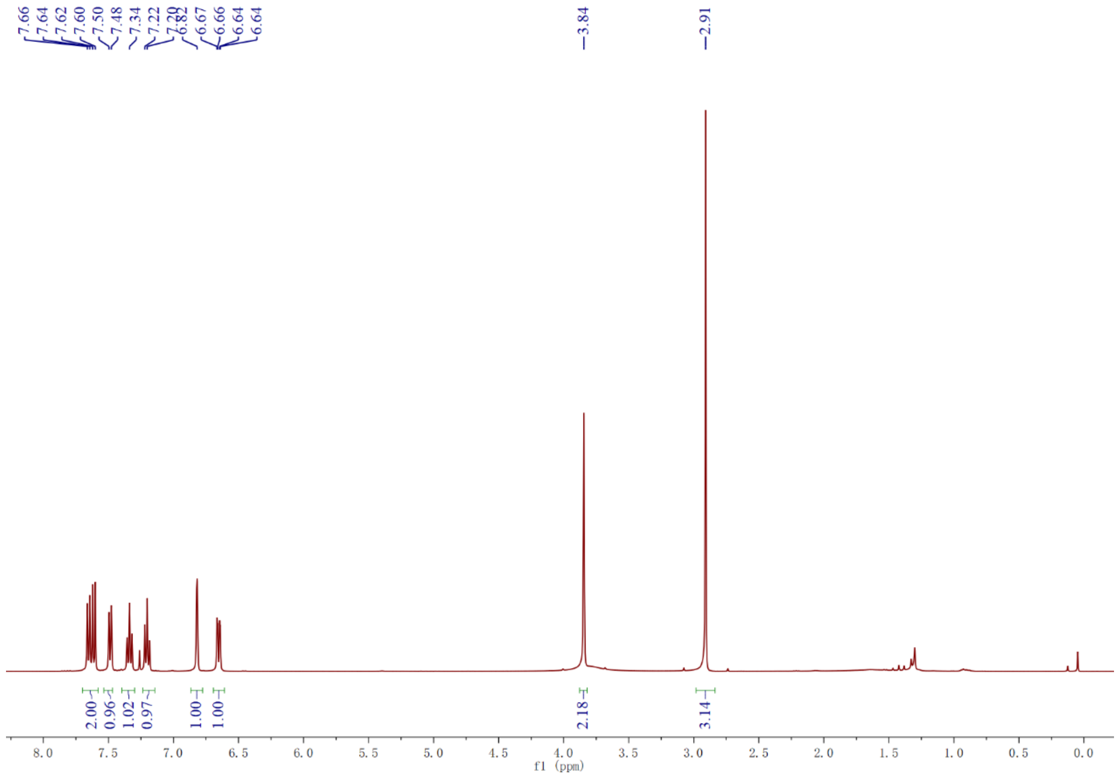
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **11j**



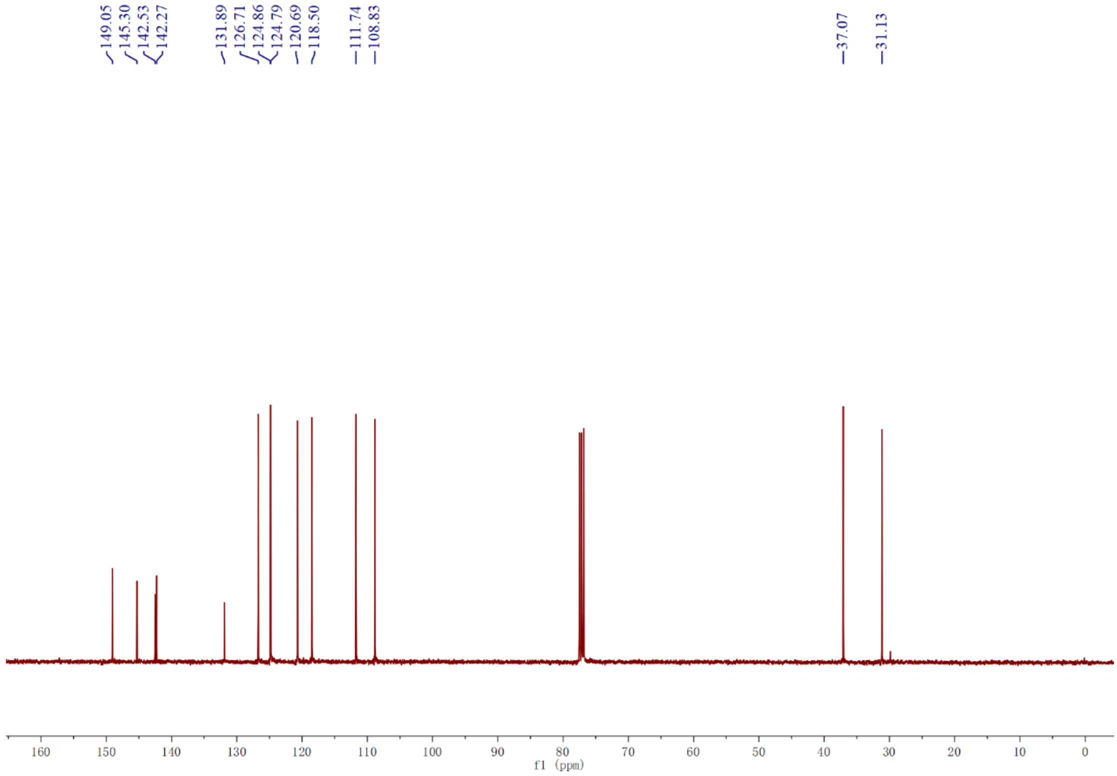
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **11k**



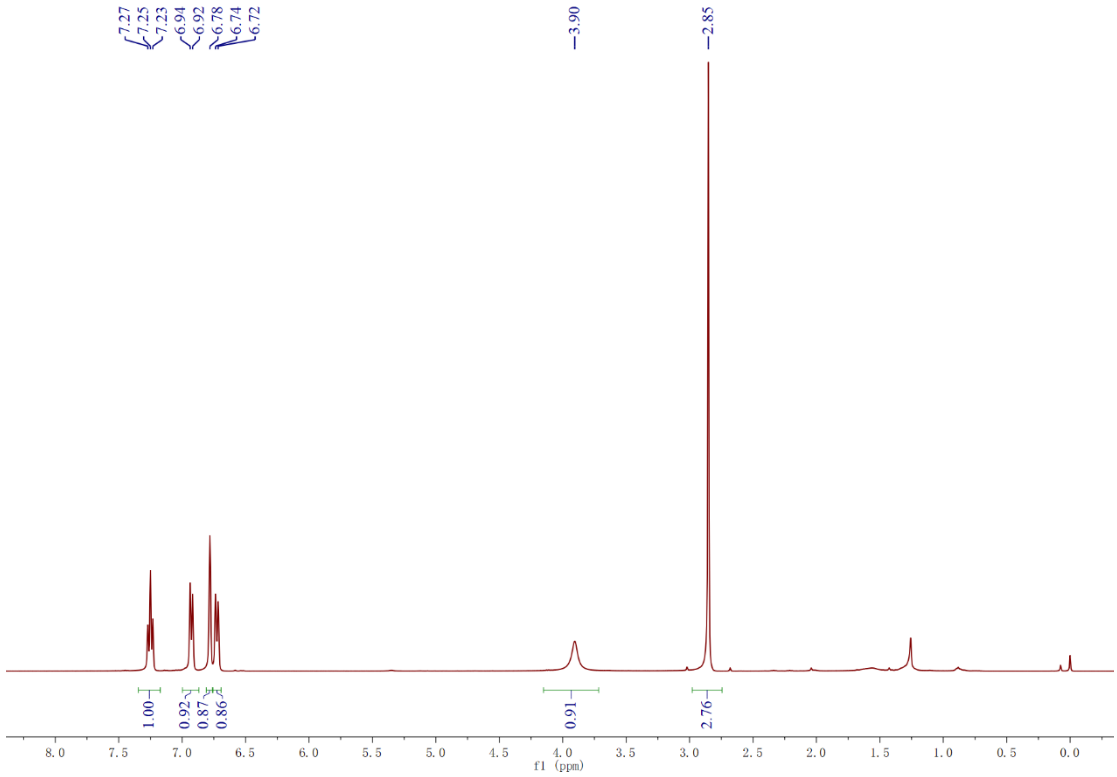
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **11k**



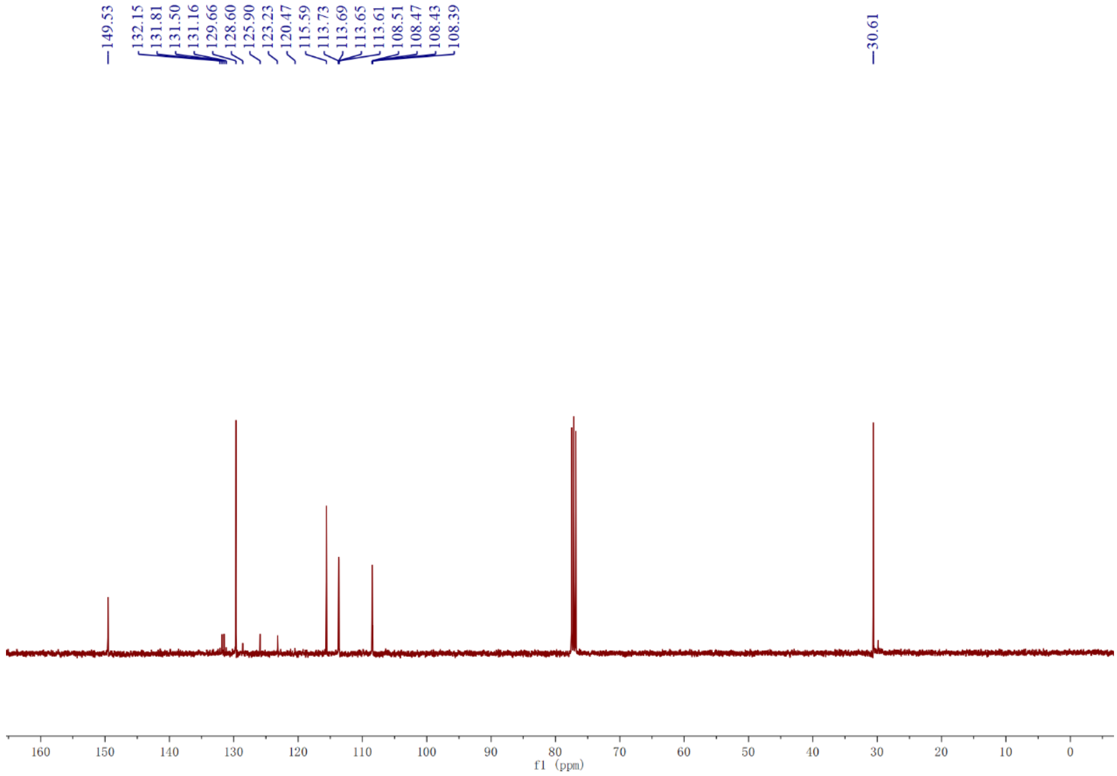
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **11l**



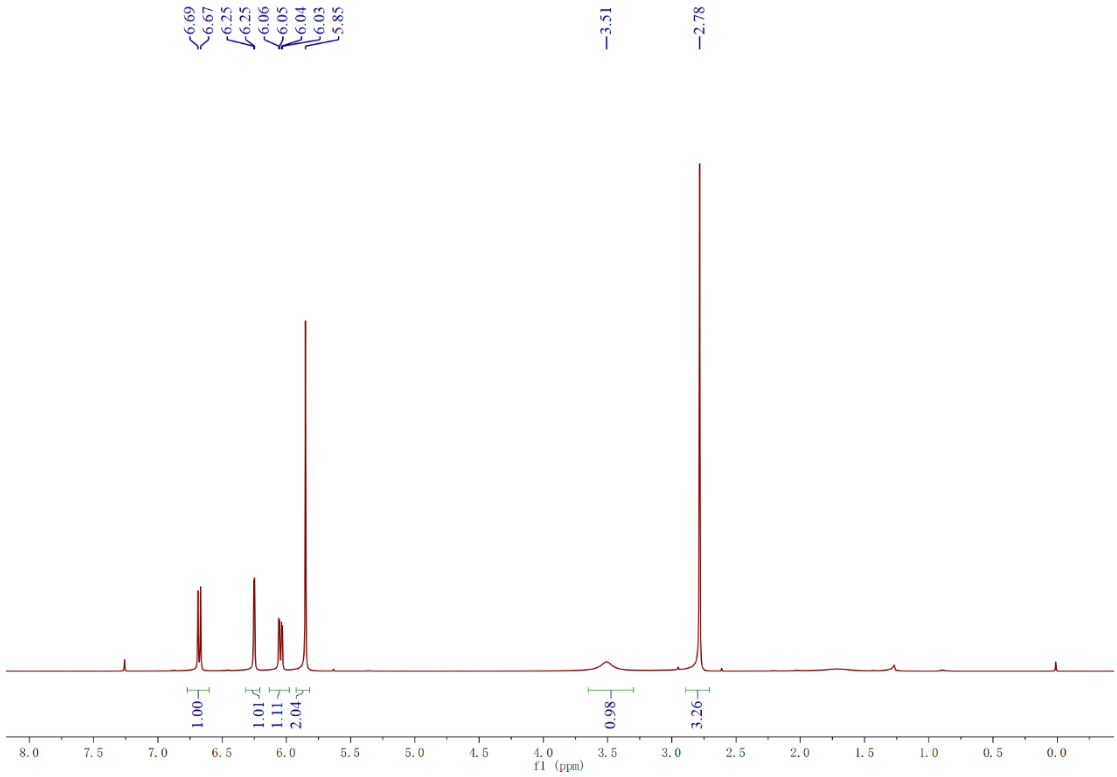
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **11l**



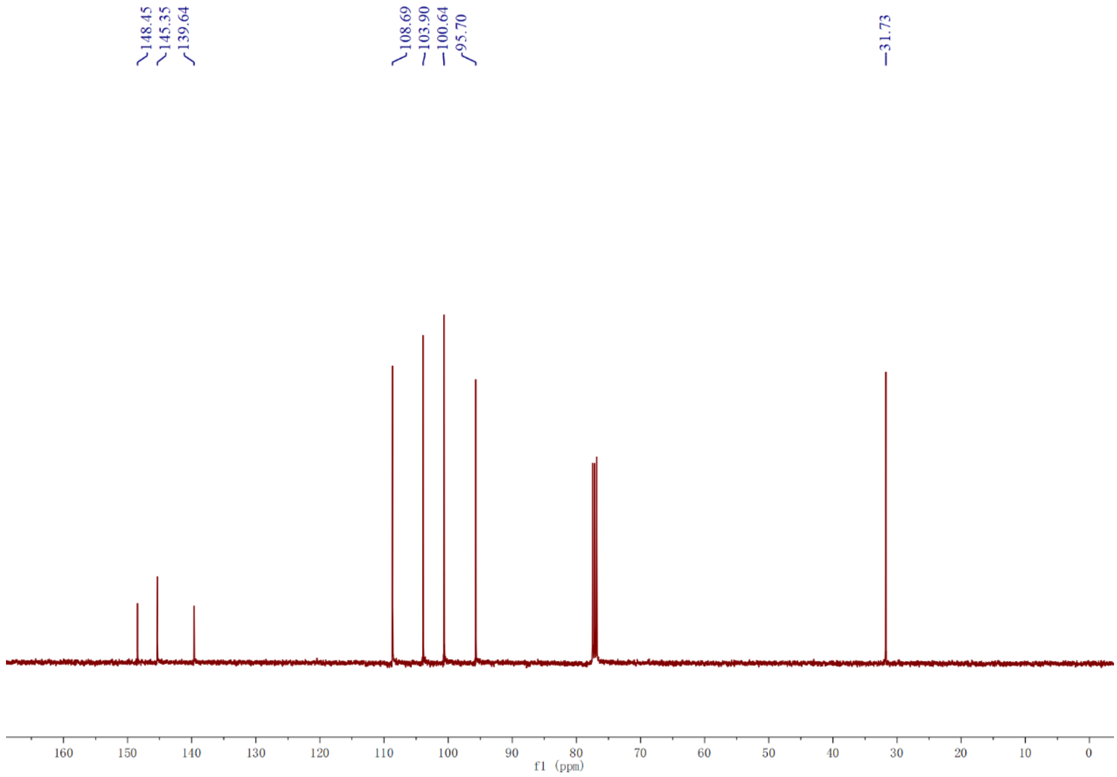
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **11m**



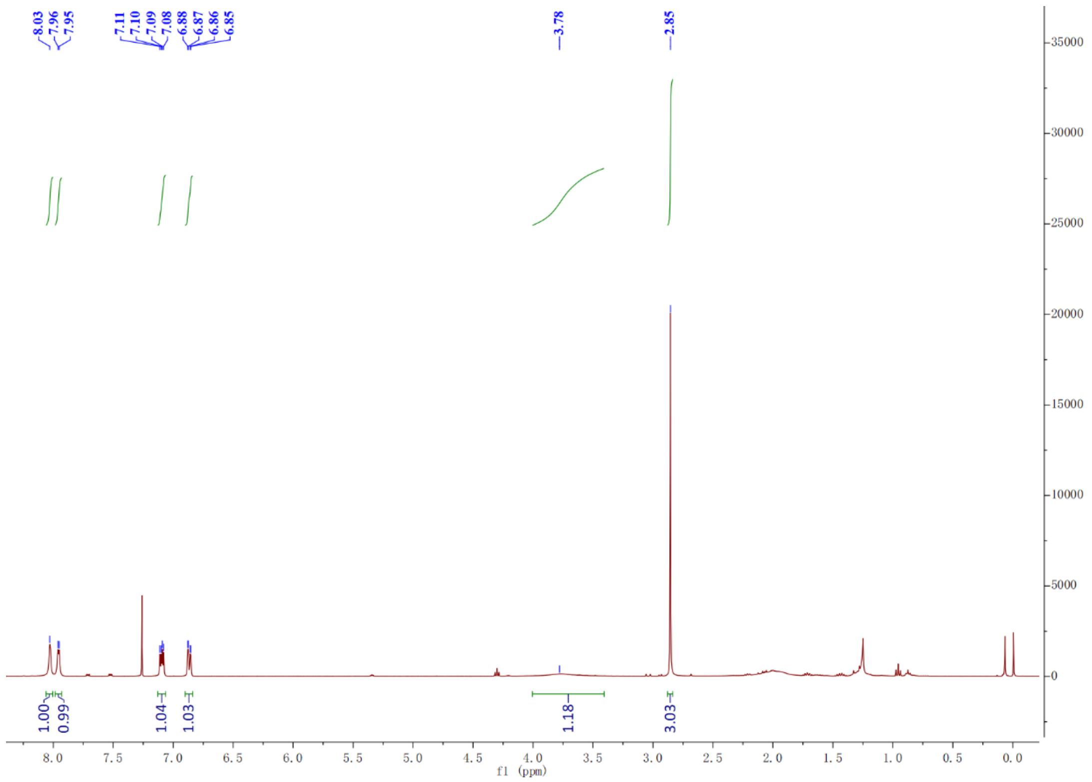
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **11m**



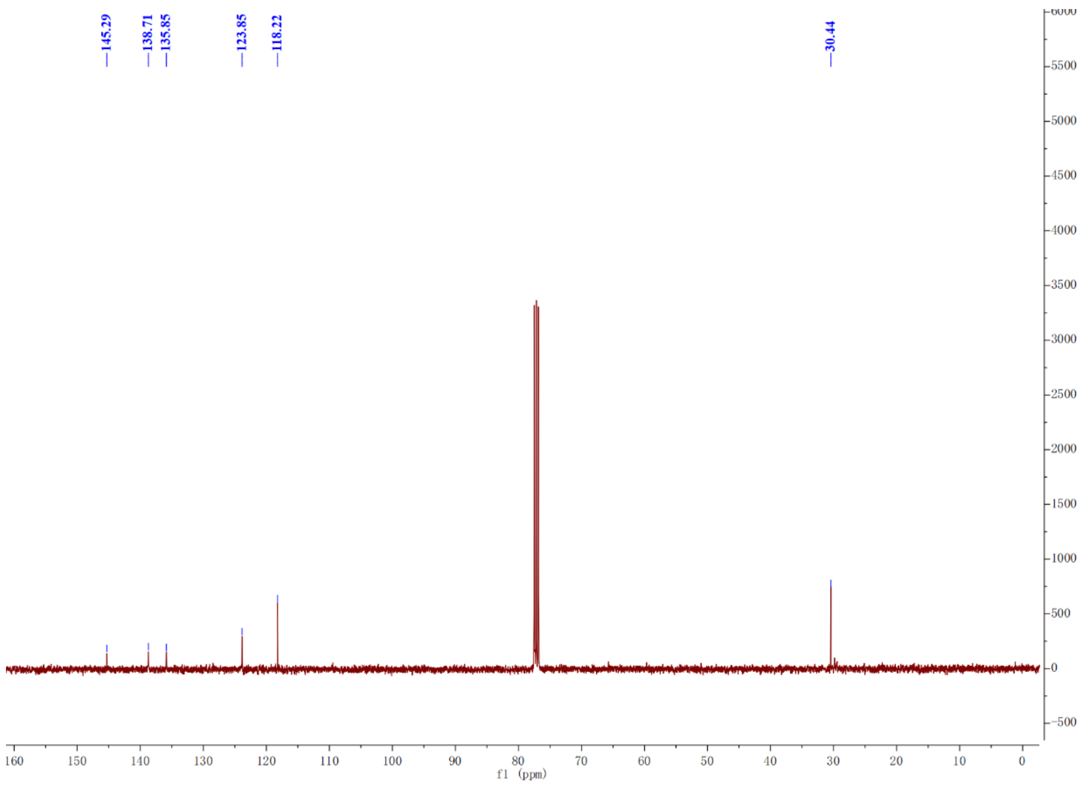
^1H NMR (400 MHz, $CDCl_3$) spectrum of **11n**



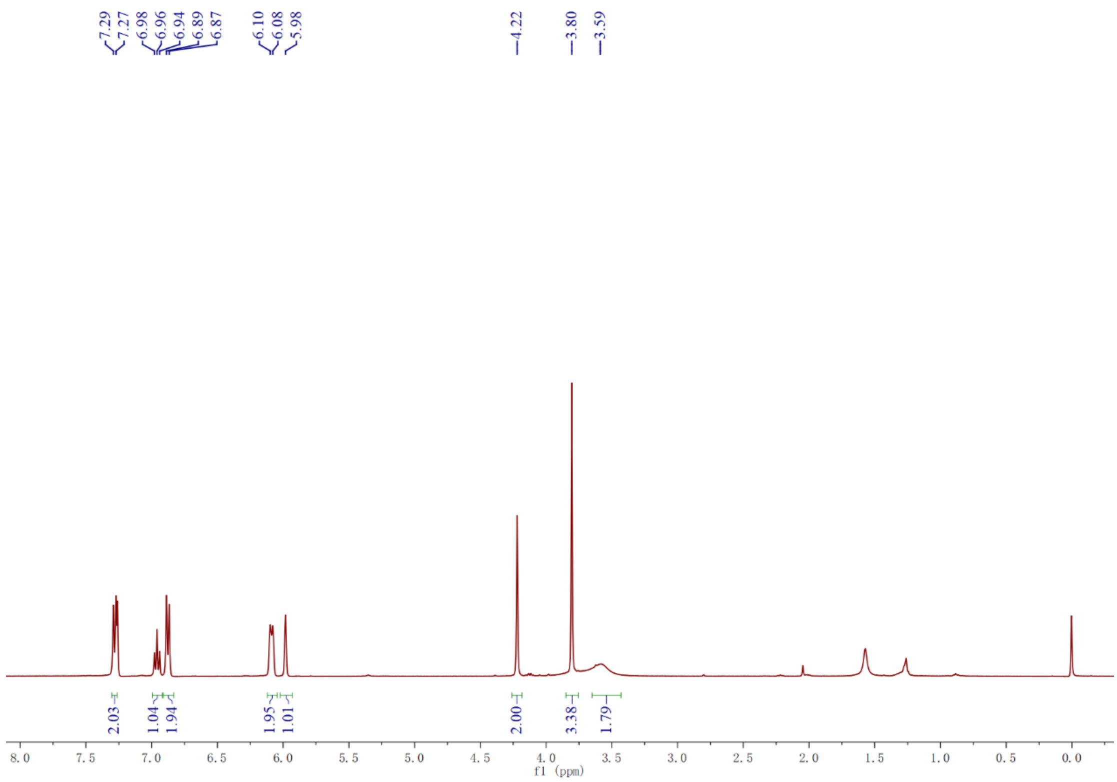
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **11n**



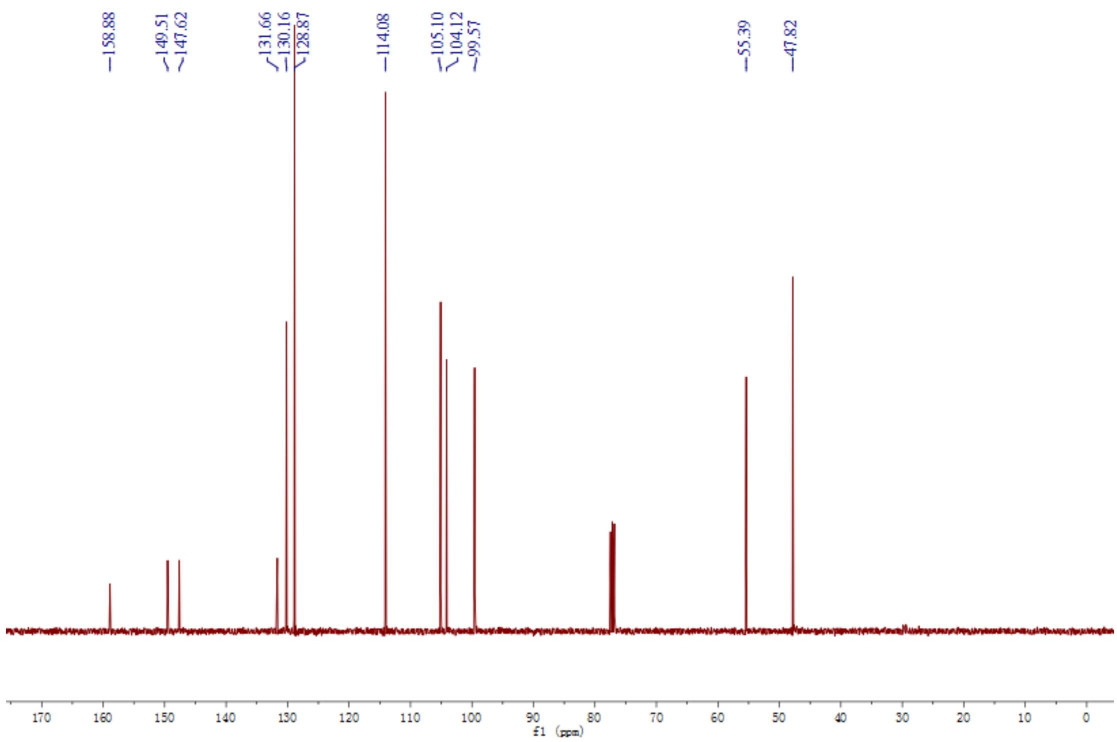
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **11o**



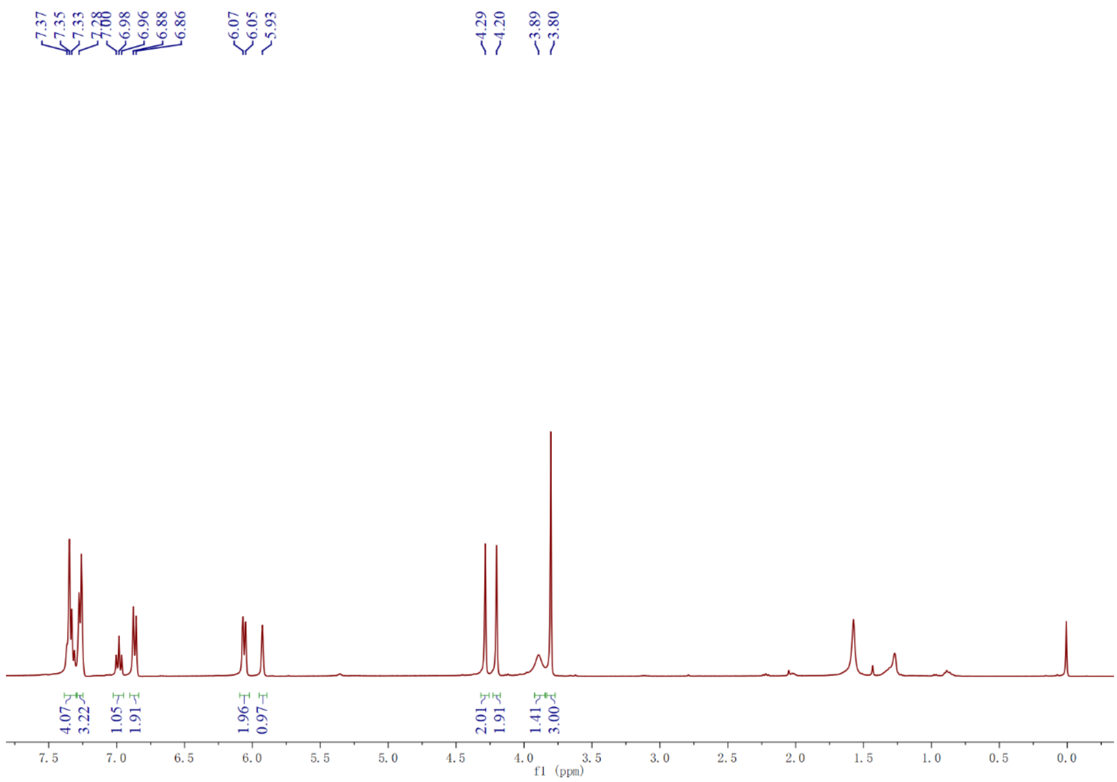
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **11o**



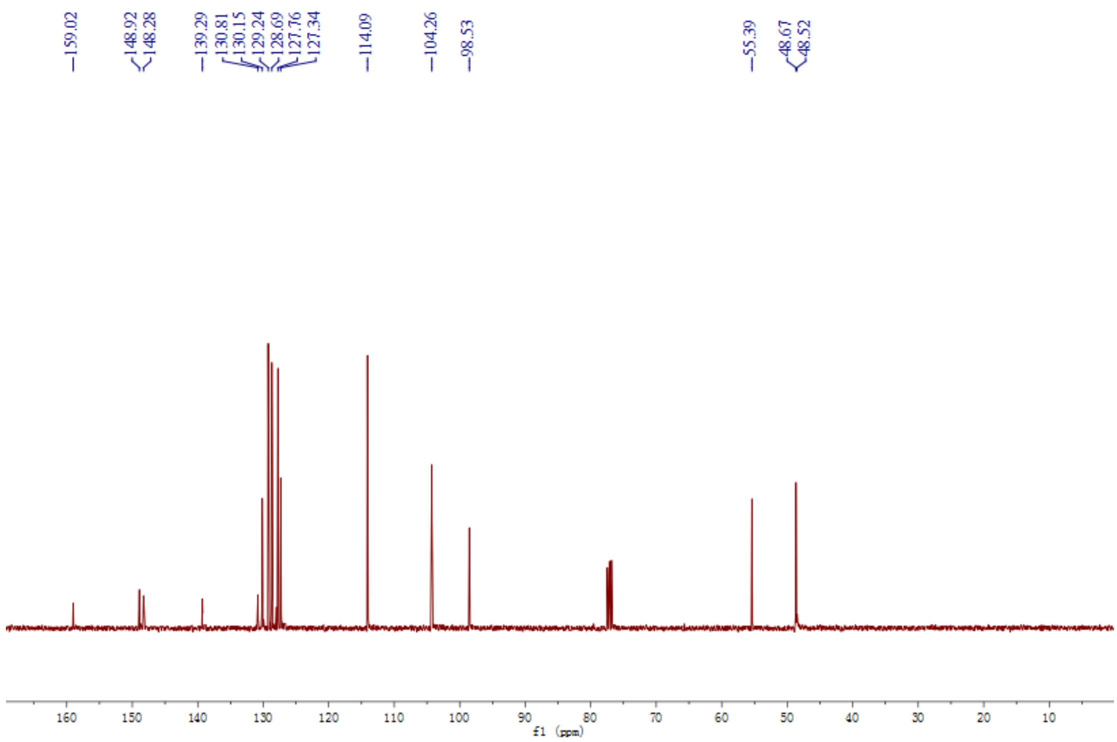
[1]H NMR (400 MHz, $CDCl_3$) spectrum of **12**



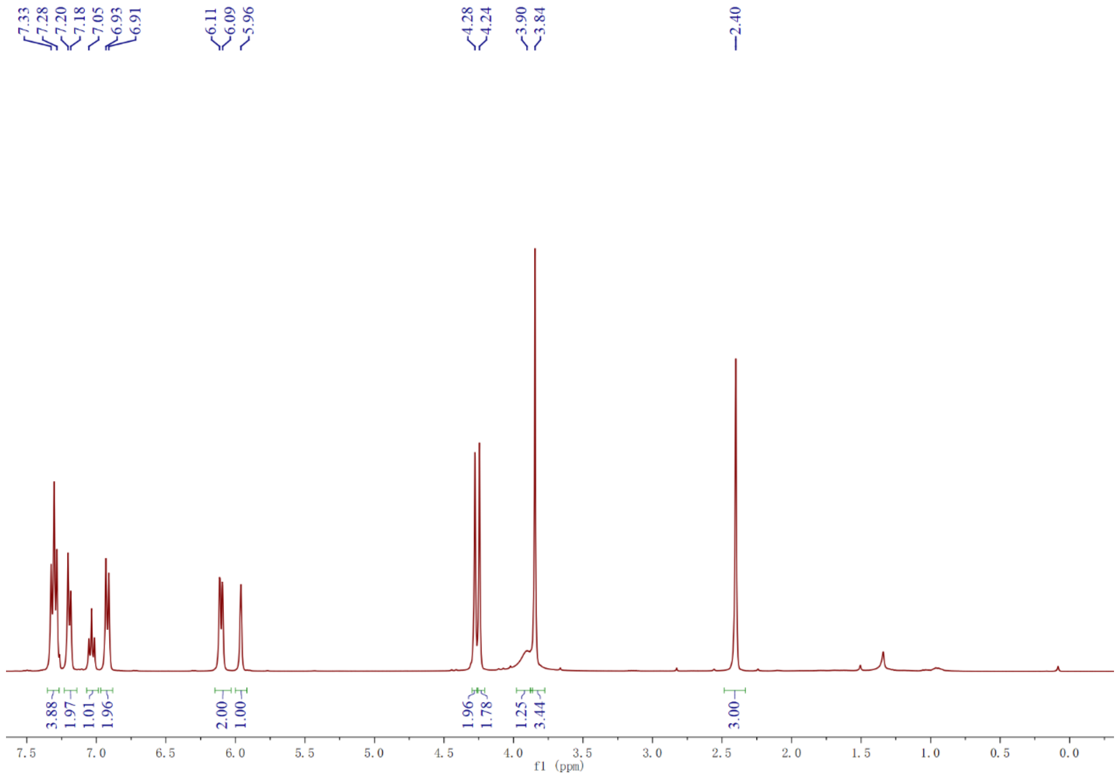
[13]C NMR (100 MHz, $CDCl_3$) spectrum of **12**



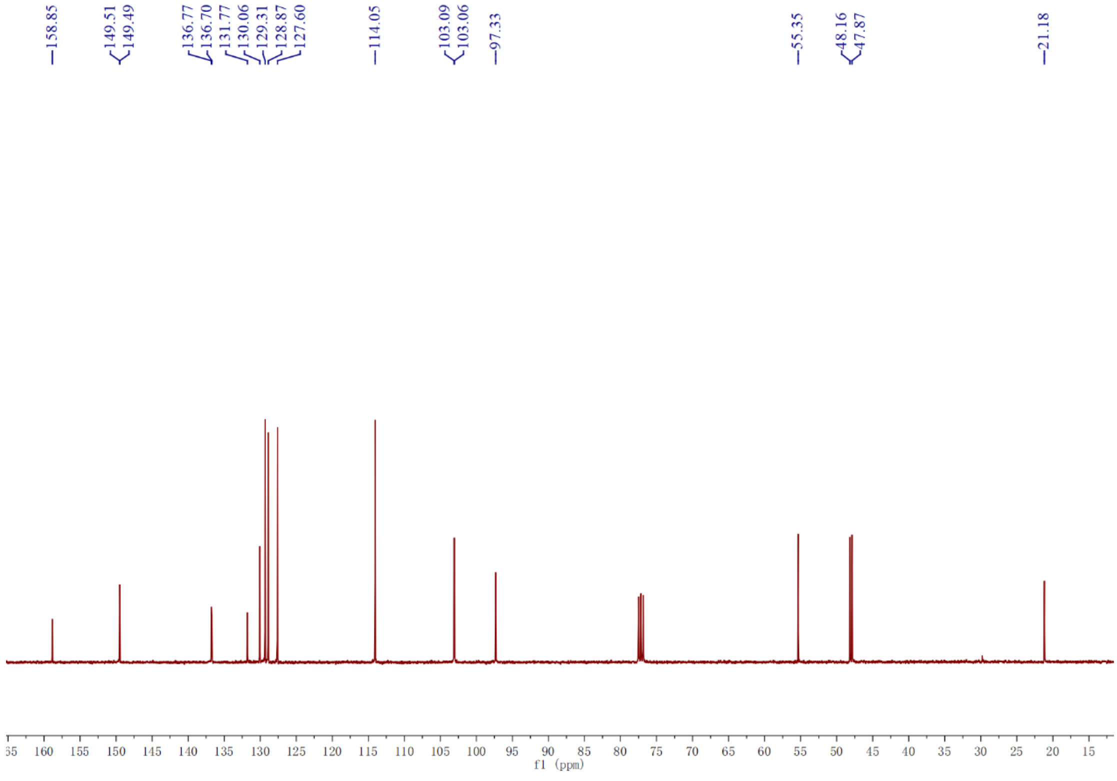
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **13a**



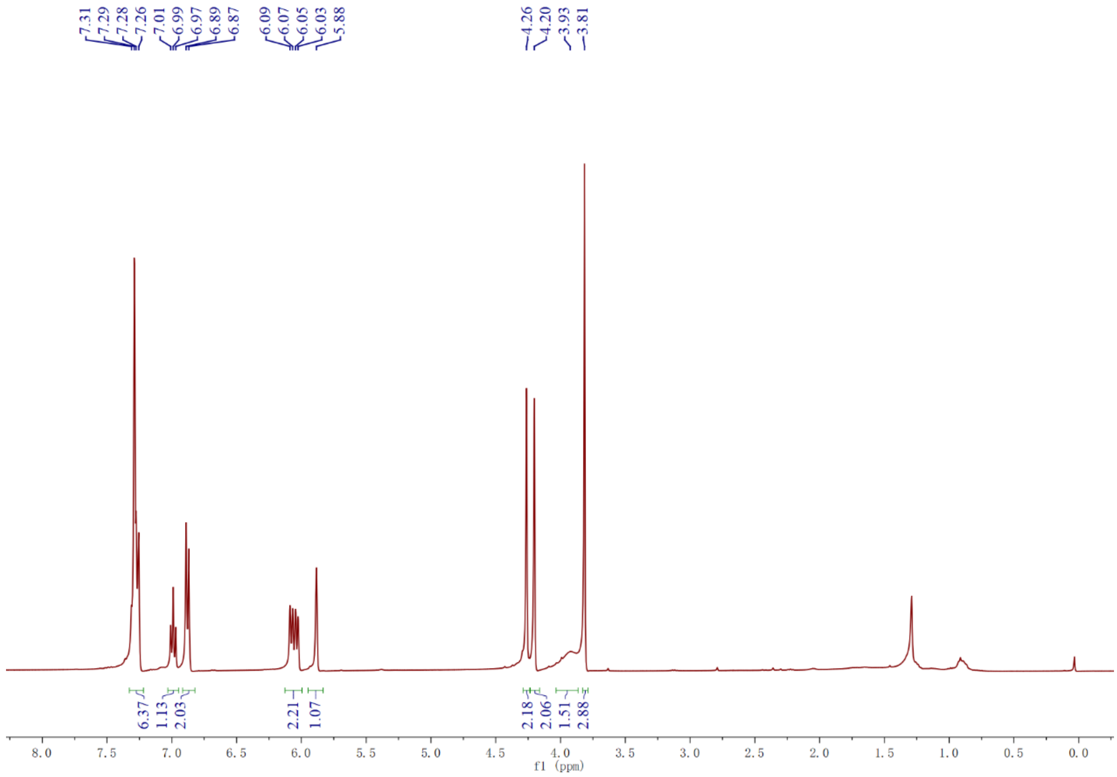
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **13a**



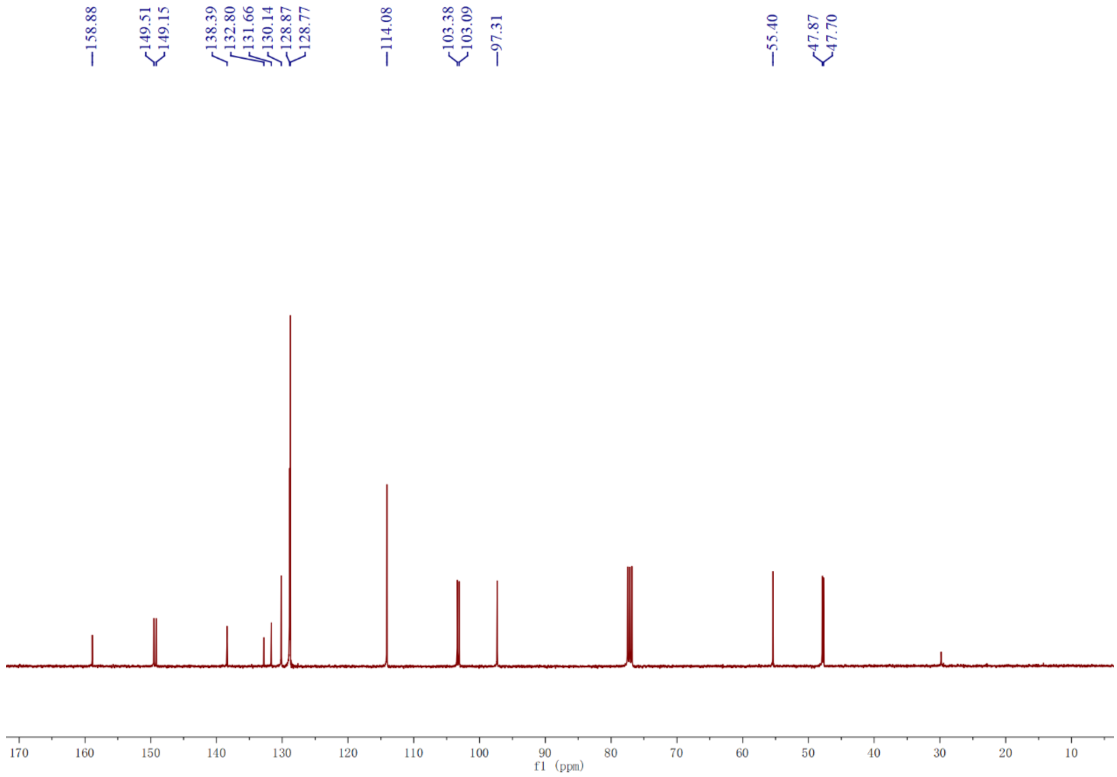
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **13b**



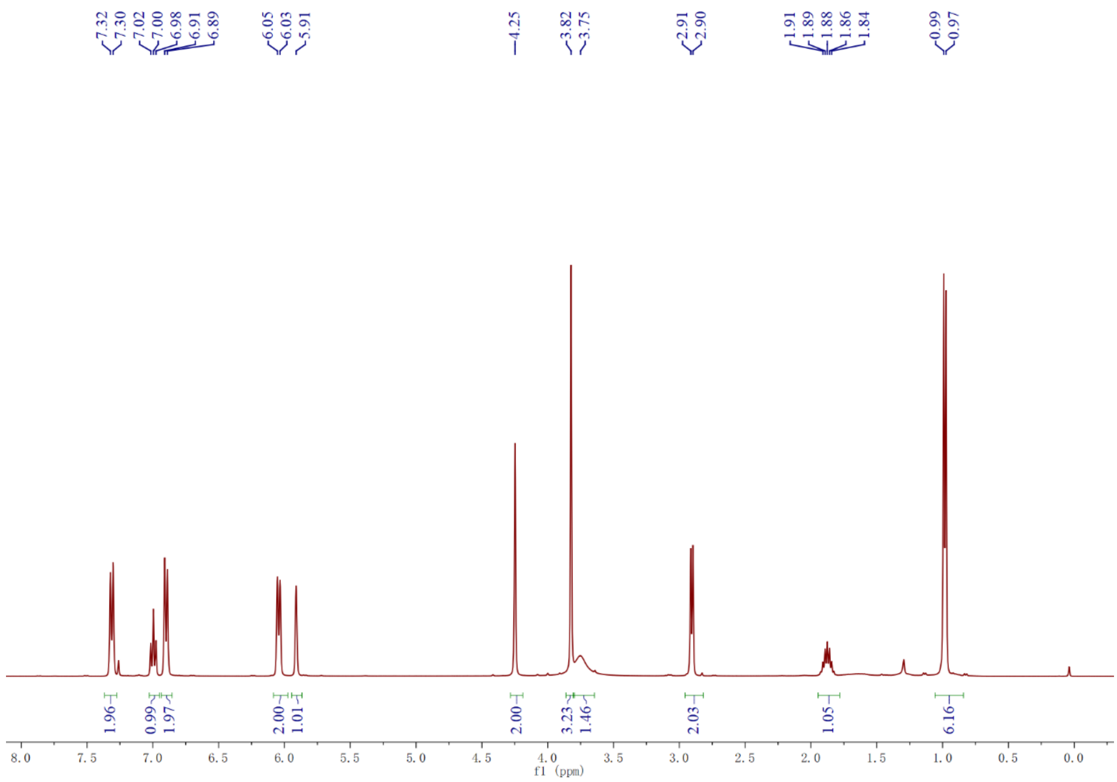
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **13b**



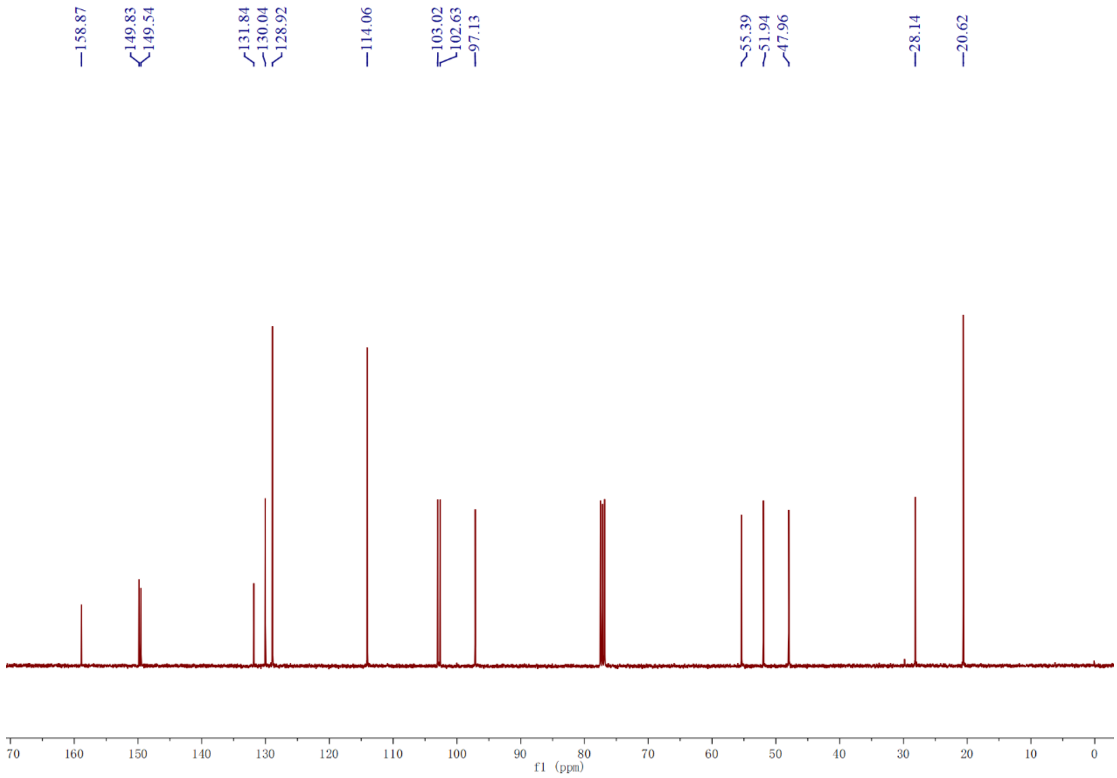
^{1}H NMR (400 MHz, CDCl$_3$) spectrum of **13c**



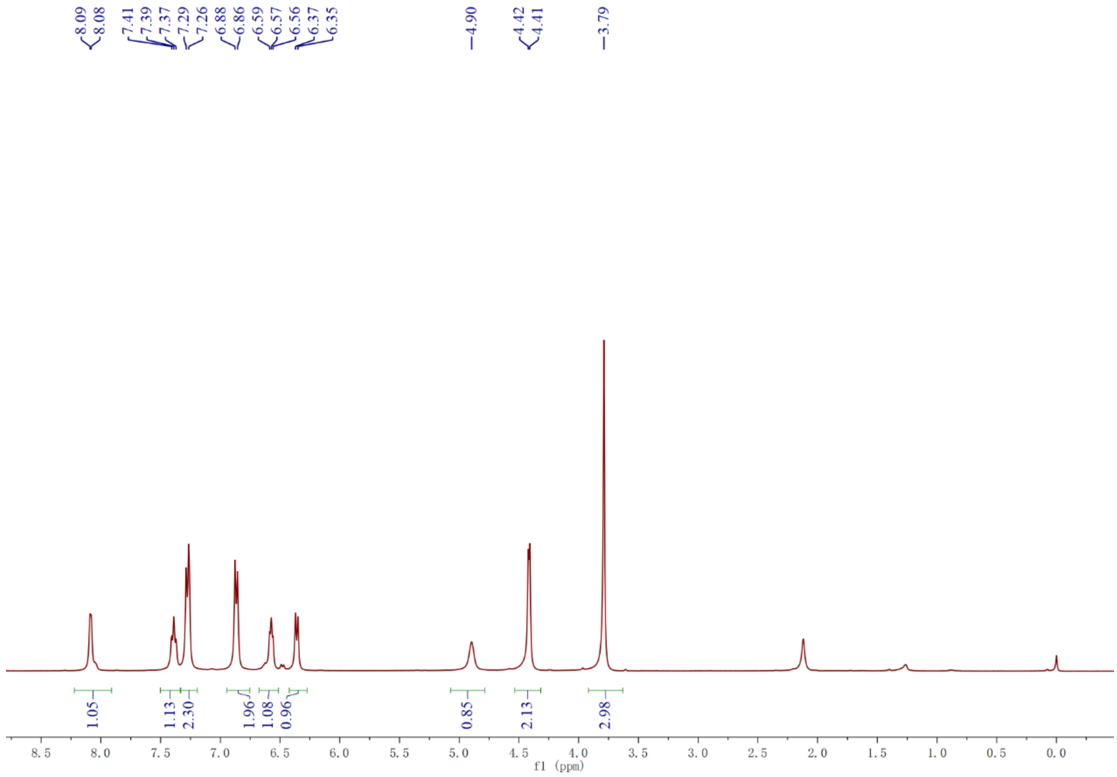
^{13}C NMR (100 MHz, CDCl$_3$) spectrum of **13c**



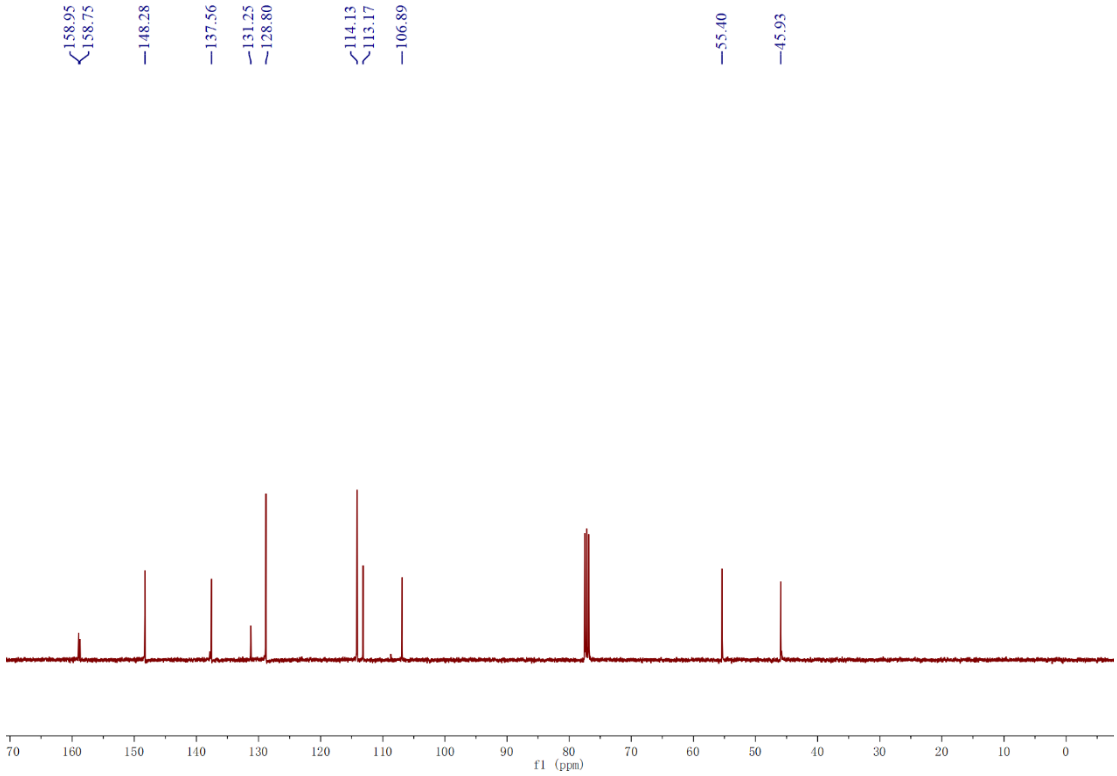
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **13d**



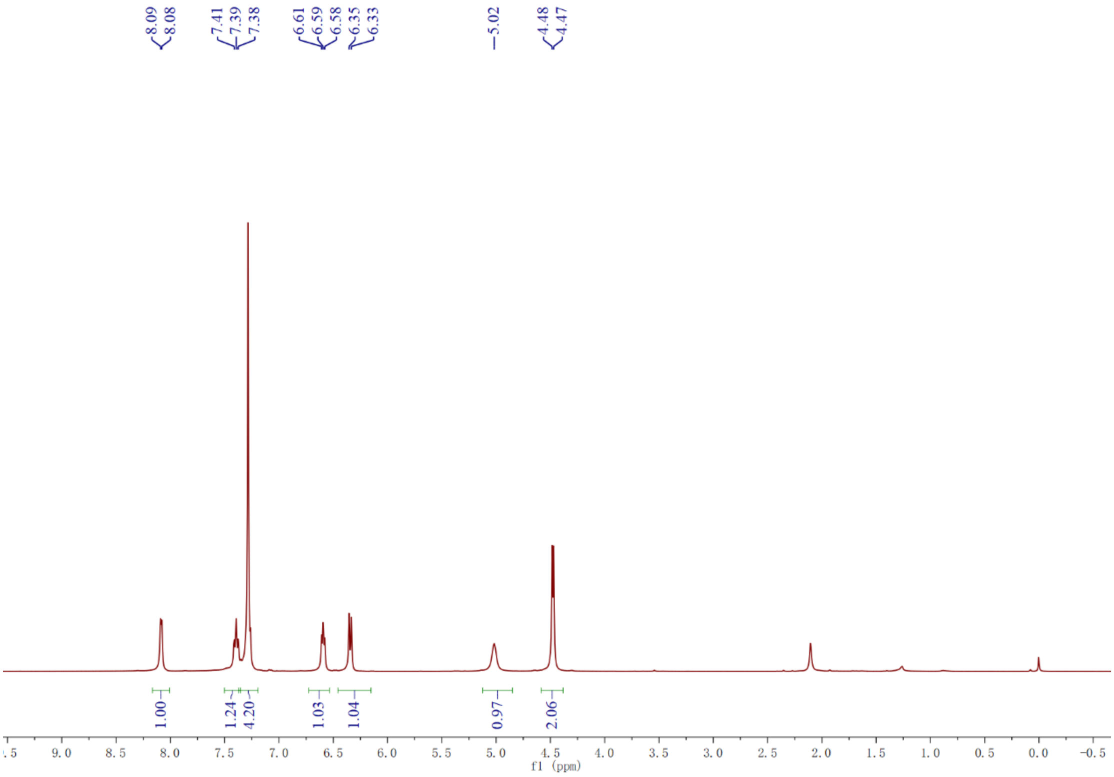
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **13d**



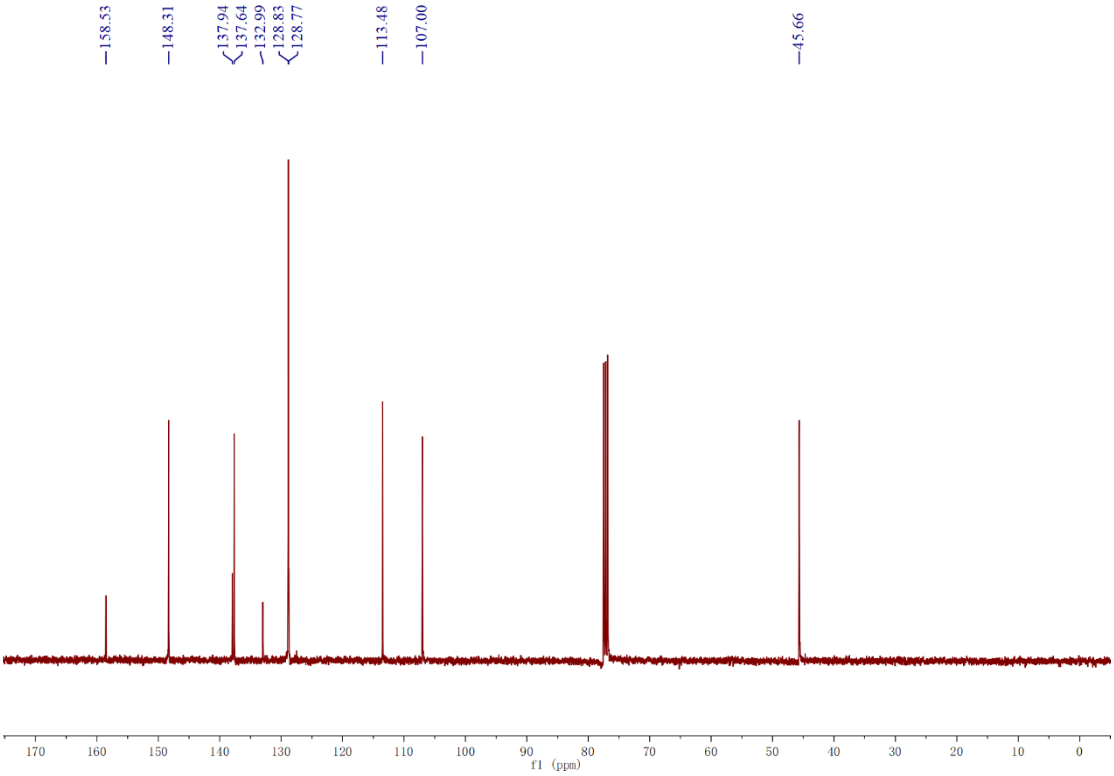
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **10q**



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **10q**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **10r**



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **10r**