Supporting information

Synthesis of sulfonated 3-sulfonylisoindolin-1-ones from olefinic amides and sodium sulfinates via electrooxidative tandem cyclization

Xuecheng Wang[a], Ziyue Zhao[a], Jiajie Guo[a], Jijin Wang[a], and Jincan Zhao*

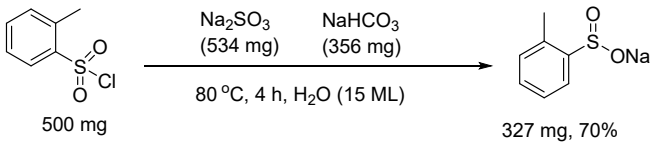
Key Laboratory of Medicinal Chemistry and Molecular Diagnosis of the Ministry of Education, College of Chemistry and Materials Science, Key Laboratory of Chemical Biology of Hebei Province, Hebei University, Baoding, Hebei, 071002, P. R. China.

Index

1. General information

All manipulations were carried out under nitrogen atmosphere. Commercially available reagents were used as received without purification. Column chromatography was carried out on silica gel (200-300 mesh). Analytical thin–layer chromatography was performed on glass plates of Silica Gel GF–254 with detection by UV. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker advance III 400M spectrometer. The chemical shift references were as follows: (^{1}H) $CDCl_3$, 7.26 ppm ($CHCl_3$), (^{13}C) $CDCl_3$, 77.00 ppm ($CDCl_3$). The yield of all compounds was obtained after separation. Cyclic voltammetry experiments were carried out in an IKA ElectraSyn 2.0. CV curves were recorded using a three-electrode scheme. The working electrode was a glassy carbon electrode, a platinum electrode served as counter electrode. Ag/AgCl was used as the reference electrode.

2. General procedure for the preparation of 2d.

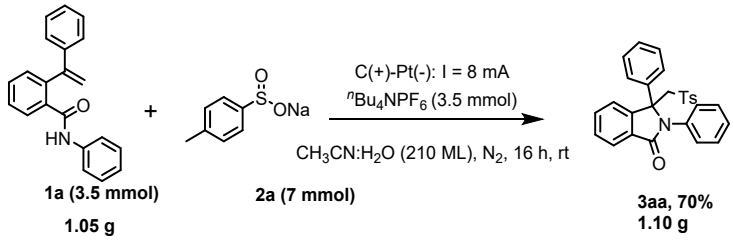


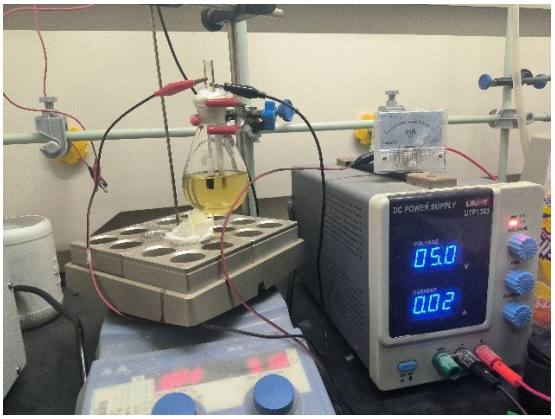
500 mg

327 mg, 70%

Sodium sulfite (4.24 mmol, 2.0 equiv), sodium bicarbonate (4.24 mmol, 2.0 equiv) and the corresponding 2-Methylbenzenesulfonyl chloride (2.12 mmol, 1.0 equiv) were dissolved in distilled water (15.0 mL). The reaction mixture was stirred for 4 h at 80 °C using oil bath. After cooling down to room temperature, The reaction solution was placed in a beaker and the water was evaporated in an oil bath at 120 °C. Ethanol (25 mL) was then added to this white residue and the resulting heterogeneous solution was filtered. The filtrate was concentrated under reduced pressure and the desired sodium sulfinates were obtained as white crystalline powders in 70% yields.

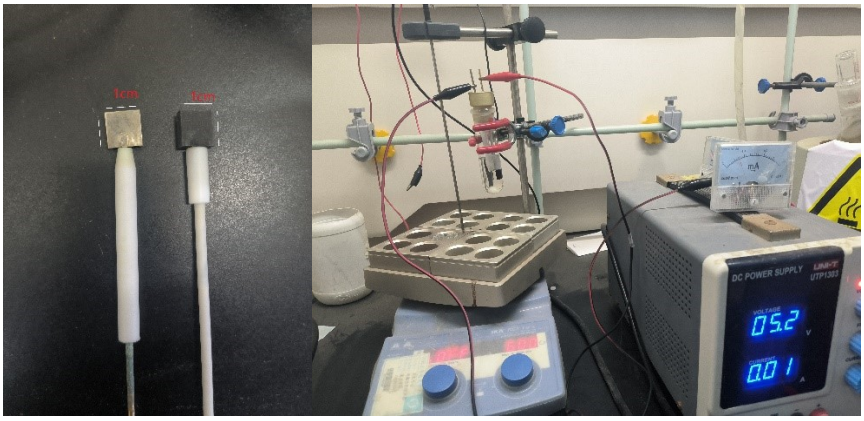
3. Gram-scale up experiment of 3aa.





4. General procedure for the preparation of 3aa.

An undivided cell was equipped with graphite anode and platinum cathode and connected to a DC power supply. A mixture of *N*-phenyl-2-(1-phenylvinyl)benzamide **1a** (0.1 mmol), sodium sulfinate **2a** (0.2 mmol), *n*-Bu_4NPF_6 (0.1mmol) in CH_3CN and H_2O (6.0 mL) was added. The reaction mixture was stirred and electrolyzed at a constant current of 8 mA under 30 ℃ for 2.5 h. When the reaction was finished, as indicated by TLC the residue was diluted with ethyl acetate and washed with NaCl saturated solution, dried over $MgSO_4$ concentrated under reduced pressure concentrated, and purified by flash chroma tography petroleum ether: ethyl acetate=5:1) to afford **3aa** in 42.1 mg, by 91% yield as white solid.



Electrode surface area: C Anode: 1 cm*1 cm = 1 cm^2.

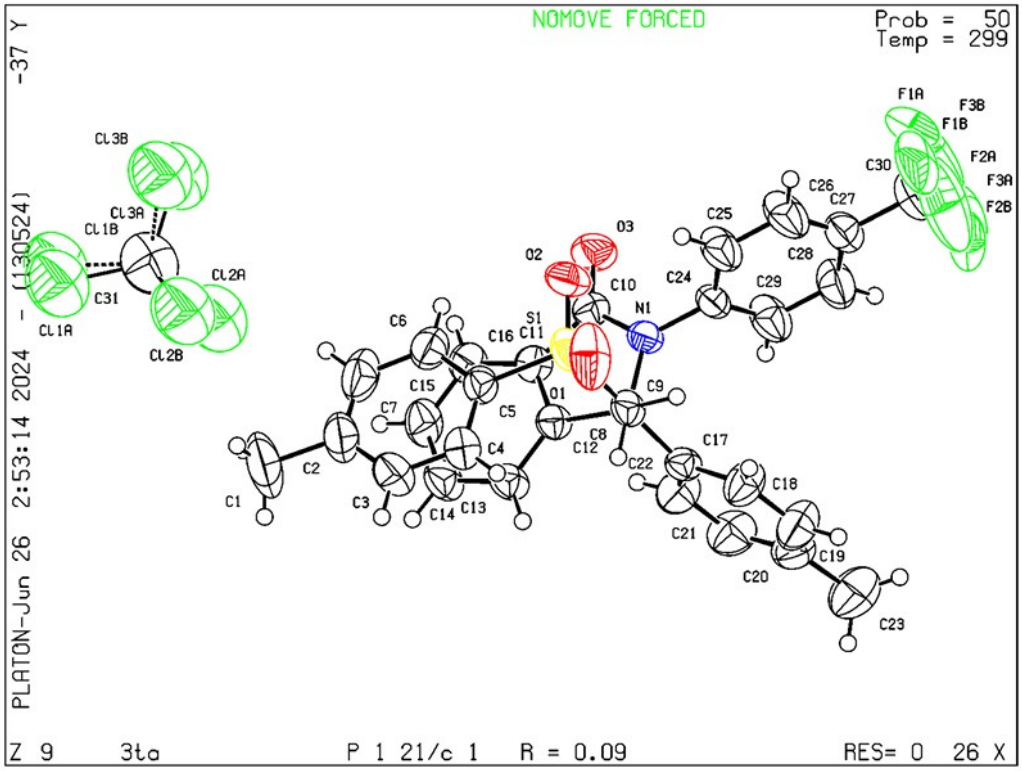
Pt Cathode: 1 cm*1 cm = 1 cm^2.

Undivided cell: Synthware Glass, 10 mL reaction tube.

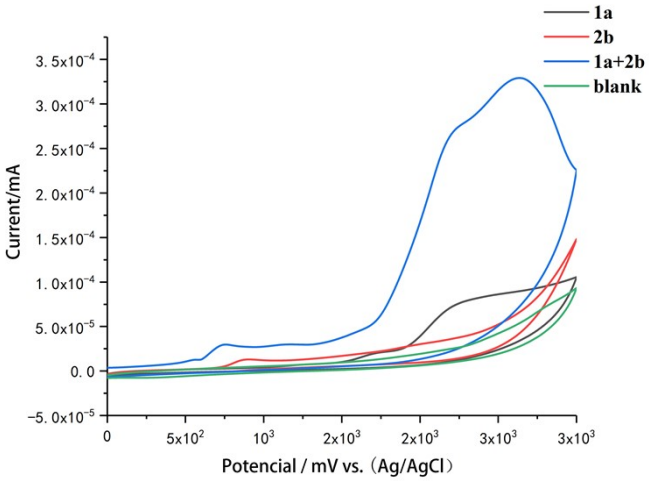
Electroradiometer: UNI-T DC power supply (UTP 1303)

5. X-ray single-crystal diffraction of 3ta.

Datablock 3ta - ellipsoid plot



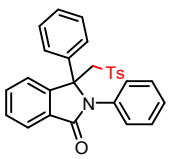
6. Cyclic voltammetry (CV) experiments.



Cyclic voltammetry was performed in a three-electrode cell under air at room temperature. Using glassy carbon electrode as working electrode, platinum wire as counter electrode. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution. 5 mL of CH_3CN containing 0.01 M *n*-Bu_4NPF_6 were poured into the electrochemical cell in all experiments. The scan rate is 0.05 V/s, ranging from 0 V to 3.0 V. The peak potentials vs. Ag/AgCl for used. The oxidation peak of *N*-phenyl-2-(1-phenylvinyl)benzamide **1a** appears at 2.20 V, and the oxidation peak of sodium sulfinate **2b** appears at 0.90 V.

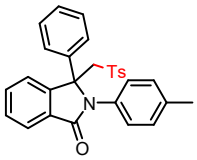
Cyclic voltammetry (CV) experiments were performed to investigate the redox potential of the substrates (Figure 1). The oxidation peaks of **1a** and **2b** were observed at 2.20 V and 0.90 V respectively. This phenomenon illustrated that sodium sulfinate **2b** was oxidized preferentially at the anode.

7. Characterization data for 3 and 4

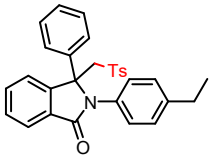


(*Z*)-*N*-(3-phenyl-3-(tosylmethyl)isobenzofuran-1(3*H*)-ylidene)anilin (3aa): white solid, m.p. 270-272 °C, (42.1 mg, 91% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.6 Hz, 1H),

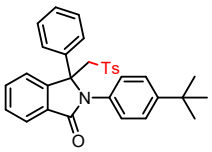
7.46 (t, J = 7.5 Hz, 1H), 7.30 – 7.19 (m, 7H), 7.15 (t, J = 8.0 Hz, 1H), 7.08 (d, J = 7.8 Hz, 4H), 7.03 (d, J = 8.1 Hz, 3H), 6.75 (d, J = 7.7 Hz, 1H), 4.40 (d, J = 14.9 Hz, 1H), 4.22 (d, J = 14.9 Hz, 1H), 2.37 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.11, 145.78, 144.36, 140.59, 137.64, 135.60, 132.02, 131.99, 129.74, 129.21, 128.96, 128.90, 128.79, 127.42, 127.16, 127.10, 125.93, 124.25, 123.51, 68.98, 57.31, 21.60. **HRMS** (ESI, m/z) calcd for $C_{28}H_{24}NO_3S$+ $[M+H]^+$ 454.1471, found 454.1473.



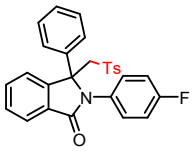
(*Z*)-4-methyl-*N*-(3-phenyl-3-(tosylmethyl)isobenzofuran-1(3*H*)-ylidene)aniline (3ba): white solid, m.p.258-260 °C, (33.7 mg, 72% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.6 Hz, 1H), 7.46 (t, J = 7.5 Hz, 1H), 7.28 (d, J = 7.6 Hz, 3H), 7.21 (d, J = 8.3 Hz, 2H), 7.13 (t, J = 7.6 Hz, 1H), 7.10 – 7.06 (m, 3H), 7.05 – 6.99 (m, 3H), 6.93 (d, J = 8.4 Hz, 2H), 6.72 (d, J = 7.7 Hz, 1H), 4.35 (d, J = 14.9 Hz, 1H), 4.22 (d, J = 14.9 Hz, 1H), 2.38 (s, 3H), 2.30 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.11, 145.60, 144.32, 140.47, 137.60, 137.25, 132.62, 132.28, 131.85, 129.73, 129.64, 129.10, 128.94, 128.79, 127.51, 127.41, 126.13, 124.21, 123.53, 68.84, 57.33, 21.64, 21.15. **HRMS** (ESI, m/z) calcd for $C_{29}H_{26}NO_3S^+$ $[M+H]^+$ 468.1628, found 468.1625.



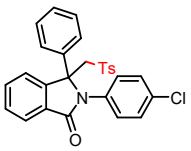
(*Z*)-4-ethyl-*N*-(3-phenyl-3-(tosylmethyl)isobenzofuran-1(3*H*)-ylidene)aniline (3ca): white solid, m.p.232-233 °C, (34.2 mg, 71% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.6 Hz, 1H), 7.45 (t, J = 7.5 Hz, 1H), 7.31 – 7.25 (m, 3H), 7.21 (d, J = 8.3 Hz, 2H), 7.13 (t, J = 7.5 Hz, 1H), 7.08 (dd, J = 8.4, 3.0 Hz, 4H), 7.02 (dd, J = 7.8, 1.7 Hz, 2H), 6.96 (d, J = 8.4 Hz, 2H), 6.72 (d, J = 7.7 Hz, 1H), 4.37 (d, J = 14.9 Hz, 1H), 4.23 (d, J = 14.9 Hz, 1H), 2.60 (q, J = 7.6 Hz, 2H), 2.37 (s, 3H), 1.20 (t, J = 7.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.17, 145.65, 144.32, 143.31, 140.52, 137.58, 132.82, 132.19, 131.89, 129.73, 129.14, 128.93, 128.78, 128.41, 127.39, 127.32, 126.08, 124.20, 123.50, 68.89, 57.23, 28.47, 21.65, 15.43. **HRMS** (ESI, m/z) calcd for $C_{30}H_{28}NO_3S^+$ $[M+H]^+$ 482.1784, found 482.1786.



(Z)-4-(tert-butyl)-N-(3-phenyl-3-(tosylmethyl)isobenzofuran-1(3*H*)-ylidene)aniline (3da): white solid, m.p.286-288 °C, (41.8 mg, 82% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.29 (dd, *J* = 5.1, 1.3 Hz, 3H), 7.24 (d, *J* = 8.6 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 8.4 Hz, 4H), 7.00 (d, *J* = 8.7 Hz, 2H), 6.73 (d, *J* = 7.7 Hz, 1H), 4.41 (d, *J* = 14.9 Hz, 1H), 4.24 (d, *J* = 14.9 Hz, 1H), 2.37 (s, 3H), 1.27 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.20, 149.75, 145.81, 144.30, 140.70, 137.59, 132.73, 131.99, 131.96, 129.70, 129.22, 128.90, 128.73, 127.40, 126.32, 125.92, 125.84, 124.21, 123.41, 68.93, 57.09, 34.55, 31.35, 21.65. **HRMS** (ESI, m/z) calcd for $C_{32}H_{32}NO_3S^+$ $[M+H]^+$ 510.2097, found 510.2093.

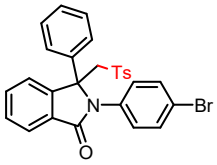


(Z)-4-fluoro-N-(3-phenyl-3-(tosylmethyl)isobenzofuran-1(3*H*)-ylidene)aniline (3ea): white solid, m.p.274-275 °C, (37.7 mg, 80% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.32 – 7.26 (m, 3H), 7.20 (d, *J* = 8.3 Hz, 2H), 7.08 (ddd, *J* = 14.1, 11.7, 6.3 Hz, 5H), 7.00 (d, *J* = 6.6 Hz, 2H), 6.94 (t, *J* = 8.7 Hz, 2H), 6.68 (d, *J* = 7.7 Hz, 1H), 4.37 (d, *J* = 15.0 Hz, 1H), 4.16 (d, *J* = 14.9 Hz, 1H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.17, 161.56 (d, $J_{C\text{-}F}$ = 249.4 Hz), 145.50, 144.46, 140.16, 137.45, 132.08, 131.99, 131.25 (d, $J_{C\text{-}F}$ = 3.0 Hz), 129.82, 129.80, 129.74, 129.25, 129.05 ($J_{C\text{-}F}$ = 4.0 Hz), 127.34, 126.11, 124.26, 123.49, 115.89 ($J_{C\text{-}F}$ = 33.3 Hz), 68.88, 57.18, 21.64. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -114.02. **HRMS** (ESI, m/z) calcd for $C_{28}H_{23}FNO_3S^+$ $[M+H]^+$ 472.1377, found 472.1375.

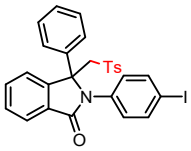


(*Z*)-4-chloro-*N*-(3-phenyl-3-(tosylmethyl)isobenzofuran-1(3*H*)-ylidene)anilin (3fa): white solid, m.p.287-289 °C, (42.9 mg, 88% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.33 – 7.28 (m, 3H), 7.23 – 7.19 (m, 4H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 8.2 Hz, 2H), 7.04 (d, *J* = 8.8 Hz, 4H), 6.72 (d, *J* = 7.7 Hz, 1H), 4.40 (d, *J* = 15.0 Hz,

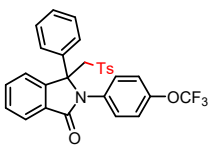
1H), 4.18 (d, *J* = 15.0 Hz, 1H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.12, 145.71, 144.51, 140.26, 137.36, 134.14, 132.77, 132.26, 131.61, 129.80, 129.40, 129.09, 129.02, 128.38, 127.36, 125.83, 124.32, 123.35, 68.87, 57.13, 21.64. **HRMS** (ESI, m/z) calcd for $C_{28}H_{23}ClNO_3S^+$ $[M+H]^+$ 488.1082, found 488.1085.



(*Z*)-4-bromo-*N*-(3-phenyl-3-(tosylmethyl)isobenzofuran-1(3*H*)-ylidene)aniline (3ga): white solid, m.p.277-278 °C, (47.6 mg, 89% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.3 Hz, 1H), 7.36 (d, *J* = 8.8 Hz, 2H), 7.30 (d, *J* = 7.2 Hz, 3H), 7.20 (d, *J* = 8.2 Hz, 2H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 8.1 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 6.72 (d, *J* = 7.7 Hz, 1H), 4.41 (d, *J* = 15.0 Hz, 1H), 4.19 (d, *J* = 15.0 Hz, 1H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.09, 145.76, 144.52, 140.27, 137.34, 134.72, 132.30, 132.05, 131.54, 129.81, 129.43, 129.09, 129.01, 128.53, 127.36, 125.78, 124.33, 123.32, 120.78, 68.84, 57.12, 21.65. **HRMS** (ESI, m/z) calcd for $C_{28}H_{23}BrNO_3S^+$ $[M+H]^+$ 532.0577, found 532.0574.

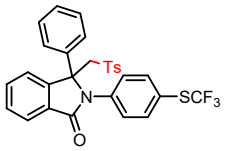


(*Z*)-4-iodo-*N*-(3-phenyl-3-(tosylmethyl)isobenzofuran-1(3*H*)-ylidene)aniline (3ha): white solid, m.p.266-268 °C, (48.3 mg, 83% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.32 – 7.27 (m, 3H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.10 – 7.03 (m, 4H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.73 (d, *J* = 7.7 Hz, 1H), 4.43 (d, *J* = 15.0 Hz, 1H), 4.20 (d, *J* = 15.0 Hz, 1H), 2.37 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.10, 145.83, 144.53, 140.28, 138.00, 137.30, 135.51, 132.35, 131.45, 129.81, 129.46, 129.08, 128.99, 128.51, 127.35, 125.70, 124.32, 123.29, 92.15, 68.83, 57.09, 21.67. **HRMS** (ESI, m/z) calcd for $C_{28}H_{23}INO_3S^+$ $[M+H]^+$ 580.0438, found 580.0440.

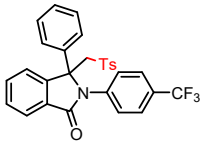


(*Z*)-*N*-(3-phenyl-3-(tosylmethyl)isobenzofuran-1(3*H*)-ylidene)-4-

(trifluoromethoxy)aniline (3ia): white solid, m.p.220-222 °C, (52.8 mg, 98% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 5.1 Hz, 3H), 7.22 – 7.13 (m, 5H), 7.07 (dd, *J* = 11.7, 6.5 Hz, 6H), 6.75 (d, *J* = 7.7 Hz, 1H), 4.42 (d, *J* = 15.0 Hz, 1H), 4.19 (d, *J* = 15.0 Hz, 1H), 2.37 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.20, 147.47, 145.79, 144.55, 140.31, 137.34, 134.18, 132.37, 131.42, 129.80, 129.48, 129.08 (d, J_{C-F} = 7.0 Hz), 128.14, 127.34, 125.73, 124.38, 123.29, 121.70 (q, J_{C-F} = 2 Hz), 121.28, 68.93, 57.02, 21.61. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -57.83. **HRMS** (ESI, m/z) calcd for $C_{29}H_{23}F_3NO_4S^+$ $[M+H]^+$ 538.1294, found 538.1290.

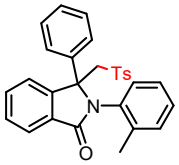


(*Z*)-*N*-(3-phenyl-3-(tosylmethyl)isobenzofuran-1(3*H*)-ylidene)-4-((trifluoromethyl)thio)aniline (3ja): white solid, m.p.235-237 °C, (54.8 mg, 99% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.6 Hz, 1H), 7.52 – 7.43 (m, 3H), 7.31 (dd, *J* = 6.1, 3.7 Hz, 4H), 7.26 – 7.17 (m, 4H), 7.12 (dd, *J* = 6.7, 2.8 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 2H), 6.86 (d, *J* = 7.7 Hz, 1H), 4.51 (d, *J* = 15.0 Hz, 1H), 4.26 (d, *J* = 15.0 Hz, 1H), 2.36 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.35, 146.22, 144.70, 140.44, 138.74, 137.16, 136.72, 132.78, 130.63, 129.83, 129.74 129.15, 128.98, 128.02, 127.36, 125.70, 125.16, 124.51, 123.13, 121.36 (q, J_{C-F} = 2.0 Hz), 69.03, 56.86, 21.60. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -42.60. **HRMS** (ESI, m/z) calcd for $C_{29}H_{23}F_3NO_3S^+$ $[M+H]^+$ 522.1345, found 522.1348.

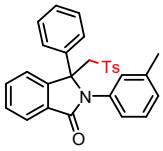


(*Z*)-*N*-(3-phenyl-3-(tosylmethyl)isobenzofuran-1(3*H*)-ylidene)-4-(trifluoromethyl)aniline (3ka): white solid, m.p.240-241 °C,(52 mg, 99% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 3H), 7.31 (t, *J* = 7.0 Hz, 5H), 7.20 (t, *J* = 8.0 Hz, 3H), 7.11 (dd, *J* = 6.4, 3.2 Hz, 2H), 7.05 (d, *J* = 8.3 Hz, 2H), 6.79 (d, *J* = 7.7 Hz, 1H), 4.52 (d, *J* = 15.1 Hz, 1H), 4.26 (d, *J* = 15.0 Hz, 1H), 2.35 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.36, 146.14, 144.63, 140.36, 139.31, 137.15, 132.73, 130.83, 129.75 (d, J_{C-F} = 11.1 Hz), 129.70, 129.08 (d, J_{C-F} = 11.1 Hz),

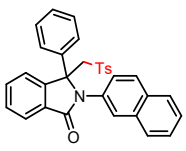
127.34, 125.85 (q, $J_{C\text{-}F}$ = 3.0 Hz), 125.38 (d, $J_{C\text{-}F}$ = 25.3 Hz), 124.48, 123.09, 68.97, 57.00, 21.59. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -62.52. **HRMS** (ESI, m/z) calcd for $C_{32}H_{32}NO_3S^+$ $[M+H]^+$ 510.2097, found 510.2095.



(*Z*)-2-methyl-*N*-(3-phenyl-3-(tosylmethyl)isobenzofuran-1(3*H*)-ylidene)aniline (3la): white solid, m.p.294-296 °C, (26 mg, 58% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.6 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.33 – 7.22 (m, 5H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.14 – 7.10 (m, 3H), 7.08 – 7.05 (m, 1H), 6.95 (d, *J* = 7.7 Hz, 1H), 6.67 (d, *J* = 7.7 Hz, 2H), 4.61 (d, *J* = 15.3 Hz, 1H), 4.08 (d, *J* = 15.3 Hz, 1H), 2.41 (s, 3H), 1.12 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.77, 144.35, 143.25, 140.06, 137.85, 137.44, 133.62, 133.28, 131.30, 131.13, 130.32, 129.79, 129.24, 129.03, 128.41, 127.40, 127.40, 127.09, 124.88, 124.54, 124.52, 69.33, 60.08, 21.63, 17.17. **HRMS** (ESI, m/z) calcd for $C_{29}H_{26}NO_3S^+$ $[M+H]^+$ 468.1628, found 468.1624.

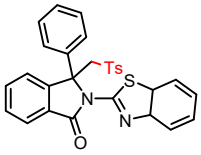


(*Z*)-3-methyl-*N*-(3-phenyl-3-(tosylmethyl)isobenzofuran-1(3*H*)-ylidene)aniline (3ma): white solid, m.p.251-253 °C, (36.5 mg, 78% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 3H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 3H), 7.02 (t, *J* = 7.1 Hz, 3H), 6.93 (s, 1H), 6.75 (dd, *J* = 16.5, 7.8 Hz, 2H), 4.37 (d, *J* = 14.9 Hz, 1H), 4.22 (d, *J* = 14.9 Hz, 1H), 2.38 (s, 3H), 2.23 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.05, 145.62, 144.32, 138.72, 137.63, 132.15, 131.90, 129.71, 129.06, 128.96, 128.75, 128.61, 128.33, 128.08, 127.42, 126.05, 124.18, 124.14, 123.59, 68.92, 57.35, 21.61, 21.51. **HRMS** (ESI, m/z) calcd for $C_{29}H_{26}NO_3S^+$ $[M+H]^+$ 468.1628, found 468.1624.

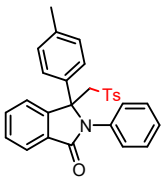


(*Z*)-*N*-(3-phenyl-3-(tosylmethyl)isobenzofuran-1(3*H*)-ylidene)naphthalen-2-amine (3na):

white solid, m.p.246-248 °C, (26.7 mg, 53% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.6 Hz, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 8.9 Hz, 1H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.46 – 7.39 (m, 3H), 7.33 – 7.28 (m, 3H), 7.26 – 7.21 (m, 4H), 7.06 (dd, *J* = 12.8, 7.5 Hz, 4H), 6.84 (d, *J* = 7.7 Hz, 1H), 4.40 (d, *J* = 14.9 Hz, 1H), 4.27 (d, *J* = 14.9 Hz, 1H), 2.33 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.35, 145.84, 144.43, 140.55, 137.49, 133.26, 133.12, 132.14, 132.10, 131.99, 129.77, 129.29, 129.08, 128.93, 128.63, 128.27, 127.54, 127.41, 126.33, 126.16, 126.07, 125.59, 125.49, 124.29, 123.57, 69.16, 57.36, 21.63. **HRMS** (ESI, m/z) calcd for $C_{32}H_{26}NO_3S^+$ $[M+H]^+$ 504.1628, found 504.1626.

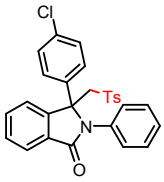


(*Z*)-*N*-(3-phenyl-3-(tosylmethyl)isobenzofuran-1(3*H*)-ylidene)benzo[d]thiazol-2-amine (3oa): white solid, m.p.202-204 °C, (45 mg, 88% yield)**.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 5.7, 2.8 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.59 – 7.55 (m, 2H), 7.50 (d, *J* = 8.1 Hz, 1H), 7.34 – 7.28 (m, 3H), 7.19 (dt, *J* = 22.9, 8.3 Hz, 7H), 6.77 (d, *J* = 8.2 Hz, 2H), 5.99 (d, *J* = 14.8 Hz, 1H), 4.60 (d, *J* = 14.8 Hz, 1H), 2.04 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.40, 154.89, 148.46, 148.26, 144.42, 139.35, 136.03, 134.40, 132.00, 129.40, 129.33, 129.06, 128.34, 128.27, 127.51, 125.76, 124.91, 124.76, 123.78, 123.09, 121.49, 120.73, 69.61, 58.06, 21.31. **HRMS** (ESI, m/z) calcd for $C_{29}H_{23}N_2O_3S_2^+$ $[M+H]^+$ 511.1145, found 511.1148.

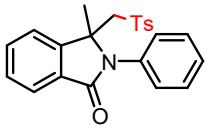


(*Z*)-*N*-(3-(p-tolyl)-3-(tosylmethyl)isobenzofuran-1(3*H*)-ylidene)aniline (3pa): white solid, m.p.255-257 °C, (44.6 mg, 95% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 7.7, 2.5 Hz, 1H), 7.41 – 7.35 (m, 1H), 7.19 – 7.12 (m, 1H), 7.11 – 7.05 (m, 1H), 7.04 – 6.99 (m, 1H), 6.84 (d, *J* = 8.3 Hz, 1H), 6.68 (t, *J* = 5.2 Hz, 1H), 4.29 (d, *J* = 14.9 Hz, 1H), 4.13 (d, *J* = 14.9 Hz, 1H), 2.30 (s, 1H), 2.24 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.33, 138.76, 137.56, 137.51, 135.59, 131.98, 131.93, 129.89, 129.74, 128.90, 127.40, 127.16, 127.09, 125.81, 124.23, 123.42, 77.30,

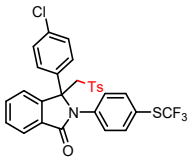
68.84, 57.29, 21.63, 21.09. **HRMS** (ESI, m/z) calcd for $C_{29}H_{26}NO_3S^+$ $[M+H]^+$ 468.1628, found 468.1624.



(*Z*)-*N*-(3-(4-chlorophenyl)-3-(tosylmethyl)isobenzofuran-1(3*H*)-ylidene)aniline (3qa): white solid, m.p.278-280 °C,(44.33 mg, 90% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.27 – 7.15 (m, 8H), 7.09 (d, *J* = 7.8 Hz, 4H), 6.97 (d, *J* = 8.6 Hz, 2H), 6.75 (d, *J* = 7.7 Hz, 1H), 4.33 (d, *J* = 14.9 Hz, 1H), 4.18 (d, *J* = 14.9 Hz, 1H), 2.38 (s, 3H). **13C NMR** (101 MHz, CDCl3) δ 168.02, 145.28, 144.53, 139.15, 137.42, 135.29, 134.86, 132.17, 131.90, 129.81, 129.39, 129.23, 129.12, 127.42, 124.42, 123.45, 68.54, 57.17, 21.65. **HRMS** (ESI, m/z) calcd for $C_{28}H_{23}ClNO_3S^+$ $[M+H]^+$ 488.1082, found 488.1080.

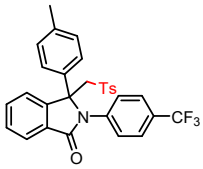


(*Z*)-*N*-(3-methyl-3-(tosylmethyl)isobenzofuran-1(3*H*)-ylidene)aniline (3ra): white solid, m.p.275-277 °C, (18 mg, 46% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.6 Hz, 1H), 7.48 (tt, *J* = 10.1, 5.1 Hz, 6H), 7.29 (dd, *J* = 14.5, 7.0 Hz, 3H), 7.20 (d, *J* = 7.7 Hz, 1H), 7.13 (d, *J* = 8.2 Hz, 2H), 3.61 (q, *J* = 15.1 Hz, 2H), 2.39 (s, 3H), 1.65 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.73, 144.48, 137.45, 135.04, 131.71, 131.56, 130.22, 129.78, 129.76, 128.82, 128.72, 127.57, 124.23, 122.64, 64.47, 60.85, 27.50, 21.61. **HRMS** (ESI, m/z) calcd for $C_{23}H_{22}NO_3S^+$ $[M+H]^+$ 392.1315, found 392.1318.

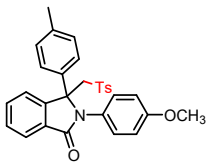


(*Z*)-*N*-(3-(4-chlorophenyl)-3-(tosylmethyl)isobenzofuran-1(3*H*)-ylidene)-4-((trifluoromethyl)thio)aniline (3sa): white solid, m.p.247-249 °C, (58 mg, 98.7% yield) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.6 Hz, 1H), 7.50 (dd, *J* = 17.3, 8.1 Hz, 3H), 7.32 – 7.27 (m, 3H), 7.25 (t, *J* = 1.9 Hz, 2H), 7.19 (d, *J* = 8.3 Hz, 2H), 7.08 – 7.05 (m, 4H), 6.85 (d, *J* = 7.7 Hz, 1H), 4.47 (d, *J* = 14.9 Hz, 1H), 4.23 (d, *J* = 14.9 Hz, 1H), 2.36 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.21,

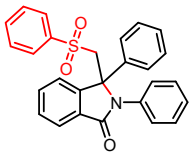
145.82, 144.83, 139.12, 138.55, 137.06, 136.81, 135.05, 132.92, 130.56, 129.90 (d, $J_{C\text{-}F}$ = 4.0 Hz), 129.38, 128.00, 127.37, 126.73, 125.76, 124.64, 123.10, 121.69 (q, $J_{C\text{-}F}$ = 2.0 Hz), 68.65, 56.74, 21.61. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -42.55. **HRMS** (ESI, m/z) calcd for $C_{29}H_{22}ClF_3NO_3S_2^+$ $[M+H]^+$ 588.0676, found 588.0679.



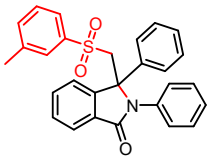
(*Z*)-*N*-(3-(p-tolyl)-3-(tosylmethyl)isobenzofuran-1(3*H*)-ylidene)-4-(trifluoromethyl)aniline (3ta): white solid, m.p.214-216 °C, (50.9 mg, 95% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.6 Hz, 1H), 7.46 (dd, *J* = 13.4, 8.1 Hz, 3H), 7.32 (d, *J* = 8.5 Hz, 2H), 7.19 (t, *J* = 7.9 Hz, 3H), 7.12 (d, *J* = 8.2 Hz, 2H), 7.05 (d, *J* = 8.1 Hz, 2H), 6.98 (d, *J* = 8.3 Hz, 2H), 6.78 (d, *J* = 7.7 Hz, 1H), 4.49 (d, *J* = 15.1 Hz, 1H), 4.24 (d, *J* = 15.0 Hz, 1H), 2.33 (d, *J* = 17.3 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.39, 146.32, 144.58, 139.39, 139.05, 137.24 (d, $J_{C\text{-}F}$ = 16.2 Hz), 132.70, 130.79, 130.35, 129.79, 129.04, 127.87 (d, $J_{C\text{-}F}$ = 33.3 Hz), 127.33, 125.83 (q, $J_{C\text{-}F}$ = 4.0 Hz), 125.79, 125.47, 125.20, 124.41, 123.04, 68.88, 57.03, 21.58, 21.06. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -62.53. **HRMS** (ESI, m/z) calcd for $C_{30}H_{25}F_3NO_3S^+$ $[M+H]^+$ 536.1502, found 536.1504.



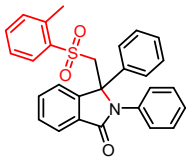
(*Z*)-4-methoxy-*N*-(3-(p-tolyl)-3-(tosylmethyl)isobenzofuran-1(3*H*)-ylidene)aniline (3ua): white solid, m.p.242-244 °C, (31.3 mg, 63% yield), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.12 – 7.04 (m, 5H), 6.98 (d, *J* = 9.0 Hz, 2H), 6.85 (d, *J* = 8.3 Hz, 2H), 6.78 (d, *J* = 9.0 Hz, 2H), 6.68 (d, *J* = 7.7 Hz, 1H), 4.30 (d, *J* = 14.9 Hz, 1H), 4.16 (d, *J* = 14.9 Hz, 1H), 3.76 (s, 3H), 2.37 (s, 3H), 2.31 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.13, 158.68, 145.64, 144.25, 138.76, 137.72, 137.32, 132.45, 131.70, 129.71, 129.69, 129.47, 128.83 , 127.91, 127.39, 126.17, 124.09, 123.58, 114.24, 68.76, 57.45, 55.41, 21.60, 21.07. **HRMS** (ESI, m/z) calcd for $C_{30}H_{28}NO_4S^+$ $[M+H]^+$ 498.1734, found 498.1736.



(*Z*)-*N*-(3-phenyl-3-((phenylsulfonyl)methyl)isobenzofuran-1(3*H*)-ylidene)anili (3ab): white solid, m.p.266-268 °C, (37 mg, 84% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.6 Hz, 1H), 7.39 (dd, *J* = 15.1, 8.0 Hz, 2H), 7.26 – 7.14 (m, 11H), 7.05 (t, *J* = 8.0 Hz, 1H), 7.01 (dd, *J* = 8.0, 1.5 Hz, 2H), 6.96 (dd, *J* = 7.7, 1.8 Hz, 2H), 6.64 (d, *J* = 7.7 Hz, 1H), 4.34 (d, *J* = 15.0 Hz, 1H), 4.17 (d, *J* = 14.9 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.52, 140.49, 135.50, 133.30, 132.09, 132.07, 129.21, 129.16, 129.04, 128.97, 128.84, 127.35, 127.24, 125.98, 124.29, 123.44, 68.92, 57.25. **HRMS** (ESI, m/z) calcd for $C_{27}H_{22}NO_3S^+$ $[M+H]^+$ 440.1315, found 440.1318.

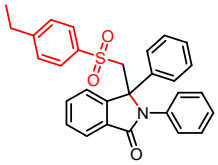


(*Z*)-*N*-(3-phenyl-3-((m-tolylsulfonyl)methyl)isobenzofuran-1(3*H*)-ylidene)aniline (3ac): white solid, m.p.267-269 °C, (22.8 mg, 50% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 6.2 Hz, 5H), 7.25 – 7.20 (m, 4H), 7.08 (dt, *J* = 18.5, 7.8 Hz, 5H), 6.98 (s, 1H), 6.69 (d, *J* = 7.7 Hz, 1H), 4.41 (d, *J* = 15.0 Hz, 1H), 4.24 (d, *J* = 15.0 Hz, 1H), 2.26 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.06, 145.57, 140.49, 140.20, 139.31, 135.45, 134.20, 132.07, 131.82, 129.19, 129.00, 128.94, 128.88, 128.81, 127.89, 12730, 127.20, 125.95, 124.35, 124.14, 123.45, 68.88, 57.28, 21.21. **HRMS** (ESI, m/z) calcd for $C_{28}H_{24}NO_3S^+$ $[M+H]^+$ 454.1471, found 454.1474.

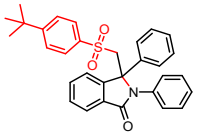


(*Z*)-*N*-(3-phenyl-3-((o-tolylsulfonyl)methyl)isobenzofuran-1(3*H*)-ylidene)aniline (3ad): white solid, m.p.247-249 °C, (28.4 mg, 62% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.33 – 7.28 (m, 3H), 7.22 (t, *J* = 6.9 Hz, 3H), 7.19 – 7.11 (m, 3H), 7.10 – 7.04 (m, 5H), 6.76 (d, *J* = 7.7 Hz, 1H), 4.44 (d, *J* = 15.0 Hz, 1H), 4.29 (d, *J* = 15.0 Hz, 1H), 2.46 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.07, 145.76, 140.62, 138.32, 136.97, 135.51, 133.37, 132.46, 132.07, 131.62, 129.67, 129.32, 129.09, 128.91, 128.81,

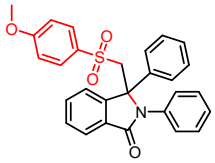
126.95, 126.81, 126.70, 125.74, 124.25, 123.01, 68.95, 55.95, 20.14. **HRMS** (ESI, m/z) calcd for $C_{28}H_{24}NO_3S^+$ $[M+H]^+$ 454.1471, found 454.1475.



(*Z*)-*N*-(3-(((4-ethylphenyl)sulfonyl)methyl)-3-phenylisobenzofuran-1(3*H*)-ylidene)aniline (3ae): white solid, m.p.270-275 °C, (33.8 mg, 72% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.52 – 7.22 (m, 9H), 7.30 – 7.26 (m, 3H), 7.24 (dd, *J* = 8.0, 3.9 Hz, 5H), 7.14 – 7.08 (m, 5H), 7.04 (dd, *J* = 7.7, 1.8 Hz, 2H), 6.73 (d, *J* = 7.7 Hz, 1H), 4.41 (d, *J* = 14.9 Hz, 1H), 4.23 (d, *J* = 14.9 Hz, 1H), 2.66 (q, *J* = 7.6 Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.14, 150.49, 145.71, 140.52, 137.68, 135.53, 132.02, 131.97, 129.22, 128.98, 128.95, 128.83, 128.67, 127.48, 127.29, 127.20, 125.97, 124.25, 123.47, 68.94, 57.20, 28.91, 15.40. **HRMS** (ESI, m/z) calcd for $C_{29}H_{26}NO_3S^+$ $[M+H]^+$ 468.1628, found 468.1625.

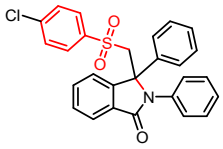


(*Z*)-*N*-(3-(((4-(tert-butyl)phenyl)sulfonyl)methyl)-3-phenylisobenzofuran-1(3*H*)-ylidene)aniline (3af): white solid, m.p.283-285 °C, (37.3 mg, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.34 – 7.27 (m, 6H), 7.24 – 7.16 (m, 3H), 7.11 – 7.07 (m, 3H), 7.04 (d, *J* = 6.0 Hz, 2H), 6.71 (d, *J* = 7.7 Hz, 1H), 4.42 (d, *J* = 14.9 Hz, 1H), 4.23 (d, *J* = 14.9 Hz, 1H), 1.31 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.08, 157.19, 145.69, 140.51, 137.35, 135.52, 131.96, 131.93, 129.19, 129.04, 128.93, 128.80, 127.31, 127.17, 126.18, 125.97, 124.23, 123.63, 123.44, 68.90, 57.14, 35.21, 31.10. **HRMS** (ESI, m/z) calcd for $C_{31}H_{30}NO_3S^+$ $[M+H]^+$ 496.1941, found 496.1943.

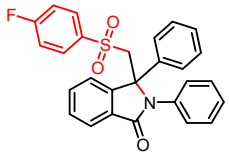


(*Z*)-*N*-(3-(((4-methoxyphenyl)sulfonyl)methyl)-3-phenylisobenzofuran-1(3*H*)-ylidene)aniline (3ag): white solid, m.p.250-252 °C, (25 mg, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.6 Hz, 1H), 7.46 (dd, *J* = 11.0, 4.0 Hz, 1H), 7.29 (t, *J* = 5.2 Hz, 3H), 7.22

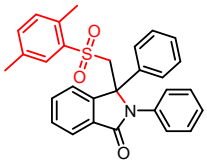
(dd, J = 15.9, 8.2 Hz, 6H), 7.09 (d, J = 8.4 Hz, 2H), 7.04 (d, J = 7.2 Hz, 2H), 6.77 (d, J = 7.7 Hz, 1H), 6.74 (d, J = 8.9 Hz, 2H), 4.38 (d, J = 14.9 Hz, 1H), 4.23 (d, J = 14.9 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.13, 163.46, 145.79, 140.54, 135.54, 132.07, 131.94, 129.56, 129.38, 129.20, 128.99, 128.91, 128.24, 127.15, 125.92, 124.27, 123.46, 114.33, 68.98, 57.38, 55.76. **HRMS** (ESI, m/z) calcd for $C_{28}H_{24}NO_4S^+$ $[M+H]^+$ 470.1421, found 470.1425.



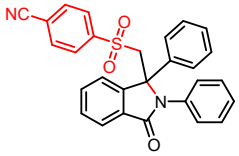
(*Z*)-*N*-(3-(((4-chlorophenyl)sulfonyl)methyl)-3-phenylisobenzofuran-1(3*H*)-ylidene)aniline (3ah): white solid, m.p.289-291 °C, (32.8 mg, 69% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, J = 7.6 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.33 – 7.26 (m, 4H), 7.23 (d, J = 8.9 Hz, 6H), 7.18 (t, J = 7.6 Hz, 1H), 7.09 (d, J = 6.6 Hz, 2H), 7.03 (d, J = 8.1 Hz, 2H), 6.72 (d, J = 7.7 Hz, 1H), 4.43 (d, J = 15.0 Hz, 1H), 4.28 (d, J = 15.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.64, 140.22, 140.15, 135.42, 132.18, 131.97, 129.42, 129.32, 129.19, 129.02, 128.95, 128.83, 127.22, 126.99, 125.85, 124.39, 123.34, 68.82, 57.33. **HRMS** (ESI, m/z) calcd for $C_{27}H_{21}ClNO_3S^+$ $[M+H]^+$ 474.0925, found 474.0921.



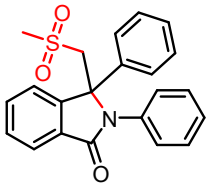
(*Z*)-*N*-(3-(((4-fluorophenyl)sulfonyl)methyl)-3-phenylisobenzofuran-1(3*H*)-ylidene)aniline (3ai): white solid, m.p.248-250 °C, (44.5 mg, 97% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.6 Hz, 1H), 7.48 (t, J = 7.5 Hz, 1H), 7.35 – 7.27 (m, 6H), 7.25 – 7.16 (m, 3H), 7.09 (d, J = 6.8 Hz, 2H), 7.03 (d, J = 7.9 Hz, 2H), 6.96 (t, J = 8.5 Hz, 2H), 6.72 (d, J = 7.7 Hz, 1H), 4.42 (d, J = 15.0 Hz, 1H), 4.28 (d, J = 15.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.05, 145.63, 140.24, 136.39 (d, $J_{C\text{-}F}$ = 3.0 Hz), 135.41, 132.15, 132.03, 130.26 (d, $J_{C\text{-}F}$ = 10.1 Hz), 129.30, 129.19, 129.03, 128.95, 127.29, 127.15, 125.91, 124.40, 123.35, 116.57, 116.44 (d, $J_{C\text{-}F}$ = 22.2 Hz), 68.86, 57.36. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -103.58. **HRMS** (ESI, m/z) calcd for $C_{27}H_{21}FNO_3S^+$ $[M+H]^+$ 458.1221, found 458.1226.



(*Z*)-*N*-(3-(((2,5-dimethylphenyl)sulfonyl)methyl)-3-phenylisobenzofuran-1(3*H*)-ylidene)aniline (3aj): white solid, m.p.210-212 °C, (39.3 mg, 84% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.32 – 7.28 (m, 3H), 7.23 (t, *J* = 7.6 Hz, 3H), 7.14 (d, *J* = 7.7 Hz, 1H), 7.09 (d, *J* = 7.8 Hz, 2H), 7.03 (dd, *J* = 9.1, 5.4 Hz, 4H), 6.85 (s, 1H), 6.67 (d, *J* = 7.7 Hz, 1H), 4.43 (d, *J* = 15.0 Hz, 1H), 4.26 (d, *J* = 15.0 Hz, 1H), 2.46 (s, 3H), 2.16 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.09, 145.65, 140.58, 137.83, 136.61, 135.50, 134.29, 133.59, 132.39, 131.89, 131.68, 130.07, 129.30, 128.95, 128.89, 128.85, 127.12 , 125.87, 123.95, 123.00, 68.94, 55.98, 20.73, 19.75. **HRMS** (ESI, m/z) calcd for $C_{29}H_{26}NO_3S^+$ $[M+H]^+$ 468.1628, found 468.1624.

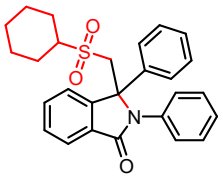


(*Z*)-4-(((1-phenyl-3-(phenylimino)-1,3-dihydroisobenzofuran-1yl)methyl)sulfonyl)benzonitrile (3al): white solid, m.p.205-207 °C, (28 mg, 60% yield). **^{1}H NMR** (400 MHz, d_6-DMSO) δ 7.85 (dd, *J* = 11.9, 7.8 Hz, 3H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 6.4 Hz, 3H), 7.27 (d, *J* = 7.7 Hz, 2H), 7.21 (dd, *J* = 7.3, 4.5 Hz, 3H), 7.16 – 7.10 (m, 3H), 6.90 (d, *J* = 7.7 Hz, 1H), 5.50 (d, *J* = 15.7 Hz, 1H), 4.49 (d, *J* = 15.7 Hz, 1H). ^{13}C NMR (400 MHz, Chloroform-*d*) δ 172.64, 151.34, 149.04, 145.29, 141.17, 138.26, 137.50, 135.85, 134.33, 133.84, 133.01, 131.51, 130.98, 128.96, 128.50, 122.84, 120.84, 60.90. **HRMS** (ESI, m/z) calcd for $C_{28}H_{21}N_2O_3S^+$ $[M+H]^+$ 468.1628, found 468.1623.

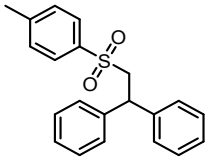


(*Z*)-3-((methylsulfonyl)methyl)-*N*,3-diphenylisobenzofuran-1(3H)-imine (3am): white solid, m.p.:200-202 °C, (27 mg, 73% yield).**^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.89 (d, *J* = 7.3 Hz, 1H), 7.70 – 7.58 (m, 2H), 7.52 (d, *J* = 7.5 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 3H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.23 (dd, *J* = 13.0, 6.7 Hz, 3H), 7.10 (d, *J* = 7.4 Hz, 2H), 5.10 (d, *J* = 15.2 Hz, 1H), 4.13 (d, *J* = 15.2 Hz, 1H),

2.51 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 167.87, 147.45, 140.85, 136.49, 133.07, 131.59, 129.77, 129.56, 129.13, 128.94, 127.08, 127.04, 126.45, 124.68, 124.01, 69.23, 55.42, 44.04. **HRMS** (ESI, m/z) calcd for $C_{22}H_{19}NO_3S^+$ $[M+H]^+$ 378.4655, found 378.4657.



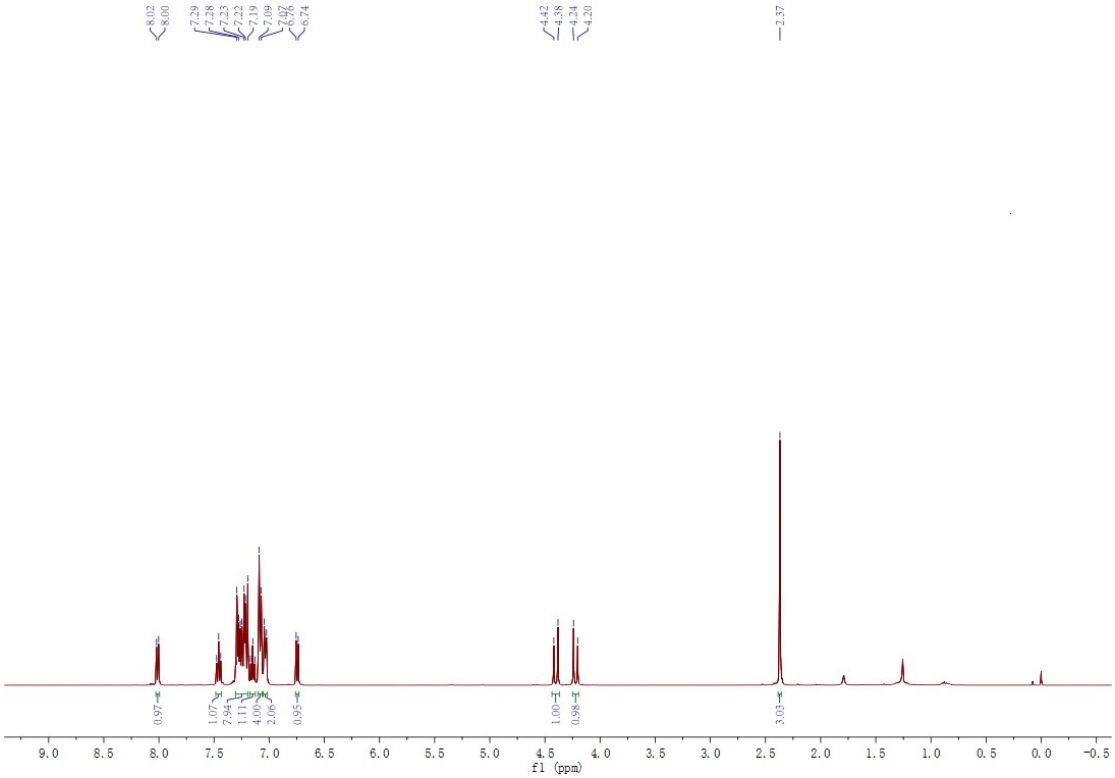
(*Z*)-3-((cyclohexylsulfonyl)methyl)-N,3-diphenylisobenzofuran-1(3H)-imine ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 – 8.04 (m, 1H), 7.64 – 7.57 (m, 2H), 7.41 – 7.34 (m, 4H), 7.30 – 7.24 (m, 3H), 7.18 (ddd, *J* = 8.8, 6.3, 2.0 Hz, 4H), 4.20 (d, *J* = 14.6 Hz, 1H), 3.94 (d, *J* = 14.5 Hz, 1H), 2.10 – 2.05 (m, 1H), 1.92 – 1.76 (m, 4H), 1.66 – 1.54 (m, 1H), 1.43 – 1.23 (m, 3H), 1.08 (d, *J* = 9.7 Hz, 1H), 0.99 – 0.89 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.20, 146.61, 140.62, 135.77, 132.32, 131.92, 129.40, 129.32, 128.97, 128.88, 127.10, 126.96, 125.97, 124.59, 123.50, 68.91, 63.07, 50.22, 25.28, 24.98, 24.13. **HRMS** (ESI, m/z) calcd for $C_{17}H_{27}NO_3S^+$ $[M+H]^+$ 445.5770, found 445.5772.



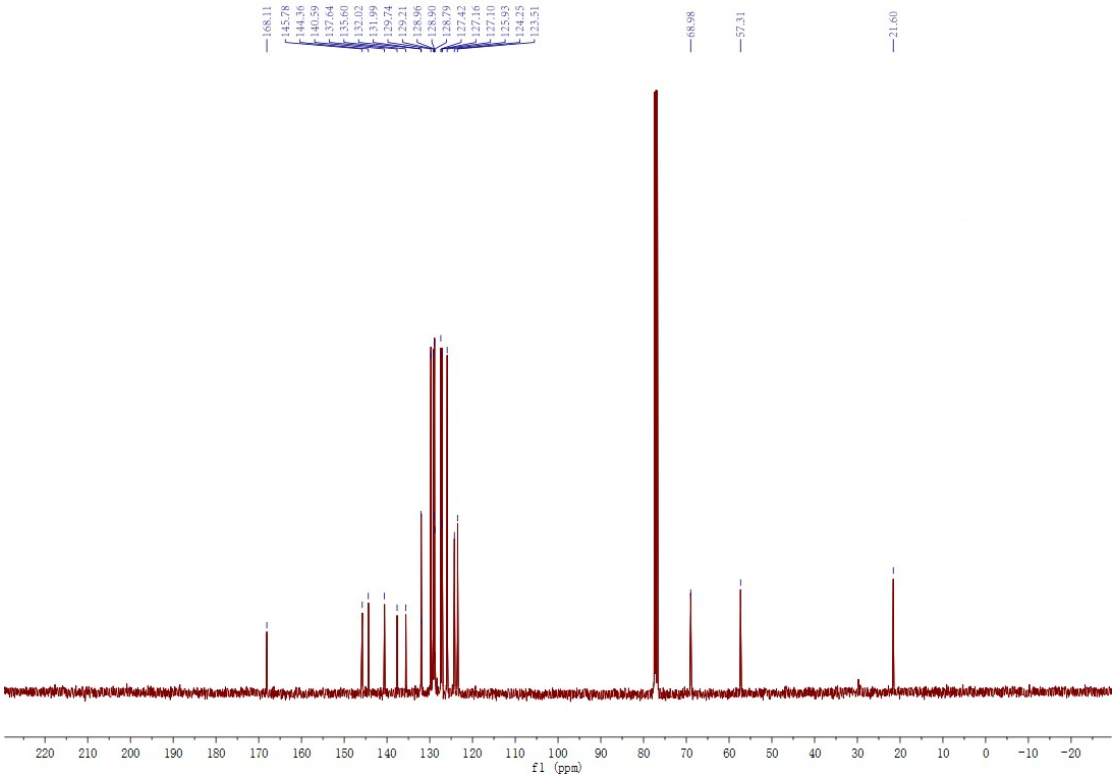
(2-tosylethane-1,1-diyl) dibenzene (4): corlorless oil, 68%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.48 – 7.44 (m, 2H), 7.41 – 7.37 (m, 4H), 7.27 – 7.22 (m, 6H), 7.16 (d, *J* = 8.1 Hz, 2H), 5.45 (d, *J* = 2.1 Hz, 1H), 4.23 (s, 2H), 2.42 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 144.58, 143.75, 137.40, 129.76, 128.34, 127.70, 127.54, 125.91, 76.71, 65.52, 21.68. **HRMS** (ESI, m/z) calcd for $C_{21}H_{21}O_2S^+$ $[M+H]^+$ 337.1257, found 337.1255.

8. NMR spectra of 3 and 4

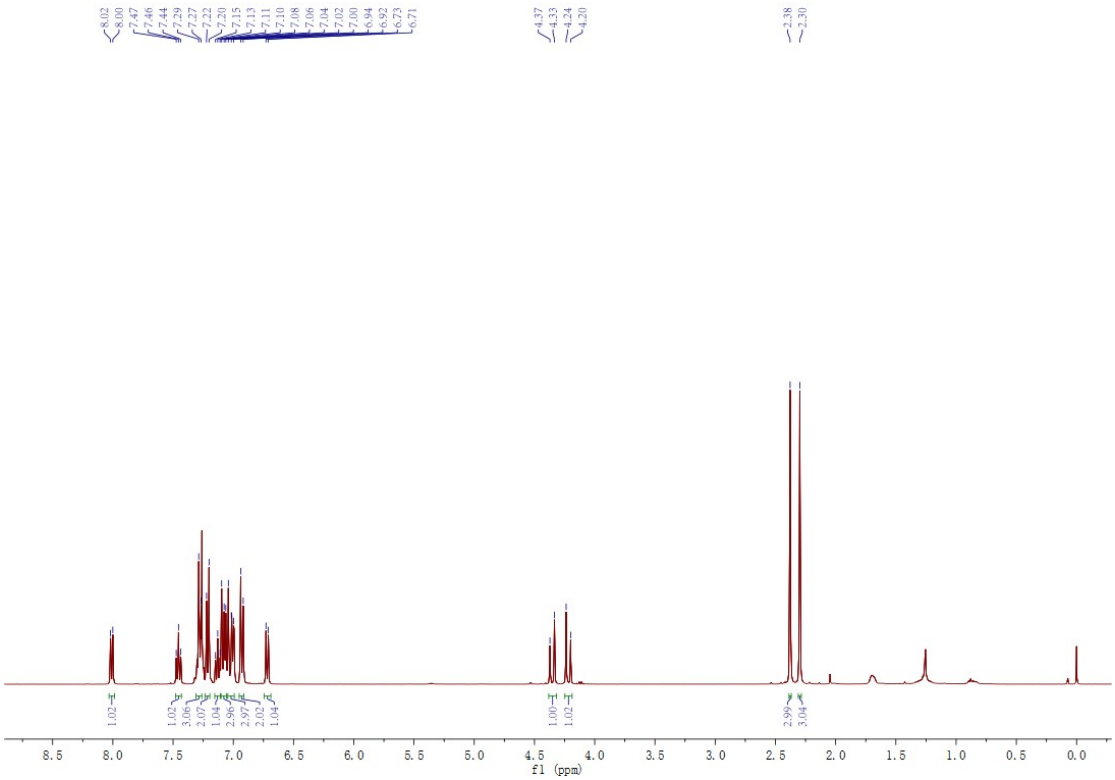
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3aa**



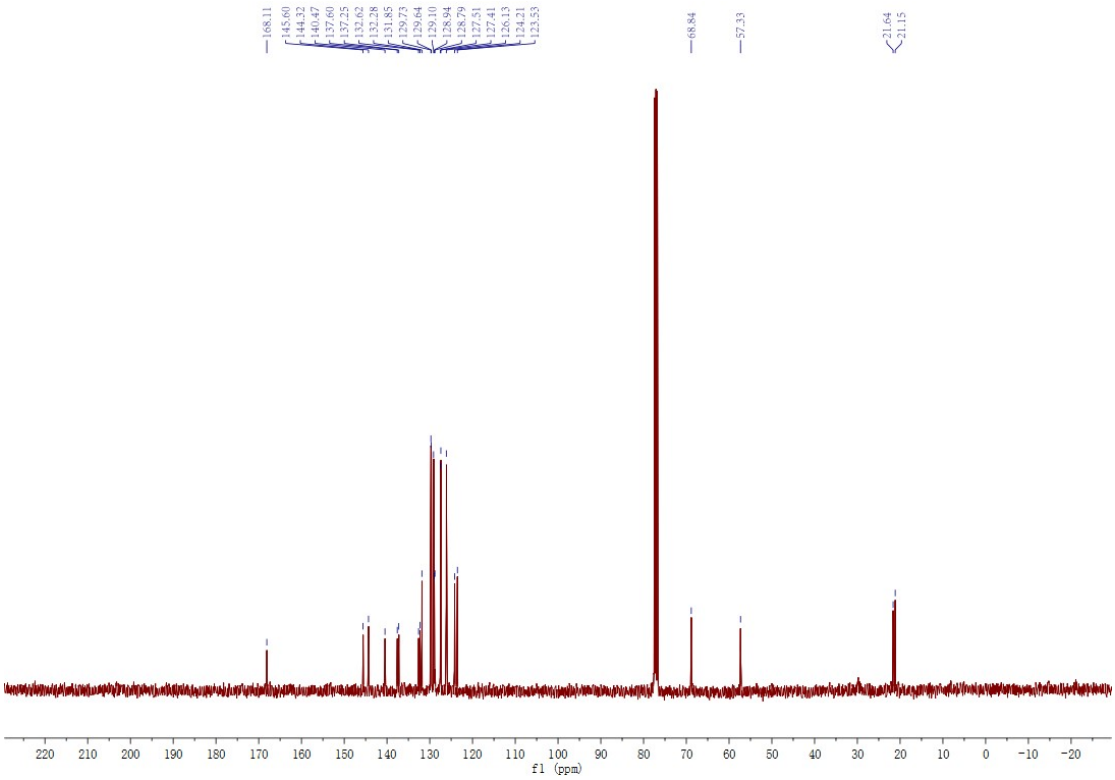
^{13}C NMR (400 MHz, $CDCl_3$) spectra of **3aa**



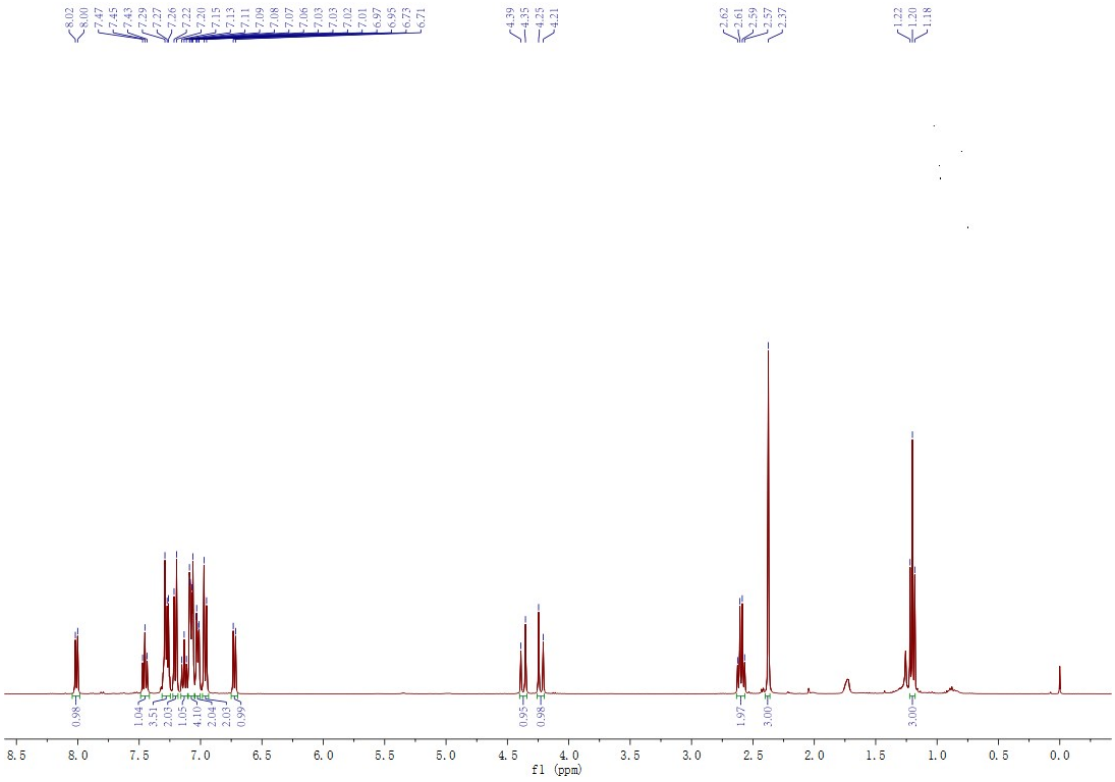
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ba**



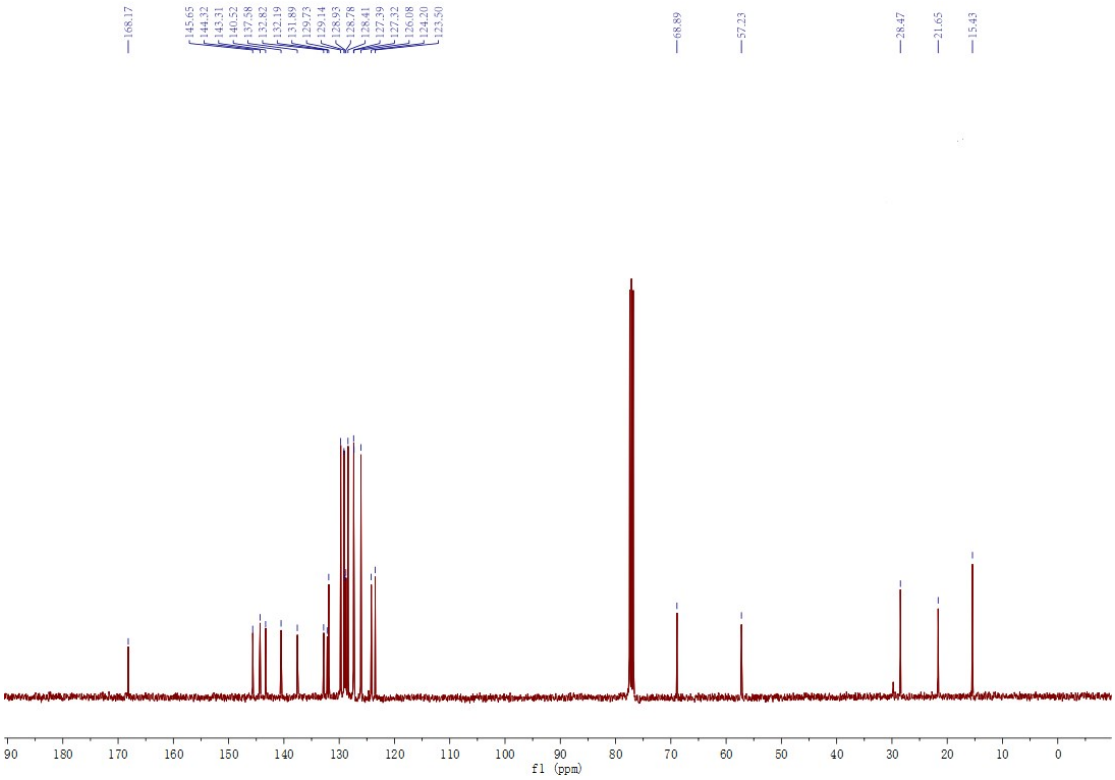
^{13}C NMR (400 MHz, $CDCl_3$) spectra of **3ba**



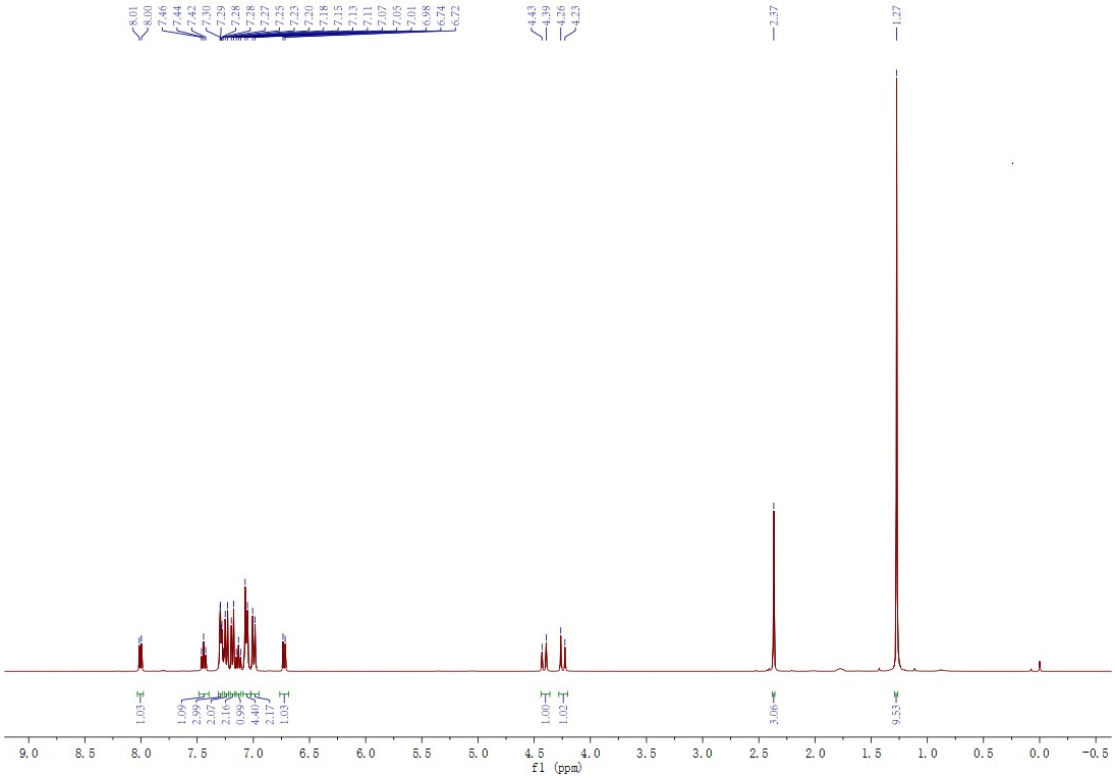
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ca**



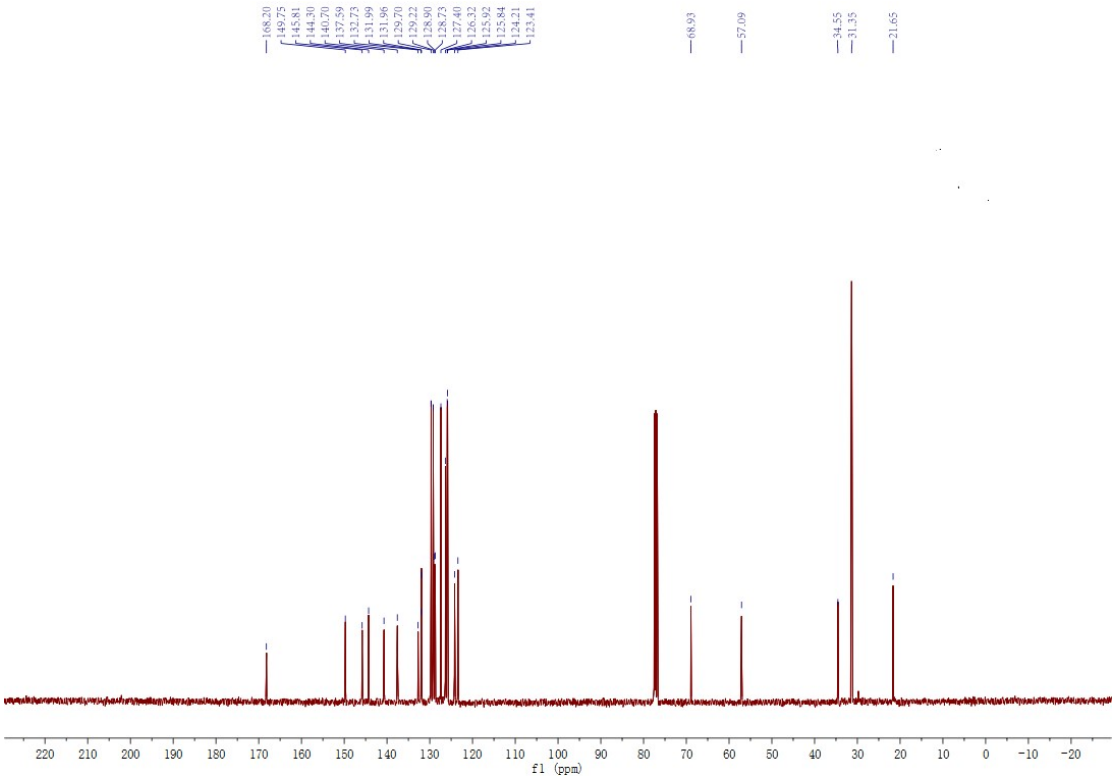
^{13}C NMR (400 MHz, $CDCl_3$) spectra of **3ca**



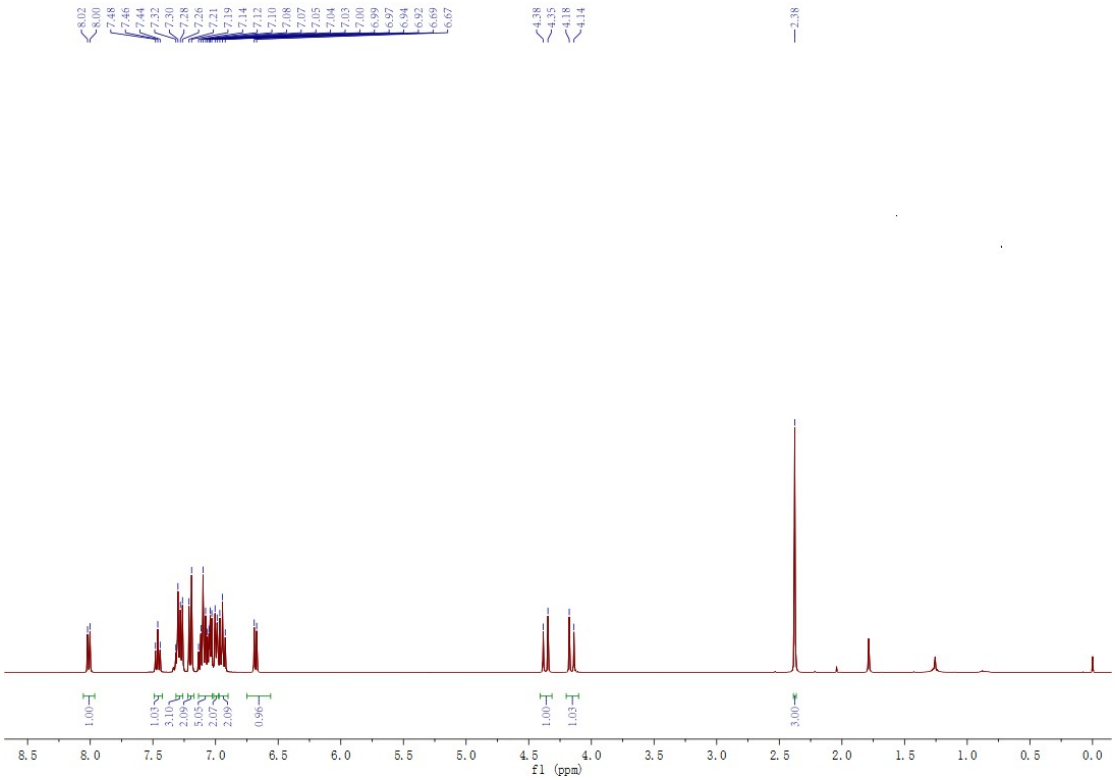
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3da**



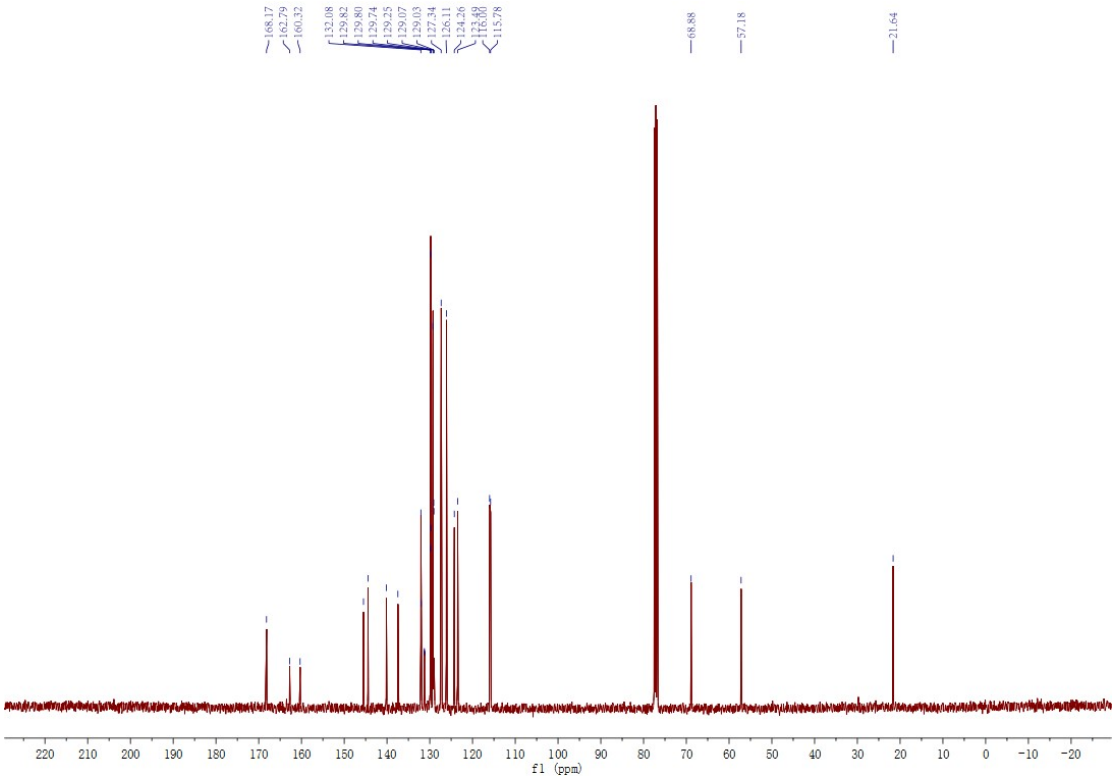
^{13}C NMR (400 MHz, $CDCl_3$) spectra of **3da**



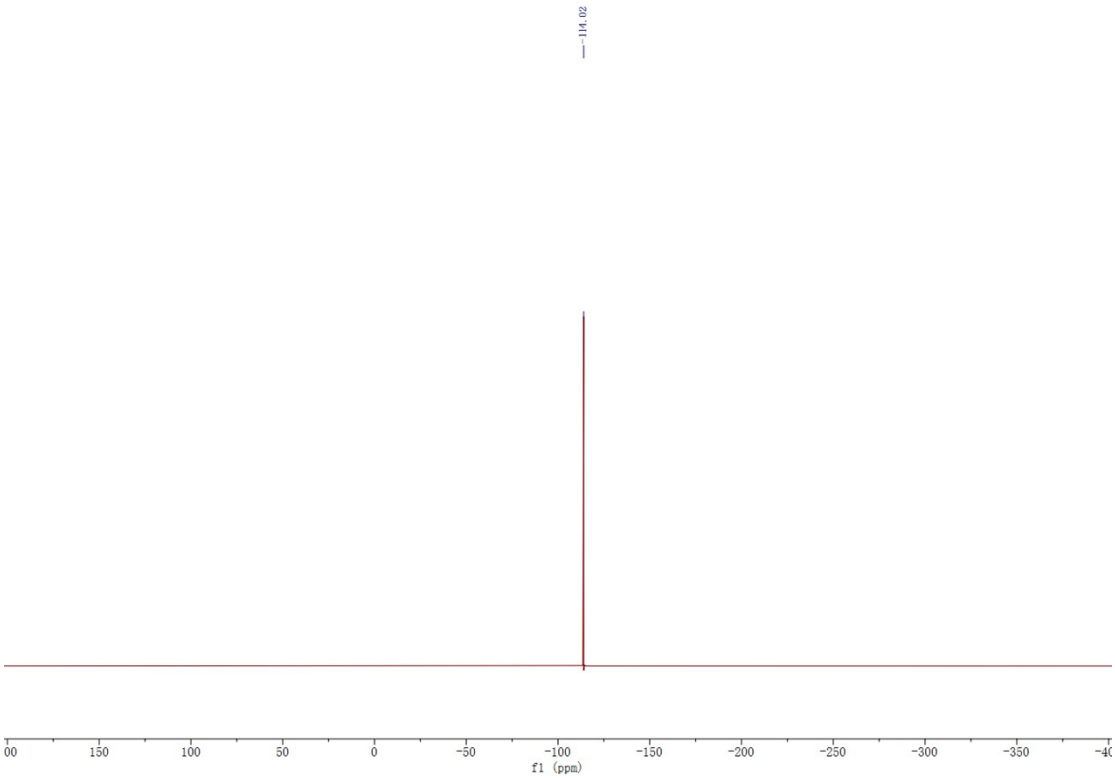
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ea**



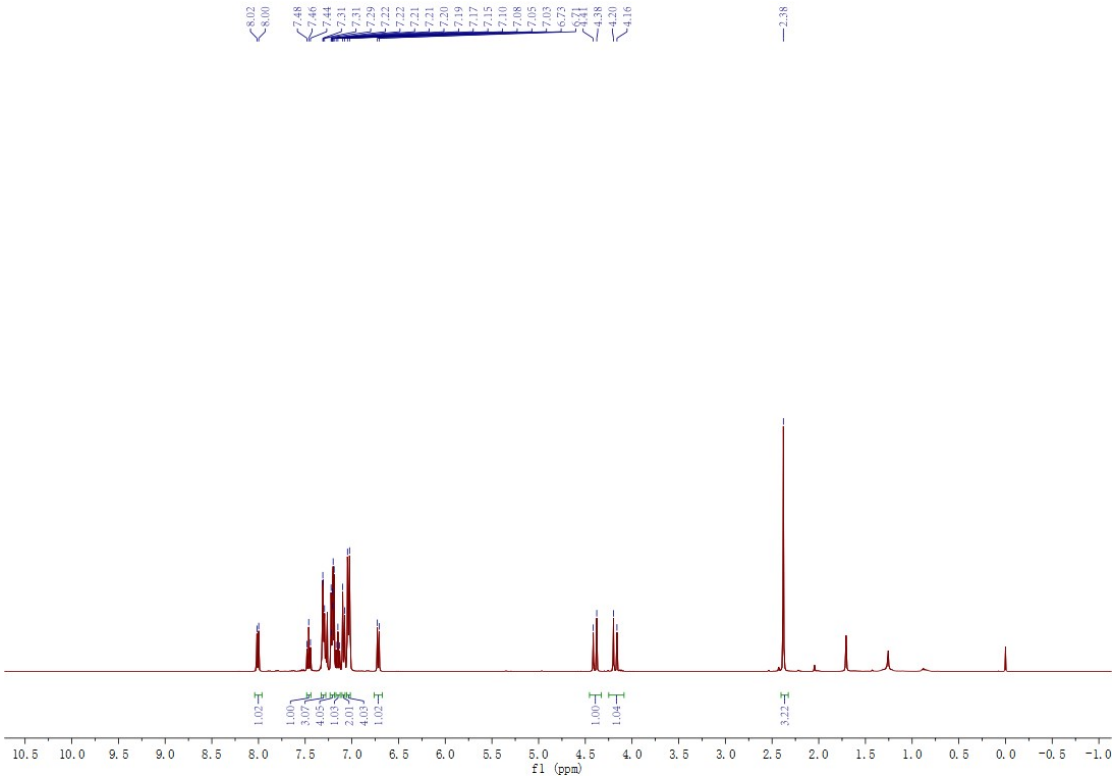
^{13}C NMR (400 MHz, $CDCl_3$) spectra of **3ea**



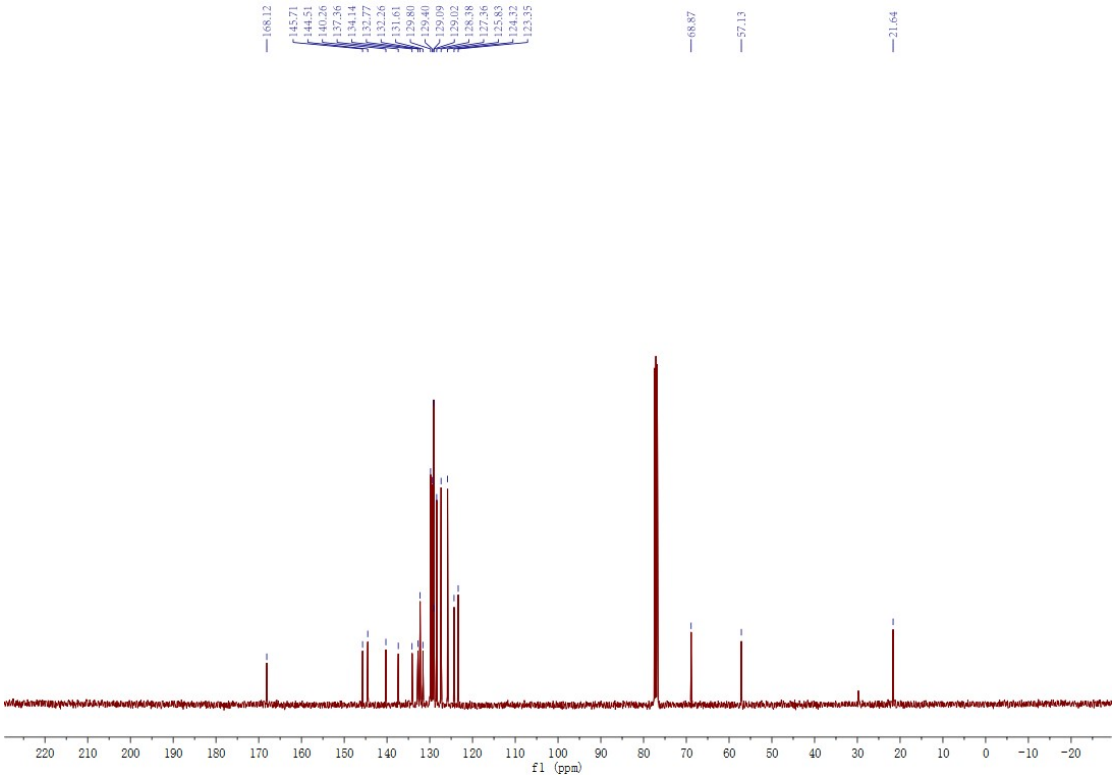
^{19}F NMR (565 MHz, Chloroform-*d*) spectra of **3ea**



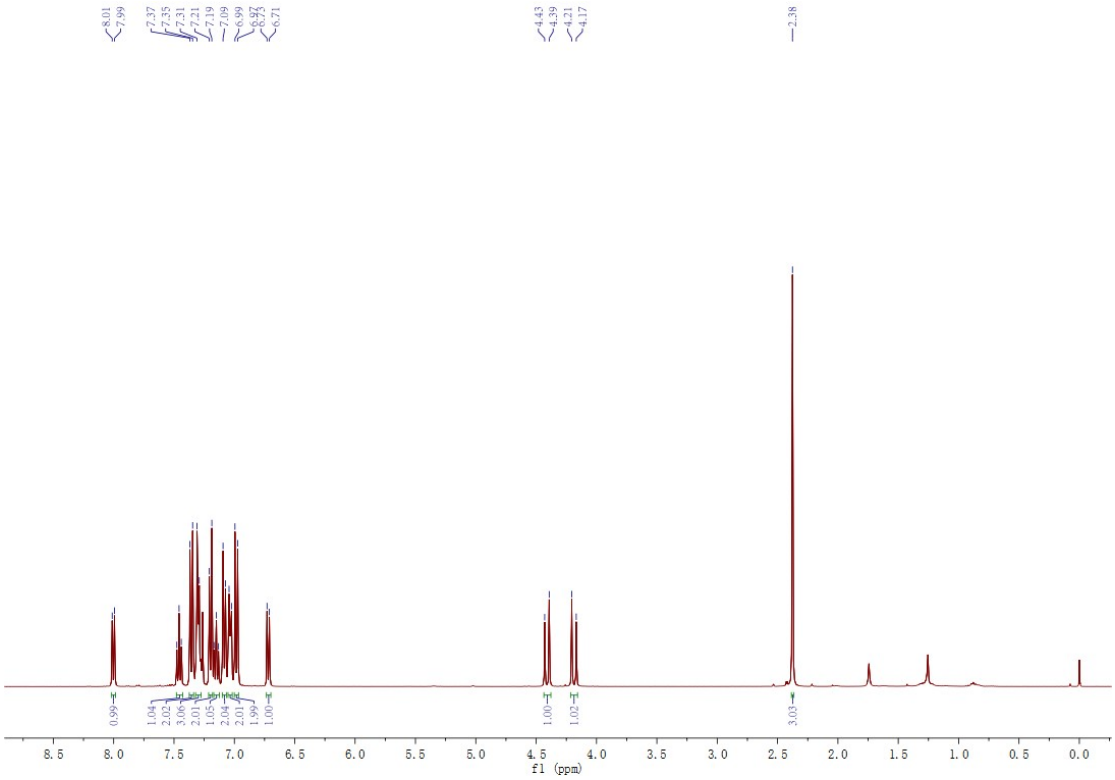
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3fa**



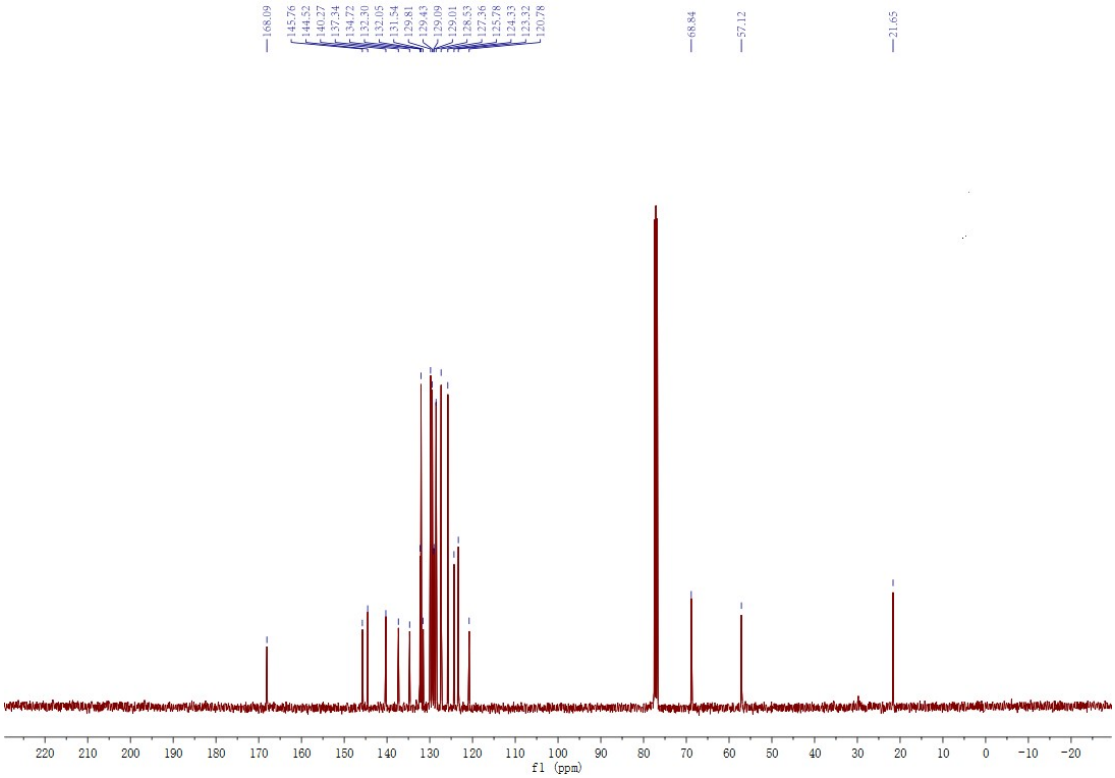
^{13}C NMR (400 MHz, $CDCl_3$) spectra of **3fa**



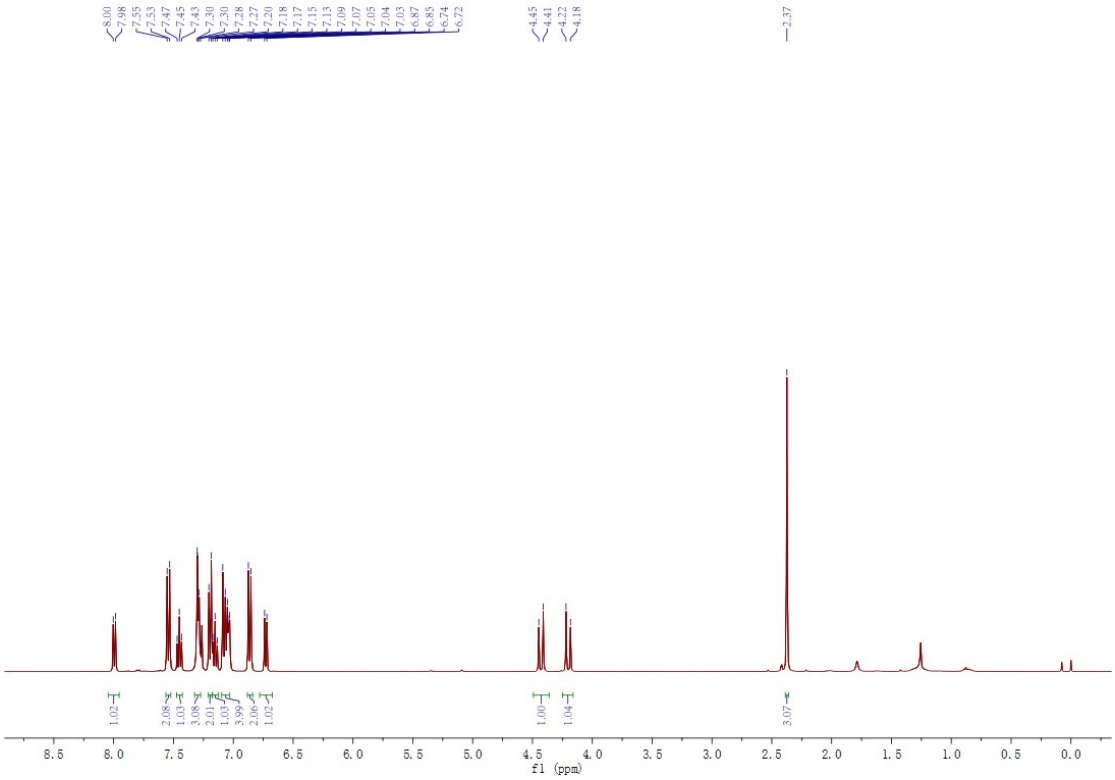
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ga**



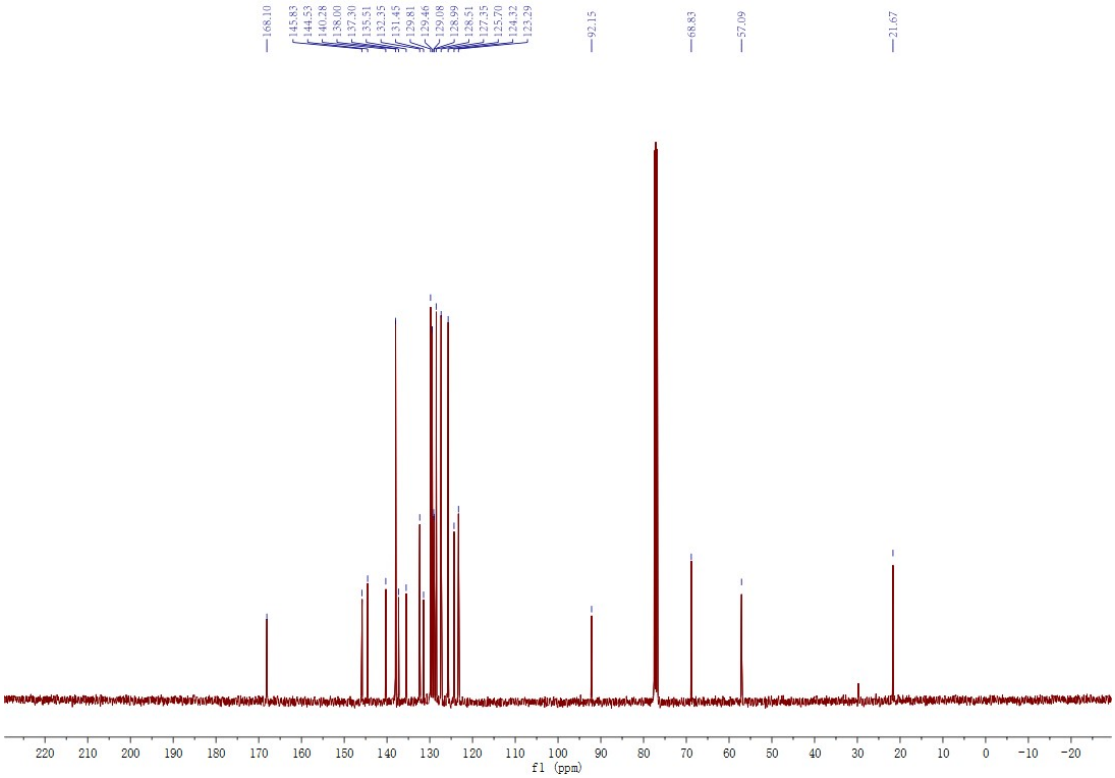
^{13}C NMR (400 MHz, $CDCl_3$) spectra of **3ga**



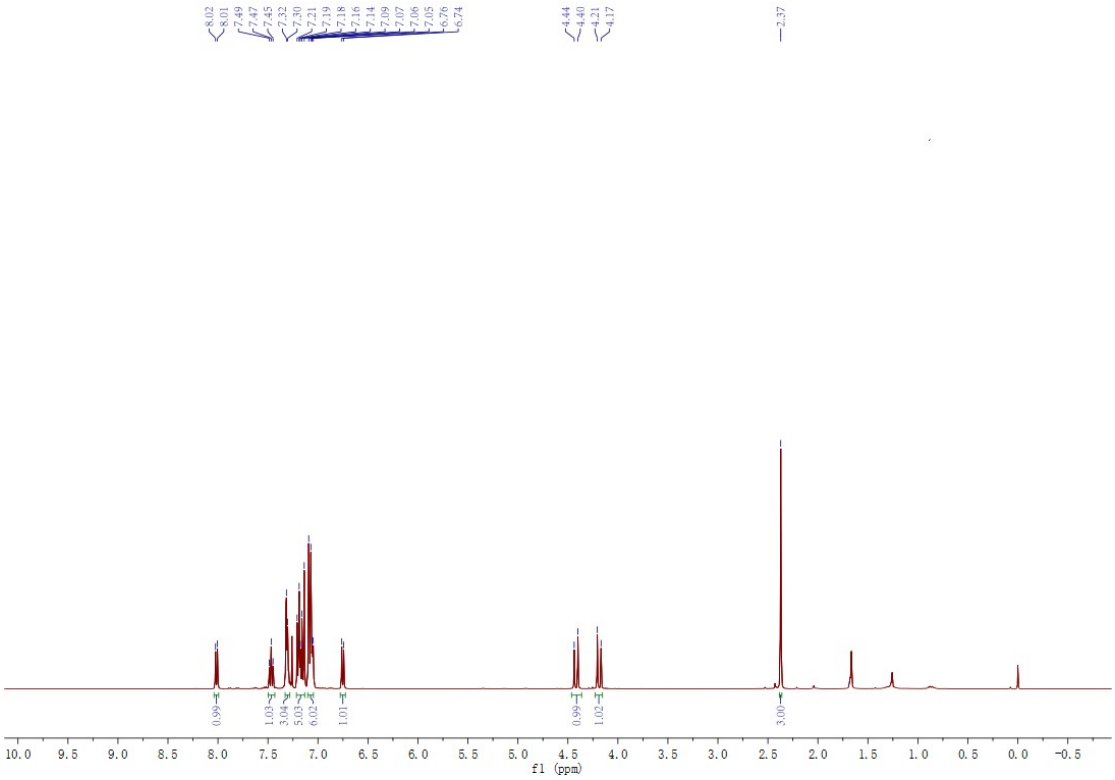
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ha**



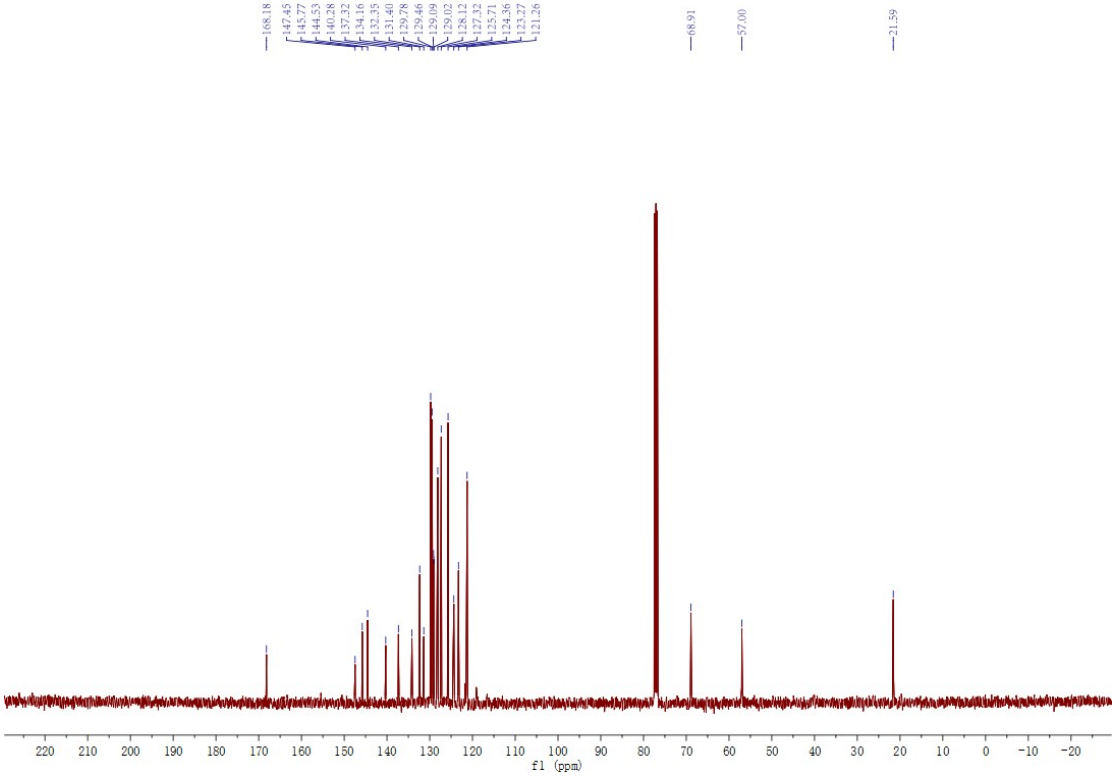
^{13}C NMR (400 MHz, $CDCl_3$) spectra of **3ha**



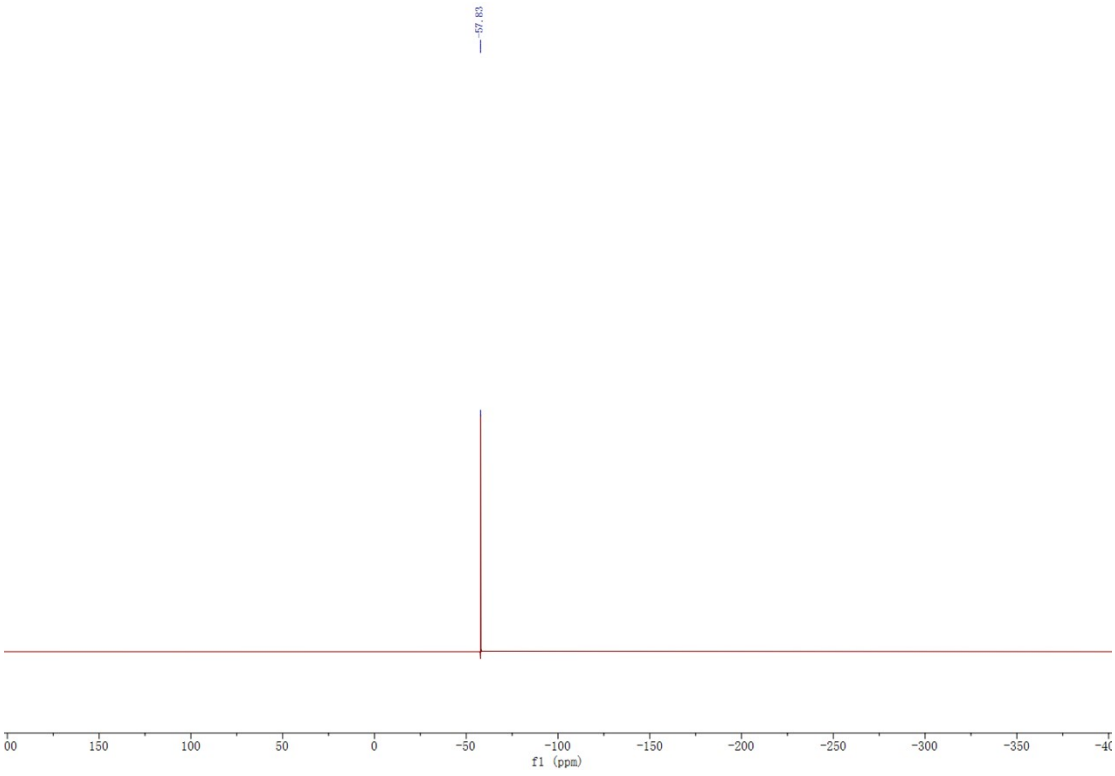
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ia**



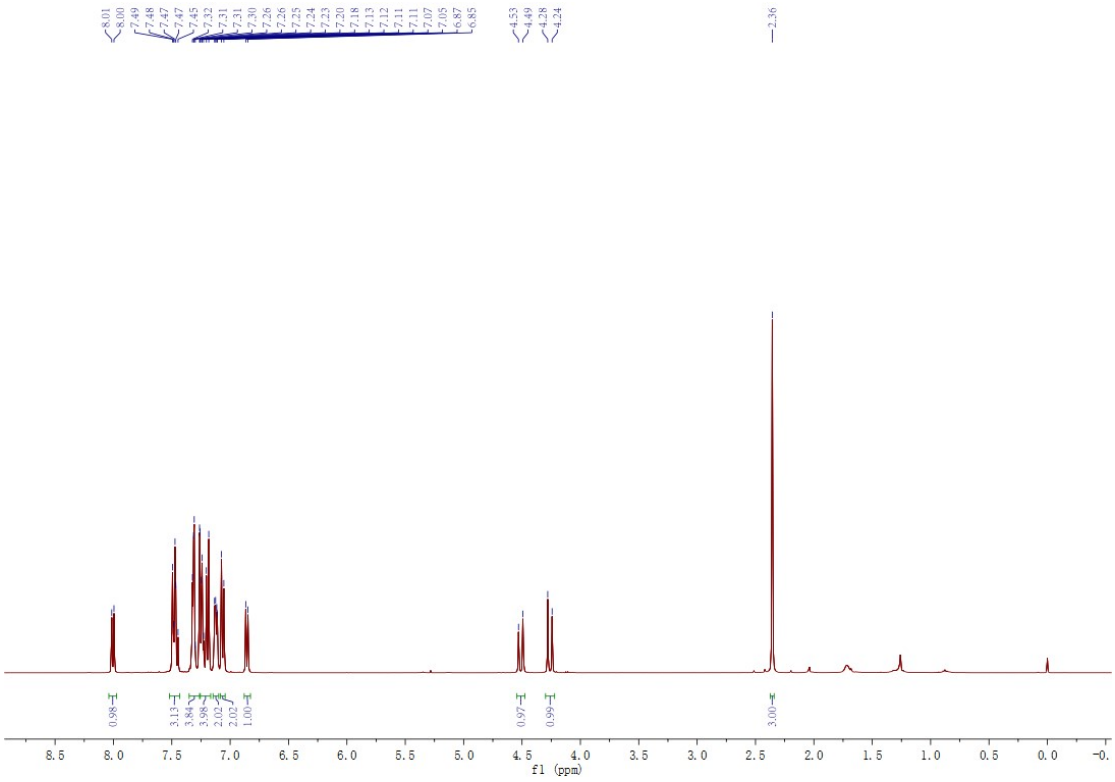
^{13}C NMR (400 MHz, $CDCl_3$) spectra of **3ia**



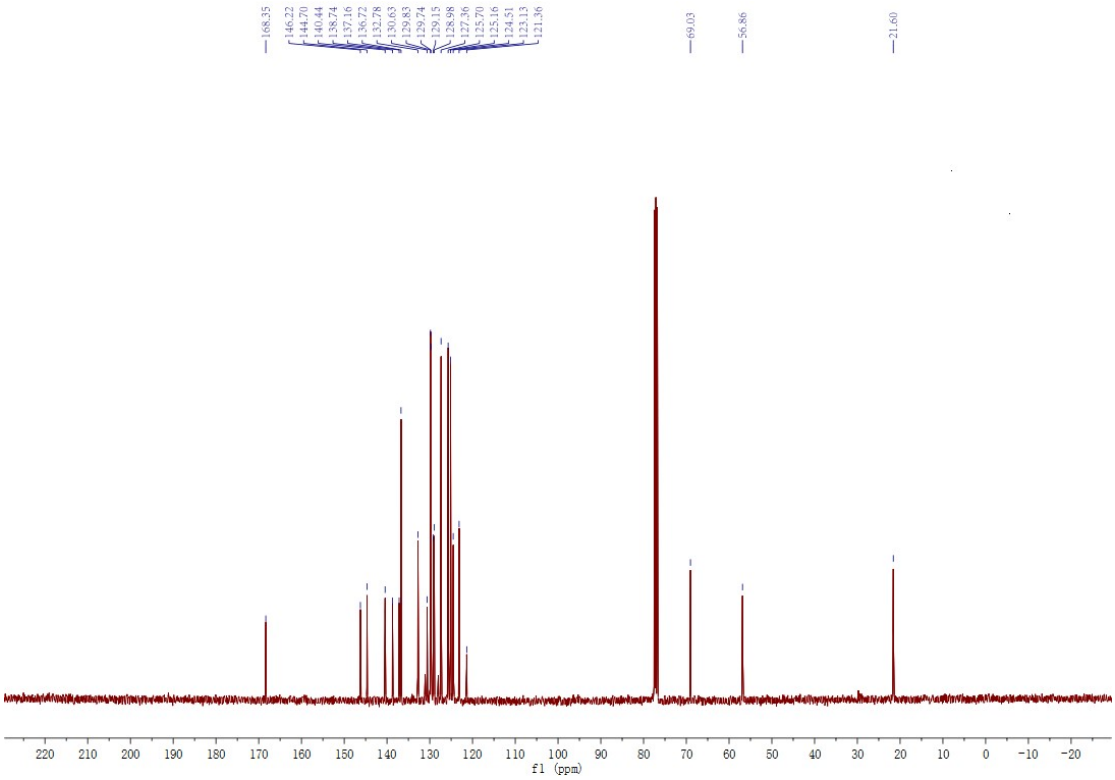
^{19}F NMR (565 MHz, Chloroform-*d*) spectra of **3ia**



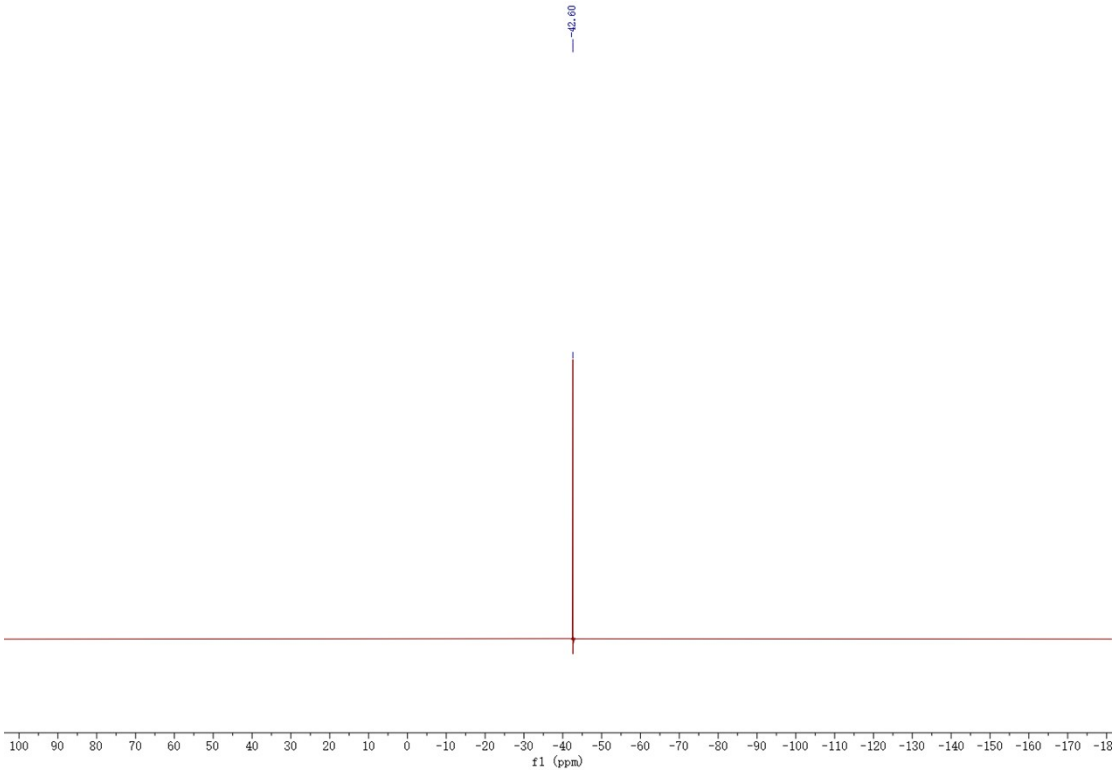
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ja**



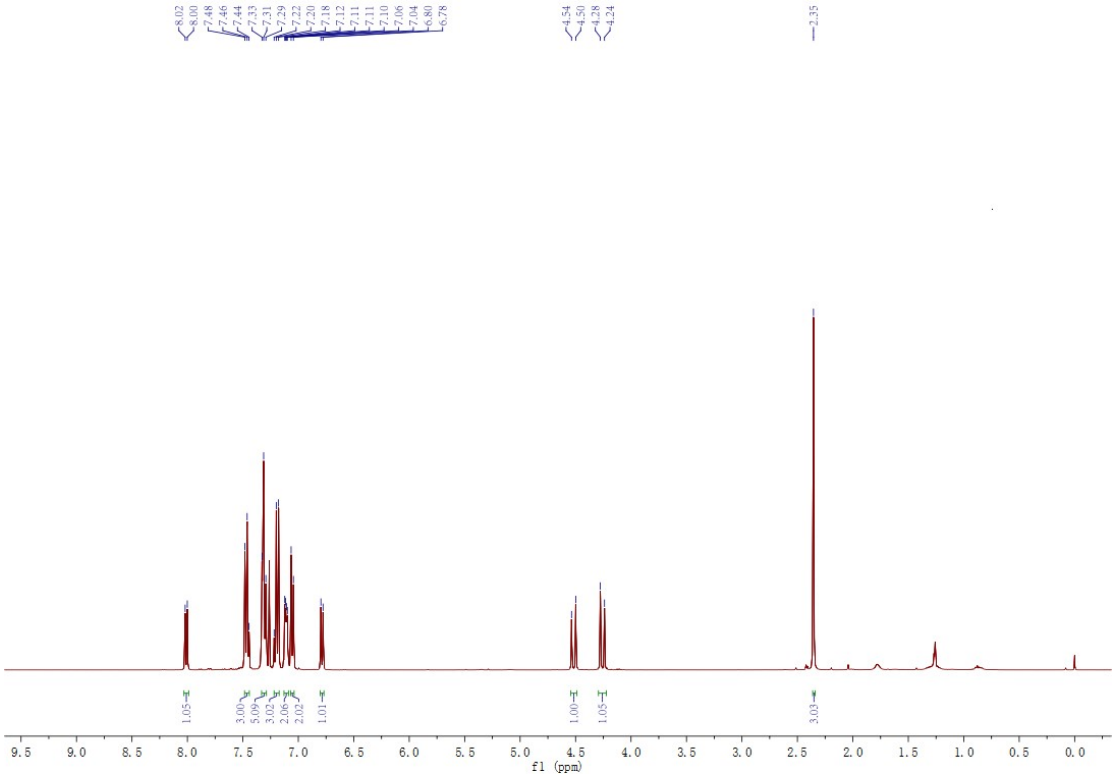
^{13}C NMR (400 MHz, $CDCl_3$) spectra of **3ja**



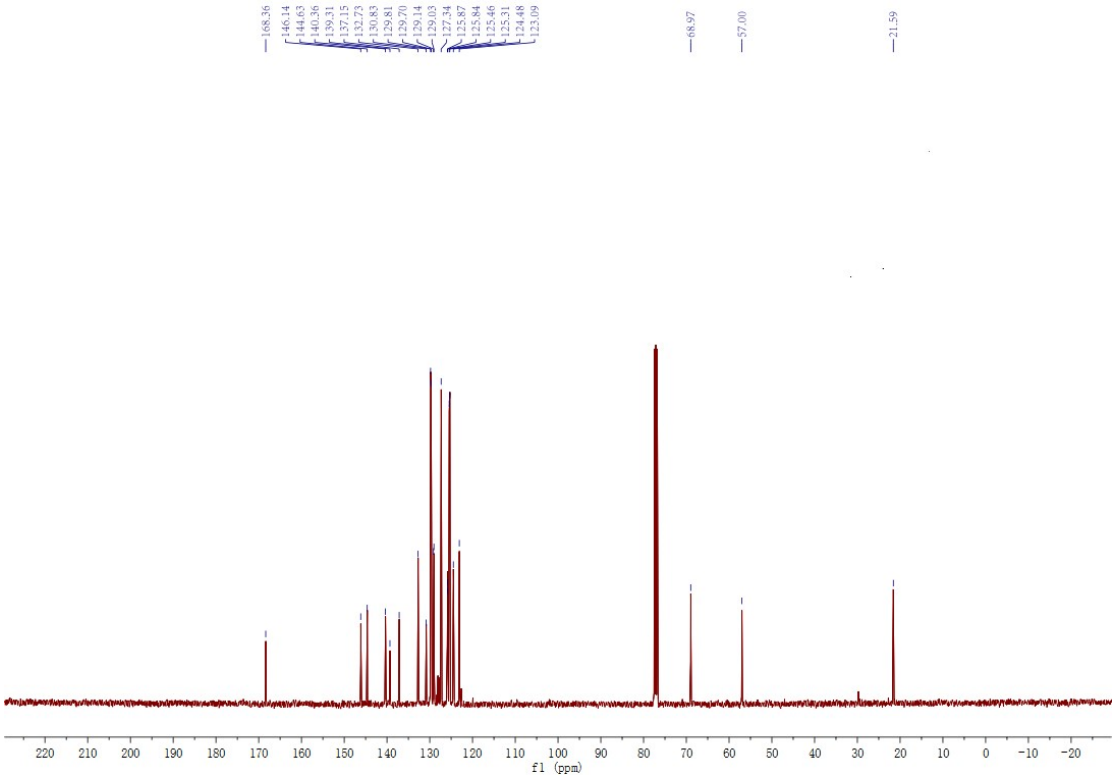
^{19}F NMR (565 MHz, Chloroform-*d*) spectra of **3ja**



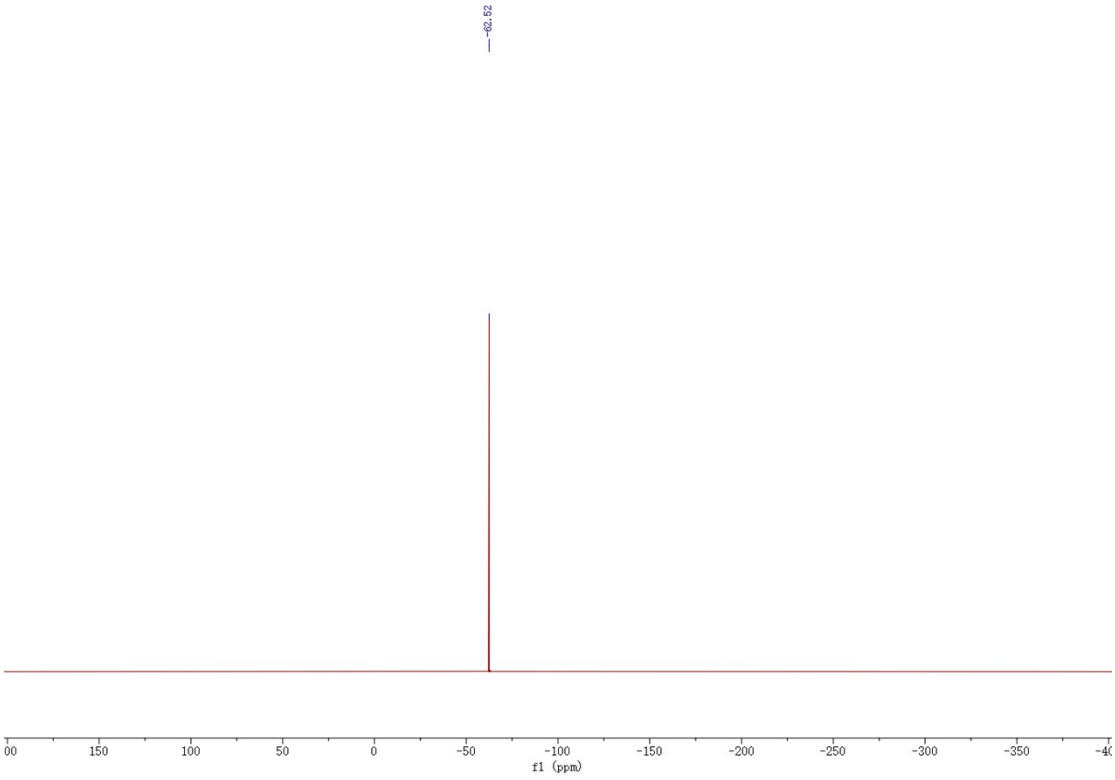
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ka**



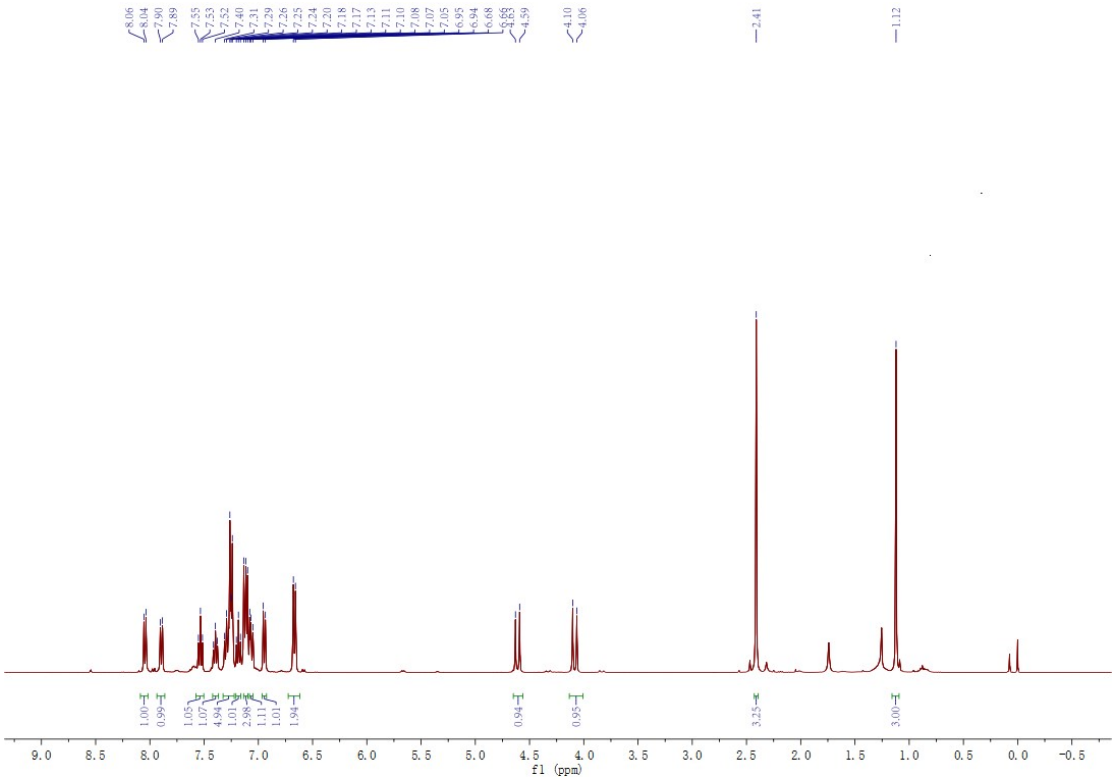
^{13}C NMR (400 MHz, $CDCl_3$) spectra of **3ka**



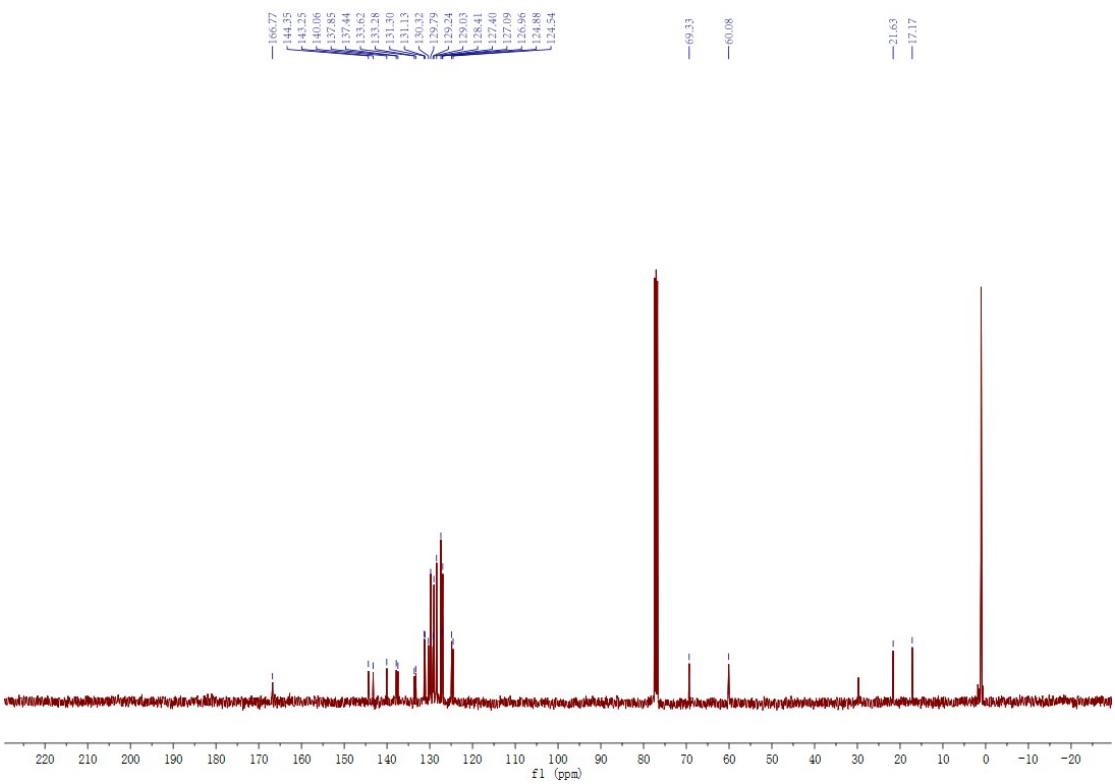
^{19}F NMR (565 MHz, Chloroform-*d*) spectra of **3ka**



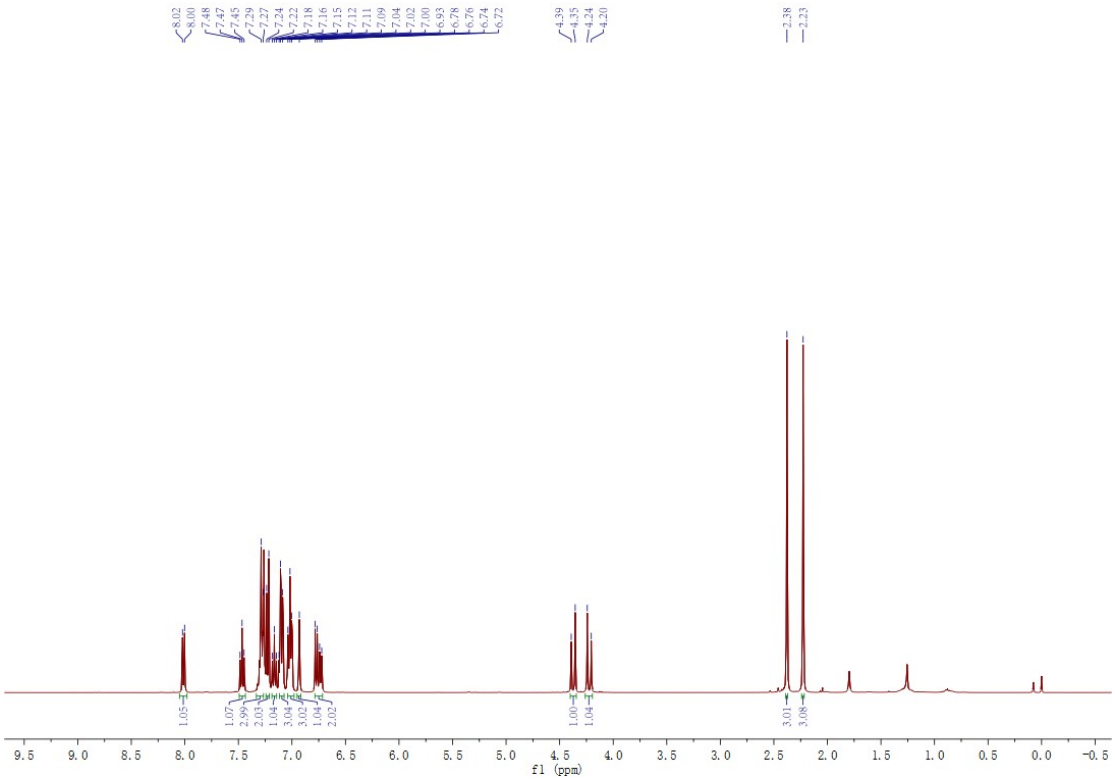
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3la**



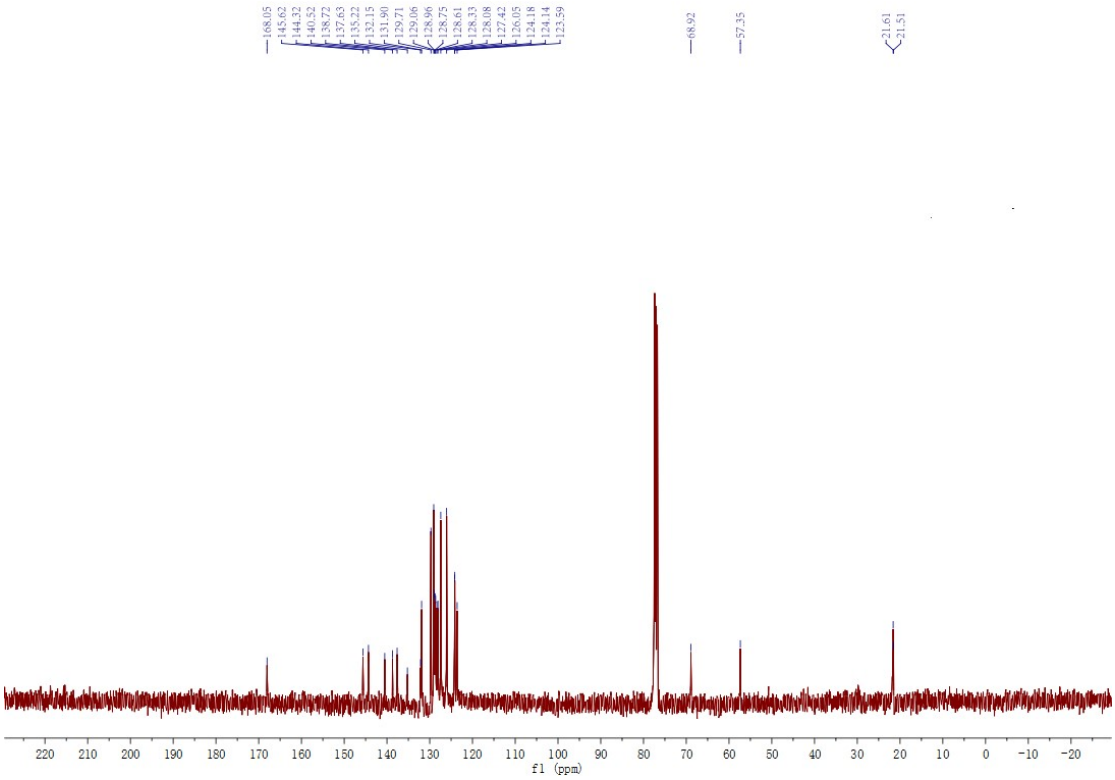
^{13}C NMR (400 MHz, $CDCl_3$) spectra of **3la**



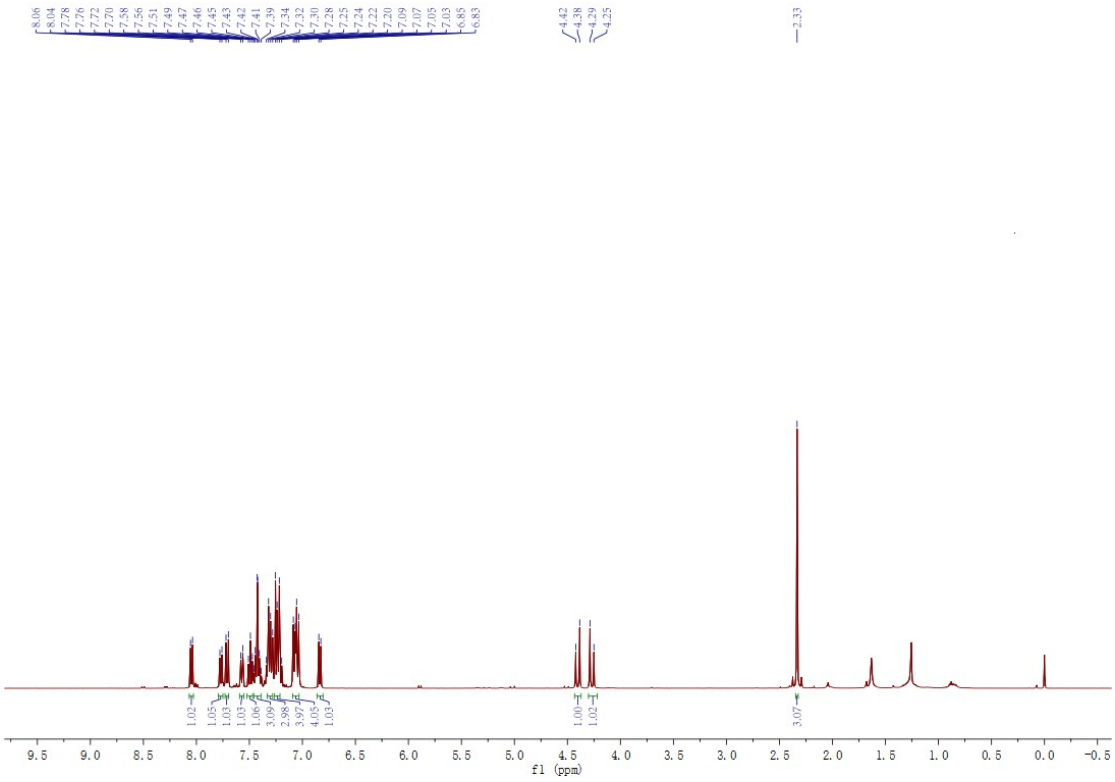
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ma**



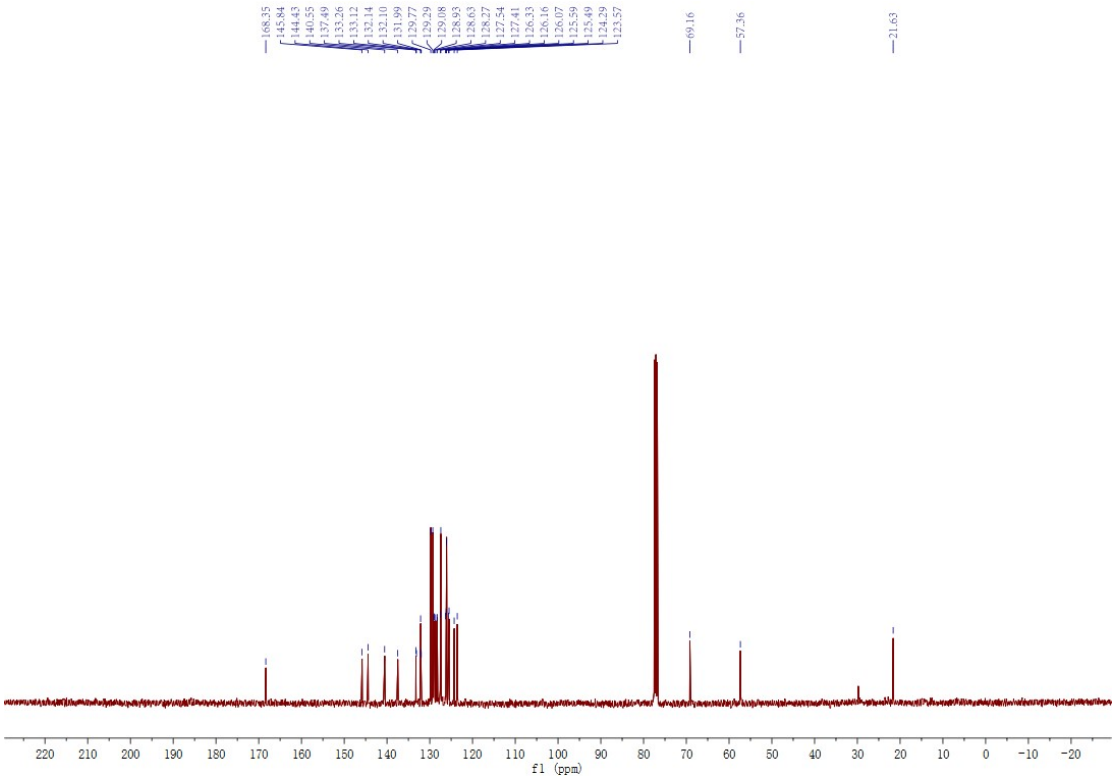
^{13}C NMR (400 MHz, $CDCl_3$) spectra of **3ma**



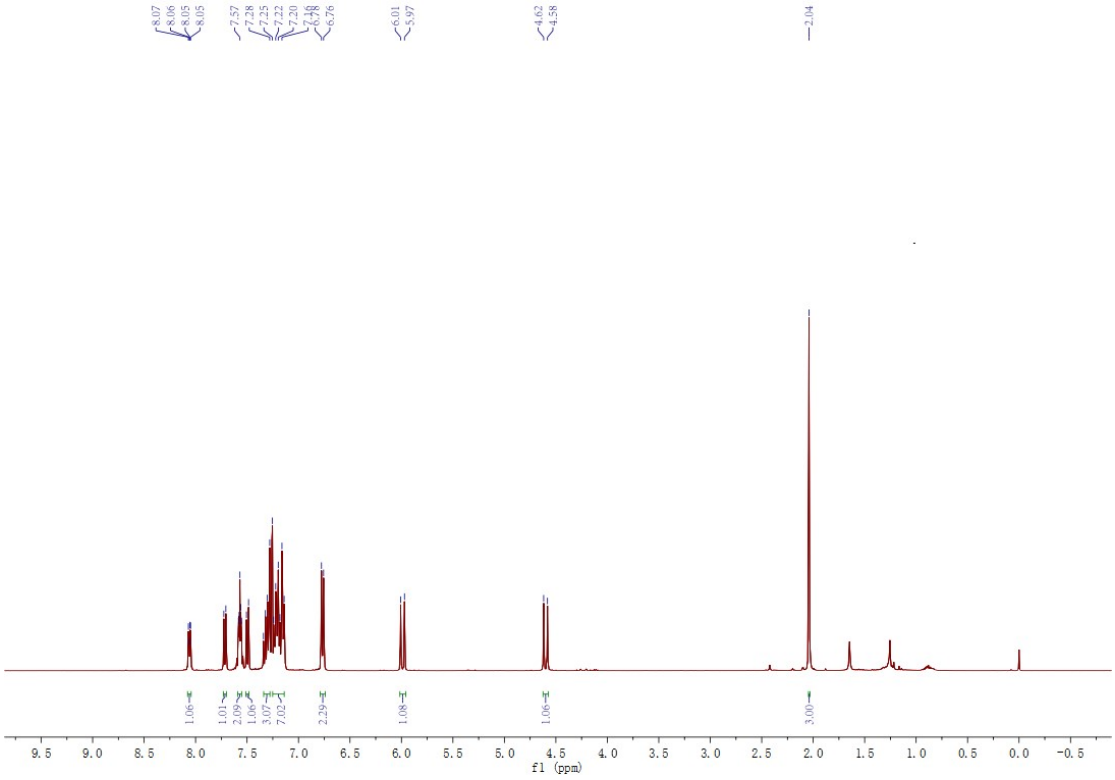
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3na**



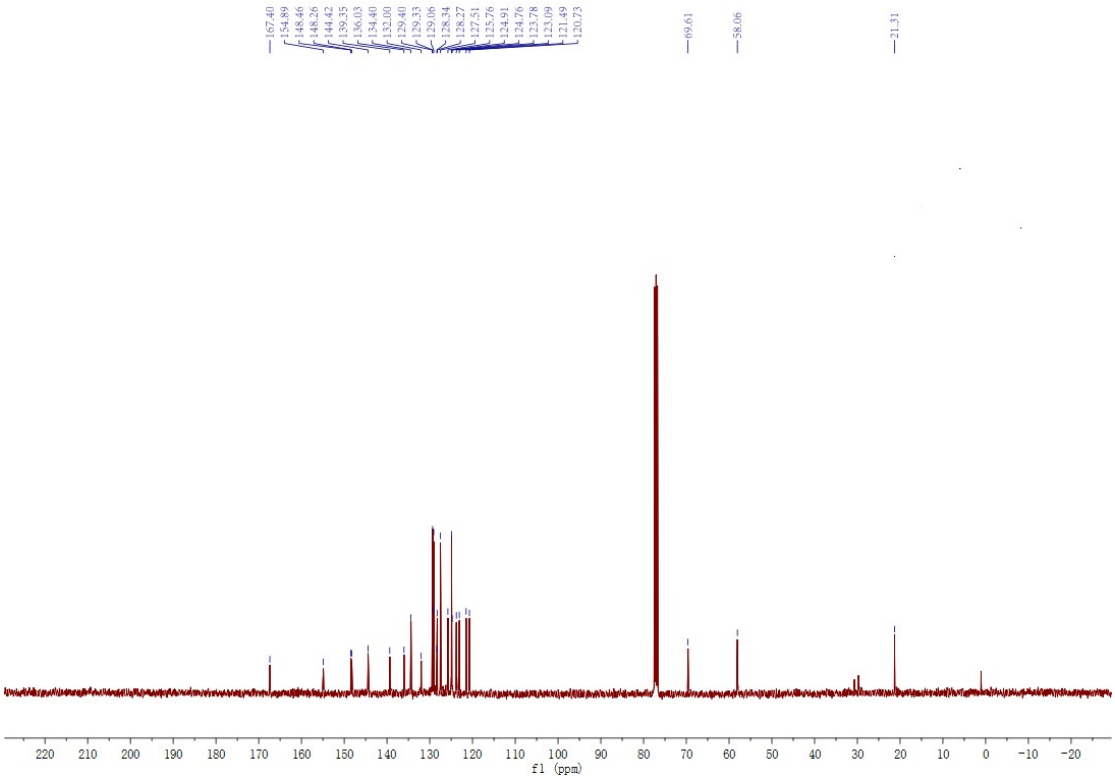
^{13}C NMR (400 MHz, $CDCl_3$) spectra of **3na**



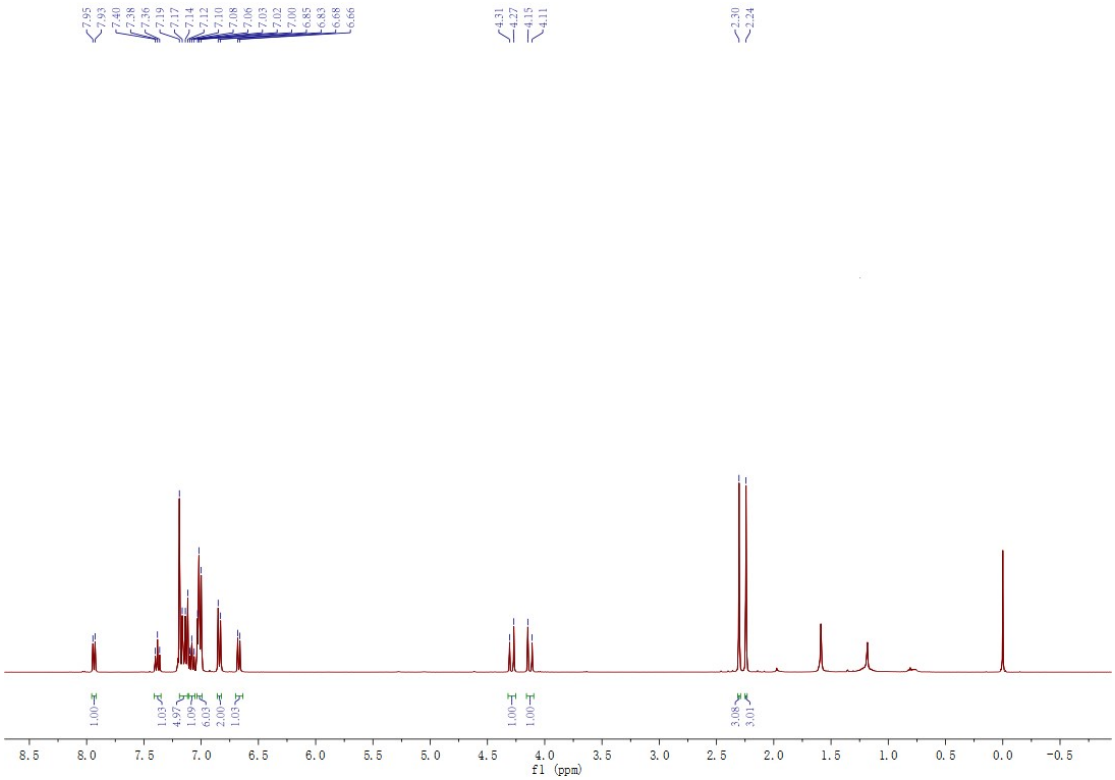
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3oa**



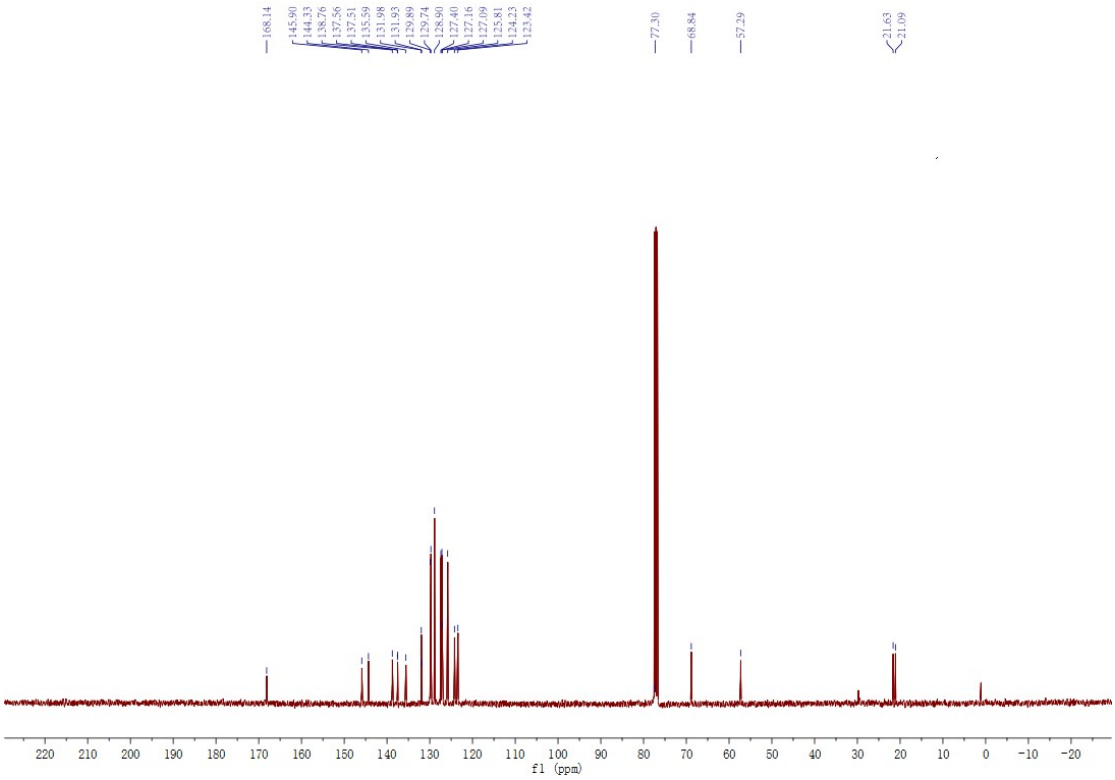
^{13}C NMR (400 MHz, $CDCl_3$) spectra of **3oa**



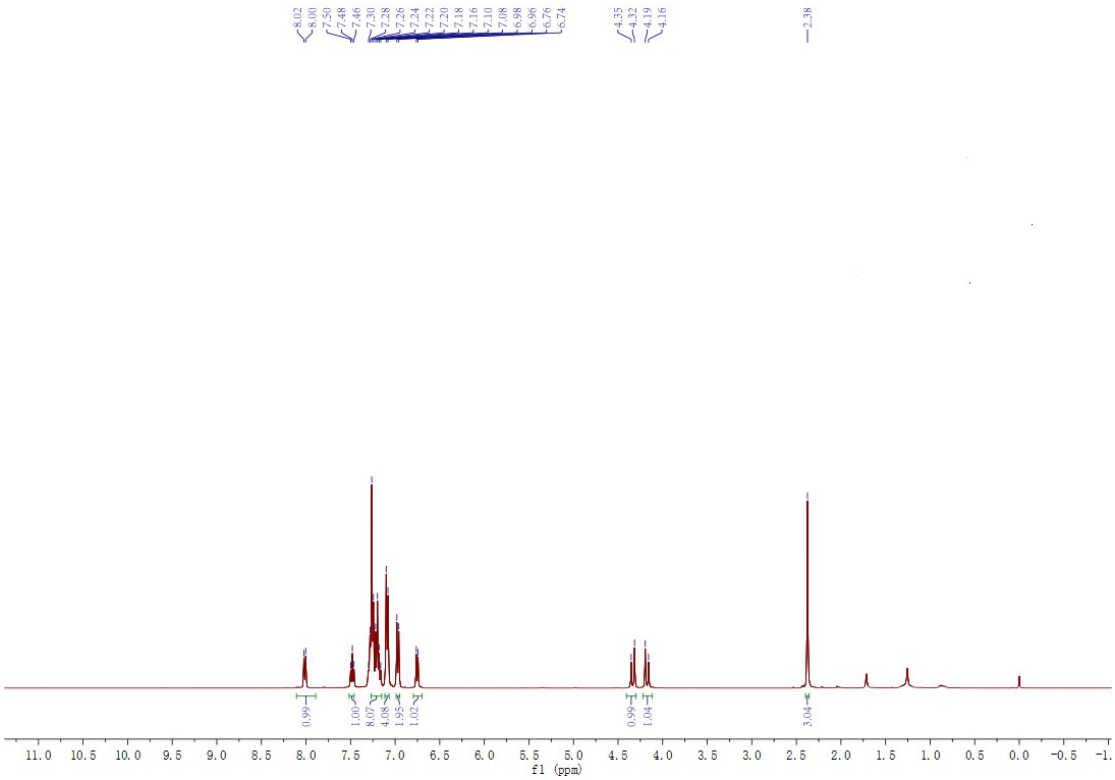
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3pa**



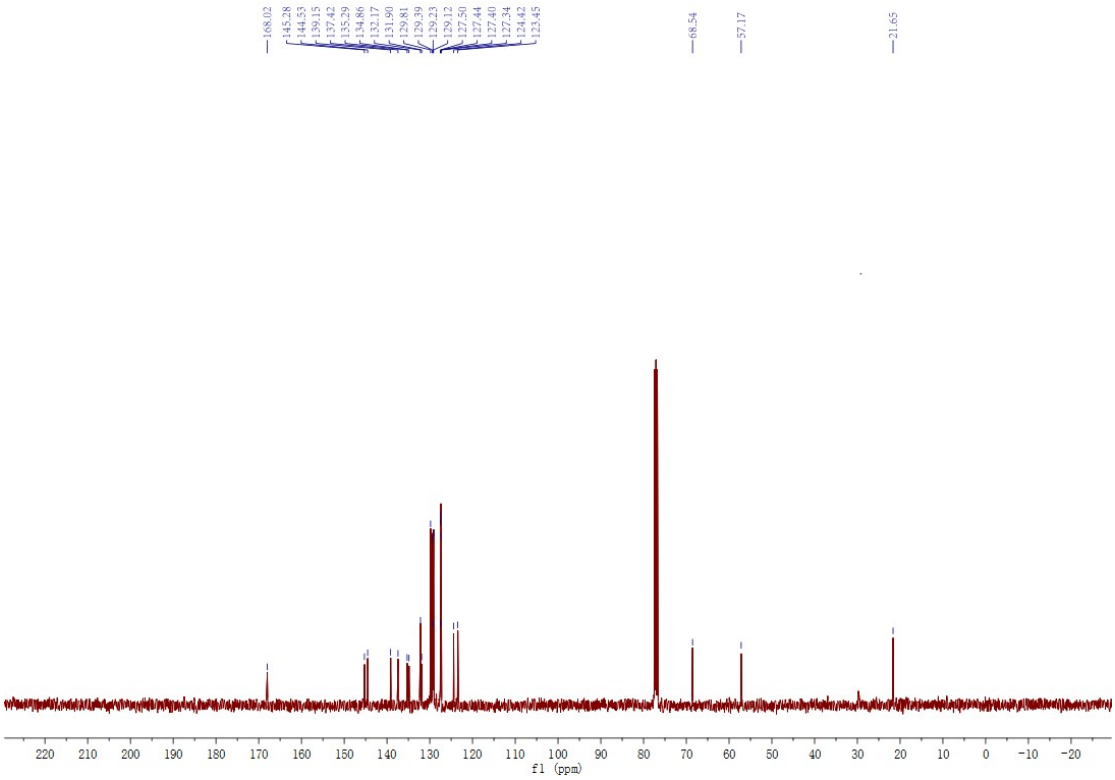
^{13}C NMR (400 MHz, $CDCl_3$) spectra of **3pa**



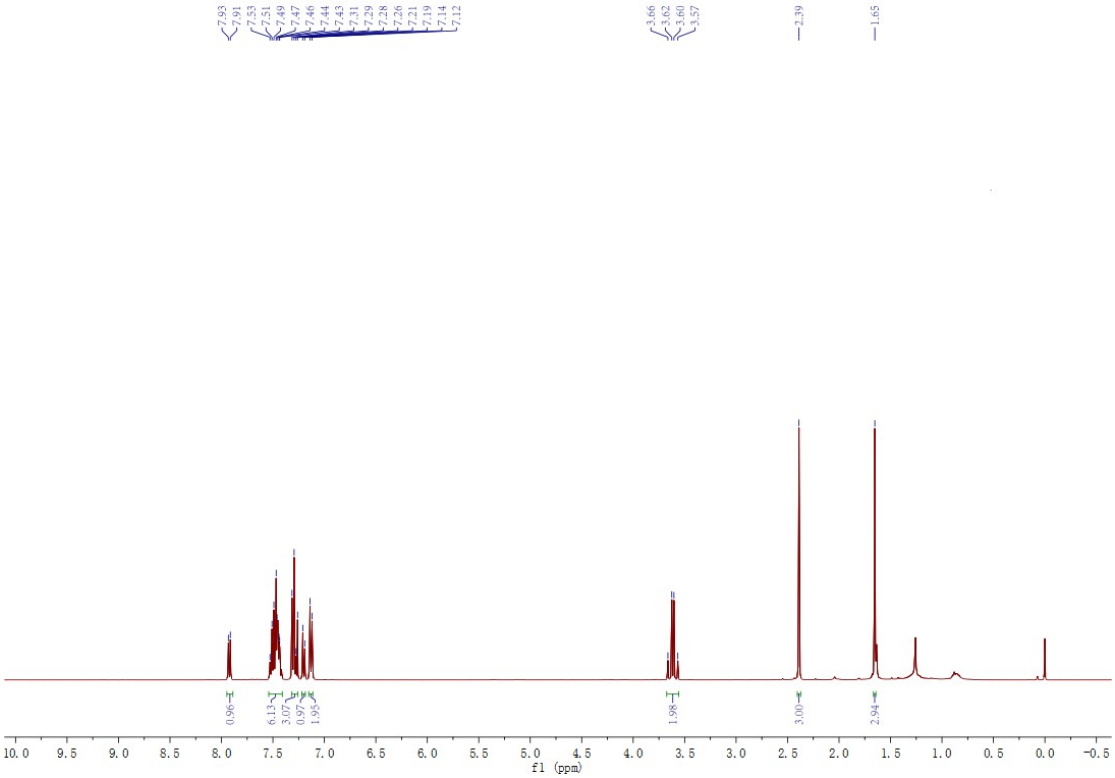
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3qa**



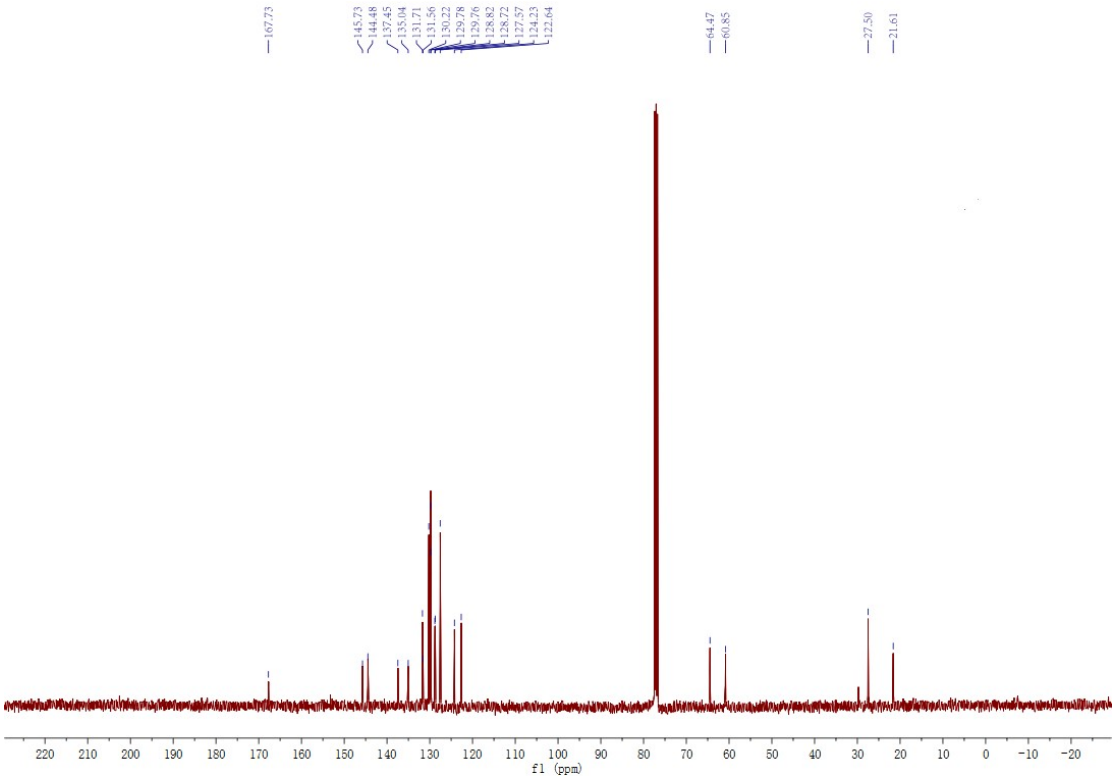
^{13}C NMR (400 MHz, $CDCl_3$) spectra of **3qa**



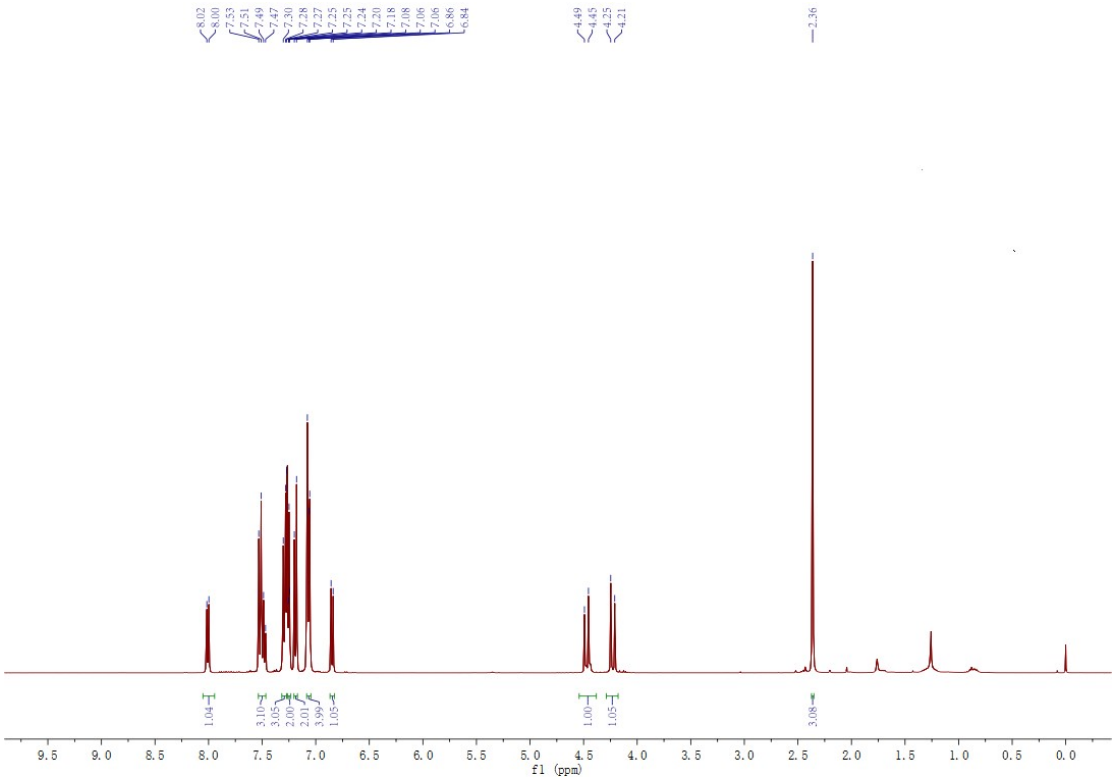
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ra**



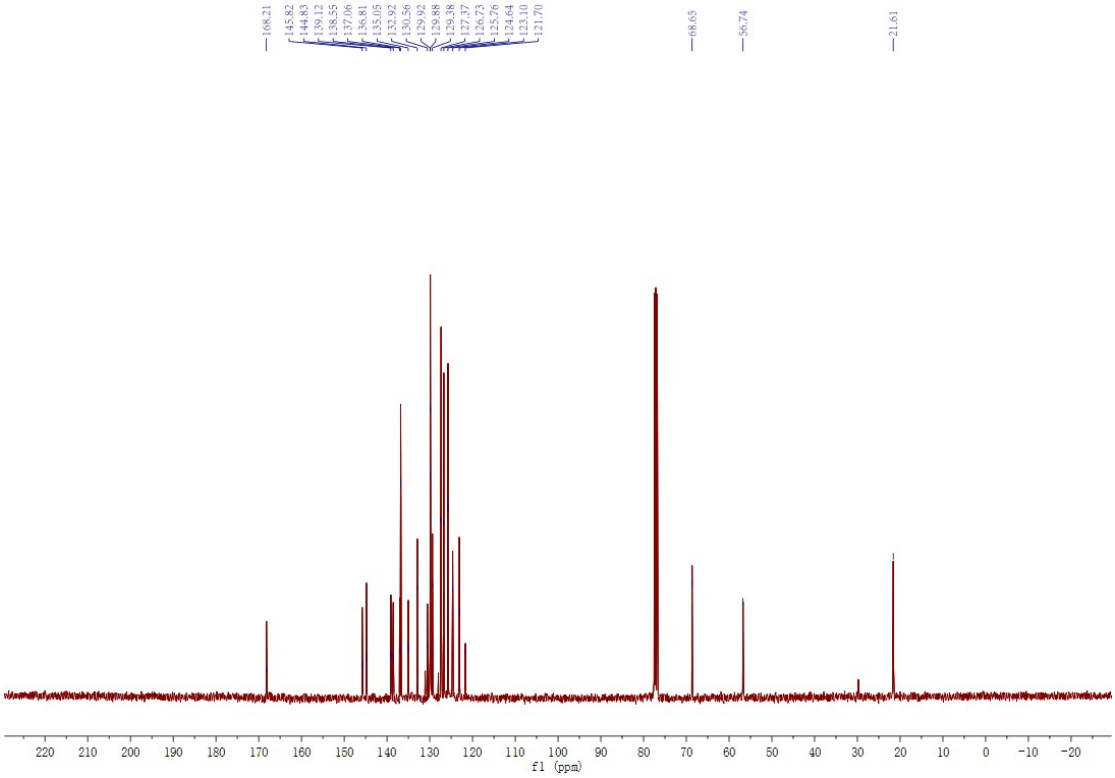
^{13}C NMR (400 MHz, $CDCl_3$) spectra of **3ra**



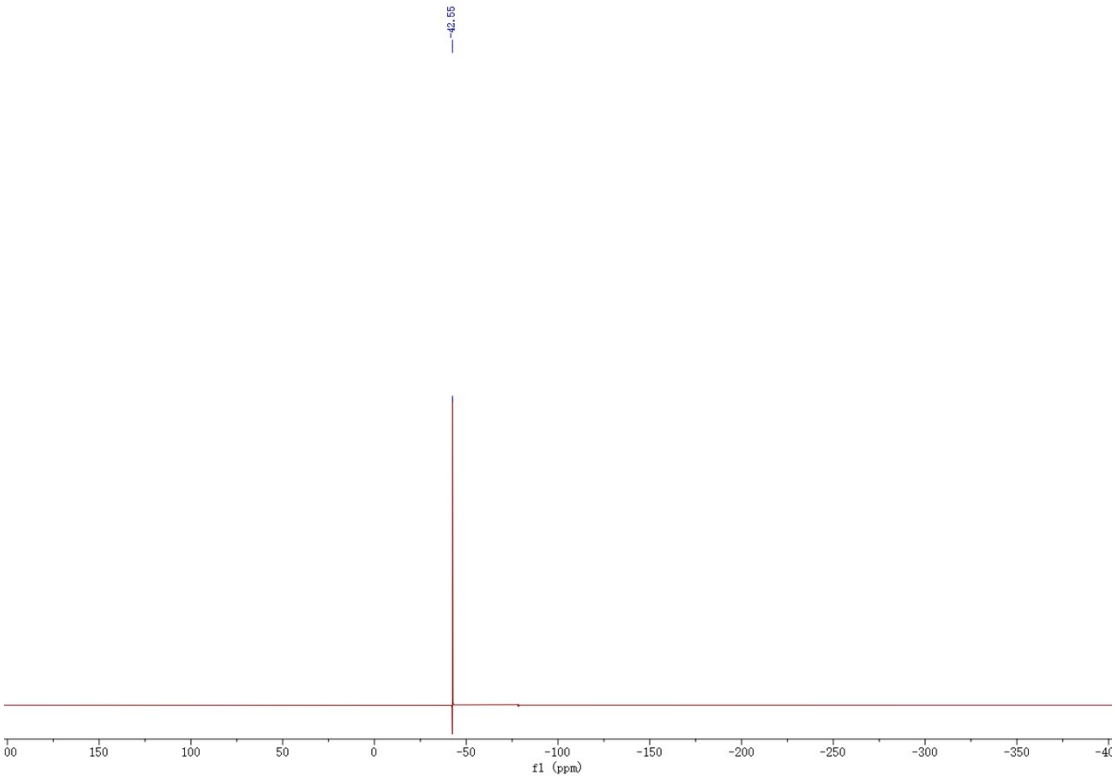
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3sa**



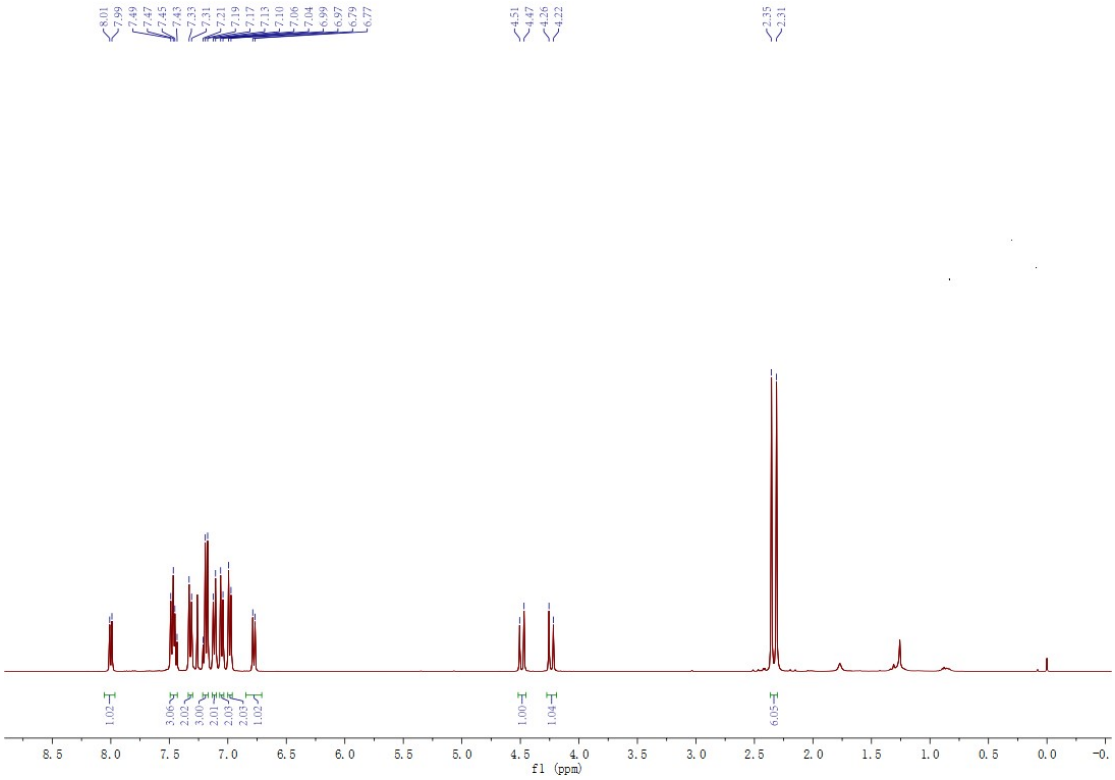
^{13}C NMR (400 MHz, $CDCl_3$) spectra of **3sa**



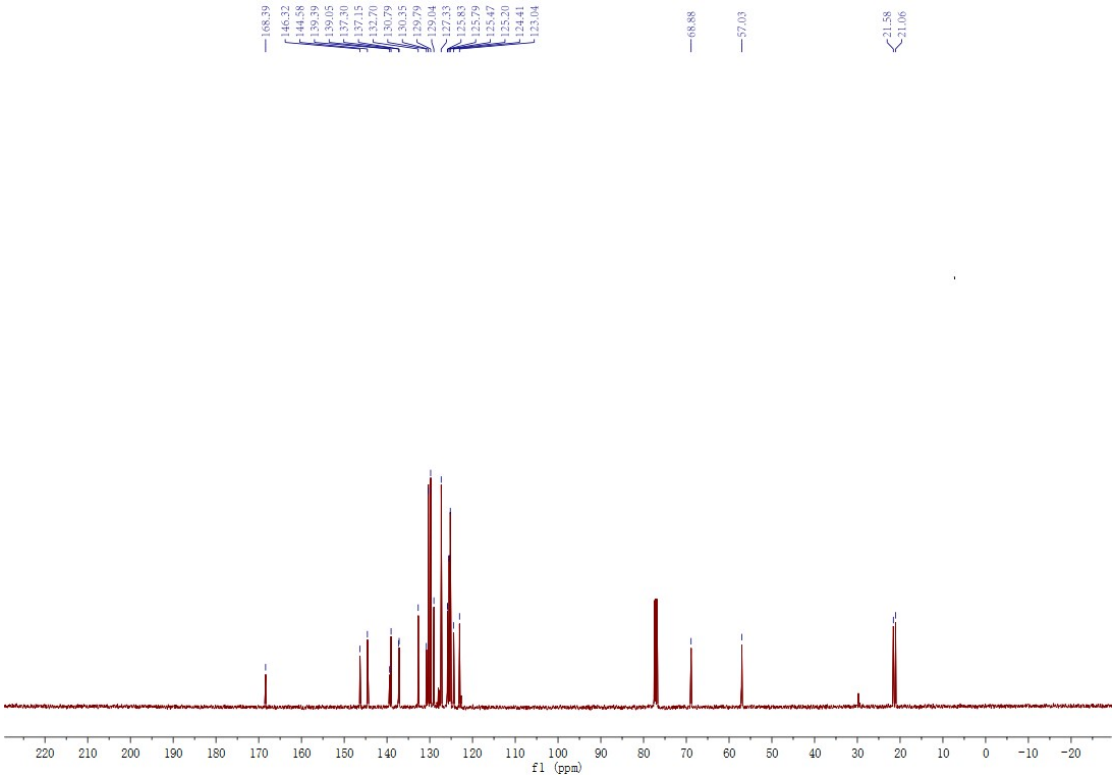
^{19}F NMR (565 MHz, Chloroform-*d*) spectra of **3sa**



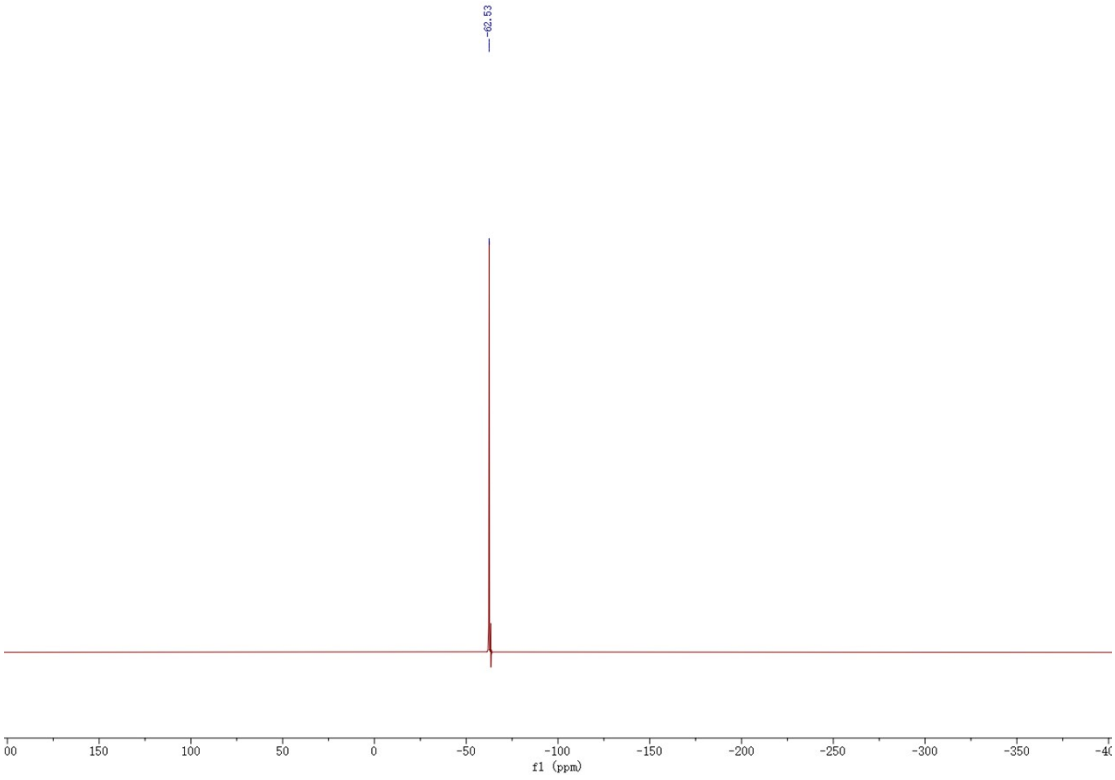
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ta**



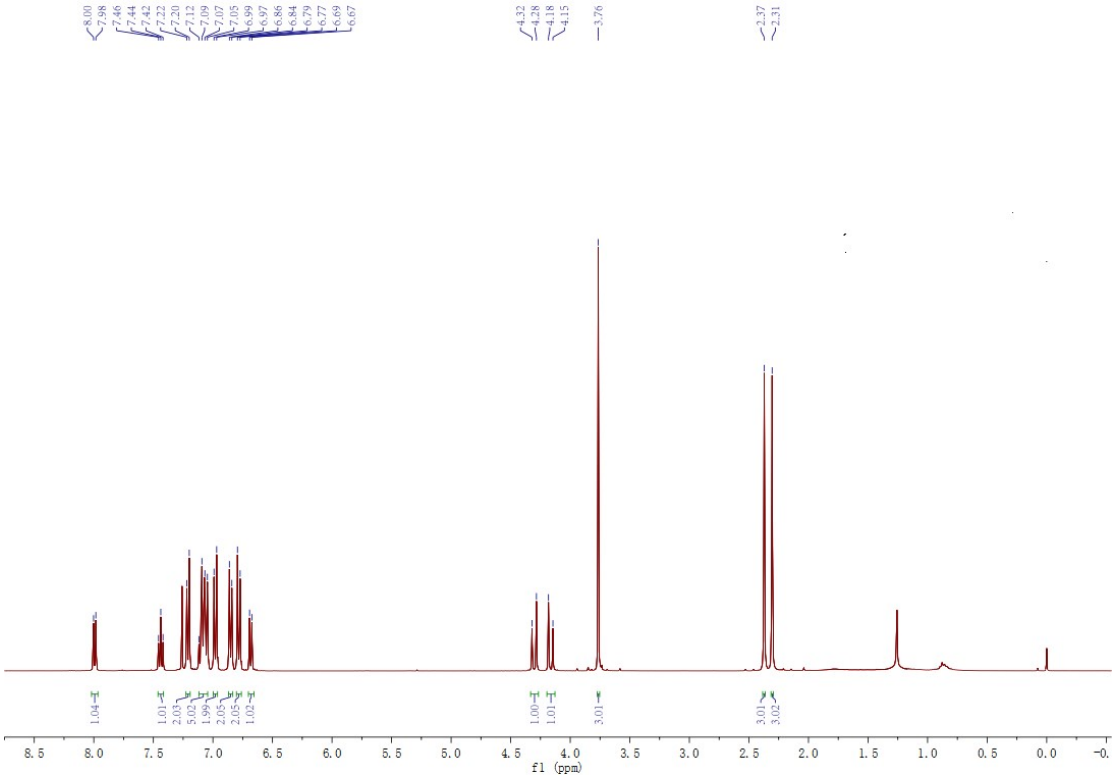
^{13}C NMR (400 MHz, $CDCl_3$) spectra of **3ta**



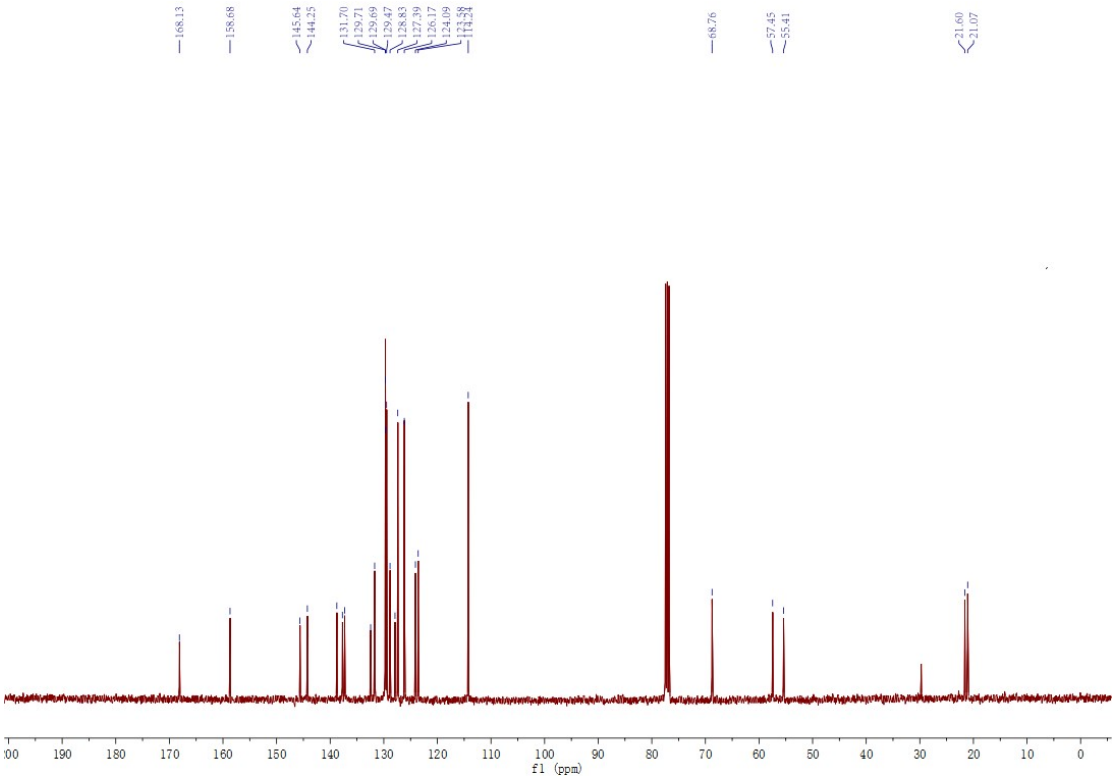
^{19}F NMR (565 MHz, Chloroform-*d*) spectra of **3ta**.



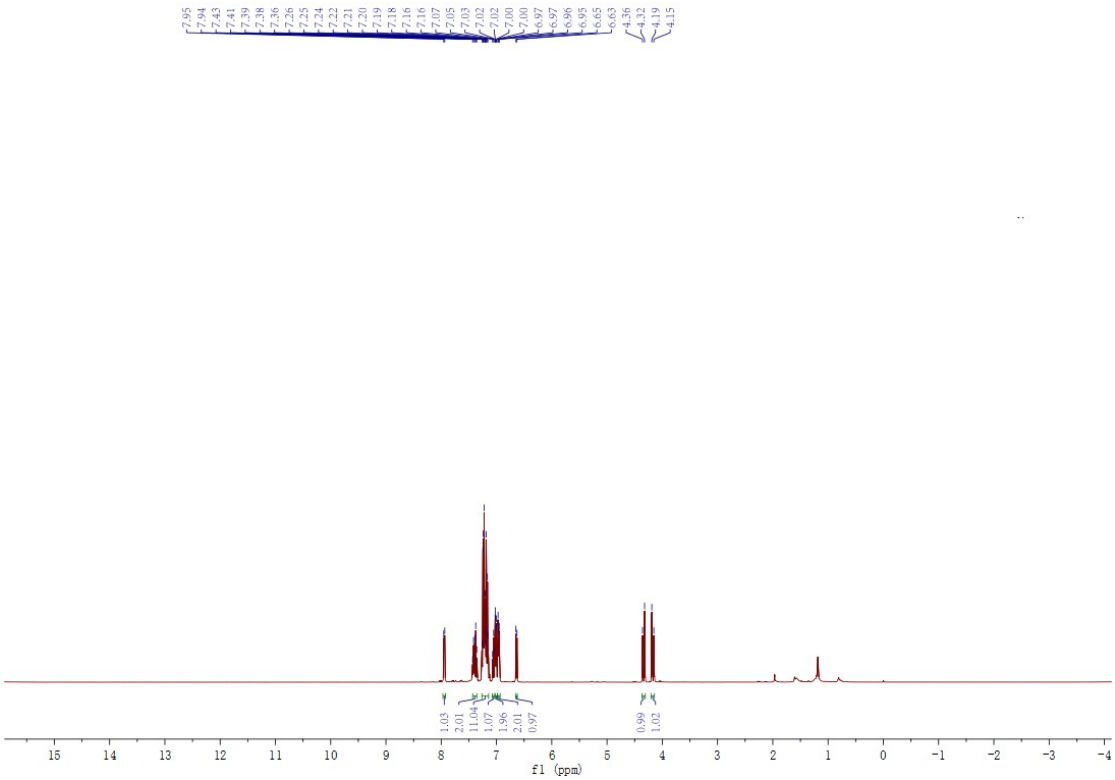
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ua**



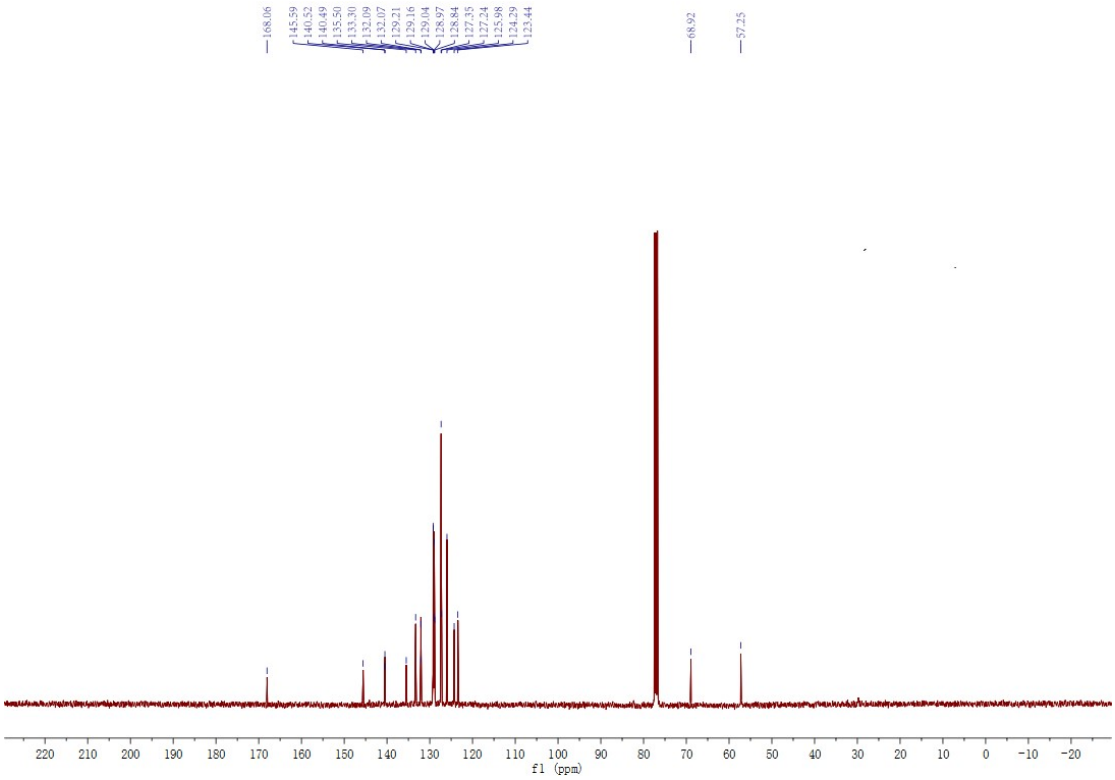
^{13}C NMR (400 MHz, $CDCl_3$) spectra of **3ua**



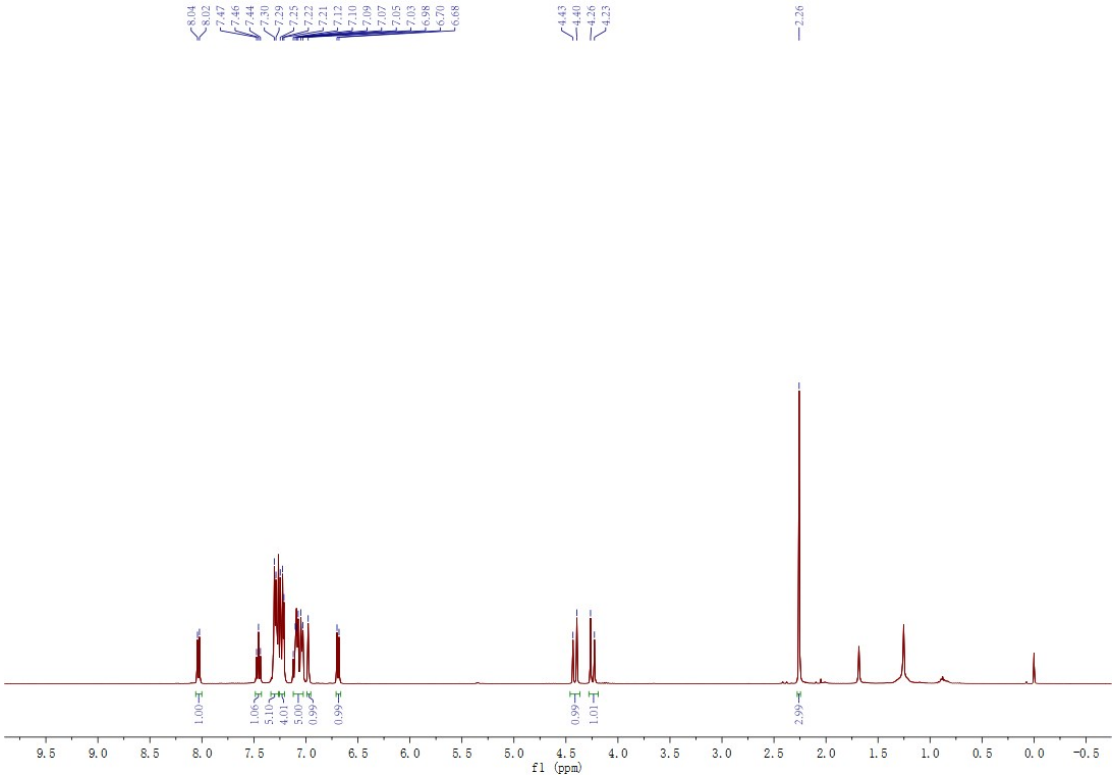
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ab**



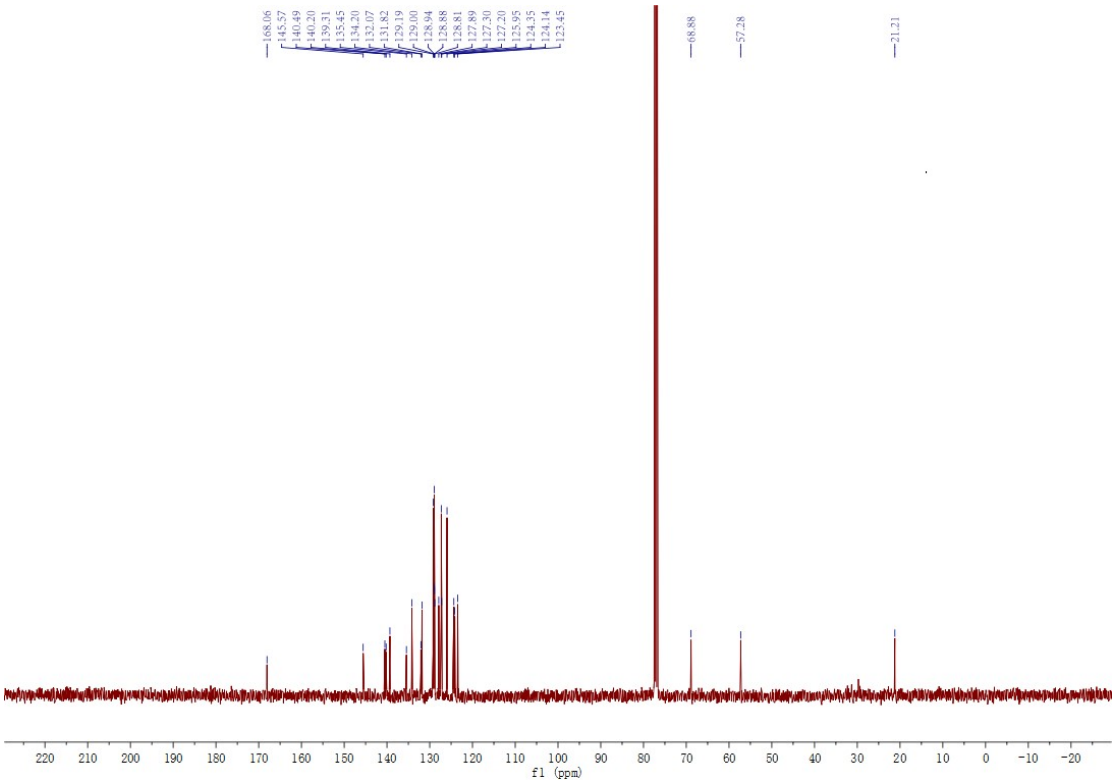
^{13}C NMR (400 MHz, $CDCl_3$) spectra of **3ab**



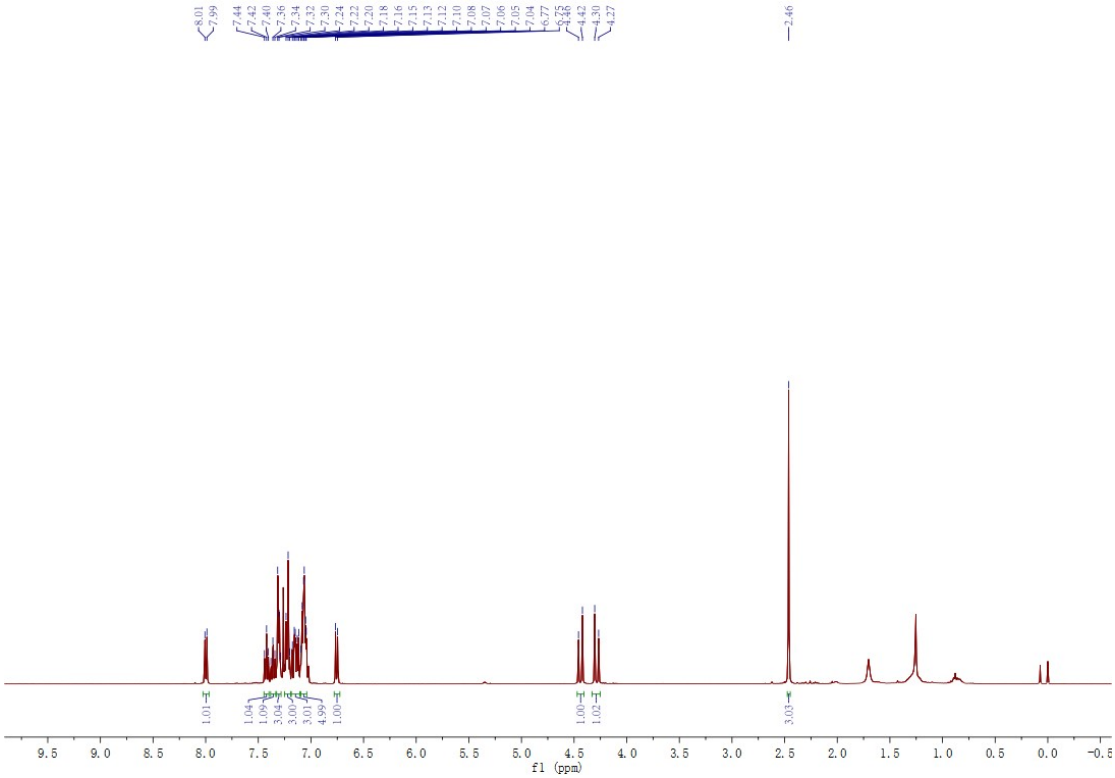
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ac**



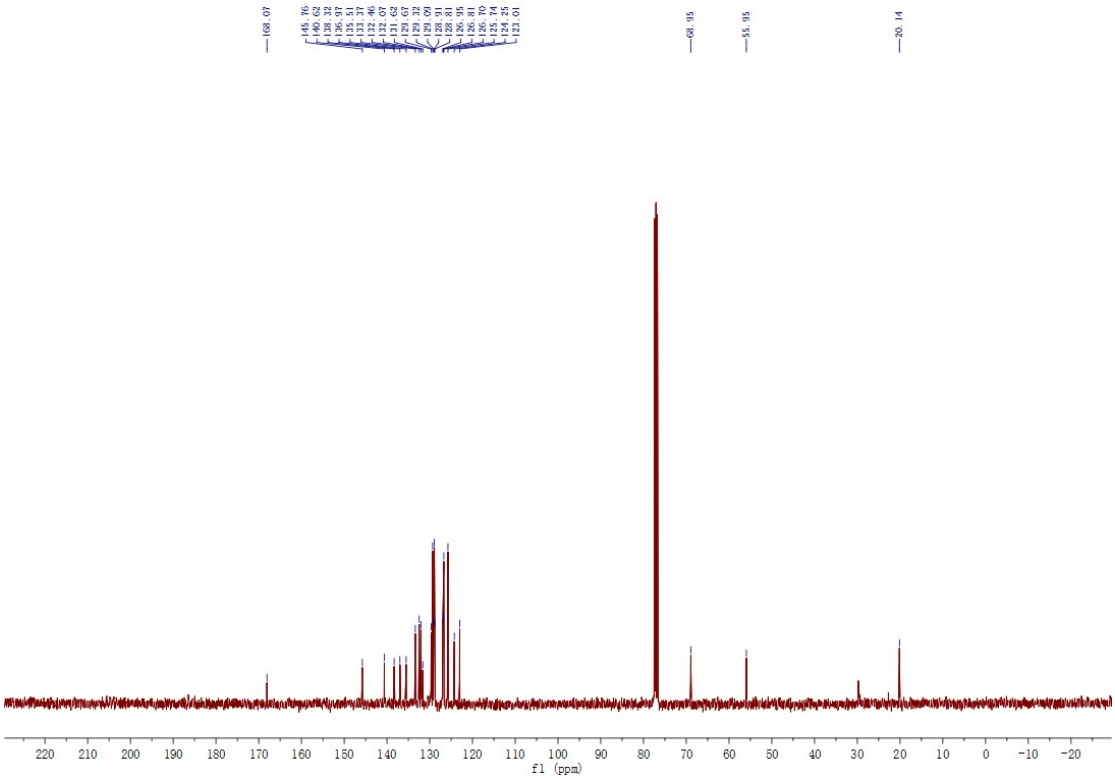
^{13}C NMR (400 MHz, $CDCl_3$) spectra of **3ac**



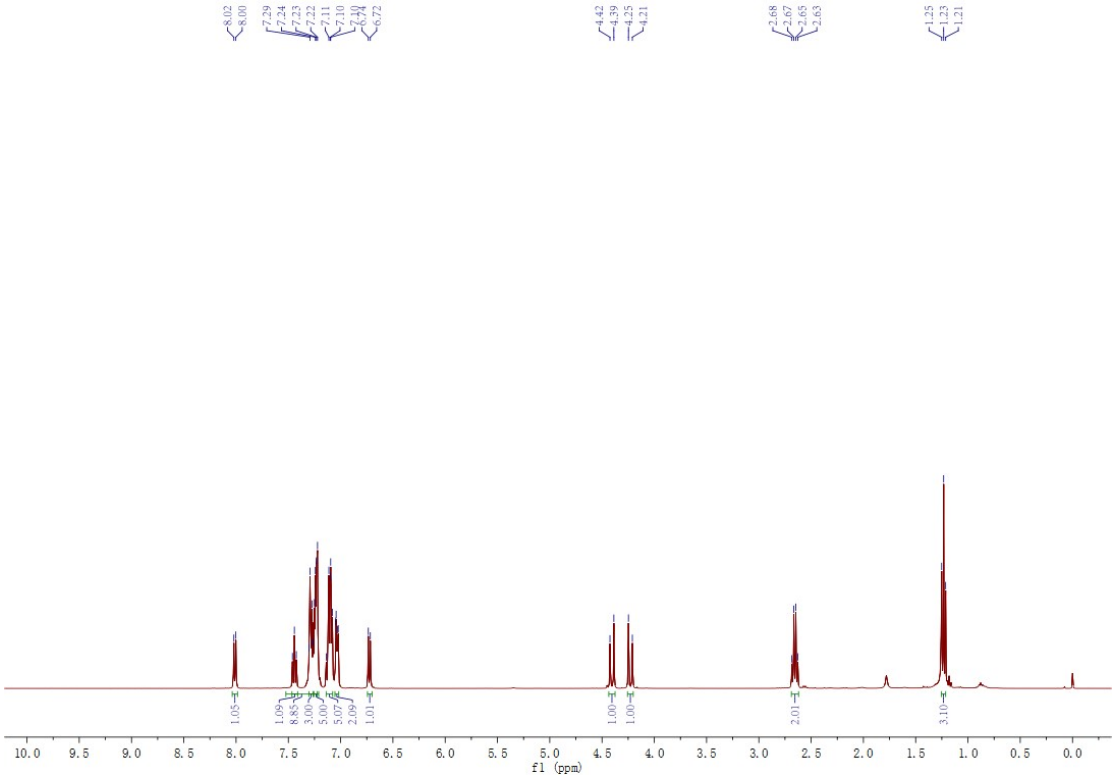
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ad**



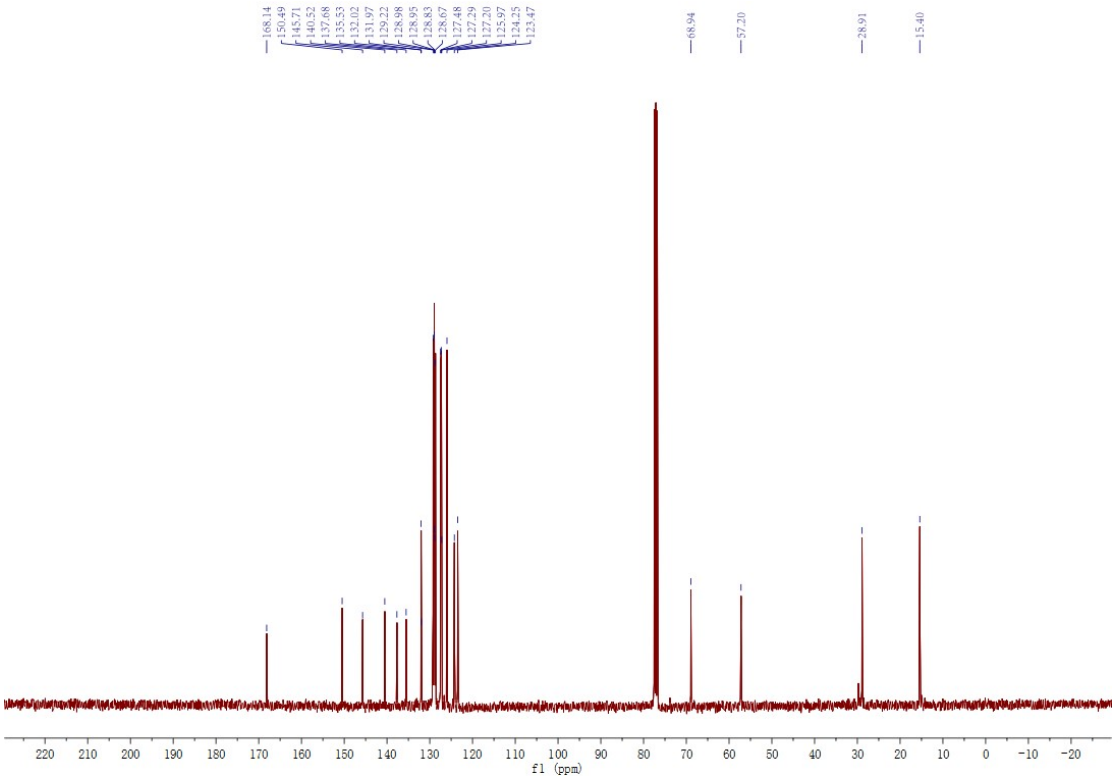
^{13}C NMR (400 MHz, $CDCl_3$) spectra of **3ad**



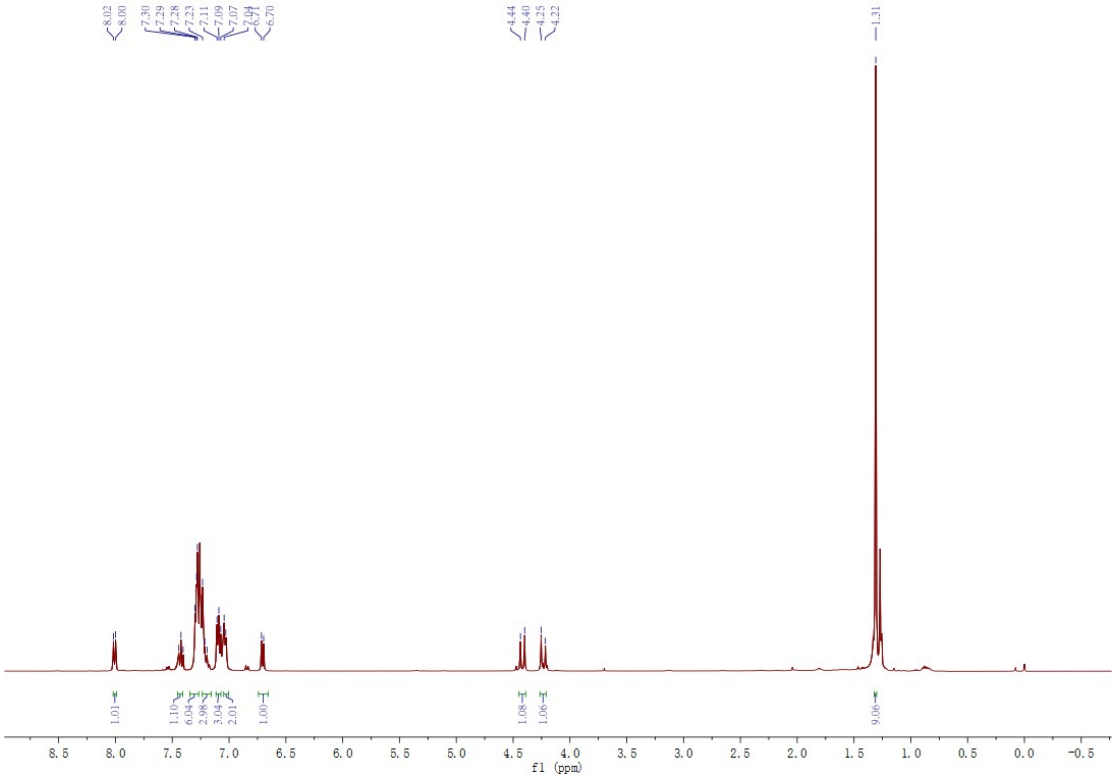
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ae**



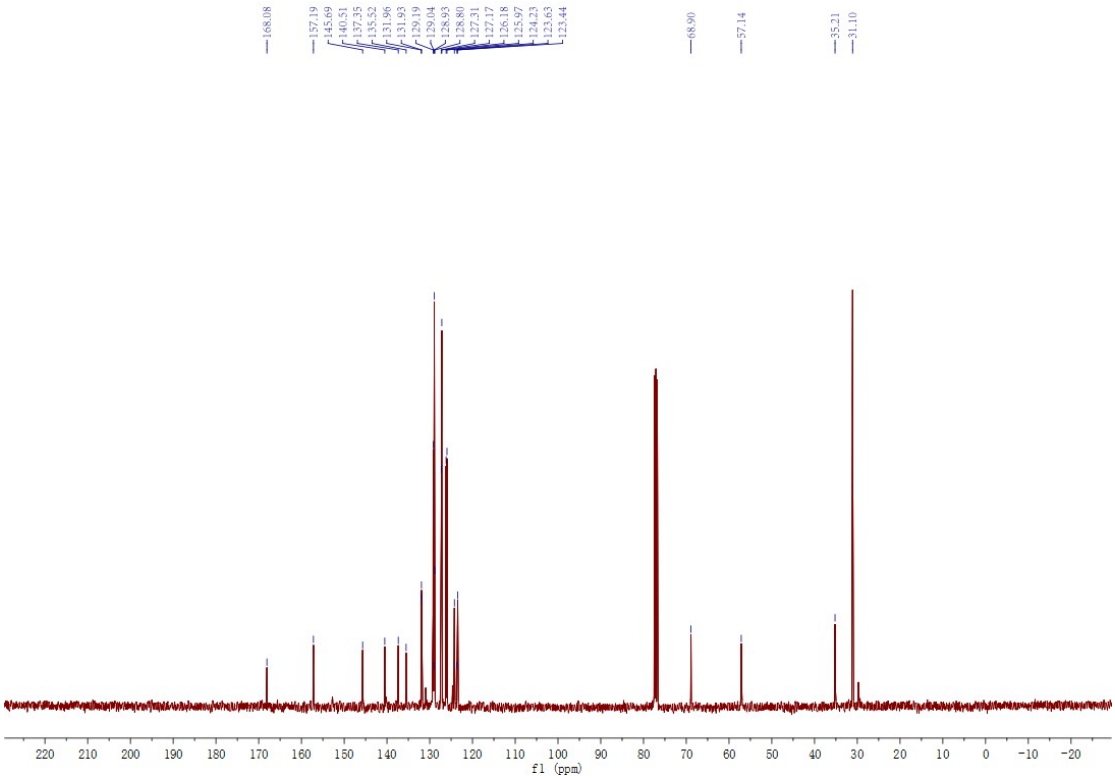
^{13}C NMR (400 MHz, $CDCl_3$) spectra of **3ae**



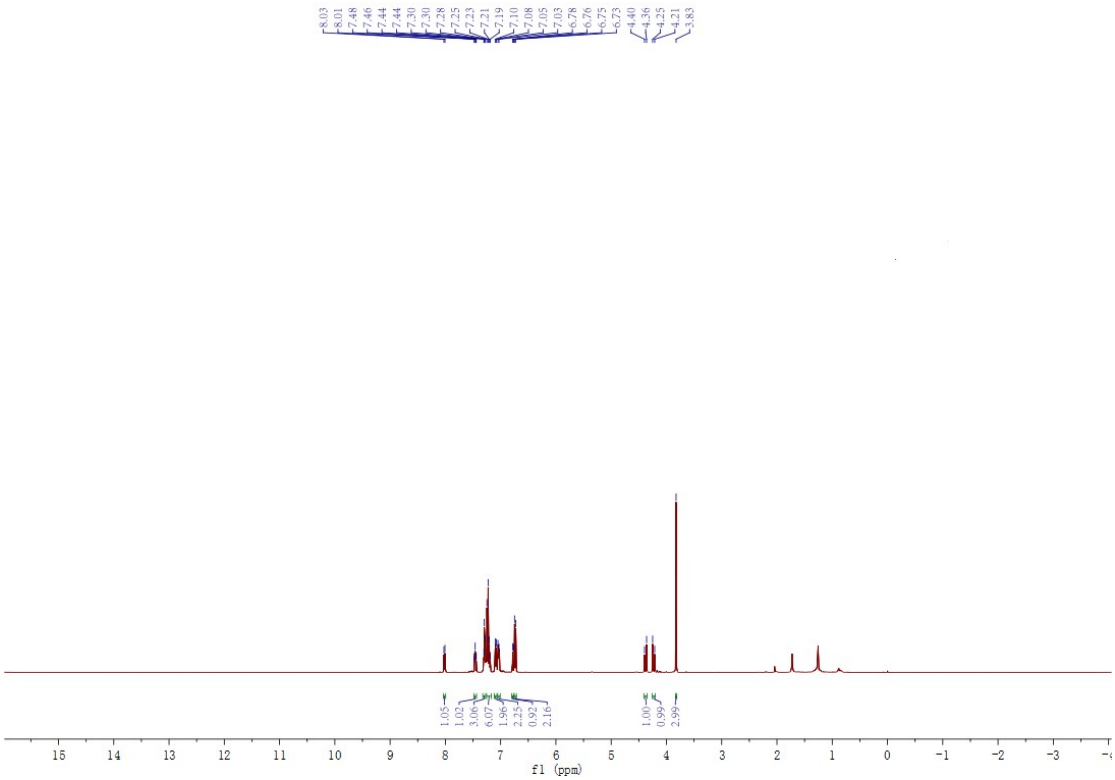
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3af**



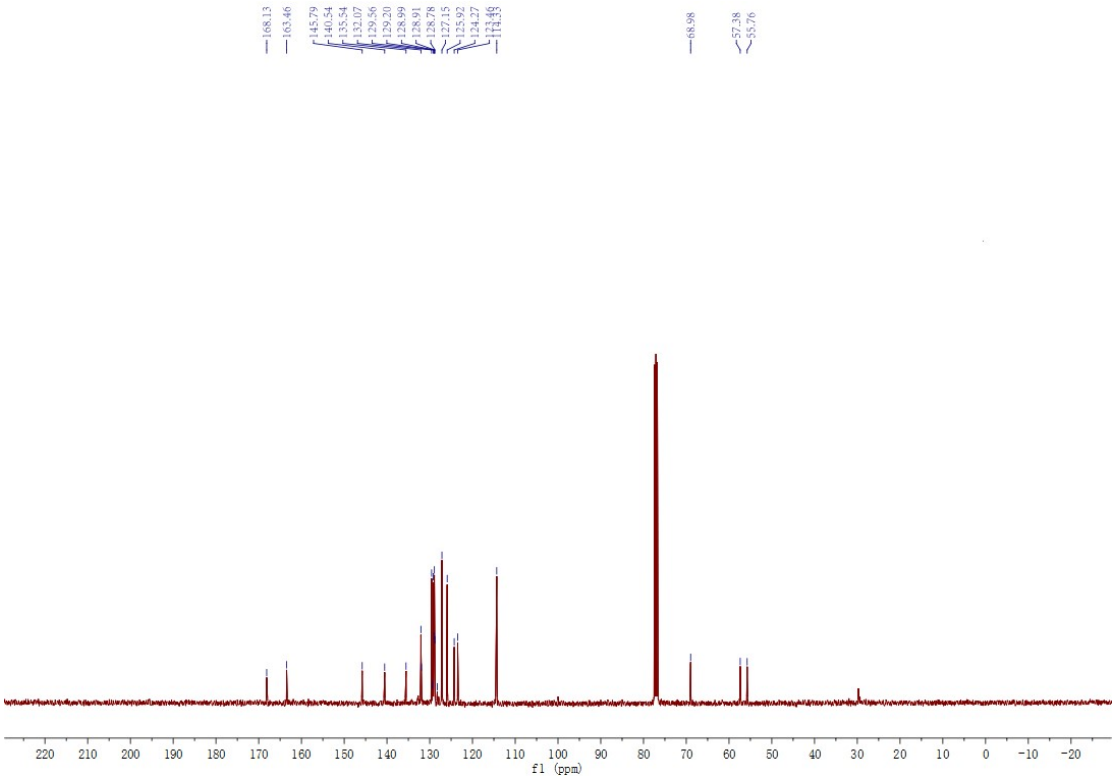
^{13}C NMR (400 MHz, $CDCl_3$) spectra of **3af**



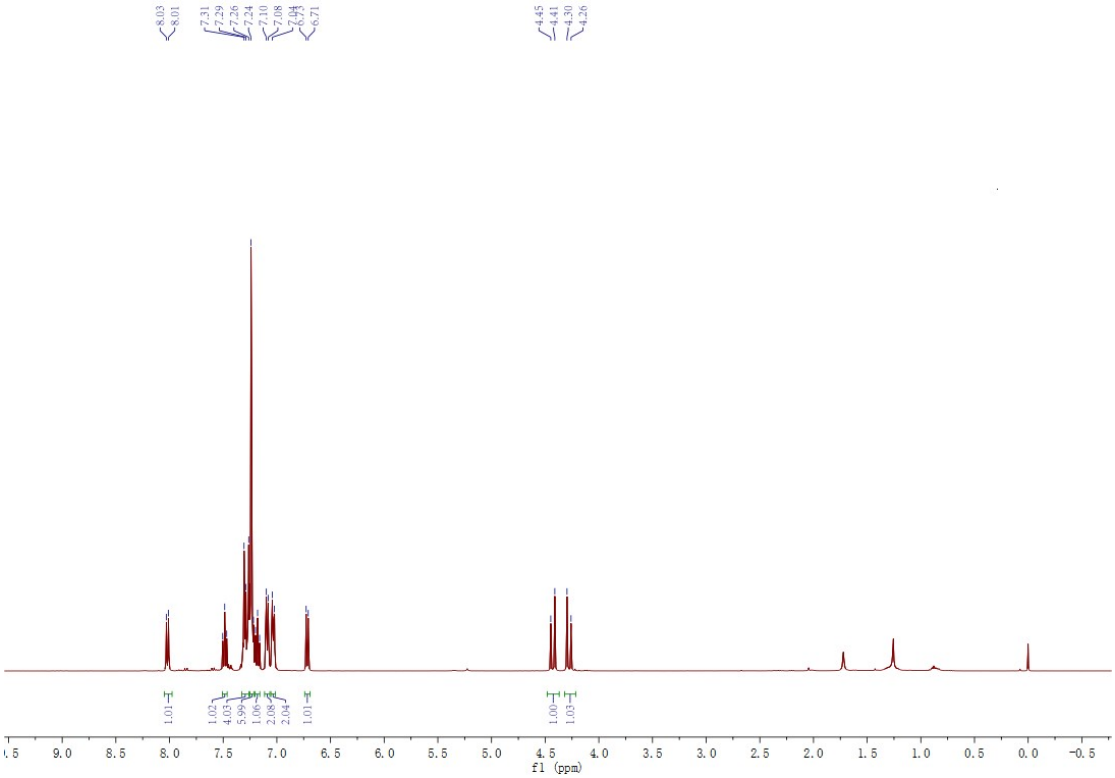
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ag**



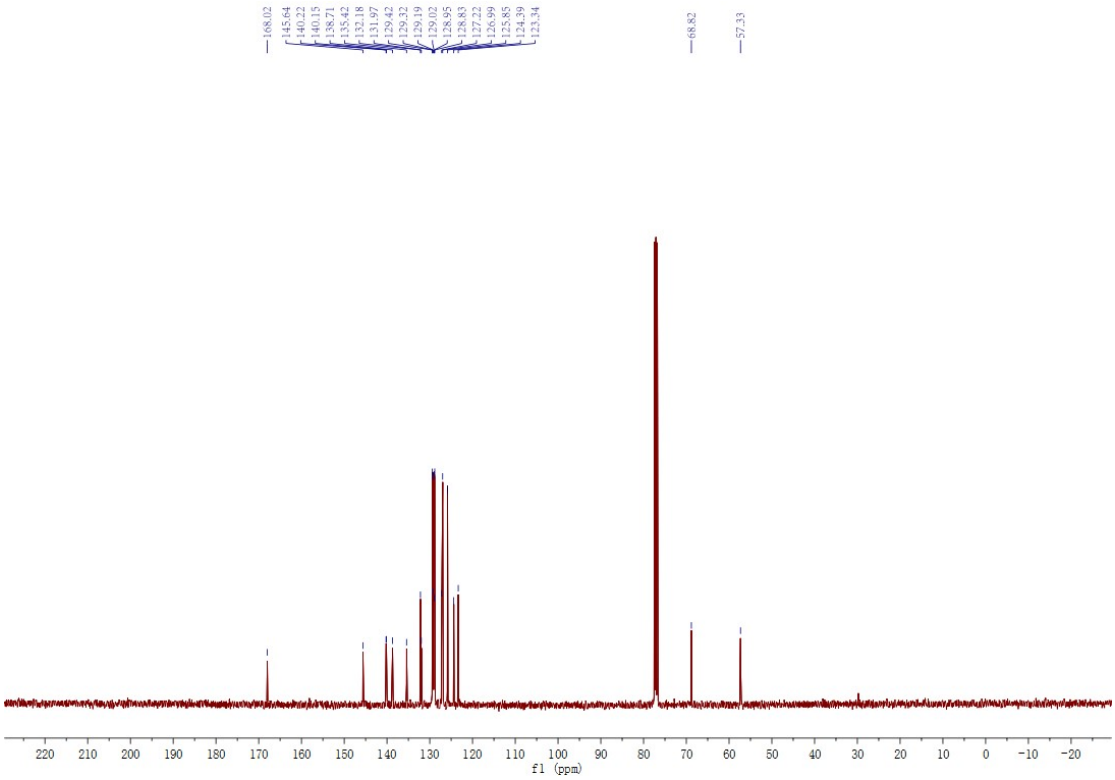
^{13}C NMR (400 MHz, $CDCl_3$) spectra of **3ag**



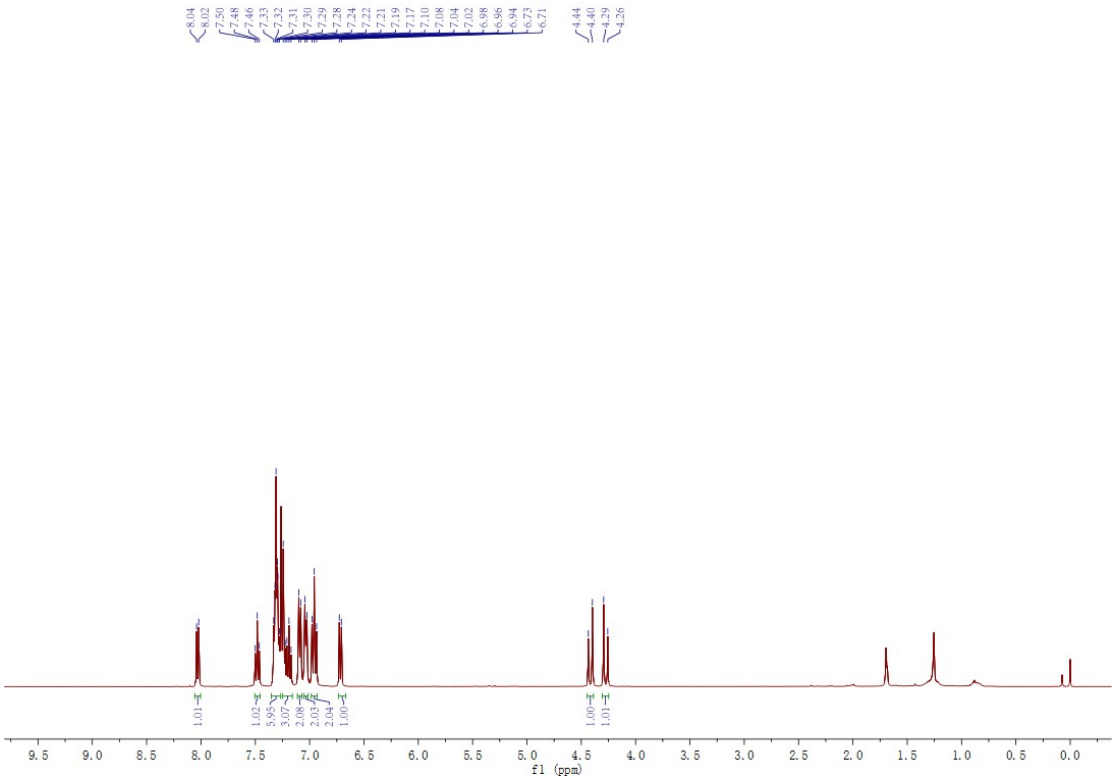
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ah**



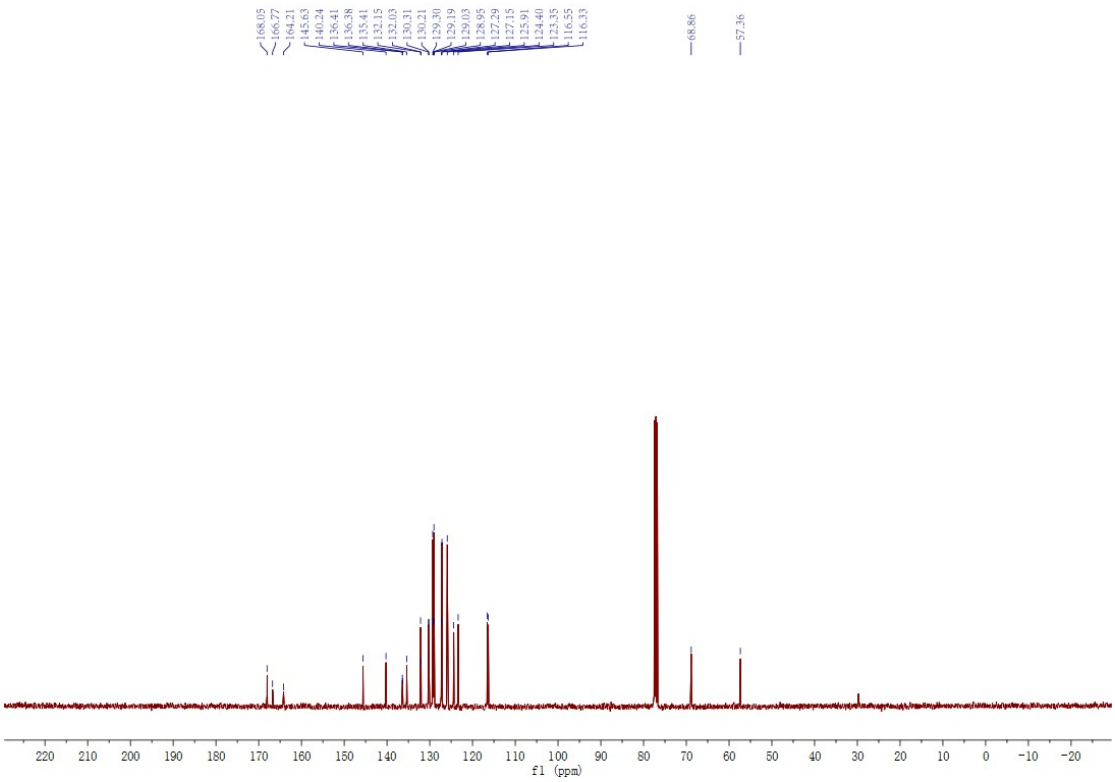
^{13}C NMR (400 MHz, $CDCl_3$) spectra of **3ah**



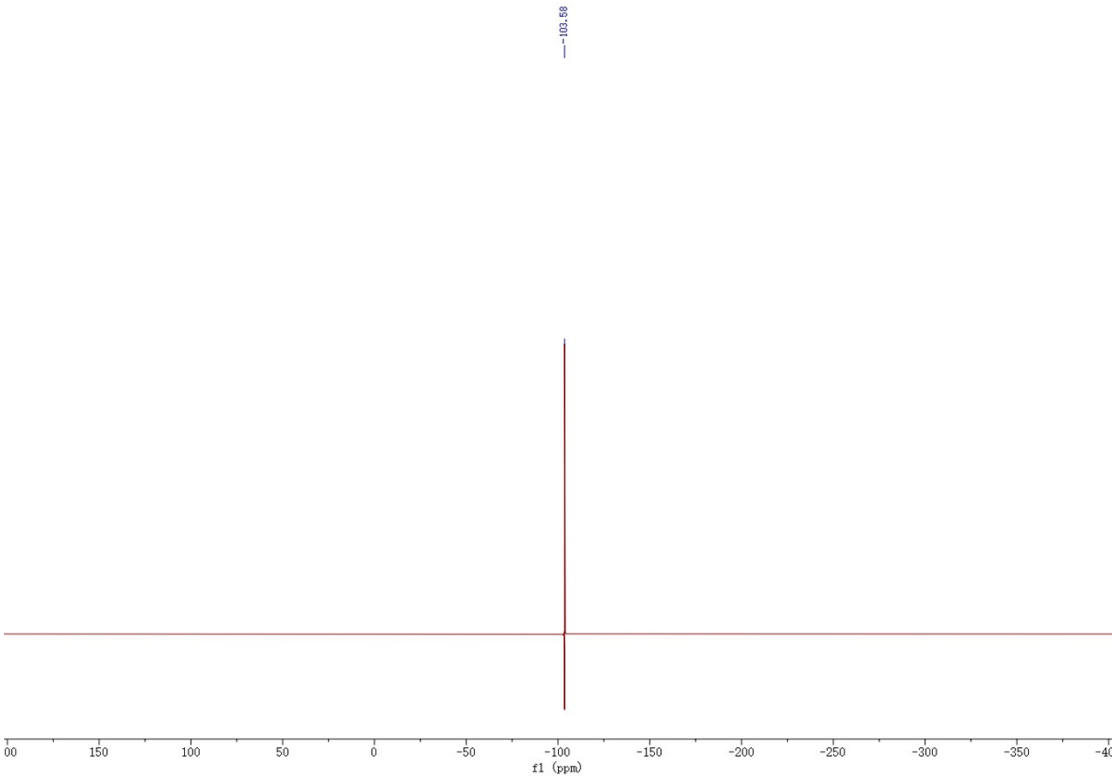
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ai**



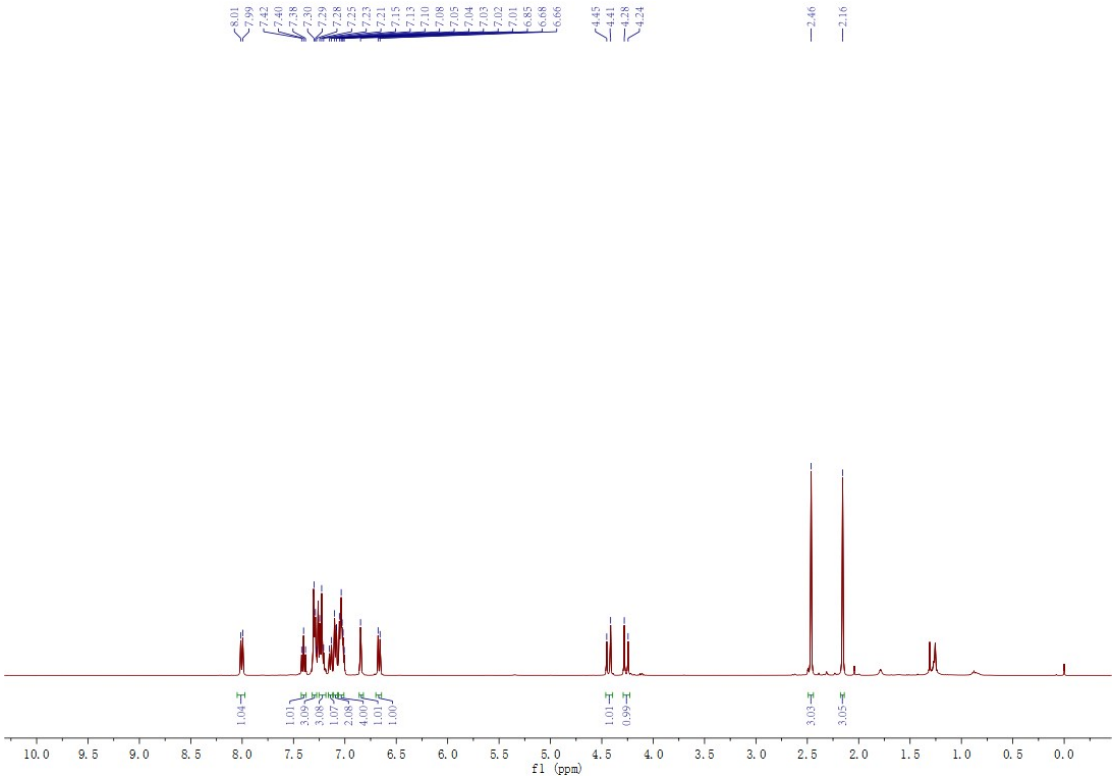
^{13}C NMR (400 MHz, $CDCl_3$) spectra of **3ai**



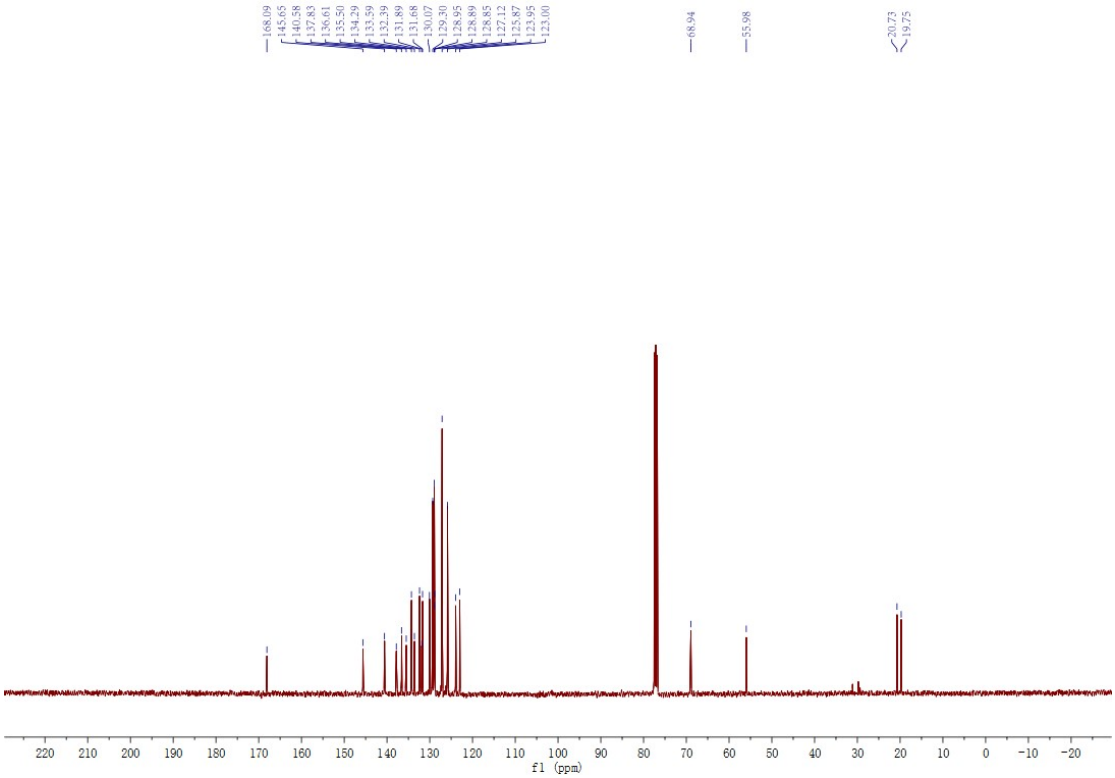
^{19}F NMR (565 MHz, Chloroform-*d*) spectra of **3ai**



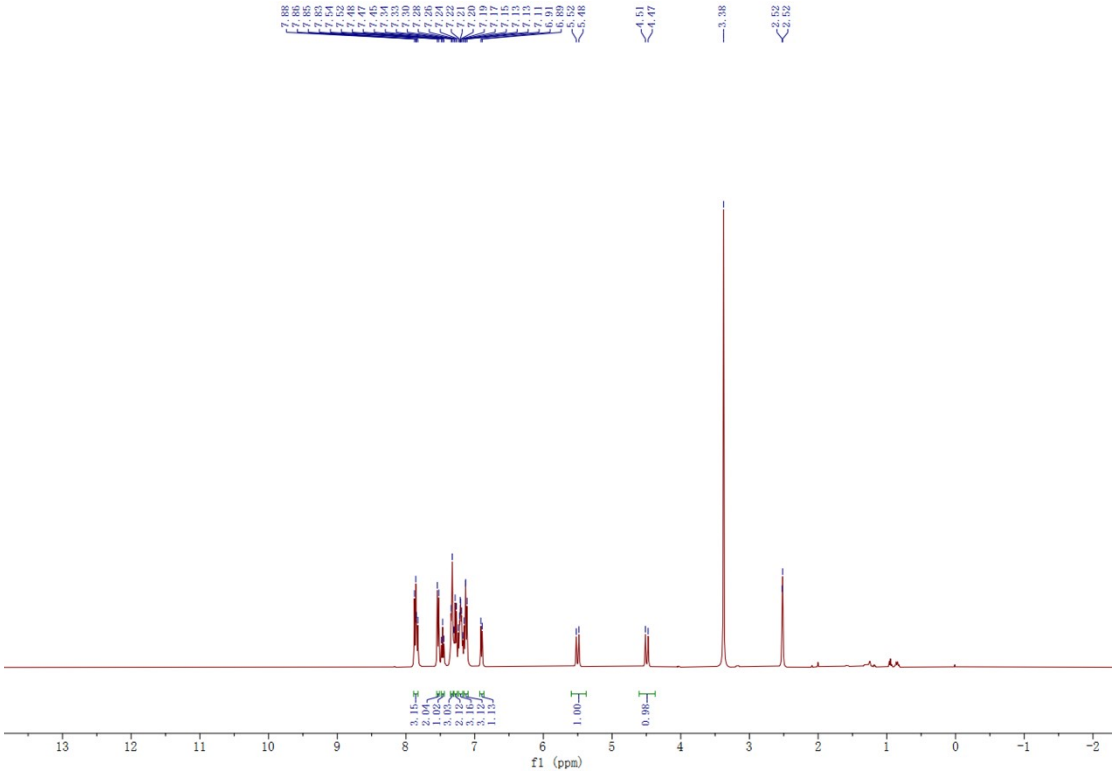
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3aj**



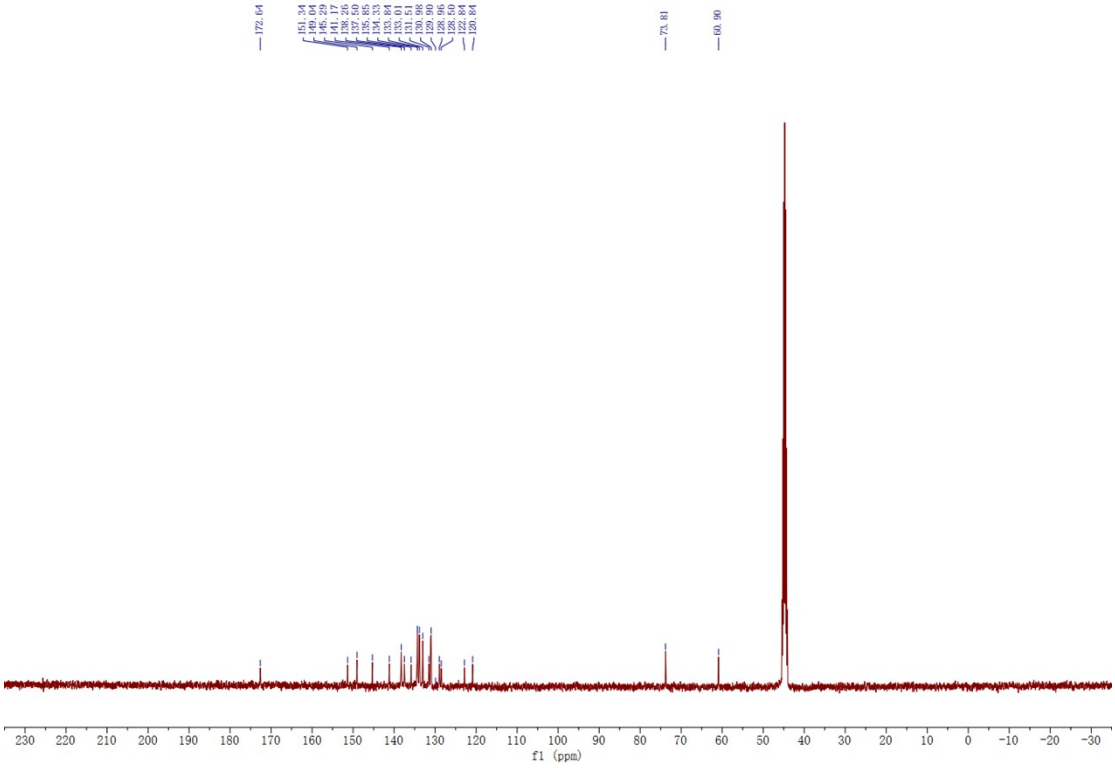
^{13}C NMR (400 MHz, $CDCl_3$) spectra of **3aj**



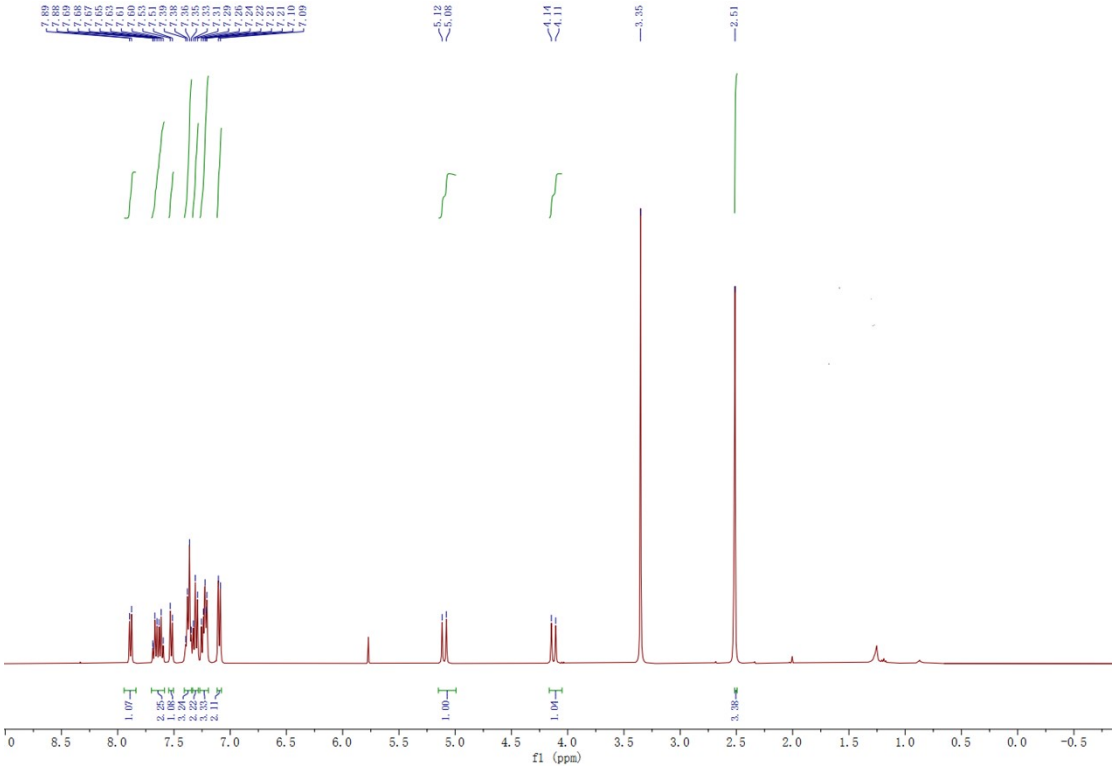
^{1}H NMR (400 MHz, d_6-DMSO) spectra of **3al**



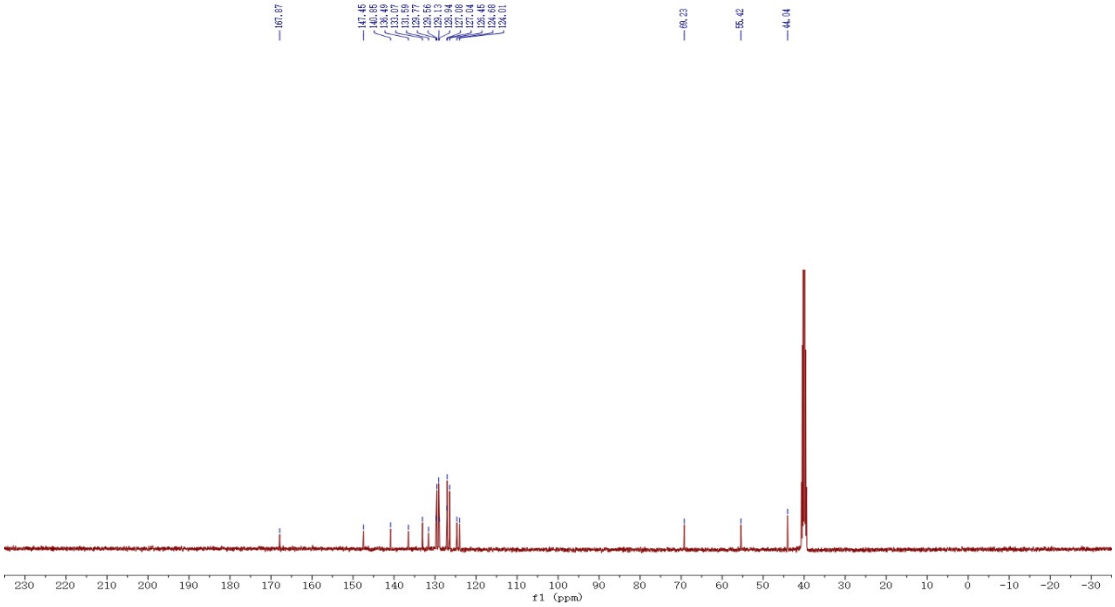
^{13}C NMR (400 MHz, d_6-DMSO) spectra of **3al**



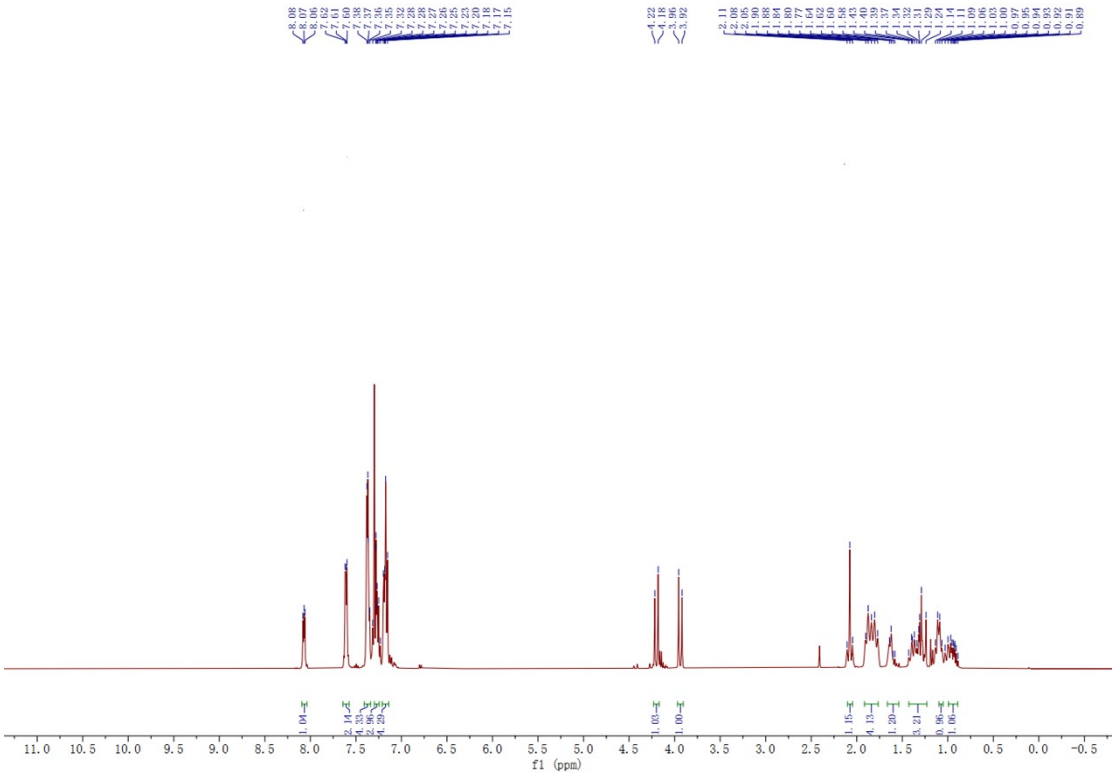
^{1}H NMR (101 MHz, d_6-DMSO) spectra of **3am**



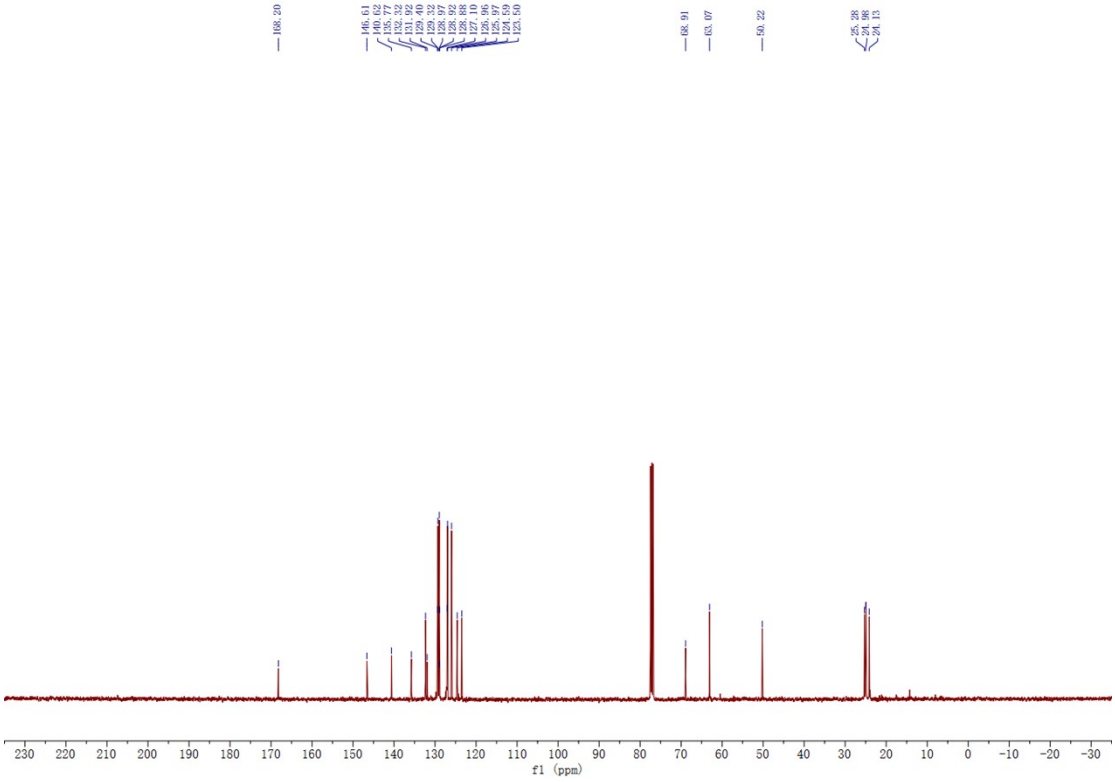
^{13}C NMR (101 MHz, d_6-DMSO) spectra of **3am**



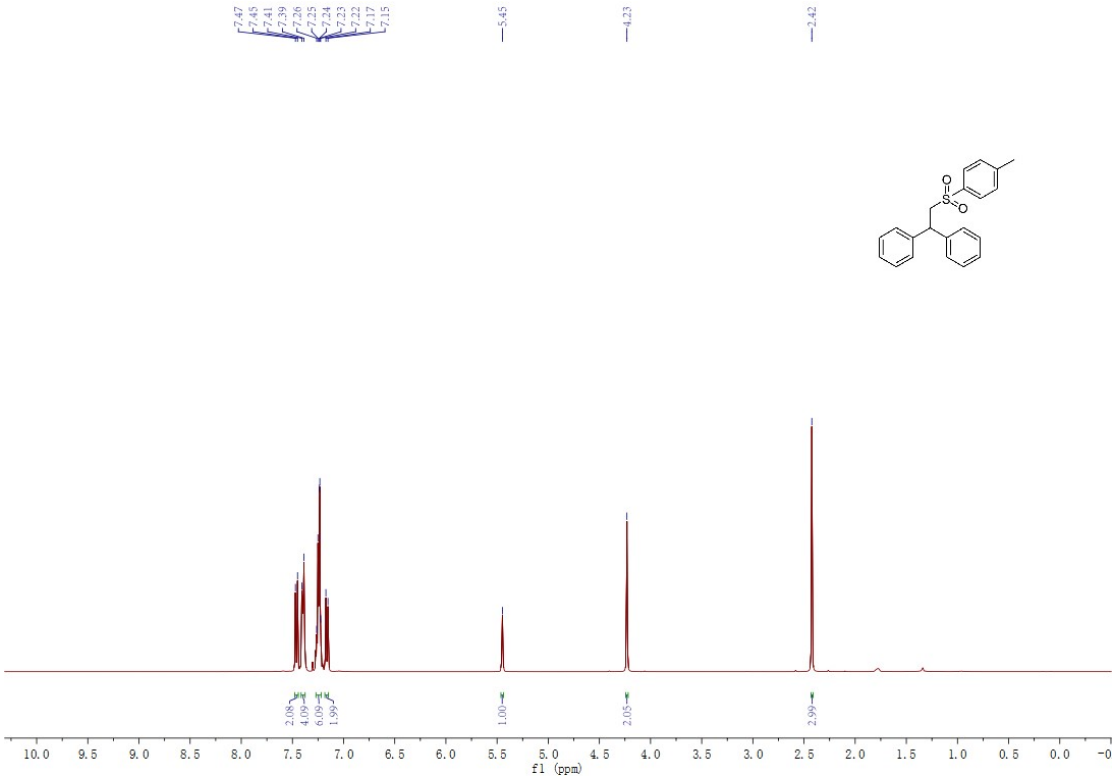
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3an**



^{13}C NMR (400 MHz, $CDCl_3$) spectra of **3an**



^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4**



^{13}C NMR (400 MHz, $CDCl_3$) spectra of **4**