# Supporting Information

## 6-*Exo-Dig* Cyclization/Dearomatization Cascade towards N-O Fused Spiro Polyheterocycles

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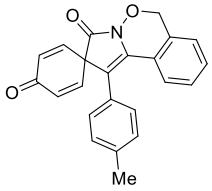
## 1. General Information

All other reagents were used as received from commercial sources. Reactions were monitored through thin layer chromatography (TLC) on 0.25-mm silica gel plates and visualized under UV light. Flash column chromatography (FCC) was performed using Flash silica gel (90-Å pore size, 200–300 μm). NMR spectra were recorded on Bruker Avance-400 or -600 instrument, calibrated to $CD(H)Cl_3$ as the internal reference (7.26 and 77.0 ppm for $^{1}H$ and $^{13}C$ NMR spectra, respectively). $^{1}H$ NMR spectral data were reported in terms of chemical shift ($\delta$, ppm), multiplicity, coupling constant (Hz), and integration. $^{13}C$ NMR spectral data were reported in terms of chemical shift ($\delta$, ppm). The following abbreviations indicated the multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. High-resolution mass spectra were recorded using a SCIEX X500R LC-Q-TOF, ESI ion Source.

## 2. Product Preparation

In a seal capped flask equipped with a stirring bar, **1** (0.1 mmol, 1 equiv), TsOBX (0.11 mmol, 1.1 equiv), and DCM (1 mL, 0.1 M) were added. The reaction mixture was reacted at room temperature for 3 h. The solvent was removed in *vacuo* and the remaining residue was purified by a silica gel column chromatography (petroleum ether/ethyl acetate from 4:1 to 2:1) to afford the products **2**.




**2a**

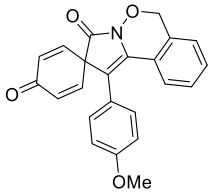
Following general procedure, **1a** (37.1 mg, 0.1 mmol) was used to give **2a** (29.9 mg, 84%). Orange solid. $R_f$ = 0.4 (Petroleum ether/EtOAc, 1:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.03 (dd, J = 21.5, 7.9 Hz, 1H), 7.49 – 7.28 (m, 3H), 7.25 (d, J = 7.7 Hz, 1H), 7.22 – 7.15 (m, 3H), 6.78 (d, J = 9.6 Hz, 2H), 6.52 (d, J = 9.6 Hz, 2H), 5.30 (s, 2H), 2.37 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 184.9, 164.5, 142.3, 138.9, 133.0, 132.2, 131.6, 129.9, 129.7, 128.7, 128.4, 128.2, 126.4, 125.3, 123.3, 113.9, 73.6, 59.2, 21.3.

**$^{13}$C NMR** (101 MHz, $CDCl_3$, DEPT-135) δ 142.3, 133.1, 130.0, 129.8, 128.8, 128.3, 126.5, 125.4, 73.7, 21.4.

**HRMS** (ESI, m/z) calcd for $C_{23}H_{17}NO_3$ $[M + H]^+$:356.1281, found: 356.1283.



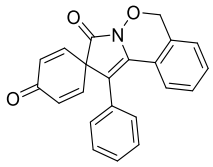

**2b**

Following general procedure, **1b** (38.7 mg, 0.1 mmol) was used to give **2b** (20.7 mg, 56%). Brown solid. $R_f$ = 0.5 (Petroleum ether/EtOAc, 1:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.37 (t, J = 7.8 Hz, 1H), 7.31 (d, J = 8.1 Hz, 1H), 7.25 (d, J = 7.7 Hz, 1H), 7.16 (dd, J = 8.8, 2.80 Hz, 3H), 6.90 – 6.84 (m, 2H), 6.80 – 6.74 (m, 2H), 6.55 – 6.49 (m, 2H), 5.30 (s, 2H), 3.83 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 185.0, 164.6, 159.9, 142.4, 133.0, 132.2, 131.6, 130.2, 129.9, 128.3, 126.3, 125.3, 123.5, 123.4, 114.5, 113.8, 73.6, 59.3, 55.2.

**HRMS** (ESI, m/z) calcd for $C_{23}H_{17}NO_4$ $[M + H]^+$: 372.1231, found: 372.1226.



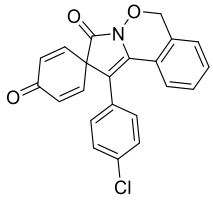
**2c**

Following general procedure, **1c** (35.7 mg, 0.1 mmol) was used to give **2c** (20.4 mg, 60%). Brown solid. $R_f$ = 0.5 (Petroleum ether/EtOAc, 1:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.36 (d, J = 5.8 Hz, 4H), 7.25 (d, J = 7.3 Hz, 4H), 7.16 (t, J = 7.8 Hz, 1H), 6.78 (d, J = 9.6 Hz, 2H), 6.51 (d, J = 9.7 Hz, 2H), 5.30 (s, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 184.8, 164.5, 142.1, 133.1, 132.5, 131.7, 131.6, 130.0, 129.0, 128.93, 128.90, 128.3, 126.4, 125.3, 123.2, 113.8, 73.6, 59.1.

**HRMS** (ESI, m/z) calcd for $C_{22}H_{15}NO_3$ $[M + H]^+$: 342.1125, found: 342.1122.



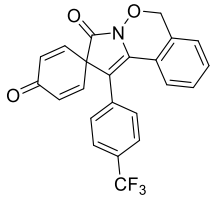
**2d**

Following general procedure, **1d** (39.2 mg, 0.1 mmol) was used to give **2d** (29.8 mg, 79%). Brown solid. $R_f$ = 0.4 (Petroleum ether/EtOAc, 1:1).

**$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.42 – 7.39 (m, 1H), 7.35 – 7.32 (m, 2H), 7.28 – 7.25 (m, 2H), 7.23 – 7.18 (m, 3H), 6.75 (d, J = 10.0 Hz, 2H), 6.53 (d, J = 10.0 Hz, 2H), 5.30 (s, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 184.6, 164.4, 141.8, 135.0, 133.3, 133.1, 131.9, 130.4, 130.2, 130.1, 129.5, 128.4, 126.4, 125.5, 123.0, 112.3, 73.7, 58.9.

**HRMS** (ESI, m/z) calcd for $C_{22}H_{14}ClNO_3$ $[M + H]^+$:376.0735, found: 376.0741.



**2e**

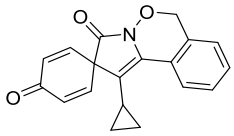
Following general procedure, **1e** (42.5 mg, 0.1 mmol) was used to give **2e** (17.3 mg, 42%). Brown solid. $R_f$ = 0.3 (Petroleum ether/EtOAc, 1:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.62 (d, J = 7.9 Hz, 2H), 7.42 (t, J = 7.8 Hz, 3H), 7.31 (s, 1H), 7.23 (d, J = 6.8 Hz, 2H), 6.80 – 6.74 (m, 2H), 6.55 (d, J = 9.5 Hz, 2H), 5.32 (s, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 184.5, 164.1, 141.7, 135.6, 133.7, 133.4, 132.1, 130.7, 129.2, 128.5, 126.4, 126.1 (q, J = 3.73 Hz), 125.7, 122.7, 111.7, 73.7, 58.8.

**$^{19}$F NMR** (377 MHz, $CDCl_3$) $\delta$ -62.8.

**HRMS** (ESI, m/z) calcd for $C_{23}H_{14}F_3NO_3$ $[M + H]^+$: 410.0999, found: 410.0998.



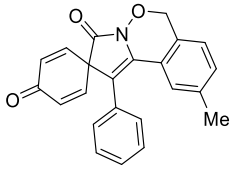
**2f**

Following general procedure, **1f** (32.1 mg, 0.1 mmol) was used to give **2f** (10.7 mg, 35%). Yellow solid. $R_f$ = 0.3 (Petroleum ether/EtOAc, 1:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 8.12 (d, J = 7.7 Hz, 1H), 7.56 – 7.39 (m, 3H), 6.71 – 6.56 (m, 4H), 5.22 (s, 2H), 1.35 (s, 1H), 0.88 (s, 2H), 0.61 (d, J = 5.6 Hz, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 185.1, 163.5, 143.4, 132.8, 131.6, 129.5, 128.5, 127.4, 125.3, 123.9, 114.8, 73.8, 58.8, 8.9, 7.1.

**HRMS** (ESI, m/z) calcd for $C_{19}H_{15}NO_3$ $[M + H]^+$: 306.1125, found: 306.1124.



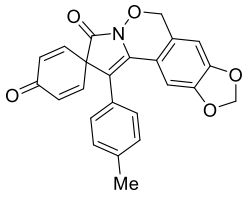
**2g**

Following general procedure, **1g** (37.1 mg, 0.1 mmol) was used to give **2g** (14.4 mg, 51%). Yellow solid. $R_f$ = 0.4 (Petroleum ether/EtOAc, 1:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.35 (d, J = 6.6 Hz, 3H), 7.25 (d, J = 7.2 Hz, 2H), 7.16 (q, J = 7.9 Hz, 2H), 7.04 (s, 1H), 6.77 (d, J = 9.5 Hz, 2H), 6.52 (d, J = 9.5 Hz, 2H), 5.26 (s, 2H), 2.14 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 184.9, 164.5, 142.3, 138.2, 133.1, 132.8, 131.7, 131.0, 128.99, 128.95, 128.9, 126.9, 125.3, 123.1, 113.5, 73.6, 59.2, 21.2.

**HRMS** (ESI, m/z) calcd for $C_{23}H_{17}NO_3$ $[M + H]^+$: 356.1281, found: 356.1277.



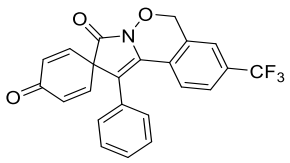
**2h**

Following general procedure, **1h** (41.5 mg, 0.1 mmol) was used to give **2h** (14.9 mg, 37%). Brown solid. $R_f$ = 0.4 (Petroleum ether/EtOAc, 1:1).

**$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.14 (d, J = 7.9 Hz, 2H), 7.09 (d, J = 8.2 Hz, 2H), 6.77 – 6.74 (m, 2H), 6.68 (d, J = 6.0 Hz, 2H), 6.51 – 6.48 (m, 2H), 5.98 (s, 2H), 5.19 (s, 2H), 2.36 (s, 3H).

**$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 185.0, 164.5, 147.6, 142.5, 138.9, 132.9, 132.1, 129.8, 128.8, 128.4, 126.8, 117.0, 111.9, 106.2, 105.6, 101.7, 73.4, 59.1, 21.3.

**HRMS** (ESI, m/z) calcd for $C_{24}H_{17}NO_5$ $[M + H]^+$: 400.1180, found: 400.1181.



**2i**

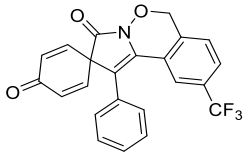
Following general procedure, **1i** (42.5 mg, 0.1 mmol) was used to give **2i** (34.6 mg, 85%). Brown solid. $R_f$ = 0.5 (Petroleum ether/EtOAc, 1:1).

**$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.43 – 7.36 (m, 4H), 7.34 (d, J = 8.3 Hz, 1H), 7.25 – 7.21 (m, 2H), 6.77 (d, J = 10.0 Hz, 2H), 6.52 (d, J = 10.0 Hz, 2H), 5.34 (s, 2H).

**$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 184.6, 164.6, 141.5, 133.2, 132.4, 131.6, 131.5, 131.3, 130.9, 130.7, 129.4, 129.3, 128.7, 126.8, 126.6, 122.5 (q, J = 4.0 Hz), 122.5 (q, J = 4.0 Hz), 116.7, 73.2, 59.2.

**$^{19}$F NMR** (377 MHz, $CDCl_3$) δ -63.1.

**HRMS** (ESI, m/z) calcd for $C_{23}H_{14}F_3NO_3$ $[M + H]^+$: 410.0999, found: 410.0991.



**2j**

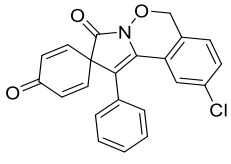
Following general procedure, **1j** (42.5 mg, 0.1 mmol) was used to give **2j** (39.2 mg, 96%). Yellow solid. $R_f$ = 0.4 (Petroleum ether/EtOAc, 1:1).

**$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.61 (dd, J = 8.0, 1.7 Hz, 1H), 7.47 (d, J = 1.7 Hz, 1H), 7.44 – 7.37 (m, 4H), 7.26 – 7.22 (m, 2H), 6.78 (d, J = 9.8 Hz, 2H), 6.54 (d, J = 9.7 Hz, 2H), 5.35 (s, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 184.6, 164.8, 141.6, 135.1, 134.3, 133.2, 131.6, 131.0, 130.8, 130.7, 130.6, 129.5, 129.3, 128.62, 128.55, 126.4 (q, J = 3.0 Hz), 126.1, 124.0, 123.3 (q, J = 3.7 Hz), 116.1, 73.1, 59.2.

**$^{19}$F NMR** (377 MHz, $CDCl_3$) δ -63.5.

**HRMS** (ESI, m/z) calcd for $C_{23}H_{14}F_3NO_3$ $[M + H]^+$: 410.0999, found: 410.0996.



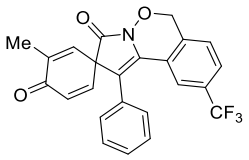
**2k**

Following general procedure, **1k** (39.2 mg, 0.1 mmol) was used to give **2k** (23.5 mg, 63%). Yellow solid. $R_f$ = 0.4 (Petroleum ether/EtOAc, 1:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.40 (d, J = 1.9 Hz, 2H), 7.38 (s, 1H), 7.34 (d, J = 8.2 Hz, 1H), 7.25 – 7.18 (m, 4H), 6.79 – 6.73 (m, 2H), 6.53 (dd, J = 9.9, 2.0 Hz, 2H), 5.27 (s, 2H).

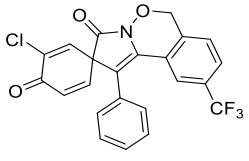
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 184.7, 164.7, 144.4, 143.1, 141.7, 134.3, 133.3, 131.6, 130.9 (q, J = 2.33 Hz), 130.1, 129.4, 129.3, 128.7, 127.6, 126.8, 126.3, 124.9, 115.5,

73.2, 59.2.
**HRMS** (ESI, m/z) calcd for $C_{22}H_{14}ClNO_3$ $[M + H]^+$: 376.0735, found: 376.0737.



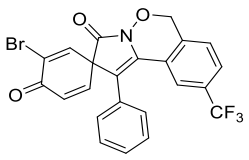
**2l**

Following general procedure, **1l** (43.9 mg, 0.1 mmol) was used to give **2l** (35.9 mg, 85%). Brown solid. $R_f$ = 0.3 (Petroleum ether/EtOAc, 1:1).
**$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.61 – 7.58 (m, 1H), 7.46 – 7.44 (m, 1H), 7.43 – 7.36 (m, 4H), 7.24 – 7.20 (m, 2H), 6.73 (dd, J = 9.8, 2.9 Hz, 1H), 6.57 – 6.55 (m, 1H), 6.52 (d, J = 9.8 Hz, 1H), 5.34 (s, 2H), 1.95 (d, J = 1.5 Hz, 3H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 185.3, 165.5, 141.0, 140.5, 136.5, 135.1, 133.0, 131.3, 130.9, 129.4, 129.2, 128.6, 126.2 (q, J = 3.69 Hz), 126.0, 124.2, 123.3 (q, J = 3.7 Hz), 121.7, 116.7, 73.1, 59.3, 16.2.
**$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -63.5.
**HRMS** (ESI, m/z) calcd for $C_{24}H_{16}F_3NO_3$ $[M + H]^+$: 424.1155, found: 424.1149.



**2m**

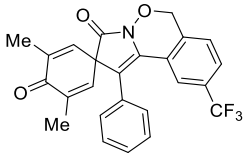
Following general procedure, **1m** (46 mg, 0.1 mmol) was used to give **2m** (36.1 mg, 81%). Brown solid. $R_f$ = 0.3 (Petroleum ether/EtOAc, 1:1).
**$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.6 (dd, J = 8.1, 1.7 Hz, 1H), 7.5 – 7.4 (m, 2H), 7.4 – 7.4 (m, 3H), 7.2 – 7.2 (m, 2H), 7.0 (d, J = 2.7 Hz, 1H), 6.8 (dd, J = 9.8, 2.7 Hz, 1H), 6.6 (d, J = 9.7 Hz, 1H), 5.4 (s, 2H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 177.7, 163.8, 141.7, 137.4, 137.2, 135.2, 132.4, 131.9, 131.1, 130.3, 129.8, 129.5, 128.6, 126.6 (q, J = 3.9 Hz), 126.1, 123.8, 123.4 (q, J = 3.8 Hz), 115.2, 73.2, 60.7.
**$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -63.5.
**HRMS** (ESI, m/z) calcd for $C_{23}H_{13}ClF_3NO_3$ $[M + H]^+$: 444.0609, found: 444.0602.



**2n**

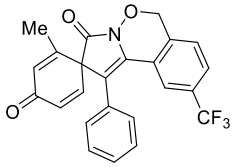
Following general procedure, **1n** (50.4 mg, 0.1 mmol) was used to give **2n** (48.4 mg, 99%). Brown solid. $R_f$ = 0.5 (Petroleum ether/EtOAc, 1:1).
**$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.61 (dd, J = 8.0, 1.7 Hz, 1H), 7.45 – 7.42 (m, 2H), 7.42 – 7.38 (m, 3H), 7.25 (d, J = 2.7 Hz, 1H), 7.24 – 7.21 (m, 2H), 6.81 (dd, J = 9.8, 2.7 Hz,

1H), 6.59 (d, J = 9.8 Hz, 1H), 5.34 (s, 2H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 177.7, 163.5, 141.8, 141.6, 135.2, 134.3, 131.9, 130.9, 130.3, 129.8, 129.5, 129.0, 128.7, 126.7 (q, J = 3.8 Hz), 126.2, 125.2, 124.4, 123.8, 123.4 (q, J = 4.1 Hz), 121.7, 115.0, 73.2, 61.7.
**$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -63.5.
**HRMS** (ESI, m/z) calcd for $C_{23}H_{13}BrF_3NO_3$ $[M + H]^+$: 488.0104, found: 488.0110.



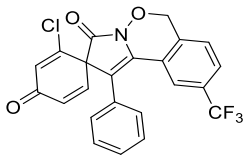
**2o**

Following general procedure, **1o** (45.4 mg, 0.1 mmol) was used to give **2o** (38.0 mg, 87%). Brown solid. $R_f$ = 0.5 (Petroleum ether/EtOAc, 1:1).
**$^{1}$H NMR** (600 MHz, $CDCl_3$) δ 7.57 (d, J = 8.1 Hz, 1H), 7.42 (s, 1H), 7.39 – 7.34 (m, 4H), 7.19 (d, J = 7.6 Hz, 2H), 6.52 (s, 2H), 5.31 (s, 2H), 1.93 (s, 6H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 186.0, 166.1, 139.9, 136.1, 135.1, 131.1, 131.0, 130.9, 130.6, 129.3, 129.2, 128.7, 126.1, 126.0, 124.5, 124.3, 123.3 (q, J = 3.8 Hz), 121.8, 117.3, 73.1, 59.0, 16.4.
**$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -63.5.
**HRMS** (ESI, m/z) calcd for $C_{25}H_{18}F_3NO_3$ $[M + H]^+$: 438.1312, found: 438.1301.



**2p**

Following general procedure, **1p** (43.9 mg, 0.1 mmol) was used to give **2p** (40.7 mg, 96%). Brown solid. $R_f$ = 0.3 (Petroleum ether/EtOAc, 1:1).
**$^{1}$H NMR** (400 MHz, $CDCl_3$) *δ* 7.62 (d, J = 8.1 Hz, 1H), 7.56 (s, 1H), 7.44 – 7.33 (m, 4H), 7.22 (d, J = 7.3 Hz, 2H), 6.73 (d, J = 9.8 Hz, 1H), 6.51 (d, J = 9.8 Hz, 1H), 6.36 (s, 1H), 5.40 – 5.29 (m, 2H), 2.02 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) *δ* 185.4, 165.1, 151.2, 141.6, 135.1, 132.2, 132.1, 131.9, 131.0, 130.7, 130.5, 129.6, 129.3, 128.3, 126.4 (q, J = 3.6 Hz), 126.1, 124.4, 124.0, 123.4 (q, J = 4.0 Hz), 121.7, 116.4, 73.4, 62.1, 19.7.
**$^{19}$F NMR** (377 MHz, $CDCl_3$) δ -63.5.
**HRMS** (ESI, m/z) calcd for $C_{24}H_{16}F_3NO_3$ $[M + H]^+$: 424.1155, found: 424.1154.



**2q**

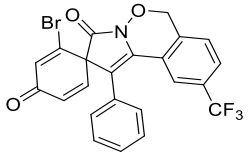
Following general procedure, **1q** (46.0 mg, 0.1 mmol) was used to give **2q** (42.5 mg, 96%). Brown solid. $R_f$ = 0.3 (Petroleum ether/EtOAc, 1:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.62 (d, J = 8.0 Hz, 1H), 7.49 – 7.35 (m, 6H), 7.29 (s, 1H), 6.81 (d, J = 9.8 Hz, 1H), 6.64 (s, 1H), 6.54 (d, J = 9.8 Hz, 1H), 5.35 (s, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 183.7, 163.2, 148.0, 140.8, 135.1, 133.0, 131.8, 131.1, 130.8, 129.8, 129.4, 128.8, 126.6 (q, J = 3.7 Hz), 126.1, 124.3, 123.8, 123.5 (q, J = 4.0 Hz), 121.6, 115.1, 73.4, 63.7.

**$^{19}$F NMR** (377 MHz, $CDCl_3$) δ -63.5.

**HRMS** (ESI, m/z) calcd for $C_{23}H_{13}ClF_3NO_3$ $[M + H]^+$: 444.0609, found: 444.0607.




**2r**

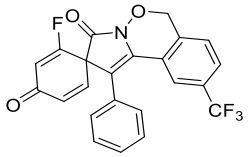
Following general procedure, **1r** (50.4 mg, 0.1 mmol) was used to give **2r** (48.6 mg, 99%). Brown solid. $R_f$ = 0.3 (Petroleum ether/EtOAc, 1:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.63 (d, J = 8.2 Hz, 1H), 7.47 (s, 1H), 7.45 – 7.36 (m, 4H), 7.31 (d, J = 7.3 Hz, 2H), 6.89 (d, J = 6.9 Hz, 2H), 6.58 (dd, J = 9.9, 2.4 Hz, 1H), 5.36 (s, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 182.9, 163.3, 141.5, 139.3, 137.0, 135.2, 132.7, 131.7, 131.1, 130.7, 129.84, 129.77, 129.3, 128.9, 126.6 (q, J = 3.6 Hz), 126.1, 123.8, 123.5 (q, J = 4.1 Hz), 121.6, 115.4, 73.4, 64.5.

**$^{19}$F NMR** (377 MHz, $CDCl_3$) δ -63.5.

**HRMS** (ESI, m/z) calcd for $C_{23}H_{13}BrF_3NO_3$ $[M + H]^+$: 488.0104, found: 488.0097.




**2s**

Following general procedure, **1s** (44.3 mg, 0.1 mmol) was used to give **2s** (33.9 mg, 80%). Brown solid. $R_f$ = 0.3 (Petroleum ether/EtOAc, 1:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.63 (d, J = 8.1 Hz, 1H), 7.48 – 7.38 (m, 5H), 7.25 (d, J = 7.3 Hz, 2H), 6.68 – 6.60 (m, 1H), 6.48 (d, J = 9.8 Hz, 1H), 6.18 (dd, J = 13.5, 2.6 Hz, 1H), 5.36 (s, 2H).

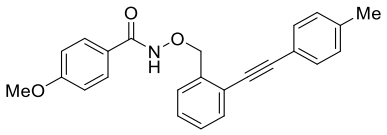
**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 186.8 (d, J = 15.2 Hz), 169.2 (d, J = 283.4 Hz), 162.9, 137.54, 137.49, 135.2, 133.1, 132.1, 131.1, 130.8, 129.9, 129.6, 128.8, 126.7 (q, J = 3.4 Hz), 126.1, 124.4, 123.5 (q, J = 4.0 Hz), 123.5, 121.7, 113.9 (d, J = 9.5 Hz), 73.3, 60.3 (d, J = 25.0 Hz).

**$^{19}$F NMR** (377 MHz, $CDCl_3$) δ -63.5, -90.9.

**HRMS** (ESI, m/z) calcd for $C_{23}H_{13}F_4NO_3$ $[M + H]^+$: 428.0905, found: 428.0901.

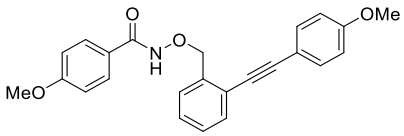
## 3. Substrate Preparation

The synthesis steps of compounds **1a-1t** were according to reported literature.[1]



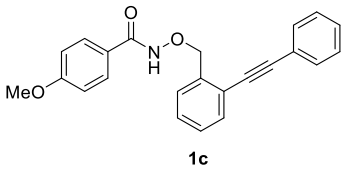
**1a**

White solid. $R_f$ = 0.4 (Petroleum ether/EtOAc, 2:1).
**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 8.50 (s, 1H), 7.65 – 7.61 (m, 2H), 7.60 – 7.55 (m, 2H), 7.42 (d, J = 8.1 Hz, 2H), 7.40 – 7.36 (m, 2H), 7.15 (d, J = 7.8 Hz, 2H), 6.88 – 6.83 (m, 2H), 5.31 (s, 2H), 3.83 (s, 3H), 2.38 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 162.5, 138.7, 136.9, 132.3, 131.5, 130.0, 129.1, 128.9, 128.6, 128.4, 124.2, 123.9, 119.7, 113.8, 94.2, 86.3, 76.6, 55.4, 21.5.
**HRMS** (ESI, m/z) calcd for $C_{24}H_{21}NO_3$ $[M + H]^+$: 372.1594, found: 372.1600.



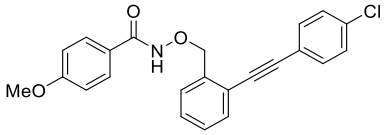
**1b**

White solid. $R_f$ = 0.4 (Petroleum ether/EtOAc, 2:1).
**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 8.78 (d, J = 12.1 Hz, 1H), 7.63 (d, J = 8.4 Hz, 2H), 7.55 (q, J = 4.8 Hz, 2H), 7.44 (d, J = 8.3 Hz, 2H), 7.40 – 7.30 (m, 2H), 6.90 – 6.78 (m, 4H), 5.29 (s, 2H), 3.82 (s, 3H), 3.80 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 166.2, 162.4, 159.7, 136.8, 134.1, 133.0, 132.0, 129.9, 128.9, 128.5, 128.1, 124.1, 123.9, 123.3, 114.9, 113.9, 113.7, 94.0, 85.7, 76.4, 55.3, 55.2.
**HRMS** (ESI, m/z) calcd for $C_{24}H_{21}NO_4$ $[M + H]^+$: 388.1544, found: 388.1543.



**1c**

White solid. $R_f$ = 0.4 (Petroleum ether/EtOAc, 2:1).
**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.67 – 7.55 (m, 5H), 7.54 – 7.50 (m, 2H), 7.40 – 7.36 (m, 2H), 7.34 (dd, J = 4.8, 2.4 Hz, 3H), 6.85 (d, J = 8.3 Hz, 2H), 5.32 (s, 2H), 3.82 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 165.9, 162.5, 137.1, 132.3, 131.6, 130.0, 128.9, 128.61, 128.57, 128.5, 128.3, 124.0, 123.6, 122.8, 113.8, 94.0, 86.9, 76.4, 55.4.
**HRMS** (ESI, m/z) calcd for $C_{23}H_{19}NO_3$ $[M + H]^+$: 358.1438, found: 358.1437.



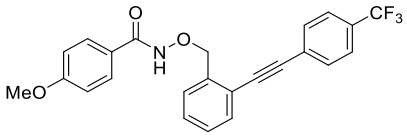

**1d**

White solid. $R_f$ = 0.4 (Petroleum ether/EtOAc, 2:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 8.67 (s, 1H), 7.62 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 6.9 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.38 (dd, J = 6.7, 3.3 Hz, 2H), 7.30 (s, 2H), 6.84 (d, J = 8.4 Hz, 2H), 5.28 (s, 2H), 3.82 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 166.2, 162.5, 137.1, 134.5, 132.8, 132.3, 130.1, 128.9, 128.8, 128.6, 124.0, 123.4, 121.3, 113.8, 92.8, 87.8, 76.3, 55.3.

**HRMS** (ESI, m/z) calcd for $C_{23}H_{18}ClNO_3$ $[M + H]^+$: 392.1048, found: 392.1041.




**1e**

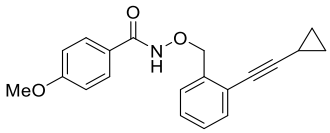
White solid. $R_f$ = 0.5 (Petroleum ether/EtOAc, 2:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 8.45 (s, 1H), 7.63 (s, 2H), 7.62 – 7.59 (m, 5H), 7.57 (s, 1H), 7.47 – 7.38 (m, 2H), 6.86 (d, J = 8.4 Hz, 2H), 5.32 (s, 2H), 3.83 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 162.6, 137.3, 132.5, 131.9, 130.3, 129.2, 128.9, 128.8, 126.6, 125.2 (q, J = 3.6 Hz), 123.8, 123.1, 113.9, 92.4, 89.2, 76.3, 55.4.

**$^{19}$F NMR** (377 MHz, $CDCl_3$) $\delta$ -62.8.

**HRMS** (ESI, m/z) calcd for $C_{24}H_{18}F_3NO_3$ $[M + H]^+$: 426.1312, found: 426.1312.



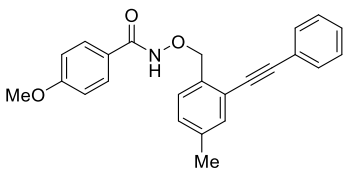

**1f**

White solid. $R_f$ = 0.5 (Petroleum ether/EtOAc, 2:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 8.48 (s, 1H), 7.68 (d, J = 8.3 Hz, 2H), 7.52 – 7.40 (m, 2H), 7.34 – 7.28 (m, 2H), 6.91 (d, J = 8.3 Hz, 2H), 5.19 (s, 2H), 3.85 (s, 3H), 1.46 – 1.38 (m, 1H), 0.87 – 0.81 (m, 2H), 0.80 – 0.74 (m, 2H).

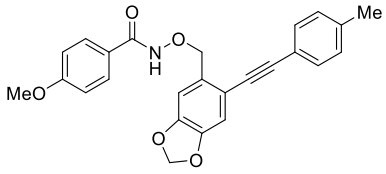
**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 162.5, 137.0, 132.3, 129.8, 128.9, 128.5, 127.7, 124.4, 113.8, 98.4, 76.3, 73.2, 55.4, 8.8, 0.2.

**HRMS** (ESI, m/z) calcd for $C_{20}H_{19}NO_3$ $[M + H]^+$: 322.1438, found: 322.1438.



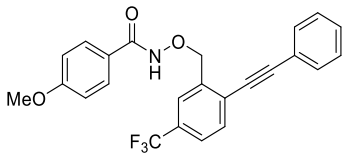

**1g**

White solid. $R_f$ = 0.5 (Petroleum ether/EtOAc, 2:1).
**$^1$H NMR** (600 MHz, $CDCl_3$) $\delta$ 8.44 (s, 1H), 7.62 (d, J = 8.8 Hz, 2H), 7.51 (dd, J = 6.8, 3.0 Hz, 2H), 7.46 – 7.42 (m, 2H), 7.35 – 7.32 (m, 3H), 7.20 (d, J = 7.8 Hz, 1H), 6.85 (d, J = 8.7 Hz, 2H), 5.28 (s, 2H), 3.83 (s, 3H), 2.39 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 162.5, 138.7, 134.0, 132.9, 131.6, 130.3, 129.5, 128.9, 128.4, 128.3, 124.2, 123.7, 122.9, 113.8, 93.5, 87.1, 76.3, 55.4, 21.0.
**HRMS** (ESI, m/z) calcd for $C_{24}H_{21}NO_3$ $[M + H]^+$: 372.1594, found: 372.1596.



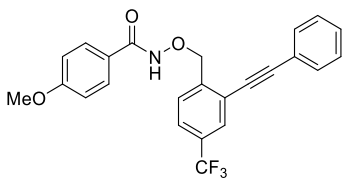
**1h**

White solid. $R_f$ = 0.4 (Petroleum ether/EtOAc, 2:1).
**$^1$H NMR** (600 MHz, $CDCl_3$) $\delta$ 8.65 (d, J = 43.6 Hz, 1H), 7.66 – 7.62 (m, 2H), 7.37 (d, J = 7.74 Hz, 2H), 7.12 (d, J = 7.8 Hz, 2H), 7.04 – 7.03 (m, 1H), 6.99 (dd, J = 3.8, 1.7 Hz, 1H), 6.86 – 6.82 (m, 2H), 6.01 (dd, J = 4.2, 1.9 Hz, 2H), 5.22 – 5.19 (m, 2H), 3.83 – 3.80 (m, 3H), 2.37 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 166.2, 162.4, 148.0, 147.7, 138.4, 131.8, 131.3, 129.1, 128.9, 124.1, 119.8, 117.5, 113.8, 111.5, 110.2, 101.6, 92.7, 86.3, 76.3, 55.3, 21.5.
**HRMS** (ESI, m/z) calcd for $C_{25}H_{21}NO_5$ $[M + H]^+$: 416.1493, found: 416.1490.



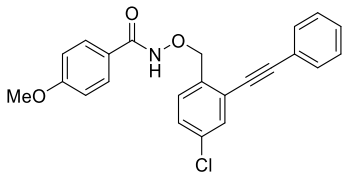
**1i**

White solid. $R_f$ = 0.4 (Petroleum ether/EtOAc, 2:1).
**$^1$H NMR** (600 MHz, $CDCl_3$) $\delta$ 8.75 (d, J = 30.2 Hz, 1H), 7.86 (s, 1H), 7.70 – 7.63 (m, 3H), 7.61 (d, J = 8.2 Hz, 1H), 7.54 (d, J = 7.1 Hz, 2H), 7.39 – 7.33 (m, 3H), 6.86 (dd, J = 8.8, 2.3 Hz, 2H), 5.35 (s, 2H), 3.82 (d, J = 2.0 Hz, 3H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 166.7, 162.7, 138.1, 132.6, 131.8, 130.2 (q, J = 32.8 Hz), 129.1, 129.0, 128.5, 127.0, 126.38, 126.35, 126.31, 126.27, 125.2 (q, J = 4.4 Hz), 123.8, 122.4, 122.2, 113.9, 96.5, 85.6, 75.8, 55.4.
**$^{19}$F NMR** (377 MHz, $CDCl_3$) $\delta$ -62.7.
**HRMS** (ESI, m/z) calcd for $C_{24}H_{18}F_3NO_3$ $[M + H]^+$: 426.1312, found: 426.1309.



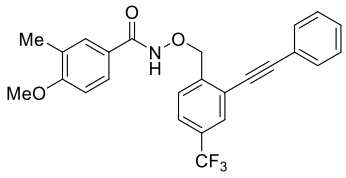
**1j**

White solid. $R_f$ = 0.4 (Petroleum ether/EtOAc, 2:1).
**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 8.90 (s, 1H), 7.82 (s, 1H), 7.72 (d, J = 8.1 Hz, 1H), 7.66 (d, J = 8.5 Hz, 2H), 7.59 (d, J = 8.2 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.36 (d, J = 6.5 Hz, 3H), 6.85 (d, J = 8.4 Hz, 2H), 5.33 (s, 2H), 3.81 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 166.6, 162.7, 140.9, 131.7, 129.73, 129.70, 129.0, 128.4, 125.0 (q, J = 5.6 Hz), 123.7, 122.7, 122.2, 113.9, 95.6, 85.4, 75.7, 55.3.
**$^{19}$F NMR** (377 MHz, $CDCl_3$) $\delta$ -62.9.
**HRMS** (ESI, m/z) calcd for $C_{24}H_{18}F_3NO_3$ $[M + H]^+$: 426.1312, found: 426.1312.



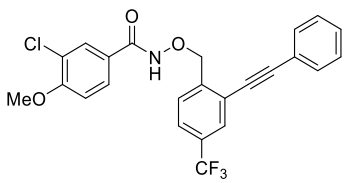
**1k**

White solid. $R_f$ = 0.4 (Petroleum ether/EtOAc, 2:1).
**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 8.48 (s, 1H), 7.64 (d, J = 8.3 Hz, 2H), 7.59 (d, J = 2.0 Hz, 1H), 7.53 (d, J = 7.3 Hz, 3H), 7.39 – 7.34 (m, 4H), 6.87 (d, J = 8.4 Hz, 2H), 5.28 (s, 2H), 3.84 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 162.6, 135.5, 134.4, 131.9, 131.7, 131.3, 128.9, 128.7, 128.4, 125.3, 123.8, 122.3, 113.9, 95.1, 85.6, 75.7, 55.4.
**HRMS** (ESI, m/z) calcd for $C_{23}H_{18}ClNO_3$ $[M + H]^+$: 392.1048, found: 392.1048.



**1l**

White solid. $R_f$ = 0.4 (Petroleum ether/EtOAc, 2:1).
**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 8.62 (s, 1H), 7.86 – 7.82 (m, 1H), 7.75 (d, J = 8.1 Hz, 1H), 7.62 (dd, J = 8.1, 1.9 Hz, 1H), 7.57 – 7.51 (m, 3H), 7.48 (d, J = 2.3 Hz, 1H), 7.40 – 7.34 (m, 3H), 6.78 (d, J = 8.5 Hz, 1H), 5.36 (s, 2H), 3.86 (s, 3H), 2.18 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 166.9, 160.9, 140.9, 131.7, 130.9, 130.6, 129.8, 129.5, 129.0, 128.4, 127.1, 126.5, 125.0 (q, J = 4.3 Hz), 124.0, 123.2, 122.2, 109.4, 95.5, 85.4, 75.8, 55.4, 16.1.
**$^{19}$F NMR** (377 MHz, $CDCl_3$) $\delta$ -62.9.
**HRMS** (ESI, m/z) calcd for $C_{25}H_{20}F_3NO_3$ $[M + H]^+$: 440.1468, found: 440.1475.



**1m**

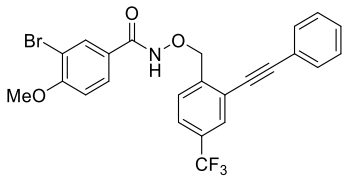
White solid. $R_f$ = 0.4 (Petroleum ether/EtOAc, 2:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 8.84 (s, 1H), 7.83 (s, 1H), 7.71 (d, J = 4.8 Hz, 2H), 7.63 – 7.56 (m, 2H), 7.53 (d, J = 7.1 Hz, 2H), 7.40 – 7.33 (m, 3H), 6.87 (d, J = 8.7 Hz, 1H), 5.34 (s, 2H), 3.91 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 157.9, 131.7, 130.0, 129.1 (q, J = 4.7 Hz), 128.5, 127.2, 125.1, 124.3, 124.1, 122.8, 122.1, 111.5, 95.6, 85.4, 75.8, 56.3.

**$^{19}$F NMR** (377 MHz, $CDCl_3$) $\delta$ -62.9.

**HRMS** (ESI, m/z) calcd for $C_{24}H_{17}ClF_3NO_3$ $[M + H]^+$: 460.0922, found: 460.0915.




**1n**

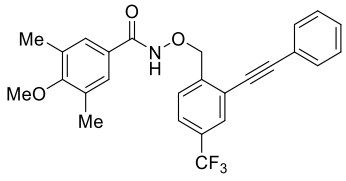
White solid. $R_f$ = 0.3 (Petroleum ether/EtOAc, 2:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 8.66 (s, 1H), 7.87 (d, J = 18.0 Hz, 2H), 7.73 (d, J = 8.1 Hz, 1H), 7.63 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 6.1 Hz, 2H), 7.41 – 7.34 (m, 3H), 6.85 (d, J = 9.0 Hz, 1H), 5.35 (s, 2H), 3.93 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 165.3, 158.9, 131.7, 129.9, 129.1, 129.0, 128.5, 128.0, 125.0 (q, J = 3.7 Hz), 122.1, 111.8, 111.3, 95.6, 85.4, 75.8, 56.4.

**$^{19}$F NMR** (377 MHz, $CDCl_3$) $\delta$ -62.9.

**HRMS** (ESI, m/z) calcd for $C_{24}H_{17}BrF_3NO_3$ $[M + H]^+$: 504.0417, found: 504.0419.




**1o**

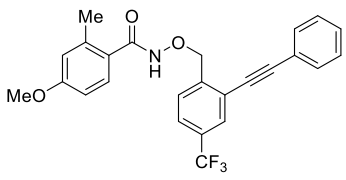
White solid. $R_f$ = 0.3 (Petroleum ether/EtOAc, 2:1).

**$^1$H NMR** (600 MHz, $CDCl_3$) $\delta$ 9.44 (s, 1H), 7.78 (s, 1H), 7.69 (d, J = 8.1 Hz, 1H), 7.56 – 7.49 (m, 3H), 7.37 – 7.30 (m, 5H), 5.32 (s, 2H), 3.67 (s, 3H), 2.19 (s, 6H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 166.6, 160.1, 140.8, 135.0, 131.6, 131.2, 130.7, 130.3, 128.9, 128.8 (q, J = 3.8 Hz), 128.3, 127.8, 126.8, 124.8 (q, J = 4.2 Hz), 124.3, 123.6, 122.2, 122.1, 95.5, 85.3, 75.5, 59.5, 15.9.

**$^{19}$F NMR** (377 MHz, $CDCl_3$) $\delta$ -62.8.

**HRMS** (ESI, m/z) calcd for $C_{26}H_{22}F_3NO_3$ $[M + H]^+$: 454.1625, found: 454.1625.




**1p**

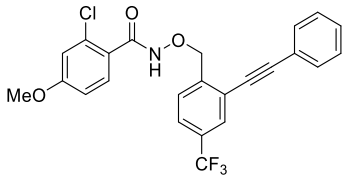
White solid. $R_f$ = 0.5 (Petroleum ether/EtOAc, 2:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 8.22 (s, 1H), 7.85 (s, 1H), 7.75 (d, J = 8.1 Hz, 1H), 7.63 (d, J = 8.1 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.38 (d, J = 5.5 Hz, 3H), 7.26 (s, 1H), 6.74 (s, 1H), 6.66 (d, J = 8.6 Hz, 1H), 5.37 (s, 2H), 3.80 (s, 3H), 2.44 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 161.2, 139.7, 131.7, 129.8, 129.1 (q, J = 3.6 Hz), 129.0, 128.9, 128.5, 125.0 (q, J = 3.3 Hz), 124.1, 122.2, 116.7, 110.8, 95.7, 85.3, 75.8, 55.3, 21.0.

**$^{19}$F NMR** (377 MHz, $CDCl_3$) $\delta$ -62.9.

**HRMS** (ESI, m/z) calcd for $C_{25}H_{20}F_3NO_3$ $[M + H]^+$: 440.1468, found: 440.1466.




**1q**

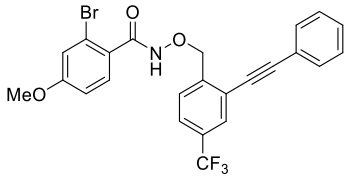
White solid. $R_f$ = 0.5 (Petroleum ether/EtOAc, 2:1).

**$^1$H NMR** (600 MHz, $CDCl_3$) $\delta$ 8.92 (s, 1H), 7.84 (s, 1H), 7.76 (s, 1H), 7.62 (d, J = 8.2 Hz, 2H), 7.59 – 7.55 (m, 2H), 7.41 – 7.36 (m, 3H), 6.88 (d, J = 2.5 Hz, 1H), 6.80 (dd, J = 8.7, 2.5 Hz, 1H), 5.39 (s, 2H), 3.81 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 161.9, 140.5, 132.1, 132.0, 131.7, 129.8, 129.0, 128.5, 125.0 (q, J = 3.6 Hz), 124.1, 122.2, 115.5, 113.0, 95.7, 85.3, 75.8, 55.7.

**$^{19}$F NMR** (377 MHz, $CDCl_3$) $\delta$ -62.9.

**HRMS** (ESI, m/z) calcd for $C_{24}H_{17}ClF_3NO_3$ $[M + H]^+$: 460.0922, found: 460.0912.




**1r**

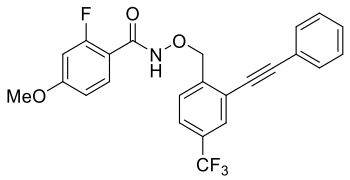
White solid. $R_f$ = 0.5 (Petroleum ether/EtOAc, 2:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 8.64 (s, 1H), 7.84 (s, 1H), 7.81 – 7.71 (m, 1H), 7.63 (d, J = 8.1 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.45 (d, J = 8.6 Hz, 1H), 7.39 (d, J = 3.7 Hz, 3H), 7.08 (d, J = 2.3 Hz, 1H), 6.83 (dd, J = 8.7, 2.4 Hz, 1H), 5.40 (s, 2H), 3.81 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 161.7, 140.5, 131.7, 131.3 (q, J = 5.9 Hz), 131.1, 130.8, 129.1, 129.0, 128.5, 126.4, 125.0 (q, J = 3.8 Hz), 124.1, 122.2, 120.6, 118.7, 113.4, 95.7, 85.3, 75.8, 55.7.

**$^{19}$F NMR** (377 MHz, $CDCl_3$) $\delta$ -62.9.

**HRMS** (ESI, m/z) calcd for $C_{24}H_{17}BrF_3NO_3$ $[M + H]^+$: 504.0417, found: 504.0409.




**1s**

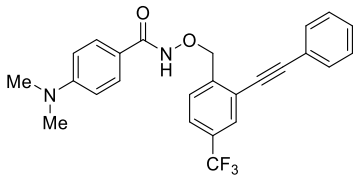
White solid. $R_f$ = 0.6 (Petroleum ether/EtOAc, 2:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 9.17 (d, J = 12.4 Hz, 1H), 8.02 (t, J = 8.5 Hz, 1H), 7.84 (s, 1H), 7.76 (d, J = 8.1 Hz, 1H), 7.63 (d, J = 8.3 Hz, 1H), 7.58 – 7.51 (m, 2H), 7.41 – 7.33 (m, 3H), 6.77 (d, J = 8.7 Hz, 1H), 6.59 (dd, J = 13.9, 2.9 Hz, 1H), 5.38 (s, 2H), 3.84 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 164.0 (d, J = 12.3 Hz), 162.5 (d, J = 15.4 Hz), 160.1, 140.6, 133.04, 132.99, 131.7, 130.9, 130.6, 129.7, 129.0 (q, J = 3.9 Hz), 128.9, 128.4, 125.0 (q, J = 3.6 Hz), 123.9, 122.2, 110.9 (d, J = 2.4 Hz), 101.5 (d, J = 28.6 Hz), 95.5, 85.3, 75.8, 55.8.

**$^{19}$F NMR** (377 MHz, $CDCl_3$) $\delta$ -62.9, -107.3.

**HRMS** (ESI, m/z) calcd for $C_{24}H_{17}F_4NO_3$ $[M + H]^+$: 444.1218, found: 444.1215.




**1t**

White solid. $R_f$ = 0.5 (Petroleum ether/EtOAc, 2:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 8.59 (s, 1H), 7.83 (s, 1H), 7.76 (d, J = 8.1 Hz, 1H), 7.64 – 7.58 (m, 3H), 7.57 – 7.51 (m, 2H), 7.37 (q, J = 3.5, 3.0 Hz, 3H), 6.61 (d, J = 8.2 Hz, 2H), 5.35 (s, 2H), 3.02 (s, 6H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 167.4, 152.9, 141.2, 131.7, 129.72, 129.68, 129.0 (q, J = 3.6 Hz), 128.9, 128.6, 128.4, 124.9 (q, J = 6.7, 2.3 Hz), 122.3, 117.9, 111.0, 95.5, 85.4, 75.8, 40.0.

**$^{19}$F NMR** (377 MHz, $CDCl_3$) $\delta$ -62.8.

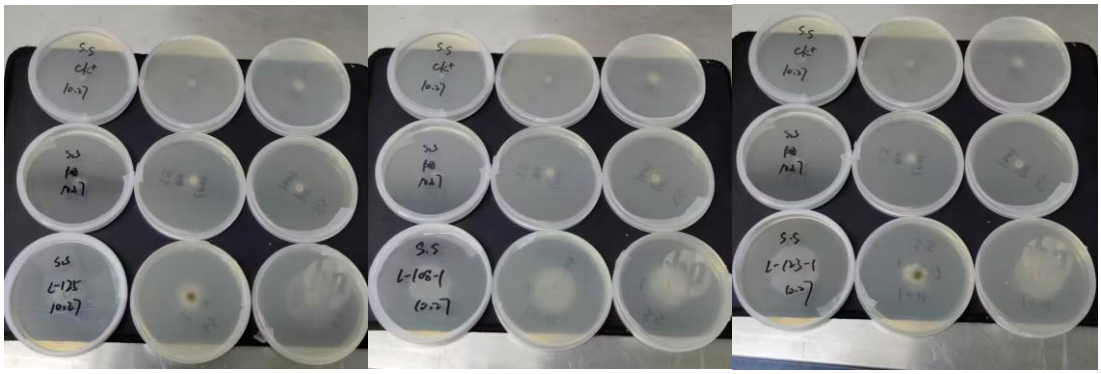
**HRMS** (ESI, m/z) calcd for $C_{25}H_{21}F_3N_2O_2$ $[M + H]^+$: 439.1628, found: 439.1619.

## 4. In Vitro Antifungal Activities.

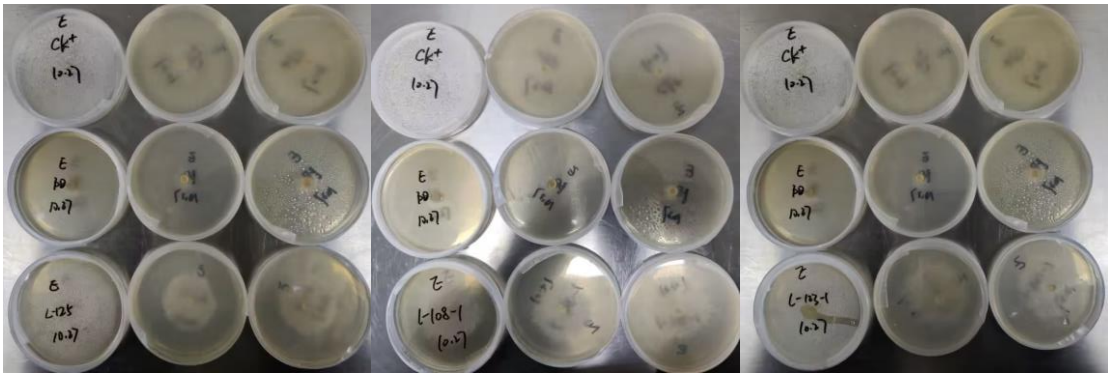
Each target compound was dissolved in DMSO to prepare the stock solution (10.0 g/L). The stock solution was added into the PDA medium, and the concentration of target compounds in the medium was 50.0 mg/L. Pure DMSO without the target compounds was utilized as the blank control, and boscalid was coassayed as the reference compound. Fresh dishes with a diameter of 5 mm were taken from the edge of the PDA-cultured fungi colonies and inoculated on the above three PDA media. Each treatment was tested for three replicates, and the antifungal effect was averaged. The relative inhibitory rate I (%) of all the tested compounds was calculated through the equation: I

(%) = [(C − T)/(C − 5)] × 100. In this equation, I is the inhibitory rate and C and T are the colony diameter of the blank control (mm) and treatment (mm), respectively.

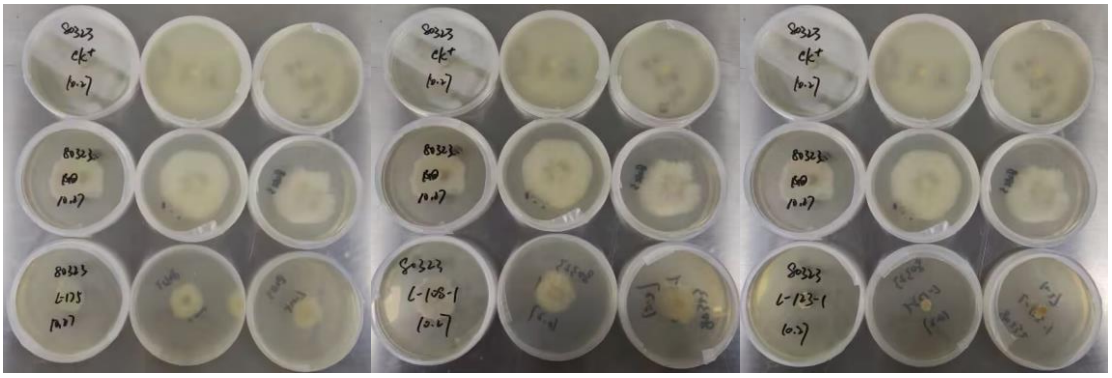
Mycelia growth of three crop pathogenic fungi and a forest pathogenic fungus after treating with the target compounds on PDA medium as illustrated in the figures (**Supplementary Figure 1**) below.



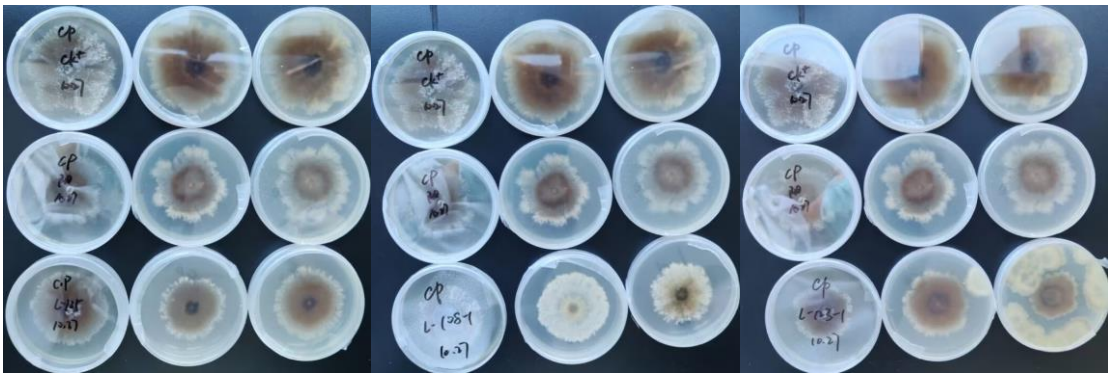
**Supplementary Figure 1-1** *S. sclerotiorum*



**Supplementary Figure 1-2** *T. cucumeris*



**Supplementary Figure 1-3** *C. chrysosperma*

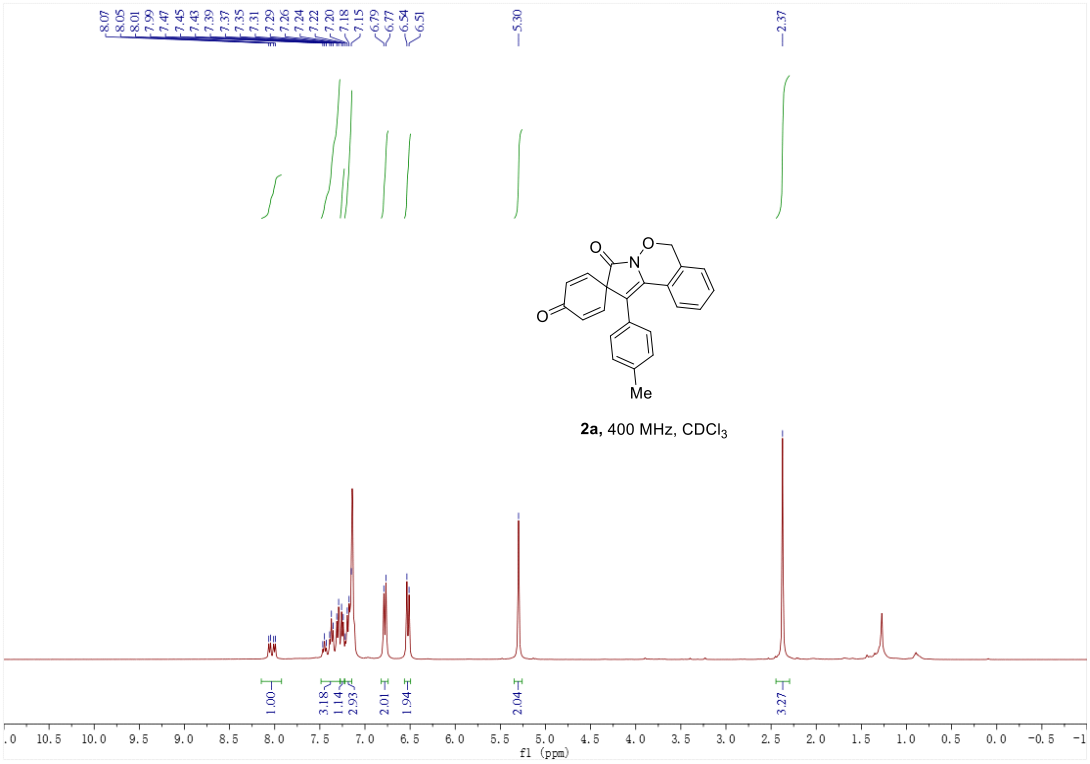


**Supplementary Figure 1-4** *C. paradoxa*

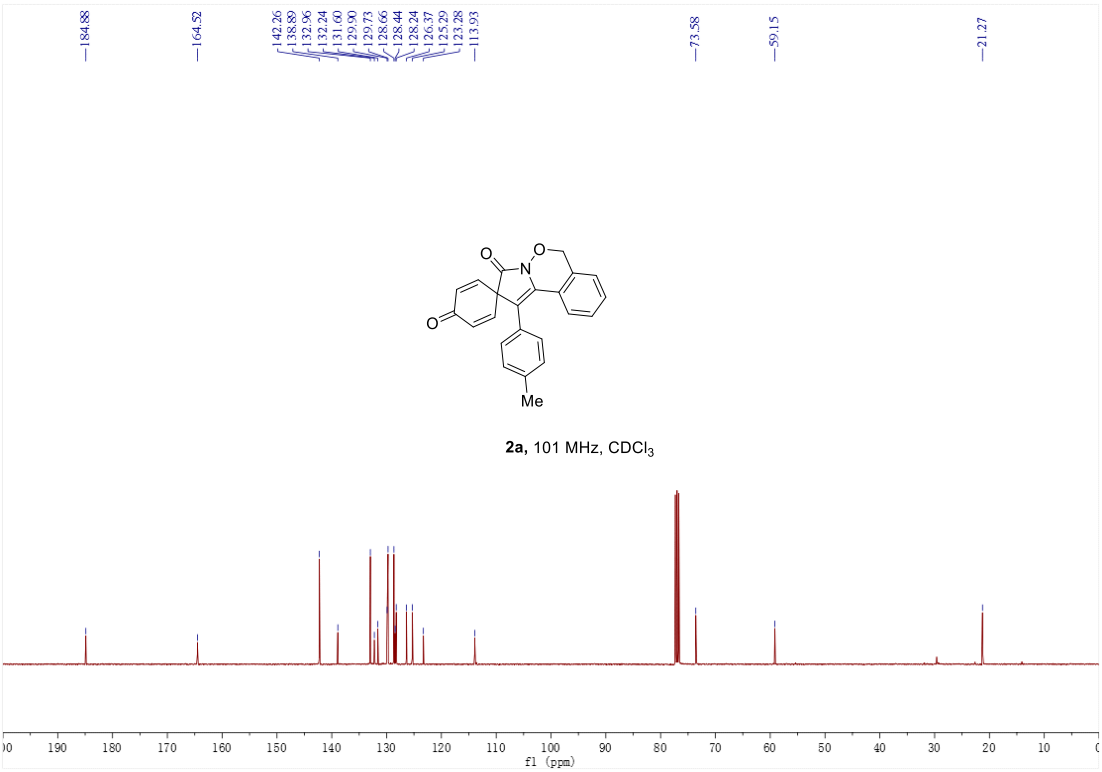
## 5. Reference


1. Song, L. *et al.* Intramolecular cascade annulation triggered by C–H activation via rhodium hydride intermediate. *Mol. Catal.* **463**, 30–36 (2019).

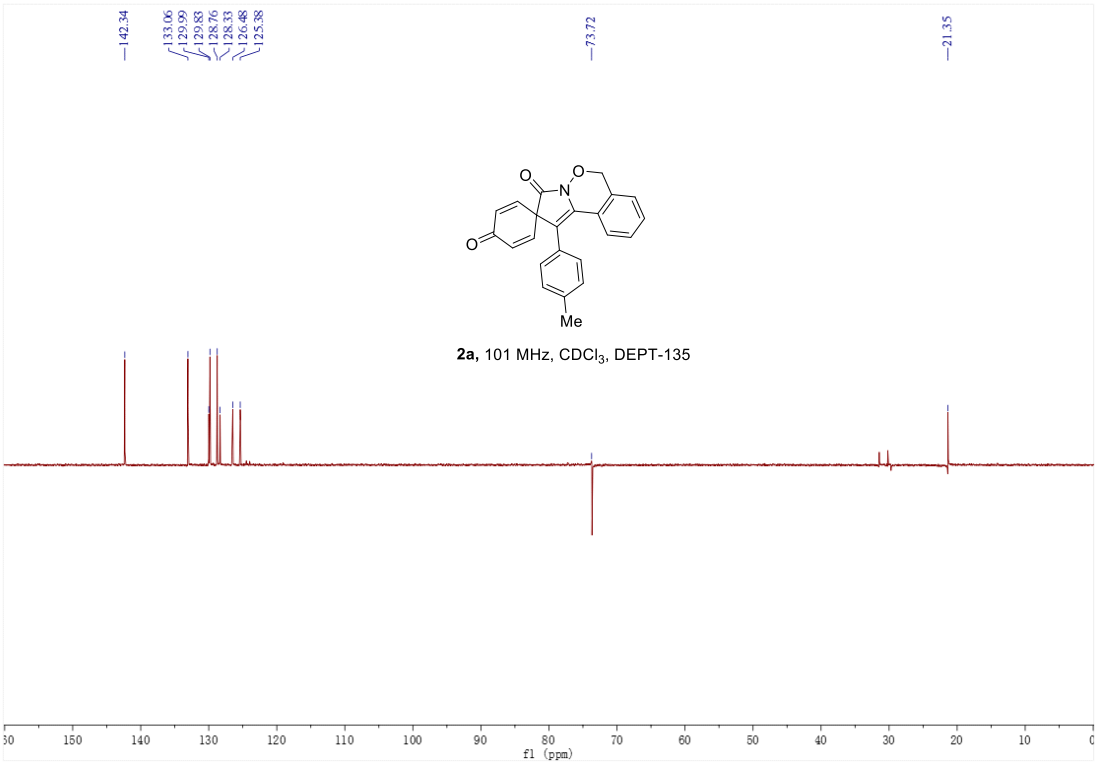
## 6. Spectra



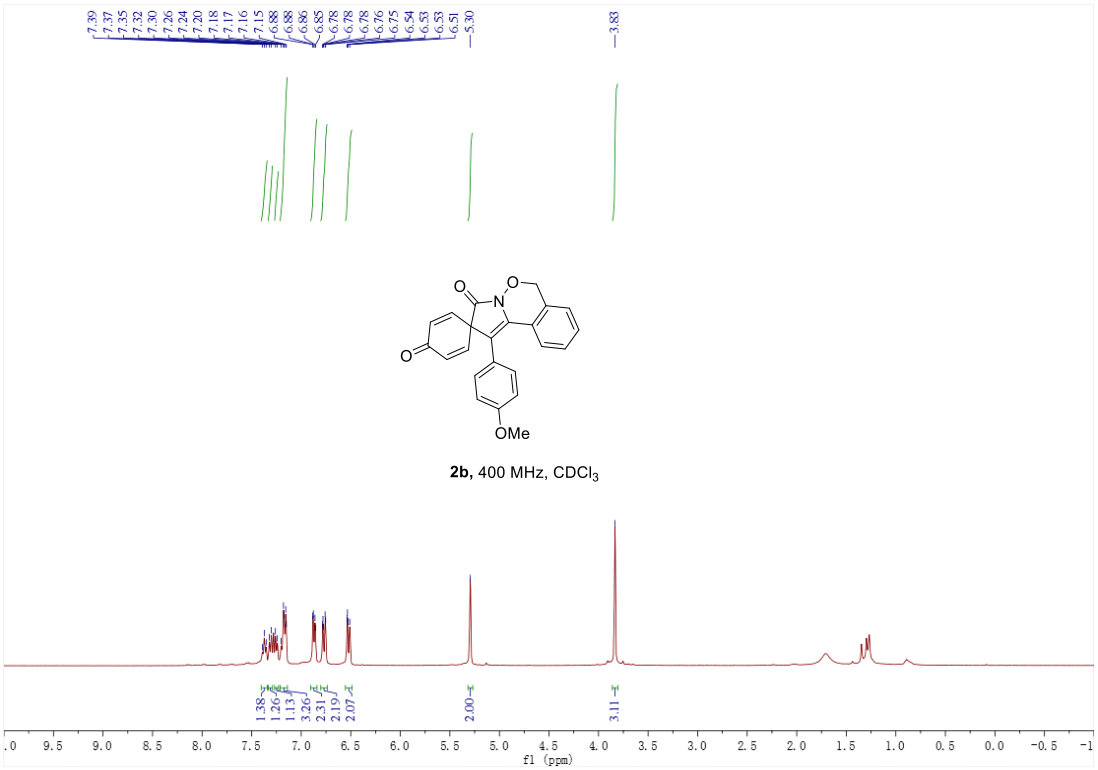

**2a**, 400 MHz, $CDCl_3$



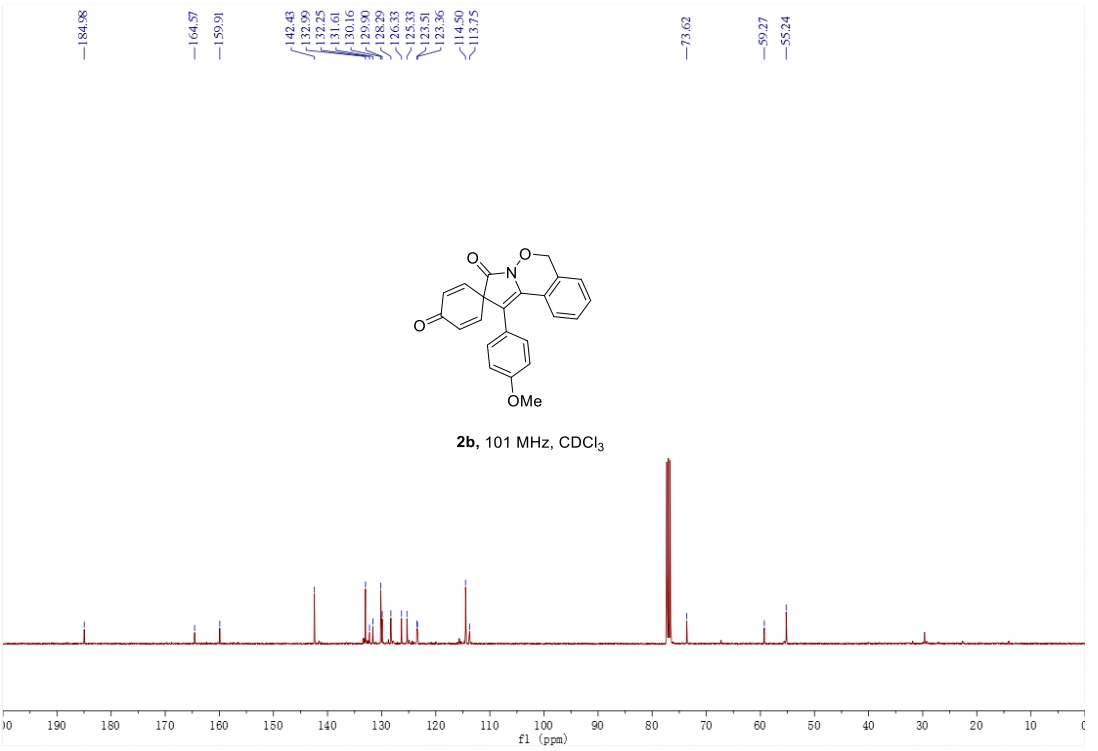

**2a**, 101 MHz, $CDCl_3$



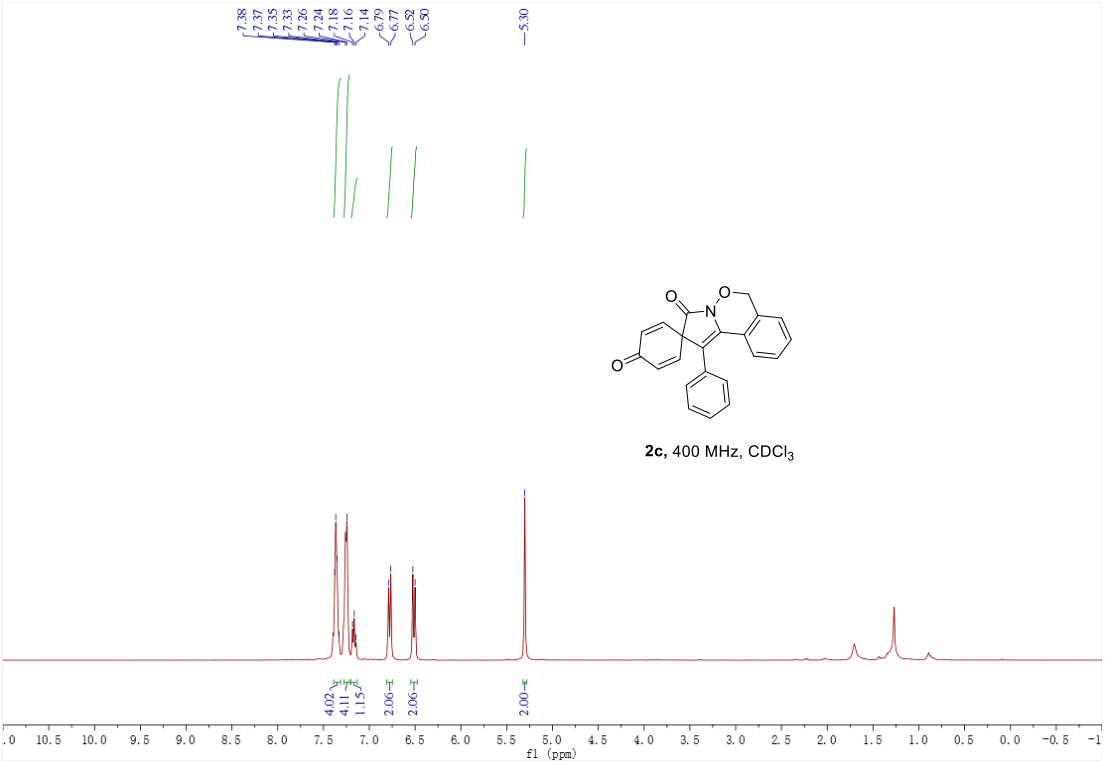

**2a,** 101 MHz, $CDCl_3$, DEPT-135



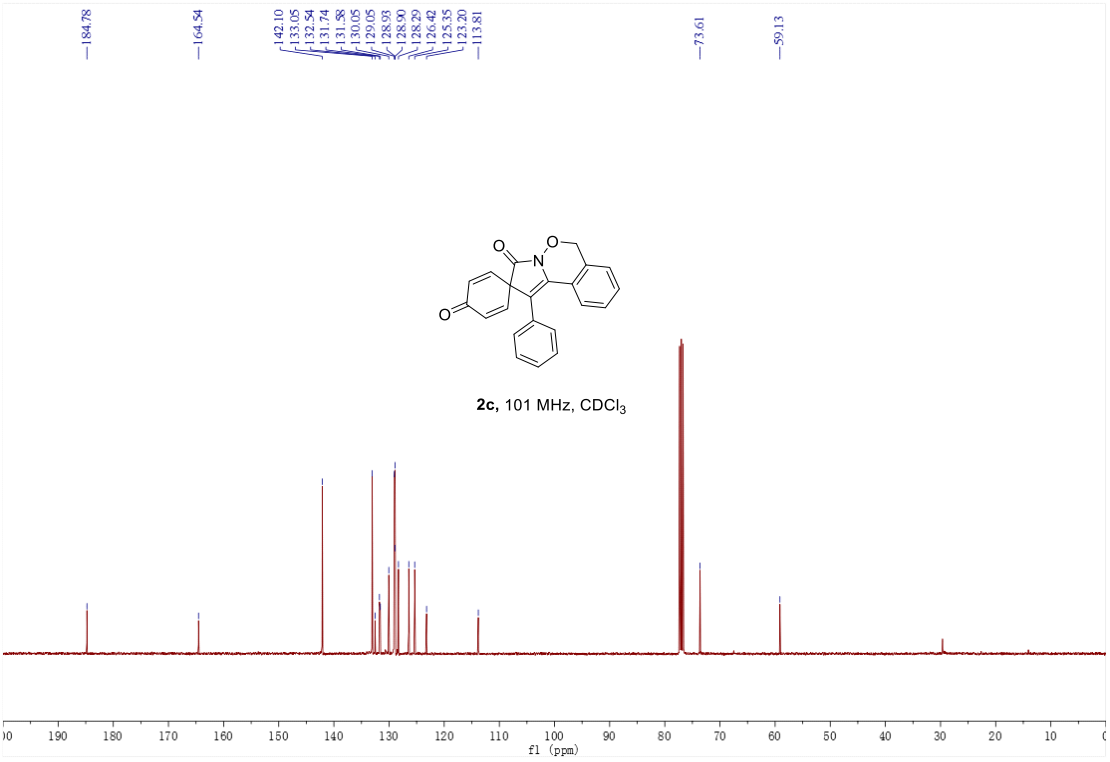

**2b,** 400 MHz, $CDCl_3$



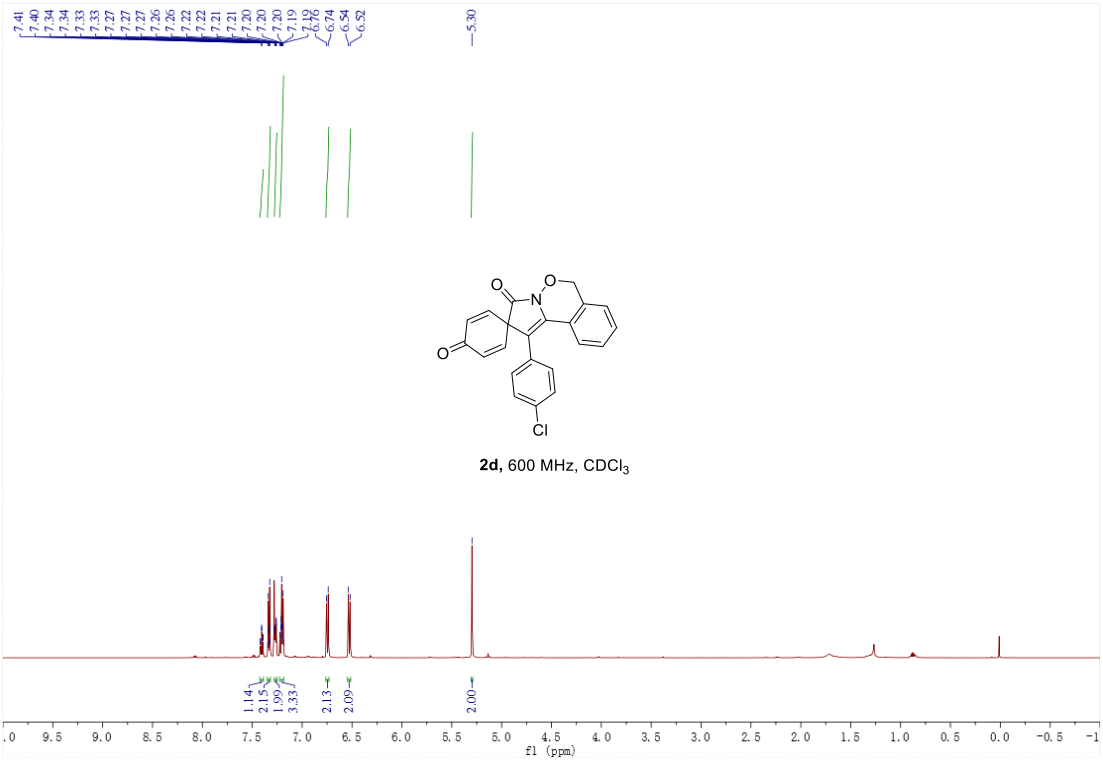

**2b,** 101 MHz, $CDCl_3$



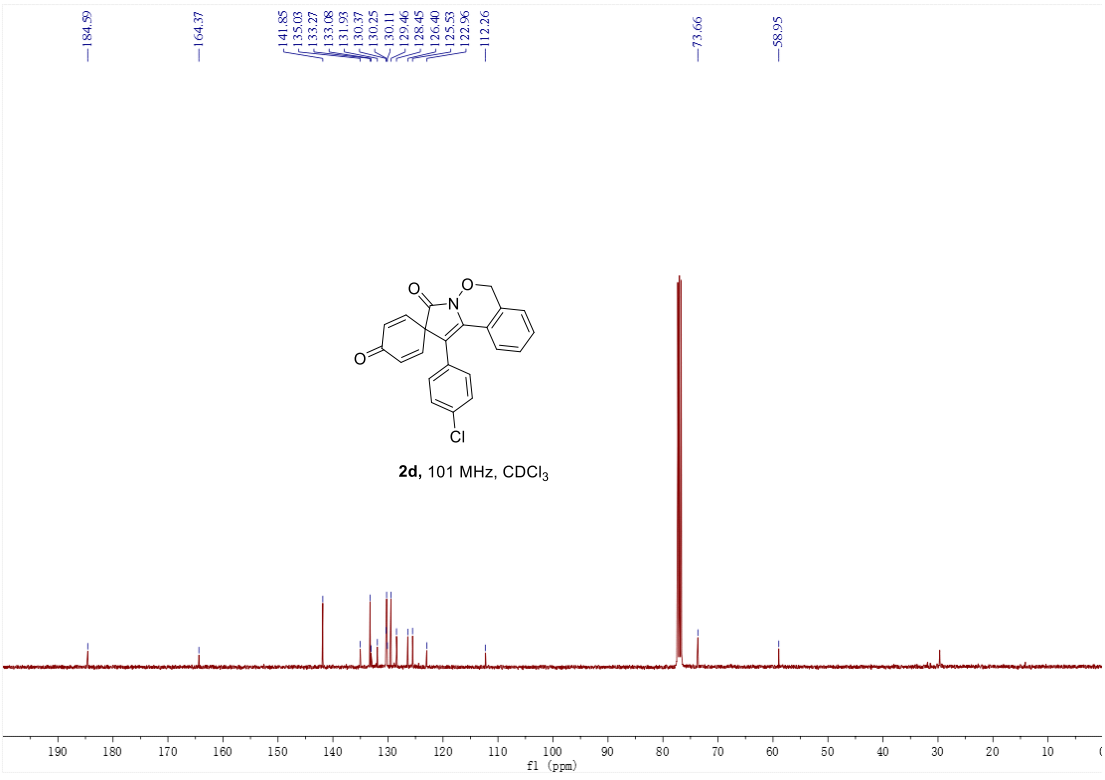

**2c,** 400 MHz, $CDCl_3$



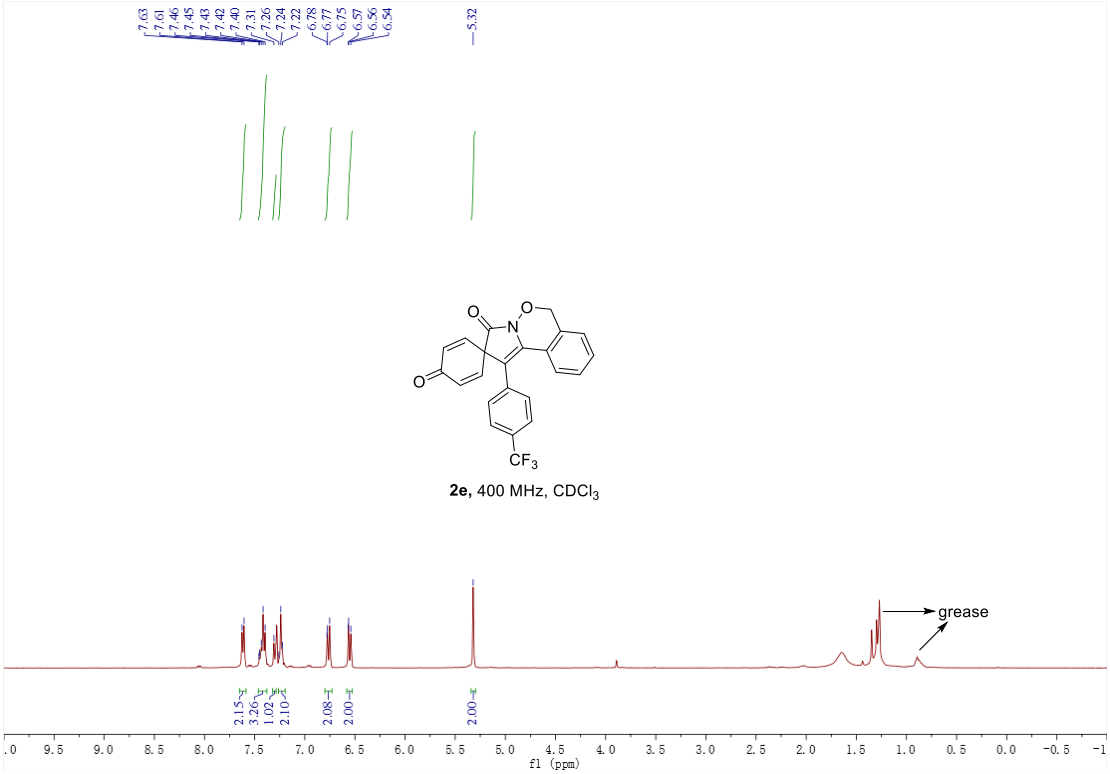

**2c,** 101 MHz, $CDCl_3$



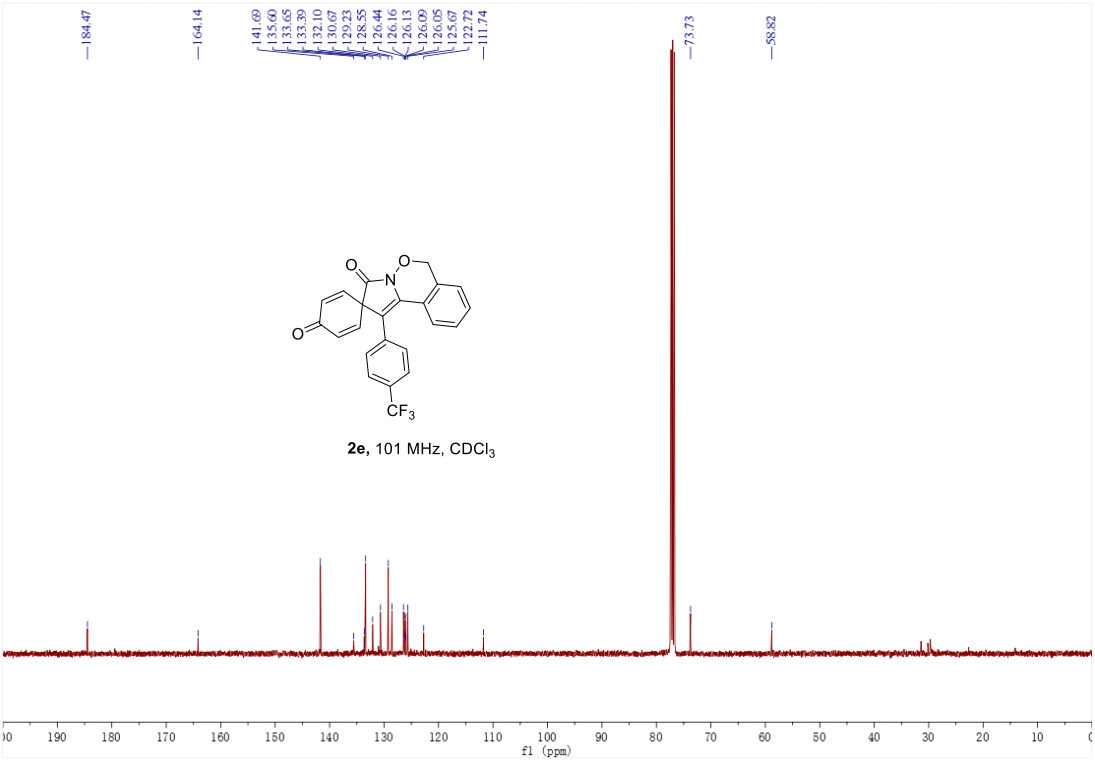

**2d,** 600 MHz, $CDCl_3$



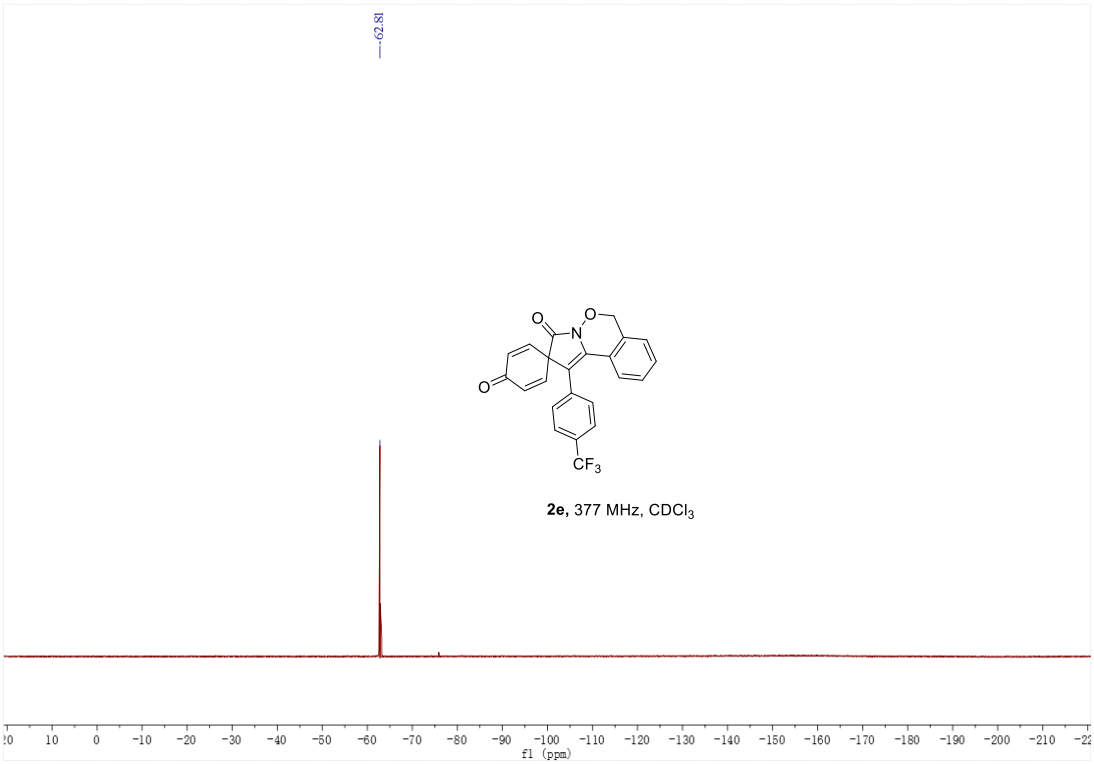

**2d,** 101 MHz, $CDCl_3$



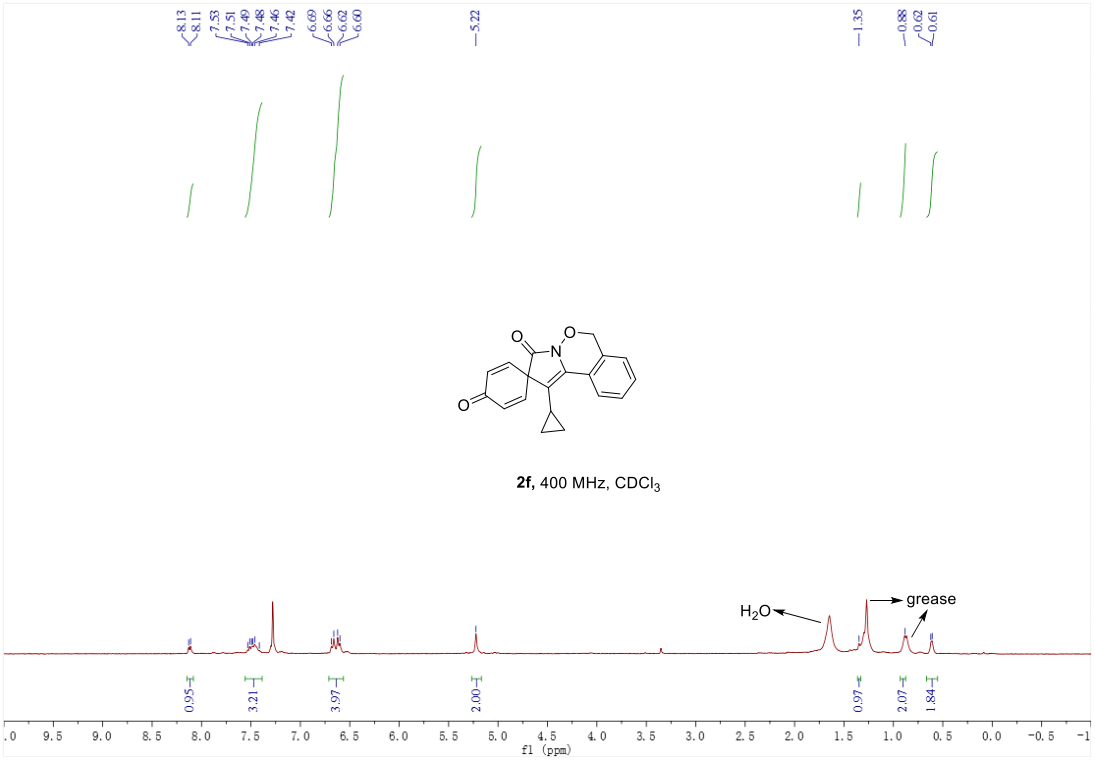

**2e,** 400 MHz, $CDCl_3$



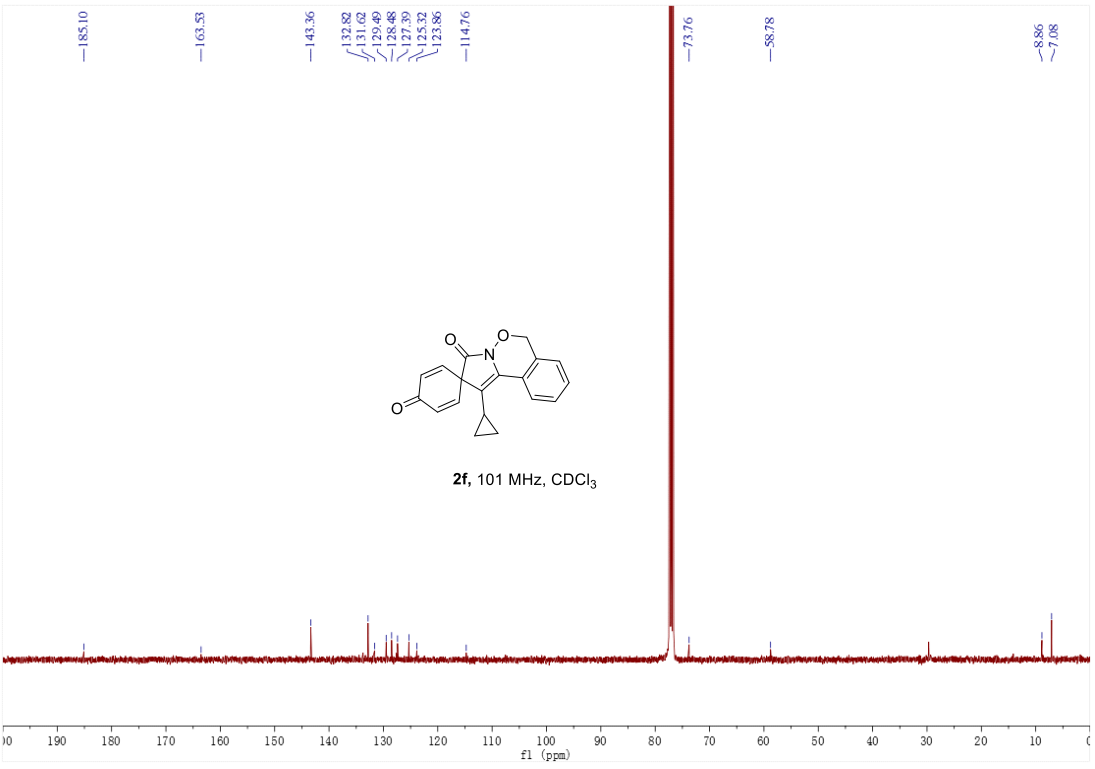

**2e,** 101 MHz, $CDCl_3$



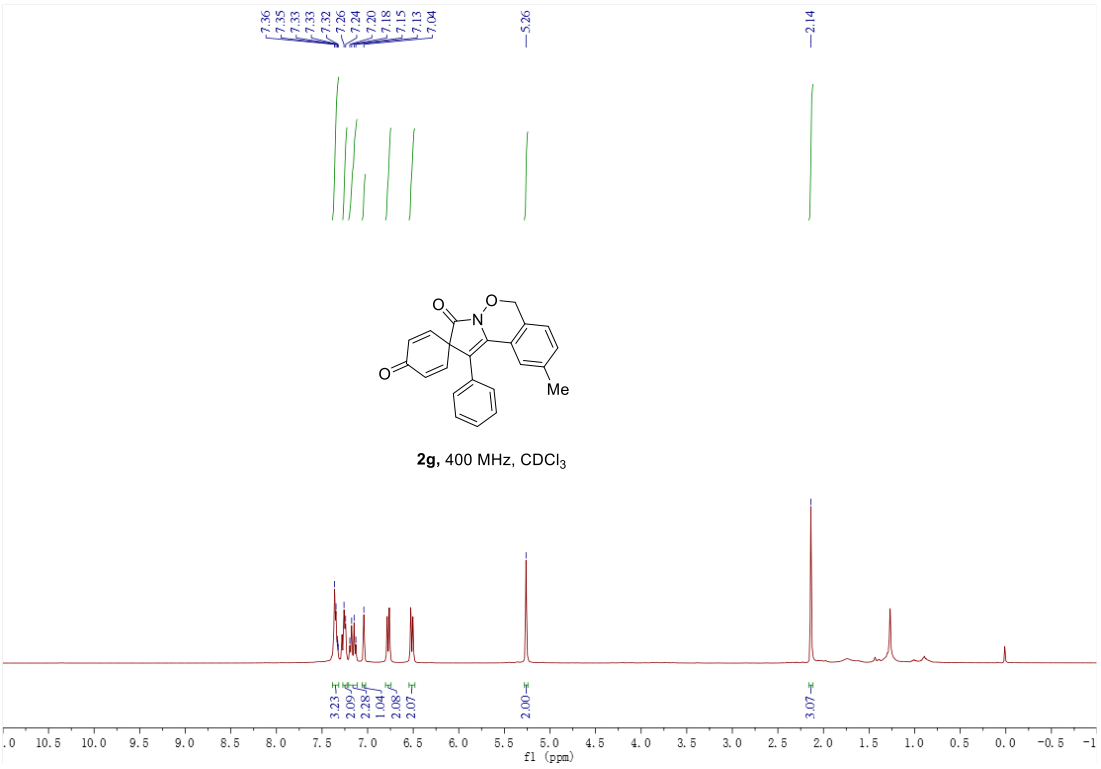

**2e,** 377 MHz, $CDCl_3$



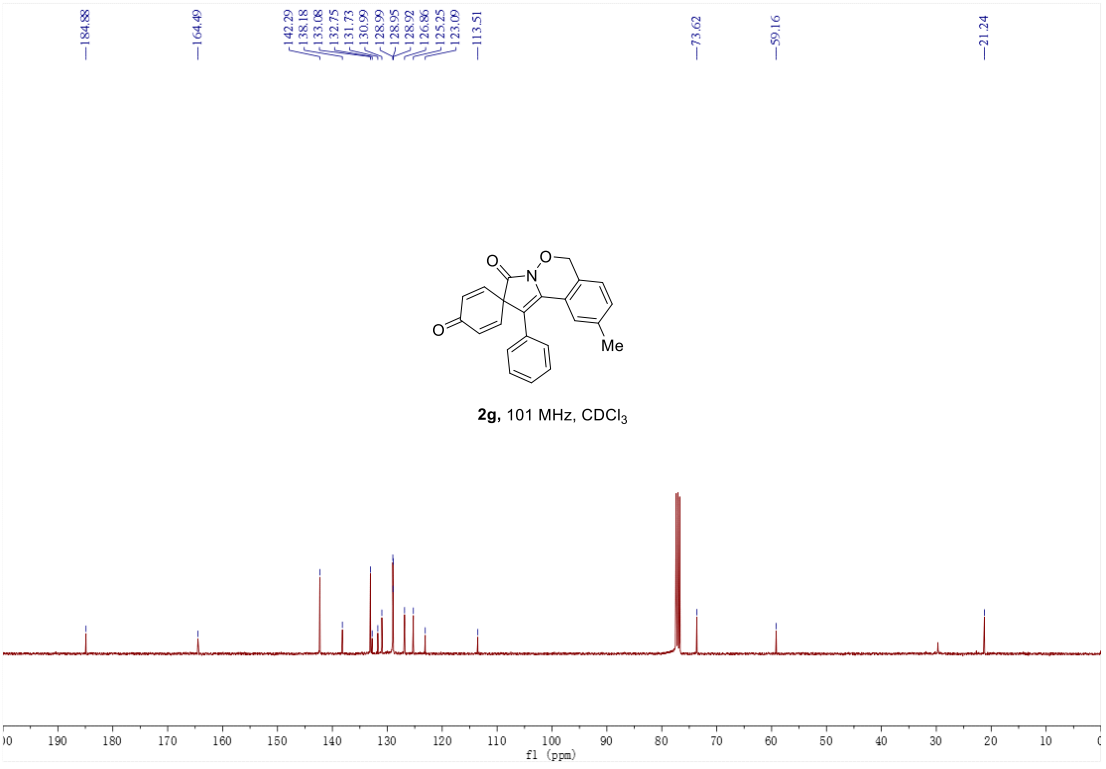

**2f,** 400 MHz, $CDCl_3$



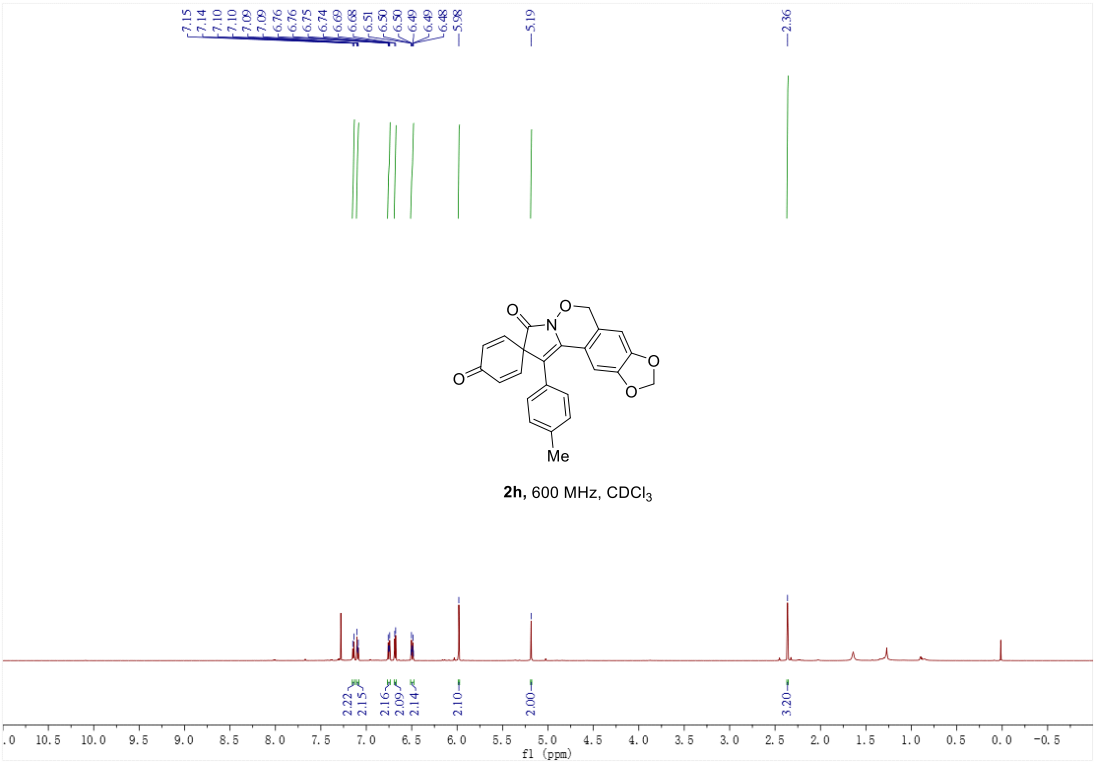

**2f,** 101 MHz, $CDCl_3$



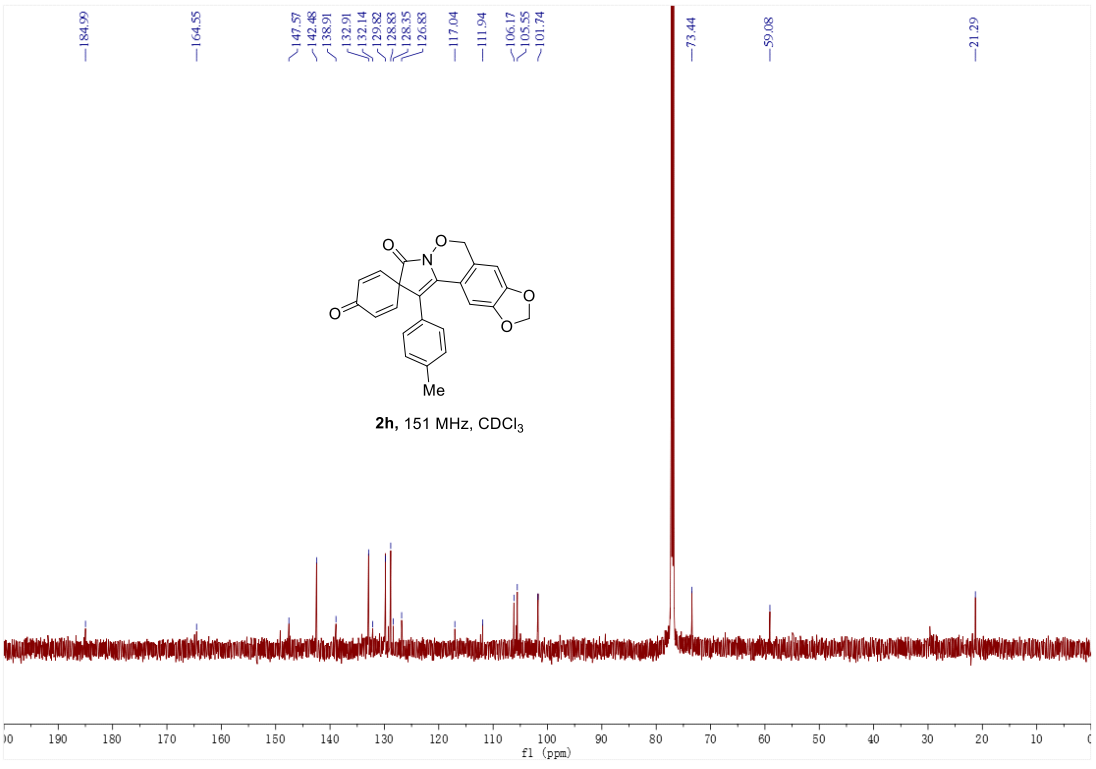

**2g,** 400 MHz, $CDCl_3$



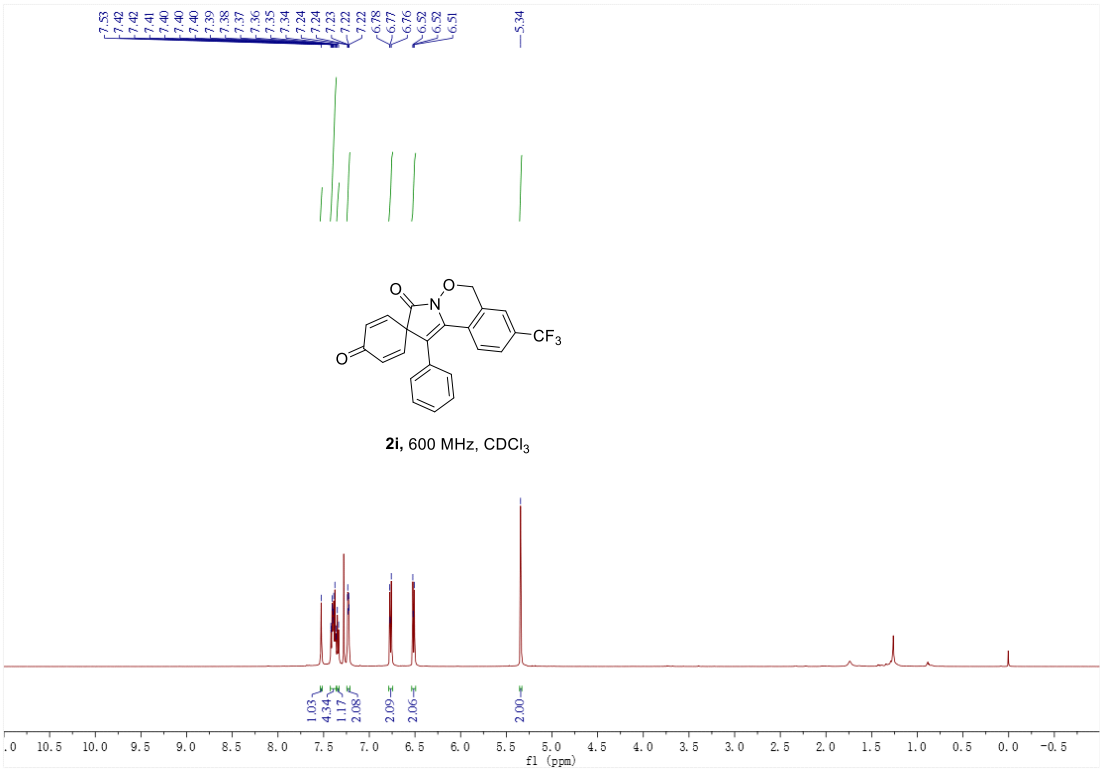

**2g,** 101 MHz, $CDCl_3$



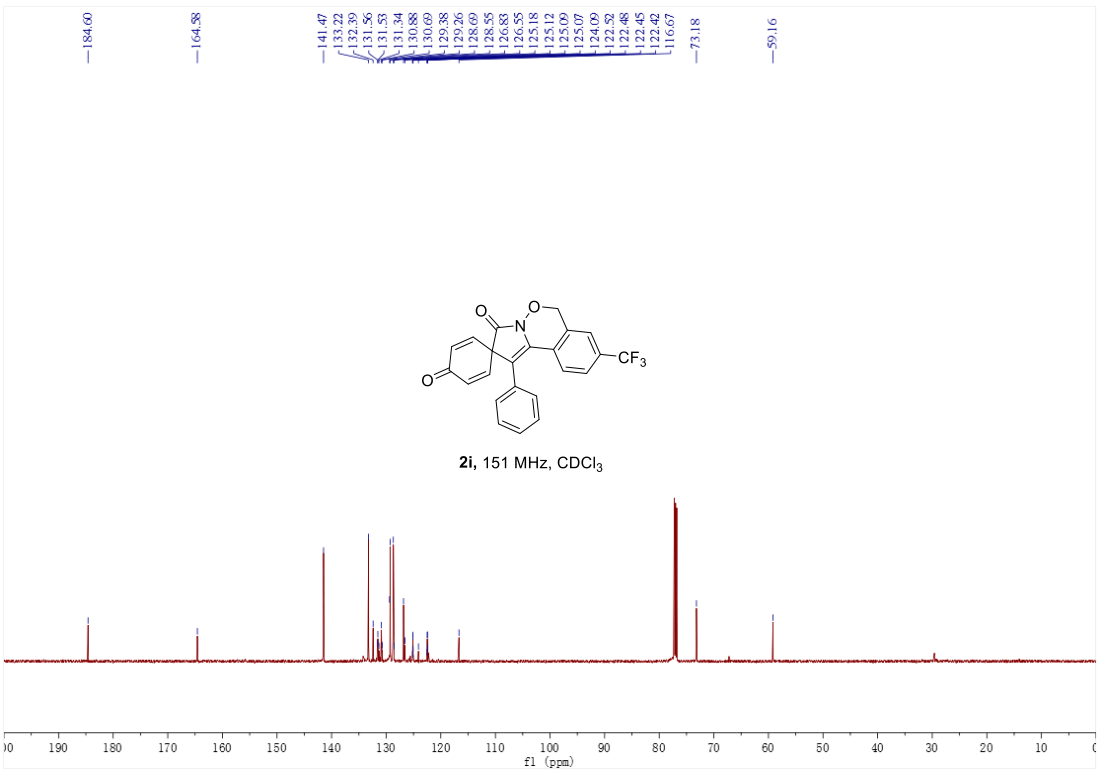

**2h,** 600 MHz, $CDCl_3$



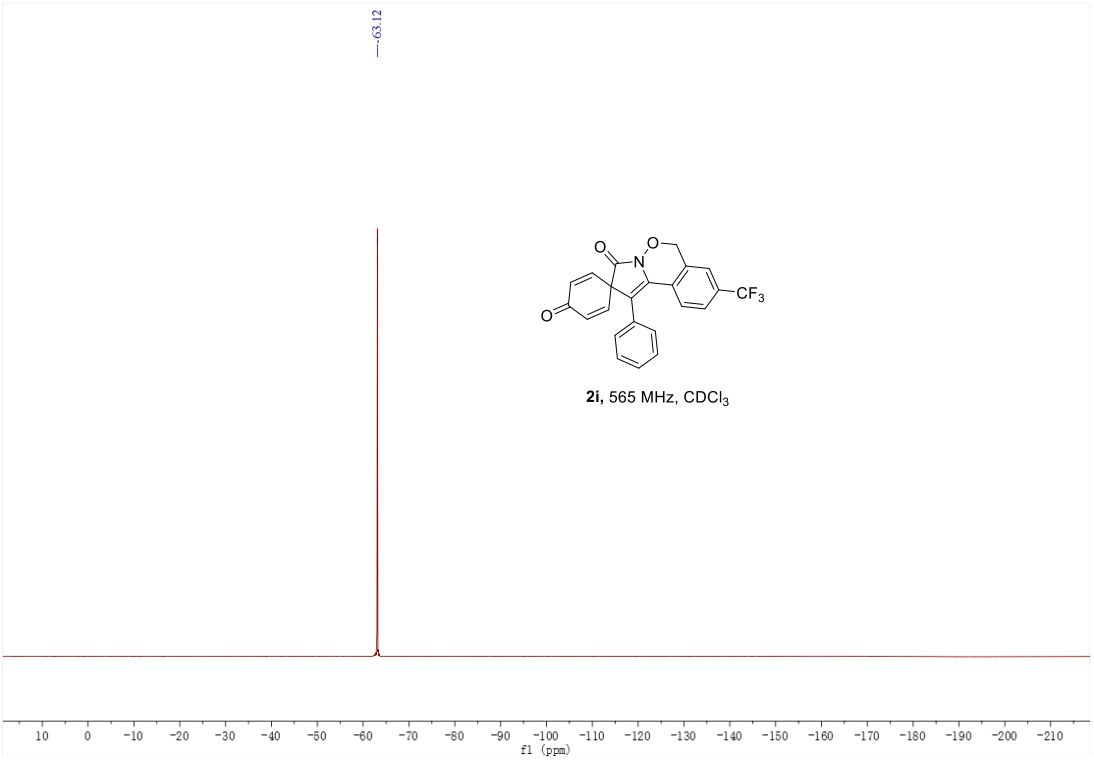

**2h,** 151 MHz, $CDCl_3$



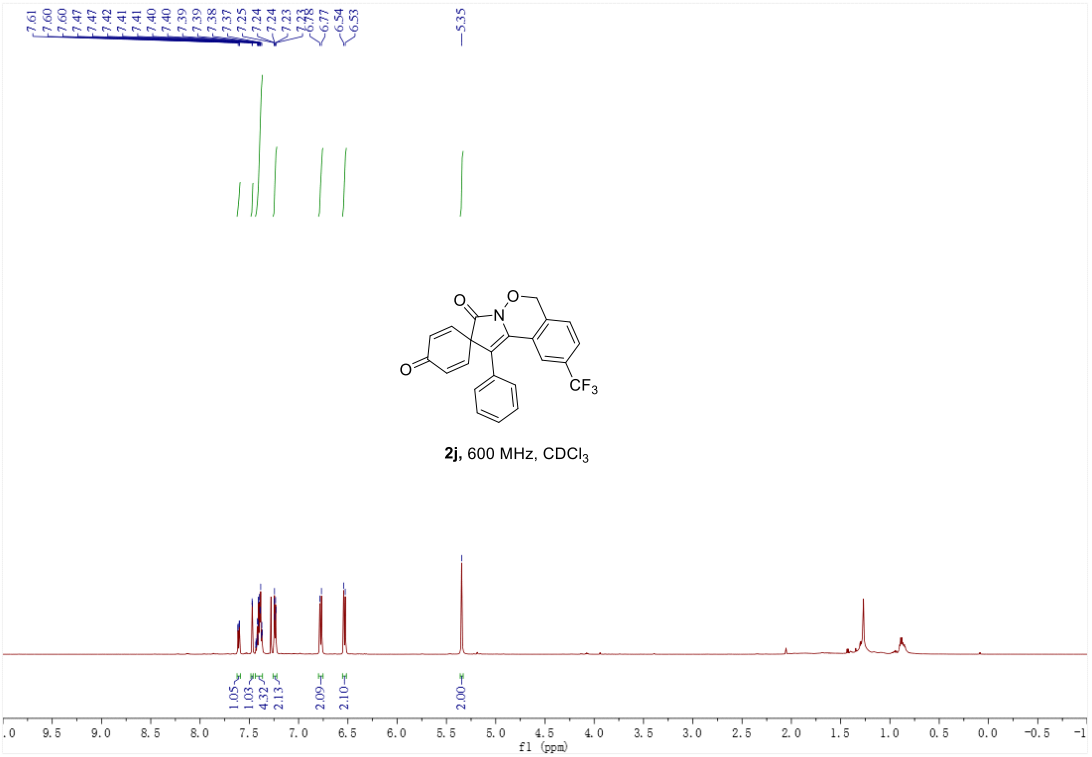

**2i,** 600 MHz, $CDCl_3$



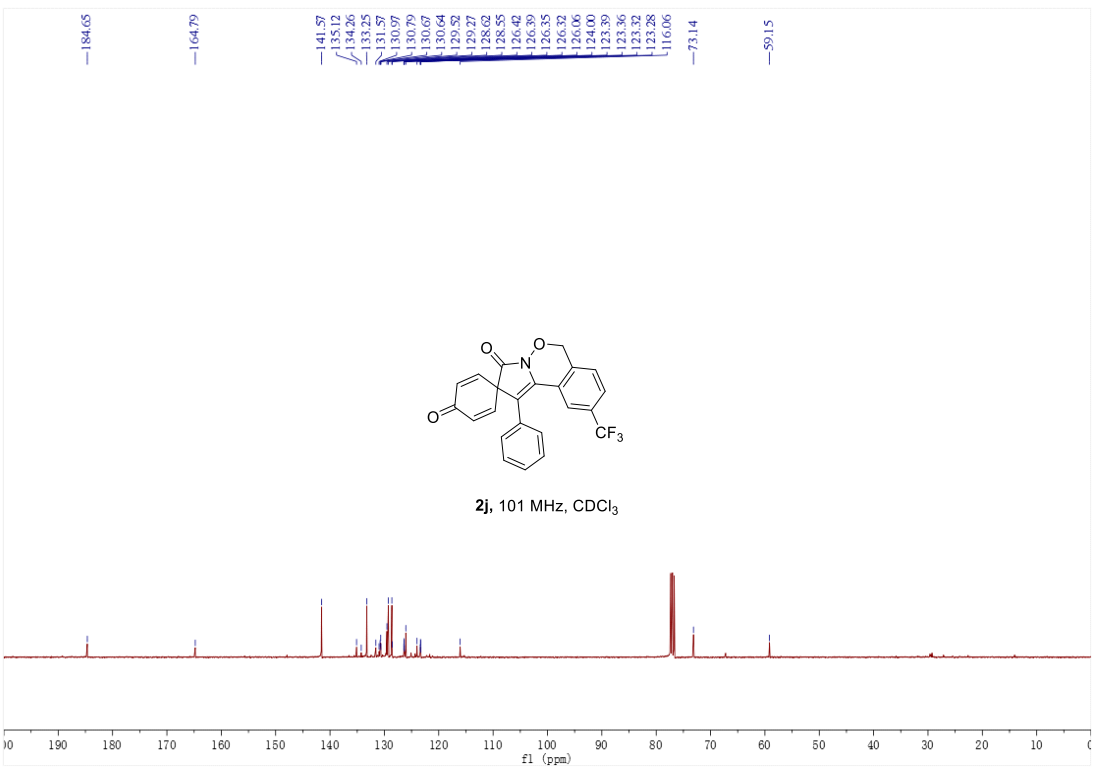

**2i,** 151 MHz, $CDCl_3$



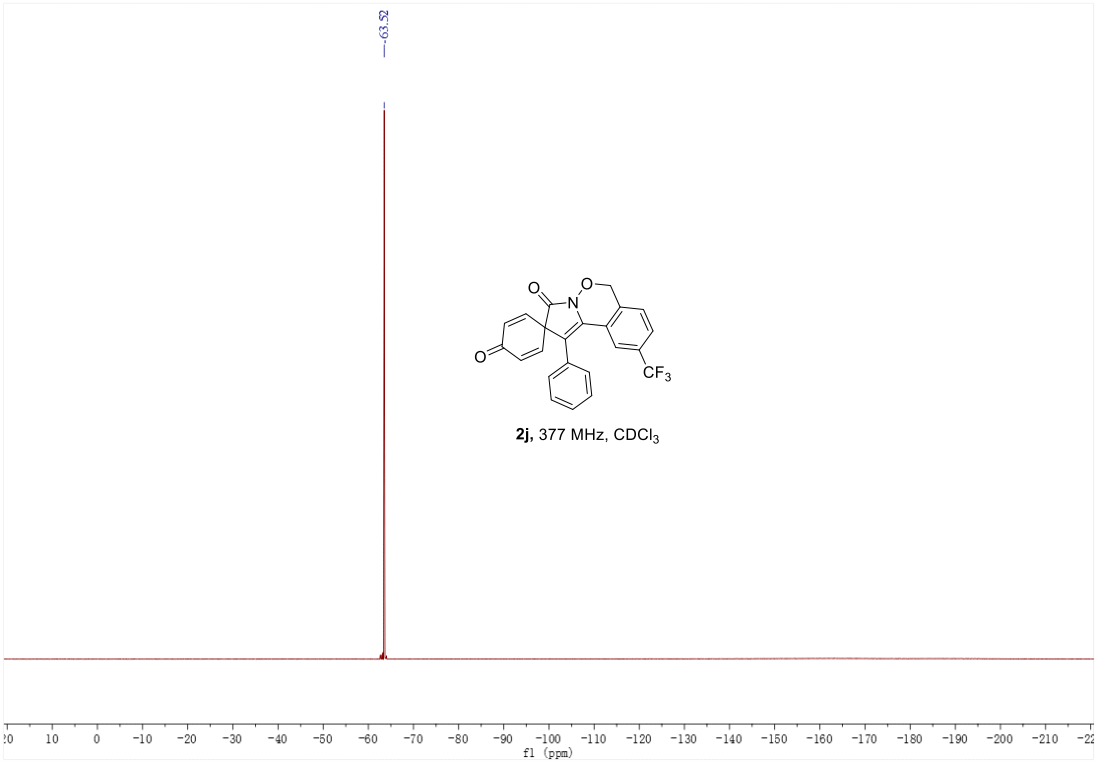

**2i,** 565 MHz, $CDCl_3$



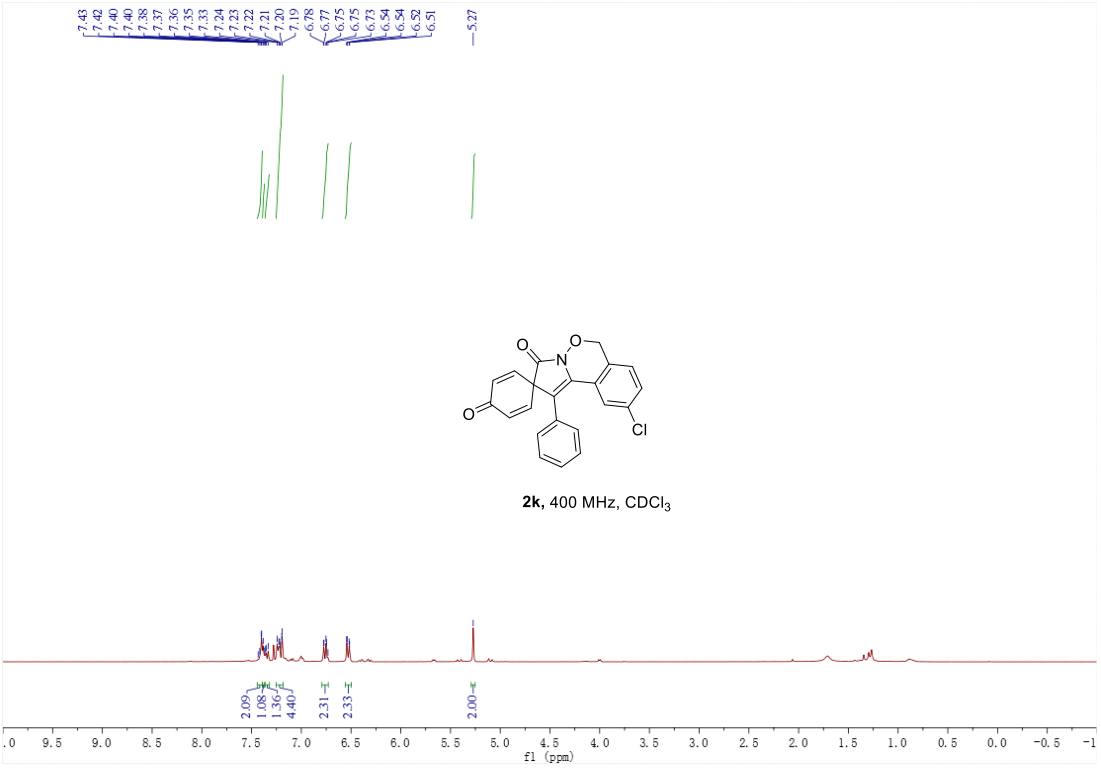

**2j,** 600 MHz, $CDCl_3$



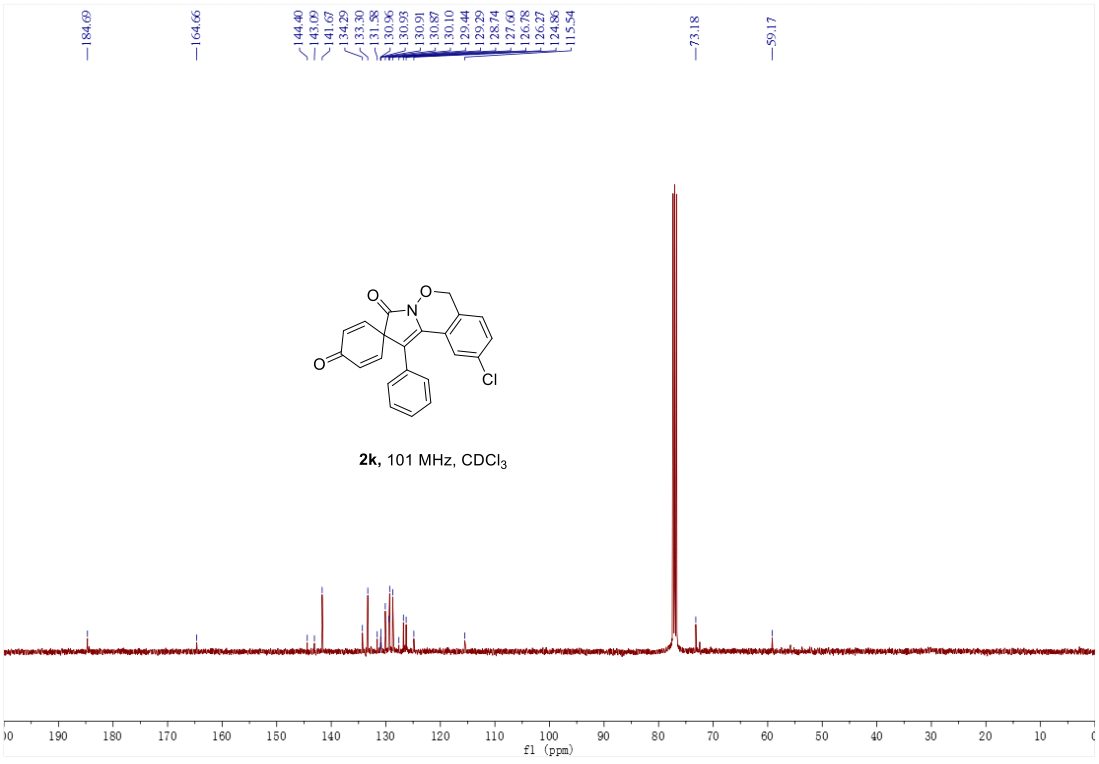

**2j,** 101 MHz, $CDCl_3$



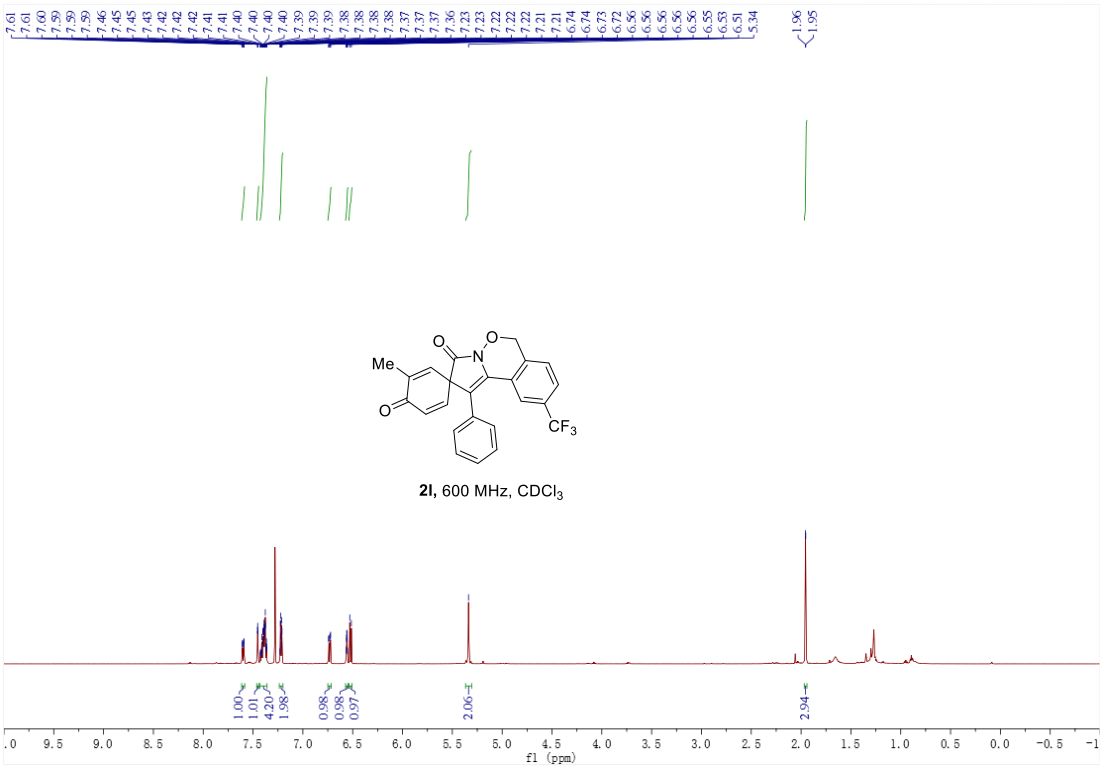

**2j,** 377 MHz, $CDCl_3$



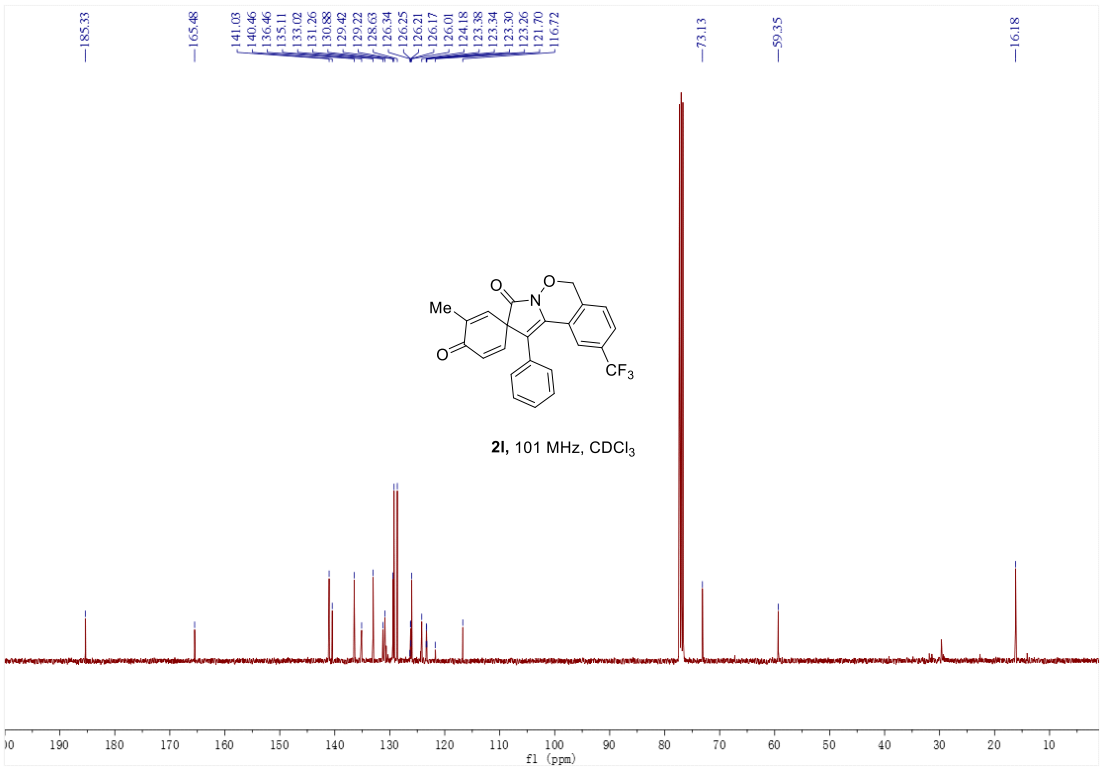

**2k,** 400 MHz, $CDCl_3$



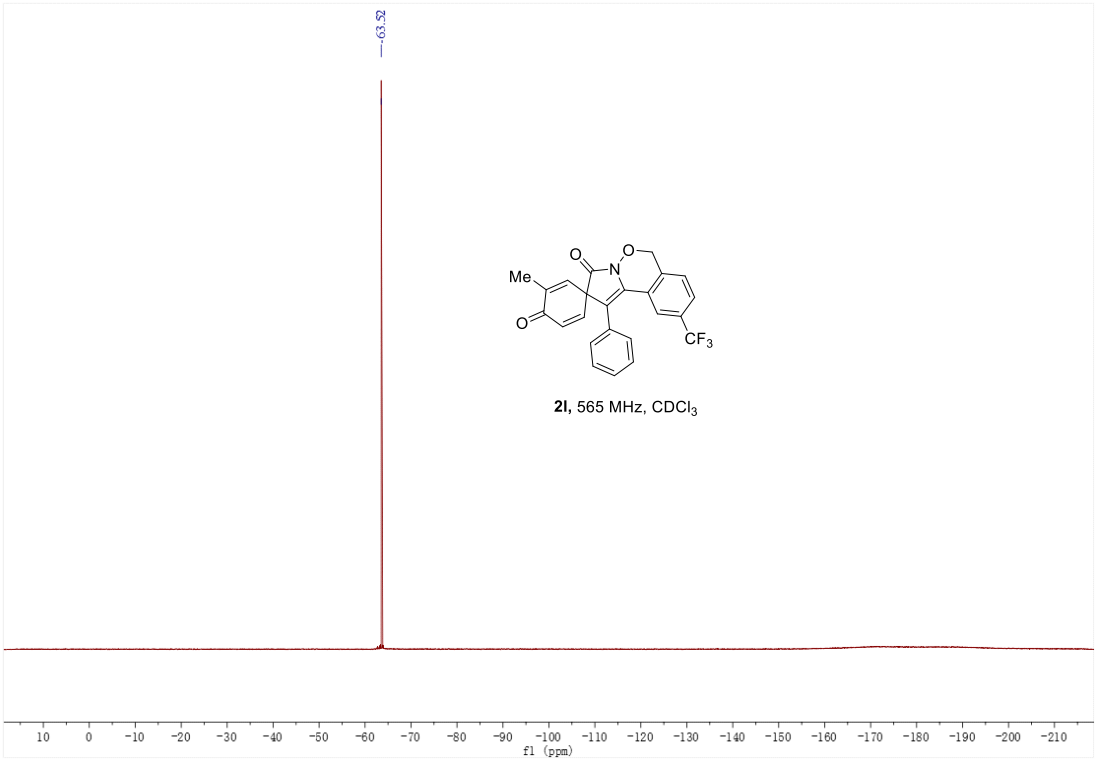

**2k,** 101 MHz, $CDCl_3$



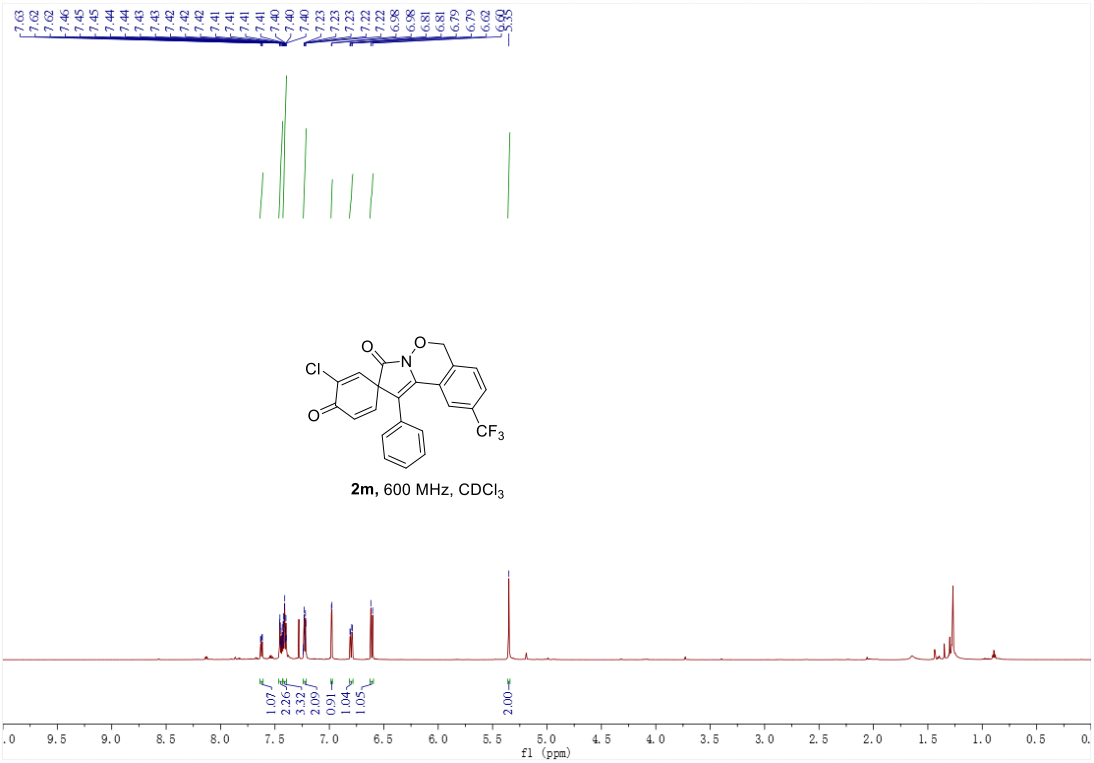

**2l,** 600 MHz, $CDCl_3$



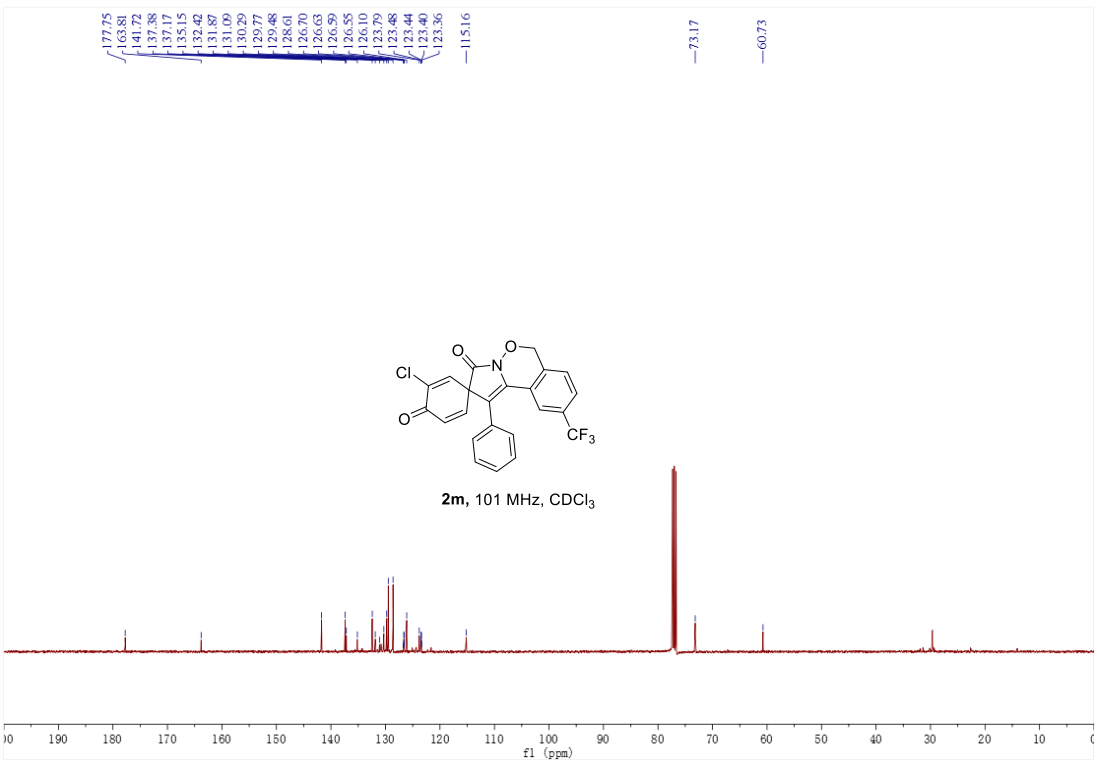

**2l,** 101 MHz, $CDCl_3$



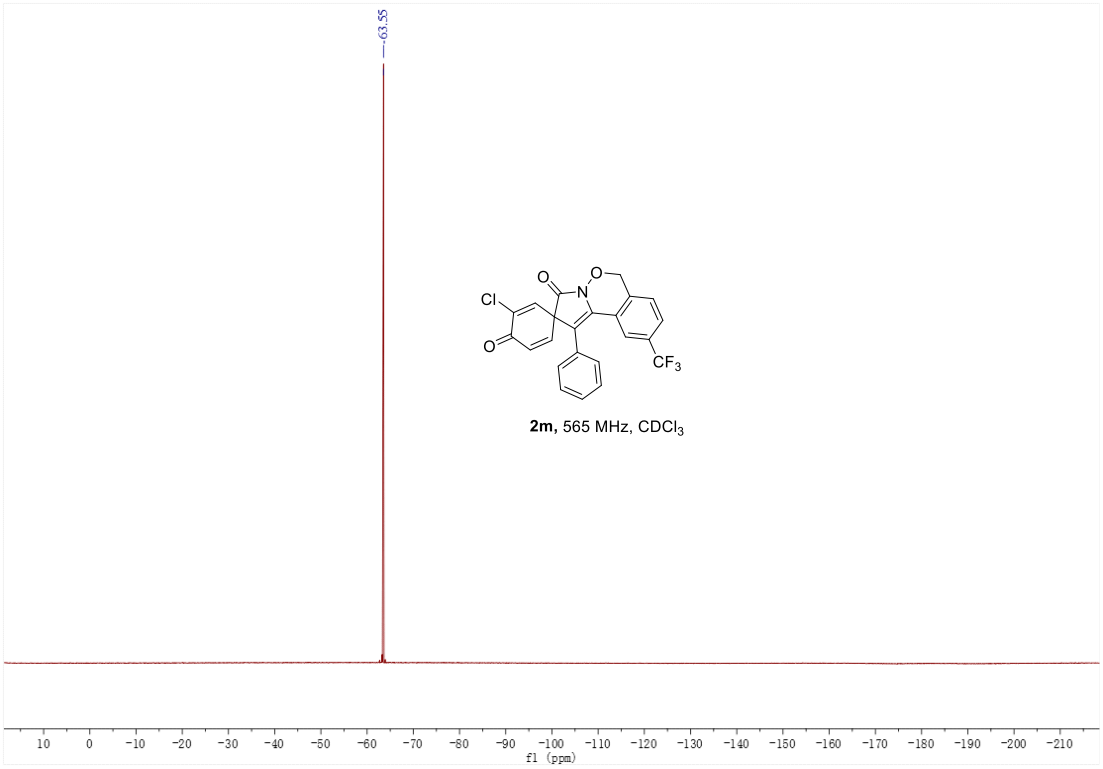

**2l,** 565 MHz, $CDCl_3$



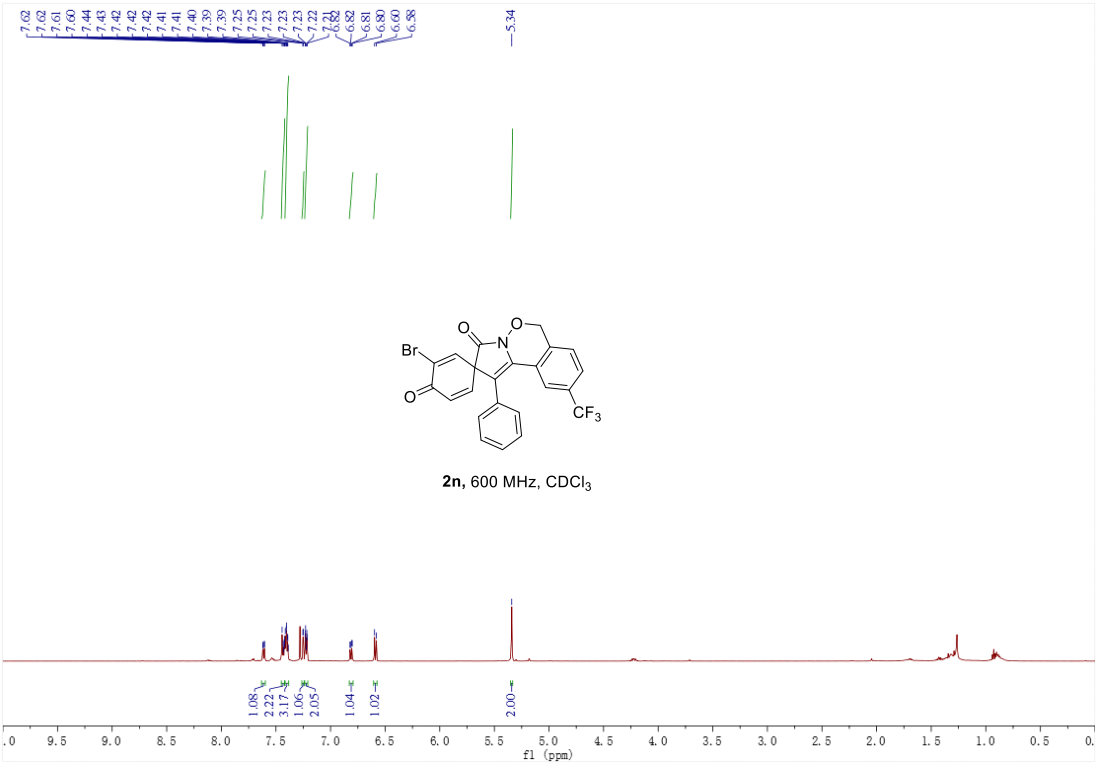

**2m,** 600 MHz, $CDCl_3$



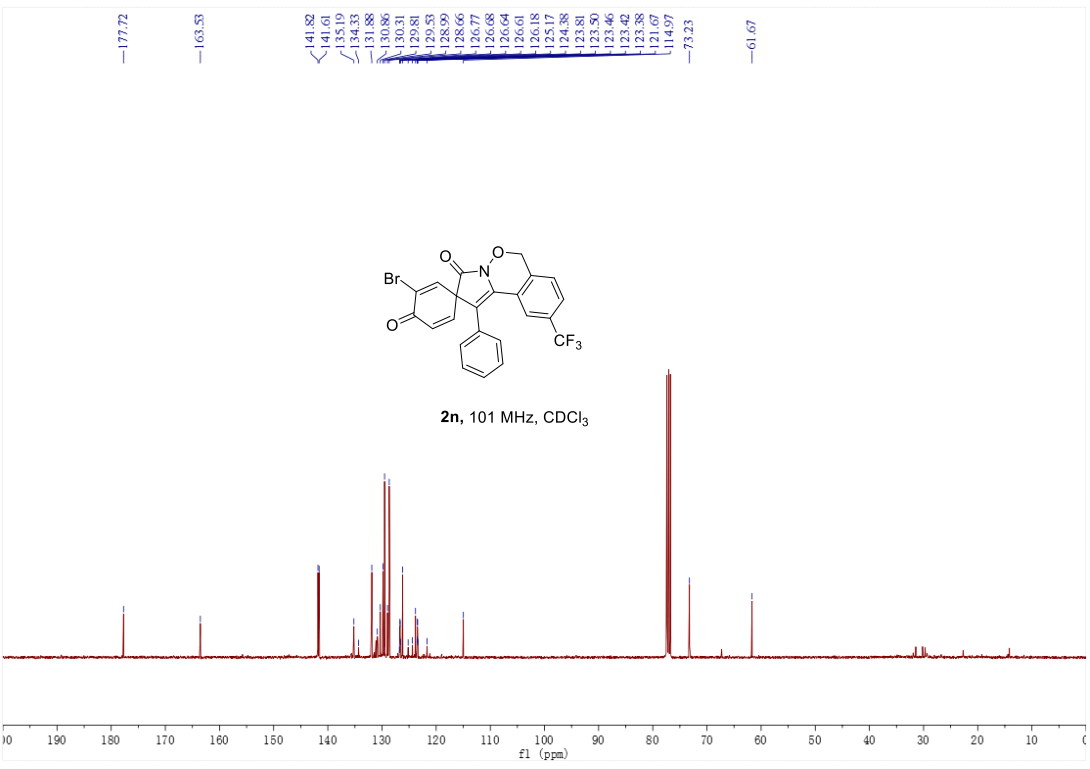

**2m,** 101 MHz, $CDCl_3$



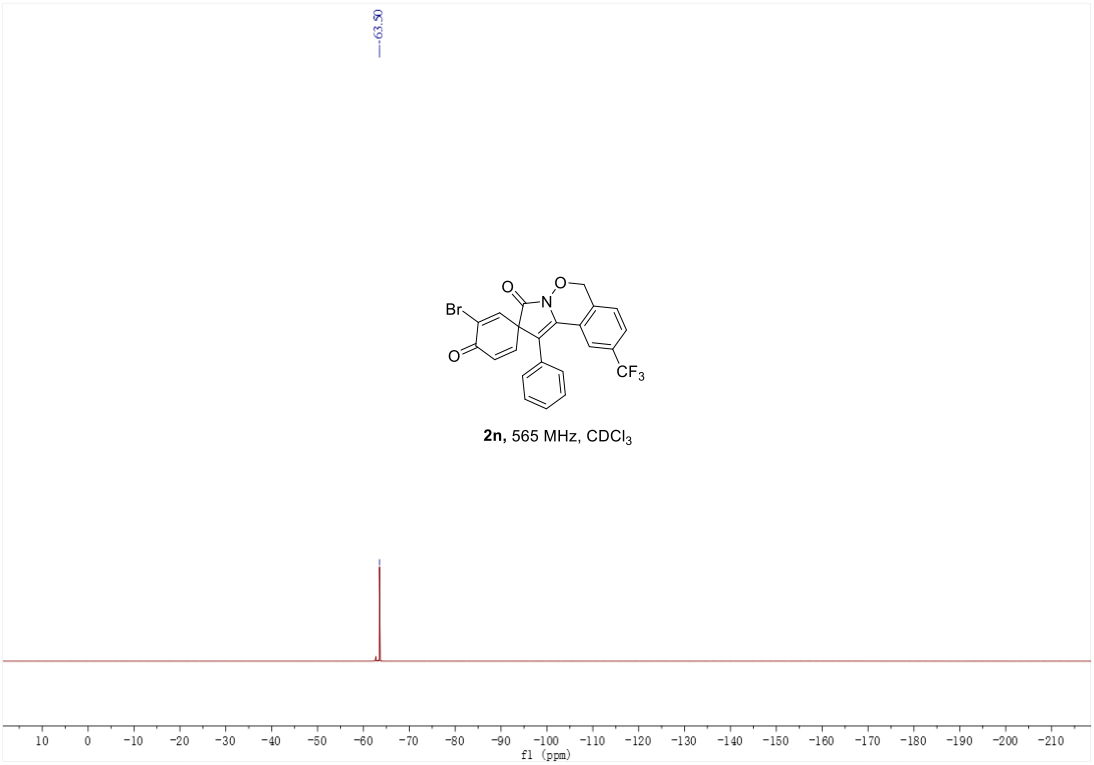

**2m,** 565 MHz, $CDCl_3$



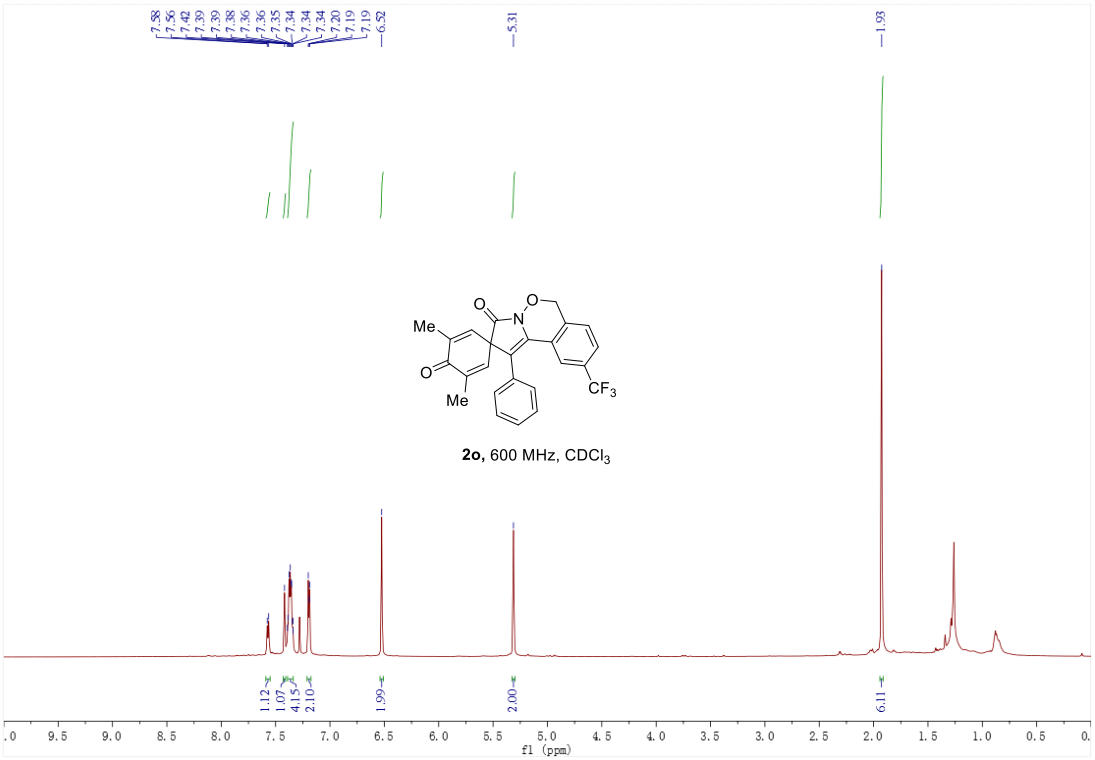

**2n,** 600 MHz, $CDCl_3$



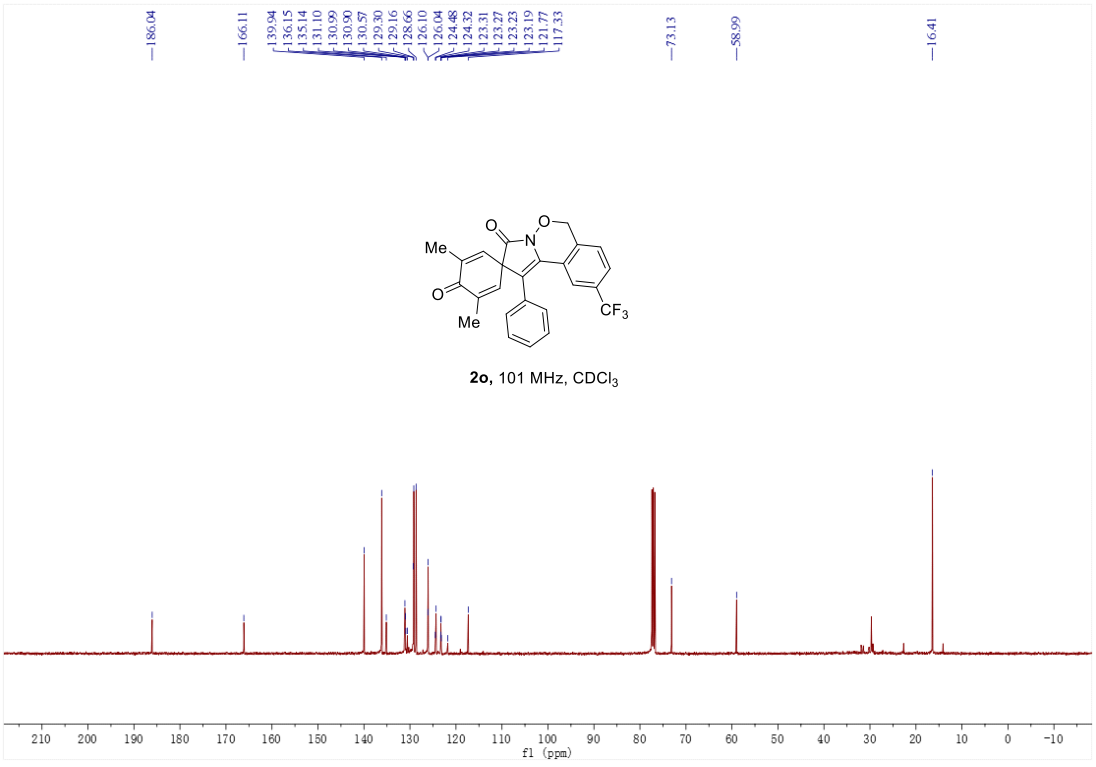

**2n,** 101 MHz, $CDCl_3$



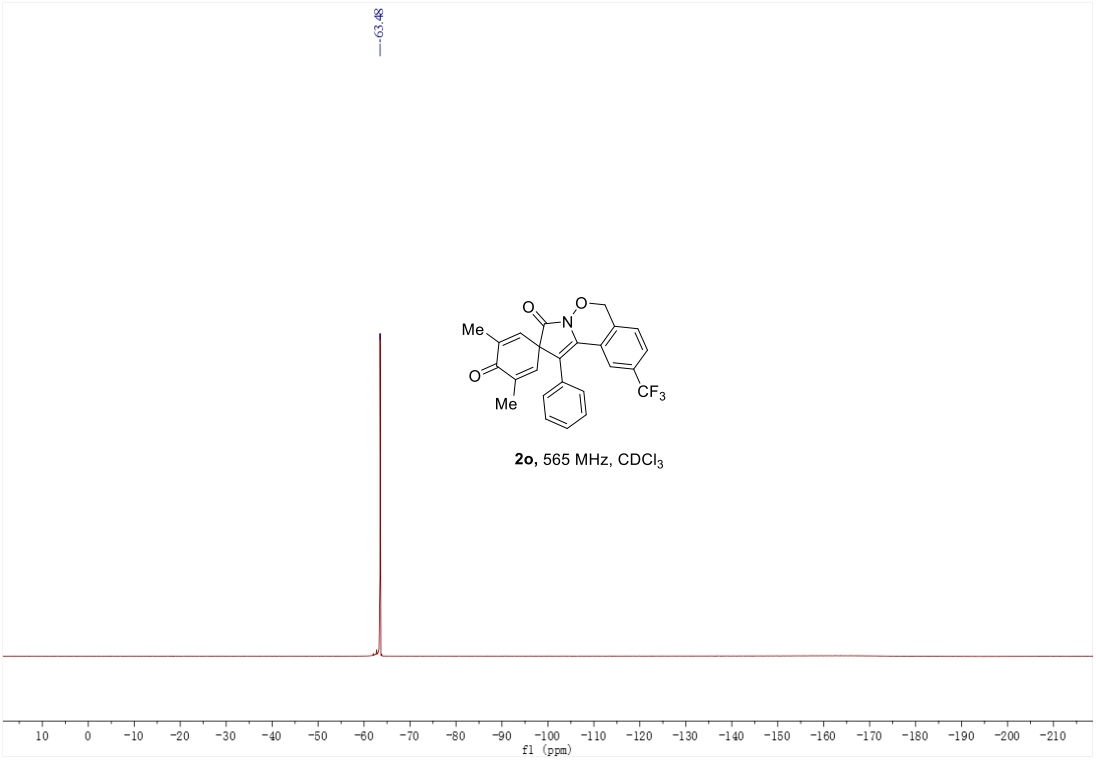

**2n,** 565 MHz, $CDCl_3$



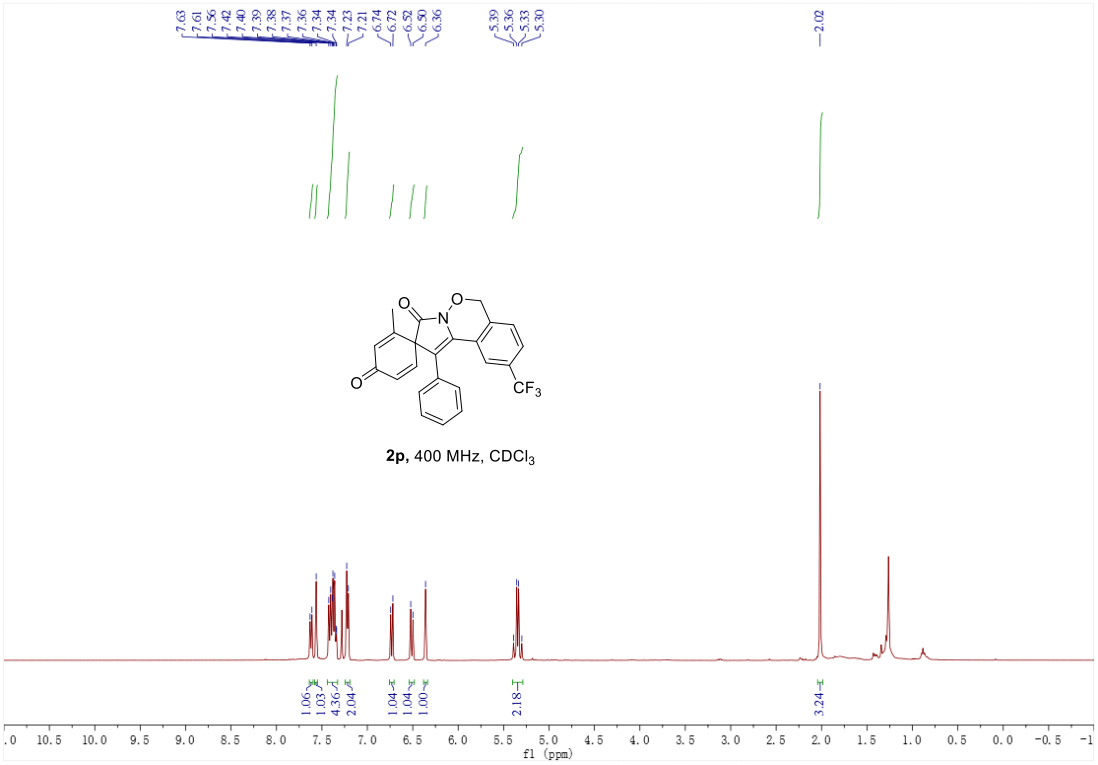

**2o,** 600 MHz, $CDCl_3$



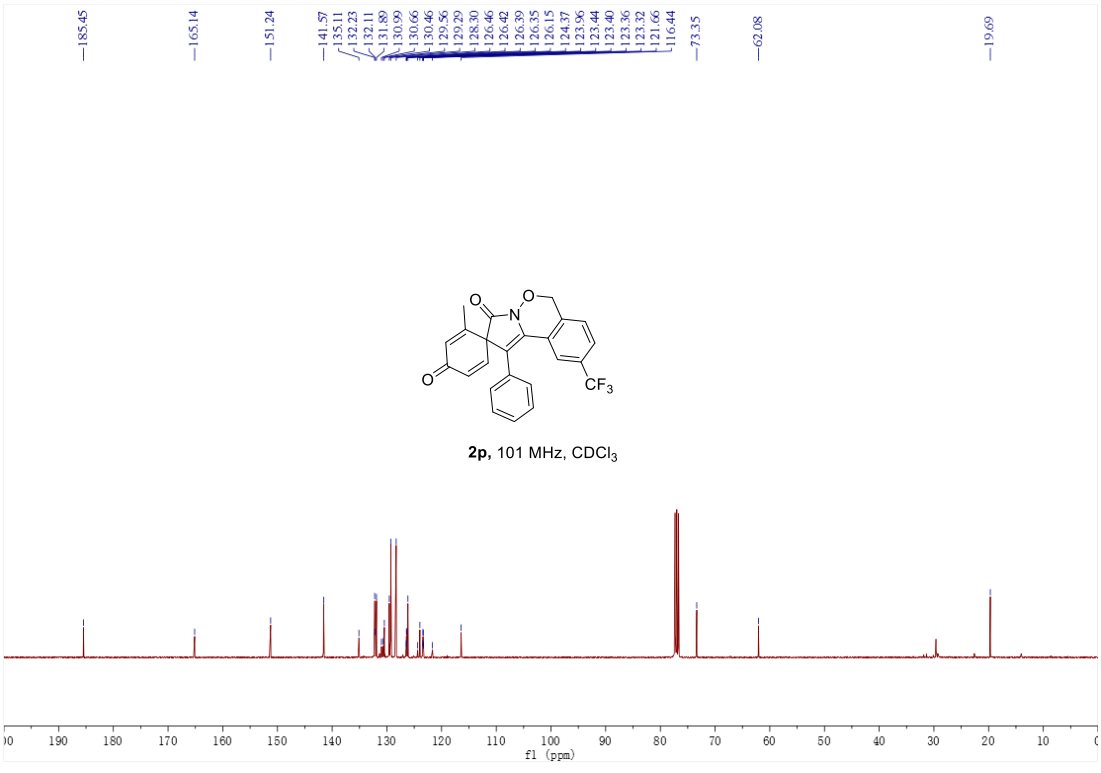

**2o,** 101 MHz, $CDCl_3$



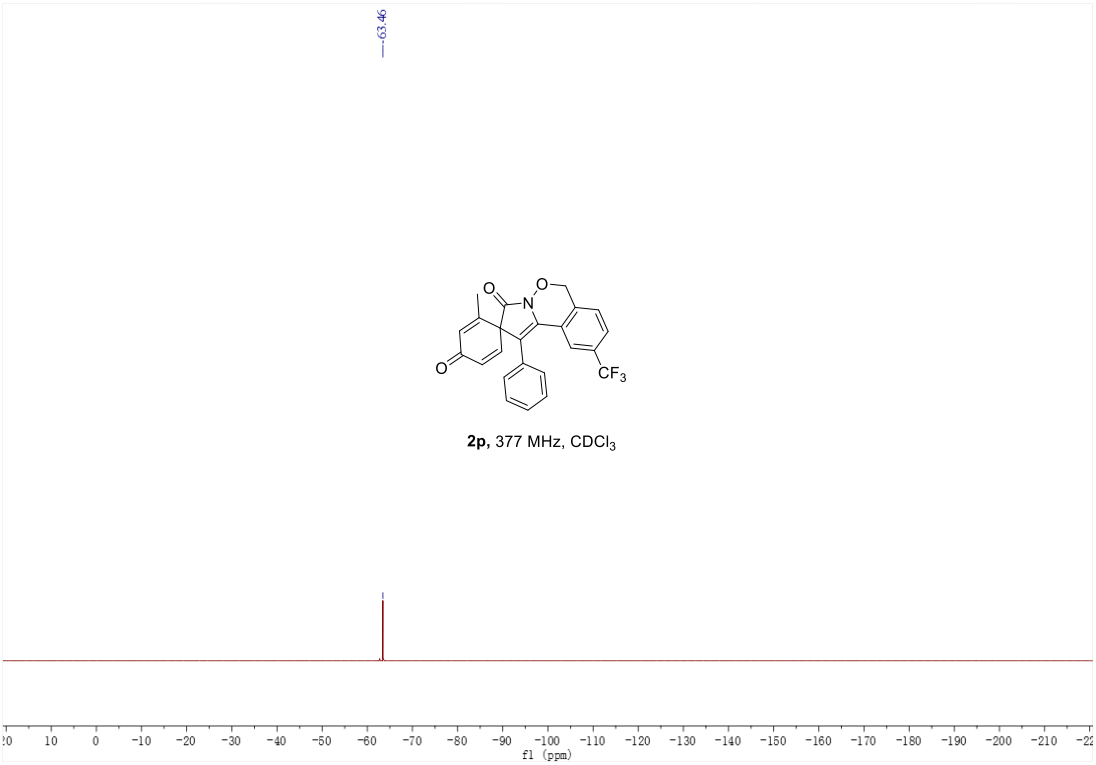

**2o,** 565 MHz, $CDCl_3$



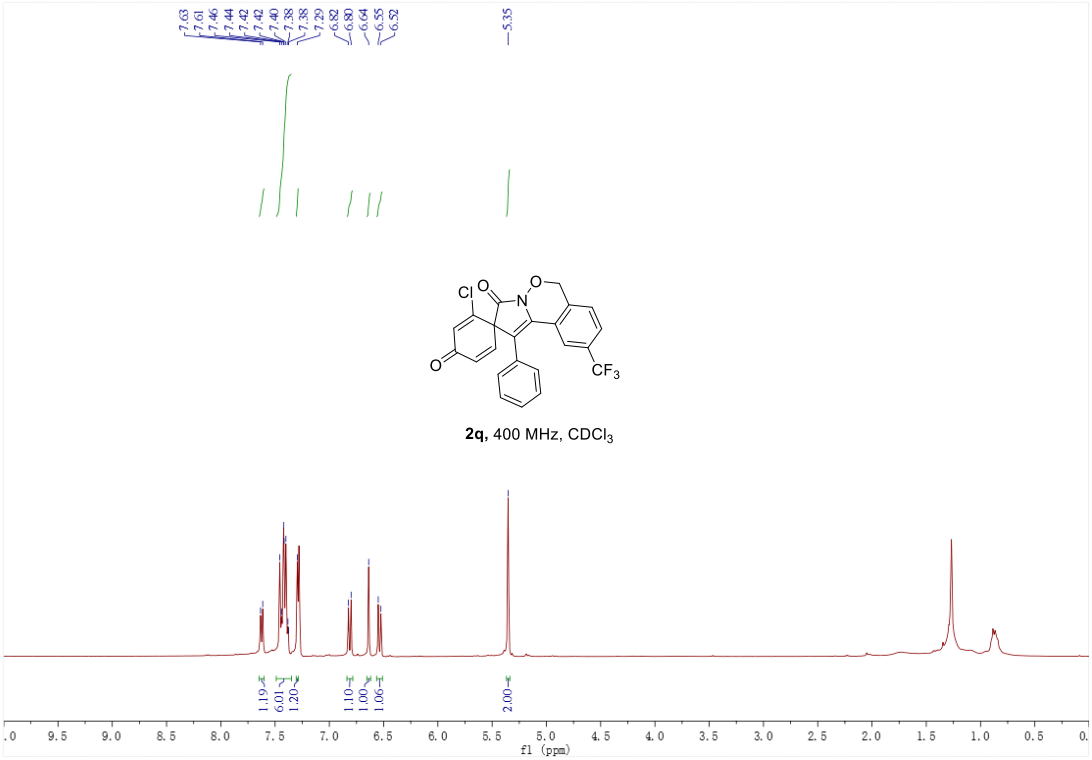

**2p,** 400 MHz, $CDCl_3$



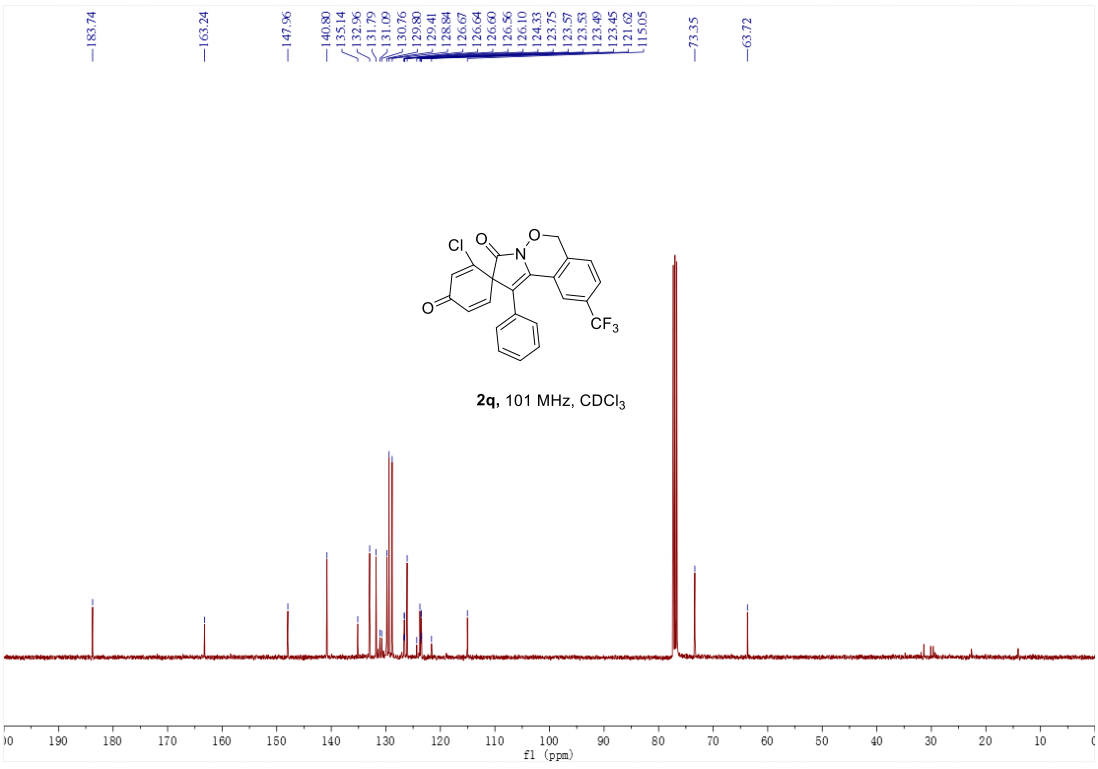

**2p,** 101 MHz, $CDCl_3$



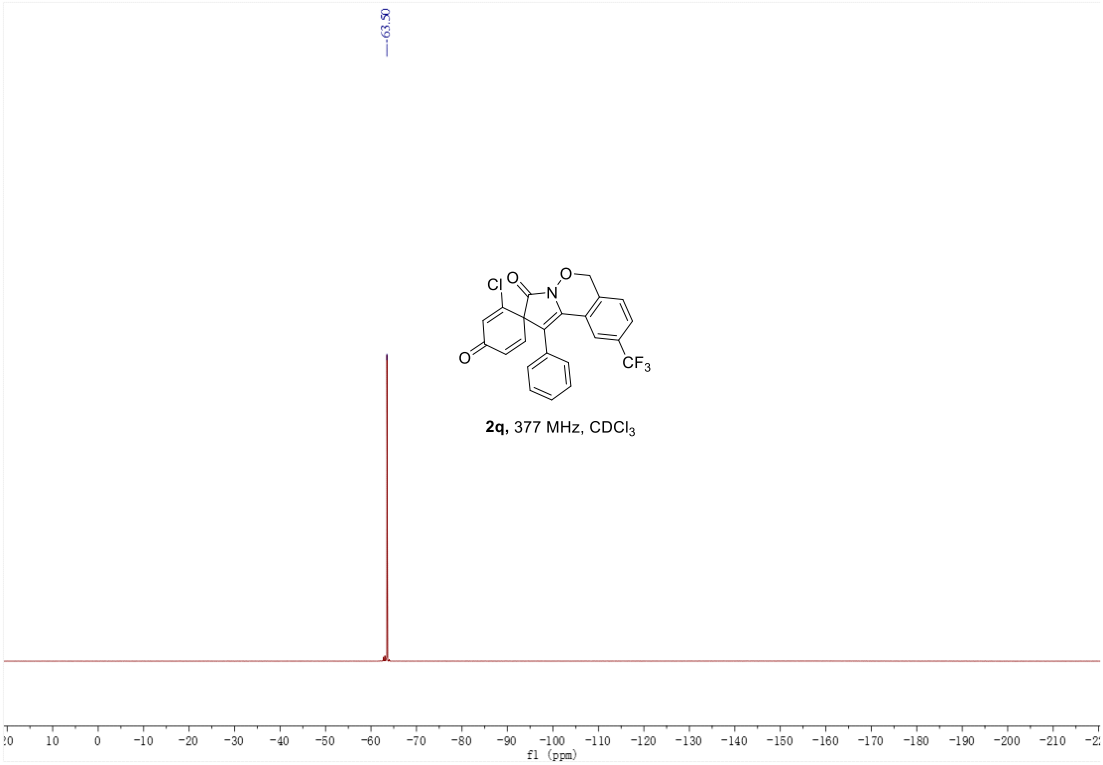

**2p,** 377 MHz, $CDCl_3$



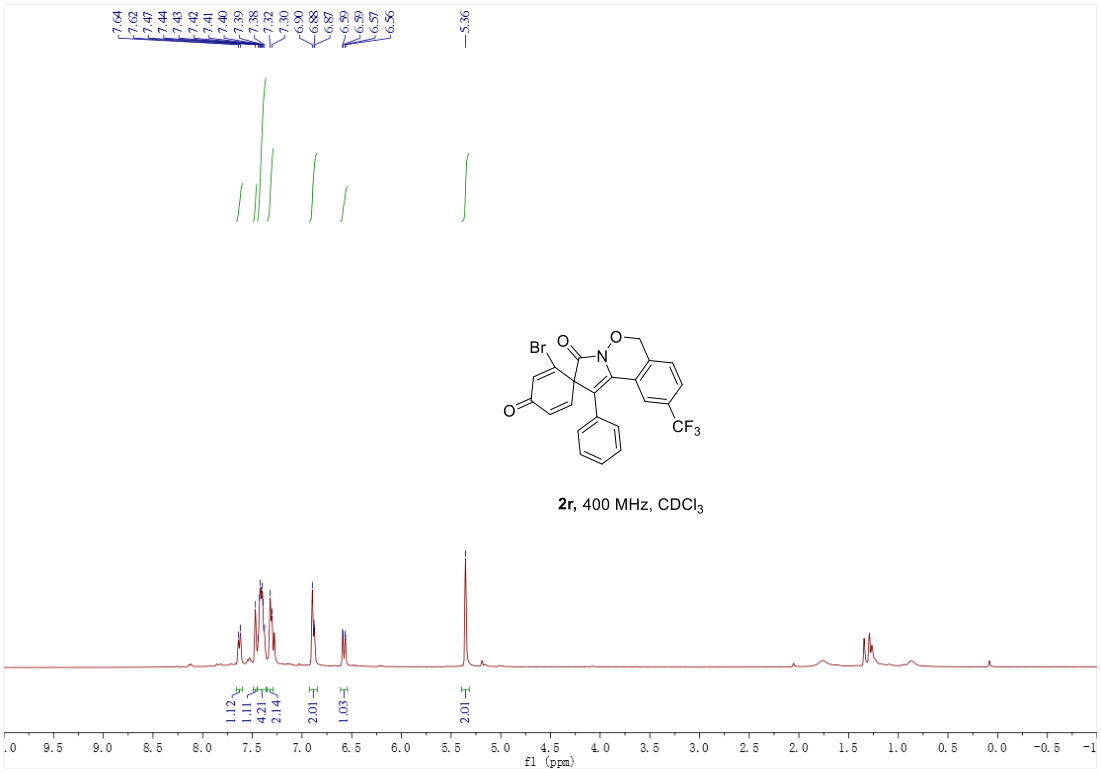

**2q,** 400 MHz, $CDCl_3$



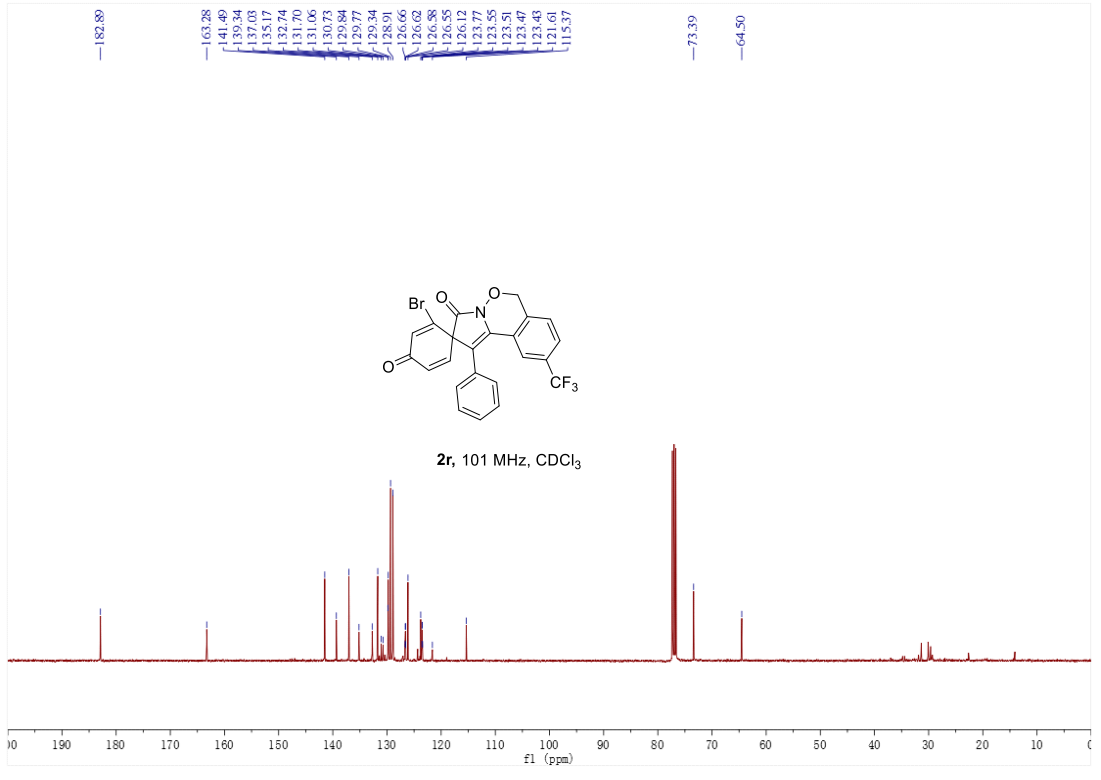

**2q,** 101 MHz, $CDCl_3$



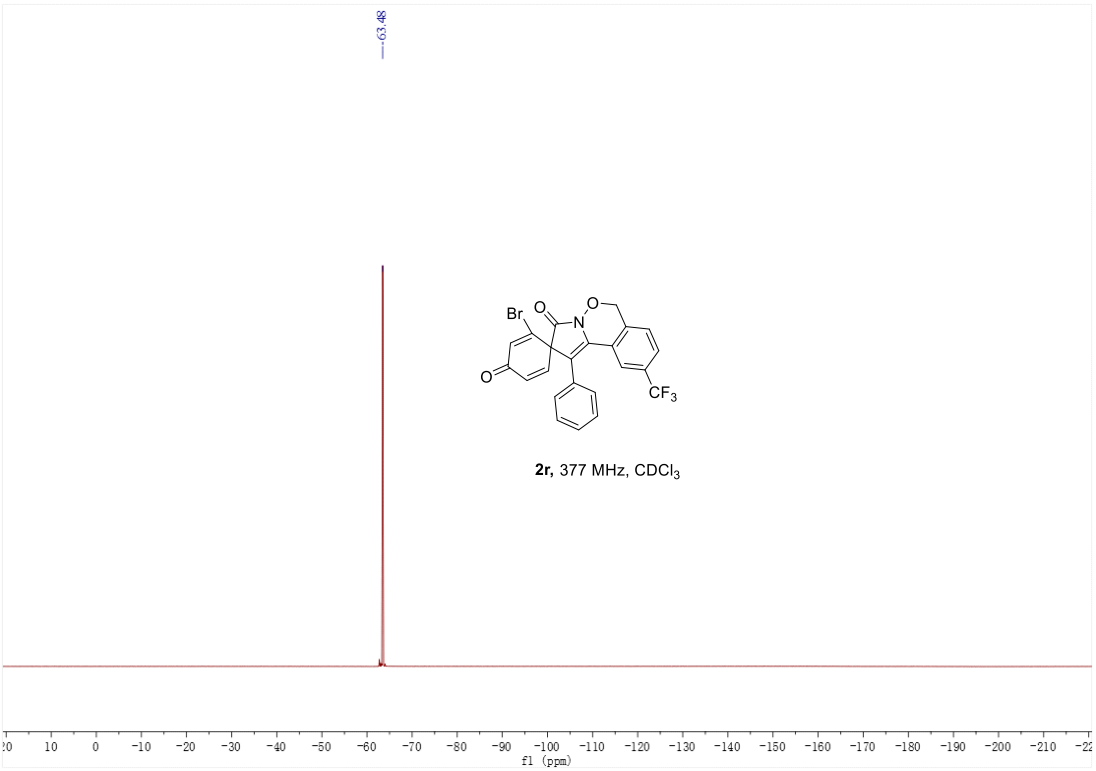

**2q,** 377 MHz, $CDCl_3$



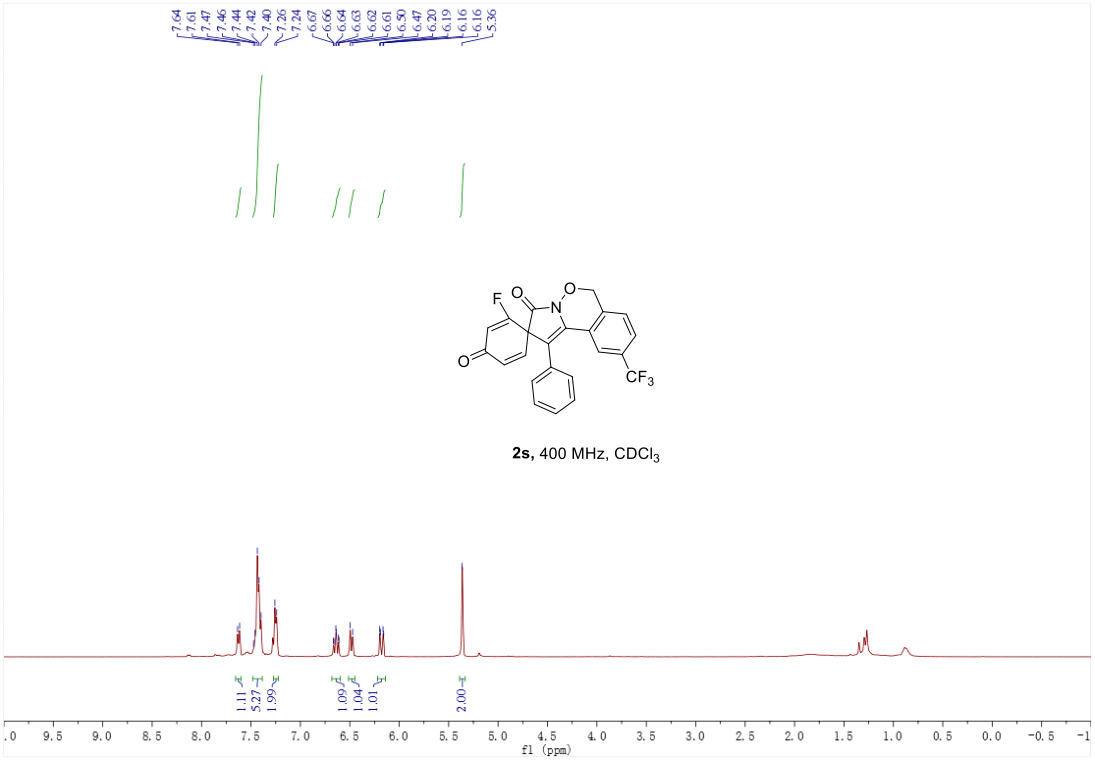

**2r,** 400 MHz, $CDCl_3$



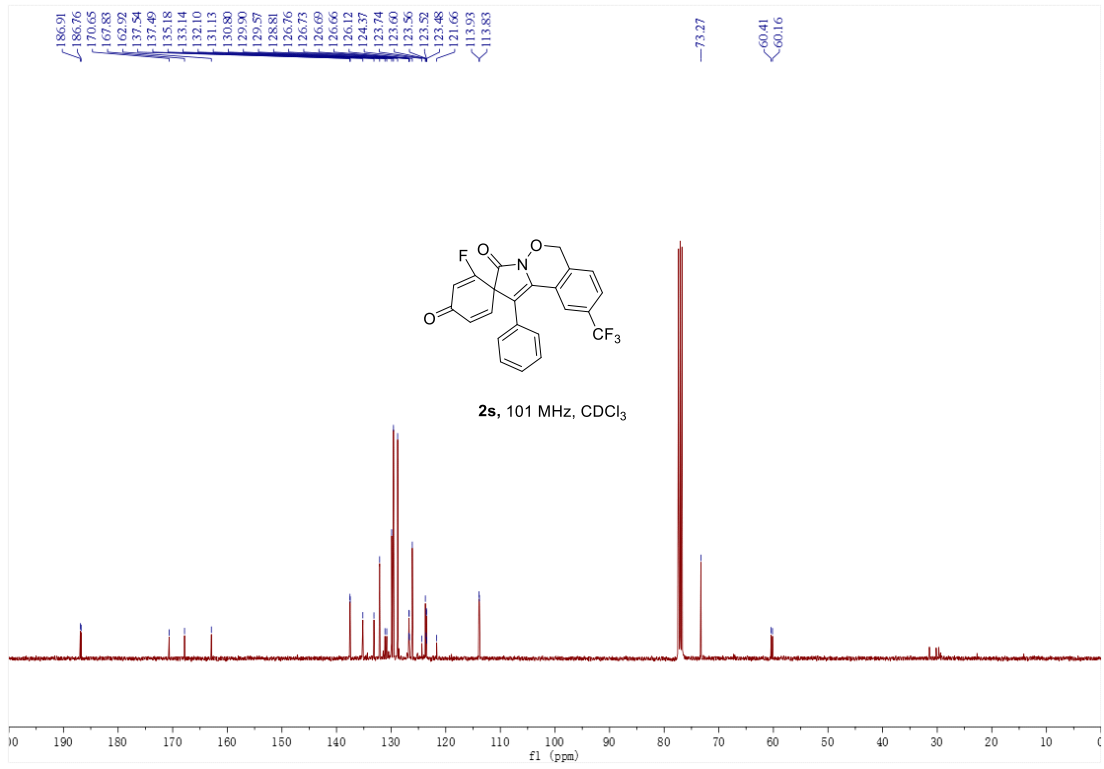

**2r,** 101 MHz, $CDCl_3$



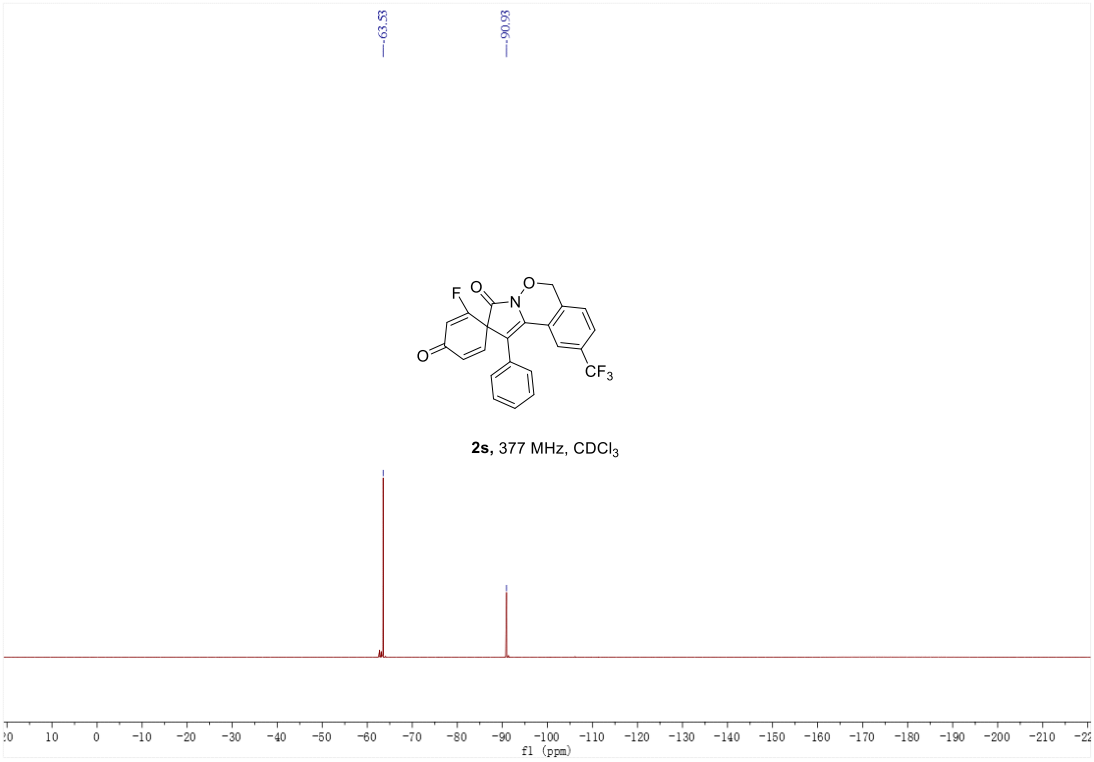

**2r**, 377 MHz, $CDCl_3$



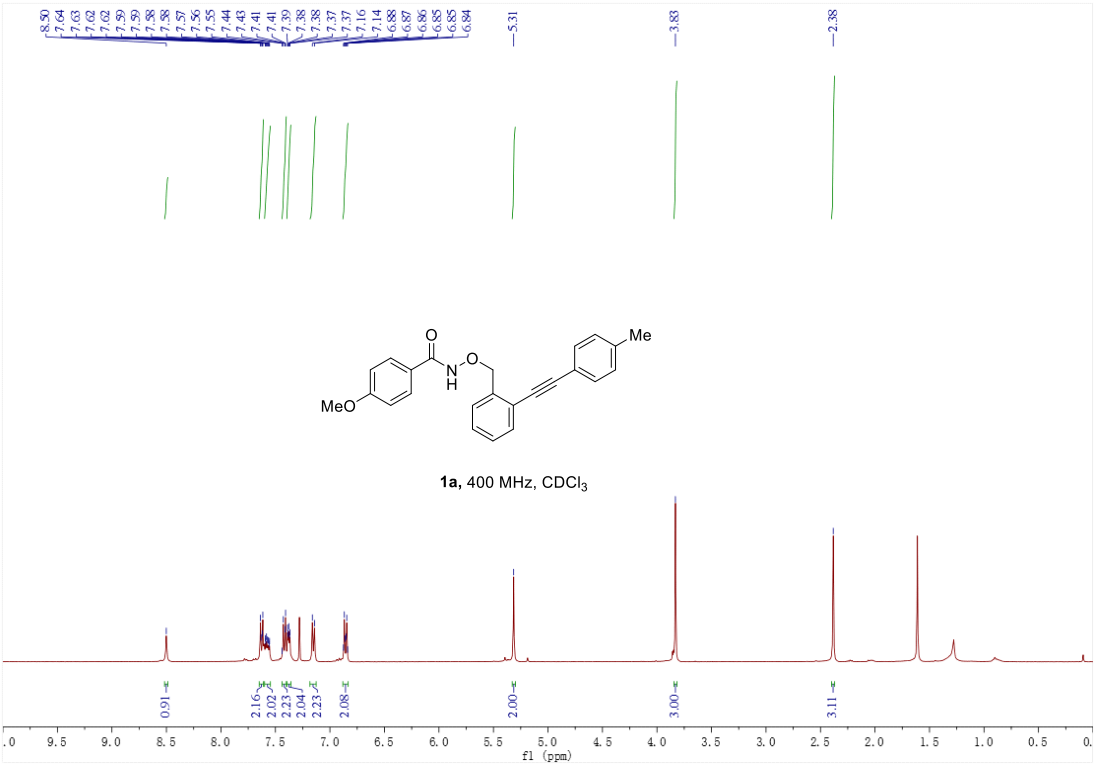

**2s,** 400 MHz, $CDCl_3$



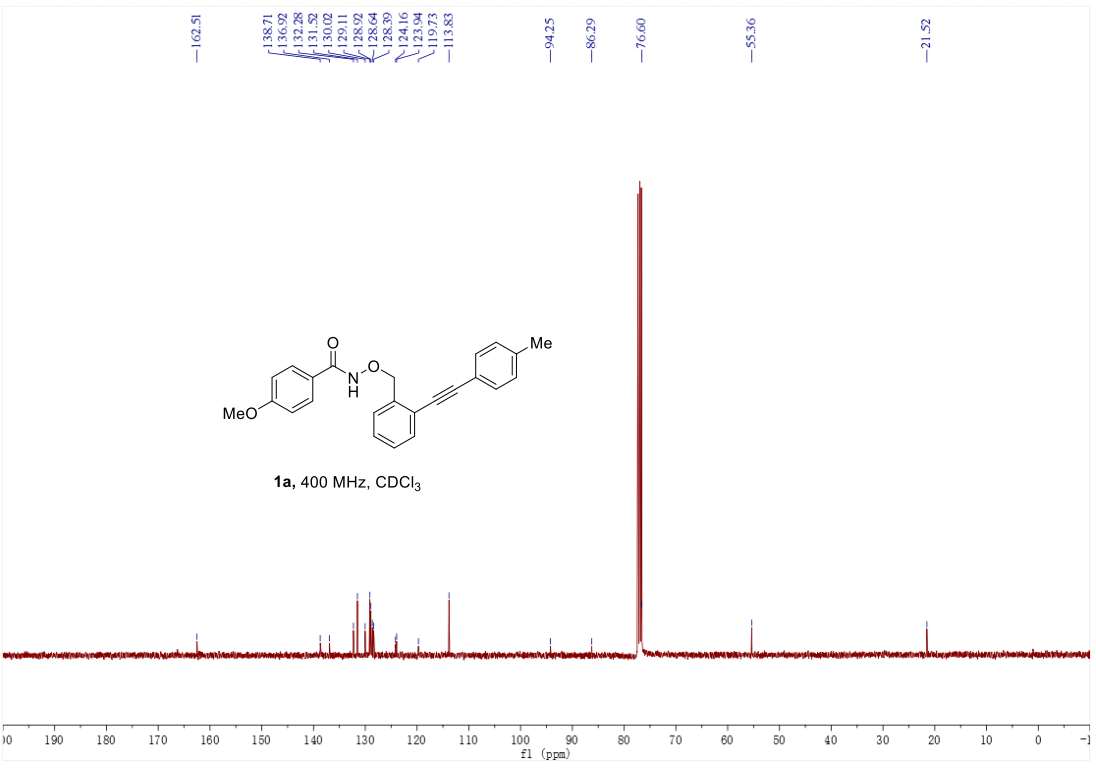

**2s,** 101 MHz, $CDCl_3$



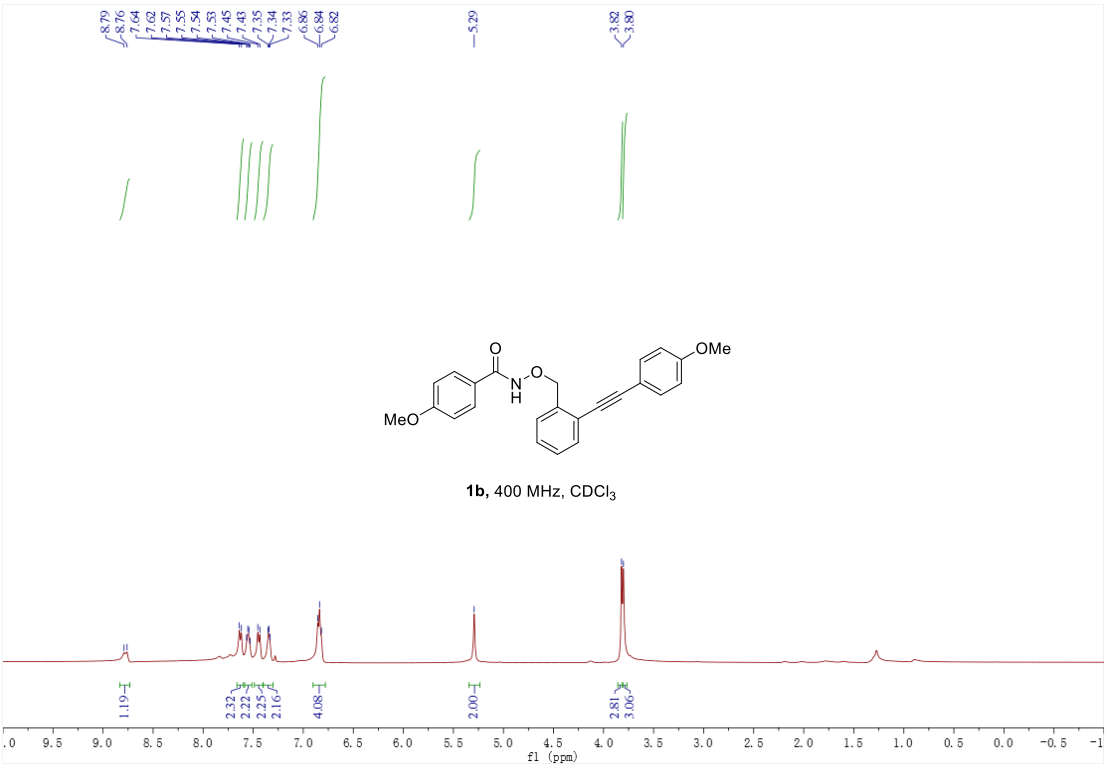

**2s**, 377 MHz, $CDCl_3$



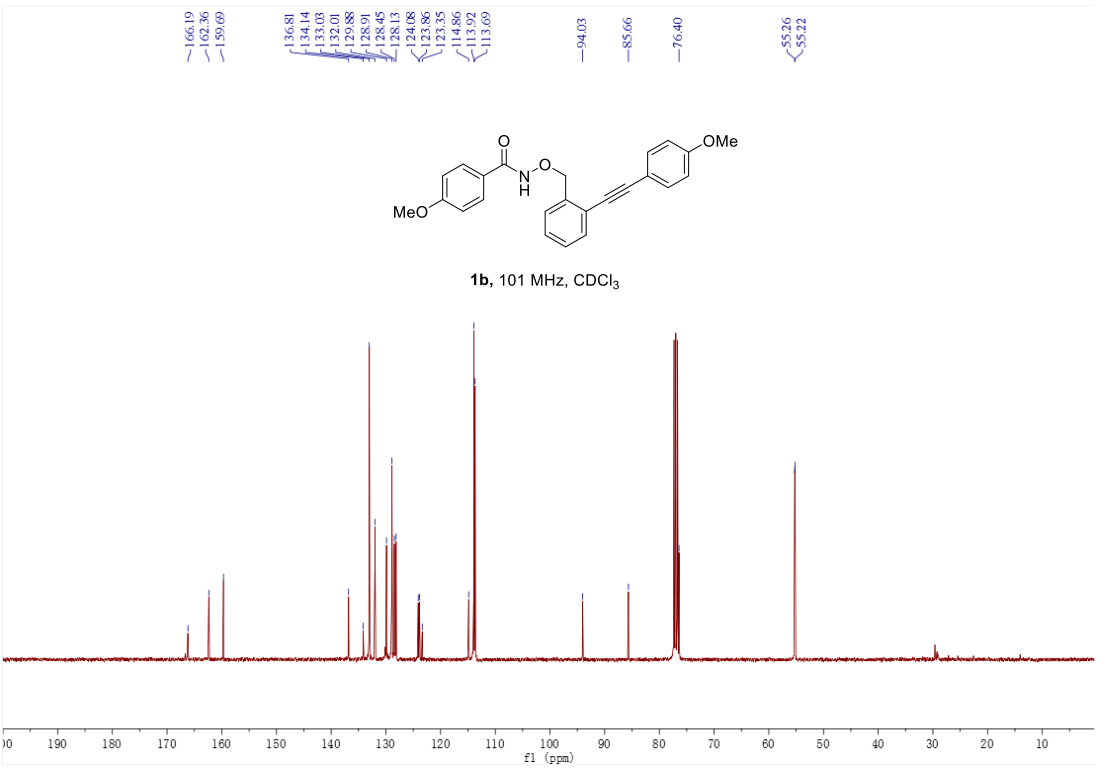

**1a,** 400 MHz, $CDCl_3$



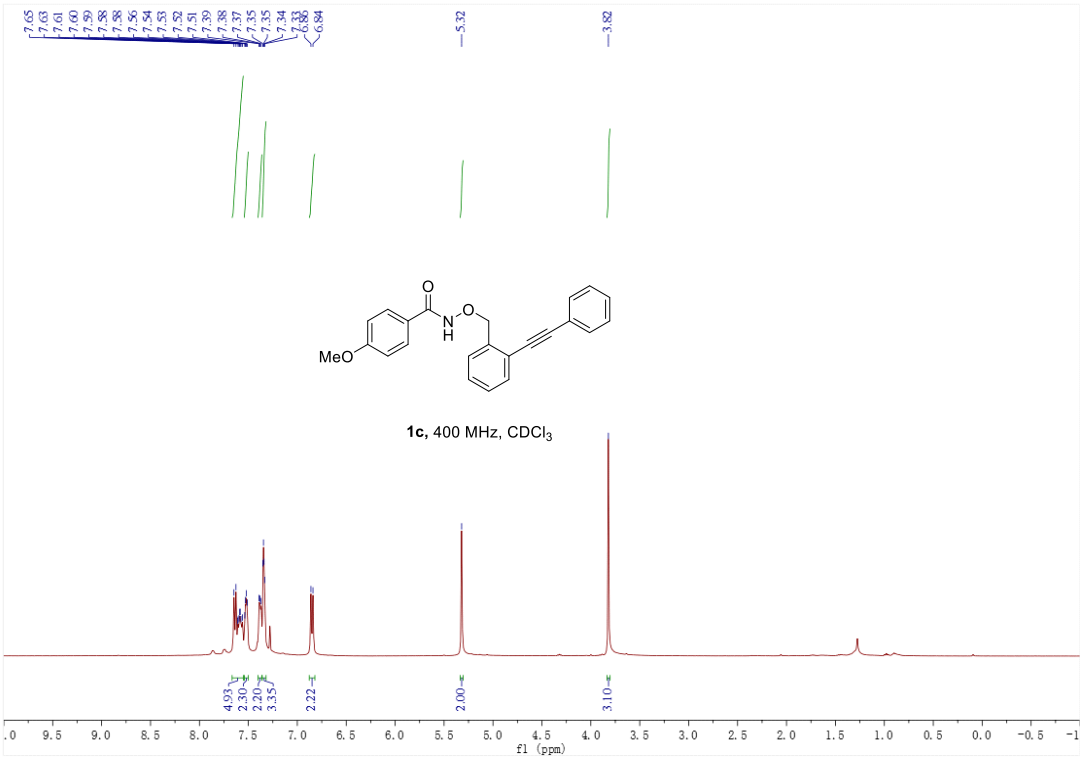

**1a,** 400 MHz, $CDCl_3$



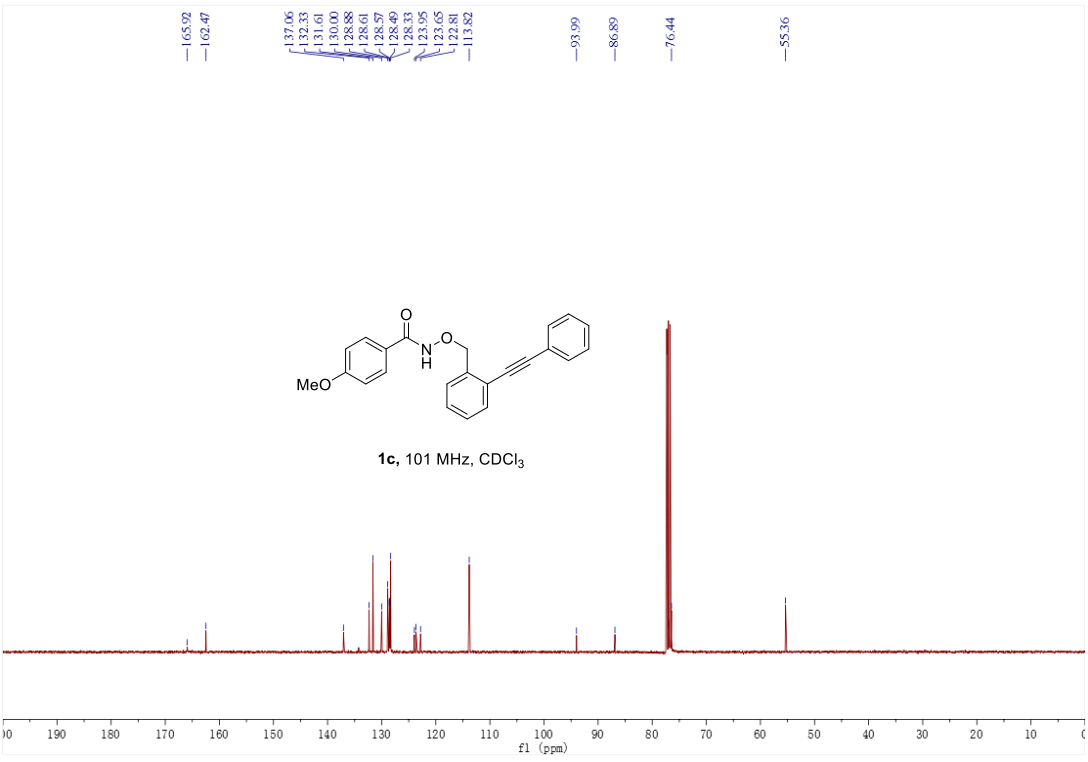

**1b,** 400 MHz, $CDCl_3$



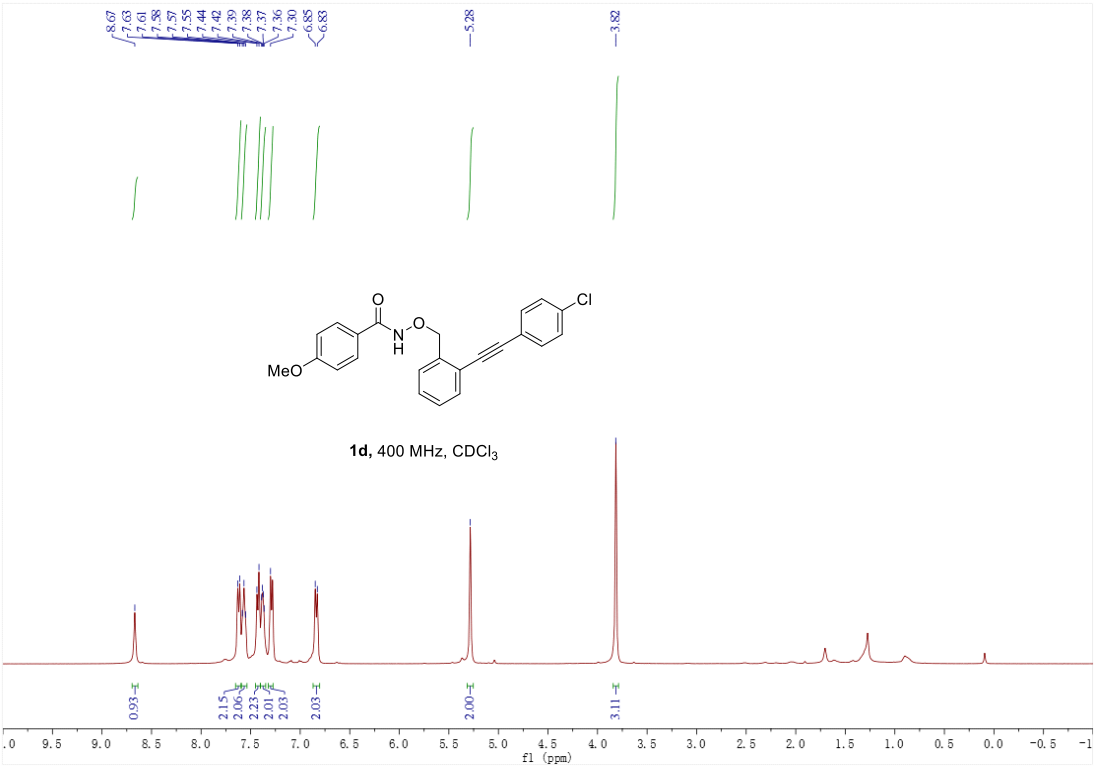

**1b,** 101 MHz, $CDCl_3$



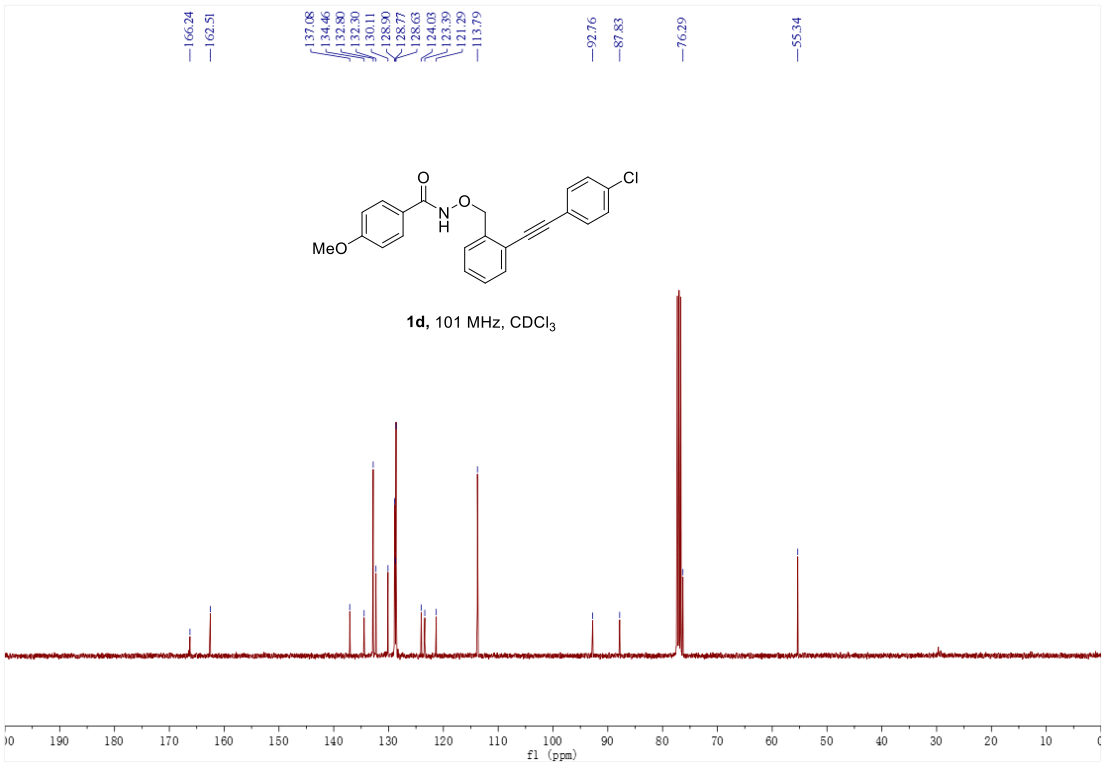

**1c**, 400 MHz, $CDCl_3$



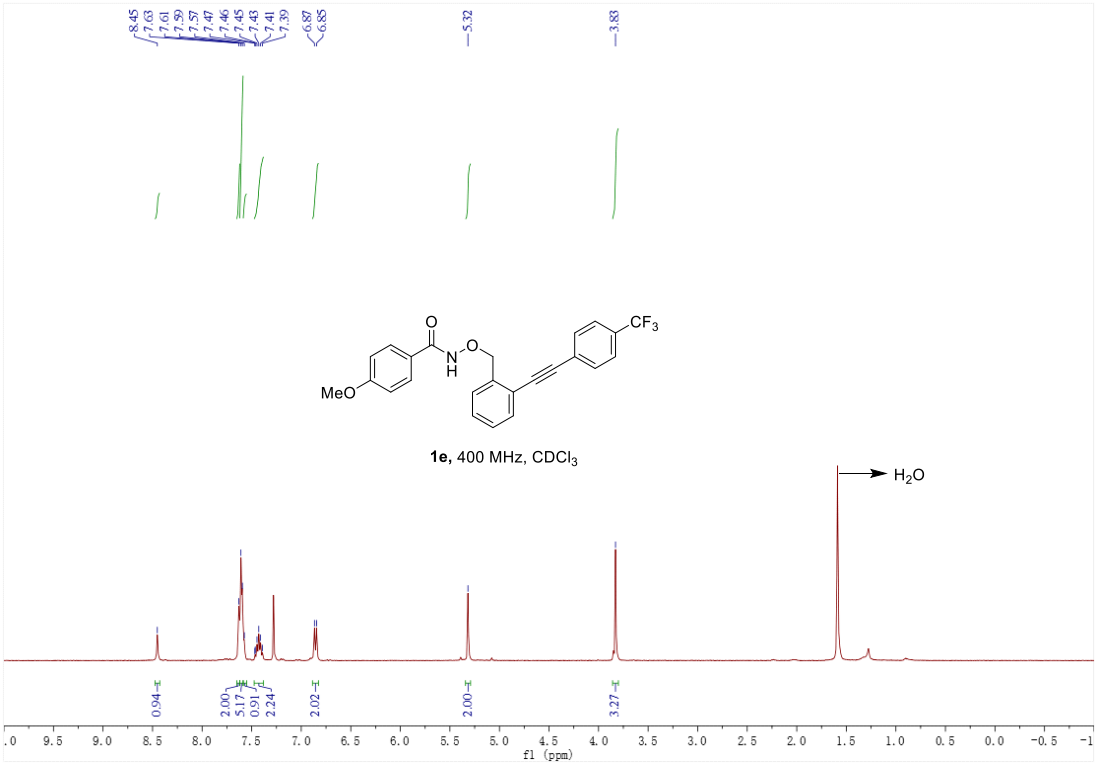

**1c**, 101 MHz, $CDCl_3$



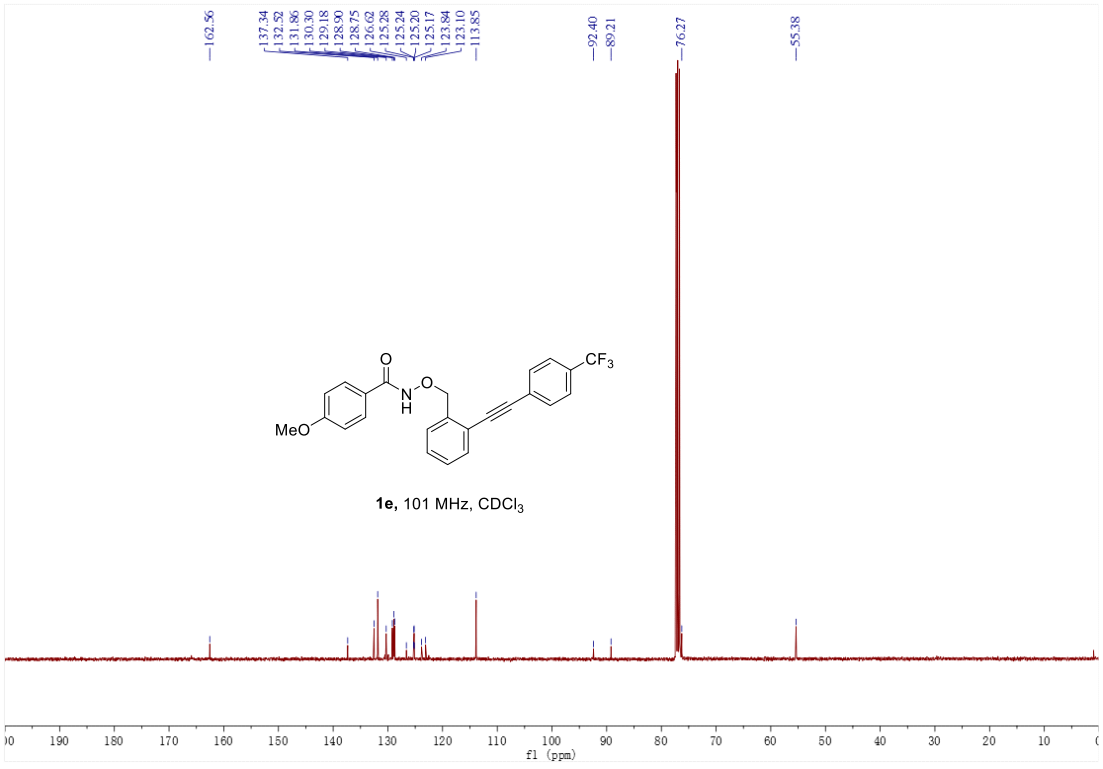

**1d,** 400 MHz, $CDCl_3$



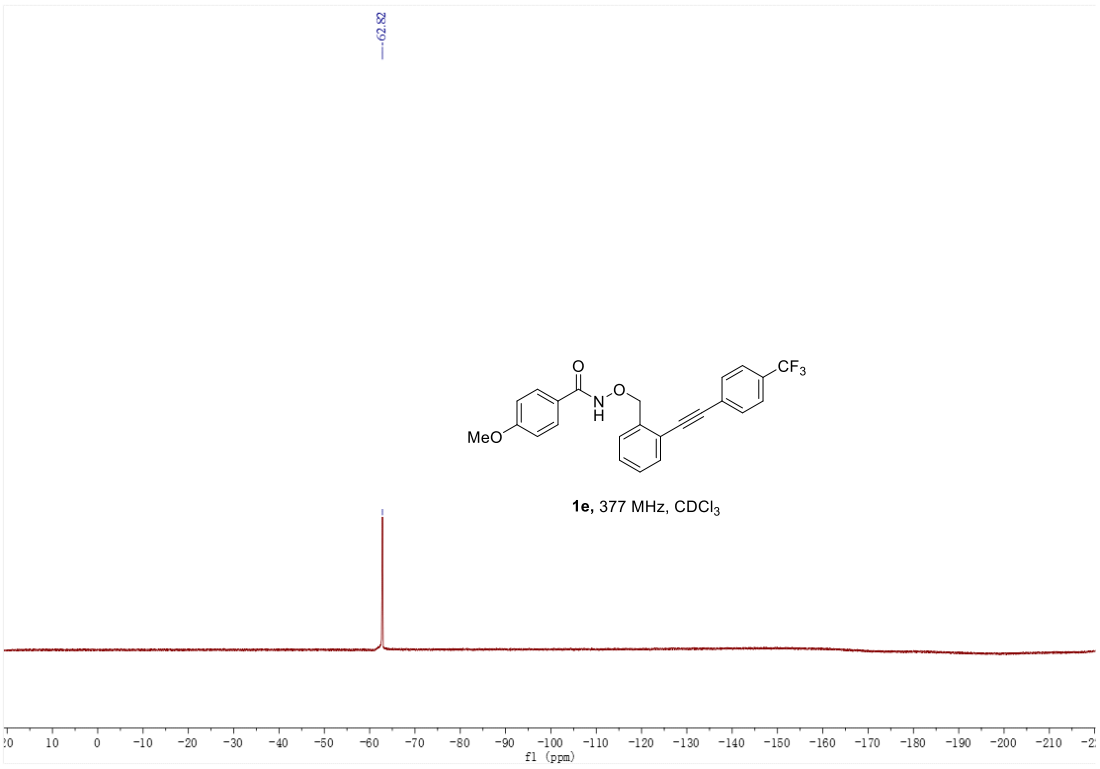

**1d,** 101 MHz, $CDCl_3$



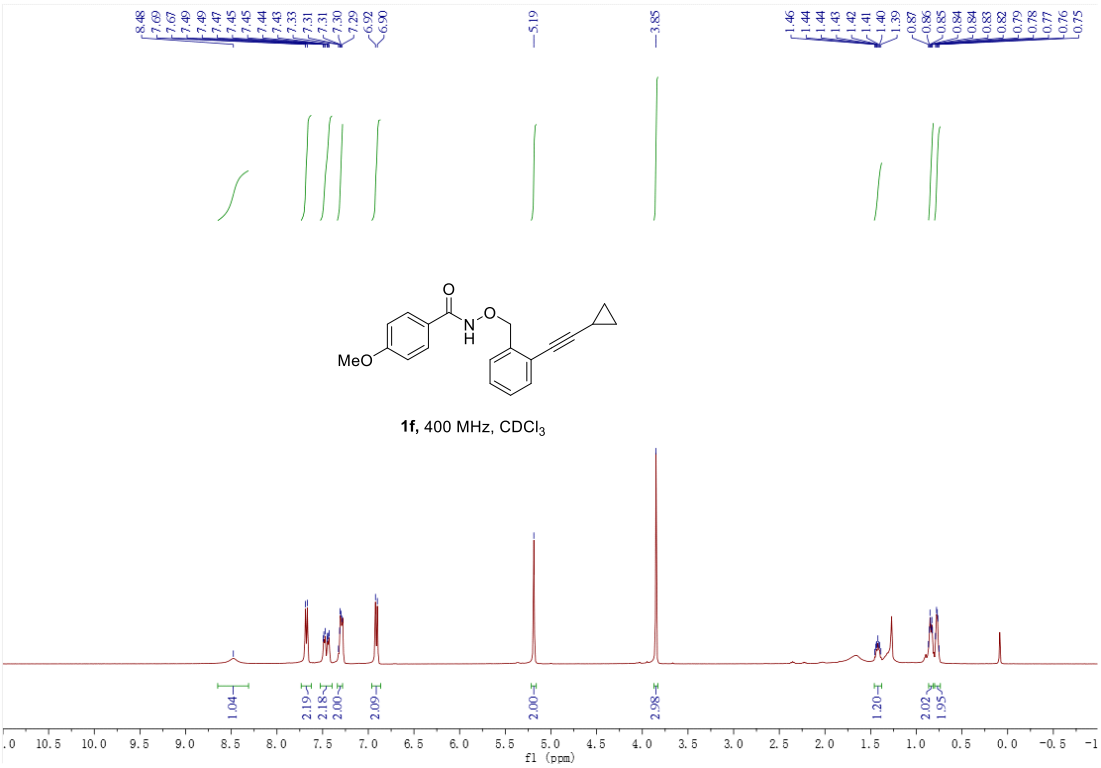

**1e,** 400 MHz, $CDCl_3$



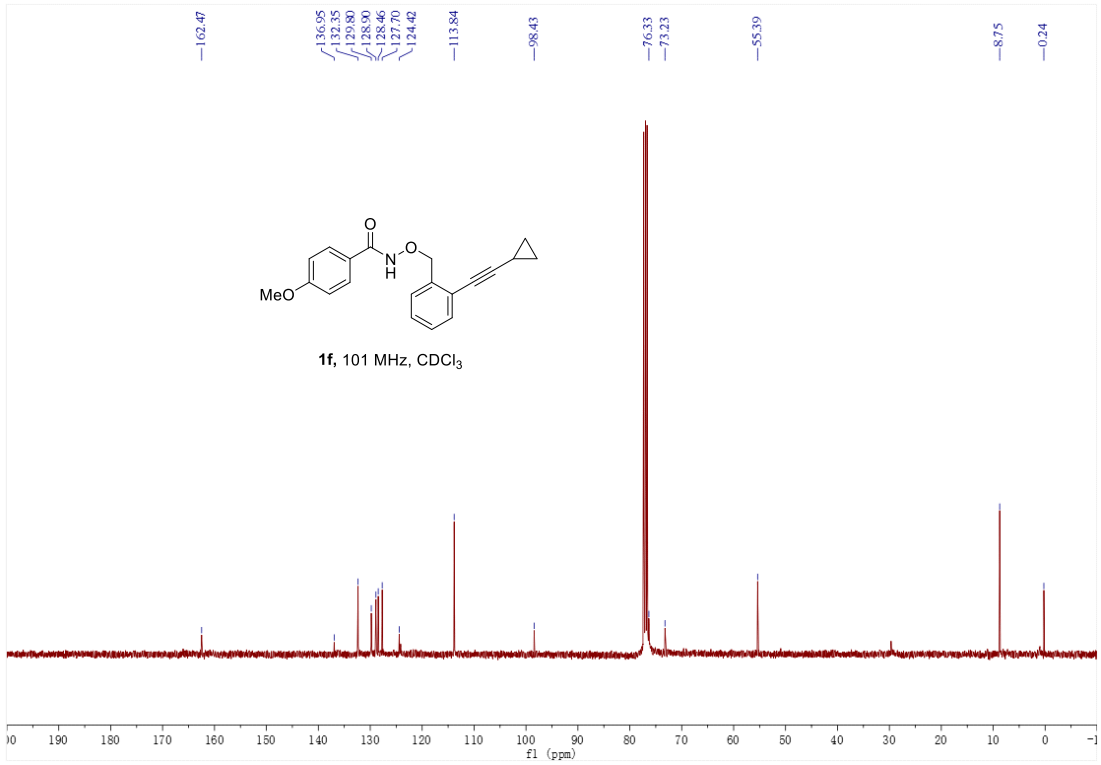

**1e,** 101 MHz, $CDCl_3$



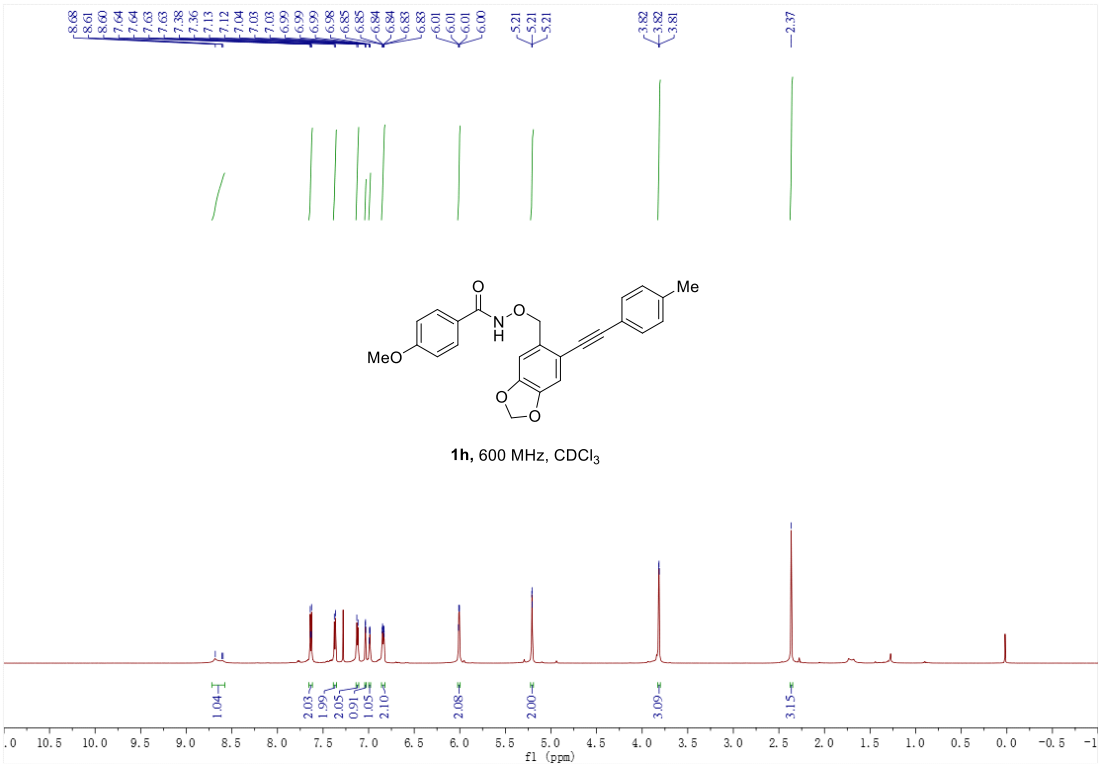

**1e**, 377 MHz, $CDCl_3$



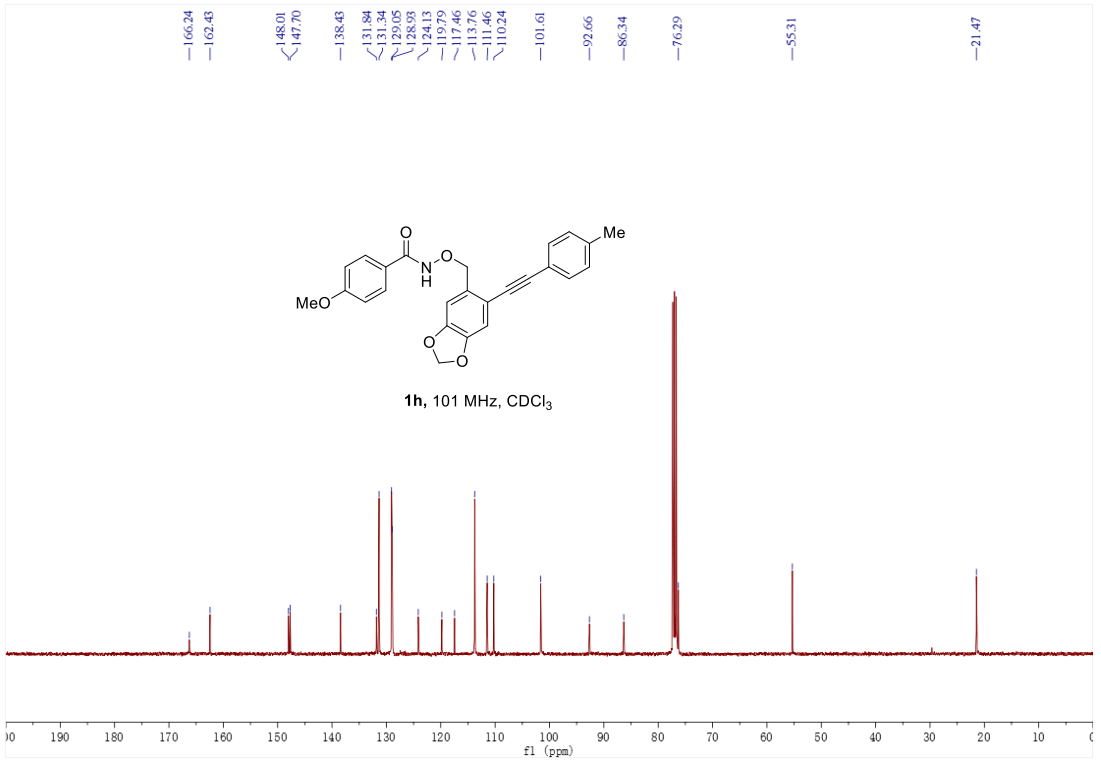

**1f,** 400 MHz, $CDCl_3$



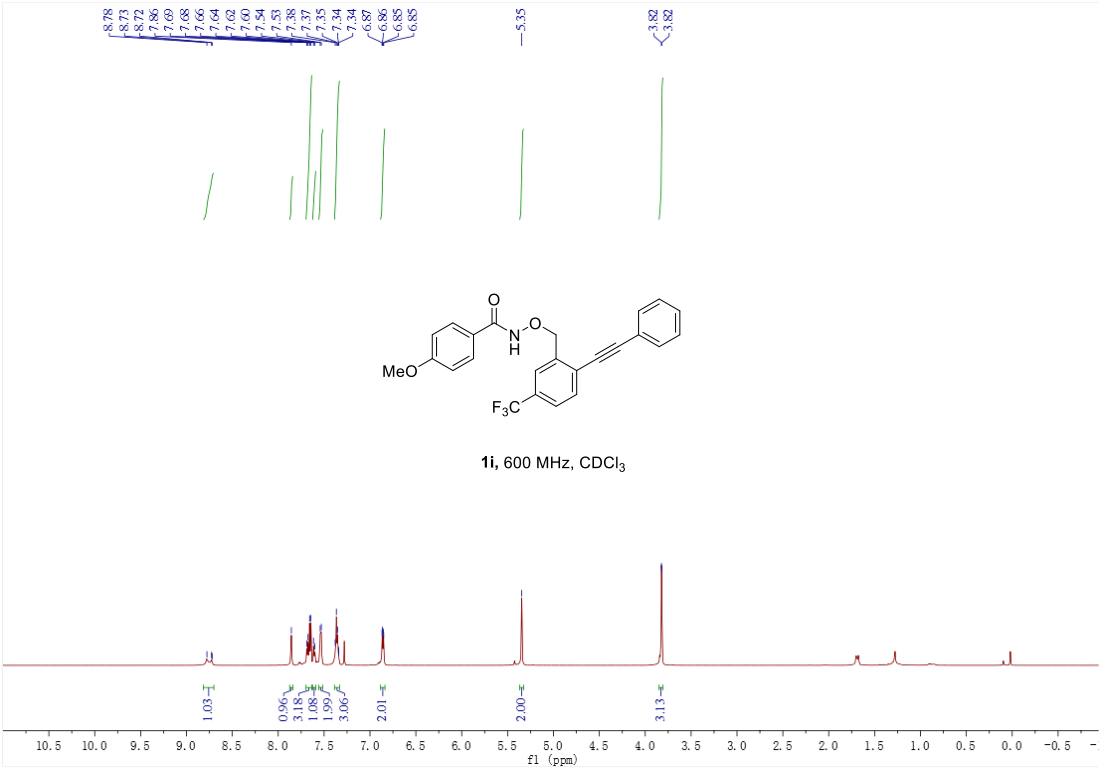

**1f,** 101 MHz, $CDCl_3$



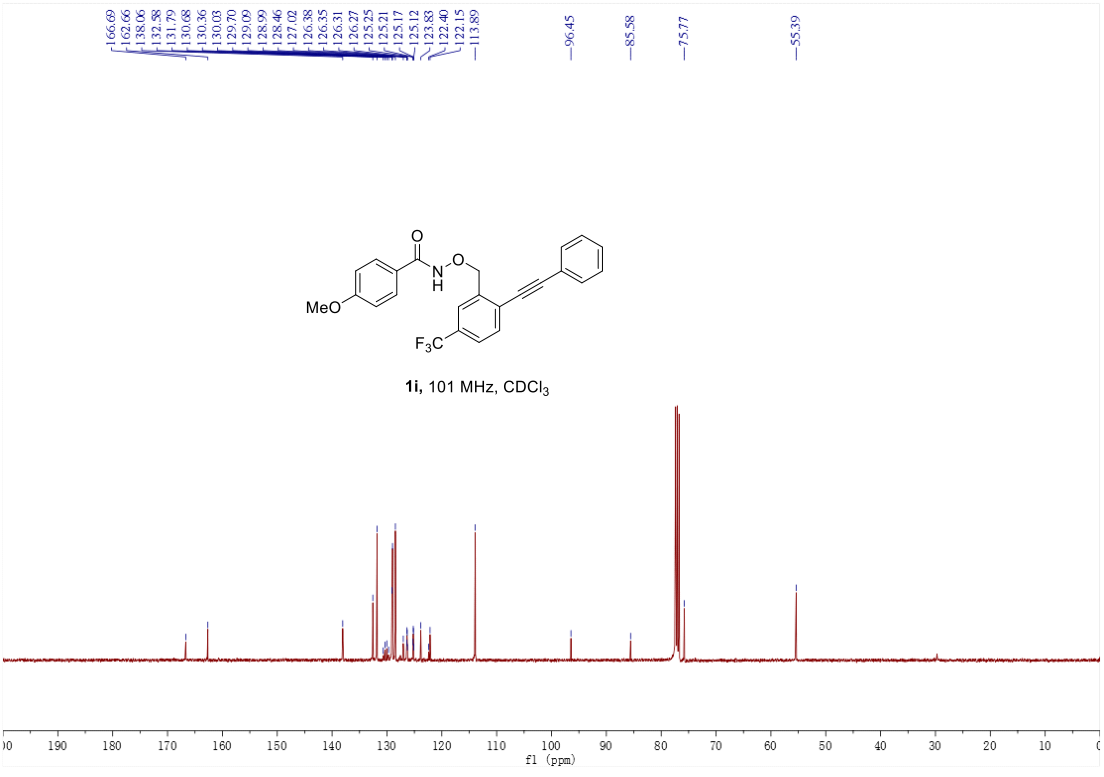

**1h,** 600 MHz, $CDCl_3$



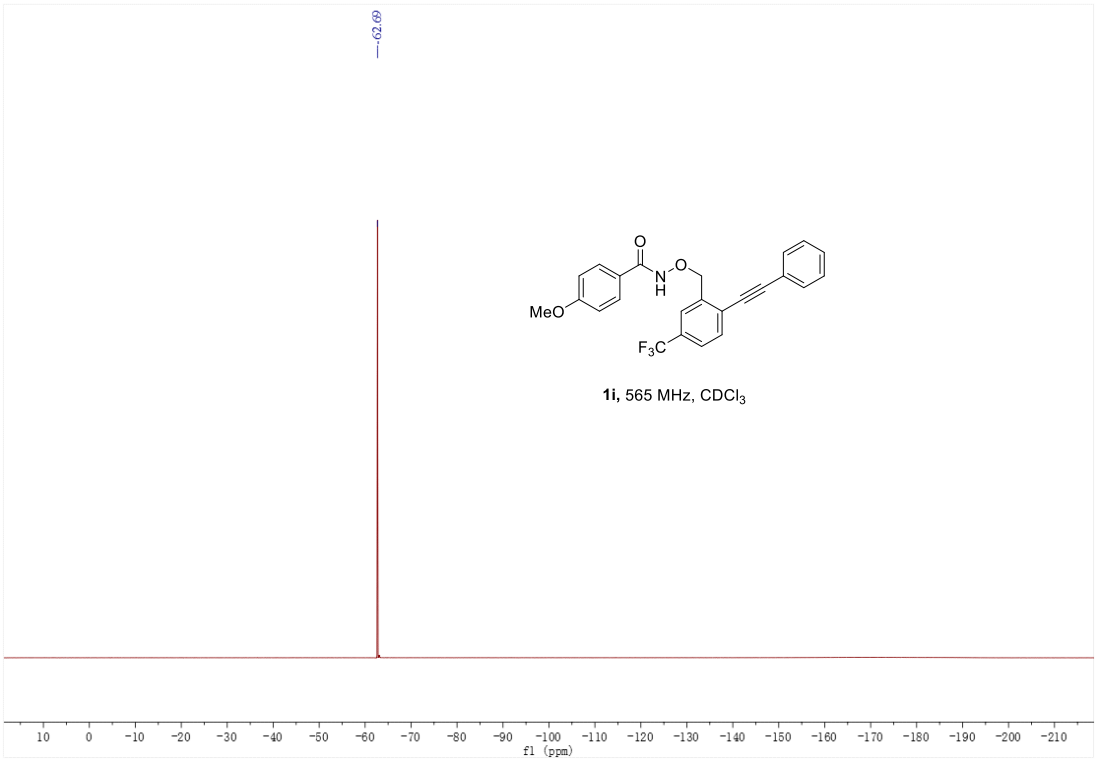

**1h,** 101 MHz, $CDCl_3$



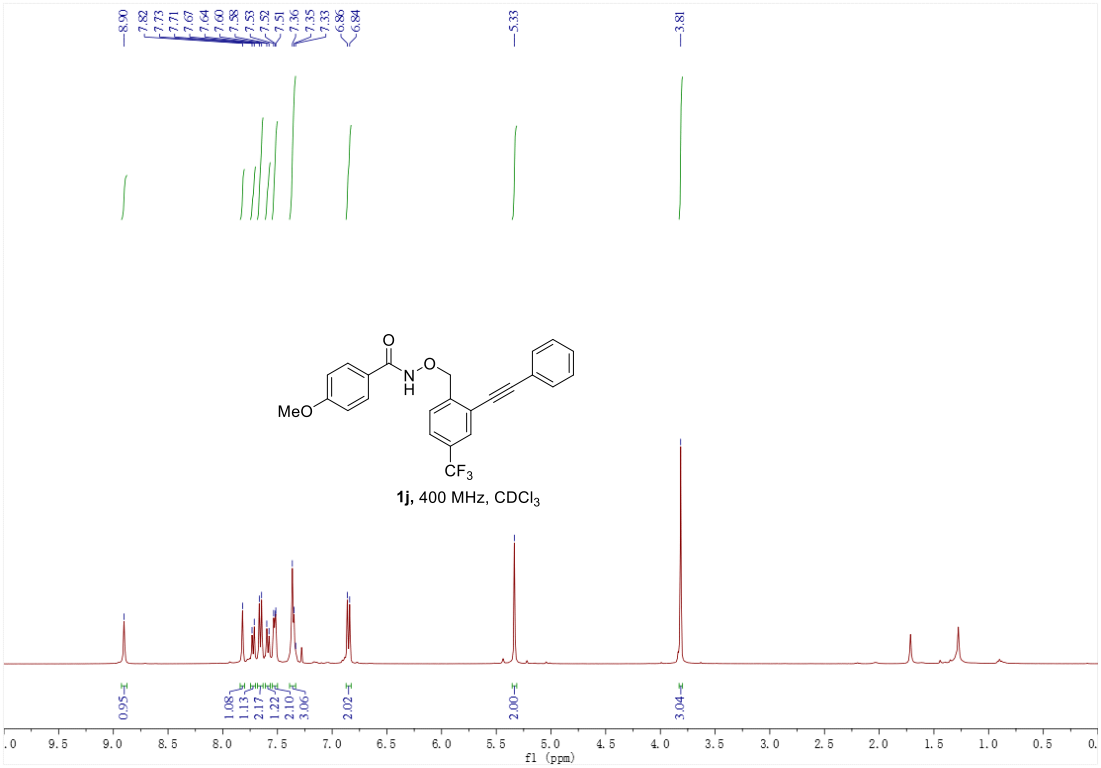

**1i,** 600 MHz, $CDCl_3$



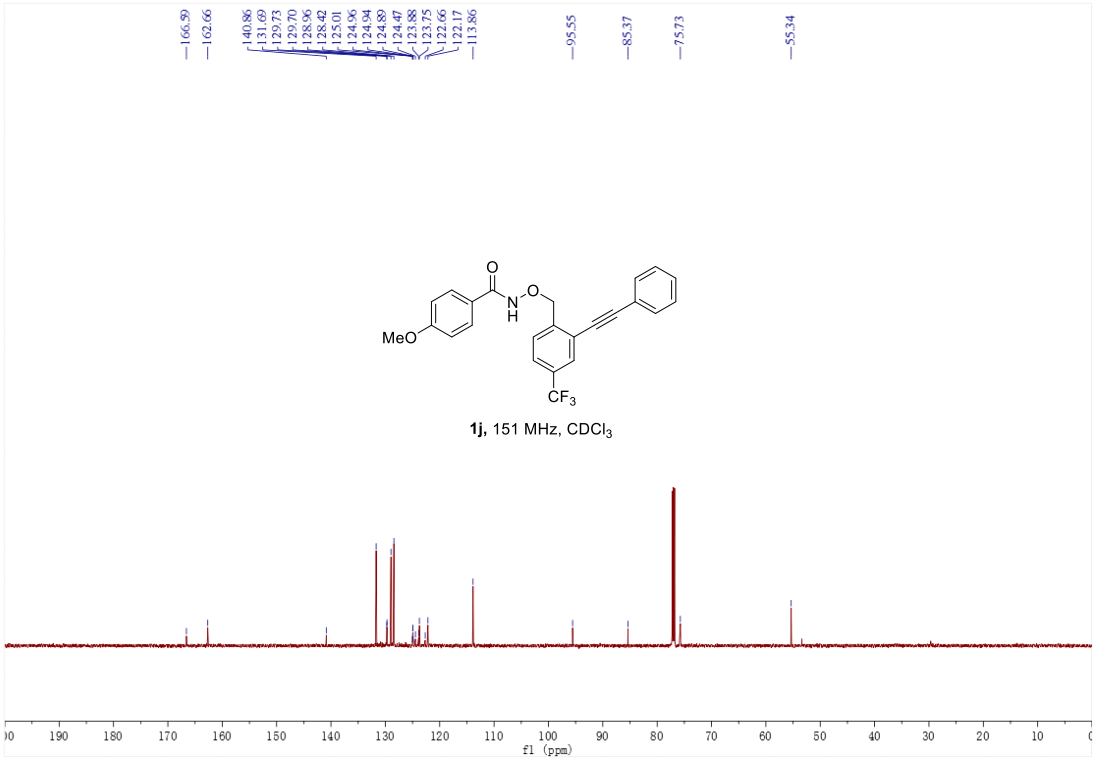

**1i,** 101 MHz, $CDCl_3$



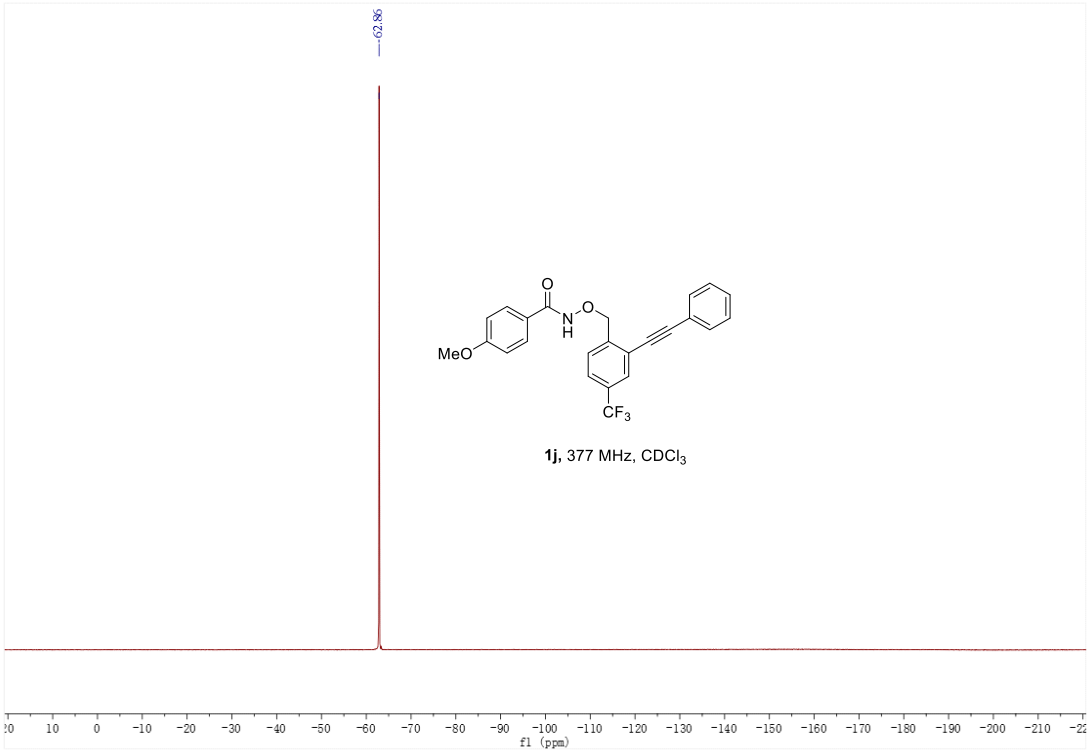

**1i,** 565 MHz, $CDCl_3$



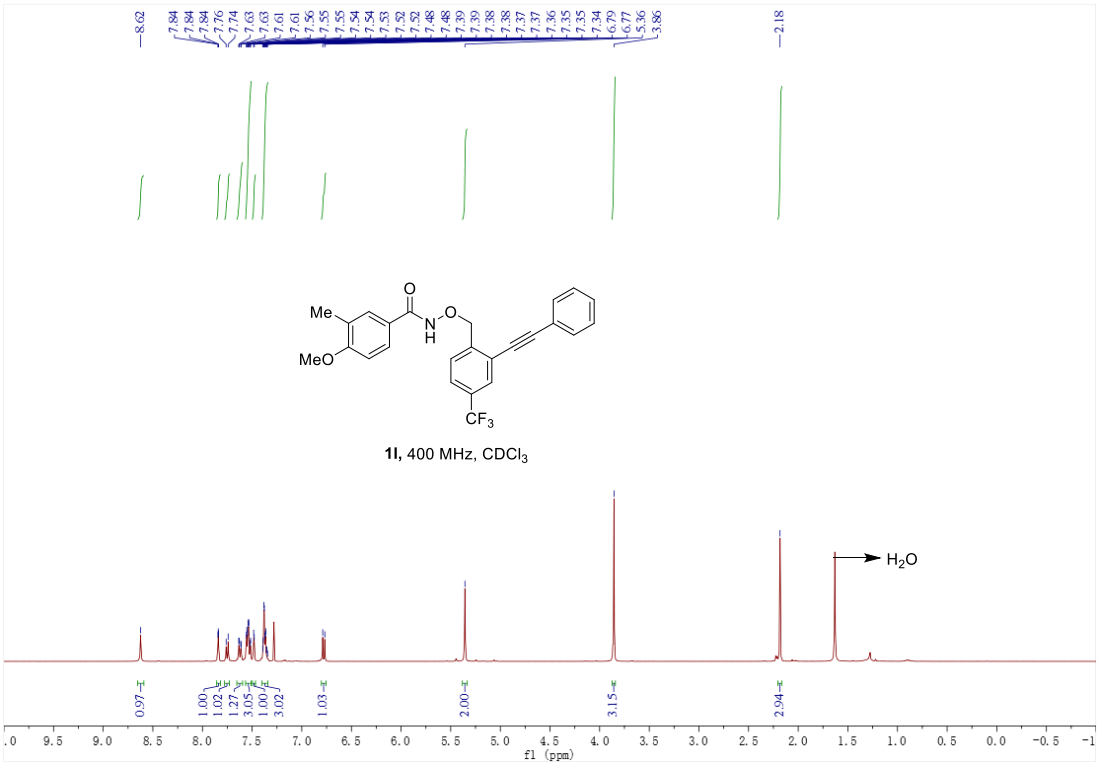

**1j**, 400 MHz, $CDCl_3$



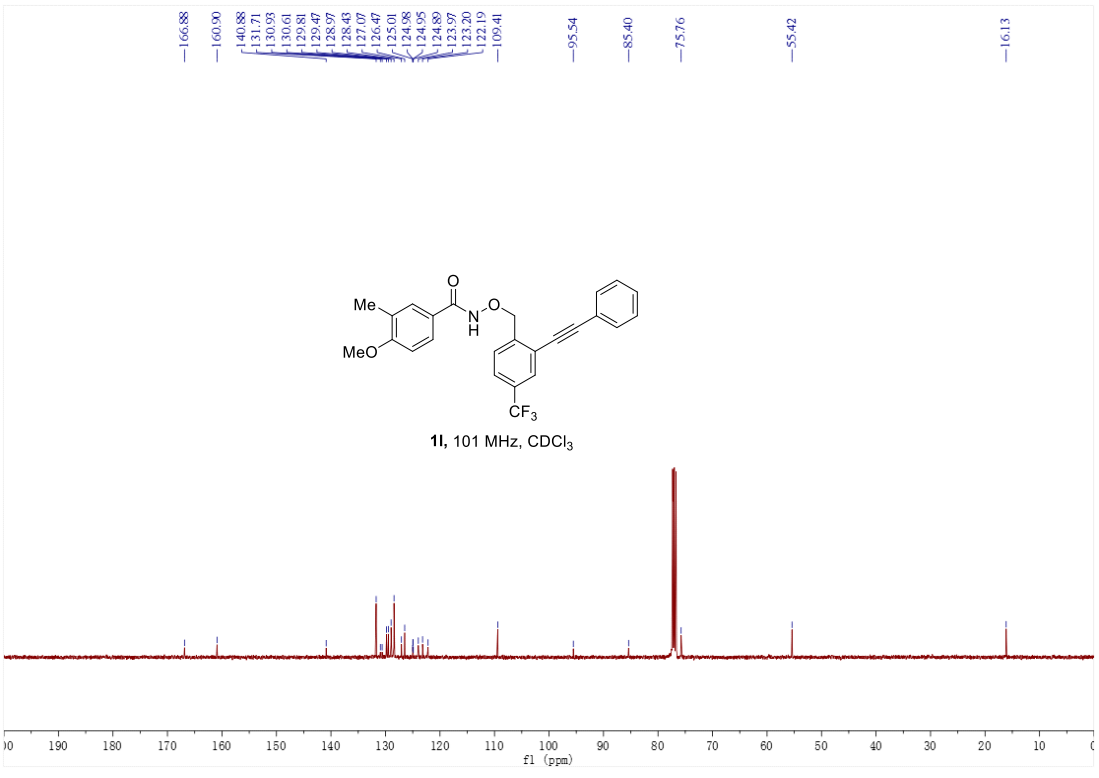

**1j**, 151 MHz, $CDCl_3$



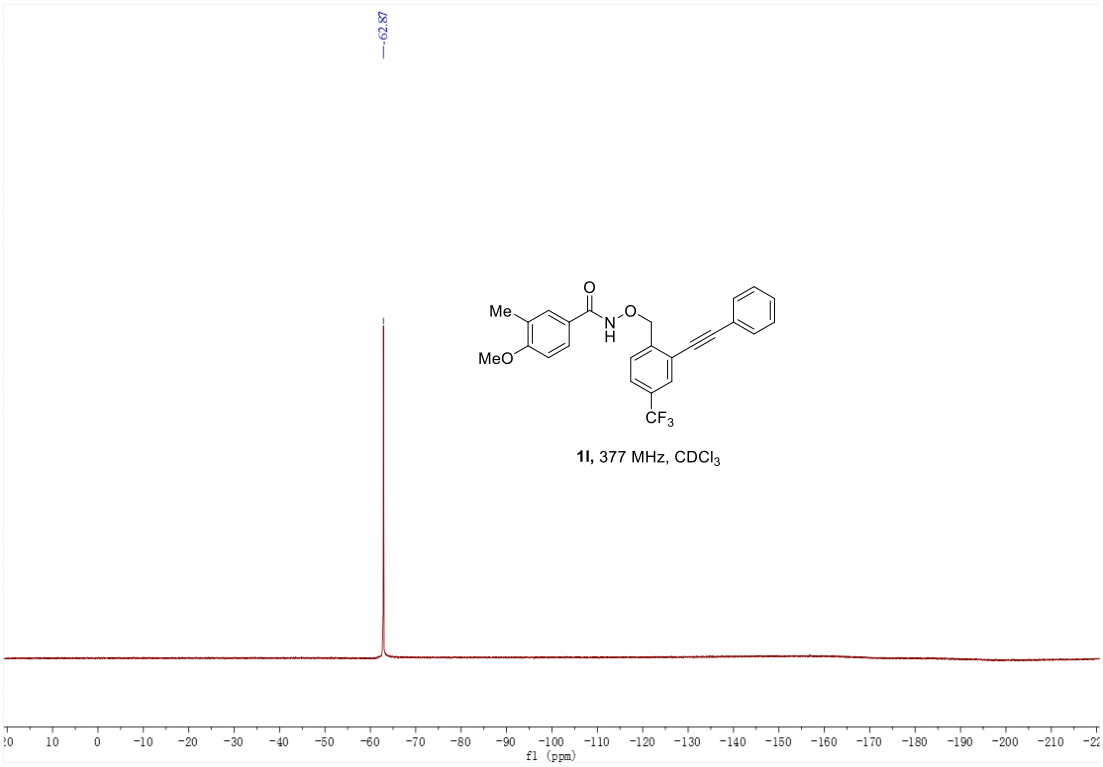

**1j,** 377 MHz, $CDCl_3$



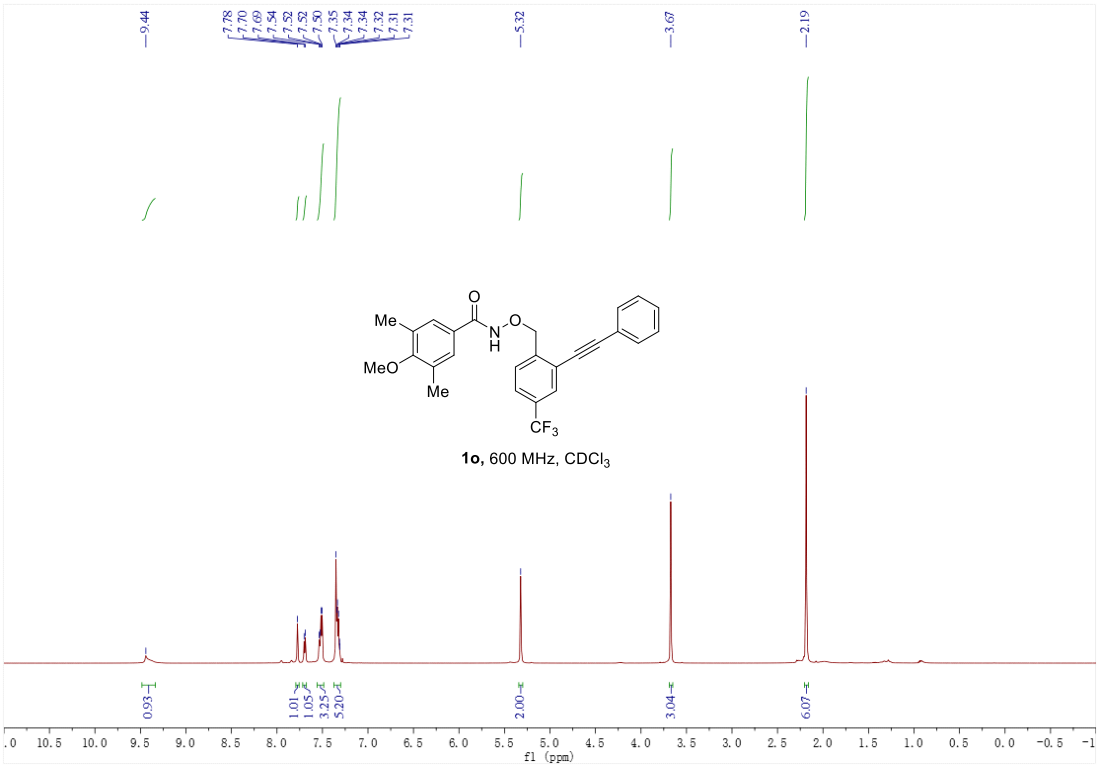

**1l**, 400 MHz, $CDCl_3$



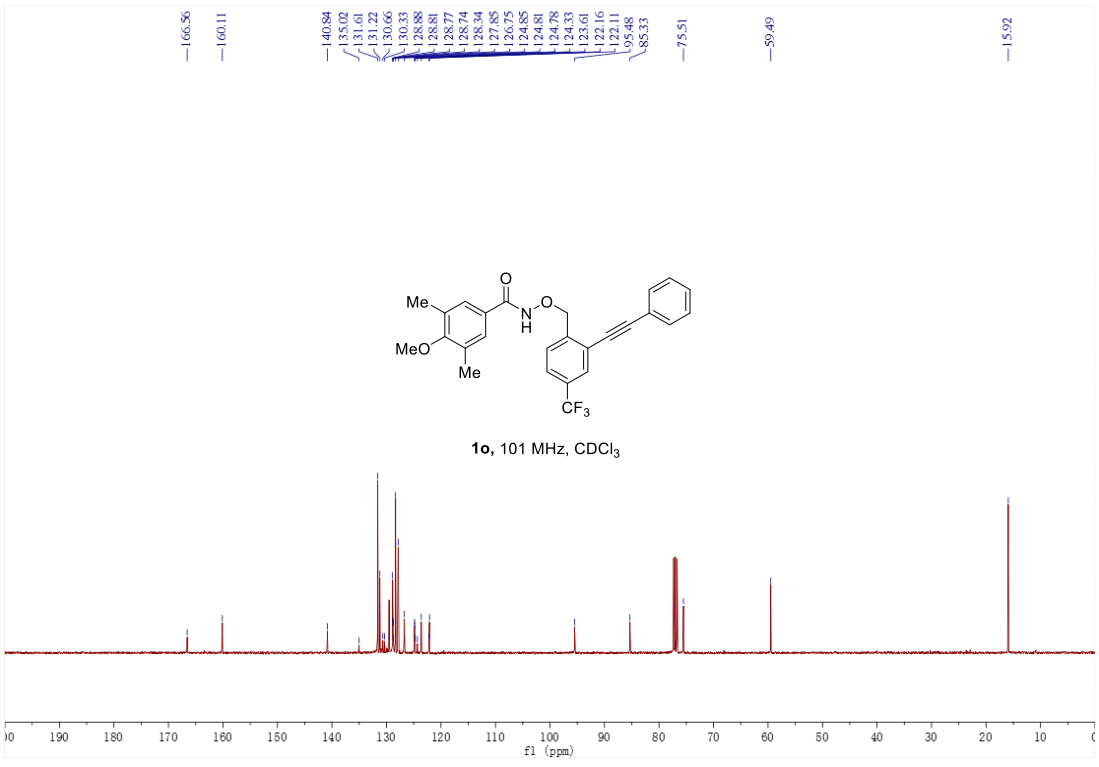

**1l**, 101 MHz, $CDCl_3$



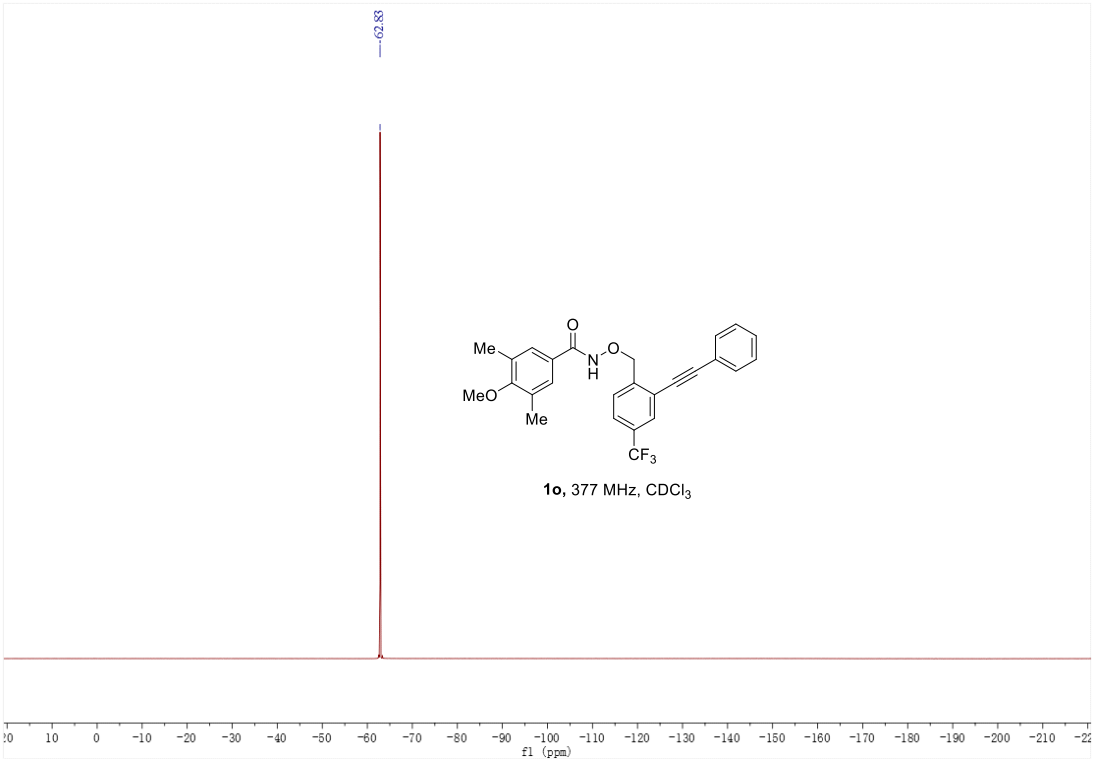

**1l,** 377 MHz, $CDCl_3$



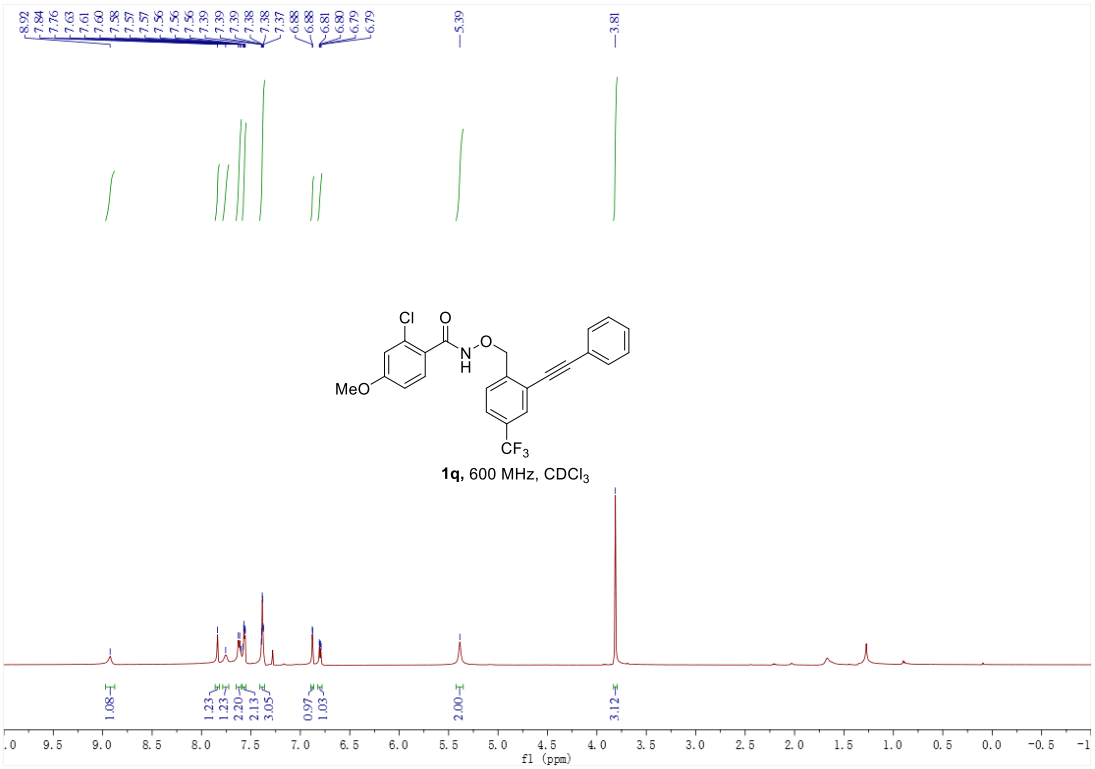

**1o,** 600 MHz, $CDCl_3$



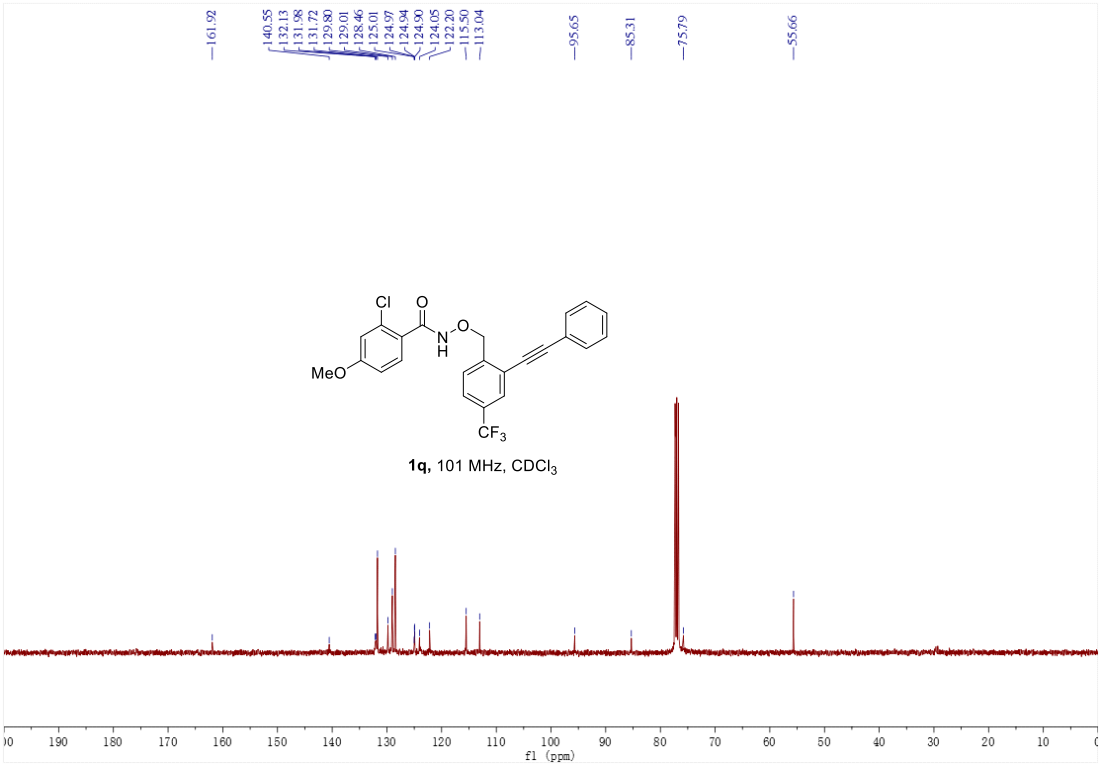

**1o,** 101 MHz, $CDCl_3$



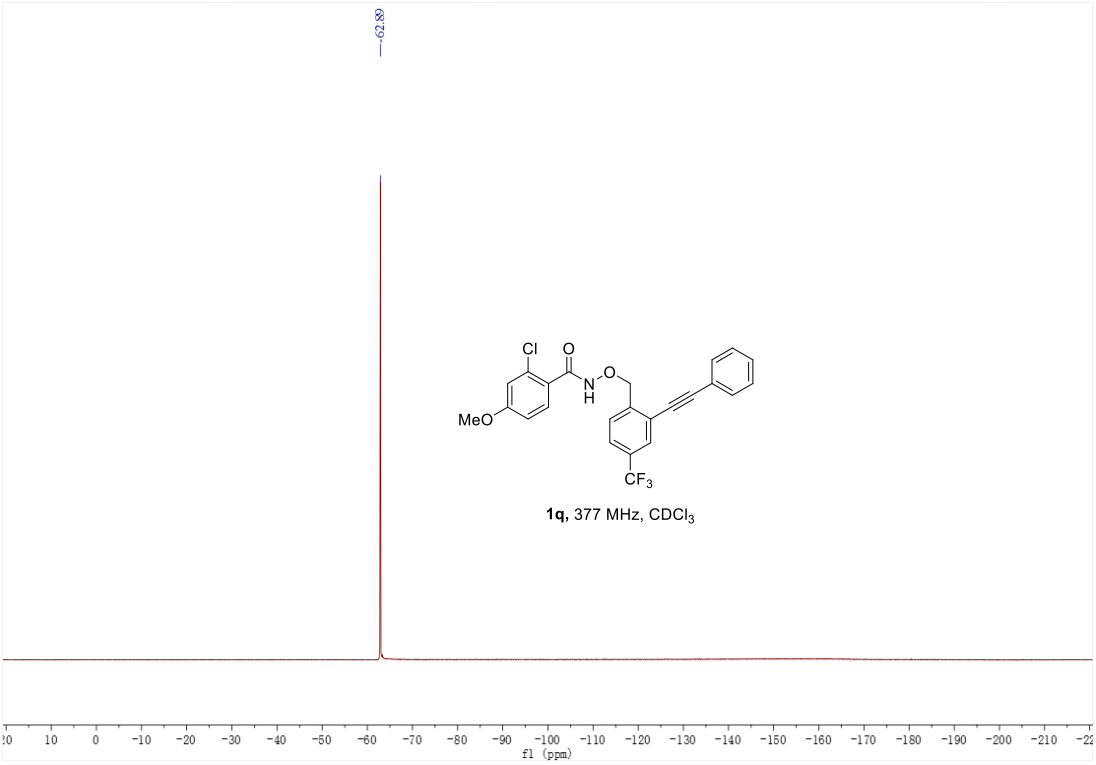

**1o,** 377 MHz, $CDCl_3$



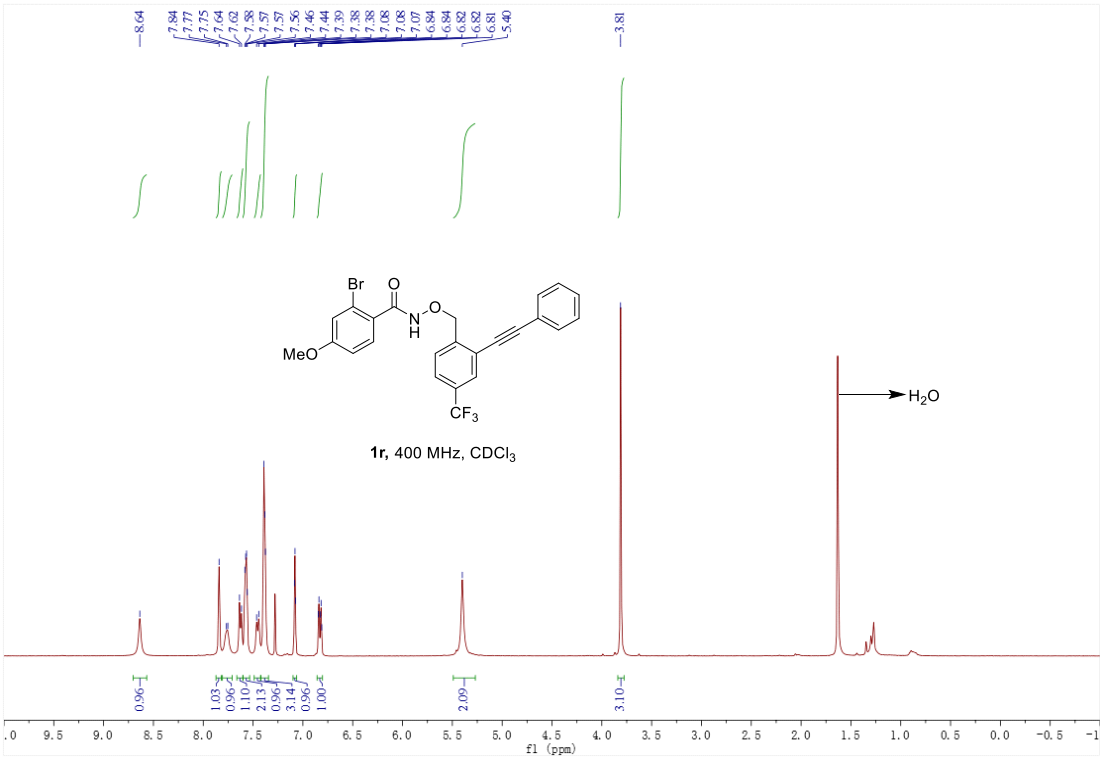

**1q,** 600 MHz, $CDCl_3$



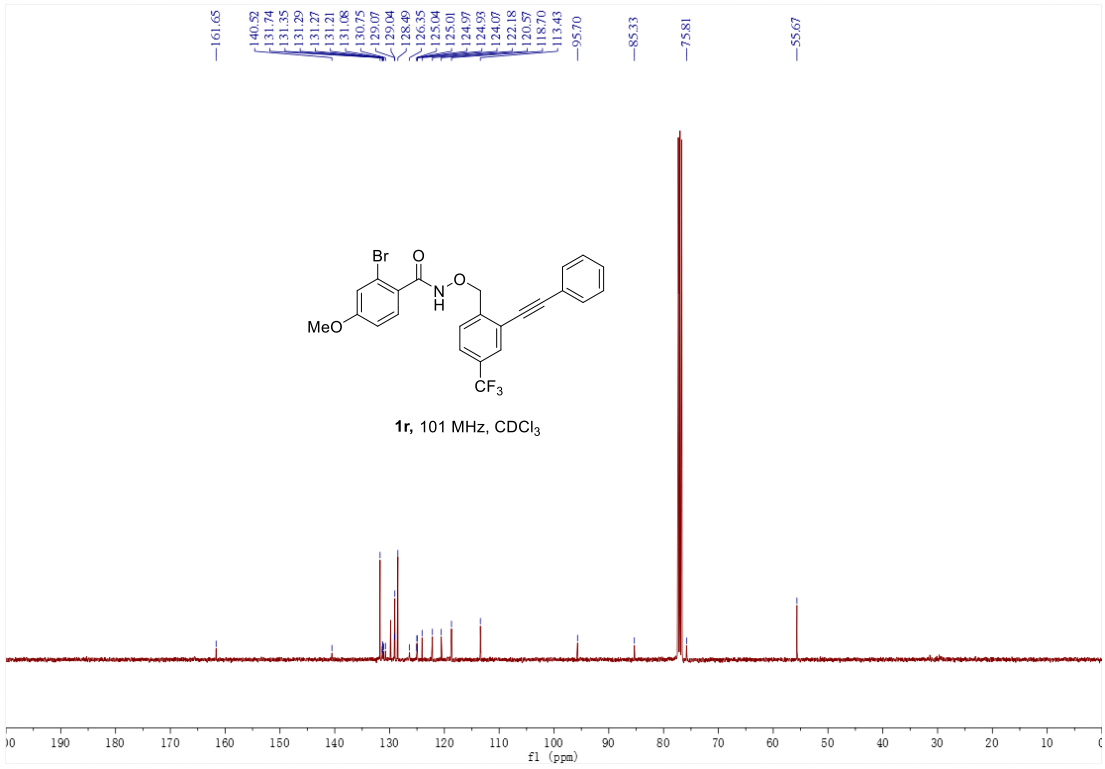

**1q,** 101 MHz, $CDCl_3$



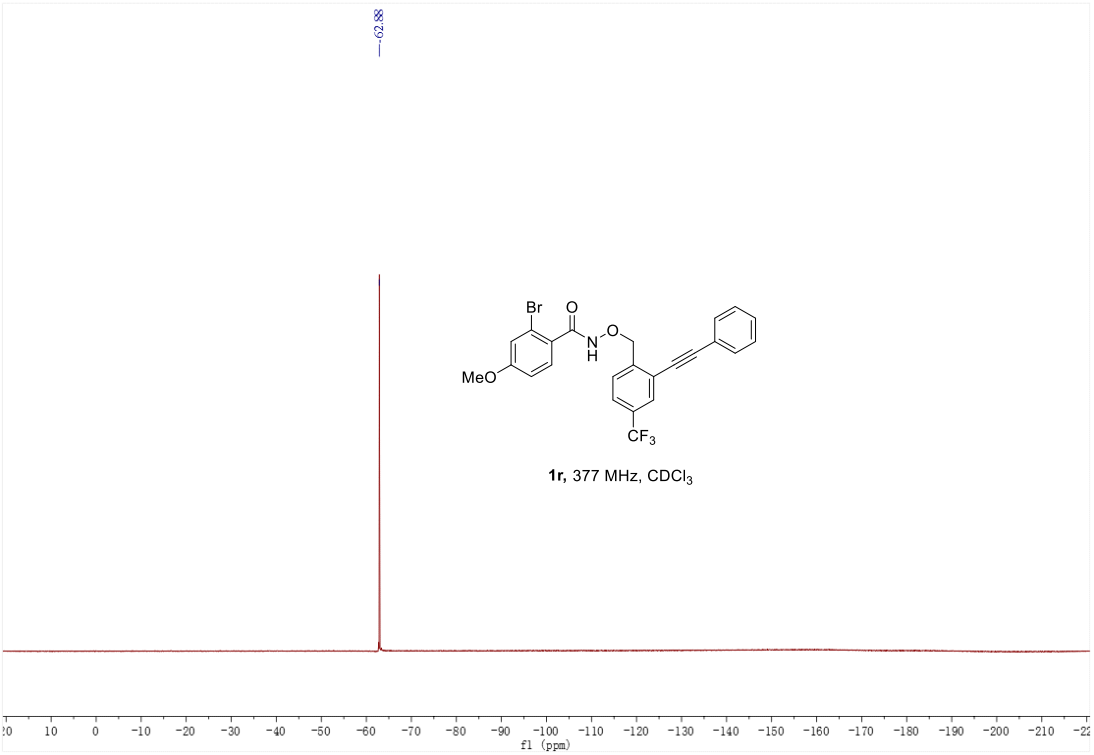

**1q**, 377 MHz, $CDCl_3$



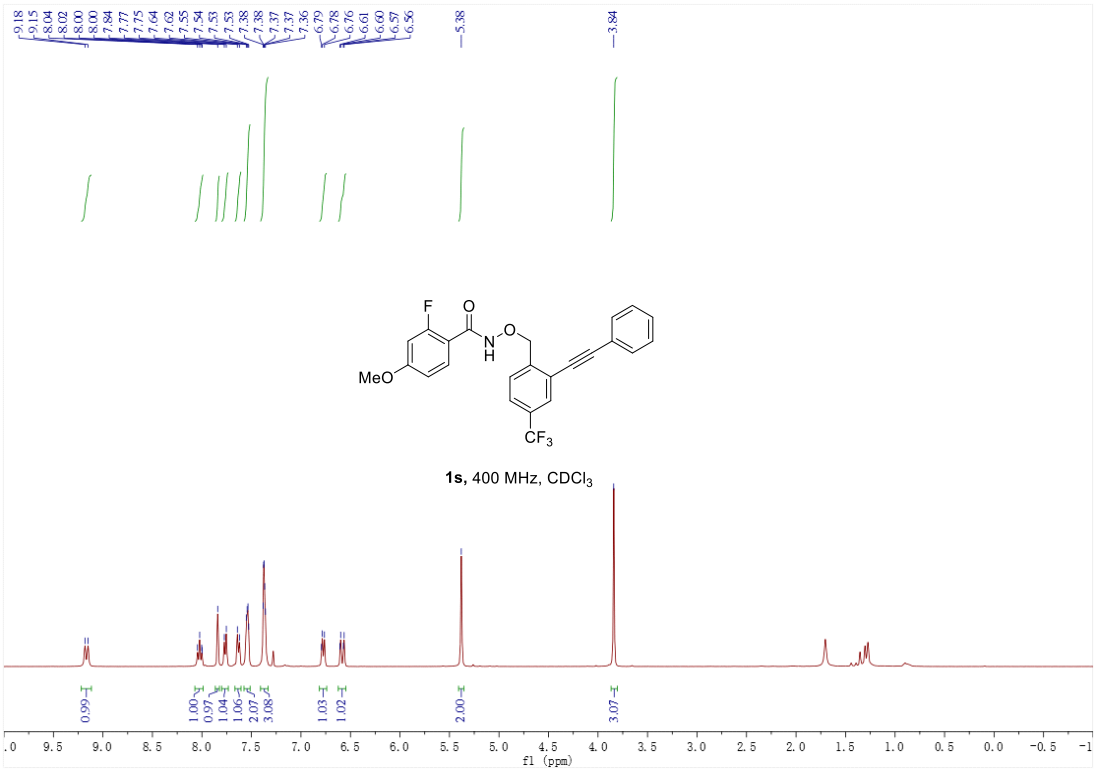

**1r,** 400 MHz, $CDCl_3$



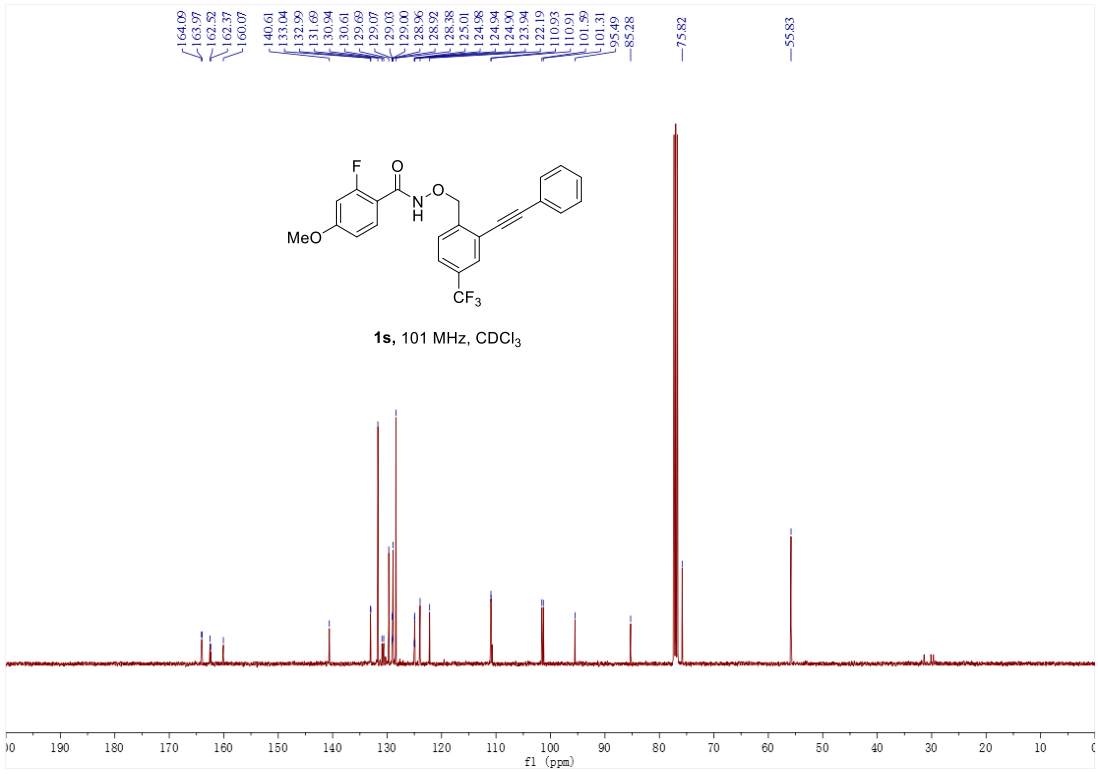

**1r,** 101 MHz, $CDCl_3$



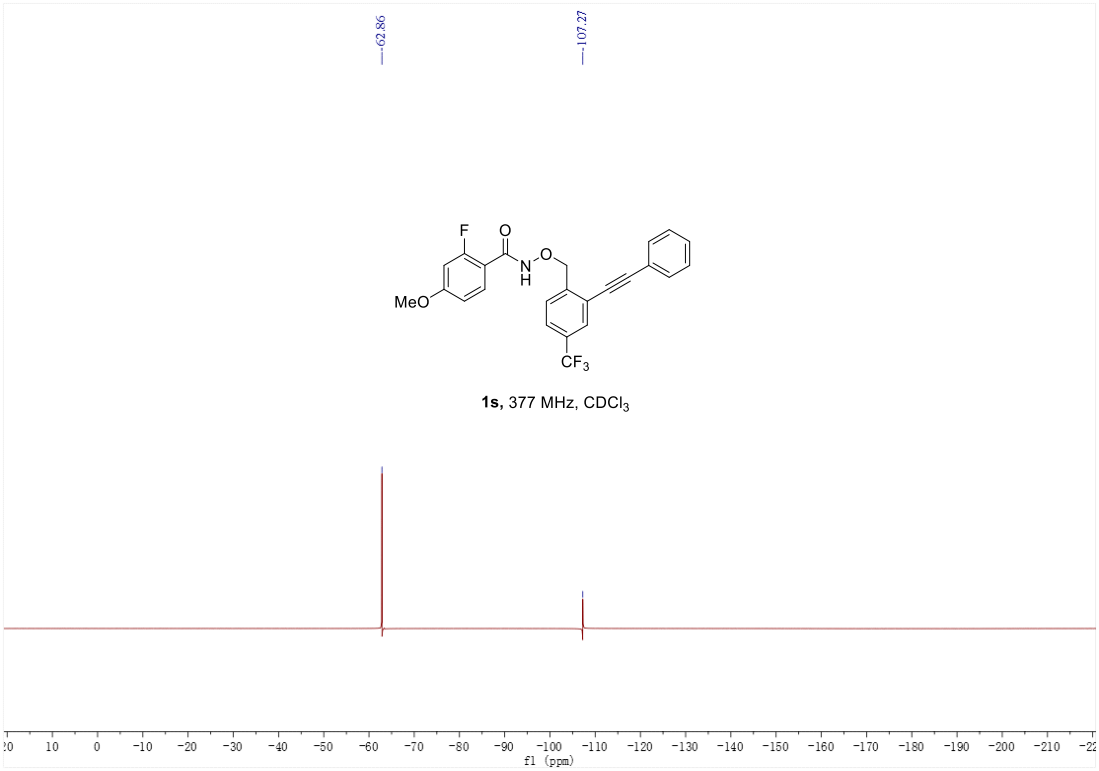

**1r**, 377 MHz, $CDCl_3$



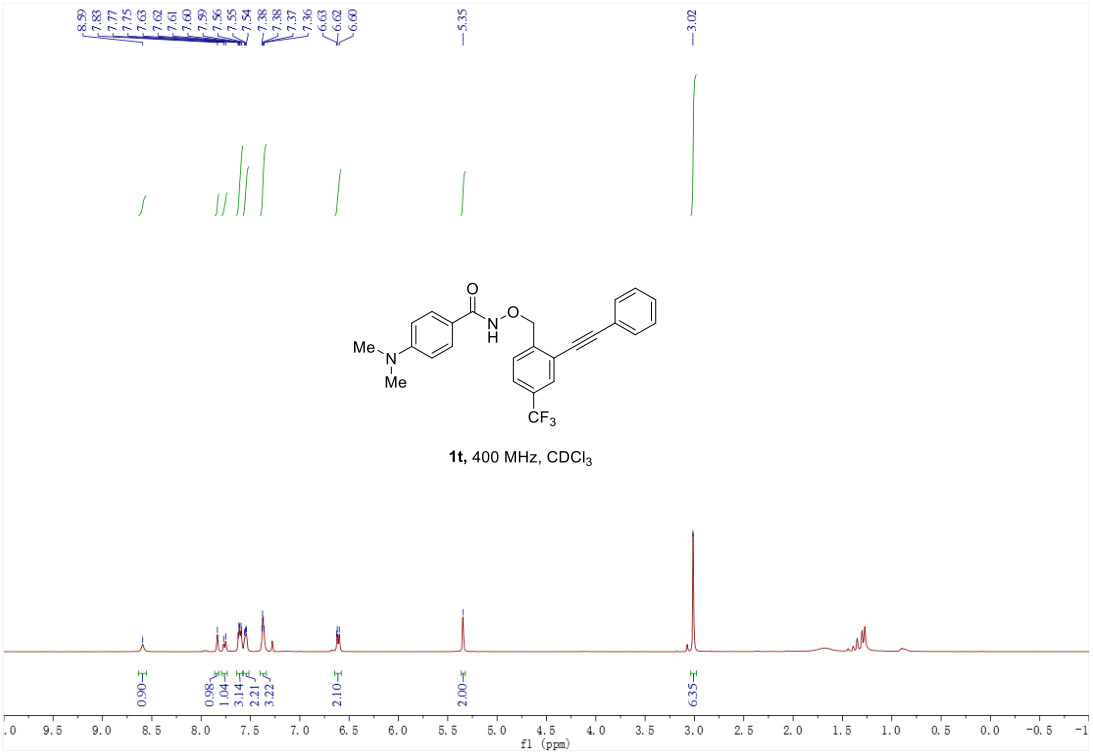

**1s,** 400 MHz, $CDCl_3$



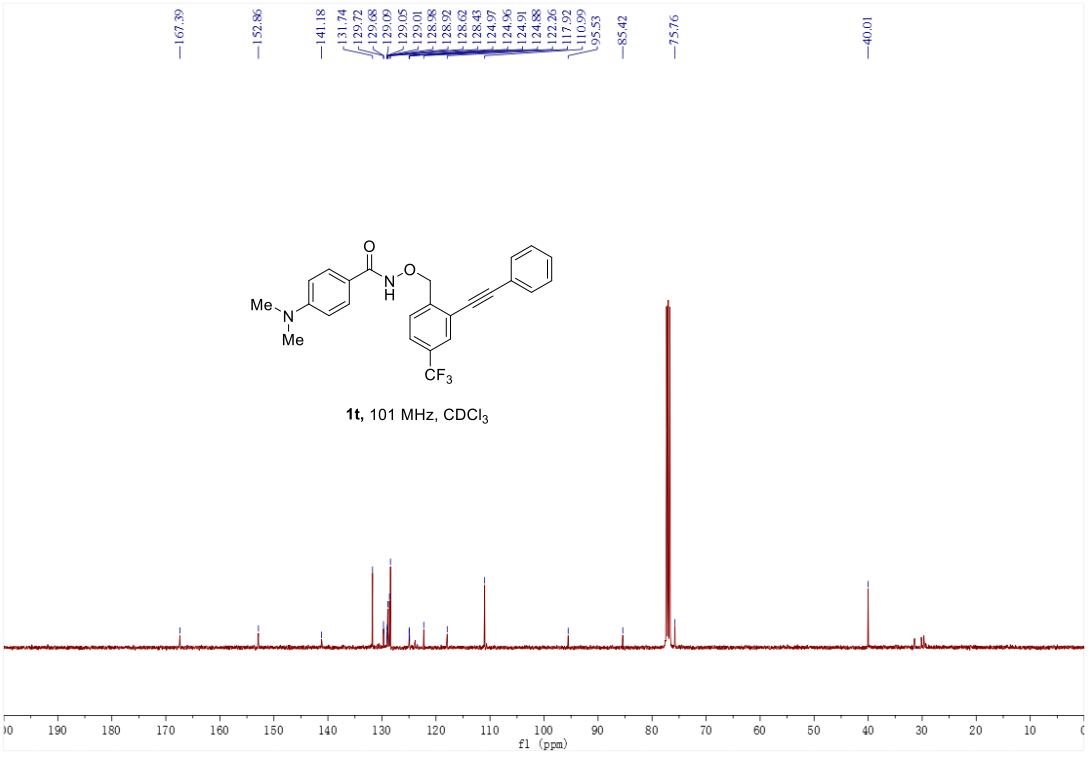

**1s,** 101 MHz, $CDCl_3$



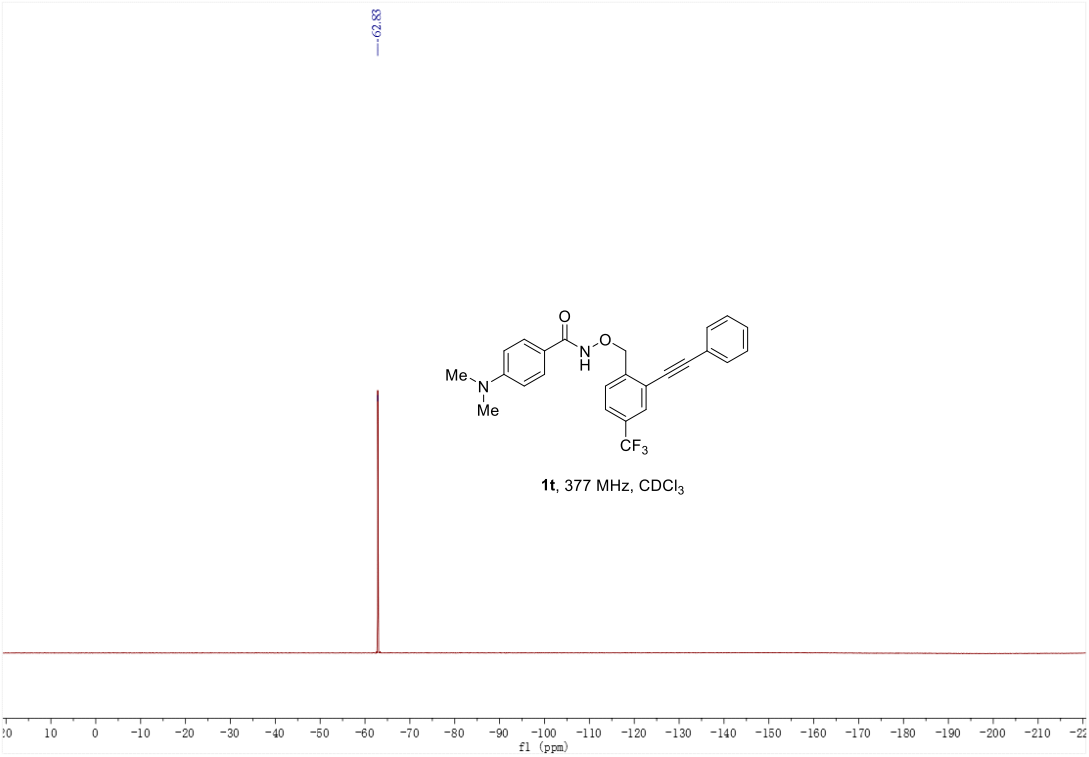

**1s,** 377 MHz, $CDCl_3$




**1t,** 400 MHz, $CDCl_3$




**1t,** 101 MHz, $CDCl_3$




**1t**, 377 MHz, $CDCl_3$