# Metal-Free three-component amino- and carbotrideuteromethylthiolation of alkenes in water

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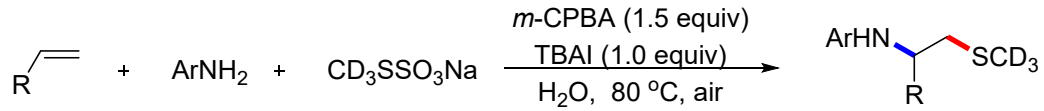
# General Information

$CD_3SSO_3Na$ is a known compound, which is prepared from our previous literature (Org. Chem. Front., 2023, 10, 3213-3218). All other reagents were purchased from Energy Chemical Company in China and used without further purification. $^1H$ NMR (500 MHz), $^{13}C$ NMR (125 MHz) and $^{19}F$ NMR (470 MHz) spectra were recorded in $CDCl_3$ and DMSO-D6 solutions using a Burker AVANCE 500 spectrometer. High-resolution mass spectra were recorded on an ESI-Q-TOF mass spectrometer. Analysis of crude reaction mixture was done on the Varian 4000 GC/MS and 1200 LC. All reactions were conducted using standard Schlenk techniques. Column chromatography was performed using EM silica gel 60 (300−400 m).

# General Experimental Procedures

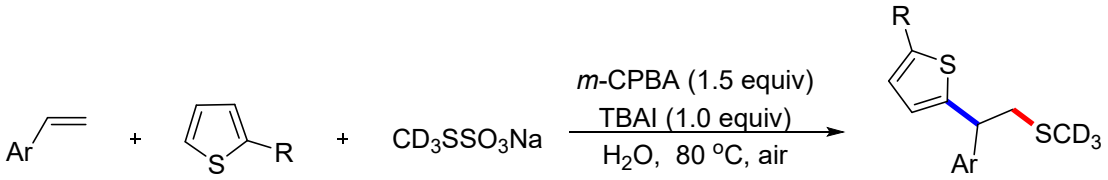
## General Procedure of Aminotrideuteromethylthiolation of Alkenes with Arylamines and $CD_3SSO_3Na$:




**1a** **2** **4, 5**

A 25 mL Schlenk tube equipped with a stir bar was charged with substituted alkene (0.2 mmol), arylamines (0.4 mmol), $CD_3SSO_3Na$ (0.4 mmol), *m*-CPBA (0.3 mmol), TBAI (0.2 mmol) and 2.0 mL water. Then, the reaction tubes are plugged tightly with teflon stoppers. The reaction mixture was stirred at 80 ℃ for 24 h. After cooling down, the reaction mixture was diluted with 10 mL of ethyl ether and filtered by silica gel powder, and concentrated under reduced pressure. The residue was then purified by flash chromatography on silica gel to provide the corresponding product.

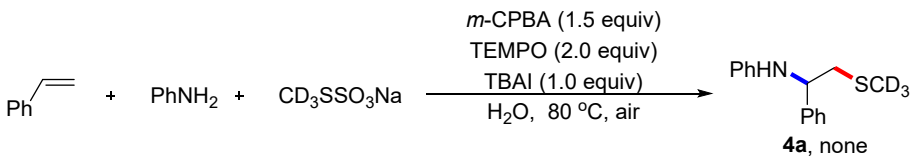
## General Procedure of Carbotrideuteromethylthiolation of Alkenes with Thiophene and $CD_3SSO_3Na$:




**1a** **3** **6**

A 25 mL Schlenk tube equipped with a stir bar was charged with substituted alkene (0.2 mmol), substituted thiophene (0.4 mmol), $CD_3SSO_3Na$ (0.4 mmol), *m*-CPBA (0.3 mmol), TBAI (0.2 mmol) and 2.0 mL water. Then, the reaction tubes are plugged tightly with teflon stoppers. The reaction mixture was stirred at 80 ℃ for 24 h. After cooling down, the reaction mixture was diluted with 10 mL of ethyl ether and filtered by silica gel powder, and concentrated under reduced pressure. The residue was then purified by flash chromatography on silica gel to provide the corresponding product.

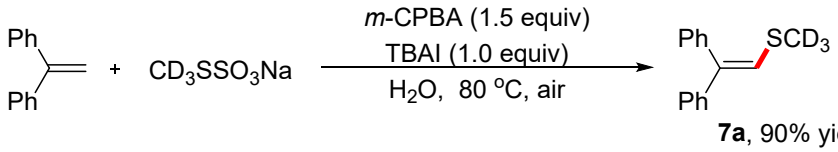
### Mechanistic Studies




**4a**, none (eq. 1)

A 25 mL Schlenk tube equipped with a stir bar was charged with styrene (0.2 mmol), aniline (0.4 mmol), $CD_3SSO_3Na$ (0.4 mmol), , *m*-CPBA (0.3 mmol), TBAI (0.2 mmol), TEMPO (0.4 mmol) and 2.0 mL water. Then, the reaction tubes are plugged tightly with teflon stoppers. The reaction

mixture was stirred at 80 ℃ for 24 h. After cooling down, the reaction mixture was diluted with 10 mL of ethyl ether and filtered by silica gel powder, none of **4a** was detected by GC-MS.

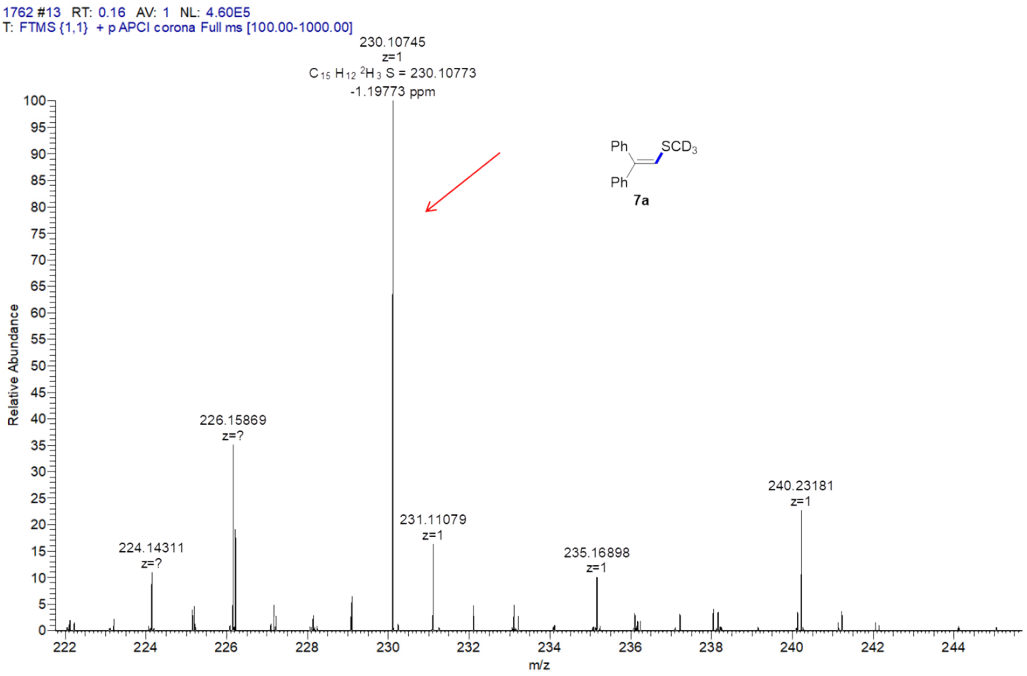


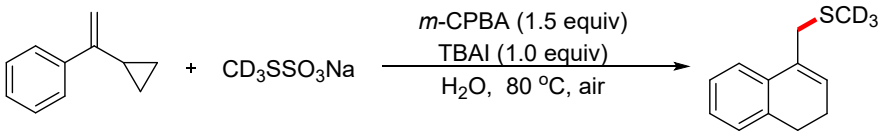

(eq. 2)

**7a**, 90% yield

A 25 mL Schlenk tube equipped with a stir bar was charged with 1,1-diphenylethylene (0.2 mmol), $CD_3SSO_3Na$ (0.4 mmol), m-CPBA (0.3 mmol), TBAI (0.2 mmol) and 2.0 mL water. The tube was fitted with a rubber septum, and then the reaction mixture was stirred at 80 ℃ for 24 h. After the reaction mixture was cooled to room temperature and the reaction was filtered through a pad of Celite and diluted with ethyl acetate (10 mL), **7a** was isolated.

The NMR data of the target product **7a** is consistent with previously our reported publication (Org. Chem. Front., 2023, 10, 3213-3218).



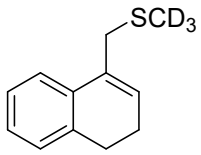




(eq. 3)

**7b**, 92% yield

A 25 mL Schlenk tube equipped with a stir bar was charged with (1-cyclopropylvinyl)benzene (0.2 mmol), $CD_3SSO_3Na$ (0.4 mmol), m-CPBA (0.3 mmol), TBAI (0.2 mmol) and 2.0 mL water. The tube was fitted with a rubber septum, and then the reaction mixture was stirred at 80 ℃ for 24 h. After the reaction mixture was cooled to room temperature and the reaction was filtered through a pad of Celite and diluted with ethyl acetate (10 mL), **7b** was isolated.

**((3,4-dihydronaphthalen-1-yl)methyl)(methyl-d3)sulfane**

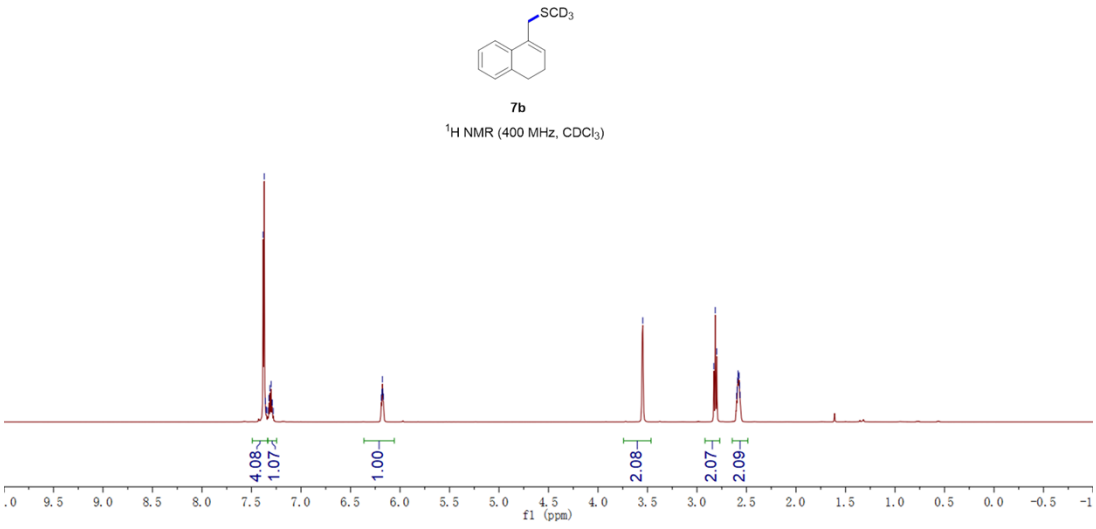


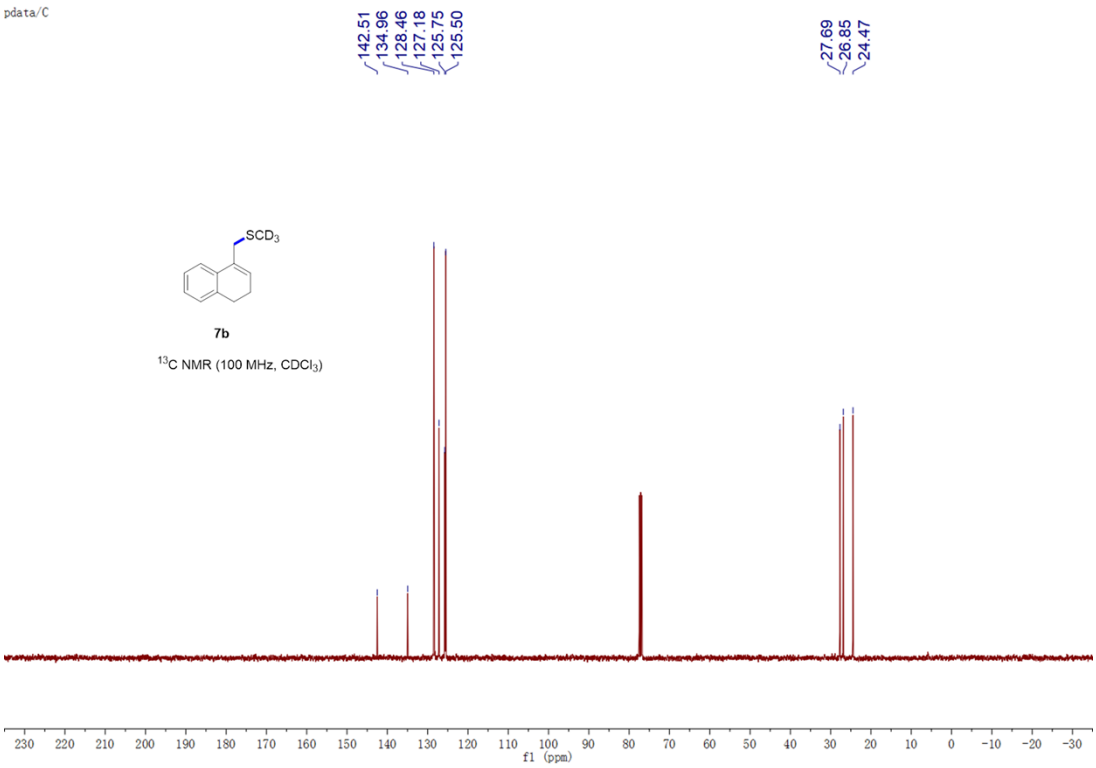

**7b**

**$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 4.3 Hz, 4H), 7.33-7.28 (m, 1H), 6.19-6.17 (m, 1H), 3.55 (s, 2H), 2.82 (t, *J* = 5.9 Hz, 2H), 2.58 (dp, *J* = 5.9, 2.0 Hz, 2H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 142.51, 134.96, 128.46, 127.18, 125.75, 125.50, 27.69, 26.85, 24.47.

**HRMS** (ESI): calcd for $C_{12}H_{12}D_3S$ $[M+H]^+$ 194.1083, found 194.1075.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128.46
127.18
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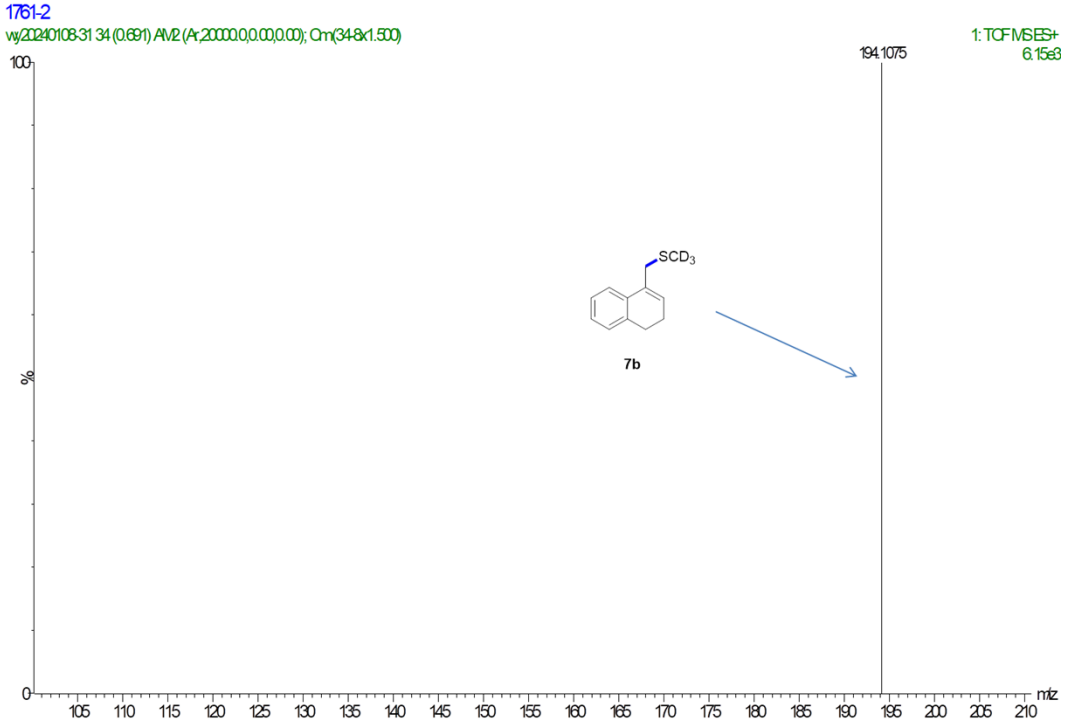
26.85
24.47
SCD3
7b
13C NMR (100 MHz, CDCl3)
f1 (ppm)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6.15e3
194.1075
100
%
0
SCD3
7b
m/z

**Cyclic Voltammetry Studies**

The cyclic voltammograms were recorded in an electrolyte of $Bu_4NPF_6$ (0.1 M) in $CH_3CN$ using a glassy carbon disk working electrode (diameter, 3 mm), a Pt wire auxiliary electrode and a SCE reference electrode. The scan rate is 100 mV/s.

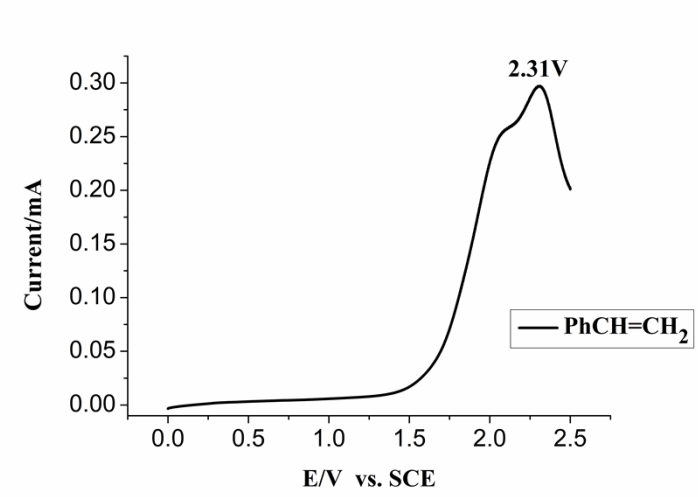



**Figure S1:**

Figure S1: Cyclic voltammogram of 10 mM $PhCH=CH_2$ obtained in $CH_3CN$ containing 0.1 M $Bu_4NPF_6$ at a 3 mm diameter planar glassy carbon (GC) electrode and at a scan rate of 0.1 V $s^{-1}$ at room temperature. Starting point is 0 v and positive direction of scan.

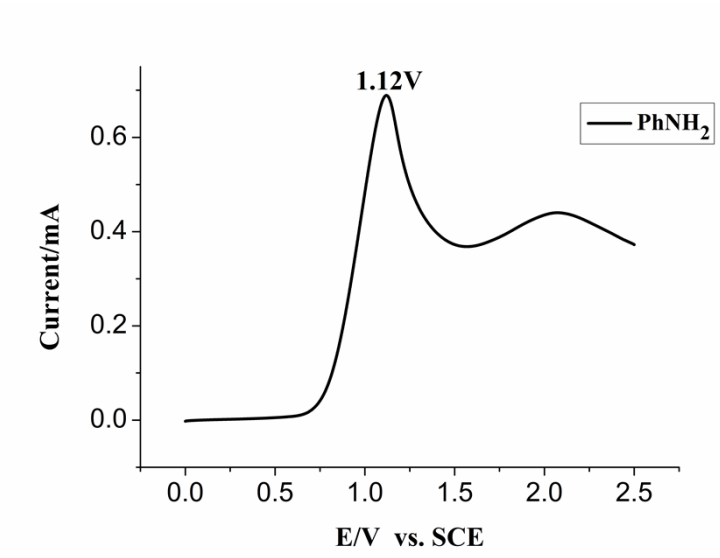



**Figure S2**

Figure S2: Cyclic voltammogram of 10 mM $PhNH_2$ obtained in $CH_3CN$ containing 0.1 M $Bu_4NPF_6$ at a 3 mm diameter planar glassy carbon (GC) electrode and at a scan rate of 0.1 V $s^{-1}$ at room temperature. Starting point is 0 v and positive direction of scan.

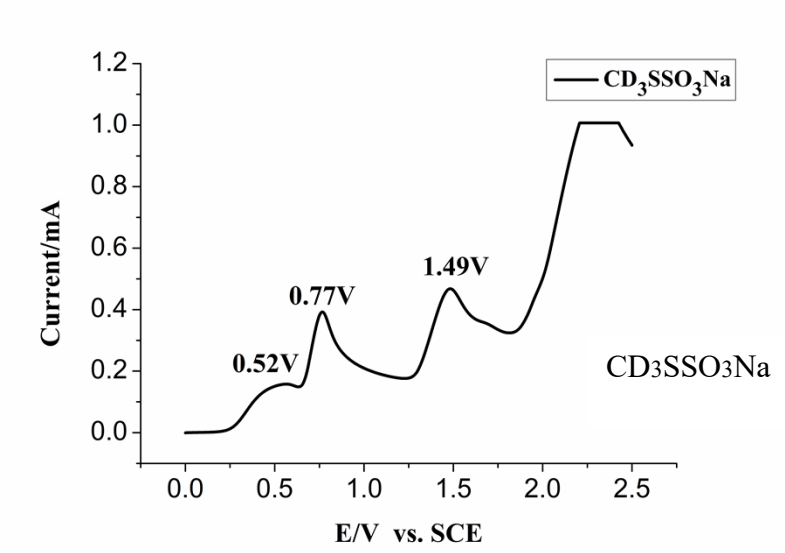
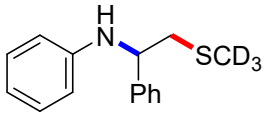



**Figure S3**

Figure S3: Cyclic voltammogram of 10 mM $CD_3SSO_3Na$ obtained in $CH_3CN$ containing 0.1 M $Bu_4NPF_6$ at a 3 mm diameter planar glassy carbon (GC) electrode and at a scan rate of 0.1 V $s^{-1}$ at room temperature. Starting point is 0 v and positive direction of scan.

# Characterization of Products in Details :

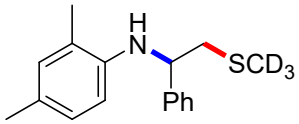
**N-(2-((methyl-d3)thio)-1-phenylethyl)aniline**




**4a**

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (42.3 mg, 86% yield). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.17 (t, *J* = 7.9 Hz, 2H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 7.8 Hz, 2H), 4.72 (s, 1H), 4.50 (dd, *J* = 9.1, 4.5 Hz, 1H), 3.06 (dd, *J* = 13.6, 4.5 Hz, 1H), 2.86 (dd, *J* = 13.6, 9.0 Hz, 1H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 147.55, 142.89, 129.20, 128.94, 127.58, 126.45, 117.95, 113.98, 56.43, 42.52. **HRMS** (ESI): calcd for $C_{15}H_{15}DNS$ $[M + H]^+$ 247.1343, found 247.1340.

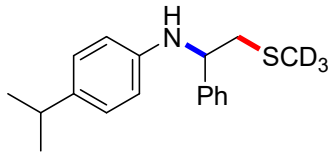
**2,4-dimethyl-N-(2-((methyl-d3)thio)-1-phenylethyl)aniline**




**4b**

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (49.8 mg, 91% yield). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 7.3 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 6.99 (s, 1H), 6.81 (d, *J* = 8.1 Hz, 1H), 6.29 (d, *J* = 8.1 Hz, 1H), 4.60 (s, 1H), 4.49 (dd, *J* = 9.3, 4.2 Hz, 1H), 3.10 (dd, *J* = 13.6, 4.3 Hz, 1H), 2.89 (dd, *J* = 13.6, 9.4 Hz, 1H), 2.37 (s, 3H), 2.27 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 143.27, 143.24, 131.01, 128.94, 127.49, 127.20, 126.66, 126.40, 123.15, 111.75, 56.45, 42.81, 20.45, 17.75. **HRMS** (ESI): calcd for $C_{17}H_{18}DNaS$ $[M + Na]^+$ 297.1481, found 297.1479.

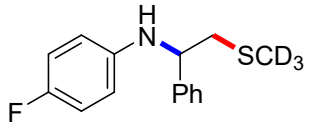
**4-isopropyl-N-(2-((methyl-d3)thio)-1-phenylethyl)aniline**




**4c**

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (51.8 mg, 90% yield). **$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 7.4 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.59 (d, *J* = 8.4 Hz, 2H), 4.64 (s, 1H), 4.46 (dd, *J* = 9.2, 4.4 Hz, 1H), 3.04 (dd, *J* = 13.6, 4.4 Hz, 1H), 2.85 (dd, *J* = 13.7, 8.7 Hz, 2H), 1.25 (d, *J* = 6.9 Hz, 6H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 145.64, 143.24, 138.39, 128.93, 127.53, 127.06, 126.50, 114.01, 56.73, 42.65, 33.23, 24.32. **HRMS** (ESI): calcd for $C_{18}H_{21}D_3NS$ $[M + H]^+$ 289.1818, found 289.1813.

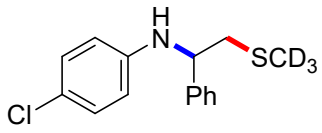
**4-fluoro-N-(2-((methyl-d3)thio)-1-phenylethyl)aniline**




**4d**

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (38.0 mg, 72% yield). **$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 7.49-7.40 (m, 4H), 7.35 (t, *J* = 7.1 Hz, 1H), 6.88 (t, *J* = 8.7 Hz, 2H), 6.56 (dd, *J* = 7.8, 5.5 Hz, 2H), 4.62 (brs, 1H), 4.43 (dd, *J* = 9.3, 4.4 Hz, 1H), 3.06 (dd, *J* = 13.7, 4.4 Hz, 1H), 2.85 (dd, *J* = 13.6, 9.2 Hz, 1H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 156.14 (d, *J* = 235.4 Hz), 143.94 (d, *J* = 1.9 Hz), 142.74, 129.02, 127.70, 126.47, 115.63 (d, *J* = 22.2 Hz), 114.85 (d, *J* = 7.3 Hz), 56.97, 42.59. **$^{19}$F NMR** (375 MHz, $CDCl_3$) δ -127.32 (1F); **HRMS** (ESI): calcd for $C_{15}H_{12}D_3NFS$ $[M - H]^+$ 263.1098, found 263.1099.

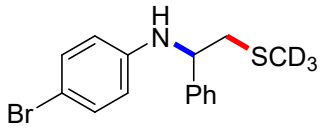
**4-chloro-N-(2-((methyl-d3)thio)-1-phenylethyl)aniline**




**4e**

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (36.4 mg, 65% yield). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.46-7.39 (m, 4H), 7.36-7.32 (m, 1H), 7.10 (d, *J* = 8.8 Hz, 2H), 6.53 (d, *J* = 8.8 Hz, 2H), 4.76 (s, 1H), 4.45 (dt, *J* = 8.2, 3.8 Hz, 1H), 3.05 (dd, *J* = 13.7, 4.4 Hz, 1H), 2.84 (dd, *J* = 13.7, 9.1 Hz, 1H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 146.08, 142.37, 129.04, 127.76, 126.39, 122.57, 115.10, 56.47, 42.44. **HRMS** (ESI): calcd for $C_{15}H_{12}D_3NSCl$ $[M - H]^+$ 279.0802, found 279.0807.

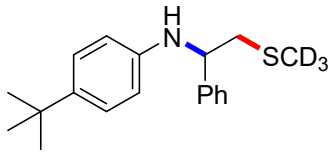
**4-bromo-N-(2-((methyl-d3)thio)-1-phenylethyl)aniline**




**4f**

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (47.9 mg, 74% yield). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.45-7.39 (m, 4H), 7.35-7.32 (m, 1H), 7.23 (d, *J* = 8.8 Hz, 2H), 6.48 (d, *J* = 8.8 Hz, 2H), 4.77 (s, 1H), 4.44 (d, *J* = 6.1 Hz, 1H), 3.05 (dd, *J* = 13.7, 4.5 Hz, 1H), 2.84 (dd, *J* = 13.7, 9.1 Hz, 1H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 146.48, 142.28, 131.91, 129.05, 127.77, 126.38, 115.60, 109.69, 56.37, 42.42. **HRMS** (ESI): calcd for $C_{15}H_{12}D_3NBrS$ $[M - H]^+$ 323.0302, found 323.0307.

**4-(tert-butyl)-N-(2-((methyl-d3)thio)-1-phenylethyl)aniline**

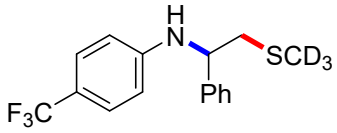



**4g**

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (54.9 mg, 91% yield). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 7.4 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.23 (d, *J* = 8.6 Hz, 2H), 6.62 (d, *J* = 8.6 Hz, 2H), 4.68 (s, 1H), 4.49 (dd, *J* = 9.3, 4.4 Hz, 1H), 3.06 (dd, *J* = 13.6, 4.4 Hz, 1H), 2.87 (dd, *J* = 13.6, 9.3 Hz, 1H), 1.34 (s, 9H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 145.31, 143.31, 140.64, 128.96, 127.56, 126.53, 125.99, 113.73, 56.75, 42.70, 33.96, 31.66. **HRMS** (ESI): calcd for $C_{19}H_{23}D_3NS$ $[M + H]^+$

303.1974, found 303.1971.

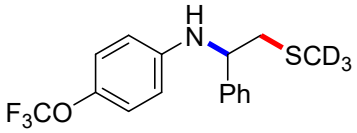
**N-(2-((methyl-d3)thio)-1-phenylethyl)-4-(trifluoromethyl)aniline**




**4h**

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (43.9 mg, 70% yield). **$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 7.45-7.35 (m, 7H), 6.62 (d, *J* = 8.4 Hz, 2H), 5.05 (s, 1H), 4.55-4.53 (m, 1H), 3.08 (dd, *J* = 13.7, 4.5 Hz, 1H), 2.87 (dd, *J* = 13.7, 9.0 Hz, 1H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 149.95, 141.91, 129.11, 127.89, 126.55 (q, *J* = 3.8 Hz), 126.30, 123.69 (q, *J* = 270.5 Hz), 119.43 (q, *J* = 32.6 Hz), 113.16, 56.05, 42.29. **$^{19}$F NMR** (375 MHz, $CDCl_3$) δ -60.93 (3F); **HRMS** (ESI): calcd for $C_{16}H_{12}D_3NF_3S$ $[M - H]^+$ 313.1066, found 313.1063.

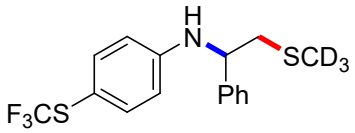
**trifluoro(4-((2-((methyl-d3)thio)-1-phenylethyl)amino)phenyl)-l6-methanone**




**4i**

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (56.1 mg, 85% yield). **$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 7.52 – 7.38 (m, 4H), 7.34 (t, *J* = 7.0 Hz, 1H), 7.01 (d, *J* = 8.6 Hz, 2H), 6.56 (d, *J* = 8.9 Hz, 2H), 4.80 (s, 1H), 4.44 (dd, *J* = 9.3, 4.4 Hz, 1H), 3.05 (dd, *J* = 13.7, 4.2 Hz, 1H), 2.84 (dd, *J* = 13.7, 9.3 Hz, 1H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 146.32, 142.37, 140.89, 129.05, 127.78, 126.35, 122.30, 119.50 (d, *J* = 255.3 Hz), 114.25, 56.58, 42.48. **$^{19}$F NMR** (375 MHz, $CDCl_3$) δ -58.35 (3F); **HRMS** (ESI): calcd for $C_{16}H_{14}D_3NOF_3S$ $[M + H]^+$ 331.1171, found 331.1162.

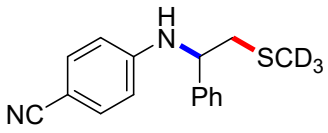
**N-(2-((methyl-d3)thio)-1-phenylethyl)-4-((trifluoromethyl)thio)aniline**




**4j**

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (56.7 mg, 82% yield). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.47-7.34 (m, 7H), 6.61 (d, *J* = 8.7 Hz, 2H), 5.05 (d, *J* = 4.0 Hz, 1H), 4.53 (dt, *J* = 8.8, 4.3 Hz, 1H), 3.08 (dd, *J* = 13.7, 4.5 Hz, 1H), 2.88 (dd, *J* = 13.7, 9.0 Hz, 1H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 149.67, 141.91, 138.16, 131.42 (d, *J* = 308.4 Hz), 129.13, 127.92, 126.31, 114.36, 110.49, 56.11, 42.32. **$^{19}$F NMR** (375 MHz, $CDCl_3$) δ -44.28 (3F); **HRMS** (ESI): calcd for $C_{16}H_{12}D_3NF_3S_2$ $[M - H]^+$ 345.0786, found 345.0784.

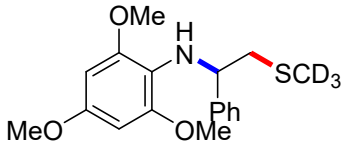
**4-((2-((methyl-d3)thio)-1-phenylethyl)amino)benzonitrile**




**4k**

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (41.7 mg, 77% yield). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.40-7.30 (m, 7H), 6.55 (d, *J* = 8.8 Hz, 2H), 5.24 (d, *J* = 4.4 Hz, 1H), 4.53 (dt, *J* = 8.9, 4.5 Hz, 1H), 3.05 (dd, *J* = 13.7, 4.5 Hz, 1H), 2.87 (dd, *J* = 13.7, 8.8 Hz, 1H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 150.56, 141.28, 133.61, 129.15, 128.02, 126.21, 120.41, 113.53, 99.49, 55.89, 42.11. **HRMS** (ESI): calcd for $C_{16}H_{14}D_3N_2S$ $[M + H]^+$ 272.1301, found 272.1299.

**2,4,6-trimethoxy-N-(2-((methyl-d3)thio)-1-phenylethyl)aniline**

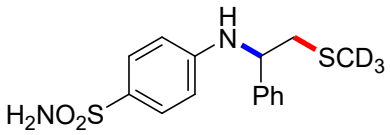



**4l**

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a

yellow solid (46.4 mg, 69% yield), Mp = 90-91℃. **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.44-7.36 (m, 4H), 7.30 (t, *J* = 7.1 Hz, 1H), 6.17 (s, 1H), 5.74 (s, 1H), 4.47-4.44 (m, 1H), 3.98 (s, 3H), 3.77 (s, 3H), 3.55 (s, 3H), 3.04 (dd, *J* = 13.6, 4.7 Hz, 1H), 2.95 (dd, *J* = 13.6, 9.0 Hz, 1H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 155.84, 154.73, 145.78, 143.04, 133.89, 128.98, 127.66, 126.35, 104.64, 92.31, 61.60, 61.16, 57.82, 55.47, 42.65. **HRMS** (ESI): calcd for $C_{18}H_{19}D_3NO_3S$ $[M - H]^+$ 335.1509, found 335.1500.

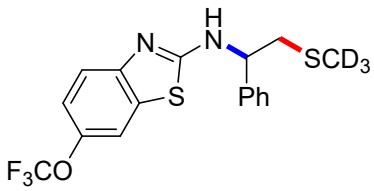
**4-((2-((methyl-d3)thio)-1-phenylethyl)amino)benzenesulfonamide**




**4m**

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (42.2 mg, 65% yield). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.8 Hz, 2H), 7.39-7.28 (m, 5H), 6.54 (d, *J* = 8.8 Hz, 2H), 5.27 (d, *J* = 4.7 Hz, 1H), 5.06 (s, 2H), 4.54 (dt, *J* = 9.1, 4.7 Hz, 1H), 3.02 (dd, *J* = 13.7, 4.7 Hz, 1H), 2.87 (dd, *J* = 13.7, 8.7 Hz, 1H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 150.74, 141.46, 129.47, 129.09, 128.29, 127.93, 126.34, 112.98, 56.02, 42.04. **HRMS** (ESI): calcd for $C_{15}H_{15}D_3N_2O_2NaS_2$ $[M + Na]^+$ 348.0896, found 348.0896.

**N-(2-((methyl-d3)thio)-1-phenylethyl)-6-(trifluoromethoxy)benzo[d]thiazol-2-amine**

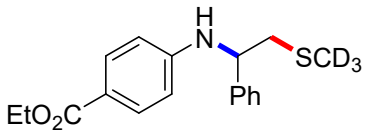



**4n**

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (68.1 mg, 88% yield). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 8.8 Hz, 1H), 7.47-7.17 (m, 6H), 7.18 (d, *J* = 8.8 Hz, 1H), 6.77 (s, 1H), 4.92 (dd, *J* = 7.6, 5.5 Hz, 1H), 3.10-3.00 (m, 2H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 167.65, 150.77, 143.74, 140.18, 131.48, 129.02, 128.32,

126.72, 124.49 (d, $J$ = 256.5 Hz), 119.78, 119.39, 114.09, 58.41, 41.32. **$^{19}$F NMR** (375 MHz, $CDCl_3$) δ -58.21 (3F); **HRMS** (ESI): calcd for $C_{17}H_{13}D_3N_2OF_3S_2$ $[M + H]^+$ 388.0844, found 388.0850.

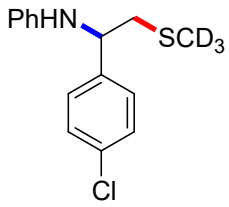
**ethyl -4-((2-((methyl-d3)thio)-1-phenylethyl)amino)benzoate**




**4o**

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (50.2 mg, 79% yield). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.86 (d, $J$ = 8.5 Hz, 2H), 7.43-7.30 (m, 5H), 6.57 (d, $J$ = 8.6 Hz, 2H), 5.16 (d, $J$ = 4.5 Hz, 1H), 4.58 (dt, $J$ = 8.9, 4.6 Hz, 1H), 4.33 (q, $J$ = 7.1 Hz, 2H), 3.05 (dd, $J$ = 13.7, 4.6 Hz, 1H), 2.88 (dd, $J$ = 13.7, 8.7 Hz, 1H), 1.37 (t, $J$ = 7.1 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 166.85, 151.07, 141.83, 131.38, 129.02, 127.81, 126.33, 119.38, 112.77, 60.27, 55.96, 42.15, 14.52. **HRMS** (ESI): calcd for $C_{18}H_{18}D_3NO_2NaS$ $[M + Na]^+$ 341.1379, found 341.1378.

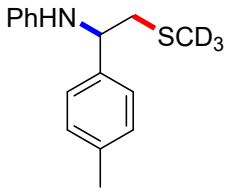
**N-(1-(4-chlorophenyl)-2-((methyl-d3)thio)ethyl)aniline**




**5a**

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (47.0 mg, 84% yield). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.39 (q, $J$ = 8.6 Hz, 4H), 7.17 (t, $J$ = 7.9 Hz, 2H), 6.77 (t, $J$ = 7.3 Hz, 1H), 6.59 (d, $J$ = 7.8 Hz, 2H), 4.71 (s, 1H), 4.46 (dd, $J$ = 8.9, 4.4 Hz, 1H), 3.02 (dd, $J$ = 13.6, 4.5 Hz, 1H), 2.82 (dd, $J$ = 13.6, 9.0 Hz, 1H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 147.23, 141.48, 133.17, 129.25, 129.12, 127.86, 118.23, 114.01, 55.84, 42.42. **HRMS** (ESI): calcd for $C_{15}H_{12}D_3NSCl$ $[M - H]^+$ 279.0802, found 279.0793.

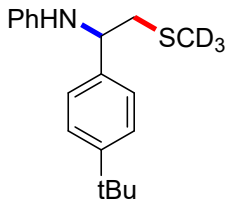
**N-(2-((methyl-d3)thio)-1-(p-tolyl)ethyl)aniline**




**5b**

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (46.8 mg, 90% yield). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.18 (t, *J* = 7.9 Hz, 2H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 8.5 Hz, 2H), 4.71 (s, 1H), 4.48 (dd, *J* = 8.9, 4.5 Hz, 1H), 3.05 (dd, *J* = 13.6, 4.6 Hz, 1H), 2.87 (dd, *J* = 13.6, 9.0 Hz, 1H), 2.42 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 147.65, 139.87, 137.18, 129.65, 129.20, 126.37, 117.89, 113.99, 56.18, 42.55, 21.26. **HRMS** (ESI): calcd for $C_{16}H_{17}D_3NS$ $[M + H]^+$ 261.1505, found 261.1507.

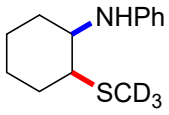
**N-(1-(4-(tert-butyl)phenyl)-2-((methyl-d3)thio)ethyl)aniline**




**5c**

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (53.1 mg, 88% yield). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.48-7.41 (m, 4H), 7.21 (t, *J* = 7.9 Hz, 2H), 6.78 (t, *J* = 7.6 Hz, 1H), 6.67 (d, *J* = 7.9 Hz, 2H), 4.72 (s, 1H), 4.52 (dd, *J* = 9.0, 4.6 Hz, 1H), 3.08 (dd, *J* = 13.6, 4.5 Hz, 1H), 2.90 (dd, *J* = 13.6, 9.0 Hz, 1H), 1.42 (s, 9H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 150.40, 147.73, 139.78, 129.22, 126.12, 125.84, 117.87, 113.98, 56.15, 42.48, 34.63, 31.56. **HRMS** (ESI): calcd for $C_{19}H_{23}D_3NS$ $[M + H]^+$ 303.1974, found 303.1972.

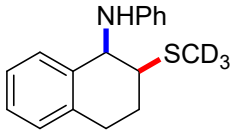
**N-2-((methyl-d3)thio)cyclohexyl)aniline**




**5d**

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (34.9 mg, 78% yield). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.25-7.21 (m, 2H), 6.77-6.69 (m, 3H), 4.12 (s, 1H), 3.21 (td, *J* = 9.5, 3.8 Hz, 1H), 2.64 (td, *J* = 10.1, 3.8 Hz, 1H), 2.43-2.36 (m, 1H), 2.21 (dp, *J* = 13.0, 3.6 Hz, 1H), 1.88-1.76 (m, 1H), 1.65 (dtd, *J* = 14.3, 10.9, 3.7 Hz, 1H), 1.53-1.36 (m, 1H), 1.32-1.23 (m, 1H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 147.76, 129.35, 117.47, 113.43, 55.33, 49.73, 33.17, 32.24, 25.75, 24.33. **HRMS** (ESI): calcd for $C_{13}H_{17}D_3NS$ $[M + H]^+$ 225.1505, found 225.1496.

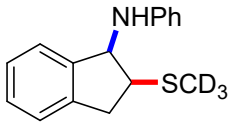
**2-((methyl-d3)thio)-N-phenyl-1,2,3,4-tetrahydronaphthalen-1-amine**




**5e**

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (48.9 mg, 90% yield). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.39 (d, *J* = 7.2 Hz, 1H), 7.29-7.18 (m, 5H), 6.79 (t, *J* = 7.3 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 2H), 4.59 (s, 1H), 4.11 (s, 1H), 3.38 (dt, *J* = 5.4, 3.4 Hz, 1H), 3.11 (ddd, *J* = 16.8, 10.8, 5.7 Hz, 1H), 2.83 (dt, *J* = 17.0, 4.8 Hz, 1H), 2.31 (dddd, *J* = 13.9, 10.7, 5.5, 3.1 Hz, 1H), 2.04 (ddd, *J* = 13.9, 7.4, 3.2 Hz, 1H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 146.96, 136.43, 135.78, 130.52, 129.58, 128.95, 127.62, 126.51, 117.68, 112.84, 55.72, 44.93, 25.32, 23.42. **HRMS** (ESI): calcd for $C_{17}H_{15}D_3NS$ $[M - H]^+$ 271.1348, found 271.1344.

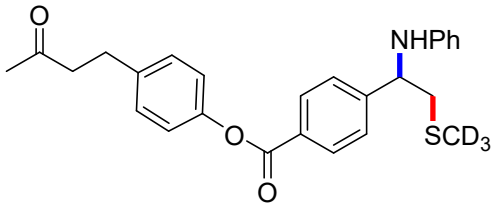
**2-((methyl-d3)thio)-N-phenyl-2,3-dihydro-1H-inden-1-amine**




**5f**

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (45.9 mg, 89% yield). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.42-7.27 (m, 6H), 6.85-6.82 (m, 3H), 4.97 (d, *J* = 5.2 Hz, 1H), 4.01 (s, 1H), 3.55-3.42 (m, 2H), 3.05 (dd, *J* = 15.8, 5.7 Hz, 1H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 147.51, 143.43, 141.42, 129.57, 128.54, 127.32, 124.95, 124.71, 117.95, 113.43, 65.44, 51.39, 37.89. **HRMS** (ESI): calcd for $C_{16}H_{15}D_3NS$ $[M + H]^+$ 259.1348, found 259.1348.

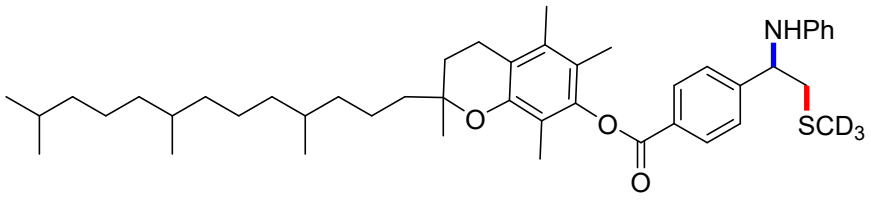
**4-(3-oxobutyl)phenyl -4-(2-((methyl-d3)thio)-1-(phenylamino)ethyl)benzoate**




**5g**

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow solid (72.4 mg, 83% yield), Mp = 40-41℃. **$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 6.83 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.95 (d, *J* = 17.6 Hz, 1H), 5.47 (d, *J* = 10.9 Hz, 1H), 3.52 (dd, *J* = 8.4, 6.5 Hz, 1H), 3.28 (dd, *J* = 14.1, 8.4 Hz, 1H), 2.94 (dd, *J* = 14.1, 6.6 Hz, 1H), 2.30 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 203.09, 165.04, 149.70, 142.68, 136.15, 135.99, 130.56, 130.14, 128.63, 126.36, 121.81, 117.06, 54.33, 34.65, 27.58. **HRMS** (ESI): calcd for $C_{26}H_{25}D_3NO_3S$ $[M + H]^+$ 437.1978, found 437.1981.

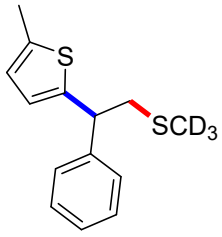
**2,5,6,8-tetramethyl-2-(4,8,12-trimethyltridecyl)chroman-7-yl 4-(-2-((methyl-d3)thio)-1-(phenylamino)ethyl)benzoate**




**5h**

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (113.7 mg, 81% yield). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.33 (d, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.21 (t, *J* = 7.9 Hz, 2H), 6.81 (t, *J* = 7.3 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 2H), 4.84 (s, 1H), 4.61 (dd, *J* = 9.1, 4.4 Hz, 1H), 3.11 (dd, *J* = 13.6, 4.4 Hz, 1H), 2.89 (dd, *J* = 13.6, 9.1 Hz, 1H), 2.72 (t, *J* = 6.8 Hz, 2H), 2.24-2.12 (m, 9H), 1.90 (dp, *J* = 20.0, 6.8 Hz, 2H), 1.69-1.15 (m, 26H), 0.99-0.95 (m, 10H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 165.03, 149.61, 149.04, 147.21, 140.77, 130.93, 129.31, 129.07, 127.05, 126.76, 125.28, 123.25, 118.34, 117.60, 115.19, 114.03, 75.19, 56.32, 42.26, 40.56, 39.75, 39.53, 37.60, 37.44, 32.95, 31.41, 31.19, 28.13, 24.96, 24.60, 24.35, 23.84, 22.90, 22.81, 21.18, 20.79, 19.93, 19.84, 13.25, 12.40, 12.02. **HRMS** (ESI): calcd for $C_{45}H_{62}D_3NO_3SNa$ $[M + Na]^+$ 725.4771, found 725.4778.

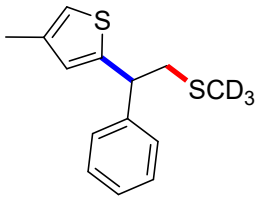
**2-methyl-5-(2-((methyl-d3)thio)-1-phenylethyl)thiophene**




**6a**

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (36.1 mg, 72% yield). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.39-7.27 (m, 5H), 6.70 (d, *J* = 3.4 Hz, 1H), 6.61 (dt, *J* = 3.3, 1.3 Hz, 1H), 4.36 (t, *J* = 7.7 Hz, 1H), 3.25 (dd, *J* = 13.0, 7.4 Hz, 1H), 3.16 (dd, *J* = 12.9, 8.0 Hz, 1H), 2.46 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 145.17, 143.25, 138.57, 128.64, 127.80, 127.07, 124.67, 124.25, 47.21, 41.57, 15.35. **HRMS** (ESI): calcd for $C_{14}H_{12}D_3S_2$ $[M - H]^+$ 250.0803, found 250.0794.

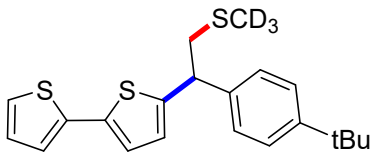
**4-methyl-2-(2-((methyl-d3)thio)-1-phenylethyl)thiophene**




**6b**

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (35.6 mg, 71% yield). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 4.3 Hz, 4H), 7.30-7.27 (m, 1H), 7.16 (d, *J* = 5.0 Hz, 1H), 6.85 (d, *J* = 5.1 Hz, 1H), 4.51 (t, *J* = 7.7 Hz, 1H), 3.23 (dd, *J* = 7.7, 2.4 Hz, 2H), 2.22 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 142.93, 140.52, 133.63, 130.18, 128.67, 127.86, 126.92, 122.12, 45.15, 41.85, 14.13. **HRMS** (ESI): calcd for $C_{14}H_{13}D_3NaS_2$ $[M + Na]^+$ 274.0779, found 274.0775.

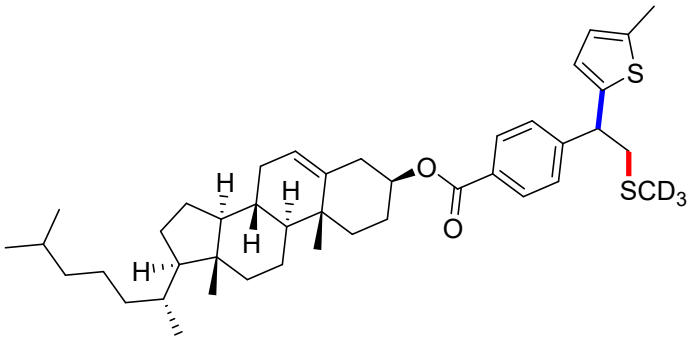
**5-(1-(4-(tert-butyl)phenyl)-2-((methyl-d3)thio)ethyl)-2,2'-bithiophene**




**6c**

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (56.2 mg, 75% yield). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 5.1 Hz, 1H), 7.14 (d, *J* = 4.4 Hz, 1H), 7.05-7.01 (m, 2H), 6.84 (d, *J* = 3.6 Hz, 1H), 4.39 (t, *J* = 7.6 Hz, 1H), 3.30-3.17 (m, 2H), 1.37 (s, 9H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 150.08, 147.01, 139.78, 136.12, 127.78, 127.52, 127.36, 125.68, 125.28, 124.14, 123.43, 123.30, 46.84, 41.59, 34.56, 31.46. **HRMS** (ESI): calcd for $C_{21}H_{21}D_3NaS_3$ $[M + Na]^+$ 398.1126, found 398.1124.

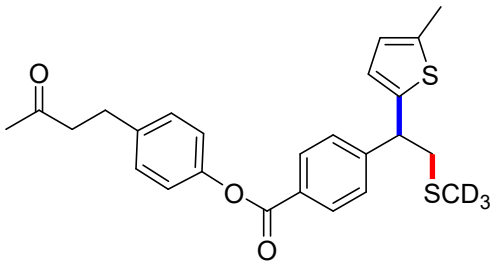
**(3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-(-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-((R)-2-((methyl-d3)thio)-1-(5-methylthiophen-2-yl)ethyl)benzoate**



**6d**

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (98.1 mg, 74% yield). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 2H), 6.67 (d, *J* = 3.4 Hz, 1H), 6.60 (d, *J* = 3.3 Hz, 1H), 5.46-5.44 (m, 1H), 4.88 (dq, *J* = 11.9, 3.9 Hz, 1H), 4.40 (t, *J* = 7.7 Hz, 1H), 3.25 (dd, *J* = 13.0, 7.0 Hz, 1H), 3.15 (dd, *J* = 13.0, 8.4 Hz, 1H), 2.49-2.45 (m, 4H), 2.09-.089 (m, 39H), 0.73 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 165.80, 148.12, 144.20, 139.72, 138.93, 129.99, 129.66, 127.82, 124.75, 124.45, 122.85, 74.56, 56.77, 56.20, 50.11, 47.06, 42.39, 41.13, 39.81, 39.59, 38.29, 37.10, 36.72, 36.26, 35.87, 32.00, 31.95, 28.31, 28.09, 27.96, 24.37, 23.90, 22.90, 22.64, 21.12, 19.45, 18.79, 15.36, 11.94. **HRMS** (ESI): calcd for $C_{42}H_{57}D_3O_2NaS_2$ $[M + Na]^+$ 686.4121, found 686.4122.

**4-(3-oxobutyl)phenyl -4-(2-((methyl-d3)thio)-1-(5-methylthiophen-2-yl)ethyl)benzoate**

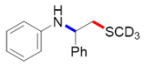


**6e**

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (59.1 mg, 67% yield). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.70 (d, *J* = 3.3 Hz, 1H), 6.62 (d, *J* = 3.3 Hz, 1H), 4.44 (t, *J* = 7.7 Hz, 1H), 3.28 (dd, *J* = 13.0, 7.0 Hz, 1H), 3.18 (dd, *J* = 13.1, 8.4 Hz, 1H), 2.97-2.94 (m, 2H), 2.83-2.80 (m, 2H), 2.46 (s, 3H), 2.19 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 207.84, 149.28, 149.11, 143.97, 139.08, 138.71, 130.62, 129.42, 128.48, 128.36, 128.13, 124.81, 124.53, 121.73, 47.08, 45.20, 41.07, 30.19, 29.15, 15.36. **HRMS** (ESI):

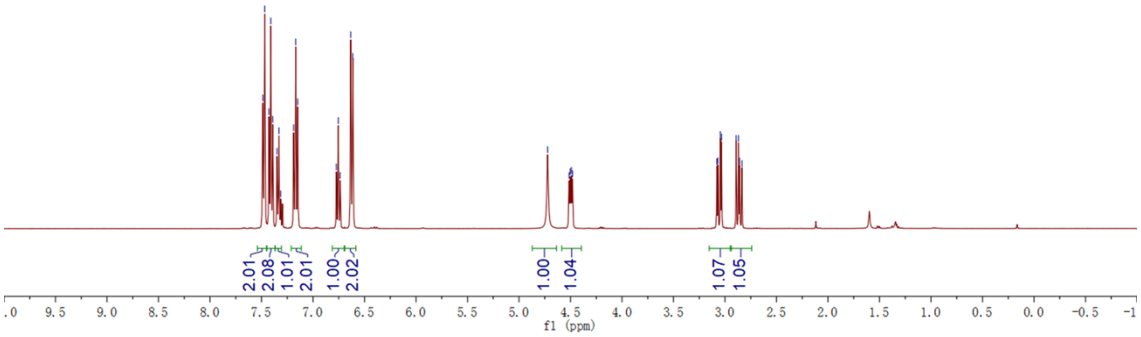
calcd for $C_{25}H_{23}D_3O_3NaS_2$ $[M + Na]^+$ 464.1409, found 464.1409.

# $^{1}H$, $^{13}C$ and $^{19}F$ NMR spectra of products

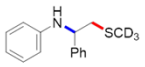




**4a**

$^{1}H$ NMR (400 MHz, $CDCl_3$)

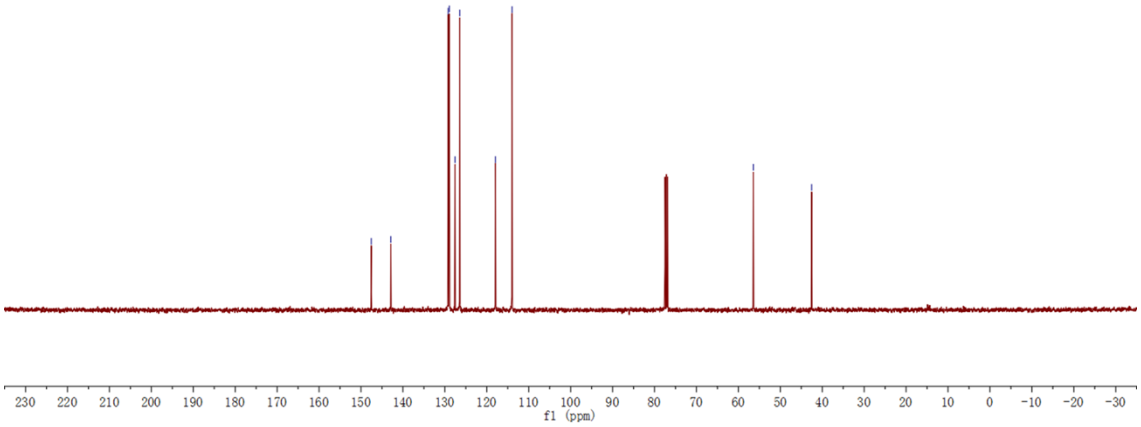




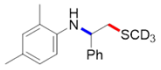



**4a**

$^{13}C$ NMR (100 MHz, $CDCl_3$)

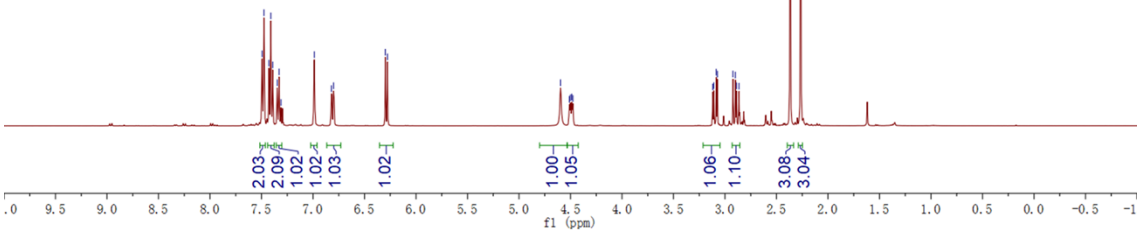


wg1469.1.1.1r


**4b**

$^{1}$H NMR (400 MHz, $CDCl_3$)

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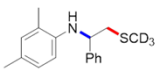
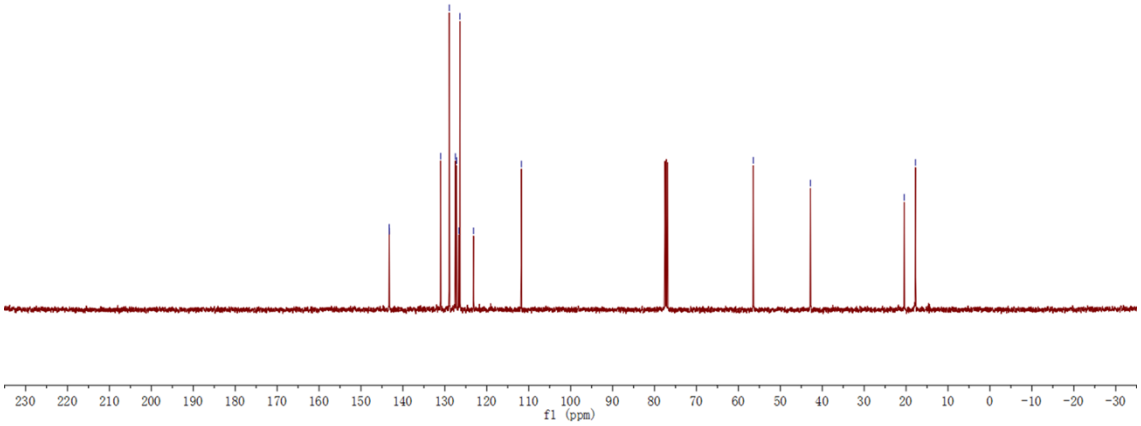


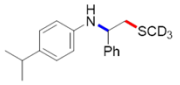

**4b**

$^{13}$C NMR (100 MHz, $CDCl_3$)



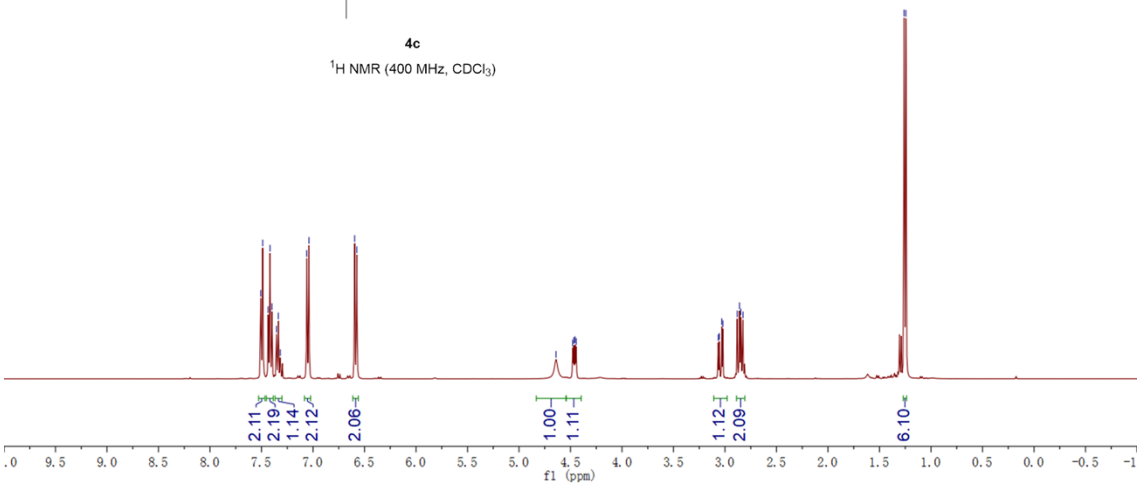
wg1493.1.1.1r

7.51 7.49 7.44 7.42 7.40 7.35 7.34 7.32 7.06 7.04 6.60 6.57 4.64 4.48 4.47 4.46 4.44 3.07 3.05 3.03 3.02 2.88 2.86 2.85 2.83 1.26 1.24



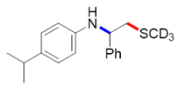

**4c**

$^{1}$H NMR (400 MHz, $CDCl_3$)



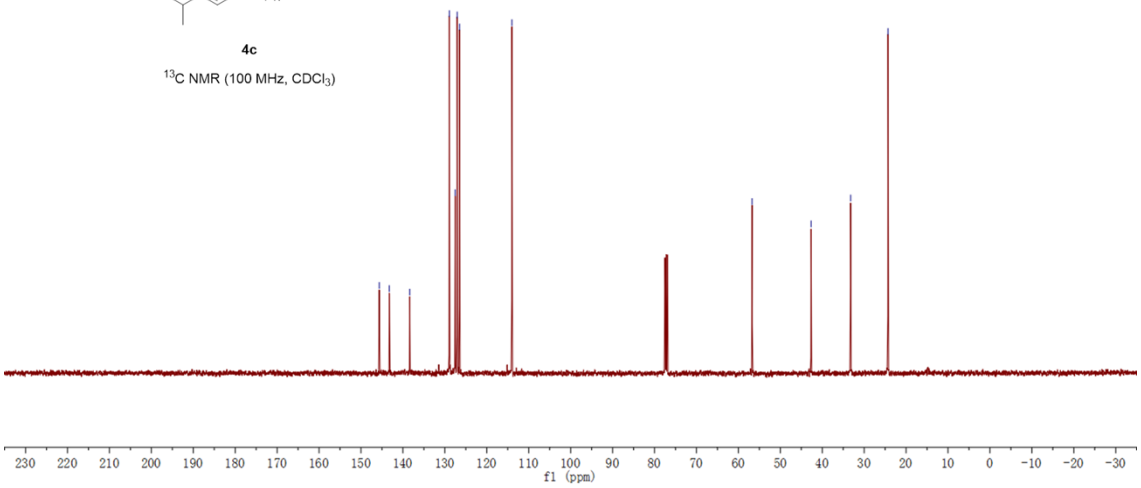

pdata/1

145.64 143.24 138.39 128.93 127.53 127.06 126.50 114.01 56.73 42.65 33.23 24.32

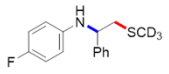



**4c**

$^{13}$C NMR (100 MHz, $CDCl_3$)

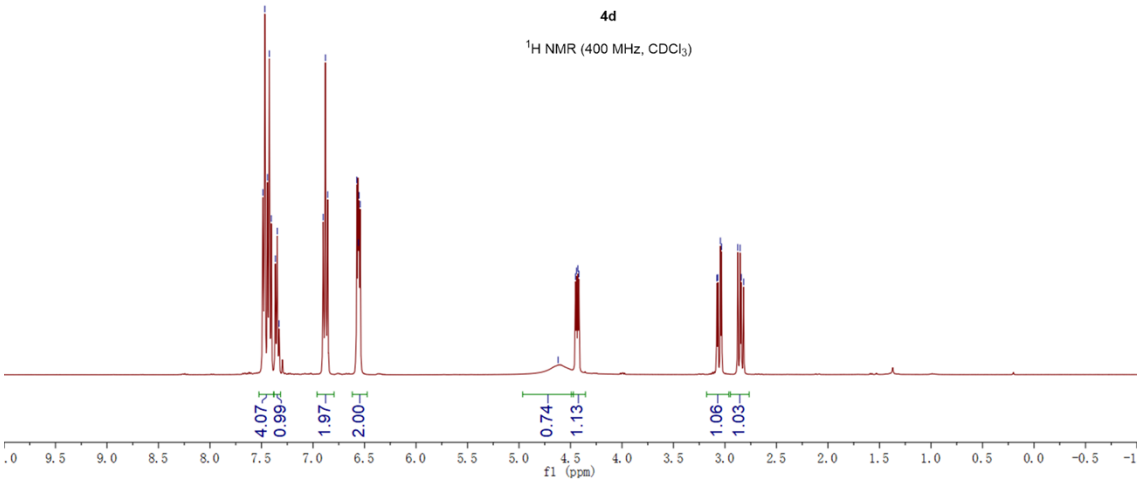


wg1482.1.1.1r


**4d**

$^{1}$H NMR (400 MHz, $CDCl_3$)

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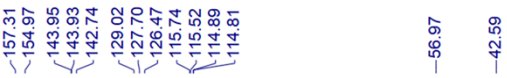
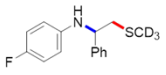
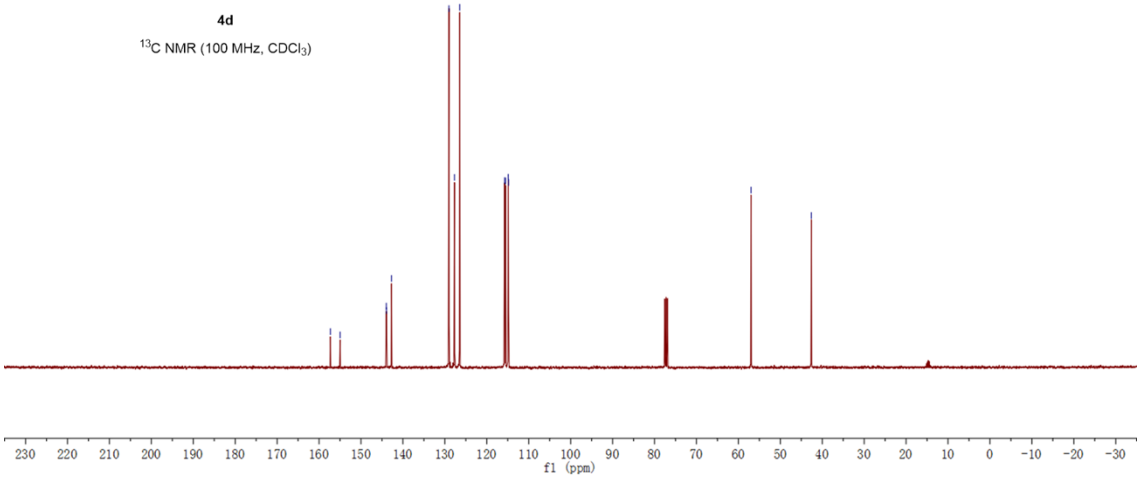



**4d**

$^{13}$C NMR (100 MHz, $CDCl_3$)



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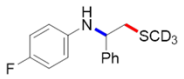
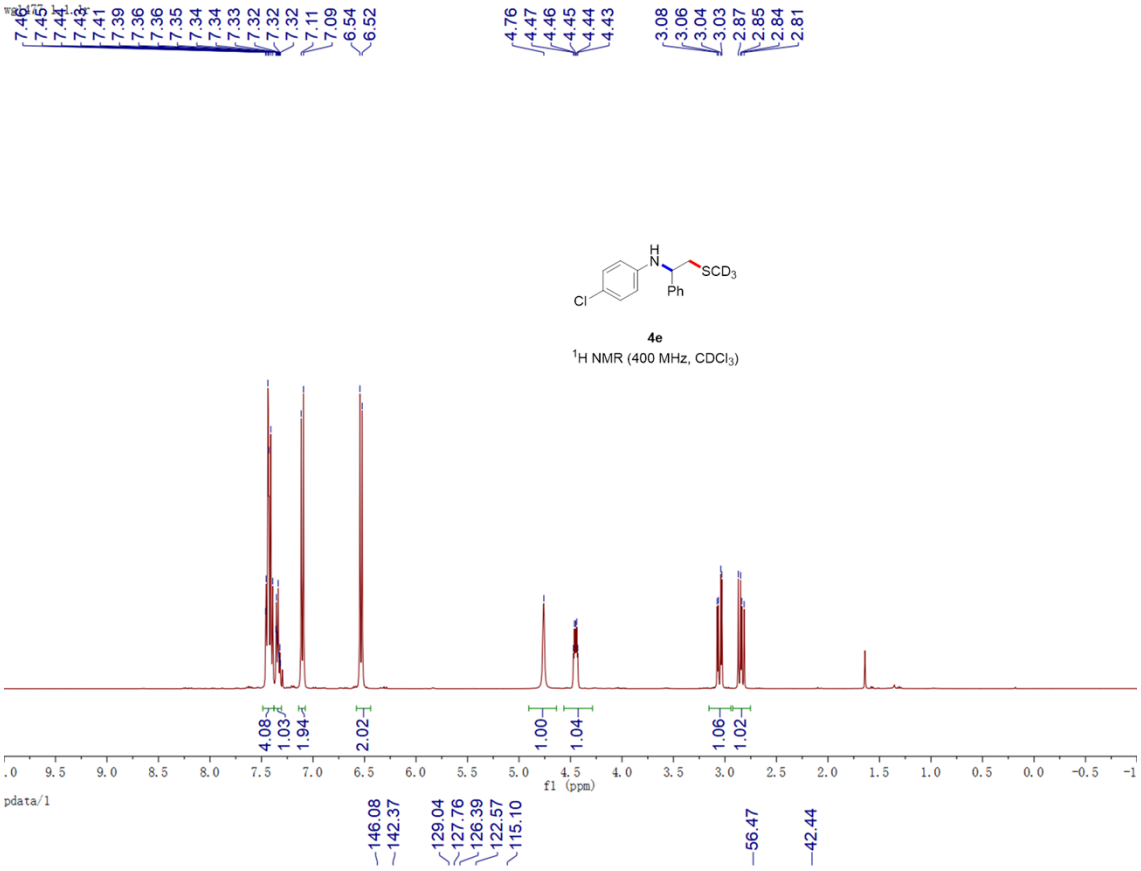
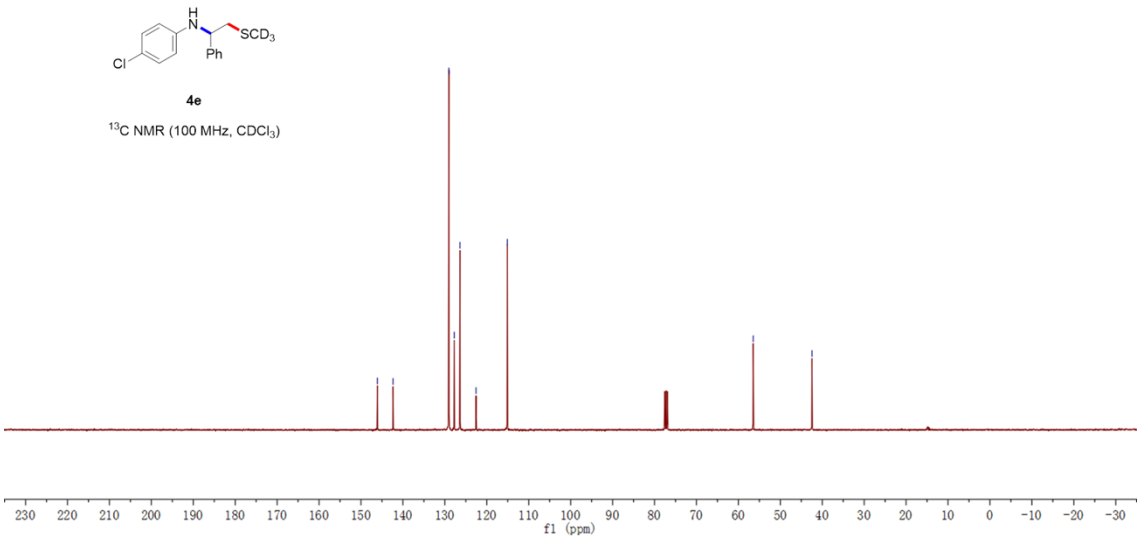


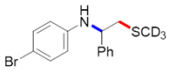

**4d**

$^{19}$F NMR (375 MHz, $CDCl_3$)


7.46
7.45
7.44
7.43
7.41
7.39
7.36
7.36
7.35
7.34
7.34
7.33
7.32
7.32
7.32
7.11
7.09
6.54
6.52
4.76
4.47
4.46
4.45
4.44
4.43
3.08
3.06
3.04
3.03
2.87
2.85
2.84
2.81
H
N
SCD3
Cl
Ph
4e
1H NMR (400 MHz, CDCl3)
4.08
1.03
1.94
2.02
1.00
1.04
1.06
1.02
f1 (ppm)
pdata/1
146.08
142.37
129.04
127.76
126.39
122.57
115.10
56.47
42.44

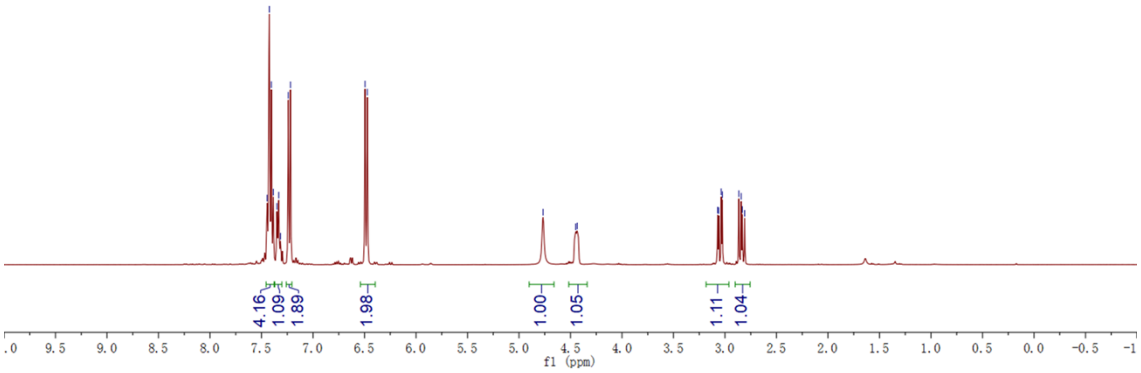

H
N
SCD3
Cl
Ph
4e
13C NMR (100 MHz, CDCl3)
f1 (ppm)

wg1468.1.1.1r


**4f**

$^{1}$H NMR (400 MHz, $CDCl_3$)

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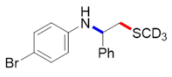
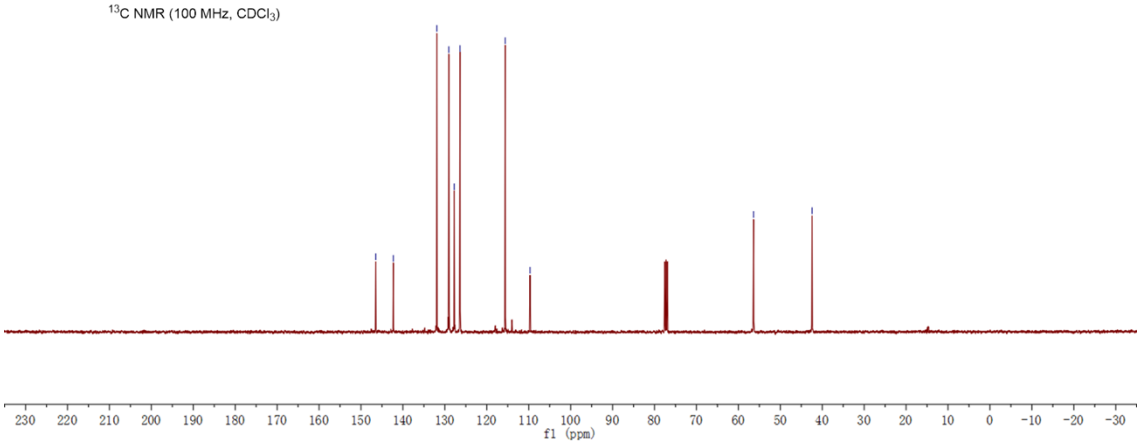
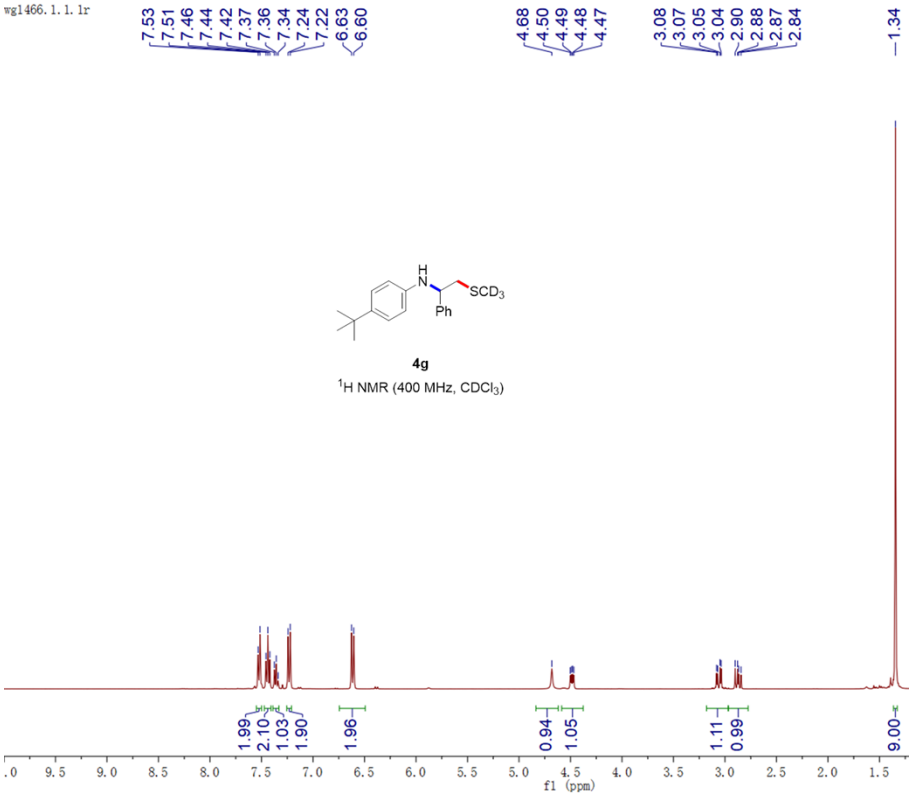



**4f**

$^{13}$C NMR (100 MHz, $CDCl_3$)



wg1466.1.1.1r



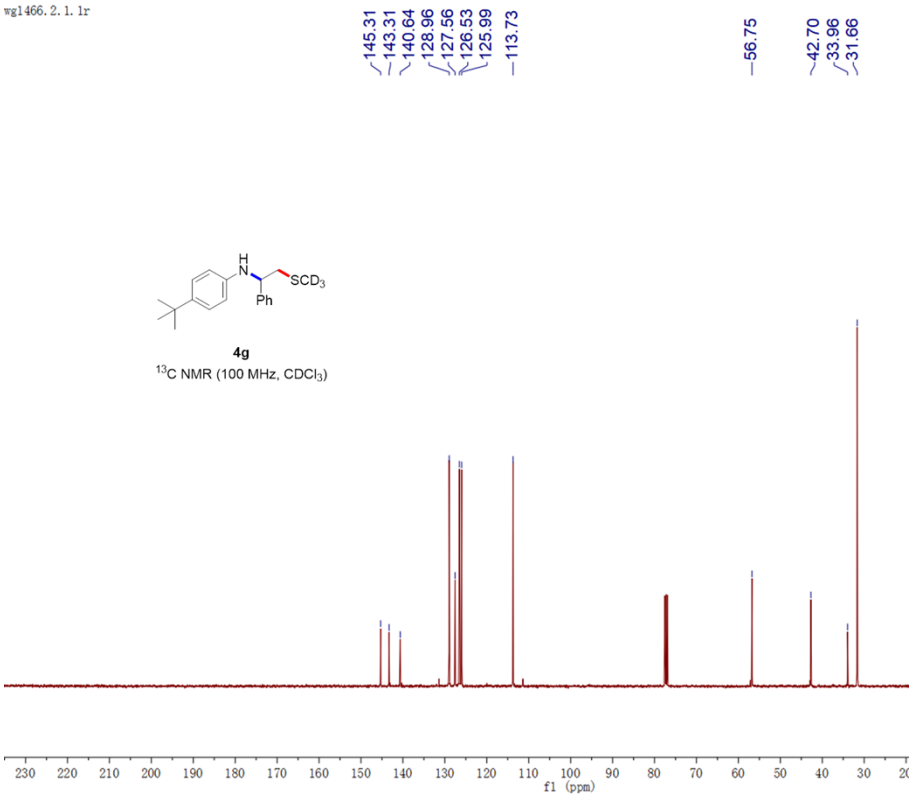




**4g**

$^{1}$H NMR (400 MHz, $CDCl_3$)

wg1466.2.1.1r





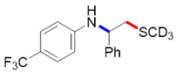


**4g**

$^{13}$C NMR (100 MHz, $CDCl_3$)

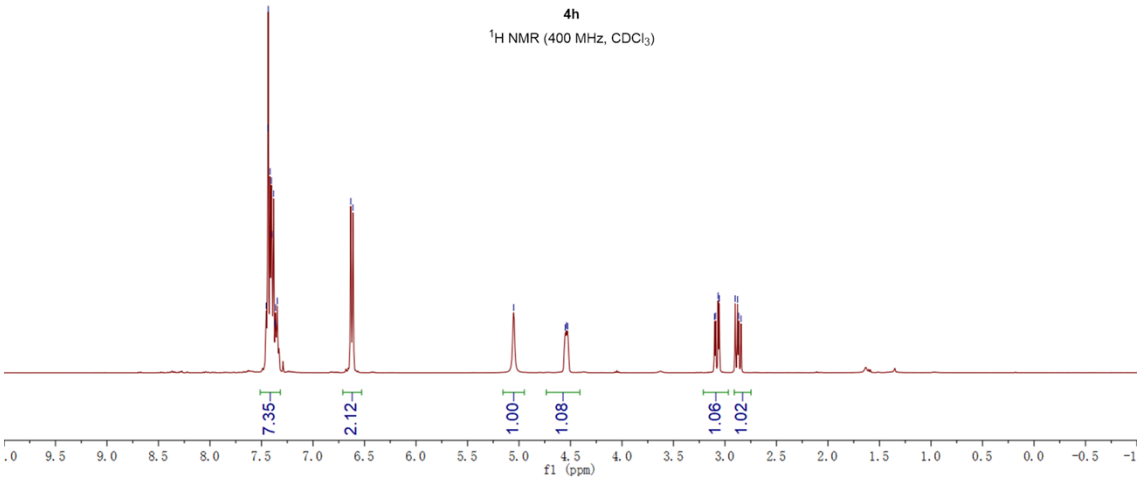
wg1481.1.1.1r

7.45 7.44 7.43 7.42 7.40 7.40 7.38 7.37 7.36 7.35 6.63 6.61 5.05 4.55 4.54 4.53 3.10 3.09 3.07 3.06 2.90 2.88 2.87 2.84



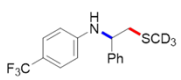

**4h**

$^{1}$H NMR (400 MHz, $CDCl_3$)



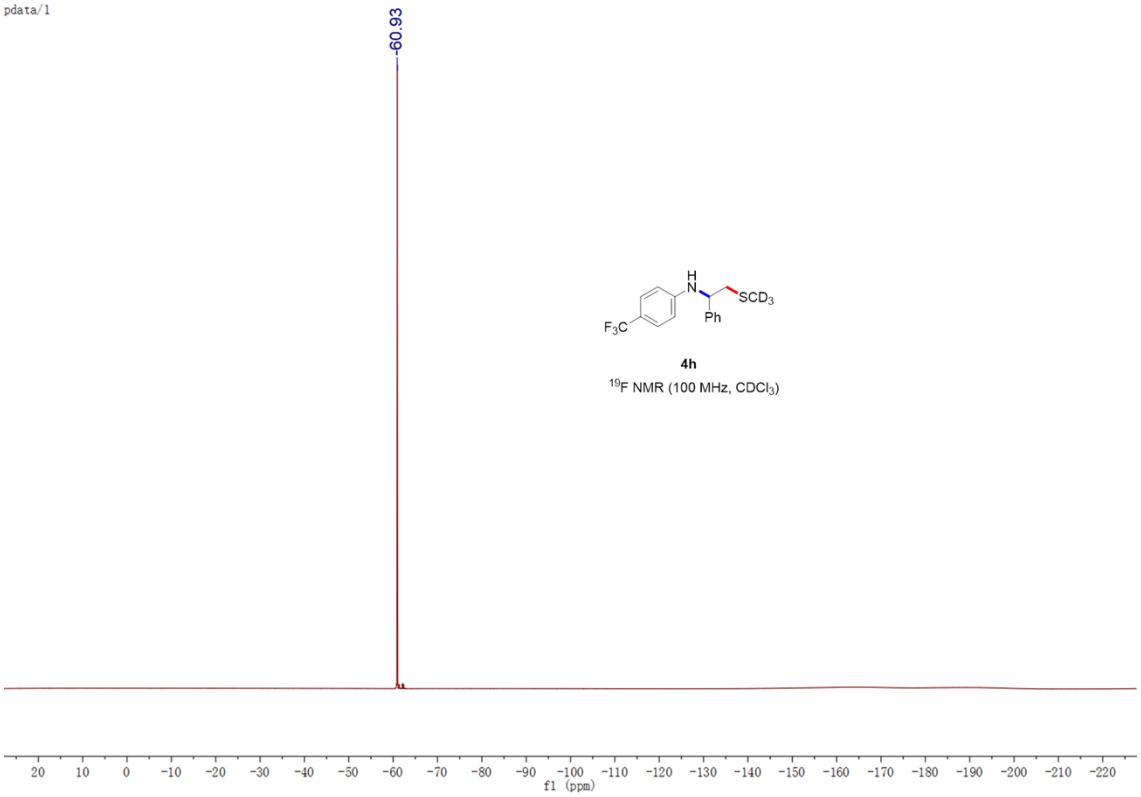

pdata/1

149.95 141.91 129.11 127.89 126.61 126.57 126.53 126.49 126.38 126.30 123.69 121.00 119.92 119.59 119.27 118.95 113.16 56.05 42.29




**4h**

$^{13}$C NMR (100 MHz, $CDCl_3$)

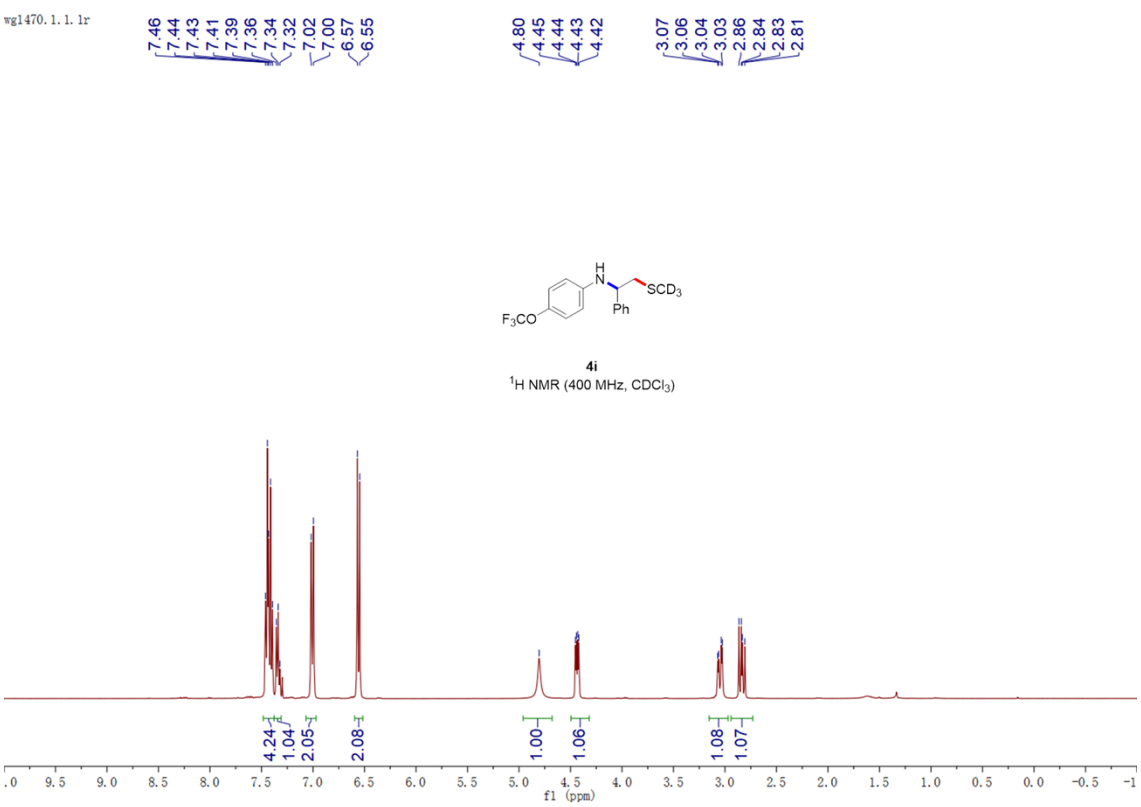






**4h**

$^{19}$F NMR (100 MHz, $CDCl_3$)

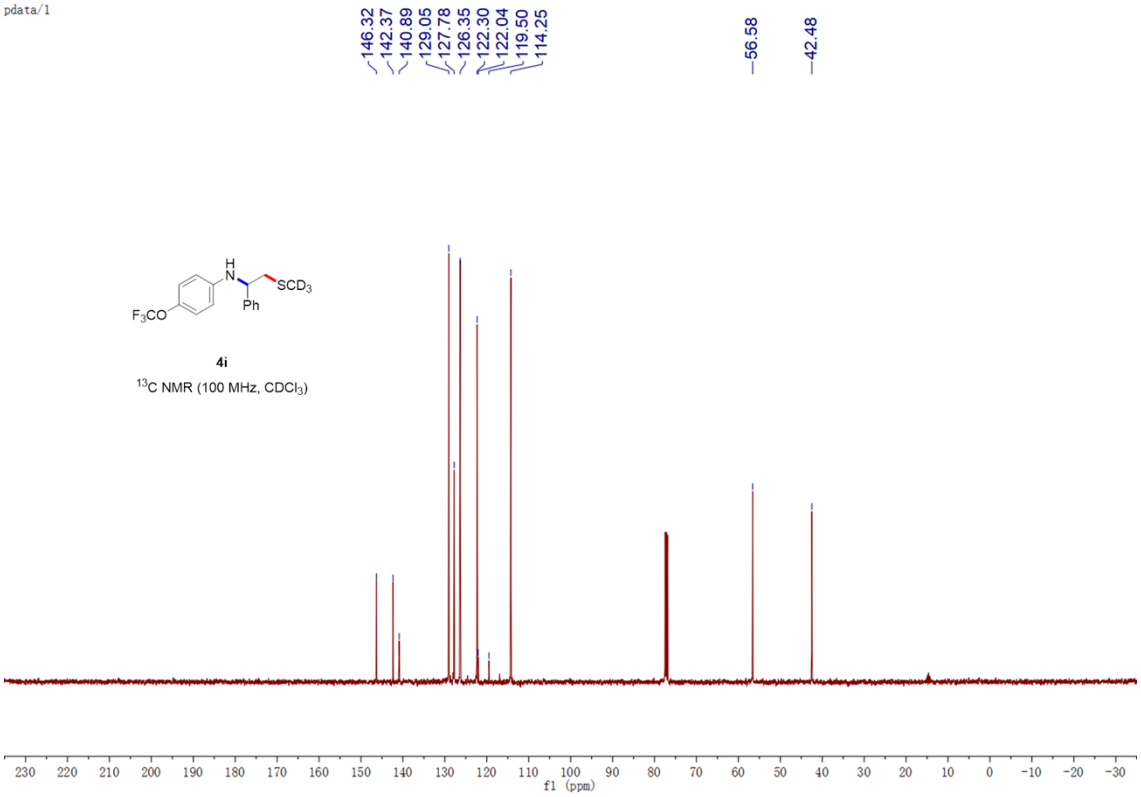


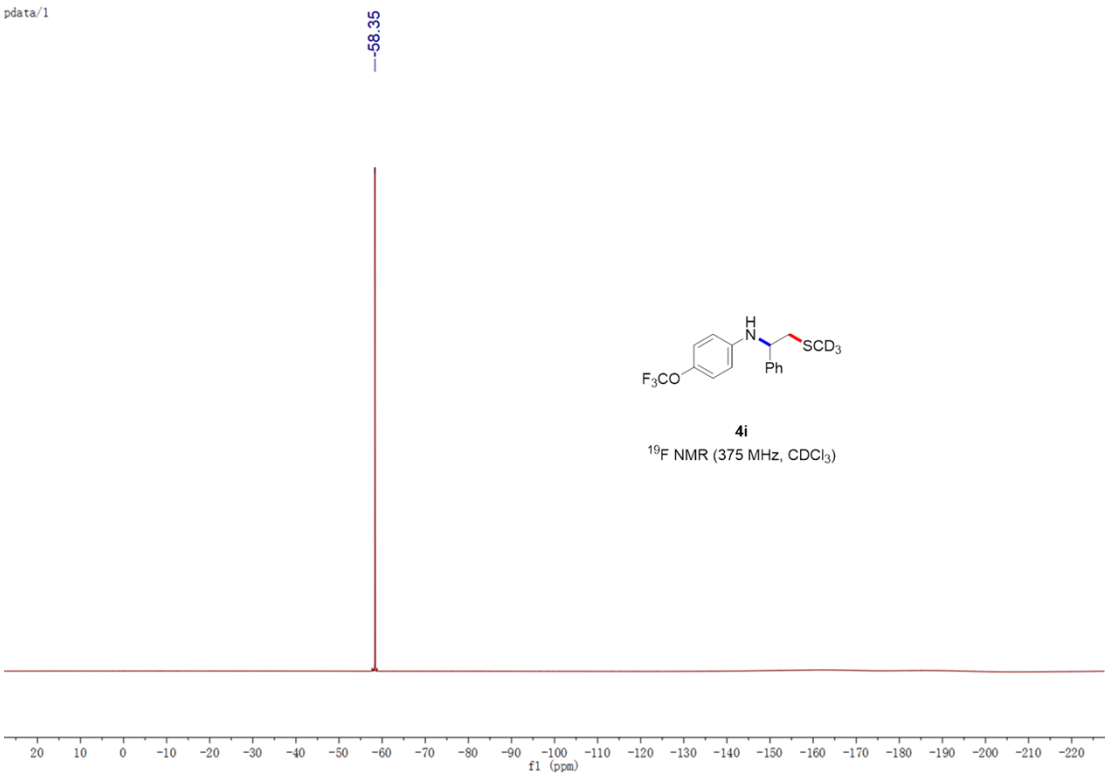


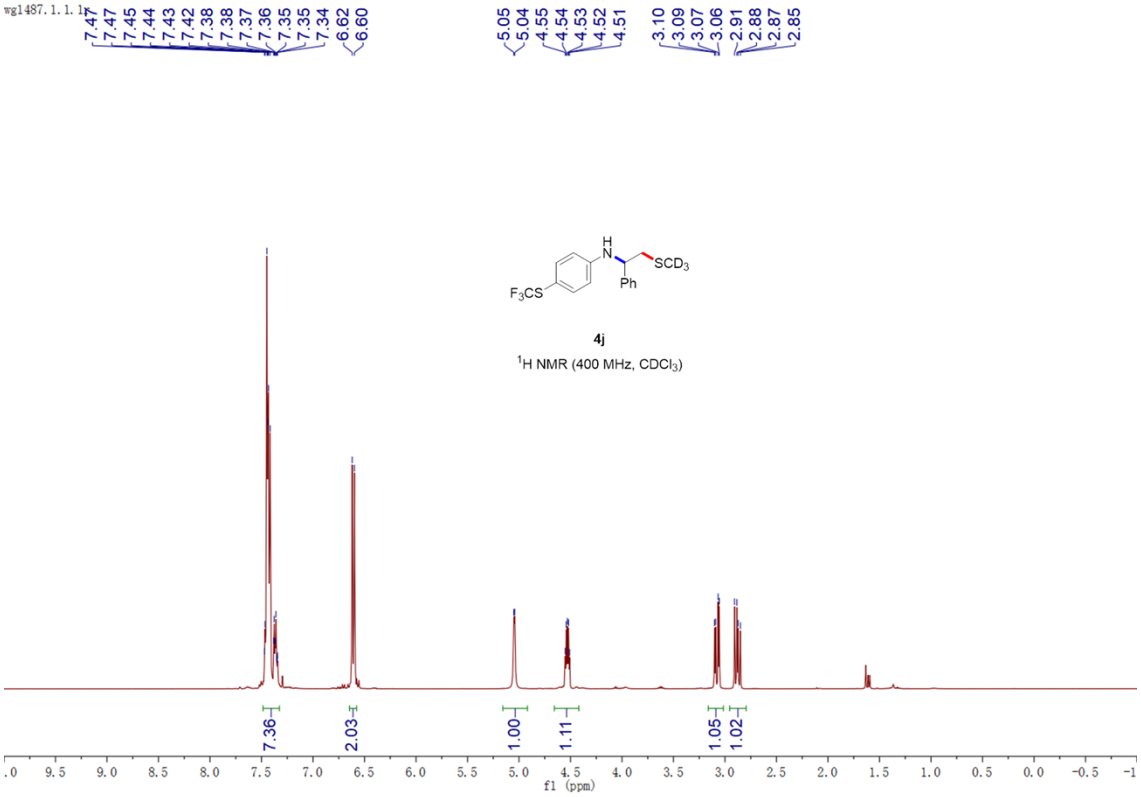


**4i**

$^{1}$H NMR (400 MHz, $CDCl_3$)

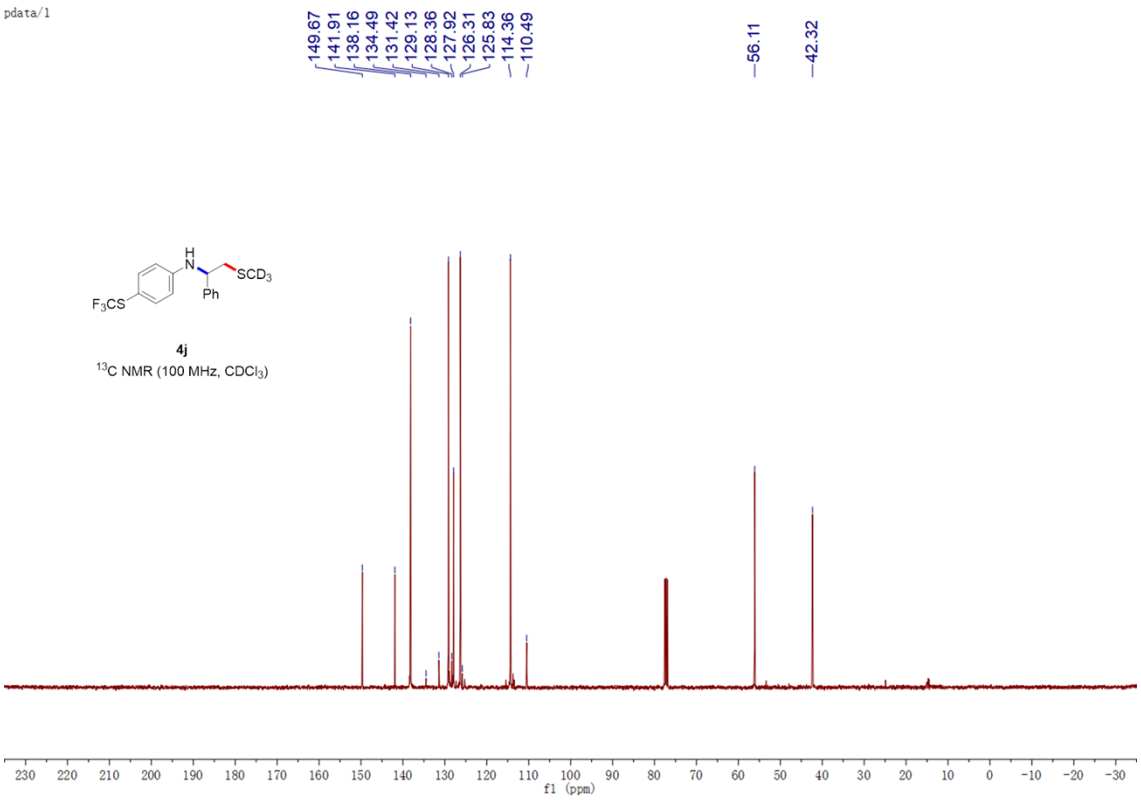

pdata/1
146.32
142.37
140.89
129.05
127.78
126.35
122.30
122.04
119.50
114.25
56.58
42.48
H
N
SCD3
Ph
F3CO
4i
13C NMR (100 MHz, CDCl3)
f1 (ppm)


pdata/1
58.35
H
N
SCD3
Ph
F3CO
4i
19F NMR (375 MHz, CDCl3)
f1 (ppm)




**4j**

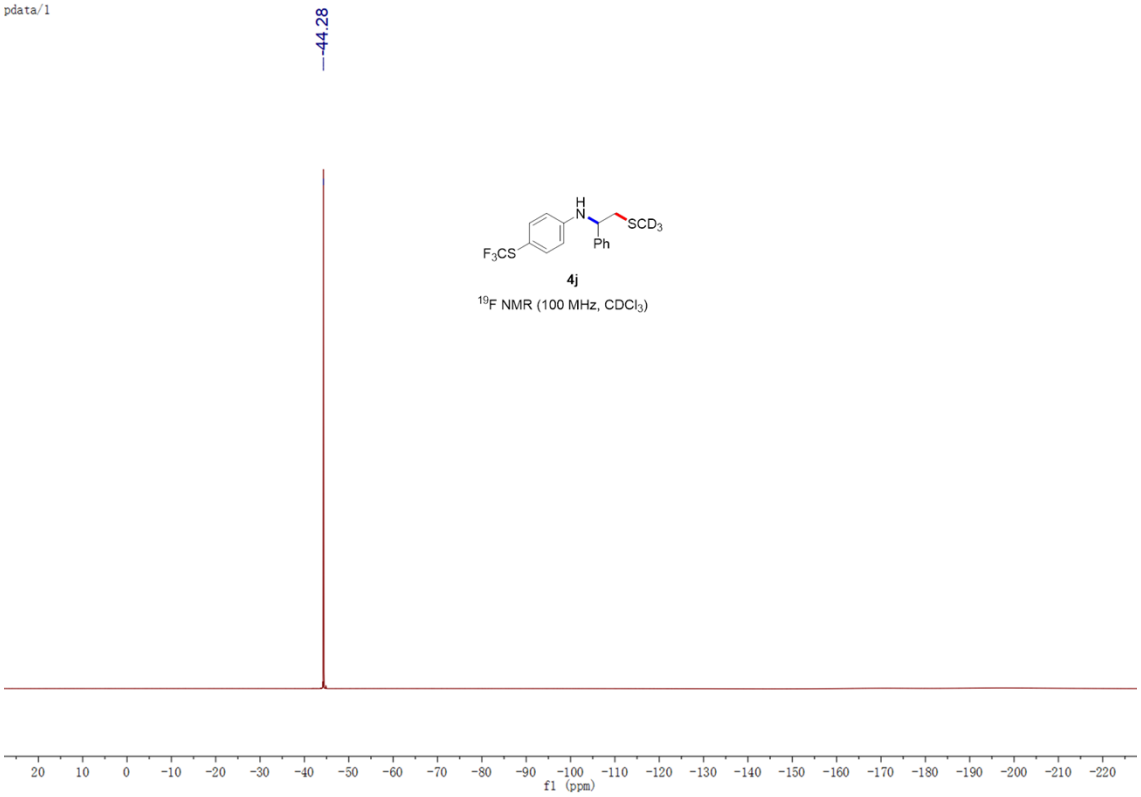
$^{1}$H NMR (400 MHz, $CDCl_3$)




**4j**

$^{13}$C NMR (100 MHz, $CDCl_3$)

pdata/1



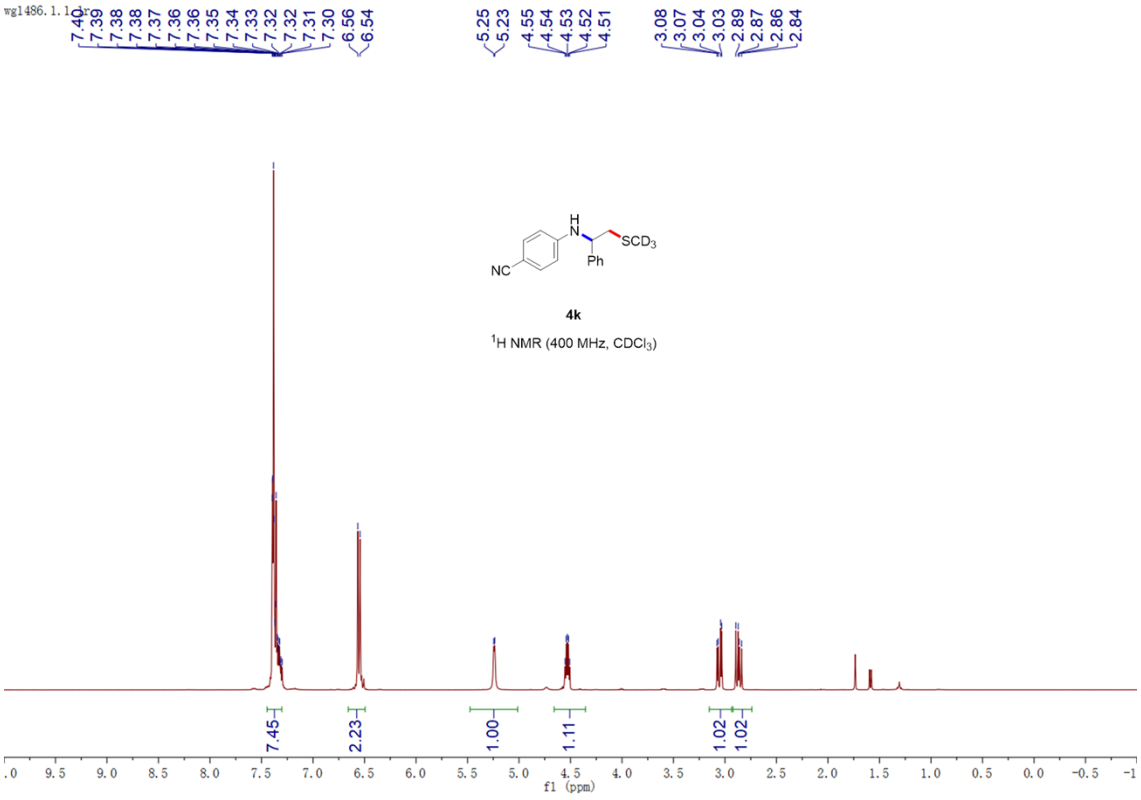




**4j**

$^{19}$F NMR (100 MHz, $CDCl_3$)

wg1486.1.1



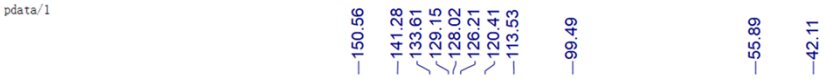


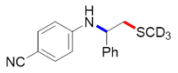


**4k**

$^{1}$H NMR (400 MHz, $CDCl_3$)

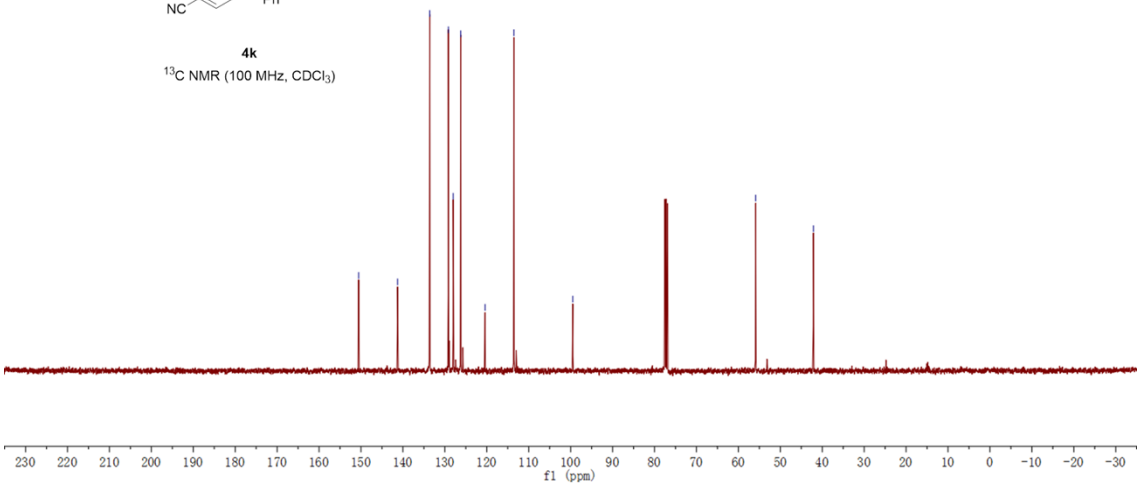
pdata/1



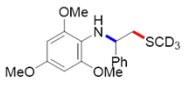




**4k**

$^{13}$C NMR (100 MHz, $CDCl_3$)

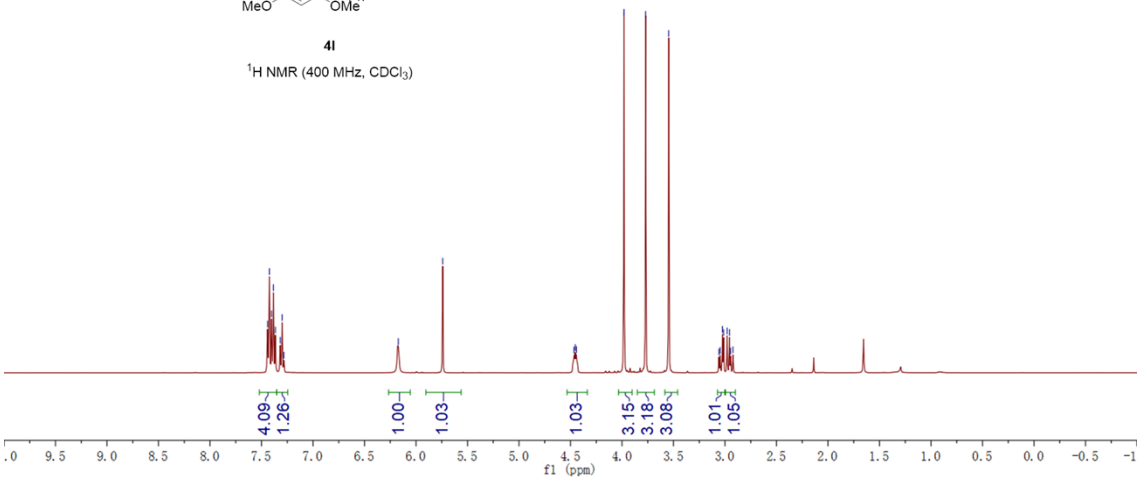


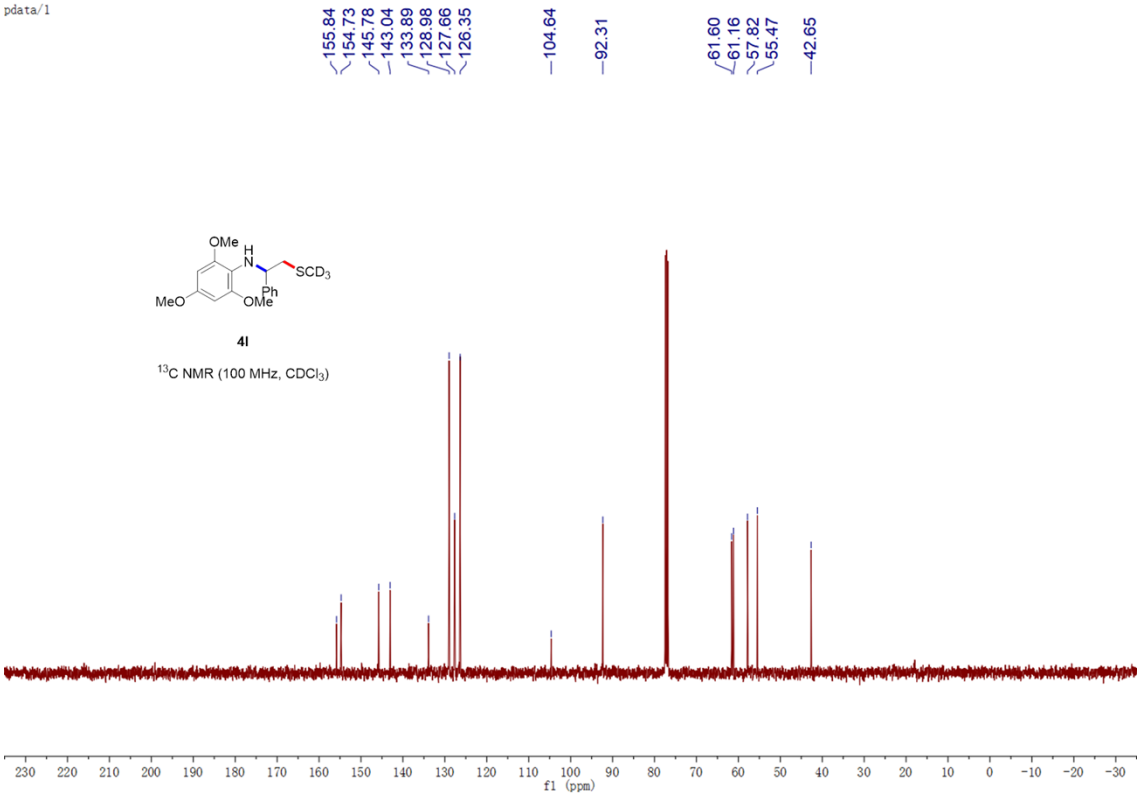

wg1488-1.1.1.1r

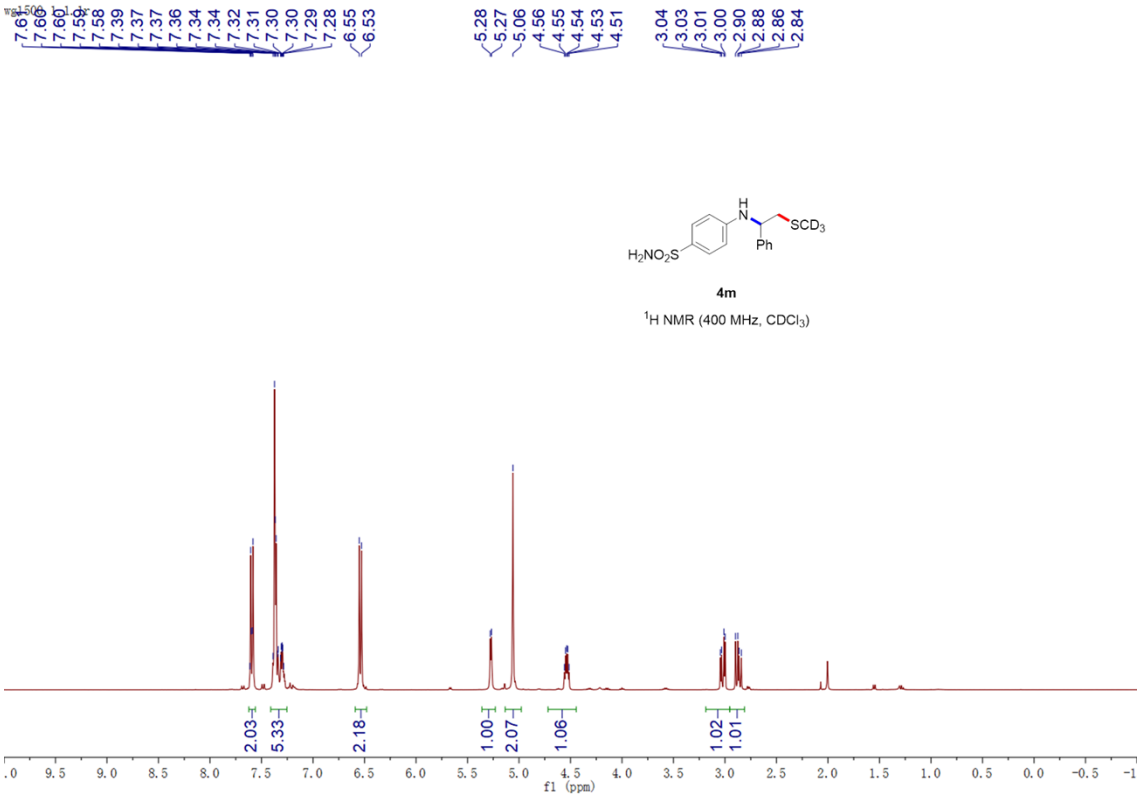



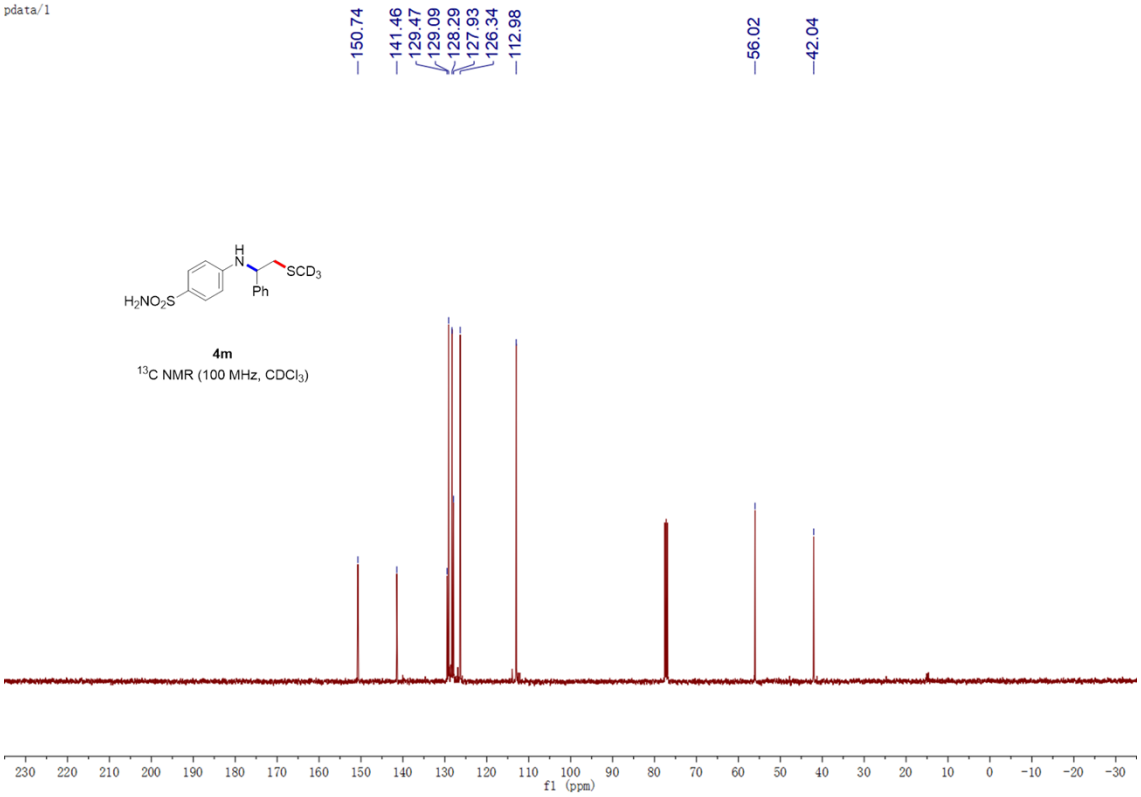

**4l**

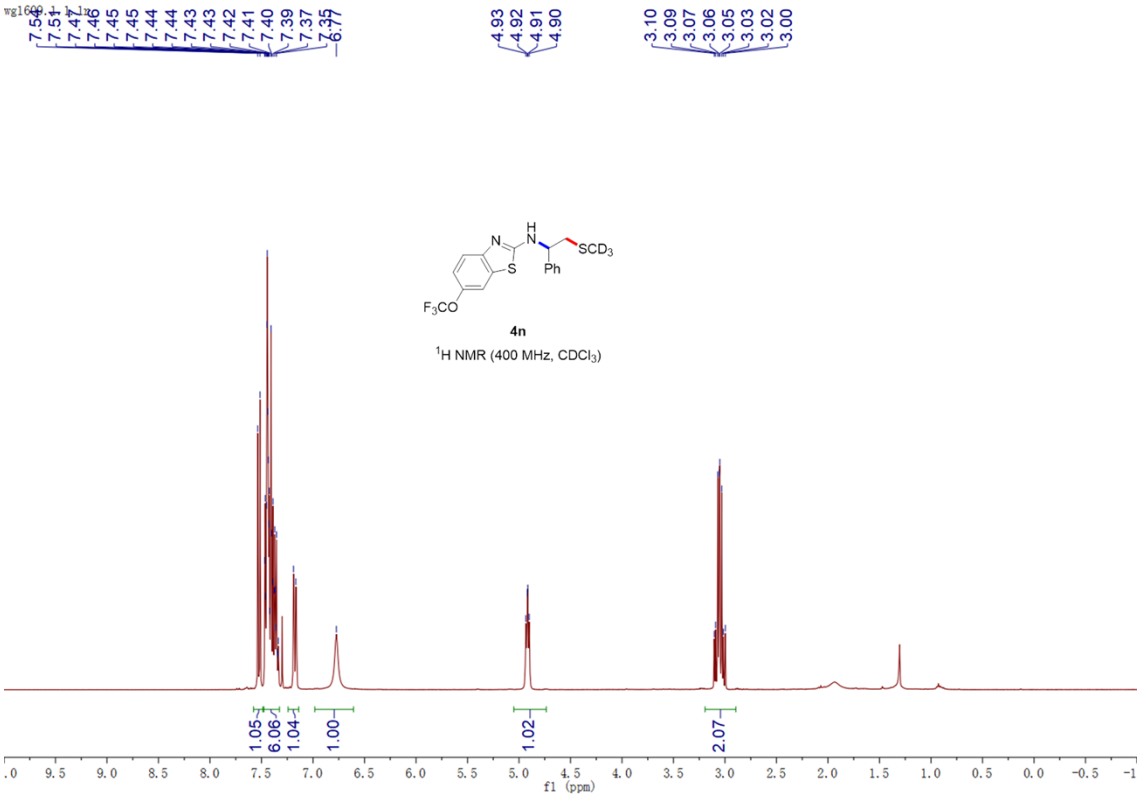
$^{1}$H NMR (400 MHz, $CDCl_3$)

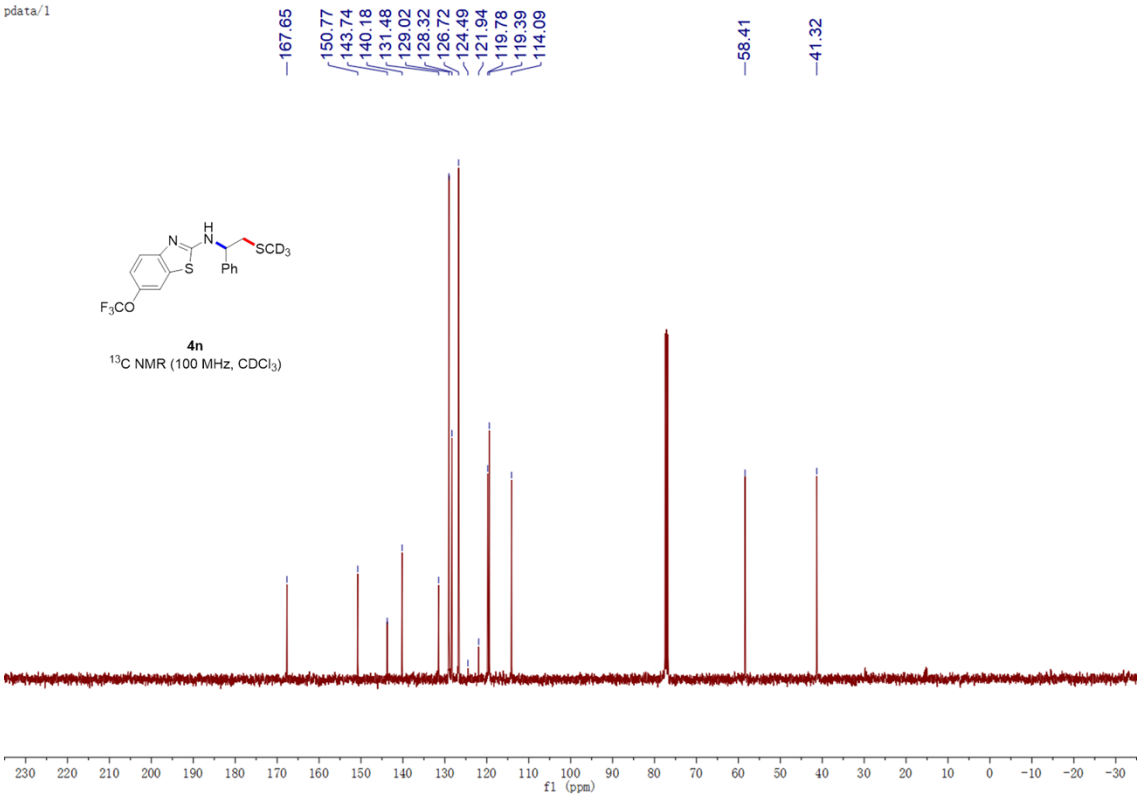



pdata/1
155.84
154.73
145.78
143.04
133.89
128.98
127.66
126.35
104.64
92.31
61.60
61.16
57.82
55.47
42.65
OMe
H
N
SCD3
MeO
OMe
Ph
4l
13C NMR (100 MHz, CDCl3)
f1 (ppm)


7.61
7.60
7.59
7.58
7.39
7.37
7.37
7.36
7.34
7.34
7.32
7.31
7.30
7.30
7.29
7.28
6.55
6.53
5.28
5.27
5.06
4.56
4.55
4.54
4.53
4.51
3.04
3.03
3.01
3.00
2.90
2.88
2.86
2.84
H
N
SCD3
Ph
H2NO2S
4m
1H NMR (400 MHz, CDCl3)
2.03
5.33
2.18
1.00
2.07
1.06
1.02
1.01
f1 (ppm)

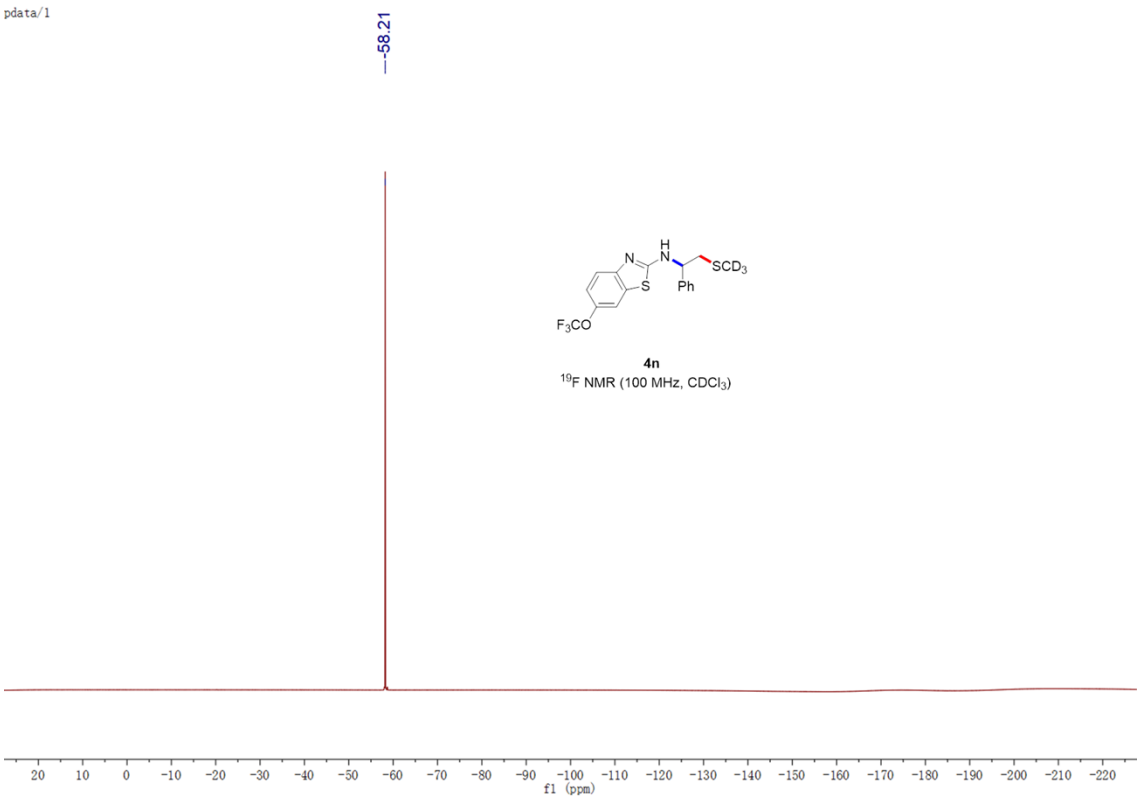

pdata/1
150.74
141.46
129.47
129.09
128.29
127.93
126.34
112.98
56.02
42.04
H
N
SCD3
Ph
H2NO2S
4m
13C NMR (100 MHz, CDCl3)
f1 (ppm)


wg1609
7.54
7.51
7.47
7.46
7.45
7.45
7.44
7.44
7.43
7.43
7.42
7.41
7.40
7.39
7.37
7.35
6.77
4.93
4.92
4.91
4.90
3.10
3.09
3.07
3.06
3.05
3.03
3.02
3.00
H
N
S
N
SCD3
Ph
F3CO
4n
1H NMR (400 MHz, CDCl3)
1.05
6.06
1.04
1.00
1.02
2.07
f1 (ppm)




**4n**

$^{13}C$ NMR (100 MHz, $CDCl_3$)




**4n**

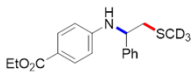
$^{19}F$ NMR (100 MHz, $CDCl_3$)

wg1648.1.1.1r

7.87 7.85 7.43 7.42 7.41 7.40 7.38 7.36 7.34 7.33 7.31 7.30 7.30 6.58 6.56

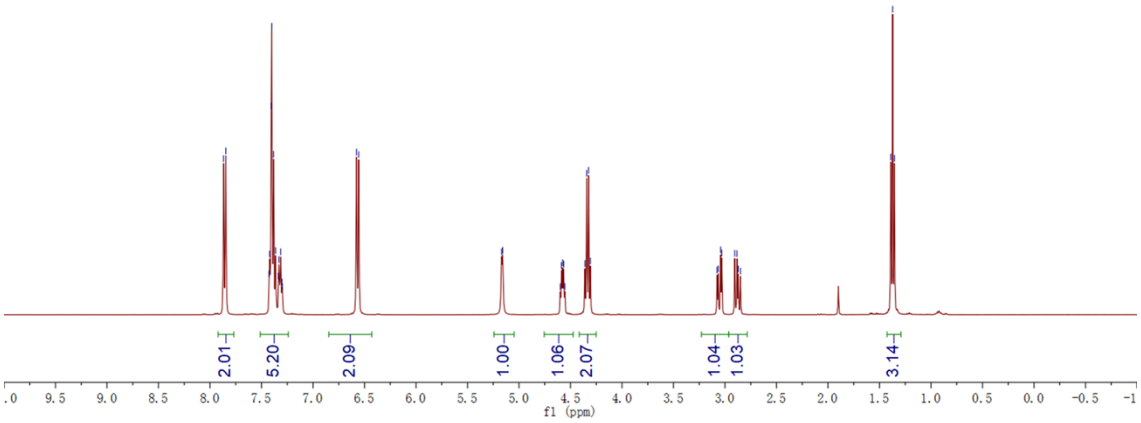
5.17 5.16 4.60 4.59 4.58 4.57 4.55 4.36 4.34 4.32 4.31 3.08 3.07 3.04 3.03 2.91 2.88 2.87 2.85

1.39 1.37 1.35




**4o**

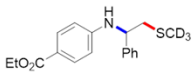
$^{1}$H NMR (400 MHz, $CDCl_3$)




pdata/1

166.85 151.07 141.83 131.38 129.02 127.81 126.33 119.38 112.77

60.27 55.96 42.15 14.52




**4o**

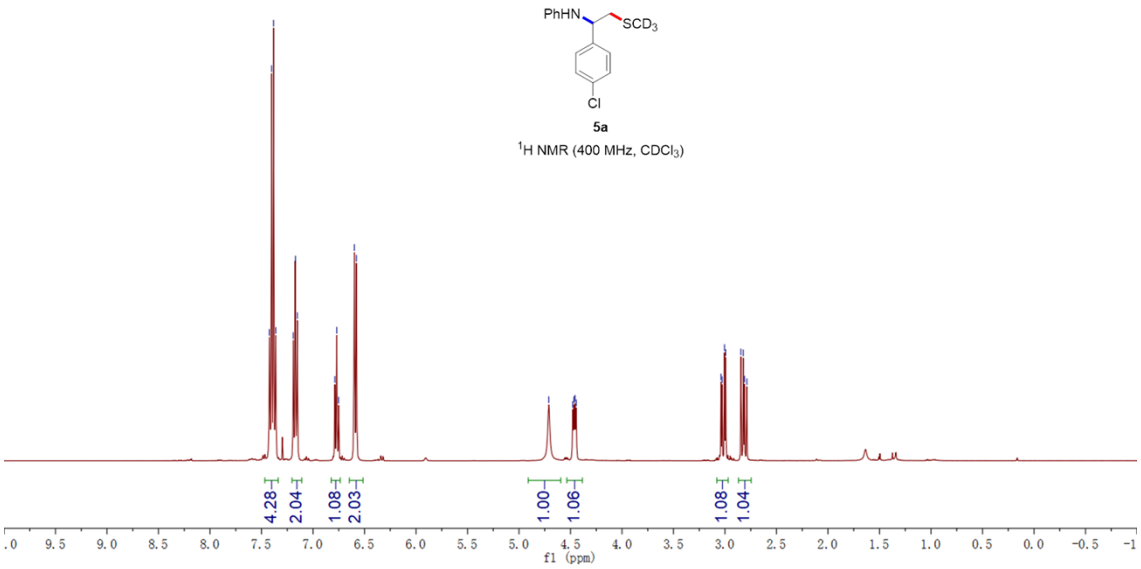
$^{13}$C NMR (100 MHz, $CDCl_3$)

wg1508.1.1.1r

7.42 7.40 7.38 7.36 7.19 7.17 7.15 6.79 6.77 6.75 6.60 6.58

4.71 4.48 4.47 4.46 4.44

3.04 3.03 3.00 2.99 2.85 2.82 2.81 2.79



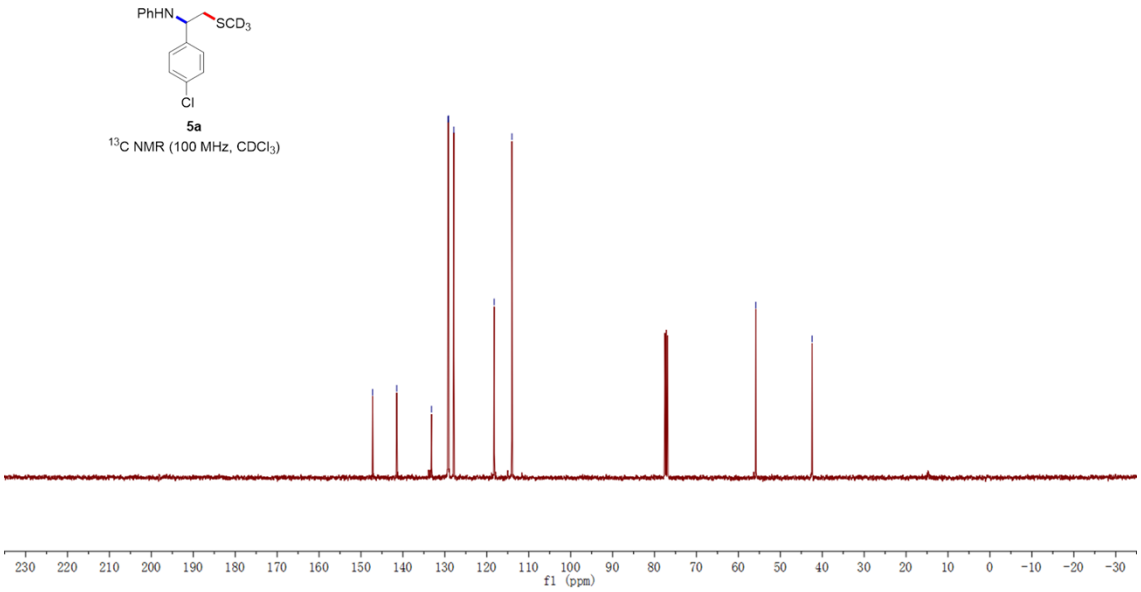

**5a**

$^{1}$H NMR (400 MHz, $CDCl_3$)

pdata/1

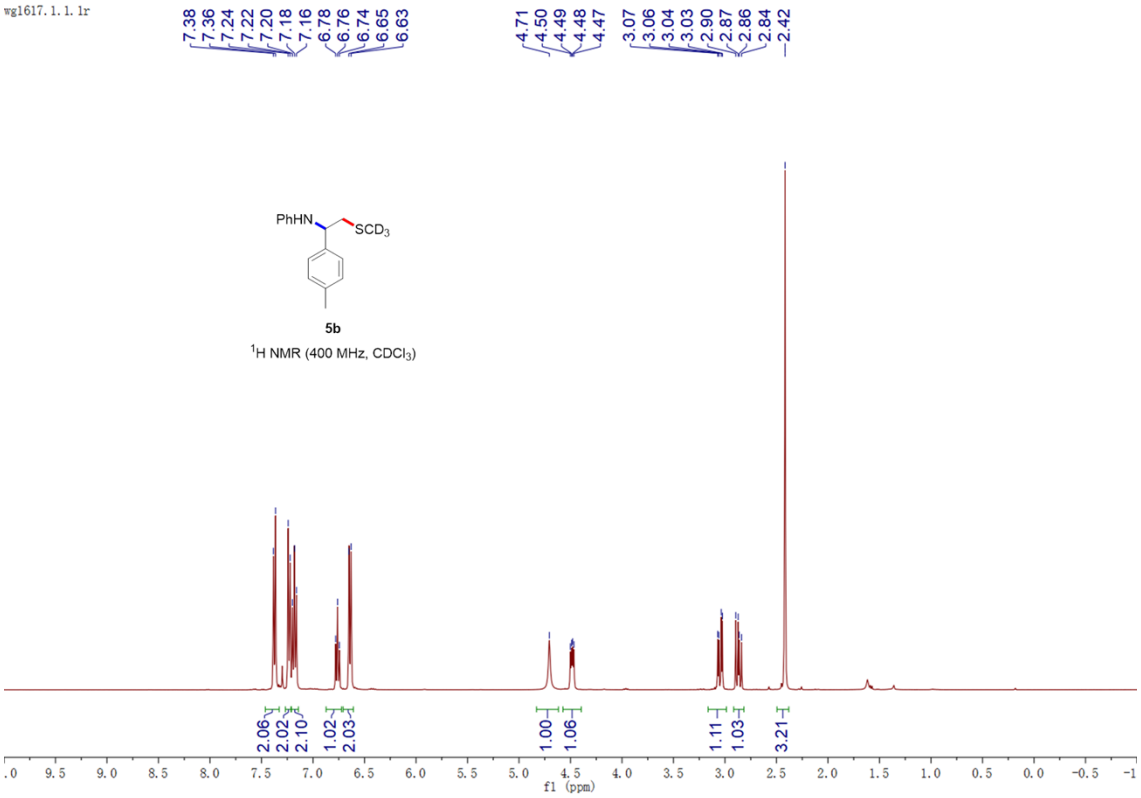
147.23 141.48 133.17 129.25 129.12 127.86 118.23 114.01

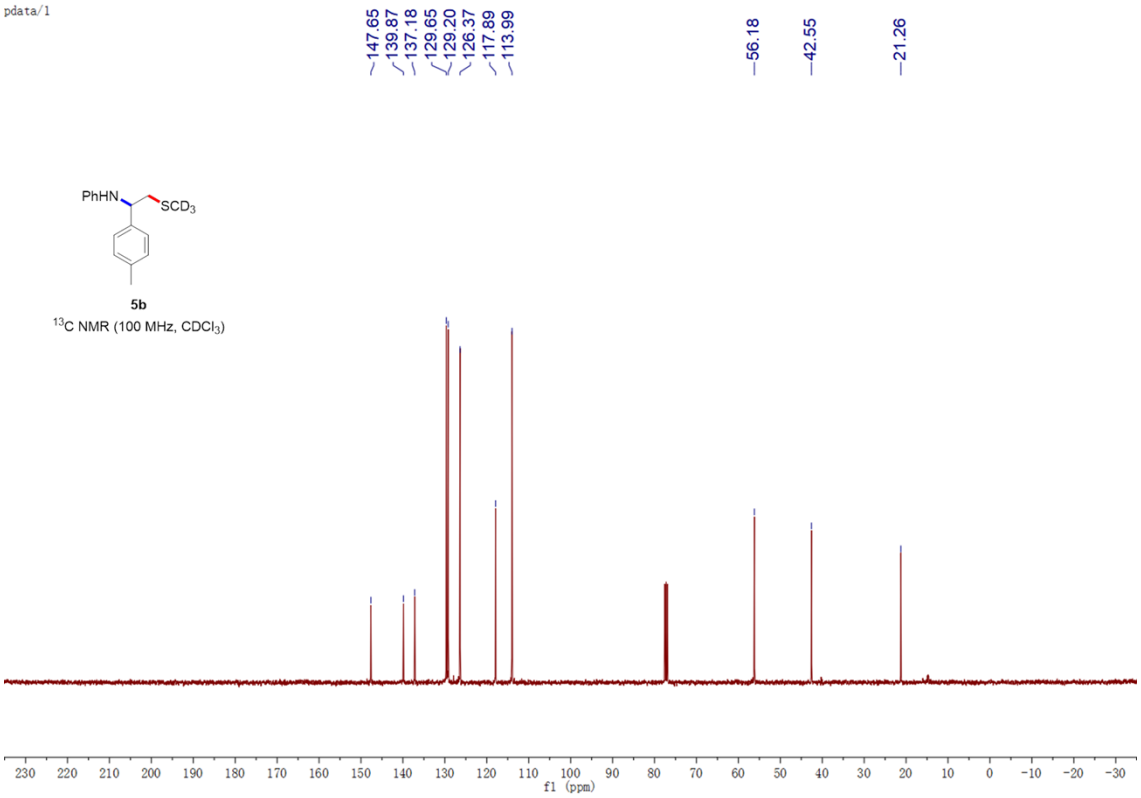
55.84 42.42

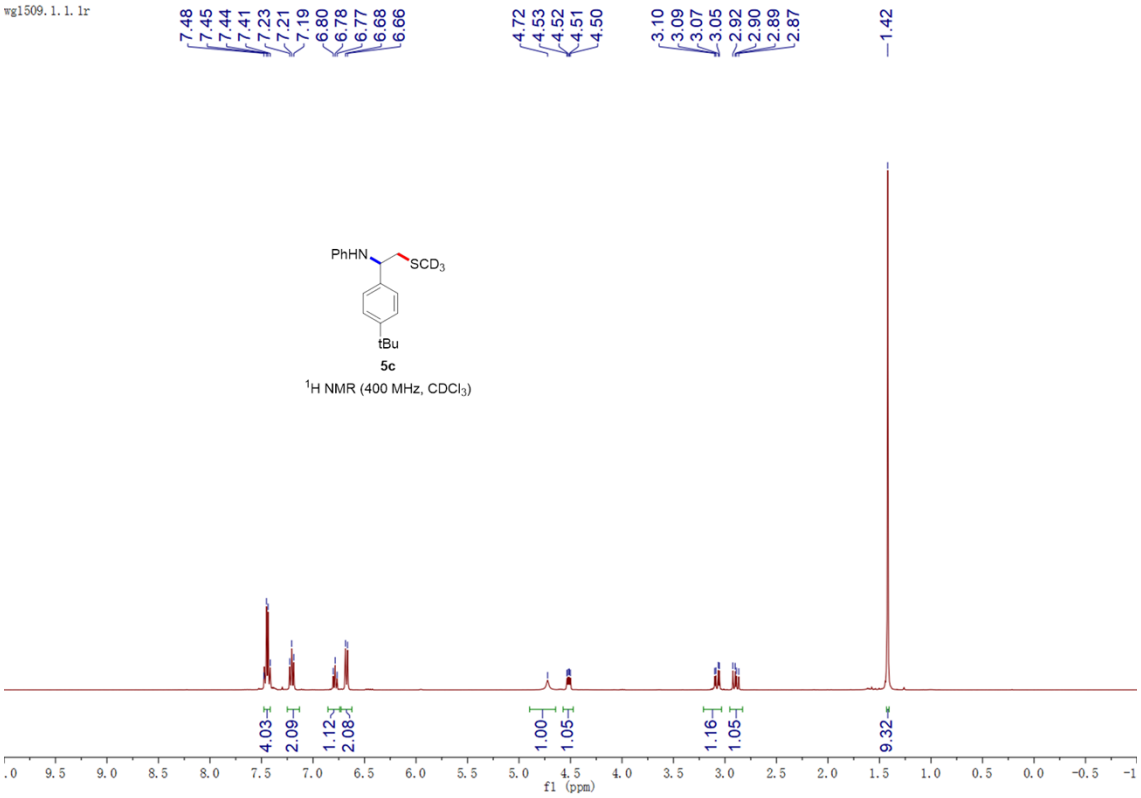


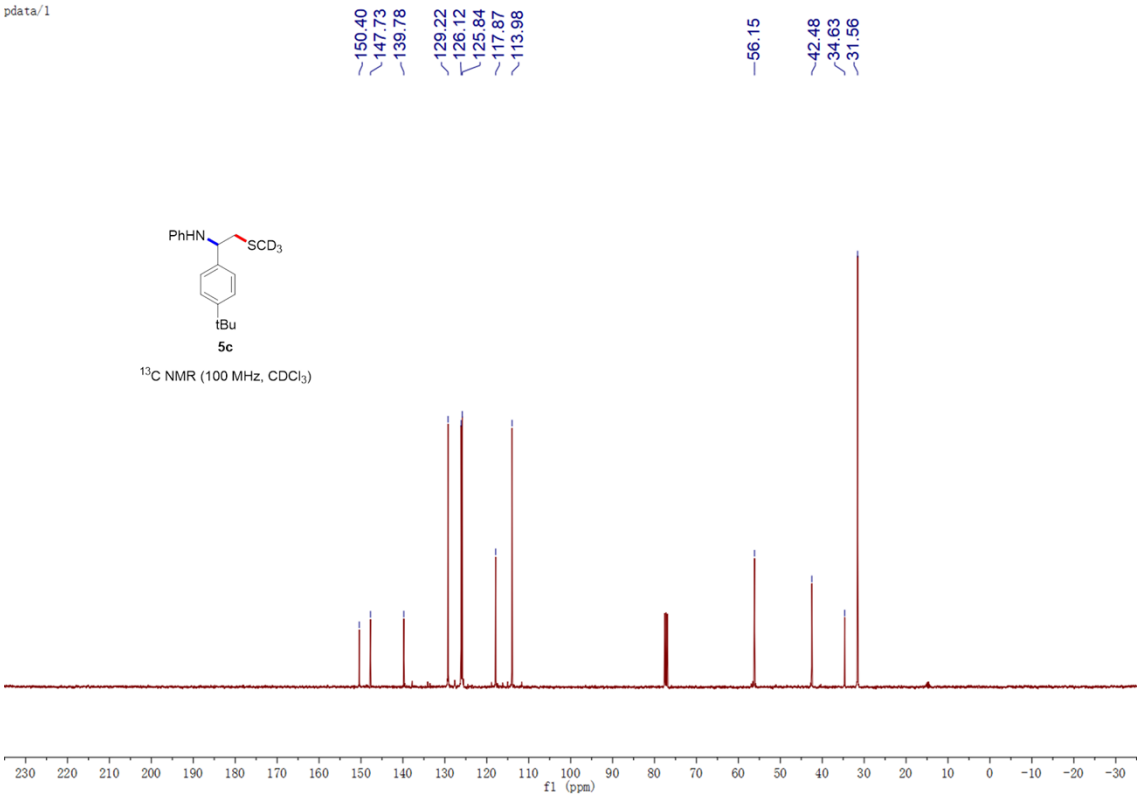

**5a**

$^{13}$C NMR (100 MHz, $CDCl_3$)


wg1617.1.1.1r
7.38
7.36
7.24
7.22
7.20
7.18
7.16
6.78
6.76
6.74
6.65
6.63
4.71
4.50
4.49
4.48
4.47
3.07
3.06
3.04
3.03
2.90
2.87
2.86
2.84
2.42
PhHN
SCD3
5b
1H NMR (400 MHz, CDCl3)
2.06
2.02
2.10
1.02
2.03
1.00
1.06
1.11
1.03
3.21
f1 (ppm)

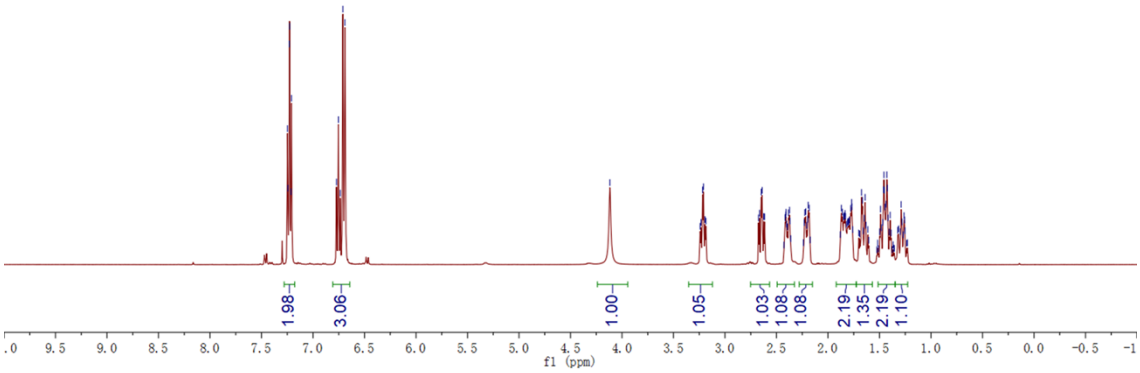

pdata/1
147.65
139.87
137.18
129.65
129.20
126.37
117.89
113.99
56.18
42.55
21.26
PhHN
SCD3
5b
13C NMR (100 MHz, CDCl3)
f1 (ppm)


wg1509.1.1.1r
7.48
7.45
7.44
7.41
7.23
7.21
7.19
6.80
6.78
6.77
6.68
6.66
4.72
4.53
4.52
4.51
4.50
3.10
3.09
3.07
3.05
2.92
2.90
2.89
2.87
1.42
PhHN
SCD3
tBu
5c
1H NMR (400 MHz, CDCl3)
4.03
2.09
1.12
2.08
1.00
1.05
1.16
1.05
9.32
f1 (ppm)


pdata/1
150.40
147.73
139.78
129.22
126.12
125.84
117.87
113.98
56.15
42.48
34.63
31.56
PhHN
SCD3
tBu
5c
13C NMR (100 MHz, CDCl3)
f1 (ppm)


**5d**

$^{1}$H NMR (400 MHz, $CDCl_3$)

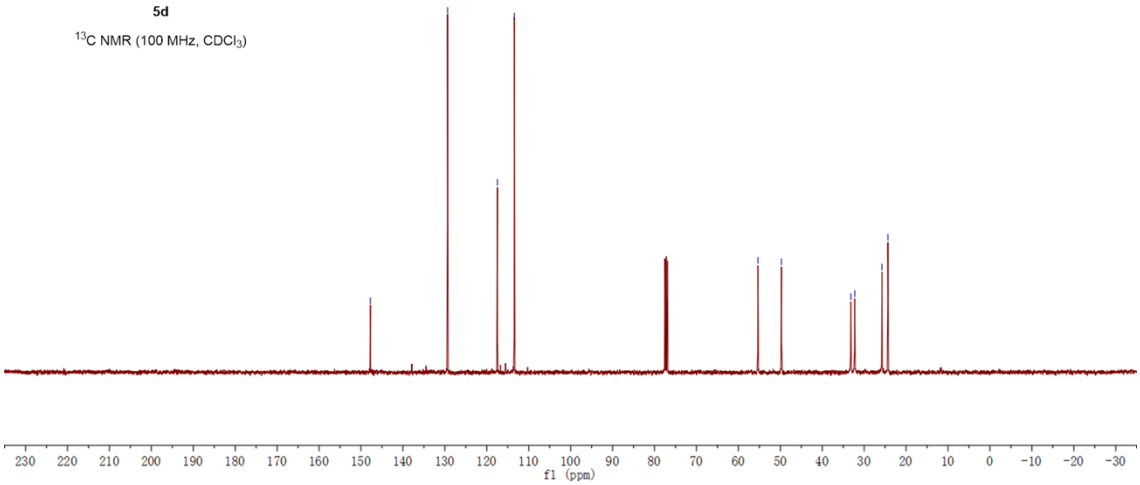


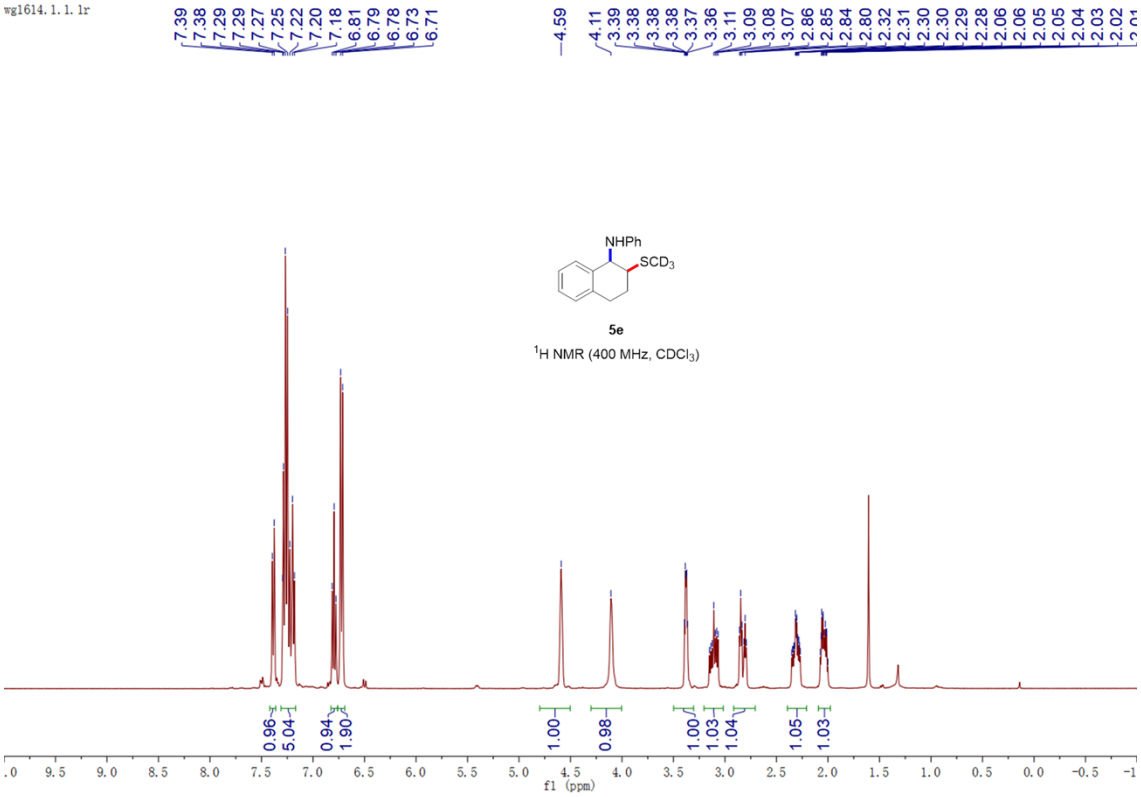

pdata/1

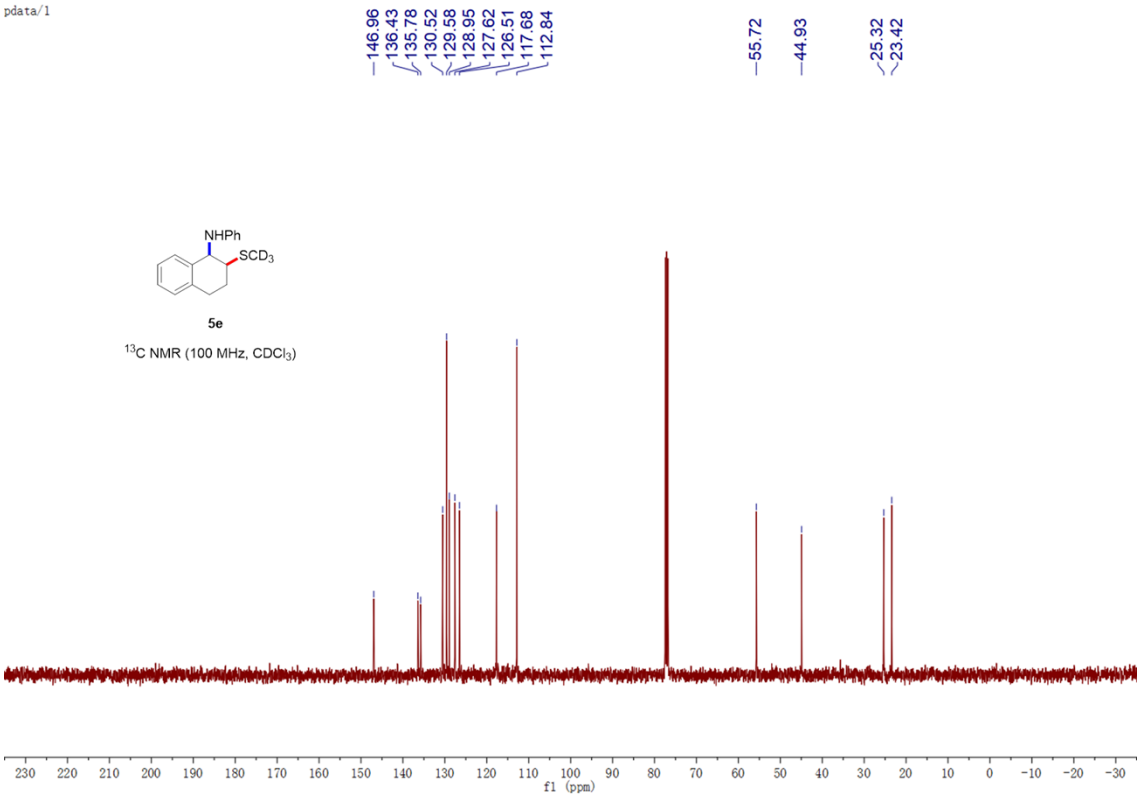


**5d**

$^{13}$C NMR (100 MHz, $CDCl_3$)



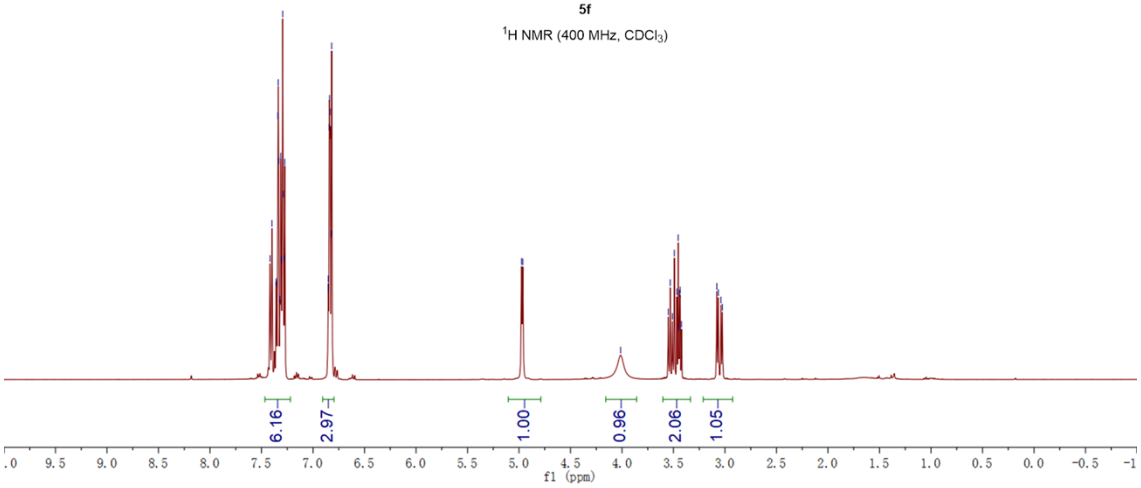

wg1614.1.1.1r
7.39
7.38
7.29
7.29
7.27
7.25
7.22
7.20
7.18
6.81
6.79
6.78
6.73
6.71
4.59
4.11
3.39
3.38
3.38
3.38
3.37
3.36
3.11
3.09
3.08
3.07
2.86
2.85
2.84
2.80
2.32
2.31
2.30
2.30
2.29
2.28
2.06
2.06
2.05
2.05
2.04
2.03
2.02
NHPh
SCD3
5e
1H NMR (400 MHz, CDCl3)
0.96
5.04
0.94
1.90
1.00
0.98
1.00
1.03
1.04
1.05
1.03
f1 (ppm)


pdata/1
146.96
136.43
135.78
130.52
129.58
128.95
127.62
126.51
117.68
112.84
55.72
44.93
25.32
23.42
NHPh
SCD3
5e
13C NMR (100 MHz, CDCl3)
f1 (ppm)

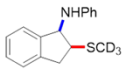


**5f**

$^{1}$H NMR (400 MHz, $CDCl_3$)

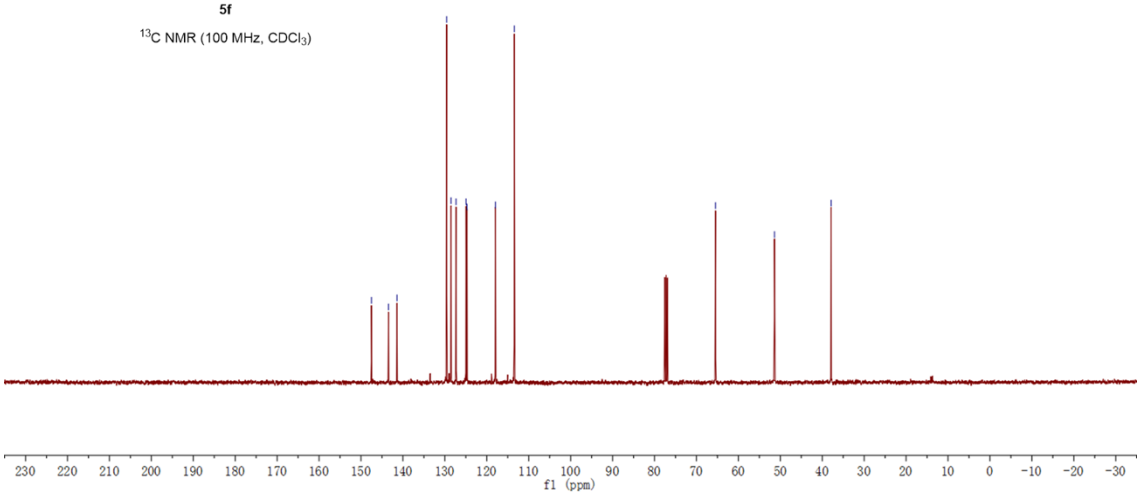


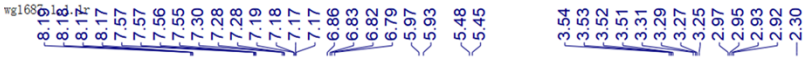

pdata/1

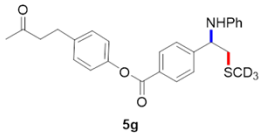




**5f**

$^{13}$C NMR (100 MHz, $CDCl_3$)

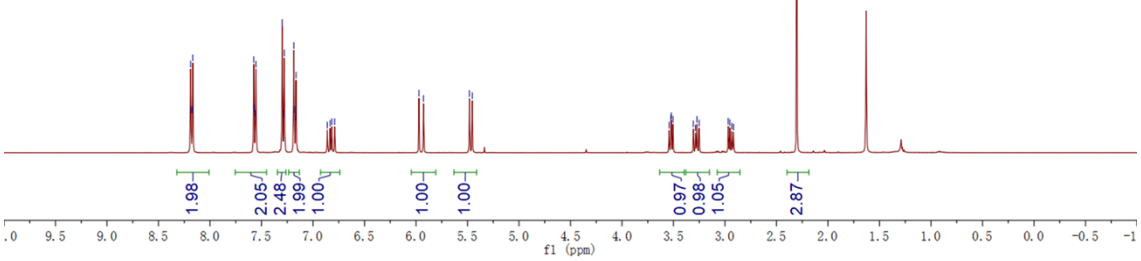


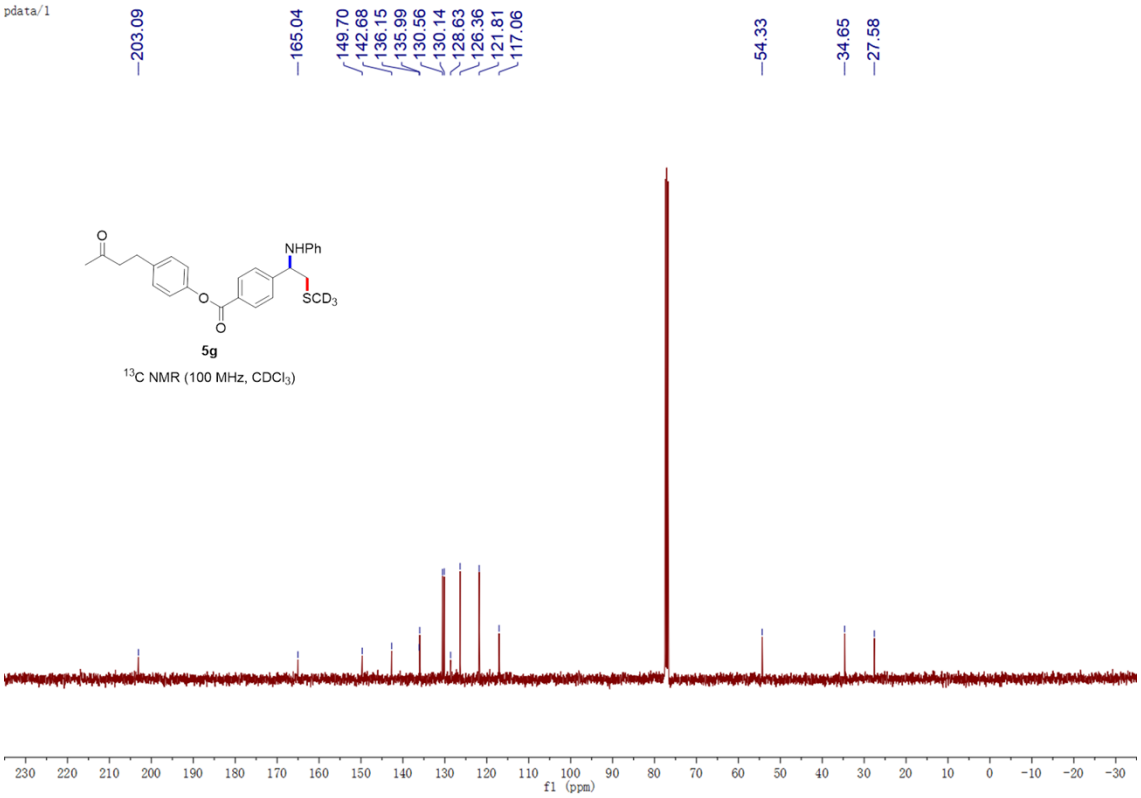



**5g**

$^{1}$H NMR (400 MHz, $CDCl_3$)



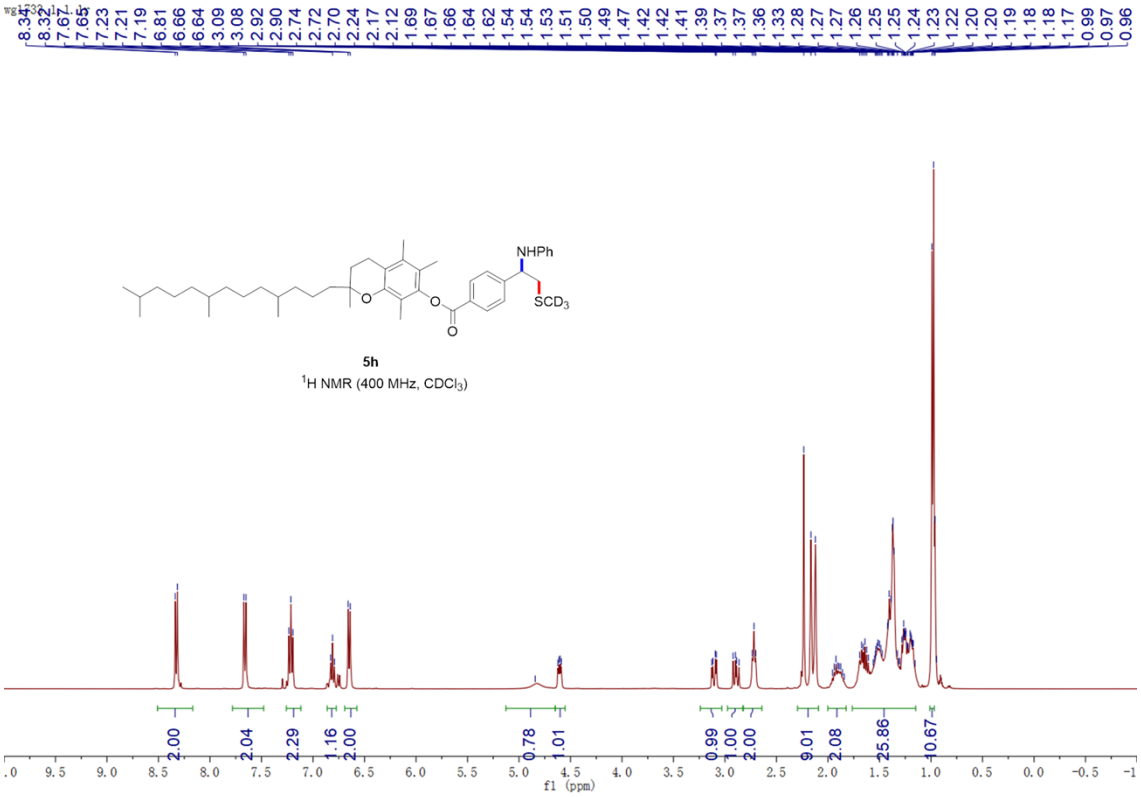







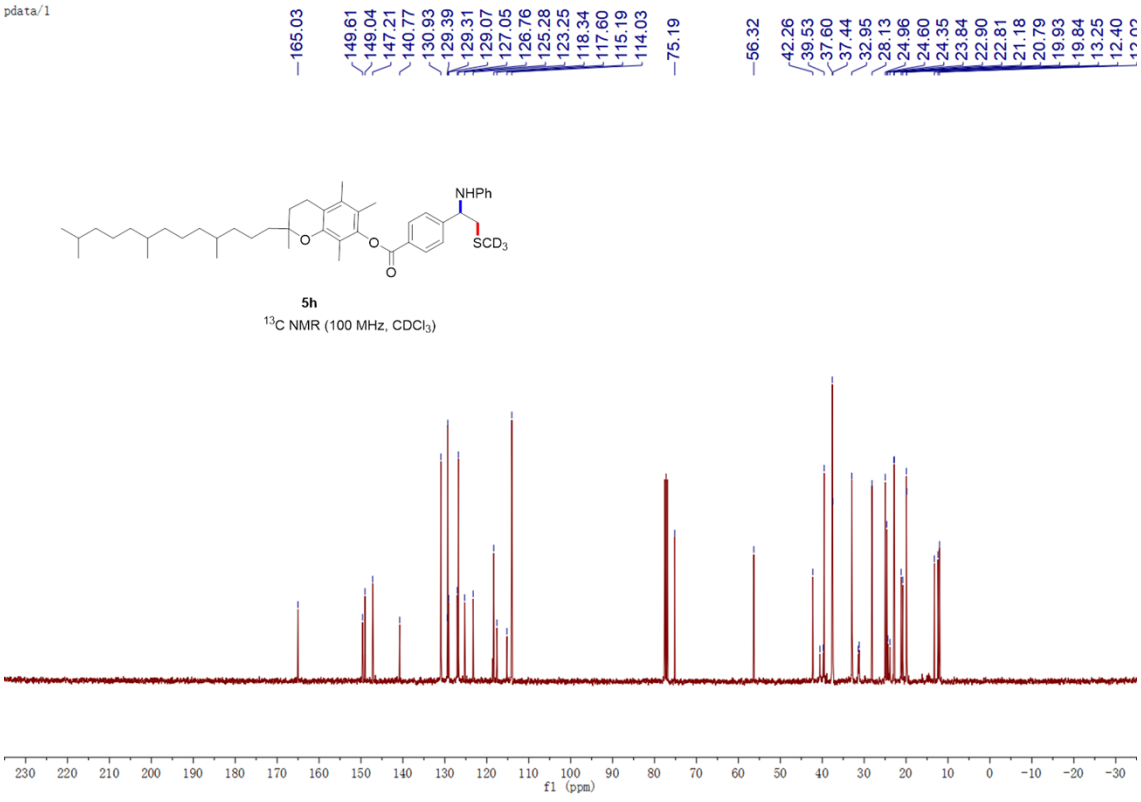
**5g**

$^{13}$C NMR (100 MHz, $CDCl_3$)



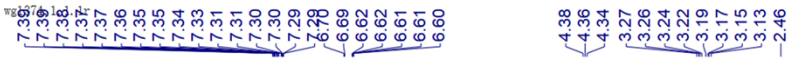

**5h**

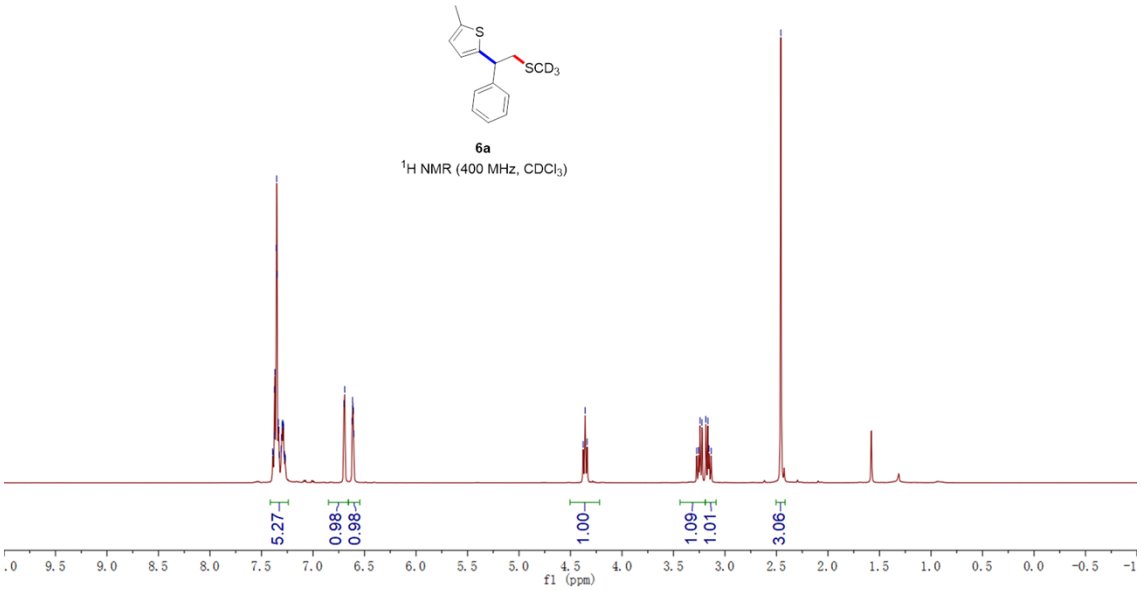
$^{1}$H NMR (400 MHz, $CDCl_3$)




**5h**

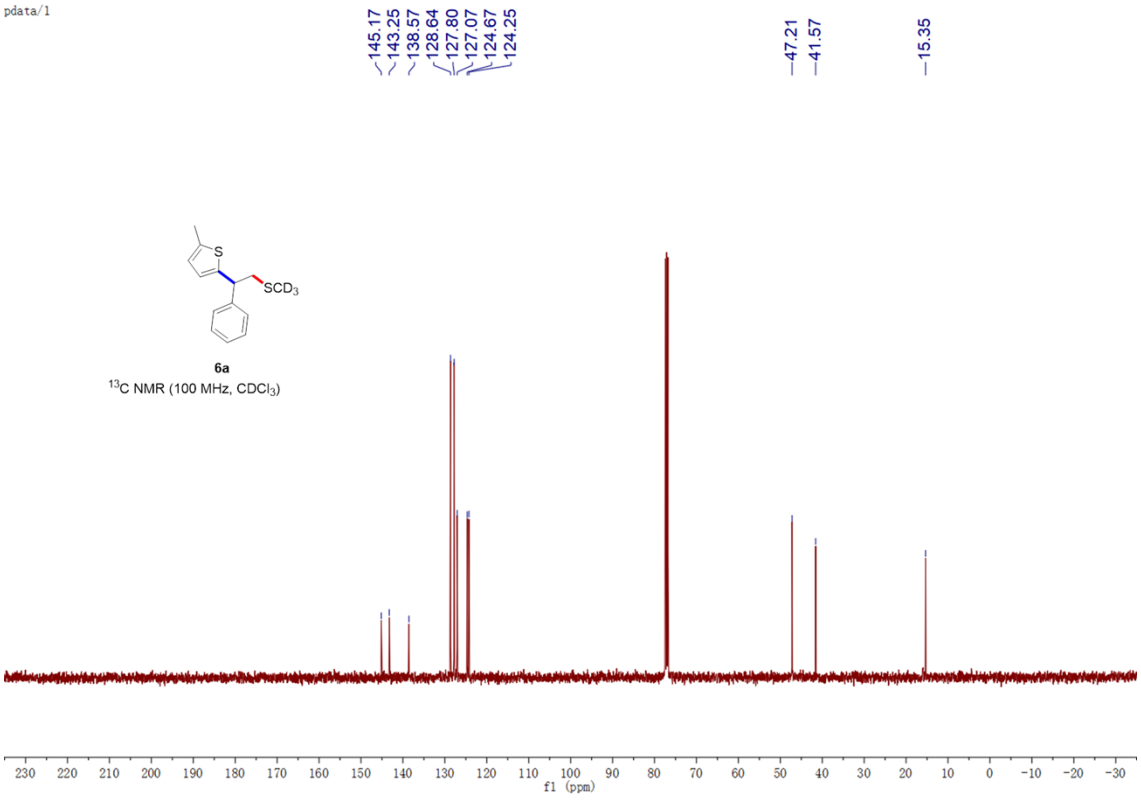
$^{13}$C NMR (100 MHz, $CDCl_3$)



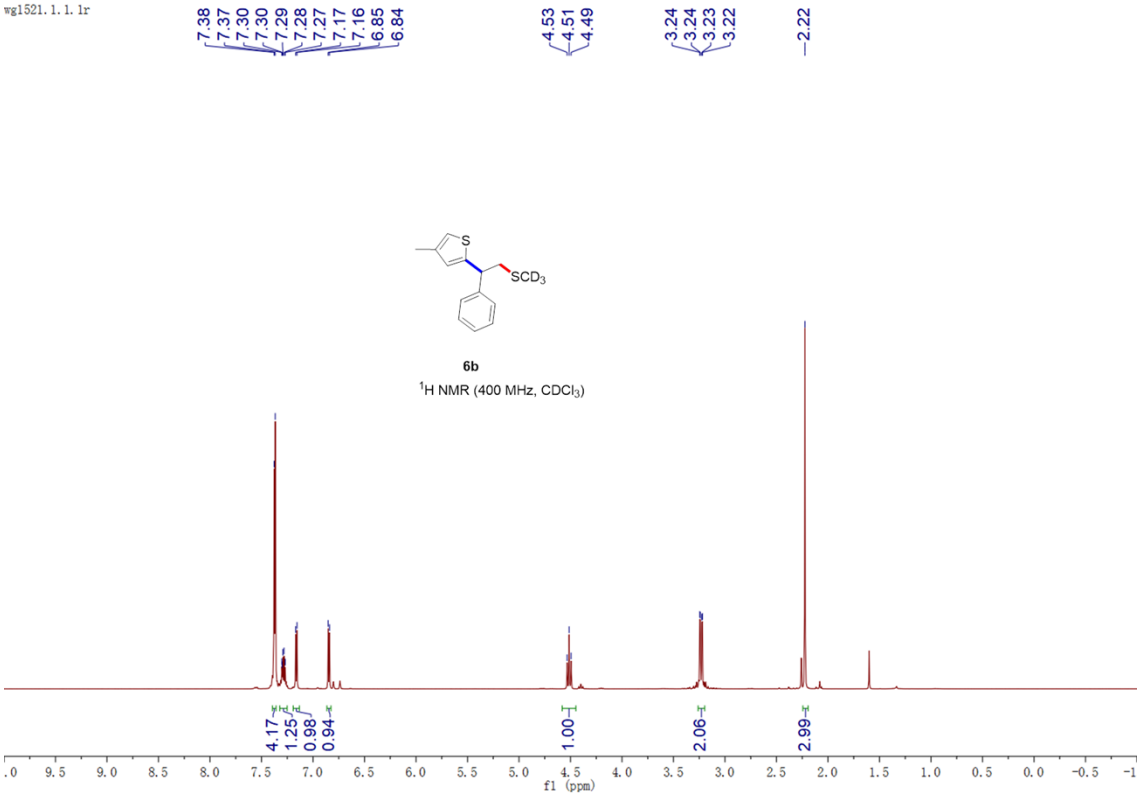

**6a**

$^{1}$H NMR (400 MHz, $CDCl_3$)



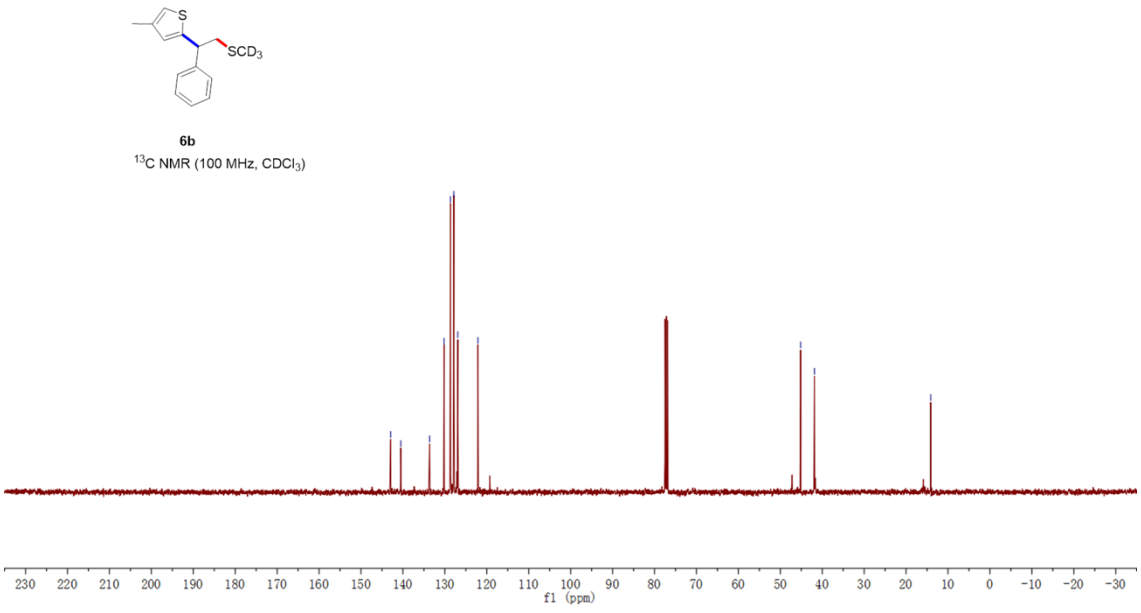

**6a**

$^{13}$C NMR (100 MHz, $CDCl_3$)



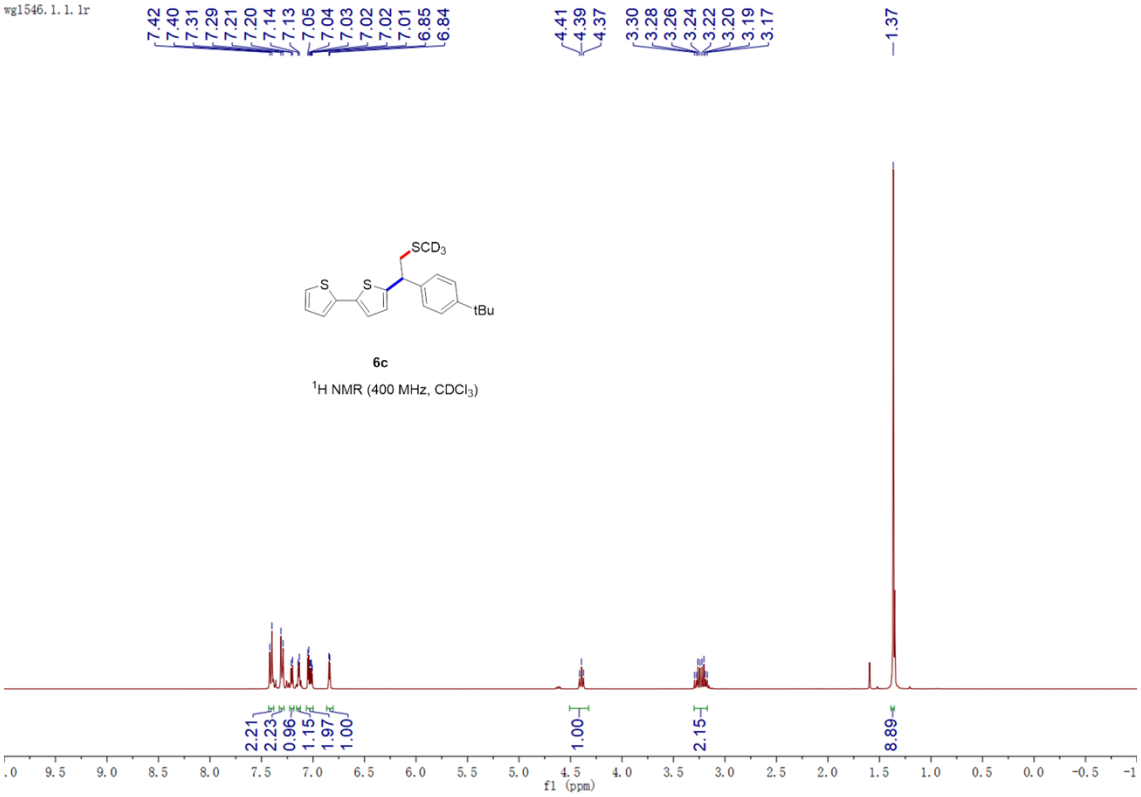

**6b**

$^{1}$H NMR (400 MHz, $CDCl_3$)



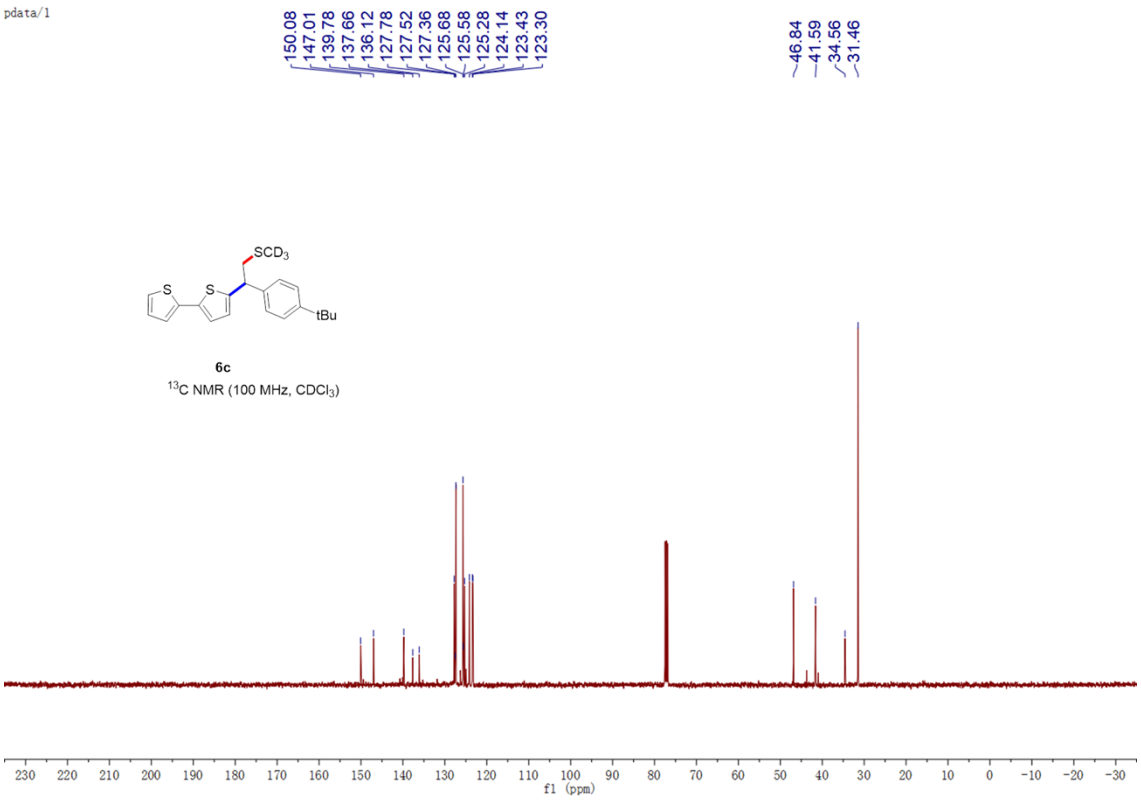

**6b**

$^{13}$C NMR (100 MHz, $CDCl_3$)



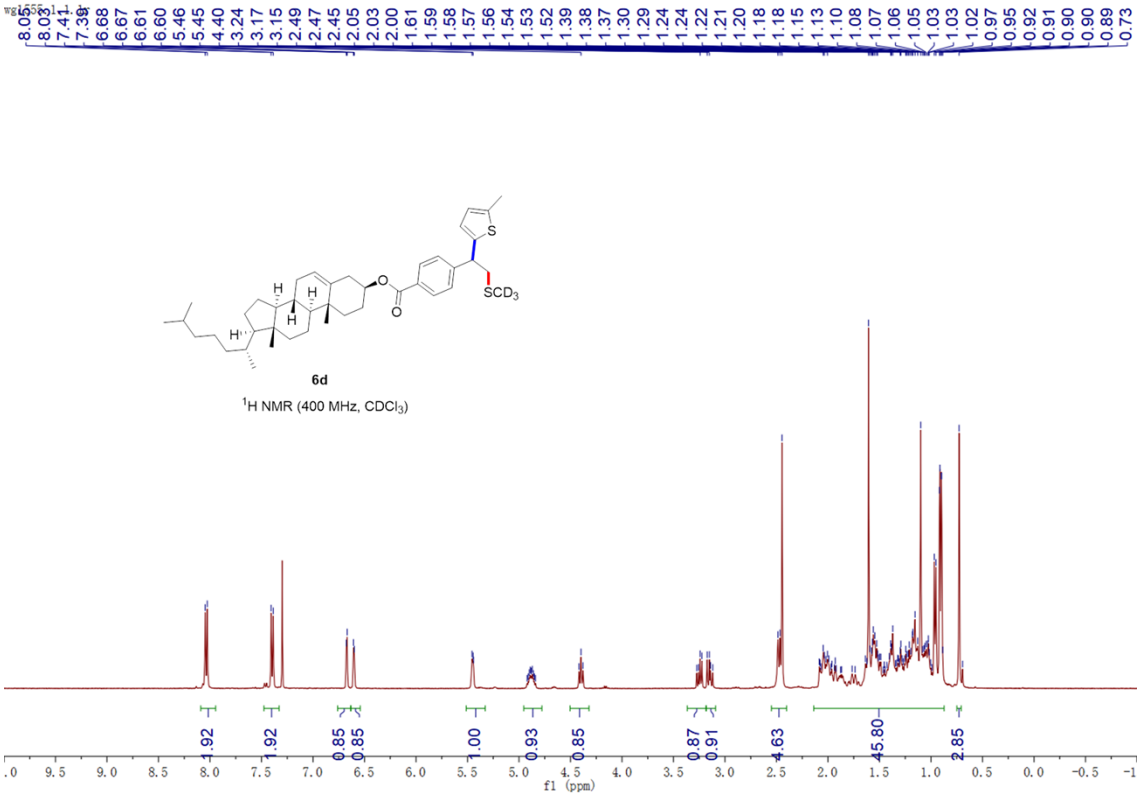

**6c**

$^{1}$H NMR (400 MHz, $CDCl_3$)



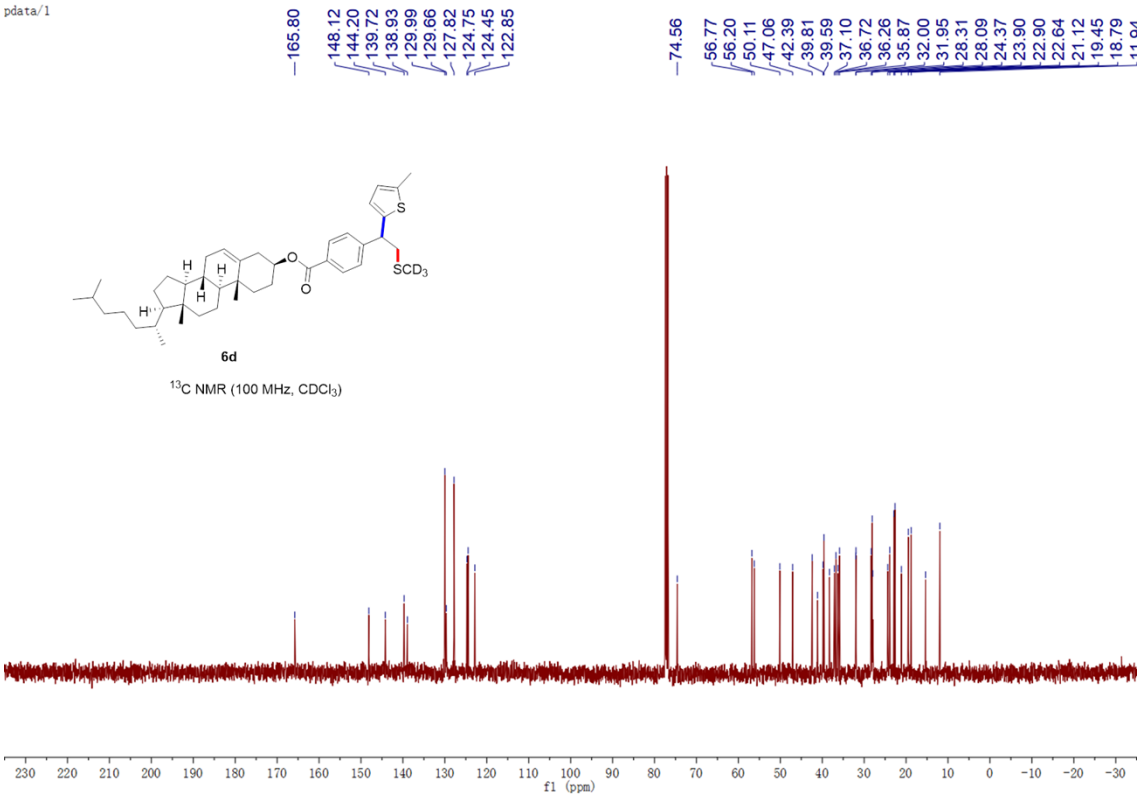

**6c**

$^{13}$C NMR (100 MHz, $CDCl_3$)



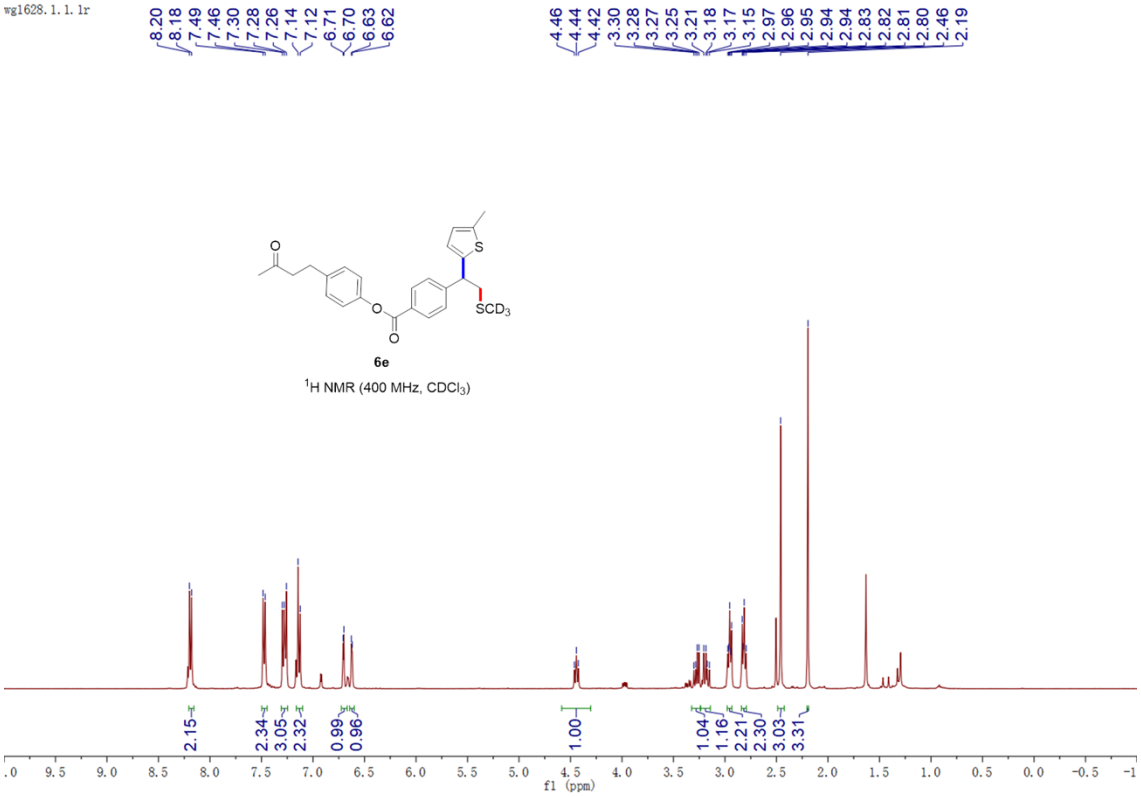

6d

$^{1}$H NMR (400 MHz, $CDCl_3$)



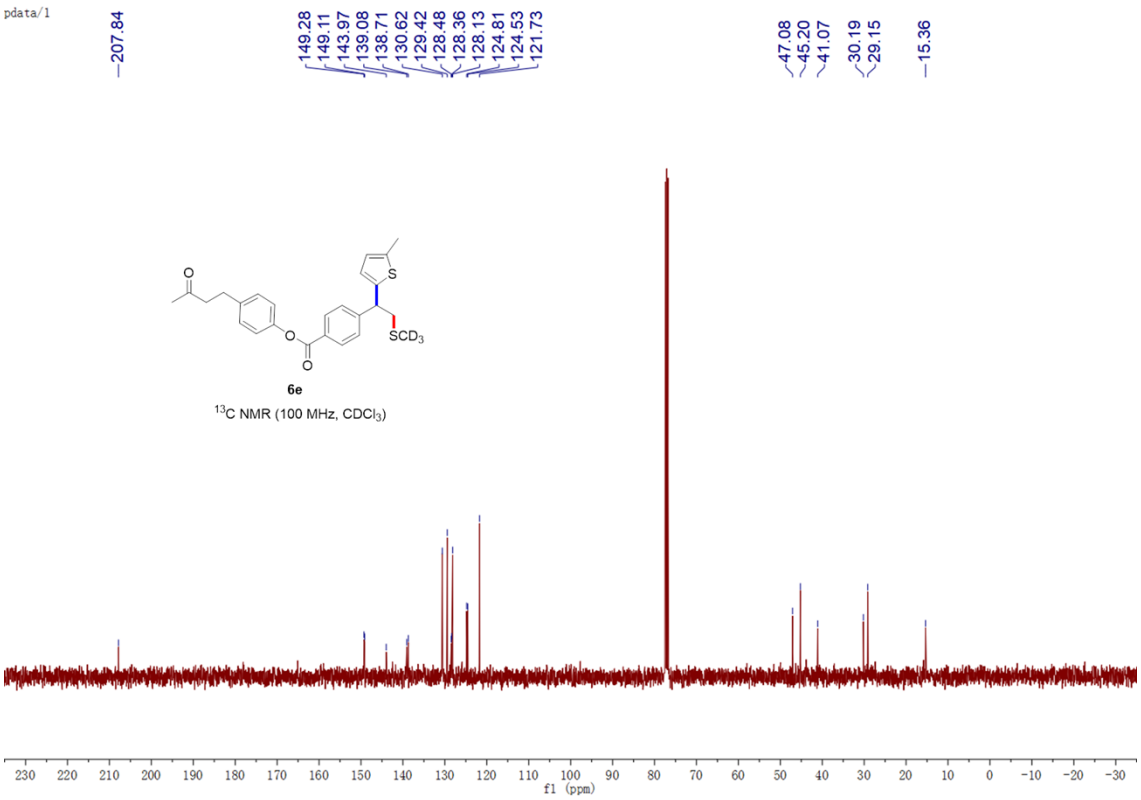

6d

$^{13}$C NMR (100 MHz, $CDCl_3$)




**6e**

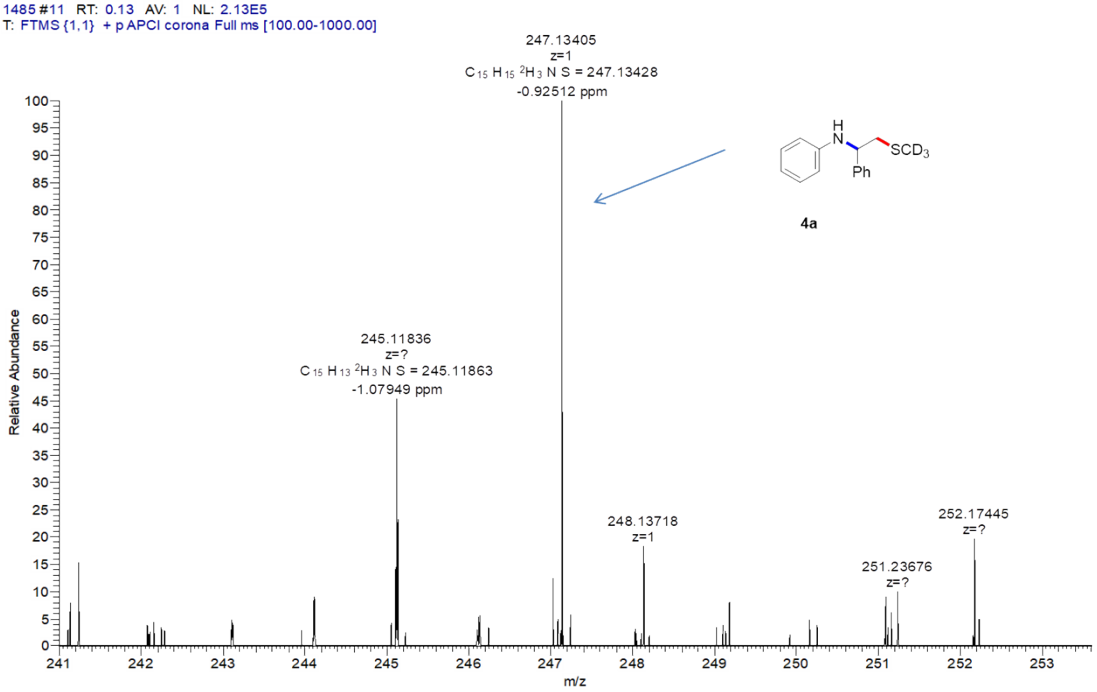
$^{1}$H NMR (400 MHz, $CDCl_3$)

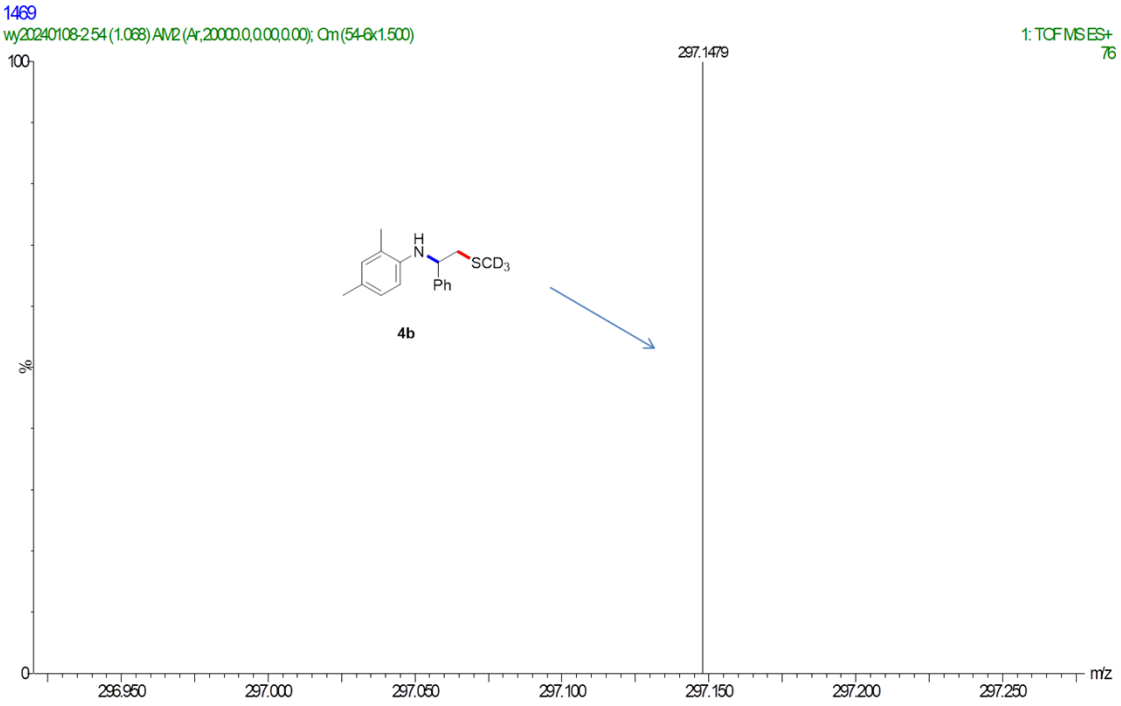


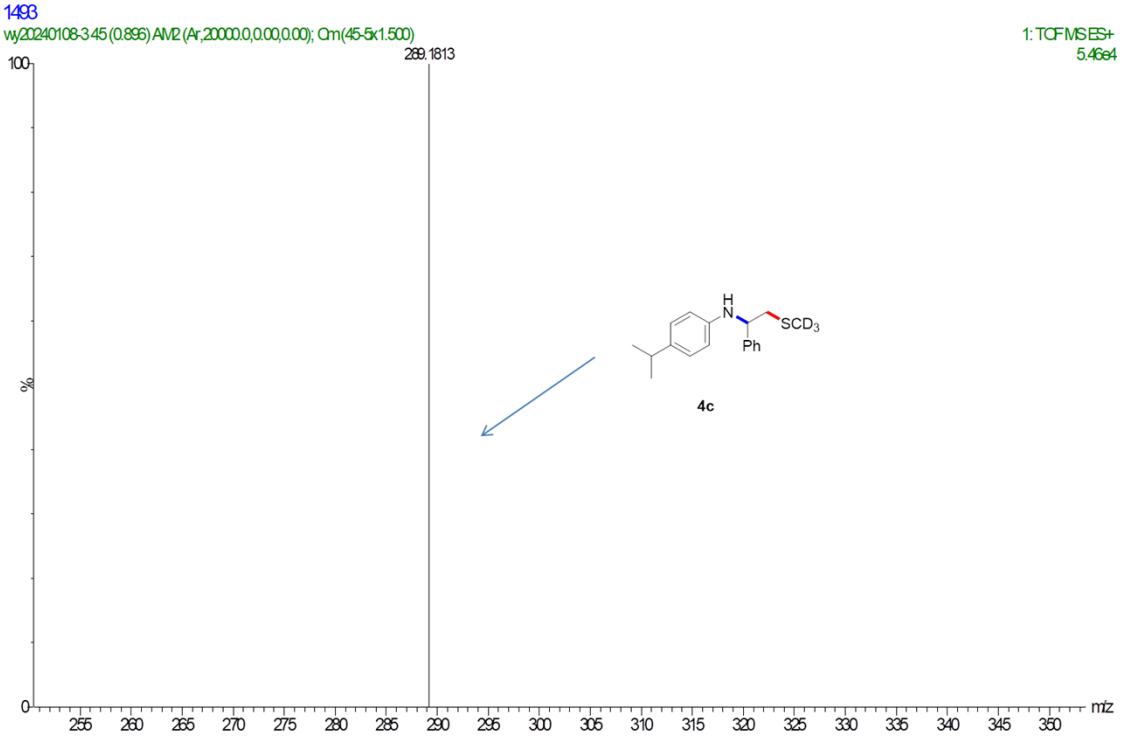

**6e**

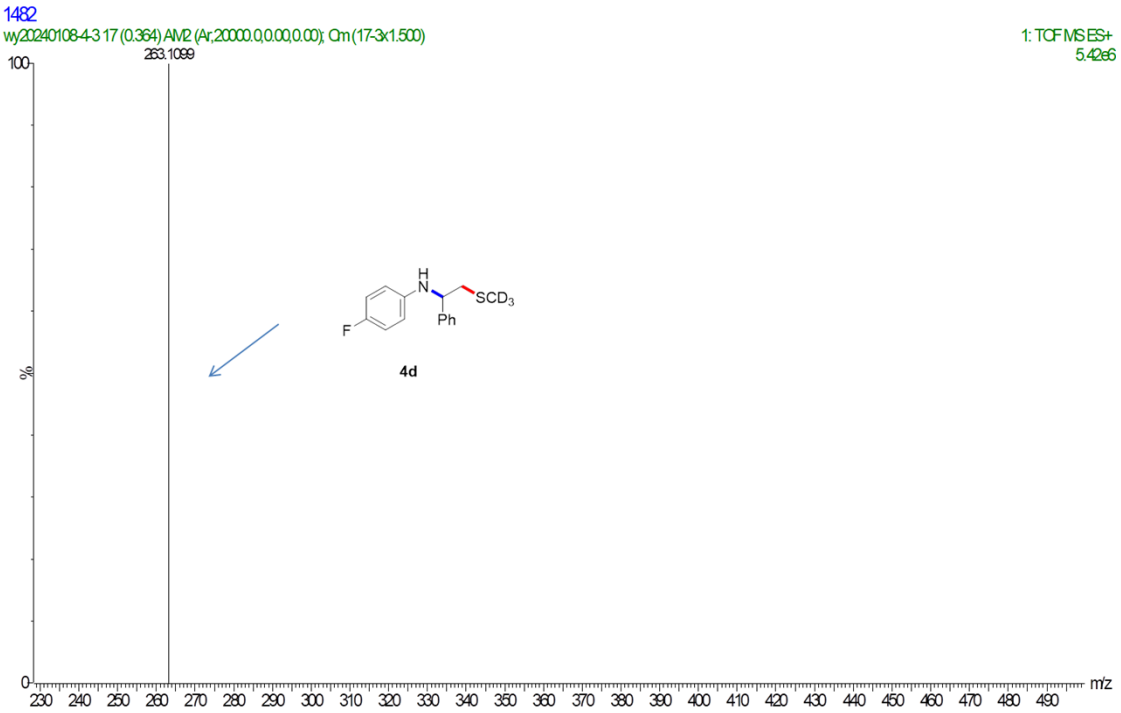
$^{13}$C NMR (100 MHz, $CDCl_3$)

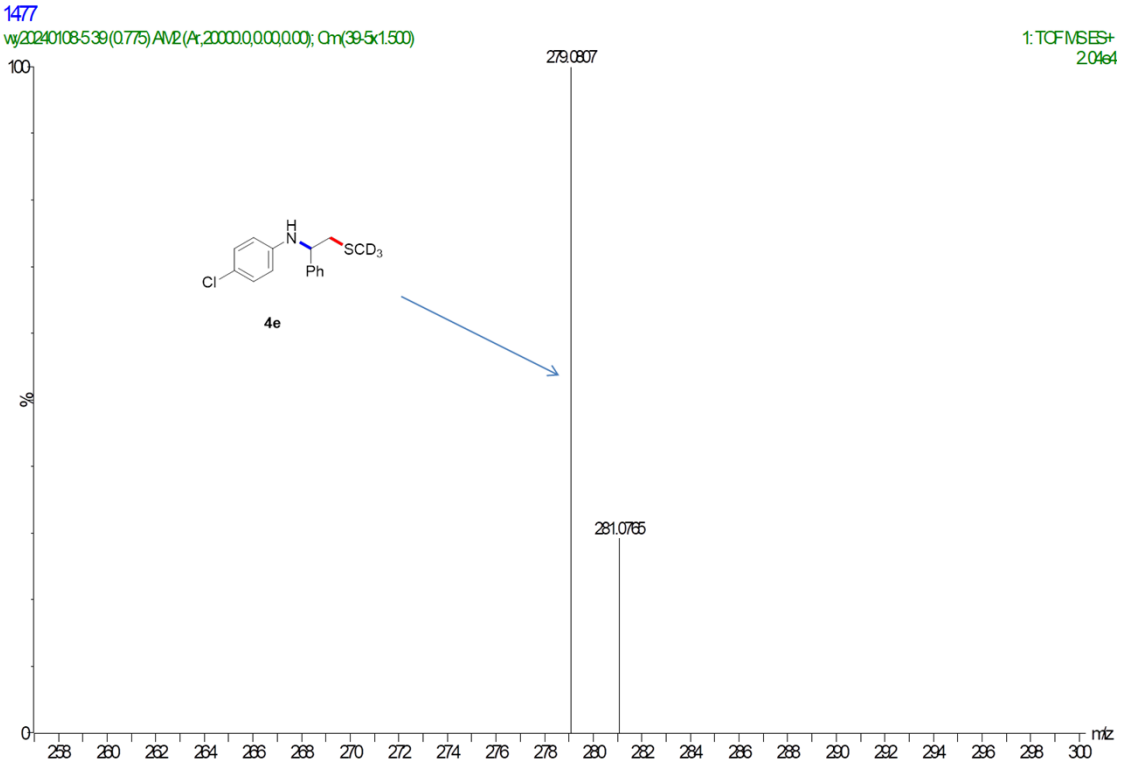
# HRMS of Products

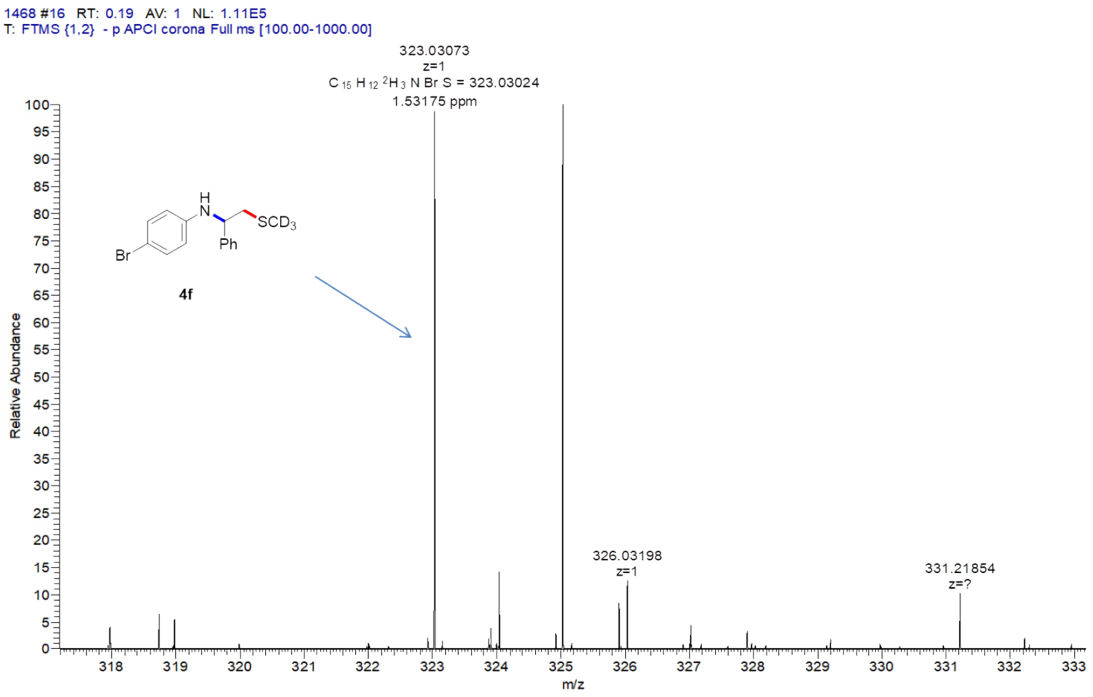


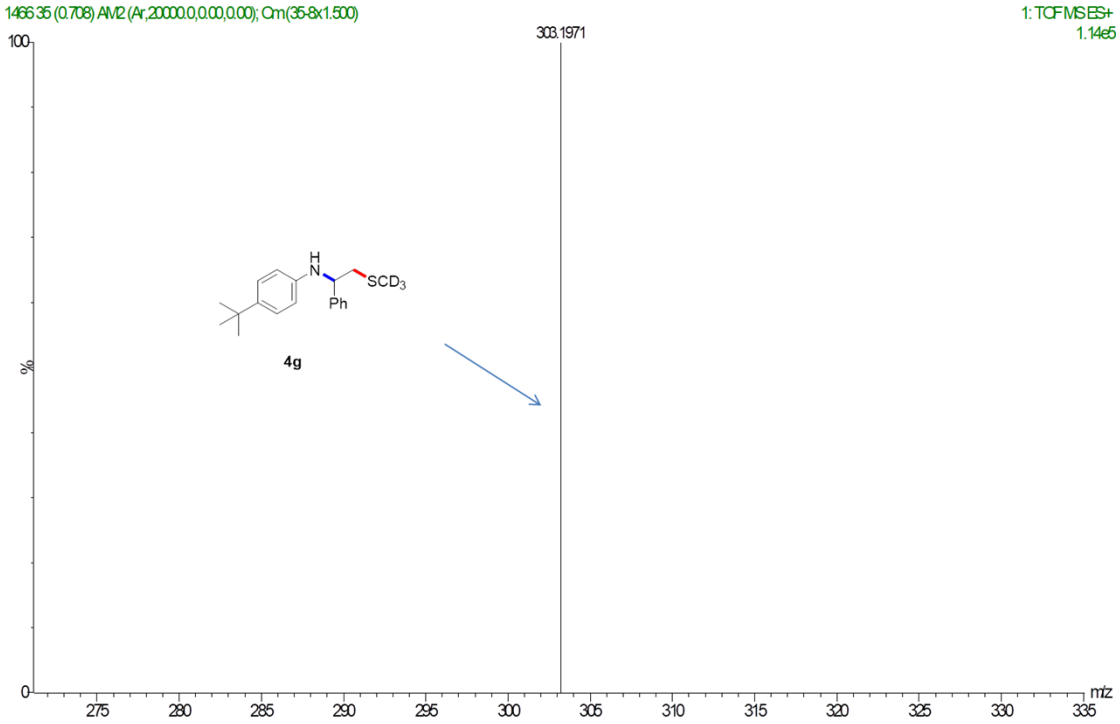

1469
wy20240108-2 54 (1.068) AM2 (Ar,20000.0,0.000,0.00); Cm (54-6x1.500)
1: TOF MS ES+
76
297.1479
100
%
0
H
N
SCD3
Ph
4b
296.950
297.000
297.050
297.100
297.150
297.200
297.250
m/z

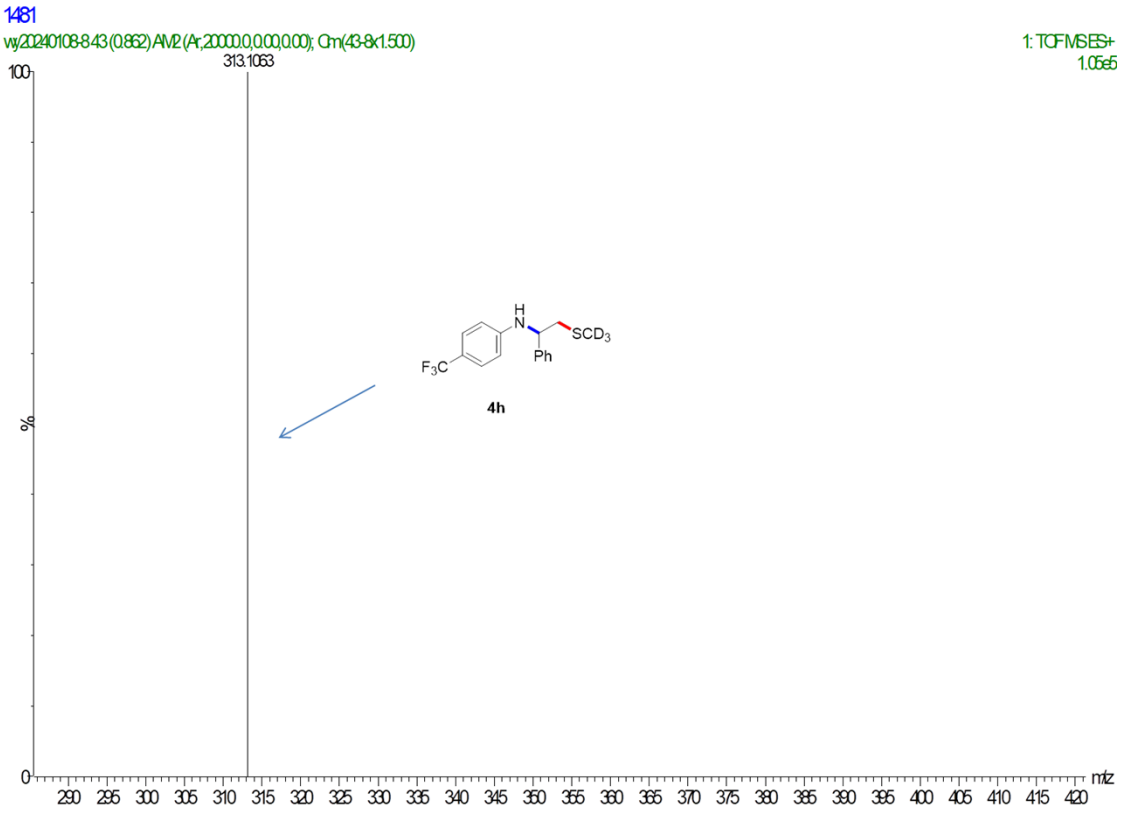

1493
wy20240108-3 45 (0.896) AM2 (Ar,20000.0,0.000,0.00); Cm (45-5x1.500)
1: TOF MS ES+
5.46e4
289.1813
100
%
0
H
N
SCD3
Ph
4c
255
260
265
270
275
280
285
290
295
300
305
310
315
320
325
330
335
340
345
350
m/z

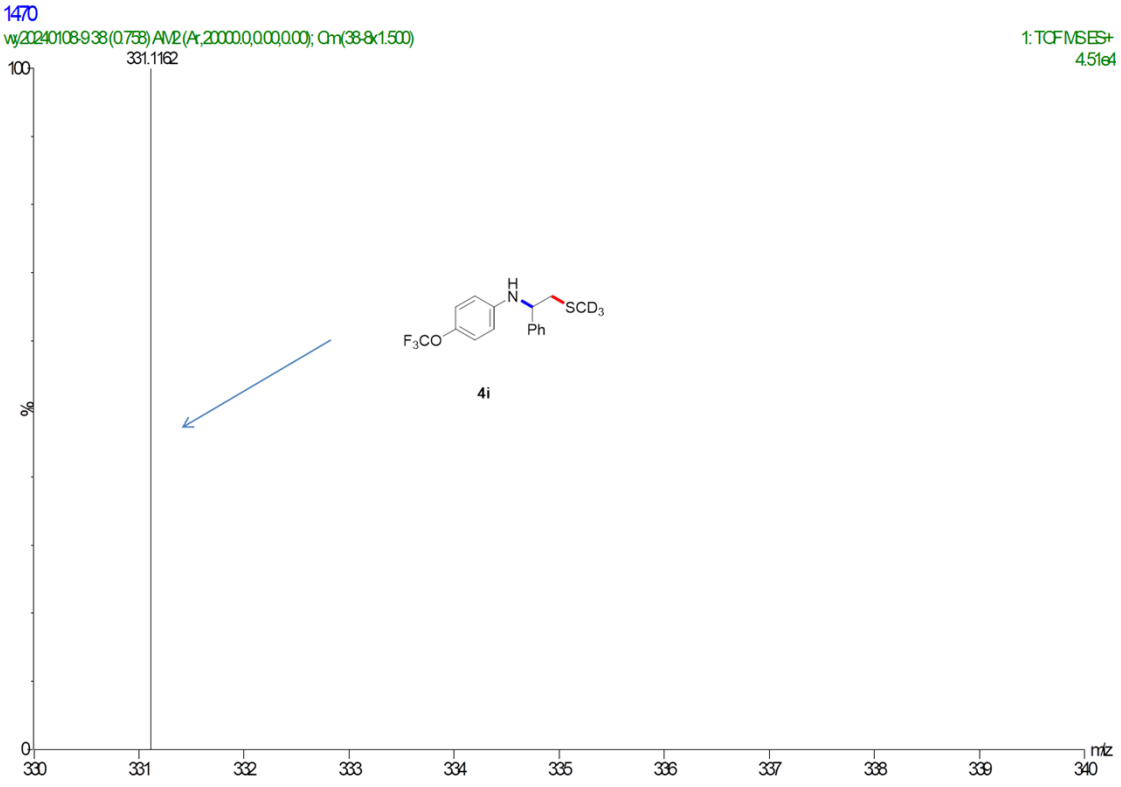

1482
wy20240108-4-3 17 (0.364) AM2 (Ar,20000.0,0.00,0.00); Cm (17-3x1.500)
1: TOF MS ES+
5.42e6
263.1099
100
%
0
230 240 250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400 410 420 430 440 450 460 470 480 490
m/z
H
N
SCD3
Ph
F
4d

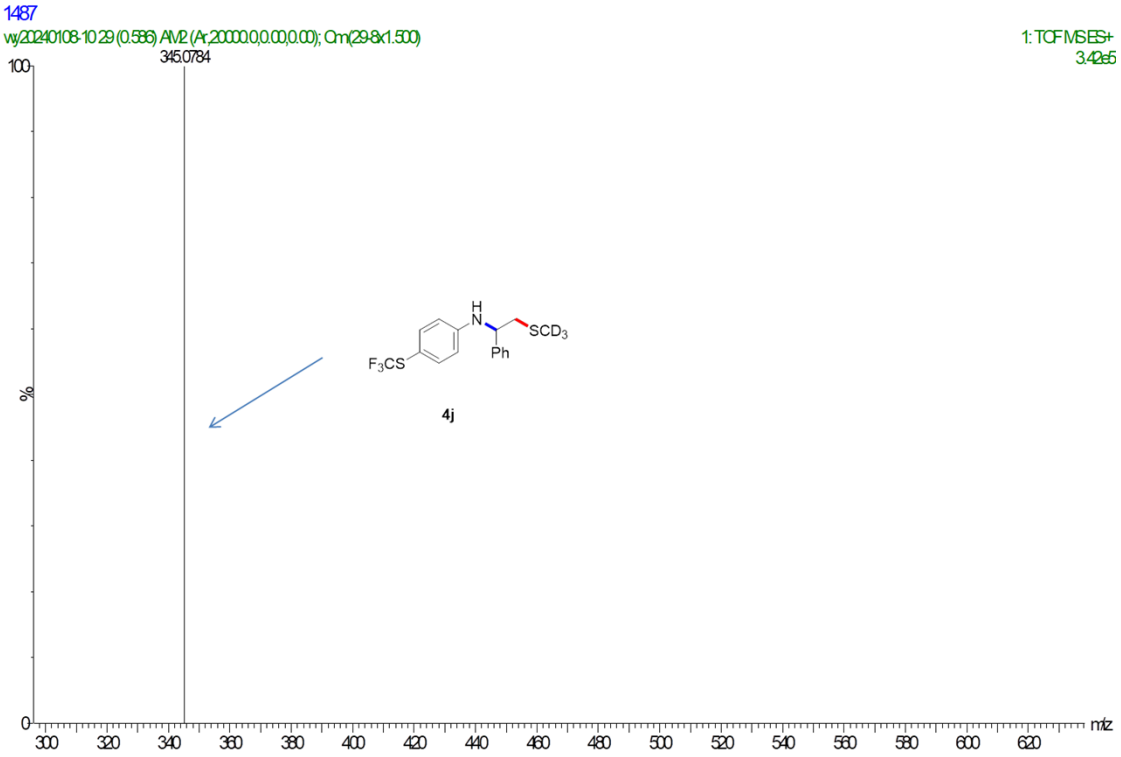

1477
wy20240108-5-39 (0.775) AM2 (Ar,20000.0,0.00,0.00); Cm (39-5x1.500)
1: TOF MS ES+
2.04e4
279.0807
281.0765
100
%
0
258 260 262 264 266 268 270 272 274 276 278 280 282 284 286 288 290 292 294 296 298 300
m/z
H
N
SCD3
Ph
Cl
4e

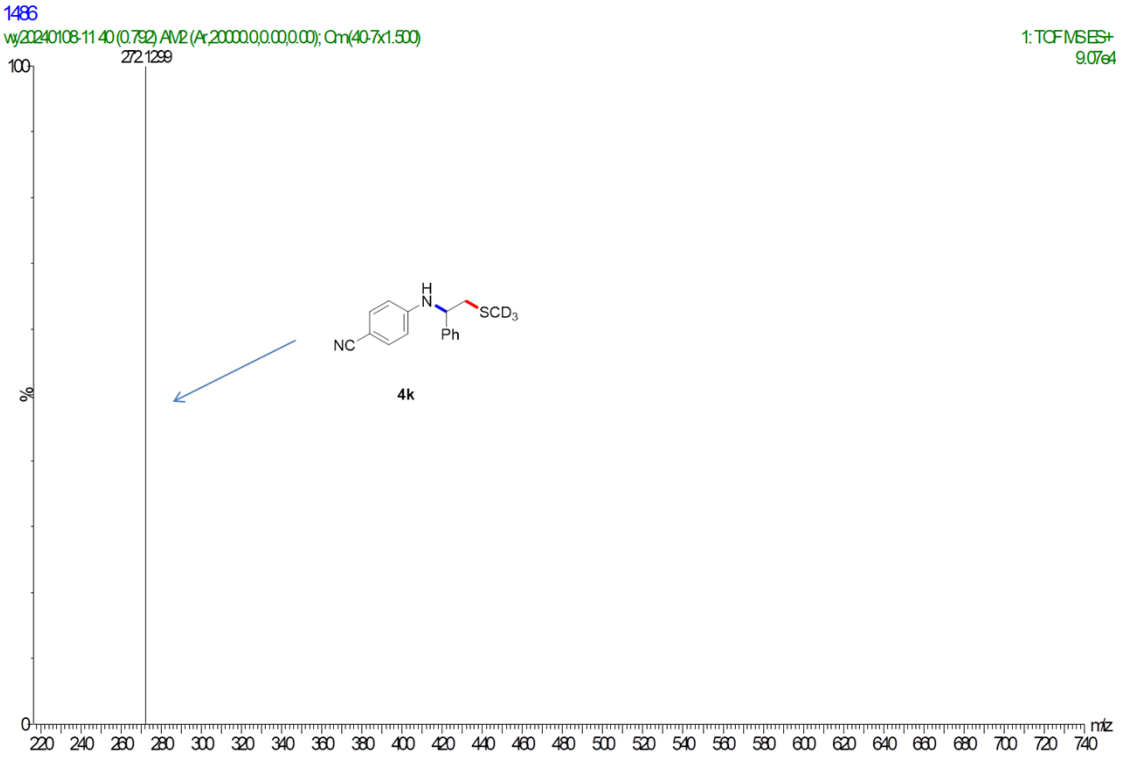

1468 #16 RT: 0.19 AV: 1 NL: 1.11E5
T: FTMS {1,2} - p APCI corona Full ms [100.00-1000.00]
323.03073
z=1
C 15 H 12 2H 3 N Br S = 323.03024
1.53175 ppm
Br
H
N
SCD3
Ph
4f
326.03198
z=1
331.21854
z=?
Relative Abundance
m/z

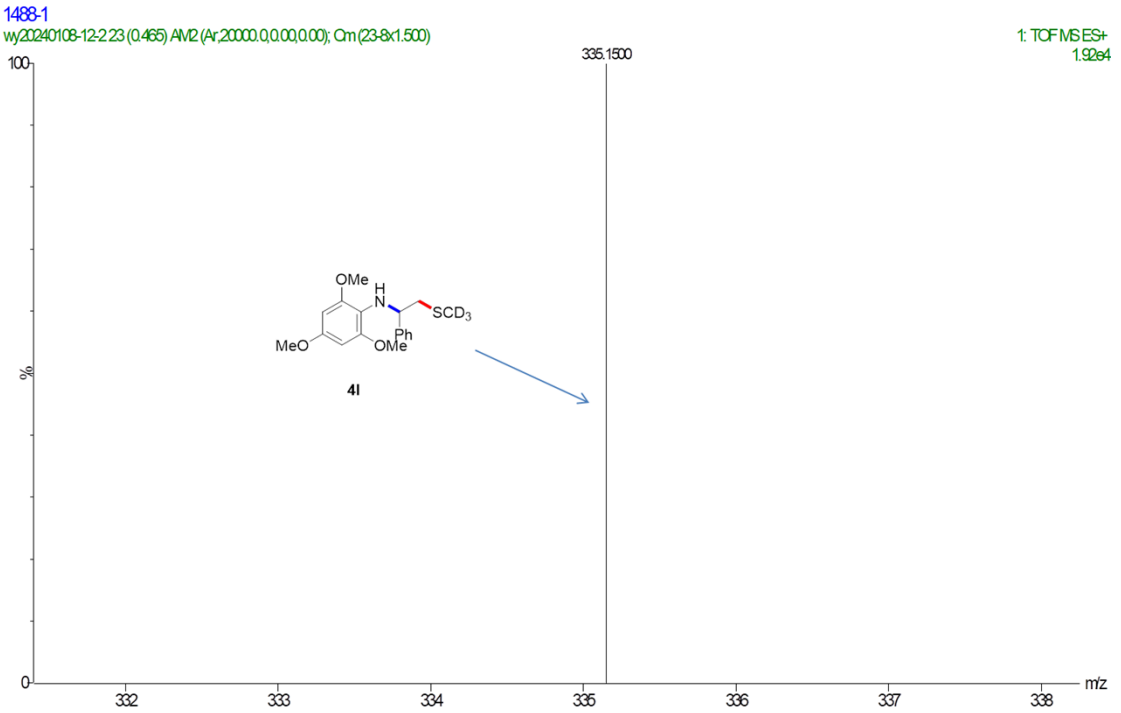

1466 35 (0.708) AM2 (Ar,20000.0,0.00,0.00); Cm (35-8x1.500)
1: TOF MS ES+
1.14e5
303.1971
H
N
SCD3
Ph
4g
%
m/z

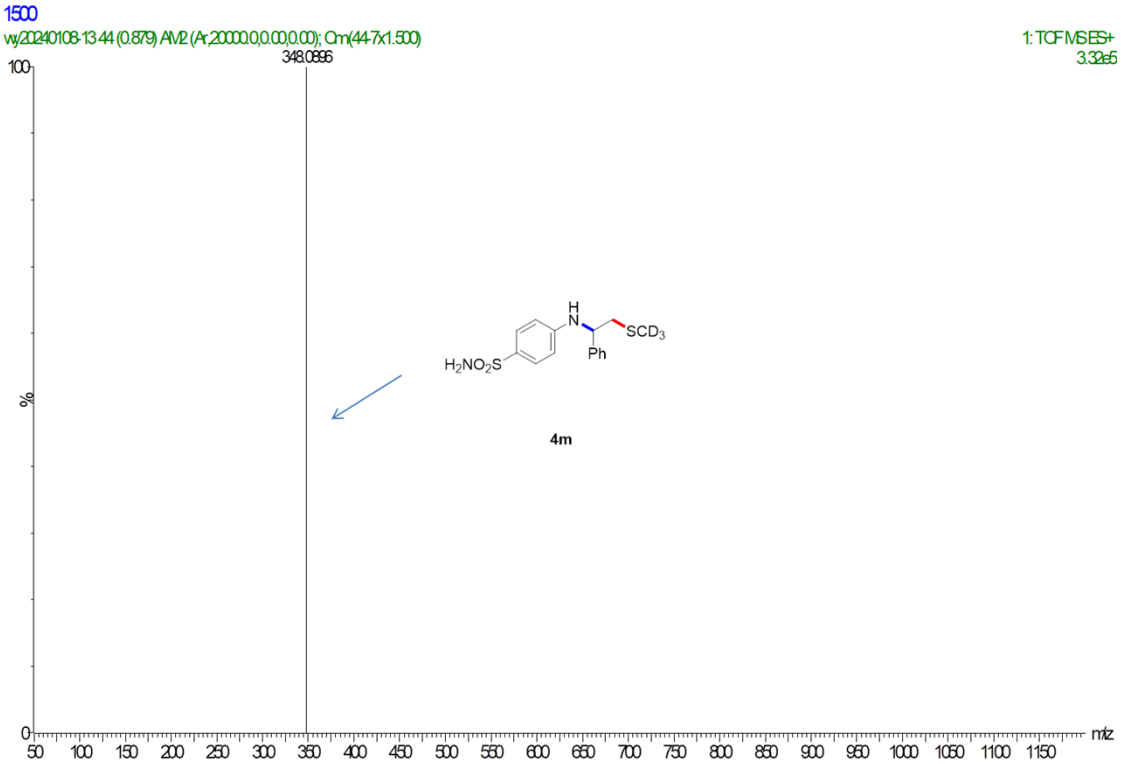

1481
wy20240108-8-43 (0.862) AM2 (Ar,20000.0,0.000,0.000); Cm(43-8x1.500)
1: TOF MS ES+
1.05e5
313.1063
100
%
0
290 295 300 305 310 315 320 325 330 335 340 345 350 355 360 365 370 375 380 385 390 395 400 405 410 415 420
m/z
H
N
SCD3
Ph
F3C
4h

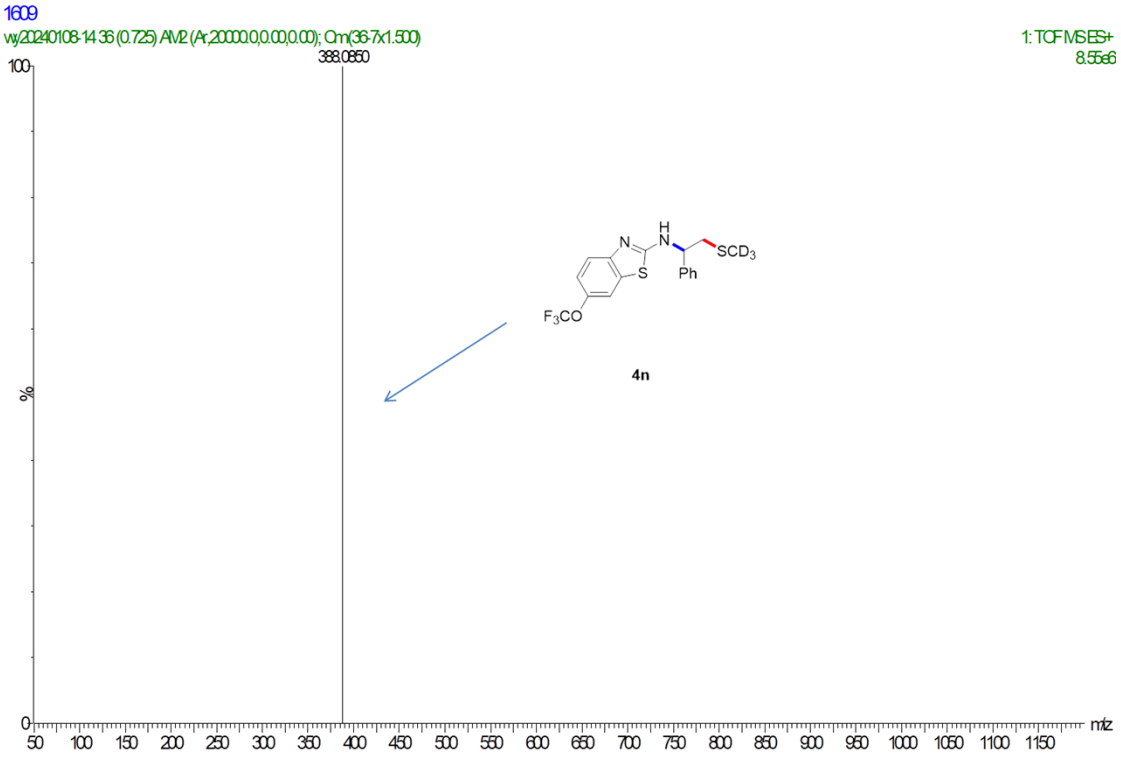

1470
wy20240108-9-38 (0.758) AM2 (Ar,20000.0,0.000,0.000); Cm(38-8x1.500)
1: TOF MS ES+
4.51e4
331.1162
100
%
0
330 331 332 333 334 335 336 337 338 339 340
m/z
H
N
SCD3
Ph
F3CO
4i

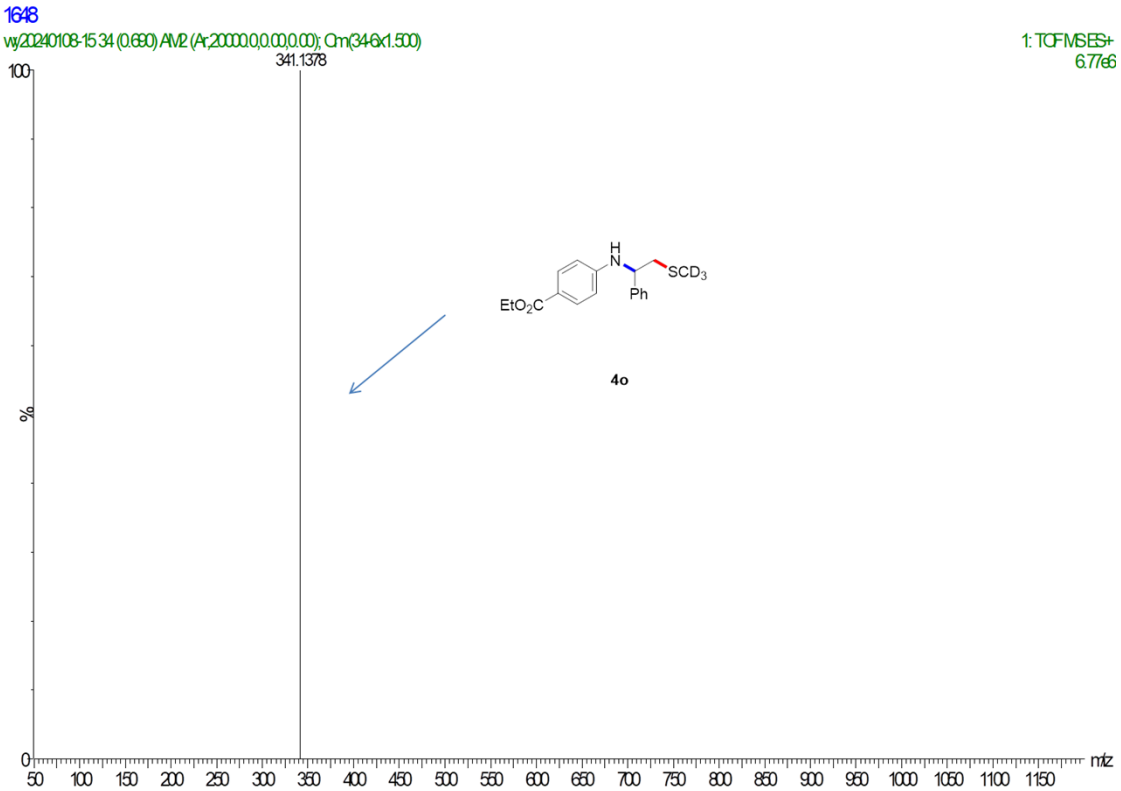

1487
wj20240108-1029 (0.586) AM2 (Ar,20000.0,0.00,0.00); Cm(29:8x1.500)
1: TOF MS ES+
3.42e5
345.0784
100
%
0
300 320 340 360 380 400 420 440 460 480 500 520 540 560 580 600 620
m/z
H
N
SCD3
Ph
F3CS
4j

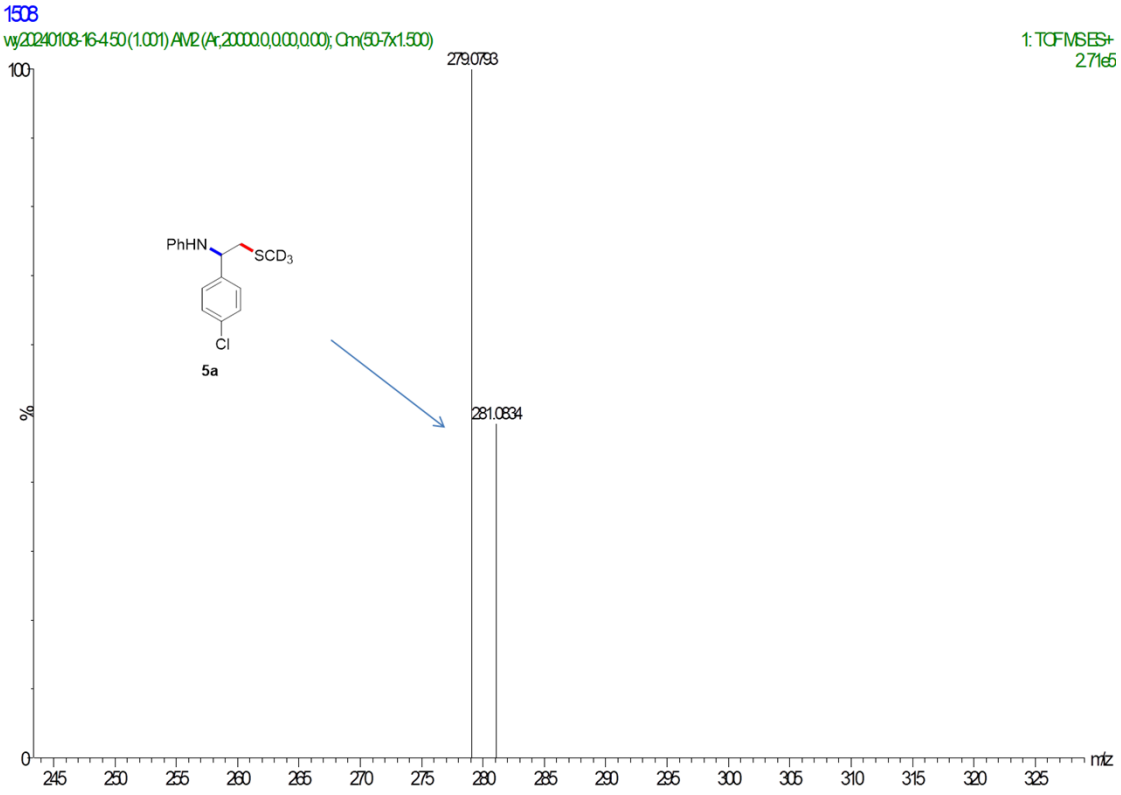

1486
wj20240108-1140 (0.792) AM2 (Ar,20000.0,0.00,0.00); Cm(40:7x1.500)
1: TOF MS ES+
9.07e4
272.1299
100
%
0
220 240 260 280 300 320 340 360 380 400 420 440 460 480 500 520 540 560 580 600 620 640 660 680 700 720 740
m/z
H
N
SCD3
Ph
NC
4k

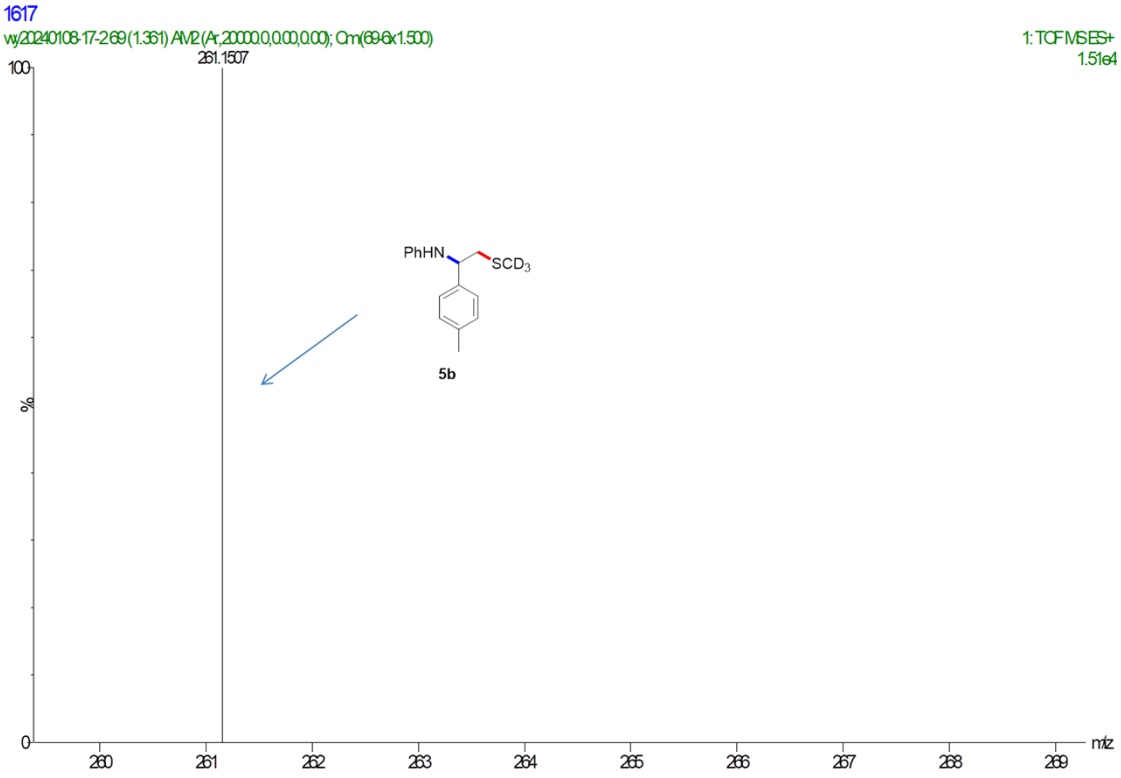

1488-1
wy20240108-12-2 23 (0.465) AM2 (Ar,20000.0,0.00,0.00); Cm (23-8x1.500)
1: TOF MS ES+
1.92e4
335.1500
100
%
0
m/z
332
333
334
335
336
337
338
OMe
H
N
SCD3
Ph
MeO
OMe
4l

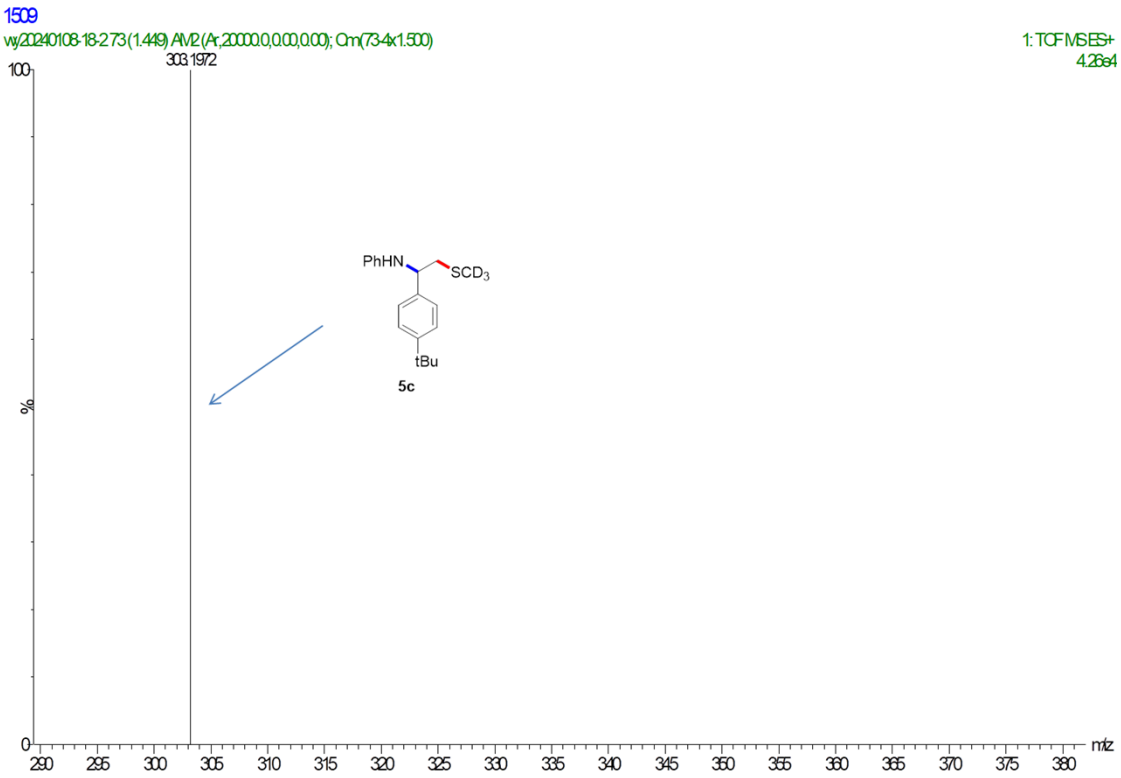

1500
wy20240108-13 44 (0.879) AM2 (Ar,20000.0,0.00,0.00); Cm (44-7x1.500)
1: TOF MS ES+
3.32e5
348.0896
100
%
0
m/z
50
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
850
900
950
1000
1050
1100
1150
H
N
SCD3
Ph
H2NO2S
4m

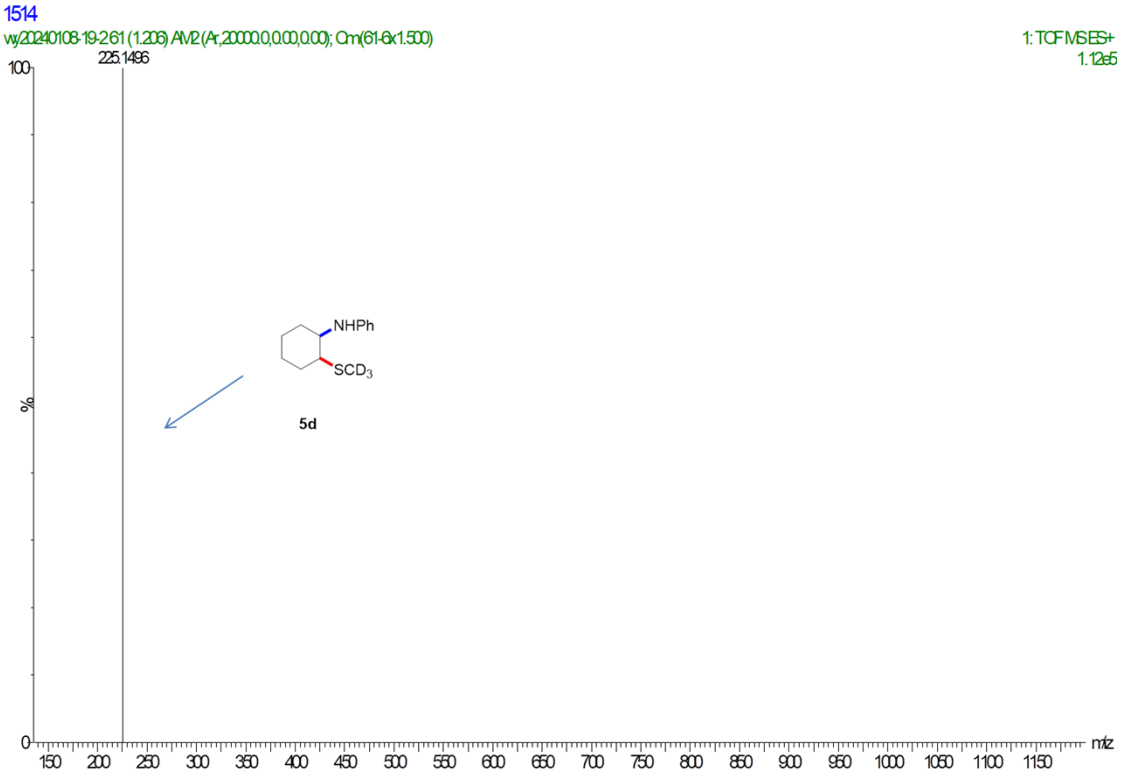

1609
wj20240108-1436 (0.725) AM2 (Ar,20000.0,0.00,0.00); Cm(36:7x1.500)
1: TOF MS ES+
8.55e6
388.0850
100
%
0
50 100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000 1050 1100 1150
m/z
N
H
N
S
SCD3
Ph
F3CO
4n

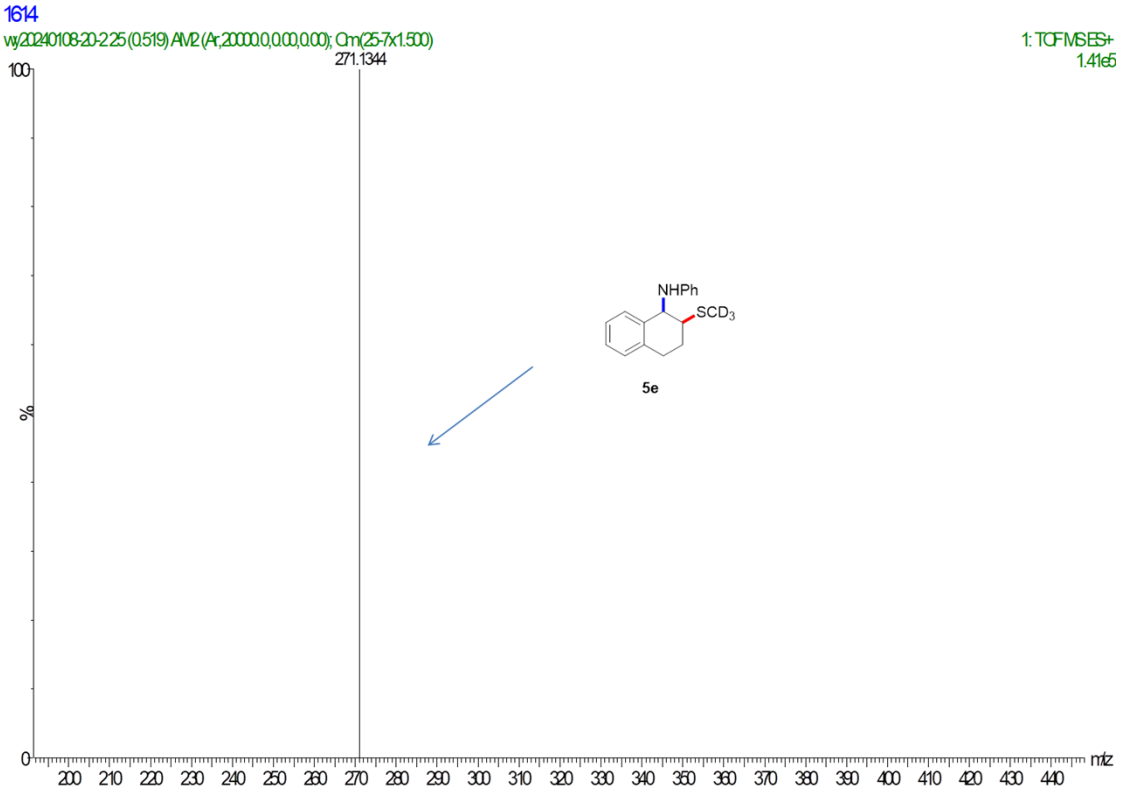

1648
wj20240108-1534 (0.690) AM2 (Ar,20000.0,0.00,0.00); Cm(34:6x1.500)
1: TOF MS ES+
6.77e6
341.1378
100
%
0
50 100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000 1050 1100 1150
m/z
H
N
SCD3
Ph
EtO2C
4o

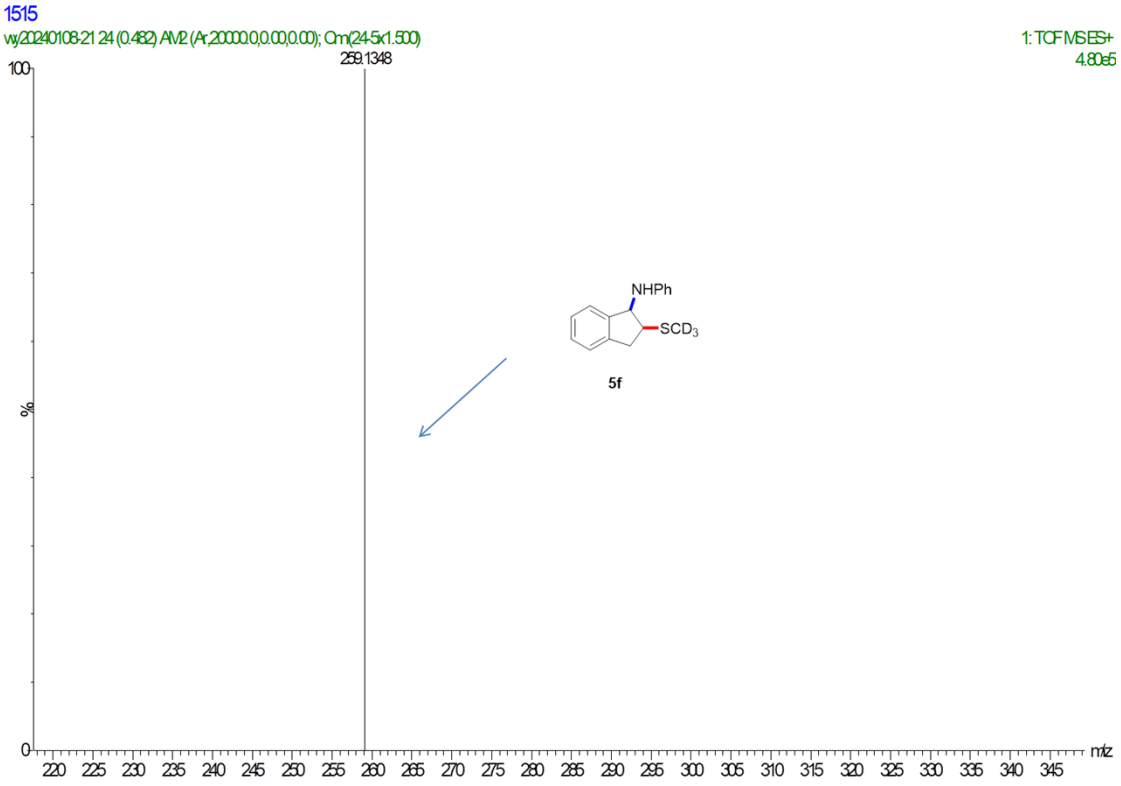

1508
wy20240108-16-4 50 (1.001) AM2 (Ar,20000.0,0.00,0.00); Cm(50-7x1.500)
1: TOF MS ES+
2.71e5
279.0793
281.0834
PhHN
SCD3
Cl
5a
%
m/z

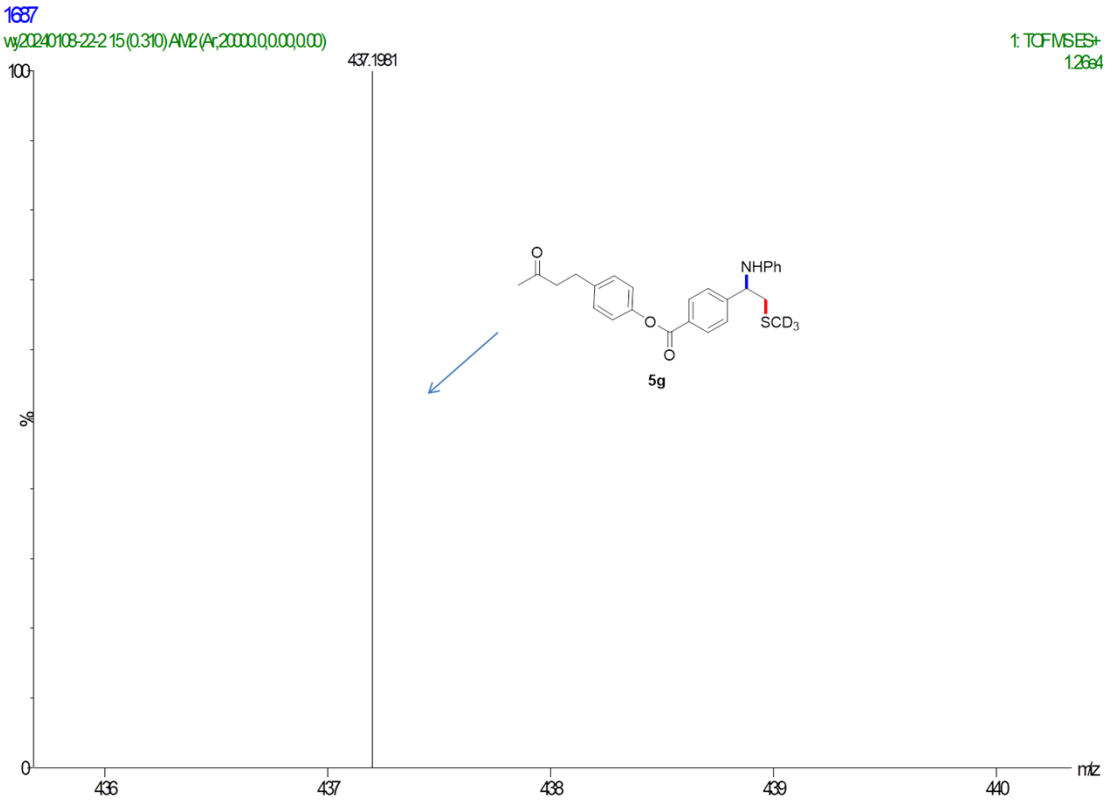

1617
wy20240108-17-2 69 (1.361) AM2 (Ar,20000.0,0.00,0.00); Cm(69-6x1.500)
1: TOF MS ES+
1.51e4
261.1507
PhHN
SCD3
5b
%
m/z

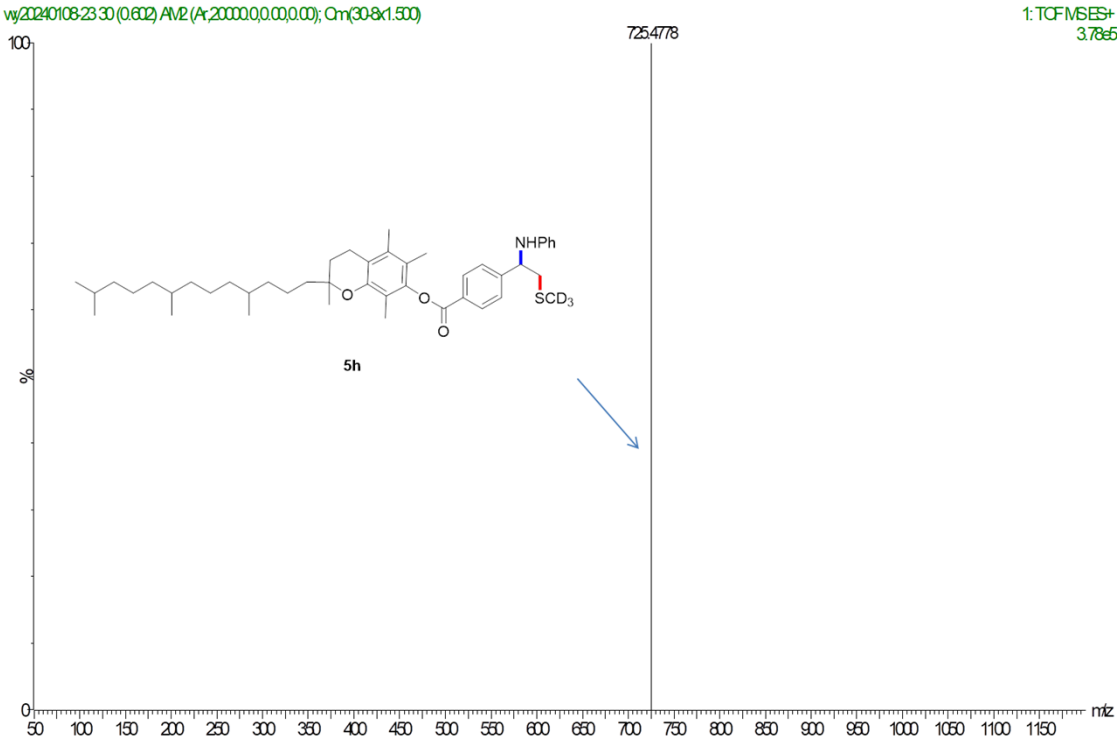

1509
wj20240108-18-273 (1.449) AM2 (Ar,20000.0,0.00,0.00); Cm(73-4x1.500)
1: TOF MS ES+
4.26e4
303.1972
100
%
0
PhHN
SCD3
tBu
5c
m/z
290 295 300 305 310 315 320 325 330 335 340 345 350 355 360 365 370 375 380

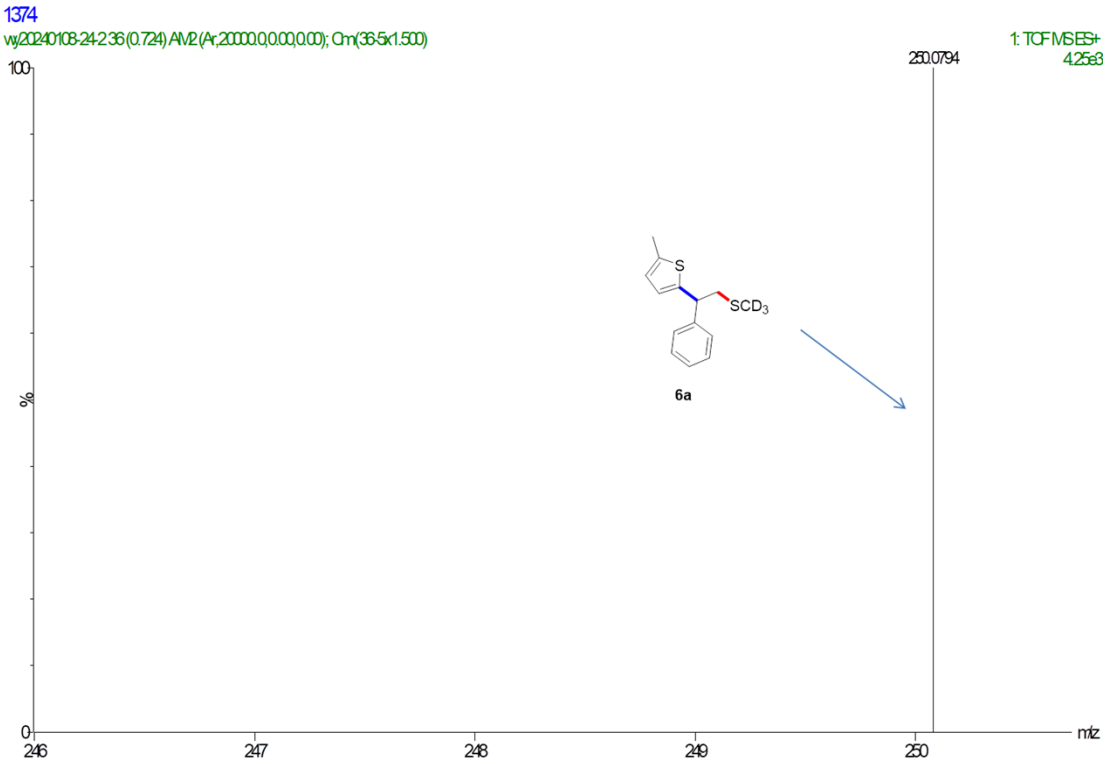

1514
wj20240108-19-261 (1.206) AM2 (Ar,20000.0,0.00,0.00); Cm(61-6x1.500)
1: TOF MS ES+
1.12e5
225.1496
100
%
0
NHPh
SCD3
5d
m/z
150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000 1050 1100 1150

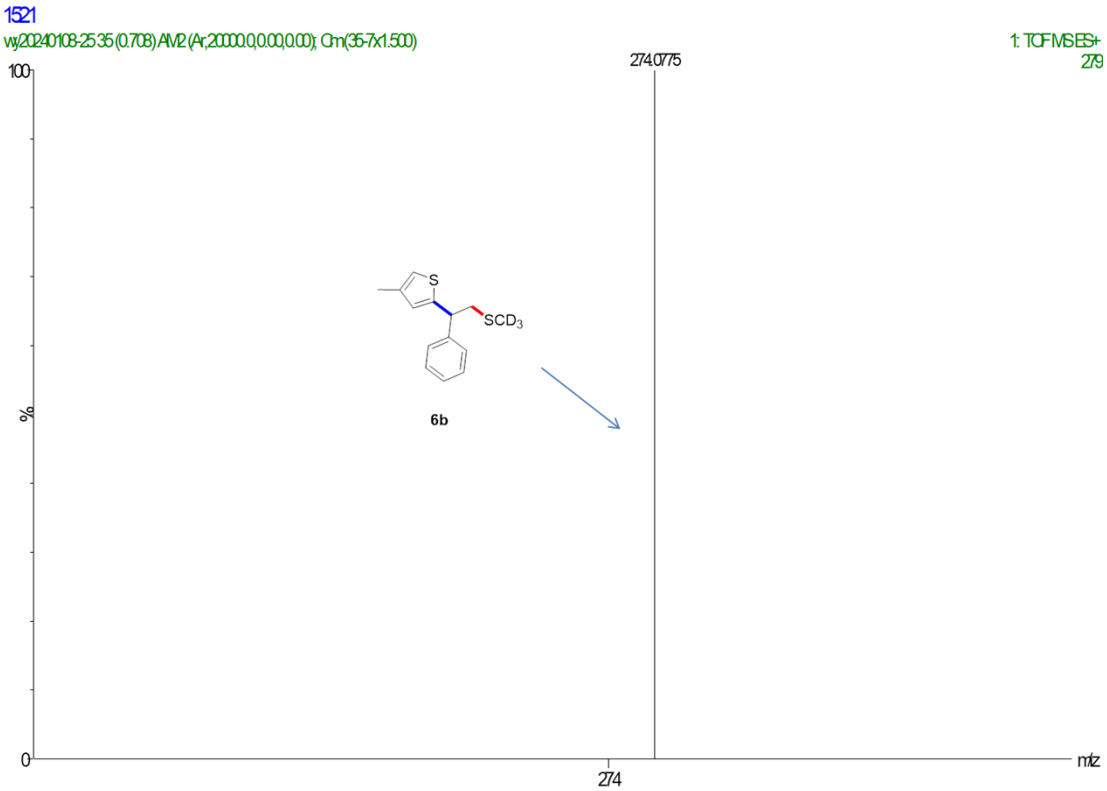

1614
wj20240108-20-2 25 (0.519) AM2 (Ar,20000.0,0.00,0.00); Cm(25-7x1.500)
1: TOF MS ES+
1.41e5
271.1344
100
%
0
NHPh
SCD3
5e
m/z
200 210 220 230 240 250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400 410 420 430 440

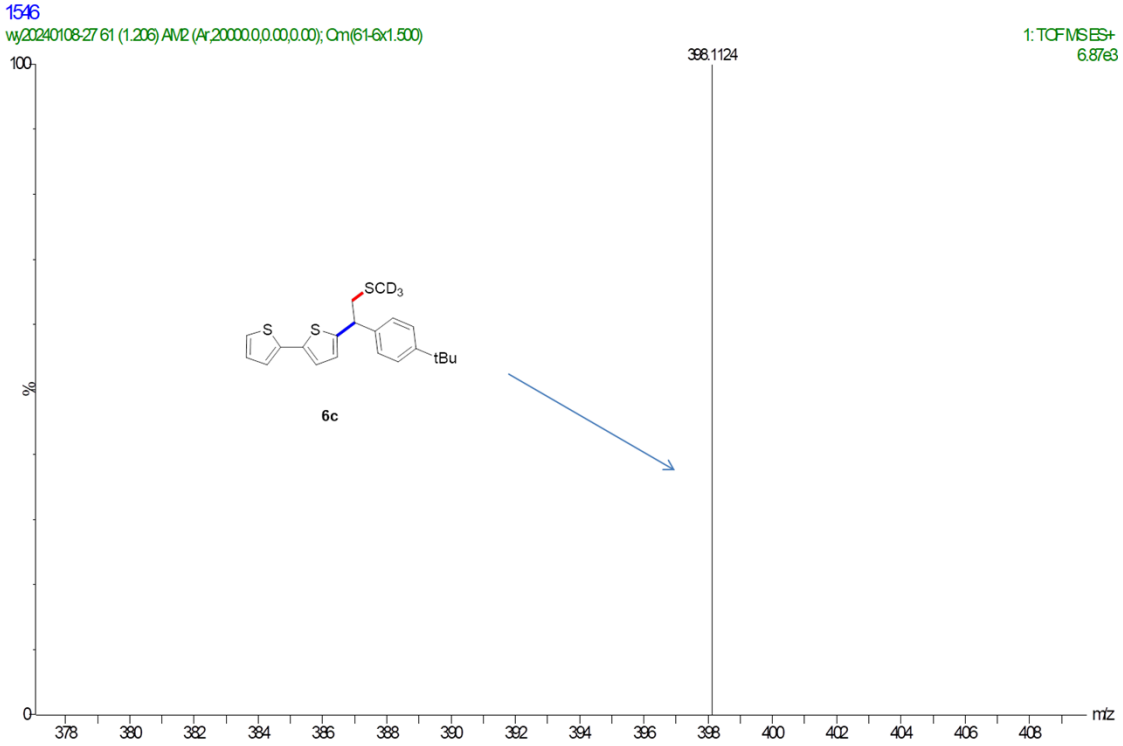

1515
wj20240108-21 24 (0.482) AM2 (Ar,20000.0,0.00,0.00); Cm(24-5x1.500)
1: TOF MS ES+
4.80e5
259.1348
100
%
0
NHPh
SCD3
5f
m/z
220 225 230 235 240 245 250 255 260 265 270 275 280 285 290 295 300 305 310 315 320 325 330 335 340 345

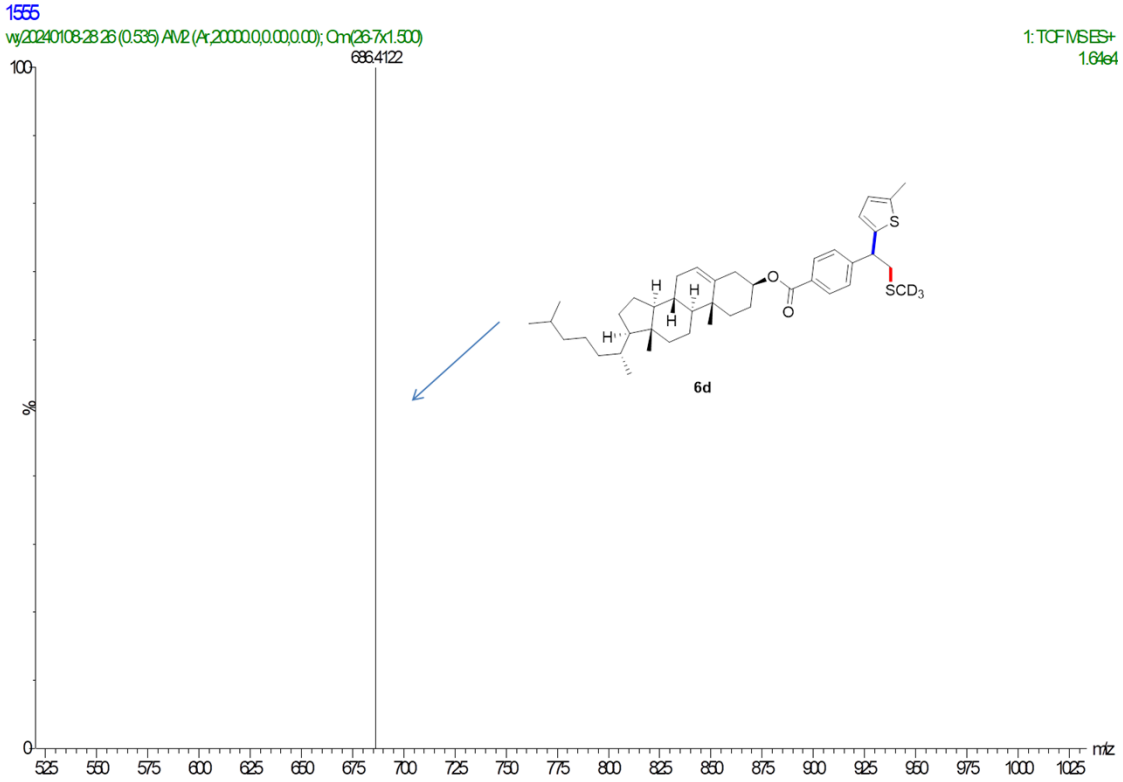

1657
wj20240108-22-2 15 (0.310) AM2 (Ar,20000.0,0.00,0.00)
1: TOF MS ES+
1.26e4
437.1981
100
%
0
436
437
438
439
440
m/z
NHPh
SCD3
O
O
O
5g

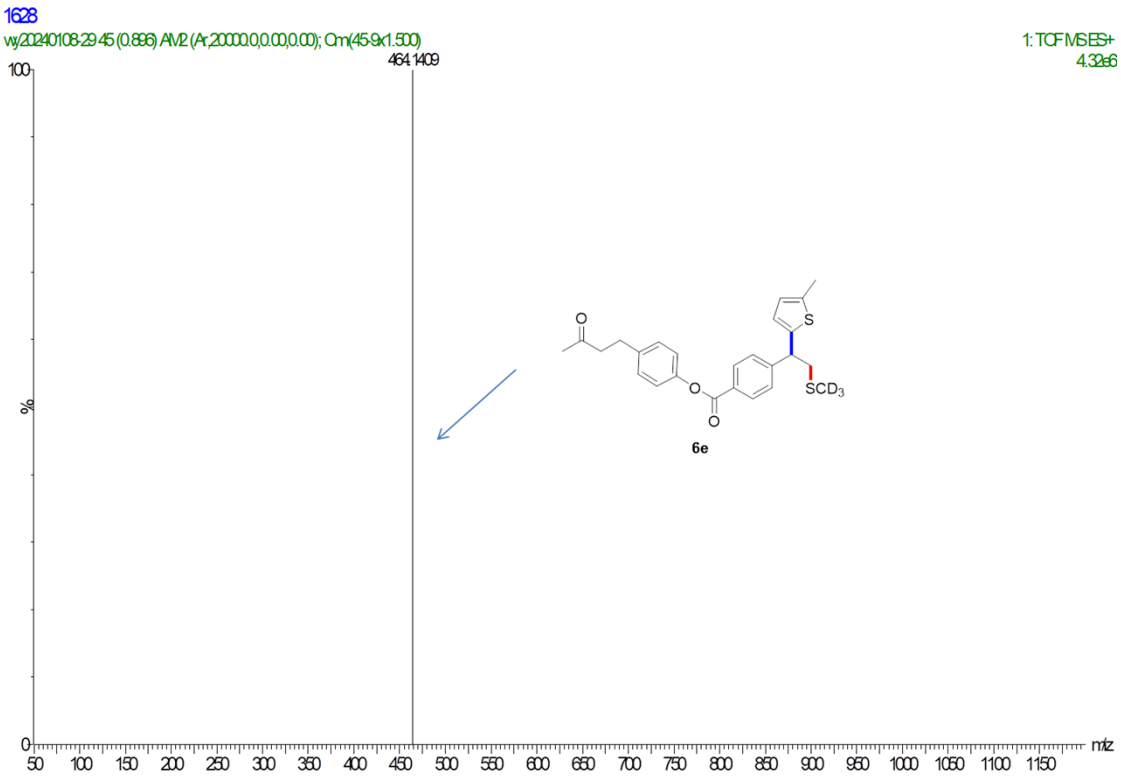

1733
wj20240108-23 30 (0.602) AM2 (Ar,20000.0,0.00,0.00); Cm(30:8x1.500)
1: TOF MS ES+
3.78e5
725.4778
100
%
0
50
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
850
900
950
1000
1050
1100
1150
m/z
NHPh
SCD3
O
O
O
5h


1374
wj20240108-24-2 36 (0.724) AM2 (Ar,20000.0,0.00,0.00); Cm(36-5x1.500)
1: TOF MS ES+
4.25e3
250.0794
100
%
0
246
247
248
249
250
m/z
S
SCD3
6a


1521
wj20240108-25 35 (0.708) AM2 (Ar,20000.0,0.00,0.00); Cm(35-7x1.500)
1: TOF MS ES+
279
274.0775
100
%
0
274
m/z
S
SCD3
6b


1546
wj20240108-27 61 (1.206) AM2 (Ar,20000.0,0.00,0.00); Cm(61-6x1.500)
1: TOF MS ES+
6.87e3
398.1124
100
%
0
SCD3
S
S
tBu
6c
m/z
378 380 382 384 386 388 390 392 394 396 398 400 402 404 406 408


1555
wj20240108-28 26 (0.535) AM2 (Ar,20000.0,0.00,0.00); Cm(26-7x1.500)
1: TOF MS ES+
1.64e4
686.4122
100
%
0
S
H
H
H
H
O
O
SCD3
6d
m/z
525 550 575 600 625 650 675 700 725 750 775 800 825 850 875 900 925 950 975 1000 1025


1628
wj20240108-29 45 (0.896) AM2 (Ar,20000.0,0.00,0.00); Cm(45:9x1.500)
1: TOF MS ES+
4.32e6
464.1409
100
%
0
50 100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000 1050 1100 1150
m/z
O
O
O
S
SCD3
6e