Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Reductive thiolation and oxidative dehydroaromatization of cyclohexanones with primary amines and sodium sulfinates to access o-sulfanylanilines

Hui Wu,[a] Lin Zhao,[a] Wenting Wang,[a] Yining Yu,[a] Ge Wu,*[a,b]

[a]School of Pharmaceutical Sciences, Wenzhou Medical University, Wenzhou 325035, China
[b]State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

*E-mail: wuge@wmu.edu.cn

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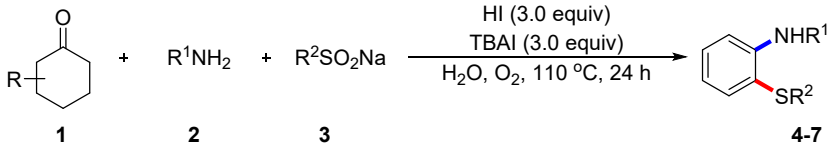
General Information

All other reagents were purchased from TCI, Sigma-Aldrich, Alfa Aesar, Acros, and Meryer and used without further purification. ^{1}H 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

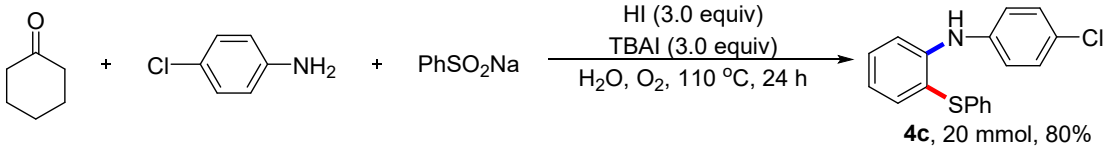
General Procedure of thioamination of cyclic ketones with primary amines and sulfinates:



1 **2** **3** **4-7**

A 25 mL Schlenk tube equipped with a stir bar was charged with substituted cyclic ketones (0.2 mmol), primary amines (0.4 mmol), sulfinates (0.4 mmol), HI (0.6 mmol, 55-57 wt.% solution in H_2O), TBAI (0.6 mmol) and H_2O (2.0 mL). The tube was fitted with a rubber septum, and then it was evacuated and refilled with O_2 three times. The reaction mixture was stirred at 110 ℃ for 24 h. After cooling down, the reaction mixture was diluted with 10 mL of ethyl ether and H_2O, after the workup of extraction, dry with Na_2SO_4, and concentrated under reduced pressure. The residue was then purified by flash chromatography on silica gel to provide the corresponding product.

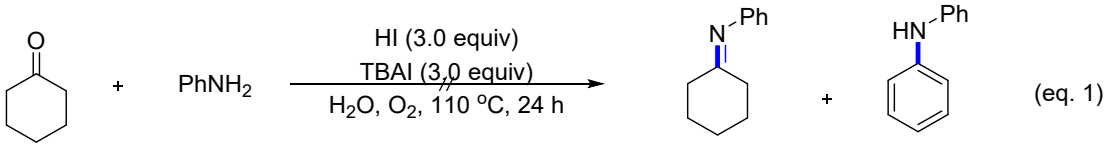
Gram-scale reaction:



4c, 20 mmol, 80%

A 250 mL Schlenk tube equipped with a stir bar was charged with substituted cyclohexanone (20 mmol), 4-chloroaniline (40 mmol), sodium benzene sulfinate (40 mmol), HI (60 mmol, 55-57 wt.% solution in H_2O), TBAI (60 mmol) and H_2O (200 mL). The tube was fitted with a rubber septum, and then it was evacuated and refilled with O_2 three times. The reaction mixture was stirred at 110 ℃ for 24 h. After cooling down, the reaction mixture was diluted with 100 mL of ethyl ether and H_2O, after the workup of extraction, dry with Na_2SO_4, and concentrated under reduced pressure. The residue was then purified by flash chromatography on silica gel to provide the corresponding product (**4c**, 80%).

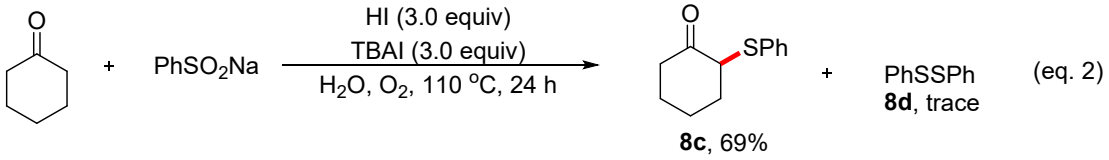
Mechanistic Studies



(eq. 1)

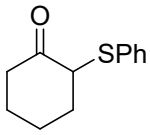
8a, 0% **8b**, 0%

A 25 mL Schlenk tube equipped with a stir bar was charged with cyclohexanone (0.2 mmol), aniline (0.4 mmol), HI (0.6 mmol, 55-57 wt.% solution in H_2O), TBAI (0.6 mmol) and H_2O (2.0 mL). The tube was fitted with a rubber septum, and then it was evacuated and refilled with O_2 three times. The reaction mixture was stirred at 110 ℃ 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), none of **8a** and **8b** were detected by GC-MS.



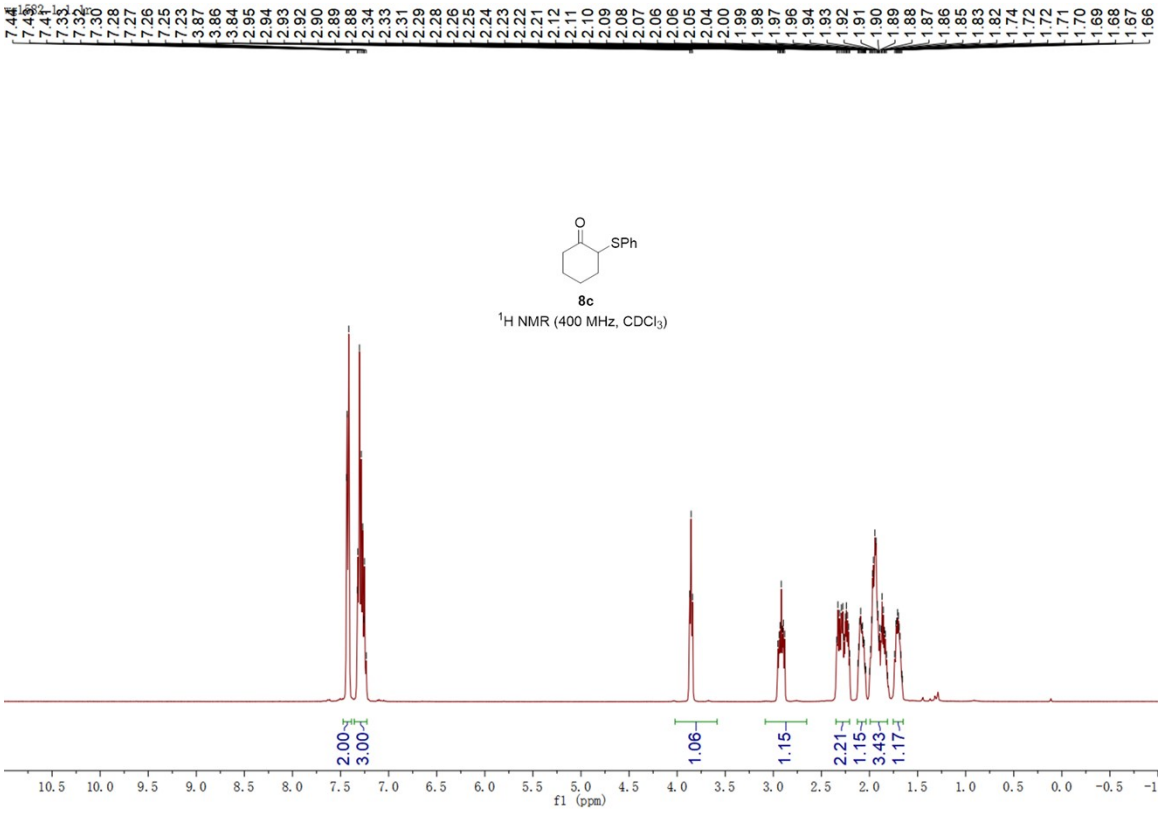
A 25 mL Schlenk tube equipped with a stir bar was charged with cyclohexanone (0.2 mmol), benzene sulfinic acid sodium salt (0.4 mmol), HI (0.6 mmol, 55-57 wt.% solution in H_2O), TBAI (0.6 mmol) and H_2O (2.0 mL). The tube was fitted with a rubber septum, and then it was evacuated and refilled with O_2 three times. The reaction mixture was stirred at 110 ℃ 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), α -thiolated product **8c** was isolated in 69% yield, and only a trace of disulfide **8d** was detected.

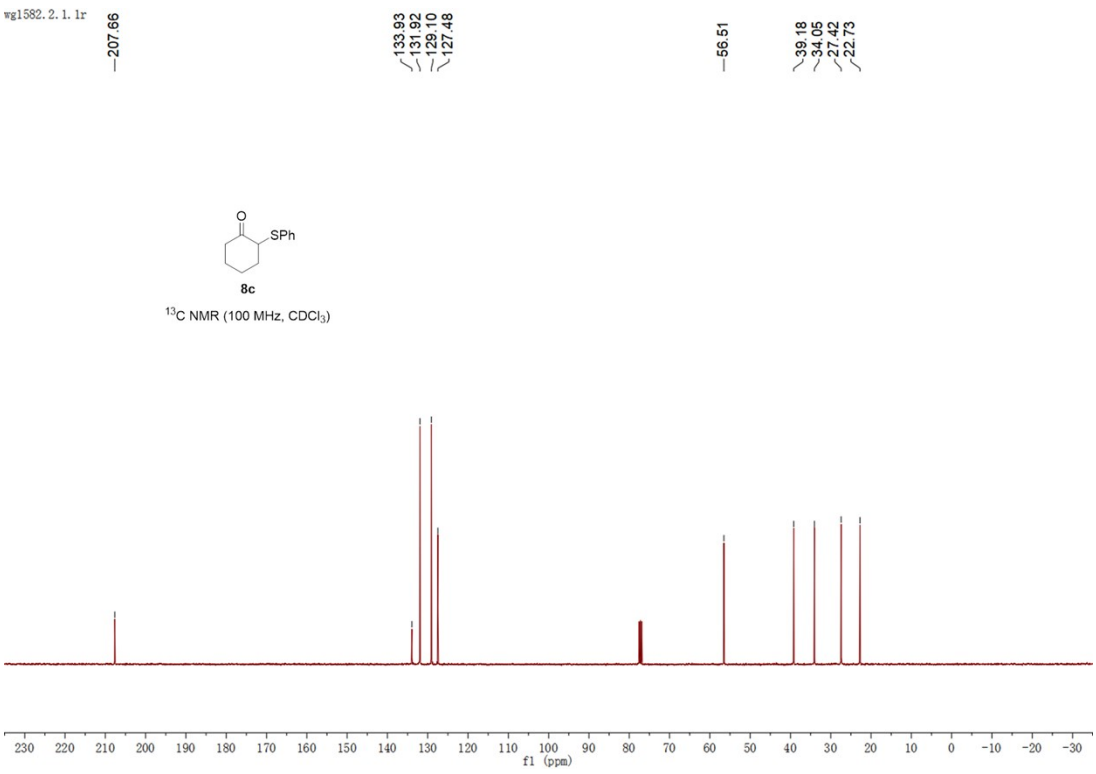
2-(phenylthio)cyclohexan-1-one

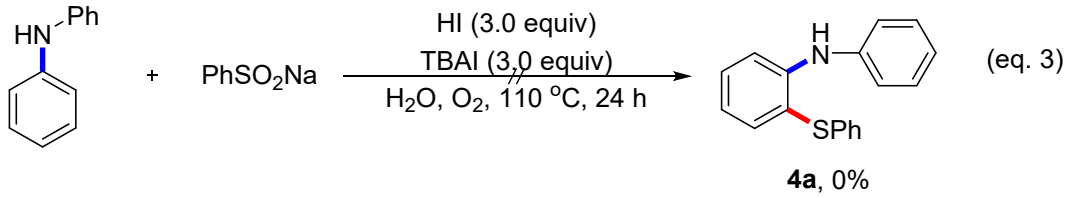


8c

The NMR of **8c** is accorded with the known reference (A. F. Vaquer, A. Frongia, F. Secci and E. Tuveria, *RSC Adv.*, 2015, **5**, 96695.)

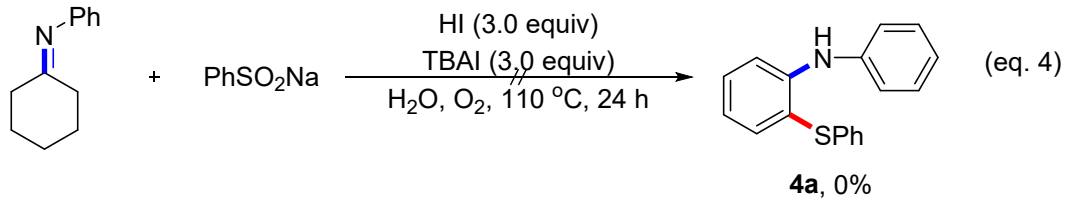






4a, 0%

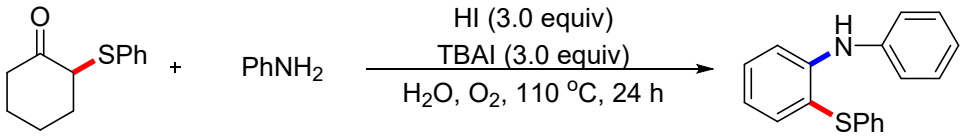
A 25 mL Schlenk tube equipped with a stir bar was charged with diphenylamine (0.2 mmol), benzene sulfinic acid sodium salt (0.4 mmol), HI (0.6 mmol, 55-57 wt.% solution in H_2O), TBAI (0.6 mmol) and H_2O (2.0 mL). The tube was fitted with a rubber septum, and then it was evacuated and refilled with O_2 three times. The reaction mixture was stirred at 110 ℃ 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), none of **4a** were detected by GC-MS.



4a, 0%

A 25 mL Schlenk tube equipped with a stir bar was charged with N-phenylcyclohexanimine (0.2 mmol), benzene sulfinic acid sodium salt (0.4 mmol), HI (0.6 mmol, 55-57 wt.% solution in H_2O), TBAI (0.6 mmol) and H_2O (2.0 mL). The tube was fitted with a rubber septum, and then it was evacuated and refilled with O_2 three times. The reaction mixture was stirred at 110 ℃ for 24 h. After the reaction mixture was cooled to room temperature and the reaction was filtered through a

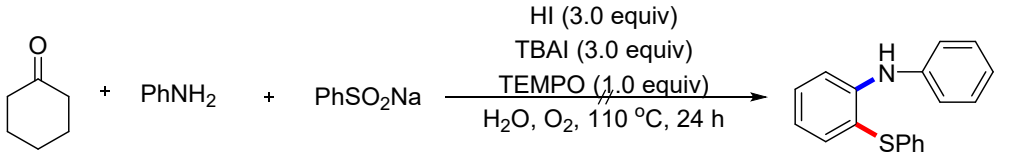
pad of Celite and diluted with ethyl acetate (10 mL), none of **4a** were detected by GC-MS.



(eq. 5)

4a, 58%

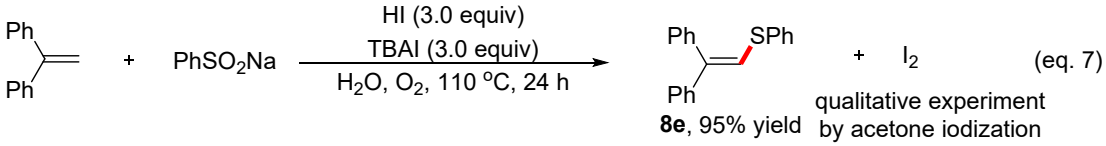
A 25 mL Schlenk tube equipped with a stir bar was charged with **8c** (0.2 mmol), aniline (0.4 mmol), HI (0.6 mmol, 55-57 wt.% solution in H_2O), TBAI (0.6 mmol) and H_2O (2.0 mL). The tube was fitted with a rubber septum, and then it was evacuated and refilled with O_2 three times. The reaction mixture was stirred at 110 ℃ 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), **4a** was isolated in 58%.



(eq. 6)

4a, 0%

A 25 mL Schlenk tube equipped with a stir bar was charged with cyclohexanone (0.2 mmol), aniline (0.4 mmol), benzene sulfinic acid sodium salt (0.4 mmol), HI (0.6 mmol, 55-57 wt.% solution in H_2O), TBAI (0.6 mmol), TEMPO (0.2 mmol) and H_2O (2.0 mL). The tube was fitted with a rubber septum, and then it was evacuated and refilled with O_2 three times. The reaction mixture was stirred at 110 ℃ 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), none of **4a** were detected by GC-MS.



(eq. 7)

8e, 95% yield

qualitative experiment by acetone iodization

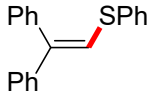
After the reaction

acetone iodization experiment

A 25 mL Schlenk tube equipped with a stir bar was charged with 1,1-diphenylethylene (0.2 mmol), benzene sulfinic acid sodium salt (0.4 mmol), HI (0.6 mmol, 55-57 wt.% solution in H_2O), TBAI (0.6 mmol) and H_2O (2.0 mL). The tube was fitted with a rubber septum, and then it was evacuated and refilled with O_2 three times. The reaction mixture was stirred at 110 ℃ for 24 h. After the reaction mixture was cooled to room temperature and the reaction was filtered through a

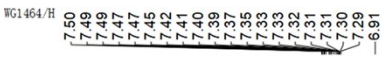
pad of Celite and diluted with ethyl acetate (10 mL), **8e** was isolated in 95%. These results indicate that a thiyl radical was involved during the reaction process. The resulting I_2 was confirmed by the acetone iodization experiment, which indicates sodium sulfinate could oxidize the HI to I_2.

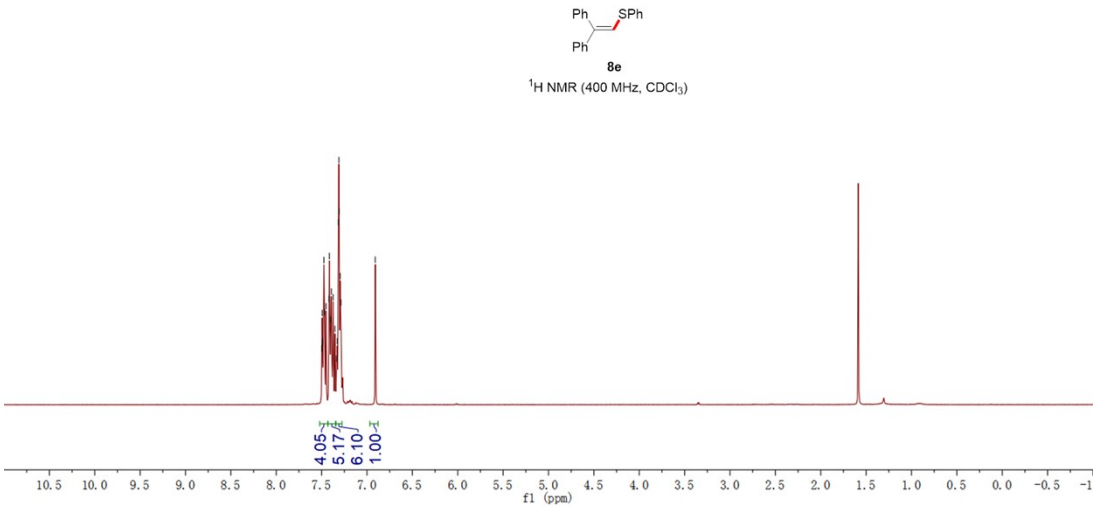
(2,2-diphenylvinyl)(phenyl)sulfane

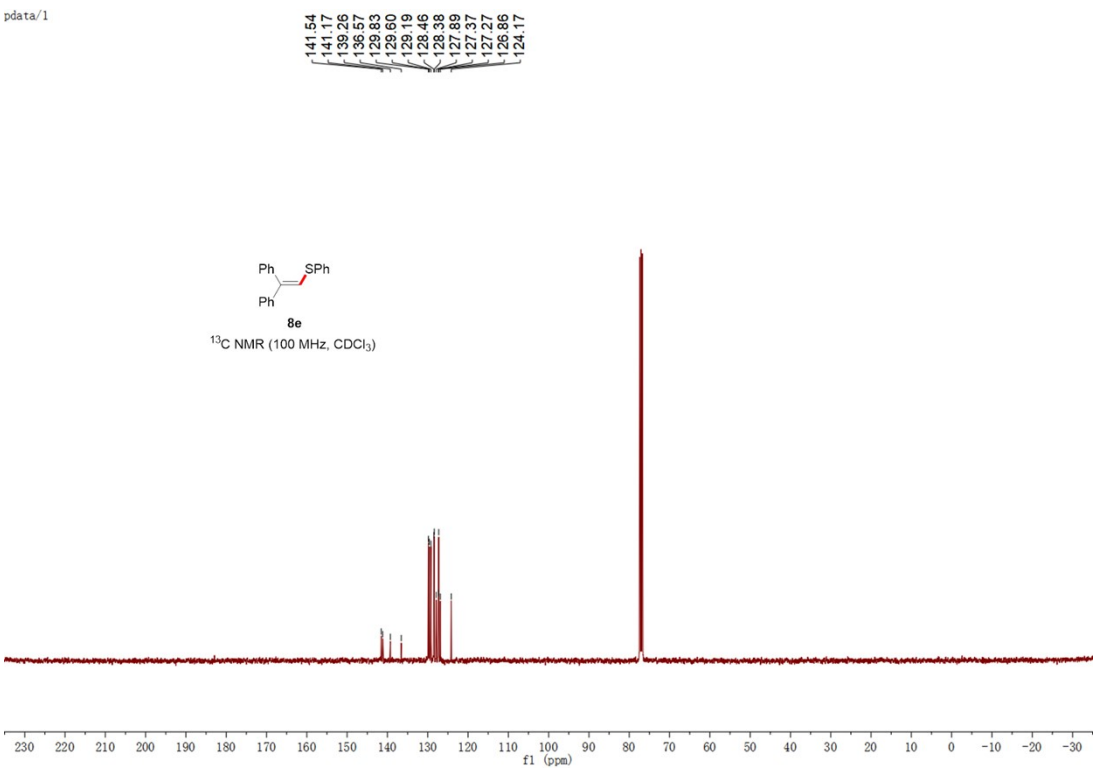


8e

The NMR of **8e** is accorded with the known reference (B.-W. Wang, K. Jiang, J.-X. Li, S.-H. Luo, Z.-Y. Wang and H.-F. Jiang, *Angew. Chem. Int. Ed.*, 2020, **59**, 2338.)

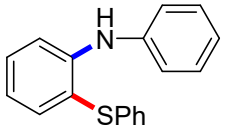






Characterization of Products in Details :

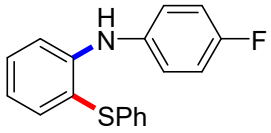
N-phenyl-2-(phenylthio)aniline[1,2]



4a

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow solid (50.4 mg, 91% yield), Mp = 83-84℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.59 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.34-7.26(m, 7H), 7.20-7.17 (m, 3H), 7.14-7.12 (m, 2H), 6.90 (ddd, *J* = 8.3, 6.4, 2.3 Hz, 1H), 6.73 (brs, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.93, 141.77, 137.51, 136.59, 130.80, 129.40, 129.21, 127.06, 125.87, 122.78, 120.81, 120.03, 117.42, 114.55. **HRMS** (ESI): calcd for $C_{18}H_{16}NS$ $[M + H]^+$ 278.1003, found 278.1016.

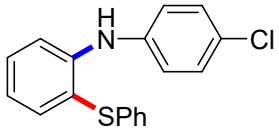
N-(4-fluorophenyl)-2-(phenylthio)aniline



4b

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (48.4 mg, 82% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.60 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.34-7.27 (m, 3H), 7.20-7.14 (m, 4H), 7.11-7.01 (m, 4H), 6.89 (td, *J* = 7.5, 1.4 Hz, 1H), 6.63 (brs, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.14 (d, *J* = 242.0 Hz), 146.73, 137.63, 136.58, 130.96, 130.93, 129.20, 126.89, 125.85, 123.76 (d, *J* = 7.9 Hz), 119.74, 116.65, 116.08 (d, *J* = 22.5 Hz), 113.76. **^{19}F NMR** (375 MHz, $CDCl_3$) δ -119.50 (1F); **HRMS** (ESI): calcd for $C_{18}H_{15}NSF$ $[M + H]^+$ 296.0909, found 296.0919.

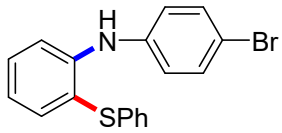
N-(4-chlorophenyl)-2-(phenylthio)aniline



4c

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (52.2 mg, 84% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.58 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.35-7.24 (m, 6H), 7.19-7.16 (m, 3H), 7.04 (d, *J* = 8.8 Hz, 2H), 6.92 (td, *J* = 7.4, 1.6 Hz, 1H), 6.65 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.37, 140.51, 137.43, 136.35, 130.78, 129.39, 129.24, 127.44, 127.15, 126.00, 121.68, 120.58, 118.13, 114.89. **HRMS** (ESI): calcd for $C_{18}H_{13}NSCl$ $[M - H]^+$ 310.0457, found 310.0456.

N-(4-bromophenyl)-2-(phenylthio)aniline

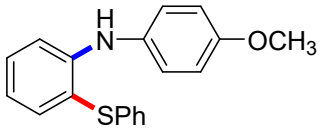


4d

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (57.5 mg, 81% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.61 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.41 (d, *J* = 8.7 Hz, 2H), 7.36-7.28 (m, 4H), 7.22-7.19 (m, 3H), 7.00 (d, *J* = 8.7 Hz, 2H), 6.95 (td,

J = 7.3, 1.7 Hz, 1H), 6.67 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.15, 141.08, 137.42, 136.34, 132.34, 130.78, 129.29, 127.24, 126.07, 121.83, 120.78, 118.43, 115.13, 114.73. **HRMS** (ESI): calcd for $C_{18}H_{13}NSBr$ $[M - H]^+$ 353.9952, found 353.9963.

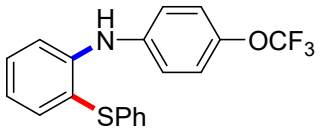
N-(4-methoxyphenyl)-2-(phenylthio)aniline



4e

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (59.6 mg, 97% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.60 (dt, *J* = 7.7, 1.5 Hz, 1H), 7.32-7.28 (m, 3H), 7.23-7.17 (m, 3H), 7.11-7.06 (m, 3H), 6.94-6.90 (m, 2H), 6.84 (td, *J* = 7.4, 1.2 Hz, 1H), 6.61 (s, 1H), 3.85 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.46, 147.89, 137.73, 136.87, 134.42, 131.08, 129.19, 126.74, 125.71, 125.00, 118.88, 115.43, 114.75, 113.14, 55.61. **HRMS** (ESI): calcd for $C_{19}H_{18}NOS$ $[M + H]^+$ 308.1109, found 308.1122.

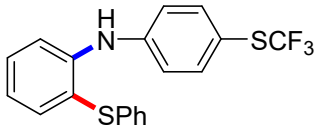
2-(phenylthio)-N-(4-(trifluoromethoxy)phenyl)aniline



4f

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (61.4 mg, 85% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.60 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.37-7.26 (m, 4H), 7.20-7.15 (m, 5H), 7.12-7.09 (m, 2H), 6.94 (td, *J* = 7.3, 1.7 Hz, 1H), 6.69 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.28, 144.10, 140.72, 137.45, 136.32, 130.81, 129.27, 127.17, 126.04, 122.31, 121.22, 120.76, 120.63 (q, *J* = 255.0 Hz), 118.27, 114.99. **^{19}F NMR** (375 MHz, $CDCl_3$) δ -58.18 (3F); **HRMS** (ESI): calcd for $C_{19}H_{15}NOF_3S$ $[M + H]^+$ 362.0826, found 362.0833.

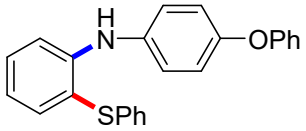
2-(phenylthio)-N-(4-((trifluoromethyl)thio)phenyl)aniline



4g

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (65.6 mg, 87% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.62 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.55 (d, *J* = 8.6 Hz, 2H), 7.49 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.40 (td, *J* = 8.2, 7.8, 1.6 Hz, 1H), 7.31-7.27 (m, 2H), 7.23-7.20 (m, 3H), 7.11-7.06 (m, 3H), 7.04 (td, *J* = 7.5, 1.4 Hz, 1H), 6.76 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.19, 143.35, 138.08, 136.92, 135.93, 130.45, 129.74 (q, *J* = 307.0 Hz), 129.35, 127.80, 126.37, 122.26, 121.07, 118.37, 117.41, 114.91. **^{19}F NMR** (375 MHz, $CDCl_3$) δ -43.76 (3F); **HRMS** (ESI): calcd for $C_{19}H_{15}NF_3S_2$ $[M + H]^+$ 378.0598, found 378.0611.

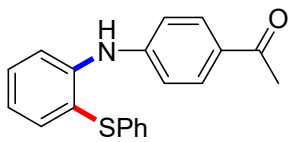
N-(4-phenoxyphenyl)-2-(phenylthio)aniline



4h

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow solid (69.4 mg, 94% yield), Mp = 88-89℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.58 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.38-7.34 (m, 2H), 7.32-7.26 (m, 3H), 7.22-7.16 (m, 4H), 7.14-7.09 (m, 3H), 7.04-6.99 (m, 4H), 6.87 (td, *J* = 7.5, 1.4 Hz, 1H), 6.66 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 157.87, 152.84, 146.76, 137.63, 137.18, 136.65, 130.95, 129.77, 129.19, 126.87, 125.79, 123.51, 122.99, 120.25, 119.58, 118.34, 116.50, 113.80. **HRMS** (ESI): calcd for $C_{24}H_{20}NOS$ $[M + H]^+$ 370.1266, found 370.1270.

1-(4-((2-(phenylthio)phenyl)amino)phenyl)ethan-1-one

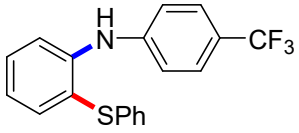


4i

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

yellow liquid (55.5 mg, 87% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.7 Hz, 2H), 7.58 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.51 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.39 (td, *J* = 8.3, 7.8, 1.6 Hz, 1H), 7.28-7.25 (m, 2H), 7.21-7.16 (m, 3H), 7.07-7.02 (m, 3H), 6.82 (s, 1H), 2.56 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 196.47, 147.05, 142.76, 136.66, 135.75, 130.46, 130.28, 130.24, 129.34, 127.98, 126.43, 122.68, 121.88, 118.17, 116.29, 26.25. **HRMS** (ESI): calcd for $C_{20}H_{18}NOS$ $[M + H]^+$ 320.1109, found 320.1122.

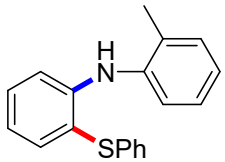
2-(phenylthio)-N-(4-(trifluoromethyl)phenyl)aniline



4j

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (54.5 mg, 79% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.59 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.38 (t, *J* = 8.2 Hz, 1H), 7.30-7.25 (m, 2H), 7.20-7.18 (m, 3H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.01 (t, *J* = 7.1 Hz, 1H), 6.76 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.51, 143.50, 136.94, 135.93, 130.45, 129.33, 127.75, 126.69 (q, *J* = 3.8 Hz), 126.34, 124.60 (q, *J* = 252.0 Hz), 123.09 (d, *J* = 15.3 Hz), 122.15, 120.87, 117.60, 117.13. **^{19}F NMR** (375 MHz, $CDCl_3$) δ -61.66 (3F); **HRMS** (ESI): calcd for $C_{19}H_{13}NSF_3$ $[M - H]^+$ 344.0721, found 344.0730.

2-methyl-N-(2-(phenylthio)phenyl)aniline

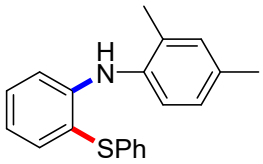


4k

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (52.4 mg, 90% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.63 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.33-7.28 (m, 5H), 7.25-7.16 (m, 4H), 7.07 (td, *J* = 7.4, 1.4 Hz, 1H), 6.99 (dd, *J* = 8.3, 1.3 Hz, 1H), 6.87 (td, *J* = 7.5, 1.3 Hz, 1H), 6.50 (s, 1H), 2.08 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.63,

139.62, 137.67, 136.61, 131.83, 131.09, 131.01, 129.20, 126.86, 126.80, 125.82, 124.04, 122.60, 119.10, 116.09, 113.71, 17.69. **HRMS** (ESI): calcd for $C_{19}H_{18}NS$ $[M + H]^+$ 292.1160, found 292.1169.

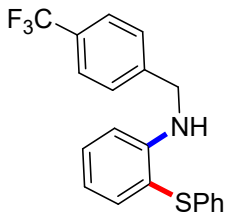
2,4-dimethyl-N-(2-(phenylthio)phenyl)aniline



4l

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (53.7 mg, 88% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 7.6 Hz, 1H), 7.35-7.31 (m, 3H), 7.28-7.26 (m, 2H), 7.24-7.18 (m, 2H), 7.11-7.06 (m, 2H), 6.91-6.85 (m, 2H), 6.49 (s, 1H), 2.40 (s, 3H), 2.09 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 147.49, 137.77, 136.89, 136.83, 134.26, 132.87, 131.86, 131.15, 129.22, 127.48, 126.88, 125.79, 124.15, 118.59, 115.36, 113.17, 21.01, 17.71. **HRMS** (ESI): calcd for $C_{20}H_{20}NS$ $[M + H]^+$ 306.1316, found 306.1318.

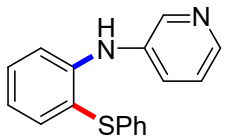
2-(phenylthio)-N-(4-(trifluoromethyl)benzyl)aniline



4m

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (46.7 mg, 65% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.59-7.54 (m, 3H), 7.31-7.27 (m, 5H), 7.22-7.18 (m, 1H), 7.15-7.13 (m, 2H), 6.77 (td, *J* = 7.5, 1.2 Hz, 1H), 6.59 (dd, *J* = 8.2, 1.2 Hz, 1H), 5.49 (t, *J* = 6.0 Hz, 1H), 4.46 (d, *J* = 5.9 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 148.73, 143.35, 137.83, 136.77, 131.51, 129.09, 127.11, 126.63, 125.66, 125.57 (q, *J* = 3.8 Hz), 121.49(q, *J* = 280.0 Hz), 117.65, 114.42, 110.88, 47.13. **^{19}F NMR** (375 MHz, $CDCl_3$) δ -62.41 (3F); **HRMS** (ESI): calcd for $C_{20}H_{17}NF_3S$ $[M + H]^+$ 360.1034, found 360.1040.

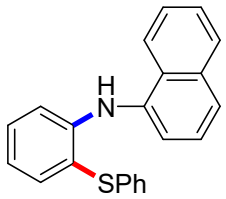
N-(2-(phenylthio)phenyl)pyridin-3-amine



4n

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (37.8 mg, 68% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.40 (d, *J* = 2.7 Hz, 1H), 8.26 (dd, *J* = 4.8, 1.4 Hz, 1H), 7.60 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.45 (ddd, *J* = 8.3, 2.8, 1.4 Hz, 1H), 7.35 (td, *J* = 7.7, 7.1, 1.5 Hz, 1H), 7.30-7.16 (m, 7H), 6.97 (td, *J* = 7.4, 1.5 Hz, 1H), 6.65 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 144.62, 143.49, 142.41, 138.58, 137.39, 136.08, 130.78, 129.29, 127.31, 126.37 (d, *J* = 41.9 Hz), 123.78, 121.29, 119.06, 115.08. **HRMS** (ESI): calcd for $C_{17}H_{15}N_2S$ $[M + H]^+$ 279.0956, found 279.0959.

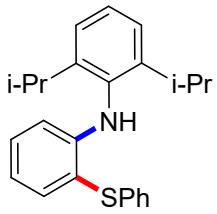
N-(2-(phenylthio)phenyl)naphthalen-1-amine



4o

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow solid (58.9 mg, 90% yield), Mp = 92-93℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.88 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.69-7.64 (m, 3H), 7.52-7.43 (m, 3H), 7.40-7.20 (m, 7H), 7.00-6.98 (m, 2H), 6.87 (td, *J* = 7.5, 1.3 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 147.44, 137.67, 137.26, 136.73, 134.78, 131.07, 129.39, 129.32, 128.46, 127.10, 126.26, 126.06, 125.95, 125.91, 124.76, 122.29, 119.74, 119.28, 116.20, 114.11. **HRMS** (ESI): calcd for $C_{22}H_{18}NS$ $[M + H]^+$ 328.1160, found 328.1158.

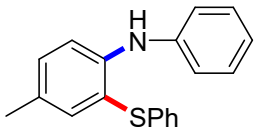
2,6-diisopropyl-N-(2-(phenylthio)phenyl)aniline



4p

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (34.7 mg, 48% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.61 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.32-7.15 (m, 9H), 6.75 (td, *J* = 7.4, 1.3 Hz, 1H), 6.27-6.21 (m, 2H), 2.93 (p, *J* = 6.9 Hz, 2H), 1.09 (d, *J* = 6.9 Hz, 6H), 0.99 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.40, 147.79, 137.85, 137.02, 134.59, 131.35, 129.01, 127.63, 126.71, 125.62, 123.85, 117.34, 113.23, 111.71, 28.28, 24.39, 23.07. **HRMS** (ESI): calcd for $C_{24}H_{28}NS$ $[M + H]^+$ 362.1942, found 362.1950.

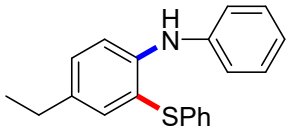
4-methyl-N-phenyl-2-(phenylthio)aniline



5a

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (53.5 mg, 92% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.47(m, 1H), 7.36-7.30 (m, 5H), 7.26-7.19 (m, 4H), 7.15-7.13 (m, 2H), 7.05 (t, *J* = 7.3 Hz, 1H), 6.63 (s, 1H), 2.37 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.27, 142.49, 137.60, 136.82, 131.47, 129.89, 129.40, 129.24, 127.15, 125.86, 122.12, 119.85, 118.05, 115.52, 20.49. **HRMS** (ESI): calcd for $C_{19}H_{18}NS$ $[M + H]^+$ 292.1160, found 292.1167.

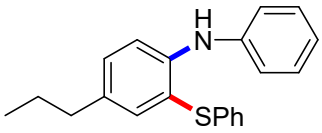
4-ethyl-N-phenyl-2-(phenylthio)aniline



5b

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (55.5 mg, 91% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 2.1 Hz, 0H), 7.34-7.26 (m, 5H), 7.22-7.15 (m, 4H), 7.12-7.09 (m, 2H), 7.01 (tt, *J* = 7.3, 1.2 Hz, 1H), 6.59 (s, 1H), 2.64 (q, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.44, 142.37, 136.79, 136.49, 136.35, 130.27, 129.34, 129.18, 126.95, 125.75, 122.10, 119.88, 117.71, 115.35, 27.92, 15.76. **HRMS** (ESI): calcd for $C_{20}H_{20}NS$ $[M + H]^+$ 306.1316, found 306.1321.

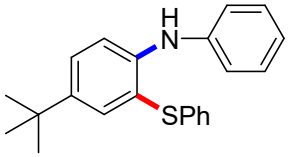
N-phenyl-2-(phenylthio)-4-propylaniline



5c

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (58.7 mg, 92% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 2.1 Hz, 1H), 7.32-7.25 (m, 5H), 7.19-7.14 (m, 4H), 7.11-7.09 (m, 2H), 7.03-6.99 (m, 1H), 6.59 (s, 1H), 2.56 (dd, *J* = 8.5, 6.7 Hz, 2H), 1.67 (h, *J* = 7.4 Hz, 2H), 0.99 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.45, 142.35, 137.13, 136.84, 134.79, 130.85, 129.34, 129.17, 126.92, 125.73, 122.10, 119.91, 117.55, 115.21, 37.04, 24.68, 13.82. **HRMS** (ESI): calcd for $C_{21}H_{22}NS$ $[M + H]^+$ 320.1473, found 320.1485.

4-(tert-butyl)-N-phenyl-2-(phenylthio)aniline

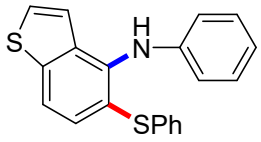


5d

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (49.9 mg, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 2.3 Hz, 1H),

7.39-7.26 (m, 6H), 7.19-7.15 (m, 3H), 7.11-7.09 (m, 2H), 7.03-6.99 (m, 1H), 6.58 (s, 1H), 1.35 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.29, 142.27, 136.86, 134.25, 129.31, 129.15, 127.82, 126.78, 125.67, 122.16, 120.04, 117.08, 114.81, 34.20, 31.45. **HRMS** (ESI): calcd for $C_{22}H_{24}NS$ $[M + H]^+$ 334.1629, found 334.1638.

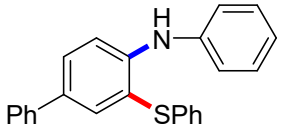
N-phenyl-5-(phenylthio)benzo[b]thiophen-4-amine



5e

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (40.6 mg, 61% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.3 Hz, 1H), 7.56 (d, *J* = 8.3 Hz, 1H), 7.33-7.30 (m, 1H), 7.25-7.12 (m, 7H), 7.00 (d, *J* = 5.6 Hz, 1H), 6.97-6.93 (m, 1H), 6.83-6.81 (m, 2H), 6.72 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 144.53, 142.80, 140.25, 137.10, 133.26, 131.98, 129.17, 129.03, 127.72, 125.99, 125.57, 123.66, 121.42, 118.61, 118.35, 117.62. **HRMS** (ESI): calcd for $C_{20}H_{16}NS_2$ $[M + H]^+$ 334.0724, found 334.0726.

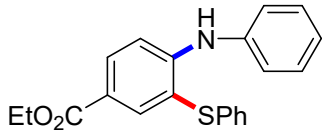
N-phenyl-3-(phenylthio)-[1,1'-biphenyl]-4-amine



5f

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (62.1 mg, 88% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 2.3 Hz, 1H), 7.62-7.58 (m, 3H), 7.48-7.42 (m, 3H), 7.37-7.31 (m, 3H), 7.30-7.23 (m, 4H), 7.21-7.16 (m, 3H), 7.10-7.05 (m, 1H), 6.80 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.17, 141.57, 140.07, 136.44, 135.91, 132.88, 129.47, 129.41, 129.28, 128.90, 127.01, 126.84, 126.42, 125.95, 122.93, 120.92, 117.66, 114.67. **HRMS** (ESI): calcd for $C_{24}H_{20}NS$ $[M + H]^+$ 354.1316, found 354.1316.

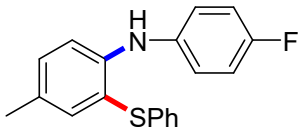
ethyl 4-(phenylamino)-3-(phenylthio)benzoate



5g

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (52.3 mg, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.34 (d, *J* = 2.1 Hz, 1H), 8.00 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.31-7.14 (m, 10H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.01, 150.11, 140.01, 139.78, 135.84, 132.89, 129.60, 129.33, 126.82, 126.11, 124.54, 122.77, 121.10, 115.60, 112.09, 60.71, 14.50. **HRMS** (ESI): calcd for $C_{21}H_{20}NO_2S$ $[M + H]^+$ 350.1215, found 350.1227.

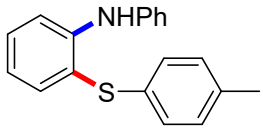
N-(4-fluorophenyl)-4-methyl-2-(phenylthio)aniline



5h

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (49.4 mg, 80% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.41 (s, 1H), 7.30-7.26 (m, 2H), 7.19-6.98 (m, 9H), 6.44 (s, 1H), 2.32 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.73 (d, *J* = 241.6 Hz), 144.06, 138.30, 137.71, 136.73, 131.59, 129.50, 129.18, 126.87, 125.77, 122.70 (d, *J* = 7.9 Hz), 117.03, 115.98 (d, *J* = 22.6 Hz), 114.52, 20.37. **^{19}F NMR** (375 MHz, $CDCl_3$) δ -120.53 (1F); **HRMS** (ESI): calcd for $C_{19}H_{17}NSF$ $[M + H]^+$ 310.1066, found 310.1073.

N-phenyl-2-(p-tolylthio)aniline[3]

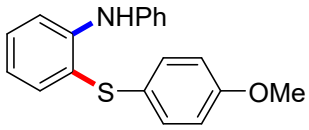


6a

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow solid (52.4 mg, 90% yield), Mp = 40-41℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.54 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.34-7.27 (m, 4H), 7.14-7.09 (m, 6H), 7.06-7.02 (m, 1H), 6.88 (td, *J* = 7.3, 1.8 Hz, 2H), 2.33 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.48, 141.88, 136.96, 135.99, 132.66,

130.39, 130.01, 129.37, 127.72, 122.57, 120.55, 120.05, 118.54, 114.62, 21.01. **HRMS** (ESI): calcd for $C_{19}H_{18}NS$ $[M + H]^+$ 292.1160, found 292.1168.

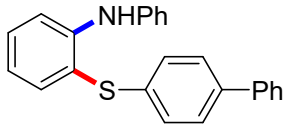
2-((4-methoxyphenyl)thio)-N-phenylaniline



6b

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (58.3 mg, 95% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.48 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.34-7.30 (m, 3H), 7.28-7.22 (m, 3H), 7.13-7.11 (m, 2H), 7.06-7.01 (m, 1H), 6.89-6.84 (m, 3H), 6.65 (s, 1H), 3.81 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.81, 144.73, 142.09, 138.20, 135.83, 130.67, 129.81, 129.39, 126.31, 122.41, 120.65, 120.25, 115.06, 115.03, 55.43. **HRMS** (ESI): calcd for $C_{19}H_{18}NOS$ $[M + H]^+$ 308.1109, found 308.1096.

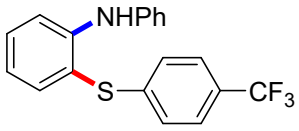
2-([1,1'-biphenyl]-4-ylthio)-N-phenylaniline



6c

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (64.3 mg, 91% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.64 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.60-7.58 (m, 2H), 7.54-7.51 (m, 2H), 7.49-7.45 (m, 2H), 7.40-7.32 (m, 5H), 7.30-7.27 (m, 2H), 7.18-7.16 (m, 2H), 7.09-7.05 (m, 1H), 6.93 (ddd, *J* = 8.3, 6.6, 2.1 Hz, 1H), 6.78 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.00, 141.77, 140.49, 138.93, 137.54, 135.72, 130.90, 129.44, 128.90, 127.91, 127.42, 127.39, 126.96, 122.84, 120.85, 120.11, 117.35, 114.64. **HRMS** (ESI): calcd for $C_{24}H_{20}NS$ $[M + H]^+$ 354.1316, found 354.1322.

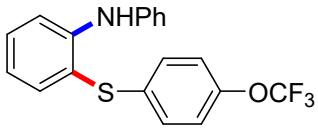
N-phenyl-2-((4-(trifluoromethyl)phenyl)thio)aniline



6d

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow solid (60.0 mg, 87% yield), Mp = 73-74℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 7.7 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.40-7.34 (m, 4H), 7.24 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.96-6.92 (m, 1H), 6.72 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.51, 142.21, 141.33, 138.11, 131.73, 129.53, 127.67 (q, *J* = 32.6 Hz), 126.04, 125.96 (q, *J* = 4.0 Hz), 124.22 (q, *J* = 270.0 Hz), 123.27, 121.21, 120.17, 114.94, 114.51. **^{19}F NMR** (375 MHz, $CDCl_3$) δ -62.32 (3F); **HRMS** (ESI): calcd for $C_{19}H_{15}NSF_3$ $[M + H]^+$ 346.0877, found 346.0878.

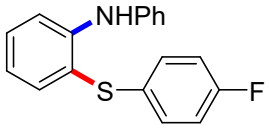
N-phenyl-2-((4-(trifluoromethoxy)phenyl)thio)aniline



6e

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (61.4 mg, 85% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 7.6 Hz, 1H), 7.38-7.34 (m, 4H), 7.23-7.14 (m, 6H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.96-6.91 (m, 1H), 6.75 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 147.42, 146.14, 141.56, 137.67, 135.61, 131.28, 129.50, 128.07, 123.09, 121.90, 121.01, 120.55 (d, *J* = 258.5 Hz), 120.18, 116.70, 114.69. **^{19}F NMR** (375 MHz, $CDCl_3$) δ -57.94 (3F); **HRMS** (ESI): calcd for $C_{19}H_{15}NOSF_3$ $[M + H]^+$ 362.0826, found 362.0823.

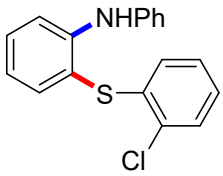
2-((4-fluorophenyl)thio)-N-phenylaniline



6f

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (49.6 mg, 84% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.4 Hz, 1H), 7.58-7.52 (m, 2H), 7.34-7.30 (m, 4H), 7.20-7.11 (m, 3H), 7.07-7.03 (m, 1H), 7.01-6.96 (m, 2H), 6.90-6.86 (m, 1H), 6.68 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.63 (d, *J* = 386.2 Hz), 136.97, 131.04, 130.70, 129.42, 129.34, 129.15, 128.76, 122.86 (d, *J* = 10.4 Hz), 120.67, 120.14, 118.25, 116.32 (d, *J* = 22.1 Hz), 114.78. **^{19}F NMR** (375 MHz, $CDCl_3$) δ -116.37 (1F); **HRMS** (ESI): calcd for $C_{18}H_{15}NSF$ $[M + H]^+$ 296.0909, found 296.0915.

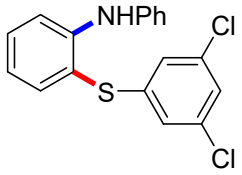
2-((2-chlorophenyl)thio)-N-phenylaniline



6g

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow solid (51.0 mg, 82% yield), Mp = 94-95℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 7.3 Hz, 1H), 7.41-7.31 (m, 5H), 7.16 (d, *J* = 7.7 Hz, 2H), 7.12-7.05 (m, 3H), 6.95-6.91 (m, 1H), 6.82-6.80 (m, 1H), 6.72 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.61, 141.46, 138.16, 135.95, 131.54, 131.51, 129.71, 129.43, 127.37, 126.83, 126.47, 123.10, 121.21, 120.12, 115.30, 114.42. **HRMS** (ESI): calcd for $C_{18}H_{15}NSCl$ $[M + H]^+$ 312.0614, found 312.0623.

2-((3,5-dichlorophenyl)thio)-N-phenylaniline

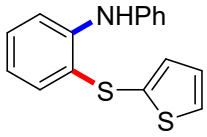


6h

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

yellow liquid (60.7 mg, 88% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 7.6 Hz, 1H), 7.39-7.34 (m, 4H), 7.19-7.16 (m, 2H), 7.14-7.09 (m, 2H), 7.01-7.01 (m, 2H), 6.94 (t, *J* = 7.3 Hz, 1H), 6.63 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.43, 141.29, 140.75, 138.02, 135.55, 131.94, 129.54, 125.78, 124.17, 123.34, 121.28, 120.29, 114.83, 114.58. **HRMS** (ESI): calcd for $C_{18}H_{14}NSCl_2$ $[M + H]^+$ 346.0224, found 346.0225.

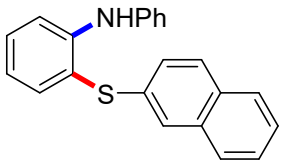
N-phenyl-2-(thiophen-2-ylthio)aniline



6i

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (37.4 mg, 66% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.47 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.37-7.27 (m, 4H), 7.24-7.20 (m, 2H), 7.17-7.14 (m, 2H), 7.08-7.00 (m, 2H), 6.87 (td, *J* = 7.5, 1.5 Hz, 1H), 6.61 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.72, 142.18, 134.13, 133.57, 132.62, 129.65, 129.45, 129.32, 127.71, 123.09, 122.32, 120.70, 119.91, 115.87. **HRMS** (ESI): calcd for $C_{16}H_{12}NS_2$ $[M - H]^+$ 282.0411, found 282.0406.

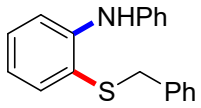
2-(naphthalen-2-ylthio)-N-phenylaniline



6j

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (59.5 mg, 91% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.82-7.76 (m, 2H), 7.72-7.69 (m, 1H), 7.65-7.61 (m, 2H), 7.50-7.43 (m, 2H), 7.40-7.29 (m, 5H), 7.15-7.12 (m, 2H), 7.06-7.02 (m, 1H), 6.95-6.91 (m, 1H), 6.77 (brs, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.95, 141.76, 137.43, 133.92, 131.82, 130.84, 129.40, 128.88, 127.81, 127.15, 126.68, 125.68, 125.50, 125.15, 122.78, 120.78, 120.15, 117.50, 114.73. **HRMS** (ESI): calcd for $C_{22}H_{18}NS$ $[M + H]^+$ 328.1160, found 328.1163.

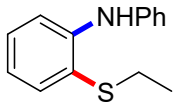
2-(benzylthio)-N-phenylaniline



6k

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (57.1 mg, 98% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.44 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.38-7.20 (m, 9H), 7.13-7.05 (m, 3H), 6.82 (td, *J* = 7.3, 1.6 Hz, 1H), 6.77 (s, 1H), 3.99 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.53, 142.18, 138.23, 136.74, 129.85, 129.39, 128.90, 128.55, 127.26, 122.23, 120.42, 119.97, 119.89, 114.42, 40.59. **HRMS** (ESI): calcd for $C_{19}H_{18}NS$ $[M + H]^+$ 292.1160, found 292.1167.

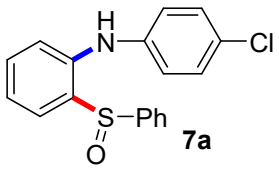
2-(ethylthio)-N-phenylaniline



6l

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (43.5 mg, 95% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 7.6 Hz, 1H), 7.41 (q, *J* = 7.8 Hz, 3H), 7.28 (d, *J* = 8.1 Hz, 3H), 7.11 (t, *J* = 7.3 Hz, 1H), 6.95-6.91 (m, 2H), 2.89 (q, *J* = 7.3 Hz, 2H), 1.36 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.09, 142.46, 135.88, 129.55, 129.36, 122.23, 121.17, 120.04, 119.87, 114.70, 29.48, 15.00. **HRMS** (ESI): calcd for $C_{14}H_{16}NS$ $[M + H]^+$ 230.1003, found 230.1014.

N-(4-chlorophenyl)-2-(phenylsulfinyl)aniline

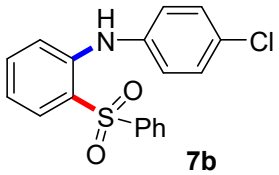


7a

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (52.3 mg, 80% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.19 (s, 1H), 7.62 (dd, *J* = 7.7, 1.6 Hz, 2H), 7.58-7.55 (m, 2H), 7.42-7.33 (m, 4H), 7.21-7.15 (m, 3H), 6.96 (td, *J* = 7.5, 1.2 Hz, 1H), 6.85 (d, *J* = 8.7 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.26, 143.35, 139.85, 133.11,

130.41, 129.29, 129.14, 128.96, 127.44, 127.17, 124.63, 120.92, 119.55, 117.20. **HRMS** (ESI): calcd for $C_{18}H_{15}NOSCl$ $[M + H]^+$ 328.0563, found 328.0571.

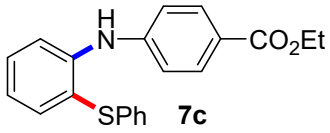
N-(4-chlorophenyl)-2-(phenylsulfonyl)aniline



7b

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow solid (63.1 mg, 92% yield), Mp = 74-75℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.03 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.97-7.92 (m, 3H), 7.59-7.55 (m, 1H), 7.49-7.45 (m, 2H), 7.38 (ddd, *J* = 8.6, 7.1, 1.7 Hz, 1H), 7.30-7.25 (m, 2H), 7.16 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.02-6.96 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.55, 141.42, 139.18, 135.06, 133.36, 130.45, 129.65, 129.18, 128.55, 127.12, 125.45, 122.55, 119.83, 116.57. **HRMS** (ESI): calcd for $C_{18}H_{15}NO_2SCl$ $[M + H]^+$ 344.0512, found 344.0524.

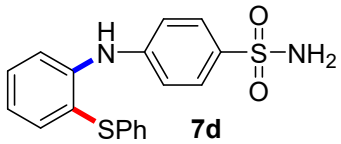
ethyl 4-((2-(phenylthio)phenyl)amino)benzoate



7c

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (56.5 mg, 81% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.8 Hz, 2H), 7.59 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.50 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.39 (td, *J* = 8.2, 7.8, 1.6 Hz, 1H), 7.30-7.25 (m, 2H), 7.21-7.16 (m, 3H), 7.08-7.01 (m, 3H), 6.83 (s, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.42, 146.65, 143.19, 136.80, 135.90, 131.34, 130.37, 129.32, 127.84, 126.36, 122.95, 122.31, 121.26, 117.68, 116.63, 60.62, 14.48. **HRMS** (ESI): calcd for $C_{21}H_{20}NO_2S$ $[M + H]^+$ 350.1215, found 350.1226.

4-((2-(phenylthio)phenyl)amino)benzenesulfonamide



7d

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow solid (49.1 mg, 69% yield), Mp = 120-121℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.7 Hz, 2H), 7.57 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.46 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.38 (td, *J* = 8.2, 7.8, 1.6 Hz, 1H), 7.30-7.24 (m, 2H), 7.20-7.16 (m, 3H), 7.08-7.04 (m, 3H), 6.77 (s, 1H), 4.97 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.88, 142.33, 136.49, 135.55, 133.06, 130.25, 129.39, 128.41, 128.16, 126.58, 123.15, 122.61, 118.56, 116.49. **HRMS** (ESI): calcd for $C_{18}H_{17}N_2O_2S_2$ $[M + H]^+$ 357.0731, found 357.0740.

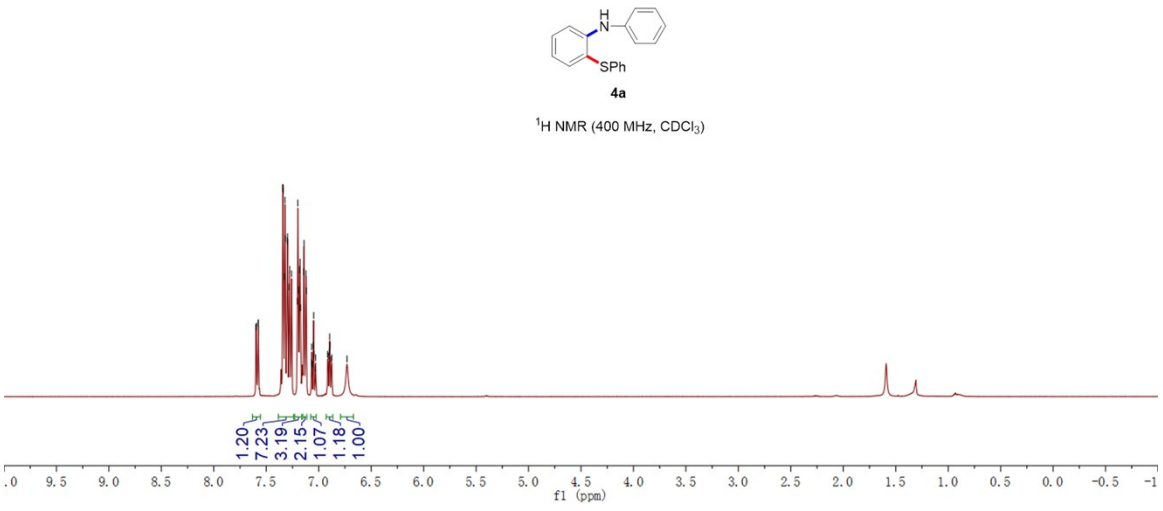
References:

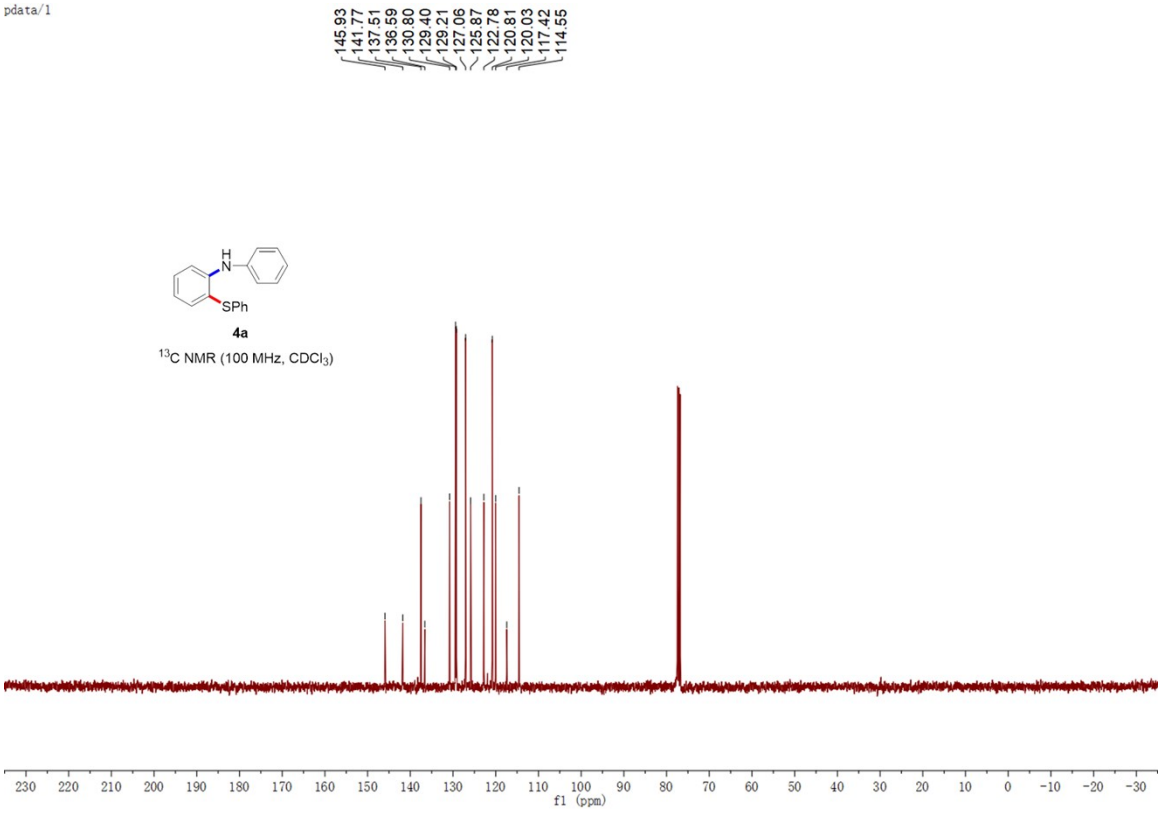
1 M. Minoshima, K. Uchida, Y. Nakamura, T. Hosoya and S. Yoshida, *Org. Lett.*, 2021, **23**, 1868.

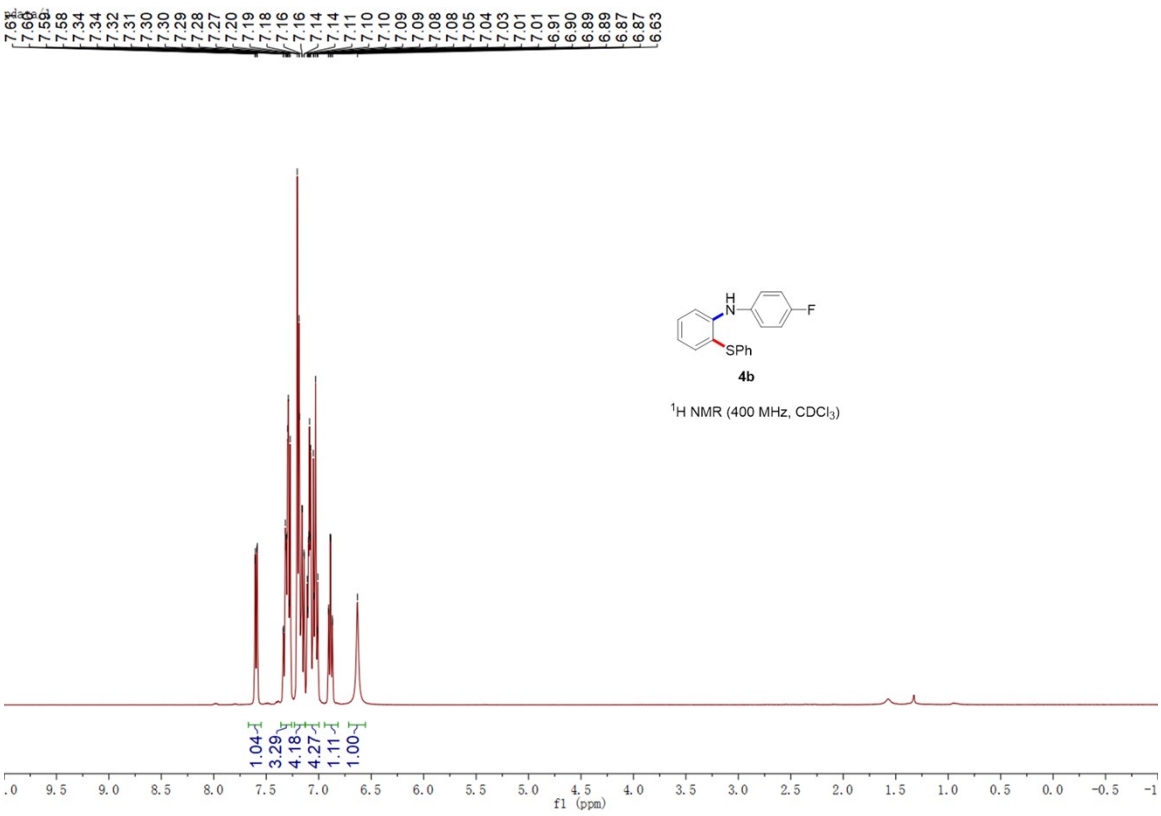
2 S. Yoshida, T. Yano, Y. Misawa, Y. Sugimura, K. Igawa, S. Shimizu, K. Tomooka and T. Hosoya, *J. Am. Chem. Soc.*, 2015, **137**, 14071.

3 M. Tang, L. Zhang, G. Mao, F. Xiao, W. Shao and G.-J. Deng, *Adv. Synth. Catal.*, 2022, **364**, 2205.

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



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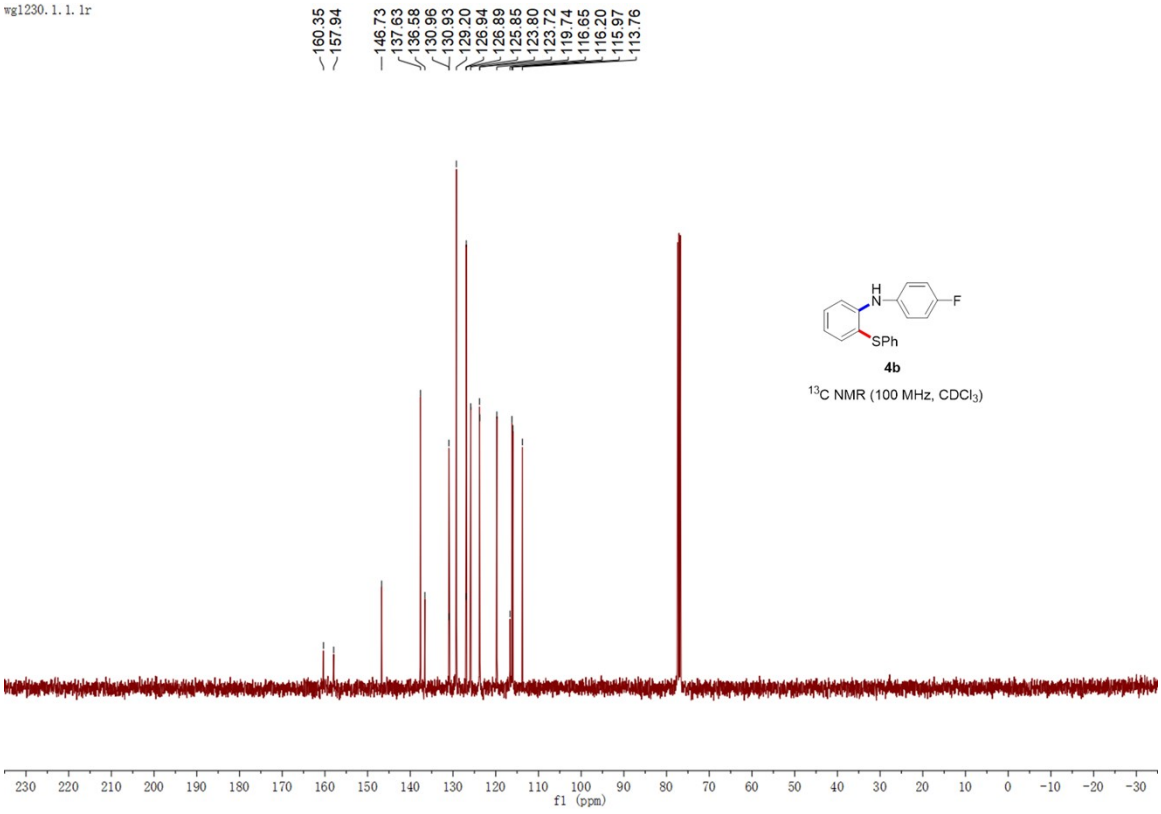
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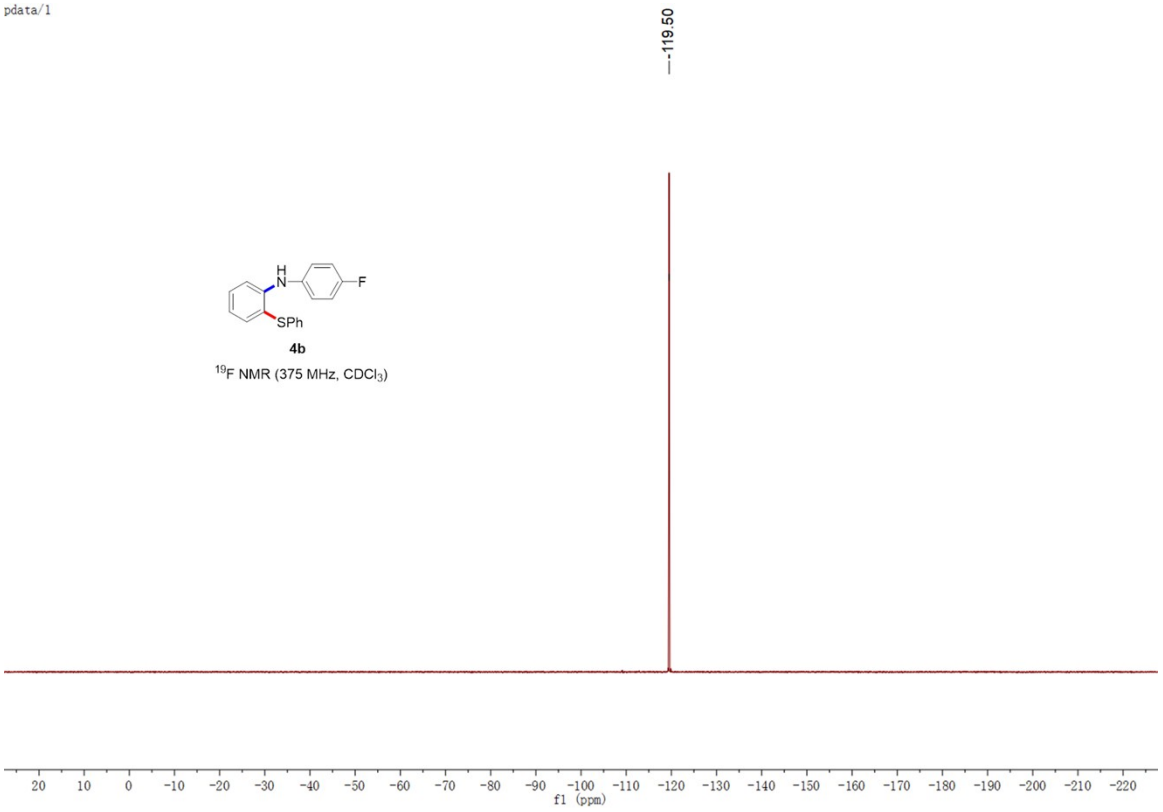
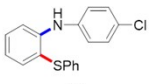


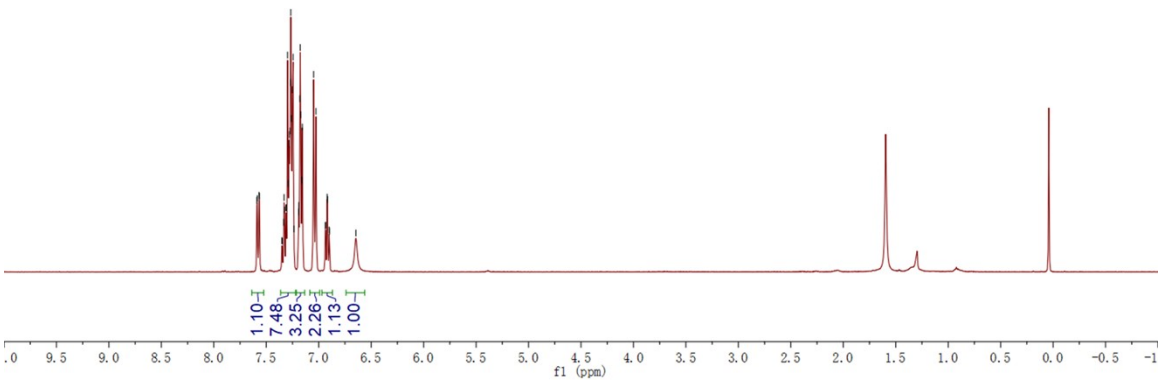
4b

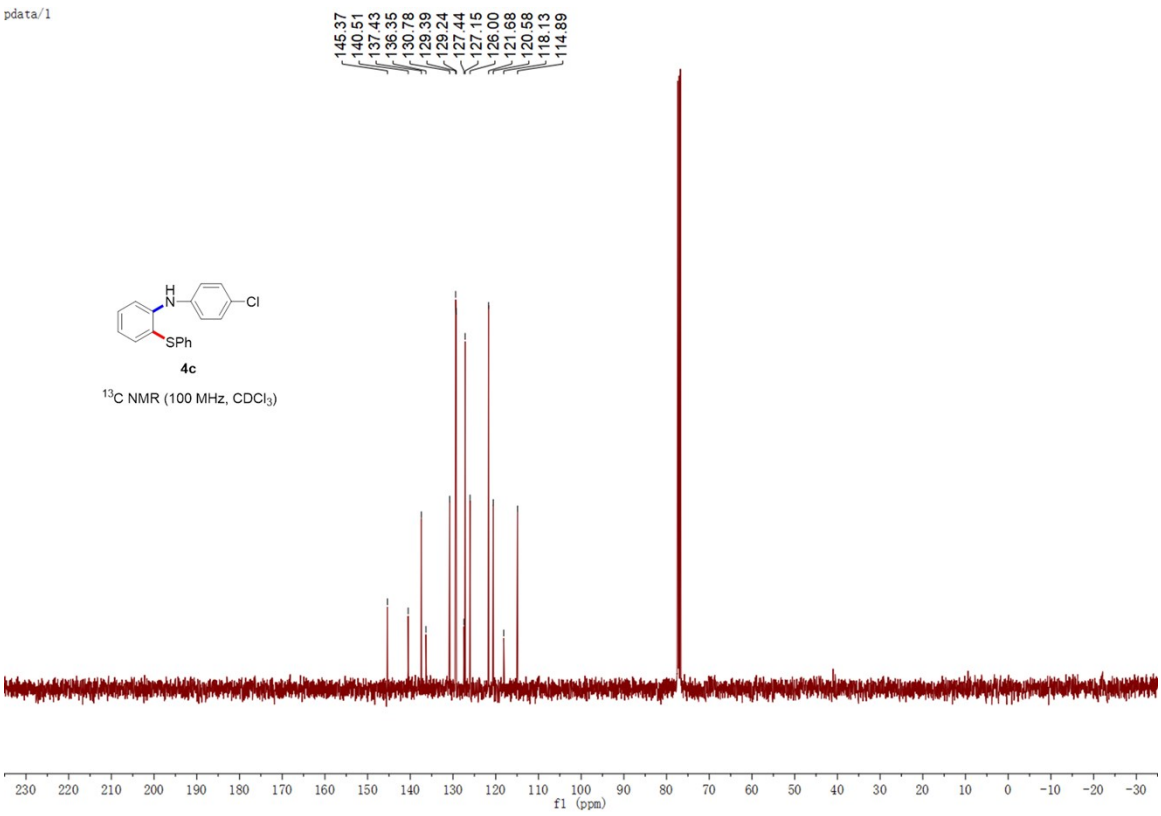
^{19}F NMR (375 MHz, $CDCl_3$)

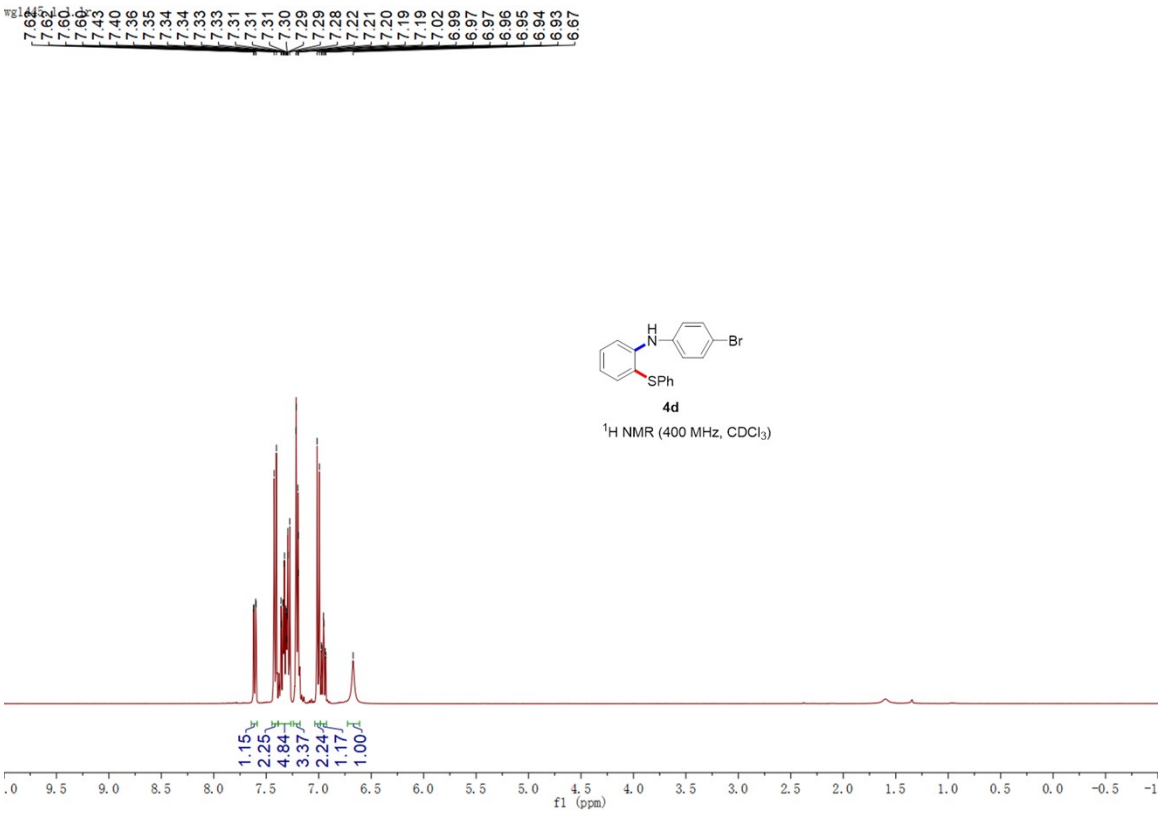


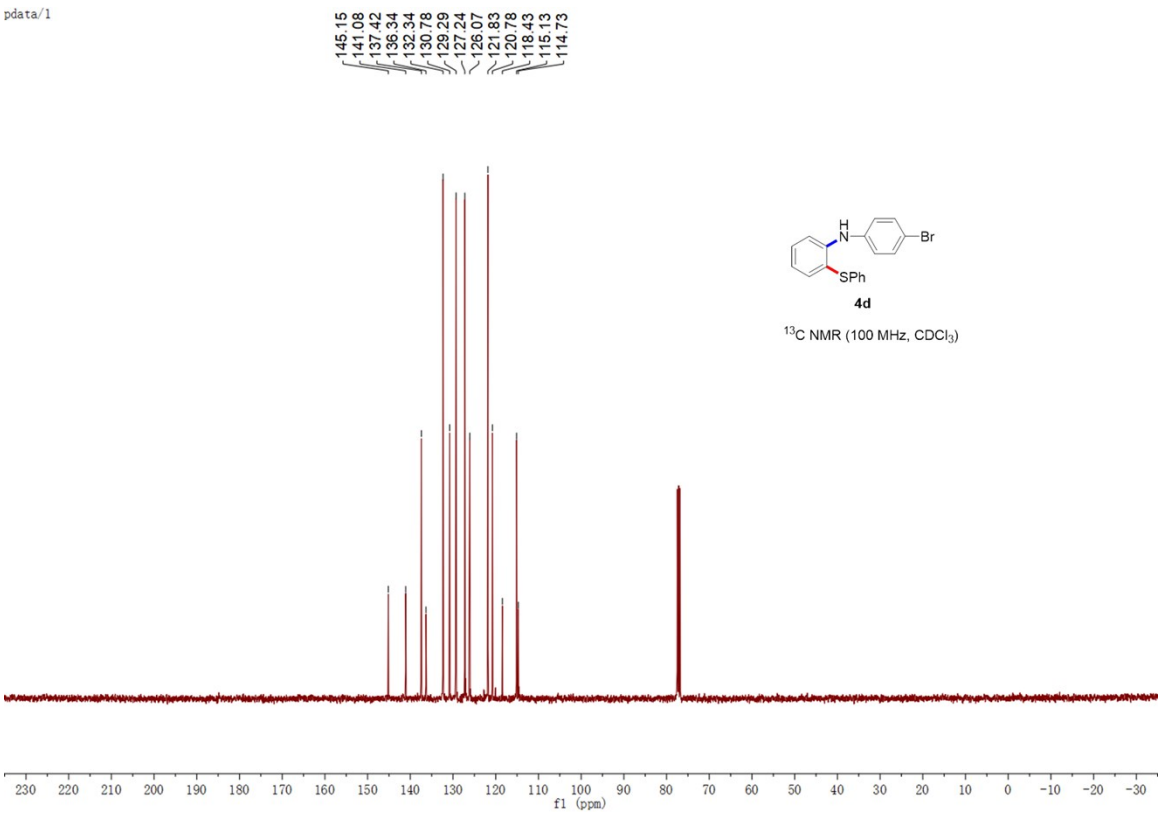
4c

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




pdata/1
145.37
140.51
137.43
136.35
130.78
129.39
129.24
127.44
127.15
126.00
121.68
120.58
118.13
114.89
H
N
Cl
SPh
4c
13C NMR (100 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)


7.62
7.62
7.60
7.60
7.43
7.40
7.36
7.35
7.34
7.34
7.33
7.33
7.31
7.31
7.31
7.30
7.29
7.29
7.28
7.22
7.21
7.20
7.19
7.19
7.02
6.99
6.97
6.97
6.96
6.95
6.94
6.93
6.67
H
N
Br
SPh
4d
1H NMR (400 MHz, CDCl3)
1.15
2.25
4.84
3.37
2.24
1.17
1.00
.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


pdata/1
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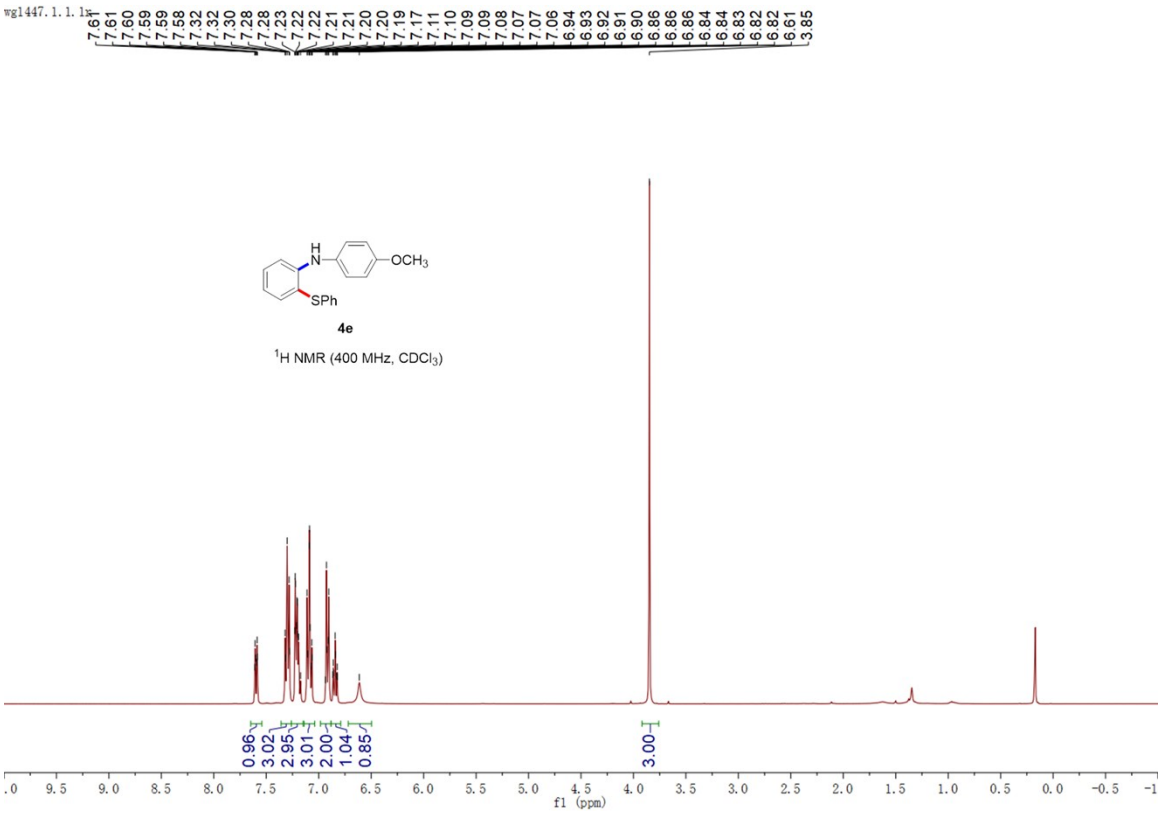
141.08
137.42
136.34
132.34
130.78
129.29
127.24
126.07
121.83
120.78
118.43
115.13
114.73
Br
SPh
4d
13C NMR (100 MHz, CDCl3)
f1 (ppm)


wgl447.1.1.1r
7.61
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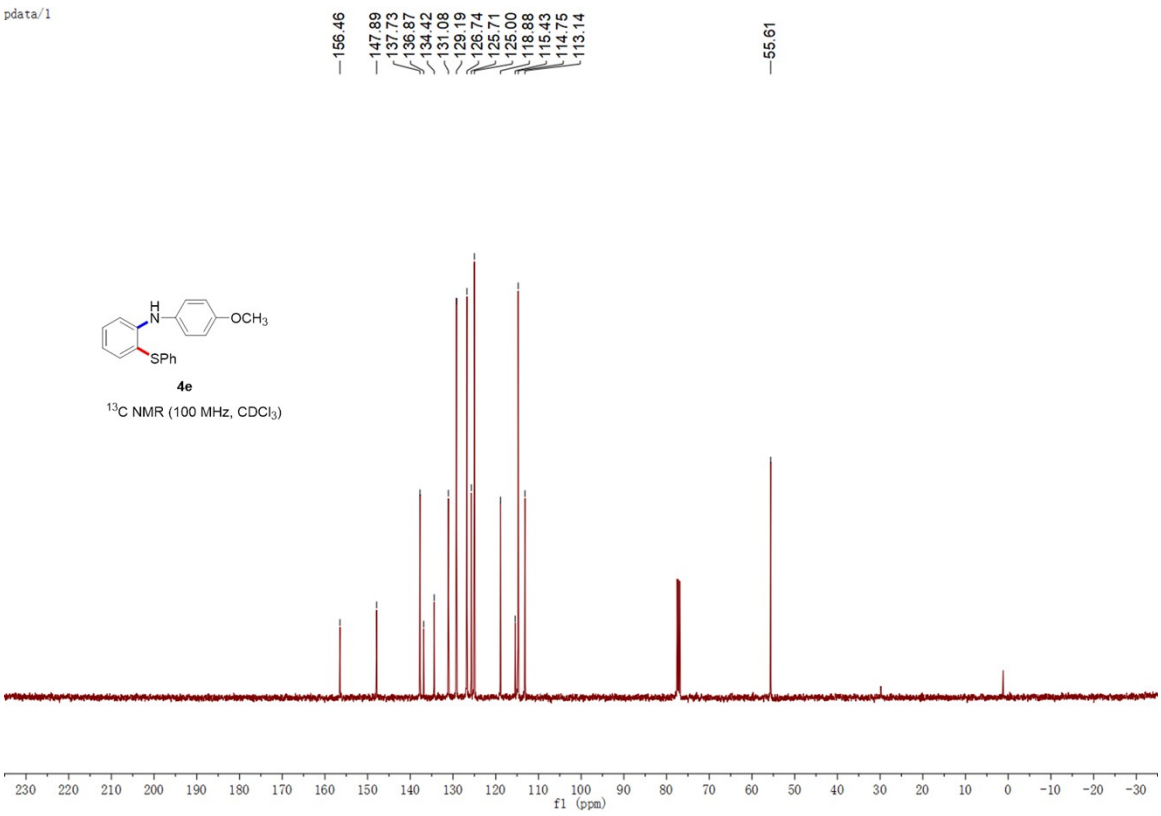
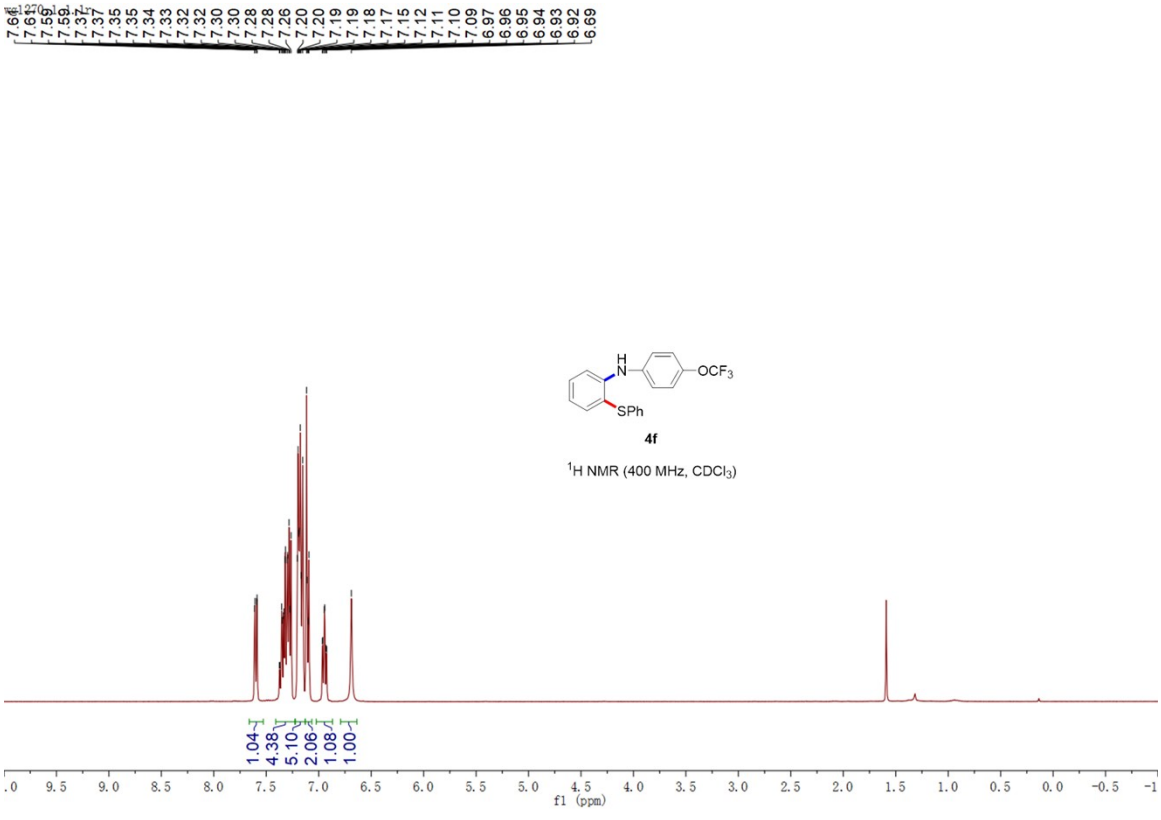
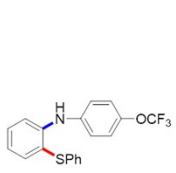
7.59
7.59
7.58
7.32
7.30
7.28
7.28
7.23
7.22
7.22
7.21
7.21
7.20
7.20
7.19
7.17
7.11
7.10
7.09
7.09
7.08
7.07
7.07
7.06
6.94
6.93
6.92
6.91
6.90
6.86
6.86
6.86
6.84
6.84
6.83
6.82
6.82
6.61
3.85
OCH3
SPh
4e
1H NMR (400 MHz, CDCl3)
0.96
3.02
2.95
3.01
2.00
1.04
0.85
3.00
f1 (ppm)


pdata/1
156.46
147.89
137.73
136.87
134.42
131.08
129.19
126.74
125.71
125.00
118.88
115.43
114.75
113.14
55.61
OCH3
SPh
4e
13C NMR (100 MHz, CDCl3)
f1 (ppm)


7.64
7.61
7.59
7.37
7.35
7.34
7.33
7.32
7.30
7.28
7.26
7.20
7.19
7.18
7.17
7.15
7.12
7.11
7.10
7.09
6.97
6.96
6.95
6.94
6.93
6.92
6.69
OCF3
SPh
4f
1H NMR (400 MHz, CDCl3)
1.04
4.38
5.10
2.06
1.08
1.00
f1 (ppm)

pdata/1

145.28
144.10
140.72
137.45
136.32
130.81
129.27
127.17
126.04
122.31
121.91
121.22
120.76
119.36
118.27
114.99



4f

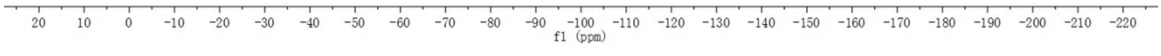
^{13}C NMR (100 MHz, $CDCl_3$)

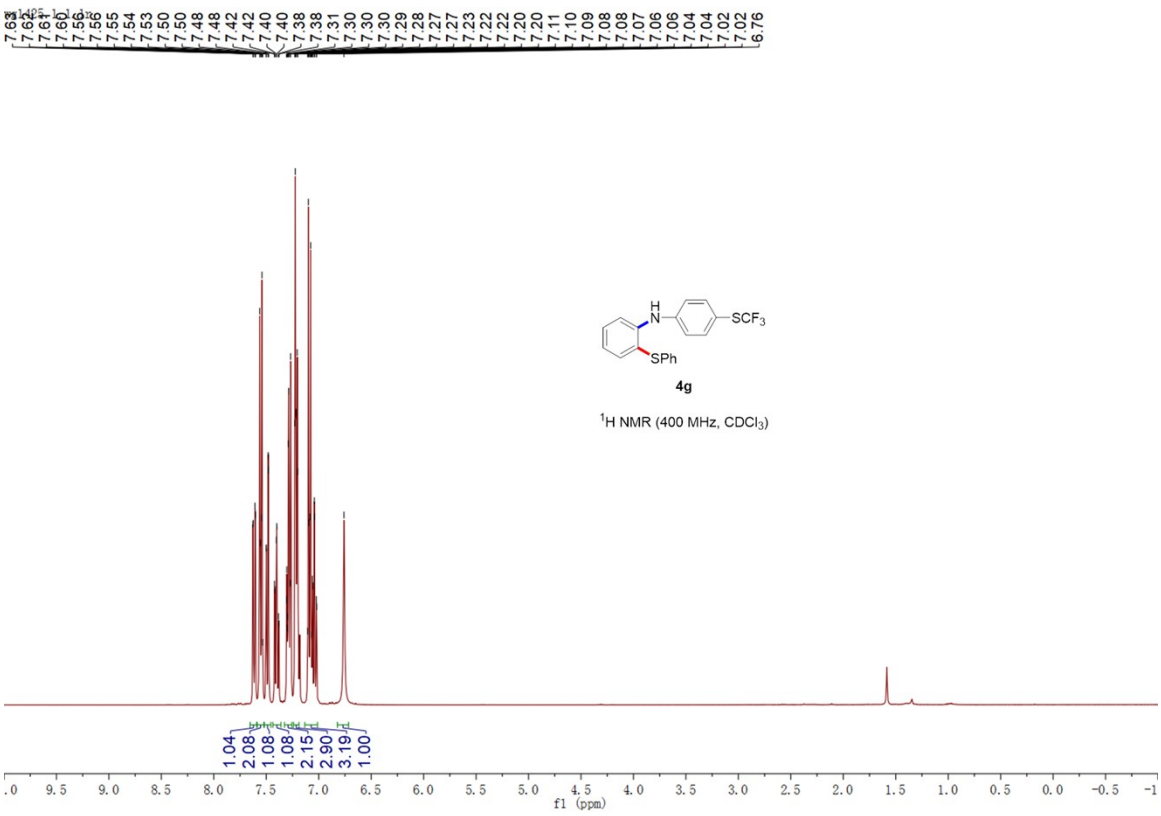
pdata/1

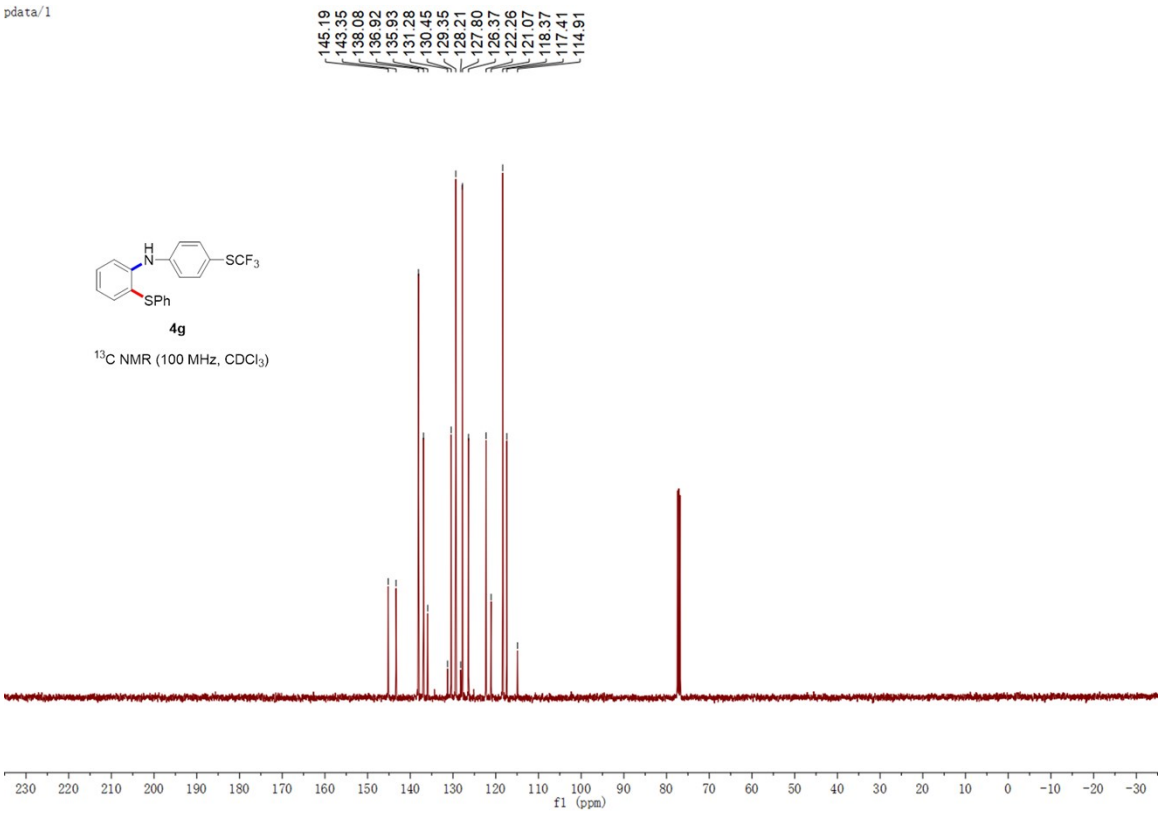
-58.18

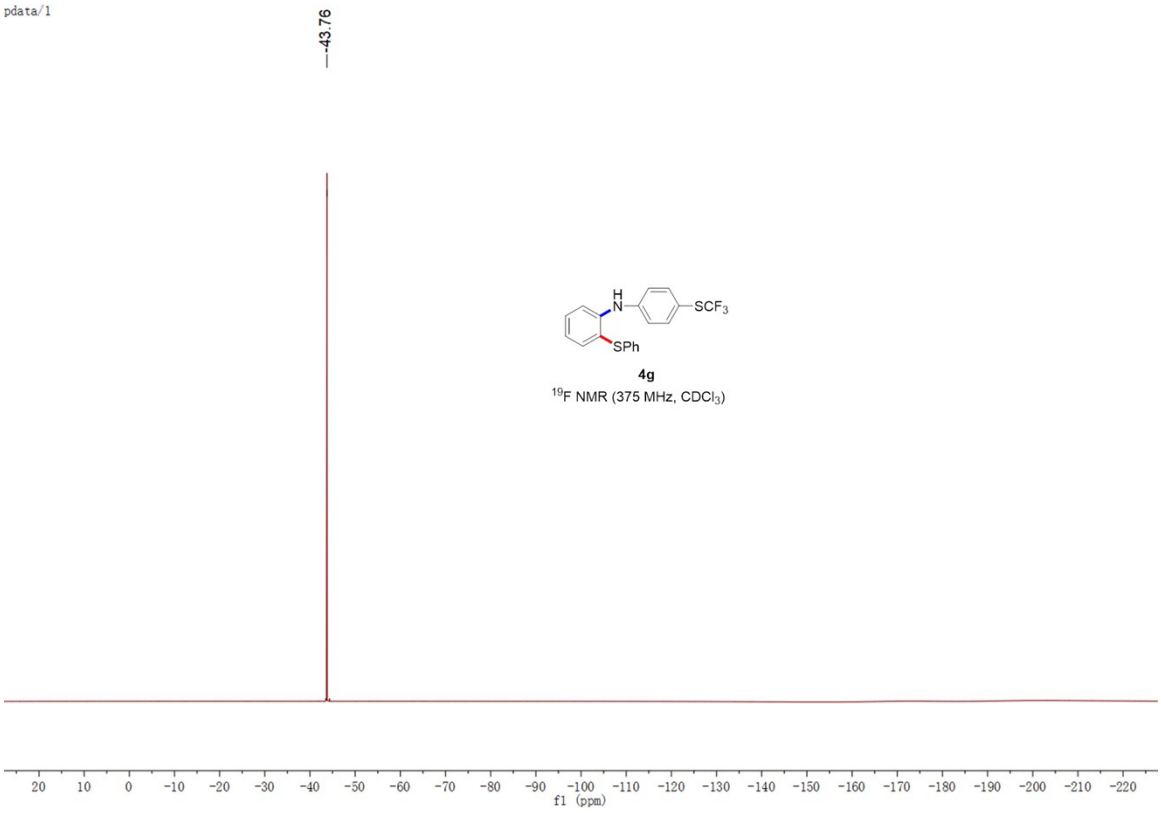
4f

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



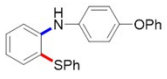

7.63
7.62
7.61
7.60
7.56
7.55
7.54
7.53
7.50
7.50
7.48
7.42
7.42
7.40
7.40
7.38
7.38
7.31
7.30
7.30
7.30
7.29
7.28
7.27
7.27
7.23
7.22
7.22
7.20
7.20
7.11
7.10
7.09
7.08
7.08
7.07
7.06
7.06
7.04
7.04
7.02
7.02
6.76
H
N
SCF3
SPh
4g
1H NMR (400 MHz, CDCl3)
1.04
2.08
1.08
1.08
2.15
2.90
3.19
1.00
f1 (ppm)


pdata/1
145.19
143.35
138.08
136.92
135.93
131.28
130.45
129.35
128.21
127.80
126.37
122.26
121.07
118.37
117.41
114.91
H
N
SCF3
SPh
4g
13C NMR (100 MHz, CDCl3)
f1 (ppm)



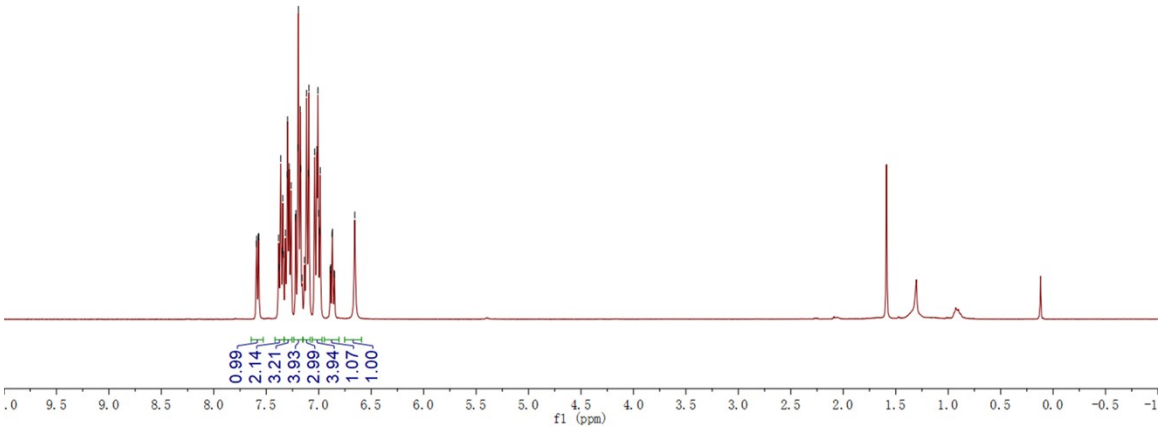
4g

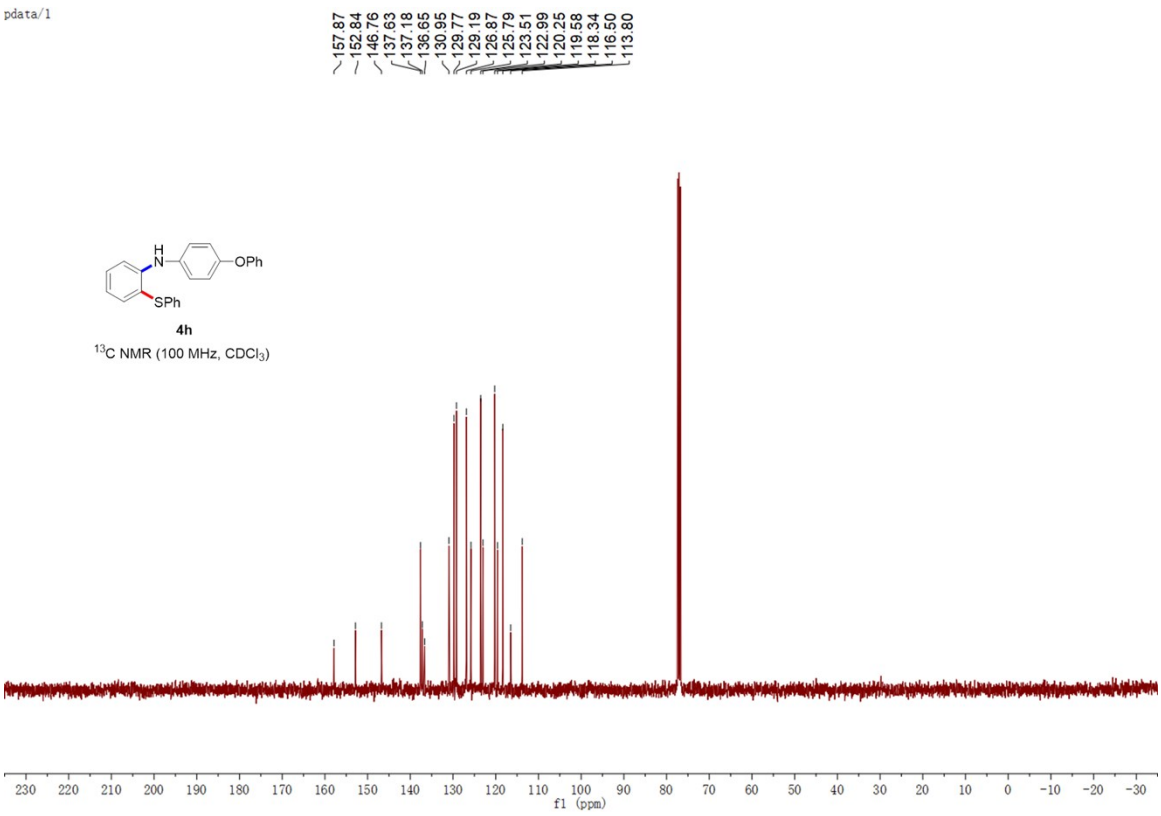
^{19}F NMR (375 MHz, $CDCl_3$)

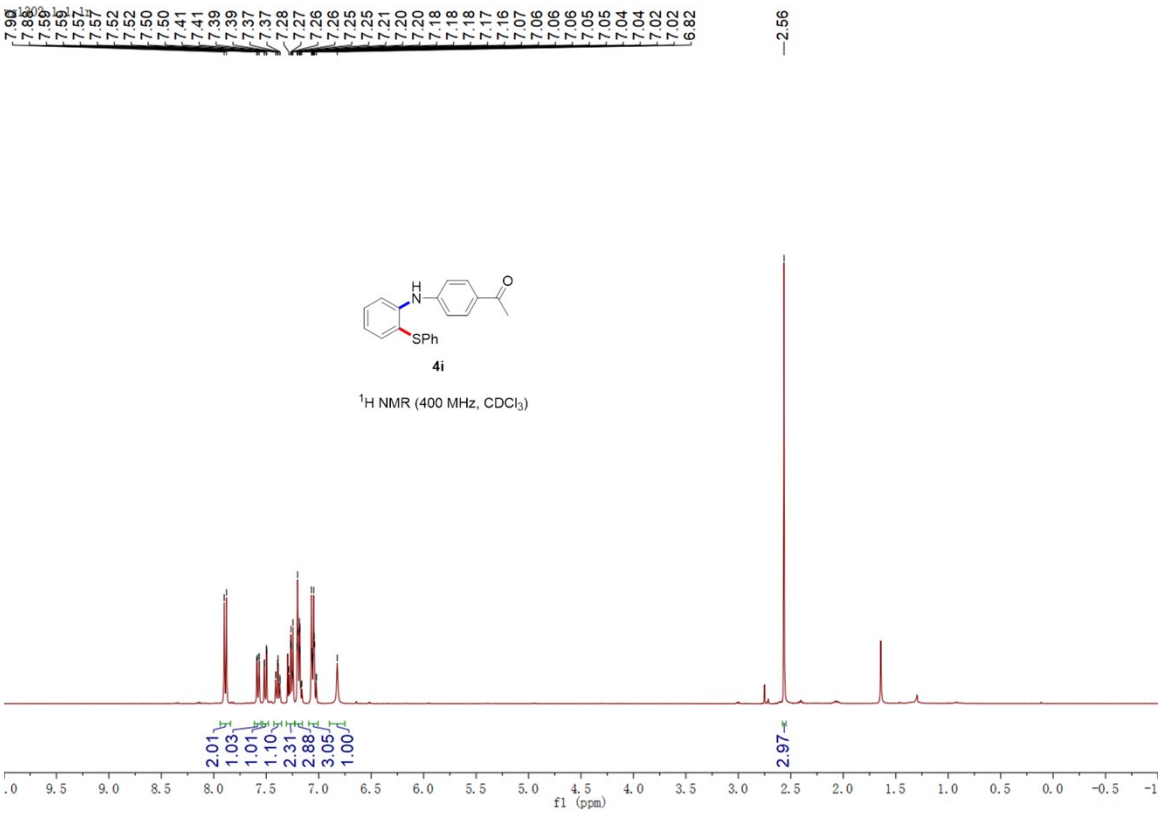


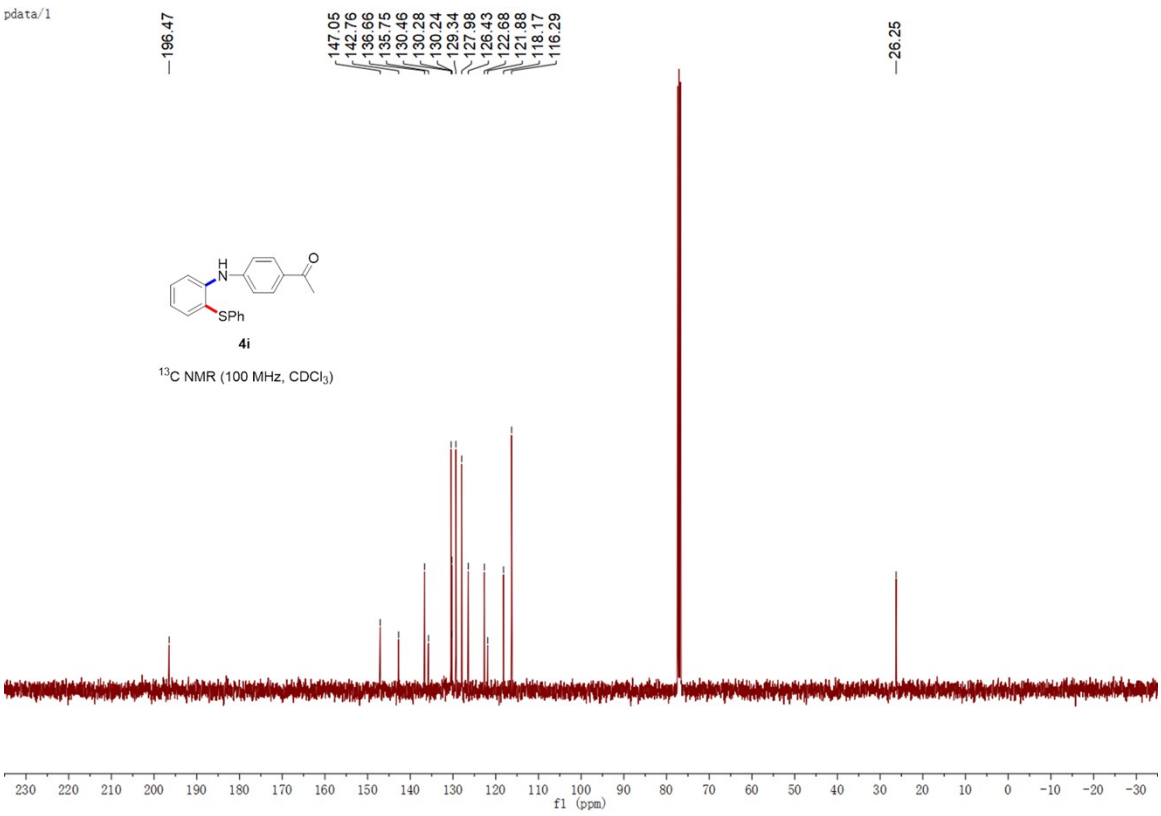
4h

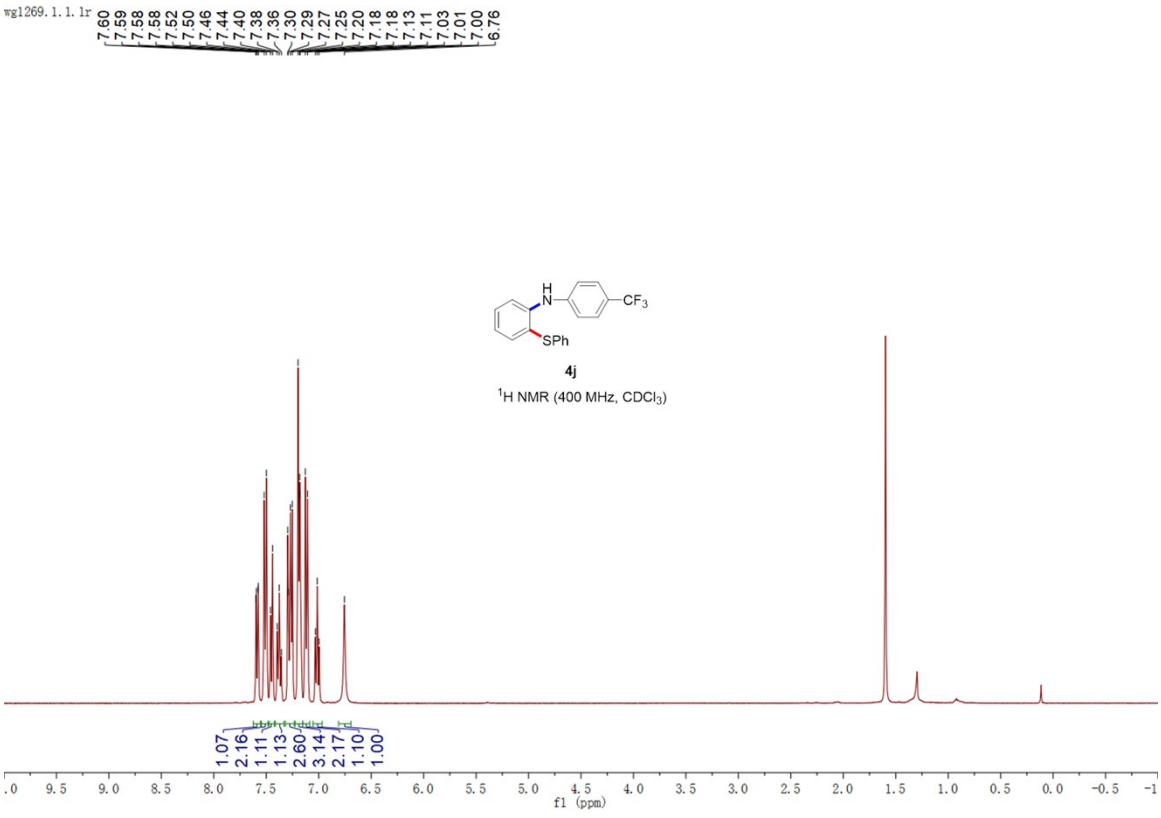
^{1}H NMR (400 MHz, $CDCl_3$)

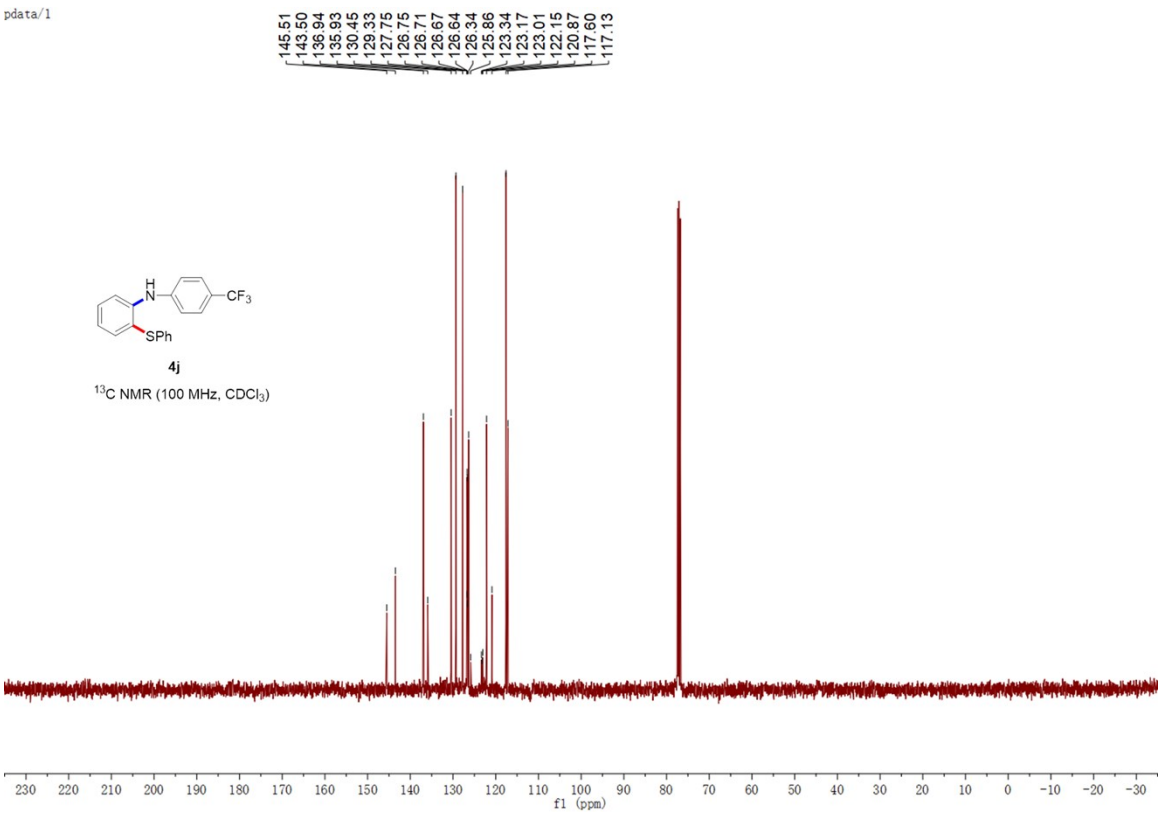



pdata/1
157.87
152.84
146.76
137.63
137.18
136.65
130.95
129.77
129.19
126.87
125.79
123.51
122.99
120.25
119.58
118.34
116.50
113.80
OPh
SPh
4h
13C NMR (100 MHz, CDCl3)
f1 (ppm)


7.90
7.88
7.58
7.57
7.52
7.50
7.41
7.39
7.37
7.28
7.27
7.26
7.25
7.21
7.20
7.18
7.17
7.16
7.07
7.06
7.05
7.04
7.02
6.82
2.56
SPh
4i
1H NMR (400 MHz, CDCl3)
2.01
1.03
1.01
1.10
2.31
2.88
3.05
1.00
2.97
f1 (ppm)


pdata/1
196.47
147.05
142.76
136.66
135.75
130.46
130.28
130.24
129.34
127.98
126.43
122.68
121.88
118.17
116.29
26.25
SPh
4i
13C NMR (100 MHz, CDCl3)
f1 (ppm)


wg1269.1.1.1r
7.60
7.59
7.58
7.58
7.52
7.50
7.46
7.44
7.40
7.38
7.36
7.30
7.29
7.27
7.25
7.20
7.18
7.18
7.13
7.11
7.03
7.01
7.00
6.76
CF3
SPh
4j
1H NMR (400 MHz, CDCl3)
1.07
2.16
1.11
1.13
2.60
3.14
2.17
1.10
1.00
f1 (ppm)


pdata/1
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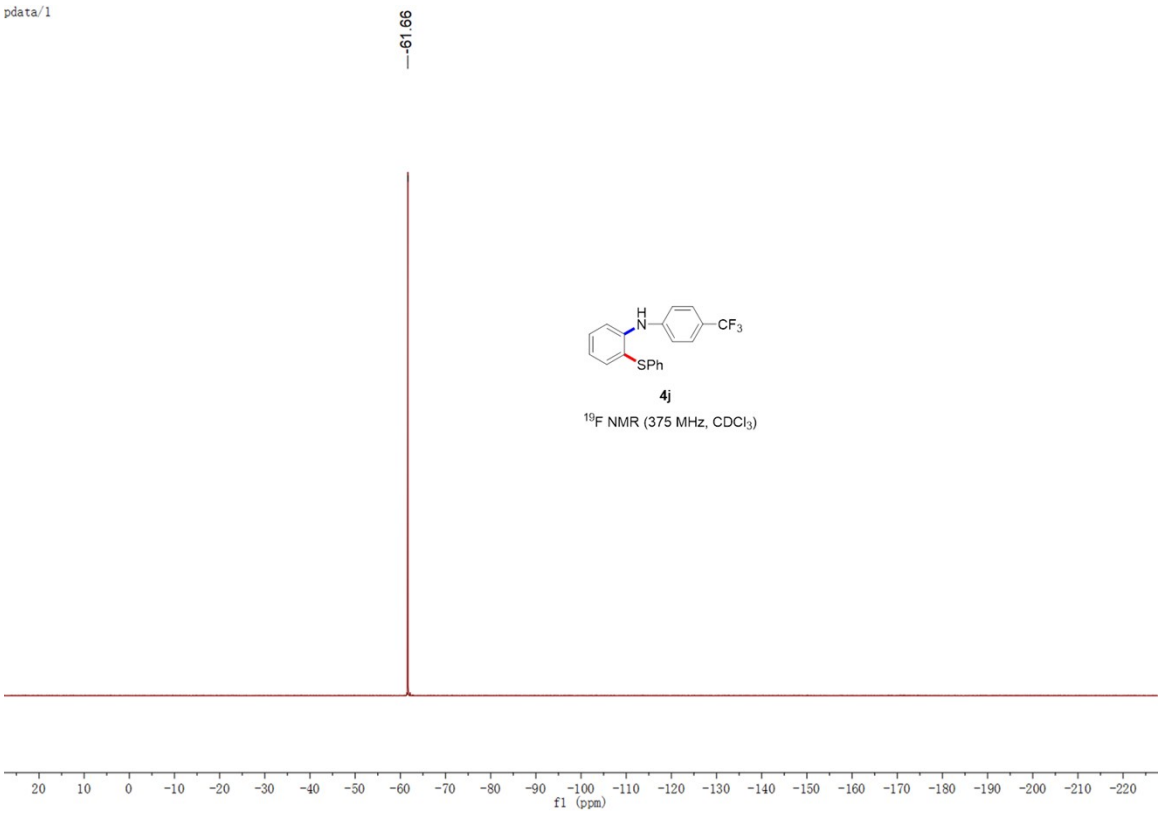
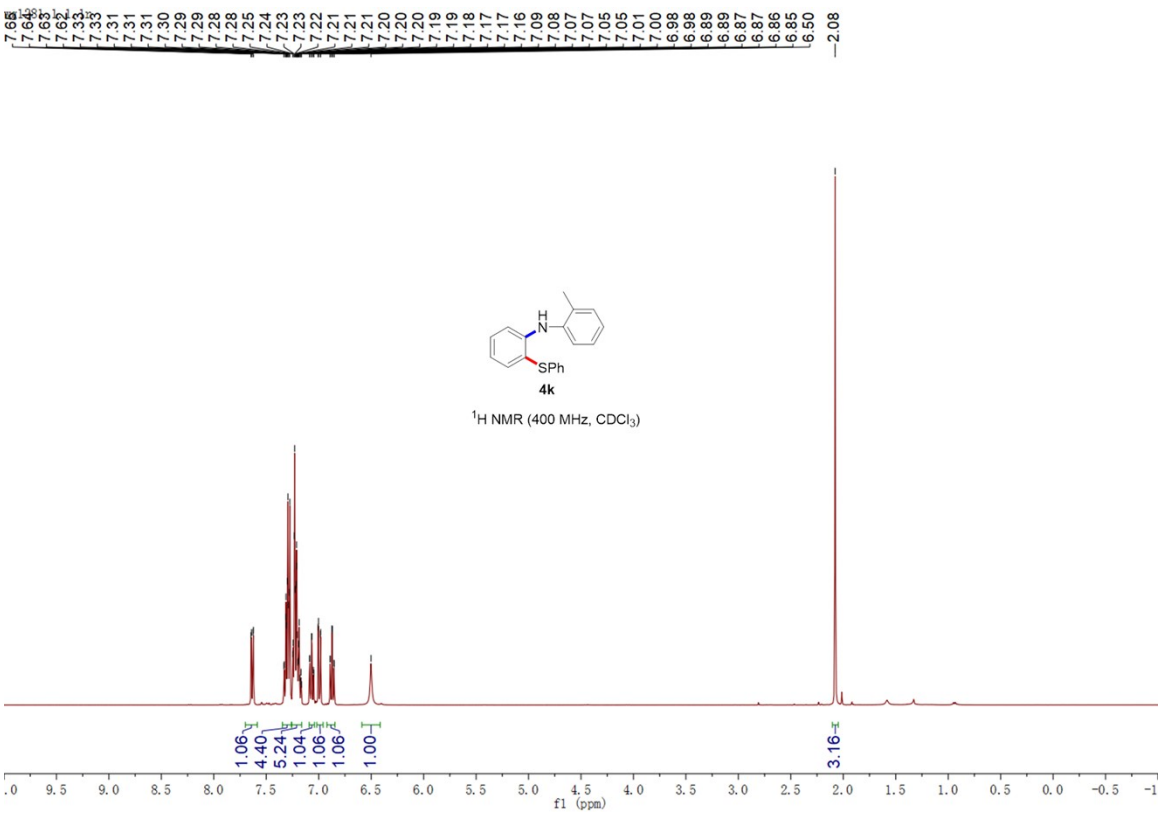
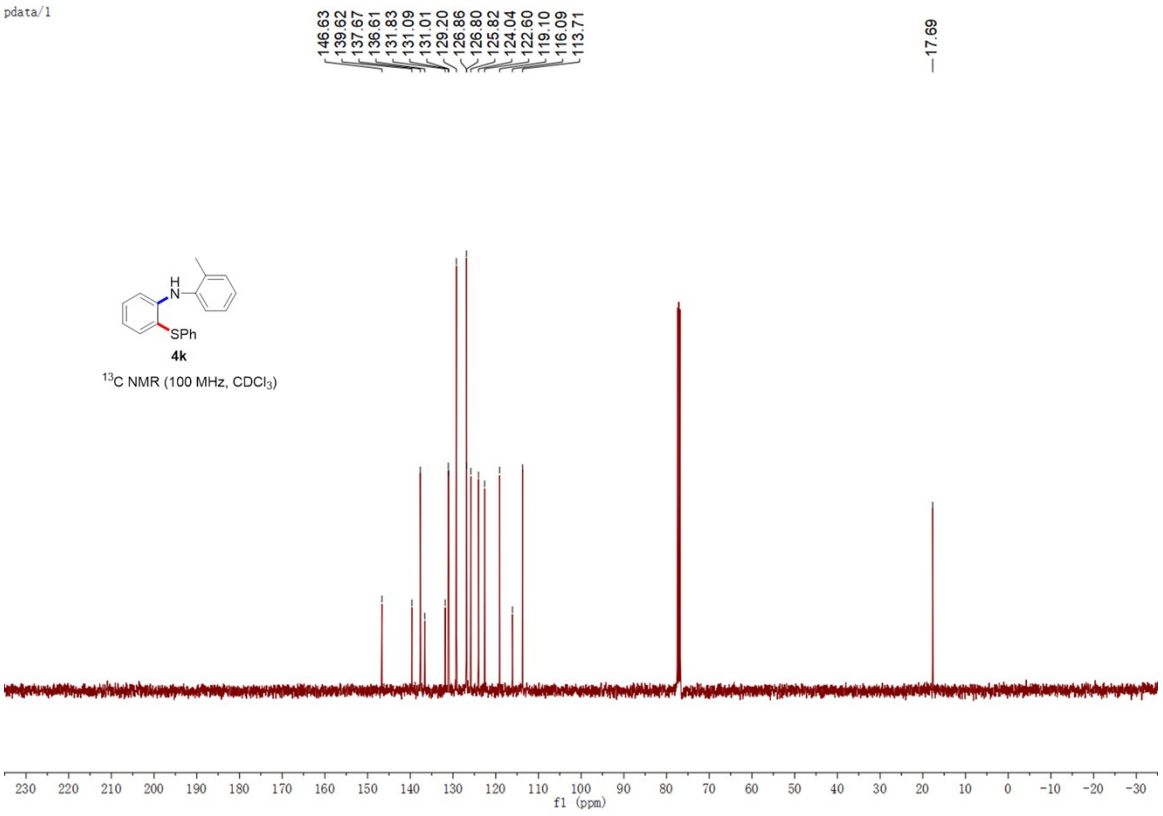
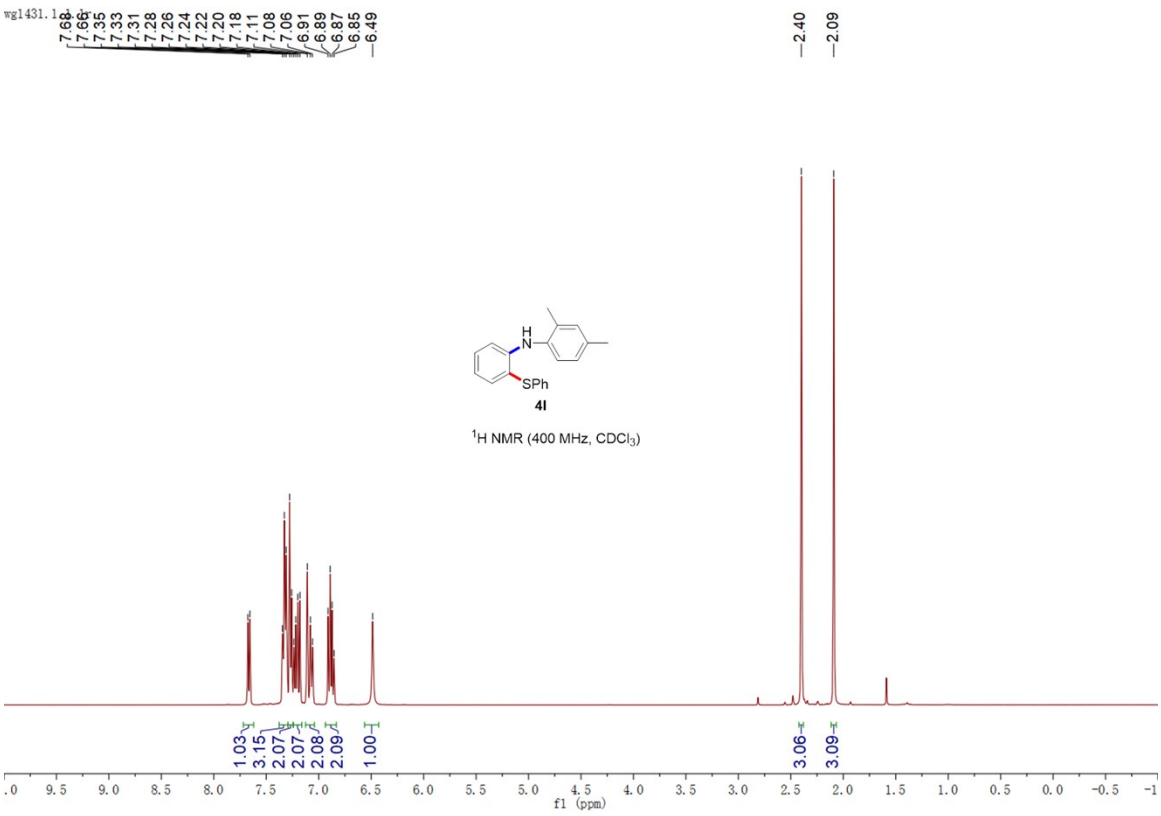
143.50
136.94
135.93
130.45
129.33
127.75
126.75
126.71
126.67
126.64
126.34
125.86
123.34
123.17
123.01
122.15
120.87
117.60
117.13
H
N
CF3
SPh
4j
13C NMR (100 MHz, CDCl3)
f1 (ppm)


pdata/1
-61.66
H
N
CF3
SPh
4j
19F NMR (375 MHz, CDCl3)
f1 (ppm)


7.65
7.64
7.63
7.62
7.33
7.31
7.31
7.30
7.29
7.29
7.28
7.28
7.25
7.24
7.23
7.23
7.22
7.21
7.21
7.21
7.20
7.20
7.20
7.19
7.19
7.18
7.17
7.17
7.16
7.09
7.08
7.07
7.07
7.05
7.05
7.01
7.00
6.98
6.89
6.89
6.87
6.87
6.86
6.85
6.50
2.08
SPh
4k
1H NMR (400 MHz, CDCl3)
1.06
4.40
5.24
1.04
1.06
1.06
1.00
3.16
f1 (ppm)


pdata/1
146.63
139.62
137.67
136.61
131.83
131.09
131.01
129.20
126.86
126.80
125.82
124.04
122.60
119.10
116.09
113.71
17.69
SPh
4k
13C NMR (100 MHz, CDCl3)
f1 (ppm)


wg1431.1.1
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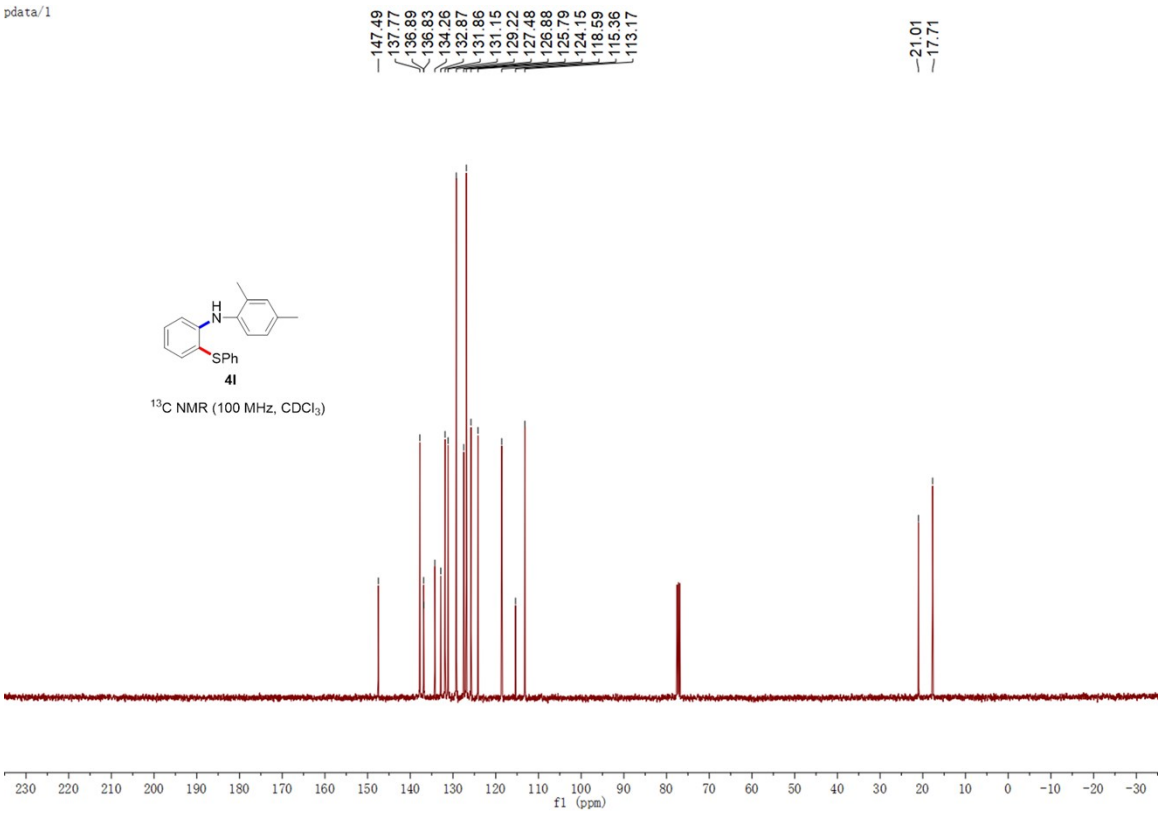
7.66
7.35
7.33
7.31
7.28
7.26
7.24
7.22
7.20
7.18
7.11
7.08
7.06
6.91
6.89
6.87
6.85
6.49
2.40
2.09
SPh
4l
1H NMR (400 MHz, CDCl3)
1.03
3.15
2.07
2.07
2.08
2.09
1.00
3.06
3.09
f1 (ppm)


pdata/1
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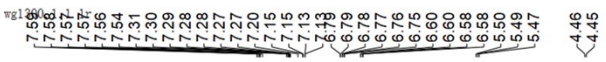
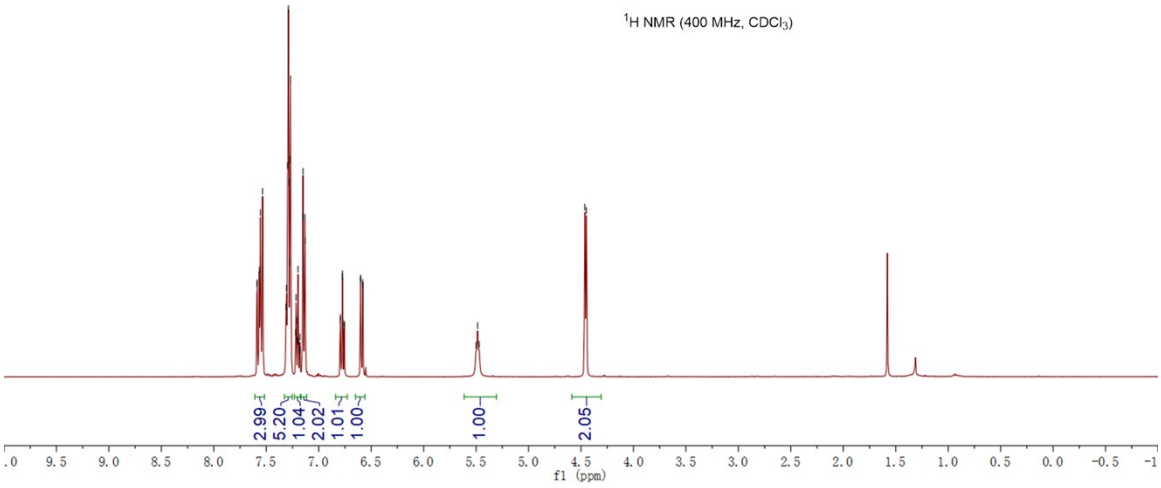
136.89
136.83
134.26
132.87
131.86
131.15
129.22
127.48
126.88
125.79
124.15
118.59
115.36
113.17
21.01
17.71
SPh
4l
13C NMR (100 MHz, CDCl3)
f1 (ppm)

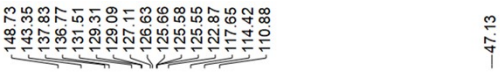


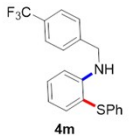
4m

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



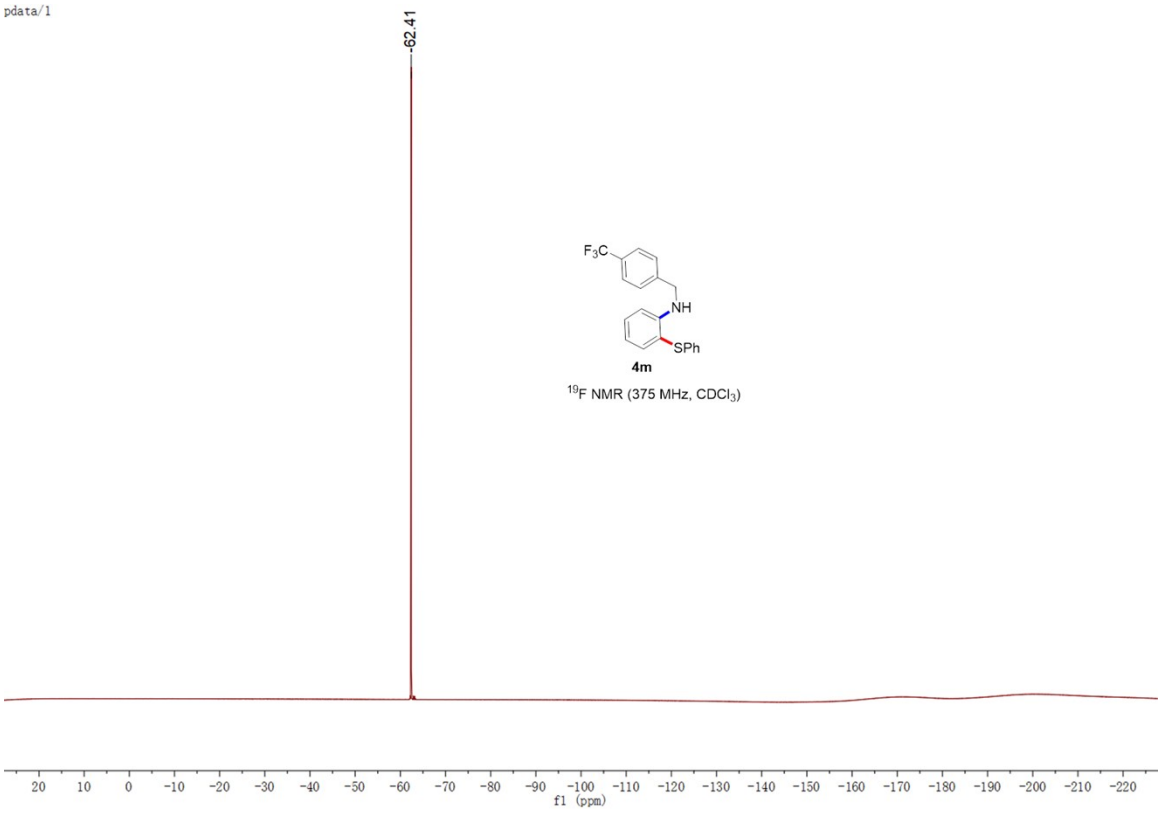
pdata/1





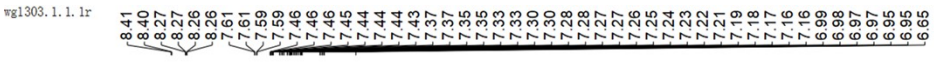
4m

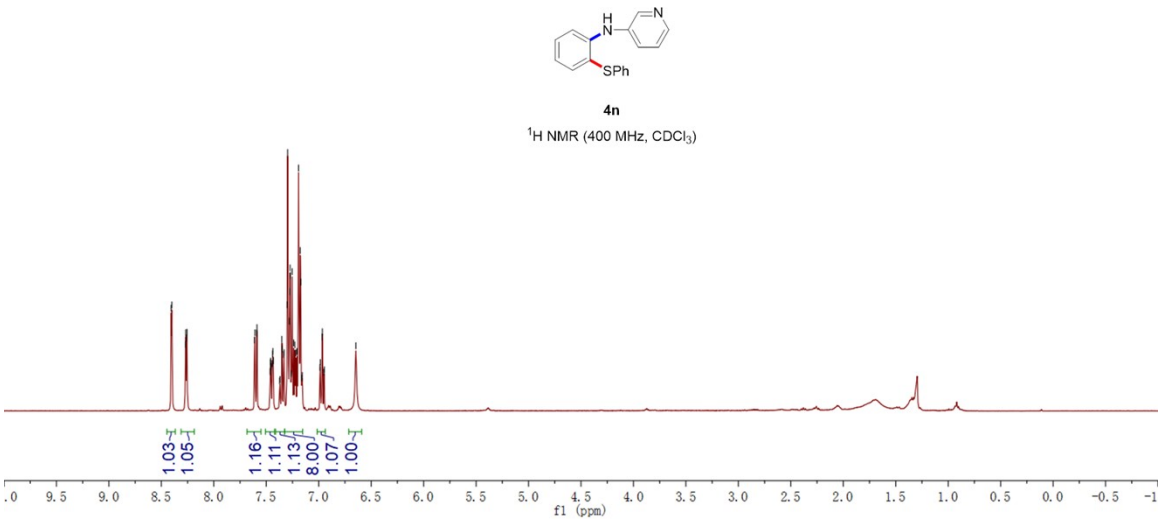
^{13}C NMR (100 MHz, $CDCl_3$)



4m

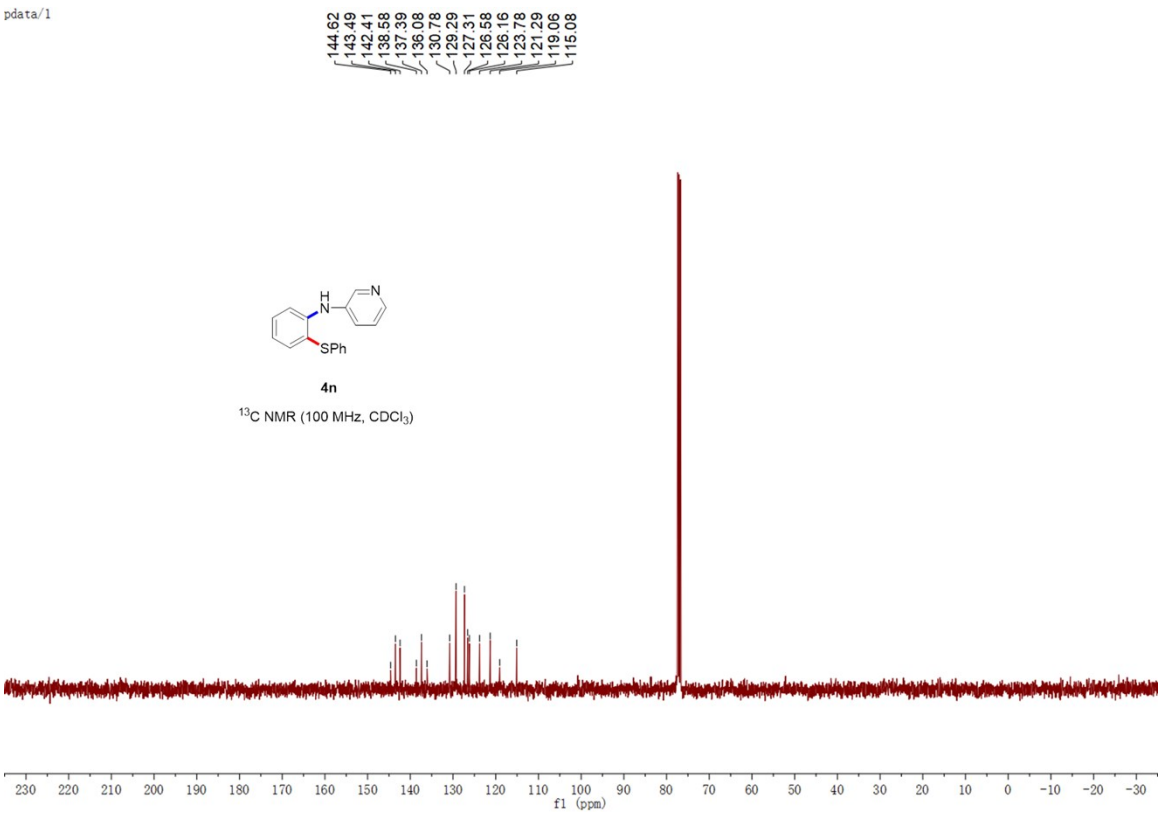
^{19}F NMR (375 MHz, $CDCl_3$)

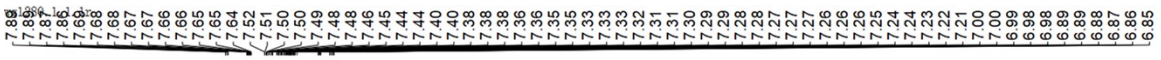




4n

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


pdata/1
144.62
143.49
142.41
138.58
137.39
136.08
130.78
129.29
127.31
126.58
126.16
123.78
121.29
119.06
115.08
H
N
N
SPh
4n
13C NMR (100 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)


7.88
7.88
7.87
7.86
7.69
7.68
7.68
7.67
7.67
7.66
7.66
7.65
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7.64
7.52
7.51
7.50
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7.49
7.48
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7.32
7.31
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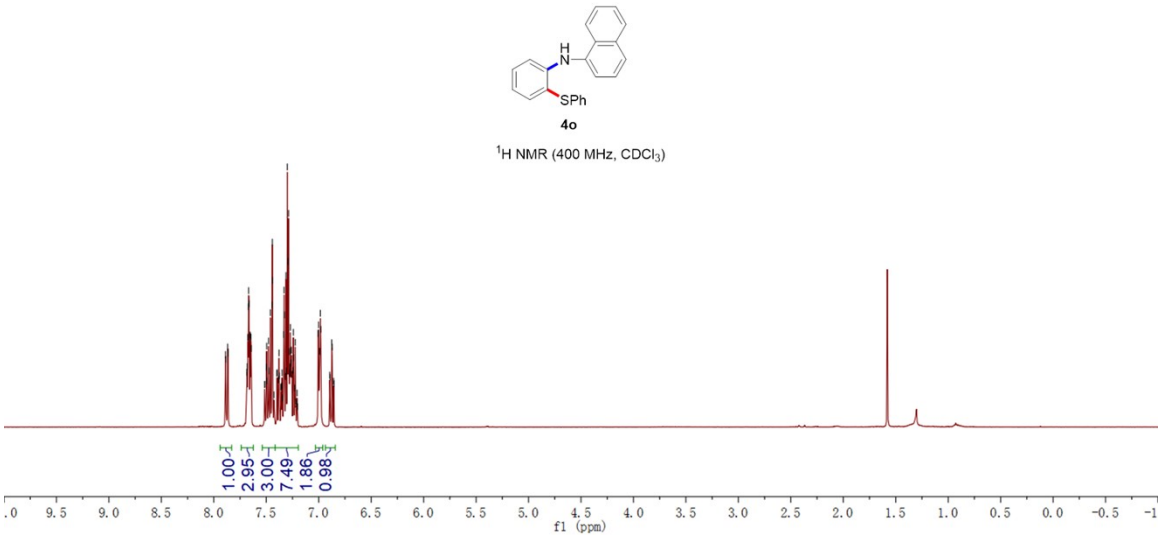
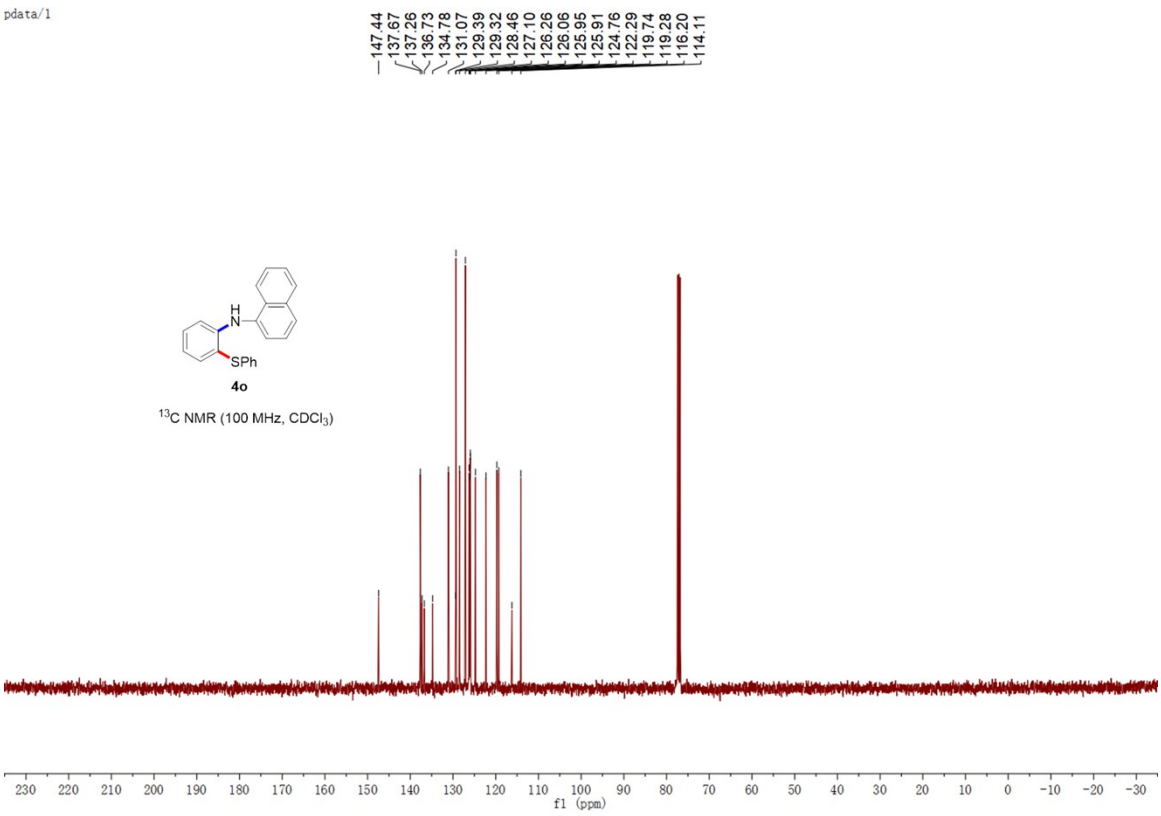
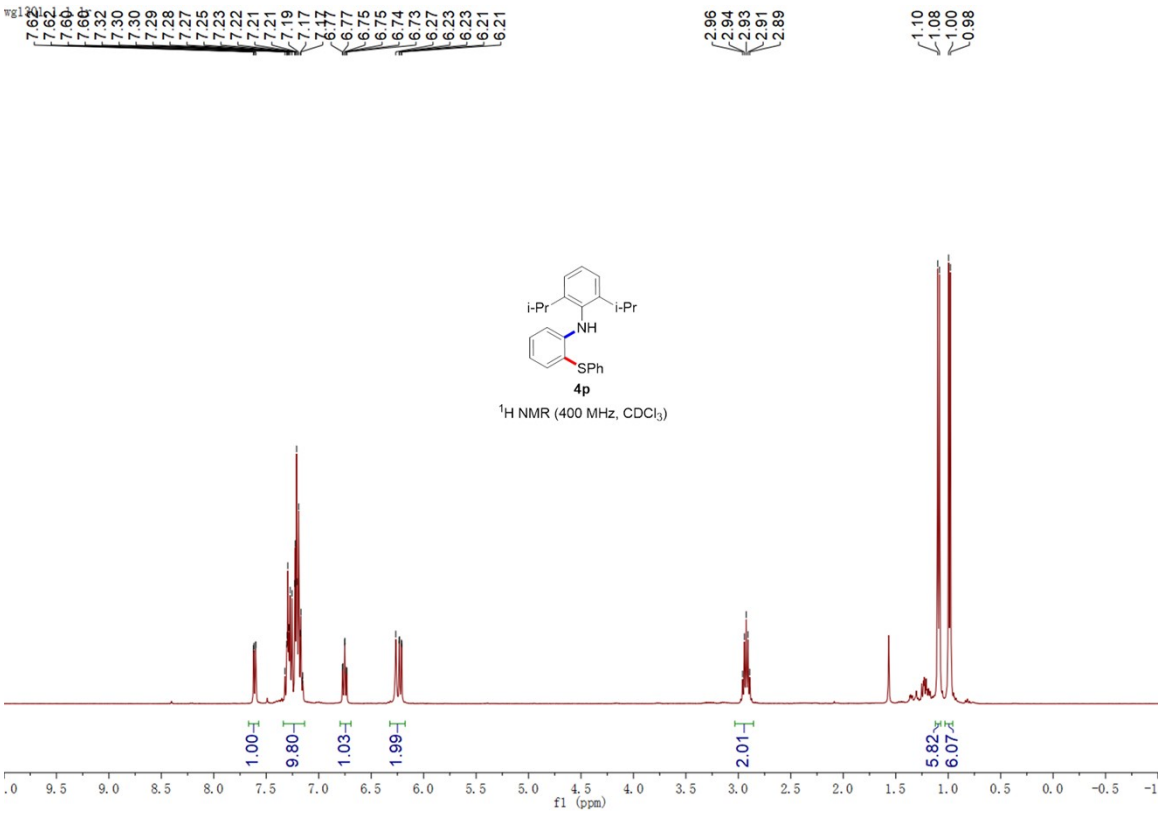
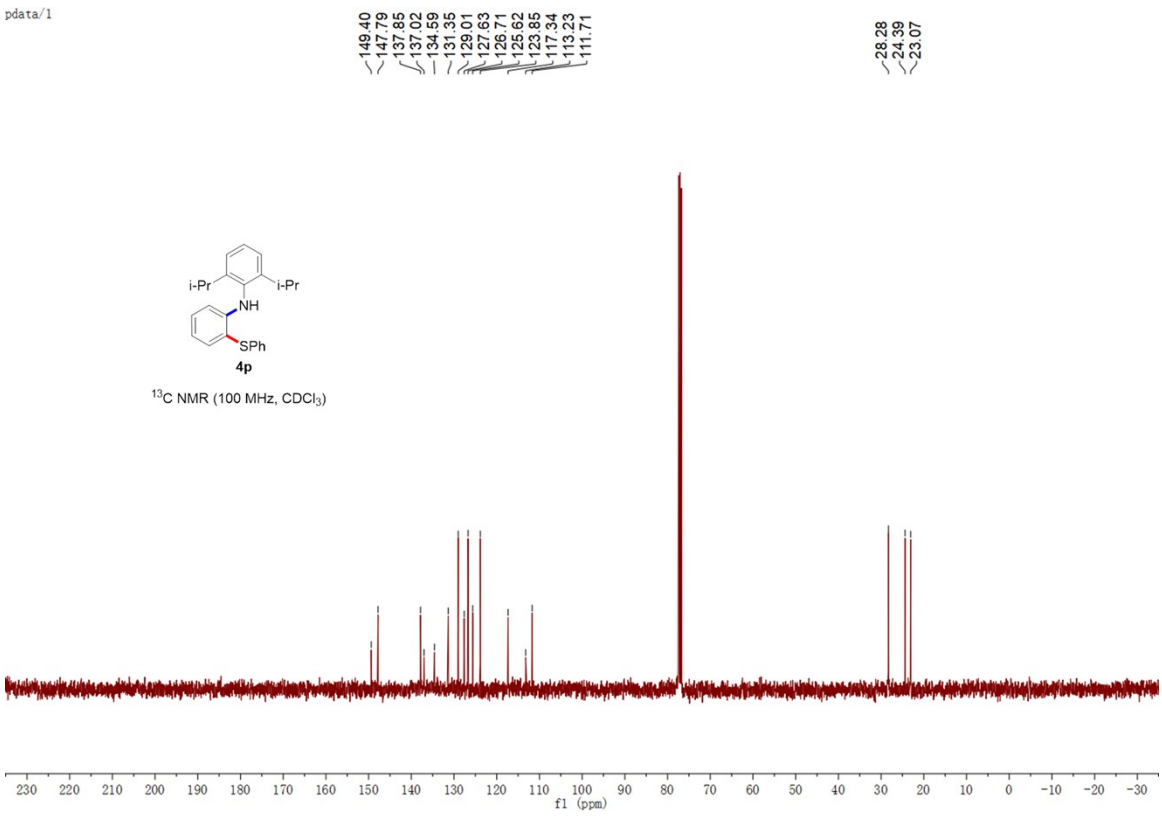
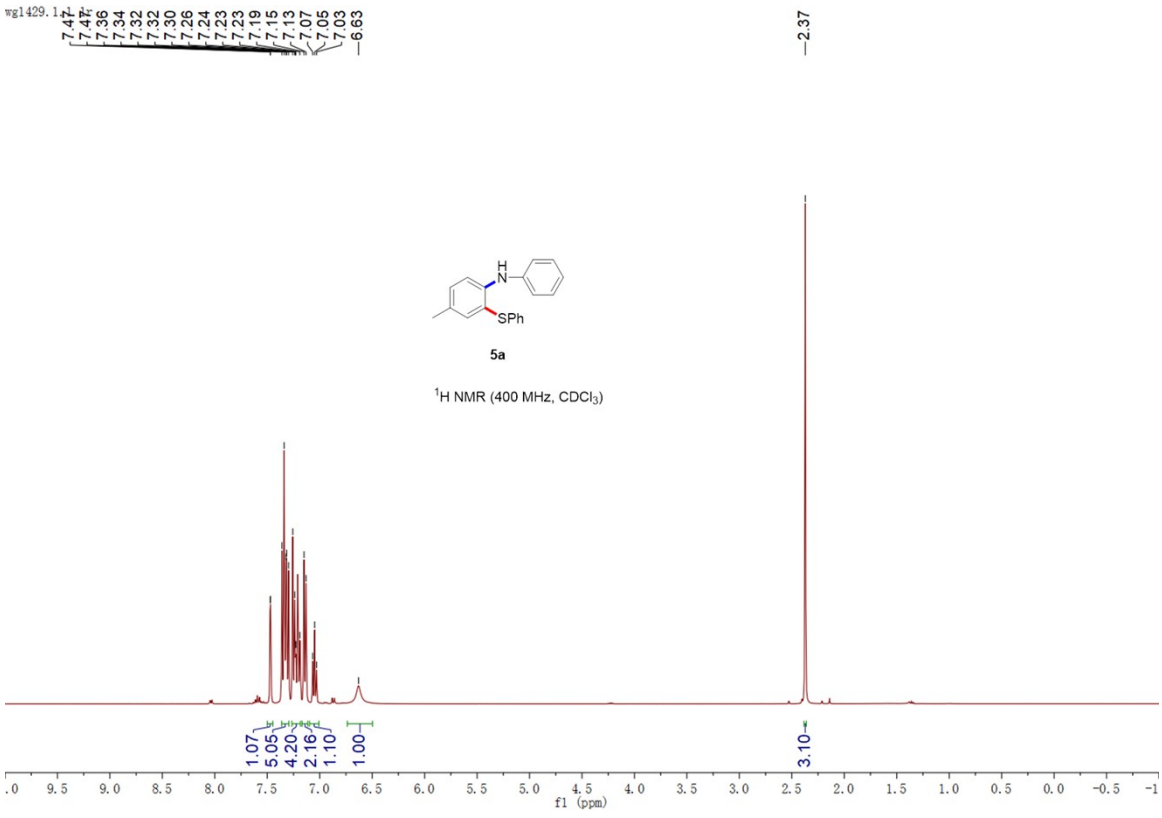
7.30
7.29
7.29
7.28
7.28
7.27
7.27
7.26
7.26
7.25
7.24
7.24
7.23
7.22
7.21
7.00
7.00
6.99
6.98
6.98
6.89
6.89
6.88
6.87
6.86
6.85


H
N
SPh
4o
1H NMR (400 MHz, CDCl3)
1.00
2.95
3.00
7.49
1.86
0.98
.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


pdata/1
147.44
137.67
137.26
136.73
134.78
131.07
129.39
129.32
128.46
127.10
126.26
126.06
125.95
125.91
124.76
122.29
119.74
119.28
116.20
114.11
SPh
4o
13C NMR (100 MHz, CDCl3)
f1 (ppm)


7.62
7.62
7.60
7.60
7.32
7.30
7.30
7.29
7.28
7.27
7.25
7.23
7.22
7.21
7.21
7.19
7.17
7.17
6.77
6.77
6.75
6.75
6.74
6.73
6.27
6.23
6.23
6.21
6.21
2.96
2.94
2.93
2.91
2.89
1.10
1.08
1.00
0.98
i-Pr
i-Pr
NH
SPh
4p
1H NMR (400 MHz, CDCl3)
1.00
9.80
1.03
1.99
2.01
5.82
6.07
f1 (ppm)


pdata/1
149.40
147.79
137.85
137.02
134.59
131.35
129.01
127.63
126.71
125.62
123.85
117.34
113.23
111.71
28.28
24.39
23.07
i-Pr
i-Pr
NH
SPh
4p
13C NMR (100 MHz, CDCl3)
f1 (ppm)


wg1429.1.1
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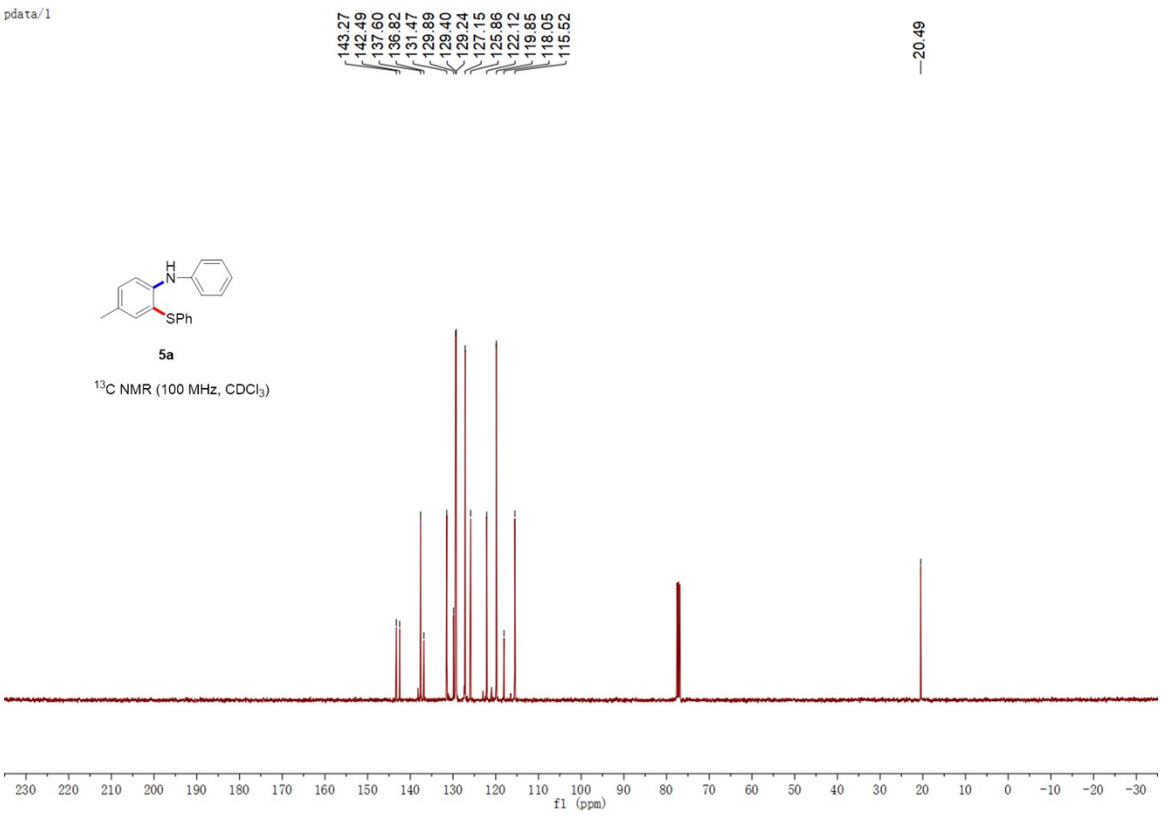
7.47
7.36
7.34
7.32
7.32
7.30
7.26
7.24
7.23
7.23
7.19
7.15
7.13
7.07
7.05
7.03
6.63
2.37
H
N
SPh
5a
1H NMR (400 MHz, CDCl3)
1.07
5.05
4.20
2.16
1.10
1.00
3.10
f1 (ppm)


pdata/1
143.27
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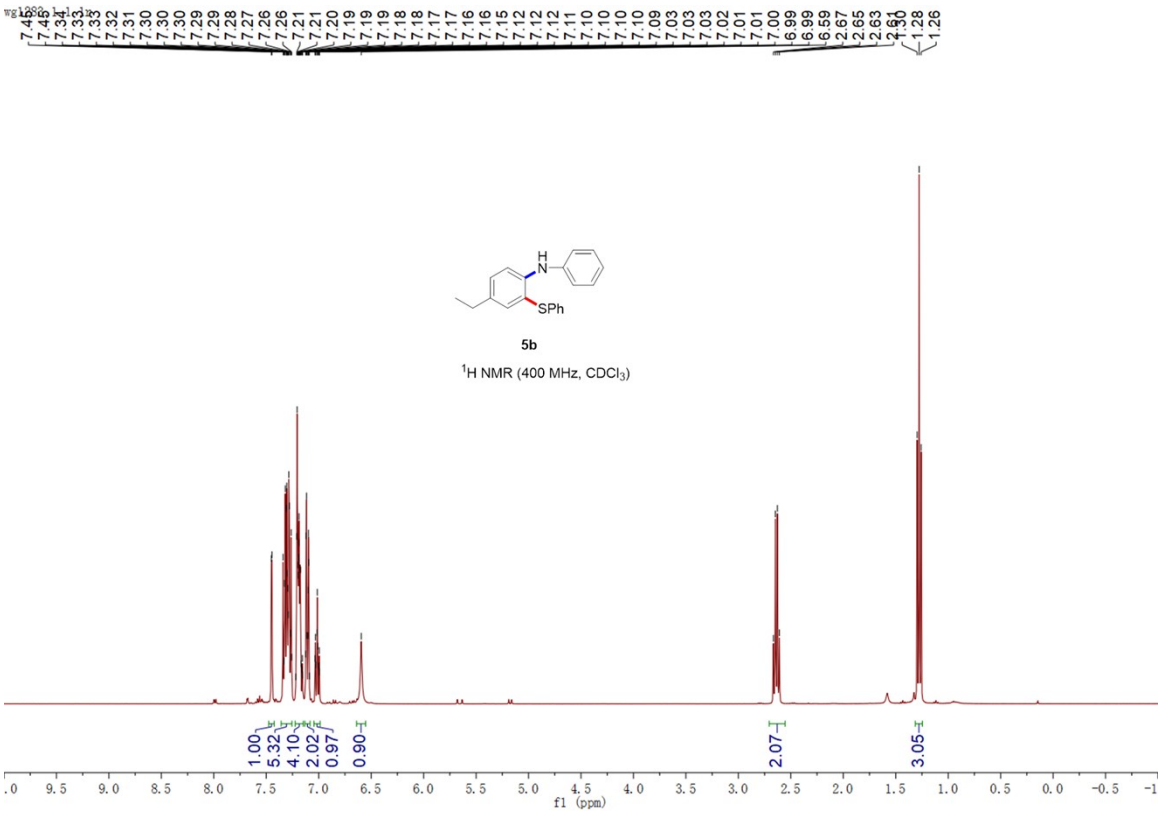
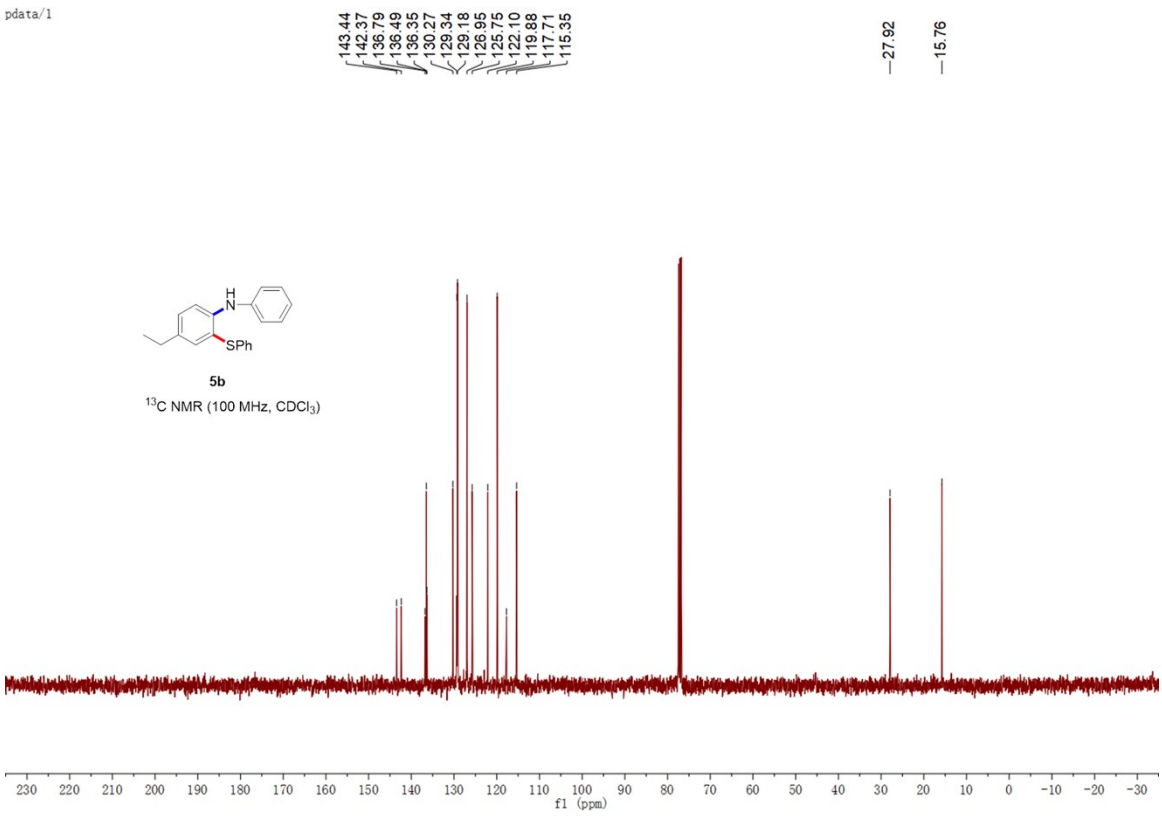
137.60
136.82
131.47
129.89
129.40
129.24
127.15
125.86
122.12
119.85
118.05
115.52
20.49
SPh
5a
13C NMR (100 MHz, CDCl3)
f1 (ppm)


SPh
5b
1H NMR (400 MHz, CDCl3)
1.00
5.32
4.10
2.02
0.97
0.90
2.07
3.05
f1 (ppm)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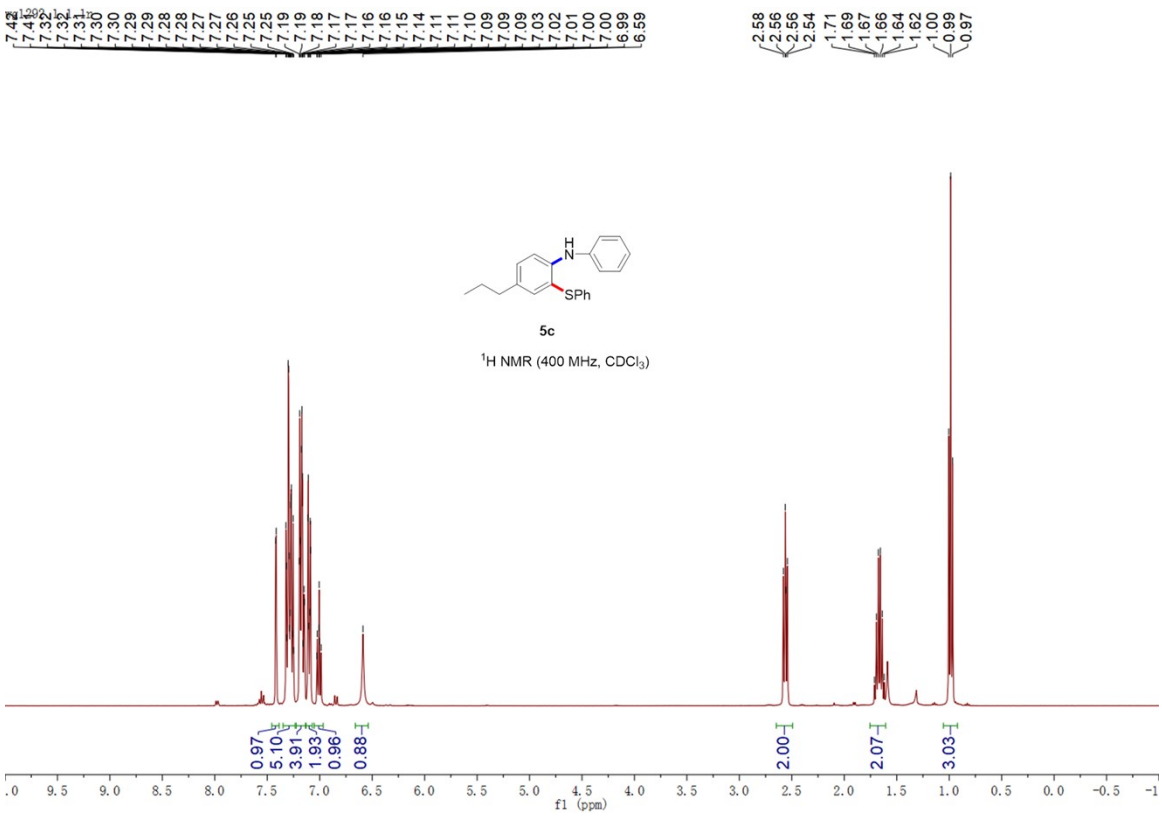
136.79
136.49
136.35
130.27
129.34
129.18
128.95
125.75
122.10
119.88
117.71
115.35
27.92
15.76
SPh
5b
13C NMR (100 MHz, CDCl3)
f1 (ppm)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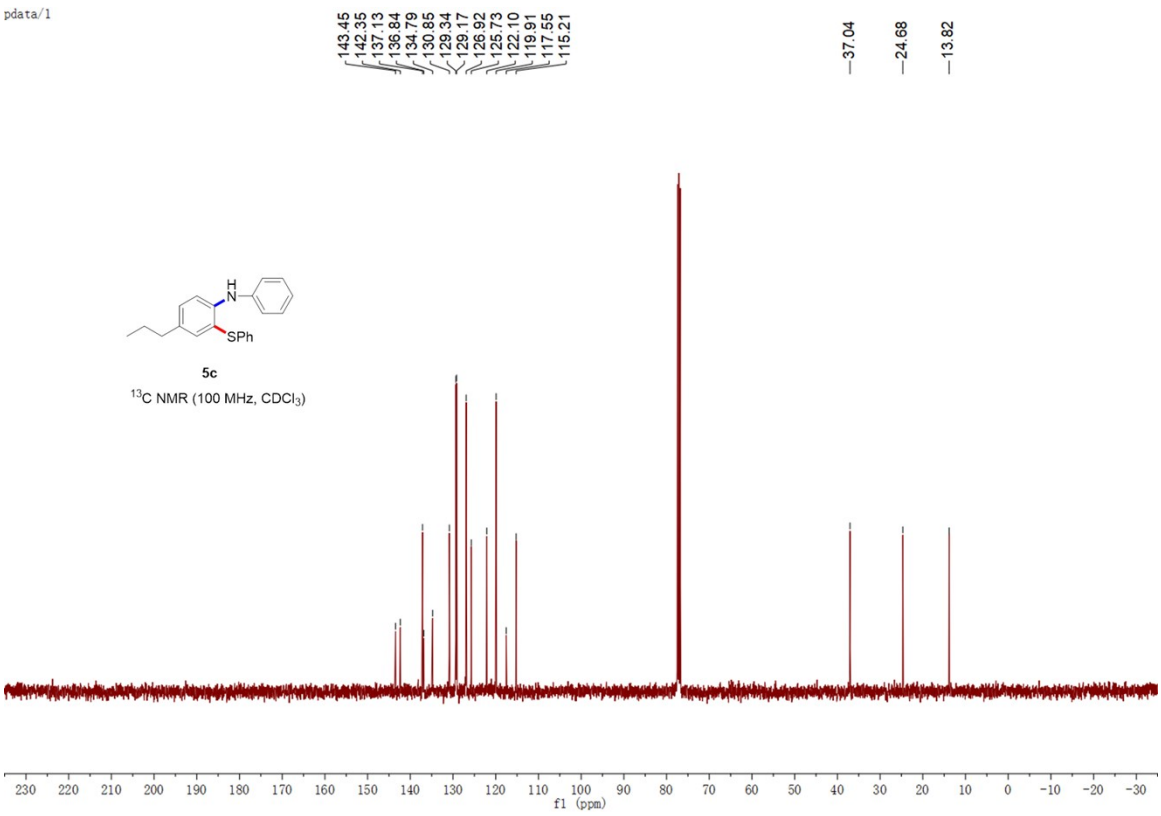
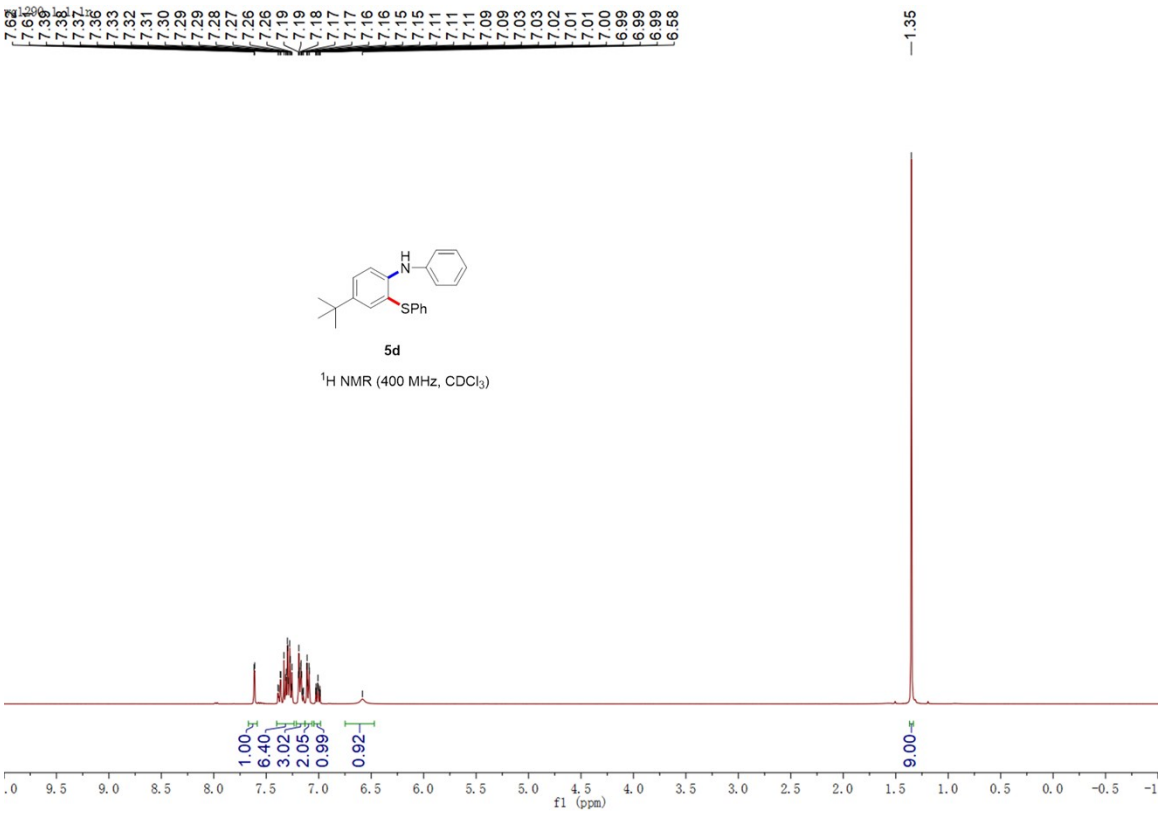
7.41
7.32
7.31
7.30
7.30
7.29
7.29
7.28
7.28
7.27
7.27
7.26
7.25
7.25
7.19
7.19
7.18
7.17
7.17
7.16
7.16
7.15
7.14
7.11
7.11
7.10
7.09
7.09
7.09
7.03
7.02
7.01
7.00
7.00
6.99
6.59
2.58
2.56
2.56
2.54
1.71
1.69
1.67
1.66
1.64
1.62
1.00
0.99
0.97
SPh
5c
1H NMR (400 MHz, CDCl3)
0.97
5.10
3.91
1.93
0.96
0.88
2.00
2.07
3.03
f1 (ppm)


pdata/1
143.45
142.35
137.13
136.84
134.79
130.85
129.34
129.17
126.92
125.73
122.10
119.91
117.55
115.21
37.04
24.68
13.82
H
N
SPh
5c
13C NMR (100 MHz, CDCl3)
f1 (ppm)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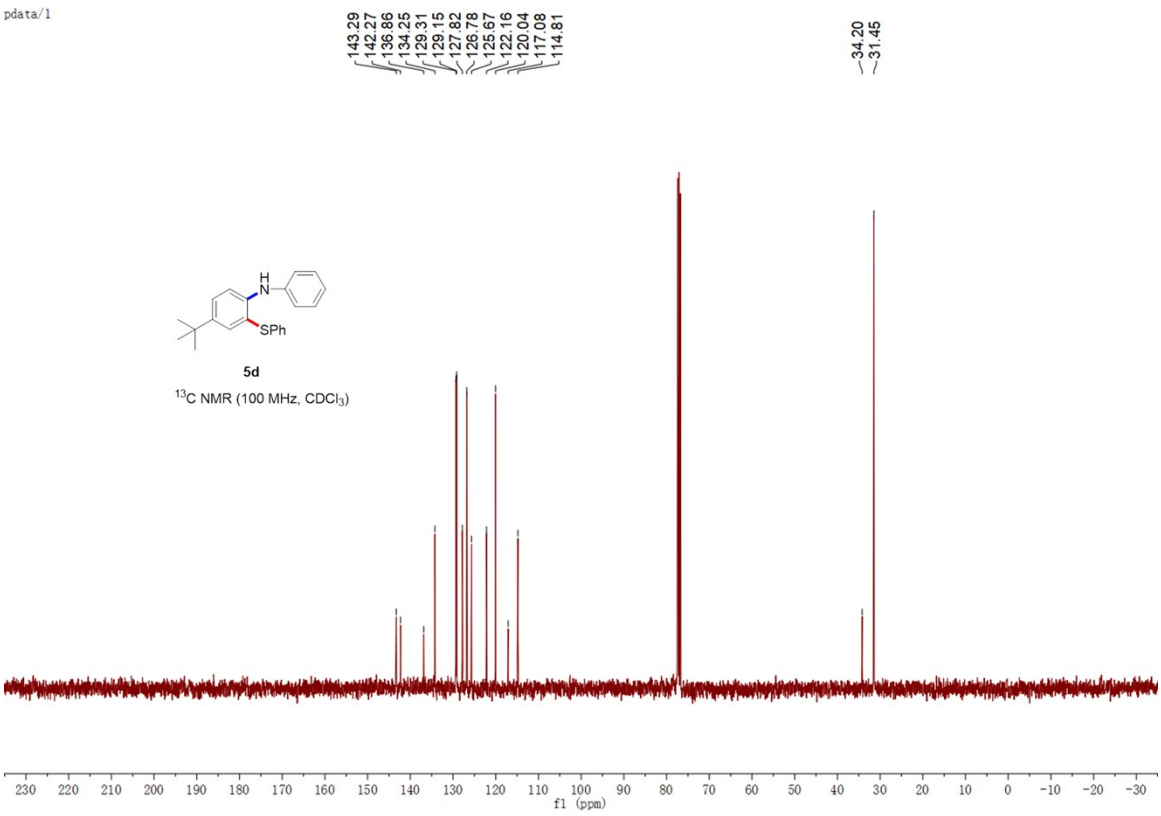
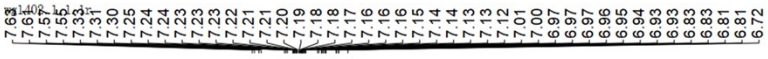
7.61
7.38
7.37
7.36
7.33
7.32
7.31
7.30
7.29
7.29
7.28
7.27
7.26
7.26
7.19
7.18
7.17
7.17
7.16
7.16
7.15
7.15
7.11
7.11
7.09
7.09
7.03
7.03
7.02
7.01
7.01
7.00
6.99
6.99
6.99
6.58
1.35
H
N
SPh
5d
1H NMR (400 MHz, CDCl3)
1.00
6.40
3.02
2.05
0.99
0.92
9.00
f1 (ppm)


pdata/1
143.29
142.27
136.86
134.25
129.31
129.15
127.82
126.78
125.67
122.16
120.04
117.08
114.81
34.20
31.45
SPh
5d
13C NMR (100 MHz, CDCl3)
f1 (ppm)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7.61
7.55
7.33
7.31
7.30
7.25
7.24
7.24
7.23
7.23
7.23
7.22
7.21
7.21
7.20
7.19
7.18
7.18
7.17
7.16
7.16
7.16
7.15
7.14
7.14
7.13
7.13
7.12
7.01
7.00
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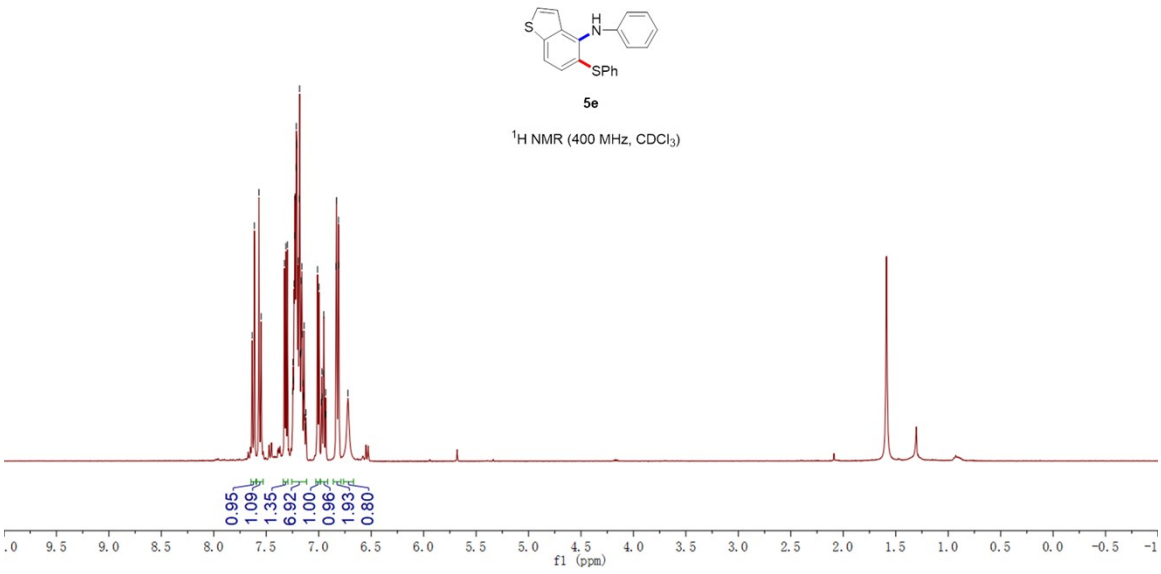
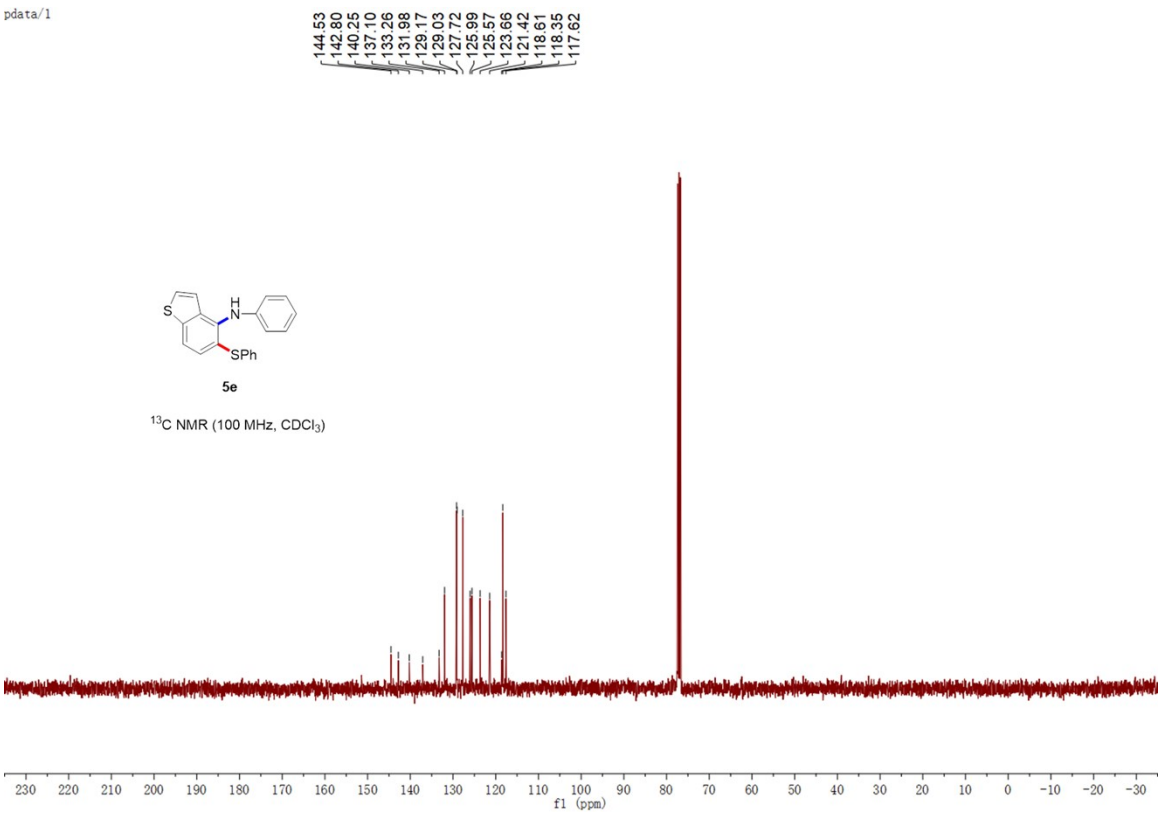
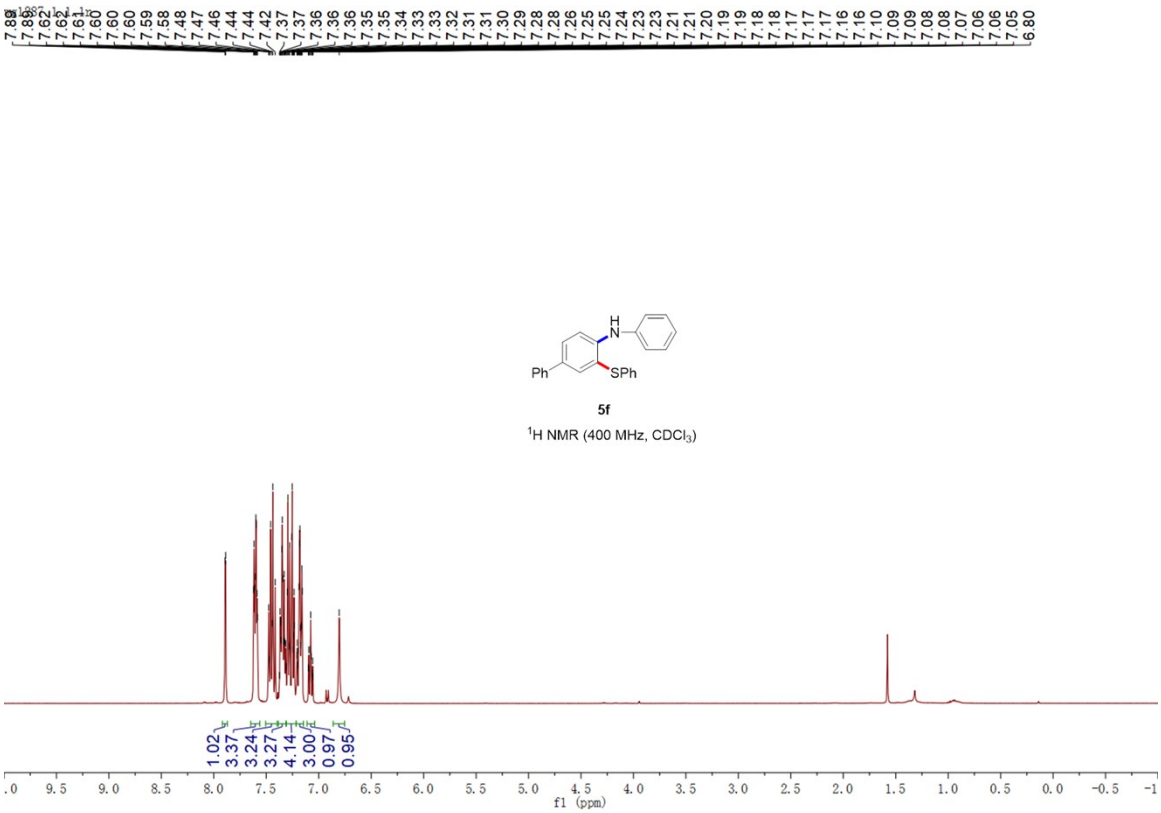
6.96
6.95
6.94
6.93
6.93
6.83
6.81
6.81
6.72

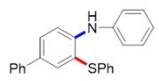

SPh
5e
1H NMR (400 MHz, CDCl3)
0.95
1.09
1.35
6.92
1.00
0.96
1.93
0.80
f1 (ppm)


pdata/1
144.53
142.80
140.25
137.10
133.26
131.98
128.17
129.03
127.72
125.99
125.57
123.66
121.42
118.61
118.35
117.62
S
H
N
SPh
5e
13C NMR (100 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)


7.88
7.86
7.62
7.62
7.61
7.60
7.60
7.60
7.59
7.58
7.48
7.47
7.46
7.44
7.44
7.42
7.37
7.37
7.36
7.36
7.36
7.35
7.35
7.34
7.33
7.33
7.32
7.31
7.31
7.30
7.29
7.28
7.28
7.26
7.25
7.24
7.23
7.23
7.21
7.21
7.20
7.19
7.19
7.18
7.18
7.17
7.17
7.17
7.16
7.16
7.10
7.09
7.09
7.08
7.08
7.07
7.06
7.06
7.05
6.80
H
N
Ph
SPh
5f
1H NMR (400 MHz, CDCl3)
1.02
3.37
3.24
3.27
4.14
3.00
0.97
0.95
.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

pdata/1

145.17
141.57
140.07
136.44
135.91
132.88
129.47
129.41
129.28
128.90
127.01
126.84
126.42
125.95
122.93
120.92
117.66
114.67



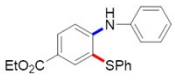
5f

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

wgl448.1.1.1r

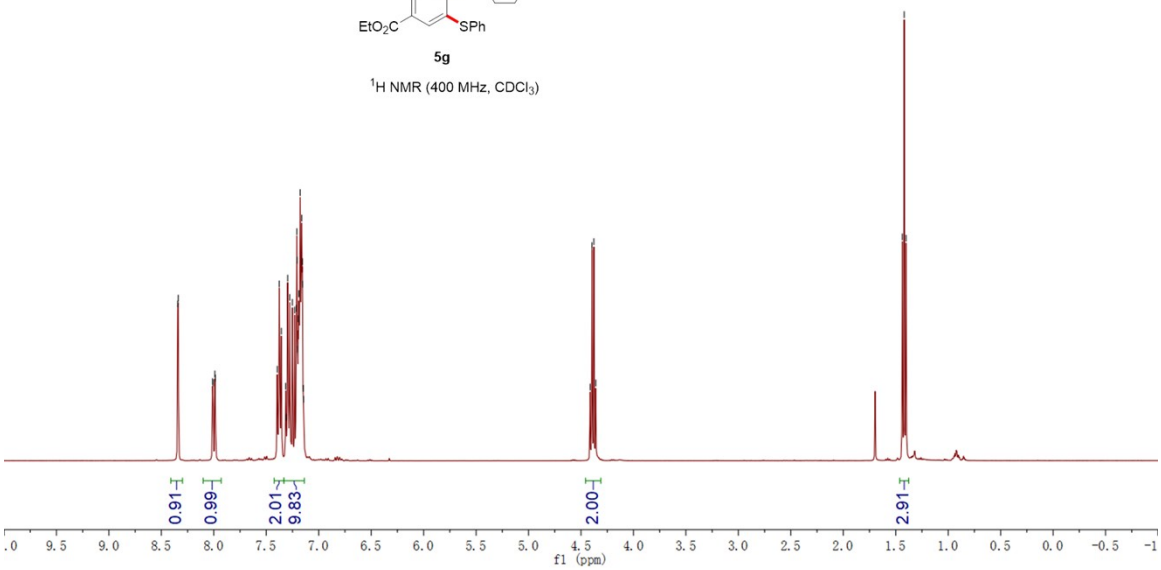
8.34
8.34
8.01
8.01
7.99
7.98
7.40
7.38
7.36
7.31
7.31
7.30
7.28
7.25
7.23
7.21
7.21
7.21
7.20
7.20
7.19
7.19
7.18
7.16
7.16
7.15
7.15
7.14
4.41
4.40
4.38
4.36

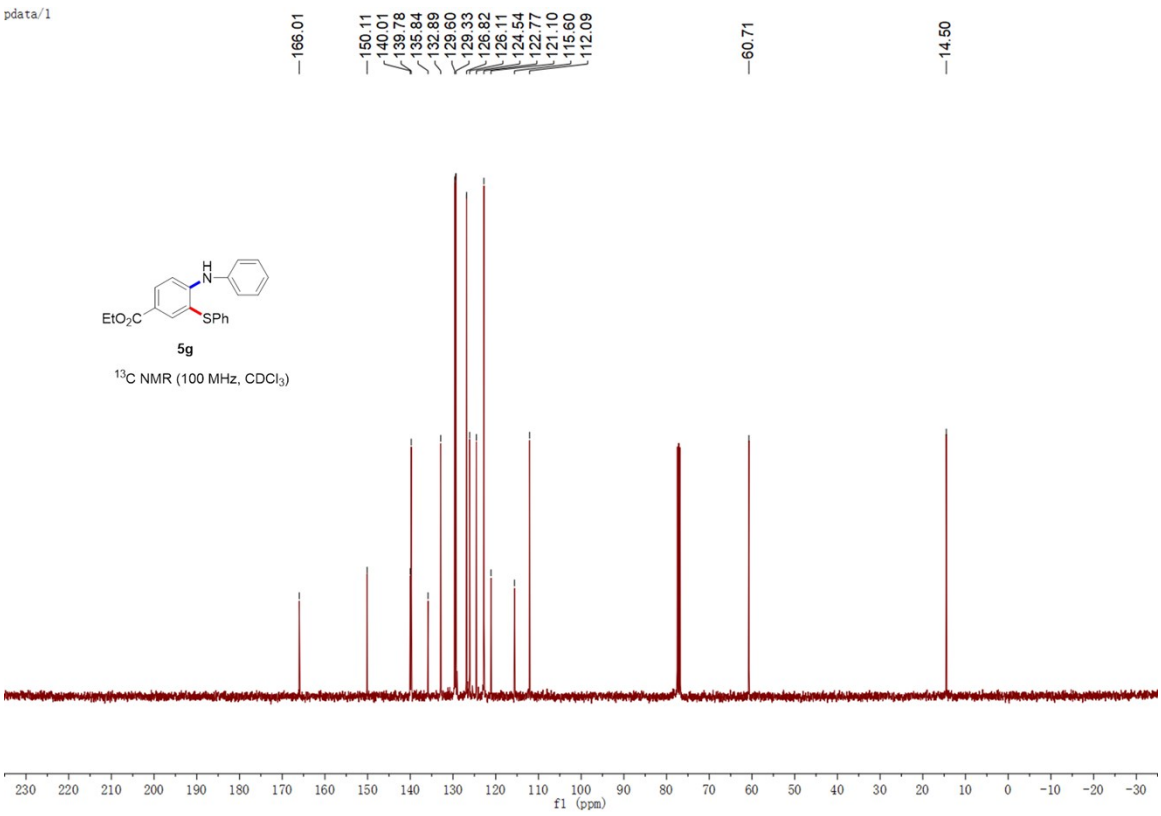
1.44
1.42
1.40

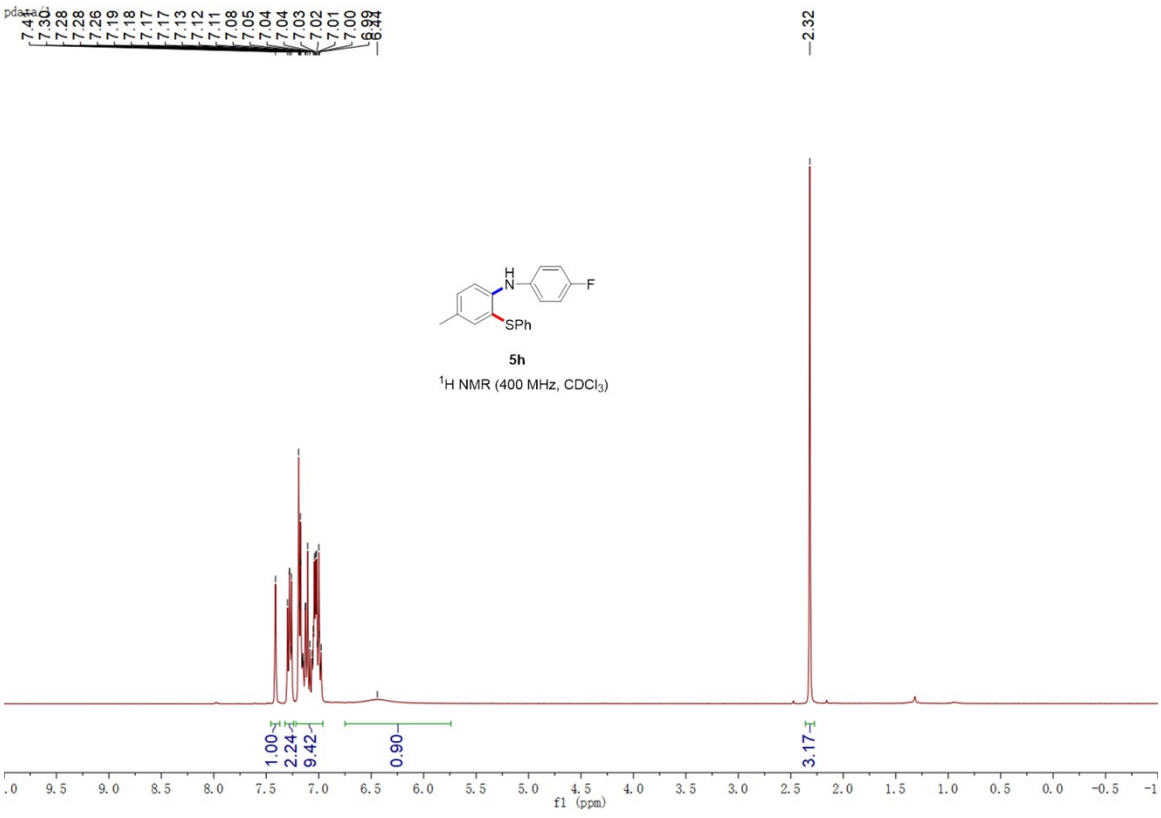


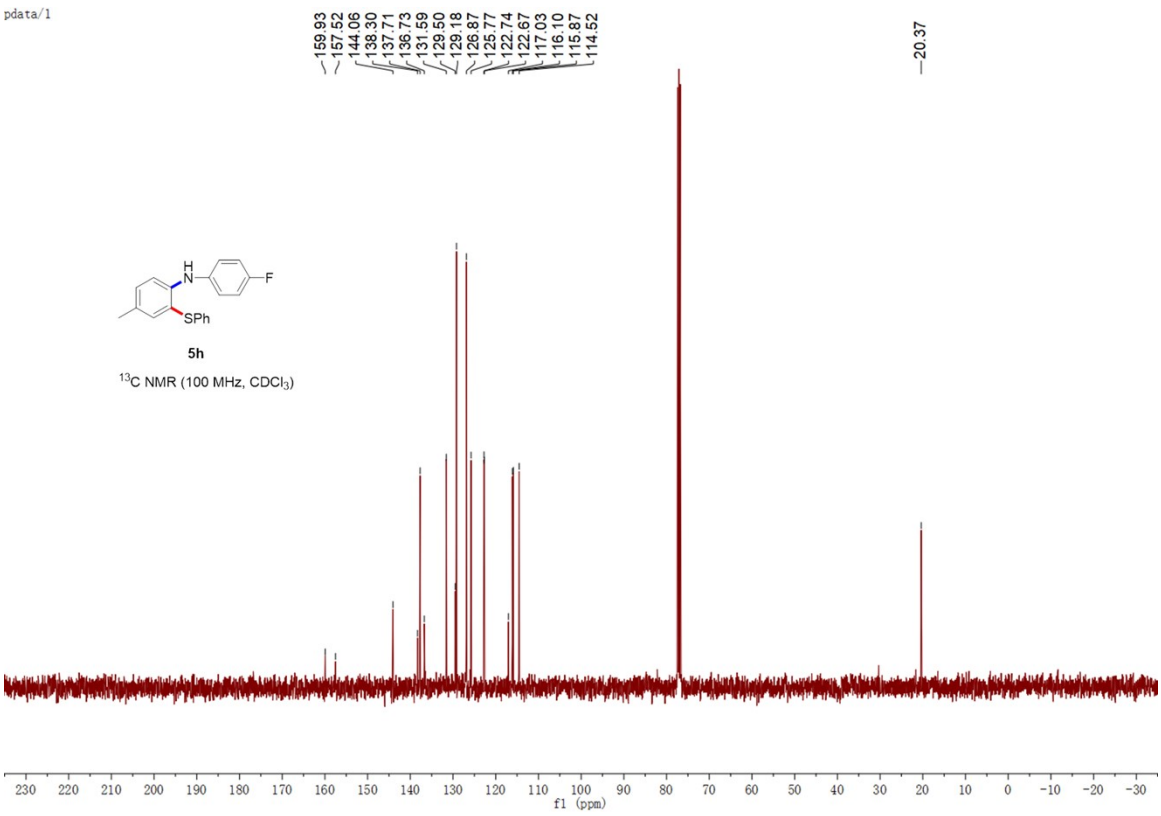
5g

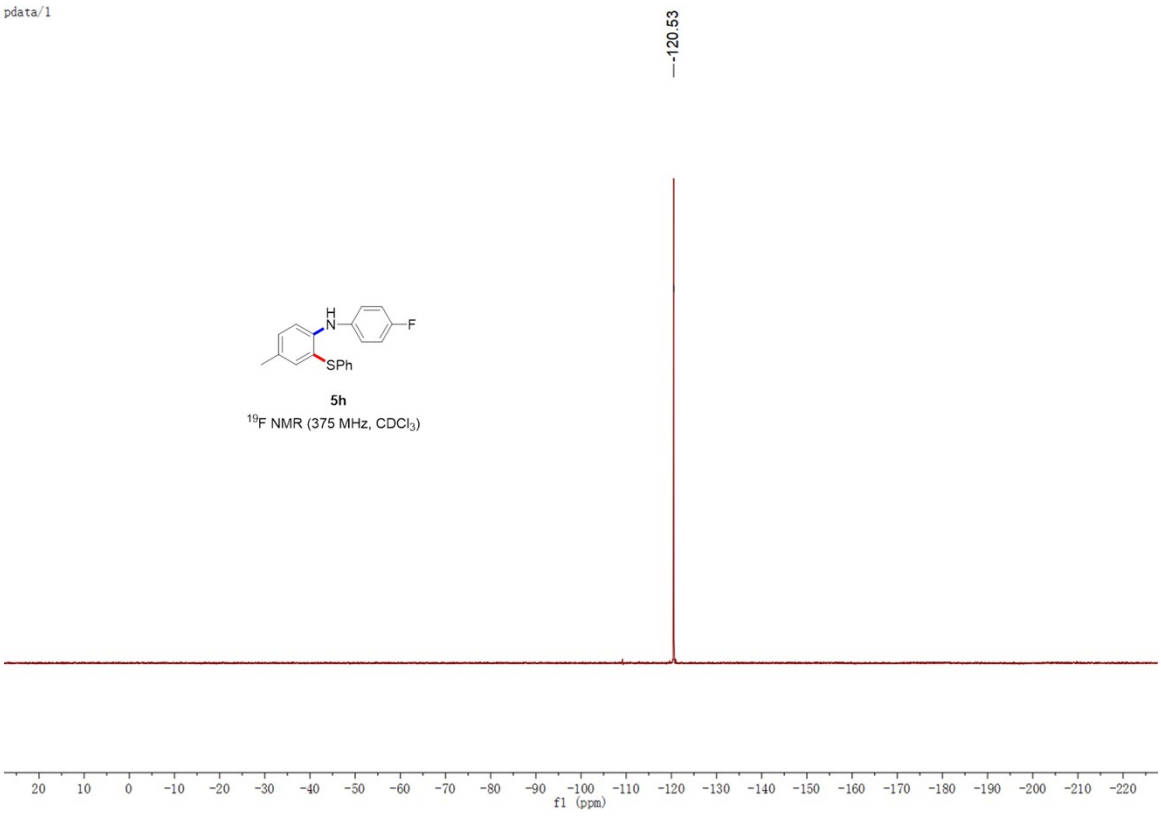
^{1}H NMR (400 MHz, $CDCl_3$)

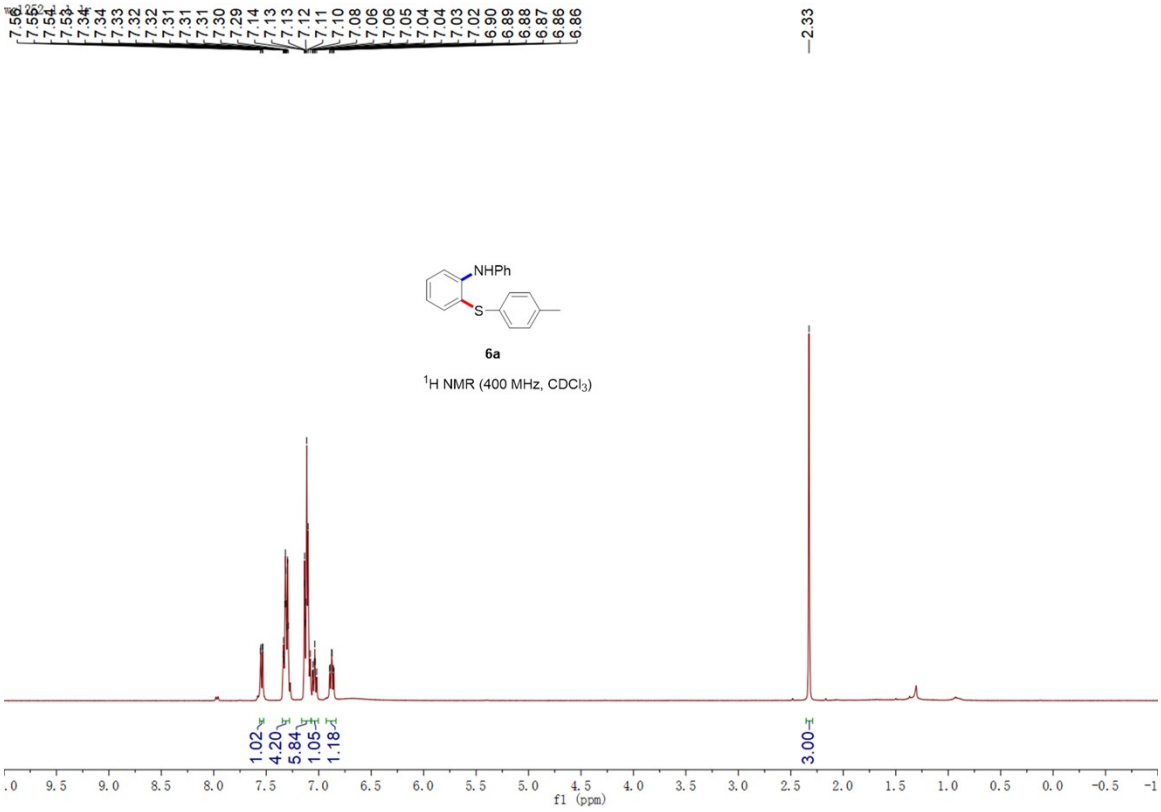



pdata/1
166.01
150.11
140.01
139.78
135.84
132.89
129.60
129.33
126.82
126.11
124.54
122.77
121.10
115.60
112.09
60.71
14.50
EtO2C
SPh
5g
13C NMR (100 MHz, CDCl3)
f1 (ppm)


pdata/1
2.32
F
SPh
5h
1H NMR (400 MHz, CDCl3)
1.00
2.24
9.42
0.90
3.17
f1 (ppm)


pdata/1
159.93
157.52
144.06
138.30
137.71
136.73
131.59
129.50
129.18
126.87
125.77
122.74
122.67
117.03
116.10
115.87
114.52
20.37
F
SPh
5h
13C NMR (100 MHz, CDCl3)
f1 (ppm)


pdata/1
-120.53
F
SPh
5h
19F NMR (375 MHz, CDCl3)
f1 (ppm)


7.56
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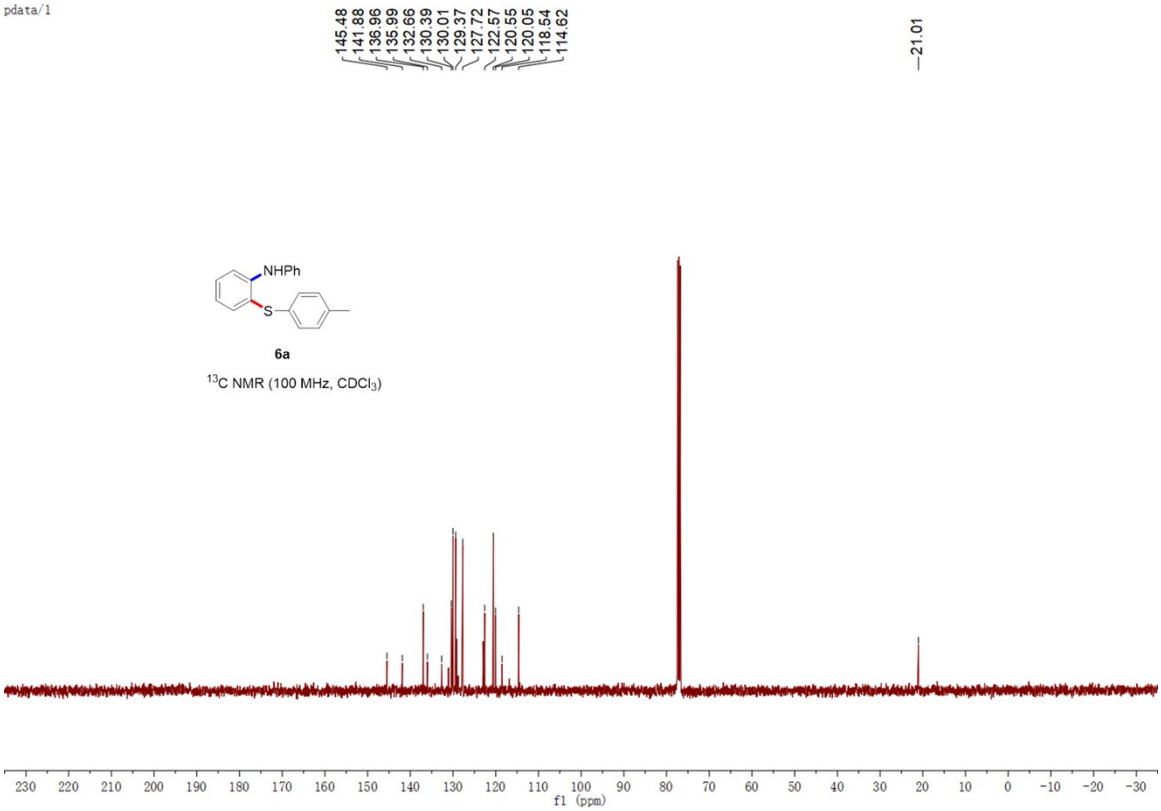
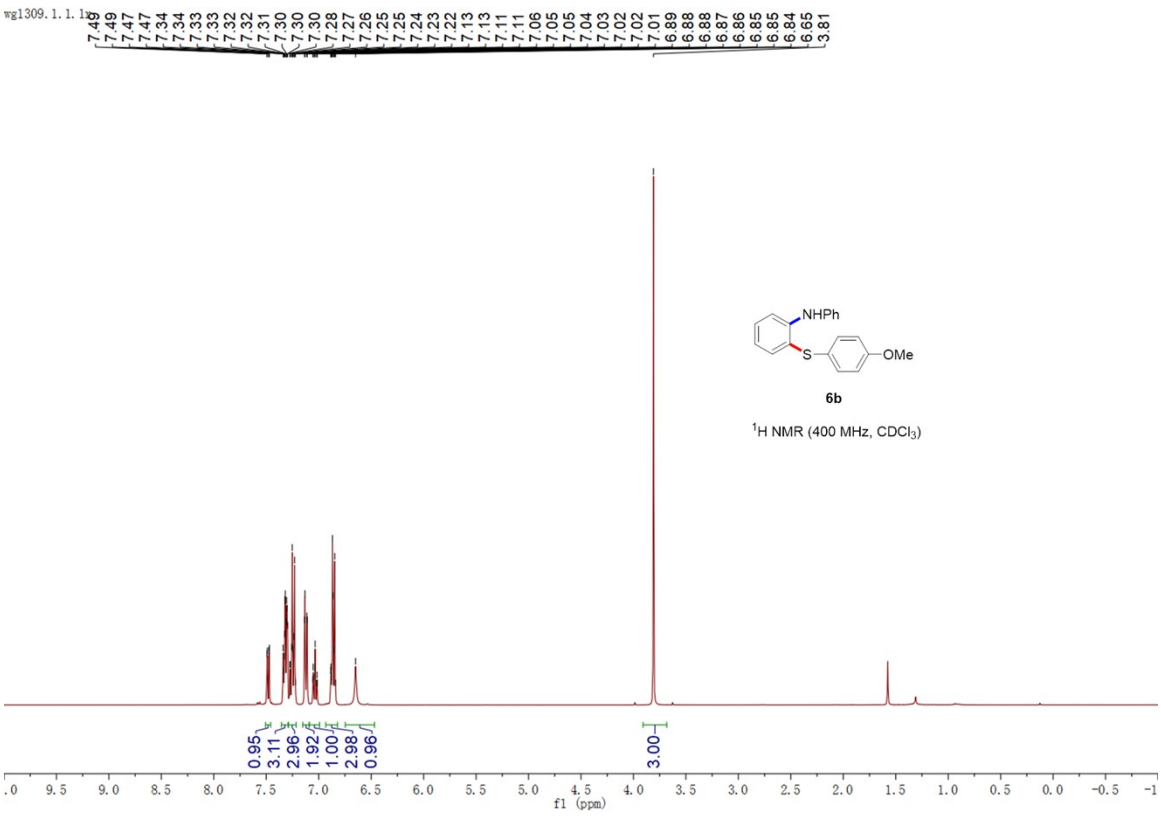
7.33
7.32
7.32
7.31
7.31
7.31
7.30
7.29
7.14
7.13
7.13
7.12
7.11
7.10
7.08
7.06
7.06
7.05
7.04
7.04
7.03
7.02
6.90
6.89
6.88
6.87
6.86
6.86
2.33
NHPh
S
6a
1H NMR (400 MHz, CDCl3)
1.02
4.20
5.84
1.05
1.18
3.00
f1 (ppm)


pdata/1
145.48
141.88
136.96
135.99
132.66
130.39
130.01
129.37
127.72
122.57
120.55
120.05
118.54
114.62
21.01
NHPh
S
6a
13C NMR (100 MHz, CDCl3)
f1 (ppm)


wgl309.1.1.1r
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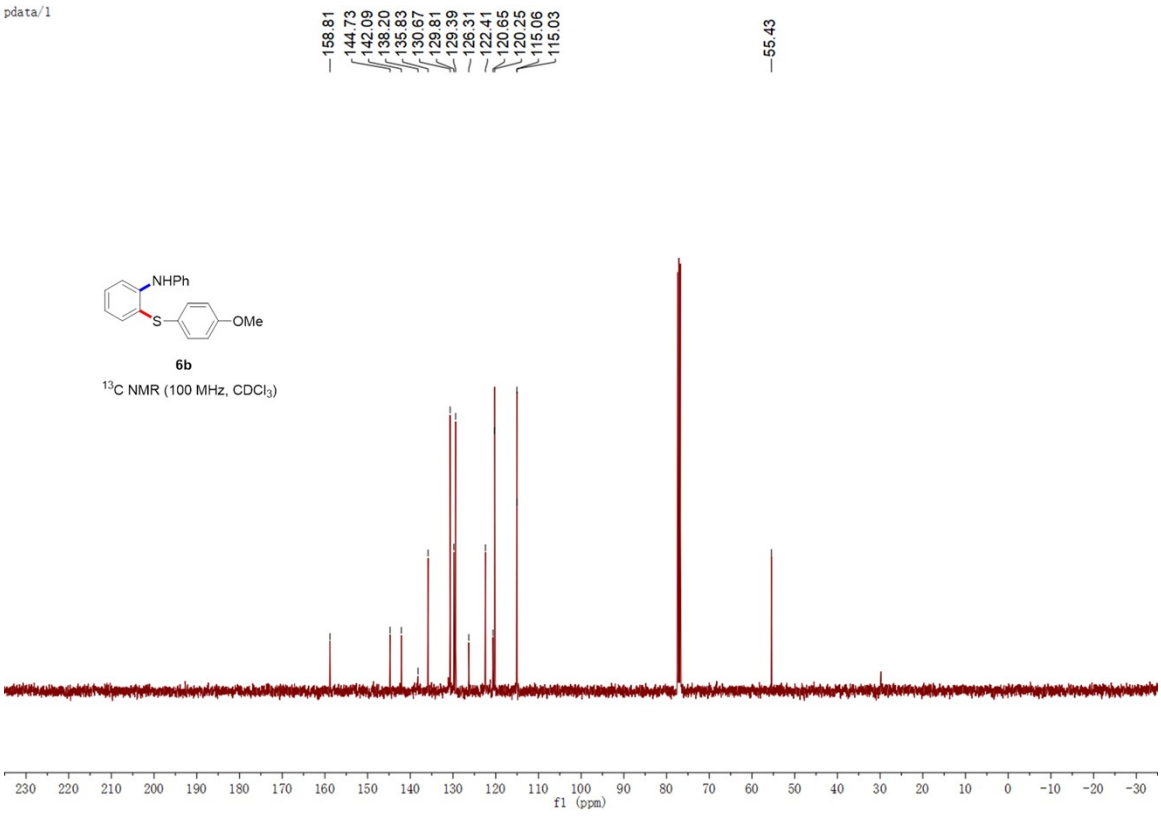
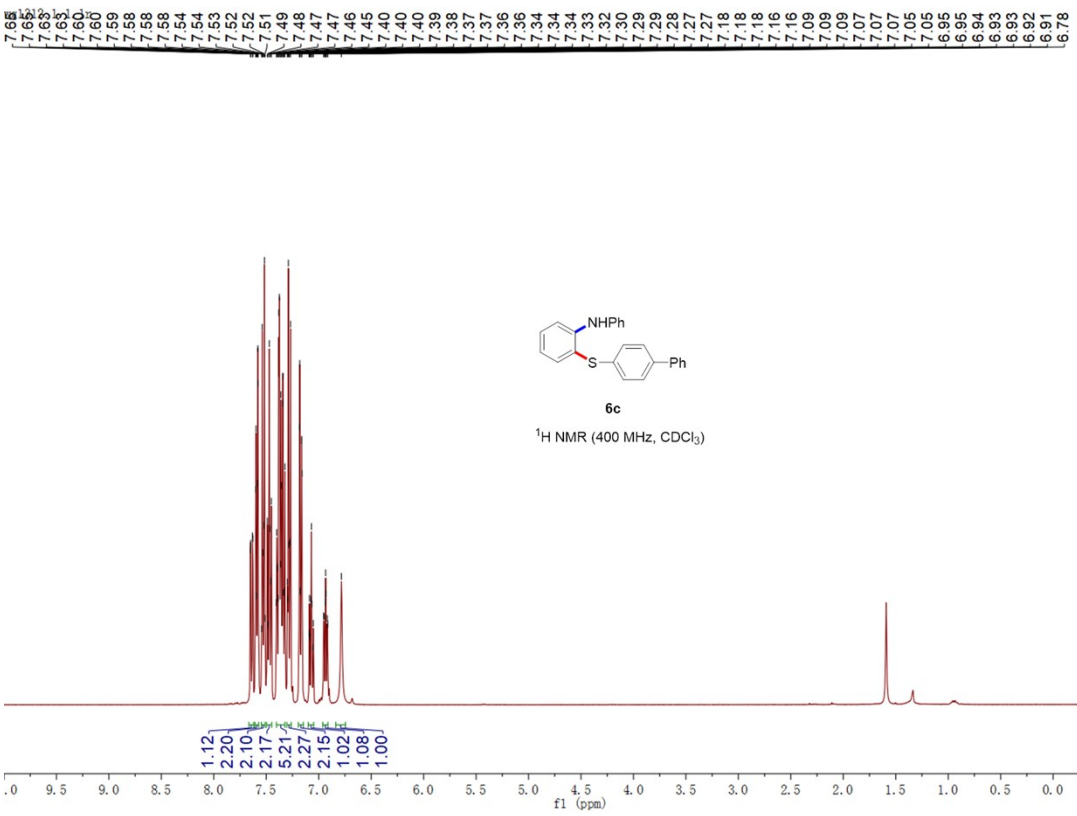
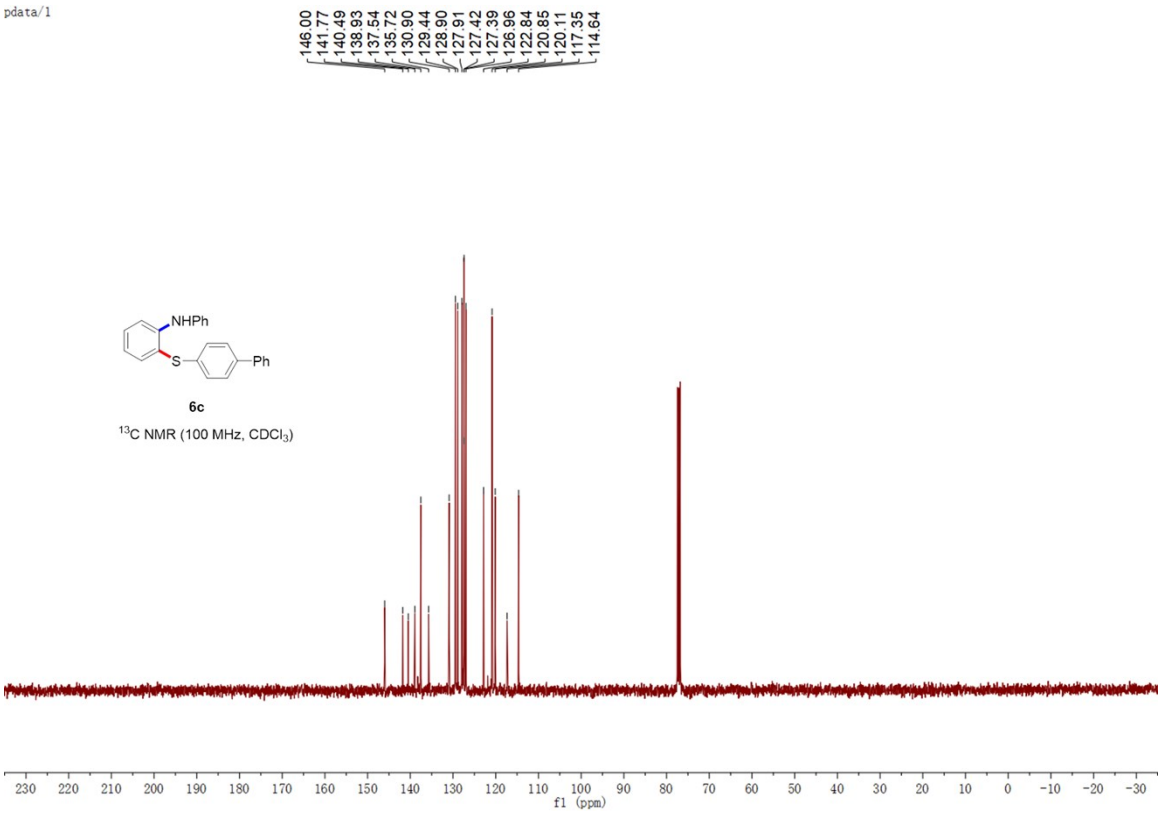
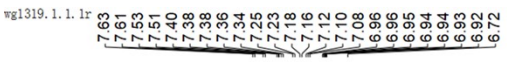
7.49
7.47
7.47
7.34
7.34
7.33
7.33
7.32
7.32
7.31
7.30
7.30
7.30
7.28
7.27
7.26
7.25
7.25
7.24
7.23
7.22
7.13
7.13
7.11
7.11
7.06
7.05
7.05
7.04
7.03
7.02
7.02
7.01
6.89
6.88
6.88
6.87
6.86
6.85
6.85
6.84
6.65
3.81
NHPh
S
OMe
6b
1H NMR (400 MHz, CDCl3)
0.95
3.11
2.96
1.92
1.00
2.98
0.96
3.00
f1 (ppm)


pdata/1
158.81
144.73
142.09
138.20
135.83
130.67
129.81
129.39
126.31
122.41
120.65
120.25
115.06
115.03
55.43
NHPh
S
OMe
6b
13C NMR (100 MHz, CDCl3)
f1 (ppm)

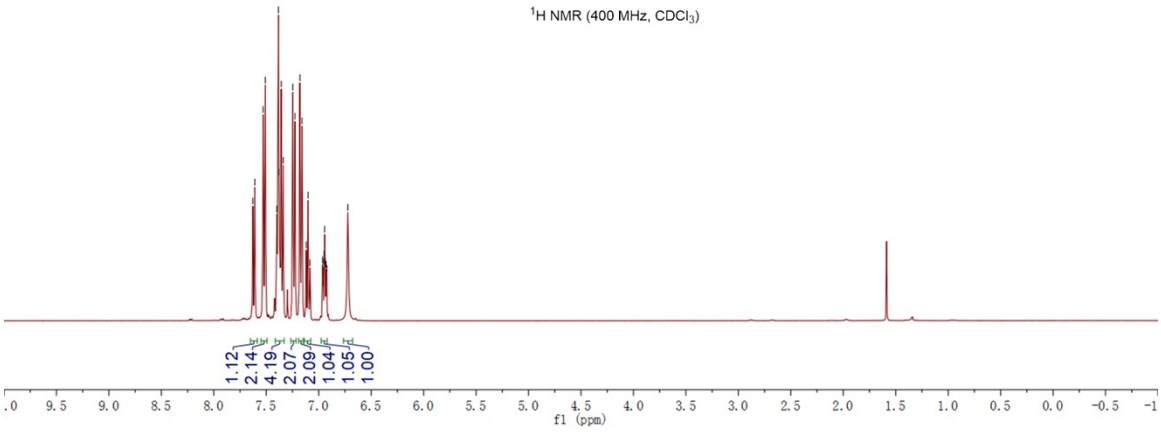

NHPh
S
Ph
6c
1H NMR (400 MHz, CDCl3)
1.12
2.20
2.10
2.17
5.21
2.27
2.15
1.02
1.08
1.00
f1 (ppm)

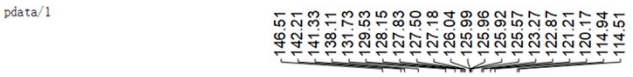

pdata/1
146.00
141.77
140.49
138.93
137.54
135.72
130.90
129.44
128.90
127.91
127.42
127.39
126.96
122.84
120.85
120.11
117.35
114.64
NHPh
S
Ph
6c
13C NMR (100 MHz, CDCl3)
f1 (ppm)

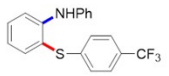


6d

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

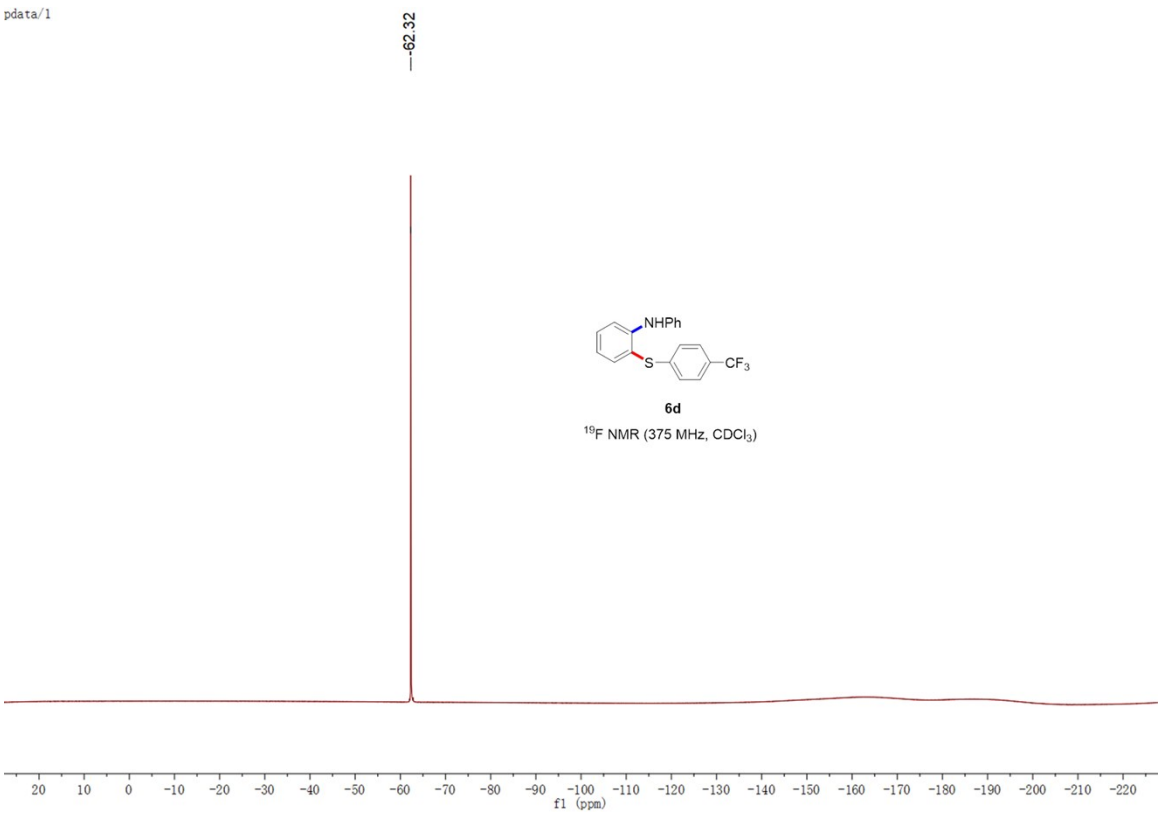






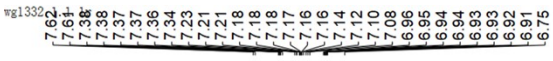
6d

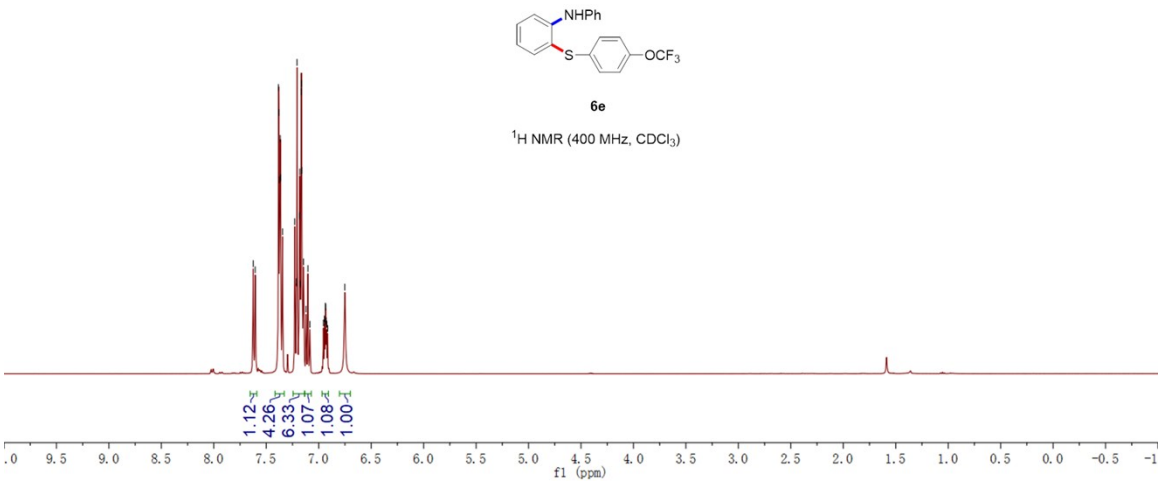
^{13}C NMR (100 MHz, $CDCl_3$)



6d

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



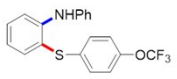


6e

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

pdata/1

147.42
146.14
141.56
137.67
135.61
131.28
129.50
128.07
123.09
121.90
121.01
120.18
119.27
116.70
114.69

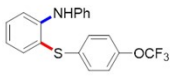


6e

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

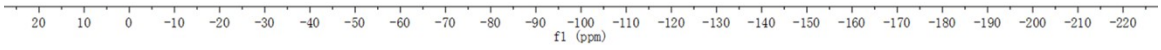
pdata/1

-57.94

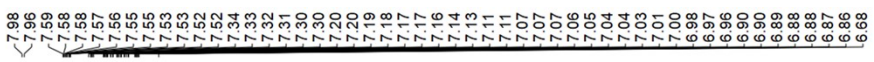


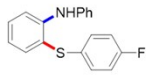
6e

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



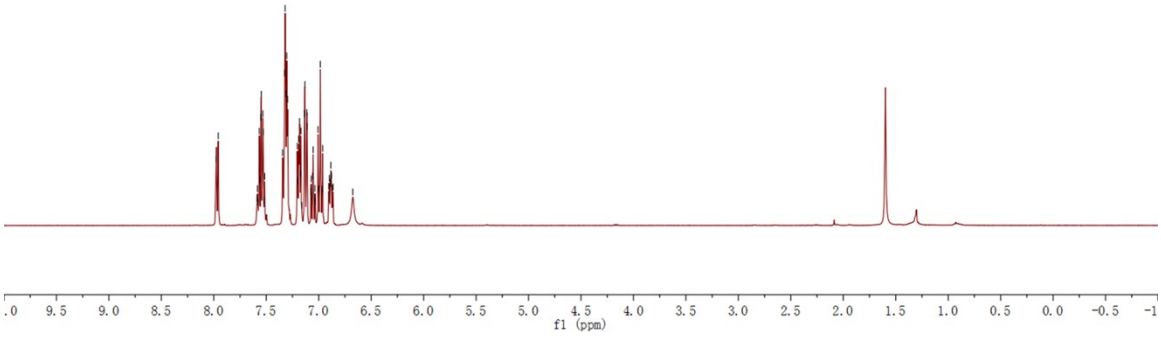
wg1321.1.1.1r



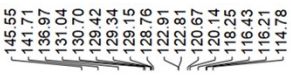


6f

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

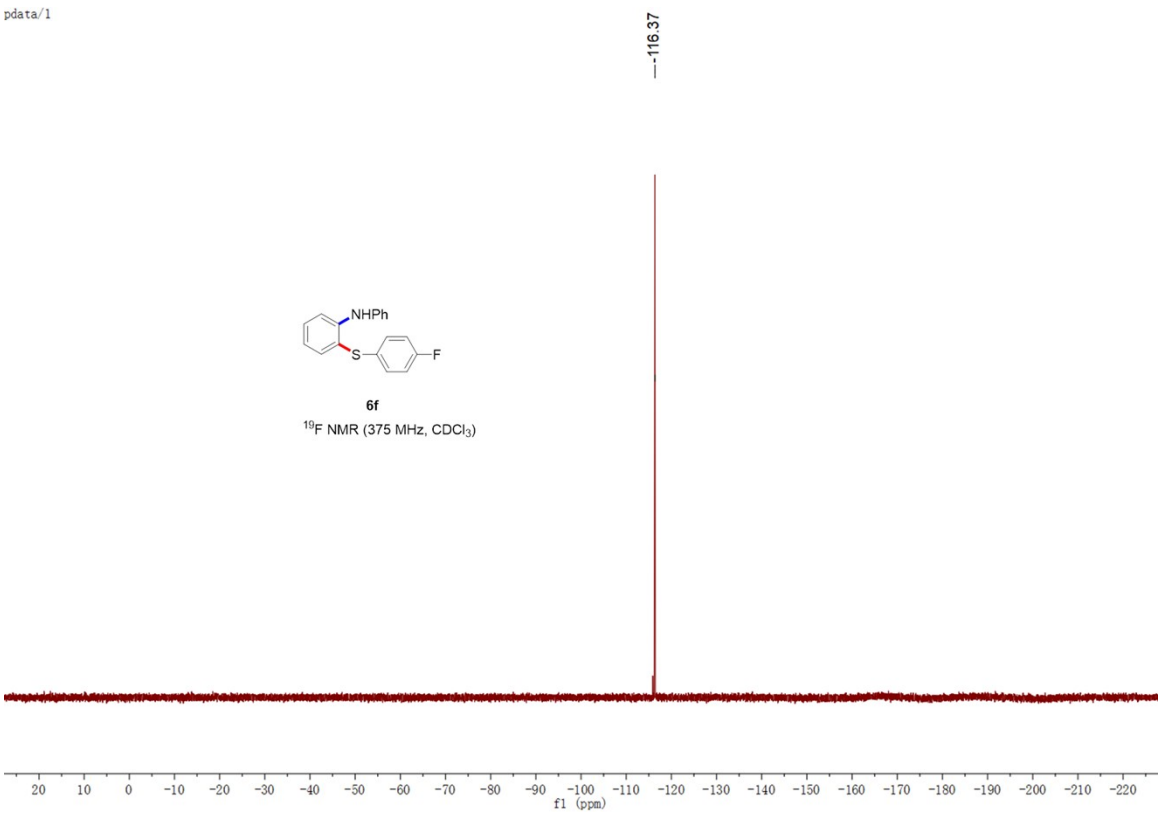


pdata/1



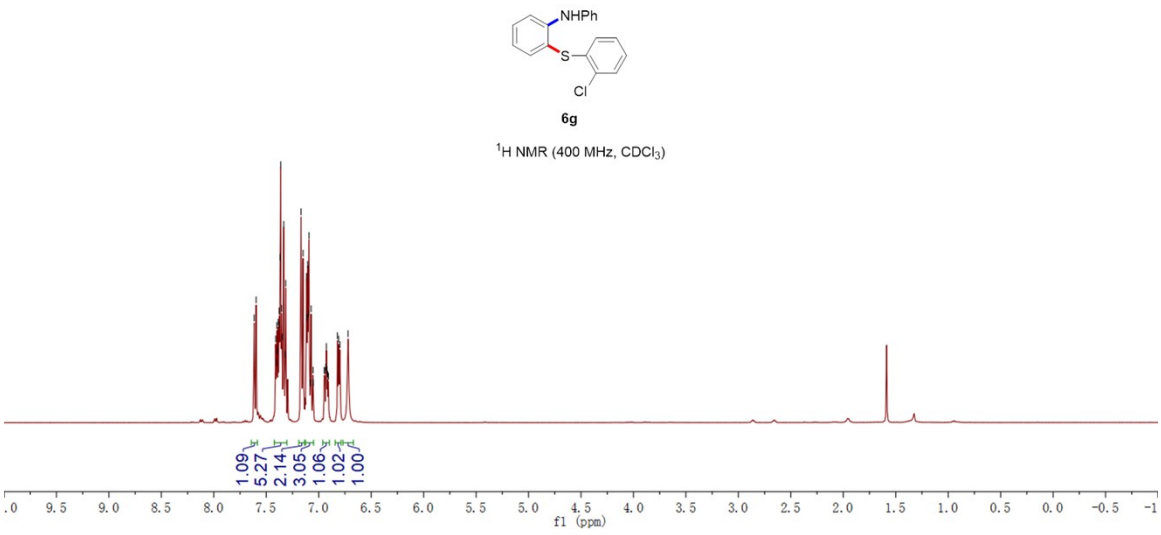
6f

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



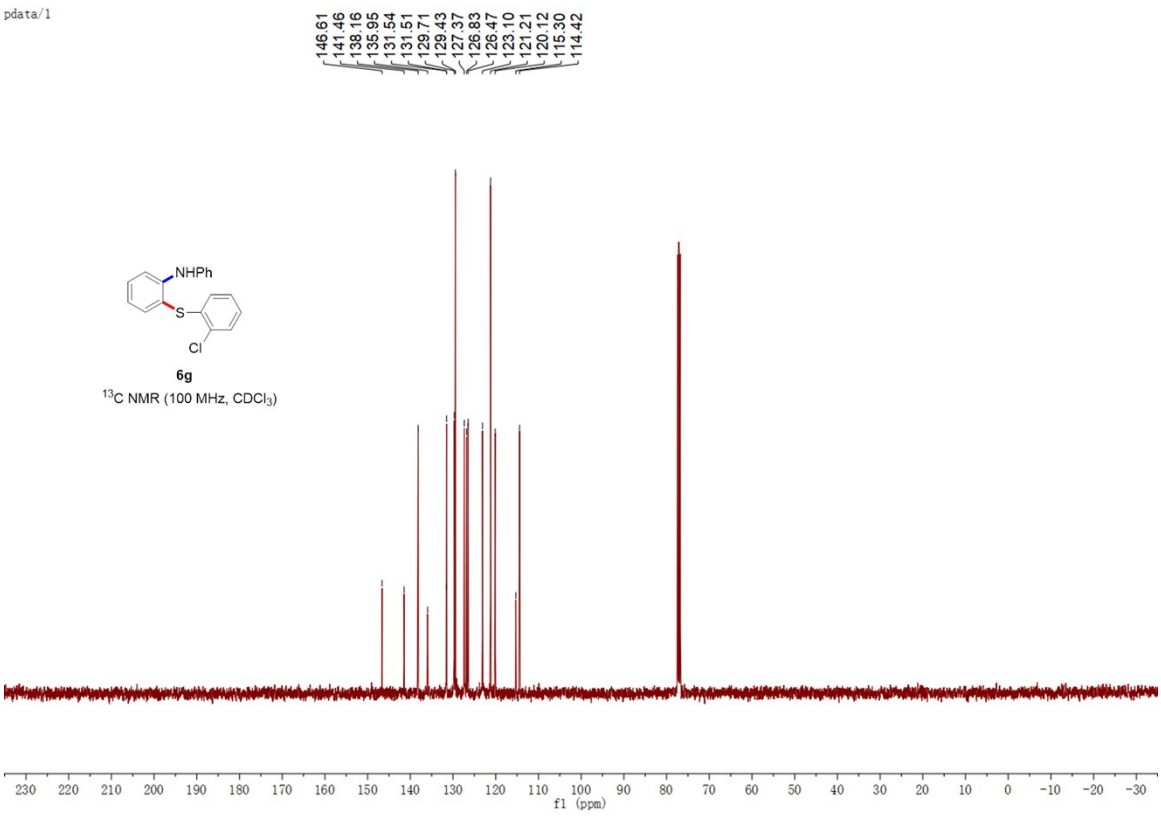
6f

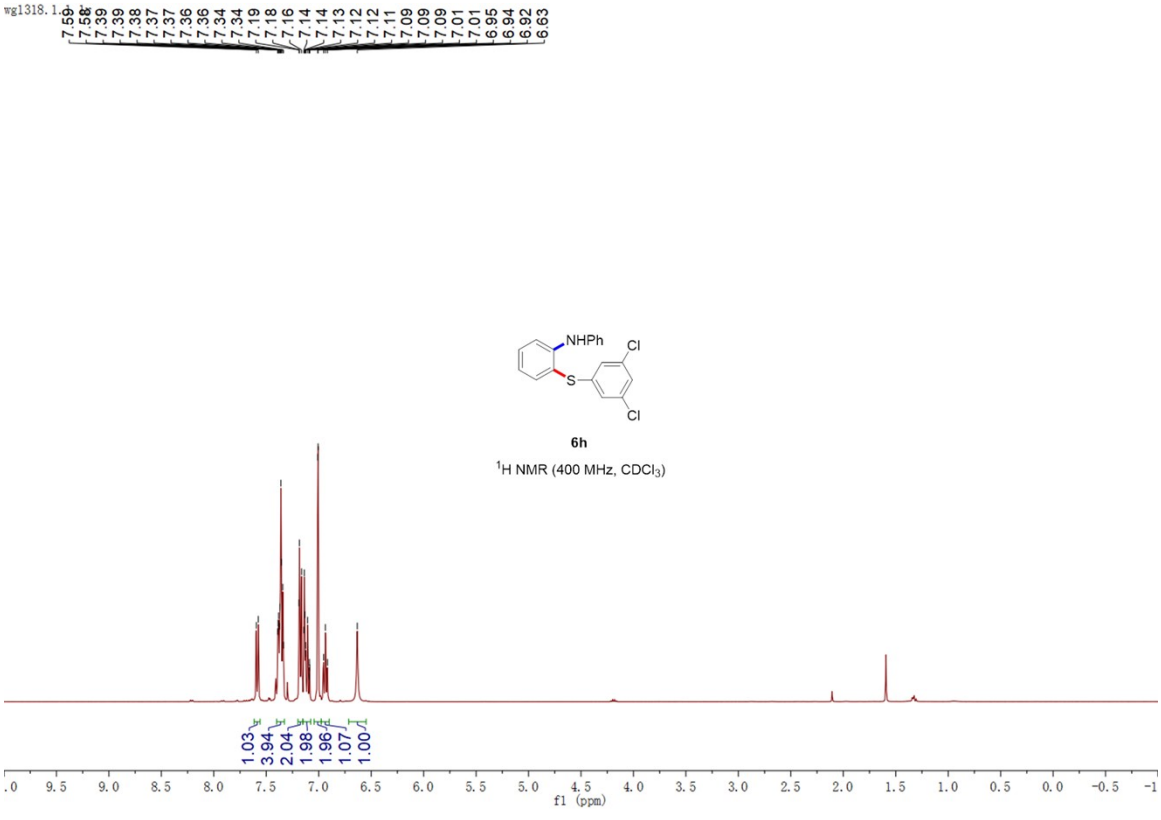
^{19}F NMR (375 MHz, $CDCl_3$)

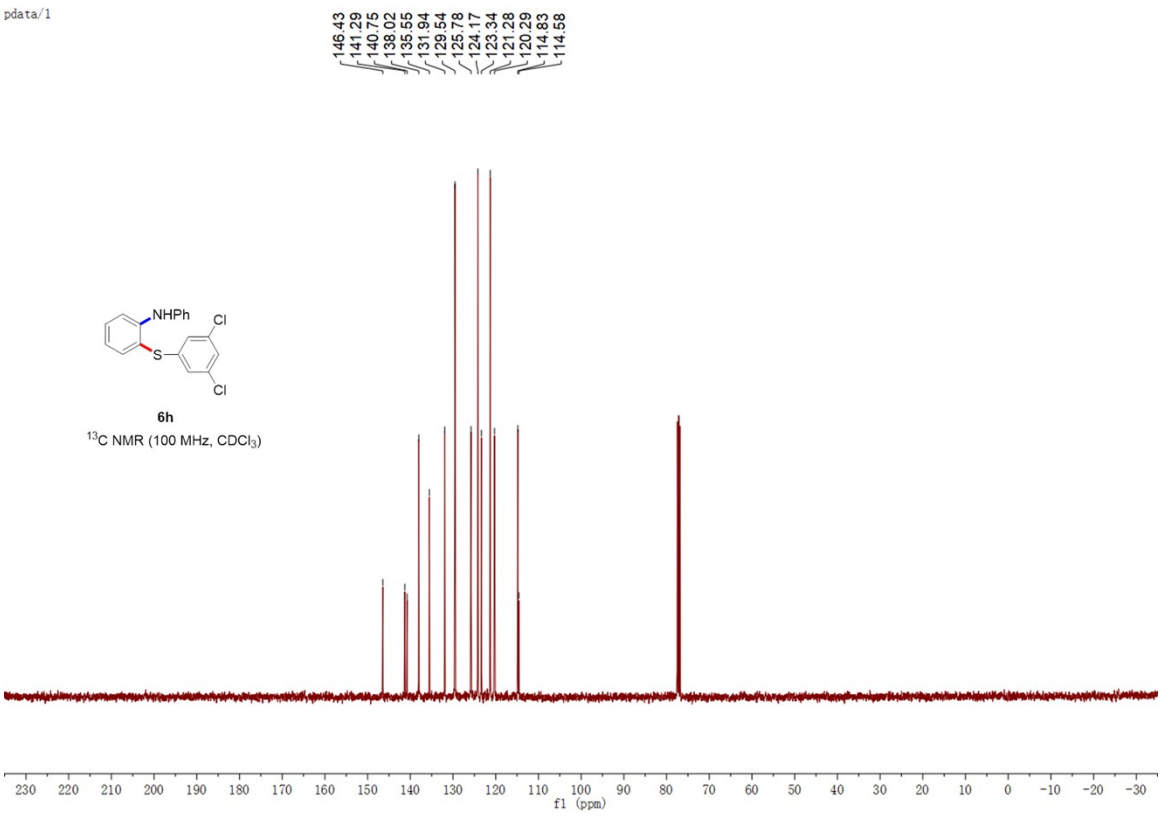


6g

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

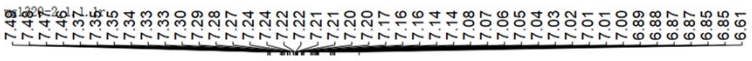

pdata/1
146.61
141.46
138.16
135.95
131.54
131.51
129.71
129.43
127.37
126.83
126.47
123.10
121.21
120.12
115.30
114.42
NHPh
S
Cl
6g
13C NMR (100 MHz, CDCl3)
f1 (ppm)

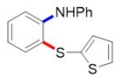

wg1318.1.1
7.59
7.58
7.39
7.39
7.38
7.37
7.37
7.36
7.36
7.34
7.34
7.19
7.18
7.16
7.14
7.14
7.13
7.12
7.12
7.11
7.09
7.09
7.09
7.01
7.01
6.95
6.94
6.92
6.63
NHPh
S
Cl
Cl
6h
1H NMR (400 MHz, CDCl3)
1.03
3.94
2.04
1.98
1.96
1.07
1.00
f1 (ppm)



6h

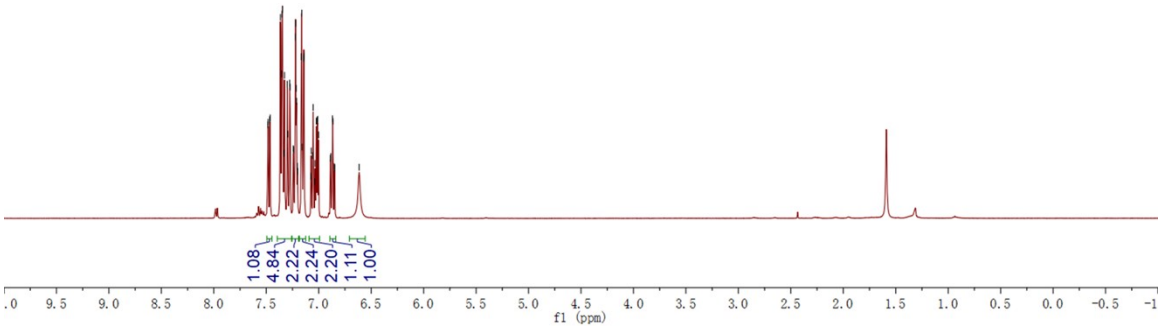
^{13}C NMR (100 MHz, $CDCl_3$)

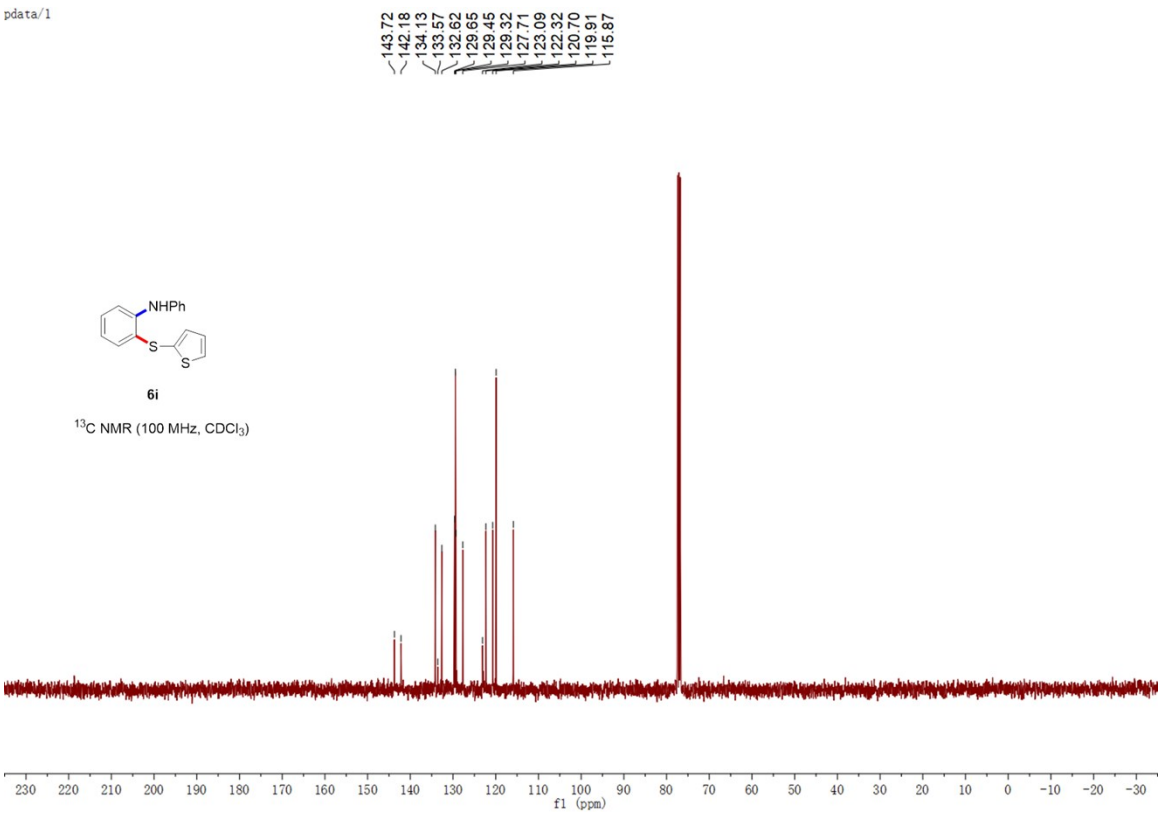


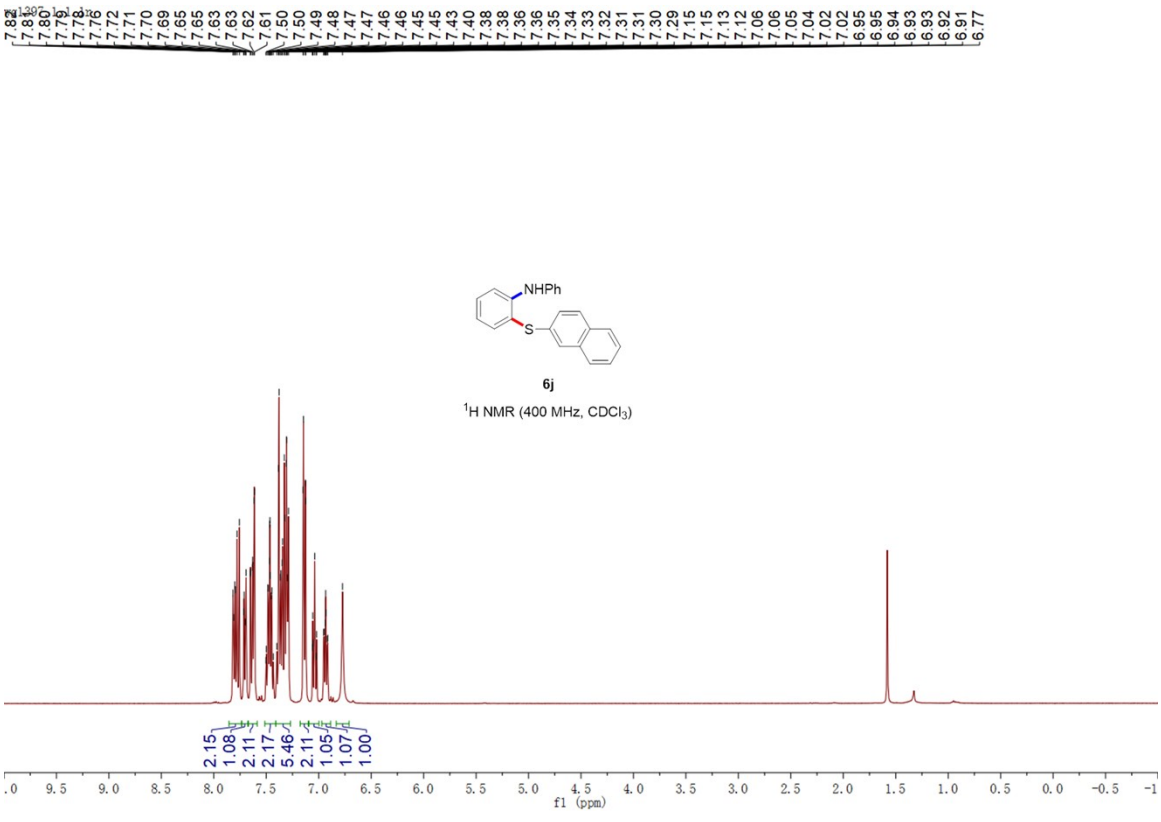


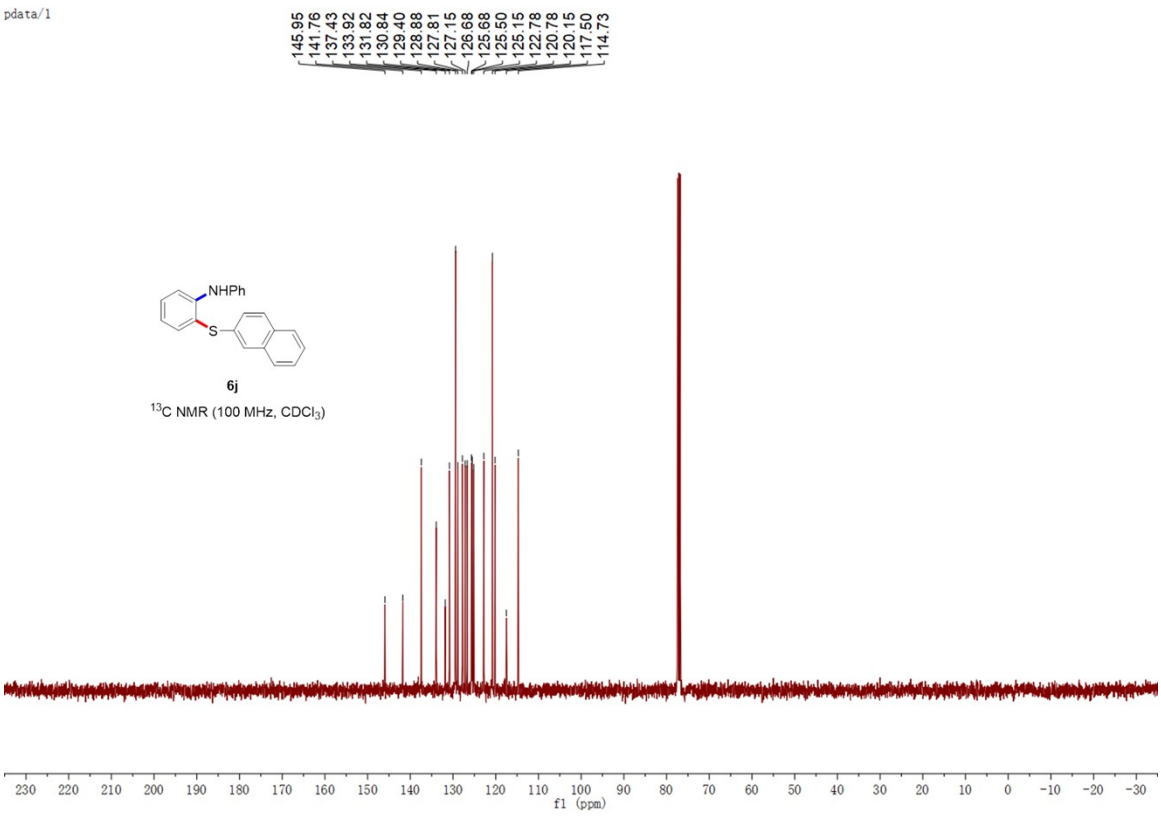
6i

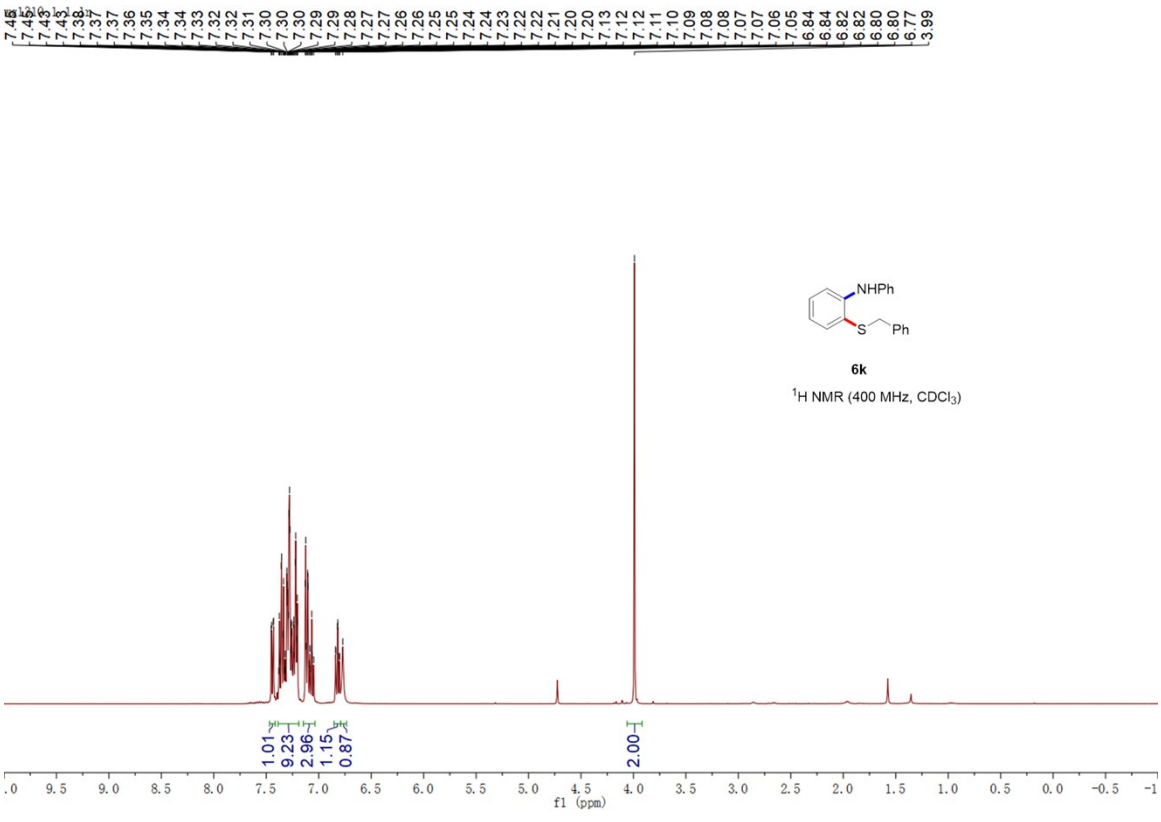
^{1}H NMR (400 MHz, $CDCl_3$)

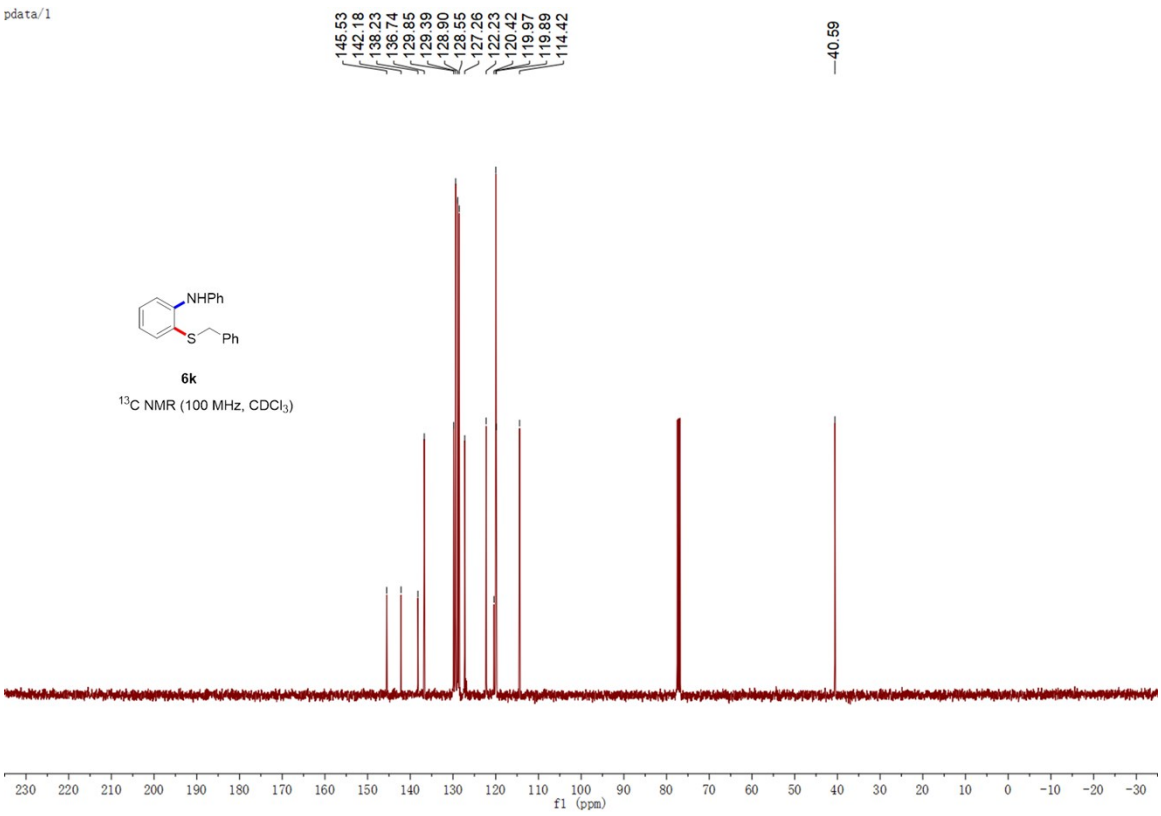


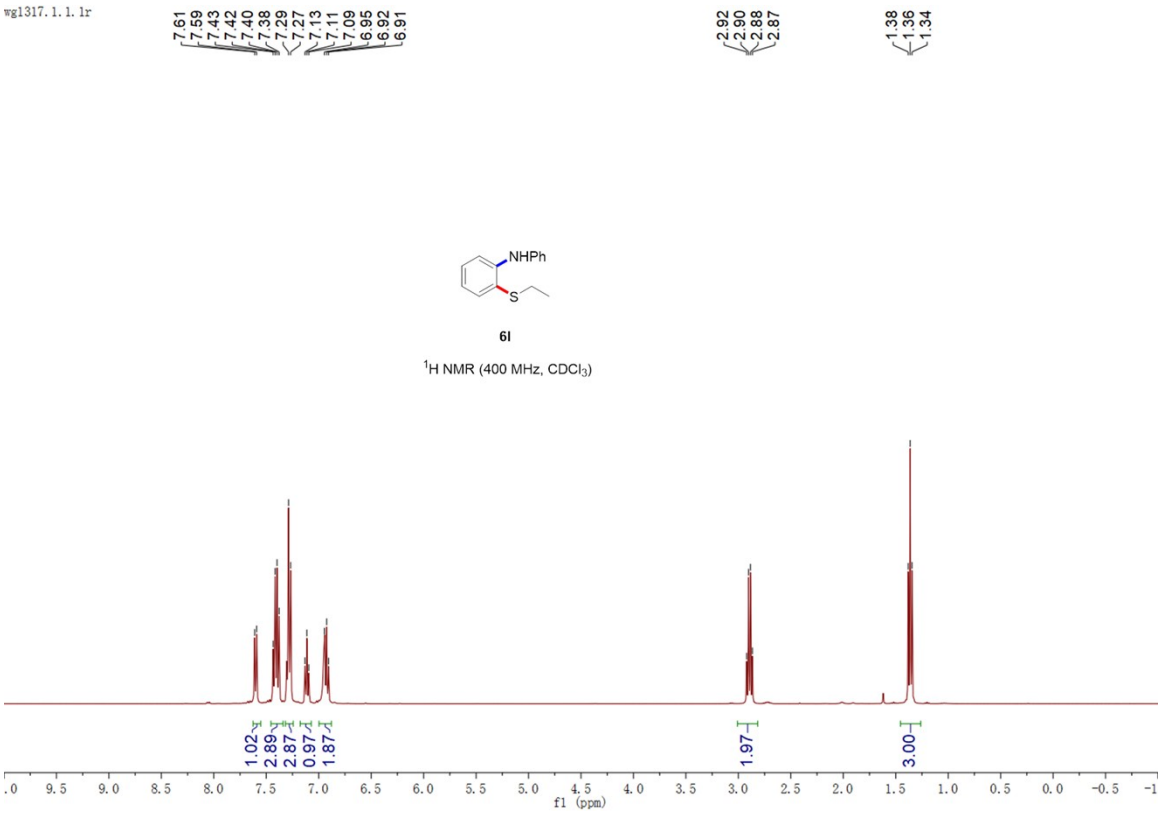

pdata/1
143.72
142.18
134.13
133.57
132.62
129.65
129.45
128.32
127.71
123.09
122.32
120.70
119.91
115.87
NHPh
S
S
6i
13C NMR (100 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)

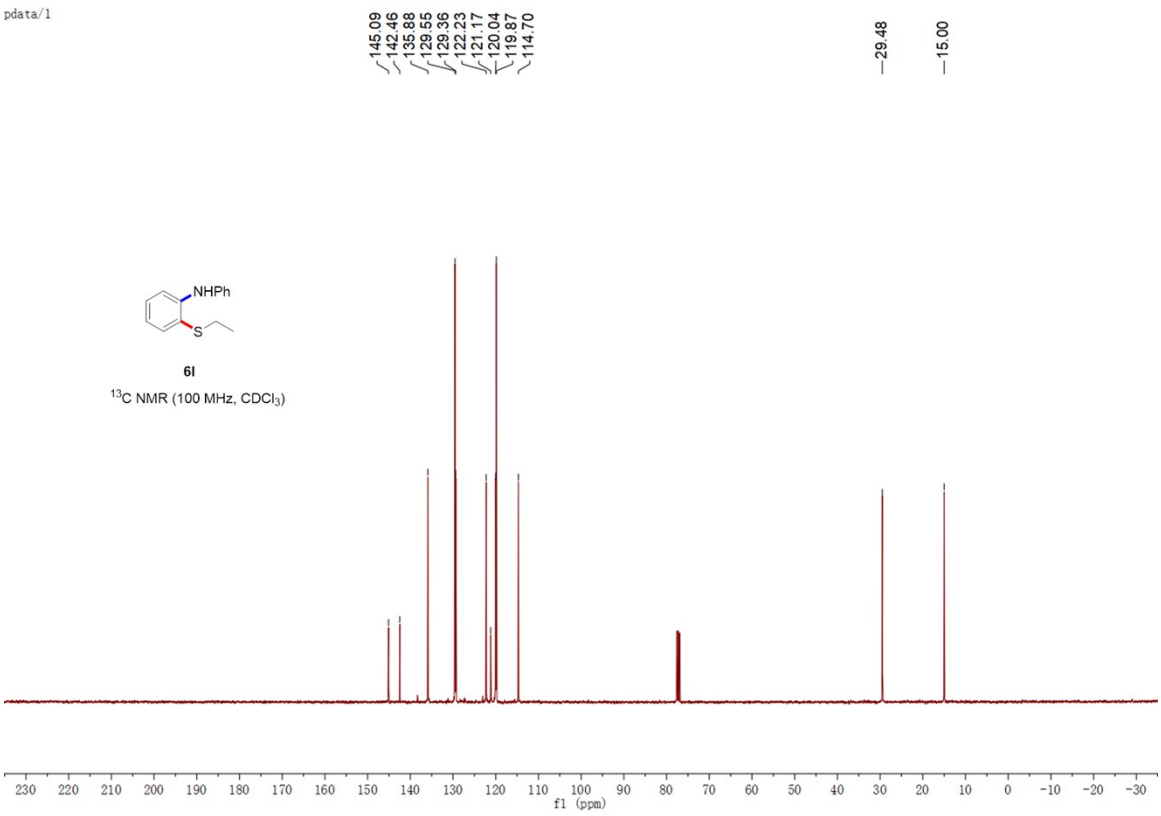

7.82
7.81
7.80
7.79
7.78
7.76
7.72
7.71
7.70
7.69
7.65
7.65
7.63
7.63
7.62
7.61
7.50
7.49
7.48
7.47
7.47
7.46
7.46
7.45
7.45
7.43
7.40
7.38
7.38
7.36
7.36
7.35
7.34
7.33
7.32
7.31
7.30
7.29
7.15
7.15
7.13
7.12
7.06
7.06
7.05
7.04
7.02
7.02
6.95
6.95
6.94
6.93
6.93
6.92
6.91
6.77
NHPh
S
6j
1H NMR (400 MHz, CDCl3)
2.15
1.08
2.11
2.17
5.46
2.11
1.05
1.07
1.00
.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

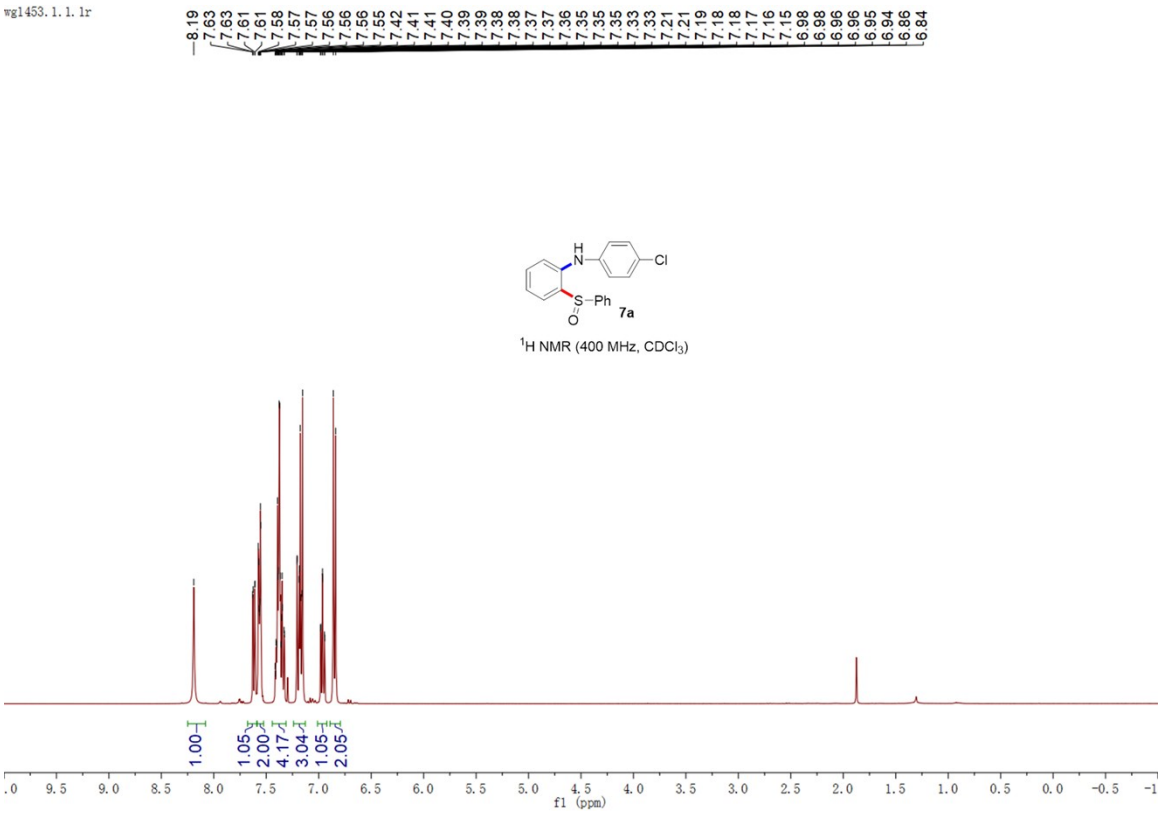

pdata/1
145.95
141.76
137.43
133.92
131.82
130.84
129.40
128.88
127.81
127.15
126.68
125.68
125.50
125.15
122.78
120.78
120.15
117.50
114.73
NHPh
S
6j
13C NMR (100 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)

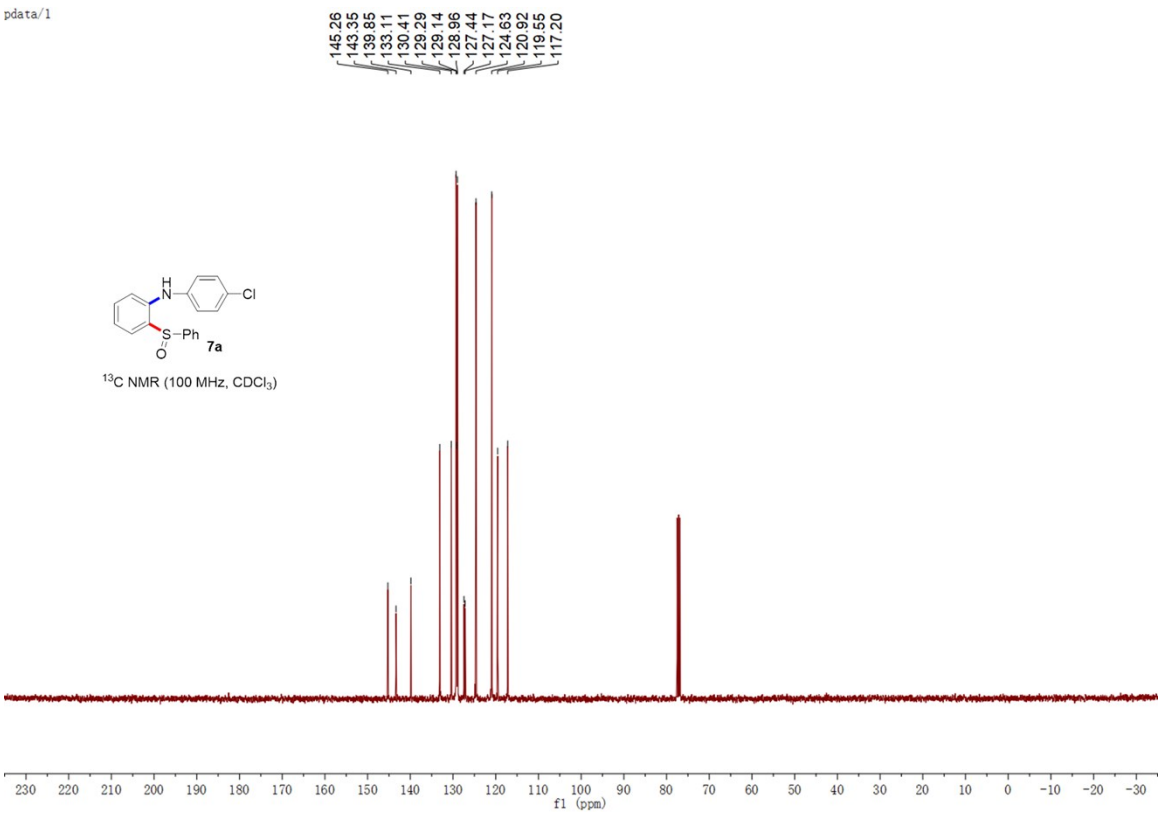

7.46
7.45
7.43
7.38
7.37
7.37
7.36
7.35
7.34
7.34
7.33
7.32
7.32
7.31
7.30
7.30
7.30
7.29
7.29
7.28
7.27
7.27
7.26
7.26
7.25
7.25
7.24
7.24
7.23
7.22
7.22
7.21
7.20
7.20
7.13
7.12
7.12
7.11
7.10
7.09
7.08
7.08
7.07
7.07
7.06
7.05
6.84
6.84
6.82
6.82
6.80
6.80
6.77
3.99
NHPh
S
Ph
6k
1H NMR (400 MHz, CDCl3)
1.01
9.23
2.96
1.15
0.87
2.00
.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

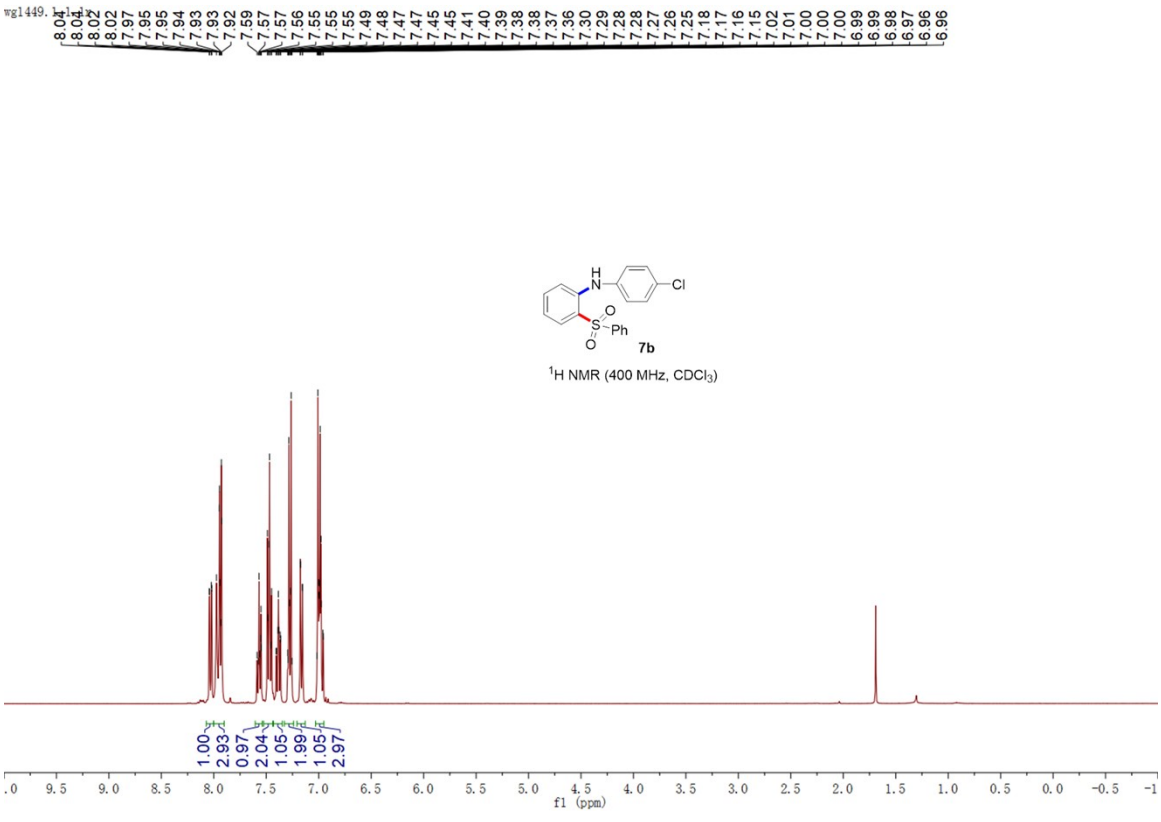

pdata/1
145.53
142.18
138.23
136.74
129.85
129.39
128.90
128.55
127.26
122.23
120.42
119.97
119.89
114.42
40.59
NHPh
S
Ph
6k
13C NMR (100 MHz, CDCl3)
f1 (ppm)


wg1317.1.1.1r
7.61
7.59
7.43
7.42
7.40
7.38
7.29
7.27
7.13
7.11
7.09
6.95
6.92
6.91
2.92
2.90
2.88
2.87
1.38
1.36
1.34
NHPh
S
6l
1H NMR (400 MHz, CDCl3)
1.02
2.89
2.87
0.97
1.87
1.97
3.00
f1 (ppm)


pdata/1
145.09
142.46
135.88
129.55
129.36
122.23
121.17
120.04
119.87
114.70
29.48
15.00
NHPh
S
6l
13C NMR (100 MHz, CDCl3)
f1 (ppm)

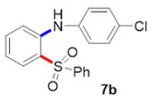

wgl453.1.1.1r
8.19
7.63
7.63
7.61
7.61
7.58
7.57
7.57
7.56
7.56
7.56
7.55
7.42
7.41
7.41
7.40
7.39
7.39
7.38
7.38
7.37
7.37
7.36
7.35
7.35
7.35
7.33
7.33
7.21
7.21
7.19
7.18
7.18
7.17
7.16
7.15
6.98
6.98
6.96
6.96
6.95
6.94
6.86
6.84
H
N
Cl
S
Ph
O
7a
1H NMR (400 MHz, CDCl3)
1.00
1.05
2.00
4.17
3.04
1.05
2.05
f1 (ppm)


pdata/1
145.26
143.35
139.85
133.11
130.41
129.29
129.14
128.96
127.44
127.17
124.63
120.92
119.55
117.20
H
N
Cl
S
Ph
O
7a
13C NMR (100 MHz, CDCl3)
f1 (ppm)


wgl449.1.1.1r
8.04
8.04
8.02
8.02
7.97
7.95
7.95
7.94
7.93
7.93
7.92
7.59
7.57
7.57
7.56
7.55
7.55
7.55
7.49
7.48
7.47
7.47
7.45
7.45
7.41
7.40
7.39
7.38
7.38
7.37
7.36
7.30
7.29
7.28
7.28
7.27
7.26
7.25
7.18
7.17
7.16
7.15
7.02
7.01
7.00
7.00
7.00
6.99
6.99
6.98
6.97
6.96
6.96
H
N
Cl
S
Ph
O
O
7b
1H NMR (400 MHz, CDCl3)
1.00
2.93
0.97
2.04
1.05
1.99
1.05
2.97
f1 (ppm)

pdata/1

143.55
141.42
139.18
135.06
133.36
130.45
129.65
129.18
128.55
127.12
125.45
122.55
119.83
116.57

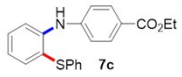


7b

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

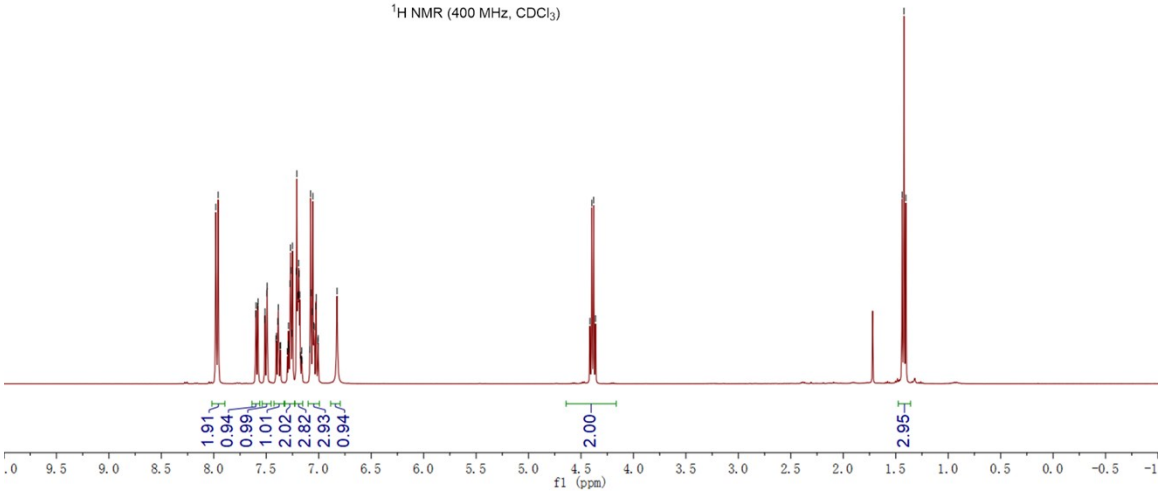
wg1426-2.1.1.1r

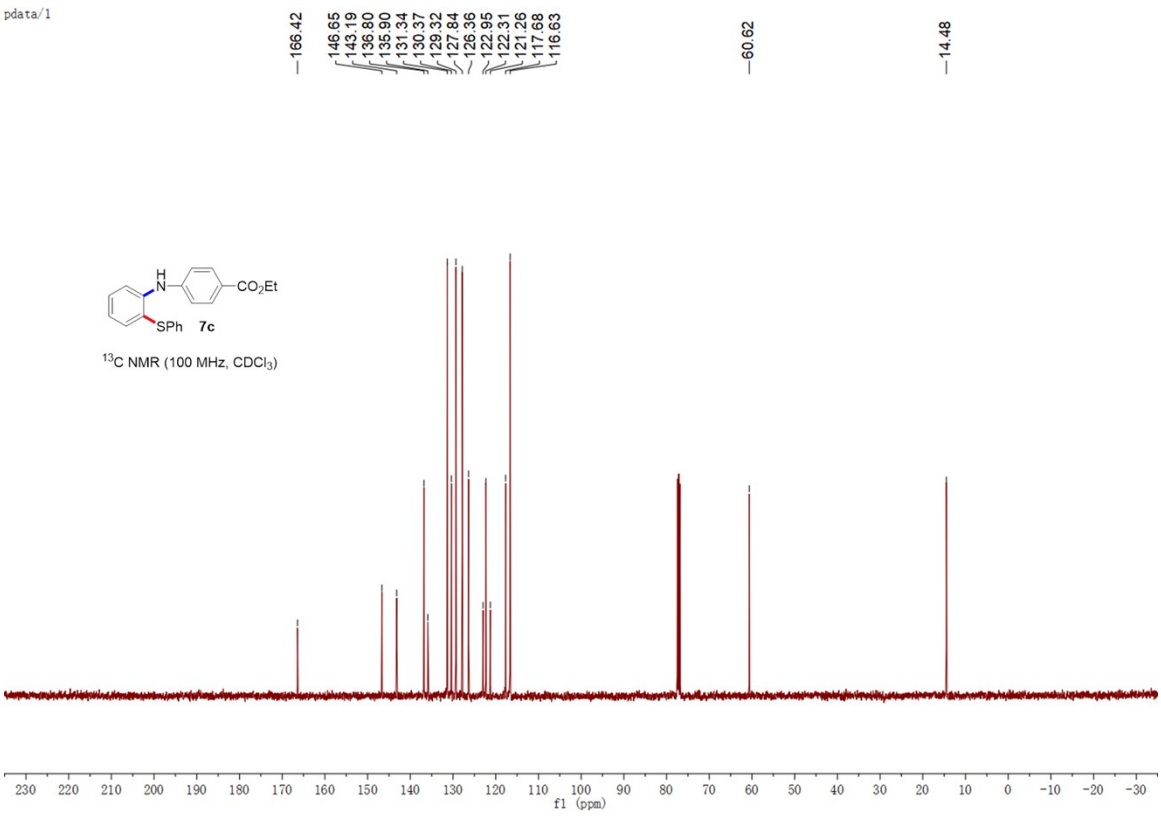
7.98
7.96
7.60
7.60
7.58
7.58
7.52
7.51
7.49
7.49
7.41
7.40
7.39
7.38
7.37
7.36
7.30
7.29
7.29
7.28
7.27
7.27
7.27
7.26
7.25
7.21
7.21
7.20
7.20
7.19
7.19
7.18
7.17
7.17
7.16
7.16
7.08
7.08
7.07
7.06
7.06
7.05
7.04
7.03
7.02
7.01
7.01
6.83
4.41
4.40
4.38
4.36
1.44
1.42
1.40

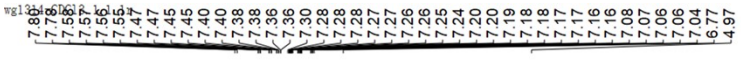


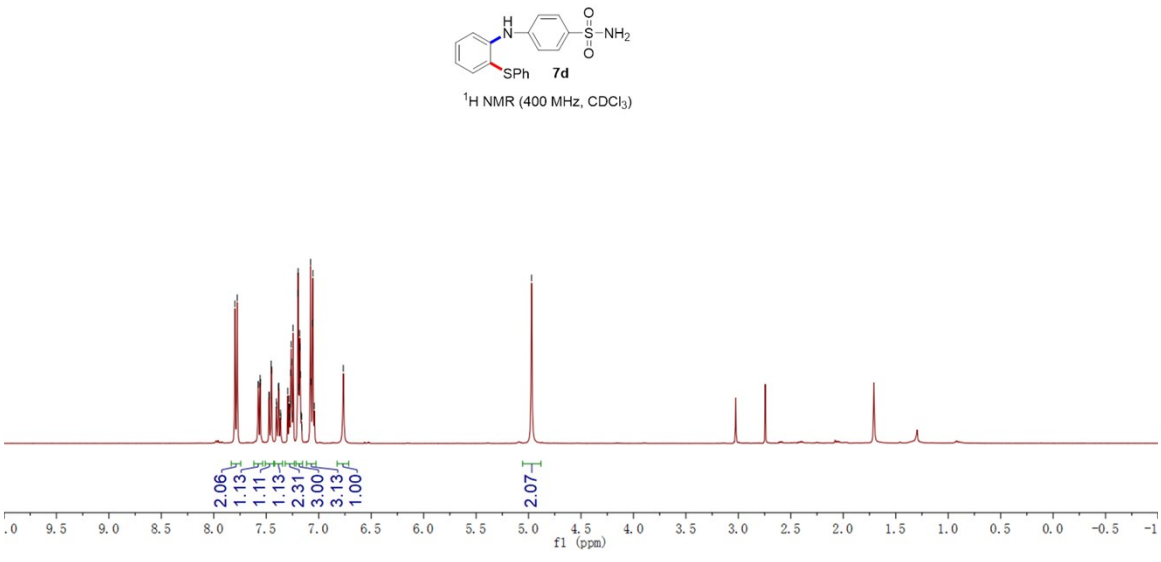
7c

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



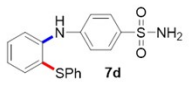

pdata/1
166.42
146.65
143.19
136.80
135.90
131.34
130.37
129.32
127.84
126.36
122.95
122.31
121.26
117.68
116.63
60.62
14.48
CO2Et
SPh 7c
13C NMR (100 MHz, CDCl3)
f1 (ppm)


7.80
7.78
7.58
7.57
7.56
7.55
7.47
7.47
7.45
7.45
7.40
7.40
7.38
7.38
7.36
7.36
7.30
7.28
7.28
7.28
7.27
7.27
7.26
7.26
7.25
7.24
7.20
7.20
7.19
7.18
7.18
7.17
7.17
7.16
7.16
7.08
7.07
7.06
7.06
7.04
6.77
4.97


NH2
SPh 7d
1H NMR (400 MHz, CDCl3)
2.06
1.13
1.11
1.13
2.31
3.00
3.13
1.00
2.07
f1 (ppm)

wg1314-CDCl3.2.1.1r

146.88
142.33
136.49
135.55
133.06
130.25
129.39
128.41
128.16
126.58
123.15
122.61
118.56
116.49



7d

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