Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Iodine (III)-Mediated Dehydroaromatization of Cyclohexanones with Primary Amines and CD_3SSO_3Na to Access *ortho*-SCD_3 Anilines

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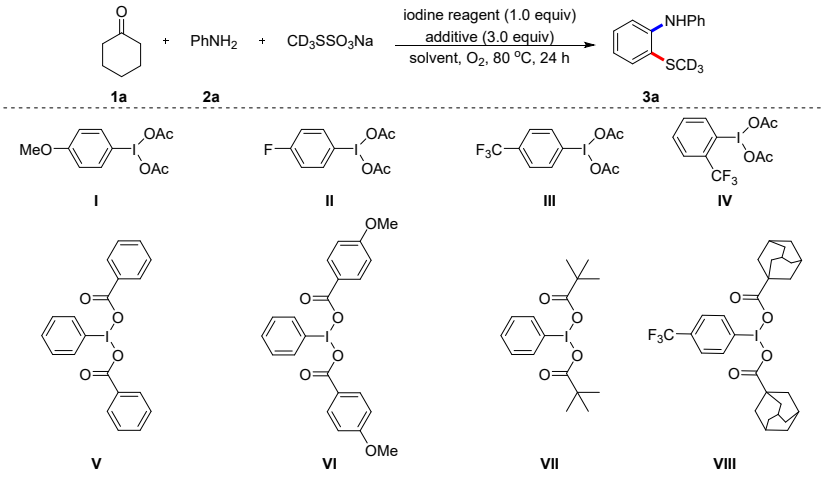
General Information

Hypervalent iodine compounds[1] were prepared from known literatures. 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).

Table 1 Reaction optimization[a]

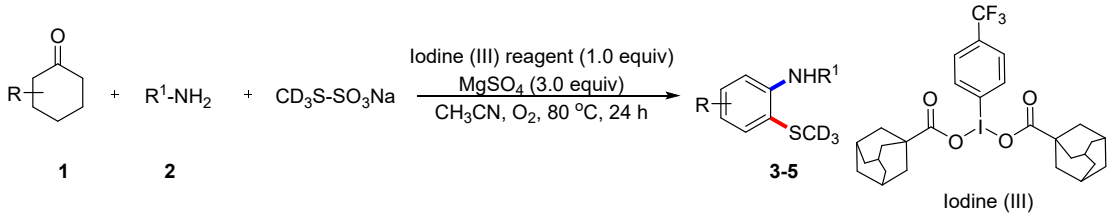


entry	catalyst	solvent	additive	yield (%)[b]
1	I_2	CH_3CN		0
2	NIS	CH_3CN		0
3	PhIO	CH_3CN		trace
4	$PhI(OAc)_2$	CH_3CN		40
5	$PhI(TFA)_2$	CH_3CN		34
6	**I**	CH_3CN		45
7	**II**	CH_3CN		40
8	**III**	CH_3CN		50
9	**IV**	CH_3CN		38
10	**V**	CH_3CN		60
11[c]	**VI**	CH_3CN		65
12	**VII**	CH_3CN		48
13	**VIII**	CH_3CN		73
14	**VIII**	CH_3CN	$MgSO_4$	89
15	**VIII**	CH_3CN	AcOH	82
16	**VIII**	DMSO	$MgSO_4$	11
17	**VIII**	DMF	$MgSO_4$	32
18	**VIII**	dioxane	$MgSO_4$	76
19	**VIII**	toluene	$MgSO_4$	81
20	**VIII**	H_2O	$MgSO_4$	0
21c	**VIII**	CH_3CN	$MgSO_4$	67
22d	**VIII**	CH_3CN	$MgSO_4$	80

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), CD_3SSO_3Na (0.6 mmol), iodine reagent (0.2 mmol), additive (0.6 mmol) and CH_3CN (1.5 ml) under O_2, heated at 80 °C for 24 h. [b] Isolated yield. [c] Under N_2 atmosphere. [d] Under air atmosphere.

General Experimental Procedures

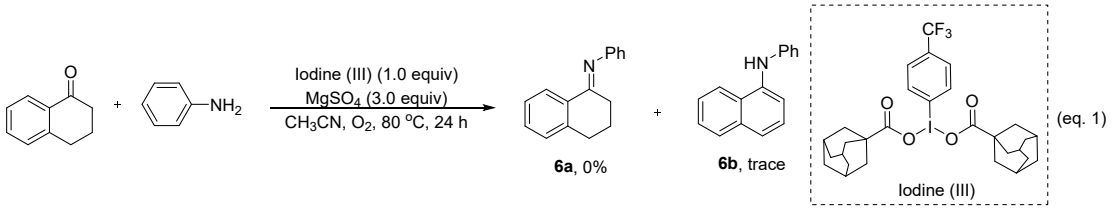
General Procedure of Hypervalent Iodine(III)-Mediated Oxidative Thioamination of Cyclohexanones with Anilines and CD_3SSO_3Na:



1 2 3-5

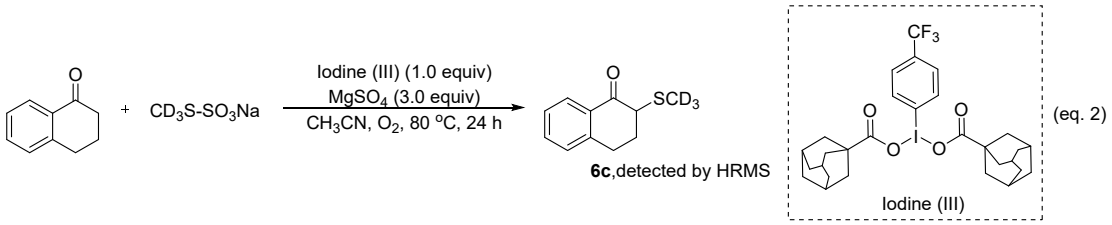
A 25 mL Schlenk tube equipped with a stir bar was charged with substituted cyclohexanone (0.2 mmol), anilines (0.6 mmol), CD_3SSO_3Na (0.6 mmol), hypervalent iodine(III) compound (0.2 mmol), $MgSO_4$ (0.6 mmol) and 2.0 mL CH_3CN. The tube was fitted with a rubber septum, and then it was evacuated and refilled with dioxygen three times, then the septum was replaced by a Teflon screwcap under oxygen flow. The reaction mixture was stirred at 80 ℃ for 24 h. After cooling down, the reaction mixture was diluted with 10 mL of ethyl ether, filtered through a pad of silica gel, followed by washing the pad of the silica gel with the same solvent (20 mL), concentrated under reduced pressure. The residue was then purified by flash chromatography on silica gel to provide the corresponding product.

Mechanistic Studies



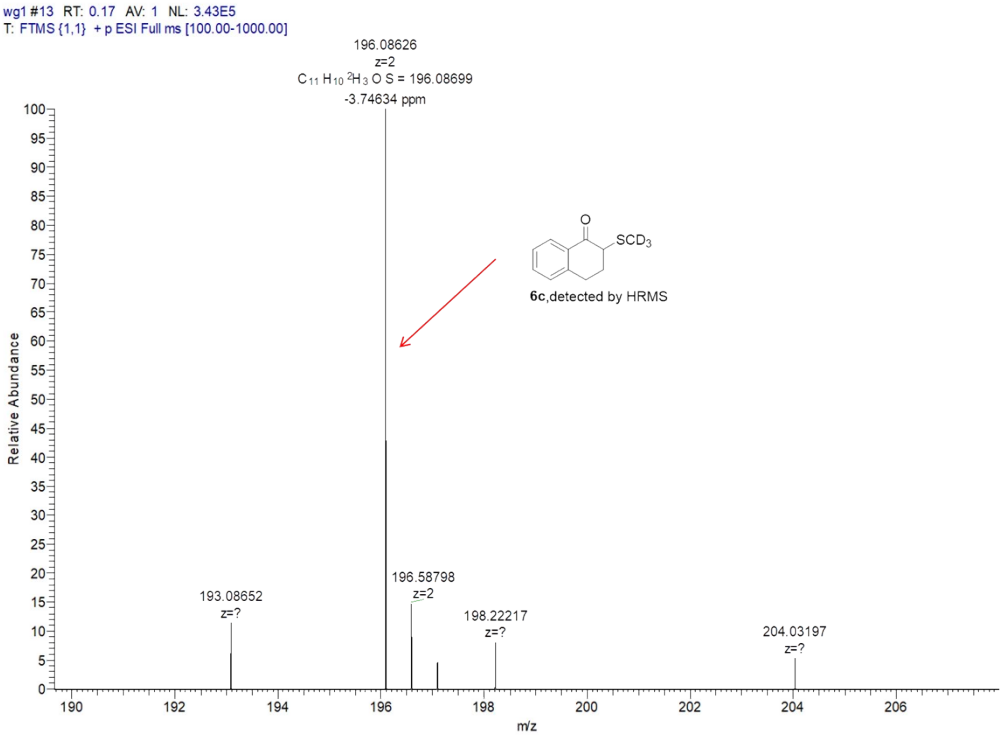
6a, 0% **6b**, trace

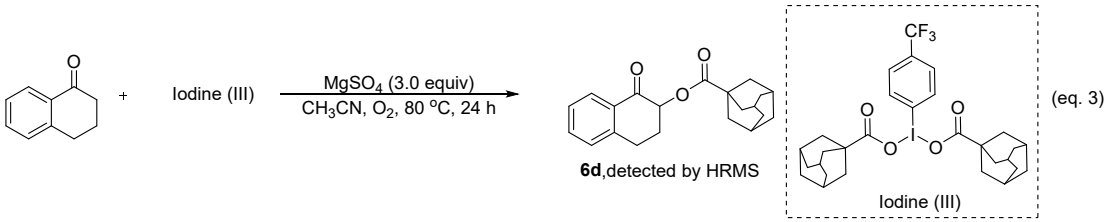
A 25 mL Schlenk tube equipped with a stir bar was charged with 1-tetralone (0.2 mmol), aniline (0.4 mmol), hypervalent iodine(III) compound (0.2 mmol), $MgSO_4$ (0.6 mmol) and 2.0 mL CH_3CN. The tube was fitted with a rubber septum, and then it was evacuated and refilled with dioxygen three times, then the septum was replaced by a Teflon screwcap under oxygen flow. 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), a large amount of 1-tetralone and aniline were remained, none of imine was detected by GC-MS, and only N-Phenyl-1-naphthylamine **6b** was detected by GC-MS, but only trace on the TLC plate.



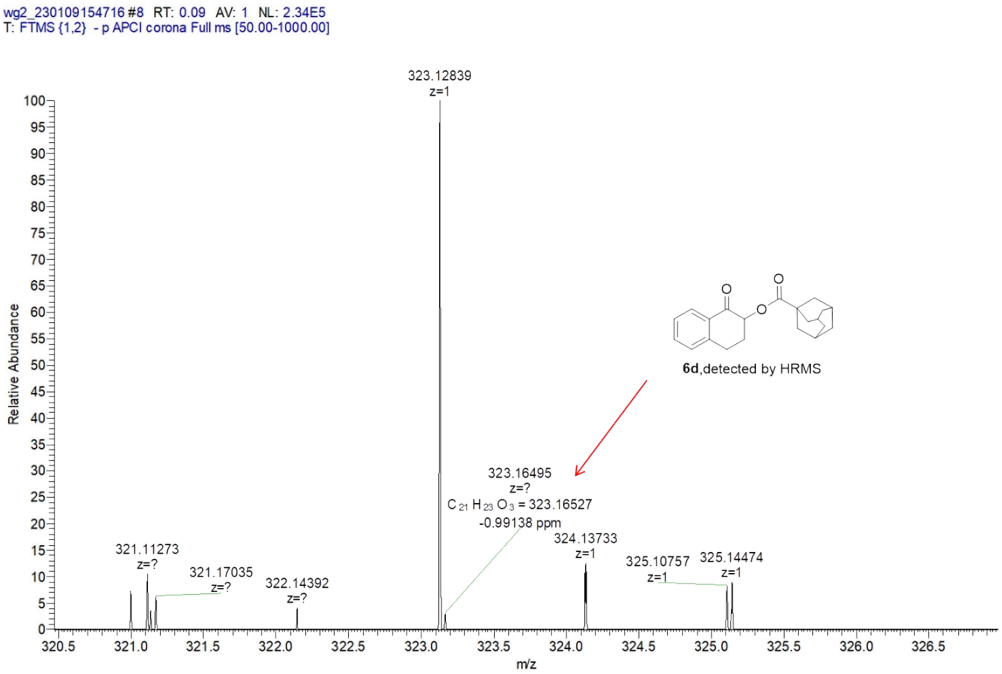
6c,detected by HRMS

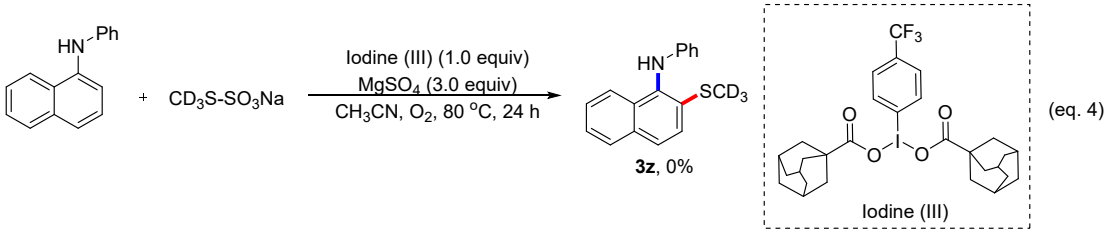
A 25 mL Schlenk tube equipped with a stir bar was charged with 1-tetralone (0.2 mmol), CD_3SSO_3Na (0.6 mmol), hypervalent iodine(III) compound (0.2 mmol), $MgSO_4$ (0.6 mmol) and 2.0 mL CH_3CN. The tube was fitted with a rubber septum, and then it was evacuated and refilled with dioxygen three times, then the septum was replaced by a Teflon screwcap under oxygen flow. 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), a large amount of 2-((methyl-d3)thio)-3,4-dihydronaphthalen-1(2H)-one was detected by TLC plate, and confirmed by HRMS. However, the polarity of remained 1-tetralone was similar to ortho-thiolated product, making it difficult to separate.





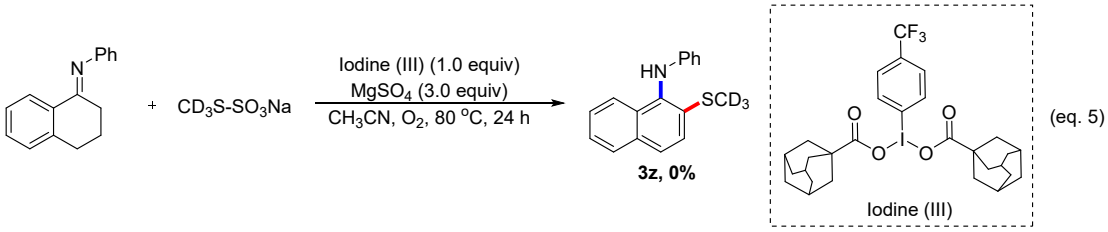
A 25 mL Schlenk tube equipped with a stir bar was charged with 1-tetralone (0.2 mmol), hypervalent iodine(III) compound (0.2 mmol), $MgSO_4$ (0.6 mmol) and 2.0 mL CH_3CN. The tube was fitted with a rubber septum, and then it was evacuated and refilled with dioxygen three times, then the septum was replaced by a Teflon screwcap under oxygen flow. 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), a large amount of 1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl adamantane-1-carboxylate was observed on TLC plate, and confirmed by HRMS. However, the polarity of remained 1-tetralone was similar to ortho- acetoxylated product, making it difficult to separate.





(eq. 4)

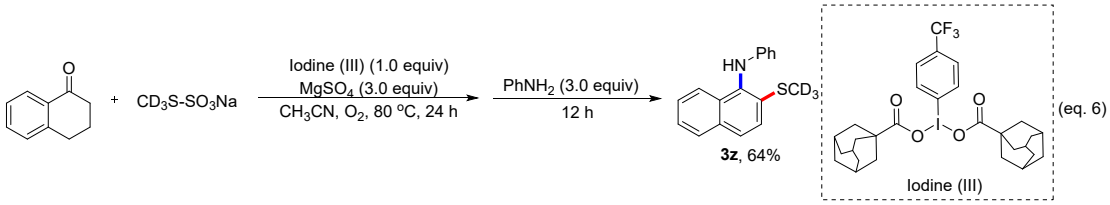
A 25 mL Schlenk tube equipped with a stir bar was charged with N-Phenyl-1-naphthylamine (0.2 mmol), CD_3SSO_3Na (0.6 mmol), hypervalent iodine(III) compound (0.2 mmol), $MgSO_4$ (0.6 mmol) and 2.0 mL CH_3CN. The tube was fitted with a rubber septum, and then it was evacuated and refilled with dioxygen three times, then the septum was replaced by a Teflon screwcap under oxygen flow. 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), N-Phenyl-1-naphthylamine almost completely remained, and no thiolation product **3z** was observed by TLC and HRMS.



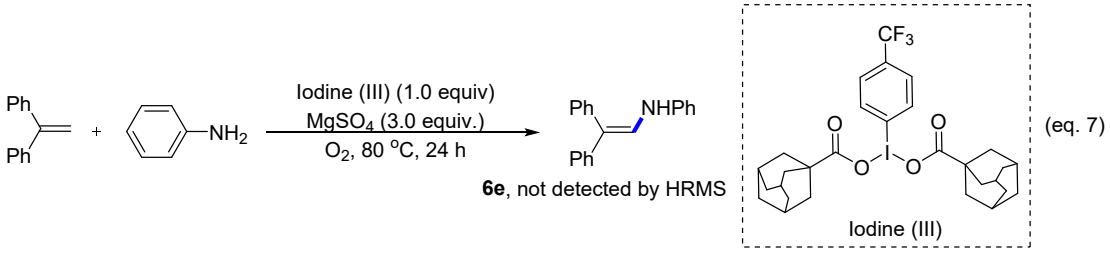
(eq. 5)

A 25 mL Schlenk tube equipped with a stir bar was charged with N-phenyl-3,4-dihydronaphthalen-1(2H)-imine (0.2 mmol), CD_3SSO_3Na (0.6 mmol), hypervalent iodine(III) compound (0.2 mmol), $MgSO_4$ (0.6 mmol) and 2.0 mL CH_3CN. The tube was fitted with a rubber septum, and then it was evacuated and refilled with dioxygen three times, then the septum was replaced by a Teflon screwcap under oxygen flow. The reaction mixture was stirred at 80 ℃ for

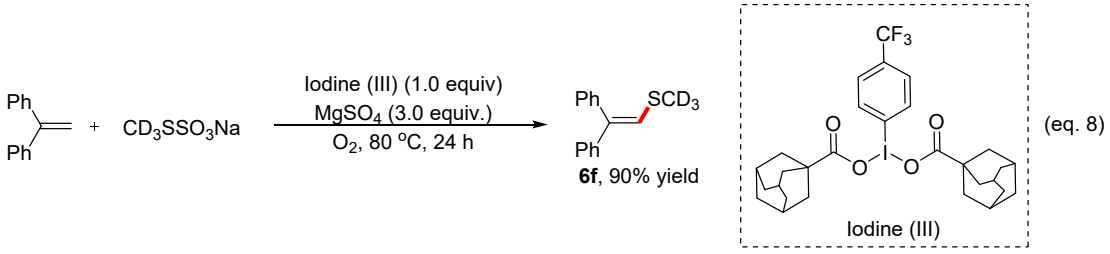
24 h. After the reaction mixture was cooled to room temperature and the reaction was filtered through a pad of Celite and diluted with ethyl acetate (10 mL), N-phenyl-3,4-dihydronaphthalen-1(2H)-imine almost completely remained, and no thiolation product **3z** was observed by TLC and HRMS.



A 25 mL Schlenk tube equipped with a stir bar was charged with 1-tetralone (0.2 mmol), CD_3SSO_3Na (0.6 mmol), hypervalent iodine(III) compound (0.2 mmol), $MgSO_4$ (0.6 mmol) and 2.0 mL CH_3CN. The tube was fitted with a rubber septum, and then it was evacuated and refilled with dioxygen three times, then the septum was replaced by a Teflon screwcap under oxygen flow. The reaction mixture was stirred at 80 ℃ for 24 h. After the reaction mixture was cooled to room temperature, the addition of aniline (0.4 mmol) into the reaction system, then continued heating at 80 ℃ for 12 h. Then, the reaction was filtered through a pad of Celite and diluted with ethyl acetate (10 mL), 64% of desired product **3z** was isolated.



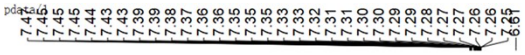
A 25 mL Schlenk tube equipped with a stir bar was charged with ethene-1,1-diyldibenzene (0.2 mmol), aniline (0.2 mmol), hypervalent iodine(III) compound (0.2 mmol), $MgSO_4$ (0.6 mmol) and 2.0 mL CH_3CN. The tube was fitted with a rubber septum, and then it was evacuated and refilled with dioxygen three times, then the septum was replaced by a Teflon screwcap under oxygen flow. 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), no amination product **6e** was observed by TLC and HRMS.

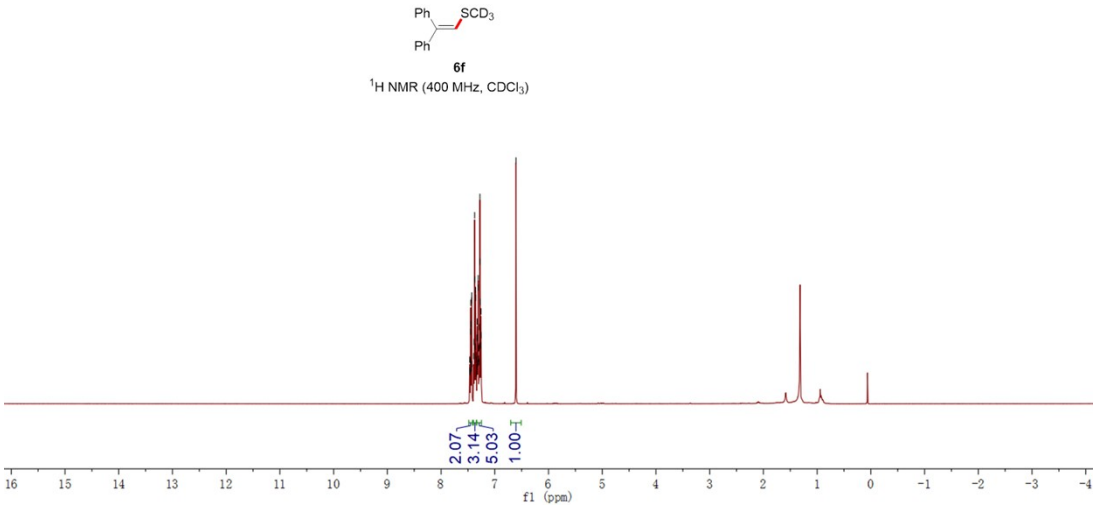


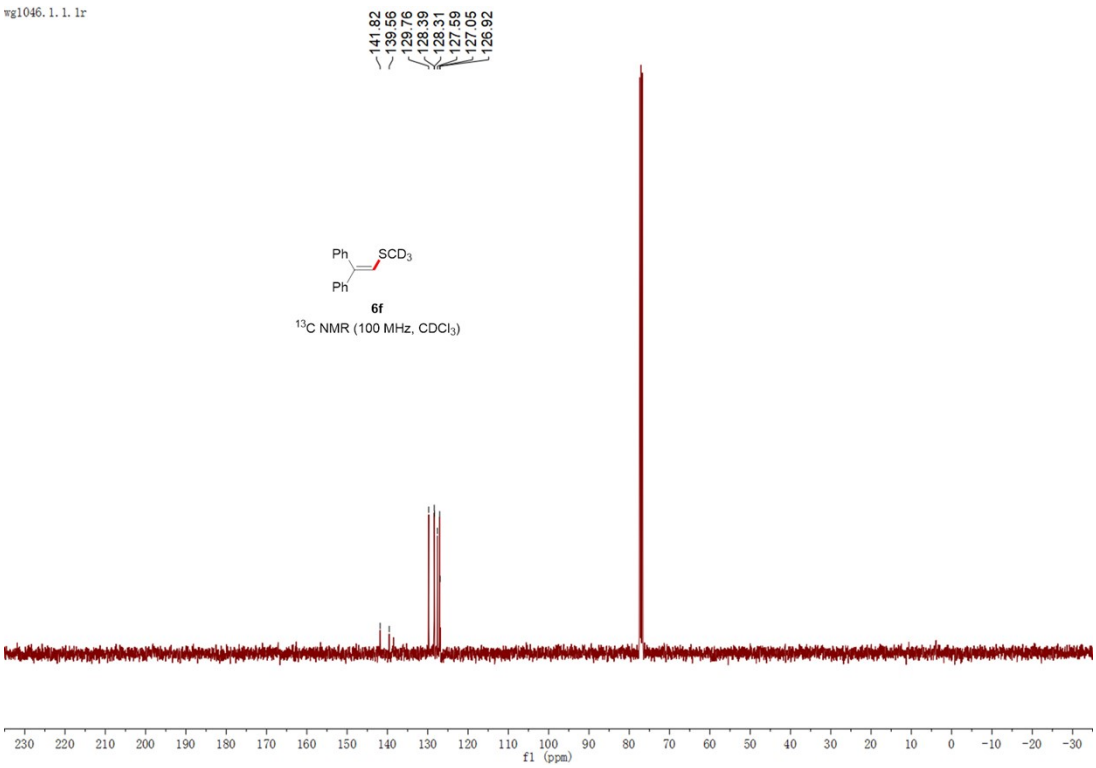
A 25 mL Schlenk tube equipped with a stir bar was charged with ethene-1,1-diyldibenzene (0.2 mmol), CD_3SSO_3Na (0.2 mmol), hypervalent iodine(III) compound (0.2 mmol), $MgSO_4$ (0.6

mmol) and 2.0 mL CH_3CN. The tube was fitted with a rubber septum, and then it was evacuated and refilled with dioxygen three times, then the septum was replaced by a Teflon screwcap under oxygen flow. 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), the corresponding thiolation product **6f** was isolated in 90% yield.

Using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (41.2 mg, 90% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.47-7.42 (m, 2H), 7.39-7.35 (m, 3H), 7.33-7.25 (m, 5H), 6.61 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 141.82, 139.56, 129.76, 128.39, 128.31, 127.59, 127.05, 126.92; **HRMS** (ESI): calcd for $C_{15}H_{11}D_3S$ $[M + H]^+$ 229.09990, found 229.10063.



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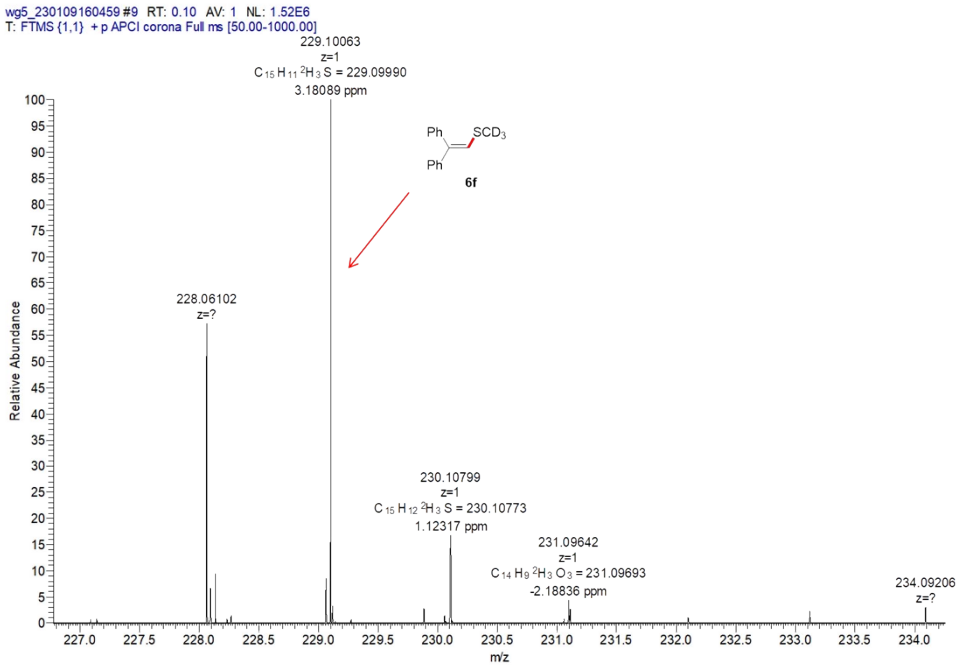
139.56
129.76
128.39
128.31
127.59
127.05
126.92
Ph
SCD3
Ph
6f
13C NMR (100 MHz, CDCl3)
f1 (ppm)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Ph
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Ph
6f
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z=?
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234.09206
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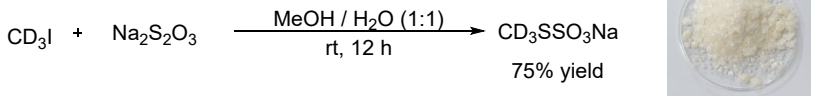
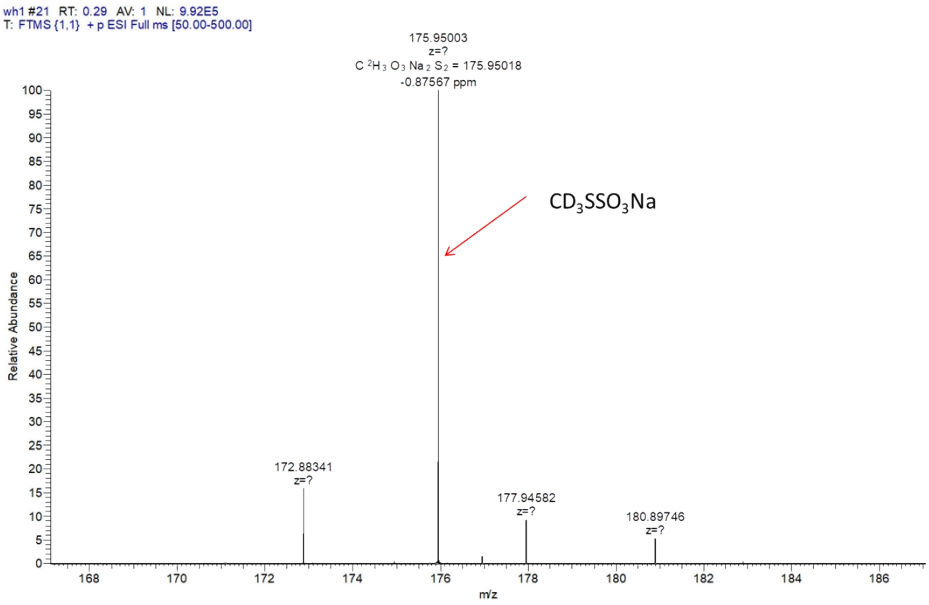
Relative Abundance
m/z

Synthesis of CD_3SSO_3Na reagent:



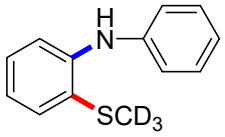
A flask was charged with deuterated iodomethane (60mmol), sodium thiosulfate (120 mmol), water (50.0 mL) and MeOH (100 mL). The reaction mixture was stirred at room temperature for 12 h. Then, the solution concentrated on a rotovap at a bath temperature of 50 ºC to remove the MeOH and water. The resultant solid was treated with MeOH (100mL), let it stand at room temperature for 6 hours, and filtered through a frit funnel. The filtrate was concentrated to a solid, trituration with hexanes, filtration, and drying under vacuum to give CD_3SSO_3Na reagent.

HRMS (ESI): calcd for $CD_3S_2O_3Na_2$ $[M + Na]^+$ 175.95018, found 175.95003.



Characterization of Products in Details :

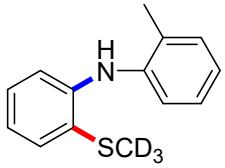
2-((methyl-d_3)thio)-N-phenylaniline



3a

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (38.8 mg, 89% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.51 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.37 (q, *J* = 8.5 Hz, 3H), 7.24-7.20 (m, 3H), 7.07 (t, *J* = 7.3 Hz, 1H), 6.93 (t, *J* = 8.1 Hz, 1H), 6.62 (brs, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.73, 142.62, 132.99, 129.48, 128.44, 124.22, 122.00, 120.66, 119.50, 115.40. **HRMS** (ESI): calcd for $C_{13}H_{11}D_3NS$ $[M + H]^+$ 219.1035, found 219.1026.

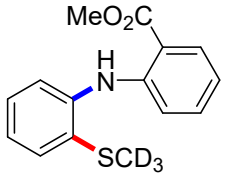
2-methyl-N-(2-((methyl-d_3)thio)phenyl)aniline



3b

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (41.8 mg, 90% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.30-7.21 (m, 2H), 7.11 (t, *J* = 7.3 Hz, 1H), 7.04 (d, *J* = 8.1 Hz, 1H), 6.91 (t, *J* = 7.4 Hz, 1H), 6.56 (brs, 1H), 2.39 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 144.78, 140.61, 133.38, 131.18, 130.48, 128.75, 126.94, 123.27, 123.02, 121.12, 119.87, 114.63, 18.10. **HRMS** (ESI): calcd for $C_{14}H_{13}D_3NS$ $[M + H]^+$ 233.1192, found 233.1187.

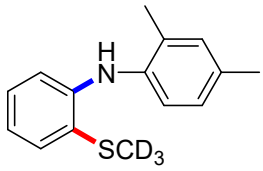
methyl 2-((2-((methyl- d_3)thio)phenyl)amino)benzoate



3c

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (45.3 mg, 82% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.55 (brs, 1H), 8.03-8.01 (m, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.38-7.33 (m, 2H), 7.17 (dq, *J* = 16.7, 7.3 Hz, 3H), 6.79 (t, *J* = 7.5 Hz, 1H), 3.97 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 168.84, 147.55, 139.14, 134.06, 132.27, 131.72, 128.31, 126.11, 124.32, 122.25, 117.54, 114.39, 112.64, 51.97. **HRMS** (ESI): calcd for $C_{15}H_{13}D_3NO_2S$ $[M + H]^+$ 277.1090, found 277.1097.

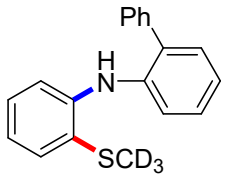
2,4-dimethyl-N-(2-((methyl-d3)thio)phenyl)aniline



3d

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (46.2 mg, 94% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.51 (dd, J = 7.7, 1.6 Hz, 1H), 7.22-7.14 (m, 3H), 7.07 (dd, J = 8.1, 2.1 Hz, 1H), 6.86-6.80 (m, 2H), 6.47 (brs, 1H), 2.39 (s, 3H), 2.30 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.73, 137.69, 133.66, 133.46, 131.83, 131.67, 128.89, 127.44, 122.85, 121.83, 119.05, 113.61, 20.91, 17.95; **HRMS** (ESI): calcd for $C_{15}H_{15}D_3NS$ $[M + H]^+$ 247.1348, found 247.1337.

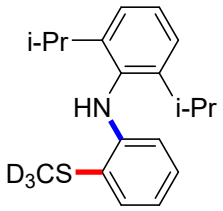
N-(2-((methyl- d_3)thio)phenyl)-[1,1'-biphenyl]-2-amine



3e

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (45.3 mg, 77% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.52-7.32 (m, 10H), 7.21 (td, *J* = 7.7, 1.6 Hz, 1H), 7.12 (td, *J* = 7.4, 1.3 Hz, 1H), 6.90 (td, *J* = 7.5, 1.4 Hz, 1H), 6.56 (brs, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.61, 139.61, 139.10, 133.16, 132.64, 131.01, 129.32, 128.82, 128.27, 128.25, 127.52, 124.98, 121.99, 120.69, 119.14, 115.55. **HRMS** (ESI): calcd for $C_{19}H_{15}D_3NS$ $[M + H]^+$ 295.1348, found 295.1348.

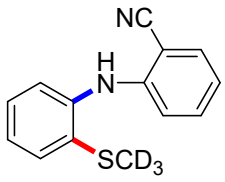
2,6-diisopropyl-N-(2-((methyl- d_3)thio)phenyl)aniline



3f

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow solid (48.9mg, 81% yield), Mp = 47-48℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.52 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.37 (dd, *J* = 8.7, 6.6 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.1-7.06(m, 1H), 6.72 (td, *J* = 7.5, 1.4 Hz, 1H), 6.44 (brs, 1H), 6.19 (dd, *J* = 8.2, 1.4 Hz, 1H), 3.17 (p, *J* = 6.9 Hz, 2H), 1.25 (d, *J* = 6.9 Hz, 6H), 1.18 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 148.45, 147.55, 135.36, 134.42, 129.51, 127.44, 123.94, 118.93, 117.60, 111.36, 28.45, 24.71, 23.02. **HRMS** (ESI): calcd for $C_{19}H_{23}D_3NS$ $[M + H]^+$ 303.1974, found 303.1963.

2-((2-((methyl- d_3)thio)phenyl)amino)benzonitrile

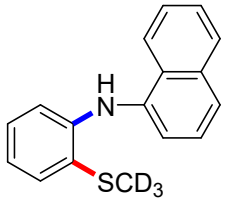


3g

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow solid (29.6 mg, 61% yield), Mp = 89-90℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.57 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.43 (ddd, *J* = 15.4, 8.2, 1.6 Hz, 2H), 7.34 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.24 (td, *J* =

7.6, 1.6 Hz, 1H), 7.19-7.11 (m, 2H), 6.93 (td, *J* = 7.6, 1.1 Hz, 1H), 6.83 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.79, 139.27, 133.92, 133.25, 130.56, 130.23, 127.27, 124.41, 120.50, 120.00, 117.47, 115.22, 99.82. **HRMS** (ESI): calcd for $C_{14}H_{10}D_3N_2S$ $[M + H]^+$ 244.0988, found 244.0982.

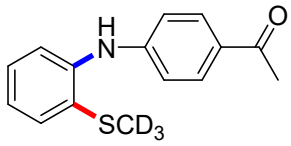
N-(2-((methyl- d_3)thio)phenyl)naphthalen-1-amine



3h

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (48.3 mg, 90% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.11-8.09 (m, 1H), 7.95-7.93 (m, 1H), 7.69 (dd, *J* = 7.4, 2.1 Hz, 1H), 7.59-7.45 (m, 5H), 7.18-7.13 (m, 1H), 7.07 (BRs, 1H), 6.98 (dd, *J* = 8.2, 1.4 Hz, 1H), 6.88 (td, *J* = 7.5, 1.4 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.68, 138.19, 134.85, 133.66, 128.89, 128.74, 128.62, 126.31, 126.09, 126.03, 124.01, 122.75, 122.32, 119.91, 118.01, 114.94. **HRMS** (ESI): calcd for $C_{17}H_{13}D_3NS$ $[M + H]^+$ 269.1192, found 269.1177.

1-(4-((2-((methyl- d_3)thio)phenyl)amino)phenyl)ethan-1-one

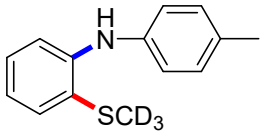


3i

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow solid (45.2 mg, 87% yield), Mp = 73-74℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.6 Hz, 2H), 7.42 (dd, *J* = 12.4, 8.0 Hz, 2H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.07 (dd, *J* = 16.6, 8.2 Hz, 3H), 6.64 (brs, 1H), 2.56 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 196.51, 148.09, 140.04, 130.89, 130.66, 129.50, 128.92, 127.50, 123.67, 119.85, 115.20, 26.27. **HRMS** (ESI): calcd for

$C_{15}H_{13}D_3NOS$ $[M + H]^+$ 261.1141, found 261.1152.

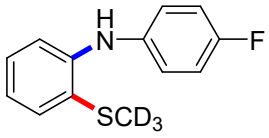
2-((methyl- d_3)thio)-N-(p-tolyl)aniline



3j

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (43.6 mg, 94% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.47 (dd, J = 7.7, 1.6 Hz, 1H), 7.22-7.15 (m, 4H), 7.12-7.09 (m, 2H), 6.86 (td, J = 7.3, 1.7 Hz, 1H), 6.56 (brs, 1H), 2.37 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 144.64, 139.75, 133.34, 131.97, 129.98, 128.61, 123.05, 120.57, 119.88, 114.39, 20.82; **HRMS** (ESI): calcd for $C_{14}H_{13}D_3NS$ $[M + H]^+$ 233.1192, found 233.1186.

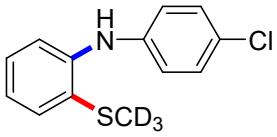
N-(4-fluorophenyl)-2-((methyl- d_3)thio)aniline



3k

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (37.3 mg, 79% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.51 (dd, J = 7.7, 1.6 Hz, 1H), 7.23-7.14 (m, 4H), 7.11-7.06 (m, 2H), 6.91 (td, J = 7.4, 1.6 Hz, 1H), 6.56 (brs, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.71 (d, J = 241.2 Hz), 144.58, 138.45 (d, J = 2.6 Hz), 133.20, 128.64, 123.36, 122.39 (d, J = 7.9 Hz), 120.33, 116.14 (d, J = 22.5 Hz), 114.33. **^{19}F NMR** (375 MHz, $CDCl_3$) δ -120.49 (1F); **HRMS** (ESI): calcd for $C_{13}H_{10}D_3NFS$ $[M + H]^+$ 237.0941, found 237.0939.

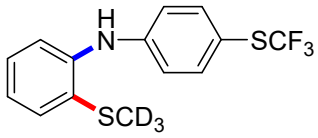
N-(4-chlorophenyl)-2-((methyl- d_3)thio)aniline



3l

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (42.3 mg, 84% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.48 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.31-7.21 (m, 4H), 7.10 (d, *J* = 8.8 Hz, 2H), 6.95 (td, *J* = 7.4, 1.6 Hz, 1H), 6.52 (brs, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.03, 141.36, 132.66, 129.44, 128.33, 126.52, 124.95, 121.29, 120.35, 115.83. **HRMS** (ESI): calcd for $C_{13}H_{10}D_3NSCl$ $[M + H]^+$ 253.0646, found 253.0645.

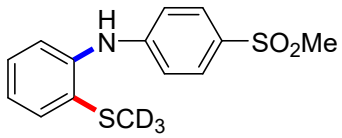
2-((methyl- d_3)thio)-N-(4-((trifluoromethyl)thio)phenyl)aniline



3m

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (54.0 mg, 85% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.2 Hz, 2H), 7.48 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.25 (t, *J* = 7.7 Hz, 1H), 7.12-7.04 (m, 3H), 6.53 (brs, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.00, 140.81, 138.23, 131.53, 129.76 (q, *J* = 308.4 Hz), 127.78, 127.69, 123.01, 118.58, 117.31, 113.90. **^{19}F NMR** (375 MHz, $CDCl_3$) δ -43.92 (3F); **HRMS** (ESI): calcd for $C_{14}H_{10}D_3NF_3S_2$ $[M + H]^+$ 319.0630, found 319.0621.

2-((methyl- d_3)thio)-N-(4-(methylsulfonyl)phenyl)aniline

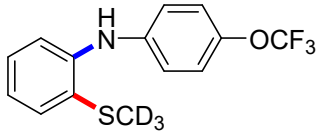


3n

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow solid (46.8 mg, 79% yield), Mp = 96-97℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.26 (t, *J* = 7.7 Hz, 1H), 7.12 (dd, *J* =

19.3, 7.8 Hz, 3H), 6.55 (brs, 1H), 3.07 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 148.69, 139.25, 130.64, 130.51, 129.90, 129.45, 127.38, 124.42, 120.59, 115.32, 44.97. **HRMS** (ESI): calcd for $C_{14}H_{13}D_3NO_2S_2$ $[M + H]^+$ 297.0811, found297.0802.

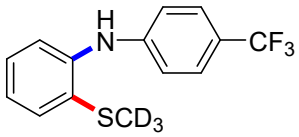
2-((methyl- d_3)thio)-N-(4-(trifluoromethoxy)phenyl)aniline



3o

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (48.9 mg, 81% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.51 (d, J = 7.7 Hz, 1H), 7.30 (d, J = 7.9 Hz, 1H), 7.25-7.15 (m, 5H), 6.98 (t, J = 7.5 Hz, 1H), 6.56 (brs, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.52, 142.91, 141.64, 132.55, 128.29, 125.22, 122.44, 121.49, 120.74 (q, J = 226.4 Hz), 119.75, 116.02. **^{19}F NMR** (375 MHz, $CDCl_3$) δ -58.16 (3F); **HRMS** (ESI): calcd for $C_{14}H_{10}D_3NOF_3S$ $[M + H]^+$ 303.0858, found 303.0845.

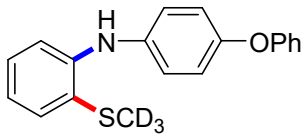
2-((methyl- d_3)thio)-N-(4-(trifluoromethyl)phenyl)aniline



3p

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow solid (40.0 mg, 70% yield), Mp = 41-42℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.57 (d, J = 8.4 Hz, 2H), 7.50 (dd, J = 7.8, 1.6 Hz, 1H), 7.41 (dd, J = 8.2, 1.4 Hz, 1H), 7.27 (td, J = 7.6, 1.6 Hz, 1H), 7.15 (d, J = 8.4 Hz, 2H), 7.08 (td, J = 7.5, 1.4 Hz, 1H), 6.52 (brs, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.44, 140.91, 131.50, 128.75, 127.79, 126.81 (q, J = 3.7 Hz), 124.71(q, J = 269.6 Hz) 123.06, 122.34 (q, J = 32.4 Hz), 118.60, 116.39. **^{19}F NMR** (375 MHz, $CDCl_3$) δ -61.37 (3F); **HRMS** (ESI): calcd for $C_{14}H_{10}D_3NF_3S$ $[M + H]^+$ 287.0909, found 287.0910.

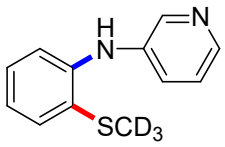
2-((methyl- d_3)thio)-N-(4-phenoxyphenyl)aniline



3q

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (49.6 mg, 80% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.20-7.17 (m, 4H), 7.12 (t, *J* = 7.3 Hz, 1H), 7.05 (t, *J* = 7.1 Hz, 4H), 6.87 (dt, *J* = 8.2, 4.3 Hz, 1H), 6.58 (brs, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.06, 152.15, 144.63, 138.04, 133.28, 129.78, 128.64, 123.07, 122.88, 122.19, 120.46, 120.07, 118.22, 114.25. **HRMS** (ESI): calcd for $C_{19}H_{15}D_3NOS$ $[M + H]^+$ 311.1297, found 311.1284.

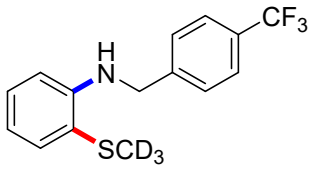
N-(2-((methyl- d_3)thio)phenyl)pyridin-3-amine



3r

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow solid (39.0 mg, 89% yield), Mp = 103-104℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.49 (s, 1H), 8.26 (s, 1H), 7.47 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.26-7.20 (m, 3H), 6.97 (td, *J* = 7.4, 1.6 Hz, 1H), 6.53 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 142.73, 142.23, 141.34, 139.35, 132.48, 128.24, 125.72, 125.16, 123.86, 121.94, 116.01. **HRMS** (ESI): calcd for $C_{12}H_{10}D_3N_2S$ $[M + H]^+$ 220.0988, found 220.0978.

2-((methyl- d_3)thio)-N-(4-(trifluoromethyl)benzyl)aniline

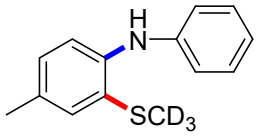


3s

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (32.4 mg, 54% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.1 Hz, 2H), 7.51

(d, J = 8.0 Hz, 2H), 7.46 (dd, J = 7.6, 1.4 Hz, 1H), 7.16 (td, J = 7.7, 1.6 Hz, 1H), 6.73 (td, J = 7.5, 1.3 Hz, 1H), 6.53 (dd, J = 8.2, 1.3 Hz, 1H), 5.49 (brs, 1H), 4.53 (d, J = 4.7 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 147.70, 143.59, 134.08, 129.46, 129.37, 127.33, 127.23, 125.69(q, J = 3.8 Hz), 121.49(d, J = 280.0 Hz), 117.76, 110.45, 47.61. **^{19}F NMR** (375 MHz, $CDCl_3$) δ -62.38 (3F); **HRMS** (ESI): calcd for $C_{15}H_{12}D_3NF_3S$ $[M + H]^+$ 301.1066, found 301.1072.

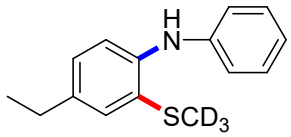
4-methyl-2-((methyl- d_3)thio)-N-phenylaniline



3t

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (40.8 mg, 88% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.35-7.30 (m, 3H), 7.26-7.24 (m, 1H), 7.14-7.12 (m, 2H), 7.04-6.98 (m, 2H), 6.37 (brs, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.38, 140.61, 132.70, 130.71, 129.43, 128.77, 125.32, 121.20, 118.33, 116.81, 20.68. **HRMS** (ESI): calcd for $C_{14}H_{13}D_3NS$ $[M + H]^+$ 233.1192, found 233.1190.

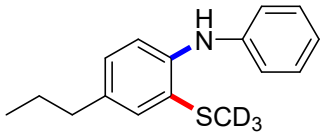
4-ethyl-2-((methyl- d_3)thio)-N-phenylaniline



3u

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (39.9 mg, 81% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.37-7.33 (m, 3H), 7.29 (d, J = 8.2 Hz, 1H), 7.17-7.15 (m, 2H), 7.07 (dd, J = 8.2, 2.1 Hz, 1H), 7.01 (t, J = 7.3 Hz, 1H), 6.40 (brs, 1H), 2.66 (q, J = 7.6 Hz, 2H), 1.31 (t, J = 7.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.32, 140.96, 137.17, 131.79, 129.44, 127.70, 125.06, 121.28, 118.48, 116.64, 28.20, 15.86. **HRMS** (ESI): calcd for $C_{15}H_{15}D_3NS$ $[M + H]^+$ 247.1348, found 247.1346.

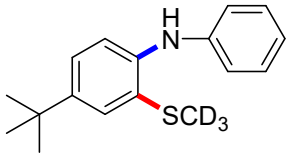
2-((methyl- d_3)thio)-N-phenyl-4-propylaniline



3v

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (42.6 mg, 82% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.35-7.25 (m, 4H), 7.15-7.13 (m, 2H), 7.04-6.97 (m, 2H), 6.41 (brs, 1H), 2.57 (t, *J* = 7.7 Hz, 2H), 1.68 (h, *J* = 7.4 Hz, 2H), 1.01 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.28, 140.93, 135.59, 132.32, 129.41, 128.25, 124.90, 121.25, 118.47, 116.45, 37.34, 24.76, 13.91. **HRMS** (ESI): calcd for $C_{16}H_{17}D_3NS$ $[M + H]^+$ 261.1505, found 261.1506.

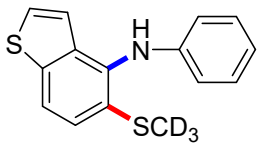
4-(tert-butyl)-2-((methyl- d_3)thio)-N-phenylaniline



3w

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow solid (46.6 mg, 85% yield), Mp = 54-55℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 2.2 Hz, 1H), 7.37-7.24 (m, 4H), 7.18-7.16 (m, 2H), 7.01 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.52 (brs, 1H), 1.37 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.79, 143.09, 141.17, 130.16, 129.41, 125.60, 123.86, 121.43, 118.80, 115.65, 34.32, 31.50. **HRMS** (ESI): calcd for $C_{17}H_{19}D_3NS$ $[M + H]^+$ 275.1661, found 275.1672.

5-((methyl- d_3)thio)-N-phenylbenzo[b]thiophen-4-amine

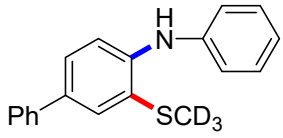


3x

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow solid (37.3 mg, 68% yield), Mp = 88-89℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.4

Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.34 (d, *J* = 5.5 Hz, 1H), 7.26 (t, *J* = 7.7 Hz, 2H), 7.06 (d, *J* = 5.6 Hz, 1H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 2H), 6.54 (brs, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.30, 140.64, 137.51, 134.40, 129.23, 128.21, 125.99, 125.18, 123.10, 120.65, 118.21, 116.91. **HRMS** (ESI): calcd for $C_{15}H_{11}D_3NS_2$ $[M + H]^+$ 275.0756, found 275.0764.

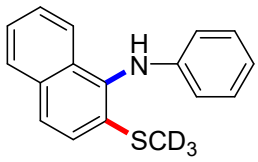
3-((methyl- d_3)thio)-N-phenyl-[1,1'-biphenyl]-4-amine



3y

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (51.1 mg, 92% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.79-7.78 (m, 1H), 7.63 (d, *J* = 7.4 Hz, 2H), 7.51-7.46 (m, 3H), 7.42-7.38 (m, 4H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.71 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.15, 142.38, 140.55, 133.52, 131.77, 129.54, 128.89, 127.25, 126.84, 126.58, 124.29, 122.21, 119.74, 115.33. **HRMS** (ESI): calcd for $C_{19}H_{15}D_3NS$ $[M + H]^+$ 295.1348, found 295.1355.

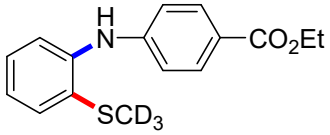
2-((methyl- d_3)thio)-N-phenylnaphthalen-1-amine



3z

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (38.1 mg, 71% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 8.7 Hz, 1H), 7.56 (d, *J* = 8.7 Hz, 1H), 7.50-7.43 (m, 2H), 7.21 (t, *J* = 7.7 Hz, 2H), 6.86 (t, *J* = 7.4 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 2H), 6.00 (brs, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.71, 135.54, 132.88, 131.71, 130.56, 129.27, 128.32, 126.63, 126.26, 125.74, 125.71, 124.06, 119.44, 114.98. **HRMS** (ESI): calcd for $C_{17}H_{13}D_3NS$ $[M + H]^+$ 269.1192, found 269.1199.

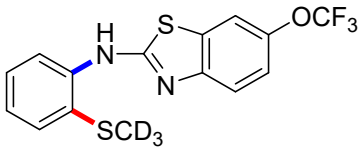
ethyl 4-((2-((methyl- d_3)thio)phenyl)amino)benzoate



4a

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow solid (46.4 mg, 80% yield), Mp = 63-64℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.99 (d, J = 8.5 Hz, 2H), 7.43 (dd, J = 17.6, 7.9 Hz, 2H), 7.24 (t, J = 7.7 Hz, 1H), 7.06 (dd, J = 13.1, 7.5 Hz, 3H), 6.60 (brs, 1H), 4.38 (q, J = 7.1 Hz, 2H), 1.41 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.53, 147.54, 140.66, 131.47, 131.41, 127.98, 127.71, 123.12, 122.20, 118.99, 115.59, 60.57, 14.51. **HRMS** (ESI): calcd for $C_{16}H_{15}D_3NO_2S$ $[M + H]^+$ 291.1247, found 291.1246.

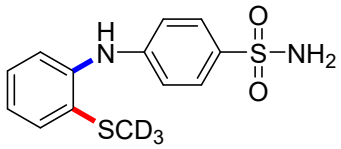
N-(2-((methyl- d_3)thio)phenyl)-6-(trifluoromethoxy)benzo[d]thiazol-2-amine



4b

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow solid (55.3 mg, 77% yield), Mp = 133-134℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.27 (d, J = 8.1 Hz, 2H), 7.69 (d, J = 8.8 Hz, 1H), 7.57-7.55 (m, 2H), 7.41 (t, J = 7.8 Hz, 1H), 7.27 (d, J = 8.8 Hz, 1H), 7.15 (t, J = 7.5 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 163.54, 153.16, 150.75, 144.59, 139.52, 132.84, 131.23, 128.93, 126.51, 124.43, 120.50, 119.96, 119.62, 113.95. **^{19}F NMR** (375 MHz, $CDCl_3$) δ -58.14 (3F); **HRMS** (ESI): calcd for $C_{15}H_9D_3N_2OF_3S_2$ $[M + H]^+$ 360.0531, found 360.0530.

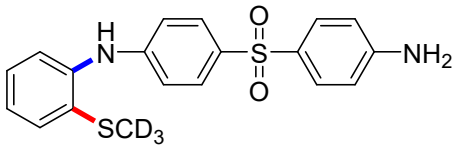
4-((2-((methyl- d_3)thio)phenyl)amino)benzenesulfonamide



4c

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (50.5 mg, 85% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.11 (s, 1H), 7.59 (d, *J* = 8.7 Hz, 2H), 7.36-7.34 (m, 1H), 7.26-7.20 (m, 1H), 7.05 (s, 2H), 6.78 (d, *J* = 8.8 Hz, 2H), 3.39 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.33, 138.33, 135.39, 133.14, 127.82, 126.78, 126.21, 126.04, 125.37, 113.73. **HRMS** (ESI): calcd for $C_{13}H_{12}D_3N_2O_2S_2$ $[M + H]^+$ 298.0763, found 298.0774.

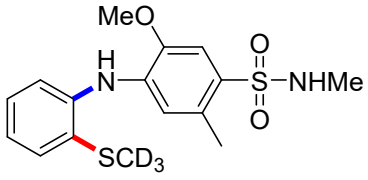
N-(4-((4-aminophenyl)sulfonyl)phenyl)-2-((methyl- d_3)thio)aniline



4d

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow solid (62.7 mg, 84% yield), Mp = 135-136℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.7 Hz, 2H), 7.71 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.22 (t, *J* = 7.7 Hz, 1H), 7.09-7.02 (m, 3H), 6.67 (d, *J* = 8.6 Hz, 2H), 6.51 (brs, 1H), 4.16 (q, *J* = 7.2 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ δ 150.84, 147.56, 139.79, 133.21, 130.85, 130.58, 129.46, 129.14, 129.04, 127.49, 123.86, 119.85, 115.64, 114.23. **HRMS** (ESI): calcd for $C_{19}H_{16}D_3N_2O_2S_2$ $[M + H]^+$ 374.1076, found 374.1086.

5-methoxy-N,2-dimethyl-4-((2-((methyl- d_3)thio)phenyl)amino)benzenesulfonamide

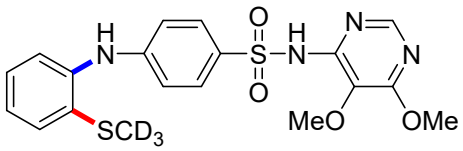


4e

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow solid (48.3 mg, 68% yield), Mp = 120-121℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.51 (s, 1H), 7.43 (ddd, *J* = 7.8, 4.0, 1.5 Hz, 2H), 7.26 (td, *J* = 7.7, 1.6 Hz, 1H), 7.10 (td, *J* = 7.5, 1.3 Hz, 1H), 7.02 (s, 1H), 6.85 (brs, 1H), 4.56 (q, *J* = 5.5 Hz, 1H), 4.00 (s, 3H), 2.65 (d, *J* = 5.5 Hz, 3H), 2.52 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.10, 139.43, 137.45, 130.86, 130.11, 129.96, 127.11,

125.27, 123.79, 120.37, 115.50, 112.36, 56.31, 29.06, 19.92. **HRMS** (ESI): calcd for $C_{16}H_{17}D_3N_2O_3NaS_2$ $[M + Na]^+$ 378.1001, found 378.1007.

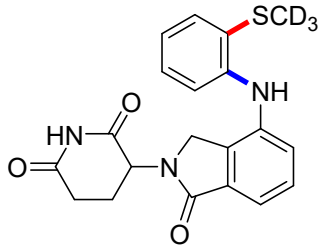
N-(5,6-dimethoxypyrimidin-4-yl)-4-((2-((methyl- d_3)thio)phenyl)amino)benzenesulfonamide



4f

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (44.4 mg, 51% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.23 (s, 1H), 8.04 (d, J = 8.7 Hz, 2H), 7.79 (s, 1H), 7.44 (d, J = 7.7 Hz, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.25 (t, J = 7.6 Hz, 1H), 7.11 (t, J = 7.6 Hz, 1H), 7.06 (d, J = 8.7 Hz, 2H), 6.54 (brs, 1H), 4.02 (s, 3H), 3.89 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 160.86, 151.22, 150.11, 148.37, 139.42, 130.69, 129.40, 129.22, 127.44, 126.38, 124.16, 120.23, 114.81, 110.46, 60.60, 54.17. **HRMS** (ESI): calcd for $C_{19}H_{17}D_3N_4O_4NaS_2$ $[M + Na]^+$ 458.1012, found 458.1017.

3-(4-((2-((methyl- d_3)thio)phenyl)amino)-1-oxoisoindolin-2-yl)piperidine-2,6-dione

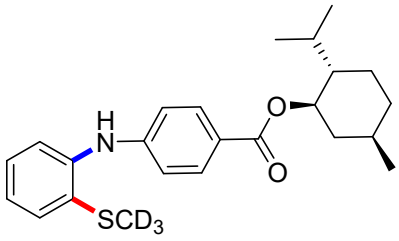


4g

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (68.4 mg, 89% yield). **^{1}H NMR** (400 MHz, DMSO-d_6): δ 11.03 (s, 1H), 7.54 (s, 1H), 7.36-7.32 (m, 2H), 7.22-7.16 (m, 3H), 7.10-7.08 (m, 1H), 6.81 (d, J = 7.9 Hz, 1H), 5.14 (dd, J = 13.3, 5.1 Hz, 1H), 4.27 (q, J = 17.2 Hz, 2H), 2.97-2.88 (m, 1H), 2.65-2.60 (m, 1H), 2.35 (qd, J = 13.1, 4.4 Hz, 1H), 2.08-2.01 (m, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6): δ 173.43, 171.71, 168.94, 141.02, 139.76, 133.59, 133.32, 129.92, 129.49, 127.35, 126.27, 125.11, 123.80, 118.70, 114.45,

52.11, 46.54, 31.76, 23.16. **HRMS** (ESI): calcd for $C_{20}H_{16}D_3N_3O_3NaS$ $[M + Na]^+$ 407.1233, found 407.1236.

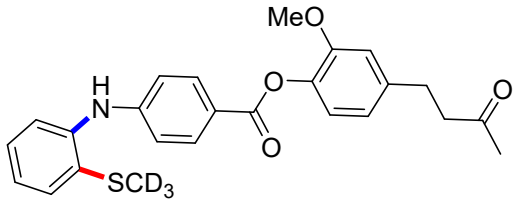
(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 4-((2-((methyl- d_3)thio)phenyl)amino)benzoate



4h

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (49.6 mg, 62% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.7 Hz, 2H), 7.44 (ddd, *J* = 17.1, 7.9, 1.5 Hz, 2H), 7.24 (td, *J* = 7.7, 1.6 Hz, 1H), 7.10-7.03 (m, 3H), 6.62 (s, 1H), 4.95 (td, *J* = 10.9, 4.3 Hz, 1H), 2.19-2.15 (m, 1H), 2.02 (td, *J* = 7.0, 2.6 Hz, 1H), 1.78-1.75 (m, 2H), 1.58 (ddt, *J* = 13.9, 10.7, 3.1 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 1H), 1.20-1.11 (m, 2H), 0.96 (dd, *J* = 6.9, 2.8 Hz, 6H), 0.85 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.99, 147.49, 140.68, 131.49, 131.39, 128.01, 127.71, 123.12, 122.55, 119.02, 115.60, 74.31, 47.41, 41.18, 34.46, 31.52, 26.60, 23.78, 22.18, 20.88, 16.69. **HRMS** (ESI): calcd for $C_{24}H_{28}D_3NO_2NaS$ $[M + Na]^+$ 423.2161, found 423.2158.

2-methoxy-4-(3-oxobutyl)phenyl 4-((2-((methyl- d_3)thio)phenyl)amino)benzoate

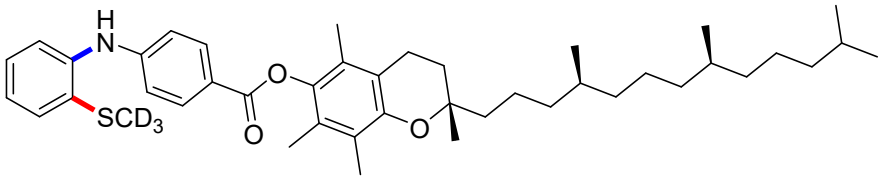


4i

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow solid (69.2 mg, 79% yield), Mp = 102-103℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8.7 Hz, 2H), 7.45 (t, *J* = 8.3 Hz, 2H), 7.26 (t, *J* = 7.7 Hz, 1H), 7.09 (dd, *J* = 11.8, 8.4 Hz, 4H), 6.87 (brs, 1H), 6.82 (d, *J* = 9.5 Hz, 1H), 6.64 (s, 1H), 3.83 (s, 3H), 2.94 (t, *J* = 7.4 Hz, 2H), 2.82 (t, *J* =

7.4 Hz, 2H), 2.20 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 208.00, 164.75, 151.35, 148.27, 140.24, 139.89, 138.48, 132.35, 131.14, 128.62, 127.63, 123.54, 123.02, 120.73, 120.43, 119.61, 115.40, 112.85, 55.99, 45.28, 30.22, 29.72. **HRMS** (ESI): calcd for $C_{25}H_{22}D_3NO_4NaS$ $[M + Na]^+$ 461.1590, found 461.1596.

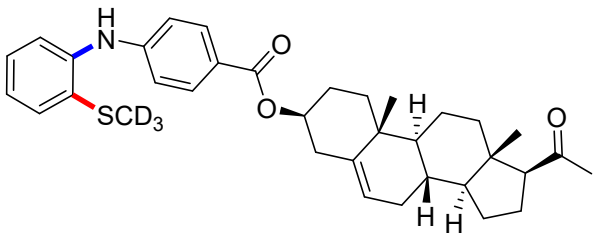
(S)-2,5,7,8-tetramethyl-2-((4S,8S)-4,8,12-trimethyltridecyl)chroman-6-yl 4-((2-((methyl-d_3)thio)phenyl)amino)benzoate



4j

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow liquid (118.7 mg, 88% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.21 (d, J = 8.7 Hz, 2H), 7.49 (ddd, J = 8.2, 4.1, 1.4 Hz, 2H), 7.31-7.29 (m, 1H), 7.16-7.09 (m, 3H), 6.66 (brs, 1H), 2.68 (t, J = 6.9 Hz, 2H), 2.19 (s, 3H), 2.13 (s, 3H), 2.09 (s, 3H), 1.87 (dtd, J = 20.1, 13.0, 6.3 Hz, 2H), 1.61 (dq, J = 19.9, 6.4 Hz, 4H), 1.46 (dq, J = 10.1, 5.3, 4.8 Hz, 4H), 1.38-1.32 (m, 11H), 1.24-1.12 (m, 7H), 0.94 (d, J = 6.6 Hz, 10H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.05, 148.23, 140.32, 132.23, 131.23, 128.59, 127.67, 127.20, 125.39, 123.53, 123.10, 121.03, 119.59, 117.49, 115.49, 75.11, 40.49, 39.74, 39.48, 37.56, 37.39, 32.90, 31.39, 28.08, 24.92, 24.56, 24.29, 23.82, 22.84, 22.75, 21.14, 20.74, 19.87, 19.78, 13.18, 12.33, 11.96. **HRMS** (ESI): calcd for $C_{43}H_{58}D_3NO_3NaS$ $[M + Na]^+$ 697.4458, found 697.4464.

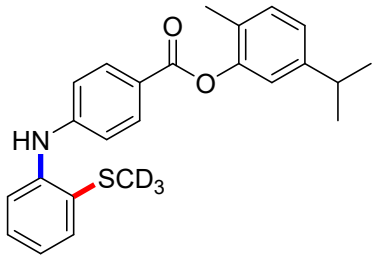
(3S,8S,9S,10R,13S,14S,17S)-17-acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-((2-((methyl- d_3)thio)phenyl)amino)benzoate



4k

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow solid (84.0 mg, 75% yield), Mp = 153-154℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.7 Hz, 2H), 7.45 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.40 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.23 (td, *J* = 7.7, 1.5 Hz, 1H), 7.08-7.02 (m, 3H), 6.60 (brs, 1H), 5.44 (d, *J* = 4.9 Hz, 1H), 4.89-4.83 (m, 1H), 2.58 (t, *J* = 8.9 Hz, 1H), 2.49 (d, *J* = 7.6 Hz, 2H), 2.23-2.21 (m, 1H), 2.16 (s, 3H), 2.11-1.92 (m, 4H), 1.81-1.50 (m, 8H), 1.32-1.19 (m, 4H), 1.10-1.09 (m, 4H), 0.67 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 209.74, 165.89, 147.48, 140.66, 139.89, 131.48, 131.41, 127.92, 127.71, 123.10, 122.39, 118.91, 115.59, 73.98, 63.76, 56.91, 49.96, 44.08, 38.87, 38.34, 37.14, 36.74, 31.90, 31.87, 31.66, 28.00, 24.56, 22.88, 21.13, 19.46, 13.31. **HRMS** (ESI): calcd for $C_{35}H_{40}D_3NO_3NaS$ $[M + Na]^+$ 583.3050, found 583.3063.

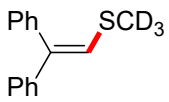
5-isopropyl-2-methylphenyl 4-((2-((methyl- d_3)thio)phenyl)amino)benzoate



4l

Following the general procedure, using (petroleum ether : EtOAc = 9 : 1) as the eluant afforded a yellow solid (48.1 mg, 61% yield), Mp = 99-100℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 8.8 Hz, 2H), 7.48 (ddd, *J* = 7.3, 5.5, 1.5 Hz, 2H), 7.31-7.23 (m, 2H), 7.16-7.09 (m, 4H), 6.66 (brs, 1H), 2.96 (p, *J* = 6.9 Hz, 1H), 2.25 (s, 3H), 1.31 (d, *J* = 7.0 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 164.81, 149.72, 148.37, 148.11, 140.17, 132.25, 131.11, 130.95, 128.76, 127.63, 124.05, 123.65, 120.86, 120.16, 119.73, 115.41, 33.70, 24.06, 16.00. **HRMS** (ESI): calcd for $C_{24}H_{22}D_3NO_2SNa$ $[M + Na]^+$ 417.1692, found 417.1697.

(2,2-diphenylvinyl)(methyl-d3)sulfane



6f

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

yellow solid (48.1 mg, 95% yield), Mp = 99-100℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 8.8 Hz, 2H), 7.48 (ddd, *J* = 7.3, 5.5, 1.5 Hz, 2H), 7.31-7.23 (m, 2H), 7.16-7.09 (m, 4H), 6.66 (brs, 1H), 2.96 (p, *J* = 6.9 Hz, 1H), 2.25 (s, 3H), 1.31 (d, *J* = 7.0 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 164.81, 149.72, 148.37, 148.11, 140.17, 132.25, 131.11, 130.95, 128.76, 127.63, 124.05, 123.65, 120.86, 120.16, 119.73, 115.41, 33.70, 24.06, 16.00. **HRMS** (ESI): calcd for $C_{24}H_{22}D_3NO_2SNa$ $[M + Na]^+$ 417.1692, found 417.1697.

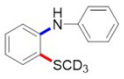
References:

(1) AtmuriOrcid, N. D. P., Reilley, D. J., D. Lubell, W. Org. Lett. 2017, 19, 19, 5066–5069

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

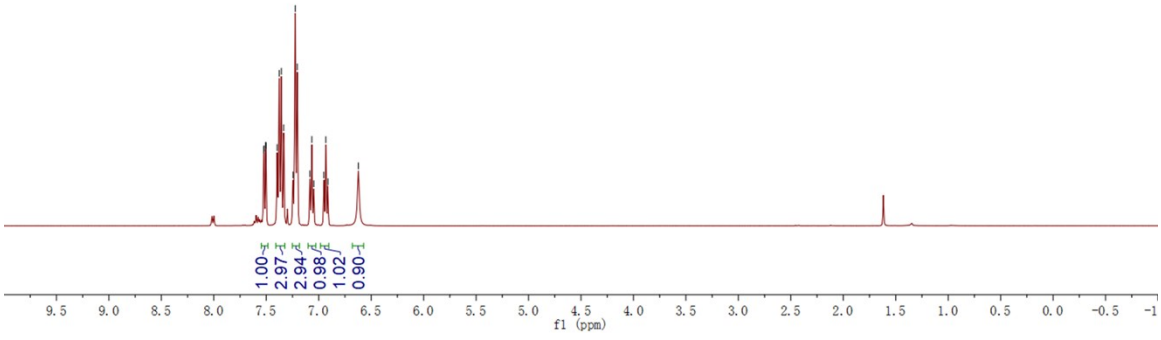
wgl128.1.1.1r

7.52
7.52
7.51
7.50
7.40
7.38
7.36
7.33
7.24
7.22
7.20
7.08
7.07
7.05
6.95
6.93
6.91
6.62



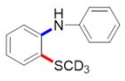
3a

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



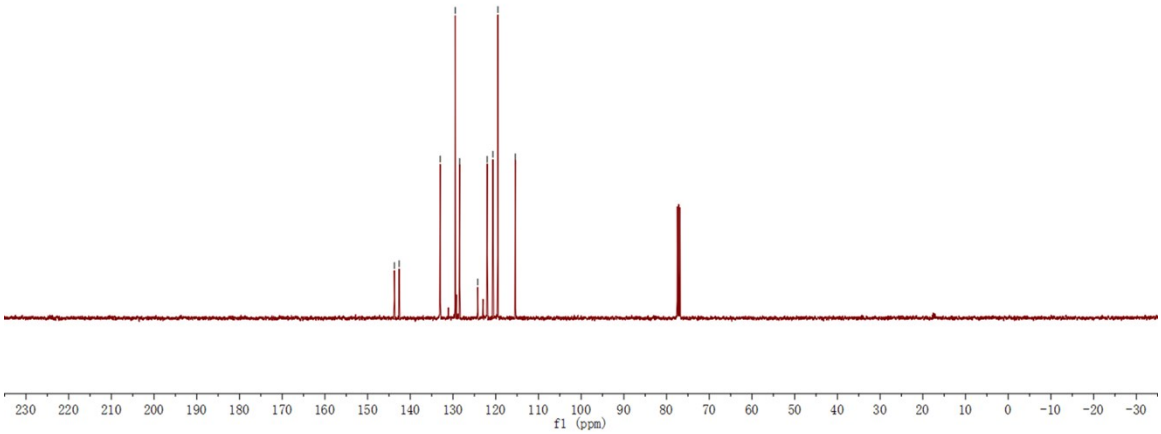
pdata/1

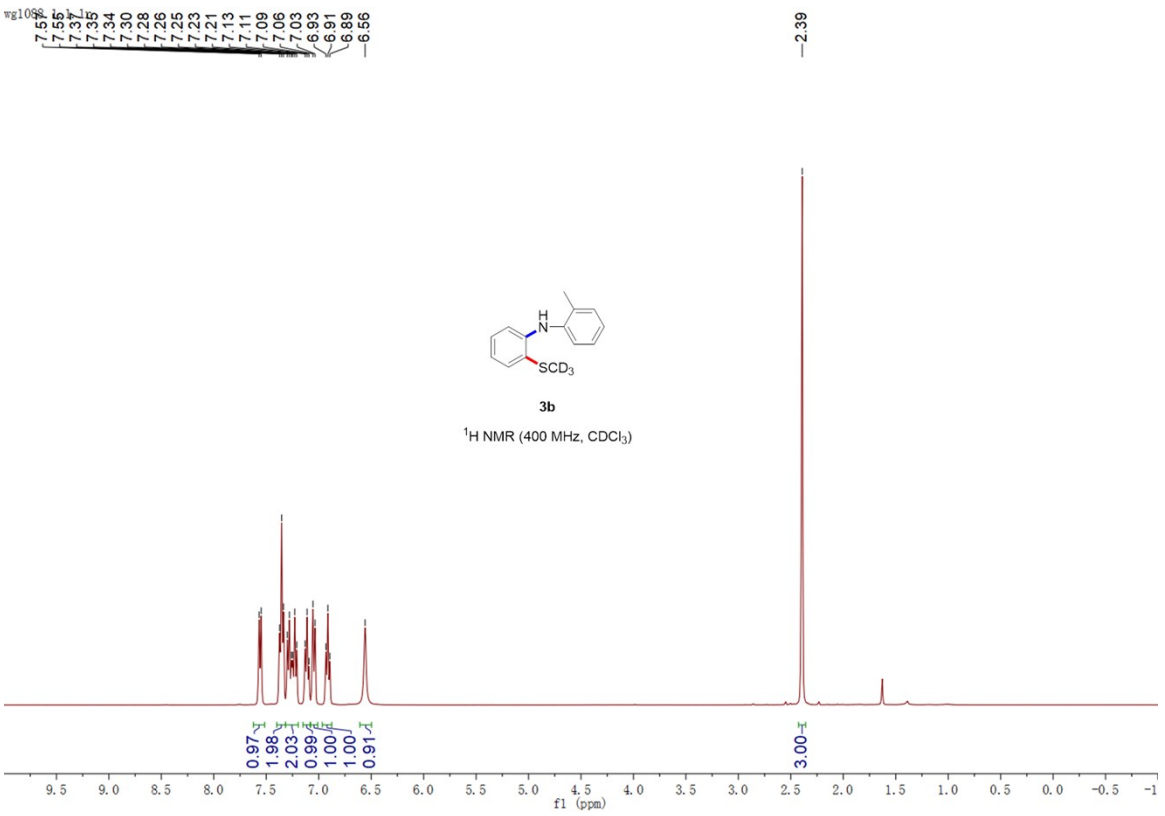
143.73
142.62
132.99
129.48
128.44
124.22
122.00
120.66
119.50
115.40



3a

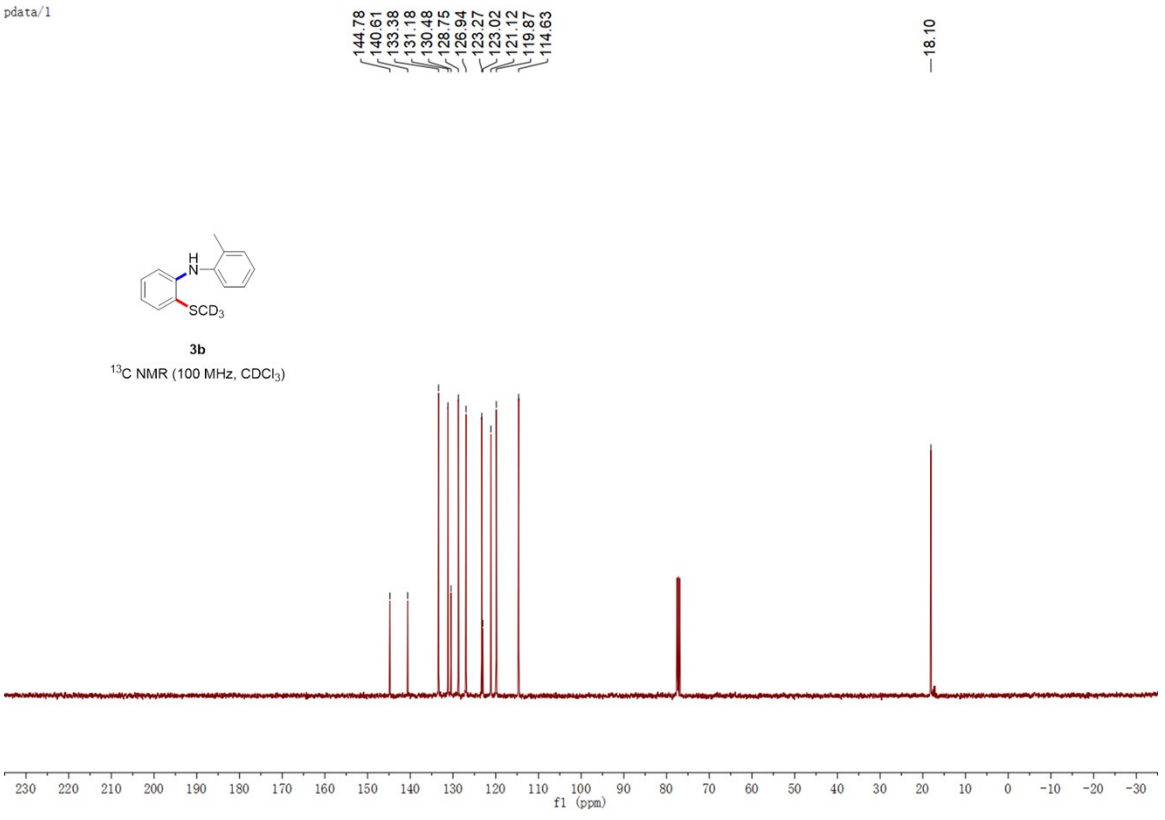
^{13}C NMR (100 MHz, $CDCl_3$)





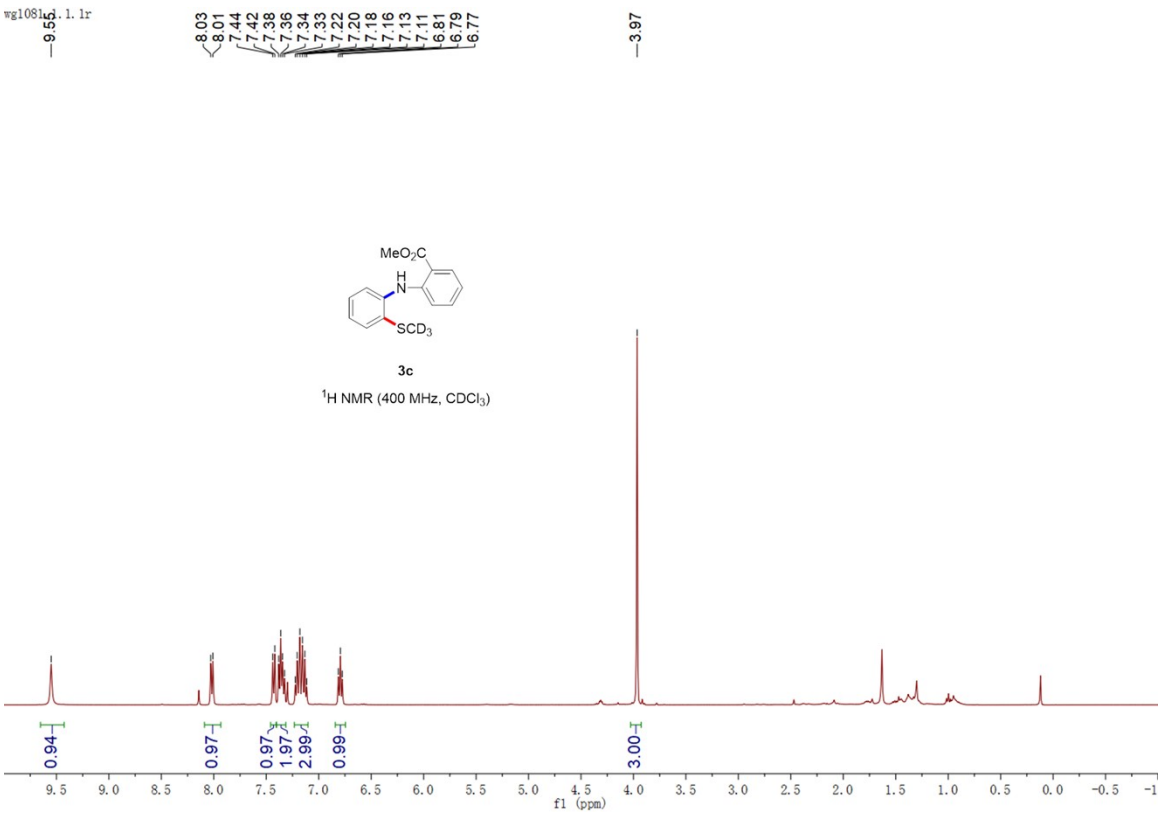
3b

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



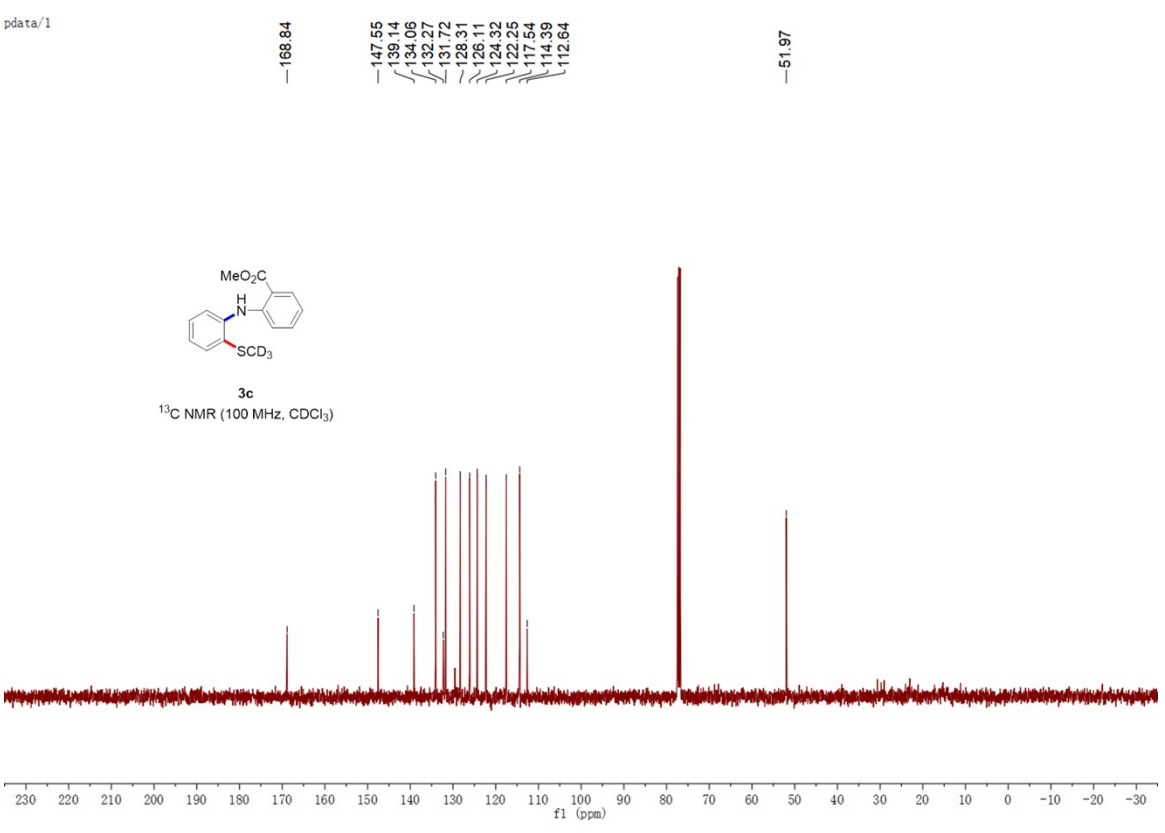
3b

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



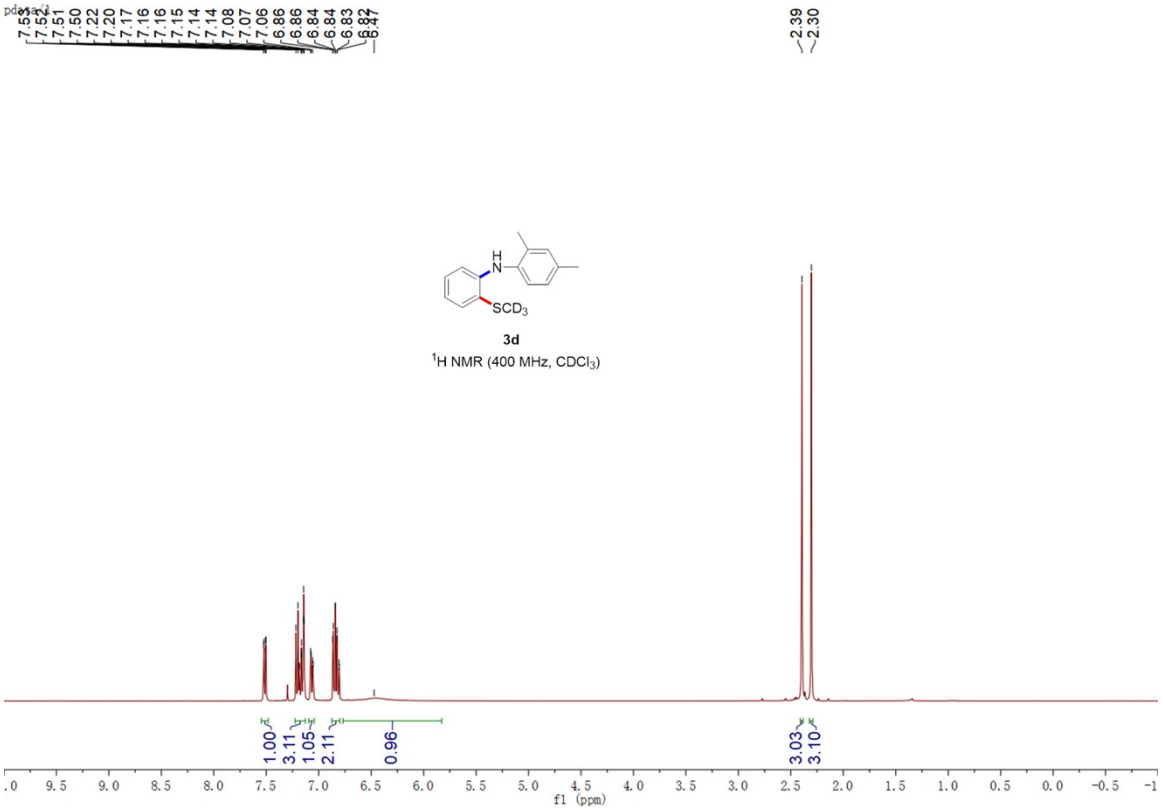
3c

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



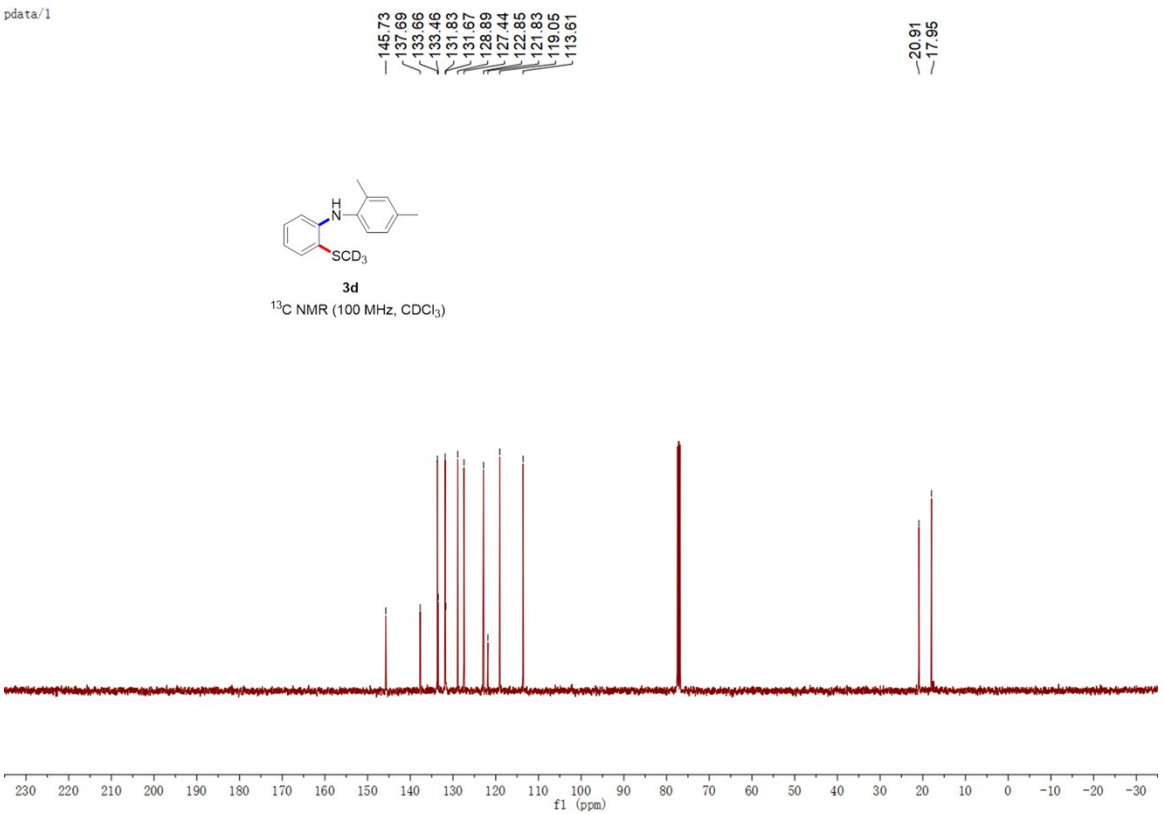
3c

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



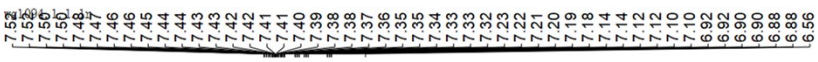
3d

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



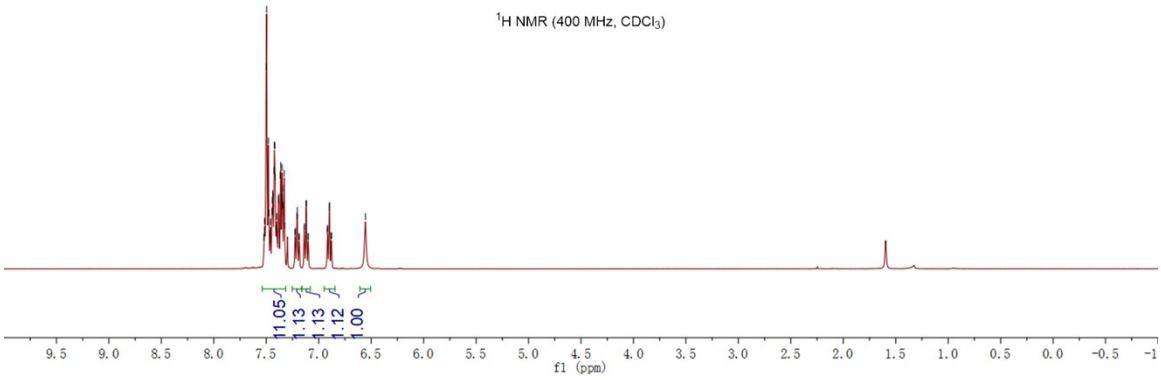
3d

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

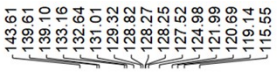


3e

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

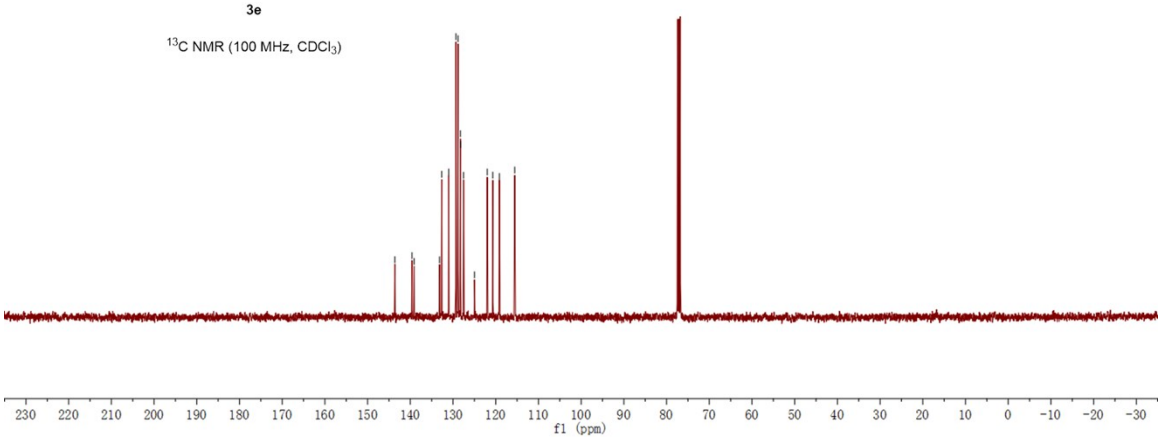


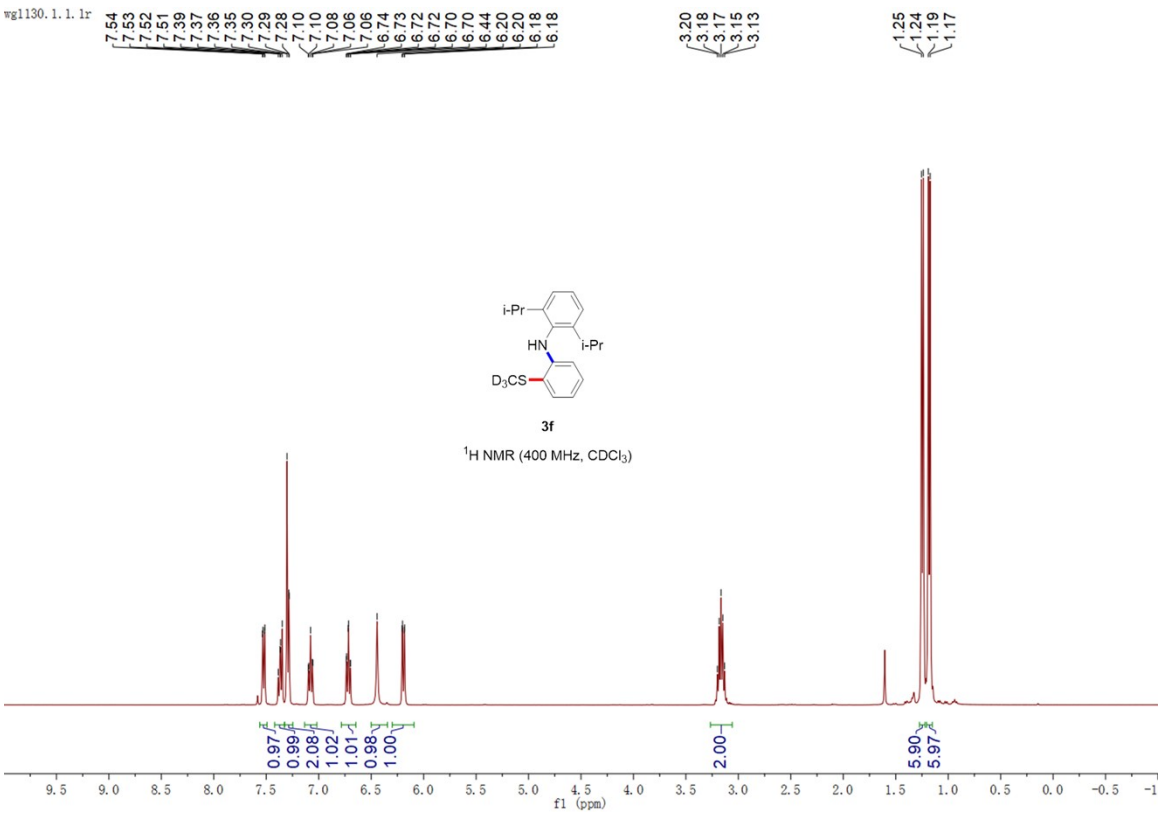
pdata/1

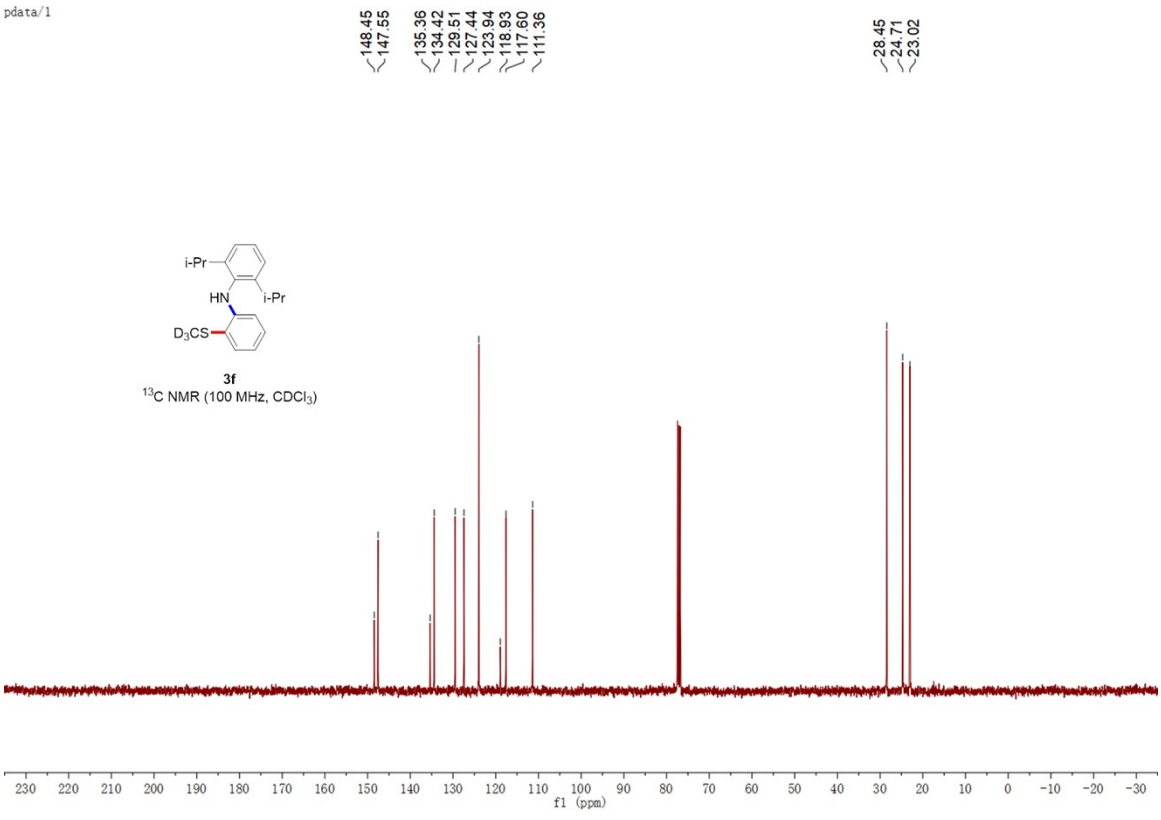


3e

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




wgl130.1.1.1r
7.54
7.53
7.52
7.51
7.39
7.37
7.36
7.35
7.30
7.29
7.28
7.10
7.10
7.08
7.06
7.06
6.74
6.73
6.72
6.72
6.70
6.70
6.44
6.20
6.20
6.18
6.18
3.20
3.18
3.17
3.15
3.13
1.25
1.24
1.19
1.17
i-Pr
HN
i-Pr
D3CS
3f
1H NMR (400 MHz, CDCl3)
0.97
0.99
2.08
1.02
1.01
0.98
1.00
2.00
5.90
5.97
f1 (ppm)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147.55
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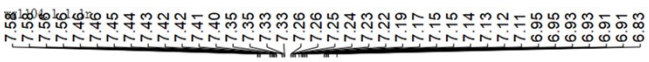
134.42
129.51
127.44
123.94
118.93
117.60
111.36
28.45
24.71
23.02
i-Pr
HN
i-Pr
D3CS
3f
13C NMR (100 MHz, CDCl3)
f1 (ppm)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7.58
7.56
7.56
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7.44
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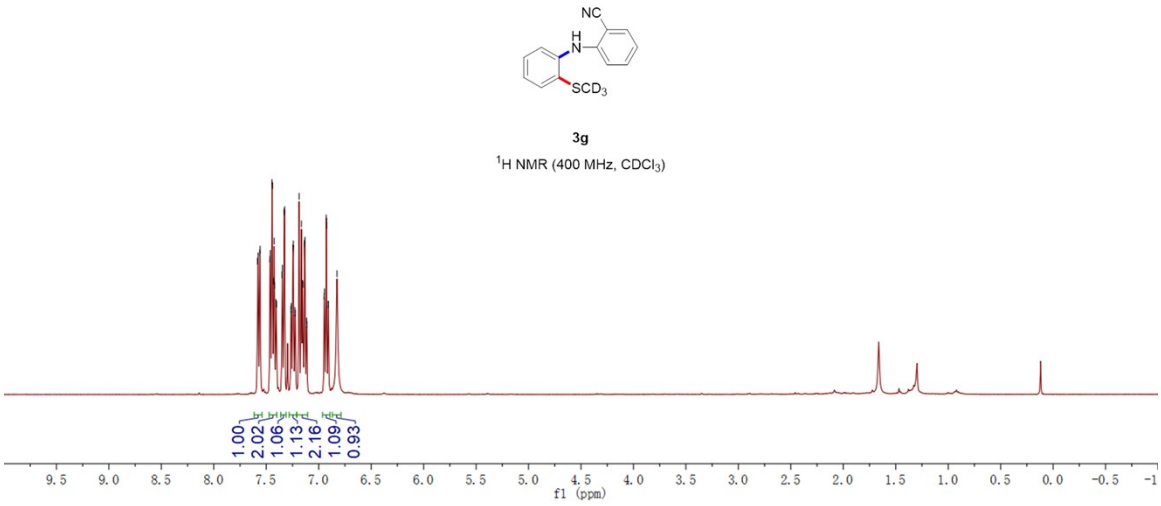
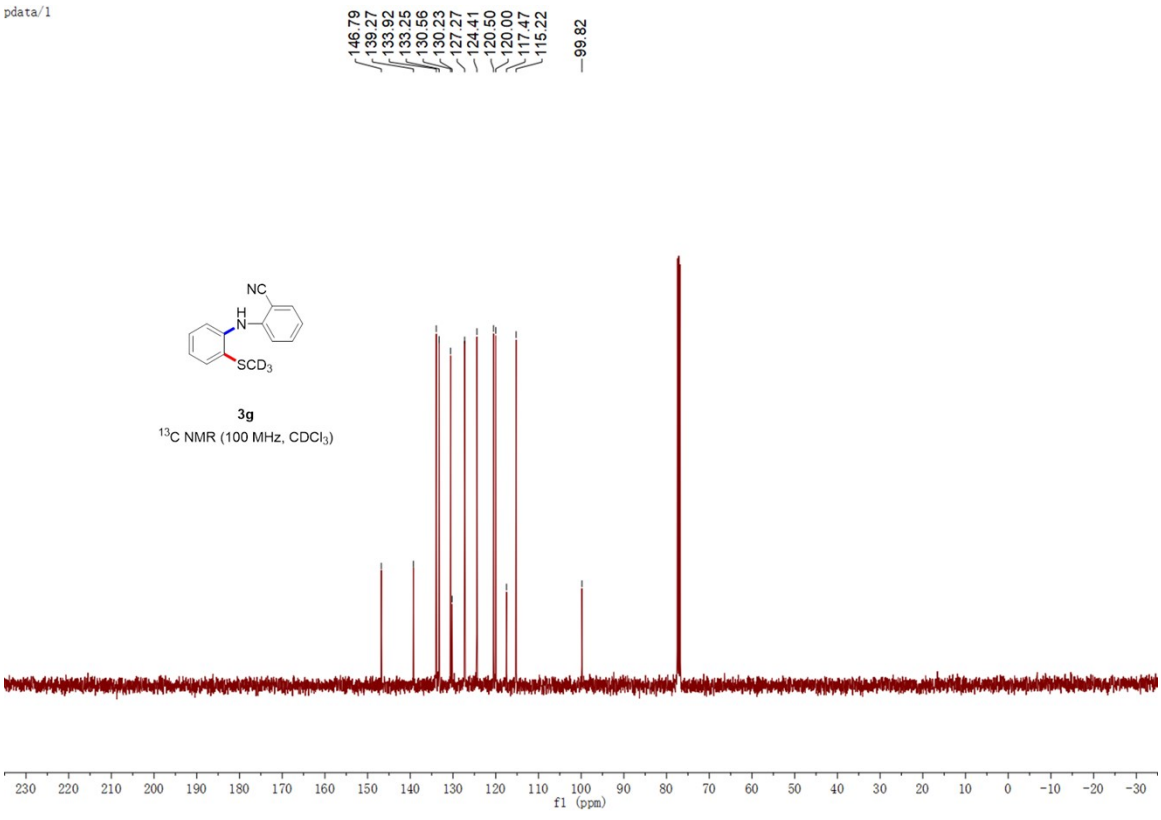
7.40
7.35
7.35
7.33
7.33
7.26
7.26
7.25
7.24
7.23
7.22
7.19
7.17
7.15
7.15
7.14
7.13
7.12
7.11
6.95
6.95
6.93
6.93
6.91
6.91
6.83


NC
H
N
SCD3
3g
1H NMR (400 MHz, CDCl3)
1.00
2.02
1.06
1.13
2.16
1.09
0.93
f1 (ppm)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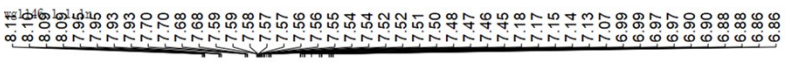
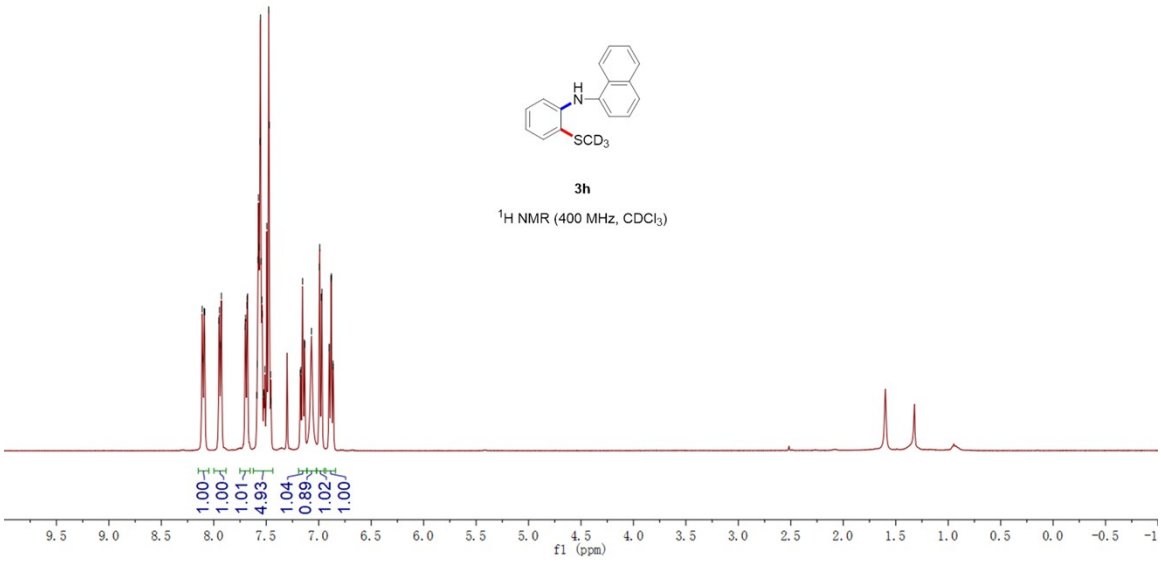
139.27
133.92
133.25
130.56
130.23
127.27
124.41
120.50
120.00
117.47
115.22
99.82
NC
H
N
SCD3
3g
13C NMR (100 MHz, CDCl3)
f1 (ppm)

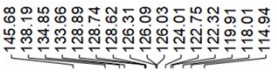




3h

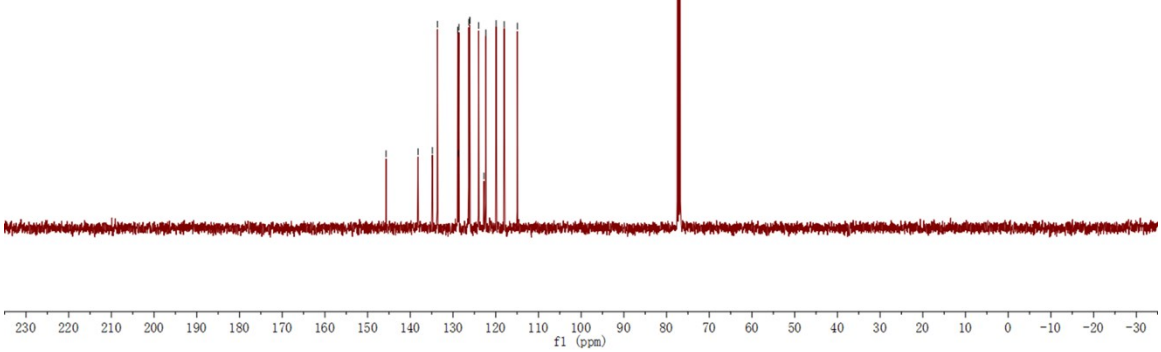
^{1}H NMR (400 MHz, $CDCl_3$)

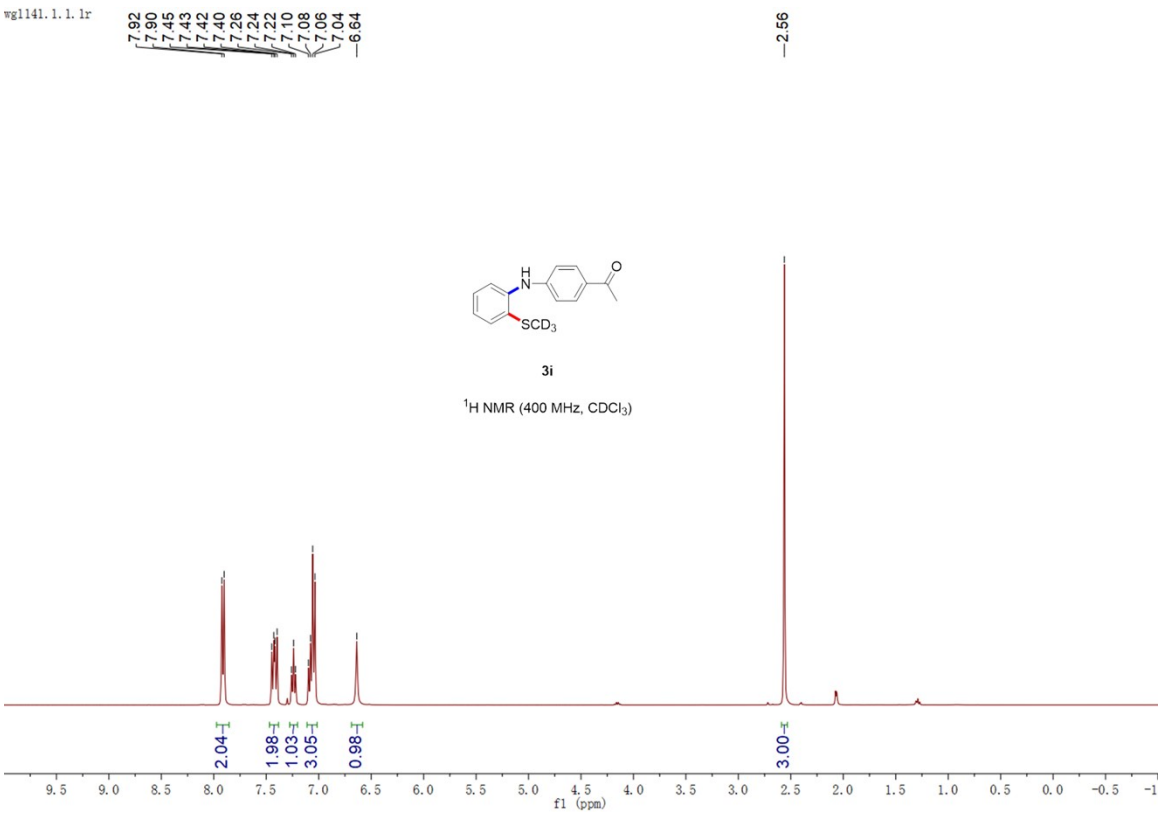
pdata/1



3h

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




wgl141.1.1.1r
7.92
7.90
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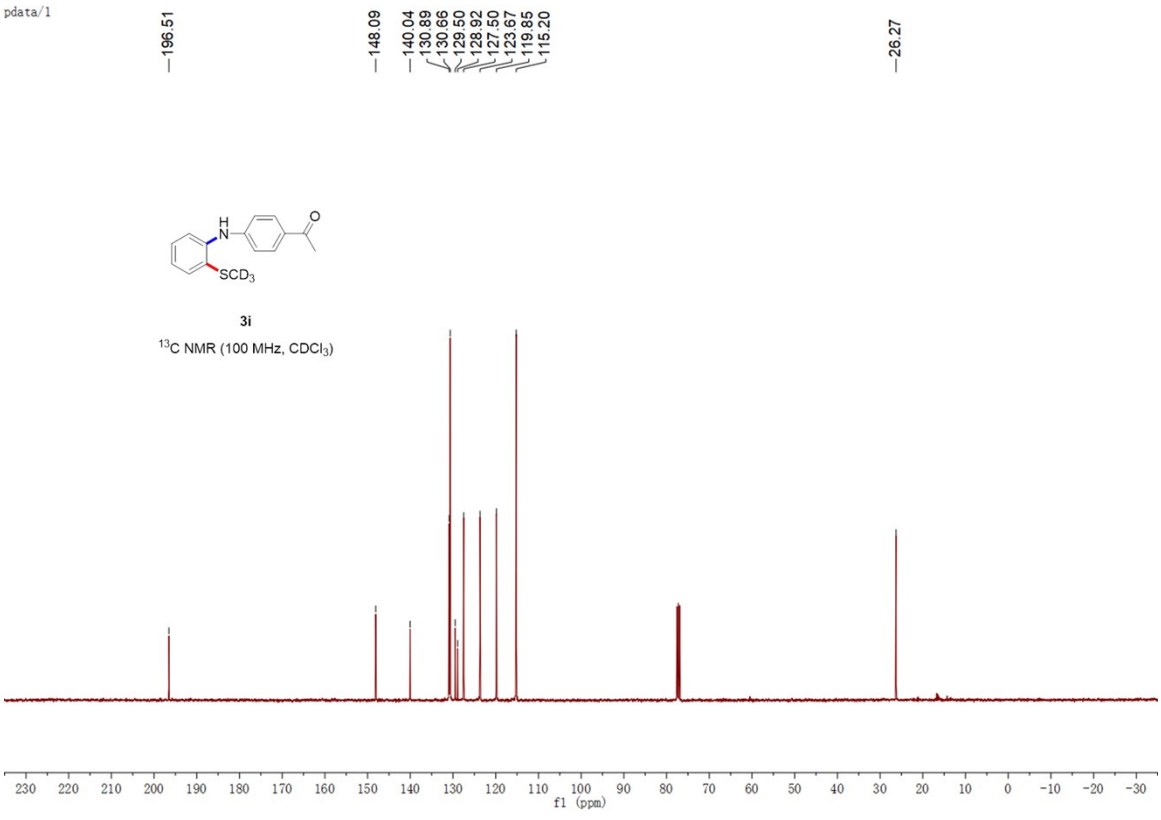
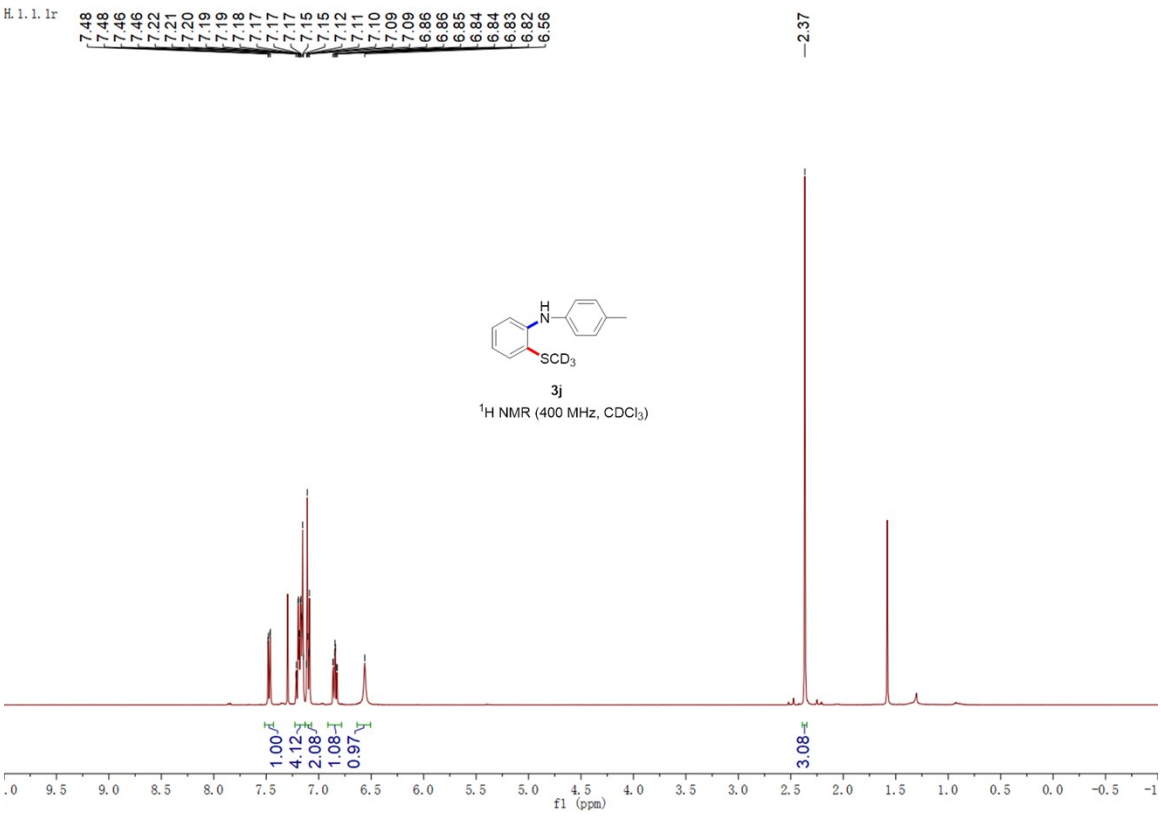
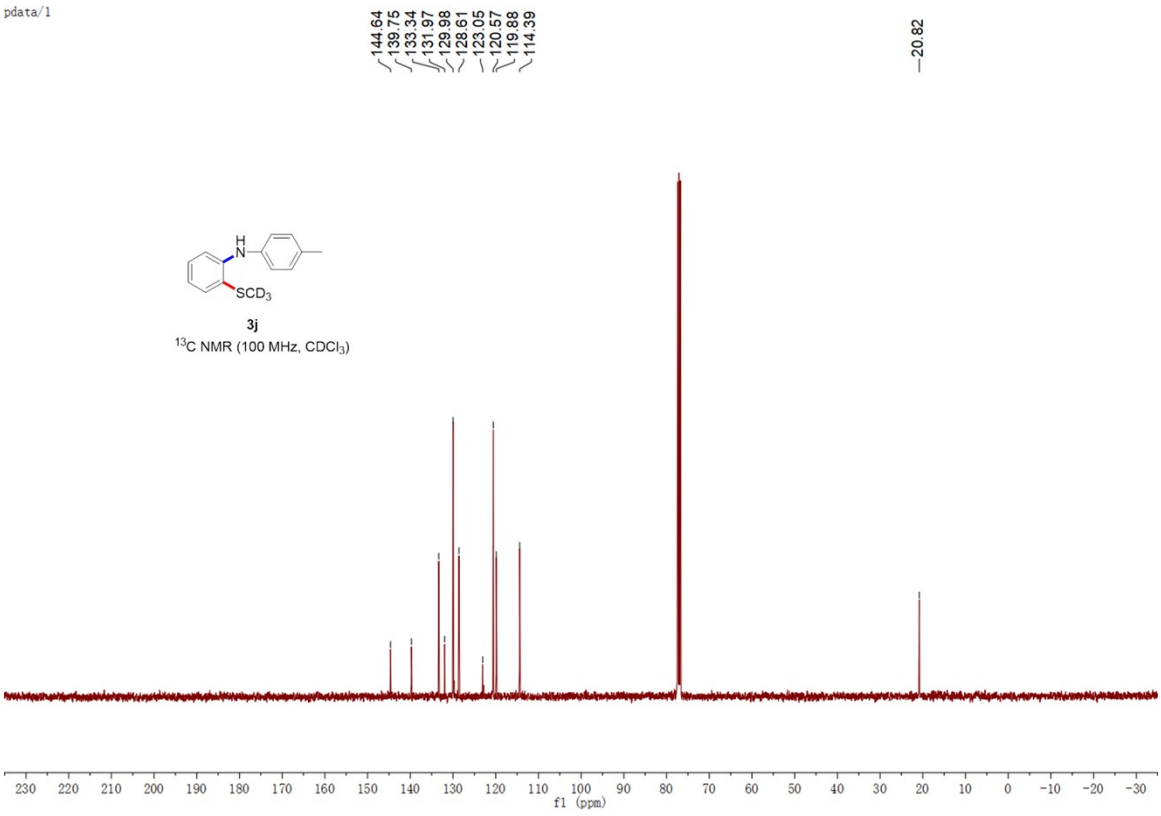
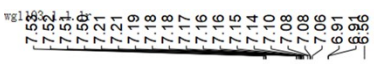
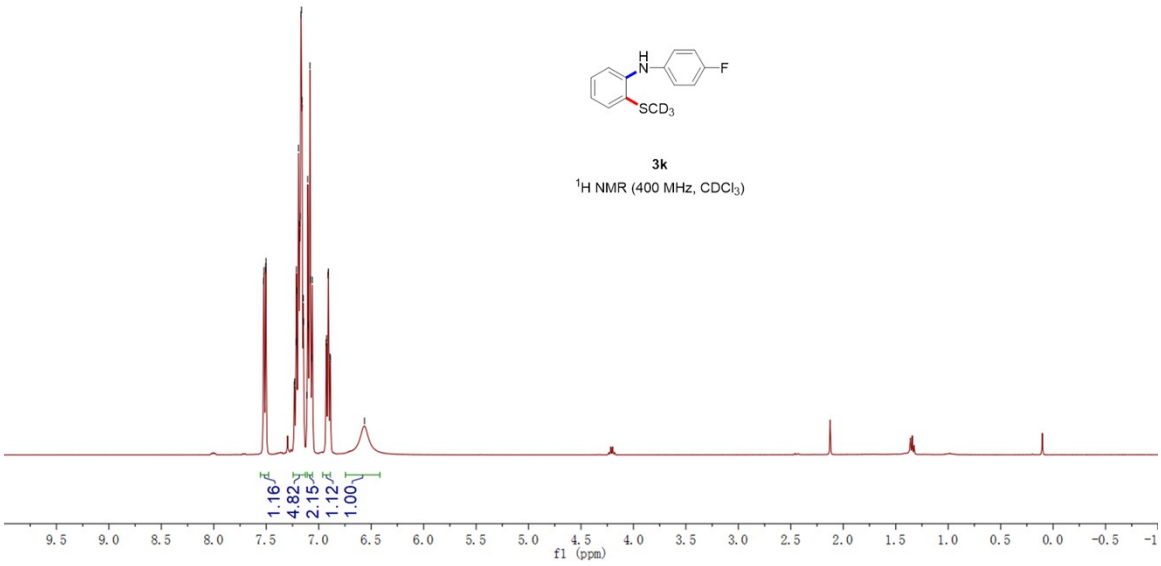
7.43
7.42
7.40
7.26
7.24
7.22
7.10
7.08
7.06
7.04
6.64
2.56
SCD3
3i
1H NMR (400 MHz, CDCl3)
2.04
1.98
1.03
3.05
0.98
3.00
f1 (ppm)


pdata/1
196.51
148.09
140.04
130.89
130.66
129.50
128.92
127.50
123.67
119.85
115.20
26.27
SCD3
3i
13C NMR (100 MHz, CDCl3)
f1 (ppm)


H.1.1.1r
7.48
7.48
7.46
7.46
7.22
7.21
7.20
7.19
7.19
7.18
7.17
7.17
7.17
7.15
7.15
7.12
7.11
7.10
7.09
7.09
6.86
6.86
6.85
6.84
6.84
6.83
6.82
6.56
2.37
SCD3
3j
1H NMR (400 MHz, CDCl3)
1.00
4.12
2.08
1.08
0.97
3.08
f1 (ppm)


pdata/1
144.64
139.75
133.34
131.97
129.98
128.61
123.05
120.57
119.88
114.39
20.82
SCD3
3j
13C NMR (100 MHz, CDCl3)
f1 (ppm)

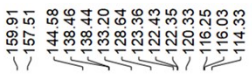


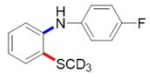


3k

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

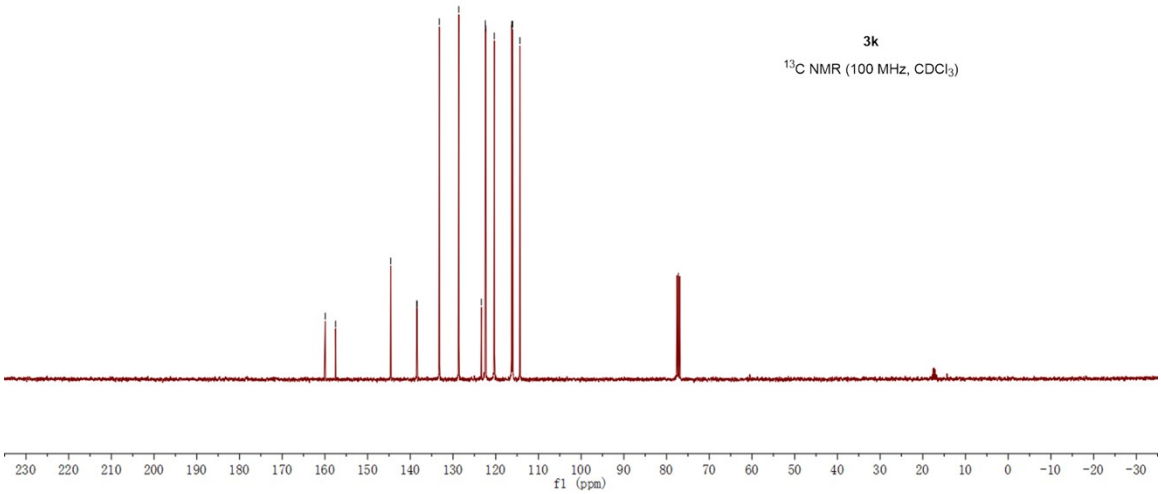
pdata/1

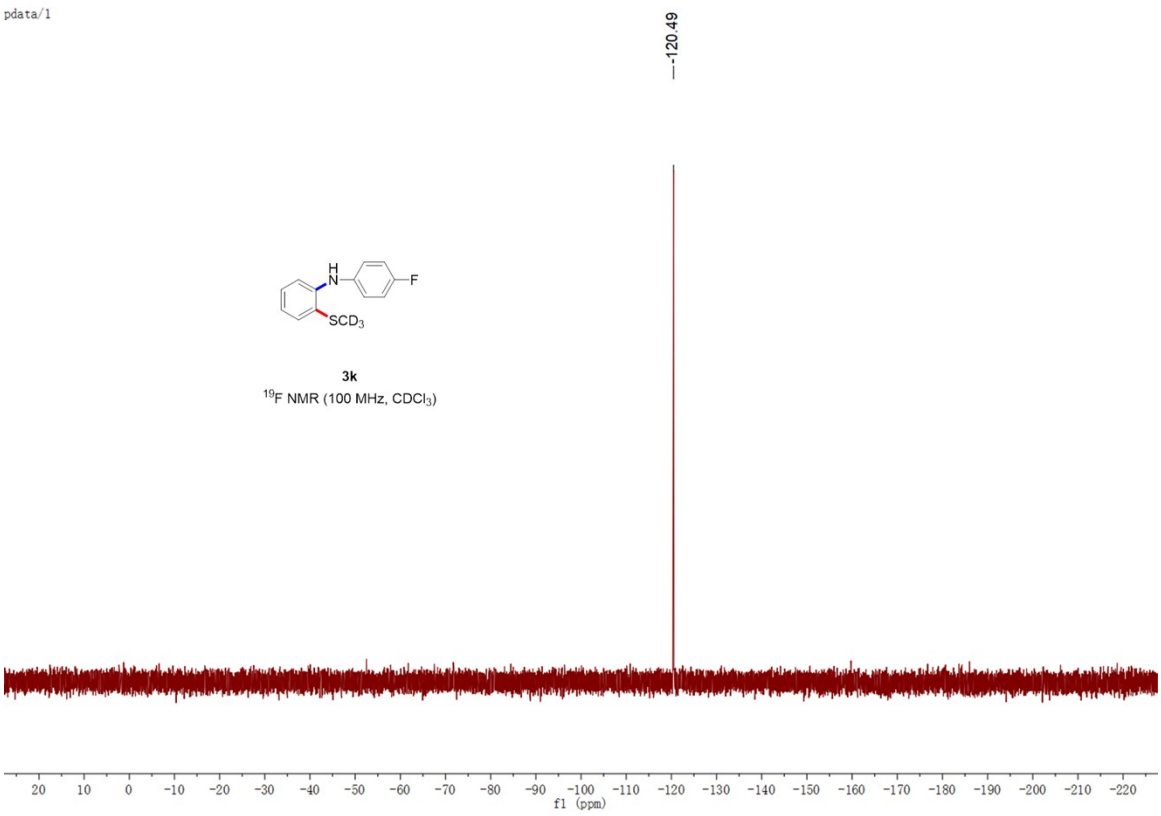




3k

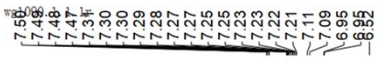
^{13}C NMR (100 MHz, $CDCl_3$)

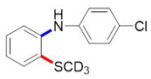




3k

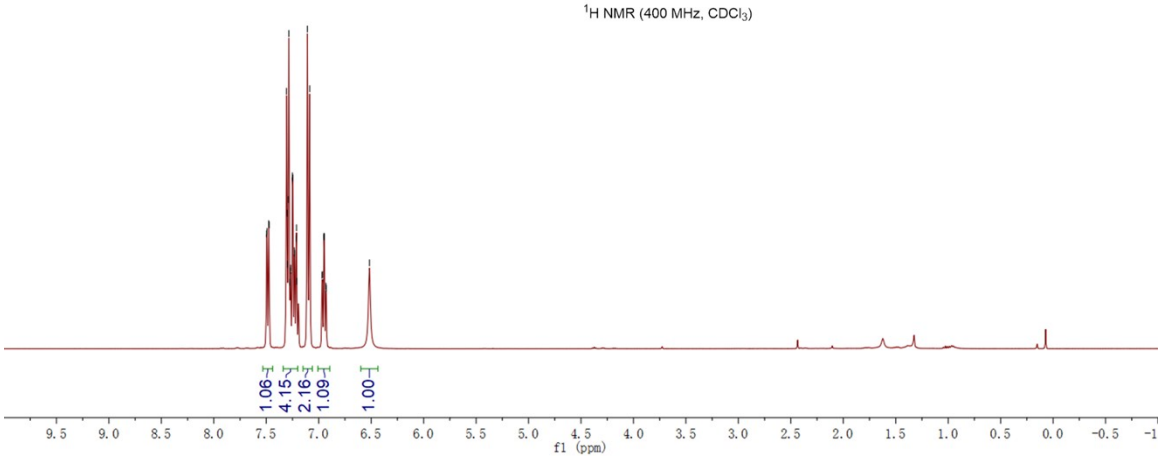
^{19}F NMR (100 MHz, $CDCl_3$)





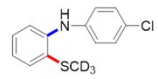
3l

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



pdata/1

143.03
141.36
132.66
129.44
128.33
126.52
124.95
121.29
120.35
115.83

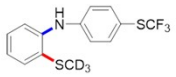


3l

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

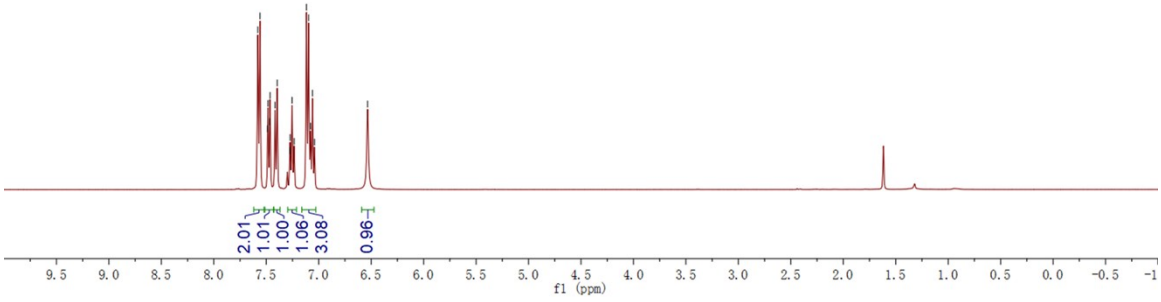
wg1106.1.1

7.58
7.56
7.49
7.48
7.47
7.46
7.42
7.40
7.28
7.27
7.25
7.23
7.12
7.10
7.08
7.06
7.04
6.53



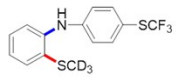
3m

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



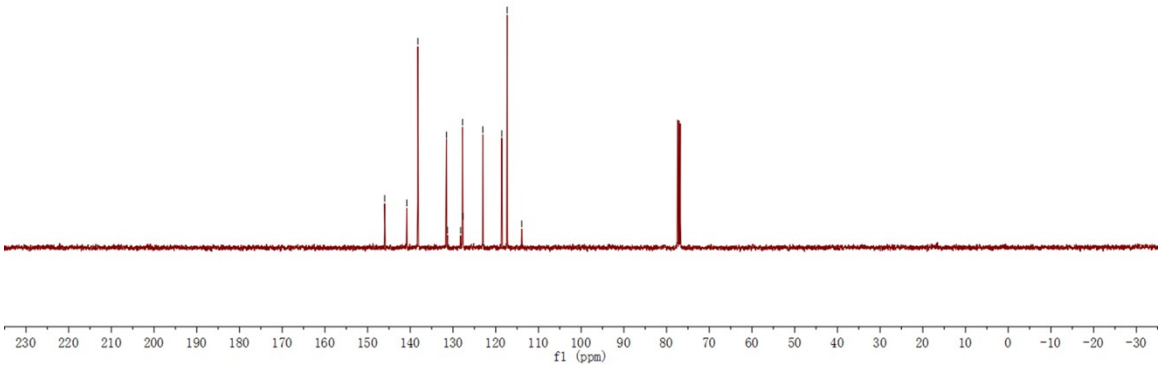
pdata/1

146.00
140.81
138.23
131.53
131.29
128.22
127.78
127.69
123.01
118.58
117.31
113.90



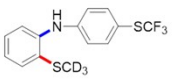
3m

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



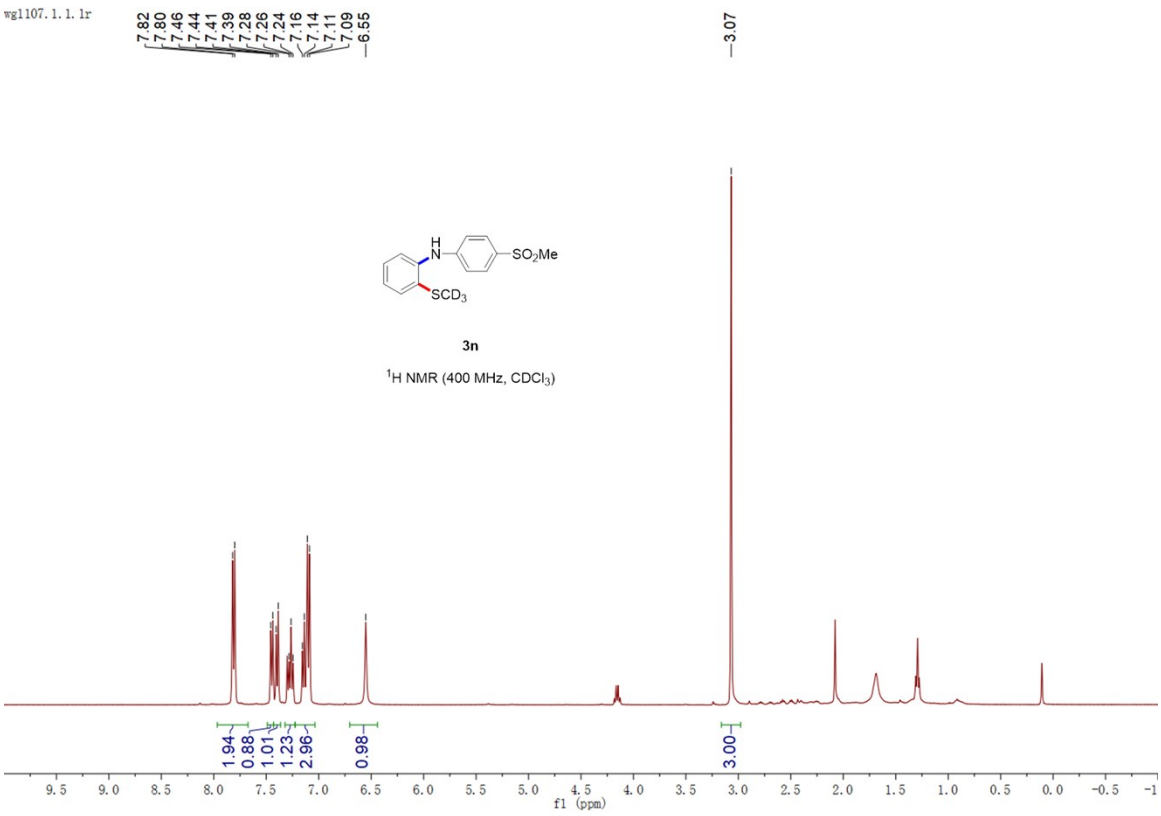
pdata/1

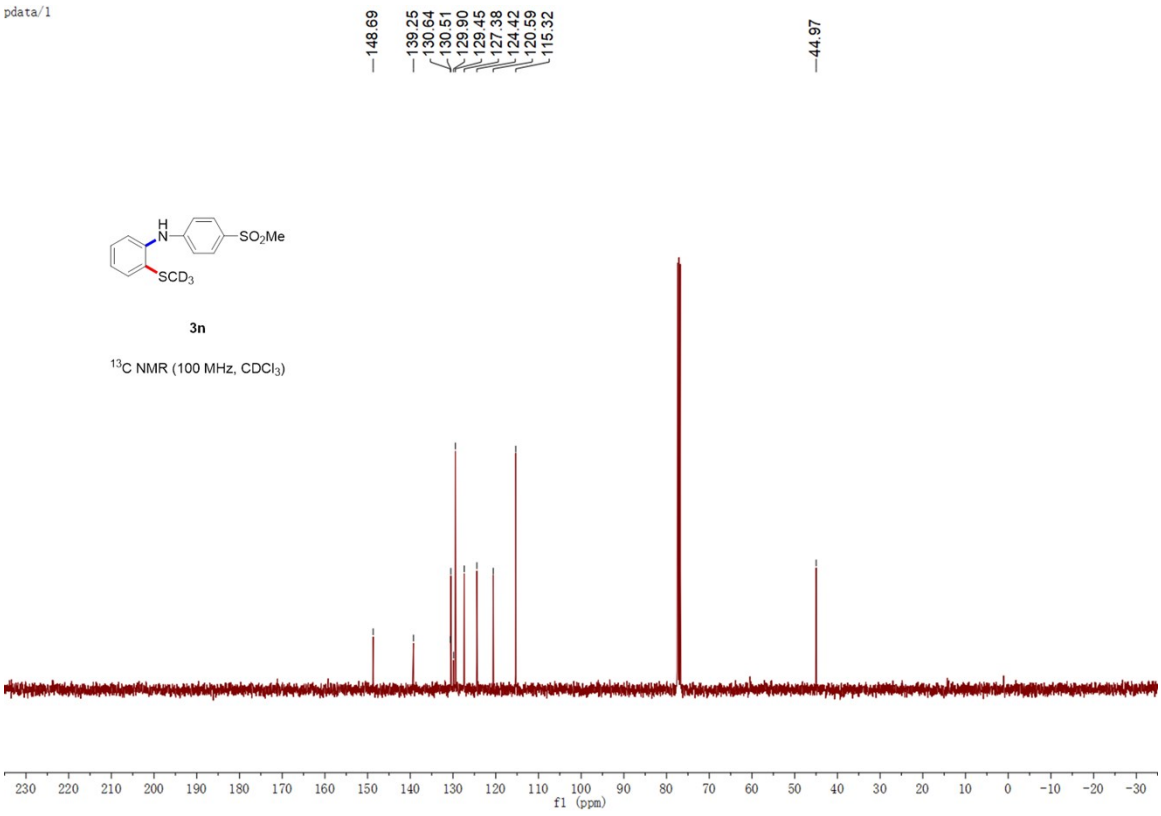
-43.92

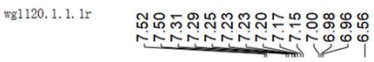


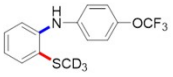
3m

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


wgl107.1.1.1r
7.82
7.80
7.46
7.44
7.41
7.39
7.28
7.26
7.24
7.16
7.14
7.11
7.09
6.55
3.07
SO2Me
SCD3
3n
1H NMR (400 MHz, CDCl3)
1.94
0.88
1.01
1.23
2.96
0.98
3.00
f1 (ppm)

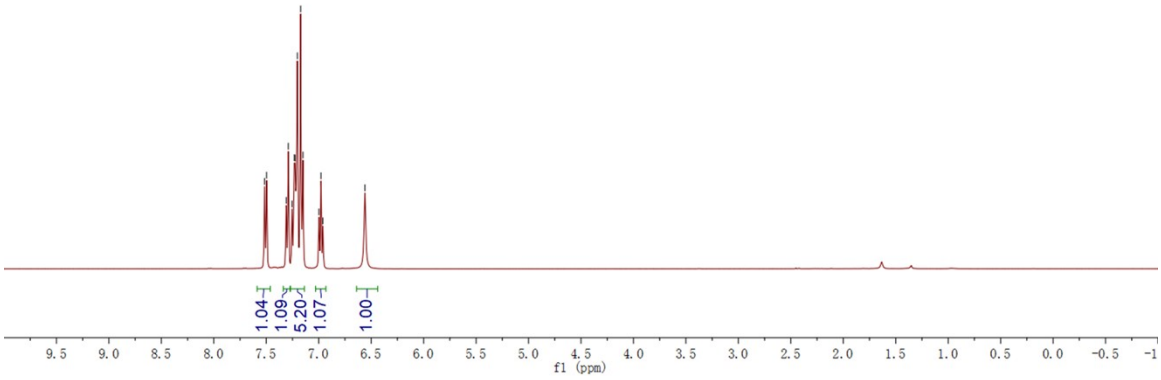

pdata/1
148.69
139.25
130.64
130.51
129.90
129.45
127.38
124.42
120.59
115.32
44.97
SO2Me
SCD3
3n
13C NMR (100 MHz, CDCl3)
f1 (ppm)

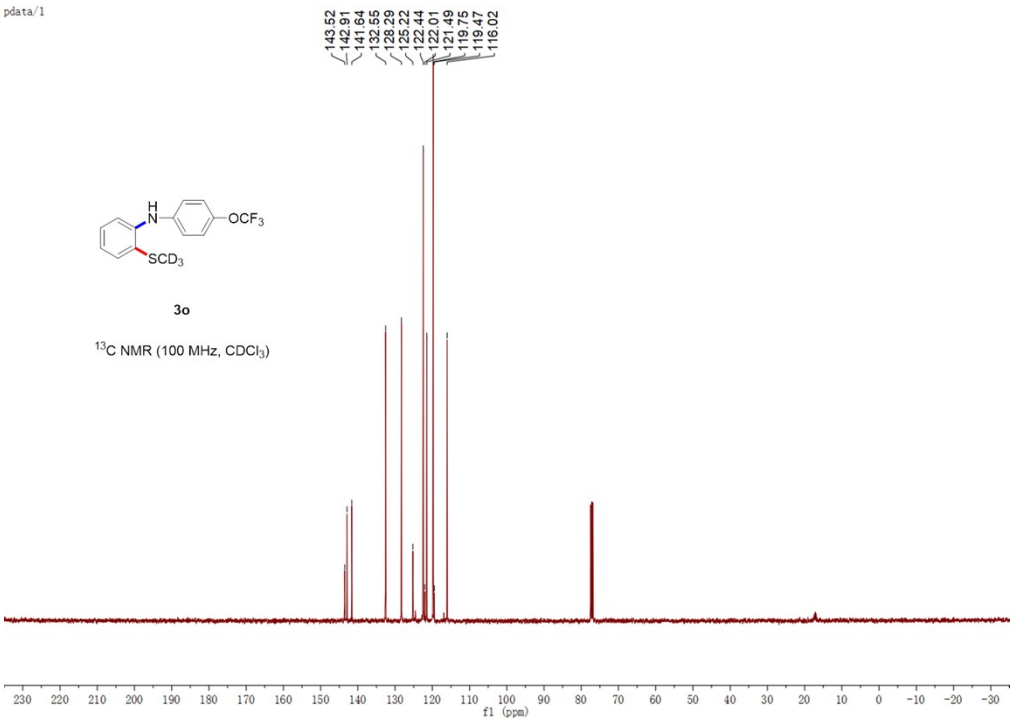




3o

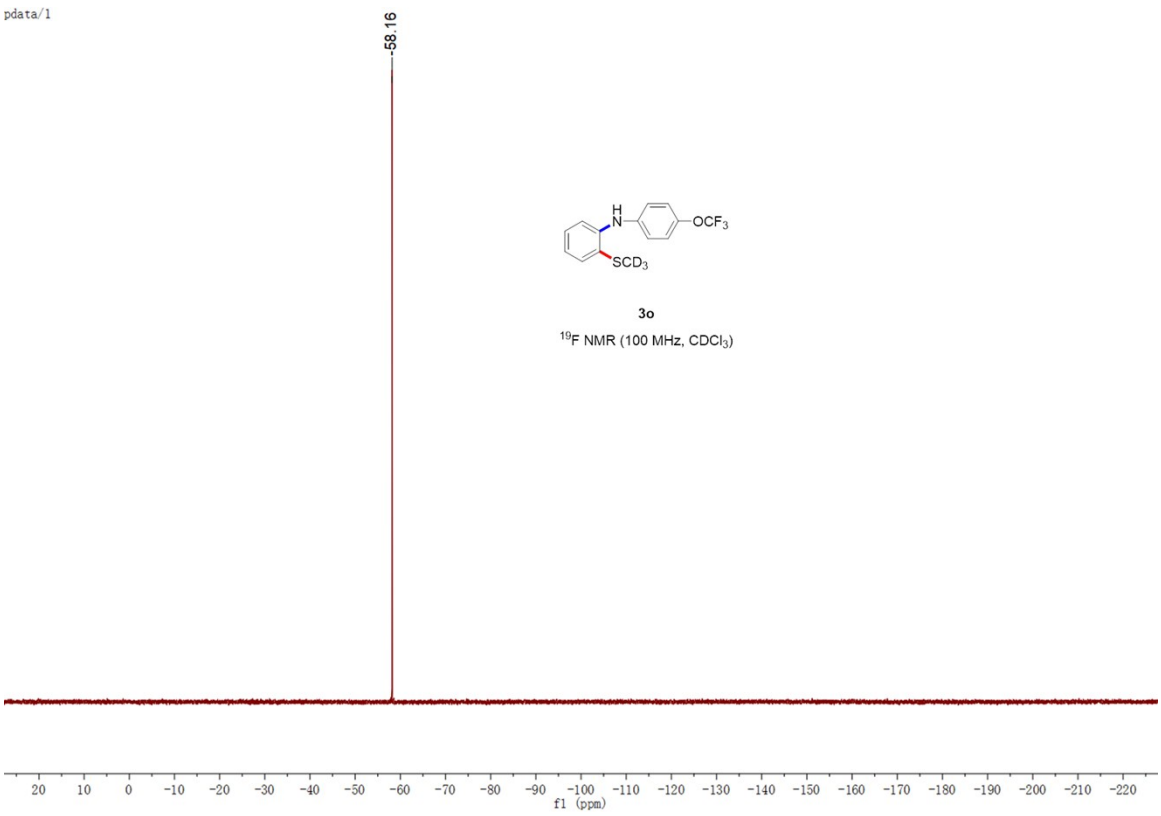
^{1}H NMR (400 MHz, $CDCl_3$)





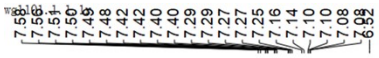
3o

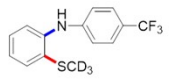
^{13}C NMR (100 MHz, $CDCl_3$)



3o

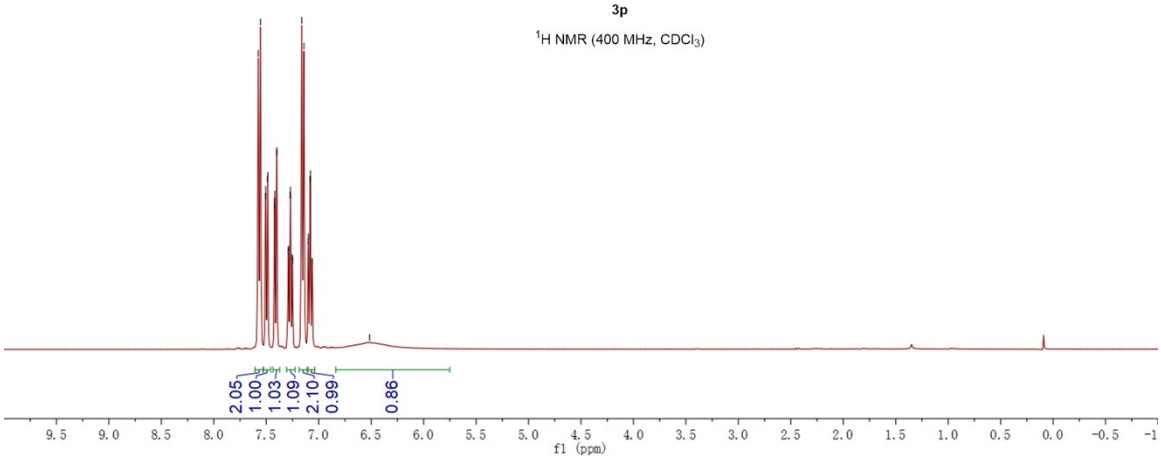
^{19}F NMR (100 MHz, $CDCl_3$)

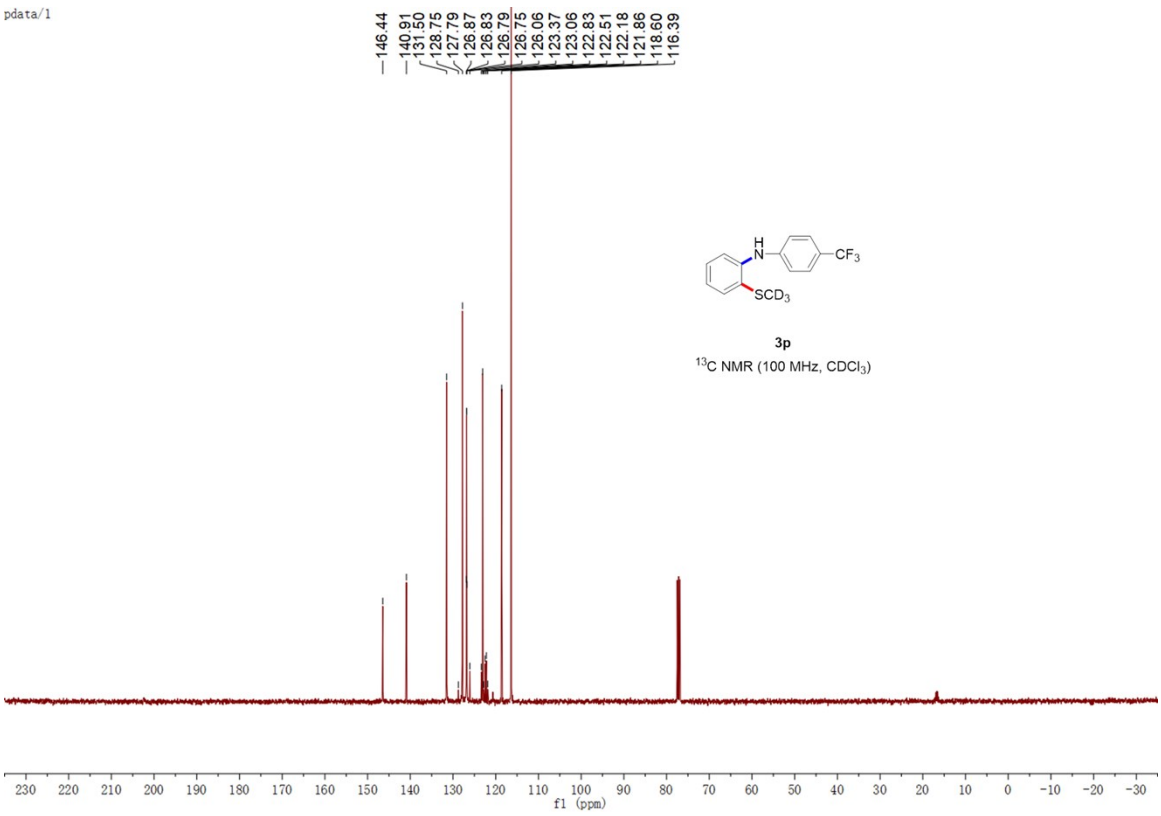




3p

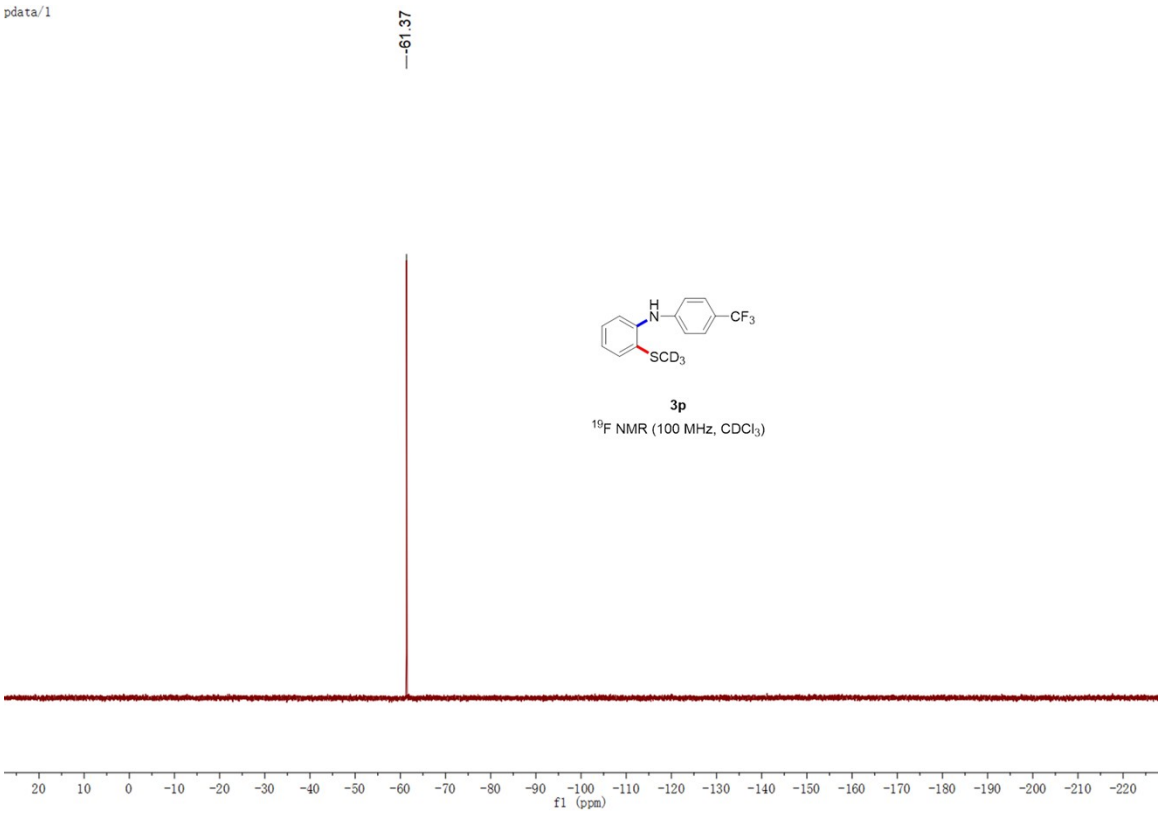
^{1}H NMR (400 MHz, $CDCl_3$)





3p

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

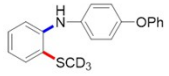


3p

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

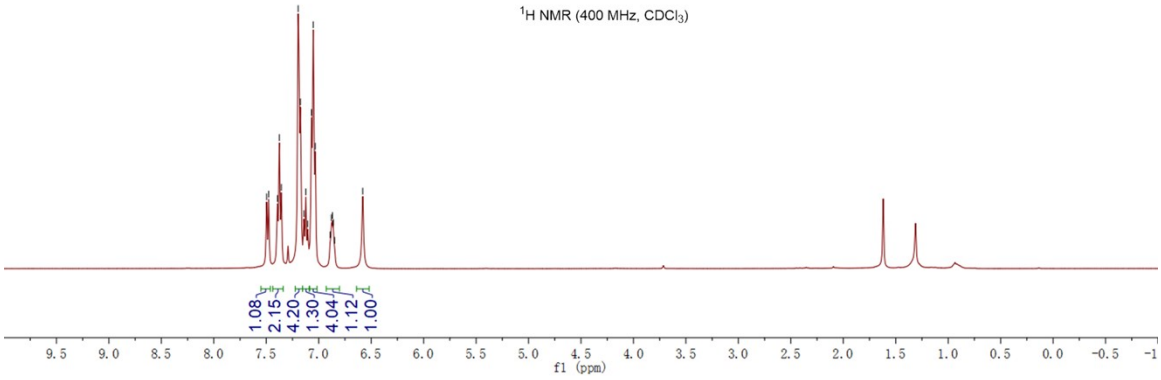
wgl122.1.1.1r

7.50
7.48
7.39
7.37
7.36
7.20
7.17
7.14
7.12
7.10
7.07
7.05
7.03
6.89
6.88
6.87
6.86
6.85
6.58



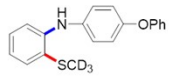
3q

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



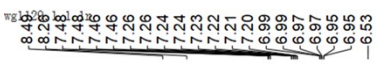
pdata/1

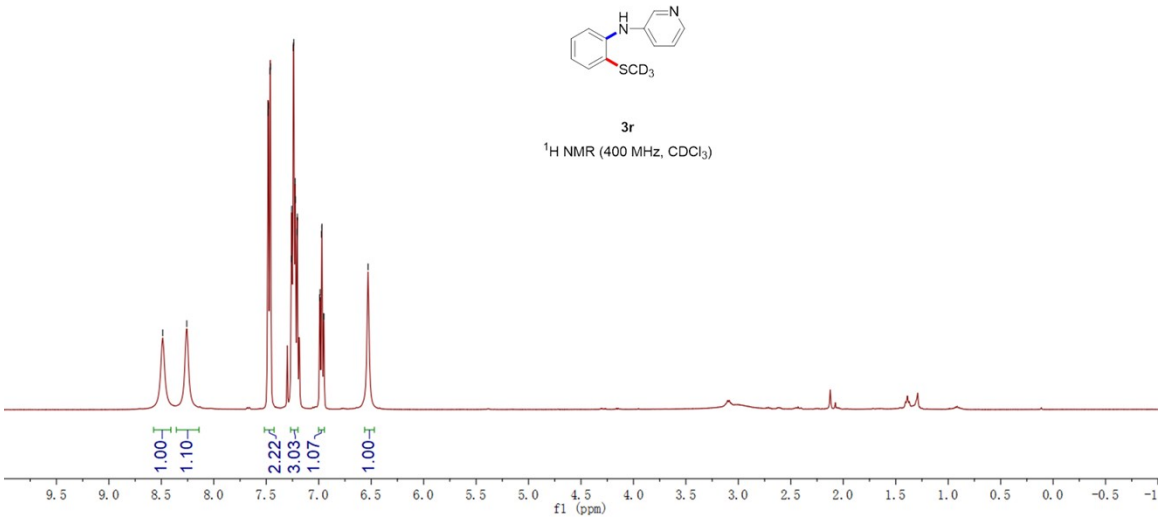
158.06
152.15
144.63
138.04
133.28
129.78
128.64
123.07
122.88
122.19
120.46
120.07
118.22
114.25



3q

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

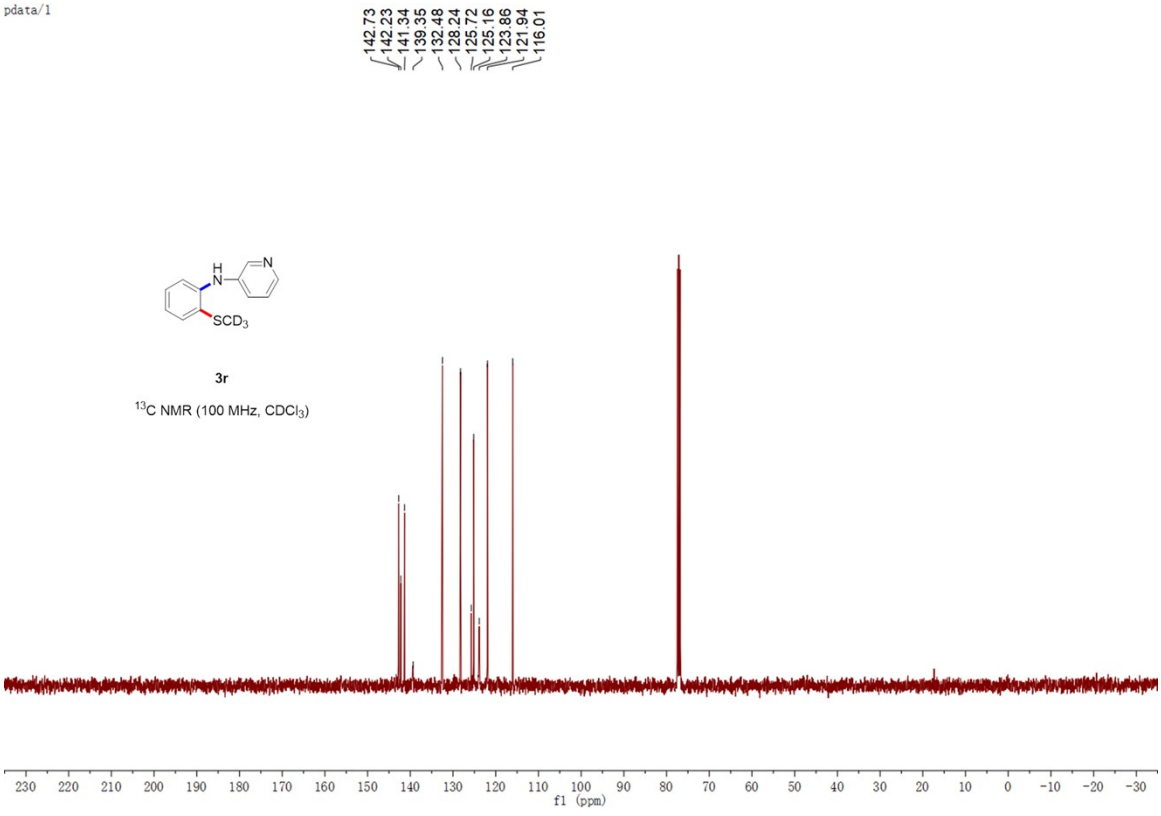




3r

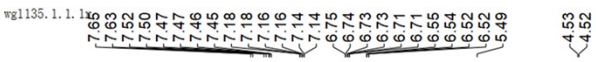
^{1}H NMR (400 MHz, $CDCl_3$)

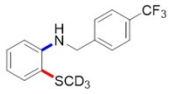
pdata/1



3r

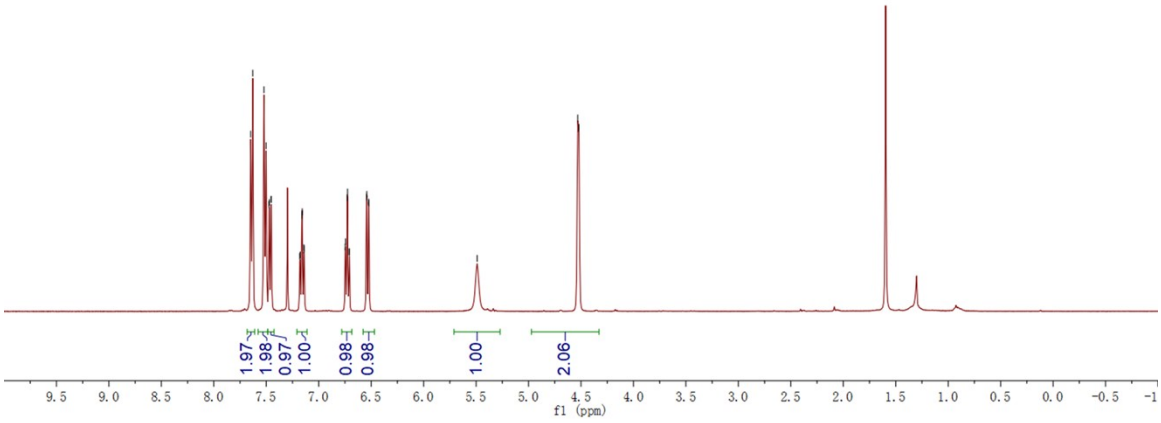
^{13}C NMR (100 MHz, $CDCl_3$)

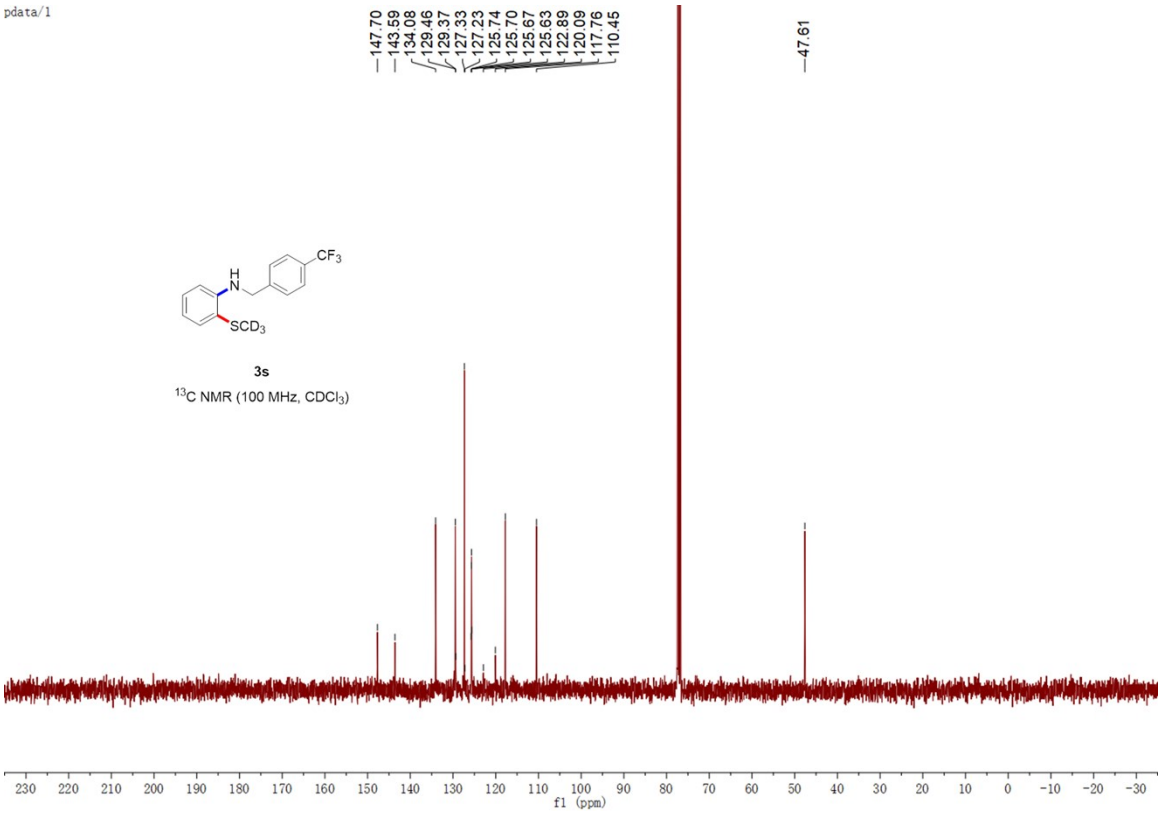




3s

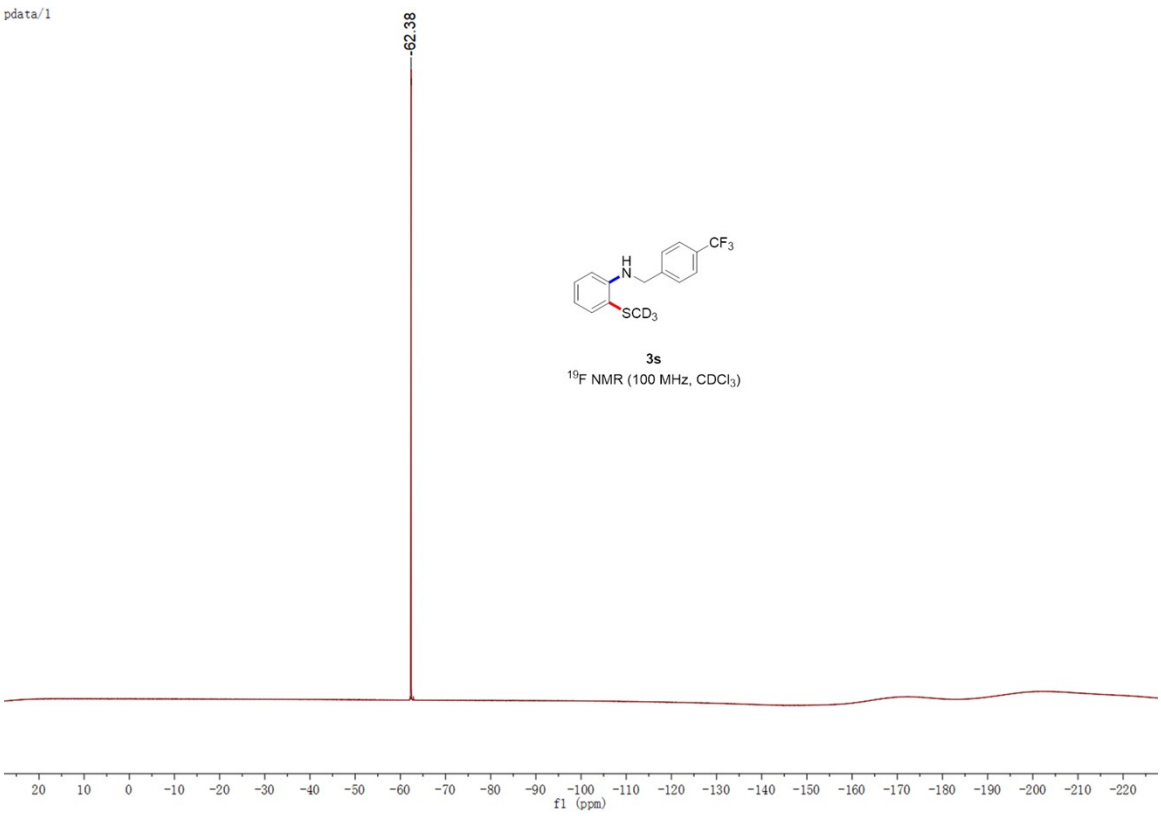
^{1}H NMR (400 MHz, $CDCl_3$)





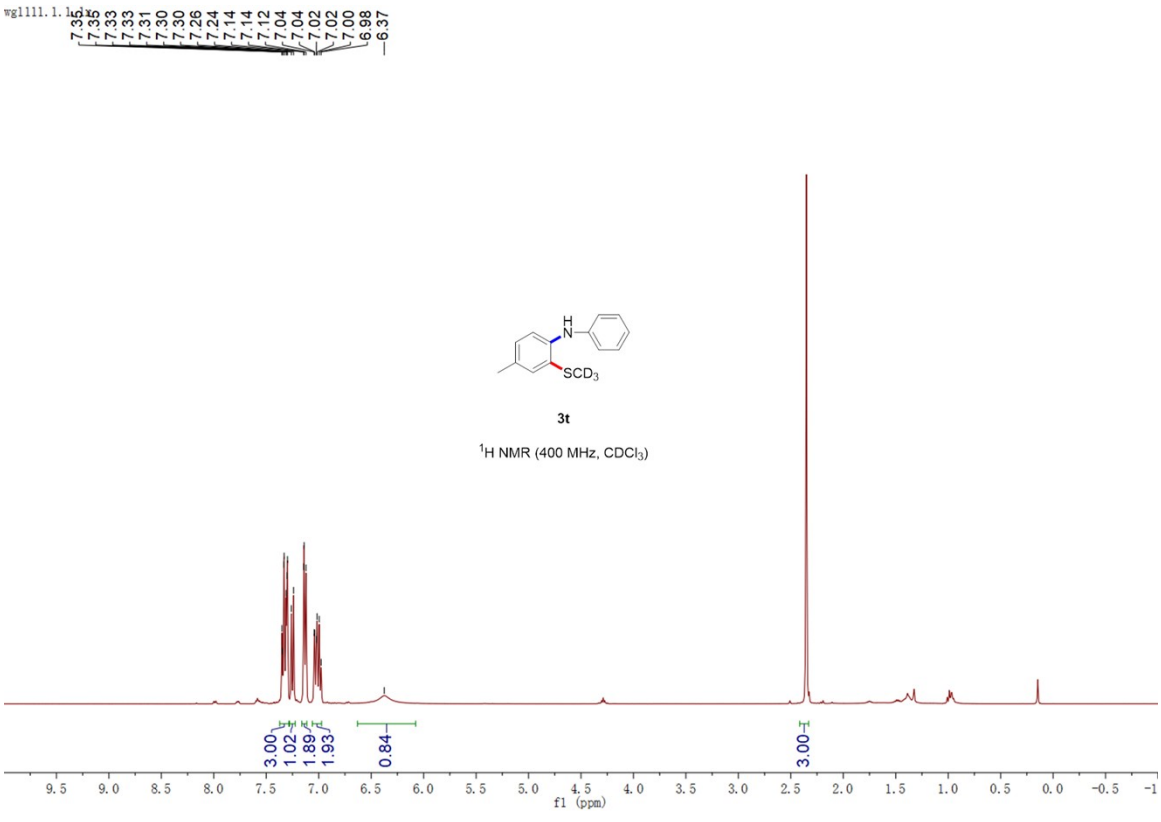
3s

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



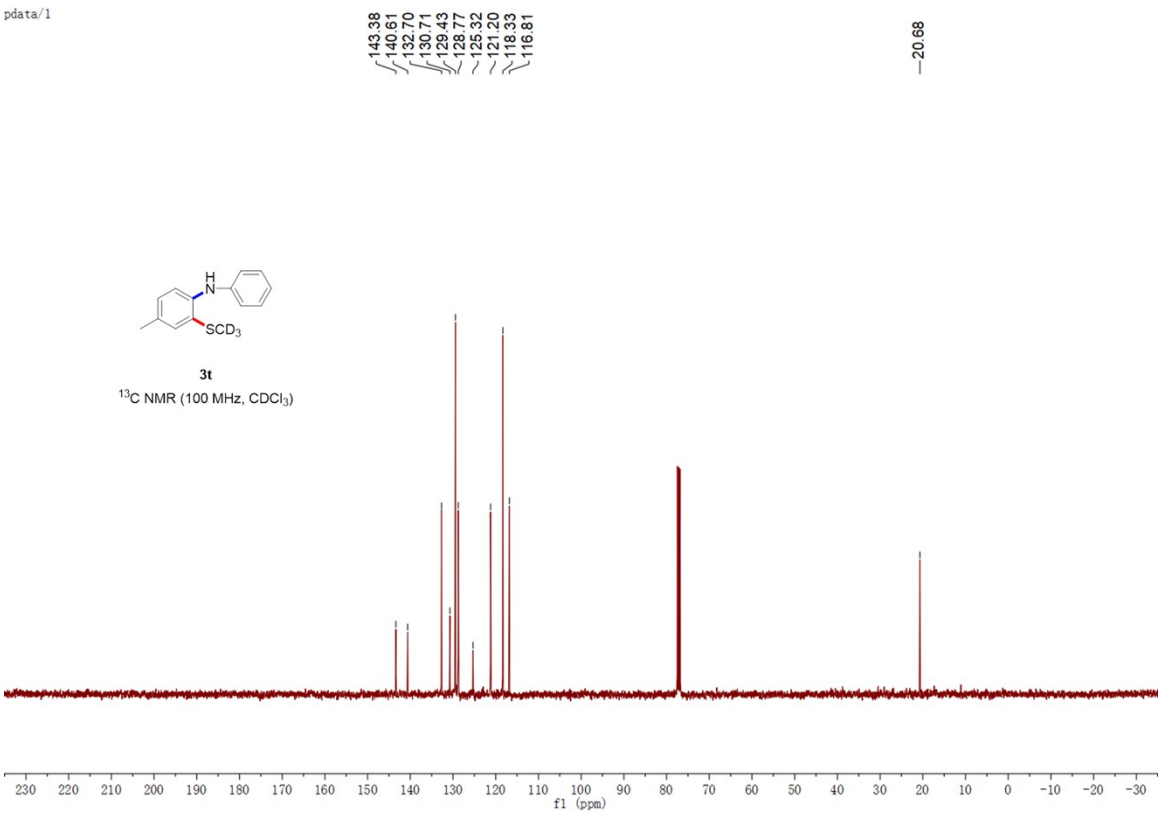
3s

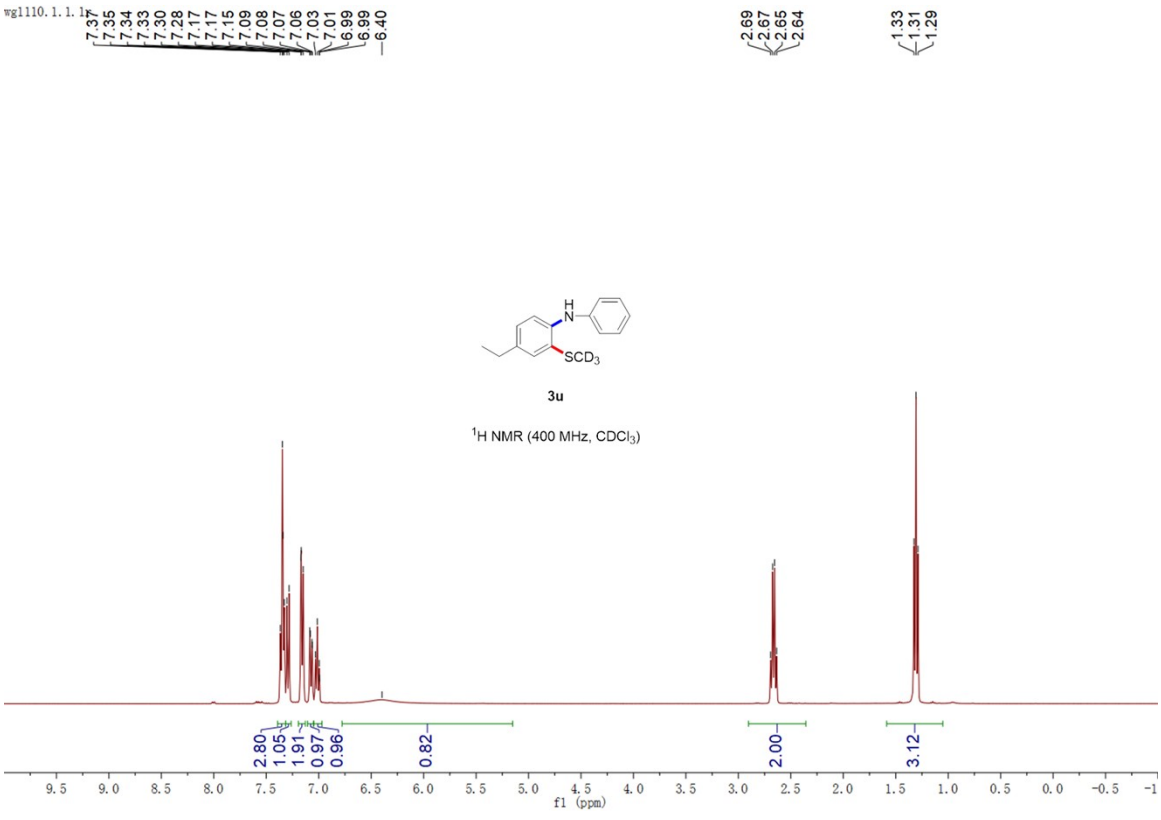
^{19}F NMR (100 MHz, $CDCl_3$)

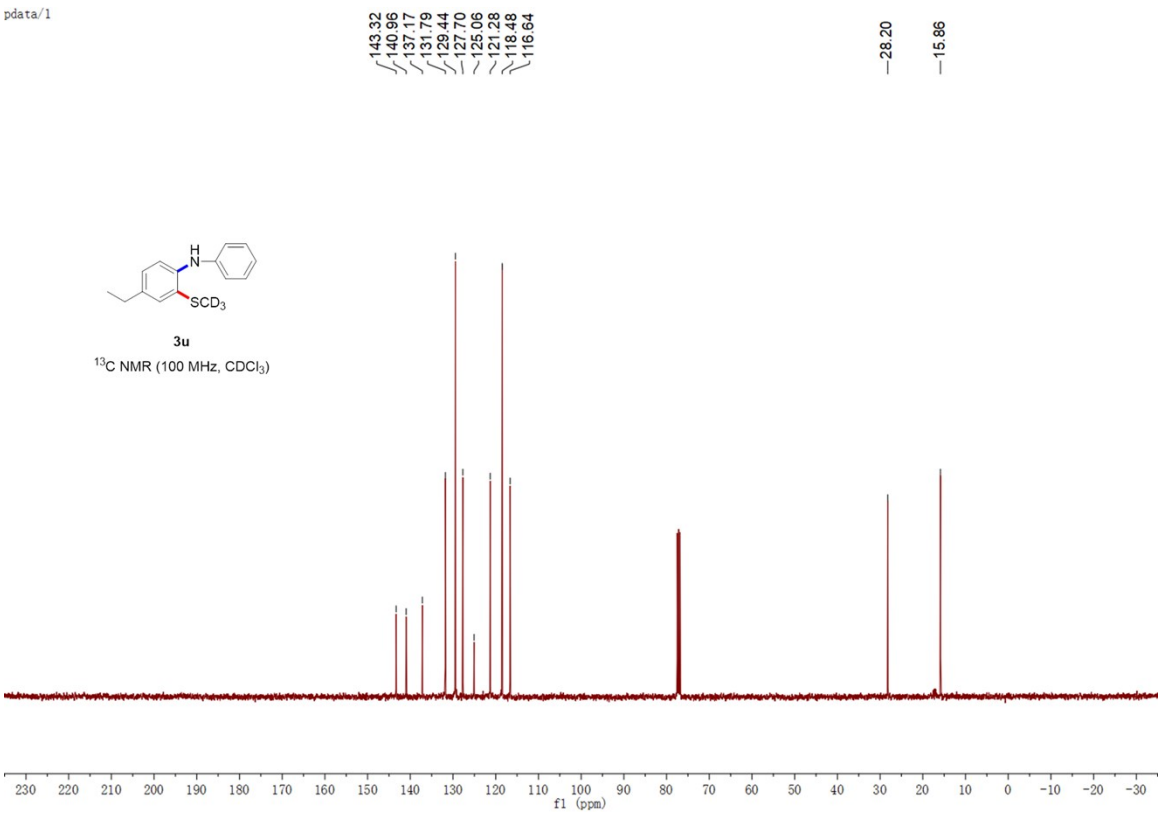


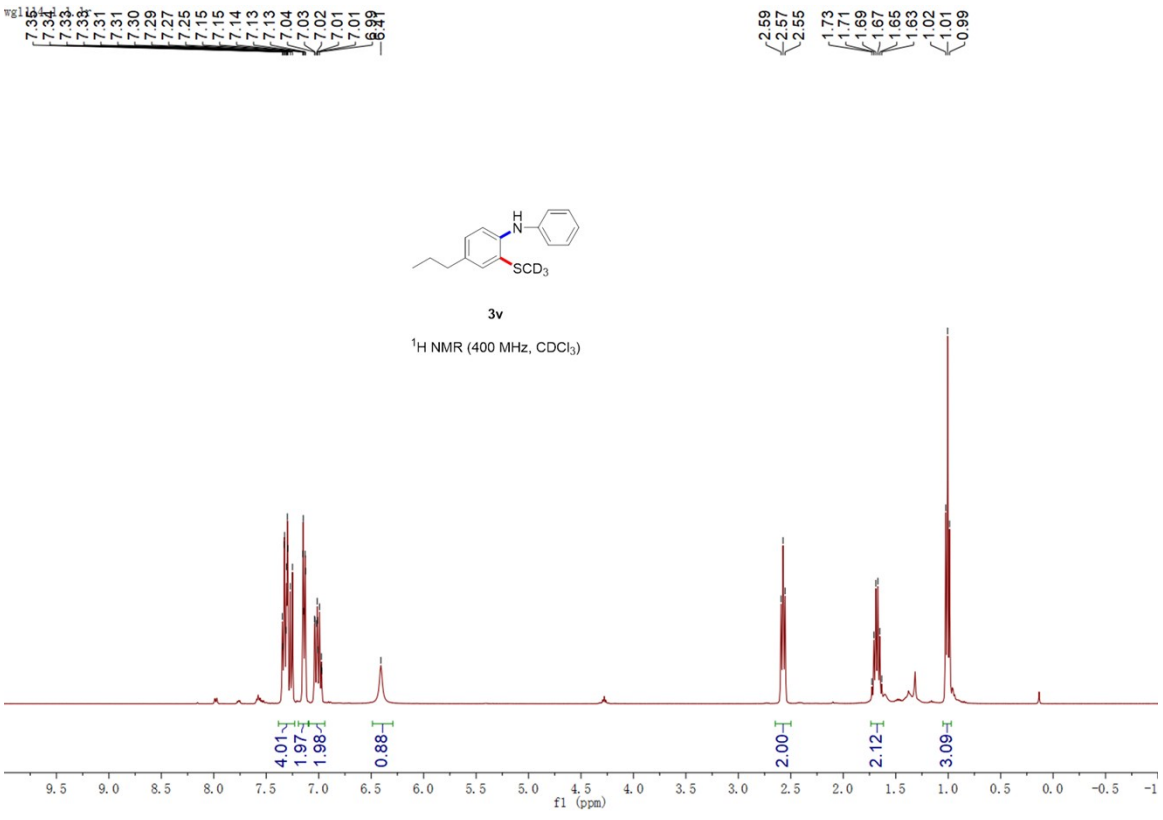
3t

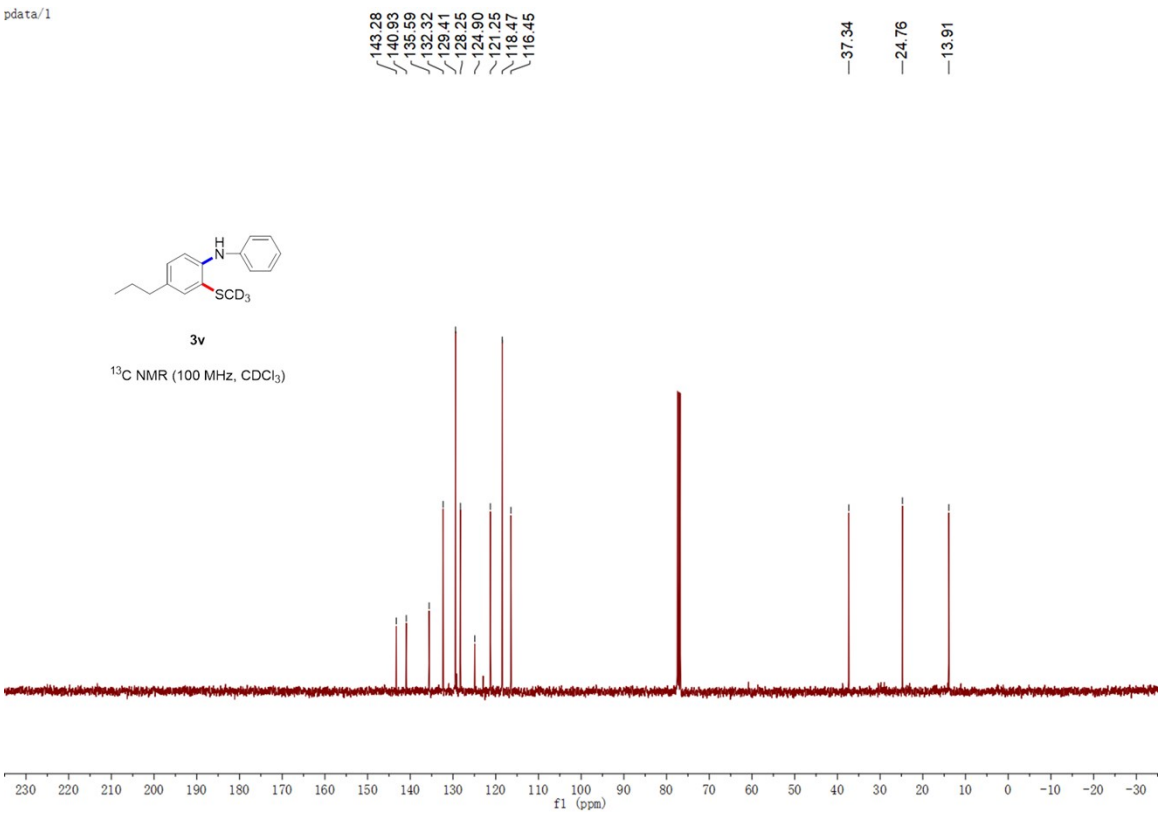
^{1}H NMR (400 MHz, $CDCl_3$)

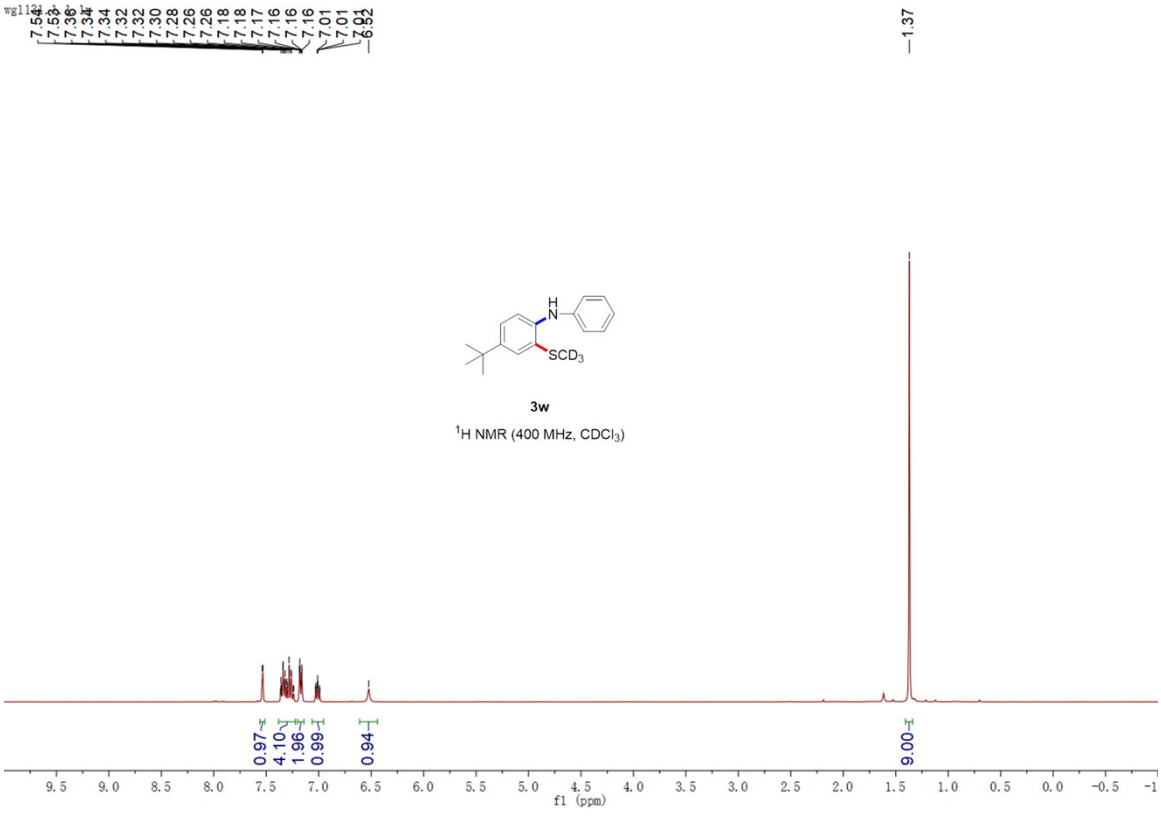

pdata/1
143.38
140.61
132.70
130.71
129.43
128.77
125.32
121.20
118.33
116.81
20.68
SCD3
3t
13C NMR (100 MHz, CDCl3)
f1 (ppm)


wg1110.1.1.1r
7.37
7.35
7.34
7.33
7.30
7.28
7.17
7.17
7.15
7.09
7.08
7.07
7.06
7.03
7.01
6.99
6.99
6.40
2.69
2.67
2.65
2.64
1.33
1.31
1.29
SCD3
3u
1H NMR (400 MHz, CDCl3)
2.80
1.05
1.91
0.97
0.96
0.82
2.00
3.12
f1 (ppm)

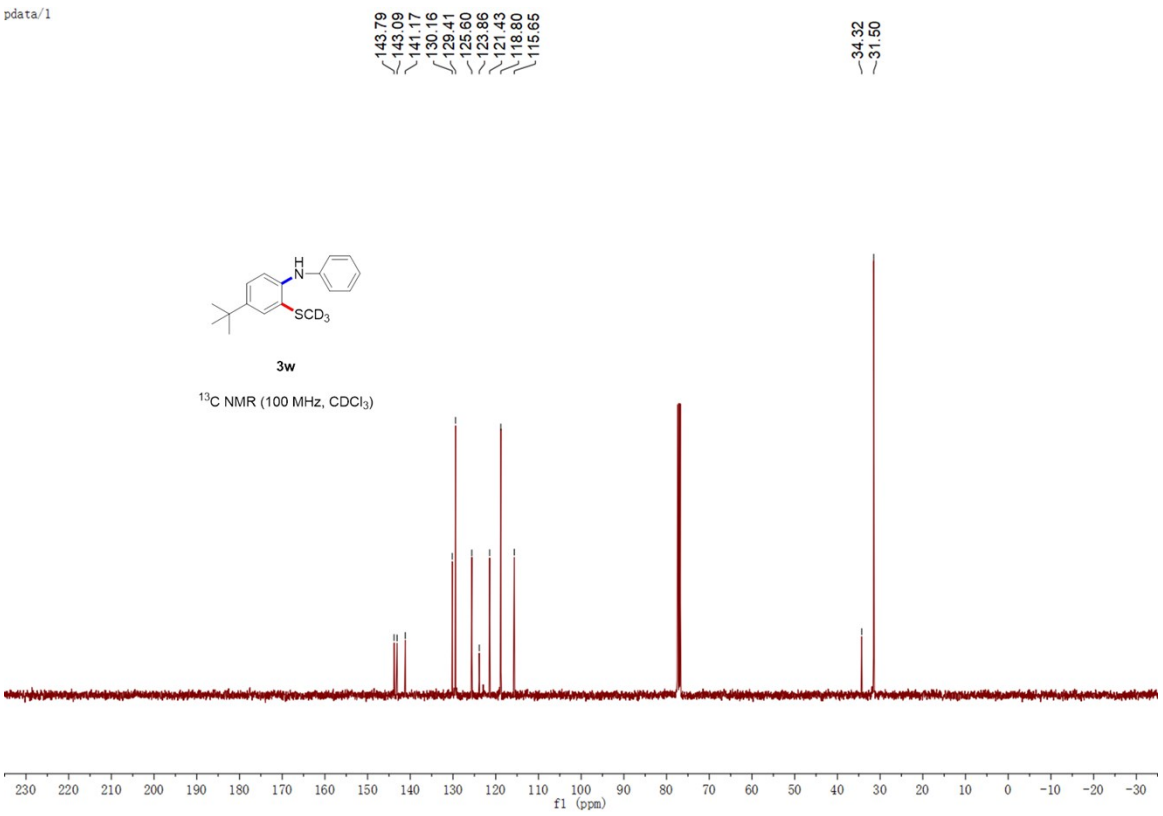

pdata/1
143.32
140.96
137.17
131.79
129.44
127.70
125.06
121.28
118.48
116.64
28.20
15.86
SCD3
3u
13C NMR (100 MHz, CDCl3)
f1 (ppm)


7.35
7.34
7.33
7.33
7.31
7.31
7.30
7.29
7.27
7.25
7.15
7.15
7.14
7.13
7.04
7.03
7.02
7.01
7.01
6.99
6.41
2.59
2.57
2.55
1.73
1.71
1.69
1.67
1.65
1.63
1.02
1.01
0.99
SCD3
3v
1H NMR (400 MHz, CDCl3)
4.01
1.97
1.98
0.88
2.00
2.12
3.09
f1 (ppm)


pdata/1
143.28
140.93
135.59
132.32
129.41
128.25
124.90
121.25
118.47
116.45
37.34
24.76
13.91
SCD3
3v
13C NMR (100 MHz, CDCl3)
f1 (ppm)


7.54
7.53
7.36
7.34
7.34
7.32
7.32
7.30
7.28
7.26
7.26
7.18
7.18
7.17
7.16
7.16
7.16
7.01
7.01
6.52
1.37
SCD3
3w
1H NMR (400 MHz, CDCl3)
0.97
4.10
1.96
0.99
0.94
9.00
f1 (ppm)

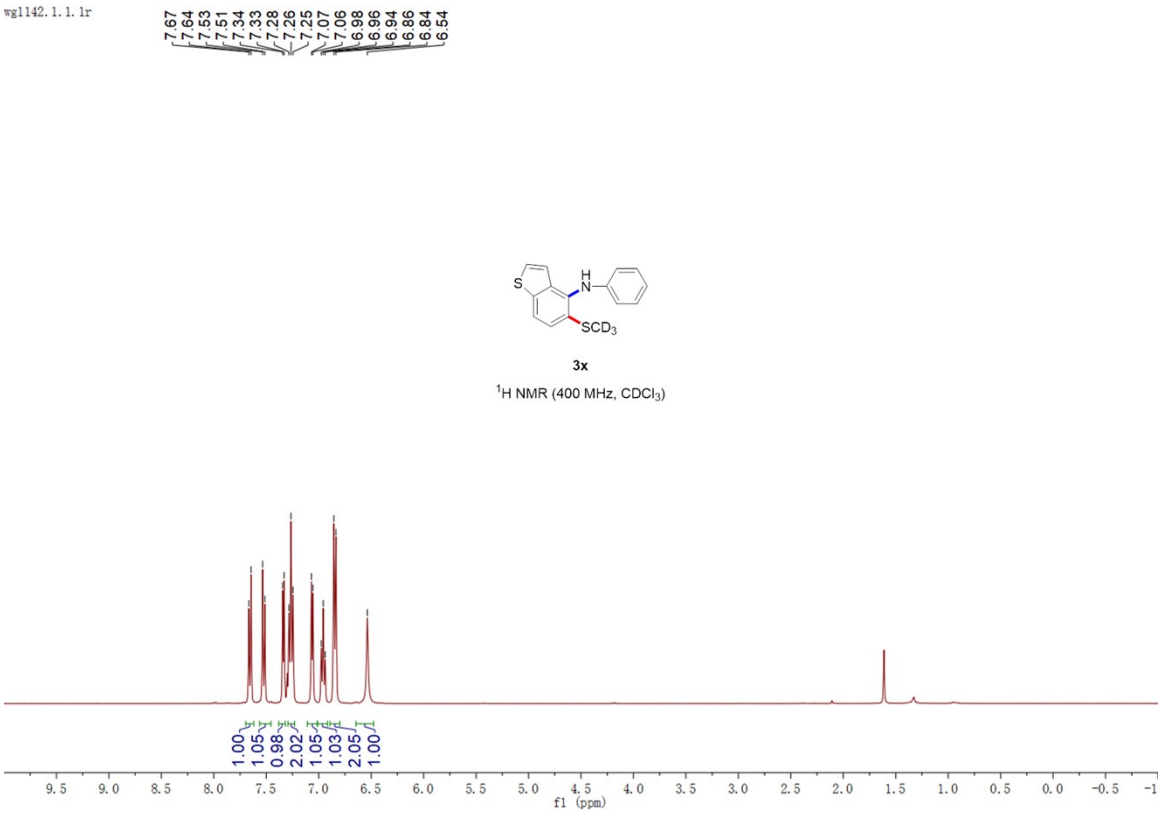
pdata/1



3w

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

wgl142.1.1.1r

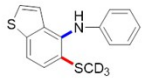


3x

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

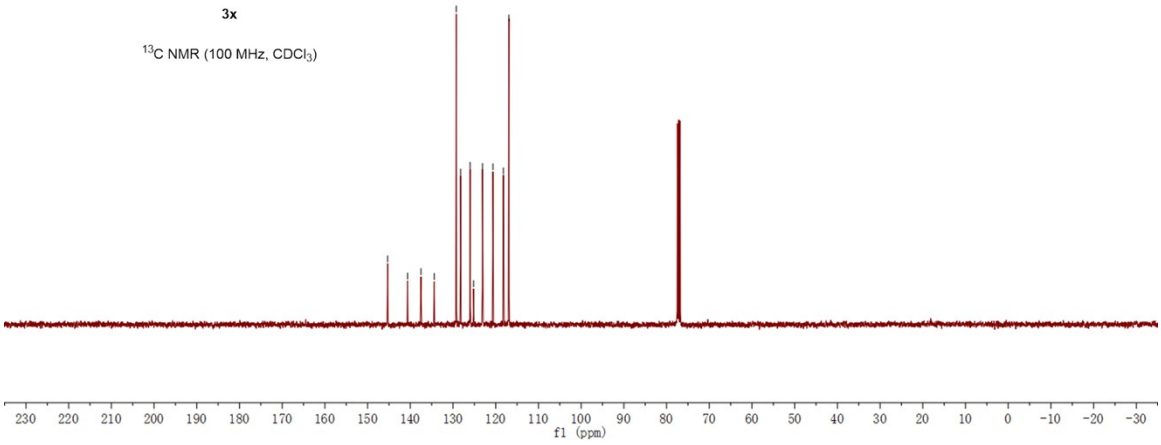
pdata/1

145.30
140.64
137.51
134.40
129.23
128.21
125.99
125.18
123.10
120.65
118.21
116.91



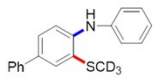
3x

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



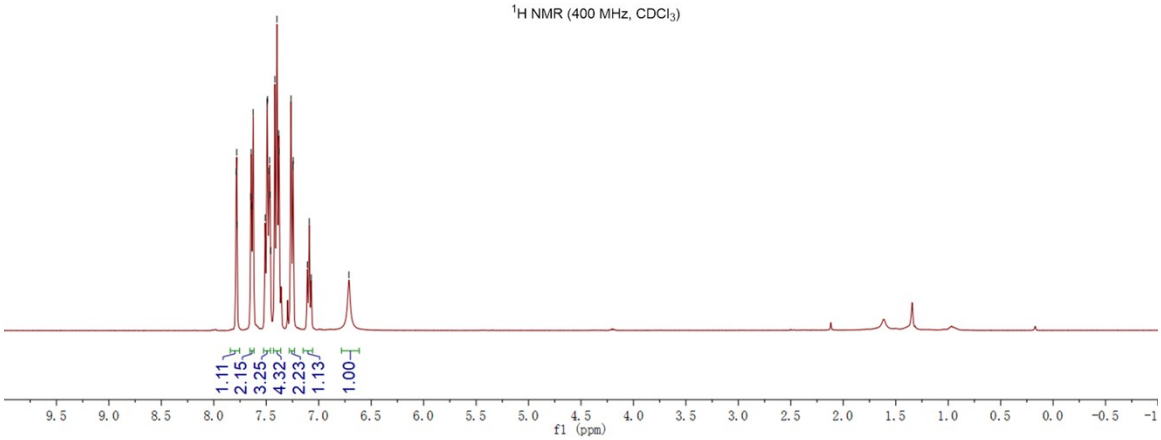
wgl160.1.1

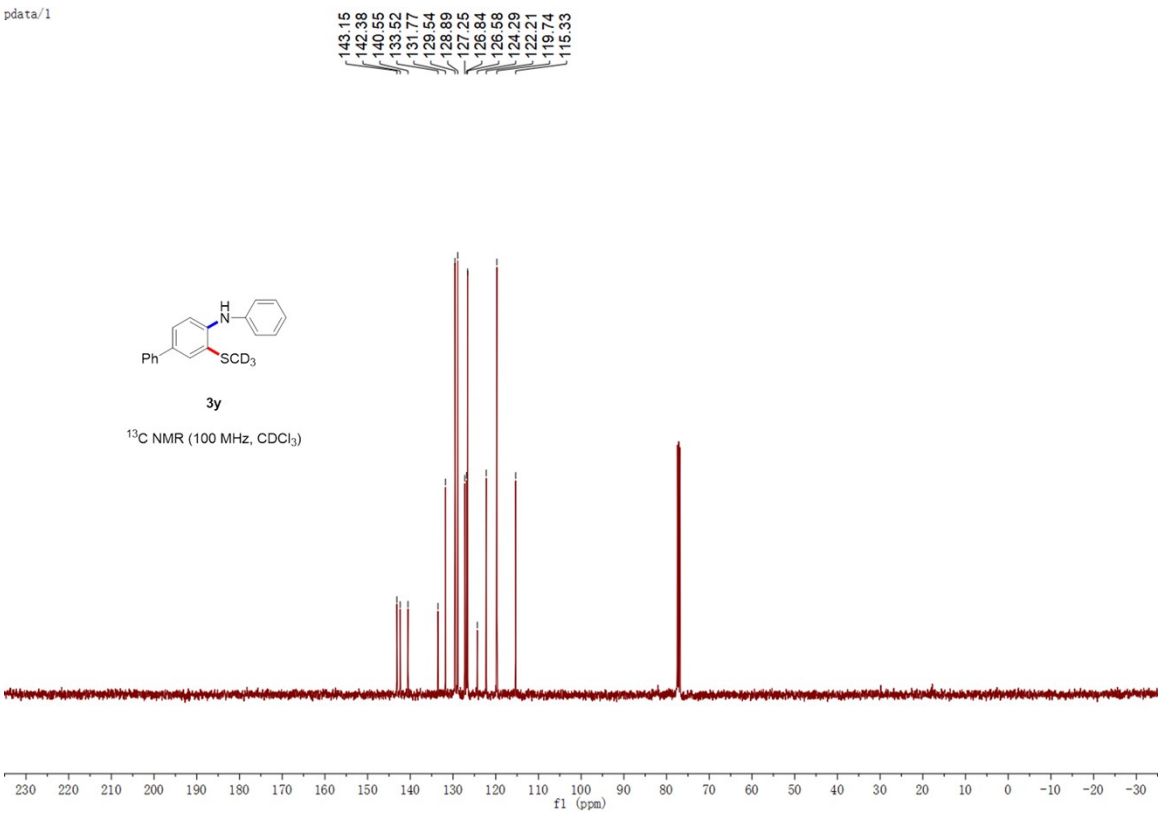
7.79
7.78
7.65
7.64
7.64
7.63
7.51
7.49
7.49
7.47
7.47
7.46
7.42
7.40
7.38
7.38
7.26
7.25
7.24
6.71

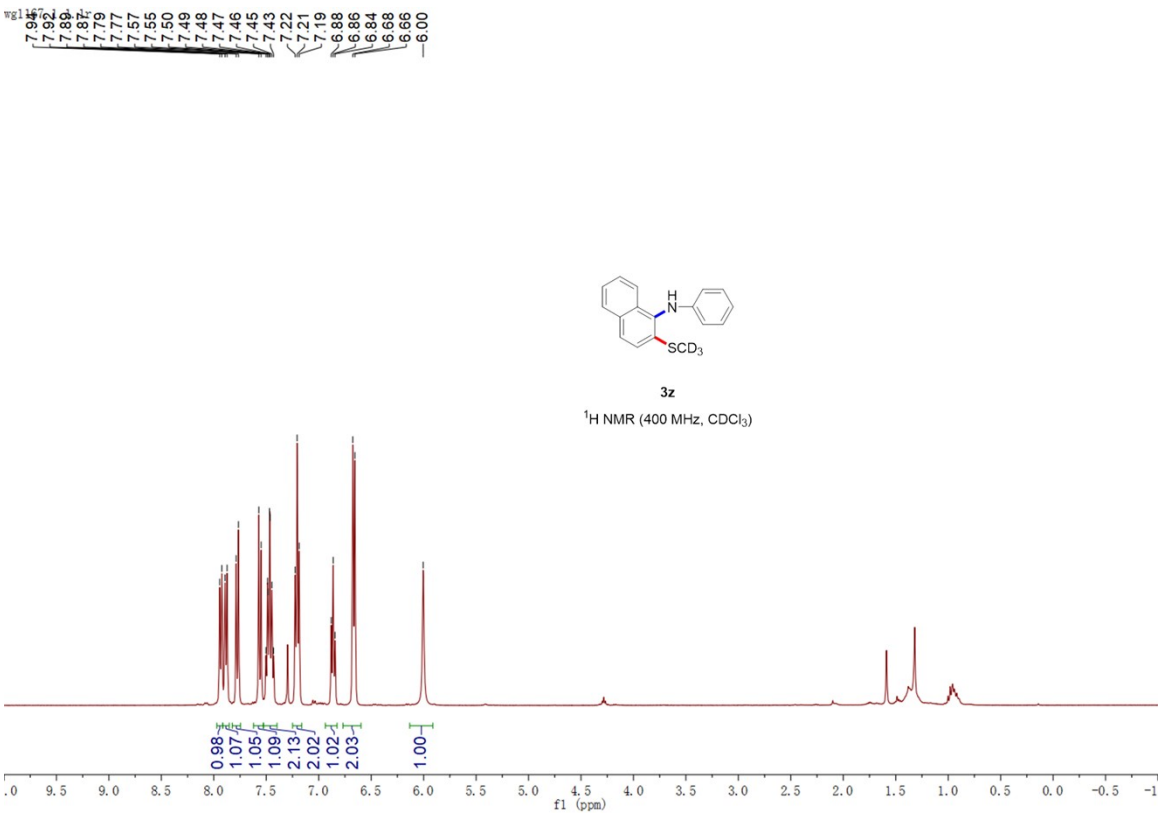


3y

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

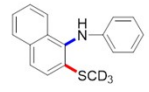



pdata/1
143.15
142.38
140.55
133.52
131.77
129.54
128.89
127.25
126.84
126.58
124.29
122.21
119.74
115.33
Ph
SCD3
3y
13C NMR (100 MHz, CDCl3)
f1 (ppm)


7.94
7.92
7.89
7.87
7.79
7.77
7.57
7.55
7.50
7.49
7.48
7.47
7.46
7.45
7.43
7.22
7.21
7.19
6.88
6.86
6.84
6.68
6.66
6.00
SCD3
3z
1H NMR (400 MHz, CDCl3)
0.98
1.07
1.05
1.09
2.13
2.02
1.02
2.03
1.00
f1 (ppm)

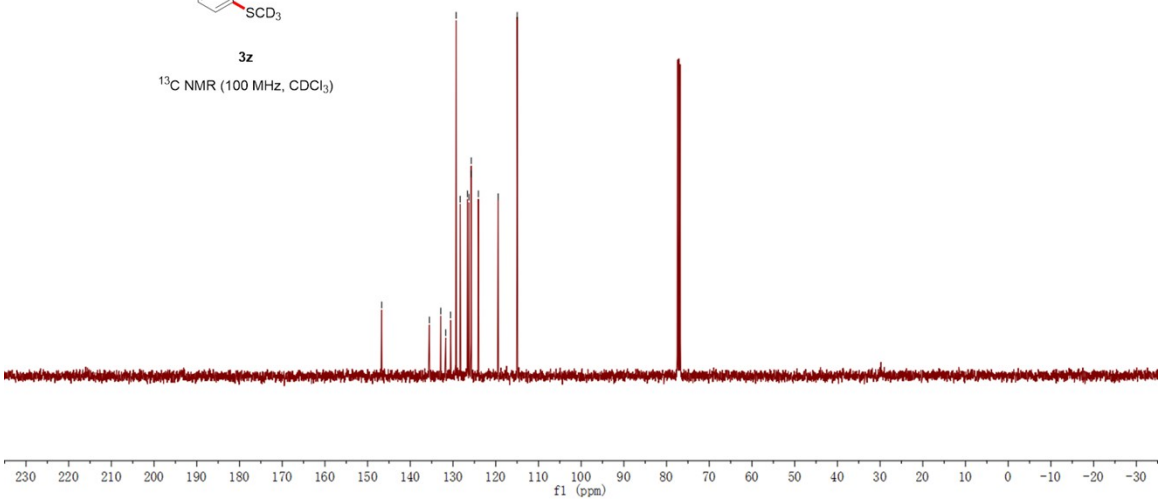
pdata/1

146.71
135.54
132.88
131.71
130.56
129.27
128.32
126.63
126.26
125.74
125.71
124.06
119.44
114.98



3z

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

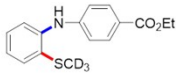


wg1092.1.1.1r

8.00
7.98
7.47
7.45
7.42
7.40
7.26
7.24
7.22
7.08
7.06
7.05
7.03
6.60

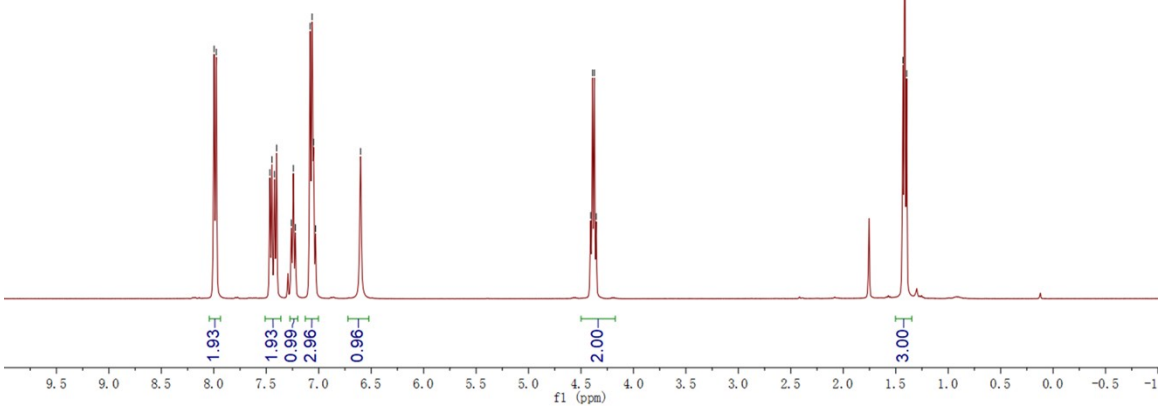
4.41
4.39
4.37
4.35

1.43
1.41
1.40



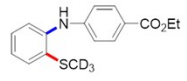
4a

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



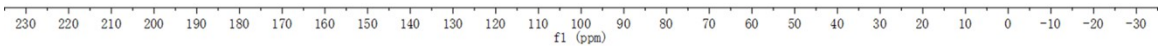
pdata/1

166.53
147.54
140.66
131.47
131.41
127.98
127.71
123.12
122.20
118.99
115.59
60.57
14.51



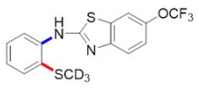
4a

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



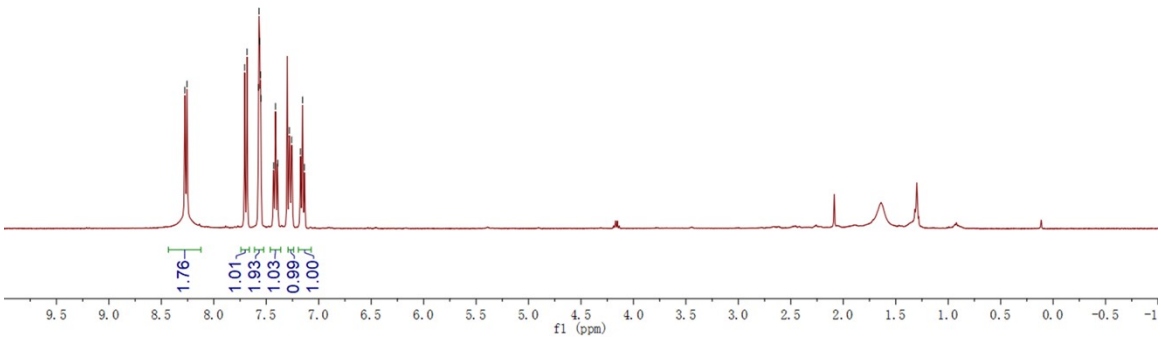
wg1115.1.1.1r

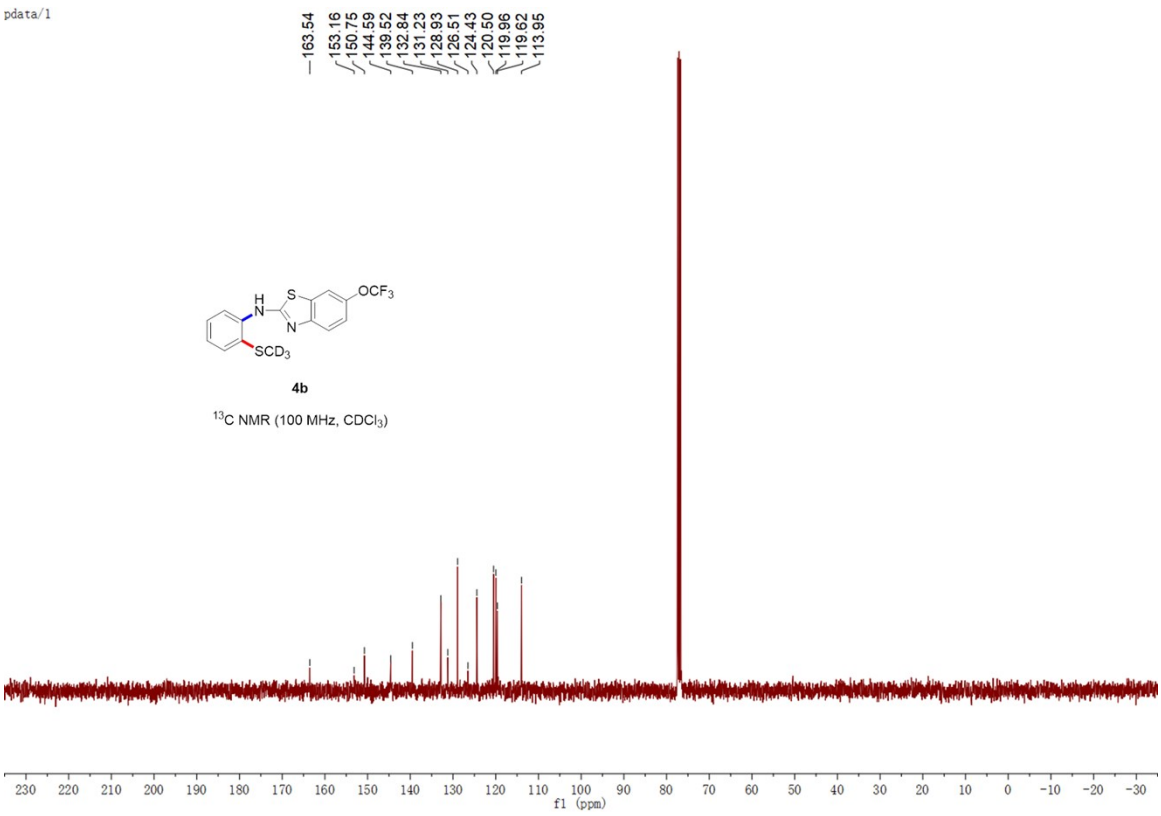
8.28
8.26
7.71
7.68
7.57
7.57
7.56
7.55
7.55
7.43
7.41
7.39
7.28
7.26
7.17
7.15
7.14

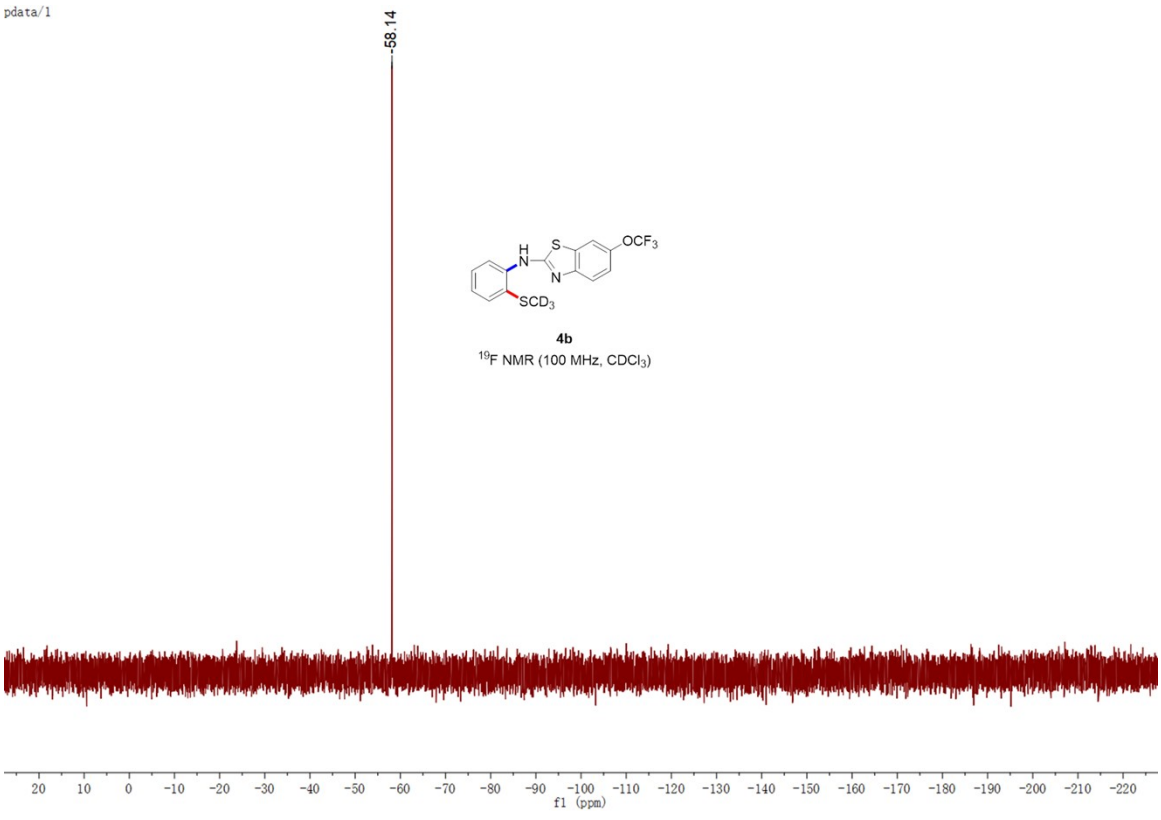


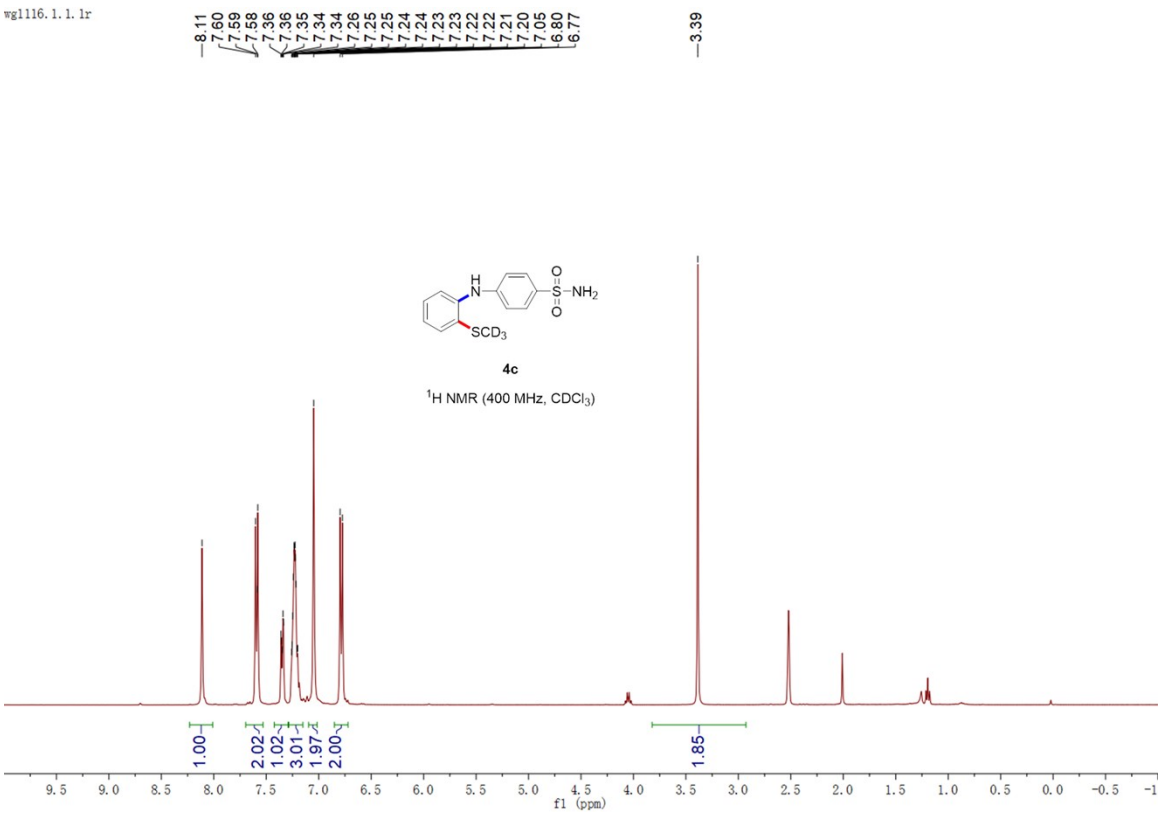
4b

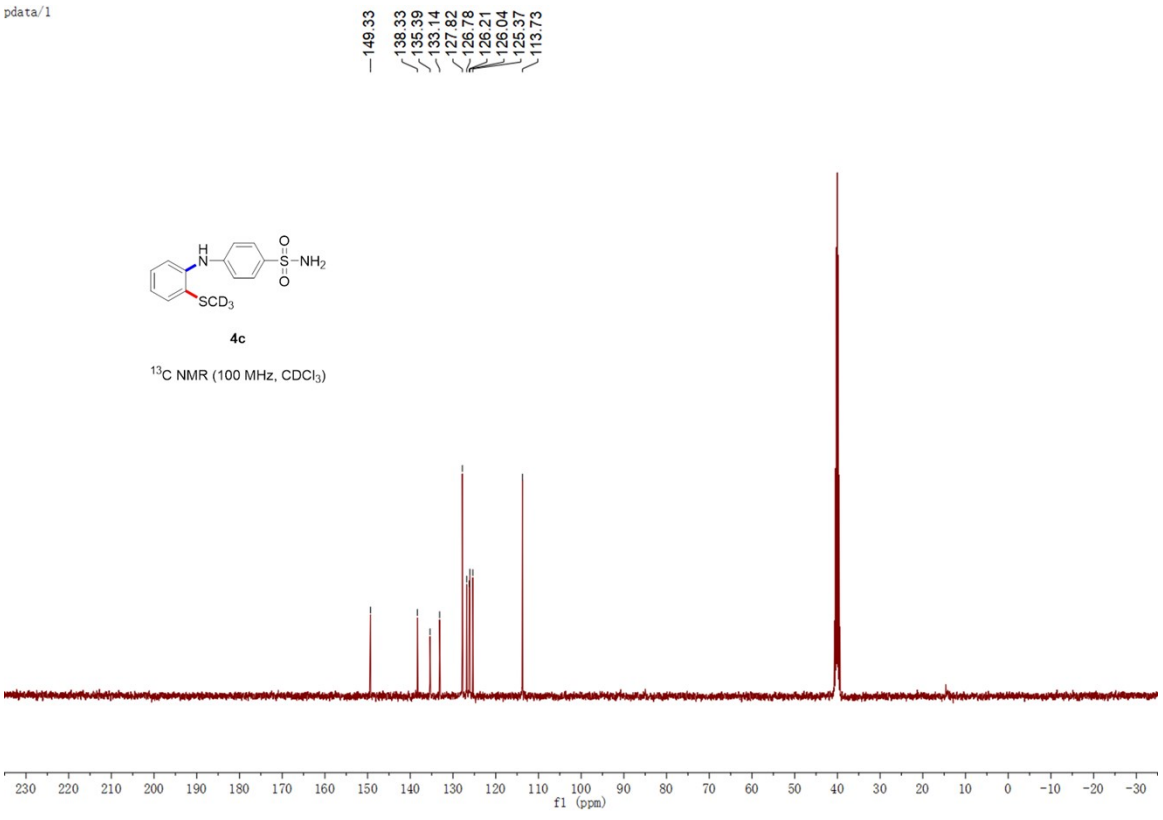
^{1}H NMR (400 MHz, $CDCl_3$)

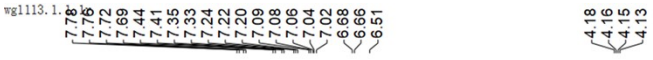


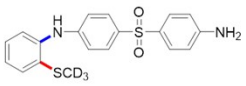

pdata/1
163.54
153.16
150.75
144.59
139.52
132.84
131.23
128.93
126.51
124.43
120.50
119.96
119.62
113.95
OCF3
H
N
S
N
SCD3
4b
13C NMR (100 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)


pdata/1
-58.14
OCF3
H
N
S
N
SCD3
4b
19F NMR (100 MHz, CDCl3)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)


wgl116.1.1.1r
8.11
7.60
7.59
7.58
7.36
7.36
7.35
7.34
7.34
7.26
7.25
7.25
7.24
7.24
7.23
7.23
7.22
7.22
7.21
7.20
7.05
6.80
6.77
3.39
4c
1H NMR (400 MHz, CDCl3)
1.00
2.02
1.02
3.01
1.97
2.00
1.85
f1 (ppm)

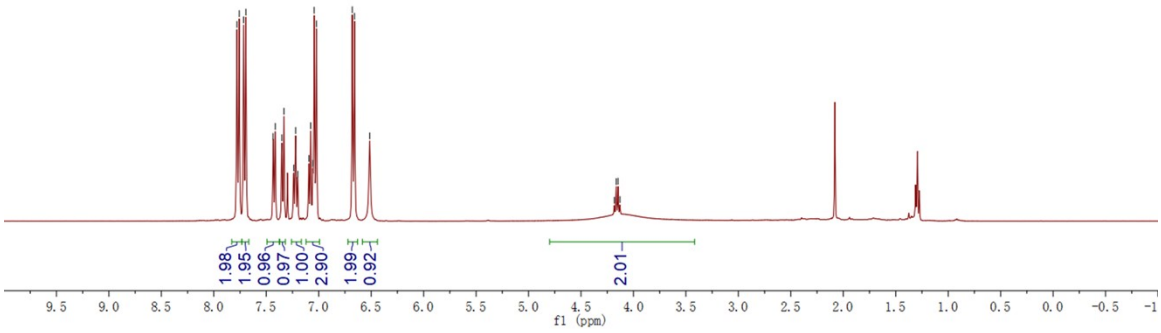

pdata/1
149.33
138.33
135.39
133.14
127.82
126.78
126.21
126.04
125.37
113.73
4c
13C NMR (100 MHz, CDCl3)
f1 (ppm)

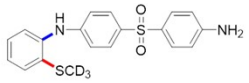




4d

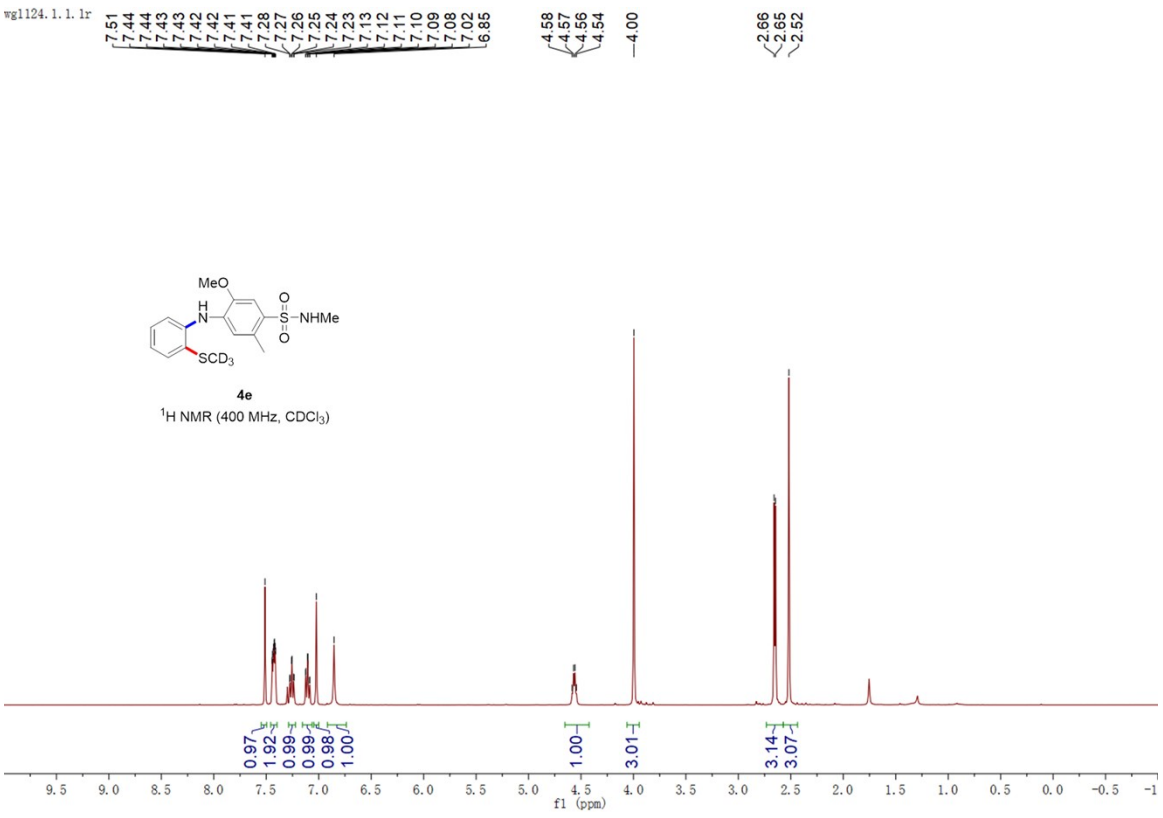
^{1}H NMR (400 MHz, $CDCl_3$)

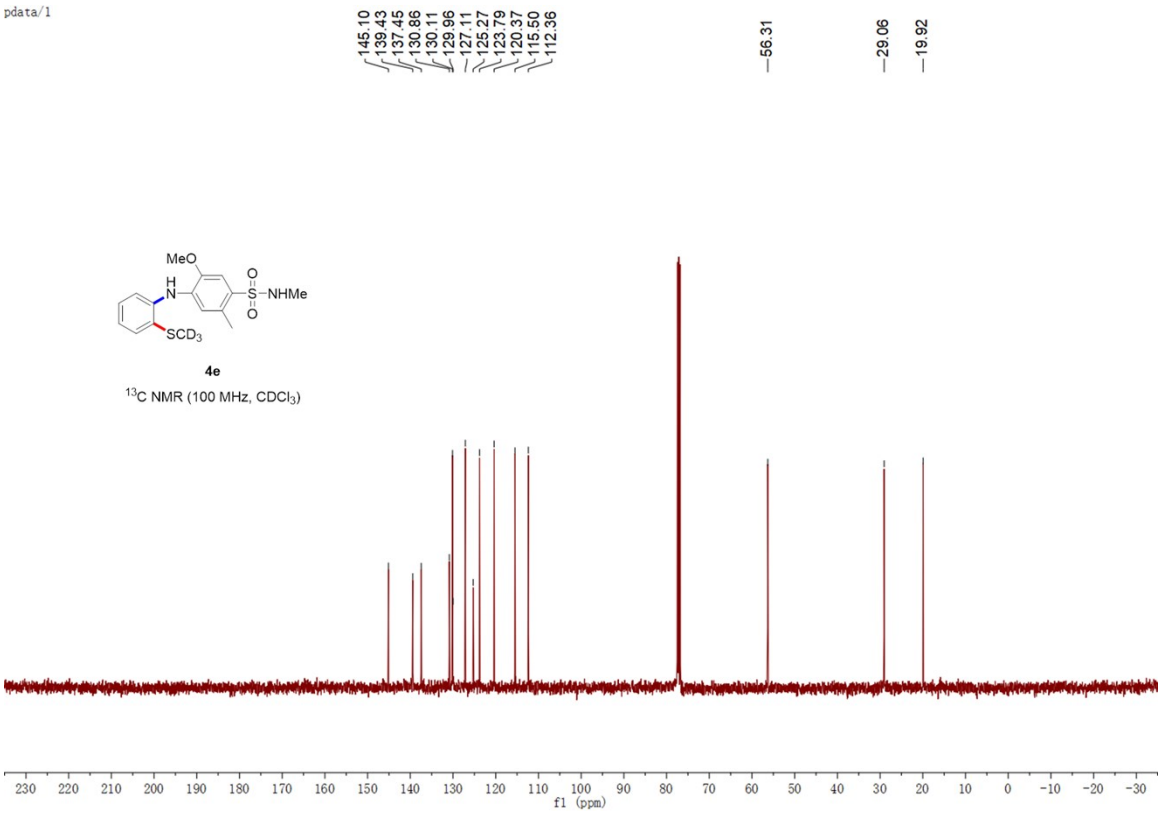


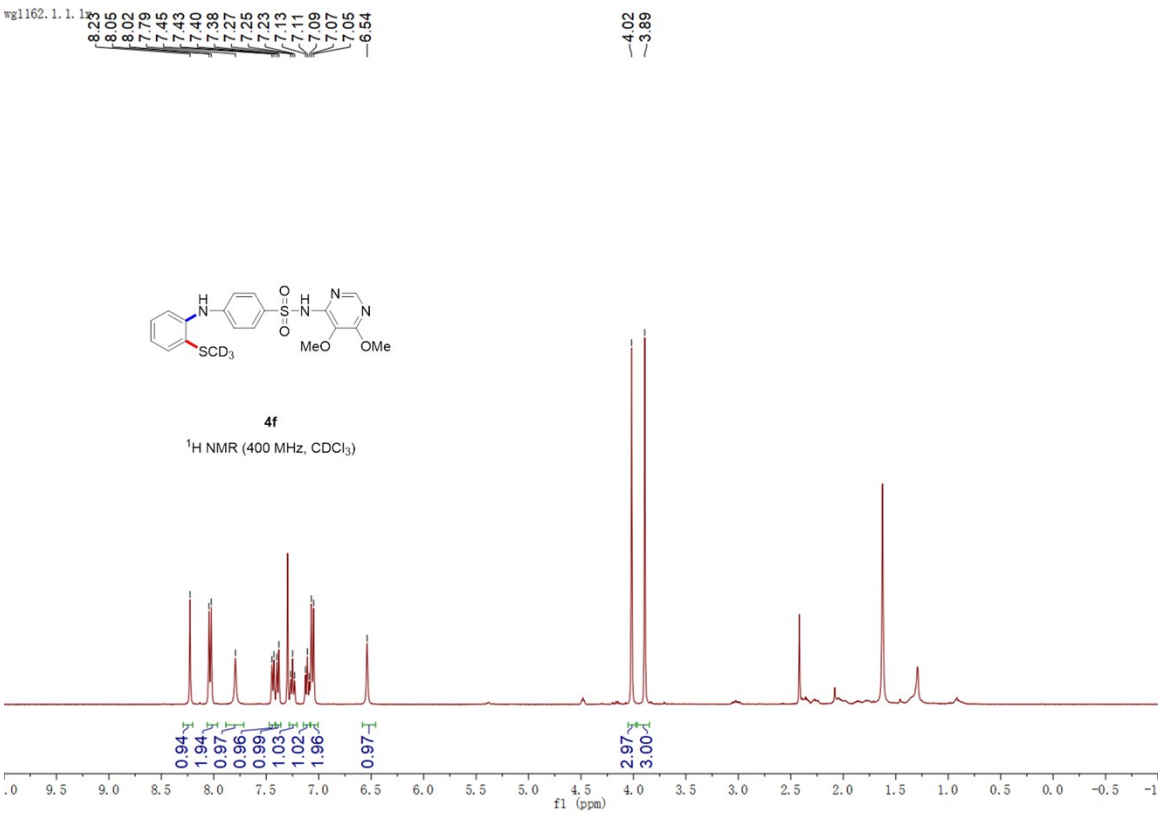


4d

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

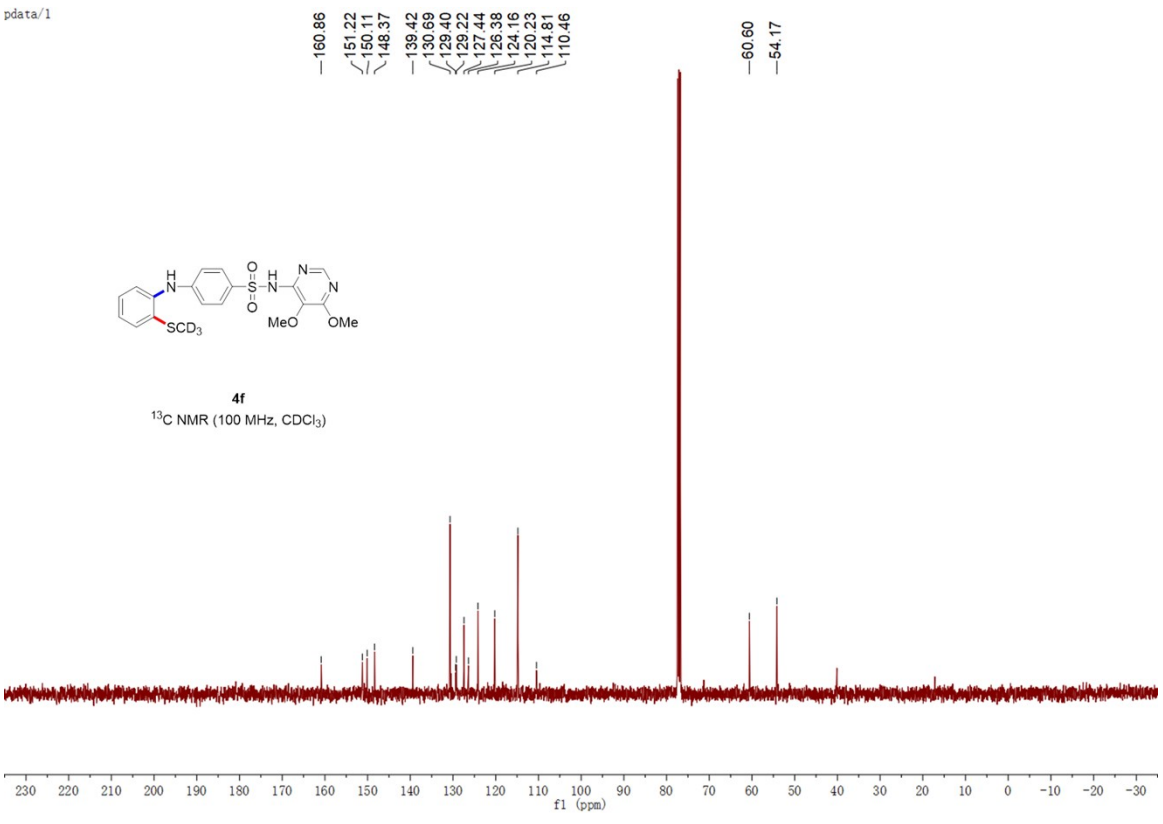

wgl124.1.1.1r
7.51
7.44
7.44
7.43
7.43
7.42
7.42
7.41
7.41
7.28
7.27
7.26
7.25
7.24
7.23
7.13
7.12
7.11
7.10
7.09
7.08
7.02
6.85
4.58
4.57
4.56
4.54
4.00
2.66
2.65
2.52
MeO
H
N
O
S
O
NHMe
SCD3
4e
1H NMR (400 MHz, CDCl3)
0.97
1.92
0.99
0.99
0.98
1.00
1.00
3.01
3.14
3.07
f1 (ppm)


pdata/1
145.10
139.43
137.45
130.86
130.11
129.96
127.11
125.27
123.79
120.37
115.50
112.36
56.31
29.06
19.92
MeO
H
N
O
S
O
NHMe
SCD3
4e
13C NMR (100 MHz, CDCl3)
f1 (ppm)



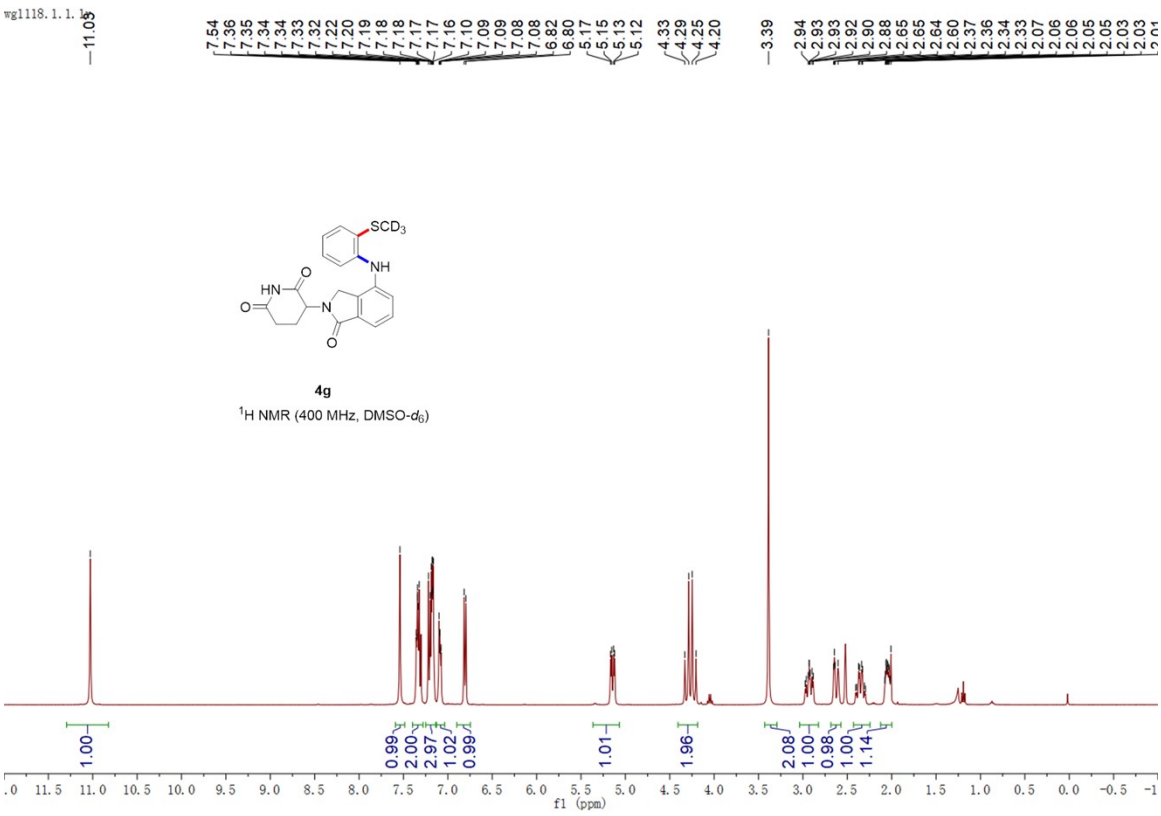
4f

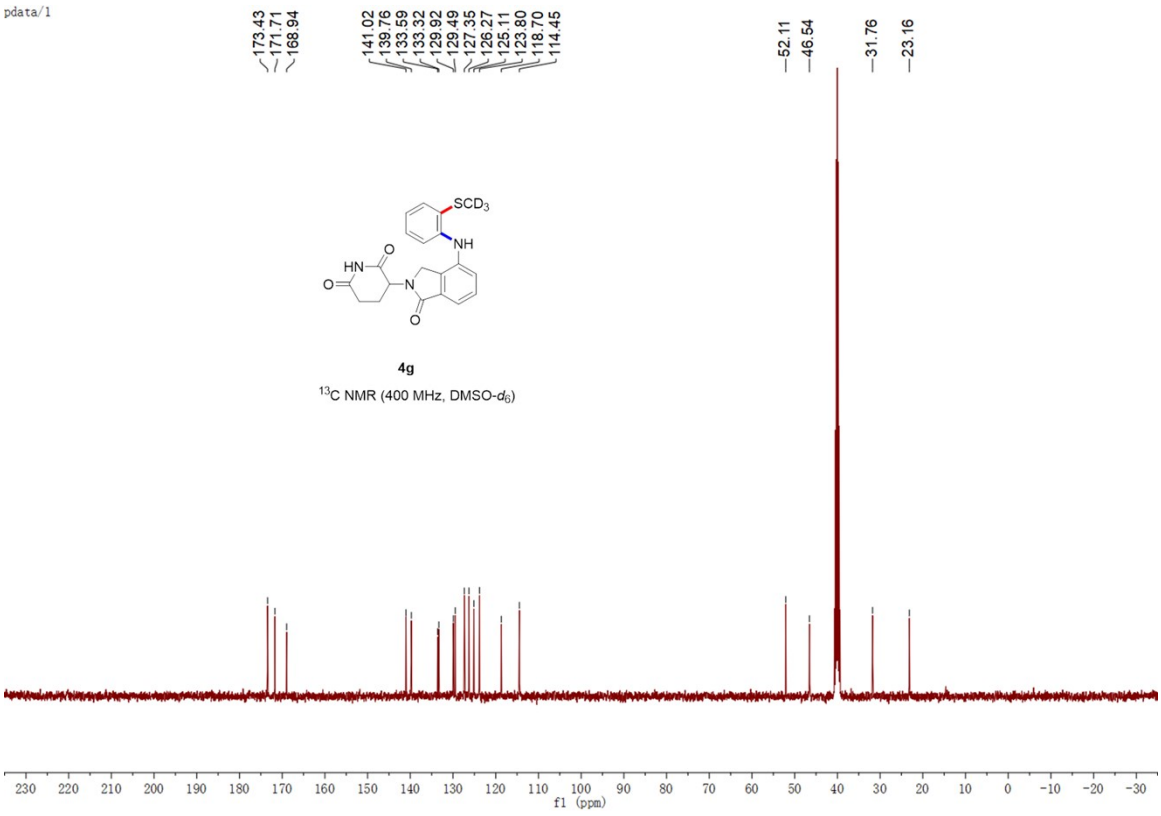
^{1}H NMR (400 MHz, $CDCl_3$)

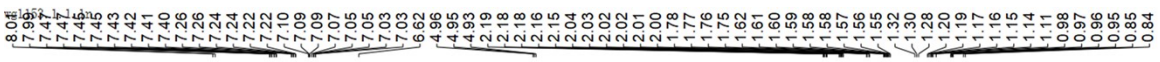


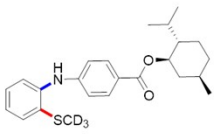
4f

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


wg1118.1.1.1
11.03
7.54
7.36
7.35
7.34
7.34
7.33
7.32
7.22
7.20
7.19
7.18
7.18
7.17
7.17
7.16
7.10
7.09
7.09
7.08
7.08
6.82
6.80
5.17
5.15
5.13
5.12
4.33
4.29
4.25
4.20
3.39
2.94
2.93
2.93
2.92
2.90
2.88
2.65
2.64
2.60
2.37
2.36
2.34
2.33
2.07
2.06
2.06
2.05
2.05
2.03
SCD3
NH
HN
O
N
O
O
4g
1H NMR (400 MHz, DMSO-d6)
1.00
0.99
2.00
2.97
1.02
0.99
1.01
1.96
2.08
1.00
0.98
1.00
1.14
f1 (ppm)

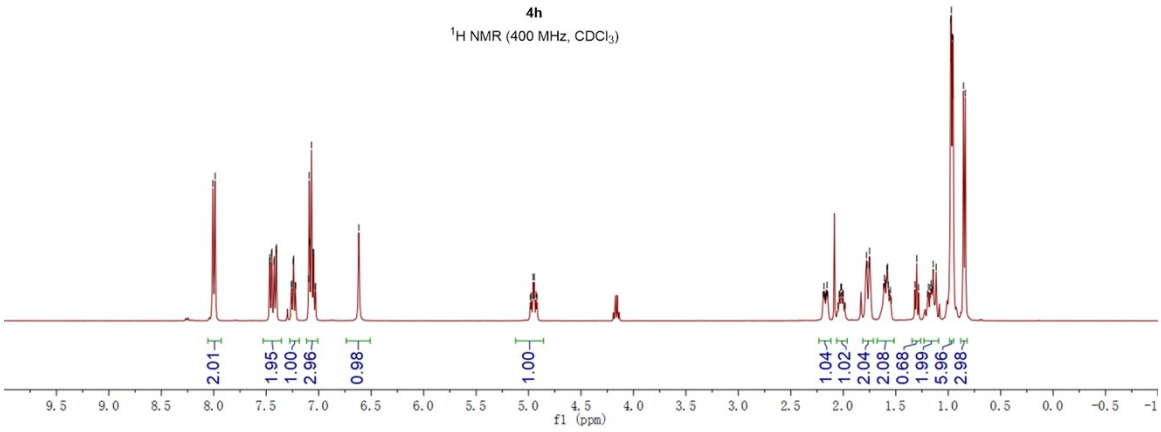

pdata/1
173.43
171.71
168.94
141.02
139.76
133.59
133.32
129.92
129.49
127.35
126.27
125.11
123.80
118.70
114.45
52.11
46.54
31.76
23.16
SCD3
NH
HN
O
N
O
O
4g
13C NMR (400 MHz, DMSO-d6)
f1 (ppm)

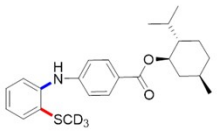




4h

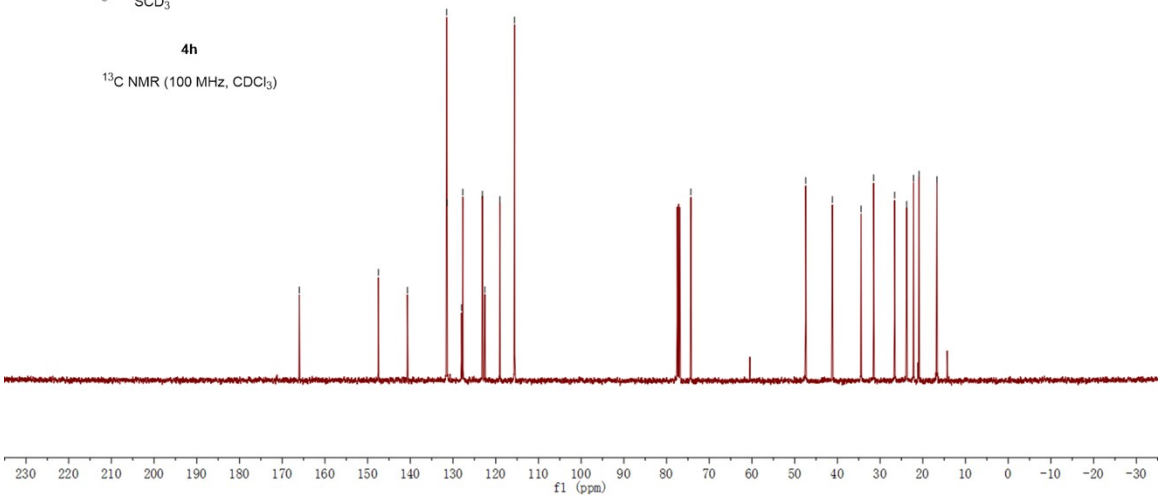
^{1}H NMR (400 MHz, $CDCl_3$)

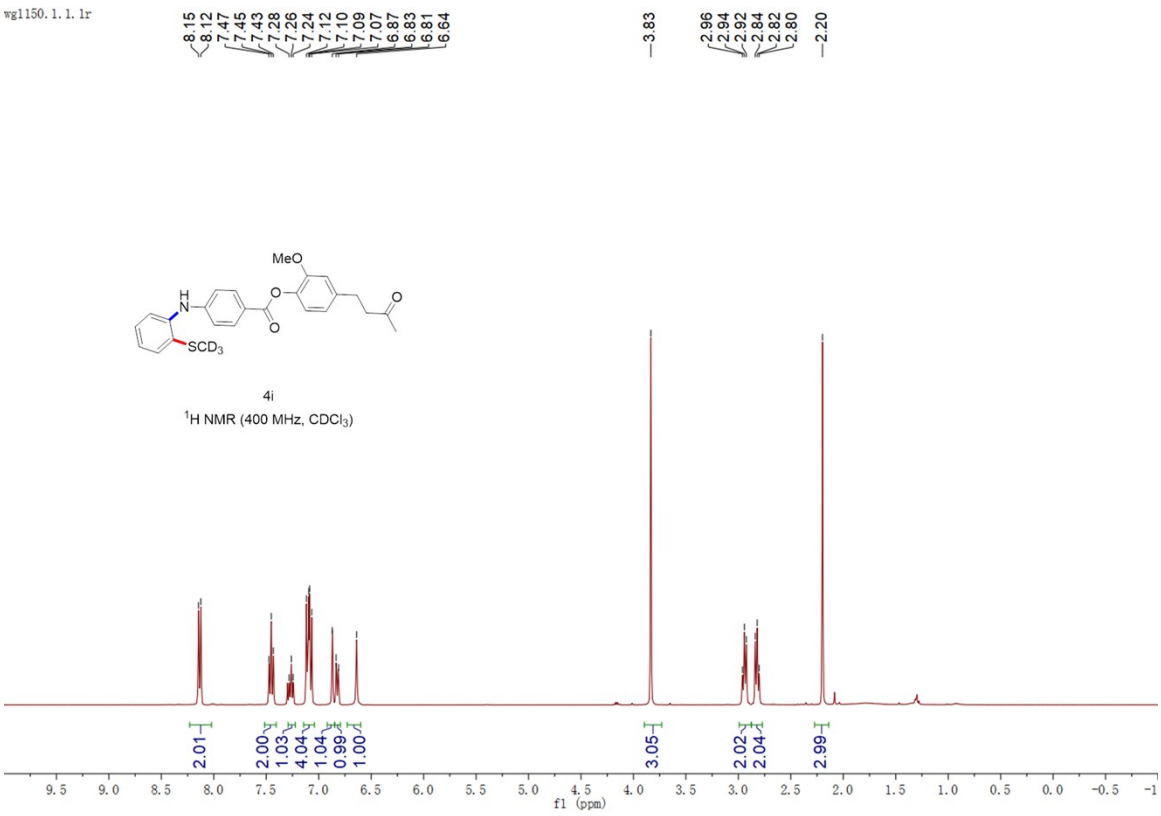




4h

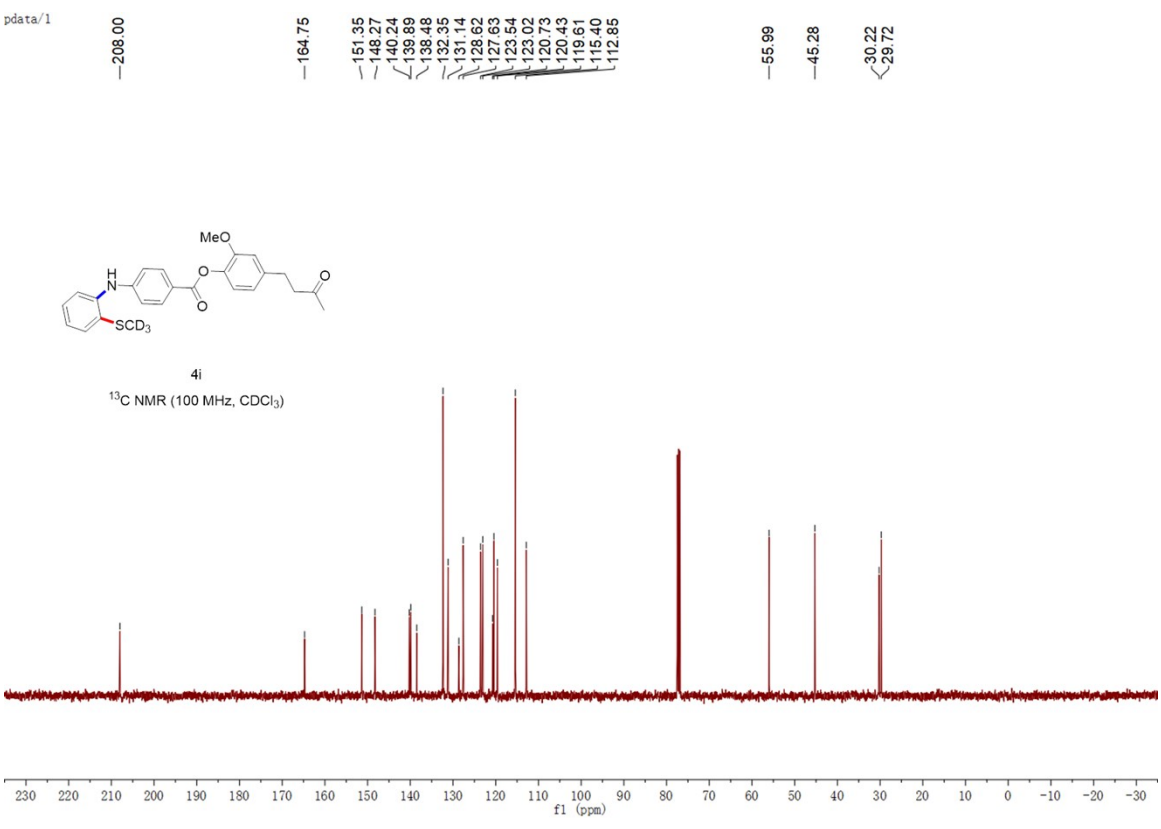
^{13}C NMR (100 MHz, $CDCl_3$)





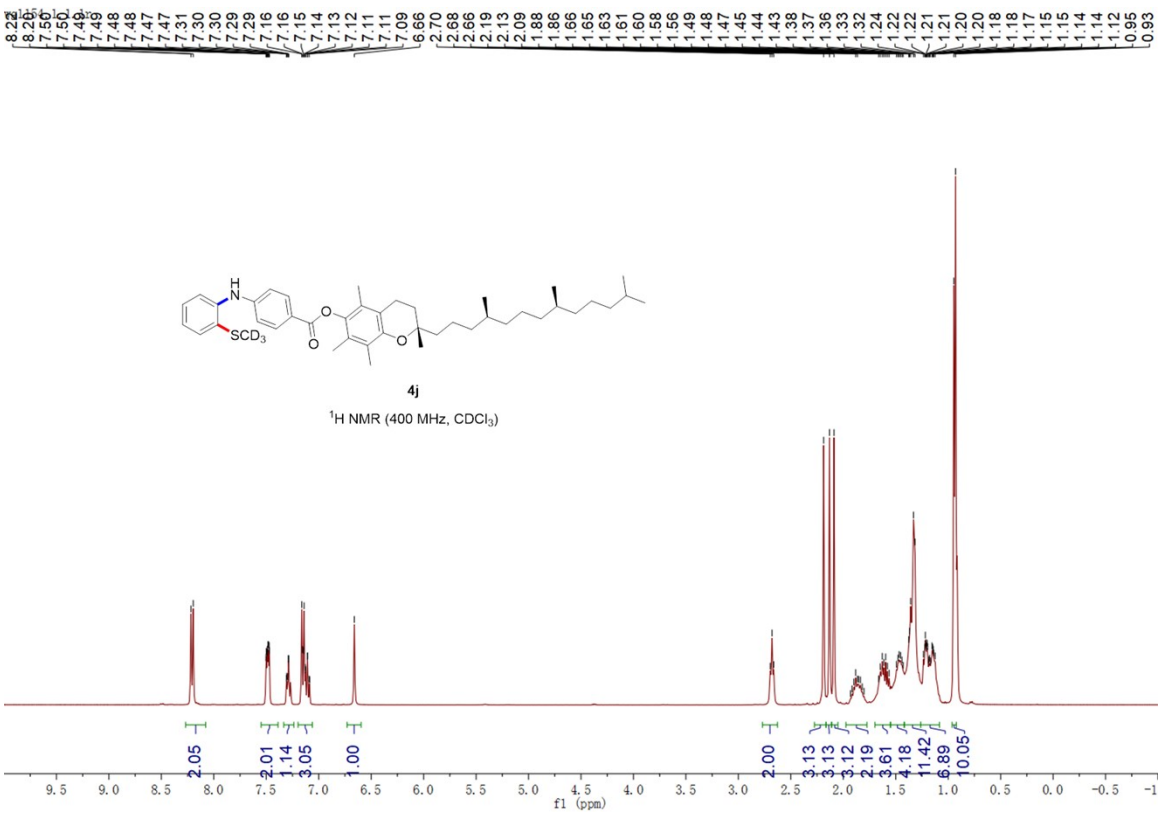
4i

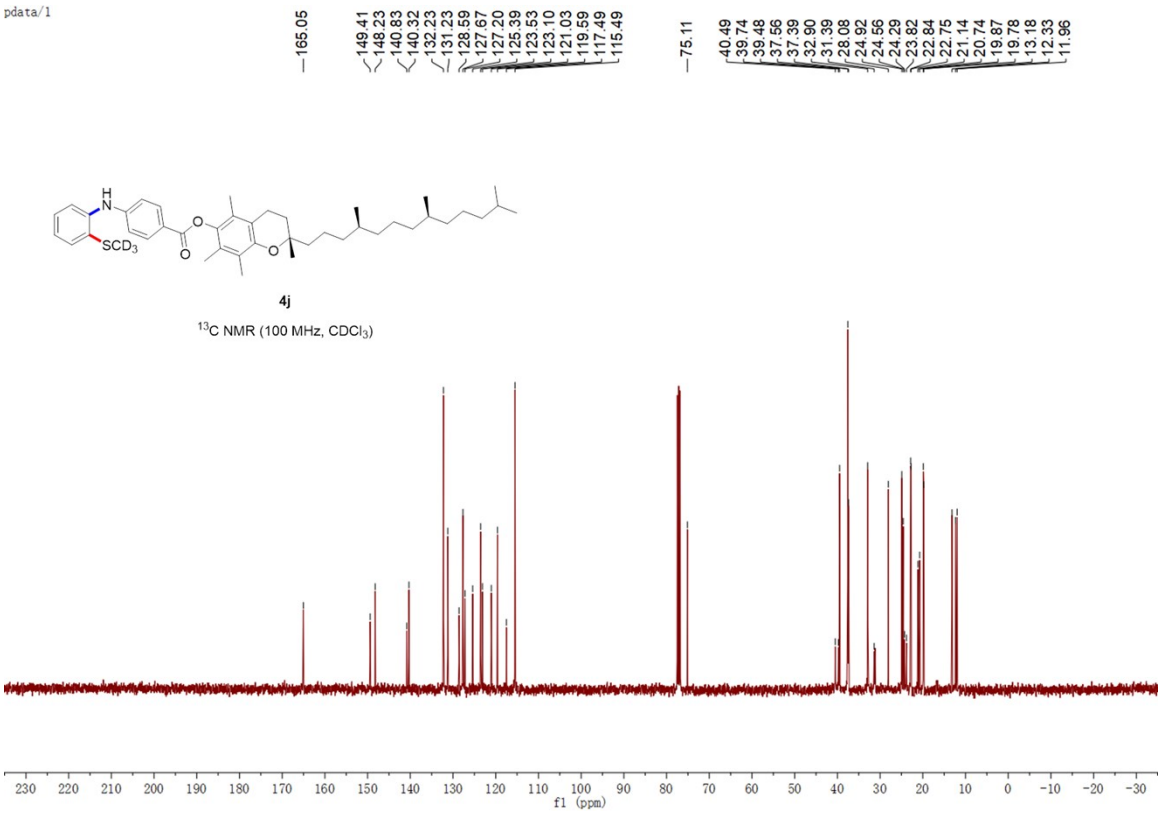
^{1}H NMR (400 MHz, $CDCl_3$)

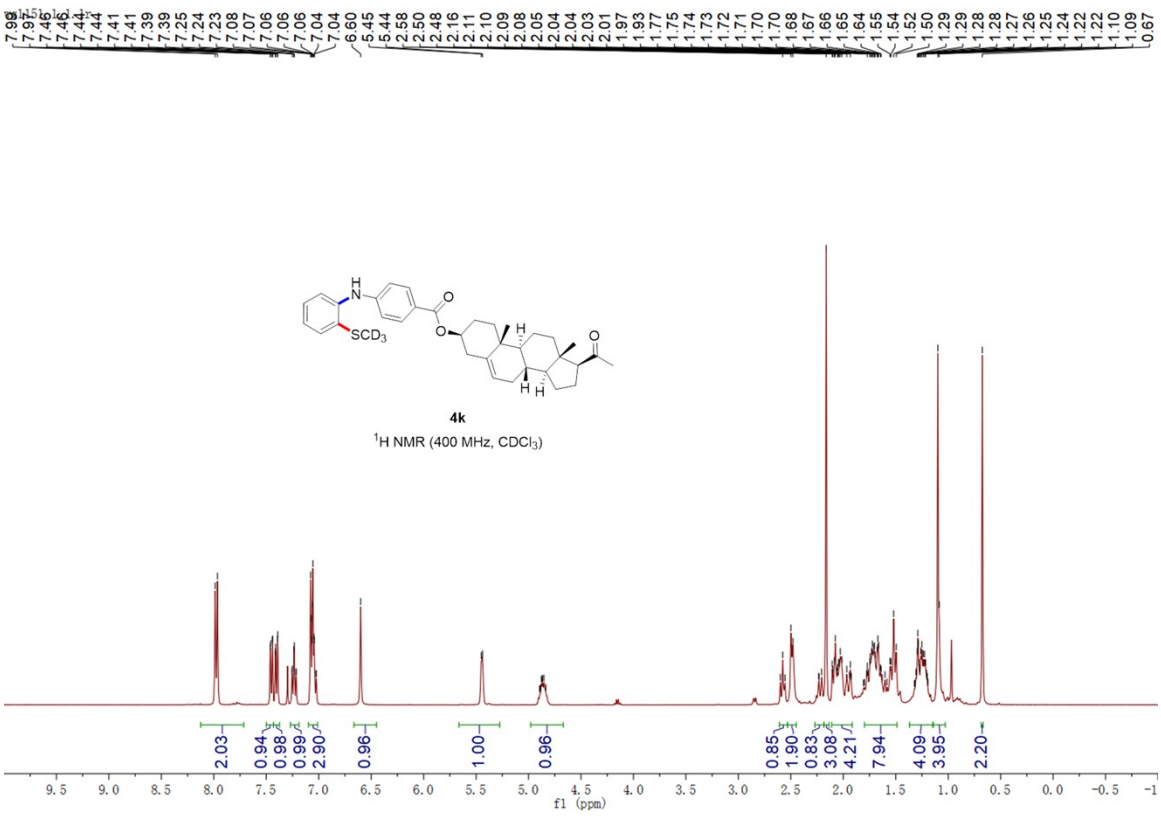


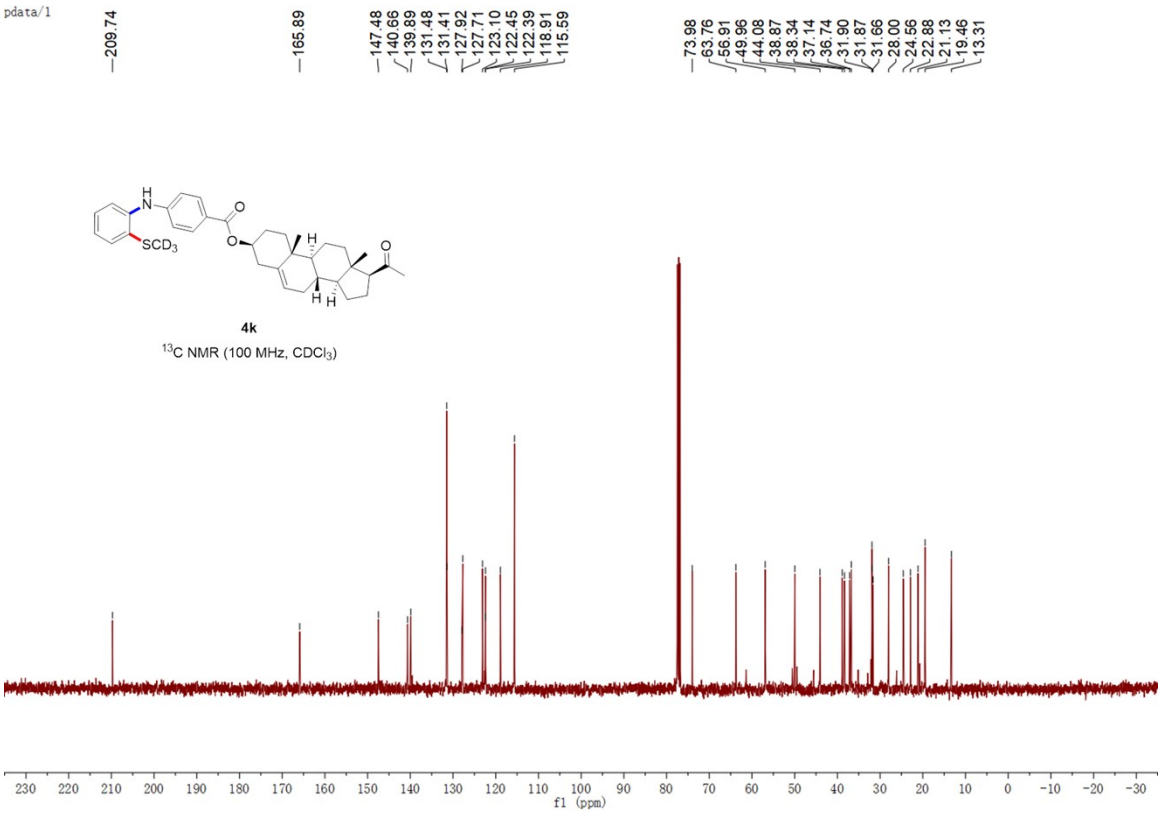
4i

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


4j
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

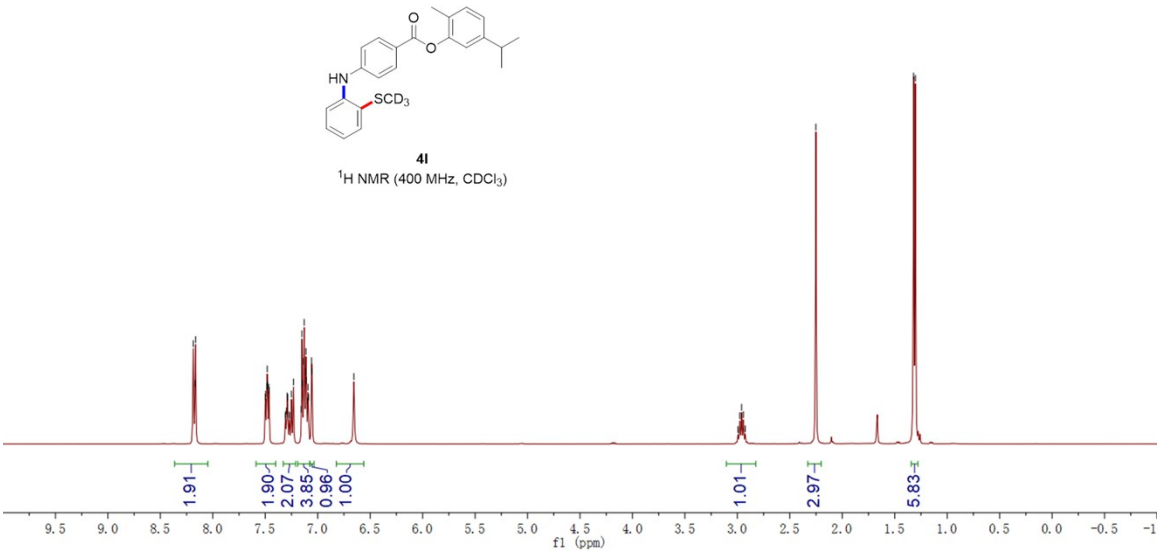

4j
^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)


SCD3
4k
1H NMR (400 MHz, CDCl3)
2.03
0.94
0.98
0.99
2.90
0.96
1.00
0.96
0.85
1.90
0.83
3.08
4.21
7.94
4.09
3.95
2.20
f1 (ppm)


pdata/1
209.74
165.89
147.48
140.66
139.89
131.48
131.41
127.92
127.71
123.10
122.45
122.39
118.91
115.59
73.98
63.76
56.91
49.96
44.08
38.87
38.34
37.14
36.74
31.90
31.87
31.66
28.00
24.56
22.88
21.13
19.46
13.31
SCD3
4k
13C NMR (100 MHz, CDCl3)
f1 (ppm)

wg1148.1.1.1r

8.19 8.17 8.16 7.50 7.50 7.49 7.48 7.48 7.47 7.46 7.31 7.31 7.30 7.29 7.29 7.27 7.27 7.25 7.23 7.16 7.15 7.15 7.13 7.13 7.12 7.11 7.11 7.10 7.09 7.09 7.06 7.05 6.66 2.99 2.98 2.96 2.94 2.93 2.25 1.32 1.30

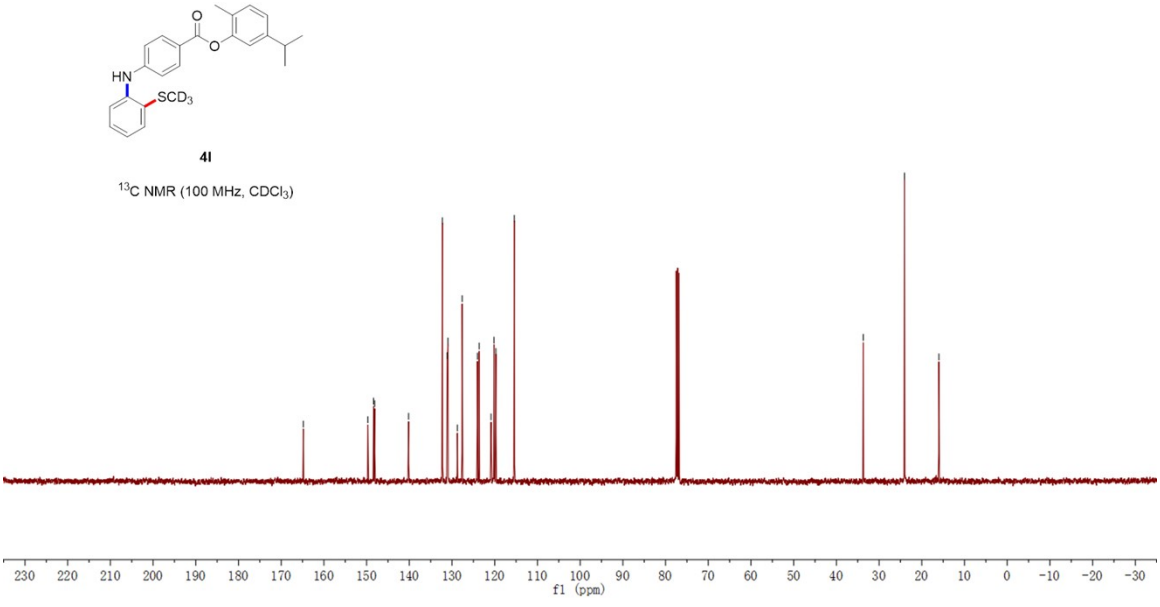


4l

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

pdata/1

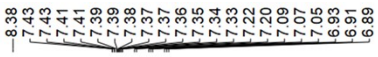
164.81 149.72 148.37 148.11 140.17 132.25 131.11 130.95 128.76 127.63 124.05 123.65 120.86 120.16 119.73 115.41 33.70 24.06 16.00

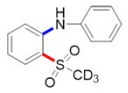


4l

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

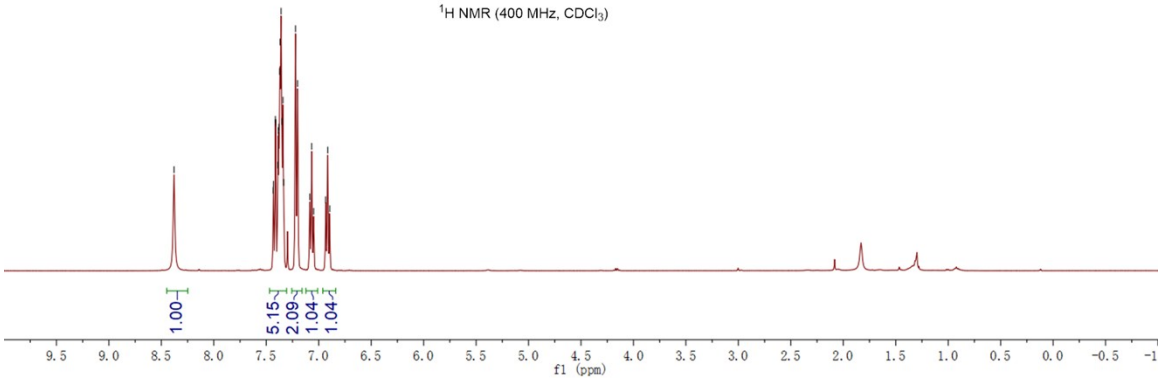
wgl156.1.1.1r



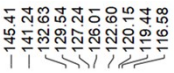


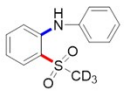
5a

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



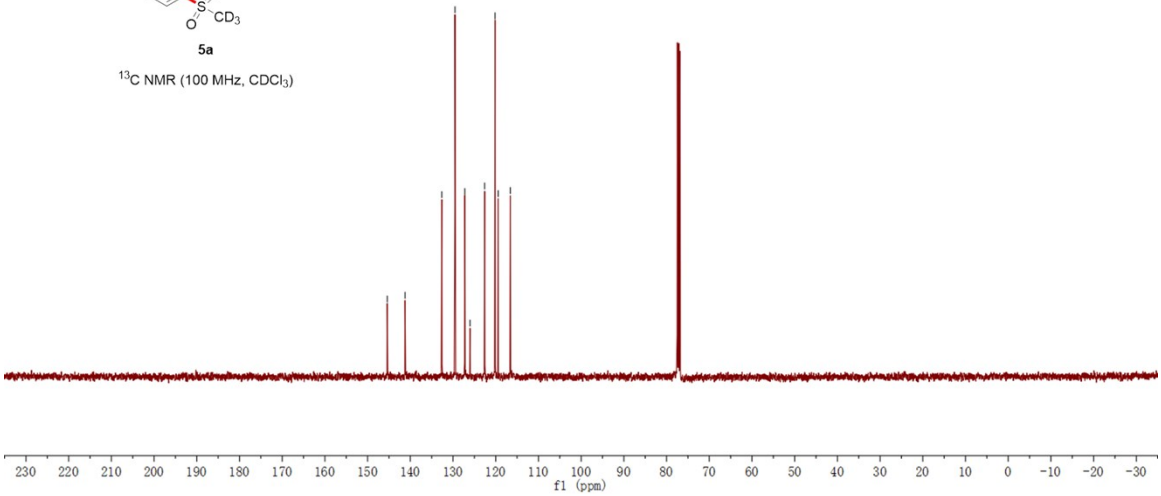
pdata/1

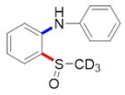




5a

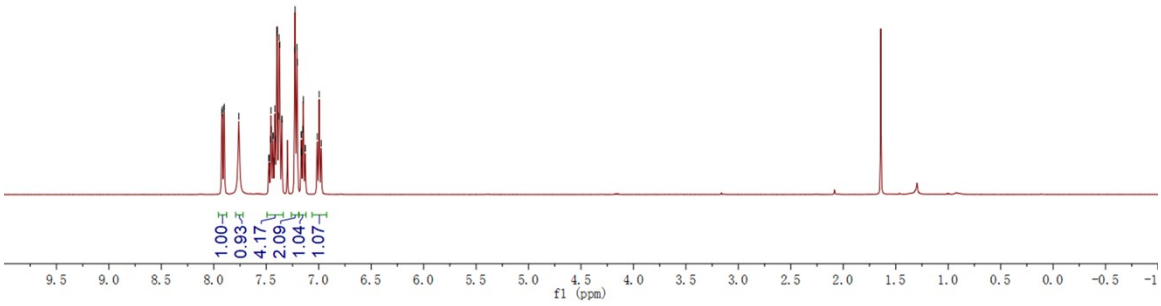
^{13}C NMR (100 MHz, $CDCl_3$)



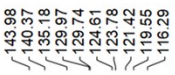


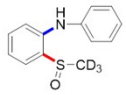
5b

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



pdata/1

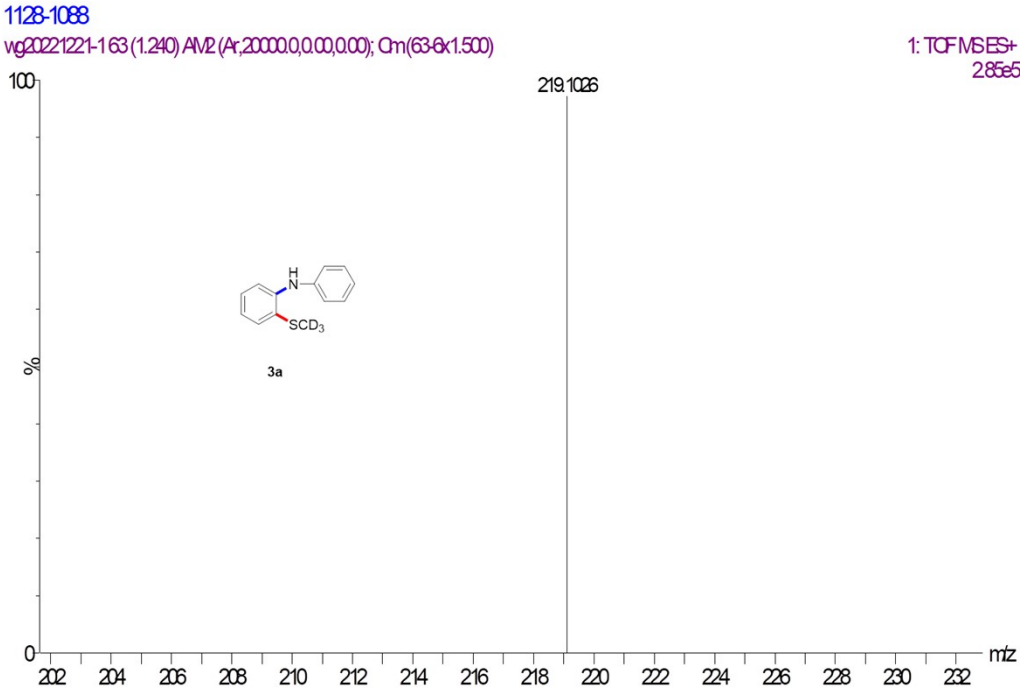


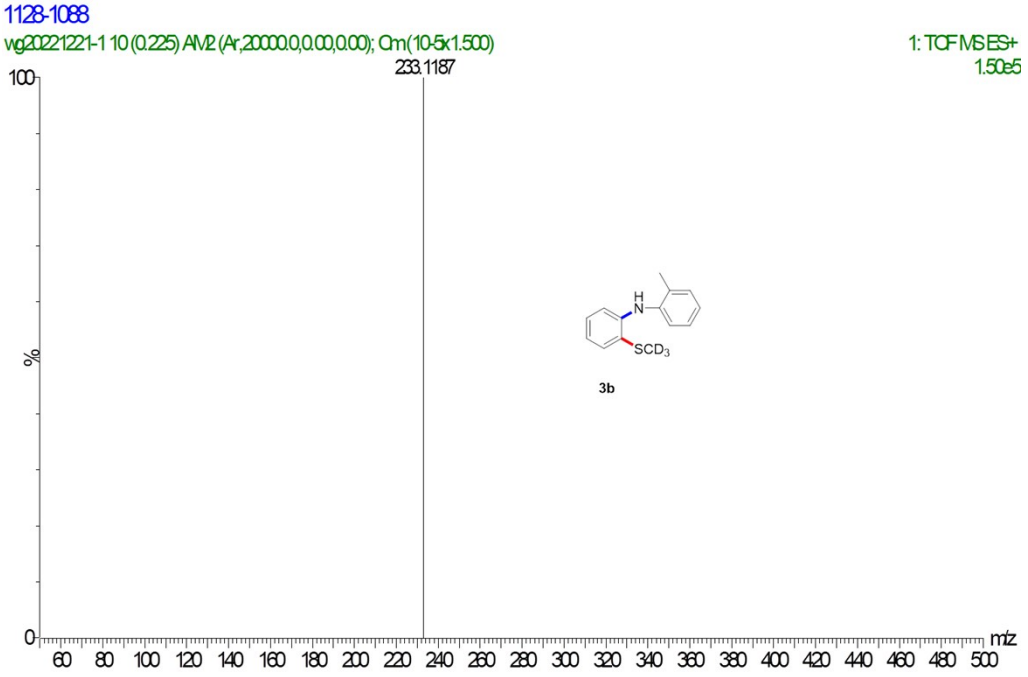


5b

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

HRMS of Products

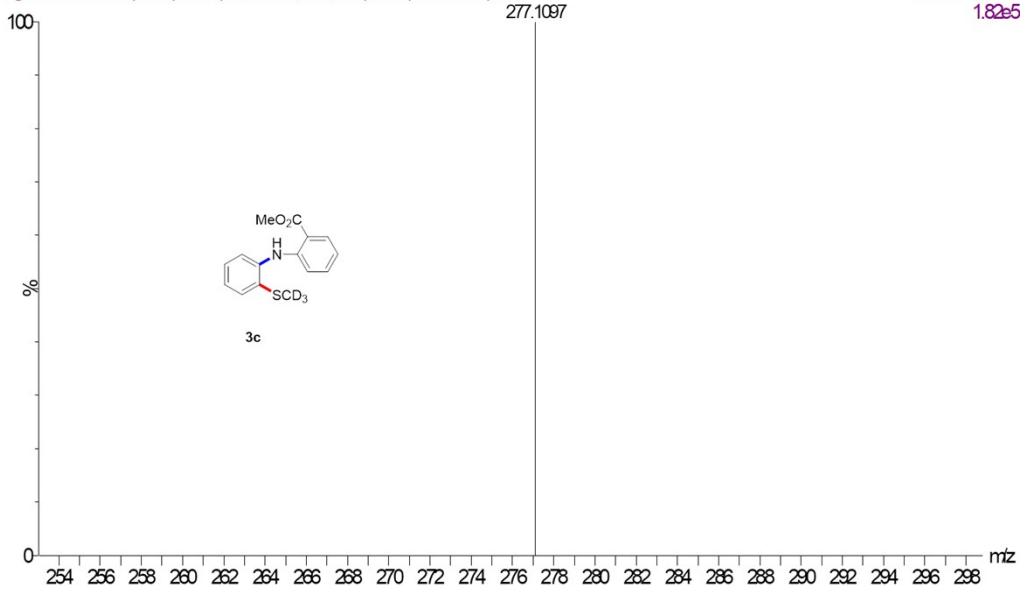




1081-1091

wg20221221-2 43 (0.862) AM2 (Ar,20000.0,0.00,0.00); Cm(43-6x1.500)

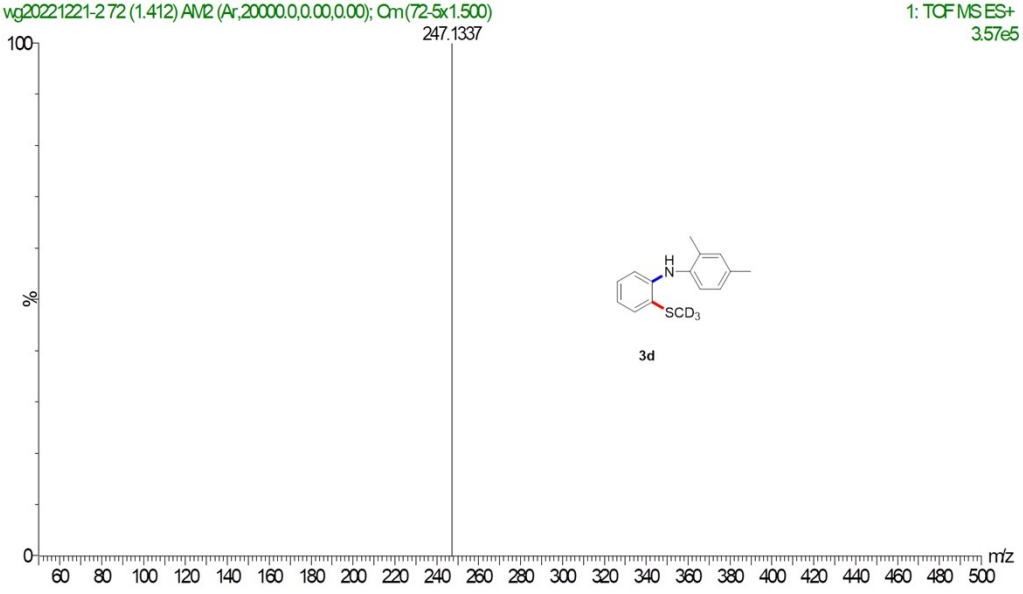
1: TOF MS ES+
1.82e5

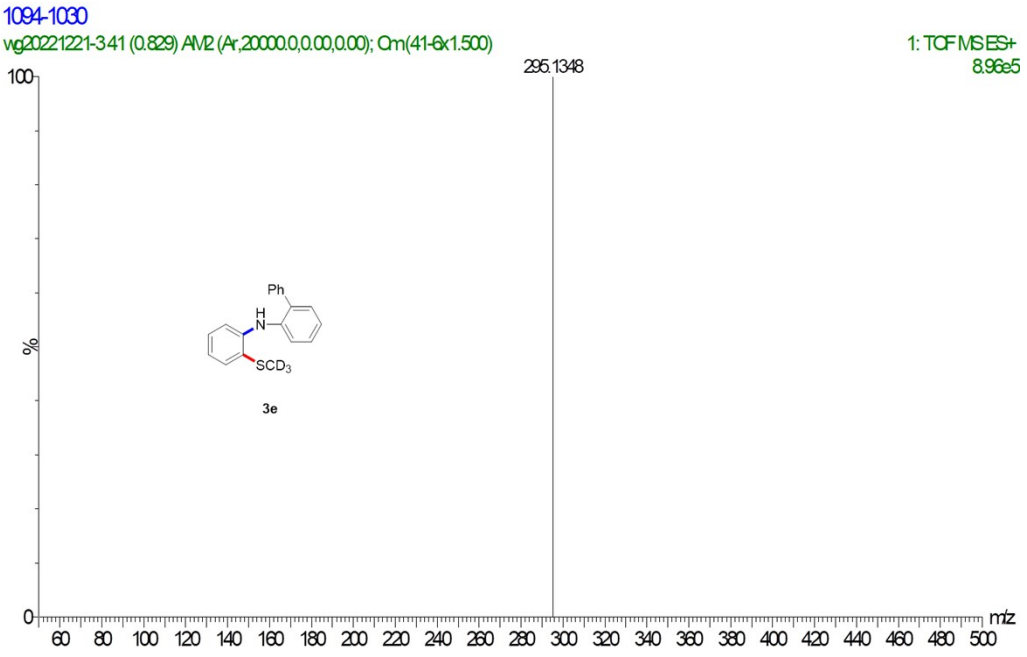


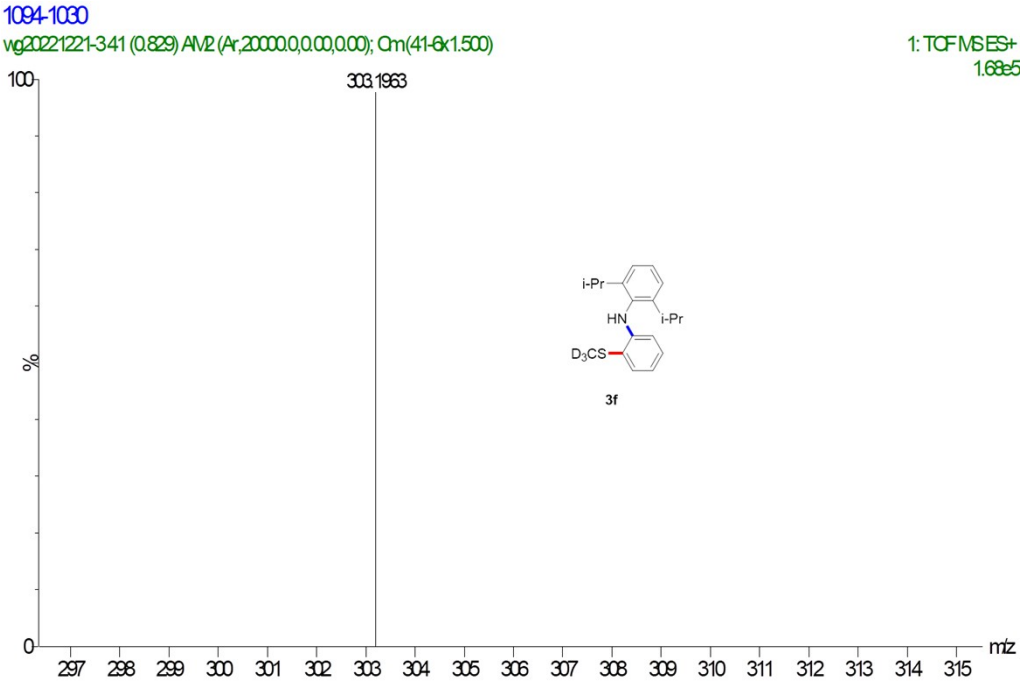
1081-1091

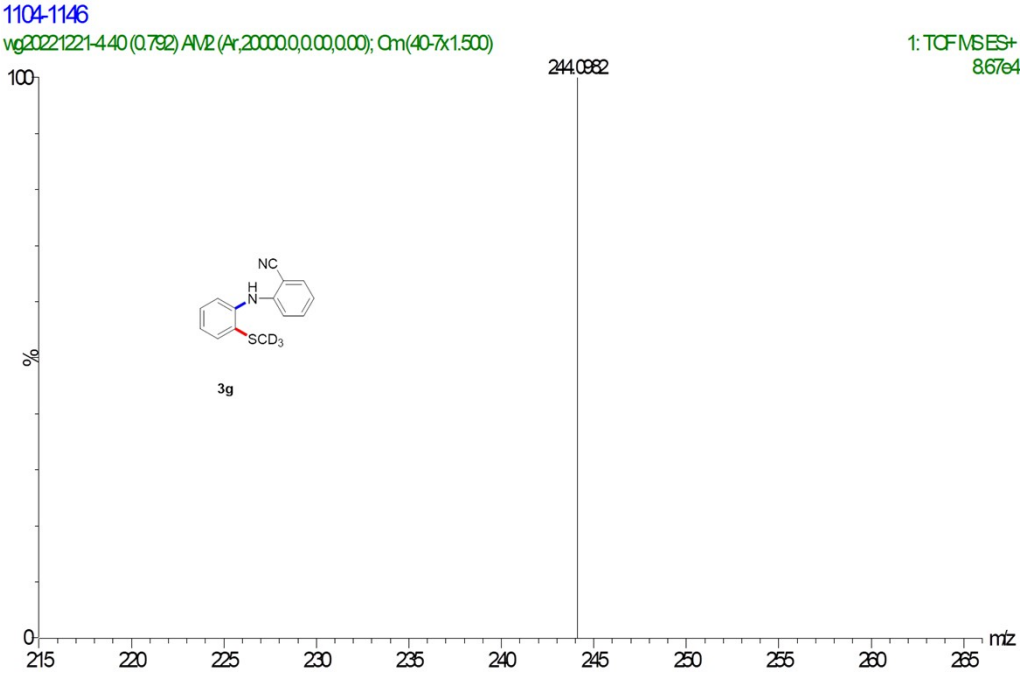
wg20221221-2 72 (1.412) AM2 (Ar,20000.0,0.00,0.00); Cm(72-5x1.500)

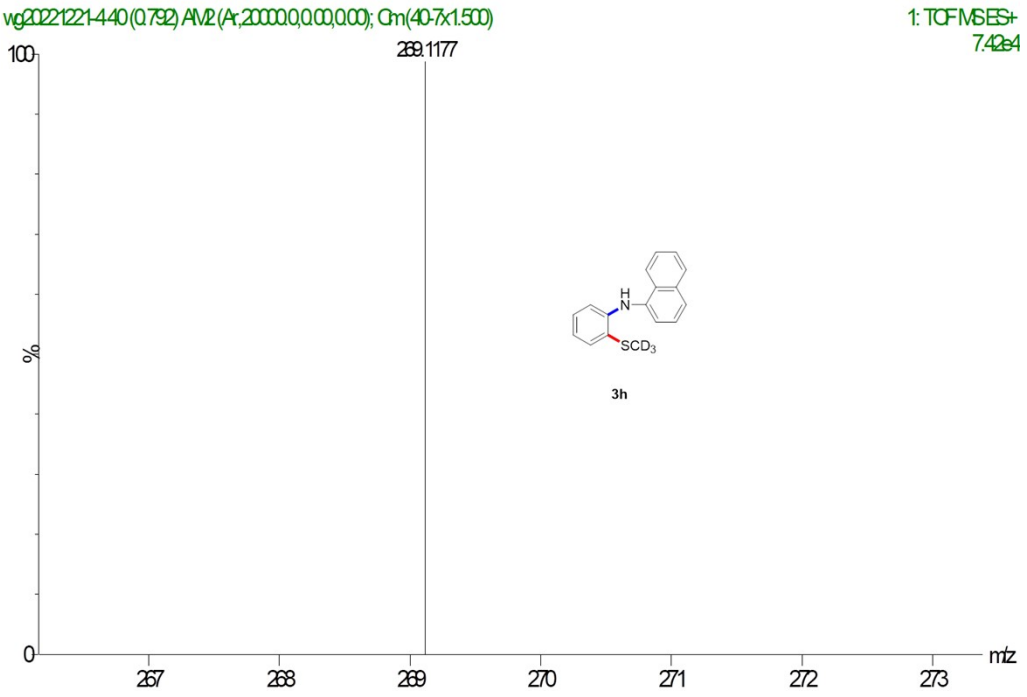
1: TOF MS ES+
3.57e5




1094-1030
vg20221221-341 (0.829) AM2 (Ar,20000.0,0.00,0.00); Cm(41-6x1.500)
1: TOF MS ES+
8.96e5
295.1348
100
%
0
Ph
H
N
SCD3
3e
60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440 460 480 500
m/z


1094-1030
vg20221221-341 (0.829) AM2 (Ar,20000.0,0.00,0.00); Cm(41-6x1.500)
1: TOF MS ES+
1.68e5
303.1963
100
%
0
i-Pr
HN
i-Pr
D3CS
3f
297 298 299 300 301 302 303 304 305 306 307 308 309 310 311 312 313 314 315
m/z

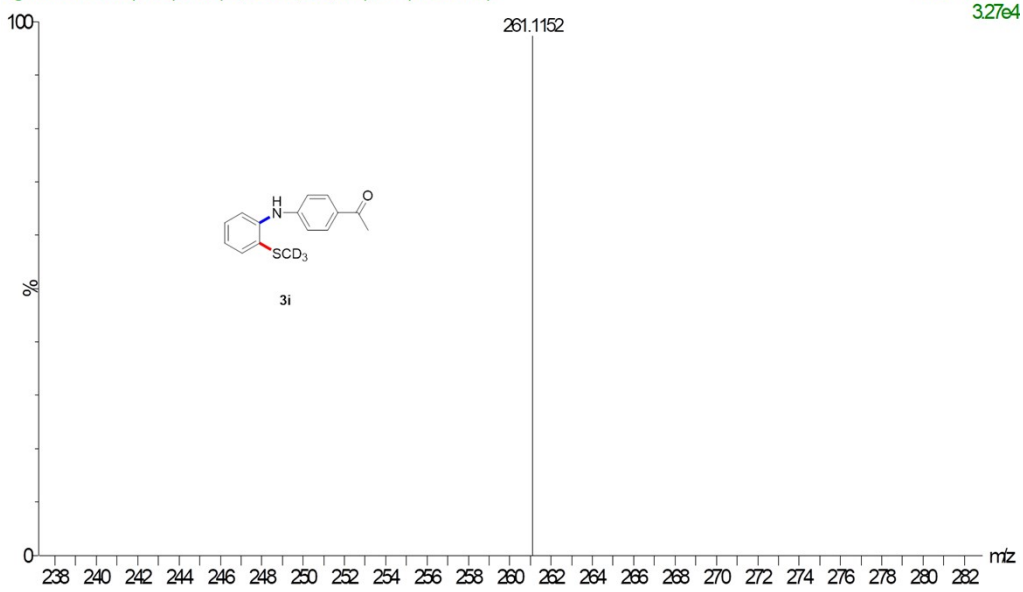

1104-1146
wg20221221-440 (0.792) AM2 (Ar,20000.0,0.00,0.00); Cm(40-7x1.500)
1: TOF MS ES+
8.67e4
244.0882
100
%
0
NC
H
N
SCD3
3g
215
220
225
230
235
240
245
250
255
260
265
m/z


1104-1146
wg20221221-440 (0.792) AM2 (Ar,20000.0,0.00,0.00); Cm(40-7x1.500)
1: TOF MS ES+
7.42e4
269.1177
100
%
0
H
N
SCD3
3h
267
268
269
270
271
272
273
m/z

1141-1089

wg20221221-5 74 (1.466) AM2 (Ar,20000.0,0.00,0.00); Cm(74-6x1.500)

1: TOF MS ES+
3.27e4

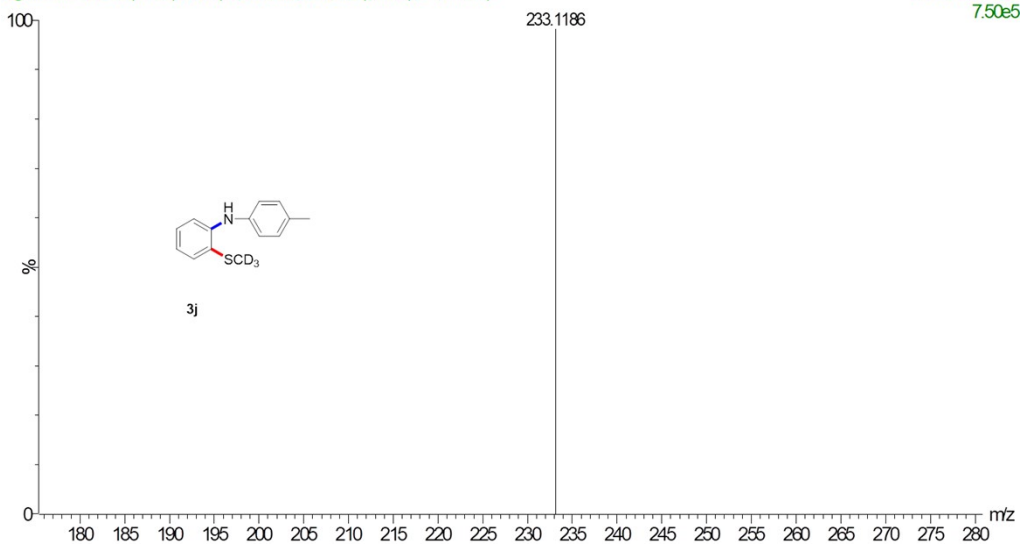


3i

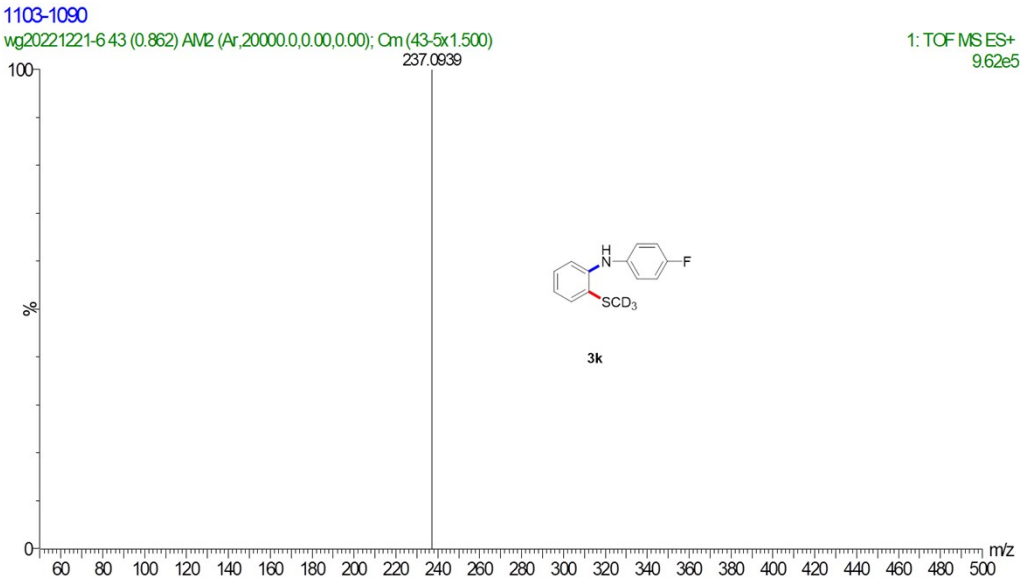
1141-1089

wg20221221-5 58 (1.156) AM2 (Ar,20000.0,0.00,0.00); Cm(58-7x1.500)

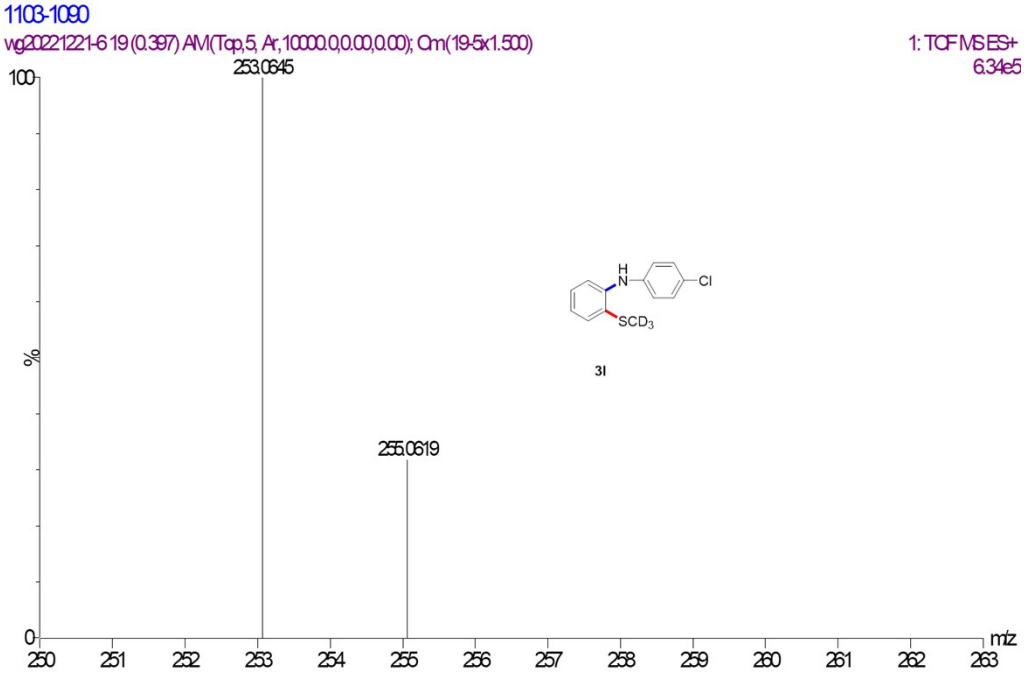
1: TOF MS ES+
7.50e5



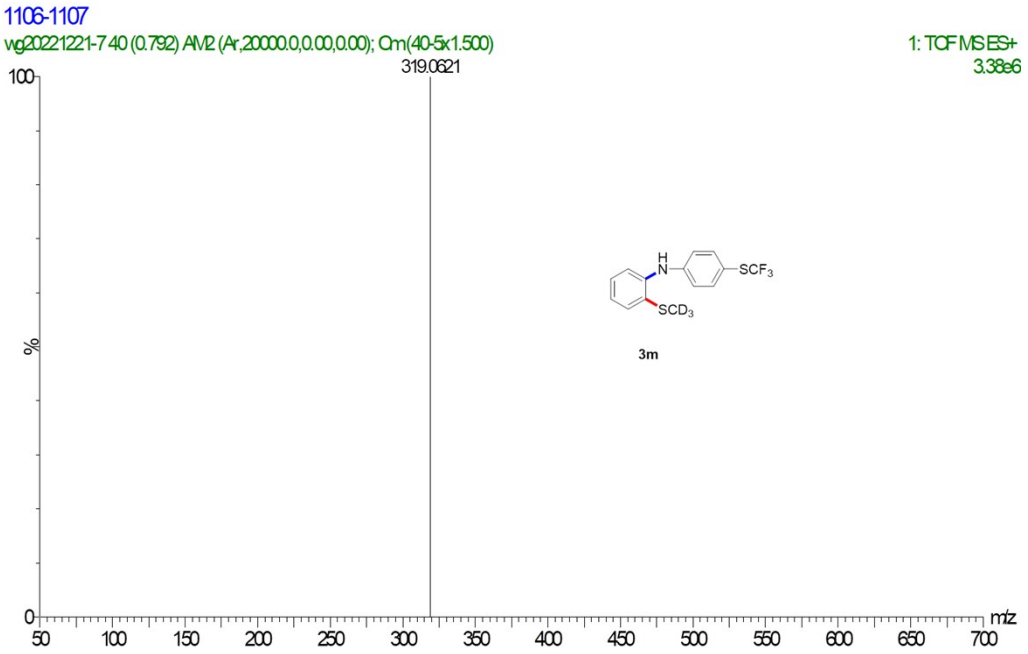
3j

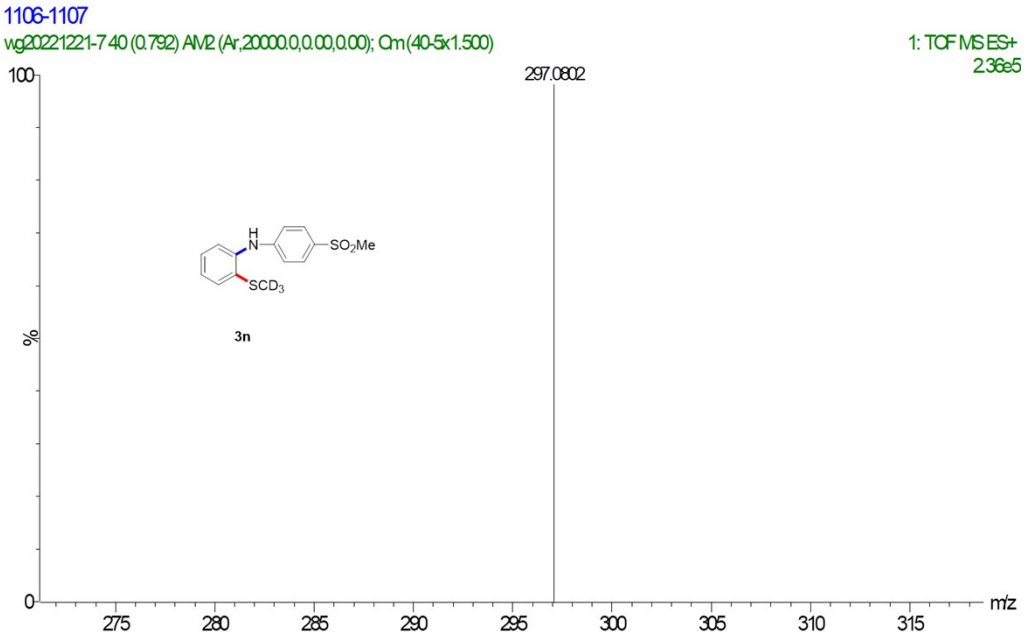

1103-1090
wg20221221-6 43 (0.862) AM2 (Ar,20000.0,0.00,0.00); Cm (43-5x1.500)
1: TOF MS ES+
9.62e5
237.0939
100
%
0
60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440 460 480 500
m/z
H
N
F
SCD3

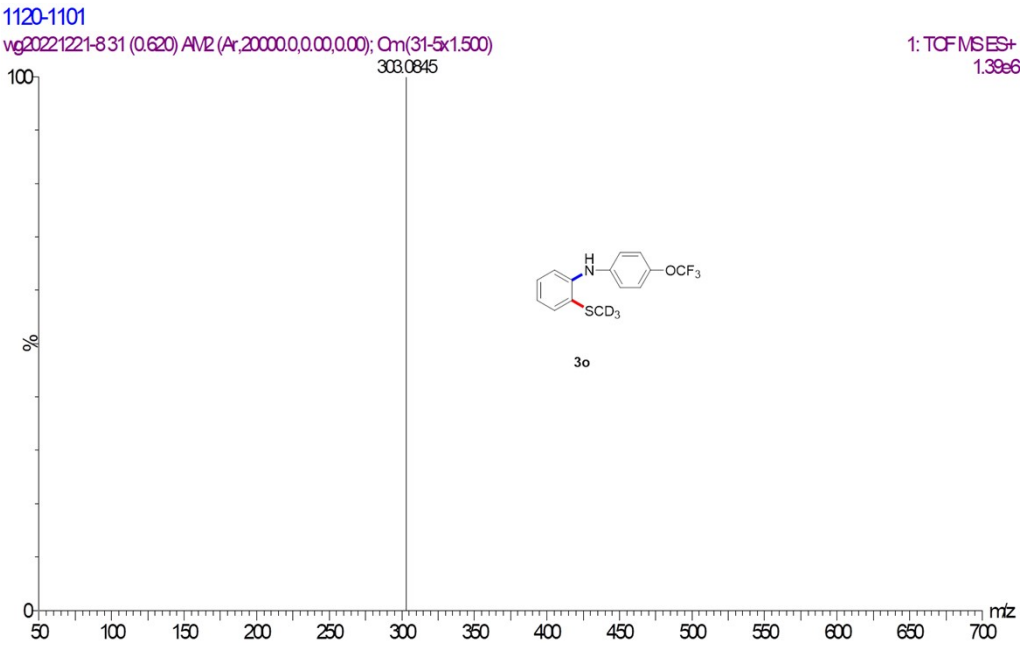
3k

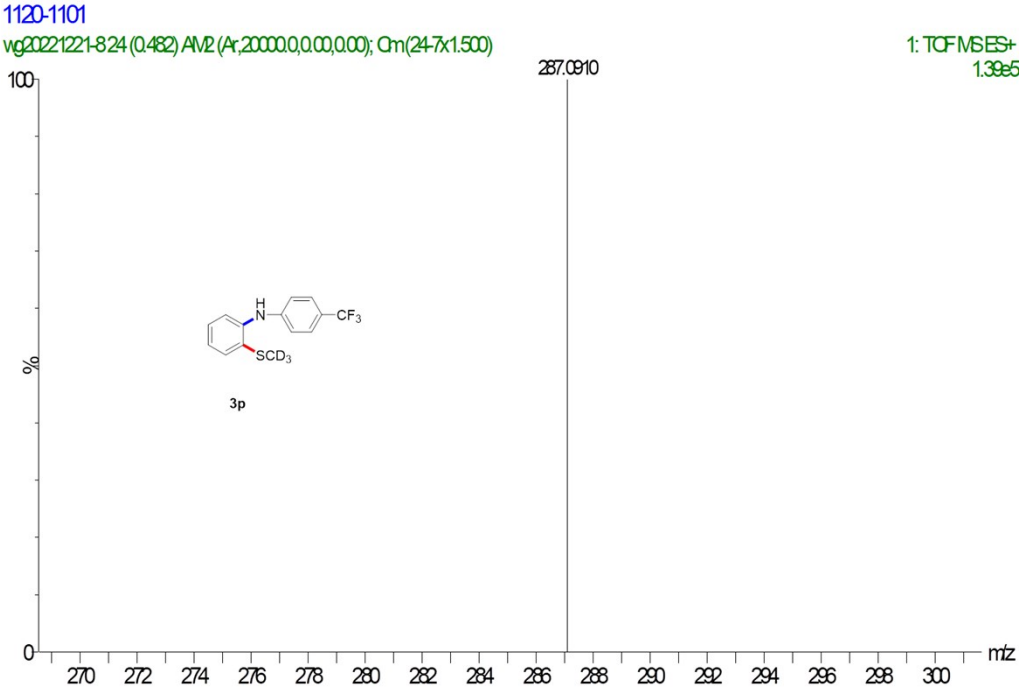

1103-1090
wg20221221-6 19 (0.397) AM (Top,5, Ar,10000.0,0.00,0.00); Cm (19-5x1.500)
1: TOF MS ES+
6.34e5
253.0645
255.0619
100
%
0
250 251 252 253 254 255 256 257 258 259 260 261 262 263
m/z
H
N
Cl
SCD3

3l


1106-1107
wg20221221-7 40 (0.792) AM2 (Ar,20000.0,0.00,0.00); Cm(40-5x1.500)
1: TOF MS ES+
3.38e6
319.0621
100
%
0
50 100 150 200 250 300 350 400 450 500 550 600 650 700
m/z
H
N
SCF3
SCD3
3m


1106-1107
wg20221221-7 40 (0.792) AM2 (Ar,20000.0,0.00,0.00); Cm(40-5x1.500)
1: TOF MS ES+
2.36e5
297.0802
100
%
0
275 280 285 290 295 300 305 310 315
m/z
H
N
SO2Me
SCD3
3n

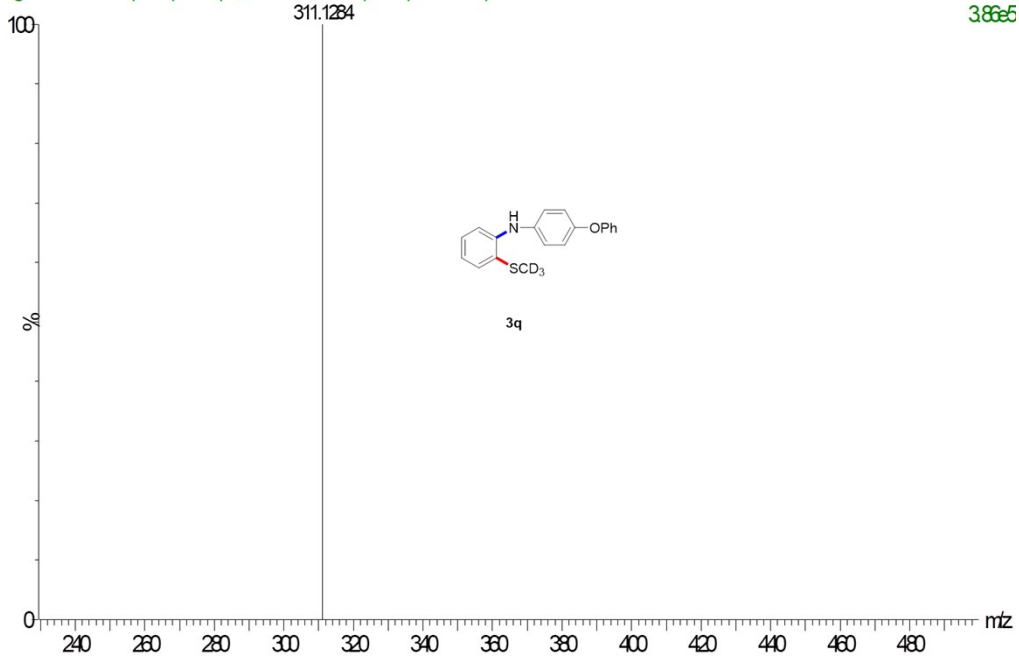

1120-1101
wg20221221-8 31 (0.620) AM2 (Ar,20000.0,0.00,0.00); Cm(31-5x1.500)
1: TOF MS ES+
1.39e6
303.0845
100
%
0
50 100 150 200 250 300 350 400 450 500 550 600 650 700
m/z
H
N
OCF3
SCD3
3o


1120-1101
wg20221221-8 24 (0.482) AM2 (Ar,20000.0,0.00,0.00); Cm(24-7x1.500)
1: TOF MS ES+
1.39e5
287.0910
100
%
0
270 272 274 276 278 280 282 284 286 288 290 292 294 296 298 300
m/z
H
N
CF3
SCD3
3p

1122-129

vg20221221-9 27 (0.552) AM2 (Ar,20000.0,0.00,0.00); Cm(27-5x1.500)

1: TOF MS ES+
3.86e5

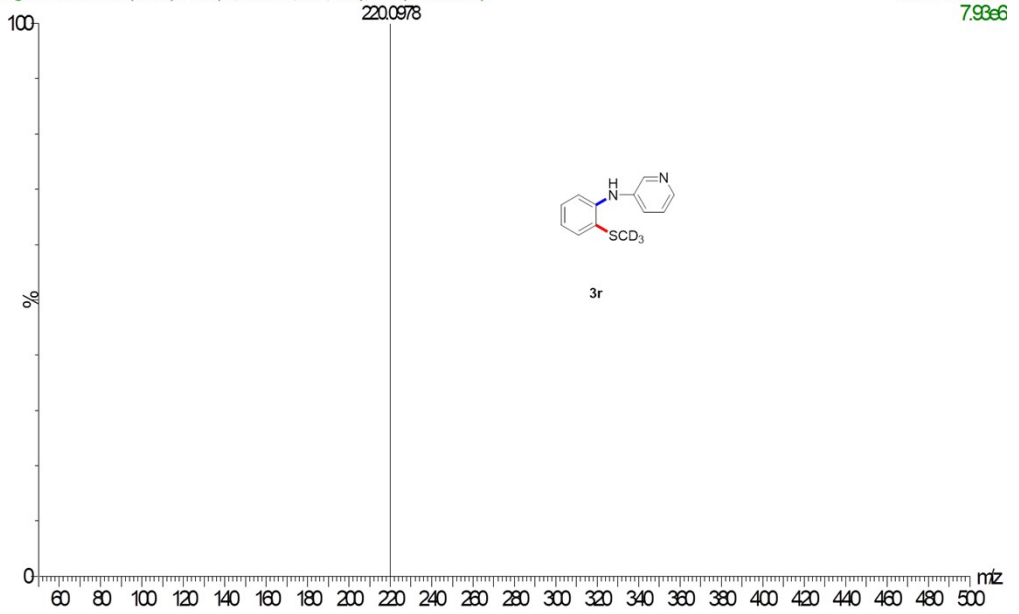


3q

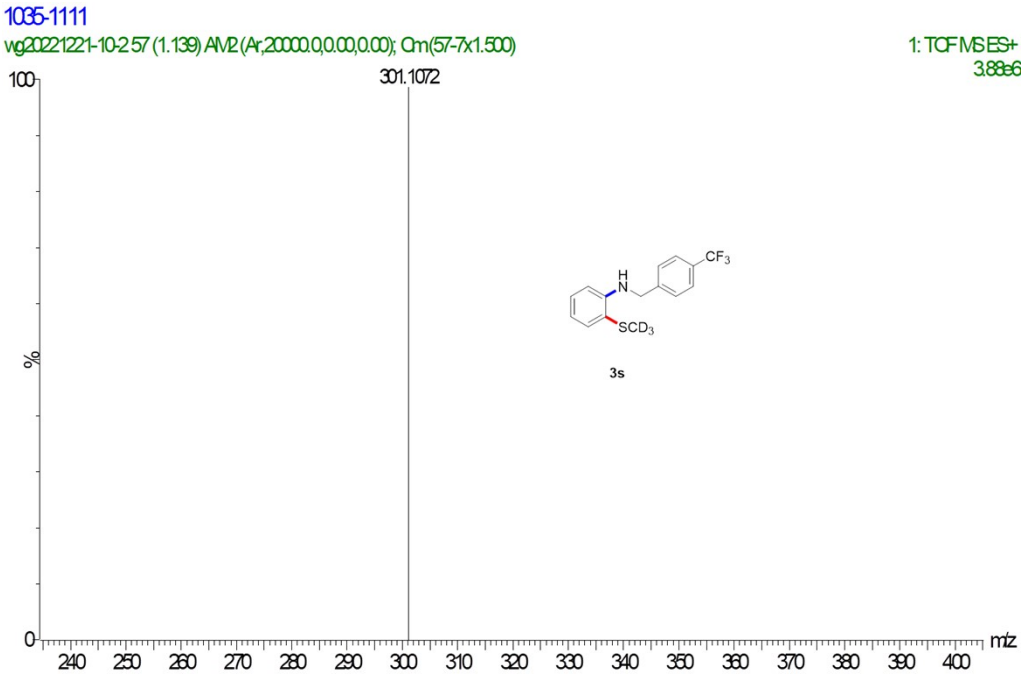
1122-129

vg20221221-9 73 (1.449) AM2 (Ar,20000.0,0.00,0.00); Cm(73-6x1.500)

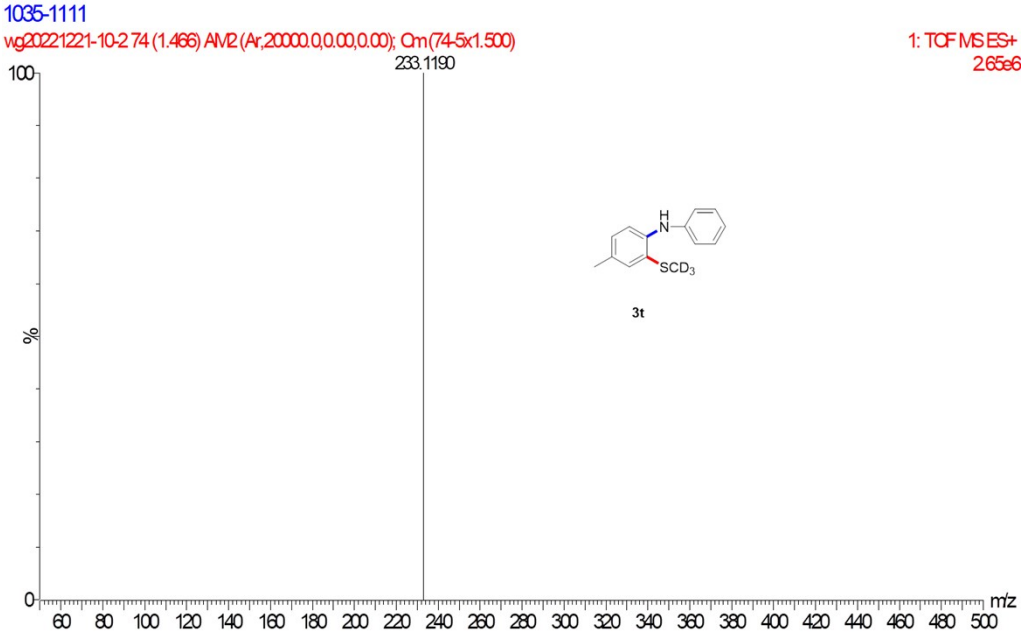
1: TOF MS ES+
7.93e6



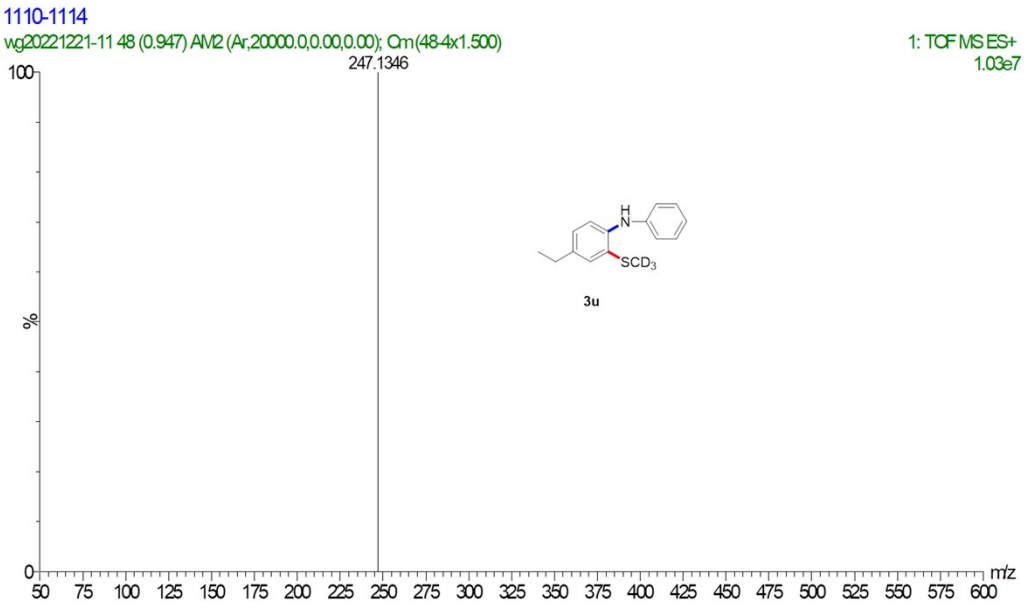
3r

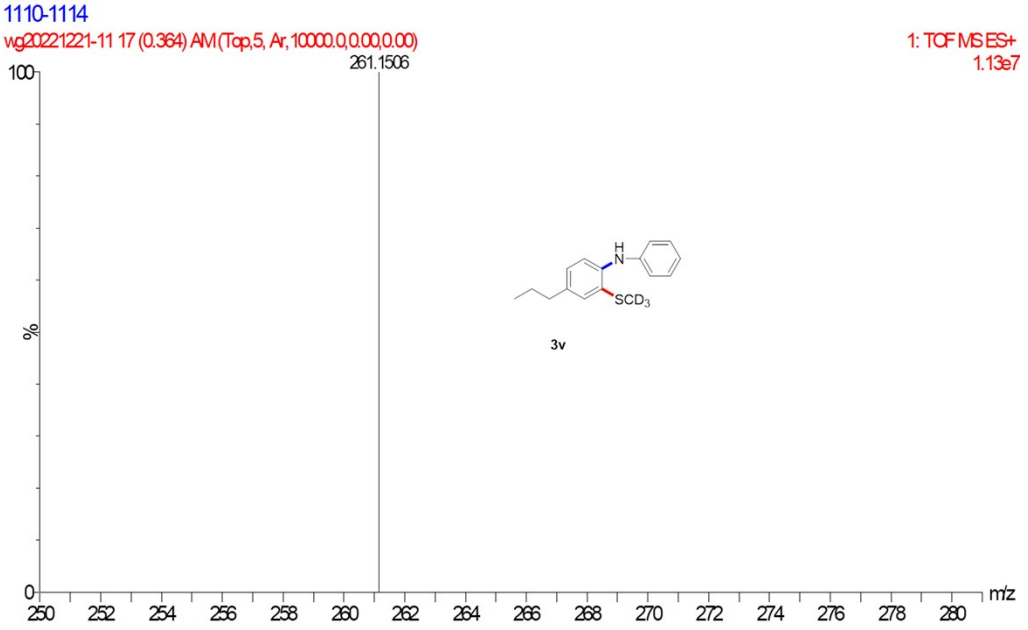

1035-1111
wg20221221-10-2 57 (1.139) AM2 (Ar,20000.0,0.00,0.00); Cm(57-7x1.500)
1: TOF MS ES+
3.88e6
301.1072
100
%
0
240 250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400
m/z
CF3
H
N
SCD3

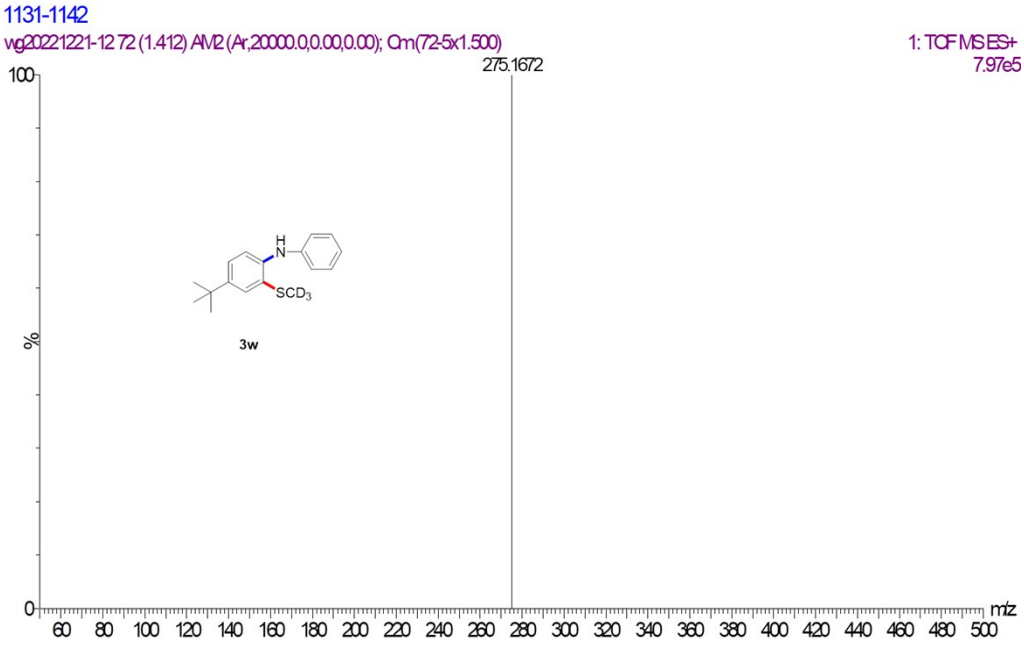
3s

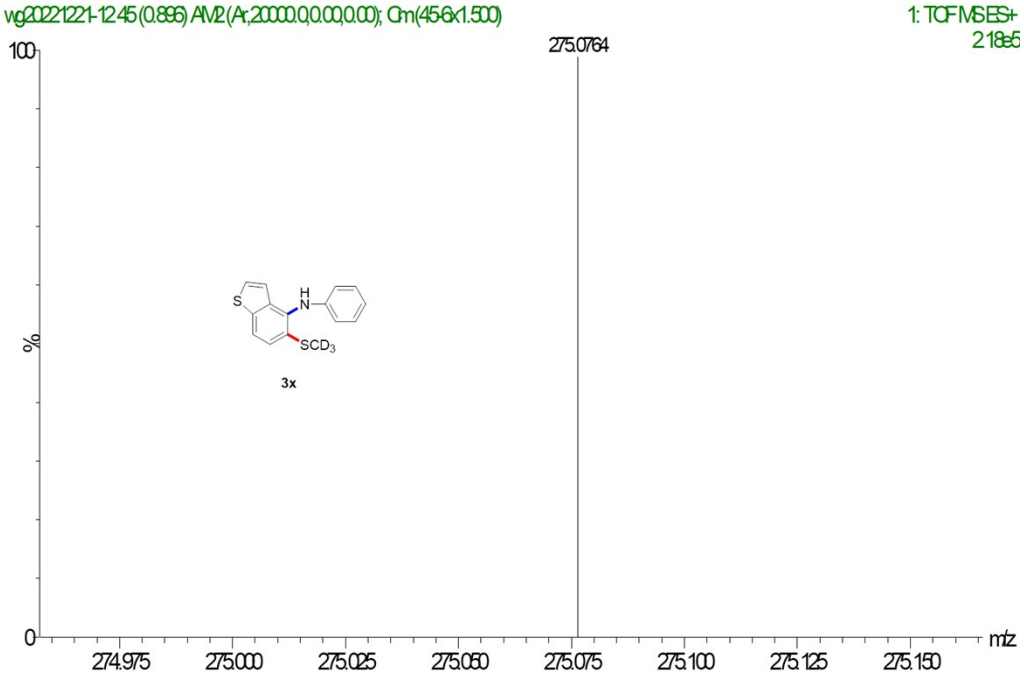

1035-1111
wg20221221-10-2 74 (1.466) AM2 (Ar,20000.0,0.00,0.00); Cm(74-5x1.500)
1: TOF MS ES+
2.65e6
233.1190
100
%
0
60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440 460 480 500
m/z
H
N
SCD3

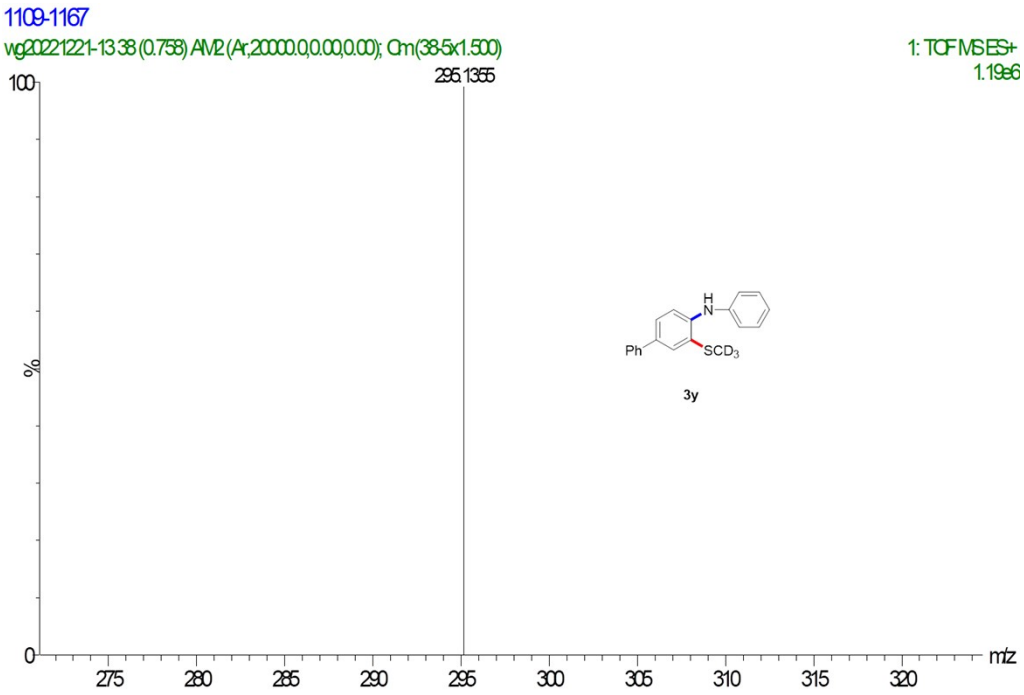
3t

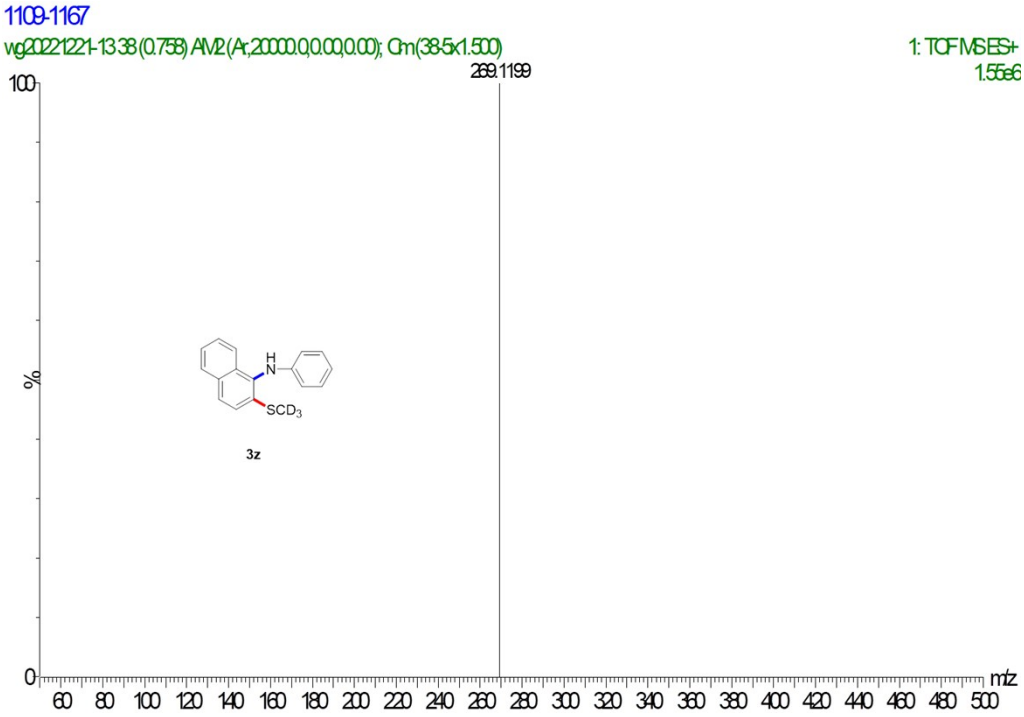

1110-1114
wg20221221-11 48 (0.947) AM2 (Ar,20000.0,0.00,0.00); Cm (48-4x1.500)
1: TOF MS ES+
1.03e7
247.1346
100
%
0
50 75 100 125 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 575 600
m/z
H
N
SCD3
3u

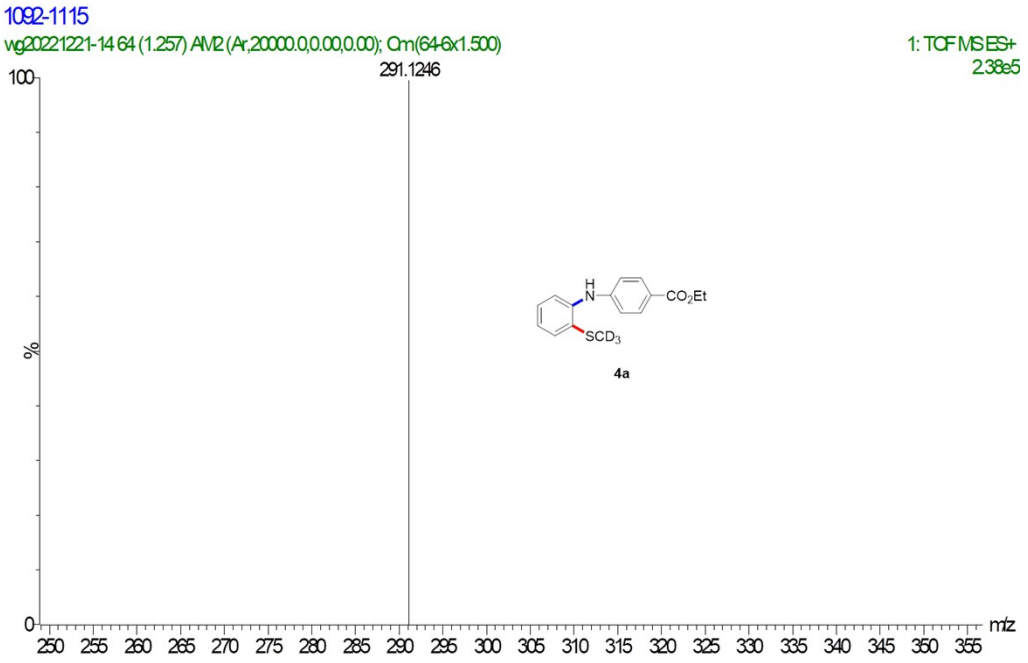

1110-1114
wg20221221-11 17 (0.364) AM (Top,5, Ar,10000.0,0.00,0.00)
1: TOF MS ES+
1.13e7
261.1506
100
%
0
250 252 254 256 258 260 262 264 266 268 270 272 274 276 278 280
m/z
H
N
SCD3
3v

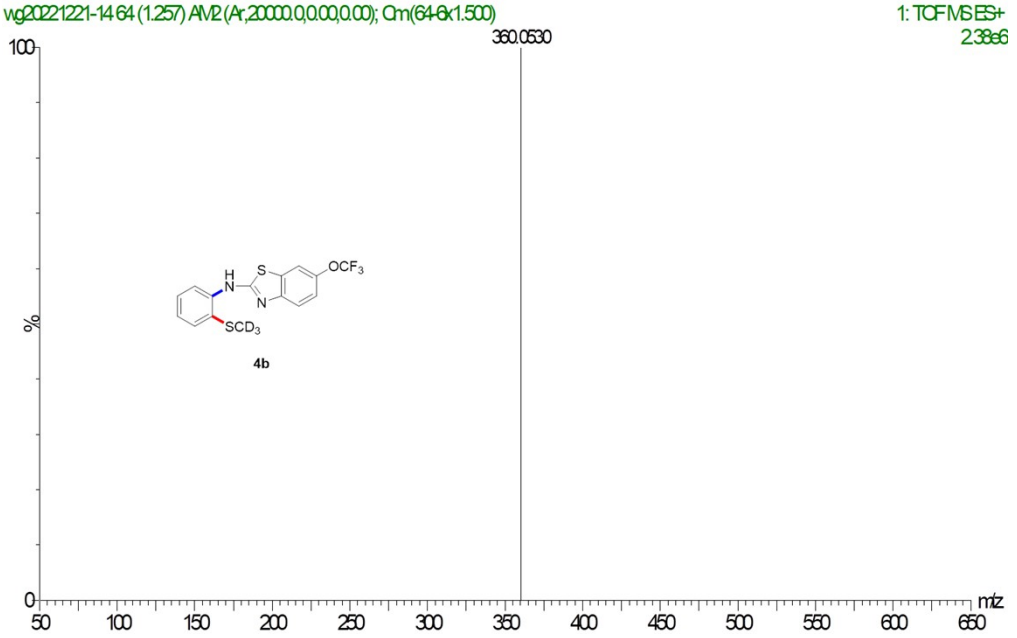

1131-1142
wg20221221-12 72 (1.412) AM2 (Ar,20000.0,0.00,0.00); Cm(72-5x1.500)
1: TOF MS ES+
7.97e5
275.1672
100
%
0
SCD3
H
N
3w
60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440 460 480 500
m/z

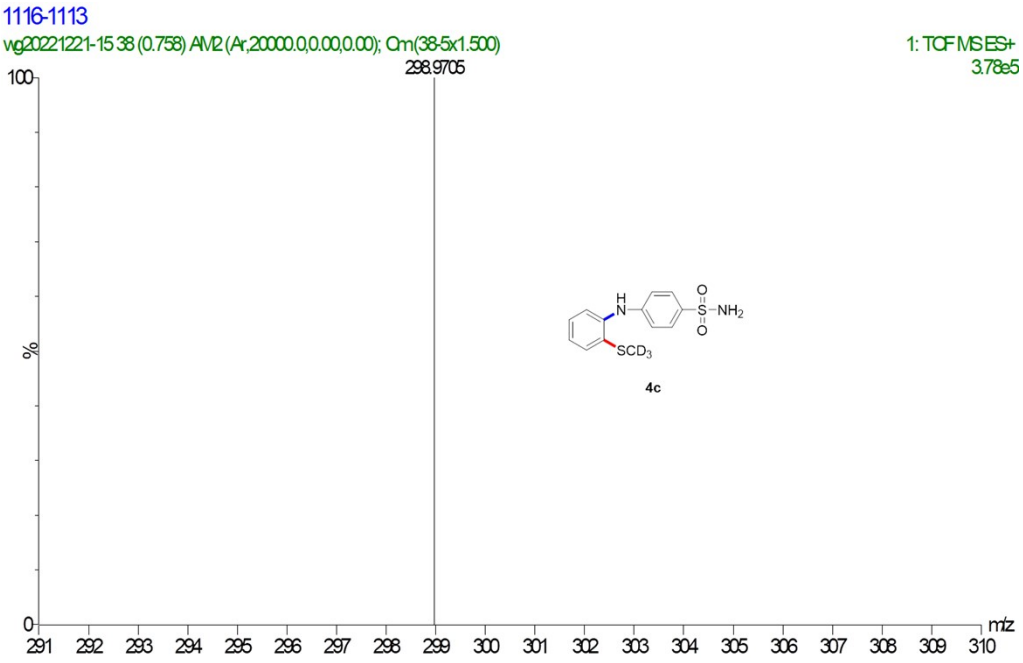

1131-1142
wg20221221-12 45 (0.896) AM2 (Ar,20000.0,0.00,0.00); Cm(45-6x1.500)
1: TOF MS ES+
2.18e5
275.0764
100
%
0
S
H
N
SCD3
3x
274.975 275.000 275.025 275.050 275.075 275.100 275.125 275.150
m/z

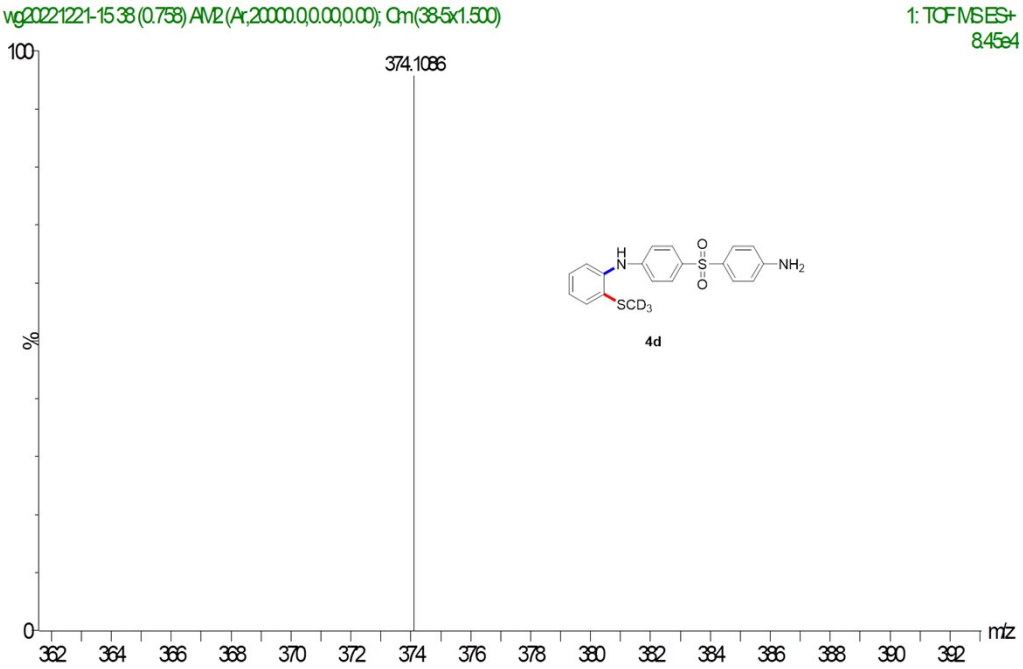

1109-1167
wg20221221-1338 (0.758) AM2 (Ar,20000.0,0.00,0.00); Cm (38:5x1.500)
1: TOF MS ES+
1.19e6
295.1355
100
%
0
275
280
285
290
295
300
305
310
315
320
m/z
H
N
Ph
SCD3
3y

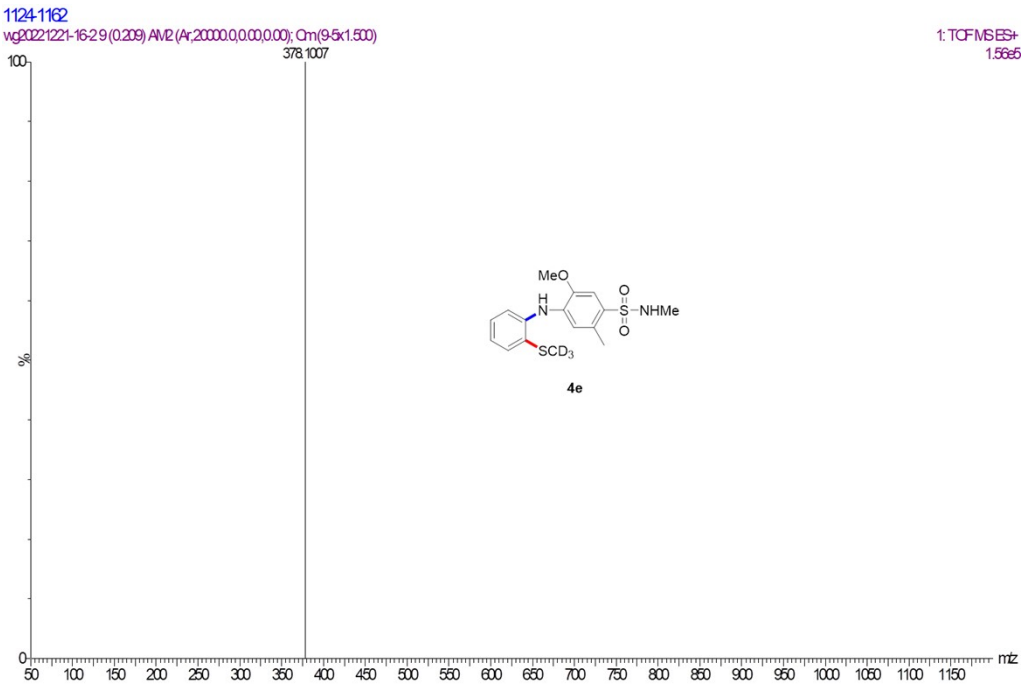

1109-1167
wg20221221-1338 (0.758) AM2 (Ar,20000.0,0.00,0.00); Cm (38:5x1.500)
1: TOF MS ES+
1.55e6
269.1199
100
%
0
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
400
420
440
460
480
500
m/z
H
N
SCD3
3z


1092-1115
wg20221221-1464 (1.257) AM2 (Ar,20000.0,0.00,0.00); Cm(64-6x1.500)
1: TOF MS ES+
2.38e5
291.1246
100
%
0
m/z
250 255 260 265 270 275 280 285 290 295 300 305 310 315 320 325 330 335 340 345 350 355
H
N
CO2Et
SCD3
4a

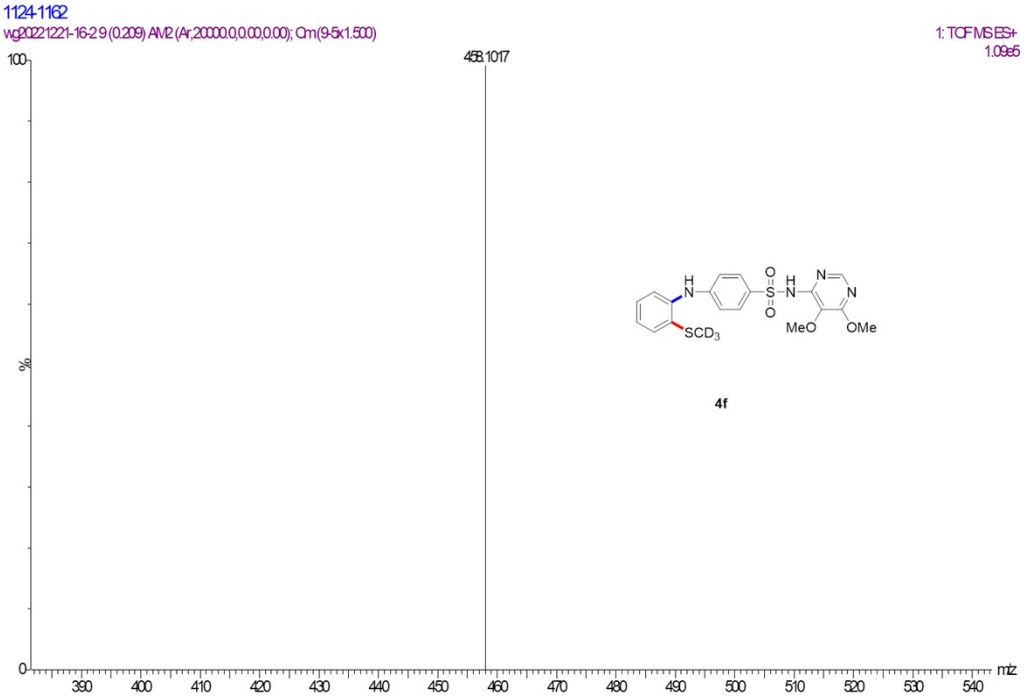

1092-1115
wg20221221-1464 (1.257) AM2 (Ar,20000.0,0.00,0.00); Cm(64-6x1.500)
1: TOF MS ES+
2.38e6
360.0530
100
%
0
m/z
50 100 150 200 250 300 350 400 450 500 550 600 650
H
N
S
N
OCF3
SCD3
4b


1116-1113
vg20221221-1538 (0.758) AM2 (Ar,20000.0,0.00,0.00); Cm(38-5x1.500)
1: TOF MS ES+
3.78e5
298.9705
100
%
0
291 292 293 294 295 296 297 298 299 300 301 302 303 304 305 306 307 308 309 310
m/z
H
N
O
S
O
NH2
SCD3
4c

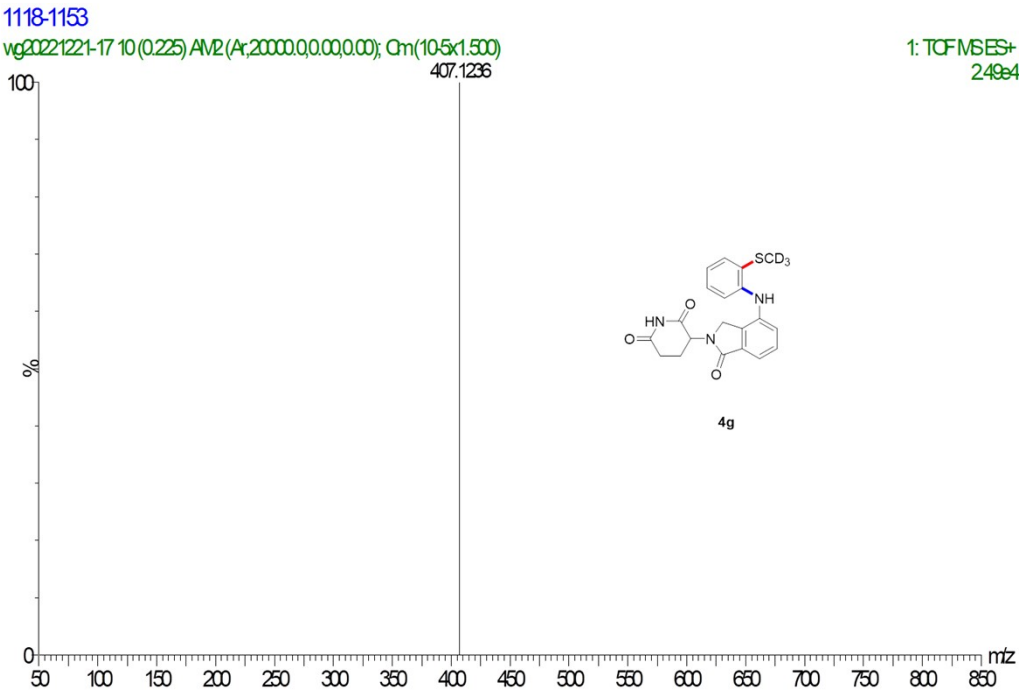

1116-1113
vg20221221-1538 (0.758) AM2 (Ar,20000.0,0.00,0.00); Cm(38-5x1.500)
1: TOF MS ES+
8.45e4
374.1086
100
%
0
362 364 366 368 370 372 374 376 378 380 382 384 386 388 390 392
m/z
H
N
O
S
O
NH2
SCD3
4d

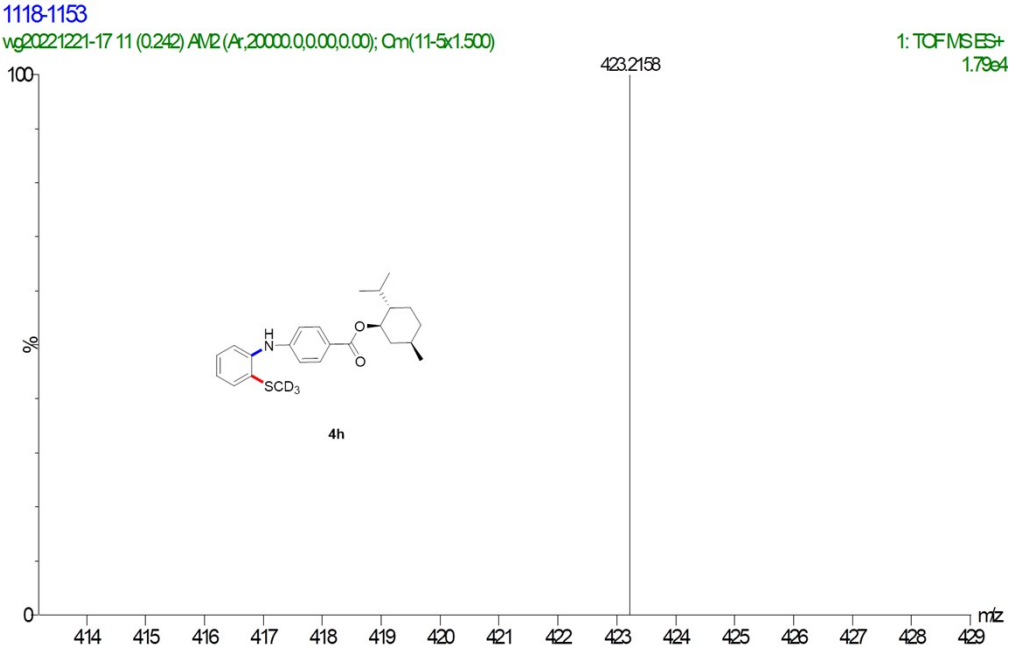

1124-1162
wg20221221-16-2 9 (0.209) AM2 (Ar,20000.0,0.00,0.00); Cm(9-5x1.500)
1: TOF MS ES+
1.56e5
378.1007
100
%
0
MeO
H
N
O
S
O
NHMe
SCD3
50 100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000 1050 1100 1150
m/z

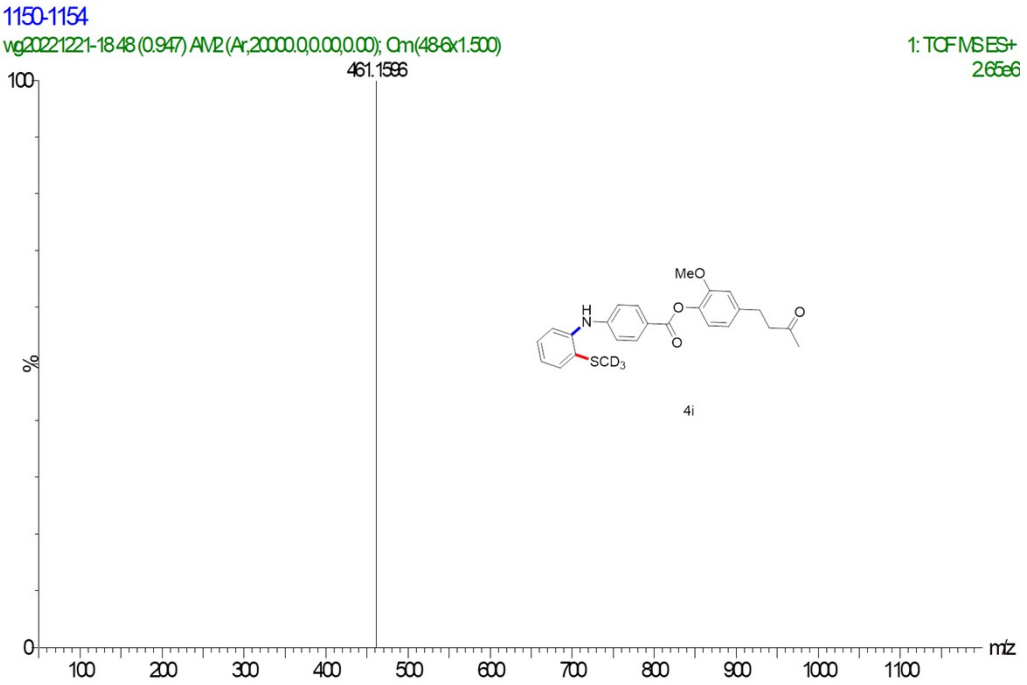
4e

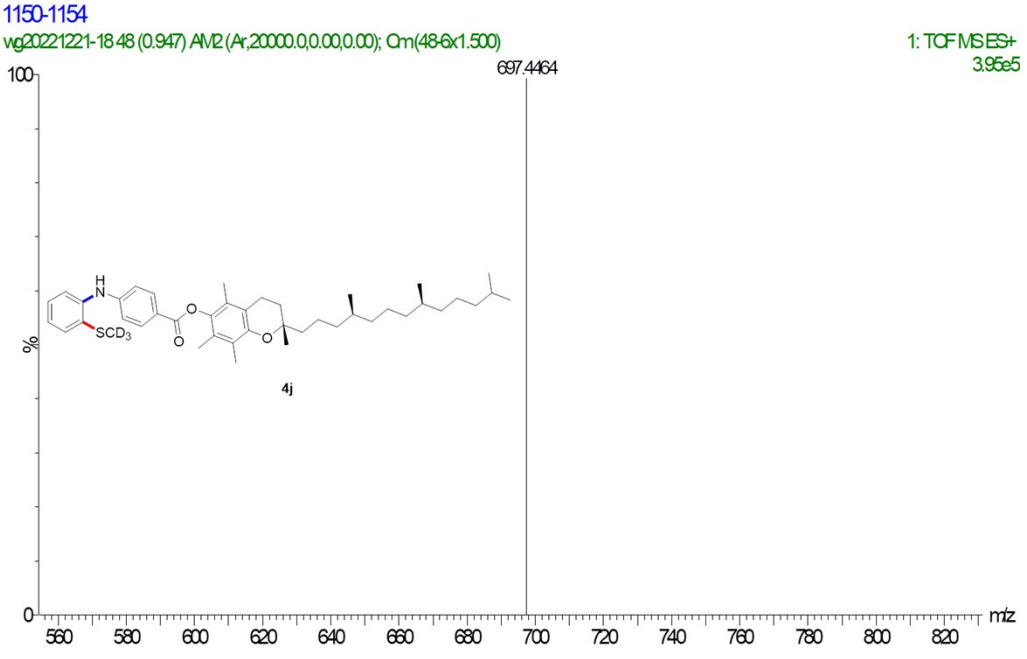

1124-1162
wg20221221-16-2 9 (0.209) AM2 (Ar,20000.0,0.00,0.00); Cm(9-5x1.500)
1: TOF MS ES+
1.09e5
458.1017
100
%
0
H
N
O
S
O
H
N
N
N
SCD3
MeO
OMe
390 400 410 420 430 440 450 460 470 480 490 500 510 520 530 540
m/z

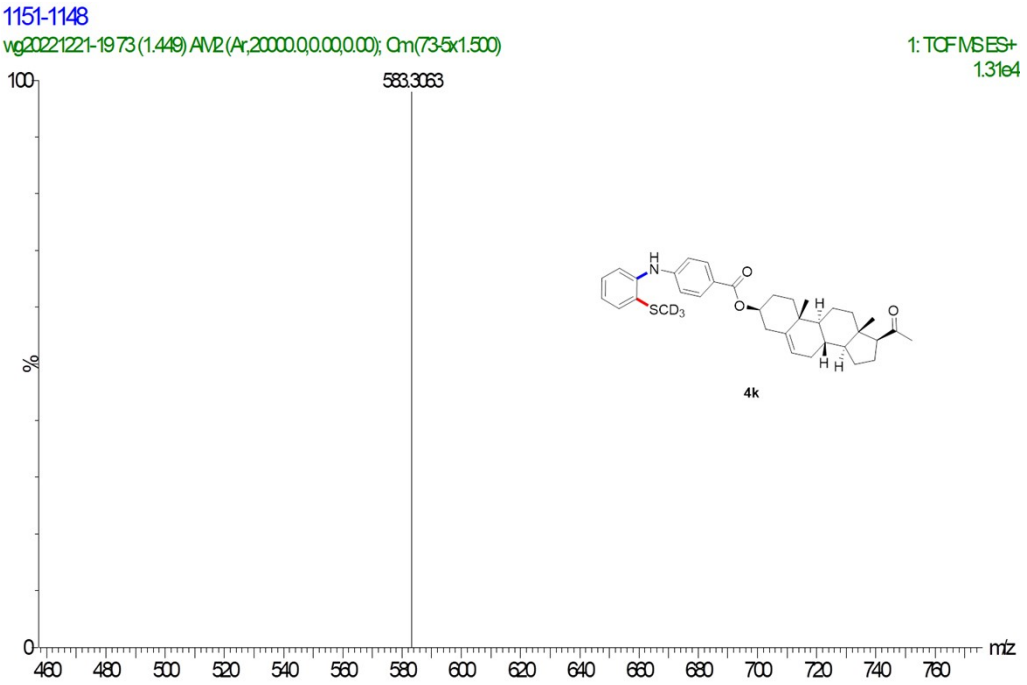
4f

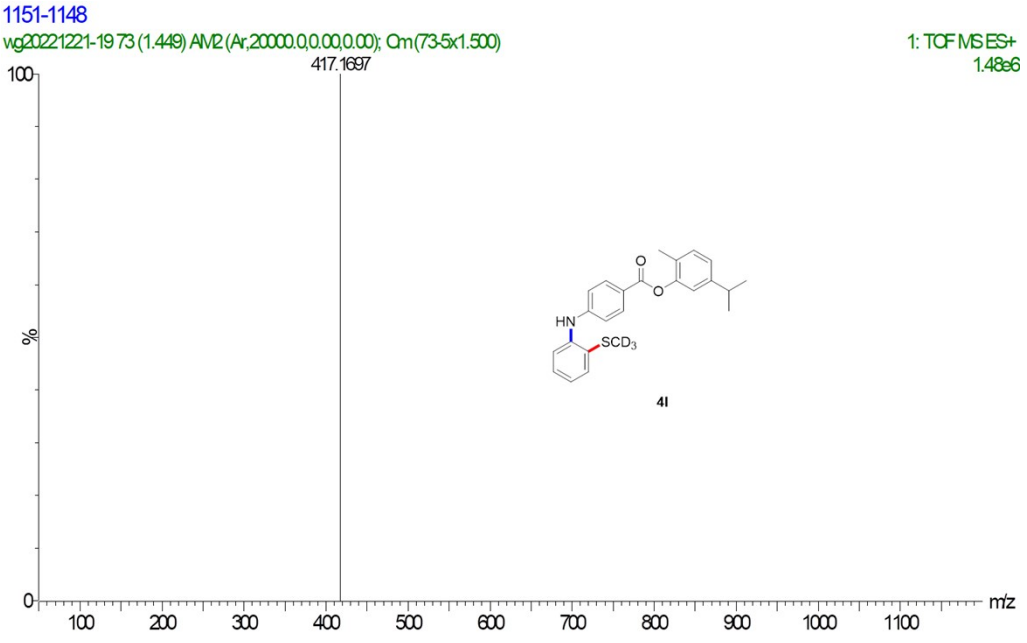

1118-1153
wg20221221-17 10 (0.225) AM2 (Ar,20000.0,0.00,0.00); Cm(10-5x1.500)
1: TOF MS ES+
2.49e4
407.1236
100
%
0
m/z
50 100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850
SCD3
NH
HN
O
N
O
O
4g


1118-1153
wg20221221-17 11 (0.242) AM2 (Ar,20000.0,0.00,0.00); Cm(11-5x1.500)
1: TOF MS ES+
1.79e4
423.2158
100
%
0
m/z
414 415 416 417 418 419 420 421 422 423 424 425 426 427 428 429
H
N
O
O
SCD3
4h


1150-1154
wg20221221-1848 (0.947) AM2 (Ar,20000.0,0.00,0.00); Cm(48-6x1.500)
1: TOF MS ES+
2.65e6
461.1596
100
%
0
100
200
300
400
500
600
700
800
900
1000
1100
m/z
MeO
H
N
O
O
O
SCD3
4i


1150-1154
wg20221221-1848 (0.947) AM2 (Ar,20000.0,0.00,0.00); Cm(48-6x1.500)
1: TOF MS ES+
3.95e5
697.4464
100
%
0
560
580
600
620
640
660
680
700
720
740
760
780
800
820
m/z
H
N
SCD3
O
O
O
4j

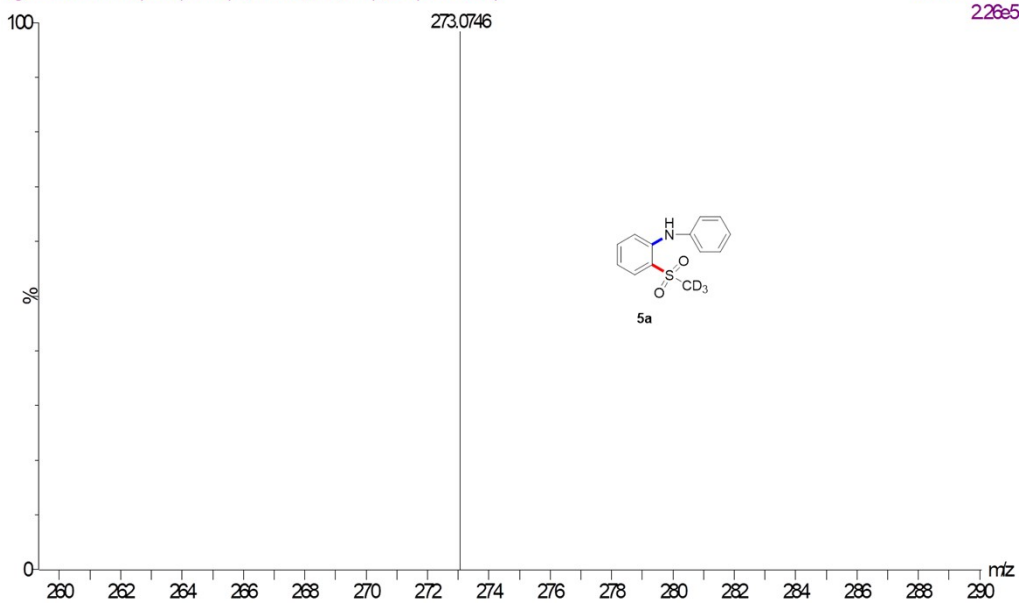

1151-1148
wg20221221-1973 (1.449) AM2 (Ar,20000.0,0.00,0.00); Cm (73-5x1.500)
1: TOF MS ES+
1.31e4
583.3063
100
%
0
460 480 500 520 540 560 580 600 620 640 660 680 700 720 740 760
m/z
4k


1151-1148
wg20221221-1973 (1.449) AM2 (Ar,20000.0,0.00,0.00); Cm (73-5x1.500)
1: TOF MS ES+
1.48e6
417.1697
100
%
0
100 200 300 400 500 600 700 800 900 1000 1100
m/z
4l

1156-1155

wg20221221-2074 (1.466) AM2 (Ar,20000.0,0.00,0.00); Cm(74:6x1.500)

1: TOF MS ES+
2.26e5

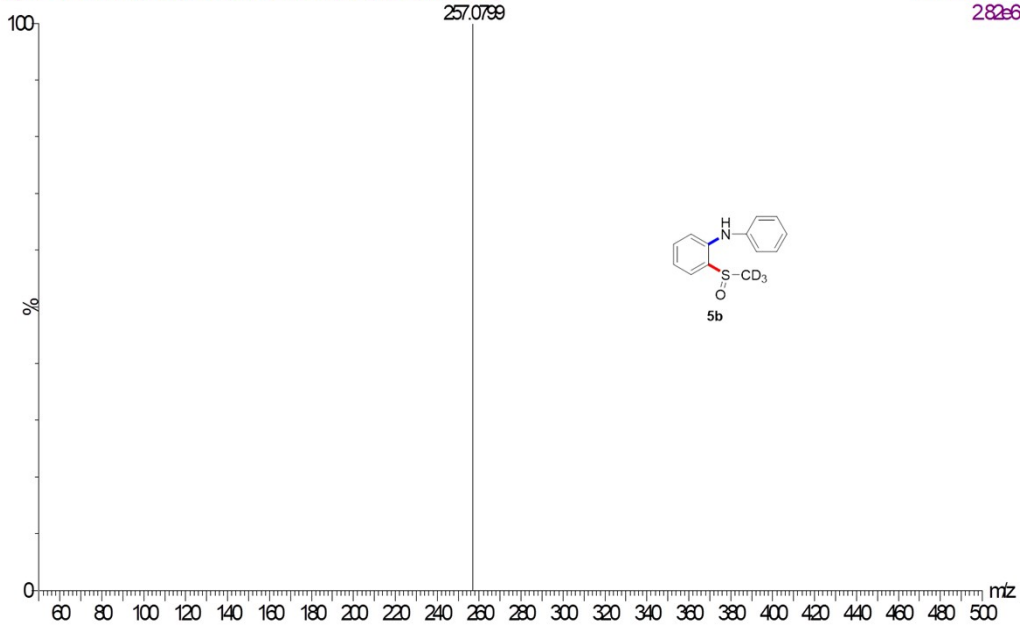


5a

1156-1155

wg20221221-2074 (1.466) AM2 (Ar,20000.0,0.00,0.00); Cm(74:6x1.500)

1: TOF MS ES+
2.82e6



5b