Copper-Catalyzed Aryl *ortho*-C–H Thiolation of Aldehydes via a Transient Directing Group Strategy

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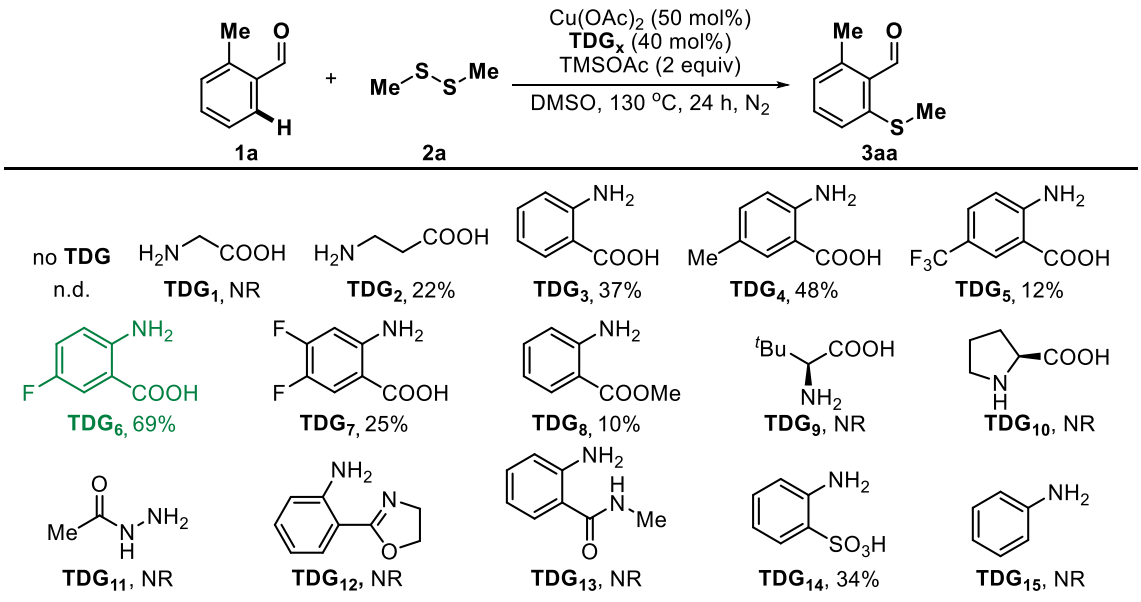
1. General information.

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker ARX400 instrument (400 MHz) or Bruker DRX-600 instrument (600 MHz). Mass spectral data were obtained from an Agilent Technologies 6230 TOF LC/MS spectrometer in electrospray ionization (ESI^{+}) mode. NMR spectra were recorded in $CDCl_3$. ^{1}H NMR spectra were referenced to residual $CHCl_3$ at 7.26 ppm, and ^{13}C NMR spectra were referenced to the central peak of $CDCl_3$ at 77.16 ppm. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

All reactions requiring anhydrous conditions were conducted in dried apparatus under an inert atmosphere of nitrogen. For reactions that require heating, an oil bath was used to warm up to the target temperatures in the process. All commercial materials were used without further purification unless there was special notice. All commercial aldehydes, were purchased from Sigma-Aldrich, Shanghai Haohong Scientific Co., Ltd, Tansoole, and Bidepharm. The disulfide derivatives[1] were prepared according to previously described methods.

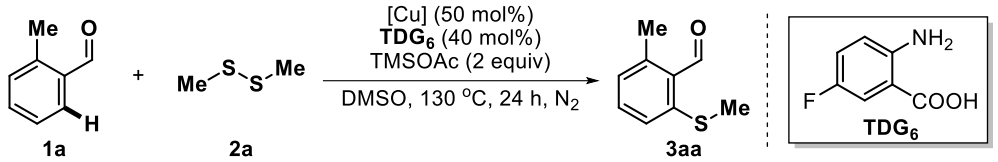
2. Condition survey for the C–H thiolation of benzaldehydes

Table S1. Transient directing group survey[a,b]



[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), $Cu(OAc)_2$ (50 mol%), TDG (40 mol %), TMSOAc (2 equiv), DMSO (2 mL), 130 °C, 24 h, N_2. [b]Determined by ^{1}H NMR analysis using CH_2Br_2 as an internal standard. NR: no reaction.

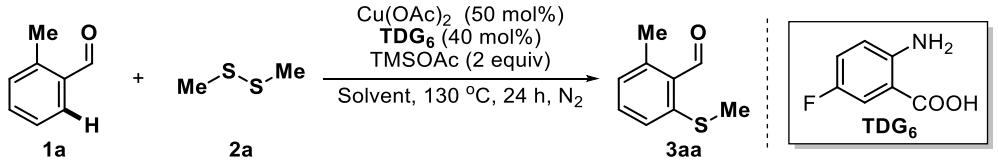
Table S2. Copper source survey[a,b]



Entry	[Cu]	Yield (%)
1	$Cu(OAc)_2$	69
2	$Cu(TFA)_2$	22
3	CuI	NR
4	$CuBr_2$	NR
5	CuF_2	trace
6	$Cu(OTf)_2$	trace

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), [Cu] (50 mol%), **TDG$_6$** (40 mol %), TMSOAc (2 equiv), DMSO (2 mL), 130 °C, 24 h, N_2. [b]Determined by ^{1}H NMR analysis using CH_2Br_2 as an internal standard. NR: no reaction.

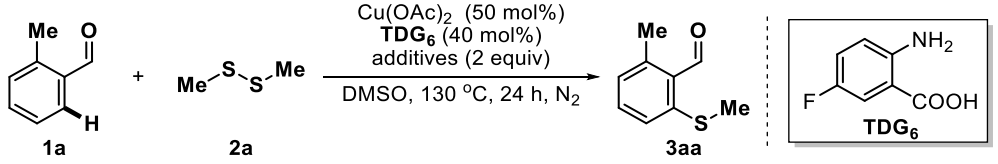
Table S3. Solvent survey[a,b]



Entry	Solvent	Yield (%)
1	DMSO	69
2	NMP	trace
3	THF	NR
4	Toluene	NR
5	DCE	NR
6	MeCN	NR
7	HFIP	13
8	DMSO/HFIP (1:1)	15

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), [Cu] (50 mol%), **TDG$_6$** (40 mol %), TMSOAc (2 equiv), solvent (2 mL), 130 °C, 24 h, N_2. [b]Determined by ^{1}H NMR analysis using CH_2Br_2 as an internal standard. NR: no reaction.

Table S4. Additives survey[a,b]

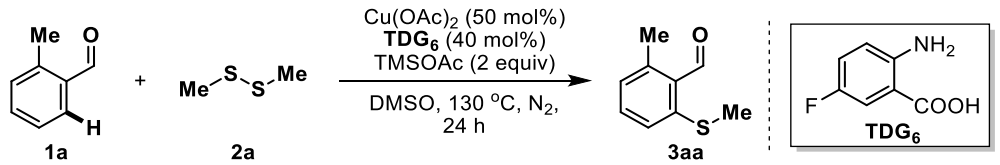


Entry	Additive	Yield (%)[b]
1	none	32

2	TMSOAc	69
3	KOAc	NR
4	Cs_2CO_3	NR
5	Pyridine	46
6	TEA	NR
7	AcOH	NR
8	Ad-COOH	trace
9	Ag_2CO_3	NR
10	MnO_2	10
11	CuF_2	78
12	AgF	trace
13	DTBP	NR

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), $Cu(OAc)_2$ (1 equiv), **TDG$_6$** (40 mol %), additives (2 equiv), DMSO (1.5 mL), 130 °C, 18 h, N_2. [b]Determined by ^1H NMR analysis using CH_2Br_2 as an internal standard. NR: no reaction.

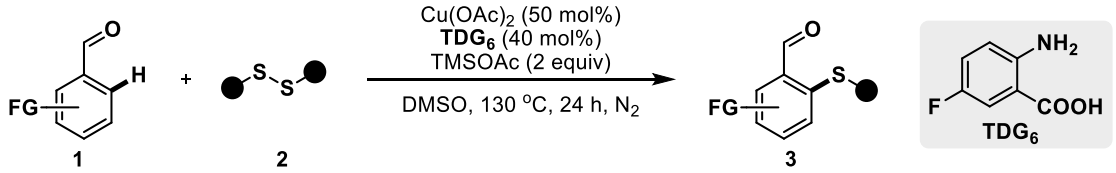
Table S5. Further condition optimization[a,b]



Entry	Variation	Yield (%)[b]
1	none	69
2	**1a (**1.2 equiv), **2a** (0.2 mmol)	60
3	**1a (**0.2 mmol), **2a** (1.2 equiv)	46
4	**1a (**0.2 mmol), **2a** (0.8 equiv)	55
5	$Cu(OAc)_2$ (25 mol%)	34
6	$Cu(OAc)_2$ (100 mol%)	71
7	**TDG$_6$** (20 mol%)	10
8	TMSOAc (1 equiv)	41
9	120 °C	40
10	18 h	63
11	DMSO = 1 mL	44
12	DMSO = 3 mL	75 (71[c])
13	DMSO = 4 mL	49

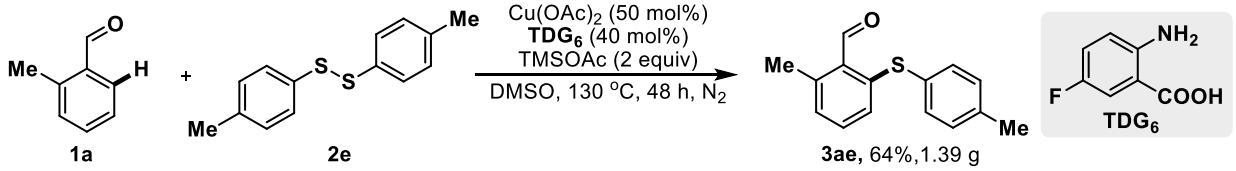
[a]Standard reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), $Cu(OAc)_2$ (1 equiv), **TDG$_6$** (40 mol %), DMSO (1.5 mL), 130 °C, 24 h, N_2. [b]Determined by ^1H NMR analysis using CH_2Br_2 as an internal standard. [c]Isolated yield.

3. General procedure for the *ortho*-C(sp^2)−H thiolation of benzaldehydes.



A 25 mL Schlenk-type tube (with a Teflon screw cap and a side arm) equipped with a magnetic stir bar was charged with $Cu(OAc)_2$ (18.1 mg, 0.1 mmol, 50 mol%), **TDG6** (12.4 mg, 0.08 mmol, 40 mol%), TMSOAc (60.0 uL, 0.4 mmol, 2.0 equiv), benzaldehydes (0.2 mmol, 1.0 equiv), and disulfides (0.2 mmol, 1.0 equiv), followed by the addition of DMSO (3.0 mL). The reaction mixture was frozen with liquid nitrogen and then the tube was evacuated and backfilled with nitrogen (6 times). After being stirred at 130 °C for 24 hours, the reaction mixture was diluted with EtOAc (20 mL) and then treated with saturated Na_2S aqueous solution (10 mL). The mixture was filtered through a pad of celite, and the filtrate was washed with brine twice. The organic layer was dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by preparative silica gel TLC with petroleum ether/EtOAc to afford **3**.

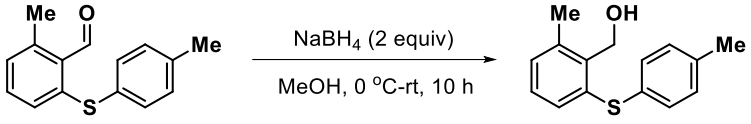
4. Gram-Scale Synthesis of Compound 3ae.



A 250 mL Schlenk-type tube (with a Teflon screw cap and a side arm) equipped with a magnetic stir bar was charged with $Cu(OAc)_2$ (815 mg, 4.5 mmol, 50 mol%), **TDG6** (558 mg, 3.6 mmol, 40 mol%), TMSOAc (2.7 mL, 18 mmol, 2.0 equiv), 2-methylbenzaldehyde (1.04 mL, 9 mmol, 1.0 equiv), and *p*-tolyl disulfide **2e** (846 mg, 9 mmol, 1.0 equiv), followed by the addition of DMSO (60 mL). The reaction mixture was frozen with liquid nitrogen and then the tube was evacuated and backfilled with nitrogen (6 times). After being stirred at 130 °C for 48 hours, the reaction mixture was diluted with EtOAc (120 mL) and then treated with saturated Na_2S aqueous solution (60 mL). The mixture was filtered through a pad of celite, and the filtrate was washed twice with brine. The organic layer was dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by silica gel column chromatography with petroleum ether/EtOAc (20:1) to afford **3ae** (1.39 g, 64% yield).

5. Procedures for product transformations and synthetic applications.

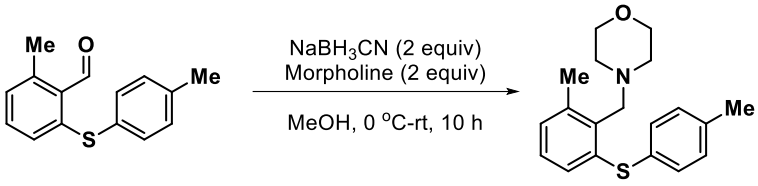
5.1 Product transformations



3ae
0.4 mmol

4
89%

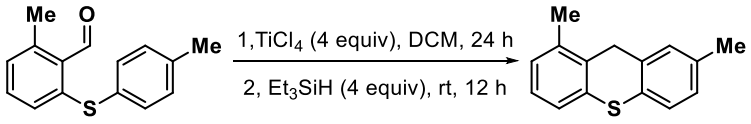
To a stirred solution of **3ae** (96.8 mg, 0.4 mmol, 1.0 equiv) in MeOH (3 mL) at 0 °C was added $NaBH_4$ (30.3 mg, 0.8 mmol, 2.0 equiv). After the reaction mixture was stirred at room temperature for 10 hours, it was diluted with EtOAc (20 mL) and then quenched by adding saturated aqueous $NaHCO_3$ solution. The reaction mixture was extracted with EtOAc (5 mL × 3). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated under vacuum. The crude product was purified by preparative silica gel TLC with petroleum ether/EtOAc (20:1) to afford **4** (87 mg, 89%).



3ae
0.4 mmol

5
48%

To a stirred solution of **3ae** (96.8 mg, 0.4 mmol, 1.0 equiv), morpholine (70 μL, 0.8 mmol, 2.0 equiv) in MeOH (3 mL) at 0 °C was added $NaBH_3CN$ (50.3 mg, 0.8 mmol, 2.0 equiv). After the reaction mixture was stirred at room temperature for 10 hours, it was diluted with EtOAc (20 mL) and then quenched by adding saturated $NaHCO_3$ solution. The mixture was extracted with EtOAc (5 mL × 3). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated under vacuum. The crude product was purified by preparative silica gel TLC with petroleum ether/EtOAc (20:1) to afford **5** (60 mg, 48%).

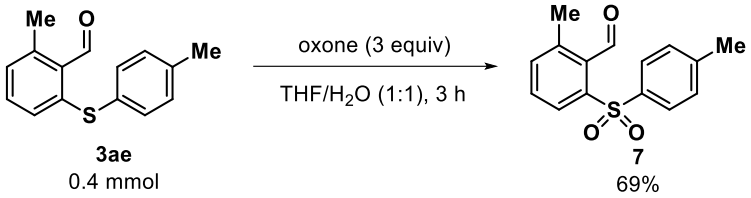


3ae
0.4 mmol

6
62%

To a solution of **3ae** (96.8 mg, 0.4 mmol, 1 equiv) in DCM (3 mL) was added $TiCl_4$ (176 μL, 1.6 mmol, 4 equiv.) at room temperature. After the reaction mixture was stirred at room temperature for 24 hours, Et_3SiH (256 μL, 1.6 mmol, 4 equiv.) was added and the reaction mixture was stirred for another 12 hours. Next, the reaction mixture was diluted with DCM (20 mL) and quenched by the addition of

H_2O (5 mL). The mixture was extracted with DCM (5 mL × 3). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude product was purified by preparative silica gel TLC with petroleum ether/EtOAc (50:1) to afford **6** (56 mg, 62%).

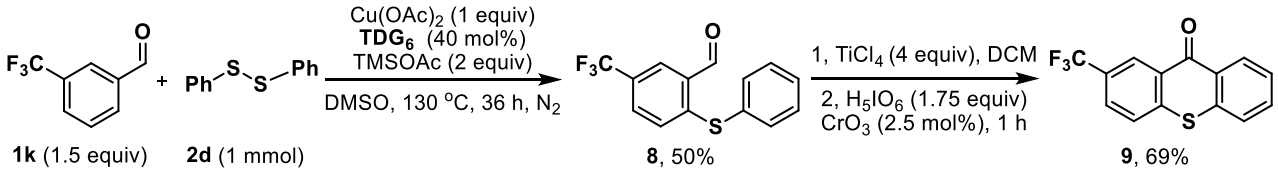


3ae
0.4 mmol

7
69%

To a solution of **3ae** (96.8 mg, 0.4 mmol, 1 equiv) in THF (3 mL) and H_2O (3 mL) was added Oxone monopersulfate (415.5 mg, 1.2 mmol, 3 equiv). After the reaction mixture was stirred at room temperature for 3 hours, it was diluted with EtOAc (20 mL) and then quenched by the addition of H_2O (5 mL). The mixture was extracted with EtOAc (5 mL × 3). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated under vacuum. The crude product was purified by preparative silica gel TLC with petroleum ether/EtOAc (5:1) to afford **7** (76 mg, 69%).

5.2 Synthetic applications

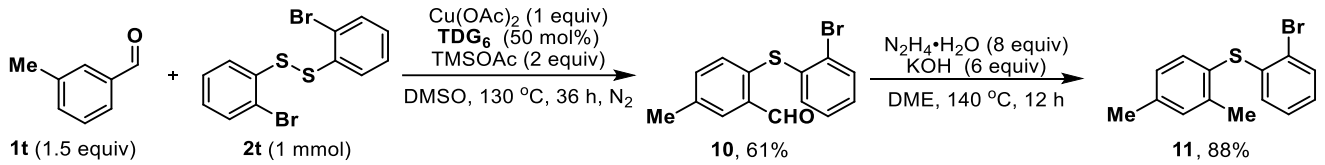


1k (1.5 equiv) **2d** (1 mmol) **8**, 50% **9**, 69%

Procedure for the synthesis of **8**. A 50 mL Schlenk-type tube (with a Teflon screw cap and a side arm) equipped with a magnetic stir bar was charged with $Cu(OAc)_2$ (181 mg, 1.0 mmol, 1.0 equiv), **TDG6** (62 mg, 0.4 mmol, 40 mol%), TMSOAc (0.3 mL, 2 mmol, 2.0 equiv), 3-(trifluoromethyl)benzaldehyde **1k** (0.20 mL, 1.5 mmol, 1.5 equiv), and phenyl disulfide **2d** (218 mg, 1 mmol, 1.0 equiv), followed by the addition of DMSO (15 mL). The reaction mixture was frozen with liquid nitrogen and then the tube was evacuated and backfilled with nitrogen (6 times). After being stirred at 130 °C for 36 hours, the reaction mixture was diluted with EtOAc (20 mL) and then treated with saturated aqueous Na_2S solution (10 mL). The mixture was filtered through a pad of celite, and the filtrate was washed with brine twice. The organic layer was dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by silica gel column chromatography with petroleum ether/EtOAc (20:1) to afford **8** (141 mg, 50% yield).

Procedure for the synthesis of **9**. To a solution of **8** (141 mg, 0.5 mmol, 1 equiv.) in DCM (1 mL) was added $TiCl_4$ (1 M solution in DCM, 2 mL, 4 equiv.) at room temperature. After the reaction mixture was stirred at room temperature for 24 hours, it was quenched by the addition of H_2O (2 mL).

The reaction mixture was extracted three times with DCM (20 mL), washed with brine, dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude product was transferred to a solution of H_5IO_6 (200 mg, 0.87 mmol, 1.75 equiv.) and CrO_3 (1.3 mg, 0.013 mmol, 2.5%) in acetonitrile (3 mL). The reaction mixture was stirred at room temperature for 1 hours, after which it was diluted with DCM (20 mL) and then washed with brine. The organic layer was dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by preparative silica gel TLC with petroleum ether/EtOAc (20:1) to afford **9** (96 mg, 69%).

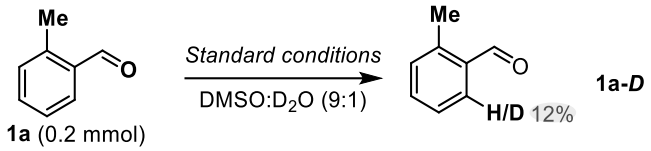


Procedure for the synthesis of **10**. A 50 mL Schlenk-type tube (with a Teflon screw cap and a side arm) equipped with a magnetic stir bar was charged with $Cu(OAc)_2$ (181 mg, 1.0 mmol, 1.0 equiv), **TDG6** (62 mg, 0.4 mmol, 40 mol%), TMSOAc (0.3 mL, 2 mmol, 2.0 equiv), 3-methylbenzaldehyde **1t** (0.18 mL, 1.5 mmol, 1.5 equiv), and phenyl disulfide **2t** (218 mg, 1 mmol, 1.0 equiv), followed by the addition of DMSO (15 mL). The reaction mixture was frozen with liquid nitrogen and then the tube was evacuated and backfilled with nitrogen (6 times). After being stirred at 130 °C for 36 hours, the reaction mixture was diluted with EtOAc (20 mL) and then treated with saturated Na_2S aqueous solution (10 mL). The mixture was filtered through a pad of celite, and the filtrate was washed with brine twice. The organic layer was dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by silica gel column chromatography with petroleum ether/EtOAc (20:1) to afford **10** (187 mg, 61% yield).

Procedure for the synthesis of **11**. A round-bottom flask (with Dean-Stark apparatus) equipped with a magnetic stir bar was charged with aldehyde **10** (184 mg, 0.6 mmol, 1 equiv), potassium hydroxide powder (202 mg, 3.6 mmol, 6 equiv) and hydrazine hydrate (291 μL, 6 mmol, 10 equiv), followed by the addition of diethylene glycol (5 mL). After being stirred at 140 °C for 12 hours, the reaction mixture was diluted with EtOAc (20 mL) and then quenched by the addition of 1 M HCl (2 mL). The mixture was extracted with EtOAc (3 × 10 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated under vacuum. The crude product was purified by preparative silica gel TLC with petroleum ether/EtOAc (50:1) to afford **11** (156 mg, 88%).

6. Mechanistic studies.

6.1 H/D exchange experiments



A 25 mL Schlenk-type tube (with a Teflon screw cap and a side arm) equipped with a magnetic stir bar was charged with $Cu(OAc)_2$ (18.1 mg, 0.1 mmol, 50 mol%), **TDG6** (12.4 mg, 0.08 mmol, 40 mol%), TMSOAc (60.0 uL, 0.4 mmol, 2.0 equiv), benzaldehyde **1a** (21 uL, 0.2 mmol, 1.0 equiv), followed by the addition of DMSO/D_2O (2.7 mL/0.3 mL). The reaction mixture was frozen with liquid nitrogen and then the tube was evacuated and backfilled with nitrogen (6 times). After being stirred at 130 °C for 24 hours, the reaction mixture was diluted with EtOAc (20 mL) and then treated with saturated Na_2S aqueous solution (10 mL). The mixture was filtered through a pad of celite, and the filtrate was washed twice with brine. The organic phase was dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by preparative silica gel TLC with petroleum ether/EtOAc (v : v = 20 : 1) to afford a mixture of **1a** and **1a**-*d*. The deuterium ratio was determined to be 12% D based on ^1H NMR analysis.

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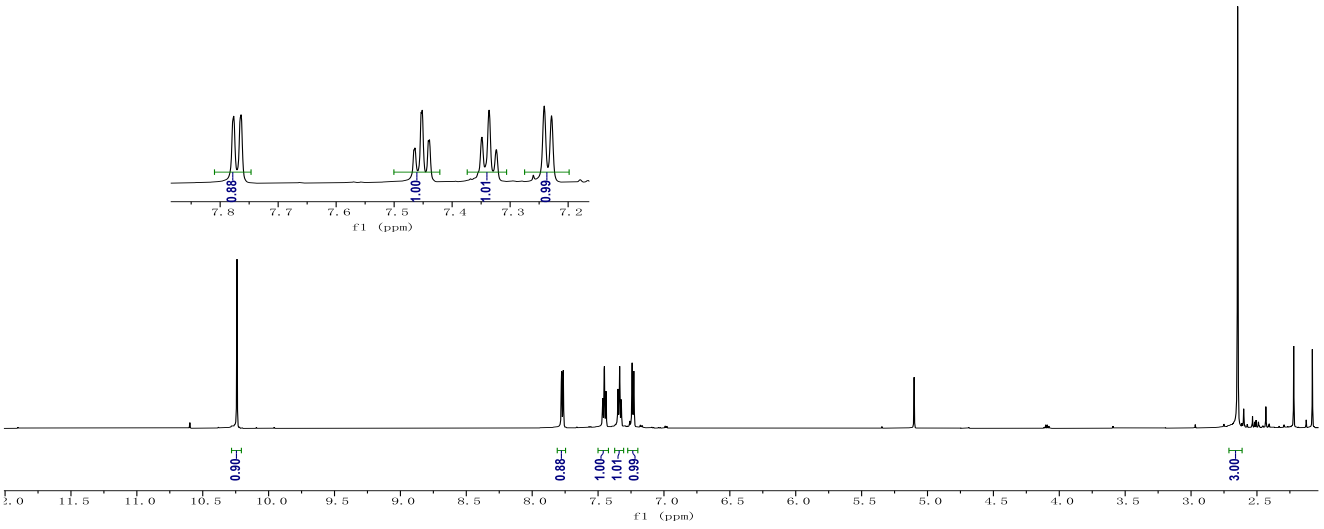
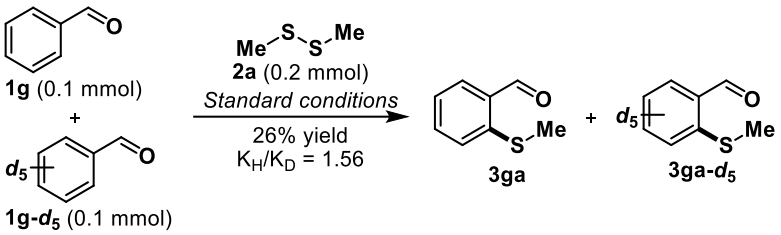
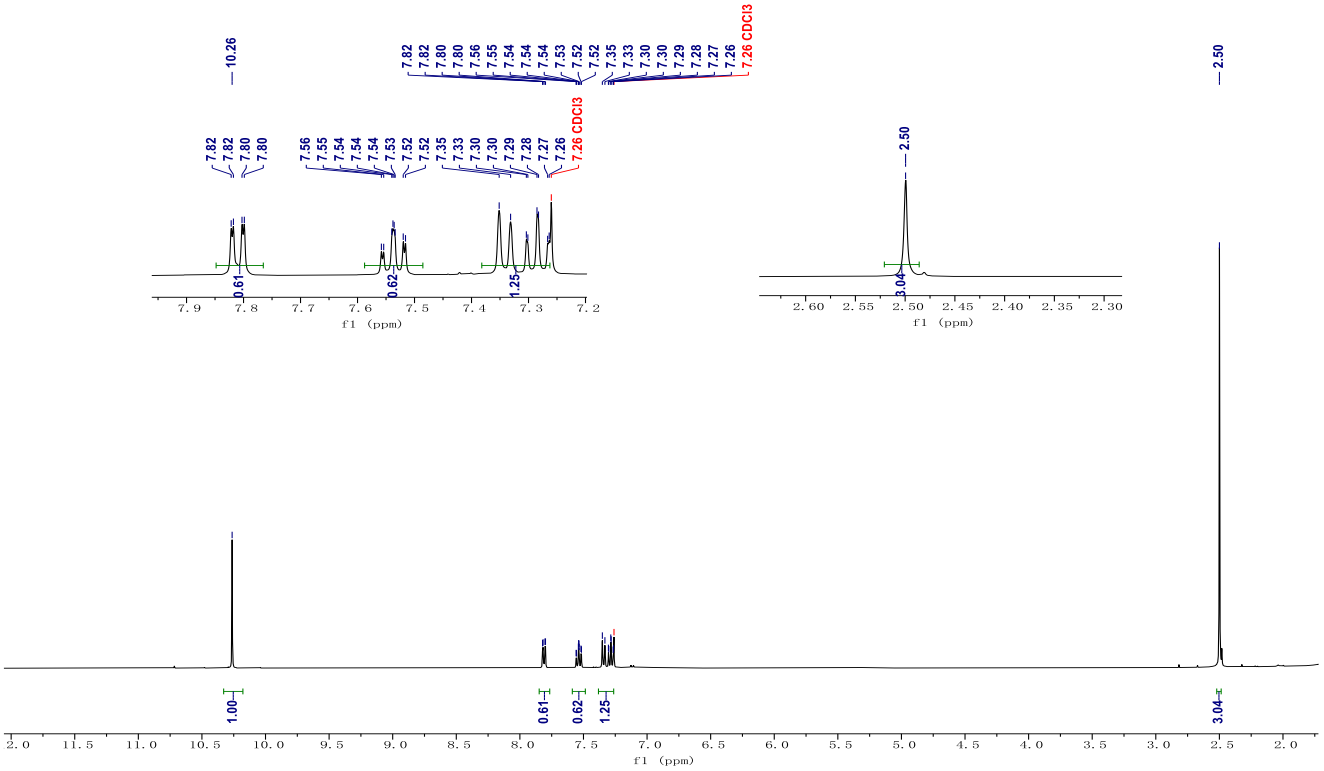


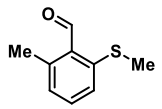
6.2 Intermolecular KIE experiments



A 25 mL Schlenk-type tube (with a Teflon screw cap and a side arm) equipped with a magnetic stir bar was charged with $Cu(OAc)_2$ (18.1 mg, 0.1 mmol, 50 mol%), **TDG6** (12.4 mg, 0.08 mmol, 40 mol%), TMSOAc (60.0 uL, 0.4 mmol, 2.0 equiv), dimethyl disulfide (0.2 mmol, 1.0 equiv), **1g** (10.6 mg, 0.1 mmol) and **1g**-d_5 (11.1 mg, 0.1 mmol), followed by the addition of DMSO (3.0 mL). The reaction mixture was frozen with liquid nitrogen and then the tube was evacuated and backfilled with nitrogen (6 times). After being stirred at 130 °C for 24 hours, the reaction mixture was diluted with EtOAc (20 mL) and then treated with saturated Na_2S aqueous solution (10 mL). The mixture was filtered through a pad of celite, and the filtrate was washed twice with brine. The organic phase was dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by preparative silica gel TLC with petroleum ether/EtOAc (v : v = 20 : 1) to afford product **3ga** and **3ga**-d_5 in 26% total yield. The ratio of **3ga** and **3ga**-d_5 was 0.61:0.39 = 1.56 based on ^{1}H NMR analysis. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.26 (s, 1H), 7.82–7.80 (m, 0.61H), 7.56–7.52 (m, 0.62H), 7.38–7.26 (m, 1.25H), 2.50 (s, 3H).



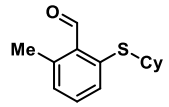
7. Characterization data of the products.



3aa

2-Methyl-6-(methylthio)benzaldehyde (3aa)[2]:

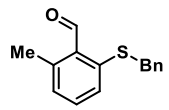
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a pale yellow oil (24 mg, 71%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.61 (s, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.18 (d, *J* = 8.1 Hz, 1H), 6.99 (d, *J* = 7.5 Hz, 1H), 2.61 (s, 3H), 2.44 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.6, 144.3, 142.4, 133.1, 131.1, 127.9, 123.9, 20.3, 16.3; **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_9H_{10}OSNa^+$: 189.0345, Found: 189.0346.



3ab

2-(Cyclohexylthio)-6-methylbenzaldehyde (3ab):

Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a pale yellow oil (29 mg, 61%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.77 (s, 1H), 7.39 (d, *J* = 7.9 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 7.4 Hz, 1H), 3.07 (tt, *J* = 10.6, 3.7 Hz, 1H), 2.57 (s, 3H), 1.98–1.93 (m, 2H), 1.79–1.74 (m, 2H), 1.62–1.60 (dd, *J* = 10.5, 5.7 Hz, 2H), 1.42–1.36 (m, 2H), 1.36–1.29 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 194.4, 141.4, 140.5, 135.0, 132.6, 131.3, 130.6, 48.0, 33.3, 26.1, 25.8, 21.2; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{19}OS^+$: 235.1151, Found: 235.1146.

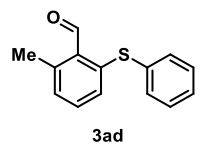


3ac

2-(Benzylthio)-6-methylbenzaldehyde (3ac)[3]:

Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a pale yellow oil (28 mg, 57%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.59 (s, 1H), 7.36–7.27 (m, 6H), 7.25–7.23 (m, 1H), 7.07 (d, *J* = 7.2 Hz, 1H), 4.11 (s, 2H), 2.58 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 192.8, 142.1, 142.0, 136.5, 133.0, 133.0, 129.6, 129.1, 128.7, 128.0, 127.6, 39.5, 20.7; **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{14}OSNa^+$: 265.0658, Found:

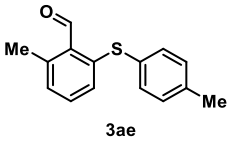
265.0662.



3ad

2-Methyl-6-(phenylthio)benzaldehyde (3ad)[3]:

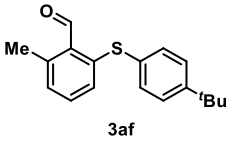
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a pale yellow oil (27 mg, 59%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.69 (s, 1H), 7.41–7.39 (m, 2H), 7.38–7.33 (m, 3H), 7.27–7.24 (m, 1H), 7.08 (d, *J* = 7.4 Hz, 1H), 6.98 (d, *J* = 7.9 Hz, 1H), 2.64 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 192.6, 142.3, 142.2, 134.3, 133.2, 133.0, 132.3, 129.9, 129.7, 129.6, 128.3, 20.6; **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{12}OSNa^+$: 251.0501, Found: 251.0497.



3ae

2-Methyl-6-(*p*-tolylthio)benzaldehyde (3ae):

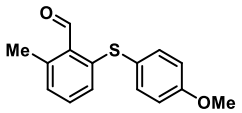
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a pale yellow solid (34 mg, 71%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.69 (s, 1H), 7.35–7.30 (m, 2H), 7.24–7.17 (m, 3H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 8.1 Hz, 1H), 2.63 (s, 3H), 2.37 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.3, 143.4, 142.1, 138.8, 133.7, 133.0, 131.8, 130. 6, 130.2, 129.4, 128.2, 21.3, 20.5; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{15}OS^+$: 243.0838, Found: 243.0838.



3af

2-((4-Methoxyphenyl)thio)-6-methylbenzaldehyde (3af):

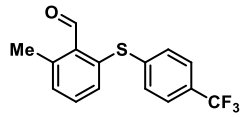
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a pale yellow oil (42 mg, 75%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.72 (s, 1H), 7.43–7.40 (m, 2H), 7.39–7.35 (m, 2H), 7.26 (t, *J* = 7.7 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 2.66 (s, 3H), 1.35 (s, 9H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 192.5, 151.8, 143.1, 142.1, 133.2, 133.1, 131.9, 130.2, 129.5, 128.4, 126.8, 34.8, 31.4, 20.6; **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{20}OSNa^+$: 307.1127, Found: 307.1111.



3ag

2-((4-Methoxyphenyl)thio)-6-methylbenzaldehyde (3ag):

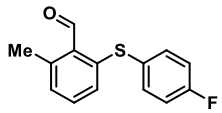
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a pale yellow solid (29 mg, 56%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.69 (s, 1H), 7.42 (d, *J* = 8.7 Hz, 2H), 7.18 (t, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 8.1 Hz, 1H), 3.84 (s, 3H), 2.63 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 191.9, 160.5, 145.0, 142.3, 136.6, 133.1, 130.9, 128.5, 126.6, 123.3, 115.5, 55.5, 20.4; **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{14}O_2SNa^+$: 281.0607, Found: 281.0603.



3ah

2-Methyl-6-((4-(trifluoromethyl)phenyl)thio)benzaldehyde (3ah):

Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a pale yellow solid (39 mg, 67%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.66 (s, 1H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.39–7.34 (m, 3H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 7.9 Hz, 1H), 2.65 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.9, 142.4, 140.9, 138.6, 133.9, 133.5, 131.8, 131.5, 130.6, 129.5 (q, *J* = 33.1, Hz), 126.4 (q, *J* = 3.9 Hz), 124.1 (q, *J* = 187.9 Hz), 20.8; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.64; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{12}F_3OS^+$: 297.0555, Found: 297.0549.

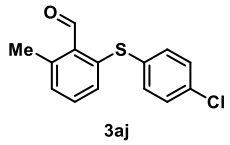


3ai

2-((4-Fluorophenyl)thio)-6-methylbenzaldehyde (3ai):

Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a pale yellow solid (40 mg, 81%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.68 (s, 1H), 7.48–7.39 (m, 2H), 7.24 (t, *J* = 7.8 Hz, 1H), 7.12–7.03 (m, 3H), 6.86 (d, *J* = 8.1 Hz, 1H), 2.64 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.1, 163.2 (d, *J* = 249.4 Hz), 143.0, 142.4, 136.0 (d, *J* = 8.4 Hz), 133.2, 131.7, 129.5, 129.0 (d, *J* = 3.7 Hz), 127.8, 117.0 (d, *J* = 22.0 Hz), 20.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.20; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{12}FOS^+$:247.0587,

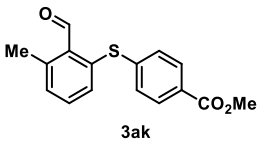
Found: 247.0584.



3aj

2-((4-Chlorophenyl)thio)-6-methylbenzaldehyde (3aj):

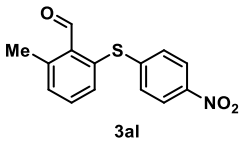
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a pale yellow solid (35 mg, 67%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.67 (s, 1H), 7.35–7.29 (m, 4H), 7.27–7.25 (m, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 7.9 Hz, 1H), 2.64 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.4, 142.4, 141.6, 134.6, 134.2, 133.3, 133.0, 132.4, 130.2, 130.0, 129.0, 20.5; **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{11}ClOSNa^+$: 285.0111, Found: 285.0118.



3ak

Methyl 4-((2-formyl-3-methylphenyl)thio)benzoate (3ak):

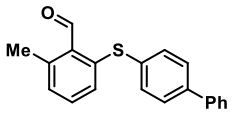
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 5 : 1 as the eluent to give the title compound as a pale yellow solid (37 mg, 66%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.65 (s, 1H), 7.95 (dd, *J* = 8.4, 3.1 Hz, 2H), 7.37 (td, *J* = 7.7, 3.0 Hz, 1H), 7.29–7.27 (m, 2H), 7.22 (t, *J* = 10.1 Hz, 2H), 3.90 (s, 3H), 2.64 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.1, 166.6, 142.4, 142.3, 138.4, 134.1, 133.4, 132.0, 131.9, 130.6, 129.7, 128.9, 52.3, 20.9; **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{14}O_3SNa^+$:309.0556, Found: 309.0548.



3al

2-Methyl-6-((4-nitrophenyl)thio)benzaldehyde (3al):

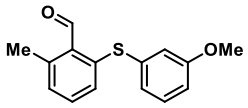
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a pale yellow oil (47 mg, 86%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.64 (s, 1H), 8.17–8.08 (m, 2H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 2.1 Hz, 1H), 7.26–7.25 (m, 1H), 2.65 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 193.1, 146.4, 146.3, 142.6, 135.9, 134.9, 133.8, 133.2, 133.2, 128.8, 124.5, 21.0; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{12}O_3NS^+$: 274.0532, Found: 274.0518.



3am

2-([1,1'-biphenyl]-4-ylthio)-6-methylbenzaldehyde (3am):

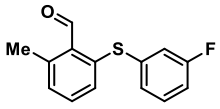
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a pale yellow oil (29 mg, 47%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.68 (s, 1H), 7.55 (d, *J* = 8.3 Hz, 4H), 7.41 (t, *J* = 8.3 Hz, 4H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.25–7.21 (m, 1H), 7.07–7.01 (m, 2H), 2.61 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.6, 142.2, 141.2, 140.2, 133.3, 133.2, 132.4, 130.0, 129.2, 129.0, 128.4, 127.8, 127.2, 20.6; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{17}OS^+$: 305.0995, Found: 305.1000.



3an

2-((3-Methoxyphenyl)thio)-6-methylbenzaldehyde (3an):

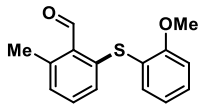
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a pale yellow oil (31 mg, 61%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.68 (s, 1H), 7.29–7.27 (m, 1H), 7.26–7.25 (m, 1H), 7.10 (d, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 6.93 (s, 1H), 6.86 (dd, *J* = 8.4, 2.5 Hz, 1H), 3.78 (s, 3H), 2.64 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.7, 160.4, 142.2, 141.8, 133.2, 130.5, 130.2, 129.5, 124.9, 117.8, 114.1, 55.5, 20.7; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{15}O_2S^+$: 259.0787, Found: 259.0792.



3ao

2-((3-Fluorophenyl)thio)-6-methylbenzaldehyde (3ao):

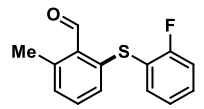
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a pale yellow oil (22 mg, 45%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.67 (s, 1H), 7.33–7.29 (m, 2H), 7.17–7.08 (m, 3H), 7.05–6.95 (m, 2H), 2.64 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 192.8, 163.2 (d, *J* = 249.2 Hz), 142.4, 140.2, 137.3 (d, *J* = 7.7 Hz), 133.4, 133.0, 131.0, 130.9 (d, *J* = 4.1 Hz), 130.2, 127.5 (d, *J* = 2.8 Hz), 118. 7 (d, *J* = 22.6 Hz), 115.0 (d, *J* = 21.5 Hz), 20.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.3; **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{11}FOSNa^+$: 269.0407, Found: 269.0394.



3ap

2-((2-Methoxyphenyl)thio)-6-methylbenzaldehyde (3ap):

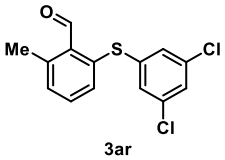
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a pale yellow oil (18 mg, 35%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.71 (s, 1H), 7.33 (td, *J* = 8.0, 1.7 Hz, 1H), 7.26–7.21 (m, 2H), 7.08 (d, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 7.9 Hz, 1H), 6.94–6.92 (m, 2H), 3.82 (s, 3H), 2.63 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 192.9, 158.6, 142.1, 141.4, 134.2, 133.1, 132.6, 130.0, 130.0, 129.1, 122.3, 121.6, 111.4, 56.0, 20.7; **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{14}O_2SNa^+$: 281.0607, Found: 281.0612.



3aq

2-((2-Fluorophenyl)thio)-6-methylbenzaldehyde (3aq):

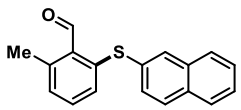
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a pale yellow oil (25 mg, 51%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.72 (s, 1H), 7.45 – 7.39 (m, 2H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.20 – 7.14 (m, 2H), 7.10 (d, *J* = 7.4 Hz, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 2.67 (s, 3H);**^{13}C NMR** (151 MHz, $CDCl_3$) δ 192.2, 162.3 (d, *J* = 248.7 Hz), 142.5, 140.9, 135.8, 133.3, 131.8, 131.1 (d, *J* = 7.7 Hz), 129.7, 127.8, 125.3 (d, *J* = 3.9 Hz), 120. 9 (d, *J* = 18.7 Hz), 116.4 (d, *J* = 22.6 Hz), 20.4; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -107.1; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{12}FOS^+$: 247.0587, Found: 247.0593.



3ar

2-((3,5-Dichlorophenyl)thio)-6-methylbenzaldehyde (3ar):

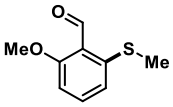
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a pale yellow solid (28 mg, 48%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.64 (s, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.26 (s, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.17 (s, 2H), 7.11 (d, *J* = 7.9 Hz, 1H), 2.65 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.5, 142.6, 139.0, 138.6, 135.9, 133.5, 131.6, 130.8, 129.2, 127.9, 20.6; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{11}Cl_2OS^+$: 296.9902, Found: 296.9898.



3as

2-Methyl-6-(naphthalen-2-ylthio)benzaldehyde (3as):

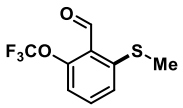
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a pale yellow solid (32 mg, 58%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.74 (s, 1H), 7.94 (s, 1H), 7.86–7.81 (m, 2H), 7.80–7.76 (m, 1H), 7.55–7.49 (m, 2H), 7.43 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 2.66 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 192.4, 142.4, 142.3, 134.0, 133.2, 132.9, 132.5, 132.2, 131.4, 130.0, 129.8, 129.4, 128.9, 127.9, 127.8, 126.9, 126.9, 20.6; **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{14}OSNa^+$: 301.0658, Found: 301.0658.



3ba

2-Methoxy-6-(methylthio)benzaldehyde (3ba)[4]:

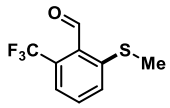
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a pale yellow oil (13 mg, 35%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.60 (s, 1H), 7.44 (t, *J* = 8.3 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 6.72 (d, *J* = 8.3 Hz, 1H), 3.91 (s, 3H), 2.42 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 190.1, 163.9, 145.8, 134.7, 121.3, 116.2, 106.4, 56.0, 15.5; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_9H_{11}O_2S^+$: 183.0474, Found: 183.0473.



3ca

2-(Methylthio)-6-(trifluoromethoxy)benzaldehyde (3ca):

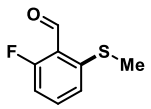
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a pale yellow oil (28 mg, 59%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.49 (s, 1H), 7.54 (t, *J* = 8.2 Hz, 1H), 7.25 (d, *J* = 8.3 Hz, 1H), 7.09 (d, *J* = 8.2 Hz, 1H), 2.47 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 188.1, 153.0, 146.9, 134.2, 124.6, 122.7, 120.4 (q, *J* = 259.7 Hz), 115.8, 15.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -57.37; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_9H_8F_3O_2S^+$: 237.0192, Found: 237.0181.



3da

2-(Methylthio)-6-(trifluoromethyl)benzaldehyde (3da):

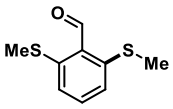
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a pale yellow oil (21 mg, 48%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.48 (q, *J* = 2.4 Hz, 1H), 7.63–7.51 (m, 3H), 2.49 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 189.3 (q, *J* = 3.3 Hz), 146.2, 133.0 (q, *J* = 31.7 Hz), 129.6, 128.5, 123.6 (q, *J* = 275.1 Hz), 121.6 (q, *J* = 6.1 Hz), 16.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -55.14; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_9H_8F_3OS^+$: 221.0242, Found: 221.0258



3ea

2-Fluoro-6-(methylthio)benzaldehyde (3ea)[5]:

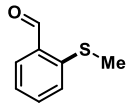
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a pale yellow oil (18 mg, 52%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.50 (s, 1H), 7.50 (td, *J* = 8.2, 5.9 Hz, 1H), 7.07 (d, *J* = 8.2 Hz, 1H), 6.90 (dd, *J* = 10.9, 7.8 Hz, 1H), 2.47 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 187.3 (d, *J* = 11.4 Hz), 166.8 (d, *J* = 259.3 Hz), 146.3, 135.1 (d, *J* = 11.0 Hz), 121.8, 120.0 (d, *J* = 3.3 Hz), 111.0 (d, *J* = 21.6 Hz), 15.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -120.30; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_8H_8FOS^+$: 171.0274, Found: 171.0278.



3fa

2,6-Bis(methylthio)benzaldehyde (3fa)[3]:

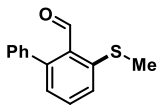
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a pale yellow oil (11 mg, 27%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.71 (s, 1H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 2.48 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 190.2, 146.0, 133.1, 129.4, 122.1, 16.4; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_9H_{11}OS_2^+$: 199.0246, Found: 199.0239.



3ga

2-(Methylthio)benzaldehyde (3ga)[6]:

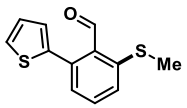
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a pale yellow oil (10 mg, 30%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.23 (s, 1H), 7.77 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.50 (td, *J* = 7.7, 1.6 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.27–7.22 (m, 1H), 2.46 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 191.4, 143.4, 134.0, 133.4, 132.8, 125.4, 124.4, 15.5; **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_8H_8OSNa^+$: 175.0188, Found: 175.0186.



3ha

3-(Methylthio)-[1,1'-biphenyl]-2-carbaldehyde (3ha):

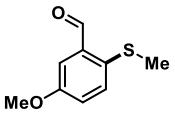
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a pale yellow solid (32 mg, 71%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.95 (s, 1H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.47–7.41 (m, 3H), 7.38–7.30 (m, 3H), 7.16 (d, *J* = 7.5 Hz, 1H), 2.50 (s, 3H);**^{13}C NMR** (151 MHz, $CDCl_3$) δ 192.5, 148.7, 144.2, 138.6, 132.6, 130.2, 130.1, 128.5, 128.3, 126.3, 123.4, 15.7; **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{12}OSNa^+$: 251.0501, Found: 251.0482.



3ia

2-(Methylthio)-6-(thiophen-2-yl)benzaldehyde (3ia):

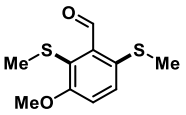
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a pale yellow solid (21 mg, 45%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.11 (s, 1H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 5.1 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.27 (d, *J* = 9.2 Hz, 1H), 7.13−7.11 (m, 1H), 7.05 (d, *J* = 2.8 Hz, 1H), 2.49 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 192.1, 144.4, 140.6, 139.3, 132.5, 130.8, 130.1, 127.7, 127.5, 126.9, 123.9, 15.7; **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{12}H_{10}OS_2Na^+$: 257.0065, Found: 226.0058.



3ja

5-Methoxy-2-(methylthio)benzaldehyde (3ja):

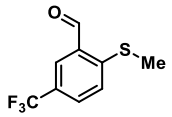
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a pale yellow oil (12 mg, 32%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.45 (s, 1H), 7.38 (s, 1H), 7.37 (d, *J* = 4.8 Hz, 1H), 7.12 (dd, *J* = 8.7, 2.9 Hz, 1H), 3.85 (s, 3H), 2.47 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 191.5, 158.3, 135.3, 134.1, 131.0, 122.0, 114.0, 55.8, 18.3; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_9H_{11}O_2S^+$: 183.0474, Found: 183.0470.



3ja'

3-Methoxy-2,6-bis(methylthio)benzaldehyde (3ja′):

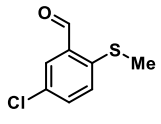
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a pale yellow oil (4 mg, 8%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.81 (s, 1H), 7.28–7.26 (m, 1H), 7.10 (d, *J* = 8.9 Hz, 1H), 3.95 (s, 3H), 2.42 (s, 3H), 2.40 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 193.1, 157.3, 135.7, 134.4, 130.1, 126.4, 115.9, 56.5, 19.3, 16.4; **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{10}H_{12}O_2S_2Na^+$: 251.0171, Found: 251.0157.



3ka

2-(Methylthio)-5-(trifluoromethyl)benzaldehyde (3ka)[4]:

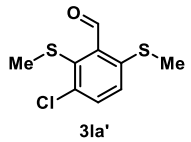
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a pale yellow oil (21 mg, 40%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.25 (s, 1H), 8.03 (s, 1H), 7.73 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 1H), 2.54 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.0, 148.5, 132.5, 130.2 (q, *J* = 4.1 Hz), 130.0 (q, *J* = 3.0 Hz), 126.8 (q, *J* =33.3 Hz), 125.3, 123.8 (q, *J* = 272.7 Hz), 15.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.56; **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_9H_8F_3OSNa^+$: 221.0242, Found: 221.0234.



3la

5-Chloro-2-(methylthio)benzaldehyde (3la)[7]:

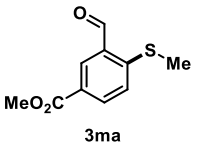
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a pale yellow oil (11 mg, 30%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.26 (s, 1H), 7.80 (d, *J* = 2.4 Hz, 1H), 7.51 (dd, *J* = 8.6, 2.5 Hz, 1H), 7.30 (d, *J* = 8.6 Hz, 1H), 2.52 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.0, 141.9, 134.2, 134.0, 132.2, 131.1, 127.6, 16.0; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_8H_8ClOS^+$: 186.9979, Found: 186.9977.



3la'

3-Chloro-2,6-bis(methylthio)benzaldehyde (3la′):

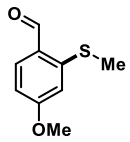
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a pale yellow oil (7 mg, 15%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.80 (s, 1H), 7.57 (d, *J* = 8.7 Hz, 1H), 7.23 (d, *J* = 8.7 Hz, 1H), 2.43 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.8, 143.5, 140.4, 136.0, 135.7, 133.7, 125.8, 20.1, 15.8; **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_9H_{10}ClOS_2Na^+$: 232.9856, Found: 232.9855.



3ma

Methyl 3-formyl-4-(methylthio)benzoate (3ma):

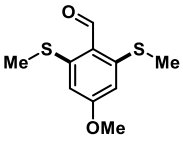
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 5 : 1 as the eluent to give the title compound as a white solid (17 mg, 40%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.20 (s, 1H), 8.44 (s, 1H), 8.14 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 3.94 (s, 3H), 2.54 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.9, 166.0, 149.7, 135.5, 134.1, 132.3, 126.1, 124.5, 52.5, 15.2; **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{10}H_{10}O_3SNa^+$: 233.0243, Found: 233.0245.



3na

4-Methoxy-2-(methylthio)benzaldehyde (3na)[4]:

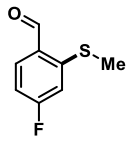
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a pale yellow oil (9.1 mg, 25%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.08 (s, 1H), 7.75 (d, *J* = 8.5 Hz, 1H), 6.79 (d, *J* = 2.3 Hz, 1H), 6.76 (dd, *J* = 8.5, 2.3 Hz, 1H), 3.90 (s, 3H), 2.47 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 190.0, 164.1, 146.0, 136.3, 126.8, 111.4, 109.2, 55.7, 15.4; **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_9H_{10}O_2SNa^+$: 205.0294, Found: 205.0309.



3na'

4-Methoxy-2,6-bis(methylthio)benzaldehyde (3na′):

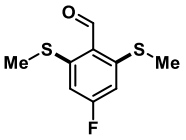
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a pale yellow oil (11.4 mg, 25%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.57 (s, 1H), 6.59 (s, 2H), 3.90 (s, 3H), 2.46 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 188.5, 163.0, 148.6, 123.3, 107.6, 55.6, 16.3; **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{10}H_{12}O_2S_2Na^+$: 251.0171, Found: 251.0175.



3oa

4-Fluoro-2-(methylthio)benzaldehyde (3oa):

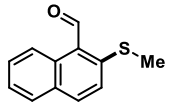
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a pale yellow oil (10.5 mg, 31%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.13 (s, 1H), 7.79 (dd, *J* = 8.5, 6.0 Hz, 1H), 7.04–6.82 (m, 2H), 2.47 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.74, 166.17 (d, *J* = 257.5 Hz), 147.24 (d, *J* = 9.2 Hz), 136.28 (d, *J* = 10.2 Hz), 129.36, 112.24 (d, *J* = 25.4 Hz), 111.58 (d, *J* = 22.4 Hz), 15.34; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.73; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_8H_8FOS^+$: 171.0274, Found: 171.0275.



3oa'

4-Fluoro-2,6-bis(methylthio)benzaldehyde (3oa′):

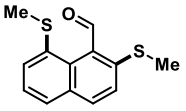
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a pale yellow oil (9 mg, 20%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.60 (s, 1H), 6.77 (d, *J* = 9.6 Hz, 2H), 2.47 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 188.3, 165.4 (d, *J* = 257.5 Hz), 149.8 (d, *J* = 9.9 Hz), 125.5, 108.6 (d, *J* = 25.3 Hz), 16.1; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -96.58; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_9H_{10}FOS_2^+$: 217.0152, Found: 217.0138.



3pa

2-(Methylthio)-1-naphthaldehyde (3pa)[8]:

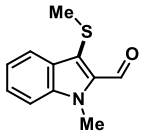
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a pale yellow oil (8.4 mg, 21%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.03 (s, 1H), 8.88 (d, *J* = 8.8 Hz, 1H), 7.98 (d, *J* = 8.8 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.64 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H), 7.57–7.49 (m, 2H), 2.61 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) 191.2, 145.8, 134.4, 132.4, 131.4, 129.4, 128.7, 126.3, 125.9, 124.3, 123.4, 17.1; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{11}OS^+$:203.0525, Found: 203.0519.



3pa'

2,8-Bis(methylthio)-1-naphthaldehyde (3pa′):

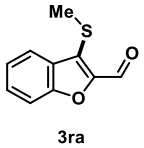
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20 : 1 as the eluent to give the title compound as a pale yellow oil (10.4 mg, 21%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 11.00 (s, 1H), 7.85 (d, *J* = 8.7 Hz, 1H), 7.81 (dd, *J* = 7.2, 1.3 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.52 (d, *J* = 8.7 Hz, 1H), 7.46–7.39 (m, 1H), 2.54 (s, 3H), 2.32 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 190.3, 138.5, 135.0, 134.5, 133.8, 132.7, 132.6, 131.7, 129.1, 126.2, 125.1, 21.5, 17.3; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{13}OS_2^+$: 249.0402, Found: 249.0403.



3qa

1-Methyl-3-(methylthio)-1*H*-indole-2-carbaldehyde (3qa)[2]:

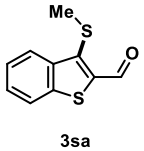
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 10 : 1 as the eluent to give the title compound as a white solid (24 mg, 57%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.41 (s, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.42–7.40 (m, 1H), 7.28–7.24 (m, 1H), 4.10 (s, 3H), 2.44 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 183.8, 139.9, 134.8, 128.5, 127.7, 122.7, 121.7, 121.5, 110.8, 31.8, 21.3; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{11}H_{12}NOS^+$: 206.0634, Found: 206.0627.



3ra

3-(Methylthio)benzofuran-2-carbaldehyde (3ra):

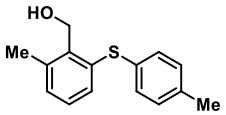
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 10 : 1 as the eluent to give the title compound as a white solid (19 mg, 49%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.15 (s, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.65–7.48 (m, 2H), 7.38 (t, *J* = 7.5 Hz, 1H), 2.62 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.8, 155.5, 150.7, 129.9, 128.6, 128.4, 124.4, 122.4, 113.2, 18.8; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{10}H_9O_2S^+$: 193.0318, Found: 193.0310.



3sa

3-(Methylthio)benzo[b]thiophene-2-carbaldehyde (3sa):

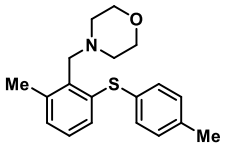
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 10 : 1 as the eluent to give the title compound as a white solid (17 mg, 41%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.55 (s, 1H), 8.16 (dd, *J* = 7.8, 2.4 Hz, 1H), 7.88 (d, *J* = 7.1 Hz, 1H), 7.52 (pd, *J* = 7.1, 1.5 Hz, 2H), 2.52 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 185.6, 144.0, 141.7, 140.3, 139.4, 128.8, 125.6, 124.9, 123.7, 20.6; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{10}H_9OS_2^+$: 209.0089, Found: 209.0089.



4

(2-Methyl-6-(*p*-tolylthio)phenyl)methanol (4):

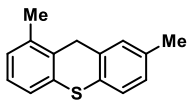
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 10 : 1 as the eluent to give the title compound as a colourless oil (87 mg, 89%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23–7.03 (m, 7H), 4.89 (s, 2H), 2.48 (s, 3H), 2.33 (s, 3H), 1.99 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.5, 138.9, 137.0, 135.7, 132.8, 131.2, 130.6, 130.4, 130.2, 128.7, 60.3, 21.1, 19.8; **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{16}OSNa^+$: 267.0814, Found: 267.0817.



5

4-(2-Methyl-6-(*p*-tolylthio)benzyl)morpholine (5):

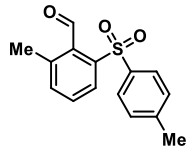
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 10 : 1 as the eluent to give the title compound as a colourless oil (60 mg, 48%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 7.06–6.85 (m, 3H), 3.72 (brs, 2H), 3.65 (brs, 4H), 2.51 (brs, 4H), 2.44 (s, 3H), 2.33 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.1, 138.8, 137.2, 131.9, 130.1, 129.5, 128.9, 127.7, 126.1, 67.3, 57.1, 53.1, 21.2, 20.5; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{29}H_{24}NOS^+$: 314.1573, Found: 314.1573.



6

1,7-Dimethyl-9H-thioxanthene (6):

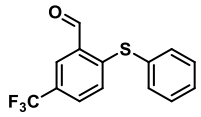
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 50 : 1 as the eluent to give the title compound as a colourless oil (56 mg, 62%);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40–7.35 (m, 2H), 7.23 (s, 1H), 7.17–7.10 (m, 2H), 7.07 (d, *J* = 7.8 Hz, 1H), 3.88 (s, 2H), 2.53 (s, 3H), 2.41 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.4, 136.4, 135.4, 135.0, 134.4, 131.0, 128.9, 128.4, 127.4, 126.6, 125.9, 125.0, 35.1, 21.1, 20.2; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{15}S^+$: 227.0889, Found: 227.0881.



7

2-Methyl-6-tosylbenzaldehyde (7)[1]:

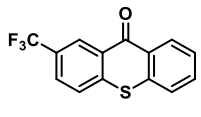
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 5 : 1 as the eluent to give the title compound as a while solid (76 mg, 69%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.79 (s, 1H), 7.96 (d, *J* = 7.7 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.47 (d, *J* = 7.2 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 2.43 (s, 3H), 2.39 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.5, 144.9, 142.2, 139.7, 138.7, 136.9, 134.8, 131.3, 130.2, 127.8, 127.3, 21.7, 20.7; **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{14}O_3SNa^+$: 297.0556, Found: 297.0554.



8

2-(Phenylthio)-5-(trifluoromethyl)benzaldehyde (8)[9]:

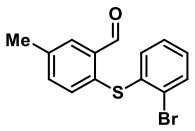
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 10 : 1 as the eluent to give the title compound as a yellow oil (141 mg, 50%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.32 (s, 1H), 8.06 (d, *J* = 2.1 Hz, 1H), 7.59–7.49 (m, 3H), 7.49–7.39 (m, 3H), 7.01 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 189.9, 147.9, 134.9, 132.5, 130.7, 130.2, 129.89 (q, *J* = 4.0 Hz), 129.8, 129.4 (q, *J* = 3.0 Hz), 128.7, 127.7 (q, *J* = 33.3 Hz), 123.6 (q, *J* = 273.7 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.7. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{14}H_9F_3OSNa^+$: 305.0218, Found: 302.0217.



9

2-(Trifluoromethyl)-9H-thioxanthen-9-one (9)[9]:

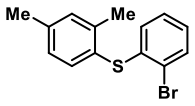
Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 10 : 1 as the eluent to give the title compound as a yellow oil (96 mg, 69%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.89 (s, 1H), 8.63 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.82 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.74–7.63 (m, 2H), 7.61–7.58 (m, 1H), 7.56–7.52 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.1, 141.2, 136.6, 133.0, 130.2, 129.3, 129.1, 128.7, 128.3 (q, *J* = 4.0 Hz), 127.4 (q, *J* = 4.1 Hz), 127.1, 127.0, 126.2, 123.8 (q, *J* = 272.7 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.6. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_8F_3OS^+$: 281.0242, Found: 281.0239.



10

2-((2-Bromophenyl)thio)-5-methylbenzaldehyde (10)[9]:

Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 10 : 1 as the eluent to give the title compound as a yellow oil (187 mg, 61%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.40 (s, 1H), 7.79 (d, *J* = 2.0 Hz, 1H), 7.60 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.38–7.34 (m, 1H), 7.23–7.16 (m, 2H), 7.09 (td, *J* = 7.6, 1.7 Hz, 1H), 6.98 (dd, *J* = 7.8, 1.7 Hz, 1H), 2.42 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.9, 139.0, 137.4, 135.7, 135.6, 134.4, 134.0, 133.5, 131.5, 131.2, 128.4, 128.3, 124.6, 21.1. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{11}BrOSNa^+$: 328.9606, Found: 328.9607.



11

(2-Bromophenyl)(2,4-dimethylphenyl)sulfane (11)[9]:

Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 50 : 1 as the eluent to give the title compound as a light yellow oil (156 mg, 88%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.17 (s, 1H), 7.11–7.02 (m, 2H), 6.96 (td, *J* = 7.6, 1.6 Hz, 1H), 6.57 (dd, *J* = 7.9, 1.6 Hz, 1H), 2.37 (s, 3H), 2.34 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.5, 140.1, 139.7, 136.3, 133.0, 132.1, 128.2, 127.8, 127.5, 127.3, 126.2, 121.4, 21.4, 20.7. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{15}O_3S^+$: 292.9994, Found: 292.9994.

8. References.

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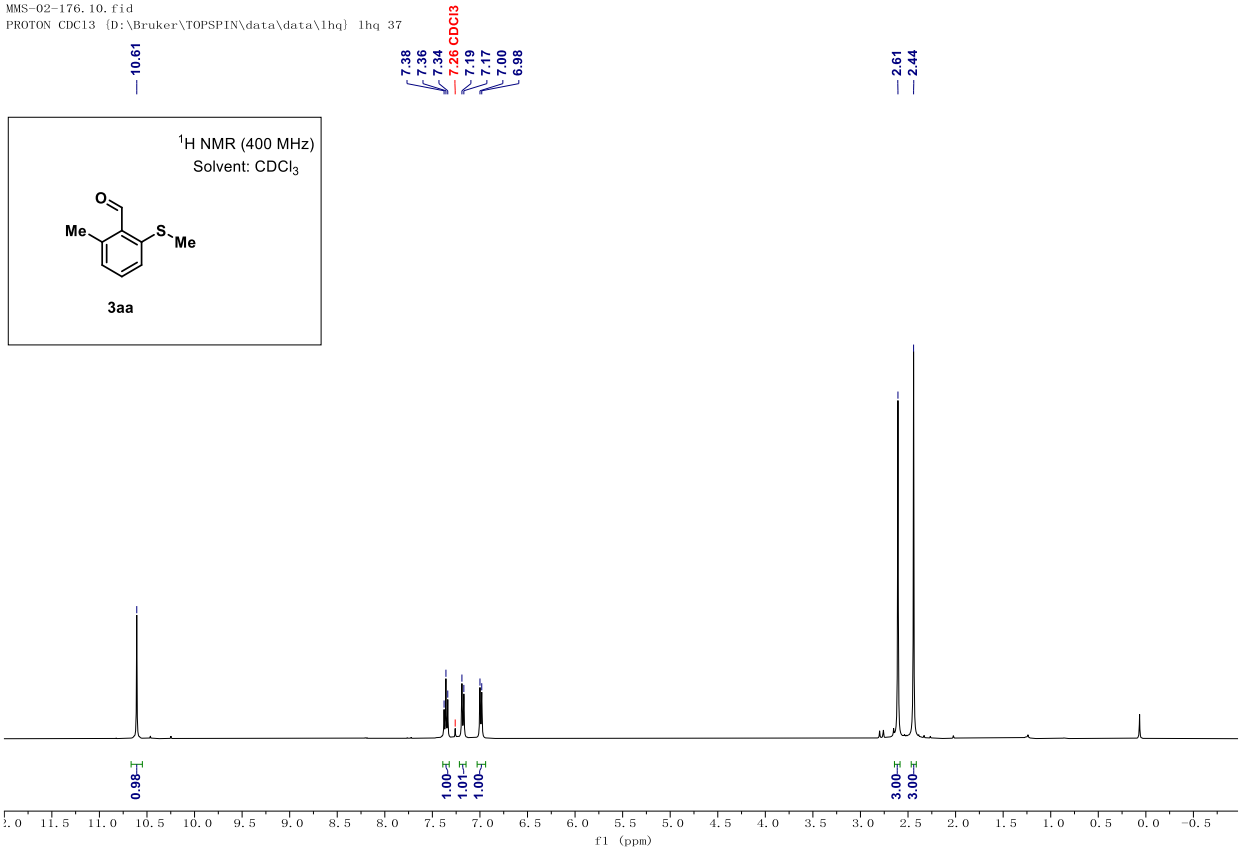
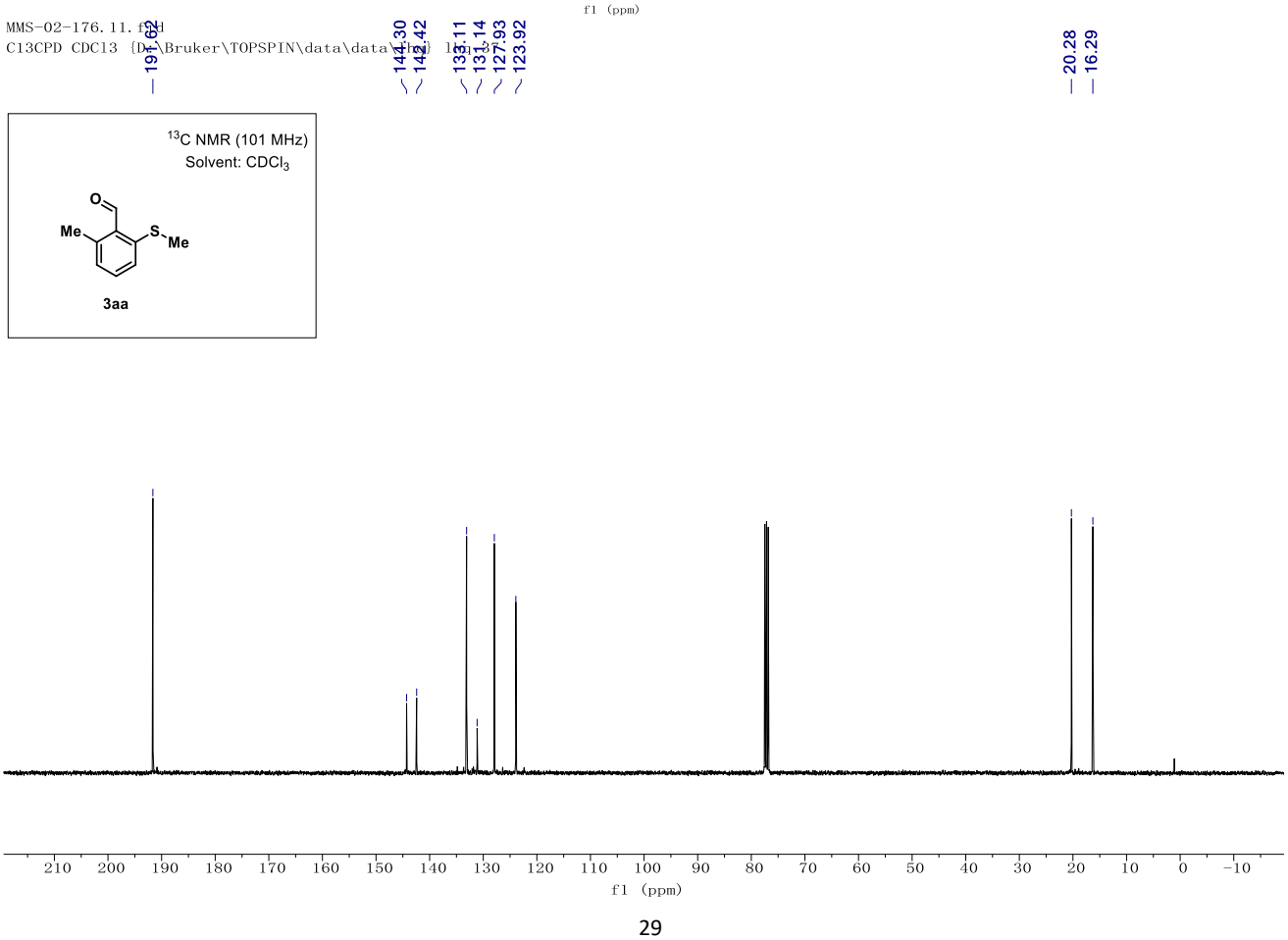
9. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra.





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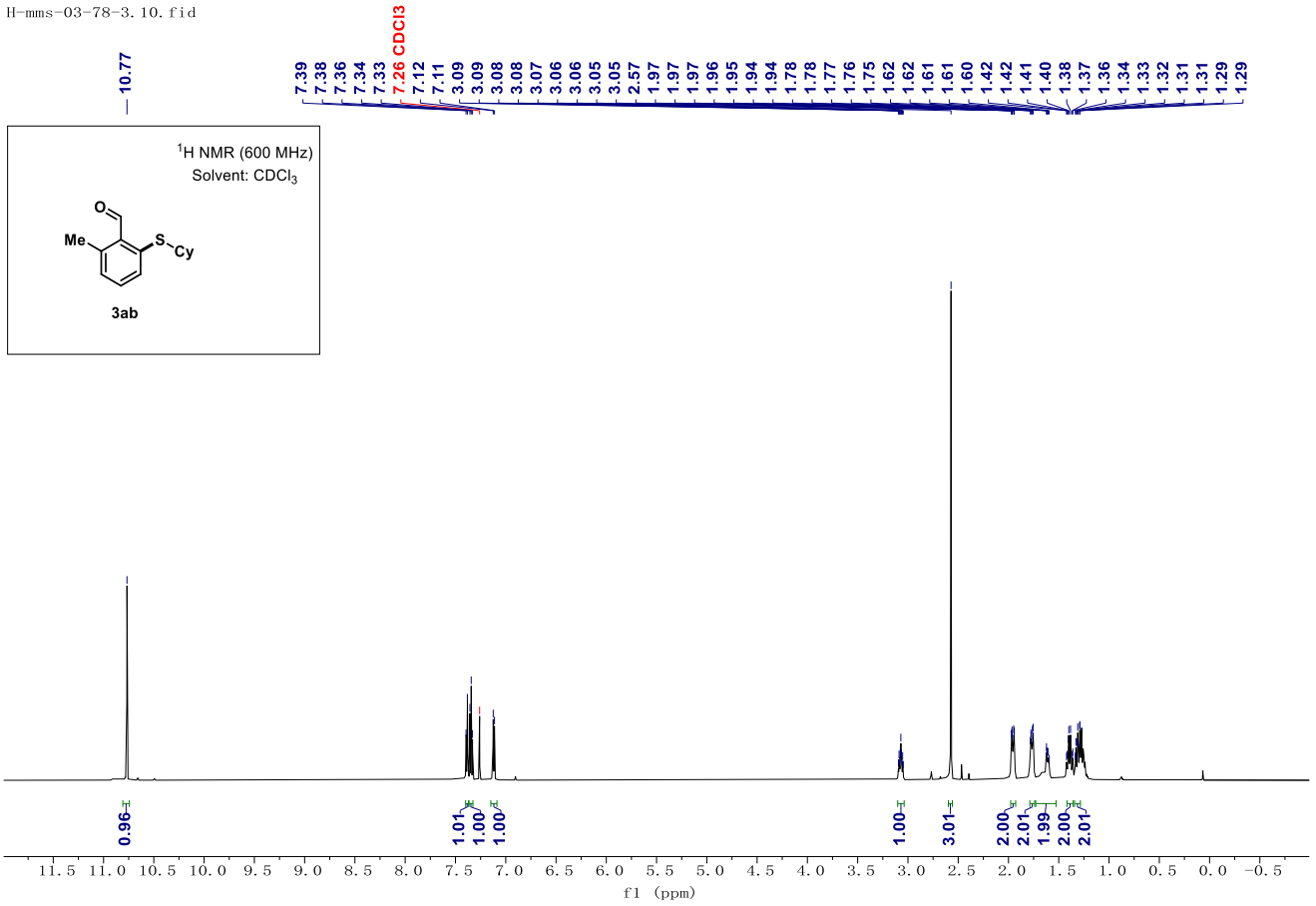

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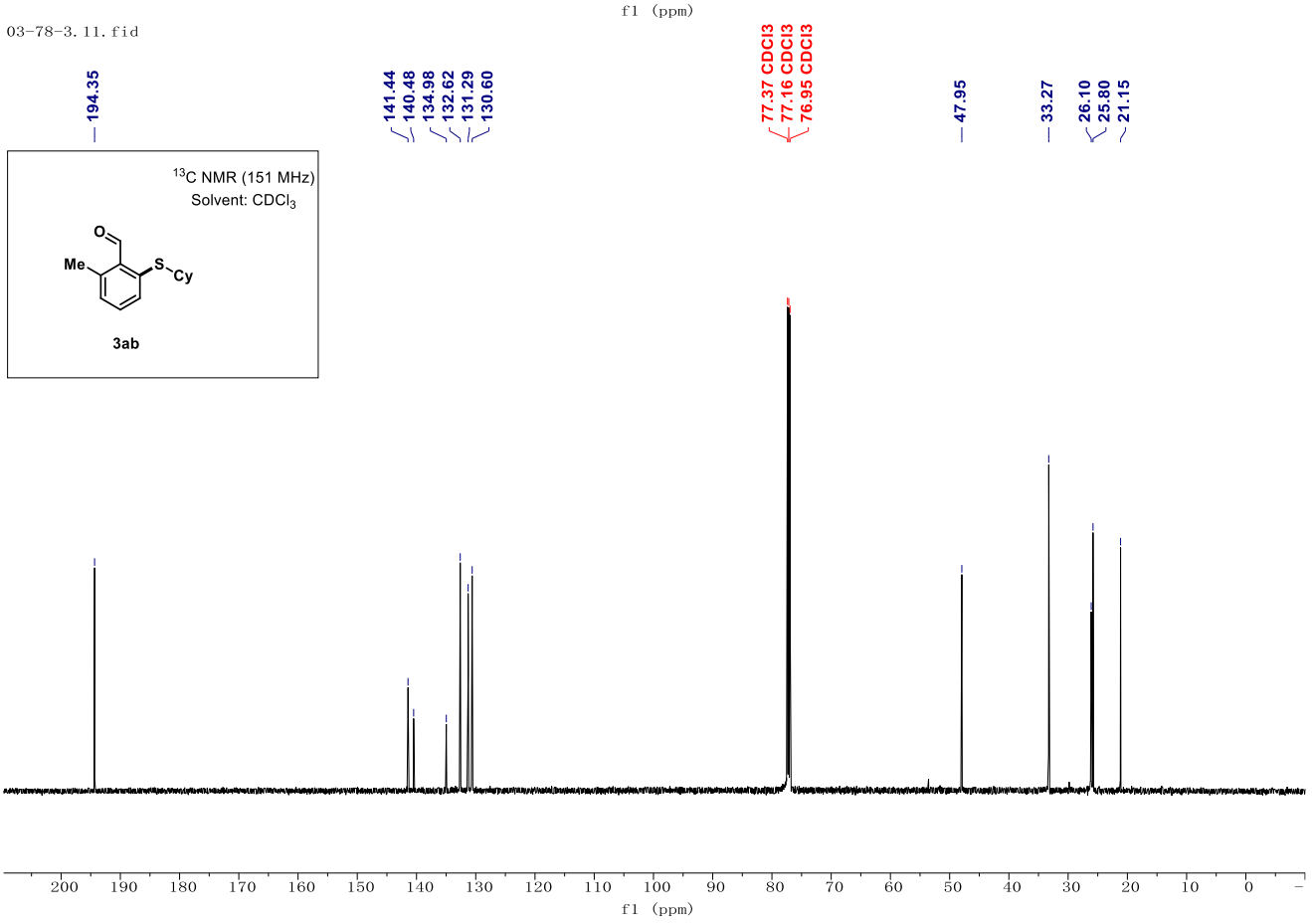

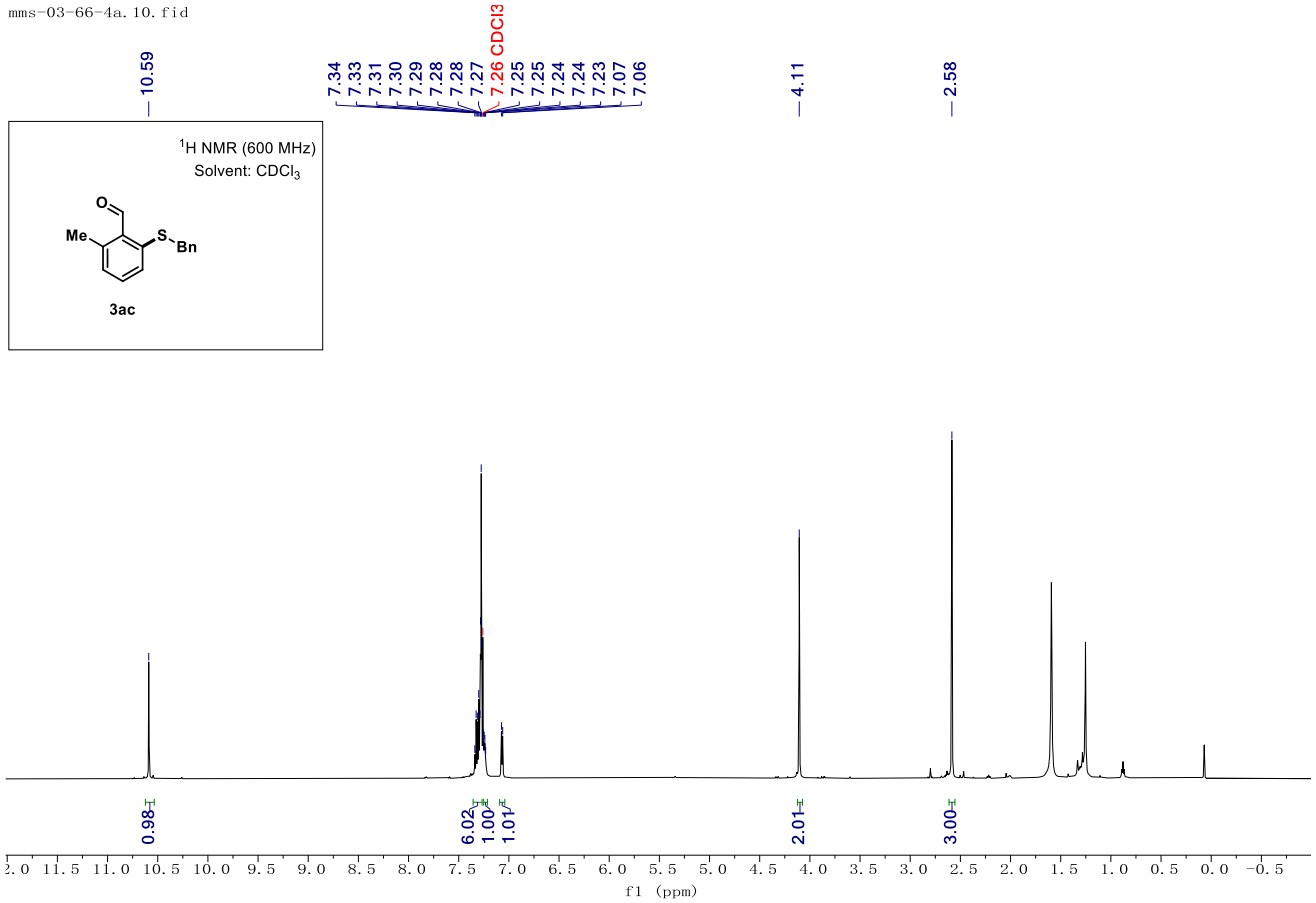
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7.23
7.07
7.06
4.11
2.58
1H NMR (600 MHz)
Solvent: CDCl3
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Bn
O
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0.98
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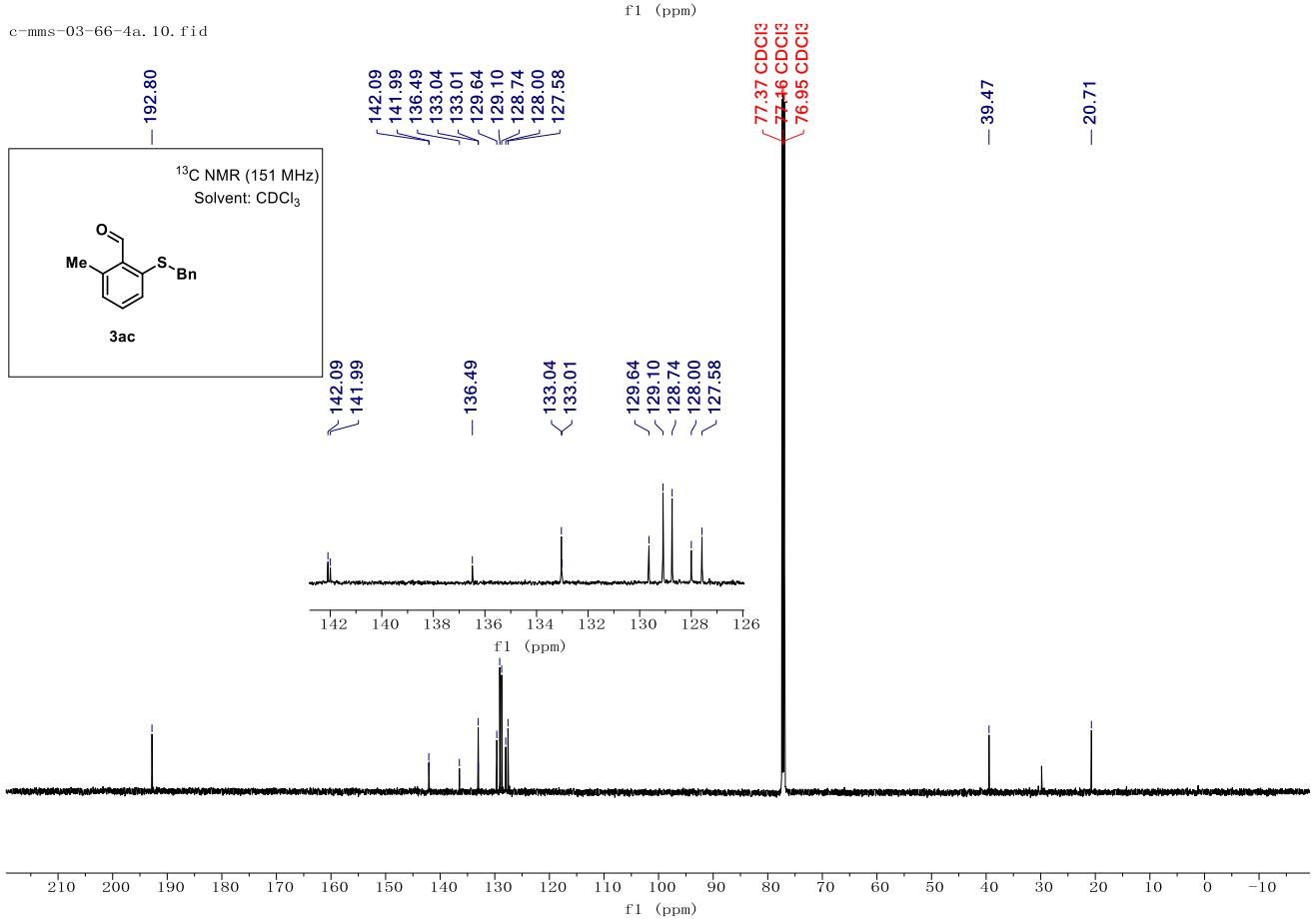
f1 (ppm)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S
Bn
O
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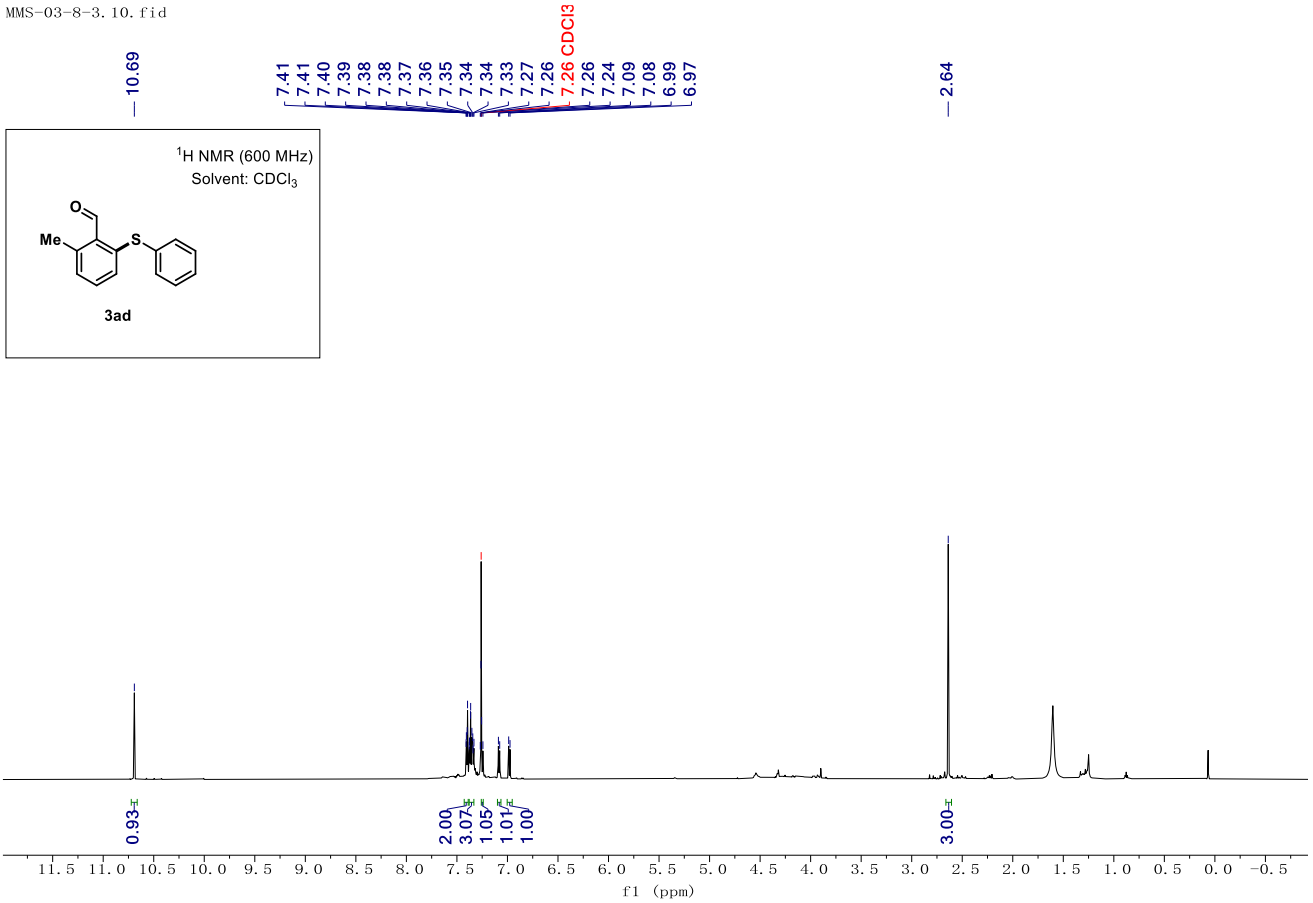
f1 (ppm)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O
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1.00
3.00
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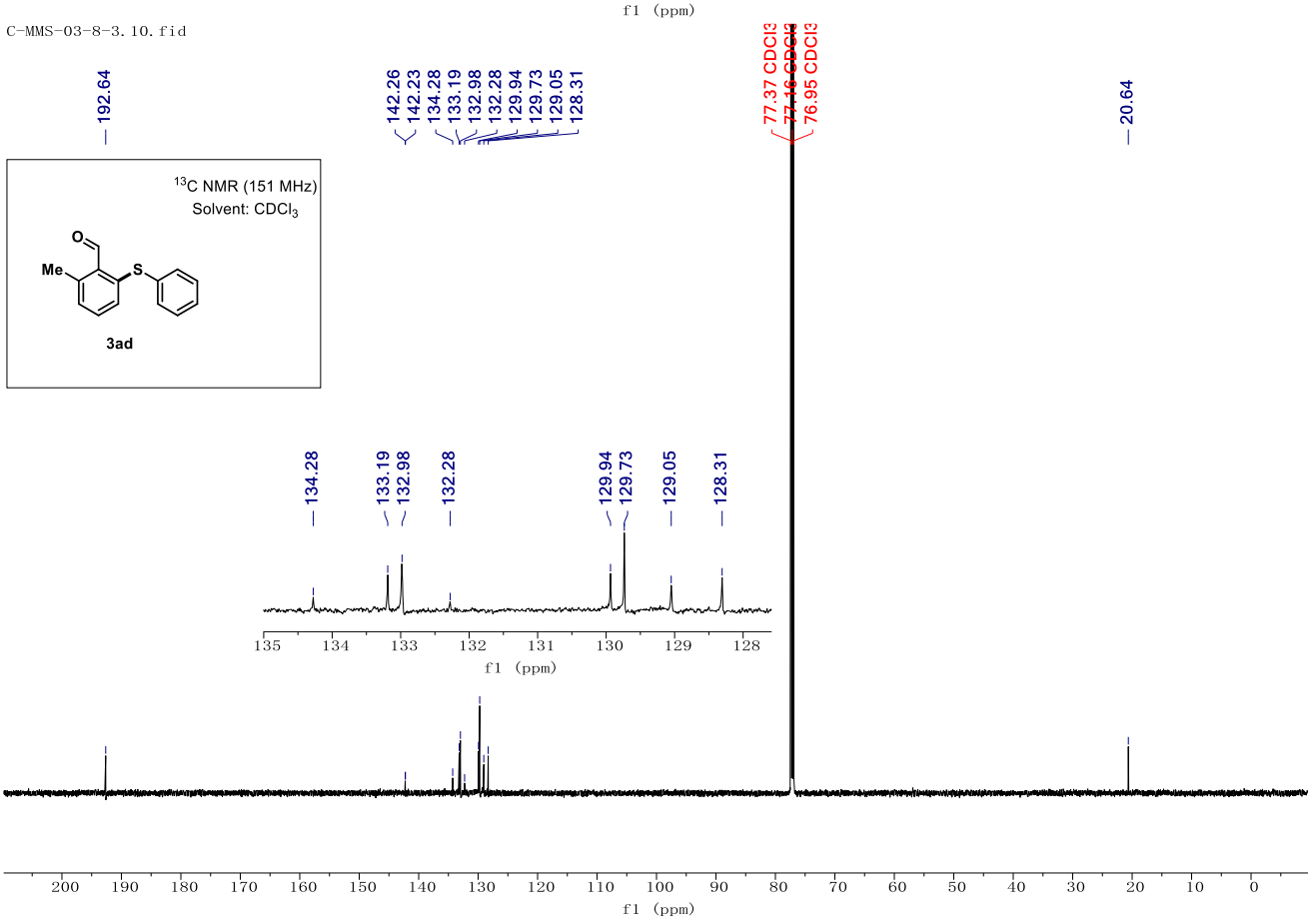
f1 (ppm)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S
O
3ad
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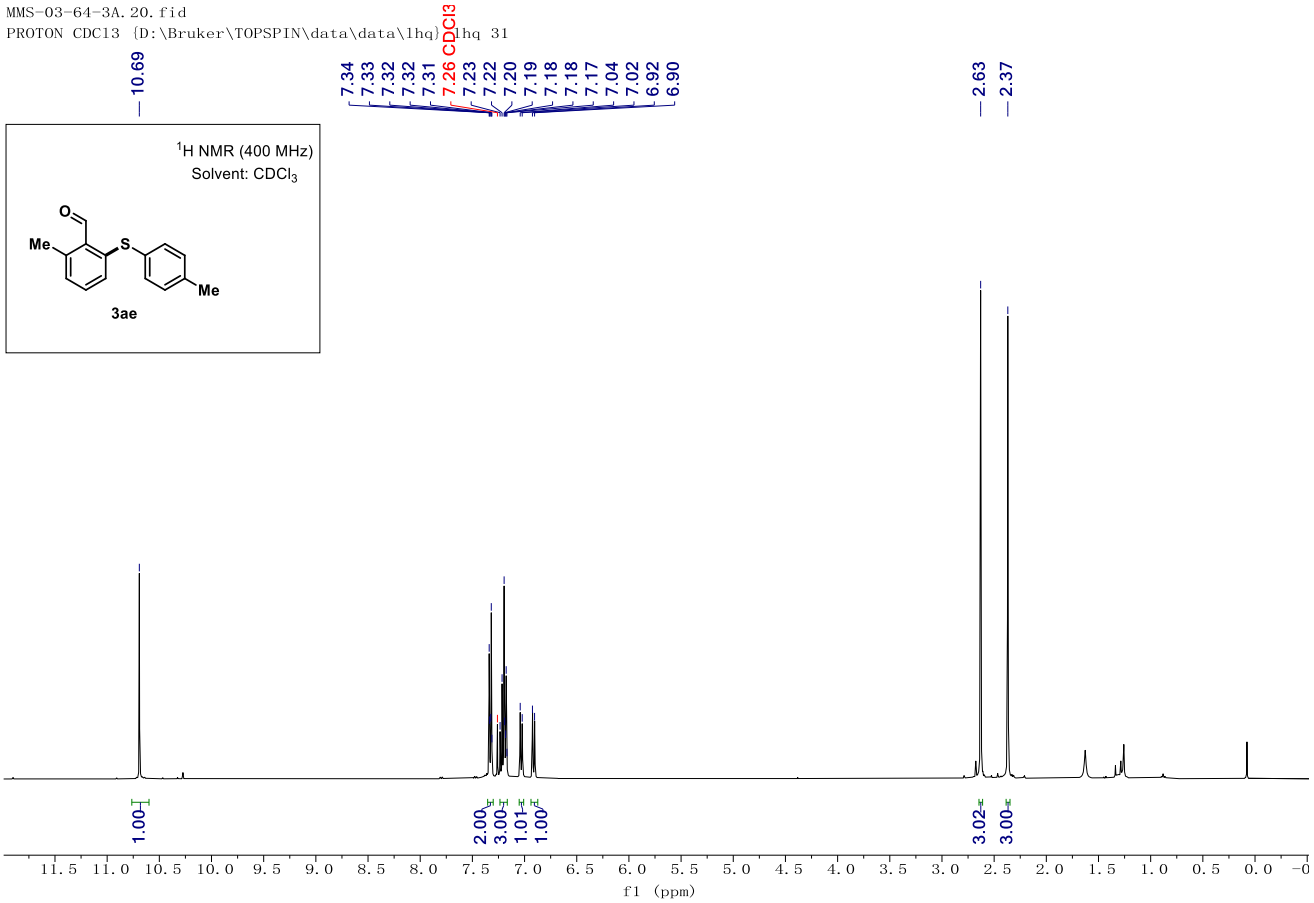
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7.02
6.92
6.90
2.63
2.37
1H NMR (400 MHz)
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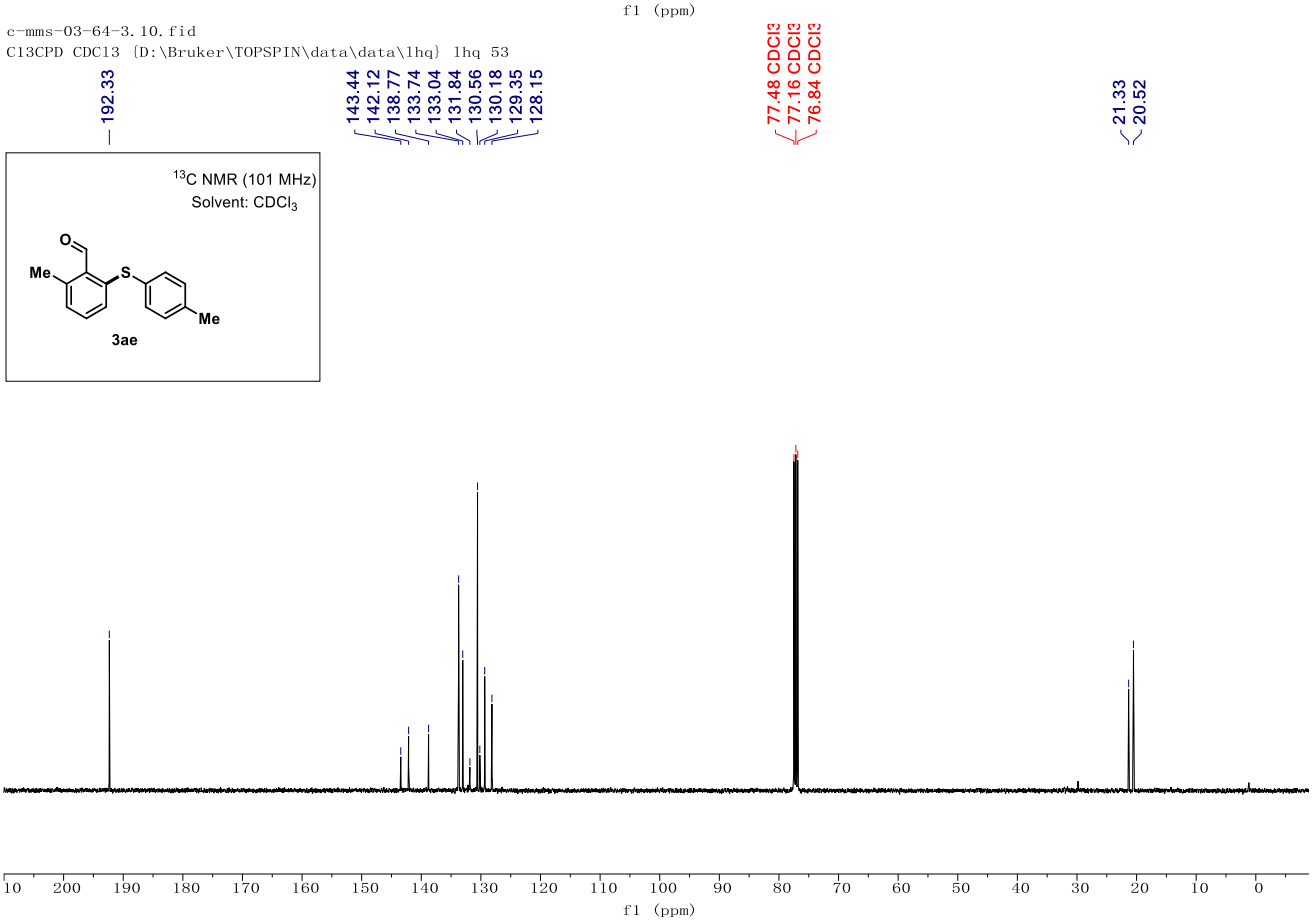
f1 (ppm)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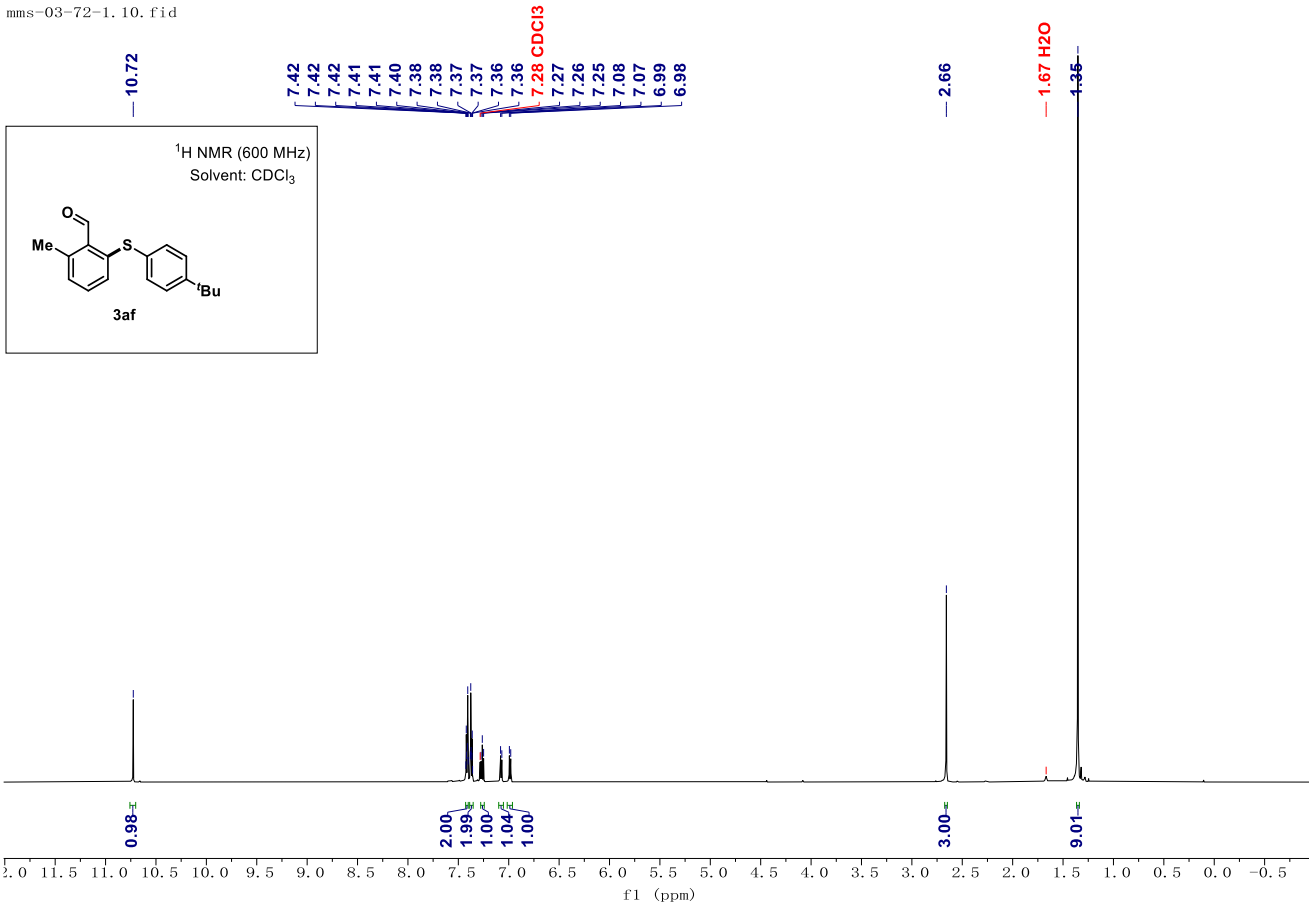
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S
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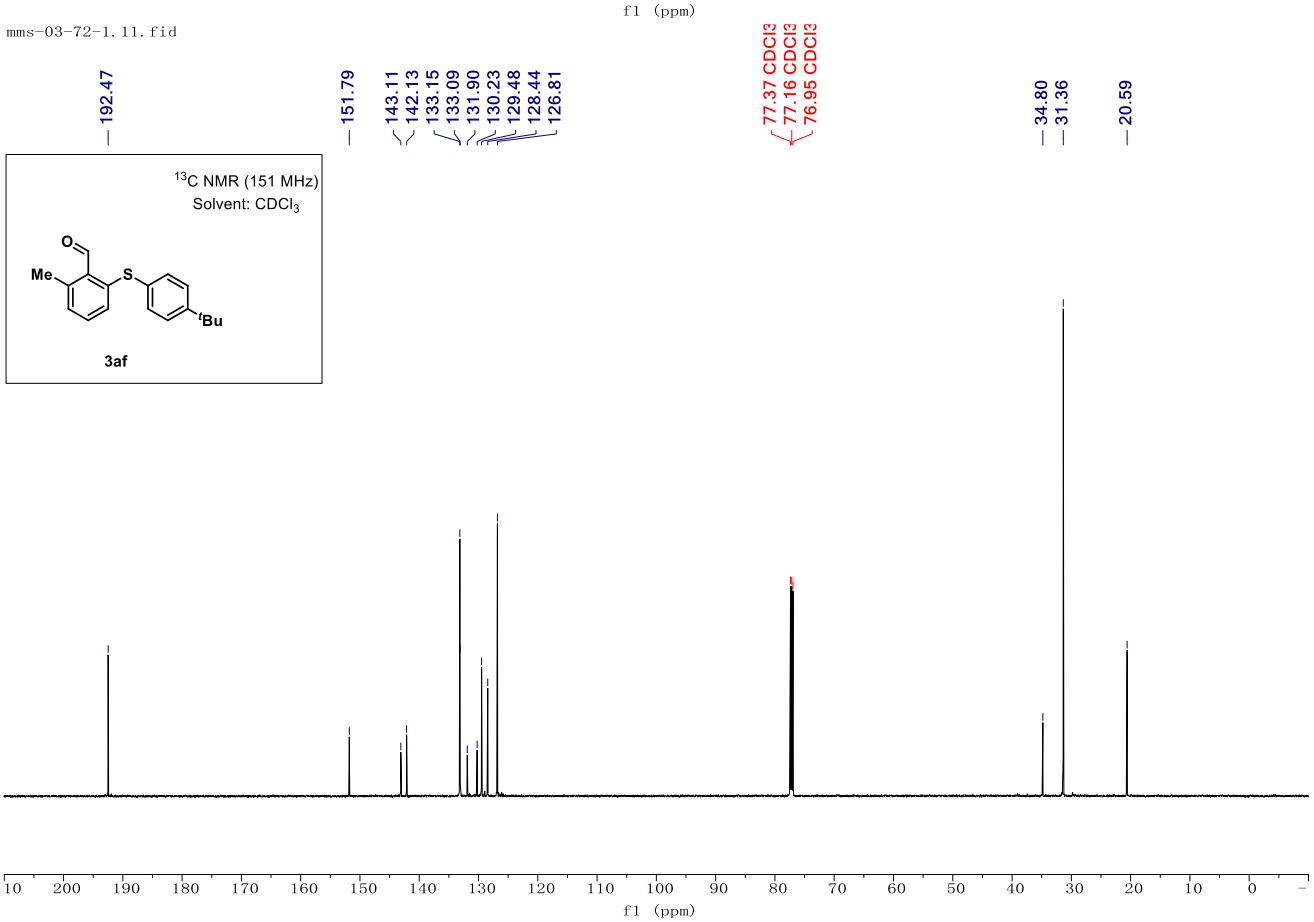
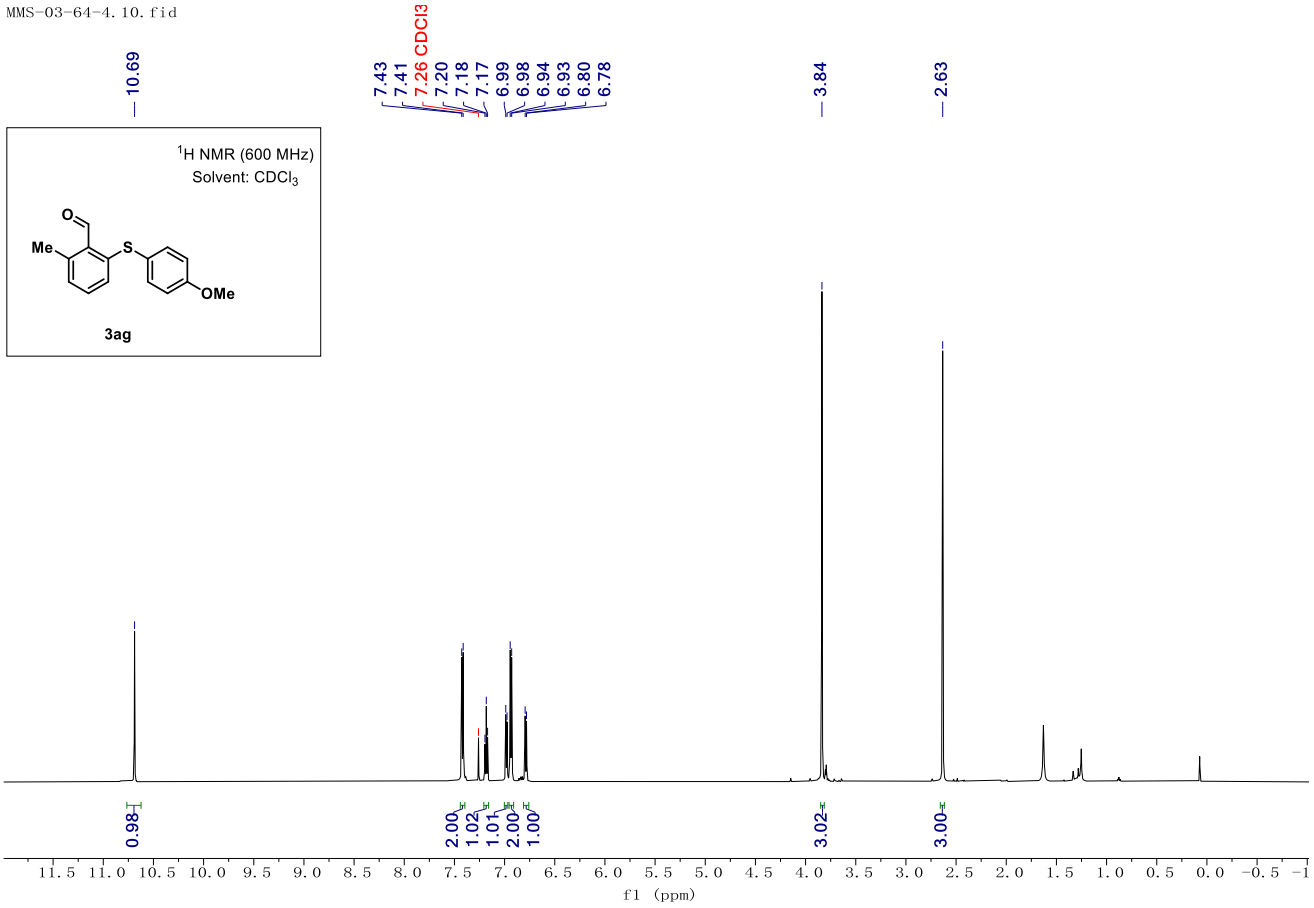
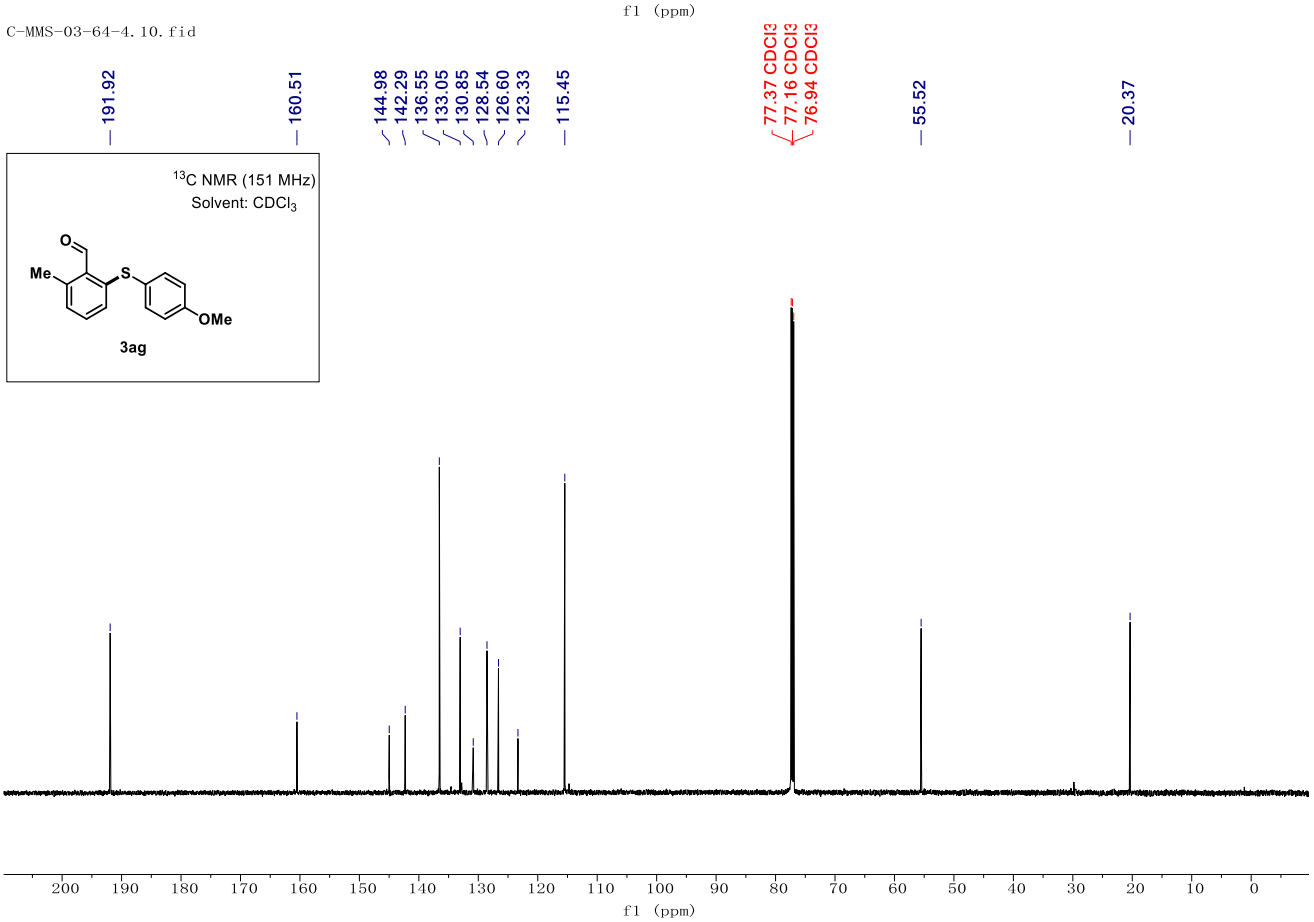
9.01
f1 (ppm)

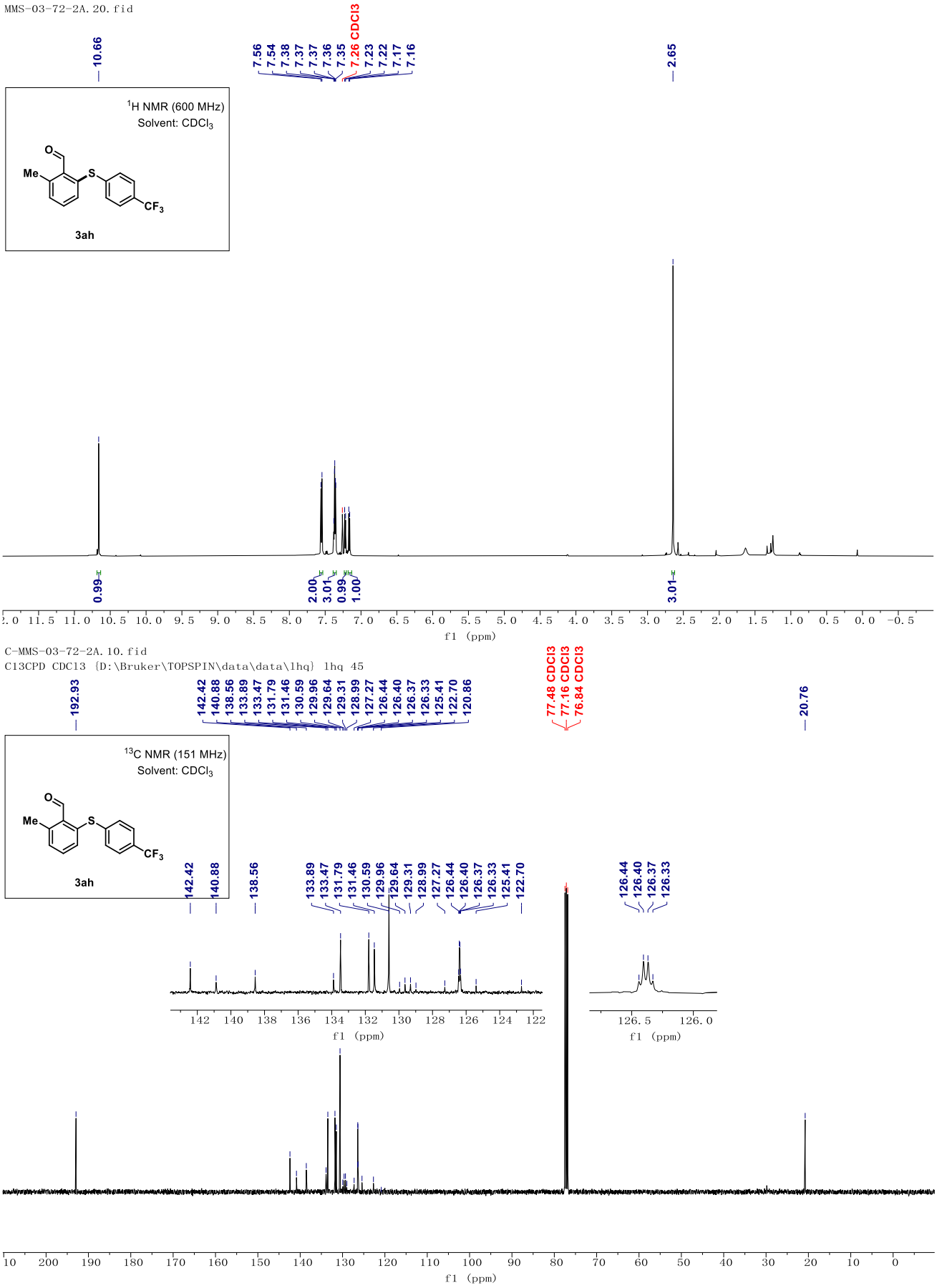

mms-03-72-1.11.fid
192.47
151.79
143.11
142.13
133.15
133.09
131.90
130.23
129.48
128.44
126.81
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
34.80
31.36
20.59
13C NMR (151 MHz)
Solvent: CDCl3
Me
S
tBu
3af
f1 (ppm)

MMS-03-64-4.10.fid



C-MMS-03-64-4.10.fid

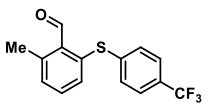



MMS-03-72-2A.20.fid
10.66
7.56
7.54
7.38
7.37
7.37
7.36
7.35
7.26 CDCl3
7.23
7.22
7.17
7.16
2.65
1H NMR (600 MHz)
Solvent: CDCl3
Me
S
CF3
3ah
0.99
2.00
3.01
0.99
1.00
3.01
f1 (ppm)
C-MMS-03-72-2A.10.fid
C13CPD CDCl3 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 45
192.93
142.42
140.88
138.56
133.89
133.47
131.79
131.46
130.59
129.96
129.64
129.31
128.99
127.27
126.44
126.40
126.37
126.33
125.41
122.70
120.86
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
20.76
13C NMR (151 MHz)
Solvent: CDCl3
Me
S
CF3
3ah
f1 (ppm)

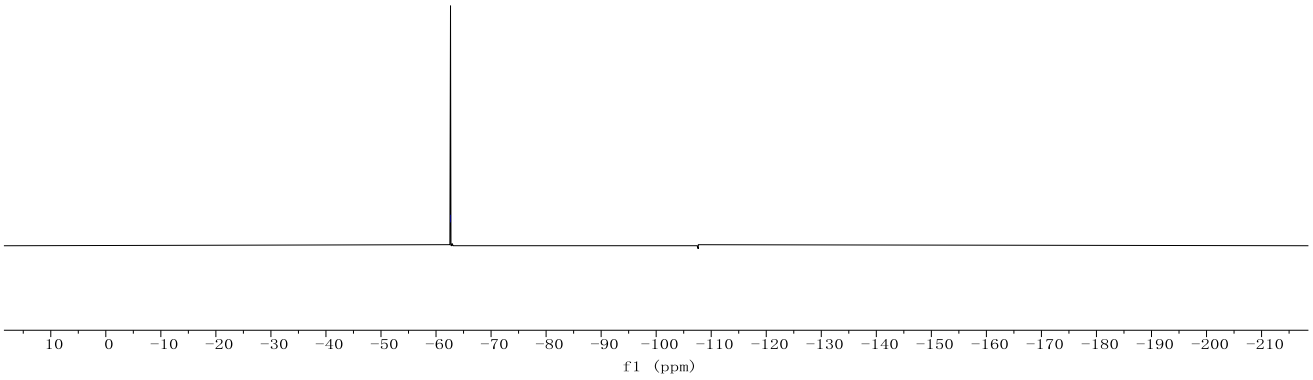
MMS-03-72-2A.21.fid

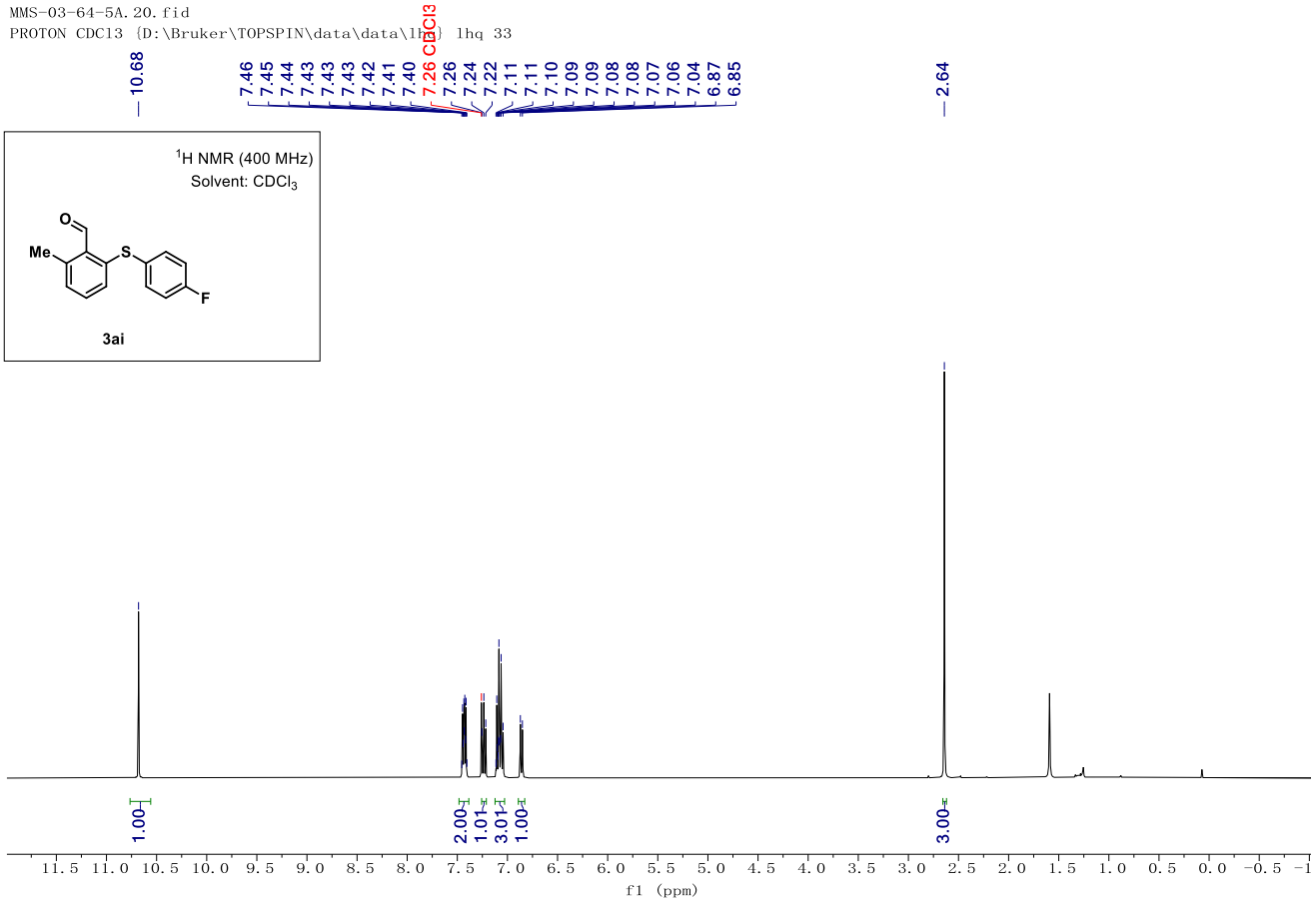
-62.64

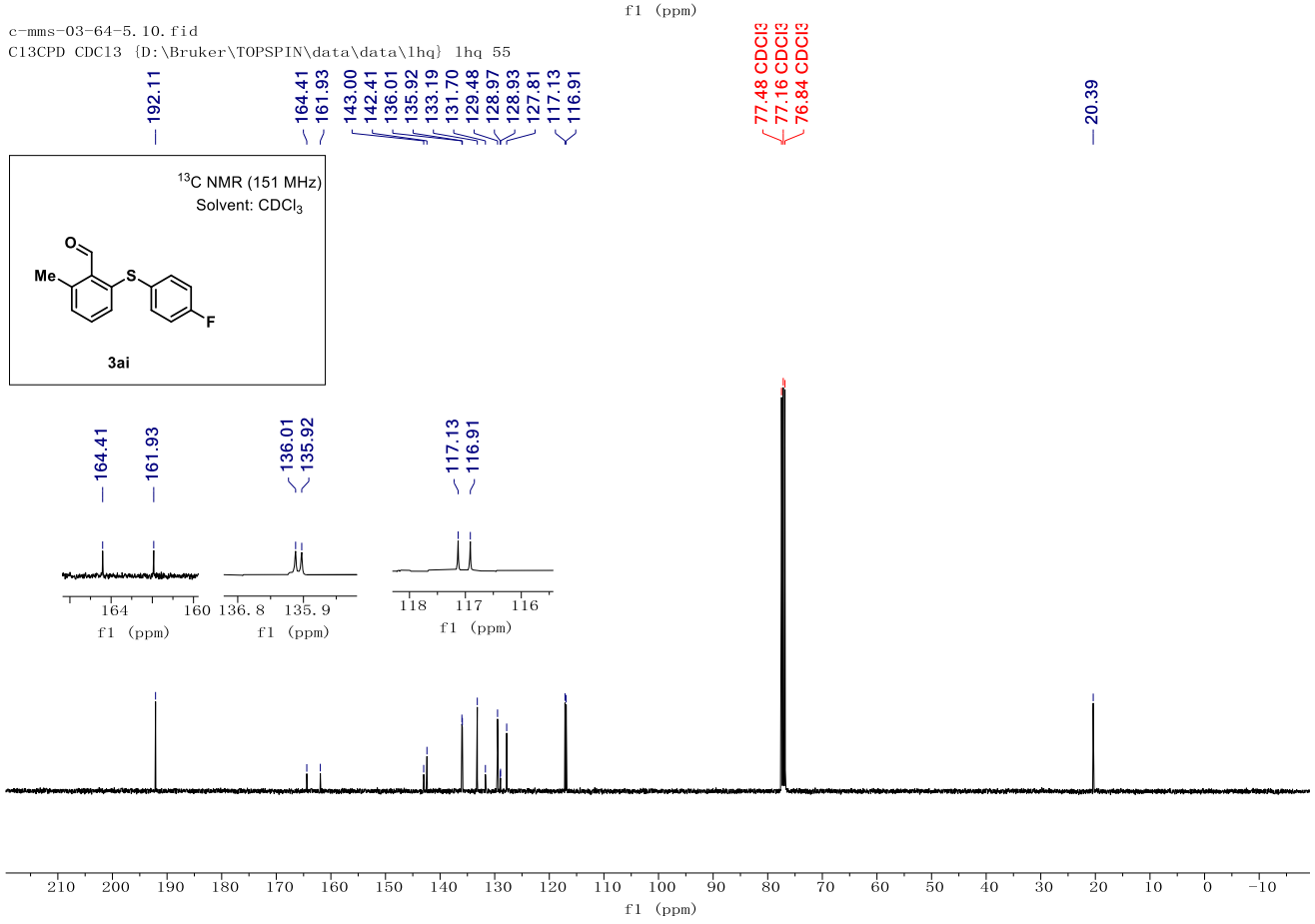
^{19}F NMR (565 MHz)
Solvent: $CDCl_3$



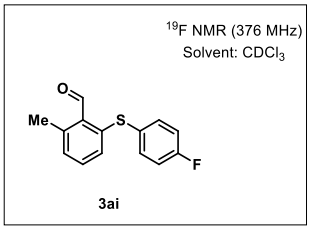
3ah

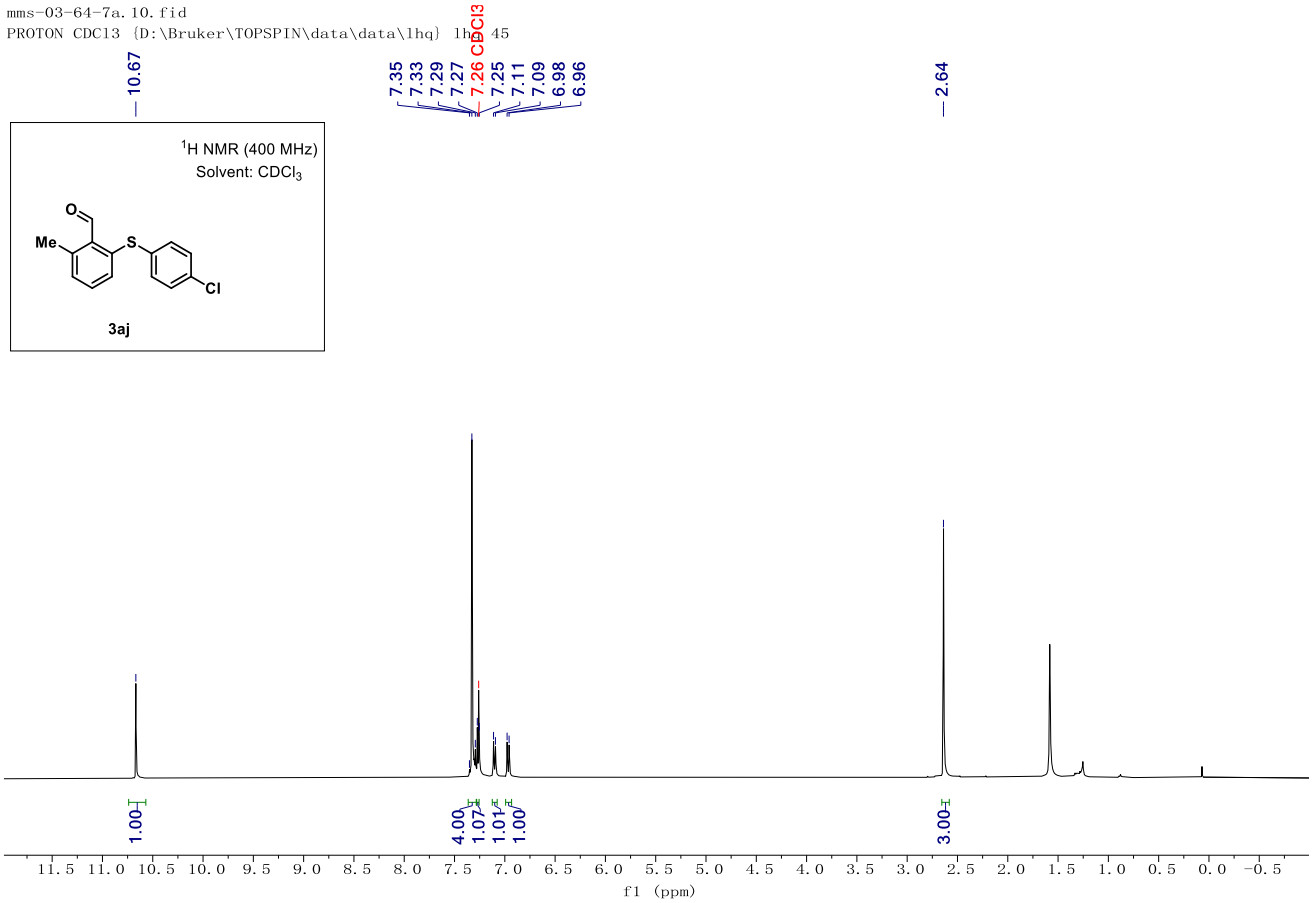


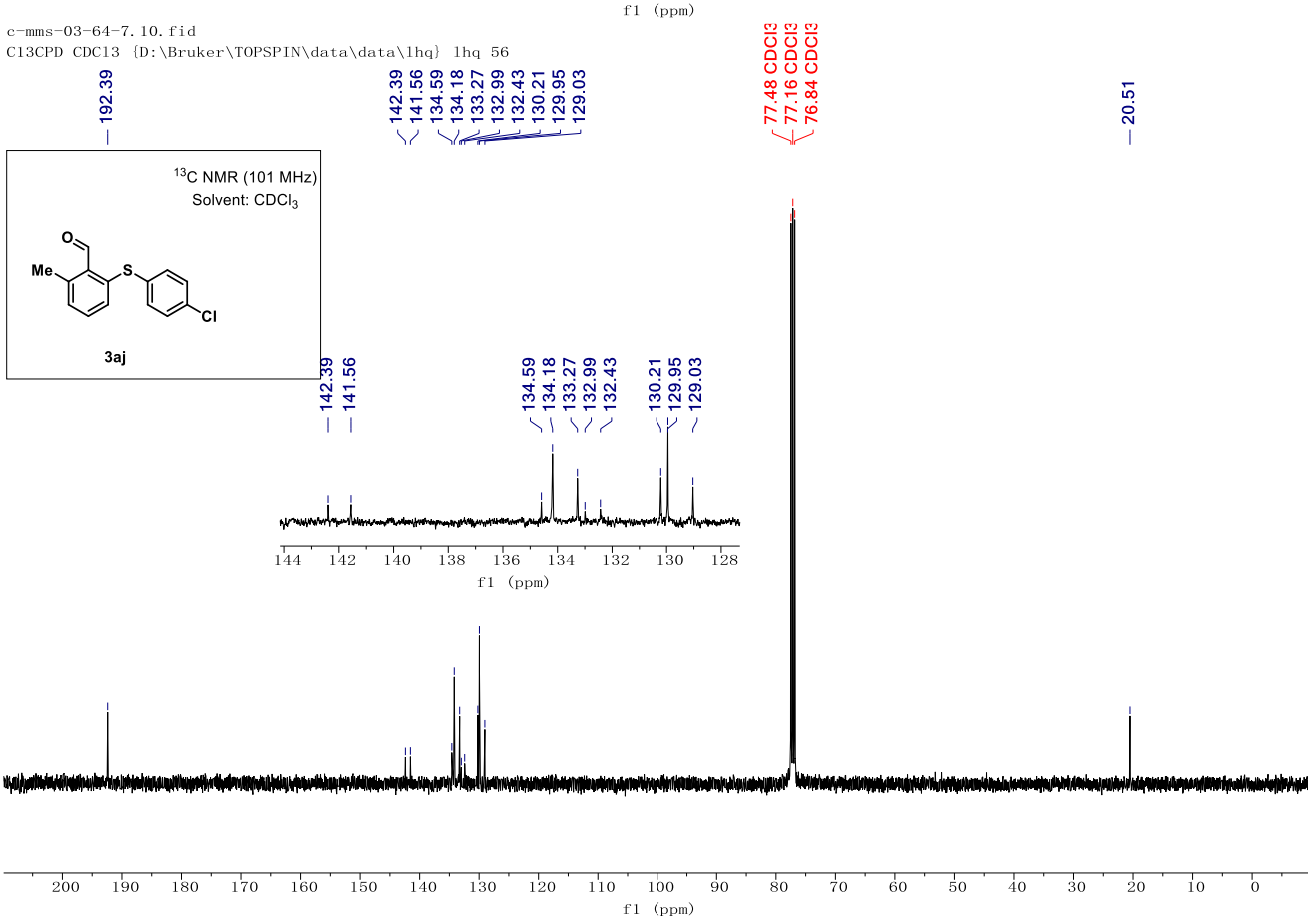

MMS-03-64-5A.20.fid
PROTON CDCl3 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 33
10.68
7.46
7.45
7.44
7.43
7.43
7.43
7.42
7.41
7.40
7.26 CDCl3
7.26
7.24
7.22
7.11
7.11
7.10
7.09
7.09
7.08
7.08
7.07
7.06
7.04
6.87
6.85
2.64
1H NMR (400 MHz)
Solvent: CDCl3
Me
S
F
3ai
1.00
2.00
1.01
3.01
1.00
3.00
f1 (ppm)

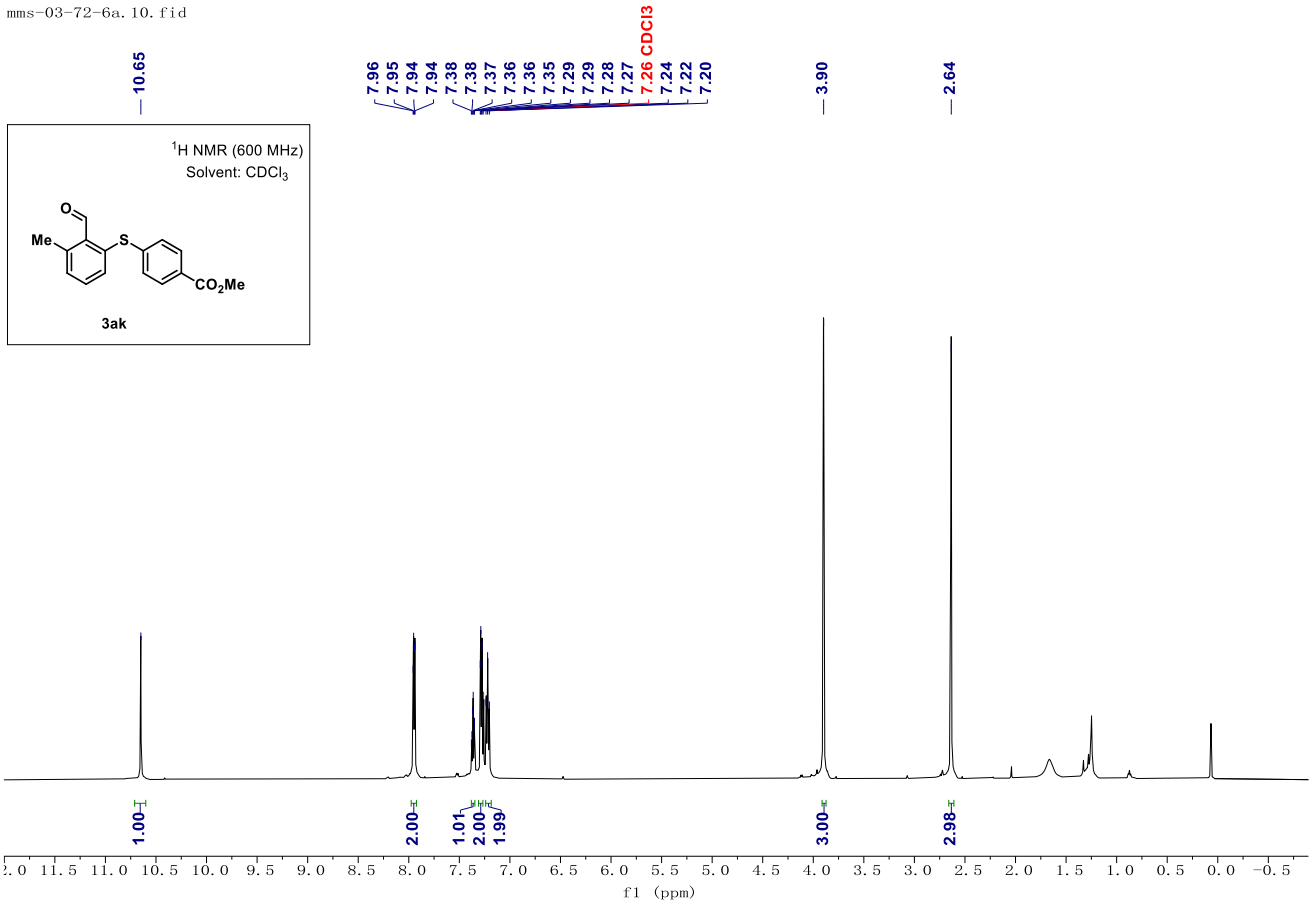

c-mms-03-64-5.10.fid
C13CPD CDCl3 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 55
192.11
164.41
161.93
143.00
142.41
136.01
135.92
133.19
131.70
129.48
128.97
128.93
127.81
117.13
116.91
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
20.39
13C NMR (151 MHz)
Solvent: CDCl3
Me
S
F
3ai
164.41
161.93
136.01
135.92
117.13
116.91
f1 (ppm)

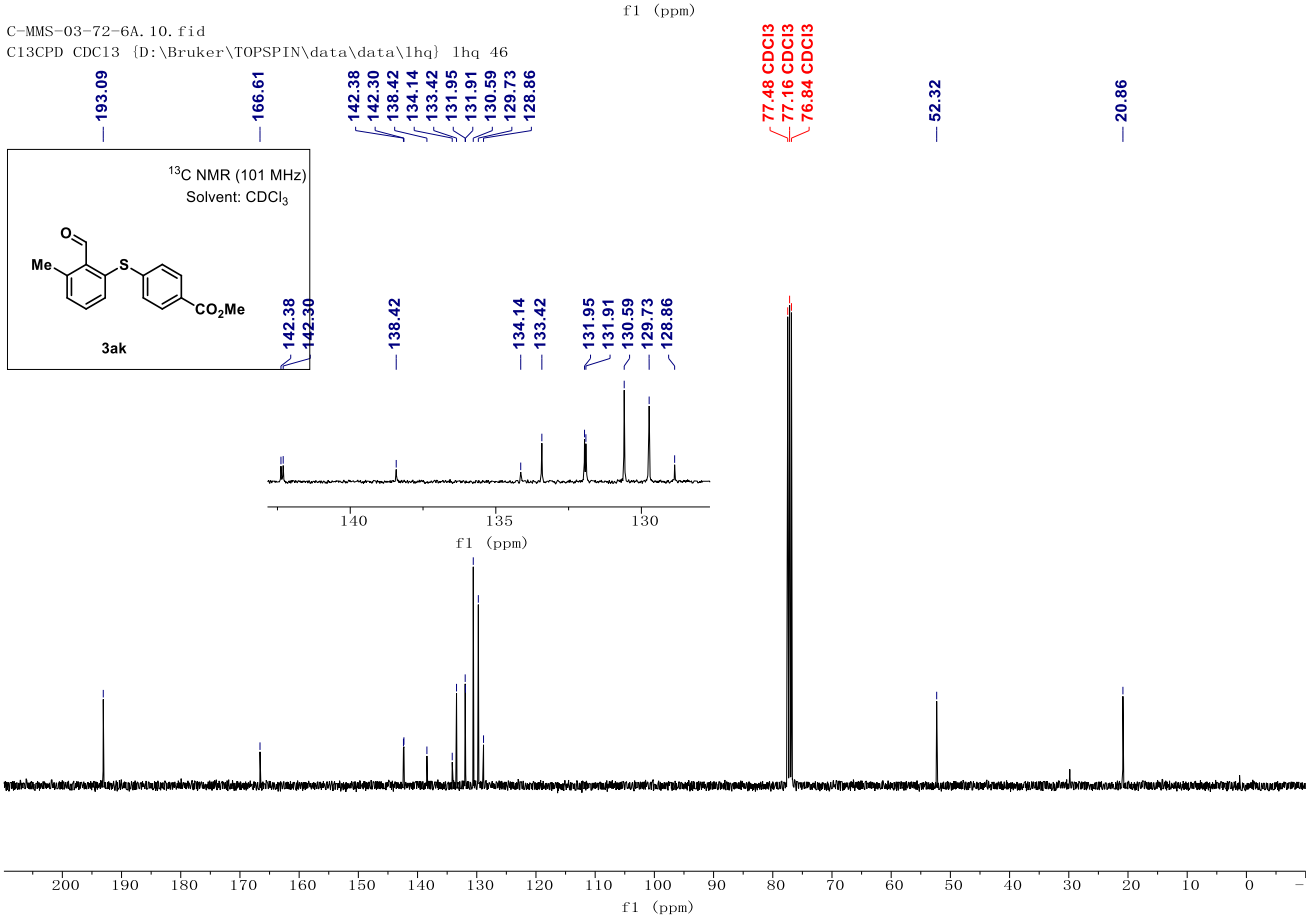
MMS-03-F-4PH-F.10.fid
F19CPD CDC13 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 19

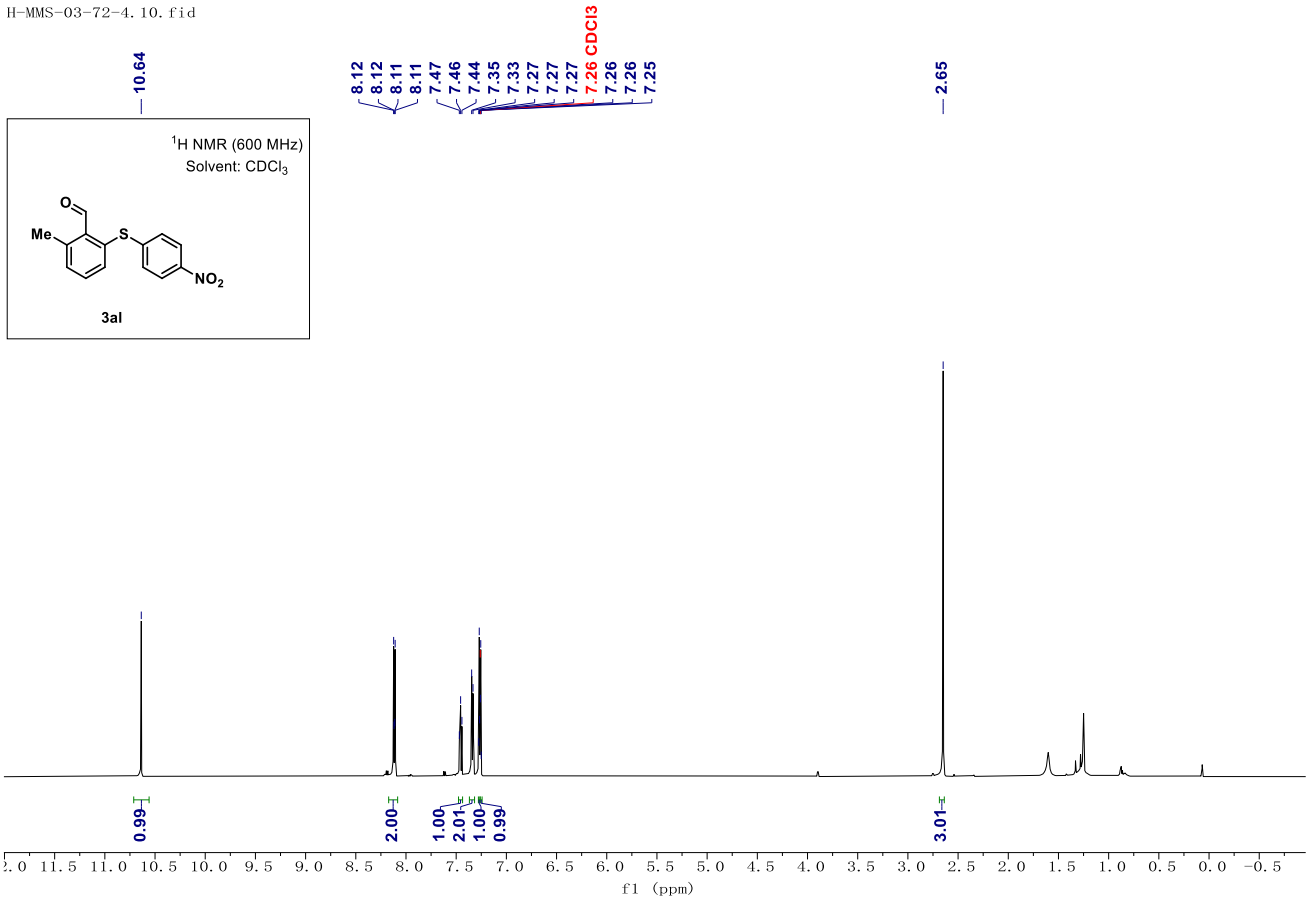


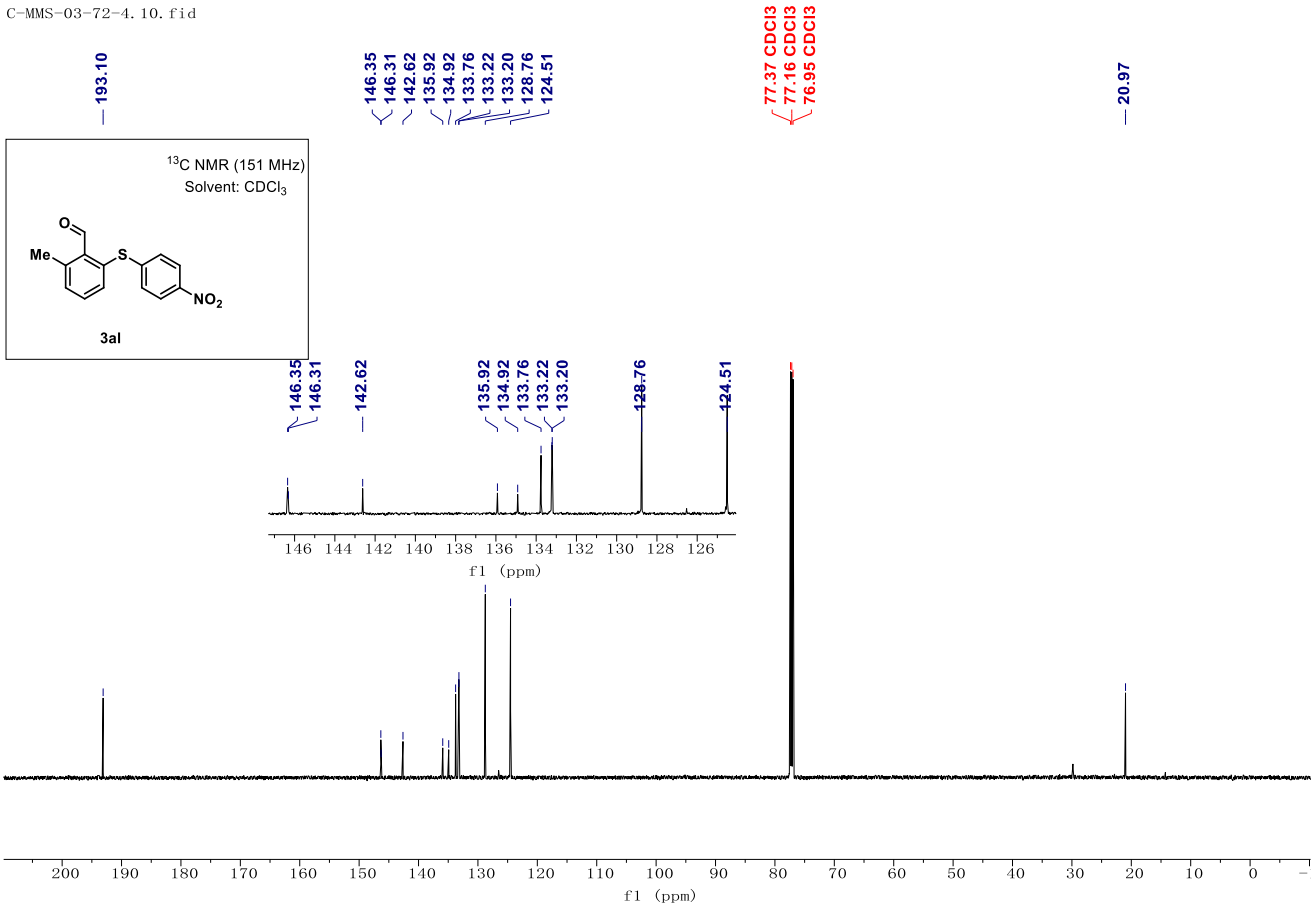

mms-03-64-7a.10.fid
PROTON CDCl3 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 45
10.67
7.35
7.33
7.29
7.27
7.26 CDCl3
7.25
7.11
7.09
6.98
6.96
2.64
1H NMR (400 MHz)
Solvent: CDCl3
Me
S
Cl
3aj
1.00
4.00
1.07
1.01
1.00
3.00
f1 (ppm)

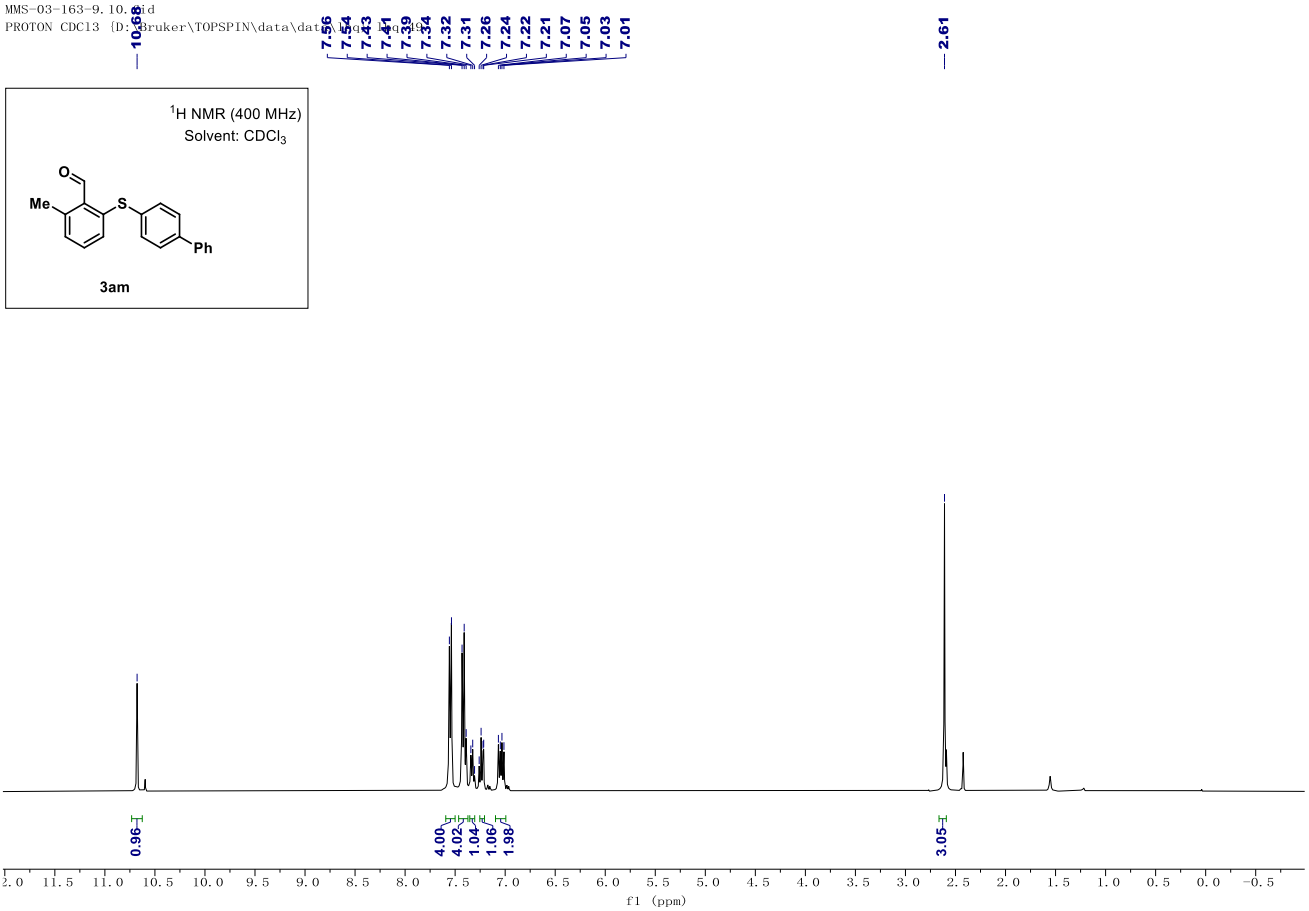

c-mms-03-64-7.10.fid
C13CPD CDCl3 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 56
192.39
142.39
141.56
134.59
134.18
133.27
132.99
132.43
130.21
129.95
129.03
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
20.51
13C NMR (101 MHz)
Solvent: CDCl3
Me
S
Cl
3aj
f1 (ppm)

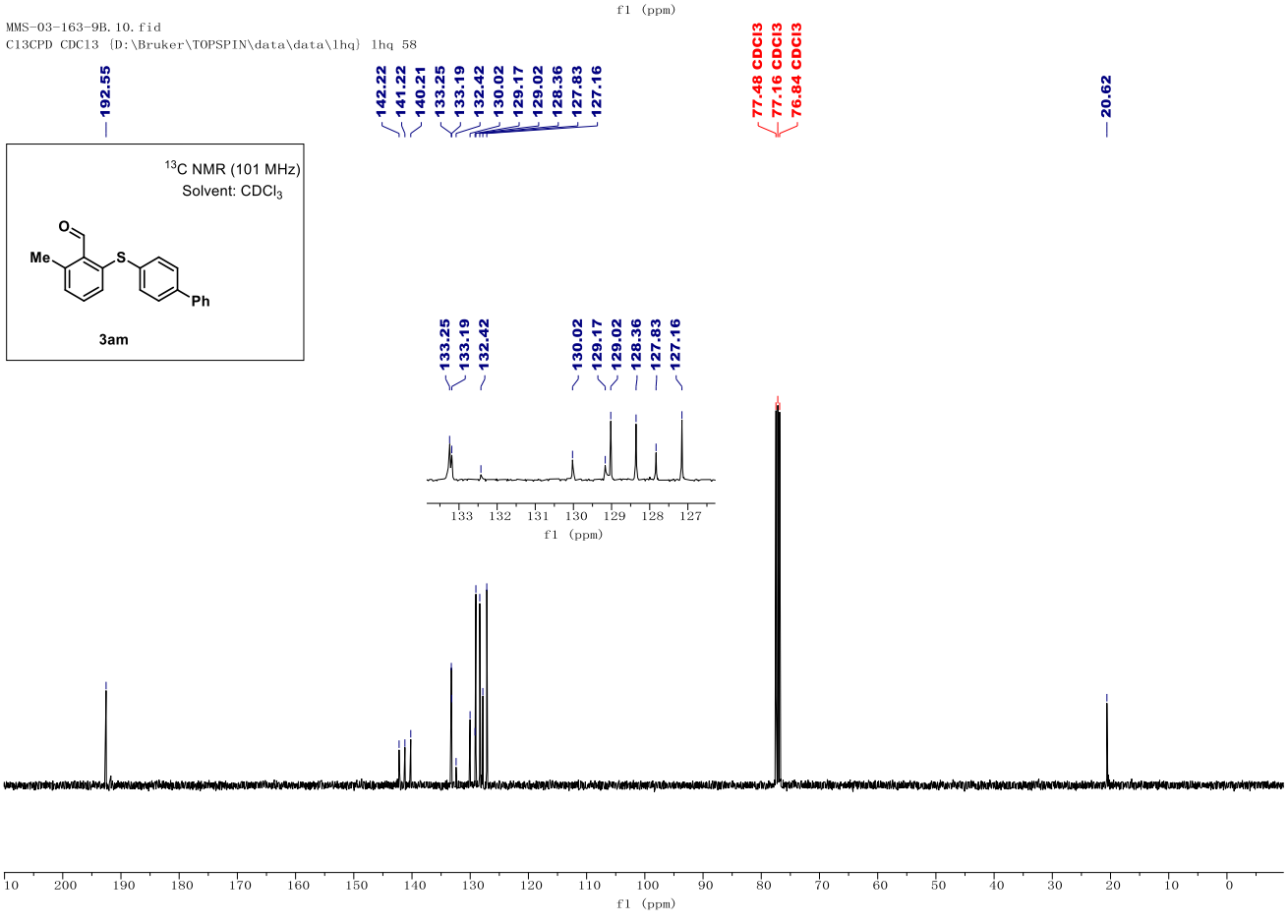

mms-03-72-6a.10.fid
10.65
7.96
7.95
7.94
7.94
7.38
7.38
7.37
7.36
7.36
7.35
7.29
7.29
7.28
7.27
7.26 CDCl3
7.24
7.22
7.20
3.90
2.64
1H NMR (600 MHz)
Solvent: CDCl3
Me
S
CO2Me
3ak
1.00
2.00
1.01
2.00
1.99
3.00
2.98
f1 (ppm)

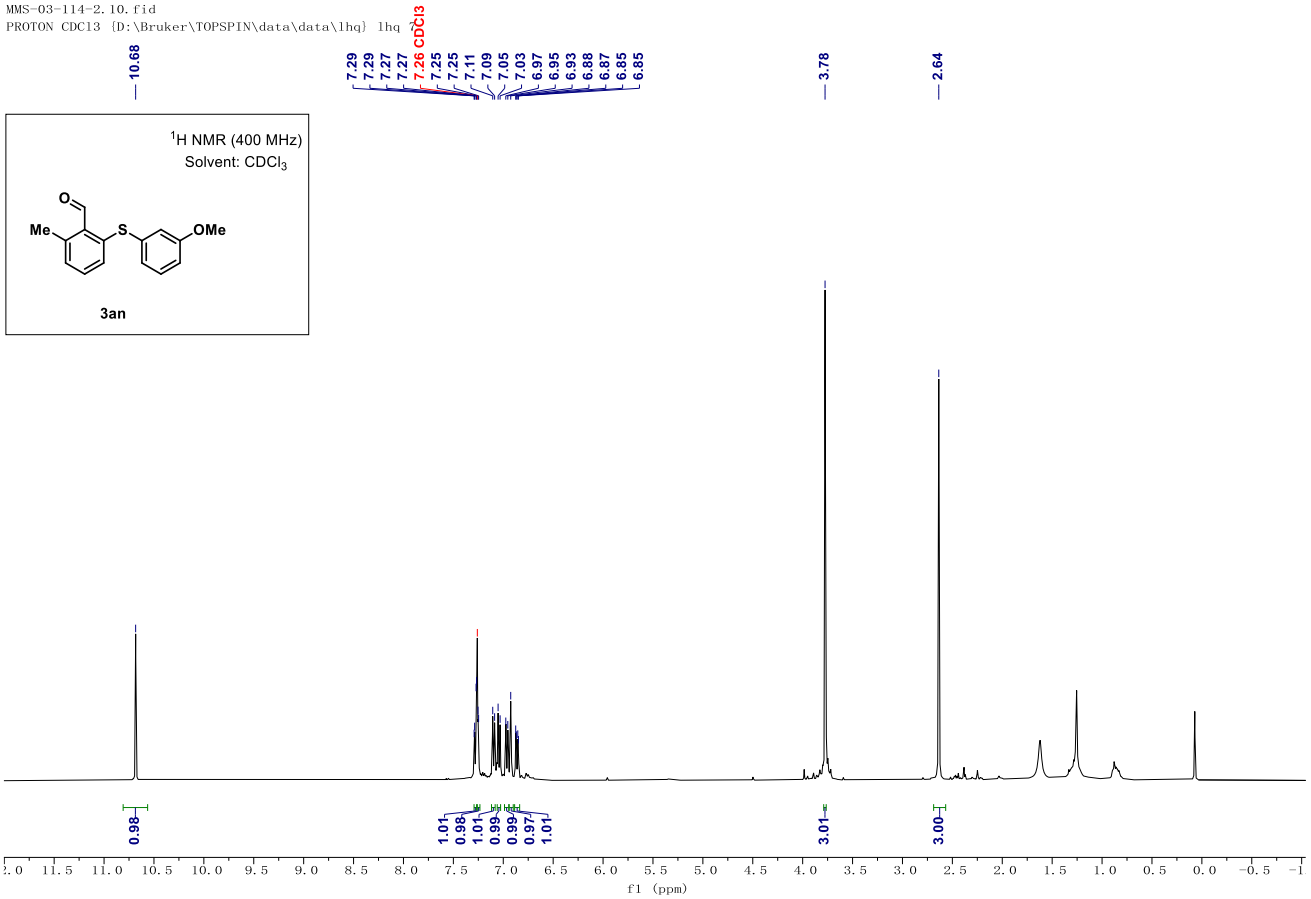

C-MMS-03-72-6A.10.fid
C13CPD CDCl3 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 46
193.09
166.61
142.38
142.30
138.42
134.14
133.42
131.95
131.91
130.59
129.73
128.86
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
52.32
20.86
13C NMR (101 MHz)
Solvent: CDCl3
Me
S
CO2Me
3ak
f1 (ppm)

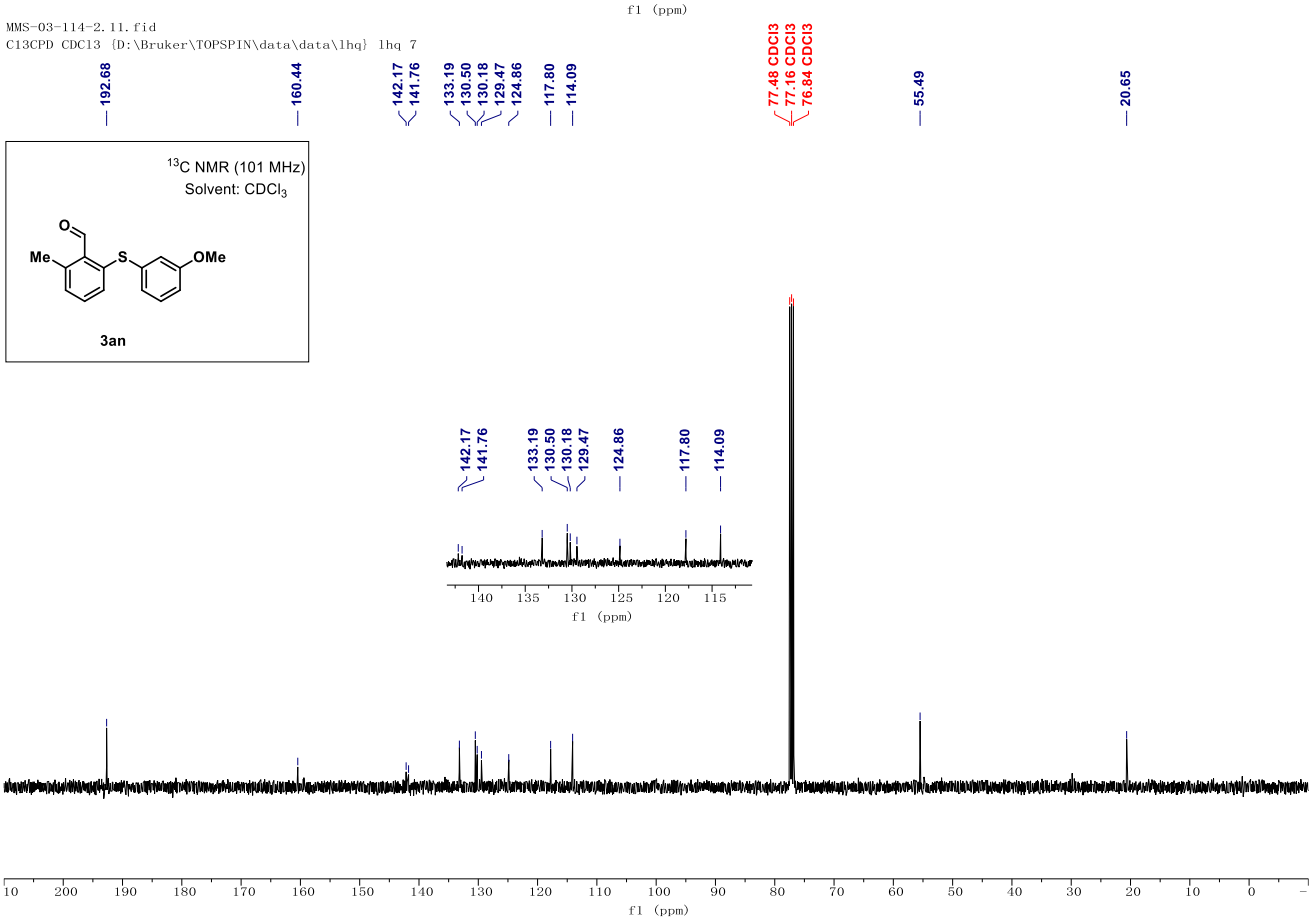

H-MMS-03-72-4.10.fid
10.64
8.12
8.12
8.11
8.11
7.47
7.46
7.44
7.35
7.33
7.27
7.27
7.27
7.26 CDCl3
7.26
7.26
7.25
2.65
1H NMR (600 MHz)
Solvent: CDCl3
Me
S
NO2
3al
0.99
2.00
1.00
2.01
1.00
0.99
3.01
f1 (ppm)

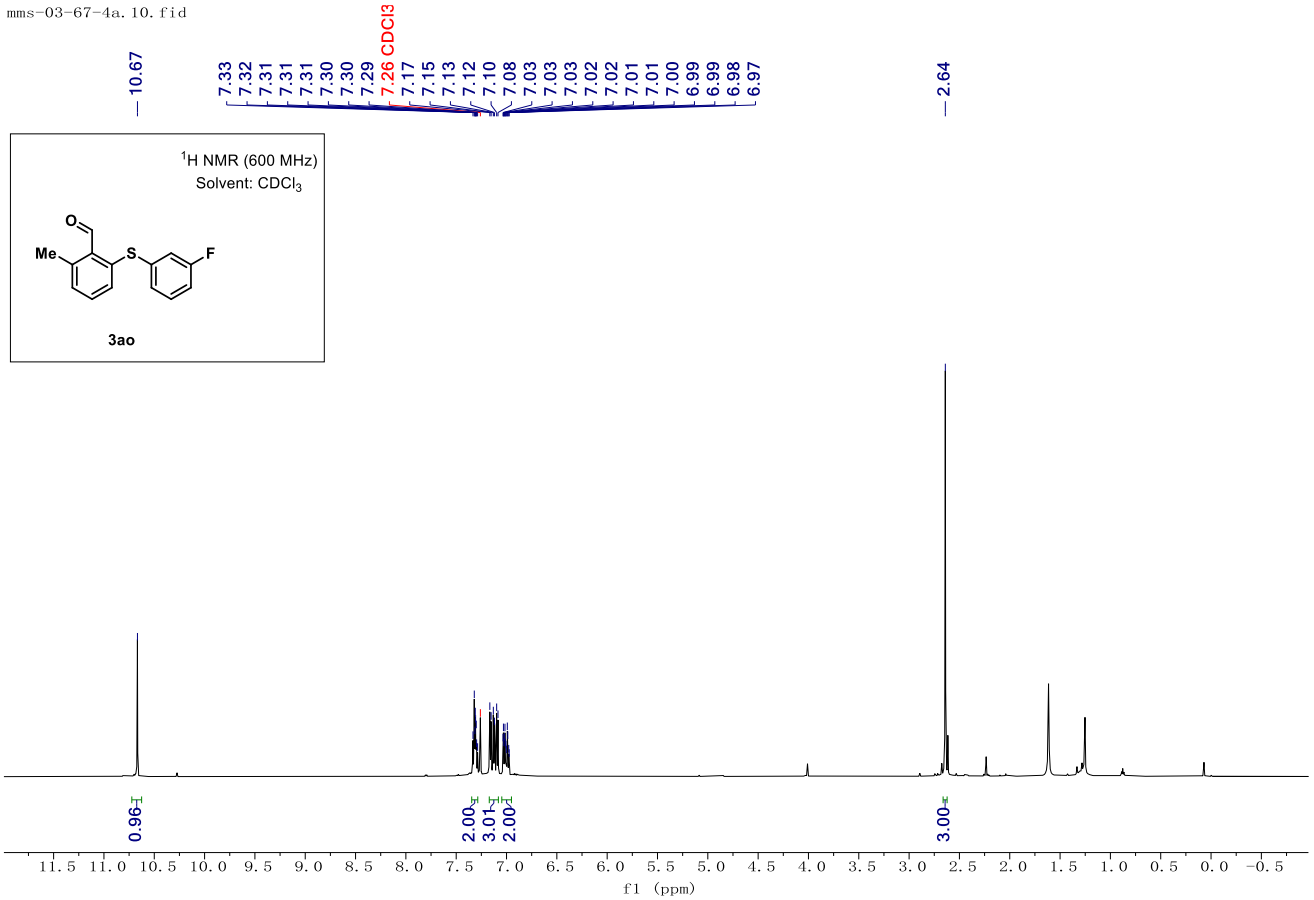

C-MMS-03-72-4.10.fid
193.10
146.35
146.31
142.62
135.92
134.92
133.76
133.22
133.20
128.76
124.51
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
20.97
13C NMR (151 MHz)
Solvent: CDCl3
Me
S
NO2
3al
f1 (ppm)

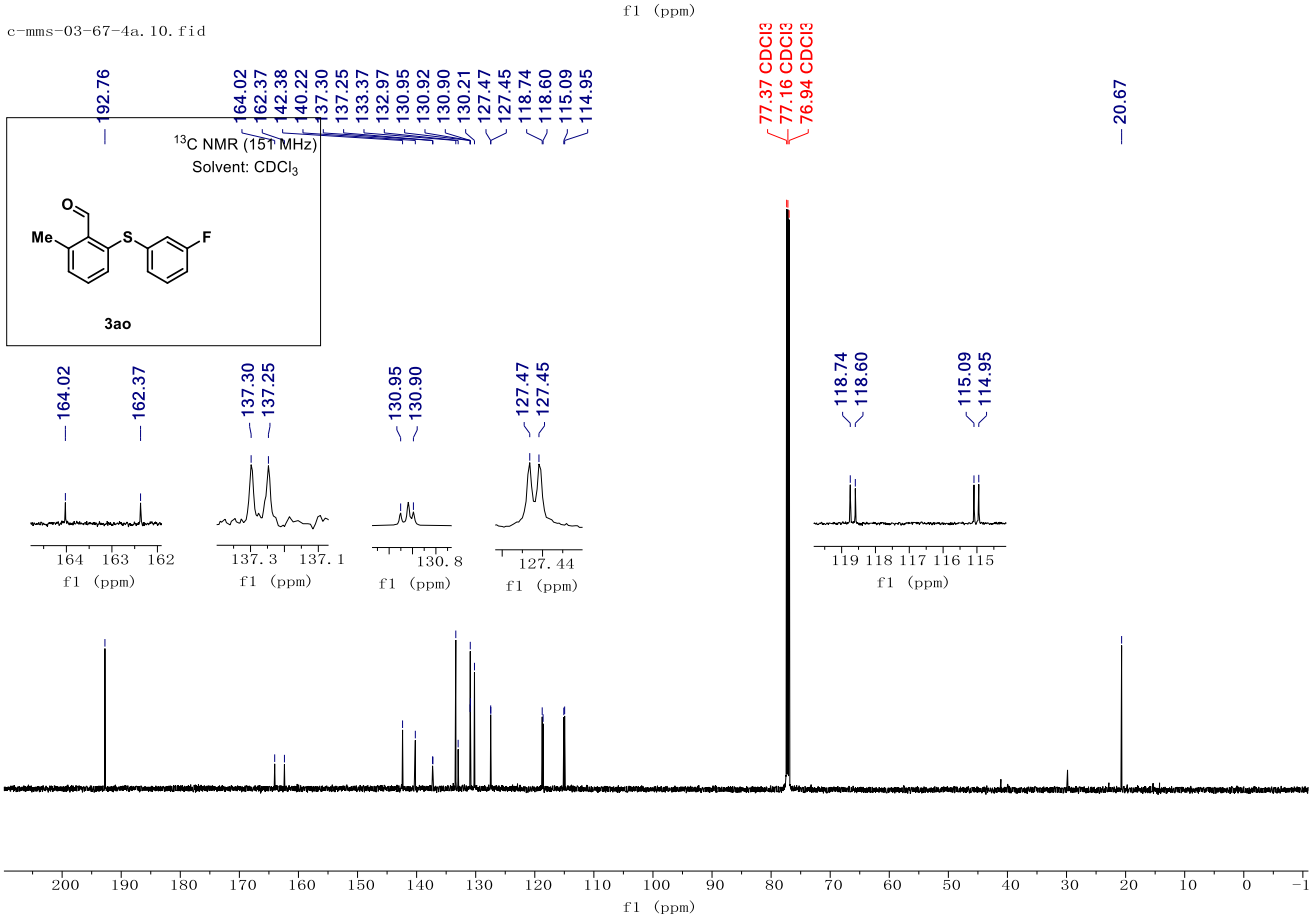

MMS-03-163-9.10.fid
PROTON CDC13 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 58
10.68
7.56
7.54
7.43
7.41
7.39
7.34
7.32
7.31
7.26
7.24
7.22
7.21
7.07
7.05
7.03
7.01
2.61
1H NMR (400 MHz)
Solvent: CDCl3
Me
S
Ph
3am
0.96
4.00
4.02
1.04
1.06
1.98
3.05
f1 (ppm)


MMS-03-163-9B.10.fid
C13CPD CDC13 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 58
192.55
142.22
141.22
140.21
133.25
133.19
132.42
130.02
129.17
129.02
128.36
127.83
127.16
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
20.62
13C NMR (101 MHz)
Solvent: CDCl3
Me
S
Ph
3am
f1 (ppm)

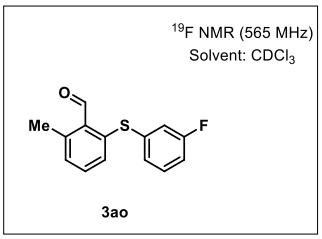

MMS-03-114-2.10.fid
PROTON CDC13 {D:\Bruker\TOPSPIN\data\data\lhq} lhq
10.68
7.29
7.29
7.27
7.27
7.26 CDCl3
7.25
7.25
7.11
7.09
7.05
7.03
6.97
6.95
6.93
6.88
6.87
6.85
6.85
3.78
2.64
1H NMR (400 MHz)
Solvent: CDCl3
Me
S
OMe
O
3an
0.98
1.01
0.98
1.01
0.99
0.99
0.97
1.01
3.01
3.00
f1 (ppm)

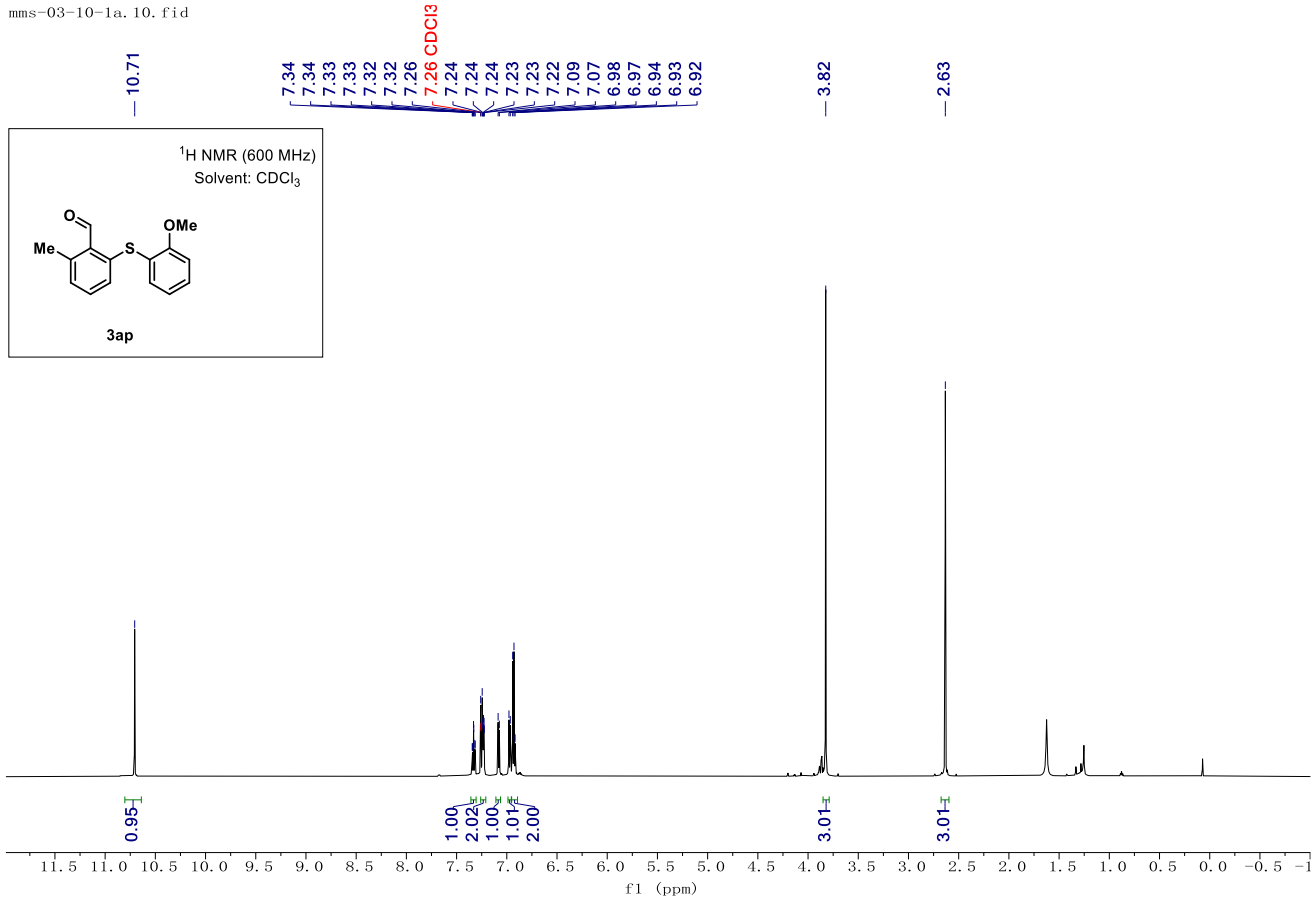

MMS-03-114-2.11.fid
C13CPD CDC13 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 7
192.68
160.44
142.17
141.76
133.19
130.50
130.18
129.47
124.86
117.80
114.09
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
55.49
20.65
13C NMR (101 MHz)
Solvent: CDCl3
Me
S
OMe
O
3an
f1 (ppm)

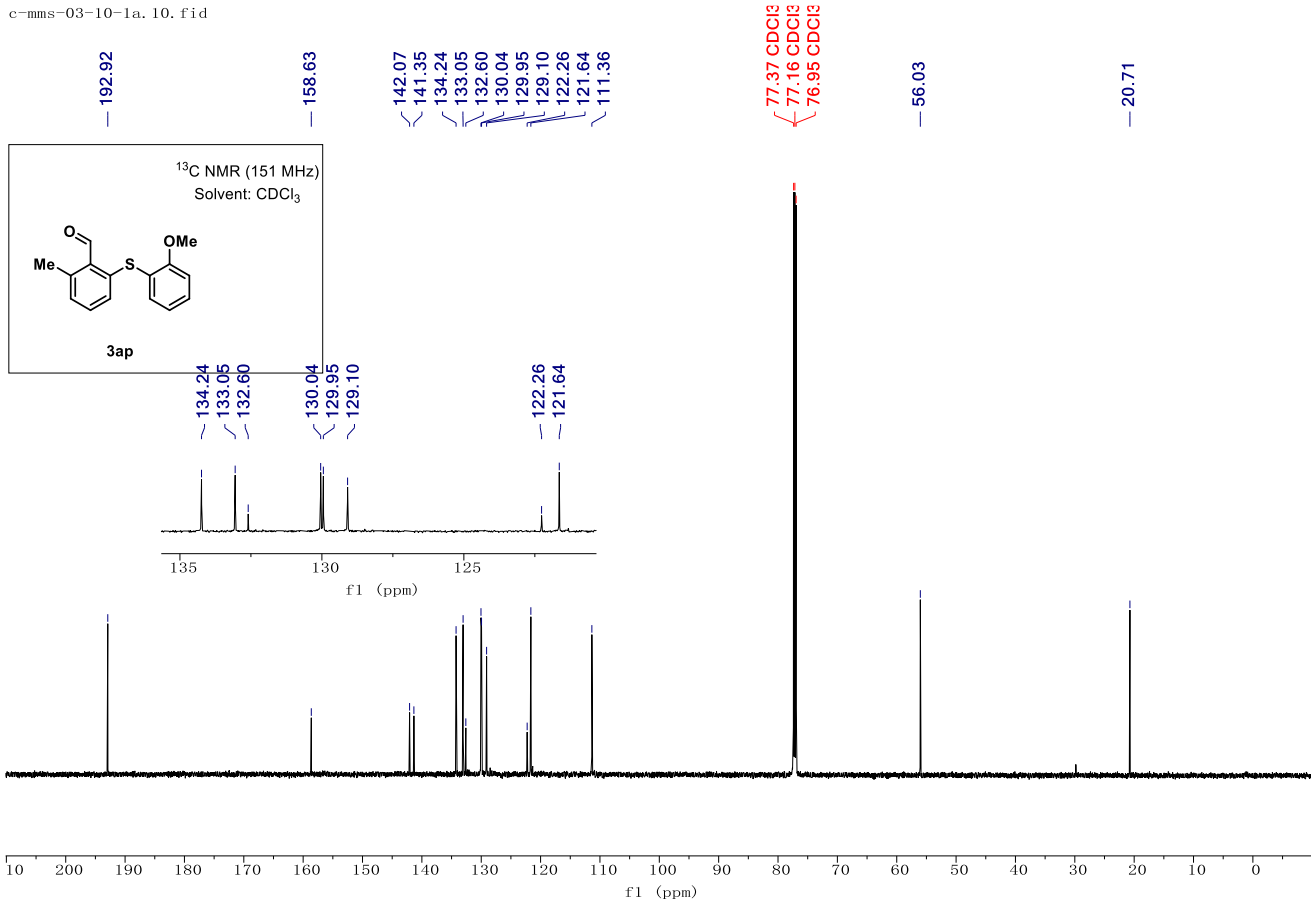

mms-03-67-4a.10.fid
10.67
7.33
7.32
7.31
7.31
7.31
7.30
7.30
7.29
7.26 CDCl3
7.17
7.15
7.13
7.12
7.10
7.08
7.03
7.03
7.03
7.02
7.02
7.01
7.01
7.00
6.99
6.99
6.98
6.97
2.64
1H NMR (600 MHz)
Solvent: CDCl3
O
Me
S
F
3ao
0.96
2.00
3.01
2.00
3.00
f1 (ppm)

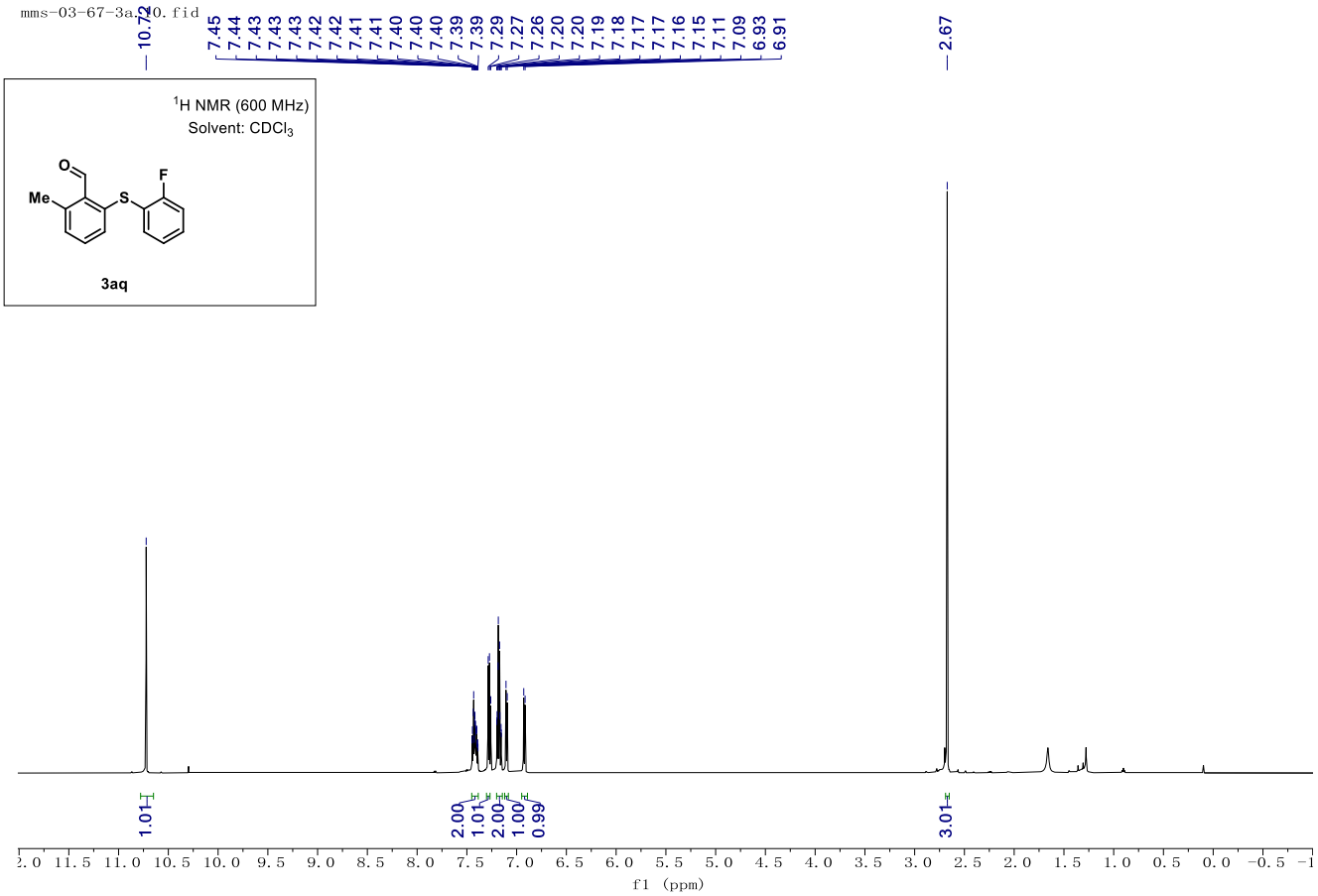

c-mms-03-67-4a.10.fid
192.76
164.02
162.37
142.38
140.22
137.30
137.25
133.37
132.97
130.95
130.92
130.90
130.21
127.47
127.45
118.74
118.60
115.09
114.95
77.37 CDCl3
77.16 CDCl3
76.94 CDCl3
20.67
13C NMR (151 MHz)
Solvent: CDCl3
O
Me
S
F
3ao
164.02
162.37
137.30
137.25
130.95
130.90
127.47
127.45
118.74
118.60
115.09
114.95
f1 (ppm)

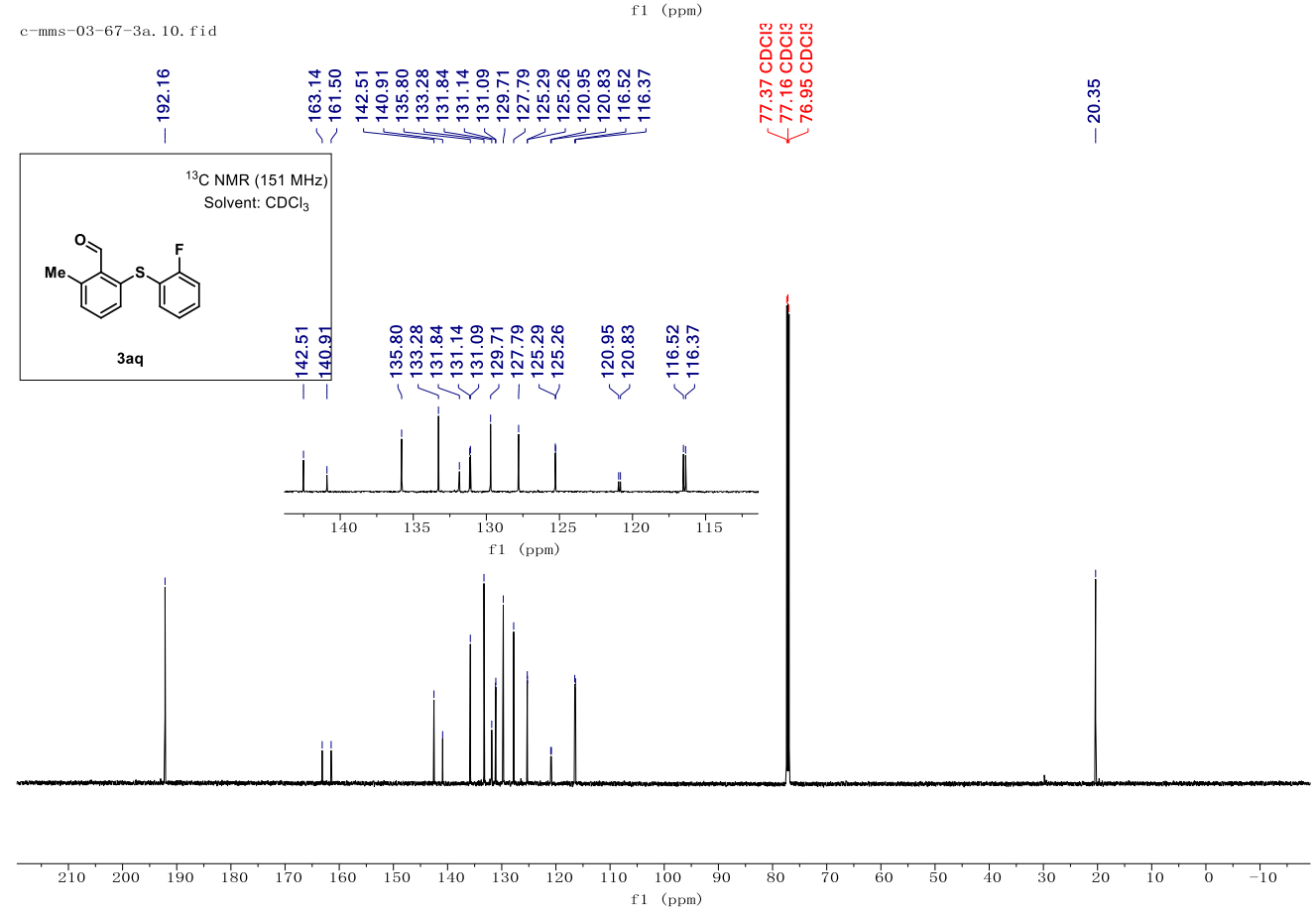
f-mms-03-67-4a.10.fid



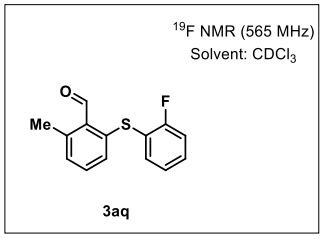

mms-03-10-1a.10.fid
10.71
7.34
7.34
7.33
7.33
7.32
7.32
7.26
7.26 CDCl3
7.24
7.24
7.24
7.23
7.23
7.22
7.09
7.07
6.98
6.97
6.94
6.93
6.92
3.82
2.63
1H NMR (600 MHz)
Solvent: CDCl3
O
Me
S
OMe
3ap
0.95
1.00
2.02
1.00
1.01
2.00
3.01
3.01
f1 (ppm)

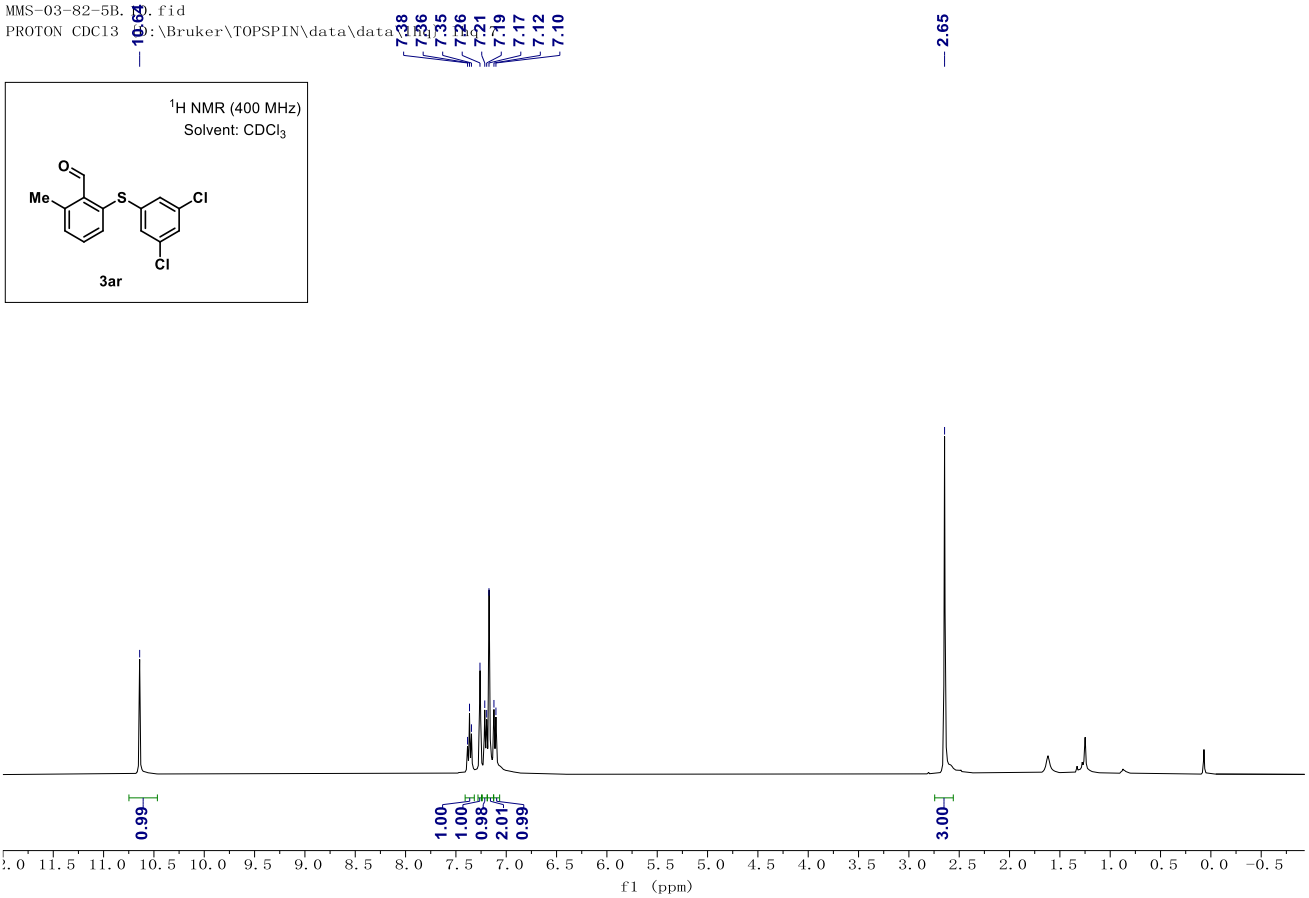

c-mms-03-10-1a.10.fid
192.92
158.63
142.07
141.35
134.24
133.05
132.60
130.04
129.95
129.10
122.26
121.64
111.36
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
56.03
20.71
13C NMR (151 MHz)
Solvent: CDCl3
O
Me
S
OMe
3ap
134.24
133.05
132.60
130.04
129.95
129.10
122.26
121.64
f1 (ppm)
f1 (ppm)

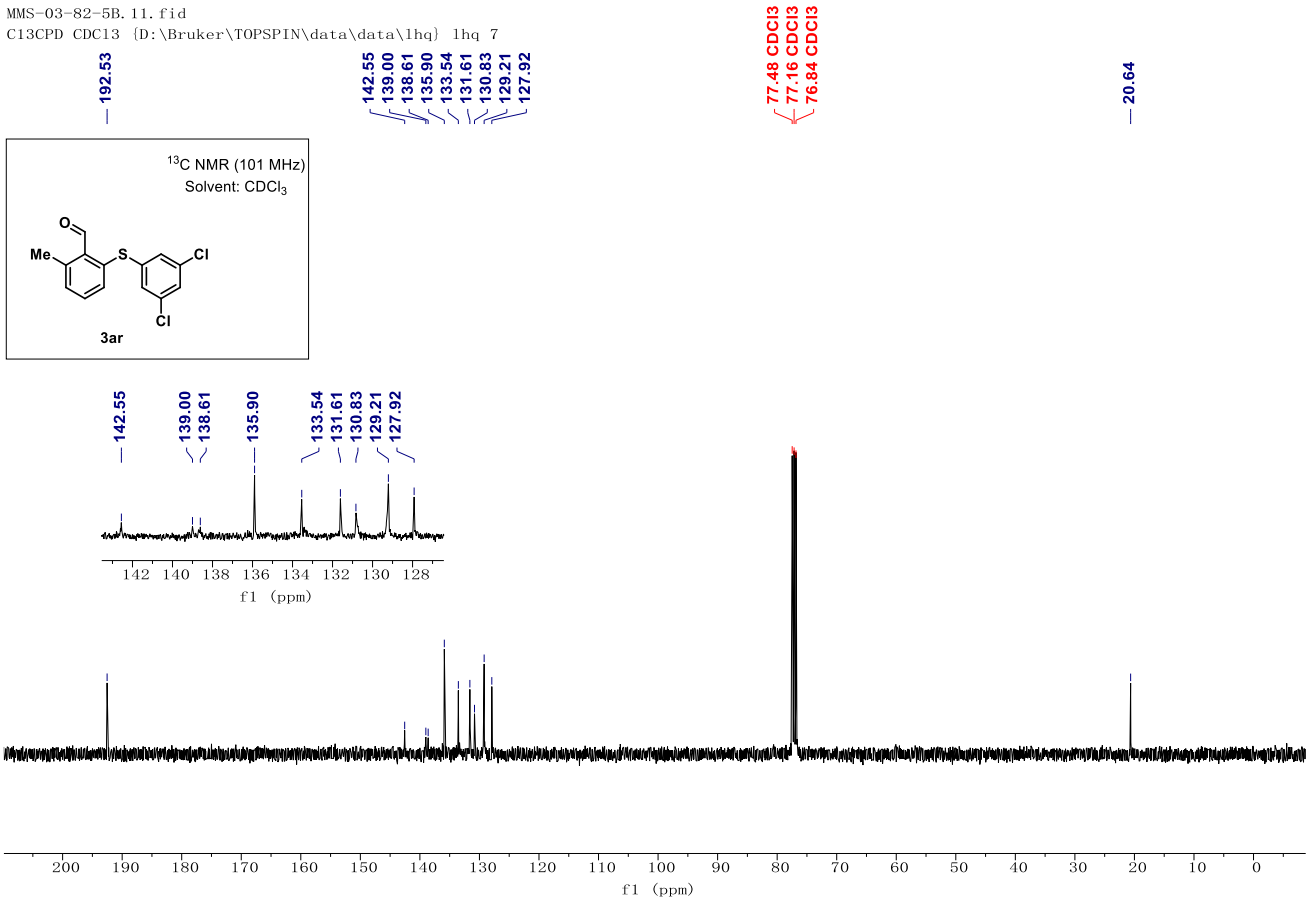

mms-03-67-3a.10.fid
10.72
7.45
7.44
7.43
7.43
7.43
7.42
7.42
7.41
7.41
7.40
7.40
7.40
7.39
7.39
7.29
7.27
7.26
7.20
7.20
7.19
7.18
7.17
7.17
7.16
7.15
7.11
7.09
6.93
6.91
2.67
1H NMR (600 MHz)
Solvent: CDCl3
Me
O
S
F
3aq
1.01
2.00
1.01
2.00
1.00
0.99
3.01
f1 (ppm)

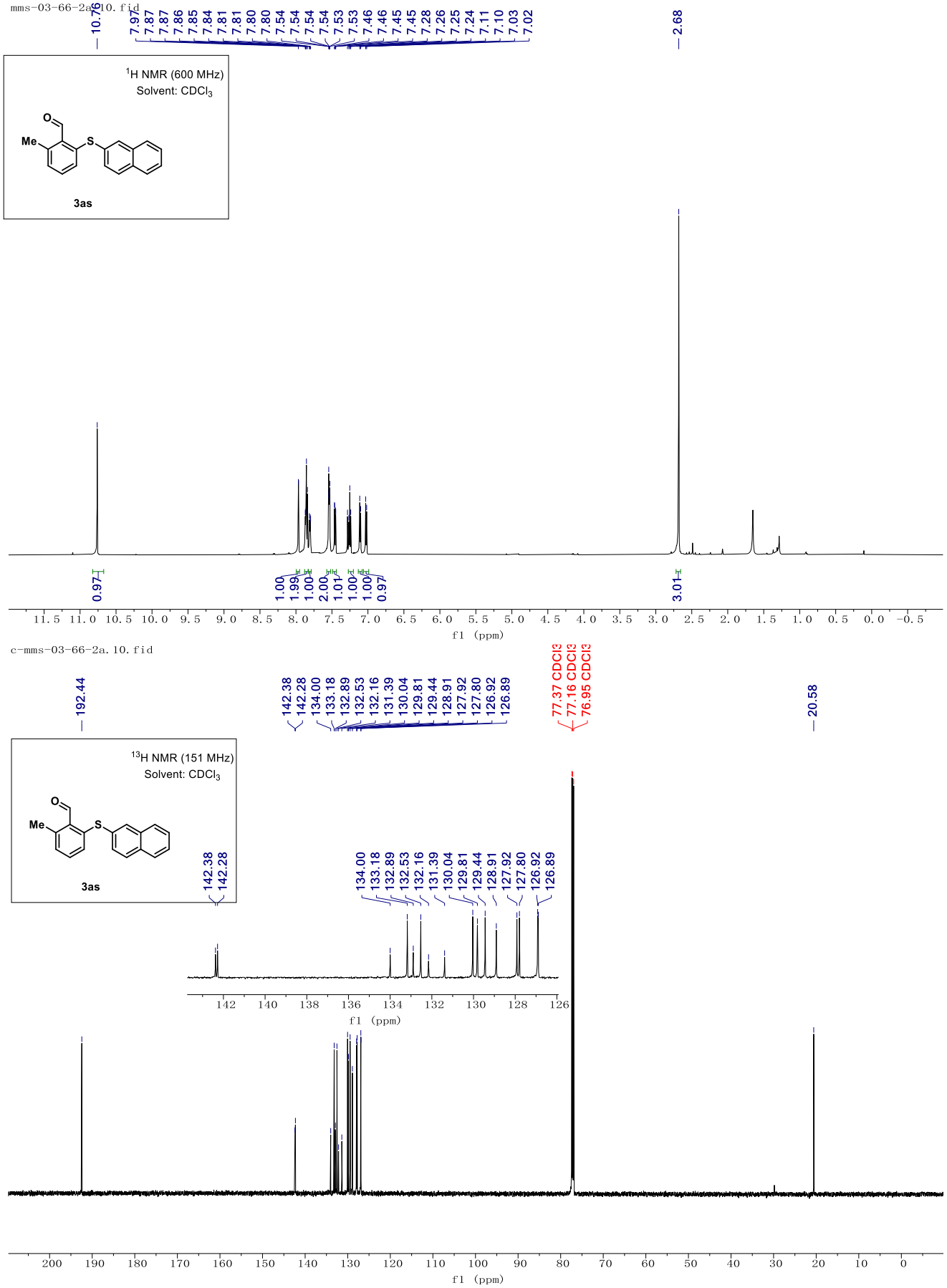

c-mms-03-67-3a.10.fid
192.16
163.14
161.50
142.51
140.91
135.80
133.28
131.84
131.14
131.09
129.71
127.79
125.29
125.26
120.95
120.83
116.52
116.37
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
20.35
13C NMR (151 MHz)
Solvent: CDCl3
Me
O
S
F
3aq
f1 (ppm)
f1 (ppm)

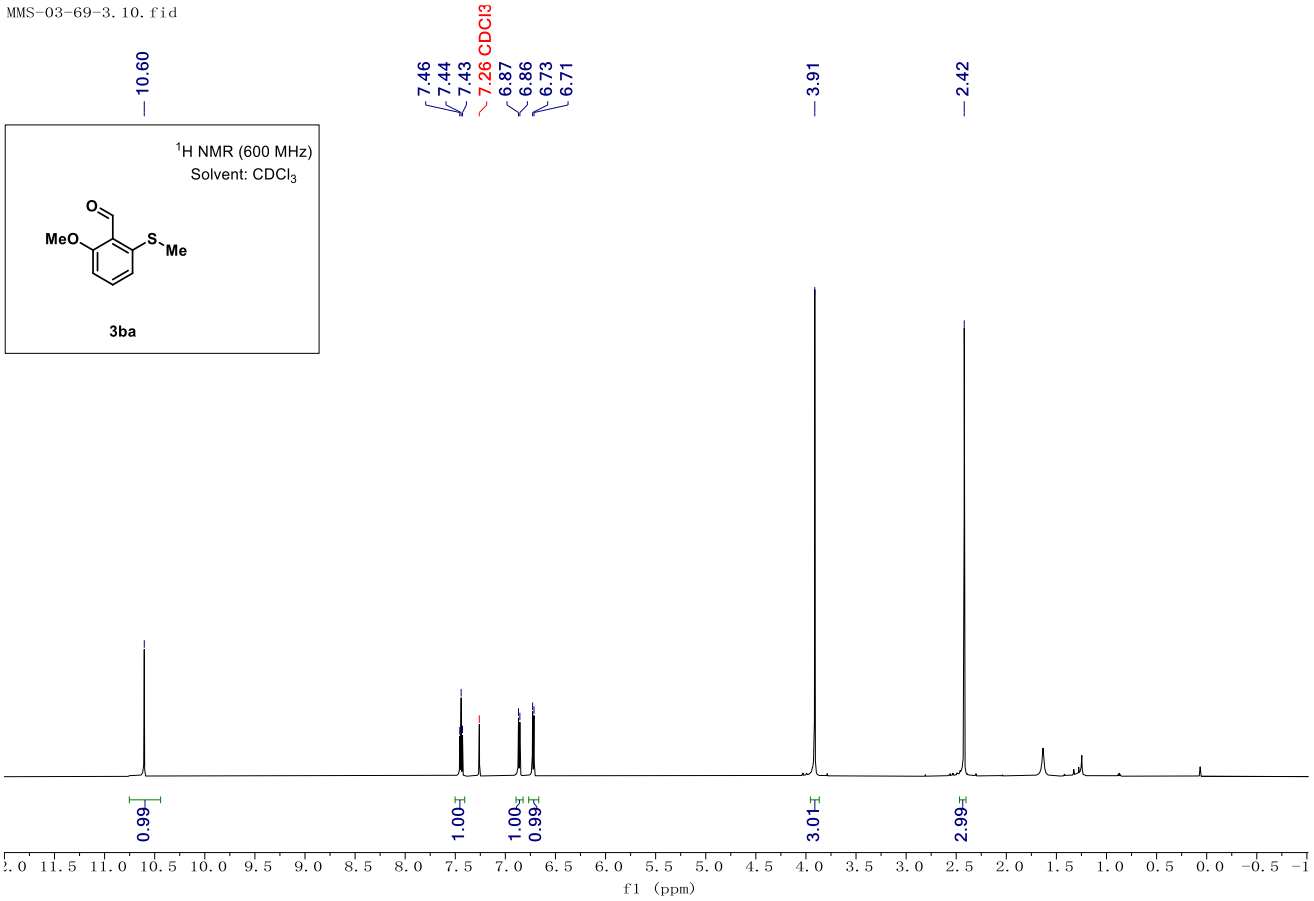
f-mms-03-67-3a.10.fid

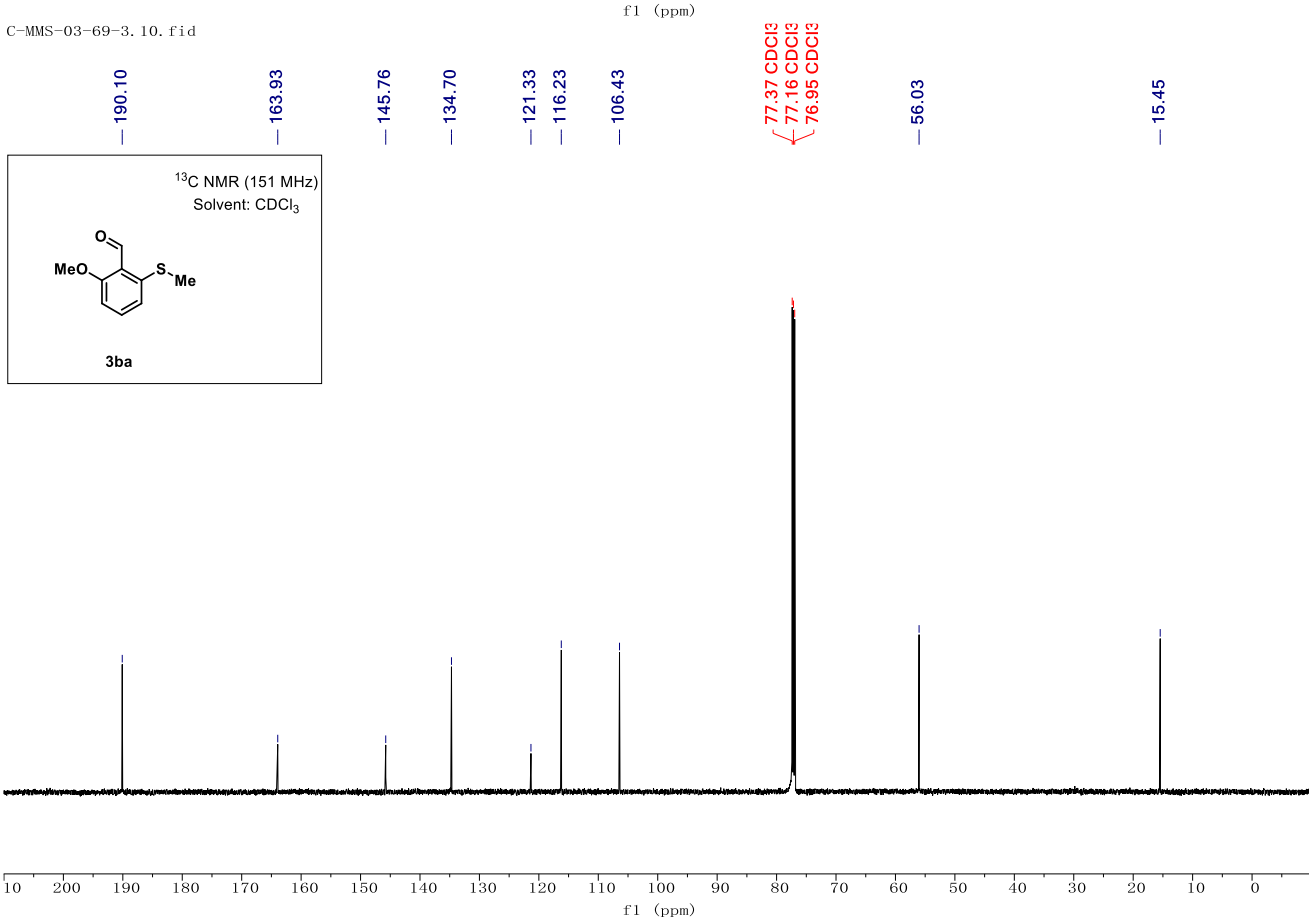


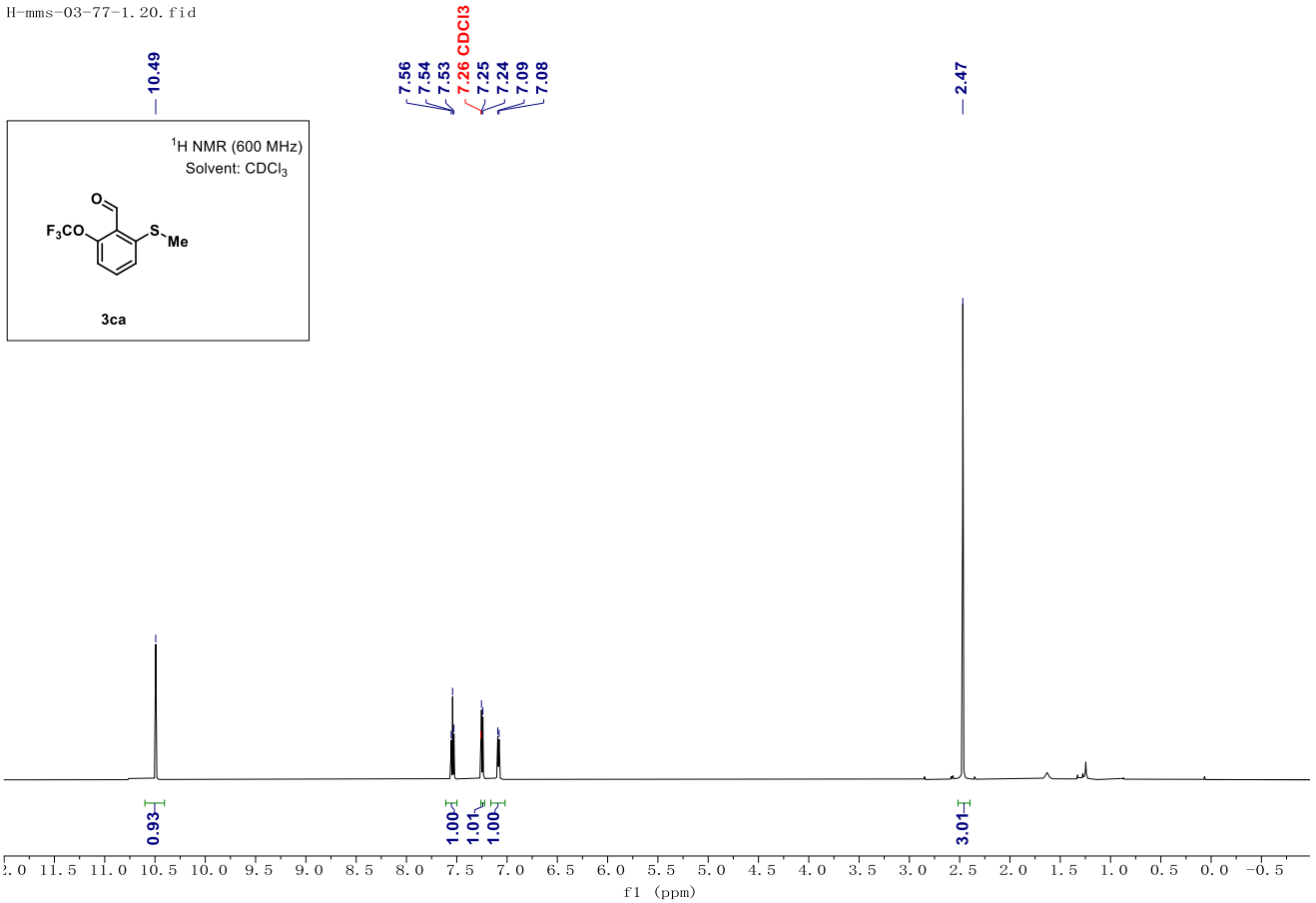

MMS-03-82-5B.10.fid
PROTON CDC13 {D:\Bruker\TOPSPIN\data\data\lhq} lhq
10.64
7.38
7.36
7.35
7.26
7.21
7.19
7.17
7.12
7.10
2.65
1H NMR (400 MHz)
Solvent: CDCl3
Me
S
Cl
Cl
O
3ar
0.99
1.00
1.00
0.98
2.01
0.99
3.00
f1 (ppm)

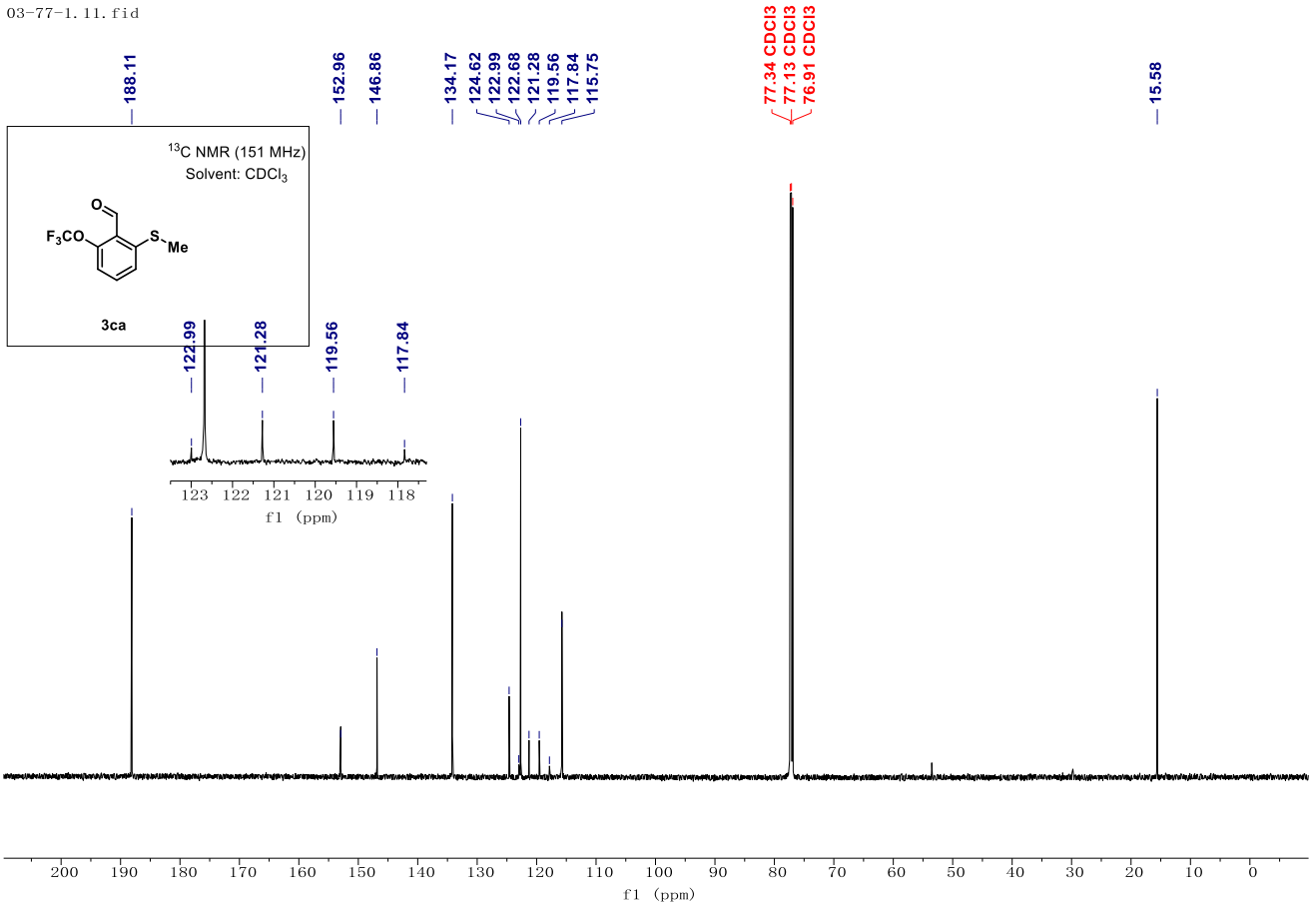

MMS-03-82-5B.11.fid
C13CPD CDC13 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 7
192.53
142.55
139.00
138.61
135.90
133.54
131.61
130.83
129.21
127.92
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
20.64
13C NMR (101 MHz)
Solvent: CDCl3
Me
S
Cl
Cl
O
3ar
f1 (ppm)


mms-03-66-2a.10.fid
10.76
7.97
7.87
7.87
7.86
7.85
7.84
7.81
7.81
7.80
7.80
7.54
7.54
7.54
7.54
7.53
7.53
7.46
7.46
7.45
7.45
7.28
7.26
7.25
7.24
7.11
7.10
7.03
7.02
2.68
1H NMR (600 MHz)
Solvent: CDCl3
O
Me
S
3as
0.97
1.00
1.99
1.00
2.00
1.01
1.00
1.00
0.97
3.01
f1 (ppm)
c-mms-03-66-2a.10.fid
192.44
142.38
142.28
134.00
133.18
132.89
132.53
132.16
131.39
130.04
129.81
129.44
128.91
127.92
127.80
126.92
126.89
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
20.58
13H NMR (151 MHz)
Solvent: CDCl3
O
Me
S
3as
f1 (ppm)
f1 (ppm)


MMS-03-69-3.10.fid
10.60
7.46
7.44
7.43
7.26 CDCl3
6.87
6.86
6.73
6.71
3.91
2.42
1H NMR (600 MHz)
Solvent: CDCl3
MeO
S
Me
3ba
0.99
1.00
1.00
0.99
3.01
2.99
f1 (ppm)


C-MMS-03-69-3.10.fid
190.10
163.93
145.76
134.70
121.33
116.23
106.43
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
56.03
15.45
13C NMR (151 MHz)
Solvent: CDCl3
MeO
S
Me
3ba
f1 (ppm)

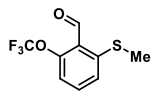

H-mms-03-77-1.20.fid
10.49
7.56
7.54
7.53
7.26 CDCl3
7.25
7.24
7.09
7.08
2.47
1H NMR (600 MHz)
Solvent: CDCl3
F3CO
S
Me
3ca
0.93
1.00
1.01
1.00
3.01
f1 (ppm)


03-77-1.11.fid
188.11
152.96
146.86
134.17
124.62
122.99
122.68
121.28
119.56
117.84
115.75
77.34 CDCl3
77.13 CDCl3
76.91 CDCl3
15.58
13C NMR (151 MHz)
Solvent: CDCl3
F3CO
S
Me
3ca
122.99
121.28
119.56
117.84
f1 (ppm)
f1 (ppm)

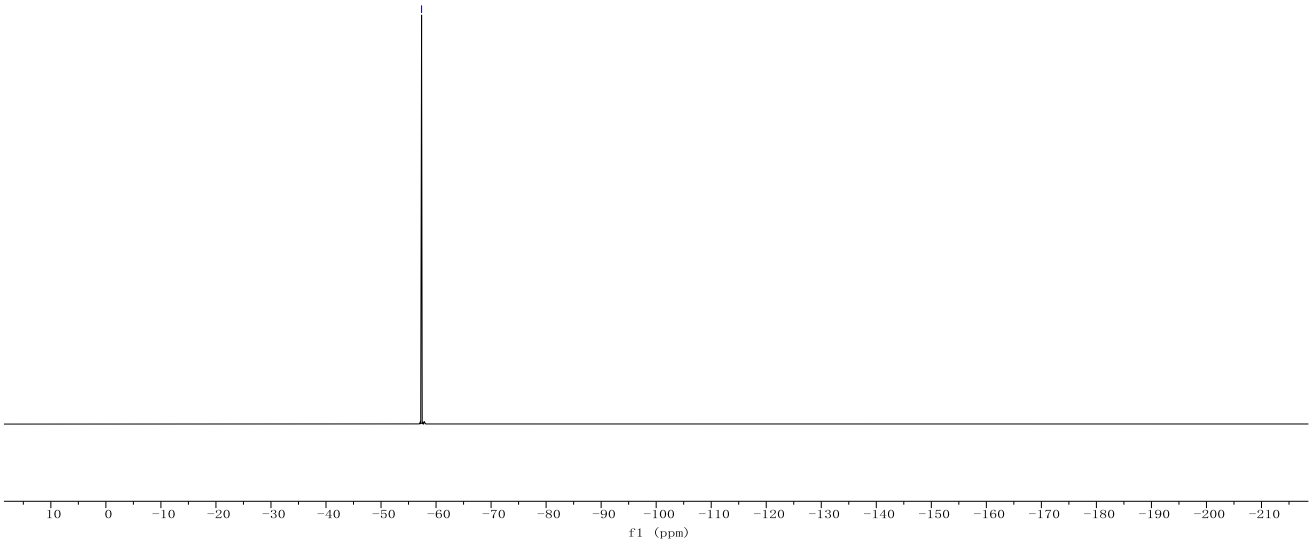
MMS-03-F-2OCF3.10.fid
F19CPD CDC13 {D:\Bruker\TOPSPIN\data\data\lhq} lhq

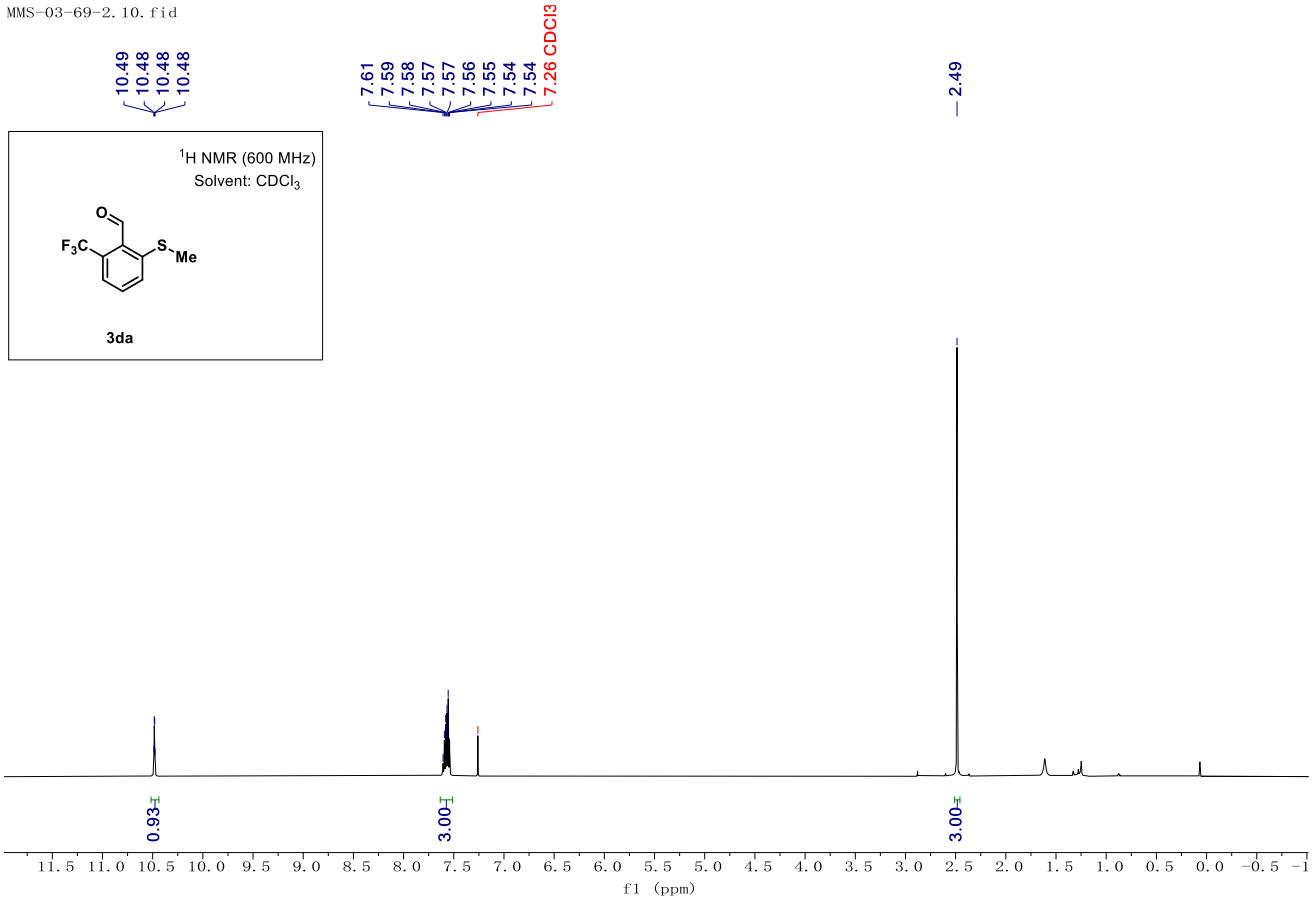
-57.37

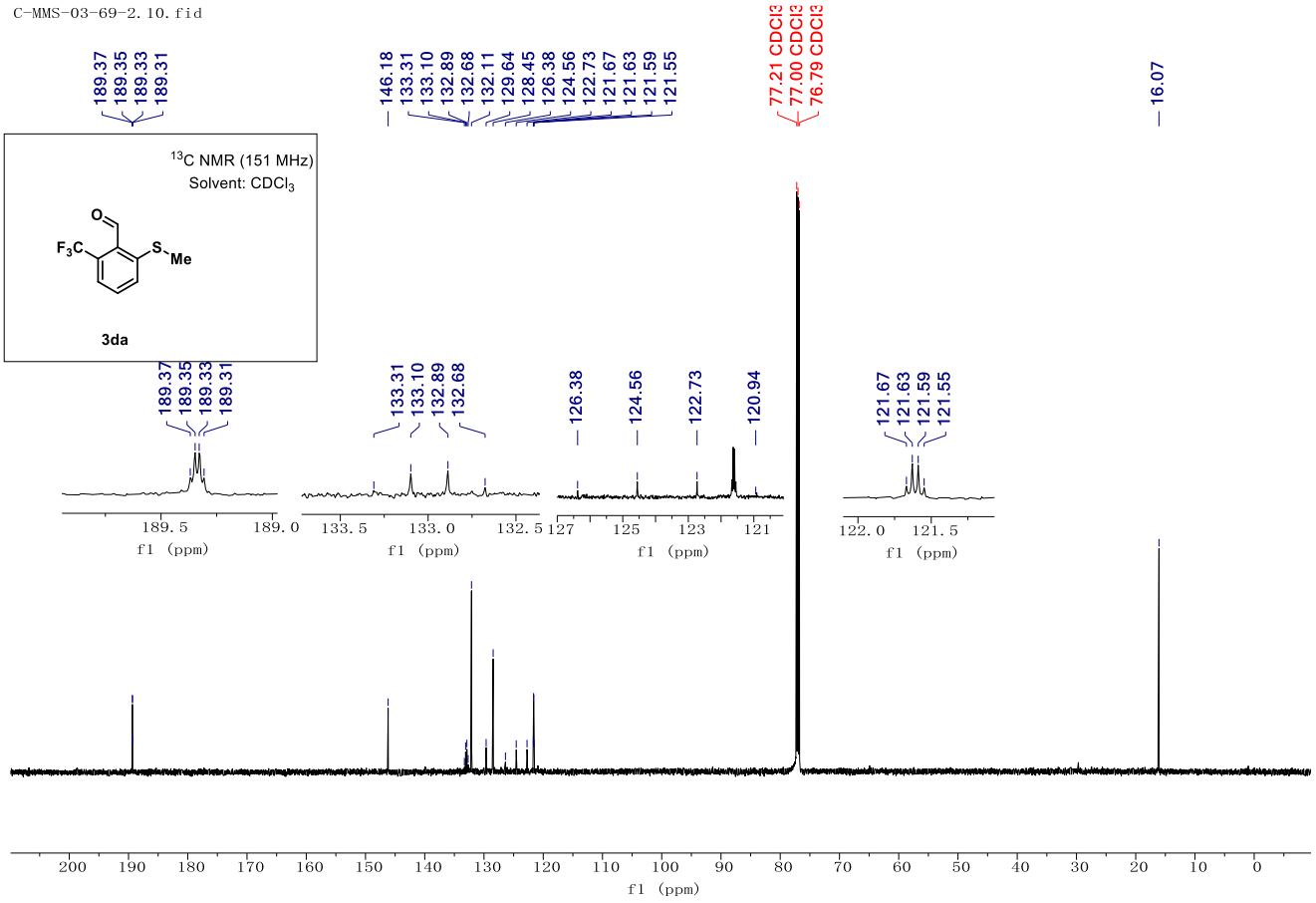
^{19}F NMR (376 MHz)
Solvent: $CDCl_3$



3ca



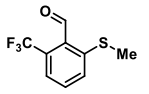

MMS-03-69-2.10.fid
10.49
10.48
10.48
10.48
7.61
7.59
7.58
7.57
7.57
7.56
7.55
7.54
7.54
7.26 CDCl3
2.49
^{1}H NMR (600 MHz)
Solvent: CDCl$_3$
O
F$_3$C
S
Me
3da
0.93
3.00
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1
f1 (ppm)


C-MMS-03-69-2.10.fid
189.37
189.35
189.33
189.31
146.18
133.31
133.10
132.89
132.68
132.11
129.64
128.45
126.38
124.56
122.73
121.67
121.63
121.59
121.55
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
16.07
^{13}C NMR (151 MHz)
Solvent: CDCl$_3$
O
F$_3$C
S
Me
3da
189.37
189.35
189.33
189.31
133.31
133.10
132.89
132.68
126.38
124.56
122.73
120.94
121.67
121.63
121.59
121.55
189.5 189.0
133.5 133.0 132.5
127 125 123 121
122.0 121.5
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

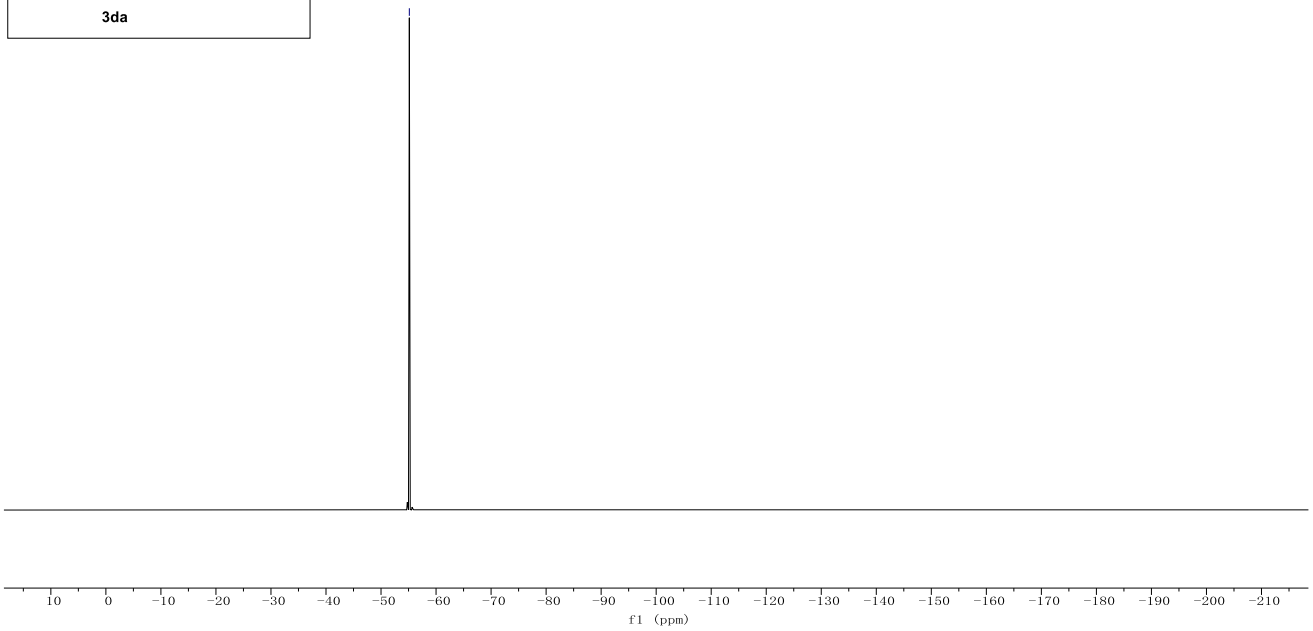
MMS-03-F-2CF3.10.fid
F19CPD CDCl3 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 20

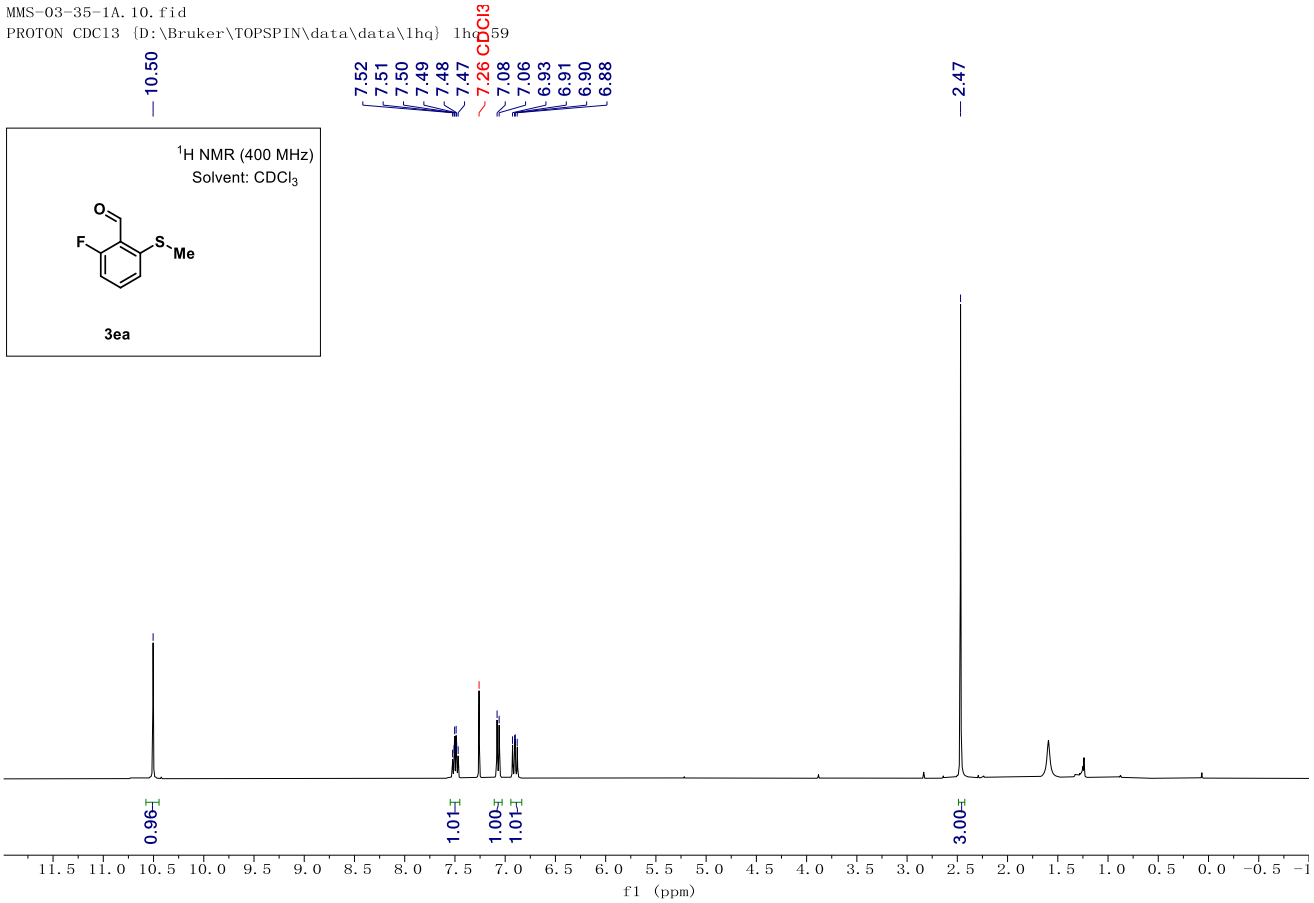
-55.14

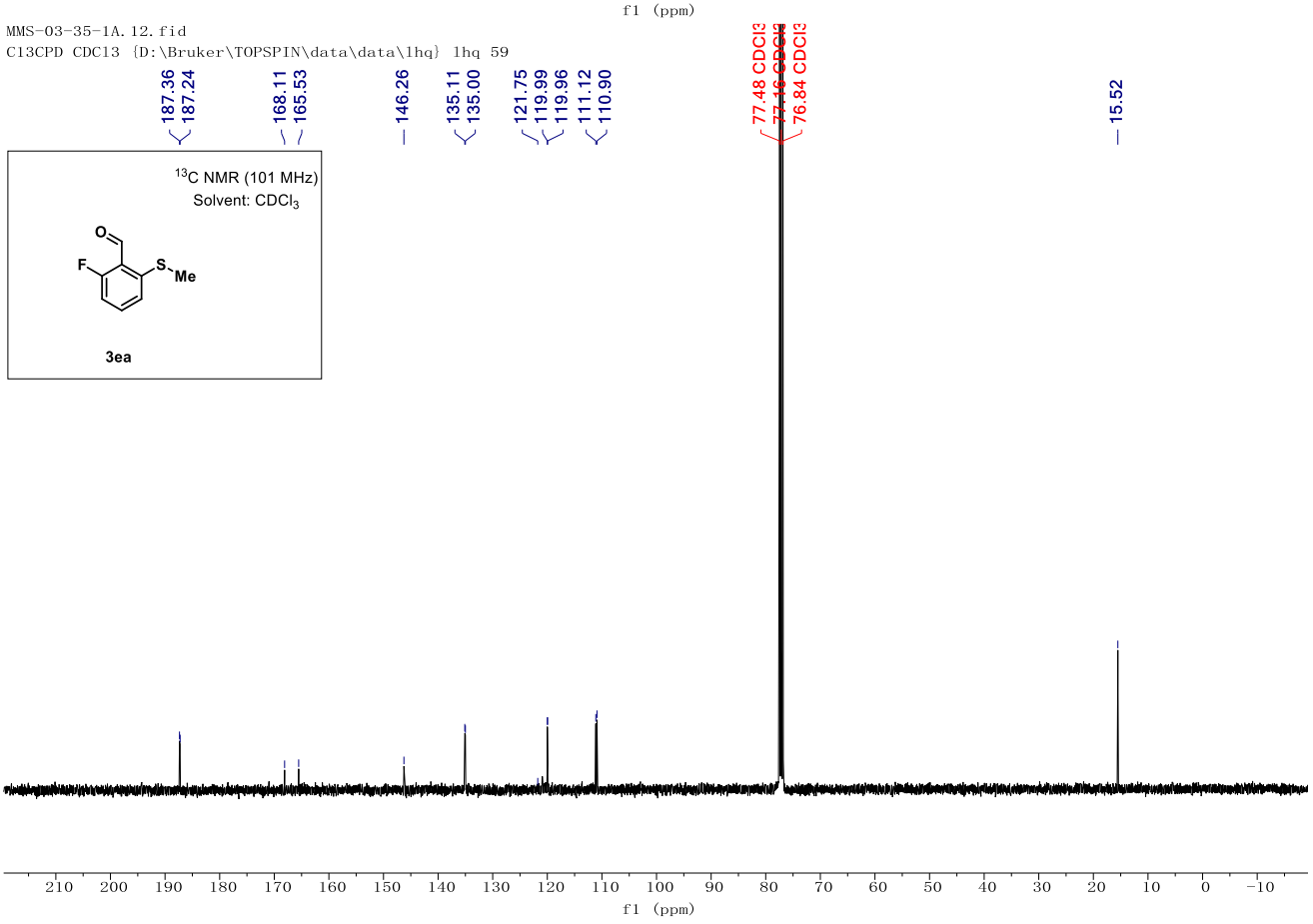
^{19}F NMR (376 MHz)
Solvent: $CDCl_3$



3da



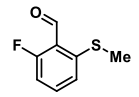

MMS-03-35-1A.10.fid
PROTON CDC13 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 59
10.50
7.52
7.51
7.50
7.49
7.48
7.47
7.26 CDCl3
7.08
7.06
6.93
6.91
6.90
6.88
2.47
1H NMR (400 MHz)
Solvent: CDCl3
O
F
S
Me
3ea
0.96
1.01
1.00
1.01
3.00
f1 (ppm)


MMS-03-35-1A.12.fid
C13CPD CDC13 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 59
187.36
187.24
168.11
165.53
146.26
135.11
135.00
121.75
119.99
119.96
111.12
110.90
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
15.52
13C NMR (101 MHz)
Solvent: CDCl3
O
F
S
Me
3ea
f1 (ppm)

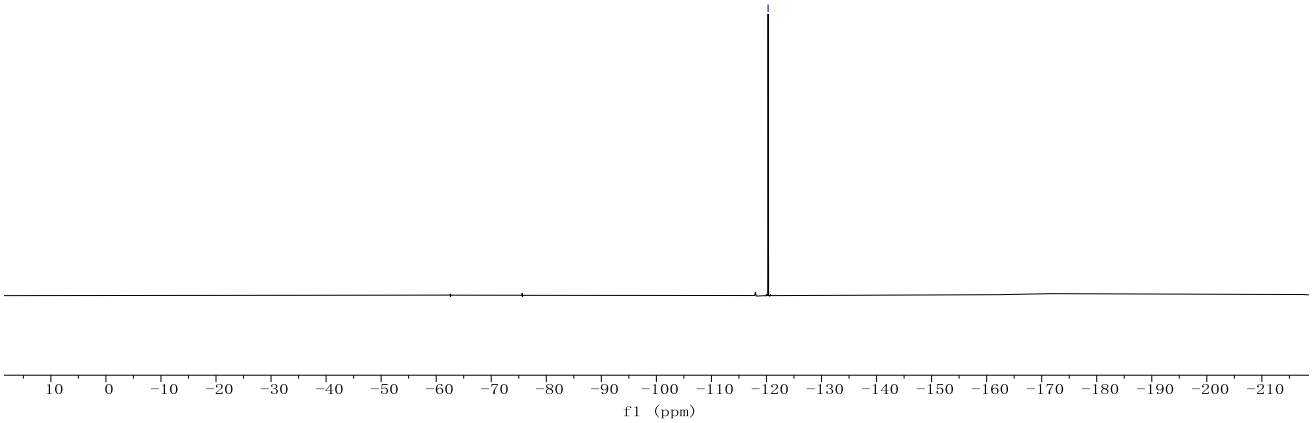
MMS-03-35-1A.11.fid
F19CPD CDCl3 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 59

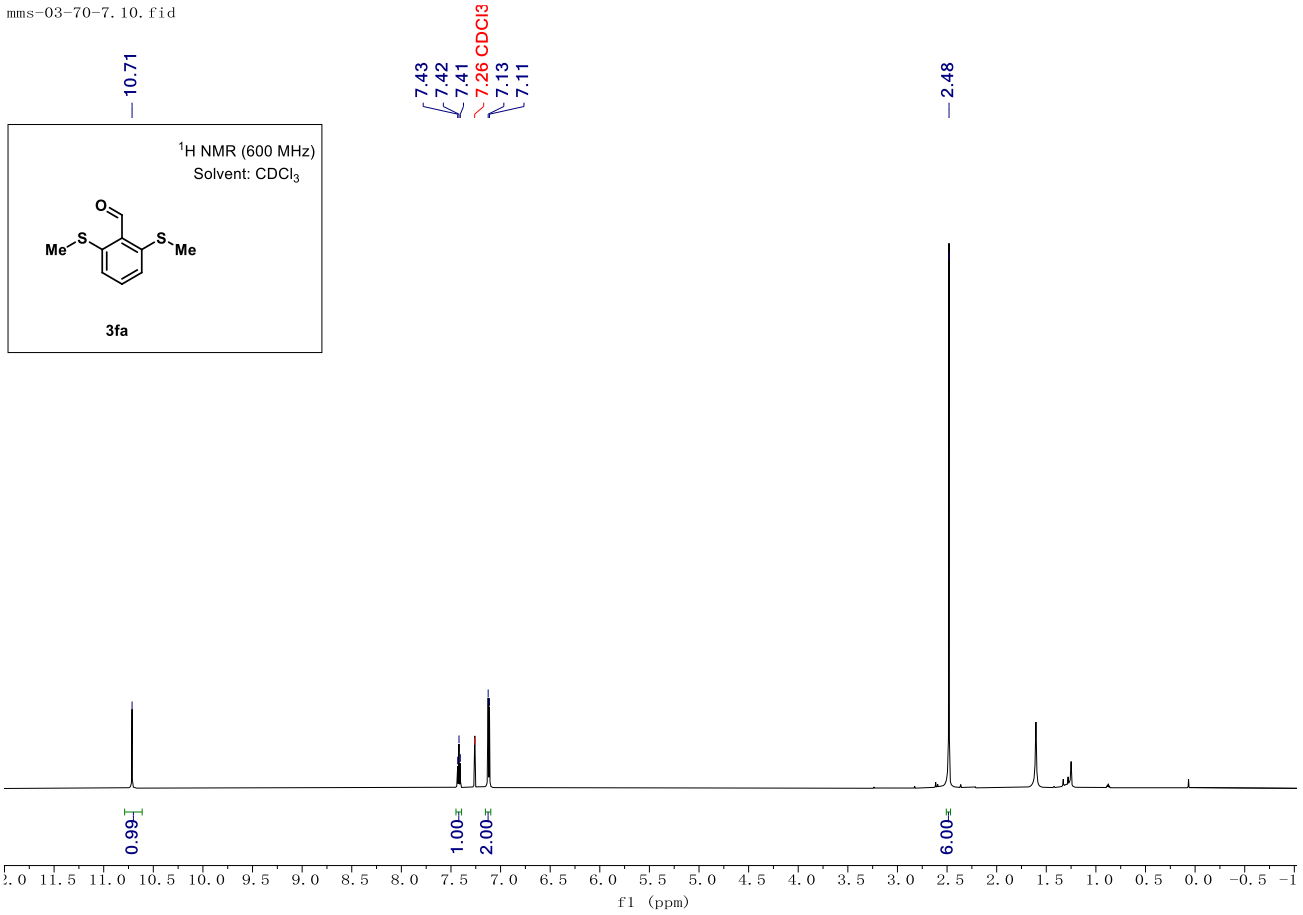
-120.30

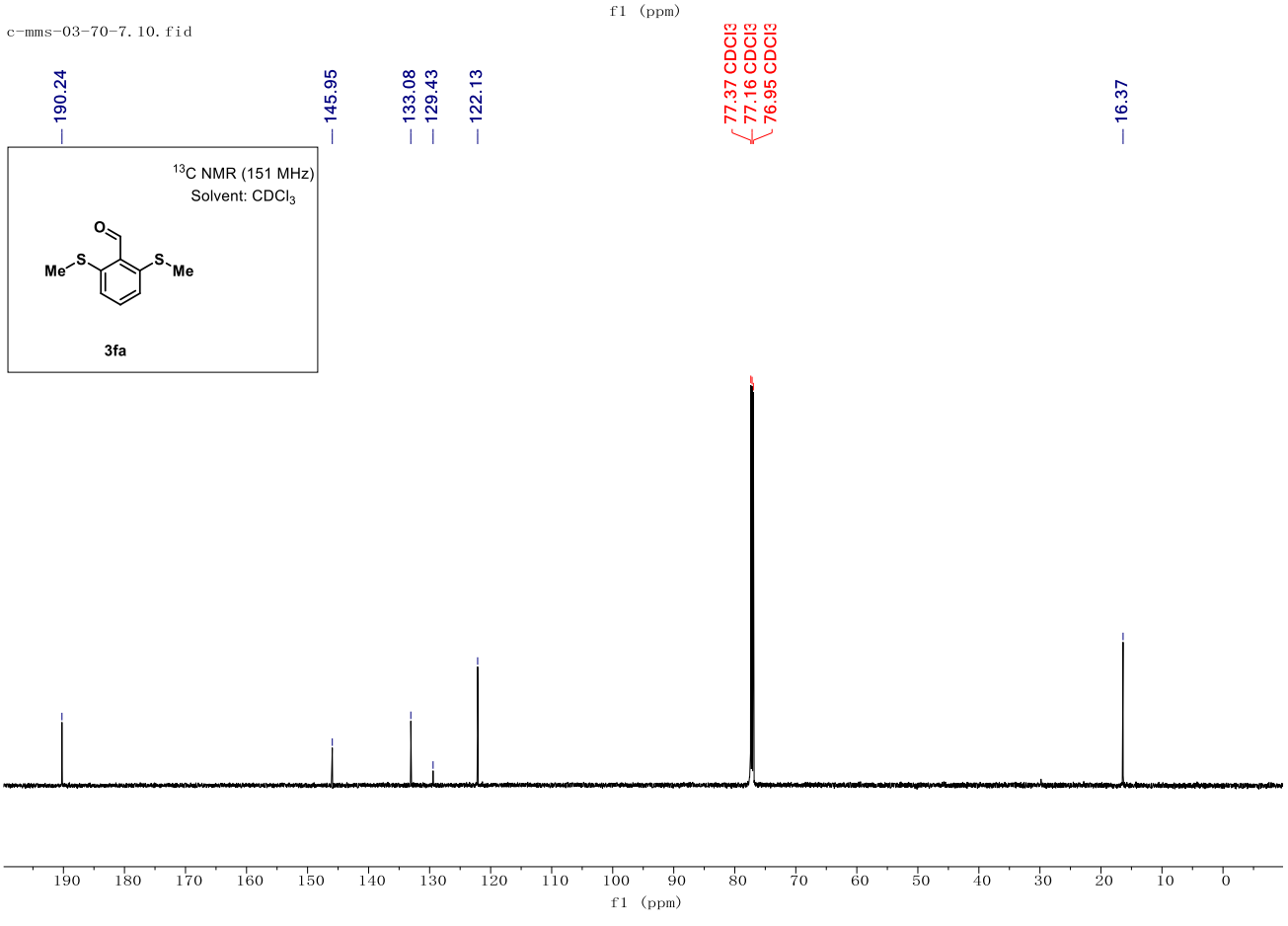
^{19}F NMR (376 MHz)
Solvent: $CDCl_3$

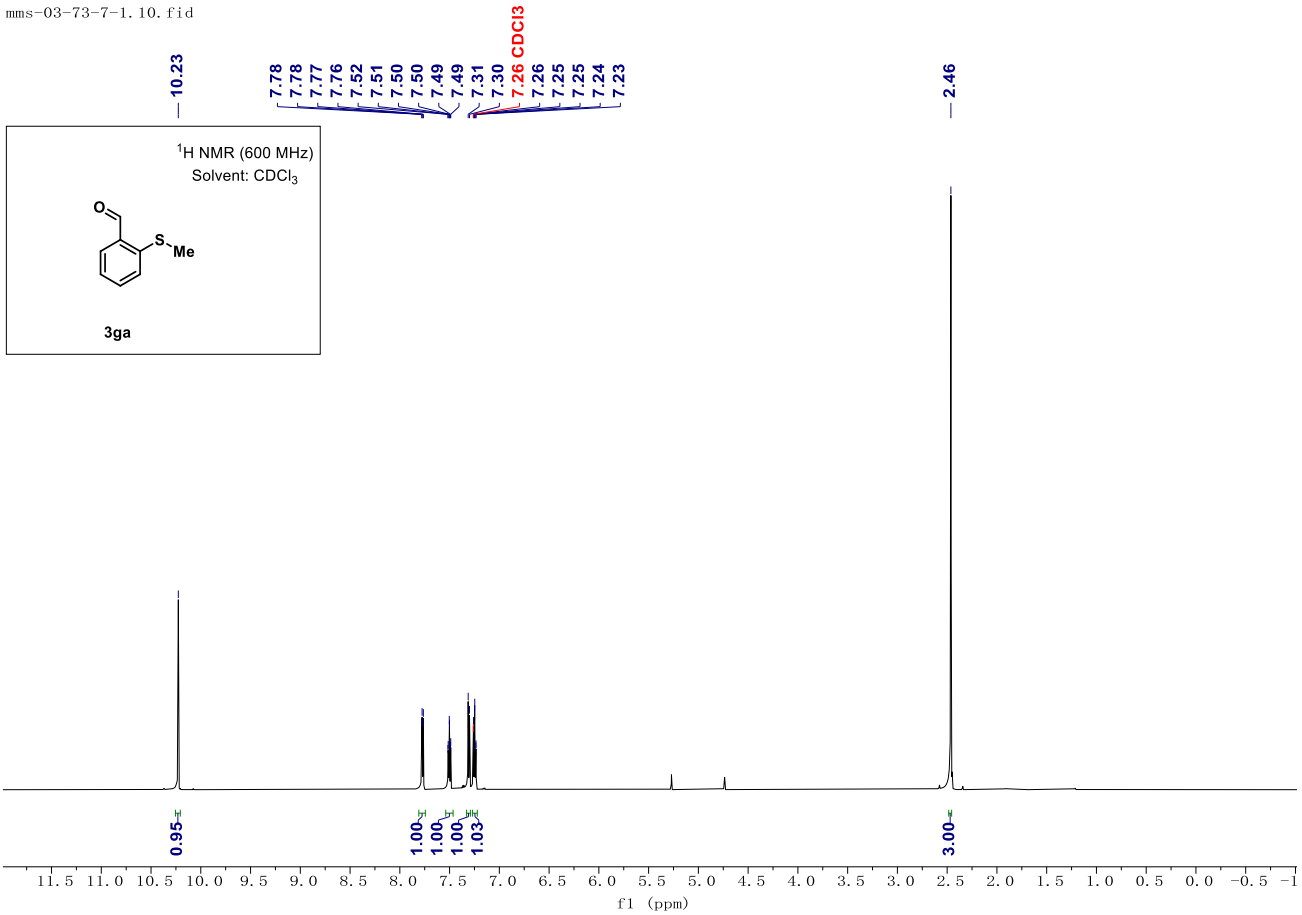


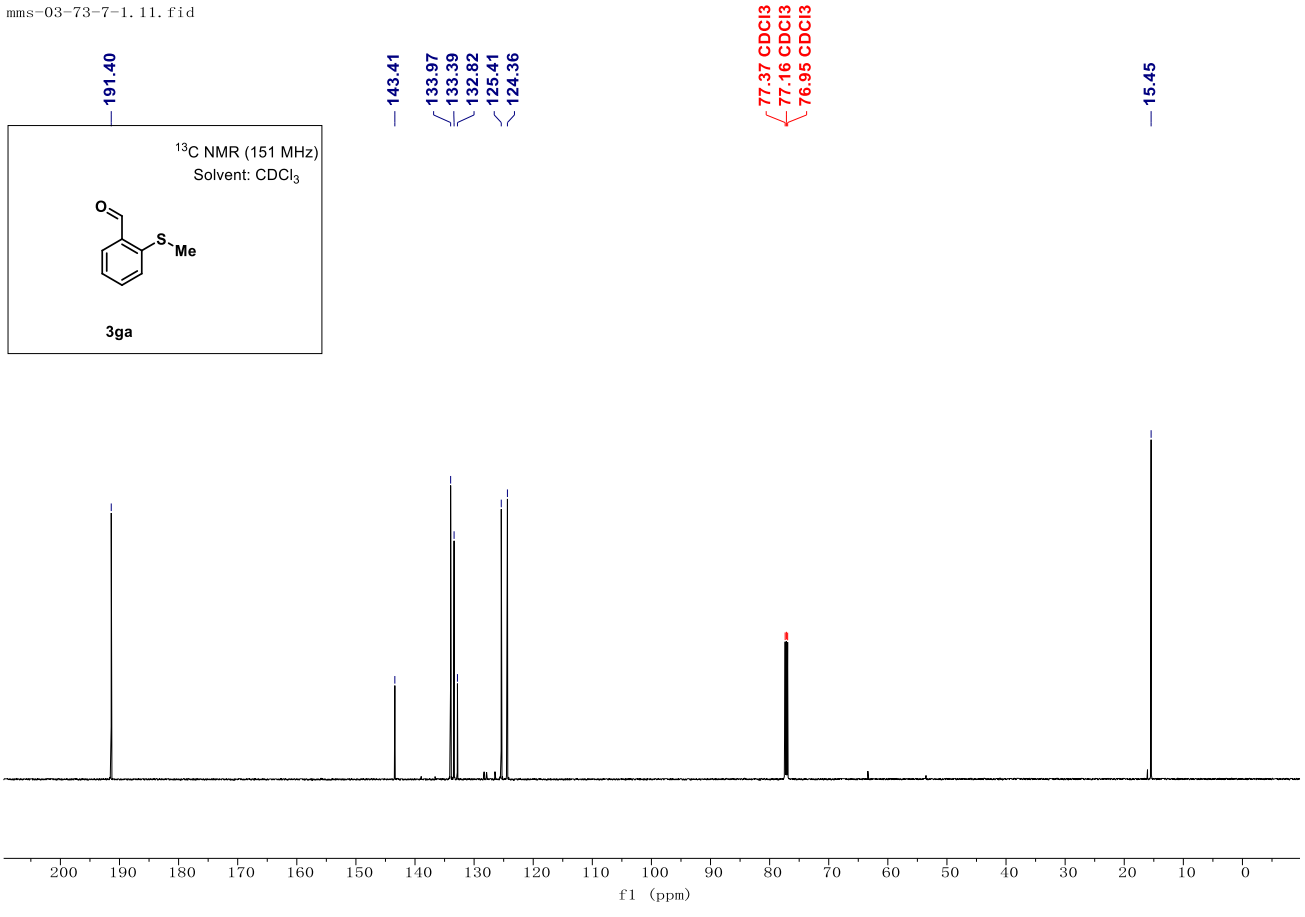
3ea

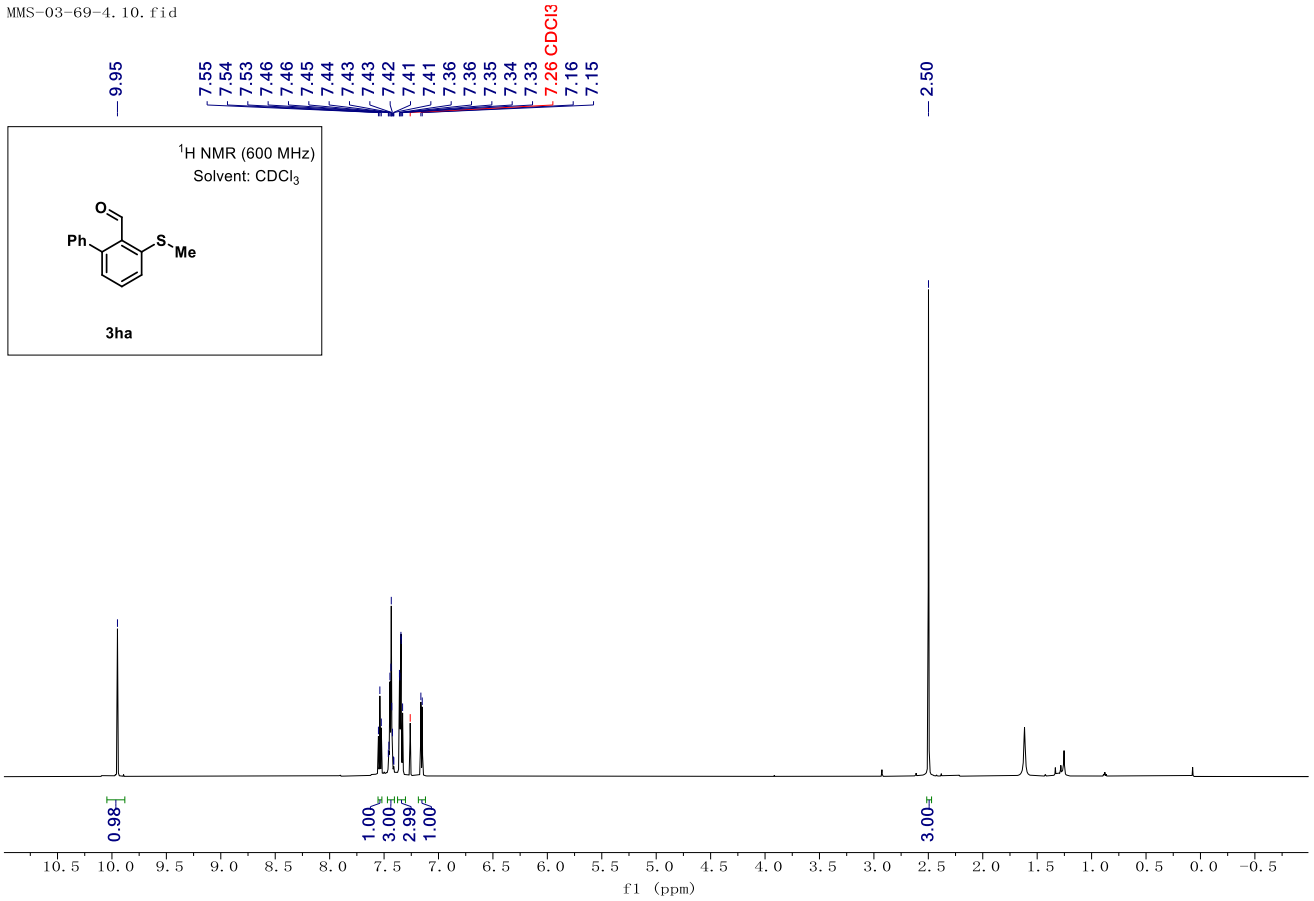


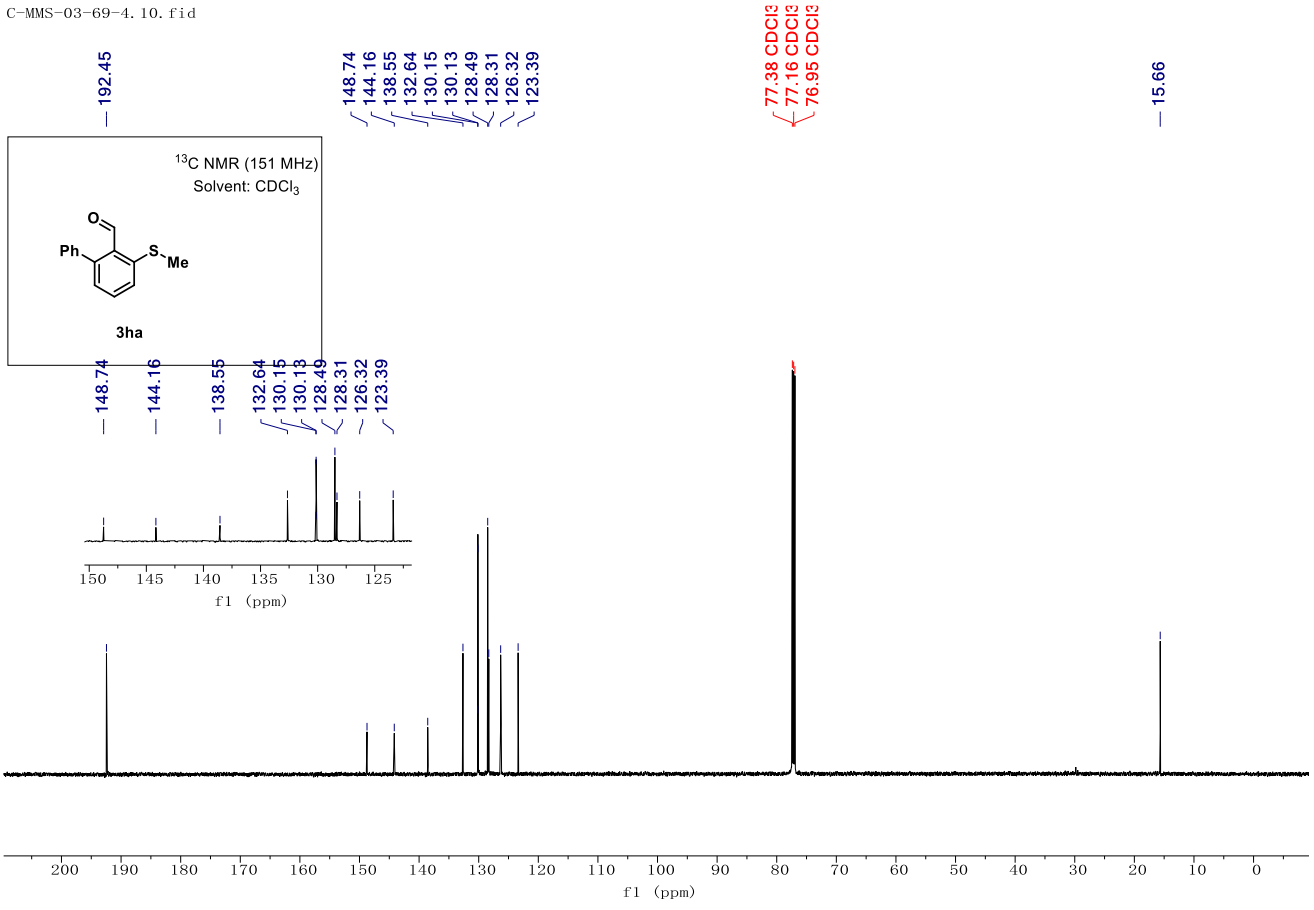

mms-03-70-7.10.fid
10.71
7.43
7.42
7.41
7.26 CDCl3
7.13
7.11
2.48
1H NMR (600 MHz)
Solvent: CDCl3
Me
S
S
Me
O
3fa
0.99
1.00
2.00
6.00
f1 (ppm)


c-mms-03-70-7.10.fid
190.24
145.95
133.08
129.43
122.13
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
16.37
13C NMR (151 MHz)
Solvent: CDCl3
Me
S
S
Me
O
3fa
f1 (ppm)

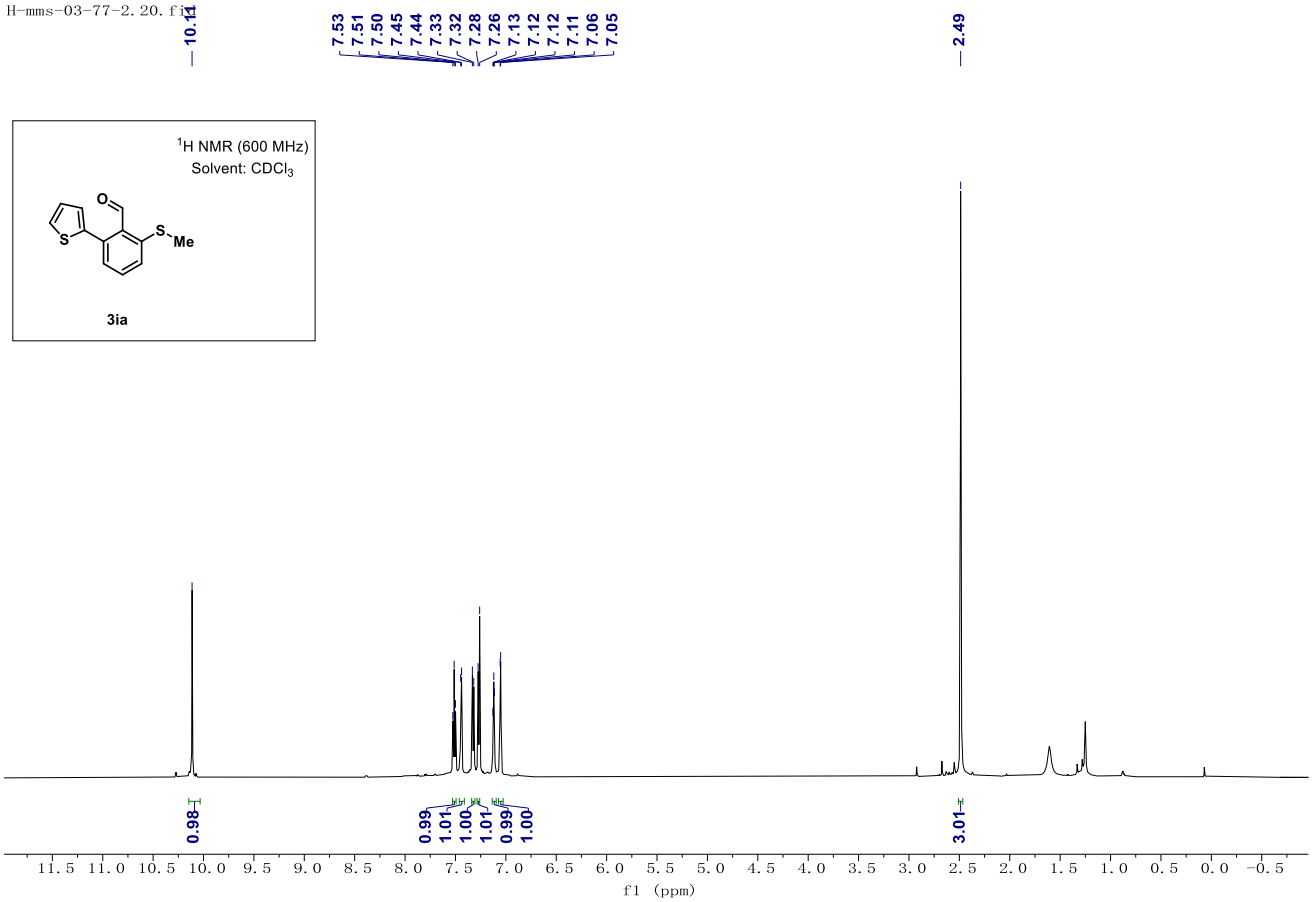

mms-03-73-7-1.10.fid
10.23
7.78
7.78
7.77
7.76
7.52
7.51
7.50
7.50
7.49
7.49
7.31
7.30
7.26 CDCl3
7.26
7.25
7.25
7.24
7.23
2.46
1H NMR (600 MHz)
Solvent: CDCl3
O
S
Me
3ga
0.95
1.00
1.00
1.00
1.03
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1
f1 (ppm)


mms-03-73-7-1.11.fid
191.40
143.41
133.97
133.39
132.82
125.41
124.36
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
15.45
13C NMR (151 MHz)
Solvent: CDCl3
O
S
Me
3ga
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

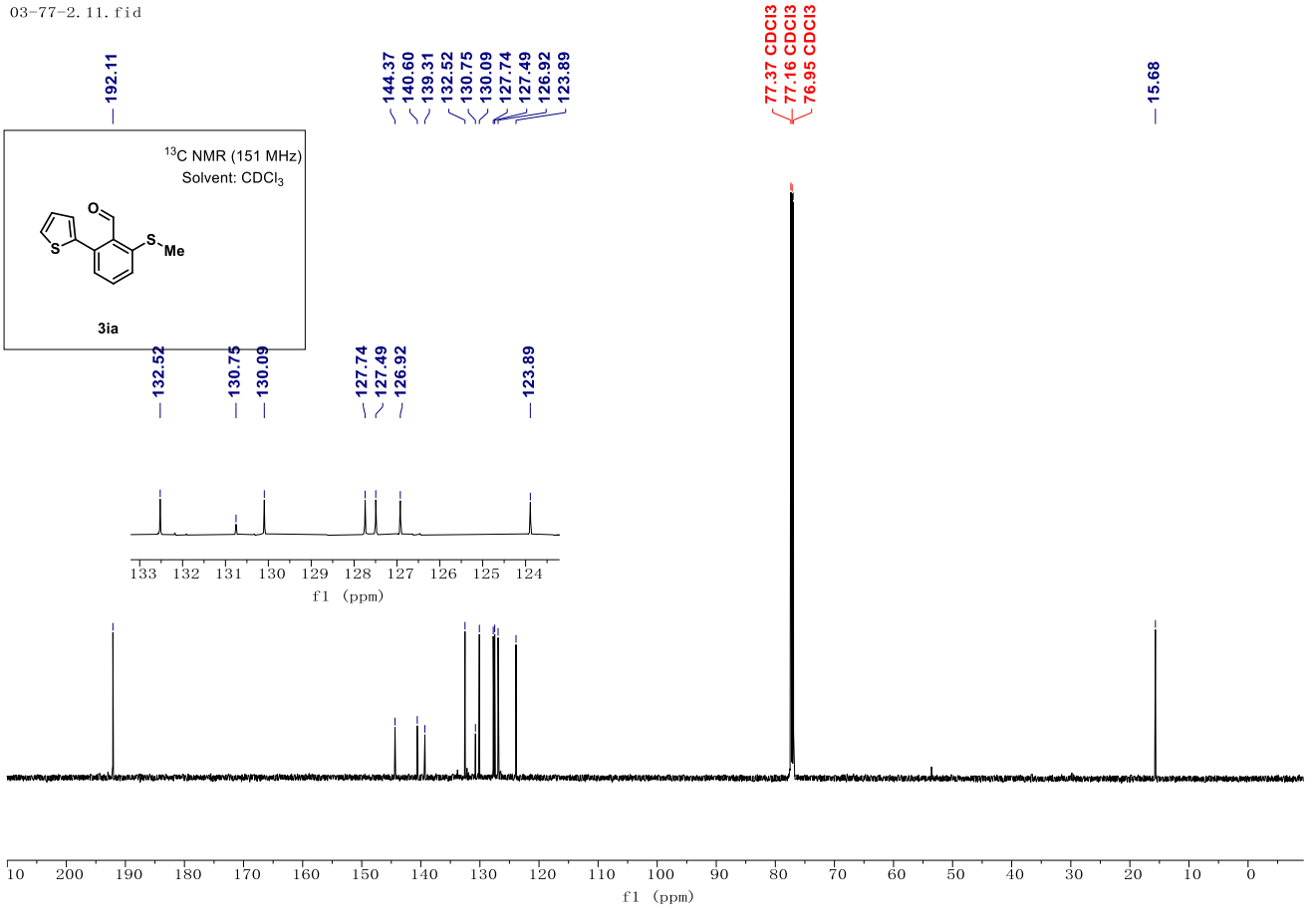

MMS-03-69-4.10.fid
9.95
7.55
7.54
7.53
7.46
7.46
7.45
7.44
7.43
7.43
7.42
7.41
7.41
7.36
7.36
7.35
7.34
7.33
7.26 CDCl3
7.16
7.15
2.50
1H NMR (600 MHz)
Solvent: CDCl3
O
Ph
S
Me
3ha
0.98
1.00
3.00
2.99
1.00
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

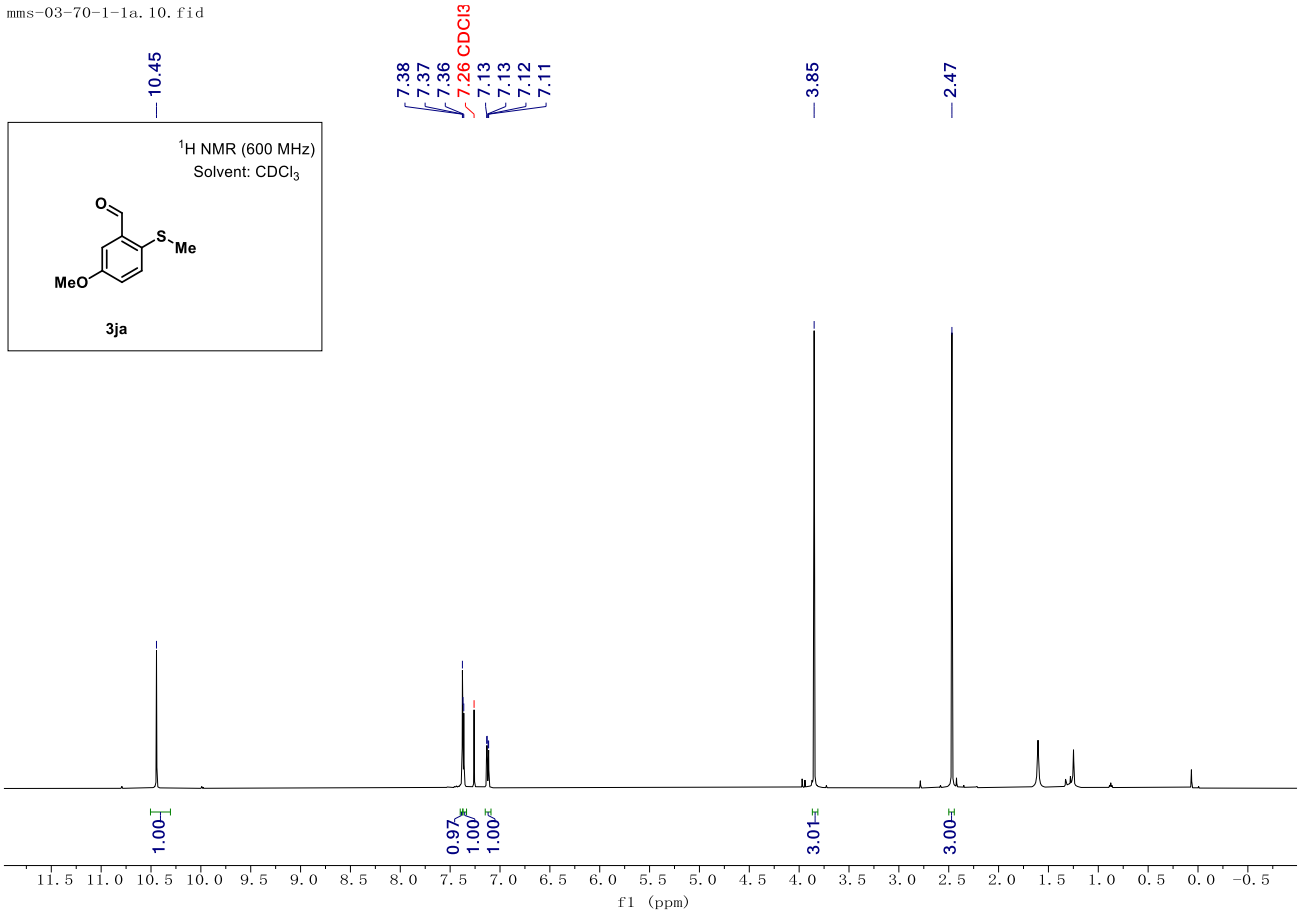

C-MMS-03-69-4.10.fid
192.45
148.74
144.16
138.55
132.64
130.15
130.13
128.49
128.31
126.32
123.39
77.38 CDCl3
77.16 CDCl3
76.95 CDCl3
15.66
13C NMR (151 MHz)
Solvent: CDCl3
O
Ph
S
Me
3ha
148.74
144.16
138.55
132.64
130.15
130.13
128.49
128.31
126.32
123.39
150 145 140 135 130 125
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

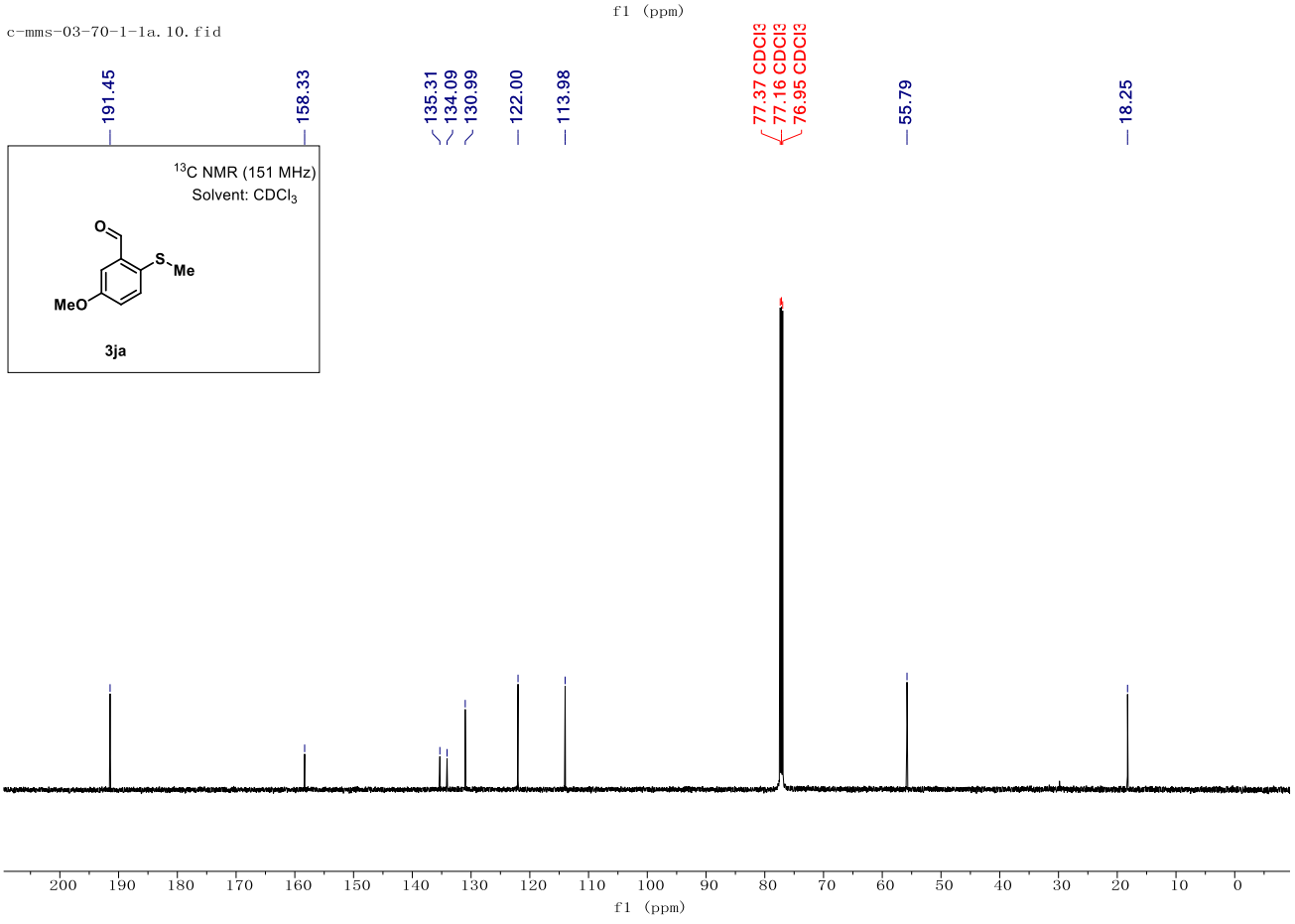
H-mms-03-77-2.20.fid



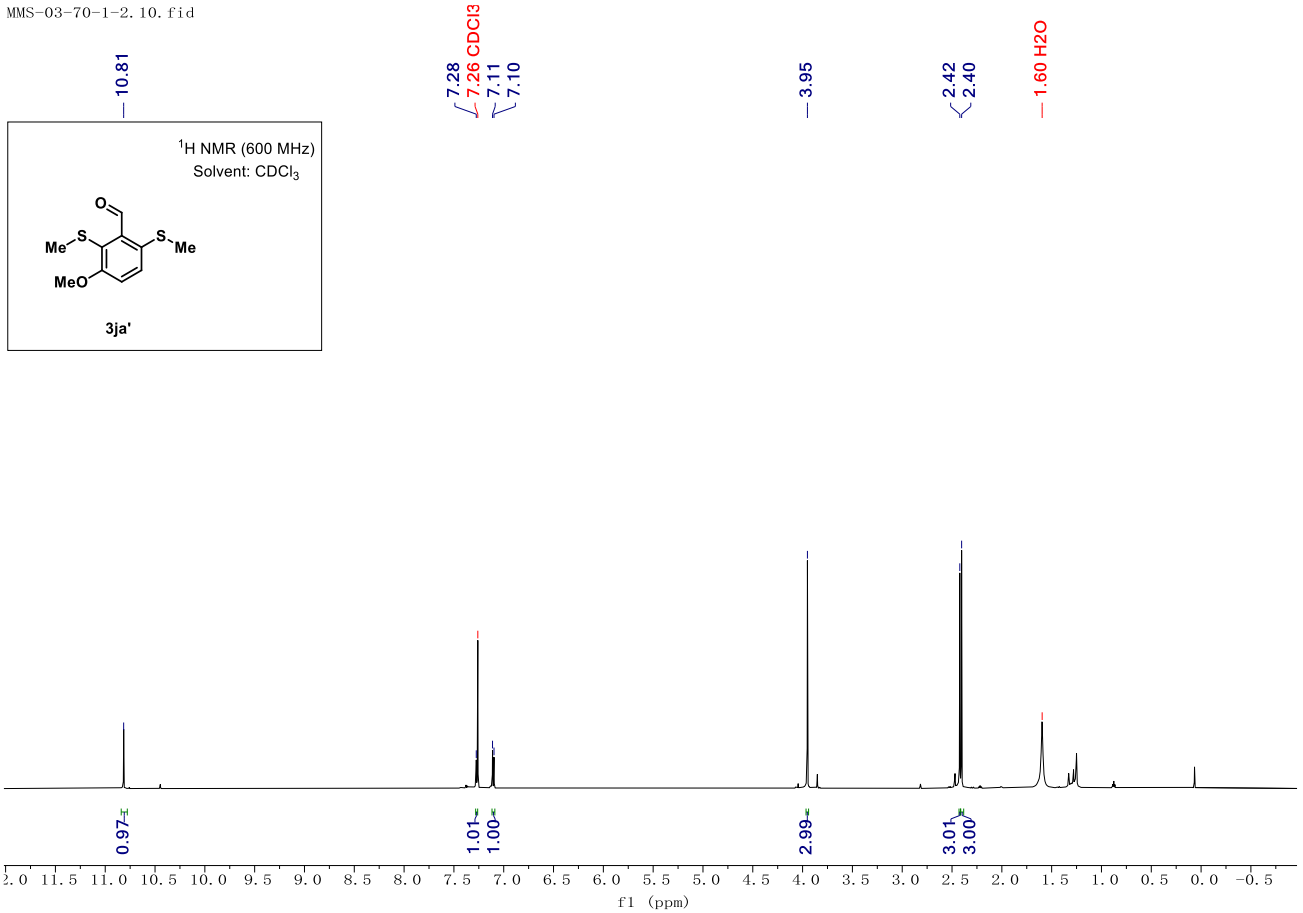
03-77-2.11.fid



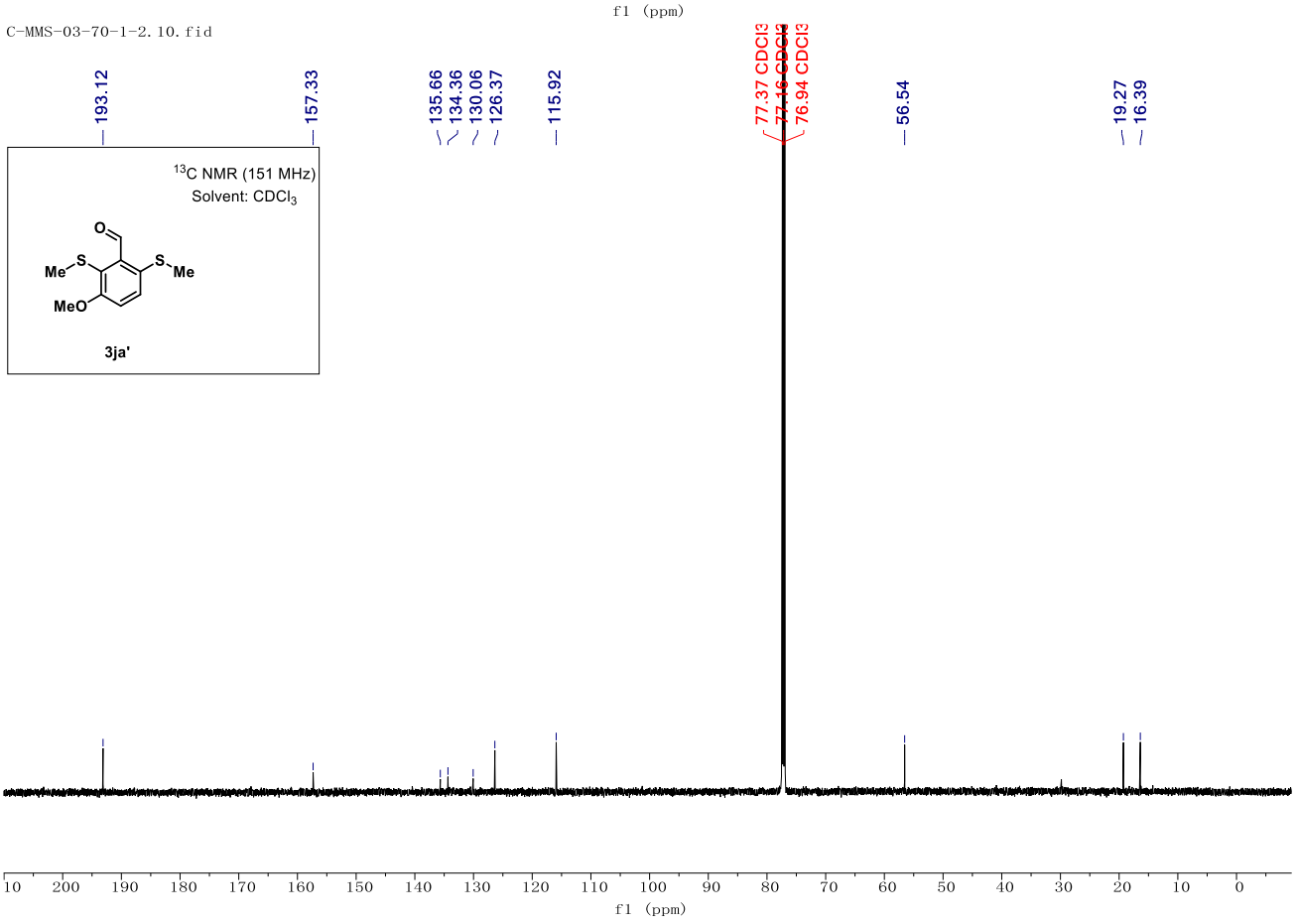

mms-03-70-1-1a.10.fid
10.45
7.38
7.37
7.36
7.26 CDCl3
7.13
7.13
7.12
7.11
3.85
2.47
1H NMR (600 MHz)
Solvent: CDCl3
O
S
Me
MeO
3ja
1.00
0.97
1.00
1.00
3.01
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

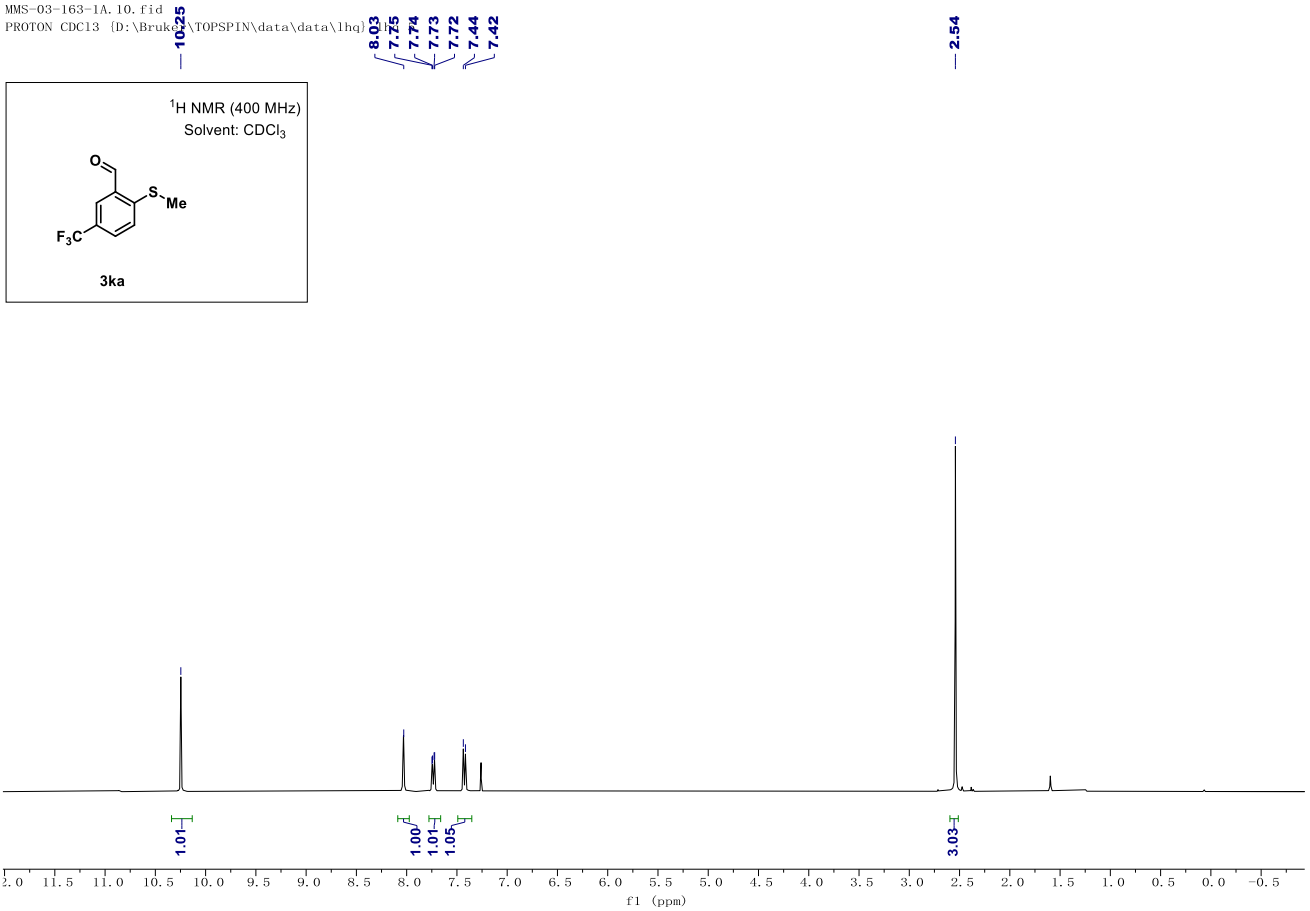

c-mms-03-70-1-1a.10.fid
191.45
158.33
135.31
134.09
130.99
122.00
113.98
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
55.79
18.25
13C NMR (151 MHz)
Solvent: CDCl3
O
S
Me
MeO
3ja
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

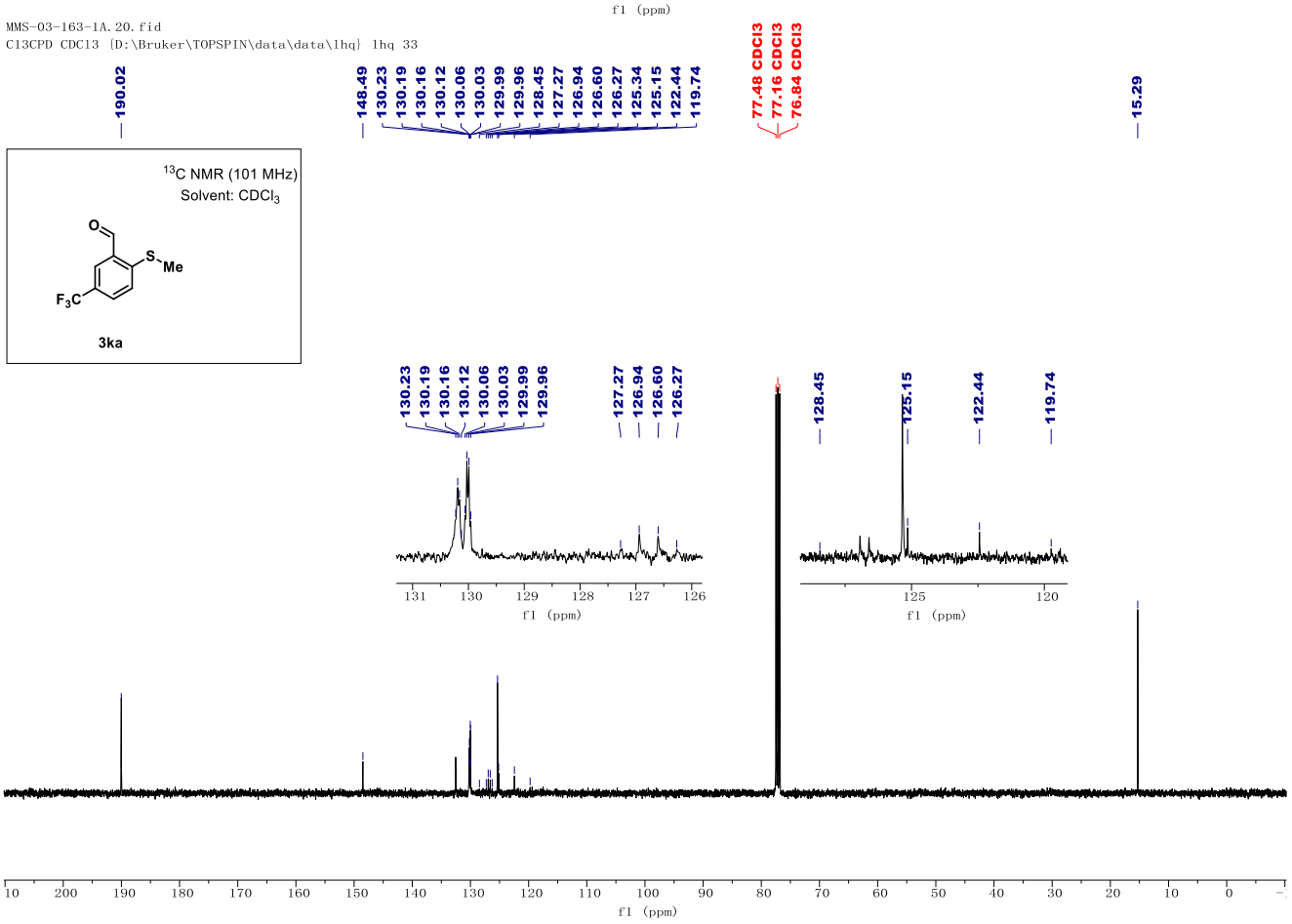
MMS-03-70-1-2.10.fid



C-MMS-03-70-1-2.10.fid



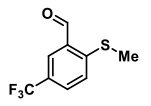

MMS-03-163-1A.10.fid
PROTON CDC13 {D:\Bruker\TOPSPIN\data\data\lhq}
10.25
8.03
7.75
7.74
7.73
7.72
7.44
7.42
2.54
1H NMR (400 MHz)
Solvent: CDCl3
O
S
Me
F3C
3ka
1.01
1.00
1.01
1.05
3.03
f1 (ppm)


MMS-03-163-1A.20.fid
C13CPD CDC13 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 33
190.02
148.49
130.23
130.19
130.16
130.12
130.06
130.03
129.99
129.96
128.45
127.27
126.94
126.60
126.27
125.34
125.15
122.44
119.74
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
15.29
13C NMR (101 MHz)
Solvent: CDCl3
O
S
Me
F3C
3ka
f1 (ppm)

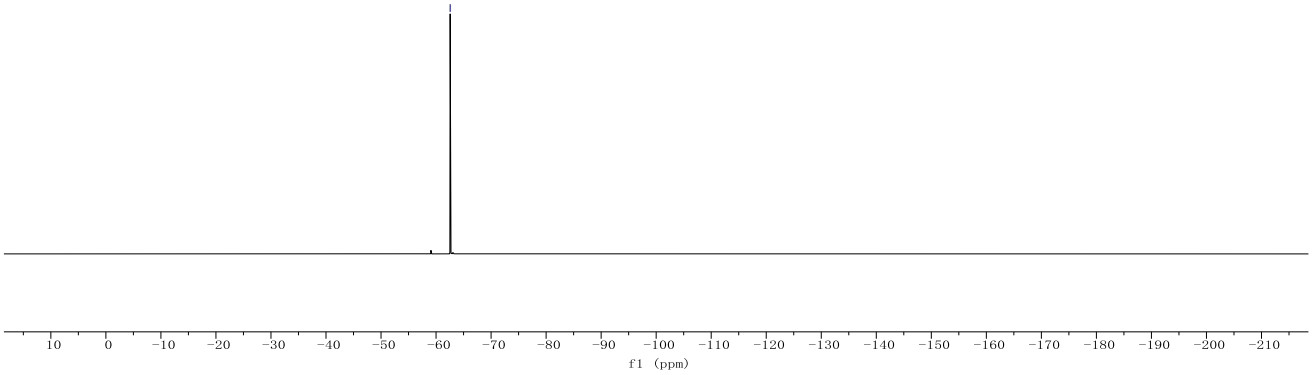
MMS-03-163-1A.11.fid
F19CPD CDC13 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 5

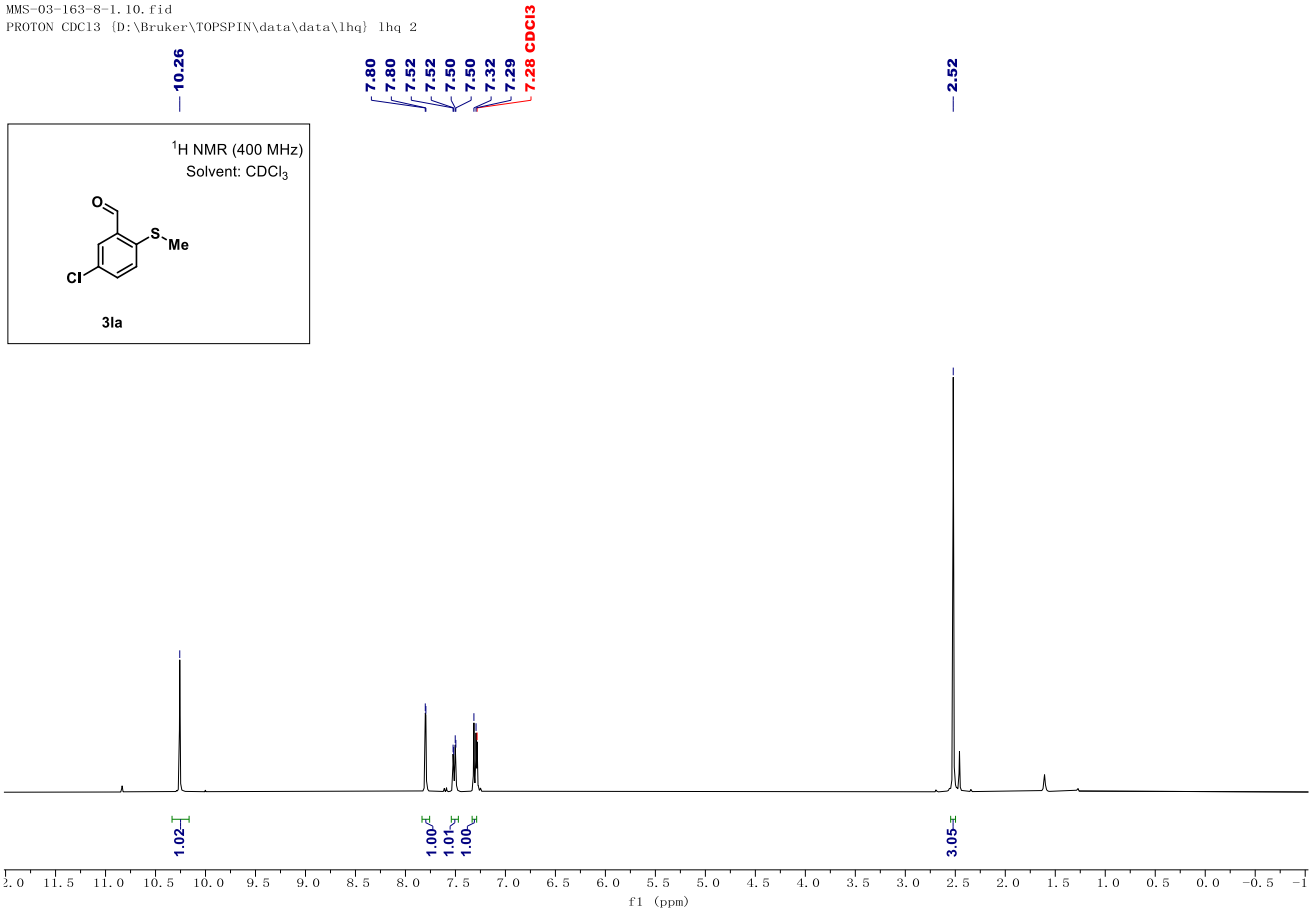
-62.56

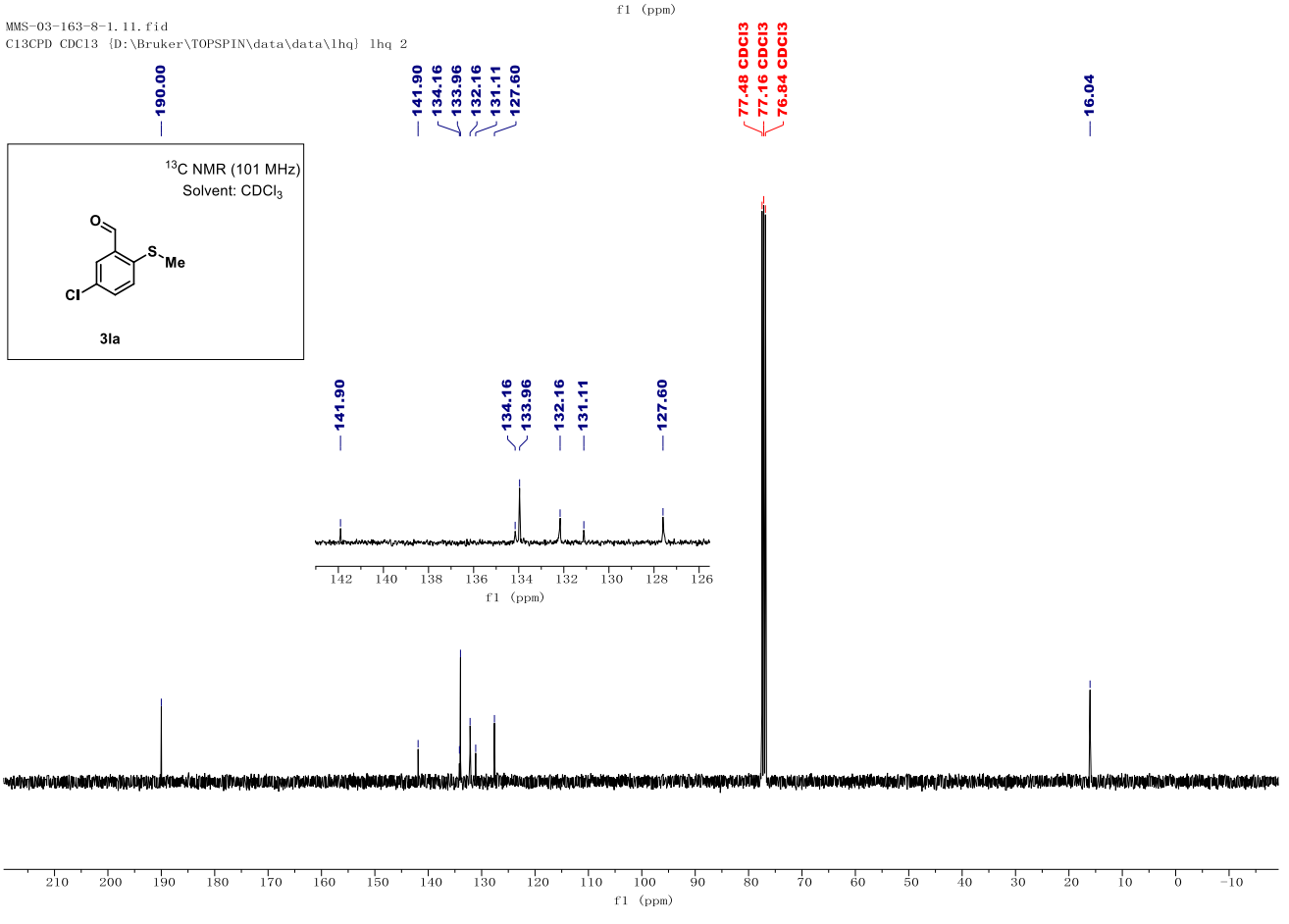
^{19}F NMR (376 MHz)
Solvent: $CDCl_3$

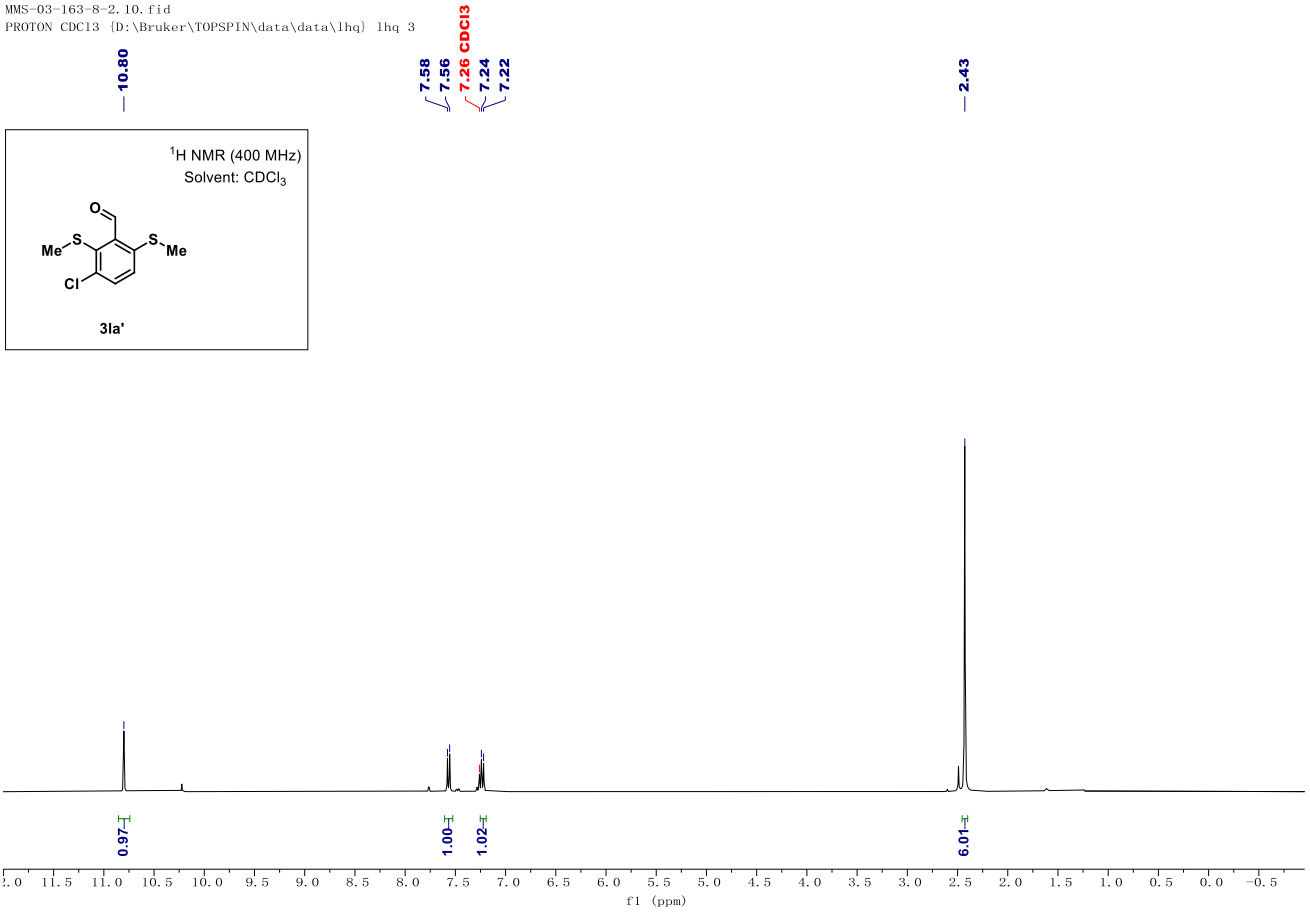


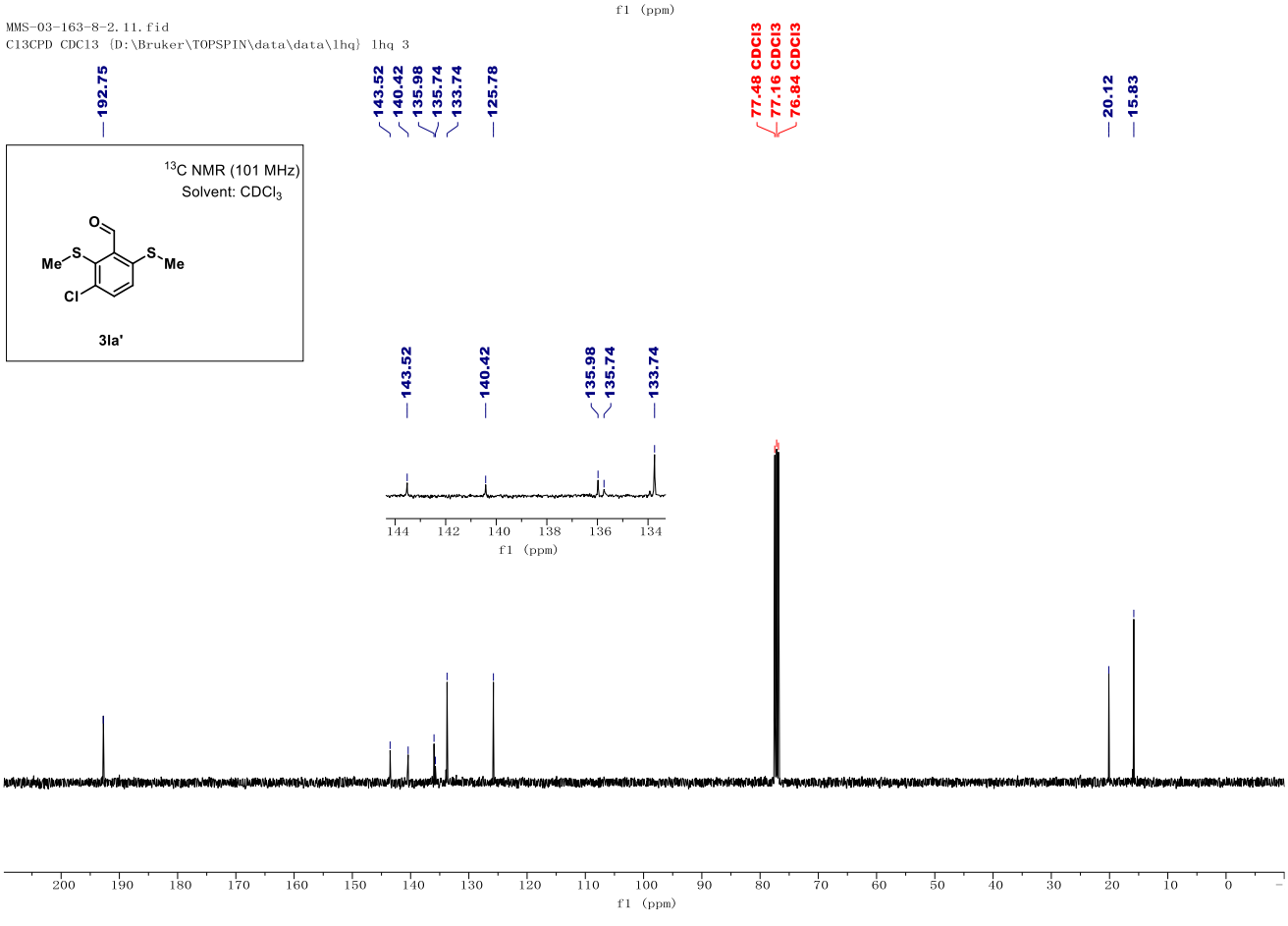
3ka

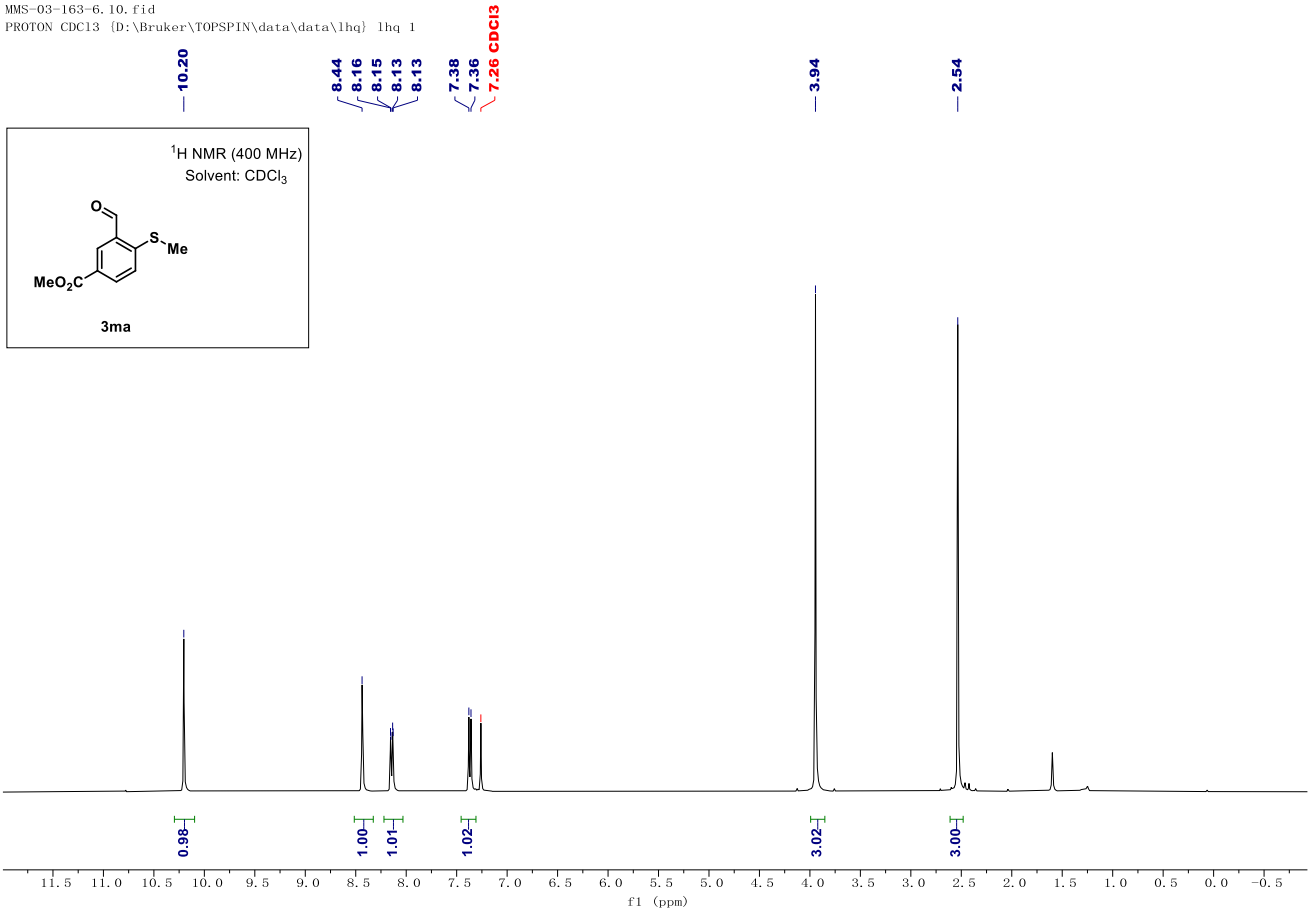


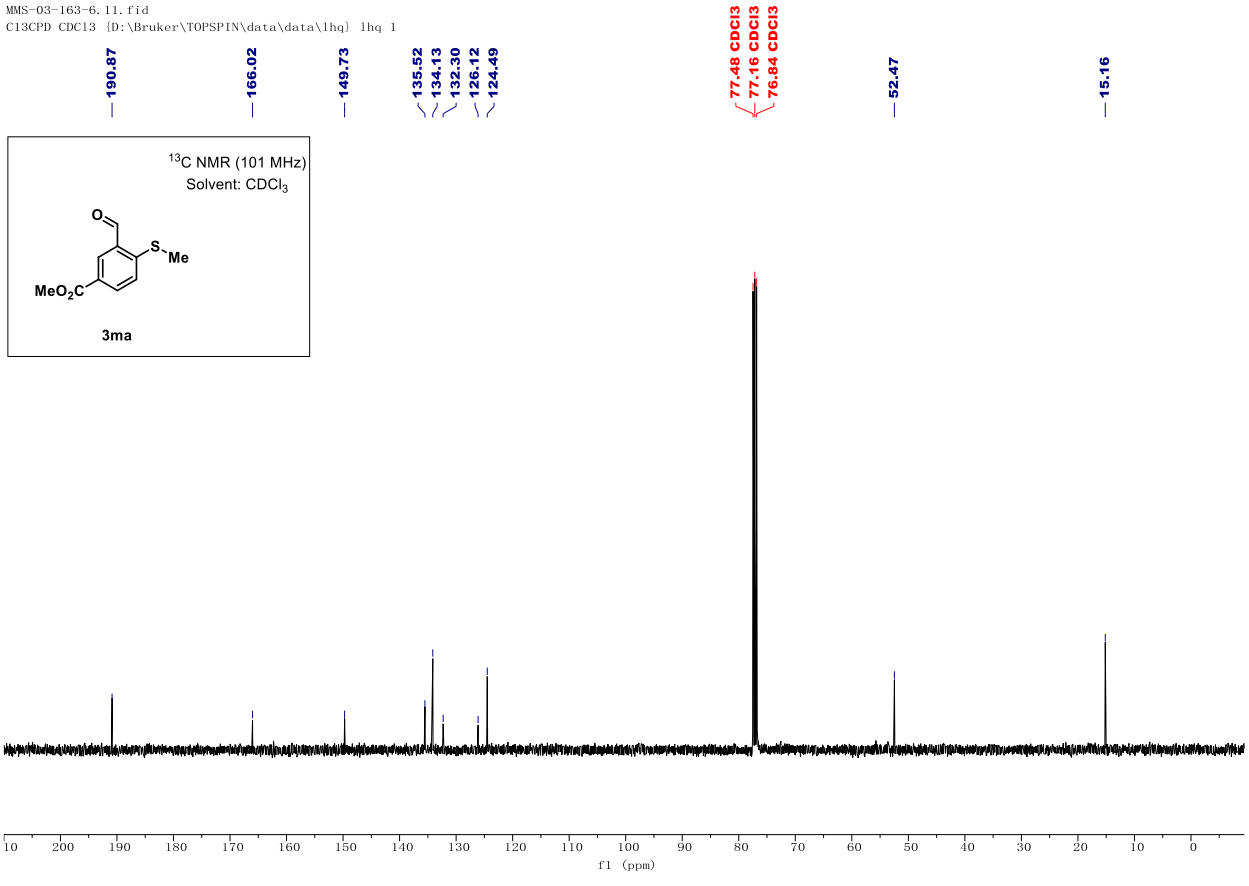

MMS-03-163-8-1.10.fid
PROTON CDCl3 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 2
10.26
7.80
7.80
7.52
7.52
7.50
7.50
7.32
7.29
7.28 CDCl3
2.52
1H NMR (400 MHz)
Solvent: CDCl3
O
S
Me
Cl
3la
1.02
1.00
1.01
1.00
3.05
f1 (ppm)


MMS-03-163-8-1.11.fid
C13CPD CDCl3 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 2
190.00
141.90
134.16
133.96
132.16
131.11
127.60
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
16.04
13C NMR (101 MHz)
Solvent: CDCl3
O
S
Me
Cl
3la
141.90
134.16
133.96
132.16
131.11
127.60
f1 (ppm)
f1 (ppm)

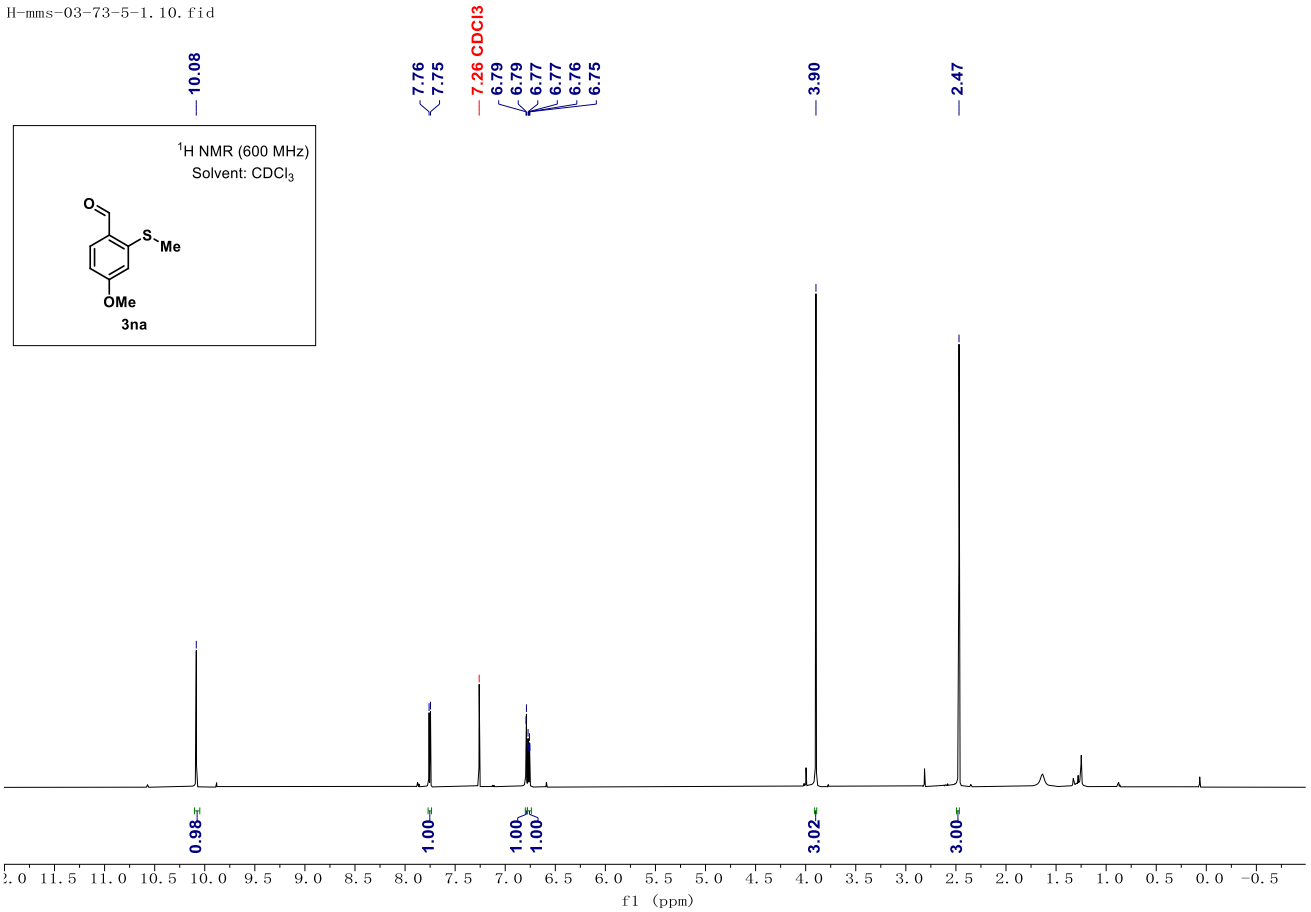

MMS-03-163-8-2.10.fid
PROTON CDC13 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 3
10.80
7.58
7.56
7.26 CDCl3
7.24
7.22
2.43
1H NMR (400 MHz)
Solvent: CDCl3
Me
S
S
Me
Cl
O
3la'
0.97
1.00
1.02
6.01
f1 (ppm)


MMS-03-163-8-2.11.fid
C13CPD CDC13 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 3
192.75
143.52
140.42
135.98
135.74
133.74
125.78
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
20.12
15.83
13C NMR (101 MHz)
Solvent: CDCl3
Me
S
S
Me
Cl
O
3la'
143.52
140.42
135.98
135.74
133.74
f1 (ppm)
f1 (ppm)

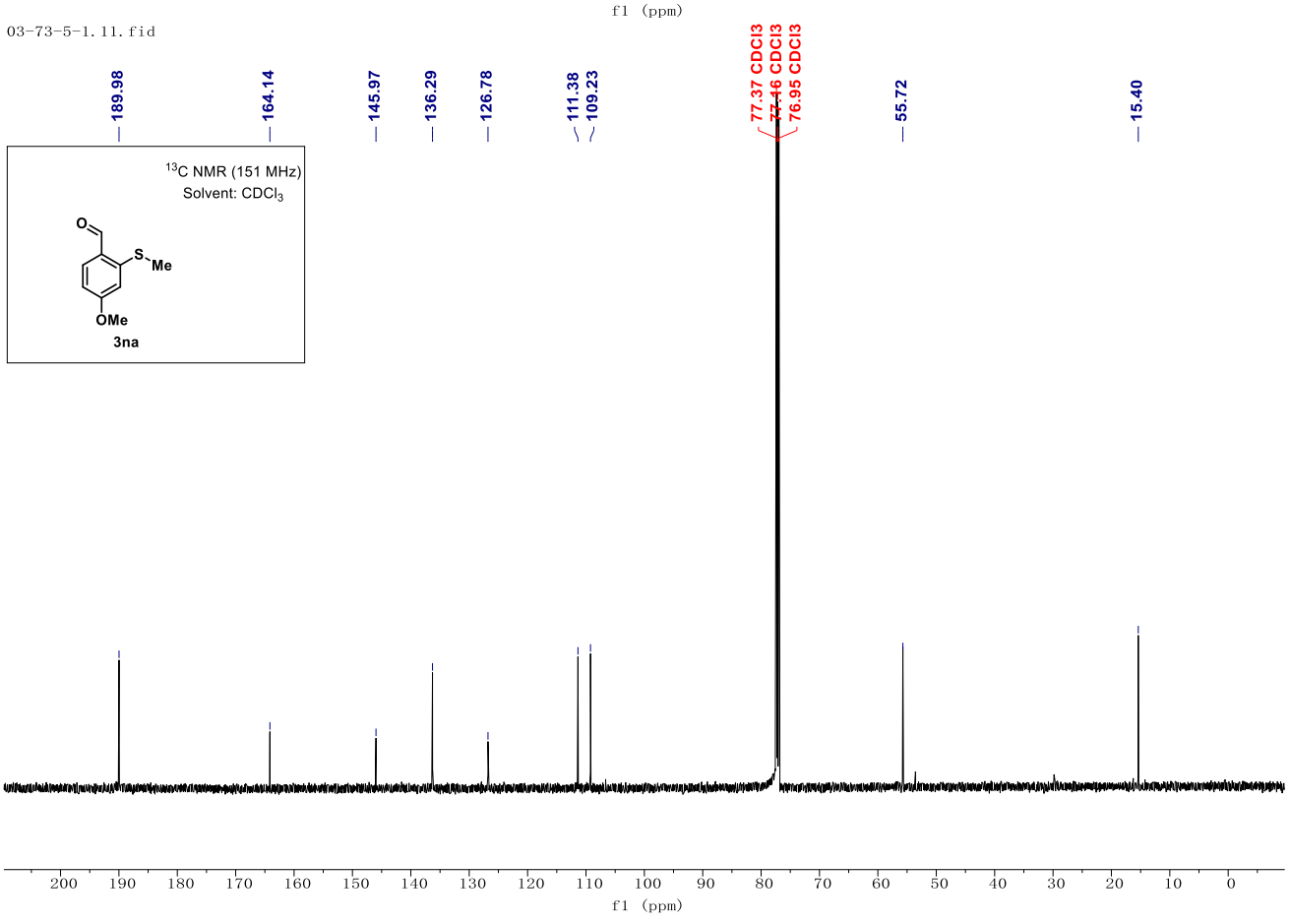

MMS-03-163-6.10.fid
PROTON CDCl3 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 1
10.20
8.44
8.16
8.15
8.13
8.13
7.38
7.36
7.26 CDCl3
3.94
2.54
1H NMR (400 MHz)
Solvent: CDCl3
O
S
Me
MeO2C
3ma
0.98
1.00
1.01
1.02
3.02
3.00
f1 (ppm)

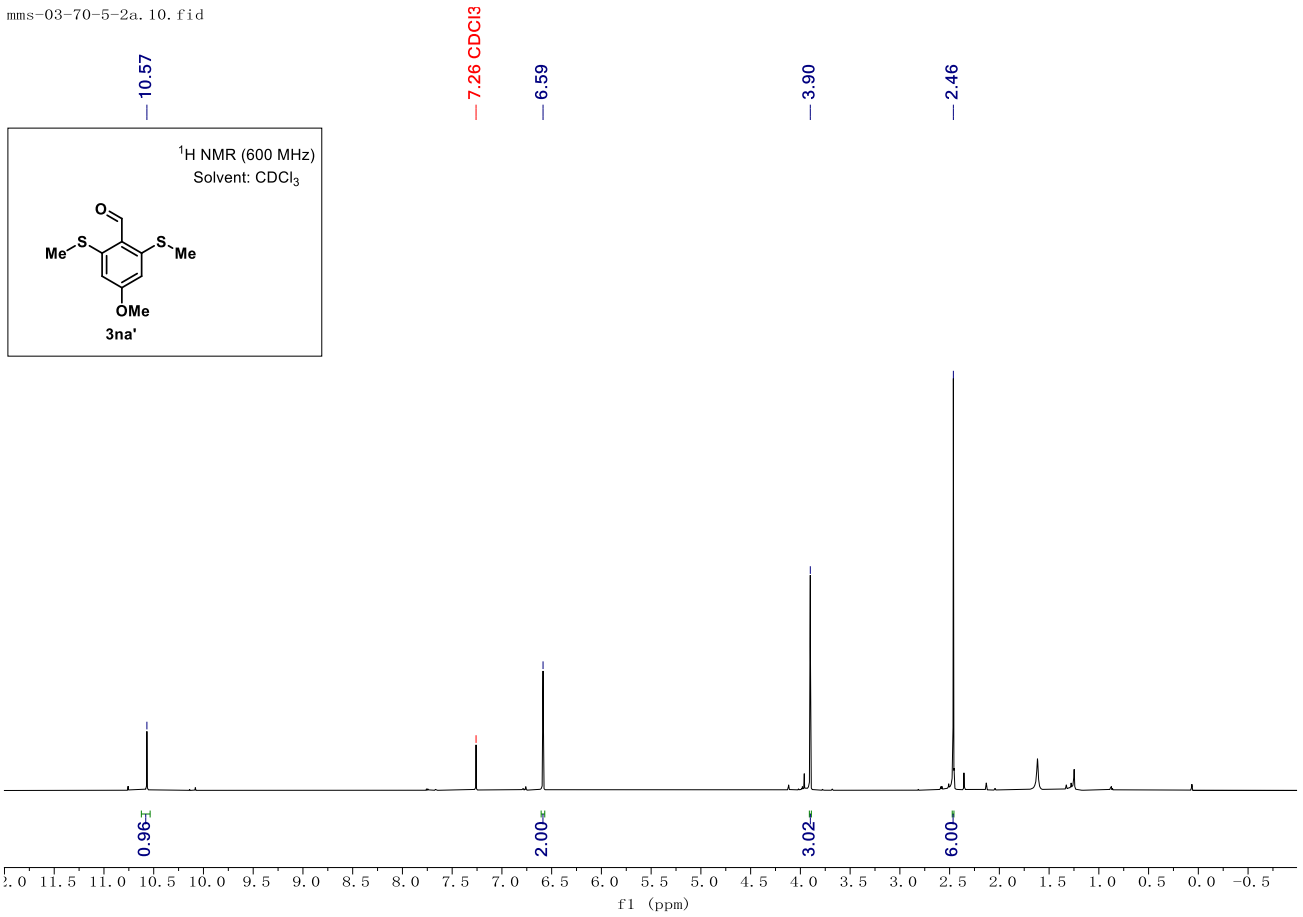

MMS-03-163-6.11.fid
C13CPD CDCl3 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 1
190.87
166.02
149.73
135.52
134.13
132.30
126.12
124.49
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
52.47
15.16
13C NMR (101 MHz)
Solvent: CDCl3
O
S
Me
MeO2C
3ma
f1 (ppm)

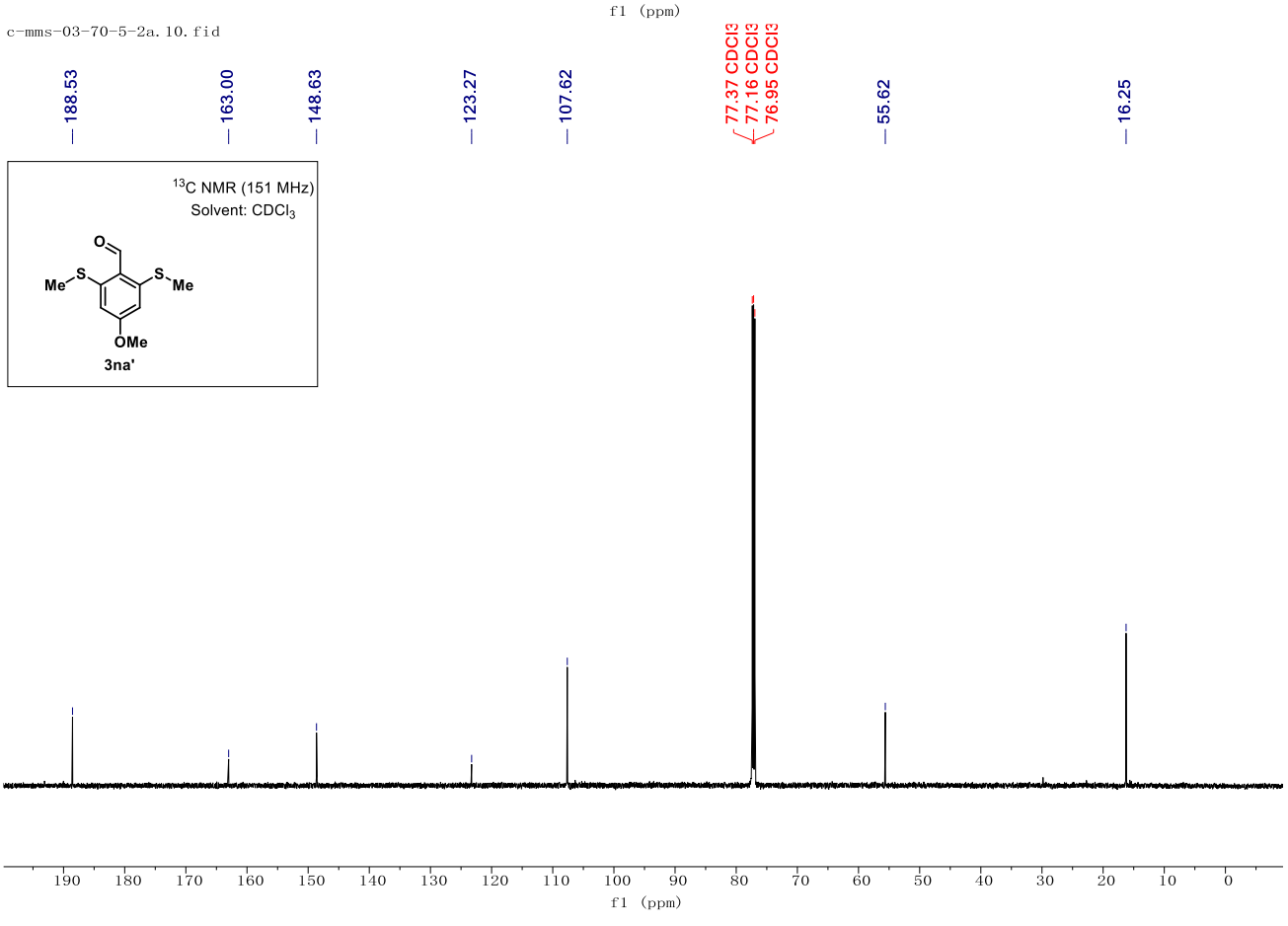
H-mms-03-73-5-1.10.fid



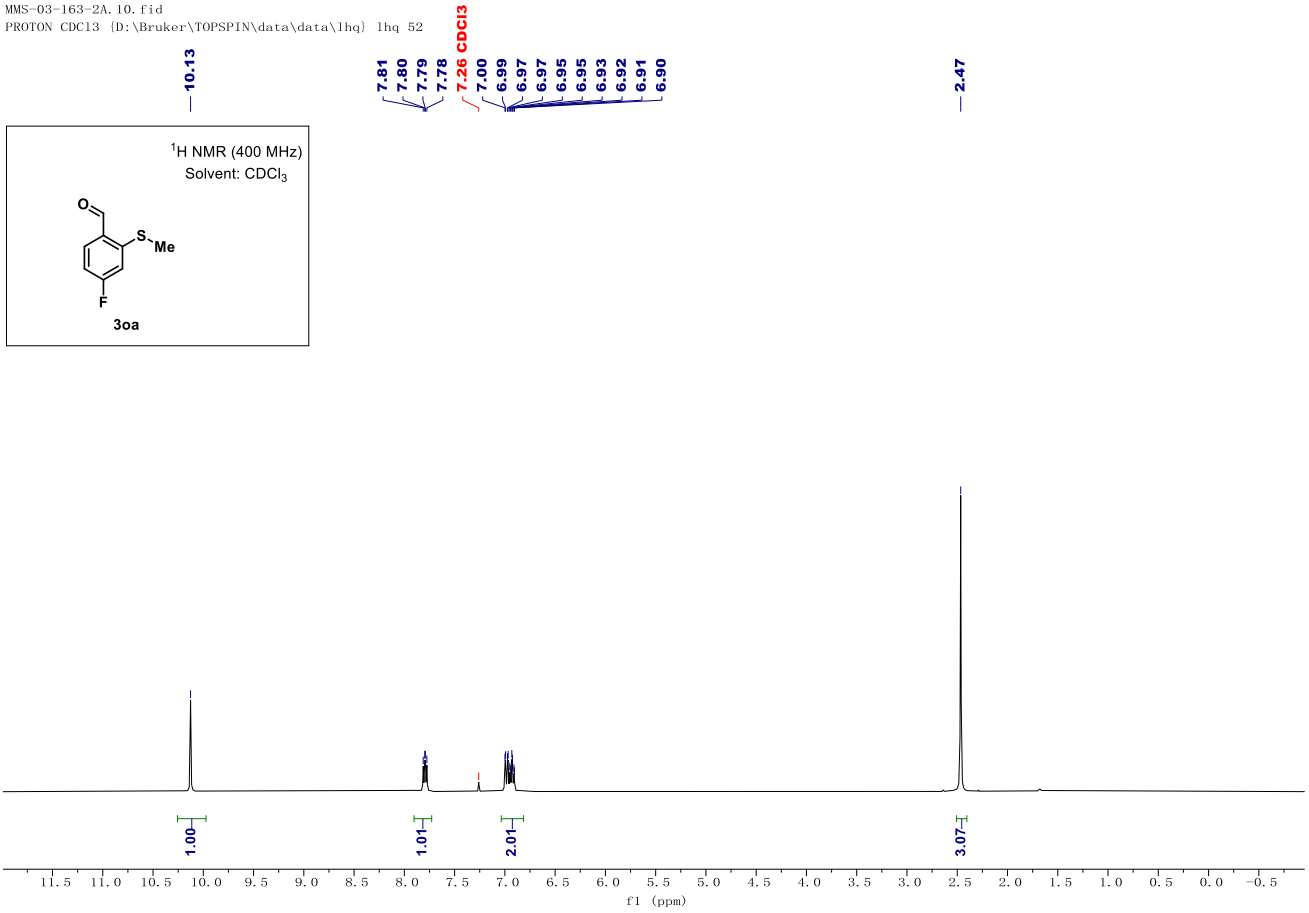
03-73-5-1.11.fid



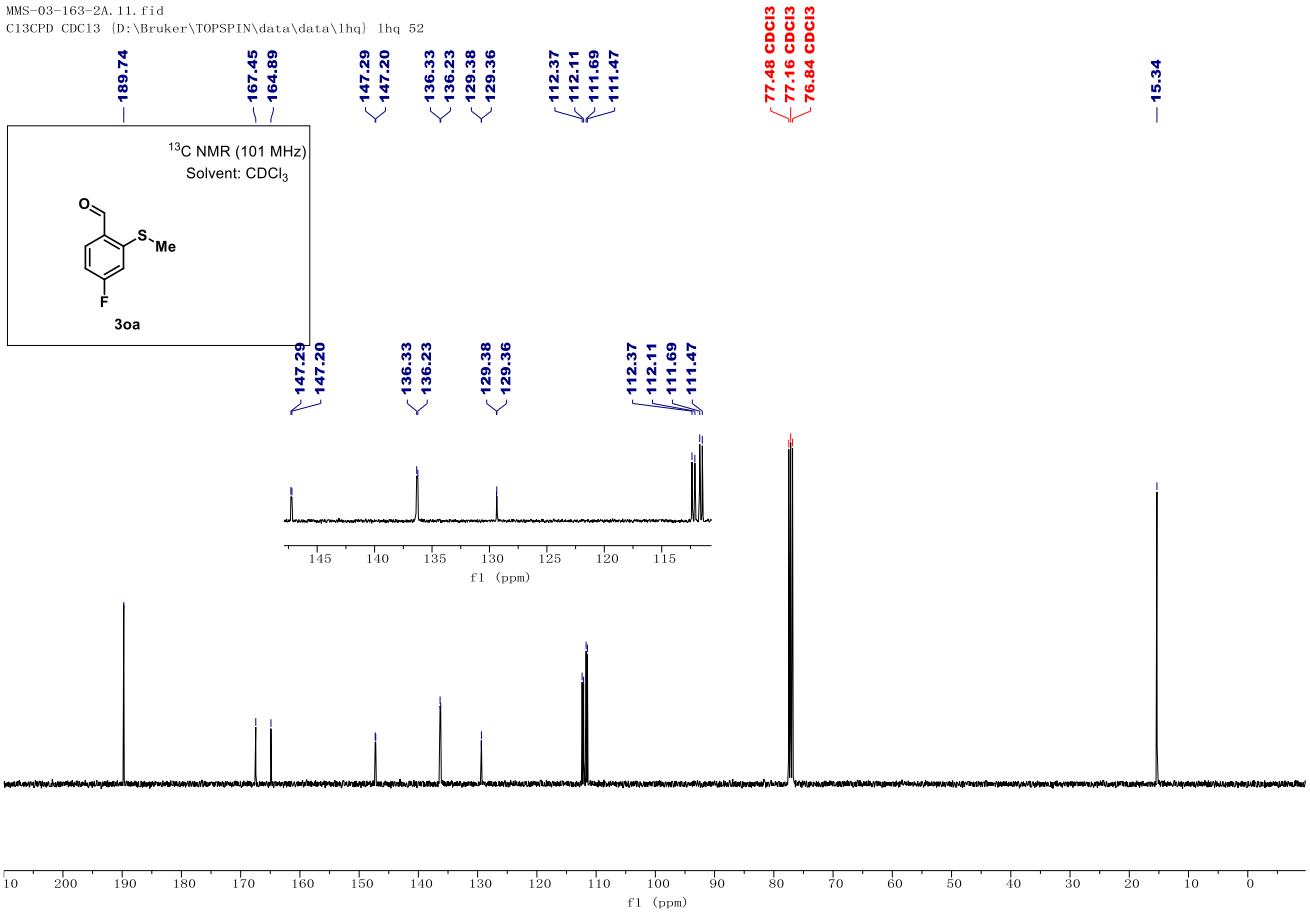

mms-03-70-5-2a.10.fid
10.57
7.26 CDCl3
6.59
3.90
2.46
1H NMR (600 MHz)
Solvent: CDCl3
Me
S
O
S
Me
OMe
3na'
0.96
2.00
3.02
6.00
f1 (ppm)


c-mms-03-70-5-2a.10.fid
188.53
163.00
148.63
123.27
107.62
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
55.62
16.25
13C NMR (151 MHz)
Solvent: CDCl3
Me
S
O
S
Me
OMe
3na'
f1 (ppm)

MMS-03-163-2A.10.fid
PROTON CDCl3 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 52



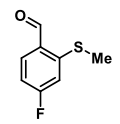
MMS-03-163-2A.11.fid
C13CPD CDCl3 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 52



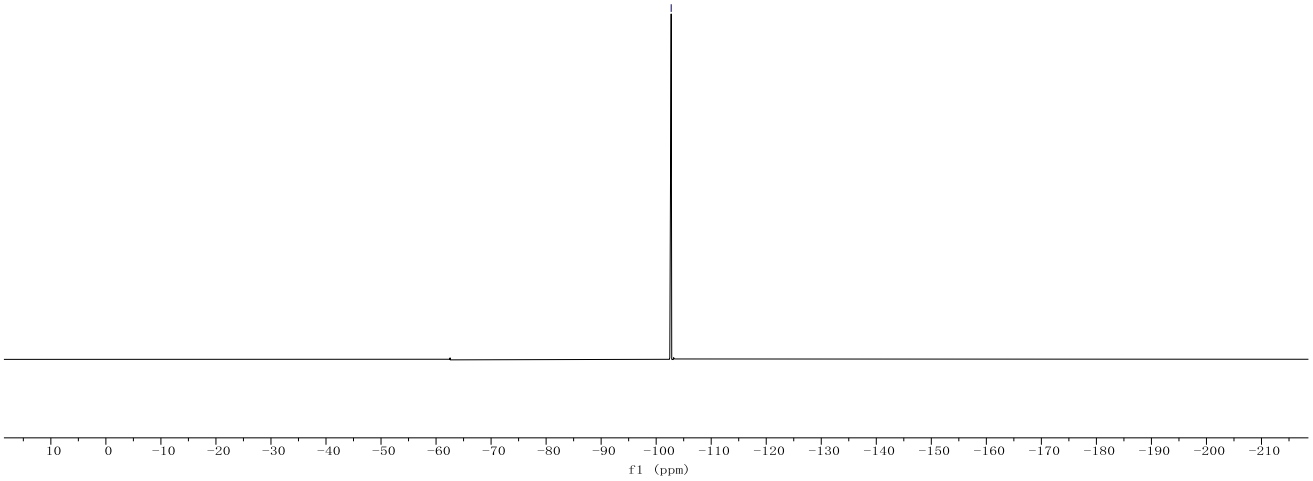
MMS-03-163-2A.12.fid
F19CPD CDCl3 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 52

-102.73

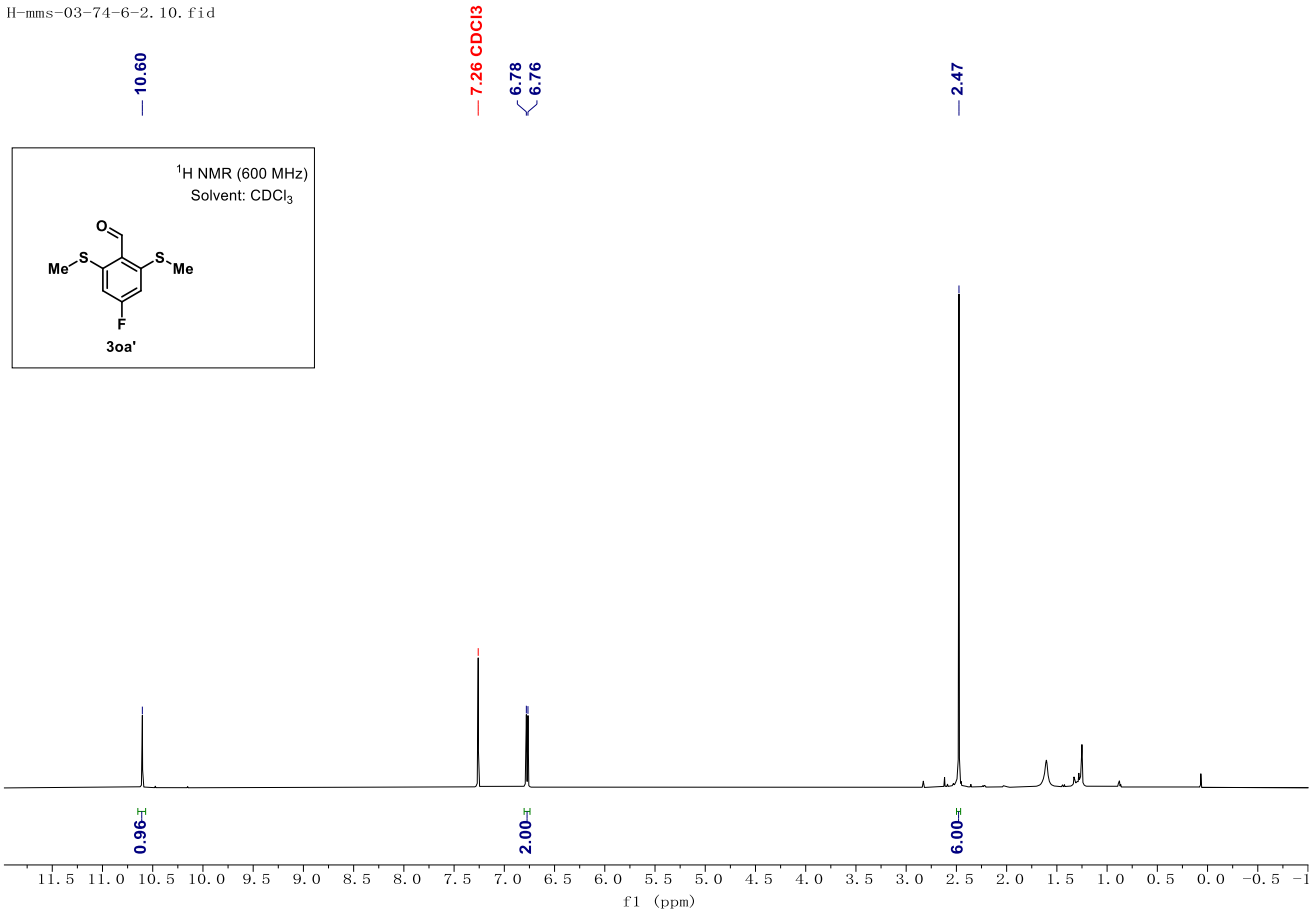
^{19}F NMR (376 MHz)
Solvent: $CDCl_3$



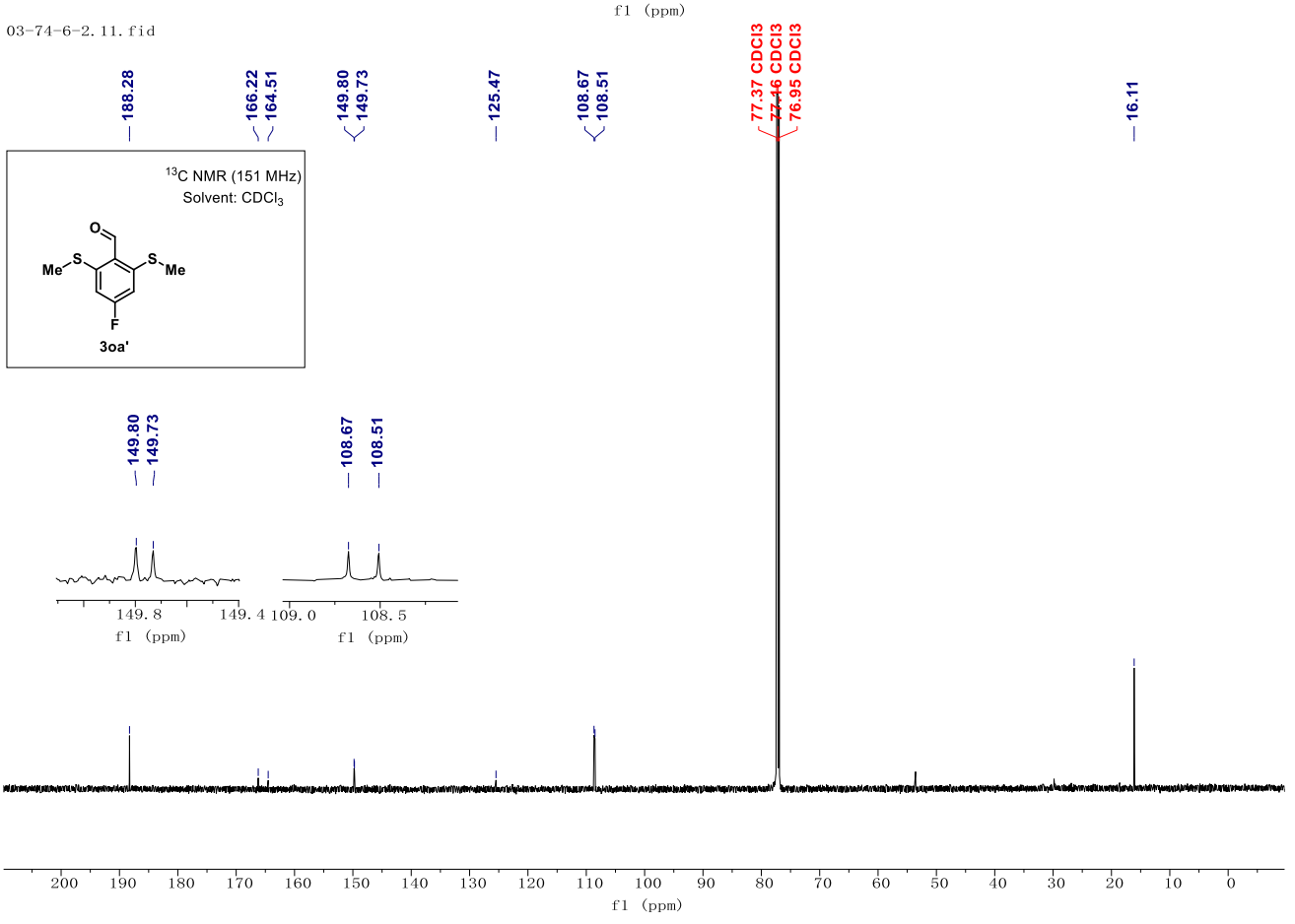
3oa



H-mms-03-74-6-2.10.fid



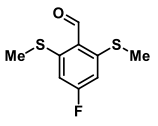
03-74-6-2.11.fid



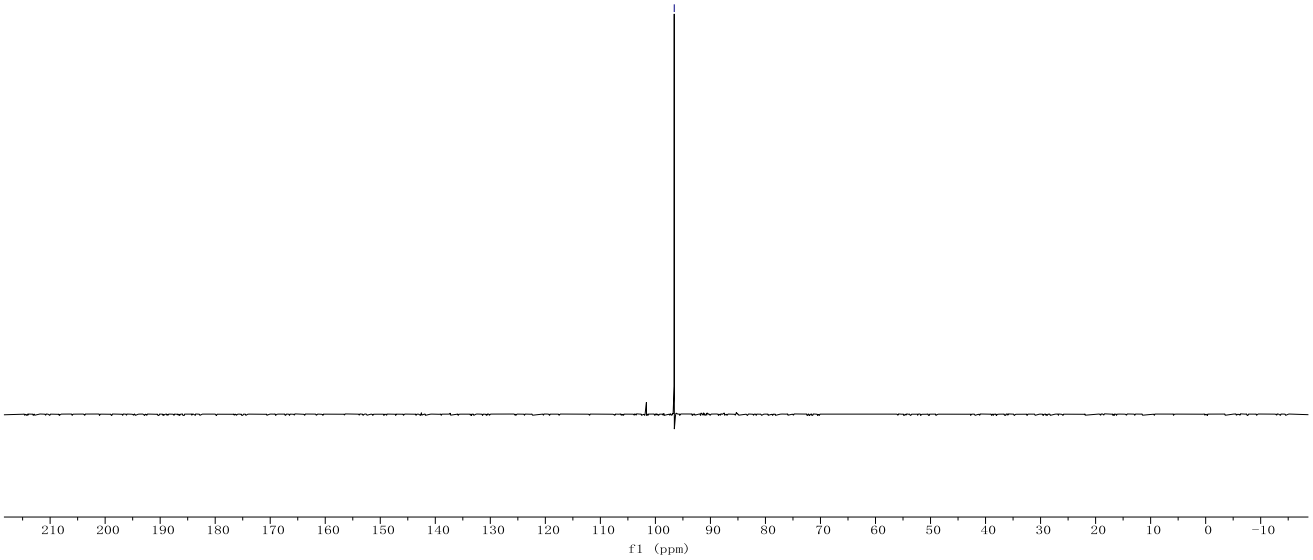
F-MMS-03-4F-2F.10.fid

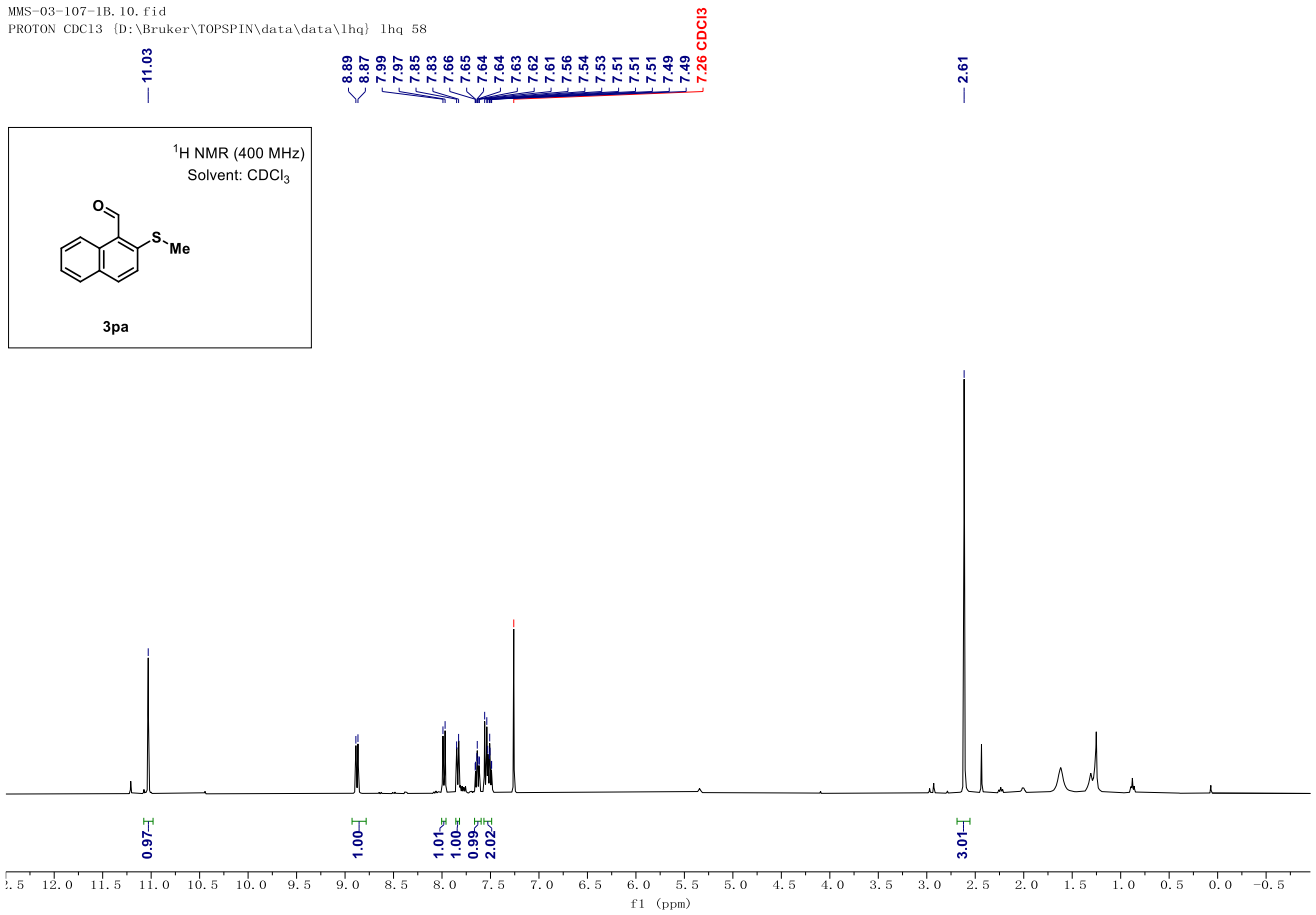
96.58

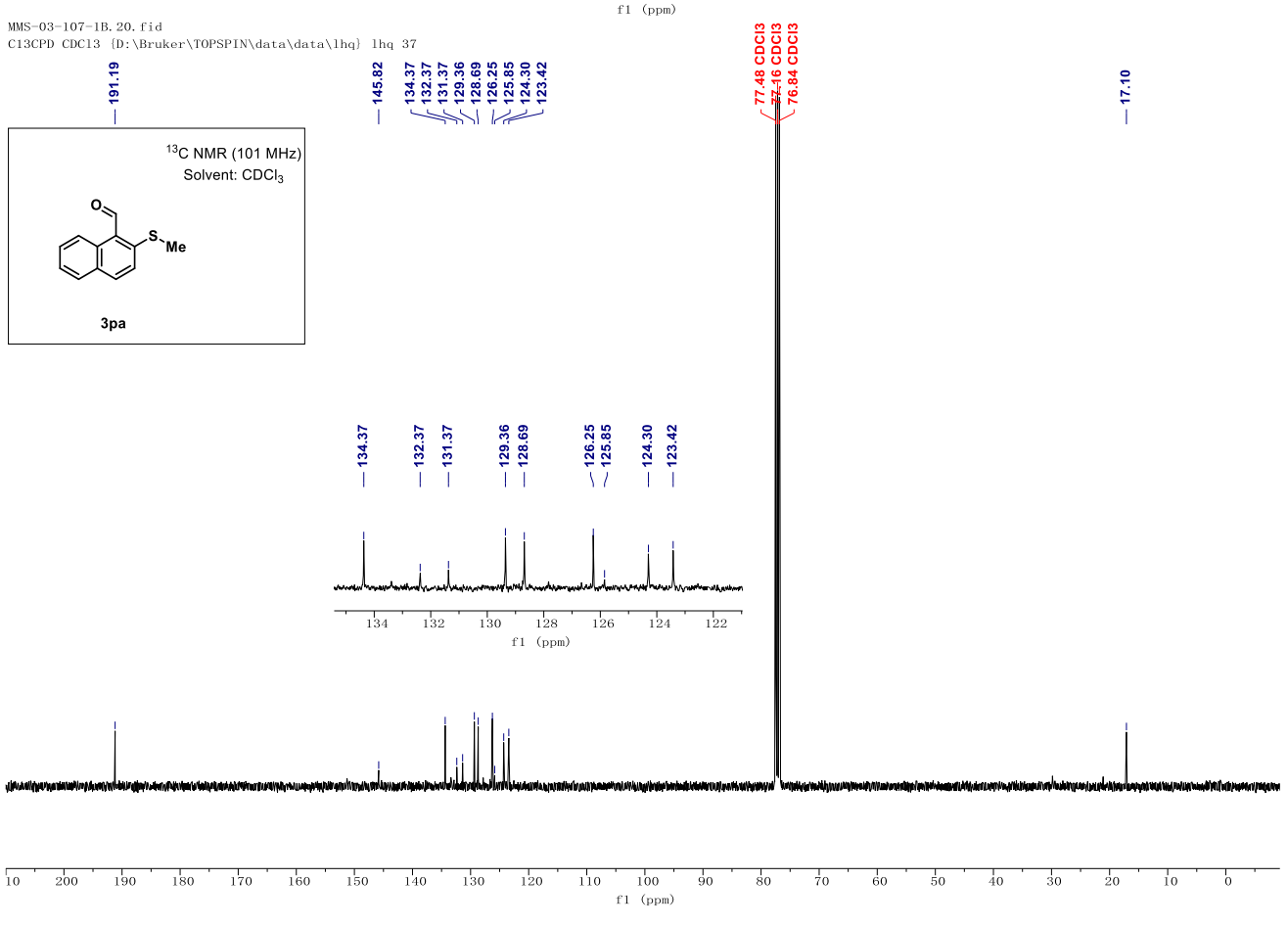
^{19}F NMR (565 MHz)
Solvent: $CDCl_3$

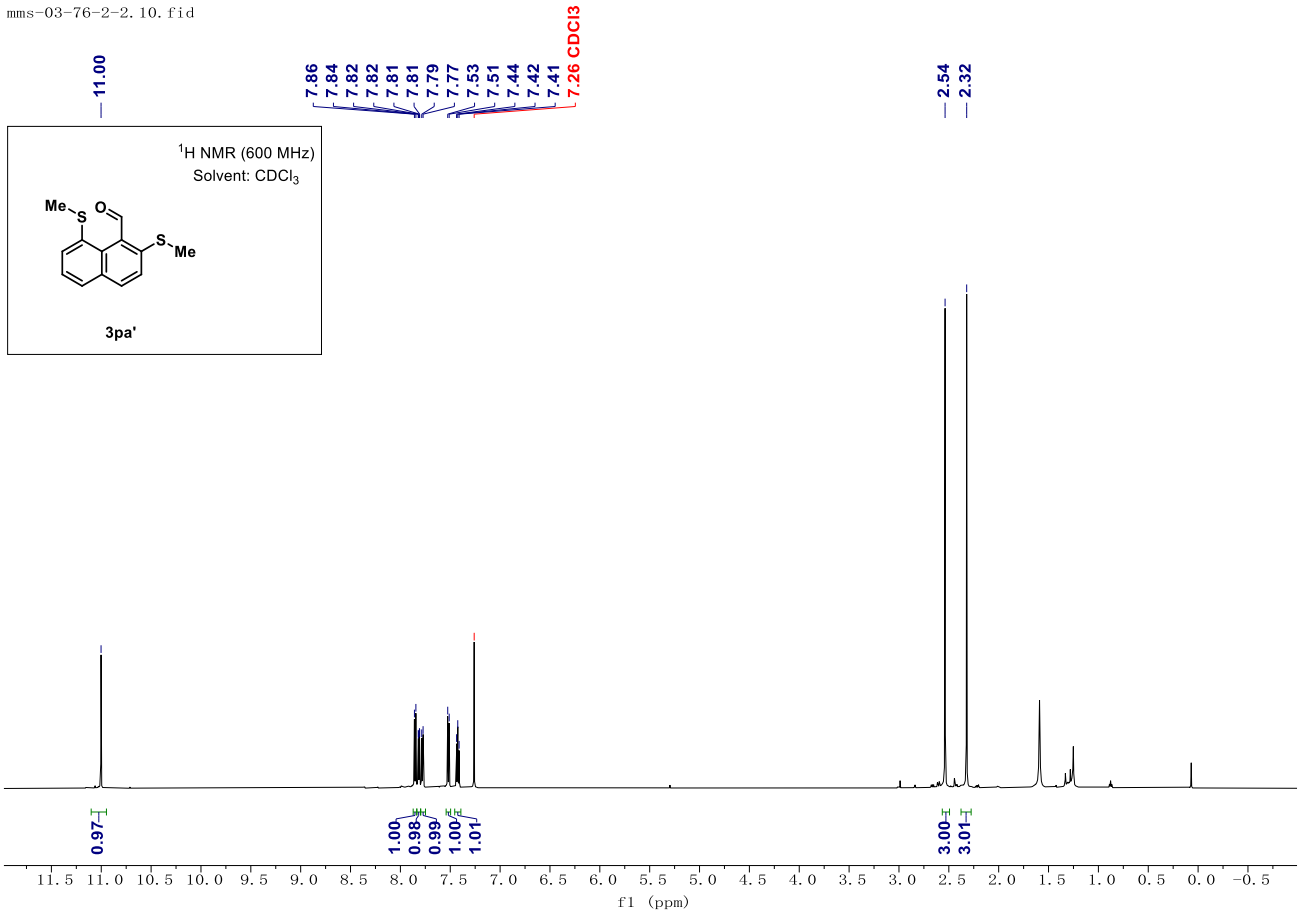


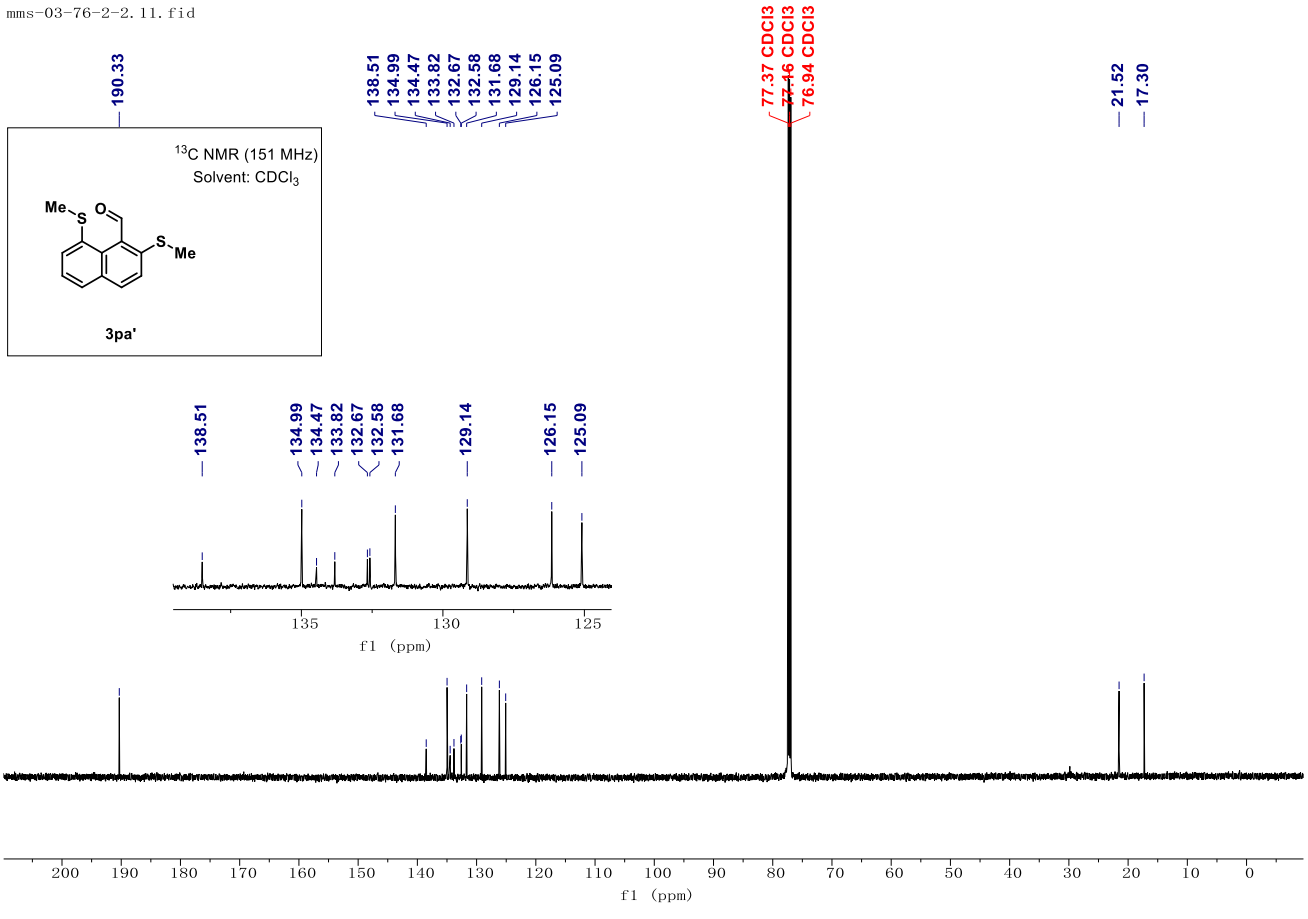
3oa'

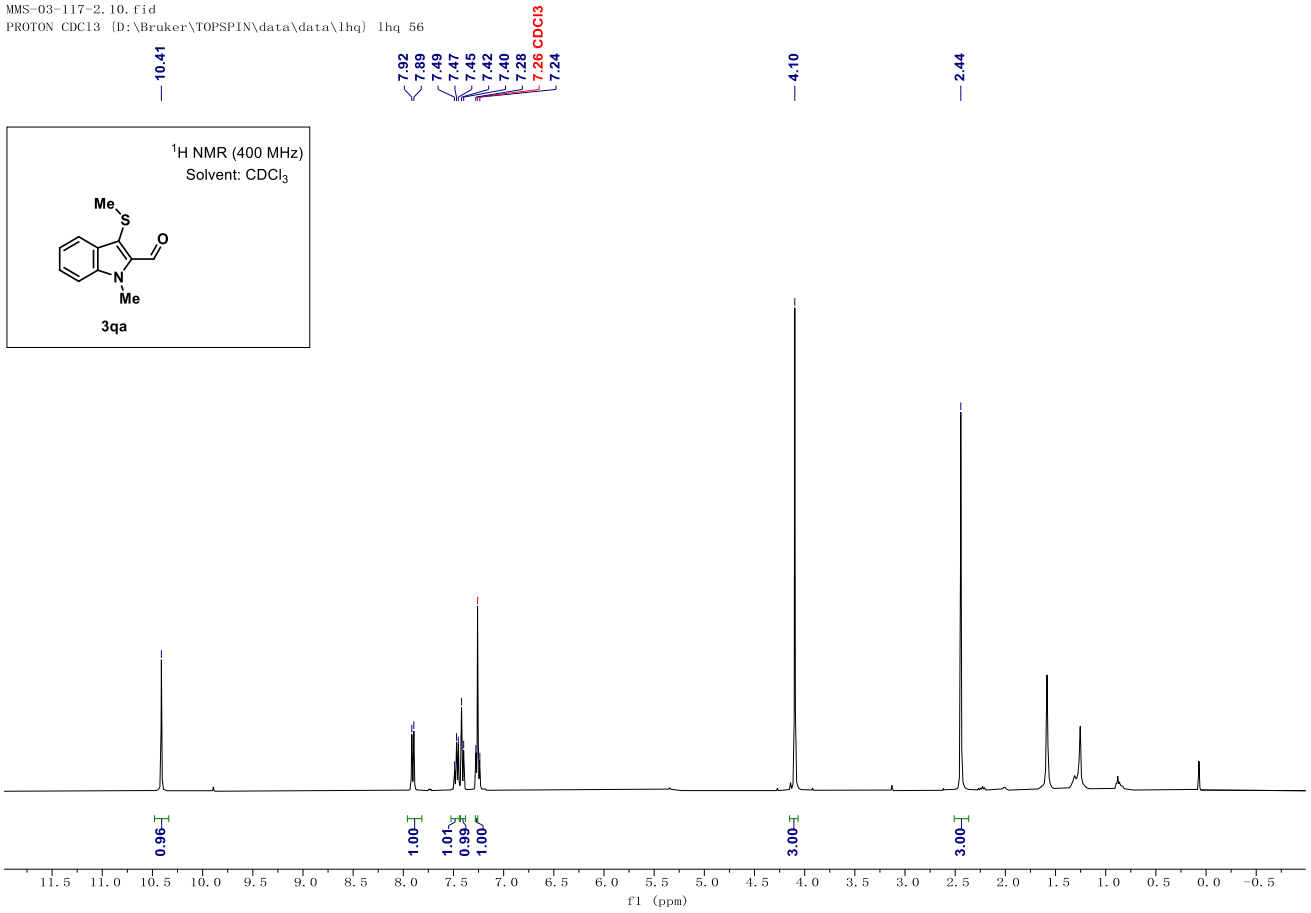


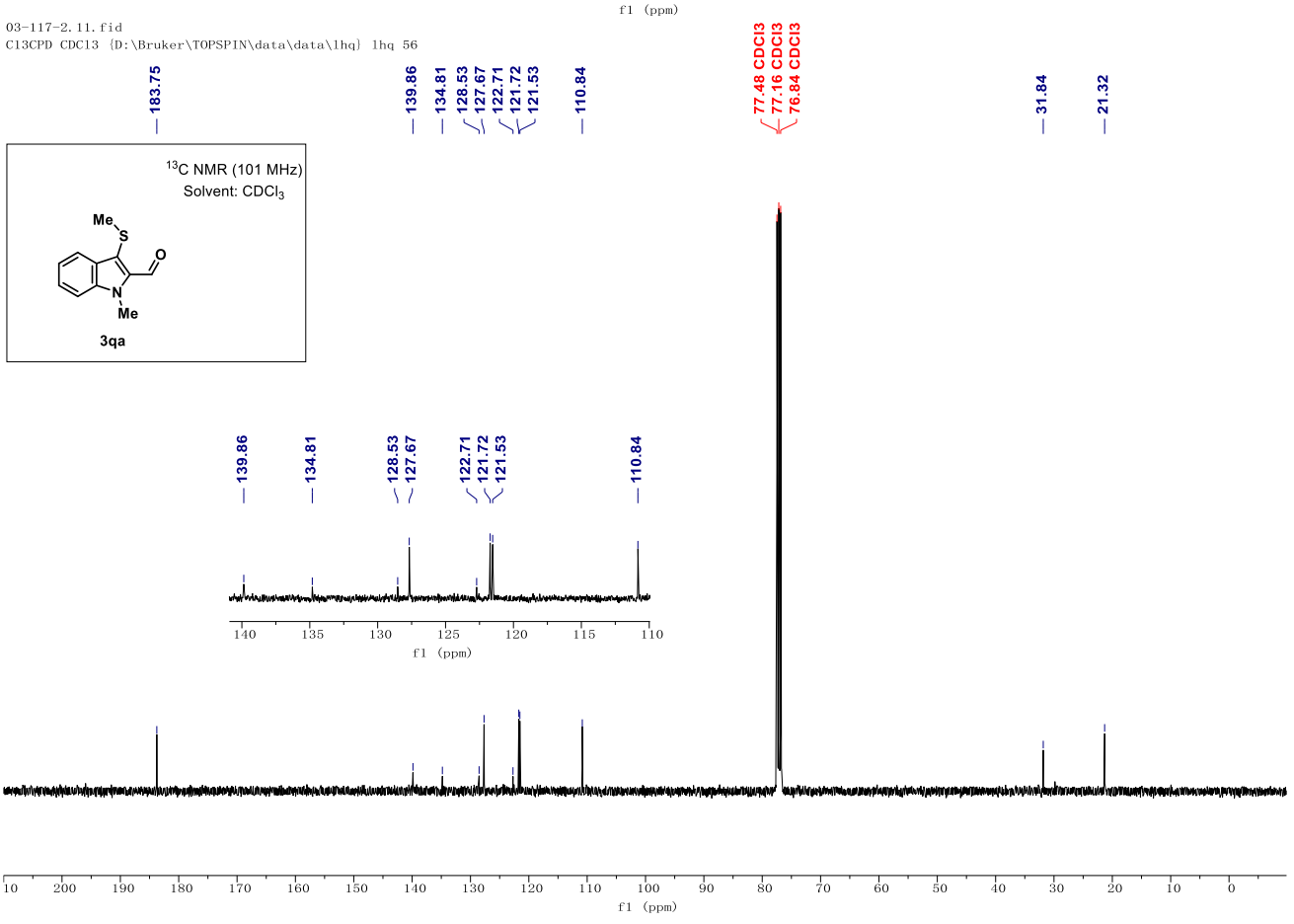

MMS-03-107-1B.10.fid
PROTON CDCl3 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 58
11.03
8.89
8.87
7.99
7.97
7.85
7.83
7.66
7.65
7.64
7.64
7.63
7.62
7.61
7.56
7.54
7.53
7.51
7.51
7.51
7.49
7.49
7.26 CDCl3
2.61
1H NMR (400 MHz)
Solvent: CDCl3
O
S
Me
3pa
0.97
1.00
1.01
1.00
0.99
2.02
3.01
f1 (ppm)

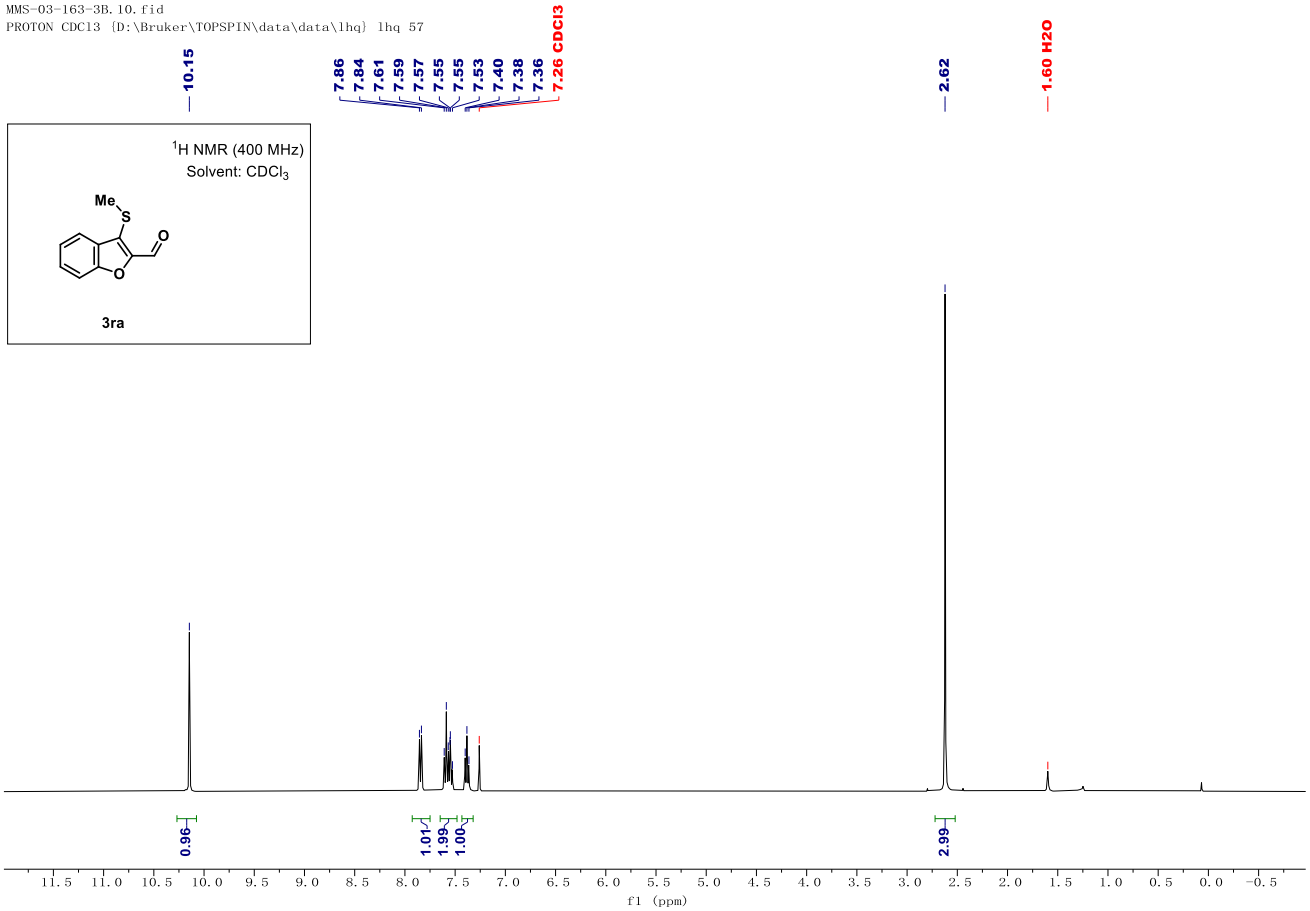

MMS-03-107-1B.20.fid
C13CPD CDCl3 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 37
191.19
145.82
134.37
132.37
131.37
129.36
128.69
126.25
125.85
124.30
123.42
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
17.10
13C NMR (101 MHz)
Solvent: CDCl3
O
S
Me
3pa
f1 (ppm)

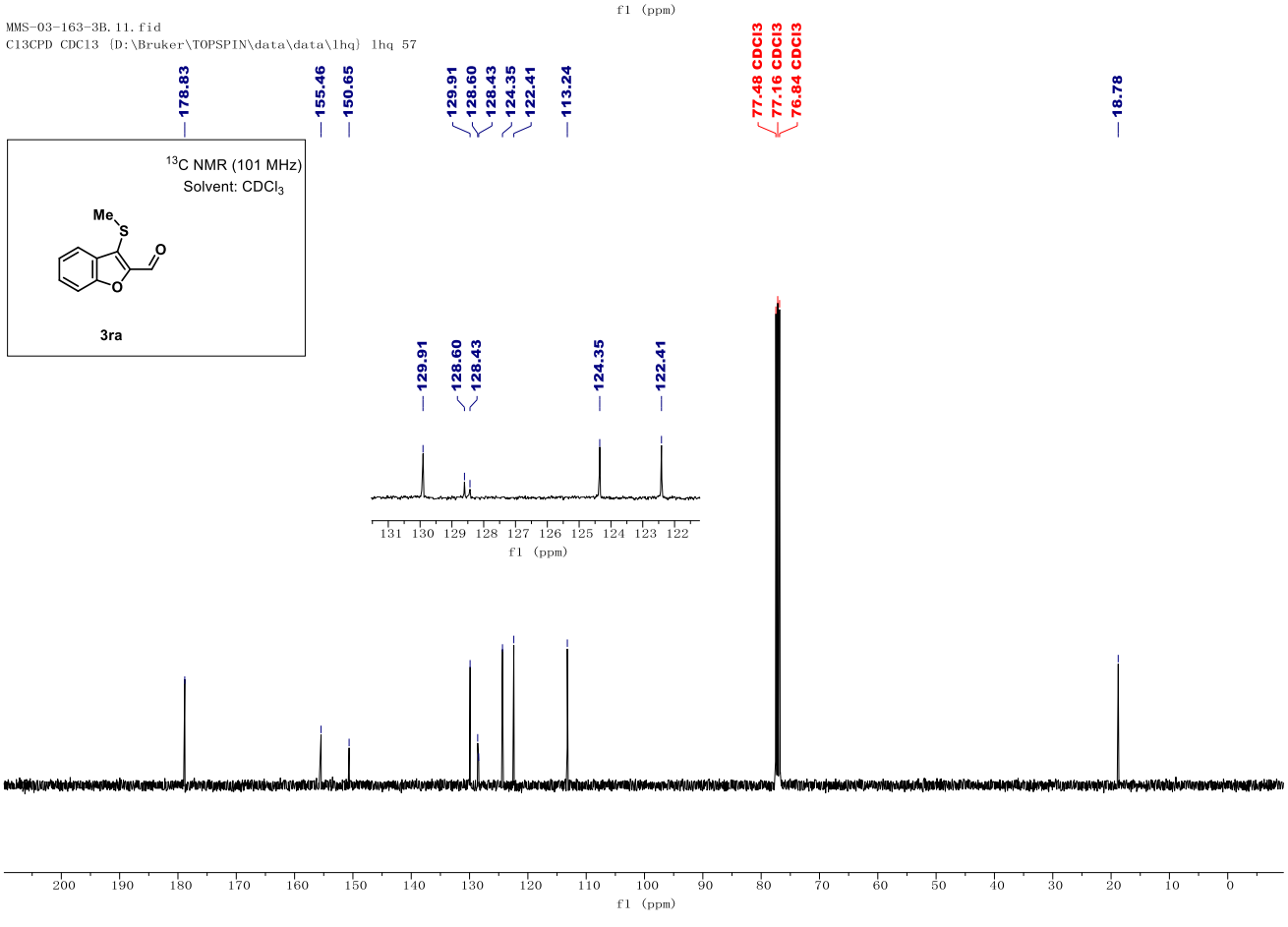

mms-03-76-2-2.10.fid
11.00
7.86
7.84
7.82
7.82
7.81
7.81
7.79
7.77
7.53
7.51
7.44
7.42
7.41
7.26 CDCl3
2.54
2.32
^{1}H NMR (600 MHz)
Solvent: CDCl$_3$
Me
S
O
S
Me
3pa'
0.97
1.00
0.98
0.99
1.00
1.01
3.00
3.01
f1 (ppm)

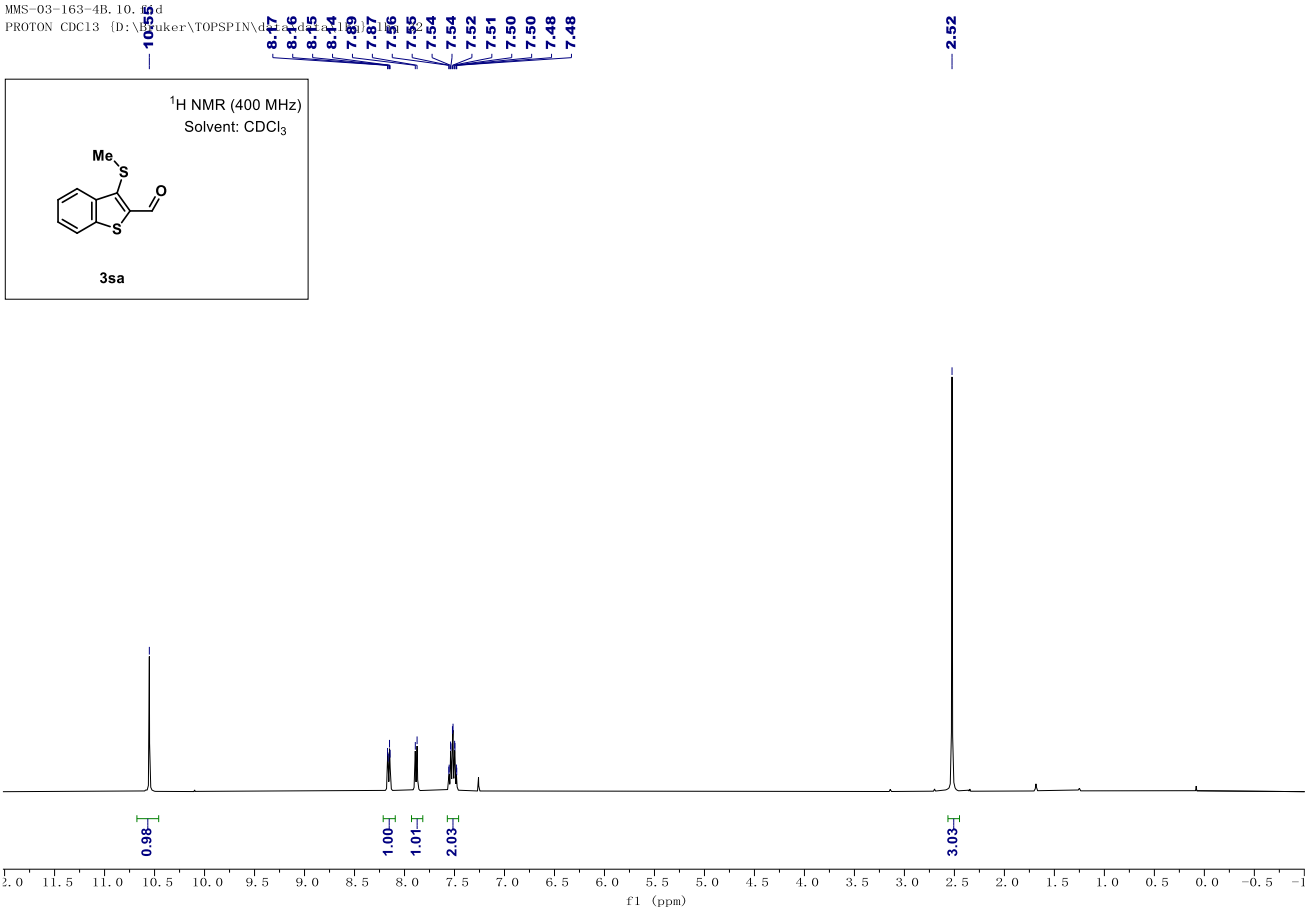

mms-03-76-2-2.11.fid
190.33
138.51
134.99
134.47
133.82
132.67
132.58
131.68
129.14
126.15
125.09
77.37 CDCl3
77.16 CDCl3
76.94 CDCl3
21.52
17.30
^{13}C NMR (151 MHz)
Solvent: CDCl$_3$
Me
S
O
S
Me
3pa'
f1 (ppm)
f1 (ppm)

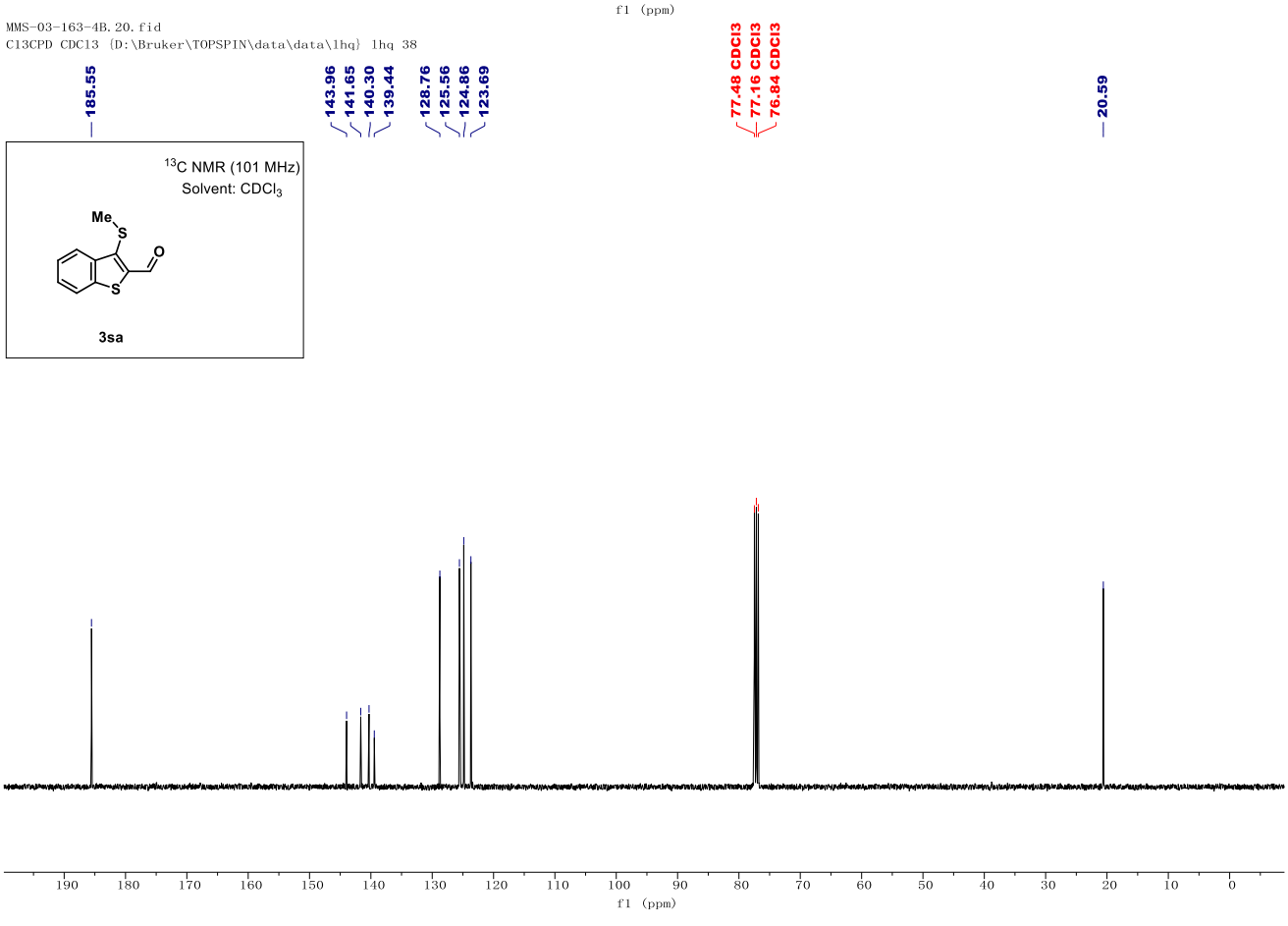

MMS-03-117-2.10.fid
PROTON CDCl3 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 56
10.41
7.92
7.89
7.49
7.47
7.45
7.42
7.40
7.28
7.26 CDCl3
7.24
4.10
2.44
1H NMR (400 MHz)
Solvent: CDCl3
Me
S
O
N
Me
3qa
0.96
1.00
1.01
0.99
1.00
3.00
3.00
f1 (ppm)

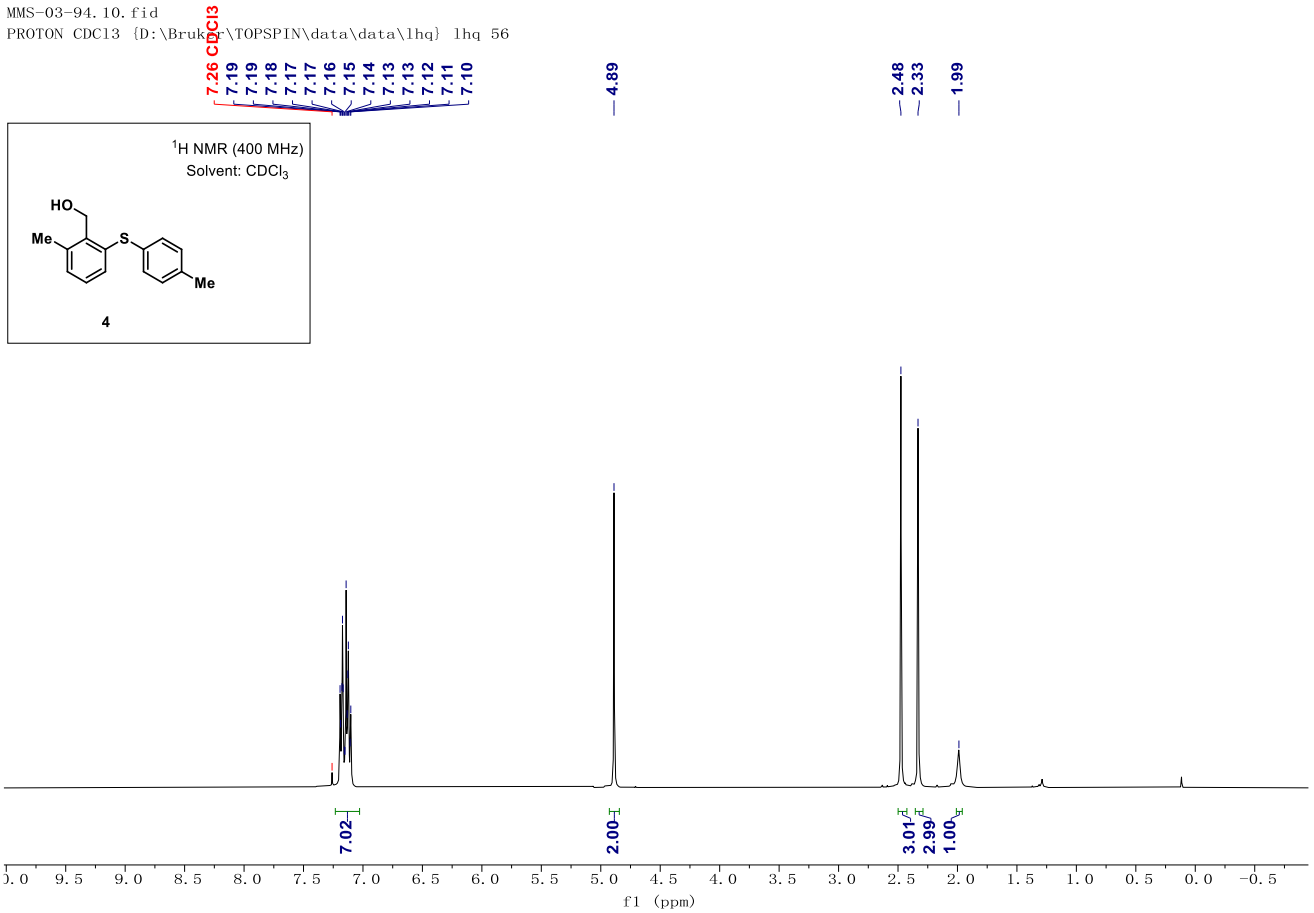

03-117-2.11.fid
C13CPD CDCl3 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 56
183.75
139.86
134.81
128.53
127.67
122.71
121.72
121.53
110.84
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
31.84
21.32
13C NMR (101 MHz)
Solvent: CDCl3
Me
S
O
N
Me
3qa
f1 (ppm)
f1 (ppm)

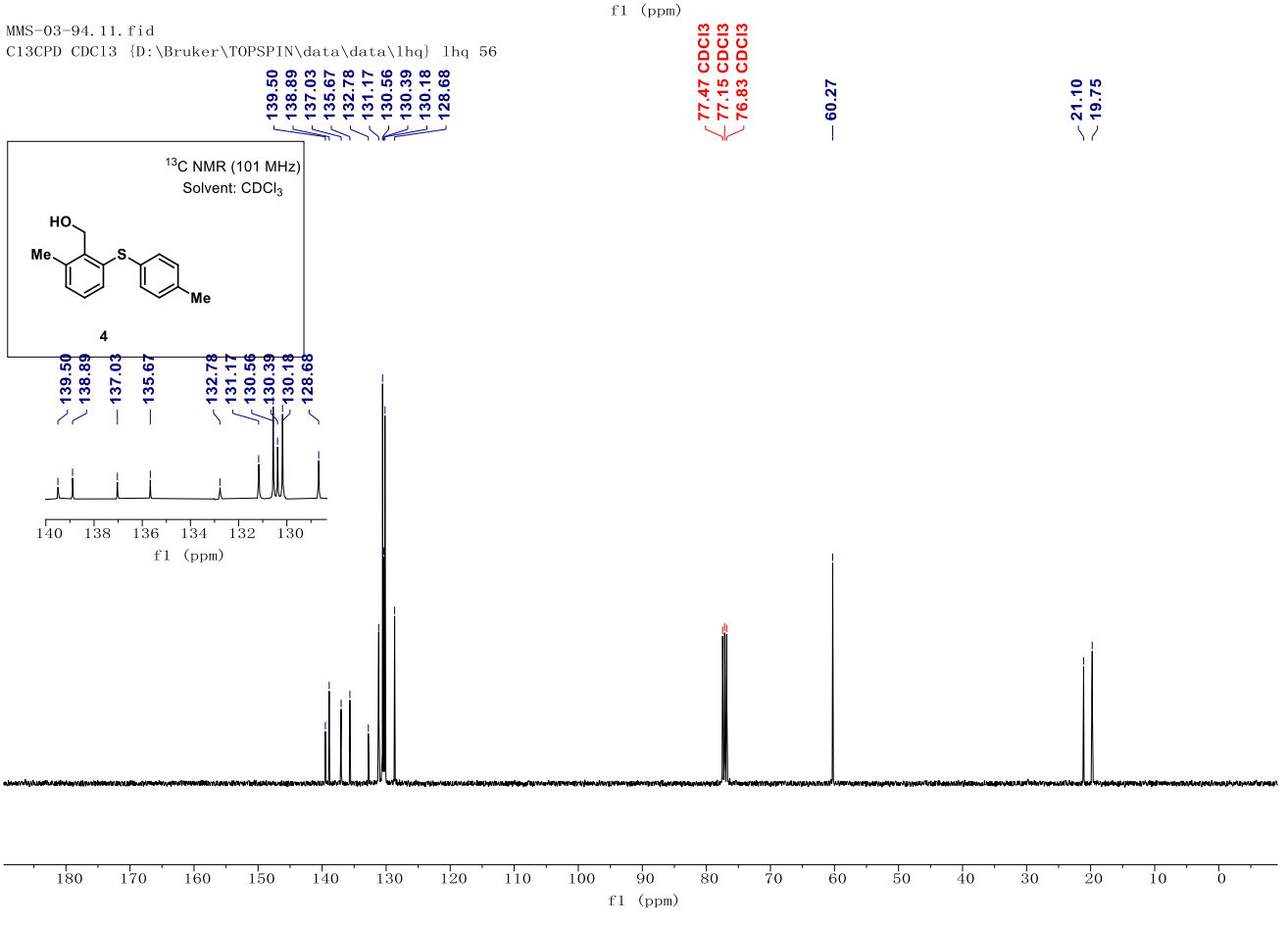

MMS-03-163-3B.10.fid
PROTON CDC13 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 57
10.15
7.86
7.84
7.61
7.59
7.57
7.55
7.55
7.53
7.40
7.38
7.36
7.26 CDCl3
2.62
1.60 H2O
1H NMR (400 MHz)
Solvent: CDCl3
Me
S
O
O
3ra
0.96
1.01
1.99
1.00
2.99
f1 (ppm)

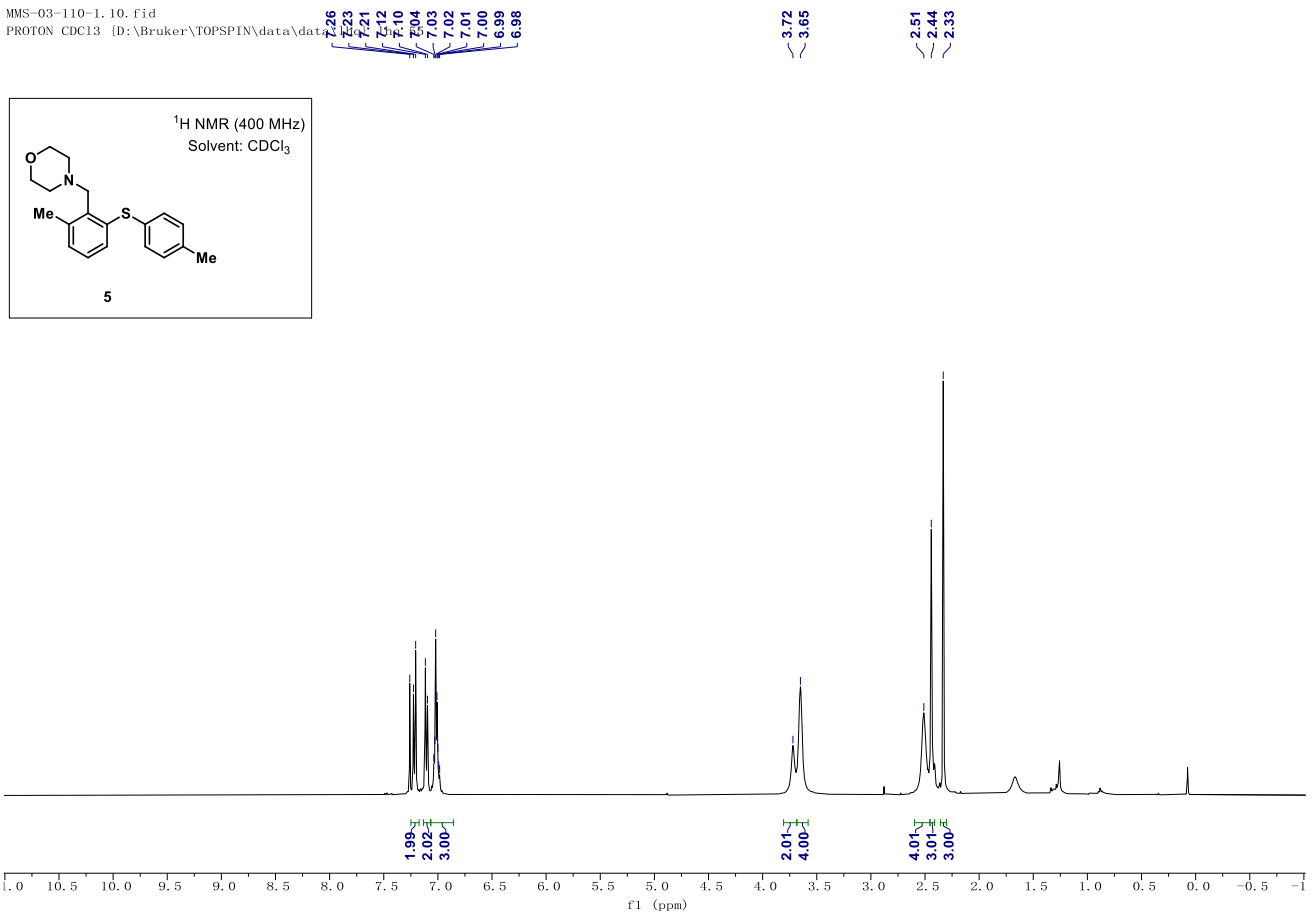

MMS-03-163-3B.11.fid
C13CPD CDC13 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 57
178.83
155.46
150.65
129.91
128.60
128.43
124.35
122.41
113.24
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
18.78
13C NMR (101 MHz)
Solvent: CDCl3
Me
S
O
O
3ra
f1 (ppm)

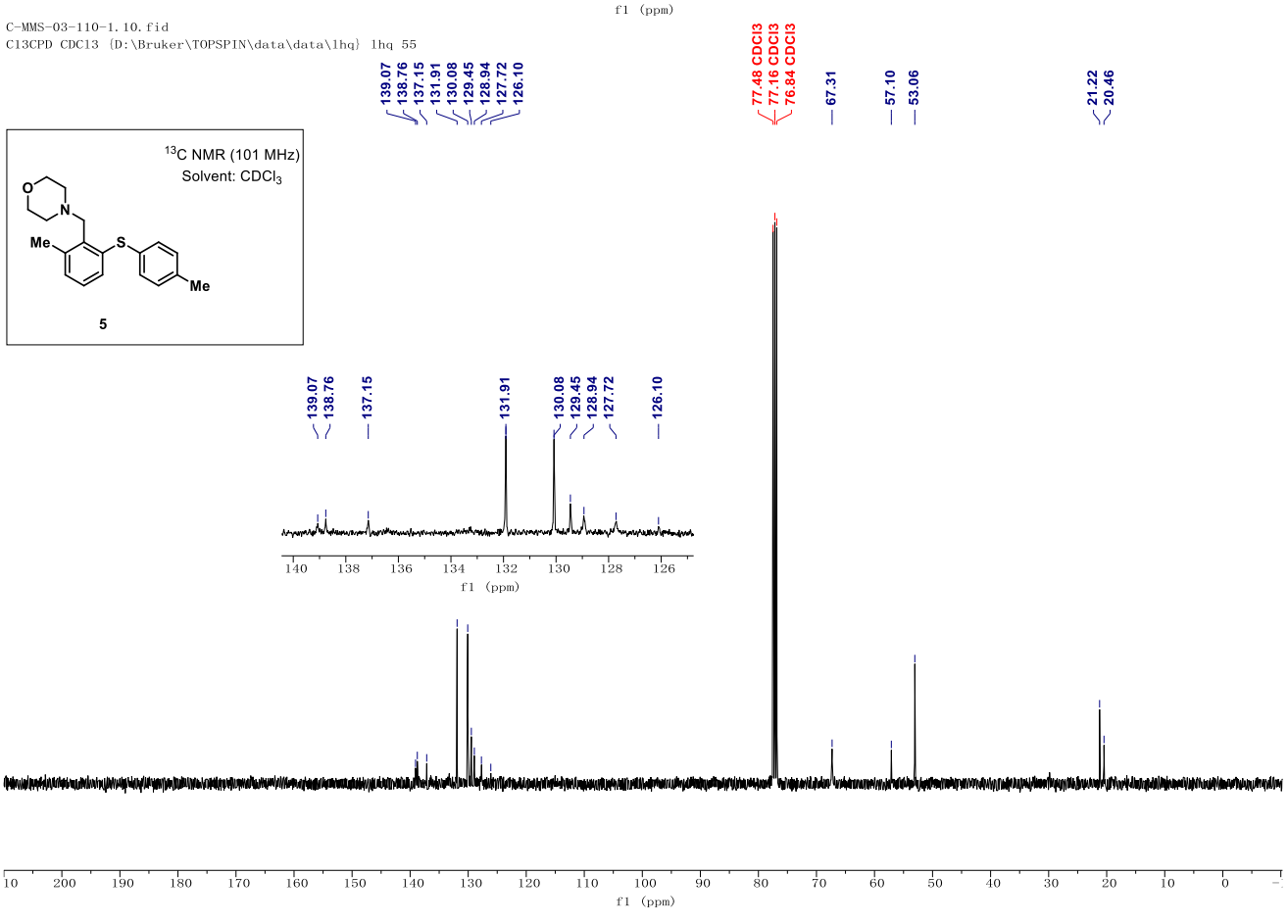

MMS-03-163-4B.10.fid
PROTON CDC13 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 38
10.55
8.17
8.16
8.15
8.14
7.89
7.87
7.56
7.55
7.54
7.54
7.52
7.51
7.50
7.50
7.48
7.48
2.52
1H NMR (400 MHz)
Solvent: CDCl3
Me
S
O
S
3sa
0.98
1.00
1.01
2.03
3.03
f1 (ppm)

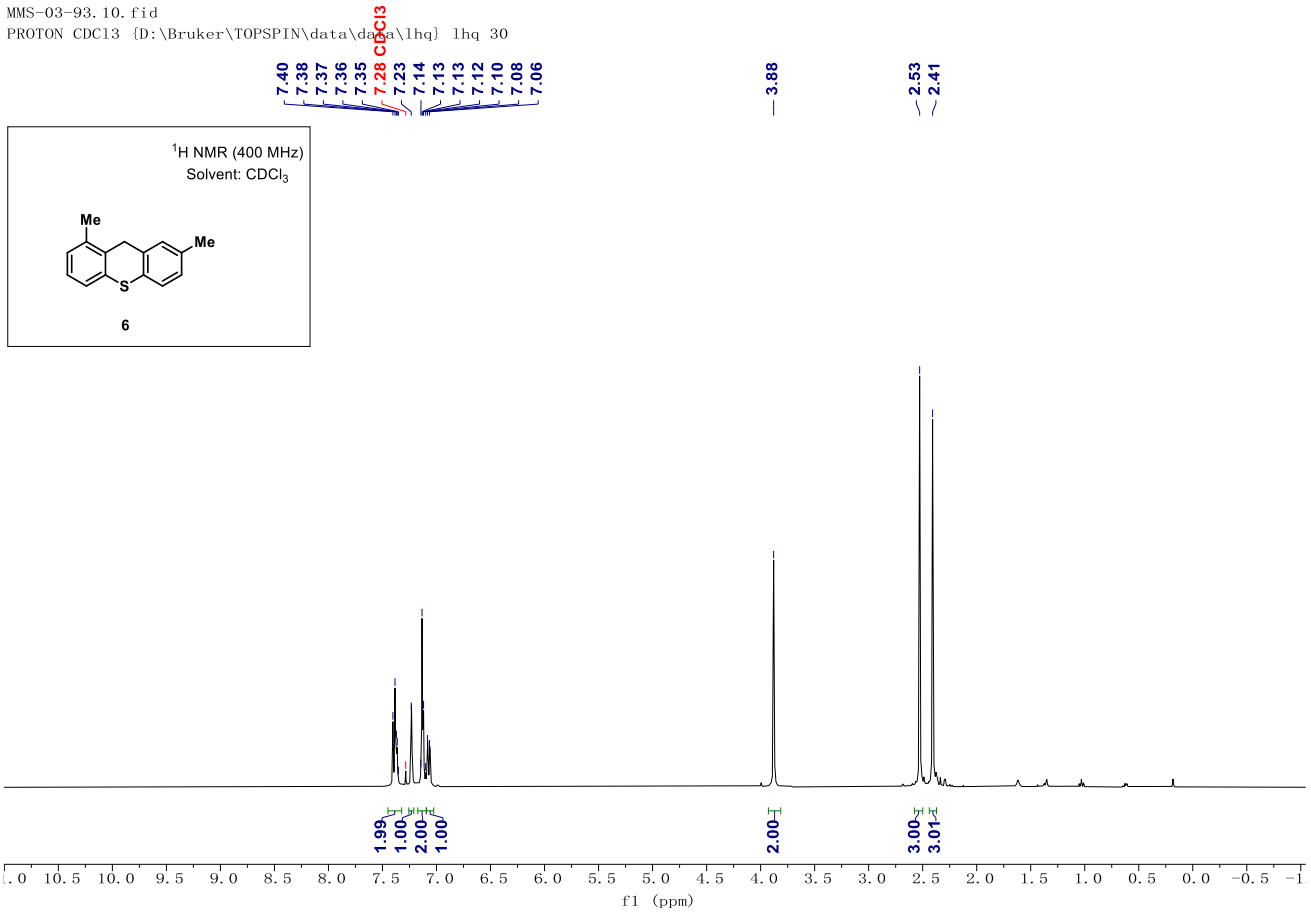

MMS-03-163-4B.20.fid
C13CPD CDC13 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 38
185.55
143.96
141.65
140.30
139.44
128.76
125.56
124.86
123.69
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
20.59
13C NMR (101 MHz)
Solvent: CDCl3
Me
S
O
S
3sa
f1 (ppm)

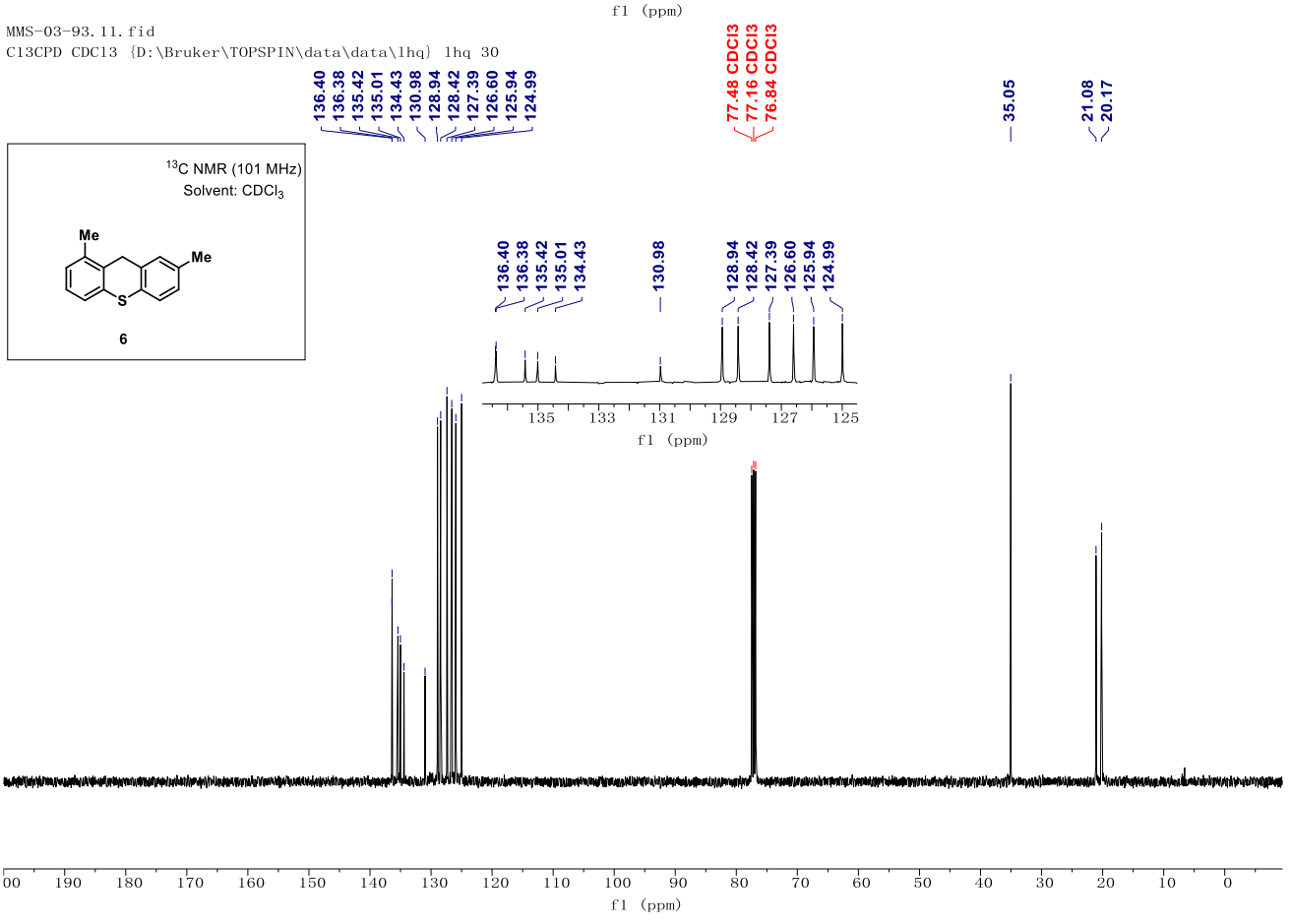

MMS-03-94.10.fid
PROTON CDCl3 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 56
7.26 CDCl3
7.19
7.19
7.18
7.17
7.17
7.16
7.15
7.14
7.13
7.13
7.12
7.11
7.10
4.89
2.48
2.33
1.99
1H NMR (400 MHz)
Solvent: CDCl3
HO
Me
S
Me
4
7.02
2.00
3.01
2.99
1.00
f1 (ppm)

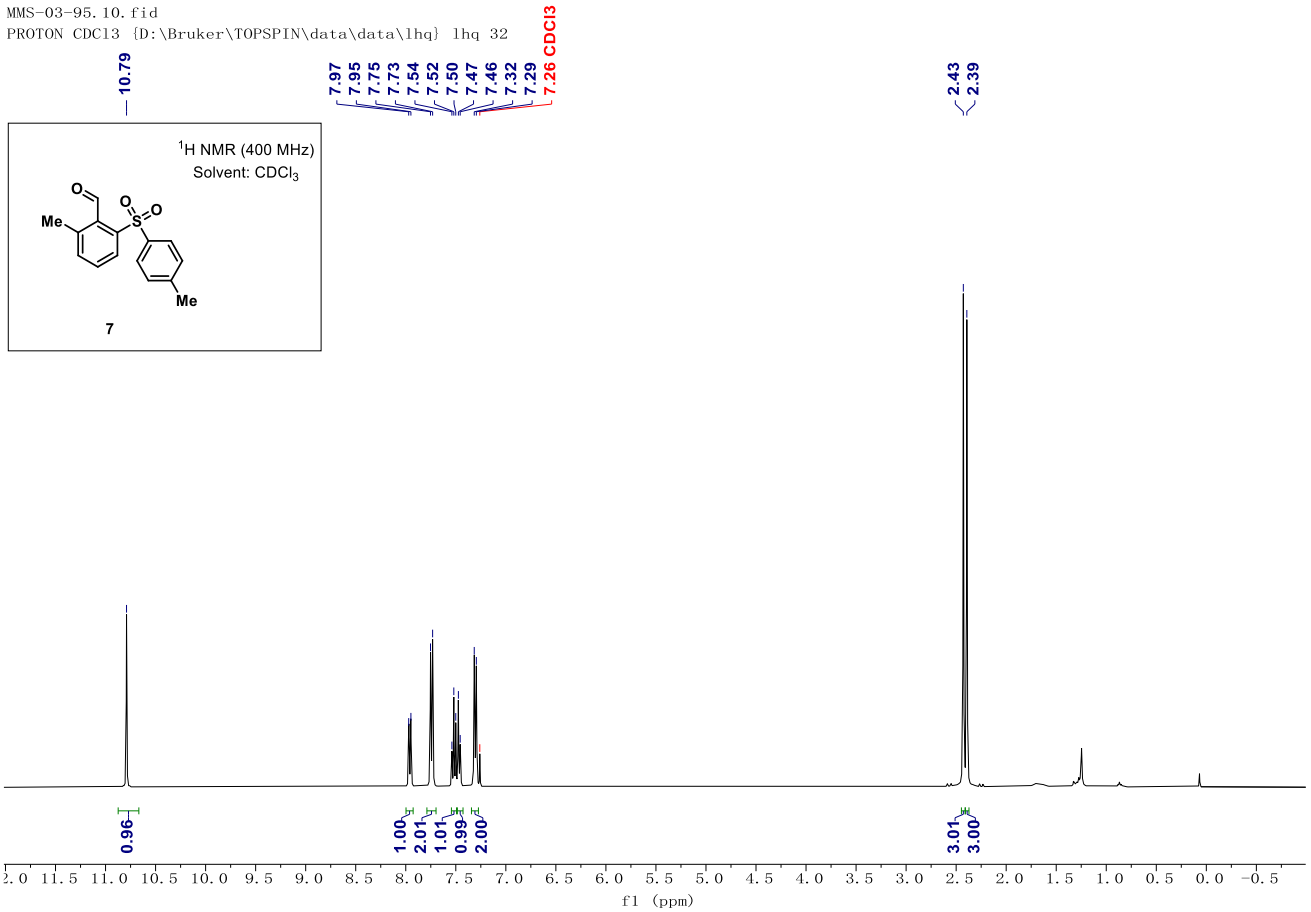

MMS-03-94.11.fid
C13CPD CDCl3 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 56
139.50
138.89
137.03
135.67
132.78
131.17
130.56
130.39
130.18
128.68
77.47 CDCl3
77.15 CDCl3
76.83 CDCl3
60.27
21.10
19.75
13C NMR (101 MHz)
Solvent: CDCl3
HO
Me
S
Me
4
f1 (ppm)

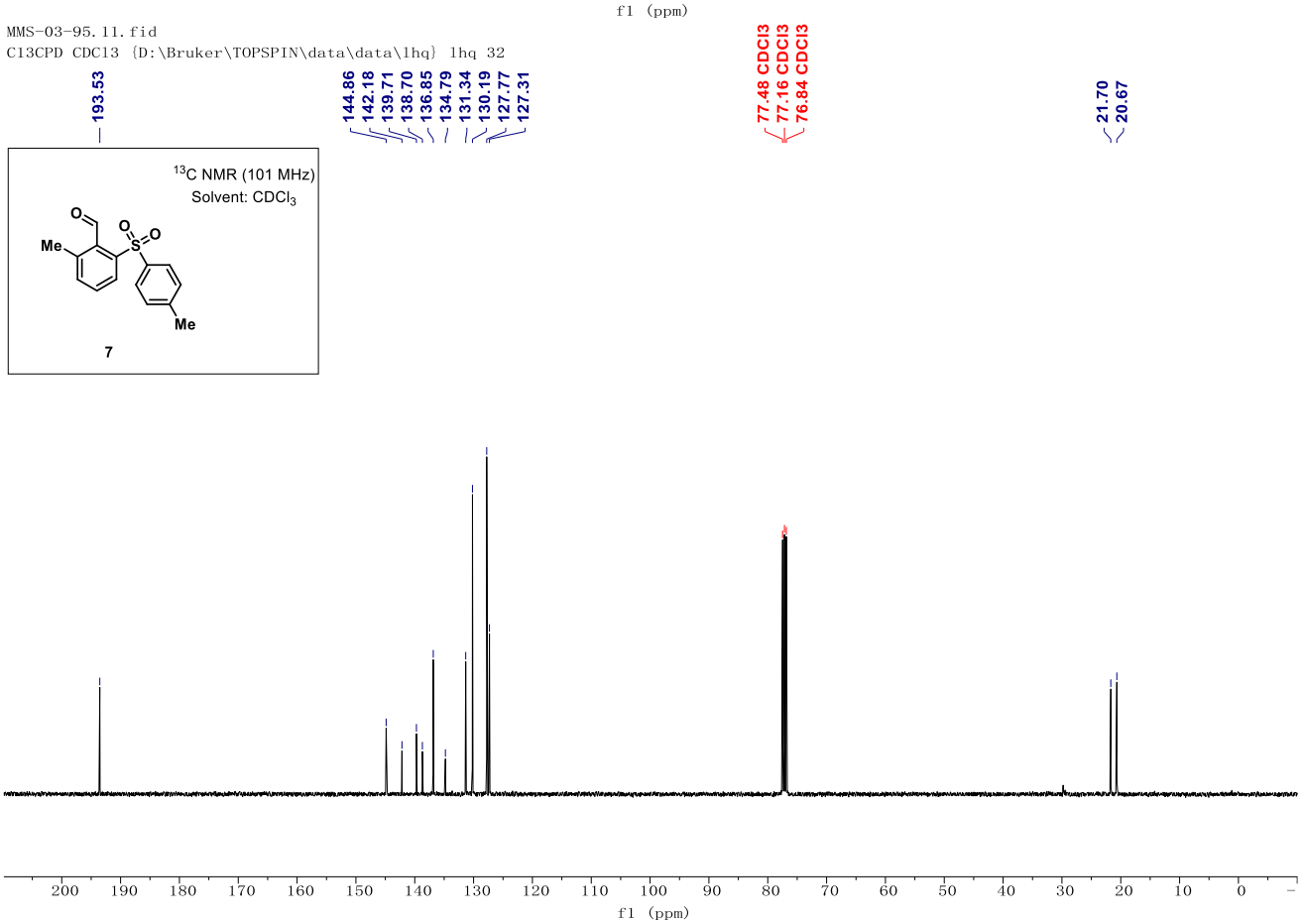

MMS-03-110-1.10.fid
PROTON CDC13 {D:\Bruker\TOPSPIN\data\data
7.26
7.23
7.21
7.12
7.10
7.04
7.03
7.02
7.01
7.00
6.99
6.98
3.72
3.65
2.51
2.44
2.33
1H NMR (400 MHz)
Solvent: CDCl3
Me
S
Me
5
1.99
2.02
3.00
2.01
4.00
4.01
3.01
3.00
f1 (ppm)

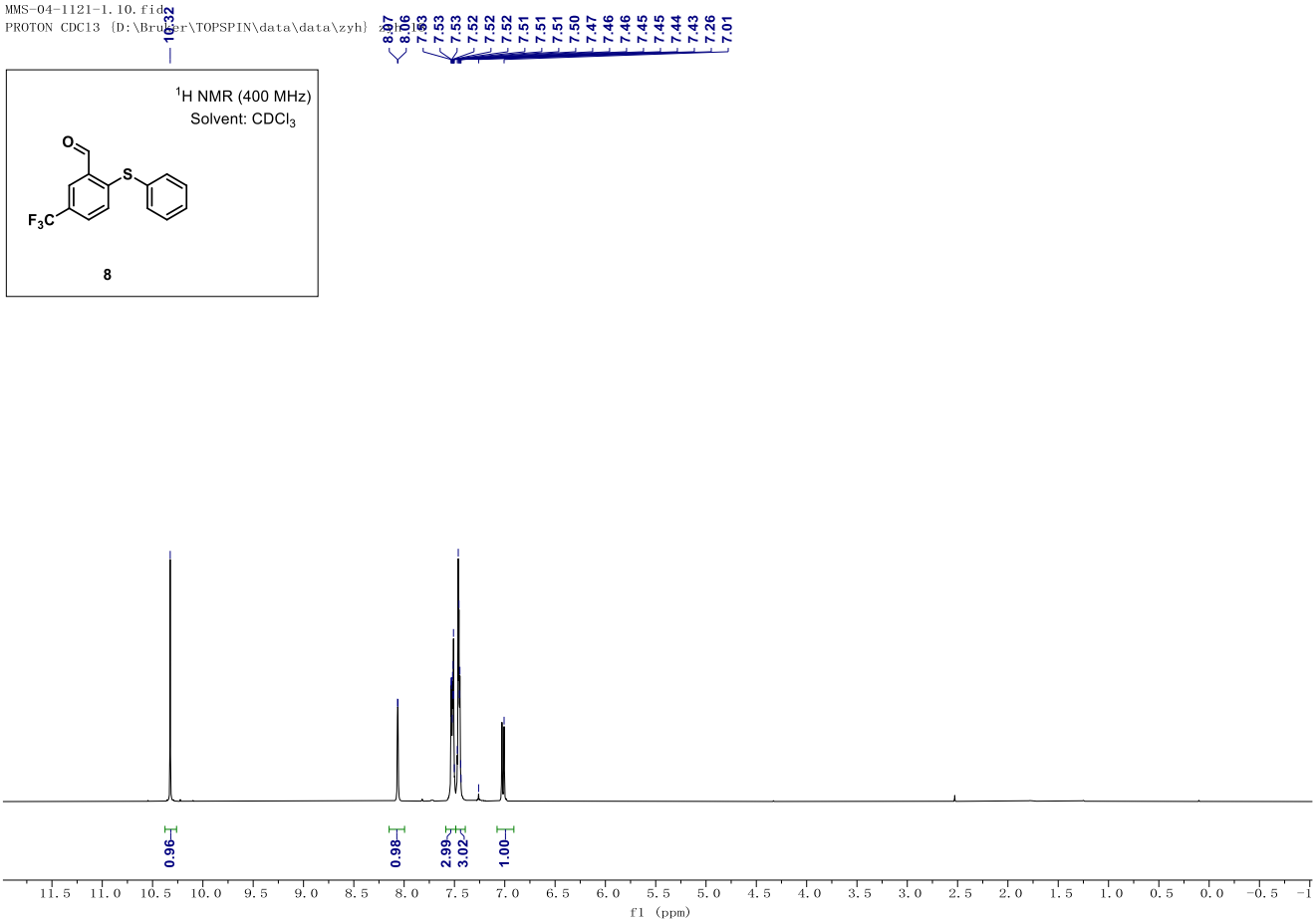

C-MMS-03-110-1.10.fid
C13CPD CDC13 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 55
139.07
138.76
137.15
131.91
130.08
129.45
128.94
127.72
126.10
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
67.31
57.10
53.06
21.22
20.46
13C NMR (101 MHz)
Solvent: CDCl3
Me
S
Me
5
f1 (ppm)
f1 (ppm)

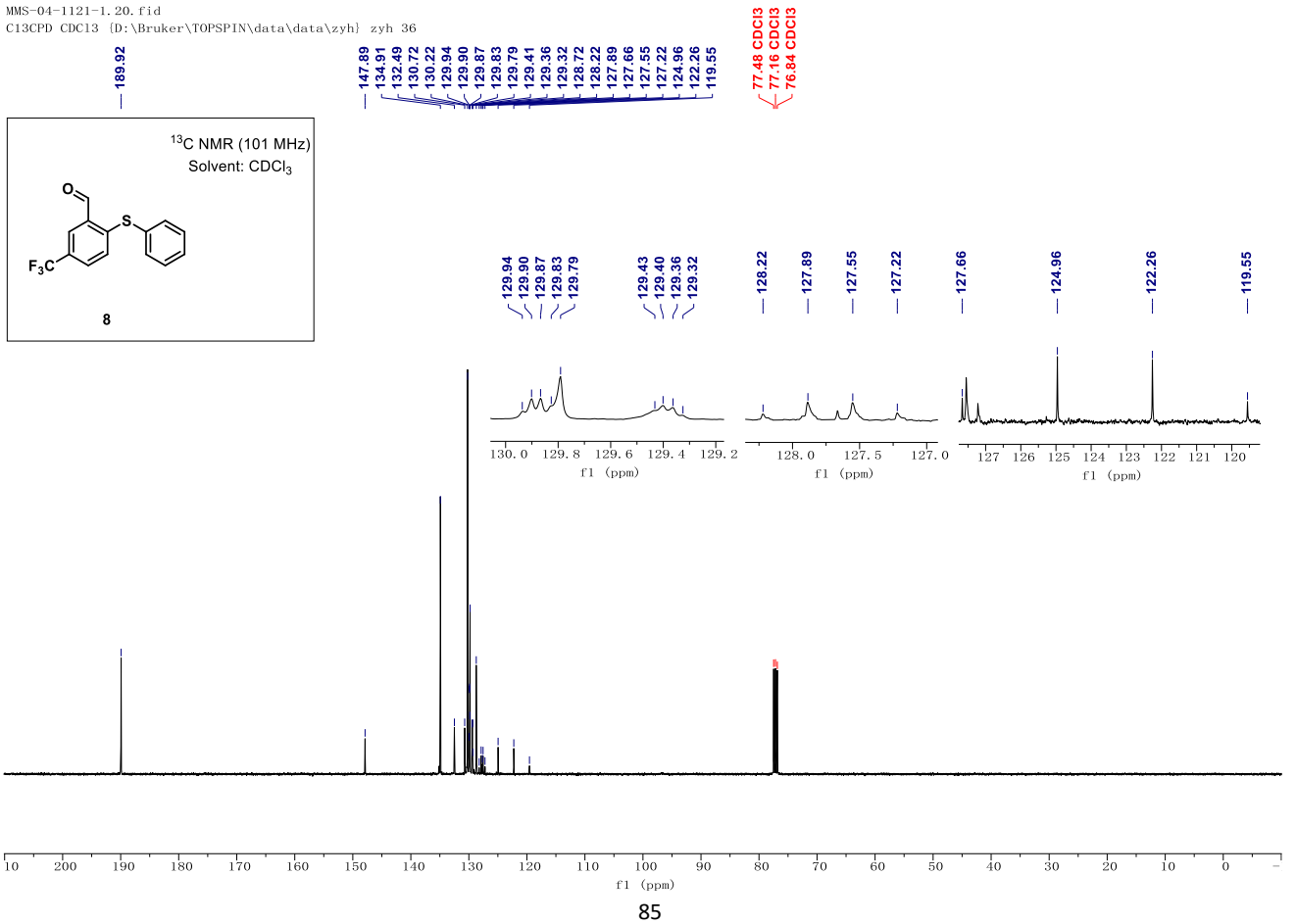

MMS-03-93.10.fid
PROTON CDCl3 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 30
7.40
7.38
7.37
7.36
7.35
7.28 CDCl3
7.23
7.14
7.13
7.13
7.12
7.10
7.08
7.06
3.88
2.53
2.41
1H NMR (400 MHz)
Solvent: CDCl3
Me
Me
S
6
1.99
1.00
2.00
1.00
2.00
3.00
3.01
f1 (ppm)


MMS-03-93.11.fid
C13CPD CDCl3 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 30
136.40
136.38
135.42
135.01
134.43
130.98
128.94
128.42
127.39
126.60
125.94
124.99
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
35.05
21.08
20.17
13C NMR (101 MHz)
Solvent: CDCl3
Me
Me
S
6
f1 (ppm)
f1 (ppm)


MMS-03-95.10.fid
PROTON CDCl3 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 32
10.79
7.97
7.95
7.75
7.73
7.54
7.52
7.50
7.47
7.46
7.32
7.29
7.26 CDCl3
2.43
2.39
1H NMR (400 MHz)
Solvent: CDCl3
Me
Me
7
0.96
1.00
2.01
1.01
0.99
2.00
3.01
3.00
f1 (ppm)

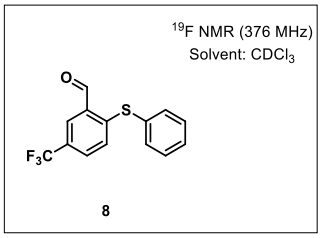

MMS-03-95.11.fid
C13CPD CDCl3 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 32
193.53
144.86
142.18
139.71
138.70
136.85
134.79
131.34
130.19
127.77
127.31
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
21.70
20.67
13C NMR (101 MHz)
Solvent: CDCl3
Me
Me
7
f1 (ppm)

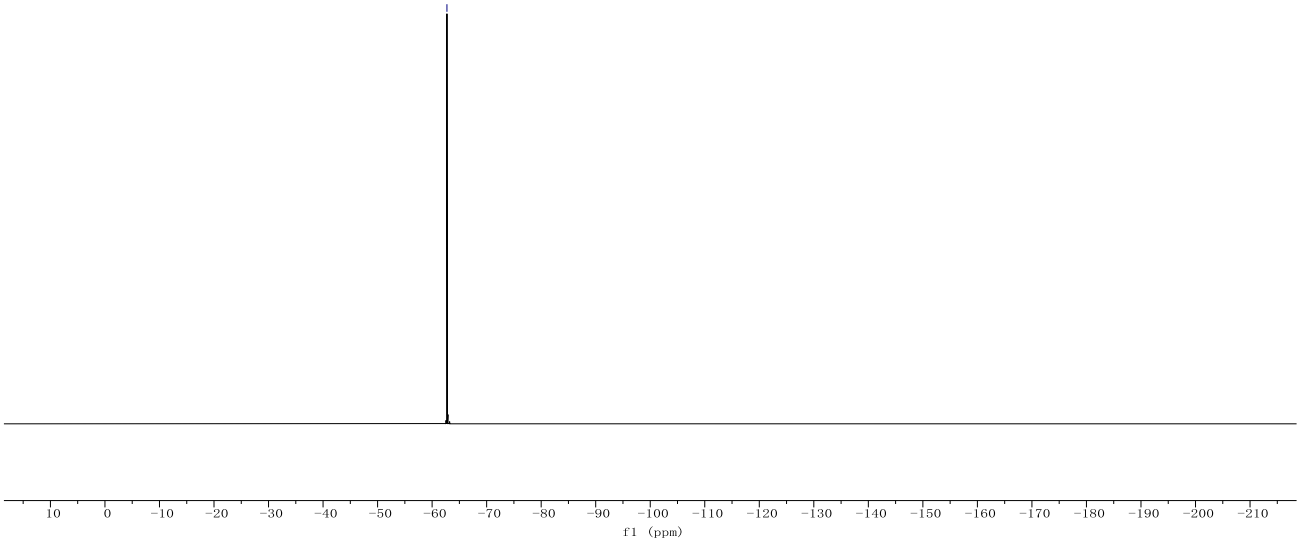

MMS-04-1121-1.10.fid
PROTON CDC13 {D:\Bruker\TOPSPIN\data\data\zyh} zyh 36
10.32
8.07
8.06
7.53
7.53
7.52
7.52
7.52
7.51
7.51
7.51
7.50
7.47
7.46
7.46
7.45
7.44
7.43
7.26
7.01
1H NMR (400 MHz)
Solvent: CDCl3
O
S
F3C
8
0.96
0.98
2.99
3.02
1.00
f1 (ppm)


MMS-04-1121-1.20.fid
C13CPD CDC13 {D:\Bruker\TOPSPIN\data\data\zyh} zyh 36
189.92
147.89
134.91
132.49
130.72
130.22
129.94
129.90
129.87
129.83
129.79
129.41
129.36
129.32
128.72
128.22
127.89
127.66
127.55
127.22
124.96
122.26
119.55
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
13C NMR (101 MHz)
Solvent: CDCl3
O
S
F3C
8
f1 (ppm)

MMS-04-1121-1.21.fid
F19CPD CDC13 {D:\Bruker\TOPSPIN\data\data\zyh} zyh 36

-62.72





MMS-04-88F.10.fid
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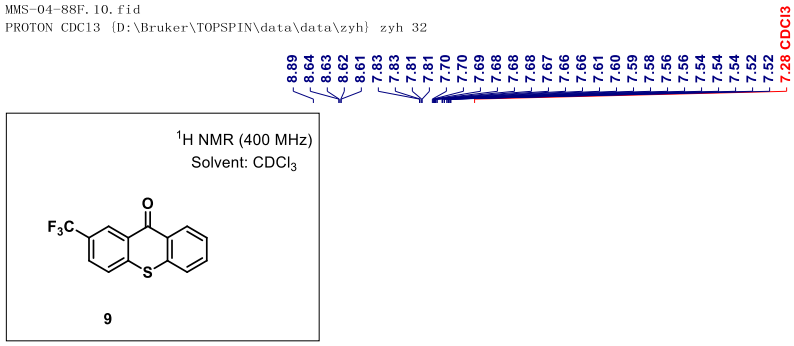
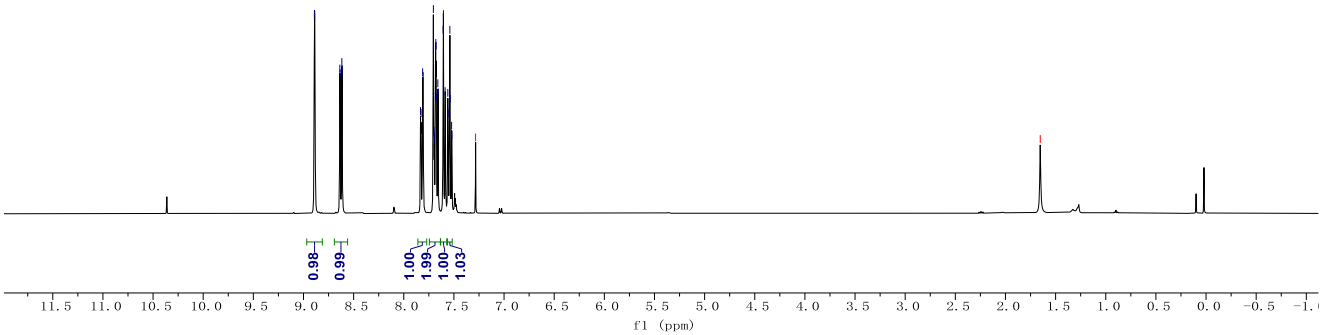
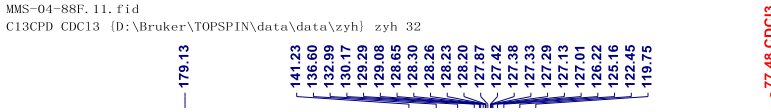


^{1}H NMR (400 MHz)
Solvent: $CDCl_3$

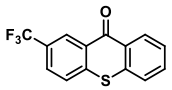
9



MMS-04-88F.11.fid
C13CPD CDC13 {D:\Bruker\TOPSPIN\data\data\zyh} zyh 32



^{13}C NMR (101 MHz)
Solvent: $CDCl_3$



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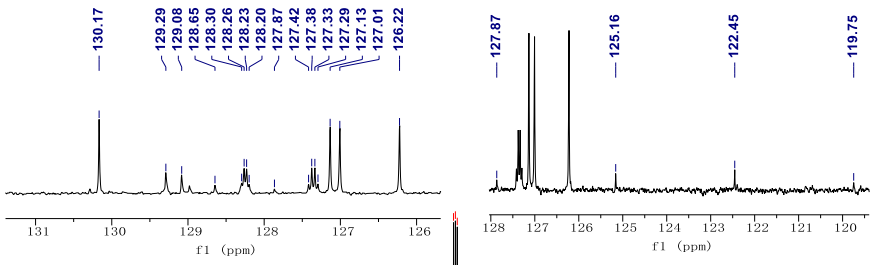
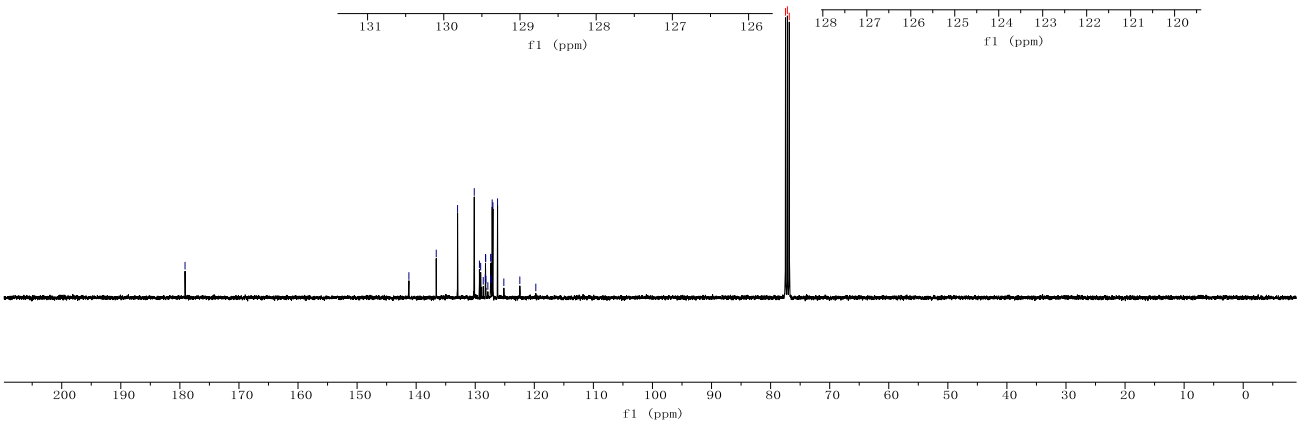
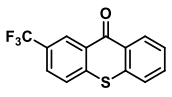




MMS-04-88F.12.fid
F19CPD CDC13 {D:\Bruker\TOPSPIN\data\data\zyh} zyh 32

-62.59

^{19}F NMR (376 MHz)
Solvent: $CDCl_3$



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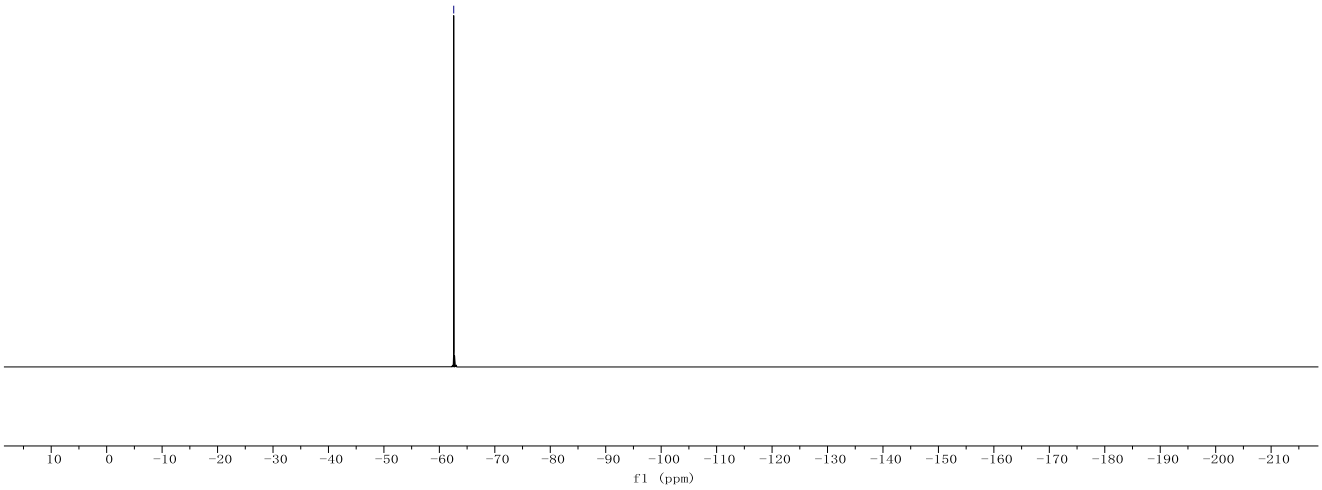
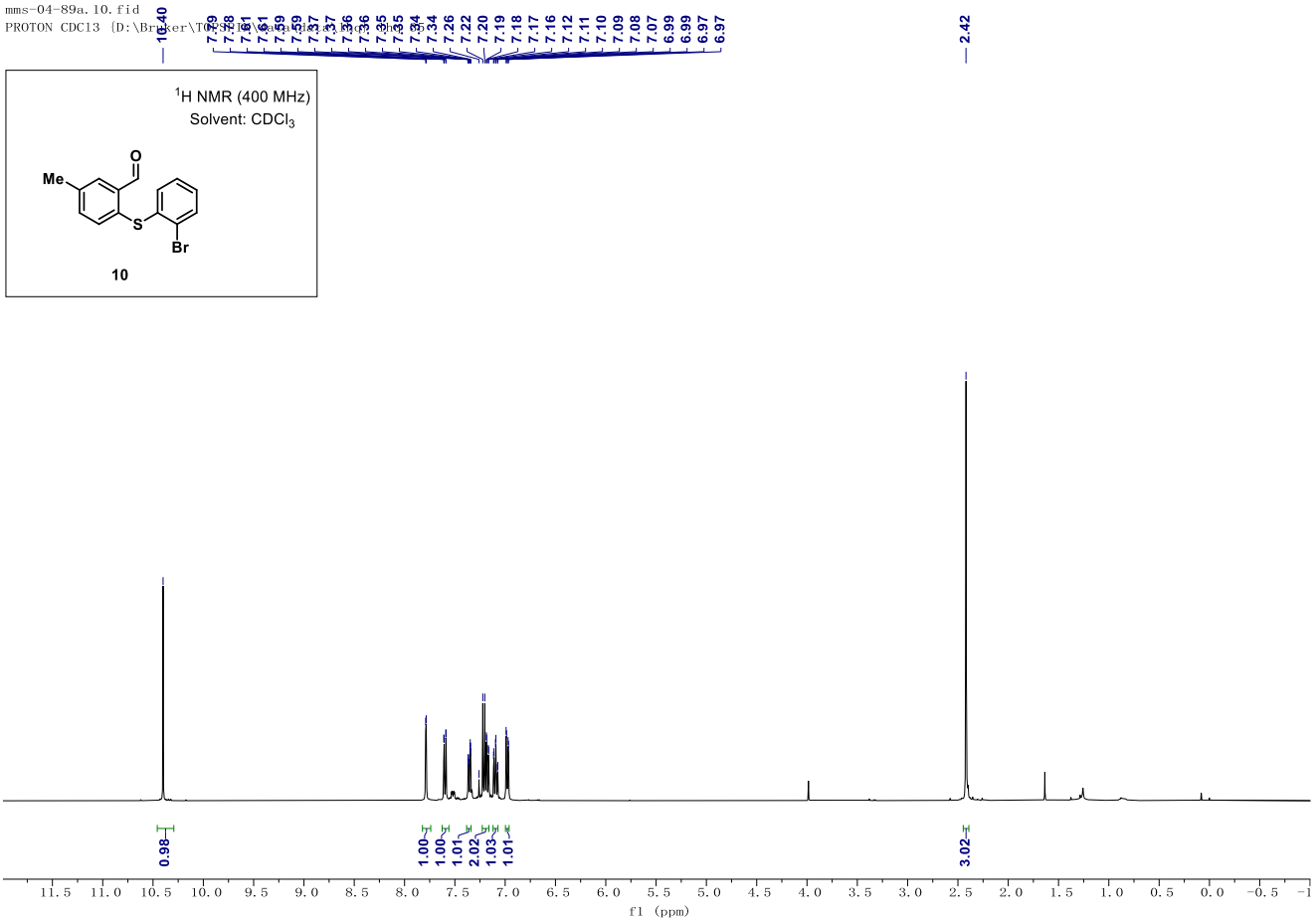
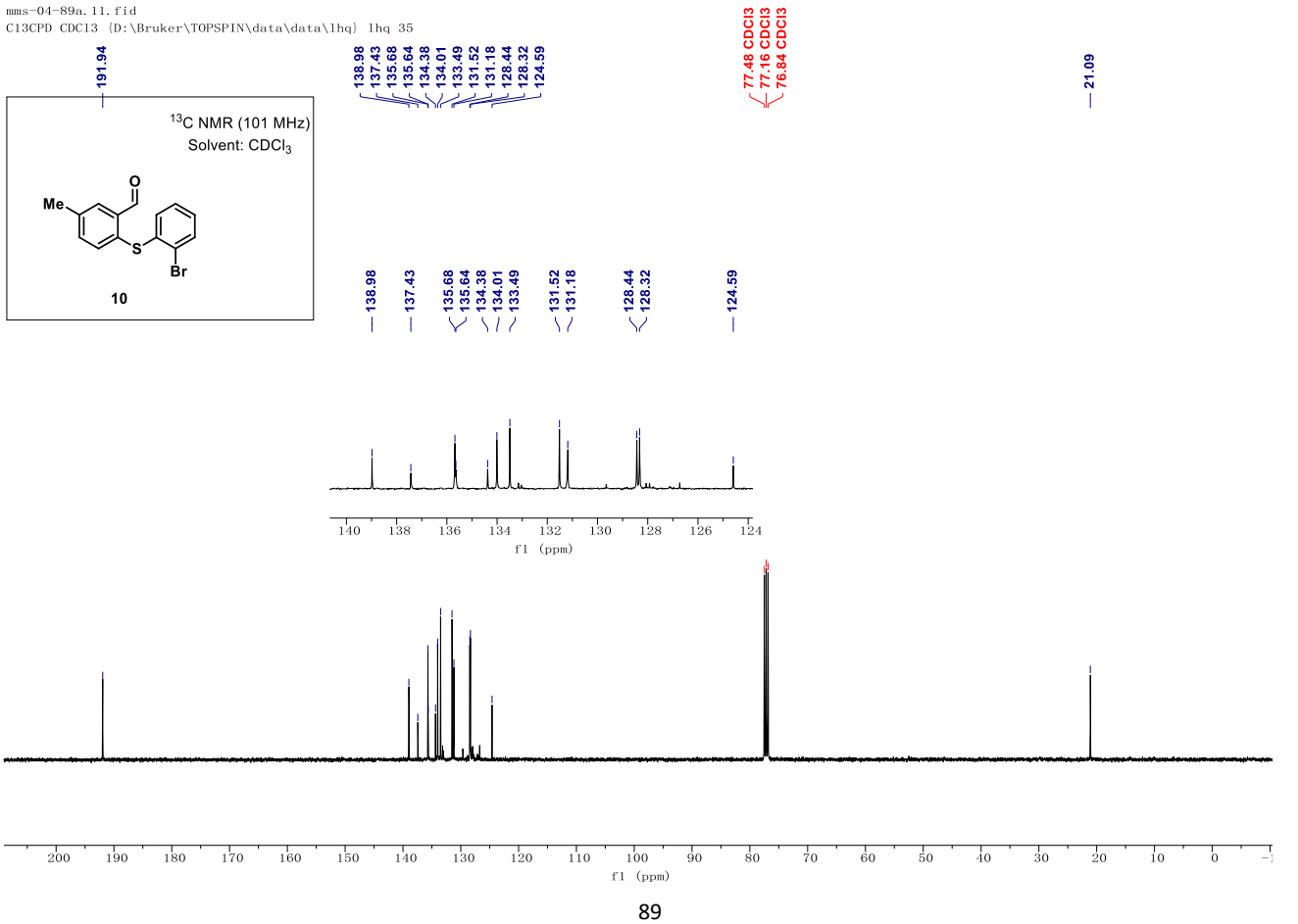
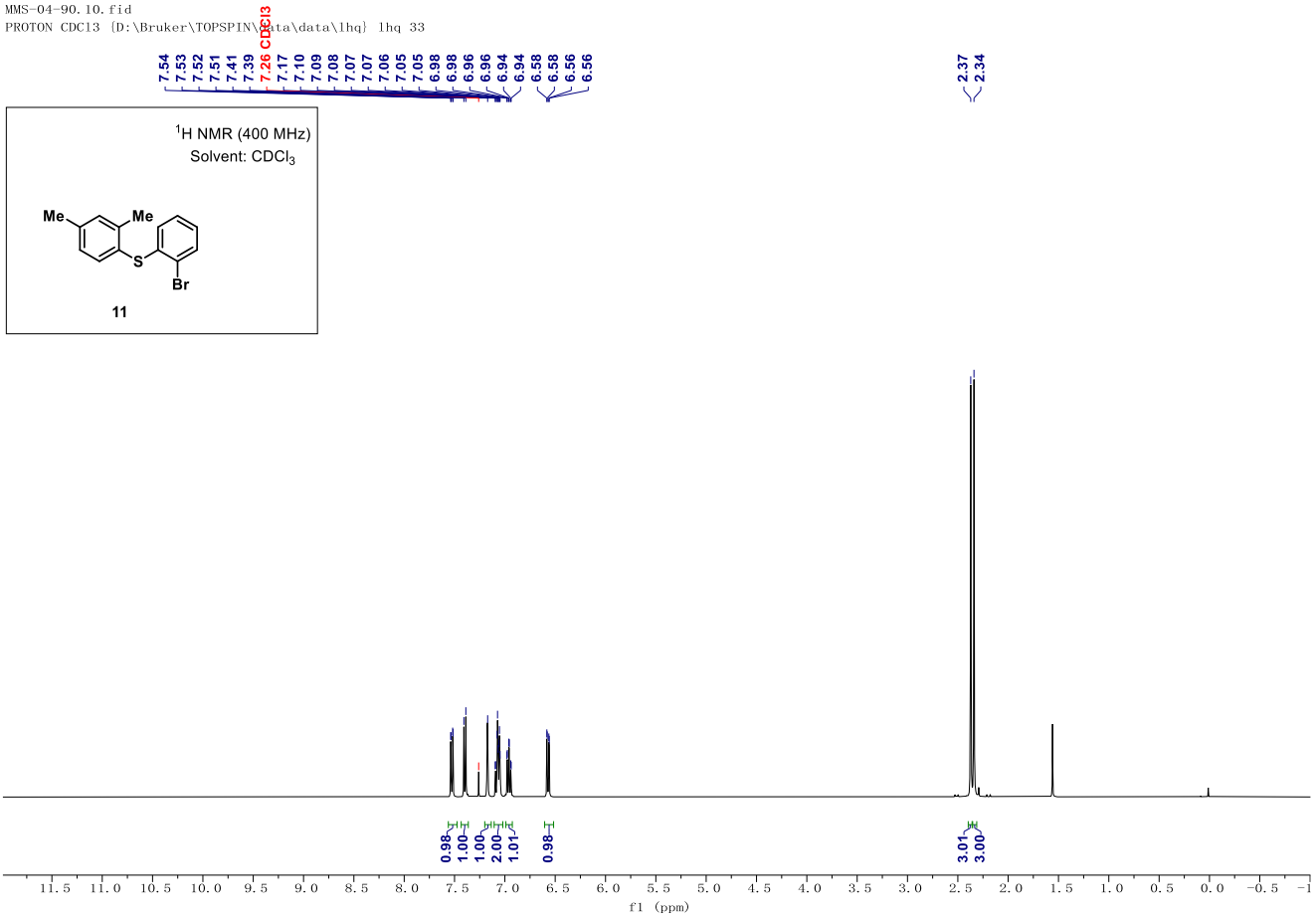
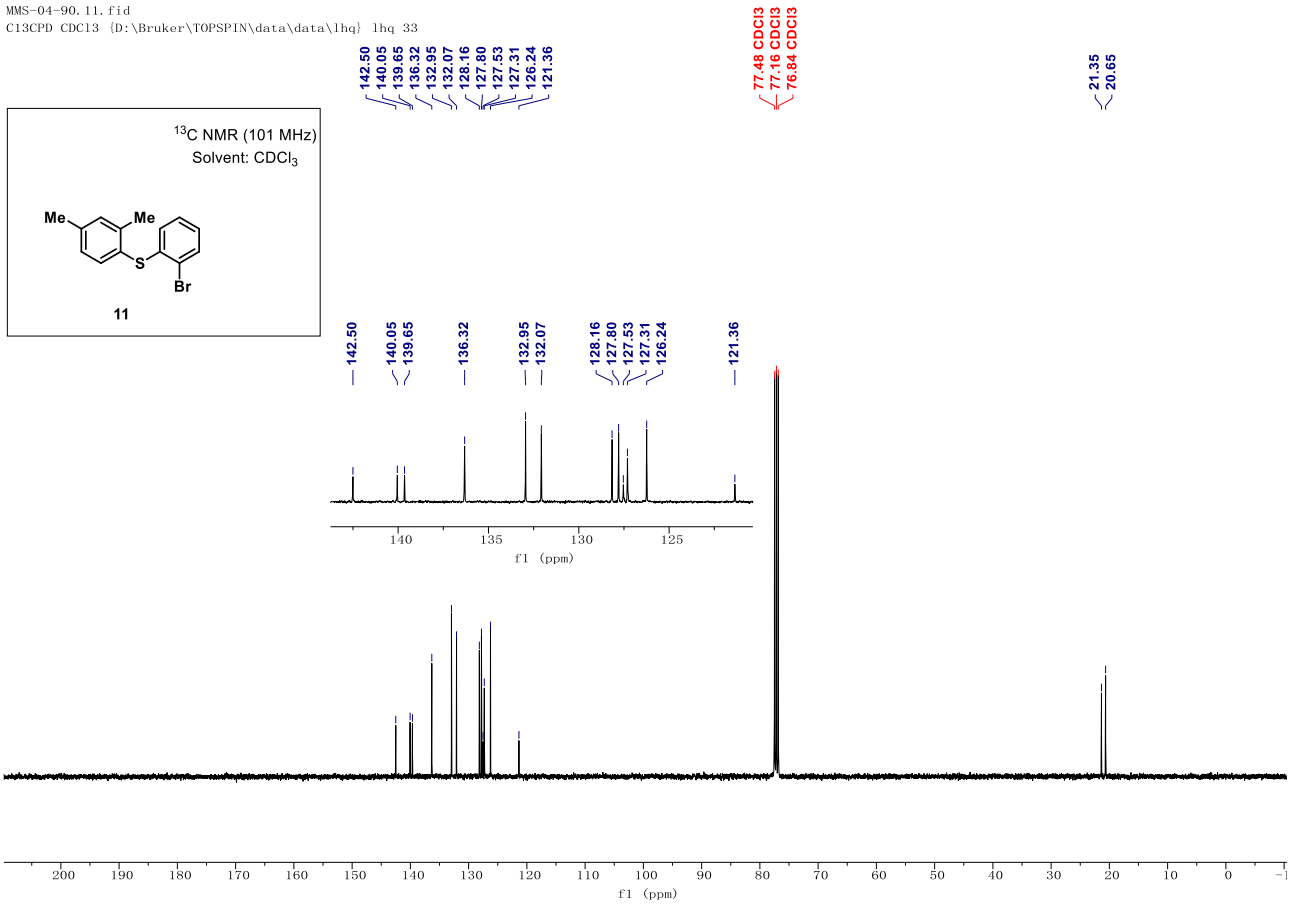



mms-04-89a.10.fid
PROTON CDC13 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 35
10.40
7.69
7.68
7.61
7.61
7.59
7.59
7.37
7.37
7.36
7.36
7.35
7.35
7.34
7.34
7.26
7.22
7.20
7.19
7.18
7.17
7.16
7.12
7.11
7.10
7.09
7.08
7.07
6.99
6.99
6.97
6.97
2.42
1H NMR (400 MHz)
Solvent: CDCl3
Me
O
S
Br
10
0.98
1.00
1.00
1.01
2.02
1.03
1.01
3.02
f1 (ppm)


mms-04-89a.11.fid
C13CPD CDC13 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 35
191.94
138.98
137.43
135.68
135.64
134.38
134.01
133.49
131.52
131.18
128.44
128.32
124.59
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
21.09
13C NMR (101 MHz)
Solvent: CDCl3
Me
O
S
Br
10
f1 (ppm)


MMS-04-90.10.fid
PROTON CDCl3 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 33
7.54 7.53 7.52 7.51 7.41 7.39 7.26 CDCl3 7.17 7.10 7.09 7.08 7.07 7.07 7.06 7.05 7.05 6.98 6.98 6.96 6.96 6.96 6.94 6.94 6.58 6.58 6.56 6.56
2.37 2.34
1H NMR (400 MHz)
Solvent: CDCl3
Me Me S Br
11
0.98 1.00 1.00 2.00 1.01 0.98 3.01 3.00
f1 (ppm)


MMS-04-90.11.fid
C13CPD CDCl3 {D:\Bruker\TOPSPIN\data\data\lhq} lhq 33
142.50 140.05 139.65 136.32 132.95 132.07 128.16 127.80 127.53 127.31 126.24 121.36
77.48 CDCl3 77.16 CDCl3 76.84 CDCl3
21.35 20.65
13C NMR (101 MHz)
Solvent: CDCl3
Me Me S Br
11
142.50 140.05 139.65 136.32 132.95 132.07 128.16 127.80 127.53 127.31 126.24 121.36
f1 (ppm)