Supporting Information

A Visible-Light Photocatalytic Thiolation of Aryl, Heteroaryl and Vinyl Iodides

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Experimental Procedures

General Information

Unless otherwise stated, reagents and solvents were purchased from commercial sources and used without further purification. 4-Iodobenzyloxybenzene,[1] *tert*-butyl 5-iodo-1H-indole-1-carboxylate[2] and 2-iodo-1-benzofuran[3] were synthesized according to literature procedures. Vinyl iodides were synthesized according to a literature procedure for the synthesis of *E*-iodostyrene[4] or [(1*E*)-2-iodo-1-methyl-vinyl]-benzene.[5]

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker 400 Ultrashield (400 MHz), Ascend 400 (400 MHz) or Varian MR-400 spectrometers. Chemical shifts are expressed in parts per million (PPM) and are referenced to the internal solvent peaks.

Mass spectrometric analyses were performed on a Thermo Scientific Q Exactive mass spectrometer fitted with an ASAP ion source. Positive ions were recorded in an appropriate mass range at 140,000 mass resolution. The APCI probe was used without flow of solvent. The nitrogen nebulizing/desolvation gas used for vaporization was heated to 350 °C in these experiments. The sheath gas flow rate was set to 25, the auxiliary gas flow rate to 5 and the sweep gas flow rate to 2 (all arbitrary units). The discharge current was 4 mA and the capillary temperature was 320 °C.

Steady-state luminescent spectra were recorded using a Perkin Elmer LS50 fluorimeter. Samples were excited at 400 nm, slit widths were 2.7 nm and the area under the spectra were used for determining the Stern-Volmer quenching values.

Time-resolved photoluminescence was measured using an Edinburgh Instruments FLSP920 time-correlated single-photon counting spectrometer comprising a pulsed diode laser excitation source operated at 378 nm. Steady-state emission spectra were collected concurrently on this instrument.

Absosrption spectra were measured using a Perkin Elmer Lambda 1050 spectrometer. Transient absorption spectra were recorded using an Edinburgh Instruments LP900 spectrometer coupled with a nanosecond pulsed Nd^{3+}-YAG laser (Quantel, Brio), operating at 355 nm and 10 Hz repetition rate as the excitation source.

Analytical Thin Layer Chromatography (TLC) was carried out using aluminium-backed Merck Kieselgel KG60 F254 silica plates. The plates were visualised by irradiation with short-wave ultraviolet light. Flash chromatography was performed on Grace Davidson Davisil LC60A 40-63 micron silica gel.

All photoredox reactions were performed using a custom built blue LED photoreactor (Figure S1). The custom reactor was comprised of a square metal frame (100 mm × 110 mm) with 14 blue LEDs (2 × SP-02-V4 LED assembly, each consisting of 7 LXML-PR02-A900 Royal-Blue LUXEON Rebel ES LEDs; www.luxeonstar.com). The photoreactor was fitted with PC cooling fans and heat sinks for temperature control (internal temperature of the reactor typically reaches 27 ± 5 °C overnight). The power of the light source can be varied using an intensity control. The emission output of the light source used was measured using a Princeton Instruments PIXIS 1024BR CCD Detector. The measurement was conducted by shining the LED light indirectly into the aperature of the detector.

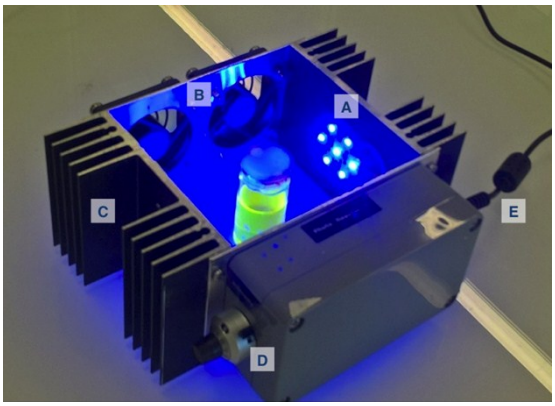
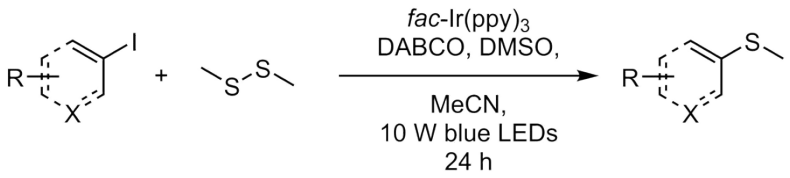


Figure S1. Custom-built LED photoreactor; a) blue LED assembly; b) PC cooling fans; c) heat sinks; d) intensity control; e) 12 V power supply.

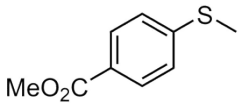
Photoredox cross-coupling reactions

General Procedure A



(Hetero)aryl iodide (0.3 mmol, 1.0 equiv.), dimethyl disulfide (1.2 mmol, 4.0 equiv.), 1,4-diazabicyclo[2.2.2]octane (1.2 mmol, 4.0 equiv.), $Ir(ppy)_3$ (6 μmol, 2 mol%) and DMSO (50.5 μL, 2.0 equiv.) were placed in a 4 mL scintillation vial and taken up in MeCN (3 mL). The vial was sealed with a plastic screw cap and stirred for 24 h at room temperature whilst being irradiated with 10 W blue LED light. The reaction mixture was concentrated under reduced pressure and the residue was purified by flash chromatography on silica to afford the final product.

Product Characterisation Data



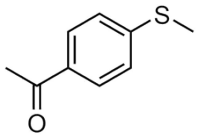
7

Methyl 4-(methylthio)benzoate (7): prepared according to general procedure A with methyl-4-iodobenzoate (79 mg, 0.3 mmol); purified by flash chromatography, eluting with 10% Et_2O/*n*-pentane, to afford the title product as a white solid (50 mg, 91%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 3.90 (s, 3H), 2.52 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.8, 145.4, 129.8, 126.2, 124.9, 51.9, 14.8.

Data matched that reported in the literature.[6]



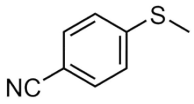
11

4-(Methylthio)acetophenone (11): prepared according to general procedure A with 4-iodoacetophenone (74 mg, 0.3 mmol); purified by flash chromatography, eluting with 20% Et_2O/*n*-pentane, to afford the title compound as a white solid (38 mg, 76%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 2.54 (s, 3H, H), 2.49 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.3, 146.0, 133.6, 128.9, 125.1, 26.6, 14.9.

Data matched that reported in the literature.[6]



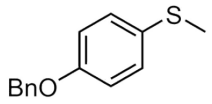
12

4-(Methylthio)benzonitrile (12): prepared according to general procedure A with 4-iodobenzonitrile (69 mg, 0.3 mmol); purified by flash chromatography eluting with *n*-pentane, to afford the title compound as a colourless oil (28 mg, 62%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 8.8 Hz, 2H), 7.23 (d, *J* = 8.8 Hz, 2H), 2.47 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.23, 132.27, 125.6, 119.10, 107.76, 14.81.

Data matched that reported in the literature.[6]



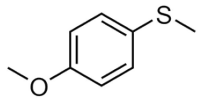
13

1-Methylthio-4-phenylmethoxy benzene (13): prepared according to general procedure A with 4-iodobenzyloxybenzene (93 mg, 0.3 mmol); purified flash chromatography eluting with 1% Et_2O/*n*-pentane, to afford the title compound as a white solid (41 mg, 60%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 – 7.32 (m, 5H), 7.25 (d, *J* = 9.0 Hz, 2H), 6.92 (d, *J* = 9.0 Hz, 2H), 5.05 (s, 2H), 2.44 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.3, 136.9, 130.0, 129.1, 128.6, 127.4, 115.6, 70.1, 18.0.

Data matched that reported in the literature.[7]



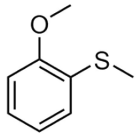
14

(4-Methoxyphenyl)(methyl)sulfane (14): prepared according to general procedure A with 4-iodoanisole (70 mg, 0.3 mmol); purified by flash chromatography, eluting with 1% Et_2O/*n*-pentane to afford the title compound as a white solid (25 mg, 55%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27 (d, *J* = 9.0 Hz, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 3.79 (s, 3H), 2.44 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ =158.3, 130.3, 128.9, 114.7, 55.5, 18.2.

Data matched that reported in the literature.[8]



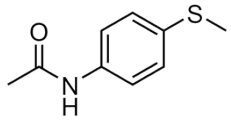
15

2-Methoxythioanisole (15): prepared according to general procedure A with 2-iodoanisole (70 mg, 0.3 mmol); purified flash chromatography eluting with 1% Et_2O/*n*-pentane to afford the title compound as a white solid (40 mg, 86%).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.18 – 7.13 (m, 2H), 6.96 (t, 1H, *J* = 7.6 Hz), 6.84 (d, *J* = 8.0 Hz, 1H), 3.90 (s, 3H), 2.44 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.3, 128.8, 126.2, 125.9, 121.2, 110.1, 55.8, 14.8.

Data matched that reported in the literature.[9]



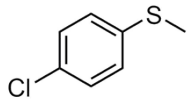
16

4-(Methylthio)acetanilide (16): prepared according to general procedure A with 4-iodoacetanilide (78 mg, 0.3 mmol); purified by flash chromatography, eluting with 1% CH_3OH/CH_2Cl_2 to afford the title compound as an orange solid (27 mg, 50%).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 2.46 (s, 3H), 2.17 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.3, 135.6, 133.7, 128.1, 120.6, 24.8, 16.8.

Data matched that reported in the literature.[6]



17

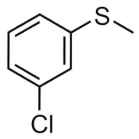
1-Chloro-4-methylthio benzene (17): prepared according to general procedure A with 4-chloro-iodobenzene (72 mg, 0.3 mmol); purified by flash chromatography, eluting with *n*-pentane to afford the title compound as a yellow oil (28 mg, 58%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 (d, *J* = 9.0 Hz), 7.17 (d, *J* = 9.0 Hz, 1H), 2.46 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.1, 131.0, 129.0, 128.0, 16.2.

HRMS (ESI) *m/z* calc. C_7H_8SCl $[M+H]^+$ 159.0035, found 159.0031.

Data matched that reported in the literature.[8]



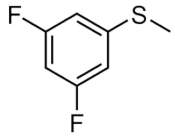
18

3-Chlorothioanisole (18): prepared according to general procedure A with 3-chloro-iodobenzene (72 mg, 0.3 mmol); purified by flash chromatography, eluting with *n*-pentane to afford the title compound as a colorless oil (36 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20 (t, *J* = 1.6 Hz), 7.18 (d, *J* = 7.6 Hz, 1H), 7.13 - 7.09 (m, 2H), 2.47 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.8, 134.9, 129.9, 126.0, 125.2, 124.6, 15.7.

Data matched that reported in the literature.[10]



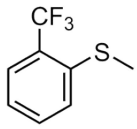
19

3,5-Diifluorothioanisole (19): prepared according to general procedure A with 1,3-difluoro-5-iodobenzene (72 mg, 0.3 mmol); purified flash chromatography, eluting with 1% Et_2O/*n*-pentane to afford the title compound as a colorless liquid (26 mg, 54%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.71 (dd, 2H, *J* = 8.4 Hz, *J* = 2.0 Hz), 6.54 (tt, 1H, *J* = 8.8 Hz, *J* = 2.0 Hz), 2.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.3 (dd, *J* = 249.7 Hz, *J* = 14.2 Hz), 142.9 (t, *J* = 9.6 Hz), 108.7 (dd, *J* = 18.8 Hz, *J* = 7.8 Hz), 100.4 (t, *J* = 25.7 Hz), 15.3.

HRMS (ESI) *m/z* calc. for $C_7H_7F_2S$ $[M+H]^+$ 161.0237, found 161.0231.



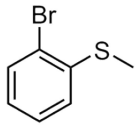
20

2-(Trifluoromethyl)thioanisole (20): prepared according to general procedure A with 1-iodo-2-(triflоromethyl)benzene (82 mg, 0.3 mmol); purified by flash chromatography, eluting with 1% Et_2O/*n*-pentane to afford the title compound as a colorless liquid (46 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (d, 1H, *J* = 8.0 Hz), 7.48 (t, 1H, *J* = 7.2 Hz), 7.37 (t, *J* = 8.0 Hz, 1H), 7.23 (t, *J* = 7.6Hz, 1H), 2.52 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.3, 131.0, 127.0 (q, *J* = 30.6 Hz), 126.4, 125.7 (q, *J* = 5.6 Hz), 122.9 (q, *J* = 272.1 Hz), 123.7, 15.4.

Data matched that reported in the literature.[10]



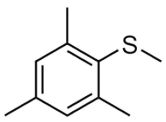
21

2-Bromothioanisole (21): prepared according to general procedure A with 1-bromo-2-iodobenzene (85 mg, 0.3 mmol); purified by flash chromatography, eluting with *n*-pentane, to afford the title compound as a colourless liquid (52 mg, 86%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (d, *J* = 6.4, 1.5 Hz), 7.30 (t, *J* = 6 Hz, 1H), 7.13 (d, *J* = 6.4 Hz), 7.00 (t, *J* = 7.2 1H), 2.48 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.6, 132.6, 127.8, 125.7, 125.4, 121.7, 15.7.

Data matched that reported in the literature.[8]



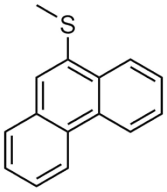
22

2-Methylthio-1,3,5-trimethylbenzene (22): prepared according to general procedure A with 2-iodo-1,3,5-trimethylbenzene (74 mg, 0.3 mmol); purified by flash chromatography, eluting with *n*-pentane to afford the title compound as a colorless liquid (24 mg, 48%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.93 (s, 2H), 2.52 (s, 6H), 2.26 (s, 3H), 2.20 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.8, 138.23, 132.0, 129.2, 21.9, 21.2, 18.7.

Data matched that reported in the literature.[11]



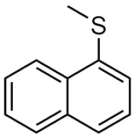
23

9-Phenanthrylmethylsulfide (23): prepared according to general procedure A with 9-iodophenanthrene (91 mg, 0.3 mmol); purified by flash chromatography, eluting with 1% Et_2O/*n*-pentane to afford the title compound as a yellow solid (49 mg, 73%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.72 (d, *J* = 1.6 Hz, 1H), 8.63 (d, *J* = 8.0 Hz, 1H), 8.36 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.83 - 7.80 (m, 1H), 7.71 - 7.64 (m, 2H), 7.62 - 7.56 (m, 3H),

^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.5, 132.0, 130.6, 130.4, 129.0, 127.7, 127.1, 127.0, 126.9, 126.1, 124.9, 123.4, 123.15, 122.7, 16. 0.

HRMS (ESI) *m/z* calc. for $C_{15}H_{13}S$ $[M+H]^+$ 225.0732, found 225.0732.



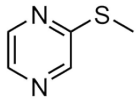
24

1-Methylthionaphalene (24): prepared according to general procedure A with 1-iodonapthalene (76 mg, 0.3 mmol); purified by flash chromatography, eluting with 1% Et_2O/*n*-pentane to afford the title compound as a white solid (48 mg, 92%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 (d, *J* = 8.0 Hz, 1H), 7.86 (dd, *J* = 8.0, 2.4 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.58-7.50 (m, 2H), 7.46-7.39(m, 2H), 2.59 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.98, 133.78, 131.81, 128.69, 126.39, 126.30, 125.99, 125.84, 124.44, 123.77, 16.38.

Data matched that reported in the literature.[8]



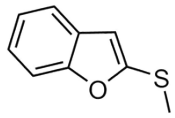
25

Methylthiopyrazine (25): prepared according to general procedure A with iodopyrazine (62 mg, 0.3 mmol); purified by flash chromatography, eluting with 20% Et_2O/*n*-pentane to afford the title compound (32 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46 (d, *J* = 1.5 Hz, 1H), 8.36 (dd, *J* = 2.5, 1.5 Hz, 1H), 8.19 (d, *J* = 2.5 Hz, 1H), 2.57 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.0, 145.1, 122.6, 122.1, 18.1.

Data matched that reported in the literature.[13]



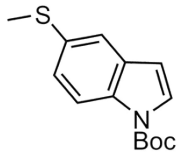
26

2-Methylthiobenzofuran (26): prepared according to general procedure A with 2-iodobenzofuran (73 mg, 0.3 mmol); purified by flash chromatography, eluting with *n*-pentane to afford the title compound (33 mg, 66%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 – 7.47 (m, 1H), 7.43 (d, *J* = 7.2 Hz), 7.27 – 7.18 (m, 2H), 6.69 (s, 1H), 2.55 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.2, 152.6, 128.9, 124.1, 123.0, 120.2, 110.9, 108.0, 17.2.

Data matched that reported in the literature.[14]



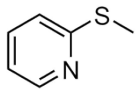
27

***N*-Boc-5-methylthioindole (27)**: prepared according to general procedure A with *tert*-butyl 5-iodo-1-H-indole-1-carboxylate (103 mg, 0.3 mmol); purified by flash chromatography, eluting 1% Et_2O/*n*-pentane to afford the title compound (51 mg, 64%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 8.3 Hz), 7.58 (d, *J* = 3.4 Hz, 1H), 7.49 (d, *J* = 1.7 Hz, 1H), 7.29 (dd, *J* = 8.3, 1.7 Hz), 6.50 (d, *J* = 3.4 Hz, 1H), 2.52 (s, 3H), 1.67 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 131. 5, 126.4, 124.5, 119.9, 115.3, 106.6, 83.6, 28.0, 17.4.

Data matched that reported in the literature.[15]



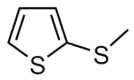
28

2-(Methylthio)pyridine (28): prepared according to general procedure A with 2-iodopyridine (62 mg, 0.3 mmol); purified by flash chromatography, eluting with 10% Et_2O/*n*-pentane, to afford the title compound as a white solid (19 mg, 50%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (dd, *J* = 5.0, 2.0 Hz, 1H), 7.48 (ddd, *J* = 8.0, 7.5, 1.9 Hz, 1H), 7.18 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.97 (ddd, *J* = 7.5, 5.0, 1.0 Hz, 1H), 2.56 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.0, 149.4, 135.7, 121.4, 119.0, 13.2.GW-B1-P2

Data matched that reported in the literature.[16]



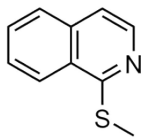
29

2-Methylthiothiophene (29): prepared according to general procedure A with 2-iodothiophene (63 mg, 0.3 mmol); purified by flash chromatography, eluting with *n*-pentane to afford the title compound as a colourless oil (32 mg, 82%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (dd, *J* = 4.4, 1.2 Hz, 1H), 7.06 (dd, *J* = 2.4, 1.2 Hz, 1H), 6.94 (td, *J* = 5.2, 3.6 Hz), 2.47 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.3, 131.2, 128.0, 127.6, 22.4.

Data matched that reported in the literature.[17]



30

1-Methylthioisoquinoline (30): prepared according to general procedure A with 1-iodoisoquinoline (77 mg, 0.3 mmol); purified by flash chromatography, eluting with 20% Et_2O/*n*-pentane, to afford the title compound as a yellow oil (48 mg, 91%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (d, *J* = 5.5 Hz, 1H), 8.20 (d, *J* = 8.5 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.66 (dd, *J* = 8.0, 7.0 Hz, 1H), 7.56 (dd, *J* = 8.5, 7.0 Hz, 1H), 7.33 (d, *J* = 5.5 Hz, 1H), 2.70 (3H).

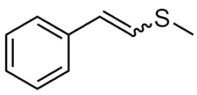
^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.1, 141.9, 135.2, 130.2, 127.0, 124.5, 117.0, 12.9.

Data matched that reported in the literature.[13]

General Procedure B

Vinyl iodide (0.3 mmol, 1.0 equiv.), dimethyl disulfide (1.2 mmol, 4.0 equiv.), 1,4-diazabicyclo[2.2.2]octane (1.2 mmol, 4.0 equiv.) and $Ir(ppy)_3$ (6 μmol, 2 mol %) were placed in a pressure-relief reaction vial and taken up in MeCN (3 mL). The vial was placed in a beaker containing ethylene glycol and heated at 60 °C for 24 h, whilst being irradiated with 10 W blue LEDs. The reaction mixture was concentrated under reduced pressure and the residue was purified by flash chromatography on silica to afford the final product.

Product Characterisation Data



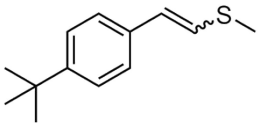
31

Methyl(styryl)sulfane (31): prepared according to general procedure B with *E*-1-(2-iodovinyl)benzene (69 mg, 0.3 mmol); purified by flash chromatography, eluting with *n*-pentane to afford title compound as a colourless oil (20 mg, 45%, *Z*/*E* = 1.3:1).

^{1}H NMR (400 MHz, $CDCl_3$): for *Z* isomer δ = 7.48 (d, *J* = 4.0 Hz, 3H), 7.31 – 7.38 (m, 3H), 6.46 (d, *J* = 10.8 Hz, 1H), 6.23 (d, *J* = 10.8 Hz, 1H), 2.43 (s, 3H); for *E* isomer δ = 7.20 –7.26 7.14 (m, 5H), 6.82 (d, *J* = 15.2 Hz, 1H), 6.31 (d, *J* = 15.2 Hz, 1H), 2.41 (s, 3H).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 137.2, 137.0, 129.1, 128.8, 128.7, 128.3, 126.8, 125.9, 125.5, 125.4, 124.8, 19.0, 14.9.

HRMS (ESI) *m/z* calc. for $C_9H_{11}S$ $[M+H]^+$ 151.0581, found 151.0576.



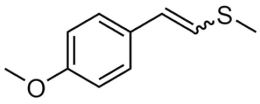
33

(4-(*tert*-Butyl)styryl)(methyl)sulfane (33): prepared according to general procedure B with 1-(*tert*-butyl)-4-(2-iodovinyl)benzene (86 mg, 0.3 mmol); purified by flash chromatography, eluting with *n*-pentane to give the title compound as a colourless oil (35 mg, 57%, *Z/E* = 1.4:1).

^{1}H NMR (400 MHz, $CDCl_3$): for *E* isomer δ = 7.33 – 7.31 (m, 2H), 7.25 – 7.22 (m, 2H), 6.74 (d, *J* = 15.4 Hz, 1H), 6.31 (d, *J* = 15.4 Hz, 1H), 2.38 (s, 3H), 1.31 (s, 9H); for *Z* isomer δ = 7.43 – 7.37 (m, 4H), 6.43 (d, *J* = 10.7 Hz, 1H), 6.16 (d, *J* = 10.7 Hz, 1H), 2.40 (s, 3H), 1.32 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$): for both *E* and *Z* isomer δ = 149.8, 149.7, 134.4, 134.1, 128.4, 128.0, 125.6, 125.22, 125.17, 125.1, 124.8, 34.6, 34.5, 31.3, 18.9, 14.9.

HRMS (ESI) *m/z* calc. for $C_{13}H_{18}S$ $[M]^+$ 206.1129, found 206.1129.



34

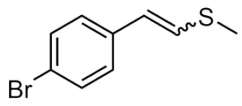
(4-(Methoxystyryl)(methyl)sulfane (34): prepared according to general procedure B with 1-(2-iodovinyl)-4-methoxybenzene (78 mg, 0.3 mmol); purified by flash chromatography, eluting with 5% Et_2O/*n*-pentane to give the title compound as a colourless oil (35 mg, 66%, *Z/E* = 0.3:1).

^{1}H NMR (400 MHz, $CDCl_3$): for *E* isomer δ = 7.25 – 7.21 (m, 2H), 6.86 – 6.82 (m, 2H), 6.62 (d, *J* = 15.4 Hz, 1H), 6.30 (d, *J* = 15.4 Hz, 1H), 3.80 (s, 3H), 2.37 (s, 3H); for *Z* isomer δ =

7.43 – 7.41 (m, 2H), 6.91 – 6.89 (m, 2H), 6.39 (d, *J* = 10.6 Hz, 1H), 6.08 (d, *J* = 10.6 Hz, 1H), 3.82 (s, 3H), 2.40 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): for *E* isomer δ = 158.7, 126.7, 124.9, 123.3, 114.2, 113.8, 55.4, 15.2; for *Z* isomer δ = 158.4, 130.2, 130.1, 129.9, 126.6, 125.1, 55.4, 18.9.

HRMS (ESI) *m/z* calc. for $C_{10}H_{13}OS$ $[M+H]^+$ 180.0687, found 180.0681.



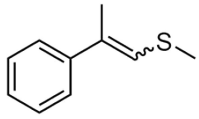
35

(4-(Bromostyryl)(methyl)sulfane (35): prepared according to general procedure B with 1-(2-iodovinyl)-4-bromobenzene (93 mg, 0.3 mmol); purified by flash chromatography, eluting with *n*-pentane to give the title compound as a colourless oil (21 mg, 31%, *Z/E* = 1.2:1).

^{1}H NMR (400 MHz, $CDCl_3$): for *E* isomer δ = 7.42 – 7.39 (m, 2H), 7.16 – 7.14 (m, 2H), 6.80 (d, *J* = 15.2 Hz, 1H), 6.23 (d, *J* = 15.2 Hz, 1H), 2.38 (s, 3H); for *Z* isomer δ = 7.48 – 7.46 (m, 2H), 7.35 – 7.33 (m, 2H), 6.36 (d, *J* = 10.9 Hz, 1H), 6.26 (d, *J* = 10.9 Hz, 1H), 2.42 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): for *E* isomer δ = 136.2, 135.9, 130.2, 127.0, 120.5, 120.3, 14.9; for *Z* isomer δ = 131.9, 131.5, 120.2, 126.9, 124.2, 123.4, 19.0.

HRMS (ESI) *m/z* calc. for $C_9H_{10}BrS$ $[M+H]^+$ 228.9687, found 228.9681.



36

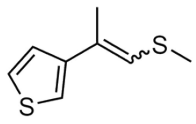
Methyl(2-phenylprop-1-en-1-yl)sulfane (36): prepared according to general procedure B with (*E*)-(1-iodoprop-1-en-2-yl)benzene (73 mg, 0.3 mmol); purified by flash

chromatography, eluting with *n*-pentane to give the title compound as a colourless oil (42 mg, 84%, *Z/E* = 1:2.8).

^{1}H NMR (400 MHz, $CDCl_3$): for *E* isomer δ = 7.40 – 7.34 (m, 5H), 5.99 (q, *J* = 1.4 Hz, 1H), 2.27 (s, 3H), 2.17 (d, *J* = 1.4 Hz, 3 H); for *Z* isomer δ = 7.32 – 7.20 (m, 5H), 6.29 (q, *J* = 0.9 Hz, 1H), 2.40 (s, 3H), 1.38 (d, *J* = 0.9 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): for *E* isomer δ = 128.4, 128.1, 127.6, 127.1, 125.1, 123.9, 24.8, 18.2; for *Z* isomer δ = 141.9, 140.6, 133.8, 133.0, 126.7, 125.3, 17.6, 17.4.

HRMS (ESI) *m/z* calc. for $C_{10}H_{12}S$ $[M]^+$ 164.0654, found 164.0654.



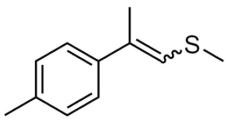
37

3-(1-(Methylthio)prop-1-en-2-yl)thiophene (37): prepared according to general procedure B with (*E*)-3-(1-iodoprop-1-en-2-yl)thiophene (75 mg, 0.3 mmol); Purified by flash chromatography, eluting with *n*-pentane to give the title compound as a colourless oil (28 mg, 55%, *Z/E* = 1:1.3).

^{1}H NMR (400 MHz, $CDCl_3$): for *E* isomer δ = 7.40 (dd, *J* = 2.9, 1.4 Hz, 1H), 7.39 (dd, *J* = 5.1, 1.4 Hz, 1H), 7.31 (dd, *J* = 5.1, 2.9 Hz, 1H), 5.94 (q, *J* = 1.3 Hz, 1H), 2.35 (s, 3H), 2.17 (d, *J* = 1.3 Hz, 3 H); for *Z* isomer δ = 7.26 (dd, *J* = 5.1, 2.9 Hz, 1H), 7.20 (dd, *J* = 5.1, 1.4 Hz, 1H), 7.07 (dd, *J* = 2.9, 1.4 Hz, 1H), 6.34 (q, *J* = 1.0 Hz, 1H), 2.38 (s, 3H), 2.10 (d, *J* = 1.0 Hz, 3 H);

^{13}C NMR (100 MHz, $CDCl_3$): for *E* and *Z* isomers δ = 143.3, 140.9, 128.7, 127.3, 125.7, 124.8, 124.7, 124.5, 123.9, 122.8, 118.5, 24.8, 18.6, 17.5.

HRMS (ESI) *m/z* calc. for $C_9H_{10}S_2$ $[M+H]^+$ 171.0302, found 171.0297.



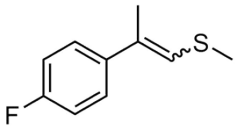
38

Methyl-(2-(*p*-tolyl)prop-1-en-1-yl)sulfane (38): prepared according to general procedure B with (*E*)-1-(1-iodoprop-1-en-2-yl)-4-methylbenzene (77 mg, 0.3 mmol); purified by flash chromatography, eluting with *n*-pentane to afford the title compound as a colourless oil (46 mg, 91%, *Z/E*-Ratio: 1:2.6).

^{1}H NMR (400 MHz, $CDCl_3$): for *E* isomer δ = 7.29 – 7.27 (m, 2H), 7.19 – 7.17 (m, 2H), 5.94 (q, *J* = 1.3 Hz, 1H), 2.35 (s, 3H), 2.25 (s, 3H), 2.14 (d, *J* = 1.3 Hz, 3 H); for *Z* isomer δ = 7.26 – 7.24 (m, 2H), 7.13 – 7.11 (m, 2H), 6.23 (q, *J* = 0.9 Hz, 1H), 2.38 (s, 3H), 2.34 (s, 3H), 2.11 (d, *J* = 0.9 Hz, 1 H)

^{13}C NMR (100 MHz, $CDCl_3$): for *E* isomer δ = 129.11, 128.9, 127.5, 125.1, 124.4, 123.4, 24.9, 21.3, 18.3; for *Z* isomer δ = 139.2, 137.7, 136.9, 136.4, 133.9, 133.1, 21.1, 17.7, 17.4.

HRMS (ESI) *m/z* calc. for $C_{10}H_{11}FS$ $[M]^+$ 178.0816, found 178.0809.



39

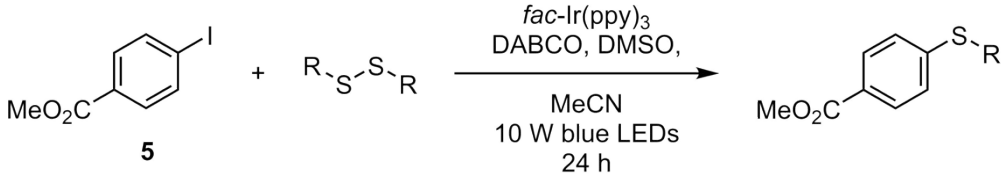
(2-(4-Fluorophenyl)prop-1-en-1-yl)(methyl)sulfane (39): prepared according to general procedure B with (*E*)-1-fluoro-4-(1-iodoprop-1-en-2-yl)benzene (79 mg, 0.3 mmol); purified by flash chromatography, eluting with *n*-pentane to afford the title compound as a colourless oil (53 mg, 84%, *Z/E*-Ratio: 1:2.9).

^{1}H NMR (400 MHz, $CDCl_3$): for *E* isomer δ = 7.37 – 7.33 (m, 2H), 7.07 – 7.02 (m, 2H), 5.97 (q, *J* = 1.3 Hz, 1H), 2.26 (s, 3H), 2.13 (d, *J* = 1.3 Hz, 3H); for *Z* isomer δ = 7.32 – 7.28 (m, 2H), 7.02 – 6.97 (m, 2H), 6.21 (q, *J* = 0.4 Hz, 1H), 2.39 (s, 3H), 2.10 (d, *J* = 0.4 Hz, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): for *E* isomer δ = 161.8 (d, *J* = 247 Hz), 136.6 (d, *J* = 3.2 Hz), 132.8, 129.4 (d, *J* = 7.9 Hz), 124.2 (d, *J* = 1.2 Hz), 115.1 (d, *J* = 21 Hz), 25.0, 18.2; for *Z* isomer δ = 161.9 (d, *J* = 247 Hz), 138.2 (d, *J* = 3.2 Hz), 132.2, 126.7 (d, *J* = 7.9 Hz), 125.3 (d, *J* = 1.2 Hz), 115.2 (d, *J* = 21 Hz), 17.8, 17.4.

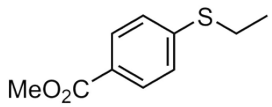
HRMS (ESI) *m/z* calc. for $C_{10}H_{11}FS$ $[M]^+$ 182.0565, found 182.0560.

General Procedure C



Methyl 4-iodobenzoate **5** (0.3 mmol, 1.0 equiv.), dialkyl disulfide (1.2 mmol, 4.0 equiv.), 1,4-diazabicyclo[2.2.2]octane (1.2 mmol, 4.0 equiv.), $Ir(ppy)_3$ (6 μmol, 2 mol%) and DMSO (50.5 μL, 2.0 equiv.) were placed in a 4 mL scintillation vial and taken up in MeCN (3 mL). The vial was sealed with a plastic screw cap and stirred for 24 h at room temperature whilst being irradiated with 10 W blue LEDs. The reaction mixture was concentrated under reduced pressure and the residue was purified by flash chromatography on silica to afford the final product.

Product Characterisation Data



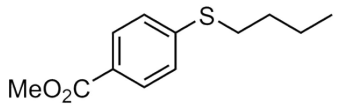
40

Methyl 4-(ethylthio)benzoate (40): prepared according to general procedure C with diethyl disulfide; purified by flash chromatography, eluting with 10% Et_2O/*n*-pentane to afford the title compound as a white solid (36 mg, 61%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.93 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 3.90 (s, 3H), 3.02 (q, *J* = 7.5 Hz, 2H), 1.37 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.0, 144.2, 130.0, 126.4, 52.2, 26.3, 14.1.

HRMS (ESI) *m/z* calc. for $C_{14}H_{20}OS$ $[M]^+$ 196.0612, found 196.0611.



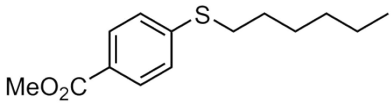
41

Methyl 4-(butylthio)benzoate (41): prepared according to general procedure C with dibutyl disulfide; purified by flash chromatography, eluting with 10 % Et_2OAc/*n*-pentane to afford the title compound (33 mg, 49%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 3.87 (s, 3H), 2.96 (t, *J* = 7.2 Hz, 2H), 1.62-1.70 (m, 2H), 1.41-1.50 (m, 2H), 0.92 (t, *J* = 7.2 Hz 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9, 144.6, 130.0, 126.7, 126.4, 52.2, 30.9, 22.1, 13.8.

Data matched that reported in the literature.[18]



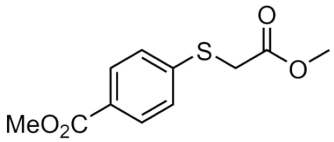
42

Methyl 4-(hexylthio)benzoate (42): prepared according to general procedure C with dihexyl disulfide; purified by flash chromatography, eluting with 10% Et_2OAc/*n*-pentane to afford the title compound (32 mg, 42%).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 8.8 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 3.89 (s, 3H), 2.98 (t, *J* = 7.2 Hz, 2H), 1.65-1.73 (m, 2H), 1.43-1.48 (m, 2H), 1.25-1.32 (m, 4H), 0.89 (t, 7.2 Hz, 3H).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 166.99, 144.6, 130.0, 126.6, 126.4, 52.2, 32.2, 31.5, 29.86, 28.7, 22.7, 14.2.

HRMS (ESI) *m/z* calc. for $C_{14}H_{20}OS$ $[M]^+$ 252.1221, found 252.1220.



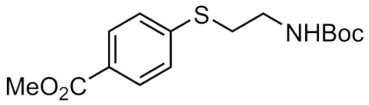
43

Methyl 4-((2-methoxy-2-oxoethyl)thio)benzoate (43): prepared according to general procedure C with dimethyl 2,2'-disulfanediyldiacetate; purified by flash chromatography, eluting with 5% Et_2OAc/*n*-pentane to afford the title compound (22 mg, 31%).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 8.6 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 2H), 3.91 (s, 3H), 3.58 (s, 3H), 3.51 (s, 2H).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 169.0, 166.5, 142.4, 130.2, 128.6, 126.3, 52.4, 52.1, 40.5, 30.3, 29.6.

HRMS (ESI) *m/z* calc. for $C_{11}H_{12}O_4S$ $[M]^+$ 140.9998, found 140.9996.



44

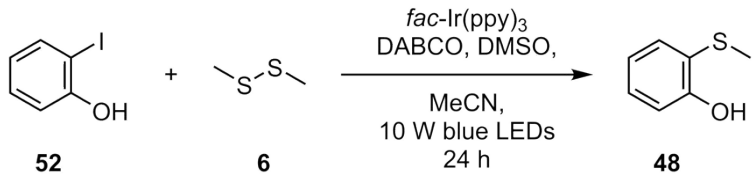
Methyl 4-((2-((tert-butoxycarbonyl)amino)ethyl)thio)benzoate (44); prepared according to general procedure C with Boc-protected 2,2'-dithio-bis(ethylamine); purified by flash chromatography, eluting with 2% Et_2OAc/*n*-pentane to afford the title compound (44 mg, 47%).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 4.9 (s, 1H), 3.80 (s, 3H), 3.36 (q, *J* = 6.4 Hz, 2H), 3.10 (t, *t* = 6.4 Hz, 2H), 1.42 (s, 3H).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 166.8, 155.8, 142.8, 130.2, 127.0, 79.7, 52.2, 39.7, 32.7, 32.5, 29.8, 28.5.

HRMS (ESI) *m/z* calc. for $C_{15}H_{21}O_4NS$ $[M]^+$ 311.1186, found 311.1186.

Synthesis of semiochemicals



52 **6** **48**

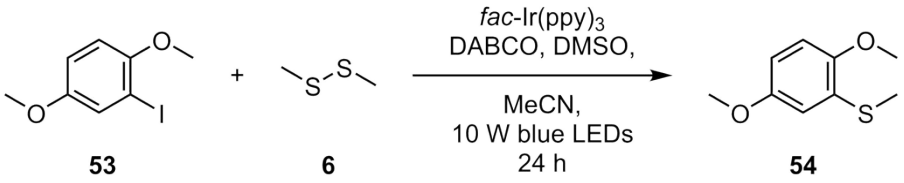
Compound **48** was synthesised according to the general procedure A. 2-Iodophenol (**52**) (66 mg, 0.3 mmol), dimethyl disulfide (0.108 mL, 1.2 mmol), 1,4-diazabicyclo[2.2.2]octane (135 mg, 1.2 mmol), $Ir(ppy)_3$ (4 mg, 6 μmol) and DMSO (50.5 μL, 0.6 mmol) were placed in a 4 mL scintillation vial and taken up in MeCN (3 mL). The vial was sealed with a plastic screw cap and stirred for 24 h at room temperature whilst being irradiated with 10 W blue LEDs. The solvent was removed under reduced pressure and the residue was purified by flash

chromatography on silica, eluting with 5 % Et_2O/*n*-pentane to afford 2-(methylthio)phenol **48** as a yellowish oil (39 mg, 93% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (dd, *J* = 6.0 & 1.6 Hz, 1H), 7.25 (td, *J* = 6.0 & 2.0 Hz, 1H), 6.92 (d, *J* = 6.8 Hz, 1H), 6.82 (td, *J* = 6.4 & 1.6 Hz, 1H), 6.40 (s, 1H). 2.33 (s, 3H).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 156.2, 134.8, 130.7, 120.9, 114.8, 19.8.

Data matched that reported in the literature.[19]

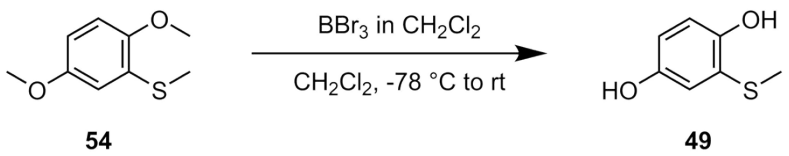


53 **6** **54**

Compound **54** was synthesised according to the general procedure A. 2-1odo-1,4-dimethoxybenene (**53**) (79 mg, 0.3 mmol), dimethyl disulfide (0.108 mL, 1.2 mmol), 1,4-diazabicyclo[2.2.2]octane (135 mg, 1.2 mmol), $Ir(ppy)_3$ (4 mg, 6 μmol) and DMSO (50.5 μL, 0.6 mmol) were placed in a 4 mL scintillation vial and taken up in MeCN (3 mL). The vial was sealed with a plastic screw cap and stirred for 24 h at room temperature whilst being irradiated with 10 W blue LEDs. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica, eluting with 2 % Et_2O/*n*-pentane to afford 2-(methylthio)-1,4-dimethoxybenzene as a yellowish oil (40 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.77 (d, *J* = 8.2 Hz, 1H), 6.74 (d, *J* = 3.2 Hz, 1H), 6.62 (dd, *J* = 6.8 Hz, *J* = 3.2 Hz, 1H), 3.84 (s, 3H), 3.78 (s, 3H), 2.43 (s, 3H).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 156.2, 154.2, 134.8, 130.7, 120.9, 114.8, 56.2, 53.2, 19.8.



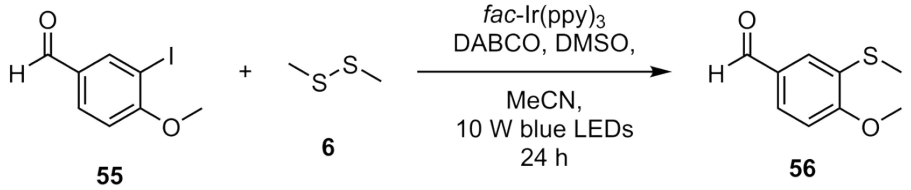
54 **49**

A solution of BBr_3 in CH_2Cl_2 (1 M, 2.1 mL, 2.1 mmol) was added dropwise, at -78 °C, to a solution of 4-methoxy-3-(methylthio)benzaldehyde (**54**) (40 mg, 0.21 mmol) in CH_2Cl_2 (1 mL). The reaction mixture was stirred at room temperature for 5 h. It was quenched with water and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were washed with brine (3 × 30 mL) and dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue purified by flash chromatography by on silica, eluting with 10% EtOAc/*n*-pentane, to give 1,4-dihydroxy-2-(methylthio)benzene (**49**) as a oil (29 mg, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.95 (d, *J* = 2.8 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 6.77 (d, *J* = 4.0 Hz, 1H), 6.74-6.75 (m, 2H), 6.16 (s, 1H). 2.38 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.1, 141.1, 118.1, 112.5, 111.8, 108.6, 19.9.

Data matched that reported in the literature.[19]



55 **6** **56**

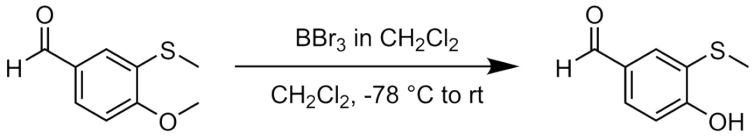
Compound **56** was synthesised according to the general procedure A. 3-Iodo-4-methoxybenzaldehyde (**55**) (79 mg, 0.3 mmol), dimethyl disulfide (0.108 mL, 1.2 mmol), 1,4-diazabicyclo[2.2.2]octane (135 mg, 1.2 mmol), $Ir(ppy)_3$ (4 mg, 6 μmol) and DMSO (50.5 μL, 0.6 mmol) were placed in a 4 mL scintillation vial and taken up in MeCN (3 mL). The vial was sealed with a plastic screw cap and stirred for 24 h at room temperature whilst being irradiated with 10 W blue LEDs. The solvent was removed under reduced pressure and the

residue was purified by flash chromatography on silica, eluting with 10 % Et_2O/*n*-pentane to afford 4-methoxy-3-(methylthio)benzaldehyde (**56**) as a colourless oil (45 mg, 83% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.87 (s, 1H), 7.67-7.63 (m, 2H), 6.94 (d, *J* = 8.2 Hz, 1H), 3.98 (s, 3H), 2.49 (s, 3H).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 190.8, 160.8, 130.5, 130.0, 129.6, 125.2, 109.5, 56.4, 14.4.

Data matched that reported in the literature.[19]



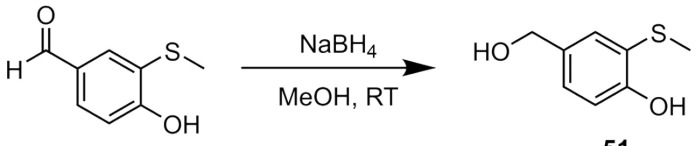
56 **50**

A solution of BBr_3 in CH_2Cl_2 (1 M, 2.7 mL, 2.7 mmol) was added dropwise, at -78 °C, to a solution of 4-methoxy-3-(methylthio)benzaldehyde (**56**) (50 mg, 0.27 mmol) in CH_2Cl_2 (1 mL). The reaction mixture was stirred at room temperature for 3 h. It was quenched with water and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were washed with brine (3 × 30 mL) and dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue purified by flash chromatography on silica, eluting with 20% EtOAc/*n*-pentane, to give 4-hydroxy-3-(methylthio)benzaldehyde (**50**) as a white solid (34 mg, 75% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.84 (s, 1H), 8.02 (d, *J* = 2.1 Hz, 1H), 7.77 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.35 (br s, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 2.38 (s, 3H).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 190.4, 161.4, 136.3, 132.7, 130.4, 123.0, 115.5, 19.5.

HRMS (ESI) *m/z* calc. for $C_8H_9O_2S$ $[M+H]^+$ 169.0323, found 169.0318.



50 **51**

Sodium borohydride (8 mg, 0.21 mmol) was added in small portions to a solution of 4-hydroxy-3-(methylthio)benzaldehyde (**50**) (30 mg, 0.18 mmol) in MeOH (1 mL) and the reaction mixture was stirred at room temperature for 14 h. It was quenched with AcOH and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (10 mL), washed with brine (3 × 10 mL), and dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue purified by flash chromatography by on silica, eluting with 30% EtOAc/*n*-pentane, to give 4-(hydroxymethyl)-2-(methylthio)phenol (**51**) as a yellowish solid (27 mg, 90% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 2.1 Hz, 1H), 7.24 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.96 (d, *J* = 8.3 Hz, 1H), 6.63 (br s, 1H), 4.60 (s, 2H), 2.34 (s, 3H).

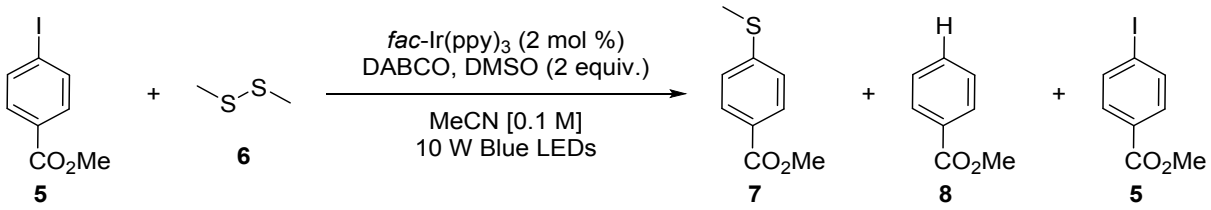
^{13}C NMR (400 MHz, $CDCl_3$): δ = 155.8, 133.6, 133.5, 129.8, 121.1, 114.9, 64.8, 19.8.

HRMS (ESI) *m/z* calc. for $C_8H_{11}O_2S$ $[M+H]^+$ 171.0480, found 171.0474.

Mechanistic Studies

Control experiments

Table S1. The effect of DABCO concentration, light and photocatalyst[a]



Entry	Deviations from general conditions	**7** [%][b]	**8** [%][b]	**5** [%][b]
1	none	100	ND	ND
2	2.0 equiv. DABCO	41	ND	59
3	1.0 equiv. DABCO	30	ND	69
4	No $Ir(ppy)_3$	1	trace	97
5	No light	ND	ND	100

[a] General conditions: **5** (0.3 mmol), *fac*-$Ir(ppy)_3$ (2 mol%), solvent (0.1 M in substrate), 24 h, 10 W blue LEDs; [b] Yields determined by ^1H NMR spectroscopic analysis using 2,5-dimethylfuran as an internal standard;

Phosphorescence quenching measurements

Samples for steady-state and time-resolved photoluminescence were prepared in the following manner. Dimethyl disulfide was added to an acetonitrile solution of $Ir(ppy)_3$ (0.01 mM) and made to a given concentration in a volumetric flask. The solution was then transferred to a septum-capped quartz cuvette and deoxygenated immediately prior to measurement by sparging with argon for approximately 10 min. A pre-weighed amount of DABCO or methyl 4-iodobenzoate was dissolved in an acetonitrile solution of $Ir(ppy)_3$ (0.01 mM) and made to a given concentration in a volumetric flask. The solution was then

transferred to a septum-capped quartz cuvette and deoxygenated immediately prior to measurement by sparging with argon for approximately 10 min.

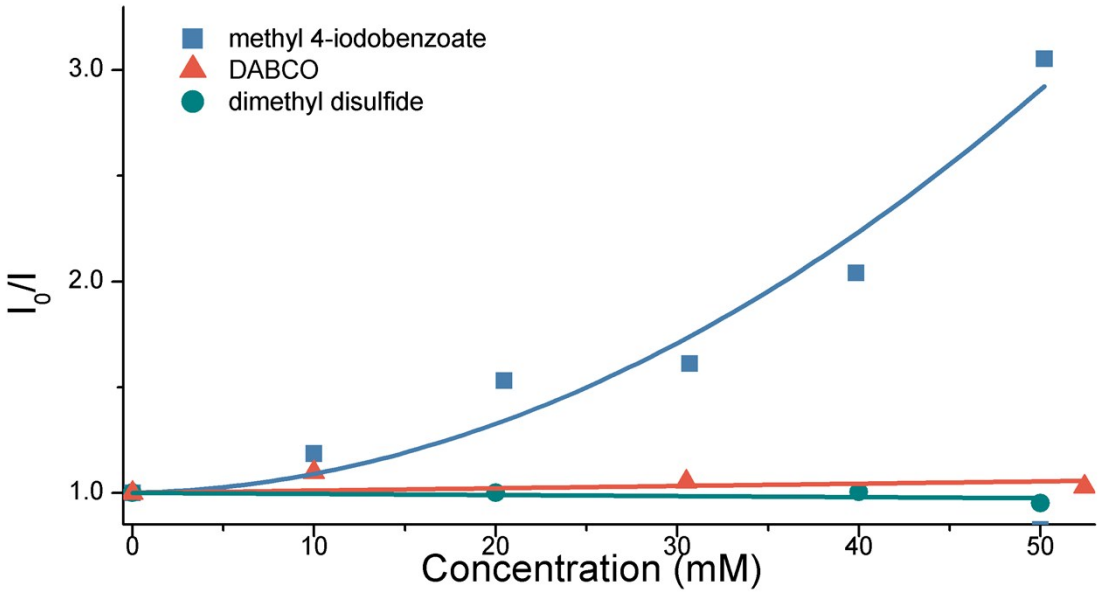


Figure S2. Stern-Volmer plot of $Ir(ppy)_3$ phosphorescence intensity in the presence of methyl 4-iodobenzoate (■), DABCO (□), dimethyl disulfide (●).

Transient absorption spectroscopy (TAS) measurements

Dimethyl disulfide was added to an acetonitrile solution of $Ir(ppy)_3$ (0.1 mM) and made to a given concentration in a volumetric flask. Pre-weighed amounts of either DABCO or methyl 4-iodobenzoate were dissolved in an acetonitrile solution of $Ir(ppy)_3$ (0.1 mM) and made to a given concentration in a volumetric flask. Solutions were deoxygenated immediately prior to measurement by sparging with argon for approximately 6 min.

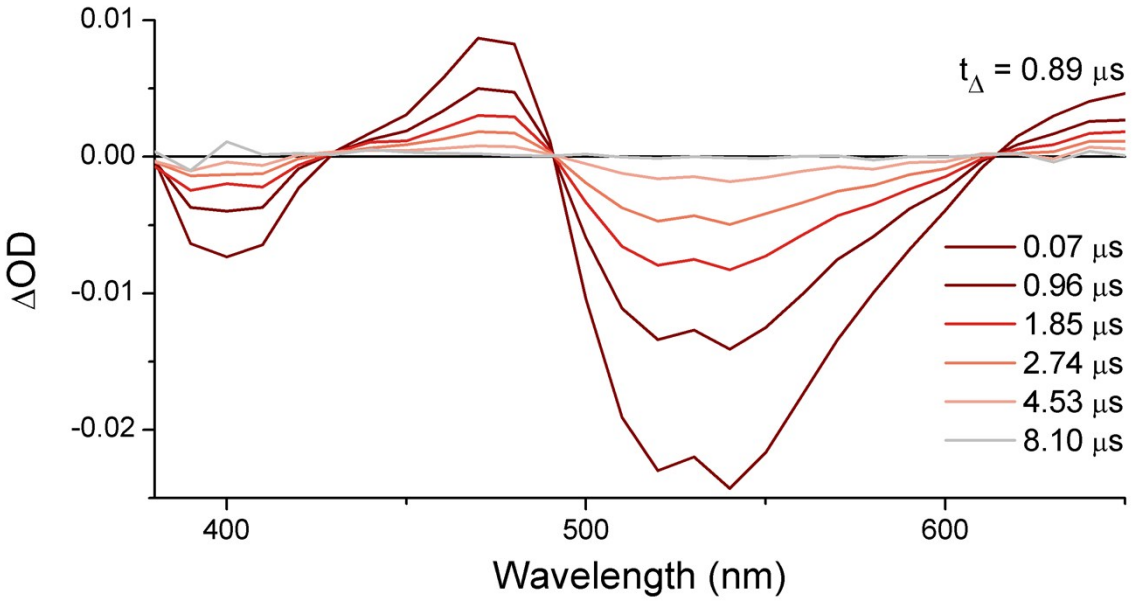


Figure S3. Transient absorption difference spectra of $Ir(ppy)_3$ (0.1 mM) with addition of DABCO (20 mM) recorded at various delay times after excitation. Solutions were prepared in acetonitrile and sparged with argon (6 min) before measurement; λ_{ex} = 355 nm.

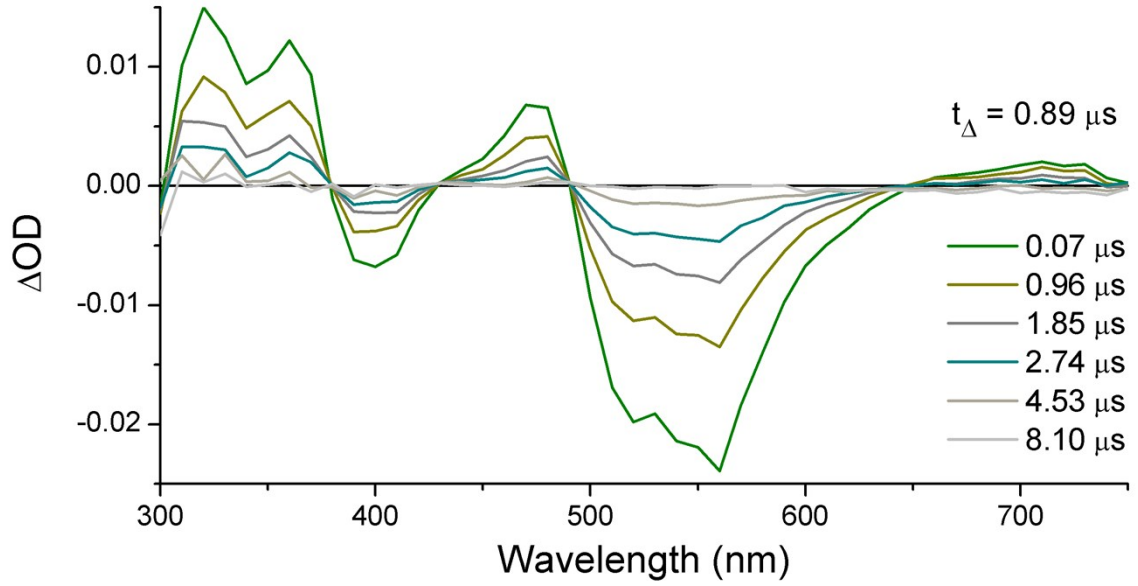


Figure S4. Transient absorption difference spectra of $Ir(ppy)_3$ (0.1 mM) with addition of dimethyl disulfide (20 mM) recorded at various delay times after excitation. Solutions were prepared in acetonitrile and sparged with argon (6 min) before measurement; λ_{ex} = 355 nm.

Disulfide exchange experiments

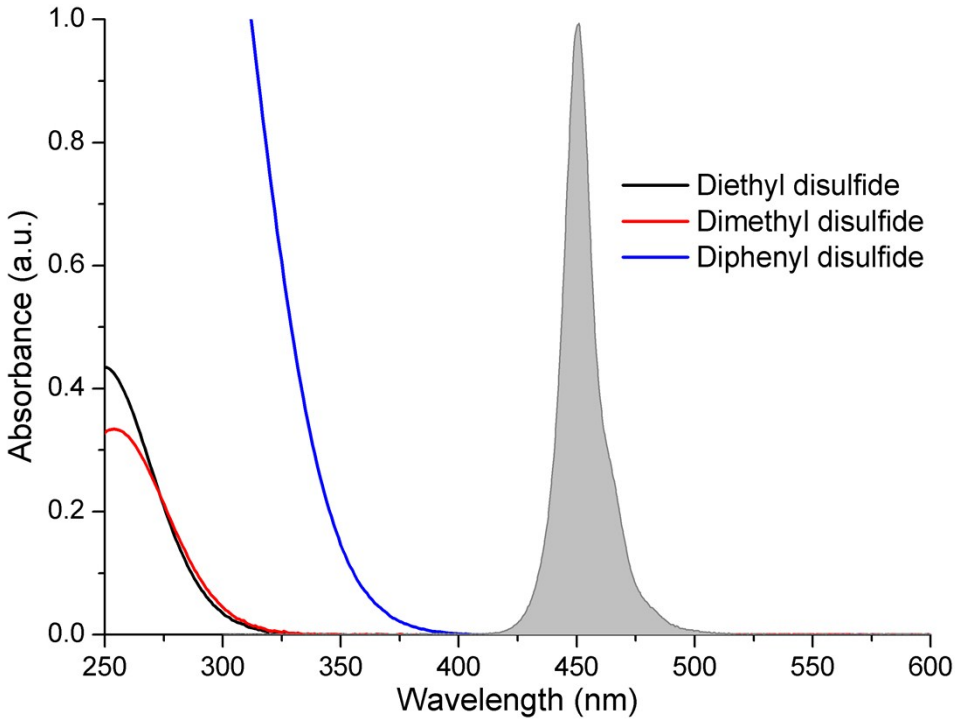
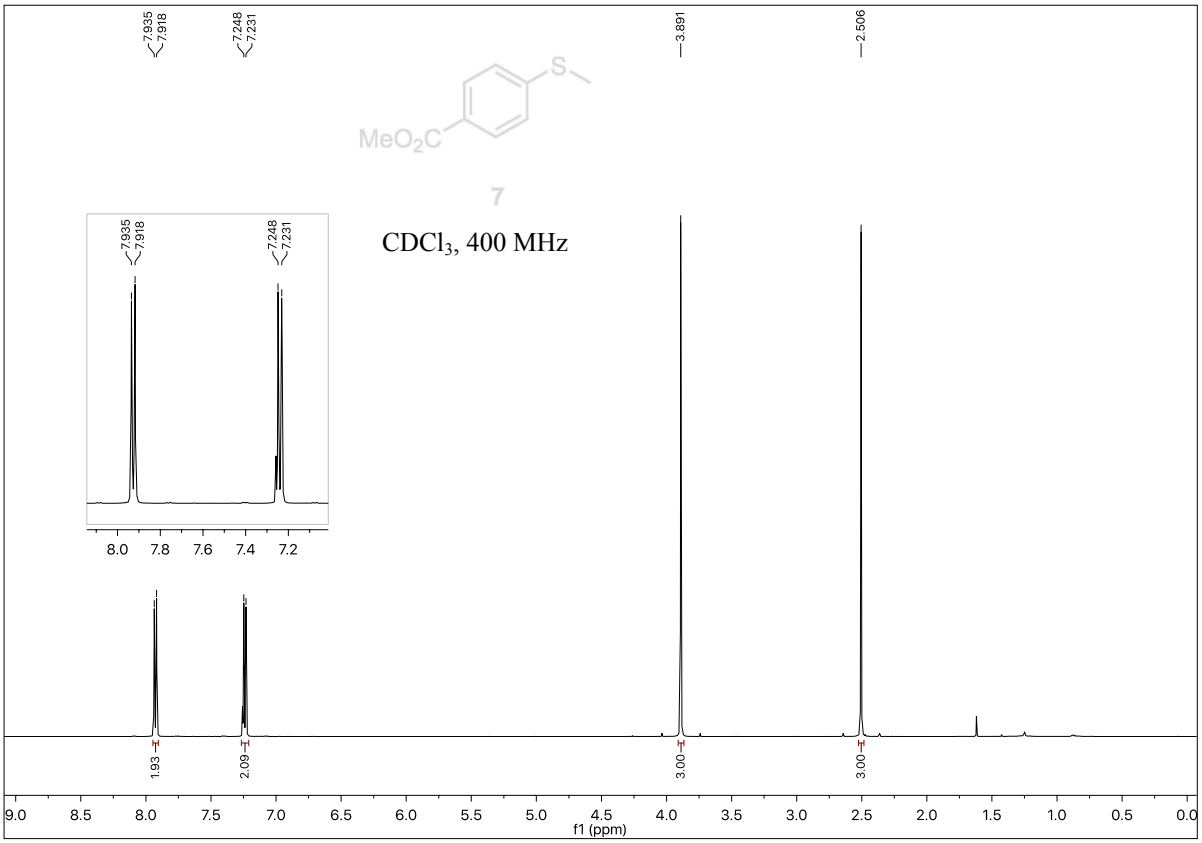
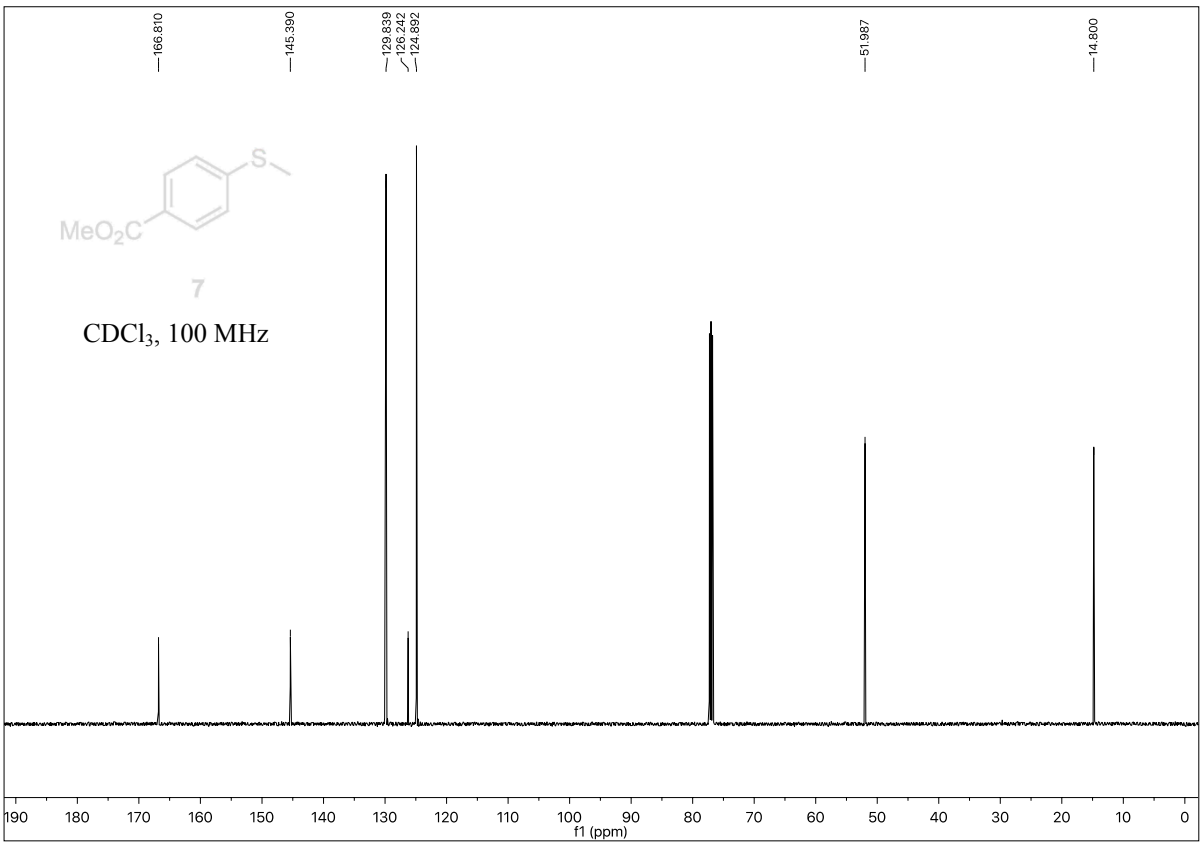
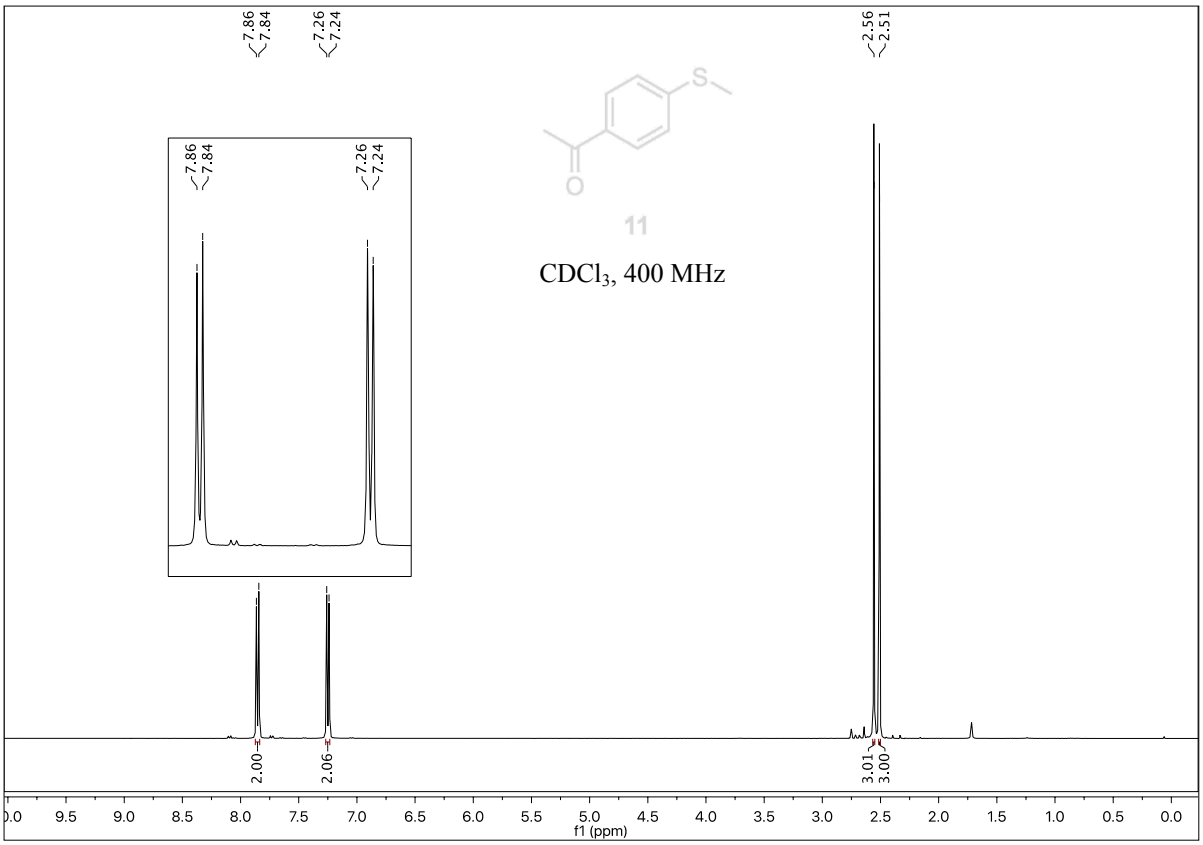


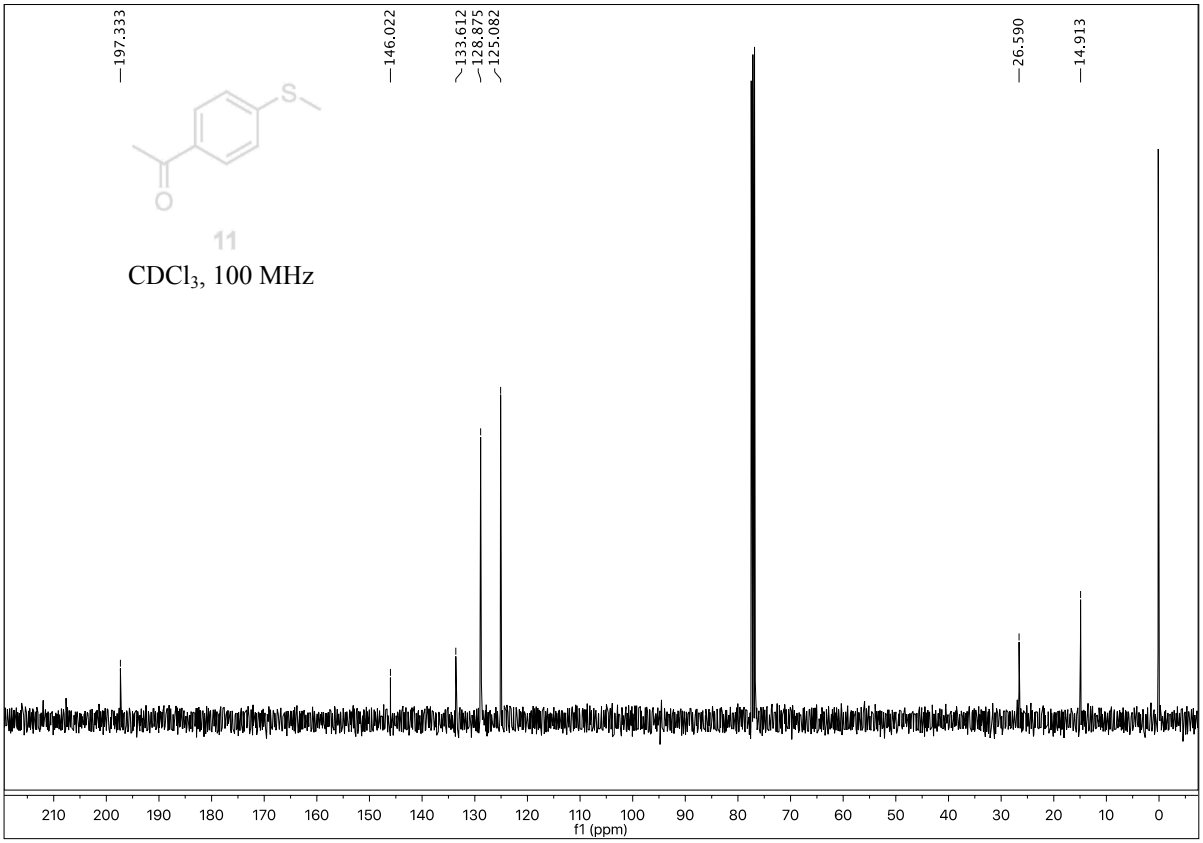
Figure S5. Absorbance spectra of 10 mM dimethyl, diethyl and diphenyl disulfides in acetonitrile, overlaid with the spectral output for the blue LED lamp (see Figure S1). Only absorbance spectrum of diphenyl disulfide (blue trace) overlaps with the emission spectrum of the blue LED lamp (grey area).

[1] H NMR and [13]C NMR Spectra






7.86
7.84
7.26
7.24
2.56
2.51
11
CDCl3, 400 MHz
2.00
2.06
3.01
3.00
f1 (ppm)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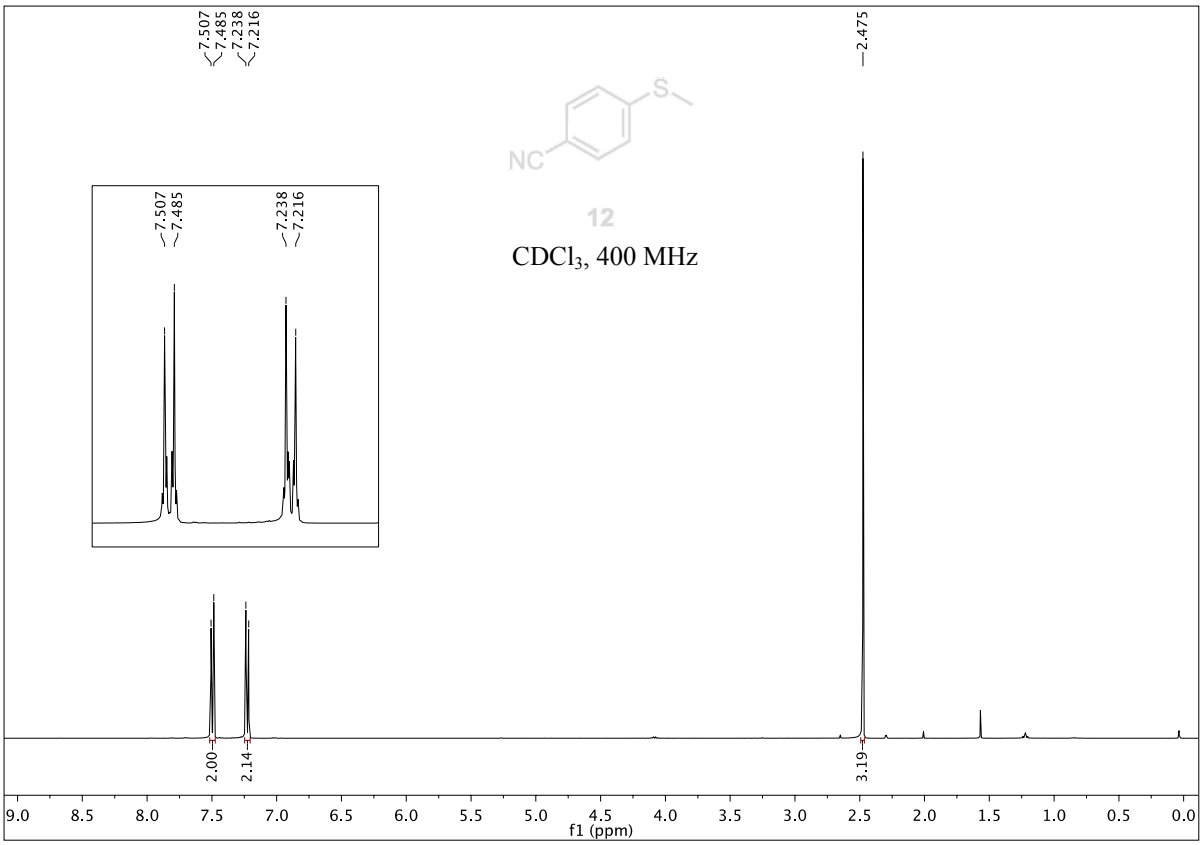
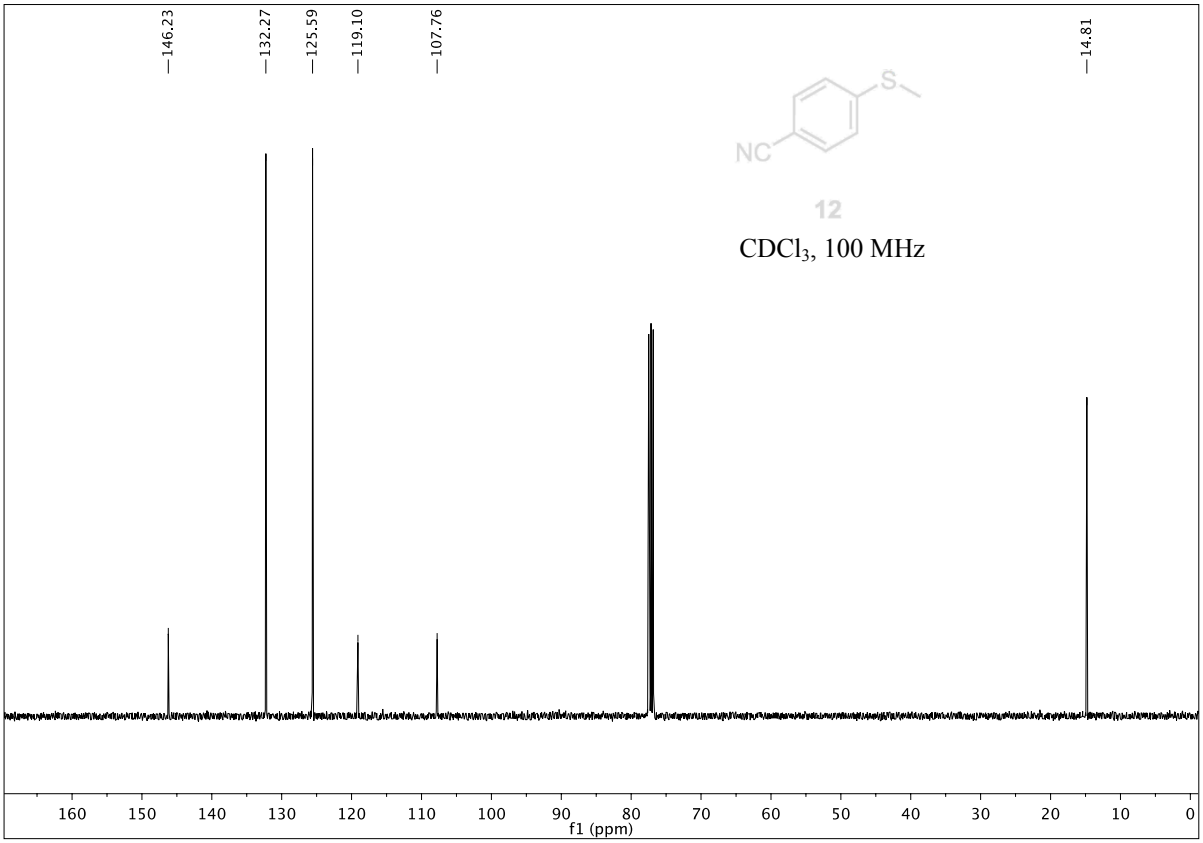
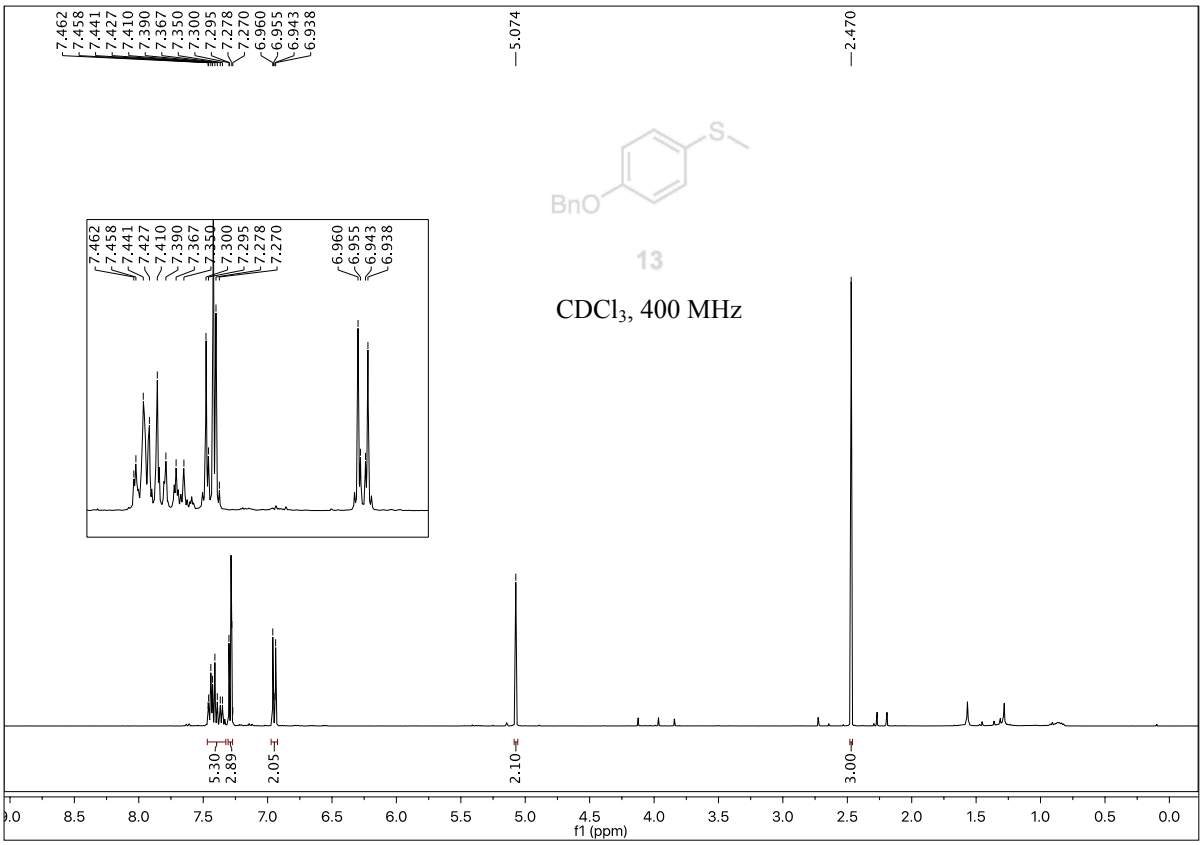
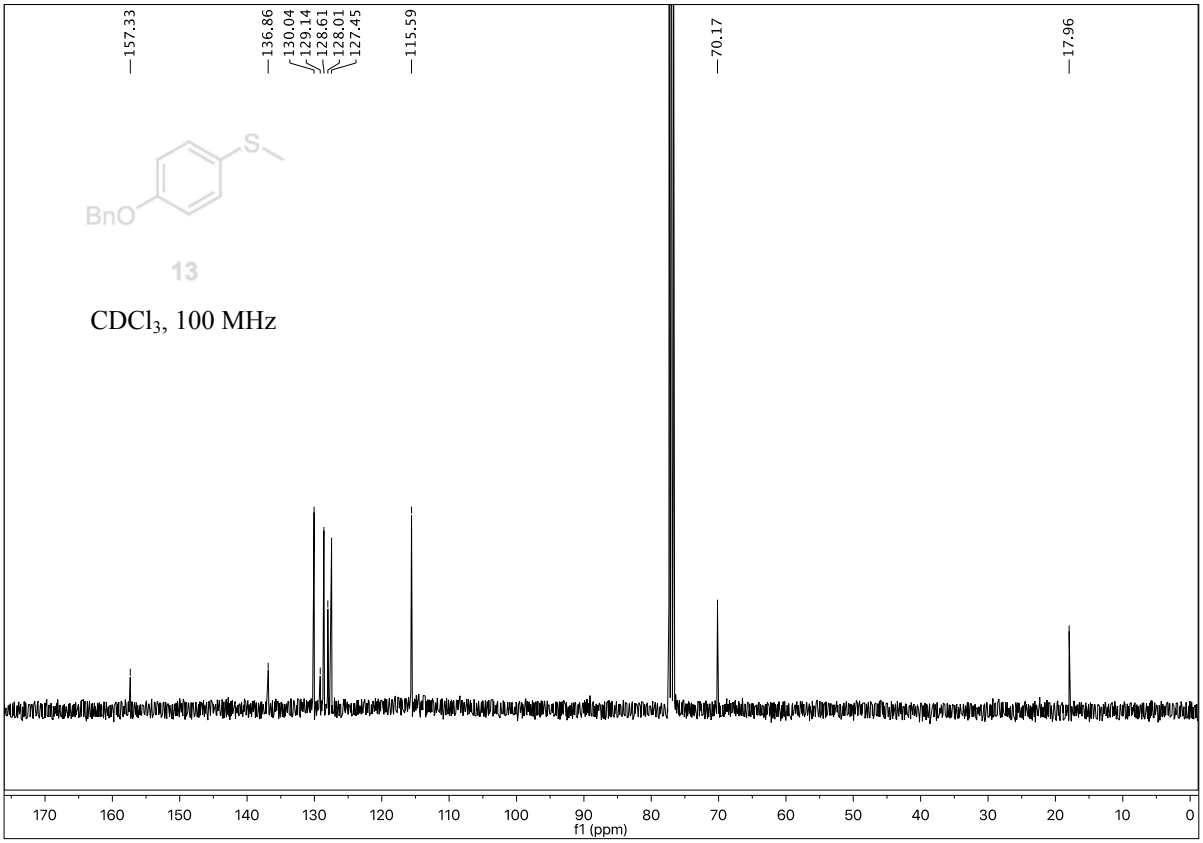
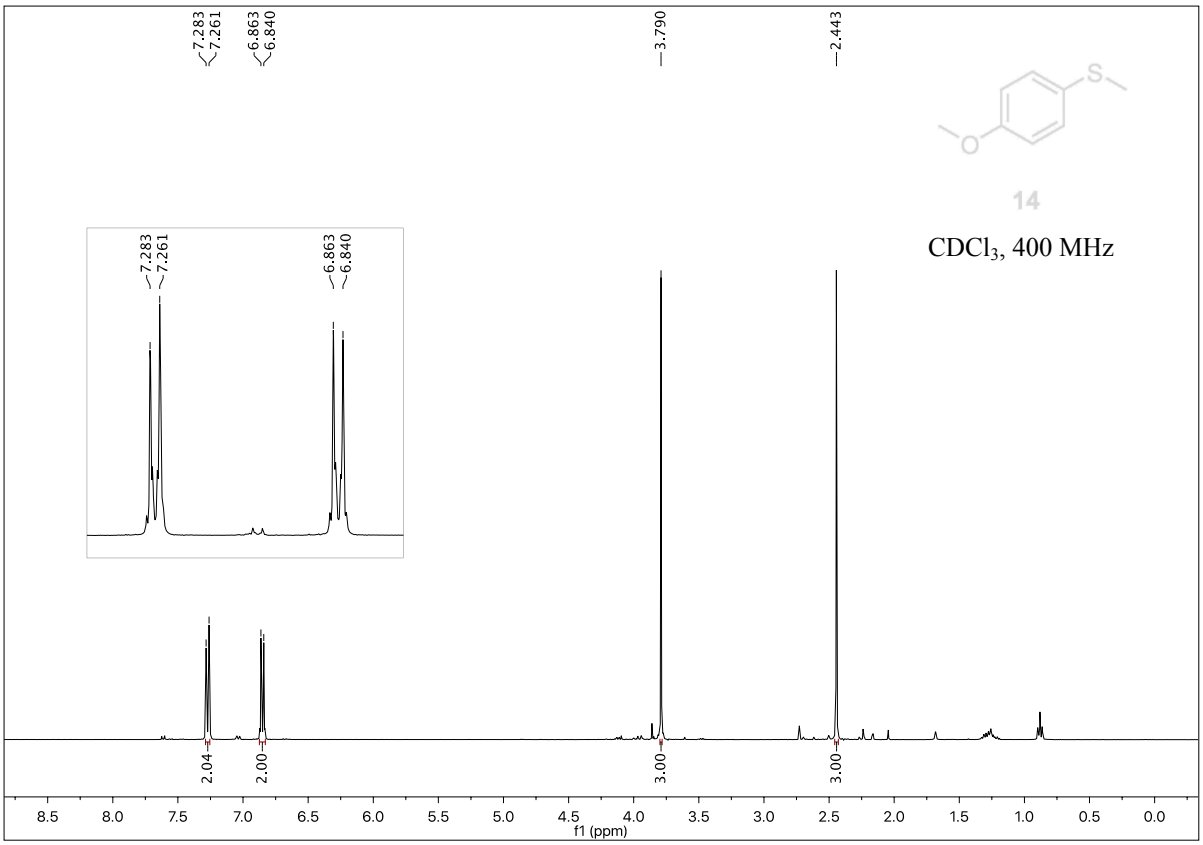
146.022
133.612
128.875
125.082
26.590
14.913
11
CDCl3, 100 MHz
f1 (ppm)

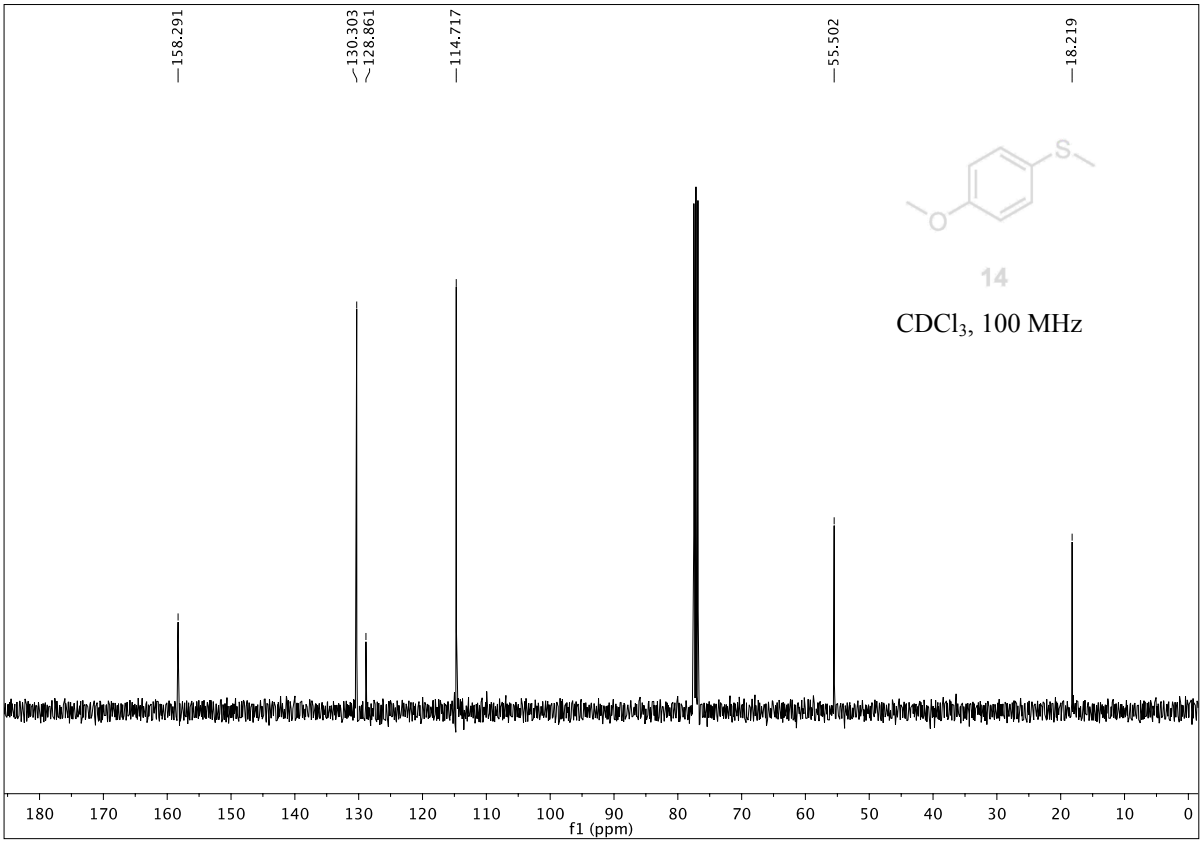

7.507
7.485
7.238
7.216
2.475
S
NC
12
CDCl3, 400 MHz
2.00
2.14
3.19
f1 (ppm)


146.23
132.27
125.59
119.10
107.76
14.81
S
NC
12
CDCl3, 100 MHz
f1 (ppm)


7.462
7.458
7.441
7.427
7.410
7.390
7.367
7.350
7.300
7.295
7.278
7.270
6.960
6.955
6.943
6.938
5.074
2.470
BnO
S
13
CDCl3, 400 MHz
5.30
2.89
2.05
2.10
3.00
f1 (ppm)


157.33
136.86
130.04
129.14
128.61
128.01
127.45
115.59
70.17
17.96
BnO
S
13
CDCl3, 100 MHz
f1 (ppm)


7.283
7.261
6.863
6.840
3.790
2.443
14
CDCl3, 400 MHz
2.04
2.00
3.00
3.00
f1 (ppm)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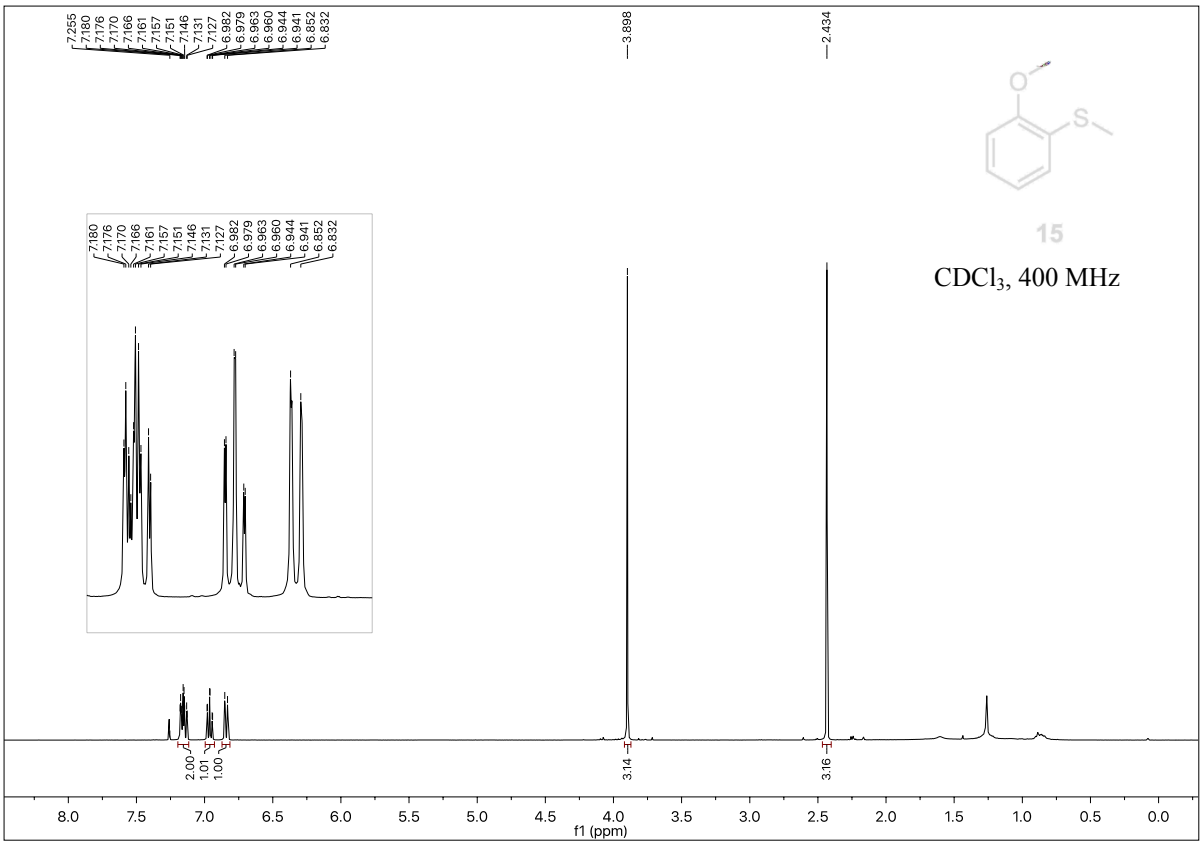
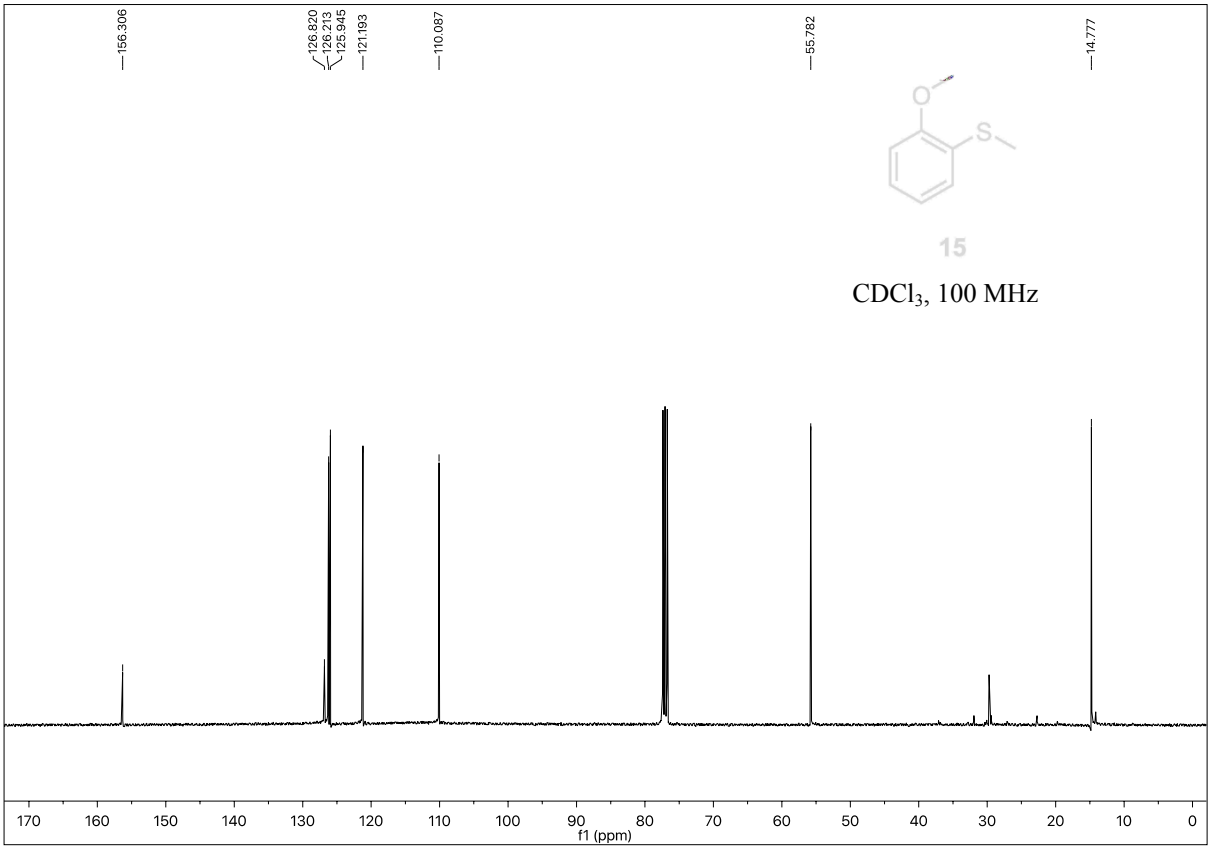
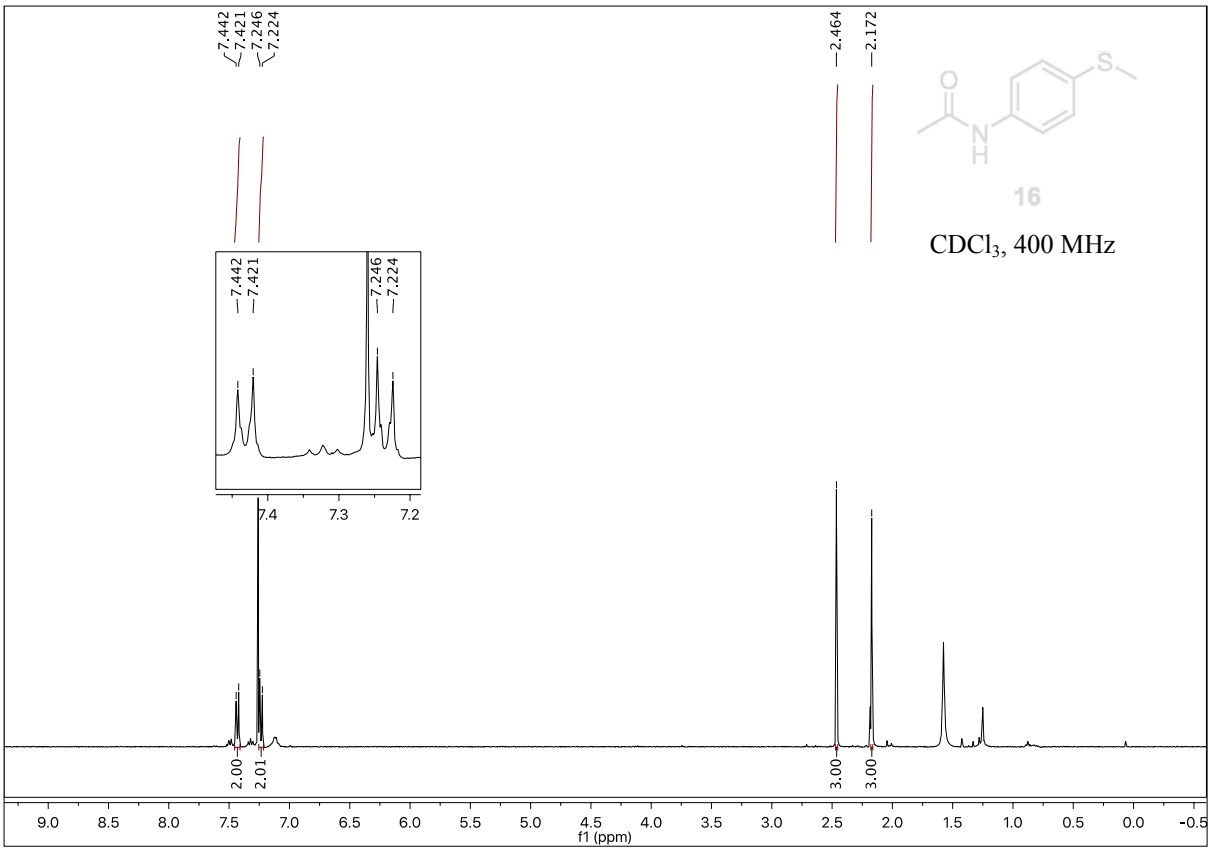
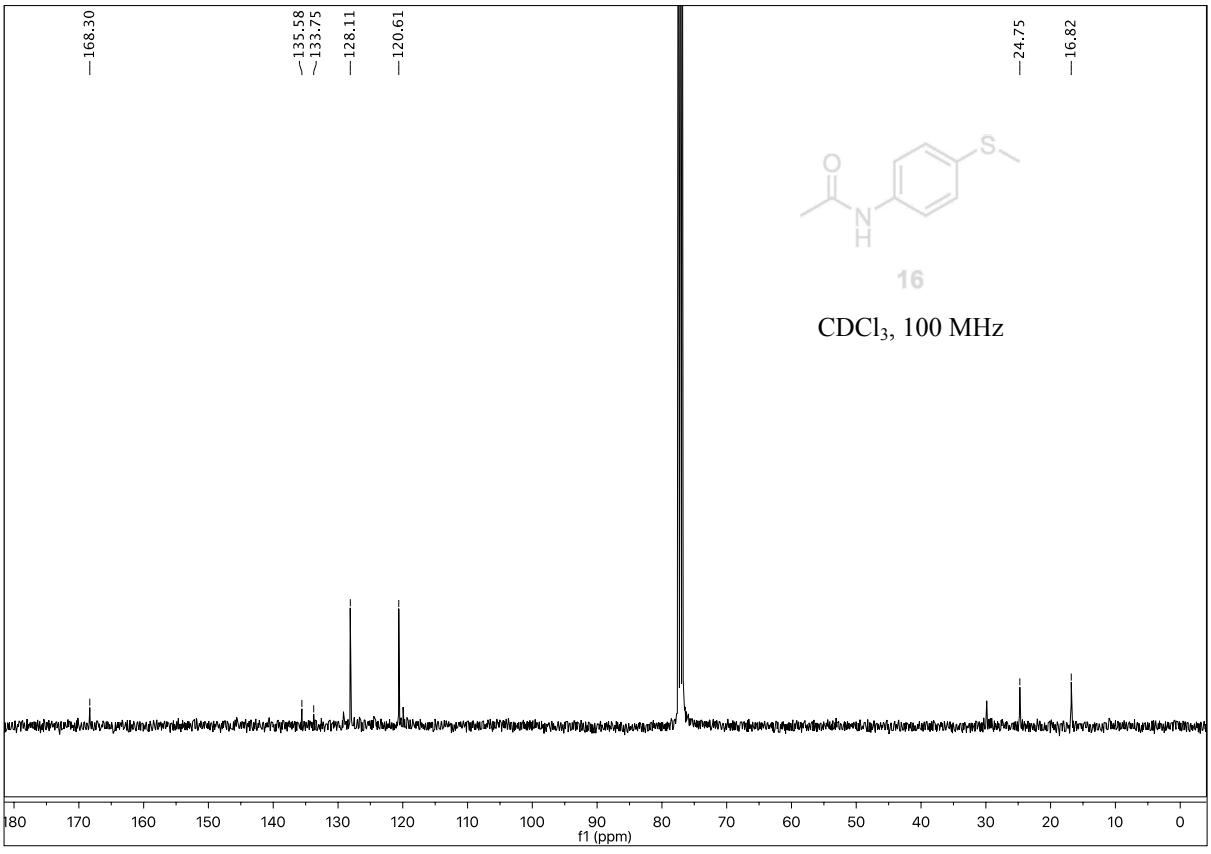
130.303
128.861
114.717
55.502
18.219
14
CDCl3, 100 MHz
f1 (ppm)


7.255
7.180
7.176
7.170
7.166
7.161
7.157
7.151
7.146
7.131
7.127
6.982
6.979
6.963
6.960
6.944
6.941
6.852
6.832
3.898
2.434
O
S
15
CDCl3, 400 MHz
2.00
1.01
1.00
3.14
3.16
f1 (ppm)

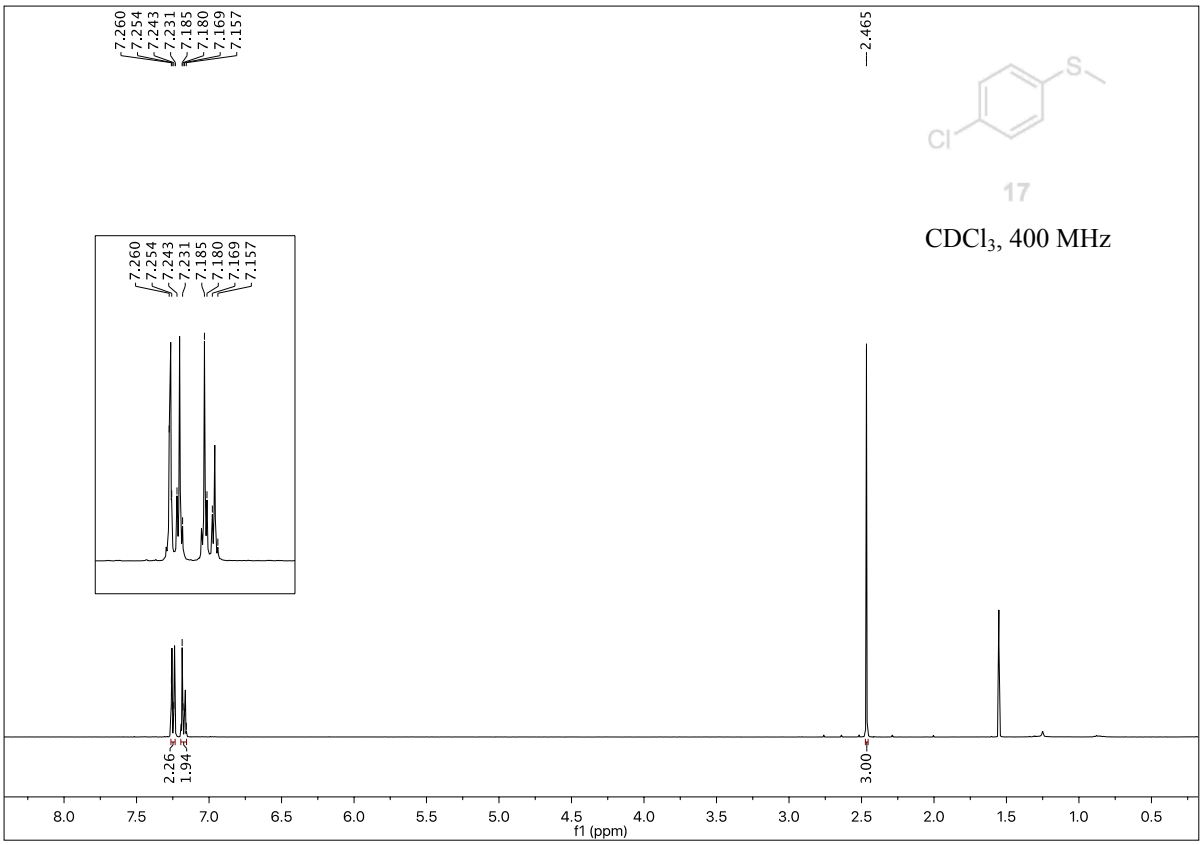

156.306
126.820
126.213
125.945
121.193
110.087
55.782
14.777
O
S
15
CDCl3, 100 MHz
f1 (ppm)

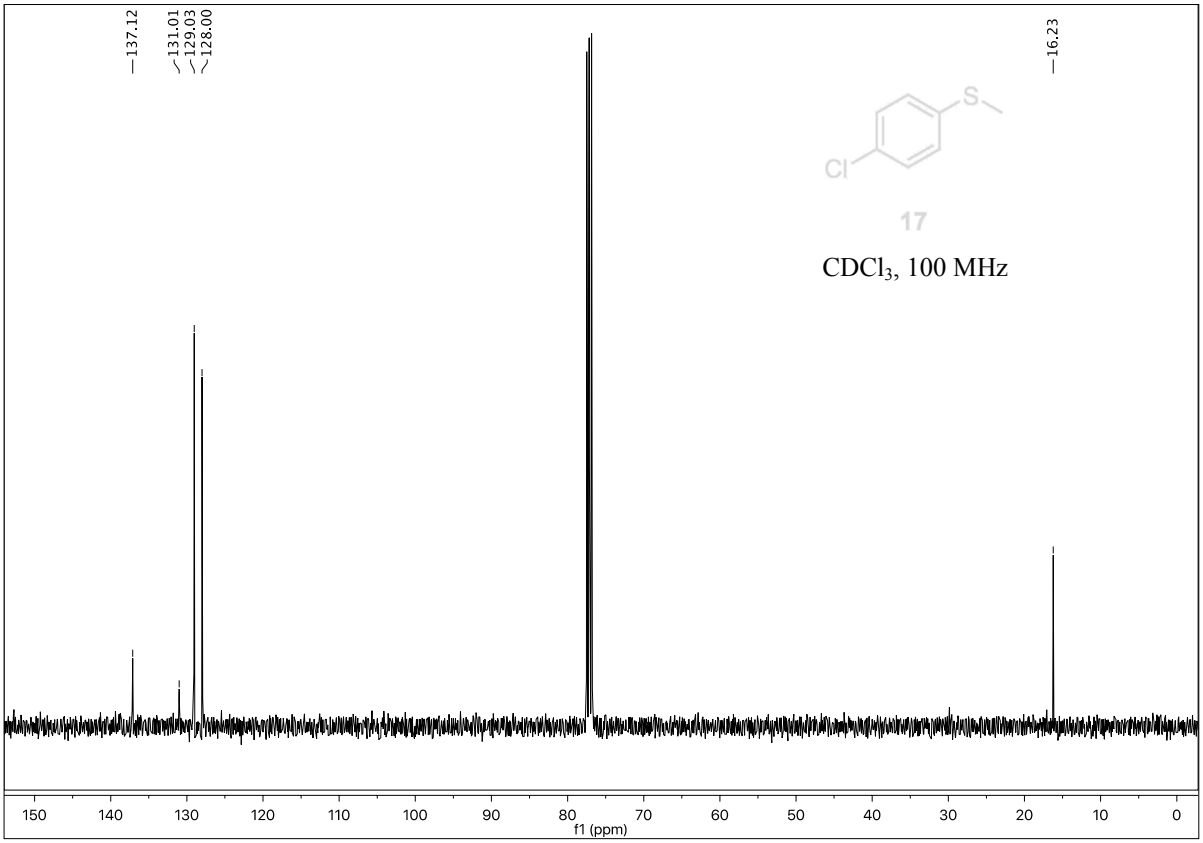


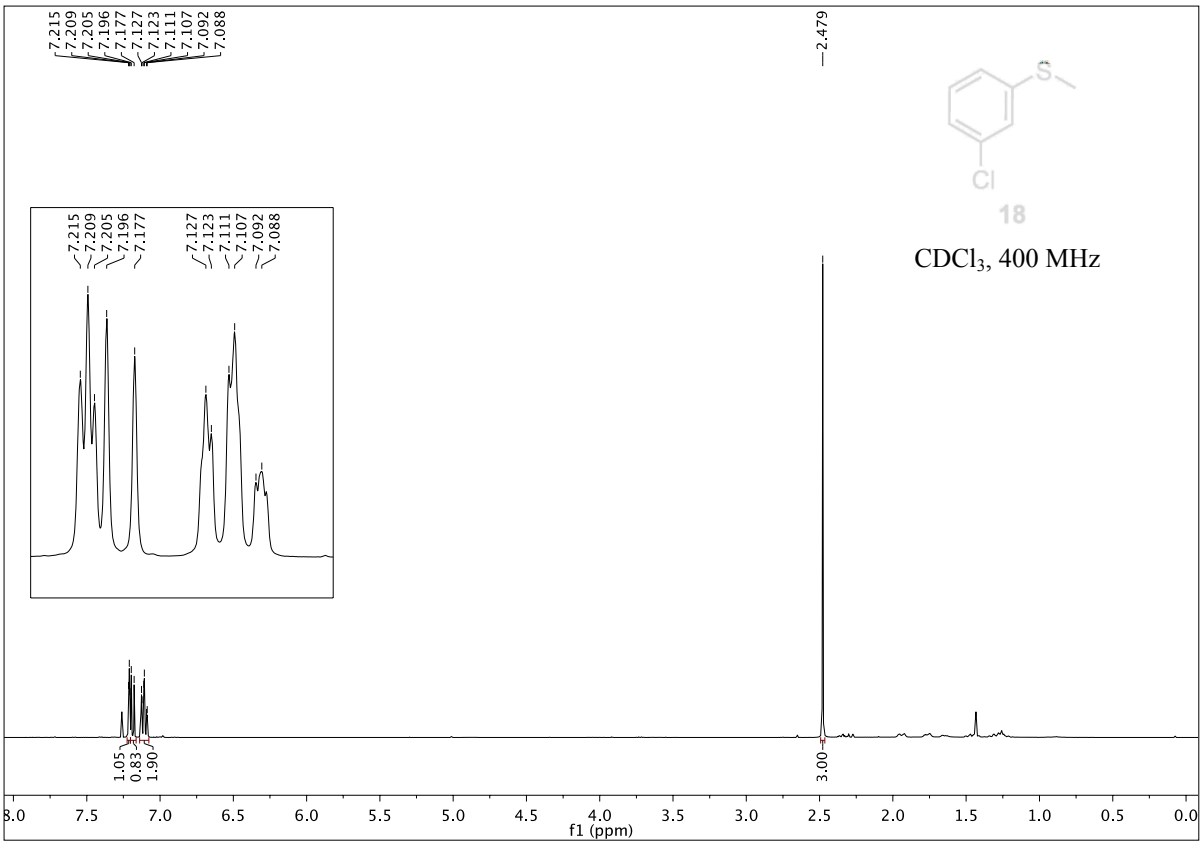
$CDCl_3$, 400 MHz



$CDCl_3$, 100 MHz


7.260
7.254
7.243
7.231
7.185
7.180
7.169
7.157
2.465
Cl
S
17
CDCl3, 400 MHz
2.26
1.94
3.00
f1 (ppm)


137.12
131.01
129.03
128.00
16.23
Cl
S
17
CDCl3, 100 MHz
f1 (ppm)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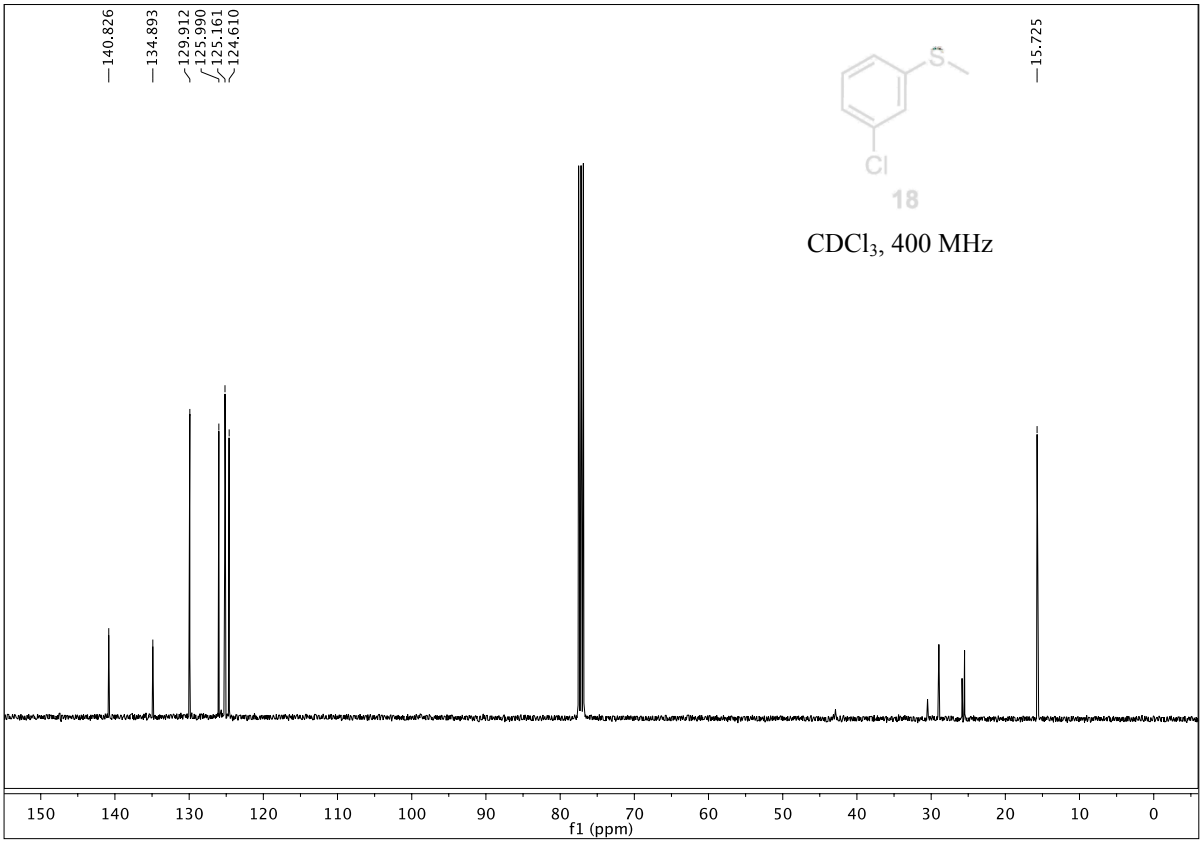
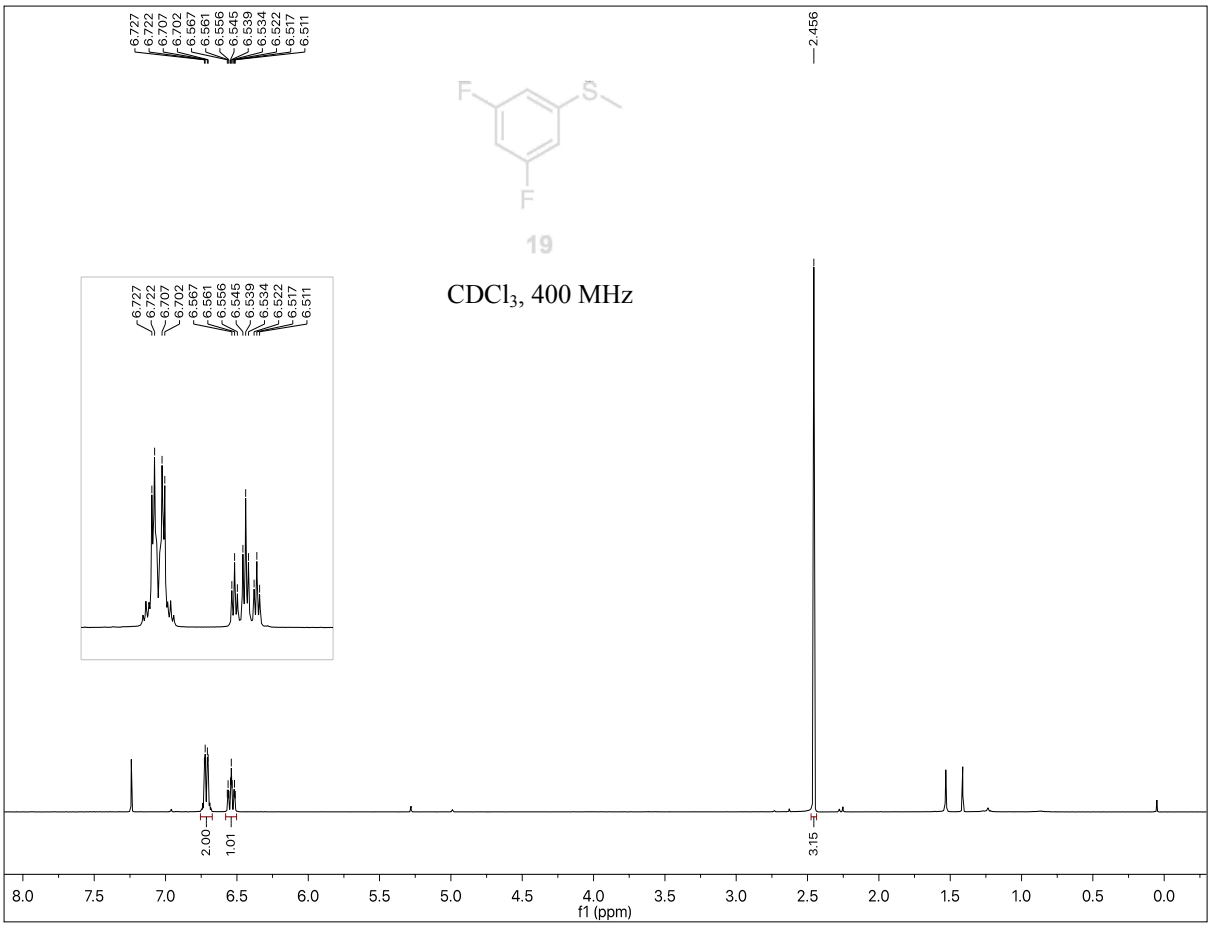
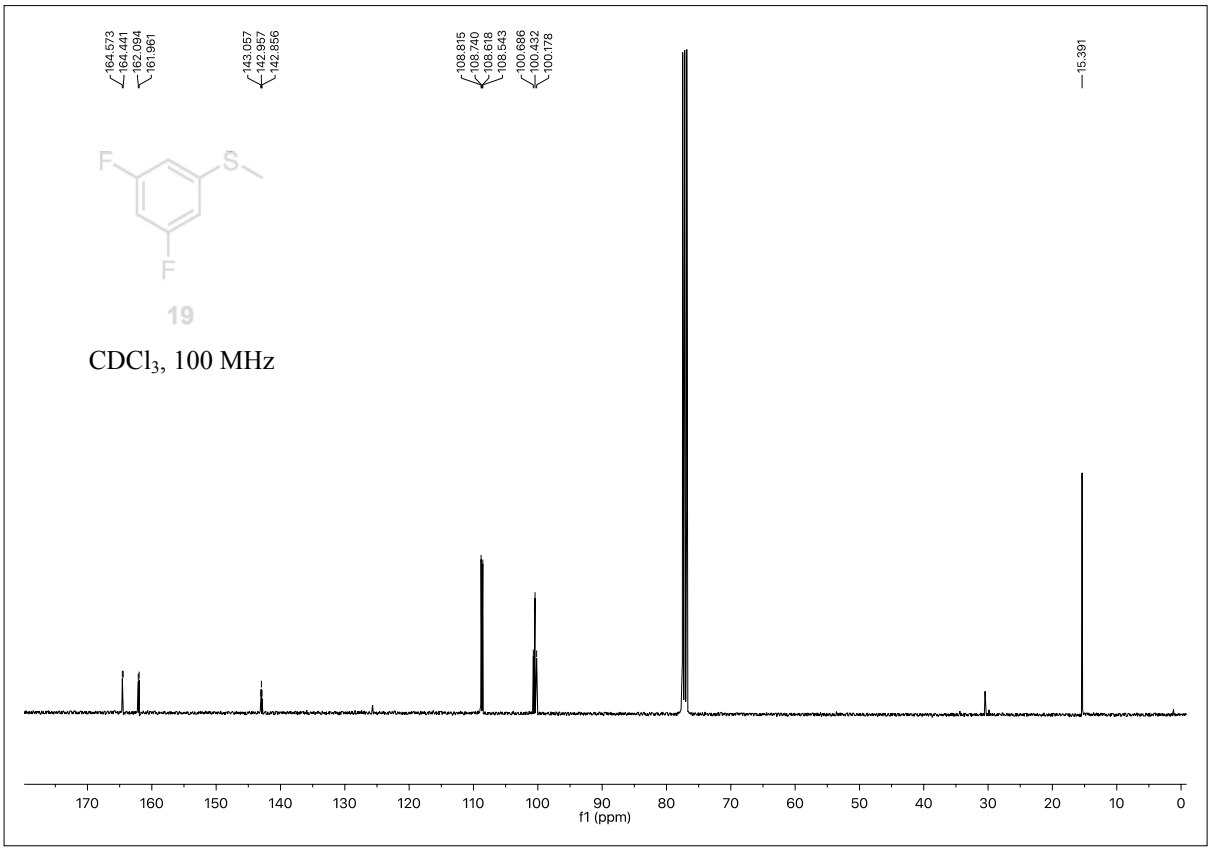
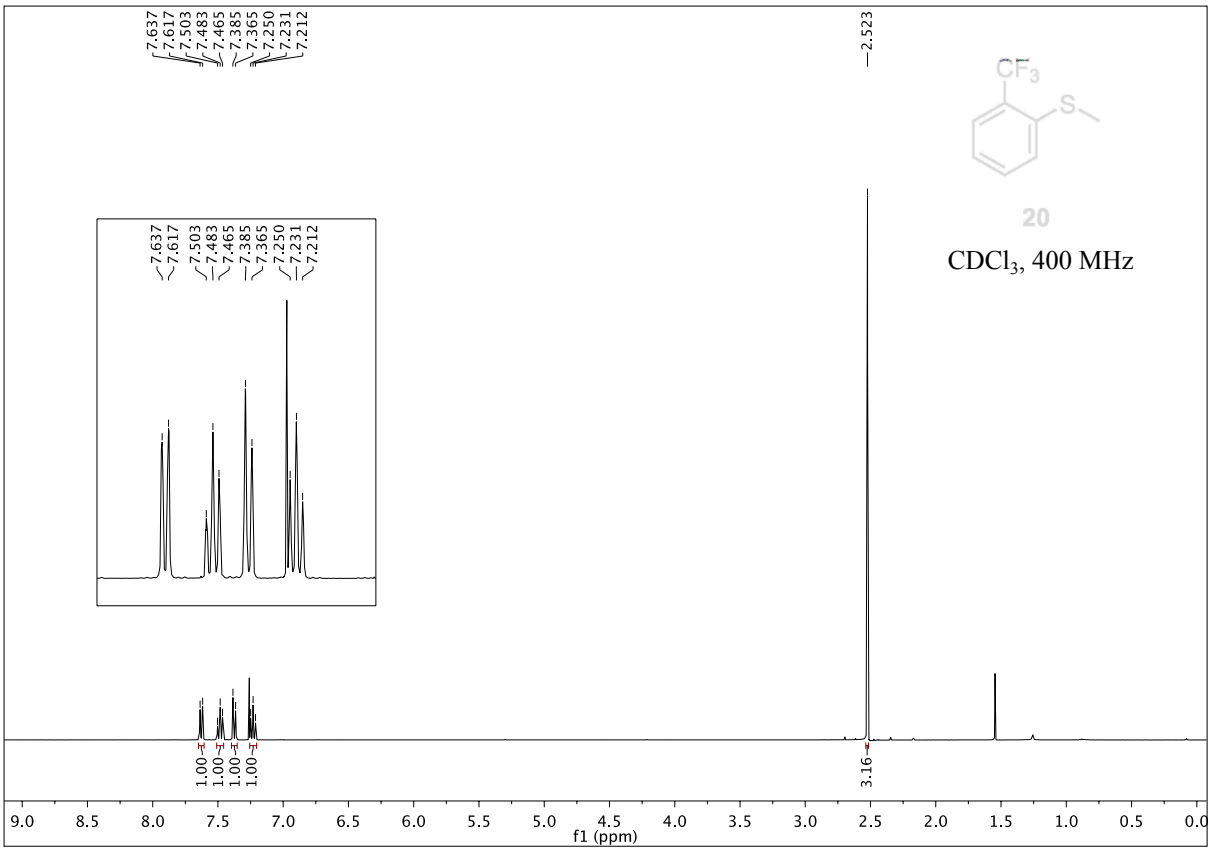
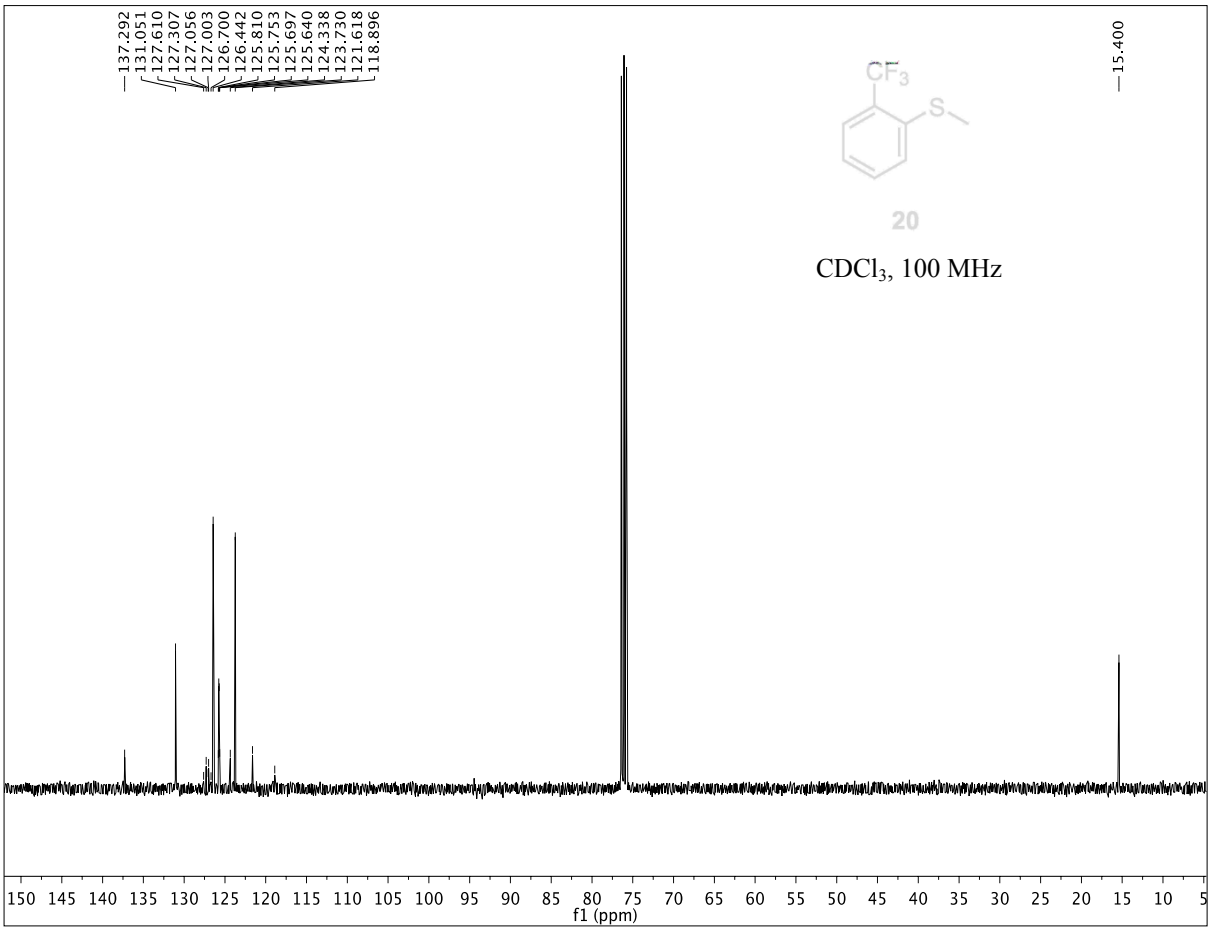
7.196
7.177
7.127
7.123
7.111
7.107
7.092
7.088
2.479
S
Cl
18
CDCl3, 400 MHz
1.05
0.83
1.90
3.00
f1 (ppm)

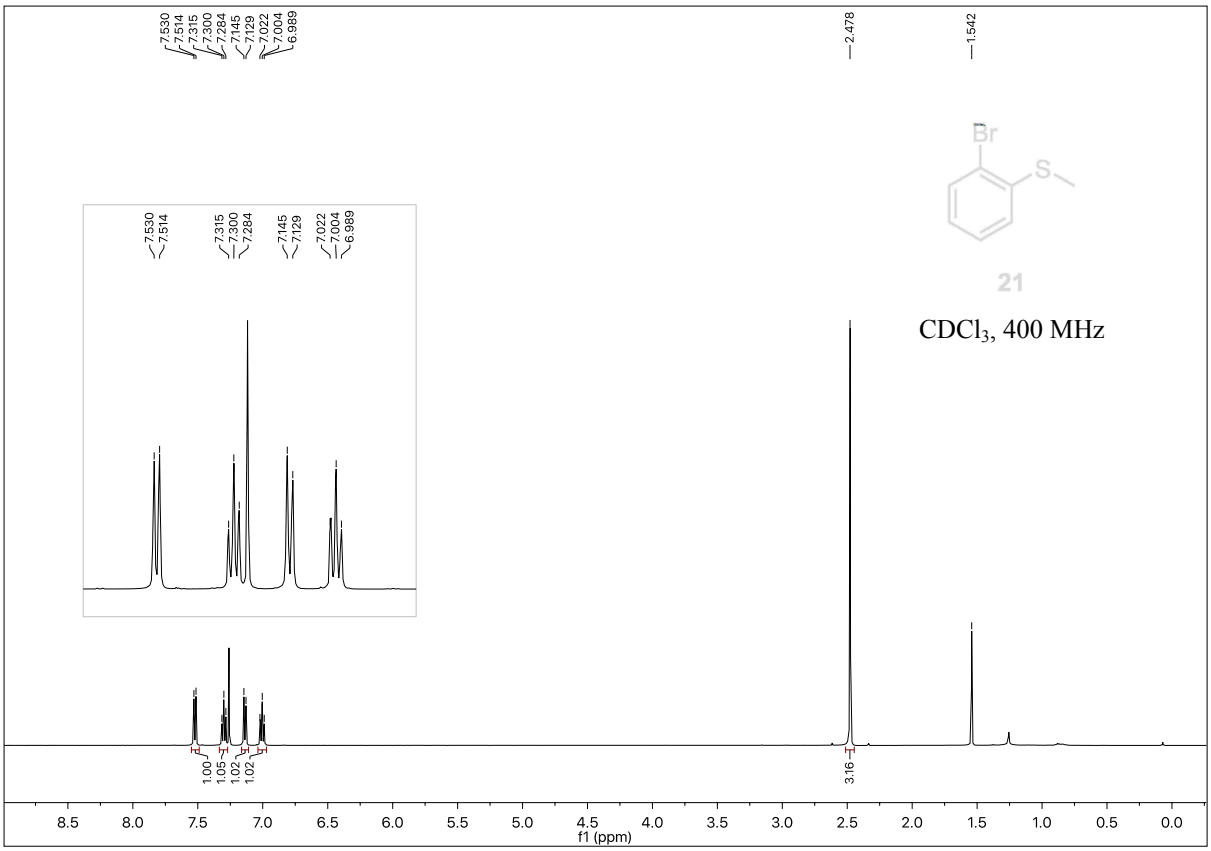

140.826
134.893
129.912
125.990
125.161
124.610
15.725
S
Cl
18
CDCl3, 400 MHz
f1 (ppm)

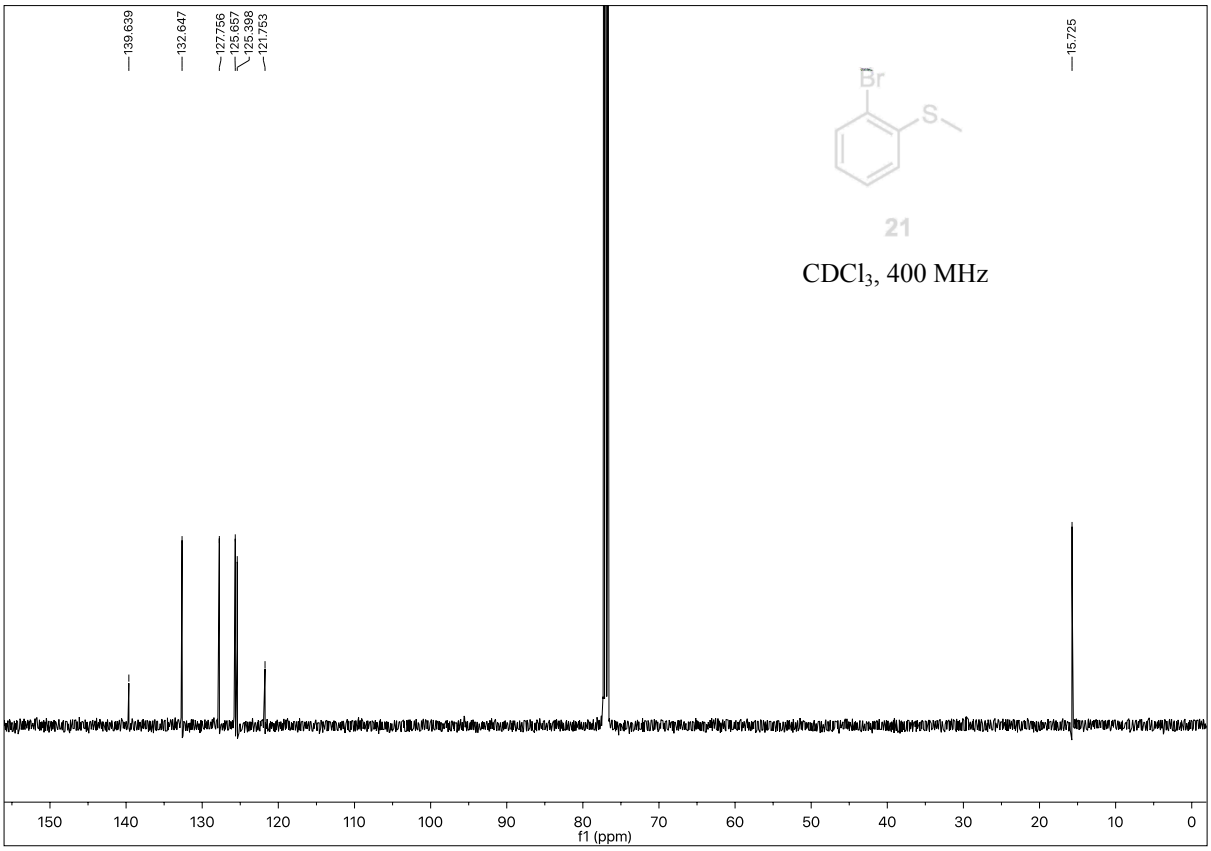

6.727
6.722
6.707
6.702
6.567
6.561
6.556
6.545
6.539
6.534
6.522
6.517
6.511
2.456
F
S
F
19
CDCl3, 400 MHz
2.00
1.01
3.15
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

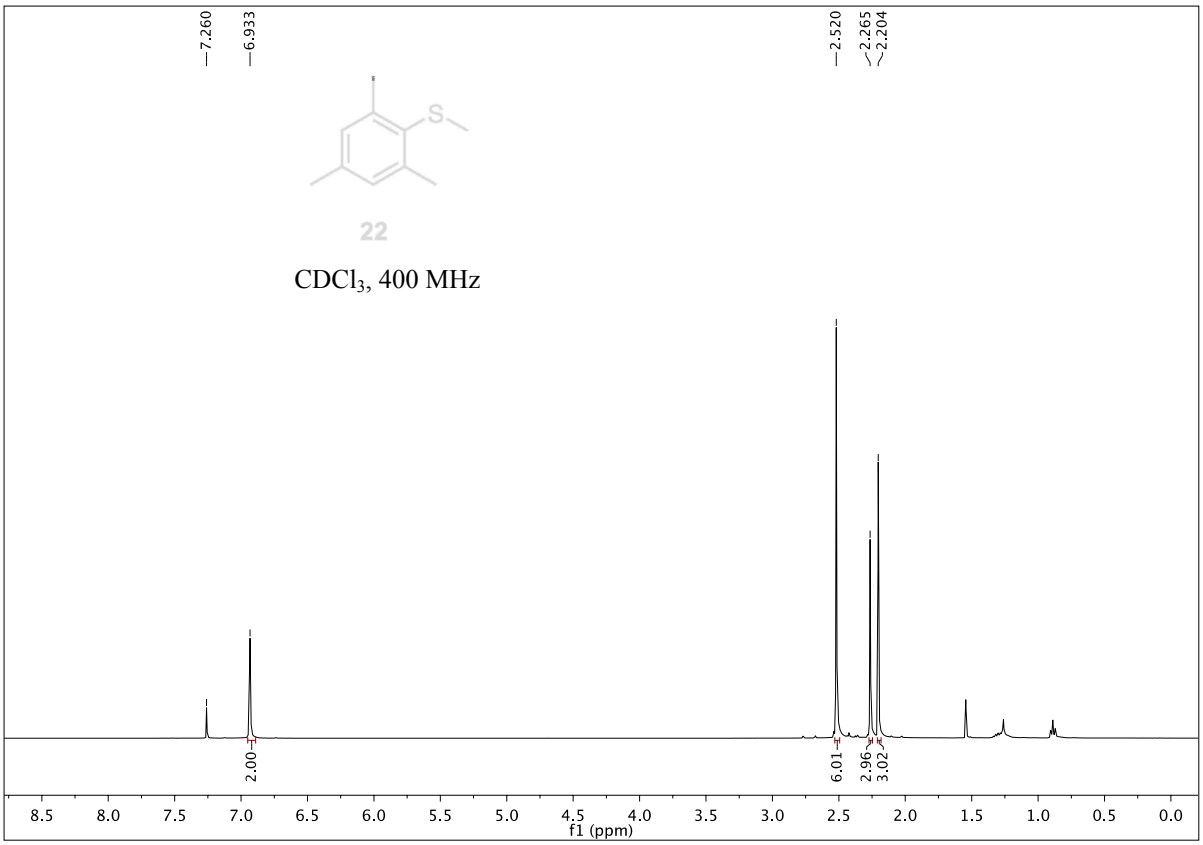

164.573
164.441
162.094
161.961
143.057
142.957
142.856
108.815
108.740
108.618
108.543
100.686
100.432
100.178
15.391
F
S
F
19
CDCl3, 100 MHz
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

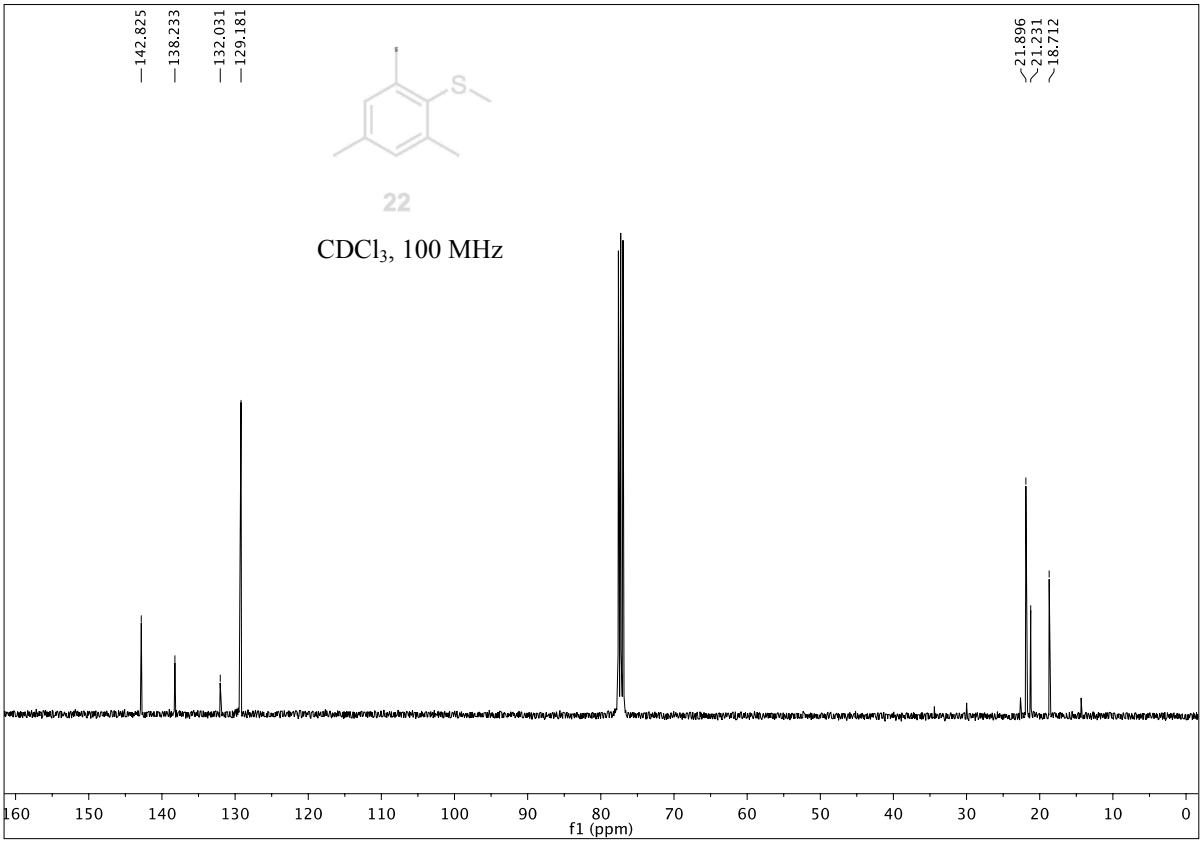

7.637
7.617
7.503
7.483
7.465
7.385
7.365
7.250
7.231
7.212
2.523
CF3
S
20
CDCl3, 400 MHz
1.00
1.00
1.00
1.00
3.16
f1 (ppm)

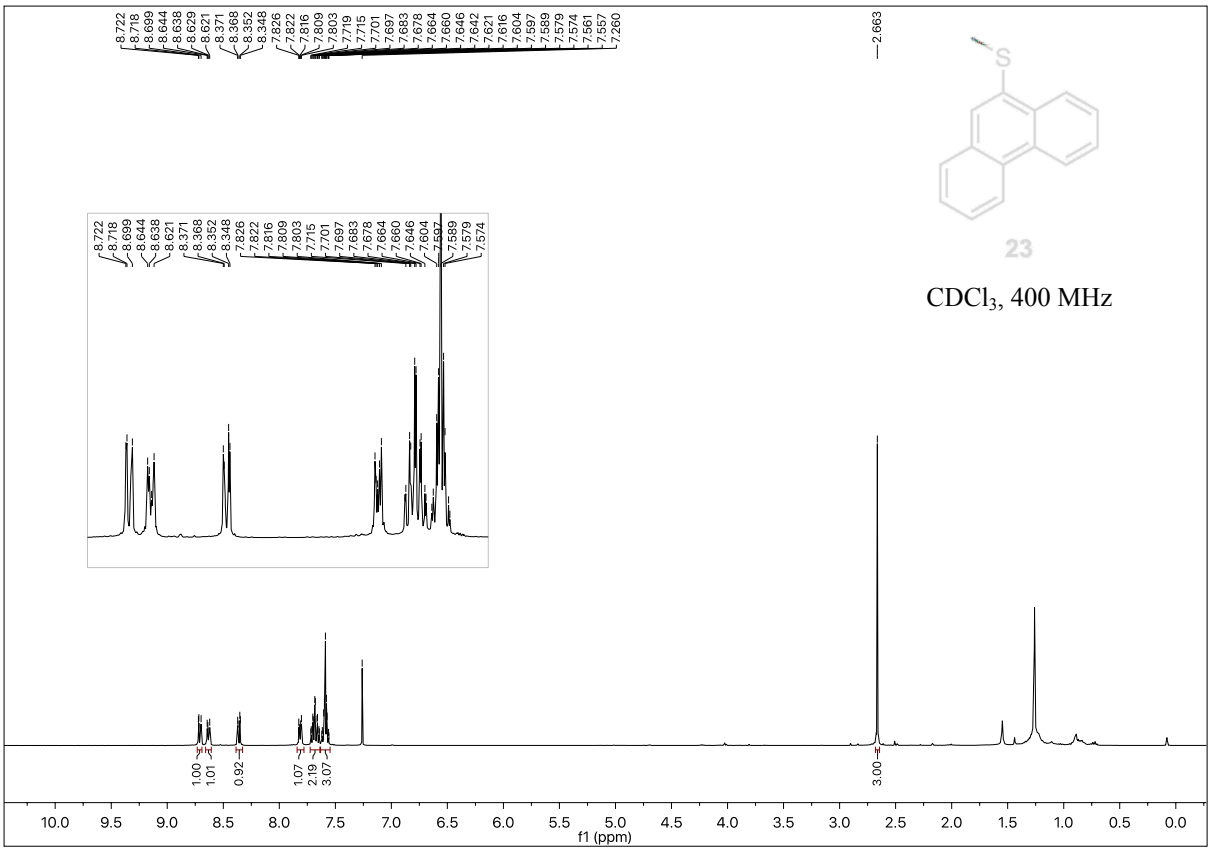

137.292
131.051
127.610
127.307
127.056
127.003
126.700
126.442
125.810
125.753
125.697
125.640
124.338
123.730
121.618
118.896
15.400
CF3
S
20
CDCl3, 100 MHz
f1 (ppm)


7.530
7.514
7.315
7.300
7.284
7.145
7.129
7.022
7.004
6.989
2.478
1.542
Br
S
21
CDCl3, 400 MHz
1.00
1.05
1.02
1.02
3.16
f1 (ppm)


139.639
132.647
127.756
125.657
125.398
121.753
15.725
Br
S
21
CDCl3, 400 MHz
f1 (ppm)

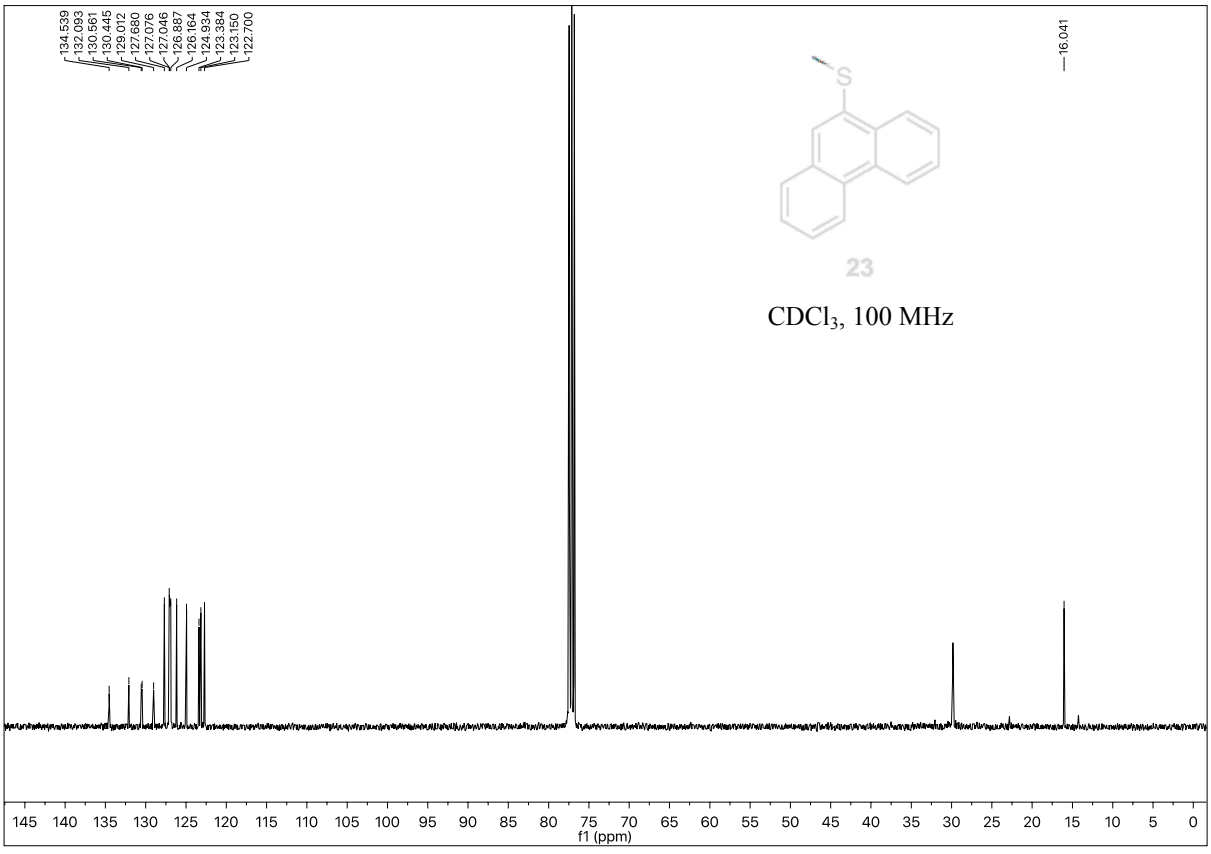

7.260
6.933
2.520
2.265
2.204
22
CDCl3, 400 MHz
2.00
6.01
2.96
3.02
f1 (ppm)


142.825
138.233
132.031
129.181
21.896
21.231
18.712
22
CDCl3, 100 MHz
f1 (ppm)



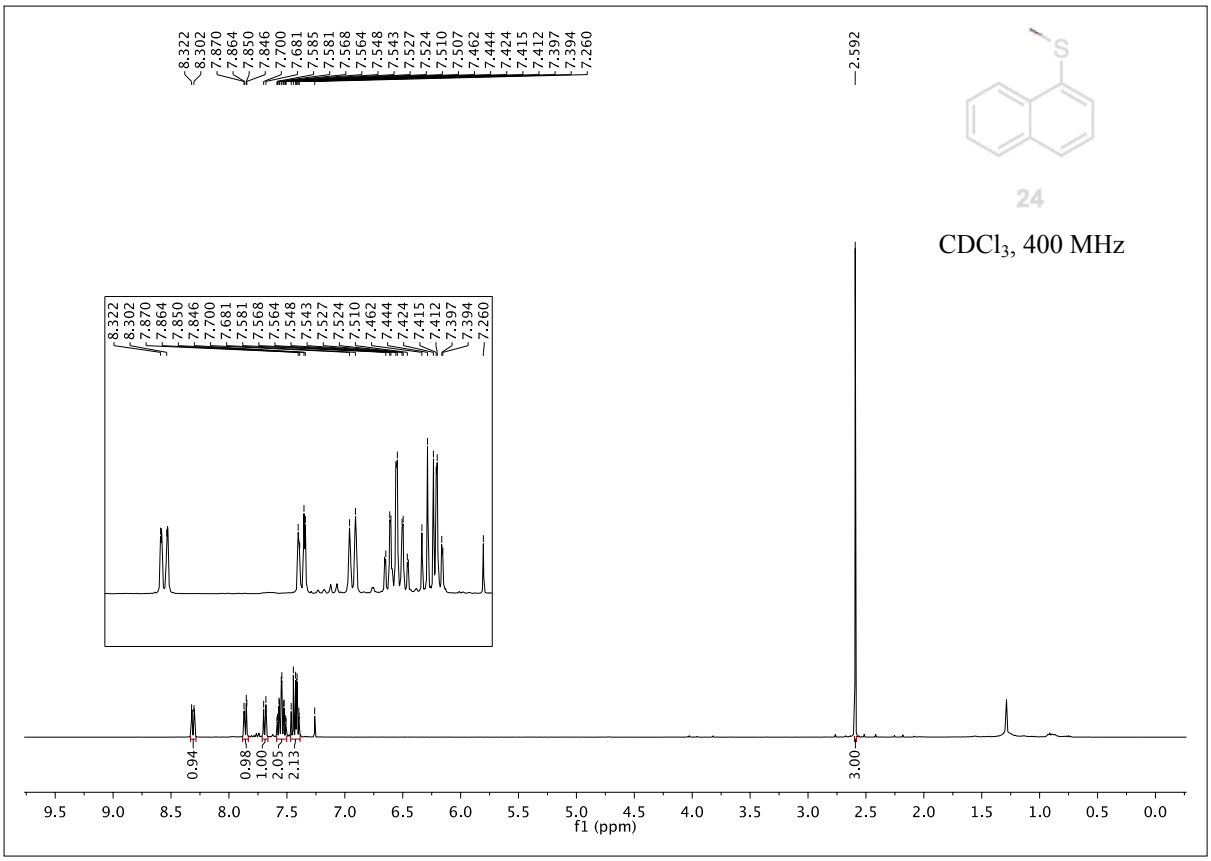
23

$CDCl_3$, 400 MHz



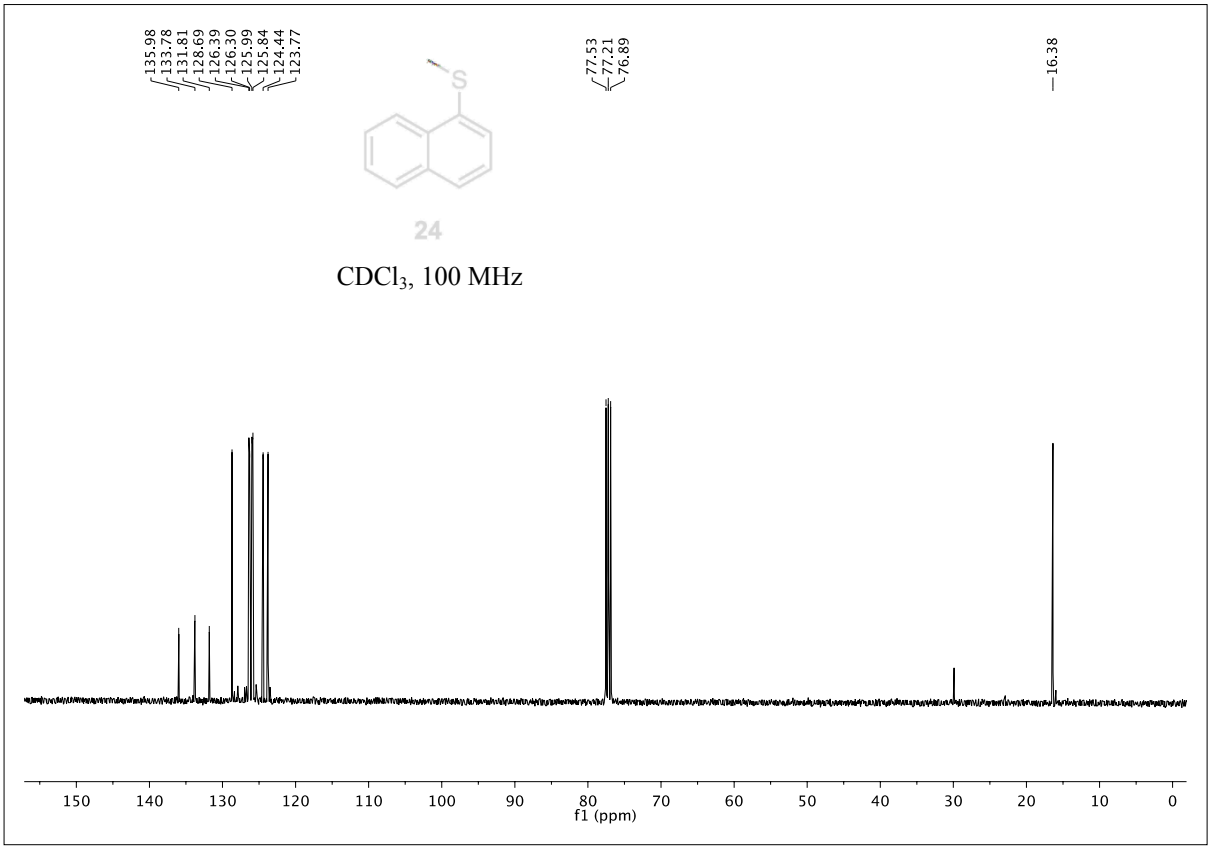
23

$CDCl_3$, 100 MHz



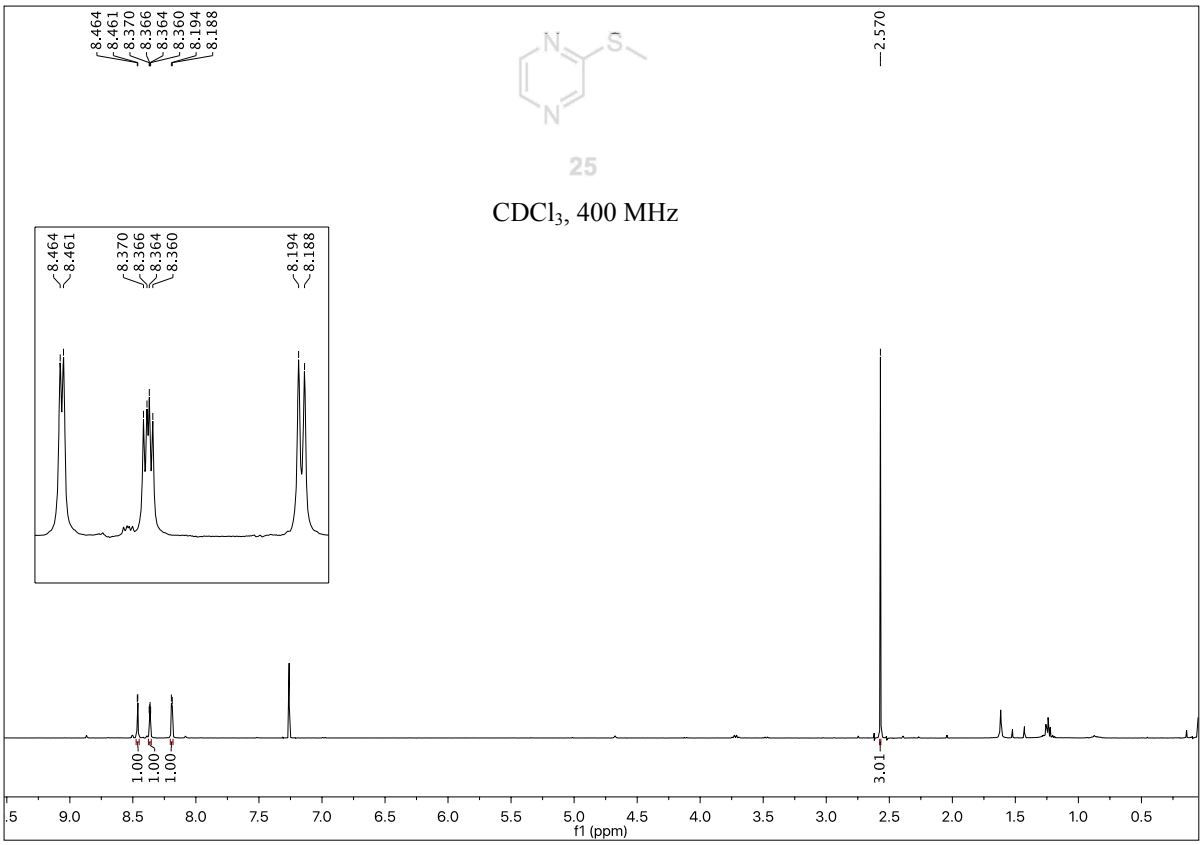
24

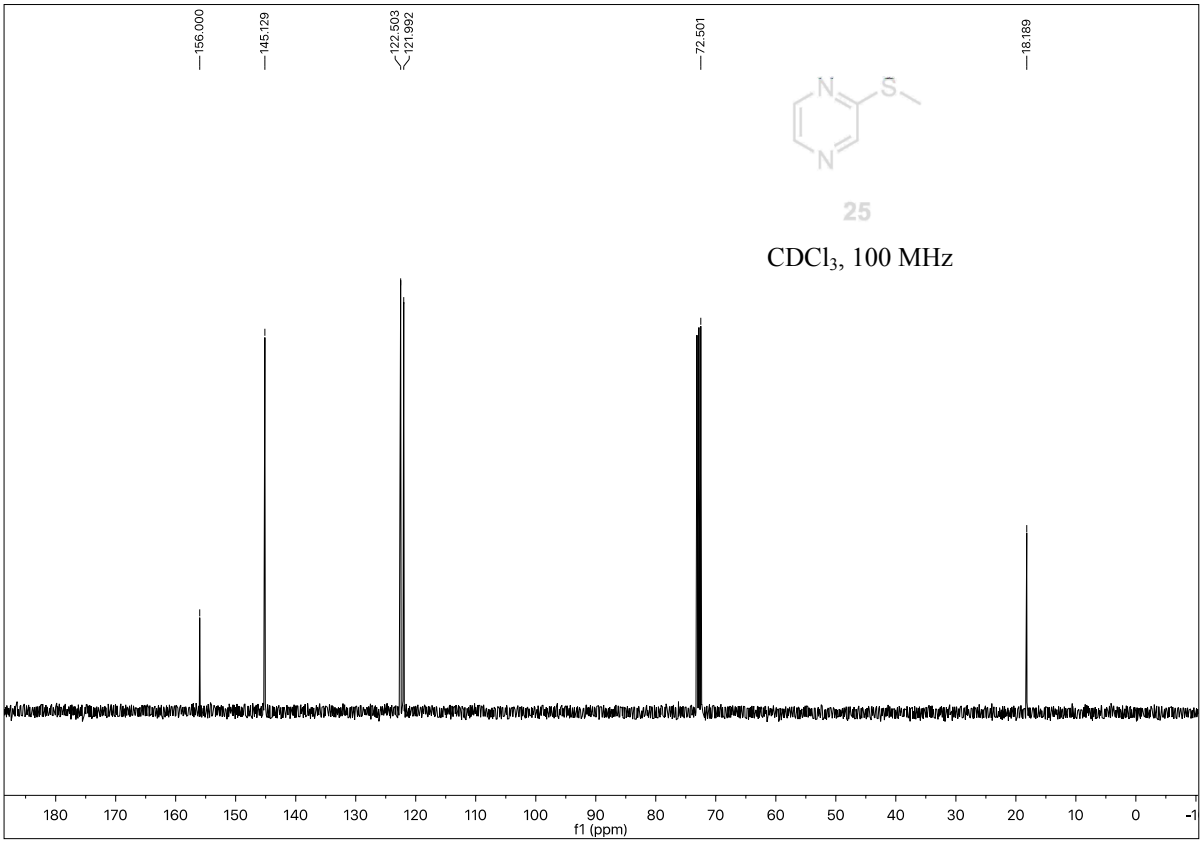
$CDCl_3$, 400 MHz

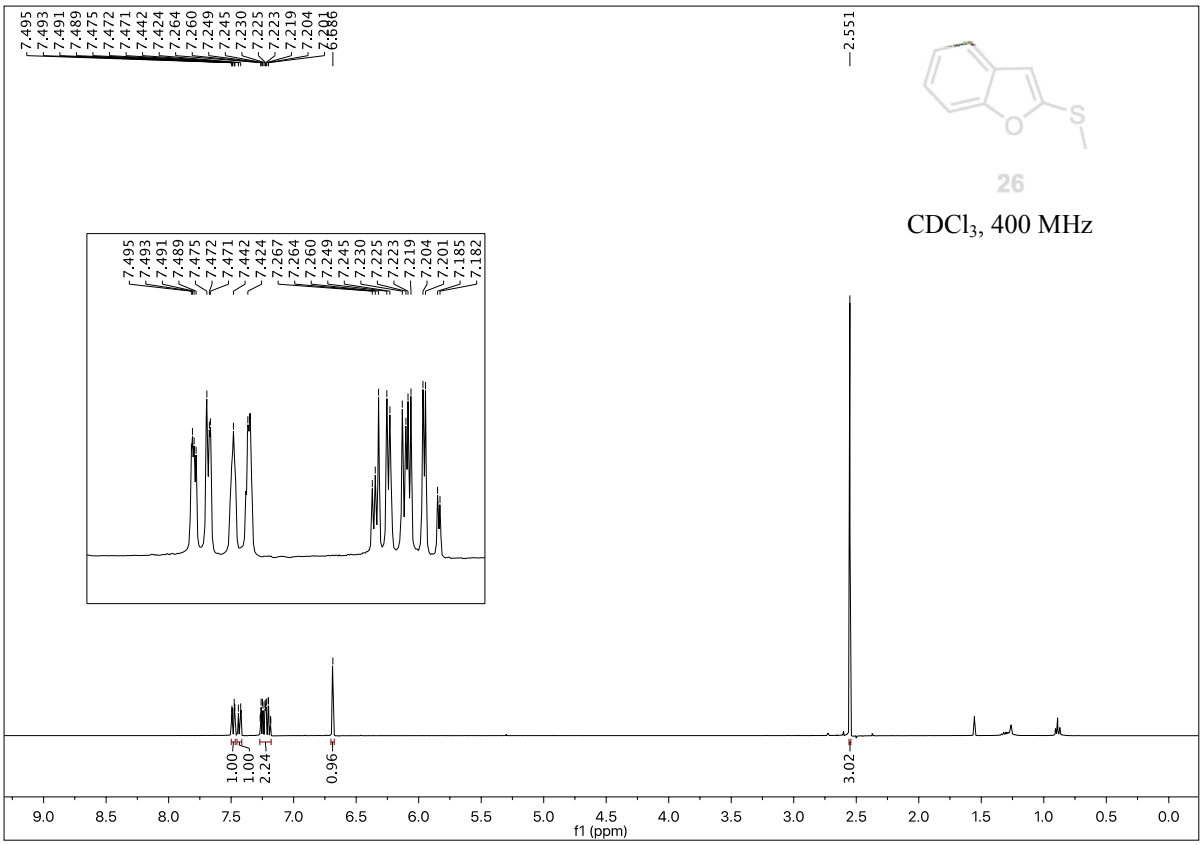


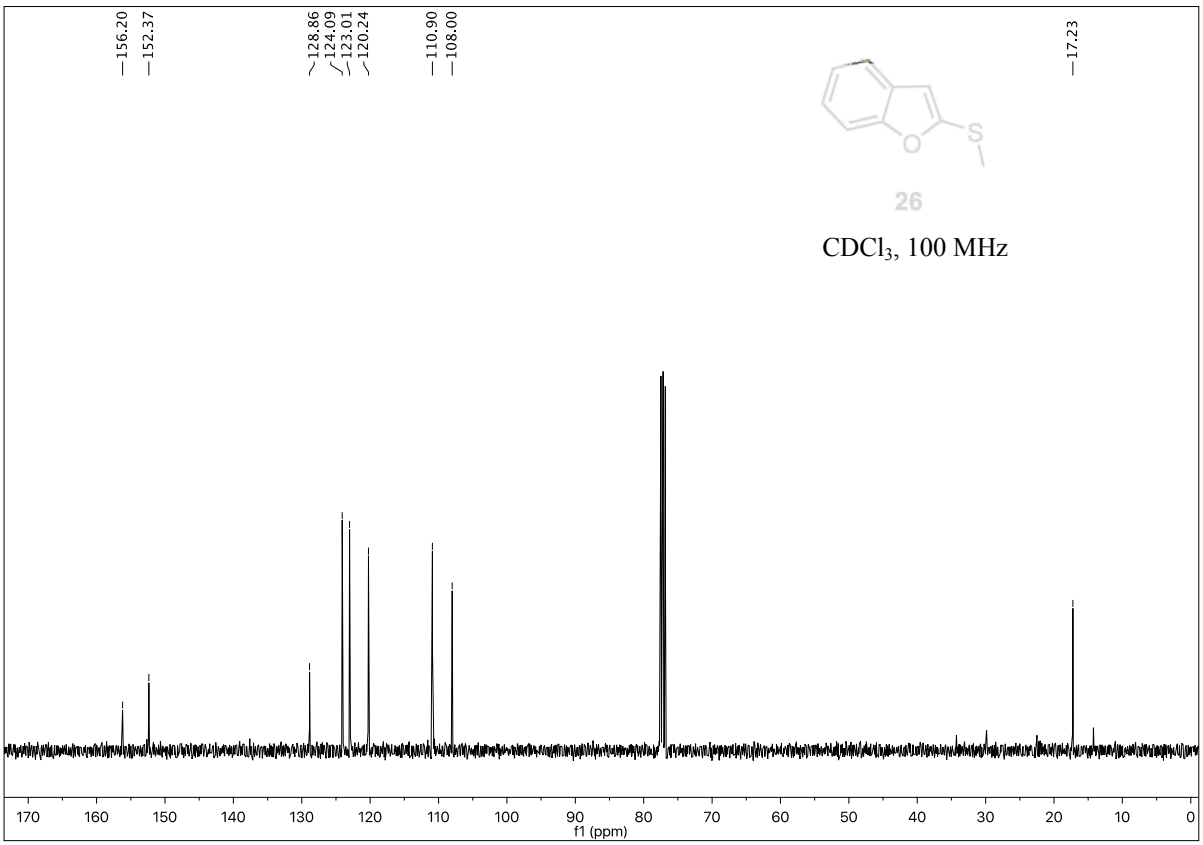
24

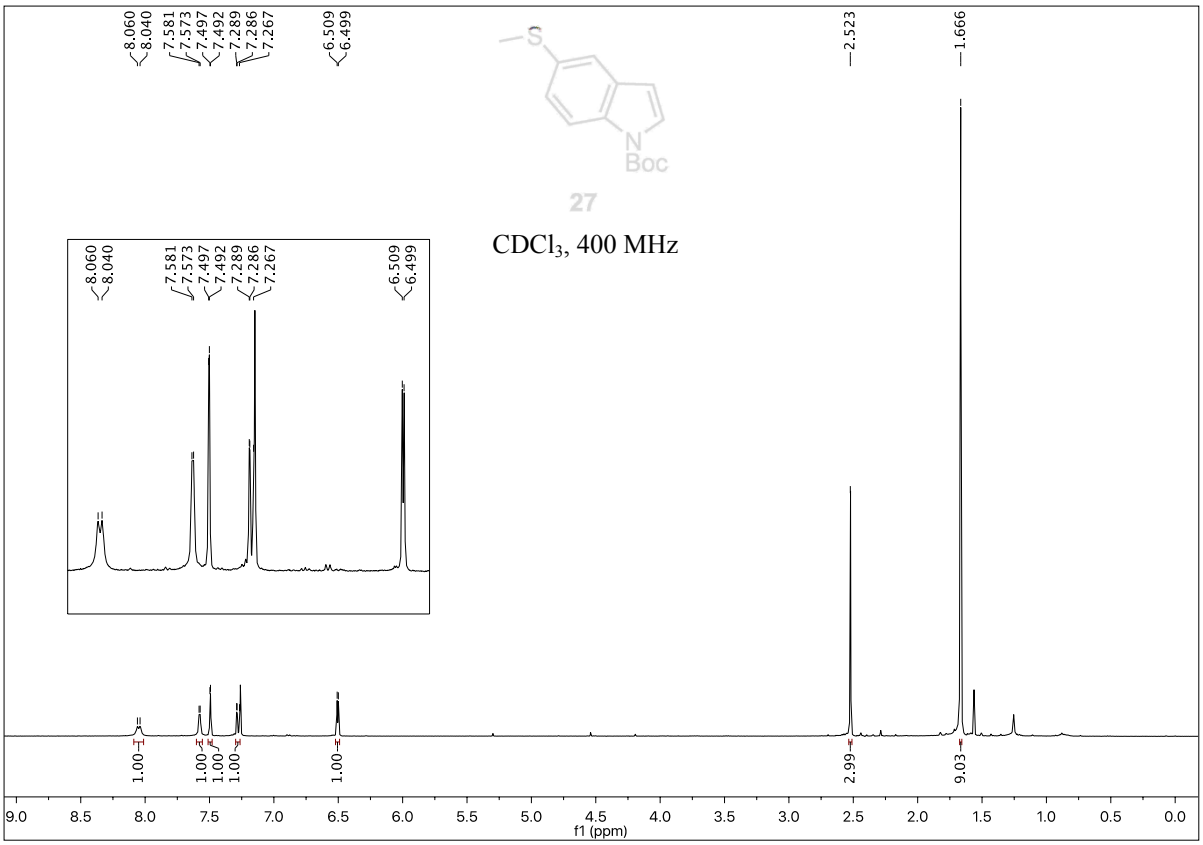
$CDCl_3$, 100 MHz

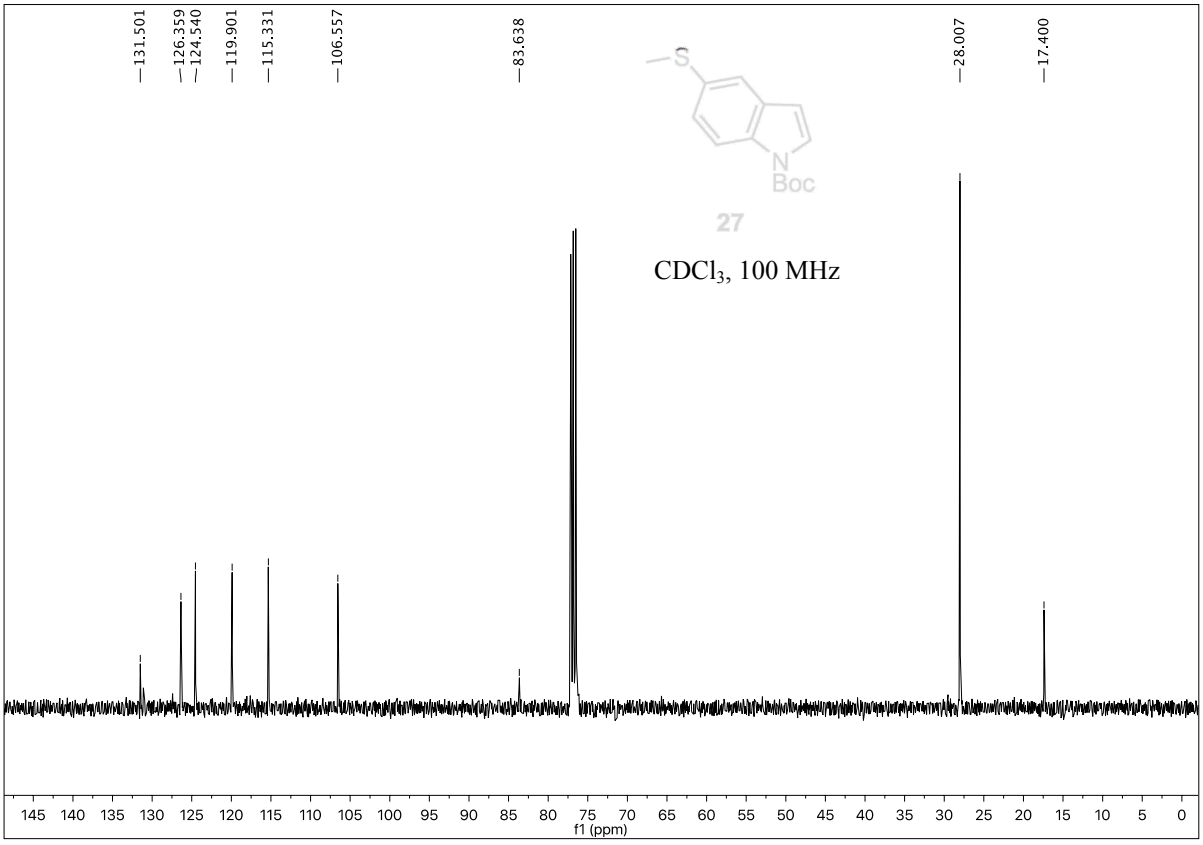

8.464
8.461
8.370
8.366
8.364
8.360
8.194
8.188
2.570
25
CDCl3, 400 MHz
1.00
1.00
1.00
3.01
f1 (ppm)

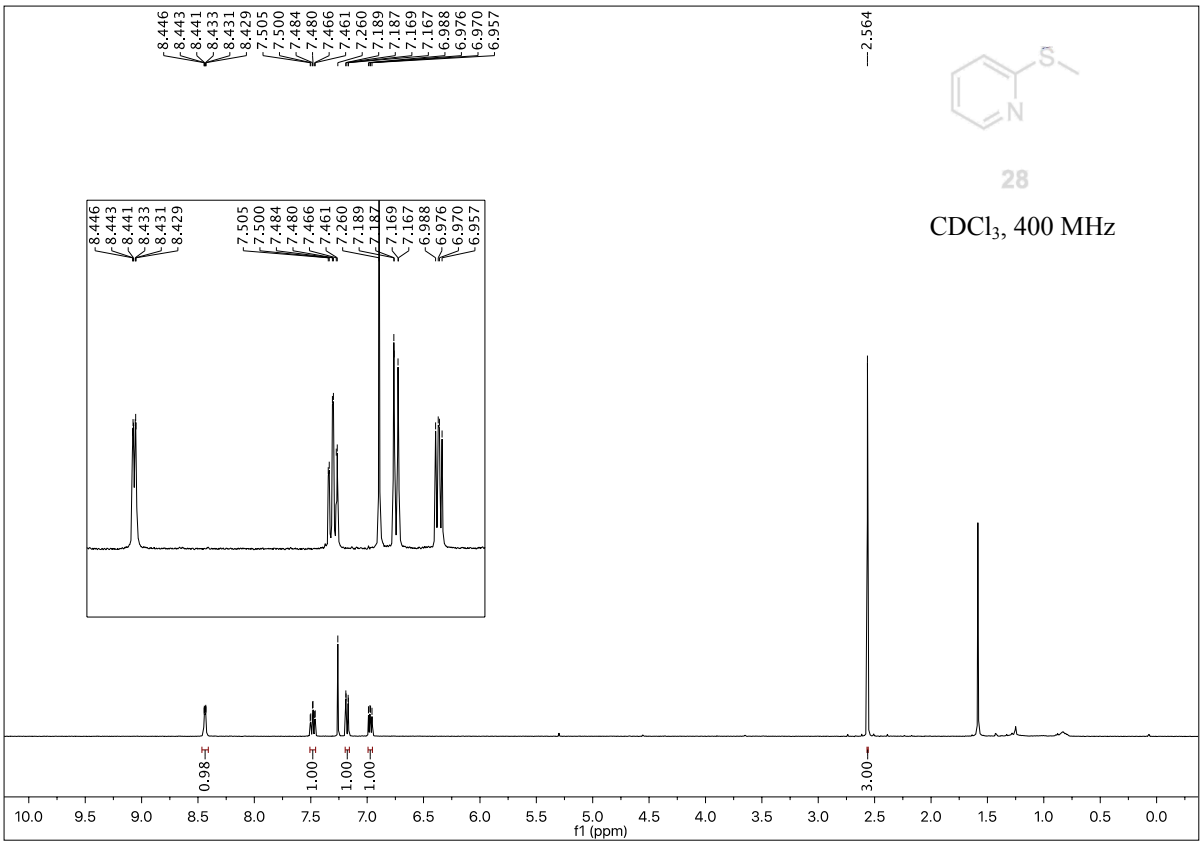

156.000
145.129
122.503
121.992
72.501
18.189
25
CDCl3, 100 MHz
f1 (ppm)


7.495
7.493
7.491
7.489
7.475
7.472
7.471
7.442
7.424
7.264
7.260
7.249
7.245
7.230
7.225
7.223
7.219
7.204
7.201
6.686
2.551
7.495
7.493
7.491
7.489
7.475
7.472
7.471
7.442
7.424
7.267
7.264
7.260
7.249
7.245
7.230
7.225
7.223
7.219
7.204
7.201
7.185
7.182
1.00
1.00
2.24
0.96
3.02
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
f1 (ppm)
26
CDCl3, 400 MHz


156.20
152.37
128.86
124.09
123.01
120.24
110.90
108.00
17.23
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
26
CDCl3, 100 MHz

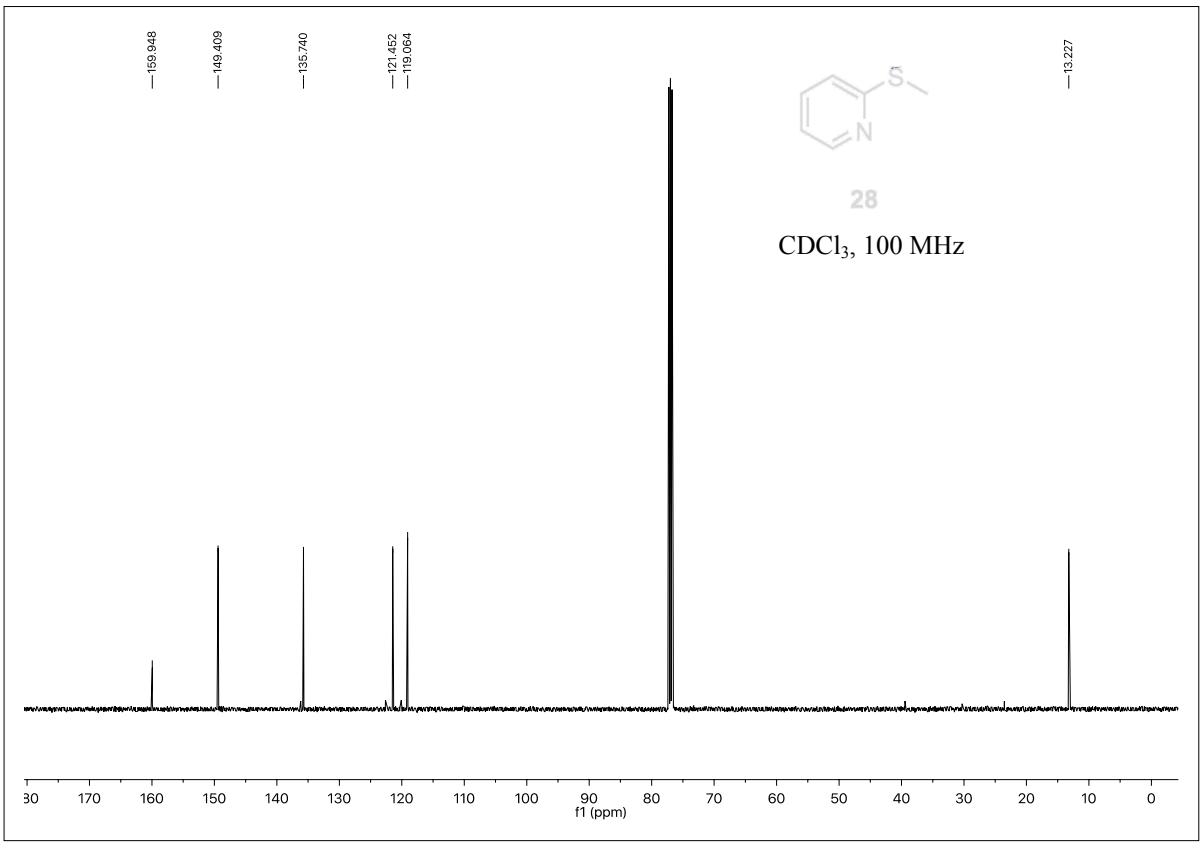

8.060
8.040
7.581
7.573
7.497
7.492
7.289
7.286
7.267
6.509
6.499
2.523
1.666
S
N
Boc
27
CDCl3, 400 MHz
1.00
1.00
1.00
1.00
1.00
2.99
9.03
f1 (ppm)


131.501
126.359
124.540
119.901
115.331
106.557
83.638
28.007
17.400
S
N
Boc
27
CDCl3, 100 MHz
f1 (ppm)



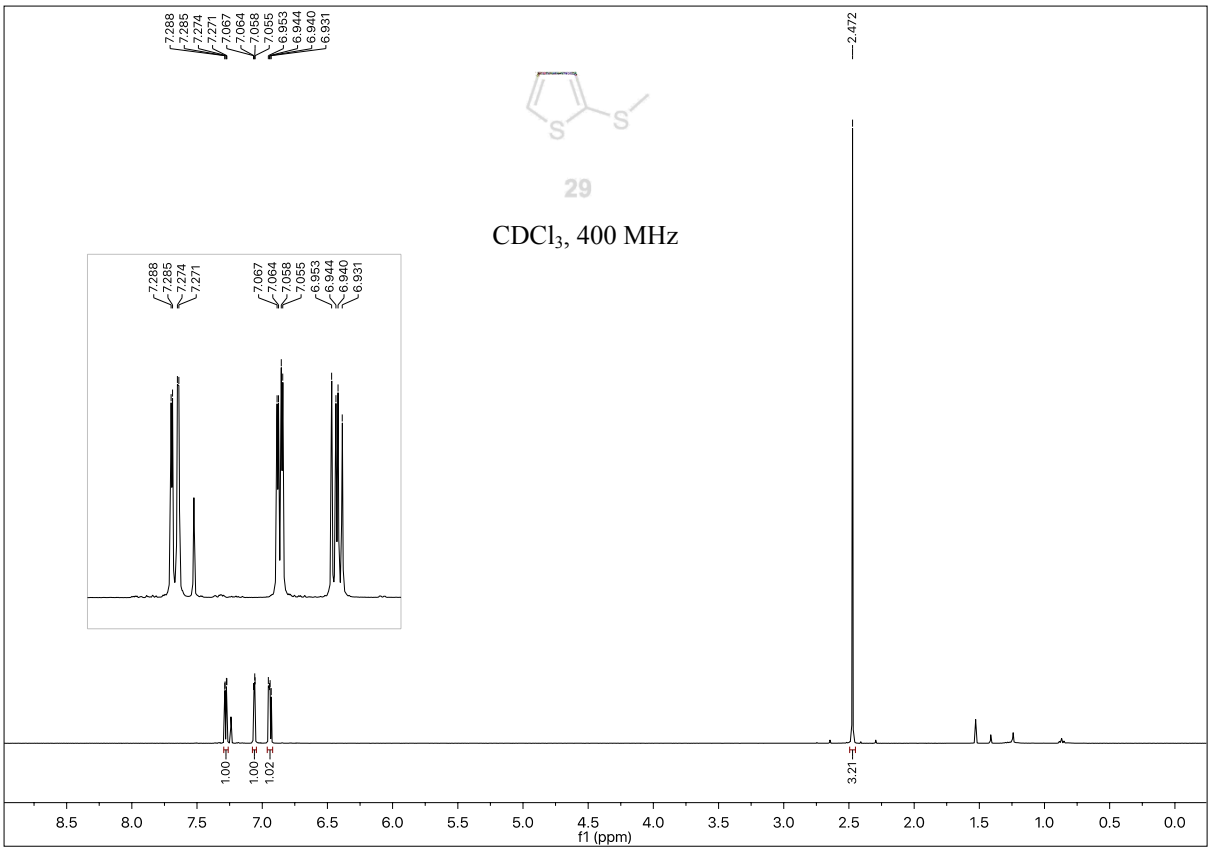
28

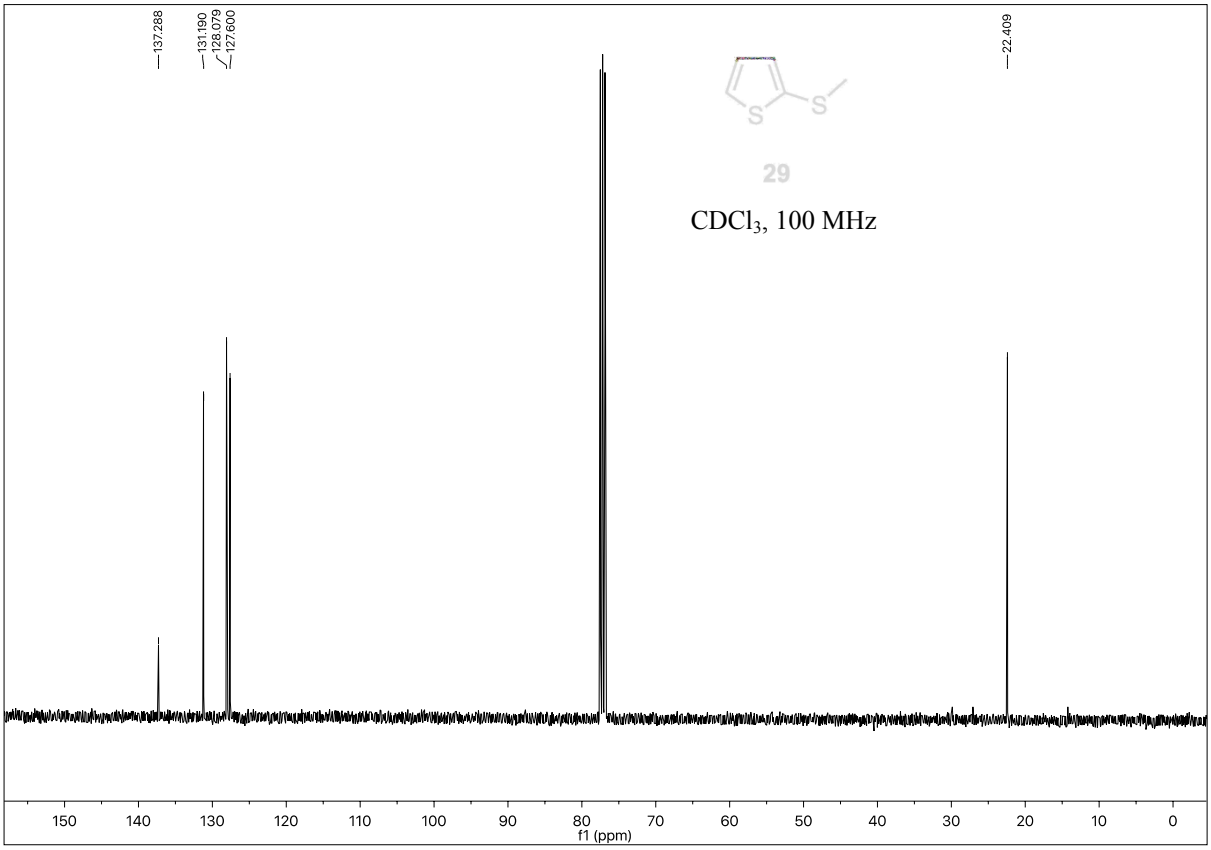
$CDCl_3$, 400 MHz

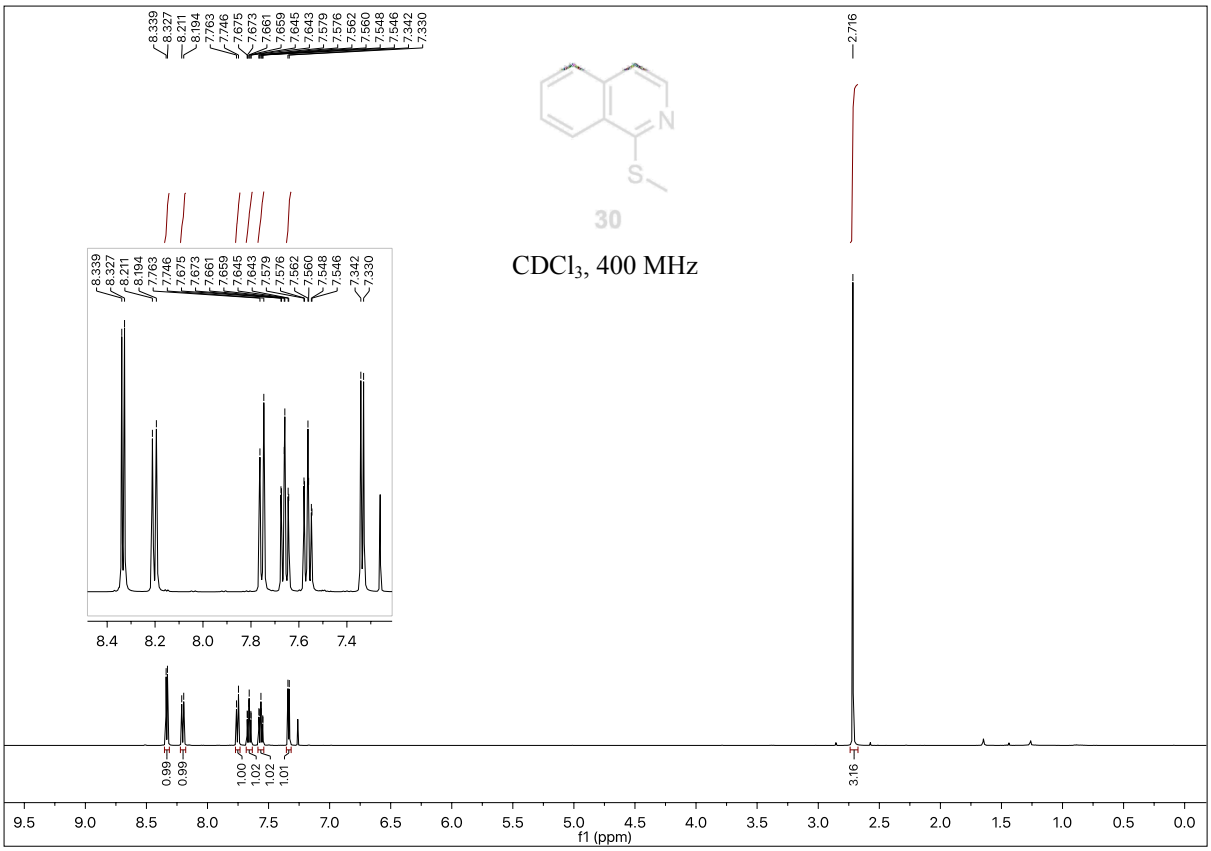


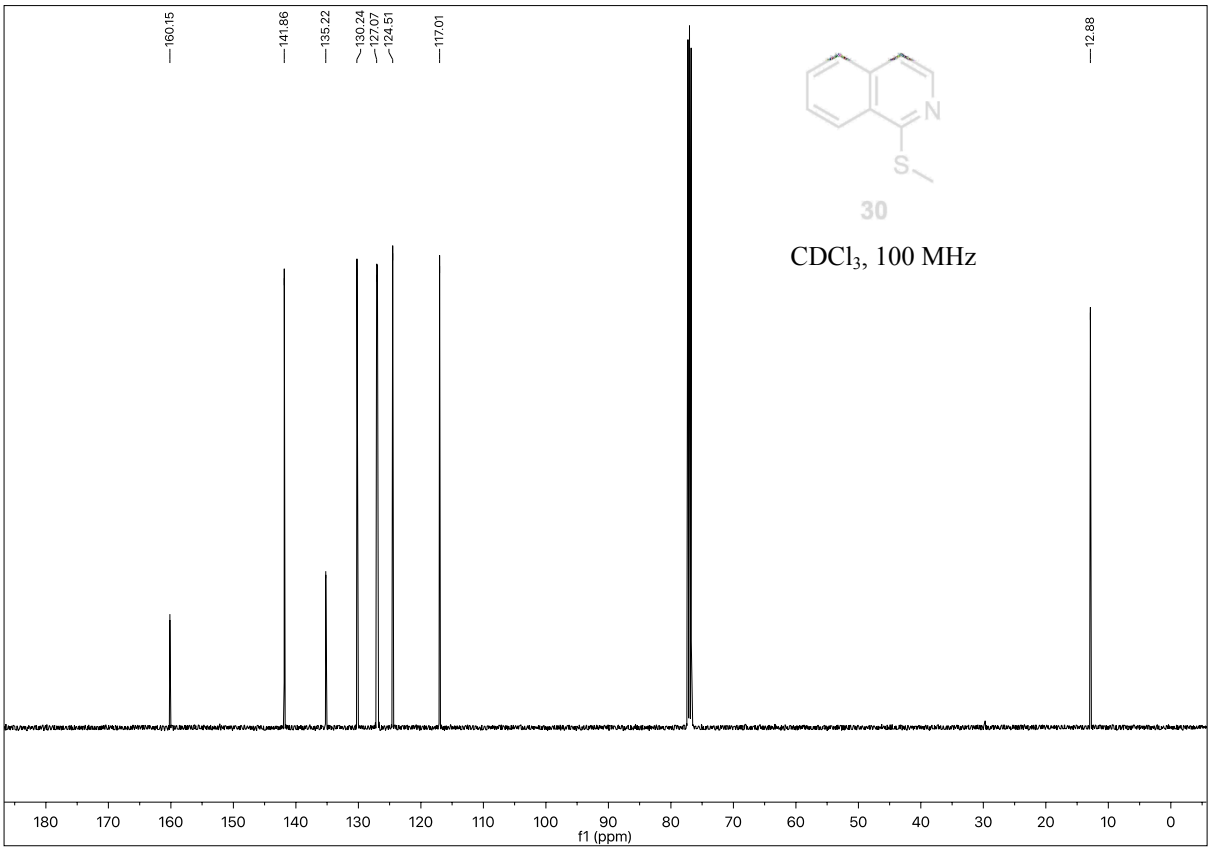
28

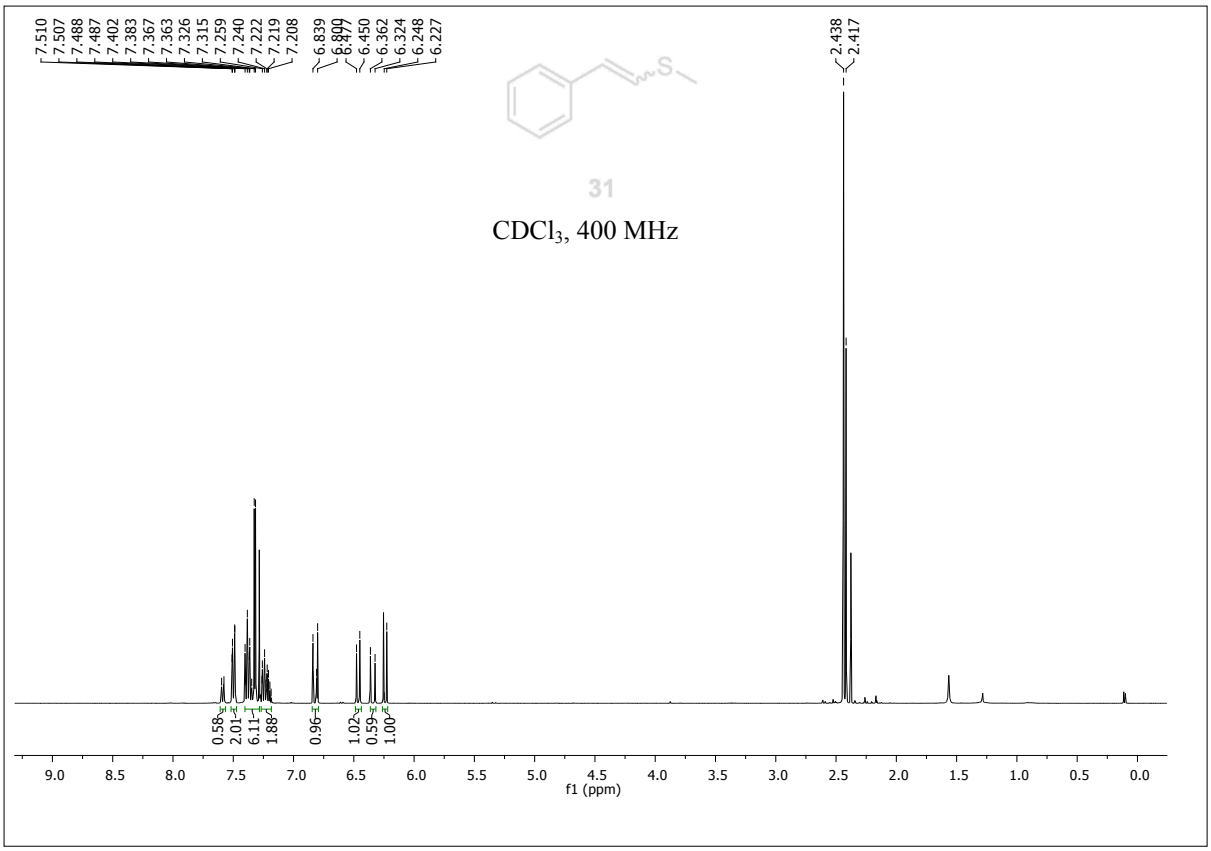
$CDCl_3$, 100 MHz


7.288
7.285
7.274
7.271
7.067
7.064
7.058
7.055
6.953
6.944
6.940
6.931
2.472
29
CDCl3, 400 MHz
1.00
1.00
1.02
3.21
f1 (ppm)

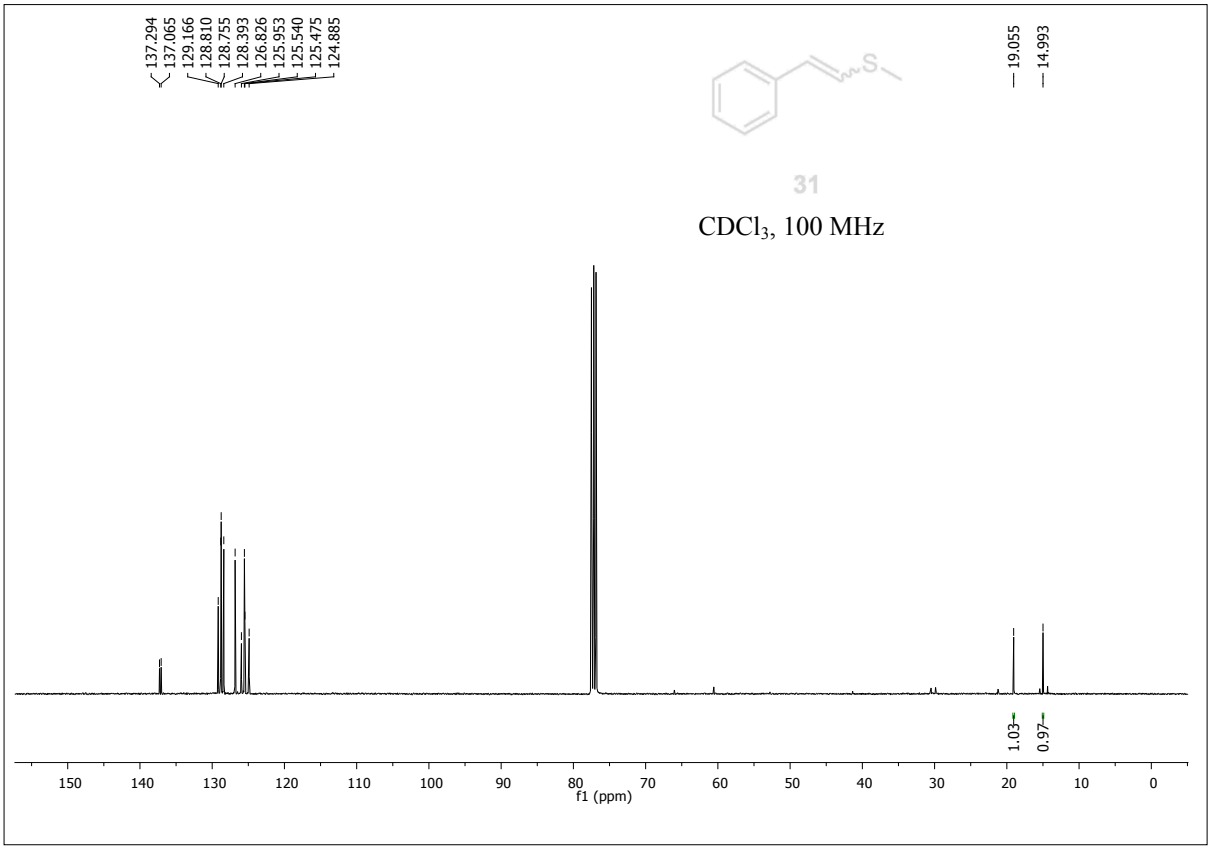

137.288
131.190
128.079
127.600
22.409
29
CDCl3, 100 MHz
f1 (ppm)


8.339
8.327
8.211
8.194
7.763
7.746
7.675
7.673
7.661
7.659
7.645
7.643
7.579
7.576
7.562
7.560
7.548
7.546
7.342
7.330
2.716
N
S
30
CDCl3, 400 MHz
0.99
0.99
1.00
1.02
1.02
1.01
3.16
f1 (ppm)

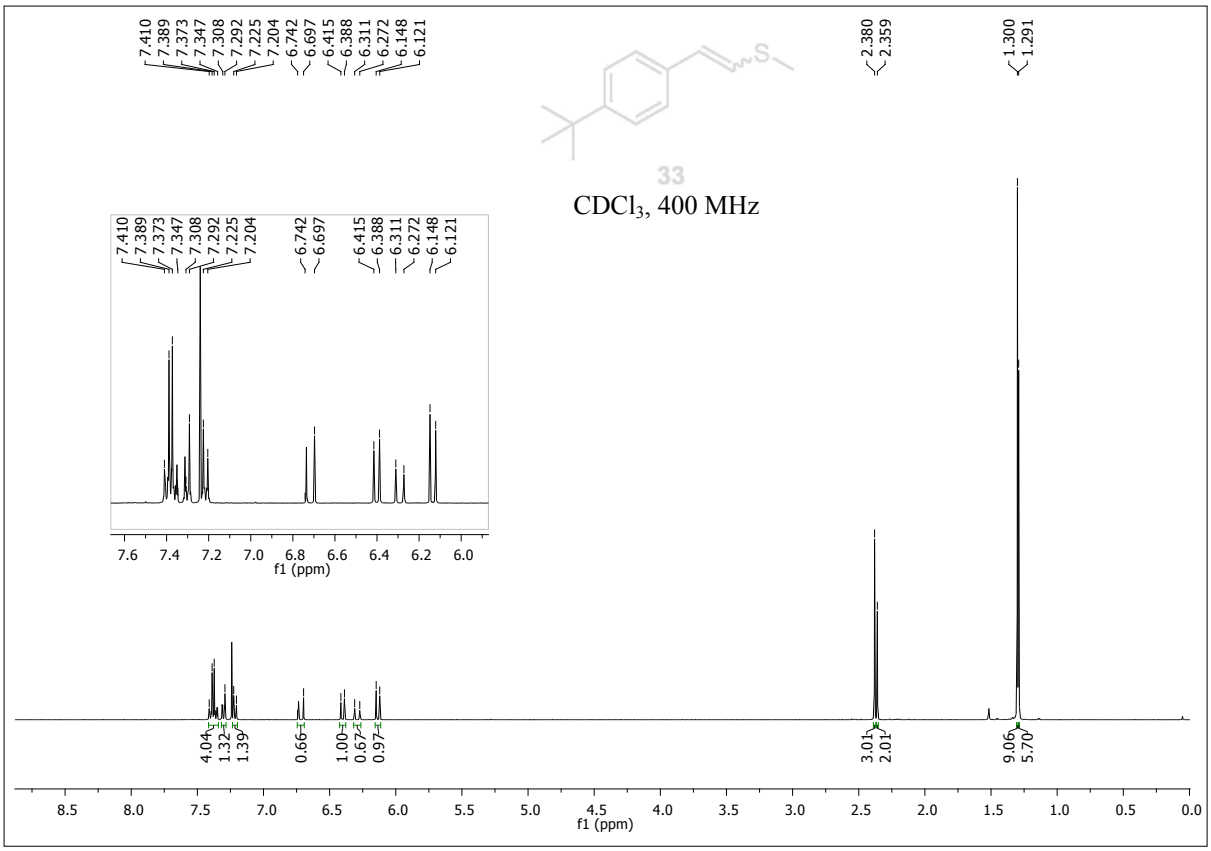

160.15
141.86
135.22
130.24
127.07
124.51
117.01
12.88
N
S
30
CDCl3, 100 MHz
f1 (ppm)

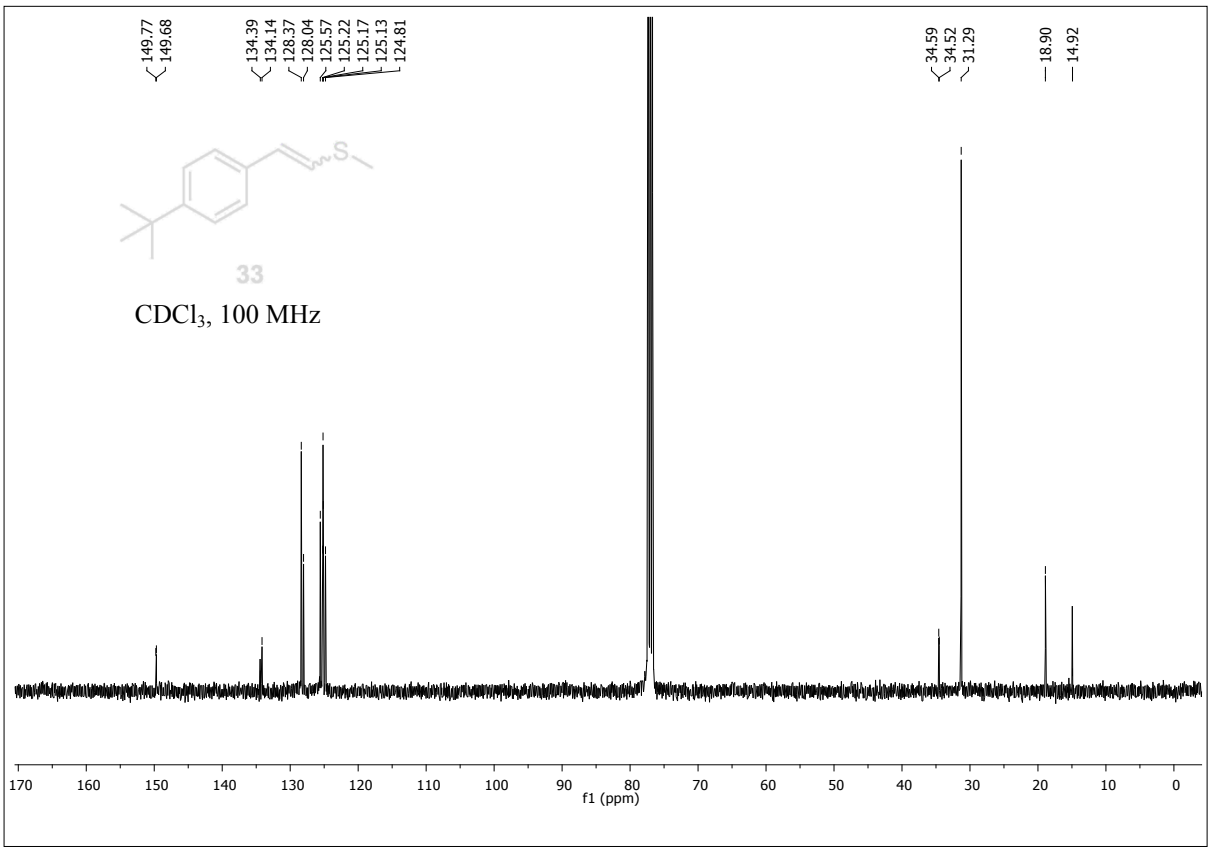


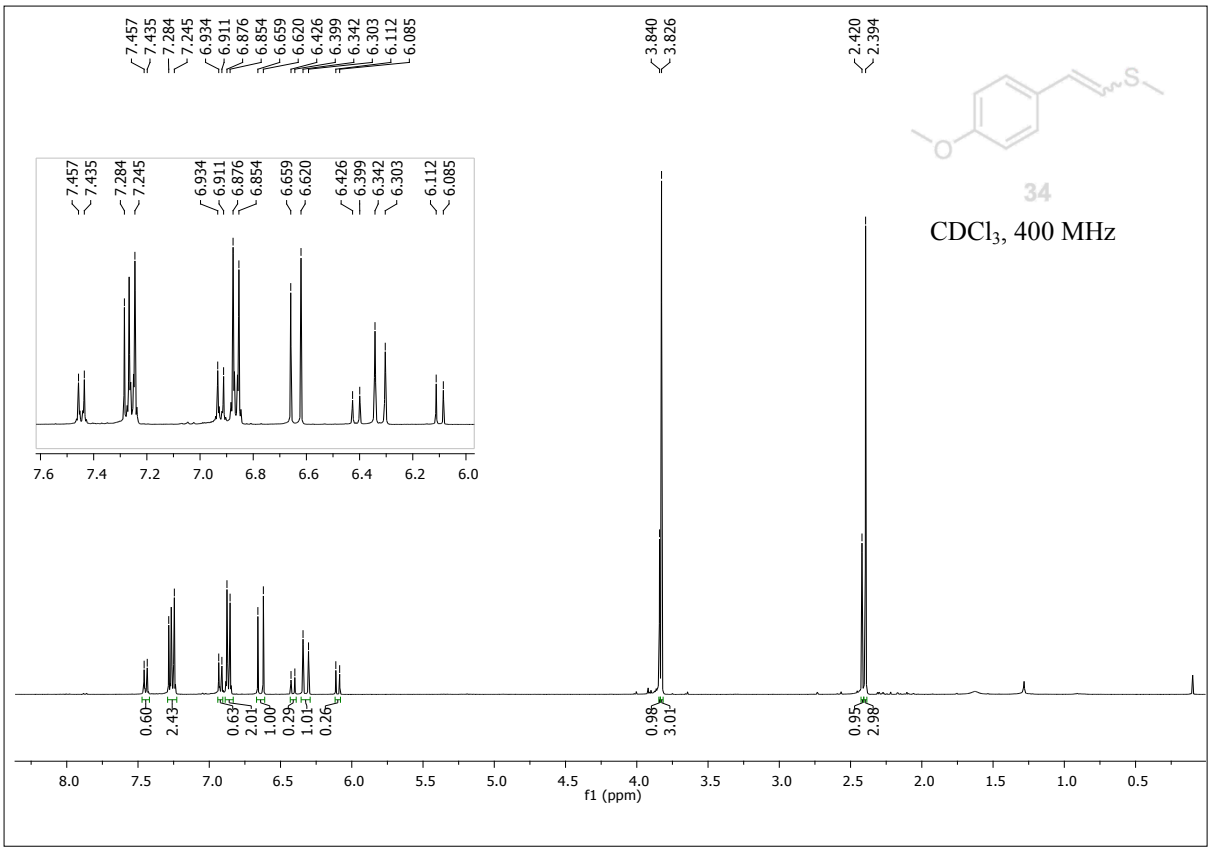
$CDCl_3$, 400 MHz

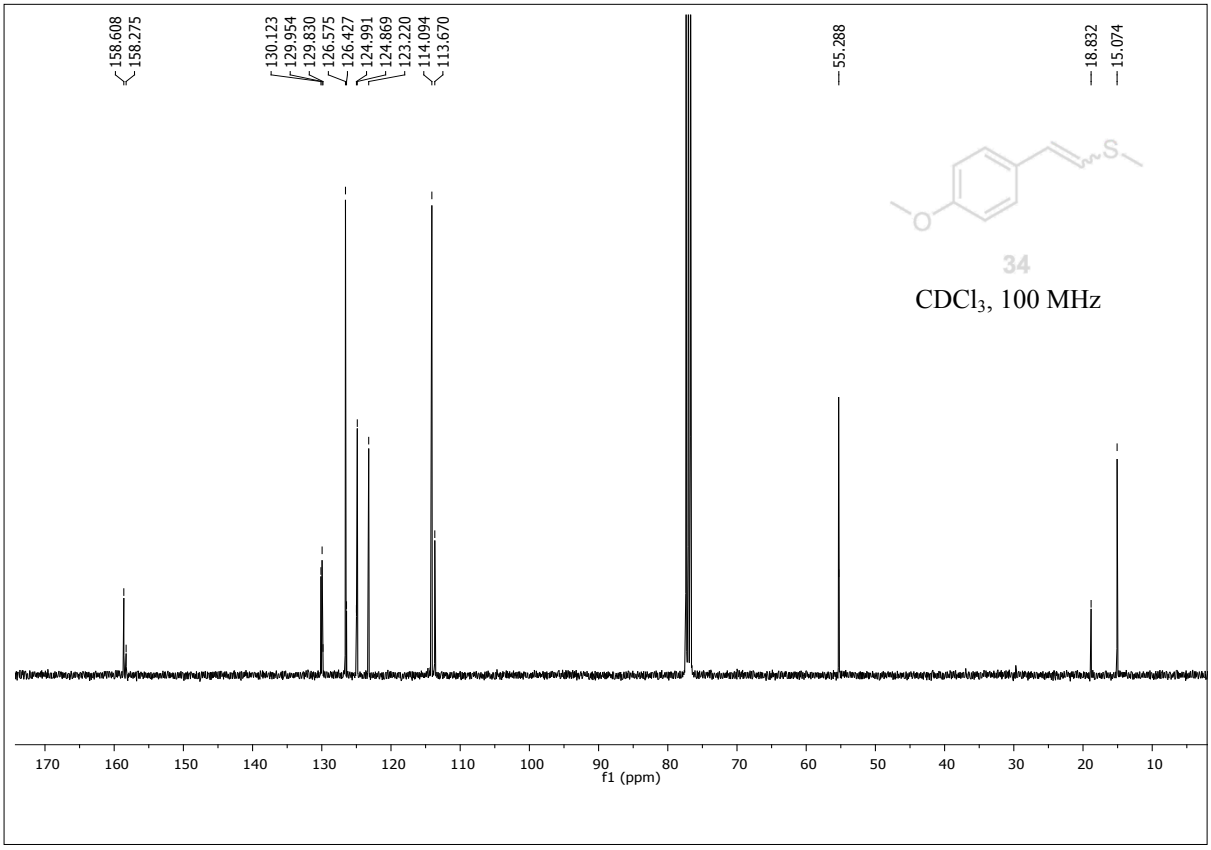


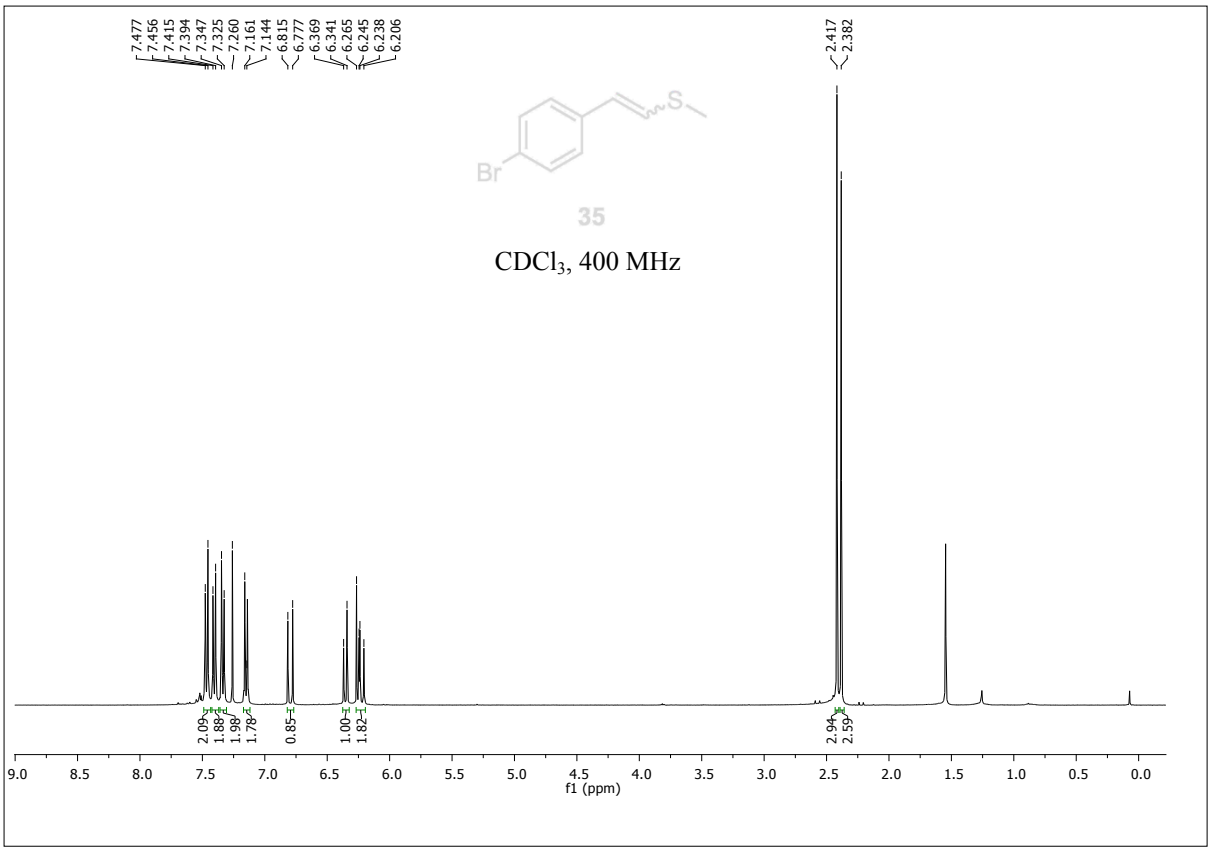
$CDCl_3$, 100 MHz


7.410
7.389
7.373
7.347
7.308
7.292
7.225
7.204
6.742
6.697
6.415
6.388
6.311
6.272
6.148
6.121
2.380
2.359
1.300
1.291
33
CDCl3, 400 MHz
f1 (ppm)
4.04
1.32
1.39
0.66
1.00
0.67
0.97
3.01
2.01
9.06
5.70

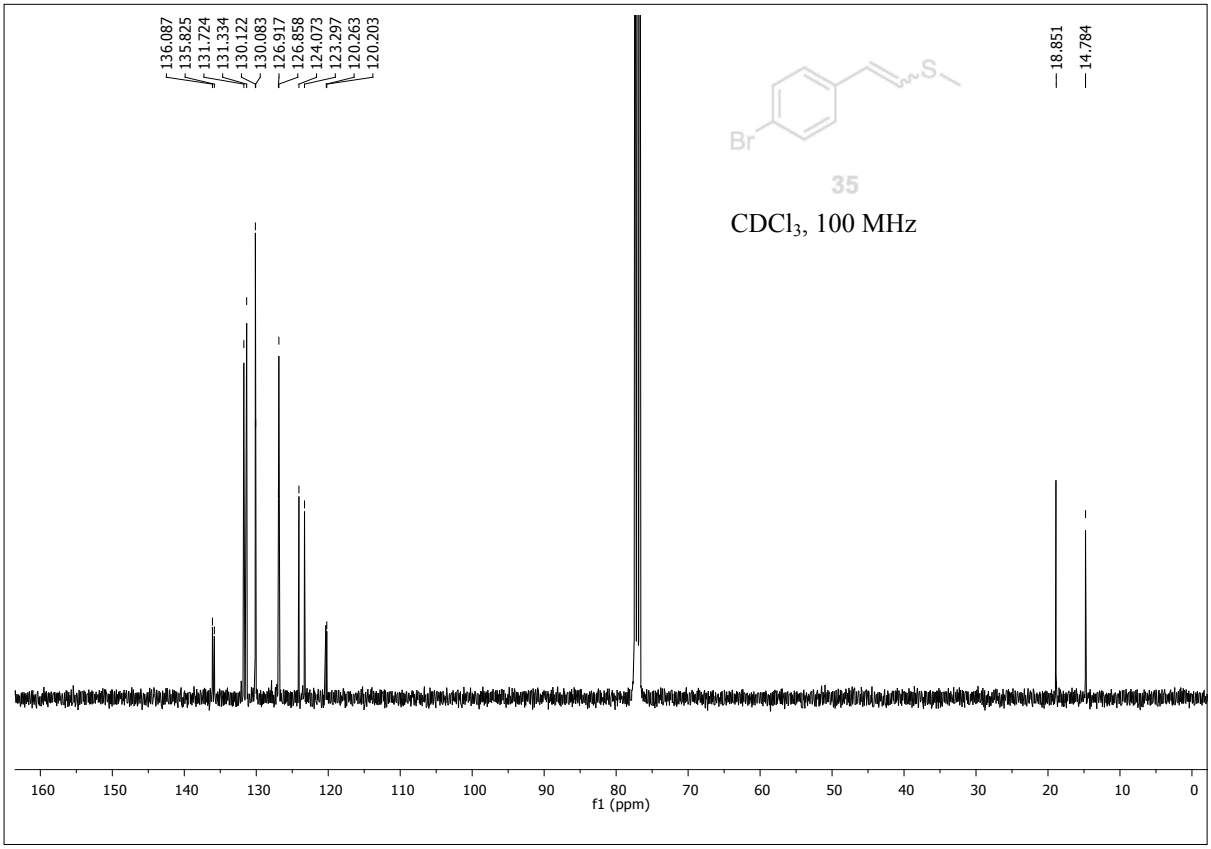

149.77
149.68
134.39
134.14
128.37
128.04
125.57
125.22
125.17
125.13
124.81
34.59
34.52
31.29
18.90
14.92
33
CDCl3, 100 MHz
f1 (ppm)


7.457
7.435
7.284
7.245
6.934
6.911
6.876
6.854
6.659
6.620
6.426
6.399
6.342
6.303
6.112
6.085
3.840
3.826
2.420
2.394
34
CDCl3, 400 MHz
f1 (ppm)

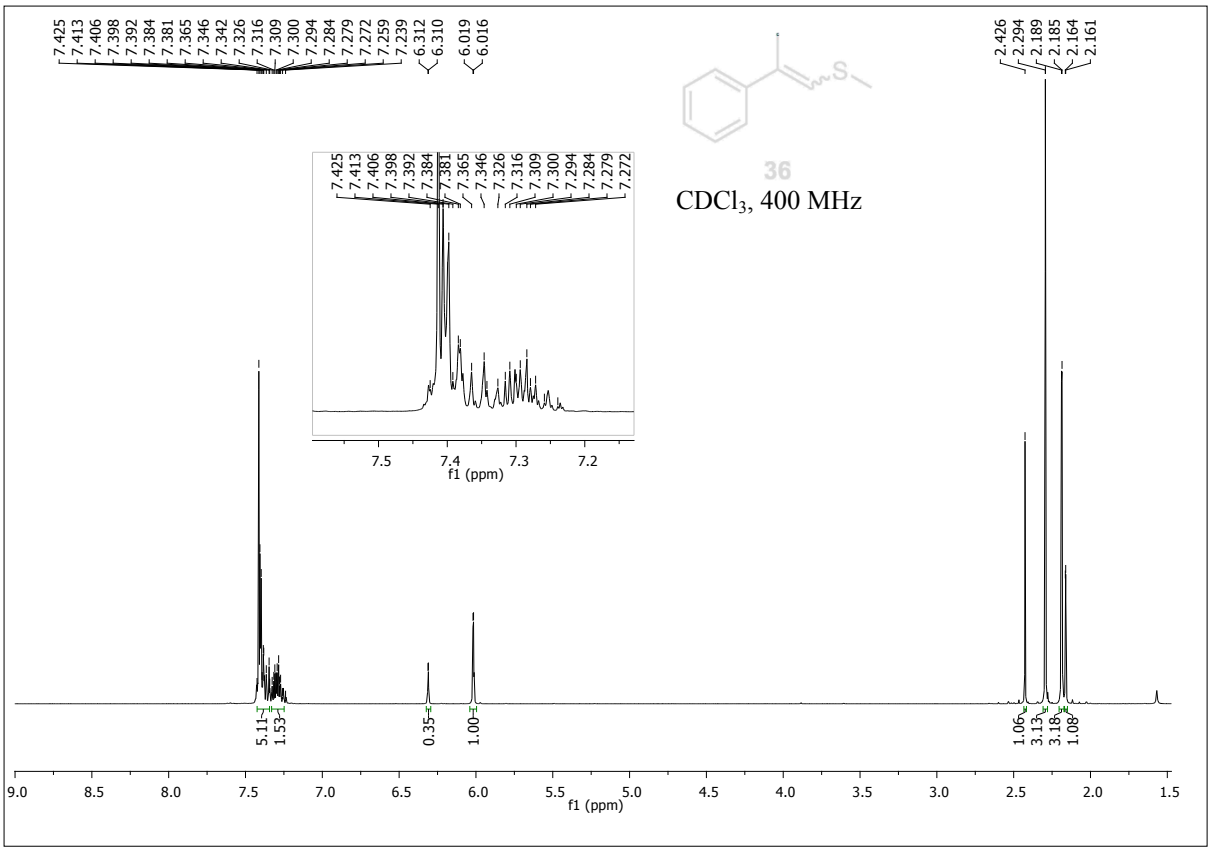

158.608
158.275
130.123
129.954
129.830
126.575
126.427
124.991
124.869
123.220
114.094
113.670
55.288
18.832
15.074
34
CDCl3, 100 MHz
f1 (ppm)

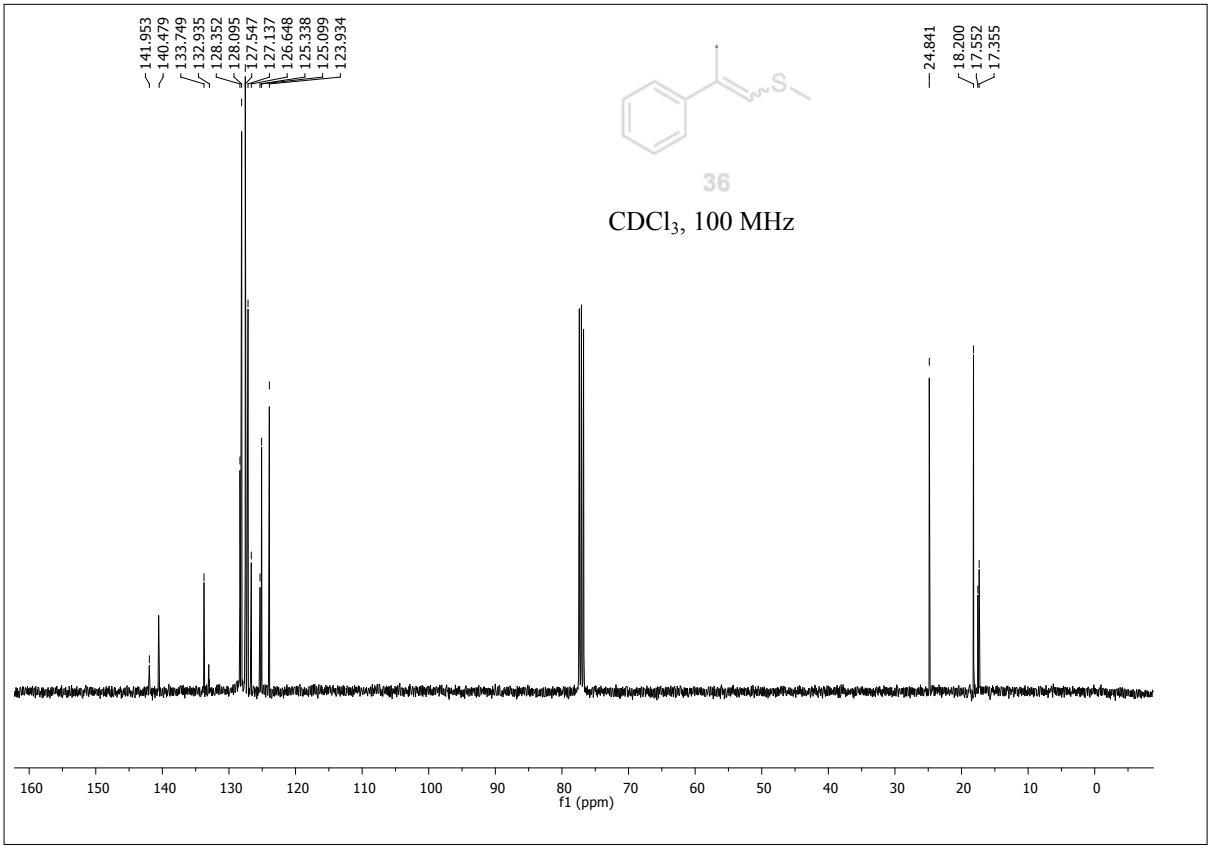


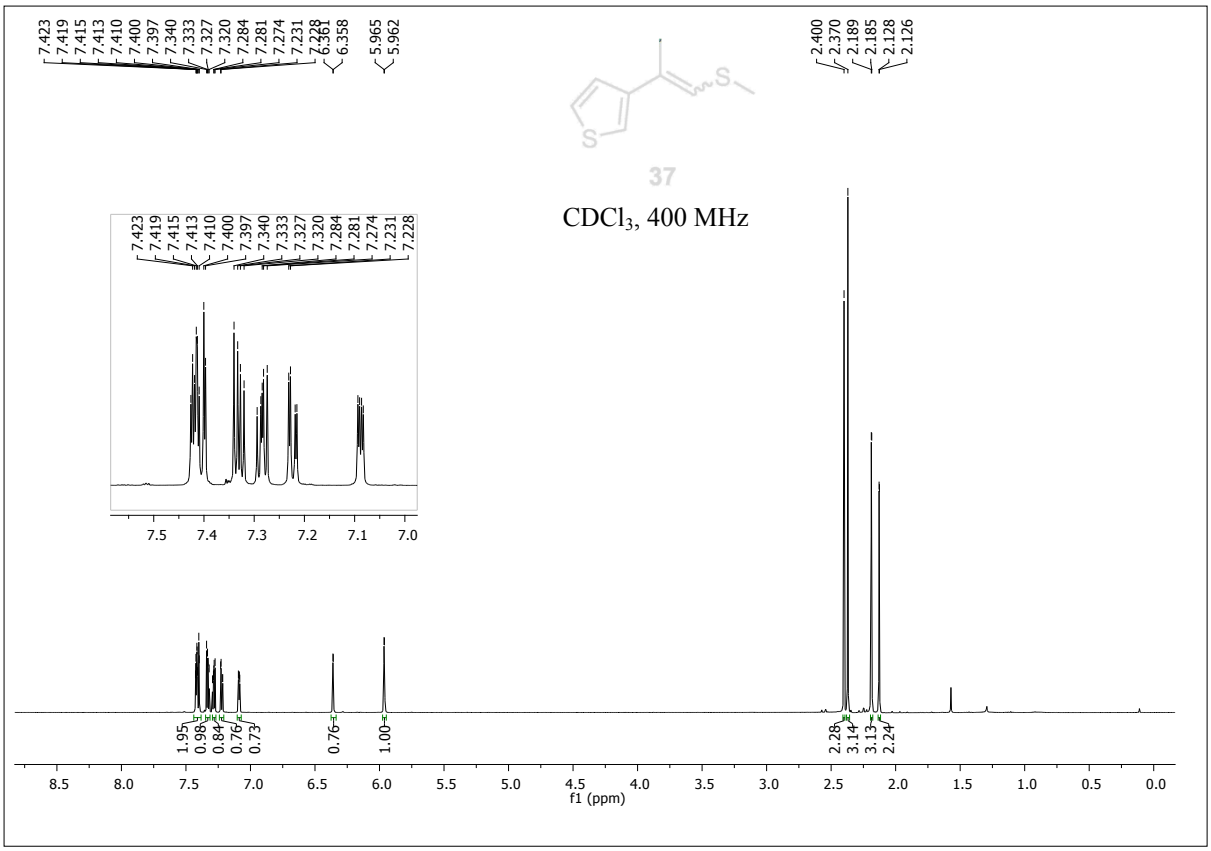
$CDCl_3$, 400 MHz

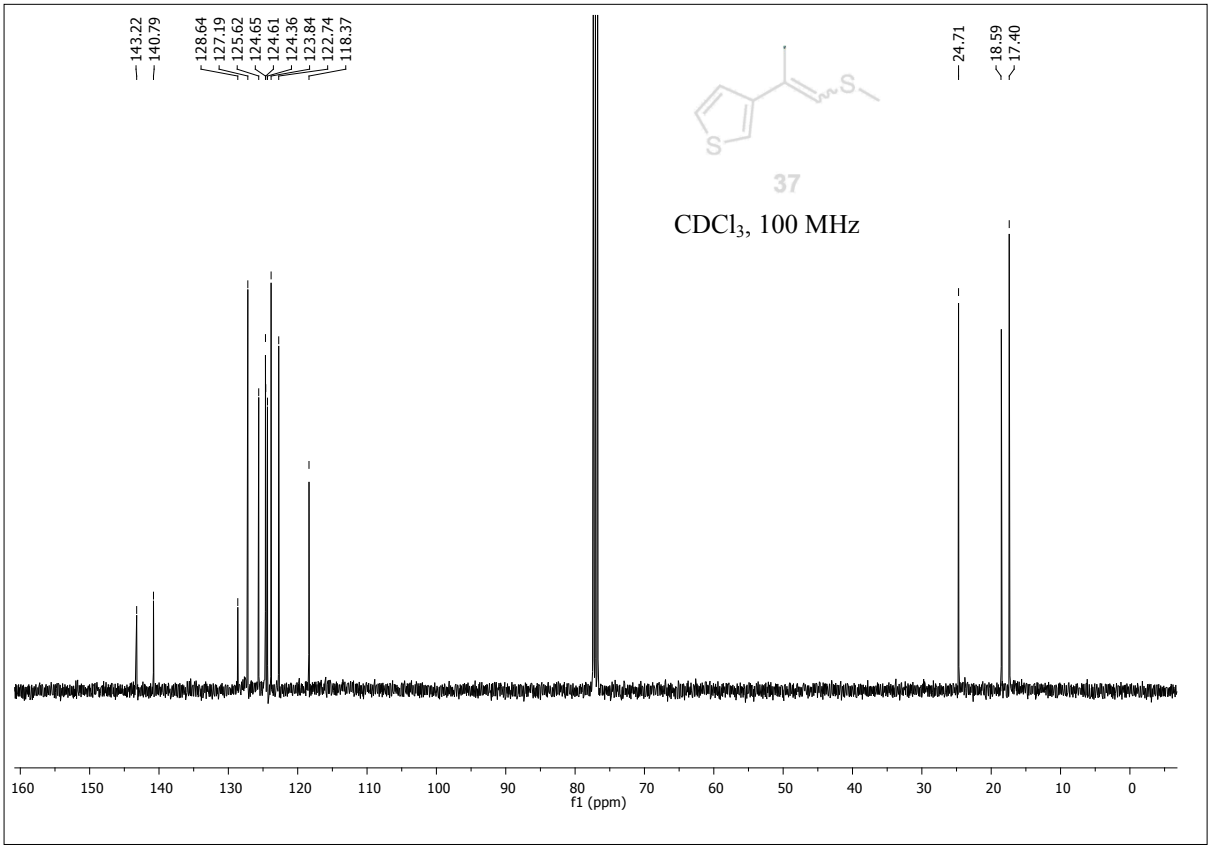


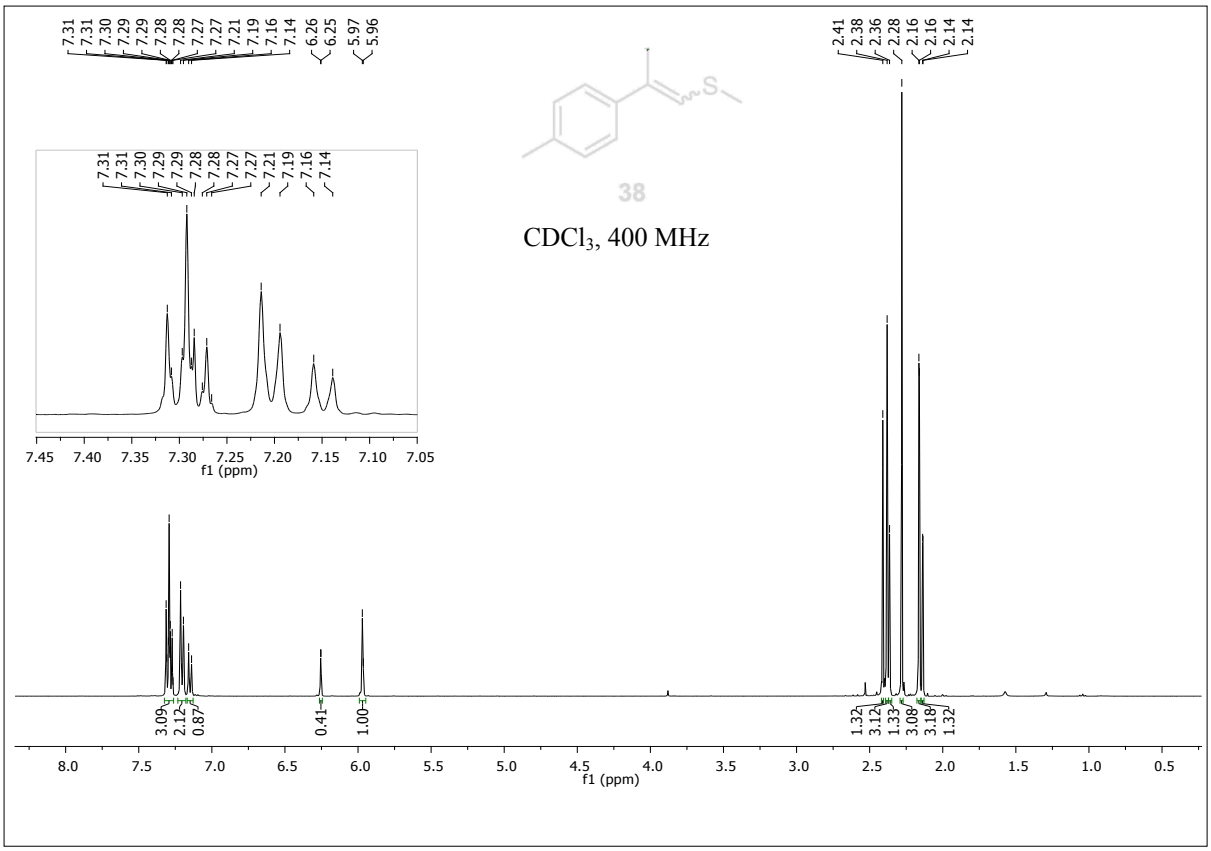
$CDCl_3$, 100 MHz

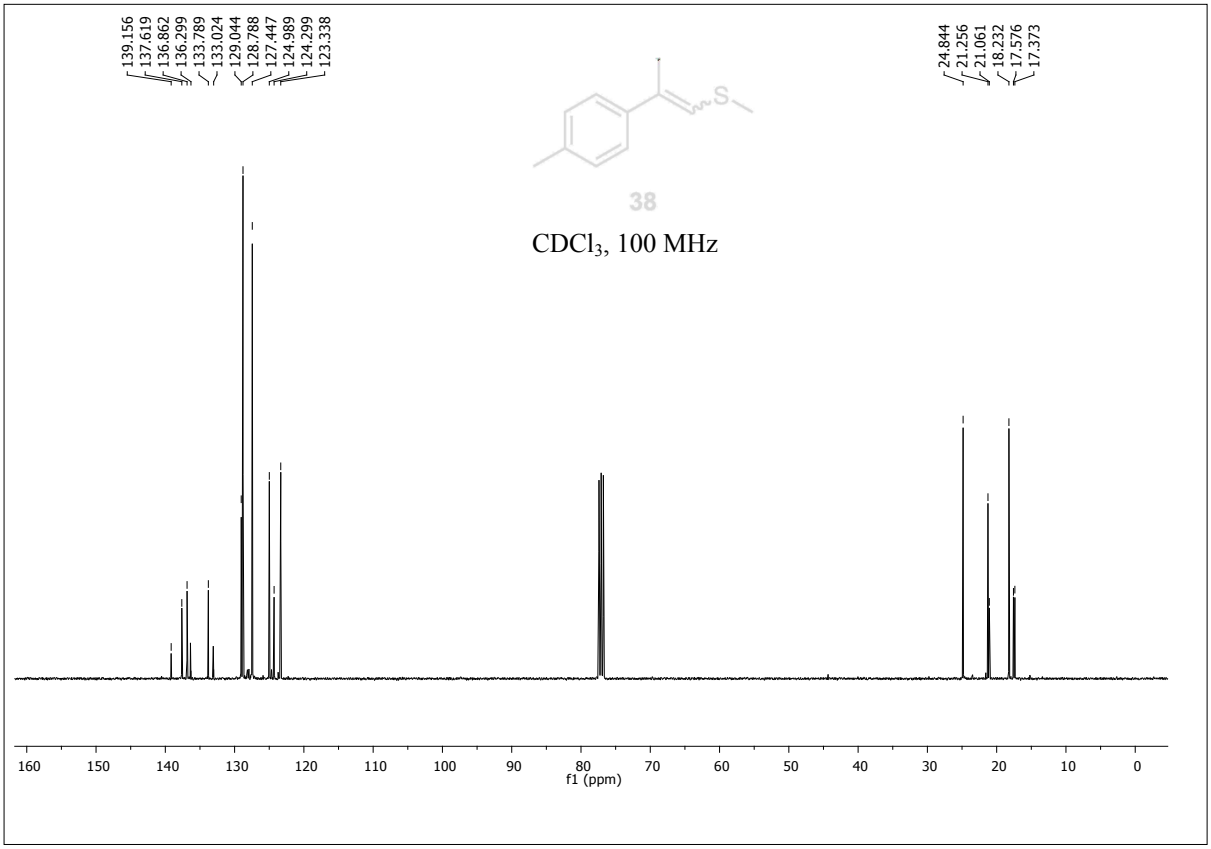

7.425
7.413
7.406
7.398
7.392
7.384
7.381
7.365
7.346
7.342
7.326
7.316
7.309
7.300
7.294
7.284
7.279
7.272
7.259
7.239
6.312
6.310
6.019
6.016
2.426
2.294
2.189
2.185
2.164
2.161
S
36
CDCl3, 400 MHz
f1 (ppm)
5.11
1.53
0.35
1.00
1.06
3.13
3.18
1.08

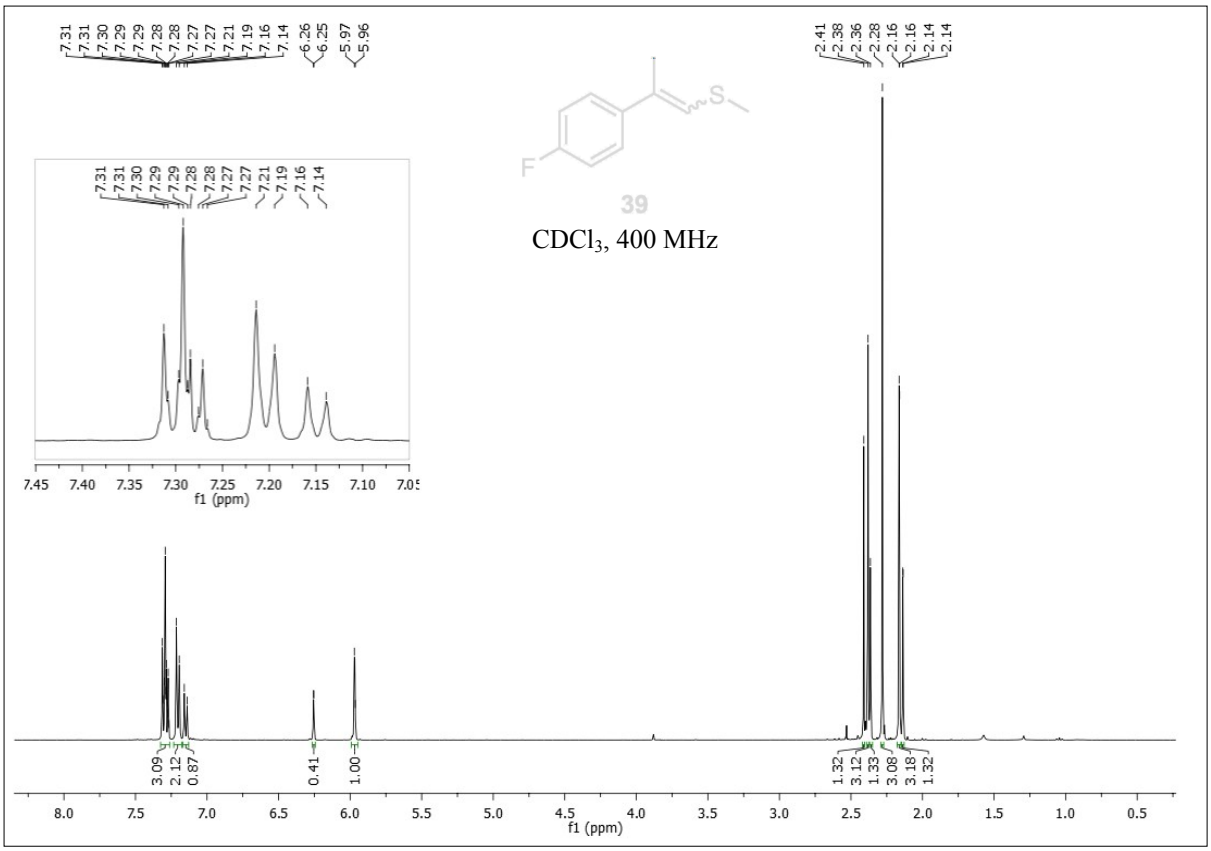

141.953
140.479
133.749
132.935
128.352
128.095
127.547
127.137
126.648
125.338
125.099
123.934
24.841
18.200
17.552
17.355
S
36
CDCl3, 100 MHz
f1 (ppm)

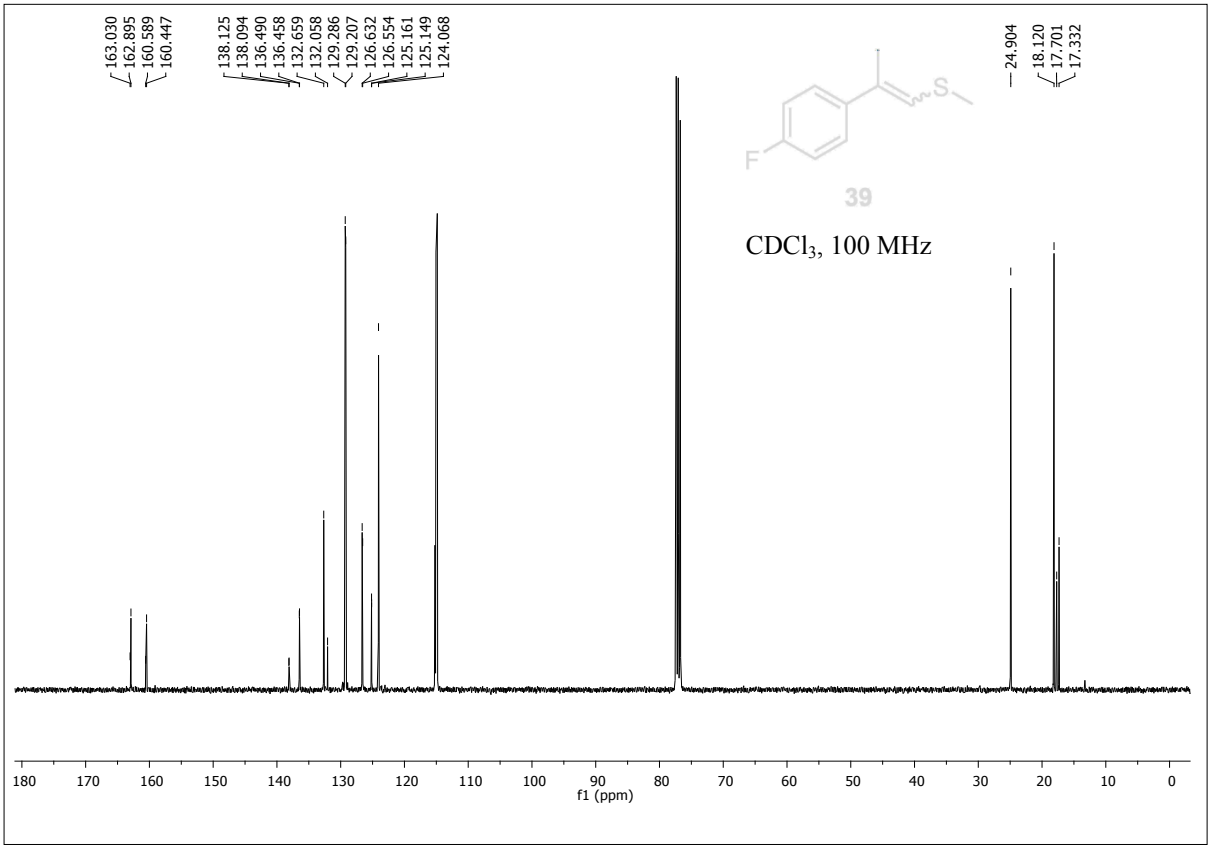

7.423
7.419
7.415
7.413
7.410
7.400
7.397
7.340
7.333
7.327
7.320
7.284
7.281
7.274
7.231
6.358
5.965
5.962
2.400
2.370
2.189
2.185
2.128
2.126
37
CDCl3, 400 MHz
1.95
0.98
0.84
0.76
0.73
0.76
1.00
2.28
3.14
3.13
2.24
f1 (ppm)

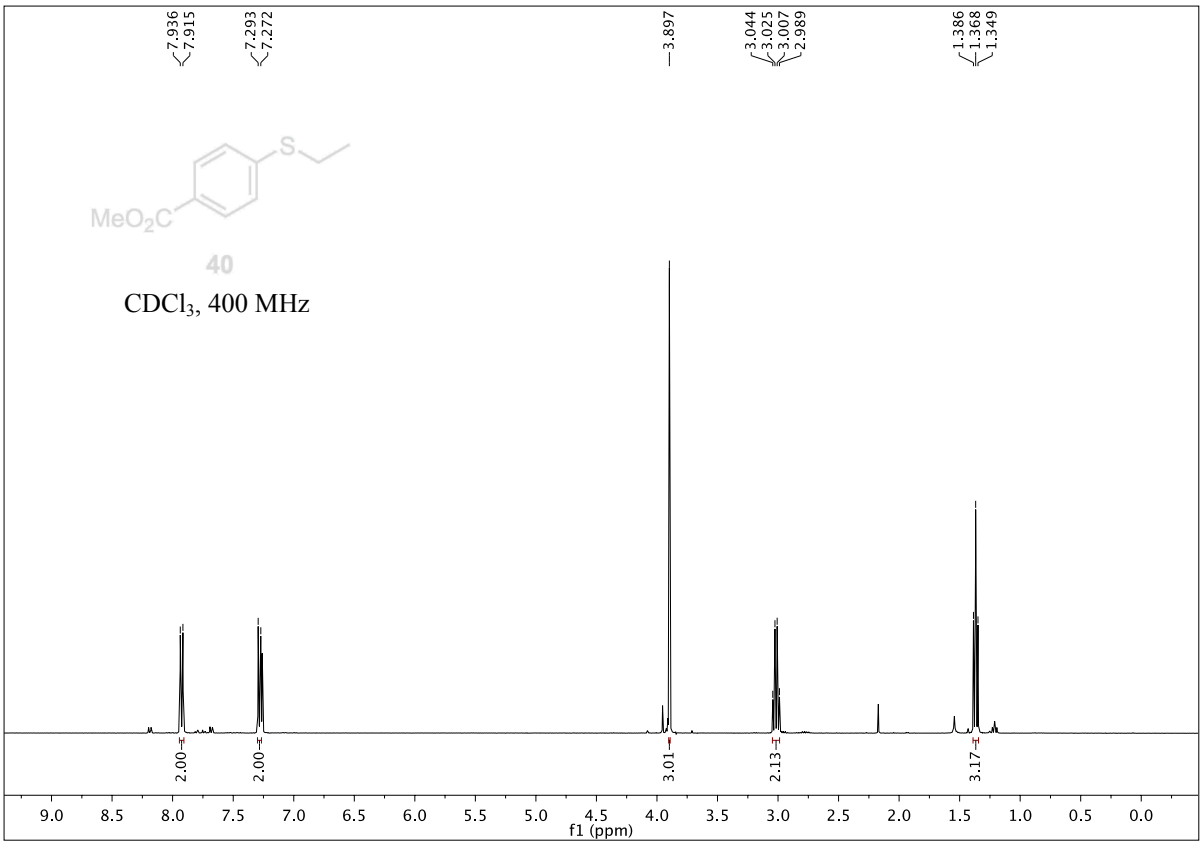

143.22
140.79
128.64
127.19
125.62
124.65
124.61
124.36
123.84
122.74
118.37
24.71
18.59
17.40
37
CDCl3, 100 MHz
f1 (ppm)


38
CDCl3, 400 MHz
f1 (ppm)

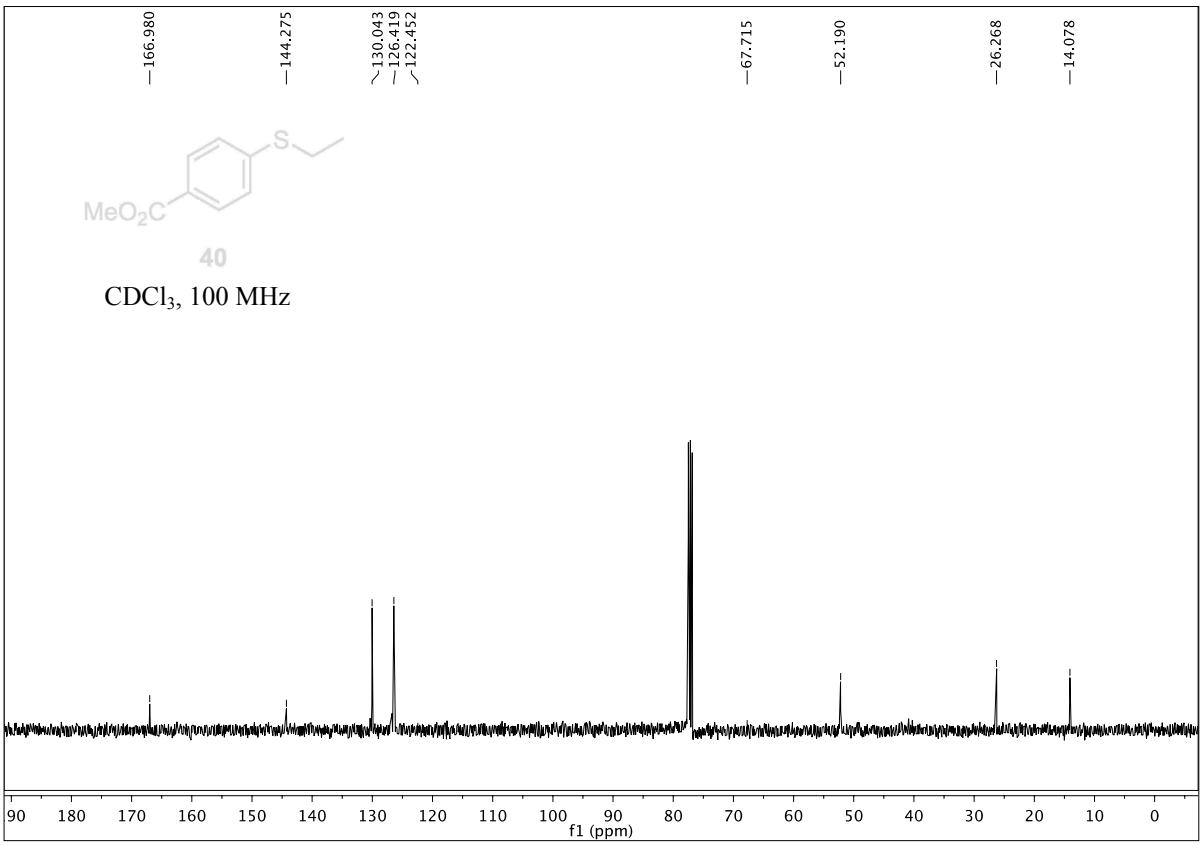

38
CDCl3, 100 MHz
f1 (ppm)


39
CDCl3, 400 MHz
f1 (ppm)

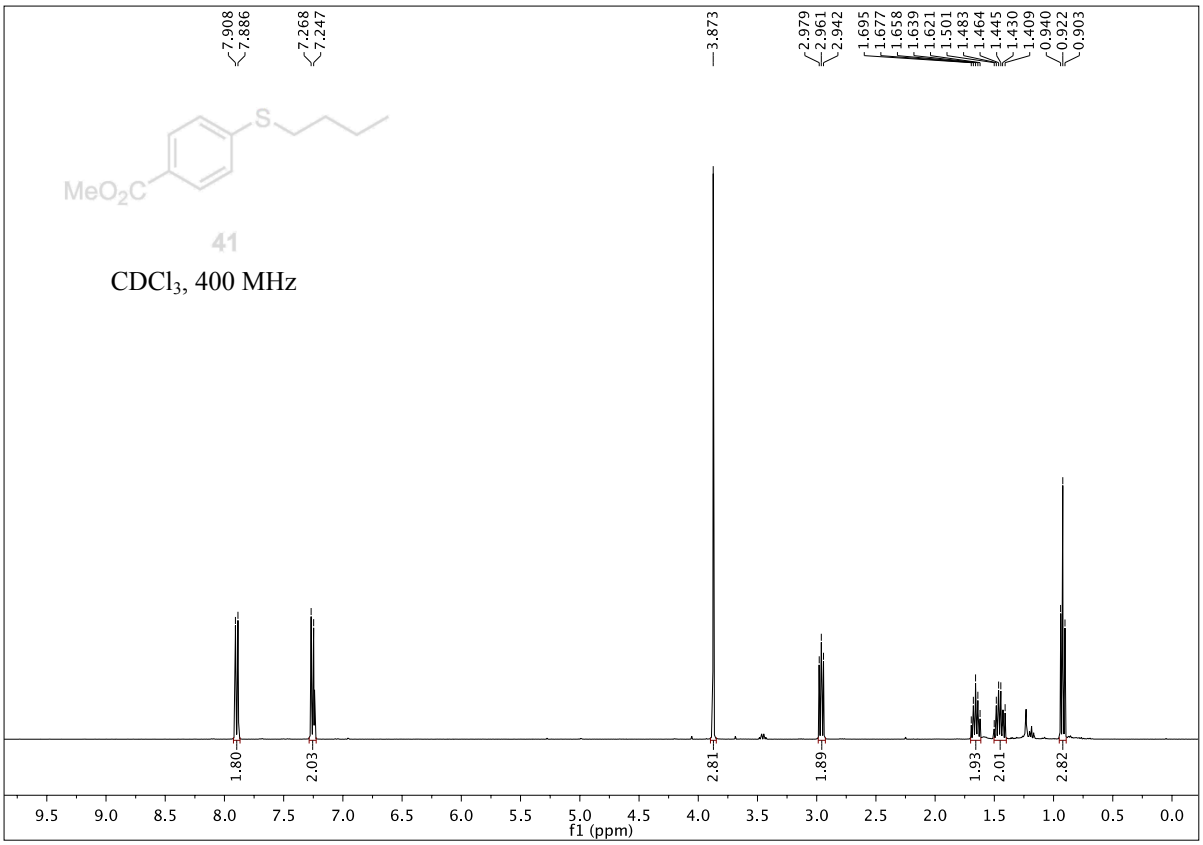

39
CDCl3, 100 MHz
f1 (ppm)

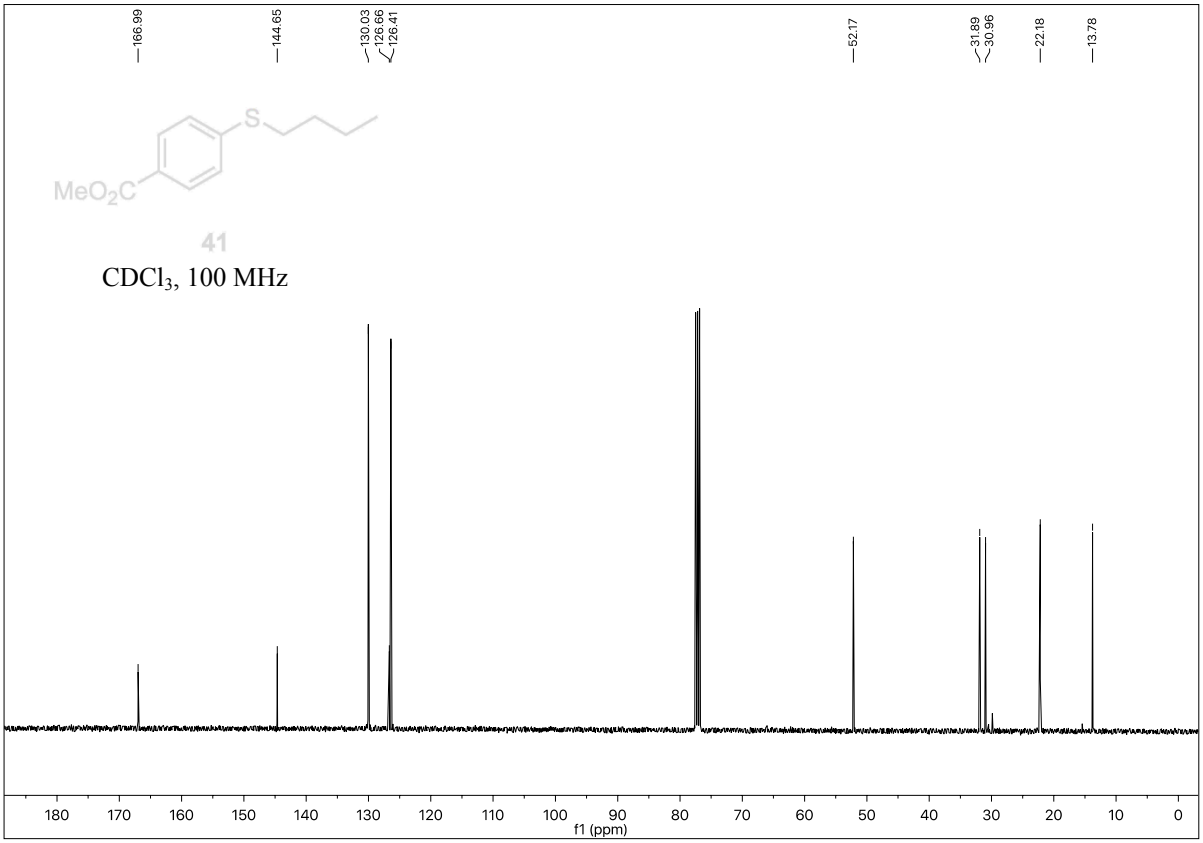


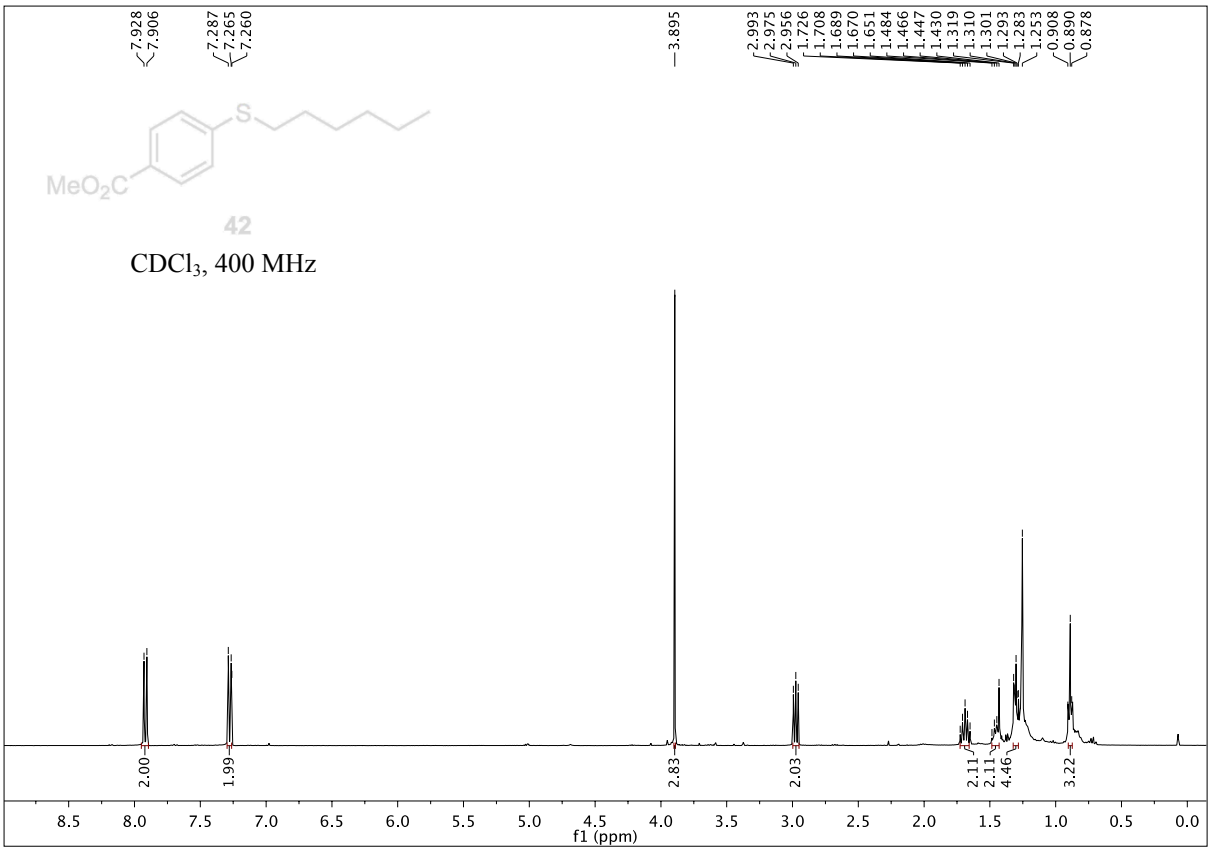
$CDCl_3$, 400 MHz

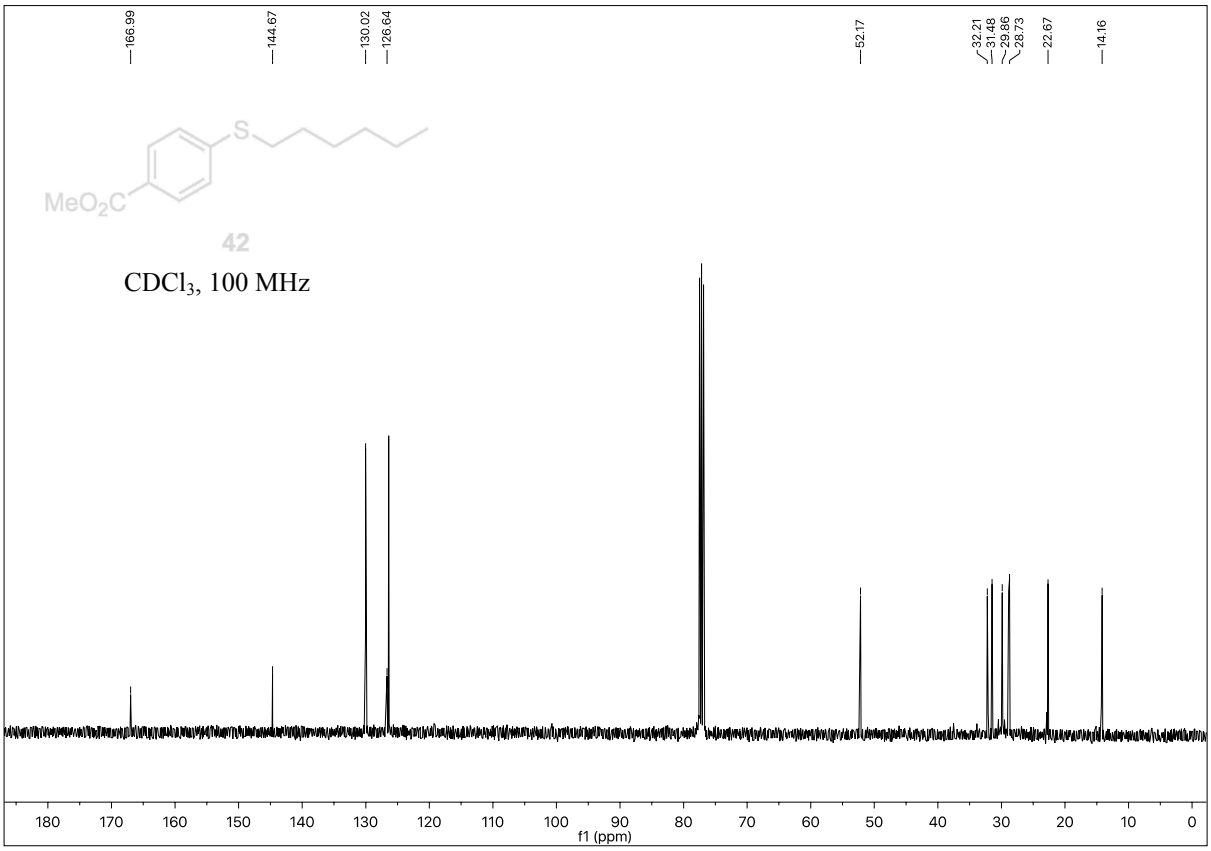


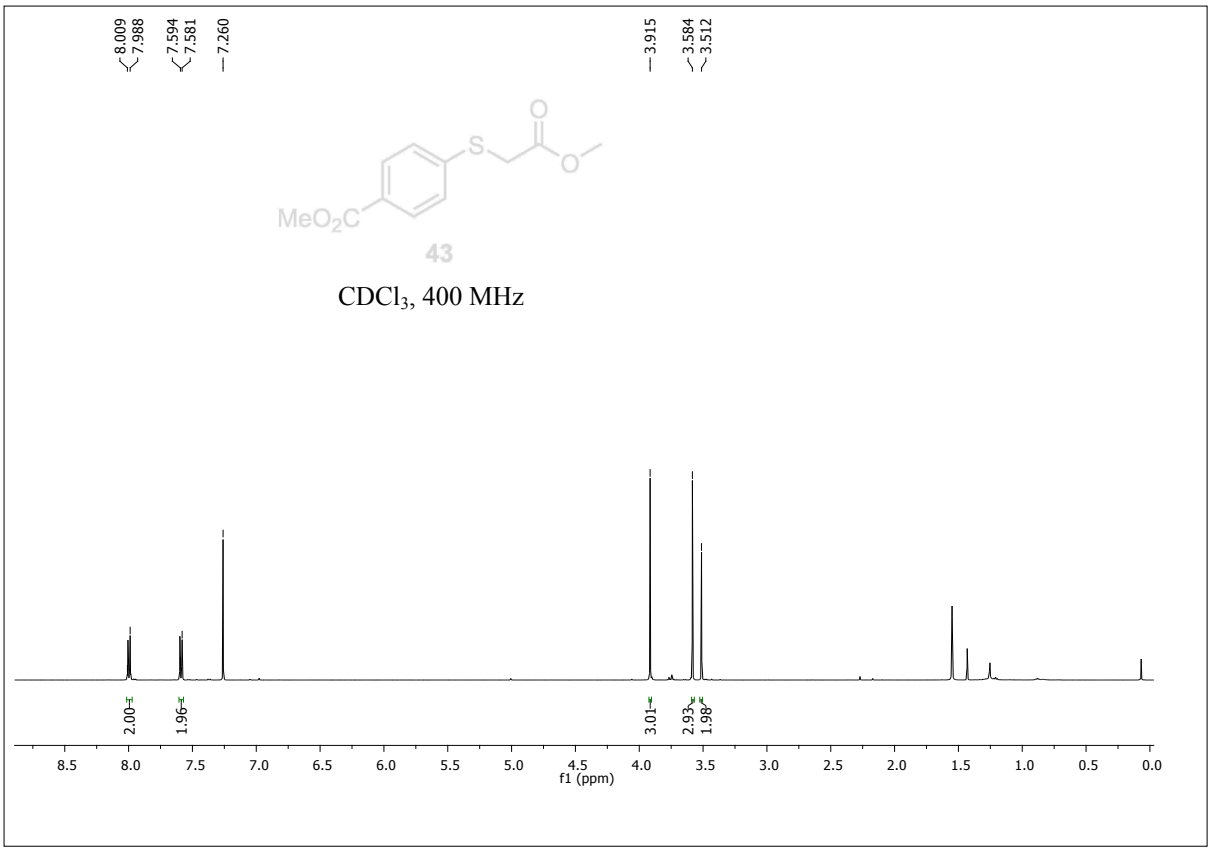
$CDCl_3$, 100 MHz


7.908
7.886
7.268
7.247
3.873
2.979
2.961
2.942
1.695
1.677
1.658
1.639
1.621
1.501
1.483
1.464
1.445
1.430
1.409
0.940
0.922
0.903
MeO2C
S
41
CDCl3, 400 MHz
1.80
2.03
2.81
1.89
1.93
2.01
2.82
f1 (ppm)

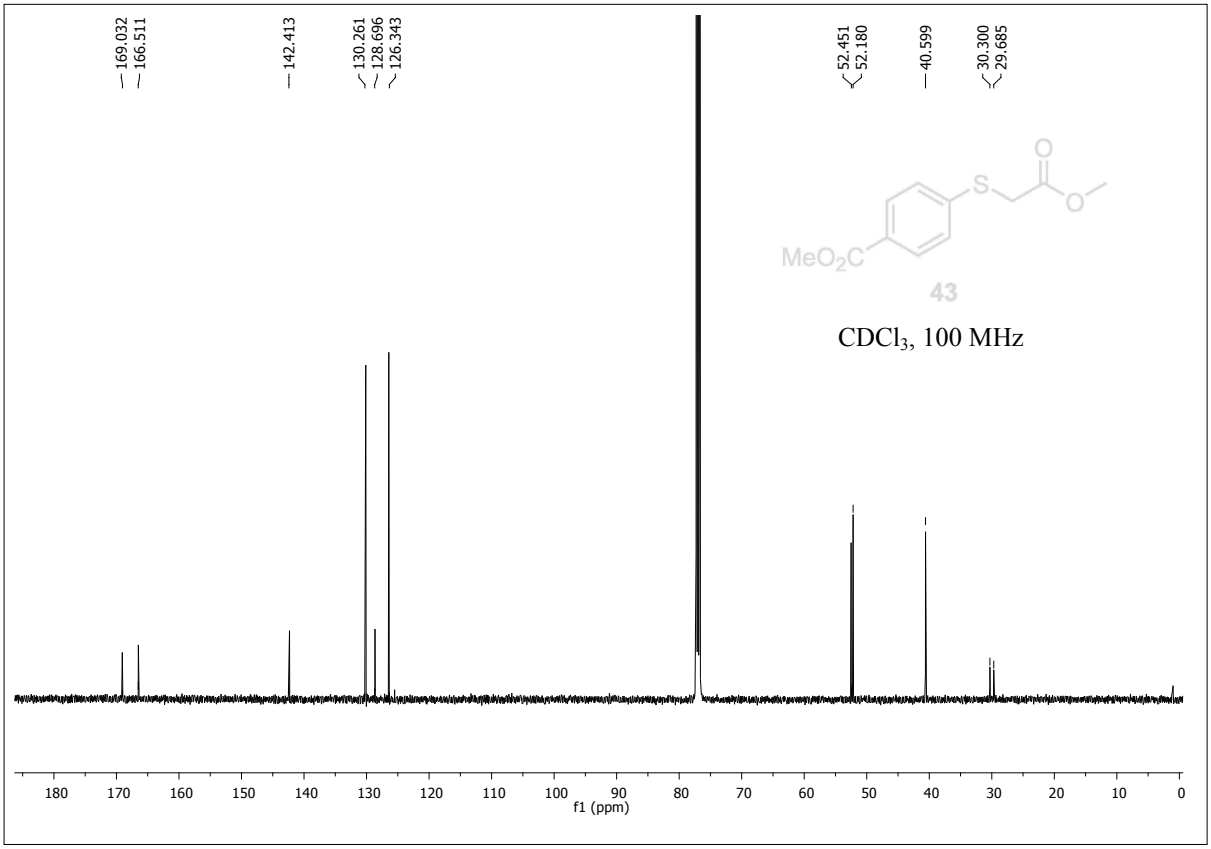

166.99
144.65
130.03
126.66
126.41
52.17
31.89
30.96
22.18
13.78
MeO2C
S
41
CDCl3, 100 MHz
f1 (ppm)


7.928
7.906
7.287
7.265
7.260
3.895
2.993
2.975
2.956
1.726
1.708
1.689
1.670
1.651
1.484
1.466
1.447
1.430
1.319
1.310
1.301
1.293
1.283
1.253
0.908
0.890
0.878
MeO2C
S
42
CDCl3, 400 MHz
2.00
1.99
2.83
2.03
2.11
2.11
4.46
3.22
f1 (ppm)

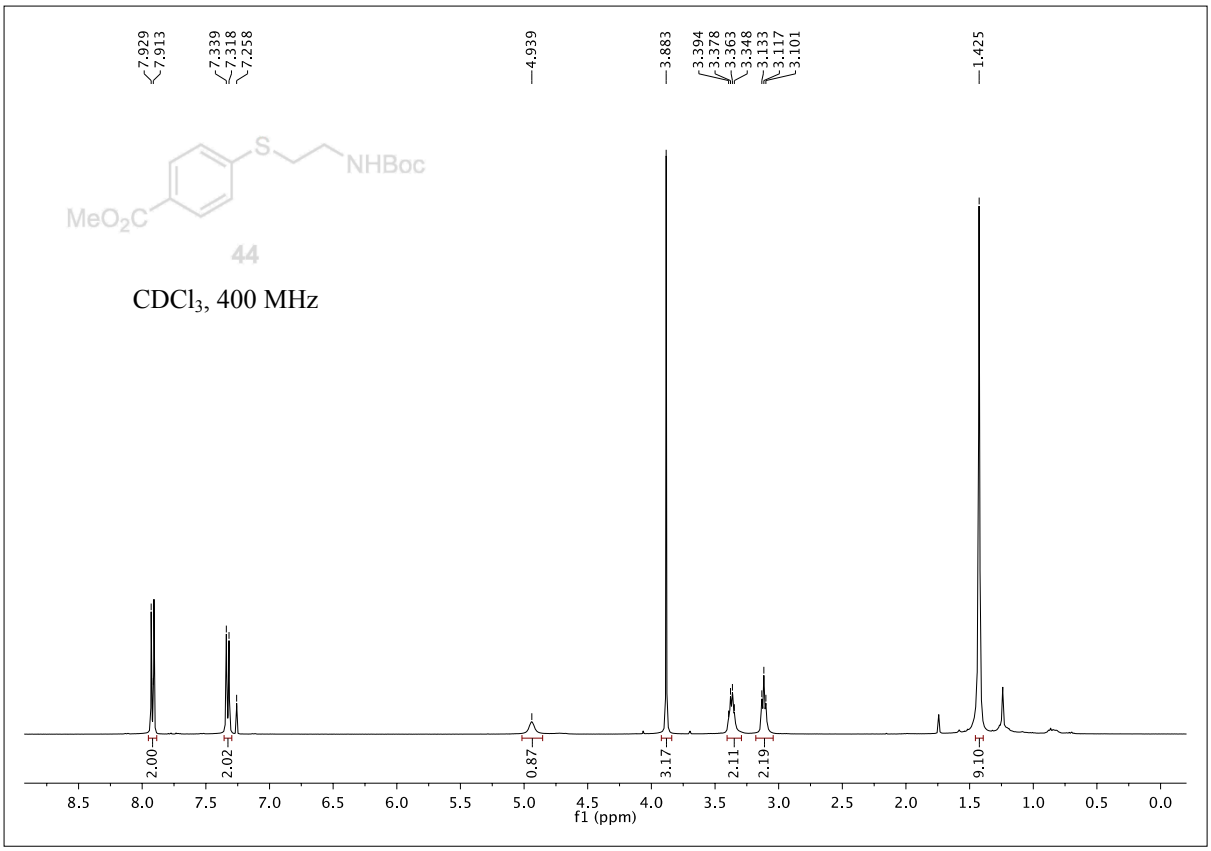

166.99
144.67
130.02
126.64
52.17
32.21
31.48
29.86
28.73
22.67
14.16
MeO2C
S
42
CDCl3, 100 MHz
f1 (ppm)



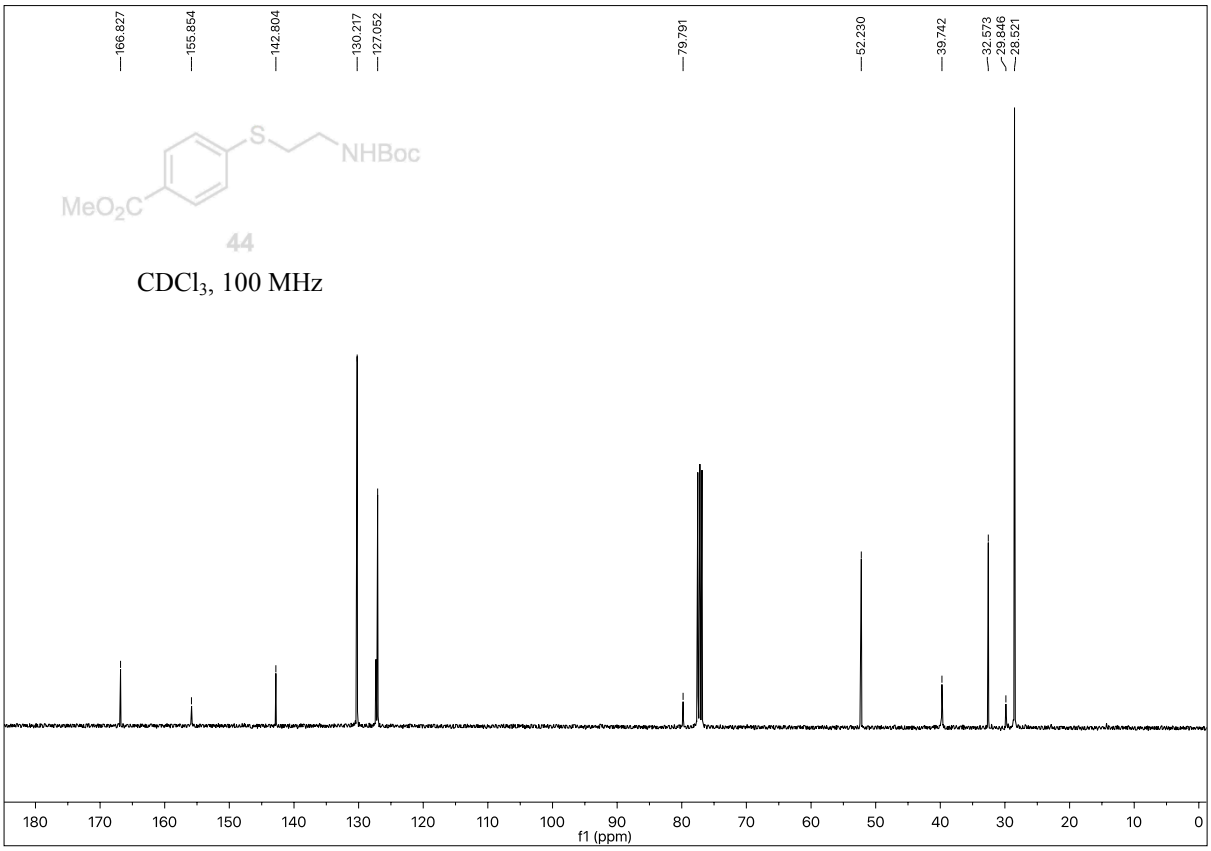
$CDCl_3$, 400 MHz



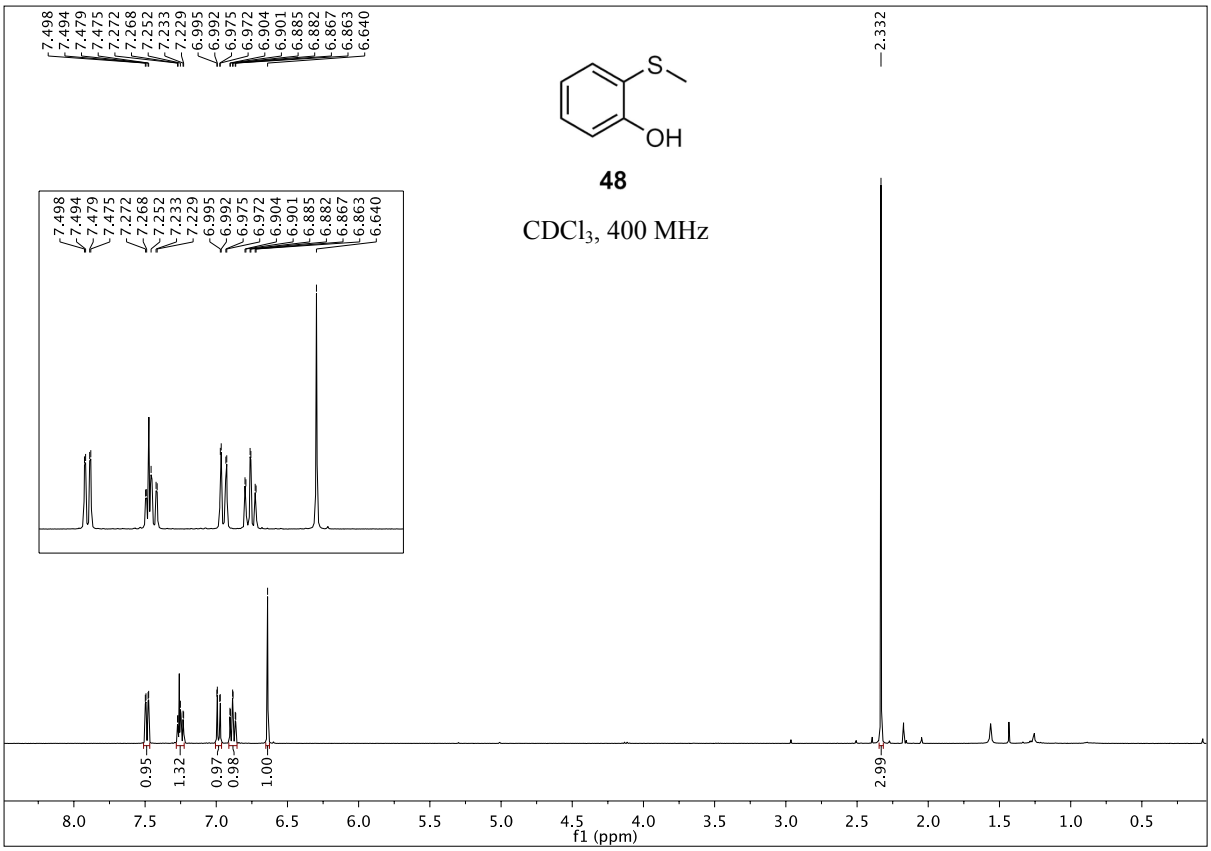
$CDCl_3$, 100 MHz

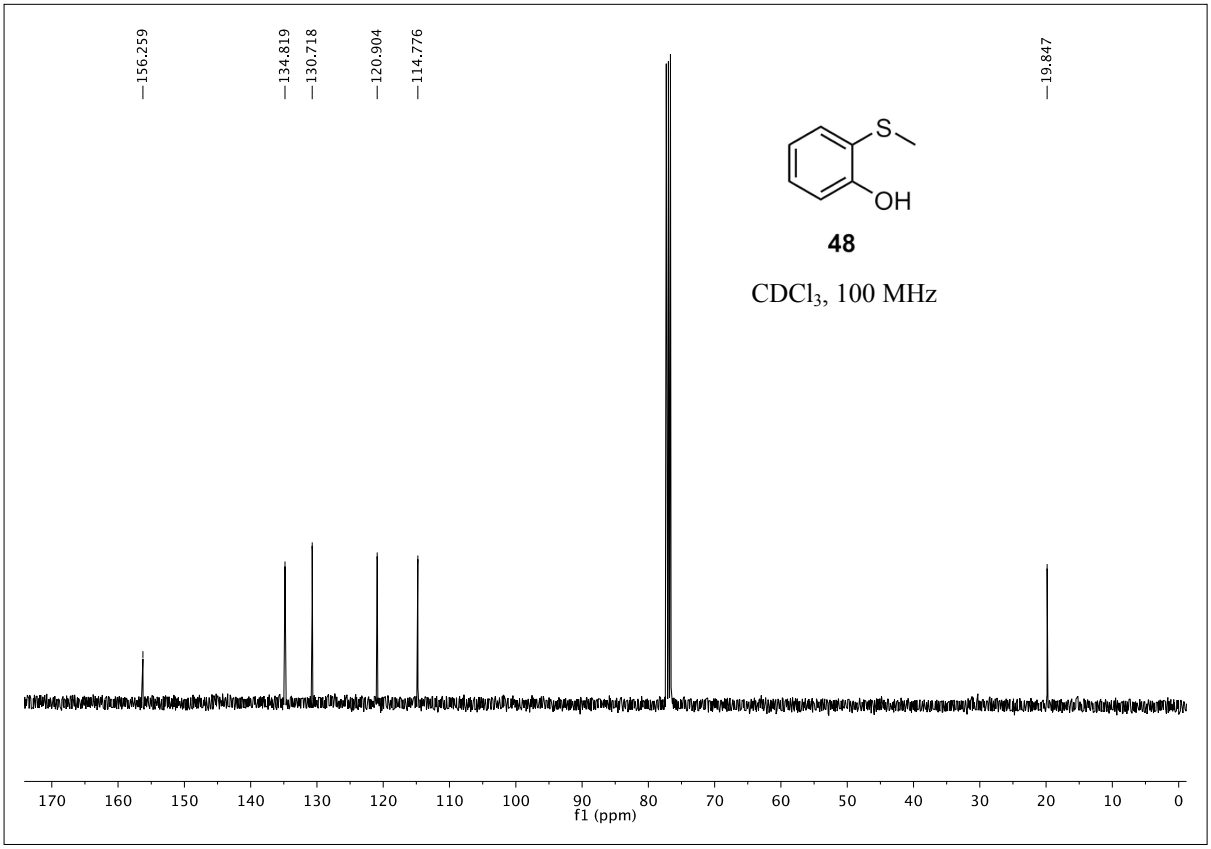


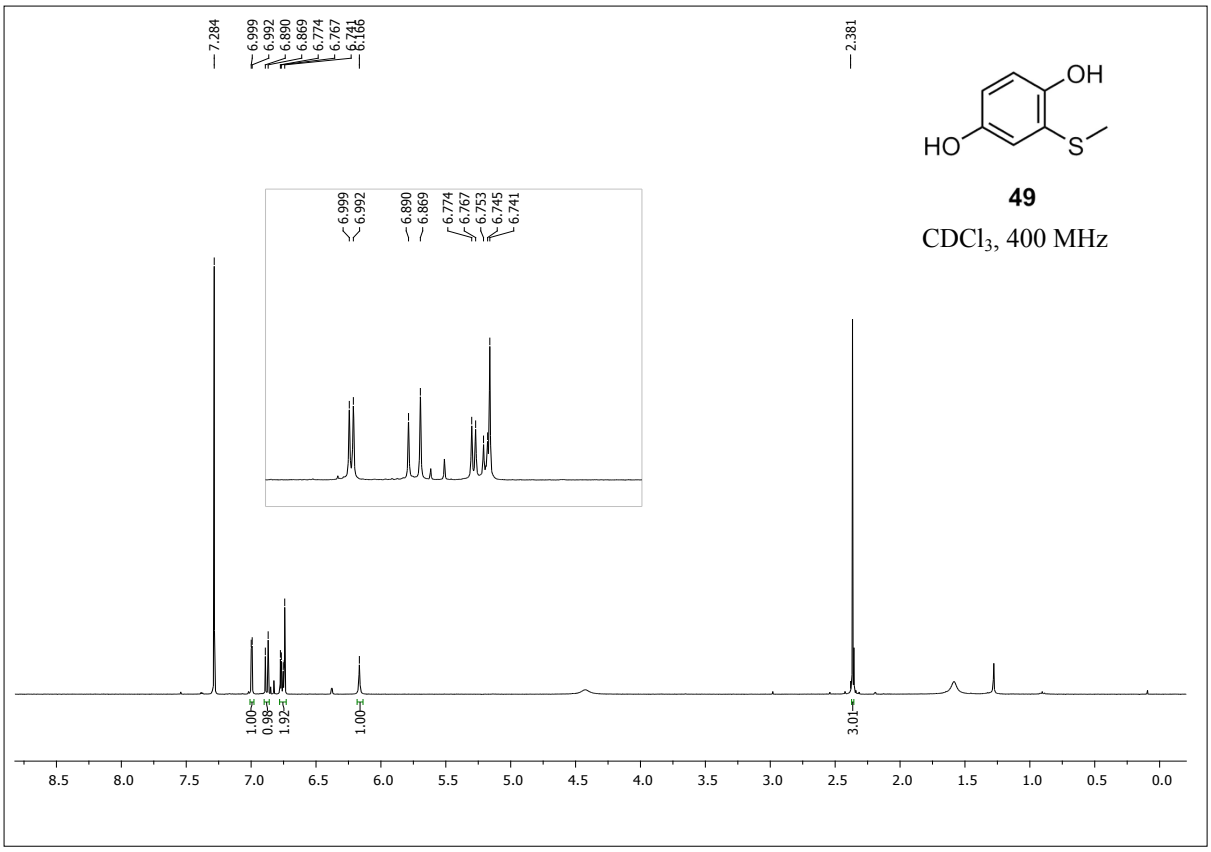
$CDCl_3$, 400 MHz

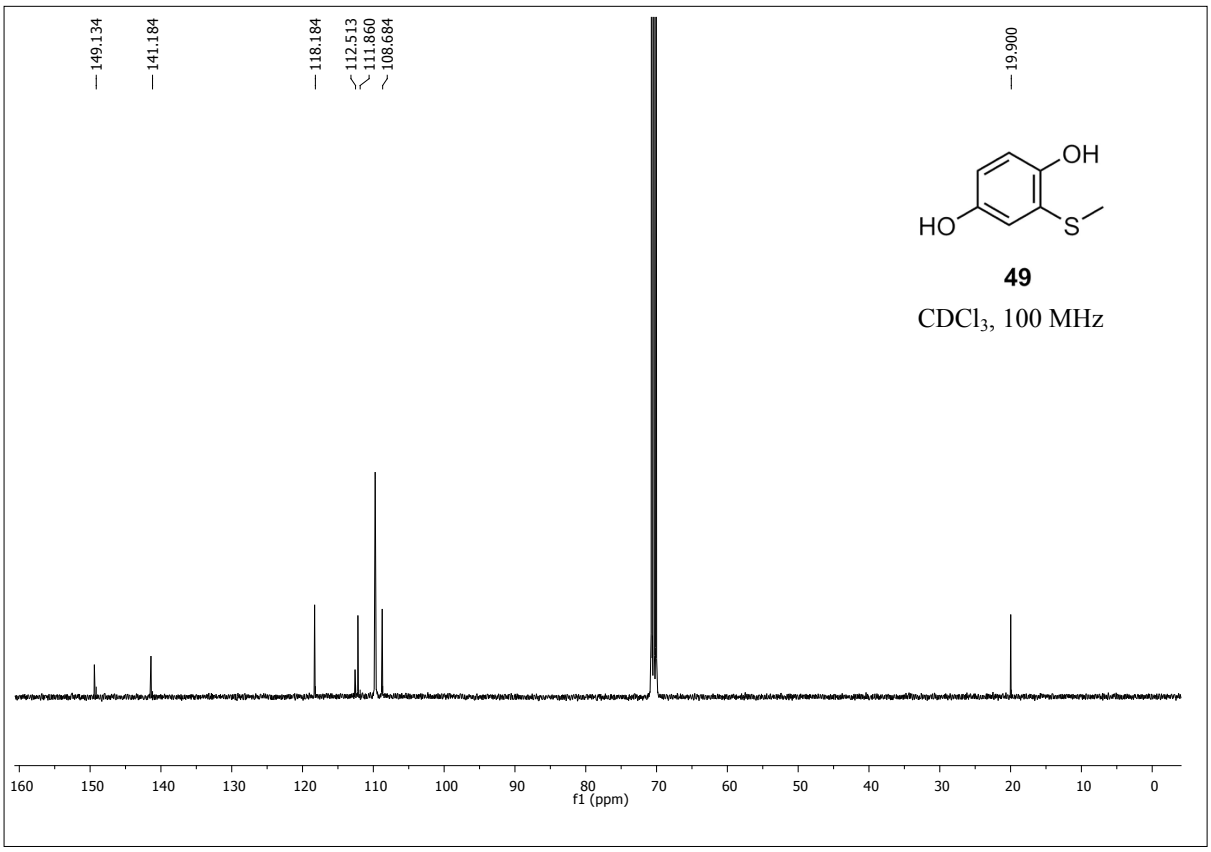


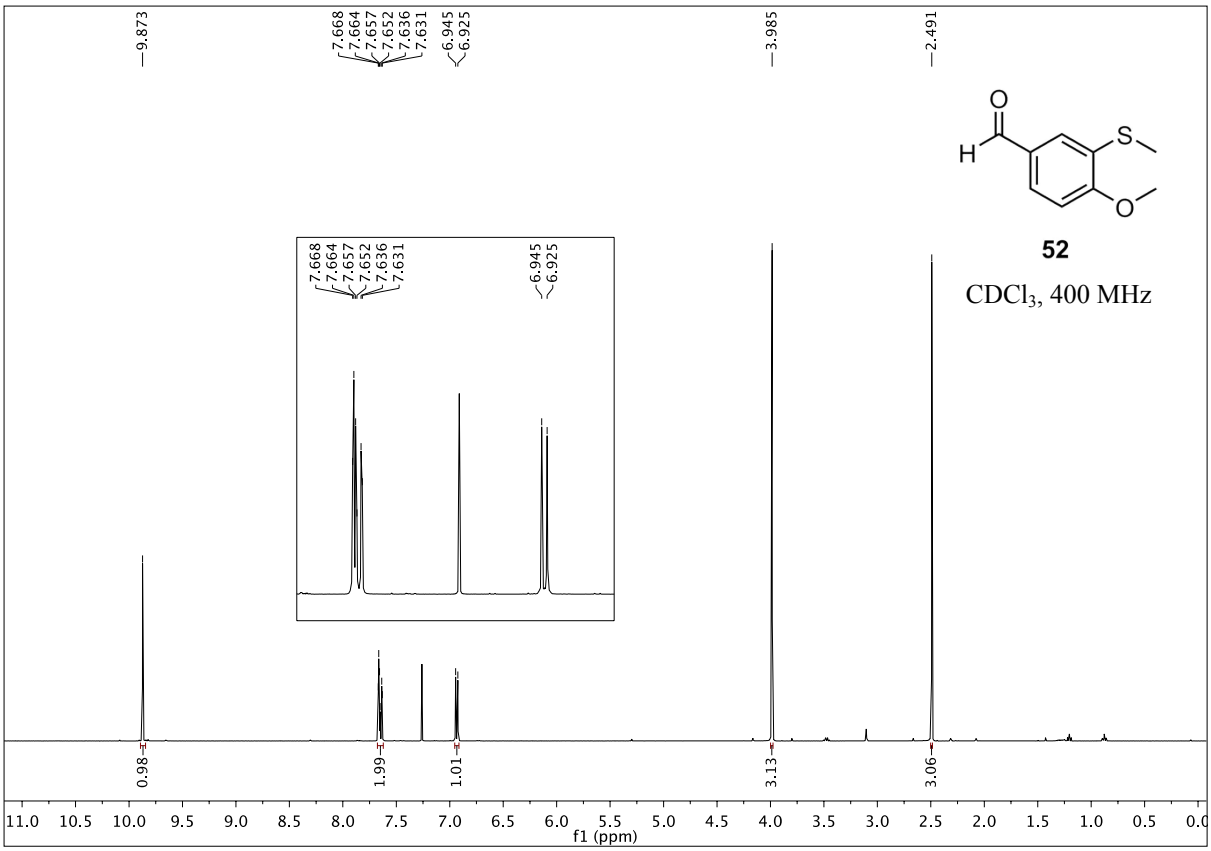
$CDCl_3$, 100 MHz

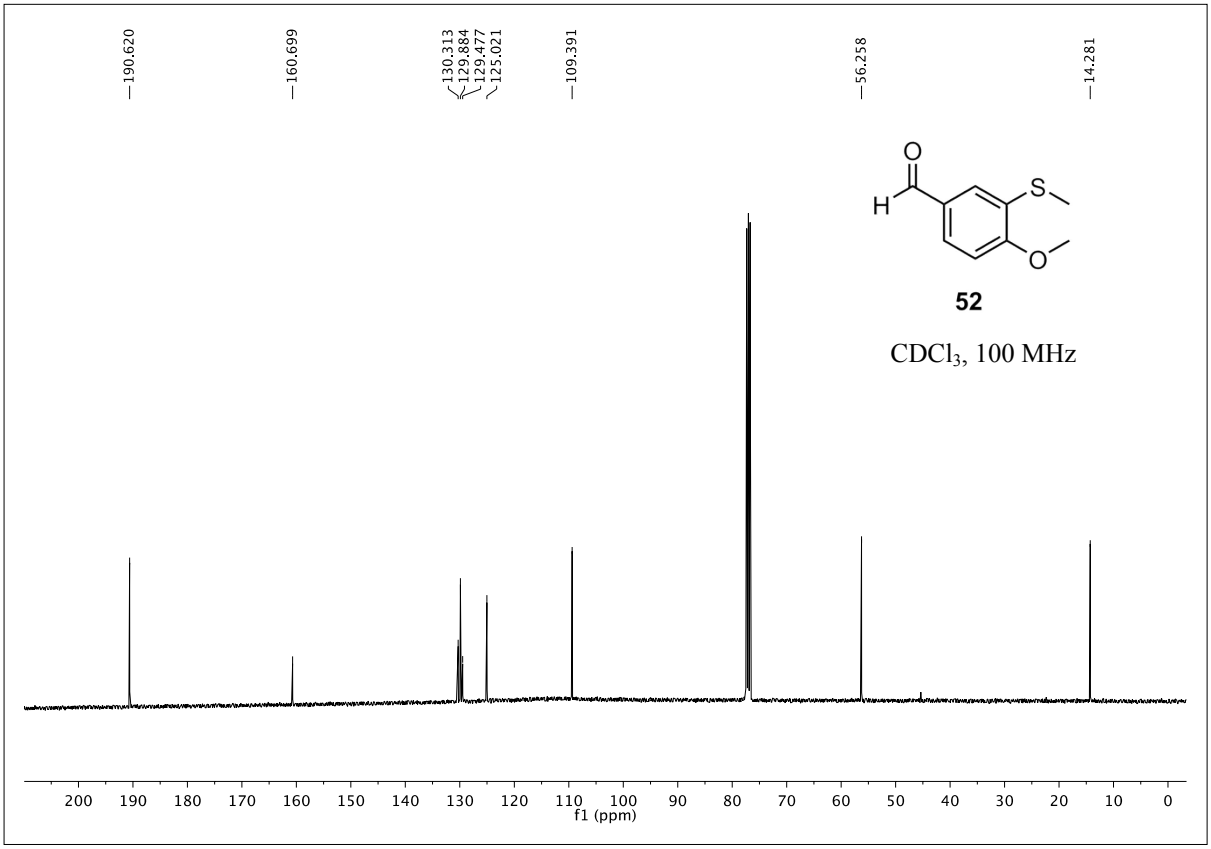

7.498
7.494
7.479
7.475
7.272
7.268
7.252
7.233
7.229
6.995
6.992
6.975
6.972
6.904
6.901
6.885
6.882
6.867
6.863
6.640
2.332
S
OH
48
CDCl3, 400 MHz
0.95
1.32
0.97
0.98
1.00
2.99
f1 (ppm)

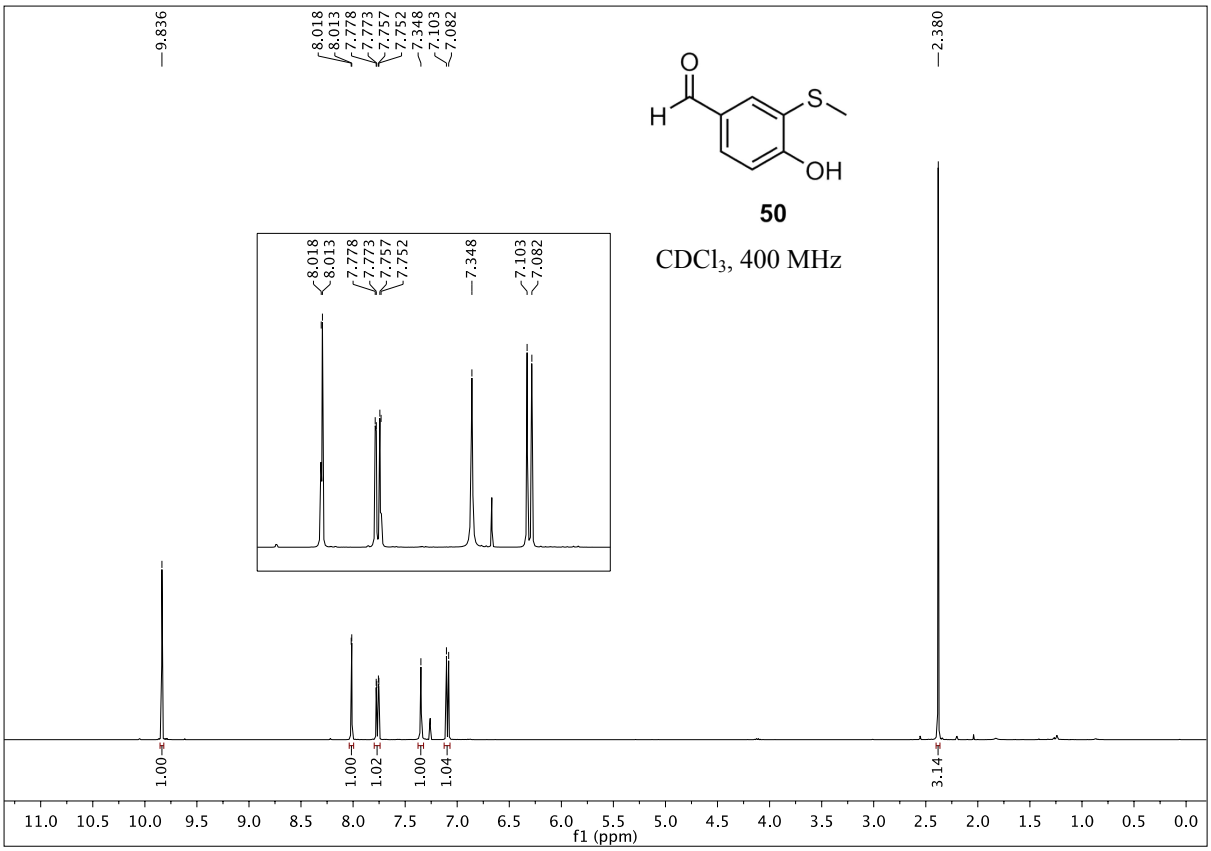

156.259
134.819
130.718
120.904
114.776
19.847
S
OH
48
CDCl3, 100 MHz
f1 (ppm)

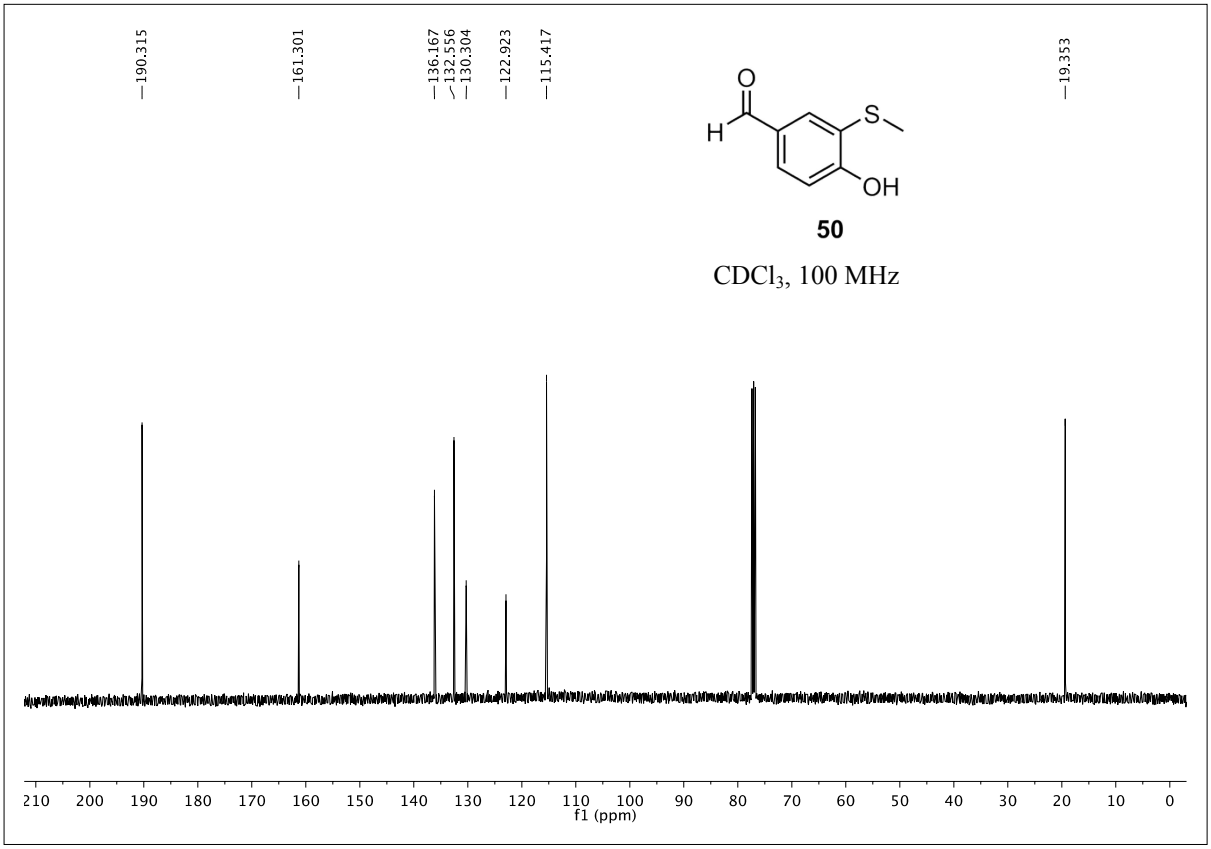

7.284
6.999
6.992
6.890
6.869
6.774
6.767
6.741
6.166
2.381
OH
HO
S
49
CDCl3, 400 MHz
1.00
0.98
1.92
1.00
3.01

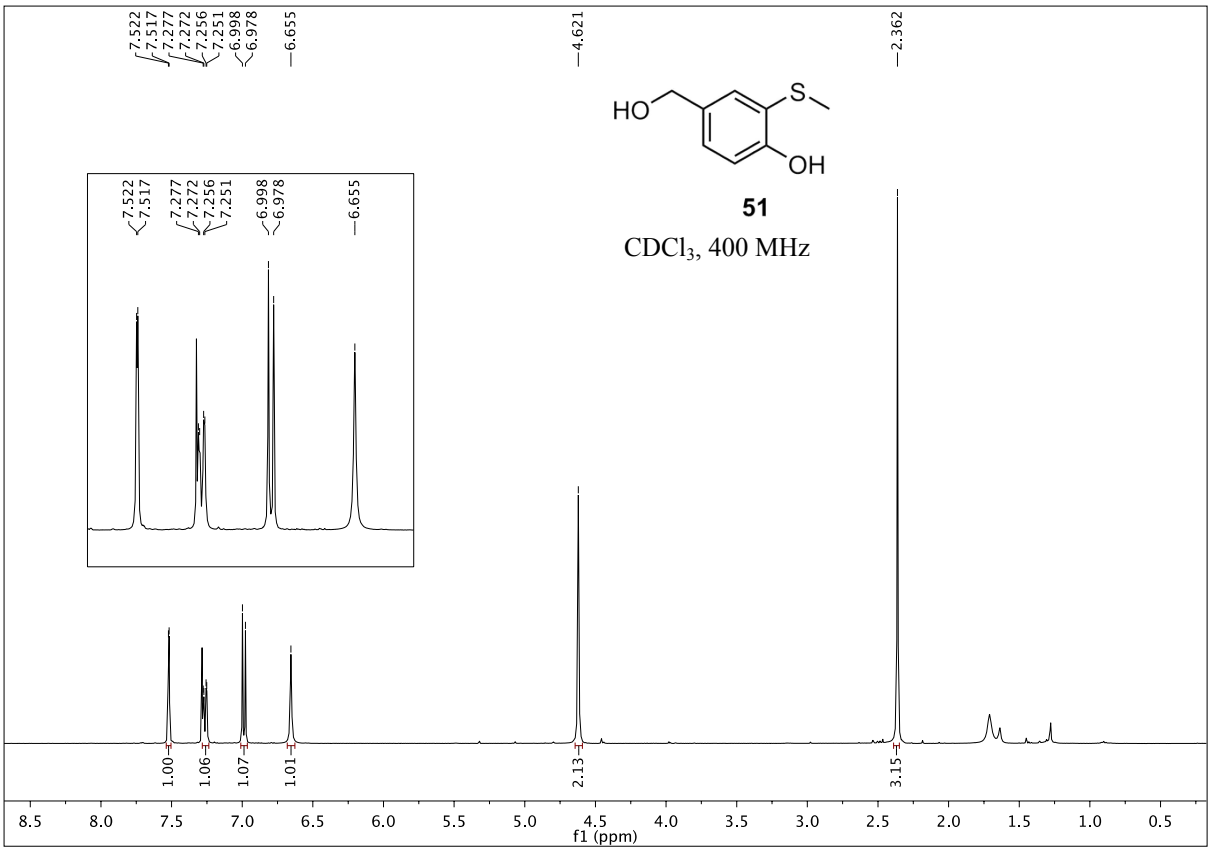

149.134
141.184
118.184
112.513
111.860
108.684
19.900
OH
HO
S
49
CDCl3, 100 MHz
f1 (ppm)


9.873
7.668
7.664
7.657
7.652
7.636
7.631
6.945
6.925
3.985
2.491
O
H
S
O
52
CDCl3, 400 MHz
0.98
1.99
1.01
3.13
3.06
f1 (ppm)


190.620
160.699
130.313
129.884
129.477
125.021
109.391
56.258
14.281
O
H
S
O
52
CDCl3, 100 MHz
f1 (ppm)

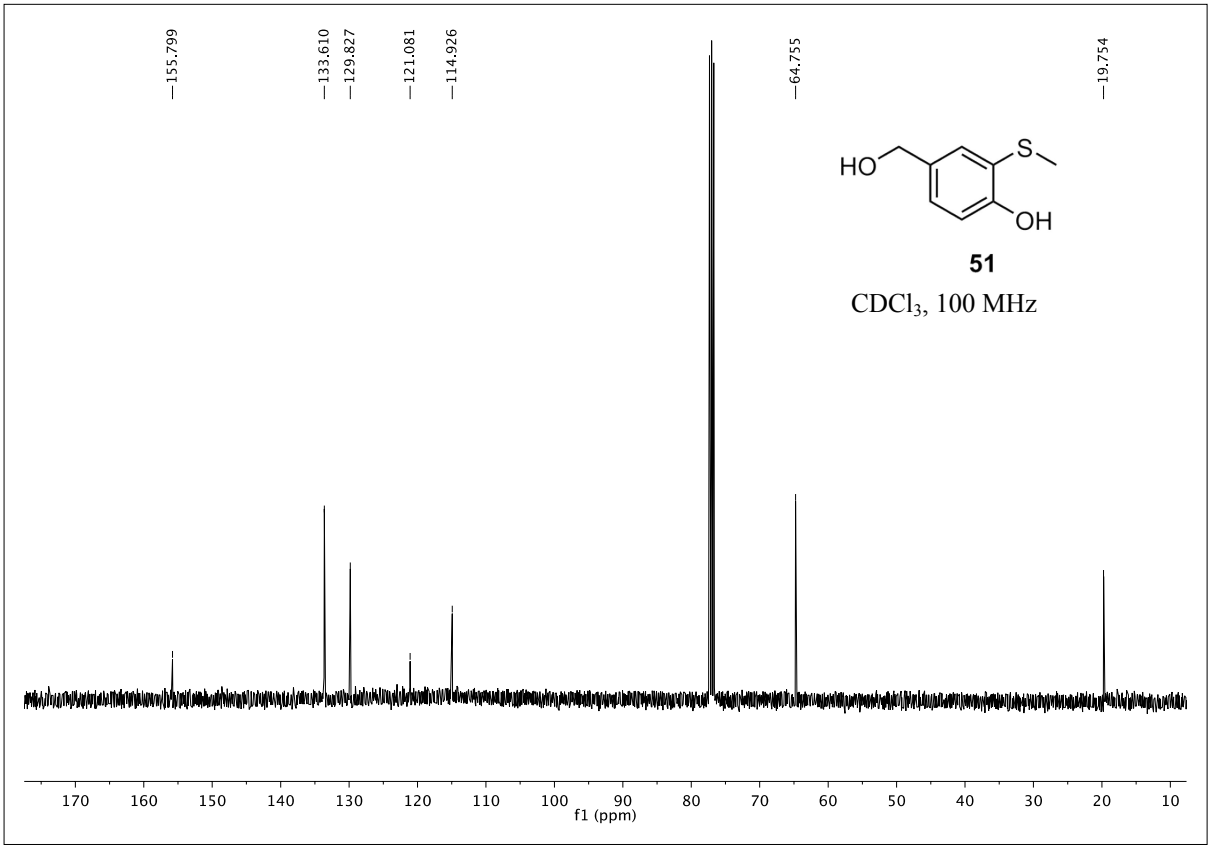

9.836
8.018
8.013
7.778
7.773
7.757
7.752
7.348
7.103
7.082
2.380
O
H
S
OH
50
CDCl3, 400 MHz
1.00
1.00
1.02
1.00
1.04
3.14
f1 (ppm)


190.315
161.301
136.167
132.556
130.304
122.923
115.417
19.353
O
H
S
OH
50
CDCl3, 100 MHz
f1 (ppm)



51

$CDCl_3$, 400 MHz



51

$CDCl_3$, 100 MHz

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