Iodine catalyzed cross-dehydrogenative C–S coupling by C(sp^2)–H bond activation: Direct access to aryl sulfides from aryl thiols

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SUPPLEMENTARY INFORMATION

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General Information:

Unless otherwise noted, chemicals were purchased from commercial suppliers at the highest purity grade available and were used without further purification. Dithioacetal derivative **2g** was synthesized according to literature procedure.[1] Thin layer chromatography was performed on Merck pre-coated 0.25 mm silica gel plates (60F–254) using UV light as visualizing agent and/or iodine as developing agent. All the final products were purified by column chromatography using silica gel (100–200 mesh).

Melting points were recorded on Opti Melt Automated Melting Point System and are uncorrected. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra were recorded on a Bruker spectrometer. Chemical shifts (δ) were reported as parts per million (ppm) in δ scale downfield from TMS. Spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.26 ppm), DMSO-d_6 (δ 2.50 ppm, the middle peak) or with tetramethylsilane (TMS, δ 0.00 ppm) as the internal standard. ^{13}C NMR spectra were referenced to $CDCl_3$ (δ 77.0 ppm, the middle peak) and DMSO (δ 39.5 ppm, the middle peak). Coupling constants were expressed in Hz. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, dt = doublet of triplet, m = multiplet, br = broad. High-resolution mass spectra (HRMS) were obtained on a Brüker micrOTOF™-Q II mass spectrometer (ESI-MS).

General procedure for the synthesis of aryl sulfides:

To a mixture of aryl thiol **1** (0.75/0.5 mmol) and electron-rich species **2** (0.5 mmol) was added DMSO (1.5 mmol, 0.1 mL) followed by iodine (10 mol%, 0.05 mmol, 0.013 g). Then the reaction mixture was heated on a pre-heated oil bath at 80 ^{o}C for 3-5 h under solvent-free conditions. The reaction was monitored by TLC. After completion of the reaction, the reaction mixture was diluted with CH_2Cl_2/ethyl acetate, and quenched with saturated sodium thiosulphate solution and extracted twice with CH_2Cl_2/ethyl acetate (2 X 15 mL). The organic layer was washed with water and dried over anhyd. sodium sulphate. The solvent was evaporated *in vacuo*, and the residue was subjected to column chromatography using ethyl acetate in hexanes as eluent to afford pure aryl sulfide derivative **3**.

Table-S1: Iodine catalyzed cross-dehydrogenative coupling of aryl thiols **1** and electron-rich species **2**.

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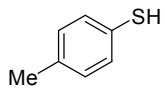
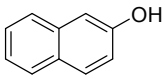
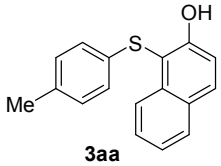
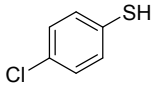
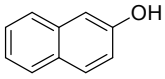
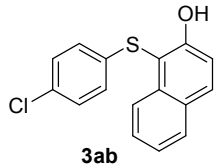
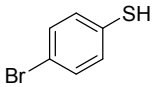
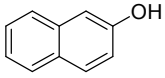
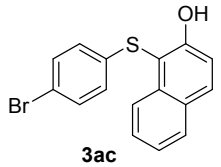
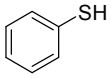
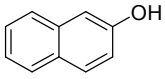
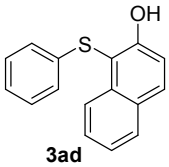
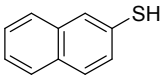
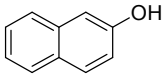
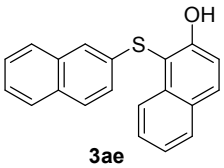
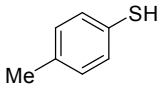
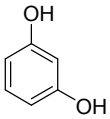
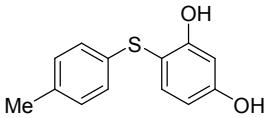
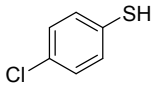
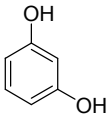
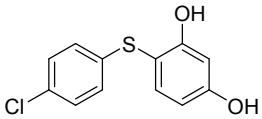
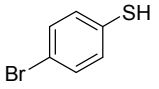
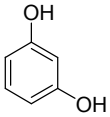
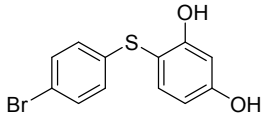
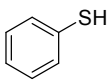
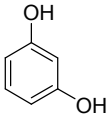
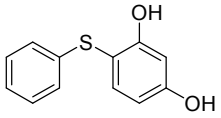
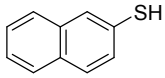
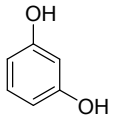
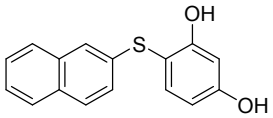
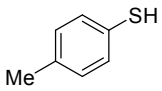
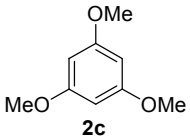
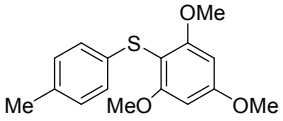
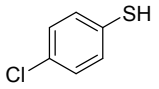
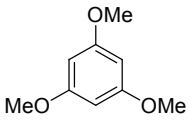
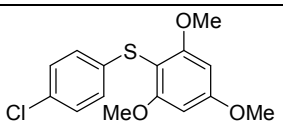
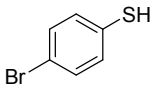
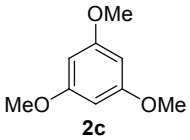
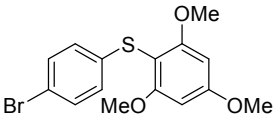
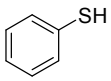
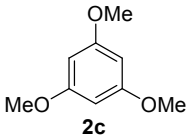
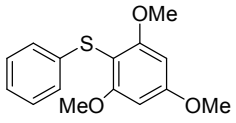
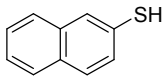
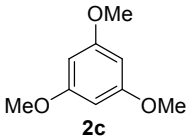
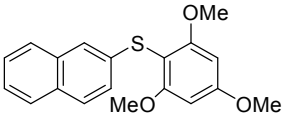
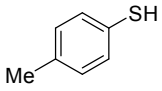
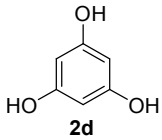
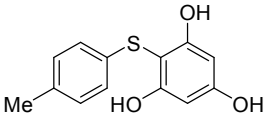
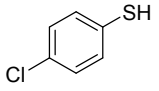
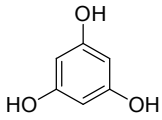
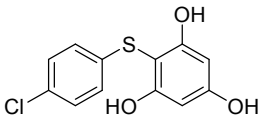
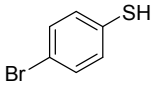
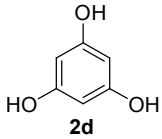
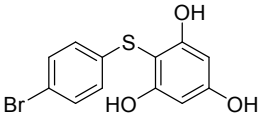
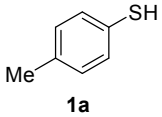
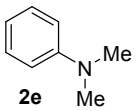
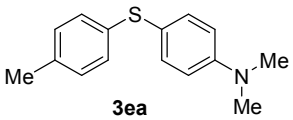
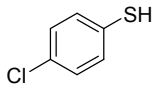
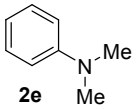
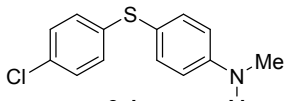
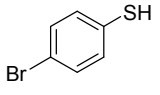
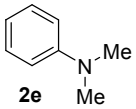
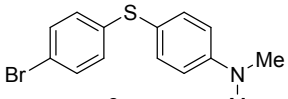
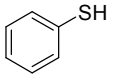
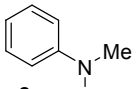
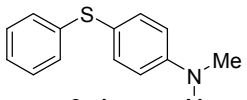
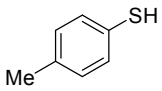
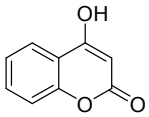
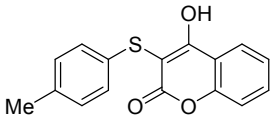
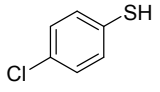
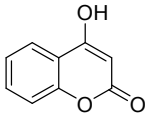
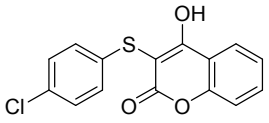
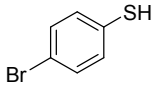
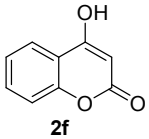
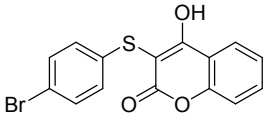
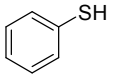
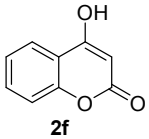
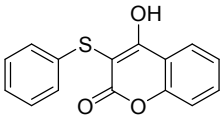
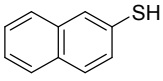
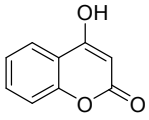
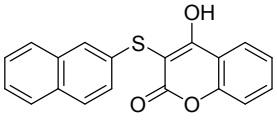
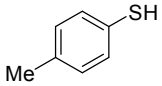
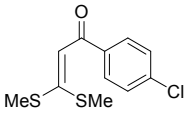
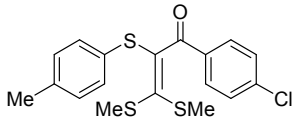
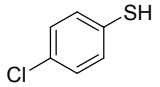
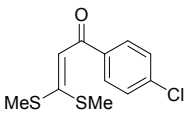
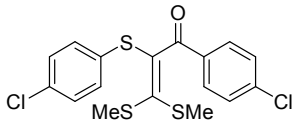
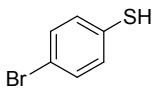
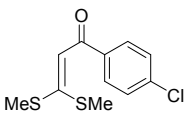
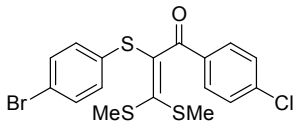
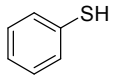
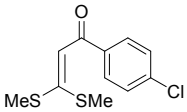
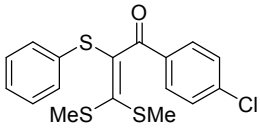
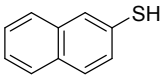
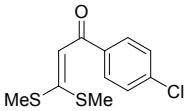
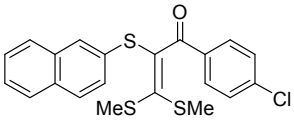
1	 **1a**	 **2a**	 **3aa**	3 h	99
2	 **1b**	 **2a**	 **3ab**	3 h	98
3	 **1c**	 **2a**	 **3ac**	3 h	91
4	 **1d**	 **2a**	 **3ad**	3 h	95
5	 **1e**	 **2a**	 **3ae**	3 h	85
6	 **1a**	 **2b**	 **3ba**	3 h	91
7	 **1b**	 **2b**	 **3bb**	3 h	92
8	 **1c**	 **2b**	 **3bc**	3 h	86
9	 **1d**	 **2b**	 **3bd**	3 h	89

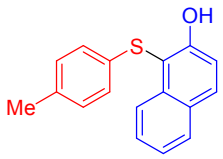
10	 **1e**	 **2b**	 **3be**	3 h	82
11	 **1a**	 **2c**	 **3ca**	3 h	92
12	 **1b**	 **2c**	 **3cb**	3 h	95
13	 **1c**	 **2c**	 **3cc**	3 h	90
14	 **1d**	 **2c**	 **3cd**	3 h	91
15	 **1e**	 **2c**	 **3ce**	3 h	94
16	 **1a**	 **2d**	 **3da**	3 h	93
17	 **1b**	 **2d**	 **3db**	3 h	84
18	 **1c**	 **2d**	 **3dc**	3 h	78
19	 **1a**	 **2e**	 **3ea**	3 h	90

20	 **1b**	 **2e**	 **3eb**	3 h	84
21	 **1c**	 **2e**	 **3ec**	3 h	76
22	 **1d**	 **2e**	 **3ed**	3 h	72
23	 **1a**	 **2f**	 **3fa**	5 h	96
24	 **1b**	 **2f**	 **3fb**	5 h	100
25	 **1c**	 **2f**	 **3fc**	5 h	90
26	 **1d**	 **2f**	 **3fd**	5 h	100
27	 **1e**	 **2f**	 **3fe**	5 h	88
28	 **1a**	 **2g**	 **3ga**	3 h	100
29	 **1b**	 **2g**	 **3gb**	3 h	100
30	 **1c**	 **2g**	 **3gc**	3 h	94

31	 **1d**	 **2g**	 **3gd**	3 h	100
32	 **1e**	 **2g**	 **3ge**	3 h	98

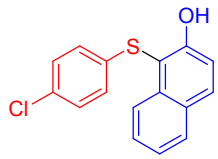
Characterization Data:

1-(*p*-Tolylthio)naphthalen-2-ol (3aa):



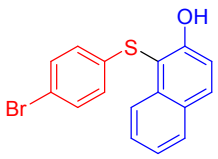
Yield: 0.130 g (99%) as yellow solid; Mp: 78–79 °C (Lit:[2] 77–79 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.31 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 9.0 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.54 (ddd, *J* = 1.0, 7.0, 8.0 Hz, 1H), 7.43–7.38 (m, 2H), 7.30 (s, 1H), 7.02 (s, 4H), 2.28 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.8 (C), 135.8 (C), 135.4 (C), 132.6 (*C*H), 131.7 (C), 129.9 (*C*H), 129.4 (C), 128.5 (*C*H), 127.8 (*C*H), 126.6 (*C*H), 124.7 (*C*H), 123.7 (*C*H), 116.8 (*C*H), 108.7 (C), 20.8 (CH_3) ppm; HRMS (ESI+): *m/z* calcd for $C_{17}H_{14}SONa$ $[M + Na]^+$: 289.0658, found 289.0657.

1-(4-Chlorophenylthio)naphthalen-2-ol (3ab):



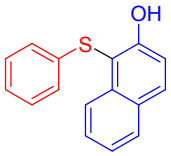
Yield: 0.139 g (98%) as brown solid; Mp: 84–85 °C (Lit:[2] 85–87 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.20 (d, *J* = 8.5 Hz, 1H), 7.93 (d, *J* = 9.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.55–7.51 (m, 1H), 7.42–7.38 (m, 1H), 7.37 (d, *J* = 9.0 Hz, 1H), 7.15 (s, 1H), 7.14 (d, *J* = 9.0 Hz, 2H), 6.97 (d, *J* = 8.5 Hz, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.0 (C), 135.1 (C), 133.9 (C), 133.1 (*C*H), 131.8 (C), 129.5 (C), 129.2 (*C*H), 128.6 (*C*H), 128.1 (*C*H), 127.6 (*C*H), 124.4 (*C*H), 124.0 (*C*H), 116.9 (*C*H), 107.6 (C) ppm; HRMS (ESI+): *m/z* calcd for $C_{16}H_{11}ClSONa$ $[M + Na]^+$: 309.0111, found 309.0111.

1-(4-Bromophenylthio)naphthalen-2-ol (3ac):



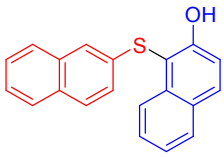
Yield: 0.150 g (91%) as brown solid; Mp: 104–105 °C (Lit:[2] 103–105 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.5 Hz, 1H), 7.80 (d, *J* = 9.0 Hz, 1H), 7.71 (d, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 9.0 Hz, 1H), 7.16 (d, *J* = 8.5 Hz, 2H), 7.00 (s, 1H), 6.77 (d, *J* = 8.5 Hz, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.0 (C), 135.1 (C), 134.6 (C), 133.1 (*C*H), 132.1 (*C*H), 129.5 (C), 128.6 (*C*H), 128.1 (*C*H), 127.8 (*C*H), 124.4 (*C*H), 124.0 (*C*H), 119.6 (C), 116.9 (*C*H), 107.4 (C) ppm; HRMS (ESI+): *m/z* calcd for $C_{16}H_{11}BrSONa$ $[M + Na]^+$: 352.9606, found 352.9596.

1-(Phenylthio)naphthalen-2-ol (3ad):



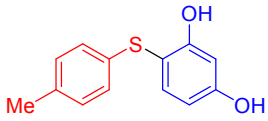
Yield: 0.119 g (95%) as white solid; Mp: 66–67 °C (Lit:[2] 65–67 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.32 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 9.0 Hz, 1H), 7.87 (d, *J* = 8.5 Hz, 1H), 7.58–7.53 (m, 1H), 7.46–7.41 (m, 2H), 7.29 (br s, 1H), 7.25–7.20 (m, 2H), 7.16 (d, *J* = 6.5 Hz, 1H), 7.11 (d, *J* = 7.5 Hz, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.9 (C), 135.4 (C), 135.3 (C), 132.7 (*C*H), 129.4 (C), 129.1 (*C*H), 128.5 (*C*H), 127.9 (*C*H), 126.3 (*C*H), 125.8 (*C*H), 124.6 (*C*H), 123.8 (*C*H), 116.8 (*C*H), 108.0 (C) ppm; HRMS (ESI+): *m/z* calcd for $C_{16}H_{12}SONa$ $[M + Na]^+$: 275.0501, found 275.0493.

1-(Naphthalen-2-ylthio)naphthalen-2-ol (3ae):



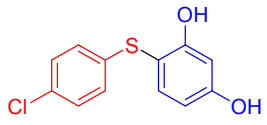
Yield: 0.128 g (85%) as white solid; Mp: 94–95 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.31 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 9.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.76–7.73 (m, 1H), 7.68 (d, *J* = 9.0 Hz, 1H), 7.60–7.57 (m, 1H), 7.51 (ddd, *J* = 1.0, 7.0, 8.0 Hz, 1H), 7.47 (d, *J* = 1.5 Hz, 1H), 7.44–7.40 (m, 4H), 7.28 (s, 1H), 7.22 (dd, *J* = 2.0, 9.0 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.1 (C), 135.4 (C), 133.7 (C), 132.9 (*C*H), 132.7 (C), 131.7 (C), 129.5 (*C*), 128.9 (*C*H), 128.6 (*C*H), 128.0 (*C*H), 127.7 (*C*H), 127.0 (*C*H), 126.6 (*C*H), 125.6 (*C*H), 124.7 (*C*H), 124.6 (*C*H), 124.5 (*C*H), 123.9 (*C*H), 116.9 (*C*H), 108.0 (C) ppm; HRMS (ESI+): *m/z* calcd for $C_{20}H_{14}SONa$ $[M + Na]^+$: 325.0658, found 325.0656.

4-(*p*-Tolylthio)benzene-1,3-diol (3ba):



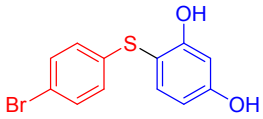
Yield: 0.105 g (91%) as brown solid; Mp: 77–78 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 (d, *J* = 8.5 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.71 (br s, 1H), 6.60 (d, *J* = 2.5 Hz, 1H), 6.48 (dd, *J* = 2.5, 8.5 Hz, 1H), 6.26 (br s, 1H), 2.29 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.1 (C), 158.2 (C), 138.0 (*C*H), 135.9 (C), 132.9 (C), 129.9 (*C*H), 126.6 (*C*H), 109.2 (*C*H), 108.0 (C), 102.4 (*C*H), 20.8 (CH_3) ppm; HRMS (ESI–): *m/z* calcd for $C_{13}H_{11}SO_2$ $[M - H]^-$: 231.0474, found 231.0482.

4-(4-Chlorophenylthio)benzene-1,3-diol (3bb):



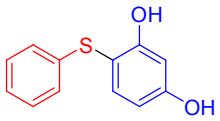
Yield: 0.115 g (92%) as white solid; Mp: 99–100 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 9.0 Hz, 2H), 6.96 (d, *J* = 8.5 Hz, 2H), 6.61 (br s, 1H), 6.59 (d, *J* = 2.5 Hz, 1H), 6.49 (dd, *J* = 2.5, 8.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.4 (C), 158.2 (C), 138.2 (*C*H), 135.2 (C), 131.8 (C), 129.2 (*C*H), 127.4 (*C*H), 109.5 (*C*H), 106.8 (C), 102.6 (*C*H) ppm; HRMS (ESI–): *m/z* calcd for $C_{12}H_8ClSO_2$ $[M - H]^-$: 250.9928, found 250.9942.

4-(4-Bromophenylthio)benzene-1,3-diol (3bc):



Yield: 0.128 g (86%) as brown solid; Mp: 116–117 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.5 Hz, 1H), 7.32 (d, *J* = 8.5 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 6.59 (br s, 1H), 6.58 (d, *J* = 2.5 Hz, 1H), 6.48 (dd, *J* = 2.5, 8.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.4 (C), 158.2 (C), 138.2 (*C*H), 135.9 (C), 132.0 (*C*H), 127.7 (*C*H), 119.6 (C), 109.5 (*C*H), 106.6 (C), 102.6 (*C*H) ppm; HRMS (ESI–): *m/z* calcd for $C_{12}H_8BrSO_2$ $[M - H]^-$: 294.9423, found 294.9433.

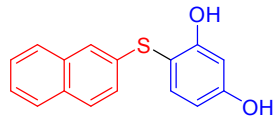
4-(phenylthio)benzene-1,3-diol (3bd):



Yield: 0.086 g (89%) as brown solid; Mp: 111–112 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.23 (d, *J* = 8.5 Hz, 1H), 7.07 (t, *J* = 7.5Hz, 2H), 6.95–6.70 (m, 1H), 6.91 (dd, *J* = 1.0, 8.5 Hz, 2H), 6.47 (d, *J* = 2.5 Hz, 1H), 6.34 (dd, *J* = 2.5, 8.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.2 (C), 158.1 (C), 138.2 (*C*H), 136.5 (C), 129.0 (*C*H), 126.1 (*C*H), 125.8 (*C*H), 109.4 (*C*H), 107.1 (C), 102.4 (*C*H) ppm; HRMS (ESI–): *m/z* calcd for $C_{12}H_9SO_2$ $[M - H]^-$: 217.0318, found 217.0324.

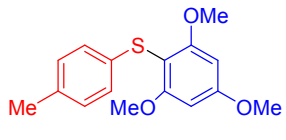
4-(Naphthalen-2-ylthio)benzene-1,3-diol (3be):

Yield: 0.110 g (82%) as white solid; Mp: 95–96 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.82 (br s, 2H), 7.82–7.75 (m, 2H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.48 (s, 1H), 7.44–7.36 (m, 2H), 7.30 (d, *J* = 8.5 Hz, 1H), 7.22 (d, *J* = 8.5 Hz, 1H), 6.58 (s, 1H), 6.41 (dd, *J* = 1.5, 8.0 Hz, 1H) ppm; ^{13}C NMR



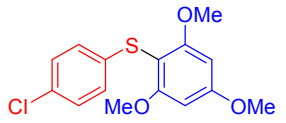
(125 MHz, DMSO-d_6): δ 160.4 (C), 159.8 (C), 137.9 (*C*H), 136.8 (C), 133.4 (C), 130.9 (C), 128.3 (*C*H), 127.7 (*C*H), 126.7 (*C*H), 126.7 (*C*H), 125.2 (*C*H), 125.0 (*C*H), 123.3 (*C*H), 108.2 (*C*H), 105.7 (C), 103.4 (*C*H) ppm; HRMS (ESI–): *m/z* calcd for $C_{16}H_{11}SO_2$ [M – H]$^-$: 267.0474, found 267.0482.

_p_-Tolyl(2,4,6-trimethoxyphenyl)sulfane (3ca):



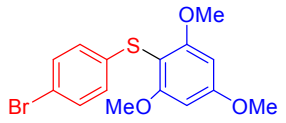
Yield: 0.132 g (92%) as white solid; Mp: 111–112 °C (Lit:[3] 112–113 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.96 (d, *J* = 2.0 Hz, 4H), 6.21 (s, 2H), 3.85 (s, 3H), 3.79 (s, 6H), 2.24 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.6 (C), 162.3 (C), 134.9 (C), 133.9 (C), 129.1 (*C*H), 125.8 (*C*H), 99.1 (C), 91.0 (*C*H), 56.1 (*C*H$_3$), 55.2 (*C*H$_3$), 20.7 (*C*H$_3$) ppm; HRMS (ESI+): *m/z* calcd for $C_{16}H_{18}SO_3Na$ [M + Na]$^+$: 313.0869, found 313.0869.

(4-Chlorophenyl)(2,4,6-trimethoxyphenyl)sulfane (3cb):



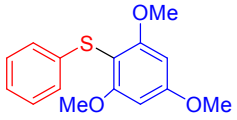
Yield: 0.146 g (95%) as white solid; Mp: 92–93 °C (Lit:[3] 93–94 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.09 (d, *J* = 8.5 Hz, 2H), 6.93 (d, *J* = 8.5 Hz, 2H), 6.19 (s, 2H), 3.84 (s, 3H), 3.78 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.0 (C), 162.3 (C), 137.3 (C), 129.9 (C), 128.4 (*C*H), 126.8 (*C*H), 98.1 (C), 91.1 (*C*H), 56.1 (*C*H$_3$), 55.3 (*C*H$_3$) ppm; HRMS (ESI+): *m/z* calcd for $C_{15}H_{15}ClSO_3Na$ [M + Na]$^+$: 333.0323, found 333.0317.

(4-Bromophenyl)(2,4,6-trimethoxyphenyl)sulfane (3cc):



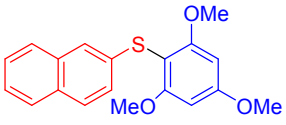
Yield: 0.158 g (90%) as white solid; Mp: 113–114 °C (Lit:[3] 114–115 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 6.20 (s, 2H), 3.85 (s, 3H), 3.78 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.0 (C), 162.3 (C), 138.1 (C), 131.3 (*C*H), 127.1 (*C*H), 117.7 (C), 97.9 (C), 91.1 (*C*H), 56.2 (*C*H$_3$), 55.3 (*C*H$_3$) ppm; HRMS (ESI+): *m/z* calcd for $C_{15}H_{15}BrSO_3Na$ [M + Na]$^+$: 376.9817, found 376.9814.

Phenyl(2,4,6-trimethoxyphenyl)sulfane (3cd):



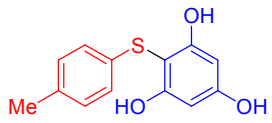
Yield: 0.125 g (91%) as white solid; Mp: 92–93 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.16–7.13 (m, 2H), 7.02 (d, *J* = 7.5 Hz, 3H), 6.21 (s, 2H), 3.84 (s, 3H), 3.78 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.8 (C), 162.3 (C), 138.6 (C), 128.3 (*C*H), 125.4 (*C*H), 124.2 (*C*H), 98.4 (C), 91.0 (*C*H), 56.1 (CH_3), 55.2 (CH_3) ppm; HRMS (ESI+): *m/z* calcd for $C_{15}H_{16}SO_3Na$ $[M + Na]^+$: 299.0712, found 299.0712.

Naphthalen-2-yl(2,4,6-trimethoxyphenyl)sulfane (3ce):



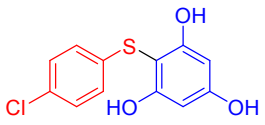
Yield: 0.152 g (94%) as white solid; Mp: 87–88 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.5 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.42–7.37 (m, 2H), 7.34 (ddd, *J* = 1.5, 7.0, 8.0 Hz, 1H), 7.24 (dd, *J* = 2.0, 9.0 Hz, 1H), 6.26 (s, 2H), 3.88 (s, 3H), 3.80 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.9 (C), 162.5 (C), 136.3 (C), 133.7 (C), 131.1 (C), 127.8 (*C*H), 127.5 (*C*H), 126.7 (*C*H), 126.0 (*C*H), 124.7 (*C*H), 124.6 (*C*H), 122.8 (*C*H), 98.5 (C), 91.2 (*C*H), 56.2 (CH_3), 55.3 (CH_3) ppm; HRMS (ESI+): *m/z* calcd for $C_{19}H_{18}SO_3Na$ $[M + Na]^+$: 349.0869, found 349.0878.

2-(*p*-Tolylthio)benzene-1,3,5-triol (3da):



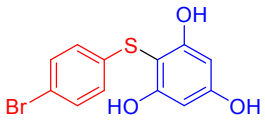
Yield: 0.115 g (93%) as brown solid; Mp: 125–126 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.50 (br s, 1H), 9.30 (br s, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 5.97 (s, 2H), 2.20 (s, 3H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ 160.8 (C), 160.4 (C), 135.8 (C), 133.4 (C), 129.2 (*C*H), 125.4 (*C*H), 94.7 (*C*H), 93.3 (C), 20.5 (CH_3) ppm; HRMS (ESI–): *m/z* calcd for $C_{13}H_{11}SO_3$ $[M - H]^-$: 247.0423, found 247.0441.

2-(4-Chlorophenylthio)benzene-1,3,5-triol (3db):



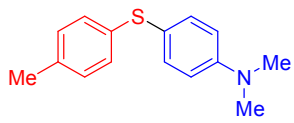
Yield: 0.112 g (84%) as brown solid; Mp: 110–111 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.53 (br s, 2H), 7.24 (d, J = 8.5 Hz, 2H), 6.93 (d, J = 8.5 Hz, 2H), 5.97 (s, 2H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ 161.1 (C), 160.9 (C), 138.9 (C), 129.0 (C), 128.8 (*C*H), 126.9 (*C*H), 95.1 (*C*H), 92.8 (C) ppm; HRMS (ESI–): *m/z* calcd for $C_{12}H_8ClSO_3$ [M – H]$^-$: 266.9877, found 266.9888.

2-(4-Bromophenylthio)benzene-1,3,5-triol (3dc):



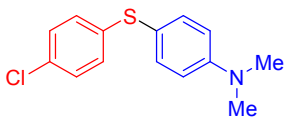
Yield: 0.122 g (78%) as brown solid; Mp: 127–128 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.56 (br s, 1H), 9.49 (br s, 2H), 7.36 (d, J = 8.5 Hz, 2H), 6.86 (d, J = 8.5 Hz, 2H), 5.95 (s, 2H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ 161.0 (C), 160.8 (C), 139.5 (C), 131.5 (*C*H), 127.1 (*C*H), 116.8 (C), 95.0 (*C*H), 92.5 (C) ppm; HRMS (ESI–): *m/z* calcd for $C_{12}H_8BrSO_3$ [M – H]$^-$: 310.9372, found 376.9378.

***N*,*N*-Dimethyl-4-(*p*-tolylthio)benzenamine (3ea):**



Yield: 0.112 g (90%) as yellow solid; Mp: 51–52 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (d, J = 9.0 Hz, 2H), 7.13 (d, J = 8.5 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 6.74 (d, J = 9.0 Hz, 2H), 3.01 (s, 6H), 2.33 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.3 (C), 136.2 (C), 135.4 (*C*H), 135.0 (C), 129.5 (*C*H), 127.7 (*C*H), 118.5 (C), 112.9 (*C*H), 40.2 (*C*H$_3$), 20.8 (*C*H$_3$) ppm; HRMS (ESI+): *m/z* calcd for $C_{15}H_{17}NSNa$ [M + Na]$^+$: 266.0974, found 266.0972.

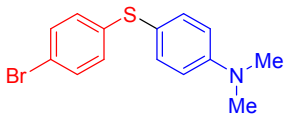
4-(4-Chlorophenylthio)-*N*,*N*-dimethylbenzenamine (3eb):



Yield: 0.110 g (84%) as yellow solid; Mp: 120–121 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (d, J = 8.5 Hz, 2H), 7.17 (d, J = 8.5 Hz, 2H), 7.03 (d, J = 9.0 Hz, 2H), 6.72 (d, J = 8.5 Hz, 2H), 3.00 (s, 6H) ppm; ^{13}C

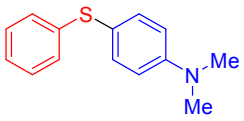
NMR (125 MHz, $CDCl_3$): δ 150.7 (C), 139.0 (C), 136.2 (*C*H), 130.6 (C), 128.7 (*C*H), 128.0 (*C*H), 116.7 (C), 113.0 (*C*H), 40.2 (CH_3) ppm; HRMS (ESI+): *m/z* calcd for $C_{14}H_{15}ClNS$ $[M + H]^+$: 264.0608, found 264.0604.

4-(4-Bromophenylthio)-*N*,*N*-dimethylbenzenamine (3ec):



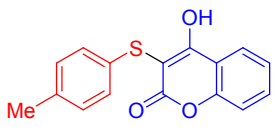
Yield: 0.117 g (76%) as yellow solid; Mp: 127–128 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 (d, *J* = 9.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 8.5 Hz, 2H), 6.72 (d, *J* = 9.0 Hz, 2H), 3.01 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.7 (C), 139.8 (C), 136.2 (*C*H), 131.6 (C), 128.1 (*C*H), 118.4 (*C*H), 116.4 (C), 112.9 (*C*H), 40.2 (CH_3) ppm; HRMS (ESI+): *m/z* calcd for $C_{14}H_{15}BrNS$ $[M + H]^+$: 308.0103, found 308.0100.

***N*,*N*-Dimethyl-4-(phenylthio)benzenamine (3ed):**



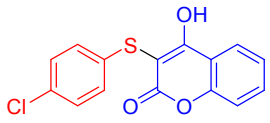
Yield: 0.082 g (72%) as brown solid; Mp: 68–69 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29–7.24 (m, 2H), 7.08–7.03 (m, 2H), 7.02–6.97 (m, 2H), 6.96–6.90 (m, 1H), 6.54 (d, *J* = 8.5 Hz, 2H), 2.80 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.5 (C), 140.2 (C), 136.0 (*C*H), 128.6 (*C*H), 126.7 (*C*H), 124.8 (*C*H), 117.2 (C), 112.8 (*C*H), 40.1 (CH_3) ppm; HRMS (ESI+): *m/z* calcd for $C_{14}H_{16}NS$ $[M + H]^+$: 230.0998, found 230.0996.

4-Hydroxy-3-(*p*-tolylthio)-2*H*-chromen-2-one (3fa):



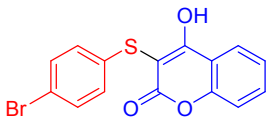
Yield: 0.135 g (96%) as white solid; Mp: 160–161 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.00 (br s, 1H), 7.94 (d, *J* = 7.5 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.41–7.30 (m, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 7.5 Hz, 2H), 2.20 (s, 3H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ 168.1 (C), 160.9 (C), 153.0 (C), 135.2 (C), 133.5 (*C*H), 132.3 (C), 129.7 (*C*H), 127.1 (*C*H), 124.3 (*C*H), 124.2 (*C*H), 116.4 (*C*H), 115.7 (C), 95.3 (C), 20.5 (CH_3) ppm; HRMS (ESI+): *m/z* calcd for $C_{16}H_{12}SO_3Na$ $[M + Na]^+$: 307.0399, found 307.406.

3-(4-Chlorophenylthio)-4-hydroxy-2*H*-chromen-2-one (3fb):



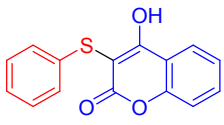
Yield: 0.151 g (100%) as white solid; Mp: 187–188 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.94 (dd, J = 0.5, 8.0 Hz, 1H), 7.68 (t, J = 8.0 Hz, 1H), 7.41–7.35 (m, 2H), 7.31 (d, J = 9.0 Hz, 2H), 7.21 (d, J = 9.0 Hz, 2H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ 168.8 (C), 161.1 (C), 153.2 (C), 135.3 (C), 133.9 (*C*H), 130.3 (C), 129.1 (*C*H), 128.2 (*C*H), 124.5 (*C*H), 124.4 (*C*H), 116.6 (*C*H), 115.9 (C), 94.2 (C) ppm; HRMS (ESI+): *m/z* calcd for $C_{15}H_9ClSO_3Na$ [M + Na]$^+$: 326.9853, found 326.9873.

3-(4-Bromophenylthio)-4-hydroxy-2*H*-chromen-2-one (3fc):



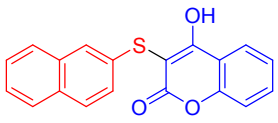
Yield: 0.156 g (90%) as light yellow solid; Mp: 197–198 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.93 (dd, J = 1.5, 8.0 Hz, 1H), 7.66 (ddd, J = 1.5, 7.0, 8.5 Hz, 1H), 7.42 (d, J = 8.5 Hz, 2H), 7.39–7.33 (m, 2H), 7.15 (d, J = 9.0 Hz, 2H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ 168.8 (C), 161.0 (C), 153.2 (C), 135.9 (C), 133.8 (*C*H), 131.9 (*C*H), 128.5 (*C*H), 124.5 (*C*H), 124.4 (*C*H), 118.5 (C), 116.6 (*C*H), 115.8 (C), 94.2 (C) ppm; HRMS (ESI+): *m/z* calcd for $C_{15}H_9BrSO_3Na$ [M + Na]$^+$: 370.9348, found 370.9361.

4-Hydroxy-3-(phenylthio)-2*H*-chromen-2-one (3fd):



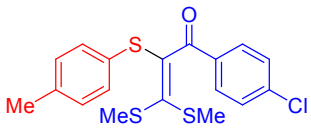
Yield: 0.135 g (100%) as white solid; Mp: 197–198 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.96 (dd, J = 1.0, 8.0 Hz, 1H), 7.74–7.68 (m, 1H), 7.45–7.39 (m, 2H), 7.31–7.25 (m, 2H), 7.19–7.13 (m, 2H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ 168.4 (C), 160.9 (C), 153.0 (C), 135.9 (C), 133.7 (*C*H), 129.1 (*C*H), 126.3 (*C*H), 125.6 (*C*H), 124.4 (*C*H), 124.3 (CH), 116.5 (*C*H), 115.6 (C), 94.5 (C) ppm; HRMS (ESI+): *m/z* calcd for $C_{15}H_{10}SO_3Na$ [M + Na]$^+$: 293.0243, found 293.0231.

4-Hydroxy-3-(naphthalen-2-ylthio)-2*H*-chromen-2-one (3fe):



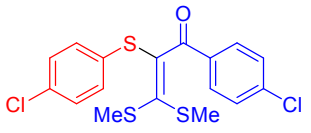
Yield: 0.140 g (88%) as light yellow solid; Mp: 160–161 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.99 (dd, J = 1.0, 7.5 Hz, 1H), 7.84–7.81 (m, 2H), 7.79 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 1.5 Hz, 1H), 7.68 (ddd, J = 1.5, 7.0, 8.5 Hz, 1H), 7.45–7.37 (m, 5H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ 168.6 (C), 161.1 (C), 153.2 (C), 133.7 (*C*H), 133.7 (C), 133.5 (C), 131.2 (C), 128.6 (*C*H), 127.7 (*C*H), 127.0 (*C*H), 126.7 (*C*H), 125.6 (*C*H), 125.0 (*C*H), 124.5 (*C*H), 124.3 (*C*H), 124.0 (*C*H), 116.6 (*C*H), 115.9 (C), 94.5 (C) ppm; HRMS (ESI+): *m/z* calcd for $C_{19}H_{12}SO_3Na$ $[M + Na]^+$: 343.0399, found 343.0392.

1-(4-Chlorophenyl)-3,3-bis(methylthio)-2-(*p*-tolylthio)prop-2-en-1-one (3ga):



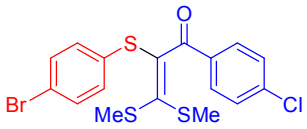
Yield: 0.190 g (100%) as yellow solid; Mp: 81–82 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, J = 8.5 Hz, 2H), 7.32 (d, J = 8.5 Hz, 2H), 7.14 (d, J = 7.5 Hz, 2H), 6.93 (d, J = 7.5 Hz, 2H), 2.47 (s, 3H), 2.22 (s, 3H), 2.15 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 189.6 (C), 139.4 (C), 139.2 (C), 138.8 (C), 134.6 (C), 134.1 (*C*H), 133.6 (C), 130.4 (*C*H), 129.5 (*C*H), 128.6 (*C*H), 126.6 (C), 21.0 (*C*H$_3$), 18.3 (*C*H$_3$), 16.3 (*C*H$_3$) ppm; HRMS (ESI+): *m/z* calcd for $C_{18}H_{17}ClS_3ONa$ $[M + Na]^+$: 403.0022, found 403.0029.

1-(4-Chlorophenyl)-2-(4-chlorophenylthio)-3,3-bis(methylthio)prop-2-en-1-one (3gb):



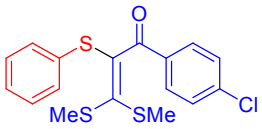
Yield: 0.200 g (100%) as yellow solid; Mp: 67–68 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 (d, J = 8.5 Hz, 2H), 7.35 (d, J = 8.5 Hz, 2H), 7.19 (d, J = 8.5 Hz, 2H), 7.11 (d, J = 8.5 Hz, 2H), 2.47 (s, 3H), 2.18 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 189.4 (C), 139.7 (C), 137.8 (C), 136.4 (C), 134.6 (C), 134.4 (*C*H), 134.3 (C), 130.4 (*C*H), 129.5 (C), 129.0 (*C*H), 128.7 (*C*H), 18.4 (*C*H$_3$), 16.4 (*C*H$_3$) ppm; HRMS (ESI+): *m/z* calcd for $C_{17}H_{14}Cl_2S_3ONa$ $[M + Na]^+$: 422.9476, found 422.9476.

2-(4-Bromophenylthio)-1-(4-chlorophenyl)-3,3-bis(methylthio)prop-2-en-1-one (3gc):



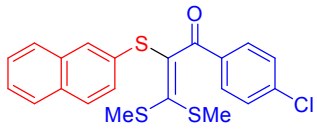
Yield: 0.210 g (94%) as yellow solid; Mp: 74–75 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 (d, J = 8.5 Hz, 2H), 7.29 (d, J = 8.5 Hz, 2H), 7.21 (d, J = 8.5 Hz, 2H), 7.06 (d, J = 8.5 Hz, 2H), 2.41 (s, 3H), 2.12 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 189.4 (C), 139.7 (C), 137.8 (C), 136.0 (C), 134.5 (*C*H), 134.4 (C), 132.0 (*C*H), 130.5 (*C*H), 130.3 (C), 128.8 (*C*H), 122.8 (C), 18.5 (*C*H$_3$), 16.5 (*C*H$_3$) ppm; HRMS (ESI+): *m/z* calcd for $C_{17}H_{14}BrClS_3ONa$ $[M + Na]^+$: 466.8971, found 466.8974.

1-(4-Chlorophenyl)-3,3-bis(methylthio)-2-(phenylthio)prop-2-en-1-one (3gd):



Yield: 0.183 g (100%) as yellow viscous liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (d, J = 8.5 Hz, 2H), 7.24 (d, J = 8.5 Hz, 2H), 7.19 (d, J = 7.0 Hz, 2H), 7.10–7.02 (m, 3H), 2.40 (s, 3H), 2.10 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 189.5 (C), 139.4 (C), 137.8 (C), 135.9 (C), 134.5 (C), 133.5 (*C*H), 130.6 (C), 130.4 (*C*H), 128.7 (*C*H), 128.6 (*C*H), 128.4 (*C*H), 18.4 (*C*H$_3$), 16.4 (*C*H$_3$) ppm; HRMS (ESI+): *m/z* calcd for $C_{17}H_{15}ClS_3ONa$ $[M + Na]^+$: 388.9866, found 388.9869.

1-(4-Chlorophenyl)-3,3-bis(methylthio)-2-(naphthalen-2-ylthio)prop-2-en-1-one (3ge):



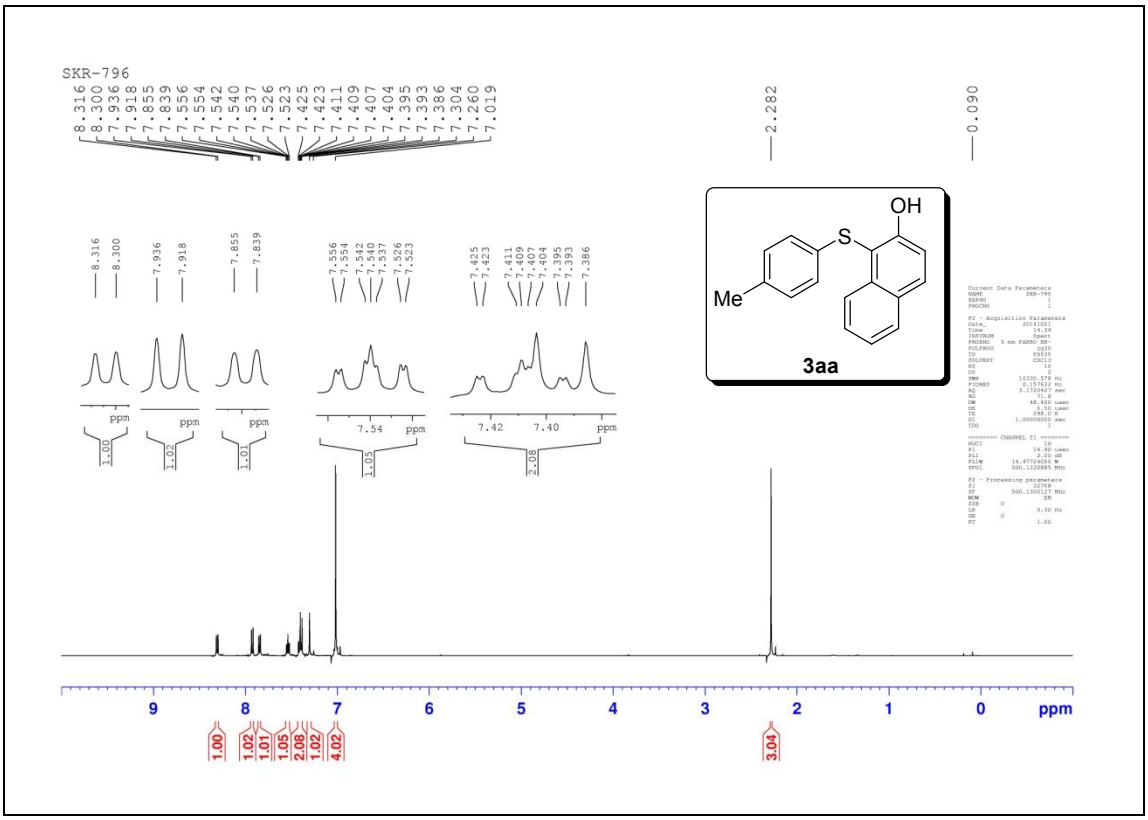
Yield: 0.204 g (98%) as yellow solid; Mp: 100–101 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (s, 1H), 7.72 (d, J = 5.0 Hz, 1H), 7.65 (dd, J = 8.5, 15.0 Hz, 4H), 7.46–7.40 (m, 2H), 7.37 (dd, J = 1.0, 8.0 Hz, 1H), 7.30 (d, J = 8.5 2H), 2.51 (s, 3H), 2.22 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 189.6 (C), 139.4 (C), 137.3 (C), 137.0 (C), 134.5 (C), 133.2 (C), 132.8 (*C*H), 132.6 (C), 130.4 (*C*H), 129.9 (*C*H), 128.6 (*C*H), 128.4 (*C*H), 128.2 (C), 127.5 (*C*H), 126.6 (*C*H), 126.4 (*C*H), 18.5 (*C*H$_3$), 16.4 (*C*H$_3$) ppm; HRMS (ESI+): *m/z* calcd for $C_{21}H_{17}ClS_3ONa$ $[M + Na]^+$: 439.0022, found 439.0022.

References

1. H. S. P. Rao, S. Sivakumar, *J. Org. Chem.* **2006**, *71*, 8715.

2. X. Kang, R. Yan, G. Yu, X. Pang, X. Liu, X. Li, L. Xiang, G. Huang, *J. Org. Chem.* **2014**, *79*, 10605.

3. S. Zhang, P. Qian, M. Zhang, M. Hu, J. Cheng, *J. Org. Chem.* **2010**, *75*, 6732.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7.936
7.918
7.855
7.839
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7.554
7.542
7.540
7.537
7.526
7.523
7.425
7.423
7.411
7.409
7.407
7.404
7.395
7.393
7.386
7.304
7.260
7.019
2.282
0.090
OH
S
Me
3aa
ppm
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7.40
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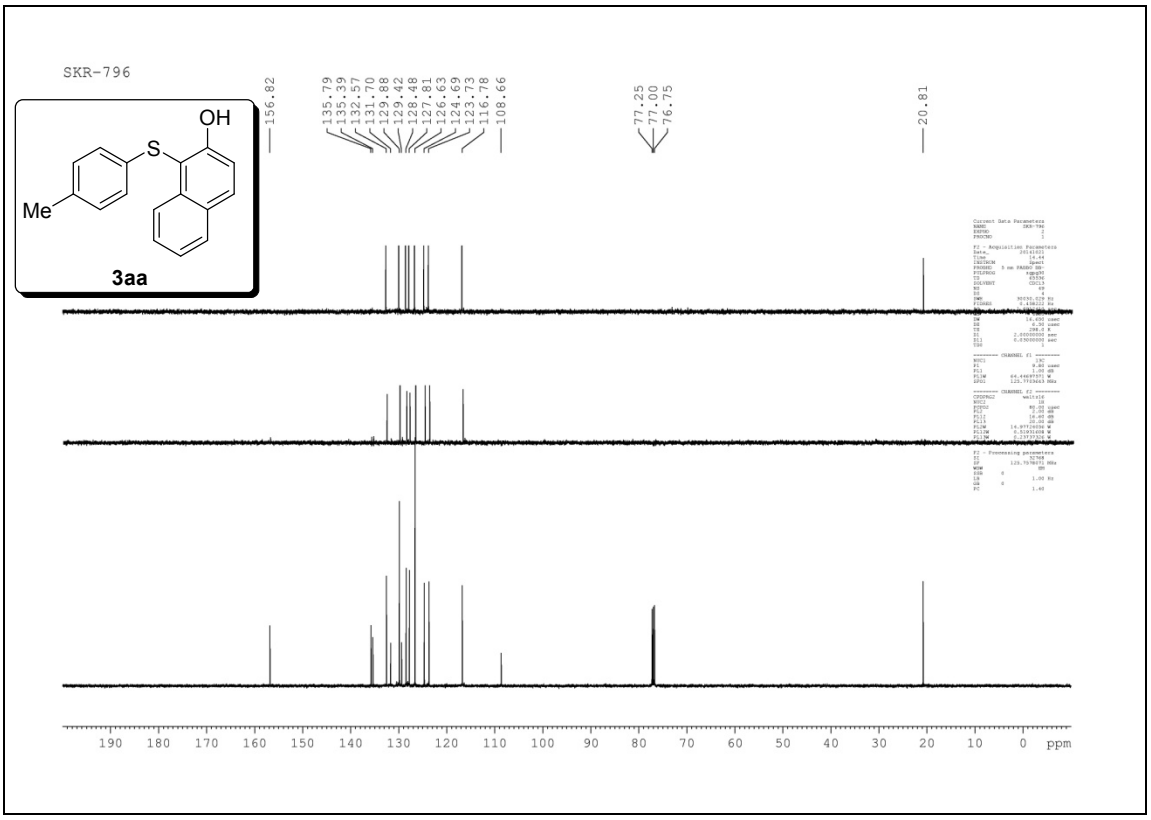
1.02
1.01
1.05
2.08
1.02
4.02
3.04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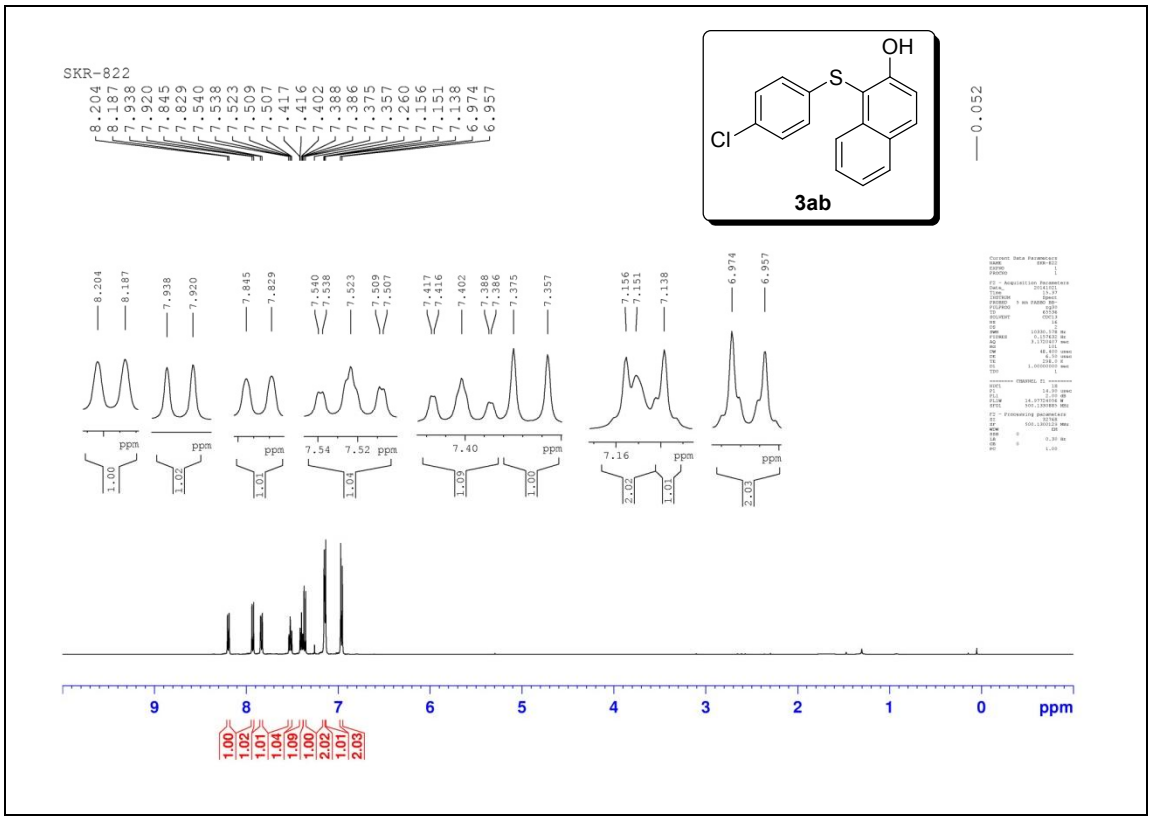
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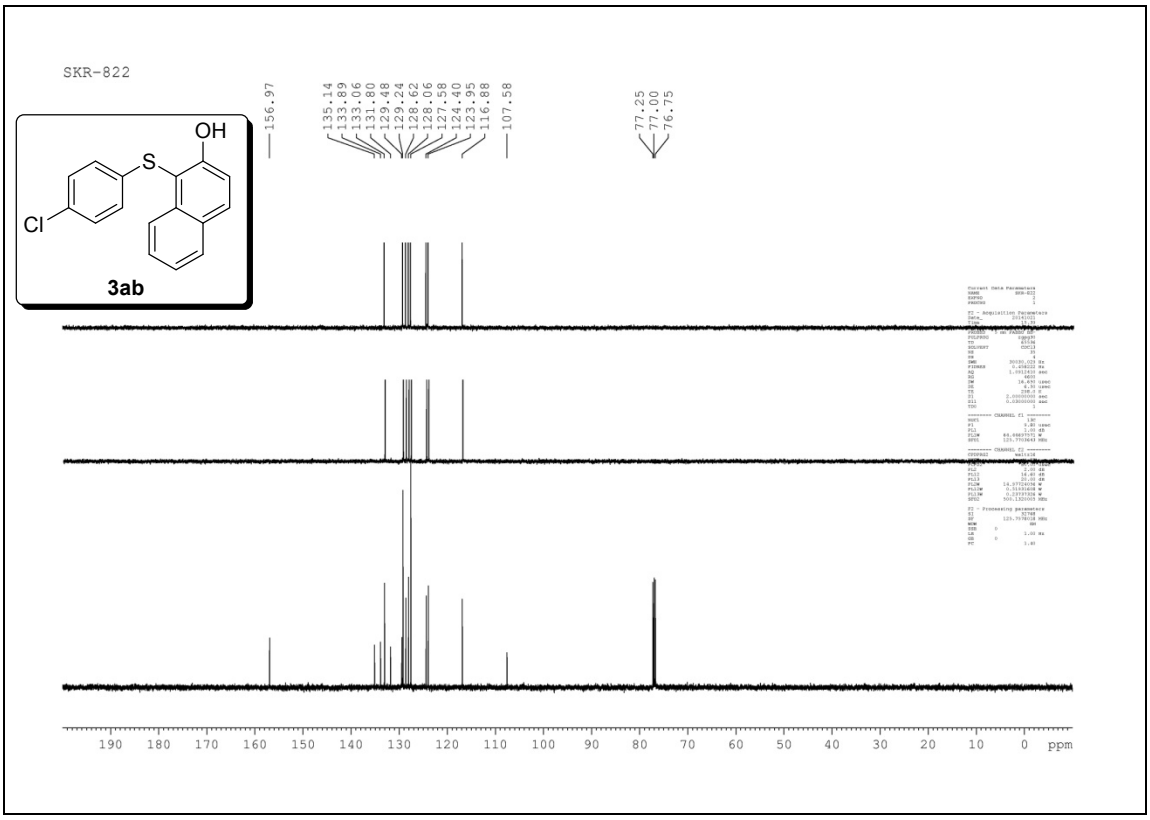
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123.95
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107.58
77.25
77.00
76.75
OH
S
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140
130
120
110
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80
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60
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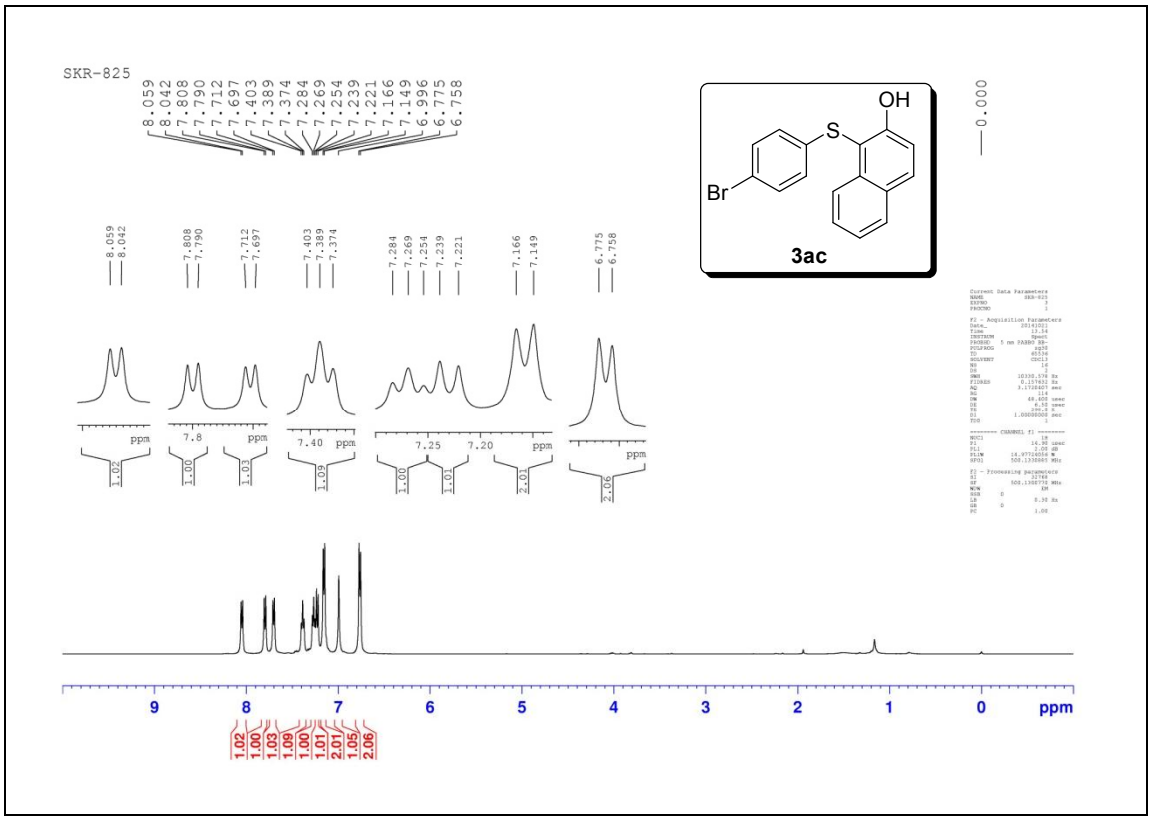
0
ppm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7.166
7.149
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1.00
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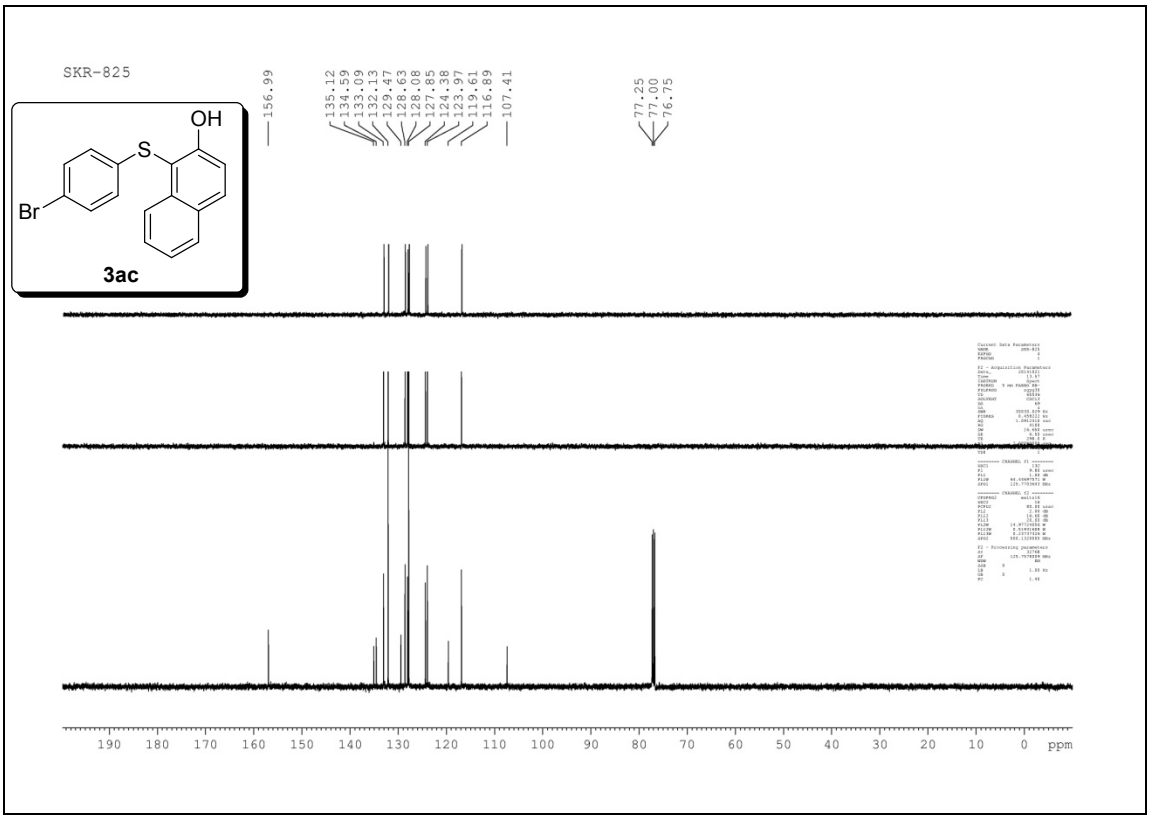
2.01
2.06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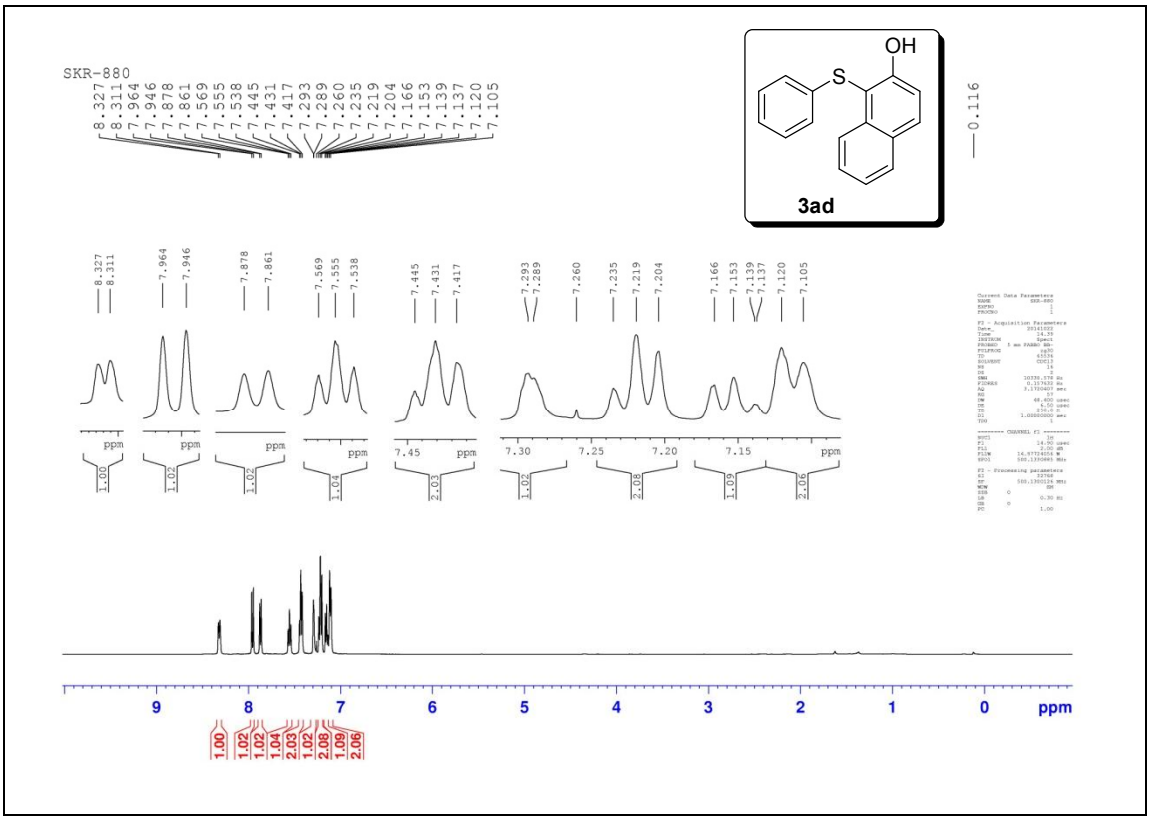
Br
3ac
ppm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7.235
7.219
7.204
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7.153
7.139
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7.120
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7.20
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1.02
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2.08
1.09
2.06
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6
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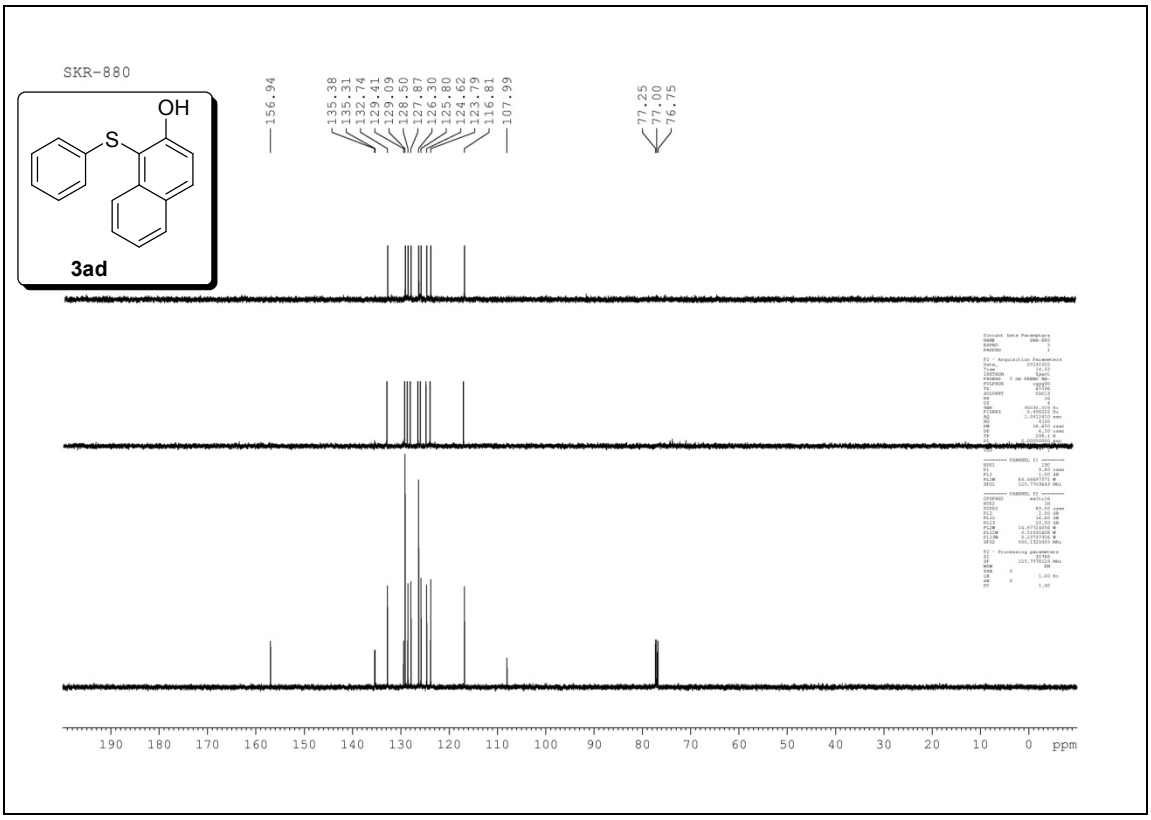
0
ppm


SKR-880
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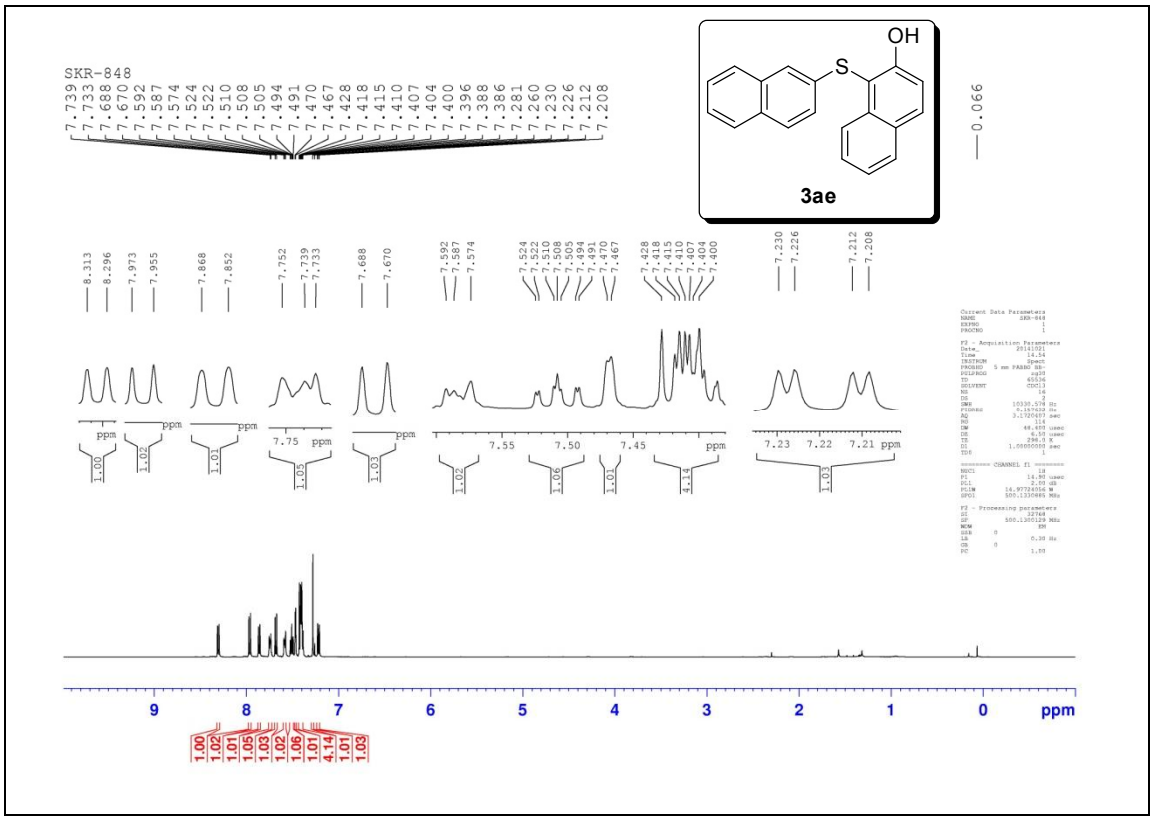
77.25
77.00
76.75
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


SKR-848
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S
3ae
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8
7
6
5
4
3
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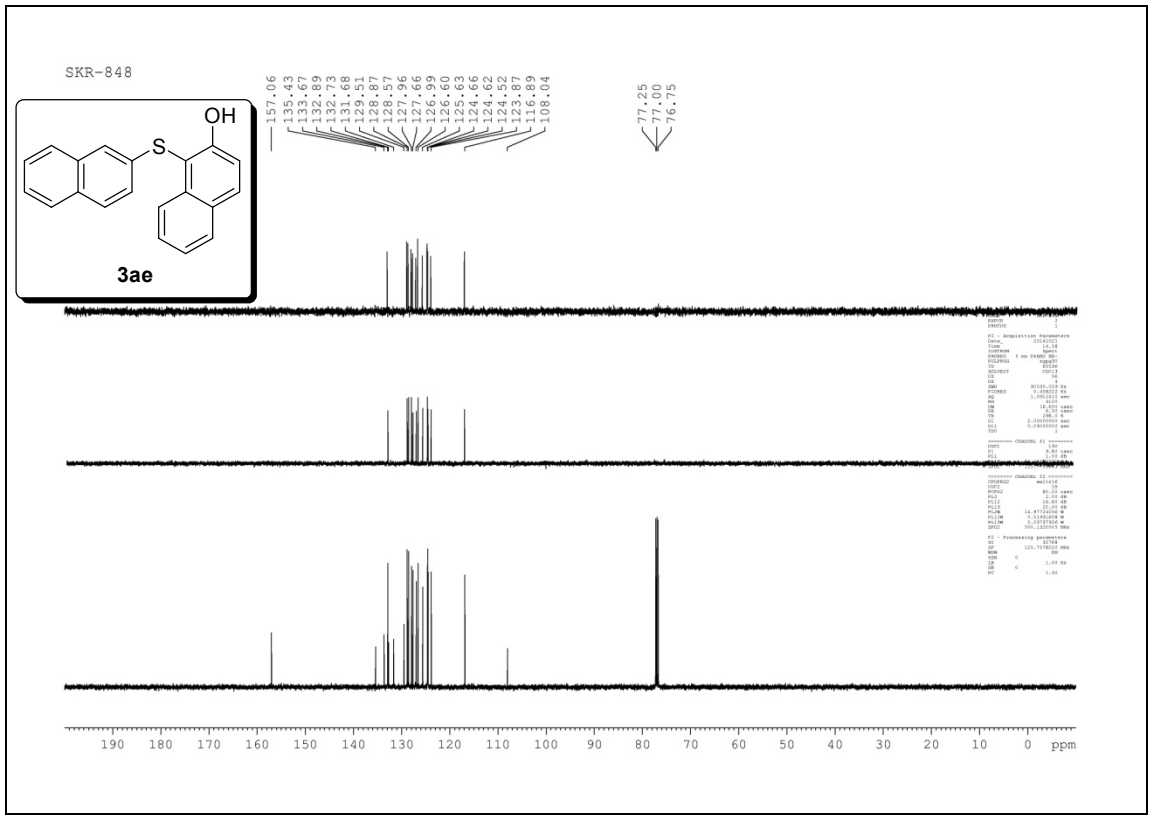
0
ppm


SKR-848
OH
S
3ae
190
180
170
160
150
140
130
120
110
100
90
80
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60
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40
30
20
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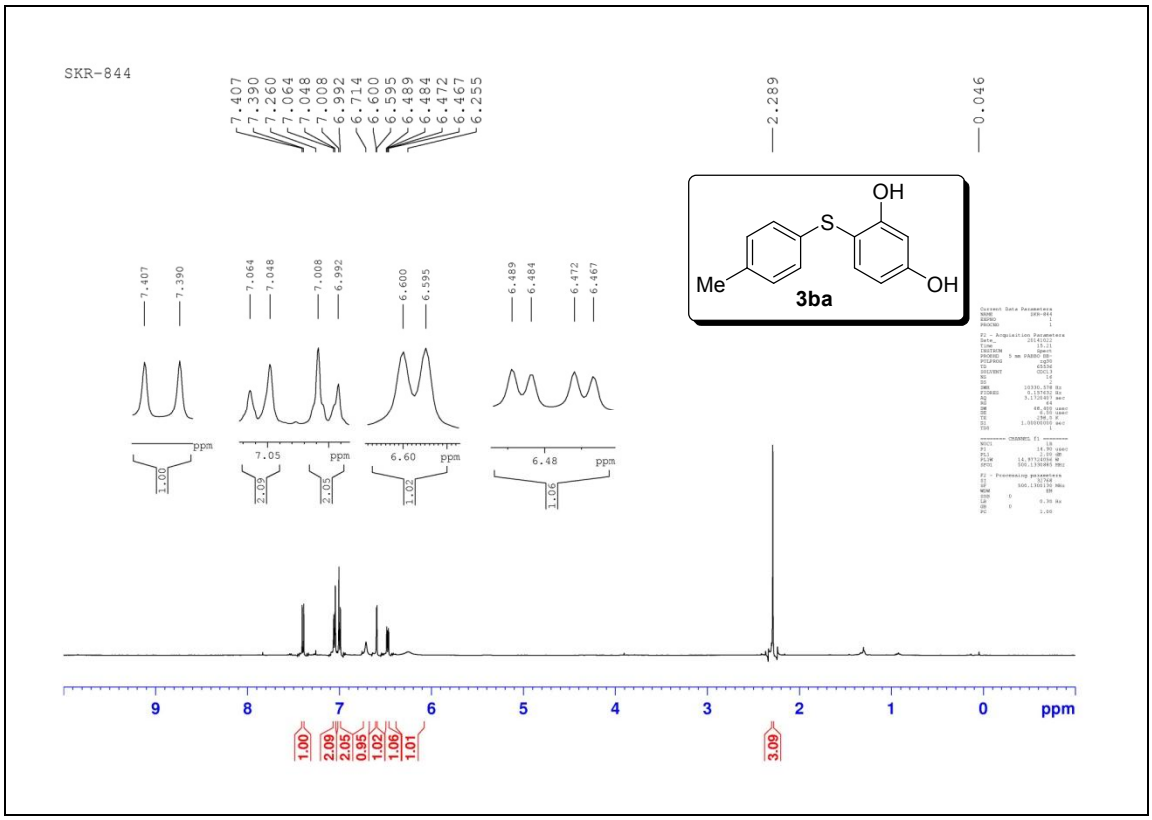
0
ppm


SKR-844
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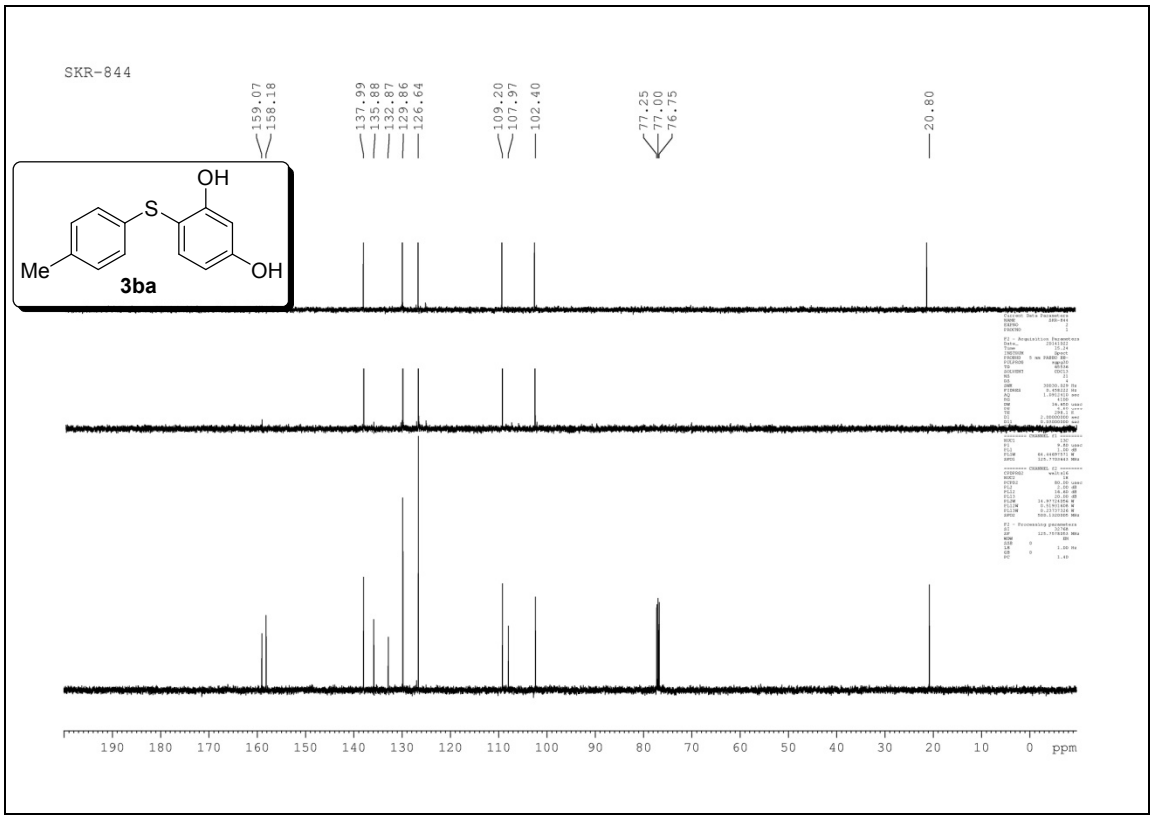
7.390
7.260
7.064
7.048
7.008
6.992
6.714
6.600
6.595
6.489
6.484
6.472
6.467
6.255
2.289
0.046
OH
S
Me
OH
3ba
ppm
7.05
6.60
6.48
1.00
2.09
2.05
1.02
1.06
9
8
7
6
5
4
3
2
1
0
ppm
1.00
2.09
2.05
0.95
1.02
1.06
1.01
3.09


SKR-844
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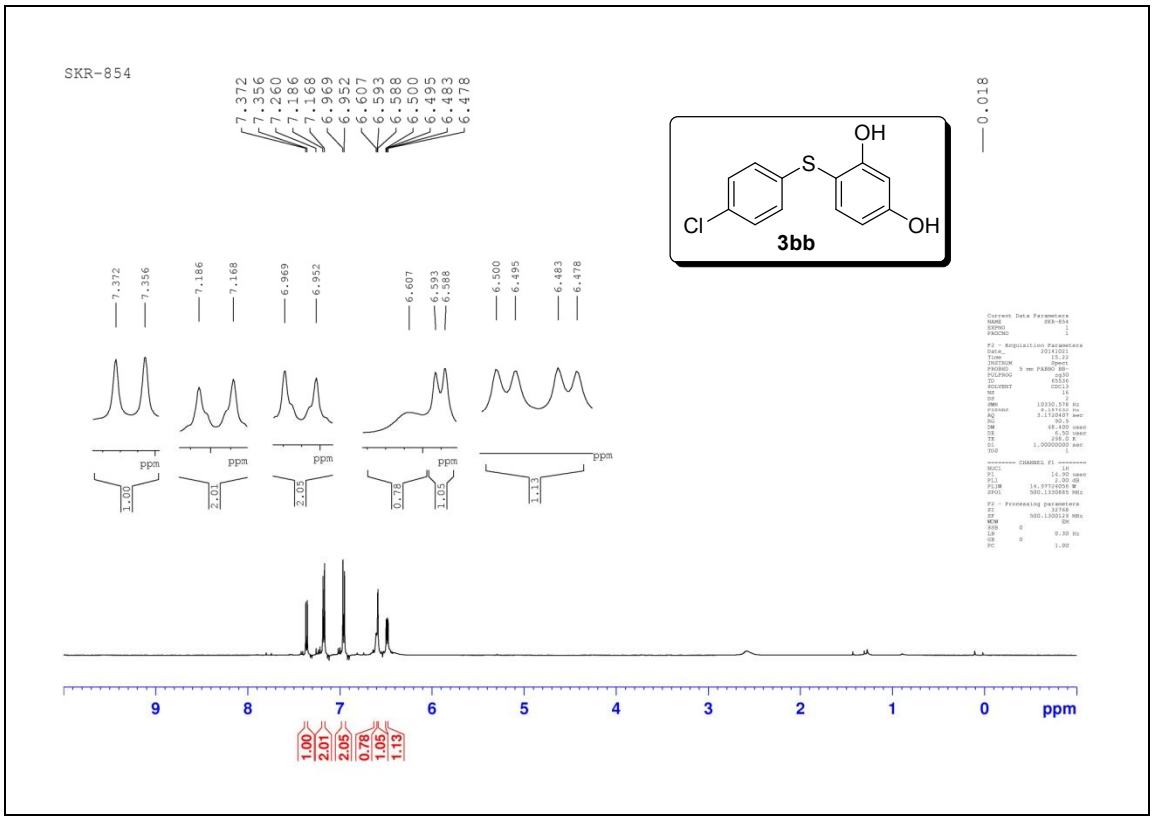
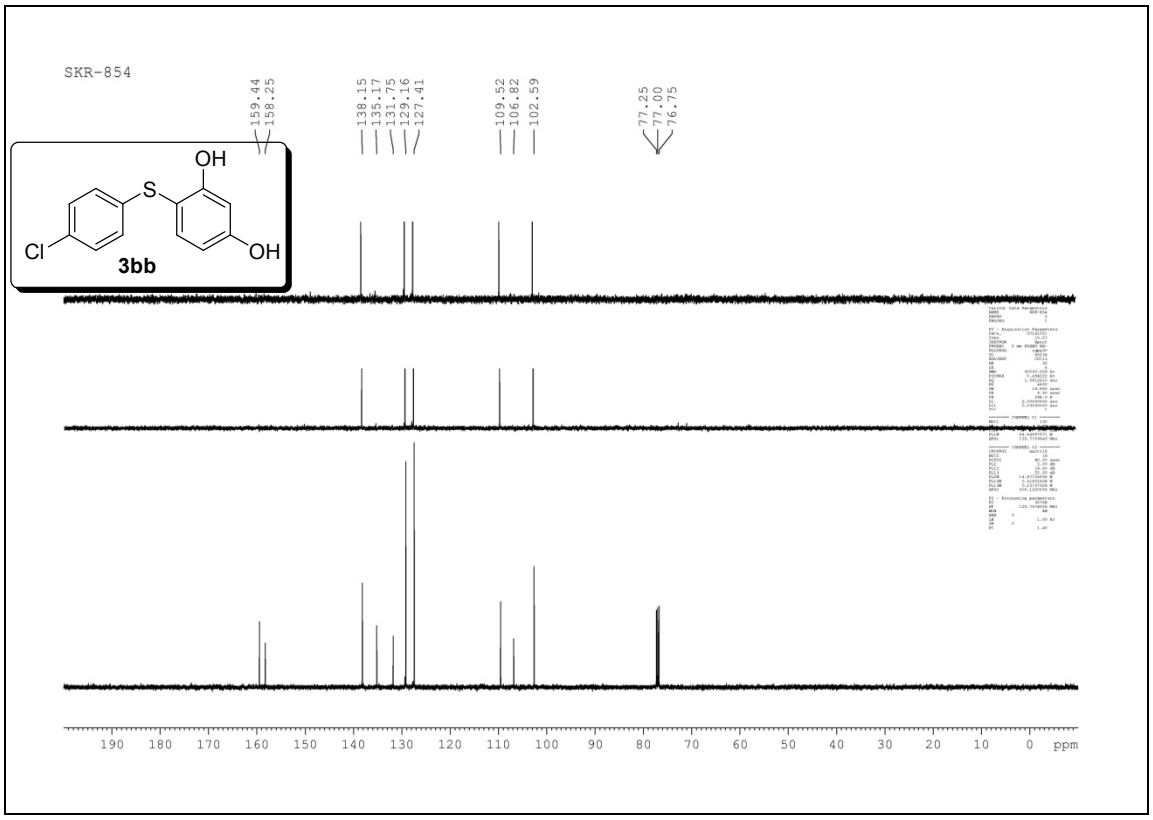
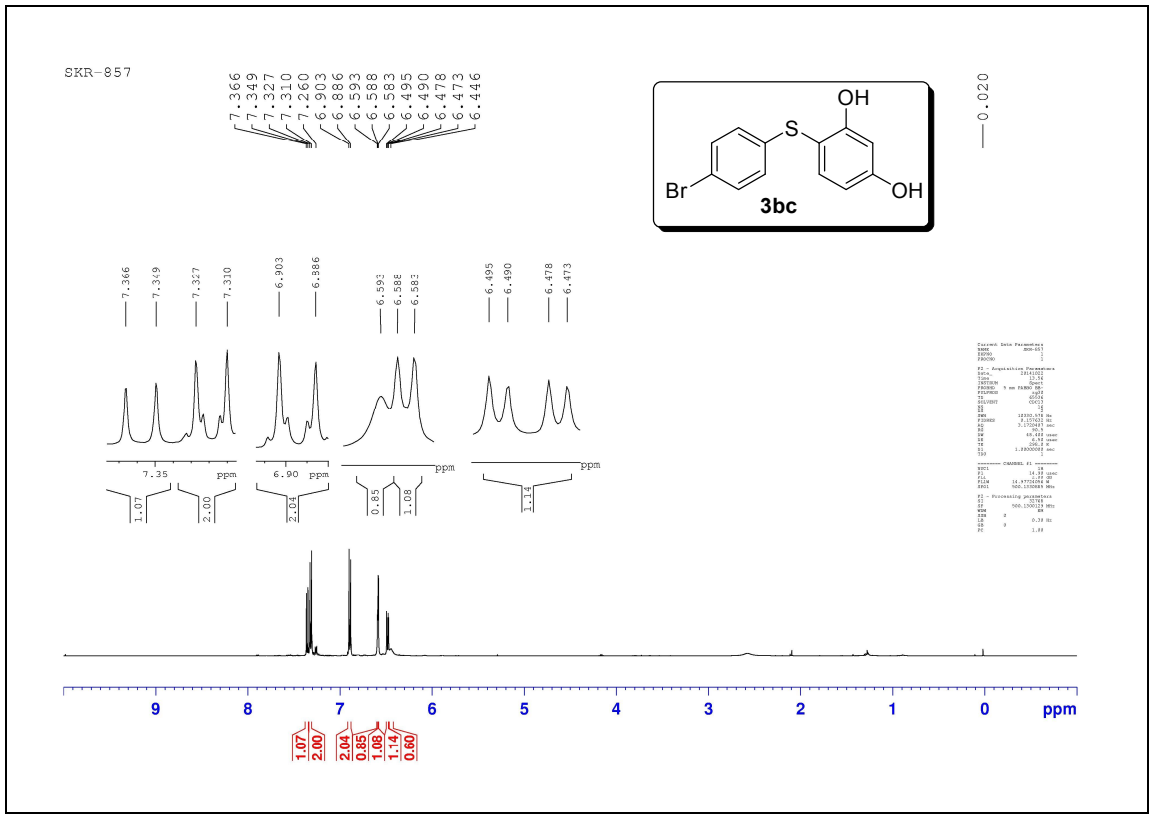
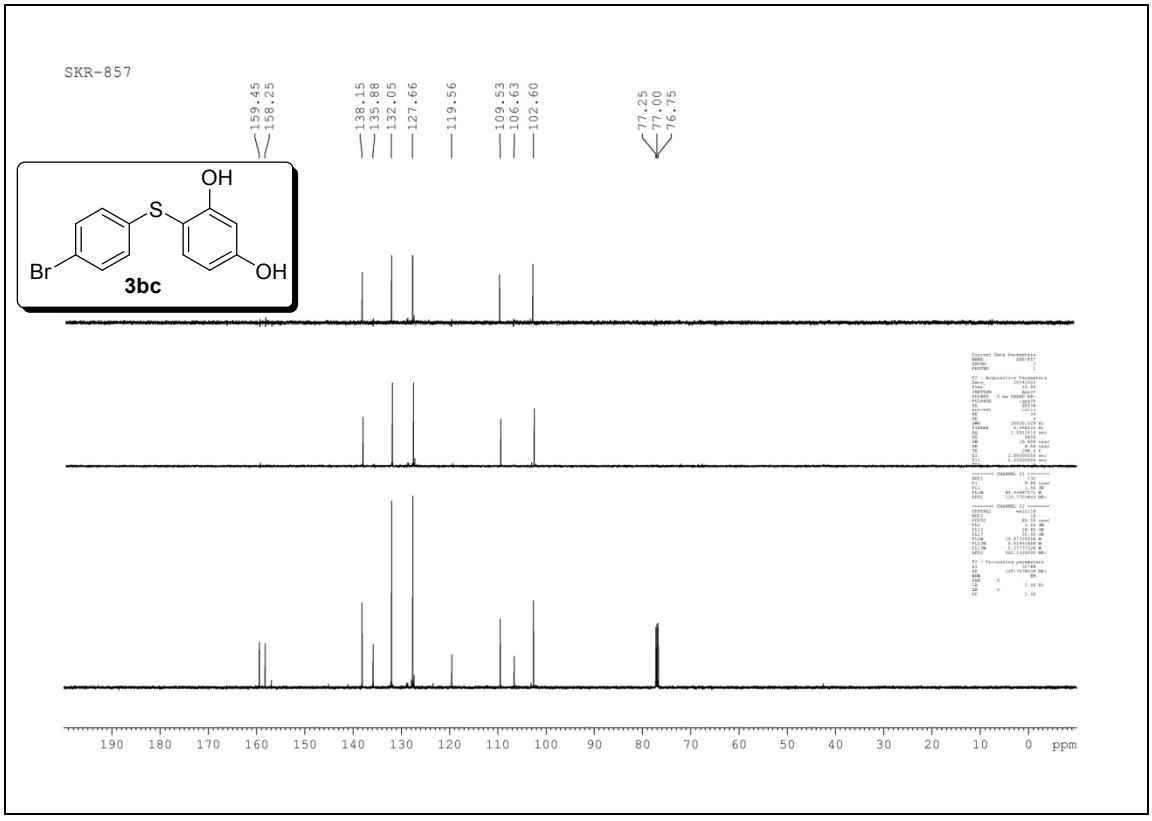
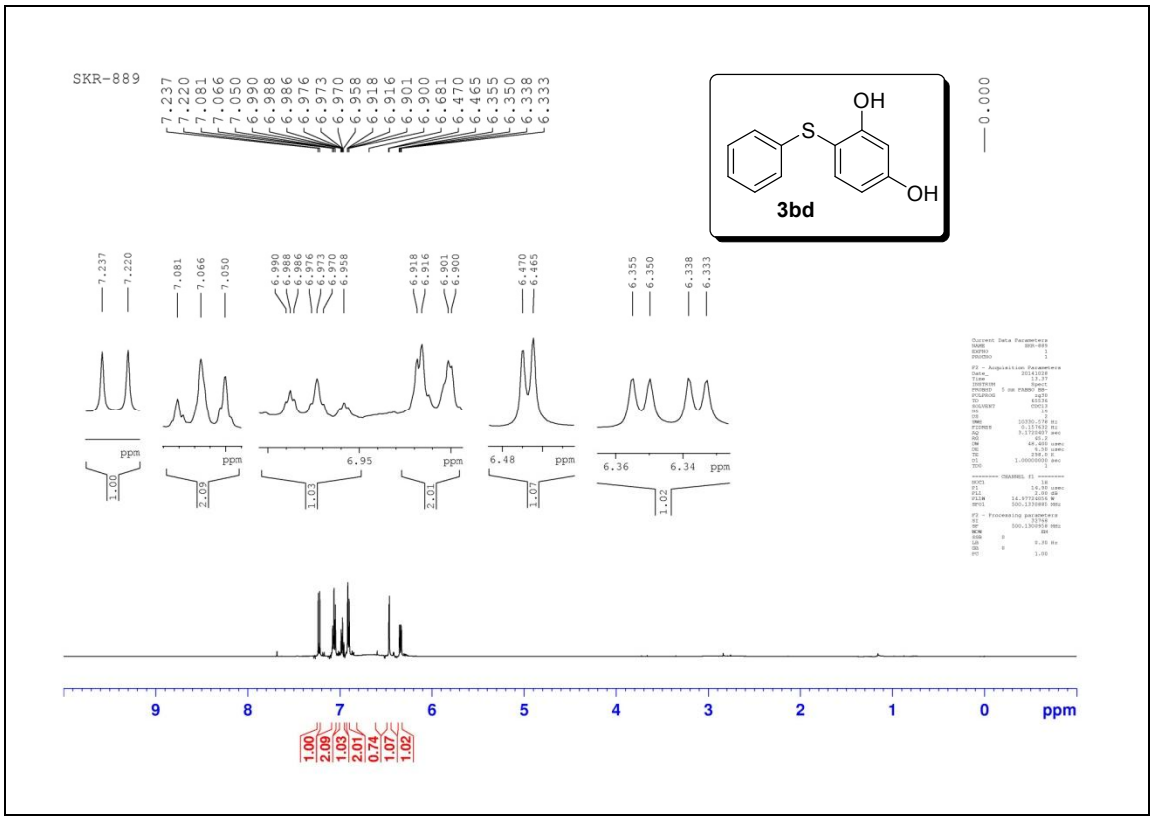
158.18
137.99
135.88
132.87
129.86
126.64
109.20
107.97
102.40
77.25
77.00
76.75
20.80
OH
S
Me
OH
3ba
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

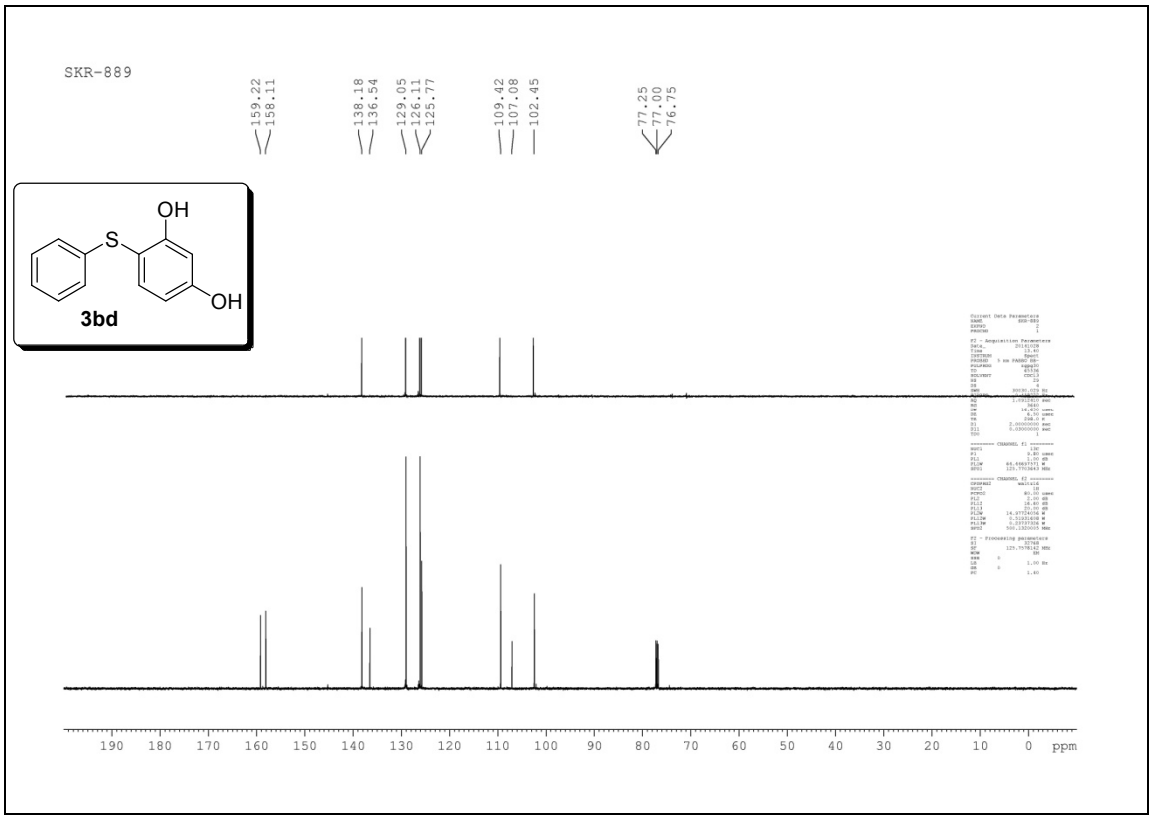

SKR-854
7.372
7.356
7.260
7.186
7.168
6.969
6.952
6.607
6.593
6.588
6.500
6.495
6.483
6.478
0.018
OH
S
Cl
OH
3bb
1.00
2.01
2.05
0.78
1.05
1.13
9
8
7
6
5
4
3
2
1
0
ppm

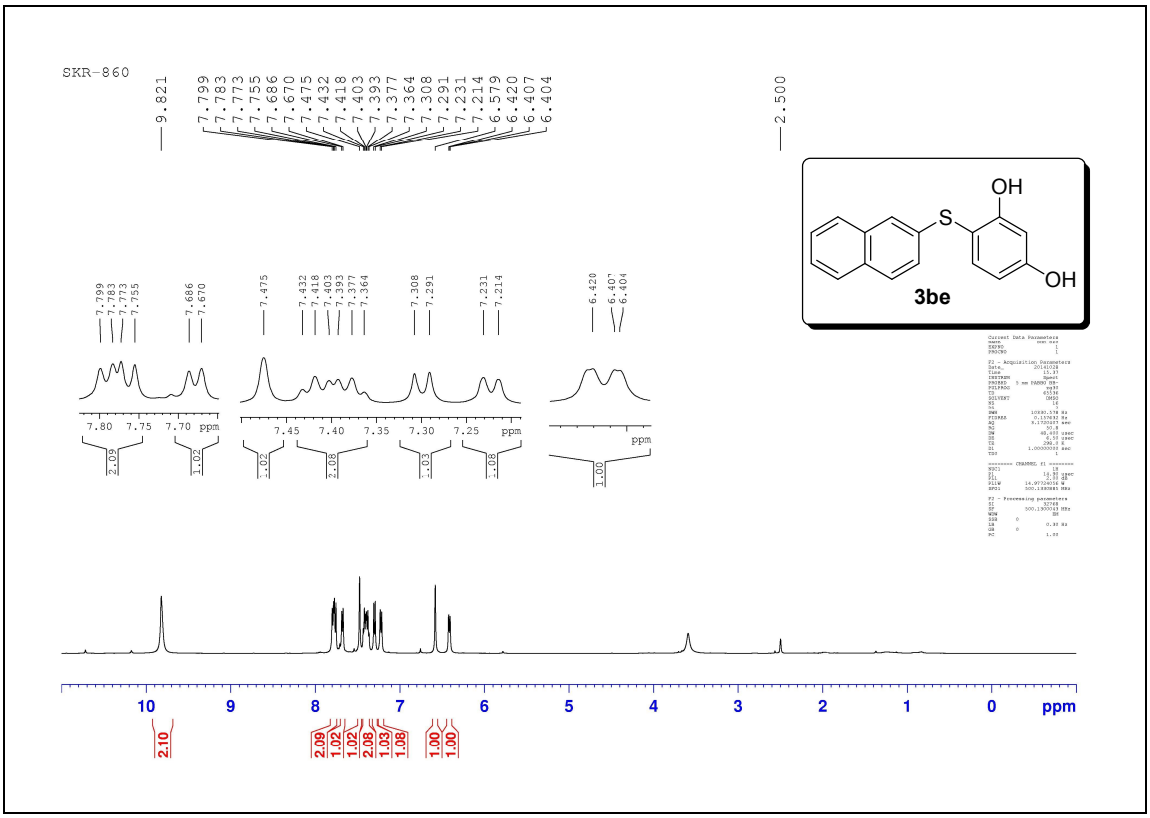

SKR-854
159.44
158.25
138.15
135.17
131.75
129.16
127.41
109.52
106.82
102.59
77.25
77.00
76.75
OH
S
Cl
OH
3bb
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


SKR-857
7.366
7.349
7.327
7.310
7.260
6.903
6.886
6.593
6.588
6.583
6.495
6.490
6.478
6.473
6.446
OH
S
Br
OH
3bc
0.020
7.35 ppm
6.90 ppm
1.07
2.00
2.04
0.85
1.08
1.14
9 8 7 6 5 4 3 2 1 0 ppm
1.07
2.00
2.04
0.85
1.08
1.14
0.60


SKR-857
159.45
158.25
138.15
135.88
132.05
127.66
119.56
109.53
106.63
102.60
77.25
77.00
76.75
OH
S
Br
OH
3bc
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


SKR-889
7.237
7.220
7.081
7.066
7.050
6.990
6.988
6.986
6.976
6.973
6.970
6.958
6.918
6.916
6.901
6.900
6.681
6.470
6.465
6.355
6.350
6.338
6.333
0.000
OH
S
OH
3bd
1.00
2.09
1.03
2.01
0.74
1.07
1.02
9
8
7
6
5
4
3
2
1
0
ppm


SKR-889
159.22
158.11
138.18
136.54
129.05
126.11
125.77
109.42
107.08
102.45
77.25
77.00
76.75
OH
S
OH
3bd
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


SKR-860
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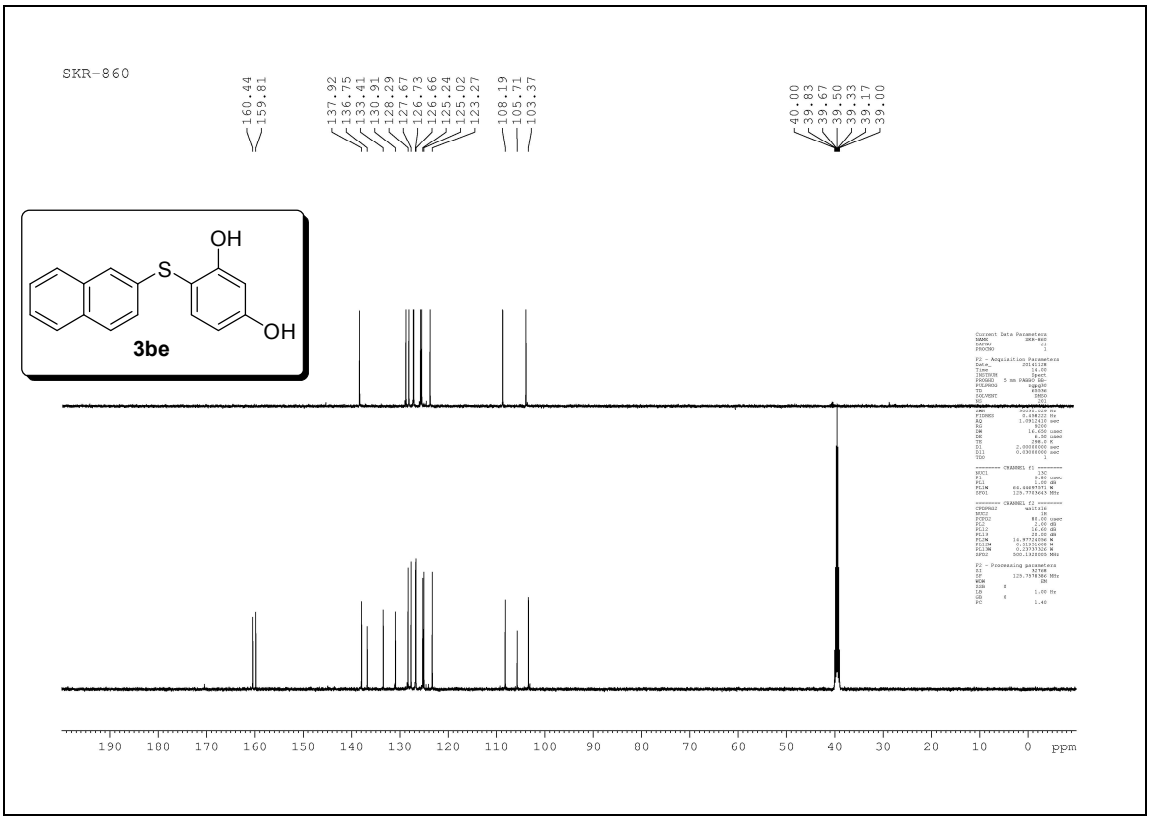
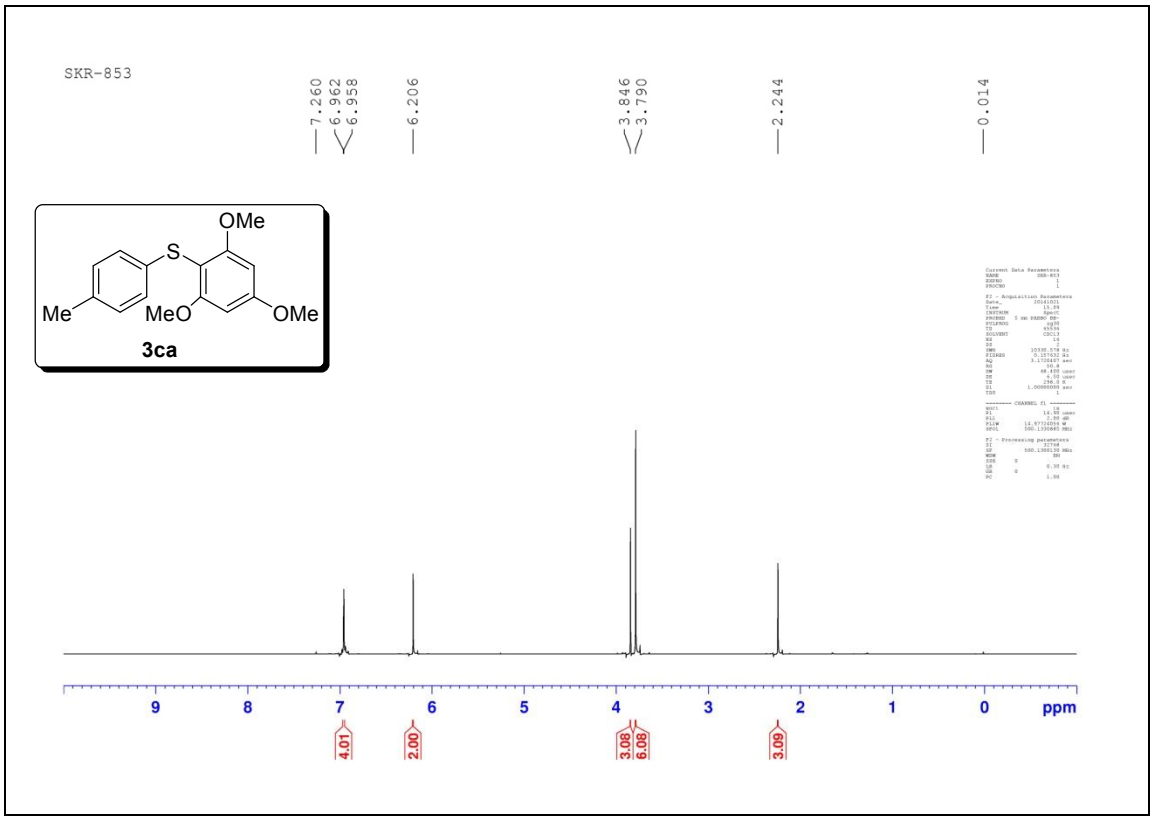
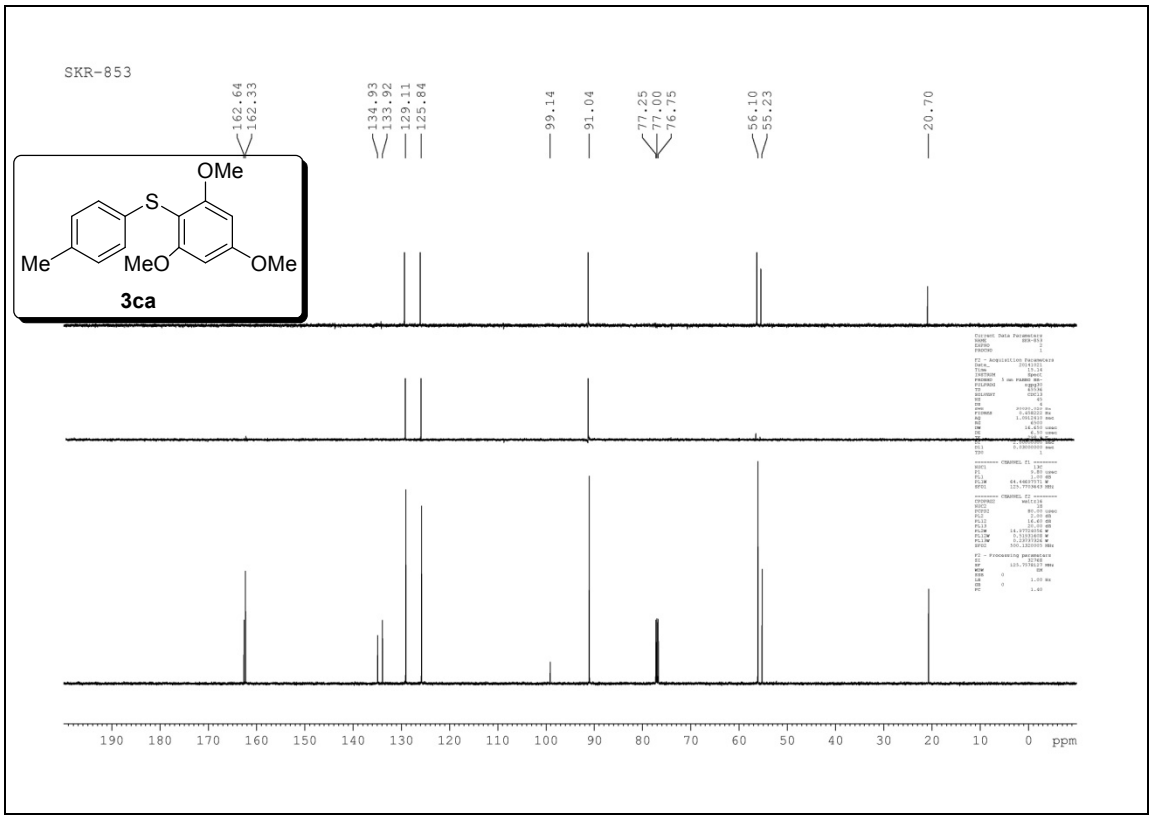
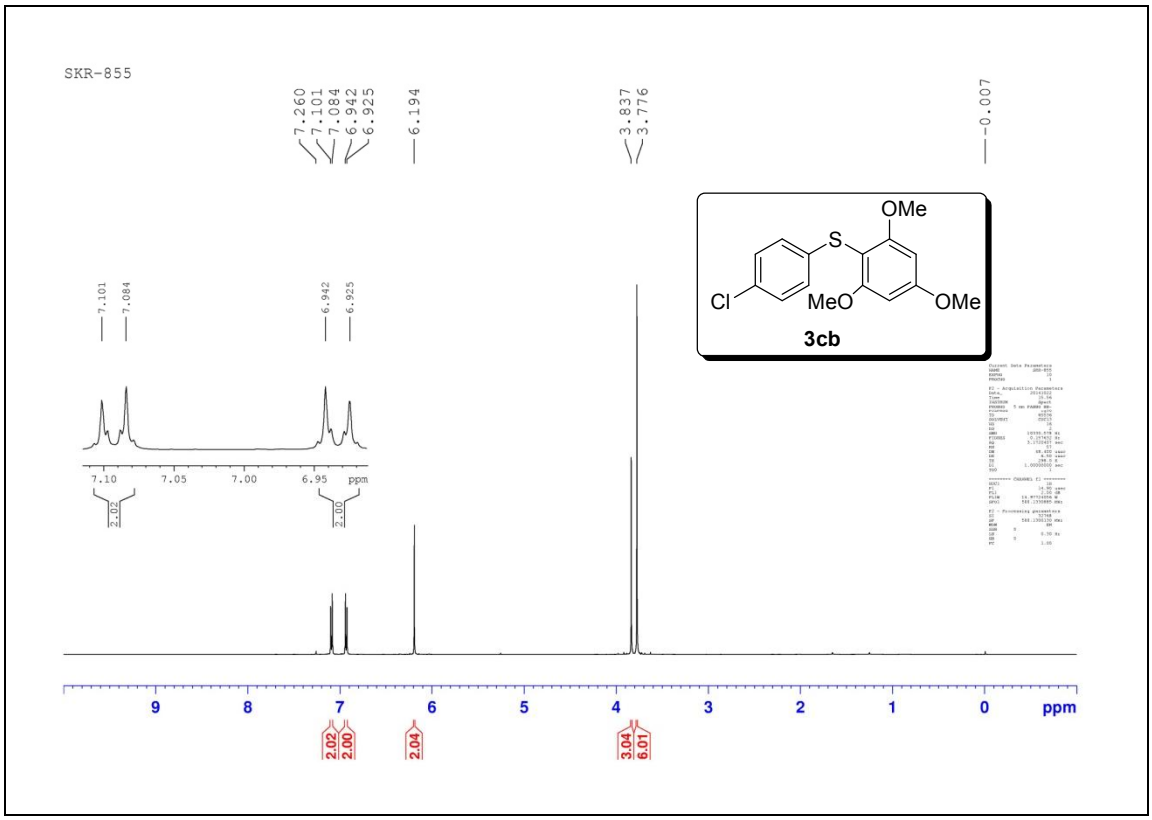
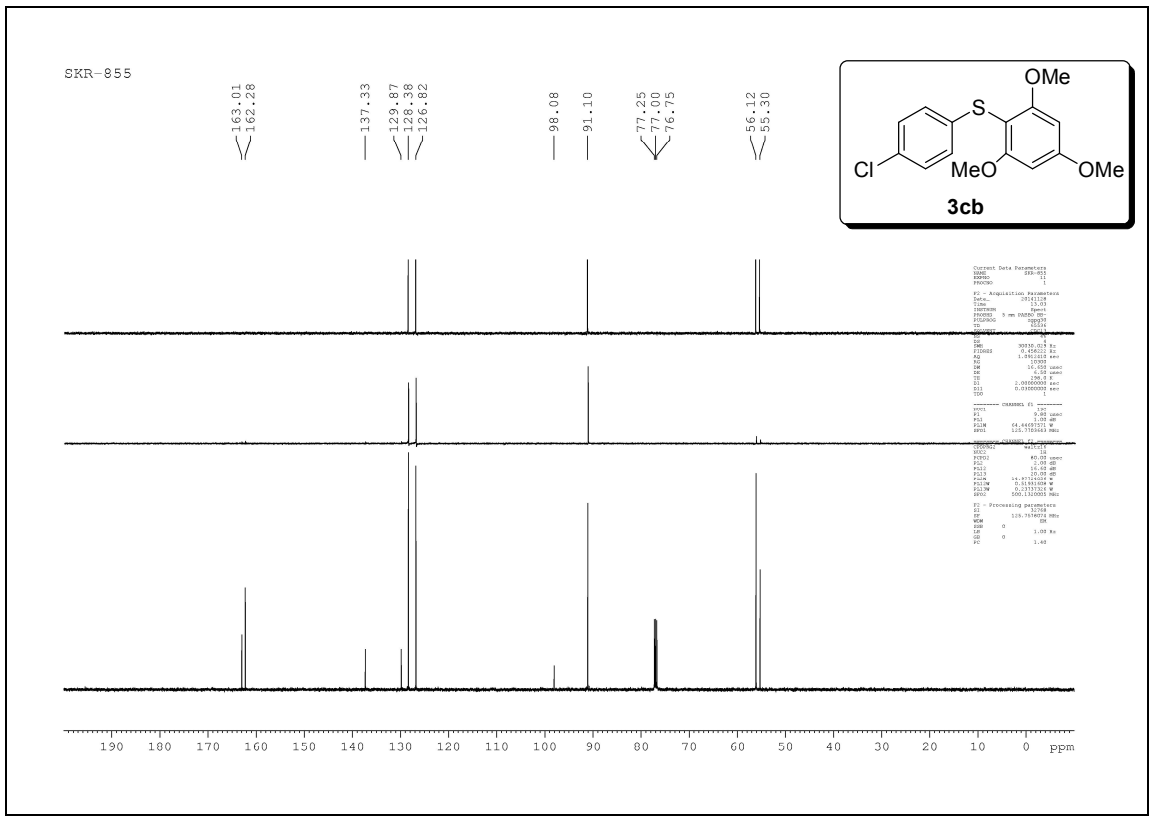
7.799
7.783
7.773
7.755
7.686
7.670
7.475
7.432
7.418
7.403
7.393
7.377
7.364
7.308
7.291
7.231
7.214
6.579
6.420
6.407
6.404
2.500
OH
S
OH
3be
7.80 7.75 7.70 ppm
7.45 7.40 7.35 7.30 7.25 ppm
ppm
10 9 8 7 6 5 4 3 2 1 0 ppm
2.10
2.09
1.02
1.02
2.08
1.03
1.08
1.00
1.00

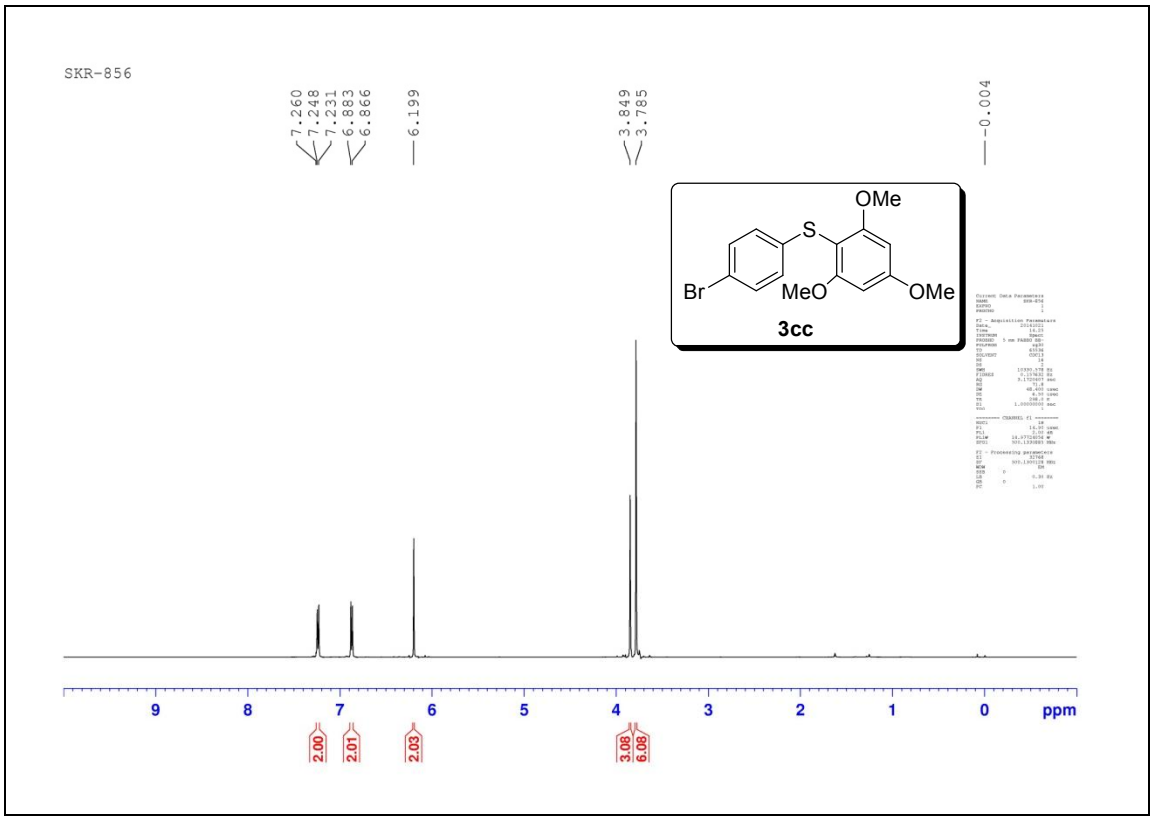

SKR-860
160.44
159.81
137.92
136.75
130.41
130.01
128.29
127.67
126.73
126.66
125.24
125.02
123.27
108.19
105.71
103.37
40.00
39.83
39.67
39.50
39.33
39.17
39.00
OH
S
OH
3be
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


SKR-853
7.260
6.962
6.958
6.206
3.846
3.790
2.244
0.014
OMe
S
Me
MeO
OMe
3ca
9
8
7
6
5
4
3
2
1
0
ppm
4.01
2.00
3.08
6.08
3.09


SKR-853
162.64
162.33
134.93
133.92
129.11
125.84
99.14
91.04
77.25
77.00
76.75
56.10
55.23
20.70
OMe
S
Me
MeO
OMe
3ca
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


SKR-855
7.260
7.101
7.084
6.942
6.925
6.194
3.837
3.776
0.007
OMe
S
Cl
MeO
OMe
3cb
7.10
7.05
7.00
6.95
ppm
2.02
2.00
2.04
3.04
6.01


SKR-855
163.01
162.28
137.33
129.87
128.38
126.82
98.08
91.10
77.25
77.00
76.75
56.12
55.30
OMe
S
Cl
MeO
OMe
3cb
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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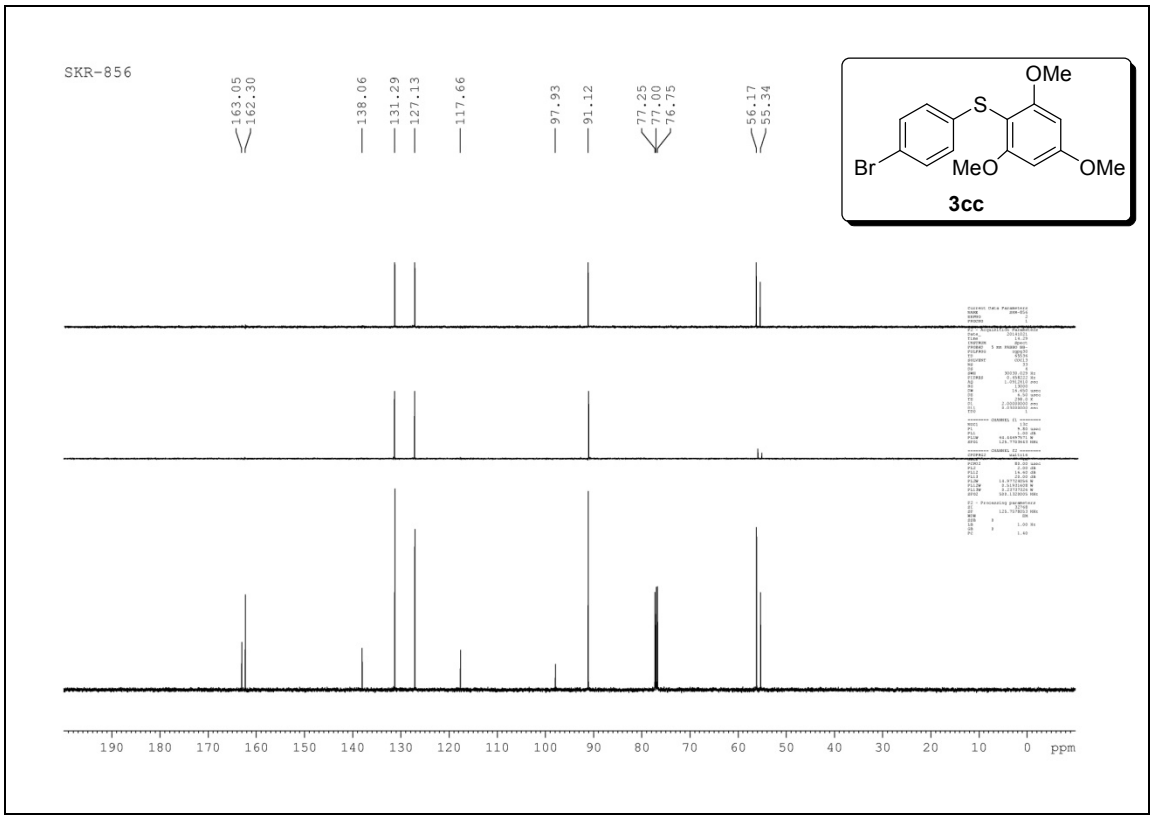
7.248
7.231
6.883
6.866
6.199
3.849
3.785
0.004
OMe
S
Br
MeO
OMe
3cc
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.01
2.03
3.08
6.08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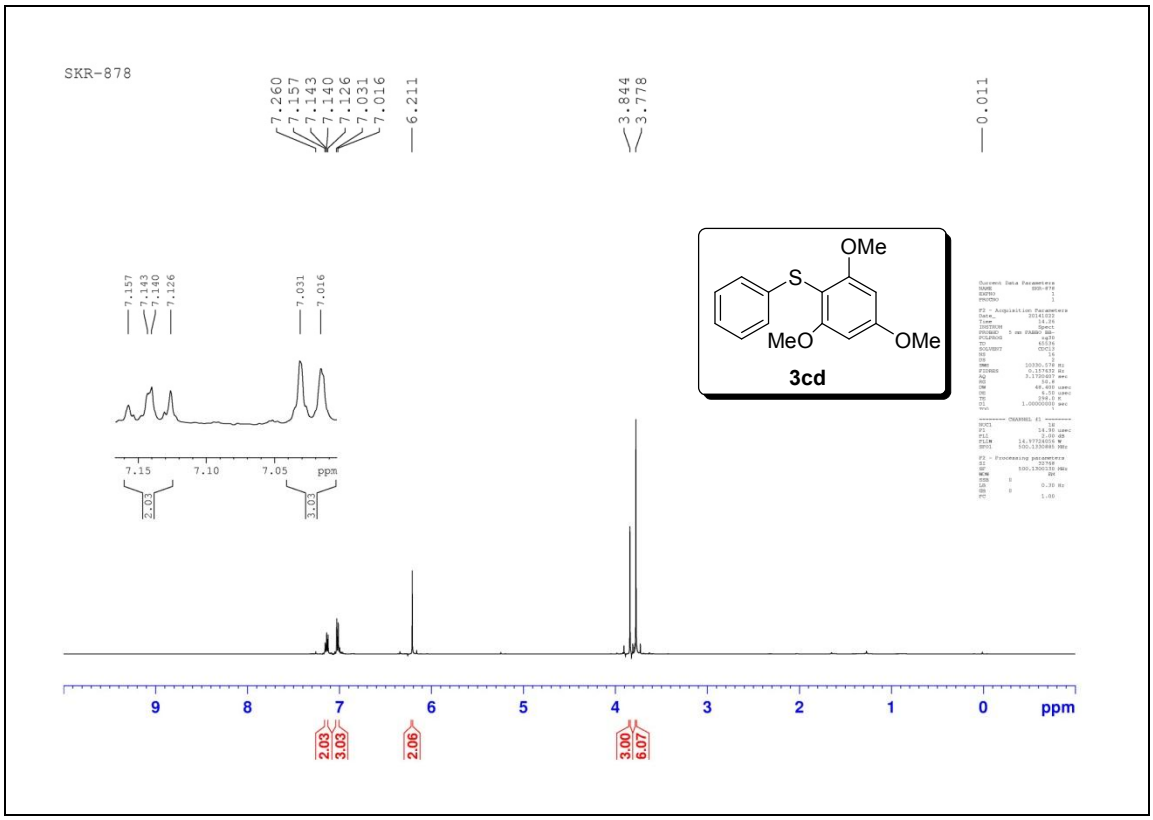
162.30
138.06
131.29
127.13
117.66
97.93
91.12
77.25
77.00
76.75
56.17
55.34
OMe
S
Br
MeO
OMe
3cc
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.126
7.031
7.016
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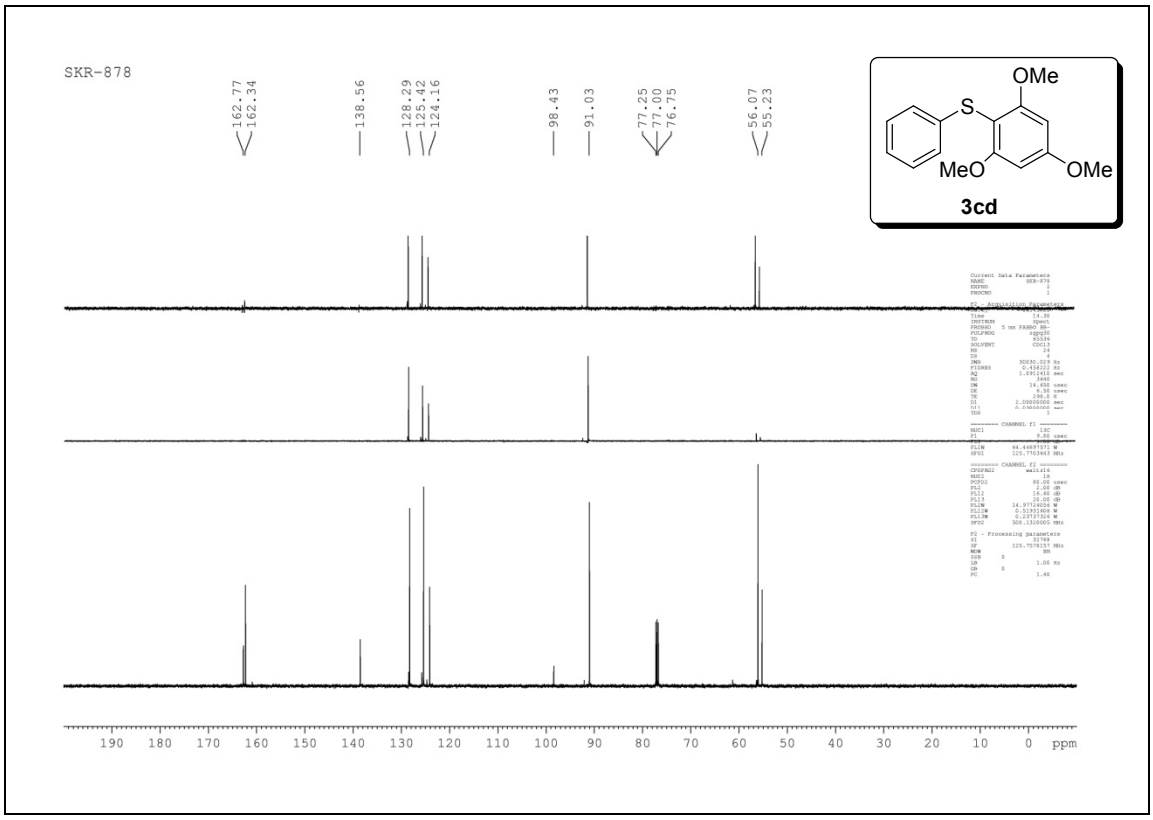
3.844
3.778
0.011
OMe
S
MeO
OMe
3cd
7.15
7.10
7.05
ppm
2.03
3.03
9
8
7
6
5
4
3
2
1
0
ppm
2.03
3.03
2.06
3.00
6.07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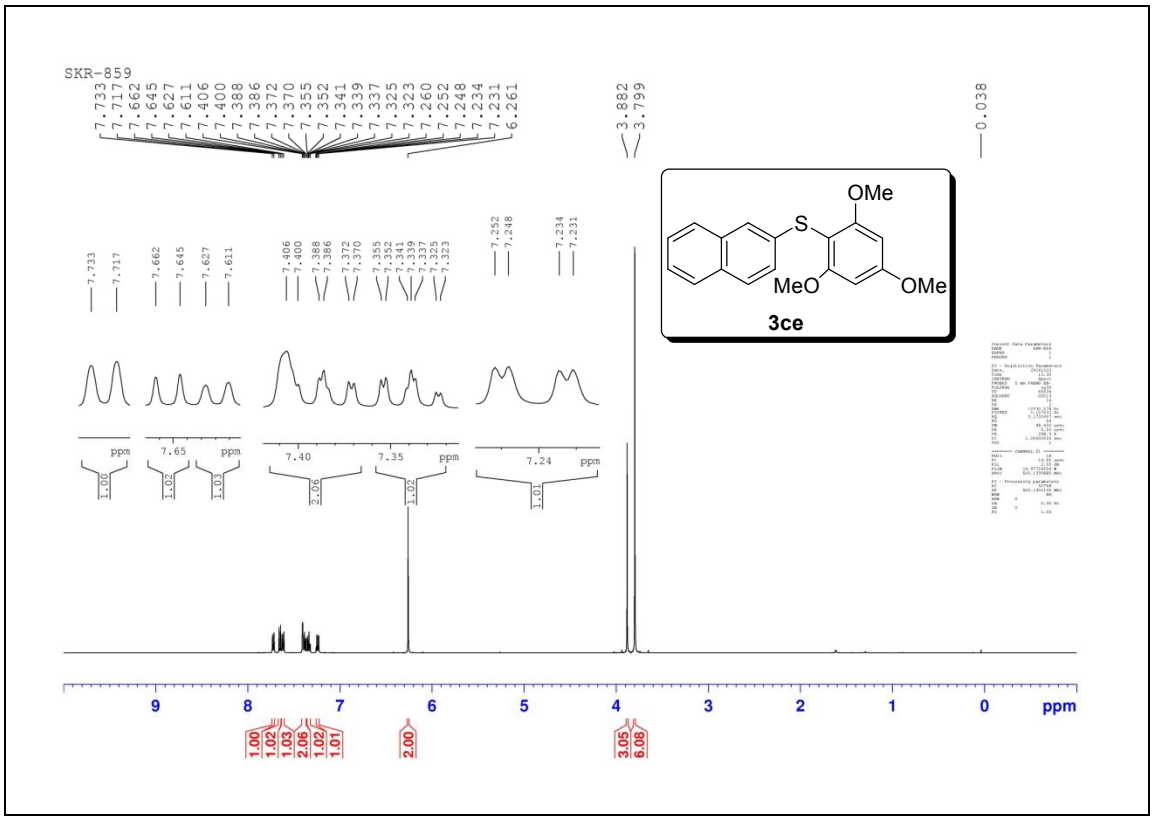
125.42
124.16
98.43
91.03
77.25
77.00
76.75
56.07
55.23
OMe
S
MeO
OMe
3cd
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


SKR-859
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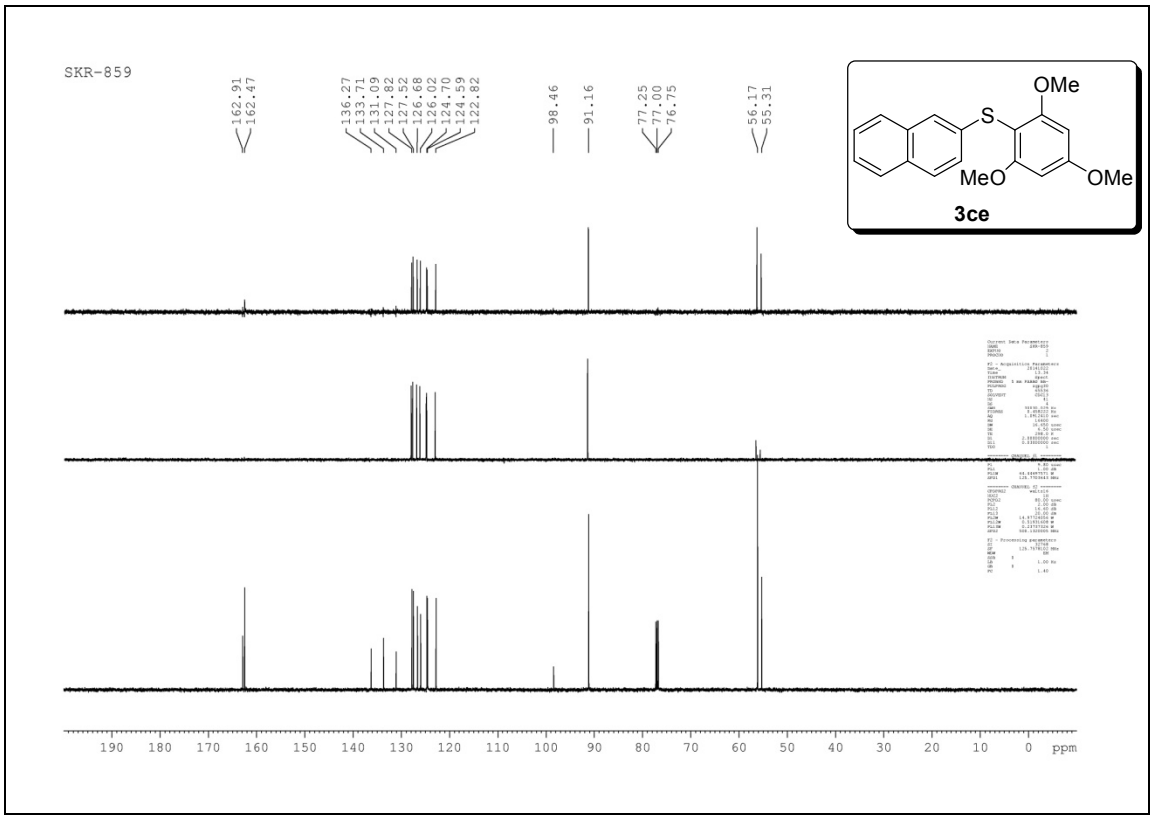
7.627
7.611
7.406
7.400
7.388
7.386
7.372
7.370
7.355
7.352
7.341
7.339
7.337
7.325
7.323
7.260
7.252
7.248
7.234
7.231
6.261
3.882
3.799
0.038
OMe
S
MeO
OMe
3ce
ppm
7.65
7.40
7.35
7.24
1.00
1.02
1.03
2.06
1.02
1.01
2.00
3.05
6.08


SKR-859
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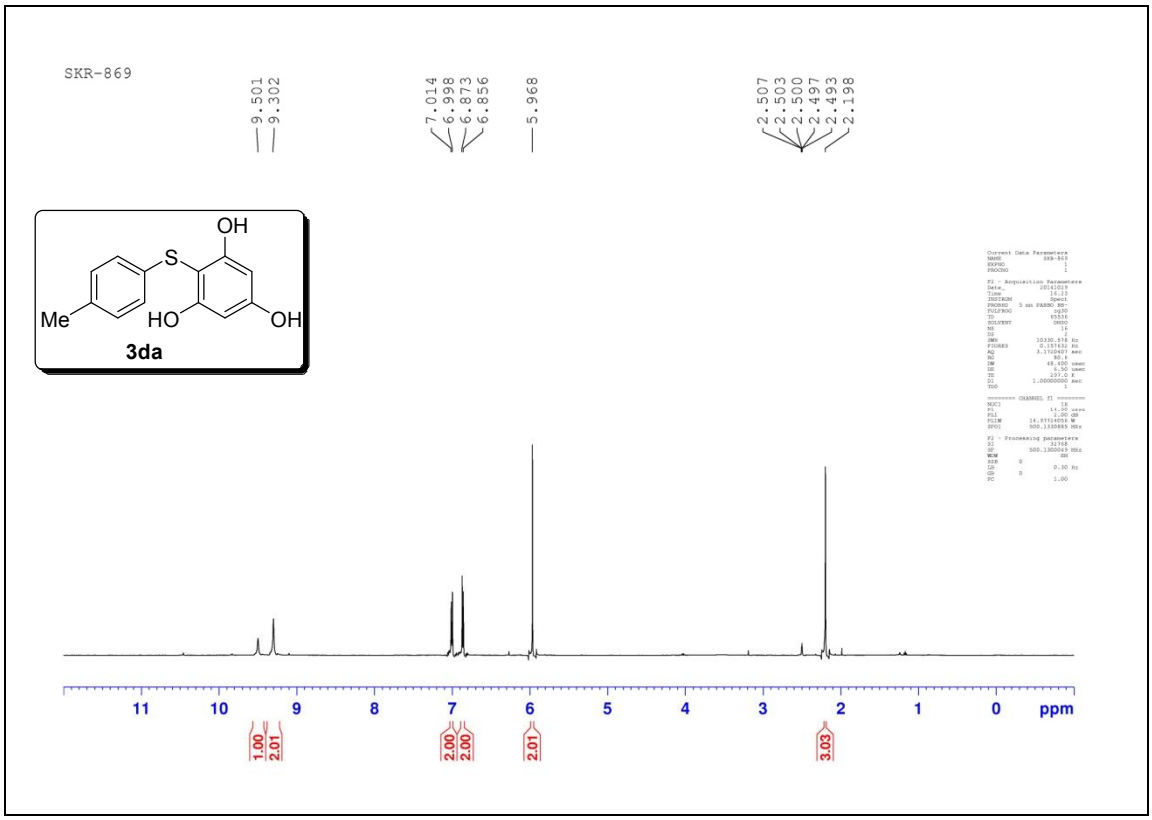
133.71
131.09
127.82
127.52
126.68
126.02
124.70
124.59
122.82
98.46
91.16
77.25
77.00
76.75
56.17
55.31
OMe
S
MeO
OMe
3ce
ppm


SKR-869
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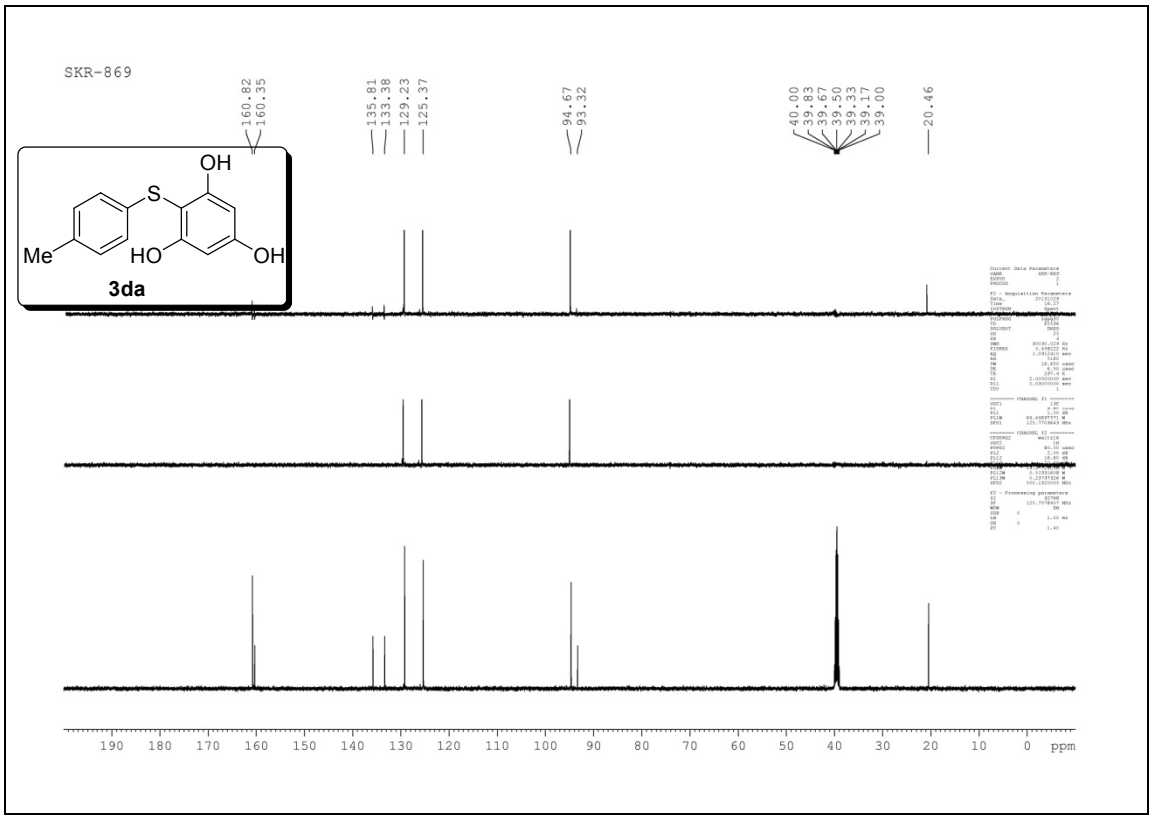
9.302
7.014
6.998
6.873
6.856
5.968
2.507
2.503
2.500
2.497
2.493
2.198
OH
S
Me
HO
OH
3da
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
2.01
2.00
2.00
2.01
3.03


SKR-869
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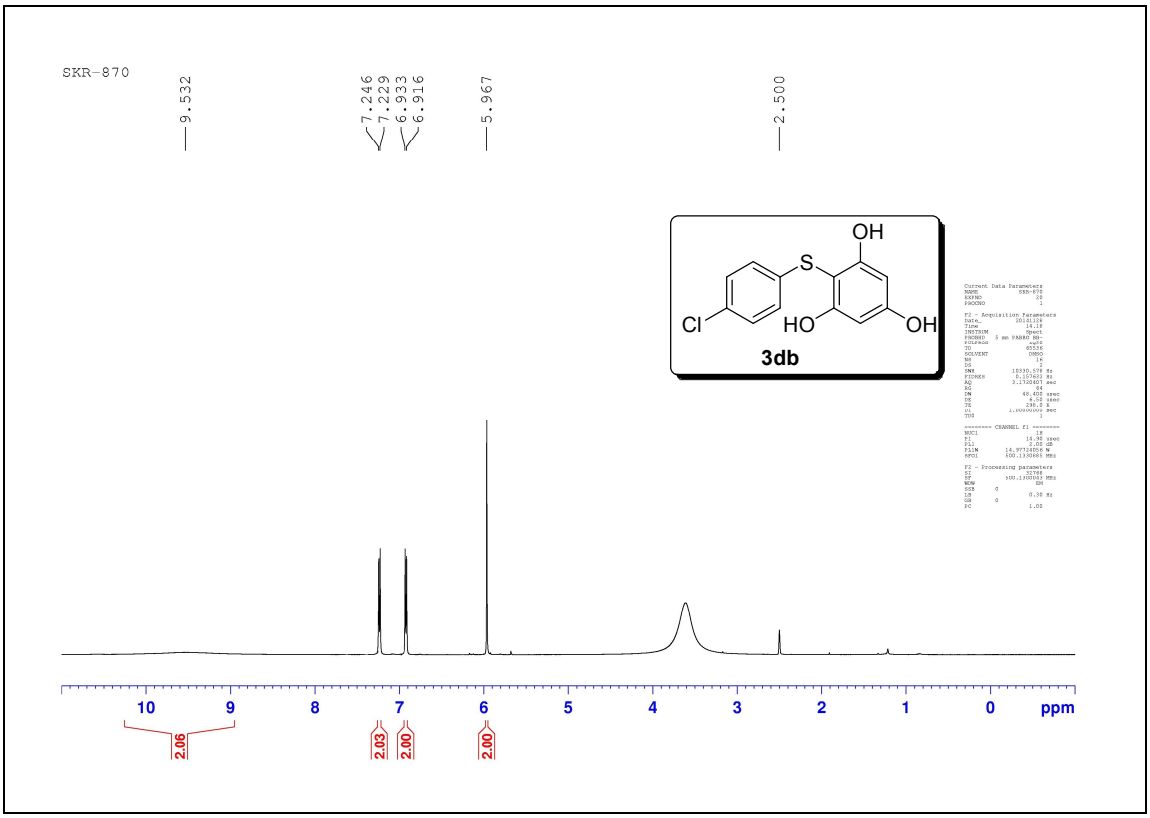
160.35
135.81
133.38
129.23
125.37
94.67
93.32
40.00
39.83
39.67
39.50
39.33
39.17
39.00
20.46
OH
S
Me
HO
OH
3da
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


SKR-870
9.532
7.246
7.229
6.933
6.916
5.967
2.500
OH
S
Cl
HO
OH
3db
10
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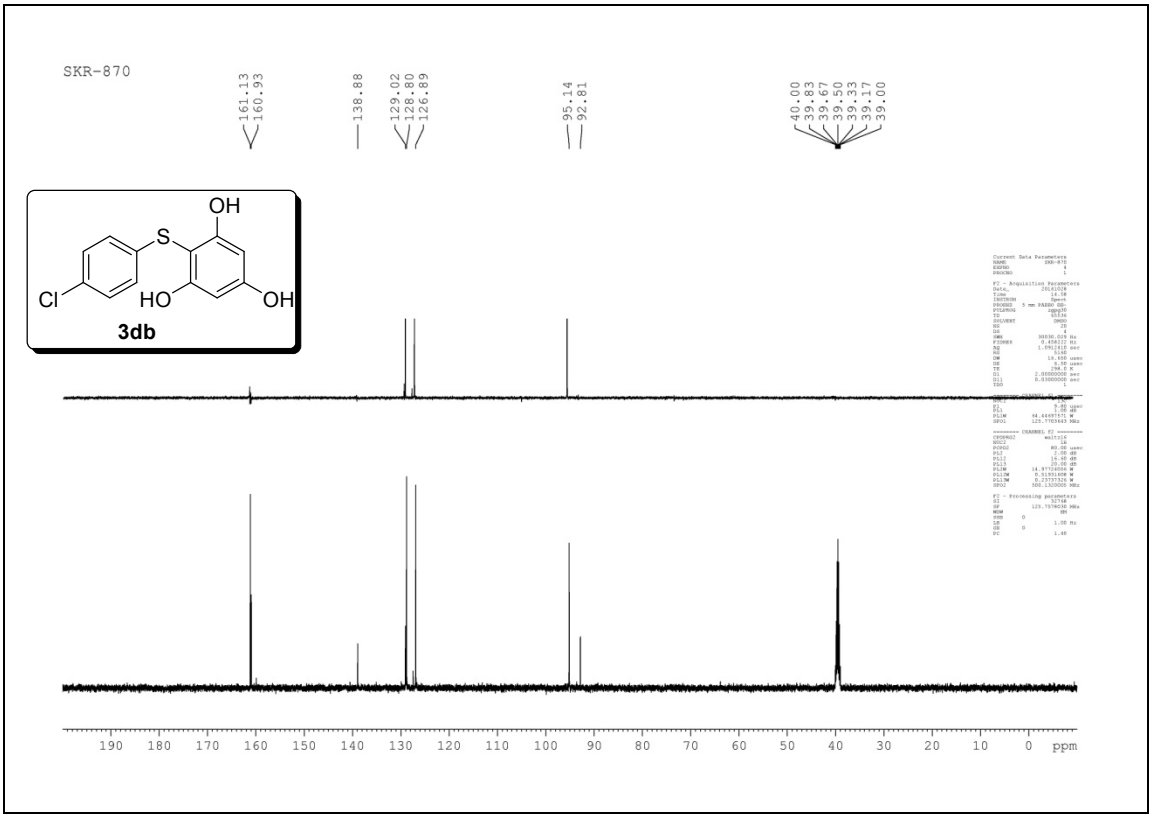
8
7
6
5
4
3
2
1
0
ppm
2.06
2.03
2.00
2.00


SKR-870
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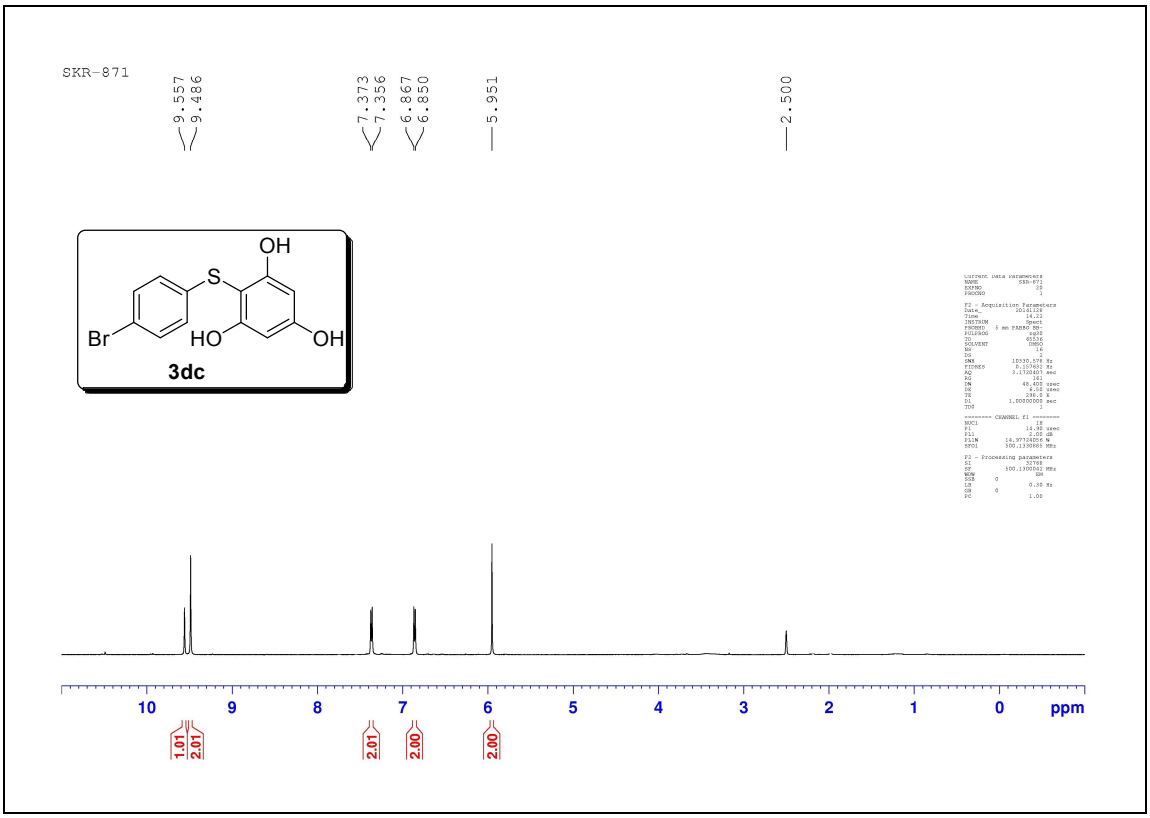
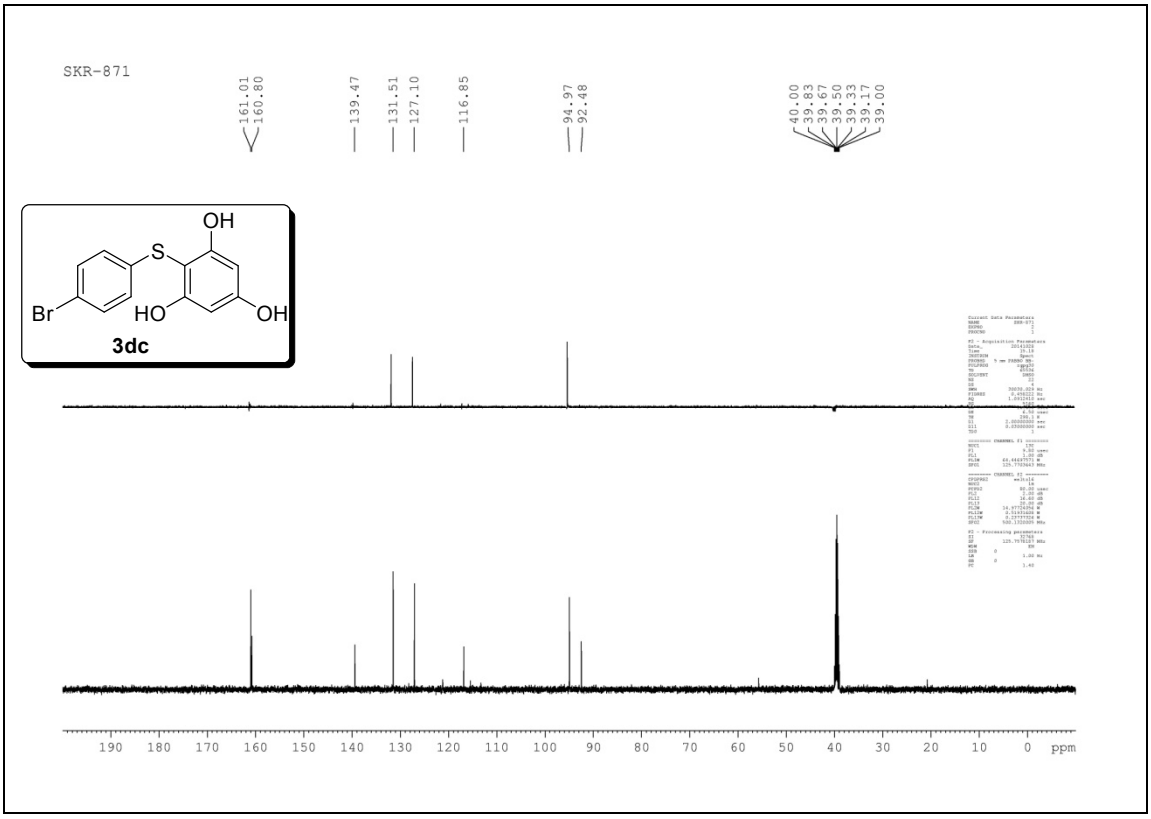
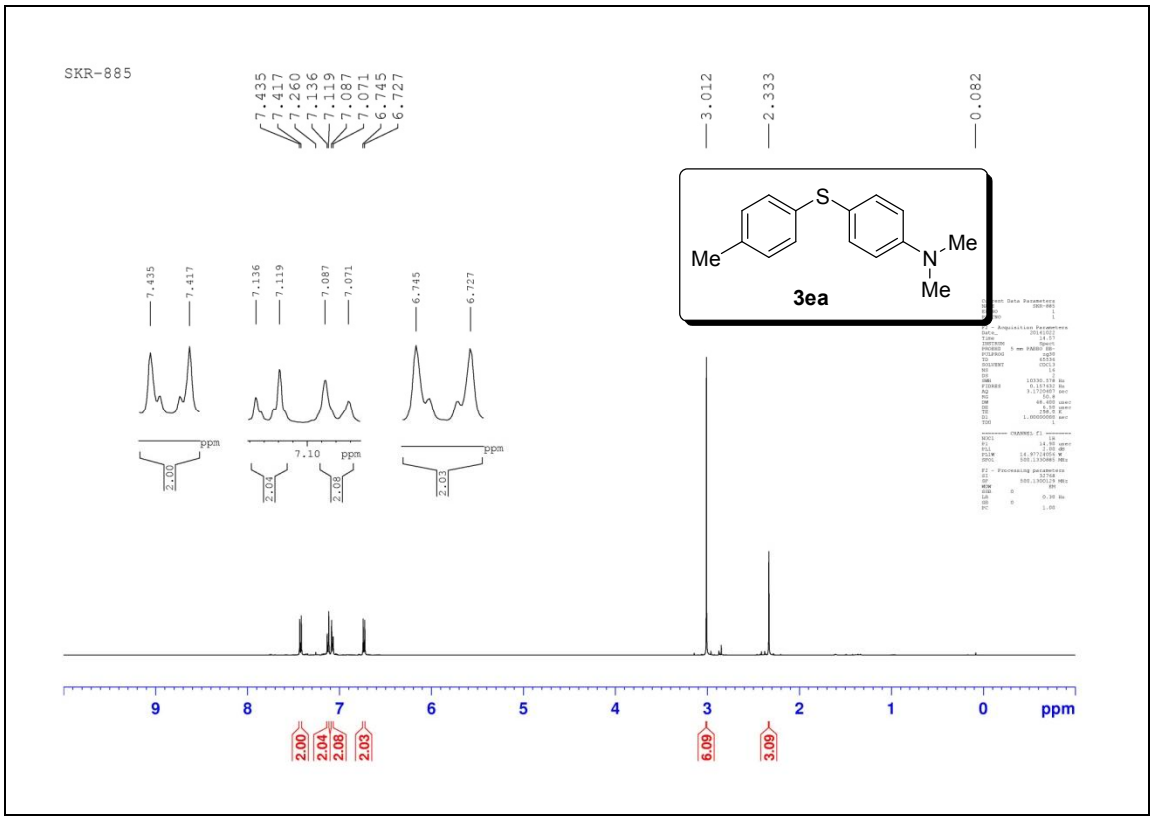
160.93
138.88
129.02
128.80
126.89
95.14
92.81
40.00
39.83
39.67
39.50
39.33
39.17
39.00
OH
S
Cl
HO
OH
3db
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


SKR-871
9.557
9.486
7.373
7.356
6.867
6.850
5.951
2.500
OH
S
Br
HO
OH
3dc
10
9
8
7
6
5
4
3
2
1
0
ppm
1.01
2.01
2.01
2.00
2.00


SKR-871
161.01
160.80
139.47
131.51
127.10
116.85
94.97
92.48
40.00
39.83
39.67
39.50
39.33
39.17
39.00
OH
S
Br
HO
OH
3dc
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


SKR-885
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7.260
7.136
7.119
7.087
7.071
6.745
6.727
3.012
2.333
0.082
Me
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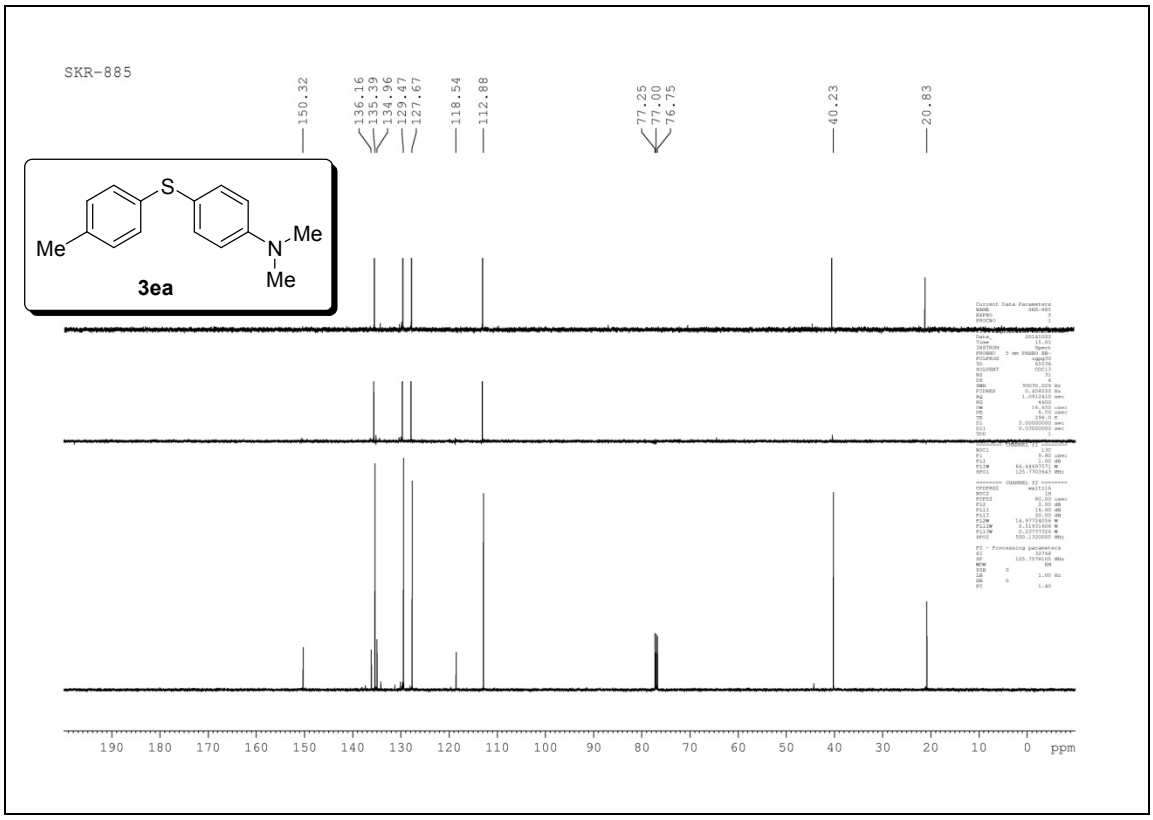
N
Me
Me
3ea
ppm
7.10
2.00
2.04
2.08
2.03
6.09
3.09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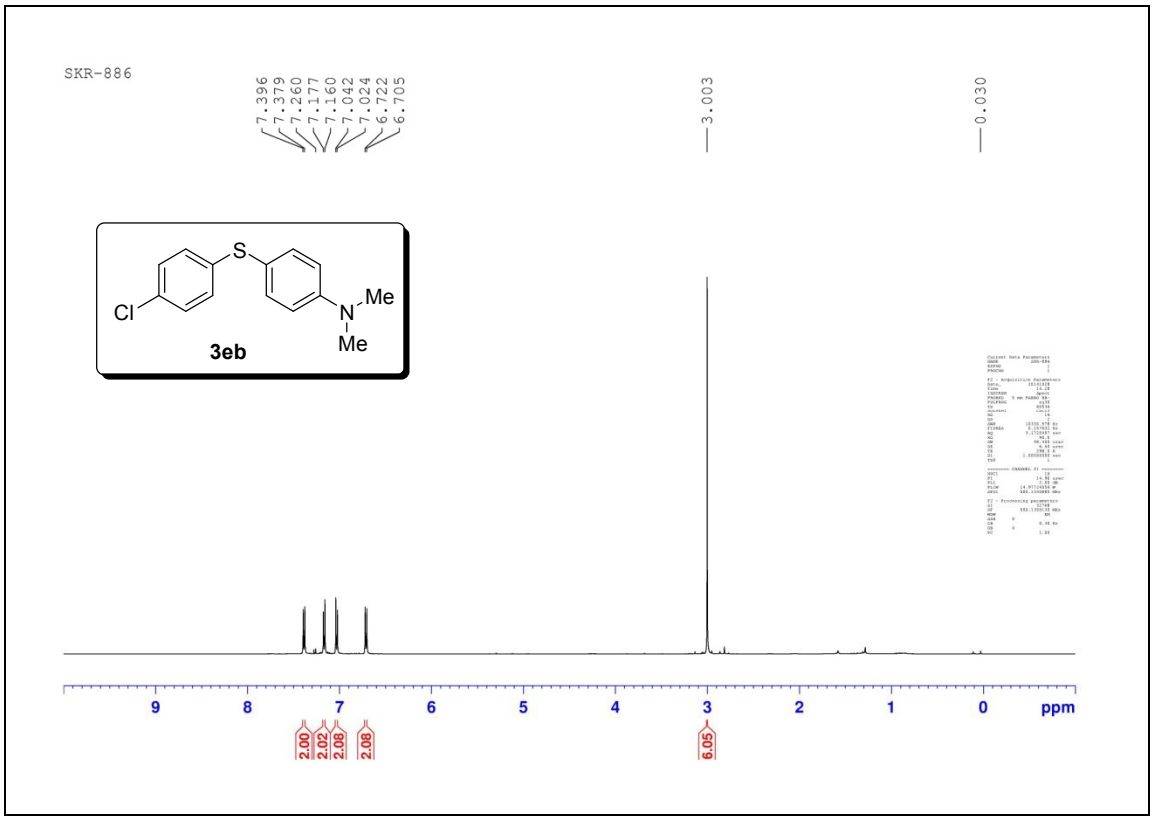
136.16
135.39
134.96
129.47
127.67
118.54
112.88
77.25
77.00
76.75
40.23
20.83
Me
S
N
Me
Me
3ea
ppm


SKR-886
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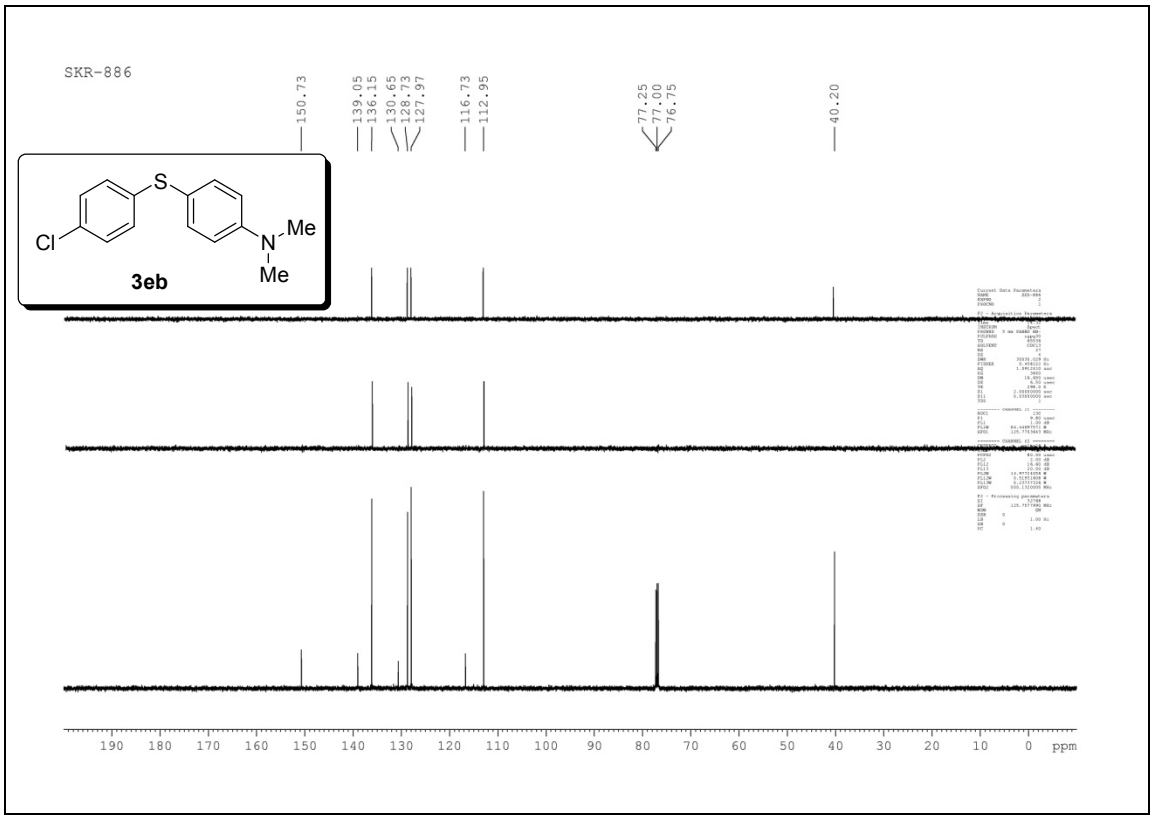
7.379
7.260
7.177
7.160
7.042
7.024
6.722
6.705
3.003
0.030
Cl
S
N
Me
Me
3eb
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.02
2.08
2.08
6.05


SKR-886
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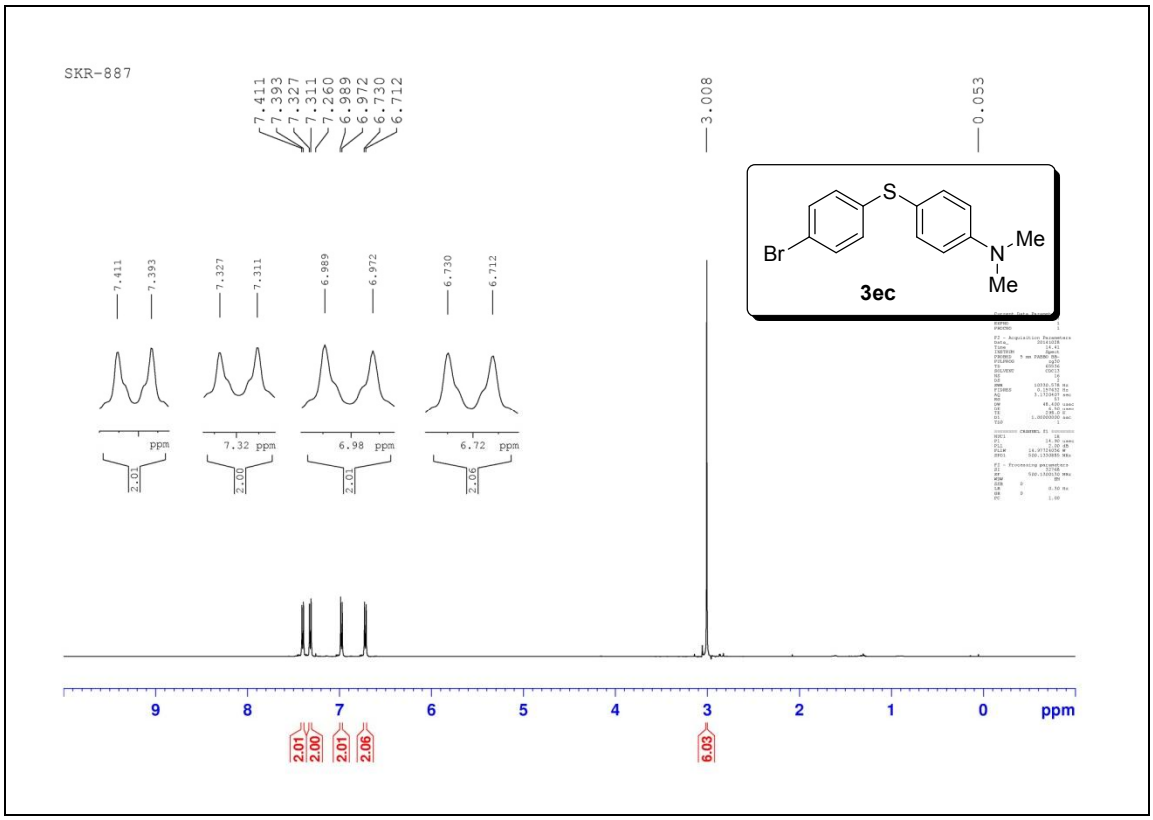
128.73
127.97
116.73
112.95
77.25
77.00
76.75
40.20
Cl
S
N
Me
Me
3eb
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


SKR-887
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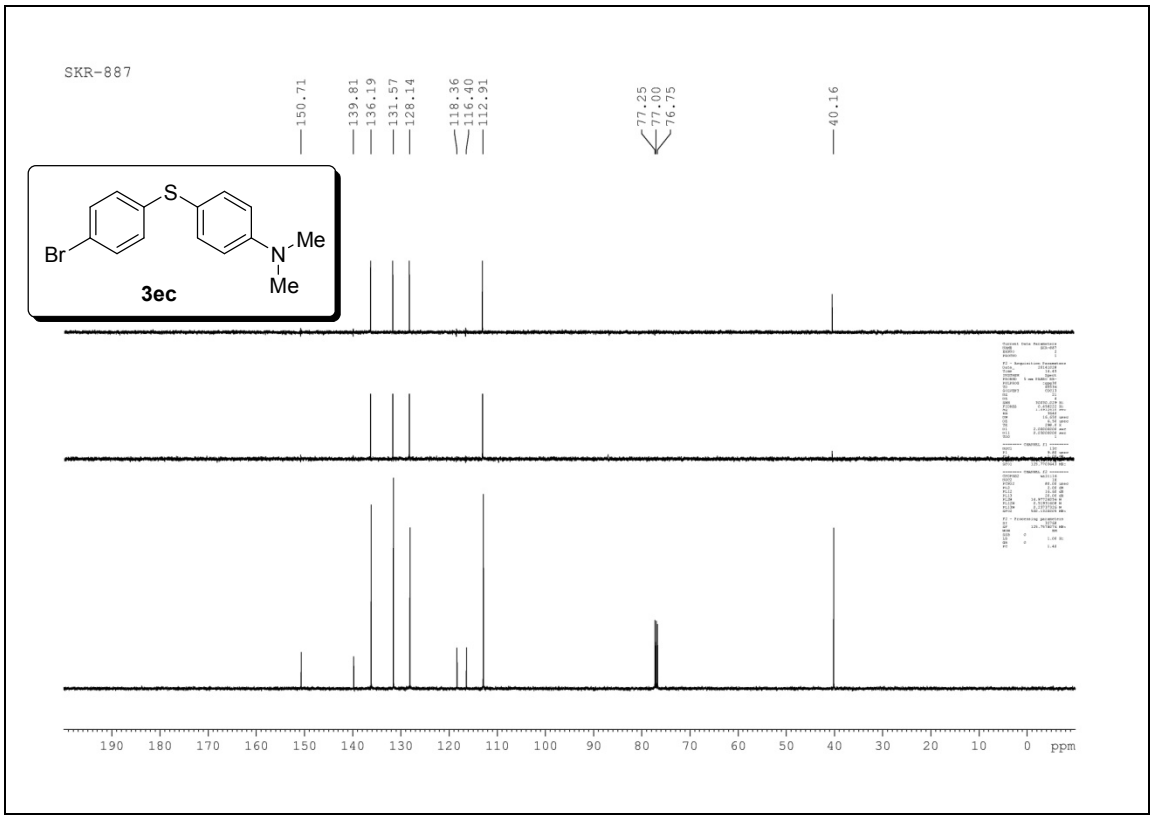
7.393
7.327
7.311
7.260
6.989
6.972
6.730
6.712
3.008
0.053
Br
S
N
Me
Me
3ec
7.32 ppm
6.98 ppm
6.72 ppm
2.01
2.00
2.01
2.06
6.03
9
8
7
6
5
4
3
2
1
0
ppm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118.36
116.40
112.91
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77.00
76.75
40.16
Br
S
N
Me
Me
3ec
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180
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140
130
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60
50
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20
10
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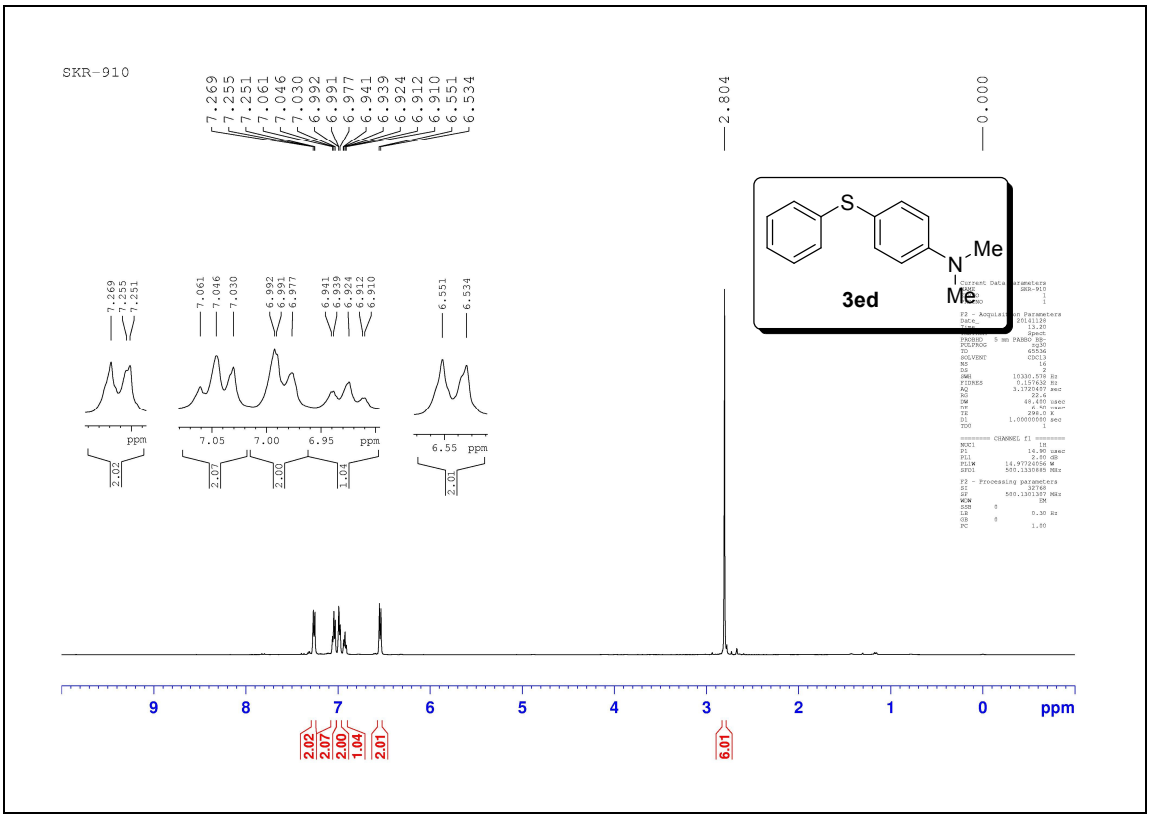
ppm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7.030
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6.991
6.977
6.941
6.939
6.924
6.912
6.910
6.551
6.534
2.804
0.000
S
N
Me
Me
3ed
ppm
7.05
7.00
6.95
6.55
2.02
2.07
2.00
1.04
2.01
9
8
7
6
5
4
3
2
1
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ppm
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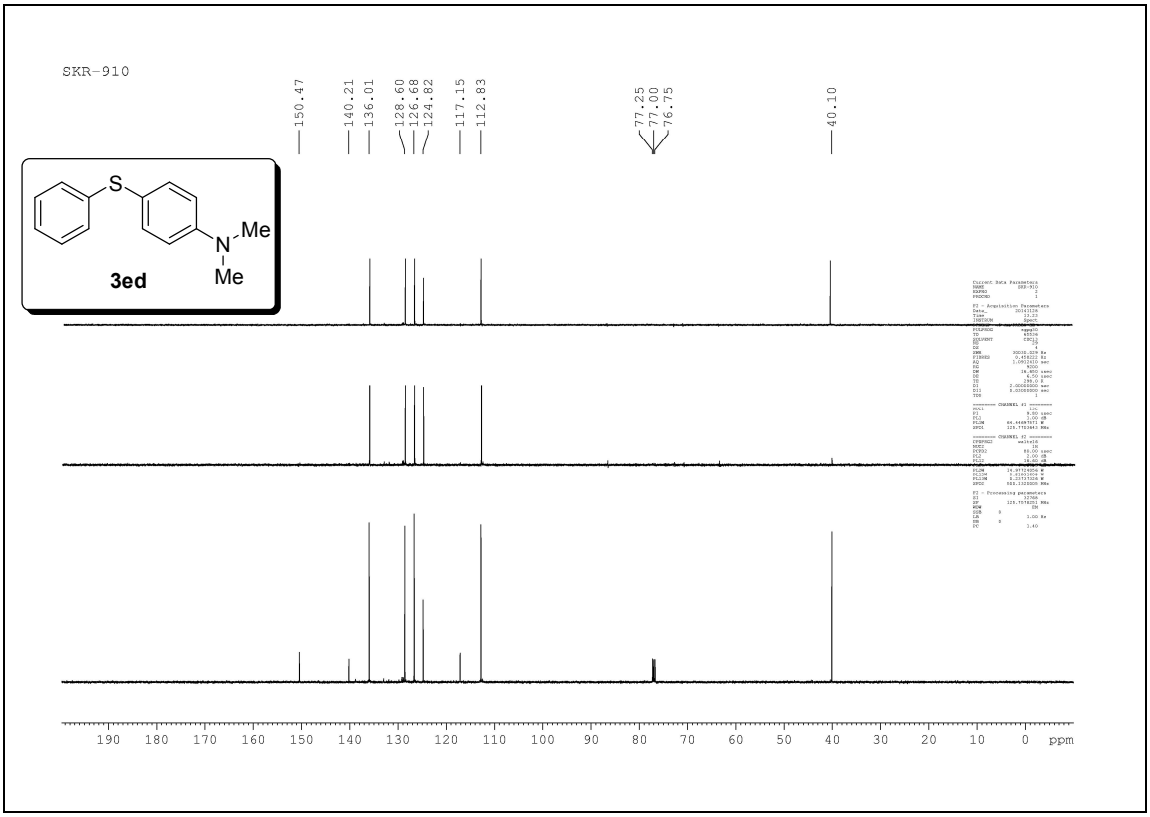
2.07
2.00
1.04
2.01
6.01


SKR-910
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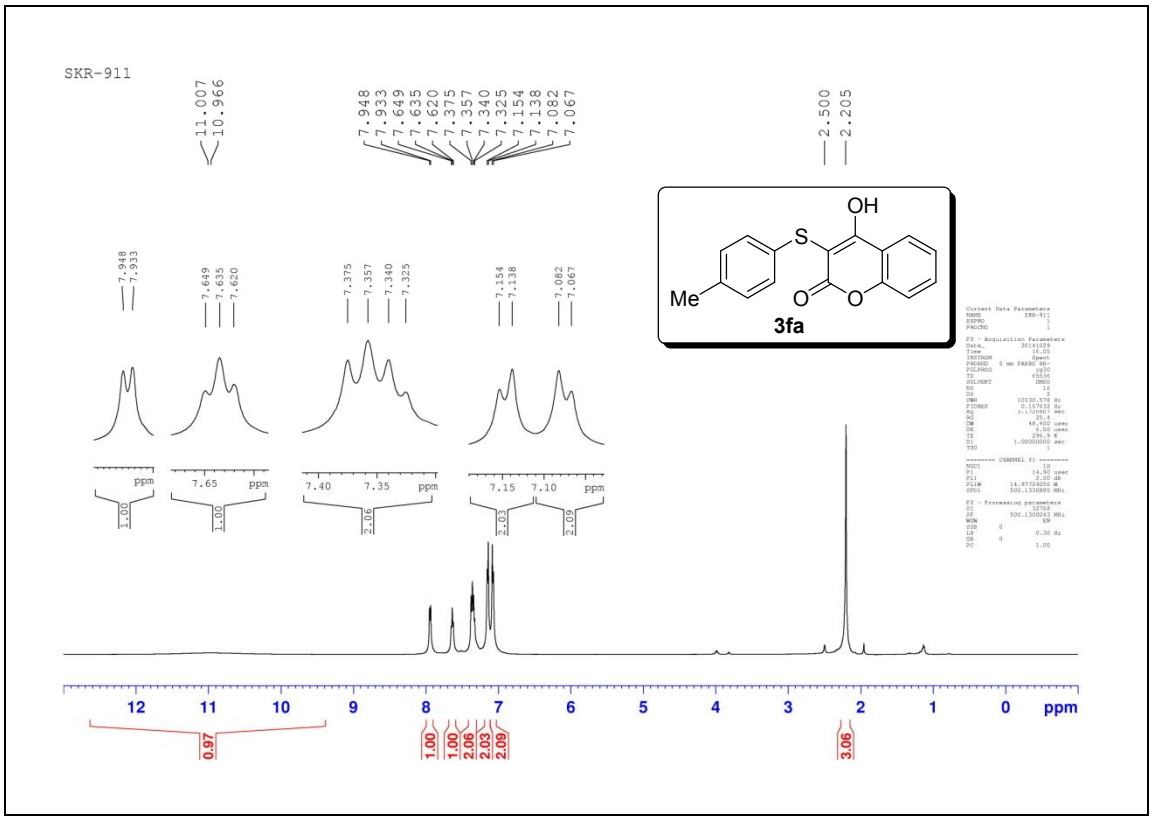
140.21
136.01
128.60
126.68
124.82
117.15
112.83
77.25
77.00
76.75
40.10
S
N
Me
Me
3ed
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


SKR-911
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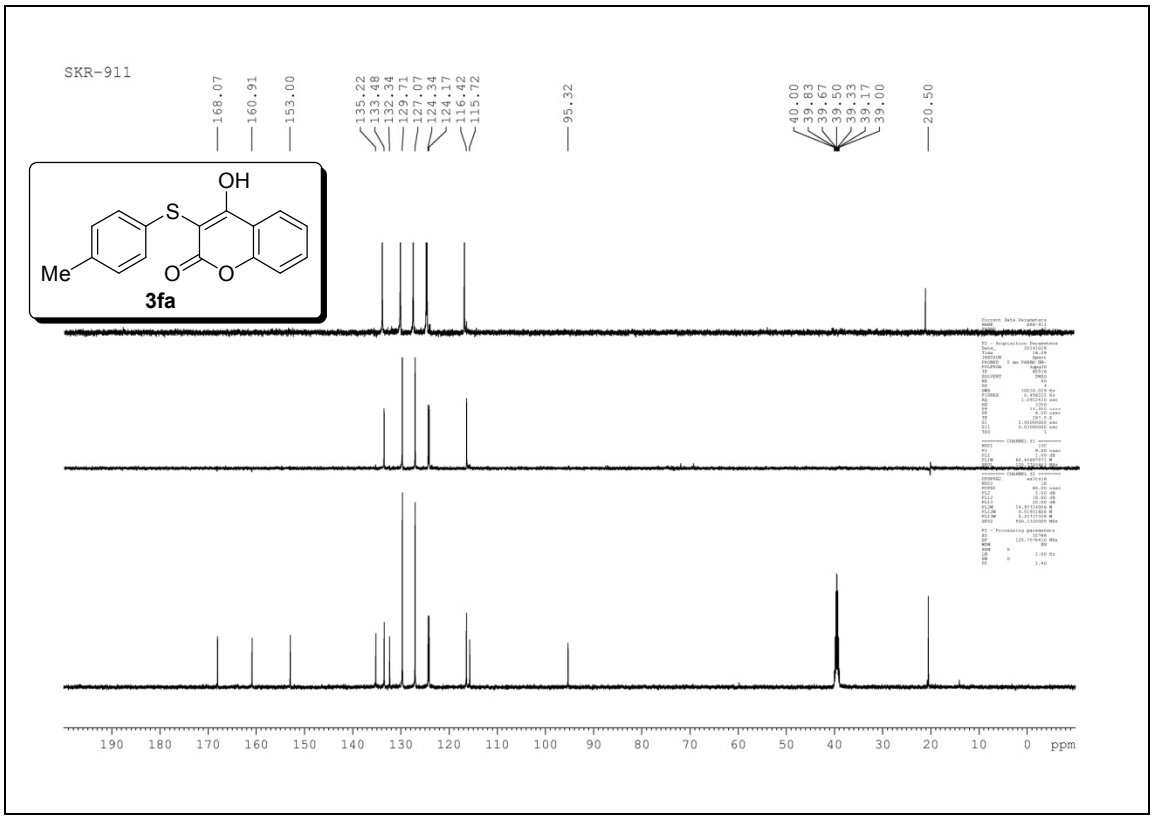
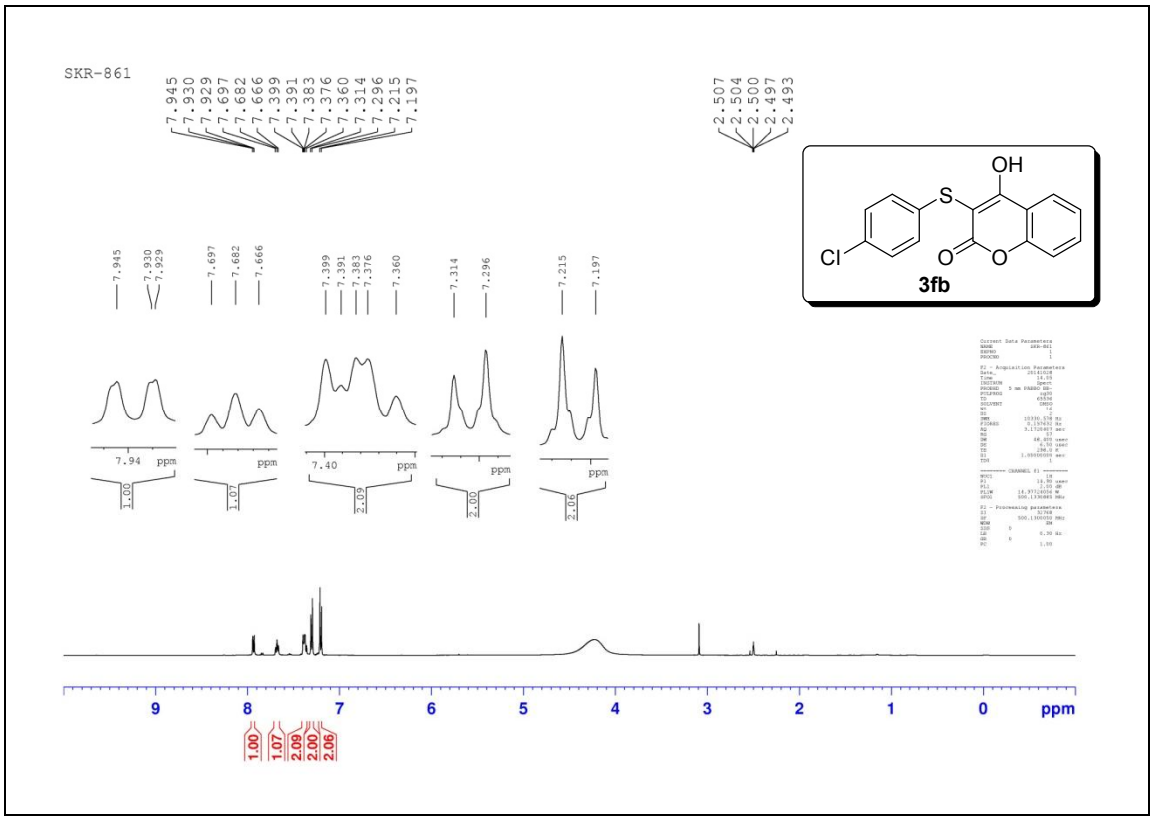
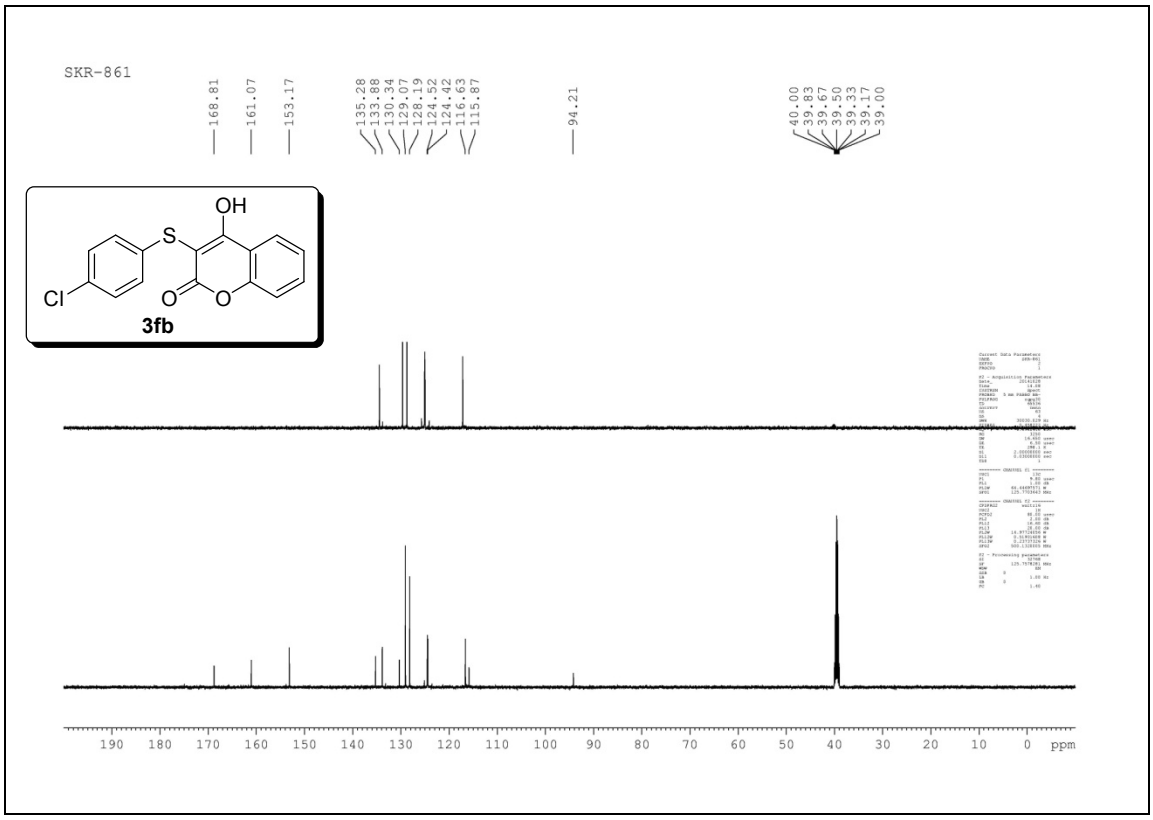
10.966
7.948
7.933
7.649
7.635
7.620
7.375
7.357
7.340
7.325
7.154
7.138
7.082
7.067
2.500
2.205
OH
S
Me
O
O
3fa
ppm
7.65
ppm
7.40
7.35
ppm
7.15
7.10
ppm
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.97
1.00
1.00
2.06
2.03
2.09
3.06


SKR-911
168.07
160.91
153.00
135.22
133.48
132.34
129.71
127.07
124.34
124.17
116.42
115.72
95.32
40.00
39.83
39.67
39.50
39.33
39.17
39.00
20.50
OH
S
Me
O
O
3fa
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


SKR-861
7.945
7.930
7.929
7.697
7.682
7.666
7.399
7.391
7.383
7.376
7.360
7.314
7.296
7.215
7.197
2.507
2.504
2.500
2.497
2.493
OH
S
Cl
O
O
3fb
7.94 ppm
7.40 ppm
1.00
1.07
2.09
2.00
2.06
9
8
7
6
5
4
3
2
1
0
ppm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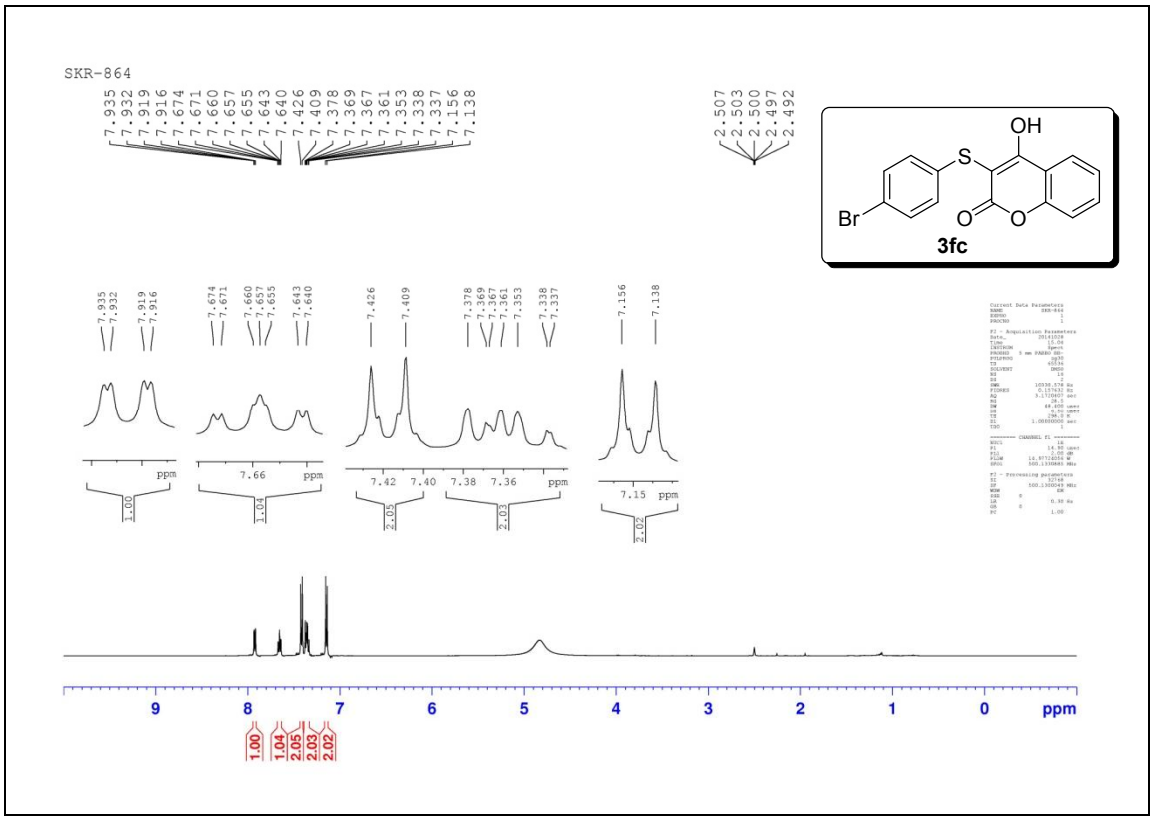
161.07
153.17
135.28
133.88
130.34
129.07
128.19
124.52
124.42
116.63
115.87
94.21
40.00
39.83
39.67
39.50
39.33
39.17
39.00
OH
S
Cl
O
O
3fb
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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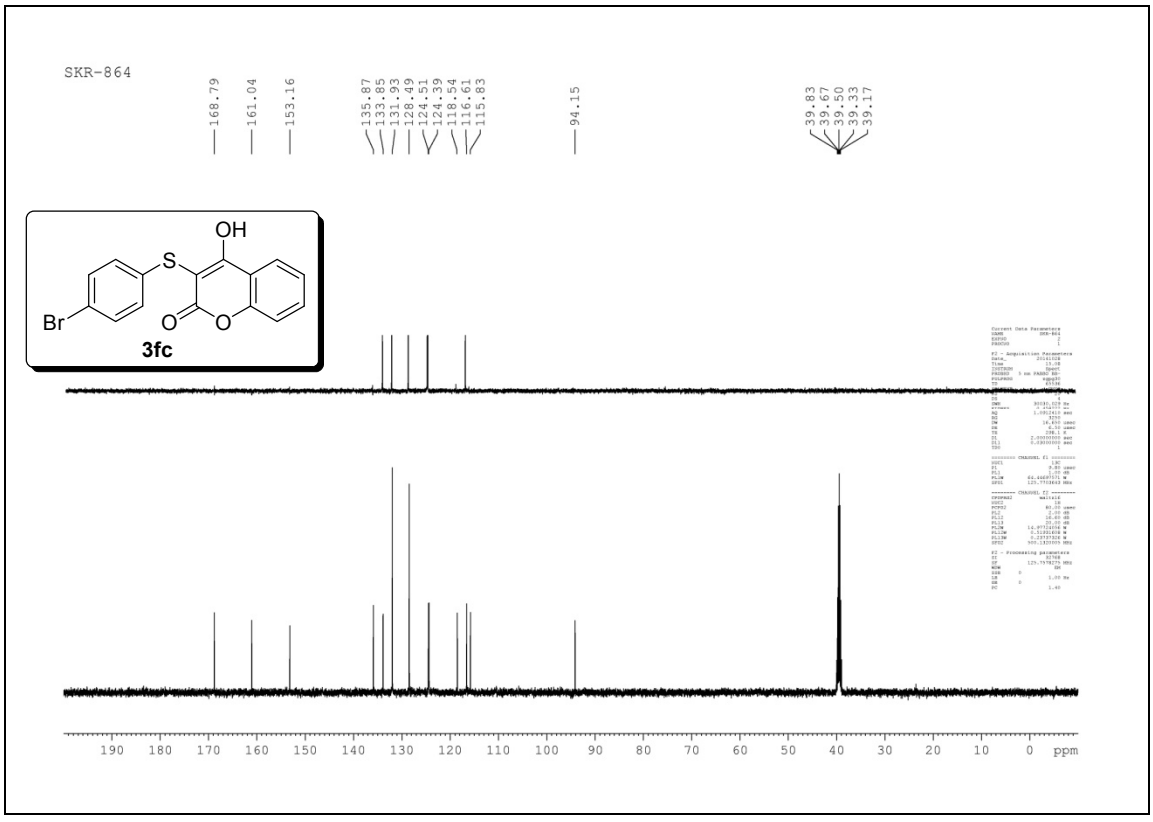
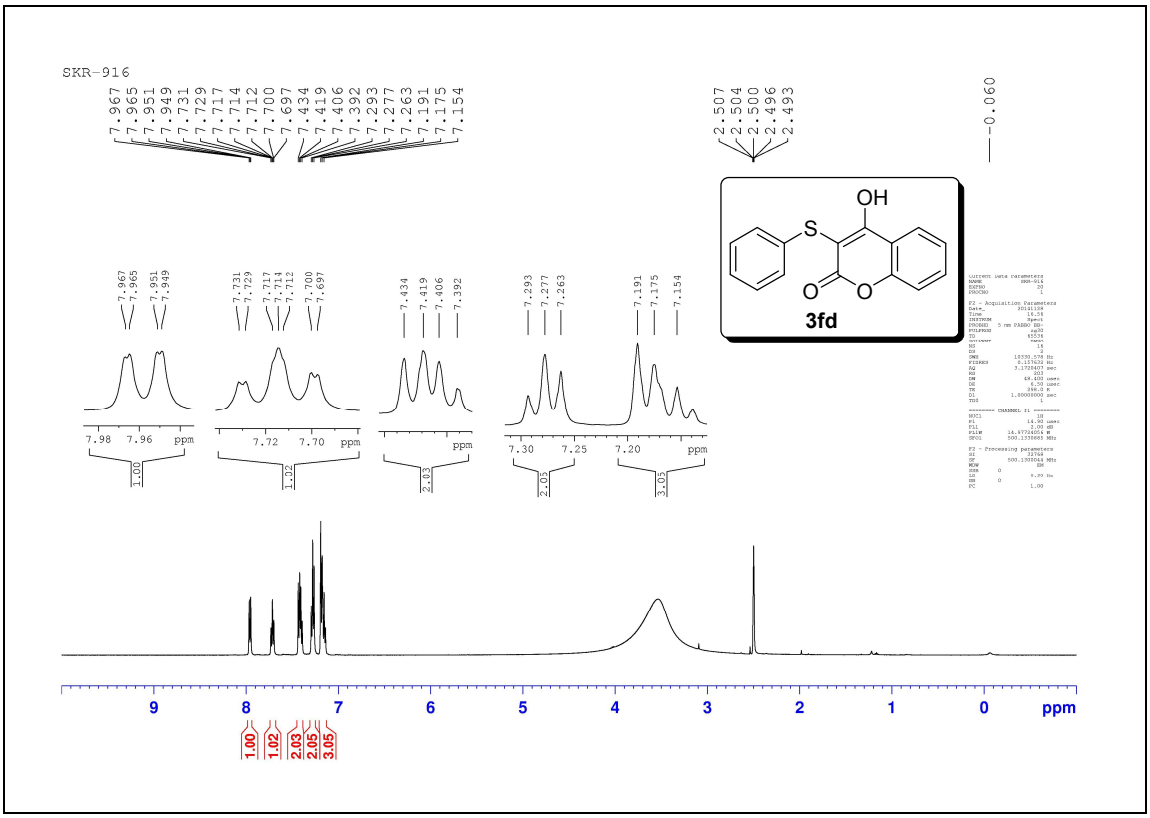
7.932
7.919
7.916
7.674
7.671
7.660
7.657
7.655
7.643
7.640
7.426
7.409
7.378
7.369
7.367
7.361
7.353
7.338
7.337
7.156
7.138
2.507
2.503
2.500
2.497
2.492
OH
S
Br
O
O
3fc
ppm
9
8
7
6
5
4
3
2
1
0
1.00
1.04
2.05
2.03
2.02


SKR-864
168.79
161.04
153.16
135.87
133.85
131.93
128.49
124.51
124.39
118.54
116.61
115.83
94.15
39.83
39.67
39.50
39.33
39.17
OH
S
Br
O
O
3fc
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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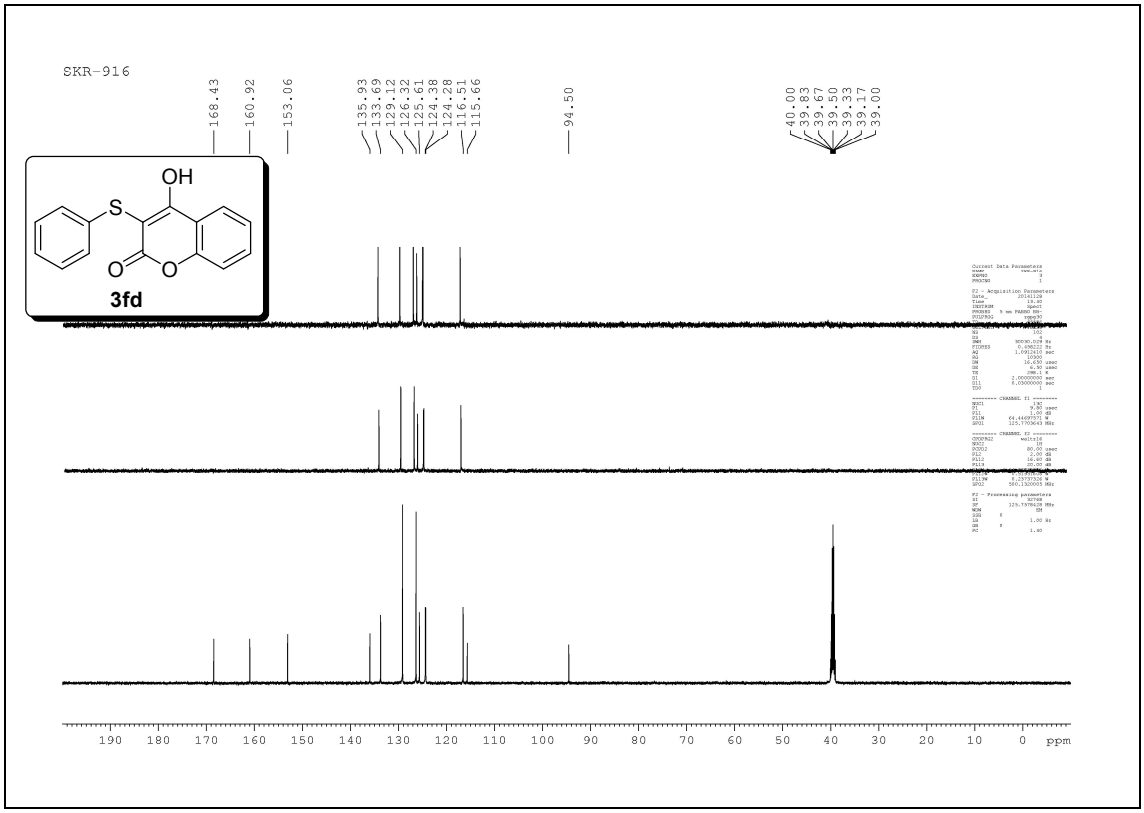
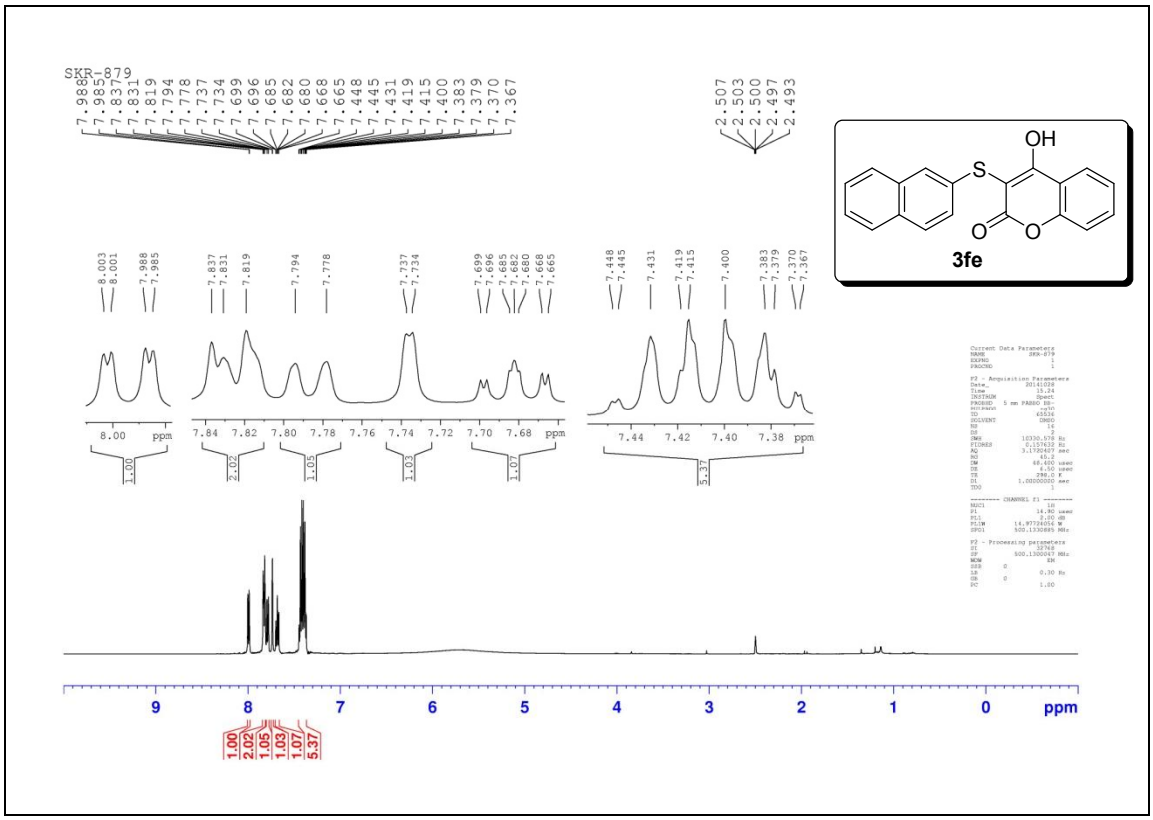
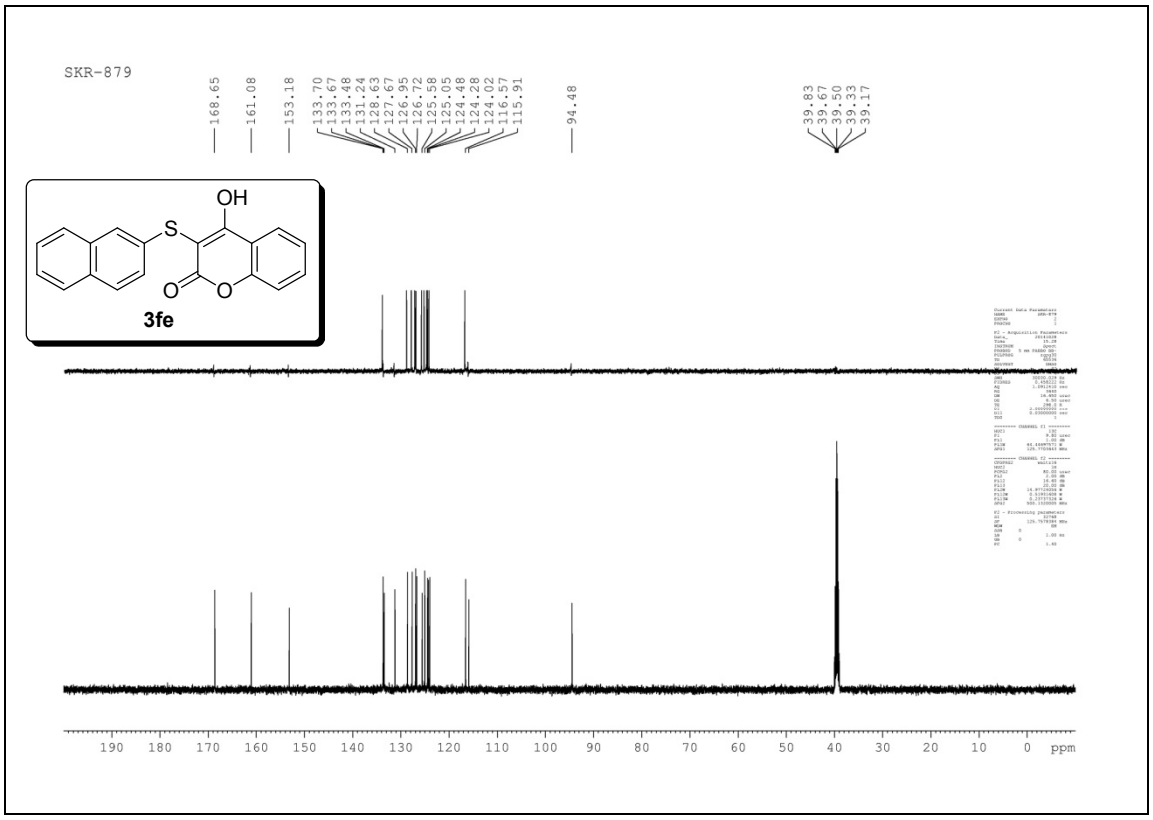
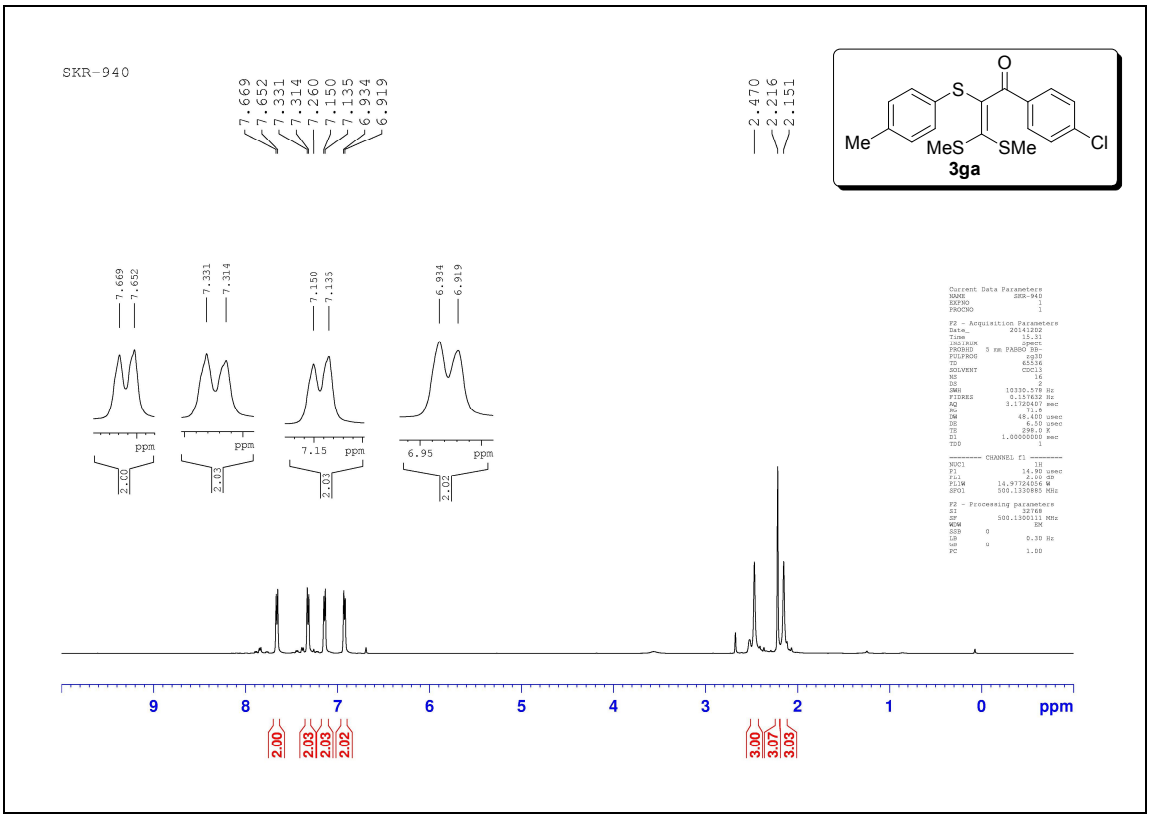
7.967
7.965
7.951
7.949
7.731
7.729
7.717
7.714
7.712
7.700
7.697
7.434
7.419
7.406
7.392
7.293
7.277
7.263
7.191
7.175
7.154
2.507
2.504
2.500
2.496
2.493
0.060
OH
S
O
O
3fd
ppm
1.00
1.02
2.03
2.05
3.05


SKR-916
168.43
160.92
153.06
135.93
133.69
129.12
126.32
125.61
124.38
124.28
116.51
115.66
94.50
40.00
39.83
39.67
39.50
39.33
39.17
39.00
OH
S
O
O
3fd
ppm


SKR-879
7.988 7.985 7.837 7.831 7.819 7.794 7.778 7.737 7.734 7.699 7.696 7.685 7.682 7.680 7.668 7.665 7.448 7.445 7.431 7.419 7.415 7.400 7.383 7.379 7.370 7.367
2.507 2.503 2.500 2.497 2.493
OH
S
O
O
3fe
8.00 ppm
7.84 7.82 7.80 7.78 7.76 7.74 7.72 7.70 7.68 ppm
7.44 7.42 7.40 7.38 ppm
1.00 2.02 1.05 1.03 1.07 5.37
9 8 7 6 5 4 3 2 1 0 ppm


SKR-879
168.65 161.08 153.18 133.70 133.67 133.48 131.24 128.63 127.67 126.95 126.72 126.58 125.05 124.48 124.28 124.02 116.57 115.91 94.48 39.83 39.67 39.50 39.33 39.17
OH
S
O
O
3fe
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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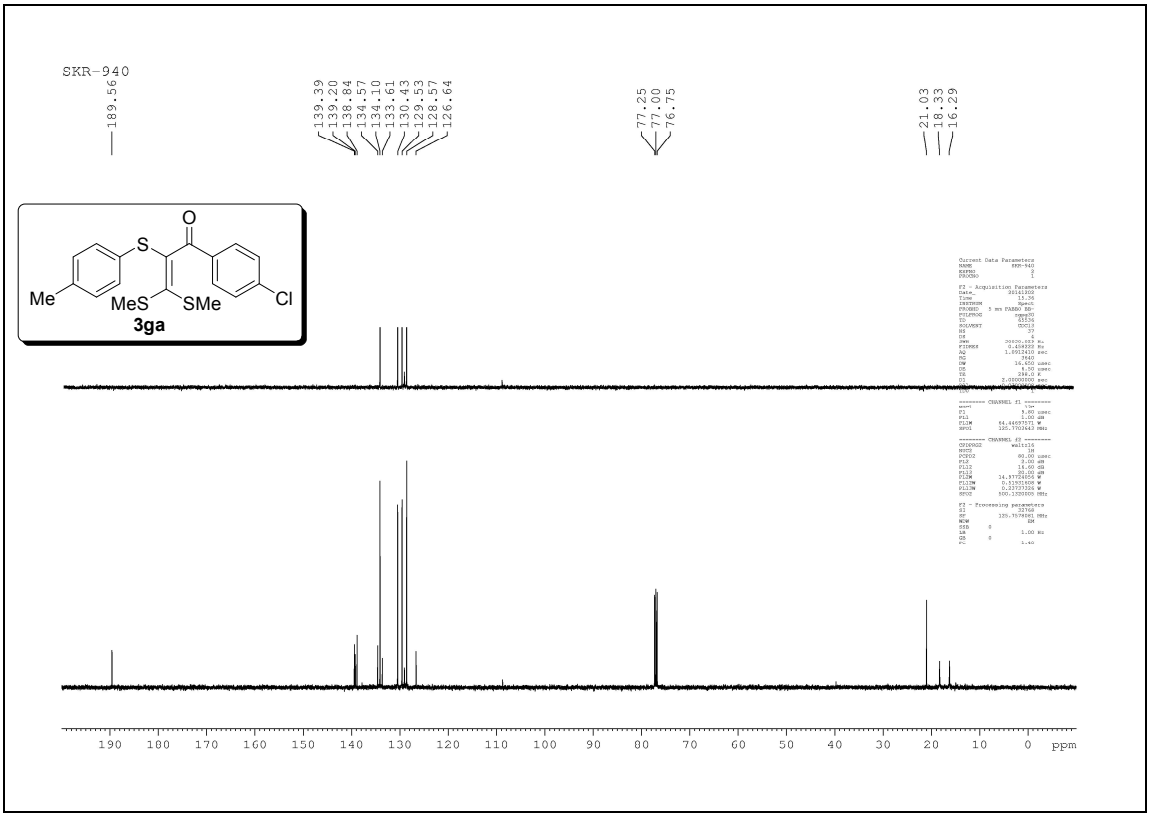
7.331
7.314
7.260
7.150
7.135
6.934
6.919
2.470
2.216
2.151
Me
MeS
SMe
Cl
3ga
ppm
7.15
6.95
2.00
2.03
2.03
2.02
3.00
3.07
3.03


SKR-940
189.56
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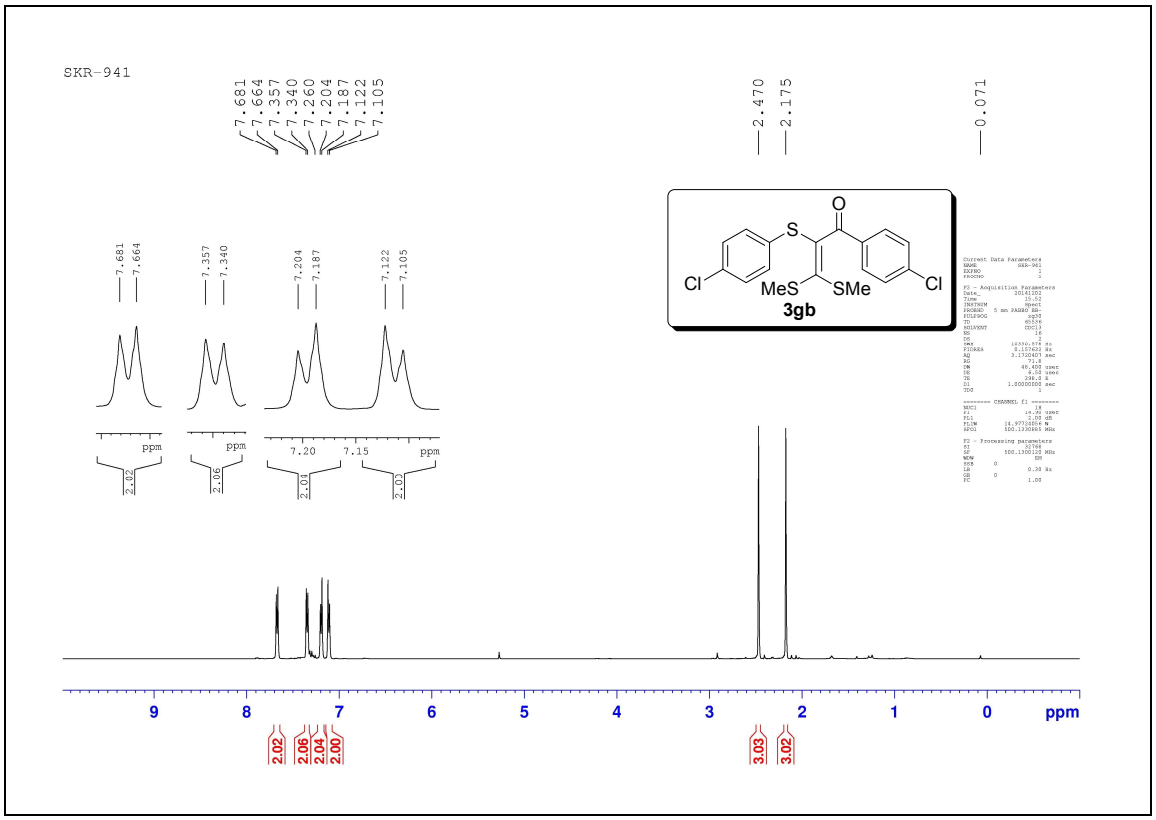
139.20
138.84
134.57
134.10
133.61
130.43
129.53
128.57
126.64
77.25
77.00
76.75
21.03
18.33
16.29
Me
MeS
SMe
Cl
3ga
ppm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7.340
7.204
7.187
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ppm
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2.06
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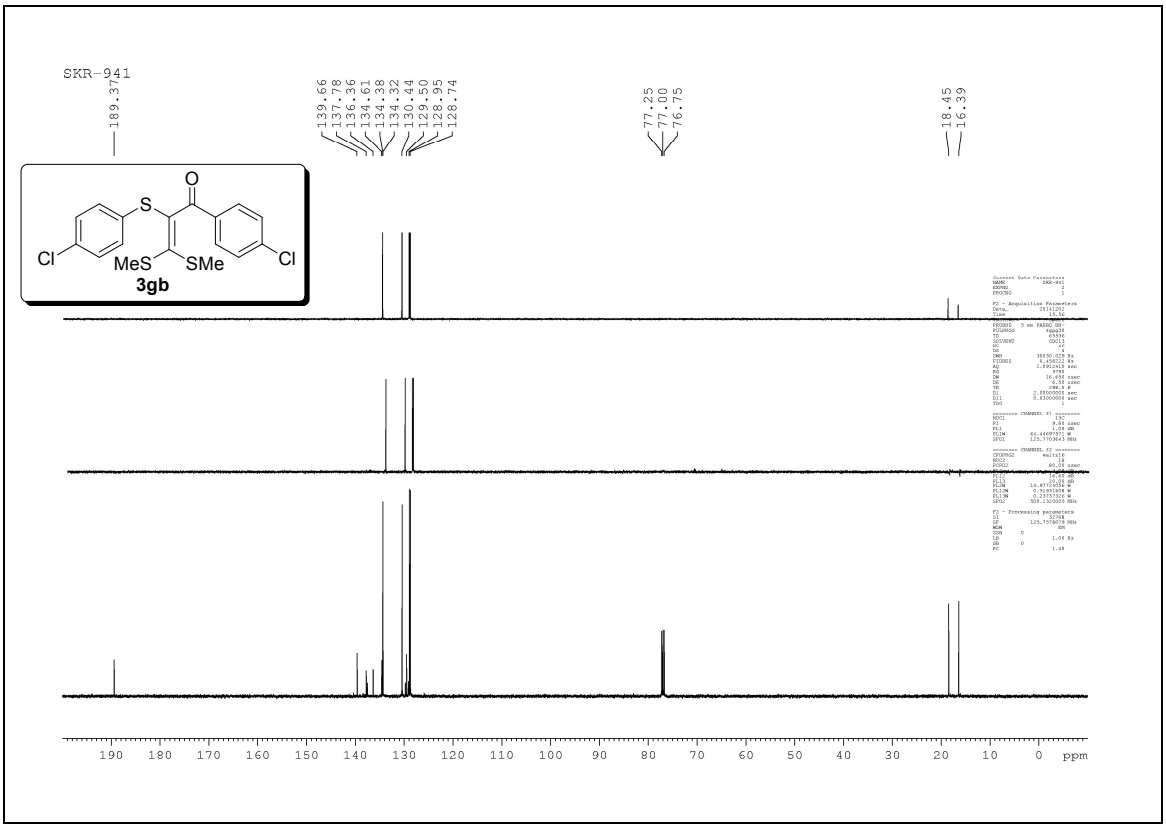
2.00
3.03
3.02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137.78
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134.61
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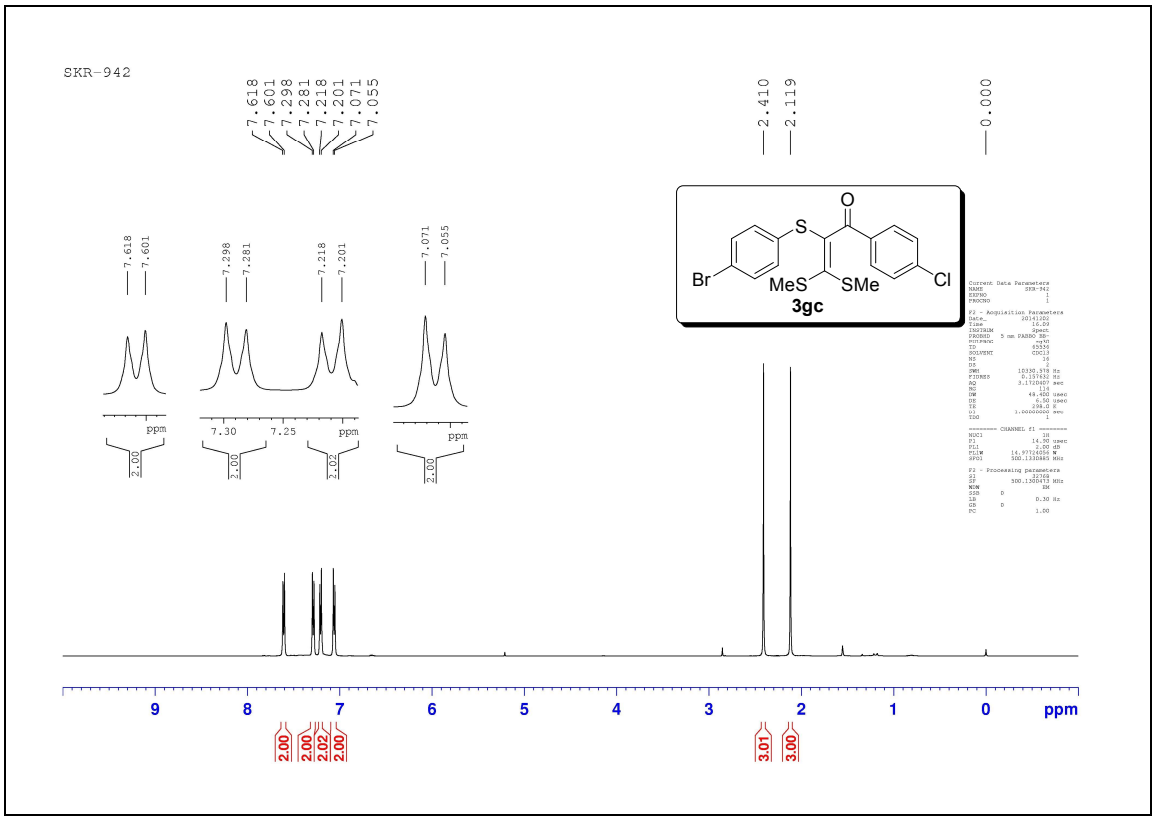
3gb
ppm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7.201
7.071
7.055
2.410
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MeS
SMe
Cl
3gc
ppm
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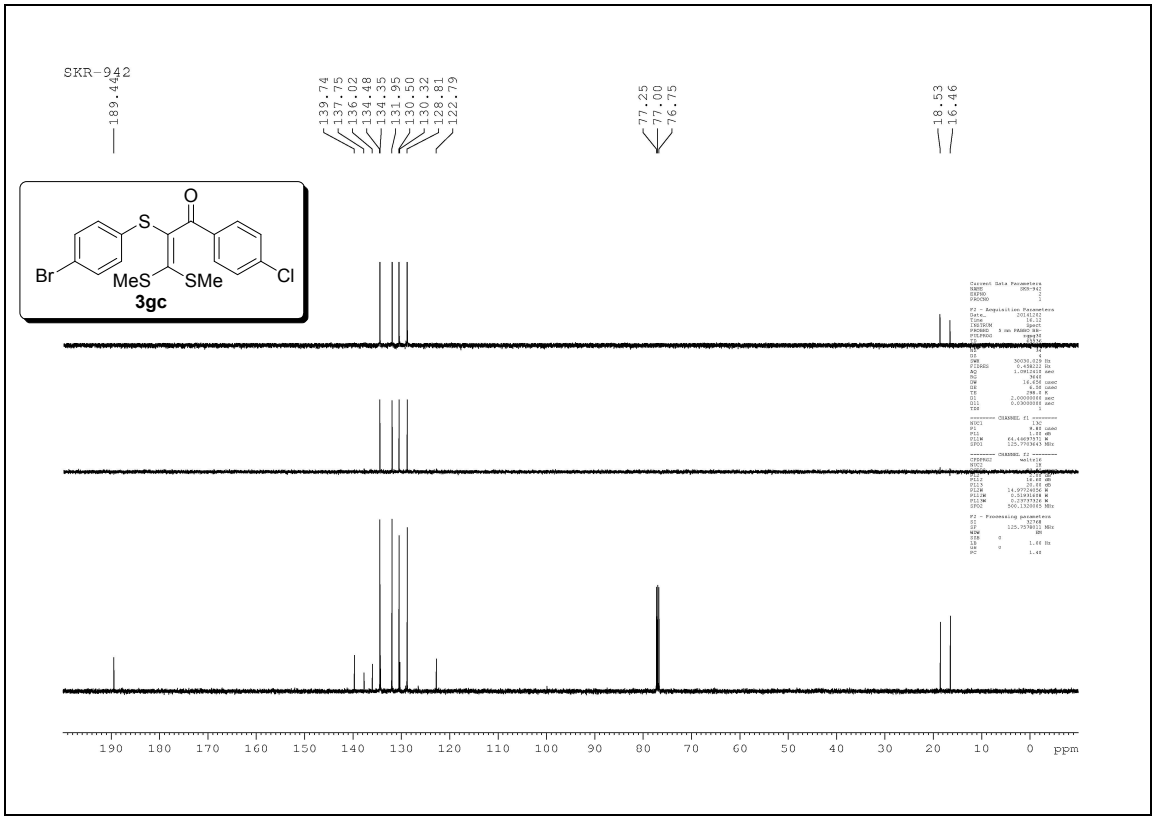
2.00
2.02
2.00
3.01
3.00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134.35
131.95
130.50
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18.53
16.46
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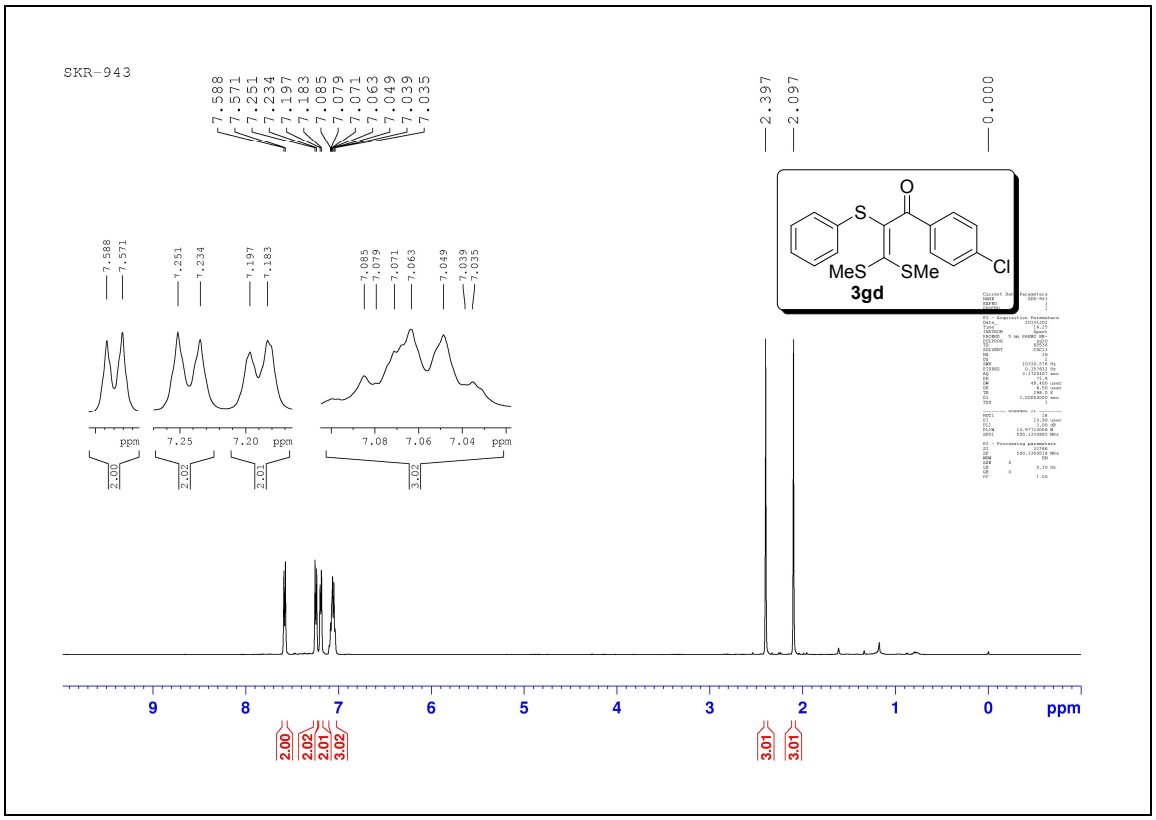
MeS
SMe
Cl
3gc
ppm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7.085
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7.039
7.035
2.397
2.097
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MeS
SMe
Cl
3gd
ppm
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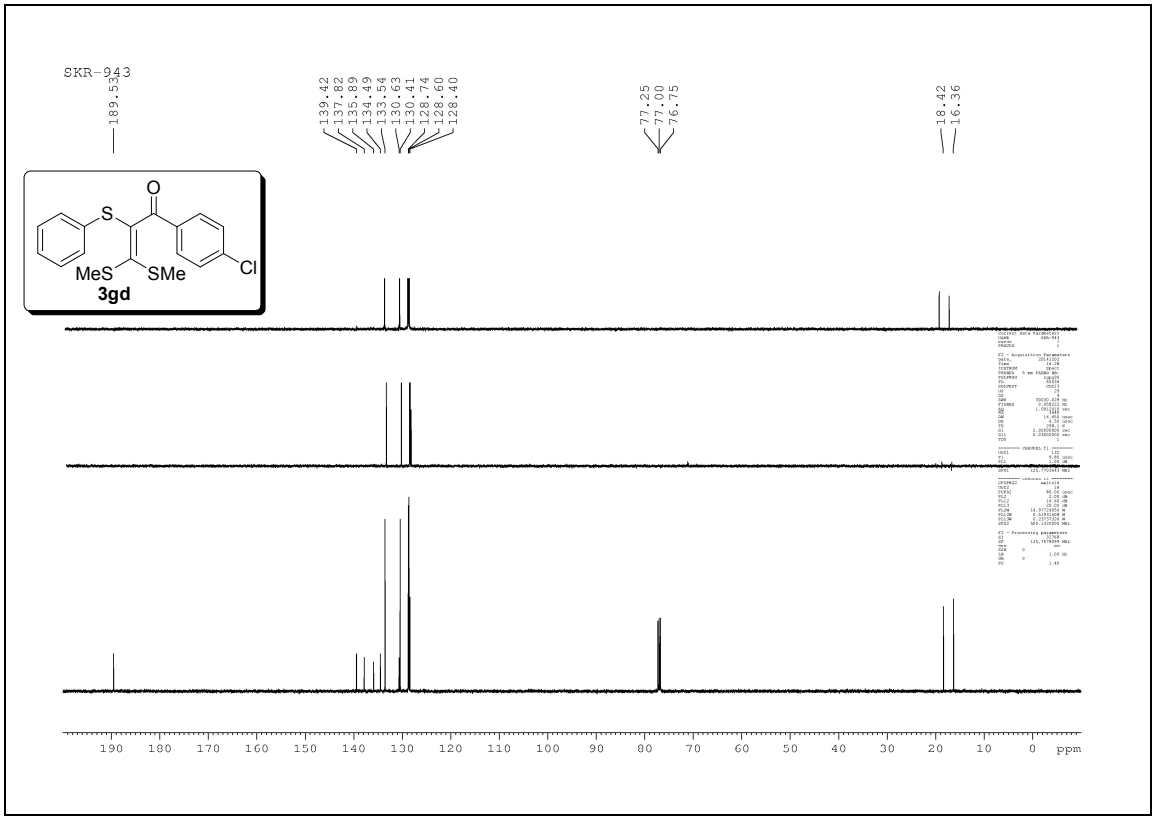
2.02
2.01
3.02
3.01
3.01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134.49
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130.63
130.41
128.74
128.60
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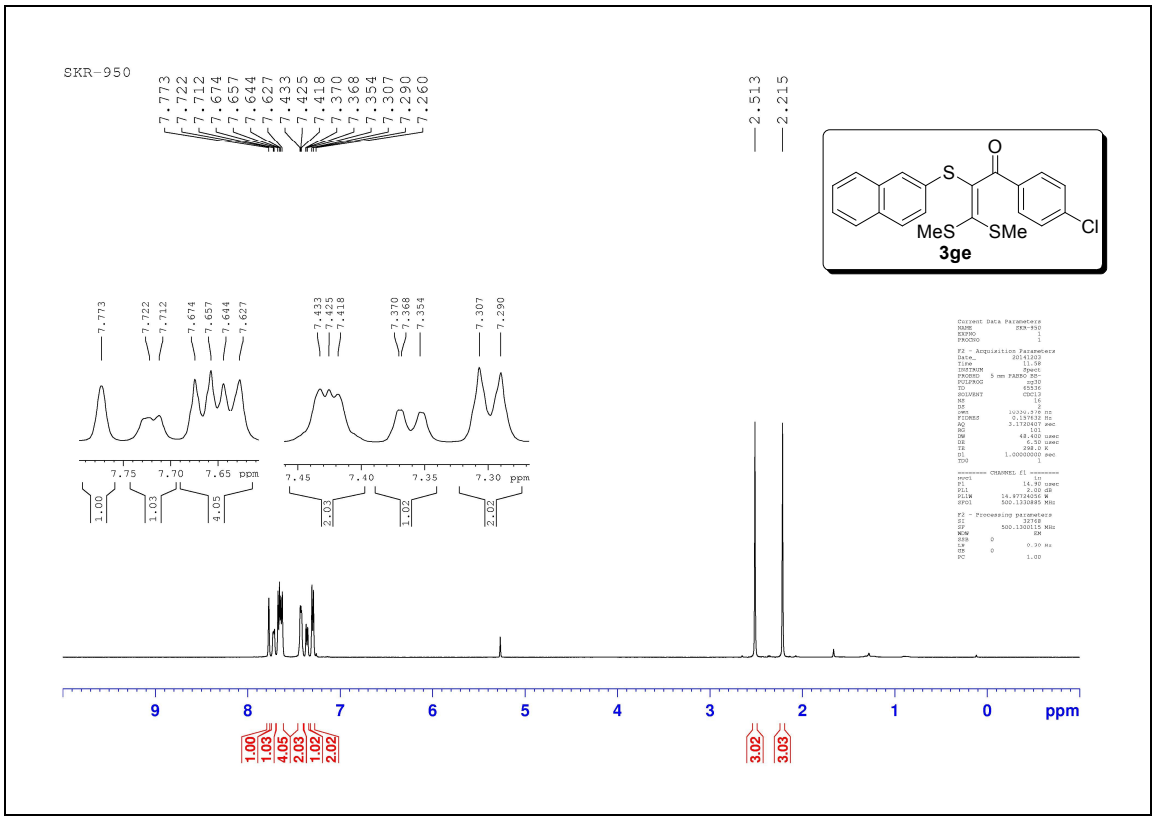
77.25
77.00
76.75
18.42
16.36
O
S
MeS
SMe
Cl
3gd
ppm


SKR-950
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7.627
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7.425
7.418
7.370
7.368
7.354
7.307
7.290
7.260
2.513
2.215
S
O
MeS
SMe
Cl
3ge
ppm
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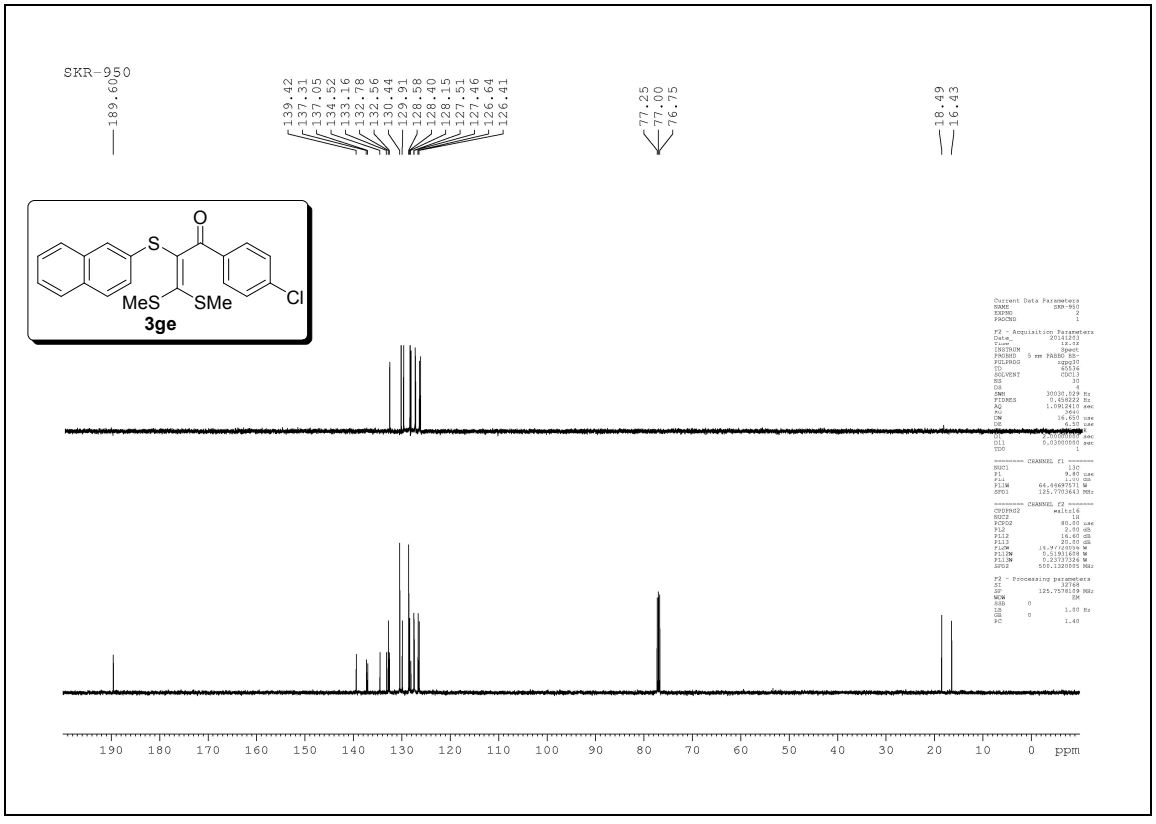
1.03
4.05
2.03
1.02
2.02
3.02
3.03


SKR-950
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129.91
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128.15
127.51
127.46
126.64
126.41
77.25
77.00
76.75
18.49
16.43
S
O
MeS
SMe
Cl
3ge
ppm