Supporting information

Reusable Cobalt-Phthalocyanine in Water: Efficient Catalytic Aerobic Oxidative Coupling of Thiols to Construct S-N/S-S Bonds

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Table of contents

(A) General information:

All thiols and amine reagents used are commercial available, without further purification unless noted. All reactions were carried out in water and oxygen atmosphere or air atmosphere, monitored by thin layer chromatography (TLC). All products were purified by flash chromatography on silica gel. The chemical yields referred are isolated products. ^{1}H NMR and ^{13}C NMR spectra were recorded on 600 MHz Bruker spectrometers (600 MHz for ^{1}H NMR and 150 MHz for ^{13}C NMR) and 400 MHz Bruker spectrometers (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR). Chemical shifts of ^{1}H were reported in part per million relative to the $CDCl_3$ residual peak (δ 7.26) or the$DMSO\text{-}d_6$ residual peak (δ 2.50). Chemical shifts of ^{13}C NMR were reported relative to $CDCl_3$ (δ 77.0) or $DMSO\text{-}d_6$ (δ 39.5). The used abbreviations are as follows: s(singlet), d (doublet), t (triplet), q(quartet), m (multiplet), br(broad). High resolution mass spectra (HRMS) data were measured on a MALDI-FTMS by means of the ESI technique, with accurate masses reported for the molecular ion $[M+H]^+$. The Low resolution mass spectra (LRMS) were performed on the SHIMADZU GCMS-QP 2010 Plus mass spectrometer (Kyoto, Japan) by means of EI technique. The melting points of these compounds were determined by an X-4 micro-melting point apparatus (Beijing, China).

(B) Typical experimental procedures

1). Condition 1: (compounds **3a-3o**): To a reactor (70 mL) was added 2-mercaptobenzothiazole (2 mmol), 0.8 wt% Co catalyst, 10 mL water. The amine was finally added to the reaction mixture under stirring at room temperature. The reactor was charged with oxygen atmosphere up to 0.3 MPa three times. Subsequently, the reactor was stirred under 0.3 MPa O_2at 60 ℃ for 4 h. After cooling to room temperature, the reaction mixture was filtered and washed with 1 mL water. The filter cake was dried and the desired product was obtained through flash chromatography on silica gel with ethyl acetate/hexane (1/10) as eluent. The filtrate was extracted with ethyl acetate (30 mL×3). The combined organic extract phase was dried over Na_2SO_4, and after filtration, the solvent was removed on rotovap under reduced pressure. The resulting residue was purified by flash chromatography on silica gel to givethe isolated productwith ethyl acetate/hexane (1/10) as eluent.The yield of desired product was calculated by combination of the obtained two parts.

2). Condition 2:(**4a**, **4m**, **4n**):To a reactor (70 mL) was added thiol (2 mmol), 0.8 wt% Co catalyst and 10 mL water. The reactor was charged with oxygen up to 0.3 MPa three times. Subsequently, the reaction mixture was stirred under 0.3 MPa O_2 at 60 ℃ for 4 h. (**4a**) After cooling to room temperature, the reaction mixture was filtered and washed with 1 mL water. The filter cake was dried and the desired productwas obtained. (**4m, 4n**) After cooling to room temperature, 10 mL water was added to the reaction mixture and extracted with ethyl acetate (30 mL×3). The combined organic extract phase was dried over Na_2SO_4, and the solvent was removed on rotovap under reduced pressure. The resulting residue was purified by flash chromatography on silica gel to give the desired product.

Condition 3: (compounds **4b-4l**): To aSchlenk tube (50 mL) was added thiol (2mmol), Co catalyst (0.8wt%), and water (10 mL). Subsequently, the reaction mixture was stirred under air atmosphereat 60 ℃and monitored by thin layer chromatography (TLC) until the thiol was converted completely.After cooling to room temperature, 10 mL water was added to the reaction mixture and extracted withethyl acetate (30 mL×3). The combined organic extract phase was dried over Na_2SO_4, and after filtration, the solvent was removed on rotovap under reduced pressure. The resulting residue was purified by flash chromatography on silica gel to give the desired product.

3) Condition 4: (compounds **5a-5d**) To a Schlenk tube (25 mL) were added thiols (**1A**, 1 mmol; 1B, 5 mmol), Co catalyst (0.8 wt%, calculated with **1A**), andwater (5 mL). Subsequently, the reaction mixture was stirred under O_2 atmosphere for 12h at 60 ℃and monitored by thin layer chromatography (TLC) until the thiol (**1A**) was converted completely. After cooling to room temperature, 10 mL water was added to

the reaction mixture and extracted with ethyl acetate (30 mL×3). The combined organic phase was dried over Na_2SO_4, and after filtration, the solvent was removed on rotovapunder reduced pressure. The resulting residue was purified by flash chromatography on silica gel to give the desired product.

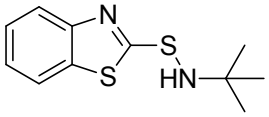
4). Large-scale testing reaction.

Condition 5: To a reactor (200 mL) was added 2-mercaptobenzothiazole (10.02g, 60 mmol), Co catalyst (0.8wt%) and water (100 mL).*tert*-Butylamine (21.94g) was finally added to the reaction mixture under stirring at room temperature. The reactor was charged with oxygen atmosphere up to 0.3 MPa three times. Subsequently, the reactor was stirred under 0.3 MPa O_2 at 60℃until the pressure did not decline any more (replenishing oxygen up to 0.3 MPa promptly if the pressure declined during the reaction period). After cooling to room temperature, the reaction mixture was filtered and washed with 3 mL water. The filter cake was dried and the desired product was obtained(12.11 g). The filtrate was extracted with ethyl acetate (80 mL×3). The combined organic extract phase was dried over Na_2SO_4, and after filtration, the solvent was removed on rotovap under reduced pressure. The resulting residue was purified by flash chromatography on silica gel toget the isolated product (0.87 g) with ethyl acetate/hexane (1/10) as eluent. The yield of desired product was calculated by combination of the obtained two parts, giving 91% as the ultimate yield.

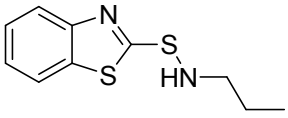
5). The circulation of the mother liquor

Condition 6: To a reactor (70 mL) was added 2-mercaptobenzothiazole (1.00g, 6 mmol), Co catalyst (0.8wt%) and the solvent water (10 mL), *tert*-Butylamine (2.19g, 30 mmol) was finally added to the reaction mixture under stirring at room temperature. The reactor was charged with O_2 up to 0.3 MPa three times. Subsequently, the reactor was stirred under 0.3 MPa O_2 at 60 ℃ for 4 h, replenishing oxygen up to 0.3 MPa promptly if the pressure declined during the reaction period. After cooling to room temperature, the reaction mixture was filtered and washed with 0.5 mL water. The filter cake was dried and the desired product **3a** was obtained, giving the yield up to 92%. The filtrate was reused directly as the solvent in the next run added 2-mercaptobenzothiazole (1.00g, 6.00mmol) and *tert*-butylamine (0.53g, 1.2 equiv.). The results are presented in **Figure 1.**We carried out the oxidation process successfully in 20 runs, with the yields varying as follow: 92%, 91%, 90%, 90%, 90%, 90%, 90%, 90%, 90%, 90%, 89%, 89%, 89%, 89%, 88%, 88%, 87%, 87%, 87%, 86%.

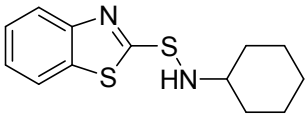
(C)^{1}H and ^{13}C spectra data of all isolated products.



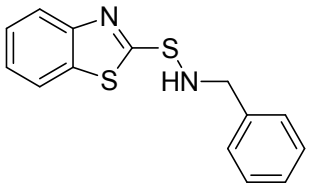
3a: White solid, isolated yield 95%, mp: 105-106℃; ^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si) δ: 7.80 (d, *J*=8.2Hz, 1H), 7.77 (d, *J*=8.0 Hz, 1H), 7.39-7.36 (m, 1H), 7.26-7.23 (m, 1H), 3.43 (s, 1H), 1.27 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$, Me_4Si) δ:181.11, 155.07, 134.87, 125.70, 123.37, 121.40, 120.86, 55.45, 28.96. HRMS (ESI)m/zcalcd. for $C_{11}H_{14}N_2S_2[M+H]^+$: 239.0671, found 239.0675. LRMS (EI) m/z calcd. for $C_{11}H_{14}N_2S_2M^+$: 238, found 238.



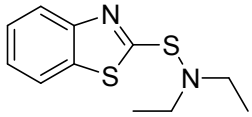
3b: Light yellow solid, isolated yield 81%, mp: 32-33 ℃;^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si) δ: 7.82 (d, *J*=8.1 Hz, 1H), 7.76 (d, *J*=7.9 Hz, 1H), 7.38-7.35 (m, 1H), 7.25-7.21 (m, 1H), 3.41 (t, *J*=5.7 Hz, 1H), 3.07-3.03 (m, 2H), 1.63-1.57 (m, 2H), 0.94 (t, *J*=7.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, Me_4Si) δ:178.81, 154.75, 134.79, 125.62, 123.36, 121.28, 120.85, 54.58, 23.56, 11.07.HRMS (ESI) m/z calcd. for $C_{10}H_{12}N_2S_2$ $[M+H]^+$: 225.0515, found 225.0515. LRMS (EI) m/z calcd. for $C_{10}H_{12}N_2S_2M^+$: 224, found 224.



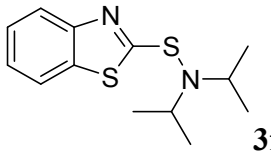
3c: White solid, isolated yield 90%, mp: 94-96 ℃; ^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si) δ: 7.80 (d, *J* = 8.1 Hz, 1H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.39-7.36 (m, 1H), 7.26-7.23 (m, 1H), 3.26 (d, *J* = 4.3 Hz, 1H), 2.91-2.87 (m, 1H), 2.08-2.06 (m, 2H), 1.77-1.74 (m, 2H), 1.62-1.59 (m, 1H), 1.28-1.15 (m, 5H); ^{13}C NMR (150 MHz, $CDCl_3$, Me_4Si) δ: 179.86, 155.04, 134.93, 125.74, 123.45, 121.45, 120.91, 60.21, 33.66, 25.57, 24.81. HRMS (ESI) m/z calcd. for $C_{13}H_{16}N_2S_2$ $[M+H]^+$: 265.0828, found 265.0830.LRMS (EI) m/z calcd. for $C_{13}H_{16}N_2S_2M^+$: 264, found 264.



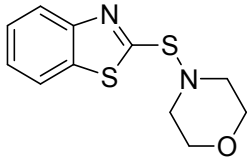
3d: White solid, isolated yield 92%, mp: 116-117 ℃; ^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si) δ: 7.87 (d, *J* = 8.2 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.44-7.38 (m, 5H), 7.35-7.28 (m, 2H), 4.27 (d, *J* = 6.0 Hz, 2H), 3.66 (t, *J* = 6.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$, Me_4Si) δ: 177.42, 154.69, 138.35, 134.88, 128.55, 128.27, 127.80, 125.79, 123.60, 121.48, 120.99, 56.84. HRMS (ESI) m/z calcd. for $C_{14}H_{12}N_2S_2$ $[M+H]^+$: 273.0515, found 273.0518. LRMS (EI) m/z calcd. for $C_{14}H_{12}N_2S_2M^+$: 272, found 272.



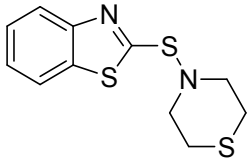
3e:Light yellow oil, isolated yield 76%; ^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si) δ: 7.80 (d, *J*=8.1 Hz, 1H), 7.77 (d,*J* = 7.9 Hz, 1H), 7.39-7.36 (m, 1H), 7.26-7.23 (m, 1H), 3.16 (q, *J*=7.1 Hz, 4H), 1.25 (t, *J*=7.1 Hz, 6H);^{13}C NMR (150 MHz, $CDCl_3$, Me_4Si) δ:179.13, 155.14, 134.95, 125.71, 123.41, 121.43, 120.85, 52.43, 13.43. HRMS (ESI) m/z calcd. for $C_{11}H_{14}N_2S_2$ $[M+H]^+$: 239.0671, found 239.0673. LRMS (EI) m/z calcd. for $C_{11}H_{14}N_2S_2M^+$: 238, found 238.



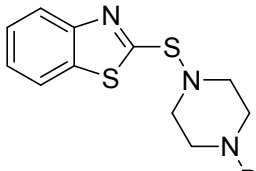
3f: White solid, isolated yield 71%, mp: 56-58℃; ^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si) δ:7.71 (d, *J*=8.0 Hz, 1H), 7.67 (d, *J*=7.7 Hz, 1H), 7.30-7.28 (m, 1H), 7.17-7.14 (m, 1H), 3.42-3.37 (m, 2H), 1.18-1.17 (m, 12H); ^{13}C NMR (150 MHz, $CDCl_3$, Me_4Si) δ:182.19, 155.05, 134.70, 125.69, 123.33, 121.31, 120.79, 55.65, 22.44, 21.62. HRMS (ESI) m/z calcd. for $C_{13}H_{18}N_2S_2$ $[M+H]^+$: 267.0984, found 267.0986. LRMS (EI) m/z calcd. for $C_{13}H_{18}N_2S_2M^+$: 266, found 266.



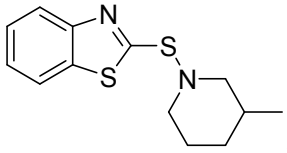
3g: White solid, isolated yield 78%, mp: 80-82 ℃; ^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si) δ:7.85 (d, *J*=8.1 Hz, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.42-7.39 (m, 1H), 7.30-7.27 (m, 1H), 3.82 (t, *J* = 4.7 Hz, 4H), 3.28 (m, *J* = 4.7 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$, Me_4Si) δ:174.73, 154.98, 134.96, 125.93, 123.88, 121.82, 120.98, 67.82, 56.52. HRMS (ESI) m/z calcd for $C_{11}H_{12}N_2OS_2$ $[M+H]^+$: 253.0464, found 253.0467.LRMS (EI) m/z calcd. for $C_{11}H_{12}N_2OS_2M^+$: 252, found 252.



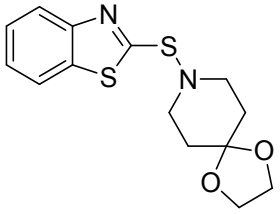
3h: White solid, isolated yield 96%, mp: 61-62 ℃; ^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si) δ:7.84 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.42-7.38 (m, 1H), 7.29-7.26 (m, 1H), 3.55 (br, 4H), 2.80-2.77 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$, Me_4Si) δ:175.61, 155.11, 134.95, 125.91, 123.82, 121.80, 120.97, 58.57, 28.50. HRMS (ESI) m/z calcd. for $C_{11}H_{12}N_2S_3$ $[M+H]^+$: 269.0235, found 269.0237.LRMS (EI) m/z calcd. for $C_{11}H_{12}N_2S_3$ M^+: 268, found 268.



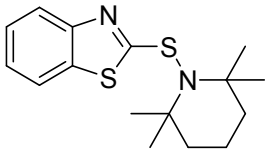
3i: White solid, isolated yield 91%, mp: 103-104 ℃; ^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si) δ:7.84 (d, *J* = 8.2 Hz, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.41-7.38 (m, 1H), 7.29-7.26 (m, 1H), 3.57-3.56 (m, 4H), 3.23 (br, 4H), 1.47 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$, Me_4Si) δ:174.62, 154.96, 154.51, 134.99, 125.94, 123.90, 121.84, 120.98, 80.13, 56.16 (2C), 28.35.HRMS (ESI) m/z calcd. for $C_{16}H_{21}N_3O_2S_2$ $[M+H]^+$: 352.1148, found 352.1150.



3j: Light yellow oil, isolated yield 79%; ^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si) δ:7.82 (d, *J* = 7.9 Hz, 1H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.40-7.36 (m, 1H), 7.27-7.24 (m, 1H), 3.29-3.25 (m, 2H), 3.08-3.05 (m, 1H), 2.76 (t, *J* = 10.9 Hz, 1H), 1.89-1.85 (m, 1H), 1.76-1.73 (m, 3H), 1.00-0.96 (m, 1H), 0.90 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, Me_4Si) δ:177.46, 155.23, 135.15, 125.71, 123.49, 121.60, 120.91, 64.85, 57.41, 32.62, 31.60, 26.63, 19.16.HRMS (ESI) m/z calcd. for $C_{13}H_{16}N_2S_2$ $[M+H]^+$: 265.0828, found 265.0831. LRMS (EI) m/z calcd. for $C_{13}H_{16}N_2S_2M^+$: 264, found 264.

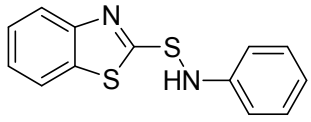


3k: White solid, isolated yield 81%, mp: 110-111℃; ^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si) δ: 7.82 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.40-7.37 (m, 1H), 7.28-7.25 (m, 1H), 3.97 (br, 4H), 3.38 (t, *J* = 5.5 Hz, 4H), 1.89 (t, *J* = 5.6 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$, Me_4Si) δ: 176.76, 155.22, 135.13, 125.79, 123.61, 121.68, 120.96, 105.75, 64.34, 55.14, 36.06. HRMS (ESI) m/z calcd. for $C_{14}H_{16}N_2O_2S_2[M+H]^+$:309.0726, found 309.0732.LRMS (EI) m/z calcd. for $C_{14}H_{16}N_2O_2S_2$ M^+: 308, found 308.

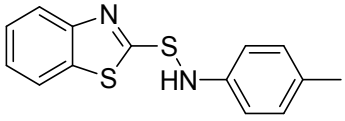


3l: White solid, isolated yield 19%, mp: 136-138 ℃; ^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si) δ: 7.79 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.39-7.36 (m, 1H), 7.26-7.23 (m, 1H), 1.74-1.71 (m, 5H), 1.57-1.54 (m, 1H), 1.41 (s, 6H), 1.27 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$, Me_4Si) δ: 182.14, 154.52, 134.60, 125.69, 123.31, 121.33, 120.71, 61.04, 40.72, 32.48, 24.85, 17.26. HRMS (ESI) m/z calcd. for

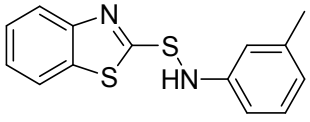
$C_{16}H_{22}N_2S_2$ [M+H]$^+$: 307.1297, found 307.1307. LRMS (EI) m/z calcd. for $C_{16}H_{22}N_2S_2M^+$: 306, found 306.



3m: Light yellow solid, isolated yield 59%, mp: 119-121℃;^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si) δ: 7.88 (d, *J* = 8.2 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.44-7.41 (m,1H), 7.30-7.26 (m, 3H), 7.13-7.12 (m, 2H), 6.98 (t, *J* = 7.3 Hz, 1H), 5.61 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si) δ: 176.27, 154.72, 144.90, 134.88, 129.43, 126.10, 124.02, 121.85, 121.79, 121.10, 115.18. HRMS (ESI) m/z calcd. for $C_{13}H_{10}N_2S_2$ [M+H]$^+$: 259.0358, found 259.0363. LRMS (EI) m/z calcd. for $C_{13}H_{10}N_2S_2M^+$: 258, found 258.

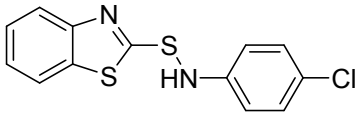


3n: Light yellow solid, isolated yield 67%, mp: 142-143 ℃; ^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si) δ:7.86 (d, *J* = 8.2 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.07-7.05 (m, 2H), 7.00-6.99 (m, 2H), 5.51 (br, 1H), 2.27 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, Me_4Si) δ:176.79, 154.74, 142.51, 134.89, 131.23, 129.90, 126.04, 123.92, 121.73, 121.08, 115.19, 20.49. HRMS (ESI) m/z calcd. for $C_{14}H_{12}N_2S_2$ [M+H]$^+$: 273.0515, found 273.0521. LRMS (EI) m/z calcd. for $C_{14}H_{12}N_2S_2M^+$: 272, found 272.

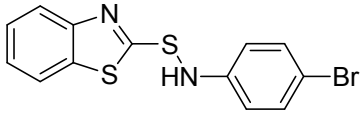


3o: Light yellow solid, isolated yield 65%, mp: 84-85℃; ^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si) δ:7.90 (d, *J* = 8.2 Hz, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.44-7.41 (m, 1H), 7.29-7.26 (m, 1H), 7.17 (t, *J* = 7.8 Hz, 1H), 6.95-6.92 (m, 2H), 6.81-6.80 (m, 1H), 5.70 (br, 1H), 2.32 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, Me_4Si)

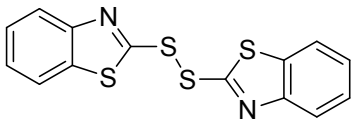
δ:176.87, 154.69, 144.86, 139.42, 134.83, 129.20, 126.03, 123.90, 122.63, 121.66, 121.06, 115.67, 112.29, 21.45. HRMS (ESI) m/z calcd. for $C_{14}H_{12}N_2S_2$ $[M+H]^+$: 273.0515, found 273.0520. LRMS (EI) m/z calcd. for $C_{14}H_{12}N_2S_2M^+$: 272, found 272.



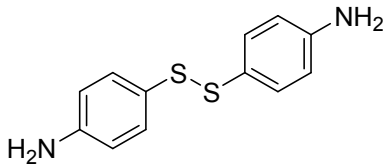
3p: Light yellow solid, isolated yield: 47%, mp: 154-156℃; ^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si) δ: 7.87 (d, *J* = 8.2 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.23 (d, *J* = 8.8 Hz, 2H), 7.05 (d, *J* = 8.8 Hz, 2H), 5.56 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$, Me_4Si) δ: 175.14, 154.64, 143.63, 134.82, 129.38, 126.79, 126.23, 124.21, 121.91, 121.15, 116.44.HRMS (ESI) m/z calcd. for $C_{13}H_9ClN_2S_2$ $[M+H]^+$: 292.9968, found 292.9965.



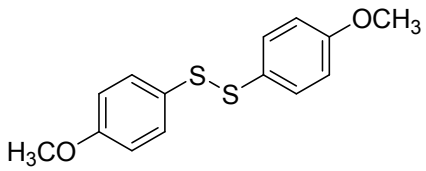
3q: Light yellow solid, isolated yield: 53%, mp: 150-152℃; ^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si) δ: 7.87 (d, *J* = 8.2 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.36 (d, *J* = 8.6 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 8.7 Hz, 2H), 5.59 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$, Me_4Si) δ:175.13, 154.59, 144.16, 134.80, 132.25, 126.22, 124.21, 121.87, 121.14, 116.85, 114.01.HRMS (ESI) m/z calcd. for $C_{13}H_9BrN_2S_2$ $[M+H]^+$:336.9463, found 336.9462.



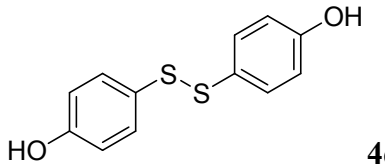
4a[1]: White solid, isolated yield: 99%, mp: 179-180 ℃; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ:7.94 (d, *J* = 8.2 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.46 (t, *J* = 7.3 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si) δ:167.83, 154.52, 136.12, 126.57, 125.29, 122.67, 121.29.



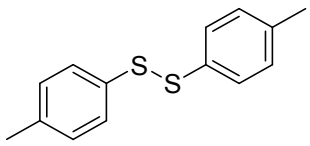
4b[2]: Yellow solid, isolated yield: 96%, mp: 75-77 ℃; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ: 7.24 (d, J = 8.4 Hz, 4H), 6.55 (d, J = 8.4 Hz, 4H), 3.76 (br, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si) δ: 147.06, 133.85, 125.48, 115.29. LRMS (EI) m/z calcd. for $C_{12}H_{12}N_2S_2M^+$: 248, found 248.



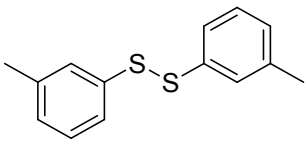
4c[1]: Light yellowsolid, isolated yield: 99%, mp: 34-35℃;^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ: 7.42 (d, J = 8.6 Hz, 4H), 6.85 (d, J = 8.6 Hz, 4H), 3.79 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si) δ: 159.81, 132.54, 128.30, 114.53, 55.25. LRMS (EI) m/z calcd. for $C_{14}H_{14}O_2S_2M^+$: 278, found 278.



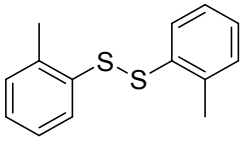
4d[3]: White solid, isolated yield: 97%, mp: 148-149 ℃; ^{1}H NMR (400 MHz, $(CD_3)_2SO$, Me_4Si) δ: 9.83 (s, 2H), 7.27 (d, J = 8.5 Hz, 4H), 6.76 (d, J = 8.4 Hz, 4H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$, Me_4Si) δ: 158.26, 133.01, 125.12, 116.30. LRMS (EI) m/z calcd. for $C_{12}H_{10}O_2S_2M^+$: 250, found 250.



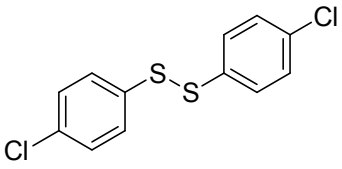
4e[1]: White solid, isolated yield: 98%, mp: 47-48℃; ^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si) δ:7.40 (d, J = 7.2 Hz, 4H), 7.12 (d, J = 7.8 Hz, 4H), 2.33 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$, Me_4Si) δ:137.41, 133.89, 129.76, 128.52, 21.03. LRMS (EI) m/z calcd. for $C_{14}H_{14}S_2$ M^+: 246, found 246.



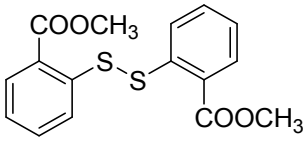
4f[4]: Light yellow oil, isolated yield: 95%; ^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si) δ: 7.29 (s, 4H), 7.16-7.13 (m, 2H), 6.99-6.98 (m, 2H), 2.28 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$, Me_4Si) δ:138.80, 136.85, 128.82, 127.93 (2C), 124.49, 21.29. LRMS (EI) m/z calcd. for $C_{14}H_{14}S_2M^+$: 246, found 246.



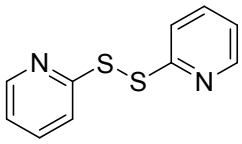
4g[5]: White solid, isolated yield: 94%, mp:38-39 ℃; ^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si) δ: 7.57-7.55 (m, 2H), 7.20-7.17 (m, 6H), 2.47 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$, Me_4Si) δ: 137.30, 135.35, 130.25, 128.58, 127.26, 126.63, 19.95.LRMS (EI) m/z calcd. for $C_{14}H_{14}S_2M^+$: 246, found 246.



4h[1]: White solid, isolated yield: 97%, mp:63-64 ℃; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ: 7.37 (d, J = 8.6 Hz, 4H), 7.24 (d, J = 8.6 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si) δ: 135.07, 133.54, 129.22 (2C).LRMS (EI) m/z calcd. for $C_{14}H_{14}Cl_2S_2M^+$: 286, found 286.

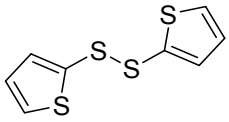


4i[6]: White solid, isolated yield: 98%, mp:126-128 ℃; ^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si) δ:8.05 (d, J = 7.8 Hz, 2H), 7.75 (d, J = 8.1 Hz, 2H), 7.42-7.38 (m, 2H), 7.24-7.21 (m, 2H), 3.98 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$, Me_4Si) δ: 166.86, 140.32, 133.03, 131.42, 127.27, 125.80, 125.44, 52.33. LRMS (EI) m/z calcd. For $C_{16}H_{14}O_4S_2$ M^+: 334, found 334.

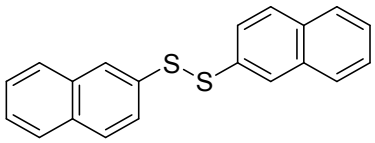


4j

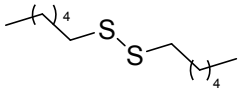
4j[1]: Yellow solid, isolated yield: 97%, yield: 51-52 ℃; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ:8.40 (d, *J* = 4.6 Hz, 2H), 7.55 (br, 4H), 7.06-7.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si) δ: 158.62, 149.33, 137.21, 120.94, 119.46.LRMS (EI) m/z calcd. For $C_{10}H_8N_2S_2$ M^+: 220, found 220.



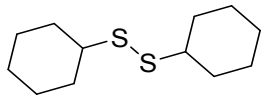
4k[7]: Light yellow solid, isolated yield: 91%, yield: 56-57℃; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ: 7.50 (d, *J* = 5.2 Hz, 2H), 7.17 (d, *J* = 3.6 Hz, 2H), 7.03-7.01 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si) δ: 135.63, 135.58, 132.22, 127.70.LRMS (EI) m/z calcd. For $C_8H_6S_4$ M^+: 230, found 230.



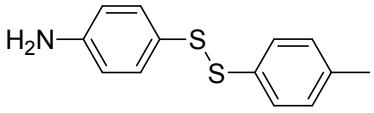
4l[8]: White solid: isolated yield: 94%, mp:139-141 ℃; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ:8.00(s, 2H), 7.81-7.63 (m, 8H), 7.49-7.44 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si) δ:134.24, 133.44, 132.47, 128.95, 127.74, 127.44, 126.71, 126.53, 126.21, 125.64.



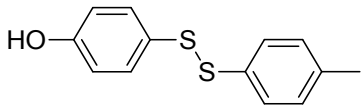
4m[9]: Colorless oil,isolated yield: 94%; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ: 2.68 (t, *J* = 7.3 Hz, 4H), 1.70-1.63 (m, 4H), 1.40-1.29 (m, 12H), 0.89 (t, *J* = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si) δ: 39.19, 31.42, 29.17, 28.19, 22.53, 14.02.LRMS (EI) m/z calcd. for $C_{12}H_{26}S_2$ M^+: 234, found 234.



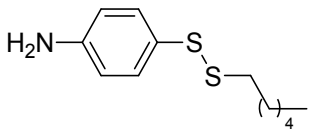
4n[10]: Colorless oil, isolated yield: 93%; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ: 2.68-2.67 (m, 2H), 2.05-2.02 (m, 4H), 1.79 (br, 4H), 1.63-1.60 (m, 2H), 1.31-1.24 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si) δ:49.94, 32.83, 26.07, 25.67. LRMS (EI) m/z calcd. for $C_{12}H_{22}S_2$ M^+: 230, found 230.



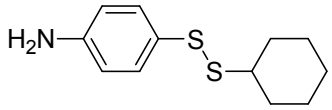
5a: Yellow solid, isolated yield: 91%, mp: 42-43℃; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ:7.40 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 7.8 Hz, 2H), 6.58 (d, J = 8.4 Hz, 2H), 3.76 (br, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si) δ: 147.01, 137.46, 134.33, 133.03, 129.66, 129.40, 125.16, 115.38, 21.05. HRMS (ESI) m/z calcd. for $C_{13}H_{13}NS_2$ $[M+H]^+$: 248.0562, found 248.0564. LRMS (EI) m/z calcd. for $C_{13}H_{13}NS_2$ M^+: 247, found 247.



5b[11]: White solid, isolated yield: 94%, mp: 67-68 ℃; ^{1}H NMR (600 MHz, $(CD_3)_2SO$, Me_4Si) δ: 9.85 (s, 1H), 7.39-7.31 (m, 4H), 7.19 (d, J = 7.9 Hz, 2H), 6.76 (d, J = 8.6 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (150 MHz, $(CD_3)_2SO$, Me_4Si) δ:158.29, 137.36, 133.07, 132.56, 129.95, 128.50, 124.65, 116.35, 20.58. LRMS (EI) m/z calcd. for $C_{13}H_{12}OS_2$ M^+: 248, found 248.



5c: Yellow oil, isolated yield: 96%; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ:7.35 (d, J = 8.4 Hz, 2H), 6.62 (d, J = 8.4 Hz, 2H), 3.77 (br, 2H), 2.73 (t, J = 7.2 Hz, 2H), 1.71-1.63 (m, 2H), 1.37-1.27 (m, 6H), 0.88 (t, J = 6.56 Hz, 3H);^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si) δ:146.64, 132.76, 125.36, 115.40, 38.67, 31.31, 28.59, 28.11, 22.45, 13.97. HRMS (ESI) m/z calcd. for $C_{12}H_{19}NS_2$ $[M+H]^+$: 242.1032, found242.1038. LRMS (EI) m/z calcd. for $C_{12}H_{19}NS_2$ M^+: 241, found 241.



5d: Yellow oil, isolated yield: 97%; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ:7.35 (d, *J* = 8.4 Hz, 2H), 6.61 (d, *J* = 8.3 Hz, 2H), 3.74 (br, 2H), 2.83-2.77 (m, 1H), 2.04-2.01 (m, 2H), 1.76-1.74 (m, 2H), 1.61-1.58 (m, 1H), 1.39-1.19 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si) δ: 146.23, 131.85, 126.21, 115.40, 49.39, 32.48, 25.91, 25.60. HRMS (ESI) m/z calcd. for $C_{12}H_{17}NS_2$ $[M+H]^+$: 240.0875, found 240.0879 . LRMS (EI) m/z calcd. for $C_{12}H_{17}NS_2$ M^+: 239, found 239.

(D)References.

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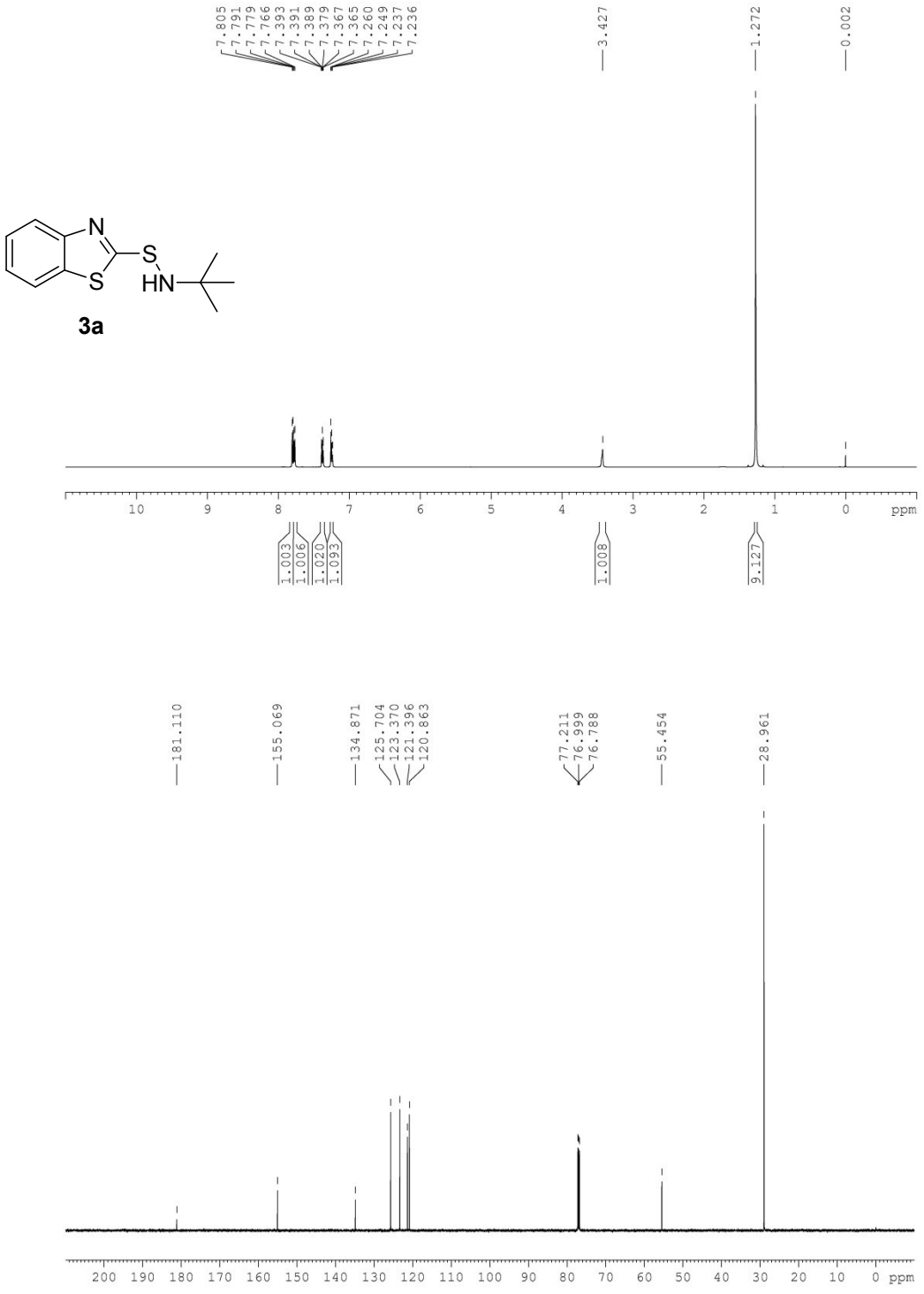
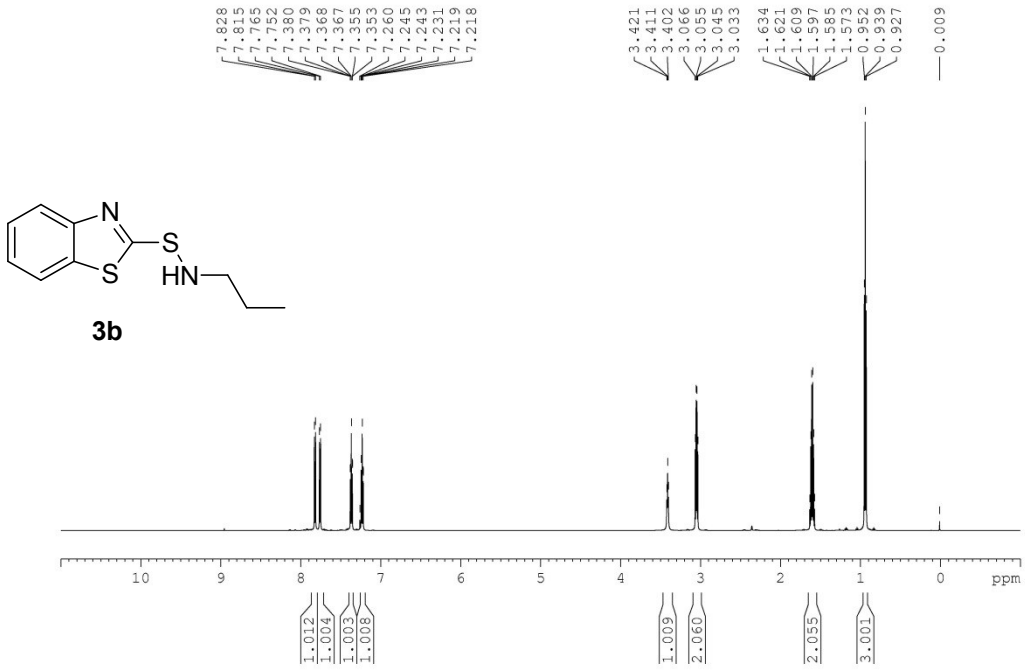
(E) Copies of all spectra.

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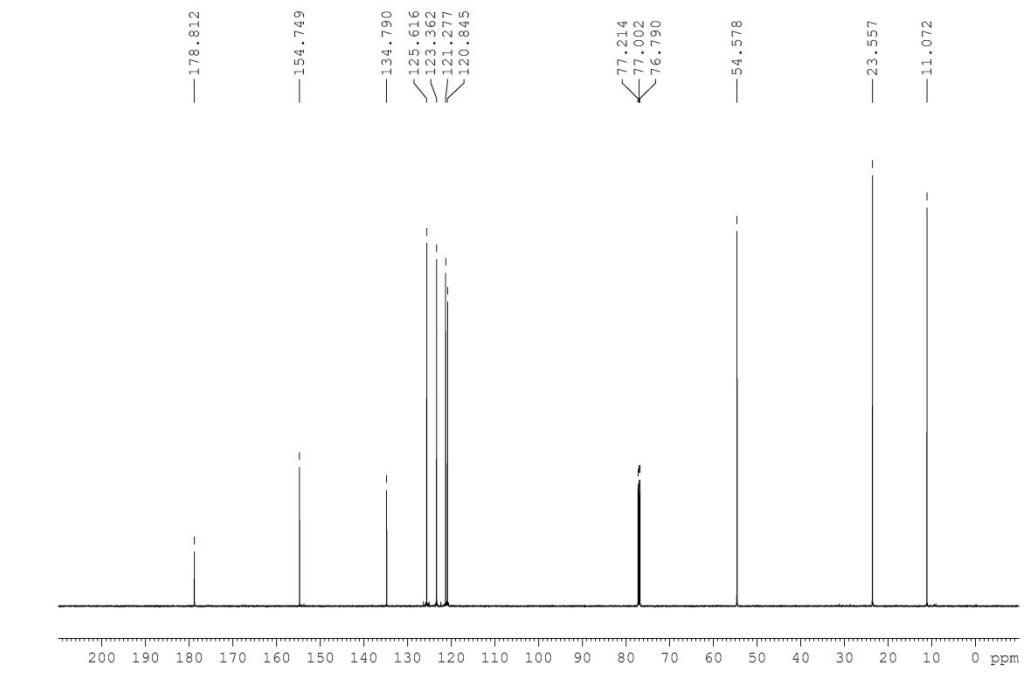
3b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134.790
125.616
123.362
121.277
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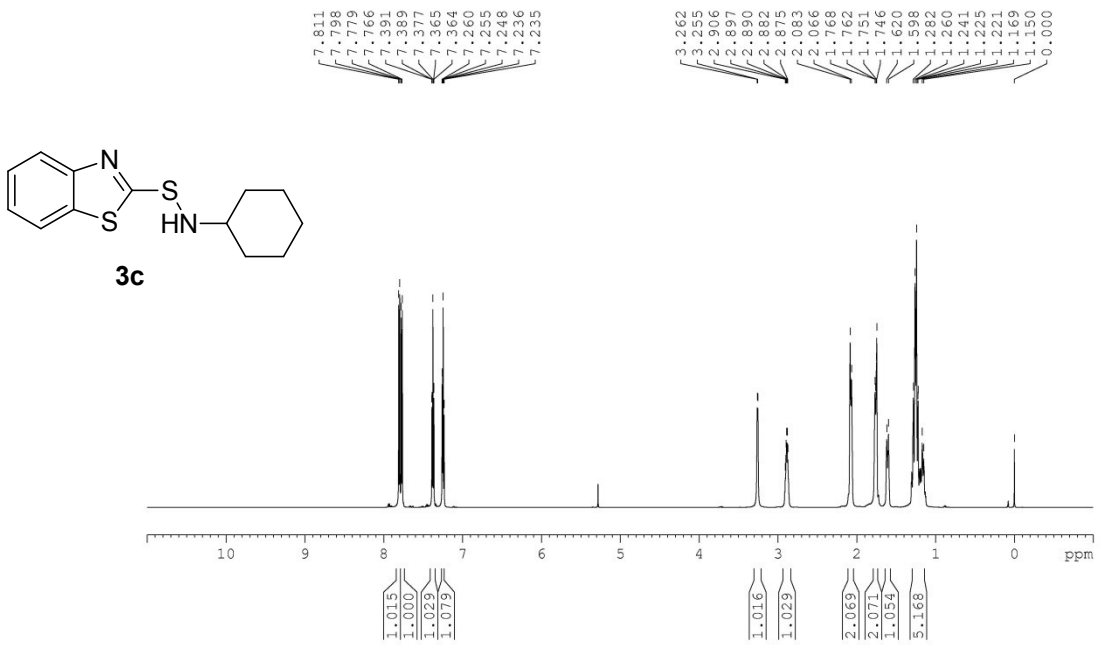
77.214
77.002
76.790
54.578
23.557
11.072
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.364
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7.236
7.235
3.262
3.255
2.906
2.897
2.890
2.882
2.875
2.083
2.066
1.768
1.762
1.751
1.746
1.620
1.598
1.282
1.260
1.241
1.225
1.221
1.169
1.150
0.000
N
S
S
HN
3c
10
9
8
7
6
5
4
3
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1.000
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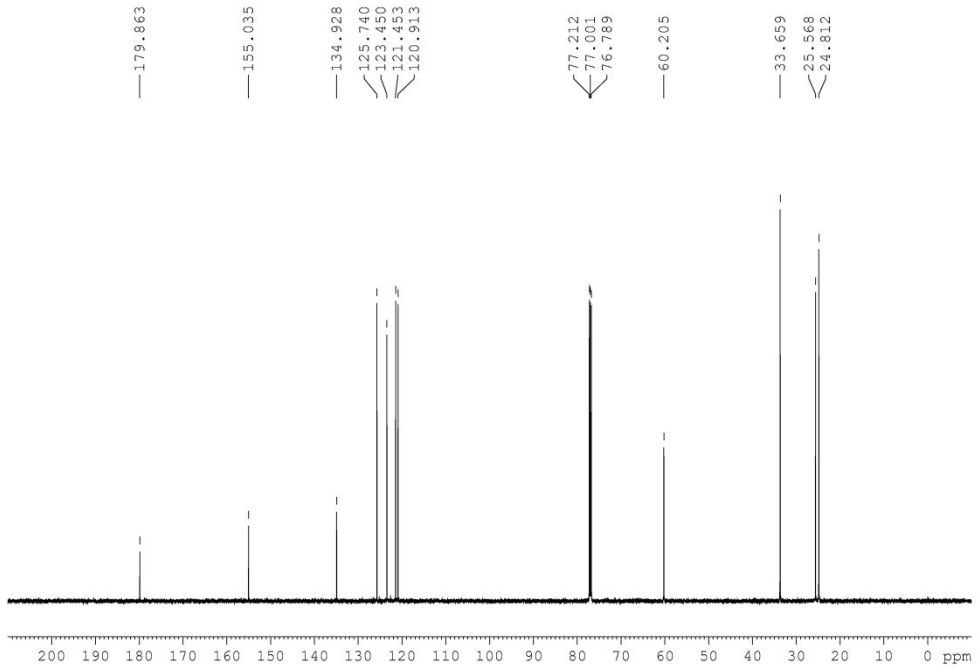
1.054
5.168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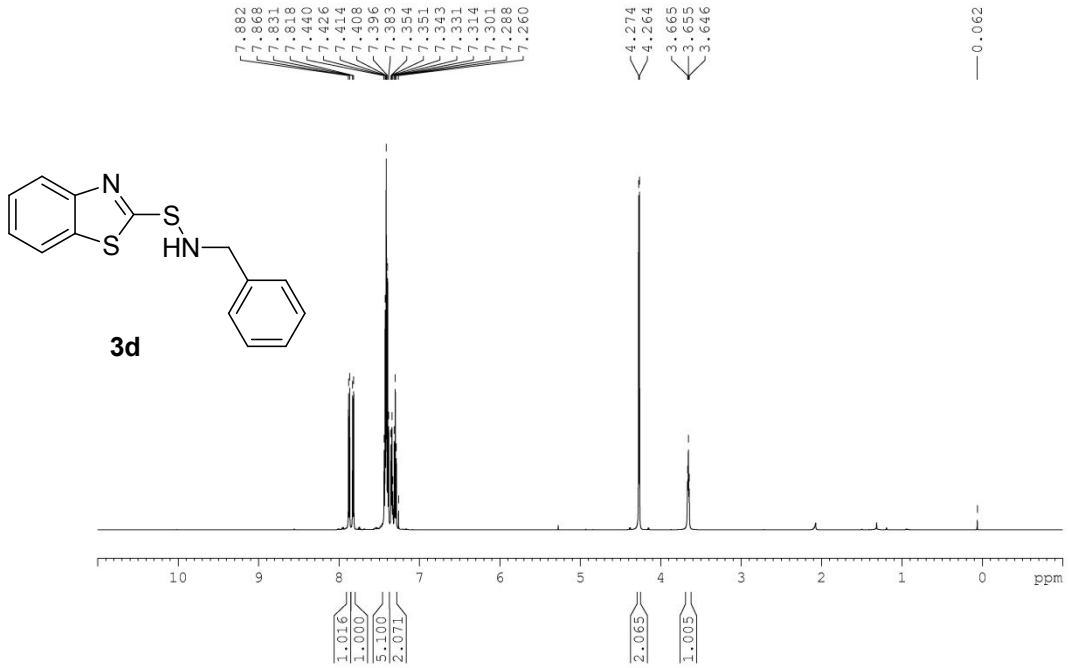
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7.408
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7.383
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7.343
7.331
7.314
7.301
7.288
7.260
4.274
4.264
3.665
3.655
3.646
0.062
N
S
S
HN
3d
10
9
8
7
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4
3
2
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1.000
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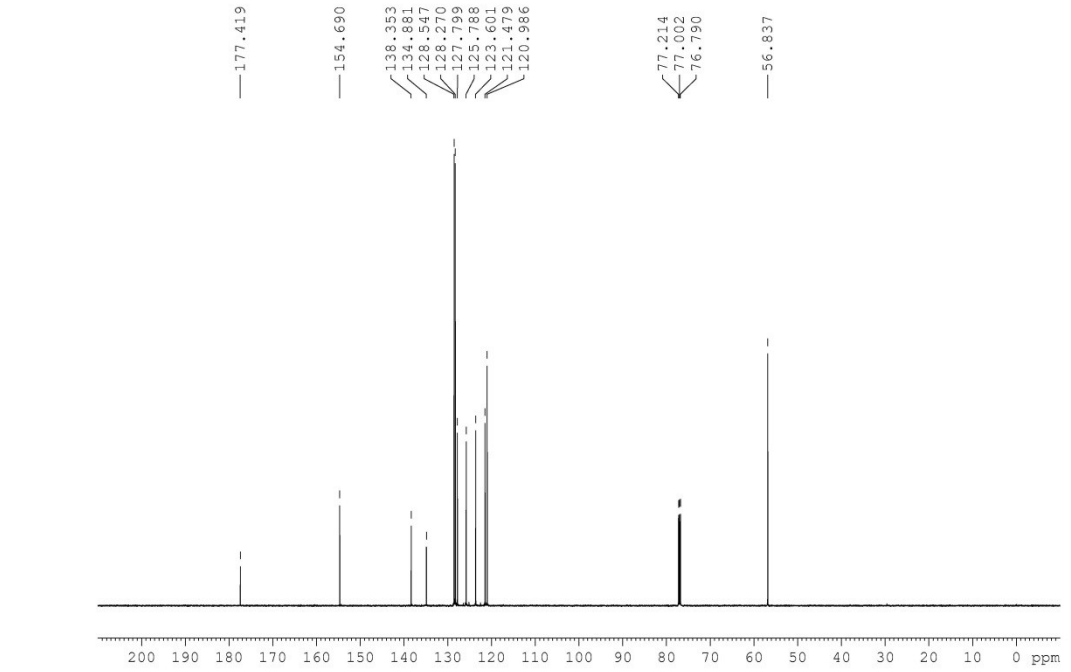
2.071
2.065
1.005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77.214
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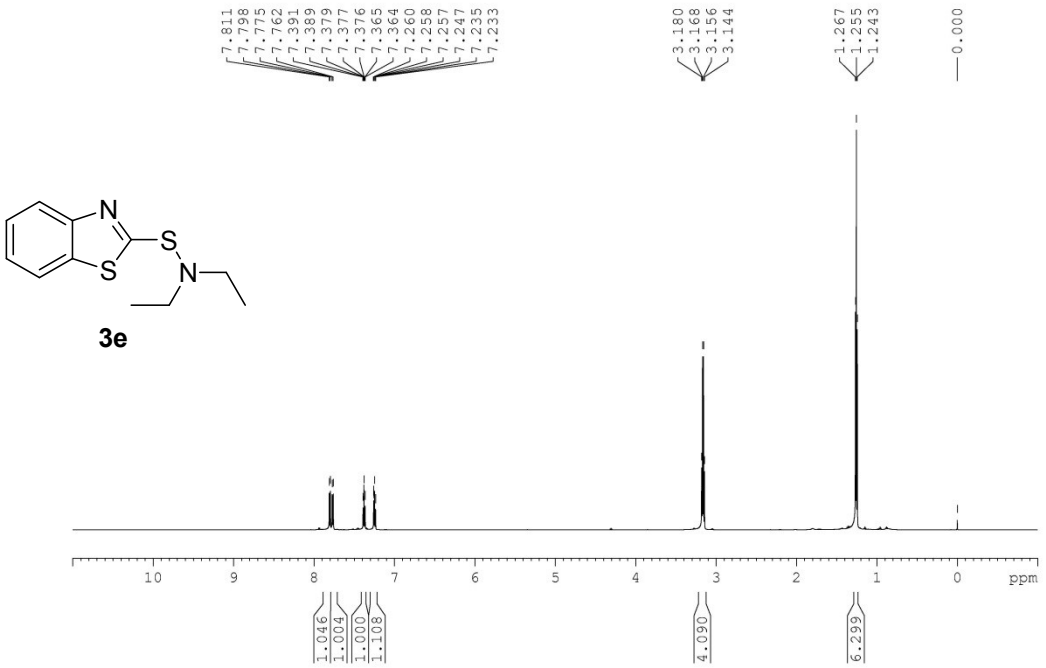
76.790
56.837
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.379
7.377
7.376
7.365
7.364
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7.258
7.257
7.247
7.235
7.233
3.180
3.168
3.156
3.144
1.267
1.255
1.243
0.000
N
S
S
N
3e
10
9
8
7
6
5
4
3
2
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0
ppm
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1.004
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1.108
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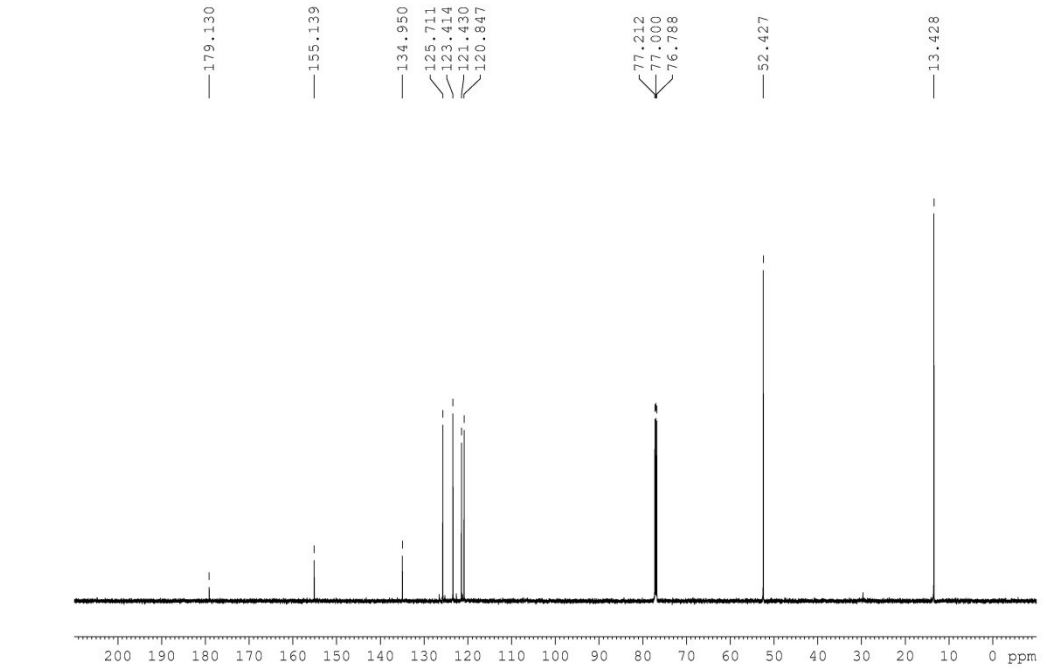
6.299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121.430
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77.212
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76.788
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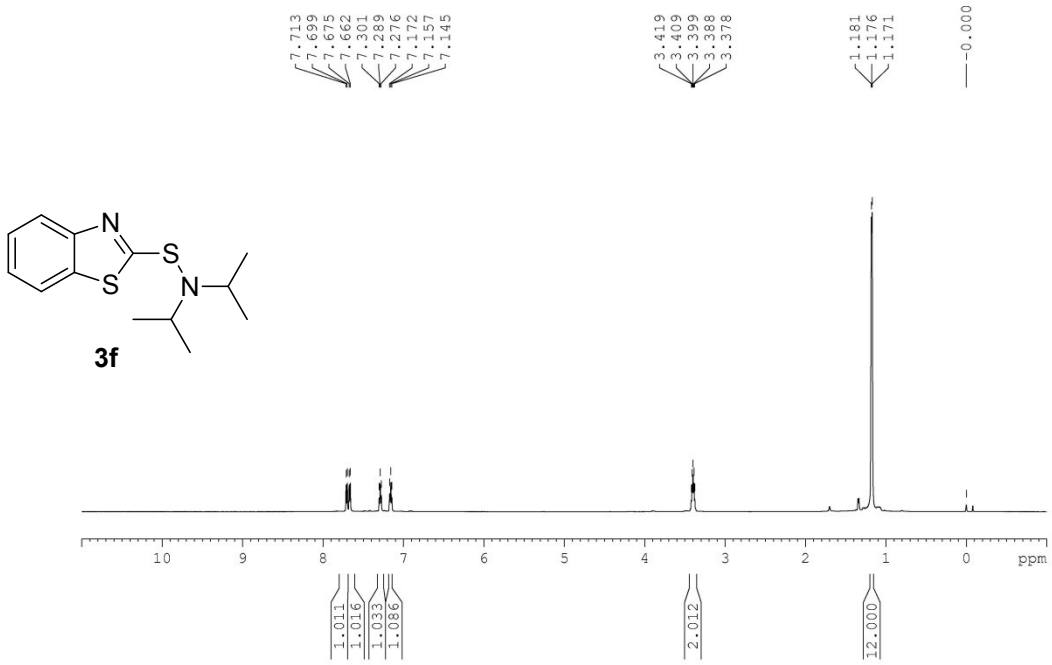
13.428
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm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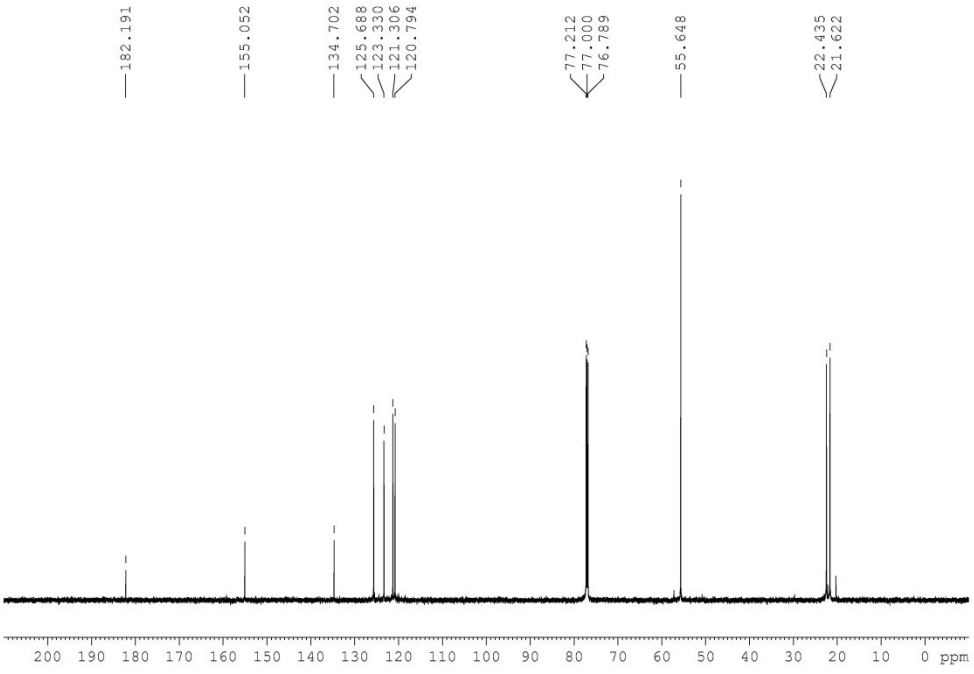
7.699
7.675
7.662
7.301
7.289
7.276
7.172
7.157
7.145
3.419
3.409
3.399
3.388
3.378
1.181
1.176
1.171
0.000
N
S
S
N
3f
10
9
8
7
6
5
4
3
2
1
0
ppm
1.011
1.016
1.033
1.086
2.012
12.000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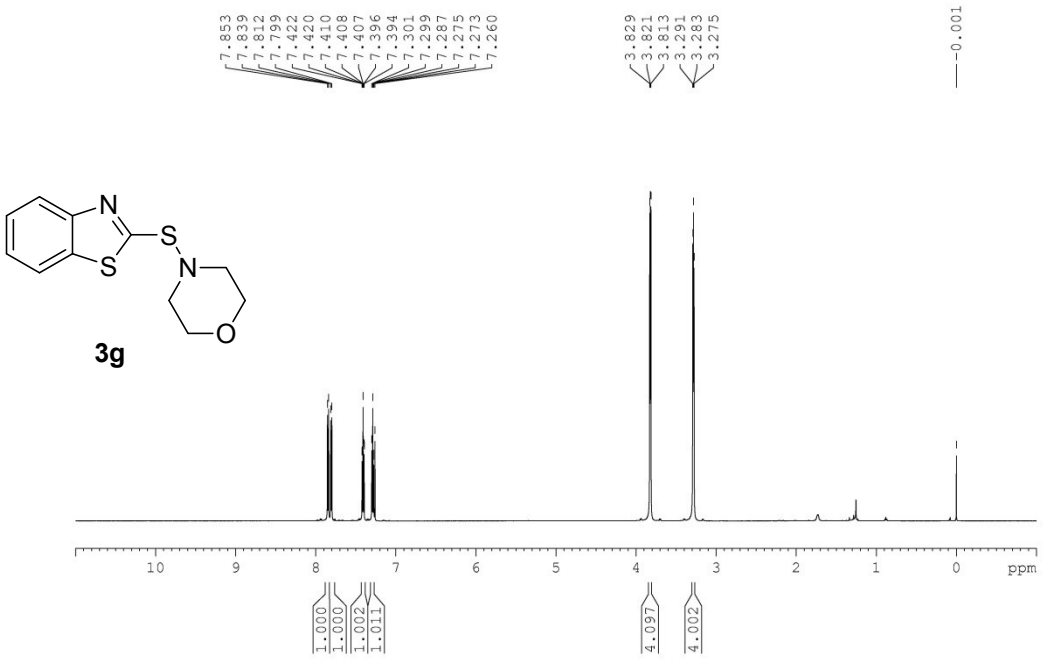
134.702
125.688
123.330
121.306
120.794
77.212
77.000
76.789
55.648
22.435
21.622
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm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7.812
7.799
7.422
7.420
7.410
7.408
7.407
7.396
7.394
7.301
7.299
7.287
7.275
7.273
7.260
3.829
3.821
3.813
3.291
3.283
3.275
0.001
N
S
S
N
O
3g
10
9
8
7
6
5
4
3
2
1
0
ppm
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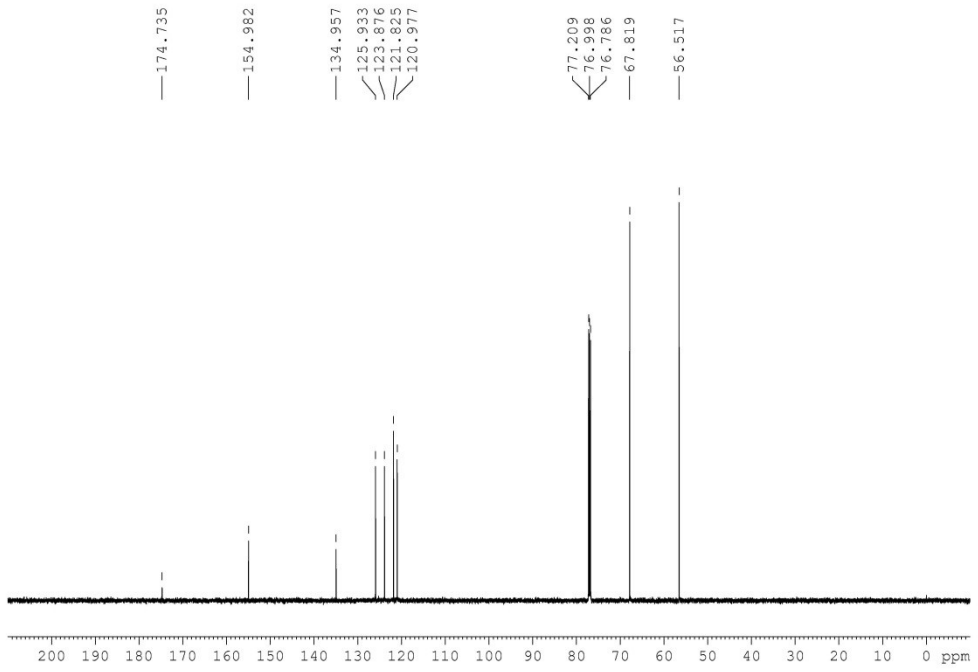
1.000
1.002
1.011
4.097
4.002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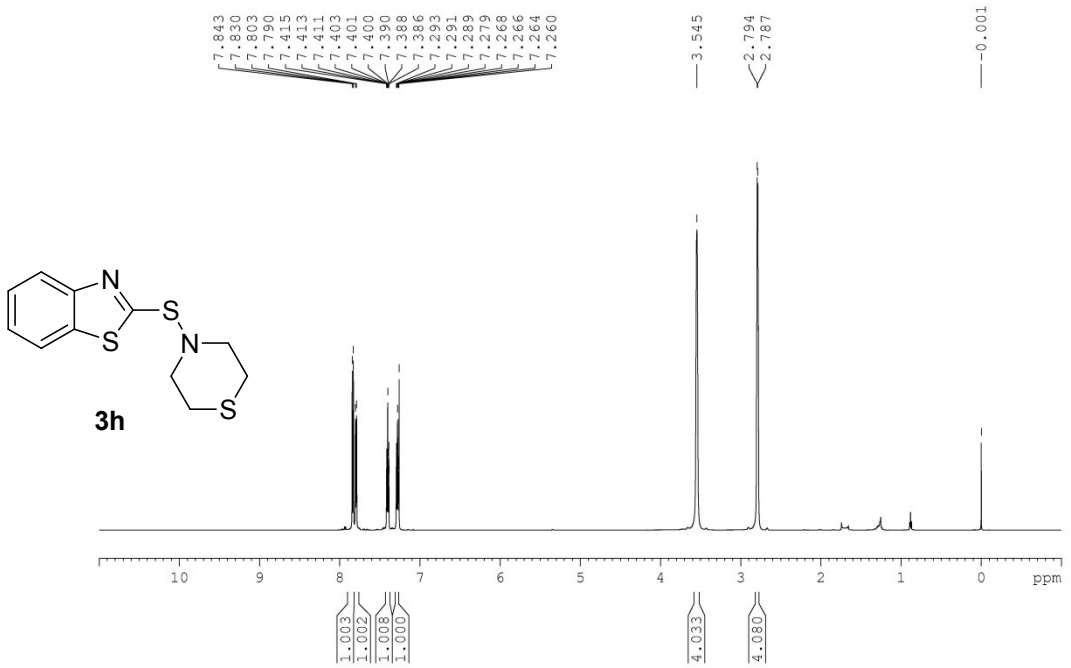
134.957
125.933
123.876
121.825
120.977
77.209
76.998
76.786
67.819
56.517
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm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7.411
7.403
7.401
7.400
7.390
7.388
7.386
7.293
7.291
7.289
7.279
7.268
7.266
7.264
7.260
3.545
2.794
2.787
0.001
N
S
S
N
S
3h
10
9
8
7
6
5
4
3
2
1
0
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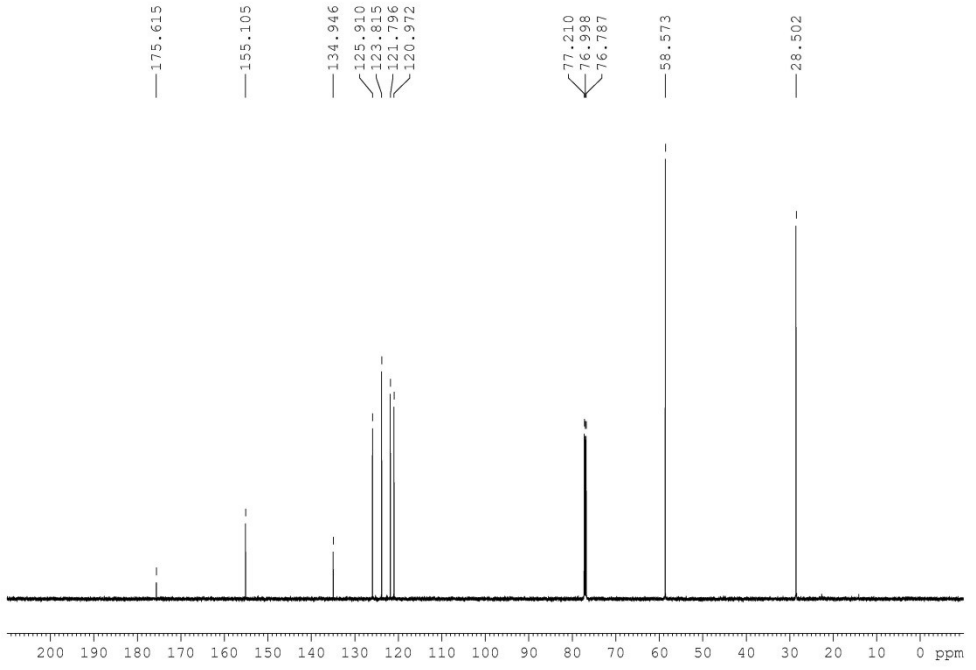
1.002
1.008
1.000
4.033
4.080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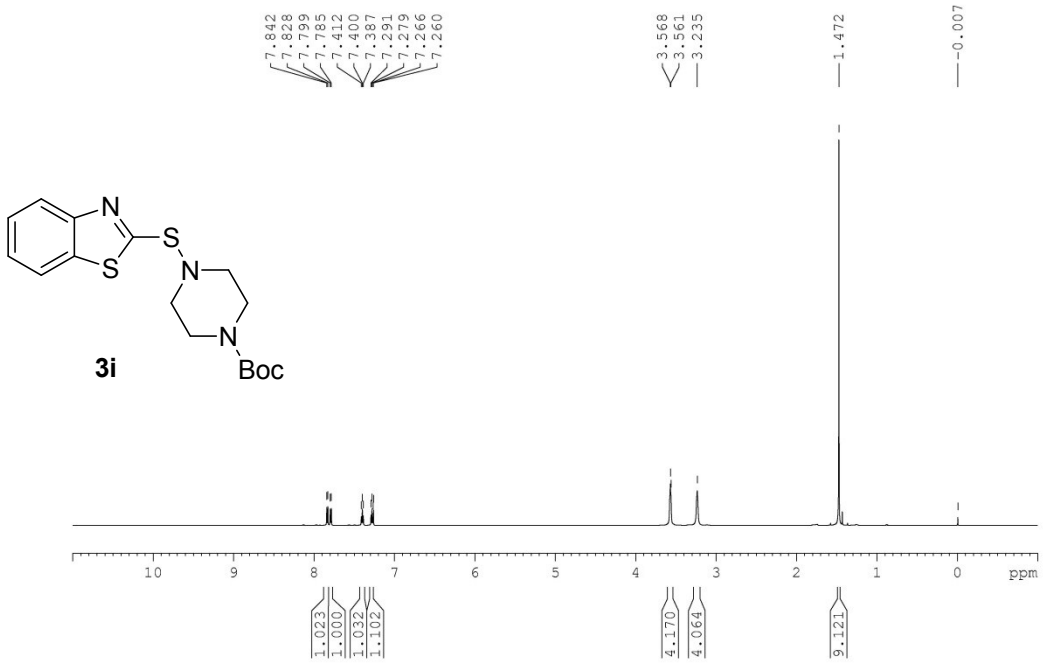
77.210
76.998
76.787
58.573
28.502
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm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7.291
7.279
7.266
7.260
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3.561
3.235
1.472
0.007
N
S
S
N
N
Boc
3i
10
9
8
7
6
5
4
3
2
1
0
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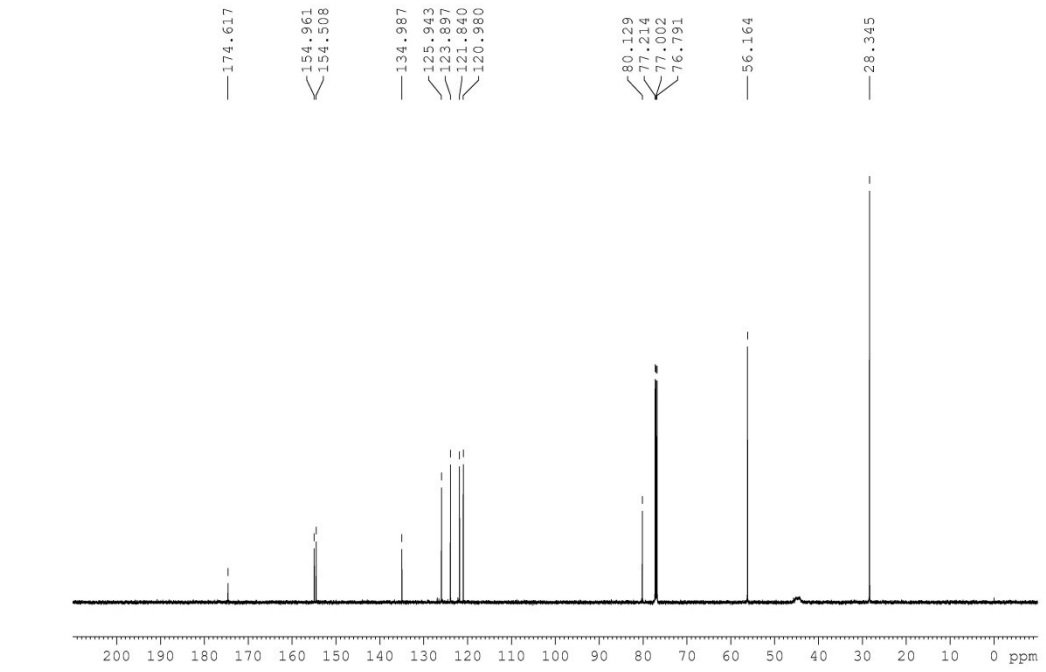
9.121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120.980
80.129
77.214
77.002
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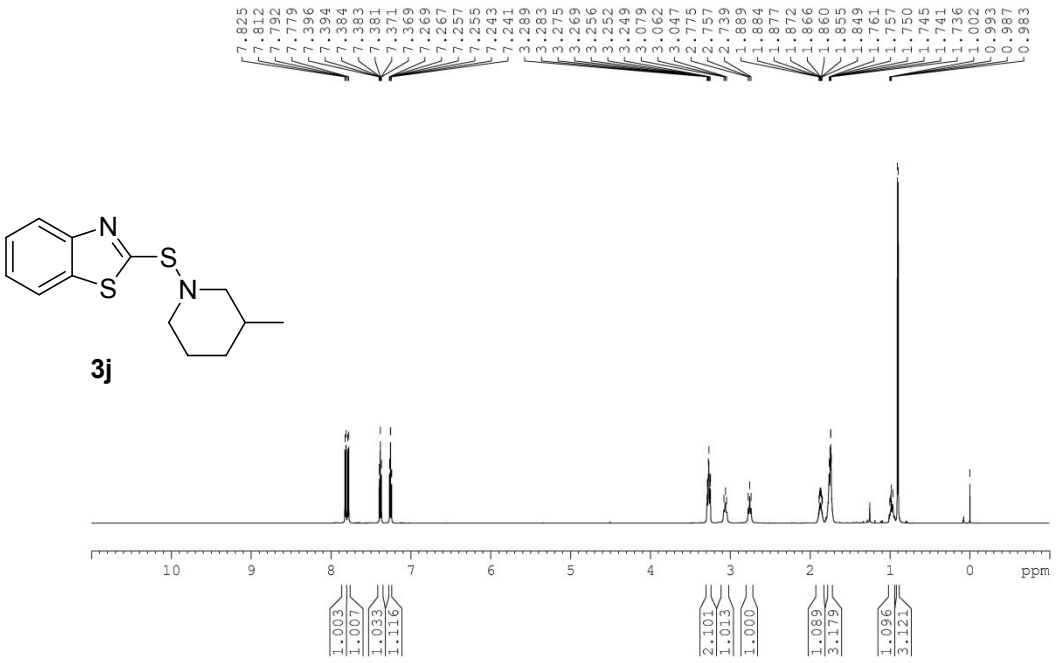
56.164
28.345
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm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7.792
7.779
7.396
7.394
7.384
7.383
7.381
7.371
7.369
7.269
7.267
7.257
7.255
7.243
7.241
3.289
3.283
3.275
3.269
3.256
3.252
3.249
3.079
3.062
3.047
2.775
2.757
2.739
1.889
1.884
1.877
1.872
1.866
1.860
1.855
1.849
1.761
1.757
1.750
1.745
1.741
1.736
1.002
0.993
0.987
0.983
N
S
S
N
10
9
8
7
6
5
4
3
2
1
0
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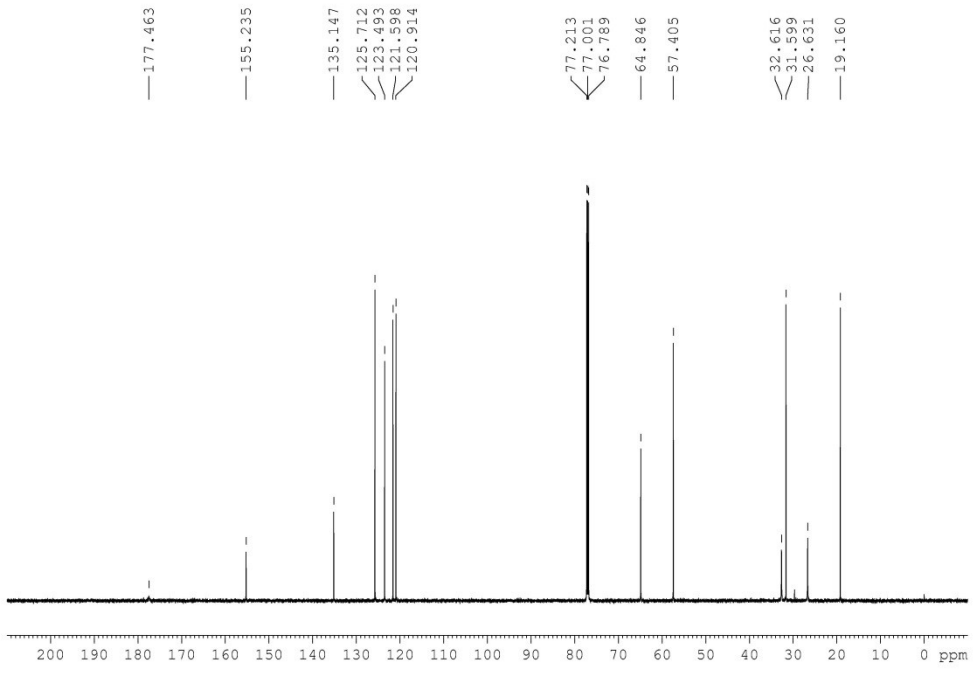
3.121

3j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77.213
77.001
76.789
64.846
57.405
32.616
31.599
26.631
19.160
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.832
7.819
7.801
7.788
7.404
7.402
7.390
7.378
7.376
7.279
7.278
7.265
7.254
7.253
3.975
3.390
3.381
3.371
1.900
1.890
1.881
0.000
N
S
S
N
O
O
3k
10
9
8
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1
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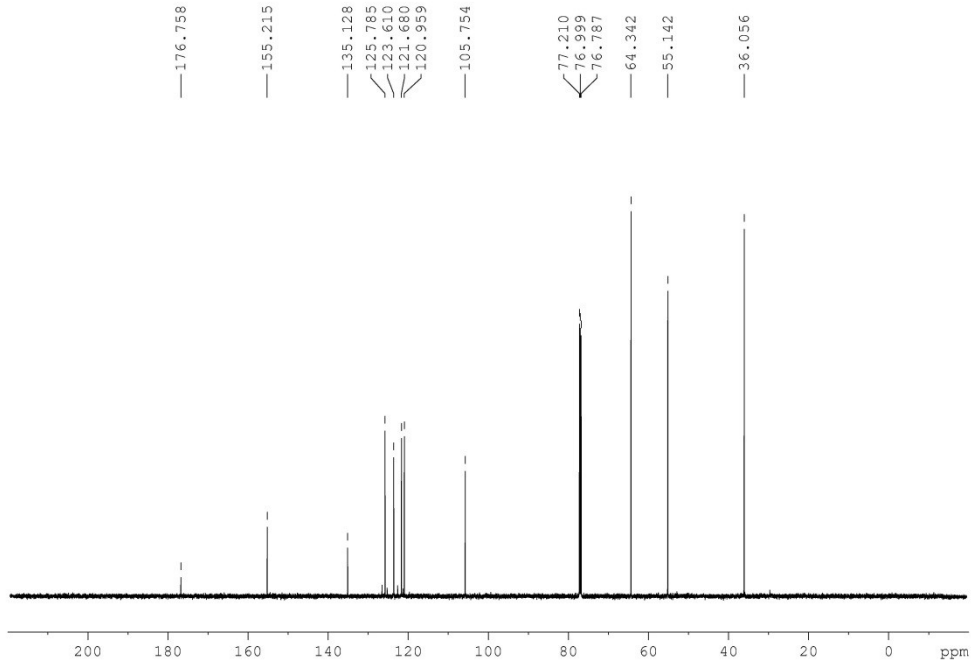
4.053
4.125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55.142
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120
100
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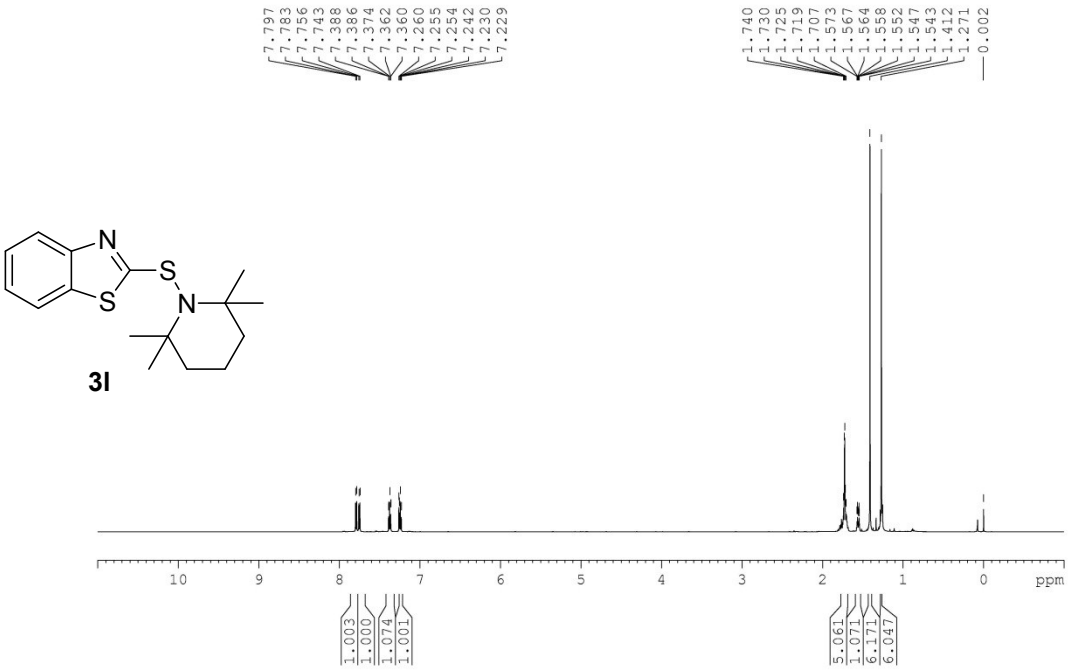
40
20
0
ppm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7.386
7.374
7.362
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7.260
7.255
7.254
7.242
7.230
7.229
1.740
1.730
1.725
1.719
1.707
1.573
1.567
1.564
1.558
1.552
1.547
1.543
1.412
1.271
0.002
10
9
8
7
6
5
4
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ppm
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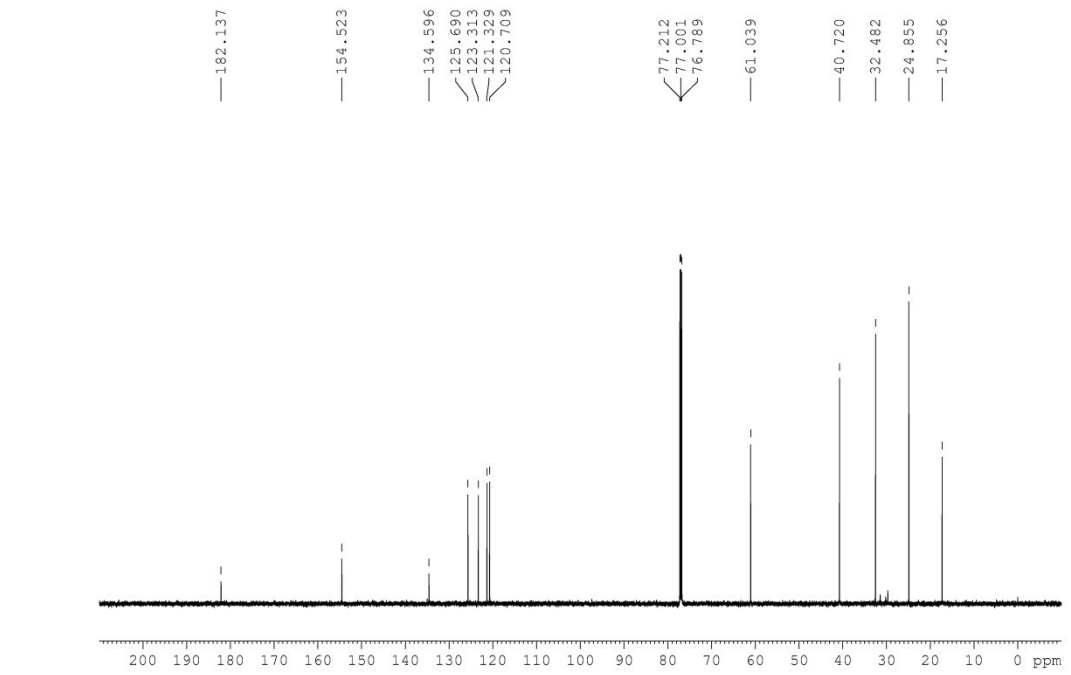
5.061
1.071
6.171
6.047

3l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134.596
125.690
123.313
121.329
120.709
77.212
77.001
76.789
61.039
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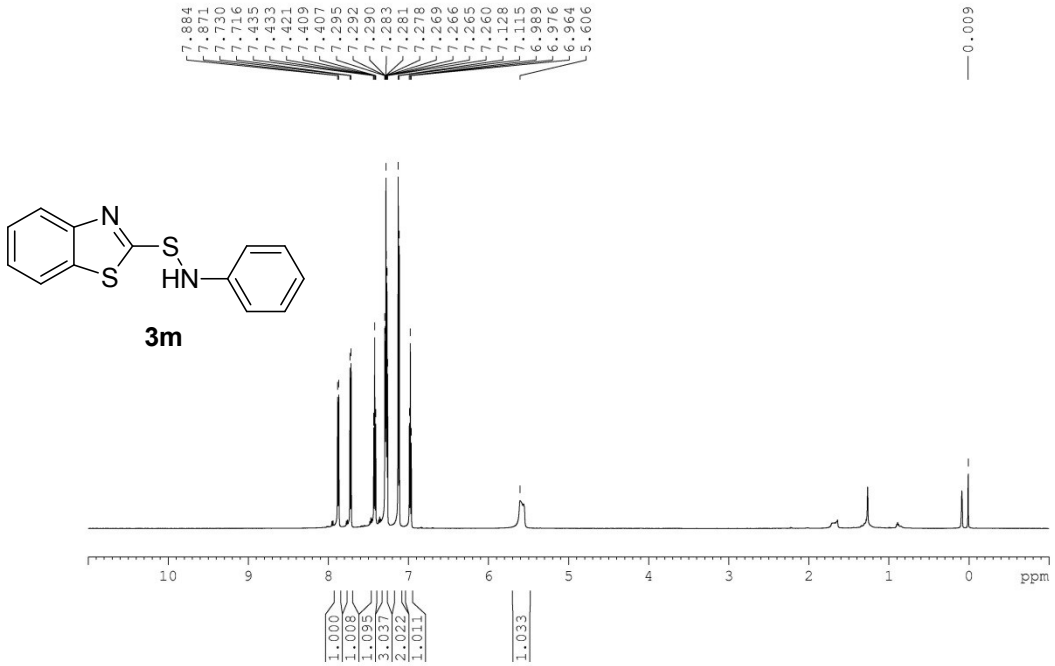
32.482
24.855
17.256
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm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7.292
7.290
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7.281
7.278
7.269
7.266
7.265
7.260
7.128
7.115
6.989
6.976
6.964
5.606
0.009
N
S
S
HN
3m
10
9
8
7
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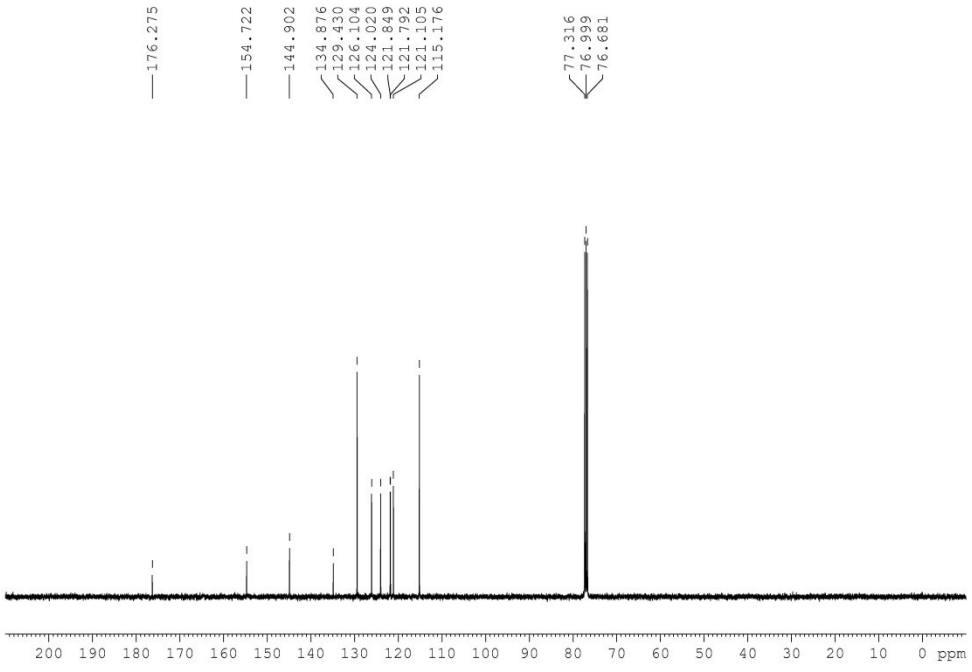
1.095
3.037
2.022
1.011
1.033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124.020
121.849
121.792
121.105
115.176
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76.999
76.681
200
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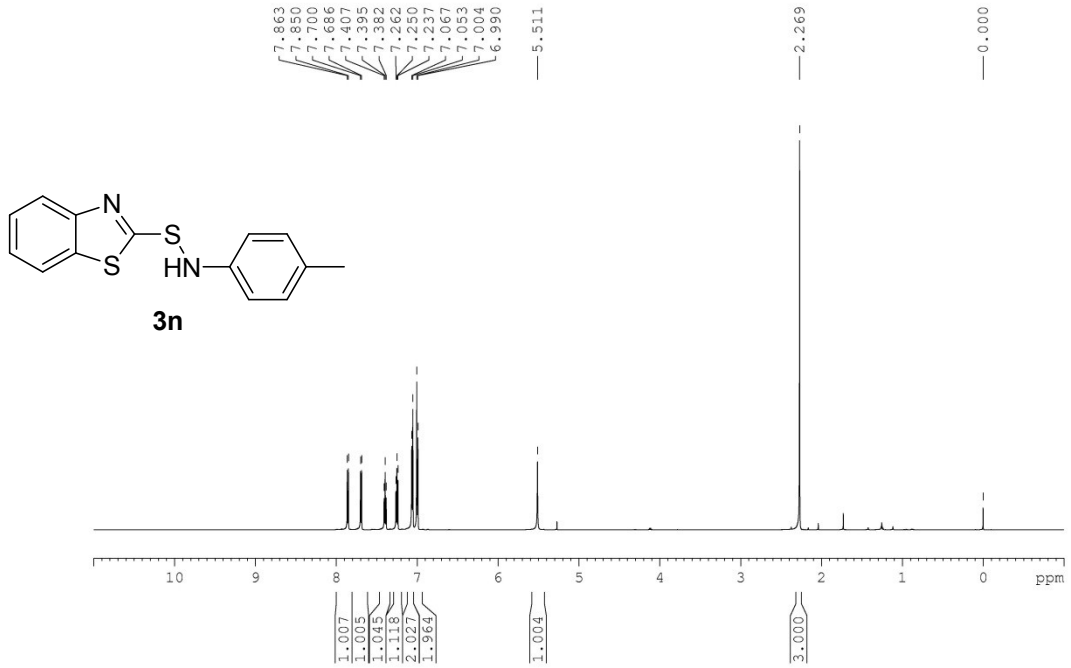
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm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7.700
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7.395
7.382
7.262
7.250
7.237
7.067
7.053
7.004
6.990
5.511
2.269
0.000
N
S
S
HN
10
9
8
7
6
5
4
3
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1
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ppm
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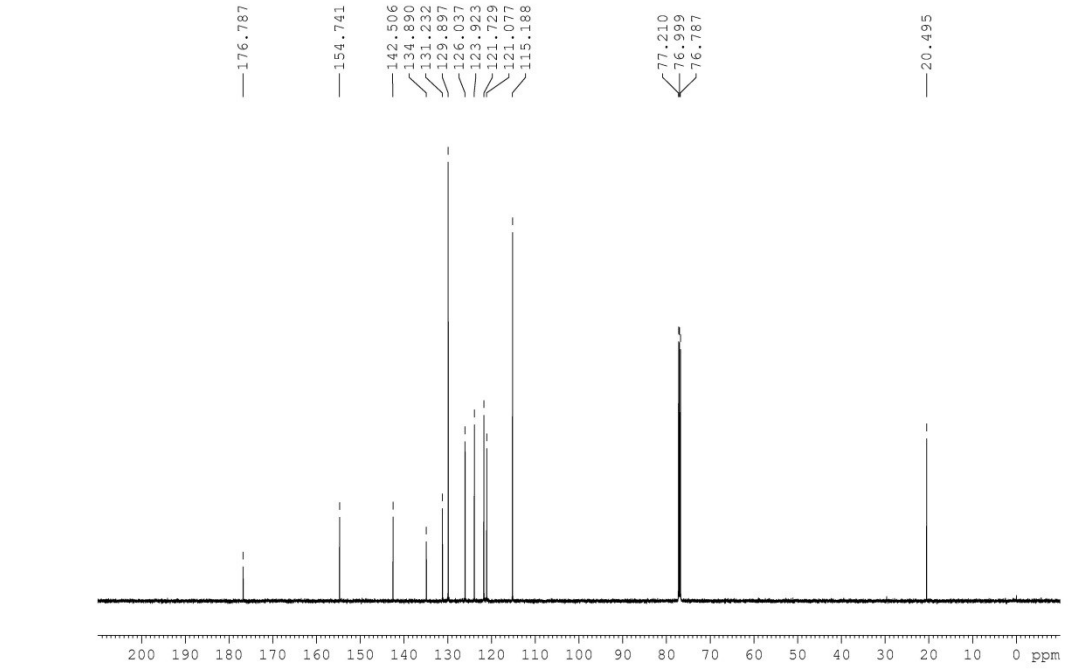
1.005
1.045
1.118
2.027
1.964
1.004
3.000

3n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142.506
134.890
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129.897
126.037
123.923
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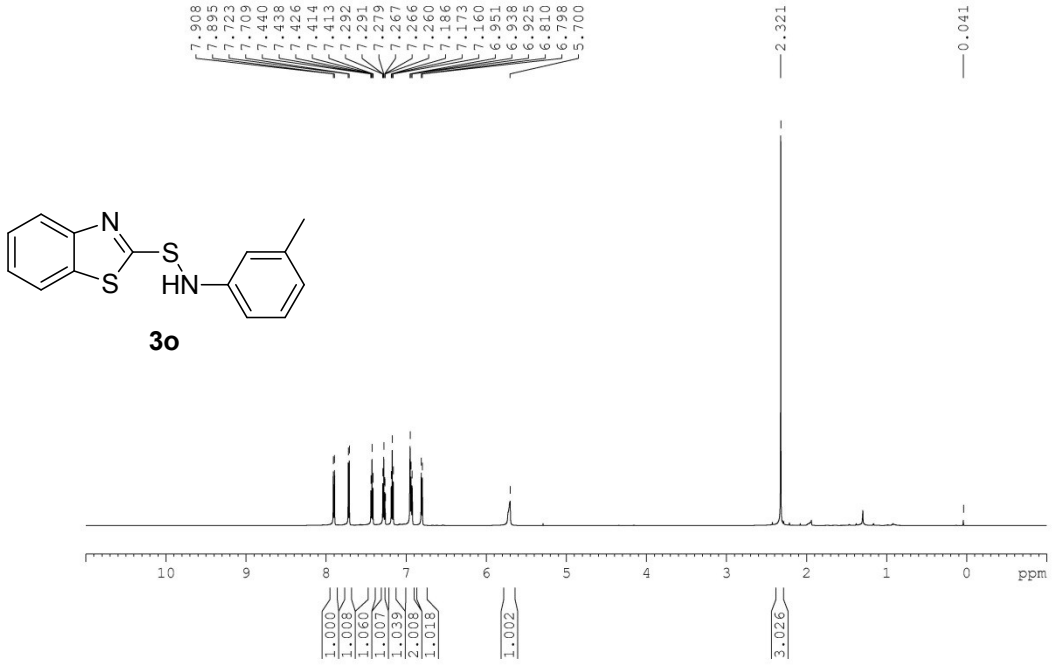
115.188
77.210
76.999
76.787
20.495
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.438
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7.414
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7.291
7.279
7.267
7.266
7.260
7.186
7.173
7.160
6.951
6.938
6.925
6.810
6.798
5.700
2.321
0.041
N
S
S
HN
10
9
8
7
6
5
4
3
2
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1.000
1.008
1.060
1.007
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2.008
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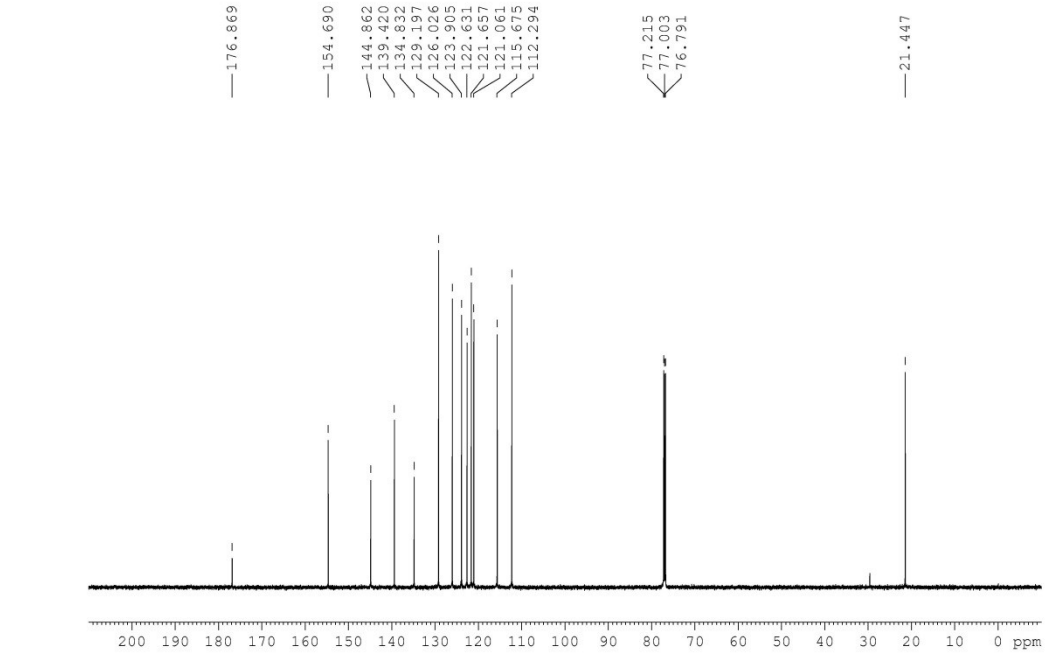
1.002
3.026

3o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123.905
122.631
121.657
121.061
115.675
112.294
77.215
77.003
76.791
21.447
200
190
180
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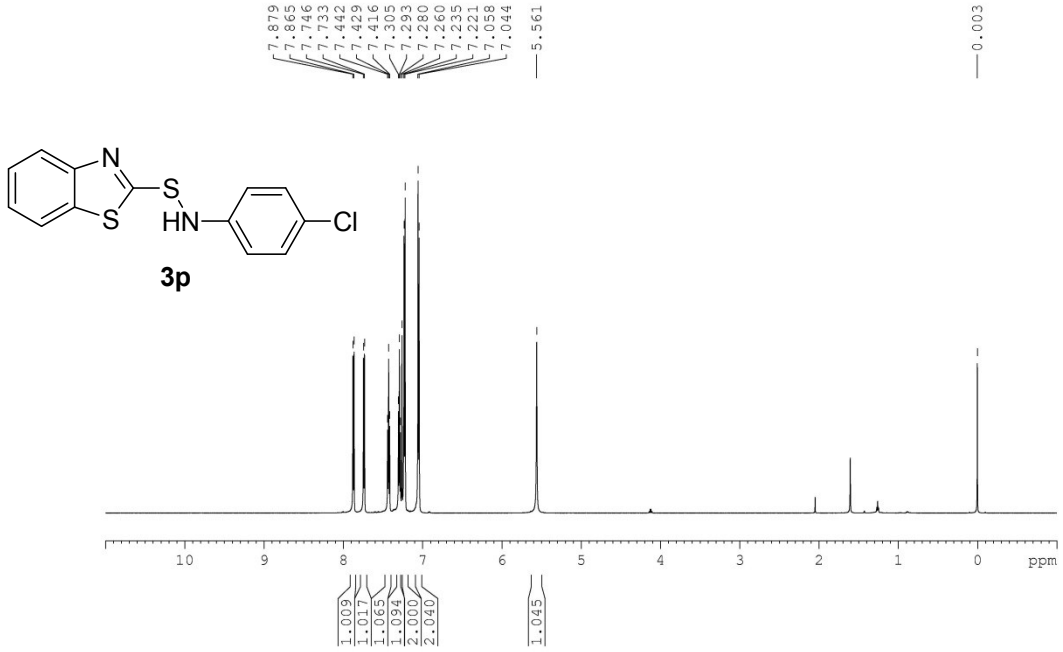
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.733
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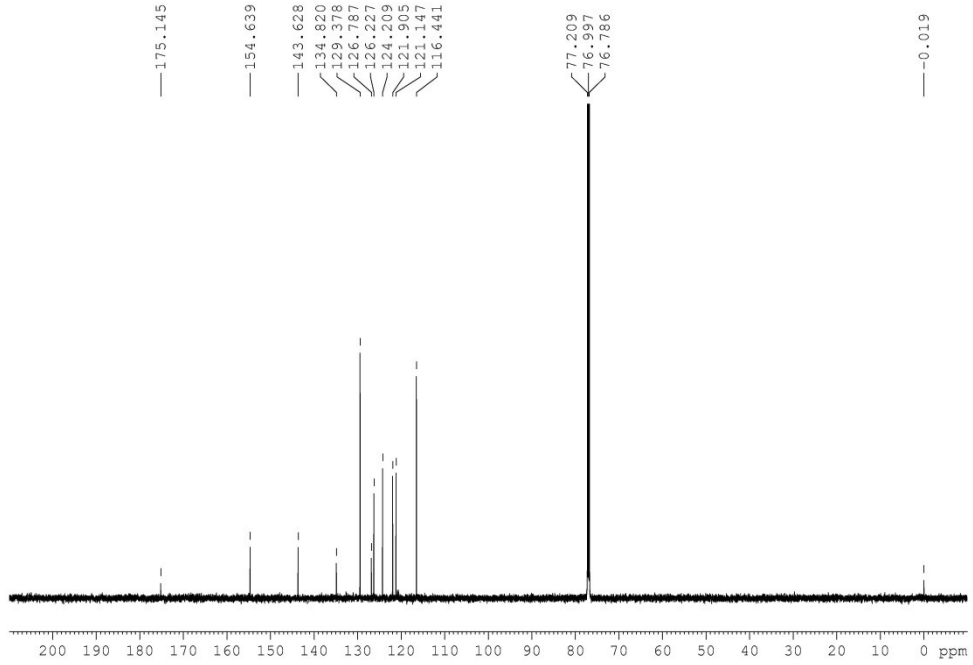
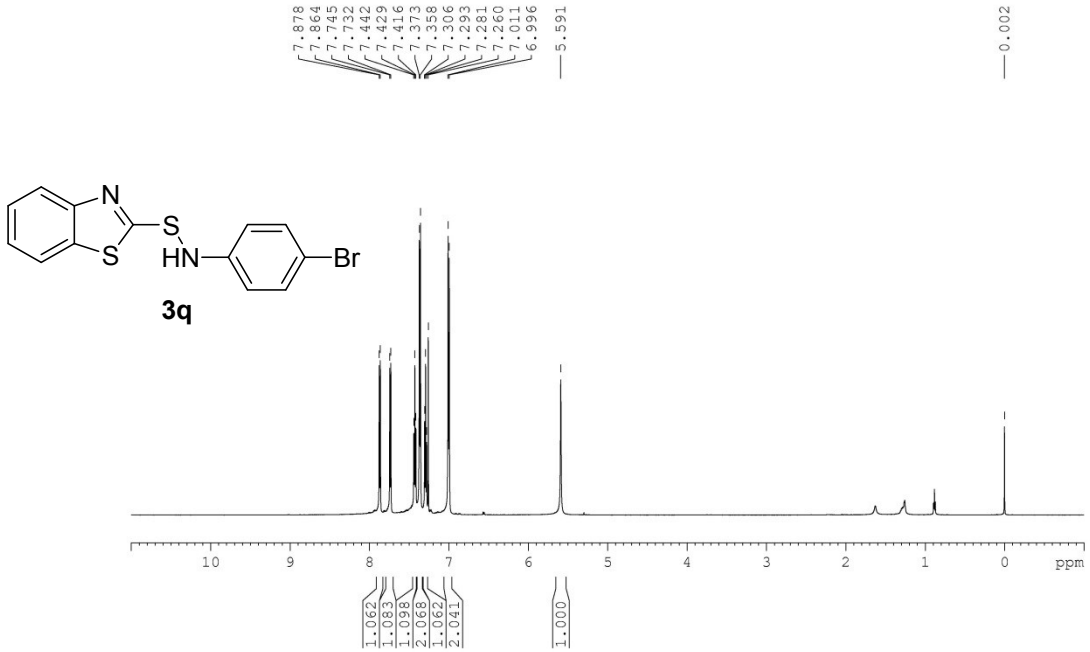
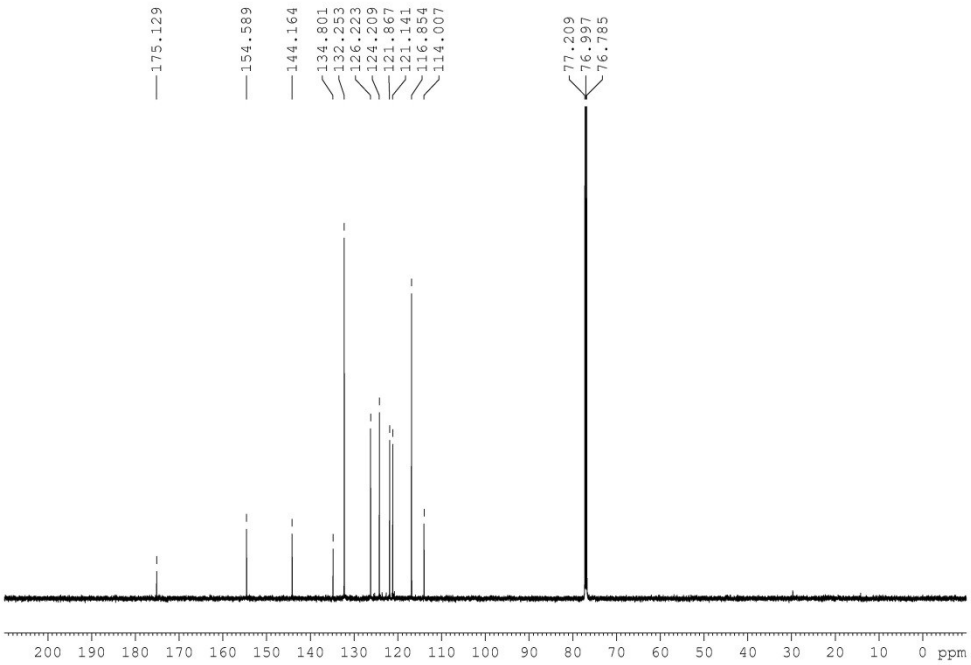
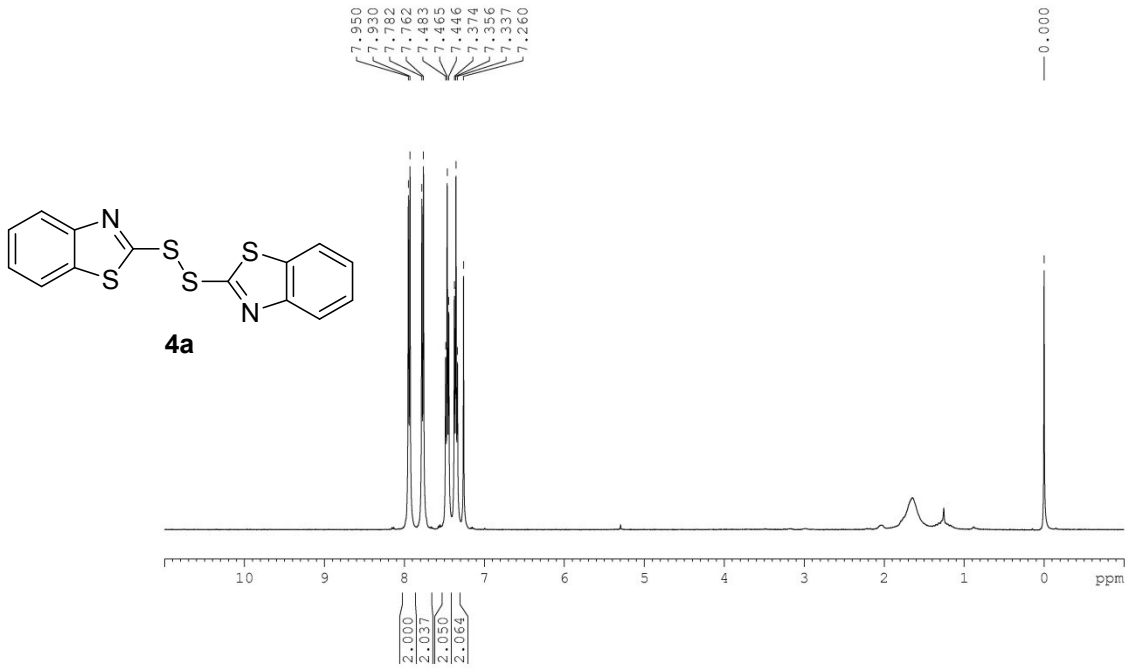
7.429
7.416
7.305
7.293
7.280
7.260
7.235
7.221
7.058
7.044
5.561
0.003
N
S
S
HN
Cl
3p
10
9
8
7
6
5
4
3
2
1
0
ppm
1.009
1.017
1.065
1.094
2.000
2.040
1.045

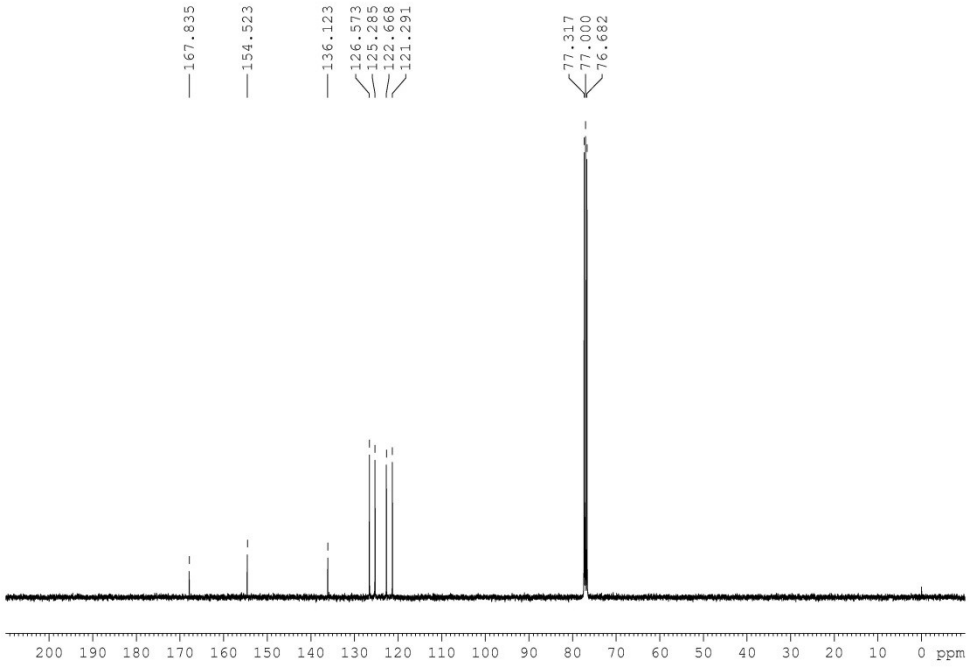

175.145
154.639
143.628
134.820
129.378
126.787
126.227
124.209
121.905
121.147
116.441
77.209
76.997
76.786
0.019
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

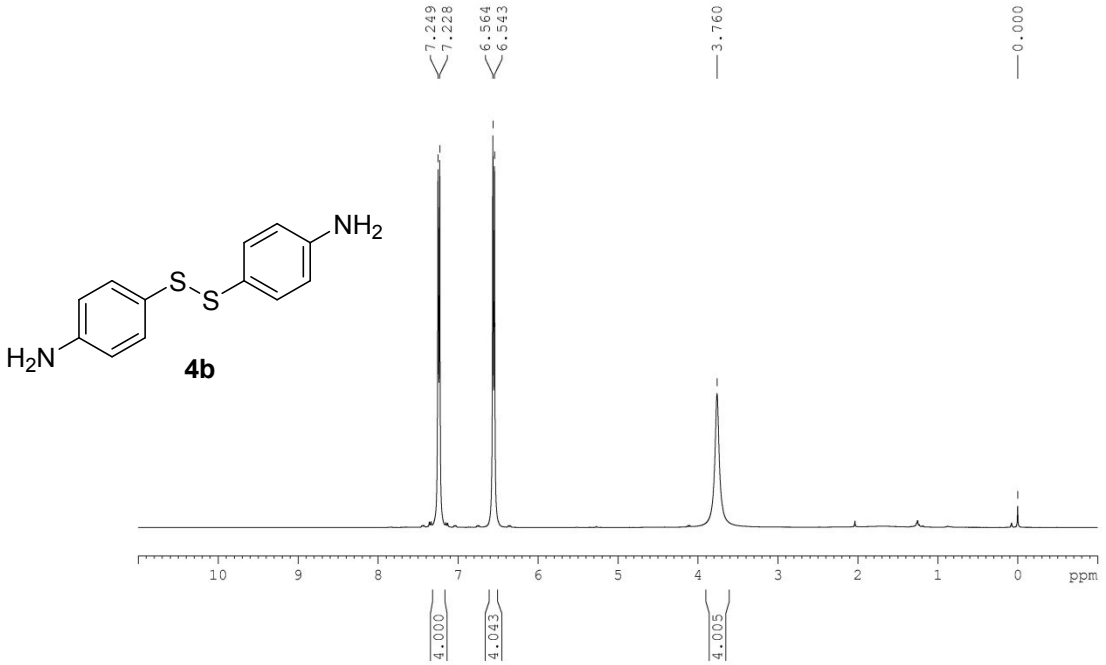

7.878
7.864
7.745
7.732
7.442
7.429
7.416
7.373
7.358
7.306
7.293
7.281
7.260
7.011
6.996
5.591
0.002
N
S
S
HN
Br
3q
10
9
8
7
6
5
4
3
2
1
0
ppm
1.062
1.083
1.098
2.068
1.062
2.041
1.000

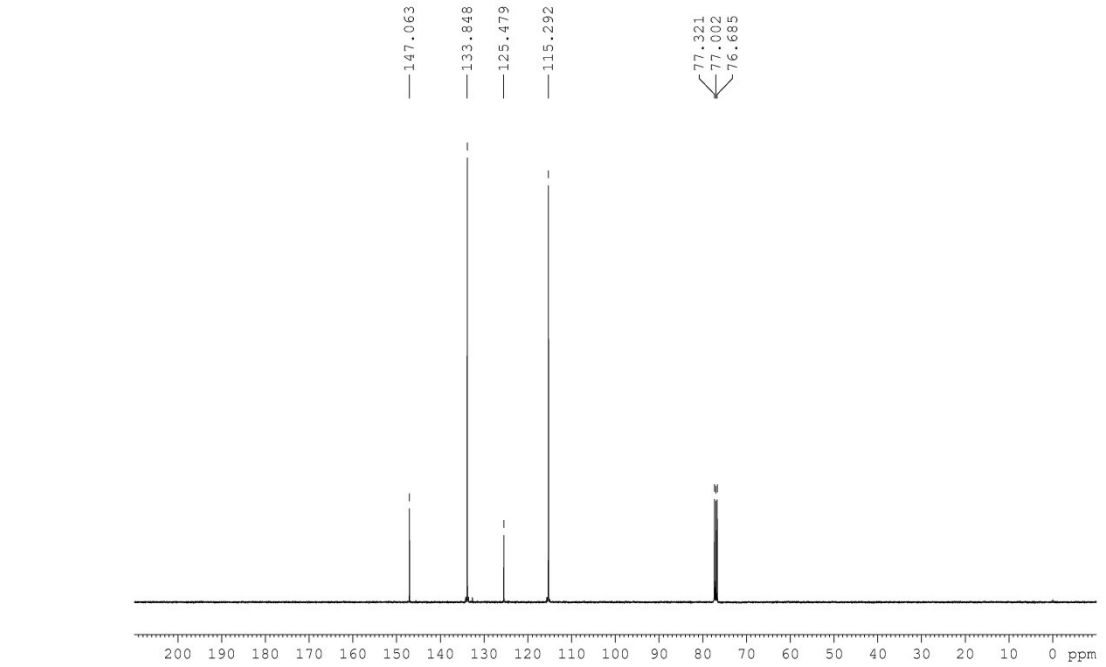

175.129
154.589
144.164
134.801
132.253
126.223
124.209
121.867
121.141
116.854
114.007
77.209
76.997
76.785
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

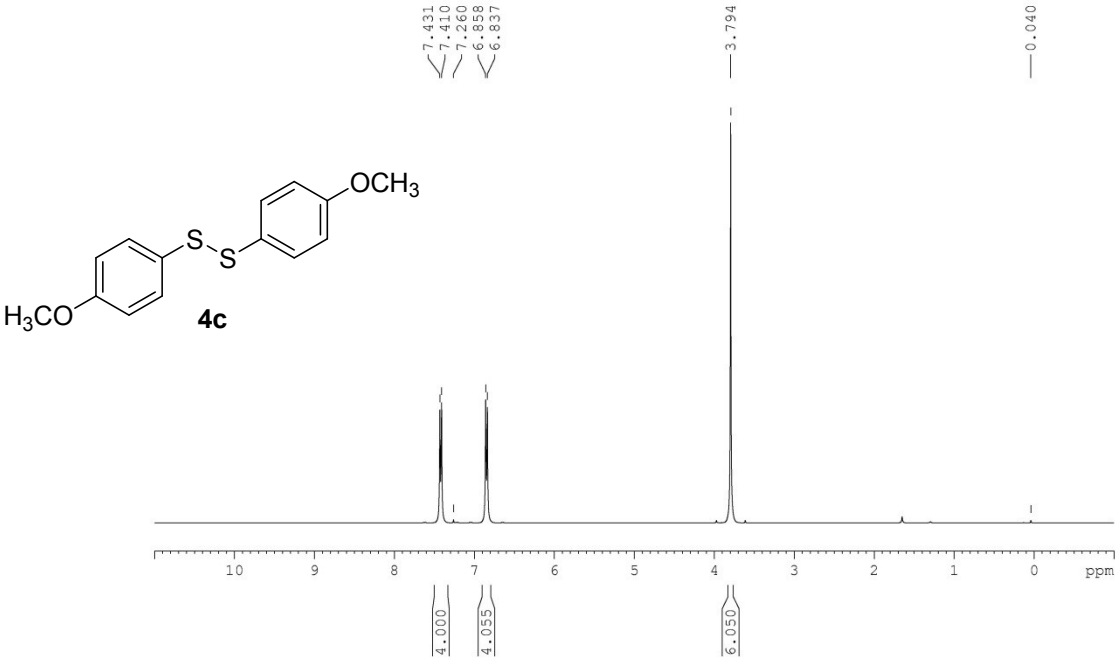

7.950
7.930
7.782
7.762
7.483
7.465
7.446
7.374
7.356
7.337
7.260
0.000
10
9
8
7
6
5
4
3
2
1
0
ppm
2.000
2.037
2.050
2.064

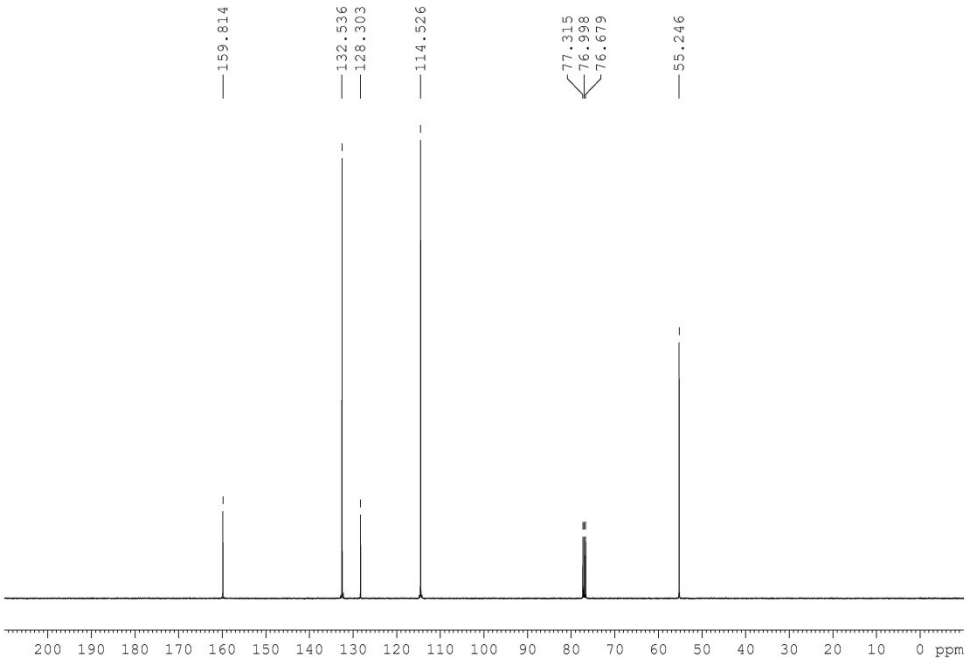
4a

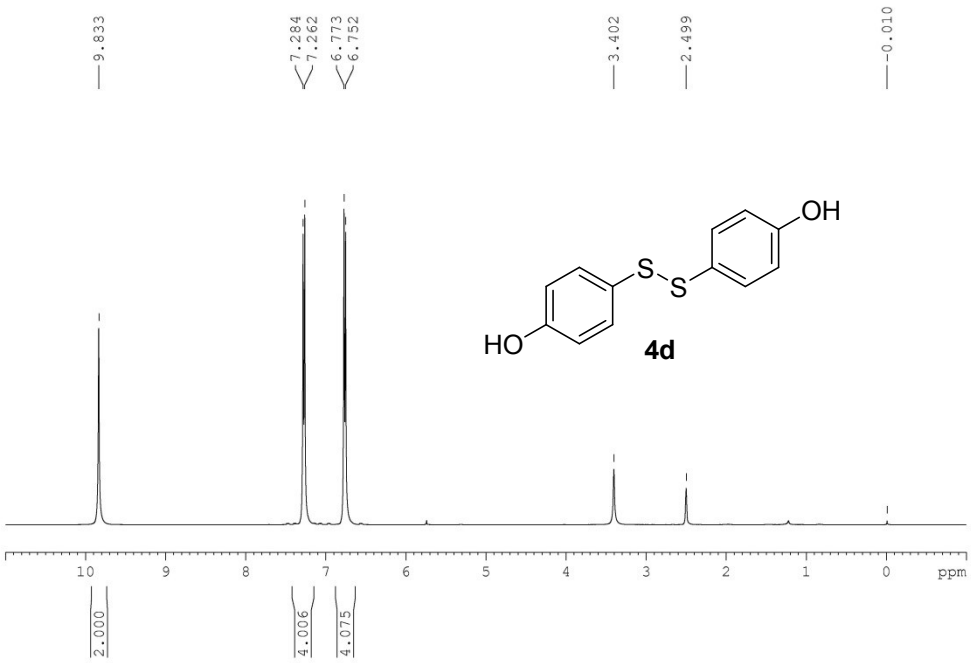

167.835
154.523
136.123
126.573
125.285
122.668
121.291
77.317
77.000
76.682
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

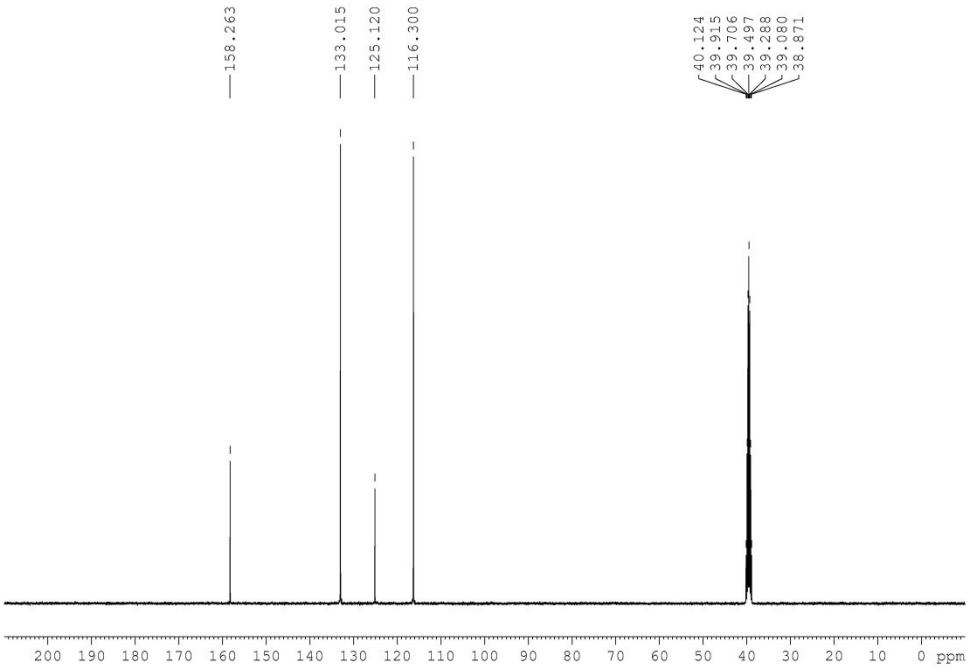

7.249
7.228
6.564
6.543
3.760
0.000
NH2
S
S
H2N
4b
10
9
8
7
6
5
4
3
2
1
0
ppm
4.000
4.043
4.005

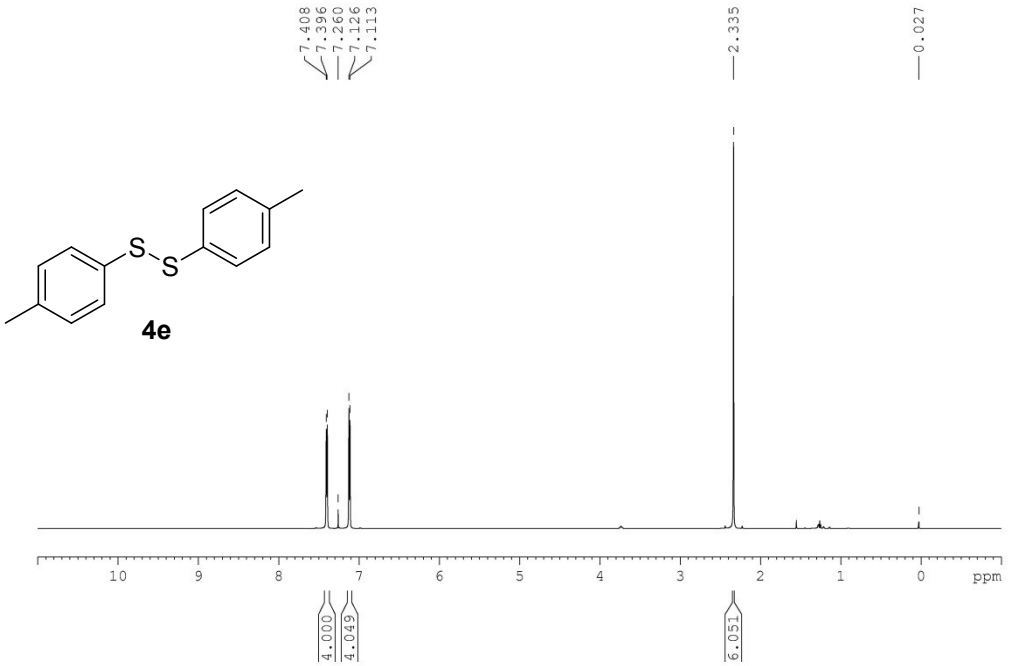

147.063
133.848
125.479
115.292
77.321
77.002
76.685
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

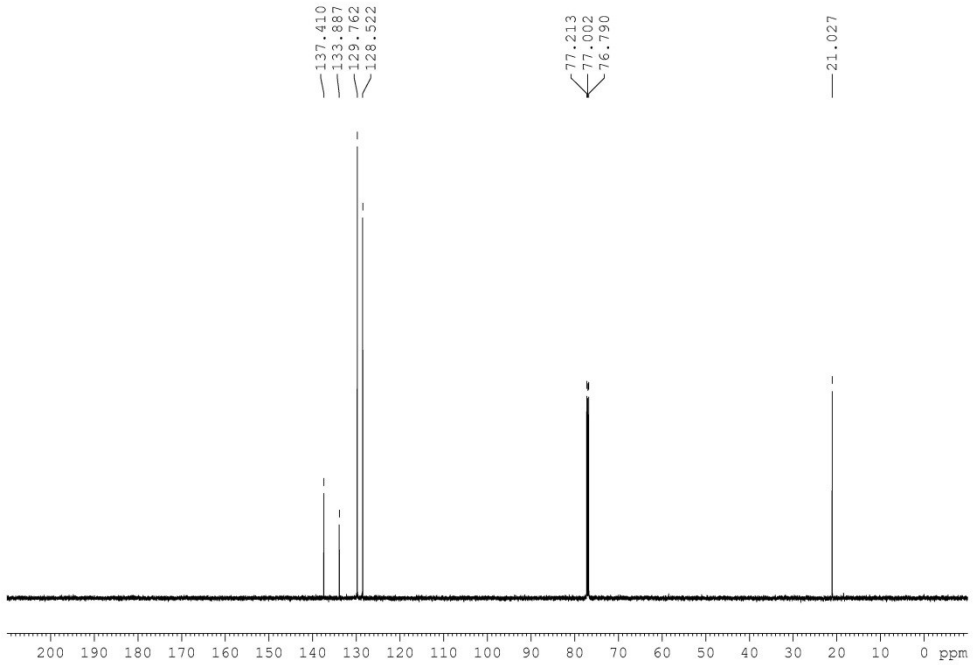

7.431
7.410
7.260
6.858
6.837
3.794
0.040
OCH3
S
S
H3CO
4c
10
9
8
7
6
5
4
3
2
1
0
ppm
4.000
4.055
6.050

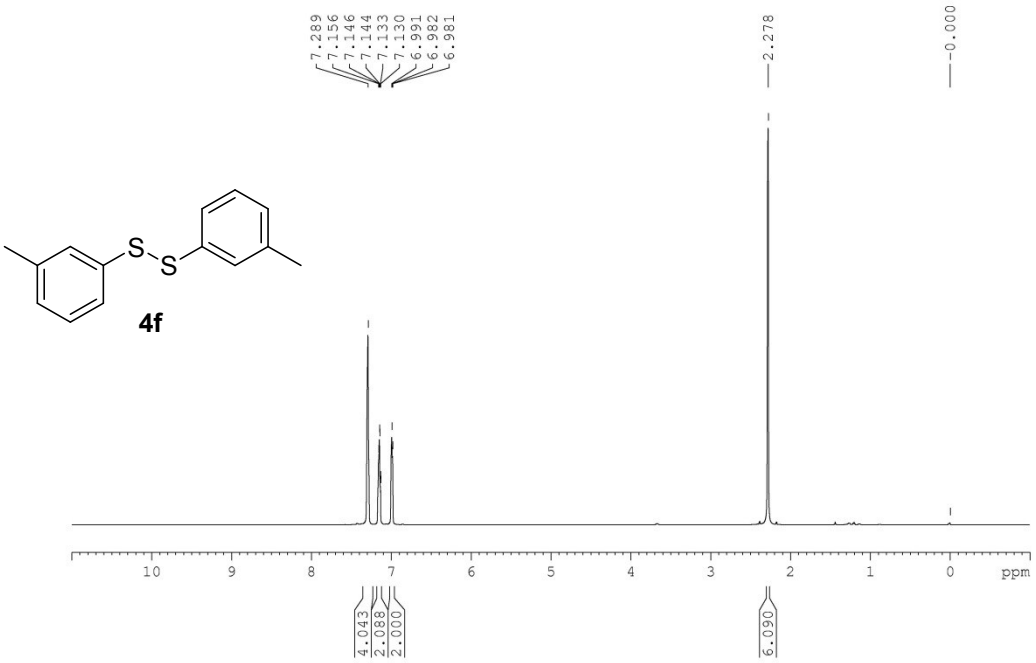

159.814
132.536
128.303
114.526
77.315
76.998
76.679
55.246
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

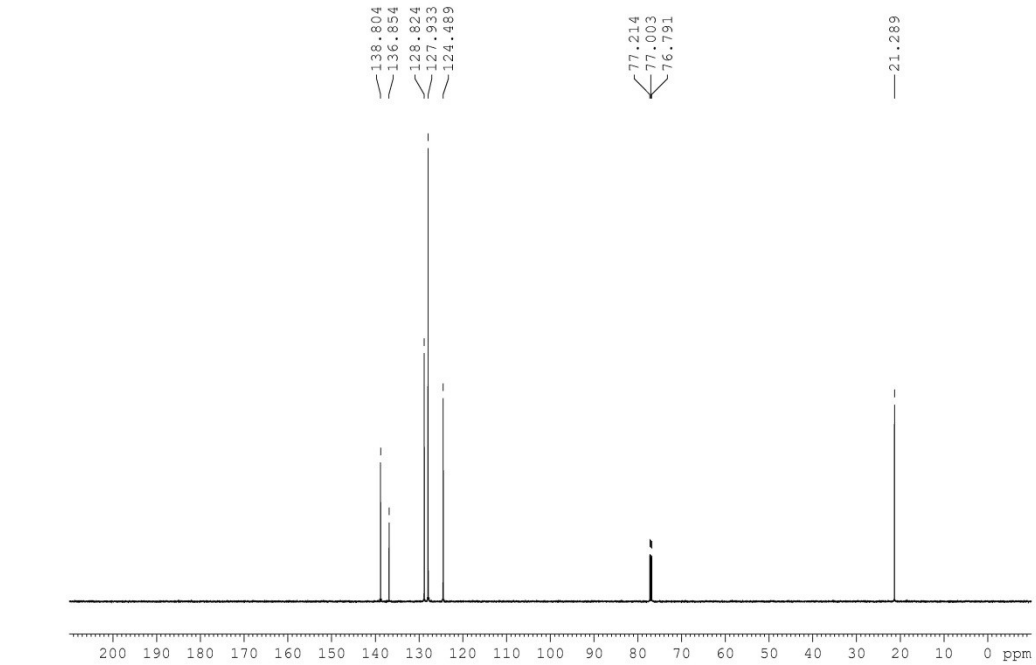

9.833
7.284
7.262
6.773
6.752
3.402
2.499
0.010
OH
S
S
HO
4d
10
9
8
7
6
5
4
3
2
1
0
ppm
2.000
4.006
4.075

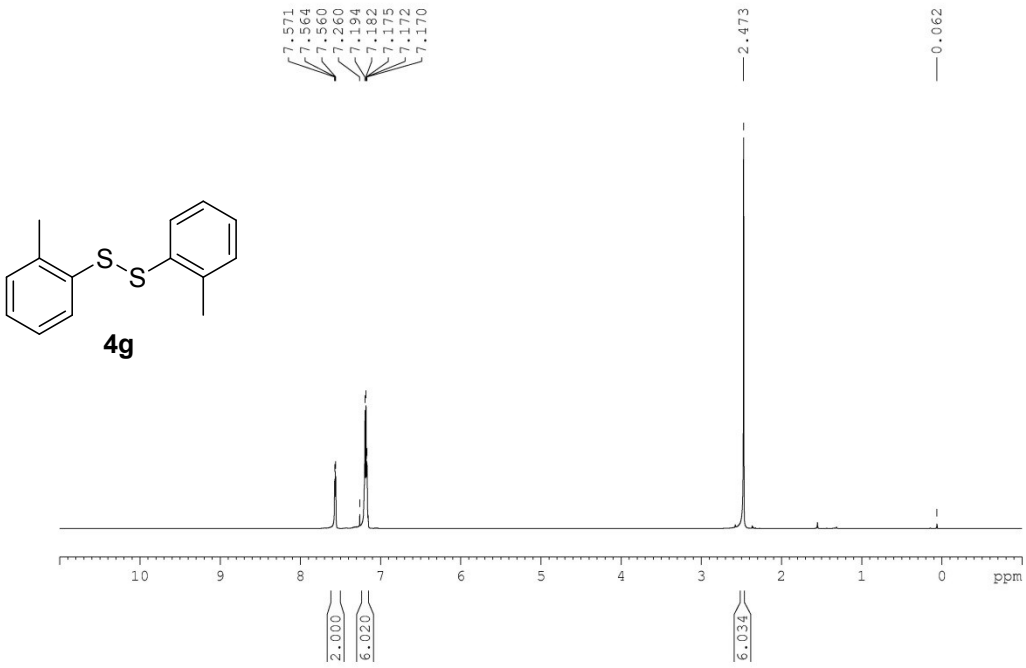

158.263
133.015
125.120
116.300
40.124
39.915
39.706
39.497
39.288
39.080
38.871
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

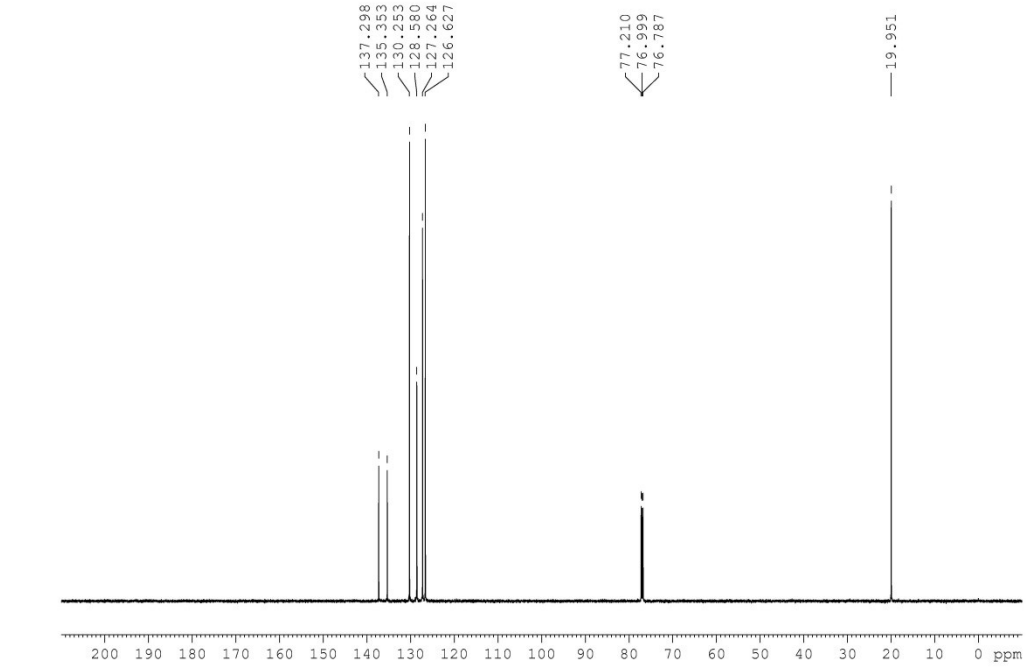

7.408
7.396
7.260
7.126
7.113
2.335
0.027
S
S
4e
10
9
8
7
6
5
4
3
2
1
0
ppm
4.000
4.049
6.051

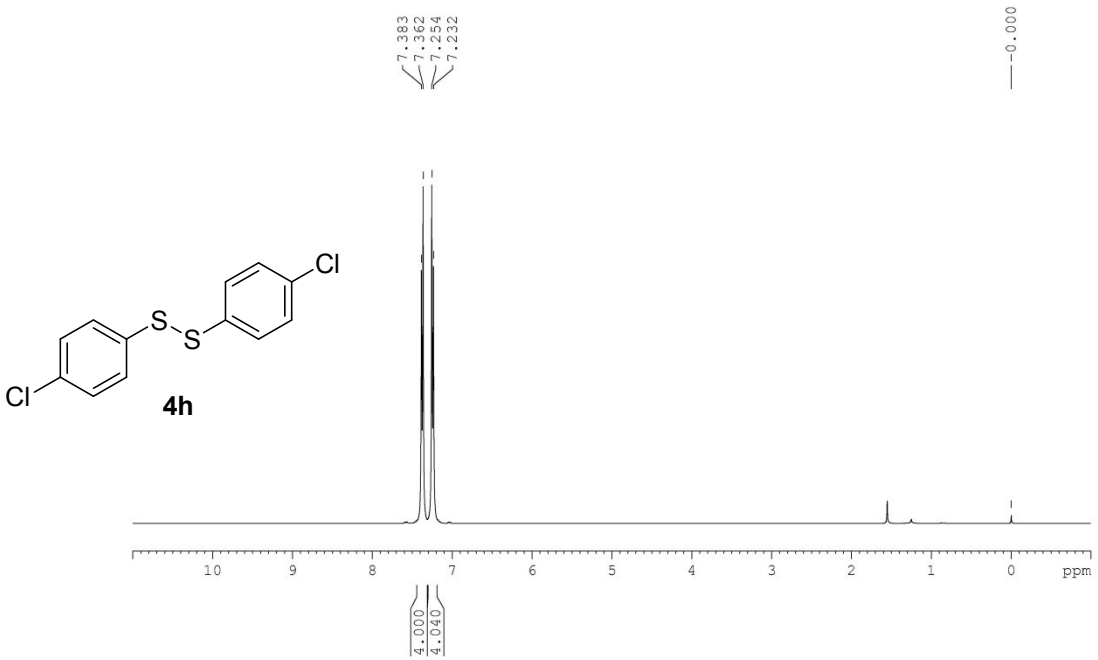

137.410
133.887
129.762
128.522
77.213
77.002
76.790
21.027
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

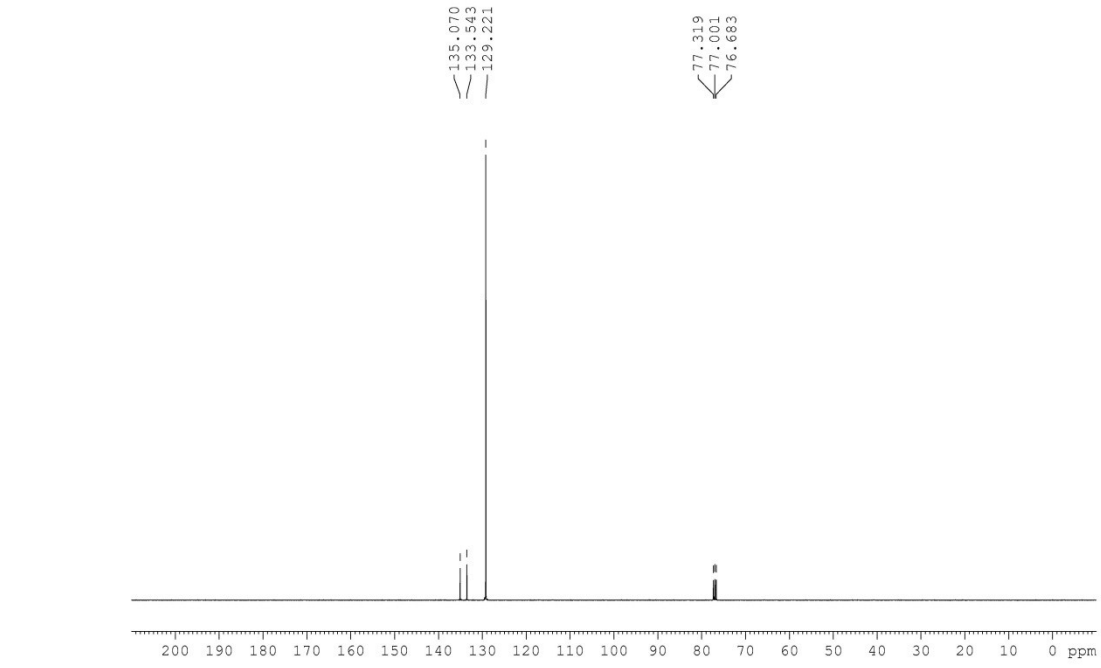

7.289
7.156
7.146
7.144
7.133
7.130
6.991
6.982
6.981
2.278
0.000
S
S
4f
10
9
8
7
6
5
4
3
2
1
0
ppm
4.043
2.088
2.000
6.090


138.804
136.854
128.824
127.933
124.489
77.214
77.003
76.791
21.289
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm


7.571
7.564
7.560
7.260
7.194
7.182
7.175
7.172
7.170
2.473
0.062
S
S
4g
10
9
8
7
6
5
4
3
2
1
0
ppm
2.000
6.020
6.034

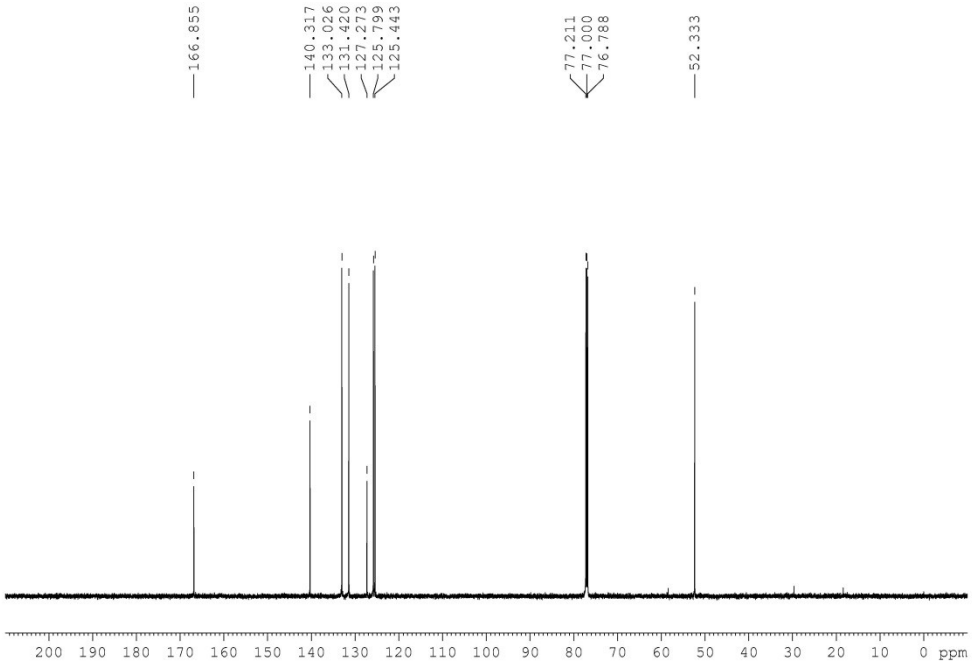

137.298
135.353
130.253
128.580
127.264
126.627
77.210
76.999
76.787
19.951
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

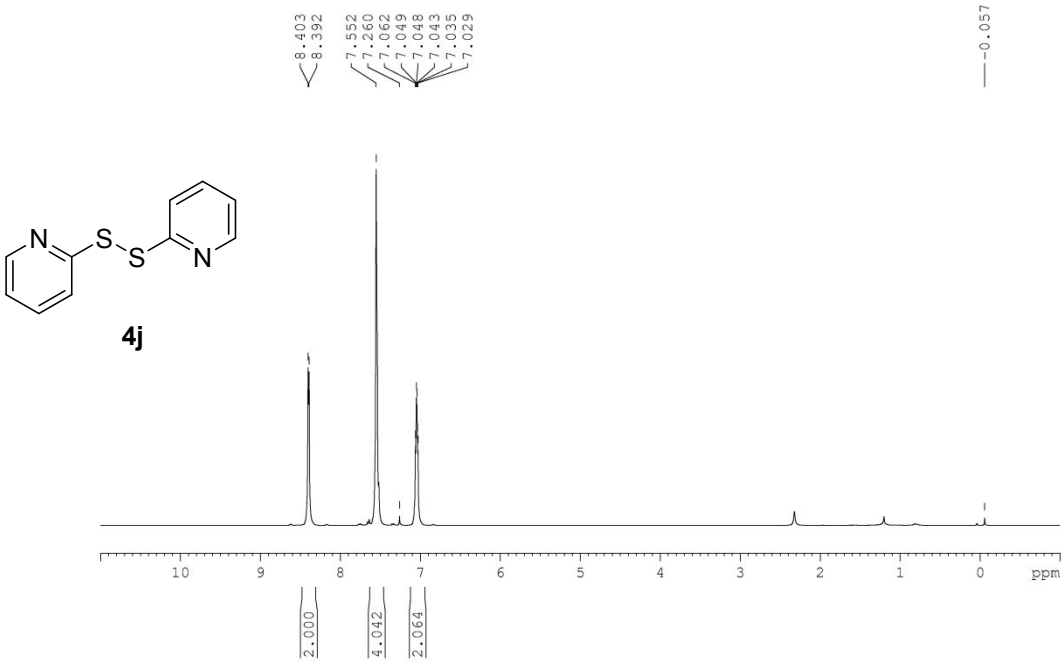

7.383
7.362
7.254
7.232
0.000
Cl
S
S
Cl
4h
10
9
8
7
6
5
4
3
2
1
0
ppm
4.000
4.040

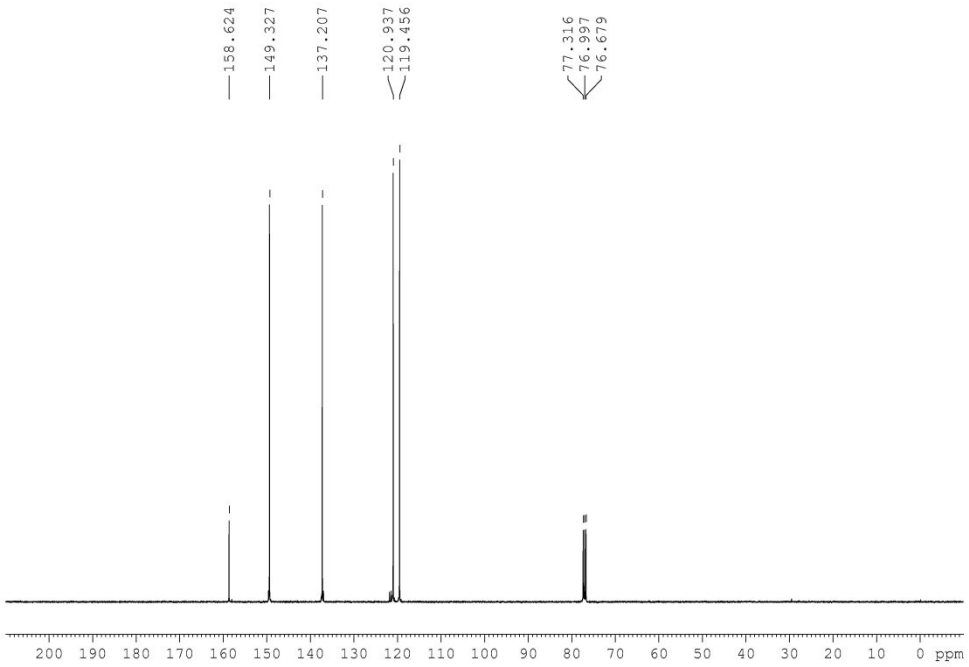

135.070
133.543
129.221
77.319
77.001
76.683
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

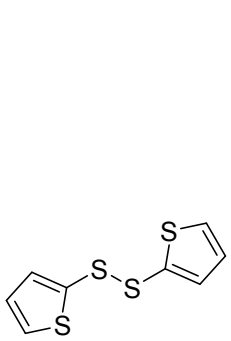

8.061
8.048
7.758
7.744
7.416
7.414
7.402
7.390
7.388
7.260
7.237
7.225
7.212
3.980
-0.005
COOCH3
S
S
COOCH3
10
9
8
7
6
5
4
3
2
1
0
ppm
2.000
2.005
2.069
2.061
6.039

4i


166.855
140.317
133.026
131.420
127.273
125.799
125.443
77.211
77.000
76.788
52.333
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

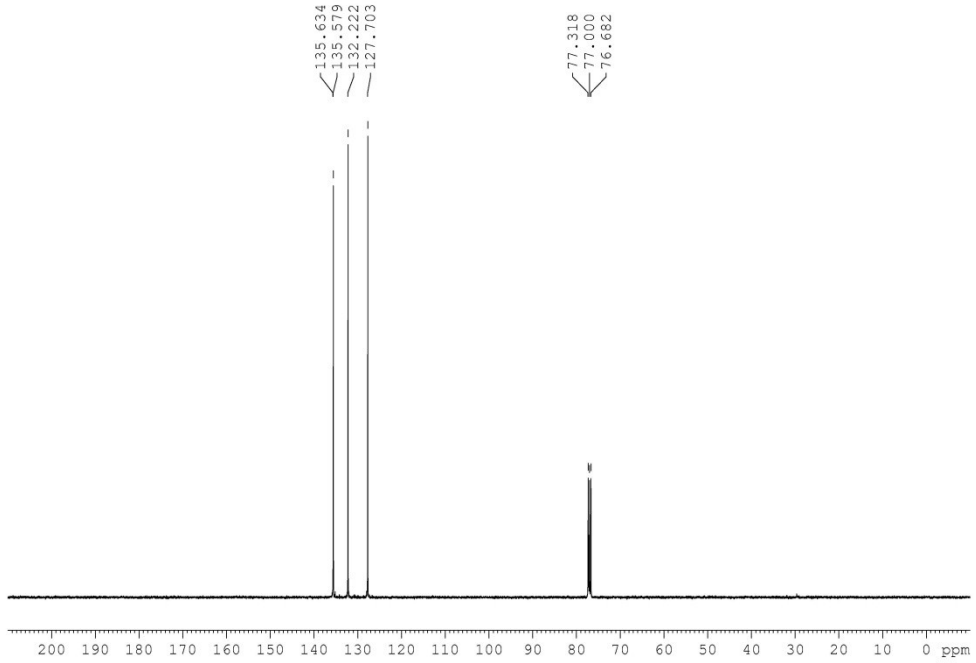

8.403
8.392
7.552
7.260
7.062
7.049
7.048
7.043
7.035
7.029
-0.057
N
S
S
N
4j
10
9
8
7
6
5
4
3
2
1
0
ppm
2.000
4.042
2.064

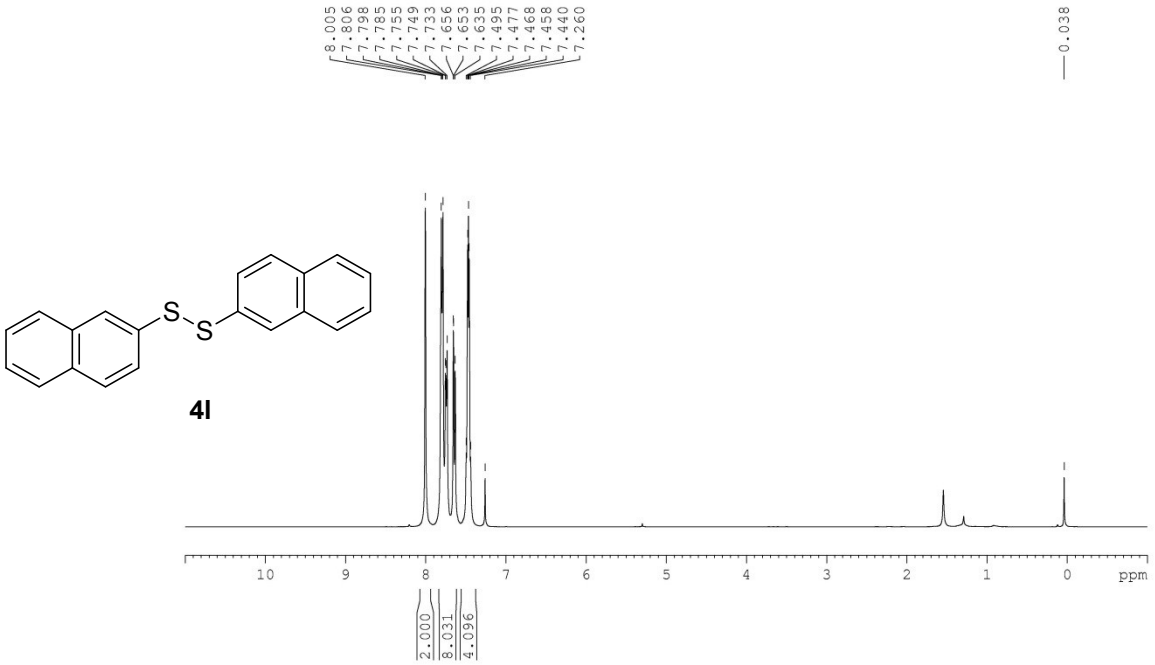

158.624
149.327
137.207
120.937
119.456
77.316
76.997
76.679
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

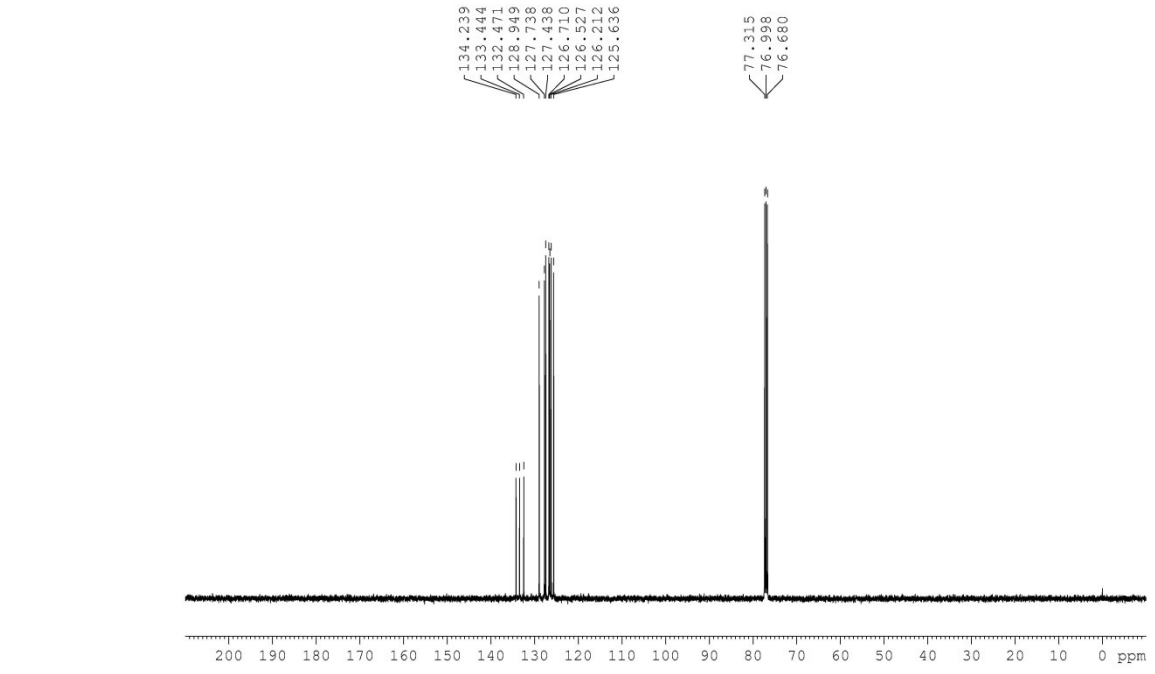


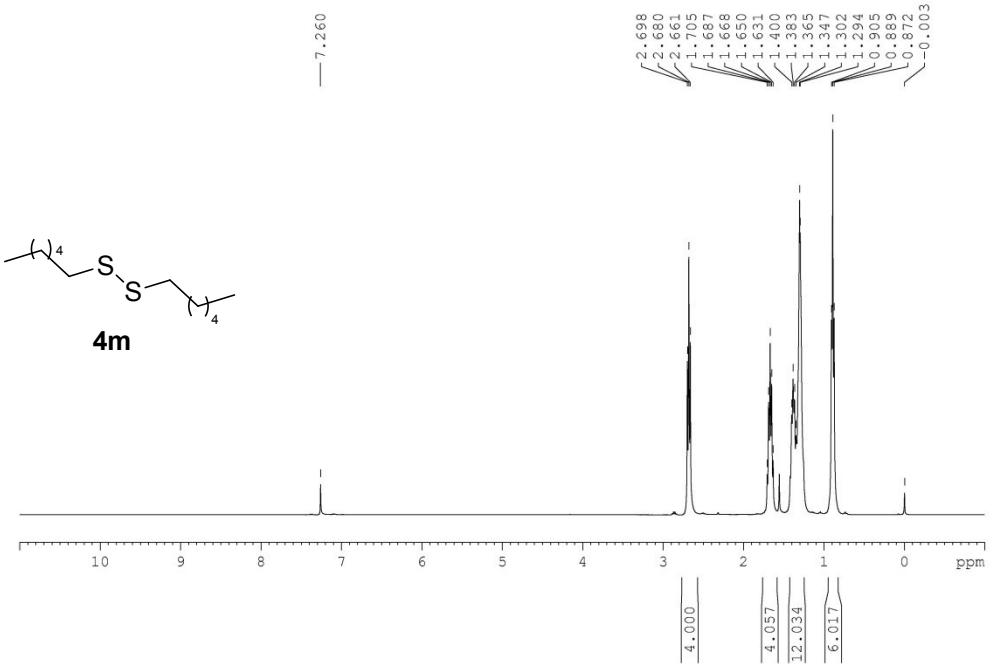
4k

7.505
7.492
7.260
7.172
7.163
7.032
7.023
7.019
7.010
0.033
10
9
8
7
6
5
4
3
2
1
0
ppm
2.004
2.000
2.122

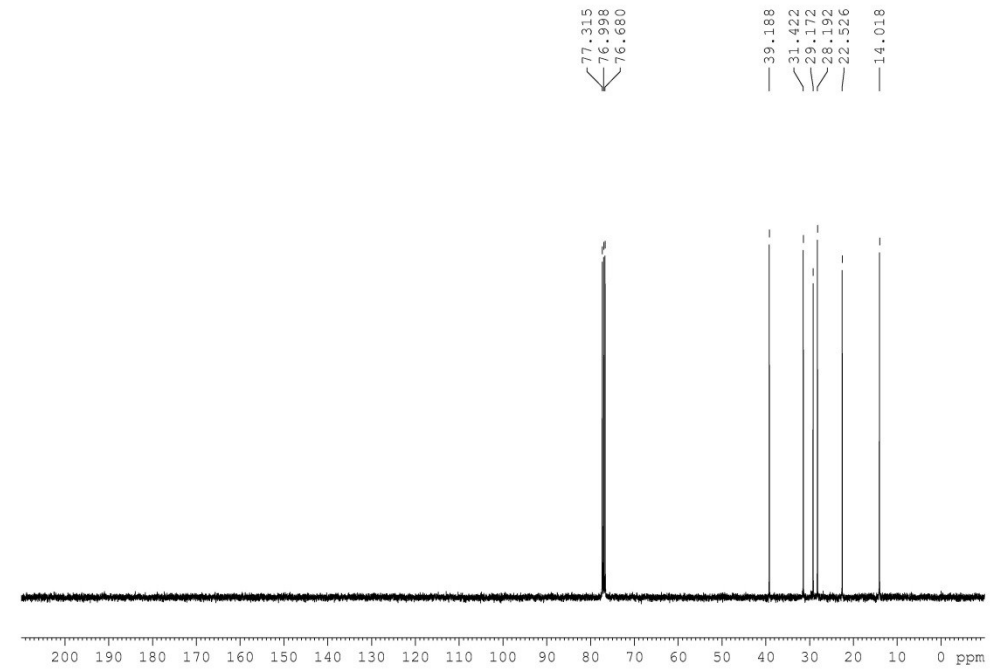

135.634
135.579
132.222
127.703
77.318
77.000
76.682
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

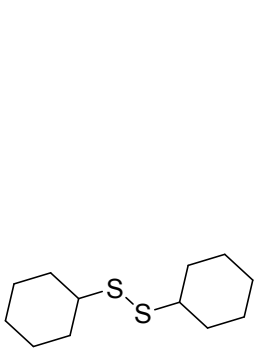

8.005
7.806
7.798
7.785
7.755
7.749
7.733
7.656
7.653
7.635
7.495
7.477
7.468
7.458
7.440
7.260
0.038
S
S
4l
10
9
8
7
6
5
4
3
2
1
0
ppm
2.000
8.031
4.096


134.239
133.444
132.471
128.949
127.738
127.438
126.710
126.527
126.212
125.636
77.315
76.998
76.680
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm


7.260
2.698
2.680
2.661
1.705
1.687
1.668
1.650
1.631
1.400
1.383
1.365
1.347
1.302
1.294
0.905
0.889
0.872
0.003
10
9
8
7
6
5
4
3
2
1
0
ppm
4.000
4.057
12.034
6.017

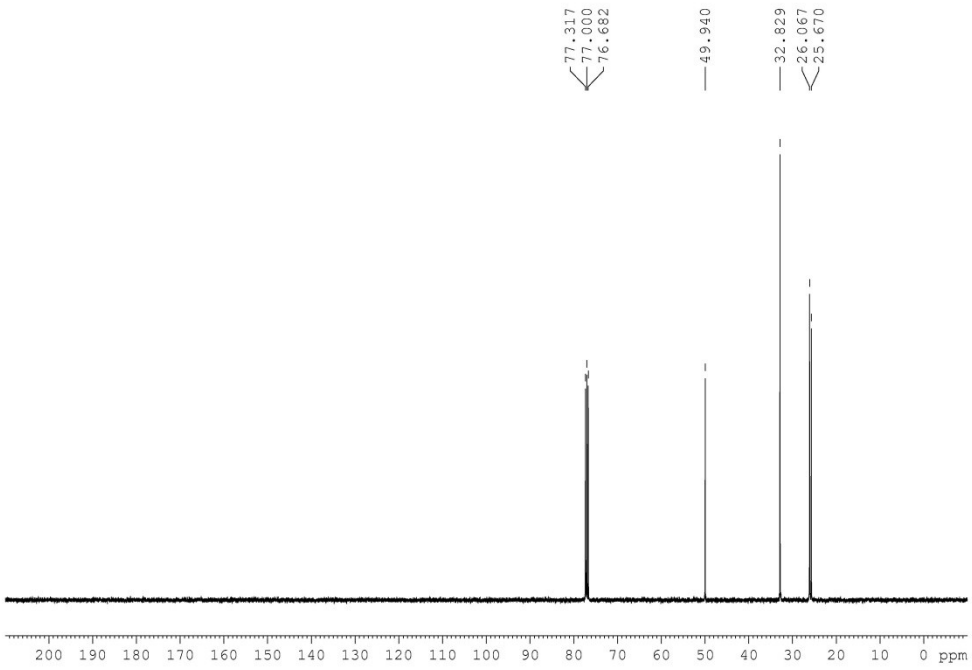
4m

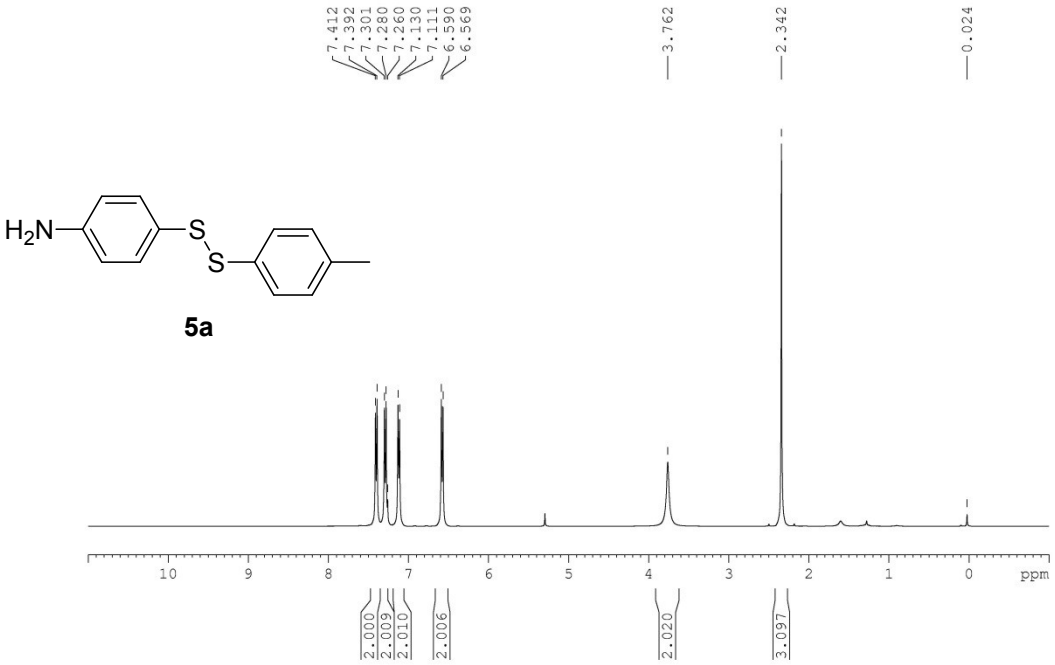

77.315
76.998
76.680
39.188
31.422
29.172
28.192
22.526
14.018
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm


S
S

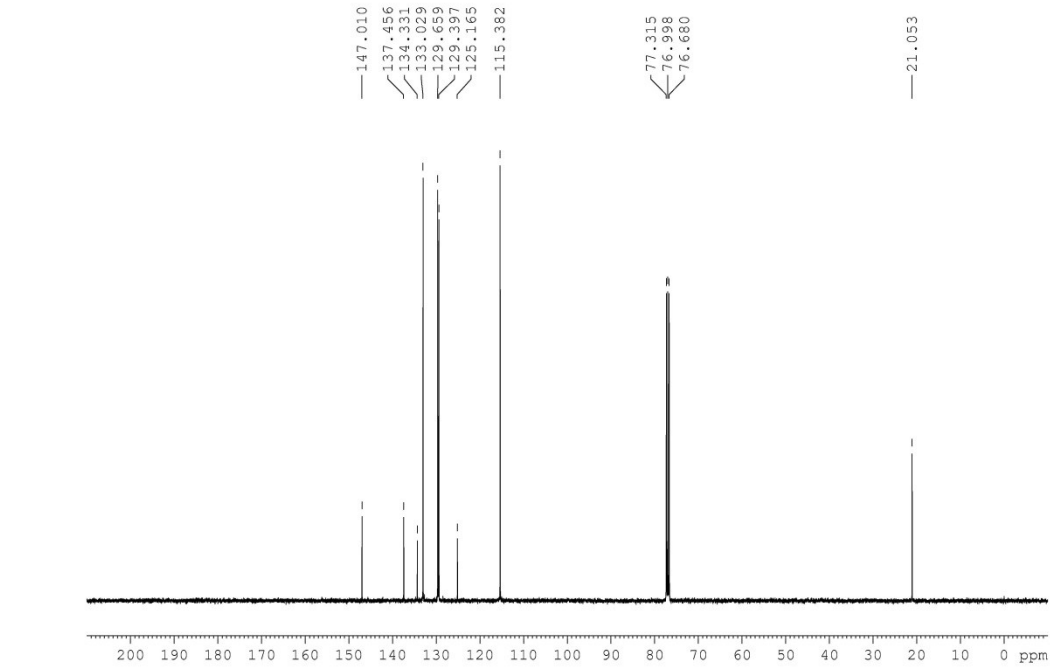
4n

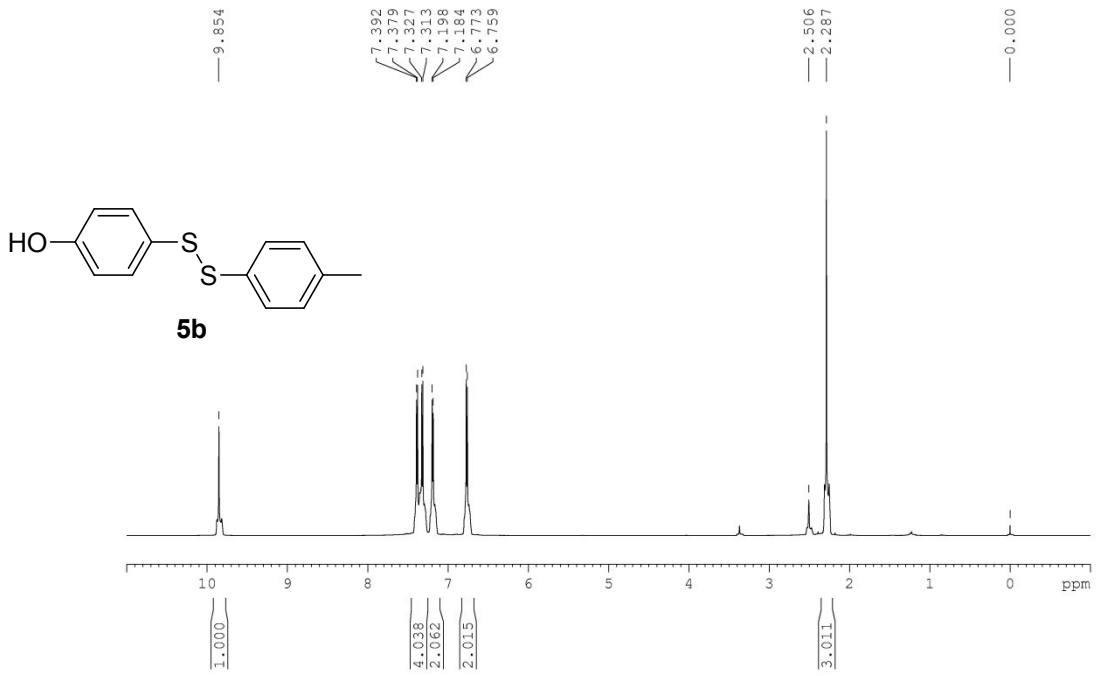
7.260
2.678
2.670
2.047
2.027
1.785
1.625
1.600
1.302
1.271
1.247
0.005
10 9 8 7 6 5 4 3 2 1 0 ppm
2.000
4.100
4.132
2.025
10.626

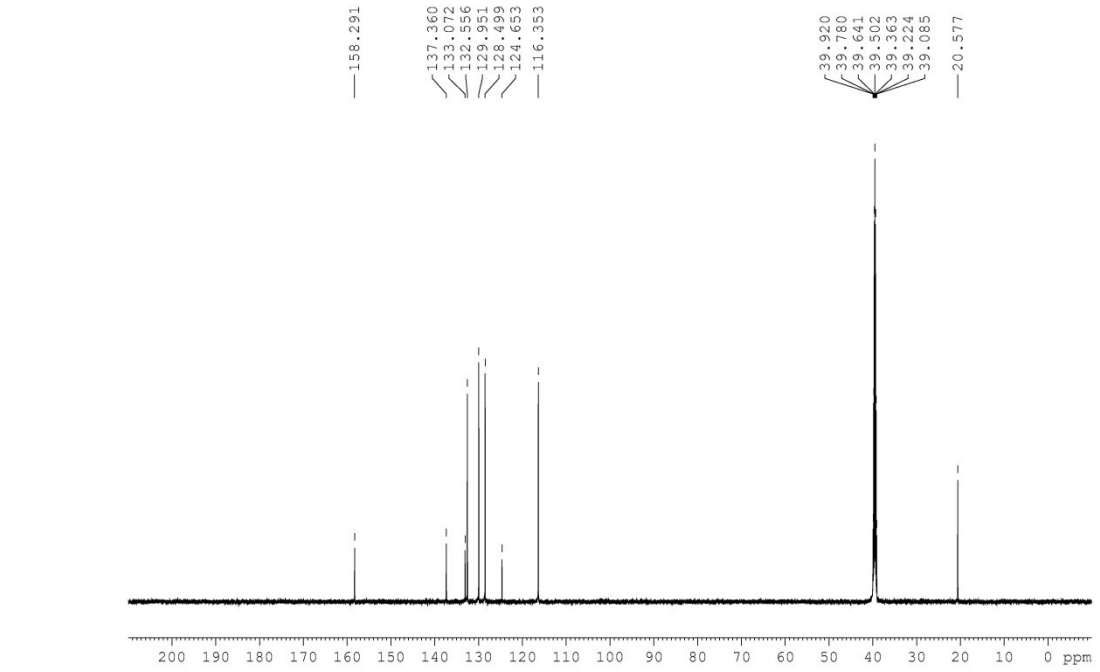

77.317
77.000
76.682
49.940
32.829
26.067
25.670
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

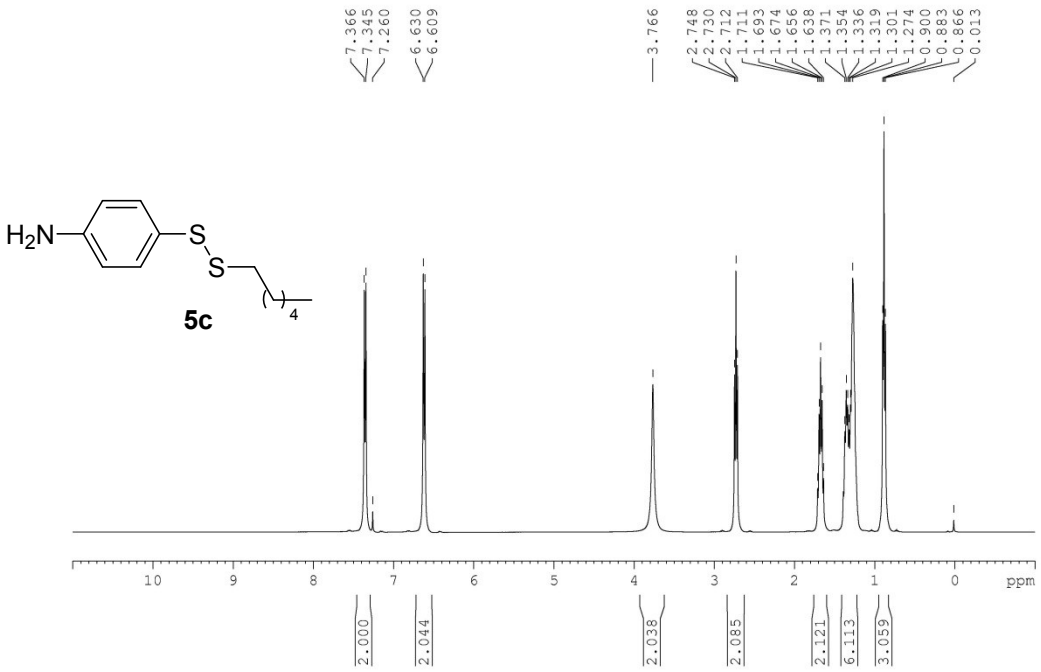

7.412
7.392
7.301
7.280
7.260
7.130
7.111
6.590
6.569
3.762
2.342
0.024
H_2N
S
S
10
9
8
7
6
5
4
3
2
1
0
ppm
2.000
2.009
2.010
2.006
2.020
3.097

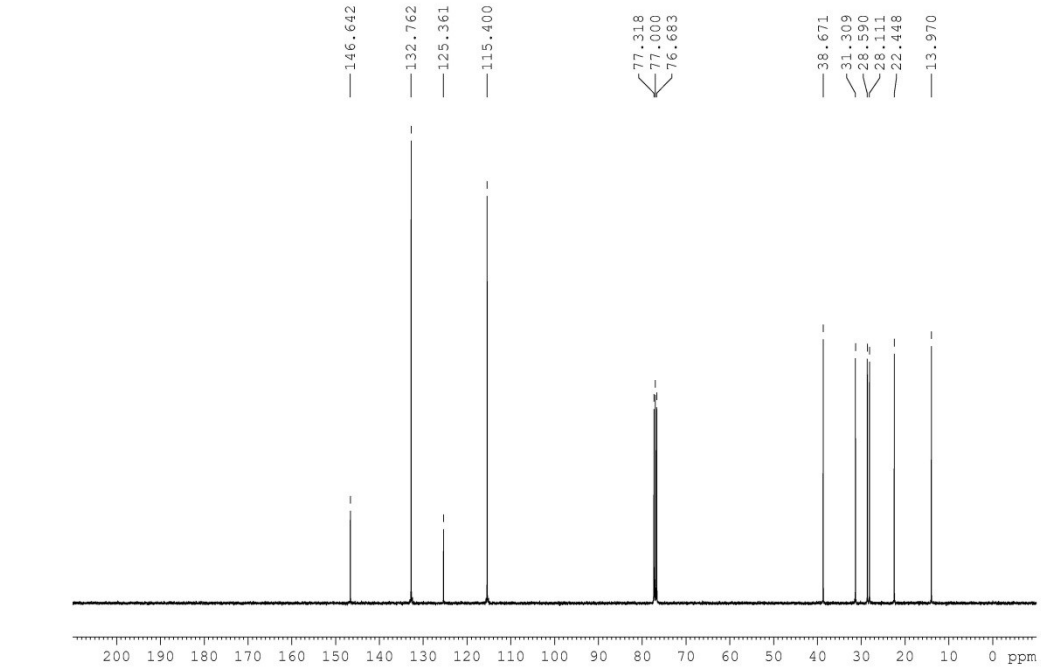
5a

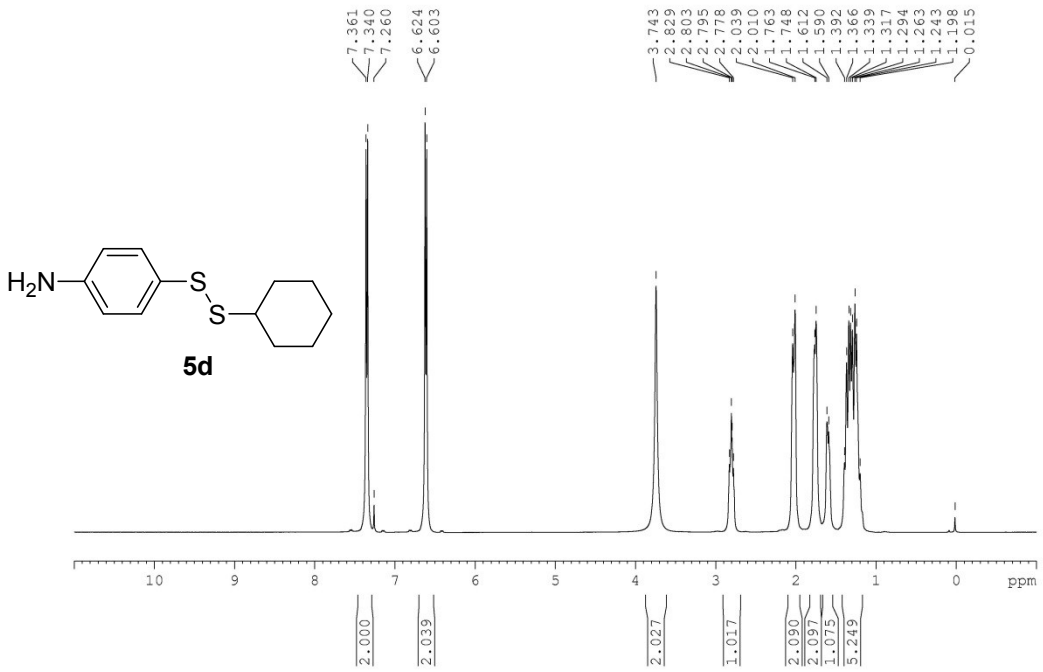

147.010
137.456
134.331
133.029
129.659
129.397
125.165
115.382
77.315
76.998
76.680
21.053
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

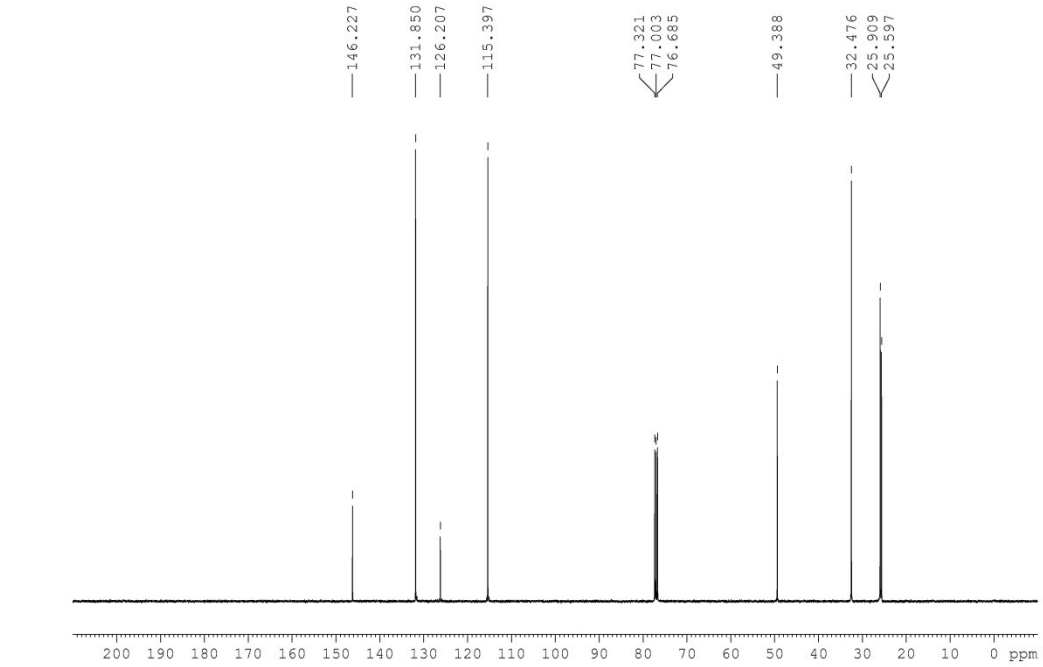

9.854
7.392
7.379
7.327
7.313
7.198
7.184
6.773
6.759
2.506
2.287
0.000
HO
S
S
5b
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
4.038
2.062
2.015
3.011


158.291
137.360
133.072
132.556
129.951
128.499
124.653
116.353
39.920
39.780
39.641
39.502
39.363
39.224
39.085
20.577
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.366
7.345
7.260
6.630
6.609
3.766
2.748
2.730
2.712
1.711
1.693
1.674
1.656
1.638
1.371
1.354
1.336
1.319
1.301
1.274
0.900
0.883
0.866
0.013
H2N
S
S
4
5c
10
9
8
7
6
5
4
3
2
1
0
ppm
2.000
2.044
2.038
2.085
2.121
6.113
3.059


146.642
132.762
125.361
115.400
77.318
77.000
76.683
38.671
31.309
28.590
28.111
22.448
13.970
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm


7.361
7.340
7.260
6.624
6.603
3.743
2.829
2.803
2.795
2.778
2.039
2.010
1.763
1.748
1.612
1.590
1.392
1.366
1.339
1.317
1.294
1.263
1.243
1.198
0.015
H_2N
S
S
5d
10 9 8 7 6 5 4 3 2 1 0 ppm
2.000
2.039
2.027
1.017
2.090
2.097
1.075
5.249


146.227
131.850
126.207
115.397
77.321
77.003
76.685
49.388
32.476
25.909
25.597
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm