Supporting Information for

Homonuclear Bond Activation Using a Stable N,N'-Diamidocarbene

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General Considerations. Unless otherwise noted, all manipulations were performed in a nitrogen purged glove box or under an atmosphere of nitrogen using standard Schlenk techniques. N,N'-Dimesityl-4,6-diketo-5,5-dimethylpyrimidin-2-ylidene (**1**),[1] N,N'-dimesityl-pyrimidin-2-ylidene (6Mes),[2] N,N'-dimesityl-imidazol-2-ylidene (SIMes)[3] and 2,3-diphenylcycloprop-2-enone[4] were prepared according to published procedures. All other reagents were commercially available and used as received after drying. Liquid reagents were dried over 3 Å molecular sieves, and solid reagents were dried under high vacuum. Unless otherwise noted, solvents were dried over 3 Å molecular sieves or using a Vacuum Atmospheres Company solvent purification system, and then subsequently stored over 3 Å molecular sieves. ^{1}H and ^{13}C NMR data were collected on a Varian Unity INOVA 400 MHz spectrometer. Chemical shifts (δ) are reported in ppm and referenced downfield from $(CH_3)_4Si$ using the residual solvent peak as an internal standard (^{1}H: $CDCl_3$, 7.24 ppm; C_6D_6, 7.15 ppm; C_7D_8, 7.09 ppm; ^{13}C: $CDCl_3$, 77.0 ppm; C_6D_6 128.0 ppm; C_7D_8, 137.5 ppm). Mass spectra (CI) were obtained with a Karatos MS9 instrument and are reported as m/z (relative intensity). IR spectra were recorded using either a Thermo Scientific Nicolet iS5 system equipped with an iD3 attenuated total reflectance (ATR) attachment (germanium crystal) or a Perkin-Elmer Spectrum BX system in the solid state in KBr. Melting points or decomposition temperatures (T_d) were collected using a Stanford Research Systems MPA100 OptiMelt automated melting point apparatus (ramp rate: 5 °C min^{-1}) and are uncorrected. Elemental analyses were performed by Midwest Microlab, LLC (Indianapolis, IN).

Synthesis of 1,3-dimesityl-4,6-diketo-5,5-dimethylpyrimidinium-2-bromo bromide (2). An oven dried 10 mL Schlenk flask was charged with **1** (162 mg, 0.44 mmol) and benzene (2 mL) and then sealed with a rubber septum. Under a positive pressure of nitrogen, 1 equiv. of bromine (11.3 μL, 0.44 mmol) was added dropwise. The immediate formation of a white precipitate was observed. After stirring the resulting mixture for 1 h, the solution was filtered under an atmosphere of nitrogen. The resulting solid was washed with pentane and dried under high vacuum to afford the desired product as a white powder (140 mg, 0.31 mmol) in 70% yield. m.p. 117 °C (decomp.) ^{1}H NMR ($CDCl_3$, 400.27 MHz): δ 1.93 (s, 6H), 2.26 (s, 12H), 2.34 (s, 6H), 7.05 (s, 4H). ^{13}C NMR ($CDCl_3$, 100.49 MHz): δ 17.58, 18.16, 19.48, 21.07, 25.17, 72.0, 129.48, 130.40, 131.08, 133.33, 134.82, 135.35, 168.04. IR (KBr): 2920.58, 1792.96, 1689.52, 1507.42, 1338.42, 1338.22, 1262.43, 1232.89, 1172.30, 1075.86, 974.48, 865.04, 847.47, 746.10. HRMS: $[M]^+$ calcd. for $C_{24}H_{28}N_2O_2Br$: 455.1334. Found: 455.1334. Anal. Calcd. for $C_{24}H_{28}N_2O_2Br_2$: C, 53.75; H, 5.26; N, 5.22. Found: C, 53.57; H, 5.31; N, 5.48. Compound **2** was found to be air sensitive and decomposed to the urea **6** upon exposure to the ambient atmosphere.

Synthesis of 1,3–dimesityl-pyrimidinium-2-bromo bromide (3). An oven dried 10 mL Schlenk flask was charged with 6Mes (115 mg, 0.35 mmol) and benzene (2 mL), and then sealed with a rubber septum. Under a positive pressure of nitrogen, 1 equiv. of bromine (9.2 μL, 0.35 mmol) was added dropwise. The immediate formation of a tan precipitate was observed. After stirring the resulting mixture for 1 h, the solution was exposed to air and the solid was isolated by filtration. The resulting solid was washed with pentane and dried under high vacuum to afford the desired product as a tan powder (126 mg, 0.32 mmol) in 90% yield. m.p. 109 °C (decomp.) ^{1}H NMR ($CDCl_3$, 400.27 MHz): δ 2.16–2.30 (m, 18H), 2.55 (m, 2H), 4.36 (t, J = 5.8 Hz, 4H), 6.88 (s, 4H). ^{13}C NMR ($CDCl_3$, 75.47 MHz): δ 17.69, 17.89, 20.85, 20.92, 51.64, 77.21, 130.47, 133.47, 139.21, 140.43, 147.90, 153.51. IR (ATR): 2980.45, 2911.47, 1613.11, 1587.16, 1477.16, 1338.57, 1314.17, 1214.65, 1024.90, 904.05. HRMS: $[M]^+$ calcd. for $C_{22}H_{28}N_2Br$:

399.1430. Found: 399.1431. Anal. Calcd. for $C_{22}H_{28}N_2Br_2$: C, 55.02; H, 5.88; N, 5.83. Found: C, 55.19; H, 6.22; N, 5.95.

Synthesis of 1,3–dimesityl-imidazolium-2-bromo Bromide (4). An oven dried 10 mL Schlenk flask was charged with SIMes (150 mg, 0.49 mmol) and benzene (2 mL), and then sealed with a rubber septum. Under a positive pressure of nitrogen, 1 equiv. of bromine (12.6 μL, 0.49 mmol) was added dropwise. The immediate formation of a tan precipitate was observed. After stirring the resulting mixture for 4 h, the solution was exposed to air and the solid was isolated by filtration. The resulting solid was washed with pentane and dried under high vacuum to afford the desired product as a tan powder (161 mg, 0.42 mmol) in 85% yield. m.p. 261 °C (decomp.) ^{1}H NMR ($CDCl_3$, 400.27 MHz): δ 2.29 (s, 12H), 2.35 (s, 6H), 4.81 (s, 4H), 6.95 (s, 4H). ^{13}C NMR ($CDCl_3$, 75.47 MHz): δ 17.74, 18.13, 21.08, 52.50, 77.21, 130.20, 130.20, 135.11, 141.26, 151.59, 159.00. IR (ATR): 2975.65, 1608.40, 1571.87, 1481.36, 1444.02, 1283.70, 1191.71, 1017.88, 915.96, 946.50, 752.82. HRMS: $[M]^+$ calcd. for $C_{21}H_{26}N_2Br$: 385.1274. Found: 385.1276. Anal. Calcd. for $C_{21}H_{26}N_2Br_2$: C, 54.10; H, 5.52; N, 6.01. Found: C, 54.49; H, 5.90; N, 6.07.

Synthesis of 1,3-dimesityl-5,5-dimethyl-4,6-dioxohexahydropyrimidine-2,2-diyl dibenzoate (5). An oven dried 8 mL vial was charged with **1** (182 mg, 0.49 mmol), 1 equiv. of benzoyl peroxide (117 mg, 0.49 mmol) and benzene (5 mL). The vial was sealed and the resulting solution stirred for 1 h after which time the reaction mixture was precipitated into hexanes (50 mL). The resulting powder was isolated by filtration and dried under high vacuum yielding the desired product as a white powder (202 mg, 0.33 mmol) in 67% yield. m.p. 157–160 °C. ^{1}H NMR (C_6D_6, 400.27 MHz): δ 1.61 (s, 6H), 2.05 (s, 6H), 2.07 (s, 12H), 6.72 (s, 4H), 6.93–6.97 (m, 4H), 7.05–7.10 (m, 2H,) 7.92–7.96 (m, 4H). ^{13}C NMR (C_6D_6, 75.47 MHz): δ 17.72, 18.61, 20.95, 25.22, 48.08, 126.09, 127.88, 128.84, 129.38, 129.67, 129.88, 130.67, 131.11, 133.95, 134.13, 135.38, 149.12, 162.63, 171.80. IR (KBr): 2922.09, 1786.73, 1724.88, 1695.42, 1599.06, 1451.66, 1387.55, 1349.91, 1245.41, 1212.76, 1173.20, 1039.07, 1016.28, 996.45, 860.83, 701.22, 506.82. HRMS: $[M]^+$ calcd. for $C_{38}H_{38}N_2O_6$: 618.2724. Found: 618.2720. Anal. Calcd. for $C_{38}H_{38}N_2O_6$: C, 73.33; H, 6.19; N, 4.53. Found: C, 73.31; H, 6.14; N, 4.92.

Synthesis of 1,3-dimesityl-5,5-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione (6). An oven dried 8 mL vial was charged with **1** (200 mg, 0.53 mmol), 1 equiv. of benzoyl peroxide (129 mg, 0.53 mmol) and benzene (5 mL). The vial was sealed and the resulting solution stirred for 5 h at 25 °C. The resulting solution was layered with pentane (5 mL) and placed in a –20 °C freezer. After 24 h, the clear crystals that formed were isolated by filtration and dried under high vacuum to afford the desired product as a white solid (190 mg, 0.48 mmol) in 91% yield. m.p. 177-180 °C. ^{1}H NMR (C_6D_6, 400.27 MHz): δ 1.61 (s, 6H), 2.05 (s, 6H), 2.07 (s, 12H), 6.72 (s, 4H). ^{13}C NMR (C_6D_6, 75.47 MHz): δ 17.48, 20.71, 24.98, 47.83, 127.64, 127.87, 129.43, 130.88, 135.14, 138.37, 148.87, 171.55. IR (ATR): 2923.93, 1694.22, 1609.97, 1464.92, 1387.21, 1348.23, 1245.58, 1199.15, 1177.88, 1034.67, 861.00, 789.94, 757.86. HRMS: $[M]^+$ calcd. for $C_{24}H_{28}N_2O_3$: 392.2904. Found: 392.2902. Anal. Calcd. for $C_{24}H_{28}N_2O_3$: C, 73.44; H, 7.19; N, 7.14. Found: C, 73.28; H, 7.18; N, 7.16. The filtrate from the recrystallization was saved and the volatiles removed under reduced pressure to yield benzoic anhydride as a pale yellow solid (99 mg, 0.44 mmol) in 83% yield. Spectral data were consistent with literature values.[5] ^{1}H NMR ($CDCl_3$, 400.27 MHz): δ 7.53 (t, J = 7.6 Hz, 2H), 7.68 (t, J = 7.6 Hz, 2H), 8.17 (d, J = 8.4 Hz,

1H). ^{13}C NMR ($CDCl_3$, 75.47 MHz): δ 129.1, 129.3, 130.9, 134.8, 162.6. HRMS: $[M]^+$ calcd. for $C_{14}H_{10}O_3$: 226.0630. Found: 226.0631.

Synthesis of 1,3-dimesityl-5,5-dimethyl-2,2-bis(methylthio)dihydropyrimidine-4,6(1H, 5H) -dione (7a). An oven dried 8 mL vial was charged with **1** (80 mg, 0.21 mmol), 1 equiv. of dimethyl disulfide (19 μL, 0.21 mmol) and benzene (5 mL). The vial was sealed and the resulting solution was stirred for 14 h, after which time the solvent was removed under reduced pressure. The resulting residue was triturated with pentane (5 mL), filtered and dried under high vacuum to afford the desired product as a white powder (85 mg, 0.18 mmol) in 86% yield. m.p. 138-141 °C. ^{1}H NMR (C_6D_6, 400.27 MHz): δ 1.28 (s, 6H), 1.98 (s, 6H), 2.07 (s, 6H), 2.47 (s, 9H), 6.71 (s, 4H). ^{13}C NMR (C_6D_6, 75.47 MHz): δ 17.37, 20.42, 20.53, 20.60, 25.08, 46.85, 99.88, 129.20, 135.03, 135.50, 135.50, 138.60, 170.98. IR (ATR): 2920.43, 1685.50, 1658.04, 1387.28, 1350.05, 1183.73, 1033.96, 857.26, 769.53, 761.89. HRMS: $[M]^+$ calcd. for $C_{26}H_{34}N_2O_2S_2$: 470.6904. Found: 470.2059. Anal. Calcd. for $C_{26}H_{34}N_2O_2S_2$: C, 66.34; H, 7.28; N, 5.95. Found: C, 66.57; H, 7.13; N, 6.14. Compound **7a** was found to be air sensitive and decomposed to the urea **6** upon exposure to the ambient atmosphere.

Synthesis of S-methyl 3-(mesityl((mesitylimino)(methylthio)methyl)amino)-2,2-dimethyl-3-oxopropanethioate (**8a**). An oven dried 8 mL vial was charged with **7a** (100 mg, 0.21 mmol) and benzene (2 mL) and stirred for 12 h at 60 °C. After 12 h, the solvent was removed under reduced pressure, and the resultant residue was triturated with pentane (5 mL). The resulting powder was isolated by filtration and dried under high vacuum to afford the desired product as a white powder (80 mg, 0.17 mmol) in 80% yield. m.p. 58-60 °C. ^{1}H NMR (C_6D_6, 400.27 MHz): δ 1.56 (s, 6H), 1.75 (s, 3H), 2.07 (s, 3H), 2.11 (s, 6H), 2.22 (s, 6H), 2.37 (s, 6H), 6.68 (s, 2H), 6.71 (s, 2H). ^{13}C NMR (C_6D_6, 75.47 MHz): δ 11.34, 15.71, 17.56, 17.72, 18.52, 19.27, 20.81, 21.08, 24.92, 25.44, 59.38, 127.01, 129.54, 1129.81, 129.91, 132.55, 135.78, 136.39, 138.73, 138.81, 142.57, 174.19, 199.72. IR (ATR): 2924.79, 1732.81, 1667.77, 1634.99, 1477.69, 1384.71, 1343.46, 1267.29, 1239.52, 1212.41, 1182.32, 1137.60, 1015.05, 944.02, 898.69, 851.24, 762.35. HRMS: $[M]^+$ calcd. for $C_{26}H_{34}N_2O_2S_2$: 470.6904. Found: 470.2057. Anal. Calcd. for $C_{26}H_{34}N_2O_2S_2$: C, 66.34; H, 7.28; N, 5.95. Found: C, 66.67; H, 7.30; N, 6.20.

Synthesis of 1,3-dimesityl-5,5-dimethyl-2,2-bis(phenylthio)dihydropyrimidine-4,6(1H,5H)-dione (7b). An oven dried 8 mL vial was charged with **1** (127 mg, 0.34 mmol), 1 equiv. of diphenyl disulfide (73.4 mg, 0.34 mmol) and benzene (5 mL). The vial was sealed and the resulting solution was stirred for 1 h at 25 °C, after which time the reaction mixture was poured into excess pentane (50 mL). The precipitate collected by filtration and dried under high vacuum to afford the desired product as a pale yellow powder (162 mg, 0.27 mmol) in 80% yield. m.p. 140-142 °C. ^{1}H NMR (C_6D_6, 400.27 MHz): δ 1.80 (s, 6H), 2.07 (s, 12H), 2.43 (s, 6H), 6.34 (s, 2H), 6.58–6.68 (m, 2H), 6.69–6.71 (m, 2H), 6.76 (s, 2H,) 6.94–6.99 (m, 6H). ^{13}C NMR (C_6D_6, 75.47 MHz): δ 18.39, 19.40, 21.81, 31.91, 47.55, 89.24, 127.22, 128.53, 129.94, 131.32, 134.39, 135.48, 137.78, 138.89, 170.71. IR (KBr): 2959.36, 1685.13, 1636.33, 1440.98, 1212.03, 1182.58, 1139.28, 1023.57, 940.03, 887.55, 748375, 705.85. HRMS: $[M]^+$ calcd. for $C_{36}H_{38}N_2O_2S_2$: 594.2369. Found: 594.2372. Anal. Calcd. for $C_{36}H_{38}N_2O_2S_2$: C, 72.69; H, 6.44; N, 4.71. Found: C, 72.37; H, 6.38; N, 4.51. Compound **7b** was found to be air sensitive and decomposed to the urea **6** upon exposure to the ambient atmosphere.

Synthesis of S-phenyl 4,6-dimesityl-2,2-dimethyl-3-oxo-5-(phenylthio) hexanethioate (**8b**). An oven dried 8 mL vial was charged with **7b** (100 mg, 0.17 mmol) and benzene (2 mL) and stirred for 2 h at 60 °C. The resulting solution was layered with pentane (5 mL) and placed in a –20 °C freezer. After 24 h, clear crystals were formed which were isolated by filtration (90 mg, 0.15 mmol) in 90% yield. m.p. 195-198 °C. ^{1}H NMR (C_6D_6, 400.27 MHz): δ 1.06 (s, 3H), 1.29 (s, 6H), 2.24-2.25 (m, 12H), 2.35 (s, 3H), 6.51 (s, 1H), 6.63 (s, 1H), 6.83 (s, 2H), 6.90 (s, 2H), 7.12–7.22 (m, 4H), 7.38–7.41 (m, 4H). ^{13}C NMR (C_6D_6, 75.47 MHz): δ 18.78, 18.83, 19.76, 20.56, 20.59 21.05, 21.08, 25.38, 61.29, 129.19, 129.70, 132.26, 134.53, 136.44, 137.81, 138.68, 149.23, 172.71, 196.14. IR (ATR): 2959.31, 1683.20, 1637.02, 1474.93, 1440.82, 1402.51, 1239.74, 1211.71, 1181.54, 1139.33, 1008.09, 940.31, 912.40, 846.53, 748.73, 741.65, 705.33. HRMS: $[M]^+$ calcd. for $C_{36}H_{38}N_2O_2S_2$: 594.2369. Found: 594.2365. Anal. Calcd. for $C_{36}H_{38}N_2O_2S_2$: C, 72.69; H, 6.44; N, 4.71. Found: C, 72.74; H, 6.46; N, 4.73.

Synthesis of 1,3-dimesityl-2,2-bis(4-methoxyphenylthio)-5,5-dimethyldihydropyrimidine-4,6(1H,5H)-dione (7c). An oven dried NMR tube was charged with a solution of **1** (20 mg, 0.053 mmol) in 0.5 mL of deuterated toluene (C_7D_8), sealed with a septum cap, and equilibrated to –78 °C in a dry ice/acetone bath. A separate 8 mL vial was charged with a solution of bis(4-methoxyphenyl) disulfide (15 mg, 0.053 mmol) in 0.4 mL of C_7D_8, sealed and then equilibrated to –78 °C in a dry ice/acetone bath. After 15 min of equilibration, the disulfide solution was added via syringe to the NMR tube which remained at –78 °C in a dry ice/acetone bath. The tube was removed from the bath, and then quickly inserted into a 400 MHz Varian NMR spectrometer with the probe previously cooled to –50 °C. The reaction proceeded to 75% conversion as determined by the relative integrations of **1** and **7c** by ^{1}H NMR spectroscopy. For clarity, the signals associated with **1** were excluded. ^{1}H NMR (C_7D_8, 400.27 MHz): δ 1.89 (bs, 6H), 2.0–2.07 (m, 12H), 2.30 (bs, 6H), 3.04 (s, 3H), 3.06 (s, 3H), 5.98 (s, 2H), 6.42 (s, 2H), 6.56–6.70 (bm, 8H). ^{13}C NMR (C_7D_8, 75.47 MHz): δ 17.42, 17.91, 18.45, 19.60, 19.69, 21.27, 28.11, 48.03, 54.41, 54.60, 61.42, 91.65, 113.38, 114.26, 114.61, 114.77, 117.89, 119.13, 131.69, 133.57, 134.87, 135.30, 135.79, 135.99, 136.29, 138.67, 139.48, 141.22, 148.33, 160.51, 170.77.

Synthesis of S-4-methoxyphenyl 3-(mesityl((mesitylimino)(4-methoxyphenylthio)methyl) amino)-2,2-dimethyl-3-oxopropanethioate (**8c**). An oven dried 8 mL vial was charged with **1** (57 mg, 0.15 mmol), 1 equiv. of bis(4-methoxyphenyl) disulfide (43 mg, 0.15 mmol) and benzene (5 mL). The vial was sealed and the resulting solution was stirred for 1 h, after which time the reaction mixture was poured into pentane (50 mL). The precipitate was isolated by filtration and dried under high vacuum to afford the desired product as an orange powder (75 mg, 0.11 mmol) in 75% yield. m.p. 171-174 °C. ^{1}H NMR (C_6D_6, 400.27 MHz): δ 1.84 (s, 6H), 2.05 (s, 3H), 2.10 (s, 3H), 2.12 (s, 6H), 2.48 (s, 6H), 3.14 (s, 3H), 3.16 (s, 3H), 6.56–6.60 (dt, J = 3 Hz, 2H), 6.77 (s, 2H), 6.99–7.03 (dt, J = 3 Hz, 2H), 7.23–7.30 (m, 4H), 7.52 (s, 2H). ^{13}C NMR (C_6D_6, 75.47 MHz): δ 18.86, 19.87, 20.60, 21.07, 54.64, 54.73, 113.76, 114.55, 114.94, 118.56, 119.97, 128.65, 129.72, 131.96, 133.25, 136.40, 137.26, 137.94, 138.63, 160.51, 197.06. IR (ATR):2920.96, 1668.29, 1635.10, 1591.05, 1493.42, 1235.82, 1248.70, 1202.10, 1175.20, 1135.83, 1019.71, 1008.41, 974.00, 903.16, 877.26, 837.32, 824.76, 747.32. HRMS: $[M]^+$ calcd. for $C_{38}H_{42}N_2O_4S_2$: 654.8811. Found: 654.8819. Anal. Calcd. for $C_{38}H_{42}N_2O_4S_2$: C, 69.69; H, 6.46; N, 4.28. Found: C, 69.75; H, 6.42; N, 4.36.

Synthesis of S-4-nitrophenyl 3-(mesityl((mesitylimino)(4-nitrophenylthio)methyl)amino)-2,2-dimethyl-3-oxopropanethioate (**8d**). An oven dried 8 mL vial was charged with **1** (55 mg, 0.15 mmol), 1 equiv. of bis(4-nitrophenyl) disulfide (45 mg, 0.15 mmol) and benzene (5 mL). The vial was sealed and the resulting solution was stirred for 1 h, after which time the reaction mixture was filtered through a 2 μm PTFE filter and then poured into pentane (50 mL). The resulting precipitate was isolated by filtration and dried under high vacuum yielding the desired product as a bright yellow-orange powder (84 mg, 0.13 mmol) in 84% yield. m.p. 131-135 °C. ^{1}H NMR (C_6D_6, 400.27 MHz): δ 1.69 (s, 3H), 1.75 (s, 6H), 1.81 (s, 6H), 1.90 (s, 3H), 2.34 (s, 6H), 6.00 (s, 2H), 6.53–6.60 (m, 4H), 6.77 (s, 2h), 7.30–7.32 (dt, *J* = 3 Hz, 2H), 7.62–7.66 (dt, *J* = 3 Hz, 2H). ^{13}C NMR (C_6D_6, 75.47 MHz): δ 18.46, 19.62, 20.24, 21.04, 25.12, 61.53, 122.43, 123.15, 124.24, 126.12, 128.46, 128.53, 129.85, 134.05, 135.28, 135.48, 135.91, 137.51, 139.46, 147.55, 148.10, 171.95, 194.64.. IR (ATR): 2918.57, 1687.68, 1636.41, 1518.37, 1475.03, 1340.22, 1213.07, 1177.67, 1137.92, 1092.25, HRMS: $[M]^+$ calcd. for $C_{36}H_{36}N_4O_6S_2$: 684.8242. Found: 684.8345. Anal. Calcd. for $C_{36}H_{36}N_4O_6S_2$: C, 63.14; H, 5.30; N, 8.18. Found: C, 62.80; H, 5.30; N, 8.11.

Synthesis of 1,3-dimesityl-5,5-dimethyl-2,2-bis(butylthio)dihydropyrimidine-4,6(1H,5H)-dione (7e). An oven dried 8 mL vial was charged with **1** (20 mg, 53 μmol), 1 equiv. of di-n-butyl disulfide (10 μL, 53 μmol) and benzene (1 mL). The vial was sealed and the resulting solution stirred for 1 h, after which time the reaction mixture was poured into pentane (10 mL). The precipitate was isolated by filtration and dried under high vacuum to afford the desired product as a pale yellow powder (20 mg, 37 μmol) in 70% yield. m.p. 110-112 °C. ^{1}H NMR (C_6D_6, 400.27 MHz): δ 0.59 (t, *J* = 7.2 Hz, 6H) 0.97–1.07 (m, 8H), 2.04 (s, 12 H), 2.08 (s, 6H), 2.13 (d, *J* = 7.2 Hz, 4H), 2.58 (s, 6H), 6.75 (s, 4H). ^{13}C NMR (C_6D_6, 75.47 MHz): δ 13.41, 20.98, 21.05, 22.21, 22.52, 25.12, 34.52, 49.51, 99.23, 126.42, 129.34, 134.21, 136.56, 139.23, 171.79. IR (KBr): 2920.95, 1735.22, 1708.73, 1487.74, 1460.33, 1384.24, 1328.65, 1236.29, 1059.24, 858.32, 509.83. HRMS: $[M]^+$ calcd. for $C_{32}H_{46}N_2O_2S_2$: 554.2995. Found: 554.2997. Anal. Calcd. for $C_{32}H_{46}N_2O_2S_2$: C, 69.27; H, 8.36; N, 5.05. Found: C, 69.57; H, 8.24; N, 5.09. Compound **7e** was found to be air sensitive and decomposed to the urea **6** upon exposure to the ambient atmosphere.

Synthesis of S-butyl 4,6-dimesityl-2,2-dimethyl-3-oxo-5-(butylthio)hexanethioate (8e). An oven dried 8 mL vial was charged with **7e** (20 mg, 37 μmol) and benzene (0.5 mL), and stirred for 4 h at 25 °C. The resulting solution was layered with pentane (3 mL) and placed in a –20 °C freezer. After 24 h, clear crystals were formed which were isolated by filtration and dried under high vacuum to afford the desired product (17 mg, 31 μmol) in 85% yield. m.p. 126-128 °C. ^{1}H NMR (C_6D_6, 400.27 MHz): δ 0.59–0.63 (t, *J* = 5.6 Hz, 3H), 0.69–0.77 (m, 5H), 1.01–1.26 (m, 10H), 1.32 (d, *J* = 10.8 Hz, 3H), 1.64 (s, 6H), 2.12 (s, 3H), 2.30 (s, 9H), 2.45 (s, 6H), 6.75 (s, 4H). ^{13}C NMR (C_6D_6, 75.47 MHz): δ 13.44, 13.66, 13.74, 17.50, 18.39, 18.74, 19.10, 19.37, 19.67, 20.70, 20.78, 20.82, 20.99, 21.61, 21.82, 22.08, 22.31, 26.00, 27.89, 28.91, 30.88, 31.17, 32.34, 47.51, 47.83, 59.72, 89.21, 127.16, 129.13, 129.67, 134.40, 135.47, 137.71, 138.71, 138.90, 170.75, 199.76. IR (ATR): 2922.33, 1688.03, 1645.95, 1484.50, 1429.56, 1377.57, 1221.65, 1200.29, 1167.30, 1136.80, 1105.03, 1037.98, 962.08, 941.50, 850.12, 766.41, 743.80. HRMS: $[M]^+$ calcd. for $C_{32}H_{46}N_2O_2S_2$: 554.2995. Found: 554.3000. Anal. Calcd. for $C_{32}H_{46}N_2O_2S_2$: C, 69.27; H, 8.36; N, 5.05. Found: C, 68.89; H, 8.33; N, 5.13.

Synthesis of 1,3-dimesityl-5,5-dimethyl-2-(methylthio)-2-(phenylthio)dihydropyrimidine-4,6(1H,5H)-dione (7f). An oven dried 8 mL vial was charged with **1** (70.7 mg, 0.19 mmol), 1 equiv. of methyl phenyl disulfide (25.5 µL, 0.19 mmol) and benzene (3 mL). The vial was sealed and the resulting solution was stirred for 1 h, after which time the reaction mixture was precipitated into pentane (50 mL). The resulting powder was isolated by filtration and dried under high vacuum to afford the desired product as a bright yellow powder (60 mg, 0.11 mmol) in 60% yield. m.p. 128 °C (decomp.) ^{1}H NMR (C_6D_6, 400.27 MHz): δ 1.70 (s, 6H), 2.08 (s, 6H), 2.14 (s, 3H), 2.18 (s, 6H), 2.33 (s, 6H), 6.70 (s, 2H), 6.74 (s, 2H,) 6.99–7.05 (m, 3H), 7.09–7.11 (m, 2H). ^{13}C NMR (C_6D_6, 75.47 MHz): δ 15.28, 17.73, 19.00, 24.93, 48.82, 124.98, 127.71, 129.00, 129.25, 129.81, 134.89, 138.41, 138.53, 170.31. IR (KBr): 2977.91, 2915.51, 1735.09, 1701.35, 1460.06, 1387.71, 1341.19, 1265.75, 1223.39, 1110.18, 1034.90, 857.68, 820.27, 510.90. HRMS: $[M]^+$ calcd. for $C_{31}H_{36}N_2O_2S_2$: 532.2213. Found: 532.2215. Anal. Calcd. for $C_{31}H_{36}N_2O_2S_2$: C, 68.89; H, 6.81; N, 5.26. Found: C, 68.95; H, 7.01; N, 5.47. Compound **7f** was found to be air sensitive and decomposed to the urea **6** upon exposure to the ambient atmosphere.

Synthesis of S-methyl 4,6-dimesityl-2,2-dimethyl-3-oxo-5-(phenylthio)hexanethioate (8f). An oven dried 8 mL vial was charged with **7f** (50 mg, 94 µmol) and benzene (1 mL) and stirred for 4 h at 60 °C. The resulting solution was layered with pentane (5 mL) and placed in a –20 °C freezer. After 24 h, a white powder had formed which was isolated by filtration and dried under high vacuum to afford the desired product as a white solid (39 mg, 73 µmol) in 78% yield. m.p. 280-282 °C. ^{1}H NMR (C_6D_6, 400.27 MHz): δ 1.70 (s, 3H), 1.75 (s, 3H), 1.92 (s, 6H), 2.20 (s, 6H), 2.34 (s, 6H), 2.59 (s, 3H), 6.70 (s, 2H), 6.74 (s, 2H), 6.88–6.92 (m, 1H), 6.98–7.03 (m, 2H) 7.43–7.45 (m, 2H). ^{13}C NMR (C_6D_6, 75.47 MHz): δ 15.99, 18.82, 18.87, 19.03, 20.80, 21.01, 25.79, 60.40, 126.89, 128.24, 128.84, 129.08, 129.24, 129.30, 129.74, 132.53, 136.52, 138.53, 138.67, 142.45, 173.26, 197.00. IR (KBr): 2915.86, 1732.39, 1702.20, 1476.51, 1438.33, 1385.57, 1333.52, 1307.66, 1265.39, 857.69, 819.97, 768.45, 739.62. HRMS: $[M]^+$ calcd. for $C_{31}H_{36}N_2O_2S_2$: 532.2213. Found: 532.2208. Anal. Calcd. for $C_{31}H_{36}N_2O_2S_2$: C, 68.89; H, 6.81; N, 5.26. Found: C, 68.89; H, 6.96; N, 5.28.

Synthesis of 1',3'-dimesityl-5',5'-dimethyl-1'H-spiro[phenalene-2,2'-pyrimidine]-1,3,4',6'(3'H,5'H)-tetraone (9a). An oven dried 8 mL vial was charged with **1** (67 mg, 0.18 mmol), 1 equiv. of acenaphthoquinone (33 mg, 0.18 mmol) and benzene (1 mL), and stirred at 60 °C. After 3 h, the mixture was exposed to the atmosphere, cooled to 25 °C, and filtered through a 0.2 µm PTFE filter. The filtrate was concentrated under reduced pressure and the resulting residue was triturated with pentane and then dried under reduced pressure to afford the desired product as a yellow powder (90 mg, 0.16 mmol) in 90% yield. m.p. 67-73 °C. ^{1}H NMR ($CDCl_3$, 400.27 MHz): δ 1.68 (s, 6H), 1.93 (2, 6H), 2.07 (s, 3H), 2.26 (s, 3H), 2.44 (s, 6H), 6.42 (s, 2H), 6.62–6.64 (d, J = 8.4 Hz, 1H), 6.75–6.79 (t, J = 7.6 Hz, 1H), 6.94 (s, 2H), 7.44–7.45 (d, J = 7.2 Hz, 1H), 7.51–7.55 (t, J = 7.6 Hz, 1H), 7.90–7.93 (d, J = 9.2 Hz, 1H), 8.16–8.19 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75.47 MHz): δ. 20.03, 20.54, 27.21, 48.58, 80.48, 122.09, 126.55, 127.07, 128.45, 128.58, 129.45, 130.10, 132.23, 132.63, 133.83, 135.61, 137.79, 137.82, 174.55, 189.72. IR (ATR): 2980.5, 1735.01, 1710.57, 1690.91, 1659.00, 1388.43, 1290.84, 1243.58, 1156.95, 1131.14, 1039.76, 851.37, 822.17, 777.33.. HRMS: $[MH]^+$ calcd. for $C_{36}H_{35}N_2O_4$: 559.2591. Found: 559.2591. Anal. Calcd. for $C_{36}H_{34}N_2O_4$: C, 77.40; H, 6.13; N, 5.01. Found: C, 77.11; H, 6.53; N, 4.95.

Synthesis of 6,10-dimesityl-2,3-dimethoxy-8,8-dimethyl-6,10-diazaspiro[4.5]dec-2-ene-1,4,7,9-tetraone (9b). An oven dried 8 mL vial was charged with **1** (73 mg, 0.19 mmol), 1 equiv. of 3,4-dimethoxycyclobut-3-ene-1,2-dione (27 mg, 0.19 mmol) and benzene (1 mL), and stirred at 25 °C. After 2 h, the reaction was exposed to the atmosphere and filtered through a 2 μm PTFE filter. The filtrate was concentrated under reduced pressure and the resulting residue triturated with pentane. Subsequent drying under high vacuum afforded the desired product as a white powder (83 mg, 0.16 mmol) in 83% yield. m.p. 193 °C (decomp.) ^{1}H NMR ($CDCl_3$, 400.27 MHz): δ 1.75 (s, 6H), 2.12 (s, 12 H), 2.32 (s, 6H), 3.27 (s, 3H), 3.40 (s, 3H), 6.72 (s, 4H). ^{13}C NMR ($CDCl_3$, 75.47 MHz): δ.17.56, 17.72, 20.15, 20.96, 24.78, 27.31, 47.18, 59.33, 59.71, 76.80, 128.24, 129.36, 129.91, 130.01, 133.70, 135.79, 138.36, 139.01, 140.03, 168.97, 173.45. IR (ATR): 2922.64, 2854.55, 1709.23, 1732.46, 1669.88, 1643.28, 1608.14, 1481.17, 1464.89, 1392.14, 1381.64, 1344.14, 1212.19, 1194.28, 1032.37, 938.24, 859.77, 832.04, 796.70, 787.54. HRMS: $[MH]^+$ calcd. for $C_{30}H_{34}N_2O_6$: 518.6008. Found:518.2418. Anal. Calcd. for $C_{30}H_{34}N_2O_6$: C, 69.48; H, 6.61; N, 5.40. Found: C, 69.70; H, 6.42; N, 5.14.

Synthesis of 2,2-dibenzoyl-1,3-dimesityl-5,5-dimethyldihydropyrimidine-4,6(1H,5H)-dione (9c). An oven dried 8 mL vial was charged with **1** (64 mg, 0.17 mmol), 1 equiv. of benzil (36 mg, 0.17 mmol) and benzene (1 mL), and stirred at 25 °C. After 1 h, the reaction was exposed to the atmosphere and volatiles were removed under reduced pressure. The resulting residue was triturated with pentane and dried under high vacuum to afford the desired product as a beige solid (75 mg, 0.13 mmol) in 75% yield. m.p. 270 °C (decomp.) ^{1}H NMR ($CDCl_3$, 400.27 MHz): δ 1.36 (s, 3H), 1.75 (s, 3H), 2.10 (s, 6H), 2.26 (s, 6H) 6.94 (s, 4H), 7.48–7.52 (t, J = 7.8 Hz, 4H), 7.63–7.67 (t, J = 8.8 Hz, 2H), 7.95–7.97 (d, J = 4.8 Hz, 4H). ^{13}C NMR ($CDCl_3$, 75.47 MHz): δ 17.51, 18.25, 18.76, 20.92, 25.28, 47.06, 88.74, 129.01, 129.47, 129.89, 132.96, 133.05, 134.79, 134.88, 138.21, 138.98, 171.82, 194.55. IR (ATR): 2920.17, 1696.51, 1595.98, 1448.97, 1387.47, 1349.52, 1244,81, 1211.33, 861.01, 720.66. HRMS: $[M]^+$ calcd. for $C_{38}H_{38}N_2O_4$: 586.2832. Found: 586.2829. Anal. Calcd. for $C_{38}H_{38}N_2O_4$: C, 77.79; H, 6.53; N, 4.77. Found: C, 77.56; H, 6.51; N, 5.01.

Synthesis of 5,9-dimesityl-7,7-dimethyl-2,3-diphenyl-5,9-diazaspiro[3.5]non-2-ene-1,6,8-trione (9d). An oven dried 8 mL vial was charged with **1** (49 mg, 0.13 mmol), 1 equiv. of 2,3-diphenylcycloprop-2-enone (27 mg, 0.13 mmol) and benzene (1 mL), and stirred at 25 °C. After 2 h, the reaction was exposed to the atmosphere and the volatiles removed under reduced pressure. The resulting residue was triturated with hexanes and dried under high vacuum to afford the desired product as a pale yellow solid (68 mg, 0.12 mmol) in 90% yield. m.p. 183 °C (decomp.) ^{1}H NMR (C_6D_6, 400.27 MHz): δ 1.93 (s, 6H), 2.05 (s, 6H), 2.06 (s, 3H), 2.30 (s, 6H), 2.42 (s, 3H), 6.21 (d, J = 7.6 Hz, 2H), 6.49 (s, 2H), 6.53 (s, 2H), 6.70–6.79 (m, 6H), 7.47–7.50 (m. 2H). ^{13}C NMR ($CDCl_3$, 75.47 MHz): δ.20.06, 20.57, 20.65, 26.28, 27.87, 48.21, 97.79, 128.34, 128.61, 129.10, 129.63, 130.03, 130.60, 130.87, 131.20, 131.91, 134.64, 138.04, 139.01, 139.02, 172.84, 189.38. IR (ATR): 2940.98, 1767.80, 1689.14, 1660.86, 1456.70, 1392.28, 1361.46, 1217.63, 1169.55, 1102.12, 965.80, 941.72, 851.30, 773.79, 763.11. HRMS: $[MH]^+$ calcd. for $C_{39}H_{39}N_2O_3$: 583.7306. Found: 583.2951. Anal. Calcd. for $C_{39}H_{38}N_2O_3$: C, 80.38; H, 6.57; N, 4.81. Found: C, 80.23; H, 6.71; N, 4.90.

Thiolate Trapping Experiment/Synthesis of S-methyl thiobenzoate. An oven dried vial was charged with **7a** (60 mg, 0.13 mmol), 5 equiv. of benzoyl chloride (74 μL, 0.64 mmol) and toluene (1.0 mL), and stirred at 60 °C. After 15 h, the reaction was exposed to the atmosphere and the volatiles removed under reduced pressure. The resulting residue was triturated with pentane which caused the precipitation of the byproduct **7a***. The resulting white precipitate was isolated by filtration and dried under high vacuum to afford **7a*** in 72% yield (43 mg, 0.09 mmol). m.p. 155–157 °C (decomp.) ^{1}H NMR ($CDCl_3$, 400.27 MHz): δ 1.76 (s, 6H), 2.11 (s, 12H), 2.27 (s, 3H) 2.30 (s, 6H), 6.95 (s, 4H). ^{13}C NMR ($CDCl_3$, 100.49 MHz): δ17.54, 21.19, 25.05, 31.58, 48.56, 121.95, 129.612, 134.31, 134.43, 138.76, 170.34. IR (ATR): 2920.76, 1723.33, 1702.94, 1461.66, 1395.37, 1334.13, 1308.13, 1265.36, 1224.37, 963.70, 857.60, 819.92. HRMS: $[M\text{-}Cl]^+$ calcd. for $C_{25}H_{31}ClN_2O_2S$: 423.5903. Found: 423.5941. Anal. Calcd. for $C_{25}H_{31}ClN_2O_2S$: C, 65.41; H, 6.81; N, 6.10. Found: C, 65.19; H, 6.58; N, 5.98. The filtrate was passed over a short column of neutral alumina and the solvent was removed under reduced pressure, to yield S-methyl thiobenzoate as a colorless oil in 67% yield (13 mg, 0.09 mmol). Spectral data were consistent with literature values.[6] ^{1}H NMR ($CDCl_3$, 400.27 MHz): δ 2.53 (s, 3H), 7.35–7.39 (m, 2H), 7.51–7.55 (m, 3H). ^{13}C NMR ($CDCl_3$, 100.49 MHz): δ 11.07, 124.24, 125.63, 127.76, 128.99, 183.06. HRMS: $[M]^+$ calcd. for C_8H_8OS: 152.2135. Found: 152.2143.

Evaluation of the Reactions Involving 1 with Various Disulfides. A 0.106 M stock solution of **1** was prepared by dissolving **1** (0.20 g, 0.44 mmol) in C_7D_8 (5 mL). An oven dried NMR tube equipped with a screw-cap septum was charged inside of a glove box with the stock solution of **1** (0.5 mL, 0.053 mmol) and a sufficient quantity of C_7D_8 such that the total volume equaled 0.9 mL upon the addition of 10 equiv. of the disulfide analyzed. The sample was then equilibrated in an NMR probe cooled to –50 °C. Upon equilibration, the sample was ejected from the instrument and 0.53 mmol (10 equiv.) was added via syringe. For the solid disulfides, 0.53 mmol (10 equiv.) of the disulfide was dissolved in C_7D_8 (0.4 mL) and added via syringe. Liquid disulfides were added neat. All of the substrates were kept in a dry ice acetone bath at –78 °C until addition to the NMR tube. The NMR tube was then vigorously shaken to ensure proper mixing, and the sample reinserted into the NMR probe. After shimming, spectra (four scans each) were run every 30 sec for 1 h. The conversion to the diamidothioketal product (**7a,e,f**, Fig. S1) was measured by comparing the ratio of the ^{1}H NMR integrals assigned to the aryl protons of **1** (δ = 6.73 ppm; s, 4H) with the corresponding aryl protons attributed to the respective product (**7a**: 6.71 ppm, s, 4H; **7e**: 6.75 ppm, s, 4H; **7f**: 6.70 ppm, s, 2H). To account for the differing number of hydrogen atoms, the integral for **7f** was doubled prior to calculating the integral ratio. Pseudo-first order rate constants were determined for these reactions by plotting the ln [**1**] versus time (Fig. S2–S4). Linear fits of all data points collected for conversions < 90% were used to calculate the observed rate constants from the corresponding slopes. For the aryl disulfides, the rate was too fast to be determined using ^{1}H NMR spectroscopy as the reactions had proceeded to > 99.9 % conversion in the < 2 min needed to shim the instrument. The lower limit of *k'* for these reactions was calculated in these cases using the following parameters: $[\mathbf{1}]_o$ = 0.059 M, t = 120 s, and [**1**] = 5.9×10^{-5} M after 2 min, assuming 99.9% conversion. By inputting these values into the pseudo first order rate equation, a k_{obs} was calculated to be > 3.45 min^{-1} for the aryl disulfides.

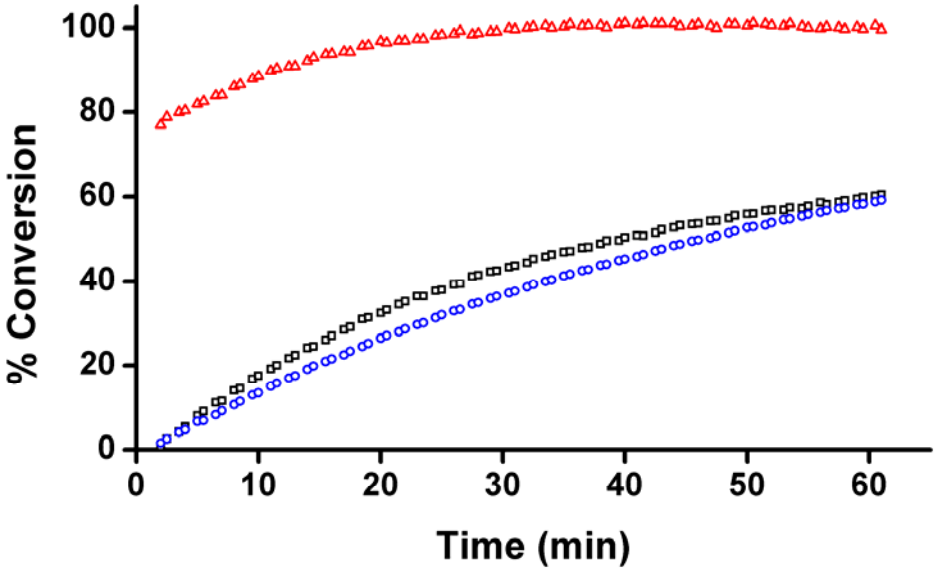


Figure S1. Plot of percent conversion versus time for the insertion of **1** into dimethyl disulfide (blue circles), di-n-butyl disulfide (black squares), or methyl phenyl disulfide (red triangles). Conditions: $[\mathbf{1}]_o$ = 0.059 M, $[\text{disulfide}]_o$ = 0.59 M (10 equiv.), C_7D_8, –50 °C. Every third data point was omitted to improve visual clarity.

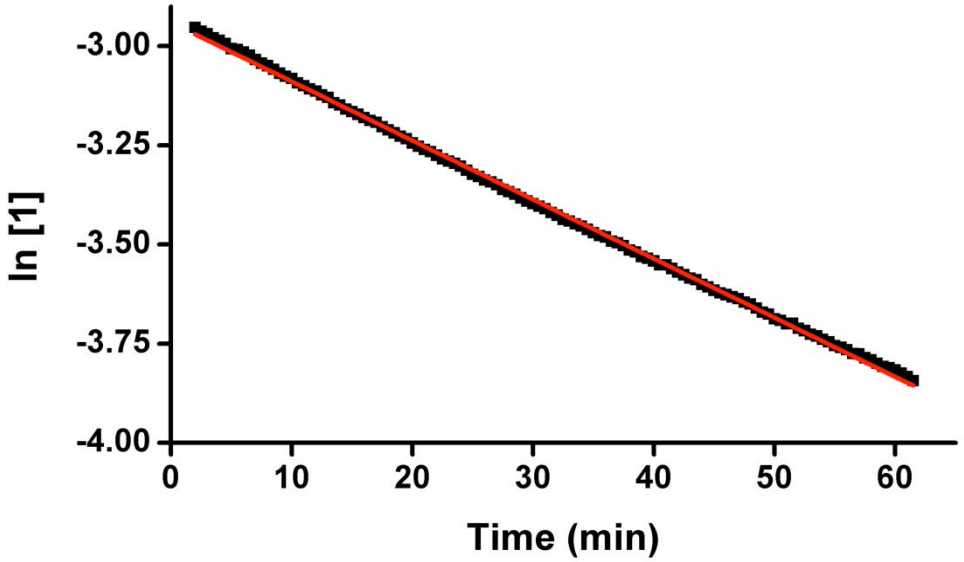


Figure S2. Plot of ln [**1**] versus time. Conditions: $[\mathbf{1}]_o$ = 0.059 M, $[\text{dimethyl disulfide}]_o$ = 0.59 M (10 equiv.), C_7D_8, –50 °C. The equation for the best fit line is as follows: y = mx + b, where m = –0.01498 ± 0.00004 s^{-1} and b = –2.9400 ± 0.0016.

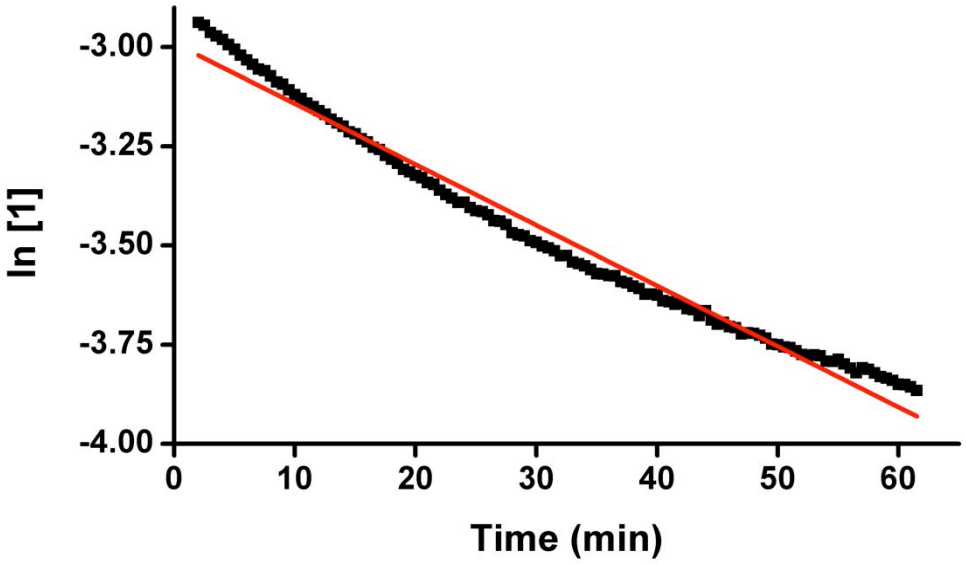


Figure S3. Plot of ln [**1**] versus time. Conditions: $[\mathbf{1}]_o$ = 0.059 M, [di-n-butyl disulfide]$_o$ = 0.59 M (10 equiv.), C_7D_8, –50 °C. The equation for the best fit line is as follows: y = mx + b, where m = –0.0153 ± 0.0002 min^{-1} and b = –2.9897 ± 0.0072.

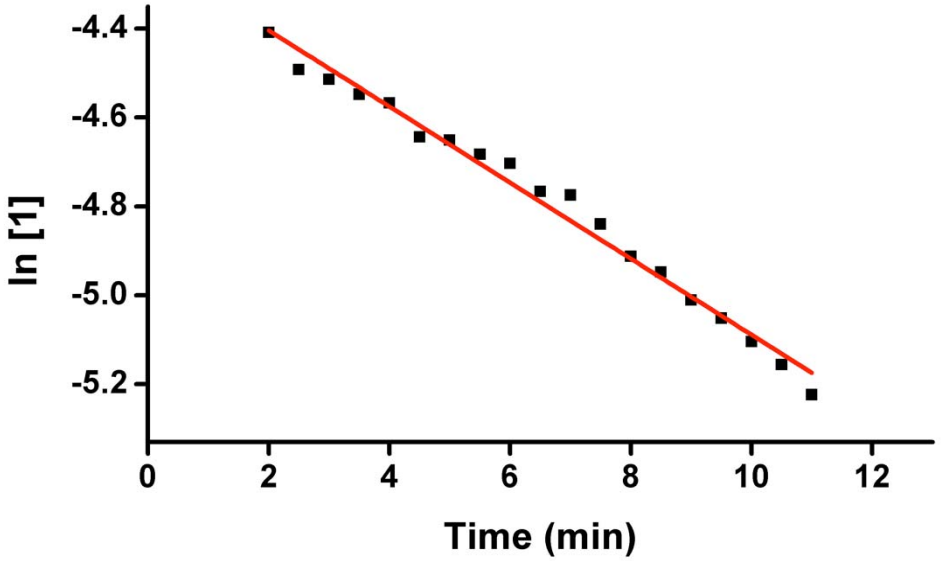


Figure S4. Plot of ln [**1**] versus time. Conditions: $[\mathbf{1}]_o$ = 0.059 M, [methyl phenyl disulfide]$_o$ = 0.59 M (10 equiv.), C_7D_8, –50 °C. The equation for the best fit line is as follows: y = mx + b, where m = –0.086 ± 0.002 s^{-1} and b = –4.233 ± 0.017.

Reaction of 1 with a Mixture of Diphenyl Disulfide and Dimethyl Disulfide. An oven dried vial was charged with **1** (100 mg, 0.26 mmol), dimethyl disulfide (12.5 μL, 0.13 mmol), diphenyl disulfide (29 mg, 0.13 mmol) and C_6D_6 (1.5 mL). The resulting solution was stirred for 30 min at 25 °C and then analyzed by ^{1}H NMR spectroscopy, which revealed a 1:1 mixture of **7a** and **7b** (Fig. S5).

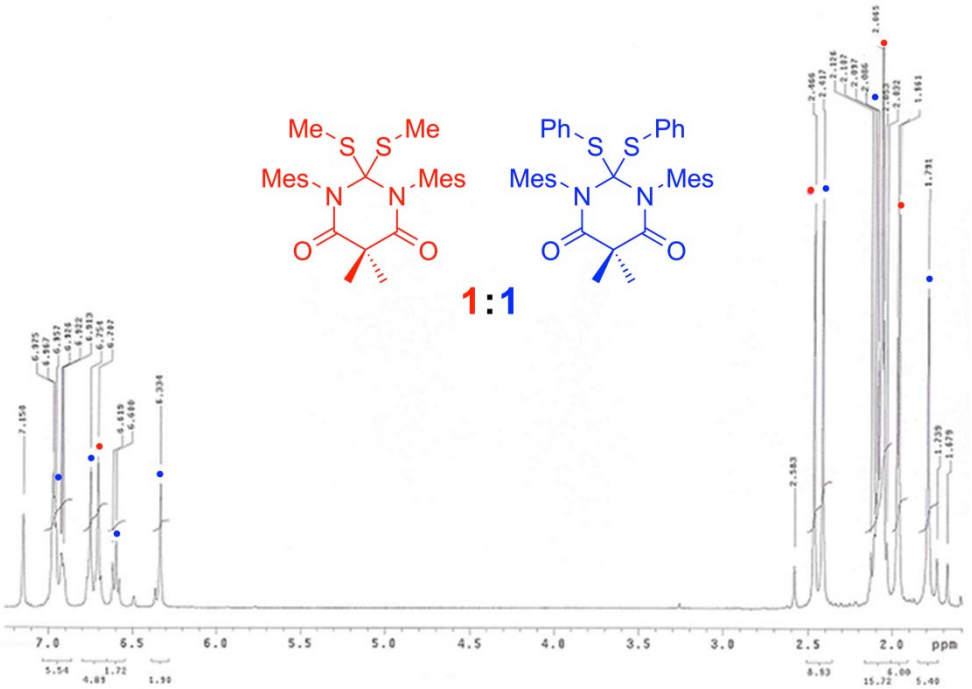


Figure S5. ^{1}H NMR spectrum showing the 1:1 mixture of **7a** (red) and **7b** (blue) observed from the treatment of **1** with a 1:1 mixture of diphenyl disulfide and dimethyl disulfide after 30 min at 25 °C in C_6D_6.

X-Ray Crystallography. Colorless single crystals of **2** were obtained by slow vapor diffusion of pentane into a saturated chloroform solution; this compound co-crystallized with one molecule of chloroform in the monoclinic space group $P2_1/n$. Pale yellow single crystals of **3** were obtained by slow vapor diffusion of pentane into a saturated chloroform solution; this compound co-crystallized with one molecule of chloroform in the monoclinic space group $P2/c$. Colorless single crystals of **4** were obtained by slow vapor diffusion of pentane into a saturated chloroform solution; this compound co-crystallized with 1.5 molecules of chloroform in the orthorhombic space group *Pbca*. Colorless single crystals of **6** were obtained by the slow diffusion of pentane into a saturated benzene solution; this compound crystallized in the triclinic space group P-1. Colorless single crystals of **7a** were obtained by slow diffusion of pentane into a saturated toluene solution at –20 °C; this compound crystallized in the monoclinic space group $P2_1/c$. Colorless single crystals of **8b** were obtained by slow vapor diffusion of pentane into a saturated benzene solution; this compound crystallized in the triclinic space group P-1. Yellow single crystals of **9a** were obtained by slow vapor diffusion of pentane into a saturated benzene solution; this compound crystallized in the monoclinic space group $P2_1/n$. Crystallographic measurements were carried out on a Rigaku Mini or Rigaku Saturn CCD area detector diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 150 or 120 K

using a Rigaku XStream low temperature device. A sample of suitable size and quality was selected and mounted onto a nylon loop. Data reductions were performed using CrystalClear. The structures were solved by direct methods which successfully located most of the non-hydrogen atoms. Subsequent refinements on F2 using the SHELXTL/PC package (version 5.1)[7] allowed location of the remaining non-hydrogen atoms. Key details of the crystal and structure refinement data are summarized in Table S1. Further crystallographic details may be found in the respective CIFs which were deposited at the Cambridge Crystallographic Data Centre, Cambridge, UK. The CCDC reference numbers for **2**, **3**, **4, 6**, **7a, 8b** and **9a** were assigned as 882670, 882671, 882672, 882673, 882674, 882675 and 882676, respectively.

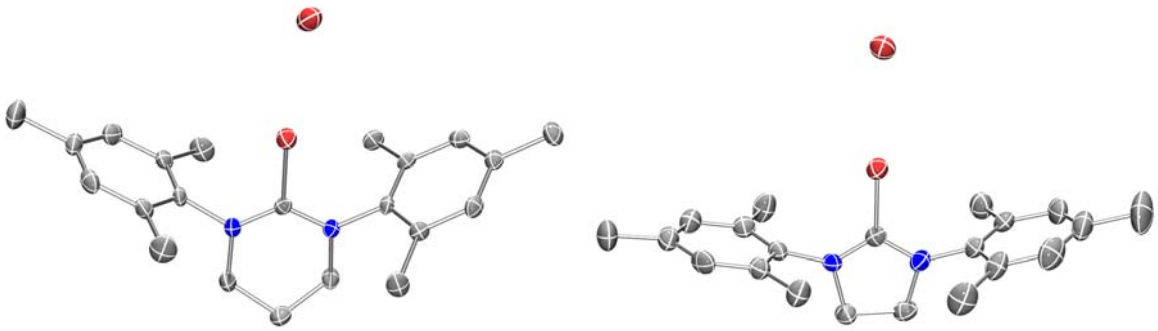


Fig. S6 ORTEP diagrams of **3** (left) and **4** (right) with thermal ellipsoids drawn at 50% probability and H-atoms omitted for clarity.

Table S1. Summary of crystal data, data collection, and structure refinement details for compounds **2**–**4** and **6**.

	2·$CHCl_3$	**3**·$CHCl_3$	**4**·1.5$CHCl_3$	**6**
Formula	$C_{25}H_{29}Cl_3N_2O_2$	$C_{23}H_{29}Br_2Cl_3N_2$	$C_{22.5}H_{27.5}Br_2Cl_{4.5}N_2$	$C_{24}H_{28}N_2O_3$
M_r	655.67	599.65	645.31	392.48
crystal size (mm^3)	0.31 × 0.18 × 0.03	0.16 × 0.15 × 0.04	0.18 × 0.18 × 0.04	0.18 × 0.14 × 0.09
crystal system	Monoclinic	Monoclinic	Orthorhombic	Triclinic
space group	$P2_1/n$	$P2/c$	$Pbca$	P-1
a (Å)	8.6872(8)	18.893(2)	28.784(3)	8.005(6)
b (Å)	24.892(2)	8.2648(9)	28.621(3)	8.772(6)
c (Å)	12.6503(12)	17.927(2)	13.8010(3)	16.048(11)
α (°)	90	90	90	91.431(9)
β (°)	92.440(2)	108/099(2)	90	103.924(9)
γ (°)	90	90	90	98.836(7)
V ($Å^3$)	2733.0(4)	2660.8(5)	11369.5(19)	1078.6(13)
Z	4	4	16	2
ρ_{calc} (g cm^{-3})	1.593	1.497	1.508	1.209
μ (mm^{-1})	3.285	3.361	3.288	0.080
F(000)	1320	1208	5168	420
T (K)	150(2)	150(2)	150(2)	150(2)
scan mode	ω	ω	ω	ω
hkl range	-10 → 10 -29 → 29 -15 → 15	-22 → 22 -9 → 9 -21 → 21	-34 → 34 -33 → 34 -16 → 16	-9 → 9 -10 → 10 -19 → 19
measd reflns	37485	36561	122939	15923
unique reflns [R_{int}]	4800 [0.0582]	4684[0.0639]	9902 [0.1031]	3779 [0.0380]
refinement reflns	4800	4694	9902	3779
refined parameters	315	277	571	270
GOF on F^2	1.006	1.006	1.006	1.006
R1[a] (all data)	0.0380 (0.0468)	0.0528 (0.0630)	0.0577 (0.0885)	0.0528 (0.0776)
wR2 (all data)	0.0861 (0.0861)	0.1352 (0.1419)	0.1340 (0.1514)	0.1531 (0.1877)
ρ_{fin} (max/min) (e $Å^{-3}$)	0.771 -0.674	1.846 -0.917	1.590 -0.970	0.563 -0.675

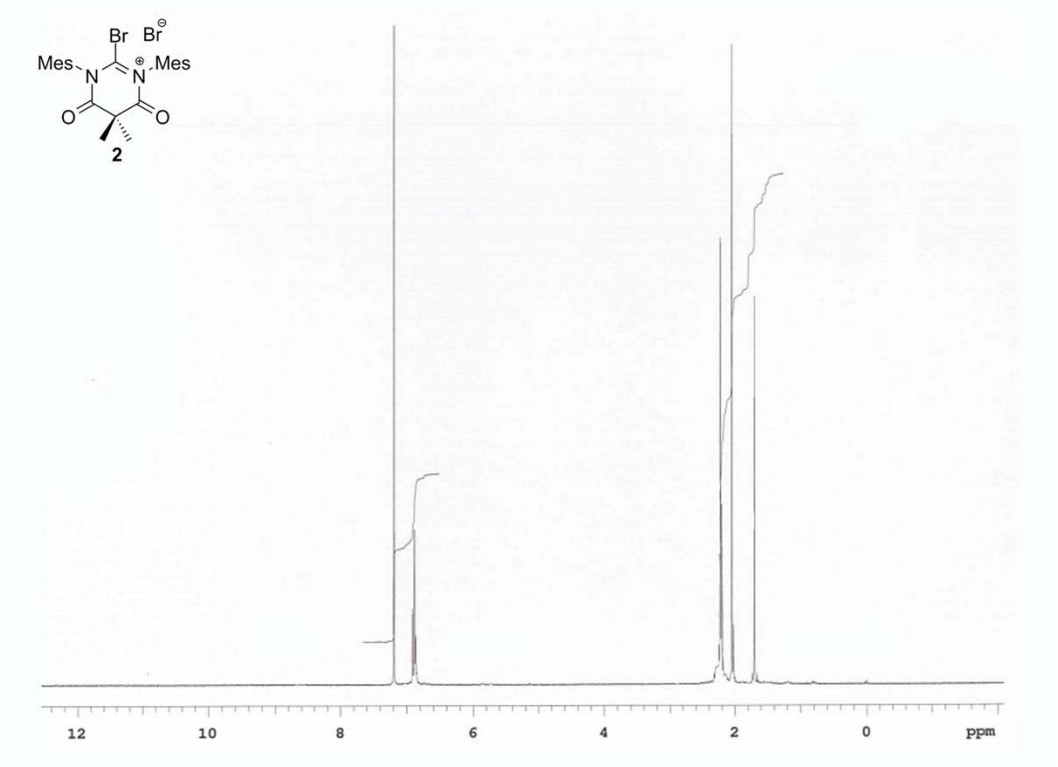
[a] $R1 = \sum||Fo| - |Fc||/\sum|Fo|$. [b] $wR2 = \{[\sum w(Fo^2 - Fc^2)^2]/[\sum w(Fo^2)^2]\}^{1/2}$.

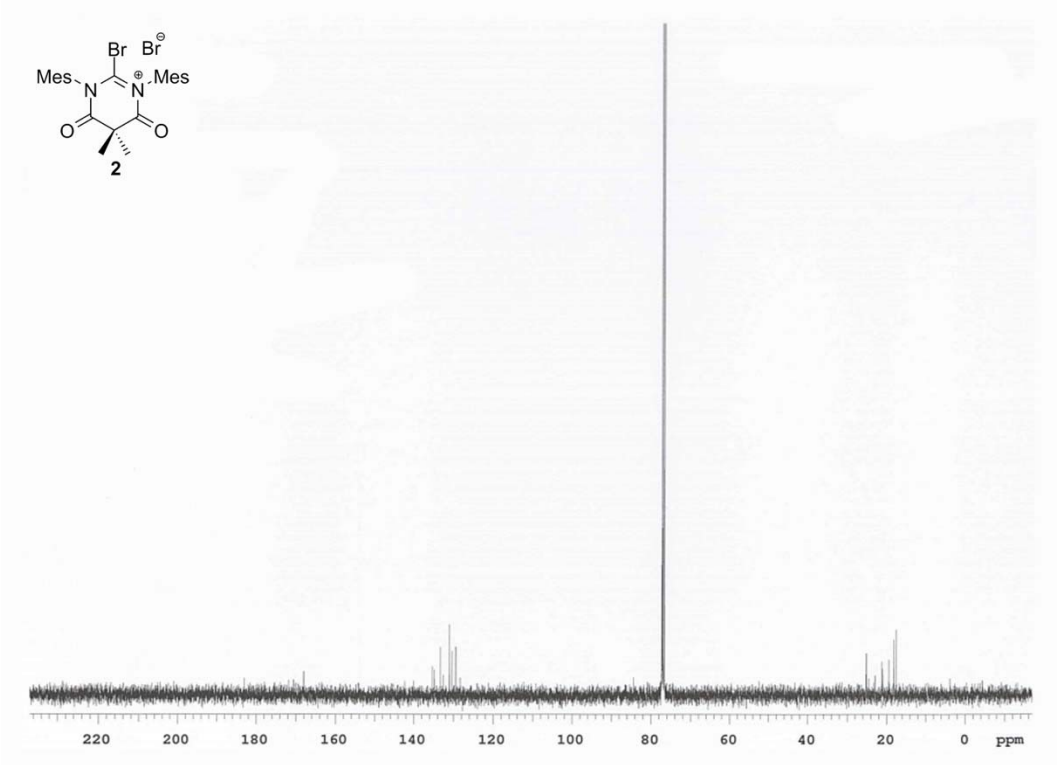
Table S2. Summary of crystal data, data collection, and structure refinement details for compounds **7a, 8b** and **9a**.

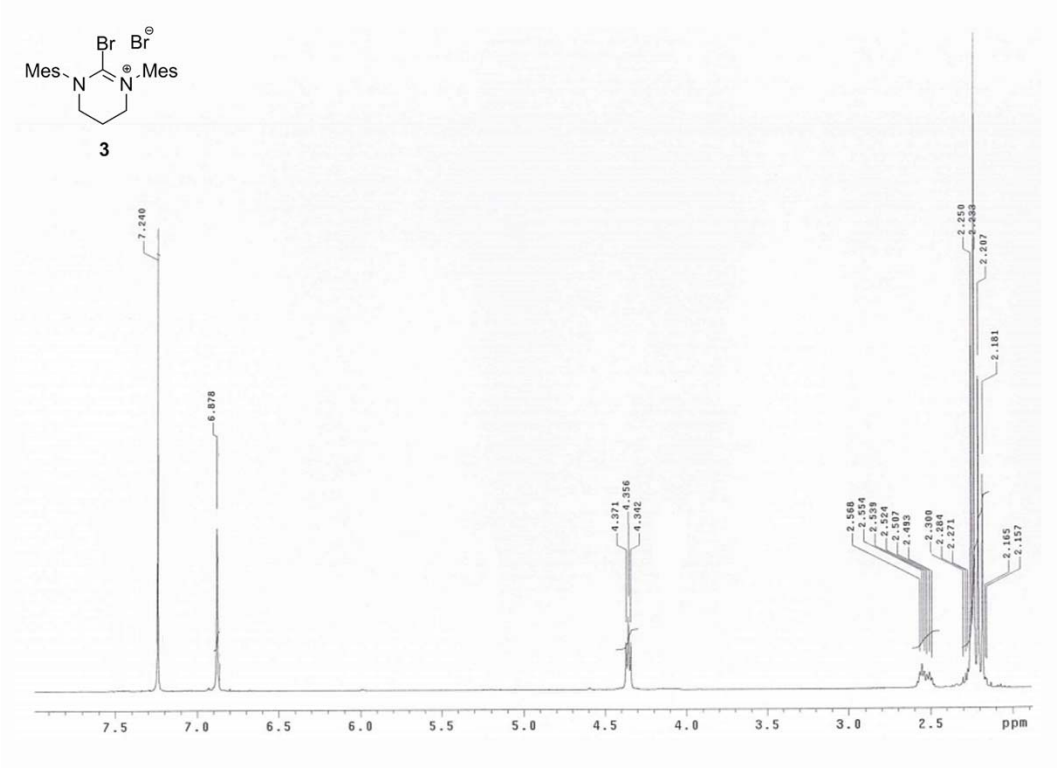
	7a	**8b**	**9a**
Formula	$C_{26}H_{34}N_2O_2S_2$	$C_{36}H_{38}N_2O_2S_2$	$C_{36}H_{34}N_2O_4$
M_r	470.67	594.80	558.65
crystal size (mm^3)	0.20 × 0.18 × 0.06	0.19 × 0.15 × 0.08	0.25 × 0.08 × 0.05
crystal system	Monoclinic	Triclinic	Monoclinic
space group	$P2_1/c$	P-1	$P2_1/n$
a (Å)	14.9337(12)	11.0307(15)	11.500(2)
b (Å)	11.8693(9)	12.1360(16)	17.626(4)
c (Å)	13.6108(11)	12.8498(17)	14.155(3)
α (°)	90	69.777(3)	90
β (°)	92.054(2)	79.796(3)	91.498(4)
γ (°)	90	85.828(3)	90
V ($Å^3$)	2411.0(3)	1588.5(4)	2868.1(10)
Z	4	2	4
ρ_{calc} (g cm^{-3})	1.297	1.244	1.294
μ (mm^{-1})	0.247	0.202	0.084
F(000)	1008	632	1184
T (K)	120(2)	150(2)	150(2)
scan mode	ω	ω	ω
hkl range	-17 → 16 -14 → 11 -16 → 16	-13 → 13 -14 → 14 -15 → 15	-13 → 13 -20 → 20 -16 → 16
measd reflns	12521	14027	40760
unique reflns [R_{int}]	4239 [0.0589]	5586 [0.0928]	5041 [0.1188]
refinement reflns	4239	5586	5041
refined parameters	299	387	387
GOF on F^2	1.006	1.006	1,006
R1[a] (all data)	0.0532 (0.1149)	0.0644 (0.1148)	0.0613 (0.1145)
wR2 (all data)	0.0635 (0.1542)	0.1335 (0.1587)	0.1312 (0.1579)
ρ_{fin} (max/min) ($e Å^{-3}$)	0.411 -0.551	0.296 -0.285	0.191 -0.185

[a] $R1 = \sum||Fo| - |Fc||/\sum|Fo|$. [b] $wR2 = \{[\sum w(Fo^2 - Fc^2)^2]/[\sum w(Fo^2)^2]\}^{1/2}$.

^{1}H and ^{13}C NMR Spectra



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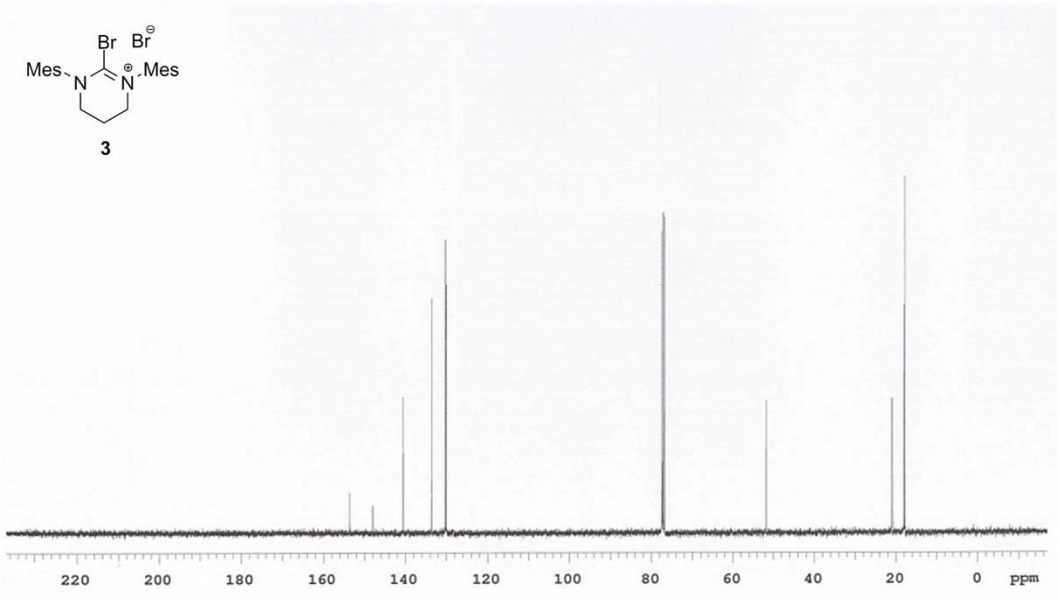
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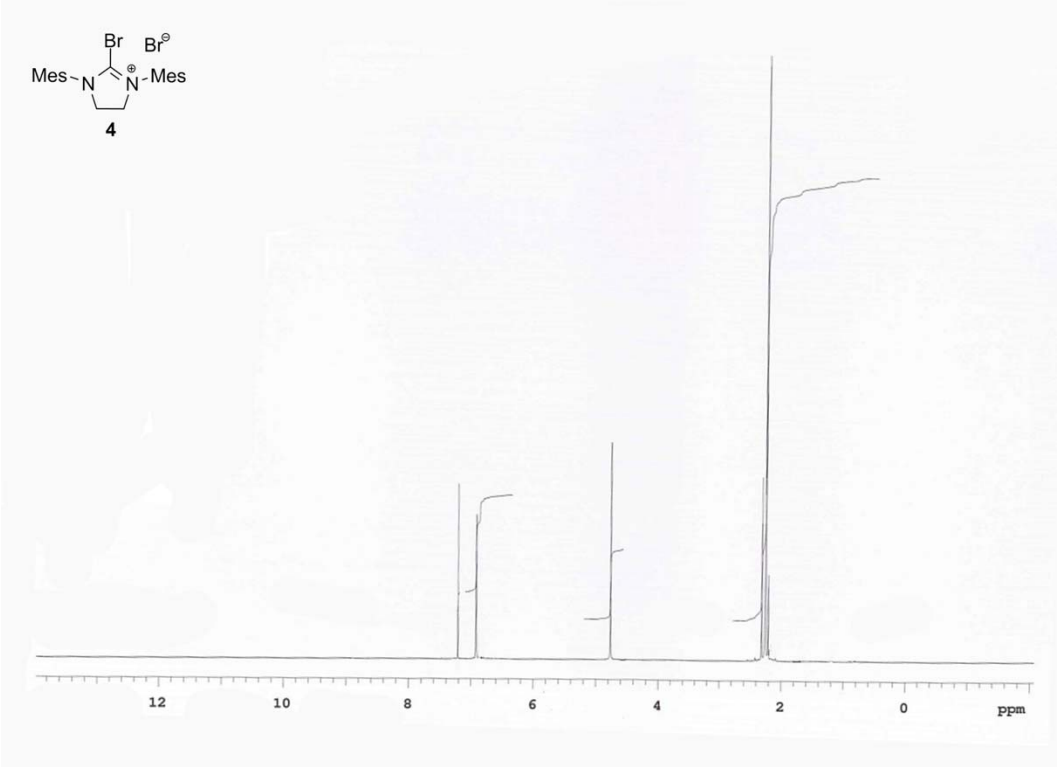

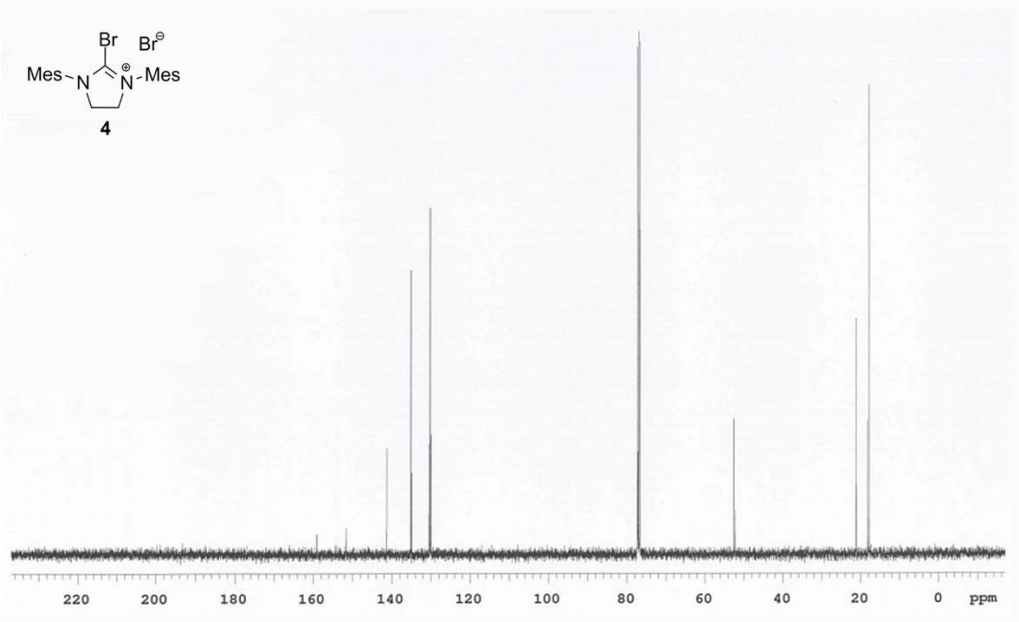

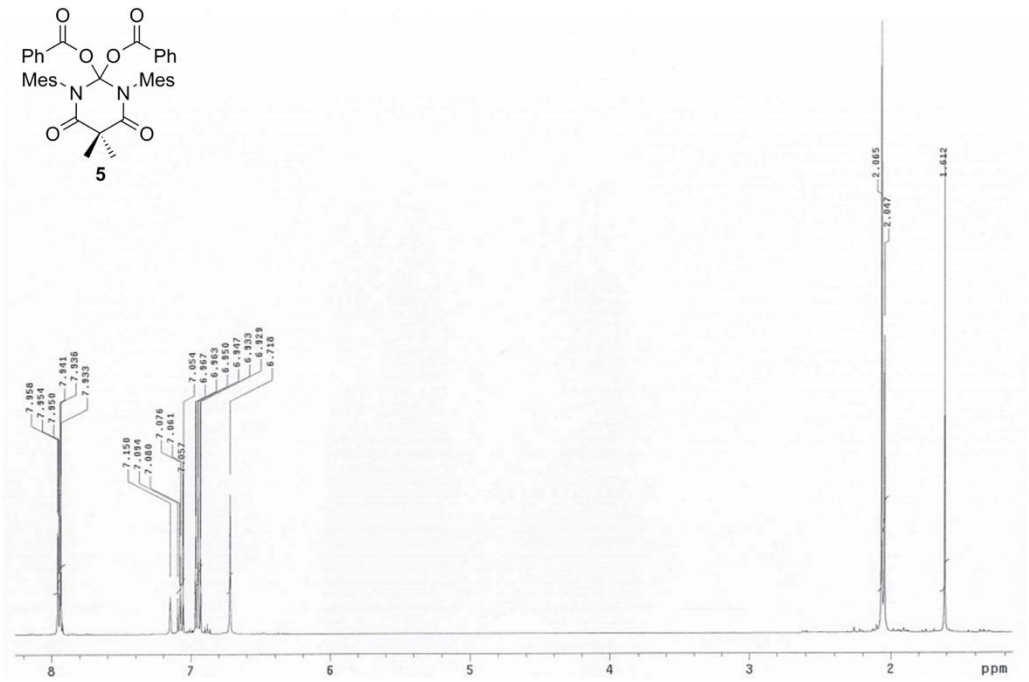
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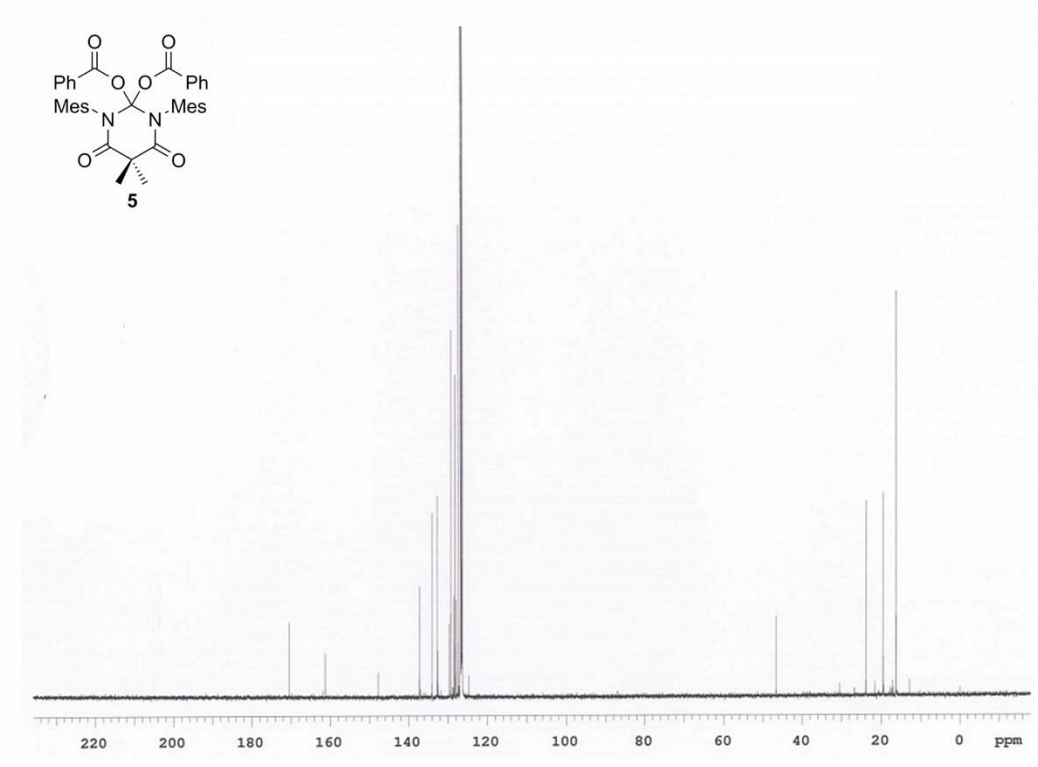
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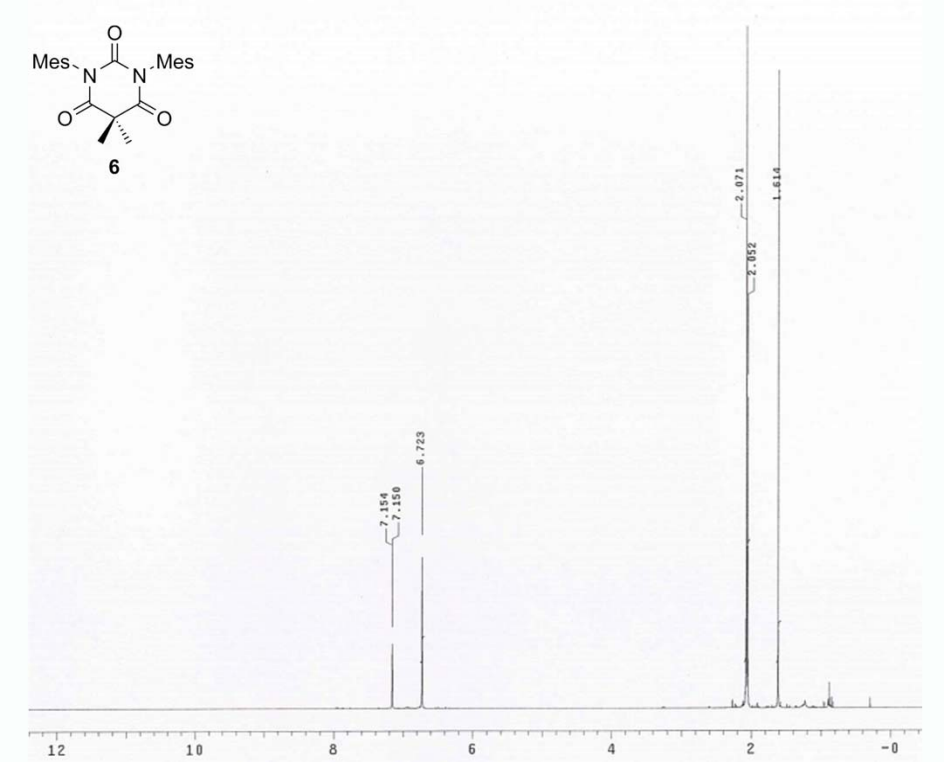

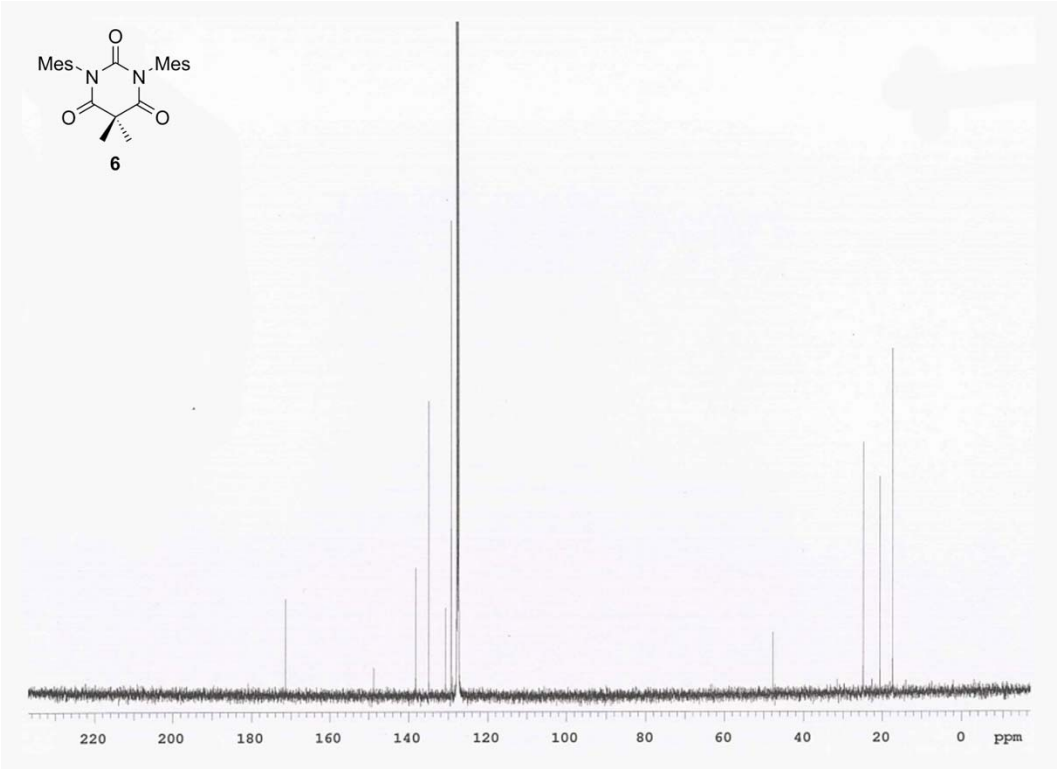

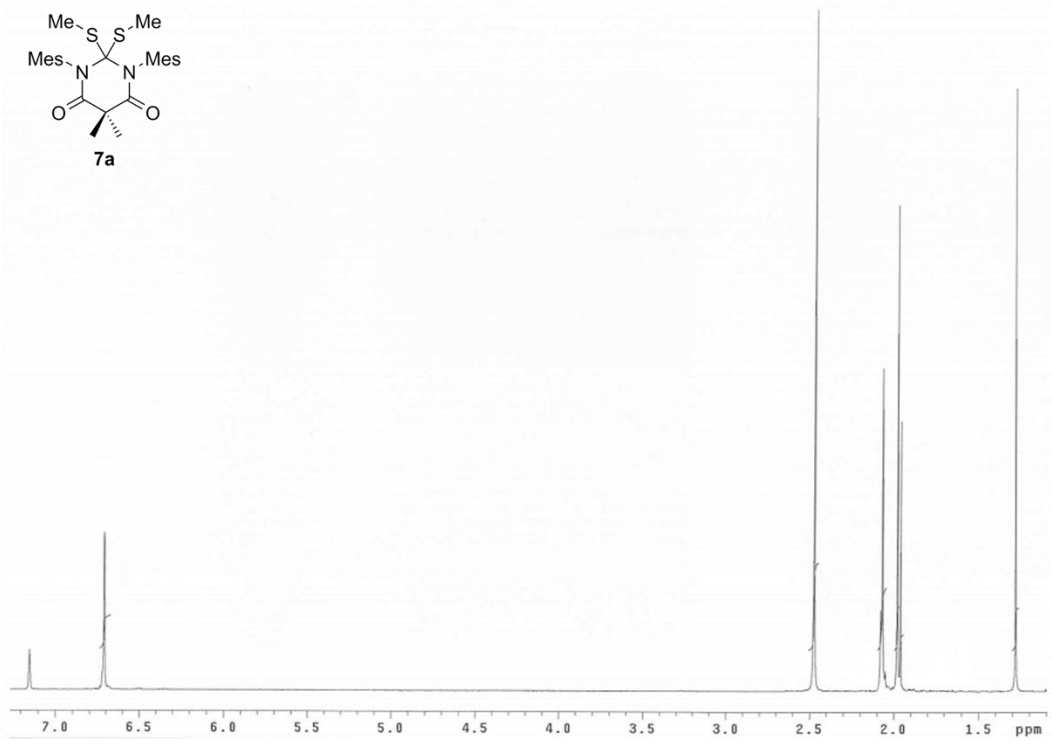

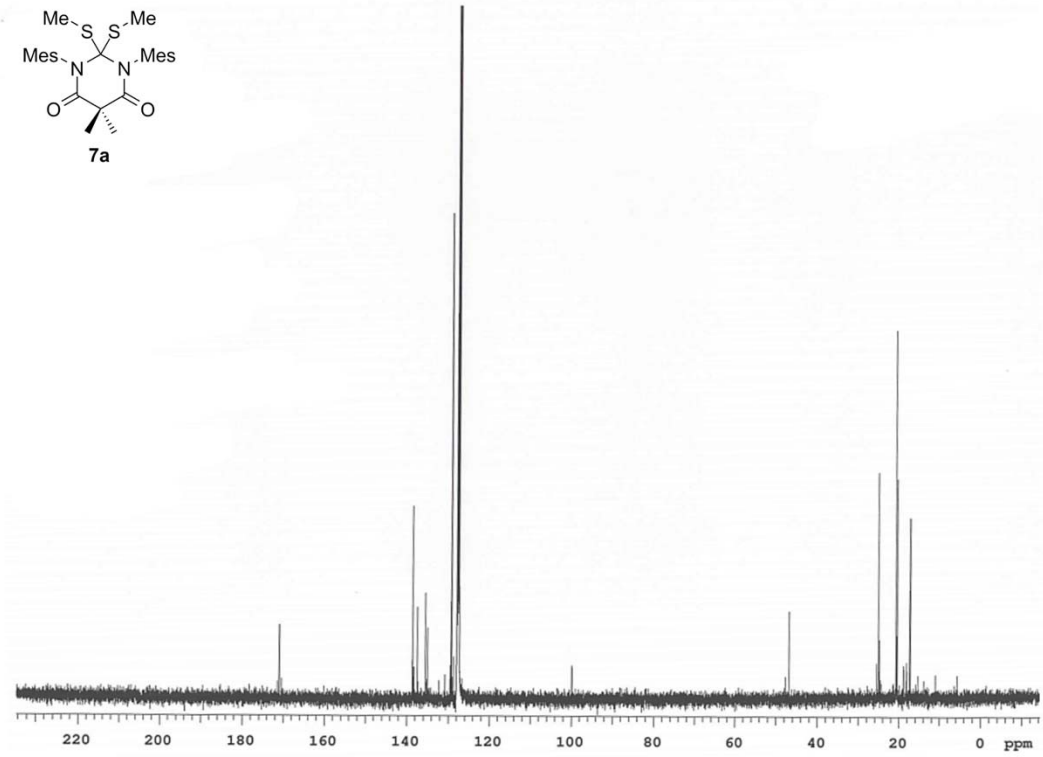

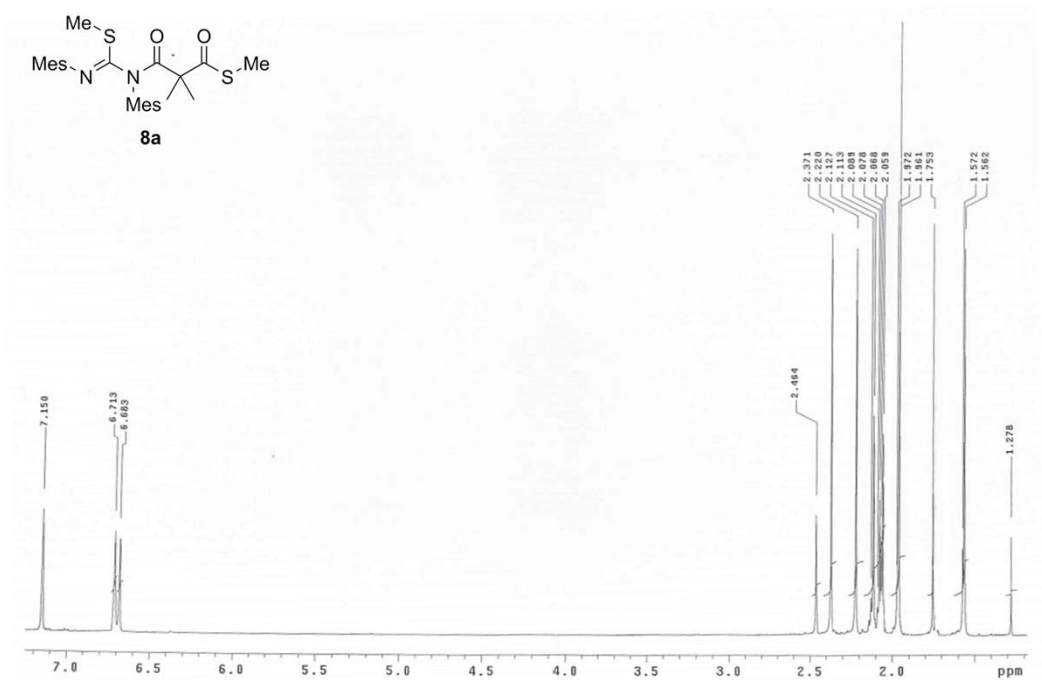
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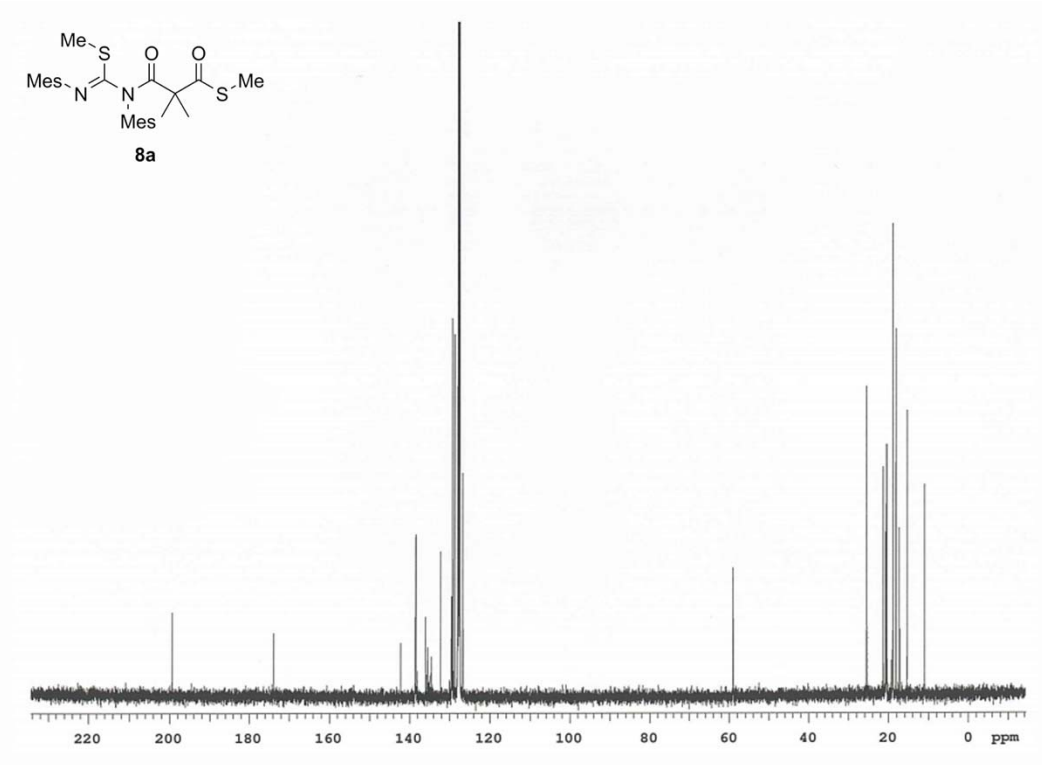
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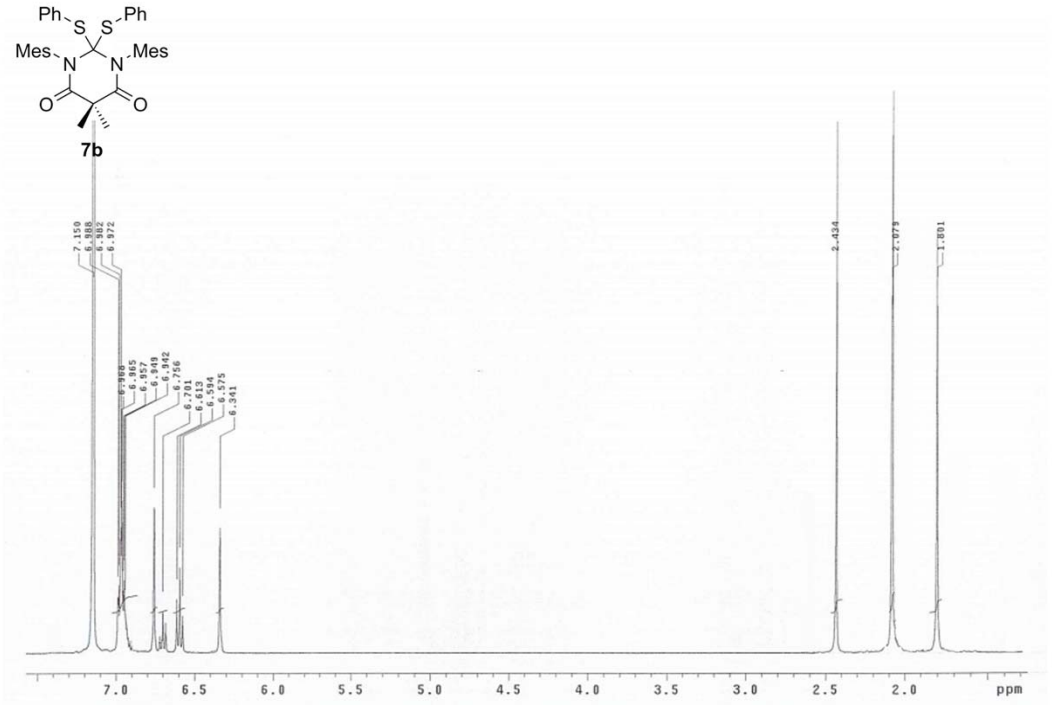

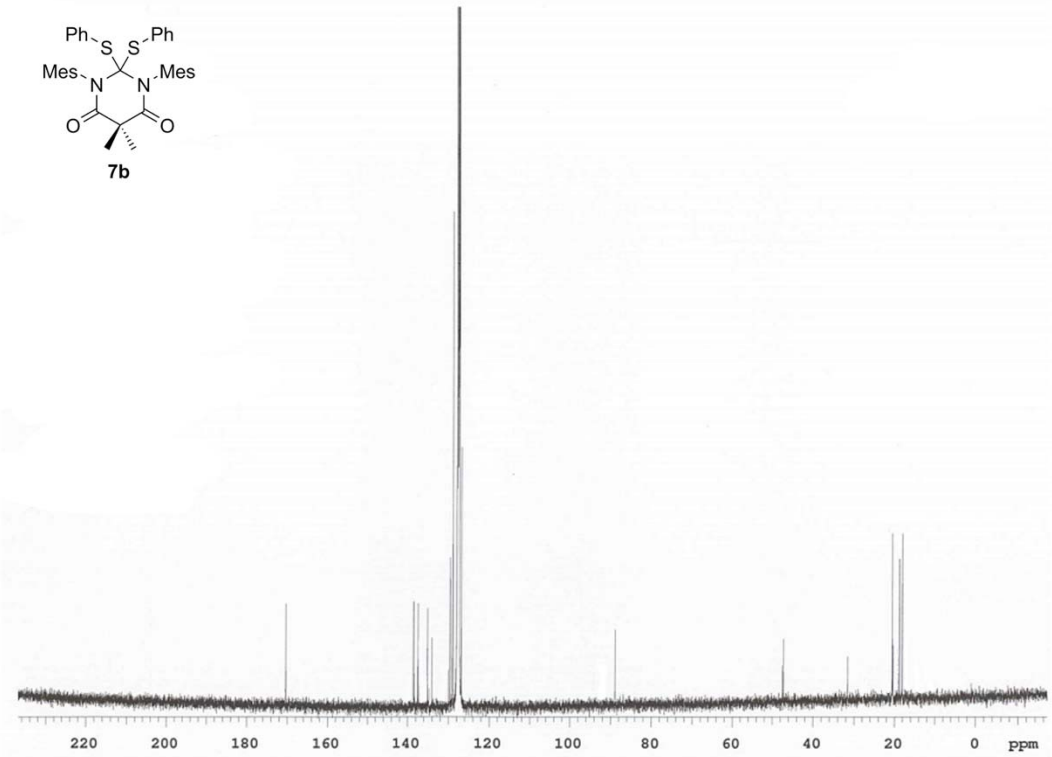

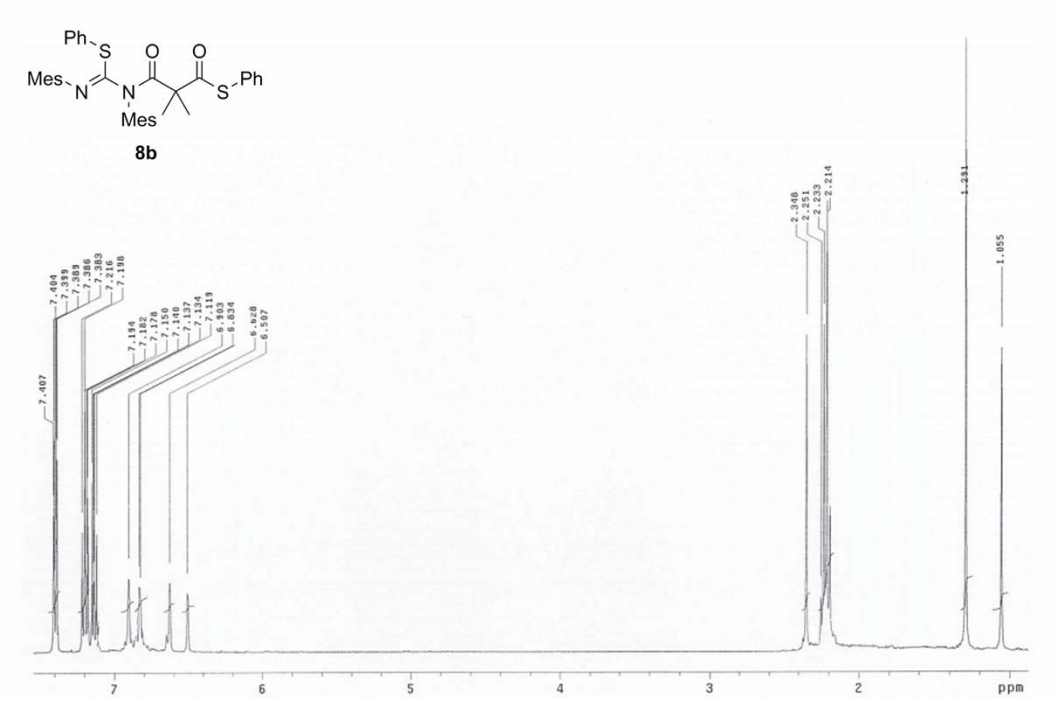
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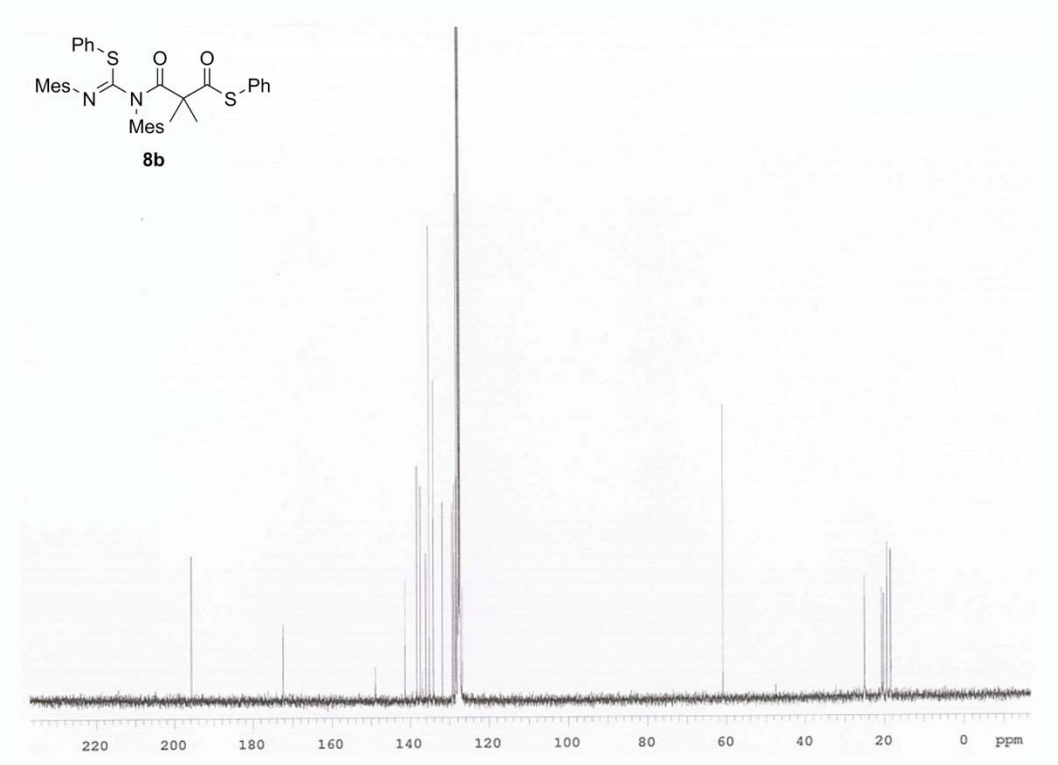
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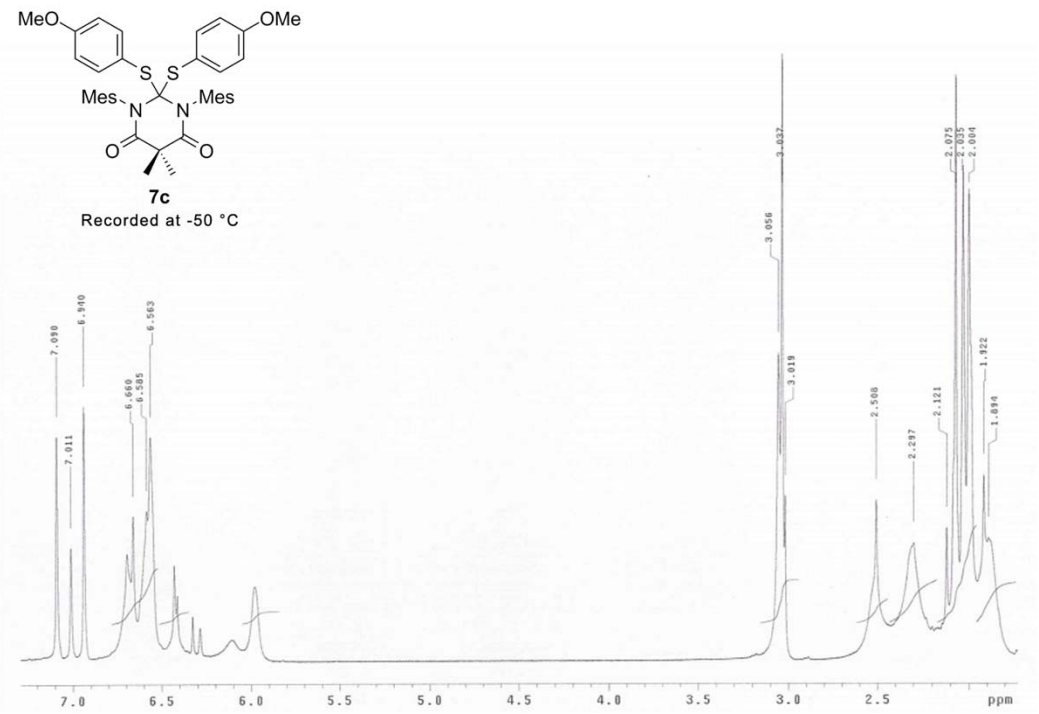
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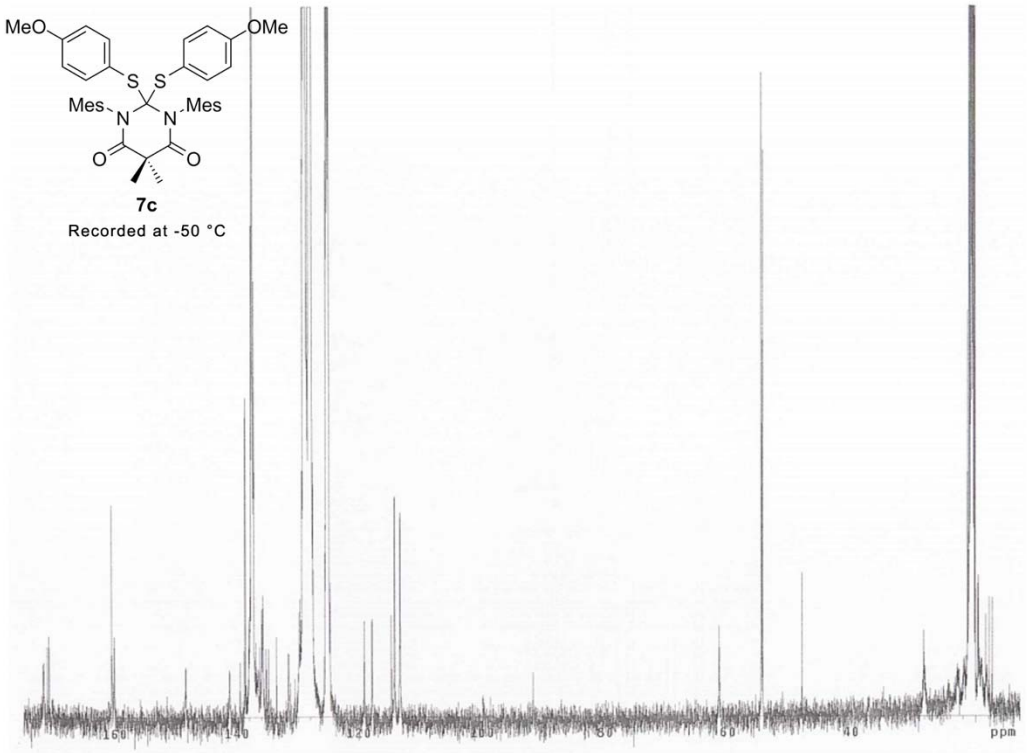
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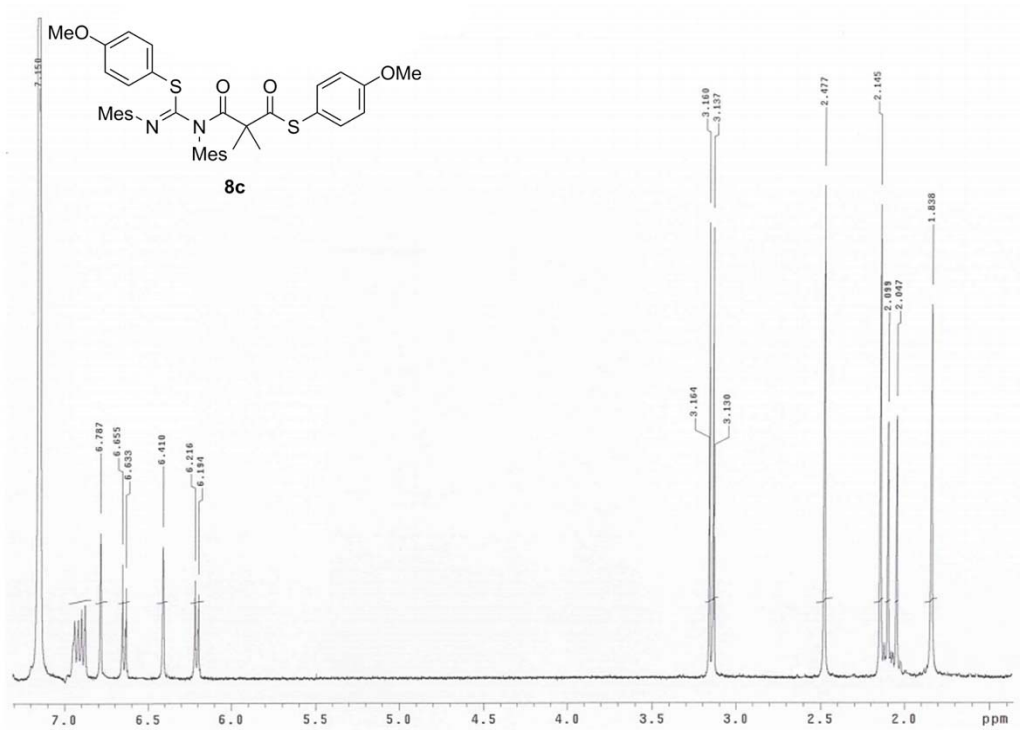

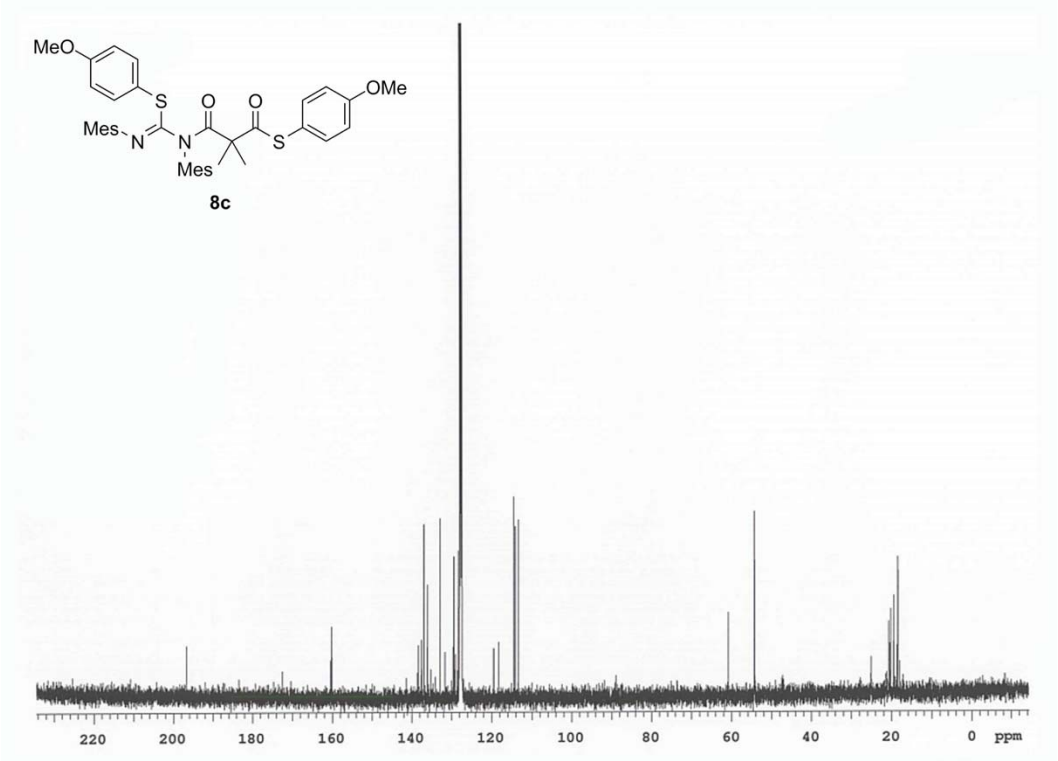

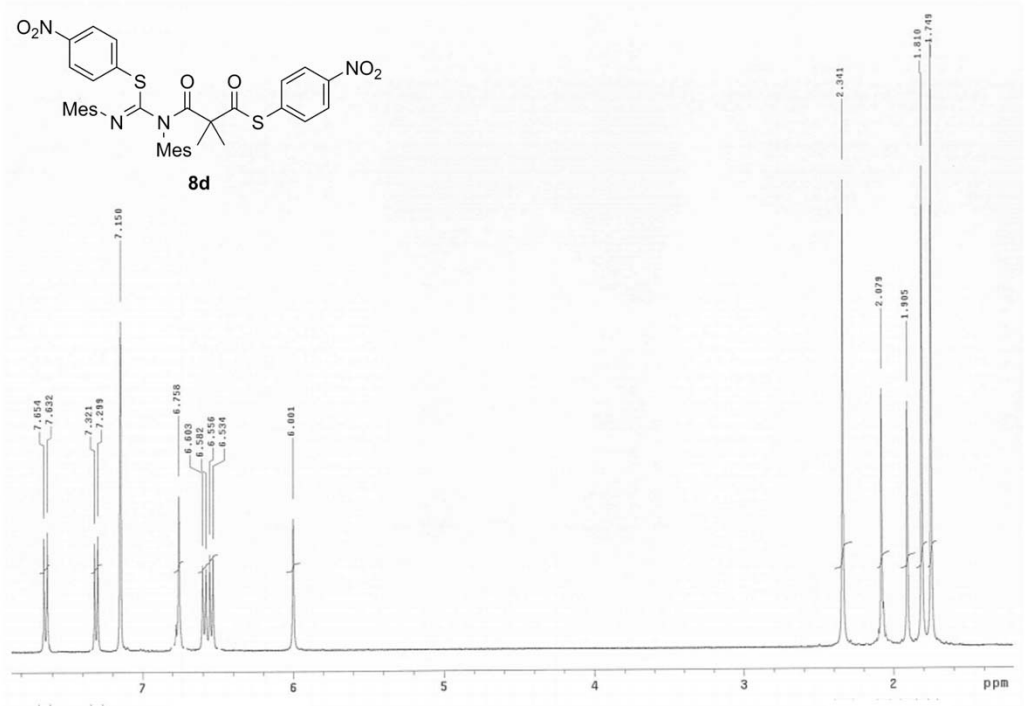
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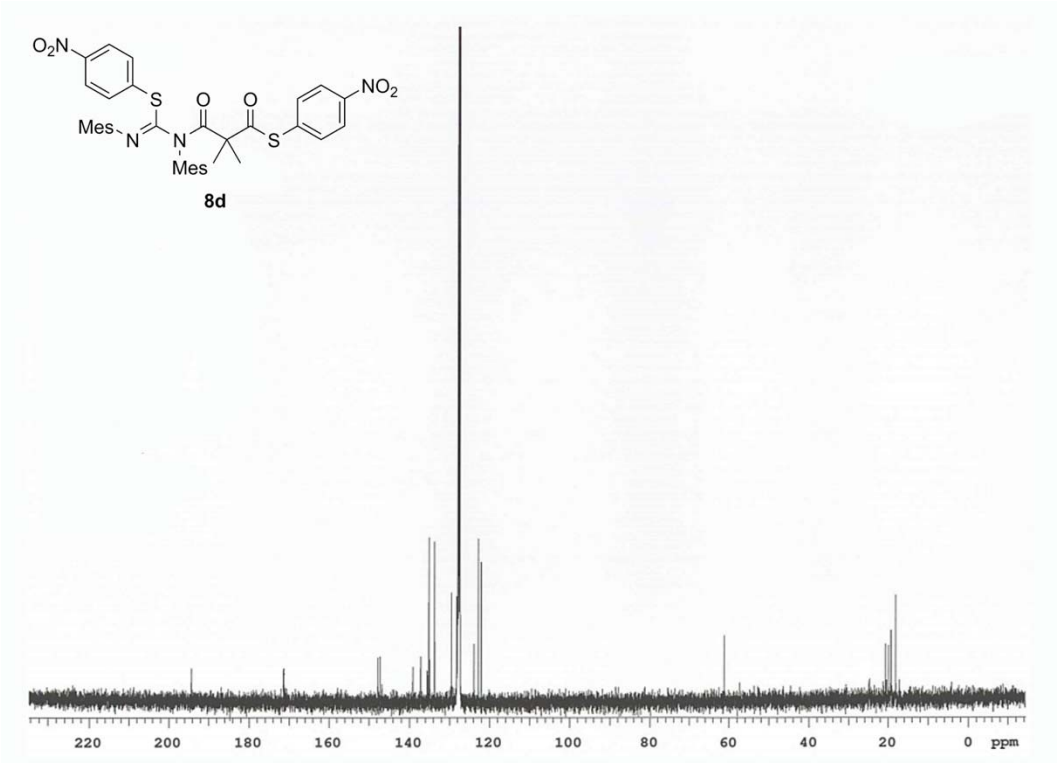
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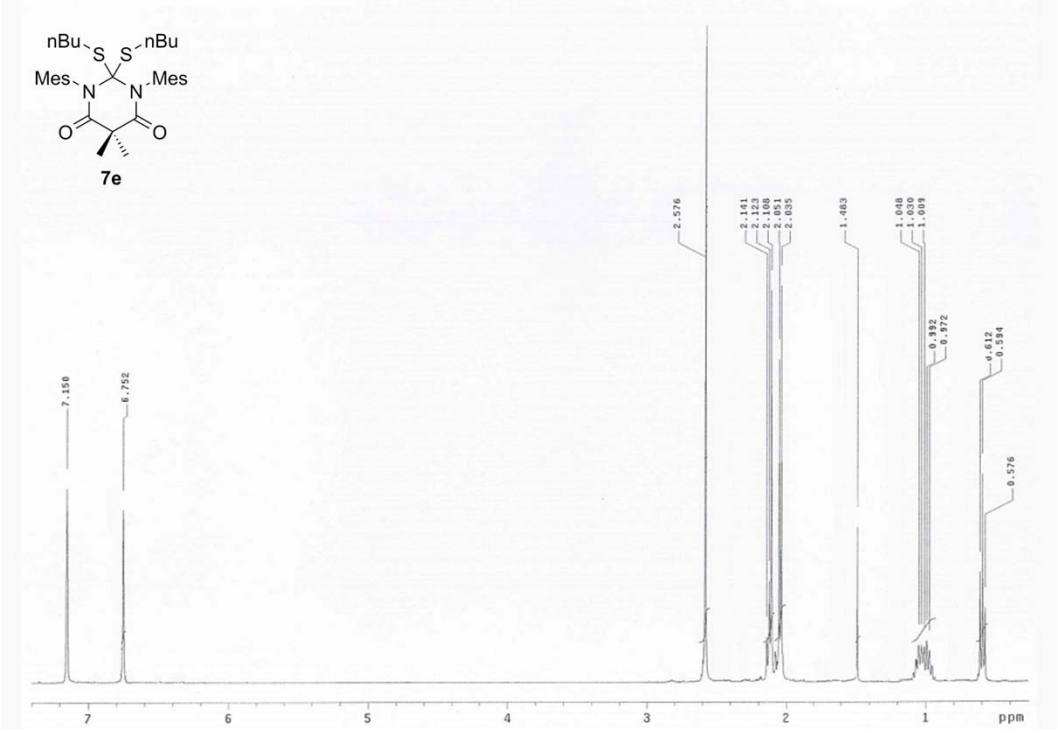
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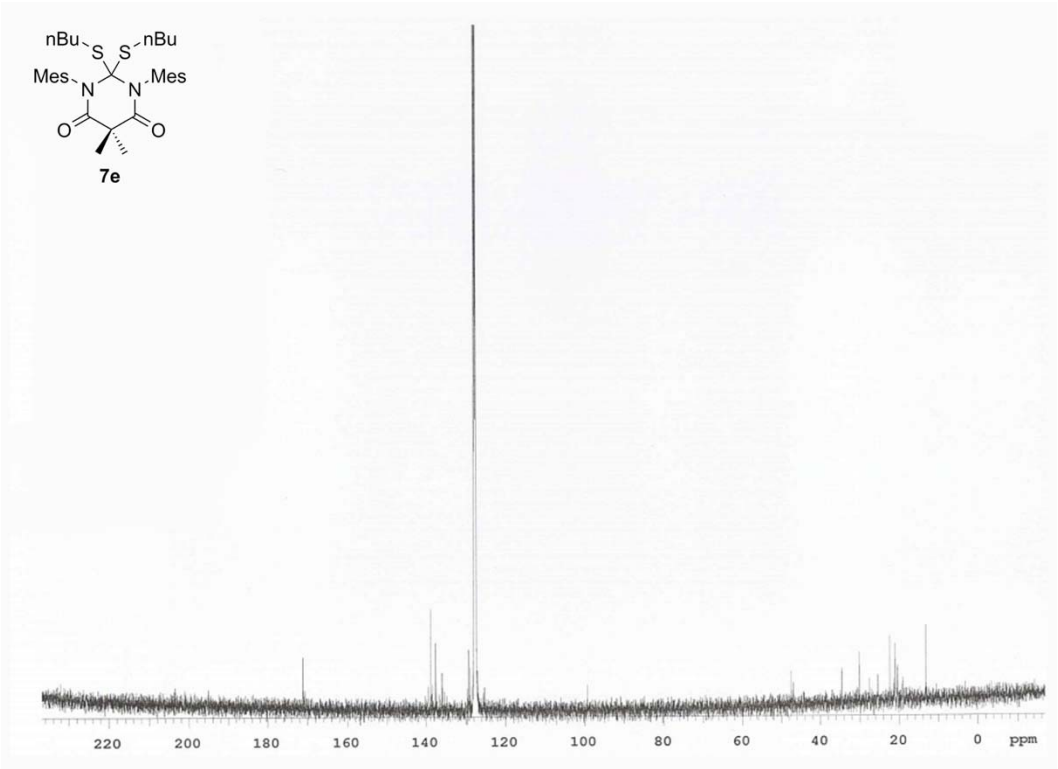
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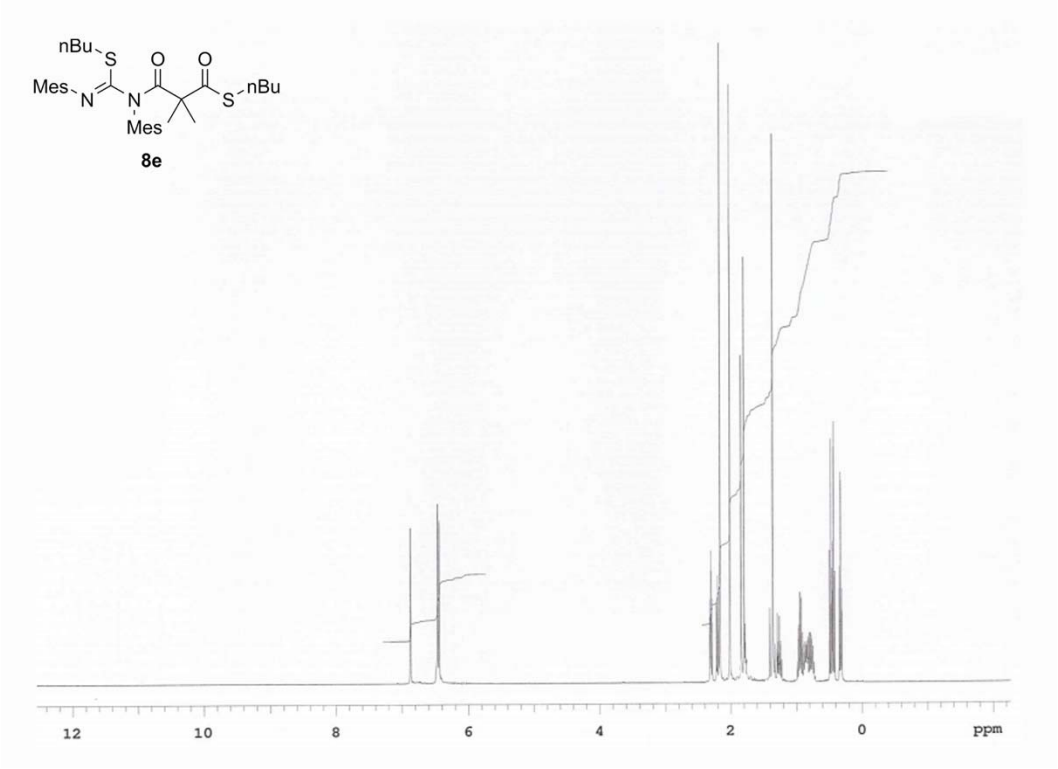
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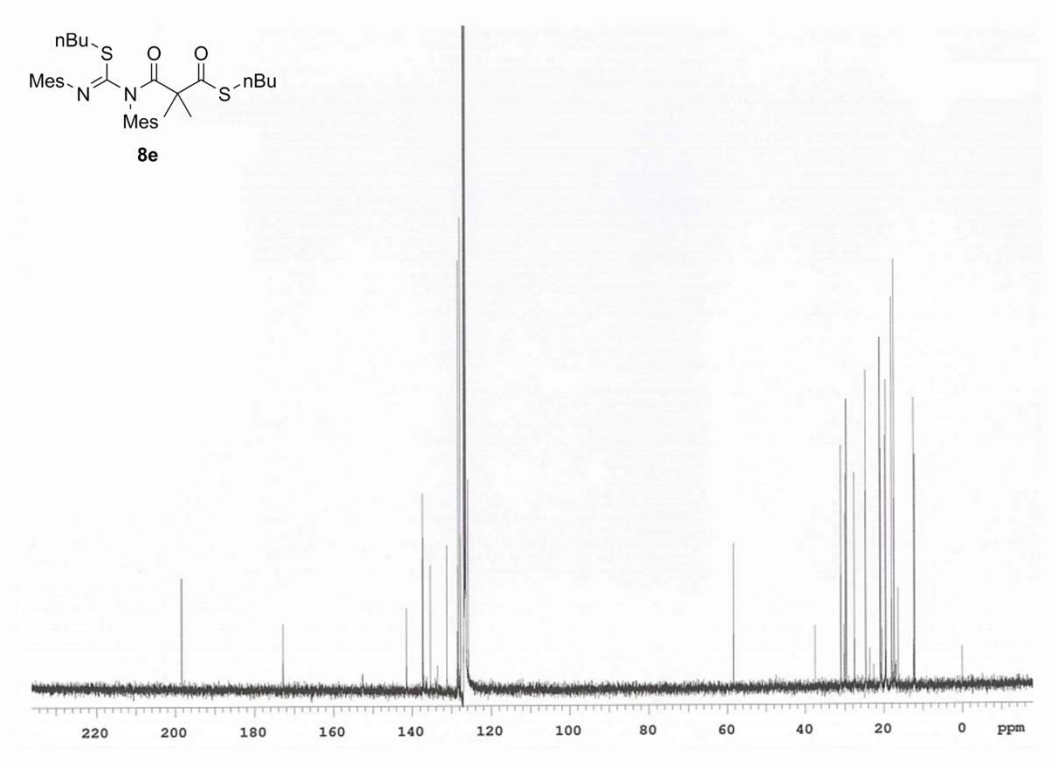
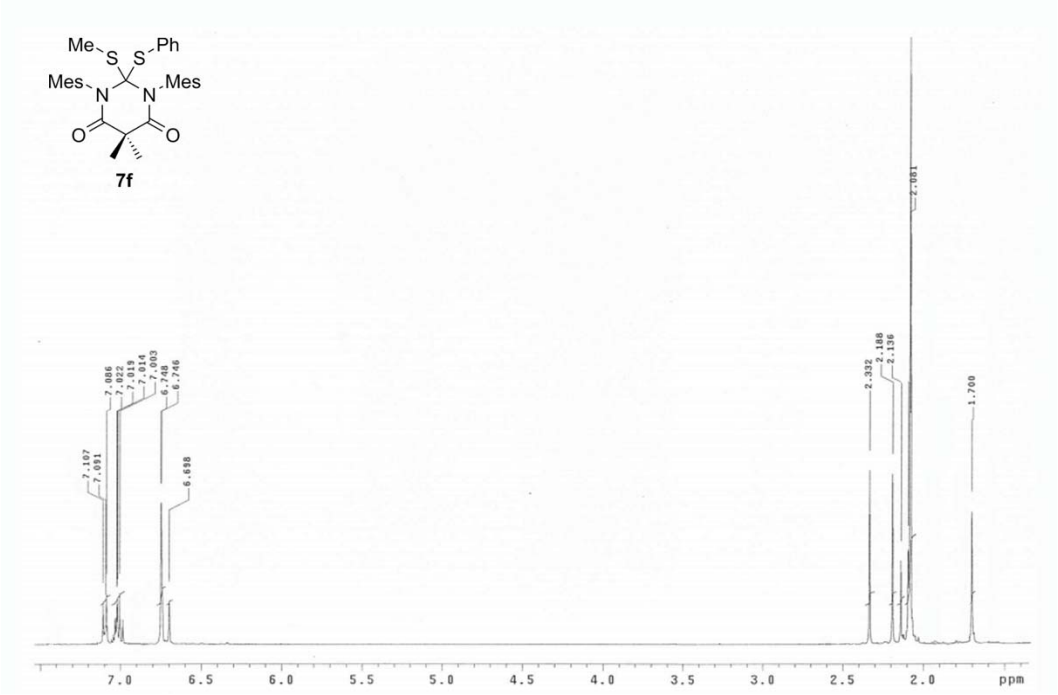
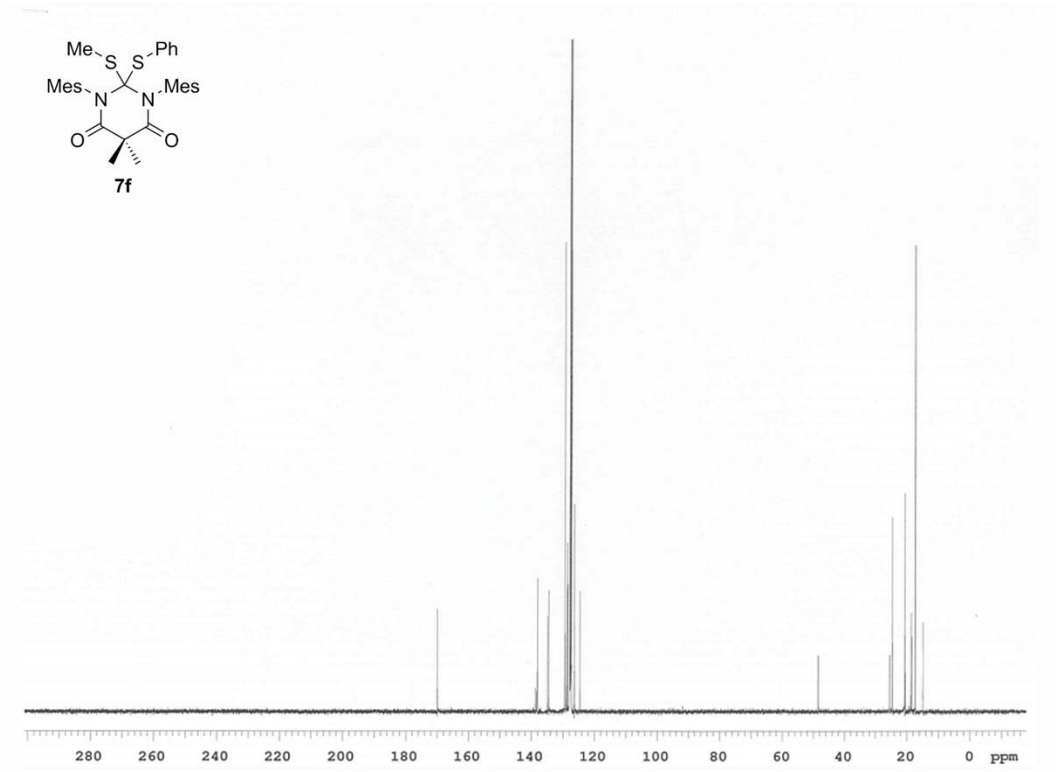
ppm

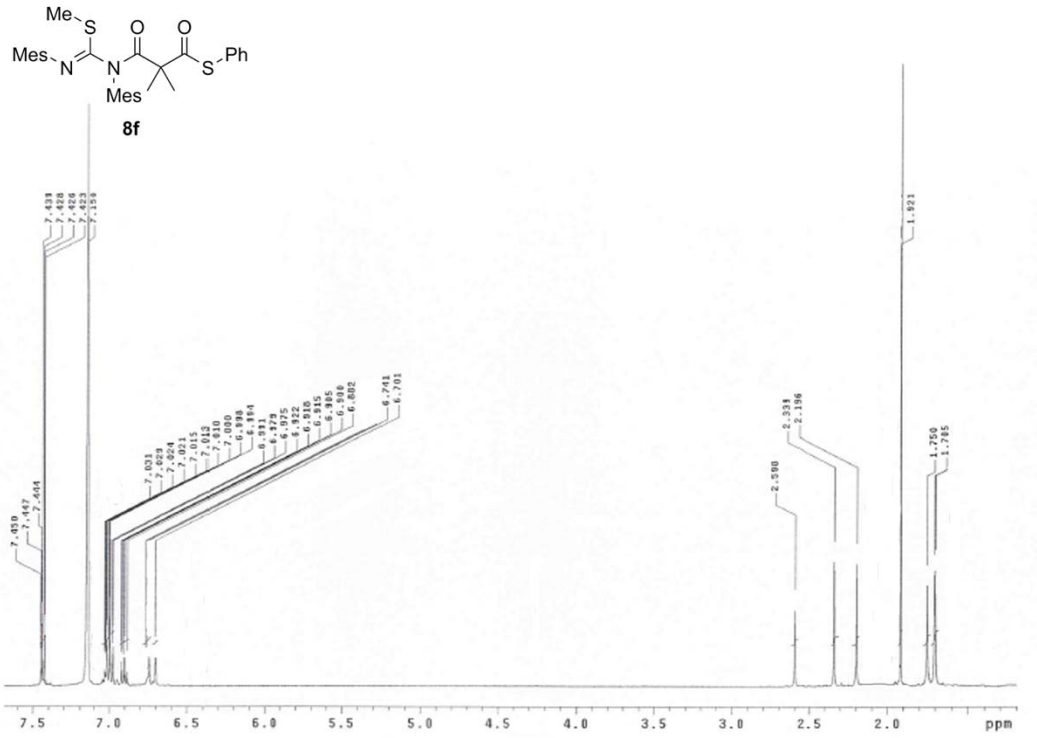
8e

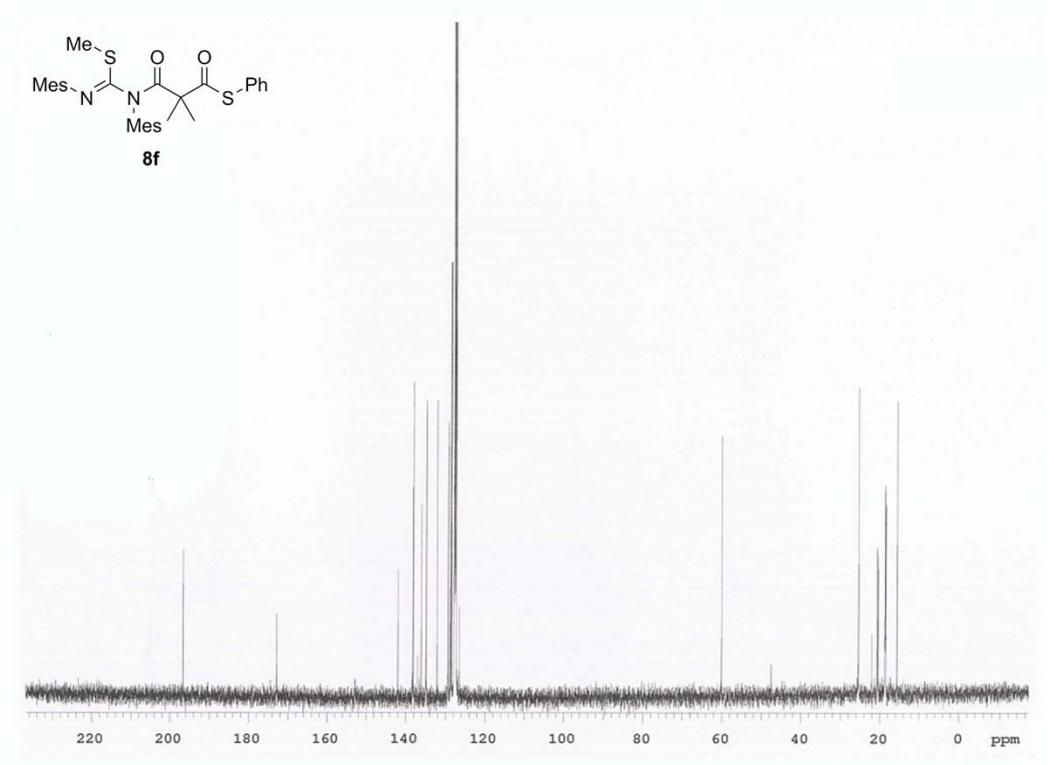

nBu
S
O
O
Mes
N
N
S
nBu
Mes
220
200
180
160
140
120
100
80
60
40
20
0
ppm

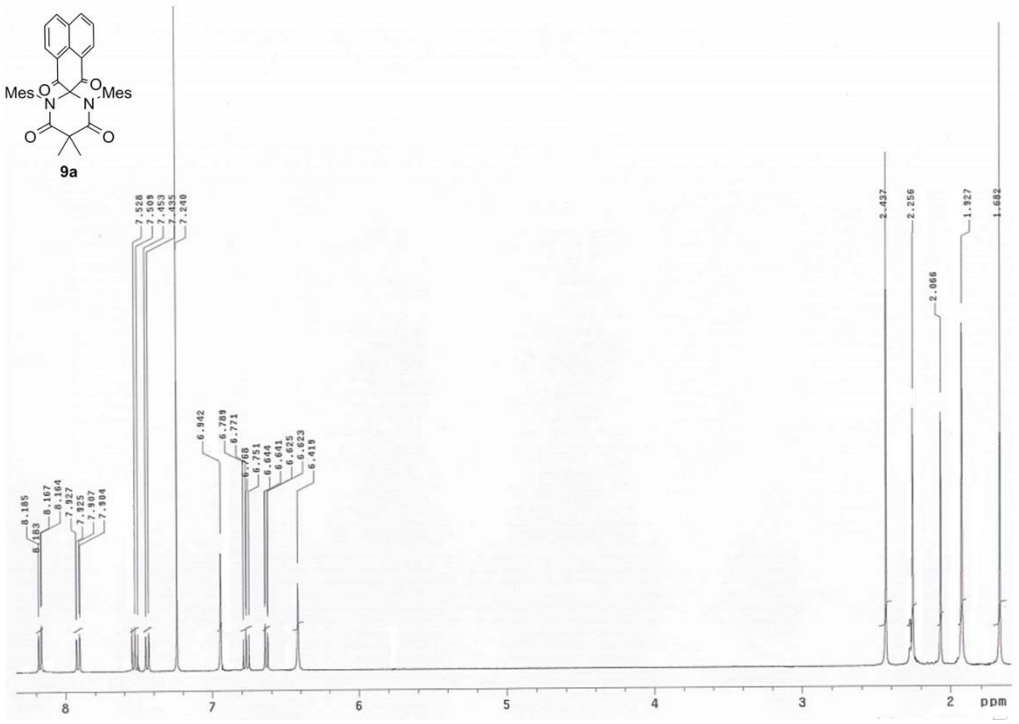
8e

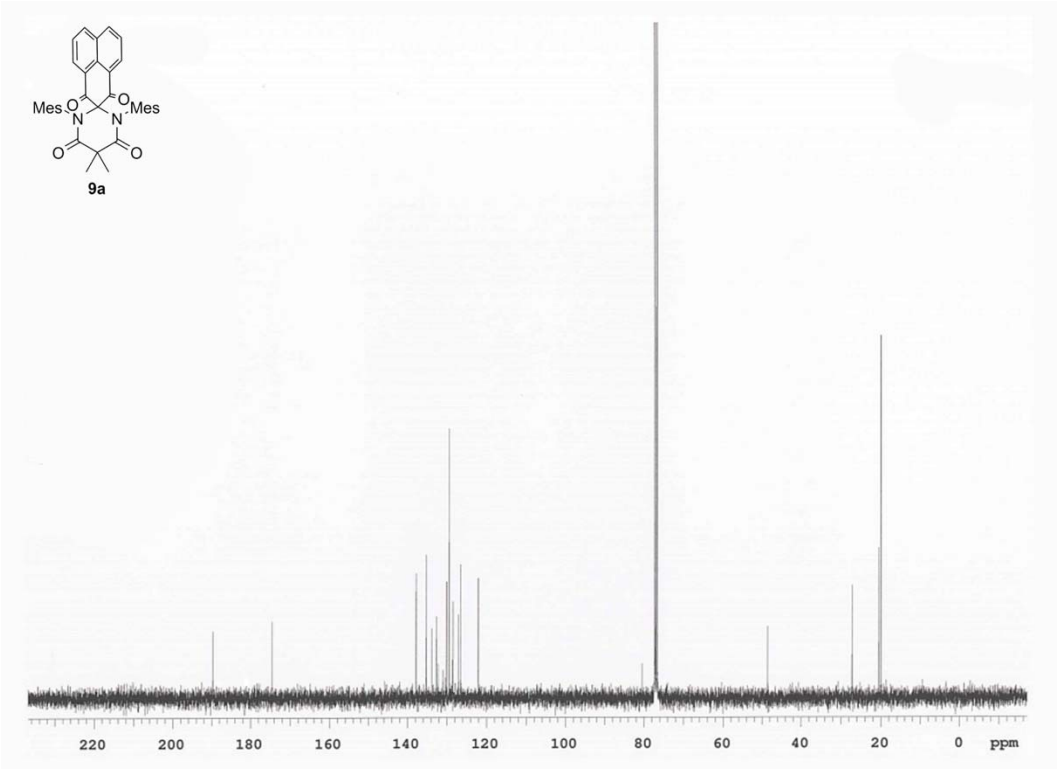


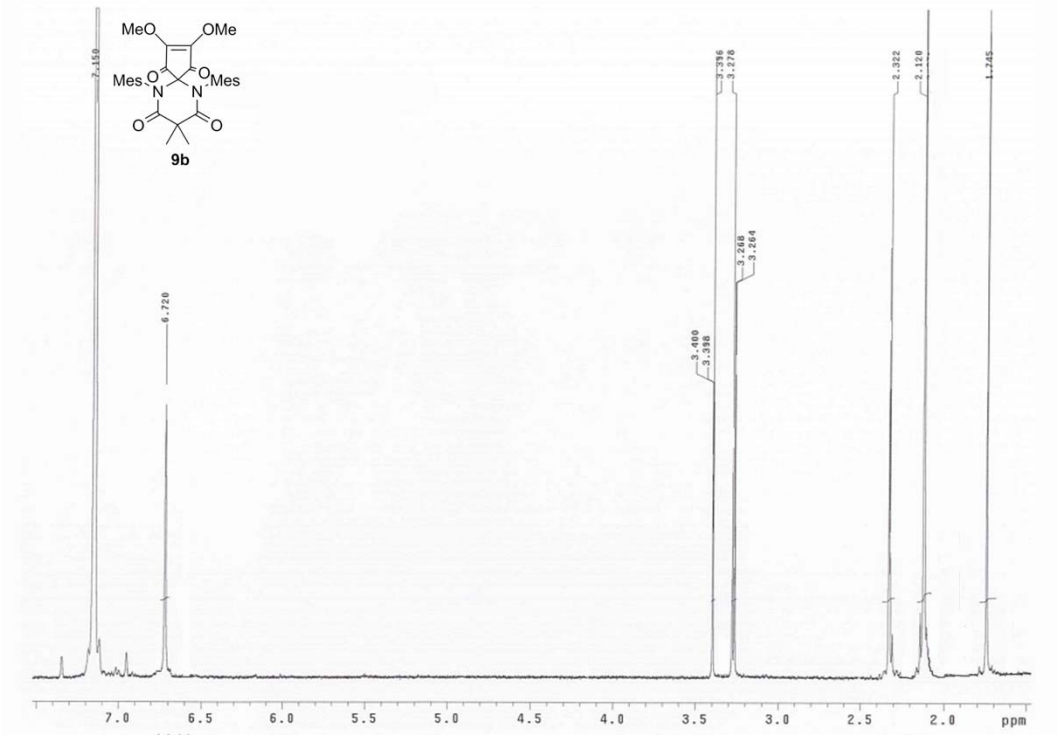


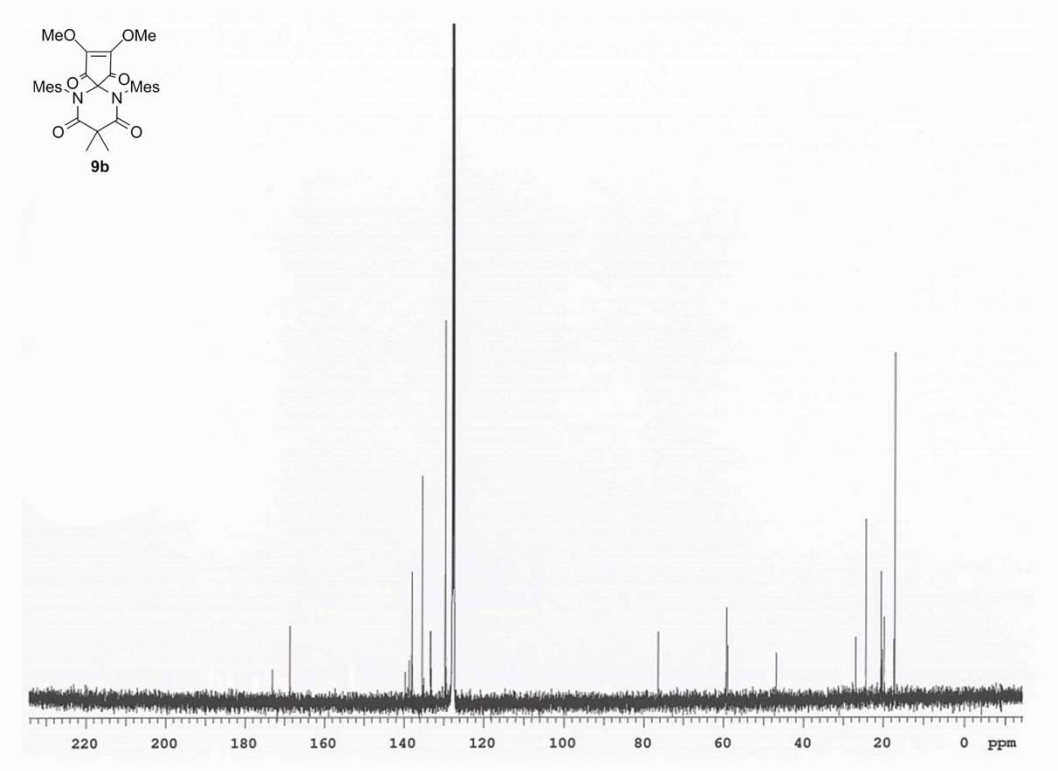

Me
S
Mes
N
O
O
N
S
Ph
Mes
8f
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm

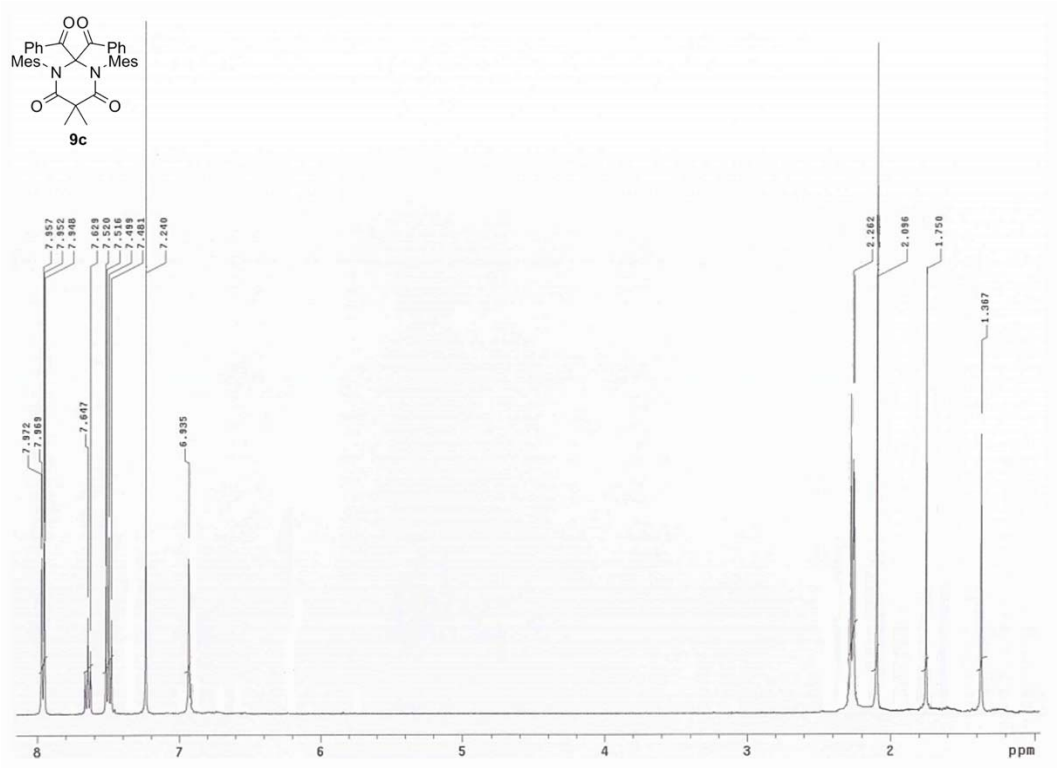

Me
S
Mes
N
O
O
N
S
Ph
Mes
8f
220
200
180
160
140
120
100
80
60
40
20
0
ppm

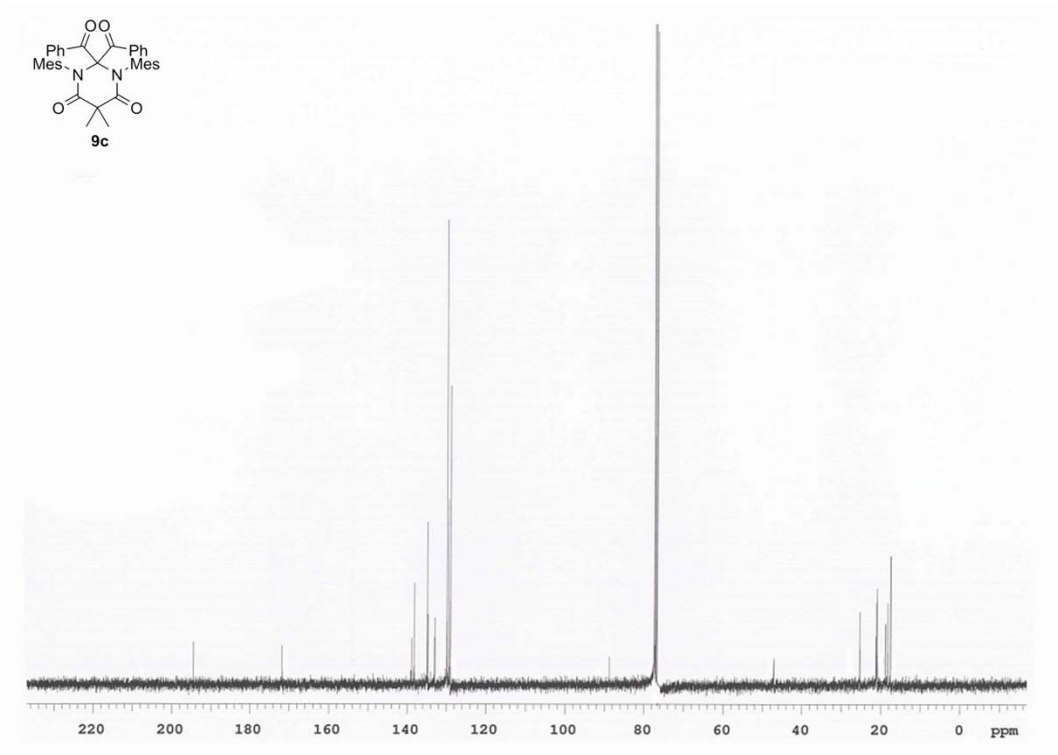

Mes
O
N
O
Mes
O
O
9a
8.185
8.183
8.167
8.165
7.927
7.925
7.907
7.904
7.528
7.509
7.453
7.435
7.240
6.942
6.789
6.771
6.768
6.751
6.644
6.641
6.625
6.623
6.419
2.437
2.256
2.066
1.927
1.682
8
7
6
5
4
3
2
ppm

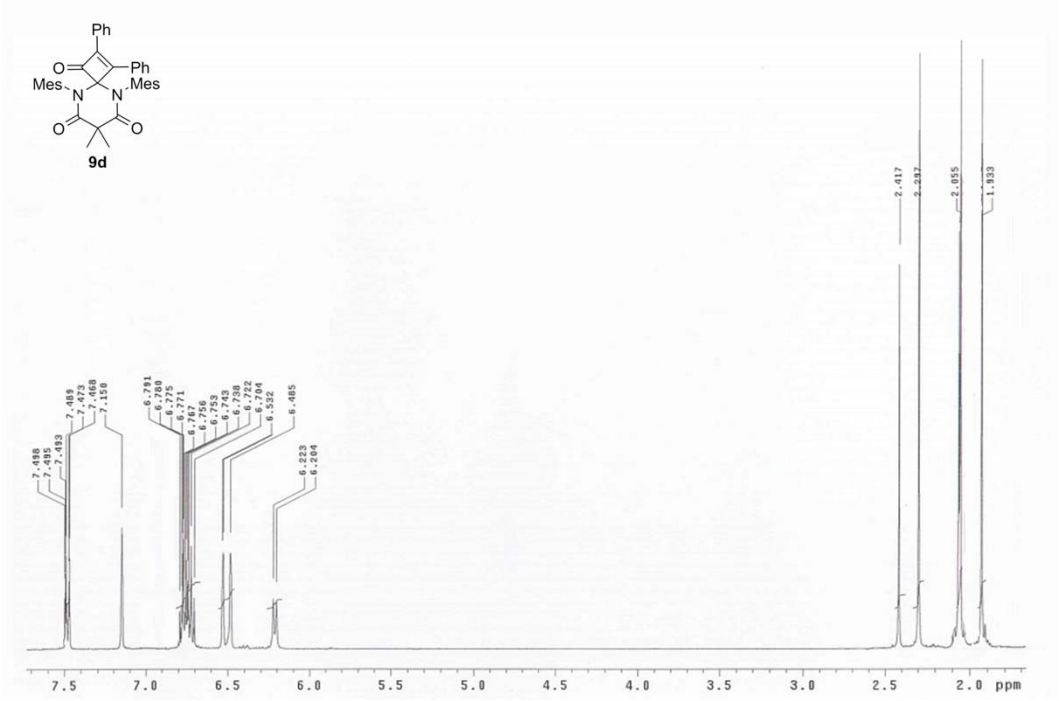

Mes
O
N
O
Mes
O
O
9a
220
200
180
160
140
120
100
80
60
40
20
0
ppm

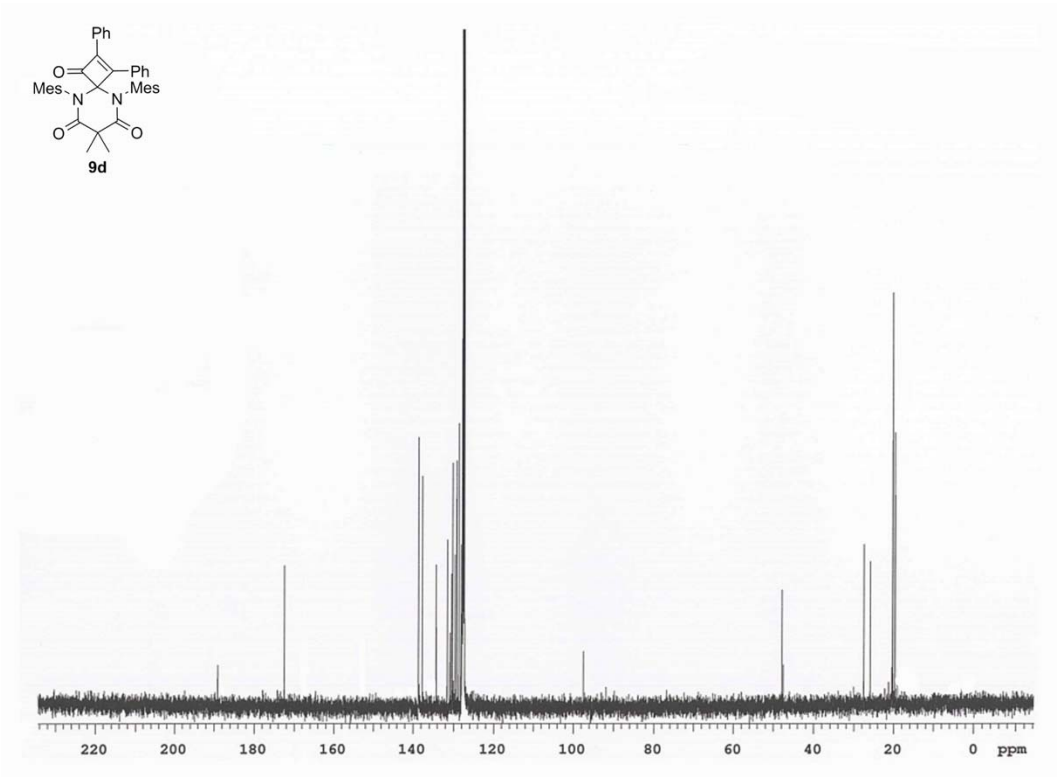

MeO
OMe
Mes
O
N
O
Mes
N
O
O
9b
2.159
6.720
3.400
3.398
3.396
3.276
3.268
3.264
2.322
2.120
1.245
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm

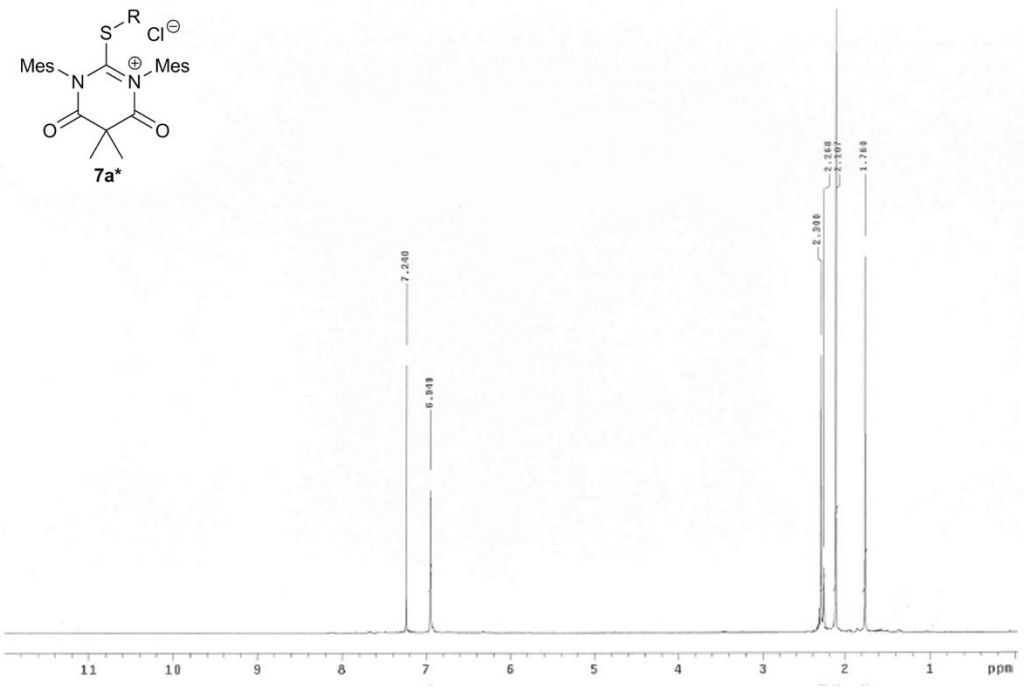

MeO
OMe
Mes
O
N
O
Mes
N
O
O
9b
220
200
180
160
140
120
100
80
60
40
20
0
ppm

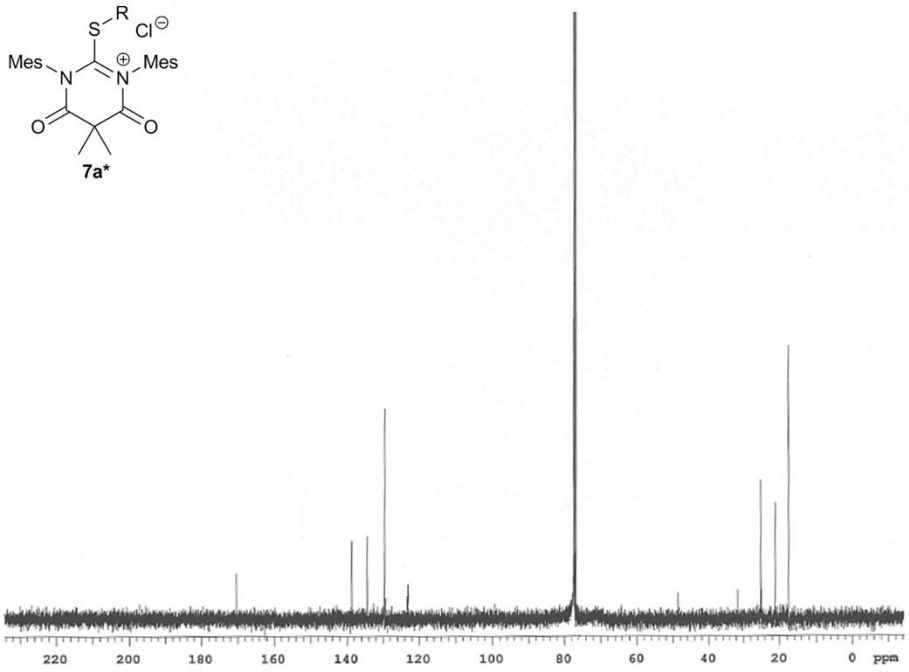

9c
7.957
7.952
7.948
7.629
7.520
7.516
7.499
7.481
7.240
7.972
7.969
7.647
6.935
2.262
2.096
1.750
1.367
8
7
6
5
4
3
2
ppm


9c
220
200
180
160
140
120
100
80
60
40
20
0
ppm


Ph
O
Ph
Mes
N
N
Mes
O
O
9d
2.417
2.297
2.055
1.933
7.498
7.495
7.493
7.489
7.473
7.468
7.150
6.791
6.788
6.775
6.771
6.767
6.766
6.759
6.743
6.738
6.722
6.704
6.532
6.485
6.223
6.204
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0 ppm


Ph
O
Ph
Mes
N
N
Mes
O
O
9d
220
200
180
160
140
120
100
80
60
40
20
0 ppm





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