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Supporting Information

Reductive Generation of Stable, Five-Membered *N,N′*-Diamidocarbenes

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General Considerations. All procedures were performed using standard Schlenk techniques under an atmosphere of nitrogen or in a nitrogen-filled glove box unless otherwise noted. Compounds **1** and **2** are highly moisture sensitive. *N*,*N*′-di-*tert*-butylcarbodiimide was purchased from Sigma Aldrich. Bromotriphenylphosphonium bromide[S1] was synthesized according to literature procedures. *N*-adamantyl-*N*′-*tert*-butylcarbodiimide[S2] was prepared using the methods reported by Palomo.[S3] Methyl acrylate, methyl vinyl ketone, 1-phenyl-1-butyne, 4-methyl anisole, and 4-chlorotoluene were dried over molecular sieves for at least 24 h prior to use. Toluene, tetrahydrofuran, benzene, diethyl ether, and pentane were dried and degassed using a Vacuum Atmospheres Company solvent purification system and stored over molecular sieves. Infrared (IR) spectra were recorded on a Perkin Elmer Spectrum BX FTIR spectrometer. High resolution mass spectra (HRMS) were obtained with a Waters Micromass Autospec-Ultima (CI). UV-vis spectra were acquired on a Perkin Elmer Lambda 35 UV-vis spectrometer. NMR spectra were recorded on a Varian Mercury 400, a Varian Directdrive 400, or an Agilent MR400 spectrometer. Chemical shifts (δ) are reported in ppm relative to the residual solvent (benzene: ^{1}H: 7.15 ppm, ^{13}C: 128.0 ppm; chloroform: ^{1}H: 7.24 ppm, ^{13}C: 77.0 ppm). Elemental analyses were performed with a ThermoScientific Flash 2000 Organic Elemental Analyzer. Melting points were obtained using a Stanford Research Systems MPA100 OptiMelt automated melting point apparatus (ramp rate: 1 °C·min^{-1}) and are uncorrected.

Synthesis of *N*,*N*′-bis(1-adamantyl)carbodiimide. A 100 mL Schlenk flask was charged with bromotriphenylphosphonium bromide (1.93 g, 4.57 mmol, 1.5 equiv), triethylamine (1.5 mL, 10.65 mmol, 3.5 equiv), dichloromethane (20 mL) and a stir bar. The heterogeneous mixture was cooled to 0 °C and *N*,*N*′-bis(1-adamantyl)urea (1.0 g, 3.0 mmol) added in four portions over 30 min. The resultant mixture was heated at 40 °C for 14 h during which time the solution became homogenous. After adding water (60 mL) to the red solution, the two layers were separated, and the aqueous layer was washed with dichloromethane (10 mL). The combined organic layers were dried over sodium sulfate and filtered. After removing the residual solvent under reduced pressure, the crude solid was extracted with diethyl ether and passed through a plug of silica gel using diethyl ether as the eluent. Concentration of the resultant solution afforded *N*,*N*′-bis(1-adamantyl)carbodiimide as a white solid (0.828 g, 2.67 mmol, 88%). m.p. = 310-312 °C. ^{1}H NMR ($CDCl_3$, 399.68 MHz): δ 1.57-1.65 (m, 12 H), 1.75 (overlapping s, 12 H), 2.05 (bs, 6H). ^{13}C NMR ($CDCl_3$, 100.50 MHz): δ 29.8, 36.0, 44.7, 54.9, 139.4. IR (KBr): 2901.8, 2848.8, 2108.3, 2037.5, 1352.7, 1300.5, 1079.8, 633.9 cm^{-1}. HRMS (CI): $[M-H]^+$ calcd. for $C_{21}H_{29}N_2$: 309.2331; Found: 309.2330. Anal. calcd. for $C_{21}H_{30}N_2$: C, 81.24; H, 9.74; N, 9.02; Found: C, 80.97; H, 9.99; N, 9.15.

Synthesis of 1a. Using a modified procedure reported by Zinner,[S4] a 100 mL Schlenk flask outfitted with a septum was charged with *N*,*N*′-di-*tert*-butylcarbodiimide (2.00 g, 12.96 mmol), dichloromethane (60 mL) and a stir bar. The resultant solution was cooled to 0 °C for 15 min whereupon oxalyl chloride (1.73 g, 1.17 mL, 13.6 mmol, 1.05 equiv) was added dropwise. The ice bath was removed and the solution was stirred for 1 h. Removal of the residual solvent under reduced pressure afforded **1a** as a white solid (3.63 g, 12.91 mmol, 99%). m.p. = 129-130 °C (decomp.) ^{1}H NMR ($CDCl_3$, 400.27 MHz): δ 1.75 (s, 18H). ^{1}H NMR (C_6D_6, 400.09 MHz): δ 1.52 (s, 18H). ^{13}C NMR ($CDCl_3$, 100.60 MHz): δ 28.0, 62.2, 101.7, 154.9. IR (KBr): 3458.9, 3002.5, 2975.8, 2940.1, 1757.7, 1483.3, 1368.8, 1295.4, 1174.1, 1129.7, 1019.9, 873.0, 771.4,

552.2 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{11}H_{19}N_2O_2{}^{35}Cl_2$: 281.0824; Found: 281.0827. Anal. calcd. for $C_{11}H_{18}Cl_2N_2O_2$: C, 46.99; H, 6.45; N, 9.96; Found: C, 46.96; H, 6.58; N, 10.23.

Synthesis of 1b. Using an adapted procedure reported by Zinner,[S4] a 25 mL Schlenk flask outfitted with a septum was charged with *N*,*N*′-bis(1-adamantyl)carbodiimide (0.500 g, 1.61 mmol), dichloromethane (10 mL) and a stir bar. To this solution, oxalyl chloride (0.225 g, 0.15 mL, 1.77 mmol, 1.1 eq) was added dropwise and the resultant mixture was stirred at ambient temperature for 1.5 h. After removing the residual solvent under reduced pressure, the resulting solid was washed with a minimal quantity of cold diethyl ether followed by a minimal quantity of pentane. Subsequent drying under reduced pressure afforded **1b** as a white solid (0.630 g, 1.44 mmol, 89%). m.p. = 200-202 °C (decomp.) ^{1}H NMR ($CDCl_3$, 399.68 MHz): δ 1.68 (m, 6H), 1.78 (m, 6H), 2.17 (bs, 6H), 2.63 (overlapping s, 12H). ^{13}C NMR ($CDCl_3$, 100.50 MHz): δ 30.1, 36.0, 38.7, 65.5, 101.8, 155.0. IR (KBr): 2914.9, 2851.9, 1758.0, 1457.1, 1376.8, 1359.0, 1343.2, 1263.8, 1200.8, 1124.5, 978.6, 866.3, 749.6 cm^{-1}. HRMS (CI): $[M-H]^+$ calcd. for $C_{23}H_{29}N_2O_2{}^{35}Cl_2$: 435.1606; Found: 435.1610. Anal. calcd. for $C_{23}H_{30}N_2O_2Cl_2$: C, 63.16; H, 6.91; N, 6.40; Found: C, 63.45; H, 6.78; N, 6.41.

Synthesis of 1c. Using an adapted procedure reported by Zinner,[S4] a 50 mL Schlenk flask outfitted with a septum was charged with *N*-adamantyl-*N*′-*tert*-butylcarbodiimide (0.450 g, 1.94 mmol), dichloromethane (10 mL) and a stir bar. To the resulting solution was added dropwise oxalyl chloride (0.18 mL, 2.13 mmol, 1.1 equiv). After stirring the resulting mixture at ambient temperature for 1.5 h, the residual solvent was removed under reduced pressure. The resulting crude residue was washed twice with a minimal quantity of cold diethyl ether followed by minimal quantity of pentane (×2). Subsequent drying of the product under reduced pressure afforded **1c** as an off-white solid (0.427 g, 1.19 mmol, 61%). m.p. = 141-143 °C (decomp.) ^{1}H NMR ($CDCl_3$, 399.68 MHz): δ 1.72 (m, 3H), 1.77-1.80 (m overlapping s, 12H), 2.18 (bs, 3H), 2.64 (overlapping s, 6H). ^{13}C NMR ($CDCl_3$, 100.50 MHz): δ 28.2, 30.07, 35.97, 38.65, 62.35, 65.48, 101.78, 154.90, 155.13. IR (KBr): 2917.4, 2852.3, 1756.8, 1374.3, 1368.6, 1345.2, 1276.3, 1123.9, 741.2 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{17}H_{25}N_2O_2{}^{35}Cl_2$: 359.1293; Found: 359.1289. Anal. calcd. for $C_{17}H_{24}N_2O_2Cl_2$: C, 56.83; H, 6.73; N, 7.80; Found: C, 56.99; H, 6.74; N, 7.47.

Synthesis of 2a. A 30 mL vial was charged with **1a** (1.0 g, 3.56 mmol), tetrahydrofuran (10 mL), potassium metal (0.292 g, 7.47 mmol, 2.1 equiv) and a stir bar. The resulting solution was observed to rapidly turn red and form a precipitate over time at ambient temperature. After 3 h, the residual solvent was removed under reduced pressure and the crude solid was extracted with pentane (4 mL), filtered through a medium porosity fritted funnel, and then washed with pentane (2 × 2 mL). Concentration of the filtrate afforded **2a** as a bright red solid (0.567 g, 2.70 mmol, 76%). m.p. = 73-75 °C. ^{1}H NMR (C_6D_6, 400.09 MHz): δ 1.37 (s, 18H). ^{13}C NMR (C_6D_6, 100.60 MHz): δ 28.6, 58.6, 154.2, 287.2. IR (KBr): 2979.5, 2935.2, 1780.1, 1754.9, 1395.4, 1325.6, 1205.0, 1066.3, 996.6, 770.9, 572.3 cm^{-1}. UV-vis (C_5H_{12}): λ_{max} = 489 nm. HRMS (CI): $[M+H]^+$ calcd. for $C_{11}H_{19}N_2O_2$: 211.1447; Found: 211.1448. Anal. calcd. for $C_{11}H_{18}N_2O_2$: C, 62.83; H, 8.63; N, 13.32; Found: C, 62.76; H, 8.82; N, 13.50.

Synthesis of 2b. An 8 mL vial was charged with **1b** (0.200 g, 0.457 mmol), tetrahydrofuran (2 mL), potassium metal (0.038 g, 0.96 mmol, 2.1 equiv) and a stir bar. Stirring the resultant

mixture at ambient temperature for 2 h afforded a red solution that was accompanied by the formation of a precipitate. The reaction mixture was concentrated under reduced pressure, and the crude solid was extracted with benzene (5 mL), filtered through a medium fritted funnel, and washed with benzene (2 × 2 mL). Concentration of the filtrate afforded **2b** as a pale purple-red solid (0.103 g, 0.281 mmol, 61%). m.p. = 197-199 °C (decomp.) ^{1}H NMR (C_6D_6, 400.09 MHz): δ 1.49 (m, 6H), 1.55 (m, 6H), 1.95 (bs, 6H), 2.24 (overlapping s, 12H). ^{13}C NMR (C_6D_6, 400.09 MHz): δ 29.9, 36.3, 41.4, 59.5, 154.2, 288.0. IR (KBr): 2906.0, 2851.2, 1777.9, 1756.4, 1342.3, 1300.6, 1222.9, 1025.1, 668.0 cm^{-1}. UV-vis (C_5H_{12}): λ_{max} = 492 nm. HRMS (CI): $[M+H]^+$ calcd. for $C_{23}H_{31}N_2O_2$: 367.2386; Found: 367.2381. Anal. calcd. for $C_{23}H_{30}N_2O_2$: C, 75.37; H, 8.25; N, 7.64; Found: C, 75.50; H, 8.47; N, 7.83.

Synthesis of 2c. An 8 mL vial was charged with **1c** (0.150 g, 0.417 mmol), benzene (2 mL), potassium metal (0.035 g, 0.090 mmol, 2.1 equiv) and a stir bar. The reaction vessel was sealed and then heated at 60 °C for 2 h. After cooling to ambient temperature, the reaction mixture was concentrated under reduced pressure. The resulting red-purple residue was extracted with pentane, filtered through a 0.2 μm PTFE filter and the residual solvent removed under reduced pressure to afford **2c** as a purple-red solid (0.072 g, 0.250 mmol, 60%). m.p. = 96-98 °C (decomp.) ^{1}H NMR (C_6D_6, 399.68 MHz): δ 1.39 (s, 9H), 1.46-1.54 (m, 6H), 1.93 (bs, 3H), 2.20-2.21 (overlapping s, 6H). ^{13}C NMR (C_6D_6, 100.60 MHz): δ 28.6, 29.9, 36.2, 41.3, 58.6, 59.5, 154.1, 154.3, 287.5. IR (KBr): 2910.2, 1855.4, 1770.8, 1756.0, 1729.7, 1357.3, 1303.7, 1007.6 cm^{-1}. UV-vis (C_5H_{12}): λ_{max} = 491 nm. HRMS (CI): $[M+H]^+$ calcd. for $C_{17}H_{25}N_2O_2$: 289.1916; Found: 289.1913. Anal. calcd. for $C_{17}H_{24}N_2O_2$: C, 70.80; H, 8.39; N, 9.71; Found: C, 70.73; H, 8.53; N, 9.43.

Synthesis of 3. A 50 mL Schlenk flask was charged with **2a** (0.075 g, 0.36 mmol), pentane (10 mL) and a stir bar. The flask was cooled to -78 °C and the atmosphere was removed from the flask under reduced pressure prior to warming back to ambient temperature. Ammonia gas was then added to the flask via a balloon which resulted in the formation of a pale yellow solution that was accompanied with a white precipitate. After stirring for 30 min at ambient temperature, the residual solvent was removed under reduced pressure and the crude solid was washed with a minimal quantity of pentane to afford **3** as a white solid (0.072 g, 0.317 mmol, 89%). m.p. = 162-165 °C (decomp.) ^{1}H NMR ($CDCl_3$, 400.09 MHz): δ 1.53 (s, 18H), 1.86 (bs, 2H), 5.64 (s, 1H). ^{13}C NMR ($CDCl_3$, 100.60 MHz): δ 27.8, 55.8, 76.1, 157.9. IR (KBr): 3438.5, 3405.5, 3312.0, 2979.2, 1717.1, 1413.5, 1366.6, 1218.7, 1128.7, 598.7 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{11}H_{22}N_3O_2$: 228.1712; Found: 228.1712. Anal. calcd. for $C_{11}H_{21}N_3O_2$: C, 58.12; H, 9.31; N, 18.49; Found: C, 57.93; H, 9.36; N, 18.31.

Synthesis of 4. An 8 mL vial was charged with **2a** (0.075 g, 0.36 mmol), benzene (1 mL), methyl vinyl ketone (0.025 g, 0.36 mmol, 1 equiv) and a stir bar. The resultant mixture was stirred at ambient temperature for 12 h after which the residual solvent was removed under reduced pressure. Subsequent washing of the residue with a minimal quantity of pentane followed by drying under reduced pressure afforded **4** as a white solid (0.083 g, 0.296 mmol, 83%). m.p. = 159-161°C (decomp.) ^{1}H NMR ($CDCl_3$, 400.09 MHz): δ 1.52 (s, 18H), 1.82 (s, 3H), 3.07 (t, J = 2 Hz, 2H), 4.88 (s, 1H). ^{13}C NMR ($CDCl_3$, 100.60 MHz): δ 14.2, 28.0, 41.5, 58.6, 97.3, 108.5, 154.5, 157.4. IR (KBr): 3115.1, 2999.6, 2964.7, 2917.3, 1739.9, 1691.8, 1407.2, 1394.8, 1368.4, 1195.0, 1158.8, 955.9, 909.2, 751.5, 584.9 cm^{-1}. HRMS (CI): $[M+H]^+$

calcd. for $C_{15}H_{25}N_2O_3$: 281.1865; Found: 281.1860. Anal. calcd. for $C_{15}H_{24}N_2O_3$: C, 64.26; H, 8.63; N, 9.99; Found: C, 64.64; H, 8.56; N, 10.01.

Synthesis of 5. An 8 mL vial was charged with **2a** (0.075 g, 0.36 mmol), benzene (1 mL), 1-phenyl-1-butyne (0.046 g, 0.36 mmol, 1 equiv) and a stir bar. The resultant mixture was stirred at ambient temperature for 6 h after which the residual solvent was removed under reduced pressure. Subsequent washing of the residue with pentane followed by drying under reduced pressure afforded **5** as a white solid (0.083 g, 0.243 mmol, 68%). m.p. = 161-163 °C (decomp.) ^{1}H NMR ($CDCl_3$, 400.09 MHz): δ 1.34 (s, 18H), 1.45 (t, J = 7.4 Hz, 3H), 2.70 (q, J = 7.4 Hz, 2H), 7.41-7.49 (m, 5H). ^{13}C NMR ($CDCl_3$, 100.60 MHz): δ 12.0, 19.64, 28.8, 57.4, 62.3, 122.1, 124.2, 126.4, 129.4, 129.6, 130.5, 159.82. IR (KBr): 3384.6, 3064.7, 3005.9, 2977.3, 2932.2, 1716.1, 1388.4, 1362.0, 1223.8, 1133.7, 766.8, 693.0, 559.6 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{21}H_{29}N_2O_2$: 341.2229; Found: 341.2235. Anal. calcd. for $C_{21}H_{28}N_2O_2$: C, 74.08; H, 8.29; N, 8.23; Found: C, 73.75; H, 8.26; N, 7.95.

Synthesis of 6. An 8 mL vial was charged with **2a** (0.075 g, 0.36 mmol), benzene (1 mL), methyl acrylate (0.031 g, 0.36 mmol, 1 equiv) and a stir bar. The resultant mixture was stirred at ambient temperature for 12 h after which the residual solvent was removed under reduced pressure. Subsequent washing of the resulting residue with a minimal quantity of pentane followed by drying under reduced pressure afforded **6** as a white solid (0.079 g, 0.267 mmol, 75%). m.p. = 129-131 °C (decomp.) ^{1}H NMR ($CDCl_3$, 400.09 MHz): δ 1.55 (s, 18H), 3.15 (s, 2H), 3.73 (s, 3H), 3.87 (s, 1H). ^{13}C NMR ($CDCl_3$, 100.60 MHz): δ 28.0, 40.4, 56.8, 58.9, 65.7, 106.3, 157.3, 160.9. IR (KBr): 3126.7, 2991.6, 2967.6, 2945.7, 1740.4, 1689.6, 1409.4, 1333.7, 1317.9, 1279.7, 1244.2, 1194.7, 1163.8, 1005.3, 954.5, 922.5, 781.3 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{15}H_{25}N_2O_4$: 297.1814; Found: 297.1817. Anal. calcd. for $C_{15}H_{24}N_2O_4$: C, 60.79; H, 8.16; N, 9.45; Found: C, 60.51; H, 8.02; N, 9.09.

Synthesis of 7. An 8 mL vial was charged with **2a** (0.075 g, 0.36 mmol), benzene (1 mL), toluene (0.164 g, 1.78 mmol, 5 equiv) and a stir bar. The resultant mixture was stirred at 80 °C for 40 h after which the reaction mixture was cooled and the residual solvent was removed under reduced pressure. Subsequent washing of the residue with a minimal quantity of pentane followed by drying under reduced pressure afforded **7** as a white solid (0.084 g, 0.278 mmol, 78%). m.p. = 149-151 °C. ^{1}H NMR ($CDCl_3$, 400.09 MHz): δ 1.46 (s, 18H), 3.28 (d, J = 3.1 Hz, 2H), 5.32 (t, J = 3.1 Hz, 1H), 7.09 (m, 2H), 7.21-7.27 (m overlapping solvent, 3H). ^{13}C NMR ($CDCl_3$, 100.60 MHz): δ 27.7, 42.0, 56.5, 67.7, 127.7, 128.9, 129.7, 133.0, 159.5. IR (KBr): 2981.6, 2965.9, 1716.3, 1396.2, 1371.2, 1361.6, 1207.6, 700.7, 632.6 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{18}H_{27}N_2O_2$: 303.2073; Found: 303.2076. Anal. calcd. for $C_{18}H_{26}N_2O_2$: C, 71.49; H, 8.67; N, 9.26; Found: C, 71.48; H, 8.69; N, 9.15.

Synthesis of 8. An 8 mL vial was charged with **2a** (0.075 g, 0.36 mmol), benzene (1 mL), 4-methyl anisole (0.218 g, 1.78 mmol, 5 equiv) and a stir bar. The resultant mixture was stirred at 80 °C for 24 h after which the reaction mixture was cooled and the residual solvent was removed under reduced pressure. Subsequent washing of the residue with a minimal quantity of pentane followed by drying under reduced pressure afforded **8** as a white solid (0.094 g, 0.283 mmol, 79%). m.p. = 143-145 °C. ^{1}H NMR ($CDCl_3$, 400.09 MHz): δ 1.46 (s, 18H), 3.21 (d, J = 2.7 Hz, 2H), 3.72 (s, 3H), 5.28 (t, J = 3.1 Hz, 1H), 6.78 (d, J = 8.6 Hz, 2H), 6.99 (d, J = 8.6 Hz, 2H). ^{13}C

NMR ($CDCl_3$, 100.60 MHz): δ 27.7, 40.9, 55.1, 56.5, 67.7, 114.2, 124.5, 130.9, 158.9, 159.6. IR (KBr): 2981.5, 2912.6, 1717.0, 1513.8, 1407.6, 1366.0, 1244.4, 1217.6, 1032.2, 802.6, 564.7 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{19}H_{29}N_2O_3$: 333.2178; Found: 333.2183. Anal. calcd. for $C_{19}H_{28}N_2O_3$: C, 68.65; H, 8.49; N, 8.43; Found: C, 68.33; H, 8.55; N, 8.39.

Synthesis of 9. An 8 mL vial was charged with **2a** (0.075 g, 0.36 mmol), benzene (1 mL), 4-chlorotoluene (0.226 g, 1.78 mmol, 5 equiv) and a stir bar. The resultant mixture was stirred at 80 °C for 48 h after which the reaction mixture was cooled and the residual solvent was removed under reduced pressure. Subsequent washing of the residue with a minimal quantity of pentane followed by drying under reduced pressure afforded **9** as a white solid (0.091 g, 0.270 mmol, 76%). m.p. = 183-185 °C (decomp.) ^{1}H NMR ($CDCl_3$, 400.09 MHz): δ 1.47 (s, 12H), 3.25 (d, J = 3.1 Hz, 2H), 5.31 (t, J = 3.1 Hz, 1H), 7.02 (d, J = 8.6 Hz, 2H), 7.24 (d overlapping solvent, J = 8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100.60 MHz): δ 27.7, 41.1, 56.7, 67.3, 129.0, 131.1, 131.3, 133.7, 159.5. IR (KBr): 2968.8, 2934.6, 1713.9, 1493.3, 1403.3, 1215.8, 1090.3, 809.4, 766.5, 603.7 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{18}H_{26}N_2O_2{}^{35}Cl$: 337.1683; Found: 337.1687. Anal. calcd. for $C_{18}H_{25}ClN_2O_2$: C, 64.18; H, 7.48; N, 8.32; Found: C, 64.08; H, 7.43; N, 8.39.

Synthesis of 10. An 8 mL vial was charged with **2a** (0.075 g, 0.36 mmol), benzene (0.3 mL), tetrahydrofuran (0.257 g, 3.6 mmol, 10 equiv) and a stir bar. The resultant mixture was stirred at 80 °C for 60 h after which the reaction mixture was cooled and the residual solvent was removed under reduced pressure. Subsequent washing of the residue with a minimal quantity of pentane followed by drying under reduced pressure afforded **10** as a white solid (0.079 g, 0.280 mmol, 78%). m.p. = 110-112 °C (decomp.) ^{1}H NMR ($CDCl_3$, 400.09 MHz): δ 1.29-1.38 (m, 1H), 1.45 (s, 9H), 1.46 (s, 9H), 1.57-1.66 (m, 1H), 1.76-1.90 (m, 2H), 3.72 (q, J = 7.8 Hz, 1H), 3.99 (m, 1H), 4.20 (m, 1H), 5.25 (d, J = 2.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.60 MHz): δ 22.9, 23.9, 27.4, 27.7, 56.0, 57.2, 68.0, 68.6, 82.0, 159.0, 160.6. IR (KBr): 2980.1, 2877.9, 1725.5, 1705.9, 1402.0, 1204.3, 1076.2 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{15}H_{27}N_2O_3$: 283.2022; Found:283.2029. Anal. calcd. for $C_{15}H_{26}N_2O_3$: C, 63.80; H, 9.28; N, 9.92; Found: C, 63.86; H, 9.60; N, 10.31.

X-Ray Crystallography. Colorless, single crystals of **1a** were obtained by the slow diffusion of pentane into a concentrated benzene solution; this compound crystallized in the monoclinic $P2_1/c$ space group. Colorless, single crystals of **1b** were obtained by the slow diffusion of pentane into a concentrated chloroform solution; this compound crystallized in the monoclinic $P2_1/c$ space group. Red-orange single crystals of **2a** were grown by cooling a concentrated pentane solution to -20 °C; this compound crystallized in the monoclinic $P2_1/n$ space group. Colorless, single crystals of **3** were obtained by the slow diffusion of pentane into a concentrated chloroform solution; this compound crystallized with two molecules of **3** in the asymmetric cell in the orthorhombic $P2_12_12_1$ space group. Colorless single crystals of **4** were obtained by the slow diffusion of pentane into a concentrated benzene solution; this compound crystallized in the monoclinic $P2_1$ space group. Colorless, single crystals of **5** were obtained by the slow diffusion of pentane into a saturated benzene solution; this compound crystallized with two molecules of **5** in the asymmetric cell in the monoclinic $P2_1/c$ space group. Colorless, single crystals of **7** were obtained by the slow diffusion of pentane into a benzene solution; two molecules of **7** co-crystallized with a solvent benzene molecule in the monoclinic $P2_1/c$ space group. Crystallographic measurements were carried out on a Rigaku Mini CCD, Enraf-Nonius Kappa

CCD, or Rigaku AFC-12 with Saturn 724+ CCD area detector diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 120 K or 150 K using an Oxford Cryostream low temperature device. A sample of suitable size and quality was selected and mounted onto a nylon loop. Data reductions were performed using DENZO-SMN.[S5] The structures were solved by direct methods which successfully located most of the non-hydrogen atoms. Subsequent refinements on F_2 using the SHELXTL/PC package (version 5.1)[S6] allowed the location of the remaining non-hydrogen atoms. Key details of the crystal and structure refinement data are summarized in Table S1-S2. 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 **1a**, **1b**, **2a**, **3**, **4**, **5**, and **7** were assigned as 983770, 983771, 983772, 983773, 983774, 983775, and 983776, respectively.

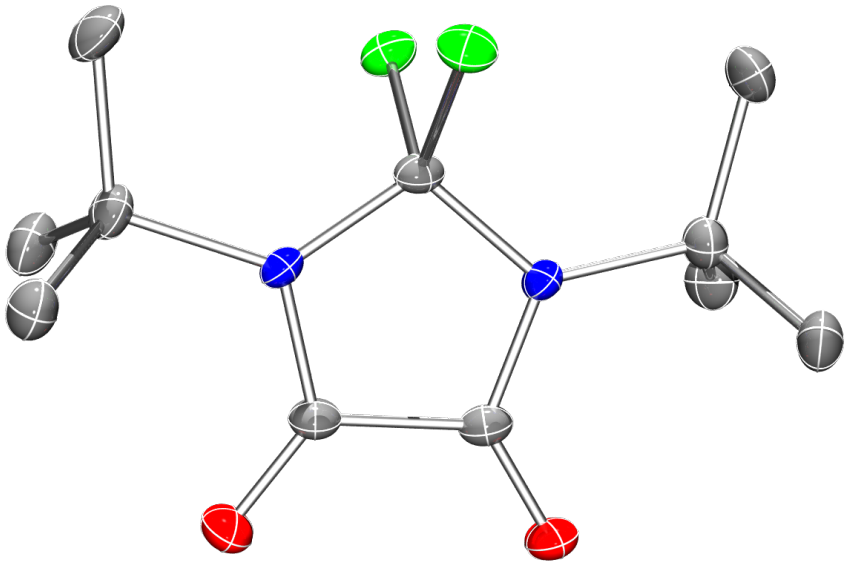


Figure S1. ORTEP diagram of **1a** with thermal ellipsoids drawn at 50% probability and H-atoms omitted for clarity.

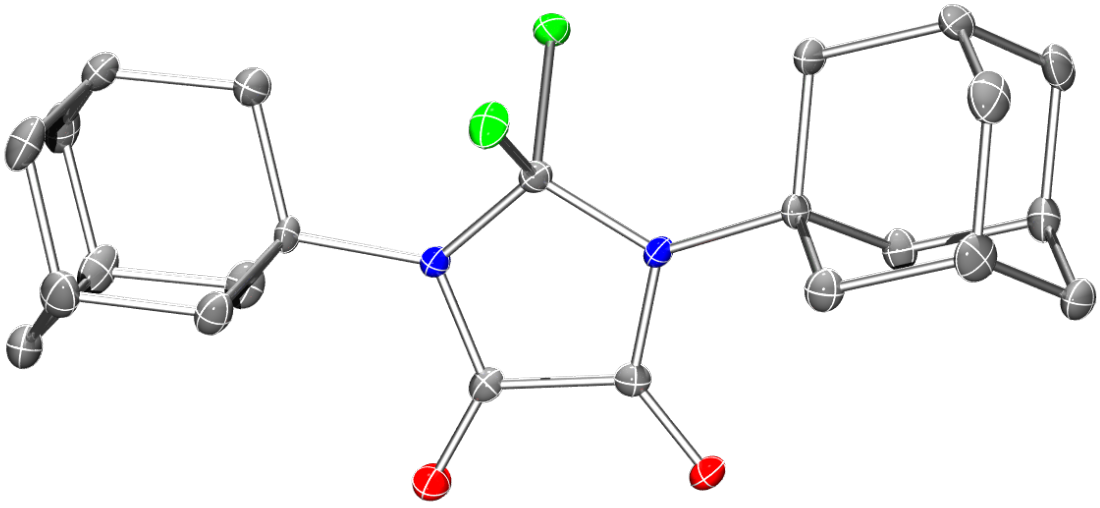


Figure S2. ORTEP diagram of **1b** with thermal ellipsoids drawn at 50% probability and H-atoms omitted for clarity.

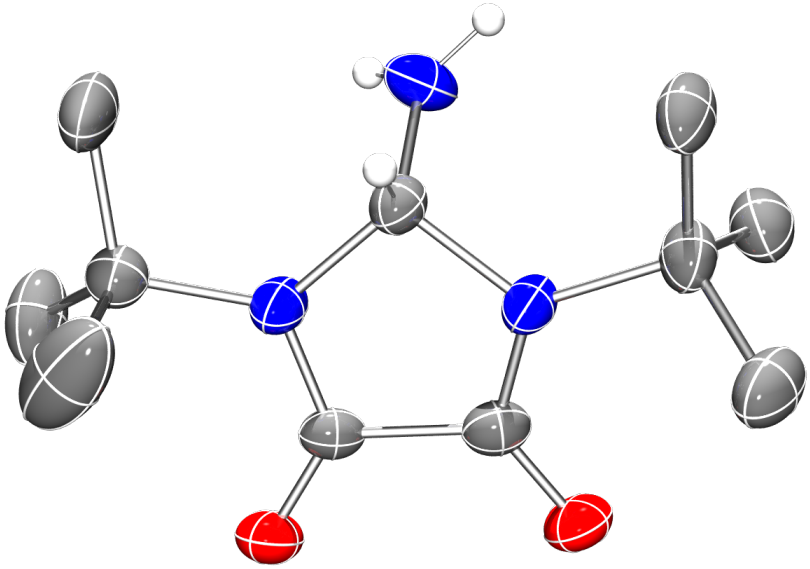


Figure S3. ORTEP diagram of **3** with thermal ellipsoids drawn at 50% probability and H-atoms, except at the nitrogens and carbenoid carbon, and a second molecule of **3** omitted for clarity.

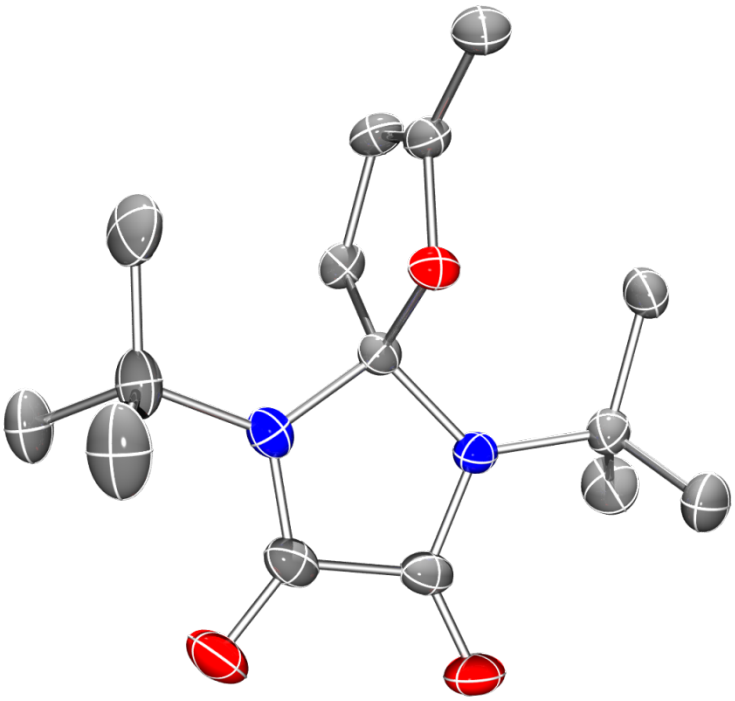


Figure S4. ORTEP diagram of **4** with thermal ellipsoids drawn at 50% probability and H-atoms omitted for clarity.

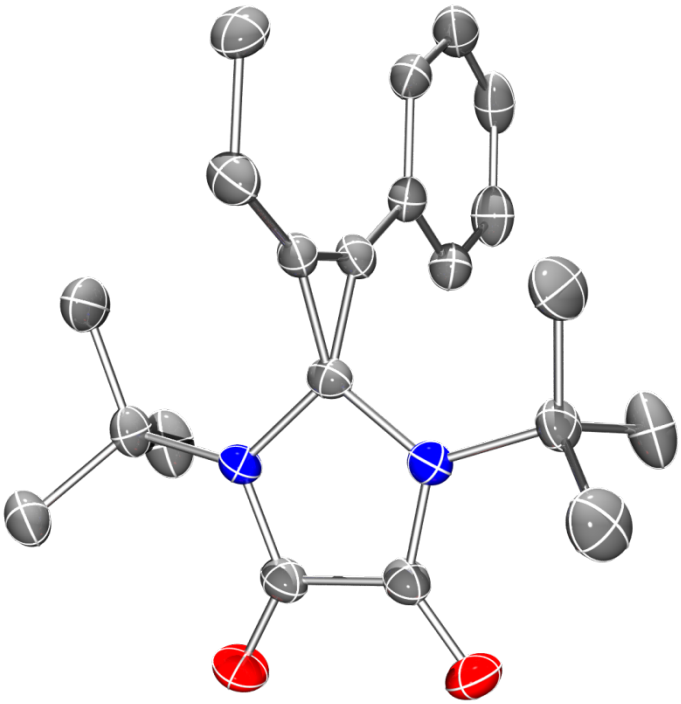


Figure S5. ORTEP diagram of **5** with thermal ellipsoids drawn at 50% probability and H-atoms and a second molecule of **5** omitted for clarity.

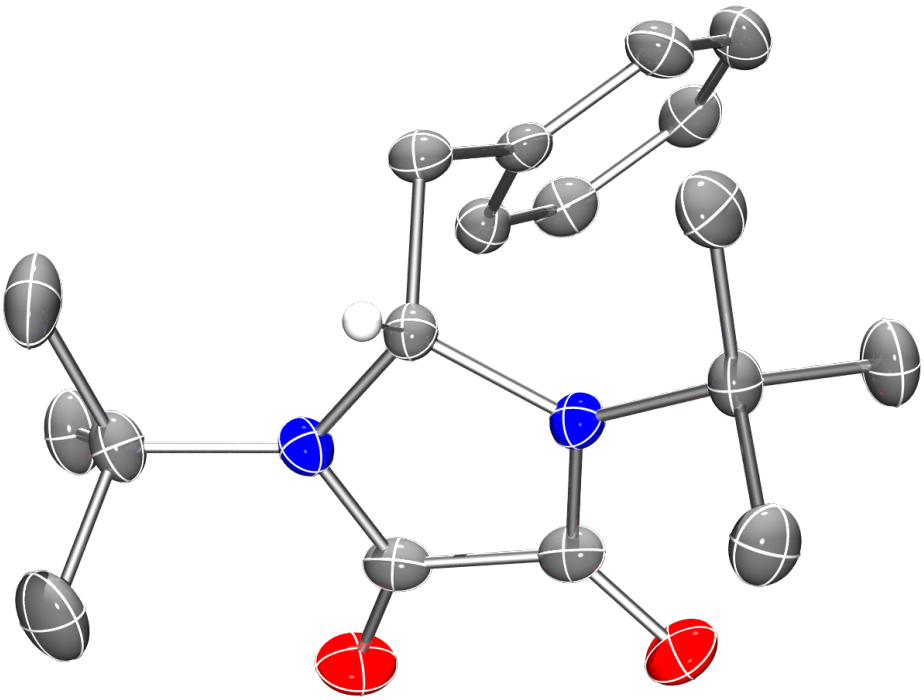


Figure S6. ORTEP diagram of **7** with thermal ellipsoids drawn at 50% probability and H-atoms, except at the carbenoid carbon, a second molecule of **7**, and a solvent benzene molecule omitted for clarity.

Table S1. Summary of crystal data, data collection, and structure refinement details for **1a**, **1b**, **2a**, and **3**.

	1a	**1b**	**2a**	**3**
Formula	$C_{11}H_{18}Cl_2N_2O_2$	$C_{23}H_{30}Cl_2N_2O_2$	$C_{11}H_{18}N_2O_2$	$C_{11}H_{21}N_3O_2$
M_r	281.17	437.39	210.27	227.31
crystal size (mm^3)	0.14 × 0.09 × 0.08	0.29× 0.26 × 0.22	0.18 × 0.13 × 0.07	0.12 × 0.07 × 0.04
crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_12_12_1$
a (Å)	8.3148(19)	14.331(4)	13.3310(12)	9.102(3)
b (Å)	14.215(3)	11.335(4)	5.9383(5)	12.188(4)
c (Å)	11.639(3)	12.768(4)	15.6507(14)	23.505(8)
α (°)	90	90	90	90
β (°)	99.688(5)	103.063(6)	105.521(3)	90
γ (°)	90	90	90	90
V ($Å^3$)	1356.1(5)	2020.3(11)	1193.78(18)	2607.5(16)
Z	4	4	4	8
ρ_{calc} (g cm^{-3})	1.377	1.438	1.170	1.158
μ (mm^{-1})	0.471	0.345	0.081	0.081
F(000)	592	928	456	992
T (K)	120(2)	120(2)	120(2)	150(2)
scan mode	ω	ω	ω	ω
hkl range	-9 → 9 -16 → 16 -13 → 13	-16 → 17 -13 → 13 -15 → 15	-15 → 15 -7 → 6 -18 → 18	-10 → 10 -14 → 14 -27 → 27
measd reflns	19296	13343	11792	34428
unique reflns [R_{int}]	2373[0.0989]	3550 [0.0356]	2089 [0.0416]	4584[0.0919]
refinement reflns	2373	3550	2089	4584
refined parameters	160	262	142	301
GOF on F^2	1.006	1.006	1.006	1.006
R1[a] (all data)	0.0449 (0.0598)	0.0366 (0.0937)	0.0452 (0.0546)	0.0851 (0.0897)
wR2 (all data)	0.0982 (0.1055)	0.0393 (0.0958)	0.1137 (0.1211)	0.1985 (0.2025)
ρ_{fin} (max/min) (e $Å^{-3}$)	0.307 -0.261	0.506 -0.299	0.305 -0.187	0.337 -0.336

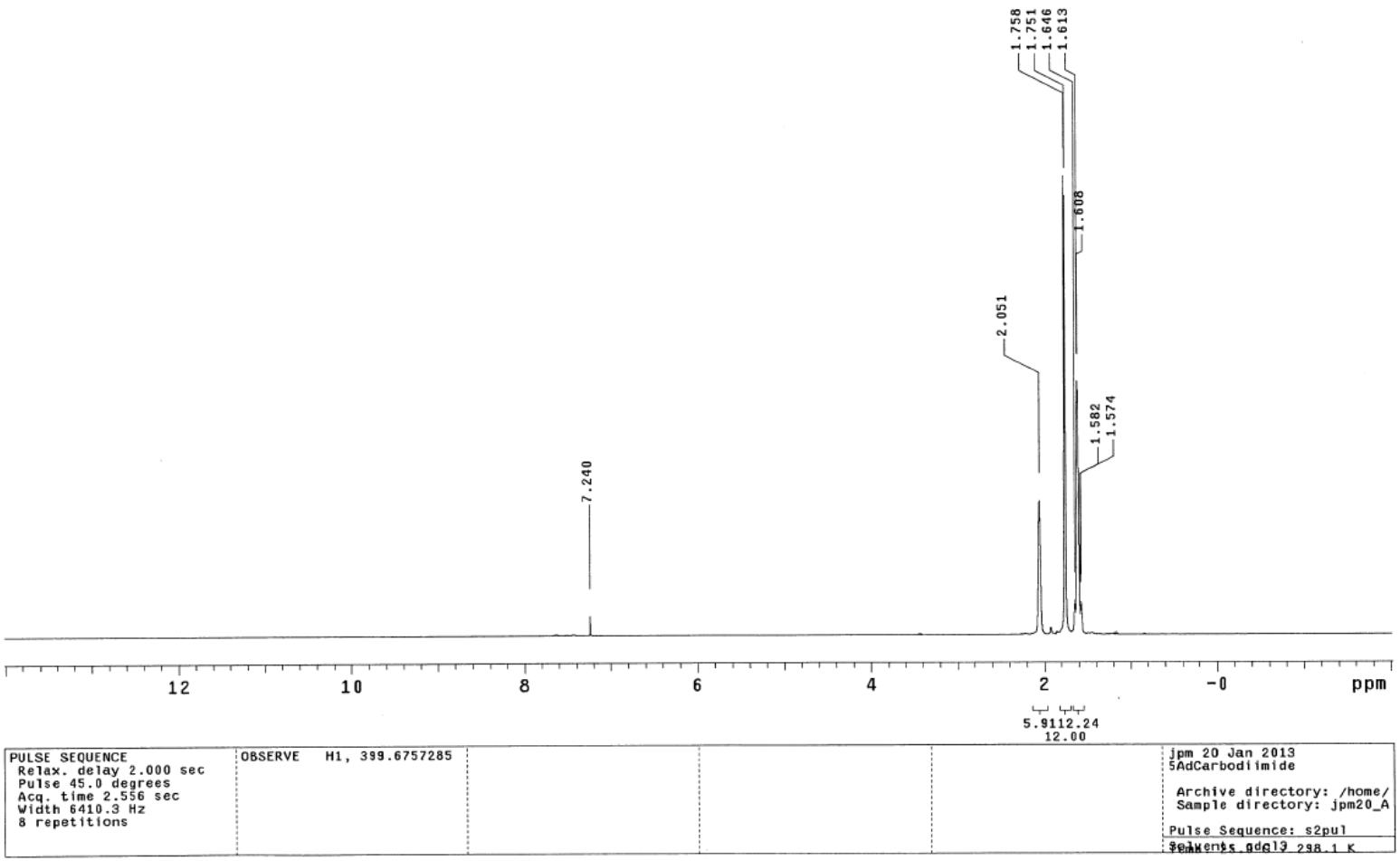
[a] $R1 = \sum||Fo| - |Fc||/\sum|Fo|$. [b] $wR2 = \{[\sum w(Fo^2 - Fc^2)^2]/[\sum w(Fo^2)^2]\}^{1/2}$.

Table S2. Summary of crystal data, data collection, and structure refinement details for **4**, **5**, and **7**.

	4	**5**	**7**·C_6H_6
Formula	$C_{15}H_{24}N_2O_3$	$C_{21}H_{28}N_2O_2$	$C_{42}H_{58}N_4O_4$
M_r	280.36	340.45	682.92
crystal size (mm^3)	0.26 × 0.24 × 0.07	0.14 × 0.09 × 0.05	0.31 × 0.26 × 0.23
crystal system	Monoclinic	Monoclinic	Monoclinic
space group	$P2_1$	$P2_1/c$	$P2_1/c$
a (Å)	6.1949(2)	9.1753(6)	17.9469(10)
b (Å)	13.0960(3)	22.7039(14)	17.5630(8)
c (Å)	9.5555(3)	18.5417(13)	12.2414(7)
α (°)	90	90	90
β (°)	93.800(2)	97.125(5)	90.152(2)
γ (°)	90	90	90
V ($Å^3$)	773.52(4)	3832.7(4)	3858.5(4)
Z	2	8	4
ρ_{calc} (g cm^{-3})	1.204	1.180	1.176
μ (mm^{-1})	0.084	0.076	0.075
F(000)	304	1472	1480
T (K)	150(2)	120(2)	120(2)
scan mode	ω	ω	ω
hkl range	-7 → 7 -15 → 15 -11 → 11	-10 → 10 -27 → 27 -22 → 22	-21 → 19 -14 → 20 -13 → 14
measd reflns	20735	144570	18906
unique reflns [R_{int}]	2727 [0.0346]	6729 [0.2417]	6694[0.0313]
refinement reflns	2727	6729	6694
refined parameters	188	465	463
GOF on F^2	1.006	1.006	1.006
R1[a] (all data)	0.0285 (0.0303)	0.0594 (0.1175)	0.0422 (0.0986)
wR2 (all data)	0.0781 (0.0798)	0.1462 (0.1648)	0.0590 (0.1113)
ρ_{fin} (max/min) (e $Å^{-3}$)	0.197 -0.217	0.224 -0.335	0.263 -0.256

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

Ad—N=C=N—Ad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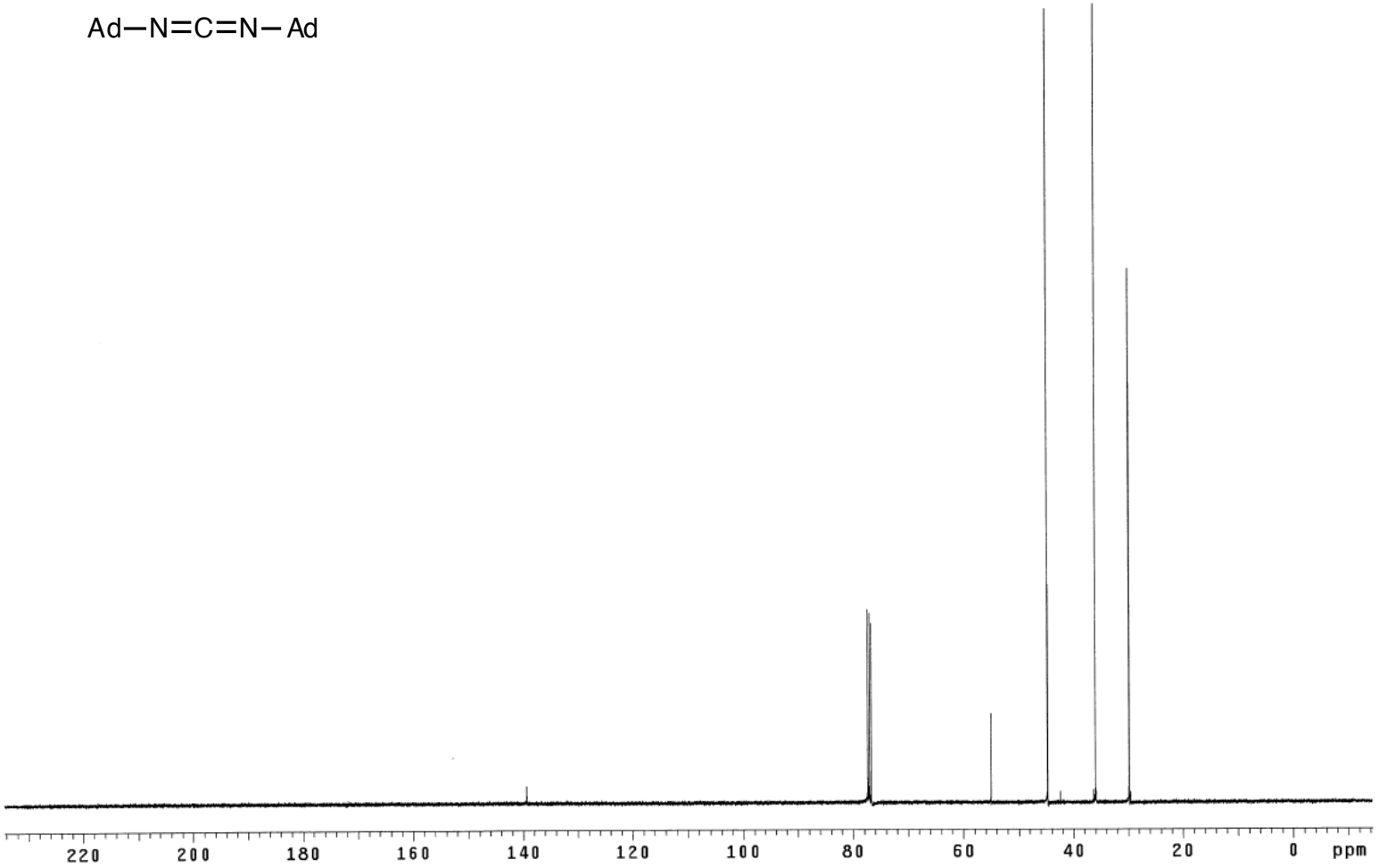
1.751
1.646
1.613
1.608
2.051
1.582
1.574
7.240
12
10
8
6
4
2
-0
ppm
5.91
12.24
12.00
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 399.6757285
jpm 20 Jan 2013
5AdCarbodiimide
Archive directory: /home/
Sample directory: jpm20_A
Pulse Sequence: s2pul
Solvent: cdcl3 298.1 K

Ad—N=C=N—Ad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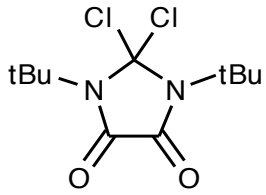
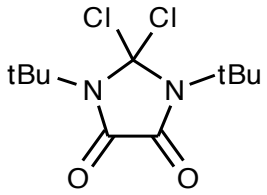
200
180
160
140
120
100
80
60
40
20
0
ppm
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 30.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
500 repetitions
OBSERVE C13, 100.4985430
jpm 20 Jan 2014
AdCarbodiimide
Archive directory: /home/
Sample directory: jpm20_A
Pulse Sequence: s2pul
Solvents: cdcl3 298.1 K


Cl
Cl
tBu
N
N
tBu
O
O

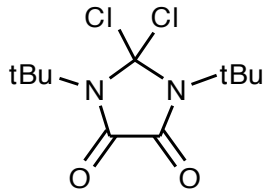
1a

1.746
12
11
10
9
8
7
6
5
4
3
2
1
-0
ppm
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 16.4 degrees
Acq. time 2.856 sec
Width 5602.2 Hz
11 repetitions
OBSERVE H1, 400.2669856
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 1 minute
jpm 19 Nov 2013
5tBuDACC12
Pulse Sequence: s2pul
Solvent: CDC13
Ambient temperature
Mercury-400 "nmr6"



1a

PULSE SEQUENCE Relax. delay 2.000 sec Pulse 45.0 degrees Acq. time 2.556 sec Width 6410.3 Hz 8 repetitions	OBSERVE H1, 400.0864171	DATA PROCESSING FT size 32768 Total time 1 minute		jpm 25 Jan 2014 5tBuDACCl2 C6D6 Solvent: c6d6 Ambient temperature Operator: moerdj File: PROTON_01


Cl
Cl
tBu
N
N
tBu
O
O

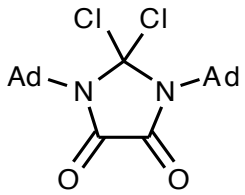
1a

Agilent Technologies
220
200
180
160
140
120
100
80
60
40
20
0
ppm
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 30.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
32 repetitions
OBSERVE C13, 100.6017503
DECOUPLE H1, 400.0881319
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 1 minutes
jpm 14 Dec 2013
5tBuDACCl2
Solvent: cdcl3
Ambient temperature
Operator: moerdj
VNMRS-400 "nhb400"


Cl
Cl
Ad
N
N
Ad
O
O

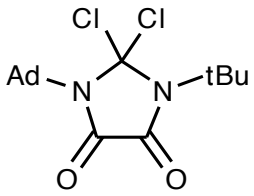
1b

2.634
2.629
2.169
1.799
1.770
1.693
1.663
7.240
12
10
8
6
4
2
-0
ppm
6.00
3.00
3.06
3.02
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
4 repetitions
OBSERVE H1, 399.6757285
jpm17_5AdDACC12
Archive directory: /home/
Sample directory: jpm17_5
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K


Cl
Cl
Ad
N
N
Ad
O
O

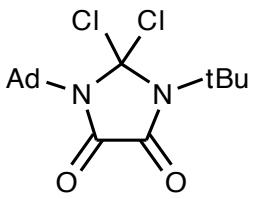
1b

220
200
180
160
140
120
100
80
60
40
20
0
ppm
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 30.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
500 repetitions
OBSERVE C13, 100.4985408
jpm17_5AdDACC12
Archive directory: /home/
Sample directory: jpm17_5
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K


Cl
Cl
Ad
N
N
tBu
O
O

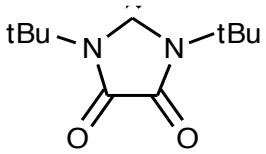
1c

7.240
2.644
2.637
2.178
1.770
1.765
1.702
12
10
8
6
4
2
-0
ppm
6.06
3.00
11.96
3.12
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
4 repetitions
OBSERVE H1, 399.6757285
jpm17_5AdtBuDACCl2
Archive directory: /home/
Sample directory: jpm17_5
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K


Cl
Cl
Ad
N
N
tBu
O
O

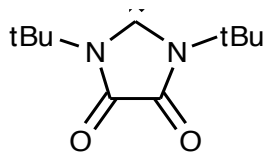
1c

220
200
180
160
140
120
100
80
60
40
20
0
ppm
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 30.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
500 repetitions
OBSERVE C13, 100.4985430
jpm 17 Jan 2014
5AdtBuDAC
Archive directory: /home/
Sample directory: jpm17_5
Pulse Sequence: s2pul
Solvent: cdcl3 298.1 K


tBu
N
N
tBu
O
O

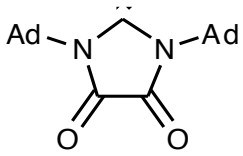
2a

Agilent Technologies
1.368
12
10
8
6
4
2
0
ppm
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 400.0861542
DATA PROCESSING
FT size 32768
Total time 1 minute
18.00
jpm 26 Nov 2013
5tBuDAC
Solvent: c6d6
Ambient temperature
Operator: moerdj
File: PROTON_01
VNMRS-400 "nhb400"


tBu
N
N
tBu
O
O

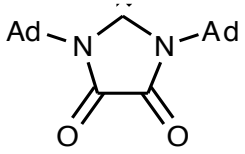
2a

Agilent Technologies
280
260
240
220
200
180
160
140
120
100
80
60
40
20
ppm
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 30.0 degrees
Acq. time 1.049 sec
Width 31250.0 Hz
480 repetitions
OBSERVE C13, 100.6017120
DECOUPLE H1, 400.0881679
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 24 minutes
jpm 14 Nov 2013
5tBuDAC
Solvent: c6d6
Ambient temperature
Operator: moerdj
File: CARBON_01
VNMRS-400 "nhb400"


Ad
N
N
Ad
O
O

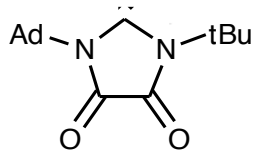
2b

Agilent Technologies
2.242
2.235
1.947
1.561
1.530
1.503
1.471
7.150
6.03
6.21
3.00
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 400.0861546
DATA PROCESSING
FT size 32768
Total time 1 minute
jpm 17 Jan 2014
5AdDAC
Solvent: c6d6
Ambient temperature
Operator: moerdj
File: PROTON_01
VNMRS-400 "nhb400"



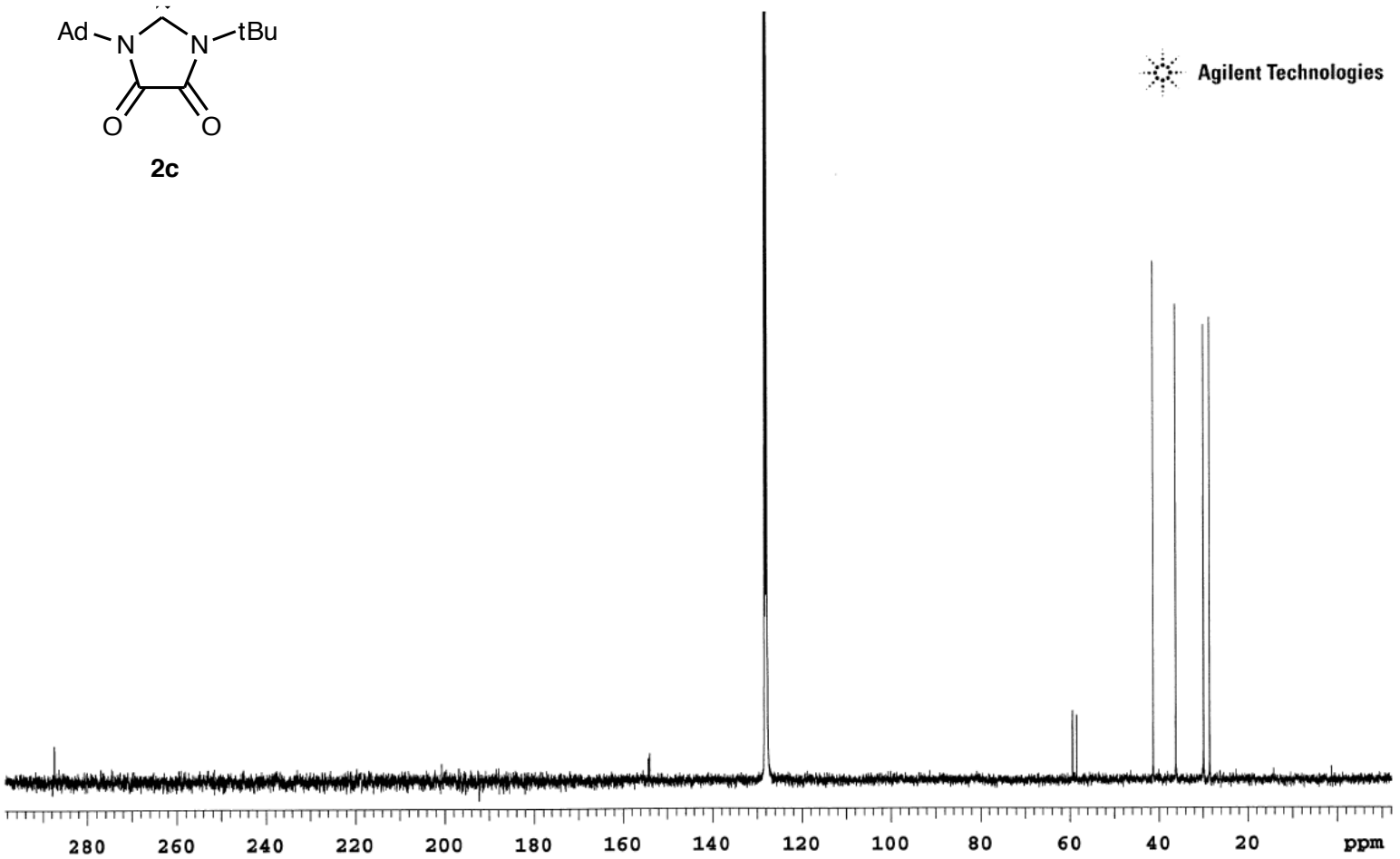
2b

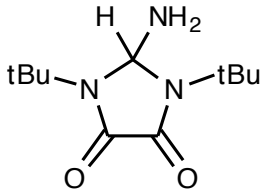
PULSE SEQUENCE Relax. delay 2.000 sec Pulse 30.0 degrees Acq. time 1.049 sec Width 31250.0 Hz 10000 repetitions	OBSERVE C13, 100.6017120 DECOUPLE H1, 400.0881679 Power 35 dB continuously on WALTZ-16 modulated	DATA PROCESSING Line broadening 0.5 Hz FT size 65536 Total time 8.5 hours			jpm20_5AdDAC Solvent: c6d6 Ambient temperature Operator: moerdj File: CARBON_02 VNMRS-400 "nhbjr"


Ad
N
N
tBu
O
O

2c

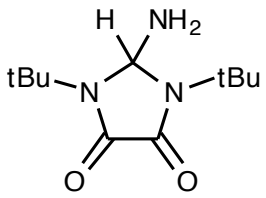
7.150
2.210
2.204
1.925
1.507
1.501
1.486
1.394
12
10
8
6
4
2
-0
ppm
5.95
3.00
6.66
9.00
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 399.6757434
jpm 21 Jan 2014
5AdtBuDAC
Archive directory: /home/
Sample directory: jpm21_5
Pulse Sequence: s2pul
Solvent: c6d6 / 298.1 K


Ad
N
N
tBu
O
O
2c
Agilent Technologies
280
260
240
220
200
180
160
140
120
100
80
60
40
20
ppm
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 30.0 degrees
Acq. time 1.049 sec
Width 31250.0 Hz
528 repetitions
OBSERVE C13, 100.6017130
DECOUPLE H1, 400.0881679
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 26 minutes
jpm 21 Jan 2014
5AdtBuDAC
Solvent: c6d6
Ambient temperature
Operator: moerdj
VNMRS-400 "nhb400"


H
NH2
tBu
N
N
tBu
O
O

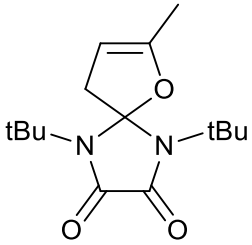
3

Agilent Technologies
7.239
5.640
1.855
1.526
1.503
12
10
8
6
4
2
0
ppm
1.00
19.32
2.00
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
16 repetitions
OBSERVE H1, 400.0861401
DATA PROCESSING
FT size 32768
Total time 1 minute
jpm 07 Jan 2014
5DAC + NH3
pentane 1 atm
Solvent: cdcl3
Ambient temperature
Operator: moerdj
File: PROTON_01


H
NH2
tBu
N
N
tBu
O
O

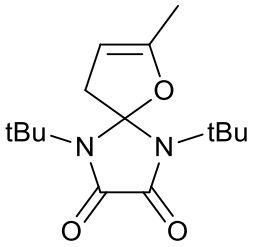
3

Agilent Technologies
220
200
180
160
140
120
100
80
60
40
20
0
ppm
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 30.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
688 repetitions
OBSERVE C13, 100.6017396
DECOUPLE H1, 400.0881319
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 37 minutes
jpm 07 Jan 2014
5DACNH3
Solvent: cdcl3
Ambient temperature
Operator: moerdj
File: CARBON_01
VNMRS-400 "nhb400"


tBu
N
O
N
tBu
O
O

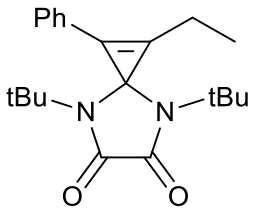
4

7.240
4.877
3.077
3.072
3.067
1.823
1.517
12
10
8
6
4
2
0
ppm
0.94
2.00
3.01
18.41
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 400.0861397
DATA PROCESSING
FT size 32768
Total time 1 minute
jpm 17 Dec 2013
5DAC Methyl vinyl ether
Solvent: cdcl3
Ambient temperature
Operator: moerdj
File: PROTON_01
VNMRS-400 "nhbjr"


tBu
N
O
N
tBu
O
O

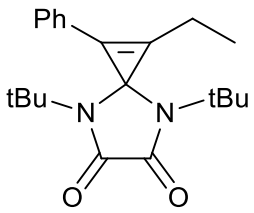
4

Agilent Technologies
220
200
180
160
140
120
100
80
60
40
20
0
ppm
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 30.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
48 repetitions
OBSERVE C13, 100.6017435
DECOUPLE H1, 400.0881319
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 2 minutes
jpm 17 Dec 2013
5DAC Methyl vinyl ketone
Solvent: cdcl3
Ambient temperature
Operator: moerdj
VNMRS-400 "nhb400"


Ph
tBu
N
N
tBu
O
O

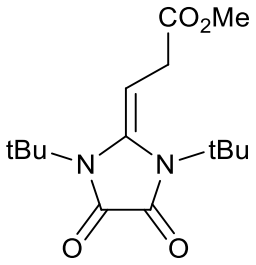
5

Agilent Technologies
1.446
1.427
1.342
7.451
7.445
7.439
2.711
2.693
1.528
1.465
12
10
8
6
4
2
0
ppm
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 400.0861393
DATA PROCESSING
FT size 32768
Total time 1 minute
4.96
2.00
3.06
17.94
jpm 13 Dec 2013
5DAC 1-Phenyl-1-butyne
Solvent: cdcl3
Ambient temperature
Operator: bielaw
File: PROTON_01
VNMRS-400 "nhb400"


Ph
tBu
N
N
tBu
O
O

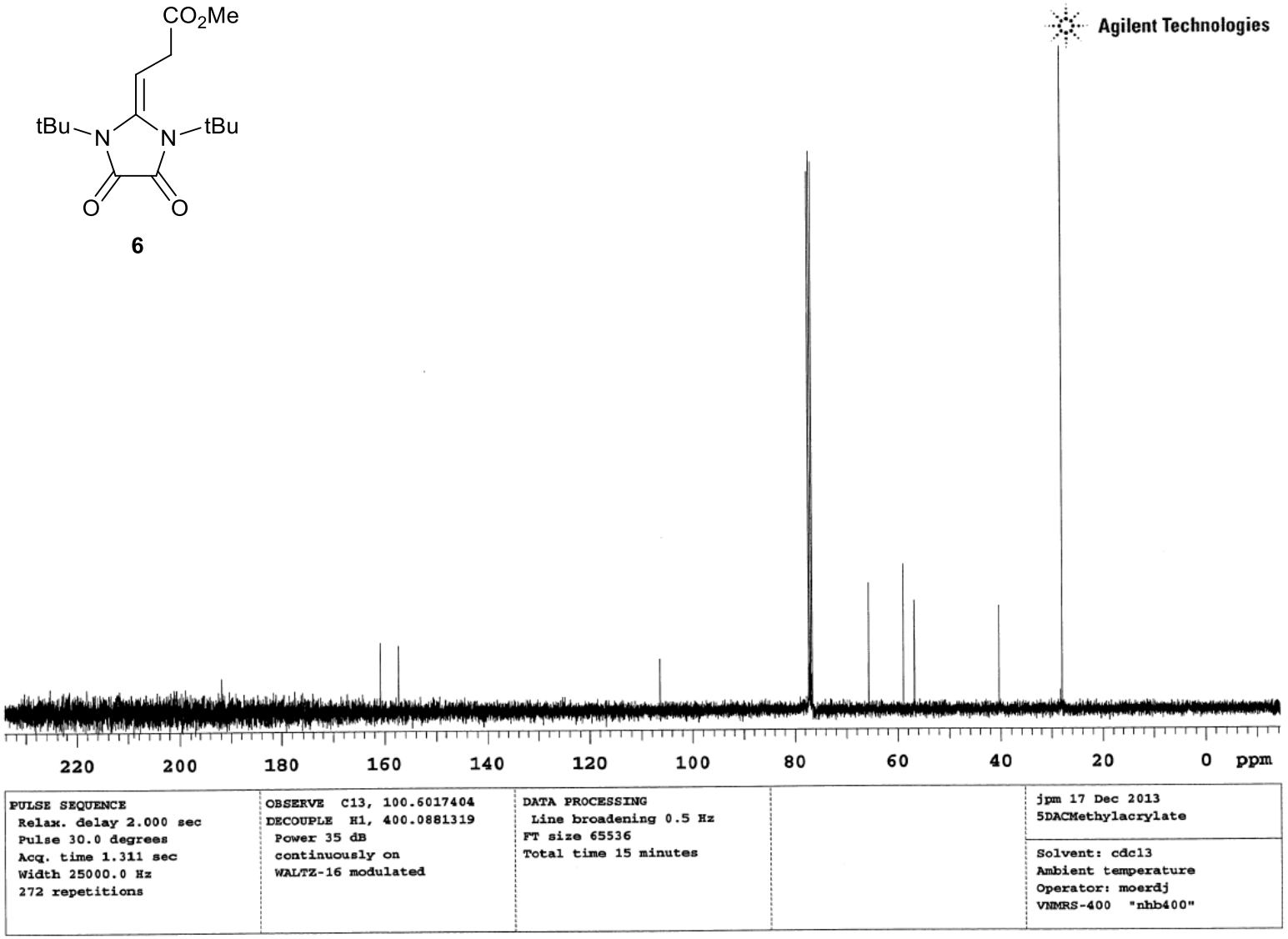
5

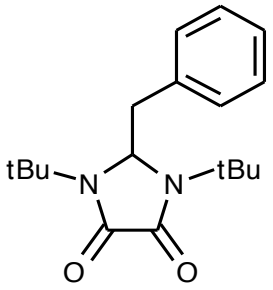
Agilent Technologies
220
200
180
160
140
120
100
80
60
40
20
0
ppm
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 30.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
224 repetitions
OBSERVE C13, 100.6017419
DECOUPLE H1, 400.0881319
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 12 minutes
jpm 13 Dec 2013
5DAC 1-Phenyl-1-butyne
Solvent: cdcl3
Ambient temperature
Operator: bielaw
VNMRS-400 "nhb400"


CO2Me
tBu
N
N
tBu
O
O

6

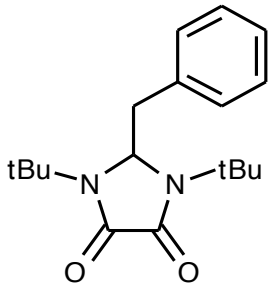
7.240
3.865
3.731
3.154
1.553
14
12
10
8
6
4
2
0
ppm
0.97
3.00
2.00
17.95
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 400.0859679
DATA PROCESSING
FT size 32768
Total time 1 minute
jpm 17 Dec 2013
5DAC Methyl acrylate
Solvent: cdcl3
Ambient temperature
Operator: moerdj
File: PROTON_01
VNMRS-400 "nhbjr"


CO2Me
tBu
N
N
tBu
O
O
6
Agilent Technologies
220
200
180
160
140
120
100
80
60
40
20
0
ppm
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 30.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
272 repetitions
OBSERVE C13, 100.6017404
DECOUPLE H1, 400.0881319
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 15 minutes
jpm 17 Dec 2013
5DACMethylacrylate
Solvent: cdcl3
Ambient temperature
Operator: moerdj
VNMRS-400 "nhb400"


tBu
N
N
tBu
O
O

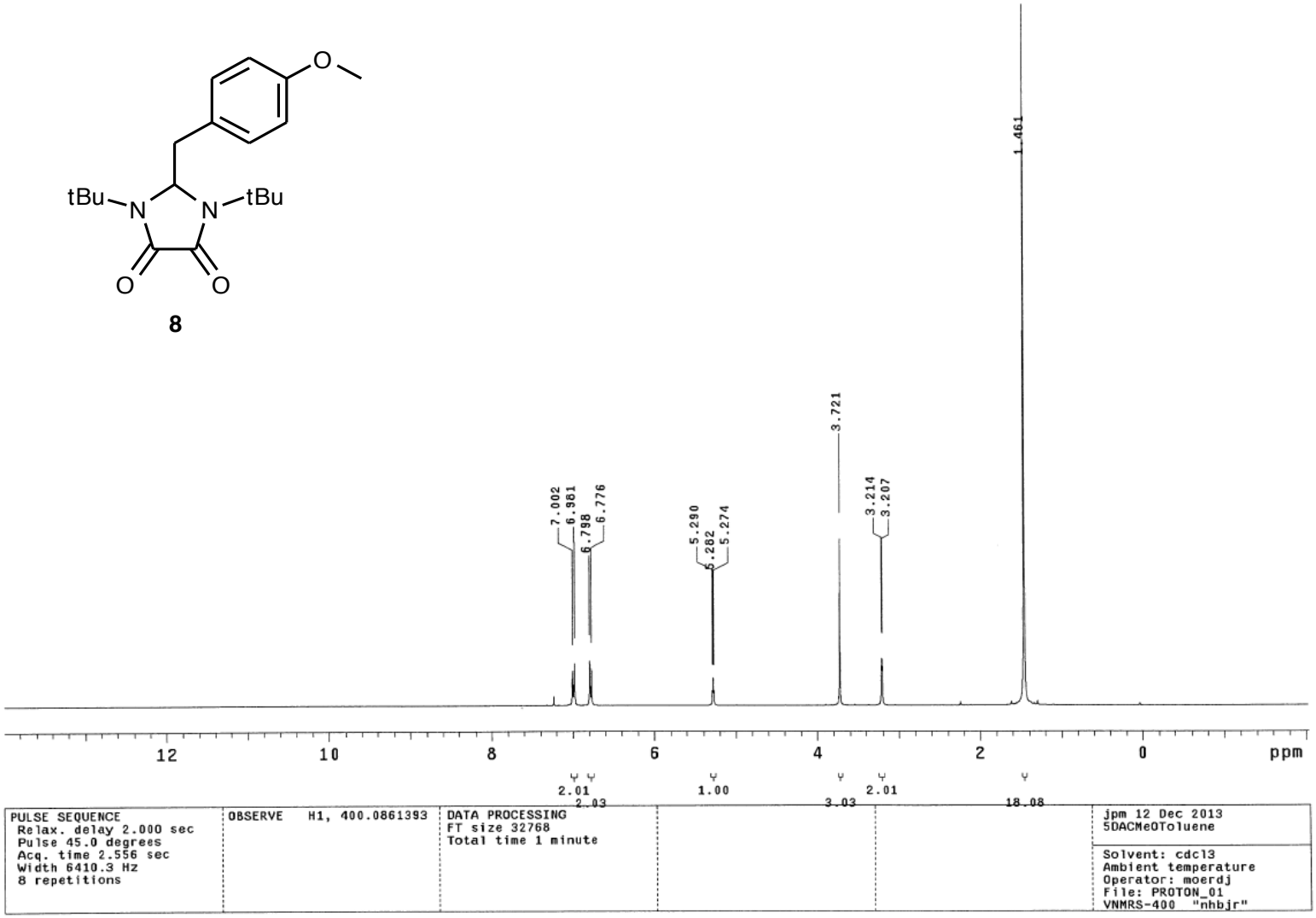
7

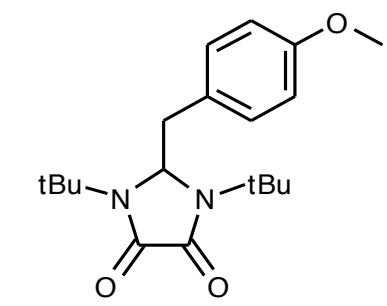
7.266
7.262
7.248
7.240
7.231
7.214
7.098
7.094
7.077
5.332
5.324
5.315
3.281
3.274
1.457
12
10
8
6
4
2
0
ppm
1.8393
0.96
1.00
2.03
18.36
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 400.0861393
DATA PROCESSING
FT size 32768
Total time 1 minute
jpm 12 Dec 2013
5DACToluene
Solvent: cdcl3
Ambient temperature
Operator: moerdj
File: PROTON_01
VNMRS-400 "nhbjr"


tBu
N
N
tBu
O
O

7

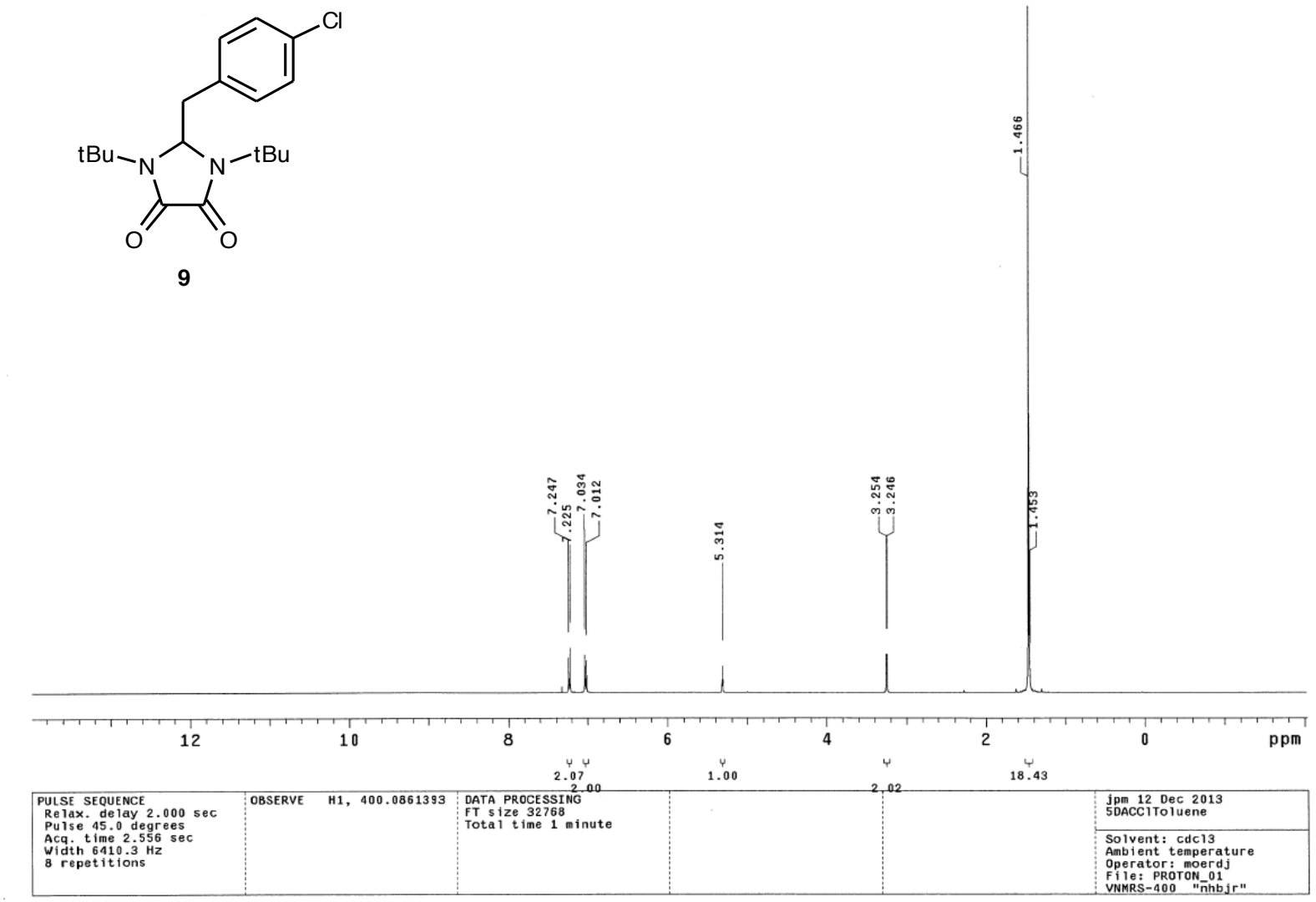
Agilent Technologies
220
200
180
160
140
120
100
80
60
40
20
0
ppm
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 30.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
128 repetitions
OBSERVE C13, 100.6017427
DECOUPLE H1, 400.0881319
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 7 minutes
jpm 12 Dec 2013
5DACToluene
Solvent: cdcl3
Ambient temperature
Operator: moerdj
File: CARBON_01
VNMRS-400 "nhb400"

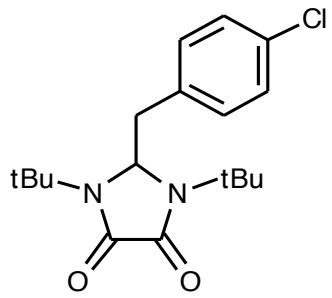

O
tBu
N
N
tBu
O
O
8
7.002
6.981
6.798
6.776
5.290
5.282
5.274
3.721
3.214
3.207
1.461
12
10
8
6
4
2
0
ppm
2.01
2.03
1.00
3.03
2.01
18.08
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 400.0861393
DATA PROCESSING
FT size 32768
Total time 1 minute
jpm 12 Dec 2013
5DACMeOToluene
Solvent: cdcl3
Ambient temperature
Operator: moerdj
File: PROTON_01
VNMRS-400 "nhbjr"


O
tBu
N
N
tBu
O
O

8

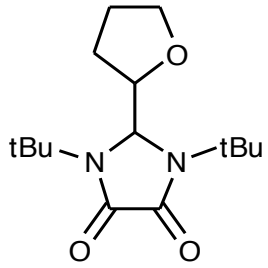
Agilent Technologies
220
200
180
160
140
120
100
80
60
40
20
0
ppm
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 30.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
96 repetitions
OBSERVE C13, 100.6017442
DECOUPLE H1, 400.0881319
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 5 minutes
jpm 12 Dec 2013
5DACMeOToluene
Solvent: cdcl3
Ambient temperature
Operator: moerdj
VNMRS-400 "nhb400"


Cl
tBu
N
N
tBu
O
O
9
7.247
7.225
7.034
7.012
5.314
3.254
3.246
1.466
1.453
12
10
8
6
4
2
0
ppm
2.07
2.00
1.00
2.02
18.43
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 400.0861393
DATA PROCESSING
FT size 32768
Total time 1 minute
jpm 12 Dec 2013
5DACClToluene
Solvent: cdcl3
Ambient temperature
Operator: moerdj
File: PROTON_01
VNMRS-400 "nhbjr"


Cl
tBu
N
N
tBu
O
O

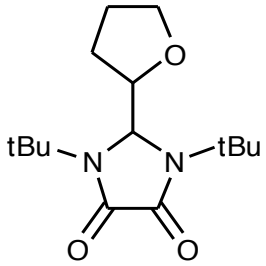
9

Agilent Technologies
220
200
180
160
140
120
100
80
60
40
20
0
ppm
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 30.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
80 repetitions
OBSERVE C13, 100.6017427
DECOUPLE H1, 400.0881319
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 4 minutes
jpm 12 Dec 2013
5DACClToluene
Solvent: cdcl3
Ambient temperature
Operator: moerdj
File: CARBON_01
VNMRS-400 "nhb400"


tBu
N
N
tBu
O
O
O

10

5.254
5.249
4.196
3.998
3.984
3.734
3.715
1.850
1.845
1.830
1.824
1.479
1.461
1.450
12
10
8
6
4
2
0
ppm
1.00
1.02
1.02 1.02
2.05
19.56
1.35
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 400.0861397
DATA PROCESSING
FT size 32768
Total time 1 minute
jpm 20 Dec 2013
5DAC THF
Solvent: cdcl3
Ambient temperature
Operator: moerdj
File: PROTON_01
VNMRS-400 "nhbjr"

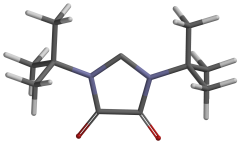
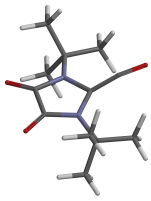
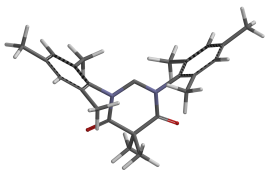
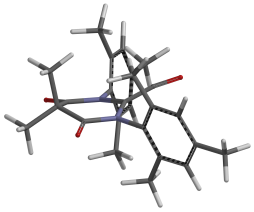
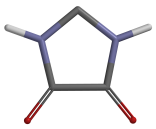
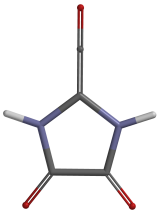
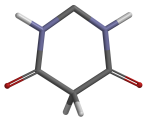
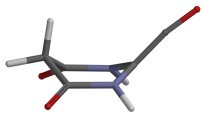

tBu
N
N
tBu
O
O
O

10

Agilent Technologies
220
200
180
160
140
120
100
80
60
40
20
0
ppm
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 30.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
224 repetitions
OBSERVE C13, 100.6017435
DECOUPLE H1, 400.0881319
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 12 minutes
jpm 20 Dec 2013
5DAC THF
Solvent: cdcl3
Ambient temperature
Operator: moerdj
VNMRS-400 "nhb400"

DFT Calculations. The DFT calculations were performed at the B3LYP/6-31g* level of theory using the Spartan'14 software package (v.1.1.3). Vibrational frequencies were calculated to identify the optimized structures as energy minima as well as to calculate the zero point energies. Truncated forms of the five- and six-membered DACs were also calculated for comparison. Key results are summarized in Table S3 and Cartesian coordinates are given in Tables S4 – S11.

Table S3. Summary of calculated structures and thermodynamic values.[a]

Carbene	Ketene	ΔH (298 K) (kcal/mol)	ΔG (298 K) (kcal/mol)	ΔH (195 K) (kcal/mol)	ΔG (195 K) (kcal/mol)
 **2a**		-6.21	6.25	-5.99	1.88
 **6DAC**		-12.2	-0.08	-12.0	-4.34
 **5DAC** (truncated)		-12.3	-1.80	-12.2	-5.69
 **6DAC** (truncated)		-11.3	-0.16	-11.1	-4.07

[a] Change in enthalpy or Gibbs free energy calculated for the reaction: DAC + CO → DAC–CO.

Table S4. Cartesian coordinates (Angstroms) for **2a**.

Atom	x	y	z
C	0.0140318	-0.8644076	0.0000000
N	0.0129201	-0.0421836	-1.1054858
N	0.0129201	-0.0421836	1.1054858
C	0.0062202	1.3130753	0.7735483
C	0.0062202	1.3130753	-0.7735483
O	-0.0006152	2.2879631	-1.4886180
O	-0.0006152	2.2879631	1.4886180
C	-0.0008231	-0.5553782	-2.5161852
C	-1.2852724	-0.0550198	-3.2023695
H	-1.3287179	1.0365460	-3.2222054
H	-2.1718672	-0.4341480	-2.6819846
H	-1.3160712	-0.4182113	-4.2352980
C	1.2509636	-0.0266895	-3.2411926
H	1.2574383	1.0650163	-3.2838657
H	1.2709952	-0.4118989	-4.2663609
H	2.1614882	-0.3648834	-2.7340148
C	0.0175259	-2.0881873	-2.4952567
H	-0.8520009	-2.4959341	-1.9736923
H	0.9113824	-2.4737439	-1.9980765
H	0.0080538	-2.4447424	-3.5309820
C	-0.0008231	-0.5553782	2.5161852
C	-1.2852724	-0.0550198	3.2023695
H	-1.3287179	1.0365460	3.2222054
H	-1.3160712	-0.4182113	4.2352980
H	-2.1718672	-0.4341480	2.6819846
C	0.0175259	-2.0881873	2.4952567
H	-0.8520009	-2.4959341	1.9736923
H	0.0080538	-2.4447424	3.5309820
H	0.9113824	-2.4737439	1.9980765
C	1.2509636	-0.0266895	3.2411926
H	1.2574383	1.0650163	3.2838657
H	2.1614882	-0.3648834	2.7340148
H	1.2709952	-0.4118989	4.2663609

Table S5. Cartesian coordinates (Angstroms) for **2a**–CO.

Atom	x	y	z
C	-0.0000100	-0.6502713	0.0546126
N	-1.1514757	0.1881901	0.0648441
N	1.1521335	0.1870549	0.0728979
C	0.7615329	1.4983202	0.2651209
C	-0.7615584	1.4985880	0.2628135
O	-1.4748624	2.4835629	0.3472445
O	1.4746516	2.4835539	0.3477330
C	-2.5833135	-0.1994251	-0.1932762
C	-3.0772662	0.5937806	-1.4197322
H	-2.5095472	0.3136231	-2.3142502
H	-2.9773964	1.6681521	-1.2591314
H	-4.1332572	0.3642957	-1.5987852
C	-2.7067257	-1.6985869	-0.4923666
H	-2.0606361	-2.0132109	-1.3179822
H	-3.7410175	-1.8996749	-0.7885522
H	-2.5020480	-2.3195734	0.3843089
C	-3.4104300	0.1468371	1.0586793
H	-3.3516984	1.2144436	1.2785777
H	-3.0487493	-0.4147176	1.9273795
H	-4.4604262	-0.1194595	0.8937617
C	2.5829635	-0.1989747	-0.1931508
C	3.0654396	0.5865024	-1.4291681
H	2.4892268	0.2998969	-2.3161503
H	4.1198135	0.3565007	-1.6169333
H	2.9660061	1.6618523	-1.2744916
C	3.4190508	0.1584752	1.0496977
H	3.3606417	1.2276612	1.2616269
H	4.4676985	-0.1085270	0.8782236
H	3.0644012	-0.3962549	1.9256196
C	2.7095285	-1.6999985	-0.4823741
H	2.0595677	-2.0225528	-1.3019595
H	2.5145989	-2.3171465	0.3993889
H	3.7424917	-1.8980572	-0.7851952
C	-0.0009794	-1.9152782	0.5102904
O	0.0010024	-3.0850891	0.6442066

Table S6. Cartesian coordinates (Angstroms) for **6DAC**.

Atom	x	y	z
N	1.1573004	0.4557478	0.0018860
N	-1.1546927	0.4491208	0.0179445
C	-2.3842301	-0.3333987	0.0271531
C	-4.7126715	-1.8806171	0.0372092
C	-2.8318441	-0.8821592	1.2369721
C	-3.0759421	-0.5286691	-1.1745893
C	-4.2373251	-1.3076858	-1.1447913
C	-3.9969862	-1.6522341	1.2168740
H	-4.7816975	-1.4698189	-2.0728072
H	-4.3532017	-2.0854070	2.1493461
C	2.3886829	-0.3236022	-0.0289022
C	4.7169848	-1.8702210	-0.1070791
C	2.8625408	-0.7805440	-1.2666839
C	3.0524372	-0.6140642	1.1702412
C	4.2141621	-1.3898154	1.1045456
C	4.0274998	-1.5517225	-1.2809978
H	4.7376442	-1.6244585	2.0291020
H	4.4029025	-1.9136810	-2.2360384
C	-1.2818815	1.8498988	0.1843321
C	1.2824905	1.8610943	0.1123993
O	2.3645155	2.3961676	0.2439579
O	-2.3570022	2.3673349	0.4075117
C	-0.0080365	2.6683663	-0.0041137
C	0.0155117	3.8371630	0.9985779
H	0.0425973	3.4712156	2.0303312
H	-0.8842041	4.4428043	0.8741582
H	0.9041519	4.4480387	0.8280003
C	-0.0510937	3.2232198	-1.4596453
H	-0.9434415	3.8439145	-1.5819178
H	-0.0820072	2.4163818	-2.1998210
H	0.8410251	3.8298780	-1.6395528
C	-2.5882635	0.0704138	-2.4716152
H	-2.5958640	1.1669497	-2.4370699
H	-3.2266872	-0.2384825	-3.3044892
H	-1.5624648	-0.2445066	-2.6977613
C	-2.0743907	-0.6652885	2.5239367
H	-2.5775405	-1.1612024	3.3591084
H	-1.9927722	0.4009551	2.7680151
H	-1.0563669	-1.0668014	2.4521005
C	-5.9495683	-2.7481260	0.0403784

H	-6.5639842	-2.5689068	0.9298898
H	-5.6862010	-3.8142688	0.0394832
H	-6.5710650	-2.5644738	-0.8421636
C	2.5433611	-0.1116683	2.4991514
H	2.6566728	0.9760771	2.5806945
H	3.0977351	-0.5685446	3.3242020
H	1.4811226	-0.3440485	2.6372357
C	5.9541761	-2.7364443	-0.1464328
H	6.5683606	-2.5214955	-1.0280656
H	5.6913395	-3.8019525	-0.1877912
H	6.5755477	-2.5878109	0.7427673
C	2.1305508	-0.4724926	-2.5499930
H	2.0103869	0.6075473	-2.7004640
H	1.1270975	-0.9155499	-2.5436609
H	2.6737189	-0.8709204	-3.4119545
C	0.0019748	-0.2753251	-0.0521685

Table S7. Cartesian coordinates (Angstroms) for **6DAC**–CO.

Atom	x	y	z
N	1.2205205	0.5749604	0.1601005
N	-1.2168502	0.5844339	0.1350377
C	-2.4313266	-0.2008415	0.0527270
C	-4.7386707	-1.7735905	-0.1389824
C	-2.8546062	-0.9319755	1.1724800
C	-3.1615269	-0.2026274	-1.1489902
C	-4.3051357	-1.0014040	-1.2219181
C	-4.0060765	-1.7161441	1.0491227
H	-4.8755469	-1.0132007	-2.1484265
H	-4.3421922	-2.2898479	1.9099976
C	2.4298636	-0.2178146	0.0819256
C	4.7432967	-1.7850207	-0.1018012
C	3.2301226	-0.1272624	-1.0698475
C	2.7768916	-1.0560495	1.1546346
C	3.9348159	-1.8289137	1.0380593
C	4.3777961	-0.9227388	-1.1387700
H	4.2156791	-2.4774505	1.8652822
H	5.0050128	-0.8591756	-2.0252152
C	-1.2900802	1.9363003	0.4206534
C	1.2996124	1.9310366	0.4297437
O	2.3592481	2.4516607	0.7440065
O	-2.3490923	2.4579721	0.7363337

C	0.0064965	2.7486105	0.2851159
C	0.0065807	3.8723541	1.3366364
H	0.0074217	3.4610468	2.3512740
H	-0.8890186	4.4847192	1.2174352
H	0.9015763	4.4854075	1.2166043
C	0.0095357	3.3692925	-1.1407785
H	-0.8774678	3.9977447	-1.2654840
H	0.0024365	2.6012371	-1.9219951
H	0.9040215	3.9863171	-1.2684923
C	-2.7686586	0.6712058	-2.3175744
H	-2.9448696	1.7281480	-2.0826659
H	-3.3609830	0.4210436	-3.2023441
H	-1.7110617	0.5657485	-2.5822230
C	-2.1216606	-0.8474284	2.4879409
H	-2.6075945	-1.4734894	3.2418685
H	-2.1092816	0.1838619	2.8598120
H	-1.0802847	-1.1739731	2.3992789
C	-5.9717130	-2.6384477	-0.2559797
H	-6.8440171	-2.0501093	-0.5653670
H	-6.2135031	-3.1218419	0.6955514
H	-5.8337525	-3.4275466	-1.0058000
C	1.9412528	-1.1228275	2.4083320
H	1.6195535	-0.1271581	2.7287909
H	2.5070742	-1.5800536	3.2253479
H	1.0377052	-1.7262364	2.2552225
C	5.9711062	-2.6578859	-0.2118841
H	6.4641110	-2.7792561	0.7586559
H	6.6998607	-2.2384520	-0.9129915
H	5.7111864	-3.6623159	-0.5718871
C	2.9020957	0.8316056	-2.1892808
H	3.0857287	1.8657769	-1.8743567
H	1.8527303	0.7628141	-2.4962304
H	3.5225247	0.6292927	-3.0669370
C	0.0031359	-0.0447492	-0.2190516
C	0.0093662	-1.1259338	-1.0118035
O	0.0113663	-2.1897969	-1.5184567

Table S8. Cartesian coordinates (Angstroms) for **5DAC** (truncated).

Atom	x	y	z
N	1.0800255	0.0000000	-0.9489894
C	0.0000000	0.0000000	-1.8043785
N	-1.0800255	0.0000000	-0.9489894
C	-0.7764145	0.0000000	0.4138059
C	0.7764145	0.0000000	0.4138059
O	-1.5237403	0.0000000	1.3582681
O	1.5237403	0.0000000	1.3582681
H	2.0318139	0.0000000	-1.2929189
H	-2.0318139	0.0000000	-1.2929189

Table S9. Cartesian coordinates (Angstroms) for **5DAC** (truncated)–CO.

Atom	x	y	z
N	-0.1107628	0.0073466	1.1231056
C	-0.9624937	0.0142984	0.0000000
N	-0.1107628	0.0073466	-1.1231056
C	1.2267524	-0.0017433	-0.7687926
C	1.2267524	-0.0017433	0.7687926
O	2.1800033	-0.0054024	-1.5158517
O	2.1800033	-0.0054024	1.5158517
C	-2.2847868	-0.0115025	0.0000000
O	-3.4639050	-0.0059750	0.0000000
H	-0.4277385	0.0177645	2.0818754
H	-0.4277385	0.0177645	-2.0818754

Table S10. Cartesian coordinates (Angstroms) for **6DAC** (truncated).

Atom	x	y	z
N	1.1332145	0.0000000	-1.0440642
C	0.0000000	0.0000000	-1.8050694
N	-1.1332145	0.0000000	-1.0440642
C	-1.2936735	0.0000000	0.3517650
C	1.2936735	0.0000000	0.3517650
O	2.3916497	0.0000000	0.8649013
O	-2.3916497	0.0000000	0.8649013
C	0.0000000	0.0000000	1.1447116
H	0.0000000	-0.8718528	1.8099297
H	0.0000000	0.8718528	1.8099297

H	-2.0132056	0.0000000	-1.5502071
H	2.0132056	0.0000000	-1.5502071

Table S11. Cartesian coordinates (Angstroms) for **6DAC** (truncated)–CO.

Atom	x	y	z
N	-0.2782762	-0.4798814	1.2126695
C	-1.0053358	-0.3858042	0.0000000
N	-0.2782762	-0.4798814	-1.2126695
C	0.9980492	0.0635772	-1.2686033
C	0.9980492	0.0635772	1.2686033
O	1.7490849	-0.1105057	2.2067281
O	1.7490849	-0.1105057	-2.2067281
C	1.3506844	0.8486339	0.0000000
H	0.7845631	1.7912723	0.0000000
H	2.4157546	1.0752383	0.0000000
C	-2.2330680	0.1545888	0.0000000
O	-3.3671893	0.4403915	0.0000000
H	-0.5012844	-1.1853242	1.9066447
H	-0.5012844	-1.1853242	-1.9066447

References

S1 H. J. Bestmann, J. Lienert and L. Mott, *Justus Liebigs Ann. Chem*., 1968, **718**, 24.

S2 R. E. Cowley, N. A. Eckert, J. Elhaïk and P. L. Holland. *Chem. Commun*., 2009, 1760.

S3 C. Palomo and R. Mestres, *Synthesis*, 1981, 373.

S4 G. Zinner and R. Vollrath, *Chem. Ber*., 1970, **103**, 766.

S5 Z. Otwinowski and W. Minor, Methods. In *Enzymology in Macromolecular Crystallography, Part A*; Carter, C. W., Jr; Sweets, R. M., Eds. (Academic Press, 1997); Vol. 276, pp 307–326.

S6 Sheldrick, G. M. SHELXL/PC package (version 5.1), program for the refinement of crystal structures, University of Gottingen, Germany, 2003.