A Facile Pd(0)-Catalyzed Regio- and Stereoselective Diamination of Conjugated Dienes and Trienes

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Supporting Information

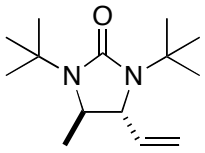
Representative diamination procedure (Table 1, entry 1). An NMR tube charged with $Pd(PPh_3)_4$ (0.0223 g, 0.020 mmol) was evacuated and then filled with argon three times. Benzene-d_6 (0.6 mL, distilled from sodium) was then added, followed by *trans*-1,3-pentadiene (**5a**) (0.0163 g, 0.24 mmol) and di-*t*-butyldiaziridinone **6** (0.034 g, 0.20 mmol). The resulting mixture was immersed into an oil bath (65 °C). Upon completion (as monitored by ^{1}H NMR) (30 min), the reaction mixture was purified by flash chromatography (silica gel, hexane:ethyl acetate = 8:1) to give compound **7a** as a colorless oil (0.045 g, 94% yield).

Bis *t*-butyl deprotection (Scheme 4). To a 5 mL-vial was added compound **7b** (0.101 g, 0.40 mmol), followed by the addition of CF_3CO_2H (0.8 ml). Upon stirring at 75-80 ^{o}C for 2 h, the reaction mixture was concentrated and purified by flash chromatography (silica gel, ether to methanol) to give compound **8** as a white solid (0.055 g, 98% yield).

Mono *t*-butyl deprotection (Scheme 4). To a 5 mL-vial was added compound **7b** (0.101 g, 0.40 mmol), followed by the addition of CF_3CO_2H (0.8 ml). Upon stirring at room temperature for 1 h, the reaction mixture was concentrated and purified by flash chromatography (silica gel, ether) to give a white solid containing both **9a** and **9b** (9.3:1) (0.077 g, 98%).

The above solid (0.059 g, 0.30 mmol) was added into a 5 mL-vial, followed by the addition of CF_3CO_2H (0.6 ml). Upon stirring at 75-80 ^{o}C for 1 h, the reaction mixture was concentrated and purified by flash chromatography (silica gel, ether to methanol) to give compound **8** as a white solid (0.0403 g, 96% yield).

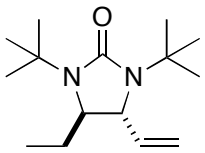
Table 1, Entry 1



7a, colorless oil; IR (film) 1688 cm^{-1}; ^{1}H NMR (300 MHz, benzene-d_6) δ 5.85 (ddd, J = 17.1, 9.9, 8.4 Hz, 1H), 4.95 (d, J = 17.1 Hz, 1H), 4.86 (d, J = 9.9 Hz, 1H), 3.25 (d, J = 8.4 Hz, 1H), 3.01 (q, J = 6.3 Hz, 1H), 1.44 (s, 9H), 1.37 (s, 9H), 0,95 (d, J = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, benzene-d_6) δ 157.8, 140.9, 115.4, 64.0, 55.7, 53.3, 52.7, 29.3, 29.2, 21.3; Anal. calcd. for

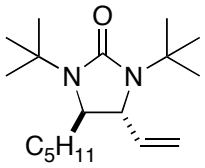
$C_{14}H_{26}N_2O$: C, 70.54; H, 10.99; N, 11.75; Found: C, 70.66; H, 11.13; N, 12.00; HRMS calcd. for $C_{14}H_{27}N_2O$ (M+1): 239.2123; Found 239.2124.

Table 1, Entry 2



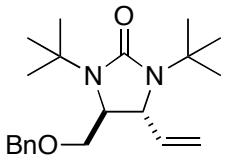
7b, colorless oil; IR (film) 1688 cm^{-1}; ^1H NMR (300 MHz, benzene-d_6) δ 5.86 (ddd, *J* = 17.1, 9.9, 8.1 Hz, 1H), 5.00 (d, *J* = 17.1 Hz, 1H), 4.86 (d, *J* = 9.9 Hz, 1H), 3.50 (d, *J* = 8.1 Hz, 1H), 3.03 (dd, *J* = 8.4, 2.7 Hz, 1H), 1.54-1.22 (m, 2H), 1.44 (s, 9H), 1.39 (s, 9H), 0.72 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, benzene-d_6) δ 158.2, 141.7, 115.0, 61.2, 60.7, 53.4, 52.8, 29.3, 29.2, 27.8, 9.3; Anal. calcd. for $C_{15}H_{28}N_2O$: C, 71.38; H, 11.18; N, 11.10; Found: C, 71.50; H, 10.91; N, 11.33; HRMS calcd. for $C_{15}H_{29}N_2O$ (M+1): 253.2280; Found 253.2284.

Table 1, Entry 3



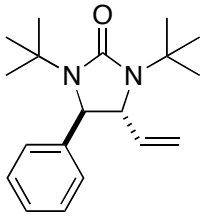
7c, colorless oil; IR (film) 1690 cm^{-1}; ^1H NMR (300 MHz, benzene-d_6) δ 5.90 (ddd, *J* = 17.1, 9.9, 8.4 Hz, 1H), 5.01 (d, *J* = 17.1 Hz, 1H), 4.88 (d, *J* = 9.9 Hz, 1H), 3.58 (d, *J* = 8.4 Hz, 1H), 3.03 (dd, *J* = 8.7, 2.1 Hz, 1H), 1.66-1.50 (m, 2H), 1.47 (s, 9H), 1.43 (s, 9H), 1.37-1.10 (m, 6H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, benzene-d_6) δ 158.2, 141.6, 115.1, 61.2, 60.1, 53.4, 52.9, 34.9, 32.5, 29.4, 29.3, 25.1, 23.4, 14.6; Anal. calcd. for $C_{18}H_{34}N_2O$: C, 73.42; H, 11.64; N, 9.51; Found: C, 73.15; H, 11.79; N, 9.78; HRMS calcd. for $C_{18}H_{35}N_2O$ (M+1): 295.2749; Found 295.2749.

Table 1, Entry 4



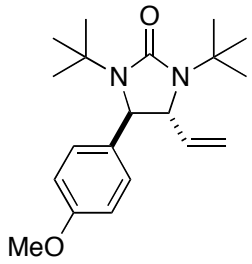
7d, colorless oil; IR (film) 1689 cm^{-1}; ^{1}H NMR (300 MHz, benzene-d_6) δ 7.25-7.17 (m, 3H), 7.16-7.05 (m, 2H), 5.90 (ddd, *J* = 18.0, 10.2, 8.1 Hz, 1H), 5.16 (d, *J* = 18.0 Hz, 1H), 4.92 (d, *J* = 10.2 Hz, 1H), 4.32 (d, *J* = 12.3 Hz, 1H), 4.20 (d, *J* = 12.3 Hz, 1H), 4.04 (d, *J* = 7.5 Hz, 1H), 3.36 (s, 3H), 1.42 (s, 9H), 1.35 (s, 9H); ^{13}C NMR (75 MHz, benzene-d_6) δ 158.4, 140.8, 138.9, 129.1, 128.1, 115.9, 73.6, 70.8, 59.4, 59.1, 53.4, 52.9, 29.3, 29.2; Anal. calcd. for $C_{21}H_{32}N_2O_2$: C, 73.22; H, 9.36; N, 8.13; Found: C, 73.34; H, 9.35; N, 8.24; HRMS calcd. for $C_{21}H_{33}N_2O_2$ (M+1): 345.2542; Found 345.2548.

Table 1, Entry 5



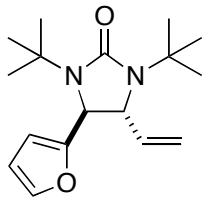
7e, colorless oil; IR (film) 1689 cm^{-1}; ^{1}H NMR (300 MHz, benzene-d_6) δ 7.27 (d, *J* = 7.2 Hz, 2H), 7.16-7.02 (m, 3H), 5.92 (ddd, *J* = 17.4, 9.9, 8.4 Hz, 1H), 4.91 (d, *J* = 17.4 Hz, 1H), 4.88 (d, *J* = 9.9 Hz, 1H), 4.05 (s, 1H), 3.55 (d, *J* = 8.4 Hz, 1H), 1.39 (s, 9H), 1.36 (s, 9H); ^{13}C NMR (75 MHz, benzene-d_6) δ 159.1, 145.0, 141.7, 129.4, 126.4, 115.6, 65.4, 63.8, 53.9, 53.7, 29.2, 29.1; Anal. calcd. for $C_{19}H_{28}N_2O$: C, 75.96; H, 9.39; N, 9.32; Found: C, 75.77; H, 9.15; N, 9.35; HRMS calcd. for $C_{19}H_{29}N_2O$ (M+1): 301.2280; Found 301.2284.

Table 1, Entry 6



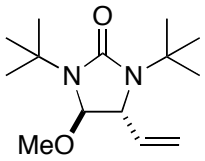
7f, colorless oil; IR (film) 1687, 1610 cm^{-1}; ^1H NMR (300 MHz, benzene-d_6) δ 7.22-7.17 (m, 2H), 6.72-6.89 (m, 2H), 5.95 (ddd, *J* = 17.4, 9.6, 8.4 Hz, 1H), 4.95 (d, *J* = 17.4 Hz, 1H), 4.90 (d, *J* = 9.6 Hz, 1H), 4.05 (s, 1H), 3.58 (d, *J* = 8.4 Hz, 1H), 2.29 (s, 3H), 1.44 (s, 9H), 1.40 (s, 9H); ^{13}C NMR (75 MHz, benzene-d_6) δ 160.2, 159.1, 141.7, 136.9, 127.6, 115.6, 114.8, 65.7, 63.3, 55.1, 53.8, 53.7, 29.2, 29.1; Anal. calcd. for $C_{20}H_{30}N_2O_2$: C, 72.69; H, 9.15; N, 8.48; Found: C, 72.34; H, 9.30; N, 8.60; HRMS calcd. for $C_{20}H_{31}N_2O_2$ (M+1): 331.2386; Found 331.2386.

Table 1, Entry 7



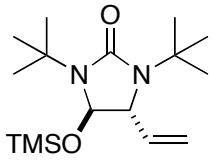
7g, light yellow oil; IR (film) 1693 cm^{-1}; ^1H NMR (300 MHz, benzene-d_6) δ 7.00 (d, *J* = 1.8 Hz 1H), 6.11 (d, *J* = 3.0 Hz, 1H), 6.02 (dd, *J* = 3.0, 1.8 Hz, 1H), 5.89 (ddd, *J* = 17.1, 9.9, 7.8 Hz, 1H), 4.97 (d, *J* = 17.1, 1H), 4.88 (d, *J* = 9.9 Hz, 1H), 4.20 (s, 1H), 3.77 (d, *J* = 8.1 Hz, 1H), 1.43 (s, 9H), 1.32 (s, 9H); ^{13}C NMR (75 MHz, benzene-d_6) δ 158.5, 156.8, 142.0, 140.6, 116.3, 111.1, 106.9, 62.6, 57.7, 53.8, 53.6, 29.1, 28.8; Anal. calcd. for $C_{17}H_{26}N_2O_2$: C, 70.31; H, 9.02; N, 9.65; Found: C, 70.49; H, 8.88; N, 9.72; HRMS calcd. for $C_{17}H_{27}N_2O_2$ (M+1): 291.2073; Found 291.2064.

Table 1, Entry 8



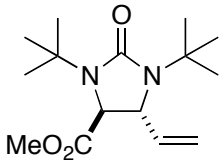
7h, colorless oil; IR (film) 1699 cm^{-1}; ^1H NMR (300 MHz, benzene-d_6) δ 5.59 (ddd, J = 17.4, 10.5, 8.1 Hz, 1H), 5.03 (d, J = 17.4 Hz, 1H), 4.89 (d, J = 10.5 Hz, 1H), 4.28 (s, 1H), 3.75 (d, J = 8.1, 1H), 2.93 (s, 3H) 1.48 (s, 9H), 1.40 (s, 9H); ^{13}C NMR (75 MHz, benzene-d_6) δ 158.2, 139.8, 116.6, 90.5, 60.4, 53.8, 53.2, 51.1, 29.1, 28.9; Anal. calcd. for $C_{14}H_{26}N_2O_2$: C, 66.10; H, 10.30; N, 11.01; Found: C, 66.05; H, 10.12; N, 11.00; HRMS calcd. for $C_{14}H_{27}N_2O_2$ (M+1): 255.2073; Found 255.2074.

Table 1, Entry 9



7i, colorless oil; IR (film) 1703 cm^{-1}; ^1H NMR (300 MHz, benzene-d_6) δ 5.66 (ddd, J = 17.4, 9.9, 8.4 Hz, 1H), 5.08 (d, J = 17.4 Hz, 1H), 4.90 (d, J = 9.9 Hz, 1H), 4.76 (s, 1H), 3.73 (d, J = 8.4, 1H), 1.52 (s, 9H) 1.45 (s, 9H), 0.08 (s, 9H); ^{13}C NMR (75 MHz, benzene-d_6) δ 158.4, 139.2, 117.0, 84.7, 65.4, 53.8, 53.2, 29.2, 1.0; HRMS calcd. for $C_{16}H_{33}N_2O_2Si$ (M+1): 313.2311; Found 313.2314.

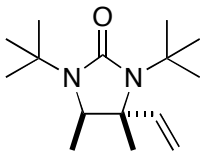
Table 1, Entry 10



7j, colorless oil; IR (film) 1756, 1737, 1698 cm^{-1}; ^1H NMR (300 MHz, benzene-d_6) δ 5.78 (ddd, J = 17.1, 9.9, 7.8 Hz, 1H), 5.05 (d, J = 17.1 Hz, 1H), 4.86 (d, J = 9.9 Hz, 1H), 3.95 (d, J = 7.8 Hz,

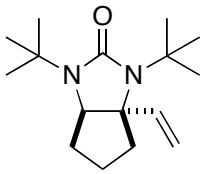
1H), 3.77 (d, J = 0.9 Hz, 1H), 3.29 (s, 3H), 1.41 (s, 9H), 1.39 (s, 9H); ^{13}C NMR (75 MHz, benzene-d_6) δ 173.2, 158.4, 140.3, 116.6, 62.0, 60.1, 53.9, 53.7, 52.1, 29.1, 28.7; Anal. calcd. for $C_{15}H_{26}N_2O_3$: C, 63.80; H, 9.28; N, 9.92; Found: C, 63.84; H, 9.37; N, 9.67; HRMS calcd. for $C_{15}H_{27}N_2O_3$ (M+1): 283.2022; Found 283.2024.

Table 1, Entry 11



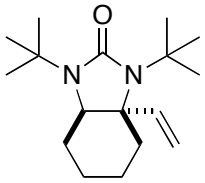
7k, white solid; mp. 39-40 °C; IR (film) 1688 cm^{-1}; ^{1}H NMR (300 MHz, benzene-d_6) δ 6.22 (dd, J = 17.4, 10.5 Hz, 1H), 4.89 (d, J = 17.4 Hz, 1H), 4.85 (d, J = 10.5 Hz, 1H), 2.84 (q, J = 6.0 Hz, 1H), 1.51 (s, 9H) 1.39 (s, 9H), 1.07 (s, 3H), 0.85 (d, J = 6.0 Hz, 3H); ^{13}C NMR (75 MHz, benzene-d_6) δ 159.8, 144.8, 112.8, 64.2, 60.0, 56.4, 53.0, 30.4, 29.1, 20.8, 16.5; Anal. calcd. for $C_{15}H_{28}N_2O$: C, 71.38; H, 11.18; N, 11.10; Found: C, 71.22; H, 10.91; N, 11.30.

Table 1, Entry 12



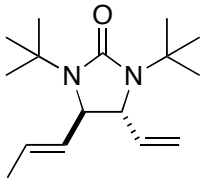
7l, colorless oil; IR (film) 1682 cm^{-1}; ^{1}H NMR (300 MHz, benzene-d_6) δ 5.85 (dd, J = 17.7, 10.5 Hz, 1H), 4.94 (d, J = 17.7 Hz, 1H), 4.80 (d, J = 10.5 Hz, 1H), 3.16 (t, J = 7.2 Hz, 1H), 1.97-1.87 (m, 1H), 1.75-1.60 (m, 2H), 1.53 (s, 9H), 1.50-1.20 (m, 2H), 1.39 (s, 9H), 1.18-0.95 (m, 1H); ^{13}C NMR (100 MHz, benzene-d_6) δ 158.9, 146.3, 111.9, 69.7, 67.3, 55.1, 53.4, 39.6, 37.8, 30.1, 29.2, 24.8; HRMS calcd. for $C_{16}H_{29}N_2O$ (M+1): 265.2280; Found 265.2281.

Table 1, Entry 13



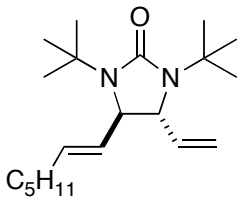
7m, colorless oil; IR (film) 1687 cm^{-1}; ^{1}H NMR (300 MHz, benzene-d_6) δ 6.19 (dd, *J* = 18.0, 11.1 Hz, 1H), 4.95 (d, *J* = 18.0 Hz, 1H), 4.91 (d, *J* = 11.1 Hz, 1H), 2.80 (dd, *J* = 9.3, 5.1 Hz, 1H), 2.10-1.95 (m, 1H), 1.53 (s, 9H), 1.51-1.21 (m, 6H), 1.38 (s, 9H), 1.00-0.84 (m, 1H); ^{13}C NMR (75 MHz, benzene-d_6) δ 160.0, 143.9, 113.1, 64.3, 60.3, 56.7, 52.7, 30.9, 30.2, 29.5, 29.1, 21.9, 20.4; HRMS calcd. for $C_{17}H_{31}N_2O$ (M+1): 279.2436; Found 279.2444.

Table 1, Entry 14



7n, white solid; mp. 63-64 °C; IR (film) 1692 cm^{-1}; ^{1}H NMR (300 MHz, benzene-d_6) δ 5.94 (ddd, *J* = 17.4, 10.2, 8.4 Hz, 1H), 5.70-5.60 (m, 1H), 5.40-5.28 (m, 1H), 4.99 (d, *J* = 17.4 Hz, 1H), 4.88 (d, *J* = 10.2 Hz, 1H), 3.52 (d, *J* = 7.5 Hz, 1H), 3.50 (d, *J* = 8.1 Hz, 1H), 1.47-1.42 (m, 21H); ^{13}C NMR (75 MHz, benzene-d_6) δ 158.4, 140.7, 133.3, 127.1, 115.8, 63.8, 63.0, 53.6, 53.5, 29.2, 17.9; HRMS calcd. for $C_{16}H_{29}N_2O$ (M+1): 265.2280; Found 265.2285.

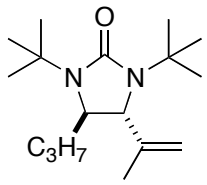
Table 1, Entry 15



7o, colorless oil; IR (film) 1692 cm^{-1}; ^{1}H NMR (300 MHz, benzene-d_6) δ 5.96 (ddd, *J* = 17.1, 9.9, 8.4 Hz, 1H), 5.68 (dd, *J* = 15.3, 8.4 Hz, 1H), 5.43 (dt, *J* = 15.3, 6.9 Hz, 1H), 5.01 (d, *J* = 17.1

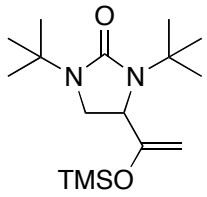
Hz, 1H), 4.90 (d, J = 9.9 Hz, 1H), 3.57 (d, J = 7.5 Hz, 1H), 3.55 (d, J = 7.8 Hz, 1H), 1.89 (dt, J = 6.9, 6.6 Hz, 2H), 1.48 (s, 9H), 1.46 (s, 9H), 1.34-1.14 (m, 6H), 0.87 (t, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, benzene-d_6) δ 158.4, 140.7, 132.8, 132.1, 115.8, 63.9, 63.0, 53.6, 53.5, 32.7, 32.0, 29,5, 29.2, 23.1, 14.6; HRMS calcd. for $C_{20}H_{37}N_2O$ (M+1): 321.2906; Found 321.2904.

Table 1, Entry 16



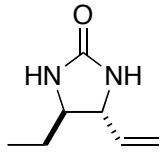
7p, colorless oil; IR (film) 1687 cm^{-1}; ^{1}H NMR (300 MHz, benzene-d_6) δ 4.90 (s, 1H), 4.72-4.68 (m, 1H), 3.52 (s, 1H), 2.99 (dd, J = 7.8, 2.1 Hz, 1H), 1.64 (s, 3H), 1.44 (s, 9H), 1.40 (s, 9H), 1.50-1.23 (m, 3H), 1.20-1.06 (m, 1H), 0.82 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, benzene-d_6) δ 158.5, 148.5, 111.8, 63.1, 59.1, 53.6, 52.8, 38.7, 29.4, 29.1, 18.4, 18.2, 14.6; Anal. calcd. for $C_{17}H_{32}N_2O$: C, 72.81; H, 11.50; N, 9.99; Found: C, 73.06; H, 11.69; N, 10.00; HRMS calcd. for $C_{17}H_{33}N_2O$ (M+1): 281.2593; Found 281.2589.

Table 1, Entry 17

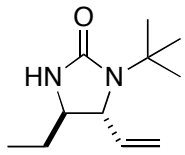


7q, colorless oil; IR (film) 1695 cm^{-1}; ^{1}H NMR (300 MHz, benzene-d_6) δ 4.33 (d, J = 1.8, Hz, 1H), 4.07 (d, J = 1.8 Hz, 1H), 3.71 (dd, J = 9.3, 3.0 Hz, 1H), 3.10 (dd, J = 9.3, 8.4 Hz, 1H), 2.99 (dd, J = 8.4, 3.0 Hz, 1H), 1.51 (s, 9H) 1.34 (s, 9H), 0.15 (s, 9H); ^{13}C NMR (75 MHz, benzene-d_6) δ 161.1, 160.8, 89.3, 56.1, 54.2, 53.0, 47.5, 29.0, 27.8, 0.3; Anal. calcd. for $C_{16}H_{32}N_2O_2Si$: C, 61.49; H, 10.32; N, 8.96; Found: C, 61.70; H, 10.14; N, 9.16; HRMS calcd. for $C_{16}H_{33}N_2O_2Si$ (M+1): 313.2311; Found 313.2314.

Scheme 4

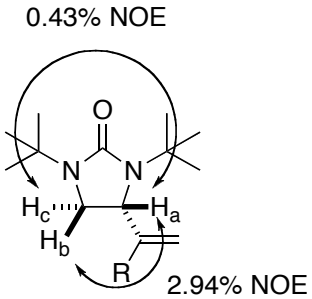


8, white solid; mp. 177-178 °C; IR (film) 3206, 1704 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.85 (ddd, *J* = 17.1, 9.9, 7.5 Hz, 1H), 5.27 (d, *J* = 17.1 Hz, 1H), 5.18 (d, *J* = 9.9 Hz, 1H), 4.95 (bs, 1H), 4.73 (bs, 1H), 3.86 (dd, *J* = 7.5, 6.9 Hz, 1H), 3.37 (td, *J* = 7.2, 6.9 Hz, 1H), 1.73-1.48 (m, 2H), 0.96 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.5, 137.8, 117.1, 61.6, 60.6, 27.9, 10.2; Anal. calcd. for $C_7H_{12}N_2O$: C, 59.98; H, 8.63; N, 19.98; Found: C, 59.78; H, 8.43; N, 20.10.

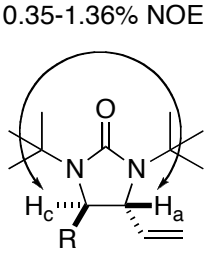


9a, white solid; mp. 58-59 °C; IR (film) 3225, 1693 cm^{-1}; ^1H NMR (300 MHz, acetontrile-d_3) δ 6.01(ddd, *J* = 17.1, 10.2, 8.1 Hz, 1H), 5.26 (d, *J* = 17.1 Hz, 1H), 5.15 (d, *J* = 10.2 Hz, 1H), 4.04 (dd, *J* = 8.1, 2.4 Hz, 1H), 3.09 (dd, *J* = 6.3, 2.4 Hz, 1H), 1.59-1.40 (m, 2H), 1.36 (s, 9H), 0.90 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, acetontrile-d_3) δ 163.4, 141.1, 117.1, 65.1, 56.0, 55.8, 29.2, 28.8, 9.6; HRMS calcd. for $C_{11}H_{21}N_2O$ (M+1): 197.1654; Found 197.1650.

NOE studies to determine stereochemistry

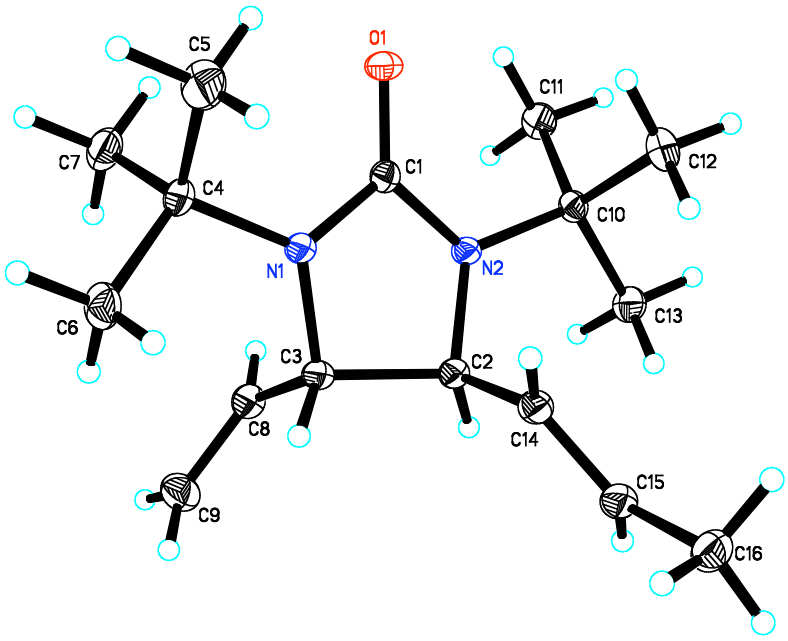


7q, R = OTMS



7b, g, h, p

X-ray structure for 7n



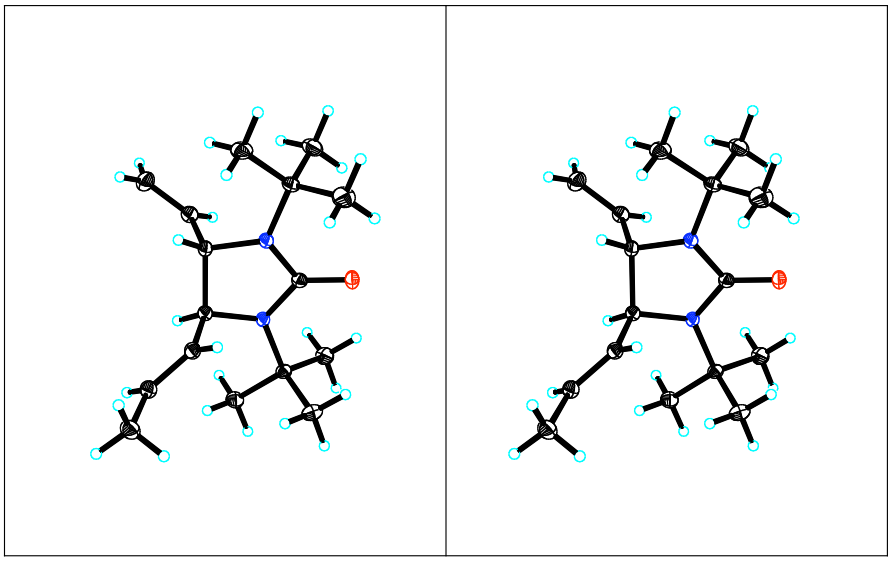


Table 1. Crystal data and structure refinement for **7n**.

Identification code	ys153	
Empirical formula	C16 H28 N2 O	
Formula weight	264.40	
Temperature	373(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 14.1771(4) Å	α= 90°.
	b = 11.7655(3) Å	β= 90°.
	c = 18.9609(5) Å	γ = 90°.
Volume	3162.69(15) $Å^3$	
Z	8	
Density (calculated)	1.111 Mg/m^3	
Absorption coefficient	0.069 mm^{-1}	
F(000)	1168	
Crystal size	0.45 x 0.29 x 0.19 mm^3	
Theta range for data collection	2.15 to 30.89°.	
Index ranges	-20<=h<=18, -16<=k<=10, -17<=l<=27	
Reflections collected	17806	
Independent reflections	4849 [R(int) = 0.0363]	
Completeness to theta = 30.89°	97.1 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.9873 and 0.9696	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4849 / 0 / 172	
Goodness-of-fit on F^2	1.071	
Final R indices [I>2sigma(I)]	R1 = 0.0562, wR2 = 0.1628	
R indices (all data)	R1 = 0.0752, wR2 = 0.1767	
Largest diff. peak and hole	0.748 and -0.754 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **7n**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	552(1)	7796(1)	2128(1)	18(1)
N(1)	1286(1)	7565(1)	1043(1)	14(1)
N(2)	2075(1)	8446(1)	1912(1)	13(1)
C(1)	1232(1)	7920(1)	1737(1)	13(1)
C(2)	2773(1)	8202(1)	1356(1)	13(1)
C(3)	2117(1)	8086(1)	711(1)	14(1)
C(4)	456(1)	7143(1)	646(1)	15(1)
C(5)	32(1)	6124(1)	1036(1)	26(1)
C(6)	784(1)	6735(1)	-80(1)	21(1)
C(7)	-287(1)	8082(1)	561(1)	22(1)
C(8)	1914(1)	9215(1)	372(1)	17(1)
C(9)	2144(1)	9479(1)	-286(1)	22(1)
C(10)	2331(1)	8733(1)	2651(1)	13(1)
C(11)	1578(1)	9514(1)	2964(1)	19(1)
C(12)	2426(1)	7655(1)	3103(1)	19(1)
C(13)	3270(1)	9375(1)	2646(1)	18(1)
C(14)	3333(1)	7132(1)	1475(1)	15(1)
C(15)	4268(1)	7100(1)	1504(1)	17(1)
C(16)	4858(1)	6057(1)	1592(1)	21(1)

Table 3. Bond lengths [Å] and angles [°] for **7n**.

O(1)-C(1)	1.2253(17)
N(1)-C(1)	1.3825(19)
N(1)-C(3)	1.4696(18)
N(1)-C(4)	1.4839(18)
N(2)-C(1)	1.3857(17)
N(2)-C(2)	1.4724(18)
N(2)-C(10)	1.4862(19)
C(2)-C(14)	1.5054(19)

C(2)-C(3)	1.542(2)
C(3)-C(8)	1.505(2)
C(4)-C(6)	1.530(2)
C(4)-C(5)	1.531(2)
C(4)-C(7)	1.535(2)
C(8)-C(9)	1.325(2)
C(10)-C(11)	1.530(2)
C(10)-C(13)	1.531(2)
C(10)-C(12)	1.538(2)
C(14)-C(15)	1.3276(19)
C(15)-C(16)	1.495(2)

C(1)-N(1)-C(3)	109.03(11)
C(1)-N(1)-C(4)	122.73(12)
C(3)-N(1)-C(4)	123.92(12)
C(1)-N(2)-C(2)	108.77(11)
C(1)-N(2)-C(10)	122.47(12)
C(2)-N(2)-C(10)	123.66(11)
O(1)-C(1)-N(1)	125.67(13)
O(1)-C(1)-N(2)	126.02(14)
N(1)-C(1)-N(2)	108.31(12)
N(2)-C(2)-C(14)	114.21(12)
N(2)-C(2)-C(3)	100.35(10)
C(14)-C(2)-C(3)	111.25(12)
N(1)-C(3)-C(8)	113.47(12)
N(1)-C(3)-C(2)	100.37(11)
C(8)-C(3)-C(2)	112.11(12)
N(1)-C(4)-C(6)	108.71(12)
N(1)-C(4)-C(5)	109.13(13)
C(6)-C(4)-C(5)	107.96(13)
N(1)-C(4)-C(7)	110.89(12)
C(6)-C(4)-C(7)	109.90(13)
C(5)-C(4)-C(7)	110.18(13)
C(9)-C(8)-C(3)	124.25(15)
N(2)-C(10)-C(11)	109.43(11)
N(2)-C(10)-C(13)	108.59(12)

C(11)-C(10)-C(13)	108.28(12)
N(2)-C(10)-C(12)	111.13(11)
C(11)-C(10)-C(12)	109.85(12)
C(13)-C(10)-C(12)	109.51(12)
C(15)-C(14)-C(2)	123.81(13)
C(14)-C(15)-C(16)	125.94(14)

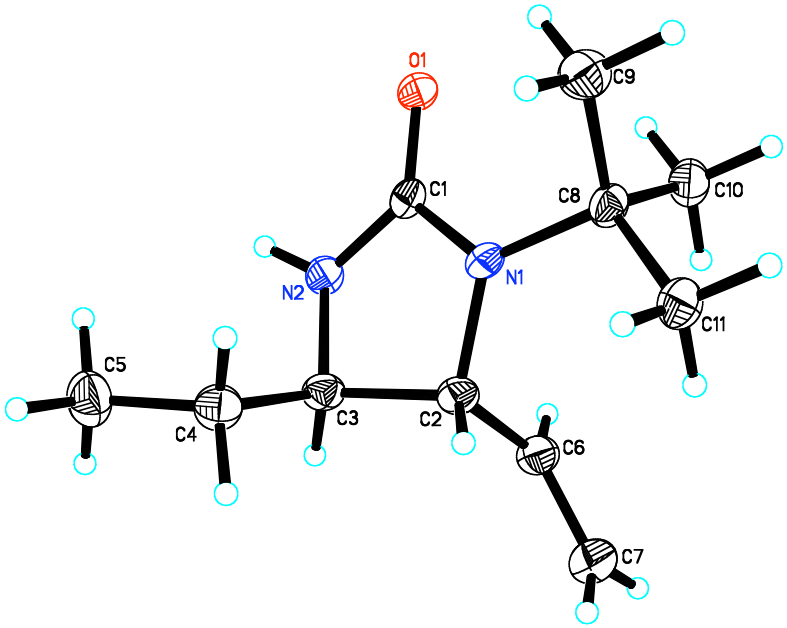
Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **7n**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + \ldots + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	14(1)	24(1)	15(1)	0(1)	3(1)	-4(1)
N(1)	12(1)	18(1)	11(1)	-2(1)	0(1)	-3(1)
N(2)	11(1)	17(1)	11(1)	-2(1)	1(1)	-2(1)
C(1)	13(1)	14(1)	13(1)	0(1)	-1(1)	-1(1)
C(2)	12(1)	16(1)	12(1)	-1(1)	0(1)	-1(1)
C(3)	12(1)	17(1)	12(1)	-1(1)	1(1)	-1(1)
C(4)	13(1)	18(1)	15(1)	-2(1)	-3(1)	-3(1)
C(5)	28(1)	24(1)	25(1)	1(1)	-6(1)	-13(1)
C(6)	21(1)	23(1)	18(1)	-7(1)	-4(1)	0(1)
C(7)	15(1)	27(1)	23(1)	-4(1)	-4(1)	2(1)
C(8)	16(1)	18(1)	17(1)	0(1)	-1(1)	-1(1)
C(9)	24(1)	25(1)	18(1)	4(1)	1(1)	-2(1)
C(10)	14(1)	15(1)	11(1)	-2(1)	-1(1)	0(1)
C(11)	19(1)	20(1)	17(1)	-5(1)	0(1)	2(1)
C(12)	24(1)	18(1)	16(1)	2(1)	-4(1)	0(1)
C(13)	17(1)	21(1)	16(1)	-4(1)	-2(1)	-4(1)
C(14)	14(1)	17(1)	13(1)	-2(1)	1(1)	0(1)
C(15)	15(1)	20(1)	15(1)	-2(1)	1(1)	1(1)
C(16)	16(1)	24(1)	21(1)	-2(1)	-1(1)	4(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **7n**.

	x	y	z	U(eq)
H(2A)	3198	8851	1295	16
H(3A)	2393	7563	366	17
H(5A)	502	5542	1085	38
H(5B)	-493	5832	773	38
H(5C)	-178	6360	1494	38
H(6A)	1251	6151	-24	31
H(6B)	1051	7361	-336	31
H(6C)	255	6436	-337	31
H(7A)	-15	8714	314	32
H(7B)	-496	8326	1018	32
H(7C)	-814	7793	299	32
H(8A)	1608	9764	641	20
H(9A)	2450	8950	-568	27
H(9B)	1998	10194	-464	27
H(11A)	1523	10186	2680	28
H(11B)	1754	9722	3436	28
H(11C)	983	9123	2974	28
H(12A)	2901	7169	2904	29
H(12B)	1834	7260	3114	29
H(12C)	2604	7862	3575	29
H(13A)	3210	10049	2364	27
H(13B)	3753	8896	2451	27
H(13C)	3437	9582	3119	27
H(14A)	3004	6454	1533	18
H(15A)	4585	7789	1464	20
H(16A)	5513	6264	1594	31
H(16B)	4739	5543	1210	31
H(16C)	4702	5694	2031	31

X-ray structure for 9a



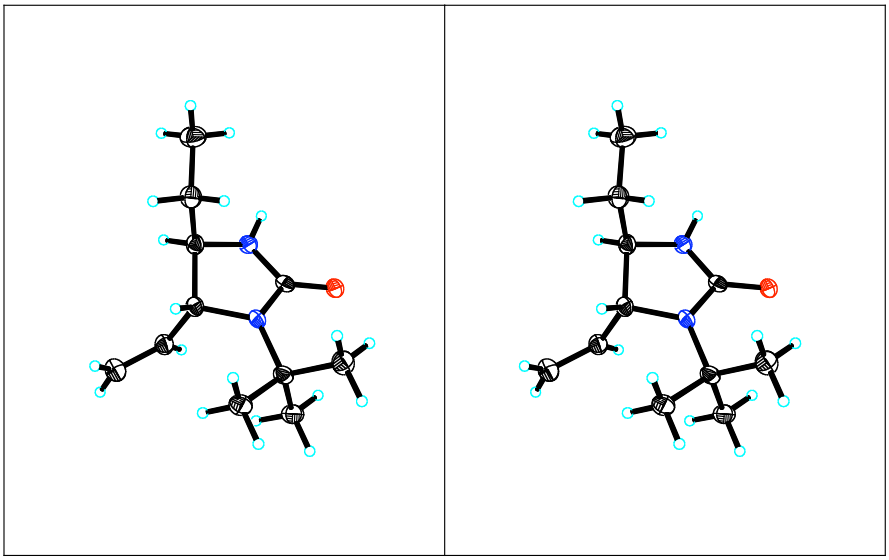


Table 1. Crystal data and structure refinement for **9a**.

Identification code	ys154_0m	
Empirical formula	C11 H20 N2 O	
Formula weight	196.29	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 6.0857(7) Å	α= 83.020(4)°.
	b = 8.7170(12) Å	β= 81.547(4)°.
	c = 11.3604(16) Å	γ = 85.252(4)°.
Volume	590.40(13) $Å^3$	
Z	2	
Density (calculated)	1.104 Mg/m^3	
Absorption coefficient	0.071 mm^{-1}	
F(000)	216	
Crystal size	0.22 x 0.17 x 0.05 mm^3	
Theta range for data collection	1.82 to 26.37°.	
Index ranges	-7<=h<=7, -10<=k<=10, -14<=l<=14	
Reflections collected	7809	
Independent reflections	2390 [R(int) = 0.0341]	
Completeness to theta = 26.37°	99.2 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.9967 and 0.9848	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2390 / 0 / 132	
Goodness-of-fit on F^2	1.033	
Final R indices [I>2sigma(I)]	R1 = 0.0415, wR2 = 0.0926	
R indices (all data)	R1 = 0.0613, wR2 = 0.1008	
Extinction coefficient	0.018(5)	
Largest diff. peak and hole	0.266 and -0.215 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **9a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	5203(2)	4788(1)	1620(1)	22(1)
N(1)	3250(2)	2657(1)	2490(1)	18(1)
N(2)	4006(2)	3057(2)	507(1)	20(1)
C(1)	4237(2)	3616(2)	1543(1)	17(1)
C(2)	2686(2)	1241(2)	2049(1)	20(1)
C(3)	2484(2)	1815(2)	720(1)	20(1)
C(4)	134(2)	2350(2)	489(1)	25(1)
C(5)	-1(3)	2957(2)	-819(1)	33(1)
C(6)	4431(3)	-77(2)	2143(1)	23(1)
C(7)	4022(3)	-1518(2)	2564(1)	32(1)
C(8)	3531(2)	2783(2)	3752(1)	20(1)
C(9)	2683(3)	4401(2)	4064(1)	28(1)
C(10)	5986(3)	2466(2)	3921(1)	26(1)
C(11)	2114(3)	1606(2)	4573(1)	26(1)

Table 3. Bond lengths [Å] and angles [°] for **9a**.

O(1)-C(1)	1.2385(17)
N(1)-C(1)	1.3752(18)
N(1)-C(2)	1.4715(18)
N(1)-C(8)	1.4866(18)
N(2)-C(1)	1.3562(18)
N(2)-C(3)	1.4583(18)
C(2)-C(6)	1.503(2)
C(2)-C(3)	1.550(2)
C(3)-C(4)	1.517(2)
C(4)-C(5)	1.527(2)
C(6)-C(7)	1.319(2)
C(8)-C(9)	1.526(2)
C(8)-C(11)	1.531(2)

C(8)-C(10)	1.532(2)
C(1)-N(1)-C(2)	109.14(11)
C(1)-N(1)-C(8)	122.55(12)
C(2)-N(1)-C(8)	124.53(11)
C(1)-N(2)-C(3)	111.33(12)
O(1)-C(1)-N(2)	125.42(12)
O(1)-C(1)-N(1)	125.73(13)
N(2)-C(1)-N(1)	108.84(12)
N(1)-C(2)-C(6)	113.80(12)
N(1)-C(2)-C(3)	101.64(11)
C(6)-C(2)-C(3)	110.93(12)
N(2)-C(3)-C(4)	113.46(12)
N(2)-C(3)-C(2)	100.33(11)
C(4)-C(3)-C(2)	114.15(12)
C(3)-C(4)-C(5)	112.95(13)
C(7)-C(6)-C(2)	124.75(15)
N(1)-C(8)-C(9)	109.08(12)
N(1)-C(8)-C(11)	108.73(12)
C(9)-C(8)-C(11)	108.14(12)
N(1)-C(8)-C(10)	110.17(12)
C(9)-C(8)-C(10)	110.56(13)
C(11)-C(8)-C(10)	110.12(12)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **9a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + \ldots + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	25(1)	19(1)	22(1)	2(1)	-4(1)	-8(1)
N(1)	20(1)	14(1)	18(1)	2(1)	-2(1)	-4(1)
N(2)	21(1)	21(1)	17(1)	3(1)	-2(1)	-8(1)
C(1)	15(1)	17(1)	19(1)	2(1)	-2(1)	0(1)
C(2)	21(1)	20(1)	19(1)	1(1)	-1(1)	-8(1)
C(3)	21(1)	19(1)	21(1)	-1(1)	-1(1)	-6(1)

C(4)	21(1)	26(1)	27(1)	1(1)	-2(1)	-7(1)
C(5)	27(1)	39(1)	33(1)	1(1)	-10(1)	-3(1)
C(6)	27(1)	20(1)	22(1)	-2(1)	-3(1)	-4(1)
C(7)	40(1)	24(1)	32(1)	-1(1)	-7(1)	-4(1)
C(8)	23(1)	20(1)	16(1)	2(1)	-1(1)	-2(1)
C(9)	34(1)	26(1)	24(1)	-4(1)	2(1)	-1(1)
C(10)	26(1)	28(1)	23(1)	1(1)	-6(1)	-3(1)
C(11)	31(1)	28(1)	18(1)	2(1)	0(1)	-7(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **9a**.

	x	y	z	U(eq)
HA	4200(30)	3660(20)	-148(16)	29(5)
H(2A)	1217	909	2477	24
H(3A)	3078	976	209	24
H(4A)	-441	3180	997	30
H(4B)	-834	1474	724	30
H(5A)	-1548	3291	-916	49
H(5B)	526	2132	-1326	49
H(5C)	933	3837	-1054	49
H(6A)	5938	145	1882	28
H(7A)	2535	-1783	2833	38
H(7B)	5214	-2291	2596	38
H(9A)	1109	4579	3960	42
H(9B)	3547	5175	3535	42
H(9C)	2850	4488	4898	42
H(10A)	6499	1421	3723	38
H(10B)	6151	2549	4756	38
H(10C)	6877	3226	3393	38
H(11A)	2633	557	4387	39
H(11B)	553	1808	4448	39
H(11C)	2249	1701	5410	39