SUPPLEMENTAL INFORMATION

A Convenient Oxazole C-2 Protecting Group; The Synthesis of 4 and 5-Substituted Oxazoles via Metallation of 2-Tri-iso-propylsilyloxazoles

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Table of Contents:

Data for compounds **5a -5l**, **6c**, **6d**, **6i**, and **6l**----------**S1-S3**

Copies of NMR data for compounds---**5f**, **5k**, **5j**, **5l** and **6l**----------**S4-S13**

1,3-oxazol-5-yl(phenyl)methanone (6i) ^{1}H NMR (399.87 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.95 (d, J = 7.0 Hz, 2H), 7.80 (s, 1H), 7.62 (tt, J = 7.4 , 2.0 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H). ^{13}C NMR (100.55 MHz, $CDCl_3$) δ 181.5, 153.8, 149.4, 136.4, 135.1, 133.6, 129.1, 128.9. IR (neat) 1656, 1558, 1473, 1332, 1130, 970, 892 cm $^{-1}$. HRMS calcd for $C_{10}H_7NO_2$ $[M+H]^+$: 174.05495, found 174.05532. Anal. Calcd for $C_{10}H_7NO_2$: C, 69.36; H, 4.07; N, 8.09; Found C, 69.01; H, 4.00; N, 7.91.

phenyl[2-[tris(1-methylethyl)silyl]-1,3-oxazol-5-yl]methanone (5i) ^{1}H NMR (399.87 MHz, $CDCl_3$) δ 8.03 (d, J = 8 Hz, 2H), 7.89 (s, 1H), 7.65 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.6 , 2H), 7.51 (t, J = 7.6 Hz, 2H), 1.5 (m, 3H), 1.2 (d, J = 7.4 Hz, 18H). ^{13}C NMR (100.55 MHz, $CDCl_3$) δ 181.8, 173.5, 151.4, 137.1, 135.5, 133.2, 129.3, 128.7, 18.4, 11.1.IR (neat) 1653, 1543, 1314, 1108, 988, 890 cm $^{-1}$. LRMS calcd for $C_{19}H_{27}NO_2Si$: 329.18, found $[M+H]^+$ = 330.2. Anal. Calcd for $C_{19}H_{27}NO_2Si$: C, 69.26; H, 8.26; N, 4.25; found C, 69.03; H, 8.37; N, 4.18.

1,3-oxazol-5-yl(phenyl)methanol (6c) ^{1}H NMR (399.87 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.4 (m, 5H), 6.77 (s, 1H), 5.84 (s, 1H), 3.70 (br s, 1H).^{13}C NMR (100.55 MHz, $CDCl_3$) δ 153.7, 151.2, 139.9, 128.7, 128.6, 126.6, 123.6, 68.3. Anal. Calcd $C_{10}H_9NO_2$: C, 68.56; H, 5.18; N, 8.00; Found C, 68.62; H, 5.09, N, 7.91. LRMS calcd $C_{10}H_9NO_2$: 175.1, found [M+H] 176.1.

2-[tris(1-methylethyl)silyl]-1,3-oxazole-5-carbaldehyde (5j) ^{1}H NMR (399.87 MHz, $CDCl_3$) δ 9.88 (s, 1H), 7.92 (s, 1H), 1.46 (m, 3H), 1.16 (d, J = 7.4 Hz,18H).^{13}C NMR (100.55 MHz, $CDCl_3$) δ 177.0, 174.9, 151.8, 136.5, 18.3, 11.0. HRMS calcd for $C_{13}H_{23}NO_2Si$ [M+H]: 254.15708, found 254.15805.

phenyl[2-[tris(1-methylethyl)silyl]-1,3-oxazol-5-yl]methanol (5c) ^{1}H NMR (399.87 MHz, $CDCl_3$) δ 7.42 (m, 5H), 6.93 (s, 1H), 5.93 (s, 1H), 1.39 (septet, J=7.5, 3H), 1.24 (d, J=0.9, 18H). ^{13}C NMR (100.56 MHz, $CDCl_3$) δ169.0, 154.9, 140.3, 128.6, 128.4, 126.6, 124.1, 68.8, 18.4, 11.0. IR (neat) 3190.49, 1042.16, 991.57, 730.81, 64.65 cm^{-1} Anal. Calcd. for $C_{19}H_{29}NO_2Si$: C 68.83, H 8.82, N 4.22. Found C 68.92, H 8.91, N 4.22. LRMS $C_{19}H_{29}NO_2Si$: calcd 331.2, found [M+H] 332.5.

5-methyl-2-[tris(1-methylethyl)silyl]-1,3-oxazole (5a) ^{1}H NMR (399.87MHz, $CDCl_3$) δ 6.81 (s, 1H), 2.38 (d, J= 1.1, 3H), 1.39 (septet, J=7.5, 3H), 1.24 (d, J=6.4,18H). ^{13}C NMR (100.55 MHz, C_6 D_6) δ 168.8, 150.3, 123.3, 18.3, 11.1, 10.2. Anal. Calcd for $C_{13}H_{25}NOSi$: C 65.21, H 10.52, N 5.85. Found C 65.15, H 10.51, N 5.83. HRMS calcd for $C_{13}H_{25}NOSi$: $[M+H]^+$ 240.17782, found 240.17882.

5-(tributylstannanyl)-2-[tris(1-methylethyl)silyl]-1,3-oxazole (5g) ^{1}H NMR (399.87 MHz, $CDCl_3$) δ 7.30 (s, 1H), 1.55 (m, 8H), 1.41 (m, 10H), 1.15 (d, J=7.4, 18H), 0.89 (t, J=7.3, 9H) ^{13}C NMR (100.56 MHz, $CDCl_3$) δ 172.5, 156.5, 136.7, 29.0, 27.2, 18.5, 13.7, 11.2, 10.3. Anal. Calcd for $C_{24}H_{49}NOSiSn$ C 56.03, H 9.60, N 2.72. Found C 55.71, H 9.54, N 2.72. LRMS calcd for $C_{24}H_{49}NOSiSn$ 515.26, found $[M+H]^+$ 516.3.

5-ethyl-2-[tris(1-methylethyl)silyl]-1,3-oxazole (5b) ^{1}H NMR (399.87 MHZ, $CDCl_3$) δ 6.81 (s, 1H), 2.70 (quartet, J= 7.4 Hz, 2H), 1.40 (septet, J= 7.5, 3H), 1.26 (t, J= 7.4, 3H), 1.14 (d, J=7.4, 18H). ^{13}C NMR (100.56 MHz, $CDCl_3$) δ 167.2, 156.2, 121.5, 19.2, 18.4, 12.0, 11.1. Anal. Calcd for $C_{14}H_{27}NOSi$: C 66.34, H 10.74, N 5.53. Found C 66.25, H 10.49, N 5.60. LRMS calcd for $C_{14}H_{27}NOSi$ 253.46, found $[M+H]^+$ 254.6.

5-(trimethylsilyl)-2-[tris(1-methylethyl)silyl]-1,3-oxazole (5d) ^{1}H NMR (399.87 MHz, $CDCl_3$) δ 7.29 (s, 1H), 1.40 (septet, J=7.5, 3H), 1.15 (d, J=7.4, 18H), 0.03 (s, 9H). ^{13}C NMR (100.56 MHz, $CDCl_3$) δ 172.2, 156.5, 135.4, 18.42, 11.1, -1.7. Anal. calcd for $C_{15}H_{31}NOSi_2$: C 60.54, H 10.50, N 4.71. Found C 60.84, H 10.43, N 4.65. LRMS calcd for $C_{15}H_{31}NOSi_2$: 297.2, found $[M+H]^+$ = 298.1.

5-(phenylmethyl)-2-[tris(1-methylethyl)silyl]-1,3-oxazole (5f) ^{1}H NMR (399.87 MHz, $CDCl_3$) δ 7.2-7.4 (m, 5H), 6.83 (s, 1H), 4.04 (s, 2H), 1.39 (septet, J= 7.4, 3H), 1.12 (d, J= 7.5, 18H). ^{13}C NMR (100.64 MHz, $CDCl_3$) δ 167.9, 153.1, 137.2, 128.6, 128.5, 126.6,

123.4, 32.0, 18.3, 10.9. HRMS calcd for $C_{19}H_{29}NOSi$. $[M+H]^+$ calcd for 316.20912; Found 316.20937.

4-methyl-5-phenyl-2-[tris(1-methylethyl)silyl]-1,3-oxazole (5k) ^{1}H NMR (400.25 MHz, $CDCl_3$) δ 7.55 (d, J= 8 Hz, 2H), 7.45 (t, J = 8 Hz, 2H), 7.2-7.3 (m, 1H), 2.48 (s, 3H), 1.39 (septet, J= 7.4, 3H), 1.12 (d, J= 7.5, 18H). ^{13}C NMR (100.64 MHz, $CDCl_3$) δ 166.1, 147.1, 131.7, 129.8, 128.7, 127.3, 125.4, 18.5, 13.5, 11.0 HRMS calcd for $C_{19}H_{29}NOSi$: $[M+H]^+$ calcd for 316.20912, found 316.20937.

4-methyl-5-phenyl-1,3-oxazole (6k) ^{1}H NMR (399.87) MHz, $CDCl_3$) δ 7.86, (s, 1H), 7.62 (dd, J = 8.4, 1.5Hz, 2H), 7.45 (m, 2H), 7.36 (m, 1H), 2.47 (s, 3H).

Phenyl[5-phenyl-2-[tris(1-methylethyl)silyl]-1,3-oxazol-4-yl]methanol (5l) ^{1}H NMR (399.87 MHz, $CDCl_3$) δ 7.55 (d, J= 7.3 Hz, 2H), 7.45 (d, J = 7.3 Hz, 2H), 7.2-7.4 (m, 6 H), 6.05 (s, 1H), 1.39 (septet, J= 7.4, 3H), 1.12 (d, J= 7.5, 18H). ^{13}C NMR (100.65 MHz, $CDCl_3$) δ 167.2, 147.6, 142.6, 136.4, 128.8, 128.6, 128.5, 128.2, 127.7, 127.2, 126.1, 69.0, 18.4, 11.0. HRMS calcd for $C_{25}H_{33}NO_2Si$ $[M+H]^+$ 408.2353, found 408.23707.

phenyl(5-phenyl-1,3-oxazol-4-yl)methanol (6l) ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.61 (d, J = 7.3 Hz, 2H),7.2-7.5 (m, 8H), 6.04 (s, 1H). ^{13}C NMR (100.61 MHz, CD_3CN) δ 150.3, 146.7, 142.7, 137.0, 129.0, 128.85, 128.2, 128.1, 127.4, 126.7, 126.6, 67.8. HRMS calcd for $C_{16}H_{13}NO_2$: $[M+Na]^+$ 274.08385, found 274.08399.

5-[(1,1-dimethylethyl)(dimethyl)silyl]-2-[tris(1-methylethyl)silyl]-1,3-oxazole (**5e)** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.24 (s, 6H), 0.91 (s, 9H), 1.12 (d. J=7.6 Hz, 18H), 1.4 (heptet, J=7.4 Hz, 3H), 7.30 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ -6.3, 11.1, 16.6, 18.4, 26.2, 136.5, 155.0, 172.3; LRMS calcd for $C_{18}H_{37}NOSi_2$: 339.2, found 339. Anal. Calcd for $C_{18}H_{37}NOSi_2$: C, 63.65; H, 10.98; N, 4.12. Found: C, 63.31: H, 11.05; N, 4.00.

5-(trimethylsilyl)-1,3-oxazole (6d) ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.29 (s, 9H), 7.22 (s, 1H), 8.04 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ -1.9, 135.3, 154.6, 155.3; LRMS calcd for $C_6H_{11}NOSi$: 141.1, found 141. Anal. Calcd for $C_6H_{11}NOSi$: C, 51.02; H, 7.85; N, 9.92. Found: C, 50.99; H, 7.46; N, 9.58.

4-prop-2-en-1-yl-2-[tris(1-methylethyl)silyl]-1,3-oxazole (5h) ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.09 (d, J=7.2 Hz, 18H), 1.35 (heptet, J=7.4 Hz, 3H), 3.40 (app dq, J=6.4, 1.2 Hz, 2H), 5.06–5.08 (m, 1H), 5.09-5.12 (m, 1H), 5.83-5.93 (m, 1H), 6.80 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.0, 18.4, 30.0, 117.3, 122.9, 132.9, 152.4, 167.7; LRMS calcd for $C_{15}H_{27}NOSi$: 265.2, found 265. Anal. Calcd for $C_{15}H_{27}NOSi$: C,67.87; H, 10.25; N, 5.28. Found: C, 67.80; H, 10.18; N, 5.28.