Intermolecular Rhodium(II)-Catalyzed Reactions with Silicon-Substituted Carbonyl Ylides

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General Remarks

The silylation of diazocompounds was conducted under an inert atmosphere of argon using standard Schlenk techniques. The solvents were distilled from sodium/benzophenone ketyl radical prior to use. ¹H- and ¹³C-NMR spectra were recorded on a Varian Unity 500 spectrometer at 500 MHz and 125 MHz, respectively, on an Inova 400 spectrometer at 400 and 100 MHz, and on a Mercury 300 spectrometer at 300 MHz and 75 MHz. The chemical shifts are given in ppm with internal referencing to the solvent peaks. IR spectra were measured on a Perkin Elmer 1760 FT spectrometer, MS spectra on a Varian MAT 212 and a Finnigan MAT 95 mass spectrometer, both with EI and CI ionization. Elemental analyses were carried out at the Institute of Organic Chemistry at the RWTH-Aachen on a Heraeus CHNO-Rapid apparatus. Melting points were measured on a Büchi Melting Point B-540 apparatus. Optical rotations were recorded on a Perkin-Elmer 241 Polarimeter.

α -Triorganylsilyl- α -Diazoacetates; General Procedure

A 1M solution of *N,N'*-dicyclohexylcarbodiimide (DCC) (52 mL, 52 mmol) in dichloromethane was added dropwise at rt to a stirred solution of Boc-glycine (8.8 g, 50 mmol), the corresponding alcohol (50 mmol), and dimethylaminopyridine (0.61 g, 5 mmol) in dichloromethane (150 mL). After addition, the reaction mixture was left stirring overnight. The precipitated urea was filtered off, and the filtrate was washed with 5% NaOH and 5% HCl. The organic phase was dried over MgSO₄, and evaporation of the solvent afforded crude Boc-protected glycine ester. HCl gas was bubbled through a stirred solution of the corresponding Boc-protected glycine ester in ethyl acetate at rt for 30 min. On cooling to ambient temperature, the precipitate was filtered off via sintered filtration, and washed with diethyl ether to afford the HCl-salt of the corresponding glycine ester. This was used without further purification in the next step. Sodium nitrite (1.7 g, 24 mmol) was added in small portions to a highly agitated ice-cooled mixture of the HCl-salt of the corresponding glycine ester (18 mmol) in water (50 mL) and chloroform (50 mL). After a minimum reaction time of 2 h, the mixture was warmed to ambient temperature. The lower organic phase was separated, and the water phase was extracted twice with chloroform. The combined organic layers were dried over MgSO₄, and removal of the solvent afforded the crude diazoacetate. This was purified via flash column chromatography (silica gel, petroleum ether/*tert*-butyl methyl ether, various gradients). To a solution of the corresponding benzyl α -diazoacetate (10 mmol) and ethyldiisopropylamine (1.29 g, 10 mmol) in diethyl ether (30 mL) was added dropwise at -78 °C a solution of trimethylsilyltriflate (2.22 g, 10 mmol) in diethyl ether (20 mL). The mixture was then stirred overnight, the precipitated ammonium salt was filtered off, and the solvent was evaporated. The crude silyldiazoacetate was purified by flash column chromatography (silica gel, petroleum ether/*tert*-butyl methyl ether, various gradients).

Compounds **1a**, **1b**, **1c** were prepared according to a known procedure.¹

(R)-(+)-1-Phenylethyl 2-diazo-2-trimethylsilylacetate (1d)

yield: 71%; yellow liquid; ¹H NMR (300 MHz, CDCl₃): δ 0.21 (s, 9H), 1.47 (d, *J* = 6.4 Hz, 3H), 5.89 (q, *J* = 6.4 Hz, 1H), 7.27-7.32 (m, 5H); ¹³C NMR (75 MHz, CDCl₃): δ -1.0, 22.9, 73.0, 126.2, 128.0, 128.7, 142.0, 169.4; MS: *m/z* = 262 (M, 3), 234 (12), 190 (13), 143 (10), 105 (100), 77 (16), 73 (53); IR (neat): $\tilde{\nu}$ = 2093, 1686, 1266, 1210, 1182, 1080, 847, 762, 698 cm⁻¹; [α]_D²³ = +12.5 (*c* 1.31, CHCl₃); Anal. calcd. for C₁₃H₁₈N₂O₂Si: C, 59.21; H, 6.91; N, 10.68. Found: C, 58.99; H, 6.95; N, 11.16

1-Phenylpropyl 2-diazo-2-trimethylsilylacetate (1e)

yield: 85%; yellow liquid; ¹H NMR (400 MHz, CDCl₃): δ 0.22 (s, 9H), 0.85 (t, *J* = 7.4 Hz, 3H), 1.72-1.83 (m, 1H), 1.84-1.95 (m, 1H), 5.69 (t, *J* = 6.9 Hz, 1H), 7.01-7.30 (m, 5H); ¹³C NMR (100 MHz, CDCl₃): δ 0.0, 11.3, 30.9, 79.0, 127.7, 128.9, 129.5, 141.8, 169.8; MS: *m/z* = 276 (M, 1), 119 (87), 91 (100), 73 (56); IR (neat): $\tilde{\nu}$ = 2969, 2091, 1687, 1266, 1211, 1182, 1079, 846, 762, 700 cm⁻¹; Anal. calcd. for C₁₄H₂₀N₂O₂Si: C, 60.83; H, 7.29; N, 10.13. Found: C, 60.40; H, 7.43; N, 10.45

Benzhydryl 2-diazo-2-trimethylsilylacetate (1f)

yield: 90%; yellow liquid; ¹H NMR (400 MHz, CDCl₃): δ 0.19 (s, 9H), 6.89 (s, 1H), 7.09-7.29 (m, 10H); ¹³C NMR (100 MHz, CDCl₃): δ 0.0, 78.4, 127.2, 128.2, 129.0, 129.2, 129.6, 129.7, 129.7, 130.1, 141.5, 169.5; MS: *m/z* = 324 (M, 5), 237 (6), 167 (100), 165 (18), 73 (9); IR (neat): $\tilde{\nu}$ = 2093, 1686, 1260, 1175, 1078, 1050, 846, 761, 699 cm⁻¹; Anal. calcd. for C₁₈H₂₀N₂O₂Si: C, 66.63; H, 6.21; N, 8.63. Found: C, 66.16; H, 6.28; N, 8.54

4-Methoxybenzyl 2-diazo-2-trimethylsilylacetate (1g)

yield: 78%; yellow liquid; ¹H NMR (500 MHz, CDCl₃): δ 0.24 (s, 9H), 3.81 (s, 3H), 5.11 (s, 2H), 6.89 (d, *J* = 8.9 Hz, 2H), 7.29 (d, *J* = 8.9 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃): δ -1.2, 27.2, 55.5, 66.4, 114.1, 128.6, 130.2, 159.8, 169.8; MS: *m/z* = 278 (M, 5), 250 (5), 121 (100), 73 (6); IR (neat): $\tilde{\nu}$ = 2958, 2091, 1683, 1614, 1516, 1375, 1303, 1250, 1211, 1174, 1079, 1037, 845, 766 cm⁻¹; Anal. calcd. for C₁₃H₁₈N₂O₃Si: C, 56.09; H, 6.52; N, 10.06. Found: C, 55.94; H, 6.60; N, 10.37

4-Nitrobenzyl 2-diazo-2-trimethylsilylacetate (1h)

yield: 82%; yellow solid; mp: 90.5-91.5 °C; ¹H NMR (300 MHz, CDCl₃): δ 0.27 (s, 9H), 5.27 (s, 2H), 7.51 (d, *J* = 8.6 Hz, 2H), 8.23 (d, *J* = 8.6 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃): δ -1.3, 65.1, 124.1, 128.5, 143.8; MS: *m/z* = 293 (M, 23), 210 (16), 136 (23), 89 (17), 73 (100), 45 (11); IR (KBr): $\tilde{\nu}$ = 2091, 1686, 1604, 1518, 1453, 1342, 1279, 1251, 1217, 1078, 849, 738 cm⁻¹; Anal. calcd. for C₁₂H₁₅N₃O₄Si: C, 49.13; H, 5.15; N, 14.32. Found: C, 49.51; H, 5.05; N, 13.96

4-Trifluoromethylbenzyl 2-diazo-2-trimethylsilylacetate (1i)

yield: 68%; yellow liquid; ^1H NMR (400 MHz, CDCl_3): δ 0.26 (s, 9H), 5.22 (s, 2H), 7.46 (d, $J = 8.2$ Hz, 2H), 7.62 (d, $J = 8.2$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ -1.3, 65.6, 125.7, 125.7, 125.8, 125.8, 128.2, 140.5; MS: $m/z = 316$ (M, 13), 233 (13), 159 (100), 140 (26), 109 (15), 73 (84), 45 (9); IR (neat): $\tilde{\nu} = 2094, 1690, 1327, 1268, 1169, 1128, 1068, 847\text{ cm}^{-1}$; Anal. calcd. for $\text{C}_{13}\text{H}_{15}\text{F}_3\text{N}_2\text{O}_2\text{Si}$: C, 49.36; H, 4.78; N, 8.86. Found: C, 49.65; H, 5.05; N, 9.10

5-Benzyl-2,2-dimethyl-5-triethylsilyl-1,3-dioxolan-4-one (3a)

yield: 71%; clear oil; ^1H NMR (300 MHz, CDCl_3): δ 0.43 (s, 3H), 0.68-0.77 (m, 6H), 1.00 (t, $J=8.2$ Hz, 9H), 1.38 (s, 3H), 2.93 (d, $J = 14.1$ Hz, 1H), 3.17 (d, $J = 14.1$ Hz, 1H), 7.12-7.21 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3): δ 2.4, 7.7, 27.8, 28.6, 41.0, 81.2, 111.1, 127.3, 128.5, 131.1, 137.2, 176.4; MS: $m/z = 320$ (M, 93), 233 (28), 173 (99), 115 (100), 91 (37), 87 (73), 59 (38); IR (neat): $\tilde{\nu} = 2955, 2915, 2879, 1769, 1383, 1265, 1230, 1086, 1010, 736, 701\text{ cm}^{-1}$; Anal. calcd. for $\text{C}_{18}\text{H}_{28}\text{O}_3\text{Si}$: C, 67.45; H, 8.80. Found: C, 67.10; H, 8.83

5-Benzyl-2-methyl-2-phenyl-5-tert-butyl dimethylsilyl-1,3-dioxolan-4-one (3b)

yield: 83%; clear syrup; ^1H NMR (400 MHz, CDCl_3): δ -0.39, -0.06, 0.21, 0.63 (4s, 6H), 0.96, 1.00, 1.15 (3s, 9H), 1.39, 1.67 (2s, 3H), 3.00-3.27 (m, 2H), 6.70-6.79 (m, 3H), 6.93-7.04 (m, 3H), 7.22-7.34 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3): δ -6.9, -6.4, -5.8, -5.5, 19.1, 19.4, 27.3, 27.4, 28.2, 28.4, 30.5, 31.4, 41.3, 41.3, 82.7, 82.7, 110.4, 110.7, 123.9, 124.7, 126.9, 127.4, 127.6, 127.8, 128.1, 128.1, 128.4, 128.6, 130.6, 131.3, 135.5, 137.1, 143.2, 143.6, 175.8, 176.0; MS: $m/z = 382$ (M, 70), 291 (11), 235 (45), 222 (70), 205 (23), 115 (14), 91 (23), 73 (100); IR (neat): $\tilde{\nu} = 2958, 2933, 2859, 1774, 1250, 1208, 1154, 1078, 839, 822, 812, 771, 698\text{ cm}^{-1}$; Anal. calcd. for $\text{C}_{23}\text{H}_{30}\text{O}_3\text{Si}$: C, 72.21; H, 7.90. Found: C, 71.86; H, 8.05

7-Benzyl-7-trimethylsilyl-5,8-dioxaspiro[3.4]octan-6-one (3c)

yield: 75%; clear oil; ^1H NMR (400 MHz, CDCl_3): δ 0.24 (s, 9H), 1.28-1.35 (m, 1H), 1.45-1.54 (m, 2H), 1.60-1.76 (m, 1H), 2.35-2.46 (m, 2H), 2.96 (d, $J = 14.0$ Hz, 1H), 3.20 (d, $J = 14.0$ Hz, 1H), 7.24-7.34 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3): δ -4.0, 10.6, 37.7, 37.8, 39.5, 81.4, 112.2, 127.1, 128.4, 128.6, 129.9, 130.6, 136.5, 175.9; MS: $m/z = 291$ (M+1, 14), 262 (62), 247 (20), 221 (80), 205 (65), 193 (52), 143 (25), 131 (100), 89 (43), 75 (94), 73 (88), 61 (48); IR (neat): $\tilde{\nu} = 3031, 3000, 2956, 2922, 1772, 1496, 1456, 1412, 1294, 1253, 1195, 1155, 1119, 1098, 1080, 976, 949, 929, 845, 772, 757, 728, 701, 626, 604\text{ cm}^{-1}$; Anal. calcd. for $\text{C}_{16}\text{H}_{22}\text{O}_3\text{Si}$: C, 66.17; H, 7.63. Found: C, 66.13; H, 7.44

2,7-Dibenzyl-7-trimethylsilyl-5,8-dioxaspiro[3.4]octan-6-one (3d)

yield: 86%; clear oil; ^1H NMR (400 MHz, CDCl_3): δ 0.14 (s, 9H), 0.84-0.96 (m, 1H), 1.30-1.42 (m, 1H), 1.72-1.79 (m, 1H), 2.09-2.24 (m, 2H), 2.33-2.74 (m, 2H), 2.94-3.26 (m, 2H), 7.09-7.33 (m, 10H); ^{13}C NMR (100 MHz, CDCl_3): δ -3.9, -3.9, 25.1, 25.8, 27.3, 27.4, 39.5, 39.6, 41.3, 42.4, 42.5, 42.6, 43.5, 43.6, 81.0, 81.4, 109.8, 110.2, 126.1, 126.2, 126.3, 127.2, 128.5, 128.5, 128.6, 128.7, 130.6, 130.7, 136.5, 136.6, 140.3, 140.6, 175.8, 176.1; MS: $m/z = 380$ (M, 3), 262 (96), 219 (7), 193 (7), 149 (7), 117 (13), 105 (100), 91 (80), 73 (75); IR (neat): $\tilde{\nu} = 2936, 1773, 1291, 1253, 1171, 1083, 847, 727, 701\text{ cm}^{-1}$; Anal. calcd. for $\text{C}_{23}\text{H}_{28}\text{O}_3\text{Si}$: C, 72.59; H, 7.42. Found: C, 73.02; H, 7.48

3-Benzyl-6-pentyl-3-trimethylsilyl-1,4-dioxaspiro[4.4]nonan-2-one (3e)

yield: 51%; clear oil; ^1H NMR (400 MHz, CDCl_3): δ 0.13 (s, 9H), 0.84-0.91 (m, 3H), 1.01-1.09 (m, 2H), 1.15-1.43 (m, 8H), 1.42-1.54 (m, 2H), 1.60-1.78 (m, 1H), 1.81-1.94 (m, 2H), 2.93-3.31 (m, 2H), 7.23-7.29 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3): δ -3.1, 14.4, 21.4, 22.9, 27.3, 28.8, 29.8, 32.1, 35.9, 37.8, 40.4, 48.1, 79.8, 120.9, 127.2, 128.4, 130.6, 136.7, 176.8; MS: m/z = 374 (M, 47), 257 (7), 227 (56), 205 (15), 165 (22), 91 (25), 73 (100); IR (neat): $\tilde{\nu}$ = 2957, 2931, 2860, 1771, 1251, 1112, 847, 700 cm^{-1} ; Anal. calcd. for $\text{C}_{22}\text{H}_{34}\text{O}_3\text{Si}$: C, 70.54; H, 9.15. Found: C, 70.27; H, 9.43

3-Benzyl-3-trimethylsilyl-1,4-dioxaspiro[4.5]decan-2-one (3f)

yield: 70%; clear crystals; mp: 83-84 $^\circ\text{C}$; ^1H NMR (500 MHz, CDCl_3): δ 0.22 (s, 9H), 1.27-1.35 (m, 4H), 1.37-1.44 (m, 1H), 1.58-1.75 (m, 5H), 2.99 (d, J = 14.0 Hz, 1H), 3.28 (d, J = 14.0 Hz, 1H), 7.23-7.31 (m, 5H); ^{13}C NMR (125 MHz, CDCl_3): δ -4.4, 22.0, 22.1, 23.4, 36.0, 36.5, 39.3, 79.0, 110.4, 126.0, 127.2, 129.6, 135.9, 175.1; MS: m/z = 318 (M, 52), 171 (100), 109 (11), 91 (20), 73.1 (53); IR (KBr): $\tilde{\nu}$ = 2965, 2947, 2927, 2848, 1760, 1452, 1287, 1266, 1248, 1197, 1098, 943, 849, 701 cm^{-1} ; Anal. calcd. for $\text{C}_{18}\text{H}_{26}\text{O}_3\text{Si}$: C, 67.88; H, 8.23. Found: C, 67.77; H, 8.26

3-Benzyl-6-phenyl-3-trimethylsilyl-1,4-dioxaspiro[4.5]decan-2-one (3g)

yield: 87%; clear crystals; mp: 159-160 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3): δ -0.46 (s, 9H), 0.96-1.02 (m, 1H), 1.41-1.56 (m, 2H), 1.68-1.76 (m, 1H), 1.79-1.87 (m, 1H), 1.91-1.97 (m, 1H), 2.01-2.09 (m, 1H), 2.29-2.37 (m, 1H), 3.18 (dd, J = 3.8 Hz, 12.1 Hz, 2H), 3.55 (d, J = 15.1 Hz, 1H), 7.30-7.52 (m, 10H); ^{13}C NMR (100 MHz, CDCl_3): δ -3.2, 24.1, 25.2, 25.4, 29.8, 39.5, 40.7, 41.6, 41.8, 50.7, 50.8, 80.2, 112.8, 126.8, 127.2, 127.4, 127.5, 128.1, 128.3, 128.4, 128.5, 130.2, 130.4, 130.7, 130.7, 130.8, 137.3, 139.3, 177.0; MS: m/z = 394 (M, 7), 174 (20), 130 (44), 117 (17), 91 (100), 73 (49); IR (KBr): $\tilde{\nu}$ = 2942, 2926, 1757, 1496, 1450, 1275, 1245, 1195, 1130, 1081, 930, 844, 761, 701 cm^{-1} ; Anal. calcd. for $\text{C}_{24}\text{H}_{30}\text{O}_3\text{Si}$: C, 73.05; H, 7.66. Found: C, 72.88; H, 7.78

2-Adamantyliden-5-benzyl-5-trimethylsilyl-1,3-dioxolan-4-one (3h)

yield: 98%; white solid; mp: 173.5-174 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3): δ 0.22 (s, 9H), 0.86-0.94 (m, 2H), 1.29-1.40 (m, 3H), 1.59-1.72 (m, 4H), 1.73-1.77 (m, 1H), 1.86-1.96 (m, 3H), 2.03-2.09 (m, 1H), 3.00 (d, J = 14.0 Hz, 1H), 3.27 (d, J = 14.0 Hz, 1H), 7.20-7.30 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3): δ -3.0, 26.7, 27.3, 27.3, 34.2, 34.4, 34.9, 37.1, 38.3, 39.2, 40.8, 80.6, 114.0, 127.2, 128.3, 130.7, 137.2, 176.3; MS: m/z = 370 (M, 100), 224 (16), 223 (78), 205 (14), 151 (9), 91 (21), 73 (60); IR (KBr): $\tilde{\nu}$ = 2933, 2891, 2860, 1761, 1251, 1203, 1116, 1095, 844, 700 cm^{-1} ; Anal. calcd. for $\text{C}_{22}\text{H}_{30}\text{O}_3\text{Si}$: C, 71.31; H, 8.16. Found: C, 71.02; H, 8.28

3-Benzyl-3-trimethylsilyl-1,4-dioxaspiro[4.4]nonan-2-one (3i)

yield: 84%; needle-like white crystals; mp: 62-63.5 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3): δ 0.24 (s, 9H), 0.61-0.69 (m, 1H), 1.03-1.11 (m, 1H), 1.39-1.56 (m, 2H), 1.60-1.68 (m, 2H), 1.83-1.96 (m, 2H), 2.97 (d, J = 14.0 Hz, 1H), 3.26 (d, J = 14.0 Hz, 1H), 7.24-7.34 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3): δ -3.5, 23.2, 23.5, 38.4, 39.0, 39.9, 80.8, 121.4, 127.2, 128.5, 130.8, 136.8, 176.1; MS: m/z = 304 (M, 61), 205 (10), 177 (11), 157 (100), 95 (16), 73 (89); IR (KBr): $\tilde{\nu}$ = 2980, 2960, 2931, 1761, 1346, 1246, 1210, 1163, 1106, 1078, 971, 844, 698, 606 cm^{-1} ; Anal. calcd. for $\text{C}_{17}\text{H}_{24}\text{O}_3\text{Si}$: C, 67.07; H, 7.95. Found: C, 66.85; H, 7.78

3-(1-Phenylethyl)-3-trimethylsilyl-1,4-dioxaspiro[4.4]nonan-2-one (3j)

yield: 78%; clear crystals; mp: 69.5-70 °C; ¹H NMR (300 MHz, CDCl₃): δ 0.06; 0.02; 0.13; 0.32 (4s, 9H), 0.60-0.68 (m, 1H), 1.38; 1.52 (2d, *J* = 7.5 Hz, 3H), 1.57-1.70 (m, 1H), 1.76-1.86 (m, 2H), 1.86-1.94 (m, 1H), 1.96-2.10 (m, 2H), 3.29; 3.46 (2q, *J* = 7.0 Hz, 2H), 7.23-7.42 (m, 5H); ¹³C NMR (75 MHz, CDCl₃): δ -2.5, -1.7, 17.7, 20.1, 22.1, 23.5, 23.7, 24.0, 39.0, 39.6, 39.8, 39.9, 43.8, 44.9, 83.6, 84.3, 121.3, 121.3, 127.2, 128.1, 128.5, 128.7, 129.3, 129.8, 141.8, 143.2, 175.7, 176.4; MS: *m/z* = 318 (M, 43), 219 (23), 214 (17), 157 (100), 105 (34), 95 (7), 73 (84); IR (KBr): $\tilde{\nu}$ = 2969, 2878, 1761, 1455, 1338, 1255, 1236, 1201, 1164, 1101, 969, 847, 768, 702 cm⁻¹; Anal. calcd. for C₁₈H₂₆O₅Si: C, 67.89; H, 8.23. Found: C, 67.89; H, 8.34

3-(1-Phenylpropyl)-3-trimethylsilyl-1,4-dioxaspiro[4.4]nonan-2-one (3k)

yield: 81%; needle-like white crystals, mp: 72.5-74 °C; ¹H NMR (400 MHz, CDCl₃): δ -0.06 (s, 9H), 0.75 (t, *J* = 7.2 Hz, 3H), 0.90-0.98 (m, 1H), 1.72-1.77 (m, 2H), 1.83-1.89 (m, 2H), 1.91-1.97 (m, 1H), 2.06-2.15 (m, 4H), 2.98 (dd, *J* = 3.0 Hz, 11.7 Hz, 1H), 7.30-7.42 (m, 5H); ¹³C NMR (100 MHz, CDCl₃): δ -2.9, -2.7, 12.5, 24.0, 24.0, 26.8, 39.8, 40.0, 52.2, 83.9, 121.3, 127.2, 128.3, 130.1, 140.7, 176.6; MS: *m/z* = 332 (M, 28), 303 (42), 157 (77), 119 (57), 105 (20), 91 (98), 73 (100); IR (KBr): $\tilde{\nu}$ = 2973, 2875, 1769, 1337, 1251, 1232, 1158, 965, 843, 703 cm⁻¹; Anal. calcd. for C₁₉H₂₈O₃Si: C, 68.63; H, 8.49. Found: C, 68.36; H, 8.62

3-Benzhydryl-3-trimethylsilyl-1,4-dioxaspiro[4.4]nonan-2-one (3l)

yield: 92%; clear oil; ¹H NMR (400 MHz, CDCl₃): δ 0.04 (s, 9H), 0.63-0.71 (m, 1H), 1.37-1.48 (m, 2H), 1.56-1.63 (m, 1H), 1.66-1.73 (m, 2H), 1.92-2.00 (m, 2H), 4.56 (s, 1H), 7.18-7.39 (m, 8H), 7.59 (d, *J* = 7.1 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ -1.7, 23.5, 23.6, 27.3, 38.9, 39.5, 56.0, 85.3, 121.5, 127.1, 127.4, 128.2, 128.4, 128.7, 130.7, 130.8, 139.9, 140.1, 175.8; MS: *m/z* = 380 (M, 29), 281 (30), 178 (22), 167 (100), 156 (53), 73 (42); IR (neat): $\tilde{\nu}$ = 2960, 1766, 1496, 1452, 1339, 1250, 1199, 1158, 1099, 968, 847, 736, 704, 594 cm⁻¹; Anal. calcd. for C₂₃H₂₈O₃Si: C, 72.59; H, 7.42. Found: C, 72.19; H, 7.57

3-(4-Methoxybenzyl)-3-trimethylsilyl-1,4-dioxaspiro[4.4]nonan-2-one (3m)

yield: 84%; clear oil; ¹H NMR (500 MHz, CDCl₃): δ 0.19 (s, 9H), 0.70-0.76 (m, 1H), 1.09-1.16 (m, 1H), 1.39-1.54 (m, 2H), 1.57-1.66 (m, 2H), 1.81-1.92 (m, 2H), 2.88 (d, *J* = 14.0 Hz, 1H), 3.16 (d, *J* = 14.0 Hz, 1H), 3.78 (s, 3H), 6.82 (d, *J* = 8.9 Hz, 2H), 7.13 (d, *J* = 8.9 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃): δ -3.6, 23.1, 23.4, 38.6, 38.9, 39.0, 55.5, 80.9, 113.9, 121.4, 128.9, 130.7, 131.8, 159.0, 176.3; MS: *m/z* = 334 (M, 29), 235 (7), 175 (12), 157 (20), 121 (100), 73 (29); IR (neat): $\tilde{\nu}$ = 2959, 1768, 1612, 1513, 1339, 1302, 1251, 1204, 1179, 1153, 1102, 1037, 966, 847 cm⁻¹; Anal. calcd. for C₁₈H₂₆O₄Si: C, 64.64; H, 7.83. Found: C, 64.58; H, 7.79

4-Nitrobenzyl 2-(1-cyclopentenyl)-2-trimethylsilylacrylate (4a)

yield: 73%; yellow/orange syrup; ¹H NMR (300 MHz, CDCl₃): δ 0.12 (s, 9H), 1.81-1.92 (m, 2H), 2.19-2.27 (m, 2H), 2.29-2.47 (m, 2H), 4.28 (s, 1H), 4.30-4.33 (m, 1H), 5.24 (q, *J* = 13.1 Hz, 31.2 Hz, 2H), 7.52 (d, *J* = 8.9 Hz, 2H), 8.20 (d, *J* = 8.9 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃): δ -3.4, 21.6, 28.9, 31.9, 64.7, 74.3, 94.8, 123.9, 124.1, 128.9, 129.1, 129.2, 143.4, 147.9, 161.7, 172.2; MS: *m/z* = 349 (M, 2), 284 (100), 212 (12), 149 (60), 138 (37), 106 (29); IR (neat): $\tilde{\nu}$ = 3476, 2959, 1727, 1607, 1524, 1349, 1320, 1252,

1192, 1111, 1062, 850, 740, 719, 700 cm^{-1} ; Anal. calcd. for $\text{C}_{17}\text{H}_{23}\text{NO}_5\text{Si}$: C, 58.43; H, 6.63. Found: C, 58.10; H, 6.43

Compounds **3n** and **4b** were obtained in a 1:5 ratio and their identification is only based on spectral data in this mixture.

3-(4-Trifluoromethylbenzyl)-3-trimethylsilyl-1,4-dioxaspiro[4.4]nonan-2-one (3n)

yield: 16%; ^1H NMR (300 MHz, CDCl_3): δ 0.20 (s, 9H), 0.64-0.74 (m, 1H), 1.11-1.19 (m, 1H), 1.43-1.56 (m, 2H), 1.59-1.67 (m, 2H), 1.81-1.92 (m, 2H), 2.98 (d, $J = 13.8$ Hz, 1H), 3.24 (d, $J = 13.8$ Hz, 1H), 7.32 (d, $J = 8.3$ Hz, 2H); 7.53 (d, $J = 8.3$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ -3.4, 23.2, 23.6, 38.6, 38.7, 39.6, 79.7, 113.9, 121.4, 125.4, 125.7, 128.7, 131.2, 177.8; MS: $m/z = 372$ (M, 24), 273 (19), 255 (12), 157 (100), 140 (35), 95 (17), 73 (68)

4-Trifluoromethylbenzyl 2-(1-cyclopentenyl-2-oxo)-2-trimethylsilylacetate (4b)

yield: 75%; ^1H NMR (300 MHz, CDCl_3): δ 0.10 (s, 9H), 1.88-1.95 (m, 2H), 2.17-2.28 (m, 2H), 2.33-2.48 (m, 2H), 4.24 (s, 1H), 4.29-4.32 (m, 1H), 5.19 (q, $J = 12.6$ Hz, 27.4 Hz, 2H), 7.46 (d, $J = 7.9$ Hz, 2H), 7.59 (d, $J = 7.9$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ -3.2, 21.6, 28.9, 31.9, 65.3, 74.3, 94.8, 125.3, 125.7, 128.7, 128.8, 129.5, 143.2, 147.4, 161.6, 172.2; MS: $m/z = 372$ (M, 2), 291 (11), 263 (6), 233 (8), 203 (5), 159 (100), 140 (3), 103 (9), 73 (14)

References

- 1) (a) Bolm, C.; Kasyan, A.; Heider, P.; Saladin, S.; Drauz, K.; Günther, K.; Wagner, C. *Org. Lett.* **2002**, 4, 2265. (b) Bolm, C.; Kasyan, A.; Drauz, K.; Günther, K.; Raabe, G. *Angew. Chem.* **2000**, 112, 2374; *Angew. Chem. Int. Ed.* **2000**, 39, 2288.