Electronic Supplementary Information for Dalton Transactions

Supporting Information

Unsuccessful attempts to add alcohols to a transient reverse-polarized silene - leading to a new benign route for base-free alcohol protection

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Experimental details

The ^{1}H and ^{13}C NMR spectra were recorded on Varian Unity 400 MHz (400 MHz for ^{1}H and 100 MHz for ^{13}C) spectrometers. Chemical shifts are reported in ppm, referenced to the residual solvent peak (chloroform, toluene). Mass spectra (m/z (relative intensity, %)) were obtained using a Finnigan MAT GCQ PLUS instrument (EI mode, 70 eV) if nothing else is noted.

Melting points are reported as their uncorrected values. FT-IR with ATR accessory, signals are reported as ($\tilde{\nu}$ / cm^{-1}, relative intensity). The microwave heated reactions were performed in a scientific microwave heating system (2.45 GHz), with control of pressure and temperature in suitable sealed reaction vessels.

Analytical TLC was performed on commercially available Merck TLC plates, coated with silica-gel 60 F_{254}, and compound visualization was achieved either with UV (254 nm) or phosphomolybdic acid reagent (20 % wt.) in ethanol, followed by heating. Preparative TLC was performed on commercially available Analtech TLC plates (20×20 cm, 1000 microns).

***N,N*-Dimethyl(*tris*(trimethylsilyl)silyl)methaneamide** $Me_2N(CO)Si(TMS)_3$ (**1**), was prepared according to literature procedure starting from TMS_4Si (5.204 g, 16.221 mmol).[i] Yield = 82 % (4.253 g, 13.301 mmol).

***N,N*-Diphenyl(*tris*(trimethylsilyl)silyl)methaneamide** $Ph_2N(CO)Si(TMS)_3$ (**12**), was prepared according to literature procedure starting from TMS_4Si (3.312 g, 10.323 mmol).[i] Yield = 67 % (3.070 g, 6.916 mmol).

N,N-Dimethyl(trimethylsilyl)methaneamide $Me_2N(CO)TMS$ (**14**) was prepared according to a literature procedure, starting from DMF (1.857 g, 25.410 mmol).[ii] Yield = 87% (3.211 g, 22.100 mmol).

***N*-cyclohexyl(triphenylsilyl)methaneamide** *c*-Hex(H)N(CO)$SiPh_3$ (**15**) was synthesized from triphenylsilyllithium (in 5 ml THF, 1.986 mmol) and *N*-cyclohexylisocyanate (0.248 g, 1.986 mmol) in a manner similar to that used by Baldwin and co-workers to prepare silylamides.[iii] Yield = 73 % (0.479 g, 1.450 mmol). Yellowish white crystals. ^{1}H NMR (toluene) δ: 6.86–7.68 (m, 15H), 4.97 (bs, 1H), 0.70 – 1.72 (m, 11H). ^{13}C NMR (toluene) δ: 160.7, 141.9, 135.26, 128.0, 127.3, 46.7, 34.1, 32.8, 25.3, 24.8. MS-CI (methane): 59.01 (29), 75 (100), 128.11 (45), 215.94 (52), 260.03 (27), 272.91 (68), 289.81 (52), 370.69 ($[M+H]^+$ 13). IR: 3392, 1673, 1427, 1108, 977, 703, 528.

Reactions with *N,N*-dimethyl(*tris*(trimethylsilyl)silyl)methaneamide (**1**):

Methoxy-*tris*(trimethylsilyl)silane $(TMS)_3SiOCH_3$ (**5a**):
Protocol 1. [MeOH (32.0 mg, 1 mmol)]:[**1** (79.9 mg, 0.250 mmol)] 4 h, 120 °C, yield = 92 % (64.1 mg, 0.230 mmol).
Protocol 2. [MeOH (32.0 mg, 1 mmol)]:[**1** (64.1 mg, 0.250 mmol)], 0.5 h, 180 °C, yield = 92 % (64.1 mg, 0.230 mmol).
Protocol 3. [MeOH (32.0 mg, 1 mmol)]:[**1** (64.1 mg, 0.250 mmol)]:[1 drop of triflic

acid], 0.5 h, r.t., yield 96 % (66.9 mg, 0.240 mmol).
Protocol 4. [MeOH (32.0 mg, 1 mmol)]:[**1** (64.1 mg, 0.250 mmol)]:[1 drop of iPr$_2$EtN], 33 h, 120 °C., yield 96 % (66.9 mg, 0.240 mmol).
Protocol 5. [MeOH (6.15 mg, 0.192 mmol)]: [**1** (79.9 mg, 0.250 mmol)], 1 h, 180 °C, yield = 93 % (49.8 mg, 0.179 mmol).[iv]

Ethoxy-*tris*(trimethylsilyl)silane $(TMS)_3SiOCH_2CH_3$ (**5b**):
Protocol 1. [EtOH (47.9 mg, 1.040 mmol)]:[**1** (84.4 mg, 0.260 mmol)], 8 h, 120 °C, yield = 90 % (68.5 mg, 0.234 mmol).
Protocol 2. [EtOH (47.9 mg, 1.040 mmol)]:[**1** (84.4 mg, 0.260 mmol)], 0.8 h, 180 °C, yield = 89 % (67.7 mg, 0.231 mmol).
Protocol 5. [EtOH (8.8 mg, 0.192 mmol)]: [**1** (79.9 mg, 0.250 mmol)], 6 h, 180 °C, yield = 96 % (53.9 mg, 0.184 mmol).
Colourless viscous oil. ^{1}H NMR δ: 0.19 (s, 27H, SiMe3), 1.13 (t, J = 5.6 Hz, 3H), 3.53 (q, J = 5.6 Hz, 2H). ^{13}C NMR δ: 0.3, 18.8, 63.6. MS: 292 (82), 277 (M^+ 100), 263 (88), 207 (86), 193 (72), 147 (29), 73 (64). IR: 2950.50, 2895.01, 144.31, 1378.23, 1366.06, 1243.40, 1170.67, 1119.23, 1006.21, 829.51, 742.98, 705.09, 686.23.

***iso*-Propoxy-*tris*(trimethylsilyl)silane** $(TMS)_3SiO$*i*Pr (**5c**):
Protocol 1. [*i*PrOH, (60.1 mg, 1 mmol)]:[**1** (79.9 mg, 0.250 mmol)], 11 h, 120 °C, yield = 87 % (66.6 mg, 0.210 mmol).
Protocol 2. [*i*PrOH, (60.1 mg, 1 mmol)]:[**1** (79.9 mg, 0.250 mmol)], 1.1 h, 180 °C yield = 85 % (65.2 mg, 0.219 mmol).
Protocol 5. [*i*PrOH (11.6 mg, 0.192 mmol),]:[**1** (79.9 mg, 0.250 mmol)], 25 h, 180 °C, yield = 89 % (52.5 mg, 0.171 mmol).[v]

***tert*-Butoxy-*tris*(trimethylsilyl)silane** $(TMS)_3SiO$*t*Bu (**5d**):
Protocol 1. [*t*BuOH (74.1 mg, 1.00 mmol)]:[**1** (79.9 mg, 0.25 mmol)], 120 °C, no reaction.
Protocol 2. [*t*BuOH (74.1 mg, 1.00 mmol)]:[**1** (79.9 mg, 0.25 mmol)], 352 h, 180 °C, yield = 18 % (14.4 mg, 0.045 mmol).
Protocol 3. [*t*BuOH, (74.1 mg, 1.00 mmol)]:[**1** (64.1 mg, 0.240 mmol)]:[1 drop of triflic acid], 33 h, r.t., yield 56 % (44.9 mg, 0.140 mmol).
Protocol 6. [*t*BuOH, (14.3 g, 0.192 mmol)]:[**1** (79.9 mg, 0.25 mmol)], 0.17 h, 240 °C, yield = 96 % (59.2 mg, 0.185 mmol).[35]
Colourless viscous oil. ^{1}H NMR δ: 1.32 (s, 9H), 0.30 (s, 27H). ^{13}C NMR δ: -0.49, 31.6. MS: 72.76 (46), 148.75 (27), 206.76 (32), 245.88 (100), 304.21 (62), 320.96 (M+ 32). IR: 2950.07, 2894.02, 1557.97, 1485.85, 1366.39, 1242.50, 1096.40, 823.08, 686.22.

Phenoxy-*tris*(trimethylsilyl)silane $(TMS)_3SiOPh$ (**5e**):
Protocol 1. [PhOH (94.1 mg, 0.192 mmol)]:[**1** (79.9 mg, 0.250 mmol)], 1.1 h, 120 °C, yield = 40 % (34.1 mg, 0.100 mmol).
Protocol 2. [PhOH (94.1 mg, 0.192 mmol)]:[**1** (79.9 mg, 0.250 mmol)], 0.5 h, 180 °C, yield = 60 % (51.1 mg, 0.150 mmol).
Protocol 5. [PhOH (18.1 mg, 0.192 mmol)]:[**1** (79.9 mg, 0.250 mmol)], 2.5 h, 180 °C, yield = 94 % (61.6 mg, 0.181 mmol).

Colourless viscous oil, ^{1}H NMR δ: 7.18-7.22 (m 2H), 6.79-6.92 (m, 3H), 0.20 (s, 27H). ^{13}C NMR δ: 158.7, 129.2, 120.9, 119.6, 0.1. MS: 73.27 (15), 149.18 (14), 207.06 (37) 249.04 (26), 325.02 (100), 340.90 (M+ 38). IR: 3037.25, 2949.61, 2894.00, 1594.14, 1489.29, 1242.66, 1161.64, 895.90, 857.12, 828.09, 756.96, 699.73, 688.67.

Allyloxy*tris*(trimethylsilyl)silane $(TMS)_3SiOCH_2CH=CH_2$ **(5f)**:
Protocol 1. [Allyl alcohol (62.7 mg, 1.080 mmol)]:[**1** (86.6 mg, 0.270 mmol)], 1 h, 120 °C, yield = 63 % (51.8 mg, 0.170 mmol).
Protocol 2. [Allyl alcohol (62.7 mg, 1.080 mmol)]:[**1** (86.6 mg, 0.270 mmol)], 0.25 h, 180 °C, yield = 78 % (64.2 mg, 0.211 mmol).
Protocol 5. [Allyl alcohol (11.2 mg, 0.192 mmol)]:[**1** (79.9 mg, 0.250 mmol)], 4 h, 180 °C, yield = 93 % (54.5 mg, 0.179 mmol).
Colourless clear crystals, ^{1}H NMR δ: 5.82-5.91 (m, 1H), 5.21-5.27 (m, 1H), 5.05-509 (m, 1H), 4.03-4.05 (m, 2H), 0.2 (s, 27H). ^{13}C NMR δ: 137.5, 113.5, 68,3, 0.3. MS: 73.24 (19), 207.06 (22), 263.10 (23), 289.01 (46), 304.84 (M+ 100). IR: 2949.47, 2893.93, 2834.67, 1645.32, 1370.84, 1243.63, 1126.98, 1066.12, 1024.79, 992.06, 917.77, 816.89, 778.68, 742.61, 685.98. m.p. 58.9-59.1 °C.

Benzyloxy-*tris*(trimethylsilyl)silane $(TMS)_3SiOCH_2C_6H_5$ (**5g**):
Protocol 1. [BnOH (92.7 mg, 0.857 mmol)]:[**1** (68.5 mg, 0.214 mmol)], 1 h, 120 °C, yield = 68 % (51,6 mg, 0.146 mmol).
Protocol 2. [BnOH (92.7 mg, 0.857 mmol)]:[**1** (68.5 mg, 0.214 mmol)], 0.25 h, 180 °C yield = 84 % (63.8 mg, 0,180 mmol).
Protocol 5. [BnOH (21.1 g, 0.192 mmol)]:[**1** (79.9 mg, 0.250 mmol)] 4 h, 180 °C, yield = 91 % (62.1 mg, 0.175 mmol).[vi]

Octoxy-*tris*(trimethylsilyl)silane $C_8H_{17}OSi(TMS)_3$ (**5h**):
Protocol 5. [Octanol (72.5 mg, 0.192 mmol)]:[**1** (79.9 mg, 0.250 mmol)] 7 h, 180 °C, yield = 91 % (66.0 mg, 0.175 mmol).
Colourless semisolid. ^{1}H NMR δ: 3.45 (t, 2H), 1.46 (m, 2H), 1.27 (m, 10H), 0.88 (m, 3H), 0.18 (s, 27H). ^{13}C NMR δ: 68.1, 33.1, 30.9, 29.4, 29.3, 25.8, 15.4, 14.1, 0.3. MS: 72.76 (32), 192.64 (87), 206.68 (100), 248.79 (10), 263.00 (75), 376.85 (M^+ 29). IR: 2950.45, 2894.84, 1440.10, 1378.39, 1365.77, 1243.59, 1170.39, 1119.63, 1007.11, 829.49, 743.70, 705.02, 685.58.

1-Methylcyclohexoxy-*tris*(trimethylsilyl)silane
1-Me-1-*c*-Hex-OSi(TMS)$_3$ (**5i**):
Protocol 5. [1-methylcyclohexan-1-ol (22.0 mg, 0.192 mmol)]:[**1** (79.9 mg, 0.250 mmol)], 1.17 h, 240 °C, yield = 92 % (61.0g, 0.177 mmol.
Colourless viscous oil). ^{1}H NMR δ: 1.63–1.80 (m, 2H), 1.22–1.58 (m, 8H), 1.17 (s, 3H), 0.42 (s, 27H), ^{13}C NMR δ: 68.4, 41.9, 30.1, 24.0, 22.2, 3.1. This substance was characterized in toluene-d_8, shifts were reported relative to the toluene methyl signal of 2.09 (^{1}H) and 20.4 (^{13}C) ppm, respectively. MS: 72.77 (22), 84.78 (100), 148.82 (26), 206.73 (15), 245.96 (9), 361.07 (M^+ 30). IR: 2950.55, 1439.10, 1243.66, 828.63, 756.96.

***Tris*(trimethylsilyl)-2-methylbutyrate** $(CH_3)_2CHCH_2CO_2Si(TMS)_3$ (**5j**):

Protocol 5. [Isovaleric acid (19.6 g, 0.192 mmol)]:[1 (79.9 mg, 0.250 mmol)], 2 h, 180 °C, conversion = 95 %. ^{1}H NMR δ: 2.91 (d, 2H), 1.77 (m, 1H), 1.13 (d, 6H), 0.41 (s, 27H). ^{13}C NMR δ: 139.1, 40.3, 23.5, 22.3, 0.9.

Reactions with *N,N*-dimethyl(trimethylsilyl)methaneamide (10):

***iso*-Propoxytrimethylsilane** *i*PrOTMS (**12c**):
Protocol 7: [*i*PrOH (25.5 mg, 0.424 mmol)]:[(80.0 mg, 0.551 mmol)], 25 h, r.t., CH_2Cl_2, conversion = 94 %.
Protocol 8: [*i*PrOH (25.5 mg, 0.424 mmol)]:[(80.0 mg, 0.551 mmol)], 28 h, r.t., DMF, conversion = 96 %.[vii]

***tert*-Butoxytrimethylsilane** *t*BuOTMS (**12d**):
Protocol 7: [*t*-BuOH (31.4 mg, 0.424 mmol)]:[(80.0 mg, 0.551 mmol)], 48 h, r.t., CH_2Cl_2, conversion = 97 %.
Protocol 8: [*t*-BuOH (31.4 mg, 0.424 mmol)]:[(80.0 mg, 0.551 mmol)], 49 h, r.t., DMF, conversion = 92 %.[viii]

Phenoxytrimethylsilane PhOTMS (**12e**):
Protocol 7: [PhOH (39.9 mg, 0.424 mmol)]:[(80.0 mg, 0.551 mmol)], 30 h, r.t., CH_2Cl_2, conversion = 99 %.
Protocol 8: [PhOH (39.9 mg, 0.424 mmol)]:[(80.0 mg, 0.551 mmol)], 33 h, r.t., DMF, conversion = 81 %.[ix]

Allyloxy-trimethylsilane AllylOTMS (**12f**):
Protocol 7: [Allyl alcohol (24.9 mg, 0.424 mmol)]:[**10** (80.0 mg, 0.551 mmol)], 15 h, r.t., CH_2Cl_2, conversion = 90 %.
Protocol 8: [Allyl alcohol (24.9 mg, 0.424 mmol)]:[**10** (80.0 mg, 0.551 mmol)], 19 h, r.t., DMF, conversion = 89 %.[x]

Benzyloxytrimethylsilane BnOTMS (**12g**):
Protocol 7: [BnOH (45.8 mg, 0.424 mmol)]:[(80.0 mg, 0.551 mmol)], 13 h, r.t., CH_2Cl_2, conversion = 97 %.
Protocol 8: [BnOH (45.8 mg, 0.424 mmol)]:[(80.0 mg, 0.551 mmol)], 16 h, r.t., DMF, conversion = 91 %.[xi]

Octoxytrimethylsilane *n*-C_8H_{17}OTMS (**12h**):
Protocol 7: [OctOH (55.2 mg, 0.424 mmol)]:[(80.0 mg , 0.551 mmol)], 18 h, r.t., CH_2Cl_2, conversion = 87 %.
Protocol 8: [OctOH (55.2 mg, 0.424 mmol)]:[(80.0 mg, 0.551 mmol)], 15 h, r.t., DMF, conversion = 88 %.[xii]

1-Methylcyclohexoxytrimethylsilane 1-Me-*c*-Hex-OTMS (**12i**):
Protocol 7: [1-Me-1-OH-*c*-Hex (40.3 mg, 0.424 mmol)]:[**10** (80.0 mg, 0.551 mmol)], 53 h, r.t., CH_2Cl_2, conversion = 96 %.[31]
Protocol 8: [1-Me-1-OH-*c*-Hex (40.3 mg, 0.424 mmol)]:[**10** (80.0 mg, 0.551 mmol)], 56 h, r.t., DMF, conversion = 86 %.[xiii]

Trimethylsilyl 2-Methylbuturate $(CH_3)_2CH_2CH_2CO_2TMS$ (**12j**):
Protocol 7: [$(CH_3)_2CHCH_2CO_2H$ (43.3 mg, 0.424 mmol)]:[**10** (80.0 mg, 0.551 mmol)] 6 h, r.t., CH_2Cl_2, conversion = 87 %,
Protocol 8: [$(CH_3)_2CHCH_2CO_2H$ (43.3 mg, 0.424 mmol)]:[**10** (80.0 mg, 0.551 mmol)] 9 h, r.t., DMF, conversion = 91 %, in agreement with commercial available material.

Butyl-trimethylsilyl thioether *n*BuSTMS (**12k**):
Protocol 7: [BuSH (40.3 mg, 0.424 mmol)]:[**10** (80.0 mg, 0.551 mmol)], 40 h, r.t., CH_2Cl_2, conversion = 84 %.
Protocol 8: [BuSH (mg, 0.424 mmol)]:[**10** (80.0 mg, 0.551 mmol)], 42 h, r.t., DMF, conversion = 82 %.[xiv]

1-Phenyl-2-trimethylsilanyloxyethanol $PhCHOHCH_2OTMS$ (**12l**):
Protocol 7: [$PhCHOHCH_2OH$ (69.2 mg, 0.501 mmol)]:[(80.0 mg, 0.551 mmol)], 27 h, r.t., CH_2Cl_2, conversion = 96 %, selective priamary alcohol protection of 85%.
Protocol 8: [$PhCHOHCH_2OH$ (69.2 mg, 0.501 mmol)]:[(80.0 mg, 0.551 mmol], 27 h, r.t., DMF, conversion = 91 %, selective primary alcohol protection of 82%.[xv]

4-Trimethylsilanyloxyphenol $4\text{-}HOC_6H_4CH_2OTMS$ (**12m**):
Protocol 7: [$HOC_6H_4CH_2OH$ (62.2 mg, 0.501 mmol)]:[(80.0 mg, 0.551 mmol)], 15 h, r.t., CH_2Cl_2, conversion = 95 %, selective priamary alcohol protection of 82%.
Protocol 8: [$HOC_6H_4CH_2OH$ (62.2 mg, 0.501 mmol)]:[(80.0 mg, 0.551 mmol)], 15 h, r.t., DMF, conversion = 94 %, selective priamary alcohol protection of 82%.[xvi]

Trimethylsilanyloxyacetic acid $HOCH_2CH_2OTMS$ (**12n**):
Protocol 7: [$HOCH_2CH_2OH$ (44.6 mg, 0.501 mmol)]:[(80.0 mg, 0.551 mmol)], 28 h, r.t., CH_2Cl_2, conversion = 86 %, selective alcohol protection of 83 %.
Protocol 8: [$HOCH_2CH_2OH$ (44.6 mg, 0.501 mmol)]:[(80.0 mg, 0.551 mmol)], 28 h, r.t., DMF, conversion = 83 %, selective alcohol protection of 78 %.[xvii]

2-Trimethylsilanyloxyethanethiol HSCH2CH2OTMS (**12o**):
Protocol 7: [$HSCH_2CH_2OH$ (39.1 mg, 0.455 mmol)]:[(80.0 mg, 0.551 mmol)], 20 h, r.t., CH_2Cl_2, conversion = 93 %, selective alcohol protection of 83 %.
Protocol 8: [$HSCH_2CH_2OH$ (39.1 mg, 0.455 mmol)]:[(80.0 mg, 0.551 mmol)], 20 h, r.t., DMF, conversion = 87 %, selective alcohol protection of 76 %.[xviii]

Reactions with *N*-cyclohexyl(triphenylsilyl)methaneamide (11):

Methoxytriphenylsilane $MeOSiPh_3$ (**13a**):
Protocol 9. [MeOH (6.2 mg, 0.192 mmol)]:[**11** (82.9 mg, 0.250 mmol)], 1 h, 180 °C, yield = 94 % (52.4 mg, 0.180 mmol.[xix]

Ethoxytriphenylsilane $EtOSiPh_3$ (**13b**):
Protocol 9. [EtOH (8.8 mg, 0.192 mmol)]:[**11** (82.9 mg, 0.250 mmol)], 1.5 h, 180 °C, yield = 93 % (54.4 mg, 0.179 mmol.[xix]

***iso*-Propoxytriphenylsilane** iPrOSiPh$_3$ (**13c**):
Protocol 9. [*i*PrOH (11.6 mg, 0.192 mmol)]:[**11** (82.9 mg, 0.250 mmol)], 2.5 h, 180 °C, yield = 88 % (53.8 mg, 0.169 mmol).[xx]

Phenoxytriphenylsilane PhOSiPh$_3$ (**13e**):
Protocol 9. [PhOH (18.1 mg, 0.192 mmol)]:[**11** (82.9 mg, 0.250 mmol)], 2 h, 180 °C, yield = 85 % (57,5 mg, 0.163 mmol).[xxi]

Allyloxytriphenylsilane AllylOSiPh$_3$ (**13f**):
Protocol 9. [Allyl alcohol (11.2 mg, 0.192 mmol)]:[**11** (82.9 mg, 0.250 mmol)], 1.75 h, 180 °C, yield = 90 % (54.7 mg, 0.173 mmol).[xxii]

Benzyloxytriphenylsilane BnOSiPh$_3$ (**13g**):
Protocol 9. [BnOH (21.1 g, 0.192 mmol)]:[**11** (82.9 mg, 0.250 mmol)], 1.75 h, 180 °C, yield = 87 % (61.2 mg, 0.167 mmol).[xxiii]

Octoxytriphenylsilane $C_8H_{17}OSiPh_3$ (**13h**):
Protocol 9. [OctOH (25.0 mg, 0.192 mmol)]:[**11** (82.9 mg, 0.250 mmol)], 2 h, 180 °C, yield = 93 % (69.4 mg, 0.179 mmol.[xxiv,xxv]

Cycloadduct formation from thermolysis of silylamides in presence of 2,3-dimethyl-buta-1,3-diene and alcohol

Reactions of 1 with 2,3-dimethylbuta-1,3-diene and *iso*-propanol:
To a solution of **1** (51.8 mg, 0.170 mmol) in toluene (0.6 ml) in a NMR-tube 2,3-dimethylbutadiene (139.7 mg, 1.700 mmol) and *iso*-propanol (11.2 mg 0.187 mmol) was added and the NMR tube was flame sealed. The NMR-tube was heated to 180 °C for 30 h. The reaction was then purified on preparative TLC (pentane:EtOAc (90:10)) yielding 27 % (0.041 mmol, 18.4 mg) of the cycloadduct (**4**),[i] and 66 % (0.112 mmol, 34.4 mg) of the proteced alcohol (**5c**).

Reactions of 8 with 2,3-dimethylbuta-1,3-diene and methanol:
To a solution of **8** (60.0 mg, 0.135 mmol) in toluene (0.7 ml) in a NMR-tube 2,3-dimethylbutadiene (22.2 mg, 0.270 mmol) and methanol (8.7 mg 0.270 mmol) was added and the NMR tube was flame sealed. The NMR-tube was heated to 120 °C for 4 h. The reaction was then purified on preparative TLC (pentane:EtOAc (90:10)) yielding 92 % (0.124 mmol, 65.2 mg) of the cycloadduct.[i]

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