Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information

Dehydrogenative Coupling of Alcohols and Carboxylic Acids with Hydrosilanes Catalyzed by a Salen Mn(V) complex

Srikanth Vijjamarri, Vamshi K. Chidara, Jana Rousova, and Guodong Du*

Department of Chemistry, University of North Dakota, 151 Cornell Street Stop 9024, Grand Forks, North Dakota 58202, United States.

Experimental Section

1. General

All the reagents and substrates were obtained from commercial sources. Deuterated solvents were obtained from Cambridge isotope laboratories. The Mn(V) nitrido Salen complex, used as a catalyst, was synthesized by the reported literature procedure. ^{1}H NMR and ^{13}C NMR analyses were performed on Bruker AVANCE-500 NMR spectrometer using Topspin 1.3 software, and signals were referenced to residual peaks of $CDCl_3$ and CD_3CN. GC analyses were performed on 5890 GC with 5972 MS equipped with an autosampler (6890 series, Agilent Technologies, Santa Clara, CA, USA). Injections were performed in the splitless mode for 0.50 min at 250 °C and the injection volume was 1 µL. The separation was performed using a 45-m long HP-5MS capillary column, with 0.25 mm internal diameter (I.D.) and 0.25 µL film thickness (J&W Scientific, Folsom, CA, USA). A constant carrier gas (helium) at a flow rate of 1.5 mL/min was maintained during the analysis. Two temperature programs were used. The first started at 40°C held for 1 min, followed by a gradient of 35 °C/min to 80 °C, then a gradient of 20 °C/min to 300 °C and held for 10 min. The second program started at 50°C held for 1 min, followed by a gradient of 35 °C/min to 80 °C, then a gradient of 20 °C/min to 320 °C and held for 3 min. The MS data in total ion chromatograms (TIC) were acquired in the mass range of m/z of 50–700 at a scan rate 2.67 scan/s using the EI of 70 eV. The solvent delay was set to 3.8 minutes.

2. General procedure for dehydrogenative coupling reactions

Reactions were performed under normal conditions without exclusion of air, or under inert conditions under N_2. Valved NMR sample tubes, capable of holding high pressure, were used as reaction vessels without stirring. ^{1}H NMR spectroscopy was used to monitor the reaction progress using phenyltrimethyl silane as an internal standard referenced to $CDCl_3$ (7.26 ppm) and CD_3CN (1.94 ppm). The resultant products were characterized by ^{1}H and ^{13}C NMR and GC-MS analysis in comparison with literature data.

Under normal benchtop conditions, 0.5 mol% catalyst (for alcohols) or 1.0 mol% catalyst (for carboxylic acids) were loaded into an NMR tube, followed by the addition of 1 equivalent substrate (0.7-0.8 mmol scale for alcohols, 0.4-0.6 mmol scale for carboxylic acids), stoichiometric equivalents of silane, 5 mol% internal standard, and 0.3–0.5 mL deuterated solvent. The reaction mixture was heated to 80 °C with an oil bath, and the reaction progress was monitored by ^{1}H NMR. After the reaction was complete or nearly complete, the mixture was transferred to a round bottomed flask with dichloromethane. After removal of solvents, the mixture was purified via flash chromatography using silica with hexane-EtOAc as eluent.

For reactions under inert conditions, all the reagents, substrates and solvents were degassed and dried prior to use. Solids substances were dried under reduced pressure and liquids were

degassed followed by drying over activated 4Å molecular sieves. Inert condition reactions were carried out under a dry nitrogen atmosphere, employing standard Schlenk line and dry box techniques. Typically, inside a glove box, 0.5 mol% catalyst was loaded into an NMR tube followed by the addition of 1 equivalent substrate, stoichiometric equivalents of silane, 5 mol% internal standard and 0.3–0.5 mL deuterated solvent. The reaction mixture was heated to 80 °C with an oil bath, and the reaction progress was monitored by ^{1}H NMR. Pure product was obtained after isolation *via* flash chromatography using ethyl acetate/hexanes solvent system.

3. NMR and GC-MS characterization data

Table 1, Entry 7: $PhCH_2OSiPh_3$: Isolated yield: 30%. ^{1}H NMR (500 MHz, $CDCl_3$, 298K, δ): 7.68-7.64 (m, 6H, Si*Ph*$_3$), 7.44-7.24 (m, 14H, OCH_2*Ph* and Si*Ph*$_3$), 4.89 (2, 2H, O*C*H_2Ph). ^{13}C {1H} NMR (500 MHz, $CDCl_3$, 298K, δ): 140.76, 135.64, 134.22, 130.25, 128.40, 128.02, 127.25, 126.55 (*Ph*), 65.78 (O*C*H_2).

Table 2, Entry 1: $(CH_3CH_2CH_2CH_2O)_2SiPh_2$ [1] **:** ^{1}H NMR (500 MHz, $CDCl_3$, 298K, δ): 7.7-7.66 (m, 4H, Ph), 7.45-7.35 (m, 6H, Ph), 3.81 (t, $J_{H\text{-}H}$ = 6.0, 2H, O*C*$H_2$$CH_3$), 1.61 (m, 2H, OCH_2*C*$H_2$$C_2H_5$), 1.24 (m, 2H, OC_2H_4*C*$H_2$$CH_3$), 0.92 (t, $J_{H\text{-}H}$ = 7.02, 3H, *C*H_3). ^{13}C {1H} NMR (500 MHz, $CDCl_3$, 298K, δ): 135.06, 134.79, 130.25, 127.93 (Ph), 63.03 (O*C*H_2), 34.75 (OCH_2*C*$H_2C_2H_5$), 19.12 (*C*H_2CH_3), 17.24 (*C*H_3).

Table 2, Entry 2: $(CH_3)_2CHOSiHPh_2$ [1]**:** ^{1}H NMR (500 MHz, $CDCl_3$, 298K, δ): 7.69 (dd, $J_{H\text{-}H}$ = 7.7, $J_{H\text{-}H}$ = 1.5, 4H, *o*-Ph), 7.6-7.35 (m, 6H, *m*,*p*-Ph), 4.85 (s, 1H, Si*H*), 4.22 (sept, $J_{H\text{-}H}$ = 6.2, 1H, C*H*), 1.27 (d, $J_{H\text{-}H}$ = 6.1, 6H, CH_3). ^{13}C {1H} NMR (500 MHz, $CDCl_3$, 298K, δ): 135.18 (*o*-Ph), 134.84 (*i*-Ph), 130.42 (*p*-Ph), 128.16 (*m*-Ph), 67.56 (O*C*H(CH_3)$_2$), 25.49 (OCH(*C*H_3)$_2$). GC/MS: t_R = 10.06 min; m/z 241 (M^+), 227, 211, 199, 183, 164 (100), 149, 136, 122, 105, 91.

Table 2, Entry 3: $(CH_3)_3COSiHPh_2$ [1,2]: ^{1}H NMR (500 MHz, $CDCl_3$, 298K, δ): 7.68-7.64 (m, 4H, *Ph*), 7.46−7.40 (m, 6H, *Ph*), 5.60 (s, 1H, Si*H*), 1.38 (s, 9H, C*H*$_3$). ^{13}C {1H} NMR (500 MHz, $CDCl_3$, 298K, δ): 135.24, 134.55, 130.62, 128.15 (Ph), 67.56 (O*C*), 25.83 (*C*H_3). GC/MS: t_R = 9.58 min; m/z 256(M^+), 241, 199, 183 (100), 178, 123, 105, 91.

Table 2, Entry 4: (OCy)$HSiPh_2$ [1]: ^{1}H NMR (500 MHz, $CDCl_3$, 298K, δ): 7.61 (dd, $J_{H\text{-}H}$ = 7.6, $J_{H\text{-}H}$ = 1.6, 4H, *Ph*), 7.46-7.40 (m, 6H, *Ph*), 5.48 (s, 1H, Si*H*), 3.82 (m, 1H, C*H*), 1.87−1.22 (m, 10H, C*H*$_2$). ^{13}C {1H} NMR (500 MHz, $CDCl_3$, 298K, δ): 134.83, 134.58, 130.37, 128.08 (Ph), 73.27 (O*C*H), 35.53, 25.76, 24.31 (*C*H_2). GC/MS: t_R = 11.7 min; m/z 281 (M^+), 267, 253, 239, 204 (100), 199, 183, 128, 105, 77. A minor component assignable to $(OCy)_2SiPh_2$ is also observed: t_R = 14.3 min; m/z 380 (M^+), 303, 281, 226 (100), 214, 205, 181, 152, 105, 77.

Table 2, Entry 5 and 6: $(PhCH_2O)_2SiPh_2$ [1,2]**:** ^{1}H NMR (500 MHz, $CDCl_3$, 298K, δ): 7.75 (dd, $J_{H\text{-}H}$ = 7.8, 1.5, 4H, *o*-$SiPh_2$), 7.45-7.40 (m, 4H, *o*-CH_2Ph), 7.39-7.35 (m, 4H, *m*-CH_2Ph), 7.34-7.29(m, 6H, *m/p*-$SiPh_2$), 7.25-7.20 (m, 2H, *p*-CH_2Ph), 4.85 (s, 4H, PhC*H*$_2$). ^{13}C {1H} NMR (500 MHz, $CDCl_3$,

298K, δ): 140.72 (*i*-PhCH$_2$), 135.42 (*o*-PhSi), 132.29 (*i*-PhSi), 130.6 (*p*-PhSi), 128.4 (*m*-PhCH$_2$), 128.2 (*m*-PhSi), 127.5 (*p*-PhCH$_2$), 127.5 (*o*-PhCH$_2$), 65.05 (O*C*H$_2$Ph). GC/MS: t_R = 16.7 min; m/z 396 (M^+), 376, 349, 335, 318, 305, 289, 275, 259, 240, 227, 212, 199, 183, 167, 151, 134, 121, 105, 91 (100).

Table 2, Entry 7: $CH_3OSi(OEt)_3$: ^{1}H NMR (500 MHz, $CDCl_3$, 298K, δ): 3.87 (q, J_{H-H} = 6.96, 6H, OC*H*$_2$CH$_3$), 3.60 (s, 3H, CH$_3$), 1.25 (t, J_{H-H} = 6.96, 9H, OCH$_2$C*H*$_3$). 0.93 (t, J_{H-H} = 6.97, 3H, CH$_3$). ^{13}C {1H} NMR (500 MHz, $CDCl_3$, 298K, δ): 59.38 (O*C*H$_2$CH$_3$), 51.30 (*C*H$_3$), 18.99 (O*C*H$_2$CH$_3$). GC/MS: t_R = 4.41 min; m/z 194 (M^+), 179 (100), 165, 149, 135, 121, 105, 93, 77.

Table 2, Entry 8: $CH_3CH_2CH_2CH_2OSi(OEt)_3$ [4]: ^{1}H NMR (500 MHz, $CDCl_3$, 298K, δ): 3.86 (q, J_{H-H} = 6.96, 6H, OC*H*$_2$CH$_3$), 3.78 (t, J_{H-H} = 6.7, 2H, OC*H*$_2$C$_3$H$_7$), 1.57 (m, 2H, OCH$_2$C*H*$_2$C$_2$H$_5$), 1.38 (m, 2H, OC$_2$H$_4$C*H*$_2$CH$_3$), 1.24 (t, J_{H-H} = 6.96, 9H, OCH$_2$C*H*$_3$). 0.93 (t, J_{H-H} = 6.99, 3H, CH$_3$). ^{13}C {1H} NMR (500 MHz, $CDCl_3$, 298K, δ): 63.37 (O*C*H$_2$C$_3$H$_7$), 59.31 (O*C*H$_2$CH$_3$), 34.56 (OCH$_2$*C*H$_2$C$_2$H$_5$), 18.99 (OCH$_2$*C*H$_3$), 18.23 (OC$_2$H$_4$*C*H$_2$CH$_3$), 13.96 (CH$_3$). GC/MS: t_R = 6.62 min; m/z 235 (M^+), 221, 207, 193, 179, 163, 149, 135, 119, 107, 91, 79 (100), 63, 45

Table 2, Entry 9: $(CH_3)_2CHCH_2CH_2OSi(OEt)_3$ [4]: ^{1}H NMR (500 MHz, $CDCl_3$, 298K, δ): 3.87 (q, 6H, J_{H-H} = 6.96, OC*H*$_2$CH$_3$), 3.80 (t, 2H, J_{H-H} = 6.86, OC*H*$_2$C$_4$H$_9$), 1.73 (m, C*H*), 1.48 (m, 2H, C*H*$_2$C$_3$H$_7$), 1.24 (t, J_{H-H} = 6.96, 6H, OCH$_2$C*H*$_3$), 0.90 (t, J_{H-H} = 6.8, 3H, C*H*$_3$). ^{13}C {1H} NMR (500 MHz, $CDCl_3$, 298K, δ): 62.03 (O*C*H$_2$C$_4$H$_9$), 59.31 (O*C*H$_2$CH$_3$), 41.38 (OCH$_2$*C*H$_2$C$_3$H$_7$), 24.70 (*C*H), 22.76 (*C*H$_3$)$_2$, 18.29 (OCH$_2$*C*H$_3$). GC/MS: t_R = 7.8 min; m/z 249 (M^+), 234, 219, 207, 191, 174, 163 (100), 149, 135, 119, 107, 91, 79, 63.

Table 2, Entry 10: $Ph_2CHOSi(OEt)_3$: ^{1}H NMR (500 MHz, $CDCl_3$, 298K, δ): 7.43 (d, J_{H-H} = 7.8, 2H, *Ph*), 7.26-7.32 (m, 8H, *Ph*), 6.09 (s, 1H, O*CH*), 3.75 (q, J_{H-H} = 6.9, 6H, OC*H*$_2$CH$_3$), 1.19 (t, J_{H-H} = 6.9, 9H, OCH$_2$C*H*$_3$). ^{13}C {1H} NMR (500 MHz, $CDCl_3$, 298K, δ): 144.20, 128.34, 127.32, 126.66 (Ph), 77.02 (O*C*H), 59.38 (O*C*H$_2$CH$_3$), 18.18 (OCH$_2$*C*H$_3$). GC/MS: t_R = 11.57 min; m/z 346 (M^+), 331, 317, 300, 289, 281, 269, 253, 239, 224, 211, 195, 181, 167 (100), 152, 135, 119, 107, 91, 79, 63.

Table 2, Entry 11: $CH_2=CHCH_2CH_2OSi(OEt)_3$: ^{1}H NMR (500 MHz, $CDCl_3$, 298K, δ): 5.84 (m, 1H, CH$_2$C*H*), 5.09 (m, 2H, C*H*$_2$CH), 3.82-3.86 (m, 8H, C*H*$_2$OSi(OC*H*$_2$CH$_3$)$_3$, 2.35 (m, 2H, C$_2$H$_3$C*H*$_2$CH$_2$O), 1.24 (t, J_{H-H} = 6.9, 9H, OCH$_2$C*H*$_3$). ^{13}C {1H} NMR (500 MHz, $CDCl_3$, 298K, δ): 135.16 (CH$_2$*C*H), 116.88 (*C*H$_2$CH), 63.19 (C$_3$H$_5$*C*H$_2$O), 59.51 (O*C*H$_2$CH$_3$), 37.03 (C$_2$H$_3$*C*H$_2$), 18.32 (OCH$_2$*C*H$_3$). GC/MS: t_R = 5.93 min; m/z 234 (M^+), 219, 204, 193 (100), 174, 163, 148, 135, 119, 105, 91.

Table 2, Entry 12: $CHCCH_2CH_2OSi(OEt)_3$: ^{1}H NMR (500 MHz, $CDCl_3$, 298K, δ): 3.82-3.88 (m, 8H, C*H*$_2$OSi(OC*H*$_2$CH$_3$), 2.49 (m, 2H, C$_2$HC*H*$_2$), 1.98 (m, C*H*), 1.24 (t, J_{H-H} = 6.9, 9H, OCH$_2$C*H*$_3$). ^{13}C {1H} NMR (500 MHz, $CDCl_3$, 298K, δ): 81.15 (CH*C*), 69.66 (*C*HC), 62.02 (C$_3$H$_3$*C*H$_2$O), 59.51 (O*C*H$_2$CH$_3$), 22.5 (CHC*C*H$_2$), 18.32 (OCH$_2$*C*H$_3$). GC/MS: t_R = 6.13 min; m/z 231 (M^+), 217, 193 (100), 163, 149, 135, 119, 107, 91.

Table 2, Entry 13: $PhCHCHCH_2OSi(OEt)_3$: ^{1}H NMR (500 MHz, $CDCl_3$, 298K, δ): 7.3-7.4 (m, 5H, *Ph*), 6.68-6.65 (m, 1H, PhC*H)*, 6.39-6.36 (m, 1H, C*H*CH_2), 4.54-4.51 (m,2H, C*H*$_2$OSi(OEt), 3.93-3.91, (m, 6H, OC*H*$_2$$CH_3$), 1.29-1.27 (m, 6H, OCH_2C*H*$_3$). ^{13}C {1H} NMR (500 MHz, $CDCl_3$, 298K, δ): 137.07, 130.78, 128.73, 128.03, 127.7, 126.63 (*Ph,* Ph*C*H, PhCH*C*H), 64.53 (O*C*H_2), 59.51 (O*C*H_2CH_3), 18.32 (OCH_2*C*H_3). GC/MS: t_R = 10.62 min; m/z 296 (M^+), 281, 267, 252, 237, 223, 208, 193, 177, 163, 149, 135, 115 (100), 97, 79.

Table 2, Entry 14: $CH_3(CO)CH_2CH_2CH_2OSi(OEt)_3$: ^{1}H NMR (500 MHz, $CDCl_3$, 298K, δ): 3.85 (q, J_{H-H} =6.99, 6H, OC*H*$_2$$CH_3$), 3.79 (t, J_{H-H} = 6.13, 2H, OC*H*$_2$), 2.56 (t, J_{H-H} = 7.3, 2H, OCH_2CH_2C*H*$_2$), 2.16 (s, 3H, C*H*$_3$), 1.85 (m, 2H, OCH_2C*H*$_2$), 1.24 (m, 9H, OCH_2C*H*$_3$). ^{13}C {1H} NMR (500 MHz, $CDCl_3$, 298K, δ): 208.9 (*CO*), 62.57, (O*C*H_2), 59.31, (O*C*H_2CH_3), 39.98 (*C*H_3), 30.25 (OCH_2CH_2*C*H_2), 26.45 (OCH_2*C*H_2), 18.32 (OCH_2*C*H_3). GC/MS: t_R = 7.77 min; m/z 264 (M^+) is not observed, 249, 234, 219, 207, 191, 175, 163 (100), 149, 135, 119, 107, 91.

Table 2, Entry 15: $(C_6H_9)CH_2OSi(OEt)_3$: ^{1}H NMR (500 MHz, $CDCl_3$, 298K, δ): ^{1}H NMR (500 MHz, $CDCl_3$, 298K, δ): 5.77-5.59 (m, 2H, C*H*=C*H*), 3.85 (q, J_{H-H} = 6.8, 6H, OC*H*$_2$$CH_3$), 3.65 (m, 2H, C*H*$_2$O), 2.36-1.54 (m, 7H, C*H*C*H*$_2$C*H*$_2$C*H*$_2$*)*, 1.25 (t, J_{H-H} = 5.7, 9H, OCH_2C*H*$_3$).

Table 2, Entry 16: $PhOSi(OEt)_3$: ^{1}H NMR (500 MHz, $CDCl_3$, 298K, δ): 7.45 (m, 1H, *o*-Ph), 7.18-7.12 (m, 2H, *p*-Ph), 6.92 (m, 2H, *m*-Ph), 3.91 (q, J_{H-H} =6.96, 6H, OC*H*$_2$$CH_3$), 1.24 (t, J_{H-H} = 6.96, 9H, C*H*$_3$). ^{13}C {1H} NMR (500 MHz, $CDCl_3$, 298K, δ): 153.93, 129.63, 122.19, 119.52 (Ph), 59.89 (O*C*H_2CH_3), 18.21 (OCH_2*C*H_3). GC/MS: t_R = 8.43 min; m/z 256 (M^+) (100), 241, 228, 211, 197, 181, 167, 155, 137, 119, 107, 94, 79, 63, 45.

Table 2, Entry 17: *p*-$MeO-C_6H_4OSi(OEt)_3$: ^{1}H NMR (500 MHz, $CDCl_3$, 298K, δ): 6.95-6.75 (m, 4H, Ph), 3.86 (m, 6H, O-C*H*$_2$), 3.77 (s, 3H, OC*H*$_3$), 1.24 (m, 9H, O-CH_2C*H*$_3$). ^{13}C {1H} NMR (500 MHz, $CDCl_3$, 298K, δ): 154.73, 147.7, 120.1, 114.5 (*Ph*), 59.86 (O-*C*H_2CH_3), 55.85 (O*C*H_3), 18.24 (O-CH_2*C*H_3). GC/MS: t_R = 9.87 min; m/z 286 (M^+), 271, 258, 242, 227, 215, 197, 185, 163 (100), 151, 135, 119, 108, 91, 79.

Table 2, Entry 18: *p*-^{t}Bu-$C_6H_4OSi(OEt)_3$: ^{1}H NMR (500 MHz, $CDCl_3$, 298K, δ): 7.25-6.58 (m, 4H, Ph), 3.96-3.92 (m, 6H, O-C*H*$_2$), 1.31 (s, 9H, ^{t}Bu), 1.23 (t, 9H, O-CH_2C*H*$_3$). ^{13}C {1H} NMR (500 MHz, $CDCl_3$, 298K, δ): 153.8, 144.2, 126.54, 118.6 (*Ph*), 59.8 (O-*C*H_2CH_3), 34.27 (4° *C*), 31.68 (^{t}Bu), 18.2 (O-CH_2*C*H_3). GC/MS: t_R = 9.6 min; m/z 312 (M^+), 297 (100), 281, 267, 253, 241, 223, 209, 194, 177, 155, 107, 91.

Table 2, Entry 19: *p*-NO_2-$C_6H_4OSi(OEt)_3$: ^{1}H NMR (500 MHz, $CDCl_3$, 298K, δ): 8.18 (m, 2H, *m*-Ph), 6.94 (m, 2H, *o*-Ph), 3.89-3.87 (m, 6H, O-C*H*$_2$), 1.25-1.22 (m, 9H, O-CH_2C*H*$_3$). ^{13}C {1H} NMR (500 MHz, $CDCl_3$, 298K, δ): 161.8, 141.72, 126.8, 115.9 (Ph), 59.69 (O-*C*H_2CH_3), 18.02 (O-CH_2*C*H_3).

Table 2, Entry 20: *p*-Cl-$C_6H_4OSi(OEt)_3$: ^{1}H NMR (500 MHz, $CDCl_3$, 298K, δ): 7.23-7.20 (m, 2H, *Ph*), 6.98-6.93 (m, 2H, *Ph*), 3.94-3.91 (m, 6H, O-C*H*$_2$), 1.27-1.23 (t, 9H, O-CH_2C*H*$_3$). ^{13}C {1H} NMR (500 MHz, $CDCl_3$, 298K, δ): 152.6, 129.6, 127.12, 117.3 (*Ph*), 59.95 (O-*C*H_2CH_3), 18.24 (O-CH_2*C*H_3).

GC/MS: t_R = 9.55 min; m/z 290 (M^+), 275, 262, 245, 230, 218, 202, 188, 174, 163, 147, 135, 119, 97, 79 (100).

Table 3, Entry 1: $(OEt)_3SiOCH_2CH_2CH_2CH_2OSi(OEt)_3$: ^{1}H NMR (500 MHz, $CDCl_3$, 298K, δ): 3.89-3.85 (m, 10H, $(CH_3CH_2O)_3SiOCH_2CH_2CH_2CH_2OSi(OCH_2CH_3)_3$, 1.64 (m, 4H, CH_2CH_2), 1.24 (m, 9H, OCH_2CH_3. ^{13}C {1H} NMR (500 MHz, $CDCl_3$, 298K, δ): 63.57 $(-C_3H_6CH_2OSi),)_3$, 59.70 (OCH_2CH_3), 28.79 ($OCH_2CH_2CH_2CH_2O$), 18.51 (OCH_2CH_3).

Table 3, Entry 2: 1,3-Dioxa-2,2-diphenyl-2-silacycloheptane [3] **:** ^{1}H NMR (500 MHz, $CDCl_3$, 298K, δ): 7.76-7.73 (m, 4H, *Ph*), 7.30-7.47 (m, 6H, *Ph*), 4.10-4.06 (m, 4H, CH_2CH_2OSi), 1.89 (m, 4H, CH_2CH_2OSi). ^{13}C {1H} NMR (500 MHz, $CDCl_3$, 298K, δ): 134.89, 133.41, 130.53, 128.12 (*Ph*), 65.37 (OCH_2), 32.67. GC/MS: t_R = 11.4 min; m/z 270 (M^+), 192 (100), 181, 114, 91, 77.

Table 3, Entry 3: 4,4,5,5-tetramethyl-2,2-diphenyl-1,3-dioxa-2-silacyclopentane [5] **:** ^{1}H NMR (500 MHz, $CDCl_3$, 298K, δ): 7.67-7.64 (m, 4H, *m*-Ph), 7.44-7.38 (m, 6H, *o,p*-Ph), 1.33 (s, 12H, CH_3). ^{13}C {1H} NMR (500 MHz, $CDCl_3$, 298K, δ): 134.8, 133.6, 130.5, 127.7 (Ph), 82.25 (OC), 25.82 (CH_3). GC/MS: t_R = 11.07 min; m/z 298 (M^+), 283, 268, 253, 240, 225, 181(100), 123, 105, 77.

Table 3, Entry 4: 2,4,4,5,5-pentamethyl-2-phenyl-1,3-dioxa-2-silacyclopentane [5] **:** ^{1}H NMR (500 MHz, $CDCl_3$, 298K, δ): 7.66 (m, 2H, o-*Ph*), 7.41-7.37 (m, 3H, *m,p-Ph*), 1.33 (s, 6H, CMe_2), 1.25 (s, 6H, CMe_2), 0.5 (s, 3H, $SiCH_3$). ^{13}C {1H} NMR (500 MHz, $CDCl_3$, 298K, δ): 135.66, 133.7, 130.42, 128.08 (Ph), 82.01 (OC), 25.96 (CH_3), -0.5 ($SiCH_3$).

Table 4, Entry 1: $PhCOOSi(OEt)_3$: ^{1}H NMR (500 MHz, $CDCl_3$, 298K, δ): 8.13-8.09 (m, 2H, *Ph*), 7.56-7.50 (m, 3H, *Ph*), 3.89-3.85 (m, 6H, O-CH_2), 1.29-1.25 (t, 9H, $O\text{-}CH_2CH_3$). ^{13}C {1H} NMR (500 MHz, $CDCl_3$, 298K, δ): 165.50 (CO), 133.57, 130.95, 130.52, 128.57 (*Ph*), 59.29 ($O\text{-}CH_2CH_3$), 18.16 ($O\text{-}CH_2CH_3$).

Table 4 Entry 2: $CH_3CH(Ph)COOSi(OEt)_3$: ^{1}H NMR (500 MHz, $CDCl_3$, 298K, δ): 7.35-7.3 (*m*, 2H, *Ph*), 7.26-7.22 (m, 3H, *Ph*), 3.85-3.82 (m, 6H, O-CH_2), 1.53-1.51 (m, 3H, CH_3), 1.25-1.22 (m, 9H, $O\text{-}CH_2CH_3$). ^{13}C {1H} NMR (500 MHz, $CDCl_3$, 298K, δ): 173.00 (CO), 140.41, 128.68, 127.66, 127.24 (*Ph*), 59.95 ($O\text{-}CH_2CH_3$), 46.82 (CH), 18.22 ($O\text{-}CH_2CH_3$), 17.80 (CH_3). GC/MS: t_R = 7.37 min; m/z 297 $[M\text{-}CH_3]^+$, 283, 269, 253, 225, 209, 150, 105 (100), 91, 77.

Table 4 Entry 3: $C_2H_5COOSi(OEt)_3$: ^{1}H NMR (500 MHz, $CDCl_3$, 298K, δ): ^{1}H NMR (500 MHz, $CDCl_3$, 298K, δ): 3.84-3.87 (m,6H, O-CH_2), 2.29 (q, 2H, CH_2), 1.21 (m, 9H, $O\text{-}CH_2CH_3$), 1.06 (t, 3H, CH_3). ^{13}C {1H} NMR (500 MHz, $CDCl_3$, 298K, δ): 173.5 (CO), 59.29 ($O\text{-}CH_2CH_3$), 28.91 (CH_2) 18.24 ($O\text{-}CH_2CH_3$), 9.3 (CH_3). GC/MS: t_R = 6.05 min; m/z 236 (M^+), 191, 163, 135, 119, 107, 91, 79 (100).

4. References

1. M. A. Esteruelas, M. Olivan, A. Vlez, *Inorg. Chem*.,2013, **52**, 12108−12119.

2. M. Kahnes, H. Gorls, L. Gonzalez, M. Westerhausen, *Organometallics*, 2010, **29**, 30198-3107.
3. A. Grajewska, M. Oestreich, *Synlett*, 2010, **16**, 2482-2484.
4. Y. Zhi, Z. Mingdong, S. De, A. Chakkittaandiyil, P. Pattiyil, R. W. Herbert, *Angew. Chem. Int. Ed*., 2015, **54**, 10225 –10229.
5. D. Mukherjee, R. R. Thompson, A. Ellern, A. D. Sadow, *ACS Catal.*, 2011, **1**, 698–702.