Self-regeneration of a silylium ion catalyst in carbonyl reduction

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Electronic Supplementary Information

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1 General Information

All reactions were performed in flame-dried glassware using a glove box (O₂ < 0.5 ppm, H₂O < 0.5 ppm) or Schlenk techniques under a static pressure of argon. Reactions at low temperatures were performed using an ethanol cooling bath and a cryostat. Liquids or solutions were transferred either with syringes or canulas. Solvents were purified and dried following standard procedures: dichloromethane (CH₂Cl₂) was distilled from calcium hydride, hexane and tetrahydrofuran (THF) were distilled from potassium prior to use. Technical grade solvents for extraction and chromatography (cyclohexane and tert-butyl methyl ether) were distilled prior to use. All ketones were obtained from commercial suppliers and purified prior to use by distillation (for liquids) or dried under vacuum (2·10⁻¹ mbar) (for solids). [Ph₃C][B(C₆F₅)₄] [1] and tert-butylferrocenylmethylsilane [2] were prepared according to reported procedures.

Analytical thin layer chromatography (TLC) was performed on silica gel SIL G-25 glass plates from Macherey-Nagel. Flash column chromatography was performed on silica gel 60 (40–63 μm, 230–400 mesh, ASTM) by Merck using the indicated solvents. ¹H, ¹³C, ¹⁹F and ²⁹Si NMR spectra were recorded in C₆D₆ on Bruker AV 300, Bruker AV 400 and Varian Inova 500 instruments. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane and referenced to the residual solvent resonance as the internal standard (C₆D₆: δ = 7.16 and 128.1 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. Infrared (IR) spectra were recorded on a Varian 3100 FT-IR spectrophotometer equipped with an ATR unit and are reported (w = weak, m = medium, s = strong) in wavenumbers (cm⁻¹). Gas liquid chromatography (GLC) was performed on a Shimadzu GC-17A gas chromatograph equipped with a SE-54 capillary column (30 m × 0.32 mm, 0.25 μm film thickness) by CS-Chromatographie Service using the following program: N₂ carrier gas, injection temperature 250 °C, detector temperature 300 °C; temperature program: start temperature 40 °C, heating rate 10 °C/min, end temperature 280 °C for 5 min. Mass spectral data as well as elemental analysis were obtained from the Analytical Facility at the Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster.


2 Experimental Details

2.1 General Procedure for the Silylium Ion-Catalysed Carbonyl Reduction

In a glove-box, a flame-dried 10-mL Schlenk tube equipped with a magnetic stir bar is charged with \([\text{Ph}_3\text{C}]^+\)[B(C6F5)4]– (9.2 mg, 0.010 mmol, 5.0 mol%). The Schlenk tube is transferred to a fume cupboard and connected to an argon–vacuum manifold. Addition of dry CH2Cl2 (1.0 mL) results in a yellow solution, which is subsequently cooled to –60 °C using an ethanol cooling bath and a cryostat. After silane addition (10, 11 mg, 0.040 mmol, 0.20 equiv.), the now brown solution is stirred for 10 min, followed by successive addition of the carbonyl compound 2 (0.20 mmol, 1.0 equiv.) and the silane 10 (57 mg, 0.20 mmol, 1.0 equiv.) dissolved in dry CH2Cl2 (0.5 mL each). The reaction mixture is maintained at –60 °C for 2½ h, and the reaction is then terminated by the addition of dry hexane (10 mL), pre-cooled to –60 °C. Filtration over a small pad of Celite® and evaporation of the solvents under reduced pressure affords crude 13, which is further purified by flash chromatography on silica gel using cyclohexane as eluent. The diastereomeric ratio is determined by GLC analysis prior to purification. All analytical data, unless stated otherwise, is reported for the mixture of diastereomers.

2.2 Control Experiments Concerning the Ipso-Substitution at Ferrocene

*Treatment of acetophenone under standard conditions at –45 ºC*: According to the general procedure, the silylium ion catalyst was prepared at –45 ºC. After the successive addition of acetophenone (2a, 24 mg, 0.20 mmol, 1.0 equiv.) and silane 10 (57 mg, 0.20 mmol, 1.0 equiv.), dissolved in dry CH2Cl2 (0.5 mL each), the reaction mixture was maintained at –45 ºC for 1 h and the reaction was then terminated by the addition of dry hexane, pre-cooled to –45 ºC, and filtered over a small pad of Celite®. The solvents were evaporated under reduced pressure and the residue was further purified by flash chromatography on silica gel using cyclohexane as eluent.

*Treatment of the silicon ether derived from acetophenone under standard conditions at –45 ºC*: According to the general procedure, the silylium ion catalyst was prepared at –45 ºC. A solution of silicon ether 13a (81 mg, 0.20 mmol, 1.0 equiv.) in dry CH2Cl2 (1 mL) was added and the reaction mixture was maintained at –45 ºC for 2½ h. The reaction was terminated as described above, the solvents were evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel using cyclohexane as eluent.
3 Characterisation Data for Compounds 13a, 13f–13p and 14a

**tert-Butylferrocenylmethyl(1-phenylethoxy)silane (13a):** Prepared from acetophenone (2a, 24.0 mg, 0.200 mmol, 1.00 equiv.) according to the general procedure; purification by flash chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product 13a (66 mg, 82%) as an orange oil. $R_f = 0.23$ (cyclohexane). Diastereomeric ratio was determined by GLC analysis prior to purification (dr = 51:49). **GLC (SE-54):** $t_R = 23.8$ min (major diastereomer), 24.0 min (minor diastereomer). **IR (ATR):** $\tilde{\nu} = 2956$ (w), 2928 (w), 2890 (w), 2855 (w), 2361 (m), 2342 (m), 1252 (m), 1163 (m), 1092 (s), 1035 (s), 958 (m), 819 (s), 801 (s), 777 (s), 753 (s), 698 (s) cm$^{-1}$. **HRMS (ESI) calculated for C$_{23}$H$_{30}$FeOSi ([M$^+$]):** 406.1410; Found: 406.1411. 

**Anal. Calcd for C$_{23}$H$_{30}$FeOSi:** C, 67.97; H, 7.44; Found: C, 68.06; H, 7.44. **NMR data for diastereomeric mixture:** 

**$^1$H NMR (400 MHz, C$_6$D$_6$):** 0.25 (s, 3H), 0.37 (s, 3H), 1.00 (s, 9H), 1.04 (s, 9H), 1.46 (d, $J = 6.3$ Hz, 3H), 1.50 (d, $J = 6.3$ Hz, 3H), 3.88 (ddd, $J = 2.3$ Hz, $J = 1.2$ Hz, $J = 1.2$ Hz, 1H), 3.93 (m, 6H), 4.07 (s, 5H), 4.09 (ddd, $J = 2.3$ Hz, $J = 2.3$ Hz, $J = 1.2$ Hz, 1H), 4.13–4.15 (m, 2H), 4.19 (ddd, $J = 2.3$ Hz, $J = 2.3$ Hz, 1H), 4.21 (ddd, $J = 2.3$ Hz, 1H), 4.24 (ddd, $J = 2.3$ Hz, 1H), 5.18 (q, $J = 6.3$ Hz, 1H), 5.22 (q, $J = 6.3$ Hz, 1H), 7.08–7.13 (m, 2H), 7.21–7.26 (m, 4H), 7.41–7.45 (m, 4H) ppm. 

**$^{13}$C NMR (100 MHz, C$_6$D$_6$):** 58.1, 60.6, 61.5, 63.8, 64.1, 65.9, 67.5, 68.1, 68.2, 68.7, 68.8, 71.0, 71.0, 71.1, 71.2, 71.6, 71.7, 73.2, 73.5, 74.2, 74.3, 125.5, 125.6, 127.2, 127.3, 128.6, 128.6, 147.3, 147.4 ppm. 

**$^{29}$Si NMR (60 MHz, C$_6$D$_6$):** 11.0, 11.1 ppm.

**tert-Butylferrocenylmethyl[1-(4-methylphenyl)ethoxy]silane (13f):** Prepared from 4-methylacetophenone (2f, 26.8 mg, 0.200 mmol, 1.00 equiv.) according to the general procedure; purification...
by flash chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product 13f (8 mg, 10%) as an orange oil. \( \text{Rf} = 0.26 \) (cyclohexane). Diastereomeric ratio was determined by GLC analysis prior to purification (dr = 52:48). **GLC (SE-54):** \( t_R = 23.8 \text{ min} \) (minor diastereomer), 24.0 min (major diastereomer). **IR (ATR):** \( \tilde{\nu} = 3096 \text{ (w)}, 2955 \text{ (w)}, 2927 \text{ (w)}, 2877 \text{ (w)}, 2855 \text{ (w)}, 2360 \text{ (w)}, 2343 \text{ (w)}, 1515 \text{ (w)}, 1472 \text{ (w)}, 1367 \text{ (w)}, 1251 \text{ (m)}, 1163 \text{ (m)}, 1093 \text{ (s)}, 1035 \text{ (s)}, 1003 \text{ (m)}, 958 \text{ (m)}, 816 \text{ (s)}, 793 \text{ (m)}, 776 \text{ (s)}, 756 \text{ (m)}, 719 \text{ (w)}, 700 \text{ (m)}, 597 \text{ (m) cm}^{-1}. **HRMS (ESI) calculated for \( \text{C}_{24}\text{H}_{32}\text{FeOSi} \) ([M]+): 420.1567; Found: 420.1557. **Anal. Calcd for \( \text{C}_{24}\text{H}_{32}\text{FeOSi} \): C, 68.56; H, 7.67; Found: C, 68.73; H, 7.68.

**NMR data for diastereomeric mixture:**

**1H NMR (400 MHz, \( \text{C}_6\text{D}_6 \)):** \( \delta = 0.28 \text{ (s, 3H)}, 0.39 \text{ (s, 3H)}, 1.02 \text{ (s, 9H)}, 1.06 \text{ (s, 9H)}, 1.49 \text{ (d, } J = 6.3 \text{ Hz, 3H)}, 1.54 \text{ (d, } J = 6.3 \text{ Hz, 3H)}, 2.13 \text{ (s, 3H)}, 2.15 \text{ (s, 3H)}, 3.90 \text{ (ddd, } J = 2.3 \text{ Hz, } J = 1.1 \text{ Hz, 1H}), 4.14 \text{ (ddd, } J = 2.3 \text{ Hz, } J = 1.1 \text{ Hz, 1H}), 4.17 \text{ (ddd, } J = 2.3 \text{ Hz, } J = 1.1 \text{ Hz, 1H}), 4.20 \text{ (ddd, } J = 2.3 \text{ Hz, } J = 1.1 \text{ Hz, 1H}), 4.22 \text{ (ddd, } J = 2.3 \text{ Hz, } J = 2.3 \text{ Hz, } J = 1.1 \text{ Hz, 1H}), 4.27 \text{ (ddd, } J = 2.3 \text{ Hz, } J = 1.1 \text{ Hz, 1H}), 5.20 \text{ (q, } J = 6.3 \text{ Hz, 1H}), 5.23 \text{ (q, } J = 6.3 \text{ Hz, 1H}), 7.07 \text{ (d, } J = 7.9 \text{ Hz, 2H}), 7.08 \text{ (d, } J = 7.9 \text{ Hz, 2H}), 7.36 \text{ (d, } J = 7.7 \text{ Hz, 2H}), 7.38 \text{ (d, } J = 7.7 \text{ Hz, 2H), ppm.} **13C NMR (100 MHz, \( \text{C}_6\text{D}_6 \)):** \( \delta = –5.1, –4.8, 19.2, 19.3, 21.1, 21.1, 26.4, 26.5, 28.1, 28.2, 68.3, 68.7, 68.8, 70.9, 71.0, 71.1, 71.2, 71.3, 71.5, 71.6, 73.2, 73.5, 74.2, 74.3, 125.5, 125.5, 129.3, 129.3, 136.5, 136.5, 144.4, 144.5 ppm. **29Si NMR (60 MHz, \( \text{C}_6\text{D}_6 \)):** \( \delta = 10.8, 10.9 \text{ ppm.}**

**tert-Butylferrocenylmethyl[1-(2-chlorophenyl)ethyloxy]silane (13g):** Prepared from 2-chloroacetophenone (2g, 30.9 mg, 0.200 mmol, 1.00 equiv.) according to the general procedure; purification by flash chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product 13g (85.5 mg, 97%) as an orange oil. \( \text{Rf} = 0.33 \) (cyclohexane). Diastereomeric ratio was determined by GLC analysis prior to purification (dr = 78:22). **GLC (SE-54):** \( t_R = 24.4 \text{ min} \) (minor diastereomer), 24.6 min (major diastereomer). **IR (ATR):** \( \tilde{\nu} = 3097 \text{ (w)}, 2956 \text{ (w)}, 2928 \text{ (w)}, 2893 \text{ (w)}, 2855 \text{ (w)}, 2360 \text{ (w)}, 1472 \text{ (m)}, 1438 \text{ (w)}, 1421 \text{ (w)}, 1368 \text{ (w)}, 1253 \text{ (m)}, 1163 \text{ (m)}, 1133 \text{ (m)}, 1096 \text{ (s)}, 1035 \text{ (s)}, 956 \text{ (s)}, 820 \text{ (s)}, 805 \text{ (s)}, 778 \text{ (s)}, 752 \text{ (s)}, 703 \text{ (m) cm}^{-1}. **HRMS (ESI) calculated for \( \text{C}_{23}\text{H}_{29}\text{ClFeOSi} \) ([M]+): 440.1021; Found: 440.1020. **Anal. Calcd for \( \text{C}_{23}\text{H}_{29}\text{ClFeOSi} \): C, 62.66; H, 6.63; Found: C, 62.60; H, 6.68. NMR data for major diastereomer: **1H NMR (400 MHz, \( \text{C}_6\text{D}_6 \)):** \( \delta = 0.25 \text{ (s, 3H)}, 1.00 \text{ (s, 9H)}, 1.57 \text{ (d, } J = 6.2 \text{ Hz, 3H}), 3.91 \text{ (ddd, } J = 2.3 \text{ Hz, } J = 1.2 \text{ Hz, 1H}), 4.11 \text{ (s, 5H)}, 4.19 \text{ (ddd, } J = 2.3 \text{ Hz, } J = 2.3 \text{ Hz, } J = 1.2 \text{ Hz, 1H}), 4.21 \text{ (ddd, } J = 2.3 \text{ Hz, } J = 2.3 \text{ Hz, } J = 1.2 \text{ Hz, 1H}), 4.28 \text{ (ddd, } J = 2.3 \text{ Hz, } J = 1.2 \text{ Hz, 1H}), 5.78 \text{ (q, } J = 6.2 \text{ Hz, 1H}), 6.80 \text{ (ddd, } J = 7.7 \text{ Hz, 1H), ppm.}
$J = 7.7 \text{ Hz, } J = 1.7 \text{ Hz, } 1\text{H}), 7.03–7.10 \text{ (m, } 1\text{H}), 7.13–7.16 \text{ (m, } 1\text{H}), 7.86 \text{ (dd, } J = 7.8 \text{ Hz, } J = 1.7 \text{ Hz, } 1\text{H}) \text{ ppm. } \mathrm{^{13}C} \text{ NMR (100 MHz, } \mathrm{C}_6\mathrm{D}_6): \delta = -5.0, 19.1, 25.9, 26.4, 67.6, 68.3, 68.8, 71.1, 71.3, 73.4, 74.0, 127.3, 127.5, 128.3, 129.4, 131.0, 144.8 \text{ ppm. } \mathrm{^{29}Si} \text{ NMR (60 MHz, } \mathrm{C}_6\mathrm{D}_6): \delta = 12.2 \text{ ppm. } $NMR data for minor diastereomer:  

$^1\mathrm{H} \text{ NMR (400 MHz, } \mathrm{C}_6\mathrm{D}_6): \delta = 0.40 \text{ (s, } 3\text{H}), 1.03 \text{ (s, } 9\text{H}), 1.52 \text{ (d, } J = 6.2 \text{ Hz, } 3\text{H}), 3.86 \text{ (ddd, } J = 2.3 \text{ Hz, } J = 1.2 \text{ Hz, } J = 1.2 \text{ Hz, } 1\text{H}), 3.97 \text{ (s, } 5\text{H}), 4.05–4.09 \text{ (m, } 2\text{H}), 4.12 \text{ (ddd, } J = 2.3 \text{ Hz, } J = 2.3 \text{ Hz, } J = 1.2 \text{ Hz, } 1\text{H}), 5.73 \text{ (q, } J = 6.2 \text{ Hz, } 1\text{H}), 6.80 \text{ (ddd, } J = 7.7 \text{ Hz, } J = 7.7 \text{ Hz, } J = 1.7 \text{ Hz, } 1\text{H}), 7.03–7.10 \text{ (m, } 1\text{H}), 7.13–7.16 \text{ (m, } 1\text{H}), 7.91 \text{ (dd, } J = 7.8 \text{ Hz, } J = 1.7 \text{ Hz, } 1\text{H}) \text{ ppm. } \mathrm{^{13}C} \text{ NMR (100 MHz, } \mathrm{C}_6\mathrm{D}_6): \delta = -5.3, 19.1, 26.0, 26.3, 67.8, 68.4, 68.6, 70.9, 71.2, 73.1, 74.1, 127.4, 127.4, 128.4, 129.4, 131.0, 144.8 \text{ ppm. } \mathrm{^{29}Si} \text{ NMR (60 MHz, } \mathrm{C}_6\mathrm{D}_6): \delta = 12.2 \text{ ppm. }$

$tet\text{-Butylferrocenylmethyl(1-pentafluorophenylethoxy)silane (13h): Prepared from pentafluoroacetophenone (2h, 42.0 mg, 0.200 mmol, 1.00 equiv.) according to the general procedure; purification by flash chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product 13h (84.6 mg, 85%) as an orange oil. } R_f = 0.33 \text{ (cyclohexane). Diastereomeric ratio was determined by GLC analysis prior to purification (dr = 52:48). } $GLC \text{ (SE-54): } t_R = 21.8 \text{ min (major diastereomer), 22.1 min (minor diastereomer). } IR \text{ (ATR): } \bar{\nu} = 3097 \text{ (w), 2932 \text{ (w), 2894 \text{ (w), 2858 \text{ (w), 2362 \text{ (w), 1653 \text{ (w), 1520 \text{ (m), 1500 \text{ (s), 1473 \text{ (w), 1420 \text{ (w), 1375 \text{ (w), 1302 \text{ (w), 1254 \text{ (w), 1151 \text{ (m), 1133 \text{ (m), 1105 \text{ (m), 1056 \text{ (m), 1036 \text{ (m), 987 \text{ (m), 964 \text{ (s), 891 \text{ (m), 821 \text{ (m), 775 \text{ (m), 746 \text{ (m), 698 \text{ (w) cm}^{-1.}} } HRMS \text{ (ESI) calculated for } C_{23}H_{25}F_5FeOSi ([M]^+) \text{: 496.0939; Found: 496.0931.}$NMR data for diastereomeric mixture:  

$^1\mathrm{H} \text{ NMR (400 MHz, } \mathrm{C}_6\mathrm{D}_6): \delta = 0.22 \text{ (s, } 3\text{H}), 0.29 \text{ (s, } 3\text{H}), 0.95 \text{ (s, } 9\text{H}), 1.00 \text{ (s, } 9\text{H}), 1.44 \text{ (d, } J = 6.6 \text{ Hz, } 3\text{H}), 1.46 \text{ (d, } J = 6.6 \text{ Hz, } 3\text{H}), 3.83 \text{ (ddd, } J = 2.3 \text{ Hz, } J = 1.2 \text{ Hz, } J = 1.2 \text{ Hz, } 1\text{H}), 3.95 \text{ (s, } 5\text{H}), 4.06 \text{ (m, } 6\text{H}), 4.08 \text{ (ddd, } J = 2.3 \text{ Hz, } J = 2.3 \text{ Hz, } J = 1.2 \text{ Hz, } 1\text{H}), 4.09 \text{ (ddd, } J = 2.3 \text{ Hz, } J = 1.2 \text{ Hz, } J = 1.2 \text{ Hz, } 1\text{H}), 4.11 \text{ (ddd, } J = 2.3 \text{ Hz, } J = 2.3 \text{ Hz, } J = 1.2 \text{ Hz, } 1\text{H}), 4.15 \text{ (ddd, } J = 2.3 \text{ Hz, } J = 2.3 \text{ Hz, } J = 1.2 \text{ Hz, } 1\text{H}), 4.18 \text{ (ddd, } J = 2.3 \text{ Hz, } J = 2.3 \text{ Hz, } J = 1.2 \text{ Hz, } 1\text{H}), 5.43 \text{ (q, } J = 6.6 \text{ Hz, } 2\text{H}) \text{ ppm. } \mathrm{^{13}C} \text{ NMR (100 MHz, } \mathrm{C}_6\mathrm{D}_6): \delta = -5.5, -5.3, 19.0, 19.1, 23.9, 24.0, 26.3, 26.3, 63.1, 63.2, 66.9, 67.0, 68.6, 68.7, 71.0, 71.1, 71.4, 71.5, 73.2, 73.3, 73.7, 73.8, 119.1 \text{ (m), 136.5 \ (m), 139.0 \ (m), 141.7 \ (m), 143.5 \ (m), 146.0 \ (m) ppm (two fluorine-substituted carbon atoms not detected). } \mathrm{^{19}F} \text{ NMR (282 MHz, } \mathrm{C}_6\mathrm{D}_6): \delta = -162.4 \text{ (2}\times), -156.3, -156.1, -143.6, -143.4. \mathrm{^{29}Si} \text{ NMR (60 MHz, } \mathrm{C}_6\mathrm{D}_6): \delta = 12.7, 13.1 \text{ ppm. }$
**tert-Butylferrocenylmethyl(1-phenylpropyloxy)silane (13i):** Prepared from propiophenone (2i, 26.8 mg, 0.200 mmol, 1.00 equiv.) according to the general procedure; purification by flash chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product 13i (69.2 mg, 82%) as an orange oil. *R*<sub>f</sub> = 0.30 (cyclohexane). Diastereomeric ratio was determined by GLC analysis prior to purification (dr = 78:22). **GLC** (SE-54): *t*<sub>R</sub> = 23.7 min (minor diastereomer), 23.8 min (major diastereomer). **IR** (ATR): ν~ = 3087 (w), 2958 (w), 2929 (w), 2883 (w), 2855 (w), 1472 (w), 1459 (w), 1420 (w), 1388 (w), 1361 (w), 1352 (w), 1252 (m), 1162 (m), 1084 (m), 1059 (m), 1035 (m), 1004 (m), 921 (w), 896 (w), 845 (m), 775 (s), 752 (m), 699 (s) cm<sup>−1</sup>. **HRMS** (ESI) calculated for C<sub>24</sub>H<sub>32</sub>FeOSi ([M]+): 420.1567; Found: 420.1554. **Anal. Calcd** for C<sub>24</sub>H<sub>32</sub>FeOSi: C, 68.56; H, 7.67; Found: C, 68.64; H, 7.87. NMR data for major diastereomer: **1H NMR** (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 0.19 (s, 3H), 0.92 (t, *J* = 7.5 Hz, 3H), 1.03 (s, 9H), 1.76–1.93 (m, 2H), 3.92 (ddd, *J* = 2.3 Hz, *J* = 1.1 Hz, *J* = 1.1 Hz, 1H), 4.08 (s, 5H), 4.19 (ddd, *J* = 2.3 Hz, *J* = 2.3 Hz, *J* = 1.1 Hz, 1H), 4.22 (ddd, *J* = 2.3 Hz, *J* = 2.3 Hz, *J* = 1.1 Hz, 1H), 4.27 (ddd, *J* = 2.3 Hz, *J* = 1.1 Hz, *J* = 1.1 Hz, 1H), 5.03 (t, *J* = 5.9 Hz, 1H), 7.08–7.13 (m, 1H), 7.20–7.25 (m, 2H), 7.38–7.42 (m, 2H) ppm. **13C NMR** (100 MHz, C<sub>6</sub>D<sub>6</sub>): δ = –4.5, 9.8, 19.2, 26.5, 34.3, 68.1, 68.8, 71.0, 71.3, 73.5, 74.2, 76.6, 126.4, 127.3, 128.4, 145.7 ppm. **29Si NMR** (60 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 10.8 ppm. NMR data for minor diastereomer: **1H NMR** (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 0.36 (s, 3H), 0.89 (t, *J* = 7.5 Hz, 3H), 1.05 (s, 9H), 1.76–1.93 (m, 2H), 3.87 (ddd, *J* = 2.3 Hz, *J* = 1.2 Hz, *J* = 1.2 Hz, 1H), 3.93 (s, 5H), 4.06–4.08 (m, 2H), 4.12 (ddd, *J* = 2.3 Hz, *J* = 2.3 Hz, *J* = 1.2 Hz, 1H), 5.00 (t, *J* = 5.8 Hz, 1H), 7.08–7.13 (m, 1H), 7.20–7.25 (m, 2H), 7.38–7.42 (m, 2H) ppm. **13C NMR** (100 MHz, C<sub>6</sub>D<sub>6</sub>): δ = –4.9, 9.4, 19.4, 26.5, 34.1, 68.2, 68.7, 70.9, 71.1, 73.3, 74.4, 76.5, 126.4, 127.3, 128.4, 145.4 ppm. **29Si NMR** (60 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 11.1 ppm.

**tert-Butylferrocenylmethyl(cyclopentyloxy)silane (13j):** Prepared from cyclopentanone (2j, 16.8 mg, 0.200 mmol, 1.00 equiv.) according to the general procedure; purification by flash chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product 13j (30.1 mg, 97%) as a yellow oil. *R*<sub>f</sub> = 0.30 (cyclohexane). Diastereomeric ratio was determined by GLC analysis prior to purification (dr = 81:19). **GLC** (SE-54): *t*<sub>R</sub> = 23.8 min (minor diastereomer), 24.0 min (major diastereomer). **IR** (ATR): ν~ = 3087 (w), 2958 (w), 2929 (w), 2883 (w), 2855 (w), 1472 (w), 1459 (w), 1420 (w), 1388 (w), 1361 (w), 1252 (m), 1162 (m), 1084 (m), 1059 (m), 1035 (m), 1004 (m), 921 (w), 896 (w), 845 (m), 775 (s), 752 (m), 699 (s) cm<sup>−1</sup>. **HRMS** (ESI) calculated for C<sub>30</sub>H<sub>42</sub>FeOSi ([M]+): 424.1554; Found: 424.1554. **Anal. Calcd** for C<sub>30</sub>H<sub>42</sub>FeOSi: C, 71.59; H, 7.87; Found: C, 71.86; H, 8.07. NMR data for major diastereomer: **1H NMR** (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 0.23 (s, 3H), 0.91 (t, *J* = 7.5 Hz, 3H), 1.03 (s, 9H), 1.76–1.93 (m, 2H), 3.90 (ddd, *J* = 2.3 Hz, *J* = 1.1 Hz, *J* = 1.1 Hz, 1H), 4.09 (s, 5H), 4.19 (ddd, *J* = 2.3 Hz, *J* = 2.3 Hz, *J* = 1.1 Hz, 1H), 4.22 (ddd, *J* = 2.3 Hz, *J* = 2.3 Hz, *J* = 1.1 Hz, 1H), 5.03 (t, *J* = 5.9 Hz, 1H), 7.08–7.13 (m, 1H), 7.20–7.25 (m, 2H), 7.38–7.42 (m, 2H) ppm. **13C NMR** (100 MHz, C<sub>6</sub>D<sub>6</sub>): δ = –4.5, 9.8, 19.2, 26.5, 34.3, 68.1, 68.8, 71.0, 71.3, 73.5, 74.2, 76.6, 126.4, 127.3, 128.4, 145.7 ppm. **29Si NMR** (60 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 10.8 ppm. NMR data for minor diastereomer: **1H NMR** (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 0.36 (s, 3H), 0.89 (t, *J* = 7.5 Hz, 3H), 1.05 (s, 9H), 1.76–1.93 (m, 2H), 3.86 (ddd, *J* = 2.3 Hz, *J* = 1.2 Hz, *J* = 1.2 Hz, 1H), 3.92 (s, 5H), 4.06–4.08 (m, 2H), 4.12 (ddd, *J* = 2.3 Hz, *J* = 2.3 Hz, *J* = 1.2 Hz, 1H), 5.00 (t, *J* = 5.8 Hz, 1H), 7.08–7.13 (m, 1H), 7.20–7.25 (m, 2H), 7.38–7.42 (m, 2H) ppm. **13C NMR** (100 MHz, C<sub>6</sub>D<sub>6</sub>): δ = –4.9, 9.4, 19.4, 26.5, 34.1, 68.2, 68.7, 70.9, 71.1, 73.3, 74.4, 76.5, 126.4, 127.3, 128.4, 145.4 ppm. **29Si NMR** (60 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 11.1 ppm.
chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product 13j (62.6 mg, 85%) as an orange oil. \( R_f = 0.26 \) (cyclohexane). GLC (SE-54): \( t_R = 21.1 \) min. IR (ATR): \( \tilde{\nu} = 3098 \) (w), 2955 (m), 2928 (m), 2855 (m), 1472 (m), 1422 (w), 1388 (w), 1360 (w), 1163 (s), 1107 (s), 1051 (s), 1035 (s), 1003 (m), 940 (w), 900 (w), 818 (s), 775 (s), 729 (w), 701 (w) cm\(^{-1}\). HRMS (ESI) calculated for C\(_{20}\)H\(_{30}\)FeOSi ([M]+): 370.1410; Found: 370.1404. Anal. Calcd for C\(_{20}\)H\(_{30}\)FeOSi: C, 64.86; H, 8.16; Found: C, 65.14; H, 8.24. \(^{1}H\) NMR (400 MHz, C\(_6\)D\(_6\)): \( \delta = 0.36 \) (s, 3H), 1.01 (s, 9H), 1.44–1.53 (m, 2H), 1.60–1.72 (m, 3H), 1.73–1.78 (m, 1H), 1.79–1.85 (m, 2H), 3.94 (ddd, \( J = 2.3 \) Hz, \( J = 1.2 \) Hz, \( J = 1.2 \) Hz, 1H), 4.10 (s, 5H), 4.20 (ddd, \( J = 2.3 \) Hz, \( J = 2.3 \) Hz, \( J = 1.2 \) Hz, 1H). GLC (SE-54): \( t_R = 22.2 \) min. IR (ATR): \( \tilde{\nu} = 2929 \) (s), 2854 (m), 2360 (m), 2342 (m), 1472 (w), 1449 (w), 1370 (w), 1250 (m), 1163 (m), 1094 (s), 1051 (m), 1034 (m), 1001 (m), 862 (m), 817 (s), 775 (s), 703 (m) cm\(^{-1}\).

**tert-Butylferrocenylmethyl(cyclohexyloxy)silane (13k):** Prepared from cyclohexanone (2k, 19.6 mg, 0.200 mmol, 1.00 equiv.) according to the general procedure; purification by flash chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product 13k (75.4 mg, 95%) as an orange oil. \( R_f = 0.28 \) (cyclohexane). GLC (SE-54): \( t_R = 22.2 \) min. IR (ATR): \( \tilde{\nu} = 2929 \) (s), 2854 (m), 2360 (m), 2342 (m), 1472 (w), 1449 (w), 1370 (w), 1250 (m), 1163 (m), 1094 (s), 1051 (m), 1034 (m), 1001 (m), 862 (m), 817 (s), 775 (s), 703 (m) cm\(^{-1}\). HRMS (ESI) calculated for C\(_{21}\)H\(_{32}\)FeOSi ([M]+): 384.1567; Found: 384.1564. Anal. Calcd for C\(_{21}\)H\(_{32}\)FeOSi: C, 65.61; H, 8.39; Found: C, 65.52; H, 8.53. \(^{13}C\) NMR (100 MHz, C\(_6\)D\(_6\)): \( \delta = -5.0 \), 19.1, 23.6, 23.6, 26.5, 26.5, 36.4, 36.4, 68.7, 68.7, 71.0, 71.1, 73.5, 74.2, 75.1 ppm. \(^{29}Si\) NMR (60 MHz, C\(_6\)D\(_6\)): \( \delta = 9.1 \) ppm.
**tert-Butylferrocenylmethyl(cyclododecyloxy)silane (13l):** Prepared from cyclododecanone (2l, 36.5 mg, 0.200 mmol, 1.00 equiv.) according to the general procedure; purification by flash chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product 13l (81.1 mg, 86%) as an orange solid. m.p. = 73 °C. R<sub>f</sub> = 0.33 (cyclohexane). GLC (SE-54): t<sub>R</sub> = 29.1 min. IR (ATR): \( \tilde{\nu} = 3092 \text{ (w)}, 2930 \text{ (s)}, 2855 \text{ (s)}, 2361 \text{ (w)}, 1472 \text{ (s)}, 1419 \text{ (w)}, 1298 \text{ (w)}, 1249 \text{ (s)}, 1097 \text{ (s)}, 1064 \text{ (s)}, 1032 \text{ (s)}, 1003 \text{ (m)}, 970 \text{ (w)}, 935 \text{ (w)}, 866 \text{ (w)}, 815 \text{ (w)}, 771 \text{ (s)}, 737 \text{ (m)}, 702 \text{ (w)} \text{ cm}^{-1}. \) HRMS (ESI) calculated for C<sub>27</sub>H<sub>44</sub>FeOSi ([M]+): 468.2506; Found: 468.2499. Anal. Calcd for C<sub>27</sub>H<sub>44</sub>FeOSi: C, 69.21; H, 9.46; Found: C, 69.40; H, 9.65. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): \( \delta = 0.40 \text{ (s, 3H)}, 1.07 \text{ (s, 9H)}, 1.34–1.51 \text{ (m, 18H)}, 1.56–1.67 \text{ (m, 2H)}, 1.73–1.85 \text{ (m, 2H)}, 3.97 \text{ (ddd, } J = 2.3 \text{ Hz, } J = 1.2 \text{ Hz, } J = 1.2 \text{ Hz, 1H}), 4.11 \text{ (s, 5H)}, 4.15–4.19 \text{ (m, 1H)}, 4.20 \text{ (ddd, } J = 2.3 \text{ Hz, } J = 2.3 \text{ Hz, } J = 1.2 \text{ Hz, 1H}), 4.22 \text{ (ddd, } J = 2.3 \text{ Hz, } J = 2.3 \text{ Hz, } J = 1.2 \text{ Hz, 1H}), 4.27 \text{ (ddd, } J = 2.3 \text{ Hz, } J = 2.3 \text{ Hz, } J = 1.2 \text{ Hz, 1H}) \text{ ppm.} \) <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>): \( \delta = -4.6, 19.3, 20.6, 20.8, 23.2, 23.2, 23.3, 23.4, 25.4, 25.8, 25.8, 26.6, 32.4, 32.6, 68.8, 68.8, 70.9, 71.2, 71.2, 73.5, 74.3 \text{ ppm.} \) <sup>29</sup>Si NMR (60 MHz, C<sub>6</sub>D<sub>6</sub>): \( \delta = 8.3 \text{ ppm.} \)

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**tert-Butylferrocenylmethyl(pent-3-yloxy)silane (13m):** Prepared from 3-pentanone (2m, 17.2 mg, 0.200 mmol, 1.00 equiv.) according to the general procedure; purification by flash chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product 13m (58.7 mg, 79%) as an orange oil. R<sub>f</sub> = 0.38 (cyclohexane). GLC (SE-54): t<sub>R</sub> = 20.9 min. IR (ATR): \( \tilde{\nu} = 2959 \text{ (w)}, 2929 \text{ (w)}, 2878 \text{ (w)}, 2855 \text{ (w), 1461 \text{ (w)}, 1251 \text{ (m)}, 1161 \text{ (m)}, 1128 \text{ (w)}, 1107 \text{ (m)}, 1065 \text{ (s)}, 1035 \text{ (s)}, 1003 \text{ (s)}, 818 \text{ (s)}, 775 \text{ (s)}, 731 \text{ (m)}, 695 \text{ (w)} \text{ cm}^{-1}. \) HRMS (ESI) calculated for C<sub>20</sub>H<sub>32</sub>FeOSi ([M]+): 372.1567; Found: 372.1565. Anal. Calcd for C<sub>20</sub>H<sub>32</sub>FeOSi: C, 64.50; H, 8.66; Found: C, 64.64; H, 8.71. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): \( \delta = 0.36 \text{ (s, 3H)}, 0.91 \text{ (t, } J = 7.5 \text{ Hz, } J = 3 \text{ Hz}), 0.94 \text{ (t, } J = 7.5 \text{ Hz, } J = 3 \text{ Hz}), 1.05 \text{ (s, 9H)}, 1.51–1.63 \text{ (m, 4H)}, 3.87 \text{ (tt, } J = 5.6 \text{ Hz, } J = 5.7 \text{ Hz, 1H}), 3.95 \text{ (ddd, } J = 2.3 \text{ Hz, } J = 1.1 \text{ Hz, } J = 1.1 \text{ Hz, } J = 1.1 \text{ Hz, 1H}). \)
4.08 (s, 5H), 4.19 (ddd, J = 2.3 Hz, J = 2.3 Hz, J = 1.1 Hz, 1H), 4.20 (ddd, J = 2.3 Hz, J = 2.3 Hz, J = 1.1 Hz, 1H), 4.22 (ddd, J = 2.3 Hz, J = 1.1 Hz, J = 1.1 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, C$_6$D$_6$): δ = –4.5, 9.5, 9.5, 19.3, 26.7, 28.9, 29.2, 68.7, 68.8, 71.0, 71.1, 73.6, 74.3, 74.7 ppm. $^{29}$Si NMR (60 MHz, C$_6$D$_6$): δ = 8.1 ppm.

**tert-Butylferrocenylmethyl(but-2-yloxy)silane (13n):** Prepared from 2-butanone (2n, 14.5 mg, 0.200 mmol, 1.00 equiv.) according to the general procedure; purification by flash chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product 13n (31.5 mg, 44%) as an orange oil. $R_f$ = 0.28 (cyclohexane). Diastereomeric ratio was determined by GLC analysis prior to purification (dr = 50:50). GLC (SE-54): $t_R$ = 19.2, 19.3 min. IR (ATR): $\nu$ = 3097 (w), 2959 (m), 2929 (m), 2880 (w), 2855 (m), 1472 (m), 1422 (w), 1373 (m), 1251 (m), 1163 (m), 1134 (w), 1107 (s), 1049 (s), 1035 (s), 947 (m), 895 (w), 818 (s), 775 (s), 730 (m), 695 (w) cm$^{-1}$. HRMS (ESI) calculated for C$_{19}$H$_{30}$FeOSi ([M] +): 358.1410; Found: 358.1408. NMR data for mixture of diastereomers: $^1$H NMR (400 MHz, C$_6$D$_6$): δ = 0.24 (s, 3H), 0.24 (s, 3H), 0.81 (t, J = 7.5 Hz, 3H), 0.82 (t, J = 7.5 Hz, 3H), 0.91 (s, 9H), 0.92 (s, 9H), 1.05 (d, J = 6.0 Hz, 3H), 1.08 (d, J = 6.0 Hz, 3H), 1.29–1.55 (m, 4H), 3.8–23.84 (m, 2H), 3.85–3.94 (m, 2H), 3.96 (s, 5H), 3.96 (s, 5H), 4.07–4.09 (m, 4H), 4.11 (ddd, J = 2.3 Hz, J = 1.1 Hz, J = 1.1 Hz, 1H), 4.12 (ddd, J = 2.3 Hz, J = 1.1 Hz, J = 1.1 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, C$_6$D$_6$): $\delta$ = –4.8, –4.7, 9.9, 9.9, 19.1, 19.3, 23.2, 23.3, 26.5, 26.6, 32.8, 32.8, 68.7, 68.7, 68.8, 68.8, 70.1, 70.3, 70.9, 71.0, 71.1, 71.1, 73.5, 73.6, 74.2, 74.3 ppm. $^{29}$Si NMR (60 MHz, C$_6$D$_6$): $\delta$ = 8.4, 8.4 ppm.

**tert-Butylferrocenylmethyl[(4-methyl)pent-2-yloxy]silane (13o):** Prepared from 4-methyl-2-pentanone (2o, 20.0 mg, 0.200 mmol, 1.00 equiv.) according to the general procedure; purification by flash chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product 13o (62.5 mg, 79%) as an orange oil. $R_f$ = 0.31 (cyclohexane). Diastereomeric ratio was determined by GLC analysis prior to purification (dr = 60:40). GLC (SE-54): $t_R$ = 20.4 min (major diastereomer).
20.5 min (minor diastereomer). IR (ATR): \( \tilde{\nu} = 3099 \) (w), 2956 (m), 2855 (m), 1427 (m), 1421 (w), 1368 (m), 1251 (m), 1160 (s), 1125 (m), 1073 (s), 1035 (s), 1001 (m), 961 (w), 892 (w), 818 (s), 775 (s), 736 (m), 693 (w) cm\(^{-1}\). HRMS (ESI) calculated for \( \text{C}_{21}\text{H}_{34}\text{FeOSi} ([M]^+): 386.1723; \) Found: 386.1722. Anal. Calcd for \( \text{C}_{21}\text{H}_{34}\text{FeOSi}: \) C, 65.27; H, 8.87; Found: C, 65.62; H, 8.50.

NMR data for major diastereomer: \(^1\text{H NMR} \) (400 MHz, \( \text{C}_6\text{D}_6 \)): \( \delta = 0.38 \) (s, 3H), 0.91 (d, \( J = 6.5 \) Hz, 3H), 0.92 (d, \( J = 6.5 \) Hz, 3H), 1.06 (s, 9H), 1.20 (d, \( J = 6.1 \) Hz, 3H), 1.33 (ddd, \( J = 13.3 \) Hz, \( J = 6.6 \) Hz, \( J = 6.6 \) Hz, 2H), 1.67–1.82 (m, 1H), 3.96–3.98 (m, 1H), 4.10 (s, 5H), 4.12–4.18 (m, 1H), 4.19–4.22 (m, 2H), 4.24–4.26 (m, 1H) ppm. \(^{13}\text{C NMR} \) (100 MHz, \( \text{C}_6\text{D}_6 \)): \( \delta = –4.6, 19.2, 23.2, 23.5, 24.2, 25.1, 26.7, 49.8, 67.5, 68.7, 68.7, 70.9, 71.2, 73.6, 74.2 \) ppm. \(^{29}\text{Si NMR} \) (60 MHz, \( \text{C}_6\text{D}_6 \)): \( \delta = 8.1 \) ppm. NMR data for minor diastereomer: \(^1\text{H NMR} \) (400 MHz, \( \text{C}_6\text{D}_6 \)): \( \delta = 0.39 \) (s, 3H), 0.92 (d, \( J = 6.5 \) Hz, 3H), 0.95 (d, \( J = 6.5 \) Hz, 3H), 1.06 (s, 9H), 1.22 (d, \( J = 6.1 \) Hz, 3H), 1.52–1.63 (m, 2H), 1.67–1.82 (m, 1H), 3.96–3.98 (m, 1H), 4.10 (s, 5H), 4.12–4.18 (m, 1H), 4.19–4.22 (m, 2H), 4.24–4.26 (m, 1H) ppm. \(^{13}\text{C NMR} \) (100 MHz, \( \text{C}_6\text{D}_6 \)): \( \delta = –4.2, 19.3, 23.2, 23.3, 24.3, 25.0, 26.7, 49.8, 67.5, 68.7, 68.8, 71.0, 71.1, 73.6, 74.4 \) ppm. \(^{29}\text{Si NMR} \) (60 MHz, \( \text{C}_6\text{D}_6 \)): \( \delta = 8.3 \) ppm.

**tert-Butylferrocenylmethyl[(3,3-dimethyl)but-2-yl]oxy]silane (13p):** Prepared from 3,3-dimethyl-2-butynone (2p, 20.0 mg, 0.200 mmol, 1.00 equiv.) according to the general procedure; purification by flash chromatography on silica gel using cyclohexane as eluent and subsequent Kugelrohr distillation to remove residual silane afforded the analytically pure product (13p (59.3 mg, 77%) as an orange oil. \( R_f = 0.50 \) (cyclohexane). Diastereomeric ratio was determined by GLC analysis prior to purification (dr = 58:42). GLC (SE-54): \( t_R = 20.7 \) min (major diastereomer), 20.8 min (minor diastereomer). IR (ATR): \( \tilde{\nu} = 2956 \) (m), 2930 (m), 2891 (w), 2856 (m), 2360 (w), 2336 (w), 1473 (w), 1391 (w), 1372 (w), 1251 (m), 1161 (m), 1116 (s), 1095 (s), 1058 (w), 1025 (s), 1003 (m), 964 (m), 818 (s), 793 (s), 776 (s), 755 (m), 696 (m) cm\(^{-1}\). HRMS (ESI) calculated for \( \text{C}_{21}\text{H}_{34}\text{FeOSi} ([M]^+): 386.1723; \) Found: 386.1720. Anal. Calcd for \( \text{C}_{21}\text{H}_{34}\text{FeOSi}: \) C, 65.27; H, 8.87; Found: C, 65.06; H, 8.96. NMR data for major diastereomer: \(^1\text{H NMR} \) (400 MHz, \( \text{C}_6\text{D}_6 \)): \( \delta = 0.37 \) (s, 3H), 0.95 (d, \( J = 6.5 \) Hz, 3H), 1.05 (s, 9H), 1.13 (d, \( J = 6.2 \) Hz, 3H), 3.82 (q, \( J = 6.2 \) Hz, 1H), 3.94 (ddd, \( J = 2.3 \) Hz, \( J = 1.2 \) Hz, \( J = 1.2 \) Hz, 1H), 4.07 (s, 5H), 4.18–4.20 (m, 2H), 4.23 (ddd, \( J = 2.3 \) Hz, \( J = 1.2 \) Hz, \( J = 1.2 \) Hz, 1H) ppm. \(^{13}\text{C NMR} \) (100 MHz, \( \text{C}_6\text{D}_6 \)): \( \delta = –3.6, 18.9, 19.3, 26.2, 26.8, 36.0, 68.7, 68.9, 71.0, 71.1, 73.7, 74.3, 76.5 \) ppm. \(^{29}\text{Si NMR} \) (60 MHz, \( \text{C}_6\text{D}_6 \)): \( \delta = 7.2 \) ppm. NMR data for minor diastereomer: \(^1\text{H NMR} \) (400 MHz, \( \text{C}_6\text{D}_6 \)): \( \delta = 0.36 \) (s, 3H), 0.97 (s, 9H), 1.06 (s, 9H), 1.14 (d, \( J = 6.2 \) Hz, 3H), 3.70 (q, \( J = 6.2 \) Hz, 1H), 3.96 (ddd, \( J = 2.3 \) Hz, \( J = 1.2 \) Hz, \( J = 1.2 \) Hz, 1H), 4.08 (s, 5H), 4.18–4.20 (m, 3H) ppm. \(^{13}\text{C NMR} \) (100 MHz, \( \text{C}_6\text{D}_6 \)): \( \delta = –4.3, 18.9, 19.3, 26.3, 26.8, 35.7, 68.9, 69.8, 70.9, 71.1, 73.7, 74.3, 76.5 \) ppm.
18.8, 19.6, 26.2, 26.9, 35.9, 68.8, 68.9, 71.0, 71.1, 73.8, 74.5, 76.9 ppm. $^{29}$Si NMR (60 MHz, C$_6$D$_6$): $\delta = 7.8$ ppm.

1-Ferrocenyl-1-phenylethane (14a): Prepared from acetophenone (2a, 24 mg, 0.20 mmol, 1.0 equiv.) and silane 10 (57.3 mg, 0.200, 1.00 equiv.); purification by flash chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product 14a (31.8 mg, 55%) as an orange oil. – Prepared from silicon ether 13a (81 mg, 0.20 mmol, 1.0 equiv.); purification by flash chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product 14a (22.0 mg, 38%) as an orange oil. $R_f = 0.32$ (cyclohexane). GLC (SE-54): $t_R = 19.9$ min. IR (ATR): $\tilde{\nu} = 3085$ (w), 3026 (w), 2967 (w), 2930 (w), 1600 (w), 1439 (m), 1450 (m), 1369 (w), 1296 (w), 1259 (w), 1181 (w), 1105 (m), 1023 (m), 1000 (m), 908 (m), 817 (s), 770 (m), 755 (m), 738 (s) cm$^{-1}$.

HRMS (ESI) calculated for C$_{18}$H$_{18}$Fe ($[M]^+$): 290.0753; Found: 290.0760. $^1$H NMR (300 MHz, C$_6$D$_6$): $\delta = 1.50$ (d, $J = 7.1$ Hz, 3H), 3.75 (q, $J = 7.1$ Hz, 1H), 3.91–3.92 (m, 1H), 3.92–3.926 (m, 1H), 3.99–4.01 (m, 1H), 4.02 (s, 5H), 4.07–4.08 (m, 1H), 7.17–7.19 (m, 5H) ppm.

$^{13}$C NMR (75 MHz, C$_6$D$_6$): $\delta = 23.0, 40.2, 57.3, 66.7, 67.3, 68.0, 68.3, 68.9, 126.3, 127.6, 128.5, 147.9$ ppm.
4  \(^1\)H, \(^{13}\)C, \(^{19}\)F and \(^{29}\)Si NMR Spectra for Compounds 13a, 13f–13p and 14

tert-Butylferrocenylmethyl(1-phenylethoxy)silane (13a):
\(^1\)H NMR:

\[^{13}\text{C}\text{ NMR}:

\[^{29}\text{Si}\text{ NMR}:

Electronic Supplementary Information (ESI) for Chemical Communications
$^{29}\text{Si NMR:}$

tert-Butylferrocenylmethyl[1-(4-methylphenyl)ethoxy]silane (13f):

$^1\text{H NMR:}$
$^{13}$C NMR:

$^{29}$Si NMR:
tert-Butylferrocenylmethyl[1-(2'-chlorophenyl)ethoxy]silane (13g):

\(^1\)H NMR:

\(^{13}\)C NMR:
$^{29}$Si NMR:

$t$-Butylferrocenylmethyl[1-(2',3',4',5',6'-pentafluorophenyl)ethoxy]silane (13h):

$^1$H NMR:
$^{13}$C NMR:

$^{19}$F NMR:
$^{29}\text{Si NMR:}$

$^{1}\text{H NMR:}$
$^{13}$C NMR:

$^{29}$Si NMR:
tert-Butylferrocenylmethyl(cyclopentyloxy)silane (13j):

$^1$H NMR:

$^{13}$C NMR:
$^{29}\text{Si}$ NMR:

**tert-Butylferrocenylmethyl(cyclohexyloxy)silane (13k):**

$^1\text{H}$ NMR:
\[^{13}\text{C} \text{ NMR:}\]

\[^{29}\text{Si} \text{ NMR:}\]
tert-Butylferrocenylmethyl(cyclododecyloxy)silane (13l):  
$^1$H NMR:

$^{13}$C NMR:
$^{29}$Si NMR:

tert-Butylferrocenylmethyl(pent-3-xyloxy)silane (13m):

$^1$H NMR:
$^{13}$C NMR:

$^{29}$Si NMR:
tert-Butylferrocenylmethyl(but-2-yloxy)silane (13n):

$^1$H NMR:

![NMR spectrum for tert-Butylferrocenylmethyl(but-2-yloxy)silane (13n)]

$^{13}$C NMR:

![NMR spectrum for tert-Butylferrocenylmethyl(but-2-yloxy)silane (13n)]
$^{29}$Si NMR:

$^{1}$H NMR:
$^{13}$C NMR:

$^{29}$Si NMR:
tert-Butylferrocenylmethyl[(3,3-dimethyl)but-2-yloxy]silane (13p):

$^1$H NMR:

$^{13}$C NMR:
29Si NMR:

1-Ferrocenyl-1-phenylethane (14a):
1H NMR:
$^{13}$C NMR: