Kinetic resolution of donor-functionalised tertiary alcohols
by Cu–H-catalysed stereoselective silylation
using a strained silicon-stereogenic silane

Betül Karatas, Sebastian Rendler, Roland Fröhlich and Martin Oestreich*

Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster,
Corrensstrasse 40, D-48149 Münster, Germany
e-mail: martin.oestreich@uni-muenster.de

Electronic Supplementary Information

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1 General information

Reagents obtained from commercial suppliers were used without further purification unless otherwise noted. All reactions were performed in flame-dried glassware under a static pressure of argon. Liquids and solutions were transferred with syringes. Solvents were dried prior to use following standard procedures. Technical grade solvents for chromatography (cyclohexane, t-butyl methyl ether) were distilled before use. Analytical thin layer chromatography was performed on silica gel SIL G-25 glass plates by Macherey-Nagel and flash chromatography on silica gel 60 (40-63 µm, 230-400 mesh, ASTM) by Merck using the indicated solvents. $^1$H and $^{13}$C NMR spectra were recorded in CDCl$_3$ or C$_6$D$_6$ on Bruker AV 300 and Bruker AV 400 instruments. Chemical shifts are reported in ppm with the solvent reference as the internal standard (CDCl$_3$: $\delta$ = 7.26, C$_6$D$_6$: $\delta$ = 7.16). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, mc = centrosymmetrical multiplet, br = broad), coupling constants (Hz) and integration. AB signals in the $^1$H NMR spectra were denoted by the symbol "◊". Residual solvent peaks for cyclohexane and t-butyl methyl ether in the $^1$H and $^{13}$C NMR spectra were shown with a star (*).

Infrared spectra were recorded on a Digilab Excalibur Series FTS 4000 spectrometer. Intensities of the bands are abbreviated as broad (br), strong (s), medium (m), and weak (w). Gas liquid chromatography (GLC) was performed on a Shimadzu GC-17A with a SE-54 (30 m × 0.32 mm × 0.25 µm film thickness) column by CS-Chromatographie Service using the following program: column flow 1.7 mL/min N$_2$, start at 40°C, heat rate 10°C/min to 280°C, 5 min at 280°C. Enantiomeric ratios were determined by analytical HPLC analysis on an Agilent 1200 Series instrument with a chiral stationary phase using Daicel Chiralpak IA and Daicel Chiralpak IB columns (n-heptane:i-propanol mixtures as solvent).

Optical rotations were measured on a Perkin Elmer 341 polarimeter. Melting points (m.p.) were determined with a Stuart Scientific MP3 apparatus and are not corrected. High resolution mass spectrometry (HRMS) was performed by electron spray ionization mass spectrometry (ESI-MS) using a Bruker MicroTOF instrument, elemental analysis were obtained using a Elementaranalysensysteme VarioEL III instrument.

2 Characterisation data of 14–24, 26 and 28

$^{(\text{SiS}^*,\text{R}^*)-2-[2-(1\text{-tert-Butyl-1-silaindan-1-yloxy)-2-phenyl-4-(trimethylsilanyl)-but-3-ynyl]pyridine}}$ $[(\text{SiS}^*,\text{R}^*)-14]$

Analytical data for $^{(\text{SiS}^*,\text{R}^*)-14}$: Yield: 51%. GLC (SE-54): $t_R = 26.6$, 26.8 min. $R_f = 0.59$ (cyclohexane–t-butyl methyl ether = 3:1). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 0.07 (s, 9H, Si(CH$_3$)$_3$), 0.83◊ (ddd, $J$ = 15.5, 9.1, 4.3 Hz, 1H, 2''-HA), 0.96◊ (m, 1H, 2''-HB), 0.96 (s, 9H, C(CH$_3$)$_3$), 2.66◊ (ddd, $J$ = 16.9, 9.9, 4.0 Hz, 1H, 3''-HA), 2.75◊ (ddd, $J$ = 16.9, 9.1, 6.4 Hz, 1H, 3''-HB), 3.26◊ (d, $J$ = 12.8 Hz, 1H, 1-H$_A$), 3.47◊ (d, $J$ = 12.8 Hz, 1H, 1-H$_B$), 6.95 (dd, $J$ = 7.2 Hz, 1H, Ar-H), 7.02–7.20 (m, 7H, Ar-H), 7.31 (d, $J$ = 7.7 Hz, 1H, 3'-H), 7.45 (dd, $J$ = 7.8, 1.8 Hz, 2H, Ar-H), 7.53 (ddd, $J$ = 7.7 Hz, $J$ = 1.7 Hz, 1H, 4'-H), 8.46 (ddd, $J$ = 4.8, 1.7, 0.8 Hz, 1H, 6'-H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ –0.2, 6.9, 19.2, 26.2, 30.2, 55.8, 75.6, 94.1,
106.2, 121.7, 125.1, 125.4, 125.9, 126.2, 127.5, 127.8, 129.5, 133.0, 135.1, 135.6, 144.5, 148.7, 153.5, 157.0. IR (film) 2173 (w, C≡C) cm⁻¹. HRMS (ESI) calcd for C₃₀H₃₇NOSi₂ (M + Na⁺): 506.2306; found: 506.2298. Anal. calcd for C₃₀H₃₇NOSi₂ (483.80): C, 74.48; H, 7.71; N, 2.90; found: C, 74.26; H, 7.86; N, 2.78. The diastereomeric ratio was determined by integration of baseline separated ¹H NMR signals of Si(CH₃)₃ at –0.04 (s, 9H, minor diastereomer) and 0.07 (s, 9H, major diastereomer) ppm.


Analytical data for (Si,R*)-15 (d.r. = 78:22, Entry 2, Table 2): Yield: 58%. [α]₁₀⁰ = +21.6, [α]₅₇⁸ = +21.9, [α]₄₃₆ = +45.2, [α]₃₆₅ = +73.3 (c = 0.660, CHCl₃).

Analytical data for (Si,S*,R)-16 (d.r. = 76:24, Entry 1, Table 2): Yield: 58%. [α]₁₀⁰ = +21.6, [α]₅₇⁸ = +21.9, [α]₄₃₆ = +25.5, [α]₃₆₅ = +45.2, [α]₃₆₅ = +73.3 (c = 0.660, CHCl₃).

Analytical data for (Si,S*,R*)-17: Yield: 61%. Rf = 0.58 (cyclohexane–t-buty methyl ether = 3:1). ¹H NMR (400 MHz, CDCl₃): δ 0.05 (s, 9H, Si(CH₃)₃), 0.81 (ddd, 15.4, 9.0, 4.4 Hz, 1H, 2''-HA), 0.94 (s, 9H, C(C₃H₇)₃), 0.95 (mc, 1H, 2''-HB), 2.69 (mc, 2H, 3''-H), 3.25 (d, J = 12.9 Hz, 1H, 1-HA), 3.46 (d, J = 12.9 Hz, 1H, 1-HB), 6.93–6.97 (m, 3H, Ar-H), 7.02 (d, J = 7.7 Hz, 1H, Ar-H), 7.09–7.13 (m, 2H, 5'-H, Ar-H), 7.17 (ddd, J = J = 7.5 Hz, J = 1.3 Hz, 1H, Ar-H), 7.32–7.34 (m, 3H, 3'-H, Ar-H), 7.54 (ddd, J = J = 7.7 Hz, J = 1.8 Hz, 1H, 4'-H), 8.46 (ddd, J = 4.9, 1.8, 0.8 Hz, 1H, 6'-H). ¹³C NMR (100 MHz, CDCl₃): δ –0.2, 7.0, 19.2, 21.3, 26.2, 30.3, 55.8, 75.5, 93.9, 106.5, 121.7, 125.1, 125.4, 125.9, 126.1, 128.5, 129.4, 133.1, 135.1, 135.7, 137.1, 141.7, 148.7, 153.5, 157.2. IR (film) 2172 (w, C≡C) cm⁻¹. HRMS (ESI) calcd for C₃₁H₃₉NOSi₂ (M + Na⁺): 520.2462; found: 520.2452. Anal. calcd for C₃₁H₃₉NOSi₂ (597.83): C, 74.79; H, 7.90; N, 2.81; found: C, 74.59; H, 8.01; N, 2.70. The diastereomeric ratio was determined by integration of baseline separated ¹H NMR signals of Si(CH₃)₃ at –0.06 (s, 9H, minor diastereomer) and 0.05 (s, 9H, major diastereomer) ppm.

Analytical data for (Si,S*,R*)-18: Yield: 59%. Rf = 0.42 (cyclohexane–t-buty methyl ether = 3:1). ¹H NMR (400 MHz, CDCl₃): δ 0.02 (s, 9H, Si(CH₃)₃), 0.77 (ddd, 15.4, 9.0, 4.4 Hz, 1H, 2''-HA), 0.94 (s, 9H, C(C₃H₇)₃), 0.95 (mc, 1H, 2''-HB), 0.94 (s, 9H, C(C₃H₇)₃), 2.60 (ddd, J = 16.1, 10.0, 4.5 Hz, 1H, 3''-HA), 2.73 (ddd, J = 16.1, 9.3, 5.9 Hz, 1H, 3''-HB), 3.60 (d, J = 13.1 Hz, 1H, 1-HA), 3.80 (d, J = 13.1 Hz, 1H, 1-HB), 3.68 (s, 3H, OCH₃), 6.72 (dd, J = 8.2, 1.0 Hz, 1H, Ar-H), 6.77 (ddd, J = 7.6 Hz, J = 1.1 Hz, 1H, Ar-H), 6.99–7.04 (m, 2H, Ar-H), 7.10 (ddd, J = 7.6, 5.0, 1.1 Hz, 1H, 5'-H), 7.16–7.20 (m, 2H, Ar-H), 7.29 (d, J = 7.9 Hz, 1H, Ar-H), 7.34 (d, J = 7.2 Hz, 1H, Ar-H), 7.52 (ddd, J = 7.6 Hz, J = 1.9 Hz, 1H, 4'-H), 7.57 (dd, J = 7.7, 1.7 Hz, 1H, Ar-H), 8.48 (ddd, J = 5.0, 1.9, 0.9 Hz, 1H, 6'-H). ¹³C NMR (100 MHz, CDCl₃): δ –0.2, 7.1, 19.3, 26.3, 30.2, 50.7, 55.1, 74.7, 92.1, 106.9, 111.5, 119.9, 121.4, 125.0, 125.5, 125.9, 128.1, 129.1, 129.3, 131.5, 133.1, 134.9, 136.2, 148.7, 153.4, 157.0, 158.0. IR (ATR) 2170 (w, C≡C) cm⁻¹.
HRMS (ESI) calcd for C$_{31}$H$_{39}$NO$_2$Si$_2$ (M + H$^+$): 514.2592; found: 514.2580. Anal. calcd for C$_{31}$H$_{39}$NO$_2$Si$_2$ (513.83): C, 72.46; H, 7.65; N, 2.73; found: C, 72.44; H, 7.95; N, 2.65. The diastereomeric ratio was determined by integration of baseline separated $^1$H NMR signals of Si(CH$_3$)$_3$ at −0.08 (s, 9H, minor diastereomer) and 0.02 (s, 9H, major diastereomer) ppm.

Analytical data for (Si$^R$,R)-16 (d.r. = 81:19, Entry 3, Table 2): Yield: 64%. $[\alpha]_{D}^{20} = -19.2$, $[\alpha]_{D}^{20} = -20.1$, $[\alpha]_{345}^{20} = -27.7$, $[\alpha]_{345}^{20} = +24.4$, $[\alpha]_{345}^{20} = +47.7$, $[\alpha]_{345}^{20} = +74.1$ (c = 0.885, CHCl$_3$).

Analytical data for (Si$^R$,S)-17: Yield: 54%. $R_f = 0.43$ (cyclohexane−$t$-butyl methyl ether = 3 : 1). $^1$H NMR (400 MHz, CDCl$_3$): δ 0.07 (s, 9H, Si(CH$_3$)$_3$), 0.21 (s, 9H, Si(CH$_3$)$_3$), 0.26 (s, 9H, Si(CH$_3$)$_3$), 0.31 (s, 9H, Si(CH$_3$)$_3$), 0.35 (s, 9H, Si(CH$_3$)$_3$), 0.4 (s, 9H, Si(CH$_3$)$_3$), 0.44 (s, 9H, Si(CH$_3$)$_3$), 0.49 (s, 9H, Si(CH$_3$)$_3$).

Analytical data for (Si$^R$,S)-18: Yield: 59%. $R_f = 0.57$ (cyclohexane−$t$-butyl methyl ether = 3 : 1). $^1$H NMR (400 MHz, CDCl$_3$): δ 0.07 (s, 9H, Si(CH$_3$)$_3$), 0.21 (s, 9H, Si(CH$_3$)$_3$), 0.26 (s, 9H, Si(CH$_3$)$_3$), 0.31 (s, 9H, Si(CH$_3$)$_3$), 0.35 (s, 9H, Si(CH$_3$)$_3$), 0.4 (s, 9H, Si(CH$_3$)$_3$), 0.44 (s, 9H, Si(CH$_3$)$_3$), 0.49 (s, 9H, Si(CH$_3$)$_3$).

Analytical data for (Si$^S$,R)-19: Yield: 56%. $R_f = 0.43$ (cyclohexane−$t$-butyl methyl ether = 3 : 1). $^1$H NMR (400 MHz, CDCl$_3$): δ 0.07 (s, 9H, Si(CH$_3$)$_3$), 0.21 (s, 9H, Si(CH$_3$)$_3$), 0.26 (s, 9H, Si(CH$_3$)$_3$), 0.31 (s, 9H, Si(CH$_3$)$_3$), 0.35 (s, 9H, Si(CH$_3$)$_3$), 0.4 (s, 9H, Si(CH$_3$)$_3$), 0.44 (s, 9H, Si(CH$_3$)$_3$), 0.49 (s, 9H, Si(CH$_3$)$_3$).

Analytical data for (Si$^S$,S)-20: Yield: 59%. $R_f = 0.57$ (cyclohexane−$t$-butyl methyl ether = 3 : 1). $^1$H NMR (400 MHz, CDCl$_3$): δ 0.07 (s, 9H, Si(CH$_3$)$_3$), 0.21 (s, 9H, Si(CH$_3$)$_3$), 0.26 (s, 9H, Si(CH$_3$)$_3$), 0.31 (s, 9H, Si(CH$_3$)$_3$), 0.35 (s, 9H, Si(CH$_3$)$_3$), 0.4 (s, 9H, Si(CH$_3$)$_3$), 0.44 (s, 9H, Si(CH$_3$)$_3$), 0.49 (s, 9H, Si(CH$_3$)$_3$).
2.79; found: C, 72.03; H, 7.56; N, 3.18. The diastereomeric ratio was determined by integration of baseline separated $^1$H NMR signals of Si(CH$_3$)$_3$ at –0.03 (s, 9H, minor diastereomer) and 0.07 (s, 9H, major diastereomer) ppm.

Analytical data for ($^6$R,S)-18 (d.r. = 81:19, Entry 5, Table 2): Yield: 55%. $[\alpha]_{D}^{20} = +27.8$, $[\alpha]_{L}^{20} = +29.0$, $[\alpha]_{378}^{20} = +33.3$, $[\alpha]_{l}^{20} = +58.9$, $[\alpha]_{365}^{20} = +96.9$ (c = 0.710, CHCl$_3$).

Analytical data for ($^6$S*,R*)-19 (d.r. = 79:21, Entry 6, Table 2): Yield: 59%. $[\alpha]_{D}^{20} = –18.2$, $[\alpha]_{L}^{20} = –19.1$, $[\alpha]_{378}^{20} = –21.7$, $[\alpha]_{l}^{20} = –35.9$, $[\alpha]_{365}^{20} = –53.3$ (c = 0.695, CHCl$_3$).

Analytical data for ($^6$S*,R*)-20: Yield: 61%. R$\_r$ = 0.46 (cyclohexane–t-butyl methyl ether = 3 : 1). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 0.82 (m, 2H, 2'-H), 0.99 (s, 9H, C(CH$_3$)$_3$), 2.56 (ddd, J = 17.0, 8.3, 5.8 Hz, 1H, 3'-H), 2.68 (m, 1H, 3''-H), 3.39 (d, J = 12.9 Hz, 1H, 1-H), 3.59 (d, J = 12.9 Hz, 1H, 1-H), 6.94 (d, J = 7.5 Hz, 2H, Ar-H), 7.02 (d, J = 6.8 Hz, 1H, Ar-H), 7.06–7.09 (m, 2H, Ar-H), 7.14–7.27 (m, 8H, 5'-H, Ar-H), 7.38 (d, J = 7.8 Hz, 1H, 3'-H), 7.58–7.64 (m, 3H, 4'-H, Ar-H), 8.56 (d, J = 4.2 Hz, 1H, 6'-H). $^{13}$C NMR (100 MHz, CDCl$_3$): 6.8, 19.2, 26.2, 30.2, 55.4, 75.5, 89.7, 90.3, 122.1, 122.5, 125.1, 125.8, 125.9, 126.0, 126.2, 128.6, 129.5, 131.7, 133.0, 135.5, 135.9, 145.0, 148.2, 153.7, 156.9. IR (film) 2233 (w, C≡C) cm$^{-1}$. HRMS (ESI) calcd for C$_{33}$H$_{33}$NOSi (M + Na$^+$): 510.2224; found: 510.2223. Anal. calcd for C$_{33}$H$_{33}$NOSi (487.72): C, 81.27; H, 6.82; N, 2.87; found: C, 81.22; H, 7.35; N, 2.65. The diastereomeric ratio was determined by integration of baseline separated $^1$H NMR signals of 6'-H at 8.49 (d, 1H, minor diastereomer) and 8.56 (d, 1H, major diastereomer) ppm.
Analytical data for \(^{(6}S, R\)-20) (d.r. = 72:28, Entry 7, Table 2): Yield: 62%. \([\alpha]_{D}^{20} = -78.1, \ [\alpha]_{D}^{378} = -81.6,\ \alpha_{347}^{20} = -94.6, \ [\alpha]_{365}^{20} = -182, \ [\alpha]_{365}^{20} = -346\ (c = 0.645, CHCl_3)\).

\((^{(R}, S\)-2-\{2-(1-tert-Butyl-1-silaindan-1-yloxy)-2-(4-methoxyphenyl)-4-phenyl-but-3-ynyl\}pyridine \[^{(R}, S\)-21\]

Analytical data for \((^{(R}, S\)-21\): Yield: 64%. \(R_f = 0.35\) (cyclohexane–tert-butyl methyl ether = 3 : 1). \(\text{H}^1\) NMR (400 MHz, CDCl_3): \(\delta\ –0.03\ (s, 9H, Si(CH_3)_3)\), \(0.01\ (s, 9H, Si(CH_3)_3)\), \(0.97\ (s, 9H, C(CH_3)_3)\), \(2.56\ (s, 9H, C(CH_3)_3)\), \(3.08\ (s, 3H, OCH_3)\), 6.74–7.68 (m, 2H, Ar-H), 7.14–7.59 (m, 7H, Ar-H), 8.49–8.52 (m, 1H, 6'-H). \(\text{C}^{13}\) NMR (75 MHz, CDCl_3) (Major diastereomer): \(\delta\ –0.2, 6.9, 18.9, 25.9, 30.3, 30.9, 31.3, 70.4, 89.5, 108.8, 121.1, 125.4, 125.5, 126.3, 129.8, 133.1, 135.4, 136.3, 148.8, 153.7, 157.3, 159.1. IR (ATR) 2168 (w, C≡C) cm\(^{-1}\). HRMS (ESI) calcd for \(C_{35}H_{36}NO_2Si\) (M + Na\(^+\)): 540.2329; found: 540.2322. Anal. calcd for \(C_{34}H_{35}NO_2Si\) (517.74): C, 78.88; H, 6.81; N, 2.71; found: C, 78.74; H, 7.21; N, 2.46. The diastereomeric ratio was determined by integration of baseline separated \(\text{H}^1\) NMR signals of 6'-H at 8.48 (ddd, 1H, minor diastereomer) and 8.54 (ddd, 1H, major diastereomer) ppm.

\((^{(R}, S\)-2-\{2-(1-tert-Butyl-1-silaindan-1-yloxy)-2-isopropyl-4-(trimethylsilanyl)-but-3-ynyl\}pyridine \[^{(R}, S\)-23\]

Analytical data for \((^{(R}, S\)-23\): Yield: 47%. \(R_f = 0.68\) (cyclohexane–tert-butyl methyl ether = 3 : 1). \(\text{H}^1\) NMR (300 MHz, CDCl_3): \(\delta\ –0.10\ (s, 9H, Si(CH_3)_3)\), \(–0.04\ (s, 9H, Si(CH_3)_3)\), \(0.69\ (m_c, 2H, 2''-H_{minor})\), \(0.91\ (s, 9H, C(CH_3)_3)\), \(0.94\ (s, 9H, C(CH_3)_3)\), \(1.00\ (m_c, 1H, 2''-H_{major})\), \(1.05\ (d, J = 6.8\ Hz, 6H, CH(CH_3)_2)\), \(1.08\ (d, J = 6.8\ Hz, 3H, CH(CH_3)_2)\), \(1.09\ (d, J = 6.8\ Hz, 3H, CH(CH_3)_2)\), \(1.28\ (m_c, 1H, 2''-H_{major})\), \(1.76\ (qq, J = 6.8\ Hz, 1H, CH(CH_3)_2)\), \(1.83\ (sep, 1H, CH(CH_3)_2)\).
2.93 (m, 2H, 3''-H), 3.08 d (d, J = 12.8 Hz, 1H, 1-H\text{minor}), 3.15 d (d, J = 12.8 Hz, 1H, 1-H\text{major}), 3.12 (s, 2H, 1-H\text{major}), 7.07–7.18 (m, 3H, Ar-H), 7.24–7.34 (m, 2H, Ar-H), 7.42 (m, 1H, 1-H\text{major}), 7.47 (dd, J = 7.7 Hz, J = 1.8 Hz, 1H, 4''-H\text{minor}), 7.61 (m, 1H, Ar-H), 8.48 (dd, J = 4.9, 1.8, 0.9 Hz, 1H, 6''-H\text{minor}). 13C NMR (75 MHz, CDCl₃): δ 0.3 [0.3], 6.8 [7.4], 17.4 [17.8], 17.8 [17.9], 19.3 [19.4], 26.1 [26.1], 30.2 [30.4], 37.5 [38.5], 47.3 [47.9], 76.6 [76.7], 92.1 [92.3], 106.9, [107.4], 121.6 [121.8], 125.2 [125.3], 125.7 [125.8], 126.3 [126.3], 129.5 [129.7], 133.0 [133.3], 135.5 [135.5], 136.3 [136.3], 148.6 [148.6], 153.3 [153.3], 157.6 [157.8]. IR (film) 2165 (w, C≡C) cm⁻¹. HRMS (ESI) calcd for C₂₇H₃₉NOSi₂ (M + H⁺): 450.2643; found: 450.2651. Anal. calcd for C₂₇H₃₉NOSi₂ (449.78): C, 72.10; H, 8.74; N, 3.11; found: C, 71.80; H, 8.79; N, 3.48. The diastereomeric ratio was determined by integration of baseline separated 1H NMR signals of Si(CH₃)₃ at –0.10 (s, 9H, minor diastereomer) and –0.04 (s, 9H, major diastereomer) ppm.

(5'R*,S*)-2-[2-(1-tert-Butyl-1-silainden-1-yloxy)-2-cyclohexyl-4-phenyl-but-3-ynyl]pyridine
[(5'S*,S*)-24]
Analytical data for (5'R*,S*)-24: Yield: 51%. Major diastereomer: Rᵥ = 0.57 (cyclohexane–t-butyl methyl ether = 9 : 2). 1H NMR (400 MHz, CDCl₃): δ 0.96 (s, 9H, C(CH₃)₃), 1.01 d (m, 1H, 2''-HA), 1.15–1.81 (m, 10H, 2''-HB and Cy-H), 2.12 (d, J = 11.6 Hz, 1H, Cy-H), 2.20 (d, J = 11.6 Hz, 1H, Cy-H), 2.80 (dd, J = 17.0, 9.3, 6.1 Hz, 1H, 3''-H A), 2.91 (ddd, J = 17.0, 10.5, 3.9 Hz, 1H, 3''-H B), 3.22 (d, J = 13.1 Hz, 1H, 1-HA), 3.26 (d, J = 13.1 Hz, 1H, 1-HB), 6.92–6.95 (m, 2H, Ar-H), 7.02 (d, J = 7.6 Hz, 1H, 3''-H), 7.09 (dd, J = 7.2 Hz, J = 0.7 Hz, 1H, Ar-H), 7.13 (ddd, J = 7.6, 4.9, 1.1 Hz, 1H, 5''-H), 7.17–7.24 (m, 4H, Ar-H), 7.33 (d, J = 7.8 Hz, 2H, Ar-H), 7.50 (ddd, J = J = 7.6 Hz, J = 1.8 Hz, 1H, 4''-H), 8.54 (ddd, J = 4.9, 1.8, 0.9 Hz, 1H, 6''-H). 13C NMR (100 MHz, CDCl₃): δ 7.4, 19.3, 26.2, 26.7, 27.5, 28.0, 30.3, 47.5, 48.3, 76.5, 88.1, 91.7, 121.6, 122.9, 125.3, 125.7, 126.3, 128.1, 128.2, 129.6, 131.6, 133.0, 135.5, 136.5, 148.9, 153.8, 157.9. IR (film) 2229 (w, C≡C) cm⁻¹. HRMS (ESI) calcd for C₃₃H₄₀NOSi (M + H⁺): 494.2874; found: 494.2866. Analytical data for (5'S*,S*)-24 (Minor diastereomer): Rᵥ = 0.46 (cyclohexane–t-butyl methyl ether = 9 : 2). 1H NMR (300 MHz, CDCl₃): δ 0.54 (dd, J = 15.5, 9.8, 6.4 Hz, 1H, 2''-Ha), 0.69 (dd, J = 15.5, 8.8, 4.4 Hz, 1H, 2''-Ha), 0.95 (s, 9H, C(CH₃)₃), 1.15–1.33 (m, 5H, Cy-H), 1.61–1.82 (m, 4H, Cy-H), 1.63 (m, 2H, Cy-H), 2.74 (m, 2H, 3''-H), 3.31 (s, 2H, 1-H), 6.86 (m, 2H, Ar-H), 7.00 (d, J = 7.5 Hz, 1H, Ar-H), 7.13–7.29 (m, 6H, Ar-H), 7.56–7.66 (m, 2H, Ar-H), 7.73 (dd, J = J = 7.1 Hz, 1H, Ar-H), 8.60 (ddd, J = 4.9, 1.8, 0.8 Hz, 1H, 6''-H). 13C NMR (75 MHz, CDCl₃): δ 6.7, 19.3, 26.2, 26.7, 27.1, 27.9, 30.1, 47.8, 48.8, 76.4, 88.3, 91.2, 121.7, 122.8, 125.3, 125.8, 126.3, 128.0, 128.2, 129.4, 131.5, 133.2, 135.4, 136.6, 150.0, 153.6, 158.1. HRMS (ESI) calcd for C₃₃H₃₀NOSi (M + H⁺): 494.2874; found: 494.2870. The diastereomeric ratio was determined by integration of baseline separated 1H NMR signals of 6''-H at 8.54 (ddd, 1H, major diastereomer) and 8.60 (ddd, 1H, minor diastereomer) ppm.
\((\text{Si}^*\text{S}^*,\text{R}^*)-2-[2-(1\text{-}\text{tert}-\text{Butyl}-1\text{-silaindan-1-yloxy})-2,4\text{-diphenyl-but-3-ynyl}]\text{-6-methylpyridine}
\)

\([\text{[\text{Si}^*\text{S}^*,\text{R}^*]}-26]\)

Analytical data for \((\text{Si}^*\text{S}^*,\text{R}^*)-26\): Yield : 60%. \(R_f = 0.57\) (cyclohexane–t-butyl methyl ether = 3 : 1). \(^1\text{H}\) NMR (300 MHz, CDCl\(_3\)): \(\delta\) 0.79 (mc, 2H, 2\(^{\prime}\)-H), 0.99 (s, 9H, C(CH\(_3\))\(_3\)), 2.53 (s, 3H, C\(_6\text{H}3\)), 2.62 (mc, 2H, 3\(^{\prime}\)-H), 3.30 \(\diamond\) (d, \(J\) = 12.9 Hz, 1H, 1-H\(_A\)), 3.52 \(\diamond\) (d, \(J\) = 12.9 Hz, 1H, 1-H\(_B\)), 6.94 (mc, 2H, Ar-H), 7.01–7.07 (m, 4H, Ar-H), 7.13–7.28 (m, 8H, Ar-H), 7.47 (dd, \(J\) = \(J\) = 7.7 Hz, 1H, Ar-H), 7.59–7.62 (m, 2H, Ar-H).

\(^{13}\text{C}\) NMR (75 MHz, CDCl\(_3\)): \(\delta\) 6.8, 19.2, 24.7, 26.2, 30.2, 55.8, 75.5, 89.5, 90.5, 121.3, 122.6, 122.7, 125.1, 125.9, 126.2, 127.5, 127.9, 128.1, 128.5, 129.4, 129.9, 131.7, 133.0, 133.6, 135.7, 145.4, 153.7, 156.5, 157.2. IR (film) 2232 (w, C\(\equiv\)C) cm\(^{-1}\). HRMS (ESI) calcd for C\(_{34}\)H\(_{35}\)NOSi (M + H\(^+\)) : 502.2561; found: 502.2553. The diastereomeric ratio was determined by integration of baseline separated \(^1\text{H}\) NMR signals of C\(_6\text{H}3\) at 2.46 (s, 3H, minor diastereomer) and 2.53 (s, 3H, major diastereomer) ppm.

Analytical data for \((\text{Si}^*\text{S}^*,\text{R}^*)-26\) (d.r. = 75:25, Scheme 3): \([\alpha]^20_D = -60.5\), \([\alpha]^20_{579} = -63.7\), \([\alpha]^20_{546} = -73.8\), \([\alpha]^20_{436} = -142\), \([\alpha]^20_{365} = -273\) (c = 0.745, CHCl\(_3\)).

\((\text{Si}^*\text{S}^*,\text{R}^*)-2-[2-(1\text{-}\text{tert}-\text{Butyl}-1\text{-silaindan-1-yloxy})-2,4\text{-diphenyl-but-3-ynyl}]\text{-quinoline}\n\)

\([\text{[\text{Si}^*\text{S}^*,\text{R}^*]}-28]\)

Analytical data for \((\text{Si}^*\text{S}^*,\text{R}^*)-28\): \(R_f = 0.70\) (cyclohexane–t-butyl methyl ether = 3 : 1). \(^1\text{H}\) NMR (300 MHz, CDCl\(_3\)): \(\delta\) 0.71 (mc, 2H, 2\(^{\prime}\)-H), 1.00 (s, 9H, C(CH\(_3\))\(_3\)), 2.57 (mc, 2H, 3\(^{\prime}\)-H), 3.75 \(\diamond\) (d, \(J\) = 12.7 Hz, 1H, 1-H\(_A\)), 3.75 \(\diamond\) (d, \(J\) = 12.7 Hz, 1H, 1-H\(_B\)), 6.90–7.01 (m, 4H, Ar-H), 7.12–7.40 (m, 8H, Ar-H), 7.46–7.51 (m, 2H, Ar-H), 7.64–7.81 (m, 4H, Ar-H), 8.02 (d, \(J\) = 11.2 Hz, 1H, Ar-H), 8.10 (d, \(J\) = 11.2 Hz, 1H, Ar-H). \(^{13}\text{C}\) NMR (75 MHz, CDCl\(_3\)): \(\delta\) 6.8, 19.1, 26.2, 30.1, 56.5, 75.6, 89.9, 90.2, 122.5, 123.9, 125.1, 125.9, 126.0, 126.2, 127.2, 127.6, 127.7, 128.0, 128.1, 128.5, 129.2, 129.4, 129.4, 131.7, 133.0, 133.9, 134.9, 135.5, 145.2, 147.9, 153.7, 157.8. IR (film) 2232 (w, C\(\equiv\)C) cm\(^{-1}\). HRMS (ESI) calcd for C\(_{37}\)H\(_{35}\)NOSi (M + H\(^+\)) : 538.2561; found: 538.2567. The diastereomeric ratio was determined by integration of baseline separated \(^1\text{H}\) NMR signals of 1-H\(_B\) at 3.71 (d, 1H, minor diastereomer) and 3.75 (d, 1H, major diastereomer) ppm.

Analytical data for \((\text{Si}^*\text{S},\text{R})-28\) (d.r. = 77:23, Scheme 3): Yield : 55%. \([\alpha]^20_D = -66.0\), \([\alpha]^20_{579} = -69.2\), \([\alpha]^20_{436} = -80.5\), \([\alpha]^20_{436} = -156\) (c = 0.655, CHCl\(_3\)).
rac-3 (¹H):

rac-3 (¹³C):
rac-4 ($^1$H):

rac-4 ($^{13}$C):
**rac-5 (¹H):**

![Chemical Structure of rac-5 (¹H)](image)

**rac-5 (¹³C):**

![Chemical Structure of rac-5 (¹³C)](image)
**rac-6 \( (^1H) \):**

![1H NMR spectrum of rac-6](image)

**rac-6 \( (^13C) \):**

![13C NMR spectrum of rac-6](image)
$\text{rac-7}$ ($^1$H):

$\text{rac-7}$ ($^{13}$C):

$$\begin{array}{c}
\text{F} \\
\text{Me}_3\text{Si} \\
\text{O} \\
\text{N}
\end{array}$$
**rac-8 (\(^{1}\text{H})\):**

![NMR Spectrum of rac-8 (\(^{1}\text{H})\)](attachment)

**rac-8 (\(^{13}\text{C})\):**

![NMR Spectrum of rac-8 (\(^{13}\text{C})\)](attachment)
rac-9 (\textsuperscript{1}H):

![NMR spectrum of rac-9 (\textsuperscript{1}H)](image)

rac-9 (\textsuperscript{13}C):

![NMR spectrum of rac-9 (\textsuperscript{13}C)](image)
**rac-10** ($^1$H):

![NMR spectrum of rac-10 (1H) with chemical shifts and peaks labeled.

**rac-10** ($^{13}$C):

![NMR spectrum of rac-10 (13C) with chemical shifts and peaks labeled.]
rac-11 (\(^1\)H):

\[
\text{Me}_3\text{Si} = \text{OH}
\]

rac-11 (\(^{13}\)C):

\[
\text{258.853} \quad 156.722 \quad 124.956 \quad 121.144 \quad 109.604 \quad 86.699 \quad 76.922 \quad 69.031 \quad 59.676 \quad 48.388
\]
rac-12 (\(^1\)H):

\[
\begin{align*}
\text{Me}_3\text{Si} & \quad \text{OH} \\
\end{align*}
\]

rac-12 (\(^{13}\)C):

\[
\begin{align*}
\text{17.307} & \quad \text{17.925} & \quad \text{37.723} & \quad \text{44.757} & \quad \text{74.766} & \quad \text{88.804} & \quad \text{107.692} & \quad \text{121.797} & \quad \text{124.738} & \quad \text{136.786} & \quad \text{148.085} & \quad \text{159.364}
\end{align*}
\]
rac-13 ($^1$H):  

![NMR spectrum of rac-13 (1H)](image)

rac-13 ($^{13}$C):  

![NMR spectrum of rac-13 (13C)](image)
\((^\text{Si}^*^\text{S}^*,^\text{R}^*)-14\) \((^1\text{H})\):

\[(\text{Si}^*^\text{S}^*,^\text{R}^*)-14\] \((^1\text{H})\):

\[
\begin{align*}
0.82 & \quad 8.86 & \quad 1.19 & \quad 10.07 \\
2.17 & \quad 1.10 & \quad 1.12 & \quad 0.92 \\
7.15 & \quad 1.08 & \quad 1.99 & \quad 1.13 \\
1.00 & & & & \\
\end{align*}
\]

\((\text{Si}^*^\text{S}^*,^\text{R}^*)-14\) \((^{13}\text{C})\):

\[(\text{Si}^*^\text{S}^*,^\text{R}^*)-14\] \((^{13}\text{C})\):

\[
\begin{align*}
-0.235 & \quad 6.942 & \quad 19.155 & \quad 26.176 \\
30.228 & \quad 55.839 & \quad 75.650 & \quad 94.120 \\
106.241 & \quad 121.745 & \quad 125.113 & \quad 126.212 \\
133.008 & \quad 135.123 & \quad 135.614 & \quad 144.503 \\
148.720 & \quad 153.525 & \quad 157.039 & \quad 2.35 \\
\end{align*}
\]
($^{\text{Si}R^*,S^*}$-15) $^1$H):

($^{\text{Si}R^*,S^*}$-15) $^{13}$C):
(\text{Si}^*,\text{R}^*)-16 (^1\text{H}):
\((^{\text{Si}^*,S^*})-17\) (\(^1\text{H}\)):
(SiR*,S*)-18 (1H):

(\text{SiR}\在我看来，(S*)-18 (13C):

\begin{align*}
\text{Si} & \quad \text{O} \\
\text{t-Bu} & \quad \text{Si} \\
\text{Me} & \quad \text{O} \\
\text{N} & \quad \text{F}
\end{align*}
\((\text{Si}^*,\text{R}^*)-19\) (\(^1\text{H}\)):
\((^{\text{Si}^*\text{R}^*})-20\) \((^1H)\):

![NMR spectrum of (\(^{\text{Si}^*\text{R}^*}\))-20 (\(^1H\)).]

\((^{\text{Si}^*\text{R}^*})-20\) \((^{13}C)\):

![NMR spectrum of (\(^{\text{Si}^*\text{R}^*}\))-20 (\(^{13}C\)).]
(\(\text{Si}R^*,S^*\))-21 (\(^1\text{H}\)):

(\(\text{Si}R^*,S^*\))-21 (\(^{13}\text{C}\)):
\((\text{Si}^*\text{R}^*,\text{S}^*)-22\) (\(^1\text{H}\)):
\((\text{Si}^R, \text{S})^\ast\text{-}23\) (\(\text{H}\)):

![Chemical Structure](image)

\((\text{Si}^R, \text{S})^\ast\text{-}23\) (\(\text{C}\)):
$(\text{Si}^* \text{R}^*, \text{S}^*)$-$24$ ($^1$H): (Major diastereomer)

$(\text{Si}^* \text{R}^*, \text{S}^*)$-$24$ ($^{13}$C):

Electronic Supplementary Information (ESI) for Organic & Biomolecular Chemistry
rac-25 (1H):

![H NMR spectrum of rac-25](image)

rac-25 (13C):

![C NMR spectrum of rac-25](image)
(\textsuperscript{Si*},\textsuperscript{R*})-26 (\textsuperscript{1}H):

(\textsuperscript{Si*},\textsuperscript{R*})-26 (\textsuperscript{13}C):
rac-27 ($^1$H):

rac-27 ($^{13}$C):

**Electronic Supplementary Information (ESI) for Organic & Biomolecular Chemistry**

S33
\((^{\text{Si}}S^*,^{\text{R}}R^*)-28\) \((^1\text{H})\):

\[
\begin{align*}
1.96 & 9.12 \\
2.04 & 1.04 \\
1.02 & 1.00 \\
4.87 & 7.00 \\
2.09 & 3.07 \\
1.08 & 1.02 \\
1.02 & 1.06 \\
\end{align*}
\]

\((^{\text{Si}}S^*,^{\text{R}}R^*)-28\) \((^{13}\text{C})\):

\[
\begin{align*}
6.767 & 19.149 \\
26.218 & 30.119 \\
56.522 & 75.624 \\
89.952 & 90.221 \\
122.498 & 123.919 \\
125.070 & 125.897 \\
126.055 & 126.189 \\
127.240 & 127.656 \\
127.678 & 127.984 \\
128.110 & 145.278 \\
147.947 & 153.732 \\
157.869 & 158.119 \\
158.149 & 3.87 \\
\end{align*}
\]
4 Molecular structures of rac-15, rac-16 and rac-19 (relative configuration) as well as (S)-8 (absolute configuration)

rac-15 [(S$^*$$^*$;S$^*$)-15]: Crystal data for C$_{31}$H$_{39}$NOSi$_2$, \( M = 497.81 \), triclinic, space group \( P1\bar{1} \) (No. 2), \( a = 10.2158(3) \), \( b = 10.5173(3) \), \( c = 16.3911(5) \) Å, \( \alpha = 72.213(2) \), \( \beta = 81.203(2) \), \( \gamma = 61.845(4) \)°, \( V = 1478.42(8) \) Å$^3$, \( D_c = 1.118 \) g cm$^{-3}$, \( \mu = 1.249 \) mm$^{-1}$, \( Z = 2 \), \( \lambda = 1.54178 \) Å, \( T = 223(2) \) K, 18283 reflections collected (±h, ±k, ±l), \( [(\sin \theta)/\lambda] = 0.60 \) Å$^{-1}$, 5176 independent \( (R_{int} = 0.038) \) and 4699 observed reflections \( [I \geq 2\sigma(I)] \), 323 refined parameters, \( R = 0.043 \), \( wR^2 = 0.117 \), CCDC 668299
rac-16 \([([S^*],R^*)-16]\): Crystal data for C\(_{31}\)H\(_{39}\)NO\(_2\)Si\(_2\), \(M = 513.81\), monoclinic, space group \(P2_1/n\) (No. 14), \(a = 14.6545(4)\) Å, \(b = 21.6938(6)\) Å, \(c = 19.1708(5)\) Å, \(\beta = 101.885(2)\)°, \(V = 5964.0(3)\) Å\(^3\), \(D_c = 1.144\) g cm\(^{-3}\), \(\mu = 1.279\) mm\(^{-1}\), \(Z = 8\), \(\lambda = 1.54178\) Å, \(T = 223(2)\) K, 55533 reflections collected \((\pm h, \pm k, \pm l)\), \([(\text{sin} \theta)/\lambda] = 0.60\) Å\(^{-1}\), 10655 independent \((R_{int} = 0.068)\) and 8195 observed reflections \([I \geq 2\sigma(I)]\), 694 refined parameters, \(R = 0.055\), \(wR^2 = 0.138\), CCDC 668298
rac-19 [(S,R*,S*)-19]: Crystal data for C\textsubscript{30}H\textsubscript{36}ClNOSi\textsubscript{2}, \(M = 518.23\), triclinic, space group \(P\overline{1}\)bar (No. 2), \(a = 10.2053(4)\), \(b = 10.5866(5)\), \(c = 16.1920(8)\) Å, \(\alpha = 72.052(2)\), \(\beta = 80.971(2)\), \(\gamma = 62.274(4)\)˚, \(V = 1472.97(12)\) Å\(^3\), \(D_c = 1.168\) g cm\(^{-3}\), \(\mu = 2.088\) mm\(^{-1}\), \(Z = 2\), \(\lambda = 1.54178\) Å, \(T = 223(2)\) K, 17954 reflections collected (±h, ±k, ±l), \([\sin(\theta)/\lambda] = 0.60\) Å\(^{-1}\), 5153 independent \((R_{int} = 0.035)\) and 4833 observed reflections \([I \geq 2\sigma(I)]\), 322 refined parameters, \(R = 0.038\), \(wR^2 = 0.114\), CCDC 668297
(S)-8: Crystal data for C_{18}H_{20}ClNOSi, \( M = 329.89 \), orthorhombic, space group \( P2_12_12_1 \) (No. 19), \( a = 5.9900(3) \), \( b = 15.6120(8) \), \( c = 19.9389(10) \) \( \AA \), \( V = 1864.60(13) \) \( \AA^3 \), \( D_c = 1.175 \) g cm\(^{-3} \), \( \mu = 2.428 \) mm\(^{-1} \), \( Z = 4 \), \( \lambda = 1.54178 \) \( \AA \), \( T = 223(2) \) K, 10021 reflections collected (\( \pm h, \pm k, \pm l \)), \( [\sin(\theta)/\lambda] = 0.60 \) Å\(^{-1} \), 3219 independent (\( R_{int} = 0.050 \)) and 2928 observed reflections \([I \geq 2\sigma(I)]\), 203 refined parameters, \( R = 0.041, wR^2 = 0.100 \), Flack parameter 0.00(2), CCDC 668300