Supporting Information

Relay Catalysis using a Gold(I) Complex/Brønsted Acid Binary System for the Synthesis of Bezoxasiloles

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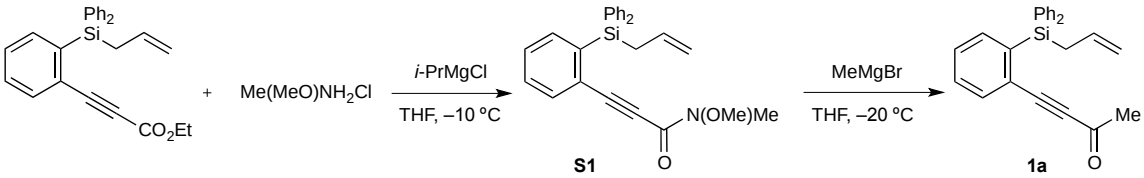
General.

All reactions were carried out in flame-dried glassware under nitrogen atmosphere. Tetrahydrofuran (THF), 1,4-dioxane, and diethyl ether (Et_2O) were purified by distillation from benzophenone ketyl. Acetonitrile (MeCN), nitoromethane and triethyl amine (Et_3N) were purified by distillation from CaH_2. Flash chromatography was performed with KANTO silica gel 60N (63-210□□m). Thin layer chromatography was carried out using Merck silica gel 60 F_{254} TLC plates coated with fluorescent indicator UV254. NMR spectra were recorded on JEOL α-GX400 or JNX-ECX500 spectrometer. Chemical shifts (δ) are reported in ppm and coupling constants are reported in Hz with $CDCl_3$ referenced at 7.26 (^{1}H) and 77.00 ppm (^{13}C), respectively. Peak multiplicities are designated by the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad and coupling constants are provided in (*J*) Hz. High resolution mass spectral data was obtained on a JEOL MStation JMS-700. HPLC analysis was carried out on a Waters 600 Controller and a detector Tosoh UV-8010 using CHIRACEL OZ-H column (250 × 4.6 mm). All commercial reagents were used as received unless otherwise noted.

Materials.

1-(Allyldiphenylsilyl)-2-ethynylbenzene and 1-(allyldiethylsilyl)-2-ethynylbenzene were prepared according to the literature procedures.[1)] chloro(triphenylphosphine)gold(I) [2)], chloro(tri-*tert*-butylphosphine)gold(I) [3)], chloro[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]gold(I) [4)], methyl(triphenylphosphine)gold(I) [5)], (*R*)-3,3′-bis[3,5-bis(trifluoromethyl)phenyl]-1,1′-binaphthyl-2,2′-diyl hydrogenphosphate [6)] were prepared according to the literature methods. (*S*)-DTBM-SEGPHOS$(AuCl)_2$ and other silver salts were obtained form Aldrich Chemical Company.

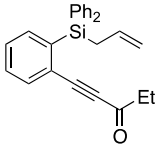
General procedures for preparation of 1-substituted 3-[2-(allyldiphenylsilyl)phenyl]propyn-1-one.



3-[2-(Allyldiphenylsilyl)phenyl]propynoic acid *N*-methoxy-*N*-methylamide (**S1**). To a mixture of ethyl 3-[2-(allyldiphenylsilyl)phenyl]propynoate (3.57 g, 11 mmol) and *N*,*O*-dimethylhydroxylamine hydrochloride (3.22 g, 33 mmol) was added *i*-PrMgBr (1.4 M in THF, 28.6 mL, 40 mmol) at -10 °C under N_2, and the mixture was stirred at -10 °C for 1 h. Upon completion, the mixture was quenched with saturated NH_4Cl solution (20 mL) and extracted with EtOAc (50 mL). The aqueous layer was re-extracted with EtOAc (2 × 20 mL). The combined organic phases were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane = 1/4 then 1/2) to give S**1** (2.5 g, 86% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.67 (d, J = 8.0 Hz, 2H), 3.04 (s, 3H), 3.44 (s, 3H), 4.88 (dm, J = 10.0, Hz, 1H), 5.00 (dm, J = 17.2 Hz, 1H), 5.90 (ddt, J = 10.0, 17.2, 8.0 Hz, 1H), 7.33-7.43 (m, 9H), 7.53 (dm, J = 7.6 Hz, 4H), 7.66 (d, J = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.9, 32.2, 61.7, 84.1, 91.5, 115.1, 126.5, 127.7, 129.1, 129.5, 134.0, 134.1, 134.3, 134.9, 135.8, 137.3, 138.4, 154.1; HRMS (EI) calcd for $C_{26}H_{25}NO_2Si$ [M^+] 411.1655; Found *m/z* 411.1658.

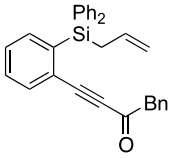
1-Methyl-3-[2-(allyldiphenylsilyl)phenyl]propyn-1-one (**1a**). To a mixture of **S1** (411 mg, 1 mmol) in THF (10 mL) was added MeMgBr (1 M in THF, 2 mL, 2 mmol) at -30 °C under N_2, and the mixture was stirred at -30 °C for 1 h. Upon completion, the mixture was quenched with saturated NH_4Cl solution (10 mL) and extracted with Et_2O (10 mL). The aqueous layer was re-extracted with Et_2O (2 × 10 mL). The combined organic phases were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (R_f 0.55, EtOAc/hexane = 1/9) to give **1a** (240.2 mg, 64% yield) as a yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.84 (s, 3H), 2.58 (dd, J = 1.2, 8.0 Hz, 2H), 4.89 (dm, J = 10.0 Hz, 1H), 4.99 (dm, J = 16.8 Hz, 1H), 5.87 (dm, J = 16.8 Hz, 1H), 7.35-7.47 (m, 9H), 7.54-7.57 (m, 4H), 7.66 (dm, J = 7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.2, 31.8, 91.5, 91.6, 115.3, 126.0, 127.9, 129.6(8), 129.7(2), 129.8, 133.8, 134.0, 134.7, 135.7, 137.4, 139.2, 184.4; HRMS (EI) calcd for $C_{25}H_{22}OSi$ [M^+] 366.1440; Found *m/z* 366.1441.

1-Ethyl-3-[2-(allyldiphenylsilyl)phenyl]propyn-1-one (**1b**).



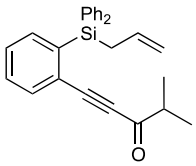
Colorless oil, purified by silica gel column chromatography (89% yield, R_f 0.62, EtOAc/hexane = 1/4). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.88 (t, J = 7.2 Hz, 3H), 2.06 (q, J = 7.2 Hz, 2H), 2.58 (dd, J = 1.2, 8.0 Hz, 2H), 4.89 (dm, J = 10.0 Hz, 1H), 4.99 (dm, J = 16.8 Hz, 1H), 5.87 (m, J = 1H), 7.35-7.47 (m, 9H), 7.55-7.57 (dm, J = 6.8 Hz, 4H), 7.66 (dd, J = 0.8, 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 7.5, 21.1, 37.9, 91.51, 91.2, 115.2, 126.1, 127.8, 129.57(2C), 129.63, 133.7, 133.9, 134.6, 135.6, 137.3, 138.9, 187.9; HRMS (EI) calcd for $C_{26}H_{24}OSi$ [M^+] 380.1596; Found *m/z* 380.1596.

1-Benzyl-4-[2-(allyldiphenylsilyl)phenyl]propyn-1-one (**1c**).



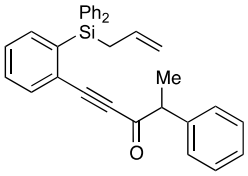
Yellow solid, purified by silica gel column chromatography (88% yield, R_f 0.62, EtOAc/hexane = 1/4). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.56 (dm, J = 8.0 Hz, 2H), 3.34 (s, 2H), 4.87 (dd, J = 1.5, 10.0 Hz, 1H), 4.97 (dq, J = 18.0, 1.5 Hz, 1H), 5.84 (ddt, J = 10.0, 18.0, 8.0 Hz, 1H), 7.00 (dm, J = 6.5 Hz, 2H), 7.22-7.29 (m, 3H), 7.35-7.44 (m, 9H), 7.55-7.57 (dd, J = 1.0, 8.0 Hz, 4H), 7.58 (dm, J = 7.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.3, 51.0, 91.5, 93.0, 115.4, 126.1, 127.2, 128.0, 128.6, 129.8(2), 129.8(6), 129.9, 132.9, 133.8, 134.1, 134.8, 135.8, 137.4, 139.3, 184.5; HRMS (EI) calcd for $C_{31}H_{26}OSi$ [M^+] 442.1753; Found *m/z* 442.1755.

2-Methyl-5-[2-(allyldiphenylsilyl)phenyl]pentyn-3-one (**1d**).



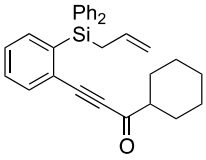
Colorless oil, purified by silica gel column chromatography (46% yield, R_f 0.66, EtOAc/hexane = 1/4). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.92 (d, J = 6.8 Hz, 6H), 2.25 (sept, J = 6.8 Hz, 1H), 2.62 (dm, J = 8.0 Hz, 2H), 4.90 (dm, J = 10.0 Hz, 1H), 5.01 (dm, J = 16.8 Hz, 1H), 5.89 (ddt, J = 10.0, 16.8, 8.0 Hz, 1H), 7.35-7.46 (m, 9H), 7.54-7.57 (m, 4H), 7.68 (d, J = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.5, 21.1, 42.5, 90.6, 91.9, 115.2, 126.3, 127.8, 129.5, 129.6(0), 129.6(2), 133.8, 134.0, 134.7, 135.7, 137.4, 138.8, 191.5; HRMS (EI) calcd for $C_{27}H_{26}OSi$ [M^+] 394.1753; Found *m/z* 394.1750.

1-Methyl-1-phenyl-4-[2-(allyldiphenylsilyl)phenyl]butyn-2-one (**1e**).



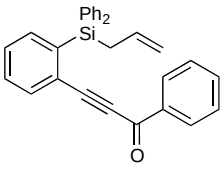
Yellow oil, purified by silica gel column chromatography (76% yield, R_f 0.49, EtOAc/hexane = 1/4). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.27 (d, J = 7.8 Hz, 3H), 2.48 (d, J = 8.0 Hz, 1H), 2.50 (d, J = 8.0 Hz, 1H), 3.43 (q, J = 7.8 Hz, 1H), 4.84 (dm, J = 10.2 Hz, 1H), 4.92 (dm, J = 18.0 Hz, 1H), 5.79, (m, 1H), 7.04 (dm, J = 7.2 Hz, 2H), 7.22-7.28 (m, 3H), 7.32-7.43 (m, 9H), 7.49-7.52 (m, 5H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 17.1, 21.1, 54.0, 91.2, 93.2, 115.3, 126.3, 127.3, 128.0, 128.3, 128.8, 129.7(1), 129.7(7), 133.9, 134.2, 134.7, 135.8, 137.4, 139.1(0), 139.1(5), 187.8; HRMS (EI) calcd for $C_{32}H_{28}OSi$ [M^+] 456.1909; Found *m/z* 456.1911.

1-Cyclohexyl-3-[2-(allyldiphenylsilyl)phenyl]propyn-1-one (**1f**).



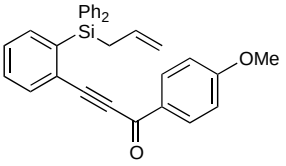
Yellow solid, purified by silica gel column chromatography (66% yield, R_f 0.45, EtOAc/hexane = 1/4). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.08-1.16 (m, 4H), 1.52-1.62 (m, 5H), 1.96 (m, 1H), 2.58 (dt, J = 8.0, 1.2 Hz, 2H), 4.89 (dm, J = 10.0 Hz, 1H), 4.99 (dm, J = 17.2 Hz, 1H), 5.87 (ddt, J = 10.0, 17.2, 8.0 Hz, 1H), 7.34-7.46 (m, 9H), 7.52-7.54 (m, 4H), 7.68 (dt, J = 7.6, 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.2, 25.3, 25.6, 27.7, 51.7, 91.0, 91.6, 115.2, 126.4, 127.8, 129.5, 129.6(0), 129.6(3), 133.8, 134.0, 134.8, 135.7, 137.3, 138.6, 190.9; HRMS (EI) calcd for $C_{30}H_{30}OSi$ [M^+] 434.2066; Found *m/z* 434.2066.

1-Phenyl-3-[2-(allyldiphenylsilyl)phenyl]propyn-1-one (**1i**).



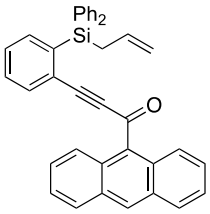
Yellow oil, purified by silica gel column chromatography (87% yield, R_f 0.67, EtOAc/hexane = 1/4). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.60 (dt, J = 8.0, 1.2 Hz, 2H), 4.85 (dm, J = 10.0 Hz, 1H), 4.93 (dm, J = 16.8 Hz, 1H), 5.87 (ddt, J = 10.0, 16.8, 8.0 Hz, 1H), 7.25-7.29 (m, 2H), 7.34-7.57 (m, 14H), 7.68 (dd, J = 1.2, 8.0 Hz, 2H), 7.80 (dt, J = 7.6, 0.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.2, 90.4, 93.6, 115.3, 126.3, 127.9, 128.4, 129.4, 129.6(5), 129.6(8), 129.7, 133.7(2C), 133.8, 135.0, 135.8, 136.5, 137.4, 138.7, 177.6; HRMS (EI) calcd for $C_{30}H_{24}OSi$ [M^+] 428.1596; Found *m/z* 428.1598.

1-(4-Methoxyphenyl)-3-[2-(allyldiphenylsilyl)phenyl]propyn-1-one (**1m**).



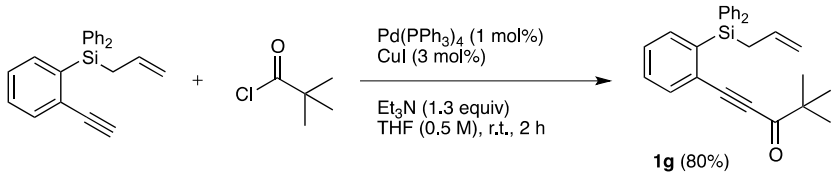
Yellow oil, purified by silica gel column chromatography (85% yield, R_f 0.50, EtOAc/hexane = 3/7). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.63 (dd, J = 1.2, 8.0 Hz, 2H), 3.86 (s, 3H), 4.87 (dm, J = 10.0 Hz, 1H), 4.95 (dm, J = 16.8 Hz, 1H), 5.89 (ddt, J = 10.0, 16.8, 8.0 Hz, 1H), 6.73 (d, J = 8.8 Hz, 2H), 7.35-7.50 (m, 9H), 7.57 (dm, J = 6.4 Hz, 4H), 7.65 (d, J = 9.2 Hz, 2H), 7.80 (d, J = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.2, 55.5, 90.5, 92.9, 113.7, 115.3, 126.6, 127.9, 129.5, 129.7(2C), 130.0, 131.8, 133.8, 134.0, 134.9, 135.9, 137.4, 138.5, 164.1, 176.2; HRMS (EI) calcd for $C_{31}H_{26}O_2Si$ [M^+] 458.1702; Found *m/z* 458.1705.

1-(9-Antracenyl)-3-[2-(allyldiphenylsilyl)phenyl]propyn-1-one (**1o**).



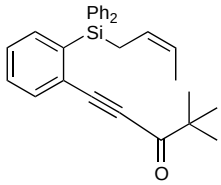
Yellow solid, purified by silica gel column chromatography (83% yield, R_f 0.43, EtOAc/hexane = 1/4). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.29 (d, J = 8.5 Hz, 2H), 4.73 (dm, J = 16.5 Hz, 1H), 4.74 (dm, J = 10.5 Hz, 1H), 5.62 (ddt, J = 10.5, 18.5, 8.0 Hz, 1H), 7.13 (t, J = 7.0 Hz, 4H), 7.23-7.26 (m, 2H), 7.30 (dm, J = 7.0 Hz, 4H), 7.34-7.40 (m, 3H), 7.42-7.51 (m, 4H), 7.64 (d, J = 7.5 Hz, 1H), 7.90 (d, J = 8.5 Hz, 2H), 8.02 (d, J = 8.5 Hz, 2H), 8.51 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 20.6, 93.8, 95.7, 115.0, 124.8, 125.6, 126.0, 127.1, 127.7, 128.1, 128.7, 129.4, 129.6, 129.7, 130.1, 131.1, 133.8(0), 133.8(5), 133.8(7), 135.3, 135.5, 137.4, 140.4, 183.4; HRMS (EI) calcd for $C_{38}H_{28}OSi$ [M^+] 528.1909; Found *m/z* 528.1909.

Synthesis of 1-*tert*-butyl-3-[2-(allyldiphenylsilyl)phenyl]propyn-1-one (**1g**).[7)]



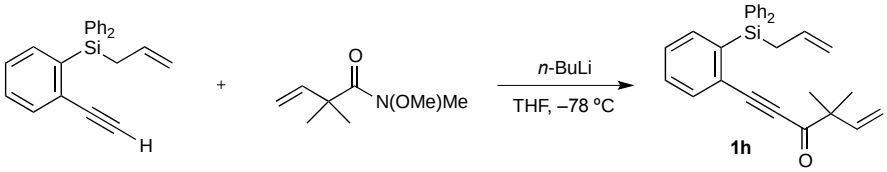
To a solution of the pivaloyl chloride (0.3 mL, 2.3 mmol) and 1-(allyldiphenylsilyl)-2-ethynylbenzene (486.8 mg, 1.5 mmol) in anhydrous THF (8 mL), under a N_2 atmosphere, was added $Pd(PPh_3)_4$ (17 mg, 1 mol%) and CuI (9 mg, 3 mol%). After stirring for 1 min, Et_3N (0.3 mL, 2.15 mmol) was added and the reaction left to stir for 2 h at ambient temperature. Upon completion, the reaction was then diluted with Et_2O (20 mL) and washed with H_2O (20 mL). The aqueous phase was then re-extracted with Et_2O (2 × 10 mL). The combined organic phases were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (R_f 0.30, EtOAc/hexane = 1/9) to afford **1g** (489.1 mg, 80% yield) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.95 (s, 9H), 2.62 (dt, J = 8.0, 1.2 Hz, 2H), 4.88 (dm, J = 10.0 Hz, 1H), 5.00 (dm, J = 17.2 Hz, 1H), 5.87 (ddt, J = 10.0, 17.2, 8.0 Hz, 1H), 7.33-7.45 (m, 9H), 7.51-7.54 (m, 4H), 7.66 (dm, J = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.9, 25.6, 44.3, 89.6, 92.7, 115.2, 126.4, 127.8, 129.3, 129.5, 129.6, 133.8, 133.9, 134.5, 135.7, 137.3, 138.7, 193.4; HRMS (EI) calcd for $C_{28}H_{28}OSi$ [M^+] 408.1909; Found *m/z* 408.1909.

(*Z*)-1-*tert*-Butyl-3-[2-(crotyldiphenylsilyl)phenyl]propyn-1-one (**1q**).



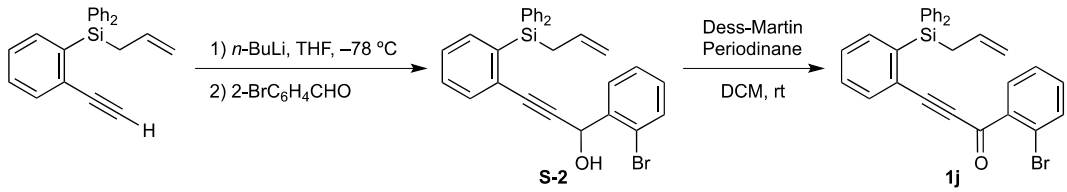
This compound was prepared from 1-[(*Z*)-crotyldiphenylsilyl]-2-ethynylbenzene.[1] Yellow oil, purified by silica gel column chromatography (91% yield, R_f 0.29, EtOAc/hexane = 1/19). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.95 (s, 9H), 1.46 (dm, J = 7.0 Hz, 3H), 2.55 (d, J = 8.0 Hz, 2H), 5.38 (m, 1H), 5.51 (m, 1H), 7.32-7.43 (m, 9H), 7.53 (dm, J = 7.5 Hz, 4H), 7.64 (dm, J = 8.0 Hz, 1H); ^{13}C NMR (CD_2Cl_2, 125 MHz) δ 13.0, 14.5, 25.8, 44.5, 89.7, 92.9, 123.8, 125.2, 126.7, 127.9, 129.4, 129.6, 134.3, 134.6, 135.9, 135.9, 137.5, 139.0, 193.6; HRMS (EI) calcd for $C_{29}H_{30}OSi$ [M^+] 422.2066; Found *m/z* 422.2060.

Synthesis of 3,3-dimethyl-6-[2-(allyldiphenylsilyl)phenyl]-5-hexyn-4-one (**1h**).



To a solution of 1-(allyldiphenylsilyl)-2-ethynylbenzene (785,5 mg, 2.4 mmol) in anhydrous THF (12 mL) was added *n*-BuLi (2.6 M in hexane, 1.15 mL, 3.0 mmol) at -78 °C under N_2, and the mixture was stirred at -78 °C for 1 h before addition of a solution of *N*-methoxy-*N*,2,2-trimethyl-3-butenamide (471.6 mg, 3.0 mmol) in anhydrous THF (5 mL) at -78 °C. The mixture was stirred for 2 h at -78 °C. Upon completion, the mixture was quenched with saturated NH_4Cl solution (10 mL) and extracted with Et_2O (10 mL). The aqueous phase was then re-extracted with Et_2O (2 × 10 mL) and washed with brine. The combined organic phases were dried over $MgSO_4$, filtrated, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (R_f 0.47, EtOAc/hexane = 1/4) to afford **1h** (516.8 mg, 49% yield) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.07 (s, 6H), 2.62 (dm, *J* = 8.0 Hz, 2H), 4.87 (dm, *J* = 10.0 Hz, 1H), 4.96-5.02 (m, 3H), 5.71 (dd, *J* = 10.5, 17.0 Hz, 1H), 5.87 (ddt, *J* = 10.0, 17.0, 8.0 Hz, 1H), 7.33-7.37 (m, 6H), 7.39-7.44 (m, 3H), 7.51-7.54 (m, 4H), 7.65 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.1, 23.2, 50.8, 89.9, 93.5, 114.7, 115.3, 126.5, 128.0, 129.5, 129.7, 129.7, 134.00, 134.1, 134.7, 135.9, 137.5, 138.9, 141.1, 190.4; HRMS (EI) calcd for $C_{29}H_{28}OSi$ [M^+] 420.1909; Found *m/z* 420.1910.

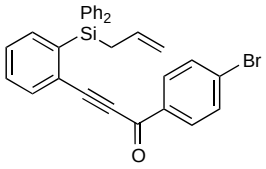
Synthesis of 1-aryl-3-[2-(allyldiphenylsilyl)phenyl]propyn-1-one (**1j**, **1k**, **1n**).



1-(2-Bromophenyl)-3-[2-(allyldiphenylsilyl)phenyl]propyn-1-one (**1j**). To a mixture of 1-(allyldiphenylsilyl)-2-ethynylbenzene (324.5 mg, 1.0 mmol) in THF (5 mL) was added *n*-BuLi (2.6 M in hexane, 462 μL, 1.2 mmol) at -78 °C under N_2, and the mixture was stirred at -78 °C for 1 h before addition of 2-bromobenzaldehyde (140 μL, 1.2 mmol) at -78 °C. The mixture was warmed up to ambient temperature and further stirred for overnight. Upon completion, the mixture was quenched with saturated NH_4Cl solution (10 mL) and extracted with Et_2O (10 mL). The aqueous phase was then re-extracted with Et_2O (2 × 10 mL) and washed with brine. The combined organic phases were dried over $MgSO_4$, filtrated, and concentrated under reduced pressure. The crude product **S-2** was used for next reaction without further purification. To a mixture of **S-2** in DCM (7 mL) was added Dess-Martin Periodinane (650 mg, 1.5 mmol) at 0 °C and stirred for 15 min. Upon completion, the mixture was quenched with saturated $NaHCO_3$ solution (10 mL) and extracted with DCM (2 × 10 mL). The combined organic phases were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (R_f 0.43, EtOAc/hexane = 1/4) to give **1j** (395.8 mg, 78% for two steps) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.54 (dt, *J* = 7.6, 1.2 Hz, 2H), 4.84 (dm, *J* = 10.0 Hz, 1H), 4.90 (dm, *J* = 17.2 Hz, 1H), 5.82 (ddt, *J* = 10.0, 17.2, 7.6 Hz, 1H), 7.11 (dt, *J* = 1.2, 7.2 Hz, 1H), 7.25-7.52 (m, 16H), 7.61 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.75 (dt, *J* = 6.4, 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz)

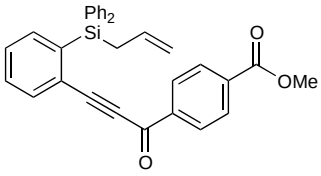
δ 21.0, 91.0, 94.5, 115.3, 120.8, 126.1, 127.1, 127.8, 129.6, 129.7, 129.8, 132.7, 132.9, 133.6, 133.8, 134.7, 134.9, 235.7, 136.8, 137.3, 139.2, 176.9; HRMS (EI) calcd for $C_{30}H_{23}BrOSi$ [M^+] 506.0702; Found *m/z* 506.0710.

1-(4-Bromophenyl)-3-[2-(allyldiphenylsilyl)phenyl]propyn-1-one (**1k**).



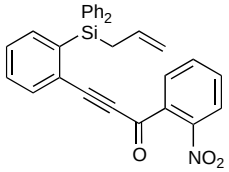
Colorless oil, purified by silica gel column chromatography (90% yield, R_f 0.51, EtOAc/hexane = 1/4). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.59 (d, *J* = 7.6 Hz, 2H), 4.87 (dm, *J* = 10.0 Hz, 1H), 4.93 (dm, *J* = 17.2 Hz, 1H), 5.87 (ddt, *J* = 10.0, 17.2, 7.6 Hz, 1H), 7.35-7.57 (m, 18H), 7.80 (dd, *J* = 0.8, 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.3, 90.1, 94.2, 115.4, 126.1, 128.0, 129.1, 129.7(7), 129.8(0), 129.9, 130.8, 131.8, 133.6, 133.8, 135.1, 135.4, 135.8, 137.5, 138.7, 176.5; HRMS (EI) calcd for $C_{30}H_{23}BrOSi$ [M^+] 506.0702; Found *m/z* 506.0708.

1-(4-Methoxycarbonylphenyl)-3-[2-(allyldiphenylsilyl)phenyl]propyn-1-one (**1l**).



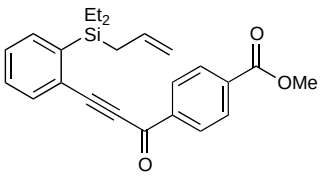
White solid, purified by silica gel column chromatography (76% yield, R_f 0.40, EtOAc/hexane = 1/4). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.58 (d, *J* = 7.5 Hz, 2H), 3.95 (s, 3H), 4.85 (dm, *J* = 10.0 Hz, 1H), 4.92 (dm, *J* = 16.5 Hz, 1H), 5.85 (ddt, *J* = 10.0, 16.5, 7.5 Hz, 1H), 7.33-7.37 (m, 4H), 7.39-7.43 (m, 4H), 7.49 (m, 1H), 7.54 (dm, *J* = 7.5 Hz, 4H), 7.69 (dm, *J* = 8.0 Hz, 2H), 7.79 (dm, *J* = 7.5 Hz, 1H), 7.91 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.3, 52.6, 90.4, 94.8, 115.5, 126.1, 128.0, 129.3, 129.7, 129.90, 129.94, 130.0, 133.7, 133.9, 134.3, 135.2, 135.9, 137.5, 139.0, 139.7, 166.2, 176.9; HRMS (EI) calcd for $C_{32}H_{26}BrO_3Si$ [M^+] 486.1651; Found *m/z* 486.1655.

1-(3-Nitorophenyl)-3-[2-(allyldiphenylsilyl)phenyl]propyn-1-one (**1n**).



Yellow solid, purified by silica gel column chromatography (66% yield, R_f 0.50, EtOAc/hexane = 1/4. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.62 (dt, *J* = 8.0, 1.5 Hz, 2H), 4.88 (dm, *J* = 10.0 Hz, 1H), 4.96 (dq, *J* = 17.0, 1.5 Hz, 1H), 5.88 (ddt, *J* = 10.0, 17.0, 8,0 Hz, 1H), 7.32-7.39 (m, 6H), 7.41-7.53 (m, 4H), 7.55-7.59 (m, 4H), 7.81 (dm, *J* = 7.5 Hz, 1H), 7.84 (dt, *J* = 7.5, 1.5 Hz, 1H), 8.36 (dm, *J* = 7.5 Hz, 1H), 8.73 (t, *J* = 2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.1, 89.6, 95.7, 115.4, 123.5, 125.5, 127.7, 127.9, 129.7, 129.7, 129.8, 130.1, 133.5, 133.7, 134.9, 135.1, 135.7, 137.4, 137.7, 139.2, 148.3, 175.0; HRMS (EI) calcd for $C_{30}H_{23}NO_3Si$ [M^+] 473.5940; Found *m/z* 473.5944.

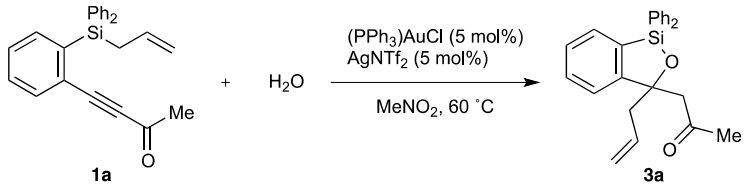
1-(4-Methoxycarbonylphenyl)-3-[2-(allyldiethylsilyl)phenyl]propyn-1-one (**1p**).



This compound was prepared from 1-(allyldiethylsilyl)-2-ethynylbenzene.[1] Yellow oil, purified by silica gel column chromatography (93% yield, R_f 0.60, EtOAc/hexane = 1/4). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.93-1.05 (m, 10H), 2.03 (dm, *J* = 8.0 Hz, 2H), 3.95 (s, 3H), 4.81 (dm, *J* = 10.0 Hz, 1H), 4.90 (dm, *J* = 17.0 Hz, 1H), 5.77 (ddt, *J* = 10.0, 17.0, 8.0 Hz, 1H), 7.40-7.47 (m, 2H), 7.55 (dm, *J* = 7.0 Hz, 1H), 7.73 (dm, *J* = 7.0 Hz, 1H), 8.17 (dm, *J* = 8.5 Hz, 2H), 8.26 (dm, *J* = 8.5 Hz, 2H); ^{13}C

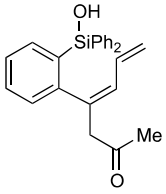
NMR ($CDCl_3$, 125 MHz) δ 3.5, 7.5, 19.5, 52.6, 89.3, 95.6, 113.9, 125.1, 129.1, 129.4, 129.9, 130.0, 134.4(2C), 134.7, 135.7, 140.1, 142.0, 166.2, 177.1; HRMS (EI) calcd for $C_{24}H_{26}NO_3Si$ [M^+] 390.1651; Found *m/z* 390.1659.

General procedure for gold(I)-catalyzed reaction

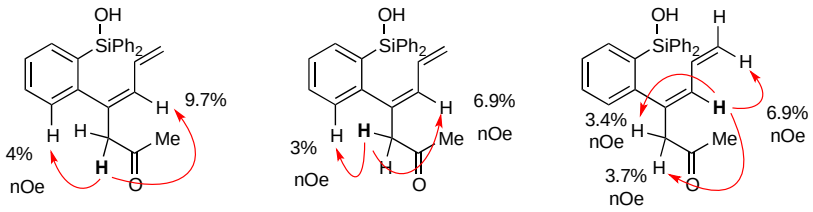


Benzoxasilole (**3a**). The cationic gold catalyst was generated in a 1 dram vial with a threaded cap by addition of $AgNTf_2$ (0.05 equiv.), $(Ph_3P)AuCl$ (0.05 equiv.) and nitromethane (0.4 M based on starting material). After allowing the catalyst mixture to sit for 10 minutes, the starting material **1a** (1 equiv.) and water (2 equiv.) in nitromethane (0.4 M) were added and stiired at 60 °C for 1 h. The resulting mixture (0.2 M) was monitored by TLC until all starting material was consumed. Upon completion, the reaction mixture was concentrated and loaded directly onto a silica gel column resulted in isolation of analytically pure product **3a** as a yellow oil (78% yield, R_f 0.48, EtOAc/hexane = 1/4). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.00 (s, 3H), 2.72 (ddm, *J* = 6.4, 13.6 Hz, 1H), 2.79 (ddm, *J* = 6.4, 13.6 Hz, 1H), 2.93 (d, *J* = 13.6 Hz, 1H), 3.02 (d, *J* = 13.6 Hz, 1H), 4.98 (dm, *J* = 10.0 Hz, 1H), 5.04 (dm, *J* = 17.2 Hz, 1H), 5.72 (ddm, *J* = 10.0, 17.2 Hz, 1H), 7.36-7.49 (m, 9H), 7.59 (dm, *J* = 8.0 Hz, 2H), 7.64 (dm, *J* = 8.0 Hz, 2H), 7.72 (dm, *J* = 7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 32.4, 46.5, 55.1, 86.6, 118.8, 123.0, 127.7, 127.8, 127.9, 130.35, 130.39, 130.5, 132.1, 132.2, 133.4, 133.9, 134.2, 135.0, 135.1, 155.3, 207.2; HRMS (EI) calcd for $C_{25}H_{24}O_2Si$ [M^+] 384.1546; Found m/z 384.1546.

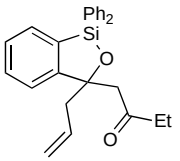
(*Z*)-4-[2-(Hydroxydiphenylsilyl)phenyl]-4,6-heptadin-2-one (**4**).



Yellow oil, purified by silica gel column chromatography (R_f 0.30, EtOAc/hexane = 1/4). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.95 (s, 3H), 3.16 (d, *J* = 16.5 Hz, 1H), 3.32 (d, *J* = 16.5 Hz, 1H), 4.06 (br s, 1H), 4.86 (dd, *J* = 2.0, 11.0 Hz, 1H), 5.14 (dd, *J* = 2.0, 17.0 Hz, 1H), 5.96 (dt, *J* = 17.0, 11.0 Hz, 1H), 6.10 (dm, *J* = 11.0 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 1 H), 7.24 (dt, *J* = 1.5, 6.0 Hz, 1 H), 7.32-7.45 (m, 8H), 7.56-7.61 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 30.3, 52.8, 118.4, 126.4, 127.6, 127.8, 129.3, 129.7, 129.8, 129.9, 133.1, 133.6, 134.2, 134.9, 135.0, 135.4, 136.8, 137.1, 137.4, 146.6, 207.5; HRMS (EI) calcd for $C_{25}H_{24}O_2Si$ [M^+] 384.1546; Found m/z 384.1550.

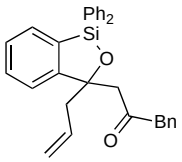


Benzoxasilole (**3b**).



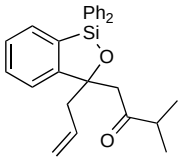
Yellow oil, purified by silica gel column chromatography (R_f 0.52, EtOAc/hexane = 1/4). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.78 (t, J = 7.2 Hz, 3H), 2.21 (dq, J = 18.4, 7.2 Hz, 1H), 2.39 (dq, J = 18.4, 7.2 Hz, 1H), 2.70 (ddm, J = 7.2, 14.0 Hz, 1H), 2.77 (ddm, J = 7.2, 14.0 Hz, 1H), 2.89 (d, J = 14.0 Hz, 1H), 2.99 (d, J = 14.0 Hz, 1H), 4.96 (dm, J = 10.0 Hz, 1H), 5.02 (dm, J = 17.2 Hz, 1H), 5.71 (ddm, J = 10.0, 17.2 Hz, 1H), 7.34-7.51 (m, 9H), 7.60 (dm, J = 8.0 Hz, 2H), 7.65 (dm, J = 8.0 Hz, 2H), 7.73 (dm, J = 7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 7.2, 38.3, 46.7, 53.8, 86.8, 118.8, 123.1, 127.6, 127.8, 127.9, 130.3, 130.4, 130.5, 132.0, 132.2, 133.6, 133.9, 134.2, 135.0, 135.1, 155.5, 209.3; HRMS (EI) calcd for $C_{26}H_{26}O_2Si$ [M^+] 398.1702; Found m/z 398.1703.

Benzoxasilole (**3c**).



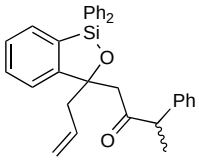
Yellow oil, purified by silica gel column chromatography (R_f 0.50, EtOAc/hexane = 1/4). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.71 (ddm, J = 6.5, 14.5 Hz, 1H), 2.79 (ddm, J = 8.0, 14.5 Hz, 1H), 2.92 (d, J =14.5 Hz, 1H), 2.96 (d, J =14.5 Hz, 1H), 3.47 (d, J = 15.0 Hz, 1H), 3.61 (d, J = 15.0 Hz, 1H), 4.93 (dm, J = 10.0 Hz, 1H), 4.99 (dm, J = 17.5 Hz, 1H), 5.67 (ddm, J = 10.0, 17.5 Hz, 1H), 6.84-6.87 (m, 2H), 7.15-7.19 (m, 3H), 7.30 (dm, J = 7.5 Hz, 1H), 7.35-7.39 (m, 5H), 7.41-7.47 (m, 3H), 7.59 (dm, J = 8.0 Hz, 2H), 7.66 (dm, J = 8.0 Hz, 2H), 7.72 (dm J = 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 46.5, 51.9, 53.3, 86.9, 118.9, 123.2, 126.8, 127.8, 127.9, 128.2, 128.5, 129.6, 130.4, 130.5, 130.7, 132.1, 132.4, 133.5, 133.9, 134.0, 134.3, 135.1, 135.3, 155.5, 206.3; HRMS (EI) calcd for $C_{31}H_{28}O_2Si$ [M^+] 460.1859; Found m/z 460.1863.

Benzoxasilole (**3d**).



Yellow oil, purified by silica gel column chromatography (R_f 0.40, EtOAc/hexane = 1/9). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.78 (d, J = 6.8 Hz, 3H), 0.93 (d, J = 6.8 Hz, 3H), 2.51 (sept, J = 6.8 Hz, 1H), 2.73 (dd, J = 6.4, 14.4 Hz, 1H), 2.84 (dd, J = 8.0, 14.4 Hz, 1H), 2.99 (s, 2H), 4.97 (dm, J = 10.0 Hz, 1H), 5.04 (dm, J = 17.2 Hz, 1H), 5.74 (dddd, J = 6.4, 8.0, 10.0, 17.2 Hz, 1H), 7.34-7.49 (m, 9H), 7.61 (dm, J = 8.0 Hz, 2H), 7.64 (dm, J = 8.0 Hz, 2H), 7.73 (d, J = 6.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.6, 17.7, 41.9, 46.5, 51.7, 86.8, 118.7, 123.1, 127.6, 127.8, 127.9, 130.3, 130.36, 130.44, 132.1, 132.2, 133.8, 134.0, 135.1, 135.2, 155.8, 212.3; HRMS (EI) calcd for $C_{27}H_{28}O_2Si$ [M^+] 412.1859; Found m/z 412.1859.

Benzoxasilole (**3e**).



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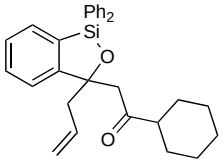
Yellow oil, purified by silica gel column chromatography (R_f 0.49, EtOAc/hexane = 1/4). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.23 (d, J = 6.5 Hz, 3H), 2.61-2.72 (m, 2.08H), 2.76-2.82 (m, 1.54H), 2.84-2.90 (m, 2H), 3.72 (q, J = 7.0 Hz, 1H), 4.90 (dm, J = 10.5 Hz, 1H), 5.00 (dm, J = 17.5 Hz, 1H), 5.59 (ddm, J = 10.0, 17.5 Hz, 1H), 6.69-6.73 (m, 2 H), 7.03-7.76 (m, 27.3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 17.6, 45.6, 53.4, 54.2, 87.10, 118.8, 123.2, 126.8, 127.0, 127.69, 127.72, 127.96(2C), 128.0, 128.2, 128.3, 128.8, 130.3, 130.40, 130.45, 134.5, 130.6, 130.7, 132.0, 132.26, 132.31, 132.38, 133.6, 133.72, 133.74, 134.2, 134.5, 134.7, 135.0, 135.3, 135.5, 140.3,

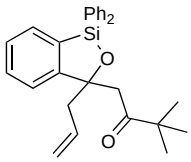
155.8, 208.8; ^{1}H NMR ($CDCl_3$, 500 MHz) δ minor isomer appeared clearly at 0.98 (d, J = 7.0 Hz, 3H), 3.11 (d, J = 14.5 Hz, 1H), 3.58 (q, J = 7.0 Hz, 1H), 4.95 (dm, J = 10.0 Hz, 1H), 4.96 (dm, J = 17.5 Hz, 1H), 5.74 (ddm, J = 10.0, 17.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 16.9, 47.8, 51.4, 54.6, 87.12, 123.3, 128.9, 140.5, 155.5, 207.9; HRMS (EI) calcd for $C_{32}H_{30}O_2Si$ [M^+] 474.2015; Found m/z 474.2015.

Benzoxasilole (**3f**).



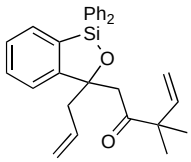
Colorless oil, purified by silica gel column chromatography (R_f 0.17, EtOAc/hexane = 1/19). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.89-1.30 (m, 5H), 1.48-1.72 (m, 5H), 2.25 (tt, J = 3.2, 11.2 Hz, 1H), 2.75 (ddm, J = 6.4, 14.0 Hz, 1H), 2.87 (dd, J = 8.0, 14.0 Hz, 1H), 2.94 (d, J = 14.0 Hz, 1H), 2.99 (d, J = 14.0 Hz, 1H), 4.98 (dm, J = 10.0 Hz, 1H), 5.05 (dm, J = 16.8 Hz, 1H), 5.74 (dddd, J = 6.4, 8.0, 10.0, 16.8 Hz, 1H), 7.36-7.50 (m, 9H), 7.64 (dm, J = 8.0 Hz, 2H), 7.67 (dm, J = 8.0 Hz, 2H), 7.75 (d, J = 7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.4, 25.6, 25.8, 27.6, 28.2, 46.2, 51.7, 51.9, 56.8, 118.6, 123.1, 127.5, 127.8, 127.9, 130.25, 130.33, 130.4, 132.0, 132.2, 133.8, 134.0, 134.4, 135.07, 135.11, 155.9, 211.8; HRMS (EI) calcd for $C_{30}H_{32}O_2Si$ [M^+] 452.2172; Found m/z 452.2173.

Benzoxasilole (**3g**).



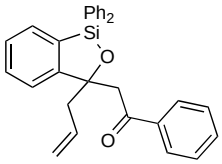
Colorless oil, purified by silica gel column chromatography (R_f 0.45, EtOAc/hexane = 1/4). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.91 (s, 9H), 2.77 (ddm, J = 6.0, 14.0 Hz, 1H), 2.94 (dd, J = 8.0, 14.0 Hz, 1H), 2.95 (d, J = 16.0 Hz, 1H), 3.21 (d, J = 16.0 Hz, 1H), 5.03 (dm, J = 10.0 Hz, 1H), 5.09 (dm, J = 17.2 Hz, 1H), 5.85 (dddd, J = 6.0, 8.0, 10.0, 17.2 Hz, 1H), 7.34-7.47 (m, 9H), 7.60 (dm, J = 8.0 Hz, 2H), 7.66 (dm, J = 8.0 Hz, 2H), 7.72 (dm, J = 7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.9, 44.6, 46.6, 46.9, 86.7, 118.5, 123.1, 127.4, 127.75, 127.79, 130.1, 130.2, 130.4, 132.1, 132.2, 134.1, 134.3, 134.4, 135.0, 135.4, 156.3, 212.2; HRMS (EI) calcd for $C_{28}H_{30}O_2Si$ [M^+] 426.2015; Found m/z 426.2015.

Benzoxasilole (**3h**).



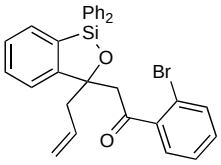
Colorless oil, purified by silica gel column chromatography (R_f 0.42, EtOAc/hexane = 1/9). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.98 (s, 3H), 0.99 (s, 3H), 2.76 (ddm, J = 6.0, 14.0 Hz, 1H), 2.91 (ddm, J = 8.0, 14.0 Hz, 1H), 2.92 (d, J = 15.0 Hz, 1H), 3.17 (d, J = 16.5 Hz, 1H), 4.95 (dm, J = 10.5 Hz, 1H), 4.96 (d, J = 17.5 Hz, 1H), 5.00 (dm, J = 10.0 Hz, 1H), 5.05 (dm, J = 17.5 Hz, 1H), 5.67 (dd, J = 10.5, 17.5 Hz, 1H), 5.81 (ddm, J = 10.0, 17.5 Hz, 1H), 7.31-7.37 (m, 6H), 7.40-7.45 (m, 3H), 7.59 (dm, J = 8.0 Hz, 2H), 7.64 (dm, J = 8.0 Hz, 2H), 7.70 (dm, J = 7.0 Hz 1H), ^{13}C NMR ($CDCl_3$, 125 MHz) δ 22.9, 23.1, 46.9, 47.6, 51.6, 86.8, 114.4, 118.6, 123.1, 127.54, 127.90, 127.94, 130.2, 130.4, 130.5, 132.2, 132.5, 134.2, 134.4, 134.5, 135.2, 135.6, 142.2, 156.3, 209.5; HRMS (EI) calcd for $C_{29}H_{30}O_2Si$ [M^+] 438.2015; Found m/z 438.2021.

Benzoxasilole (**3i**).



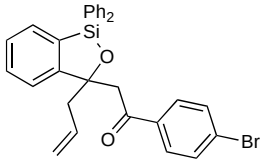
Colorless oil, purified by silica gel column chromatography (R_f 0.46, EtOAc/hexane = 1/4). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.84 (ddm, J = 6.4, 14.4 Hz, 1H), 2.92 (ddm, J = 8.0, 14.4 Hz, 1H), 3.41 (d, J = 14.4 Hz, 1H), 3.62 (d, J = 14.4 Hz, 1H), 5.01 (dm, J = 10.4 Hz, 1H), 5.09 (dm, J = 17.2 Hz, 1H), 5.83 (dddd, J = 6.4, 8.0, 10.4, 17.2 Hz, 1H), 7.20-7.29 (m, 4H), 7.33-7.49 (m, 10H), 7.63 (dm, J = 8.0 Hz, 2H), 7.71-7.74 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 47.0, 49.1, 87.2, 118.8, 123.4, 127.6, 127.8(2C), 128.1(2C), 128.8, 130.2, 130.29, 130.30, 132.2, 132.6, 133.8, 134.06, 134.13, 135.1, 135.2, 138.0, 155.6, 198.0; HRMS (EI) calcd for $C_{30}H_{26}O_2Si$ [M^+] 446.1702; Found m/z 446.1702.

Benzoxasilole (**3j**).



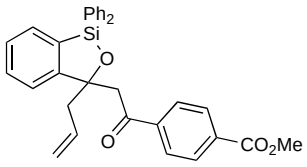
Yellow oil, purified by silica gel column chromatography (R_f 0.50, EtOAc/hexane = 1/4). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.83 (dd, J = 6.4, 14.0 Hz, 1H), 2.96 (dd, J = 8.0, 14.0 Hz, 1H), 3.47 (d, J = 14.8 Hz, 1H), 3.55 (d, J = 14.8 Hz, 1H), 4.97 (dm, J = 10.0 Hz, 1H), 5.05 (dm, J = 17.2 Hz, 1H), 5.74 (dddd, J = 6.4, 8.0, 10.0, 17.2 Hz, 1H), 7.06-7.16 (m, 3H), 7.26-7.29 (m, 2H), 7.34-7.48 (m, 10H), 7.62 (dm, J = 7.6 Hz, 2H), 7.72 (d, J = 7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 46.5, 53.3, 87.11, 118.4, 118.9, 123.1, 127.1, 127.6, 127.8(2C), 129.0, 130.28(2C), 130.32, 131.0, 132.18, 132.22, 133.1, 133.6, 134.0, 134.1, 135.05, 135.07, 142.7, 155.4, 201.6; HRMS (EI) calcd for $C_{30}H_{25}BrO_2Si$ [M^+] 524.0807; Found m/z 524.0817.

Benzoxasilole (**3k**).



Yellow oil, purified by silica gel column chromatography (R_f 0.57, EtOAc/hexane = 3/7). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.81 (dd, J = 6.4, 14.4 Hz, 1H), 2.86 (dd, J = 8.0, 14.4 Hz, 1H), 3.30 (d, J = 14.0 Hz, 1H), 3.62 (d, J = 14.0 Hz, 1H), 5.05 (dm, J = 10.0 Hz, 1H), 5.11 (dm, J = 17.2 Hz, 1H), 5.85 (dddd, J = 6.4, 8.0, 10.0, 17.2 Hz, 1H), 7.24-7.29 (m, 3H), 7.33-7.44 (m, 9H), 7.49-7.54 (m, 3H), 7.62 (dm, J = 8.0 Hz, 2H), 7.73 (dm, J = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 47.4, 49.0, 87.3, 119.0, 123.4, 127.7, 127.77, 127.82, 130.28, 130.33, 130.35, 130.44, 131.2, 131.9, 132.2, 132.4, 133.6, 133.8, 134.0, 134.9, 135.1, 136.5, 155.2, 197.2; HRMS (EI) calcd for $C_{30}H_{25}BrO_2Si$ [M^+] 524.0807; Found m/z 524.0820.

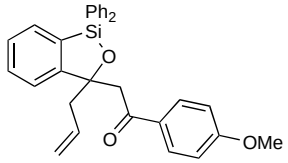
Benzoxasilole (**3l**).



Yellow oil, purified by silica gel column chromatography (R_f 0.59, EtOAc/hexane = 1/4). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.81 (ddm, J = 6.0, 14.0 Hz, 1H), 2.87 (dd, J = 8.0, 14.0 Hz, 1H), 3.38 (d, J = 14.0 Hz, 1H), 3.66 (d, J = 14.0 Hz, 1H), 3.91 (s, 3H), 5.04 (dm, J = 10.0 Hz, 1H), 5.10 (dm, J = 17.0 Hz, 1H), 5.85 (dddd, J = 6.0, 8.0, 10.0, 17.0 Hz, 1H), 7.23 (t, J = 7.5 Hz, 2H), 7.32-7.42 (m, 8H), 7.48 (dm, J = 7.5 Hz, 1H), 7.61 (dm, J = 8.0 Hz, 2H), 7.69-7.73 (m, 3H), 7.82 (dm, J = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 47.4, 49.3, 52.4, 87.3, 119.1, 123.4, 127.8, 127.92, 127.94, 128.8, 129.4,

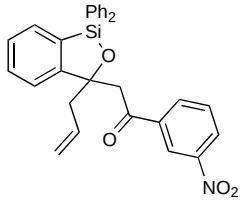
130.4, 130.5, 132.1, 132.3, 133.3, 133.7, 134.0, 134.1, 135.1, 135.2, 141.1, 155.4, 166.4, 197.8; HRMS (EI) calcd for $C_{32}H_{28}BrO_4Si$ [M^+] 504.1757; Found m/z 504.1756.

Benzoxasilole (**3m**).



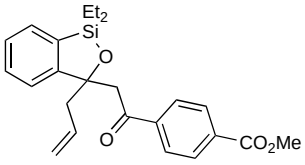
Yellow oil, purified by silica gel column chromatography (R_f 0.45, EtOAc/hexane = 3/7). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.83 (ddm, J = 6.4, 14.0 Hz, 1H), 2.91 (dd, J = 8.0, 14.0 Hz, 1H), 3.34 (d, J = 14.0 Hz, 1H), 3.57 (d, J = 14.0 Hz, 1H), 3.79 (s, 3H), 5.01 (dm, J = 10.0 Hz, 1H), 5.08 (dm, J = 17.2 Hz, 1H), 5.83 (dddd, J = 6.4, 8.0, 10.0, 17.2 Hz, 1H), 6.66 (dm, J = 9.2 Hz, 2H), 7.26-7.29 (m, 2H), 7.33-7.54 (m, 10H), 7.63 (dm, J = 8.0 Hz, 2H), 7.70 (dm, J = 9.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 47.1, 49.0, 55.3, 87.3, 113.2, 118.7, 123.5, 127.6, 127.7, 127.8, 130.17, 130.20, 130.3, 131.1, 131.2, 132.0, 132.1, 133.9, 134.2, 135.0, 135.2, 135.4, 155.6, 163.1, 196.5; HRMS (EI) calcd for $C_{31}H_{28}O_3Si$ [M^+] 476.1808; Found m/z 476.1811.

Benzoxasilole (**3n**).



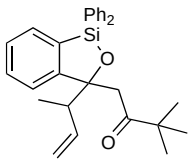
Yellow oil, purified by silica gel column chromatography (R_f 0.46, EtOAc/hexane = 1/4). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.79 (ddm, J = 6.5, 14.0 Hz, 1H), 2.83 (dd, J = 8.0, 14.0 Hz, 1H), 3.28 (d, J = 13.5 Hz, 1H), 3.84 (d, J = 13.5 Hz, 1H), 5.14 (dm, J = 10.5 Hz, 1H), 5.17 (dm, J = 17.0 Hz, 1H), 5.96 (dddd, J = 6.5, 8.0, 10.5, 17.0 Hz, 1H), 7.11-7.16 (m, 2 H), 7.23-7.29 (m, 4H), 7.31-7.36 (m, 2H), 7.38-7.42 (m, 2H), 7.45 (dm, J = 7.0 Hz, 1H), 7.51 (m, 1H), 7.58 (dm, J = 6.5 Hz, 2H), 7.70 (dm, J = 7.0 Hz, 1H), 7.93 (dm, J = 8.0 Hz, 1H), 8.11 (dm, J = 8.0 Hz, 1H), 8.44 (t, J = 7.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 48.3, 48.8, 87.5, 119.6, 123.5, 123.8, 126.8, 127.8, 127.99, 128.02, 129.1, 130.4, 130.49, 130.52, 131.8, 132.4, 133.5, 133.6, 133.9, 134.7, 134.9, 135.1, 138.9, 148.0, 154.9, 196.2; HRMS (EI) calcd for $C_{30}H_{25}NO_4Si$ [M^+] 491.1553; Found m/z 491.1555.

Benzoxasilole (**3o**).



Yellow oil, purified by silica gel column chromatography (R_f 0.59, EtOAc/hexane = 1/4). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.56 (q, J = 8.0 Hz, 2H), 0.78 (q, J = 8.0 Hz, 1H), 0.79 (q, J = 8.0 Hz, 1H), 0.83 (t, J = 8.0, 3H), 0.96, (t, J = 8.0 Hz, 3H), 2.66 (ddm, J = 6.0, 14.0 Hz, 1H), 2.75, (dd, J = 8.5, 14.0 Hz, 1H), 3.29 (d, J = 14.0 Hz, 1H), 3.67 (d, J = 14.0 Hz, 1H), 3.92 (s, 3H), 5.08 (dm, J = 10.5 Hz, 1H), 5.09 (dm, J = 17.0 Hz, 1H), 5.76 (ddm, J = 10.5, 17.0 Hz, 1H), 7.27-7.32 (m, 2H), 7.39 (dt, J = 1.0, 7.0 Hz, 1H), 7.50 (d, J = 7.0 Hz, 1H), 7.92 (d, J = 8.5 Hz, 2H), 8.04 (d, J = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 6.6, 6.8, 6.95, 7.01, 48.0, 49.4, 52.5, 86.4, 118.9, 123.1, 127.3, 128.8, 129.6, 129.8, 131.6, 133.5, 133.7, 134.2, 141.6, 154.5, 166.4, 197.8; HRMS (EI) calcd for $C_{24}H_{28}O_4Si$ [M^+] 408.1757; Found m/z 408.1757.

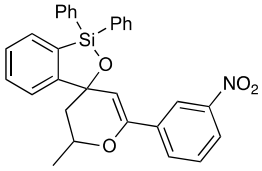
Benzoxasilole (**3p**).



dr = 1.5:1

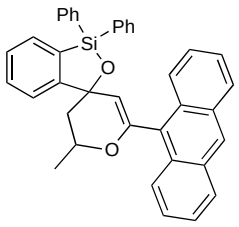
Major: Yellow oil, purified by silica gel column chromatography (R_f 0.51, toluene). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.64 (d, J = 7.0 Hz, 3H), 0.86 (s, 9H), 3.06 (d, J = 17.0 Hz, 1H), 3.17 (d, J = 17.0 Hz, 1H), 3.28 (dq, J = 9.5, 7.0 Hz, 1H), 5.08 (dd, J = 2.0, 10.0 Hz, 1H), 5.14 (dd, J = 2.0, 17.0 Hz, 1H), 6.04 (ddd, J = 9.5, 10.0, 17.0 Hz, 1H), 7.33-7.44 (m, 9H), 7.59 (dm, J = 8.0 Hz, 2H), 7.65 (dm, J = 8.0 Hz, 2H), 7.74 (dm, J = 7.0 Hz, 1H) ^{13}C NMR ($CDCl_3$, 125 MHz) δ 15.7, 26.1, 44.7, 46.4, 47.5, 89.3, 116.0, 123.8, 127.5, 127.9, 128.0, 130.25, 130.34, 132.1, 133.0, 134.3, 135.08, 135.13, 135.3, 135.8, 141.0, 155.7, 212.5; Minor: Yellow oil, purified by silica gel column chromatography (R_f 0.40, toluene). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.91 (s, 9H), 1.07 (d, J = 8.0 Hz, 3H), 3.05 (d, J = 17.0 Hz, 1H), 3.18 (d, J = 17.0 Hz, 1H), 3.33 (quint, J = 8.0 Hz, 1H), 4.79 (dm, J = 10.0 Hz, 1H), 4.86 (dm, J = 17.0 Hz, 1H), 5.67 (ddd, J = 8.0, 10.5, 17.0 Hz, 1H), 7.33-7.43 (m, 9H), 7.57 (dm, J = 8.0 Hz, 2H), 7.65 (dm, J = 8.0 Hz, 2H), 7.72, (dm, J = 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.7, 26.0, 44.7, 45.7, 45.9, 89.1, 115.5, 123.8, 127.3, 127.8, 127.9, 129.9, 130.2, 132.0, 132.6, 134.1, 135.0, 135.2(2C), 135.5, 140.4, 155.7, 212.5; HRMS (EI) calcd for $C_{29}H_{32}O_2Si$ [M^+] 440.2172; Found m/z 440.2175.

Spirodihydropyran (**5a**).



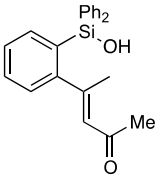
Yellow oil, purified by silica gel column chromatography (R_f 0.29, EtOAc/hexane = 1/4). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.51 (d, J = 6.4 Hz, 3H), 2.05-2.18 (m, 2H), 4.67 (m, 1H), 5.56 (d, J = 1.6 Hz, 1H), 7.30 (dm, J = 3.6 Hz, 1H), 7.35-7.52 (m, 9H), 7.63-7.69 (m, 4H), 7.73 (dm, J = 6.8 Hz, 1H), 7.95 (ddd, J = 1.2, 1.6, 8.0 Hz, 1H), 8.17 (ddd, J = 1.5, 2.4, 8.0 Hz, 1H), 8.42 (dd, J = 1.6, 2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.8, 46.9, 70.9, 81.1, 104.9, 120.4, 123.27, 123.29, 127.9, 128.0, 128.1, 129.1, 130.53, 130.59, 130.62, 131.2, 132.1, 132.7, 133.9, 134.3, 134.9, 135.1, 137.2, 148.3, 151.9, 155.9; HRMS (EI) calcd for $C_{30}H_{25}NO_4Si$ [M^+] 491.1553; Found m/z 491.1560.

Spirodihydropyran (**5b**).



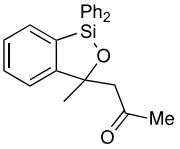
Yellow solid, purified by silica gel column chromatography (R_f 0.59, EtOAc/hexane = 3/7). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.51 (d, J = 6.5 Hz, 3H), 2.29 (dm, J = 14.0 Hz, 1H), 2.51 (dd, J = 12.5, 14.0 Hz, 1H), 5.02 (m, 1H), 5.27 (d, J = 1.5 Hz, 1H), 7.33 (t, J = 7.5 Hz, 2H), 7.39 (t, J = 7.5 Hz, 2H), 7.47-7.66 (m, 9H), 7.69-7.74 (m, 3H), 7.76-7.79 (m, 2H), 8.01 (d, J = 8.5 Hz, 2H), 8.40 (d, J = 7.5 Hz, 1H), 8.48 (m, 1H), 8.52 (d, J = 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.2, 47.3, 71.2, 81.6, 110.9, 123.3, 125.2, 125.4, 126.1, 126.6, 127.9, 128.1, 128.2, 128.5, 128.6, 130.5, 130.7, 131.0, 131.45, 131.54, 132.2, 133.2, 134.3, 134.7, 135.2, 135.3, 152.1, 156.5; HRMS (EI) calcd for $C_{38}H_{30}O_2Si$ [M^+] 546.2015; Found m/z 546.2015.

(*E*)-4-[2-(hydroxydiphenylsilyl)phenyl]-3-penten-2-one (**6**).



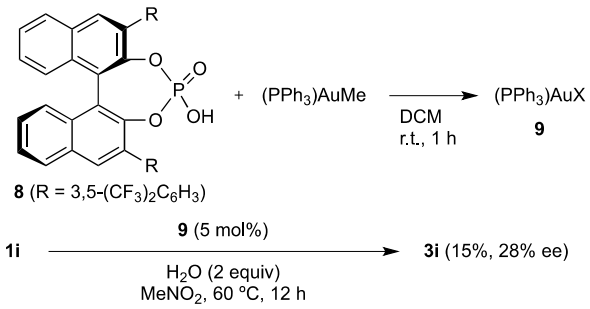
White solid, ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 1.77 (s, 3H), 2.14 (d, J = 1.5 Hz, 3H), 5,91 (d, J = 1.5 Hz, 1H), 7.20 (dm, J = 7.5 Hz, 1H), 7.29 (dt, J = 8.0, 1.5 Hz, 1H), 7.36-7.40 (m, 4H), 7.41-7.46 (m, 3H), 7.53 (ddd, J = 0.5, 1.5, 7.5 Hz, 1H), 7.55-7.58 (m, 4H); ^{13}C NMR (CD_2Cl_2, 125 MHz) δ 20.7, 30.8, 126.3, 126.8, 127.5, 127.6, 129.5, 129.6, 132.0, 134.3, 136.1, 136.6, 151.2, 156.3, 198.3; HRMS (EI) calcd for $C_{23}H_{22}O_2Si$ [M^+] 358.1389; Found *m/z* 358.1391.

Benzoxasilole (**7**).

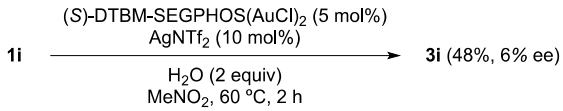


Yellow solid, purified by silica gel column chromatography (R_f 0.26, EtOAc/hexane = 1/4). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.68 (s, 3H), 2.05 (s, 3H), 2.89 (s, 2H), 7.30-7.51 (m, 9H), 7.63 (tm, J = 8.4 Hz, 4H), 7.71 (dm, J = 6.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 29.8, 32.4, 56.9, 84.7, 122.5, 127.7, 127.9, 128.0, 130.5, 130.5(6), 130.5(9), 131.3, 132.2, 133.9, 134.0, 134.9, 135.0, 157.2, 207.7; HRMS (EI) calcd for $C_{23}H_{22}O_2Si$ [M^+] 358.1389; Found m/z 358.1389.

General procedure for Scheme 2.



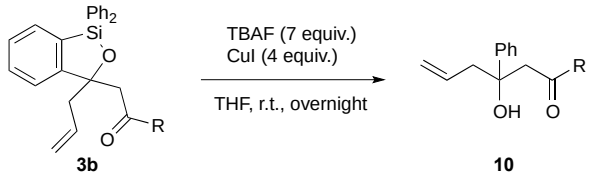
To a 2 dram vial was added (Ph_3P)AuMe (4.7 mg, 0.01 mmol) and (*R*)-3,3′-Bis[3,5-bis(trifluoromethyl)phenyl]-1,1′-binaphthyl-2,2′-diyl hydrogenphosphate **8** (7.7 mg, 0.01 mmol). The mixture was dissolved in dichloromethane (1 mL) and stirred for 30 minutes at room temperature. After this time, dichloromethane was removed in reduced pressure and redissolved in nitromethane (0.5 mL). **1i** (85.7 mg, 0.2 mmol) and H_2O (0.4 mmol) was added as a solution in nitromethane (0.5 mL) and THF (0.2 mL). The resulting mixture was stirred for 60 °C for 12 h, then filtered through a silica gel plug and concentrated. Purification by flash column chromatography afforded the desired product **3i** (15% yield, R_f 0.61, EtOAc/hexane = 1/4). Enantiopurity was determined by HPLC analysis (CHIRACEL OZ-H column, hexanes/isopropanol = 98/2, 1.0 mL/min, 254 nm) t_r 8.2 min (major), 14.0 min (minor): 28% ee.



The cationic gold catalyst was generated in a 1 dram vial with a threaded cap by addition of $AgNTf_2$ (7.6 mg, 0.02 mml), (*S*)-DTBM-SEGPHOS($AuCl)_2$ (18.0 mg, 0.011 mmol) and nitromethane (0.4 M based on starting material). After allowing the catalyst mixture to sit for 10 minutes, the starting material **1i** (85.7 mg, 0.2 mmol) and water (2 equiv.) in nitromethane (0.4 M) were added and stiired at 60 °C for 2 h. The resulting mixture (0.2

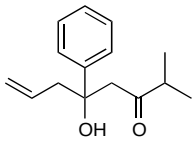
M) was monitored by TLC until all starting material was consumed. Upon completion, the reaction mixture was concentrated and loaded directly onto a silica gel column resulted in isolation of analytically pure product **3i** as a yellow oil (48% yield, R_f 0.61, EtOAc/hexane = 1/4). Enantiopurity was determined by HPLC analysis (CHIRACEL OZ-H column, hexanes/isopropanol = 90/10, 0.5 mL/min, 254 nm) t_r 9.5 min (minor), 11.9 min (major): 6% ee.

General procedure for deprotection of benzoxasilole 3b, 3d, and 3f.



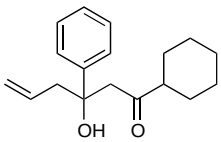
4-Hydroxy-4-phenyl-1-octen-6-one (**10a**). To a solution of **3b** (39.9 mg, 0.10 mmol) and CuI (76.2 mg, 0.40 mmol) in THF (0.3 mL) was added TBAF (1 M in THF, 0.7 mL, 0.7 mmol) at 0 °C, and the reaction mixture was stirred at ambient temperature for overnight. Upon completion, the mixture was diluted with Et_2O (10 mL) and washed with H_2O (2 × 10 mL). The aqueous layer was then re-extracted with Et_2O (2 × 10 mL). The combined organic phases were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (R_f 0.30, EtOAc/hexane = 1/9) to afford **10a** (16.6 mg, 76% yield) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.91 (t, J = 7.2 Hz, 3H), 2.26 (dq, J = 18.0, 7.2 Hz, 1H), 2.39 (dq, J = 18.0, 7.2 Hz, 1H), 2.48 (dd, J = 7.6, 14.0 Hz, 1H), 2.56 (dd, J = 6.4, 14.0 Hz, 1H), 2.83 (d, J = 16.8 Hz, 1H), 3.16 (d, J = 16.8 Hz, 1H), 4.66 (s, 1H), 5.05 (dm, J = 18.0 Hz, 1H), 5.08 (dm, J = 11.2 Hz, 1H), 5.68 (m, 1H), 7.22 (m, 1H), 7.29-7.34 (m, 2H), 7.36-7.40 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 7.2, 38.0, 47.8, 50.7, 75.1, 118.4, 124.8, 126.8, 128.2, 133.4, 145.8, 213.5; HRMS (EI) calcd for $C_{14}H_{18}O_2$ [M^+] 218.1307; Found m/z 218.1307.

4-Hydroxy-4-phenyl-7-methyl-1-octen-6-one (**10b**).



Colorless oil, purified by silica gel column chromatography (R_f 0.26, EtOAc/hexane = 1/9). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.91 (t, J = 7.2 Hz, 2H), 1.02 (d, J = 7.2 Hz, 2H), 2.46 (sept, J = 7.2 Hz, 1H), 2.50 (dd, J = 8.0, 14.0 Hz, 1H), 2.57 (dd, J = 6.8, 14.0 Hz, 1H), 2.85 (d, J = 17.2 Hz, 1H), 3.21 (d, J = 17.2 Hz, 1H), 4.83 (s, 1H), 5.04 (dm, J = 18.4 Hz, 1H), 5.05 (dm, J = 11.2 Hz, 1H), 5.70 (m, 1H), 7.22 (m, 1H), 7.28-7.34 (m, 2H), 7.39 (dm, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.4, 17.7, 42.2, 47.7, 48.9, 75.2, 118.3, 124.8, 126.7, 128.1, 133.5, 145.8, 216.8; HRMS (EI) calcd for $C_{15}H_{20}O_2$ [M^+] 232.1463; Found m/z 232.1463.

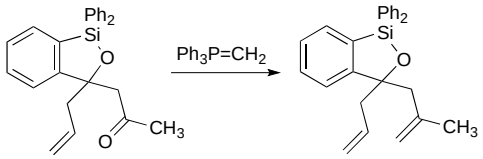
2-Hydroxy-2-phenyl-4-pentenyl cyclohexyl ketone (**10c**).



Colorless oil, purified by silica gel column chromatography (R_f 0.28, EtOAc/hexane = 1/9). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.05-1.29 (m, 5H), 1.58-1.80 (m, 5H), 2.20 (m, 1H), 2.48 (ddd, J = 0.8, 8.0, 14.0 Hz, 1H), 2.55 (ddm, J = 6.4, 14.0 Hz, 1H), 2.84 (d, J = 17.2 Hz, 1H), 3.21 (d, J = 17.2 Hz, 1H), 4.85 (s, 1H), 5.04 (dm, J = 18.0 Hz, 1H),

5.05 (dm, *J* = 10.8 Hz, 1H), 5.69 (ddm, *J* = 10.8, 18.0 Hz, 1H), 7.21 (m, 1H), 7.28-7.34 (m, 2H), 7.36-7.40 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.3, 25.4, 25.6, 27.6, 27.9, 47.8, 49.0, 52.0, 75.2, 118.2, 124.8, 126.7, 128.1, 133.5, 145.9, 216.2; HRMS (EI) calcd for $C_{18}H_{24}O_2$ [M^+] 272.1766; Found m/z 272.1767.

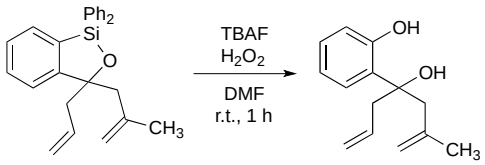
Synthesis of Benzoxasilole (11).



3a **11** (75%)

To a suspension of dry methyltriphenylphosphonium bromide (115 mg, 0.42 mmol) in dry THF (3 mL) was added dropwise *n*-butyllithium (2.6 M in hexane, 100 µL, 0.26 mmol) at –40 °C. After 30 min, the resulting yellow mixture was allowed to warm to room temperature and stirred for an additional 90 min. The yellow suspension was recooled to –78 °C and a solution of benzoxasilole **3a** (45 mg, 0.14 mmol) in dry THF (2 mL) was added via syringe and stirred for 30 min. The cooling bath was removed and the mixture was stirred for an additional 60 min, poured into a stirred 10% aqueous solution of NH_4Cl (5 mL) and diluted with diethyl ether (10 mL). The layers were separated and the aqueous phase was extracted with diethyl ether (3 × 10 mL). The combined organic layers were washed with water (2 × 5 mL) and brine (5 mL), dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. Purification of the residue by silica gel chromatography (R_f 0.64, EtOAc/hexane = 1/4) gave **11** (33.8 mg, 0.105 mmol, 75%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.52 (s, 3H), 2.52 (d, *J* = 14.0 Hz, 1H), 2.63 (ddt, *J* = 6.4, 14.0, 1.2 Hz, 1H), 2.66 (d, *J* = 14.0 Hz, 1H), 2.73 (dd, *J* = 7.6, 14.0 Hz, 1H), 4.59 (dm, 1H), 4.60 (br s, 1H), 4.69 (m, 1H), 4.89 (dm, *J* = 10.0 Hz, 1H), 4.96 (dm, *J* = 17.2 Hz, 1H), 5.68 (dddd, *J* = 6.4, 7.6, 10.0, 17.2 Hz, 1H), 7.29-7.38 (m, 6H), 7.40-7.50 (m, 3H), 7.60-7.68 (m, 4H), 7.71 (dm, *J* = 6.5 Hz, 1H); ^{13}C NMR ($CDCl_3$,125 MHz) δ 24.9, 46.8, 50.2, 88.6, 115.6, 118.1, 123.4, 127.3, 127.7, 127.8, 129.9, 130.2, 130.3, 132.2, 132.8, 134.3, 134,6, 134.9, 135.2, 135.3, 142.0, 156.3; HRMS (EI) calcd for $C_{26}H_{26}OSi$ [M^+] 382.1753; Found m/z 382.1753.

Synthesis of 2-(4-hydroxy-2-methylhepta-1,6-dien-4-yl)phenol (12).[8)]



11 **12** (63%)

To a mixture of **11** (33.8 mg, 0.105 mmol) and TBAF (1 M in THF, 110 µL, 0.11 mmol) in DMF (0.5 mL) was added a 30% H_2O_2 (120 µL, 0.95 mmol) at room temperature. After being stirring for 1 h at room temperature, the resulting mixture was poured into 10% aqueous sodium thiosulfate (10 mL) and extracted with Et_2O (3 ×5 mL). The extracts were concentrated followed by chromatography on silica gel (R_f 0.40, EtOAc/hexane = 1/4) to afford 14.6 mg (0.066 mmol, 63%) of **12** as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.58 (s, 3H), 2.53 (dm, *J* = 14.0 Hz, 1H), 2.54 (dm, *J* = 14.0 Hz, 1H), 2.76 (dd, *J* = 0.8, 14.0 Hz, 1H), 2.87 (ddt, *J* = 6.4, 14.0, 1.2 Hz, 1H), 3.08 (br s, 1H), 4.76 (q, *J* = 0.8 Hz, 1H), 4.95 (m, 1H), 5.17 (dm, *J* = 18.0 Hz, 1H), 5.18 (dm, *J* = 9.2

Hz, 1H), 5.77 (dddd, *J* = 6.4, 8.0, 9.2, 18.0 Hz, 1H), 6.78-6.86 (m, 2H), 7.01 (dd, *J* = 1.6, 7.6 Hz, 1H), 7.14 (dt, *J* = 1.6, 7.6 Hz, 1H), 9.37 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 24.4, 46.0, 48.8, 78.8, 116.5, 117.8, 119.1, 120.4, 126.8, 127.0, 128.8, 132.9, 141.6, 156.7; HRMS (EI) calcd for $C_{14}H_{18}O_2$ [M^+] 218.1307; Found m/z 218.1307.

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