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Supporting Information

Carboazidation of Chiral Allylsilanes. Experimental and Theoretical Investigations

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Supporting information

- Synthesis of **3a-h**, **4a-b**, **13a-f**, **14a-b**, **17a-b**, **19**, **23**, **25a-b**, **27**, **28**, **29**.
- EPR spectrum of radical **I** from xanthate **7** and allylsilane **13a**.
- Geometries of transition states optimized at the B3LYP/6-31G(d) level.

General Remarks. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Brüker Avance 300 (^{1}H: 300 MHz, ^{13}C: 75.5 MHz) or a Brüker AC-250 FT (^{1}H: 250 MHz, ^{13}C: 62.9 MHz), using $CDCl_3$ as internal reference. The chemical shifts (δ) and coupling constants (*J*) are expressed in ppm and hertz respectively. IR spectra were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer as neat films on NaCl windows or as KBr pellets. HRMS were recorded on a Varian MAT 311 aparatus (for EI) or a Micromass ZABSpec TOF apparatus (for ESI). Melting points were determined by using a Büchi Totolli apparatus and are uncorrected. Merck silica gel (0.043-0.063 mm) was used for flash chromatography. All reactions were carried out under nitrogen atmosphere unless specified. CH_2Cl_2 was distilled over CaH_2. Benzene and THF were distilled from sodium/benzophenone prior to use. All reagent-grade chemicals were obtained from commercial suppliers and were used as received, unless otherwise stated.

Preparation of b**-hydroxyallylsilanes (General procedure A**): To a solution of allylsilane (1 eq.) in dry THF was added a solution of *n*-butyllithium in hexane (1.1 eq.) followed by TMEDA (1.5 eq.) at 0°C. The resulting pale-yellow solution was stirred at 0°C for 2h, turning reddish brown, then cooled to -78°C. Titanium isopropoxide (1 eq.) was added at -78°C and the mixture was stirred for 1h at this temperature. Finally, a solution of aldehyde (1 eq.) in dry THF was added at -78°C, and the reaction mixture was then stirred for 75 min. The reaction was quenched with an aqueous solution of NH_4Cl at -78°C. The organic layer was decanted and the aqueous layer extracted with ether. The combined organic layers were then washed with H_2O, dried over $MgSO_4$ and the solvents were removed under reduced pressure. The residue was purified by chromatography.

2-(Dimethyl-phenyl-silanyl)-1-phenyl-but-3-en-1-ol (3a): Prepared according to general procedure A from dimethylphenyl allylsilane (1 g, 5.68 mmol) in dry THF (9 mL), *n*-butyllithium in hexane (2.5 mL, 6.25 mmol), TMEDA (1.4 mL, 9.37 mmol), titanium isopropoxide (1.68 mL, 5.68 mmol) and benzaldehyde (0.52 mL, 5.11 mmol) in dry THF (1.0 mL). The residue was purified by chromatography (EP/EtOAc : 97/3) to afford a colorless oil (955 mg, 66 %). All spectroscopic data were in agreement with those previously reported.[1]

4-(Dimethyl-phenyl-silanyl)-2-methyl-hex-5-en-3-ol (3b): Prepared according to general procedure A from dimethylphenyl allylsilane (1 g, 5.68 mmol) in dry THF (10 mL), *n*-butyllithium in hexane (2.5 mL, 6.25 mmol), TMEDA (1.41 mL, 9.37 mmol), titanium isopropoxide (1.68 mL, 5.68 mmol), isobutyraldehyde (0.46 mL, 5.11 mmol). The residue was purified by chromatography (EP/EtOAc : 98/2) to afford a colorless oil (1 g, 79%). All spectroscopic data were in agreement with those previously reported.[2]

4-(Dimethyl-phenyl-silanyl)-2,2-dimethyl-hex-5-en-3-ol (3c): Prepared according to general procedure A from dimethylphenyl allylsilane (381 mg, 2.16 mmol) in dry THF (5 mL), *n*-butyllithium in hexane (1 mL, 2.4 mmol), TMEDA (0.5 mL, 5.1 mmol), titanium isopropoxide (0.64 mL, 2.16 mmol), pivalaldehyde (0.23 mL, 2.16 mmol). The residue was purified by chromatography (hexane/EtOAc : 95/5) to afford a colorless oil (390 mg, 69%). IR (neat) ν_{max} = 3583, 3070-2869, 1621, 1247, 1113 cm^{-1}. ^{1}H NMR (250MHz, $CDCl_3$) δ 7.60-7.50 (m, 2H), 7.40-7.30 (m, 3H), 6.00 (ddd, *J* = 17.1, 10.4, 10.4 Hz, 1H), 4.91 (dd, *J* = 10.4, 2.1 Hz, 1H), 4.79 (dd, *J* = 17.1, 2.1 Hz, 1H), 3.40 (d, *J* = 5.8 Hz, 1H), 2.19 (d, *J* = 10.4 Hz, 1H), 1.35 (d, *J* = 5.8 Hz, 1H), 0.84 (s, 9H), 0.35 (s, 3H), 0.33 ppm (s, 3H). ^{13}C NMR (75MHz, $CDCl_3$) δ 138.0, 135.9, 134.1, 129.0, 127.7, 112.9, 78.4, 38.1, 37.4, 26.6, -4.0, -4.2 ppm.

Ethyl 2-hydroxy-3-(dimethyl(phenyl)silyl)pent-4-enoate (3d): Prepared according to general procedure A from dimethylphenyl allylsilane (1 g, 5.67 mmol) in dry THF (15 mL), *n*-butyllithium in hexane (2.5 mL, 6.24 mmol), TMEDA (1.1 mL, 7.4 mmol), titanium isopropoxide (1.7 mL, 5.67 mmol), ethylglyoxalate (50% solution in toluene, 1.23 mL, 6.24 mmol). The residue was purified by chromatography (PE) to afford a yellow oil (320 mg, 22%). IR (neat) ν_{max} = 3515, 3071-2856, 1732, 1626 cm^{-1}. ^{1}H NMR (250MHz, $CDCl_3$) δ 7.60 (m, 2H), 7.37 (m, 3H), 5.80 (ddd, *J* = 17.2, 10.4, 10.2 Hz, 1H), 4.97 (m, 1H), 4.87 (m, 1H), 4.22 (m, 1H), 4.15 (m, 2H), 2.88 (dd, *J* = 4.9, 0.9 Hz, 1H), 2.18 (dd, *J* = 10.5, 2.3 Hz, 1H), 1.22 (t, *J* = 7.0 Hz, 3H), 0.42 (s, 3H), 0.36 ppm (s, 3H). ^{13}C NMR (63MHz, $CDCl_3$) δ 175.1, 137.2, 134.1, 133.1, 129.1, 127.7, 115.8, 71.1, 61.6, 39.9, 14.3, -4.0, -4.2 ppm. MS (LSIMS); *m/z* (%) : 261 (100) [M-OH].

3-(dimethyl(phenyl)silyl)hepta-1,5-dien-4-ol (3e): Prepared according to general procedure A from dimethylphenyl allylsilane (2 g, 11.36 mmol) in dry THF (20 mL), *n*-butyllithium in hexane (5 mL, 12.5 mmol), TMEDA (2.8 mL, 18.7 mmol), titanium isopropoxide (3.36 mL, 11.4 mmol), crotonaldehyde (0.94 mL, 11.4 mmol). The residue was purified by chromatography (pentane/EtOAc : 95/5) to afford a colorless oil (1.90 g, 68%). IR (neat) ν_{max} = 3443, 3070-2879, 1625 cm^{-1}. ^{1}H NMR (300MHz, $CDCl_3$) δ 7.55-7.46 (m, 2H), 7.40-7.32 (m, 3H), 5.81 (ddd, *J* = 17.1, 10.4, 10.4 Hz, 1H), 5.55 (dq, *J* = 15.3, 6.3 Hz, 1H), 5.36 (m, 1H), 5.09 (dd, *J* = 10.2, 1.9 Hz, 1H), 4.97 (dl, *J* = 17.0 Hz, 1H), 4.14 (dd, *J* = 7.5, 7.5 Hz, 1H), 2.00 (dd, *J* = 10.6, 7.3 Hz, 1H), 1.72 (br, 1H), 1.59 (dd, *J* = 6.4, 1.5 Hz, 3H), 0.34 (s, 3H), 0.32 ppm (s, 3H). ^{13}C NMR (75MHz, $CDCl_3$) δ 137.7, 135.9, 134.1, 133.8, 128.9, 127.6, 127.3, 115.7, 72.9, 43.4, 17.5, -3.2, -3.8 ppm. MS (ESI); *m/z* : 269 (100) [M+Na]. HRMS [M+Na] $C_{15}H_{22}OSiNa$: calcd. 269.1338; found. 269.1336.

1-Phenyl-2-triisopropylsilanyl-but-3-en-1-ol (3f): Prepared according to general procedure A from allyltriisopropylsilane (1.24 g, 6.23 mmol) in dry hexane (15 mL), *n*-butyllithium in hexane (2.8 mL, 6.85 mmol), TMEDA (1.55 mL, 10.28 mmol) at 0°C. The resulting pale-yellow solution was stirred at RT overnight, turning reddish brown, then cooled to -78°C. Titanium isopropoxide (1.84 mL, 6.23 mmol) was added at -60°C and the mixture was stirred for 1h at this temperature. Finally, a solution of benzaldehyde (0.57 mL, 5.6 mmol) was added at -78°C, and the reaction mixture was then stirred for 2h. The reaction was quenched with an aqueous solution of NH_4Cl at -78°C. The organic layer was decanted and the aqueous layer extracted with ether. The combined organic layers were then washed with H_2O, dried over $MgSO_4$ and the solvents were removed under reduced pressure. The residue was purified by chromatography (PE/EtOAc : 95/5) to afford a white solid (1.36 g, 79%). All spectroscopic data were in agreement with those previously reported.[3]

1-Phenyl-2-triphenylsilanyl-but-3-en-1-ol 5 (3g): Prepared according to general procedure A from allyltriphenylsilane (2 g, 6.6 mmol) in dry THF (17 mL), *n*-butyllithium in hexane (3 mL, 7.33 mmol), titanium isopropoxide (1.96 mL, 6.66 mmol), benzaldehyde (0.61 mL, 6 mmol). The residue was washed with petroleum ether to afford a white solid (1.54 g, 63%). All spectroscopic data were in agreement with those previously reported.[4]

2-Methyl-4-triphenylsilanyl-hex-5-en-3-ol (3h): Prepared according to general procedure A from allyltriphenylsilane (900 mg, 3 mmol) in dry THF (8 mL), *n*-butyllithium in hexane (1.5 mL, 3.3 mmol), titanium isopropoxide (0.88 mL, 3 mmol), isobutyraldehyde (0.27 mL, 3 mmol). The residue was purified by chromatography (hexane/EtOAc : 9/1) to afford a white solid (765 mg, 68%). mp = 105-107°C. IR (neat) ν_{max} = 3564, 3069-2958, 1623, 1428, 1107, 700 cm^{-1}. ^1H NMR (300MHz, $CDCl_3$) δ 7.66-7.59 (m, 6H), 7.46-7.31 (m, 9H), 6.05 (dt, *J* = 17.1, 10.5 Hz, 1H), 5.07 (dd, *J* = 10.2, 1.9 Hz, 1H), 4.99 (dd, *J* = 17.1, 1.9 Hz, 1H), 3.54 (m, 1H), 2.89 (dd, *J* = 10.7, 2.4 Hz, 1H), 1.76 (m, 1H), 1.52 (d, *J* = 5.1 Hz, 1H), 0.91 (d, *J* = 6.6 Hz, 3H), 0.84 ppm (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (75MHz, $CDCl_3$) δ 136.4, 134.4, 134.2, 129.4, 127.7, 116.9, 77.1, 37.8, 32.6, 19.2, 18.9 ppm. MS (ESI); *m*/*z* : 395 (10) [M+Na]. HRMS [M+Na] $C_{25}H_{28}OSiNa$: calcd. 395.1807; found. 395.1805.

2-(dimethyl(phenyl)silyl)-1-phenylbut-3-en-1-ol (4a): To a stirred solution of allylsilane (608 mg, 3.47 mmol) and TMEDA (0.53 mL, 3.47 mmol) in THF (6 mL), at 0°C was added *n*-BuLi (1.4 mL, 3.47 mmol). The mixture was stirred for 2h then Bu_3SnCl (1.02 mL, 3.82 mmol) was added dropwise at -30°C and stirred for additional 15 min. The reaction was quenched with saturated $NaHCO_3$ and the aqueous layer extracted with ether. The combined organic layers were then washed with H_2O, dried over $MgSO_4$ and the solvents were removed under reduced pressure. To a solution of aldehyde (0.35 mL, 3.47 mmol)

and crude vinylsilane in CH_2Cl_2 (10 mL) at -78°C was added $BF_3.OEt_2$ (0.45 mL, 3.47 mmol) dropwise. After stirring at -78°C for 30 min, the reaction mixture was carefully quenched with saturated $NaHCO_3$ at this temperature, followed by removal of the cold bath and warning to RT. The organic layer was decanted and the aqueous layer extracted with ether. The combined organic layers were then washed with H_2O, dried over $MgSO_4$ and the solvents were removed under reduced pressure. The residue was purified by chromatography (PE/EtOAc : 98/2) to afford a colorless oil (490 mg, 50%). IR (neat) ν_{max} = 3440, 3069-2872, 1627, 1248, 1112 cm^{-1}. ^1H NMR (250MHz, $CDCl_3$) δ 7.63-7.55 (m, 2H), 7.41-7.35 (m, 3H), 5.56 (ddd, *J* = 17.0, 10.4, 10.4 Hz, 1H), 4.86 (dd, *J* = 10.4, 1.8 Hz, 1H), 4.78-4.69 (m, 2H), 2.41 (dd, *J* = 10.4, 8.5 Hz, 1H), 1.84 (d, *J* = 4.3 Hz, 1H), 0.35 (s, 3H), 0.28 ppm (s, 3H). ^{13}C NMR (75MHz, $CDCl_3$) δ 144.3, 138.0, 135.4, 134.2, 129.0, 128.1, 127.7, 127.4, 126.6, 115.2, 75.5, 44.5, -2.6, -3.6 ppm.

4-(Dimethyl-phenyl-silanyl)-2-methyl-hex-5-en-3-ol (4b): To a stirred solution of allylsilane (298 mg, 1.7 mmol) and TMEDA (0.26 mL, 1.7 mmol) in THF (3 mL), at 0°C was added *n*-BuLi (0.7 mL, 1.7 mmol). The mixture was stirred for 2h then Bu_3SnCl (0.51 mL, 1.87 mmol) was added dropwise at -30°C and stirred for additional 15 min. The reaction was quenched with saturated $NaHCO_3$ and the aqueous layer extracted with ether. The combined organic layers were then washed with H_2O, dried over $MgSO_4$ and the solvents were removed under reduced pressure. To a solution of aldehyde (0.16 mL, 1.79 mmol) and crude vinylsilane in CH_2Cl_2 (5 mL) at -78°C was added $BF_3.OEt_2$ (0.22 mL, 1.79 mmol) dropwise. After stirring at -78°C for 30 min, the reaction mixture was carefully quenched with saturated $NaHCO_3$ at this temperature, followed by removal of the cold bath and warning to RT. The organic layer was decanted and the aqueous layer extracted with ether. The combined organic layers were then washed with H_2O, dried over $MgSO_4$ and the solvents were removed under reduced pressure. The residue was purified by chromatography (hexane/EtOAc : 95/5) to afford a colorless oil (216 mg, 44%). IR (neat) ν_{max} = 3490, 3070-2872, 1626, 1248, 1112 cm^{-1}. ^1H NMR (300MHz, $CDCl_3$) δ 7.61-7.53 (m, 2H), 7.40-7.32 (m, 3H), 5.56 (ddd, *J* = 17.0, 10.4, 10.4 Hz, 1H), 4.91 (dd, *J* = 10.2, 1.9 Hz, 1H), 4.84 (dd, *J* = 17.0, 1.9 Hz, 1H), 3.59 (m, 1H), 2.10 (m, 1H), 1.74 (m, 1H), 1.05 (dd, *J* = 6.4, 1.0 Hz, 1H), 0.89 (d, *J* = 7.0 Hz, 3H), 0.77 (d, *J* = 6.8 Hz, 3H), 0.36 ppm (s, 6H). ^{13}C NMR (75MHz, $CDCl_3$) δ 138.6, 136.8, 134.1, 128.9, 127.7, 113.6, 76.9, 41.2, 31.3, 20.1, 13.5, -2.4, -3.7 ppm.

Acetylation of b**- and** g**-Hydroxysilanes (General Procedure B)** : To a stirred solution of alcohol (1 eq) in dry CH_2Cl_2 (6.5 mL/mmol) were added acetic anhydride (2 eq), NEt_3 (2 eq), and a catalytic amount of 4-DMAP (0.1 eq). The resulting mixture was then stirred at RT under nitrogen for 18 h and was treated with saturated aqueous $NaHCO_3$ solution. The organic layer was decanted and the aqueous layer extracted

with ether. The combined extracts were washed with brine and dried over $MgSO_4$, and the solvents were concentrated in vacuo. The crude product was purified by chromatography through silica.

Acetic acid 2-(dimethyl-phenyl-silanyl)-1-isopropyl-but-3-enyl ester (13a): Prepared according to general procedure B from alcohol **3b** (495 mg, 1.99 mmol), Ac_2O (0.38 mL, 4 mmol), Et_3N (0.56 mL, 4 mmol) and 4-DMAP (24 mg, 0.2 mmol). The crude was purified by chromatography (hexane/EtOAc : 98/2) to afford a colorless oil in quantitative yield (579 mg, 100%). IR (neat) ν_{max} = 3051-2874, 1732, 1625, 1237, 1114 cm^{-1}. ^1H NMR (300MHz, $CDCl_3$) d 7.50-7.43 (m, 2H), 7.37-7.30 (m, 3H), 5.87 (dt, *J* = 17.2, 10.5 Hz, 1H), 5.02 (dd, *J* = 10.2, 2.1 Hz, 1H), 4.89 (dd, *J* = 8.0, 3.7 Hz, 1H), 4.85 (ddd, *J* = 17.2, 2.0, 0.7 Hz, 1H), 2.13 (dd, *J* = 10.5, 3.6 Hz, 1H), 1.81 (m, 1H), 1.74 (s, 3H), 0.82 (d, *J* = 6.8 Hz, 3H), 0.76 (d, *J* = 6.6 Hz, 3H), 0.34 (s, 3H), 0.29 ppm (s, 3H). ^{13}C NMR (75MHz, $CDCl_3$) d 170.5, 137.4, 134.9, 134.1, 129.0, 127.6, 115.1, 77.8, 38.3, 31.7, 20.9, 18.8, 18.3, -3.7, -4.2 ppm. MS (ESI); *m*/*z* (%) : 313 [M+Na]. HRMS [M+Na] $C_{17}H_{26}O_2SiNa$: calcd. 313.1599; found. 313.1592.

[Dimethyl-(3-methyl-2-triethylsilanyloxy-1-vinyl-butyl)-silanyl]-benzene (13b): To a stirred solution of alcohol **3b** (316 mg, 1.21 mmol) in dry CH_2Cl_2 (3 mL) were added NEt_3 (0.67 mL, 4.83 mmol), TESCl (0.61 mL, 3.63 mmol) and a catalytic amount of 4-DMAP. The resulting mixture was then stirred at RT under nitrogen for 18 h and was diluted with EtOAc and washed with $KHSO_4$ (1N), followed by saturated aqueous $NaHCO_3$ solution and brine. The crude product was purified by chromatography through silica (hexane) to afford colorless oil (438 mg, 100%). IR (neat) ν_{max} = 2955-2876, 1621, 1246, 1113 cm^{-1}. ^1H NMR (300MHz, $CDCl_3$) δ 7.52-7.45 (m, 2H), 7.37-7.30 (m, 3H), 5.96 (dt, *J* = 17.1, 10.4 Hz, 1H), 4.85 (dd, *J* = 10.3, 2.2 Hz, 1H), 4.74 (ddd, *J* = 17.2, 2.2, 0.8 Hz, 1H), 3.73 (dd, *J* = 4.5, 3.4 Hz, 1H), 2.11 (dd, *J* = 10.3, 4.6, 1H), 1.70 (m, 1H), 0.91 (m, 6H), 0.83 (d, *J* = 7.0 Hz, 3H), 0.72 (d, *J* = 6.8 Hz, 3H), 0.32 (s, 3H), 0.27 ppm (s, 3H). ^{13}C NMR (75MHz, $CDCl_3$) δ 138.4, 138.1, 134.0, 128.8, 127.5, 112.6, 76.7, 38.9, 35.3, 18.8, 17.8, 7.1, 6.8, 6.4, 5.6, -3.1, -4.1 ppm. MS (ESI); *m*/*z* (%)*:* 362 (7) [M], 319 (79) [M-*i*-Pr], 135 (100) [$PhMe_2Si$], 115 (72) [Et_3Si]. HRMS [M] $C_{21}H_{38}OSi_2$: calcd. 362.246123; found. 362.245390.

2,2-dimethyl-4-(dimethyl(phenyl)silyl)hex-5-en-3-yl acetate (13c): Prepared according to general procedure B from alcohol **3c** (1.31 g, 5 mmol), Ac_2O (1.41 mL, 15 mmol), Et_3N (2.1 mL, 15 mmol) and 4-DMAP (61 mg, 0.5 mmol). The crude was purified by chromatography (PE/EtOAc : 98/2) to afford a colorless oil (1.25 g, 82%). IR (neat) ν_{max} = 3072-2958, 1740, 1621, 1370, 1246 cm^{-1}. ^1H NMR (250MHz, $CDCl_3$) δ 7.51-7.43 (m, 2H), 7.37-7.29 (m, 3H), 6.01 (dt, *J* = 17.4, 10.4 Hz, 1H), 4.98-4.89 (m, 2H), 4.76 (dd, *J* = 17.4, 1.4 Hz, 1H), 2.21 (d, *J* = 10.4 Hz, 1H), 1.71 (s, 3H), 0.83 (s, 9H), 0.34 (s, 3H), 0.27 ppm (s, 3H). ^{13}C NMR (75MHz, $CDCl_3$) δ 170.3, 137.1, 136.3, 134.3, 128.9, 127.4, 113.2, 77.8, 37.6, 36.8, 26.8,

20.7, -3.8, -4.7 ppm. MS (LSIMS); *m*/*z* (%) : 327 (42) [M+Na], 288 (100), 245 (39). HRMS [M+Na] $C_{18}H_{28}O_2SiNa$: calcd. 327.175629; found. 327.177304.

2-(dimethyl(phenyl)silyl)-1-phenylbut-3-enyl acetate (13d): Prepared according to general procedure B from alcohol **3a** (209 mg, 0.74 mmol), Ac_2O (0.14 mL, 1.48 mmol), Et_3N (0.21 mL, 1.48 mmol) and 4-DMAP (8 mg, 0.07 mmol). The crude was purified by chromatography (hexane/EtOAc : 9/1) to afford a colorless oil (203 mg, 84%). IR (neat) ν_{max} = 3070-2956, 1734, 1233, 1114 cm^{-1}. ^1H NMR (300MHz, $CDCl_3$) d 7.46-7.39 (m, 2H), 7.36-7.31 (m, 3H), 7.27-7.16 (m, 5H), 5.94 (d, *J* = 7.0 Hz, 1H), 5.85 (ddd, *J* = 17.2, 10.4, 10.4 Hz, 1H), 4.97 (dd, *J* = 10.4, 1.9 Hz, 1H), 4.82 (dl , *J* = 17.1 Hz, 1H), 2.38 (dd, *J* = 10.2, 7Hz, 1H), 1.92 (s, 3H), 0.20 (s, 3H), 0.16 (s, 3H). ^{13}C NMR (75MHz, $CDCl_3$) d 169.9, 140.4, 136.8, 135.0, 133.9, 129.1, 128.1, 127.7, 127.6, 126.8, 115.4, 75.9, 42.6, 21.0, -3.6, -4.2 ppm.

3-(dimethyl(phenyl)silyl)hepta-1,5-dien-4-yl acetate (13e): Prepared according to general procedure B from alcohol **3e** (100 mg, 0.40 mmol), Ac_2O (0.08 mL, 0.813 mmol), Et_3N (0.11 mL, 0.813 mmol) and 4-DMAP (5 mg, 0.04 mmol). The crude was purified through neutral alumine (PE/EtOAc : 95/5) to afford a colorless oil (100 mg, 86%). IR (neat) ν_{max} = 3071-2857, 1740, 1627, 1369, 1235 cm^{-1}. ^1H NMR (300MHz, $CDCl_3$) δ 7.49-7.42 (m, 2H), 7.37-7.31 (m, 3H), 5.77 (ddd, *J* = 17.2, 10.3, 10.3 Hz, 1H), 5.62 (dd, *J* = 14.9, 6.6 Hz, 1H), 5.37 (dd, *J* = 8.1, 6.6 Hz, 1H), 5.27 (m, 1H), 5.00 (dd, *J* = 10.5, 1.9 Hz, 1H), 4.87 (dl, *J* = 17 Hz, 1H), 2.11 (dd, *J* = 10.2, 6.4 Hz, 1H), 1.88 (s, 3H), 1.56 (dd, *J* = 6.6, 1.7 Hz, 3H), 0.31 ppm (s, 6H). ^{13}C NMR (75MHz, $CDCl_3$) δ 170.0, 137.4, 135.3, 134.0, 129.8, 129.4, 129.0, 127.6, 115.1, 75.2, 41.1, 21.2, 17.5, -3.5, -3.9 ppm.

Ethyl 2-acetoxy-3-(dimethyl(phenyl)silyl)pent-4-enoate (13f): Prepared according to general procedure B from alcohol **3d** (291 mg, 1.09 mmol), Ac_2O (0.2 mL, 2.18 mmol), Et_3N (0.3 mL, 2.18 mmol) and DMAP (12 mg, 0.1 mmol). The crude was purified by chromatography (PE/ EtOAc : 95/5) to afford a colorless oil (220 mg, 63%). IR (neat) ν_{max} =3000-2958, 1748, 1231, 1113 cm^{-1}. ^1H NMR (250MHz, $CDCl_3$) δ 7.52-7.44 (m, 2H), 7.40-7.32 (m, 3H), 5.85 (ddd, *J* = 17.0, 10.3, 10.3 Hz, 1H), 5.05-4.95 (m, 2H), 4.90 (dd, *J* = 17.1, 1.5 Hz, 1H), 4.10 (dd, *J* = 7.3 Hz, 2H), 2.36 (dd, *J* = 10.4, 3.0 Hz, 1H), 2.04 (s, 3H), 1.20 (t, *J* = 7.2 Hz, 3H), 0.37 (s, 3H), 0.36 ppm (s, 3H). ^{13}C NMR (63MHz, $CDCl_3$) δ 170.0, 169.5, 136.2, 133.7, 133.0, 129.4, 127.8, 116.2, 73.0, 61.1, 37.2, 20.5, 14.2, -4.2, -4.4 ppm. MS (LSIMS); *m*/*z* (%) : 343 (14) [M+Na], 261 (100) [M-OAc]. HRMS [M+Na] $C_{17}H_{24}O_4SiNa$: calcd. 343.134158; found. 343.134046.

2-(dimethyl(phenyl)silyl)-1-phenylbut-3-enyl acetate (14a): Prepared according to general procedure B from alcohol **4a** (419 mg, 1.48 mmol), Ac_2O (0.42 mL, 4.45 mmol), Et_3N (0.62 mL, 4.45 mmol) and 4-DMAP (18 mg, 0.15 mmol). The crude was purified by chromatography (hexane/EtOAc : 98/2) to afford

a white solid (312 mg, 65%). IR (neat) ν_{max} = 3000- 2950, 1732, 1236 cm^{-1}. ^1H NMR (300MHz, $CDCl_3$) δ 7.59-7.50 (m, 2H), 7.42-7.33 (m, 3H), 7.32-7.16 (m, 5H), 5.84 (d, *J* = 9.4 Hz, 1H), 5.58 (ddd, *J* = 16.9, 10.4, 10.4 Hz, 1H), 4.88 (dd, *J* = 10.4, 1.7 Hz, 1H), 4.76 (dd, *J* = 16.9, 0.7 Hz, 1H), 2.64 (dd, *J* = 9.8, 9.8 Hz, 1H), 1.76 (s, 3H), 0.32 (s, 3H), 0.31 ppm (s, 3H). ^{13}C NMR (75MHz, $CDCl_3$) δ 169.7, 140.5, 137.6, 134.4, 133.8, 128.9, 127.9, 127.7, 127.6, 127.1, 115.6, 76.6, 41.5, 20.9, -2.8, -4.4 ppm. MS (LSIMS); *m*/*z* (%) : 347 (29) [M+Na], 329 (22), 288 (100), 265 (10). HRMS [M+Na] $C_{20}H_{24}O_2SiNa$: calcd. 347.144328; found. 347.144430.

Acetic acid 2-(dimethyl-phenyl-silanyl)-1-isopropyl-but-3-enyl ester (14b): Prepared according to general procedure B from alcohol **4b** (216 mg, 0.87 mmol), Ac_2O (0.17 mL, 1.74 mmol), Et_3N (0.24 mL, 1.74 mmol) and 4-DMAP (11 mg, 0.09 mmol). The crude was purified by chromatography (hexane/EtOAc : 95/5) to afford a colorless oil (154 mg, 61%). IR (neat) ν_{max} = 3070-2965, 1736, 1627, 1240, 1114 cm^{-1}. ^1H NMR (300MHz, $CDCl_3$) δ 7.52-7.45 (m, 2H), 7.36-7.31 (m, 3H), 5.60 (dt, *J* = 16.9, 10.4 Hz, 1H), 5.10 (dd, *J* = 9.5, 3.7 Hz, 1H), 4.96 (dd, J = 10.3, 1.8 Hz, 1H), 4.89 (ddd, 17.0, 1.7, 0.8 Hz, 1H), 2.35 (m, 1H), 1.86 (m, 1H), 1.58 (s, 1H), 0.82 (d, *J* = 3.2 Hz, 3H), 0.80 (d, *J* = 3.2 Hz, 3H), 0.37 (s, 3H), 0.24 ppm (s, 3H). ^{13}C NMR (75MHz, $CDCl_3$) δ 170.7, 138.3, 136.0, 133.9, 128.8, 127.5, 114.5, 77.5, 38.0, 31.4, 20.6, 19.7, 15.2, -2.5, -4.5 ppm. MS (ESI); *m*/*z* (%) : 313 (100) [M+Na], 135 (75) [$PhMe_2Si$]. HRMS [M+Na] $C_{17}H_{26}O_2SiNa$: calcd. 313.1599; found. 313.1614.

Acetic acid 1-isopropyl-2-triphenylsilanyl-but-3-enyl ester (17a): Prepared according to general procedure B from alcohol **3h** (500 mg, 1.34 mmol), Ac_2O (0.25 mL, 2.68 mmol), Et_3N (0.38 mL, 2.68 mmol) and 4-DMAP (16 mg, 0.13 mmol). The crude was purified by chromatography (hexane/EtOAc : 95/5) to afford a white solid (496 mg, 89%). mp = 90-91°C. IR (neat) ν_{max} = 3070-2873, 1731, 1428, 1236, 1108 cm^{-1}. ^1H NMR (300MHz, $CDCl_3$) δ 7.62-7.53 (m, 2H), 7.45 -7.31 (m, 3H), 6.11 (dt, *J* = 17.3, 10.5 Hz, 1H), 5.15 (dd, *J* = 8.5, 2.4 Hz, 1H), 5.03 (dd, *J* = 10.4, 1.9 Hz, 1H), 4.91 (dd, *J* = 17.2, 1.8 Hz, 1H), 2.89 (dd, *J* = 10.5, 2.6 Hz, 1H), 1.93 (m, 1H), 1.48 (s, 3H), 0.86 (d, *J* = 6.6 Hz, 3H), 0.78 ppm (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (75MHz, $CDCl_3$) δ 170.1, 136.3, 134.2, 133.7, 129.4, 127.7, 117.3, 77.4, 36.3, 31.8, 20.5, 18.9, 18.8 ppm. MS (ESI); *m*/*z* (%) : 437 (38) [M+Na], 259 (100) [$SiPh_3$], 241 (95). HRMS [M+Na] $C_{27}H_{30}O_2SiNa$: calcd.437.1912; found. 437.1911.

Acetic acid 2-(triisopropylsilyl)-1-phenylbut-3-enyl ester (17b): Prepared according to general procedure B from alcohol **3f**[1] (190 mg, 0.625 mmol), Ac_2O (0.18 mL, 1.87 mmol), Et_3N (0.26 mL, 1.87 mmol) and 4-DMAP (7.5 mg, 0.06 mmol). The crude was purified by chromatography (hexane/EtOAc : 95/5) to afford a white solid (205 mg, 95%). mp 53-55°C. IR (neat) ν_{max} = 3073-2867, 1748 (ester), 1464, 1370, 1228 cm^{-1}. ^1H NMR (300MHz, $CDCl_3$) δ 7.35-7.13 (m, 5H), 6.17-5.99 (m, 2H), 4.93 (dd, *J* = 10.2,

1.9 Hz, 1H), 4.69 (dd, *J* = 17.1, 2.1 Hz, 1H), 2.33 (dd, *J* = 10.9, 3.0 Hz, 1H), 2.11 (s, 3H), 1.17-1.11 ppm (m, 21H). ^{13}C NMR (75MHz, $CDCl_3$) δ 169.9, 141.7, 135.0, 127.9, 127.2, 125.9, 116.1, 75.8, 39.7, 21.3, 19.1, 18.9, 11.5 ppm.

1-phenyl-3-(triphenylsilyl)pent-4-enyl acetate (19): Prepared according to general procedure B from alcohol **5b**[2] (500 mg, 1.19 mmol), Ac_2O (0.23 mL, 2.37 mmol), Et_3N (0.33 mL, 2.37 mmol) and 4-DMAP (15 mg, 0.12 mmol). The crude was purified by chromatography (hexane/EtOAc : 95/5) to afford a colorless oil (506 mg, 92%). IR (neat) ν_{max} = 3069, 1738, 1428, 1237, 1109 cm^{-1}. ^{1}H NMR (300MHz, $CDCl_3$) δ 7.44-7.27 (m, 20H), 5.86-5.72 (m, 2H), 5.08 (dd, *J* = 10.4, 1.3 Hz, 1H), 4.97 (dl, *J* = 17.0 Hz, 1H), 2.27-2.10 (m, 3H), 1.96 ppm (s, 3H). ^{13}C NMR (63MHz, $CDCl_3$) δ 170, 139.3, 137.4, 136.0, 135.7, 133.2, 129.5, 128.3, 127.7, 127.5, 115.7, 75.6, 34.9, 28.0, 21.3 ppm.

dimethyl(2-methyl-1-phenylallyl)(phenyl)silane (23): To a solution of (2E)-2-methyl-3-phenyl-2-propenoic acid (3.25 g, 20 mmol) in dry ether (20 mL) was added dropwise a solution of $LiAlH_4$ in ether (1M, 15 mL, 15 mmol) at 0°C. The mixture was stirred under reflux for 2h, then carefully quenched at 0°C with aqueous saturated NH_4Cl. The solvent was evaporated. $SOCl_2$ (3.4 mL, 46.6 mmol) was added at RT to a solution of alcohol (2.3 g, 15.5 mmol) in THF (25 mL). The mixture was stirred for 1h, followed by addition of water (50 mL) and extraction with CH_2Cl_2. The solvent was evaporated under reduce pressure. The residue was distillated under reduce pressure (bp = 85°C, 0.5 mbar) to afford a colorless oil (1.1 g, 33% over two steps). To a suspension of CuCN (653 mg, 7.3 mmol) in dry THF (55 mL) was added at -30°C under nitrogen atmosphere, a 0.87M solution of dimethylphenylsilyl lithium in THF (16.7 mL, 14.6 mmol). The mixture was stirred for 1h at -30°C, and allylchloride (1.1 mL, 6.57 mmol) was added at -78°C. The resulting mixture was then stirred for 1h at -78°C. The reaction mixture was quenched with a saturated solution of NH_4Cl at -78°C, and the aqueous layer was extracted with ether. The combined extracts were washed with brine, dried over $MgSO_4$ and the solvent were evaporated in vacuo. The residue was purified by chromatography over silica gel with petroleum ether affording the product as a colorless oil (1.57 g, 90%). All spectroscopic data were in agreement with those previously reported.[5]

1-((but-3-en-2-yloxy)methyl)benzene (25a): A solution of NaH (4.8 g, 100 mmol), in dry THF (10 mL), was warmed to 45°C and BnBr (6 mL, 50 mmol), was added. Alcohol (1.3 mL, 15 mmol), in THF (20 mL), was added dropwise during 20 min. After being heated for an additional 45 min, the reaction mixture was allowed to cool to RT and water was added until evolution of H_2 ceased. The aqueous layer was extracted with ether, and the combiend extract washed with brine. The solvent was evaporated and

the residue purified over silica gel (hexane) to afford a colorless oil (2.44 g, 100%). All spectroscopic data were in agreement with those previously reported.[6]

Tert-butyl(but-3-en-2-yloxy)dimethylsilane (25b): To a solution of alcohol (2 mL, 23.1 mmol) in CH_2Cl_2 (25 mL) was added TBSCl (7 g, 46.2 mmol), NEt_3 (6.4 mL, 46.2 mmol) and a catalytic amount of 4-DMAP (280 mg, 2.3 mmol). The mixture was stirred at RT for 5h under N_2 atmosphere. The solution was washed with brine. The solvent was evaporated under vacuo and the residue purified over silica gel (hexane) to afford a colorless oil (2.13 g, 50%). All spectroscopic data were in agreement with those previously reported.[6]

(1R,2S)-2-(dimethyl(phenyl)silyl)-1-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)but-3-enyl acetate (27): Prepared according to general procedure B from the corresponding alcohol (9.88 g, 32.3 mmol), Ac_2O (6.1 mL, 64.5 mmol), Et_3N (9.0 mL, 64.5 mmol) and 4-DMAP (390 mg, 3.2 mmol). The crude product was purified by chromatography (petroleum ether/EtOAc : 95/5) to afford a colorless oil (10.5 g, 93 %). IR (neat) ν_{max} = 3071-2891, 1746, 1626, 1428, 1371, 1279, 1114, 1069 cm^{-1}. ^1H NMR (300MHz, $CDCl_3$) d 7.53-7.41 (m, 2H), 7.40-7.29 (m, 3H), 5.84 (ddd, *J* = 17.1, 10.4, 10.4 Hz, 1H), 5.29 (dd, *J* = 6.2, 3.0 Hz, 1H), 5.08 (dd, *J* = 10.4, 1.9 Hz, 1H), 4.98 (ddd, *J* = 17.1, 1.9, 0.6 Hz, 1H), 4.01 (m, 1H), 3.75 (m, 1H), 3.68 (m, 1H), 2.16 (dd, *J* = 10.5, 3.1 Hz, 1H), 1.75 (s, 3H), 1.31 (s, 3H), 1.26 (s, 3H), 0.35 (s, 3H), 0.31 ppm (s, 3H). ^{13}C NMR (75MHz, $CDCl_3$) d 169.8, 136.8, 134.0, 133.9, 129.1, 127.6, 116.2, 108.7, 76.6, 72.1, 65.6, 37.4, 26.4, 25.3, 20.6, -4.2, -4.3. MS (ESI); *m*/*z* (%) : 371 [M+Na] (100), 329 (21), 231 (10), 209 (10). HRMS [M+Na] $C_{19}H_{28}O_4SiNa$: calcd. 372.1654; found. 371.1648. Elemental Analysis : $C_{19}H_{28}O_4Si$ (348.51): calcd C 65.48, H 8.10; found C 65.73, H 8.02.

6-Acetoxy-4-azido-6-(2,2-dimethyl-[1,3]dioxolan-4-yl)-5-(dimethyl-phenyl-silanyl)-hexanoic acid ethyl ester (28): Prepared according to general procedure C from allylsilane **27** (244 mg, 0.7 mmol), xanthate (71 mg, 0.34 mmol), 3-pyridinesulfonyl azide (194 mg, 1.05 mmol), $(Bu_3Sn)_2$ (0.26 mL, 0.52 mmol), DTBHN (11 mg, 0.06 mmol) in benzene (1 mL) at 60°C under N_2 atmosphere. The product was obtained as a colorless oil (137 mg, 84%, *syn/anti* 85/15) after purification through silica gel (pentane/EtOAc : 95/5). Major diastereomer : a_D^{20} = + 74.7° (C = 1.08, $CHCl_3$). IR (neat) ν_{max} = 3070-2984, 2105, 1732 cm^{-1}. ^1H NMR (300MHz, $CDCl_3$) d 7.58-7.51 (m, 2H), 7.38-7.32 (m, 3H), 5.09 (dd, *J* = 6.9, 1.6 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 4.10-3.97 (m, 2H), 3.81 (dd, *J* = 8.6, 6.3 Hz, 1H), 3.54 (dd, *J* = 8.6, 6.1 Hz, 1H), 2.42 (m, 2H), 1.96 (s, 3H), 1.81 (m, 2H), 1.69 (m, 1H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.27 (s, 3H), 1.23 (s, 3H), 0.42 ppm (s, 6H). ^{13}C NMR (75MHz, $CDCl_3$) d 172.8, 170.4, 137.4, 134.2, 129.2, 127.8, 109.4, 75.8, 72.4, 66.8, 62.9, 60.4, 35.0, 32.2, 31.6, 26.3, 25.2, 21.6, 14.2, -2.0, -3.2 ppm. MS (ESI); *m*/*z* (%) : 500 (100) [M+Na], 435 (21) [M-N3], 418 (20), 329 (28), 317 (53), 223 (54). HRMS

[M+Na] $C_{23}H_{35}N_3O_6SiNa$: calcd. 500.2192, found. 500.2177. Elemental Analysis : $C_{28}H_{37}N_3O_6Si$ (539.7): calcd C 57.84, H 7.39, Si 5.88; found C 57.89, H 7.51, Si 5.86. Minor diastereomer : IR (neat) ν_{max} = 3070-2984, 2105, 1732 cm^{-1}. ^1H NMR (300MHz, $CDCl_3$) d 7.56-7.47 (m, 2H), 7.41-7.32 (m, 3H), 5.24 (dd, *J* = 7.3, 4.0 Hz, 1H), 4.21 (m, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.82 (m, 1H), 3.73-3.60 (m, 2H), 2.38 (m, 2H), 2.11-2.02 (m, 1H), 2.01 (s, 3H), 1.81 (m, 1H), 1.77-1.66 (m, 1H), 1.31-1.21 (m, 9H), 0.44 ppm (s, 6H). ^{13}C NMR (75MHz, $CDCl_3$) d 172.7, 170.0, 137.7, 134.7, 129.3, 128.0, 109.3, 76.2, 73.1, 67.0, 62.2, 60.4, 33.2, 31.5, 30.3, 26.4, 25.2, 21.1, 14.2, -2.3, -2.4 ppm. MS (LSIMS); *m*/*z* (%) : 500 (100) [M+Na], 435 (21) [M-N3], 393 (17), 305 (40), 241 (52). HRMS [M+Na] $C_{23}H_{35}N_3O_6SiNa$: calcd. 500.219284, found. 500.217543.

(R)-methyl 4-azido-4-((4S,5R)-5-((R)-1,2-dihydroxyethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)butanoate (29) The diacetonide (78 mg, 0.228 mmol) was dissolved in CH_3CN (1.2 mL) and $Zn(NO_3)_2.6H_2O$ (342 mg, 1.15 mmol) was added. The resulting mixture was stirred at 50°C for 6h. The solvent was evaporated and the oily residue dissolved in CH_2Cl_2, washed with brine and dried over Na_2SO_4. The solvent was evaporated under vacuo and the residue purified through silica gel (PE/EtOAc : 5/5) to afford a colorless oil (39 mg, 56%, corrected yield 75%). IR (neat) ν_{max} = 3428, 2990-2930, 2106, 1732 cm^{-1}. ^1H NMR (300MHz, $CDCl_3$) d 4.20 (m, 1H), 4.10-3.95 (m, 2H), 3.92-3.81 (br, 1H), 3.70 (s, 3H), 3.69-3.57 (m, 2H), 3.17 (br, 1H), 2.55 (dd, *J* = 7.6, 6.4 Hz, 2H), 2.23-2.02 (m, 2H), 1.99-1.82 (m, 1H), 1.48 (s, 3H), 1.36 ppm (s, 3H). ^{13}C NMR (75MHz, $CDCl_3$) d 173.8, 108.9, 80.0, 77.0, 69.2, 64.6, 58.7, 51.9, 30.4, 27.2, 26.8, 25.0 ppm. MS (LSIMS); *m*/*z* (%) : 326 (58) [M+Na]. HRMS [M+Na] $C_{12}H_{21}N_3O_6Na$: calcd. 326.132805; found. 326.133367.

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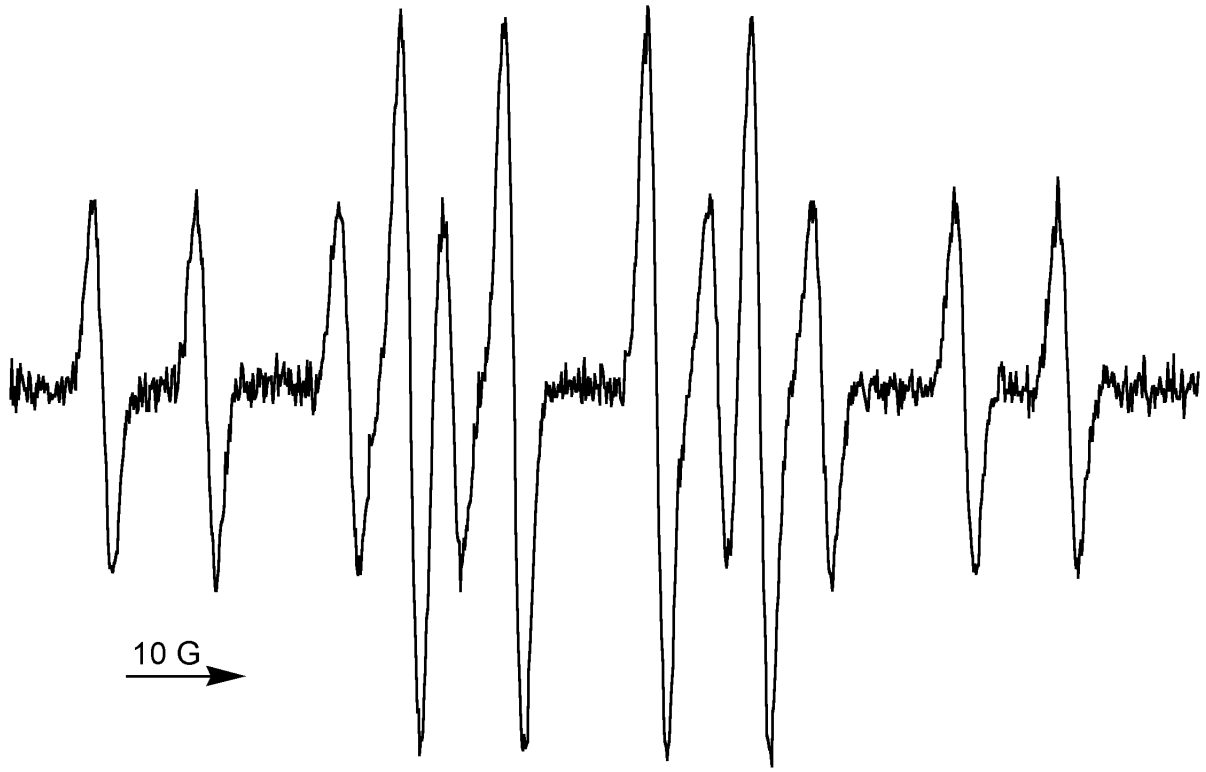

Figure. Room temperature EPR spectrum of radical **I** obtained by photolysis of a benzene solution containing $(Bu_3Sn)_2$, xanthate **7** and allylsilane **13a**.

Geometries of transition states optimized at the B3LYP/6-31G(d) level.

IIA-1

6	1.048972	1.164356	.102801
7	-.945690	1.246584	-1.033654
6	1.609366	-.126857	-.367895
6	4.502287	.222977	.889638
6	2.166122	-.841747	2.619962
1	4.954836	.300383	-.105329
1	4.296491	1.240488	1.241846
1	5.253687	-.206626	1.563128
1	1.220197	-1.395563	2.641985
1	2.846204	-1.325827	3.330624
1	1.967989	.171863	2.988042
14	2.927313	-.826423	.886753
7	-1.579513	.304624	-.812522
7	-1.896493	-.799290	-.281692
16	-3.383927	-1.466698	-.941296
8	-3.538503	-1.027328	-2.330549
8	-3.304285	-2.876147	-.570698
6	2.138231	-.120306	-1.814163
1	2.990264	.557663	-1.939674
1	2.466931	-1.121368	-2.109212
1	1.356447	.196199	-2.515127
6	1.608295	2.493600	-.306353
1	2.669673	2.560919	-.019491
1	1.594892	2.579899	-1.401105
6	.847491	3.678080	.314440
1	-.202719	3.662632	.015558
1	.885620	3.600380	1.410066
1	.817935	-.889089	-.284096
1	.508525	1.138375	1.049011
6	-4.663662	-.685726	.041939
6	-4.980864	-1.223126	1.291546
6	-5.308130	.448328	-.456065
6	-5.964313	-.601272	2.059556
1	-4.474506	-2.116737	1.640462
6	-6.290082	1.059765	.323991
1	-5.054476	.826847	-1.440473

6	-6.614581	.538339	1.578362
1	-6.226748	-1.009794	3.031198
1	-6.804913	1.939255	-.051754
1	-7.381051	1.017785	2.180958
6	3.313466	-2.595401	.345641
6	4.612912	-2.998555	-.011931
6	2.292729	-3.565142	.287804
6	4.885265	-4.310515	-.405639
1	5.430166	-2.281568	.016450
6	2.557668	-4.876741	-.106269
1	1.270275	-3.299770	.551789
6	3.857172	-5.252412	-.453649
1	5.899049	-4.595675	-.675635
1	1.750779	-5.603972	-.143820
1	4.065965	-6.273762	-.761420
6	1.403419	5.035196	-.070294
8	.755744	5.961879	-.504288
8	2.739471	5.102054	.149880
6	3.352803	6.360386	-.175407
1	4.412640	6.237001	.049774
1	3.208762	6.596293	-1.233055
1	2.922576	7.164380	.427715

IIA-2

6	1.682335	-.648320	-.451750
7	-.066495	-2.089284	-.314747
6	1.127263	.613459	.100359
6	3.854416	2.224448	.304851
6	2.337735	2.064999	-2.388616
1	3.800861	2.207258	1.399234
1	4.471943	1.375458	-.010594
1	4.387065	3.137576	.012948
1	1.370342	1.957986	-2.893160
1	2.807956	2.978431	-2.771167
1	2.965209	1.217748	-2.689344
14	2.146499	2.160566	-.508524
7	-1.049078	-1.619823	-.708105
7	-1.825726	-.743705	-1.187859
16	-3.444902	-1.363960	-1.484652

8	-4.036987	-.336046	-2.334644
8	-3.358376	-2.768116	-1.894077
6	.923957	.625122	1.626834
1	1.871370	.537633	2.170379
1	.445480	1.556398	1.945410
1	.283269	-.206976	1.944016
6	2.716897	-1.463061	.266221
1	3.616465	-.852315	.443533
1	2.347794	-1.739460	1.262783
6	3.123855	-2.733019	-.503278
1	2.265104	-3.392347	-.641986
1	3.500062	-2.450985	-1.496031
1	.155836	.797050	-.385591
1	1.665402	-.745696	-1.536965
6	-4.224906	-1.297768	.129145
6	-4.270147	-2.453043	.911670
6	-4.761514	-.086923	.572863
6	-4.864445	-2.387208	2.172433
1	-3.864113	-3.382652	.527507
6	-5.351551	-.036351	1.834892
1	-4.726784	.787465	-.068230
6	-5.400387	-1.182625	2.633051
1	-4.913495	-3.278725	2.790974
1	-5.778176	.896270	2.192731
1	-5.863088	-1.137649	3.615083
6	1.139260	3.692702	-.046614
6	1.622192	4.662427	.850628
6	-.139368	3.899197	-.601053
6	.866845	5.790359	1.178984
1	2.604612	4.542173	1.301332
6	-.899343	5.023177	-.277146
1	-.554529	3.174190	-1.299083
6	-.396156	5.972780	.614909
1	1.264940	6.525637	1.873845
1	-1.882238	5.158877	-.721146
1	-.985942	6.850048	.868092
6	4.204823	-3.535205	.193886
8	4.125715	-4.701773	.508552
8	5.306246	-2.777414	.423447
6	6.392707	-3.455713	1.074950
1	7.182172	-2.710939	1.181384

1	6.081592	-3.829397	2.054145
1	6.737825	-4.297740	.469106

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6	.944670	.402575	.781196
7	-.463950	-1.287632	.982209
6	2.150032	-.269114	.226037
6	3.882150	2.337549	-.322798
6	3.804598	1.085918	2.507590
1	3.795194	2.185507	-1.404622
1	3.090927	3.034547	-.023024
1	4.841496	2.834394	-.134561
1	3.695730	.176355	3.110143
1	4.754830	1.554355	2.789277
1	2.999106	1.771468	2.796079
14	3.776438	.716786	.650751
7	-1.281388	-1.351476	.157966
7	-1.893861	-.984855	-.890259
16	-3.328383	-1.938165	-1.221700
8	-3.712184	-1.484824	-2.554541
8	-3.074908	-3.352415	-.931042
6	2.072325	-.617443	-1.272721
1	1.998784	.278348	-1.899472
1	2.964828	-1.166977	-1.587594
1	1.199706	-1.244248	-1.491234
6	.163760	1.420486	-.001137
1	.830280	2.245156	-.299609
1	-.191126	.980008	-.940644
6	-1.028641	2.008141	.776404
1	-1.709821	1.222785	1.109929
1	-.661623	2.530072	1.670824
1	2.299224	-1.199789	.796305
1	.921333	.514528	1.864077
6	-4.496819	-1.317283	-.007801
6	-5.129707	-2.225762	.841156
6	-4.758124	.054448	.052775
6	-6.052983	-1.744884	1.771226
1	-4.895413	-3.282248	.769335
6	-5.672496	.520181	.996160

1	-4.245440	.752356	-.599898
6	-6.321971	-.376998	1.849042
1	-6.557226	-2.439963	2.436622
1	-5.868924	1.586022	1.062550
1	-7.036433	-.007548	2.579798
6	5.234423	-.401214	.204167
6	6.060915	-.136901	-.903264
6	5.523573	-1.546963	.970645
6	7.128118	-.975350	-1.231926
1	5.874332	.738015	-1.521500
6	6.587461	-2.389592	.648111
1	4.912350	-1.789179	1.838371
6	7.393350	-2.104292	-.456164
1	7.751675	-.746731	-2.092548
1	6.788669	-3.266920	1.257594
1	8.223185	-2.758853	-.709659
6	-1.851482	2.992111	-.032492
8	-3.057535	2.961407	-.162681
8	-1.072987	3.942967	-.595101
6	-1.766502	4.919610	-1.391837
1	-.993037	5.584224	-1.777468
1	-2.301795	4.433832	-2.211515
1	-2.481405	5.475452	-.779562

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6	.927913	1.326194	.944261
7	-.877445	.392218	1.801783
6	1.704525	.190901	.379356
6	3.991038	1.922036	-.987921
6	4.157629	1.226987	2.023834
1	3.623810	1.645272	-1.982421
1	3.541696	2.886740	-.725228
1	5.073425	2.079898	-1.066911
1	3.901335	.519213	2.821107
1	5.245071	1.364215	2.045216
1	3.698021	2.189824	2.275924
14	3.608825	.610691	.320456
7	-1.735978	.163245	1.051452
7	-2.300466	.107555	-.082493

16	-3.962802	-.448936	.023150
8	-4.511549	-.105824	1.338273
8	-4.556572	.032164	-1.220612
6	1.202105	-.344766	-.975830
1	1.273961	.410869	-1.766394
1	1.795511	-1.208643	-1.291750
1	.153426	-.657475	-.921871
6	.332679	2.401970	.079739
1	1.115606	2.805199	-.585914
1	-.424869	1.980153	-.591598
6	-.281583	3.557125	.891215
1	-1.075107	3.162589	1.537407
1	.469362	4.029840	1.530414
1	1.684023	-.627309	1.117026
1	1.195842	1.623106	1.956288
6	-3.808017	-2.233431	-.072436
6	-3.679584	-2.836187	-1.325796
6	-3.808793	-2.981811	1.106082
6	-3.542393	-4.221977	-1.393903
1	-3.702334	-2.227391	-2.223346
6	-3.671503	-4.367782	1.022359
1	-3.933142	-2.484309	2.062000
6	-3.536011	-4.985054	-.223132
1	-3.446501	-4.706479	-2.361370
1	-3.677171	-4.964674	1.929893
1	-3.431125	-6.064875	-.282668
6	4.513450	-.999917	-.085364
6	5.147957	-1.208387	-1.323617
6	4.567448	-2.046809	.855357
6	5.807445	-2.405368	-1.611246
1	5.133707	-.425590	-2.078394
6	5.222958	-3.245711	.574811
1	4.095085	-1.927327	1.828917
6	5.845691	-3.427177	-.661970
1	6.291599	-2.538866	-2.575383
1	5.250703	-4.036430	1.320298
1	6.358732	-4.359516	-.883154
6	-.874621	4.648292	.019984
8	-.556500	5.817612	.046669
8	-1.821079	4.148045	-.803193
6	-2.464587	5.099958	-1.666270

1	-3.191273	4.526139	-2.241420
1	-2.963689	5.873768	-1.077088
1	-1.734090	5.573743	-2.327755

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7	.876346	.073553	-1.352995
6	-.802545	.650136	.040033
6	-.708407	2.132297	-.180368
1	-.752416	2.342634	-1.256218
1	-1.593115	2.625534	.253034
6	-1.998068	-.113291	-.395547
1	-.229769	.230133	.868664
6	-1.694857	-1.579341	-.783736
1	-2.459654	.394514	-1.255625
1	-2.615936	-2.146326	-.953992
1	-1.105091	-1.615637	-1.704997
1	-1.119629	-2.090508	-.003648
6	-2.786768	-1.160569	2.453015
6	-3.765350	1.638285	1.600178
1	-2.545402	-2.188883	2.163426
1	-1.886845	-.729486	2.907636
1	-3.557971	-1.205608	3.230970
1	-4.038391	2.318806	.785457
1	-4.613716	1.604446	2.294244
1	-2.919885	2.083077	2.137477
14	-3.375226	-.112602	.993089
6	.561177	2.765168	.415965
1	1.441029	2.337453	-.079823
1	.641977	2.553258	1.485911
7	1.566731	-.739295	-.895915
7	1.946485	-1.560321	-.009236
16	3.350198	-2.488493	-.504882
8	3.293978	-3.667028	.354066
8	3.382602	-2.584251	-1.966931
6	-4.938448	-.853693	.228116
6	-5.320865	-2.187773	.461259
6	-5.759892	-.081915	-.616080
6	-6.469438	-2.728321	-.120580
1	-4.717484	-2.818299	1.110094

6	-6.908164	-.615334	-1.201972
1	-5.505519	.956574	-.820166
6	-7.265463	-1.942359	-.954657
1	-6.742366	-3.761586	.078320
1	-7.524905	.003499	-1.848879
1	-8.159958	-2.360534	-1.408959
6	4.724288	-1.462710	.021239
6	5.147175	-1.524915	1.350857
6	5.336591	-.617534	-.905965
6	6.205459	-.713442	1.757730
1	4.662235	-2.206752	2.041273
6	6.394821	.188215	-.484531
1	4.998002	-.610537	-1.936515
6	6.825597	.142224	.843284
1	6.549351	-.753376	2.787286
1	6.886111	.846457	-1.195344
1	7.650938	.770940	1.165798
6	.616522	4.272117	.261092
8	.797395	5.063902	1.160243
8	.445430	4.640060	-1.030581
6	.492876	6.054613	-1.279347
1	1.465120	6.462646	-.990424
1	.332420	6.168828	-2.351809
1	-.288737	6.570864	-.715594

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7	1.007801	1.228249	-.808824
6	-.981621	1.013653	.206456
6	-1.539705	2.329509	-.253503
1	-1.418594	2.413638	-1.340947
1	-2.626106	2.350381	-.073830
6	-1.565064	-.269697	-.257800
1	-.474019	.996319	1.172374
6	-.547591	-1.432237	-.315804
1	-2.004434	-.129697	-1.256830
1	-1.042890	-2.384783	-.529698
1	.192365	-1.254167	-1.102763
1	-.004176	-1.535813	.630159
6	-2.404028	-1.200800	2.616914

6	-4.380232	.540848	1.008734
1	-1.640406	-1.986268	2.613384
1	-1.955600	-.310971	3.074482
1	-3.218324	-1.530571	3.272829
1	-4.742182	.869489	.027499
1	-5.244662	.152646	1.560835
1	-4.019150	1.424960	1.546116
14	-3.057997	-.809101	.886567
6	-.892622	3.547140	.431365
1	.174409	3.574427	.182189
1	-.988538	3.480836	1.518713
7	1.896544	.891456	-.142735
7	2.442402	.400868	.889699
16	4.193766	.484315	.826880
8	4.597703	1.642347	.024614
8	4.585709	.326554	2.223662
6	-3.836398	-2.345124	.102749
6	-3.658441	-3.631453	.644634
6	-4.620716	-2.235258	-1.061931
6	-4.235818	-4.757083	.053108
1	-3.064026	-3.762020	1.545880
6	-5.199035	-3.355261	-1.659543
1	-4.790355	-1.258889	-1.512646
6	-5.007158	-4.620947	-1.101543
1	-4.084474	-5.738788	.494866
1	-5.800915	-3.241294	-2.557614
1	-5.457900	-5.495316	-1.563823
6	4.649599	-1.002652	-.066736
6	4.896731	-.924945	-1.438601
6	4.741323	-2.210102	.629227
6	5.237041	-2.089632	-2.127361
1	4.840909	.032751	-1.944990
6	5.082086	-3.365796	-.072319
1	4.563136	-2.232325	1.699040
6	5.326492	-3.306061	-1.446964
1	5.438708	-2.044347	-3.193745
1	5.162838	-4.311669	.455605
1	5.593724	-4.209595	-1.988014
6	-1.520327	4.861213	.011619
8	-2.065323	5.649282	.753191
8	-1.402415	5.054477	-1.323360

6	-1.965878	6.279516	-1.819794
1	-1.482061	7.141190	-1.352344
1	-1.781183	6.272464	-2.894432
1	-3.038829	6.321506	-1.613579

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7	-.755598	.049079	-2.125273
6	.934188	1.267091	-1.270137
6	.130838	2.153895	-.360988
1	-.374503	1.559203	.409257
1	.816168	2.824230	.185551
6	1.853555	.211722	-.772426
1	1.180904	1.690052	-2.244338
6	2.353651	-.703455	-1.911822
1	1.334443	-.395900	-.014975
1	2.991774	-1.503728	-1.529119
1	1.513076	-1.161619	-2.442926
1	2.935926	-.136752	-2.649487
6	4.142515	2.374215	-.785914
6	2.841255	1.561226	1.917324
1	4.430548	2.066829	-1.797934
1	3.435446	3.206332	-.883994
1	5.039098	2.762951	-.289096
1	2.298725	.784594	2.469131
1	3.727854	1.822541	2.507495
1	2.199776	2.447721	1.877889
14	3.379671	.954058	.205228
6	-.890947	3.033437	-1.108763
1	-1.628915	2.393592	-1.604818
1	-.396545	3.633473	-1.877767
7	-1.153329	-.722092	-1.354690
7	-1.226594	-1.331904	-.247297
16	-2.370515	-2.667494	-.289441
8	-2.492143	-3.160176	-1.664377
8	-1.928318	-3.518756	.810841
6	4.642764	-.430729	.454251
6	5.887949	-.427626	-.199951
6	4.364077	-1.509461	1.316334
6	6.816235	-1.452070	-.002573

1	6.143742	.387069	-.873356
6	5.284966	-2.538248	1.515054
1	3.413177	-1.553154	1.844384
6	6.515584	-2.510517	.855301
1	7.772595	-1.423486	-.518723
1	5.043538	-3.359979	2.184375
1	7.235447	-3.310120	1.009689
6	-3.925103	-1.901454	.171724
6	-4.815202	-1.511194	-.830501
6	-4.211146	-1.708733	1.525064
6	-6.018175	-.907495	-.463183
1	-4.572694	-1.697416	-1.871251
6	-5.417210	-1.104230	1.877058
1	-3.506809	-2.042624	2.279462
6	-6.316648	-.702547	.885750
1	-6.724371	-.604461	-1.230844
1	-5.657778	-.953508	2.925580
1	-7.256321	-.234637	1.166184
6	-1.622850	3.997815	-.197002
8	-1.648955	5.202706	-.321780
8	-2.263416	3.338897	.797691
6	-2.991426	4.169094	1.717125
1	-3.774990	4.724690	1.194898
1	-3.427050	3.485641	2.446557
1	-2.321322	4.880195	2.207489

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7	-1.150025	1.018923	-1.742646
6	1.009661	1.348107	-1.217411
6	.783261	2.514670	-.295862
1	.058157	2.242916	.481673
1	1.714611	2.740953	.247036
6	1.498546	.036892	-.721824
1	1.230268	1.583701	-2.258507
6	1.158268	-1.135118	-1.670331
1	1.066575	-.163641	.269936
1	1.611335	-2.070076	-1.326925
1	.076645	-1.289377	-1.731218
1	1.518044	-.938710	-2.687208

6	4.317339	.304826	-2.080561
6	3.980041	1.384632	.789157
1	4.054496	-.452121	-2.827707
1	4.063973	1.284832	-2.502171
1	5.405264	.277341	-1.947964
1	3.391259	1.384547	1.713510
1	5.026328	1.211731	1.069016
1	3.921357	2.387879	.352926
14	3.434445	.040504	-.428102
6	.316661	3.787437	-1.026719
1	-.628997	3.582084	-1.541454
1	1.050182	4.098079	-1.776040
7	-1.745052	.605001	-.835684
7	-1.893899	.159588	.342040
16	-3.578150	-.127450	.745938
8	-3.566489	-.167910	2.205000
8	-4.426837	.800958	-.006285
6	3.884236	-1.643612	.306467
6	4.565713	-2.625498	-.435903
6	3.542353	-1.957009	1.636515
6	4.893556	-3.862975	.122163
1	4.851878	-2.425151	-1.465816
6	3.865082	-3.191642	2.200056
1	3.017346	-1.226737	2.249865
6	4.543137	-4.148689	1.442163
1	5.423397	-4.602278	-.473300
1	3.589771	-3.406359	3.229509
1	4.797525	-5.110971	1.878865
6	-3.878651	-1.785445	.130719
6	-3.491541	-2.877945	.910108
6	-4.486192	-1.950006	-1.115385
6	-3.715213	-4.164358	.421502
1	-3.039713	-2.715296	1.882797
6	-4.704512	-3.243449	-1.591043
1	-4.795368	-1.080043	-1.684763
6	-4.317788	-4.346273	-.826323
1	-3.424596	-5.024670	1.017563
1	-5.182406	-3.388339	-2.555670
1	-4.491582	-5.351298	-1.200830
6	.109179	4.965176	-.094481
8	.664043	6.038961	-.184461

8	-.791761	4.668082	.868698
6	-1.072631	5.722674	1.803606
1	-1.475005	6.596717	1.284739
1	-1.810073	5.312129	2.493552
1	-.164358	6.014630	2.337747