Highly Stereospecific, Palladium-Catalyzed Cross-Coupling of Alkenylsilanols

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SUPPORTING INFORMATION

General Experimental

^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a Varian Unity 400 (400 MHz, ^{1}H; 100 MHz, ^{13}C) or Unity 500 (500 MHz, ^{1}H; 126 MHz, ^{13}C; 100 MHz, ^{29}Si) spectrometer. Spectra are referenced to residual chloroform (δ 7.26 ppm, ^{1}H; δ 77.0 ppm, ^{13}C) or tetramethylsilane (δ 0.00 ppm, ^{1}H, ^{13}C, ^{29}Si).

Chemical shifts are reported in ppm (δ); multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), qn (quintet), sext (sextet), m (multiplet) and br (broad). Coupling constants, *J*, are reported in Hertz. Mass spectroscopy was performed by the University of Illinois Mass Spectrometer Center. Electron impact (EI) spectra were performed on a Finnigan-MAT CH-5 spectrometer. Data are reported in the form of m/z (intensity relative to base peak= 100). Infrared spectra (IR) were recorded on an Mattson Galaxy 5020 spectrophotometer. Peaks are reported in cm^{-1} with indicated relative intensities: s (strong, 67-100%); m (medium, 34-66%); w (weak, 0-33%). Elemental analyses were performed by the University of Illinois Microanalytical Service Laboratory.

Analytical thin-layer chromatography was performed on Merck silica gel plates with QF-254 indicator. Visualization was accomplished with UV light and/or potassium permanganate. Methanol was of reagent grade and used as received; other solvents for chromatography and filtration were technical grade and distilled from the indicated drying agents: hexane and pentane ($CaCl_2$); ethyl acetate (K_2CO_3). Column chromatography was performed using EM Science 230-400 mesh silica gel or ICN silica RP C18 (32-63 μm) 60A.

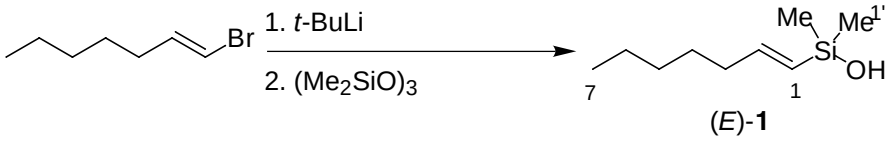
Analytical capillary gas chromatography (GC) was performed using the following gas chromatography fitted with a flame ionization detector (H_2 carrier gas, 1 mL/min): Hewlett Packard 5890 Series II. The following column was used: HP-5 50-m cross-linked 5-Phenyl methyl silicone gum phase. The injector temperature was 225 °C, the detector temperature was 300 °C. Retention times (t_R) and integrated ratios were obtained from Hewlett Packard 3393A integrators.

Kugelrohr distillations were performed on a Büchi GKR-50 Kugelrohr; boiling points (bp) corresponding to uncorrected air-bath temperatures. All commercial reagents were purified by distillation r recrystalisation prior to use. All reactions were performed under an inert atmosphere of dry N_2.

Literature Preparations

(*E*)-6-iodo-5-hexen-1-ol[4]and (*Z*)-6-iodo-5-hexen-1-ol[5] were prepared by literature methods

Preparation of (*E*)-Dimethyl-(1-heptenyl)silanol ((*E*)-1) [DW-IV-59]



To a solution of (*E*)-1-bromo-1-heptene (5.313 g, 30.0 mmol) in dry ether (30 mL) under dry N_2 at -78 °C, *t*-butyllithium (38.7 mL, 60 mmol, 1.55M) was added over 10 min. The reaction mixture was stirred at -78 °C for 1 h. The hexamethylcyclotrisiloxane (2.225 g, 10.0 mmol) in dry ether (30 mL) was then added over 5 min at -78 °C. The reaction was warmed to room temperature and stirred for 24 h. The solution was then cooled to 0 °C and quenched with water (30 mL). The aqueous phase was extracted with ether (3 × 10 mL) and the combined organic phases were washed with water (1 × 10 mL) and brine (3 × 30 mL). The organic layer was dried with magnesium sulfate (anhydrous) and filtered. The solvent was then evaporated *in vacuo* to give a yellow oil which was purified by distillation to afford 3.836 g (74%) of (*E*)-**1** (3.836 g, 74 %) as a colorless oil.

Data for (*E*)-**1**:

bp: 120 °C (0.9 mmHg)

^{1}H NMR: (400 MHz, $CDCl_3$)

6.18 (dt, *J* = 18.7, 6.2 Hz, HC(2), 1 H); 5.64 (dt, *J* = 18.7, 1.5 Hz, HC(1), 1 H); 2.11 (qd, *J* = 6.2, 1.5 Hz, HC(3), 2 H); 1.82 (brs, OH, 1 H); 1.40 (qn, *J* = 7.3 Hz, HC(4), 2 H); 1.29 (m, HC(5) and HC(6), 4 H); 0.88 (t, *J* = 7.1 Hz, HC(7), 3 H); 0.19 (s, HC(1'), 6 H).

^{13}C NMR: (100.6 MHz, $CDCl_3$)

149.5 (C1), 128.2 (C(2)), 36.5 (C(3)), 31.4 (C(4)), 28.1 (C(5)), 22.5 (C(6)), 14.0 (C(7)), 0.0 (C(1')).

^{29}Si NMR: (99.3 MHz, THF-d_8)

-0.30

IR: (NaCl)

3267 (s,br), 2958 (s), 2928 (s), 2874 (s), 2859 (s), 1618 (s), 1251 (s), 992 (s), 866 (s); 793 (s).

MS: (EI, 70 eV)

172 (M^+, 0.9), 157 (100), 116 (24), 95 (14), 75 (78), 61 (54).

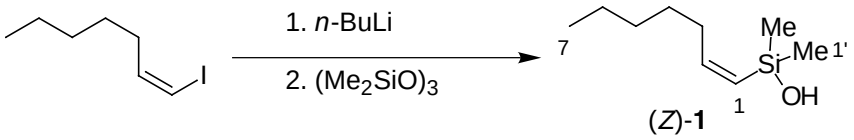
TLC: R_f: 0.12 (pentane/EtOAc=19/1)

GC: t_R (*E*)-**1** 5.67 min (100%) (HP5, 200 °C, 15 psi).

Analysis: $C_9H_{20}OSi$ (172.34)

Caculated	C, 62.72;	H, 11.70;	Si, 16.30%
Found	C, 62.64;	H, 11.68;	Si, 16.58%

Preparation of (*Z*)-Dimethyl-(1-heptenyl)silanol ((*Z*)-1) [DW-VII-30]



(*Z*)-**1**

To a solution of (*Z*)-1-iodo-1-heptene (2.241 g, 10.0 mmol) in dry ether (30 mL) under dry N_2 at -78 °C, *n*-butyllithium (6.1 mL, 10 mmol, 1.64M) was added over 10 min. The reaction mixture was stirred at -78 °C for 30 min. The hexamethylcyclotrisiloxane (742 mg, 3.3 mmol) in dry ether (10 mL) was then added over 5 min at -78 °C. The reaction was warmed to room temperature and stirred for 24 h. The solution was then cooled to 0 °C and was quenched with water (5 mL). The aqueous phase was extracted with ether (3 × 10 mL) and the combined organic phases were washed with water (1 × 10 mL) and brine (3 × 30 mL). The organic layer was dried with magnesium sulfate (anhydrous) and filtered. The filtrate was then evaporated *in vacuo* to give a yellow oil which was purified by distillation to afford 1.344 g (78%) of (*Z*)-**1** as a colorless oil. Repeated distillation provided analytically pure material.

Data for (*Z*)-**1**:

bp: 120 °C (0.9 mmHg)

^{1}H NMR: (400 MHz, $CDCl_3$)

6.36 (dt, *J* = 14.2, 7.9 Hz, HC(2), 1 H); 5.47 (dt, *J* = 14.2, 1.0 Hz, HC(1), 1 H); 2.19 (qd, *J* = 7.3, 1.2 Hz, HC(3), 2 H); 1.58 (brs, OH, 1 H); 1.39 (qn, *J* = 7.6 Hz, HC(4), 2 H); 1.30 (m, HC(5) and HC(6), 4 H); 0.89 (t, *J* = 6.8 Hz, HC(7), 3 H); 0.25 (s, HC(1'), 6 H).

^{13}C NMR: (100.6 MHz, $CDCl_3$)

151.0, 127.5, 33.6 (C(3)), 31.5 (C(4)), 29.3 (C(5)), 22.6 (C(6)), 14.0 (C(7)), 1.7 (C(1')).

IR: (NaCl)

3294 (s, br), 2962 (s), 2928 (s), 1607 (s), 1467 (m), 1377 (m), 1253 (s), 856 (s), 785 (s).

MS: (EI, 70 eV)

172 (M^+, 0.9), 157 (87), 116 (21), 95 (18), 75 (100), 61 (70).

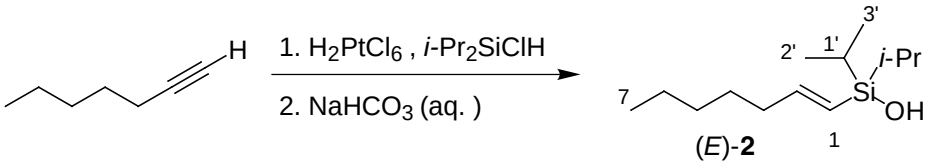
TLC: R_f: 0.12 (pentane/EtOAc=19/1)

GC: t_R (*Z*)-**1** 5.12 min (100%) (HP5, 200 °C, 15 psi).

Analysis: $C_9H_{20}OSi$ (172.34)

Caculated	C, 62.72;	H, 11.70;	Si, 16.30%
Found	C, 62.56;	H, 11.57;	Si, 16.56%

Preparation of (*E*)-Diisopropyl-(1-heptenyl)silanol ((*E*)-2) [DW-VI-60]



Hexachloroplatinic acid (26.6 mg, 65µmol, 0.005 equiv) was dissolved in 2-propanol (1 mL) and diethyl ether (30 mL) in a dry, two-neck, round-bottom flask equipped with a stir bar and a reflux condenser under an atmosphere of dry argon. Chlorodiisopropylsilane (2.155 g, 14.3 mmol, 1.1 equiv) was then added and the mixture was heated to reflux. A solution of 1-heptyne (1.250 g, 13.0 mmol) in dry ether (10 mL) was then added dropwise over 10 min, at a rate to maintain reflux of the reaction mixture. After the addition was complete, the mixture was heated in an oil bath to reflux for 4 h. After cooling to room temperature, the solvent was evaporated *in vacuo* and the residual oil was distilled (114 °C at 6 mmHg) to give the chlorosilane (2.682 g, 83.6%) as a colorless liquid.

The intermediate chlorosilane (2.731 g, 11.1 mmol) was dissolved in ether (20 mL) and saturated, aqueous sodium bicarbonate solution (10 mL) was added. The mixture was stirred at room temperature for 30 min and was then pourred into pentane (30 mL). The aqueous phase was washed with pentane (3 × 10 mL). The combined organic phases were then washed with water (3 × 10 mL) and brine (2 × 10 mL). The organic layer was dried with $MgSO_4$, filtered and the solvents evaporated *in vacuo* to give a oil which was distilled twice to give (*E*)-**2** (2.408 g, 95.3%) as a colorless oil.

Data for (*E*)-**2**:

bp: 88 °C (0.1 mmHg)

^{1}H NMR: (500 MHz, $CDCl_3$)

6.22 (dt, *J* = 18.7, 6.4 Hz, HC(2), 1 H); 5.54 (dt, *J* = 18.7, 1.7 Hz, HC(1), 1 H); 2.16 (qd, *J* = 6.9, 1.5 Hz, HC(3), 2 H); 1.50 (s, OH, 1 H); 1.43 (qn, *J* = 7.5 Hz, HC(4), 2 H); 1.31 (m, HC(5) and HC(6), 4 H); 1.03 (d, *J* = 5.4 Hz, HC(2'), 6 H); 1.01 (d, *J* = 5.4 Hz, HC(3'), 6 H); 1.00 (overlapping m, HC(1'), 2 H); 0.90 (t, *J* = 6.9 Hz, HC(7), 3 H).

^{13}C NMR: (125 MHz, $CDCl_3$)

150.8 (C(1)), 123.3 (C(2)), 36.9 (C(3)), 31.3 (C(4)), 28.3 (C(5)), 22.5 (C(6)), 17.2 (C(3')), 17.0 (C(2')), 14.0 (C(1')), 12.6 (C(7)).

IR: (NaCl)

3343 (m), 2928 (s), 2865 (s), 1618 (m), 1463 (s), 994 (s), 821 (s).

MS: (EI, 70 eV)

228 (M^+, 2), 227 (8), 219 (2), 185 (100), 157 (55), 143 (9), 101 (23), 75 (27), 61 (47).

TLC: R_f: 0.12 (pentane/EtOAc=19/1)

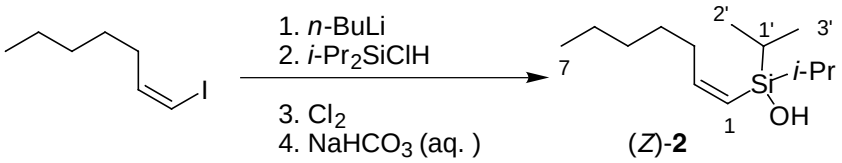
GC: t_R (*E*)-**2** 8.77 min (100%) (HP5, 200 ^oC, 15 psi).

t_R (*E*)-**2** 20.91 min (100%) (U2, 200 ^oC, 15 psi).

Analysis: $C_9H_{20}OSi$ (172.34)

Caculated	C, 68.35;	H, 12.35;	Si, 12.29%
Found	C, 68.22;	H, 12.29;	Si, 12.07%

Preparation of (*Z*)-Diisopropyl-(1-heptenyl)silanol ((*Z*)-2) [DW-VII-7]



To a solution of (*Z*)-1-iodo-1-heptene (2.017 g, 9.0 mmol) in dry ether (30 mL) under dry N_2 at -78 ^oC, was added *n*-butyllithium (5.5 mL, 9 mmol, 1.64M, 1 equiv) over 10 min. The reaction mixture was stirred at -78 ^oC for 30 min whereupon a solution of chlorodiisopropylsilane (1.359 g, 9.0 mmol) in dry ether (10 mL) was then added over 5 min at -78 ^oC.

The mixture was allowed to warm to room temperature, was stirred for 12 h, then was poured into pentane (30 mL) and water (10 mL). The aqueous phase was extracted with pentane (3 × 10 mL) and the combined organic phases were washed with brine (3 × 10 mL). The organic layer was then dried with $MgSO_4$, filtered and the solvent evaporated to give 1.803 g of the intermediate hydridosilane as an oil. The crude intermediate was dissolved in CCl_4 (20 mL) and cooled with an ice bath. A solution of chlorine in CCl_4 (9.44 mL, 0.9 M, 8.5 mmol, 1.0 equiv) was then added dropwise and the mixture was stirred for 30 min further at 0 ^oC. The solvent was then evaporated *in vacuo* and the residual oil was taken up in diethyl ether (20 mL). Saturated, aqueous sodium bicarbonate solution (10 mL) was added and the reaction was stirred at room temperature for 30 min and then pourred into pentane (30 mL). The aqueous phase was washed with pentane (3 × 10 mL). The combined organic phases were then washed with water (3 × 10 mL) and brine (2 × 10 mL). The organic layer was dried with $MgSO_4$, filtered and the solvents evaporated *in*

vacuo to give an oil which was distilled twice to afford the desired silanol (*Z*)-**2** (1.742 g, 85%) as a colorless oil.

Data for (*Z*)-**2**:

bp: 120 °C (1.0 mmHg)

^{1}H NMR: (400 MHz, $CDCl_3$)

6.47 (dt, *J* = 14.4, 7.3 Hz, HC(2), 1 H); 5.34 (dt, *J* = 14.4, 1.3 Hz, HC(1), 1 H); 2.22 (qd, *J* = 7.3, 1.3 Hz, HC(3), 2 H); 1.82 (brs, OH, 1 H); 1.40 (m, HC(4) and OH, 3 H); 1.30 (m, HC(5) and HC(6), 4 H); 1.03 (d, *J* = 5.2 Hz, HC(2'), 6 H); 1.00 (d, *J* = 5.2 Hz, HC(3'), 6 H); 1.00 (overlapping m, HC(1'), 2 H); 0.89 (t, *J* = 7.1 Hz, HC(7), 3 H).

^{13}C NMR: (100.6 MHz, $CDCl_3$)

152.4 (C(1)), 122.8 (C(2)), 34.0 (C(3)), 31.6 (C(4)), 29.4 (C(5)), 22.6 (C(6)), 17.2 (C(2')), 17.0 (C(3')), 14.0 (C(1')), 13.4 (C(7)).

IR: (NaCl)

3466 (s, br), 2953 (s), 2865 (s), 1607 (s), 1464 (s), 1380 (m), 1244 (w), 995 (m), 810 (s), 708 (s).

MS: (EI, 70 eV)

208 (M^+, 0.2), 219 (3), 185 (100), 157 (33), 143 (6), 115 (12), 101 (24), 75 (25), 61 (47).

TLC: R_f: 0.14 (*n*-hexane/EtOAc=97/3)

GC: t_R (*Z*)-**2** 8.64 min (100%) (HP5, 200 °C, 15 psi).

t_R (*Z*)-**2** 20.54 min (100%) (U2, 200 °C, 15 psi).

Analysis: $C_9H_{20}OSi$ (172.34)

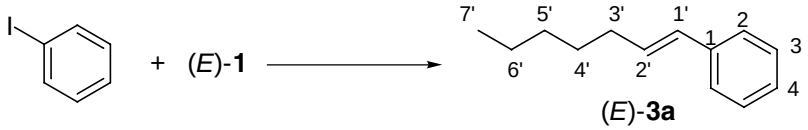
Caculated	C, 68.35;	H, 12.35;	Si, 12.29%
Found	C, 68.13;	H, 12.28;	Si, 12.20%

General Procedure: Palladium Catalyzed Cross Coupling Reaction of Alkenylsilanes with Aryl or Alkenyl halides.

Tetrabutylammonium fluoride (2.0 mmol, 2.0 equiv) was dissolved in dry THF (2 mL) at room temperature under an atmosphere of dry nitrogen. The silanol (1.0 - 1.2 mmol) was added neat and the mixture was stirred for 10 minutes at room temperature. The corresponding aryl- or alkenyl iodide (1.0 mmol) was added to the mixture, followed by the palladium catalyst (2.5 mol% or 5 mol%) and the mixture was stirred at room temperature for 10 min-5 h. The reaction mixture was then filtered through a short silica gel column (20 g). The plug was washed with diethyl ether (100 mL) and the solvent was evaporated

in vacuo. The residue was purified by column chromatography (Reverse Phase C18 or SiO_2, 25 g) to afford the corresponding product which was further purified by distillation.

Preparation of (1*E*)-1-Heptenylbenzene[6] ((*E*)-3a) [DW-VI-30]. (Table 1, entry 1)



Following the General Procedure, (*E*)-**1** (201 mg, 1.1 equiv), TBAF (631 mg, 2.0 equiv) in THF (2 mL), iodobenzene (112 µL, 1.0 mmol) and $Pd(dba)_2$ (29 mg, 0.05 equiv) was stirred at rt for 10 min, and then was filtered through SiO_2. Purification by column chromatography (RP C18, MeOH/H_2O=9/1) and Kugelrohr distillation afforded 159 mg (91%) of (*E*)-**3a** as colorless oil.

Data for (*E*)-**3a**:

bp: 100 °C (10 mmHg).

^{1}H NMR: (400 MHz, $CDCl_3$)

7.36 (d, *J* =7.7, 2 H), 7.30 (dd, *J* =7.7, 7.5, 2 H), 7.19 (t, *J* =7.5, 1 H), 6.38 (d, *J* =15.8, 1 H), 6.24 (dt, *J* =15.6, 6.8, 1 H), 2.21 (q, *J* =7.6, 2 H), 1.48 (m, 2 H), 1.34 (m, 4 H), 0.91 (t, *J* =7.3, 3 H).

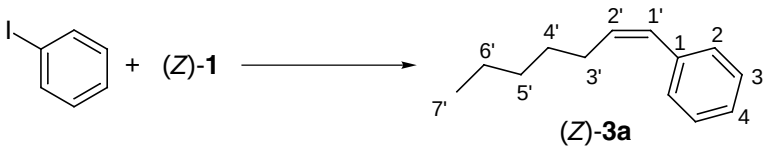
^{13}C NMR: (126 MHz, $CDCl_3$)

137.8, 131.1, 129.5, 128.3, 126.6, 125.7, 32.9, 31.3, 28.9, 22.4, 14.0.

TLC: R_f: 0.25 (MeOH/H_2O=9/1)

GC: t_R (*E*)-**3a** 8.20 min (97.8%); t_R (*Z*)-**3a** 7.37 min (2.2%) (HP5, 200 °C, 15 psi).

Preparation of (*Z*)-1-Heptenylbenzene[7] ((*Z*)-3a) [DW-VI-50]. (Table 1, entry 2)



Following the General Procedure, (*Z*)-**1** (201 mg, 1.1 equiv), TBAF (631 mg, 2.0 equiv) in THF (2 mL), iodobenzene (112 µL, 1.0 mmol) and $Pd(dba)_2$ (29 mg, 0.05 equiv) was stirred at rt for 10 min and then was filtered through SiO_2. Purification by column chromatography (RP C18, MeOH/H_2O=9/1) and Kugelrohr distillation afforded 157 mg (90%) of (*Z*)-**3a** as colorless oil.

Data for (*Z*)-**3a** :

bp: 115 ^{o}C (13 mmHg).

^{1}H NMR: (500 MHz, $CDCl_3$)

7.34 (m, 2 H), 7.29 (m, 2 H), 7.22 (tt, *J* =7.2, 1.5, 1 H), 6.41 (d, *J* =11.6, 1 H), 5.67 (dt, *J* =11.6, 7.2, 1 H), 2.34 (qd, *J* =7.5, 1.7, 2 H), 1.45 (qn, *J* =7.9, 2 H), 1.32 (m, 4 H), 0.90 (t, *J* =7.1, 3 H).

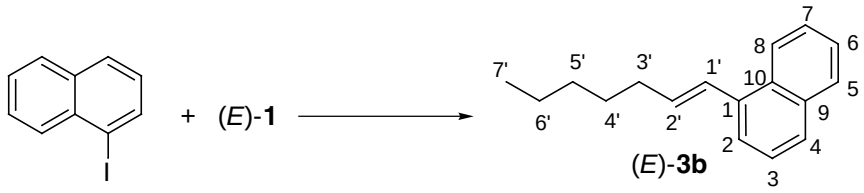
^{13}C NMR: (126 MHz, $CDCl_3$)

137.8, 133.3, 128.7, 128.6, 128.0, 126.4, 31.6, 29.7, 28.6, 22.5, 14.0.

TLC: R_f: 0.25 (MeOH/H_2O=9/1).

GC: t_R (*Z*)-**3a** 7.37 min (97.3%); t_R (*E*)-**3a** 8.20 min (2.7%) (HP5, 200 ^{o}C, 15 psi).

Preparation of (*E*)-1-(1-Heptenyl)naphthalene[8]((*E*)-3b) [DW-VI-31]. (Table 1, entry 3)



Following the General Procedure, (*E*)**-1** (201 mg, 1.1 equiv), TBAF (631 mg, 2.0 equiv) in THF (2 mL), 1-iodonaphthalene (146 μL, 1.0 mmol) and $Pd(dba)_2$ (29 mg, 0.05 equiv) was stirred at rt for 30 min, and then filtered through SiO_2. Purification by column chromatography (RP C18, MeOH/H_2O=9/1) and Kugelrohr distillation afforded 199 mg (89%) of (*E*)-**3b** as colorless oil.

Data for (*E*)-**3b**:

bp: 155 ^{o}C (0.3 mmHg)

^{1}H NMR: (500 MHz, $CDCl_3$)

8.13 (d, *J* =8.4, 1 H), 7.84 (dd, *J* =7.2, 1.7, 1 H), 7.74 (d, *J* =8.3, 1 H), 7.56 (d, *J* =7.0, 1 H), 7.50 (m, 2 H), 7.46 (dd, *J* =8.0, 7.4, 1 H), 7.12 (d, *J* =15.6, 1 H), 6.25 (dt, *J* =15.4, 7.0, 1 H), 2.34 (qd, *J* =7.5, 1.3, 2 H), 1.54 (m, 2 H), 1.39 (m, 4 H), 0.94 (t, *J* =7.0, 3 H)

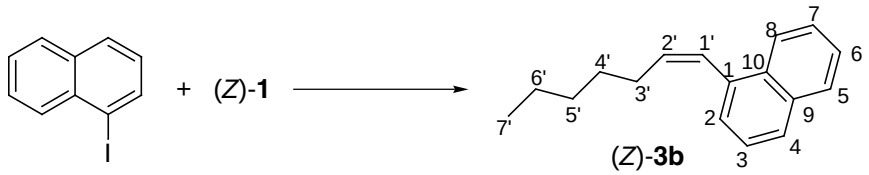
^{13}C NMR: (125 MHz, $CDCl_3$)

135.8, 134.6, 133.6, 131.1, 128.4, 127.1, 126.8, 125.7, 125.6, 125.57, 123.9, 123.4, 33.4, 31.5, 29.1, 22.6, 14.1

TLC: R_f: 0.18 (MeOH/H_2O=9/1)

GC: t_R (*E*)-**3b** 9.88 min (96.5%); t_R (*Z*)-**3b** 8.43 min (3.5%) (HP5, 260 ^{o}C, 15 psi).

Preparation of (Z)-1-(1-Heptenyl)naphthalene ((*Z*)-3b) [DW-VI-64]. (Table 1, entry 4)



Following the General Procedure, (*Z*)-**1** (201 mg, 1.1 equiv), TBAF (631 mg, 2.0 equiv) in THF (2 mL), 1-iodonaphthalene (146 µL, 1.0 mmol) and $Pd(dba)_2$ (29 mg, 0.05 equiv) was stirred at rt for 30 min, and then filtered through SiO_2. Purification by column chromatography (RP C18, MeOH/H_2O=9/1) and Kugelrohr distillation afforded 191 mg (85%) of (*Z*)-**3b** as colorless oil.

Data for (*Z*)-**3b**:

bp: 145 ^{o}C (0.5 mmHg).

^{1}H NMR: (500 MHz, $CDCl_3$)

8.02 (dd, *J* =9.8, 4.1, 1 H), 7.87 (dd, *J* =6.5, 2.4, 1 H), 7.77 (d, *J* =8.1, 1 H), 7.50 (m, 2 H), 7.46 (dd, *J* =7.7, 7.6, 1 H), 7.35 (d, *J* =7.0, 1 H), 6.88 (d, *J* =11.4, 1 H), 5.95 (dt, *J* =11.4, 7.4, 1 H), 2.16 (q, *J* =7.4, 2 H), 1.42 (pentett, *J* =7.2, 2 H), 1.25 (m, 4 H), 0.84 (t, *J* =6.6, 3 H).

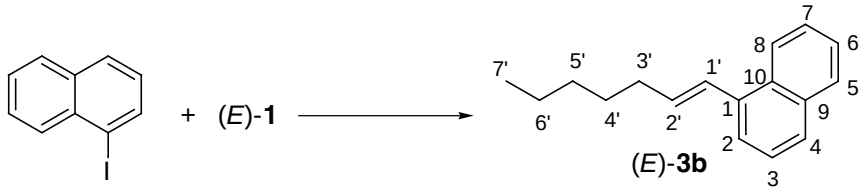
^{13}C NMR: (100.6 MHz, CDCl3)

134.9, 134.7, 133.5, 131.9, 128.3, 127.0, 126.7, 126.3, 125.7, 125.6, 125.2, 125.1, 31.4, 29.5, 28.6, 22.5, 14.0.

TLC: R_f: 0.18 (MeOH/H_2O=9/1)

GC: t_R (*Z*)-**3b** 8.43 min (96.7%); t_R (*E*)-**3b** 9.88 min (3.3%) (HP5, 260 ^{o}C, 15 psi).

Preparation of (*E*)-1-(1-Heptenyl)naphthalene[8]((*E*)-3b) methanolic with Tetrabutylammonium hydroxide [DW-VI-84]. (Table 1, entry 5)



Following the General Procedure, (*E*)-**1** (201 mg, 1.1 equiv), TBAOH (1.00 mL, 2.0 mmol, 2M in MeOH) in THF (1.0 mL), 1-iodonaphthalene (146 μL, 1.0 mmol) and $Pd(dba)_2$ (29 mg, 0.05 equiv) was stirred at rt for 30 min, and then filtered through SiO_2. Purification by column chromatography (RP C18, MeOH/H_2O=9/1) and Kugelrohr distillation afforded 170 mg (76%) of (*E*)-**3b** as colorless oil.

Data for (*E*)-**3b**:

bp: 155 at 0.3 mmHg

^{1}H NMR: (500 MHz, $CDCl_3$)

8.13 (d, *J* =8.4, 1 H), 7.84 (dd, *J* =7.2, 1.7, 1 H), 7.74 (d, *J* =8.3, 1 H), 7.56 (d, *J* =7.0, 1 H), 7.50 (m, 2 H), 7.46 (dd, *J* =8.0, 7.4, 1 H), 7.12 (d, *J* =15.6, 1 H), 6.25 (dt, *J* =15.4, 7.0, 1 H), 2.34 (qd, *J* =7.5, 1.3, 2 H), 1.54 (m, 2 H), 1.39 (m, 4 H), 0.94 (t, *J* =7.0, 3 H)

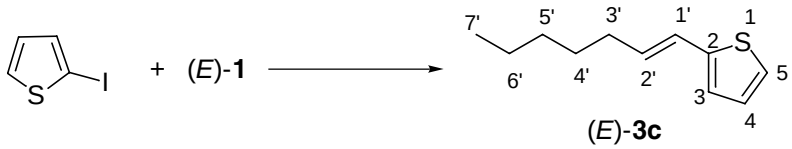
^{13}C NMR: (125 MHz, $CDCl_3$)

135.8, 134.6, 133.6, 131.1, 128.4, 127.1, 126.8, 125.7, 125.6, 125.57, 123.9, 123.4, 33.4, 31.5, 29.1, 22.6, 14.1

TLC: R_f: 0.18 (MeOH/H_2O=9/1)

GC: t_R (*E*)-**3b** 9.88 min (94.2%); t_R (*Z*)-**3b** 8.43 min (3.3%); t_R cine 7.96 min (2.5%)(HP5, 260 ^{o}C, 15 psi).

Preparation of (*E*)-2-(1-Heptenyl)thiophene ((*E*)-3c) [DW-VI-32]. (Table 1, entry 6)



Following the General procedure, (*E*)-**1** (201 mg, 1.2 equiv), TBAF (631 mg, 2.0 equiv) in THF (2 mL), 1-iodothiophene (111 μL, 1.0 mmol) and $Pd(dba)_2$ (29 mg, 0.05 equiv) was stirred at rt for 3 h, and

then filtered through SiO_2. Purification by column chromatography (RP C18, MeOH/H_2O=9/1) and Kugelrohr distillation afforded 150 mg (83%) of (*E*)-**3c** as colorless oil.

Data for (*E*)-**3c**:

bp: 110 ^oC (10 mmHg).

^{1}H NMR: (500 MHz, $CDCl_3$)

7.08 (d, *J* =5.1, C(5)*H*, 1 H), 6.93 (dd, *J* =5.1, 3.5, C(4)*H*, 1 H), 6.86 (d, *J* =3.3, C(3)*H*, 1 H), 6.51 (dd, *J* =15.6, 0.6, C(1')*H*, 1 H), 6.08 (dt, *J* =15.6, 7.0, C(2')*H*, 1 H), 2.17 (qd, *J* =7.2, 1.5, C(3')H_2, 2 H), 1.46 (qn, *J* =7.3, C(4')H_2, 2 H), 1.33 (m, C(5',6')H_2, 4 H), 0.91 (t, *J* =6.8, C(7')*H*, 3 H).

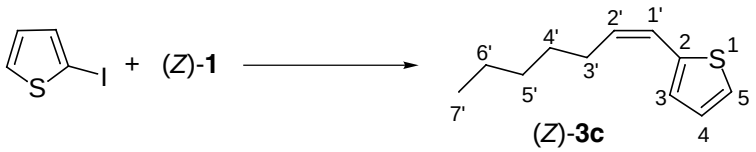
^{13}C NMR: (126 MHz, $CDCl_3$)

143.2 (C(2)), 131.3 (C(1')), 127.2 (C(2')), 124.1, 122.93, 122.92, 32.8 (C(3')), 31.4 (C(4')), 28.9 (C(5')), 22.5 (C(6')), 14.0 (C(7')).

TLC: R_f: 0.32 (MeOH/H_2O=9/1).

GC: t_R (*E*)-**3c** 6.51 min (95.7%); t_R (*Z*)-**3c** 5.81 min (4.3%) (HP5, 200 ^oC, 15 psi).

Preparation of (*Z*)-1-(1-Heptenyl)thiophene ((*Z*)-3c) [DW-VI-65]. (Table 1, entry 7)



Following the General procedure, (*Z*)-**1** (201 mg, 1.2 equiv), TBAF (631 mg, 2.0 equiv) in THF (2 mL), 1-iodothiophene (111 μL, 1.0 mmol) and $Pd(dba)_2$ (29 mg, 0.05 equiv) was stirred at rt for 3 h, and then filtered through SiO_2. Purification by column chromatography (RP C18, MeOH/H_2O=9/1) and Kugelrohr distillation afforded 146 mg (81%) of (*Z*)-**3c** as colorless oil.

Data for (*Z*)-**3c**:

bp: 90 ^oC (11 mmHg).

^{1}H NMR: (500 MHz, $CDCl_3$)

7.24 (d, *J* =5.0, 1 H), 7.00 (dd, *J* =5.0, 3.5, 1 H), 6.97 (d, *J* =3.5, 1 H), 6.53 (dt, *J* =11.4, 1.8, 1 H), 5.59 (dt, *J* =11.4, 1.8, 1 H), 2.41 (qd, *J* =7.6, 1.8, 2 H), 1.51 (qn, *J* =7.4, 2 H), 1.36 (m, 4 H), 0.91 (t, *J* =7.4, 3 H).

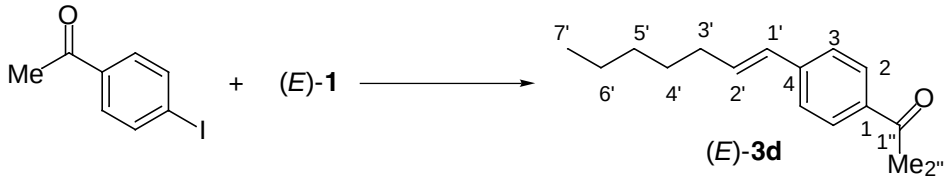
^{13}C NMR: (100 MHz, $CDCl_3$)

141.1, 131.6, 127.3, 127.0, 125.2, 121.9, 31.9, 29.6, 29.5, 22.9, 14.4.

TLC: R_f: 0.32 (MeOH/H_2O=9/1).

GC: t_R (*Z*)-**3c** 5.81 min (97.5%); t_R (*E*)-**3c** 6.46 min (2.5%) (HP5, 200 ^{o}C, 15 psi).

Preparation of (*E*)-4-(1-Heptenyl)acetophenone ((*E*)-3d) [DW-VI-28]. (Table 1, entry 8)



Following the General Procedure, (*E*)-**1** (201 mg, 1.1 equiv), TBAF (631 mg, 2.0 equiv) in THF (2 mL), 4'-iodoacetophenone (246 mg, 1.0 mmol) and $Pd(dba)_2$ (29 mg, 0.05 equiv) was stirred at rt for 10 min and then was filtered through SiO_2. Purification by column chromatography (RP C18, MeOH/H_2O=9/1) and Kugelrohr distillation afforded 201 mg (93%) of (*E*)-**3d** as colorless oil.

Data for (*E*)-**3d**:

bp: 110 ^{o}C (1.2 mmHg).

^{1}H NMR: (400 MHz, $CDCl_3$)

7.89 (d, *J* =8.4, 2 H), 7.41 (d, *J* =8.3, 2 H), 6.39 (m, 2 H), 2.58 (s, 3 H), 2.24 (qd, *J* =7.4, 1.6, 2 H), 1.49 (qn, *J* =7.2, 2 H), 1.33 (m, 4 H), 0.91 (t, *J* =7.0, 3 H).

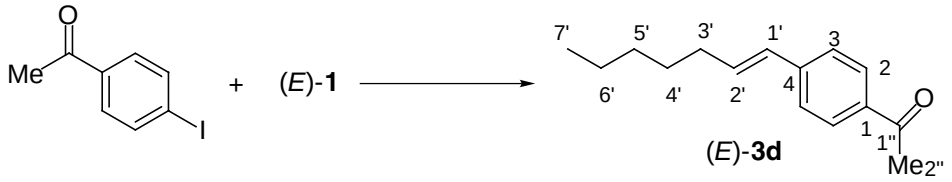
^{13}C NMR: (100.6 MHz, $CDCl_3$)

197.6, 142.7, 135.4, 134.6, 128.9, 128.7, 125.9, 33.2, 31.4, 28.8, 26.5, 22.5, 14.0.

TLC: R_f: 0.39 (MeOH/H_2O=9/1)

GC: t_R (*E*)-**3d** 9.54 min (96.5%); t_R (*Z*)-**3d** 8.44 min (3.5%) (HP5, 250 ^{o}C, 15 psi).

Preparation of (*E*)-4-(1-Heptenyl)acetophenone ((*E*)-3d) with 1 equivalent of TBAF [DW-VII-35]. (Table 1, entry 9)



Following the General Procedure, (*E*)-**1** (201 mg, 1.1 equiv), TBAF (1.00 mL, 1M in THF, 1.0 equiv) in THF (2 mL), 4'-iodoacetophenone (246 mg, 1.0 mmol) and $Pd(dba)_2$ (29 mg, 0.05 equiv) was

stirred at rt for 60 min and then was filtered through SiO_2. Purification by column chromatography (RP C18, MeOH/H_2O=9/1) and Kugelrohr distillation afforded 188 mg (87%) of (*E*)-**3d** as colorless oil.

Data for (*E*)-**3d**:

bp: 110 °C (1.2 mmHg).

^{1}H NMR: (400 MHz, $CDCl_3$)

7.89 (d, *J* =8.4, 2 H), 7.41 (d, *J* =8.3, 2 H), 6.39 (m, 2 H), 2.58 (s, 3 H), 2.24 (qd, *J* =7.4, 1.6, 2 H), 1.49 (qn, *J* =7.2, 2 H), 1.33 (m, 4 H), 0.91 (t, *J* =7.0, 3 H).

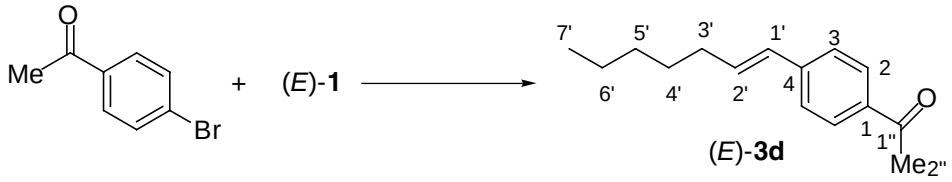
^{13}C NMR: (100.6 MHz, $CDCl_3$)

197.6, 142.7, 135.4, 134.6, 128.9, 128.7, 125.9, 33.2, 31.4, 28.8, 26.5, 22.5, 14.0.

TLC: R_f: 0.39 (MeOH/H_2O=9/1)

GC: t_R (*E*)-**3d** 9.54 min (95.5%); t_R (*Z*)-**3d** 8.44 min (4.5%) (HP5, 250 °C, 15 psi).

Preparation of (*E*)-4-(1-Heptenyl)acetophenone ((*E*)-3d) from 4-Bromoacetophenone [DW-VI-89]. (Table 1, entry 10)



Following the General Procedure, (*E*)-**1** (219 mg, 1.2 equiv), TBAF (631 mg, 2.0 equiv) in THF (2 mL), 4'-bromoacetophenone (199 mg, 1.0 mmol) and $[allylPdCl]_2$ (9.1 mg, 0.025 equiv) was stirred at rt for 120 min. An additional equivalent of TBAF (315 mg) and 1.25 mol% of $[allylPdCl]_2$ (4.5 mg, 0.013 equiv) was added and the reaction was stirred for one more hour. Filtration through SiO_2, followed by purification by column chromatography (RP C18, MeOH/H_2O=9/1) and Kugelrohr distillation afforded 160 mg (74%) of (*E*)-**3d** as colorless oil.

Data for (*E*)-**3d**:

bp: 110 °C (1.2 mmHg).

^{1}H NMR: (400 MHz, $CDCl_3$)

7.89 (d, *J* =8.4, 2 H), 7.41 (d, *J* =8.3, 2 H), 6.39 (m, 2 H), 2.58 (s, 3 H), 2.24 (qd, *J* =7.4, 1.6, 2 H), 1.49 (qn, *J* =7.2, 2 H), 1.33 (m, 4 H), 0.91 (t, *J* =7.0, 3 H).

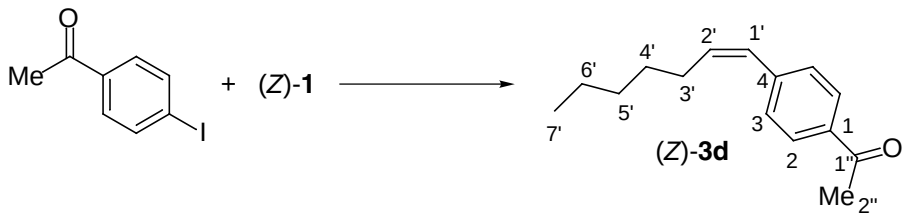
^{13}C NMR: (100.6 MHz, $CDCl_3$)

197.6, 142.7, 135.4, 134.6, 128.9, 128.7, 125.9, 33.2, 31.4, 28.8, 26.5, 22.5, 14.0.

TLC: R_f: 0.39 (MeOH/H_2O=9/1)

GC: t_R (*E*)-**3d** 9.54 min (96.9%); t_R (*Z*)-**3d** 8.44 min (3.1%) (HP5, 250 ^oC, 15 psi).

Preparation of (*Z*)-4-(1-Heptenyl)acetophenone ((*Z*)-3d) [DW-VI-48]. (Table 1, entry 11)



Following the General Procedure, (*Z*)-**1** (201 mg, 1.1 equiv), TBAF (631 mg, 2.0 equiv) in THF (2 mL), 4'-iodoacetophenone (246 mg, 1.0 mmol) and $Pd(dba)_2$ (29 mg, 0.05 equiv) was stirred at rt for 10 min and then was filtered through SiO_2. Purification by column chromatography (RP C18, MeOH/H_2O=9/1) and Kugelrohr distillation afforded 199 mg (92%) of (*Z*)-**3d** as colorless oil.

Data for (*Z*)-**3d**:

bp: 100 (1.2 mmHg).

^{1}H NMR: (400 MHz, $CDCl_3$)

7.92 (d, *J* =8.3, 2 H), 7.36 (d, *J* =8.5, 2 H), 6.43 (d, *J* =11.7, 1 H), 5.79 (dt, *J* =11.7, 7.3, 1 H), 2.60 (s, 3 H), 2.31 (q, *J* =7.3, 2 H), 1.46 (m, 2 H), 1.30 (m, 4 H), 0.88 (t, *J* =6.5, 3 H).

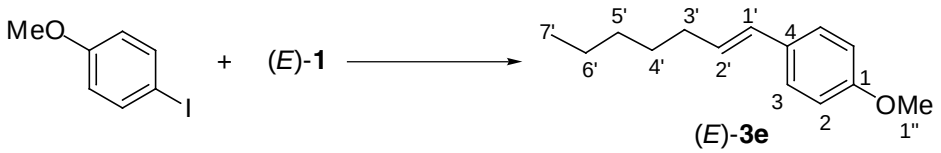
^{13}C NMR: (100.6 MHz, $CDCl_3$)

197.6, 142.7, 135.7, 135.0, 128.8, 128.3, 127.8, 31.5, 29.5, 28.8, 26.6, 22.5, 14.0.

TLC: R_f: 0.39 (H_2O/MeOH=1/9)

GC: t_R (*Z*)-**3d** 8.44 min (95.2%); t_R (*E*)-**3d** 9.54 min (4.8%) (HP5, 250 ^oC, 15 psi).

Preparation of (*E*)-1-(1-Heptenyl)-4-methoxybenzene ((*E*)-3e) [DW-VI-29]. (Table 1, entry 12)



Following the General Procedure, (*E*)-**1** (201 mg, 1.1 equiv), TBAF (631 mg, 2.0 equiv) in THF (2 mL), 4-iodoanisole (234 mg, 1.0 mmol) and $Pd(dba)_2$ (29 mg, 0.05 equiv) was stirred at rt for 10 min and then was filtered through SiO_2. Purification by column chromatography (RP C18, MeOH/H_2O=9/1) and Kugelrohr distillation afforded 194 mg (95%) of (*E*)-**3e** as colorless oil.

Data for (*E*)-**3e**:

bp: 90 °C (1.2 mmHg).

^{1}H NMR: (500 MHz, $CDCl_3$)

7.28 (d, *J* =8.8, 2 H), 6.83 (d, *J* =8.6, 2 H), 6.32 (d, *J* =15.8, 1 H), 6.09 (dt, *J* =15.8, 7.0, 1 H), 3.80 (s, 3 H), 2.18 (qd, *J* =7.3, 1.5, 2 H), 1.46 (qn, *J* =7.3, 2 H), 1.33 (m, 4 H), 0.90 (t, *J* =7.2, 3 H).

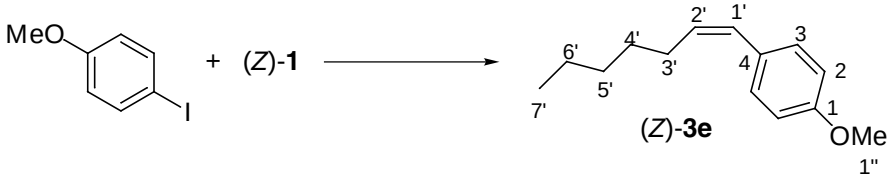
^{13}C NMR: (126 MHz, $CDCl_3$)

158.5, 130.8, 129.1, 128.9, 126.9, 113.9, 55.3, 33.0, 31.4, 29.2, 22.6, 14.1.

TLC: R_f: 0.28 (MeOH/H_2O=9/1)

GC: t_R (*E*)-**3e** 7.54 min (97.2%); t_R (*Z*)-**3a** 6.97 min (2.8%) (HP5, 250 °C, 15 psi).

Preparation of (*Z*)-1-(1-Heptenyl)-4-methoxybenzene ((*Z*)-3e) [DW-VI-49]. (Table 1, entry 13)



Following the General Procedure, (*Z*)-**1** (201 mg, 1.1 equiv), TBAF (631 mg, 2.0 equiv) in THF (2 mL), 4-iodoanisole (234 mg, 1.0 mmol) and $Pd(dba)_2$ (29 mg, 0.05 equiv) was stirred at rt for 10 min and then filtered through SiO_2. Purification by column chromatography (RP C18, MeOH/H_2O=9/1) and Kugelrohr distillation afforded 192 mg (94%) of (*Z*)-**3e** as colorless oil.

Data for **(*Z*)-3e**:

bp: 80- 85 °C (1.3 mmHg).

^{1}H NMR: (400 MHz, $CDCl_3$)

7.23 (d, *J* =8.4, 2 H), 6.87 (d, *J* =8.6, 2 H), 6.34 (dt, *J* =11.6, 1.7, 1 H), 5.57 (dt, *J* =11.6, 7.2, 1 H), 3.82 (s, 3 H), 2.32 (qd, *J* =7.7, 1.7, 2 H), 1.45 (qn, *J* =7.2, 2 H), 1.31 (m, 4 H), 0.89 (t, *J* =7.2, 3 H).

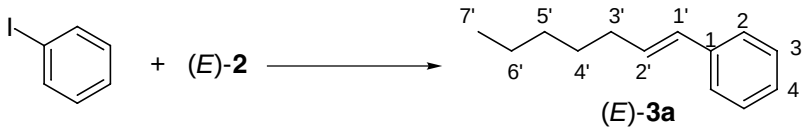
^{13}C NMR: (126 MHz, CDCl3)

158.1, 131.7, 130.5, 129.9, 128.0, 113.5, 55.2, 31.6, 29.7, 28.6, 22.6, 14.1.

TLC: R_f : 0.18 ($MeOH/H_2O$=9/1)

GC: t_R (*Z*)-**3a** 6.97 min (97.4%); t_R (*E*)-**3e** 7.54 min (2.6%) (HP5, 250 °C, 15 psi).

Preparation of (1*E*)-1-Heptenylbenzene[6] ((*E*)-3a) with di(iso-propyl)heptenylsilanol (*E*)-2 [DW-VII-8]. (Table 2, entry 1)



Following the General Procedure, (*E*)-**2** (251 mg, 1.1 equiv), TBAF (631 mg, 2.0 equiv) in THF (2 mL), iodobenzene (112 µL, 1.0 mmol) and $Pd(dba)_2$ (29 mg, 0.05 equiv) was stirred at rt for 10 min, and then was filtered through SiO_2. Purification by column chromatography (RP C18, $MeOH/H_2O$=9/1) and Kugelrohr distillation afforded 143 mg (82%) of (*E*)-**3a** as colorless oil.

Data for (*E*)-**3a**:

bp: 100 °C (10 mmHg).

^{1}H NMR: (400 MHz, $CDCl_3$)

7.36 (d, *J* =7.7, 2 H), 7.30 (dd, *J* =7.7, 7.5, 2 H), 7.19 (t, *J* =7.5, 1 H), 6.38 (d, *J* =15.8, 1 H), 6.24 (dt, *J* =15.6, 6.8, 1 H), 2.21 (q, *J* =7.6, 2 H), 1.48 (m, 2 H), 1.34 (m, 4 H), 0.91 (t, *J* =7.3, 3 H).

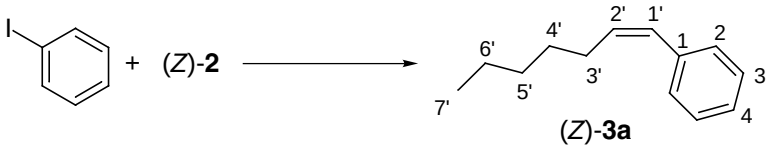
^{13}C NMR: (126 MHz, $CDCl_3$)

137.8, 131.1, 129.5, 128.3, 126.6, 125.7, 32.9, 31.3, 28.9, 22.4, 14.0.

TLC: R_f: 0.25 ($MeOH/H_2O$=9/1)

GC: t_R (*E*)-**3a** 8.26 min (99.2%); t_R (*Z*)-**3a** 7.42 min (0.8%) (HP5, 200 °C, 15 psi).

Preparation of (*Z*)-1-Heptenylbenzene[7] ((*Z*)-3a) with di(iso-propyl)heptenylsilanol (*Z*)-2 [DW-VII-10]. (Table 2, entry 2)



Following the General Procedure, (*Z*)-**1** (251 mg, 1.1 equiv), TBAF (631 mg, 2.0 equiv) in THF (2 mL), iodobenzene (112 µL, 1.0 mmol) and $Pd(dba)_2$ (29 mg, 0.05 equiv) was stirred at rt for 10 min and then was filtered through SiO_2. Purification by column chromatography (RP C18, MeOH/H_2O=9/1) and Kugelrohr distillation afforded 141 mg (81%) of (*Z*)-**3a** as colorless oil.

Data for (*Z*)-**3a** :

bp: 115 (13 mmHg).

^{1}H NMR: (500 MHz, $CDCl_3$)

7.34 (m, 2 H), 7.29 (m, 2 H), 7.22 (tt, *J* =7.2, 1.5, 1 H), 6.41 (d, *J* =11.6, 1 H), 5.67 (dt, *J* =11.6, 7.2, 1 H), 2.34 (qd, *J* =7.5, 1.7, 2 H), 1.45 (qn, *J* =7.9, 2 H), 1.32 (m, 4 H), 0.90 (t, *J* =7.1, 3 H).

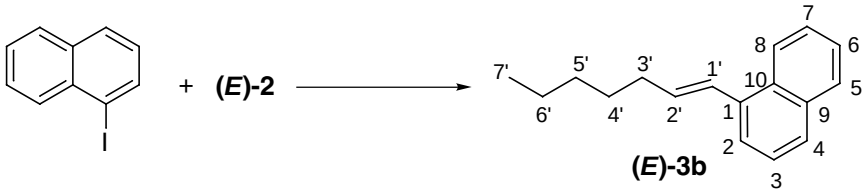
^{13}C NMR: (126 MHz, $CDCl_3$)

137.8, 133.3, 128.7, 128.6, 128.0, 126.4, 31.6, 29.7, 28.6, 22.5, 14.0.

TLC: R_f: 0.25 (MeOH/H_2O=9/1).

GC: t_R (*Z*)-**3a** 7.42 min (99.4%); t_R (*E*)-**3a** 8.26 min (0.6%) (HP5, 200 ^{o}C, 15 psi).

Preparation of (*E*)-1-(1-Heptenyl)naphthalene[8] ((*E*)-3b) with di(iso-propyl)heptenylsilanol (*E*)-2 [DW-VI-43]. (Table 2, entry 3)



Following the General Procedure, (*E*)-**2** (251 mg, 1.1 equiv), TBAF (631 mg, 2.0 equiv) in THF (2 mL), 1-iodonaphthalene (146 µL, 1.0 mmol) and $Pd(dba)_2$ (29 mg, 0.05 equiv) was stirred at rt for 30 min, and then filtered through SiO_2. Purification by column chromatography (RP C18, H_2O/ MeOH=1/9) and Kugelrohr distillation afforded 191 mg (85%) of (*E*)-**3b** as colorless oil.

Data for (*E*)-**3b**:

bp: 155 (0.3 mmHg).

^{1}H NMR: (500 MHz, $CDCl_3$)

8.13 (d, *J* =8.4, 1 H), 7.84 (dd, *J* =7.2, 1.7, 1 H), 7.74 (d, *J* =8.3, 1 H), 7.56 (d, *J* =7.0, 1 H), 7.50 (m, 2 H), 7.46 (dd, *J* =8.0, 7.4, 1 H), 7.12 (d, *J* =15.6, 1 H), 6.25 (dt, *J* =15.4, 7.0, 1 H), 2.34 (qd, *J* =7.5, 1.3, 2 H), 1.54 (m, 2 H), 1.39 (m, 4 H), 0.94 (t, *J* =7.0, 3 H)

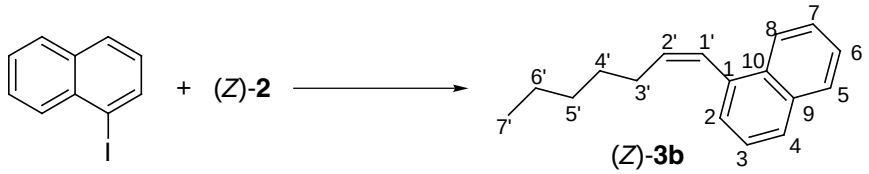
^{13}C NMR: (125 MHz, $CDCl_3$)

135.8, 134.6, 133.6, 131.1, 128.4, 127.1, 126.8, 125.7, 125.6, 125.57, 123.9, 123.4, 33.4, 31.5, 29.1, 22.6, 14.1

TLC: R_f: 0.18 (H_2O/MeOH=1/9)

GC: t_R (*E*)-**3b** 9.88 min (98.4%); t_R (*Z*)-**3b** 8.43 min (1.6%) (HP5, 260 ^oC, 15 psi).

Preparation of (Z)-1-(1-Heptenyl)naphthalene ((*Z*)-3b) with di(iso-propyl)heptenylsilanol (*Z*)-2 [DW-VII-11]. (Table 2, entry 4)



Following the General Procedure, (*Z*)-**1** (251 mg, 1.1 equiv), TBAF (631 mg, 2.0 equiv) in THF (2 mL), 1-iodonaphthalene (146 μL, 1.0 mmol) and $Pd(dba)_2$ (29 mg, 0.05 equiv) was stirred at rt for 30 min, and then filtered through SiO_2. Purification by column chromatography (RP C18, MeOH/H_2O=9/1) and Kugelrohr distillation afforded 178 mg (79%) of (*Z*)-**3b** as colorless oil.

Data for (*Z*)-**3b**:

bp: 145 ^oC (0.5 mmHg).

^{1}H NMR: (500 MHz, $CDCl_3$)

8.02 (dd, *J* =9.8, 4.1, 1 H), 7.87 (dd, *J* =6.5, 2.4, 1 H), 7.77 (d, *J* =8.1, 1 H), 7.50 (m, 2 H), 7.46 (dd, *J* =7.7, 7.6, 1 H), 7.35 (d, *J* =7.0, 1 H), 6.88 (d, *J* =11.4, 1 H), 5.95 (dt, *J* =11.4, 7.4, 1 H), 2.16 (q, *J* =7.4, 2 H), 1.42 (pentett, *J* =7.2, 2 H), 1.25 (m, 4 H), 0.84 (t, *J* =6.6, 3 H).

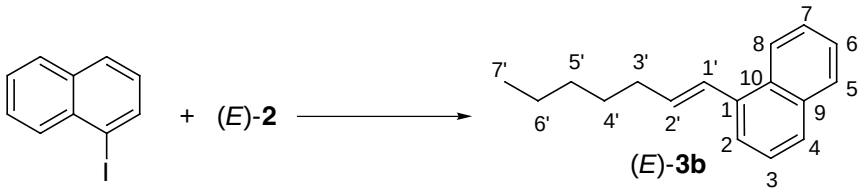
^{13}C NMR: (100.6 MHz, CDCl3)

134.9, 134.7, 133.5, 131.9, 128.3, 127.0, 126.7, 126.3, 125.7, 125.6, 125.2, 125.1, 31.4, 29.5, 28.6, 22.5, 14.0.

TLC: R_f: 0.18 (MeOH/H_2O=9/1)

GC: t_R (*Z*)-**3b** 8.43 min (97.7%); t_R (*E*)-**3b** 9.88 min (2.3%) (HP5, 260 ^oC, 15 psi).

Preparation of (*E*)-1-(1-Heptenyl)naphthalene[8] ((*E*)-3b) with di(iso-propyl)heptenylsilanol (*E*)-2 and with methanolic Tetrabutylammonium hydroxide [DW-VII-18]. (Table 2, entry 5)



Following the General Procedure, (*E*)-**2** (251 mg, 1.1 equiv), TBAOH (1.00 mL, 2.0 mmol, 2M in MeOH) in THF (1.0 mL), 1-iodonaphthalene (146 μL, 1.0 mmol) and $Pd(dba)_2$ (29 mg, 0.05 equiv) was stirred at rt for 30 min, and then filtered through SiO_2. Purification by column chromatography (RP C18, MeOH/H_2O=9/1) and Kugelrohr distillation afforded 174 mg (78%) of (*E*)-**3b** as colorless oil.

Data for (*E*)-**3b**:

bp: 155 (0.3 mmHg).

^{1}H NMR: (500 MHz, $CDCl_3$)

8.13 (d, *J* =8.4, 1 H), 7.84 (dd, *J* =7.2, 1.7, 1 H), 7.74 (d, *J* =8.3, 1 H), 7.56 (d, *J* =7.0, 1 H), 7.50 (m, 2 H), 7.46 (dd, *J* =8.0, 7.4, 1 H), 7.12 (d, *J* =15.6, 1 H), 6.25 (dt, *J* =15.4, 7.0, 1 H), 2.34 (qd, *J* =7.5, 1.3, 2 H), 1.54 (m, 2 H), 1.39 (m, 4 H), 0.94 (t, *J* =7.0, 3 H)

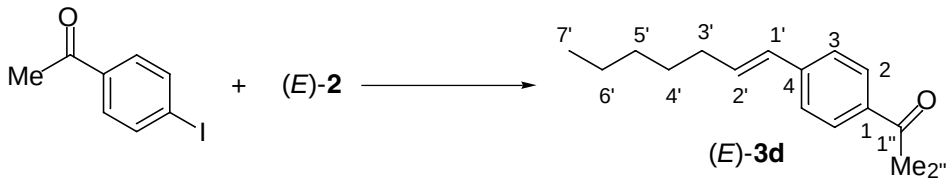
^{13}C NMR: (125 MHz, $CDCl_3$)

135.8, 134.6, 133.6, 131.1, 128.4, 127.1, 126.8, 125.7, 125.6, 125.57, 123.9, 123.4, 33.4, 31.5, 29.1, 22.6, 14.1

TLC: R_f: 0.18 (MeOH/H_2O=9/1)

GC: t_R (*E*)-**3b** 9.88 min (99.2%); t_R (*Z*)-**3b** 8.43 min (0.8%) (HP5, 260 ^{o}C, 15 psi).

Preparation of (*E*)-4-(1-Heptenyl)acetophenone ((*E*)-3d) with di(iso-propyl)heptenylsilanol (*E*)-2 [DW-VI-95]. (Table 2, entry 6)



Following the General Procedure, (*E*)-**1** (251 mg, 1.1 equiv), TBAF (631 mg, 2.0 equiv) in THF (2 mL), 4'-iodoacetophenone (246 mg, 1.0 mmol) and $Pd(dba)_2$ (29 mg, 0.05 equiv) was stirred at rt for 10 min and then was filtered through SiO_2. Purification by column chromatography (RP C18, MeOH/H_2O=9/1) and Kugelrohr distillation afforded 173 mg (80%) of (*E*)-**3d** as colorless oil.

Data for (*E*)-**3d**:

bp: 110 °C (1.2 mmHg).

^{1}H NMR: (400 MHz, $CDCl_3$)

7.89 (d, *J* =8.4, 2 H), 7.41 (d, *J* =8.3, 2 H), 6.39 (m, 2 H), 2.58 (s, 3 H), 2.24 (qd, *J* =7.4, 1.6, 2 H), 1.49 (qn, *J* =7.2, 2 H), 1.33 (m, 4 H), 0.91 (t, *J* =7.0, 3 H).

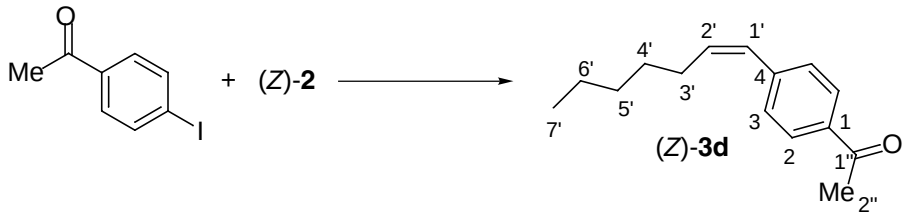
^{13}C NMR: (100.6 MHz, $CDCl_3$)

197.6, 142.7, 135.4, 134.6, 128.9, 128.7, 125.9, 33.2, 31.4, 28.8, 26.5, 22.5, 14.0.

TLC: R_f: 0.39 (MeOH/H_2O=9/1)

GC: t_R (*Z*)-**3d** 8.44 min (100%); t_R (*E*)-**3d** 9.54 min (not detected) (HP5, 250 °C, 15 psi).

Preparation of (*Z*)-4-(1-Heptenyl)acetophenone ((*Z*)-3d) with di(iso-propyl)heptenylsilanol (*E*)-2 [DW-VII-9]. (Table 2, entry 7)



Following the General Procedure, (*Z*)-**1** (251 mg, 1.1 equiv), TBAF (631 mg, 2.0 equiv) in THF (2 mL), 4'-iodoacetophenone (246 mg, 1.0 mmol) and $Pd(dba)_2$ (29 mg, 0.05 equiv) was stirred at rt for 10 min and then was filtered through SiO_2. Purification by column chromatography (RP C18, MeOH/H_2O=9/1) and Kugelrohr distillation afforded 186 mg (86%) of (*Z*)-**3d** as colorless oil.

Data for (*Z*)-**3d**:

bp: 100 ^{o}C (1.2 mmHg).

^{1}H NMR: (400 MHz, $CDCl_3$)

7.92 (d, *J* =8.3, 2 H), 7.36 (d, *J* =8.5, 2 H), 6.43 (d, *J* =11.7, 1 H), 5.79 (dt, *J* =11.7, 7.3, 1 H), 2.60 (s, 3 H), 2.31 (q, *J* =7.3, 2 H), 1.46 (m, 2 H), 1.30 (m, 4 H), 0.88 (t, *J* =6.5, 3 H).

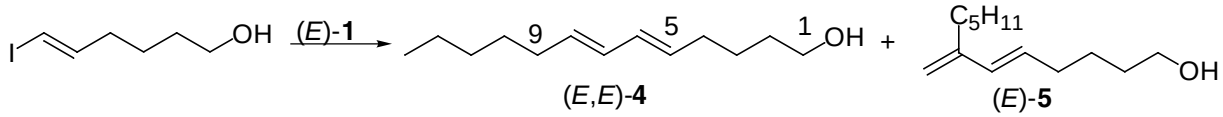
^{13}C NMR: (100.6 MHz, $CDCl_3$)

197.6, 142.7, 135.7, 135.0, 128.8, 128.3, 127.8, 31.5, 29.5, 28.8, 26.6, 22.5, 14.0.

TLC: R_f: 0.39 (H_2O/MeOH=1/9)

GC: t_R (*E*)-**3d** 9.54 min (99.0%); t_R (*Z*)-**3d** 8.44 min (1.0%) (HP5, 250 ^{o}C, 15 psi).

Preparation of (*E*,*E*)-5,7-Tridecadien-1-ol ((*E*, *E*)-4) [DW-VI-73]. (Table 3, entry 1)



Following the General Procedure, (*E*)-**1** (201 mg, 1.1 equiv), TBAF (631 mg, 2.0 equiv) in THF (2 mL), (*E*)-6-iodo-5-hexen-1-ol (226 mg, 1.0 mmol) and $Pd(dba)_2$ (29 mg, 0.05 equiv) was stirred at rt for 1.5 h and then was filtered through SiO_2. Purification by column chromatography (SiO_2, *n*-hexane/EtOAc=4/1) and Kugelrohr distillation afforded 178 mg (91%) of a mixture of (*E*, *E*)-**4** and (*E*)-7-pentyl-5,7-octadien-1-ol ((*E*)-**5**) as colorless oil.

Data for (*E*, *E*)-**4**:

bp: 80-85 ^{o}C (1.3 mmHg).

^{1}H NMR: (500 MHz, $CDCl_3$)

6.04 (m, C(6, 7)*H*, 2 H), 5.56 (m, C(5, 8)*H*, 2 H), 4.97 and 4.84 (2s, $H_2C{=}CR_1R_2$ ((*E*)-**5**), 3.63 (t, *J* =6.6, C(1)H2, 2 H), 2.06 (m, C(4, 9)*H*, 2 H), 1.57 (m, C(2)H_2, 2 H), 1.45 (m, C(3)H_2, 2 H), 1.37 (m, C(10)H_2, 2 H), 1.28 (m, C(11, 12)H_2, 4 H), 0.88 (t, *J* =7.1, C(13)H_3, 3 H).

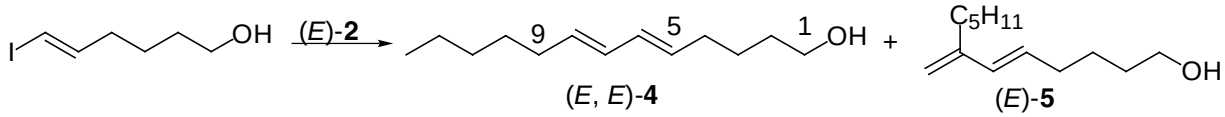
^{13}C NMR: (126 MHz, $CDCl_3$)

132.80 (C(5)), 131.64 (C(8)), 130.78 (C(6)), 130.14 (C(7)), 62.81 (C(1)), 32.53 (C(4)), 32.22 and 32.19 (C2 and C9), 31.39 (C(11)), 29.04 (C(10)), 25.45 (C(3)), 22.50 (C(12)), 14.00 (C(13)).

TLC: R_f: 0.25 (*n*-hexane/EtOAc=4/1).

GC: t_R (*E,E*)-**4** 6.83 min (82.5%); t_R (*Z,E*)-**4** and (*E,Z*)-**4** 6.69 min (4.2%); t_R (*E*)-**5**, 6.43 min) (13.3%) (HP5, 200 ^{o}C, 15 psi).

Preparation of (*E*,*E*)-5,7-Tridecadien-1-ol ((*E*, *E*)-4c) with di(iso-propyl)heptenylsilanol (*E*)-2 [DW-VII-14]. (Table 3, entry 2)



Following the General Procedure, (*E*)-**2** (251 mg, 1.1 equiv), TBAF (631 mg, 2.0 equiv) in THF (2 mL), (*E*)-6-iodo-5-hexen-1-ol (226 mg, 1.0 mmol) and $Pd(dba)_2$ (29 mg, 0.05 equiv) was stirred at rt for 1.5 h and then was filtered through SiO_2. Purification by column chromatography (SiO_2, *n*-hexane/EtOAc=4/1) and Kugelrohr distillation afforded 170 mg (87%) of a mixture of (*E*, *E*)-**4** and (*E*)-7-pentyl-5,7-octadien-1-ol ((*E*)-**5**) as colorless oil.

Data for (*E*, *E*)-**4**:

bp: 80-85 ^{o}C (1.3 mmHg).

^{1}H NMR: (500 MHz, $CDCl_3$)

6.04 (m, C(6, 7)*H*, 2 H), 5.56 (m, C(5, 8)*H*, 2 H), 4.97 and 4.84 (2s, $H_2C{=}CR_1R_2$ ((*E*)-**5**), 3.63 (t, *J* =6.6, C(1)H2, 2 H), 2.06 (m, C(4, 9)*H*, 2 H), 1.57 (m, C(2)H_2, 2 H), 1.45 (m, C(3)H_2, 2 H), 1.37 (m, C(10)H_2, 2 H), 1.28 (m, C(11, 12)H_2, 4 H), 0.88 (t, *J* =7.1, C(13)H_3, 3 H).

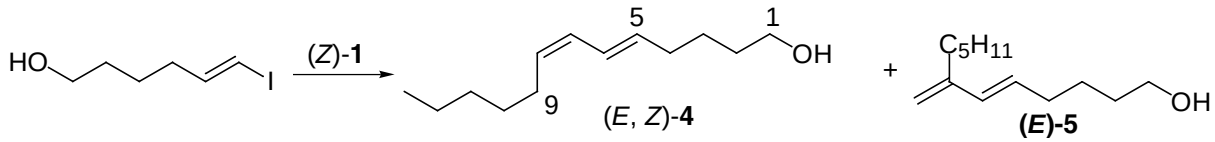
^{13}C NMR: (126 MHz, $CDCl_3$)

132.80 (C(5)), 131.64 (C(8)), 130.78 (C(6)), 130.14 (C(7)), 62.81 (C(1)), 32.53 (C(4)), 32.22 and 32.19 (C2 and C9), 31.39 (C(11)), 29.04 (C(10)), 25.45 (C(3)), 22.50 (C(12)), 14.00 (C(13)).

TLC: R_f: 0.25 (*n*-hexane/EtOAc=4/1).

GC: t_R (*E,E*)-**4** 6.87 min (93.8%); t_R (*Z,E*)-**4** and (*E,Z*)-**4** 6.72 min (2.2%); t_R (*E*)-**5**, 6.46 min (4.0%) (HP5, 200 ^{o}C, 15 psi).

Preparation of (*E*, *Z*)-5,7-Tridecadien-1-ol ((*E*, *Z*)-4c) [DW-VI-75]. (Table 3, entry 3)



Following the General Procedure, (*Z*)-**1** (201 mg, 1.1 equiv), TBAF (631 mg, 2.0 equiv) in THF (2 mL), (*E*)-6-iodo-5-hexen-1-ol (226 mg, 1.0 mmol) and $Pd(dba)_2$ (29 mg, 0.05 equiv) was stirred at rt for 1.5 h and then was filtered through SiO_2. Purification by column chromatography (SiO_2, *n*-hexane/EtOAc=4/1) and Kugelrohr distillation afforded 141 mg (72%) of a mixture of (*E*, *Z*)-**4** and (*E*)-**5** as colorless oil.

Data for (*E*, *Z*)-**4**:

bp: 75-80 °C (1.5 mmHg).

^{1}H NMR: (400 MHz, $CDCl_3$)

6.30 (dd, *J* =11.0, 15.0, C(6)*H*, 1H), 3.92 (t, *J* =11.0, C(7)*H*, 1H), 5.63 (td, *J* =7.5, 15.0, C(5)*H*, 1H), 5.29 (td, *J* =6.5, 11.0, C(8)*H*, 1H), 3.62 (t, *J* =6.6, C(1)H_2, 2 H), 2.12 (m, C(4,9)H_2, 4 H), 1.57 (m, C(12)H_2, 2 H), 1.45 (m, C(3)H_2, 2 H), 1.36 (m, C(10)H_2, 2 H), 1.29 (m, C(11, 12)H_2, 4 H), 0.88 (t, *J* =7.1, C(13)H_3, 3 H).

^{13}C NMR: (100.6 MHz, $CDCl_3$)

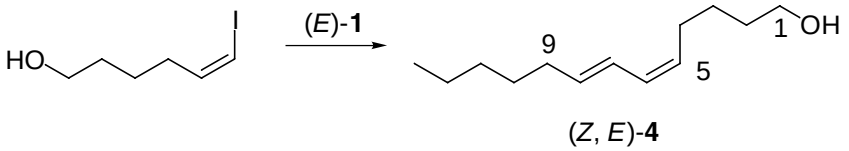
133.91 (C(5)), 130.36 (C(8)), 128.39 (C(7)), 125.98 (C(6)), 62.64 (C(1)), 32.49 (C(4)), 32.17 (C(2)), 31.41 (C(11)), 29.33 (C(10)), 27.59 (C(9)), 25.44 (C(3)), 22.48 (C(12)), 13.97 (C(13)).

TLC: R_f: 0.25 (*n*-hexane/EtOAc=4/1)

GC: t_R (*E,Z*)-**4** 10.78 min (87.5%); t_R (*E,E*)-**4** 11.44 min (5.3%); t_R (*E*)-**5**, 9.77 min (7.1%) (U2, 200 °C, 15 psi).

t_R (*E,Z*)-**4** 6.97 min (86.5%); t_R (*E,E*)-**4** 7.11 min (4.2%); t_R (*E*)-**5**, 6.46 min (9.3%) (HP5, 200 °C, 15 psi).

Preparation of (*Z*, *E*)-5,7-Tridecadien-1-ol[11] ((Z, E)-4) [DW-VI-74]. (Table 3, entry 4)



(*Z*, *E*)-**4**

Following the General Procedure, (*E*)-**1** (201 mg, 1.1 equiv), TBAF (631 mg, 2.0 equiv) in THF (2 mL), (*Z*)-6-iodo-5-hexen-1-ol (226 mg, 1.0 mmol) and $Pd(dba)_2$ (29 mg, 0.05 equiv) was stirred at rt for 1.5 h and then was filtered through SiO_2. Purification by column chromatography (SiO_2, *n*-hexane/EtOAc=4/1) and Kugelrohr distillation afforded 143 mg (73%) of (*Z*, *E*)-**4** as colorless oil.

Data for (*Z*, *E*)-**4**:

bp: 75-80 °C (1.5 mmHg).

^{1}H NMR: (400 MHz, $CDCl_3$)

6.27 (dd, *J* =10.7, 14.6, C(7)*H*, 1 H), 5.95 (t, *J* =10.7, C(6)*H*, 1 H), 5.65 (td, *J* =7.5, 14.6, C(8)*H*, 1 H), 5.27 (td, *J* =7.5, 10.7, C(5)*H*, 1 H), 3.63 (t, *J* =6.6, C(1)H_2, 2 H), 2.19 (m, C(4)H_2, 2 H), 2.08 (m, C(9)H_2, 2 H), 1.80 (b, OH, 1 H), 1.58 (m, C(2)H_2, 2 H), 1.44 (m, C(3)H_2, 2 H), 1.38 (m, C(10)H_2, 2 H), 1.28 (m, C(11, 12)H_2, 4 H), 0.88 (t, C(10)H_3,*J* =7.1).

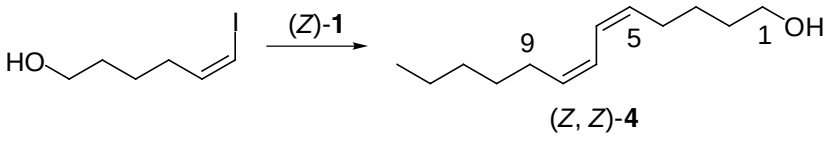
^{13}C NMR: (100.6 MHz, $CDCl_3$)

135.02 (C(7)), 129.30 (C(6)), 128.97 (C(8)), 125.37 (C(5)), 32.81 (C(9)), 32.21 (C(2)), 31.40 (C(11)), 29.02 (C(10)), 27.31 (C(4)), 25.78 (C(3)), 22.49 (C(12)), 14.01 (C(13)).

TLC: R_f: 0.25 (*n*-hexane/EtOAc=4/1).

GC: t_R (*Z,E*)-**4** 10.76 min (95.9%); t_R (*E,E*)-**4** 11.45 min (4.1%) (U2, 200 °C, 15 psi).
t_R (*Z,E*)-**4** 6.68 min (94.1%); t_R (*E,E*)-**4** 6.81 min (5.9%) (HP5, 200 °C, 15 psi).

Preparation of (*Z*,*Z*)-5,7-Tridecadien-1-ol[11] ((*Z*, *Z*)-4c) [DW-VI-76]. (Table 3, entry 5)



(*Z*, *Z*)-**4**

Following the General Procedure, (*Z*)-**1** (219 mg, 1.2 equiv), TBAF (631 mg, 2.0 equiv) in THF (2 mL), (*Z*)-6-iodo-5-hexen-1-ol (226 mg, 1.0 mmol) and $(allylPdCl)_2$ (9 mg, 0.025 eq) was stirred at rt for 6

h and then was filtered through SiO_2. Purification by column chromatography (SiO_2, *n*-hexane/EtOAc=4/1) and Kugelrohr distillation afforded 126 mg (64%) of (*Z*, *Z*)-**4** as colorless oil.

Data for (*Z*, *Z*)-**4**:

bp: 76-81 °C (2.0 mmHg).

^{1}H NMR: (500 MHz, $CDCl_3$)

6.24 (m, C(6, 7)*H*, 2 H), 5.44 (m, C(5, 8)*H*, 2 H), 3.63 (t, *J* =6.6, C(1)H_2, 2 H), 2.18 (m, C(4, 9)H_2, 4 H), 1.58 (m, C(2)H_2 and OH, 3 H), 1.45 (m, C(3)H_2, 2 H), 1.37 (m, C(10)H_2, 2 H), 1.29 (m, C(11, 12)H_2, 4 H), 0.88 (t, *J* =7.1, C(13), 3 H).

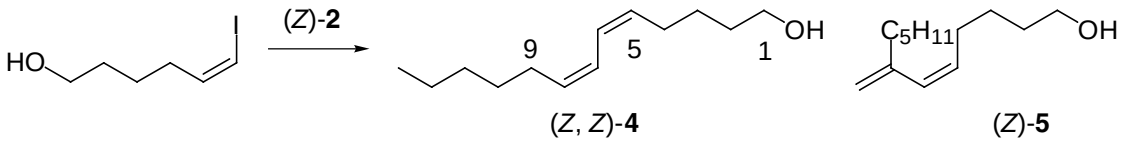
^{13}C NMR: (126 MHz, $CDCl_3$)

132.42 (C(6)), 131.33 (C(11)), 123.98 (C(5)), 123.39 (C(8)), 62.74 (C(1)), 32.24 (C(2)), 31.44 (C(11)), 29.25 (C(10)), 27.40 (C(4)), 27.08 (C(9)), 25.70 (C(3)), 22.49 (C(12)), 13.99 (C(13)).

TLC: R_f: 0.25 (*n*-hexane/EtOAc=4/1)

GC: t_R (*Z,Z*)-**4** 6.81 min (87.8%); t_R (*E,Z*)-**4** and (*Z,E*)-**4** 6.68 min (12.2%) (HP5, 200 °C, 15 psi).

Preparation of (*Z,Z*)-5,7-Tridecadien-1-ol[11] ((*Z*, *Z*)-4c) with di(iso-propyl)heptenylsilanol [DW-VII-33]. (Table 3, entry 6)



(*Z*, *Z*)-**4** (*Z*)-**5**

Following the General Procedure, (*Z*)-**2** (274 mg, 1.2 equiv), TBAF (631 mg, 2.0 equiv) in THF (2 mL), (*Z*)-6-iodo-5-hexen-1-ol (226 mg, 1.0 mmol) and (allylPdCl)$_2$ (9 mg, 0.025 eq) was stirred at rt for 6 h and then was filtered through SiO_2. Purification by column chromatography (SiO_2, *n*-hexane/EtOAc=4/1) and Kugelrohr distillation afforded 134 mg (68%) of (*Z*, *Z*)-**4** as colorless oil.

Data for (*Z*, *Z*)-**4**:

bp: 76-81 °C (2.0 mmHg).

^{1}H NMR: (500 MHz, $CDCl_3$)

6.24 (m, C(6, 7)*H*, 2 H), 5.44 (m, C(5, 8)*H*, 2 H), 3.63 (t, *J* =6.6, C(1)H_2, 2 H), 2.18 (m, C(4, 9)H_2, 4 H), 1.58 (m, C(2)H_2 and OH, 3 H), 1.45 (m, C(3)H_2, 2 H), 1.37 (m, C(10)H_2, 2 H), 1.29 (m, C(11, 12)H_2, 4 H), 0.88 (t, *J* =7.1, C(13), 3 H).

^{13}C NMR: (126 MHz, $CDCl_3$)

132.42 (C(6)), 131.33 (C(11)), 123.98 (C(5)), 123.39 (C(8)), 62.74 (C(1)), 32.24 (C(2)), 31.44 (C(11)), 29.25 (C(10)), 27.40 (C(4)), 27.08 (C(9)), 25.70 (C(3)), 22.49 (C(12)), 13.99 (C(13)).

TLC: R_f: 0.25 (*n*-hexane/EtOAc=4/1)

GC: t_R (*Z,Z*)-**4** 6.81 min (87.5%); t_R (*E,Z*)-**4** and (*Z,E*)-**4** 6.68 min (12.6%) (HP5, 200 ^{o}C, 15 psi). t_R (*Z,Z*)-**4** 11.21 min (86.1%); t_R (*E,Z*)-**4** and (*Z,E*)-**4** 11.80 min (6.7%); t_R (*Z*)-**5** 10.53 min (6.8%) (HP5, 200 ^{o}C, 15 psi).

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