Cross-Coupling Reactions of Alkenylsilanols with Fluoroalkylsulfonates

Scott E. Denmark* and Ramzi F. Sweis

*Roger Adams Laboratory, Department of Chemistry, University of Illinois, Urbana, Illinois,
61801*

SUPPORTING INFORMATION

General Experimental

All reactions were performed in oven (180 °C) and/or flame dried glassware under an atmosphere of dry argon. All reaction temperatures corresponded to internal temperatures unless otherwise noted. All the solvents used were technical grade and distilled from the indicated drying agents: dichloromethane: P₂O₅; diethyl ether and tetrahydrofuran: Na, benzophenone; pentane, hexane, dimethylformamide, and dimethoxyethane: CaH₂; methanol: Mg(OMe)₂; ethyl acetate: K₂CO₃. “Brine” refers to a saturated solution of NaCl. Bulb-to-bulb distillations were performed on a Büchi GKR-50 Kugelrohr and boiling points (bp) correspond to the uncorrected, recorded air bath temperatures (ABT). All reaction temperatures correspond to internal temperatures measured with Teflon-coated thermocouples unless otherwise noted.

¹H and ¹³C NMR were recorded on a Varian Unity-500 (500 MHz ¹H, 126 MHz ¹³C) and Varian Unity Inova 500 (500 MHz ¹H, 100 MHz ²⁹Si) spectrometer in deuteriochloroform unless otherwise stated using chloroform as an internal reference (7.26 ppm, ¹H; 77.2 ppm, ¹³C). Chemical shifts are reported in ppm (d); multiplicities are indicated by s (singlet), d (doublet), q (quartet), qn (quintet), sext (sextet), m (multiplet), and br (broad). Coupling constants, *J*, are reported in Hertz (Hz); integration is provided; and assignments are indicated.

Mass spectrometry 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 the base peak = 100). Infrared spectra (IR) were recorded on a Mattson Galaxy 5020 spectrophotometer. Peaks are reported in cm⁻¹ with the 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 Reverse-Phase C18 silica gel plates (RP C18) with F-254 indicator or Merck silica gel plates with F-254 indicator. Visualization was accomplished with UV light, an aqueous KMnO_4 solution, or phosphomolybdic acid in ethanol. Column chromatography was performed using 230-400 mesh silica gel purchased from EM Science or 230-400 mesh C18 Reverse Phase (RP) silica gel purchased from Fluka.

Analytical gas chromatography (GC) was performed using a Hewlett Packard 5890 Series II Gas Chromatograph fitted with a flame ionization detector. Injections were made on a Hewlett-Packard HP-5 (50 meter) or a Hewlett-Packard Ultra-2 (50 meter) capillary column. The injector temperature was 225 °C, the detector temperature was 300 °C, with a split ratio of 100:1. Retention times (t_R) and integrated ratios were obtained using Agilent Chemstation Software.

Literature Preparations

(*E*)-Dimethyl-(1-heptenyl)silanol,¹ (*Z*)-dimethyl-(1-heptenyl)silanol,¹ phenyl triflate,² phenyl nonaflate,³ 1-naphthyltriflate,⁴ 2-methylphenyl triflate,⁵ 4-methoxyphenyl triflate,⁴ 4-acetylphenyl nonaflate,^{3,6} and 4-*t*-butylcyclohex-1-enyl triflate,⁷ were prepared by literature methods.

General Procedure I: Palladium-Catalyzed Cross-Coupling Reaction of (*E*)-1 with Phenyl Nonaflate or Phenyl Triflate.

The selected tetralkylammonium fluoride (0.4 mmol, 2.0 equiv) was dissolved in dry dioxane or DMF (325 μL or 375 μL) at room temperature in a 1 mL conical vial with a magnetic stir bar and fitted with a septum. To this solution was added the appropriate amount of water, followed by naphthalene (internal standard), di-*t*-butylbiphenylphosphine (BPTBP) (0.02 mmol, 0.10 equiv), the palladium bromide or palladium chloride (0.01 mmol, 0.05 equiv), (*E*)-1 (0.22 mmol, 1.1 equiv), and either the phenyl nonaflate or phenyl triflate (2.0 mmol, 1.0 equiv). The mixture was then purged with dry argon gas via a needle through the septum. The reaction was monitored by GC analysis at certain intervals until completion. Sampling of the reaction

was done by removing 10 μ L of the mixture via syringe, and adding it to a 20% solution of 2-dimethylaminoethanethiol hydrochloride to quench. The resultant mixture was then filtered through a small plug of silica gel and was eluted with 4 mL of diethyl ether. This sample was then analyzed by GC. Conversions were calculated relative to the internal standard. Response factors were obtained by equation 1 and are shown below:

$$\text{Response factor for A} = \frac{(\text{mass A} * \text{area naphthalene})}{(\text{mass naphthalene} * \text{area A})}$$

mg naphthalene	area naphthalene	mg product	area product	response factor
75	2762150	25	516170	1.78
75	2665150	25	517107	1.72
75	2716090	25	516004	1.75
50	1025480	50	512044	2.00
50	1820290	50	1052880	1.73
50	1674250	50	998519	1.68
25	951807	75	1617150	1.77
25	879020	75	1515560	1.74
25	945583	75	1621300	1.75
				1.77

mg naphthalene	area naphthalene	mg phenol	area phenol	response factor
75	2723480	75	2061860	1.32
75	2642280	75	2003680	1.32
75	2504850	75	1892990	1.32
50	1802430	50	1287940	1.40
50	1955660	50	1396620	1.40
50	1868430	50	1334090	1.40
25	967172	75	1989740	1.46
25	898562	75	1847360	1.46
25	1034210	75	2121570	1.46
				1.39

t_R : naphthalene, 2.98 min ; t_R : phenol, 0.91 min; t_R : (*E*)-1-heptenylbenzene, 5.92 min
(HP-5, 250 °C, 15 psi)

Table 1, entry 1:

Following General Procedure I, a solution of TBAF•3H₂O (126 mg, 0.4 mmol, 2.0 equiv), naphthalene (15.3 mg), (*E*)-**1** (37.9 mg, 0.22 mmol, 1.1 equiv), phenyl nonaflate (75.2 mg, 0.2 mmol), BPTBP (6.0 mg, 0.02 mmol, 0.10 equiv), and PdCl₂ (1.8 mg, 0.01 mmol, 0.05 equiv) in dioxane (325 µL) was stirred at room temperature for 12 h. An aliquot of the mixture was then taken for GC analysis.

phenol	naphthalene	product	% phenol	% product
64748	325962	168659	22.44	40.20

Table 1, entry 2:

Following General Procedure I, a solution of TMAF•4H₂O (66 mg, 0.4 mmol, 2.0 equiv), naphthalene (17.5 mg), (*E*)-**1** (37.9 mg, 0.22 mmol, 1.1 equiv), phenyl nonaflate (75.2 mg, 0.2 mmol), BPTBP (6.0 mg, 0.02 mmol, 0.10 equiv), and PdCl₂ (1.8 mg, 0.01 mmol, 0.05 equiv) in DMF (325 µL) was stirred at room temperature for 24 h. An aliquot of the mixture was then taken for GC analysis.

phenol	naphthalene	product	% phenol	% product
22646	554380	657396	5.28	105.37

Table 1, entry 3:

Following General Procedure I, a solution of TBAF•3H₂O (126 mg, 0.4 mmol, 2.0 equiv), naphthalene (17.5 mg), (*E*)-**1** (37.9 mg, 0.22 mmol, 1.1 equiv), phenyl nonaflate (75.2 mg, 0.2 mmol), BPTBP (6.0 mg, 0.02 mmol, 0.10 equiv), and PdCl₂ (1.8 mg, 0.01 mmol, 0.05 equiv) in dioxane (325 µL) and water (7.2 µL, 0.4 mmol, 2 equiv) was stirred at room temperature for 12 h. An aliquot of the mixture was then taken for GC analysis.

phenol	naphthalene	product	% phenol	% product
46984	319442	254332	19.01	70.75

Table 1, entry 4:

Following General Procedure I, a solution of TBAF•3H₂O (126 mg, 0.4 mmol, 2.0 equiv), naphthalene (14.7 mg), (*E*)-**1** (37.9 mg, 0.22 mmol, 1.1 equiv), phenyl nonaflate (75.2 mg, 0.2

mmol), BPTBP (6.0 mg, 0.02 mmol, 0.10 equiv), and PdCl₂ (1.8 mg, 0.01 mmol, 0.05 equiv) in dioxane (325 µL) and water (21.6 µL, 1.2 mmol, 6 equiv) was stirred at room temperature for 12 h. An aliquot of the mixture was then taken for GC analysis.

phenol	naphthalene	product	% phenol	% product
10880	298672	297202	5.17	97.01

Table 1, entry 5:

Following General Procedure I, a solution of TBAF•3H₂O (126 mg, 0.4 mmol, 2.0 equiv), naphthalene (17.3 mg), (*E*)-**1** (37.9 mg, 0.22 mmol, 1.1 equiv), phenyl nonaflate (75.2 mg, 0.2 mmol), BPTBP (6.0 mg, 0.02 mmol, 0.10 equiv), and PdCl₂ (1.8 mg, 0.01 mmol, 0.05 equiv) in dioxane (325 µL) and water (36.0 µL, 2.0 mmol, 10 equiv) was stirred at room temperature for 12 h. An aliquot of the mixture was then taken for GC analysis.

phenol	naphthalene	product	% phenol	% product
4011	473397	428010	1.21	88.60

Table 1, entry 6:

Following General Procedure I, a solution of TBAF•3H₂O (126 mg, 0.4 mmol, 2.0 equiv), naphthalene (17.5 mg), (*E*)-**1** (37.9 mg, 0.22 mmol, 1.1 equiv), phenyl nonaflate (75.2 mg, 0.2 mmol), BPTBP (6.0 mg, 0.02 mmol, 0.10 equiv), and PdCl₂ (1.8 mg, 0.01 mmol, 0.05 equiv) in dioxane (325 µL) and water (50.4 µL, 2.8 mmol, 14 equiv) was stirred at room temperature for 12 h. An aliquot of the mixture was then taken for GC analysis.

phenol	naphthalene	product	% phenol	% product
1507	366691	314062	0.53	76.11

Table 1, entry 7:

Following General Procedure I, a solution of TMAF (37 mg, 0.4 mmol, 2.0 equiv), naphthalene (15.4 mg), (*E*)-**1** (37.9 mg, 0.22 mmol, 1.1 equiv), phenyl nonaflate (75.2 mg, 0.2 mmol), BPTBP (6.0 mg, 0.02 mmol, 0.10 equiv), and PdCl₂ (1.8 mg, 0.01 mmol, 0.05 equiv) in DMF (350 µL) was stirred at room temperature for 24 h. An aliquot of the mixture was then taken for GC analysis.

phenol	naphthalene	product	% phenol	% product
101714	569770	10219	20.30	1.40

Table 1, entry 8:

Following General Procedure I, a solution of TMAF•4H₂O (66 mg, 0.4 mmol, 2.0 equiv), naphthalene (15.7 mg), (*E*)-**1** (37.9 mg, 0.22 mmol, 1.1 equiv), phenyl nonaflate (75.2 mg, 0.2 mmol), BPTBP (6.0 mg, 0.02 mmol, 0.10 equiv), and PdCl₂ (1.8 mg, 0.01 mmol, 0.05 equiv) in DMF (325 µL) and water (14.4 µL, 0.8 mmol, 4 equiv) was stirred at room temperature for 24 h. An aliquot of the mixture was then taken for GC analysis.

phenol	naphthalene	product	% phenol	% product
3145	442023	561337	0.82	101.24

Table 1, entry 9:

Following General Procedure I, a solution of TMAF•4H₂O (66 mg, 0.4 mmol, 2.0 equiv), naphthalene (18.6 mg), (*E*)-**1** (37.9 mg, 0.22 mmol, 1.1 equiv), phenyl nonaflate (75.2 mg, 0.2 mmol), BPTBP (6.0 mg, 0.02 mmol, 0.10 equiv), and PdCl₂ (1.8 mg, 0.01 mmol, 0.05 equiv) in DMF (325 µL) and water (28.8 µL, 1.6 mmol, 8 equiv) was stirred at room temperature for 24 h. An aliquot of the mixture was then taken for GC analysis.

phenol	naphthalene	product	% phenol	% product
1910	468064	409018	0.56	82.53

Table 1, entry 10:

Following General Procedure I, a solution of TBAF•3H₂O (126 mg, 0.4 mmol, 2.0 equiv), naphthalene (13.7 mg), (*E*)-**1** (37.9 mg, 0.22 mmol, 1.1 equiv), phenyl nonaflate (75.2 mg, 0.2 mmol), BPTBP (6.0 mg, 0.02 mmol, 0.10 equiv), and PdBr₂ (2.7 mg, 0.01 mmol, 0.05 equiv) in dioxane (325 µL) and water (21.6 µL, 1.2 mmol, 6 equiv) was stirred at room temperature for 8 h. An aliquot of the mixture was then taken for GC analysis.

phenol	naphthalene	product	% phenol	% product
14744	572692	795802	2.60	96.67

Table 1, entry 11:

Following General Procedure I, a solution of TBAF•3H₂O (126 mg, 0.4 mmol, 2.0 equiv), naphthalene (13.7 mg), (*E*)-**1** (37.9 mg, 0.22 mmol, 1.1 equiv), phenyl triflate (45.2 mg, 0.2 mmol), BPTBP (6.0 mg, 0.02 mmol, 0.10 equiv), and PdBr₂ (2.7 mg, 0.01 mmol, 0.05 equiv) in

dioxane (325 μ L) was stirred at room temperature for 3 h. An aliquot of the mixture was then taken for GC analysis.

phenol	naphthalene	product	% phenol	% product
117076	532928	597356	22.23	77.98

Table 1, entry 12:

Following General Procedure I, a solution of TBAF•3H₂O (126 mg, 0.4 mmol, 2.0 equiv), naphthalene (10.7 mg), (*E*)-**1** (37.9 mg, 0.22 mmol, 1.1 equiv), phenyl triflate (45.2 mg, 0.2 mmol), BPTBP (6.0 mg, 0.02 mmol, 0.10 equiv), and PdBr₂ (2.7 mg, 0.01 mmol, 0.05 equiv) in dioxane (325 μ L) and water (7.2 μ L, 0.4 mmol, 2 equiv) was stirred at room temperature for 8 h. An aliquot of the mixture was then taken for GC analysis.

phenol	naphthalene	product	% phenol	% product
119125	570742	894570	16.49	85.16

Table 1, entry 13:

Following General Procedure I, a solution of TBAF•3H₂O (126 mg, 0.4 mmol, 2.0 equiv), naphthalene (15.7 mg), (*E*)-**1** (37.9 mg, 0.22 mmol, 1.1 equiv), phenyl triflate (45.2 mg, 0.2 mmol), BPTBP (6.0 mg, 0.02 mmol, 0.10 equiv), and PdBr₂ (2.7 mg, 0.01 mmol, 0.05 equiv) in dioxane (325 μ L) and water (21.6 μ L, 1.2 mmol, 6 equiv) was stirred at room temperature for 8 h. An aliquot of the mixture was then taken for GC analysis.

phenol	naphthalene	product	% phenol	% product
34217	531383	618320	7.47	92.76

Table 1, entry 14:

Following General Procedure I, a solution of TBAF•3H₂O (126 mg, 0.4 mmol, 2.0 equiv), naphthalene (14.8 mg), (*E*)-**1** (37.9 mg, 0.22 mmol, 1.1 equiv), phenyl triflate (45.2 mg, 0.2 mmol), BPTBP (6.0 mg, 0.02 mmol, 0.10 equiv), and PdBr₂ (2.7 mg, 0.01 mmol, 0.05 equiv) in dioxane (325 μ L) and water (36.0 μ L, 2.0 mmol, 10 equiv) was stirred at room temperature for 8 h. An aliquot of the mixture was then taken for GC analysis.

phenol	naphthalene	product	% phenol	% product
11026	354088	474234	3.40	100.65

General Procedure II: Palladium-Catalyzed Cross-Coupling Reaction of (*E*)- or (*Z*)-Alkenylsilanols with Aryl Triflates/Nonaflates and Alkenyl Triflates.

The selected tetralkylammonium fluoride (4.0 mmol, 2.0 equiv) was dissolved in dry dioxane or DMF (3.25 or 3.75 mL) at room temperature in a 2-necked round-bottom flask fitted to a dry argon line and fitted with a septum. To this solution was added the appropriate amount of water, followed by di-*t*-butylbiphenylphosphine (BPTBP) (0.20 mmol, 0.10 equiv) and the palladium bromide (0.10 mmol, 0.05 equiv). This mixture first was stirred at room temperature for 30 min when a *Z*-silanol was employed. The silanol (2.2 mmol, 1.1 equiv) and either the aryl triflate, nonaflate or alkenyl triflate (2.0 mmol, 1.0 equiv) was then added to the mixture. When a *Z*-silanol was employed, the reaction mixture was first quenched by addition of 400 μ L of a 20% solution of 2-dimethylaminoethanethiol hydrochloride. It was then filtered through a short silica gel column (20 g). The plug was eluted with diethyl ether (100 mL) and the eluate was evaporated in vacuo. The residue was purified by column chromatography (Reverse Phase C18 or SiO₂, 25 g) to afford the corresponding product which was further purified by bulb-to-bulb distillation.

Preparation of (*E*)-1-Heptenylbenzene ((*E*)-2a) (Table 2, entry 1).

Following General Procedure II, a mixture of TBAF (1.26 g, 4.0 mmol, 2.0 equiv), (*E*)-1 (379 mg, 2.2 mmol, 1.1 equiv), phenyl triflate (452 mg, 2.0 mmol), BPTBP (60 mg, 0.2 mmol, 0.10 equiv), and PdBr₂ (26.6 mg, 0.10 mmol, 0.05 equiv) was stirred in dioxane (3.25 mL) and water (360 μ L, 20.0 mmol, 10 equiv) at room temperature for 8 h, and then was quenched and filtered through SiO₂. Purification of the residue by column chromatography (RP C18, MeOH/H₂O, 9/1) and Kugelrohr distillation afforded 317 mg (91%) of (*E*)-2a as a colorless oil. The spectroscopic data matched those from the literature.¹

Data for (E)-2a:

bp: 160 °C (0.5 mm Hg, ABT)

¹H NMR: (500 MHz, CDCl₃)
 7.35 (dt, *J* = 8.4, 1.7, 2 H, HC(2)), 7.29 (td, *J* = 7.4, 2.1, 2 H, HC(3)), 7.19 (tt, *J* = 7.3, 1.3, 1 H, HC(4)), 6.38 (d, *J* = 15.7, 1 H, HC(1')), 6.24 (dt, *J* = 15.8, 6.9, 1 H, HC(2')), 2.21 (qd, *J* = 7.7, 1.5, 2 H, HC(3')), 1.48 (m, 2 H, HC(4')), 1.34 (m, 4 H, HC(5') and HC(6')), 0.91 (t, *J* = 7.2, 3 H, HC(7'))

¹³C NMR: (126 MHz, CDCl₃)
 138.2, 131.5, 129.9, 128.7, 127.0, 126.1, 33.2, 31.6, 29.3, 22.8, 14.3

TLC: *R*_f 0.25 (MeOH/H₂O, 9/1) [RP C18, UV]

GC: *t*_R (E)-2a, 8.35 min (99.5%); *t*_R (Z)-2a, 7.48 min (0.5%) (U2, 200 °C, 15 psi)

Preparation of (Z)-1-Heptenylbenzene ((Z)-2a) (Table 2, entry 2).

Following General Procedure II, a mixture of TBAF (1.26 g, 4.0 mmol, 2.0 equiv), (Z)-1 (379 mg, 2.2 mmol, 1.1 equiv), phenyl nonaflate (752 mg, 2.0 mmol), BPTBP (60 mg, 0.2 mmol, 0.10 equiv), and PdBr₂ (26.6 mg, 0.10 mmol, 0.05 equiv) was stirred in dioxane (3.25 mL) and water (216 µL, 12.0 mmol, 6 equiv) at room temperature for 14 h, and then was quenched and filtered through SiO₂. Purification of the residue by column chromatography (RP C18, MeOH/H₂O, 9/1) and Kugelrohr distillation afforded 306 mg (88%) of (Z)-2a as a colorless oil. The spectroscopic data matched those from the literature.¹

Data for (Z)-2a:

bp: 160 °C (0.5 mm Hg, ABT)

¹H NMR: (500 MHz, CDCl₃)
 7.34 (m, 2 H), 7.29 (m, 2 H), 7.22 (tt, *J* = 7.2, 1.5, 1 H), 6.41 (d, *J* = 11.8, 1 H), 5.67 (dt, *J* = 11.6, 7.3, 1 H), 2.33 (qd, *J* = 7.5, 1.7, 2 H), 1.45 (qn, *J* = 7.6, 2 H), 1.32 (m, 4 H), 0.89 (t, *J* = 7.1, 3 H)

¹³C NMR: (126 MHz, CDCl₃)
 138.0, 133.5, 129.0, 128.8, 128.3, 126.6, 31.8, 29.9, 28.8, 22.8, 14.2

TLC: R_f 0.25 (MeOH/H₂O, 9/1) [RP C18, UV]

GC: t_R (Z)-**2a**, 7.43 min (97.5%); t_R (E)-**2a**, 8.24 min (2.5%) (U2, 200 °C, 15 psi)

Preparation of (E)-1-(1-Heptenyl)naphthalene ((E)-2b) (Table 2, entry 3).

Following General Procedure II, a mixture of TBAF (1.26 g, 4.0 mmol, 2.0 equiv), (E)-**1** (379 mg, 2.2 mmol, 1.1 equiv), 1-naphthyl triflate (552 mg, 2.0 mmol), BPTBP (60 mg, 0.2 mmol, 0.10 equiv), and PdBr₂ (26.6 mg, 0.10 mmol, 0.05 equiv) was stirred in dioxane (3.25 mL) and water (216 μ L, 12.0 mmol, 6 equiv) at room temperature for 14 h, and then was quenched and filtered through SiO₂. Purification of the residue by column chromatography (RP C18, MeOH/H₂O, 9/1) and Kugelrohr distillation afforded 366 mg (82%) of (E)-**2b** as a colorless oil. The spectroscopic data matched those from the literature.¹

Data for (E)-2b:

bp: 190 °C (0.5 mm Hg, ABT)

¹H NMR: (500 MHz, CDCl₃)

8.13 (d, J = 8.2, 1 H), 7.84 (dd, J = 7.7, 1.9, 1 H), 7.74 (d, J = 8.1, 1 H), 7.56 (d, J = 7.1, 1 H), 7.49 (m, 2 H), 7.43 (dd, J = 8.0, 7.7, 1 H), 7.11 (d, J = 15.6, 1 H), 6.25 (dt, J = 15.5, 7.1, 1 H), 2.33 (qd, J = 7.3, 1.5, 2 H), 1.54 (m, 2 H), 1.39 (m, 4 H), 0.94 (t, J = 7.2, 3 H)

¹³C NMR: (126 MHz, CDCl₃)

136.0, 134.8, 133.8, 131.4, 128.7, 127.4, 127.1, 126.0, 125.9, 125.8, 124.2, 123.7, 33.6, 31.7, 29.3, 22.8, 14.3

TLC: R_f 0.18 (MeOH/H₂O, 9/1) [RP C18, UV]

GC: t_R (E)-**2b**, 10.97 min (99.1%); t_R (Z)-**2b**, 9.18 min (0.9%) (U2, 250 °C, 15 psi)

Preparation of (Z)-1-(1-Heptenyl)naphthalene ((Z)-2b) (Table 2, entry 4).

Following General Procedure II, a mixture of TBAF (1.26 g, 4.0 mmol, 2.0 equiv), (Z)-1 (379 mg, 2.2 mmol, 1.1 equiv), 1-naphthyl triflate (552 mg, 2.0 mmol), BPTBP (60 mg, 0.2 mmol, 0.10 equiv), and PdBr₂ (26.6 mg, 0.10 mmol, 0.05 equiv) was stirred in dioxane (3.25 mL) and water (216 μ L, 12.0 mmol, 6 equiv) at room temperature for 15 h, and then was quenched and filtered through SiO₂. Purification of the residue by column chromatography (RP C18, MeOH/H₂O, 9/1) and Kugelrohr distillation afforded 368 mg (82%) of (Z)-2b as a colorless oil. The spectroscopic data matched those from the literature.¹

Data for (Z)-2a:

- bp:** 190 °C (0.5 mm Hg, ABT)
- ¹H NMR:** (500 MHz, CDCl₃)
 8.02 (dd, *J* = 9.6, 4.3, 1 H), 7.86 (dd, *J* = 6.4, 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* = 6.9, 1 H), 6.87 (d, *J* = 11.4, 1H), 5.94 (dt, *J* = 11.5, 7.5, 1 H), 2.15 (qd, *J* = 7.3, 1.5, 2 H), 1.42 (qn, *J* = 7.3, 2H), 1.25 (m, 4 H), 0.83 (t, *J* = 6.6, 3 H)
- ¹³C NMR:** (126 MHz, CDCl₃)
 135.2, 134.9, 133.7, 132.2, 128.5, 127.3, 127.0, 126.6, 125.9, 125.8, 125.5, 125.3, 31.7, 29.7, 28.8, 22.7, 14.2
- TLC:** *R*_f 0.18 (MeOH/H₂O, 9/1) [RP C18, UV]
- GC:** *t*_R (Z)-2b, 9.29 min (98.9%); *t*_R (E)-2b, 11.10 min (1.1%) (U2, 250 °C, 15 psi)

Preparation of (*E*)-1-(1-Heptenyl)-2-methylbenzene ((*E*)-2c) (Table 2, entry 5).

Following General Procedure II, a mixture of TBAF (1.26 g, 4.0 mmol, 2.0 equiv), (*E*)-1 (379 mg, 2.2 mmol, 1.1 equiv), 2-methylphenyl triflate (480 mg, 2.0 mmol), BPTBP (119.4 mg, 0.4 mmol, 0.20 equiv), and PdBr₂ (53.2 mg, 0.20 mmol, 0.10 equiv) was stirred in dioxane (3.25 mL) and water (216 μ L, 12.0 mmol, 6.0 equiv) at room temperature for 16 h, and then was quenched and filtered through SiO₂. Purification of the residue by column chromatography (silica gel, pentane) and Kugelrohr distillation afforded 319 mg (85%) of (*E*)-2c as a colorless oil.

Data for (*E*)-2c:

<u>bp</u> :	170 °C (0.6 mm Hg, ABT)
<u>¹H NMR</u> :	(500 MHz, CDCl ₃) 7.42 (d, <i>J</i> = 7.7, 1 H, HC(2)), 7.13 (m, 3 H, HC(3), HC(4), and HC(5)), 6.57 (d, <i>J</i> = 15.7, 1 H HC(1')), 6.10 (dt, <i>J</i> = 15.7, 7.1, 1 H, HC(2')), 2.34 (s, 3 H, HC(7)), 2.24 (qd, <i>J</i> = 7.2, 1.5, 2 H, HC(3')), 1.50 (qn, <i>J</i> = 7.3, 2 H, HC(4')), 1.35 (m, 4 H, HC(5') and HC(6')), 0.92 (t, <i>J</i> = 7.2, 3 H, HC(7'))
<u>¹³C NMR</u> :	(126 MHz, CDCl ₃) 137.3 (C(1)), 135.1 (C(6)), 132.8 (C(2')), 130.3 (C(2)), 127.7 (C(1')), 126.9 (C(3)), 126.2 (C(4)), 125.6 (C(5)), 33.5 (C(3')), 31.6 (C(5')), 29.3 (C(4')), 22.7 (C(6')), 20.0 (C(7)), 14.3 (C(7'))
<u>TLC</u> :	<i>R_f</i> 0.67 (pentane) [SiO ₂ , UV]
<u>IR</u> :	(NaCl) 2956 (s), 2930 (s), 2860 (m), 1720 (s), 1603 (w), 1491 (w), 1461 (m), 1380 (w), 1288 (w), 1256 (m), 1130 (w), 1078 (m), 889 (w), 753 (s)
<u>MS</u> :	(EI, 70 eV) 188 (M ⁺ , 28), 145 (5), 131 (100), 118 (52), 105 (15), 91 (22), 77 (4)
<u>GC</u> :	<i>t_R</i> (<i>E</i>)-2c, 76 min (99.96%); <i>t_R</i> (<i>Z</i>)-2c, 6.95 min (0.04%) (U2, 220 °C, 15 psi)
<u>Analysis</u> :	C ₁₄ H ₂₀ (188.31) Calculated: C, 89.30; H, 10.70 % Found: C, 89.61; H, 10.73 %

Preparation of (Z)-1-(1-Heptenyl)-2-methylbenzene ((Z)-2c) (Table 2, entry 6).

Following General Procedure II, a mixture of TBAF (1.26 g, 4.0 mmol, 2.0 equiv), (Z)-1 (379 mg, 2.2 mmol, 1.1 equiv), 2-methylphenyl triflate (480 mg, 2.0 mmol), BPTBP (119.4 mg, 0.4 mmol, 0.20 equiv), and PdBr_2 (53.2 mg, 0.20 mmol, 0.10 equiv) was stirred in dioxane (3.25 mL) and water (216 μL , 12.0 mmol, 6.0 equiv) at room temperature for 25 h, and then was quenched and filtered through SiO_2 . Purification of the residue by column chromatography (silica gel, pentane) and Kugelrohr distillation afforded 323 mg (86%) of (Z)-2c as a colorless oil.

Data for (Z)-2c:

<u>bp</u> :	170 °C (0.6 mm Hg, ABT)
<u>^1H NMR</u> :	(500 MHz, CDCl_3) 7.16 (m, 4 H, HC(2), HC(3), HC(4), and HC(5)), 6.42 (d, $J = 11.6$, 1 H HC(1')), 5.72 (dt, $J = 11.6, 7.5$, 1 H, HC(2')), 2.26 (s, 3 H, HC(7)), 2.14 (qd, $J = 7.5, 1.7$, 2 H, HC(3')), 1.40 (qn, $J = 7.2$, 2 H, HC(4')), 1.26 (m, 4 H, HC(5') and HC(6')), 0.87 (t, $J = 7.2$, 3 H, HC(7'))
<u>^{13}C NMR</u> :	(126 MHz, CDCl_3) 137.3 (C(1)), 136.4 (C(6)), 133.2 (C(2')), 129.9 (C(2)), 129.2 (C(1')), 128.0 (C(3)), 126.9 (C(4)), 125.4 (C(5)), 31.6 (C(5')), 29.7 (C(4')), 28.5 (C(3')), 22.7 (C(6')), 20.1 (C(7)), 14.2 (C(7'))
<u>TLC</u> :	R_f 0.67 (pentane) [SiO_2 , UV]
<u>IR</u> :	(NaCl) 2958 (s), 2927 (s), 2857 (s), 1721 (m), 1700 (m), 1601 (w), 1486 (m), 1460 (s), 1377 (m), 1289 (w), 1254 (m), 1078 (m), 1043 (m), 785 (m), 750 (s)
<u>MS</u> :	(EI, 70 eV) 188 (M^+ , 33), 145 (6), 131 (100), 118 (43), 105 (17), 91 (20), 77 (6)
<u>GC</u> :	t_R (Z)-2c, 6.94 min (99.6%); t_R (E)-2c, 7.76 min (0.4%) (U2, 220 °C, 15 psi)
<u>Analysis</u> :	$\text{C}_{14}\text{H}_{20}$ (188.31) Calculated: C, 89.30; H, 10.70 % Found: C, 89.03; H, 10.90 %

Preparation of (*E*)-1-(1-Heptenyl)-4-methoxybenzene ((*E*)-2d) (Table 2, entry 7).

Following General Procedure II, a mixture of TBAF (1.26 g, 4.0 mmol, 2.0 equiv), (*E*)-**1** (379 mg, 2.2 mmol, 1.1 equiv), 4-methoxyphenyl triflate (512 mg, 2.0 mmol), BPTBP (60 mg, 0.2 mmol, 0.10 equiv), and PdBr₂ (26.6 mg, 0.10 mmol, 0.05 equiv) was stirred in dioxane (3.25 mL) and water (216 μ L, 12.0 mmol, 6.0 equiv) at room temperature for 5 h, and then was quenched and filtered through SiO₂. Purification of the residue by column chromatography (silica gel, pentane/ethyl acetate, 50/1) and Kugelrohr distillation afforded 382 mg (93%) of (*E*)-**2d** as a colorless oil. The spectroscopic data matched those from the literature.¹

Data for (*E*)-2d:

- bp: 180 °C (0.5 mm Hg, ABT)
- ¹H NMR: (500 MHz, CDCl₃)
 7.28 (dd, *J* = 6.5, 2.0, 2 H, HC(2)), 6.84 (dd, *J* = 6.6, 2.1, 2 H, HC(3)), 6.32 (d, *J* = 15.8, 1 H HC(1')), 6.09 (dt, *J* = 15.8, 7.2, 1 H, HC(2')), 3.80 (s, 3 H, HC(5)), 2.18 (qd, *J* = 7.4, 1.3, 2 H, HC(3')), 1.46 (qn, *J* = 7.3, 2 H, HC(4')), 1.33 (m, 4 H, HC(5') and HC(6')), 0.90 (t, *J* = 7.1, 3 H, HC(7'))
- ¹³C NMR: (126 MHz, CDCl₃)
 158.8 (C(4)), 131.0 (C(1)), 129.3 (C(2')), 129.2 (C(1')), 127.2 (C(2)), 114.1 (C(3)), 55.5 (C(5)), 33.2 (C(3')), 31.6 (C(5')), 29.4 (C(4')), 22.8 (C(6')), 14.3 (C(7'))
- TLC: *R_f* 0.31 (pentane/ethyl acetate, 50/1) [SiO₂, UV]
- GC: *t_R* (*E*)-**2d**, 10.21 min (98.5%); *t_R* (*Z*)-**2d**, 8.99 min (1.5%) (U2, 220 °C, 15 psi)

Preparation of (Z)-1-(1-Heptenyl)-4-methoxybenzene ((Z)-2d) (Table 2, entry 8).

Following General Procedure II, a mixture of TBAF (1.26 g, 4.0 mmol, 2.0 equiv), (Z)-1 (379 mg, 2.2 mmol, 1.1 equiv), 4-methoxyphenyl triflate (512 mg, 2.0 mmol), BPTBP (60 mg, 0.2 mmol, 0.10 equiv), and PdBr₂ (26.6 mg, 0.10 mmol, 0.05 equiv) was stirred in dioxane (3.25 mL) and water (216 μ L, 12.0 mmol, 6.0 equiv) at room temperature for 13 h, and then was quenched and filtered through SiO₂. Purification of the residue by column chromatography (silica gel, pentane/ethyl acetate, 50/1) and Kugelrohr distillation afforded 355 mg (87%) of (Z)-2d as a colorless oil. The spectroscopic data matched those from the literature.¹

Data for (Z)-2d:

- bp: 180 °C (0.5 mm Hg, ABT)
- ¹H NMR: (500 MHz, CDCl₃)
 7.23 (d, *J* = 8.6, 2 H, HC(2)), 6.87 (d, *J* = 8.8, 2 H, HC(3)), 6.34 (d, *J* = 11.8, 1 H, HC(1')), 5.57 (dt, *J* = 11.8, 7.3, 1 H, HC(2')), 3.82 (s, 3 H, HC(5)), 2.32 (qd, *J* = 7.4, 1.8, 2 H, HC(3')), 1.45 (qn, *J* = 7.5, 2 H, HC(4')), 1.31 (m, 4 H, HC(5') and HC(6')), 0.89 (t, *J* = 7.2, 3 H, HC(7'))
- ¹³C NMR: (126 MHz, CDCl₃)
 158.3 (C(4)), 131.9 (C(2')), 130.7 (C(1)), 130.1 (C(2)), 128.2 (C(1')), 113.7 (C(3)), 55.4 (C(5)), 31.8 (C(5')), 29.9 (C(4')), 28.8 (C(3')), 22.8 (C(6')), 14.3 (C(7'))
- TLC: *R*_f 0.31 (pentane/ethyl acetate, 50/1) [SiO₂, UV]
- GC: *t*_R (Z)-2d, 9.01 min (98.5%); *t*_R (E)-2d, 10.27 min (1.5%) (U2, 220 °C, 15 psi)

Preparation of (*E*)-1-[4-(1-heptenyl)phenyl]ethanone ((*E*)-2e) (Table 2, entry 9).

Following General Procedure II, a mixture of TMAF (661 mg, 4.0 mmol, 2.0 equiv), (*E*)-**1** (379 mg, 2.2 mmol, 1.1 equiv), 4-acetylphenyl nonaflate (837 mg, 2.0 mmol), BPTBP (60 mg, 0.2 mmol, 0.10 equiv), and PdBr₂ (26.6 mg, 0.10 mmol, 0.05 equiv) was stirred in DMF (2.13 mL) and water (1.87 mL, 104 mmol, 6.0 equiv) at 50 °C for 27 h, and then was quenched and filtered through SiO₂. Purification of the residue by column chromatography (silica gel, pentane/ethyl acetate, 30/1) and Kugelrohr distillation afforded 377 mg (87%) of (*E*)-**2e** as a colorless oil. The spectroscopic data matched those from the literature.¹

Data for (*E*)-2e:

bp: 160 °C (0.5 mm Hg, ABT)

¹H NMR: (500 MHz, CDCl₃)

7.89 (dd, *J* = 8.4, 2 H, HC(3)), 7.41 (d, *J* = 8.4, 2 H, HC(2)), 6.39 (m, 2 H, HC(1') and HC(2')), 2.58 (s, 3 H, HC(6)), 2.24 (qd, *J* = 7.4, 1.6, 2 H, HC(3')), 1.49 (qn, *J* = 7.2, 2 H, HC(4')), 1.33 (m, 4 H, HC(5') and HC(6')), 0.91 (t, *J* = 7.1, 3 H, HC(7'))

¹³C NMR: (126 MHz, CDCl₃)

197.9 (C(5)), 142.9 (C(4)), 135.6 (C(1)), 134.8 (C(2')), 129.1 (C(1')), 129.0 (C(3)), 126.1 (C(2)), 33.4 (C(3')), 31.6 (C(5')), 29.0 (C(4')), 26.8 (C(6)), 22.7 (C(6')), 14.2 (C(7'))

TLC: *R_f* 0.25 (pentane/ethyl acetate, 50/1) [SiO₂, UV]

GC: *t_R* (*E*)-**2e**, 9.40 min (93.2%); *t_R* (*Z*)-**2e**, 8.91 min (6.8%) (U2, 250 °C, 15 psi)

Preparation of (Z)-1-[4-(1-Heptenyl)phenyl]ethanone ((Z)-2e) (Table 2, entry 10).

Following General Procedure II, a mixture of TMAF (661 mg, 4.0 mmol, 2.0 equiv), (*E*)-**1** (379 mg, 2.2 mmol, 1.1 equiv), 4-acetylphenyl nonaflate (837 mg, 2.0 mmol), BPTBP (60 mg, 0.2 mmol, 0.10 equiv), and PdBr₂ (26.6 mg, 0.10 mmol, 0.05 equiv) was stirred in DMF (2.13 mL) and water (1.87 mL, 104 mmol, 6.0 equiv) at 50 °C for 24 h, and then was quenched and filtered through SiO₂. Purification of the residue by column chromatography (silica gel, pentane/ethyl acetate, 30/1) and Kugelrohr distillation afforded 193 mg (91% based on 49% conversion in crude ¹H NMR) of a mixture of (*E*)-**2e** and (*Z*)-**2e** in an 80/20 ratio as a colorless oil. The spectroscopic data matched those from the literature.¹

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

See above

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

bp: 160 °C (0.5 mm Hg, ABT)

¹H NMR: (500 MHz, CDCl₃)

7.92 (d, *J* = 8.3, 2 H, HC(3)), 7.36 (d, *J* = 8.5, 2 H, HC(2)), 6.43 (d, *J* = 11.7, 1 H, HC(1')), 5.79 (dt, *J* = 11.7, 7.3, 1 H, HC(2')), 2.60 (s, 3 H, HC(6)), 2.31 (q, *J* = 7.3, 2 H, HC(3')), 1.46 (m, 2 H, HC(4')), 1.30 (m, 4 H, HC(5') and HC(6')), 0.88 (t, *J* = 6.5, 3 H, HC(7'))

¹³C NMR: (126 MHz, CDCl₃)

197.6 (C(5)), 142.7 (C(4)), 135.7 (C(2')), 135.0 (C(1)), 128.8 (C(2)), 128.3 (C(3)), 127.8 (C(1')), 31.5 (C(5')), 29.5 (C(4')), 28.8 (C(3')), 26.6 (C(6)), 22.5 (C(6')), 14.0 (C(7'))

TLC: *R_f* 0.25 (pentane/ethyl acetate, 50/1) [SiO₂, UV]

Preparation of (*E*)-1-(1-Heptenyl)-4-*tert*-butyl-1-cyclohexene ((*E*)-3) (Figure #3).

Following General Procedure II, a mixture of TBAF (1.26 g, 4.0 mmol, 2.0 equiv), (*E*)-1 (379 mg, 2.2 mmol, 1.1 equiv), 4-*t*-butylcyclohex-1-enyl triflate (573 mg, 2.0 mmol), BPTBP (60 mg, 0.2 mmol, 0.10 equiv), and PdBr₂ (26.6 mg, 0.10 mmol, 0.05 equiv) was stirred in DMF (3.25 mL) at 50 °C for 5 h, and then was quenched and filtered through SiO₂. Purification of the residue by gravity column chromatography (RP C18, MeOH/H₂O, 9/1) and Kugelrohr distillation afforded 289 mg (62%) of (*E*)-3 as a colorless oil.

Data for (*E*)-3:

bp:	175 °C (0.45 mm Hg, ABT)
¹H NMR:	(500 MHz, CDCl ₃) 6.03 (d, <i>J</i> = 15.9, 1 H, HC(1')), 5.63 (m, 1 H, HC(2)), 5.53 (dt, <i>J</i> = 15.6, 6.8 1 H, HC(2')), 1.81-2.33 (m, 6H, HC(3'), HC(3) and HC(6)), 1.10-1.42 (m, 9 H, HC(4'), HC(5'), HC(6'), HC(4) and HC(5)), 0.87 (m, 12 H, HC(7') and HC(8))
¹³C NMR:	(126 MHz, CDCl ₃) 135.8, 133.0, 127.4, 127.3, 44.5, 36.7, 33.0, 32.4, 31.6, 29.6, 27.5, 27.4, 26.2, 22.7, 14.2
TLC:	<i>R_f</i> 0.03 (RP C18, MeOH/H ₂ O, 9/1) [RP C18, UV]
IR:	(NaCl) 2960 (s), 2934 (s), 1721 (m), 1652 (w), 1454 (m), 1325 (m), 1289 (w), 1078 (m), 968 (m), 742 (w)
MS:	(EI, 70 eV) 234 (M ⁺ , 38), 219 (7), 191 (15), 177 (27), 163 (29), 149 (8), 135 (19), 121 (28), 107 (57), 93 (77), 79 (84), 67 (35), 57 (100)
GC:	<i>t_R</i> (<i>E</i>)-3, 9.16 min (98.7%); <i>t_R</i> (<i>Z</i>)-3, 8.81 min (1.3%) (HP-1, 15 psi, 100 °C (3 min), 20 °C/min to 150 °C, 150 °C (2 min), 50 °C/min to 270 °C)
Analysis:	C ₁₄ H ₂₀ (234.43) Calculated: C, 87.10; H, 12.90 % Found: C, 86.93; H, 12.94 %

Preparation of (Z)-1-(1-Heptenyl)-4-*tert*-butyl-1-cyclohexene ((Z)-3) (Figure #3).

Following General Procedure II, a mixture of TBAF (1.26 g, 4.0 mmol, 2.0 equiv), (Z)-1 (379 mg, 2.2 mmol, 1.1 equiv), 4-*t*-butylcyclohex-1-enyl triflate (573 mg, 2.0 mmol), BPTBP (60 mg, 0.2 mmol, 0.10 equiv), and PdBr₂ (26.6 mg, 0.10 mmol, 0.05 equiv) was stirred in DMF (3.25 mL) at 50 °C for 12 h, and then was quenched and filtered through SiO₂. Purification of the residue by gravity column chromatography (RP C18, MeOH/H₂O, 9/1) and Kugelrohr distillation afforded 303 mg (65%) of (Z)-3 as a colorless oil. Purity was assayed at >97% by GC (small disiloxane contaminant) due to difficulty obtaining a sample with suitable microanalytical standards.

Data for (Z)-3:

- bp:** 175 °C (0.45 mm Hg, ABT)
- ¹H NMR:** (500 MHz, CDCl₃)
 5.75 (d, *J* = 11.8, 1 H, HC(1')), 5.63 (m, 1 H, HC(2)), 5.26 (dt, *J* = 11.8, 7.5 1 H, HC(2')), 1.81-2.32 (m, 6 H, HC(3'), HC(3) and HC(6)), 1.10-1.42 (m, 9 H, HC(4'), HC(5'), HC(6'), HC(4) and HC(5)), 0.87 (m, 12 H, HC(7') and HC(8))
- ¹³C NMR:** (126 MHz, CDCl₃)
 135.7, 131.3, 130.0, 127.8, 43.9, 32.4, 31.8, 30.7, 30.3, 29.9, 29.1, 27.4, 27.3, 24.5, 22.8, 14.2
- TLC:** *R_f* 0.03 (RP C18, MeOH/H₂O, 9/1) [RP C18, UV]
- IR:** (NaCl)
 2957 (s), 2946 (s), 1708 (m), 1631 (w), 1463 (m), 1324 (m), 1292 (w), 1078 (m), 952 (m), 720 (w)
- MS:** (EI, 70 eV)
 234 (M⁺, 36), 219 (7), 191 (17), 177 (25), 163 (27), 149 (8), 135 (18), 121 (27), 107 (49), 93 (64), 79 (71), 67 (35), 57 (100)

HRMS: (EI)

Calcd. For (C₁₇H₃₀): 234.2348

Found: 234.2354

GC: *t*_R (Z)-**3**, 8.86 min (96.6%); *t*_R (E)-**3**, 9.21 min (3.4%) (HP-1, 15 psi, 100 °C (3 min), 20 °C/min to 150 °C, 150 °C (2 min), 50 °C/min to 270 °C.)

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