

## Sequential Silylcarbocyclization/Silicon-Based Cross-Coupling Reactions

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### SUPPORTING INFORMATION

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#### General Experimental

All reactions were performed in oven-dried (150 °C) and/or flame-dried glassware under an atmosphere of dry argon unless otherwise specified. Commercial reagents were purified by distillation or recrystallization prior to use. All syringes were glass. Reaction solvents tetrahydrofuran (Fisher, HPLC grade), diethyl ether (Fisher, BHT stabilized ACS grade), and methylene chloride (Fisher, unstabilized HPLC grade) were dried by percolation through two columns packed with neutral alumina under a positive pressure of argon. Reaction solvents hexane (Fisher, OPTIMA grade), and toluene (Fisher, ACS grade) were dried by percolation through a column packed with neutral alumina and a column packed with Q5 reactant, a supported copper catalyst for scavenging oxygen, under a positive pressure of argon. All reaction temperatures correspond to internal temperatures measured by Teflon-coated thermocouples unless otherwise noted. A 1.0 M solution of tetrabutylammonium fluoride in THF was prepared from solid tetrabutylammonium fluoride trihydrate (TBAF•3H<sub>2</sub>O, Fluka, Acros) and THF in a volumetric flask and was stored in a Schlenk flask. Rh<sub>4</sub>(CO)<sub>12</sub> and Rh(acac)(CO)<sub>2</sub> were obtained

from Strem Chemicals, Inc., and were used as received.

All reactions using carbon monoxide were performed in a well-ventilated hood. Because of the toxic nature of CO, all the procedures involving the use of CO employed a dedicated manifold for filling the apparatus with CO and maintaining an atmosphere. Reactions using the pressure bomb were also conducted in the hood. The bomb was filled directly from the CO tank and vented slowly into the hood with the doors closed. All practices were in accordance with *Prudent Practices in the Laboratory: Handling and Disposal of Chemicals*, National Research Council: Washington, DC, 1995. A CO monitor (Nighthawk KN-COPP-3) was used as a safety precaution.

“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). Melting points (mp) were determined in sealed tubes using a Thomas Unimelt Hoover capillary melting point apparatus and were corrected. Analytical thin-layer chromatography was performed on Merck silica with QF-254 indicator. Visualization was accomplished with UV light and/or KMnO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub> solution. Diethyl ether, ethyl acetate, hexanes, dimethoxy ethane, dichloromethane, acetonitrile and methanol were of reagent grade and used as received. Column chromatography was performed using Silicycle Silia-P flash silica gel or Aldrich 150-mesh aluminum oxide, activated, neutral, Brockmann I.

Analytical high pressure liquid chromatography (HPLC) was performed on a Hewlett-Packard 1090 Series II liquid chromatograph equipped with an Agilent Zorbax 300SB-C8 column or an Agilent Zorbax Rx-C8 column. Compounds were detected using a UV detection unit with a wavelength of 254 nm. Response factors were generated by mixing 1:1 molar ratios of compound to naphthalene internal standard in HPLC grade acetonitrile. Retention times ( $t_R$ ) and integrated ratios were obtained using SRI Peaksimple software.

<sup>1</sup>H NMR spectra were recorded on a Varian Inova (500 MHz, <sup>1</sup>H), Varian Unity-500 (500 MHz, <sup>1</sup>H, 126 MHz, <sup>13</sup>C), Varian 500 VXR (500 MHz, <sup>1</sup>H, 126 MHz, <sup>13</sup>C) spectrometer in chloroform-*d* or benzene-*d*<sub>6</sub> using chloroform (7.27 ppm, <sup>1</sup>H, 77.23 ppm, <sup>13</sup>C) or benzene (7.15 ppm, <sup>1</sup>H, 128.06 ppm, <sup>13</sup>C) as an internal reference for <sup>1</sup>H. Chemical shifts are reported in ppm (δ); 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. All  $^{13}\text{C}$  NMR and most  $^1\text{H}$  NMR assignments are corroborated by 2-D experiments (HETCOR and COSY). Spectra available on request from [denmark@scs.uiuc.edu](mailto:denmark@scs.uiuc.edu).

Infrared (IR) spectra were as thin films (neat) in NaCl cells, using a Perkin Elmer Spectrum BX spectrophotometer, and peaks are reported in  $\text{cm}^{-1}$  along with relative signal intensities: s (strong); m (medium); w (weak).

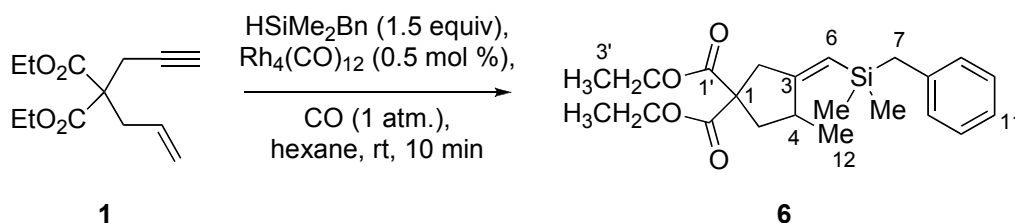
Low-resolution and high-resolution electron impact mass spectrometry (EI) was performed at 70 eV, on a Micromass 70-VSE spectrometer; low-resolution and high-resolution chemical ionization mass spectra (CI) were obtained using methane as the carrier gas, on a Micromass 70-VSE spectrometer. Data are reported in the form of  $m/z$  (intensity relative to base peak = 100.0).

Microanalysis (CHN) was performed on an Exeter CE440 analyzer. All results are reported as % by weight.

## Literature Preparations

Bis(dibenzylidene)palladium chloroform adduct,<sup>1</sup> 4,4-bis(carboethoxy)-6-hepten-1-yne (1),<sup>2</sup> *N*-benzyallylpropargylamine (2),<sup>2</sup> allyl propargyl ether (3),<sup>2</sup> 5,5-bis(carboethoxy)-7-octen-1-yne (4),<sup>2</sup> diethyl propargylmalonate,<sup>3</sup> and methyl 3-bromocrotonate<sup>4</sup> were prepared according literature procedures.

## Silylcarbocyclization Reaction of 4,4-Bis(carboethoxy)-6-hepten-1-yne (1) with Benzyldimethylsilane. Preparation of (Z)-3-Benzyldimethylsilylmethylene-4-methylcyclopentane-1,1-dicarboxylate (6).



4,4-Bis(carboethoxy)-6-hepten-1-yne (**1**) (2.009 g, 8.39 mmol, 1.0 equiv) and benzyldimethylsilane (1.7 mL, 10.7 mmol, 1.0 equiv) were dissolved in hexane (12 mL), in an oven-dried, 50-mL, round-bottomed flask with a magnetic stirrer and a gas inlet adaptor. In

another oven-dried, 50-mL, round-bottomed flask equipped with a magnetic stirrer and a gas inlet adaptor, a red-orange solution of  $\text{Rh}_4(\text{CO})_{12}$  (31 mg, 0.04 mmol, 0.5 mol %) and benzyldimethylsilane (0.3 mL, 1.89 mmol, 0.5 equiv) in hexane (8 mL) was prepared. Both flasks were purged with CO. The solution containing  $\text{Rh}_4(\text{CO})_{12}$  was stirred at room temperature under CO for 3 min, and this solution was added to the solution containing 4,4-bis(carboethoxy)-6-hepten-1-yne (**1**) via cannulation under CO. Upon the mixing of the two solutions, the color quickly changed from orange to yellow, and the reaction was noticeably exothermic. After 10 min of stirring under a CO atmosphere at room temperature, the reaction mixture was concentrated under reduced pressure, and the residue was dissolved in EtOH (5 mL). To this solution was added 0.1 g of decolorizing charcoal and stirred for 5 min to remove the rhodium-containing species. This suspension was subsequently filtered through a pad of Celite (approximately 3 cm) and was washed with more EtOH (70 mL). The yellow filtrate was concentrated under reduced pressure, and the resulting crude product was purified using flash chromatography (silica gel (200 g), hexane/ $\text{CH}_2\text{Cl}_2$ , 40/1 (500 mL), 20/1 (1 L), 10/1 (1 L)) and diffusion pump distillation to afford 2.724 g (84%) of **6** as a colorless, viscous liquid.

Data for **6**:

b.p.: 125 °C (ABT) at  $1.0 \times 10^{-4}$  mmHg

$^1\text{H}$  NMR: (500 MHz,  $\text{CDCl}_3$ )

7.21 (t, 2 H,  $J = 7.6$ ,  $2 \times \text{HC}(10)$ ), 7.06 (t, 1 H,  $J = 7.3$ ,  $\text{HC}(11)$ ), 6.99 (d, 2 H,  $J = 7.0$ ,  $2 \times \text{HC}(9)$ ), 5.31 (dd, 1 H,  $J = 1.1$ , 1.1,  $\text{HC}(6)$ ), 4.19 (qd, 2 H,  $J = 7.1$ , 2.2,  $\text{H}_2\text{C}(2')$ ), 4.17 (qd, 2 H,  $J = 7.1$ , 0.6,  $\text{H}_2\text{C}(2')$ ), 3.25 (dt, 1 H,  $J = 17.2$ , 2.0,  $\text{HC}(2)$ ), 2.76 (d, 1 H,  $J = 16.4$ ,  $\text{HC}(2)$ ), 2.67-2.62 (m, 1 H,  $\text{HC}(4)$ ), 2.64 (qd, 1 H,  $J = 8.0$ , 1.0,  $\text{HC}(5)$ ), 2.12 (d, 2 H,  $J = 2.1$ ,  $\text{H}_2\text{C}(7)$ ), 1.89 (dd, 1 H,  $J = 12.6$ , 3.8,  $\text{HC}(5)$ ), 1.25 (t, 3 H,  $J = 7.2$ ,  $\text{H}_3\text{C}(3')$ ), 1.23 (t, 3 H,  $J = 7.2$ ,  $\text{H}_3\text{C}(3')$ ), 1.03 (d, 3 H,  $J = 6.8$ ,  $\text{H}_3\text{C}(12)$ ), 0.07 (s, 3 H,  $\text{H}_3\text{CSi}$ ), 0.06 (s, 3 H,  $\text{H}_3\text{CSi}$ ).

$^{13}\text{C}$  NMR: (126 MHz,  $\text{CDCl}_3$ )

172.4 ( $\text{C}(1')$ ), 172.1 ( $\text{C}(1')$ ), 164.3 ( $\text{C}(3)$ ), 140.3 ( $\text{C}(8)$ ), 128.5 ( $\text{C}(10)$ ), 128.3 ( $\text{C}(9)$ ), 124.2 ( $\text{C}(11)$ ), 118.9 ( $\text{C}(6)$ ), 61.7 ( $\text{C}(2')$ ), 61.6 ( $\text{C}(2')$ ), 58.6 ( $\text{C}(1)$ ), 44.6 ( $\text{C}(2)$ ), 42.0 ( $\text{C}(5)$ ), 37.0 ( $\text{C}(4)$ ), 27.0 ( $\text{C}(7)$ ), 22.7 ( $\text{C}(12)$ ), 14.2 ( $\text{C}(3')$ ), 14.2 ( $\text{C}(3')$ ), -1.6 ( $\text{CSi}$ ), -1.7 ( $\text{CSi}$ ).

IR: (neat)

3463 (s), 2979 (m), 1373 (s), 1629 (m), 1493 (m), 1451 (m), 1366 (m), 1246 (s),  
1159 (m), 1096 (m), 837 (m), 761 (m).

LRMS: (CI):

55 (3.4), 57 (5.3), 59 (3.0), 62 (25.8), 63 (100.0), 71 (2.2), 107 (2.0), 389 (2.7,  
[M+H]<sup>+</sup>).

HRMS: (CI, [M+H]<sup>+</sup>):

calcd.: 389.214813

found: 389.214541

Analysis: C<sub>22</sub>H<sub>37</sub>O<sub>4</sub>Si (388.57)

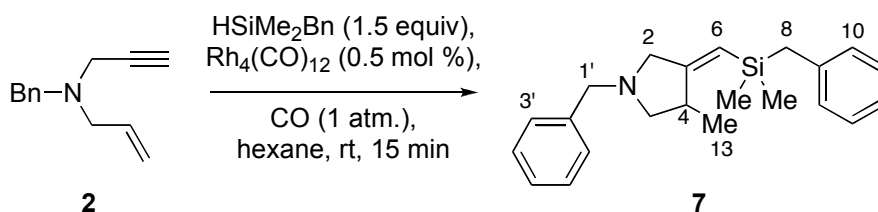
calcd.: C, 68.00; H, 8.30.

found: C, 67.99; H, 8.20.

R<sub>f</sub>: 0.78 (silica gel, hexane/EtOAc, 5/1, UV)

t<sub>R</sub>: 9.866 min (Agilent Zorbax 300SB-C8, 60% (MeCN in H<sub>2</sub>O) to 100% ramp at  
4%/min, 100% for 2 min, 100% to 60% gradient at 11.4%/min)

**Silylcarbocyclization Reaction of *N*-Benzyallylpropargylamine (2) with Benzyldimethylsilane. Preparation of *N*-Benzyl-(*Z*)-3-benzyldimethylsilylmethylene-4-methylpyrrolidine (7).**



*N*-Benzyallylpropargylamine (2) (1.112 g, 6.00 mmol, 1.0 equiv) and benzyldimethylsilane (1.0 mL, 6.00 mmol, 1.0 equiv) were dissolved in hexane (9 mL), in a flame-dried, 25-mL, round-bottomed flask with a magnetic stirrer and a gas inlet adaptor. In another flame-dried, 50-mL, round-bottomed flask equipped with a gas inlet adaptor, a red-orange solution of Rh<sub>4</sub>(CO)<sub>12</sub> (22 mg, 0.03 mmol, 0.5 mol %) and benzyldimethylsilane (0.5 mL, 3.00 mmol, 0.5 equiv) in hexane (6 mL) was prepared. Both flasks were purged with CO. The solution containing Rh<sub>4</sub>(CO)<sub>12</sub> was stirred at room temperature under CO for 3 min, and this solution was added to the solution containing *N*-benzyallylpropargylamine (2) via cannulation

under CO. Upon the mixing of the two solutions, the color quickly changed from red-orange to yellow, and the reaction was noticeably exothermic. After 15 min of stirring under a CO atmosphere at room temperature, the reaction was quenched by adding a solution of thiourea (50 mg, 0.60 mmol, 10 mol %) in EtOH (15 mL). This mixture was stirred at room temperature under air for approximately 50 min, during which time the reaction mixture turned into a yellow suspension. It was then filtered through a layer of silica gel (approximately 3 cm), and the silica gel was washed with 60 mL of EtOAc. The yellow filtrate was concentrated under reduced pressure. The resulting crude product was purified using flash chromatography (neutral alumina activity I (300 g), hexane/EtOAc, 8/1 (500 mL), 6/1 (500 mL)), reverse phase chromatography (reverse phase silica gel (250 g), MeCN), and diffusion pump distillation to afford 1.914 g (95%) of **7** as a colorless, viscous liquid.

Data for 7:

b.p.: 177 °C (ABT) at  $5.5 \times 10^{-5}$  mmHg

<sup>1</sup>H NMR: (500 MHz, C<sub>6</sub>D<sub>6</sub>)

7.34 (d, 2 H,  $J = 7.6$ ,  $2 \times \text{HC}(3')$ ), 7.19 (t, 2 H,  $J = 7.6$ ,  $2 \times \text{HC}(4')$ ), 7.14 (t, 2 H,  $J = 7.6$ ,  $2 \times \text{HC}(11)$ ), 7.09 (d, 1 H,  $J = 7.3$ ,  $\text{HC}(5')$ ), 7.00 (t, 1 H,  $J = 7.3$ ,  $\text{HC}(12)$ ), 6.97 (d, 2 H,  $J = 8.1$ ,  $2 \times \text{HC}(10)$ ), 5.20 (d, 1 H,  $J = 1.5$ ,  $\text{HC}(6)$ ), 3.46 (d, 1 H,  $J = 12.9$ ,  $\text{HC}(1')$ ), 3.37 (dd, 1 H,  $J = 13.9$ , 2.4,  $\text{HC}(1')$ ), 3.36 (d, 1 H,  $J = 24.4$ ,  $\text{HC}(2)$ ), 2.84 (dd, 1 H,  $J = 13.9$ , 1.5,  $\text{HC}(2)$ ), 2.55-2.52 (m, 1 H,  $\text{HC}(4)$ ), 2.43-2.37 (m, 2 H,  $\text{H}_2\text{C}(5)$ ), 2.09 (d, 1 H,  $J = 13.6$ ,  $\text{HC}(8)$ ), 1.11 (d, 3 H,  $J = 7.1$ ,  $\text{H}_3\text{C}(13)$ ), 0.09 (s, 3 H,  $\text{H}_3\text{CSi}$ ), 0.08 (s, 3 H,  $\text{H}_3\text{CSi}$ ).

<sup>13</sup>C NMR: (126 MHz, C<sub>6</sub>D<sub>6</sub>)

165.5 (C(3)), 140.7 (C(2')), 140.2 (C(9)), 129.2 (C(3')), 129.0 (C(3')), 128.9 (C(aryl)), 128.8 (C(aryl)), 128.6 (C(aryl)), 128.4 (C(aryl)), 127.6 (C(5')), 124.8 (C(12)), 116.2 (C(6)), 63.1 (C(2)), 62.9 (C(1')), 60.9 (C(5)), 38.2 (C(4)), 27.4 (C(8)), 22.3 (C(13)), -1.4 (CSi), -1.6 (CSi).

IR: (neat)

3025 (m), 2958 (s), 2925 (s), 2785 (s), 1632 (s), 1600 (s), 1493 (s), 1452 (s), 1340 (m), 1248 (s), 1207 (s), 1153 (s), 1056 (m), 1028 (s), 835 (s), 760 (m), 698 (m).

LRMS: (CI):

336 (100.0,  $[\text{M}+\text{H}]^+$ ), 320 (20.0), 244 (24.2), 186 (29.1), 149 (34.0), 91 (20.7), 75

(12.2).

HRMS: (CI,  $[M+H]^+$ ):

calcd.: 336.214754

found: 336.214403

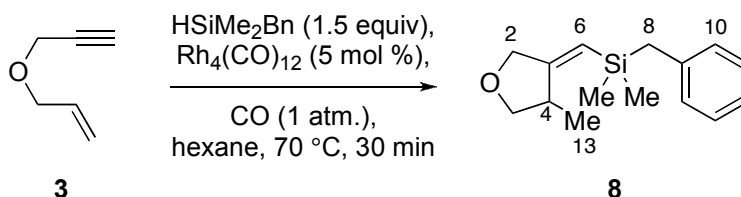
Analysis:  $C_{22}H_{37}O_4Si$  (335.56)

calcd.: C, 78.75; H, 8.71; N, 4.17.

found: C, 78.55; H, 8.56; N, 4.44.

 $R_f$ : 0.57 (silica gel, hexane/EtOAc, 5/1, UV) $t_R$ : 20.71 min (HP-5, 150 °C to 270 °C ramp at 10 °C/min, 270 °C for 15 min)

**Silylcarbocyclization Reaction of Allyl Propargyl Ether (3) with Benzyldimethylsilane.**  
**Preparation of (Z)-3-Benzyldimethylsilylmethylene-4-methyltetrahydrofuran (8).**



Allyl propargyl ether (**3**) (384 mg, 4.00 mmol, 1.0 equiv) was dissolved in toluene (4 mL), in a flame-dried, 10-mL, round-bottomed flask with a magnetic stirrer and a gas inlet adaptor. In another flame-dried, 50-mL, round-bottomed flask equipped with a magnetic stirrer and a gas inlet adaptor, a light green solution of  $Rh(acac)(CO)_2$  (52 mg, 0.20 mmol, 5 mol %) and benzyldimethylsilane (1.3 mL, 8.00 mmol, 2.0 equiv) in hexane (16 mL) was prepared. Both flasks were purged with CO. The solution containing  $Rh(acac)(CO)_2$  was placed in an oil bath preheated to 70 °C, and this solution was stirred in the oil bath for 3 min. Then, the solution containing allyl propargyl ether (**3**) was added to the solution containing  $Rh_4(CO)_{12}$  via cannulation under CO. Upon the mixing of the two solutions, the color changed from light-green to yellow. After 30 min of stirring under a CO atmosphere in the oil bath, the reaction was quenched by adding a solution of thiourea (78 mg, 1.00 mmol, 2.5 mol %) in EtOH (5 mL). This mixture immediately turned red, and the color quickly faded to red-orange and then to yellow-orange. It was stirred at room temperature under air for approximately 20 min, during which time the reaction mixture turned into a yellow suspension. The suspension was then filtered through a layer of silica gel, and the silica gel was washed with 100 mL of EtOAc. The bright-yellow

filtrate was concentrated under reduced pressure. The resulting crude product was purified using flash chromatography (silica gel (100 g), hexane/Et<sub>2</sub>O, 60/1) and Kugelrohr distillation to afford 520 mg (53%) of **8** as a colorless, viscous liquid.

Data for **8**:

b.p.: 190 °C (ABT) at 0.2 mmHg

<sup>1</sup>H NMR: (500 MHz, CDCl<sub>3</sub>)

7.22 (t, 2 H, *J* = 7.7, 2 × HC(11)), 7.08 (t, 1 H, *J* = 7.3, HC(12)), 7.01 (d, 2 H, *J* = 7.6, 2 × HC(10)), 5.29 (d, 1 H, *J* = 1.5, HC(6)), 4.44 (dt, 1 H, *J* = 13.7, 1.7, HC(2)), 4.15 (dd, 1 H, *J* = 13.7, 1.7, HC(2)), 3.82 (dd, 1 H, *J* = 8.3, 5.4, HC(5)), 3.67 (dd, 1 H, *J* = 8.3, 1.0, HC(5)), 2.63-2.60 (m, 1 H, HC(4)), 2.17 (s, 2 H, H<sub>2</sub>C(8)), 1.08 (d, 3 H, *J* = 7.1, H<sub>3</sub>C(13)), 0.14 (s, 3 H, H<sub>3</sub>CSi), 0.13 (s, 3 H, H<sub>3</sub>CSi).

<sup>13</sup>C NMR: (126 MHz, CDCl<sub>3</sub>)

163.5 (C(3)), 140.1 (C(9)), 128.4 (C(11)), 124.2 (C(12)), 115.0 (C(6)), 76.2 (C(5)), 73.4 (C(2)), 38.3 (C(4)), 27.0 (C(8)), 20.7 (C(13)), -1.7 (CSi), -1.9 (CSi).

IR: (neat)

2963 (m), 2850 (w), 1636 (w), 1600 (w), 1493 (m), 1348 (m), 1248 (m), 1087 (m), 922 (w), 837 (s), 699 (s).

LRMS: (EI):

246 (14.2, [M]<sup>+</sup>), 155 (100.0), 125 (26.6), 113 (17.9), 91 (20.7), 75 (49.3), 59 (36.2).

HRMS: (EI, [M]<sup>+</sup>):

calcd.: 246.14085

found: 246.14369

Analysis: C<sub>22</sub>H<sub>37</sub>O<sub>4</sub>Si (246.42)

calcd.: C, 73.11; H, 9.00.

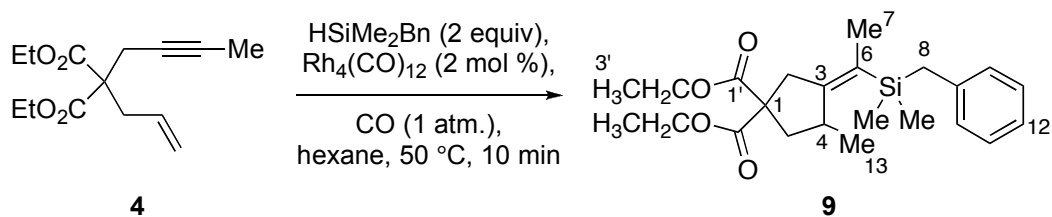
found: C, 73.18; H, 8.95.

R<sub>f</sub>: 0.67 (silica gel, hexane/EtOAc, 5/1, UV)

t<sub>R</sub>: 3.19 min (Agilent Zorbax Rx-C8, 100% MeCN (1 mL/min))



**Silylcarbocyclization Reaction of 5,5-Bis(carboethoxy)-7-octen-1-yne (4) with Benzyldimethylsilane. Preparation of Diethyl (Z)-3-Benzyldimethylsilylmethylmethylene-4-methylcyclopentane-1,1-dicarboxylate (9).**



5,5-Bis(carboethoxy)-7-octen-1-yne (**4**) (1.262 g, 5.00 mmol, 1.0 equiv) was dissolved in hexane (5 mL), which was saturated with CO by bubbling for approximately 20 min, in a flame-dried, 25-mL, round-bottomed flask with a magnetic stirrer and a gas inlet adaptor. In another flame-dried, 100-mL, round-bottomed flask equipped with a magnetic stirrer a gas inlet adaptor, a red-orange solution of Rh<sub>4</sub>(CO)<sub>12</sub> (75 mg, 0.10 mmol, 2 mol %) and benzyldimethylsilane (1.60 mL, 10.00 mmol, 2.0 equiv) in hexane (20 mL) was prepared. Both flasks were purged with CO. The solution containing Rh<sub>4</sub>(CO)<sub>12</sub> heated to 50 °C by placing in an oil bath, and it was stirred at room temperature under CO for 3 min. The color of the solution containing Rh<sub>4</sub>(CO)<sub>12</sub> darkened somewhat upon heating. Then, this solution was added to the solution containing 5,5-bis(carboethoxy)-7-octen-1-yne (**4**) via cannulation under CO. Upon the mixing of the two solutions, the color turned from red-brown to yellow-brown. After 10 min of stirring under a CO atmosphere at 50 °C, the reaction mixture was allowed to cool down, and the reaction mixture was treated with a solution of thiourea (76.8 mg, 1.00 mmol, 20 mol %) in EtOH (5 mL). This mixture was stirred at room temperature under air for 20 min, and it quickly turned into a yellow-brown suspension. This mixture was then filtered through a layer of silica gel, and the yellow filtrate was concentrated under reduced pressure. The resulting crude product was purified using flash chromatography (silica gel (200 g), hexane/EtOAc, 80/1 (500 mL), 60/1 (500 mL), 40/1 (1 L), 30/1 (500 mL), 20/1 (500 mL), 10/1 (500 mL)) and diffusion pump distillation to afford 1.637 g (81%) of **9** as a colorless, viscous liquid.

**Data for 9:**

**b.p.:** 160 °C (ABT) at  $1.0 \times 10^{-4}$  mmHg

**<sup>1</sup>H NMR:** (500 MHz, CDCl<sub>3</sub>)

7.19 (t, 2 H,  $J = 7.7$ , 2 × HC(11)), 7.06 (t, 1 H,  $J = 7.3$ , HC(12)), 6.97 (d, 2 H,  $J = 7.0$ , 2 × HC(10)), 4.22 (q, 2 H,  $J = 7.2$ , H<sub>2</sub>C(2')), 4.19 (qd, 2 H,  $J = 7.2$ , 1.1,

H<sub>2</sub>C(2')), 3.14 (d, 1 H,  $J = 17.3$ , HC(2)), 2.90 (d, 1 H,  $J = 17.3$ , HC(2)), 2.75-2.72 (m, 1 H, HC(4)), 2.48 (dd, 1 H,  $J = 13.4, 7.8$ , HC(5)), 2.16 (s, 2 H, H<sub>2</sub>C(8)), 2.12 (dd, 1 H,  $J = 12.4, 2.4$ , HC(5)), 1.63 (s, 3 H, H<sub>3</sub>C(7)), 1.28 (t, 3 H,  $J = 7.2$ , H<sub>3</sub>C(3')), 1.25 (t, 3 H,  $J = 7.1$ , H<sub>3</sub>C(3')), 0.89 (s, 3 H,  $J = 7.1$ , H<sub>3</sub>C(13)), 0.02 (s, 3 H, H<sub>3</sub>CSi), 0.01 (s, 3 H, H<sub>3</sub>CSi).

<sup>13</sup>C NMR: (126 MHz, CDCl<sub>3</sub>)

173.0 (C(1')), 172.6 (C(1')), 156.9 (C(3)), 140.4 (C(6)), 128.4 (C(10)), 128.3 (C(11)), 124.1 (C(12)), 123.9 (C(9)), 61.7 (C(2')), 61.7 (C(2')), 58.5 (C(1)), 41.3 (C(2)), 38.6 (C(5)), 37.8 (C(4)), 26.2 (C(8)), 23.2 (C(13)), 23.2 (C(7)), 14.3 (C(3')), 14.3 (C(3')), -1.6 (CSi), -1.6 (CSi).

IR: (neat)

2978 (s), 1732 (s), 1624 (m), 1600 (m), 1494 (s), 1452 (s), 1367 (s), 1298 (s), 1248 (s), 1811 (s), 1110 (s), 1096 (s), 1071 (s), 1035 (s), 831 (s), 792 (s), 761 (s), 699 (s).

LRMS: (CI):

403 (73.8, [M+H]<sup>+</sup>), 387 (17.7), 311 (100.0), 239 (25.1), 209 (28.9), 181 (43.8), 149 (34.2), 135 (24.4), 107 (33.7).

HRMS: (CI, [M+H]<sup>+</sup>):

calcd.: 403.230463

found: 403.230952

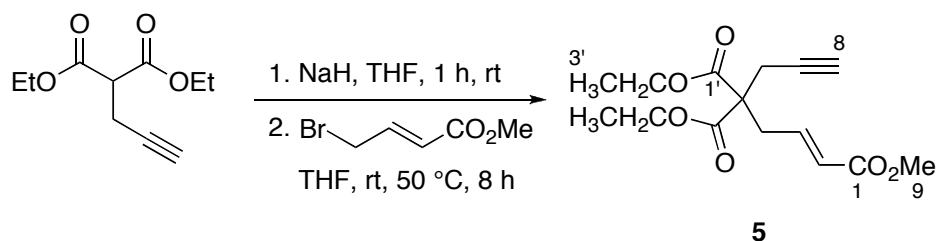
Analysis: C<sub>23</sub>H<sub>34</sub>O<sub>4</sub>Si (402.60)

calcd.: C, 68.62; H, 8.51.

found: C, 68.74; H, 8.61.

R<sub>f</sub>: 0.69 (silica gel, hexane/EtOAc, 5/1, UV)

t<sub>R</sub>: 3.13 min (Agilent Zorbax 300SB-C8, 100% MeCN (1 mL/min))

**Preparation of Methyl 5,5-Bis(carboethoxy)-2-octene-7-ynoate (5).**

In a flamed-dried, 100-mL, round-bottomed flask equipped with a magnetic stirrer and a gas inlet adaptor, NaH (60 % wt in mineral oil, 529 mg, 13.2 mmol, 1.2 equiv) was dispersed in THF (25 mL). To this suspension was added a solution of diethyl propargylmalonate (2.180 g, 11.0 mmol, 1.0 equiv) in THF (10 mL) in the course of 2 min at room temperature. Bubbling and heat evolution were observed, and the reaction mixture was stirred at room temperature under Ar. When the bubbling subsided, the reaction mixture became a slightly opaque, light-yellow solution. After 30 min of stirring, the reaction mixture was added a solution methyl 3-bromocrotonate (2.180 g, 13.2 mmol, 1.2 equiv) in THF (25 mL). The reaction mixture immediately turned into a yellow suspension, and an exotherm was observed. The reaction mixture was heated to 50 °C and was stirred under Ar for 2 h. Then, the reaction mixture was allowed to cool down, and it was subsequently quenched with a saturated solution of NH<sub>4</sub>Cl (10 mL). Consequently, all the solid quickly dissolved, and the reaction mixture was poured into a 125-mL separatory funnel containing 20 mL of water. The aqueous layer was extracted with Et<sub>2</sub>O (3 × 20 mL). The combined organic layers were washed with brine (20 mL), dried over anhydrous MgSO<sub>4</sub>, and filtered, and the filtrate was concentrated under reduced pressure. The resulting crude product was purified by flash chromatography (silica gel (200 g), hexane/EtOAc, 20/1 (750 mL), 10/1 (250 mL), 5/1 (750 mL)) and Kugelrohr distillation to afford 2.922 g (91%) of **5** as a colorless, viscous liquid.

Data for **5**:

b.p.: 193 °C (ABT) at 0.2 mmHg

<sup>1</sup>H NMR: (500 MHz, CDCl<sub>3</sub>)

6.78 (dt, 1 H, *J* = 15.6, 7.8, HC(3)), 5.96 (dt, 1H, *J* = 15.6, 1.4, HC(2)), 4.23 (qd, 4 H, *J* = 7.1, 0.7, 2 × H<sub>2</sub>C(2')), 3.73 (s, 3 H, H<sub>3</sub>(9)), 2.96 (dd, 2 H, *J* = 7.8, 1.3, H<sub>2</sub>C(4)), 2.81 (d, 2 H, *J* = 2.6, H<sub>2</sub>C(6)), 2.06 (t, 1 H, *J* = 2.7, HC(8)), 1.27 (q, 6 H, *J* = 7.1, 2 × H<sub>3</sub>C(3')).

$^{13}\text{C}$  NMR: (126 MHz,  $\text{CDCl}_3$ )

169.4 (C(1')), 166.5 (C(1)), 142.4 (C(3)), 125.5 (C(2)), 78.5 (C(7)), 72.2 (C(8)), 62.2 (C(2')), 56.5 (C(5)), 51.8 (C(9)), 25.0 (C(4)), 23.2 (C(6)), 14.2 (C(3')).

IR: (neat)

3282 (m), 2984 (m), 2123 (w), 1732 (s), 1661 (m), 1438 (m), 1278 (s), 1194 (s), 1097 (m), 1071 (m), 835 (w).

LRMS: (CI):

297 (71.6,  $[\text{M}+\text{H}]^+$ ), 265 (100.0), 251 (59.0), 237 (72.2), 223 (61.0), 191 (66.9), 177 (45.0), 163 (58.7), 151 (24.2), 119 (15.8), 91 (21.2).

HRMS: (CI,  $[\text{M}+\text{H}]^+$ ):

calcd.: 297.1338

found: 297.1332

Analysis:  $\text{C}_{24}\text{H}_{34}\text{O}_6\text{Si}$  (296.32)

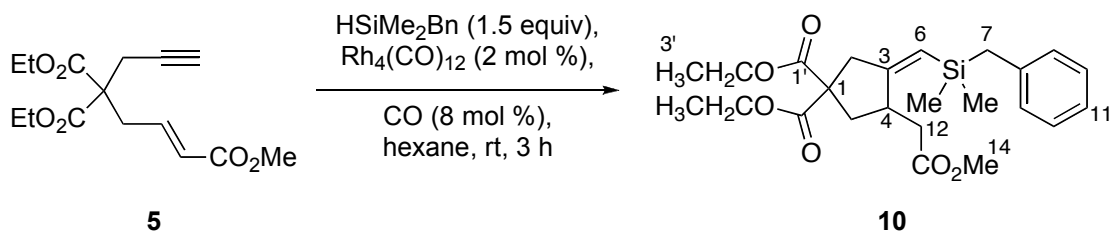
calcd.: C, 60.80; H, 6.80.

found: C, 60.46; H, 6.78.

$R_f$ : 0.24 (silica gel, hexane/EtOAc, 5/1, UV)

$t_R$ : 2.23 min (YMC-Pac Pro C18, 100% MeCN (1 mL/min))

**Silylcarbocyclization Reaction of Methyl 5,5-Bis(carboethoxy)-2-octene-7-ynoate (**5**) with Benzyldimethylsilane. Preparation of Diethyl (Z)-3-Benzyldimethylsilylmethylene-4-methoxycarbonylmethylcyclopentane-1,1-dicarboxylate (**10**).**



In an flame-dried, 25-mL, Schlenk flask with a magnetic stirrer, **5** (1.482 g, 5.00 mmol, 1.0 equiv) and benzyldimethylsilane (0.8 mL, 5.00 mmol, 1.0 equiv) were dissolved in hexane (15 mL). The Schlenk flask was purged with Ar and was subsequently sealed. In another flame-dried, 25-mL, round-bottomed flask equipped with a magnetic stirrer and a gas inlet adaptor, a dark red solution of  $\text{Rh}_4(\text{CO})_{12}$  (75 mg, 0.10 mmol, 2 mol %) and benzyldimethylsilane (0.4 mL, 2.5 mmol, 0.5 equiv) in hexane (10 mL) was prepared by stirring at room temperature under Ar

for 5 min. This solution was subsequently added into the Schlenk flask via cannulation under Ar, followed by the addition of CO (9.7 mL, 0.4 mmol, 8 mol %) via a gas-tight syringe. Upon the addition of the solution containing  $\text{Rh}_4(\text{CO})_{12}$  the reaction mixture turned from red to yellow in approximately 5 min. When the additions were completed, the reaction mixture was stirred at room temperature for 3 h. When the reaction period had completed, the reaction mixture was treated with a solution of thiourea (60 mg, 0.80 mmol, 16 mol %) in EtOH (5 mL). The reaction mixture quickly turned red and then turned into a brown suspension. This mixture was stirred at room temperature under air for approximately 20 min. This brown suspension was filtered through a layer of silica gel and it was washed with 100 mL of EtOH. The yellow filtrate was concentrated under reduced pressure. The resulting crude product was purified using flash chromatography (silica gel (210 g), hexane/DME, 40/1 (2.5 L), 20/1 (1.5 L)) and diffusion pump distillation to afford 866 mg (87%) of **10** as a colorless, viscous liquid.

Data for **10**:

b.p.: 180 °C (ABT) at  $6.0 \times 10^{-5}$  mmHg

$^1\text{H}$  NMR: (500 MHz,  $\text{CDCl}_3$ )

7.21 (t, 2 H,  $J = 7.7$ ,  $2 \times \text{HC}(10)$ ), 7.07 (t, 1 H,  $J = 7.5$ ,  $\text{HC}(11)$ ), 6.99 (d, 2 H,  $J = 7.1$ ,  $2 \times \text{HC}(9)$ ), 5.41 (d, 1 H,  $J = 1.0$ ,  $\text{HC}(6)$ ), 4.20 (dq, 2 H,  $J = 7.2$ , 1.9,  $\text{H}_2\text{C}(2')$ ), 4.17 (q, 2 H,  $J = 7.1$ ,  $\text{H}_2\text{C}(2')$ ), 3.68 (s, 3 H,  $\text{H}_3\text{C}(14)$ ), 3.17 (dt, 1 H,  $J = 16.4$ , 2.0,  $\text{HC}(2)$ ), 3.04-3.00 (m, 1 H,  $\text{HC}(4)$ ), 2.81 (d, 1 H,  $J = 16.4$ ,  $\text{HC}(2)$ ), 2.67 (dd, 1 H,  $J = 14.1$ , 8.2,  $\text{HC}(5)$ ), 2.30 (d, 1 H,  $J = 1.5$ ,  $\text{HC}(12)$ ), 2.28 (dd, 1 H,  $J = 22.4$ , 15.8,  $\text{HC}(12)$ ), 2.14 (s, 2 H,  $\text{H}_2\text{C}(7)$ ), 2.07 (dd, 1 H,  $J = 14.1$ , 4.5,  $\text{HC}(5)$ ), 1.26 (t, 3 H,  $J = 7.1$ ,  $\text{H}_3\text{C}(3')$ ), 1.23 (t, 3 H,  $J = 7.2$ ,  $\text{H}_3\text{C}(3')$ ), 0.11 (s, 3 H,  $\text{H}_3\text{CSi}$ ), 0.10 (s, 3 H,  $\text{H}_3\text{CSi}$ ).

$^{13}\text{C}$  NMR: (126 MHz,  $\text{CDCl}_3$ )

172.5 ( $\text{C}(1')$ ), 172.2 ( $\text{C}(1')$ ), 171.1 ( $\text{C}(13)$ ), 161.1 ( $\text{C}(3)$ ), 140.0 ( $\text{C}(8)$ ), 128.4 ( $\text{C}(9)$ ), 128.3 ( $\text{C}(10)$ ), 124.3 ( $\text{C}(11)$ ), 120.8 ( $\text{C}(6)$ ), 61.9 ( $\text{C}(2')$ ), 61.7 ( $\text{C}(2')$ ), 58.5 ( $\text{C}(1)$ ), 51.8 ( $\text{C}(14)$ ), 44.8 ( $\text{C}(2)$ ), 40.8 ( $\text{C}(12)$ ), 39.4 ( $\text{C}(5)$ ), 39.1 ( $\text{C}(4)$ ), 26.8 ( $\text{C}(7)$ ), 14.3 ( $\text{C}(3')$ ), 14.2 ( $\text{C}(3')$ ), -1.8 ( $\text{CSi}$ ).

IR: (neat)

2982 (m), 2954 (m), 1732 (s), 1630 (w), 1494 (m), 1437 (m), 1366 (m), 1250 (s), 1179 (s), 1073 (m), 1059 (m), 834 (m), 700 (m).

LRMS: (CI):

477 (44.4,  $[M+H]^+$ ), 431 (16.4), 355 (100.0), 267 (14.0), 207 (16.2), 63 (28.0).

HRMS: (CI,  $[M+H]^+$ ):

calcd.: 447.2171

found: 447.2200

Analysis: C<sub>24</sub>H<sub>34</sub>O<sub>6</sub>Si (446.61)

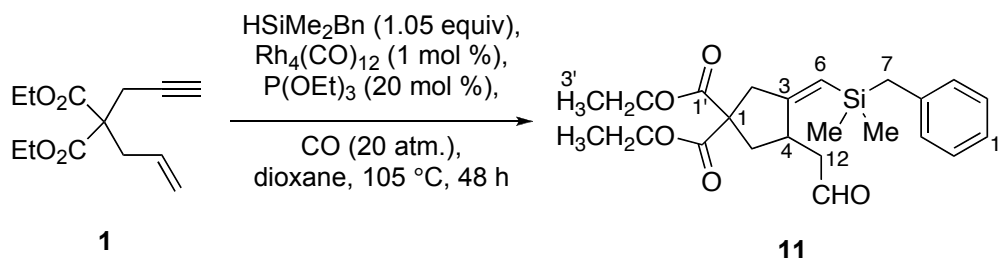
calcd.: C, 64.54; H, 7.67.

found: C, 64.42; H, 7.87.

R<sub>f</sub>: 0.39 (silica gel, hexane/EtOAc, 5/1, UV)

t<sub>R</sub>: 2.75 min (Agilent Zorbax 300SB-C8, 100% MeCN (1 mL/min))

**Carbonylative Silylcarbocyclization Reaction of 4,4-Bis(carboethoxy)-6-hepten-1-yne (1) with Benzyldimethylsilane. Preparation of Diethyl (Z)-3-Benzyldimethylsilylmethylene-4-oxoethylcyclopentane-1,1-dicarboxylate (11).**



In an flame-dried glass liner ( $\varnothing = 7$  cm) with a magnetic stirrer and a gas inlet adaptor, 4,4-bis(carboethoxy)-6-hepten-1-yne (**1**) (715 mg, 3.00 mmol, 1.0 equiv) and benzyldimethylsilane (0.5 mL, 3.15 mmol, 1.05 equiv) were dissolved in dioxane (150 mL), which was saturated with CO by bubbling for approximately 30 min. In another flame-dried, 25-mL, round-bottomed flask equipped with a magnetic stirrer and a gas inlet adaptor, a red solution of Rh<sub>4</sub>(CO)<sub>12</sub> (22 mg, 0.03 mmol, 1 mol %) in dioxane (6 mL) was prepared by stirring at room temperature under CO for 5 min. Both vessels were purged with CO. The solution containing Rh<sub>4</sub>(CO)<sub>12</sub> was added a solution of P(OEt)<sub>3</sub> (0.1 mL, 0.60 mmol, 20 mol %) in dioxane (6 mL), and the color of the mixture immediately turned to dark-red. This dark-red solution was stirred at room temperature under a CO atmosphere for 10 min, and it was subsequently added to the solution containing 4,4-bis(carboethoxy)-6-hepten-1-yne (**1**) in the liner via cannulation under CO. When the addition was completed, the liner was removed from the CO manifold and was

quickly transferred into the autoclave. The autoclave was sealed and was then purged with CO by pressurize to approximately 20 atm followed by venting. The purging process was repeated twice. Then the autoclave was pressurized with CO to 20 atm and was placed in an oil bath, in which the reaction mixture was heated to 105 °C and was stirred for 48 h. When the reaction period had completed, the autoclave was allowed to cool down to room temperature before the CO was vented. The reaction mixture, which had turned into a bright-yellow solution, was treated with a solution of thiourea (22 mg, 0.30 mmol, 10 mol %) in EtOH (5 mL). This mixture was stirred at room temperature under air for approximately 20 min, and it was concentrated under reduced pressure. The resulting crude product was purified using flash chromatography (silica gel (120 g), hexane/EtOAc, 40/1 (500 mL), 30/1 (500 mL), 20/1 (500 mL), 10/1 (500 mL), 5/1 (500 mL)) and diffusion pump distillation to afford 891 mg (71%) of **11** as a colorless, viscous liquid.

Data for **11**:

b.p.: 200 °C (ABT) at  $1.6 \times 10^{-4}$  mmHg

<sup>1</sup>H NMR: (500 MHz, CDCl<sub>3</sub>)

9.63 (d, 1 H,  $J = 0.4$ , HC(13)), 7.21 (t, 2 H,  $J = 7.6$ , 2 × HC(10)), 7.08 (t, 1 H,  $J = 7.6$ , HC(11)), 6.98 (d, 2 H,  $J = 7.1$ , 2 × HC(9)), 5.41 (d, 1 H,  $J = 1.0$ , HC(6)), 4.19 (q, 2 H,  $J = 7.1$ , H<sub>2</sub>C(2')), 4.19 (q, 2 H,  $J = 7.1$ , H<sub>2</sub>C(2')), 3.17 (dt, 1 H,  $J = 16.6$ , 2.1, HC(2)), 3.04-3.01 (m, 1 H, HC(4)), 2.86 (d, 1 H,  $J = 16.4$ , HC(2)), 2.67 (dd, 1 H,  $J = 14.1$ , 8.2, HC(5)), 2.45 (ddd, 1 H,  $J = 17.8$ , 11.2, 1.7, HC(12)), 2.23 (dd, 1 H,  $J = 17.8$ , 2.9, HC(12)), 2.12 (s, 2 H, H<sub>2</sub>C(7)), 1.96 (dd, 1 H,  $J = 13.9$ , 4.4, HC(5)), 1.25 (t, 3 H,  $J = 7.3$ , H<sub>3</sub>C(3')), 1.24 (t, 3 H,  $J = 7.1$ , H<sub>3</sub>C(3')), 0.09 (s, 3 H, H<sub>3</sub>CSi), 0.08 (s, 3 H, H<sub>3</sub>CSi).

<sup>13</sup>C NMR: (126 MHz, CDCl<sub>3</sub>)

200.8 (C(13)), 172.3 (C(1')), 171.6 (C(1')), 161.4 (C(3)), 140.0 (C(8)), 128.5 (C(9) or C(10)), 128.4 (C(9) or C(10)), 124.4 (C(11)), 120.4 (C(6)), 61.9 (C(2')), 61.8 (C(2')), 58.6 (C(1)), 50.7 (C(5)), 44.8 (C(2)), 39.6 (C(12)), 36.5 (C(4)), 26.9 (C(7)), 14.3 (C(3')), 14.2 (C(3')), -1.6 (CSi), -1.8 (CSi).

IR: (neat)

2981 (m), 1730 (s), 1631 (w), 1494 (m), 1452 (w), 1367 (w), 1249 (s), 1186 (m), 1158 (m), 1082 (w), 1060 (w), 837 (m), 700 (m).

LRMS: (CI):

417 (22.5,  $[M+H]^+$ ), 399 (15.1), 343 (15.2), 325 (51.6), 297 (6.4), 279 (12.1), 251 (57.5), 223 (8.9), 205 (15.1), 177 (100.0), 149 (13.5).

HRMS: (CI,  $[M+H]^+$ ):

calcd.: 417.209399

found: 417.209265

Analysis:  $C_{22}H_{32}O_5Si$  (416.58)

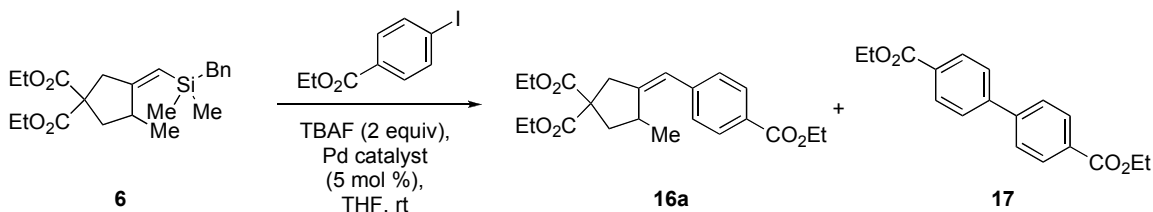
calcd.: C, 66.31; H, 7.74.

found: C, 66.22; H, 7.95.

$R_f$ : 0.38 (silica gel, hexane/EtOAc, 5/1, UV)

$t_R$ : 2.83 min (Agilent Zorbax 300SB-C8, 100% MeCN (1 mL/min))

**General Procedure of the Survey of Palladium Catalysts for the Cross-Coupling of **6** with Ethyl 4-Iodobenzoate.**



Alkylidenesilane **6** (78 mg, 0.20 mmol, 1.0 equiv) and naphthalene (26 mg, 0.20 mmol) were dissolved in a solution of TBAF $\cdot$ 3H<sub>2</sub>O (1.0 M in THF, 0.40 mL, 0.40 mmol, 2.0 equiv) in a 5-mL, round-bottomed flask with a magnetic stir bar fitted with a gas inlet adaptor, and the resulting light-yellow solution was stirred for approximately 3 min. Then ethyl 4-iodobenzoate (34  $\mu$ L, 0.20 mmol, 1.0 equiv) and the palladium complex (5 mol % Pd used) were added to the solution sequentially. The flask was purged with Ar, and the reaction mixture was stirred at room temperature under Ar atmosphere. The reaction was monitored by GC analysis at certain intervals until the formation of desired product **16a** stopped. Sampling of the reaction was performed by removing 20  $\mu$ L aliquot of the mixture via syringe. The aliquot was quenched by a solution (40  $\mu$ L) of dimethylaminoethanethiol $\cdot$ HCl (10 wt % in water), and the mixture was loaded onto a small plug of silica gel and eluted with 8 mL of MeCN. The aliquot was then



analyzed by HPLC using the general HPLC shown below. Response factors ( $R_f$ ) were obtained by equation 1 and are shown below:

$$\text{Eq 1: Response factor for A} = \frac{(\text{mmol A} \times \text{area naphthalene})}{(\text{mmol naphthalene} \times \text{area A})}$$

naphthalene (mmol)	naphthalene (area)	Ethyl 4- iodobenzoate (mmol)	Ethyl 4- iodobenzoate (area)	response factor ( $R_f$ )
0.09519	6201.1740	0.09345	12326.3780	0.4939
0.09519	5291.1790	0.09345	11694.1890	0.4442
0.09519	7150.4010	0.09345	13121.7800	0.5134

naphthalene (mmol)	naphthalene (area)	<b>16a</b> (mmol)	<b>16a</b> (area)	response factor ( $R_f$ )
0.09987	858.3210	0.05196	1814.9010	0.2461
0.09987	1733.6155	0.05196	3407.5163	0.2647
0.09987	1078.3440	0.05196	2257.7180	0.2485
0.1030	1406.8980	0.04894	2552.8720	0.2619
0.1030	1011.8490	0.04894	1911.9770	0.2515
0.1030	809.1140	0.04894	1529.8480	0.2512

naphthalene (mmol)	naphthalene (area)	<b>17</b> (mmol)	<b>17</b> (area)	response factor ( $R_f$ )
0.09753	7027.8688	0.03063	5293.7525	0.4169
0.09753	6476.3840	0.03063	5067.9850	0.4013
0.09753	7272.048.	0.03063	5832.5085	0.3916
0.1061	5634.4310	0.03627	4930.0545	0.3906
0.1061	7744.4018	0.03627	6920.7515	0.3825
0.1061	7426.8445	0.03627	6701.0830	0.3789

$$\text{Eq 2: HPLC yield of A} = \frac{(\text{area A} / \text{mmol A})}{(\text{area naphthalene} / \text{mmol naphthalene})} \times \text{Rf A}$$

### General HPLC Method

Injectons were made onto an Agilent Zorbax 300-SB C8 column. Compounds were separated using a gradient of increasing concentration of acetonitrile in a mobile phase of MeCN/water, 60/40 (1 mL/min). The column solvent gradient program is as follows: 60% (MeCN) to 100% ramp at 4%/min, 100% for 2 min, 100% to 60% gradient at 11.4%/min. The total run time is 16 min.

#### Table 2, entry 1

Following the General Procedure, **6** (78 mg, 0.20 mmol, 1.0 equiv) and naphthalene (26 mg, 0.20 mmol, 1.0 equiv) in a 10-mL, round-bottomed flask equipped with a gas inlet adaptor and a magnetic stirrer was dissolved in a solution of TBAF•3H<sub>2</sub>O (1.0 M in THF, 0.4 mL, 0.40 mmol, 2.0 equiv), and stirred for approximately 3 min. Then ethyl 4-iodobenzoate (34 µL, 0.20 mmol) and Pd(dba)<sub>2</sub> (6 mg, 0.05 mmol, 5 mol %) were added to the solution sequentially. The flask was purged with Ar, and the reaction mixture was stirred at room temperature under Ar atmosphere for 4 h. An aliquot of the mixture was then taken for HPLC analysis using the general HPLC method. 2 h: **17**, *t<sub>R</sub>* 6.86 min (33.9, 1%); **16a**, *t<sub>R</sub>* 7.70 min (2009.6, 92%) 4 h: **17**, *t<sub>R</sub>* 6.88 min (29.7, 2%); **16a**, *t<sub>R</sub>* 7.72 min (1134.6, 104%).

#### Table 2, entry 2

Following the General Procedure, **6** (78 mg, 0.20 mmol, 1.0 equiv) and naphthalene (26 mg, 0.20 mmol, 1.0 equiv) in a 10-mL, round-bottomed flask equipped with a gas inlet adaptor and a magnetic stirrer were dissolved in a solution of TBAF•3H<sub>2</sub>O (1.0 M in THF, 0.4 mL, 0.40 mmol, 2.0 equiv), and stirred for approximately 3 min. Then ethyl 4-iodobenzoate (34 µL, 0.20 mmol, 1.0 equiv) and Pd<sub>2</sub>(dba)<sub>3</sub> (5 mg, 0.025 mmol, 2.5 mol %) were added to the solution sequentially. The flask was purged with Ar, and the reaction mixture was stirred at room temperature under Ar atmosphere for 4 h. An aliquot of the mixture was then taken for HPLC analysis using the general HPLC method. 2 h: **17**, *t<sub>R</sub>* 6.73 min (45.0, 1%); **16a**, *t<sub>R</sub>* 7.55 min (1785.4, 83%). 4 h: **17**, *t<sub>R</sub>* 6.73 min (50.8, 2%); **16a**, *t<sub>R</sub>* 7.54 min (1306.9, 90%).

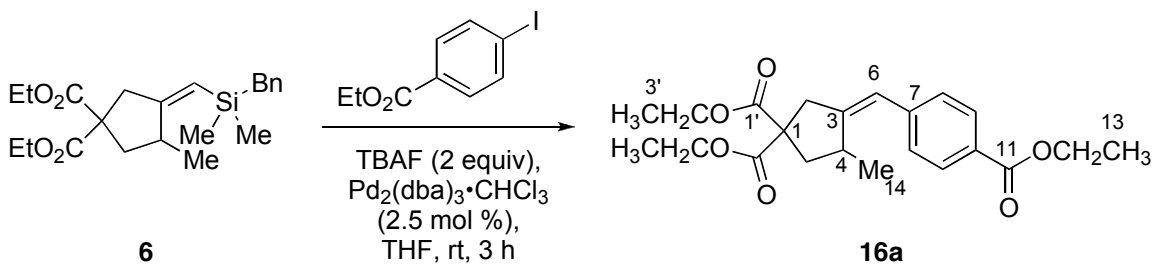
**Table 2, entry 3**

Following the General Procedure, **6** (78 mg, 0.20 mmol, 1.0 equiv) and naphthalene (26 mg, 0.20 mmol, 1.0 equiv) in a 10-mL, round-bottomed flask equipped with a gas inlet adaptor and a magnetic stirrer was dissolved in a solution of TBAF•3H<sub>2</sub>O (1.0 M in THF, 0.4 mL, 0.40 mmol, 2.0 equiv), and stirred for approximately 3 min. Then ethyl 4-iodobenzoate (34  $\mu$ L, 0.20 mmol, 1.0 equiv) and Pd<sub>2</sub>(dba)<sub>3</sub>•CHCl<sub>3</sub> (5 mg, 0.025 mmol, 2.5 mol %) were added to the solution sequentially. The flask was purged with Ar, and the reaction mixture was stirred at room temperature under Ar atmosphere for 4 h. An aliquot of the mixture was then taken for HPLC analysis using the general HPLC method. 2 h: **17**, *t*<sub>R</sub> 6.89 min (18.2, 1%); **16a**, *t*<sub>R</sub> 7.73 min (881.8, 99%). 4 h: **17**, *t*<sub>R</sub> 6.88 min (47.9, 2%); **16a**, *t*<sub>R</sub> 7.72 min (1489.5, 100%).

**Table 2, entry 4**

Following the General Procedure, **6** (78 mg, 0.20 mmol, 1.0 equiv) and naphthalene (26 mg, 0.20 mmol, 1.0 equiv) in a 10-mL, round-bottomed flask equipped with a gas inlet adaptor and a magnetic stirrer was dissolved in a solution of TBAF•3H<sub>2</sub>O (1.0 M in THF, 0.4 mL, 0.40 mmol, 2.0 equiv), and stirred for approximately 3 min. Then ethyl 4-iodobenzoate (34  $\mu$ L, 0.20 mmol, 1.0 equiv) and [π-allylPdCl]<sub>2</sub> (2 mg, 0.025 mmol, 2.5 mol %) were added to the solution sequentially. The flask was purged with Ar, and the reaction mixture was stirred at room temperature under Ar atmosphere for 4 h. An aliquot of the mixture was then taken for HPLC analysis using the general HPLC method. 2 h: **17**, *t*<sub>R</sub> 6.88 min (17.8, 1%); **16a**, *t*<sub>R</sub> 7.71 min (1033.4, 80%) 4 h: **17**, *t*<sub>R</sub> 6.89 min (24.3, 3%); **16a**, *t*<sub>R</sub> 7.70 min (460.4, 78%).

**Cross-Coupling Reaction of 6 with Ethyl 4-Iodobenzoate. Preparation of Diethyl (Z)-3-(4-Ethoxycarbonylbenzylidene)-4-methylcyclopentane-1,1-dicarboxylate (16a).**



Alkylidenesilane **6** (428 mg, 1.10 mmol, 1.1 equiv) in a 5-mL, round-bottomed flask with a magnetic stir bar and fitted with a gas inlet adaptor was dissolved in a solution of

TBAF•3H<sub>2</sub>O (1.0 M in THF, 2.0 mL, 2.0 mmol, 2.0 equiv), and the resulting light-yellow solution was stirred at room temperature under Ar for 3 min. Then ethyl 4-iodobenzoate (167  $\mu$ L, 1.00 mmol, 1.0 equiv) and Pd<sub>2</sub>(dba)<sub>3</sub>•CHCl<sub>3</sub> (26 mg, 0.025 mmol, 2.5 mol %) were added to the solution sequentially. The flask was purged with Ar, and the reaction mixture was stirred at room temperature under Ar atmosphere for 3 h. Then, the reaction mixture was passed through thin layer of silica gel (approximately 1 cm) followed by a wash of EtOAc (100 mL). The dark-brown filtrate was added silica gel (1 g) and was concentrated under reduced pressure. The crude product adsorbed on silica gel was purified using flash chromatography (first column: silica gel (45 g), hexane/EtOAc, 40/1 (500 mL), 20/1 (1.25 L), second column: silica gel (45 g), hexane/EtOAc = 50/1 (250 mL), 40/1 (750 mL), 20/1 (500 mL), 10/1 (500 mL)), reverse phase flash chromatography (reverse phase silica gel (20 g), MeCN/H<sub>2</sub>O, 1/1 (250 mL), 2/1 (250 mL), 3/1 (250 mL)), and diffusion pump distillation to afford 350 mg (90%) of **16a** as a colorless, viscous liquid.

Data for **16a**:

b.p.: 175 °C (ABT) at  $9.0 \times 10^{-5}$  mmHg

<sup>1</sup>H NMR: (500 MHz, CDCl<sub>3</sub>)

7.98 (dd, 2 H,  $J = 6.6, 1.7, 2 \times \text{HC}(9)$ ), 7.33 (d, 2 H,  $J = 8.4, 2 \times \text{HC}(8)$ ), 6.37 (s, 1 H, HC(6)), 4.37 (q, 2 H,  $J = 7.1, \text{H}_2\text{C}(12)$ ), 4.26-4.17 (m, 4 H,  $2 \times \text{H}_2\text{C}(2')$ ), 3.30 (dt, 1 H,  $J = 16.3, 2.1, \text{HC}(2)$ ), 3.36-3.33 (m, 1 H, HC(4)), 3.00 (d, 1 H,  $J = 16.3, \text{HC}(2)$ ), 2.76 (ddd, 1 H,  $J = 13.3, 8.0, 1.4, \text{HC}(5)$ ), 1.97 (dd, 1 H,  $J = 13.3, 6.2, \text{HC}(5)$ ), 1.40 (t, 3 H,  $J = 7.1, \text{H}_3\text{C}(13)$ ), 1.39 (t, 3 H,  $J = 6.6, \text{H}_3\text{C}(3')$ ), 1.25 (t, 3 H,  $J = 6.5, \text{H}_3\text{C}(3')$ ), 1.06 (d, 3 H,  $J = 7.9, \text{H}_3\text{C}(14)$ ).

<sup>13</sup>C NMR: (126 MHz, CDCl<sub>3</sub>)

172.0 (C(1')), 171.9 (C(1')), 166.7 (C(11)), 149.9 (C(3)), 142.3 (C(7)), 129.8 (C(9)), 129.8 (C(10), C(8)), 122.0 (C(6)), 61.8 (C(2')), 61.8 (C(2')), 61.1 (C(12)), 58.4 (C(1)), 43.4 (C(2)), 42.6 (C(5)), 34.9 (C(4)), 19.6 (C(14)), 14.5 (C(13)), 14.2 (C(3')).

IR: (neat)

3463 (w), 2980 (s), 1732 (s), 1606 (s), 1447 (m), 1367 (m), 1274 (s), 1178 (s), 1108 (s), 1068 (s), 1021 (s), 877 (m), 772 (m).

LRMS: (EI):

241 (53.0), 268 (13.5), 269 (13.7), 314 (100.0), 343 (13.4), 388 (21.0,  $[M]^+$ ).

HRMS: (EI,  $[M]^+$ ):

calcd.: 388.188589

found: 388.188594

Analysis: C<sub>22</sub>H<sub>28</sub>O<sub>6</sub> (388.45)

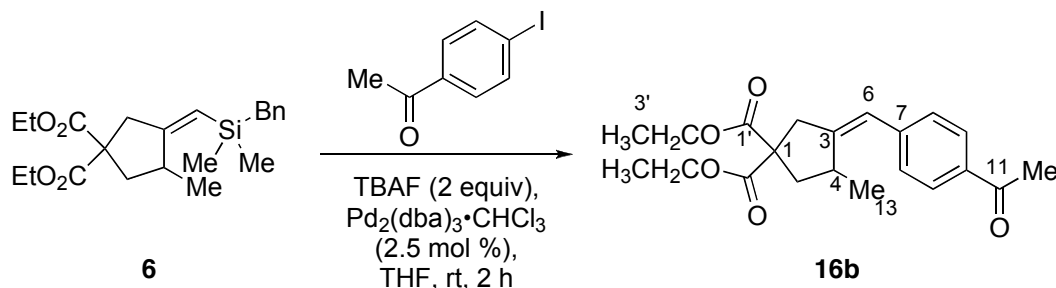
calcd.: C, 68.02; H, 7.27.

found: C, 68.27; H, 7.37.

R<sub>f</sub>: 0.35 (silica gel, hexane/EtOAc, 5/1, UV)

t<sub>R</sub>: 3.075 min (Agilent Zorbax 300SB-C8, 100% MeCN (1 mL/min))

**Cross-Coupling Reaction of 6 with 4-Iodoacetophenone. Preparation of Diethyl (Z)-3-(4-Methylcarbonylbenzylidene)-4-methylcyclopentane-1,1-dicarboxylate (16b).**



Alkylidenesilane **6** (426 mg, 1.10 mmol, 1.1 equiv) in a 5-mL, round-bottomed flask with a magnetic stir bar and fitted with a gas inlet adaptor, was dissolved in a solution of TBAF·3H<sub>2</sub>O (1.0 M in THF, 2.0 mL, 2.0 mmol, 2.0 equiv) and the resulting light-yellow solution was stirred at room temperature under Ar for approximately 3 min. Then 4-iodoacetophenone (247 mg, 1.00 mmol, 1.0 equiv) and Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub> (26 mg, 0.025 mmol, 2.5 mol %) were added to the solution sequentially. The flask was purged with Ar, and the reaction mixture was stirred at room temperature under Ar atmosphere for 2 h. Then, the reaction mixture was passed through thin layer of silica gel (approximately 1 cm) followed by a wash of EtOAc (100 mL). The dark-brown filtrate was added silica gel (1 g) and was concentrated under reduced pressure. The crude product adsorbed on silica gel was purified using flash chromatography (silica gel (40 g), hexane/EtOAc, 40/1 (250 mL), 20/1 (250 mL), 10/1 (500 mL), 5/1 (500 mL)) and diffusion pump distillation to afford 308 mg (86%) of **16b** as a colorless,

viscous liquid.

**Data for 16b:**

**b.p.:** 162 °C (ABT) at  $1.2 \times 10^{-4}$  mmHg

**<sup>1</sup>H NMR:** (500 MHz, CDCl<sub>3</sub>)  
7.90 (d, 2 H,  $J = 7.9$ , HC(9)), 7.36 (d, 2 H,  $J = 8.4$ , HC(8)), 6.37 (s, 1 H, HC(6)), 4.25-4.17 (m, 4 H,  $2 \times \text{H}_2\text{C}(2')$ ), 3.30 (dt, 1 H,  $J = 16.3, 2.4$ , HC(2)), 3.30-3.28 (m, 1 H, HC(4)), 3.00 (d, 1 H,  $J = 16.3$ , HC(2)), 2.77 (dd, 1 H,  $J = 13.2, 8.0$ , HC(5)), 2.60 (s, 3H, H<sub>3</sub>C(12)), 1.98 (dd, 1 H,  $J = 13.3, 5.8$ , HC(5)), 1.28 (td, 3 H,  $J = 7.2, 0.8$ , H<sub>3</sub>C(3')), 1.25 (ts, 3 H,  $J = 7.1, 0.6$ , H<sub>3</sub>C(3')), 1.07 (d, 3 H,  $J = 6.9$ , H<sub>3</sub>C(12)).

**<sup>13</sup>C NMR:** (126 MHz, CDCl<sub>3</sub>)  
197.9 (C(11)), 172.0 (C(1')), 171.8 (C(1')), 150.3 (C(3)), 142.6 (C(10)), 135.0 (C(7)), 128.6 (C(9)), 128.5 (C(8)), 121.9 (C(6)), 61.8 (C(2')), 61.8 (C(2')), 58.4 (C(12)), 43.4 (C(1)), 43.4 (C(2)), 42.6 (C(5)), 35.0 (C(4)), 26.7 (C(12)), 19.6 (C(14)), 19.6 (C(13)), 14.2 (C(3')).

**IR:** (neat)

3462 (w), 2980 (s), 2256 (w), 1732 (s), 1682 (s), 1602 (s), 1447 (m), 1412 (m), 1365 (s), 1268 (s), 1182 (s), 1099 (s), 1067 (s), 1033 (m), 916 (m), 870 (m), 733 (s).

**LRMS:** (EI):

211 (56.8), 284 (100.0), 313 (5.2), 358 (25.1, [M]<sup>+</sup>)

**HRMS:** (EI, [M]<sup>+</sup>):

calcd.: 358.178024

found: 358.178071

**Analysis:** C<sub>21</sub>H<sub>26</sub>O<sub>5</sub> (358.43)

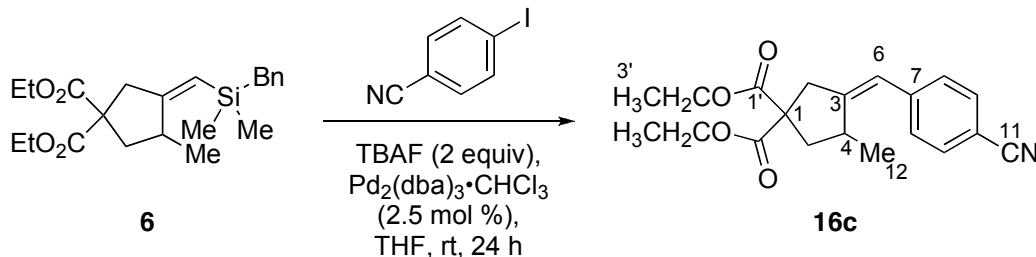
calcd.: C, 70.37; H, 7.31.

found: C, 70.40; H, 7.32.

**R<sub>f</sub>:** 0.34 (silica gel, hexane/EtOAc, 5/1, UV)

**t<sub>R</sub>:** 3.050 min (Agilent Zorbax 300SB-C8, 100% MeCN (1 mL/min))

**Cross-Coupling Reaction of 6 with 2-Iodotoluene. Preparation of Diethyl (Z)-3-(4-Cyanobenzylidene)-4-methylcyclopentane-1,1-dicarboxylate (16c).**



Alkydienesilane **6** (427 mg, 1.10 mmol, 1.1 equiv) in a 10-mL, round-bottomed flask with a magnetic stir bar and fitted with a gas inlet adaptor, was dissolved in a solution of TBAF·3H<sub>2</sub>O (1.0 M in THF, 2.0 mL, 2.0 mmol, 2.0 equiv) and the resulting light-yellow solution was stirred at room temperature under Ar for approximately 3 min. Then 4-iodobenzonitrile (229 mg, 1.00 mmol, 1.0 equiv) and Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub> (26 mg, 0.025 mmol, 2.5 mol %) were added to the solution sequentially. The flask was purged with Ar, and the reaction mixture was stirred at room temperature under Ar atmosphere for 24 h. Then, the reaction mixture was passed through thin layer of silica gel (approximately 1 cm) followed by a wash of EtOAc (100 mL). The dark-brown filtrate was added silica gel (1 g) and was concentrated under reduced pressure. The crude product adsorbed on silica gel was purified using flash chromatography (silica gel (45 g), hexane/EtOAc, 40/1 (500 mL), 30/1 (500 L), 20/1 (1.5 L)), reverse phase flash chromatography (reverse phase silica gel (30 g), MeCN/H<sub>2</sub>O, 5/1), and diffusion pump distillation to afford 259 mg (76%) of **16c** as a colorless, viscous liquid.

**Data for 16c:**

**b.p.:** 167 °C (ABT) at  $9.0 \times 10^{-5}$  mmHg

**<sup>1</sup>H NMR:** (500 MHz, CDCl<sub>3</sub>)

7.57 (d, 2 H,  $J = 8.3$ , HC(9)), 7.34 (d, 2 H,  $J = 8.3$ , HC(8)), 5.33 (s, 1 H, HC(6)), 4.24-4.15 (m, 4 H,  $2 \times \text{H}_2\text{C}(2')$ ), 3.29 (dt, 1 H,  $J = 16.4, 2.4$ , HC(2)), 3.24 (dd, 1 H,  $J = 8.0, 1.7$ , HC(4)), 2.98 (d, 2 H,  $J = 16.4$ , HC(2)), 2.74 (ddd, 1 H,  $J = 13.4, 8.2, 1.4$ , HC(5)), 1.97 (dd, 1 H,  $J = 13.4, 5.9$ , H<sub>3</sub>C(5)), 1.26 (t, 3 H,  $J = 7.1$ , H<sub>3</sub>C(3')), 1.23 (t, 3 H,  $J = 7.1$ , H<sub>3</sub>C(3')), 1.04 (d, 3 H,  $J = 6.8$ , H<sub>3</sub>C(12)).

**<sup>13</sup>C NMR:** (126 MHz, CDCl<sub>3</sub>)

171.8 (C(1')), 171.7 (C(1')), 151.4 (C(3)), 142.3 (C(7)), 132.2 (C(9)), 128.9 (C(8)), 121.3 (C(6)), 119.3 (C(11)), 109.7 (C(10)), 61.8 (C(2')), 61.8 (C(2')), 58.2

(C(1)), 43.3 (C(2)), 42.4 (C(5)), 34.9 (C(4)), 14.5 (C(12)), 14.2 (C(3')).

IR: (neat)

3458 (w), 2981 (m), 2226 (m), 1731 (s), 1604 (m), 1367 (m), 1276 (s), 1247 (s), 1178 (s), 1099 (m), 1068 (m), 1033 (m), 870 (m), 757 (w).

LRMS: (EI):

341 (16.0,  $[M]^+$ ), 267 (91.3), 194 (87.5), 154 (26.2), 130 (100.0), 116 (21.0), 102 (60.2), 76 (28.3), 62 (39.3).

HRMS: (EI,  $[M]^+$ ):

calcd.: 341.162708

found: 341.162604

Analysis:  $C_{20}H_{26}NO_4$  (341.40)

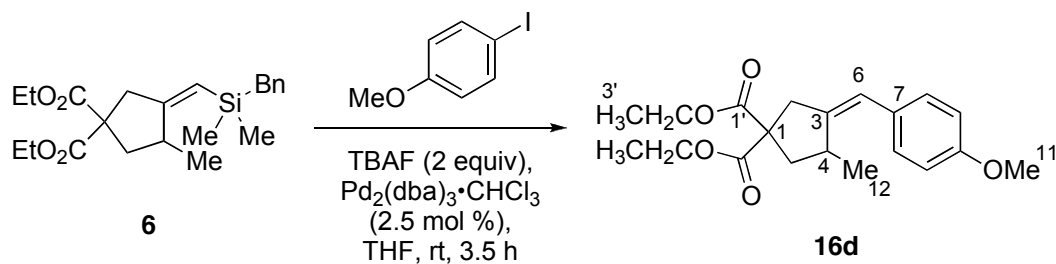
calcd.: C, 70.36; H, 6.79; N, 4.10.

found: C, 70.05; H, 6.76; N, 4.25.

R<sub>f</sub>: 0.31 (silica gel, hexane/EtOAc, 5/1, UV)

t<sub>R</sub>: 3.20 min (Agilent Zorbax 300SB-C8, 100% MeCN (1 mL/min))

**Cross-Coupling Reaction of 6 with 4-Iodoanisole. Preparation of Diethyl (Z)-3-(4-Methoxybenzylidene)-4-methylcyclopentane-1,1-dicarboxylate (16d).**



Alkylidenesilane **6** (427 mg, 1.10 mmol, 1.1 equiv) in a 5-mL, round-bottomed flask with a magnetic stir bar and fitted with a gas inlet adaptor, was dissolved in a solution of TBAF·3H<sub>2</sub>O (1.0 M in THF, 2.0 mL, 2.0 mmol, 2.0 equiv) and the resulting light-yellow solution was stirred at room temperature under Ar for approximately 3 min. Then 4-iodoanisole (234 mg, 1.00 mmol, 1.0 equiv) and  $Pd_2(dba)_3 \cdot CHCl_3$  (26 mg, 0.025 mmol, 2.5 mol %) were added to the solution sequentially. The flask was purged with Ar, and the reaction mixture was stirred at room temperature under Ar atmosphere for 3.5 h. Then, the reaction mixture was passed through thin layer of silica gel (Approximately 1 cm) followed by a wash of EtOAc (100



mL). The dark-brown filtrate was added silica gel (1 g) and was concentrated under reduced pressure. The crude product adsorbed on silica gel was purified using flash chromatography (silica gel (40 g), hexane/EtOAc, 40/1 (1 L), 20/1 (750 mL)), reverse phase flash chromatography (reverse phase silica gel (30 g), MeOH/H<sub>2</sub>O, 1/1 (250 mL), 2/1 (300 mL), 3/1 (450 mL)), and diffusion pump distillation to afford 286 mg (82%) of **16d** as a yellow, viscous liquid.

Data for **16d**:

b.p.: 147 °C (ABT) at  $8.5 \times 10^{-5}$  mmHg

<sup>1</sup>H NMR: (500 MHz, CDCl<sub>3</sub>)

7.19 (d, 2 H,  $J = 8.5$ , 2 × HC(8)), 6.83 (d, 2 H,  $J = 8.7$ , 2 × HC(9)), 6.26 (s, 1 H, HC(6)), 4.24-4.15 (m, 4 H, 2 × H<sub>2</sub>C(2')), 3.80 (s, 3 H, H<sub>3</sub>C(11)), 3.26 (dt, 1 H,  $J = 16.9$ , 2.5, HC(2)), 3.24-3.20 (m, 1 H, HC(4)), 2.93 (d, 1 H,  $J = 17.0$ , HC(2)), 2.74 (ddd, 1 H,  $J = 15.9$ , 8.2, 1.1, HC(5)), 1.93 (dd, 1 H,  $J = 13.2$ , 6.4, HC(5)), 1.26 (t, 3 H,  $J = 7.4$ , H<sub>3</sub>C(3')), 1.23 (t, 3 H,  $J = 7.2$ , H<sub>3</sub>C(3')), 1.07 (d, 3 H,  $J = 7.2$ , H<sub>3</sub>C(12)).

<sup>13</sup>C NMR: (126 MHz, CDCl<sub>3</sub>)

172.3 (C(1')), 172.0 (C(1')), 158.1 (C(3)), 145.0 (C(7)), 130.4 (C(10)), 129.6 (C(9)), 122.0 (C(6)), 113.8 (C(8)), 61.7 (C(2')), 61.6 (C(2')), 58.5 (C(1)), 55.4 (C(11)), 43.1 (C(2)), 42.7 (C(5)), 34.5 (C(4)), 19.6 (C(12)), 14.2 (C(3')).

IR: (neat)

3462 (s), 2979 (s), 1373 (s), 1732 (s), 1608 (s), 1511 (s), 1493 (m), 1463 (m), 1367 (m), 1246 (s), 1178 (s), 1098 (m), 1066 (m), 1034 (s), 863 (m), 824 (m).

LRMS: (EI):

121 (67.3), 199 (81.6), 272 (100.0), 346 (44.0, [M]<sup>+</sup>).

HRMS: (EI, [M]<sup>+</sup>):

calcd.: 346.178024

found: 346.177374

Analysis: C<sub>20</sub>H<sub>26</sub>O<sub>5</sub> (346.42)

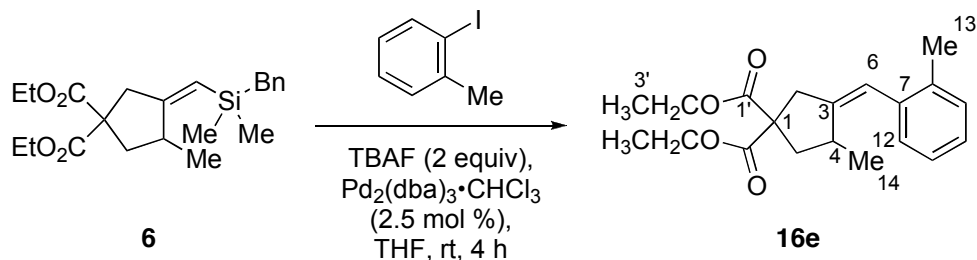
calcd.: C, 69.34; H, 7.56.

found: C, 69.30; H, 7.50.

R<sub>f</sub>: 0.37 (silica gel, hexane/EtOAc, 5/1, UV)

$t_R$ : 6.875 min (general HPLC method)

**Cross-Coupling Reaction of 6 with 2-Iodotoluene. Preparation of Diethyl (Z)-3-(2-Methylbenzylidene)-4-methylcyclopentane-1,1-dicarboxylate (16e).**



Benzylidenesilane **6** (427 mg, 1.10 mmol, 1.1 equiv) in a 5-mL, round-bottomed flask with a magnetic stir bar and fitted with a gas inlet adaptor, was dissolved in a solution of TBAF•3H<sub>2</sub>O (1.0 M in THF, 2.0 mL, 2.0 mmol, 2.0 equiv) and the resulting light-yellow solution was stirred at room temperature under Ar for approximately 3 min. Then 2-iodotoluene (127  $\mu\text{L}$ , 1.00 mmol, 1.0 equiv) and Pd<sub>2</sub>(dba)<sub>3</sub>•CHCl<sub>3</sub> (26 mg, 0.025 mmol, 2.5 mol %) were added to the solution sequentially. The flask was purged with Ar, and the reaction mixture was stirred at room temperature under Ar atmosphere for 4 h. Then, the reaction mixture was passed through thin layer of silica gel (approximately 1 cm) followed by a wash of EtOAc (100 mL). The dark-brown filtrate was added silica gel (1 g) and was concentrated under reduced pressure. The crude product adsorbed on silica gel was purified using flash chromatography (silica gel (75 g), hexane/EtOAc, 40/1) and diffusion pump distillation to afford 279.2 mg (85%) of **16e** as a colorless, viscous liquid.

**Data for 16e:**

**b.p.:** 128 °C (ABT) at  $9.0 \times 10^{-5}$  mmHg

**<sup>1</sup>H NMR:** (500 MHz, CDCl<sub>3</sub>)

7.20-7.17 (m, 1 H, HC(12)), 7.16-7.11 (m, 3 H, HC(Aryl)), 6.37 (s, 1 H, HC(6)), 4.25-4.19 (m, 4 H, 2 × H<sub>2</sub>C(2')), 3.23 (ddd, 1 H,  $J = 15.9, 2.3, 2.3$ , H<sub>3</sub>C(2)), 3.03-2.99 (m, 1 H, HC(4)), 3.01 (d, 1 H,  $J = 16.1$ , HC(2)), 2.68 (ddd, 1 H,  $J = 13.3, 8.2, 1.4$ , HC(5)), 2.22 (s, 3 H, H<sub>3</sub>C(13)), 1.84 (dd, 1 H,  $J = 13.3, 7.2$ , HC(5)), 1.28 (t, 3 H,  $J = 7.1$ , H<sub>3</sub>C(3')), 1.28 (t, 3 H,  $J = 7.1$ , H<sub>3</sub>C(3')), 0.83 (d, 3 H,  $J = 6.8$ , H<sub>3</sub>C(12)).

$^{13}\text{C}$  NMR: (126 MHz,  $\text{CDCl}_3$ )

172.2 (C(1')), 172.0 (C(1')), 146.7 (C(3)), 137.5 (C(7)), 136.2 (C(8)), 129.8 (C(Aryl)), 128.5 (C(12)), 126.8 (C(Aryl)), 125.7 (C(Aryl)), 121.9 (C(6)), 61.7 (C(2')), 61.7 (C(2')), 58.9 (C(1)), 42.5 (C(5)), 42.4 (C(2)), 34.6 (C(4)), 20.1 (C(13)), 19.7 (C(14)), 14.3 (C(3')), 14.3 (C(3')).

IR: (neat)

3464 (w), 2980 (m), 1372 (s), 1459 (m), 1366 (s), 1244 (s), 1176 (m), 1098 (m), 1066 (m), 1034 (m), 1178 (s), 1098 (m), 1066 (m), 1034 (s), 863 (s), 737 (m).

LRMS: (EI):

105 (43.9), 183 (87.0), 256 (100.0), 330 (32.7,  $[\text{M}]^+$ ).

HRMS: (EI,  $[\text{M}]^+$ ):

calcd.: 330.183110

found: 330.182732

Analysis:  $\text{C}_{20}\text{H}_{26}\text{O}_5$  (330.42)

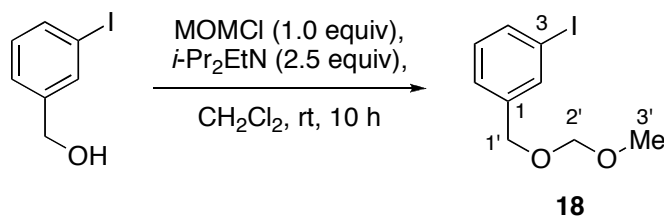
calcd.: C, 72.70; H, 7.93.

found: C, 72.42; H, 7.97.

$R_f$ : 0.54 (silica gel, hexane/EtOAc, 5/1, UV)

$t_R$ : 3.183 min (Agilent Zorbax 300SB-C8, 100% MeCN (1 mL/min))

### MOM-Protection of 3-Iodobenzyl Alcohol. Preparation of 3-Iodobenzyl Methoxymethyl Ether (18).



3-Iodobenzyl alcohol (0.64 mL, 5.0 mmol, 1.0 equiv) in a 25-mL, flame-dried round-bottomed flask equipped with a gas inlet adaptor and a magnetic stirrer was dissolved in 5 mL of  $\text{CH}_2\text{Cl}_2$ . This solution was cooled in an ice bath before it was treated with *i*- $\text{Pr}_2\text{EtN}$  (8.7 mL, 50.0 mmol, 10.0 equiv). The reaction mixture was stirred for 1 h in the ice bath under Ar, and subsequently, MOMCl (0.95 mL, 50.0 mmol, 10.0 equiv) was added dropwise in the course of 3 min. The evolution of a white smoke was observed during the addition. The reaction mixture

remained stirring in the ice bath under Ar or 20 min after the addition had completed before the ice bath was removed. The reaction mixture was allowed to warm up to room temperature and it was stirred at room temperature under Ar for 9 h and 40 min. Then, the reaction mixture was poured into a 250-mL separatory funnel containing 20 mL of water. The aqueous layer was extracted with Et<sub>2</sub>O (3 × 20 mL). The combined organic layers were washed with 20 mL of saturated NH<sub>4</sub>Cl aqueous solution followed by 20 mL of brine, dried over anhydrous MgSO<sub>4</sub>, and were filtered. The filtrate was concentrated under reduced pressure. The resulting crude product was purified by flash chromatography (silica gel (100 g), hexane/EtOAc = 80/1 (1 L), 40/1 (900 mL)) and Kugelrohr distillation to afford 1.323 g (95%) of **18** as a colorless liquid.

Data for **18**:

b.p.: 175 °C (ABT) at 0.8 mmHg

<sup>1</sup>H NMR: (500 MHz, CDCl<sub>3</sub>)  
7.74 (s, 1 H, HC(2)), 7.64 (d, 1 H, *J* = 8.0, HC(4)), 7.32 (d, 1 H, *J* = 7.7, HC(6)), 7.10 (t, 1 H, *J* = 7.8, HC(5)), 4.71 (s, 2 H, H<sub>2</sub>C(2')), 4.55 (s, 2 H, H<sub>2</sub>C(1')), 3.42 (s, 3 H, HC(3')).

<sup>13</sup>C NMR: (126 MHz, CDCl<sub>3</sub>)  
140.5 (C(3)), 136.9 (C(2) or C(4)), 136.9 (C(2) or C(4)), 130.4 (C(5)), 127.1 (C(6)), 96.0 (C(2')), 94.6 (C(1)), 68.4 (C(1')), 55.6 (C(3')).

IR: (neat)

2944 (s), 2884 (s), 1594 (m), 1567 (s), 1471 (m), 1423 (m), 1376 (m), 1210 (m), 1150 (s), 1106 (s), 1048 (s), 918 (m), 776 (s).

LRMS: (EI):

278.0 (62.3, [M]<sup>+</sup>), 246 (14.5), 218 (100.0), 217 (87.9), 119 (16.8), 91 (78.1), 76 (9.3), 63 (13.4).

HRMS: (EI, [M]<sup>+</sup>):

calcd.: 277.980382

found: 277.980448

Analysis: C<sub>9</sub>H<sub>11</sub>O<sub>2</sub>I (278.09)

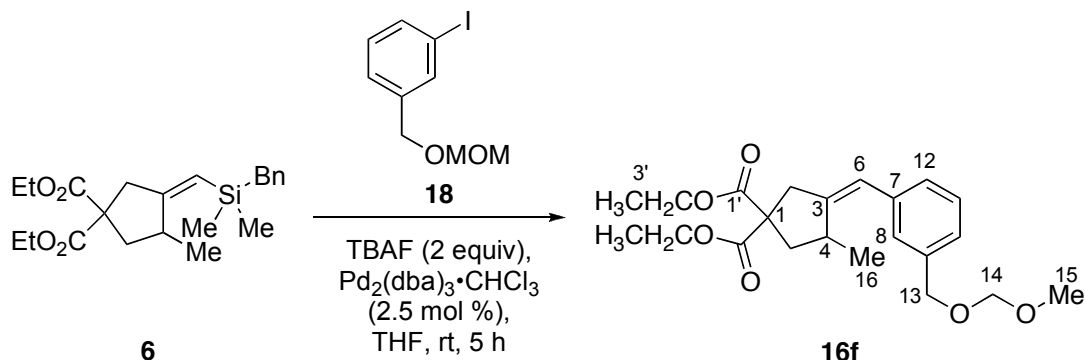
calcd.: C, 38.87; H, 3.99.

found: C, 38.70; H, 3.85.

R<sub>f</sub>: 0.62 (silica gel, hexane/EtOAc, 5/1, UV)

$t_R$ : 2.99 min (Agilent Zorbax 300SB-C8, 100% MeCN (1 mL/min))

**Cross-Coupling Reaction of 6 with 3-Iodobenzyl Methoxymethyl Ether (18). Preparation of Diethyl (Z)-3-(2-Methylbenzylidene)-4-methylcyclopentane-1,1-dicarboxylate (16f).**



Alkydenylsilane **6** (427 mg, 1.10 mmol, 1.1 equiv) in a 5-mL, round-bottomed flask with a magnetic stir bar and fitted with a gas inlet adaptor, was dissolved in a solution of TBAF·3H<sub>2</sub>O (1.0 M in THF, 2.0 mL, 2.0 mmol, 2.0 equiv) and the resulting light-yellow solution was stirred at room temperature under Ar for approximately 3 min. Then methoxymethyl 3-iodobenzyl ether (**18**) (292 mg, 1.00 mmol, 1.0 equiv) and  $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$  (26 mg, 0.025 mmol, 2.5 mol %) were added to the solution sequentially. The flask was purged with Ar, and the reaction mixture was stirred at room temperature under Ar atmosphere for 5 h. Then, the reaction mixture was passed through thin layer of silica gel (approximately 1 cm) followed by a wash of EtOAc (100 mL). The dark-brown filtrate was added silica gel (1 g) and was concentrated under reduced pressure. The crude product adsorbed on silica gel was purified using flash chromatography (silica gel (45 g), hexane/EtOAc, 40/1 (250 mL), 30/1 (250 mL), 20/1 (250 mL), 10/1 (500 mL), 5/1 (250 mL)), reverse phase flash chromatography (reverse phase silica gel (30 g), MeCN/H<sub>2</sub>O, 1/1 (250 mL), 2/1 (250 mL)), and diffusion pump distillation to afford 318 mg (81%) of **16f** as a colorless, viscous liquid.

**Data for 16f:**

**b.p.:** 167 °C (ABT) at  $9.0 \times 10^{-5}$  mmHg

**<sup>1</sup>H NMR:** (500 MHz, CDCl<sub>3</sub>)

7.29 (t, 1 H,  $J = 7.6$ , HC(11)), 7.26 (s, 1 H, HC(8)), 7.22 (d, 1 H,  $J = 7.6$ ,

HC(10)), 7.18 (d, 1 H,  $J = 7.3$ , HC(12)), 6.34 (s, 1 H, HC(6)), 4.17 (s, 2 H, H<sub>2</sub>C(14)), 4.58 (s, 2 H, H<sub>2</sub>C(13)), 4.25-4.18 (m, 4 H, 2 × H<sub>2</sub>C(2')), 3.42 (s, 3 H, H<sub>3</sub>C(15)), 3.30-3.27 (m, 1 H, HC(4)), 3.28 (dd, 2 H,  $J = 16.1, 2.2$ , H<sub>2</sub>C(2)), 2.97 (d, 1 H,  $J = 16.1$ , HC(2)), 2.74 (dd, 1 H,  $J = 13.3, 8.2$ , HC(5)), 1.87 (dd, 1 H,  $J = 13.3, 6.0$ , H<sub>3</sub>C(5)), 1.28 (t, 3 H,  $J = 7.0$ , H<sub>3</sub>C(3')), 1.25 (t, 3 H,  $J = 7.0$ , H<sub>3</sub>C(3')), 1.07 (d, 3 H,  $J = 7.1$ , H<sub>3</sub>C(16)).

<sup>13</sup>C NMR: (126 MHz, CDCl<sub>3</sub>)

172.2 (C(1')), 171.9 (C(1')), 147.3 (C(3)), 137.9 (C(7)), 128.5 (C(Aryl)), 128.1 (C(Aryl)), 127.7 (C(Aryl)), 126.0 (C(10)), 122.5 (C(6)), 95.8 (C(14)), 69.3 (C(13)), 61.7 (C(2')), 61.7 (C(2')), 58.4 (C(1)), 55.5 (C(15)), 43.1 (C(2)), 42.6 (C(5)), 34.7 (C(4)), 19.7 (C(16)), 14.2 (C(3')).

IR: (neat)

3459 (w), 2980 (m), 1732 (s), 1464 (w), 1448 (w), 1246 (m), 1150 (m), 1104 (m), 1049 (m), 918 (w), 861 (w), 785 (w).

LRMS: (EI):

390 (0.9, [M]<sup>+</sup>), 372 (5.3), 328 (39.9), 254 (100.0), 200 (17.5), 181 (47.2), 154 (30.3), 119 (67.9), 91 (34.3).

HRMS: (EI, [M]<sup>+</sup>):

calcd.: 390.205576

found: 390.204924

Analysis: C<sub>22</sub>H<sub>30</sub>O<sub>6</sub> (390.00)

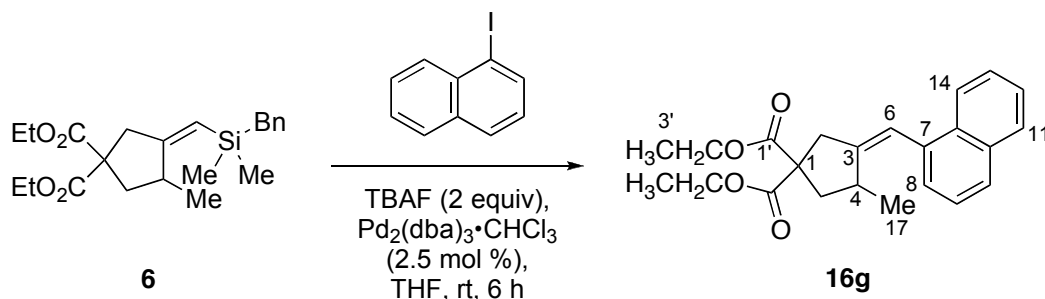
calcd.: C, 67.67; H, 7.74.

found: C, 67.62; H, 7.75.

R<sub>f</sub>: 0.30 (silica gel, hexane/EtOAc, 5/1, UV)

t<sub>R</sub>: 3.08 min (Agilent Zorbax 300SB-C8, 100% MeCN (1 mL/min))

**Cross-Coupling Reaction of 6 with 1-Iodonaphthalene. Preparation of Diethyl (Z)-3-(1-Naphthylidene)-4-methylcyclopentane-1,1-dicarboxylate (16g).**



Alkydienesilane **6** (426 mg, 1.10 mmol, 1.1 equiv) in a 5-mL, round-bottomed flask with a magnetic stir bar and fitted with a gas inlet adaptor, was dissolved in a solution of TBAF·3H<sub>2</sub>O (1.0 M in THF, 2.0 mL, 2.0 mmol, 2.0 equiv) and the resulting light-yellow solution was stirred at room temperature under Ar for approximately 3 min. Then 1-iodonaphthalene (146  $\mu$ L, 1.00 mmol, 1.0 equiv) and Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub> (26 mg, 0.025 mmol, 2.5 mol %) were added to the solution sequentially. The flask was purged with Ar, and the reaction mixture was stirred at room temperature under Ar atmosphere for 6 h. Then, the reaction mixture was passed through thin layer of silica gel (approximately 1 cm) followed by a wash of EtOAc (100 mL). The dark-brown filtrate was added silica gel (1 g) and was concentrated under reduced pressure. The crude product adsorbed on silica gel was purified using flash chromatography (silica gel (45 g), hexane/EtOAc, 80/1 (250 mL), 40/1 (1 L)), reverse phase chromatography (first column: reverse phase silica gel (20 g), MeCN/H<sub>2</sub>O, 1/1 (250 mL), 2/1 (500 mL), second column: reverse phase silica gel (20 g), MeCN/H<sub>2</sub>O, 1/1 (500 mL), 2/1 (125 mL), 3/1 (125 mL), 4/1 (250 mL)) and diffusion pump distillation to afford 330 mg (93%) of **16g** as a light-yellow, viscous liquid.

**Data for 16g:**

**b.p.:** 161 °C (ABT) at  $9.0 \times 10^{-5}$  mmHg

**<sup>1</sup>H NMR:** (500 MHz, CDCl<sub>3</sub>)

7.98-7.96 (m, 1 H, HC(14)), 7.85-7.84 (m, 1 H, HC(11)), 7.75 (d, 1 H, *J* = 8.1, HC(10)), 7.50-7.47 (m, 2 H, HC(12), HC(13)), 7.43 (t, 1 H, *J* = 7.6, HC(9)), 7.37 (d, 1 H, *J* = 7.5, HC(8)), 6.81 (s, 1 H, HC(6)), 4.28 (q, 2 H, *J* = 7.3, H<sub>2</sub>C(2')), 4.27-4.21 (m, 2 H, H<sub>2</sub>C(2')), 3.33 (d, 1 H, *J* = 16.1, HC(2)), 3.17 (d, 1 H, *J* = 15.8, HC(2)), 3.05-2.99 (m, 1 H, HC(4)), 2.68 (dd, 1 H, *J* = 13.2, 8.1, HC(5)), 1.87 (dd,

1 H,  $J = 13.2, 7.3$ , H<sub>3</sub>C(5)), 1.32 (t, 3 H,  $J = 7.2$ , H<sub>3</sub>C(3')), 1.30 (t, 3 H,  $J = 7.1$ , H<sub>3</sub>C(3')), 0.73 (d, 3 H,  $J = 7.8$ , H<sub>3</sub>C(17)).

<sup>13</sup>C NMR: (126 MHz, CDCl<sub>3</sub>)

172.2 (C(1')), 172.1 (C(1')), 148.7 (C(3)), 135.6 (C(7)), 133.7 (C(16)), 131.9 (C(15)), 128.5 (C(14)), 127.2 (C(11)), 125.9 (C(Aryl)), 125.6 (C(Aryl)), 125.3 (C(Aryl)), 120.8 (C(8)), 61.8 (C(6)), 61.7 (C(2')), 61.7 (C(2')), 59.0 (C(1)), 42.4 (C(2) or C(5)), 42.4 (C(2) or C(5)), 35.0 (C(4)), 19.8 (C(17)), 14.3 (C(3')), 14.2 (C(3')).

IR: (neat)

3462 (w), 2980 (m), 1371 (s), 1447 (m), 1366 (m), 1245 (s), 1178 (s), 1098 (m), 1066 (m), 1032 (m), 862 (w), 782 (m), 772 (m).

LRMS: (EI):

141 (48.0), 203 (24.5), 292 (100.0), 366 (56.4, [M]<sup>+</sup>).

HRMS: (EI, [M]<sup>+</sup>):

calcd.: 366.184447

found: 366.183812

Analysis: C<sub>20</sub>H<sub>26</sub>O<sub>5</sub> (366.45)

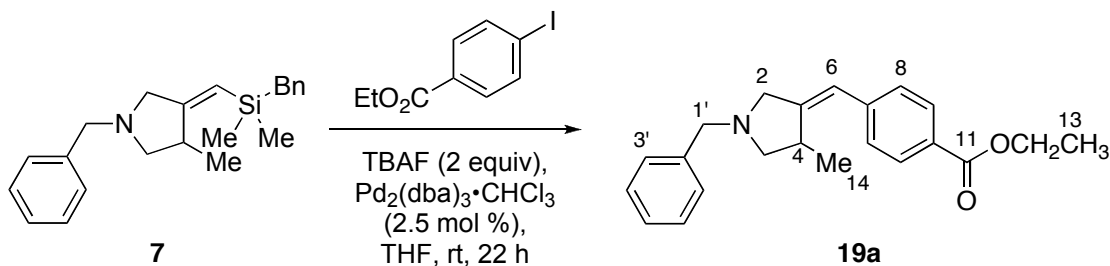
calcd.: C, 75.38; H, 7.15.

found: C, 75.15; H, 7.11.

R<sub>f</sub>: 0.55 (silica gel, hexane/EtOAc, 5/1, UV)

t<sub>R</sub>: 3.133 min (Agilent Zorbax 300SB-C8, 100% MeCN (1 mL/min))

**Cross-Coupling Reaction of 7 with Ethyl 4-Iodobenzoate. Preparation of *N*-Benzyl-(*Z*)-3-(4-ethoxycarbonylbenzylidene)-4-methylpyrrolidine (19a).**



Alkylidenesilane **7** (370 mg, 1.10 mmol, 1.1 equiv) in a 10-mL, round-bottomed flask with a magnetic stir bar and fitted with a gas inlet adaptor, was dissolved in a solution of



TBAF•3H<sub>2</sub>O (1.0 M in THF, 2.0 mL, 2.0 mmol, 2.0 equiv) and the resulting light-yellow solution was stirred at room temperature under Ar for approximately 3 min. Then ethyl 4-iodobenzoate (274 mg, 1.00 mmol, 1.0 equiv) and Pd<sub>2</sub>(dba)<sub>3</sub>•CHCl<sub>3</sub> (26 mg, 0.025 mmol, 2.5 mol %) were added to the solution sequentially. The flask was purged with Ar, and the reaction mixture was stirred at room temperature under Ar atmosphere for 22 h. Then, the reaction mixture was passed through thin layer of silica gel (approximately 1 cm) followed by a wash of EtOAc (100 mL). The dark-brown filtrate was added silica gel (1 g) and was concentrated under reduced pressure. The crude product adsorbed on silica gel was purified using flash chromatography (first column: silica gel (45 g), hexane/EtOAc, 60/1 (250 mL), 40/1 (250 mL), 30/1 (250 mL), 20/1 (250 mL), 10/1 (1 L), second column: silica gel (45 g), hexane/EtOAc, 60/1 (250 mL), 40/1 (250 mL), 30/1 (250 mL), 20/1 (500 mL), 5/1 (750 mL)) to afford 254.6 mg (72%) of **19a** as a yellow, viscous liquid. Product **19a** was unable to be obtained analytically pure. Analytical sample obtained by further purification using flash chromatography (silica gel (30 g), hexane/EtOAc, 40/1 (500 mL), 20/1 (500 mL), 5/1 (500 mL)).

Data for **19a**:

<sup>1</sup>H NMR: (500 MHz, CDCl<sub>3</sub>)

8.30 (d, 2 H, *J* = 8.3, HC(9)), 7.38-7.32 (m, 4 H, *J* = 7.3, 2 × HC(3'), 2 × HC(4')), 7.34 (d, 2 H, *J* = 8.3, 2 × HC(8)), 7.27 (t, 1 H, *J* = 6.0, HC(5')), 6.31 (d, 1 H, *J* = 1.5, HC(6)), 4.37 (q, 2 H, *J* = 7.1, H<sub>2</sub>C(12)), 3.66 (d, 1 H, *J* = 12.7, HC(1')), 3.63 (d, 1 H, *J* = 12.9, HC(1')), 3.44 (d, 2 H, *J* = 13.4, HC(2)), 3.33-3.25 (m, 1 H, HC(4)), 3.27 (d, 1 H, *J* = 14.6, HC(2)), 2.89 (dd, 1 H, *J* = 8.7, 7.0, HC(5)), 2.46 (dd, 1 H, *J* = 8.8, 4.4, HC(5)), 1.39 (t, 3 H, *J* = 7.1, H<sub>3</sub>C(13)), 1.10 (d, 3 H, *J* = 6.8, H<sub>3</sub>C(14)).

<sup>13</sup>C NMR: (126 MHz, CDCl<sub>3</sub>)

166.7 (C(11)), 150.3 (C(2')), 142.3 (C(10)), 139.0 (C(7)), 129.8 (C(9)), 128.9 (C(aryl)), 128.5 (C(aryl)), 128.2 (C(aryl)), 128.1 (C(aryl)), 127.2 (C(aryl)), 120.1 (C(6)), 63.0 (C(5)), 61.8 (C(2)), 61.0 (C(12)), 60.6 (C(1')), 35.8 (C(3)), 17.9 (C(14)), 14.6 (C(13)).

IR: (neat)

3410 (w), 2975 (m), 2930 (m), 2790 (m), 1714 (s), 1606 (s), 1453 (m), 1367 (s), 1275 (s), 1180 (s), 1108 (s), 1121 (m), 876 (m), 741 (m), 700 (s).

LRMS: (CI):

336 (100.0,  $[M+H]^+$ ), 290 (5.6), 258 (3.2), 244 (1.8), 91 (6.7), 86 (7.9), 84 (12.8).

HRMS: (CI,  $[M+H]^+$ ):

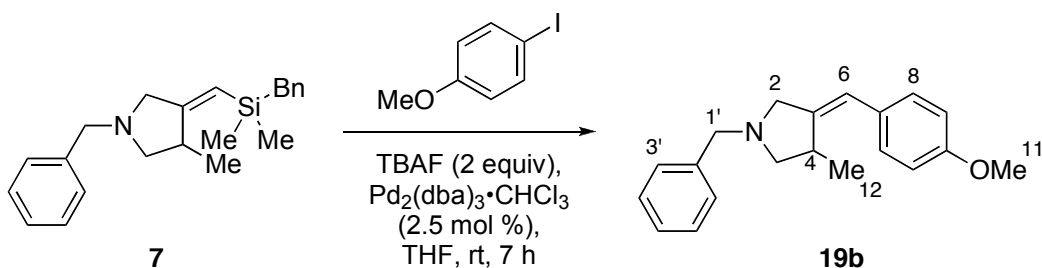
calcd.: 336.1937

found: 336.1970

R<sub>f</sub>: 0.33 (silica gel, hexane/EtOAc, 5/1, UV)

t<sub>R</sub>: 4.45 min (Agilent Zorbax Rx-C8, MeCN/H<sub>2</sub>O = 1/1 (H<sub>2</sub>O contained 0.1% of HOAc and 0.1% of TFA) (1 mL/min))

**Cross-Coupling Reaction of 7 with 4-Iodoanisole. Preparation of *N*-Benzyl-(*Z*)-3-(4-methoxybenzylidene)-4-methylpyrrolidine (19b).**



Alkylidenesilane **7** (369 mg, 1.10 mmol, 1.1 equiv) in a 10-mL, round-bottomed flask with a magnetic stir bar and fitted with a gas inlet adaptor, was dissolved in a solution of TBAF·3H<sub>2</sub>O (1.0 M in THF, 2.0 mL, 2.0 mmol, 2.0 equiv) and the resulting light-yellow solution was stirred at room temperature under Ar for approximately 3 min. Then 4-iodoanisole (234 mg, 1.00 mmol, 1.0 equiv) and  $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$  (26 mg, 0.025 mmol, 2.5 mol %) were added to the solution sequentially. The flask was purged with Ar, and the reaction mixture was stirred at room temperature under Ar atmosphere for 7 h. Then, the reaction mixture was passed through thin layer of silica gel (approximately 1 cm) followed by a wash of EtOAc (100 mL). The dark-brown filtrate was added silica gel (1 g) and was concentrated under reduced pressure. The crude product adsorbed on silica gel was purified using flash chromatography (first column: silica gel (45 g), hexane/EtOAc, 60/1 (250 mL), 40/1 (500 mL), 30/1 (250 mL), 20/1 (250 mL), 10/1 (1 L), second column: silica gel (45 g), hexane/Et<sub>2</sub>O, 80/1 (250 mL), 60/1 (250 mL), 40/1 (250 mL), 10/1 (500 mL), 5/1 (250 mL)) to afford 265 mg (90%) of **19b** as a yellow solid. Product **19b** was unable to be obtained analytically pure.

Data for 19b:m.p.: 51-53 °C<sup>1</sup>H NMR: (500 MHz, CDCl<sub>3</sub>)

7.39 (d, 2 H,  $J = 7.3$ , 2 × HC(3')), 7.34 (t, 2 H,  $J = 7.5$ , 2 × HC(4')), 7.28 (d, 2 H,  $J = 7.3$ , HC(5')), 7.26 (d, 2 H,  $J = 8.8$ , 2 × HC(8)), 6.86 (d, 2 H,  $J = 8.8$ , 2 × HC(9)), 6.23 (s, 1 H, HC(6)), 3.81 (s, 3 H, H<sub>3</sub>C(11)), 3.67 (d, 1 H,  $J = 12.7$ , HC(1')), 3.63 (d, 1 H,  $J = 12.7$ , HC(1')), 3.42 (d, 2 H,  $J = 13.2$ , HC(2)), 3.27-3.23 (m, 1 H, HC(4)), 3.25 (d, 1 H,  $J = 13.4$ , HC(2)), 2.88 (dd, 1 H,  $J = 7.8$ , 7.8, HC(5)), 2.46 (dd, 1 H,  $J = 8.7$ , 4.3, HC(5)), 1.10 (d, 3 H,  $J = 6.8$ , H<sub>3</sub>C(12)).

<sup>13</sup>C NMR: (126 MHz, CDCl<sub>3</sub>)

158.1 (C(3)), 145.2 (C(2')), 139.3 (C(7)), 130.5 (C(10)), 129.5 (C(5')), 129.0 (C(3')), 128.5 (C(4')), 127.2 (C(8)), 120.1 (C(6)), 113.9 (C(9)), 63.2 (C(5)), 61.8 (C(2)), 60.7 (C(1')), 55.4 (C(11)), 35.5 (C(4)), 17.9 (C(13)).

IR: (neat)

3029 (w), 2960 (m), 2929 (m), 2787 (m), 2360 (w), 1608 (s), 1511 (s), 1544 (s), 1454 (m), 1250 (s), 1178 (s), 1126 (m), 1036 (s), 865 (m), 822 (m), 743 (m), 700 (s).

LRMS: (EI):

293 (100.0, [M]<sup>+</sup>), 278 (8.0), 250 (24.9), 159 (18.3), 121 (78.3), 91 (87.4).

HRMS: (EI, [M]<sup>+</sup>):

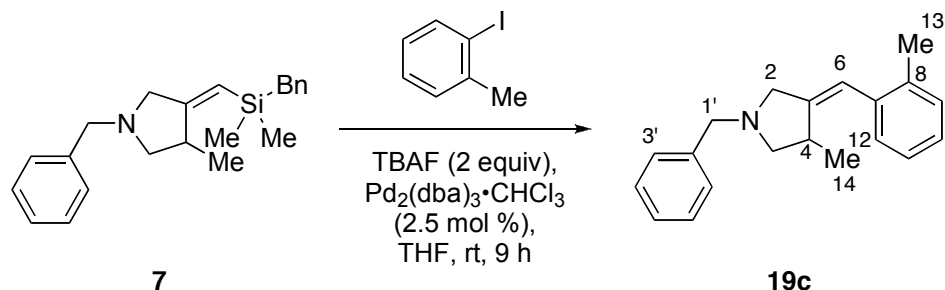
calcd.: 293.177965

found: 293.177930

R<sub>f</sub>: 0.26 (silica gel, hexane/EtOAc, 5/1, UV)

t<sub>R</sub>: 9.22 min (Agilent Zorbax Rx-C8, MeCN/H<sub>2</sub>O = 1/1 (H<sub>2</sub>O contained 0.1% of HOAc and 0.1% of TFA) (0.5 mL/min))

**Cross-Coupling Reaction of 7 with 2-Iodotoluene. Preparation of *N*-Benzyl-(*Z*)-3-(2-methylbenzylidene)-4-methylpyrrolidine (19c).**



Alkylidenesilane **7** (369 mg, 1.10 mmol, 1.1 equiv) in a 10-mL, round-bottomed flask with a magnetic stir bar and fitted with a gas inlet adaptor, was dissolved in a solution of TBAF·3H<sub>2</sub>O (1.0 M in THF, 2.0 mL, 2.0 mmol, 2.0 equiv) and the resulting light-yellow solution was stirred at room temperature under Ar for approximately 3 min. Then 2-iodobenzene (229.0 mg, 1.00 mmol, 1.0 equiv) and  $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$  (26 mg, 0.025 mmol, 2.5 mol %) were added to the solution sequentially. The flask was purged with Ar, and the reaction mixture was stirred at room temperature under Ar atmosphere for 9 h. Then, the reaction mixture was passed through thin layer of silica gel (approximately 1 cm) followed by a wash of EtOAc (100 mL). The dark-brown filtrate was added silica gel (1 g) and was concentrated under reduced pressure. The crude product adsorbed on silica gel was purified using flash chromatography (first column: silica gel (45 g), hexane/EtOAc, 30/1 (250 mL), 20/1 (250 mL), 10/1 (1 L), second column: silica gel (45 g), hexane/Et<sub>2</sub>O, 80/1 (500 mL), 40/1 (250 mL), 20/1 (250 mL), 10/1 (250 mL), 5/1 (250 mL)) and reverse phase flash chromatography (reverse phase silica gel (30 g), MeCN), to afford 237.0 mg (85%) of **19c** as a yellow, viscous liquid. Product **19c** was unable to be obtained analytically pure.

**Data for 19c:**

<sup>1</sup>H NMR: (500 MHz, CDCl<sub>3</sub>)

7.42 (d, 2 H,  $J = 7.1$ ,  $2 \times \text{HC}(3')$ ), 7.37 (t, 2 H,  $J = 7.5$ ,  $2 \times \text{HC}(4')$ ), 7.35-7.29 (m, 2 H, HC(12), HC(5')), 7.19-7.15 (m, 3 H, HC(9), HC(10), HC(11)), 6.37 (d, 1 H,  $J = 1.5$ , HC(6)), 3.71 (d, 1 H,  $J = 12.7$ , HC(1')), 3.65 (d, 1 H,  $J = 12.9$ , HC(1')), 3.39 (s, 2 H, H<sub>2</sub>C(2)), 3.21-3.17 (m, 1 H, HC(4)), 2.96 (dd, 1 H,  $J = 8.8$ , 7.1, HC(5)), 2.34 (dd, 1 H,  $J = 8.9$ , 5.8, HC(5)), 2.27 (s, 3 H, H<sub>3</sub>C(13)), 0.87 (d, 3 H,  $J = 6.8$ , H<sub>3</sub>C(12)).

$^{13}\text{C}$  NMR: (126 MHz,  $\text{CDCl}_3$ )

147.1 (C(3)), 139.1 (C(2')), 137.4 (C(7) or C(8)), 136.2 (C(7) or C(8)), 129.8 (C(5')), 129.1 (C(3')), 128.5 (C(4')), 128.1 (C(9), C(10), C(11) or C(12)), 127.2 (C(9), C(10), C(11) or C(12)), 126.7 (C(9), C(10), C(11) or C(12)), 125.8 (C(9), C(10), C(11) or C(12)), 119.6 (C(6)), 63.1 (C(5)), 61.3 (C(5)), 60.9 (C(1')), 35.3 (C(4)), 20.1 (C(13)), 17.7 (C(14)).

IR: (neat)

3026 (m), 2960 (m), 2925 (m), 2786 (m), 1732 (w), 1676 (w), 1602 (w), 1494 (m), 1453 (m), 1376 (m), 1323 (m), 1131 (m), 1028 (m), 853 (w), 738 (s), 699 (s).

LRMS: (EI):

277 (66.4,  $[\text{M}]^+$ ), 262 (20.3), 234 (4.5), 220 (2.6), 200 (2.6), 186 (12.8), 172 (7.8), 143 (16.5), 128 (14.1), 115 (9.7), 105 (35.4), 91 (100.0), 77 (5.8), 65 (14.0).

HRMS: (EI,  $[\text{M}]^+$ ):

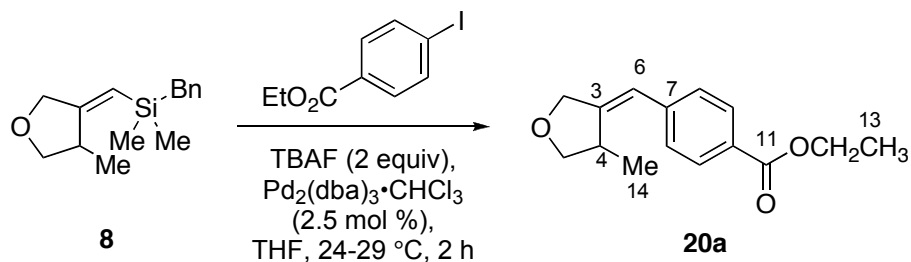
calcd.: 277.183050

found: 277.183168

$R_f$ : 0.44 (silica gel, hexane/EtOAc, 5/1, UV)

$t_R$ : 10.43 min (Agilent Zorbax Rx-C8, MeCN/ $\text{H}_2\text{O}$  = 1/1 ( $\text{H}_2\text{O}$  contained 0.1% of HOAc and 0.1% of TFA) (0.5 mL/min))

**Cross-Coupling Reaction of 8 with Ethyl 4-Iodobenzoate. Preparation of (Z)-3-(4-Ethoxycarbonylbenzylidene)-4-methyltetrahydrofuran (20a).**



Alkylidenesilane **8** (270 mg, 1.10 mmol, 1.1 equiv) in a 10-mL, two-necked, round-bottomed flask with a magnetic stir bar and fitted with a gas inlet adaptor, was dissolved in a solution of TBAF $\cdot 3\text{H}_2\text{O}$  (1.0 M in THF, 2.0 mL, 2.0 mmol, 2.0 equiv) and the resulting light-yellow solution was stirred under Ar for approximately 11 min. A thermocouple was inserted to monitor the internal temperature. Then,  $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$  (26 mg, 0.025 mmol, 2.5 mol %) was

added, and to this dark purple solution, ethyl 4-iodobenzoate (276 mg, 1.00 mmol, 1.0 equiv) was added dropwise in the course of 26 min, during which the internal temperature was maintained between 26-29 °C. After the addition was completed, the internal temperature slowly decreased to 24 °C in approximately 1 h. The reaction mixture was stirred at room temperature under Ar atmosphere for 2 h. Then, the reaction mixture was passed through thin layer of silica gel (approximately 1 cm) followed by a wash of EtOAc (100 mL). The dark-brown filtrate was added silica gel (1 g) and was concentrated under reduced pressure. The crude product adsorbed on silica gel was purified using flash chromatography (silica gel (50 g), hexane/EtOAc, 60/1 (1.5 L), 4/1 (500 mL), 20/1 (750 mL)) to afford 215.8 mg (88%) of **20a** as a yellow, viscous liquid. Product **20a** was unable to be obtained analytically pure. Analytical sample obtained by further purification using flash chromatography (first column: silica gel (30 g), hexane/EtOAc, 40/1 (500 mL), 20/1 (500 mL), second column: silica gel (40 g), hexane/EtOAc, 40/1 (750 mL), 20/1 (500 mL)) and diffusion pump distillation.

Data for **20a**:

b.p.: 140 °C (ABT) at  $4.0 \times 10^{-5}$  mmHg

<sup>1</sup>H NMR: (500 MHz, CDCl<sub>3</sub>)

8.02 (d, 2 H,  $J = 8.3$ ,  $2 \times \text{HC}(9)$ ), 7.40 (d, 2 H,  $J = 8.3$ ,  $2 \times \text{HC}(8)$ ), 6.33 (d, 1 H,  $J = 1.7$ , HC(6)), 4.60 (dt, 1 H,  $J = 13.7$ , 1.7, HC(2)), 4.40 (dd, 1 H,  $J = 13.5$ , 1.8, HC(2)), 4.38 (q, 2 H,  $J = 7.2$ , H<sub>2</sub>C(12)), 3.99 (dd, 1 H,  $J = 8.5$ , 5.9, HC(5)), 3.76 (dd, 1 H,  $J = 8.4$ , 2.6, HC(5)), 3.20-3.27 (m, 1 H, HC(4)), 1.40 (t, 3 H,  $J = 7.1$ , H<sub>3</sub>C(13)), 1.18 (d, 3 H,  $J = 6.8$ , H<sub>3</sub>C(14)).

<sup>13</sup>C NMR: (126 MHz, CDCl<sub>3</sub>)

166.6 (C(11)), 149.2 (C(10)), 141.7 (C(7)), 129.9 (C(9)), 128.6 (C(3)), 128.1 (C(8)), 119.0 (C(6)), 76.6 (C(5)), 73.1 (C(2)), 61.1 (C(12)), 36.5 (C(4)), 17.6 (C(14)), 14.6 (C(13)).

IR: (neat)

2974 (m), 1716 (s), 1606 (m), 1276 (s), 1179 (m), 1104 (m), 1020 (w), 879 (w), 769 (w), 700 (w).

LRMS: (CI):

247 (30.5, [M+H]<sup>+</sup>), 21.9 (4.3), 201 (6.3), 185 (4.4), 157 (6.1), 145 (3.3), 131 (2.1), 119 (2.1), 102 (3.5), 86 (11.7), 86 (69.4), 83 (100.0).

**HRMS:** (CI,  $[M+H]^+$ ):

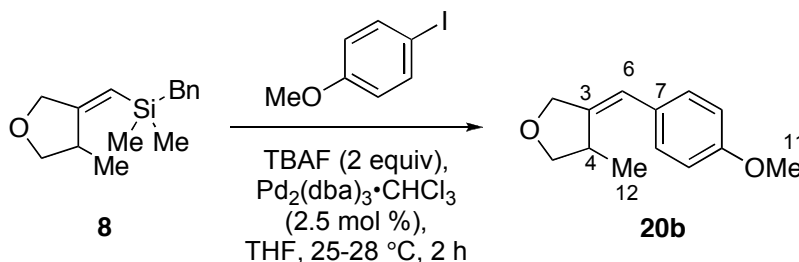
calcd.: 247.13343

found: 247.13406

$R_f$ : 0.36 (silica gel, hexane/EtOAc, 5/1, UV)

$t_R$ : 1.541 min (Agilent Zorbax 300SB-C8, 100% MeCN (2 mL/min))

**Cross-Coupling Reaction of 8 with 4-Iodoanisole. Preparation of (Z)-3-(4-Methoxybenzylidene)-4-methyltetrahydrofuran (20b).**



Alkylidenesilane **8** (271 mg, 1.10 mmol, 1.1 equiv) in a 10-mL, two-necked, round-bottomed flask with a magnetic stir bar and fitted with a gas inlet adaptor, was dissolved in a solution of TBAF·3H<sub>2</sub>O (1.0 M in THF, 2.0 mL, 2.0 mmol, 2.0 equiv) and the resulting light-yellow solution was stirred under Ar for approximately 11 min. A thermocouple was inserted to monitor the internal temperature. Then, Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub> (26 mg, 0.025 mmol, 2.5 mol %) was added, and to this dark purple solution, a solution of 4-iodoanisole (234 mg, 1.00 mmol, 1.0 equiv) in THF (0.2 mL) was added dropwise in the course of 30 min, during which the internal temperature was maintained between 26-28 °C. After the addition was completed, the internal temperature slowly decreased to 25 °C in approximately 1 h. The reaction mixture was stirred at room temperature under Ar atmosphere for 2 h. Then, the reaction mixture was passed through thin layer of silica gel (approximately 1 cm) followed by a wash of EtOAc (100 mL). The dark-brown filtrate was added silica gel (1 g) and was concentrated under reduced pressure. The crude product adsorbed on silica gel was purified using flash chromatography (silica gel (50 g), hexane/EtOAc, 80/1) to afford 286 mg (89%) of **20b** as a yellow, viscous liquid. Product **20b** was unable to be obtained analytically pure. Analytical sample obtained by further purification using flash chromatography (first column: silica gel (40 g), hexane/DME, 80/1) and diffusion pump distillation.

**Data for 20b:**b.p.: 110 °C (ABT) at  $5.5 \times 10^{-5}$  mmHg<sup>1</sup>H NMR: (500 MHz, CDCl<sub>3</sub>)7.29 (d, 2 H,  $J = 8.8$ ,  $2 \times \text{HC}(8)$ ), 7.40 (d, 2 H,  $J = 8.3$ ,  $2 \times \text{HC}(9)$ ), 6.24 (d, 1 H,  $J = 1.7$ , HC(6)), 4.57 (dt, 1 H,  $J = 13.2$ , 1.8, HC(2)), 4.37 (dd, 1 H,  $J = 13.0$ , 1.9, HC(2)), 3.97 (dd, 1 H,  $J = 8.4$ , 5.8, HC(5)), 3.82 (s, 3 H, H<sub>3</sub>C(11)), 3.75 (dd, 1 H,  $J = 8.4$ , 2.3, HC(5)), 3.25-3.23 (m, 1 H, HC(4)), 1.20 (d, 3 H,  $J = 7.1$ , H<sub>3</sub>C(12)).<sup>13</sup>C NMR: (126 MHz, CDCl<sub>3</sub>)

158.5 (C(10)), 144.1 (C(3)), 130.0 (C(7)), 129.4 (C(8)), 119.0 (C(6)), 114.1 (C(9)), 76.7 (C(5)), 73.0 (C(2)), 55.5 (C(11)), 36.1 (C(4)), 17.7 (C(12)).

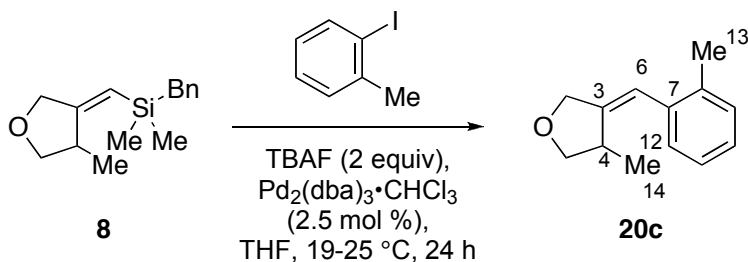
IR: (neat)

2966 (m), 2837 (m), 1608 (s), 1513 (s), 1463 (m), 1297 (m), 1250 (s), 1178 (s), 1089 (m), 1034 (s), 926 (s), 869 (m), 824 (m).

LRMS: (CI):205 (100.0,  $[\text{M}+\text{H}]^+$ ), 187 (57.4), 175 (11.7), 162 (9.2), 147 (14.8), 137 (6.4), 121 (38.5).HRMS: (CI,  $[\text{M}+\text{H}]^+$ ):

calcd.: 205.12286

found: 205.12278

R<sub>f</sub>: 0.43 (silica gel, hexane/EtOAc, 5/1, UV)t<sub>R</sub>: 1.450 min (Agilent Zorbax 300SB-C8, 100% MeCN (2 mL/min))**Cross-Coupling Reaction of 8 with 2-Iodotoluene. Preparation of (Z)-3-(2-Methylbenzylidene)-4-methyltetrahydrofuran (20c).**

Alkylidenesilane **8** (271 mg, 1.10 mmol, 1.1 equiv) in a 10-mL, two-necked, round-bottomed flask with a magnetic stir bar and fitted with a gas inlet adaptor that was immersed in a



room temperature water bath, was dissolved in a solution of TBAF•3H<sub>2</sub>O (1.0 M in THF, 2.0 mL, 2.0 mmol, 2.0 equiv) and the resulting light-yellow solution was stirred under Ar for approximately 3 min. A thermocouple was inserted to monitor the internal temperature. Then, Pd<sub>2</sub>(dba)<sub>3</sub>•CHCl<sub>3</sub> (26 mg, 0.025 mmol, 2.5 mol %) was added, and to this dark purple solution, 2-iodotoluene (273 mg, 1.00 mmol, 1.0 equiv) was added dropwise in the course of 5 min, during which the internal temperature was maintained between 19-21 °C. After the addition was completed, the internal temperature slowly rose to 25 °C in approximately 1 h. The reaction mixture was stirred at room temperature under Ar atmosphere for 24 h. Then, the reaction mixture was passed through thin layer of silica gel (approximately 1 cm) followed by a wash of EtOAc (100 mL). The dark-brown filtrate was added silica gel (1 g) and was concentrated under reduced pressure. The crude product adsorbed on silica gel was purified using flash chromatography (first column: silica gel (45 g), hexane/EtOAc, 80/1 (500 mL), 60/1 (500 mL), second column: silica gel (45 g), hexane/EtOAc, 80/1 (500 mL), 60/1 (500 mL)) and diffusion pump distillation to afford 145 mg (77%) of **20c** as a colorless, viscous liquid.

Data for **20c**:

b.p.: 82 °C (ABT) at  $8.0 \times 10^{-5}$  mmHg

<sup>1</sup>H NMR: (500 MHz, CDCl<sub>3</sub>)

7.32-7.30 (m, 1 H, HC(12)), 7.20-7.15 (m, 3 H, HC(9), HC(10), HC(11)), 6.39 (d, 1 H,  $J = 1.9$ , HC(6)), 4.56 (dt, 1 H,  $J = 12.9, 2.0$ , HC(2)), 4.43 (dd, 1 H,  $J = 13.0, 1.7$ , HC(2)), 4.01 (dd, 1 H,  $J = 8.3, 6.4$ , HC(5)), 3.63 (dd, 1 H,  $J = 8.5, 3.8$ , HC(5)), 3.12-3.09 (m, 1 H, HC(4)), 2.28 (s, 3 H, H<sub>3</sub>C(13)), 0.96 (d, 3 H,  $J = 6.8$ , H<sub>3</sub>C(14)).

<sup>13</sup>C NMR: (126 MHz, CDCl<sub>3</sub>)

146.6 (C(3)), 136.9 (C(7)), 136.3 (C(aryl)), 130.0 (C(aryl)), 128.1 (C(12)), 127.1 (C(aryl)), 125.9 (C(aryl)), 118.5 (C(3)), 76.5 (C(5)), 72.6 (C(6)), 36.0 (C(4)), 20.2 (C(13)), 17.5 (C(14)).

IR: (neat)

2965 (s), 2851 (s), 1602 (w), 1480 (m), 1458 (m), 1379 (m), 1317 (m), 1150 (w), 1072 (s), 1042 (s), 926 (s), 745 (s).

LRMS: (ESI):

187 (100.0, [M-1]<sup>+</sup>).

**HRMS:** (ESI,  $[M-1]^+$ ):

calcd.: 187.1123

found: 187.1123

**Analysis:**  $C_{13}H_{16}O$  (188.27)

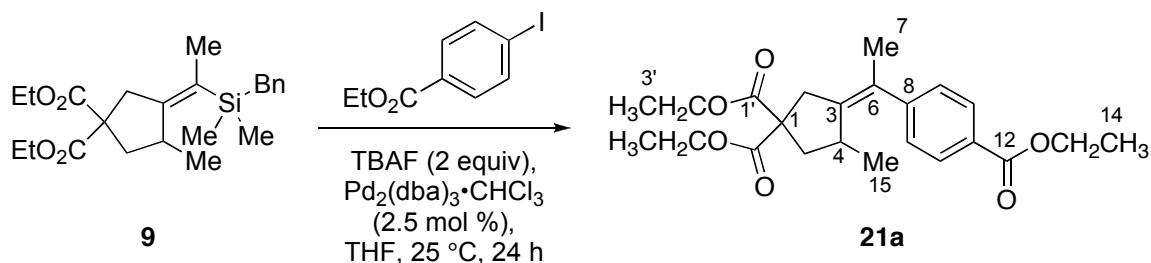
calcd.: C, 82.94; H, 8.57.

found: C, 82.94; H, 8.74.

$R_f$ : 0.51 (silica gel, hexane/EtOAc, 5/1, UV)

$t_R$ : 5.222 min (HP-1, 100 °C, 25.0 °C/min, 250 °C)

**Cross-Coupling Reaction of 9 with Ethyl 4-Iodobenzoate. Preparation of Diethyl (Z)-3-(4-Ethoxycarbonylphenyl)methylmethylidene-4-methylcyclopentane-1,1-dicarboxylate (21a).**



Alkylidenesilane **9** (442 mg, 1.10 mmol, 1.1 equiv) in a 10-mL, round-bottomed flask with a magnetic stir bar and fitted with a gas inlet adaptor, was dissolved in a solution of TBAF·3H<sub>2</sub>O (1.0 M in THF, 2.0 mL, 2.0 mmol, 2.0 equiv) and the resulting light-yellow solution was stirred at room temperature under Ar for approximately 3 min. Then ethyl 4-iodobenzoate (273 mg, 1.00 mmol, 1.0 equiv) and  $Pd_2(dba)_3 \cdot CHCl_3$  (26 mg, 0.025 mmol, 2.5 mol %) were added to the solution sequentially. The flask was purged with Ar, and the reaction mixture was stirred at 35 °C under Ar atmosphere for 24 h. Then, the reaction mixture was passed through thin layer of silica gel (approximately 1 cm) followed by a wash of EtOAc (100 mL). The dark-brown filtrate was added silica gel (1 g) and was concentrated under reduced pressure. The crude product adsorbed on silica gel was purified using flash chromatography (first column: silica gel (45 g), hexane/EtOAc, 40/1 (250 mL), 30/1 (750 mL), 20/1 (500 mL), second column: silica gel (50 g), hexane/DME, 40/1 (500 mL), 30/1 (500 mL), third column: silica gel (60 g), hexane/Et<sub>2</sub>O, 40/1 (750 mL), 30/1 (500 mL), 20/1 (500 mL), 10/1 (250 mL), 5/1 (250 mL), 3/1 (250 mL)), reverse phase flash chromatography (first column: reverse phase silica gel (70 g), MeOH/H<sub>2</sub>O, 5/1, second column: reverse phase silica gel (71 g), MeOH/H<sub>2</sub>O, 3/1 (325

mL), 5/1 (300 mL)), and diffusion pump distillation to afford 289 mg (72%) of **21a** as a white solid.

Data for **21a**:

m.p.: 55-56 °C

b.p.: 150 °C (ABT) at  $6.0 \times 10^{-5}$  mmHg

<sup>1</sup>H NMR: (500 MHz, CDCl<sub>3</sub>)

7.98 (d, 2 H,  $J = 8.5$ , 2 × HC(10)), 7.23 (d, 2 H,  $J = 8.5$ , 2 × HC(9)), 4.38 (q, 2 H,  $J = 7.2$ , H<sub>2</sub>C(13)), 4.24 (q, 2 H,  $J = 7.1$ , H<sub>2</sub>C(2')), 4.22 (q, 2 H,  $J = 7.4$ , H<sub>2</sub>C(2')), 3.06 (s, 2 H, HC(2)), 2.91-2.87 (m, 1 H, HC(4)), 2.58 (dd, 1 H,  $J = 13.3$ , 8.0, HC(5)), 1.97 (s, 3 H, H<sub>3</sub>C(7)), 1.85 (dd, 1 H,  $J = 13.2$ , 7.1, HC(5)), 1.40 (t, 3 H,  $J = 7.1$ , H<sub>3</sub>C(14)), 1.29 (t, 3 H,  $J = 6.7$ , H<sub>3</sub>C(3')), 1.28 (t, 3 H,  $J = 6.7$ , H<sub>3</sub>C(3')), 0.61 (d, 3 H,  $J = 6.8$ , H<sub>3</sub>C(15)).

<sup>13</sup>C NMR: (126 MHz, CDCl<sub>3</sub>)

172.3 (C(1')), 172.3 (C(1')), 166.8 (C(12)), 149.2 (C(3)), 141.2 (C(8)), 129.7 (C(10)), 128.8 (C(11)), 128.6 (C(11)), 128.1 (C(9)), 61.7 (C(2')), 61.7 (C(2')), 61.1 (C(13)), 59.1 (C(1)), 42.4 (C(5)), 39.3 (C(2)), 35.7 (C(4)), 22.3 (C(7)), 20.2 (C(15)), 14.6 (C(14)), 14.3 (C(3')), 14.3 (C(3')).

IR: (neat)

2981 (m), 1731 (s), 1607 (m), 1447 (s), 1367 (m), 1273 (s), 1179 (s), 1102 (s), 1076 (s), 1020 (m), 861 (m), 777 (m), 712 (m).

LRMS: (EI):

402 (27.6, [M]<sup>+</sup>), 357 (16.9), 328 (100.0), 283 (14.2), 255 (49.1), 177 (22.2).

HRMS: (EI, [M]<sup>+</sup>):

calcd.: 402.2042

found: 402.2039

Analysis: C<sub>20</sub>H<sub>26</sub>O<sub>5</sub> (402.48)

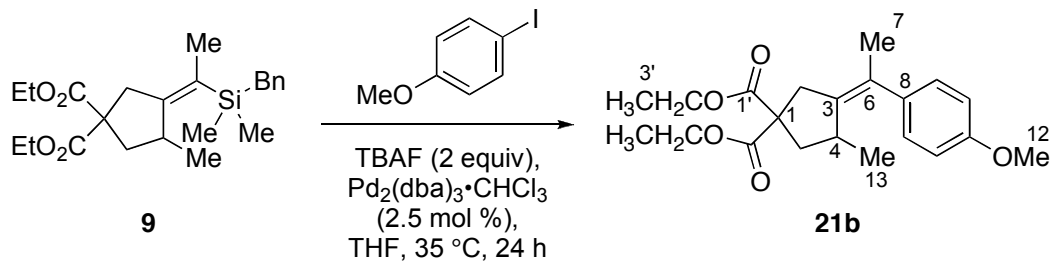
calcd.: C, 68.64; H, 7.51.

found: C, 68.63; H, 7.35.

R<sub>f</sub>: 0.44 (silica gel, hexane/EtOAc, 5/1, UV)

t<sub>R</sub>: 2.758 min (Agilent Zorbax 300SB-C8, 100% MeCN (1 mL/min))

**Cross-Coupling Reaction of 9 with 4-Iodoanisole. Preparation of Diethyl (Z)-3-(4-Methoxyphenyl)methylmethylidene-4-methylcyclopentane-1,1-dicarboxylate (21b).**



Alkylidenesilane **9** (443 mg, 1.10 mmol, 1.1 equiv) in a 10-mL, round-bottomed flask with a magnetic stir bar and fitted with a gas inlet adaptor, was dissolved in a solution of TBAF·3H<sub>2</sub>O (1.0 M in THF, 2.0 mL, 2.0 mmol, 2.0 equiv) and the resulting light-yellow solution was stirred at room temperature under Ar for approximately 3 min. Then 4-iodoanisole (234 mg, 1.00 mmol, 1.0 equiv) and Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub> (26 mg, 0.025 mmol, 2.5 mol %) were added to the solution sequentially. The flask was purged with Ar, and the reaction mixture was stirred at 35 °C under Ar for 24 h. Then, the reaction mixture was passed through thin layer of silica gel (approximately 1 cm) followed by a wash of EtOAc (100 mL). The dark-brown filtrate was added silica gel (1 g) and was concentrated under reduced pressure. The crude product adsorbed on silica gel was purified using flash chromatography (first column: silica gel (45 g), hexane/EtOAc, 60/1 (250 mL), 20/1 (750 mL), 10/1 (500 mL), second column silica gel (45 g), hexane/EtOAc, 60/1 (250 mL), 40/1 (500 mL), 30/1 (500 mL), 20/1 (250 mL)) and diffusion pump distillation to afford 278 mg (77%) of **21a** as a yellow, viscous liquid.

**Data for 21a:**

**b.p.:** 159 °C (ABT) at  $6.0 \times 10^{-5}$  mmHg

**<sup>1</sup>H NMR:** (500 MHz, CDCl<sub>3</sub>)

7.07 (d, 2 H, *J* = 8.1, 2 × HC(9)), 6.84 (d, 2 H, *J* = 8.1, 2 × HC(10)), 4.23 (q, 2 H, *J* = 7.2, H<sub>2</sub>C(2')), 4.21 (q, 2 H, *J* = 7.2, H<sub>2</sub>C(2')), 3.80 (s, 3 H, H<sub>3</sub>C(12)), 3.04 (s, 2 H, HC(2)), 2.91-2.87 (m, 1 H, HC(4)), 2.56 (dd, 1 H, *J* = 13.1, 8.0, HC(5)), 1.94 (s, 3 H, H<sub>3</sub>C(7)), 1.82 (dd, 1 H, *J* = 13.1, 7.2, HC(5)), 1.28 (td, 3 H, *J* = 6.7, 1.0, H<sub>3</sub>C(3')), 1.27 (td, 3 H, *J* = 6.7, 0.8, H<sub>3</sub>C(3')), 0.64 (d, 3H, *J* = 6.8, H<sub>3</sub>C(13)).

**<sup>13</sup>C NMR:** (126 MHz, CDCl<sub>3</sub>)

172.3 (C(1')), 172.2 (C(1')), 158.1 (C(3)), 139.7 (C(11)), 136.7 (C(8)), 129.0 (C(9)), 113.7 (C(10)), 61.6 (C(2')), 61.6 (C(2')), 59.2 (C(1)), 55.4 (C(12)), 42.5

(C(5)), 39.2 (C(2)), 35.7 (C(4)), 22.7 (C(7)), 20.2 (C(13)), 14.3 (C(3')), 14.3 (C(3')).

IR: (neat)

2980 (s), 1731 (s), 1608 (m), 1511 (s), 1464 (m), 1296 (s), 1243 (s), 1181 (s), 1105 (m), 1044 (m), 833 (m).

LRMS: (EI):

360 (40.3,  $[M]^+$ ), 286 (100.0), 271 (15.8), 213 (40.7), 197 (11.1), 173 (15.4), 135 (36.4), 77 (9.8).

HRMS: (EI,  $[M]^+$ ):

calcd.: 360.1937

found: 360.1944

Analysis: C<sub>20</sub>H<sub>26</sub>O<sub>5</sub> (360.44)

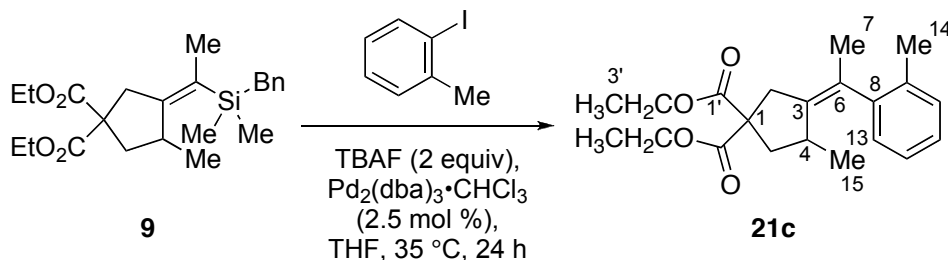
calcd.: C, 69.98; H, 7.83.

found: C, 69.87; H, 7.92.

R<sub>f</sub>: 0.61 (silica gel, hexane/EtOAc, 5/1, UV)

t<sub>R</sub>: 2.73 min (Agilent Zorbax 300SB-C8, 100% MeCN (1 mL/min))

**Cross-Coupling Reaction of 9 with 2-Iodotoluene. Preparation of Diethyl (Z)-3-(2-Methylphenyl)methylmethylidene-4-methylcyclopentane-1,1-dicarboxylate (21c).**



Alkylidenylsilane **9** (443 mg, 1.10 mmol, 1.1 equiv) in a 5-mL, round-bottomed flask with a magnetic stir bar and fitted with a gas inlet adaptor, was dissolved in a solution of TBAF·3H<sub>2</sub>O (1.0 M in THF, 2.0 mL, 2.0 mmol, 2.0 equiv) and the resulting light-yellow solution was stirred at room temperature under Ar for approximately 3 min. Then 2-iodotoluene (224 mg, 1.00 mmol, 1.0 equiv) and Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub> (26 mg, 0.025 mmol, 2.5 mol %) were added to the solution sequentially. The flask was purged with Ar, and the reaction mixture was stirred at room temperature under Ar atmosphere for 24 h. Then, the reaction mixture was passed

through thin layer of silica gel (approximately 1 cm) followed by a wash of EtOAc (100 mL). The dark-brown filtrate was added silica gel (1 g) and was concentrated under reduced pressure. The crude product adsorbed on silica gel was purified using flash chromatography (silica gel (50 g), hexane/EtOAc, 60/1 (500 mL), 40/1 (500 mL), 20/1 (500 mL)), reverse phase flash chromatography (reverse phase silica gel (90 g), MeOH/H<sub>2</sub>O, 3/1 (1 L), 5/1 (500 mL)), and diffusion pump distillation to afford 221 mg (64%) of **21c** as a colorless, viscous liquid.

Data for **21c**:

b.p.: 120 °C (ABT) at  $7.5 \times 10^{-5}$  mmHg

<sup>1</sup>H NMR: (500 MHz, CDCl<sub>3</sub>)

7.17-7.10 (m, 3 H, HC(10), HC(11), HC(12)), 7.03-7.00 (m, 0.5 H, HC(13)), 6.95 (d, 0.5 H,  $J = 7.6$ , HC(13)), 4.23-4.18 (m, 4 H,  $2 \times$  H<sub>2</sub>C(2')), 3.14 (d, 0.5 H,  $J = 16.6$ , HC(2)), 3.04 (dm, 1.5 H,  $J = 18.1$ , H<sub>2</sub>C(2)), 2.72-2.68 (m, 0.5 H, HC(4) (A)), 2.57 (ddd, 1 H,  $J = 12.9, 8.0, 1.1$ , HC(5)), 2.37-2.33 (m, 0.5 H, HC(4) (B)), 2.22 (s, 1.5 H, H<sub>3</sub>C(14)), 2.14 (s, 1.5 H, H<sub>3</sub>C(14)), 1.88 (s, 1.5 H, H<sub>3</sub>C(7)), 1.87 (d, 1.5 H,  $J = 1.2$ , H<sub>3</sub>C(7)), 1.82 (dd, 0.5 H,  $J = 13.0, 6.6$ , HC(5)), 1.80 (dd, 0.5 H,  $J = 12.9, 7.6$ , HC(5)), 1.29 (t, 1.5 H,  $J = 7.3$ , H<sub>3</sub>C(3')), 1.28 (t, 1.5 H,  $J = 7.3$ , H<sub>3</sub>C(3')), 0.67 (d, 1.5 H,  $J = 7.1$ , H<sub>3</sub>C(15)(B)), 0.54 (d, 1.5 H,  $J = 6.8$ , H<sub>3</sub>C(15)(A)).

<sup>13</sup>C NMR: (126 MHz, CDCl<sub>3</sub>)

172.5 (C(1')), 172.4 (C(1')), 172.2 (C(1')), 172.2 (C(1')), 143.8 (C(3)), 143.2 (C(3)), 159.7 (C(8)), 139.6 (C(8)), 135.7 (C(9)), 134.5 (C(9)), 130.2 (C(aryl)), 130.1 (C(aryl)), 130.0 (C(13)), 129.2 (C(aryl)), 129.0 (C(13)), 126.8 (C(aryl)), 126.6 (C(aryl)), 126.1 (C(aryl)), 125.5 (C(aryl)), 61.7 (C(2')), 61.6 (C(2')), 59.3 (C(1)), 42.5 (C(5)), 42.2 (C(5)), 38.8 (C(2)), 38.4 (C(2)), 36.2 (C(4)), 35.7 (C(4)), 22.2 (C(7)), 21.5 (C(7)), 21.0 (C(15)), 19.7 (C(14)), 19.0 (C(14)), 18.9 (C(15)), 14.3 (C(3')), 14.3 (C(3')).

IR: (neat)

2980 (m), 1732 (s), 1448 (m), 1367 (m), 1277 (s), 1244 (s), 1282 (s), 1100 (m), 1075 (m), 1048 (m), 863 (w), 764 (m), 732 (m).

LRMS: (EI):

344 (43.9,  $[M]^+$ ), 299 (7.9), 270 (100.0), 241 (10.7), 197 (54.3), 181 (13.5), 119 (32.4).

HRMS: (EI,  $[M]^+$ ):

calcd.: 344.1988

found: 344.1986

Analysis:  $C_{21}H_{28}O_4$  (344.44)

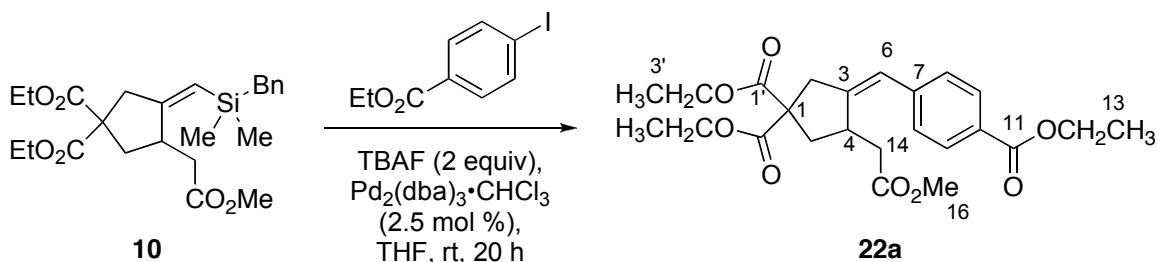
calcd.: C, 73.23; H, 8.19.

found: C, 72.96; H, 8.05.

R<sub>f</sub>: 0.64 (silica gel, hexane/EtOAc, 5/1, UV)

t<sub>R</sub>: 2.703 min (Agilent Zorbax 300SB-C8, 100% MeCN (1 mL/min))

**Cross-Coupling Reaction of 10 with Ethyl 4-Iodobenzoate. Preparation of Diethyl (Z)-3-(4-Ethoxycarbonylbenzylidene)-4-methoxycarbonylcyclopentane-1,1-dicarboxylate (22a).**



Alkylidenesilane **10** (491 mg, 1.10 mmol, 1.1 equiv) in a 10-mL, round-bottomed flask with a magnetic stir bar and fitted with a gas inlet adaptor, was dissolved in a solution of TBAF·3H<sub>2</sub>O (1.0 M in THF, 2.0 mL, 2.0 mmol, 2.0 equiv) and the resulting light-yellow solution was stirred at room temperature under Ar for approximately 3 min. Then ethyl 4-iodobenzoate (491 mg, 1.00 mmol, 1.0 equiv) and  $Pd_2(dba)_3 \cdot CHCl_3$  (26 mg, 0.025 mmol, 2.5 mol %) were added to the solution sequentially. The flask was purged with Ar, and the reaction mixture was stirred at room temperature under Ar atmosphere for 20 h. Then, the reaction mixture was passed through thin layer of silica gel (approximately 1 cm) followed by a wash of EtOAc (100 mL). The dark-brown filtrate was added silica gel (1 g) and was concentrated under reduced pressure. The crude product adsorbed on silica gel was purified using flash chromatography (silica gel (45 g), hexane/EtOAc, 30/1 (250 mL), 20/1 (500 mL), 10/1 (500 mL), 5/1 (500 mL)), reverse phase flash chromatography (reverse phase silica gel (74 g),

MeOH/H<sub>2</sub>O, 5/1), and diffusion pump distillation to afford 333 mg (74%) of **22a** as a colorless, viscous liquid.

Data for **22a**:

b.p.: 188 °C (ABT) at  $6.0 \times 10^{-5}$  mmHg

<sup>1</sup>H NMR: (500 MHz, CDCl<sub>3</sub>)

7.20 (d, 2 H,  $J = 8.3$ ,  $2 \times \text{HC}(9)$ ), 6.86 (d, 2 H,  $J = 8.3$ ,  $2 \times \text{HC}(8)$ ), 6.45 (s, 1 H, HC(6)), 4.37 (q, 2 H,  $J = 7.1$ , H<sub>2</sub>C(12)), 4.24-4.18 (m, 4 H,  $2 \times \text{H}_2\text{C}(2')$ ), 3.72-3.64 (m, 1 H, HC(4)), 3.64 (s, 3H, H<sub>3</sub>C(16)), 3.25 (dt, 1 H,  $J = 16.6$ , 2.3, HC(2)), 3.05 (d, 1 H,  $J = 16.6$ , HC(2)), 4.22 (ddd, 1 H,  $J = 13.7$ , 8.4, 1.2, HC(5)), 2.55 (dd, 1 H,  $J = 16.1$ , 3.4, HC(14)), 2.17 (dd, 1 H,  $J = 16.1$ , 11.2, HC(14)), 2.11 (dd, 1 H,  $J = 13.7$ , 6.1, HC(5)), 1.39 (t, 3H,  $J = 8.1$ , H<sub>3</sub>C(13)), 1.27 (t, 3 H,  $J = 7.2$ , H<sub>3</sub>C(3')), 1.25 (t, 3 H,  $J = 7.2$ , H<sub>3</sub>C(3')).

<sup>13</sup>C NMR: (126 MHz, CDCl<sub>3</sub>)

172.6 (C(1')), 171.7 (C(1')), 171.5 (C(11)), 166.6 (C(15)), 146.7 (C(3)), 141.6 (C(7)), 130.0 (C(9)), 128.7 (C(10)), 128.2 (C(8)), 123.0 (C(6)), 61.9 (C(2')), 61.9 (C(2')), 61.1 (C(12)), 58.5 (C(1)), 51.9 (C(16)), 43.6 (C(2)), 40.3 (C(5)), 37.5 (C(14)), 36.7 (C(4)), 14.5 (C(13)), 14.2 (C(3')), 14.2 (C(3')).

IR: (neat)

2983 (s), 1731 (s), 1607 (s), 1446 (m), 1367 (s), 1276 (s), 1179 (s), 1105 (s), 1074 (s), 1021 (s), 864 (m), 769 (m), 705 (m).

LRMS: (CI):

447 (56.1, [M+H]<sup>+</sup>), 415 (23.6), 401 (100.0), 373 (50.0), 355 (13.0), 341 (12.4), 327 (62.9), 299 (7.2).

HRMS: (CI, [M+H]<sup>+</sup>):

calcd.: 447.2019

found: 447.2025

Analysis: C<sub>20</sub>H<sub>26</sub>O<sub>5</sub> (446.49)

calcd.: C, 64.56; H, 6.77.

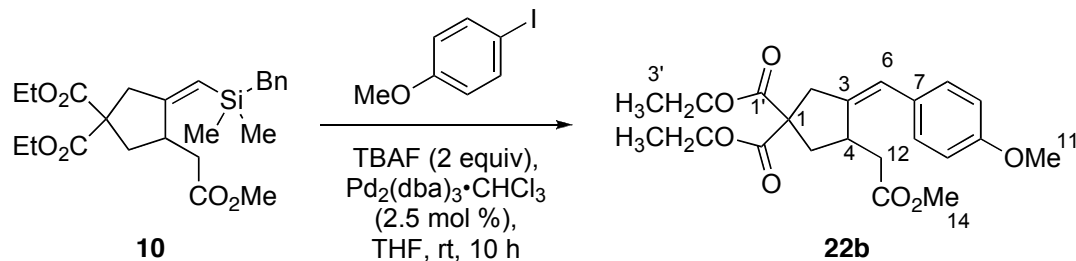
found: C, 64.69; H, 6.67.

R<sub>f</sub>: 0.10 (silica gel, hexane/EtOAc, 5/1, UV)

t<sub>R</sub>: 2.608 min (Agilent Zorbax 300SB-C8, 100% MeCN (1 mL/min))



**Cross-Coupling Reaction of 10 with 4-Iodoanisole. Preparation of Diethyl (Z)-3-(4-Methoxybenzylidene)-4-methoxycarbonylcyclopentane-1,1-dicarboxylate (22b).**



Alkylidenesilane **10** (476 mg, 1.10 mmol, 1.1 equiv) in a 10-mL, round-bottomed flask with a magnetic stir bar and fitted with a gas inlet adaptor, was dissolved in a solution of TBAF·3H<sub>2</sub>O (1.0 M in THF, 2.0 mL, 2.0 mmol, 2.0 equiv) and the resulting light-yellow solution was stirred at room temperature under Ar for approximately 3 min. Then 4-iodoanisole (234 mg, 1.00 mmol, 1.0 equiv) and Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub> (26 mg, 0.025 mmol, 2.5 mol %) were added to the solution sequentially. The flask was purged with Ar, and the reaction mixture was stirred at room temperature under Ar atmosphere for 10 h. Then, the reaction mixture was passed through thin layer of silica gel (approximately 1 cm) followed by a wash of EtOAc (100 mL). The dark-brown filtrate was added silica gel (1 g) and was concentrated under reduced pressure. The crude product adsorbed on silica gel was purified using flash chromatography (first column: silica gel (45 g), hexane/EtOAc, 30/1 (250 mL), 20/1 (250 mL), 10/1 (250 mL), 5/1 (500 mL), second column: silica gel (50 g), hexane/DME, 40/1 (500 mL), 30/1 (250 mL), 20/1 (1 L), 10/1 (500 mL), third column: silica gel (15 g), hexane/DME, 20/1) and diffusion pump distillation to afford 311 mg (77%) of **22b** as a yellow, viscous liquid.

**Data for 22b:**

b.p.: 185 °C (ABT) at  $6.5 \times 10^{-5}$  mmHg

<sup>1</sup>H NMR: (500 MHz, CDCl<sub>3</sub>)

7.20 (d, 2 H,  $J = 8.8$ , 2 × HC(8)), 6.86 (d, 2 H,  $J = 8.8$ , 2 × HC(9)), 6.26 (s, 1 H, HC(6)), 4.24-4.17 (m, 4 H, 2 × H<sub>2</sub>C(2')), 3.81 (s, 3 H, H<sub>3</sub>C(11)), 3.70-3.60 (m, 1 H, HC(4)), 3.65 (s, 3H, H<sub>3</sub>C(14)), 3.21 (dt, 1 H,  $J = 16.1$ , 2.3, HC(2)), 3.00 (d, 1 H,  $J = 16.1$ , HC(2)), 2.80 (ddd, 1 H,  $J = 13.6$ , 8.3, 1.5, HC(5)), 2.64 (dd, 1 H,  $J = 16.1$ , 3.4, HC(12)), 2.17 (dd, 1 H,  $J = 16.1$ , 11.1, HC(12)), 2.09 (dd, 1 H,  $J = 13.7$ , 5.9, HC(5)), 1.27 (t, 3 H,  $J = 7.1$ , H<sub>3</sub>C(3')), 1.25 (t, 3 H,  $J = 7.1$ , H<sub>3</sub>C(3')).

$^{13}\text{C}$  NMR: (126 MHz,  $\text{CDCl}_3$ )

173.1 (C(13)), 171.9 (C(1')), 171.6 (C(1')), 158.4 (C(3)), 141.9 (C(7)), 129.7 (C(10)), 129.5 (C(8)), 123.2 (C(6)), 114.1 (C(9)), 61.8 (C(2')), 61.7 (C(2')), 58.6 (C(1)), 55.5 (C(11)), 51.8 (C(14)), 43.4 (C(2)), 40.4 (C(5)), 36.5 (C(4)), 14.3 (C(3')), 14.2 (C(3')).

IR: (neat)

2982 (s), 2939 (m), 1731 (s), 1608 (s), 1512 (s), 1443 (m), 1367 (m), 1252 (s), 1178 (s), 1074 (s), 1032 (s), 863 (m), 832 (m).

LRMS: (EI):

404 (67.9,  $[\text{M}]^+$ ), 330 (100.0), 257 (59.5), 205 (26.8), 197 (32.4), 183 (19.5), 121 (79.0).

HRMS: (EI,  $[\text{M}]^+$ ):

calcd.: 404.1835

found: 404.1839

Analysis:  $\text{C}_{20}\text{H}_{26}\text{O}_5$  (404.45)

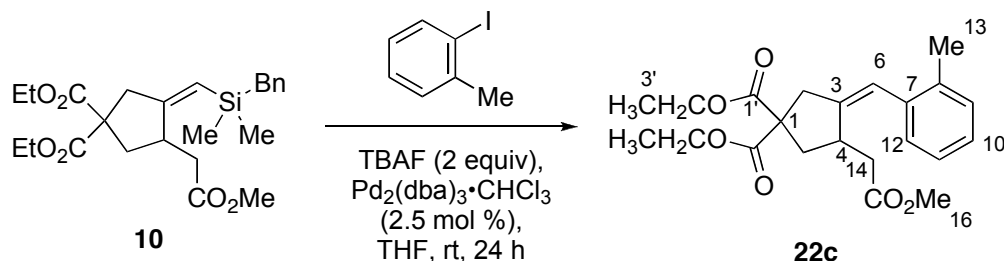
calcd.: C, 65.77; H, 6.98.

found: C, 65.36; H, 6.91.

$R_f$ : 0.21 (silica gel, hexane/EtOAc, 5/1, UV)

$t_R$ : 2.675 min (Agilent Zorbax 300SB-C8, 100% MeCN (1 mL/min))

**Cross-Coupling Reaction of 10 with 2-Iodobenzene. Preparation of Diethyl (Z)-3-(2-Methylbenzylidene)-4-methoxycarbonylcyclopentane-1,1-dicarboxylate (22c).**



Alkylidenesilane **10** (476 mg, 1.10 mmol, 1.1 equiv) in a 10-mL, round-bottomed flask with a magnetic stir bar and fitted with a gas inlet adaptor, was dissolved in a solution of TBAF·3H<sub>2</sub>O (1.0 M in THF, 2.0 mL, 2.0 mmol, 2.0 equiv) and the resulting light-yellow solution was stirred at room temperature under Ar for approximately 3 min. Then 2-iodotoluene

(220 mg, 1.00 mmol, 1.0 equiv) and  $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$  (26 mg, 0.025 mmol, 2.5 mol %) were added to the solution sequentially. The flask was purged with Ar, and the reaction mixture was stirred at room temperature under Ar atmosphere for 24 h. Then, the reaction mixture was passed through thin layer of silica gel (approximately 1 cm) followed by a wash of EtOAc (100 mL). The dark-brown filtrate was added silica gel (1 g) and was concentrated under reduced pressure. The crude product adsorbed on silica gel was purified using flash chromatography (silica gel (45 g), hexane/EtOAc, 40/1 (500 mL), 30/1 (500 mL), 20/1 (500 mL), 10/1 (1 L), 5/1 (250 mL)), reverse phase flash chromatography (first column: reverse phase silica gel (80 g), MeOH/ $\text{H}_2\text{O}$ , 3/1 (500 mL), 5/1 (250 mL), second column: reverse phase silica gel (60 g), MeOH/ $\text{H}_2\text{O}$ , 3/1 (300 mL), 5/1 (200 mL)), and diffusion pump distillation to afford 284 mg (73%) of **22c** as a colorless, viscous liquid.

Data for **22c**:

b.p.: 180 °C (ABT) at  $5.5 \times 10^{-5}$  mmHg

$^1\text{H}$  NMR: (500 MHz,  $\text{CDCl}_3$ )

7.20-7.16 (m, 3 H, HC(9), HC(10), HC(11)), 7.15-7.12 (m, 1 H, HC(12)), 6.44 (s, 1 H, HC(6)), 4.26-4.13 (m, 2 H,  $\text{H}_2\text{C}(2')$ ), 4.24 (q, 2 H,  $J = 7.6$ ,  $\text{H}_2\text{C}(2')$ ), 3.56 (s, 3H,  $\text{H}_3\text{C}(16)$ ), 3.47-3.39 (m, 1 H, HC(4)), 3.20 (dt, 1 H,  $J = 16.1$ , 2.4, HC(2)), 3.06 (dt, 1 H,  $J = 16.1$ , 1.5, HC(2)), 2.75 (ddd, 1 H,  $J = 13.4$ , 8.3, 1.4, HC(5)), 2.29 (dd, 1 H,  $J = 16.0$ , 4.1, HC(14)), 2.21 (s, 3 H,  $\text{H}_3\text{C}(13)$ ), 2.05 (dd, 1 H,  $J = 15.9$ , 10.4, HC(14)), 2.01 (dd, 1 H,  $J = 13.6$ , 7.2, HC(5)), 1.28 (t, 3 H,  $J = 7.1$ ,  $\text{H}_3\text{C}(3')$ ), 1.27 (t, 3 H,  $J = 7.2$ ,  $\text{H}_3\text{C}(3')$ ).

$^{13}\text{C}$  NMR: (126 MHz,  $\text{CDCl}_3$ )

172.8 (C(15)), 171.8 (C(1')), 171.6 (C(1')), 143.8 (C(3)), 136.7 (C(7)), 136.1 (C(8)), 130.0 (C(aryl)), 128.2 (C(12)), 127.2 (C(aryl)), 126.0 (C(aryl)), 123.1 (C(6)), 61.8 (C(2')), 61.8 (C(2')), 58.6 (C(1)), 51.6 (C(16)), 42.6 (C(2)), 40.0 (C(5)), 37.6 (C(14)), 36.2 (C(4)), 20.1 (C(13)), 14.3 (C(3')), 14.2 (C(3')).

IR: (neat)

2982 (m), 1732 (s), 1436 (m), 1367 (m), 1247 (s), 1188 (s), 1075 (s), 1024 (m), 863 (w), 749 (m).

LRMS: (EI):

388 (33.6,  $[\text{M}]^+$ ), 314 (100.0), 268 (37.5), 241 (48.3), 181 (44.1), 167 (53.1), 105

(78.7), 83 (42.3).

HRMS: (EI,  $[M]^+$ ):

calcd.: 388.1886

found: 388.1881

Analysis:  $C_{22}H_{29}O_6$  (388.45)

calcd.: C, 68.02; H, 7.27.

found: C, 67.85; H, 7.09.

R<sub>f</sub>: 0.40 (silica gel, hexane/EtOAc, 5/1, UV)

t<sub>R</sub>: 2.700 min (Agilent Zorbax 300SB-C8, 100% MeCN (1 mL/min))

**Results of the NOE Experiments****Alkylidenesilanes 6-11**

Table 1, entry 1

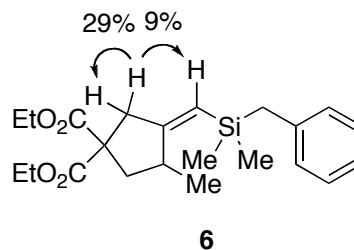
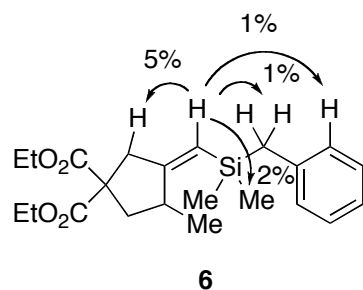


Table 1, entry 2

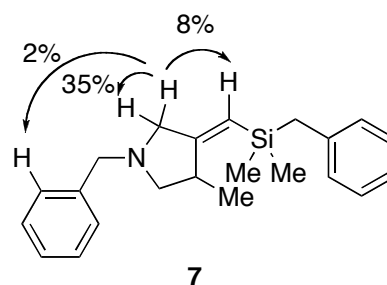
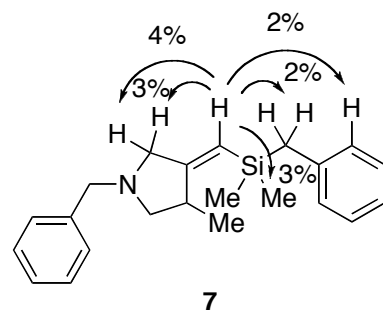


Table 1, entry 3

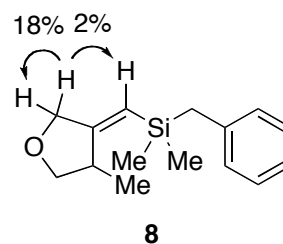
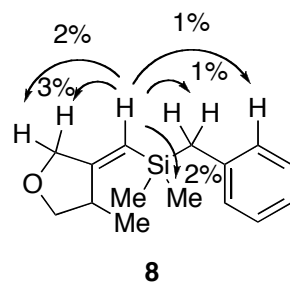


Table 1, entry 4

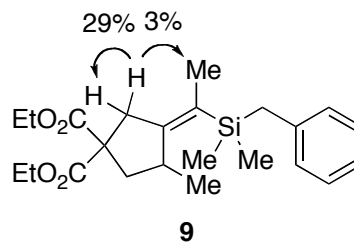
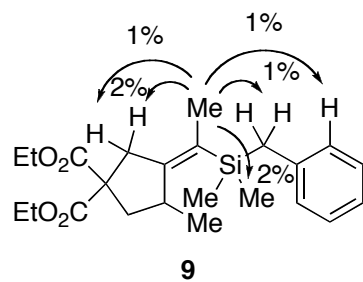


Table 1, entry 5

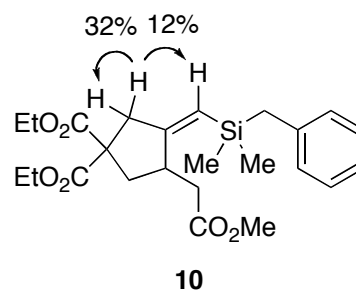
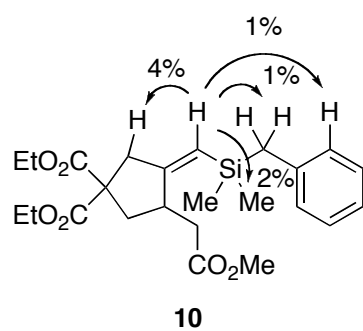


Table 1, entry 6

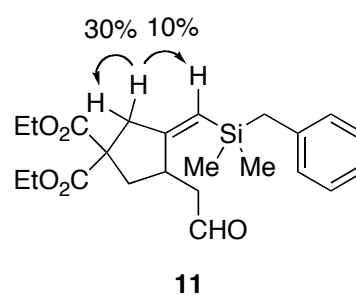
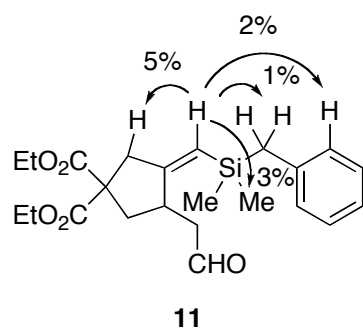
**Benzylidene-cyclopentanes 16, 19-22**

Table 5, entry 1

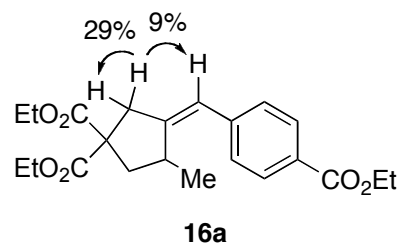
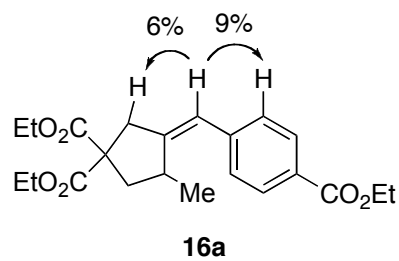


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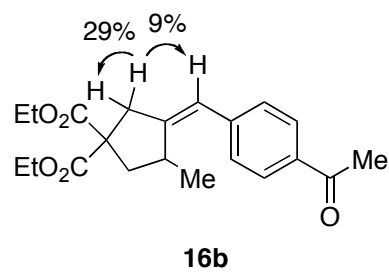
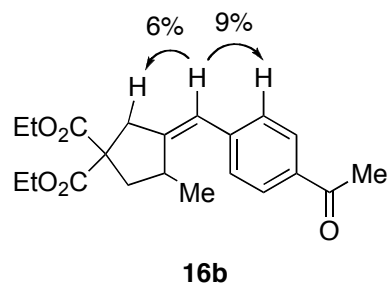


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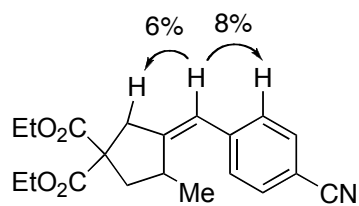
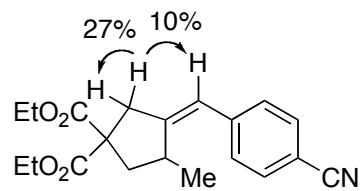
**16c****16c**

Table 5, entry 4

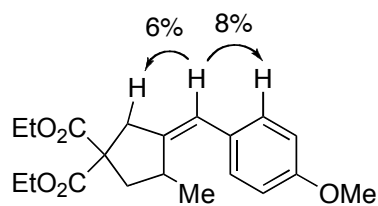
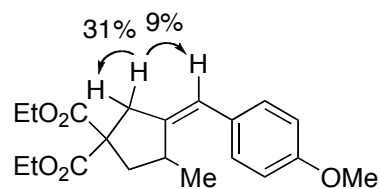
**16d****16d**

Table 5, entry 5

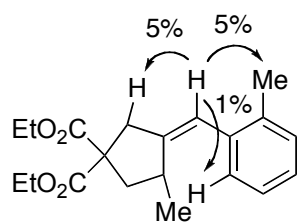
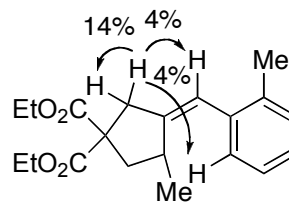
**16e****16e**

Table 5, entry 6

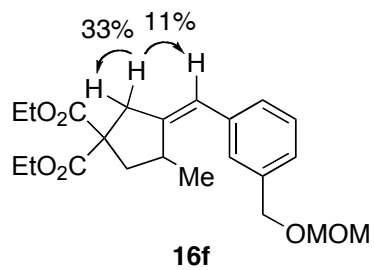
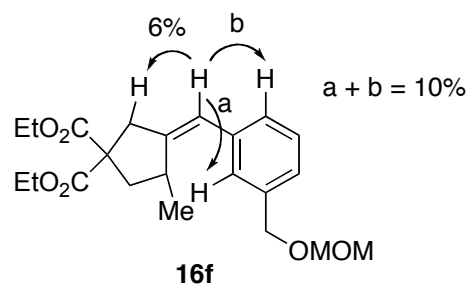
**16f****16f**

Table 5, entry 7

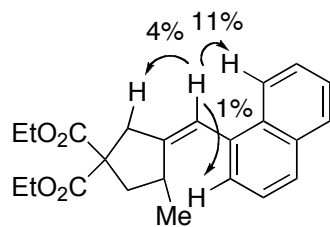
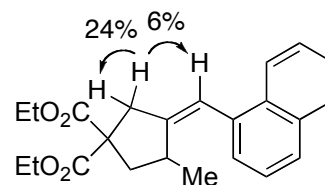
**16g****16g**

Table 6, entry 1

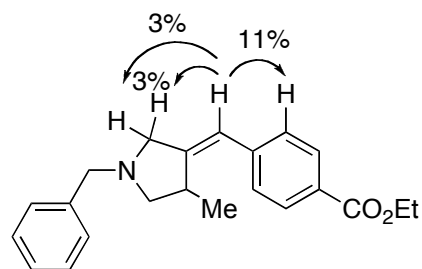
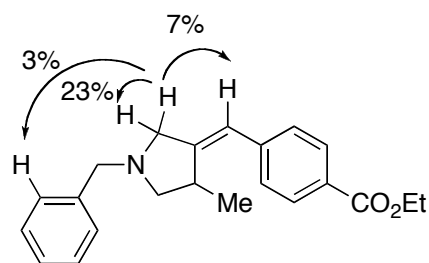
**18a****18a**

Table 6, entry 2

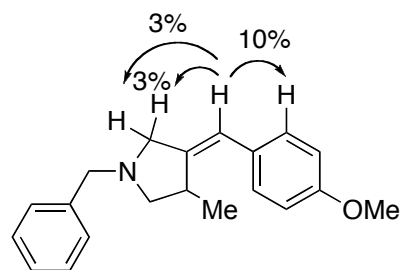
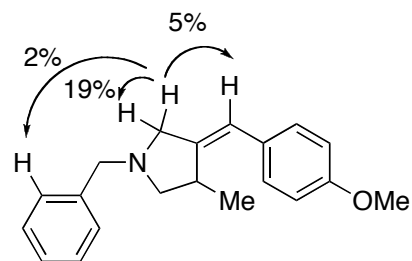
**18b****18b**

Table 6, entry 3

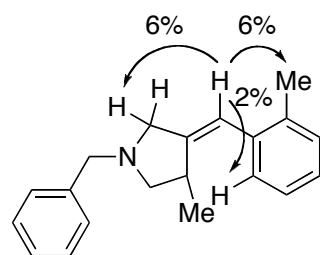
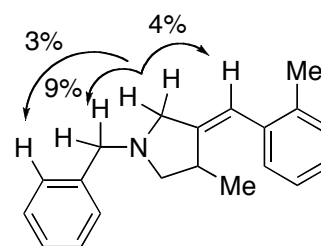
**18c****18c**



Table 6, entry 4

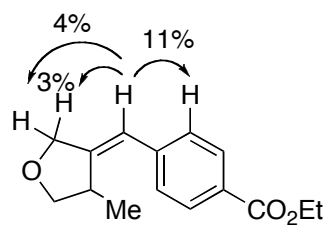
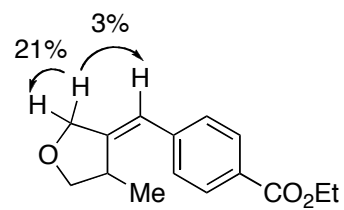
**20a****20a**

Table 6, entry 5

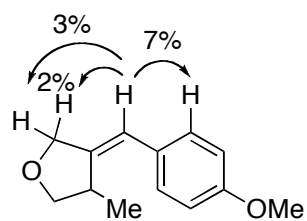
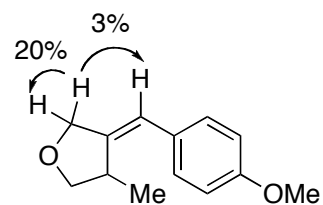
**20b****20b**

Table 6, entry 6

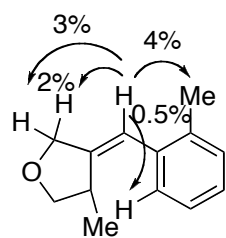
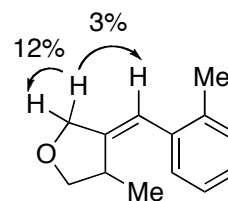
**20c****20c**

Table 6, entry 7

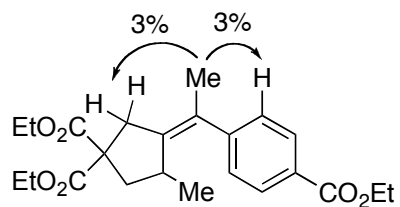
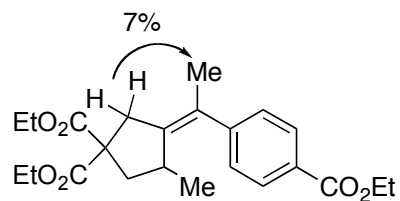
**21a****21a**

Table 6, entry 8

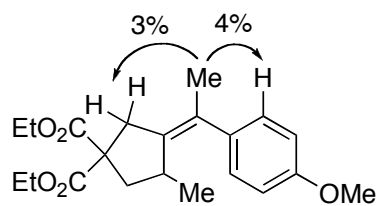
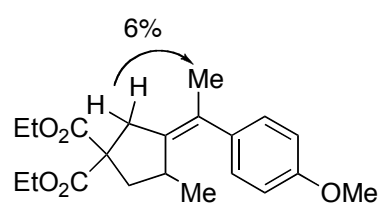
**21b****21b**

Table 6, entry 9

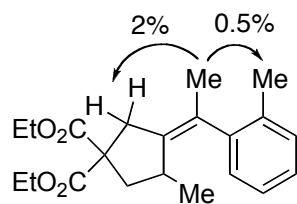
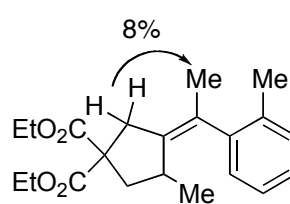
**21c****21c**

Table 6, entry 10

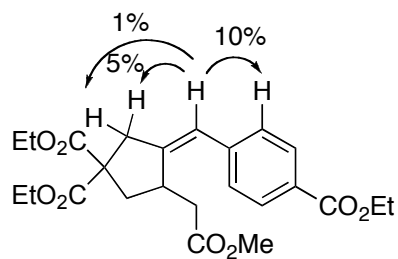
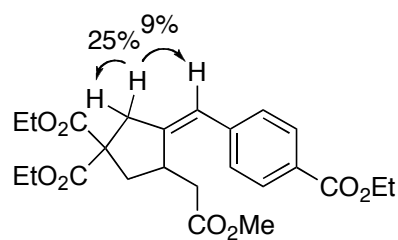
**22a****22a**

Table 6, entry 11

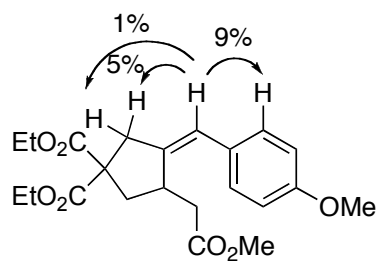
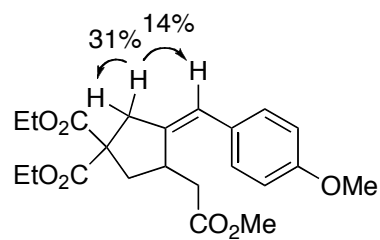
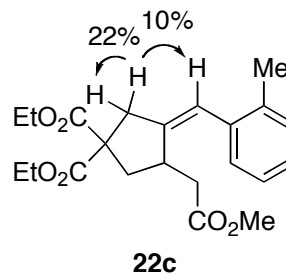
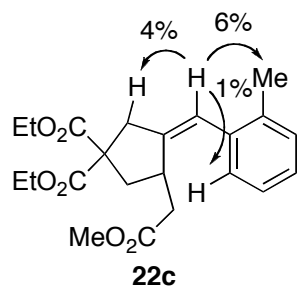
**22b****22b**

Table 6, entry 12



### Procedure of the VT NMR Experiments

Approximately 20 mg of **21c** was dissolved in approximately 0.5 mL of toluene-*d*<sub>8</sub>, in a 5-mm NMR tube. This sample was placed in a Varian Unity-500 NMR spectrometer. <sup>1</sup>H NMR spectra were measured at 25, 40, 60, 80, and 100 °C.

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