

## **Supporting Information**

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Direct Substitution of the Hydroxyl Group in Alcohols with Silyl Nuculeophiles Catalyzed by Indium Trichloride

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**General.** IR spectra were recorded as thin films or as solids in KBr pellets on a HORIBA FT-720 spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained with a 270 and 67.9 MHz spectrometer, respectively, with TMS as internal or external standard. Mass spectra were recorded on a JEOL JMS-DS303 or a Shimadzu GCMS-QP2000A spectrometer. GLC analyses were performed on a Shimadzu GC-8A with FID using a 2 m x 3 mm column packed with SE-52. Column chromatography was performed on silica gel (Wakogel C-300). Bulb-to-bulb distillation (Kugelrohr) was accomplished in a Sibata GTO-250RS at the oven temperature and pressure indicated. Yields were determined by GLC or <sup>1</sup>H NMR using internal standards.

**Materials.** Dichloromethane and 1,2-dichloroethane were distilled from  $CaH_2$ . THF and hexane were distilled from sodium and benzophenone. DMF was distilled after stirring with molecular sieves 4A. All catalysts in Table 1 were commercially available. Allylsilanes 1, 7, and alkynylsilane 14 were commercially available.  $\gamma$ -Substituted allylsilanes 8,<sup>[1]</sup> 10,<sup>[2]</sup> and propargylsilane 12<sup>[3]</sup> were prepared according to the literature. The alcohols 2d, 2k, and 2m were prepared according to our paper.<sup>[4]</sup> All other starting alcohols are commercially available.

General Procedure for InCl<sub>3</sub>-Catalyzed Allylation of Alcohols Using Allylic Silanes (1, 7, 8, 10, 12, or 14). To a mixture of InCl<sub>3</sub> (0.05 mmol) and the alcohol (1.0 mmol) in dry dichloromethane or 1,2-dichloroethane (1 mL) was added allylsilane (2.0 mmol) under nitrogen. The reaction mixture was stirred under the reaction conditions noted in the text. The resulting mixture was poured into  $Et_2O$  (50 mL) and  $NaHCO_3$  aq (15%, 30 mL). The solution was extracted with  $Et_2O$  and the organic layer was dried over MgSO<sub>4</sub>. The evaporation of the ether

solution gave the crude product which was analyzed by GLC and NMR. The details of further purification are performed for the new compound and described in product data section.

**Product data.** The products **3b**,<sup>[5]</sup> **3f**<sup>[5]</sup> and **5**<sup>[6]</sup>, and **15a**<sup>[7]</sup> showed spectra in an excellent agreement with the reported data. The spectral data of **6** was in an excellent agreement with the sample which is commercially available. Spectral data for the products, **3a**, **3c-e**, **3g-m**, **9**, **11a** and **11g** are shown below.

**4,4-Diphenyl-1-butene (3a).** According to the general procedure, this compound was prepared from **1**, **2a**, and InCl<sub>3</sub> to give the product as a colorless liquid after chromatography (hexane). Further purification was performed by distillation under reduced pressure: bp: 100 °C/0.011mmHg; IR: (neat) 1643 (C=C) cm<sup>-1</sup>;  $^{1}$ H NMR: (270 MHz, CDCl<sub>3</sub>) 7.31-7.14 (m, 5H, aroma), 5.80-5.64 (m, 1H, 2-H), 5.07-4.92 (m, 2H, 1-H<sub>2</sub>), 4.01 (t, J = 7.8 Hz, 1H, 4-H), 2.82 (t, J = 7.8 Hz, 2H, 3-H<sub>2</sub>);  $^{13}$ C NMR: (67.9 MHz, CDCl<sub>3</sub>) 144.45 (s, Ph-*ipso*), 136.79 (d, C-2), 128.36 (d, Ph-o), 127.90 (d, Ph-m), 126.14 (d, Ph-p), 116.27 (t, C-1), 51.19 (d, C-4), 39.92 (t, C-3); MS: (EI, 70 eV) m/z 208 (M<sup>+</sup>, 0.6), 167 (M<sup>+</sup> -CH<sub>2</sub>CH=CH<sub>2</sub>, 100), 165 (30); HRMS: (EI, 70 eV) calcd for C<sub>16</sub>H<sub>16</sub> 208.1252, found m/z 208.1266, 208.1262, 208.1234 (M<sup>+</sup>). Anal. Calcd for C<sub>16</sub>H<sub>16</sub>: C, 92.26; H, 7.74. Found: C, 92.20; H, 7.73.

**4-(4-Chlorophenyl)-4-phenyl-1-butene (3c)**. According to the general procedure, this compound was prepared from **1**, **2c**, and InCl<sub>3</sub> to give the product as a colorless liquid after chromatography (hexane). Further purification was performed by distillation under reduced pressure: bp: 118 °C/0.3 mmHg; IR: (neat) 1643 (C=C), 1095 (Ph-Cl) cm<sup>-1</sup>; <sup>1</sup>H NMR: (270 MHz, CDCl<sub>3</sub>) 7.13-7.31 (m, 9H, aroma), 5.69 (ddt, J = 17.1, 10.3, 6.8 Hz, 1H, 2-H), 5.02 (ddd, J = 17.1, 2.0, 1.5 Hz, 1H, 1-H<sup>A</sup>), 4.95 (ddd, J = 10.3, 2.0, 1.2 Hz, 1H, 1-H<sup>B</sup>), 3.98 (t, J = 8.1 Hz, 1H, 4-H), 2.75-2.80 (m, 2H, 3-H<sub>2</sub>), 2.76 (ddd, J = 8.1, 6.8, 1.5 Hz, 1H, 3-H<sup>B</sup>); <sup>13</sup>C NMR: (67.9 MHz, CDCl<sub>3</sub>) 143.90 (s, ipso), 142.87 (s, ipso), 136.32 (d, C-2), 131.82 (s, C-Cl), 129.24 (d, aroma-CH), 128.45 (d, aroma-CH), 127.75 (d, aroma-CH), 126.33 (d, p-Ph), 116.57 (t, C-1), 50.54 (d, C-4), 39.83 (t, C-3); MS: (EI, 70 eV) m/z 244 (M<sup>+</sup> + 2, 0.11), 242 (M<sup>+</sup>, 0.41), 203 (45), 201 (M<sup>+</sup> - CH<sub>2</sub>CH=CH<sub>2</sub>, 100), 165 (51); HRMS: (EI, 70 eV) calcd for C<sub>16</sub>H<sub>15</sub>Cl 242.0862, found m/z 242.0858, 242.0878, 242.0852 (M<sup>+</sup>). Anal. Calcd for C<sub>16</sub>H<sub>15</sub>Cl: C, 79.17; H, 6.23. Found: C, 78.86; H, 6.30.

**4-Phenyl-4-(4-nitrophenyl)-1-butene (3d).** According to the general procedure, this compound was prepared from **1**, **2d**, and InCl<sub>3</sub> to give the product as a colorless liquid after chromatography (hexane/Et<sub>2</sub>O, 4/1). Further purification was performed by distillation under reduced pressure: bp: 150-165 °C/ 0.011mmHg; IR: (neat) 1640 (C=C), 1520 (NO<sub>2</sub>), 1350 (NO<sub>2</sub>) cm<sup>-1</sup>; <sup>1</sup>H NMR: (270 MHz, CDCl<sub>3</sub>) 8.14 (d, J = 8.8 Hz, 2H, aroma), 7.40-7.20 (m, 7H, aroma), 5.77-5.62 (m, 1H, 2-H), 5.04 (d, J = 17.6 Hz, 1H, 1-H<sup>A</sup>), 4.98 (d, J = 10.3 Hz, 1H, 1-H<sup>B</sup>), 4.13 (t,

J = 7.8 Hz, 1H, 4-H), 2.85 (m, 2H, 3-H<sub>2</sub>); <sup>13</sup>C NMR: (67.9 MHz, CDCl<sub>3</sub>) 152.06 (s, <sup>1</sup>Ph-*ipso*), 146.31 (s, <sup>1</sup>Ph-*p*), 142.67 (s, <sup>2</sup>Ph-*ipso*), 135.58 (d, C-2), 128.74 (d, <sup>1</sup>Ph-*o*), 128.68 (d, <sup>2</sup>Ph-*o*), 127.77 (d, <sup>2</sup>Ph-*m*), 126.77 (d, <sup>2</sup>Ph-*p*), 123.62 (d, <sup>1</sup>Ph-*m*), 117.13 (t, C-1), 50.89 (d, C-4), 39.41 (t, C-3); MS: (EI, 70 eV) m/z 253 (M<sup>+</sup>, 1.0), 212 (M<sup>+</sup> - CH<sub>2</sub>=CHCH<sub>2</sub>, 100), 166 (M<sup>+</sup> - CH<sub>2</sub>=CHCH<sub>2</sub> - NO<sub>2</sub>, 31), 165 (M<sup>+</sup>, 41), 103 (37); HRMS: (EI, 70 eV) calcd for C<sub>16</sub>H<sub>15</sub>NO<sub>2</sub> 253.1103, found m/z 253.1128, 253.1086, 253.1084 (M<sup>+</sup>). Anal. Calcd for C<sub>16</sub>H<sub>15</sub>NO<sub>2</sub>: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.51; H, 6.22; N, 5.50.

**4-Phenyl-4-(4-methoxyphenyl)-1-butene (3e).** According to the general procedure, this compound was prepared from **1**, **2e**, and InCl<sub>3</sub> to give the product as a colorless liquid after chromatography (hexane/AcOEt, 9/1). Further purification was performed by distillation under reduced pressure: bp:  $103 \, ^{\circ}\text{C}/ \, 0.11 \, \text{mmHg}$ ; IR: (neat)  $1635 \, (\text{C=C}) \, \text{cm}^{-1}$ ;  $^{1}\text{H NMR}$ : (270 MHz, CDCl<sub>3</sub>) 7.30-7.13 (m, 7H, aroma), 6.82 (d,  $J = 8.9 \, \text{Hz}$ , 2H, aroma), 5.795.64 (m, 1H, 2-H), 5.06-4.92 (m, 2H, 1-H<sub>2</sub>), 3.96 (t,  $J = 7.8 \, \text{Hz}$ , 1H, 4-H), 3.76 (s, 3H, Ar-CH<sub>3</sub>), 2.78 (t,  $J = 7.8 \, \text{Hz}$ , 2H, 3-H<sub>2</sub>);  $^{13}\text{CNMR}$ : (67.9 MHz, CDCl<sub>3</sub>) 157.88 (s,  $^{1}\text{Ph-}p$ ), 144.89 (s,  $^{2}\text{Ph-ipso}$ ), 136.93 (d, C-2), 136.61 (s,  $^{1}\text{Ph-ipso}$ ), 128.81 (d,  $^{1}\text{Ph-o}$ ), 128.36 (d,  $^{2}\text{Ph-o}$ ), 127.81 (d,  $^{2}\text{Ph-m}$ ), 126.05 (d,  $^{2}\text{Ph-}p$ ), 16.18 (t, C-1), 113.73 (d,  $^{1}\text{Ph-}m$ ), 55.17 (q, OMe), 50.35 (d, C-4), 40.10 (t, C-3); MS: (EI, 70 eV) m/z 238 (M<sup>+</sup>, 1.6), 197 (M<sup>+</sup> -CH<sub>2</sub>=CHCH<sub>2</sub>, 100), 165 (15); HRMS: (EI, 70 eV) calcd for C<sub>17</sub>H<sub>18</sub>O 238.1358, found m/z 238.1371, 238.1353, 238.1347 (M<sup>+</sup>). Anal. Calcd for C<sub>17</sub>H<sub>18</sub>O: C, 85.67; H, 7.61. Found: C, 85.46; H, 7.65.

**4-Phenyl-1-pentene** (**3g**). According to the general procedure, this compound was prepared from **1**, **2g**, and InCl<sub>3</sub> to give the product as a colorless liquid after chromatography (hexane). Further purification was performed by distillation under reduced pressure: bp: 40-50 °C/ 0.011mmHg; IR: (neat) 1643 (C=C) cm<sup>-1</sup>;  $^{1}$ H NMR: (270 MHz, CDCl<sub>3</sub>) 7.32-7.09 (m, 5H, aroma), 5.70-5.55 (m, 1H, 2-H), 4.85-4.93 (m, 2H, 1-H<sub>2</sub>), 2.77-2.64 (m, 1H, 4-H), 2.36-2.14 (m, 1H, 3-H<sub>2</sub>), 1.17 (d, J = 6.8 Hz, 3H, 5-H<sub>3</sub>);  $^{13}$ C NMR: (67.9 MHz, CDCl<sub>3</sub>) 147.01 (s, Ph-*ipso*), 137.14 (d, C-2), 128.28 (d, Ph-*o*), 126.97 (d, Ph-*m*), 125.93 (d, Ph-*p*), 115.87 (t, C-1), 42.67 (t, C-3), 39.75 (d, C-4), 21.49 (q, C-5); MS: (EI, 70 eV) m/z 146 (M<sup>+</sup>, 6.5), 105 (M<sup>+</sup> - CH<sub>2</sub>=CHCH<sub>2</sub>· 100), 91 (PhCH<sub>2</sub>, 3.2), 77 (Ph, 8.9); HRMS: (EI, 70 eV) calcd for C<sub>11</sub>H<sub>14</sub> 146.1096, found m/z 146.1103, 146.1100, 146.1087 (M<sup>+</sup>).

**4-Methyl-4-phenyl-1-pentene (3h).** According to the general procedure, this compound was prepared from **1**, **2h**, and InCl<sub>3</sub> to give the product as a colorless liquid after chromatography (hexane). Further purification was performed by distillation under reduced pressure: bp: 30 °C/0.11 mmHg; IR: (neat) 1643 (C=C) cm<sup>-1</sup>;  $^{1}$ H NMR: (270 MHz, CDCl<sub>3</sub>) 7.37-7.13 (m, 5H, aroma), 5.62-5.47 (m, 1H, 2-H), 5.00-4.91 (m, 2H, 1-H<sub>2</sub>), 2.37 (d, J = 6.8 Hz, 2H, 3-H<sub>2</sub>), 1.30 (s, 6H, 5-H<sub>3</sub> and 4-CH<sub>3</sub>);  $^{13}$ CNMR: (67.9 MHz, CDCl<sub>3</sub>) 149.18 (s, Ph-ipso), 135.52 (d, C-2), 128.00

(d, Ph-m), 125.80 (d, Ph-o), 125.50 (d, Ph-p), 116.88 (t, C-1), 48.82 (t, C-3), 37.56 (s, C-4), 28.50 (q, C-5 and 4-C); MS: (EI, 70 eV) m/z 160 (M<sup>+</sup>, 0.4), 119 (M<sup>+</sup> -CH<sub>2</sub>=CHCH<sub>2</sub>, 100), 91 (46); HRMS: (EI, 70 eV) calcd for C<sub>12</sub>H<sub>16</sub> 160.1252, found m/z 160.1260, 160.1271, 160.1261 (M<sup>+</sup>). Anal. Calcd for C<sub>12</sub>H<sub>16</sub>: C, 89.94; H, 10.06. Found: C, 89.70; H, 9.99.

**4-Chloro-(4-chlorophenyl)1-pentene (3i).** According to the general procedure, this compound was prepared from **1**, **2i**, and InCl<sub>3</sub> to give the product as a colorless liquid after chromatography (hexane). Further purification was performed by distillation under reduced pressure: bp: 50-60 °C/ 0.011mmHg; IR: (neat) 1643 (C=C), 1095 (Ph-Cl) cm<sup>-1</sup>; <sup>1</sup>H NMR: (270 MHz, CDCl<sub>3</sub>) 7.15 (d, J = 8.8 Hz, 2H, aroma), 7.01 (d, J = 8.8 Hz, 2H, aroma), 5.65-5.50 (m, 1H, 2-H), 4.88 (d, J = 18.6 Hz, 1H, 1-H<sup>A</sup>), 4.86 (d, J = 10.3 Hz, 1H, 1-H<sup>B</sup>), 2.70-2.60 (m, 1H, 4-H), 2.29-2.10 (m, 2H, 3-H<sub>2</sub>), 1.13 (d, J = 7.3 Hz, 3H, 5-H<sub>3</sub>); <sup>13</sup>C NMR: (67.9 MHz, CDCl<sub>3</sub>) 145.36 (s, Ph-*ipso*), 136.62 (d, C-2), 131.50 (s, Ph-*p*), 128.37 (d), 128.32 (d), 116.21 (t, C-1), 42.53 (t, C-3), 39.20 (d, C-4), 21.44 (q, C-5); MS: (EI, 70 eV) m/z 182 (M<sup>+</sup> + 2, 3.0), 180 (M<sup>+</sup>, 7.9), 141 (M<sup>+</sup> + 2 - CH<sub>2</sub>=CHCH<sub>2</sub>, 39), 139 (M<sup>+</sup> - CH<sub>2</sub>=CHCH<sub>2</sub>, 100), 103 (37); HRMS: (EI, 70 eV) calcd for C<sub>11</sub>H<sub>13</sub>Cl 180.0706, found m/z 180.0726, 180.0713, 180.0706 (M<sup>+</sup>).

**2-Allyl-bicyclo[2.2.1]heptane (3j).** According to the general procedure, this compound was prepared from **1**, **2j**, and InCl<sub>3</sub> to give the product as a colorless liquid after chromatography (hexane). Further purification was performed by distillation under reduced pressure: bp:  $105 \, ^{\circ}\text{C}/27 \, \text{mmHg}$ ; IR: (neat)  $1639 \, (\text{C=C}) \, \text{cm}^{-1}$ ;  $^{1}\text{H NMR}$ : (270 MHz, CDCl<sub>3</sub>) 5.84- $5.69 \, (\text{m}, 1\text{H}, 2\text{-H})$ , 5.01- $4.83 \, (\text{m}, 2\text{H}, 1\text{-H}_2)$ , 2.19- $2.17 \, (\text{m}, 1\text{H}, 4\text{-H})$ , 2.04- $1.79 \, (\text{ddd}, J = 14.1, 7.0, 7.2 \, \text{Hz}, 2\text{H}, 3\text{-H}_2)$ ,  $1.96 \, (\text{m}, 1\text{H}, 9\text{-H})$ , 1.52- $1.41 \, (\text{m}, 2\text{H}, 8\text{-H})$ , 1.39- $1.31 \, (\text{m}, 1\text{H}, 6\text{-H})$ ,  $1.35 \, (\text{dd}, J = 3.6, 2.2 \, \text{Hz}, 2\text{H}, 10\text{-H})$ ,  $1.28 \, (\text{dd}, J = 3.8, 1.9 \, \text{Hz}, 2\text{H}, 5\text{-H})$ , 1.18- $1.01 \, (\text{m}, 2\text{H}, 7\text{-H})$ ;  $^{13}\text{CNMR}$ : (67.9 MHz, CDCl<sub>3</sub>)  $138.10 \, (\text{d}, \text{C-2})$ ,  $114.76 \, (\text{t}, \text{C-1})$ ,  $41.58 \, (\text{d}, \text{C-6})$ ,  $41.08 \, (\text{t}, \text{C-3})$ ,  $40.65 \, (\text{d}, \text{C-4})$ ,  $37.78 \, (\text{t}, \text{C-10})$ ,  $36.66 \, (\text{d}, \text{C-9})$ ,  $35.13 \, (\text{t}, \text{C-5})$ ,  $30.01 \, (\text{t}, \text{C-8})$ ,  $28.82 \, (\text{t}, \text{C-7})$ ; MS: (EI,  $70 \, \text{eV}$ )  $m/z \, 136 \, (\text{M}^+, 0.4)$ ,  $95 \, (\text{M}^+ \text{-CH}_2 = \text{CHCH}_2, 100)$ ; HRMS: (EI,  $70 \, \text{eV}$ ) calcd for  $\text{C}_{10}\text{H}_{16} \, 136.1252$ , found  $m/z \, 136.1232$ , 136.1244,  $136.1272 \, (\text{M}^+)$ .

**Ethyl 3-phenyl-5-hexenate (3k).** According to the general procedure, this compound was prepared from **1**, **2k**, and InCl<sub>3</sub> to give the product as a colorless liquid after purification by TLC (hexane/Et<sub>2</sub>O, 8/1, R<sub>f</sub> = 0.57): IR: (neat) 1736 (C=O), 1643 (C=C) cm<sup>-1</sup>; <sup>1</sup>H NMR: (270 MHz, CDCl<sub>3</sub>) 7.32-7.16 (m, 5H, aroma), 5.66 (ddt, J = 17.1, 10.3, 6.8 Hz, 1H, 5-H), 5.00 (dd, J = 17.1, 1.5 Hz, 1H, 6-H<sup>A</sup>), 4.97 (dd, J = 10.3, 1.5 Hz, 1H, 6-H<sup>B</sup>), 4.02 (q, J = 7.1 Hz, 2H, OCH<sub>2</sub>), 3.26-3.16 (m, 1H, 3-H), 2.68 (dd, J = 15.1, 6.8 Hz, 1H, 2-H<sup>A</sup>), 2.55 (dd, J = 15.1, 8.5 Hz, 1H, 2-H<sup>B</sup>), 2.39 (td, J = 6.8, 1.2 Hz, 2H, 4-H<sub>2</sub>), 1.13 (t, J = 7.1 Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR: (67.9 MHz, CDCl<sub>3</sub>) 172.21 (s, C-1), 143.48 (s, ipso), 135.88 (d, C-5), 128.30 (d, aroma-CH), 127.37 (d, aroma-CH), 126.42 (d, aroma-CH), 116.77 (t, C-6), 60.22 (t, OCH<sub>2</sub>), 41.83 (d, C-3), 40.65 (t, C-1)

2 and C-4), 14.12 (q, CH<sub>3</sub>); MS: (EI, 70 eV) m/z 218 (M<sup>+</sup>, 9), 177 (M<sup>+</sup> - CH<sub>2</sub>CH=CH<sub>2</sub>, 23), 144 (35), 135 (100), 130 (45), 105 (53), 91 (33), 77 (11); HRMS: (EI, 70 eV) calcd for C<sub>14</sub>H<sub>18</sub>O<sub>2</sub> 218.1307, found m/z 218.1300, 218.1326, 218.1292 (M<sup>+</sup>). Anal. Calcd for C<sub>14</sub>H<sub>18</sub>O<sub>2</sub>: C, 77.03; H, 8.31. Found: C, 76.91; H, 8.39.

**6-Chloro-4-phenyl-1-hexene (3l).** According to the general procedure, this compound was prepared from **1**, **2l**, and InCl<sub>3</sub> to give the product as a colorless liquid after chromatography (hexane/Et<sub>2</sub>O, 4/1). Further purification was performed by distillation under reduced pressure: bp: 110 °C/ 0.011mmHg; IR: (neat) 1643 (C=C) cm<sup>-1</sup>;  $^{1}$ H NMR: (270 MHz, CDCl<sub>3</sub>) 7.34-7.16 (m, 5H, aroma), 5.74-5.59 (m, 1H, 2-H), 5.04-4.94 (m, 2H, 1-H<sub>2</sub>), 3.47-3.38 (ddd, J = 10.7, 8.5, 6.8 Hz, 1H, 6-H<sup>A</sup>), 3.30-3.20 (ddd, J = 10.8, 7.3, 4.9 Hz, 1H, 6-H<sup>B</sup>), 2.92-2.84 (m, 1H, 4-H), 2.39 (m, 2H, 3-H<sub>2</sub>), 2.20-2.10 (m, 1H, 5-H<sup>A</sup>), 2.05-1.92 (m, 1H, 5-H<sup>B</sup>);  $^{13}$ C NMR: (67.9 MHz, CDCl<sub>3</sub>) 143.30 (s, Ph-*ipso*), 136.32 (d, C-2), 128.54 (d, Ph-*o*), 127.64 (d, Ph-*m*), 126.54 (d, Ph-*p*), 114.45 (t, C-1), 43.08 (t), 42.73 (d), 40.89 (t, C-4), 38.53 (t); MS: (EI, 70 eV) m/z 196 (M<sup>+</sup> + 2, 1.7), 194 (M<sup>+</sup>, 5.2), 155 (M<sup>+</sup> + 2 -CH<sub>2</sub>CH=CH<sub>2</sub>, 22), 153 (M<sup>+</sup> -CH<sub>2</sub>CH=CH<sub>2</sub>, 63), 91 (100); HRMS: (EI, 70 eV) calcd for C<sub>12</sub>H<sub>15</sub>Cl 194.0862, found m/z 194.0872, 194.0862, 194.0858 (M<sup>+</sup>).

**7-Hydroxy-4-phenyl-1-heptene (3m).** According to the general procedure, this compound was prepared from **1**, **2m**, and InCl<sub>3</sub> to give the product as a colorless liquid after chromatography (hexane/AcOEt, 3/1). Further purification was performed by distillation under reduced pressure: bp: 125 °C/ 0.11 mmHg; IR: (neat) 3340 (OH), 1643 (C=C) cm<sup>-1</sup>; <sup>1</sup>H NMR: (270 MHz, CDCl<sub>3</sub>) 7.31-7.13 (m, 5H, aroma), 5.74-5.59 (m, 1H, 2-H), 4.99-4.91 (m, 2H, 1H<sub>2</sub>), 3.55 (t, J = 6.7 Hz, 2H, 7-H<sub>2</sub>), 2.66-2.56 (m, 1H, 4-H), 2.37 (t, J = 6.8 Hz, 2H, 3-H<sub>2</sub>), 1.85-1.52 (m, 2H, 5-H<sub>2</sub>), 1.50-1.34 (m, 2H, 6-H<sub>2</sub>); <sup>13</sup>CNMR: (67.9 MHz, CDCl<sub>3</sub>) 144.89 (s, Ph-ipso), 136.93 (d, C-2), 128.30 (d), 127.64 (d), 126.09 (d, Ph-p), 115.93 (t, C-1), 62.93 (t, C-7), 45.66 (d, C-4), 41.38 (t, C-3), 31.94 (t, C-5), 30.69 (t, C-6); MS: (EI, 70 eV) m/z 190 (M<sup>+</sup>, 3.7), 149 (M<sup>+</sup>, -CH<sub>2</sub>=CHCH<sub>2</sub>, 40), 131 (100), 91 (44); HRMS: (EI, 70 eV) calcd for C<sub>13</sub>H<sub>18</sub>O 190.1358, found m/z 190.1362, 190.1333, 190.1366 (M<sup>+</sup>). Anal. Calcd for C<sub>13</sub>H<sub>18</sub>O: C, 82.06; H, 9.53. Found: C, 81.94; H, 9.38.

**4,4-Diphenyl-3-phenyl-1-butene (9a).** According to the general procedure, this compound was prepared from **8**, **2a**, and InCl<sub>3</sub> to give the product as a white solid after recrystallization (hexane): mp: 85-88 °C; IR: (KBr) 1635 (C=C) cm<sup>-1</sup>; <sup>1</sup>H NMR: (270 MHz, CDCl<sub>3</sub>) 7.38-6.97 (m, 15H, aroma), 5.92 (ddd, J = 17.1, 10.1, 7.3 Hz, 1H, 2-H), 4.88 (dd, J = 17.1, 10.1 Hz, 2H, 1-H<sub>2</sub>), 4.30 (d, J = 7.3 Hz, 1H, 4-H), 4.17 (dd, J = 7.3 Hz, 2H, 3-H<sub>2</sub>); <sup>13</sup>C NMR: (67.9 MHz, CDCl<sub>3</sub>) 143.46 (s), 143.17 (s), 142.69 (s), 140.90 (d, C-2), 128.71 (d), 128.64 (d), 128.38 (d), 128.32 (d), 128.22 (d), 128.08 (d), 126.28 (d), 126.08 (d), 125.83 (d), 115.95 (t, C-1), 57.00 (t, C-4), 54.42 (d, C-3); MS: (EI, 70 eV) m/z 284 (M<sup>+</sup>, 2.5), 167 (M<sup>+</sup> -

- CHPhCH=CH<sub>2</sub>, 100); HRMS: (EI, 70 eV) calcd for  $C_{22}H_{20}$  284.1565, found m/z 284.1571, 284.1563, 284.1553 (M<sup>+</sup>). Anal. Calcd for  $C_{22}H_{20}$ : C, 92.91; H, 7.09. Found: C, 92.52; H, 6.99.
- **3,3-Dimethyl-4,4-diphenyl-1-butene** (**11a**). According to the general procedure, this compound was prepared from **10**, **2a**, and InCl<sub>3</sub> to give the product as a colorless liquid. Further purification was performed by distillation and TLC (hexane/Et<sub>2</sub>O, 8/1, R<sub>f</sub> = 0.74): bp: 138 °C/0.3 mmHg; IR: (neat) 1635 (C=C) cm<sup>-1</sup>; <sup>1</sup>H NMR: (270 MHz, CDCl<sub>3</sub>) 7.11-7.40 (m, 10H, aroma), 6.07 (ddd, J = 17.6, 11.0, 1.2 Hz, <sup>1</sup>H, 4-H), 5.06 (dd, J = 11.0, 1.2 Hz, 1H, 1-H<sup>A</sup>), 4.99 (dd, J = 17.6, 1.2 Hz, 1H, 1-H<sup>B</sup>), 3.79 (s, 1H, 4-H), 1.07 (d, J = 1.2 Hz, 6H, CH<sub>3</sub>); <sup>13</sup>C NMR: (67.9 MHz, CDCl<sub>3</sub>) 145.76 (d, C-2), 142.44 (s, ipso), 129.79 (d, aroma-CH), 127.76 (d, aroma-CH), 126.02 (d, aroma-CH), 112.11 (t, C-1), 63.70 (d, C-4), 40.47 (s, C-3), 27.60 (q, CH<sub>3</sub>); MS: (EI, 70 eV) m/z 236 (M<sup>+</sup>, 0.09), 167 (M<sup>+</sup> C(CH<sub>3</sub>)<sub>2</sub>CH=CH<sub>2</sub>, 100); HRMS: (EI, 70 eV) calcd for C<sub>18</sub>H<sub>20</sub> 236.1565, found m/z 236.1587, 236.1548, 236.1543 (M<sup>+</sup>). Anal. Calcd for C<sub>18</sub>H<sub>20</sub>: C, 91.47; H, 8.53. Found: C, 91.28; H, 8.50.
- **3,3-dimethyl-4-phenyl-1-pentene (11g).** According to the general procedure, this compound was prepared from **10**, **2g**, and InCl<sub>3</sub> to give the product as a colorless liquid. Further purification was performed by distillation and TLC (hexane,  $R_f = 0.60$ ): bp: 85 °C/0.1 mmHg; IR: (neat) 1639 (C=C) cm<sup>-1</sup>; <sup>1</sup>H NMR: (270 MHz, CDCl<sub>3</sub>) 7.28-7.14 (m, 5H, aroma), 5.84 (dd, J = 17.3, 10.7 Hz, 1H, 2-H), 4.97 (dd, J = 10.7, 1.2 Hz, 1H, 1-H<sup>A</sup>), 4.89 (dd, J = 17.3, 1.2 Hz, 1H, 1-H<sup>B</sup>), 2.62 (q, J = 7.1 Hz, 3H, 4-H), 1.22 (d, 7.1 Hz, 3H, 5-H<sub>3</sub>),0.96 (s, 1H, 3-CH<sub>3</sub><sup>A</sup>), 0.92 (s, 3H, 3-CH<sub>3</sub><sup>B</sup>); <sup>13</sup>C NMR: (67.9 MHz, CDCl<sub>3</sub>) 146,78 (d, C-1), 144.19 (s, ipso), 129.13 (d, aroma-CH), 127.36 (d, aroma-CH), 125.89 (d, aroma-CH), 111.38 (t, C-2), 49.35 (d, C-4), 39.95 (s, C-3), 26.30 (q, 3-C<sup>A</sup>), 23.78 (q, 3-C<sup>B</sup>), 16.19 (q, C-5); MS: (EI, 70 eV) m/z 174 (M<sup>+</sup>, 1), 105 (100), 77(6); HRMS: (EI, 70 eV) calculated for C<sub>13</sub>H<sub>18</sub> 174.1409, found m/z 174.1414 (M<sup>+</sup>).
- **4,4-Diphenyl-1,2-butadiene** (13a). According to the general procedure, this compound was prepared from 12, 2a, and InCl<sub>3</sub> to give the product as a colorless liquid after chromatography (hexane). Further purification was performed by distillation under reduced pressure: bp: 128 °C/0.1 mmHg; IR: (neat) 1955 (C=C=C) cm<sup>-1</sup>; <sup>1</sup>H NMR: (270 MHz, CDCl<sub>3</sub>) 7.33-7.17 (m, 10H, aroma), 5.62 (dt, J = 6.6, 6.6 Hz, 1H, 3-H), 4.77-4.73 (m, 1H, 4-H), 4.72-4.69 (m, 2H, 1-H<sub>2</sub>); <sup>13</sup>C NMR: (67.9 MHz, CDCl<sub>3</sub>) 208.58 (s, C-2), 143.41 (s, ipso), 128.28 (d, o- and m-Ph), 126.39 (d, p-Ph), 93.92 (d, C-3), 76.34 (t, C-1), 50.76 (d, C-4); MS: (EI, 70 eV) m/z 206 (M<sup>+</sup>, 73), 191 (24), 167 (M<sup>+</sup> CH=C=CH<sub>2</sub>, 100), 165 (68), 152 (33), 128 (29), 91 (36); HRMS: (EI, 70 eV) calcd for C<sub>16</sub>H<sub>14</sub> 206.1096, found m/z 206.1083 (M<sup>+</sup>).
- **4-Phenyl-1,2-pentadiene (13g)**. According to the general procedure, this compound was prepared from **12**, **2g**, and InCl<sub>3</sub> to give the product as a colorless liquid after chromatography (hexane). Further purification was performed by distillation under reduced pressure: bp: 68

°C/0.2 mmHg; IR: (neat) 1955 (C=C=C) cm<sup>-1</sup>; <sup>1</sup>H NMR: (270 MHz, CDCl<sub>3</sub>) 7.34-7.15 (m, 5H, aroma), 5.34 (dt, J = 6.6, 6.6 Hz, 1H, 3-H), 4.79 (dd, J = 3.4, 6.6 Hz, 2H, 1-H<sub>2</sub>), 3.53-3.41 (m, 1H, 4-H), 1.35 (d, J = 7.1 Hz, 3H, 5-H<sub>3</sub>); <sup>13</sup>C NMR: (67.9 MHz, CDCl<sub>3</sub>) 207.63 (s, C-2), 145.95 (s, ipso), 128.32 (d, aroma-CH), 127.03 (d, aroma-CH), 126.20 (d, aroma-CH), 95.76 (d, C-3), 76.48 (t, C-1), 38.58 (d, C-4), 21.60 (q, C-5); MS: (EI, 70 eV) m/z 144 (M<sup>+</sup>, 11), 129 (100), 105 (M<sup>+</sup> - CH=C=CH<sub>2</sub>, 61), 77 (17); HRMS: (EI, 70 eV) calcd for C<sub>11</sub>H<sub>12</sub>, 144.0939, found m/z 144.0941 (M<sup>+</sup>).

**1,3-Diphenyl-1-butyne (15g)**. According to the general procedure, this compound was prepared from **14**, **2g**, and InCl<sub>3</sub> to give the product as a colorless liquid after chromatography (hexane). Further purification was performed by distillation under reduced pressure: bp: 119 °C/0.15 mmHg; IR: (neat) 2233 (alkyne) cm<sup>-1</sup>; <sup>1</sup>H NMR: (270 MHz, CDCl<sub>3</sub>) 7.47-7.16 (m, 10H, aroma), 3.98 (q, J = 7.1 Hz, 1H, 3-H), 1.58 (d, J = 7.1 Hz, 3H, 4-H<sub>3</sub>); <sup>13</sup>C NMR: (67.9 MHz, CDCl<sub>3</sub>) 143.24 (s, ipso), 131.55 (d, aroma-CH), 128.49 (d, aroma-CH), 128.13 (d, aroma-CH), 127.68 (d, aroma-CH), 126.87 (d, aroma-CH), 126.60 (d, aroma-CH), 123.66 (s, ipso), 92.56 (s, C-2), 82.40 (s, C-1), 32.49 (d, C-3), 24.55 (q, C-4); MS: (EI, 70 eV) m/z 206 (M<sup>+</sup>, 57), 191 (M<sup>+</sup> - CH<sub>3</sub>, 100), 189 (18); HRMS: (EI, 70 eV) calcd for C<sub>16</sub>H<sub>14</sub> 206.1096, found m/z 206.1087 (M<sup>+</sup>).

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