

## Electronic Supporting Information

### Regio- and Stereoselective Formation of Conjugated Dienes by Titanocene(II)- Promoted Alkylation of Propargyl Carbonates

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#### General

<sup>1</sup>H and <sup>13</sup>C NMR spectra (300 and 75 MHz, respectively) were recorded in CDCl<sub>3</sub> and chemical shifts (δ) are quoted in parts per million from tetramethylsilane for <sup>1</sup>H NMR and from CDCl<sub>3</sub> for <sup>13</sup>C NMR spectroscopy. IR absorptions are reported in cm<sup>-1</sup>.

#### Characterization Data

##### Formation of Conjugated Dienes **3**

(*5E*)-2-Methyl-7-phenyl-4-[(*E*)-phenylmethylidene]-1,5-heptadiene (**3a**): IR (neat) 3081, 3025, 2968, 2910, 1651, 1599, 1495, 1451, 1030, 962, 891, 750, 698; <sup>1</sup>H NMR (CDCl<sub>3</sub>) 1.80 (s, 3H), 3.07 (s, 2H), 3.48 (d, *J* = 7.0 Hz, 2H), 4.72–4.79 (m, 1H), 4.83–4.89 (m, 1H), 5.85 (dt, *J* = 15.6, 7.0 Hz, 1H), 6.25 (d, *J* = 15.6 Hz, 1H), 6.60 (s, 1H), 7.12–7.36 (m, 10H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) 23.5, 36.2, 39.2, 111.0, 126.0, 126.7, 128.2, 128.4, 128.55, 128.59, 128.8, 131.4, 135.4, 137.2, 137.6, 140.5, 143.0; HRMS (FAB) Calcd for C<sub>21</sub>H<sub>22</sub>: [M]<sup>+</sup> 274.1722; Found: 274.1703; Anal. Calcd for C<sub>21</sub>H<sub>22</sub>: C, 91.92; H, 8.08. Found: C, 91.72; H, 8.20.

(*1E*, *3E*)-2-Benzyl-1,5-diphenyl-1,3-pentadiene (**3b**): IR (neat) 3082, 3060, 3025, 2974, 2925, 1601, 1494, 1452, 1118, 1074, 1030, 964, 731, 697; <sup>1</sup>H NMR (CDCl<sub>3</sub>) 3.41 (d, *J* = 7.0 Hz, 2H), 3.88 (s, 2H), 5.78 (dt, *J* = 15.6, 7.0 Hz, 1H), 6.30 (d, *J* = 15.6 Hz, 1H), 6.74 (s, 1H), 7.01–7.34 (m, 15H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) 33.7, 39.0, 125.8, 126.0, 126.8, 128.1, 128.27, 128.30, 128.46, 128.49, 128.6, 129.9, 132.0, 135.1, 137.1, 137.4, 139.8, 140.3; HRMS (FAB) Calcd for C<sub>24</sub>H<sub>22</sub>: [M]<sup>+</sup> 310.1722; Found: 310.1712.

(*1E*, *3E*)-2-Cyclohexyl-1,5-diphenyl-1,3-pentadiene (**3c**): IR (neat) 3081, 3060, 3025, 2925, 2851, 1601, 1494, 1449, 1074, 1029, 965, 913, 770, 745, 697; <sup>1</sup>H NMR (CDCl<sub>3</sub>) 1.07–1.39 (m, 5H),

1.39–1.85 (m, 5H), 2.70–2.84 (m, 1H), 3.49 (d,  $J = 6.6$  Hz, 6H), 6.08 (dt,  $J = 15.4, 6.6$  Hz, 1H), 6.21 (d,  $J = 15.4$  Hz, 1H), 6.52 (s, 1H), 7.12–7.38 (m, 10H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) 26.1, 26.3, 31.7, 39.1, 39.5, 124.5, 126.0, 128.1, 128.4, 128.6, 128.7, 128.9, 129.5, 131.6, 138.2, 140.6, 145.6; HRMS (FAB) Calcd for  $\text{C}_{23}\text{H}_{26}$ :  $[\text{M}]^+$  302.2035; Found: 302.2024.

(*E*)-2,6-Diphenyl-3-[(*Z*)-phenylmethylidene]-4-hexen-1-ol (**3d**): IR (neat) 3416, 3059, 3025, 2929, 1724, 1601, 1494, 1451, 1383, 1288, 1116, 1029, 969, 751, 698;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 3.39 (d,  $J = 6.8$  Hz, 2H), 4.07 (dd,  $J = 10.8, 8.6$  Hz, 1H), 4.16 (dd,  $J = 10.8, 6.7$  Hz, 1H), 4.48 (dd,  $J = 8.6, 6.7$  Hz, 1H), 5.99 (dt,  $J = 15.6, 6.8$  Hz, 1H), 6.12 (d,  $J = 15.6$  Hz, 1H), 6.93 (s, 1H), 7.04–7.52 (m, 15H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) 39.3, 46.6, 64.1, 126.1, 126.5, 127.0, 127.7, 128.3, 128.4, 128.5, 128.6, 128.9, 130.7, 131.1, 131.3, 137.2, 138.9, 140.1, 140.3; HRMS (FAB) Calcd for  $\text{C}_{25}\text{H}_{24}\text{O}$ :  $[\text{M}]^+$  340.1827; Found: 340.1810.

(*2E, 4E*)-1-Phenyl-4-(2-propen-1-yl)-2,4-undecadiene (**3e**): IR (neat) 3062, 3027, 2925, 1637, 1604, 1495, 1453, 1378, 1073, 1030, 991, 963, 909, 746, 698;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 0.88 (t,  $J = 7.1$  Hz, 3H), 1.00–1.43 (m, 8H), 2.10 (dt,  $J = 7.3, 7.1$  Hz, 2H), 2.98 (d,  $J = 6.0$  Hz, 2H), 3.42 (d,  $J = 7.0$  Hz, 2H), 4.80–5.08 (m, 2H), 5.49 (t,  $J = 7.3$  Hz, 1H), 5.63–5.88 (m, 2H), 6.05 (d,  $J = 15.6$  Hz, 1H), 7.09–7.33 (m, 5H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) 14.1, 22.6, 28.1, 29.1, 29.6, 31.2, 31.8, 39.2, 114.8, 125.9, 126.0, 128.3, 128.5, 132.9, 134.6, 135.2, 136.1, 140.8; HRMS (FAB) Calcd for  $\text{C}_{20}\text{H}_{27}$ :  $[\text{M}]^+$  267.2113; Found: 267.2126.

(*2E, 4E*)-1-Phenyl-4-(2-methyl-2-propen-1-yl)-2,4-undecadiene (**3f**): IR (neat) 3063, 3026, 2925, 1731, 1651, 1604, 1495, 1453, 1376, 1272, 1118, 1073, 1030, 963, 888, 745, 698;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.88 (t,  $J = 6.6$  Hz, 3H), 1.15–1.44 (m, 8H), 1.71 (s, 3H), 2.07 (dt,  $J = 7.2, 7.2$  Hz, 2H), 2.91 (s, 2H), 3.41 (d,  $J = 6.8$  Hz, 2H), 4.66 (s, 1H), 4.72 (s, 1H), 5.54 (t,  $J = 7.2$  Hz, 1H), 5.68 (dt,  $J = 15.6, 6.8$  Hz, 1H), 6.06 (d,  $J = 15.6$  Hz, 1H), 7.10–7.32 (m, 5H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) 14.1, 22.6, 22.8, 28.3, 29.1, 29.5, 31.8, 35.2, 39.2, 110.4, 125.87, 125.91, 128.3, 128.5, 133.4, 135.0, 135.1, 140.9, 143.2; HRMS (FAB) Calcd for  $\text{C}_{21}\text{H}_{29}$ :  $[\text{M}]^+$  281.2269; Found: 281.2254.

(*2E, 4E*)-4-Benzyl-1-phenyl-2,4-undecadiene (**3g**): IR (neat) 3084, 3061, 3026, 2925, 1603, 1495, 1453, 1378, 1074, 1030, 964, 729, 696;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.86 (t,  $J = 6.6$  Hz, 3H), 1.15–1.50 (m, 8H), 2.16 (dt,  $J = 7.2, 7.2$  Hz, 2H), 3.34 (d,  $J = 6.8$  Hz, 2H), 3.61 (s, 2H), 5.54–5.74 (m, 2H), 6.10 (d,  $J = 15.6$  Hz, 1H), 7.03 (d,  $J = 7.2$  Hz, 1H), 7.08–7.32 (m, 10H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) 14.1, 22.6, 28.4, 29.1, 29.6, 31.7, 32.8, 39.0, 125.6, 125.8, 126.8, 128.0, 128.2, 128.4, 133.7, 134.9, 135.7, 140.1, 140.7; HRMS (FAB) Calcd for  $\text{C}_{24}\text{H}_{30}$ :  $[\text{M}]^+$  318.2348; Found: 318.2337.

(*Z*)-2-Phenyl-3-[(*E*)-3-phenyl-1-propen-1-yl]-3-decen-1-ol (**3h**): IR (neat) 3353, 3084, 3060, 3026, 2925, 1602, 1495, 1453, 1378, 1029, 967, 734, 698; <sup>1</sup>H NMR (CDCl<sub>3</sub>) 0.87 (t, *J* = 6.6 Hz, 3H), 1.15–1.45 (m, 8H), 1.51 (s, 1H), 2.18 (dt, *J* = 7.3, 7.3 Hz, 2H), 3.32 (d, *J* = 6.8 Hz, 2H), 3.93–4.07 (m, 1H), 4.07–4.25 (m, 2H), 5.69–5.83 (m, 2H), 5.95 (d, *J* = 15.6 Hz, 1H), 7.00–7.35 (m, 10H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) 14.1, 22.6, 28.3, 29.1, 29.8, 31.7, 39.2, 46.5, 63.7, 125.9, 126.3, 127.6, 128.3, 128.4, 128.5, 128.9, 131.7, 132.8, 136.7, 140.4, 140.6; HRMS (FAB) Calcd for C<sub>25</sub>H<sub>31</sub>: [M-OH]<sup>+</sup> 331.2426; Found: 331.2438.

(*5E*)-2,7-Dimethyl-4-[(*E*)-phenylmethylidene]-1,5-octadiene (**3i**): IR (neat) 3080, 2960, 1652, 1598, 1494, 1448, 1377, 1338, 1297, 1225, 1076, 1031, 963, 917, 891, 750, 699, 610; <sup>1</sup>H NMR (CDCl<sub>3</sub>) 1.03 (d, *J* = 6.8 Hz, 6H), 1.83 (s, 3H), 2.29–2.46 (m, 1H), 3.05 (s, 2H), 4.71–4.75 (m, 1H), 4.82–4.87 (m, 1H), 5.68 (dd, *J* = 15.8, 6.8 Hz, 1H), 6.14 (d, *J* = 15.8 Hz, 1H), 6.58 (s, 1H), 7.15–7.35 (m, 5H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) 22.5, 23.5, 31.4, 36.1, 111.0, 126.5, 128.1, 128.5, 130.5, 130.8, 137.6, 137.8, 137.9, 143.1; HRMS (FAB) Calcd for C<sub>17</sub>H<sub>22</sub>: [M]<sup>+</sup> 226.1722, Found 226.1728; Anal. Calcd for C<sub>17</sub>H<sub>22</sub>: C, 90.20; H, 9.80. Found: C, 90.07; H, 9.98.

(*1E, 3E*)-2-Benzyl-5-methyl-1,3-hexadiene (**3j**): IR (neat) 3060, 3025, 2958, 2866, 1601, 1494, 1453, 965, 751, 731, 697; <sup>1</sup>H NMR (CDCl<sub>3</sub>) 0.95 (d, *J* = 6.6 Hz, 6H), 2.21–2.39 (m, 1H), 3.86 (s, 2H), 5.62 (dd, *J* = 15.9, 6.8 Hz, 1H), 6.20 (d, *J* = 15.9 Hz, 1H), 6.71 (s, 1H), 7.10–7.34 (m, 10H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) 22.3, 31.3, 33.6, 125.7, 128.1, 128.2, 128.3, 128.40, 128.43, 128.6, 131.2, 137.4, 137.6, 140.1, 141.8; HRMS (FAB) Calcd for C<sub>20</sub>H<sub>22</sub>: [M]<sup>+</sup> 262.1722; Found: 262.1742.

(*5E*)-4-[(*E*)-2-Furylmethylidene]-2-methyl-7-phenyl-1,5-heptadiene (**3k**): IR (neat) 3083, 3027, 2927, 1727, 1651, 1602, 1495, 1451, 1375, 1269, 1122, 1074, 1018, 961, 886, 797, 733, 699, 593; <sup>1</sup>H NMR (CDCl<sub>3</sub>) 1.80 (s, 3H), 3.26 (s, 2H), 3.48 (d, *J* = 7.2 Hz, 2H), 4.68 (s, 1H), 4.76 (s, 1H), 5.88 (dt, *J* = 15.6, 7.2 Hz, 1H), 6.16–6.27 (m, 2H), 6.34–6.41 (m, 2H), 7.10–7.41 (m, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) 23.1, 36.4, 39.2, 109.5, 110.3, 111.5, 119.2, 126.0, 128.4, 128.6, 129.1, 135.0, 135.7, 140.4, 141.7, 142.2, 153.0; HRMS (FAB) Calcd for C<sub>19</sub>H<sub>20</sub>O: [M]<sup>+</sup> 264.1514; Found: 264.1510.

(*5E*)-4-[(*E*)-Cyclohexylmethylidene]-2-methyl-7-phenyl-1,5-heptadiene (**3l**): IR (neat) 3062, 3026, 2924, 2849, 1651, 1604, 1495, 1447, 963, 888, 746, 698; <sup>1</sup>H NMR (CDCl<sub>3</sub>) 0.92–1.36 (m, 5H), 1.54–1.76 (m, 8H), 2.20 (dt, *J* = 9.7, 10.3, 3.6 Hz, 1H), 2.92 (s, 2H), 3.40 (d, *J* = 6.8 Hz, 2H), 4.68 (br s, 1H), 4.73 (br s, 1H), 5.36 (d, *J* = 9.7 Hz, 1H), 5.36 (dt, *J* = 15.6, 6.8 Hz, 1H), 6.02 (d, *J* = 15.6 Hz, 1H), 7.10–7.32 (m, 5H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) 22.9, 25.9, 26.0, 33.0, 35.4, 37.3, 39.2, 110.4, 125.9, 126.2, 128.3, 128.5, 133.1, 135.2, 139.1, 140.9, 143.4; HRMS (FAB) Calcd for C<sub>21</sub>H<sub>27</sub>: [M-H]<sup>+</sup> 279.2113; Found: 279.2106.

(*5E*)-2,6-Dimethyl-4-[(*E*)-phenylmethylidene]-1,5-heptadiene (**3m**): IR (neat) 3079, 3023, 2966, 1651, 1599, 1492, 1445, 1374, 920, 888, 748, 699; <sup>1</sup>H NMR (CDCl<sub>3</sub>) 1.75 (s, 3H), 1.83 (d, *J* = 1.1 Hz, 3H), 1.90 (d, *J* = 1.1 Hz, 3H), 2.94 (s, 2H), 4.75 (s, 1H), 4.84 (s, 1H), 5.71 (s, 1H), 6.47 (s, 1H), 7.15–7.45 (m, 5H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) 19.7, 23.2, 26.9, 40.3, 111.0, 126.4, 128.1, 128.2, 128.4, 130.1, 134.6, 137.1, 137.9, 143.9; HRMS (FAB) Calcd for C<sub>16</sub>H<sub>19</sub>: [M-H]<sup>+</sup> 211.1487; Found: 211.1480.

#### Formation of the dideuterated alkene **10**

(*Z*)-1-Deuterio-2-(1-deuteriomethyl)-1,3-diphenyl-1-propene (**10**): IR (neat) 3060, 3025, 2961, 2908, 2846, 2217, 1728, 1643, 1599, 1574, 1494, 1452, 1277, 1236, 1156, 1074, 1030, 1015, 915, 751, 728, 697, 627, 607; <sup>1</sup>H NMR (CDCl<sub>3</sub>) 1.79 (t, *J* = 2.0 Hz, 3H), 3.61 (s, 2H), 7.00–7.35 (m, 10H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) 23.7 (t, *J* = 19.3 Hz), 38.4, 126.0, 126.3, 128.2, 128.36, 128.42, 128.5, 136.9, 138.1, 139.7; HRMS (FAB) Calcd for C<sub>16</sub>H<sub>14</sub>D<sub>2</sub>: [M]<sup>+</sup> 210.1378; Found: 210.1402.

#### Formation of the (*Z*)-alkene **11**

(*Z*)-3-Phenethyl-1-phenyl-1-heptene (**11**): IR (neat) 3060, 3026, 3000, 2927, 2856, 1602, 1495, 1455, 1378, 1073, 1030, 914, 748, 697; <sup>1</sup>H NMR (CDCl<sub>3</sub>) 0.84 (t, *J* = 7.1 Hz, 3H), 1.12–1.38 (m, 5H), 1.40–1.64 (m, 2H), 1.66–1.80 (m, 1H), 2.48 (ddd, *J* = 13.7, 10.2, 6.2 Hz, 1H), 2.57–2.76 (m, 2H), 5.43 (dd, *J* = 11.7, 10.8 Hz, 1H), 6.50 (d, *J* = 11.7 Hz, 1H), 7.00–7.35 (m, 10H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) 14.0, 22.9, 29.4, 33.6, 35.4, 37.0, 37.7, 125.5, 126.4, 128.1, 128.2, 128.4, 128.6, 129.1, 137.97, 138.01, 142.7; HRMS (FAB) Calcd for C<sub>21</sub>H<sub>26</sub>: [M]<sup>+</sup> 278.2035; Found: 278.2018.