Supporting Information

Iridium-Catalyzed Allyl-Allyl Cross-Coupling of Allylic Carbonates with (E)-1,3-Diarylpropenes

Qianjia Yuan,† Kun Yao,‡ Delong Liu‡ and Wanbin Zhang*,†,‡

† School of Chemistry and Chemical Engineering ‡ School of Pharmacy, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, P. R. China
Fax: (+)-86-21-54743265; Phone: (+)-86-21-54743265; e-mail: wanbin@sjtu.edu.cn

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1. General Information

All the reactions were monitored by TLC (thin layer chromatography) using UV light to visualize the course of reaction. The solvent water was distilled before used. Anhydrous THF, DME, Et\textsubscript{2}O, 1,4-dioxane and toluene were prepared by distillation over sodium-benzophenone prior to use. \textsuperscript{1}H, \textsuperscript{19}F, \textsuperscript{13}C NMR spectra were obtained using a Varian MERCURY plus-400 spectrometer with TMS as an internal standard. HRMS was performed on a Bruck solariX FTICR Mass Spectrometer at the Instrumental Analysis Center of Shanghai Jiao Tong University. Melting points were measured with SGW X-4 micro melting point apparatus. All commercially available reagents were used as received.

2. Preparation of Allylic tert-Butyl Carbonates

**General Procedure A:** To a solution of allylic alcohol (30 mmol) in THF (150 mL) under a nitrogen atmosphere was added \textit{n}-BuLi (33 mmol, 2.5 M in hexane) at 0 °C and the mixture was stirred for 30 min. Boc\textsubscript{2}O (36 mmol) was added at 0 °C and the reaction mixture was stirred overnight at r.t.. The reaction was quenched with H\textsubscript{2}O and the solvent was removed in vacuo. The residue was diluted with ethanol (50 mL) and imidazole (9 mmol) was added to remove the unreacted Boc\textsubscript{2}O. After stirring for 1 h at r.t., the solvent was removed and the residue was purified by flash column chromatography (SiO\textsubscript{2}; petroleum ether: ethyl acetate = 100:1) to give the corresponding allylic tert-butyl carbonate.

**General Procedure B:** To a solution of allylic alcohol (5.2 mmol) in DCM (6 mL) was added Boc\textsubscript{2}O (5.7 mmol, 1.1 equiv.) and Bu\textsubscript{4}NHSO\textsubscript{4} (0.26 mmol, 0.05 equiv.). The solution was cooled to 0 °C and aqueous NaOH (2.6 mL, 30% solution) was added dropwise and then the solution was stirred overnight at r.t.. The reaction mixture was extracted with DCM (30 mL × 3). The combined organic phase was washed with 1M HCl, H\textsubscript{2}O and brine, dried over anhydrous Na\textsubscript{2}SO\textsubscript{4} and then concentrated in vacuo. The residue was purified by flash column chromatography (SiO\textsubscript{2}; petroleum ether : ethyl acetate = 100 : 1) to give the corresponding allylic tert-butyl carbonate.
**1a**

**tert-Butyl cinnamyl carbonate:**[1] General procedure A was followed on a 30.0 mmol scale. A yellow oil (6.9 g, 98%); ¹H NMR (400 MHz, CDCl₃): δ 7.42 – 7.40 (m, 2H), 7.36 – 7.32 (m, 2H), 7.30 – 7.26 (m, 1H), 6.69 (d, J = 16.0 Hz, 1H), 6.30 (dt, J = 15.6, 6.4 Hz 1H), 4.74 (dd, J = 6.4, 1.2 Hz, 2H), 1.52 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 153.5, 135.4, 134.6, 128.8, 128.3, 126.8, 123.3, 82.4, 67.6, 28.0.

**1b**

**tert-Butyl 4-fluorocinnamyl carbonate:**[2] General procedure B was followed on a 5.2 mmol scale. A colorless oil (1.4 g, 86%); ¹H NMR (400 MHz, CDCl₃): δ 7.37 – 7.33 (m, 2H), 7.03 – 6.98 (m, 2H), 6.63 (d, J = 16.0 Hz, 1H), 6.21 (dt, J = 16.0, 6.8 Hz, 1H), 4.70 (dd, J = 6.4, 0.8 Hz, 2H), 1.50 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 162.6 (d, J_C-F = 246.0 Hz), 153.3, 132.3 (d, J_C-F = 3.2 Hz), 133.2, 128.2 (d, J_C-F = 8.0 Hz, 2C), 122.6 (d, J_C-F = 2.1 Hz), 115.6 (d, J_C-F = 21.6 Hz, 2C), 82.9, 67.3, 27.7; ¹⁹F NMR (376 MHz, CDCl₃): δ –113.6.

**1c**

**tert-Butyl 4-chlorocinnamyl carbonate:**[3] General procedure B was followed on a 4.0 mmol scale. A colorless oil (0.8 g, 74%); ¹H NMR (400 MHz, CDCl₃): δ 7.35 – 7.29 (m, 4H), 6.64 (d, J = 15.9 Hz, 1H), 6.29 (dt, J = 16.0, 6.4 Hz, 1H), 4.73 (dd, J = 6.4, 1.3 Hz, 2H), 1.53 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 153.2, 134.6, 133.7, 133.0, 128.7, 127.8, 123.6, 82.3, 67.2, 27.7.

**1d**

**tert-Butyl 4-bromocinnamyl carbonate:**[4] General procedure B was followed on a 5.2 mmol scale. A white crystal (1.2 g, 83%); ¹H NMR (400 MHz, CDCl₃): δ 7.44 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 9.6 Hz, 2H), 6.60 (d, J = 16.0 Hz, 1H), 6.31 – 6.24 (dt, J = 16.0, 6.4 Hz, 1H), 4.70 (dd, J = 6.4, 1.2 Hz, 2H), 1.50 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 153.0, 135.1, 133.0, 131.7,
128.1, 123.7, 121.9, 82.3, 67.1, 27.7.

**1e**

*tert*-Butyl 4-methoxycinnamyl carbonate: General procedure A was followed on a 5.0 mmol scale. A yellow oil (0.9 g, 68%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.34 (d, $J = 8.4$ Hz, 2H), 6.88 (d, $J = 7.6$ Hz, 2H), 6.64 (d, $J = 16.0$ Hz, 1H), 6.18 (dt, $J = 15.2$, 6.8 Hz, 1H), 4.72 (d, $J = 6.4$ Hz, 2H), 3.83 (s, 3H), 1.52 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 159.6, 153.4, 134.2, 128.9, 127.9, 120.5, 114.0, 82.1, 67.7, 55.2, 27.8.

**1f**

*tert*-Butyl 4-methylcinnamyl carbonate: General procedure A was followed on a 5.0 mmol scale. A white solid (1.2 g, 99%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.28 (d, $J = 8.0$ Hz, 2H), 7.13 (d, $J = 8.0$ Hz, 2H), 6.64 (d, $J = 15.6$ Hz, 1H), 6.24 (dt, $J = 16.0$, 6.4 Hz, 1H), 4.71 (dd, $J = 6.4$, 1.2 Hz, 2H), 2.33 (s, 3H), 1.50 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 153.6, 138.2, 134.7, 133.6, 129.5, 126.8, 122.0, 82.3, 67.8, 28.0, 21.4.

**1g**

*tert*-Butyl 3-methylcinnamyl carbonate: General procedure A was followed on a 8.1 mmol scale. A yellow oil (1.1 g, 57%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.23 – 7.18 (m, 3H), 7.09 – 7.07 (m, 1H), 6.64 (d, $J = 15.6$ Hz, 1H), 6.28 (dt, $J = 16.0$, 6.4 Hz, 1H), 4.71 (dd, $J = 6.8$, 1.2 Hz, 2H), 2.34 (s, 3H), 1.50 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 153.6, 138.3, 136.3, 134.7, 129.1, 128.7, 127.6, 124.0, 122.9, 82.3, 67.7, 28.0, 21.6; IR: 2979, 2932, 1739, 1605, 1585, 1457, 1393, 1368, 1275, 1254, 1162, 1117, 1090, 965, 859, 793, 778, 763, 691. HRMS (ESI+) [M+H]$^+$ calcd for C$_{15}$H$_{21}$O$_3$, 249.1491; found 249.1492.
**tert-Butyl 2-methylcinnamyl carbonate:** General procedure A was followed on a 8.1 mmol scale. A yellow oil (1.7 g, 83%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.48 – 7.44 (m, 1H), 7.23 – 7.16 (m, 3H), 6.92 (d, $J$ = 15.6 Hz, 1H), 6.21 (dt, $J$ = 15.6, 6.4 Hz, 1H), 4.77 (dd, $J$ = 6.4, 1.2 Hz, 2H), 2.38 (s, 3H), 1.54 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 153.5, 135.9, 135.5, 132.6, 130.5, 128.1, 126.3, 126.1, 124.4, 82.4, 67.9, 28.0, 19.9; IR: 2979, 2933, 2872, 1739, 1482, 1457, 1393, 1386, 1277, 1262, 1107, 1035, 966, 928, 861, 793, 764, 744.

![1i](image)

**tert-Butyl (E)-3-(2-furyl)-prop-2-enyl carbonate:** General procedure B was followed on a 6.4 mmol scale. A yellow oil (1.3 g, 90%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.34 (s, 1H), 6.47 (d, $J$ = 16.0 Hz, 1H), 6.36 (dd, $J$ = 3.2, 1.6 Hz, 1H), 6.27 (d, $J$ = 3.2 Hz, 1H), 6.21 (dt, $J$ = 15.6, 6.4 Hz, 1H), 4.68 (d, $J$ = 6.4 Hz, 2H), 1.49 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 153.5, 152.0, 142.4, 122.4, 121.6, 111.5, 109.1, 82.4, 67.2, 28.0.

![1j](image)

**tert-Butyl (E,E)-2,4-hexadienyl carbonate:** General procedure A was followed on a 10.0 mmol scale. A yellow oil (1.8 g, 91%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 6.25 (dd, $J$ = 15.2, 10.4 Hz, 1H), 6.04 (ddd, $J$ = 14.8, 10.8, 1.2 Hz, 1H), 5.75 (dq, $J$ = 14.8, 6.8 Hz, 1H), 5.66 – 5.59 (m, 1H), 4.55 (d, $J$ = 6.4 Hz, 2H), 1.75 (dd, $J$ = 6.4, 0.4 Hz, 3H), 1.48 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 153.5, 135.3, 131.5, 130.6, 123.5, 82.1, 67.6, 27.9, 18.3.

![1k](image)

**tert-Butyl geranyl carbonate:** General procedure A was followed on a 10.0 mmol scale. A yellow oil (2.5 g, 99%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 5.36 (t, $J$ = 6.4 Hz, 1H), 5.08 (t, $J$ = 6.4 Hz, 1H), 4.58 (d, $J$ = 7.2 Hz, 2H), 2.11 – 2.01 (m, 4H), 1.69 (s, 3H), 1.67 (s, 3H), 1.59 (s, 3H), 1.48 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 153.6, 142.5, 131.8, 123.7, 118.0, 81.8, 63.7, 39.5, 27.8, 26.2, 25.6, 17.6, 16.5.
3. Preparation of Nucleophiles

**General Procedure:** A solution of phenylacetaldehydes (0.167 mol) and KOH (0.179 mol) in 95% ethanol (80 mL) was heated at refluxed for 12 h. After cooling, the solvent was removed in vacuo and the residue was dissolved in H₂O (30 mL) and the mixture was extracted with ethyl acetate (60 mL × 3). The combined organic layer was washed with H₂O and brine, dried over anhydrous Na₂SO₄ and then concentrated in vacuo. The residue was purified by flash column chromatography (SiO₂; petroleum ether) to give the corresponding (E)-1,3-diphenylpropenes.

![2a](image)

**(E)-1,3-Diphenylpropene:**[6] The general procedure was followed on a 0.167 mol scale. A yellow oil (2.5 g, 99%); ¹H NMR (400 MHz, CDCl₃): δ 7.38 – 7.19 (m, 10H), 6.46 (d, J = 15.6 Hz, 1H), 6.47 (dt, J = 15.6, 6.8 Hz, 1H), 3.56 (d, J = 6.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 140.6, 137.9, 131.5, 129.6, 129.1, 128.9, 127.5, 126.6, 126.6, 39.8.

![2l](image)

**(E)-1,3-Di-(4-fluorophenyl)propene:**[7] The general procedure was followed on a 12.0 mmol scale. A colorless oil (0.5 g, 36%); ¹H NMR (400 MHz, CDCl₃): δ 7.31 – 7.26 (m, 2H), 7.19 – 7.14 (m, 2H), 7.01 – 6.93 (m, 4H), 6.37 (d, J = 15.6 Hz, 1H), 6.21 (dt, J = 16.0, 6.8 Hz, 1H), 3.48 (d, J = 6.8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 163.0 (d, J₇C,F = 58.0 Hz), 160.6 (d, J₇C,F = 55.9 Hz), 135.6 (d, J₇C,F = 2.7 Hz), 133.4 (d, J₇C,F = 2.9 Hz), 130.0, 130.0, 129.9, 128.7, 127.5 (d, J₇C,F = 7.8 Hz), 115.3 (dd, J₇C,F = 21.3, 13.7 Hz), 38.4; ¹⁹F NMR (376 MHz, CDCl₃): δ −115.1, −117.1.

![2m](image)

**(E)-1,3-Di-(4-chlorophenyl)propene:**[6] The general procedure was followed on a 10.0 mmol scale. A colorless oil (0.6 g, 46%); ¹H NMR (400 MHz, CDCl₃): δ 7.31 – 7.26 (m, 6H), 7.18 – 7.15 (m, 2H), 6.39 (dt, J = 15.6, 1.2 Hz, 1H), 6.30 (dt, J = 15.6, 6.4 Hz, 1H), 3.51 (d, J = 6.4 Hz,
$\text{C NMR}$ (100 MHz, CDCl$_3$): $\delta$ 138.5, 136.0, 133.1, 132.3, 130.5, 130.2, 129.6, 128.9, 128.9, 127.6, 39.0.

**(E)-1,3-Di-(4-bromophenyl)propene:** The general procedure was followed on a 13.3 mmol scale. A white solid (1.6 g, 67%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.45 – 7.38 (m, 4H), 7.22 – 7.18 (m, 2H), 7.12 – 7.09 (m, 2H), 6.36 (d, $J$ = 15.6 Hz, 1H), 6.29 (dt, $J$ = 16.0, 6.0 Hz, 1H), 3.48 (d, $J$ = 6.4 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 138.9, 136.4, 131.8, 130.8, 130.5, 129.5, 127.9, 121.2, 120.3, 38.8.

**(E)-1,3-Di-(4-methylphenyl)propene:** The general procedure was followed on a 14.0 mmol scale. A yellow oil (1.4 g, 90%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.26 (d, $J$ = 8.0 Hz, 2H), 7.16 – 7.09 (m, 6H), 6.42 (d, $J$ = 15.6 Hz, 1H), 6.29 (dt, $J$ = 15.6, 6.8 Hz, 1H), 3.51 (d, $J$ = 6.8 Hz, 2H), 2.34 (s, 3H), 2.33 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 137.5, 137.0, 136.8, 135.0, 130.9, 129.4, 128.8, 128.7, 126.2, 39.1, 21.4, 21.2.

**(E)-1,3-Di-(4-biphenyl)propene:** The general procedure was followed on a 30.0 mmol scale. A white solid (1.1 g, 10%); mp: 144.1 – 144.9 ºC; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.66 – 7.59 (m, 8H), 7.51 – 7.46 (m, 6H), 7.41 – 7.36 (m, 4H), 6.59 (d, $J$ = 15.6 Hz, 1H), 6.49 (dt, $J$ = 16.0, 6.4 Hz, 1H), 3.67 (d, $J$ = 6.4 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 141.2, 141.0, 140.1, 139.5, 136.7, 131.0, 129.5, 129.4, 129.0, 127.55, 127.51, 127.4, 127.3, 127.1, 126.8, 39.3; IR: 3027, 2918, 2849, 1485, 1405, 964, 834, 756, 689; HRMS (APCI) calcd for C$_{23}$H$_{21}$: 346.1722; found 346.1713.
(E)-1,3-Di-(3-fluorophenyl)propene: The general procedure was followed on a 18.0 mmol scale. A colorless oil (0.75 g, 18%); ¹H NMR (400 MHz, CDCl₃): δ 7.31 – 7.23 (m, 2H), 7.13 – 7.01 (m, 4H), 6.96 – 6.89 (m, 2H), 6.43 (d, J = 16.0 Hz, 1H), 6.34 (dt, J = 15.6, 6.4 Hz, 1H), 3.55 (d, J = 6.8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 164.5 (d, J_C-F = 10.4 Hz), 162.0 (d, J_C-F = 11.4 Hz), 142.5 (d, J_C-F = 6.9 Hz), 139.8 (d, J_C-F = 7.8 Hz), 130.8, 130.2, 130.1, 130.0, 124.5, 122.3, 115.7 (d, J_C-F = 20.9 Hz), 114.3 (d, J_C-F = 21.2 Hz), 113.4 (d, J_C-F = 20.9 Hz), 112.85 (d, J_C-F = 21.6 Hz), 39.1; ¹⁹F NMR (376 MHz, CDCl₃): δ −113.4, −113.6; IR: 3034, 2914, 1611, 1583, 1522, 1487, 1447, 1338, 1248, 1143, 1074, 1002, 969, 947, 932, 871, 778, 733, 682, 520.

2r

(E)-1,3-Di-(2-fluorophenyl)propene: The general procedure was followed on a 18.0 mmol scale. A colorless oil (0.8 g, 20%); ¹H NMR (400 MHz, CDCl₃): δ 7.45 (td, J = 7.6, 1.6 Hz, 1H), 7.29 – 7.16 (m, 3H), 7.10 – 7.01 (m, 4H), 6.66 (d, J = 16.0 Hz, 1H), 6.45 (dt, J = 15.6, 6.8 Hz, 1H), 3.62 (d, J = 6.8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 162.0 (d, J_C-F = 91.7 Hz), 159.5 (d, J_C-F = 94.9 Hz), 130.9 (d, J_C-F = 4.4 Hz), 130.5 (d, J_C-F = 4.2 Hz), 128.6 (d, J_C-F = 8.2 Hz), 128.3 (d, J_C-F = 7.9 Hz), 127.5 (d, J_C-F = 3.4 Hz), 127.1 (d, J_C-F = 15.6 Hz), 125.3 (d, J_C-F = 12.3 Hz), 124.4 (d, J_C-F = 3.3 Hz), 124.3 (d, J_C-F = 3.0 Hz), 124.1 (d, J_C-F = 2.9 Hz), 115.9 (d, J_C-F = 22.0 Hz), 115.6 (d, J_C-F = 21.8 Hz), 32.9; ¹⁹F NMR (376 MHz, CDCl₃): δ −118.4, −118.5; IR: 3043, 2914, 1611, 1583, 1522, 1487, 1447, 1338, 1248, 1143, 1074, 1002, 969, 947, 932, 871, 778, 733, 682, 520.

2s

(E)-1,3-Di-(α-naphthyl)propene: The general procedure was followed on a 15.0 mmol scale. A yellow oil (0.8 g, 35%); ¹H NMR (400 MHz, CDCl₃): δ 8.18 (d, J = 8.4 Hz, 1H), 8.06 – 8.02 (m, 1H), 7.90 (dd, J = 7.6, 1.2 Hz, 1H), 7.84 – 7.82 (m, 1H), 7.80 (dd, J = 7.2, 2.4 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.57 – 7.51 (m, 3H), 7.49 – 7.45 (m, 4H), 7.41 (t, J = 7.6 Hz, 1H), 7.22 (d, J = 15.6 Hz, 1H), 6.54 (dt, J = 15.2, 6.8 Hz, 1H), 4.14 (dd, J = 6.4, 1.6 Hz, 2H); ¹³C NMR (100 MHz,
CDCl₃): δ 136.2, 135.3, 133.9, 133.5, 132.1, 131.1, 128.7, 128.4, 127.5, 127.1, 126.4, 125.9, 125.8, 125.7, 125.66, 125.62, 124.0, 123.8, 123.7, 127.5, 127.1, 126.4, 125.9, 125.8, 125.7, 125.66, 125.62, 124.0, 123.8, 123.7, 35.8; IR: 3043, 2953, 2900, 1923, 1868, 1807, 1732, 1688, 1646, 1622, 1595, 1432, 1393, 1352, 1318, 1260, 1212, 1167, 1141, 1029, 1011, 934, 905, 884, 859, 732, 713, 649, 637, 593, 548; HRMS (APCI) [M] calcd for C₂₃H₁₈, 294.1409; found 294.1400.

2t

(E)-1,3-Di-(β-naphthyl)propene: The general procedure was followed on a 15.0 mmol scale. A white solid (1.0 g, 48%); mp: 133.2 – 134.1 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.84 – 7.76 (m, 6H), 7.72 (s, 2H), 7.61 (d, J = 8.8 Hz, 1H), 7.48 – 7.42 (m, 5H), 6.68 (m, J = 16.0, 1H), 6.61-6.54 (m, 1H), 3.78 (d, J = 6.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 137.9, 135.2, 134.0, 133.1, 132.5, 131.7, 129.8, 128.4, 128.2, 127.9, 127.8, 127.8, 127.1, 126.5, 126.3, 126.1, 125.9, 125.6, 123.9, 39.9. IR: 3046, 2920, 2889, 1596, 1506, 1412, 1363, 1307, 1271, 959, 950, 933, 897, 860, 814, 803, 740, 640, 617; HRMS (APCI) [M] calcd for C₂₃H₁₈, 294.1409; found 294.1400.

4. General Procedure for Ir-Catalyzed Cross-Coupling Reactions

To oven-dried glassware were added [Ir(cod)Cl]₂ (2.7 mg, 2.0 mol %), dppf (4.8 mg, 4.4 mol %) and anhydrous THF (2 mL). The mixture was stirred at r.t. under a nitrogen atmosphere for 30 min. Then the allylic carbonate 1 (0.2 mmol), (E)-1,3-diarylpropene 2 (0.3 mmol, 1.5 equiv.) and NaHMDS (0.3 mmol, 2M in THF, 1.5 equiv.) were added. The reaction mixture was stirred for the indicated time until complete consumption of starting material as monitored by TLC. The reaction was quenched with H₂O, extracted with EtOAc (20 mL x 3). The combined organic layer was washed with brine, dried over anhydrous Na₂SO₄ and then concentrated in vacuo. The ratio of regioisomers (linear to branched l/b) was determined by ¹H NMR of the crude reaction mixture. Then the crude reaction mixture was then purified by flash column chromatography (SiO₂; petroleum ether: ethyl acetate = 100:1) to give the desired product.
\((E,E)-1,3,6\)-Tri-phenyl-1,5-hexadiene: A colorless oil (61.5 mg, 99%); \(^1H\) NMR (400 MHz, CDCl\(_3\)): \(\delta 7.37 - 7.17 \text{ (m, 15H)}, 6.47 - 6.39 \text{ (m, 3H)}, 6.18 \text{ (dt, } J = 15.6, 7.2 \text{ Hz, 1H}), 3.64 - 3.58 \text{ (m, 1H)}, 2.80 - 2.71 \text{ (m, 2H)}; \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 144.0, 137.8, 137.6, 133.6, 131.8, 130.1, 128.8, 128.7, 128.5, 128.0, 127.4, 127.2, 126.6, 126.4, 126.3, 49.6, 39.7; IR: 3081, 3058, 2923, 2852, 1598, 1494, 1449, 1072, 1028, 962, 910, 742, 692, 541.

\((E,E)-1,3\)-Diphenyl-6-(4-fluorophenyl)-1,5-hexadiene: A colorless oil (63.7 mg, 97%); \(^1H\) NMR (400 MHz, CDCl\(_3\)): \(\delta 7.37 - 7.19 \text{ (m, 12H)}, 6.95 \text{ (t, } J = 8.4 \text{ Hz, 2H)}, 6.46 - 6.36 \text{ (m, 3H)}, 6.08 \text{ (dt, } J = 16.0, 7.2 \text{ Hz, 1H}), 3.60 \text{ (dd, } J = 12.4, 6.8 \text{ Hz, 1H}), 2.77 - 2.71 \text{ (m, 2H)}; \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 162.2 \text{ (d, } J_{\text{C-F}} = 244.4 \text{ Hz)}, 143.9, 137.6, 133.9 \text{ (d, } J_{\text{C-F}} = 3.2 \text{ Hz)}, 133.5, 130.6, 130.2, 128.7 \text{ (d, } J_{\text{C-F}} = 8.8 \text{ Hz)}, 128.2, 127.9, 127.7 \text{ (d, } J_{\text{C-F}} = 7.7 \text{ Hz)}, 127.4, 126.7, 126.4, 115.5 \text{ (d, } J_{\text{C-F}} = 21.4 \text{ Hz}), 49.5, 39.6; \(^19\)F NMR (376 MHz, CDCl\(_3\)): \(\delta -115.4; IR: 3059, 3026, 2924, 2852, 1600, 1507, 1492, 1452, 1227, 1157, 1092, 1014, 965, 834, 745, 699, 518; HRMS (APCI) [M-H] \(^{-}\) caled for C\(_{24}\)H\(_{20}\)F, 327.1549; found 327.1540.

\((E,E)-1,3\)-Diphenyl-6-(4-chlorophenyl)-1,5-hexadiene: A colorless oil (49.7 mg, 72%). \(^1H\) NMR (400 MHz, CDCl\(_3\)): \(\delta 7.41 - 7.23 \text{ (m, 14H)}, 6.51 - 6.39 \text{ (m, 3H)}, 6.19 \text{ (dt, } J = 15.6, 7.2 \text{ Hz, 1H}), 3.65 \text{ (dd, } J = 13.2, 7.2 \text{ Hz, 1H}), 2.84 - 2.72 \text{ (m, 2H)}; \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 143.9, 137.6, 136.3, 133.5, 132.8, 130.7, 130.2, 129.3, 128.8, 128.8, 128.7, 127.9, 127.5, 126.7, 126.4, 49.5, 39.7; IR: 3081, 3059, 3025, 2920, 2850, 1599, 1490, 1451, 1091, 1012, 965, 799, 744, 698, 546, 508; HRMS (APCI) [M-H] \(^{-}\) caled for C\(_{24}\)H\(_{20}\)Cl, 343.1254; found 343.1244.
(E,E)-1,3-Diphenyl-6-(4-bromophenyl)-1,5-hexadiene: A yellow oil (48.3 mg, 62%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.40 – 7.14 (m, 14H), 6.47 – 6.34 (m, 3H), 6.17 (dt, $J$ = 15.6, 7.2 Hz, 1H), 3.61 (dd, $J$ = 13.2, 7.6 Hz, 1H), 2.79 – 2.68 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 143.8, 137.5, 136.7, 133.4, 131.7, 130.7, 130.2, 129.4, 128.8, 128.7, 127.9, 127.8, 127.4, 126.7, 126.4, 120.9, 49.4, 39.7; IR: 3060, 3027, 2922, 2851, 1715, 1688, 1681, 1599, 1488, 1453, 1397, 1374, 1338, 1269, 1071, 1028, 1010, 965, 756, 699, 518; HRMS (APCI) [M-H]$^-$ calcd for C$_{24}$H$_{29}$Br, 387.0748; found 387.0739.

(E,E)-1,3-Diphenyl-6-(4-methoxyphenyl)-1,5-hexadiene: A yellow oil (66.7 mg, 98%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.37 – 7.19 (m, 12H), 6.84 – 6.80 (m, 2H), 6.44 – 6.36 (m, 3H), 6.03 (dt, $J$ = 15.6, 7.2 Hz, 1H), 3.80 (s, 3H), 3.60 (dd, $J$ = 6.8, 3.2 Hz, 1H), 2.75 – 2.70 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 158.7, 143.9, 137.4, 133.4, 130.9, 130.4, 129.8, 128.5, 128.4, 127.7, 127.14, 127.12, 126.3, 126.2, 126.1, 113.8, 55.2, 49.4, 39.5; IR: 3059, 3024, 2923, 1646, 1599, 1492, 1451, 1378, 1260, 1072, 1029, 964, 744, 698, 543; HRMS (APCI) [M-H]$^-$ calcd for C$_{25}$H$_{23}$O, 339.1749; found 339.1740.

(E,E)-1,3-Diphenyl-6-(4-methylphenyl)-1,5-hexadiene: A colorless oil (68.4 mg, 99%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.37 – 7.18 (m, 12H), 7.08 (d, $J$ = 8.0 Hz, 2H), 6.43 – 6.38 (m, 3H), 6.12 (dt, $J$ = 16.0, 6.8 Hz, 1H), 3.62 – 3.57 (m, 1H), 2.79 – 2.67 (m, 2H), 2.31 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 143.9, 137.5, 136.7, 134.8, 133.4, 131.4, 129.9, 129.1, 128.6, 128.5, 127.8, 127.3, 127.1, 126.4, 126.2, 126.0, 49.4, 39.5, 21.1; IR: 3082, 3024, 2920, 2854, 1738, 1599, 1512,
1494, 1451, 1311, 1072, 1029, 961, 828, 795, 743, 693, 596, 548, 505; HRMS (APCI) [M-H] calcd for C_{25}H_{23}, 323.1800; found 323.1791.

3g

(\textit{E,E})-1,3-Diphenyl-6-(3-methylphenyl)-1,5-hexadiene: A colorless oil (62.3 mg, 96%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.35 – 7.12 (m, 13H), 6.99 (d, $J$ = 7.6 Hz, 1H), 6.45 – 6.36 (m, 3H), 6.14 (dt, $J$ = 16.0, 7.2 Hz, 1H), 3.61 – 3.56 (m, 1H), 2.78 – 2.66 (m, 2H), 2.29 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 144.1, 138.2, 137.8, 137.7, 133.7, 131.9, 130.1, 128.8, 128.7, 128.6, 128.3, 128.1, 128.0, 127.4, 127.0, 126.6, 126.4, 123.4, 49.6, 39.8, 21.6; IR: 3081, 3058, 3025, 2921, 2857, 1738, 1600, 1493, 1451, 1029, 962, 744, 692, 537; HRMS (APCI) [M-H]$^-$ calcd for C$_{25}$H$_{23}$, 323.1800; found 323.1791.

3h

(\textit{E,E})-1,3-Diphenyl-6-(2-methylphenyl)-1,5-hexadiene: A colorless oil (59.7 mg, 92%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.39 – 7.11 (m, 14H), 6.60 (d, $J$ = 15.6 Hz, 1H), 6.46 – 6.45 (m, 2H), 6.04 (dt, $J$ = 15.6, 6.8 Hz, 1H), 3.66 – 3.61 (m, 1H), 2.82 – 2.74 (m, 2H), 2.25 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 144.0, 137.6, 137.1, 135.2, 133.6, 130.3, 130.1, 129.9, 129.9, 128.8, 128.7, 128.0, 127.3, 127.1, 126.6, 126.4, 126.2, 125.9, 49.5, 40.0, 20.0; IR: 3059, 3024, 2923, 1646, 1599, 1492, 1451, 1378, 1029, 964, 744, 698, 543; HRMS (APCI) [M-H]$^-$ calcd for C$_{25}$H$_{23}$, 323.1800; found 323.1791.

3i

(\textit{E,E})-1,3-Diphenyl-6-(2-furyl)-1,5-hexadiene: A yellow oil (58.3 mg, 97%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.42 – 7.12 (m, 11H), 6.43 – 6.35 (m, 2H), 6.30 (dd, $J$ = 3.2, 1.6 Hz, 1H), 6.23 (d, $J$ = 15.6 Hz, 1H), 6.14 – 6.07 (m, 2H), 3.58 (dd, $J$ = 13.2, 6.8 Hz, 1H), 2.73 – 2.66 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 153.2, 143.9, 141.6, 137.6, 133.5, 130.2, 128.8, 128.7, 127.9, 127.5,
127.4, 126.6, 126.4, 120.4, 111.3, 106.7, 49.4, 39.6; IR: 3102, 3058, 3026, 2921, 2849, 1599, 1493, 1451, 1251, 1180, 1150, 1073, 1012, 925, 883, 594, 543; HRMS (APCI) [M-H]⁻ calcd for C_{22}H_{18}O, 299.1436; found 299.1428.

(E,E,E)-1,3-Diphenyl-1,5,7-nonatriene: A colorless oil (51.6 mg, 94%); \(^1\)H NMR (400 MHz, CDCl₃): \(\delta\) 7.36 – 7.18 (m, 10H), 6.43 – 6.34 (m, 2H), 6.09 – 5.96 (m, 2H), 5.63 – 5.47 (m, 2H), 3.52 (dd, \(J = 12.8, 6.8\) Hz, 1H), 2.60 (t, \(J = 7.2\) Hz, 2H), 1.72 (d, \(J = 6.8\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl₃): 144.1, 137.7, 133.7, 132.2, 131.7, 129.9, 129.3, 128.7, 128.6, 127.9, 127.7, 127.3, 126.5, 126.4, 49.6, 39.3, 18.2; IR: 3081, 3059, 2958, 2912, 2851, 1599, 1493, 1450, 1071, 987, 964, 927, 744, 698, 545, 517; HRMS (APCI) [M-H]⁻ calcd for C_{21}H_{21}, 273.1643; found 273.1635.

(E,E,E)-6,9-Dimethyl-1,3-diphenyl-1,5,9-undecatriene: General procedure was followed with \(1k\) (0.3 mmol), \(2a\) (0.2 mmol) and NaHMDS (0.2 mmol, 2 M in THF) in the presence of Ir catalyst. A colorless oil (39.7 mg, 60% yield based on \(2a\)); \(^1\)H NMR (400 MHz, CDCl₃): \(\delta\) 7.37 – 7.18 (m, 10H), 6.40 (d, \(J = 3.6\) Hz, 2H), 5.18 – 5.04 (m, 2H), 3.50 – 3.45 (m, 1H), 2.58 – 2.46 (m, 2H), 2.04 – 1.97 (m, 4H), 1.67 (s, 3H), 1.59 (s, 6H); \(^{13}\)C NMR (100 MHz, CDCl₃): \(\delta\) 144.5, 137.8, 136.7, 134.0, 131.5, 129.7, 128.7, 128.6, 128.0, 127.2, 126.4, 126.3, 124.5, 122.3, 49.5, 40.0, 34.6, 26.9, 25.9, 17.9, 16.4; IR: 3082, 3059, 3025, 2923, 2853, 1599, 1494, 1451, 1375, 1107, 1073, 1029, 962, 829, 743, 698, 548; HRMS (APCI) [M-H]⁻ calcd for C_{25}H_{29}, 329.2269; found 329.2263.

(E,E)-1,3-Di-(4-fluorophenyl)-6-phenyl-1,5-hexadiene: General procedure was followed with \(1a\) (0.2 mmol), \(2l\) (0.3 mmol) and LiHMDS (0.3 mmol, 1 M in THF) in the presence of Ir catalyst. A colorless oil (67.9 mg, 98%); \(^1\)H NMR (400 MHz, CDCl₃): \(\delta\) 7.32 – 7.17 (m, 9H), 7.05 – 6.96
(m, 4H), 6.40 (dt, J = 15.6, 1.6 Hz, 1H), 6.34 – 6.25 (m, 2H), 6.12 (dt, J = 15.6, 7.2 Hz, 1H), 3.58 (q, J = 7.2 Hz, 1H), 2.76 – 2.63 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 163.2 (d, J = 62.5 Hz), 160.8 (d, J = 60.6 Hz), 139.4, 137.6, 133.6 (d, J = 3.1 Hz), 133.1, 132.0, 129.3 (d, J = 7.7 Hz), 129.0, 128.6, 128.0, 127.8 (d, J = 7.7 Hz), 127.3, 126.2, 115.5 (d, J = 21.5 Hz), 48.6, 39.7; $^{19}$F NMR (376 MHz, CDCl$_3$): δ −115.0, −116.6; IR: 3026, 2920, 2850, 1646, 1601, 1507, 1471, 1260, 1224, 1157, 1094, 1014, 965, 831, 787, 741, 693, 518; HRMS (APCI) [M-H]$^-$ calcd for C$_{24}$H$_{19}$F$_2$, 345.1446; found 345.1446.

3m

![Structure](image)

(E,E)-1,3-Di-(4-chlorophenyl)-6-phenyl-1,5-hexadiene: A white solid (75.1 mg, 99%); mp: 104.6 – 105.8 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.31 – 7.25 (m, 10H), 7.21 – 7.18 (m, 3H), 6.41 (dt, J = 15.6, 1.2 Hz, 1H), 6.35 – 6.34 (m, 2H), 6.11 (dt, J = 15.6, 7.2 Hz, 1H), 3.58 (m, 1H), 2.78 – 2.64 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 142.1, 137.6, 135.9, 133.7, 133.1, 132.4, 132.2, 129.3, 128.9, 128.8, 128.7, 127.8, 127.6, 127.3, 48.8, 39.5; IR: 3080, 3025, 2924, 2851, 1646, 1596, 1490, 1448, 1405, 1091, 1013, 965, 825, 805, 744, 693, 535, 507; HRMS (APCI) [M-H]$^-$ calcd for C$_{24}$H$_{19}$Cl$_2$, 377.0864; found 377.0854.

3n

![Structure](image)

(E,E)-1,3-Di-(4-bromophenyl)-6-phenyl-1,5-hexadiene: A white solid (90.8 mg, 99%); mp: 126.4 – 127.2 °C; $^1$H NMR (400 MHz): δ 7.47 – 7.39 (m, 4H), 7.28 – 7.13 (m, 9H), 6.41 (dt, J = 15.6, 1.2 Hz, 1H), 6.35 – 6.30 (m, 2H), 6.11 (dt, J = 15.6, 7.2 Hz, 1H), 3.56 (q, J = 7.2 Hz, 1H), 2.76 – 2.65 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 142.6, 137.5, 136.3, 133.7, 132.2, 131.9, 131.8, 129.7, 129.4, 128.7, 127.9, 127.7, 127.4, 126.2, 121.2, 120.5, 48.9, 39.4. IR: 3566, 3545, 3523, 3420, 3025, 2924, 1715, 1681, 1487, 1275, 1260, 1055, 763, 749, 695; HRMS (APCI) [M-H]$^-$ calcd for C$_{24}$H$_{19}$Br$_2$, 464.9854; found 464.9844.
(E,E)-1,3-Di-(4-methylphenyl)-6-phenyl-1,5-hexadiene: A colorless solid (60.9 mg, 90%); mp: 75.0 – 76.4 °C; $^1$H NMR (400 MHz): $\delta$ 7.30 – 7.23 (m, 6H), 7.19 – 7.08 (m, 7H), 6.44 – 6.31 (m, 3H), 6.17 (dt, $J = 15.6, 7.2$ Hz, 1H), 3.55 (q, $J = 7.2$ Hz, 1H), 2.77 – 2.65 (m, 2H), 2.33 (s, 3H), 2.31 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 141.1, 137.9, 137.0, 136.0, 134.9, 132.8, 131.6, 129.7, 129.4, 129.3, 128.8, 128.6, 127.8, 127.1, 126.3, 126.2, 49.1, 39.8, 21.3, 21.2; IR: 3081, 3023, 2857, 1512, 1495, 1447, 1020, 797, 745, 692, 525, 506; HRMS (APCI) [M+H]$^+$ calcd for C$_{26}$H$_{27}$, 339.2113; found 339.2106.

(3p)

(E,E)-1,3-Di-(4-biphenyl)-6-phenyl-1,5-hexadiene: A colorless oil (86.0 mg, 93%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.60 – 7.51 (m, 8H), 7.44 – 7.15 (m, 15H), 6.52 – 6.43 (m, 3H), 6.21 (dt, $J = 15.6, 7.2$ Hz, 1H), 3.68 – 3.65 (m, 1H), 2.82 – 2.74 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 143.1, 141.2, 141.0, 140.2, 139.6, 137.8, 136.7, 133.7, 132.0, 129.9, 129.0, 128.7, 128.5, 128.4, 127.6, 127.5, 127.4, 127.3, 127.2, 126.9, 126.3, 49.3, 39.8; IR: 3023, 1748, 1731, 1715, 1697, 1681, 1646, 1594, 1543, 1507, 1487, 1398, 1275, 1260, 1071, 1008, 964, 801, 764, 749, 692, 500; HRMS (APCI) [M-H]$^-$ calcd for C$_{36}$H$_{29}$, 461.2269; found 461.2259.

(3q)

(E,E)-1,3-Di-(3-fluorophenyl)-6-phenyl-1,5-hexadiene: General procedure was followed with 1a (0.2 mmol), 2q (0.3 mmol) and LiHMDS (0.3 mmol, 1 M in THF) in the presence of Ir catalyst. A colorless oil (67.2 mg, 97%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.32 – 7.19 (m, 7H), 7.11 – 6.88 (m, 6H), 6.46 – 6.39 (m, 3H), 6.16 – 6.08 (m, 1H), 3.62 – 3.59 (m, 1H), 2.74 – 2.68 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 164.5 (d, $J_{C,F} = 4.2$ Hz), 162.0 (d, $J_{C,F} = 5.4$ Hz), 146.2 (d, $J_{C,F} = 6.8$ Hz).
Hz), 139.7 (d, $J_{C,F} = 7.5$ Hz), 137.6, 134.2, 132.3, 130.2 (dd, $J_{C,F} = 10.8, 8.7$ Hz, 2C), 129.6, 128.7, 127.7, 127.4, 126.3, 123.6, 122.3, 114.7 (d, $J_{C,F} = 21.2$ Hz), 114.3 (d, $J_{C,F} = 21.4$ Hz), 113.7 (d, $J_C = 21.0$ Hz), 112.9 (d, $J_{C,F} = 21.6$ Hz), 49.2, 39.4; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -112.9, -113.6; IR: 3080, 3059, 3027, 2923, 2845, 1941, 1748, 1647, 1611, 1584, 1521, 1487, 1447, 1249, 1143, 1073, 1002, 963, 937, 892, 872, 780, 746, 693, 521; HRMS (APCI) [M-H]$^-$ calcd for C$_{24}$H$_{19}$F$_2$, 345.1455; found 345.1446.

$^{3r}$

$(E,E)$-1,3-Di-(2-fluorophenyl)-6-phenyl-1,5-hexadiene: General procedure was followed with $1a$ (0.2 mmol), $2r$ (0.3 mmol) and LiHMDS (0.3 mmol, 1 M in THF) in the presence of Ir catalyst. A colorless oil (65.1 mg, 94%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.44 (td, $J = 7.6, 1.6$ Hz, 1H), 7.32 – 6.98 (m, 12H), 6.64 (d, $J = 16.4$ Hz, 1H), 6.53 (ddd, $J = 16.0, 7.6, 0.8$ Hz, 1H), 6.43 (d, $J = 15.6$ Hz, 1H), 6.17 (dt, $J = 15.6, 7.6$ Hz, 1H), 3.98 (q, $J = 7.6$ Hz, 1H), 2.83 – 2.70 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 161.6 (d, $J_{C,F} = 53.0$ Hz), 159.1 (d, $J_{C,F} = 56.4$ Hz), 137.5, 134.3 (d, $J_{C,F} = 4.5$ Hz), 131.9, 130.4 (d, $J_{C,F} = 14.3$ Hz), 128.9 (d, $J_{C,F} = 4.9$ Hz), 128.5, 128.4, 127.9 (d, $J_{C,F} = 8.3$ Hz), 127.8, 127.30 (d, $J_{C,F} = 3.8$ Hz), 127.0, 126.0, 125.0 (d, $J_{C,F} = 12.2$ Hz), 124.2 (d, $J_{C,F} = 3.5$ Hz), 124.0 (d, $J_{C,F} = 3.5$ Hz), 123.0 (d, $J_{C,F} = 3.5$ Hz), 115.7, 115.5, 43.0, 38.4; $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -117.8, -118.2; IR: 3026, 2924, 2849, 1796, 1715, 1697, 1578, 1540, 1507, 1488, 1455, 1361, 1229, 1093, 964, 830, 753, 692, 518; HRMS (APCI) [M-H]$^-$ calcd for C$_{24}$H$_{19}$F$_2$, 345.1455; found 345.1447.

$^{3s}$

$(E,E)$-1,3-Di-(α-naphthyl)-6-phenyl-1,5-hexadiene: A colorless oil (77.1 mg, 94%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.29 (d, $J = 8.4$ Hz, 1H), 7.97 (d, $J = 8.4$ Hz, 1H), 7.91 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.80 (t, $J = 8.4$ Hz, 2H), 7.74 (d, $J = 8.0$ Hz, 1H), 7.58 – 7.49 (m, 5H), 7.46 – 7.25 (m, 8H), 7.22 – 7.18 (m, 1H), 6.58 – 6.51 (m, 2H), 6.37 (dt, $J = 16.0, 6.8$ Hz, 1H), 4.60 (q, $J = 6.4$ Hz, 1H),
3.01 – 2.97 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 140.1, 137.8, 136.5, 135.7, 134.4, 133.8, 132.1, 131.9, 131.4, 129.3, 128.9, 128.7, 128.6, 128.5, 127.8, 127.4, 127.3, 126.4, 126.3, 126.1, 126.0, 125.9, 125.8, 124.6, 124.3, 124.0, 123.7, 44.5, 39.5; IR: 3055, 2924, 2851, 1595, 1576, 1507, 1494, 1394, 1262, 1027, 963, 796, 740, 692; HRMS (APCI) [M-H]$^-$ calcd for C$_{32}$H$_{25}$, 409.1956; found 409.1946.

$^{3t}$

(E,E)-1,3-Di-(β-naphthyl)-6-phenyl-1,5-hexadiene: A white solid (75.5 mg, 97%); mp: 99.7 – 101.6 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.86 – 7.75 (m, 7 H), 7.70 (s, 1H), 7.60 (dd, J = 8.4, 2.8 Hz, 1H), 7.50 – 7.41 (m, 5H), 7.31 – 7.16 (m, 5H), 6.64 – 6.63 (m, 2H), 6.50 (d, J = 16.0 Hz, 1H), 6.23 (dt, J = 15.6, 7.2 Hz, 1H), 3.87 – 3.82 (m, 1H), 2.90 (t, J = 7.2 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 141.4, 137.7, 135.0, 134.0, 133.9, 133.8, 133.0, 132.6, 131.9, 130.5, 128.7, 128.5, 128.3, 128.1, 127.9, 127.8, 127.2, 126.6, 126.4, 126.3, 126.2, 126.1, 125.8, 125.7, 123.8, 49.8, 39.6; IR: 3054, 3023, 2962, 2922, 2850, 1628, 1597, 1507, 1495, 1447, 1345, 1368, 1121, 1018, 962, 893, 857, 842, 812, 744, 692, 475; HRMS (APCI) [M-H]$^-$ calcd for C$_{32}$H$_{25}$, 409.1956; found 409.1946.

A mixture of $^{3u}$ and $^{4u}$ in a ratio of 3:1;[9] To oven-dried glassware were added [Ir(cod)Cl]$_2$ (2.7 mg, 2.0 mol %), dppf (4.8 mg, 4.4 mol %) and anhydrous THF (1 mL). The mixture was stirred at r.t. under a nitrogen atmosphere for 30 min, and allylic carbonate 1a (0.2 mmol) was added. Then the nucleophile which was prepared from allylbenzene (35.4 mg, 0.3 mmol) and n-BuLi (0.3 mmol, 1.6 M in hexane) stirring at 0 °C in THF (1 mL) for 1 h was added. The reaction mixture was stirred overnight. The reaction was quenched with H$_2$O, extracted with EtOAc (20 mL x 3). The combined organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$ and then concentrated in vacuo. The ratio of regioisomers (linear to branched l/b) was determined by $^1$H NMR of the crude reaction mixture. Then the crude reaction mixture was then purified by flash column chromatography (SiO$_2$; petroleum ether) to give the desired product (46.3 mg, 99% yield) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.42 – 7.12 (m, 40H), 6.47 – 6.26 (m, 7H), 6.17 –
5.99 (m, 6H), 5.10 – 5.05 (m, 6H), 3.44 (q, \(J = 7.2 \text{ Hz}, 3\text{H}\)), 2.67 – 2.63 (m, 6H), 2.41 – 2.40 (m, 4H); \(^{13}\text{C}\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 141.6, 131.6, 130.6, 130.2, 128.7, 128.6, 127.9, 127.1, 126.5, 126.2, 114.8, 50.2, 39.2, 33.1.

5. The Efficiency of the Catalytic System

\[
\begin{align*}
\text{Ph} & \text{OBoc} + \text{Ph} & \begin{array}{c}
\text{[Ir(cod)Cl\(_2\), dppf, NaHMDS, THF, r.t.]} \\
\text{3a (linear)} & \text{4a (branched)}
\end{array}
\end{align*}
\]

To oven-dried glassware were added [Ir(cod)Cl\(_2\)] (2.7 mg, 0.004 mmol), dppf (4.8 mg, 0.0088 mmol) and anhydrous THF (2 mL). The mixture was stirred at r.t. under a nitrogen atmosphere for 30 min, then anhydrous THF (8 mL) was added to the mixture.

(a) S/C = 1000. To oven-dried glassware were added the aforementioned mixture (0.5 mL) and anhydrous THF (3 mL). tert-Butyl cinnamyl carbonate \(1\text{a}\) (0.4 mmol), \((E)-1,3\text{-diphenylpropene 2a}\) (0.6 mmol, 1.5 equiv.) and NaHMDS (0.6 mmol, 2M in THF, 1.5 equiv.) were added. The reaction mixture was stirred for 12 h at r.t.. The reaction was quenched with H\(_2\)O and extracted with EtOAc (20 mL × 3). The combined organic layer was washed with brine, dried over anhydrous Na\(_2\)SO\(_4\) and then concentrated in vacuo. The ratio of regioisomers (linear to branched, \(3\text{a}/4\text{a} > 99/1\)) was determined by \(^1\text{H}\) NMR of the crude reaction mixture. The crude reaction mixture was then purified by flash column chromatography (SiO\(_2\); petroleum ether: ethyl acetate = 100:1) to give product \(3\text{a}\) (111.8 mg, 90%).

(b) S/C = 2000. To oven-dried glassware were added the aforementioned mixture (0.25 mL) and anhydrous THF (3 mL). \(t\)-Butyl cinnamyl carbonate \(1\text{a}\) (0.4 mmol), \((E)-1,3\text{-diphenylpropene 2a}\) (0.6 mmol, 1.5 equiv.) and NaHMDS (0.6 mmol, 2 M in THF, 1.5 equiv.) were added. The reaction mixture was stirred for 24 h at r.t. The reaction was quenched with H\(_2\)O and extracted with EtOAc (20 mL × 3). The combined organic layer was washed with brine, dried over anhydrous Na\(_2\)SO\(_4\) and then concentrated in vacuo. The ratio of regioisomers (linear to branched, \(3\text{a}/4\text{a} > 99/1\)) was determined by \(^1\text{H}\) NMR of the crude reaction mixture. The crude reaction mixture was then purified by flash column chromatography (SiO\(_2\); petroleum ether: ethyl acetate = 100:1) to give product \(3\text{a}\) (98.1 mg, 79%).
6. Stereochemical Studies

a) Synthesis of (rac)-cis-tert-butyl(5-phenyl-2-cyclohexenyl)carbonate 5

\[ \mathrm{HO-C(Ph)_2-C(5-PhC_6H_{10})OC(Ph)_2} \]

\[ \mathrm{n-BuLi, Boc_2O} \]

\[ \mathrm{-78 \degree C, THF} \]

\[ \mathrm{Ph} \]

\[ \mathrm{BocO} \]

\[ \mathrm{Ph} \]

\[ \mathrm{n-BuLi} \] (3.44 mL, 2.5 M in hexane) was added to a solution of (rac)-cis-5-phenyl-2-cyclohexen-1-ol (1.5 g, 8.6 mmol) in THF (8 mL) at \(-78 \degree C\). \[11\] The reaction mixture was warmed and stirred at 0 \degree C for 30 min. A solution of Boc\(_2\)O (1.98 mL, 8.6 mmol) in THF (4 mL) was then added. The reaction mixture was stirred for 12 h, quenched with saturated aqueous NaHCO\(_3\) and extracted with EtOAc (50 mL × 3). The combined organic layer was washed with brine, dried over anhydrous MgSO\(_4\) and concentrated in vacuo. The crude product was purified by flash column chromatography (SiO\(_2\); petroleum ether: ethyl acetate = 100:1) to give the desired product (1.8 g, 76\%) as colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.33 – 7.29 (m, 2H), 7.23 – 7.19 (m, 3H), 5.94 – 5.90 (m, 1H), 5.76 – 5.73 (m, 1H), 5.37 – 5.32 (m, 1H), 2.99 – 2.92 (m, 1H), 2.38 – 2.28 (m, 2H), 2.20 – 2.13 (m, 1H), 1.88 (ddd, \(J=13.2, 12.0, 10.4\) Hz, 1H), 1.49 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 153.4, 145.3, 130.6, 128.8, 127.0, 126.9, 126.7, 82.2, 74.0, 39.2, 35.3, 33.7, 28.0.

b) Determination of the relative stereochemistry of compound 6

\[ \begin{array}{c}
\text{BocO} \\
\text{Ph}
\end{array} \]

\[ \begin{array}{c}
\text{Ph}
\end{array} \]

\[ \begin{array}{c}
\text{[Ir(cod)Cl\(_2\)]/dpf}\end{array} \]

\[ \begin{array}{c}
\text{NaHMDS, THF}
\end{array} \]

\[ \begin{array}{c}
50 \degree C, 12 h
\end{array} \]

\[ \begin{array}{c}
\text{6}
\end{array} \]

To oven-dried glassware were added [Ir(cod)Cl\(_2\)] (10.7 mg, 4 mol %), dppf (19.5 mg, 8.8 mol %) and anhydrous THF (4 mL). The mixture was stirred at r.t. under a nitrogen atmosphere for 30 min. Carbonate 5 (0.4 mmol), (E)-1,3-diarylpropene 2t (0.6 mmol, 1.5 equiv.) and NaHMDS (0.6 mmol, 2 M in THF, 1.5 equiv.) were then added. The reaction mixture was stirred for 12 h at 50 \degree C. The reaction was quenched with H\(_2\)O and extracted with EtOAc (20 mL × 3). The combined organic layer was washed with brine, dried over anhydrous Na\(_2\)SO\(_4\) and then concentrated in vacuo. The crude product was purified by flash column chromatography (SiO\(_2\); petroleum ether: ethyl acetate = 50:1) to give the desired products (63 mg, 35\%) as a colorless oil. The \(^1\)H NMR
spectra of the products showed two sets of peaks in 2:1 ratio (Figure 1). The products were isolated by chiral preparative HPLC (Chiralcel OD-H, iPrOH/Hexane = 1:99, 4 ml/min, 220 nm), affording two samples (sample 1, 39 mg; sample 2, 20 mg). Through analysis of the $^1$H NMR and $^{13}$C NMR spectra, it can be known: (1) The spectrum of sample 1 (Figure 2) also contains two sets of NMR peaks similar to Figure 1, representing a pairs of enantiomers (A + B) and another diastereomer C, but in a ratio of 1:1. (2) The spectrum of sample 2 shows only one isomer, D (Figure 3), which is the enantiomer of C. Through analysis of $^1$H NMR coupling constants,$^{[12]}$ we know that the relative stereochemistry of compounds C and D is trans. We were unable to determine if the other set of peaks corresponded to cis- or trans-isomers in spectrum of sample 1 (Figure 2). According to the method for the preparation of mixtures 3a and 4a in the following comparative experiments (see section 7), the two pairs of cis-isomers of product 6 were prepared as a mixture in a ratio of 7:4 (Figure 4). Comparison of the $^1$H NMR spectra shown in Figure 2 and Figure 4 indicates that compounds A and B are also trans-isomers.

Sample 1. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.87 – 7.41 (m, 14H), 7.34 – 7.14 (m, 5H), 6.68 – 6.57 (m, 2H), 6.02 – 5.94 (m, 1H), 5.82 – 5.77 (m, 0.5 H), 5.48 – 5.44 (m, 0.5 H), 3.73 – 3.66 (m, 1H), 3.08 – 3.00 (m, 1H), 2.81 (m, 1H), 2.43 – 2.34 (m, 1H), 2.28 – 2.19 (m, 1H), 2.01 (ddd, $J$ = 13.2, 11.2, 5.6 Hz, 0.6H), 1.84 – 1.70 (m, 0.7H); $^{13}$C NMR (100 MHz, CDCl$_3$): 146.9, 146.7, 141.4, 140.9, 135.1, 135.0, 133.9, 133.8, 133.7, 133.6, 133.1, 133.0, 132.5, 131.2, 129.8, 129.5, 128.6, 128.5, 128.3, 128.0, 127.9, 127.8, 127.7, 127.2, 126.8, 126.6, 126.5, 126.4, 126.2, 126.1, 126.0, 125.8, 125.6, 123.9, 123.8, 55.5, 55.4, 39.2, 39.1, 36.1, 35.9, 33.6, 33.5, 32.6; IR: 3734, 3648, 3618, 3594, 3586, 3545, 3523, 3022, 2919, 1748, 1731, 1704, 1697, 1688, 1549, 1507, 1488, 1472, 1396, 1362, 813, 744, 698;

Sample 2. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.88 – 7.14 (m, 14H), 6.70 – 6.57 (m, 2H), 5.82 – 5.78 (m, 1H), 5.48 – 5.45 (m, 1H), 3.67 (dd, $J$ = 10.0, 8.0 Hz, 1H), 3.08 – 3.01 (m, 1H), 2.82 (m, 1H), 2.42 – 2.35 (m, 1H), 2.27 – 2.19 (m, 1H), 2.01 (ddd, $J$ = 13.2, 10.8, 5.6 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 146.7, 140.7, 134.8, 133.7, 133.5, 133.4, 132.7, 132.3, 131.0, 129.3, 128.4, 128.2, 128.0, 127.8, 127.61, 127.65, 127.66, 127.5, 127.0, 126.6, 126.4, 126.1, 126.0, 125.8, 125.6, 125.4, 123.6, 55.3, 39.0, 35.7, 33.4, 32.4. IR: 3734, 3648, 3613, 3586, 3022, 2920, 1748, 1731, 1715, 1681, 1597, 1507, 1489, 1362, 959, 813, 744, 698; HRMS (APCI) [M+H]$^+$ calcd for C$_{33}$H$_{31}$, 451.2426; found 451.2419.
cis-Isomers 6: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.88 – 7.13 (m, 14 H), 6.73 – 6.62 (m, 2H), 6.02 – 6.00 (m, 0.7H), 5.92 – 5.88 (m, 0.7H), 5.80 – 5.76 (m, 0.4 H), 5.57 – 5.54 (m, 0.4H), 3.50 (t, $J$ = 8.4 Hz, 1H), 2.99 – 2.83 (m, 2H), 2.34 – 2.29 (m, 1H), 2.21 – 2.16 (m, 1.69 H), 1.79 – 1.76 (m, 0.78H), 1.63 (dt, $J$ = 13.2, 12.4 Hz, 0.48), 1.52 (dt, $J$ = 13.2, 12.0 Hz, 0.94); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 147.1, 147.0, 141.0, 140.9, 135.1, 135.0, 133.9, 133.88, 133.81, 133.05, 133.00, 132.8, 132.6, 132.5, 131.2, 129.7, 129.4, 128.7, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.2, 127.1, 126.8, 126.4, 126.38, 126.31, 126.2, 126.1, 125.9, 125.8, 125.7, 125.6, 123.9, 123.8, 66.1, 65.8, 42.3, 42.2, 36.0, 34.3, 34.2.

Figure 1 $^1$H NMR Spectra of Compound A, B, C, D

Figure 2 $^1$H NMR Spectra of Compound A, B, C
Figure 3 $^1$H NMR Spectrum of Compound D

Figure 4 $^1$H NMR Spectra of cis-Isomers 6
7. References

8. NMR Spectra

1g

\[
\text{Me} - \text{C} = \text{C} - \text{OBoc}
\]
1h

Me

O

O

Boc
2t

![Chemical Structure](image1)

![NMR Spectrum](image2)
3f

Ph

Me

Ph
3h

\[ \text{Me} \]
\[ \text{Ph} \]
\[ \text{Ph} \]

![NMR Spectrum](image_url)
\[
\text{Ph} = C \xrightarrow{\text{Ph}} \text{Ph} + \text{Ph} = C \xrightarrow{\text{Ph}} \text{Ph}
\]

\[
3u + 4u
\]
Sample 1
Sample 2
cis-Isomers 6