Supporting Information

Asymmetric Synergy between Chiral Dienes and Diphosphines in Cationic Rh(I)-Catalyzed Intramolecular [4+2] Cycloaddition

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General:

^1H NMR and ^{13}C NMR spectra were measured on Varian Gemini 300 (300 MHz) and Bruker AV300M (300 MHz) spectrometers, ^{19}F NMR were measured on Varian Gemini 400 (400 MHz) spectrometers.

Analytical thin layer chromatography (TLC) were performed on a glass plates and /or aluminum sheets pre-coated with silica-gel (Merck Kieselgal 60 F₂₅₄, layer thickness 0.25 and 0.2 mm). Column chromatography was performed on Merck Kieselgel 60 and KANTO Silica Gel 60N (spherical, neutral).

Capillary gas chromatographic analysis (GC) was conducted on Shimadzu GC-14B instrument equipped with FID detector and capillary column coated with PEG-20 M by using He as a carrier gas. Peak area was calculated by Shimadzu C-R6A as an automatic integrator. CP-Cyclodextrin- β -2,3,6-M-19 (i.d. 0.25 mm x 25 m, CHROMPACK; GL Science) was used as chiral columns. Split ratio was 100:1.

Optical rotations were measured on a JASCO P-1020.

2-(3,5-Dimethylphenyl)-8-methoxy-1,8-dimethylbicyclo[2.2.2]octa-2,5-diene (3)

To a mixture of 3,5-dimethylphenylboronic acid (112.5 mg, 0.75 mmol) and trifluoromethanesulfonic acid 8-methoxy-1,8-dimethyl-bicyclo[2.2.2]octa-2,5-dien-2-yl ester¹ (156.2 mg, 0.5 mmol) in THF (8.0 ml) and 2.0 M K₂CO₃/H₂O (8.0 ml) was added Pd(PPh₃)₄ (11.6 mg, 0.01 mmol) under argon atmosphere. The mixture was refluxed for 18 h. After cooling to room temperature, THF was evaporated under reduced pressure. Ether was added to the mixture, and then the organic layer was washed with brine, and then dried over NaSO₄. After evaporated under reduced pressure, the residue was purified by silica-gel chromatography (hexane/ethyl acetate = 10/1) to give the titled compound (yield 82%).

¹H NMR (300 MHz, CDCl₃) δ 1.320 (s, 3H), 1.324 (d, J = 11.7 Hz, 1H), 1.34 (s, 3H), 1.65 (d, J = 11.7, 1H), 2.32 (s, 6H), 3.24 (s, 3H), 3.64 (td, J = 6.3, 1.2 Hz, 1H), 6.16 (td, J = 6.0, 1.2 Hz, 2H), 6.39 (t, J = 6.9 Hz, 1H), 6.78 (s, 2H), 6.90 (s, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 21.24, 21.71, 24.77, 45.33, 47.59, 49.86, 50.70, 84.09, 126.23, 128.09, 130.85, 134.06, 136.94, 139.49, 141.71, 150.05.

$[\alpha]_D^{20}$ = -22.3 (c = 0.36 in CHCl₃).

8-Methoxy-1,8-dimethyl-2-phenylbicyclo[2.2.2]octa-2,5-diene (4)¹

The titled compound was prepared from phenylboronic acid and trifluoromethanesulfonic acid 8-methoxy-1,8-dimethyl-bicyclo[2.2.2]octa-2,5-dien-2-yl ester¹ according to the procedure as diene **3** (yield 67%).

¹H NMR (300 MHz, CDCl₃) δ 1.299 (s, 3H), 1.302 (d, J = 12.0 Hz, 1H), 1.319 (s, 3H), 1.63 (d, J = 12.0, 1H), 3.21 (s, 3H), 3.63 (td, J = 6.0, 1.2 Hz, 1H), 6.16 (dd, J = 7.5, 1.2 Hz, 1H), 6.17 (d, J = 6.0 Hz, 1H), 6.38 (t, J = 6.6 Hz, 1H), 7.13-7.16 (m, 2H), 7.24-7.32 (m, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 21.72, 24.78, 45.41, 47.74, 49.90, 50.58, 84.15, 126.44, 127.62, 128.51, 131.44, 134.04, 139.65, 141.68, 149.83.

2-(3,5-Dimethylphenyl)-8-methoxy-1,8-dimethylbicyclo[2.2.2]octa-2,5-diene (5)¹

The titled compound was prepared from 4-*tert*-butylphenylboronic acid and trifluoromethanesulfonic acid 8-methoxy-1,8-dimethyl-bicyclo[2.2.2]octa-2,5-dien-2-yl ester¹ according to the procedure as diene **3** (yield 81%).

¹H NMR (300 MHz, CDCl₃) δ 1.314 (d, *J* = 11.7 Hz, 1H), 1.317 (s, 3H), 1.343 (s, 9H), 1.369 (s, 3H), 1.65 (d, *J* = 11.7, 1H), 3.22 (s, 3H), 3.63 (td, *J* = 6.0, 1.2 Hz, 1H), 6.17 (dd, *J* = 7.2, 1.2 Hz, 1H), 6.18 (d, *J* = 6.0 Hz, 1H), 6.39 (t, *J* = 6.6 Hz, 1H), 7.09-7.13 (m, 2H), 7.30-7.35 (m, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 21.85, 24.80, 31.38, 34.41, 45.44, 47.77, 49.87, 50.58, 84.13, 124.50, 128.10, 131.19, 133.98, 136.61, 141.77, 149.20, 149.63.

[RhCl(3)]₂

A mixture of diene **3** (53.6 mg, 0.2 mmol) and [RhCl(ethylene)₂] (42.8 mg, 0.11 mmol) in benzene (4.0 ml) was stirred under argon atmosphere at room temperature for 24 h, and then the reaction mixture was filtered through celite. After the filtrate was evaporated under reduced pressure, the yellow residue was washed with ether. Prolonged evacuation of the product at 100 °C gave the solvent free complex (yield 90%).²

¹H NMR (300 MHz, CDCl₃) δ 0.68 (d, *J* = 13.8 Hz, 1H), 1.04 (s, 3H), 1.13 (d, *J* = 13.8, 1H), 1.65 (br s, 3H), 2.26 (br s, 6H), 3.22 (s, 3H), 3.32 (br s, 1H), 3.64 (br s, 1H), 3.71 (br m, 1H), 4.25 (br t, *J* = 6.0 Hz, 1H), 6.80 (br s, 1H), 7.32 (br s, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 21.40, 21.53, 21.82, 48.22, 49.22, 49.31, 50.23 (d, *J*_{Rh-C} = 2.5 Hz), 51.55 (d, *J*_{Rh-C} = 11.0 Hz), 57.00 (d, *J*_{Rh-C} = 10.9 Hz), 71.26 (br s), 77.19, 80.90 (d, *J*_{Rh-C} = 2.5 Hz), 128.77, 128.85, 136.14, 137.37.

Anal. Calcd for C₃₈H₄₈Cl₂O₂Rh₂: C, 56.10; H, 5.95%. Found: C, 55.41; H, 5.95%.

[α]_D²⁸ = -13.8 (c = 1.36 in CHCl₃).

[RhCl(4)]₂

The titled compound was prepared from diene **4** and [RhCl(ethylene)₂] according to the procedure as [RhCl(**3**)]₂ (yield 94%).

¹H NMR (300 MHz, CDCl₃) δ 0.72 (d, *J* = 13.8 Hz, 1H), 1.06 (s, 3H), 1.21 (d, *J* = 13.8, 1H), 1.69 (br s, 3H), 3.23 (s, 3H), 3.34 (d, *J* = 4.2 Hz, 1H), 3.67 (br s, 1H), 3.76 (br m, 1H), 4.29 (br t, *J* = 6.0 Hz, 1H), 7.21 (br s, 3H), 7.90 (br s, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 21.53, 29.68, 48.42, 49.22 (d, *J*_{Rh-C} = 3.7 Hz), 49.37, 50.23 (d, *J*_{Rh-C} = 2.5 Hz), 52.16 (d, *J*_{Rh-C} = 10.9 Hz), 57.00 (d, *J*_{Rh-C} = 10.9 Hz), 71.20 (d, *J*_{Rh-C} = 14.3 Hz), 77.19, 80.75 (d, *J*_{Rh-C} = 2.4 Hz), 126.97, 127.07, 130.97, 137.70.

Anal. Calcd for C₃₄H₄₀Cl₂O₂Rh₂: C, 53.92; H, 5.32%. Found: C, 50.33; H, 5.29%.

[α]_D²⁹ = +83.8 (c = 0.43 in CHCl₃).

[RhCl(5)]₂

The titled compound was prepared from diene **5** and [RhCl(ethylene)₂] according to the procedure as [RhCl(**3**)]₂ (yield 91%).

¹H NMR (300 MHz, CDCl₃) δ 0.70 (d, *J* = 13.8 Hz, 1H), 1.04 (s, 3H), 1.17 (d, *J* = 13.8, 1H), 1.28 (s, 9H), 1.66 (br s, 3H), 3.21 (s, 3H), 3.29 (d, *J* = 5.4 Hz, 1H), 3.65 (br s, 1H), 3.73 (br m, 1H), 4.26 (br t, *J* = 6.0 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.73 (br s, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 21.55, 21.64, 31.33, 34.46, 48.32, 49.29, 49.34, 50.33 (d, *J*_{Rh-C} = 3.7 Hz), 51.82 (d, *J*_{Rh-C} = 11.0 Hz), 56.80 (d, *J*_{Rh-C} = 11.0 Hz), 71.50 (d, *J*_{Rh-C} = 12.2 Hz), 77.21, 80.82 (d, *J*_{Rh-C} = 2.4 Hz), 123.86, 130.48, 134.59, 149.73.

Anal. Calcd for C₄₂H₅₆Cl₂O₂Rh₂: C, 58.01; H, 6.49%. Found: C, 57.76; H, 6.68%.

[α]_D²⁵ = +27.4 (c = 1.21 in CHCl₃).

1-Prop-2-ynoxy-hexa-2,4-diene

To a solution of NaH (105.6 mg, 4.4 mmol) in THF (2.0 ml) was added *trans,trans*-2,4-hexadiene-1-ol (0.45 ml, 4.0 mmol) in THF (0.5 ml) at 0 °C under argon atmosphere. After stirred for 45 min at room temperature, the reaction mixture was added propargyl bromide (0.33

ml, 4.4 mmol) at 0 °C. After stirred for 12 h, the reaction mixture was added carefully ice water and extracted with ether twice times. The organic layer was washed with brine and dried over MgSO₄. After concentration under reduced pressure, the residue was purified by silica-gel chromatography (pentane/ether = 20/1) to give the titled compound (yield 78%).

¹H NMR (300 MHz, CDCl₃) δ 1.75 (d, *J* = 6.6 Hz, 3 H), 2.41 (s, 1 H), 4.12 (s, 2 H), 4.07 (d, *J* = 6.6 Hz, 2 H), 5.59 (dt, *J* = 15.3, 6.5 Hz, 1 H), 5.72 (dq, *J* = 14.9, 6.7 Hz, 1 H), 6.05 (dd, *J* = 15.0, 15.0 Hz, 1 H), 6.23 (dd, *J* = 15.2, 10.4 Hz, 1 H).

¹³C NMR (CDCl₃, 75 MHz) δ 18.1, 56.7, 70.0, 74.3, 79.8, 125.5, 130.5, 130.6, 134.2.

HRMS (EI), Calcd for C₉H₁₂O [M⁺]: 136.0888, Found: 136.0887.

(3-Hexa-2,4-dienyloxy-prop-1-ynyl)-benzene (1a)

To a suspension of PdCl₂(PPh₃)₂ (70.2 mg, 0.10 mmol) and CuI (9.5 mg, 0.05 mmol) was added iodobenzene (1.12 ml, 10.0 mmol), diethylamine (15 ml), and 1-prop-2-ynyloxy-hexa-2,4-diene (0.68 g, 5.0 mmol) under argon atmosphere, and the mixture was refluxed for 3 h (monitored by TLC). After cooled to room temperature, the resultant mixture was added to ether, and then filtered by celite. After evaporation under reduced pressure, the resultant residue was purified by silica-gel chromatography to give the titled compound (yield 90%).

¹H NMR (300 MHz, CDCl₃) δ 1.79 (dd, *J* = 6.9, 0.6 Hz, 3H), 4.17 (d, *J* = 6.3 Hz, 2H), 4.38 (s, 2H), 5.63-5.82 (m, 2H), 6.06-6.15 (m, 1H), 6.29 (dd, *J* = 15.0, 10.5 Hz, 1H), 7.31-7.36 (m, 3H), 7.46-7.49 (m, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 18.1, 57.6, 70.1, 85.2, 86.2, 122.7, 125.8, 128.2, 128.4, 130.5, 130.7, 131.7, 134.2.

HRMS (EI), Calcd for C₁₅H₁₆O [M⁺]: 212.1201, Found: 212.1205.

1-(3-Hexa-2,4-dienyloxy-prop-1-ynyl)-4-methoxy-benzene (1b)

¹H NMR (300 MHz, CDCl₃) δ 1.76 (d, *J* = 6.0 Hz, 3H), 3.81 (s, 3H), 4.13 (d, *J* = 6.6 Hz, 2H), 4.34 (s, 2H), 5.60-5.79 (m, 2H), 6.00-6.12 (m, 1H), 6.26 (dd, *J* = 14.7, 10.2 Hz, 1H), 6.83 (d, *J* = 9.0 Hz, 2H), 7.39 (d, *J* = 9.0 Hz, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 17.8, 54.9, 57.5, 69.8, 83.6, 85.9, 113.7, 114.6, 125.8, 129.9, 130.6, 133.0, 133.7, 159.5.

HRMS (EI), Calcd for C₁₆H₁₈O₂ [M⁺]: 242.1307, Found: 242.1313.

1-Fluoro-4-(3-hexa-2,4-dienyloxy-prop-1-ynyl)-benzene (1c)

¹H NMR (300 MHz, CDCl₃) δ 1.76 (d, *J* = 6.6 Hz, 3H), 4.13 (d, *J* = 6.6 Hz, 2H), 4.33 (s, 2H), 5.58-5.80 (m, 2H), 6.02-6.13 (m, 1H), 6.21-6.31 (m, 1H), 6.95-7.04 (m, 2H), 7.38-7.46 (m, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 18.0, 57.5, 70.1, 84.9, 85.0, 115.5 (d, *J*_{C-F} = 22.0 Hz), 118.8 (d, *J*_{C-F} = 3.7 Hz), 125.7, 130.3, 130.7, 133.6 (d, *J*_{C-F} = 8.5 Hz), 134.0, 162.5 (d, *J*_{C-F} = 249.2 Hz).

¹⁹F NMR (376 MHz, CDCl₃) δ -111.2 (m, 1F).

HRMS (EI), Calcd for C₁₅H₁₅FO [M⁺]: 230.1107, Found: 230.1112.

1-Chloro-4-(3-hexa-2,4-dienyloxy-prop-1-ynyl)-benzene (1d)

¹H NMR (300 MHz, CDCl) δ 1.73 (d, *J* = 6.6 Hz, 3H), 4.01 (d, *J* = 6.3 Hz, 2H), 4.32 (s, 2H), 5.57-5.75 (m, 2H), 6.04 (ddd, *J* = 14.7, 10.5, 1.2 Hz, 1H), 6.24 (dd, *J* = 15.3, 10.5, 1H), 7.25 (dt, *J* = 8.7, 2.1 Hz, 2H), 7.34 (dt, *J* = 8.7, 2.1 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz) 17.9, 57.4, 70.0, 84.9, 86.3, 121.1, 125.6, 128.4, 130.2, 130.6, 132.8, 133.9, 134.3.

HRMS (EI), Calcd for C₁₅H₁₅³⁵ClO [M⁺]: 246.0811, Found: 246.0818.

1-(3-Hexa-2,4-dienyloxy-prop-1-ynyl)-4-trifluoromethyl-benzene (1e)

¹H NMR (300 MHz, CDCl) δ 1.76 (d, *J* = 6.6 Hz, 3H), 4.12 (d, *J* = 6.6 Hz, 2H), 4.37 (s, 2H), 5.61-5.80 (m, 2H), 6.08 (dd, *J* = 14.1, 10.5 Hz, 1H), 6.27 (dd, *J* = 15.3, 10.5, 1H), 7.54 (d, *J* = 9.0 Hz, 2H), 7.57 (d, *J* = 9.0 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz) 18.09, 57.43, 70.34, 84.78, 87.80, 123.85 (q, *J*_{C-F} = 271.7 Hz), 125.20 (q, *J*_{C-F} = 3.8 Hz), 125.52, 126.48, 130.12 (q, *J*_{C-F} = 33.2 Hz), 130.63, 130.67, 131.96, 134.37.

¹⁹F NMR (376 MHz, CDCl₃) δ -63.4 (s, 3F).

HRMS (ESI), Calcd for C₁₆H₁₅F₃O [M⁺]: 280.1075, Found: 280.1068.

Typical experimental procedure (Table 2)

To a solution of $[\text{RhCl}(\text{diene}^*)]_2$ (0.01 mmol) and (*R,R*)-Me-Duphos (6.7 mg, 0.022 mmol) in dry dichloromethane (2.0 ml) was added diene **1** (0.2 mmol) under argon atmosphere at room temperature. After the mixture was stirred for 1 min, AgSbF_6 (13.7 mg, 0.04 mmol) was added to the mixture at room temperature. The reaction was monitored by TLC. After the reaction was complete, the reaction mixture directly loaded onto a silica-gel column to give cyclization product **2** as a colorless oil.

6-Methyl-7-phenyl-1,3,3a,6-tetrahydroisobenzofuran (**2a**)

^1H NMR (300 MHz, CDCl_3) δ 0.94 (d, $J = 7.5$ Hz, 3H), 3.10-3.30 (m, 2H), 3.39 (dd, $J = 11.4, 7.5$, 1H), 4.13 (d, $J = 13.5$ Hz, 1H), 4.24 (d, $J = 7.5$ Hz, 1H), 4.30 (d, $J = 13.5$ Hz, 1H), 5.80 (s, 2H), 7.09-7.13 (m, 2H), 7.21-7.27 (m, 1H), 7.30-7.36 (m, 2H).

^{13}C NMR (75 MHz, CDCl_3) δ 20.19, 34.57, 41.04, 68.25, 72.15, 121.76, 126.60, 128.02, 128.28, 132.10, 134.62, 134.94, 140.30.

HRMS (EI), Calcd for $\text{C}_{15}\text{H}_{16}\text{O}$ $[\text{M}^+]$: 212.1201, Found: 212.1202.

$[\alpha]_{\text{D}}^{24} = +85.3$ ($c = 2.71$ in CHCl_3) (88% *ee*).

GC (column, CP-Cyclodextrin- β -2,3,6-M-19, i.d. 0.25 mm x 25 m, CHROMPACK; carrier gas, nitrogen 75 kPa; column, 150 $^\circ\text{C}$; injection temp, 180 $^\circ\text{C}$), t_{R} of minor-isomer 48.8 min, t_{R} of major-isomer 50.7 min.

7-(4-Methoxy-phenyl)-6-methyl-1,3,3a,6-tetrahydroisobenzofuran (**2b**)

^1H NMR (300 MHz, CDCl_3) δ 0.95 (d, $J = 7.5$ Hz, 3H), 3.08-3.28 (m, 2H), 3.38 (dd, $J = 11.4, 7.5$, 1H), 3.81 (s, 3H), 4.14 (d, $J = 14.4$ Hz, 1H), 4.23 (d, $J = 7.5$ Hz, 1H), 4.28 (d, $J = 14.4$ Hz, 1H), 5.79 (s, 2H), 6.87 (d, $J = 8.7$ Hz, 1H), 7.03 (d, $J = 8.7$ Hz, 1H).

^{13}C NMR (75 MHz, CDCl_3) δ 20.24, 34.78, 41.10, 55.19, 68.36, 72.20, 113.74, 121.76, 129.14, 131.73, 132.62, 134.72, 135.04, 158.27.

HRMS (EI), Calcd for $\text{C}_{16}\text{H}_{18}\text{O}_2$ $[\text{M}^+]$: 242.1307, Found: 242.1305.

$[\alpha]_{\text{D}}^{23} = +59.8$ ($c = 1.01$ in CHCl_3) (81% *ee*).

GC (column, CP-Cyclodextrin- β -2,3,6-M-19, i.d. 0.25 mm x 25 m, CHROMPACK; carrier gas,

nitrogen 75 kPa; column, 180 °C; injection temp, 180 °C), t_R of minor-isomer 49.4 min, t_R of major-isomer 50.9 min.

7-(4-Fluoro-phenyl)-6-methyl-1,3,3a,6-tetrahydroisobenzofuran (2c)

^1H NMR (300 MHz, CDCl_3) δ 0.93 (d, $J = 7.2$ Hz, 3H), 3.08-3.28 (m, 2H), 3.38 (dd, $J = 10.8, 6.9$, 1H), 4.12 (d, $J = 13.2$ Hz, 1H), 4.24 (d, $J = 13.2$ Hz, 1H), 4.26 (d, $J = 6.9$ Hz, 1H), 5.79 (s, 2H), 6.99-7.11 (m, 4H).

^{13}C NMR (75 MHz, CDCl_3) δ 20.12, 34.65, 41.10, 68.22, 72.16, 115.25 (d, $J_{\text{C-F}} = 20.8$ Hz), 121.81, 129.65 (d, $J_{\text{C-F}} = 8.53$ Hz), 131.19, 134.51, 135.69, 136.10 (d, $J_{\text{C-F}} = 3.6$ Hz), 161.65 (d, $J_{\text{C-F}} = 245.4$ Hz).

^{19}F NMR (376 MHz, CDCl_3) δ -116.4 (m, 1F).

HRMS (EI), Calcd for $\text{C}_{15}\text{H}_{15}\text{FO}$ [M^+]: 230.1107, Found: 230.1108.

$[\alpha]_D^{22} = +95.7$ ($c = 1.90$ in CHCl_3) (93% *ee*).

GC (column, CP-Cyclodextrin- β -2,3,6-M-19, i.d. 0.25 mm x 25 m, CHROMPACK; carrier gas, nitrogen 75 kPa; column, 180 °C; injection temp, 180 °C), t_R of minor-isomer 18.6 min, t_R of major-isomer 19.0 min.

7-(4-Chloro-phenyl)-6-methyl-1,3,3a,6-tetrahydroisobenzofuran (2d)

^1H NMR (300 MHz, CDCl_3) δ 0.93 (d, $J = 6.9$ Hz, 3H), 3.07-3.28 (m, 2H), 3.38 (dd, $J = 11.4, 7.2$, 1H), 4.12 (d, $J = 13.5$ Hz, 1H), 4.24 (d, $J = 13.5$ Hz, 1H), 4.26 (d, $J = 7.2$ Hz, 1H), 5.79 (s, 2H), 7.05 (d, $J = 8.4$ Hz, 1H), 7.31 (d, $J = 8.4$ Hz, 1H).

^{13}C NMR (75 MHz, CDCl_3) δ 20.12, 34.47, 41.10, 68.17, 72.13, 121.79, 128.59, 129.46, 131.00, 132.52, 134.43, 135.80, 138.68.

HRMS (EI), Calcd for $\text{C}_{15}\text{H}_{15}\text{ClO}$ [M^+]: 246.0811, Found: 246.0805.

$[\alpha]_D^{24} = +83.3$ ($c = 2.19$ in CHCl_3) (86% *ee*).

GC (column, CP-Cyclodextrin- β -2,3,6-M-19, i.d. 0.25 mm x 25 m, CHROMPACK; carrier gas, nitrogen 75 kPa; column, 180 °C; injection temp, 180 °C), t_R of minor-isomer 39.9 min, t_R of major-isomer 41.0 min.

6-Methyl-7-(4-trifluoromethyl-phenyl)-1,3,3a,6-tetrahydro-isobenzofuran (2e)

^1H NMR (300 MHz, CDCl_3) δ 0.95 (d, $J = 7.2$ Hz, 3H), 3.16-3.33 (m, 2H), 3.41 (dd, $J = 11.1, 7.2$, 1H), 4.14 (ddd, $J = 13.5, 3.0, 1.2$ Hz, 1H), 4.27 (d, $J = 13.5$ Hz, 1H), 4.30 (d, $J = 7.2$ Hz, 1H), 5.82 (s, 2H), 7.26 (d, $J = 8.1$ Hz, 1H), 7.62 (d, $J = 8.1$ Hz, 1H).

^{13}C NMR (75 MHz, CDCl_3) δ 20.10, 34.32, 41.07, 68.06, 72.06, 121.78, 124.17 (q, $J_{\text{C-F}} = 272.4$ Hz), 125.37 (q, $J_{\text{C-F}} = 3.8$ Hz), 128.41, 129.13 (q, $J_{\text{C-F}} = 32.5$ Hz), 130.93, 134.28, 136.14, 144.07.

^{19}F NMR (376 MHz, CDCl_3) δ -63.0 (s, 3F).

HRMS (ESI), Calcd for $\text{C}_{16}\text{H}_{15}\text{F}_3\text{O}$ [M^+]: 280.1075, Found: 280.1074.

$[\alpha]_{\text{D}}^{25} = +97.5$ ($c = 2.80$ in CHCl_3) (98% *ee*).

GC (column, CP-Cyclodextrin- β -2,3,6-M-19, i.d. 0.25 mm x 25 m, CHROMPACK; carrier gas, nitrogen 75 kPa; column, 170 $^{\circ}\text{C}$; injection temp, 180 $^{\circ}\text{C}$), t_{R} of minor-isomer 25.1 min, t_{R} of major-isomer 26.0 min.

References

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