Enantioselective Cyclization of 4-Alkenoic Acids via an Oxidative Allylic C–H Esterification

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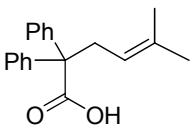
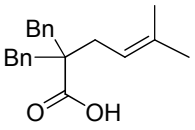
SUPPORTING INFORMATION 1

General: All reactions were carried out with standard Schlenk technique under a nitrogen atmosphere. All NMR spectra were recorded at 25 °C on a JEOL ECS400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C). Chemical shifts are reported in δ ppm referenced to an internal tetramethylsilane standard for ^{1}H NMR. Chemical shifts of ^{13}C NMR are given relative to $CDCl_3$ (δ 77.0), CD_2Cl_2 (δ 53.1), or CD_3OD (δ 49.0). ESI and APCI mass spectra were recorded on a Thermo Fisher, LTQ ORBITRAP XL. Melting points were measured using a Yanaco melting point apparatus MP-S9 and were uncorrected. IR spectra were obtained using a JASCO FT/IR-4100 instrument. Optical rotations were measured with a JASCO P-1030 polarimeter. HPLC analyses were performed on JASCO HPLC system (JASCO PU 2080 pump and MD-2010 UV/Vis detector). Anhydrous diethyl ether, THF and toluene were purchased from Kanto Chemicals and were used without further purification. Other solvents were purified prior to use by standard techniques.[1] *p*-Benzoquinone was purified by sublimation under vacuum. SPRIXs were prepared according to the methods reported by our laboratory.[2] 4-Alkenoic acids **1f** (CAS registry number: 75380-42-6),[3] **1i** (CAS registry number: 91764-08-8),[4] and **1m** (CAS registry number: 6966-03-6)[5] were prepared by the reported procedures. All other chemicals were purchased from commercial suppliers and used as received. Column chromatography was conducted on Kishida Silica Gel (spherical, 63–200 μm).

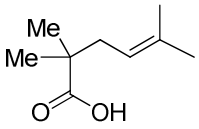


5-Methyl-2,2-diphenylhex-4-enoic acid (1a). To a solution of diisopropylamine (2.9 mL, 21 mmol) in THF (21 mL) was added *n*-BuLi (2.6 M solution in hexane; 8.1 mL) slowly at 0 °C, which was stirred at that temperature for 30 min. To this solution was added a solution of diphenylacetic acid (2.12 g, 10.0 mmol) in THF (10 mL). The reaction mixture was allowed to warm to rt and stirred for an additional 30 min. Then 1-chloro-3-methyl-2-butene (1.24 mL, 11 mmol) was added dropwise at 0 °C and the resulting solution was stirred at rt for 16 h. After being quenched by the addition of 1 M aq HCl, the mixture was extracted with EtOAc. The organic layer was washed with brine and dried over Na_2SO_4. After removal of the volatiles under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/EtOAc = 5/1, Rf 0.2) and recrystallization from hexane/EtOAc to give **1a** (2.38 g, 8.5 mmol) in 85% yield. Colorless crystal. Mp: 139–141 °C. HRMS (ESI): calcd for $C_{19}H_{20}NaO_2$: *m/z* 303.1360 ([M+Na]$^+$), found: *m/z* 303.1353. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34–7.18 (m, 10H), 5.03 (t, 1H, *J* = 7.1 Hz), 3.07 (d, 2H, *J* = 7.1 Hz), 1.55 (s, 3H), 1.24 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 180.0 (C=O), 142.1 (C), 135.1 (CH), 129.2 (CH), 127.8 (CH), 126.9 (CH), 119.2 (CH), 60.5 (C), 36.7 (CH_2), 25.8 (CH_3), 17.5 (CH_3). IR (KBr): 3060, 3037, 2969, 2927, 2911, 2856, 2808, 2686, 2637, 2589, 1692, 1302, 1244, 954, 723, 698, 657 cm^{-1}.

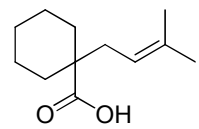


2,2-Dibenzyl-5-methylhex-4-enoic acid (1b). To a solution of diisopropylamine (0.59 mL, 4.2 mmol) in THF (4 mL) was added *n*-BuLi (2.6 M solution in hexane; 1.6 mL) slowly at 0 °C, which was stirred at that temperature for 30 min. To this solution was added a solution of dibenzylacetic acid (500 mg, 2 mmol) in THF (2 mL). The reaction mixture was allowed to warm to rt and stirred for an additional 30 min. Then 1-chloro-3-methyl-2-butene (0.34 mL, 3.0 mmol) was added dropwise at 0 °C and the resulting solution was stirred at rt for 12 h. After being quenched by the addition of 1 M aq HCl, the mixture was extracted with EtOAc. The organic layer was washed with brine and dried over Na_2SO_4. After removal of the volatiles under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/EtOAc = 5/1, Rf 0.2) and recrystallization from hexane/EtOAc to give **1b** (413 mg, 1.34 mmol) in 67% yield. White solid. Mp: 107–109 °C. HRMS (ESI): calcd for $C_{21}H_{24}NaO_2$: *m/z* 331.1673 ([M+Na]$^+$), found: *m/z* 331.1665. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27–7.16 (m, 10H), 5.38 (t, 1H, *J* = 6.2 Hz), 3.12 (d, 2H, *J* = 13.7 Hz), 2.93 (d, 2H, *J* = 13.7 Hz), 2.14 (d, 2H, *J* = 6.2 Hz), 1.83 (s, 3H), 1.51 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 182.1 (C=O), 137.1 (CH), 134.5 (C), 130.1 (CH), 128.1 (CH), 126.6 (CH), 119.1 (CH), 52.2 (C), 41.7 (CH_2), 29.1 (CH_2), 26.3 (CH_3), 18.4 (CH_3). IR (KBr): 3029, 2959, 2927, 1698, 1496, 1455, 1220, 1163,

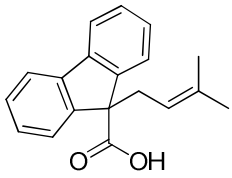
1154, 1117, 1107, 1084, 737, 700, 675, 572, 566, 516, 491, 475, 467, 457, 441, 423, 406 cm^{-1}.



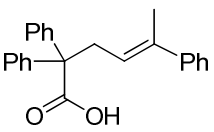
2,2,5-Trimethylhex-4-enoic acid (1c). To a solution of diisopropylamine (2.83 mL, 20.2 mmol) in THF (20 mL) was added *n*-BuLi (2.6 M solution in hexane; 7.77 mL, 20.2 mmol) slowly at 0 °C, which was stirred at that temperature for 30 min. To this solution was added carboxylic acid methyl isobutyrate (2.16 g, 16.8 mmol). The reaction mixture was allowed to warm to rt and stirred for an additional 30 min. Then 1-chloro-3-methyl-2-butene (2.46 g, 20.2 mmol) was added dropwise at 0 °C and the resulting solution was stirred at rt for 24 h. After being quenched by the addition of 1 M aq HCl, the mixture was extracted with EtOAc. The organic layer was washed with brine and dried over Na_2SO_4. After removal of the volatiles under reduced pressure, the residue was redissolved in EtOH. To this solution was added 5 M aq LiOH and the mixture was refluxed for 44 h. After being cooled to rt, the mixture was extracted with EtOAc. The organic layer was washed with brine and dried over Na_2SO_4. The crude product was purified by column chromatography on silica gel (hexane/EtOAc = 5/1, Rf 0.3) to give **1c** (2.39 g, 15.3 mmol) in 91% yield. Colorless liquid. HRMS (APCI): calcd for $C_9H_{16}O_2$: *m/z* 157.1229 ($[M+Na]^+$), found: *m/z* 157.1222. ^1H NMR (400 MHz, $CDCl_3$): δ 5.13 (t, 1H, J = 7.5 Hz), 2.25 (d, 2H, J = 7.5 Hz), 1.71 (s, 3H), 1.61 (s, 3H), 1.18 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 185.0 (C=O), 134.5 (C), 119.6 (CH), 42.7 (C), 38.4 (CH_2), 26.0 (CH_3), 24.5 (CH_3), 17.9 (CH_3). IR (KBr): 2972, 2929, 2876, 2725, 2671, 2619, 1701, 1474, 1453, 1409, 1385, 1379, 1315, 1265, 1241, 1201, 1163, 944, 782, 768, 601, 555 cm^{-1}.



1-(3-Methylbut-2-enyl)cyclohexanecarboxylic acid (1d). To a solution of diisopropylamine (2.83 mL, 20.2 mmol) in THF (20 mL) was added *n*-BuLi (2.6 M solution in hexane; 7.77 mL, 20.2 mmol) slowly at 0 °C, which was stirred at that temperature for 30 min. To this solution was added carboxylic acid methyl cyclohexanecarboxylate (2.38 g, 16.8 mmol). The reaction mixture was allowed to warm to rt and stirred for an additional 30 min. Then 1-chloro-3-methyl-2-butene (2.46 g, 20.2 mmol) was added dropwise at 0 °C and the resulting solution was stirred at rt for 24 h. After being quenched by the addition of 1 M aq HCl, the mixture was extracted with EtOAc. The organic layer was washed with brine and dried over Na_2SO_4. After removal of the volatiles under reduced pressure, the residue was redissolved in EtOH. To this solution was added 5 M aq LiOH and the mixture was refluxed for 44 h. After being cooled to rt, the mixture was extracted with EtOAc. The organic layer was washed with brine and dried over Na_2SO_4. The crude product was purified by column chromatography on silica gel (hexane/EtOAc = 5/1, Rf 0.3) to give **1d** (2.22 g, 11.3 mmol) in 67% yield. Colorless crystal. Mp: 102–104 °C. HRMS (APCI): calcd for $C_{12}H_{21}O_2$: *m/z* 197.1542 ($[M+Na]^+$), found: *m/z* 197.1537. ^1H NMR (400 MHz, CD_3OD): δ 5.09 (t, 1H, J = 8.0 Hz), 2.19 (d, 2H, J = 8.0 Hz), 2.02 (d, 2H, J = 16.0 Hz), 1.68 (s, 3H), 1.60–1.18 (m, 13H). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3OD): δ 181.4 (C=O), 135.7 (C), 121.3 (CH), 49.4 (C), 40.8 (CH_2), 35.8 (CH_2), 27.9 (CH_2), 27.0 (CH_3), 25.3 (CH_2), 18.9 (CH_3). IR (KBr): 2970, 2928, 2855, 2727, 2631, 1735, 1718, 1701, 1686, 1678, 1656, 1648, 1457, 1380, 1330, 1250, 1192, 1138, 969, 951, 932, 840 cm^{-1}.

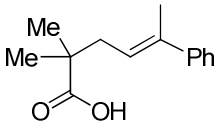


9-(3-Methylbut-2-enyl)-9H-fluorene-9-carboxylic acid (1e). To a solution of diisopropylamine (1.47 mL, 10.5 mmol) in THF (10 mL) was added *n*-BuLi (2.6 M solution in hexane; 4.04 mL, 10.5 mmol) slowly at 0 °C, which was stirred at that temperature for 30 min. To this solution was added a solution of 9*H*-fluorene-9-carboxylic acid (1.05 g, 5.00 mmol) in THF (5 mL). The reaction mixture was allowed to warm to rt and stirred for an additional 30 min. Then 1-chloro-3-methylbut-2-ene (0.65 mL, 5.75 mmol) was added dropwise at 0 °C and the resulting solution was stirred at rt for 14 h. After being quenched by the addition of 1 M aq HCl, the mixture was extracted with EtOAc. The organic layer was washed with brine and dried over Na_2SO_4. After removal of the volatiles under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/EtOAc = 5/1, Rf 0.3) and recrystallization from hexane/EtOAc to give **1e** (1.09 g, 3.9 mmol) in 78% yield. Light yellow needle. Mp: 129–131 °C. HRMS (ESI): calcd for $C_{19}H_{18}NaO_2$: *m/z* 301.1204 ($[M+Na]^+$), found: *m/z* 301.1197. ^1H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, 2H, J = 7.2 Hz), 7.58 (d, 2H, J = 7.2 Hz), 7.39 (t, 2H, J = 7.2 Hz), 7.30 (t, 2H, J = 7.2 Hz), 4.82 (t, 1H, J = 7.2 Hz), 2.92 (d, 2H, J = 7.2 Hz) 1.53 (s, 3H), 1.38 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 179.4 (C=O), 144.7 (C), 140.7 (C), 135.4 (C), 128.1 (CH), 127.3 (CH), 125.1 (CH), 119.9 (CH), 118.2 (CH), 61.0 (C), 36.5 (CH_2), 25.7 (CH_3), 18.6 (CH_3). IR (KBr): 3064, 3021, 2968, 2935, 2879, 2637, 2517, 1699, 1687, 1678, 1656, 1648, 1638, 1449, 1402, 1272, 739, 680 cm^{-1}.

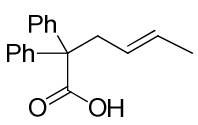


(*E*)-2,2,5-Triphenylhex-4-enoic acid (1g). To a solution of diisopropylamine (2.6mL, 18.6 mmol) in THF (19 mL) was added *n*-BuLi (2.6 M solution in hexane; 7.2 mL, 18.6 mmol) slowly at 0 °C, which was stirred at that temperature for 30 min. To this solution was added a solution of diphenylacetic acid (1.88 g, 8.86 mmol) in THF (9 mL). The reaction mixture was allowed to warm to rt and stirred for an additional 30 min. Then (*E*)-(4-chlorobut-2-en-2-yl)benzene (1.77 g, 10.6 mmol) was added dropwise at 0 °C and the resulting solution was stirred at rt for 24 h. After being quenched by the addition of 1 M aq HCl, the mixture was extracted with EtOAc. The organic layer was washed with brine and dried over Na_2SO_4. After removal of the volatiles under

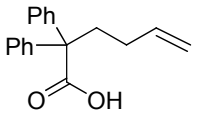
reduced pressure, the residue was purified by column chromatography on silica gel (hexane/EtOAc = 5/1, Rf 0.3) and recrystallization from hexane/EtOAc to give **1g** (911 mg, 2.66 mmol) in 30% yield. White solid. Mp: 143–145 °C. HRMS (ESI): calcd for $C_{24}H_{22}NaO_2$: *m/z* 365.1517 ($[M+Na]^+$), found: *m/z* 365.1510. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.13 (m, 15H), 5.63 (t, 1H, *J* = 7.1 Hz), 3.28 (d, 2H, *J* = 7.1 Hz), 1.66 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 180.3 (C=O), 144.0 (C), 141.9 (C), 138.0 (C), 129.2 (CH), 128.0 (CH), 127.9 (CH), 127.1 (CH), 126.6 (CH), 125.7 (CH), 123.3 (CH), 60.6 (C), 37.3 (CH_2), 15.8 (CH_3). IR (KBr): 3074, 3021, 2979, 2937, 2915, 2872, 2810, 2639, 2516, 1698, 1599, 1493, 1450, 1443, 1408, 1271, 1249, 1029, 941, 912, 905, 869, 761, 741, 723, 699, 680 cm^{-1}.



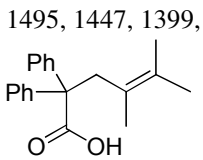
(*E*)-2,2-Dimethyl-5-phenylhex-4-enoic acid (1h). To a solution of diisopropylamine (2.0 mL, 14.0 mmol) in THF (14 mL) was added *n*-BuLi (2.6 M solution in hexane; 5.4 mL, 14.0 mmol) slowly at 0 °C, which was stirred at that temperature for 30 min. To this solution was added carboxylic acid methyl isobutyrate (1.19 g, 11.7 mmol). The reaction mixture was allowed to warm to rt and stirred for an additional 30 min. Then (*E*)-(4-chlorobut-2-en-2-yl)benzene (2.34 g, 14.1 mmol) was added dropwise at 0 °C and the resulting solution was stirred at rt for 24 h. After being quenched by the addition of 1 M aq HCl, the mixture was extracted with EtOAc. The organic layer was washed with brine and dried over Na_2SO_4. After removal of the volatiles under reduced pressure, the residue was redissolved in EtOH. To this solution was added 5 M aq LiOH and the mixture was refluxed for 44 h. After being cooled to rt, the mixture was extracted with EtOAc. The organic layer was washed with brine and dried over Na_2SO_4. The crude product was purified by column chromatography on silica gel (hexane/EtOAc = 5/1, Rf 0.3) to give **1h** (1.99 g, 9.13 mmol) in 78% yield. Colorless liquid. HRMS (ESI): calcd for $C_{14}H_{18}NaO_2$: *m/z* 241.1204 ($[M+Na]^+$), found: *m/z* 241.1194. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, 2H, *J* = 7.2 Hz), 7.29 (dd, 2H, *J* = 7.7 Hz, *J* = 7.2 Hz), 7.22 (d, 1H, *J* = 7.7 Hz), 5.75 (t, 1H, *J* = 7.6 Hz), 2.48 (d, 2H, *J* = 7.6 Hz), 2.03 (s, 3H), 1.26 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 184.5 (C=O), 144.0 (C), 137.6 (C), 128.1 (CH), 126.7 (CH), 125.8 (CH), 123.4 (CH), 42.9 (C), 39.0 (CH_2), 24.7 (CH_3), 16.1 (CH_3). IR (KBr): 2974, 2923, 2878, 1698, 1473, 1445, 756, 698, 625, 608, 549, 505, 496, 466, 453, 445 cm^{-1}.



(*E*)-2,2-Diphenylhex-4-enoic acid (1j). To a solution of diisopropylamine (1.1 mL, 7.77 mmol) in THF (8 mL) was added *n*-BuLi (2.6 M solution in hexane; 3.0 mL, 7.77 mmol) slowly at 0 °C, which was stirred at that temperature for 30 min. To this solution was added a solution of diphenylacetic acid (784 mg, 3.70 mmol) in THF (10 mL). The reaction mixture was allowed to warm to rt and stirred for an additional 30 min. Then (*E*)-1-bromobut-2-ene (0.48 mL, 4.44 mmol) was added dropwise at 0 °C and the resulting solution was stirred at rt for 16 h. After being quenched by the addition of 1 M aq HCl, the mixture was extracted with EtOAc. The organic layer was washed with brine and dried over Na_2SO_4. After removal of the volatiles under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/EtOAc = 5/1, Rf 0.2) and recrystallization from hexane/EtOAc to give **1j** (839 mg, 3.15 mmol) in 85% yield (*E*/*Z* = 86:14). White crystalline solid. Mp: 114–116 °C. HRMS (ESI): calcd for $C_{18}H_{18}NaO_2$: *m/z* 289.1204 ($[M+Na]^+$), found: *m/z* 289.1188. For *E* isomer, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31–7.22 (m, 10H), 5.31–5.19 (m, 2H), 3.08 (d, 2H, *J* = 6.4 Hz), 1.50 (dd, 3H, *J* = 5.6 Hz, *J* = 0.9 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 179.9 (C=O), 142.1 (CH), 129.3 (C), 129.1 (CH), 127.8 (CH), 126.9 (CH), 125.9 (CH), 60.5 (C), 41.3 (CH_2), 18.0 (CH_3). IR (KBr): 3087, 3062, 3030, 2969, 2913, 2853, 2804, 2730, 2525, 1701, 1294, 1270, 1240, 965, 937, 920, 761, 699, 660, 638, 494 cm^{-1}.

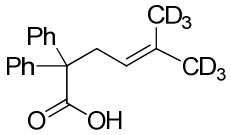


2,2-Diphenylhex-5-enoic acid (1j'). To a solution of diisopropylamine (4.4 mL, 31.5 mmol) in THF (31 mL) was added *n*-BuLi (2.6 M solution in hexane; 12.1 mL, 31.5 mmol) slowly at 0 °C, which was stirred at that temperature for 30 min. To this solution was added a solution of diphenylacetic acid (3.18 g, 15 mmol) in THF (15 mL). The reaction mixture was allowed to warm to rt and stirred for an additional 30 min. Then 4-bromobut-1-ene (1.8 mL, 8.16 mmol) was added dropwise at 0 °C and the resulting solution was stirred at rt for 12 h. After being quenched by the addition of 1 M aq HCl, the mixture was extracted with EtOAc. The organic layer was washed with brine and dried over Na_2SO_4. After removal of the volatiles under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/EtOAc = 5/1, Rf 0.3) and recrystallization from hexane/EtOAc to give **1j'** (3.4 g, 12.8 mmol) in 85% yield. White crystalline solid. Mp: 132–134 °C. HRMS (ESI): calcd for $C_{18}H_{18}NaO_2$: *m/z* 289.1204 ($[M+Na]^+$), found: *m/z* 289.1188. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34–7.25 (m, 10H), 5.75 (ddt, 1H, *J* = 17.0 Hz, *J* = 10.2 Hz, *J* = 6.5 Hz), 4.95 (dd, 1H, *J* = 17.0 Hz, *J* = 1.6 Hz), 4.91 (dd, 1H, *J* = 10.2 Hz, *J* = 1.6 Hz), 2.45 (m, 2H), 2.45 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 179.7 (C=O), 142.2 (C), 138.1 (CH), 129.0 (CH), 128.0 (CH), 127.0 (CH), 114.6 (CH_2), 60.0 (C), 37.1 (CH_2), 29.6 (CH_2). IR (KBr): 3077, 3019, 3000, 2973, 2934, 2901, 2636, 2503, 1703, 1495, 1447, 1399, 1262, 911, 759, 700, 656 cm^{-1}.

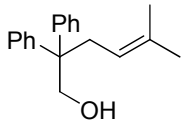


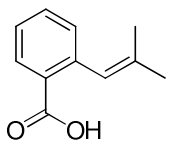
4,5-Dimethyl-2,2-diphenylhex-4-enoic acid (1k). To a solution of diisopropylamine (2.0 mL, 14.3 mmol) in THF (21 mL) was added *n*-BuLi (2.6 M solution in hexane; 5.5 mL, 14.3 mmol) slowly at 0 °C, which was stirred at that temperature for 30 min. To this solution was added a solution of diphenylacetic acid (1.44 g, 6.80 mmol) in THF (10 mL). The reaction mixture was allowed to warm to rt and

stirred for an additional 30 min. Then 1-bromo-2,3-dimethylbut-2-ene (1.10 mL, 8.16 mmol) was added dropwise at 0 °C and the resulting solution was stirred at rt for 18 h. After being quenched by the addition of 1 M aq HCl, the mixture was extracted with EtOAc. The organic layer was washed with brine and dried over Na_2SO_4. After removal of the volatiles under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/EtOAc = 5/1, Rf 0.2) and recrystallization from hexane/EtOAc to give **1k** (1.58 g, 5.37 mmol) in 79% yield. White crystalline solid. Mp: 135–137 °C. HRMS (ESI): calcd for $C_{20}H_{22}NaO_2$: *m/z* 317.1517 ($[M+Na]^+$), found: *m/z* 317.1509. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (m, 10H), 3.24 (s, 2H), 1.58 (s, 3H), 1.44 (s, 3H), 0.80 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 180.0 (C=O), 142.5 (CH), 130.9 (C), 129.1 (CH), 127.5 (CH), 126.8 (CH), 122.9 (C), 59.9 (C), 42.4 (CH_2), 20.6 (CH_3), 19.6 (CH_3), 19.1 (CH_3). IR (KBr): 3089, 3064, 3024, 2995, 2925, 2796, 2730, 2710, 2683, 2640, 2596, 1698, 1494, 1445, 1300, 1231, 1190, 1128, 911, 727, 698, 652, 632 cm^{-1}.

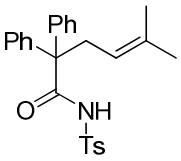


5-Methyl-2,2-diphenylhex-4-enoic acid-d_6 (1a-*d*). To a solution of diisopropylamine (0.29 mL, 3.91 mmol) in THF (4 mL) was added *n*-BuLi (2.6 M solution in hexane; 1.5 mL, 3.91 mmol) slowly at 0 °C, which was stirred at that temperature for 30 min. To this solution was added a solution of diphenylacetic acid (394 mg, 1.86 mmol) in THF (2 mL). The reaction mixture was allowed to warm to rt and stirred for an additional 30 min. Then 1-chloro-3-methyl-2-butene-d_6 (400 mg, 2.6 mmol) was added dropwise at 0 °C and the resulting solution was stirred at rt for 16 h. After being quenched by the addition of 1 M aq HCl, the mixture was extracted with EtOAc. The organic layer was washed with brine and dried over Na_2SO_4. After removal of the volatiles under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/EtOAc = 5/1, Rf 0.2) and recrystallization from hexane/EtOAc to give **1a-*d*** (453 mg, 1.58 mmol) in 85% yield. Colorless crystal. Mp: 139–141 °C. HRMS (ESI): calcd for $C_{19}H_{14}D_6NaO_2$: *m/z* 309.1737 ($[M+Na]^+$), found: *m/z* 309.1722. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30–7.26 (m, 10H), 5.04 (t, 1H, *J* = 7.1 Hz), 3.08 (d, 2H, *J* = 7.1 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 179.7 (C=O), 142.1 (C), 129.1 (CH), 127.8 (CH), 126.9 (CH), 119.2 (CH), 60.4 (C), 36.6 (CH_2) (signals of the deuterated carbons could not be detected). IR (KBr): 2962, 2927, 2874, 2861, 1790, 1467, 1379, 1161, 1066, 884, 758, 724, 697, 513, 505, 496, 481, 468, 450, 431, 421, 407 cm^{-1}.





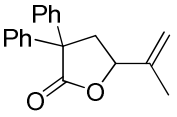
2-(2-Methylprop-1-enyl)benzoic acid (1l). To a solution of 1-bromo-2-(2-methylprop-1-enyl)benzene [6] (1.86 g, 8.86 mmol) in THF (30 mL) was added *n*-BuLi (1.65 M solution in hexane; 8.06 mL, 13.3 mmol) at −80 °C, which was stirred for 30 min. To this solution was bubbled CO_2 gas for 2 h and allowed to warm to rt. The reaction mixture was extracted with EtOAc, which was washed with brine and dried over Na_2SO_4. After removal of the solvents in vacuo, the residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 5/1, Rf 0.3) to afford **1l** (1.25 g, 7.09 mmol) in 80% yield**.** White needle. Mp: 137–139 °C. HRMS (ESI): calcd for $C_{11}H_{12}NaO_2$: *m/z* 199.0734 ($[M+Na]^+$), found: *m/z* 199.0727. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, 1H, *J* = 7.2 Hz), 7.51 (dd, 1H, *J* = 7.6 Hz, *J* = 7.4 Hz), 7.33-7.26 (m, 2H), 6.72 (br, 1H), 1.95 (s, 3H), 1.74 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 172.9 (C=O), 140.8 (C), 135.3 (C), 132.3 (CH), 131.5 (CH), 131.2 (CH), 128.1 (C), 126.2 (CH), 124.7 (CH), 26.3 (CH_3), 19.4 (CH_3). IR (KBr): 3064, 2979, 2930, 2911, 2817, 2653, 2552, 1689, 1599, 1569, 1483, 1454, 1406, 1377, 1303, 1266, 1142, 1054, 932, 831, 796, 742, 706, 663, 409 cm^{-1}.



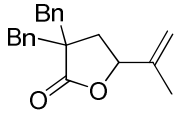
5-Methyl-2,2-diphenyl-*N*-tosylhex-4-enamide (4). [7] To a solution of **1a** (224 mg, 0.80 mmol) in THF (4 mL) was added tosyl isocyanate (0.15 mL, 1.0 mmol) and triethylamine (0.14 mL, 1.0 mmol) at 25 °C, which was stirred for 3 hours. After being quenched by the addition of 1 M aq HCl, the mixture was extracted with EtOAc. The organic layer was washed with brine and dried over Na_2SO_4. After removal of the solvents in vacuo, the residue was purified by recrystallization from hexane/EtOAc to give **4** (329 mg, 0.76 mmol) in 95% yield**.** Yellow needle. Mp: 137–139 °C. HRMS (ESI): calcd for $C_{26}H_{27}NNaO_3S$: *m/z* 456.1609 ($[M+Na]^+$), found: *m/z* 456.1598. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.75 (d, 2H, *J* = 8.4 Hz), 7.35-7.29 (m, 8H), 7.13-7.11 (m, 4H), 4.93 (t, 1H, *J* = 7.0 Hz), 3.03 (d, 2H, *J* = 7.0 Hz), 2.47 (s, 3H), 1.56 (s, 3H), 1.35 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 172.5 (C=O), 146.1 (C), 141.5 (C), 137.3 (C), 135.9 (C), 130.2 (CH), 129.5 (CH), 129.2 (CH), 129.1 (CH), 128.2 (CH), 119.5 (CH), 62.3 (C), 37.3 (CH_2), 26.3 (CH_3), 22.2 (CH_3), 18.3 (CH_3). IR (KBr): 3276, 3093, 3050, 3033, 2970, 2941, 2918, 1730, 1595, 1497, 1407, 1339, 1189, 1174, 1085, 1036, 979, 790, 699, 659, 579, 556 cm^{-1}.

5-Methyl-2,2-diphenylhex-4-en-1-ol (6). To a solution of $LiAlH_4$ (356 mg, 9.36 mmol) in THF (10 mL) was added a solution of **1a** (1.31 g, 4.68 mmol) in THF (10 mL) slowly at 0 °C. Then the reaction mixture was refluxed 5 h. After being quenched by the addition of 1 M aq HCl, the mixture was extracted with EtOAc. The organic layer was washed with brine and dried over Na_2SO_4. The volatiles were removed by evaporation to give the crude product, which was chromatographed on silica gel (hexane/EtOAc = 5/1, Rf 0.2). Pure **6** (1.25 g, 4.68 mmol) was obtained quntitatively. Colorless liquid. HRMS (ESI): calcd for $C_{19}H_{22}NaO$: *m/z* 289.1568 ($[M+Na]^+$), found: *m/z* 289.1559. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.18 (m, 10H), 4.84 (t, 1H, *J* = 7.2 Hz), 4.11 (d, 2H, *J* = 6.8 Hz), 2.88 (d, 2H, *J* = 7.2 Hz), 1.59 (s, 3H), 1.53 (s, 3H), 1.18 (t, 1H, *J* = 6.8 Hz). $^{13}C\{^1H\}$ NMR

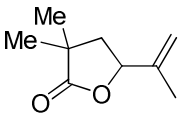
(100 MHz, $CDCl_3$): δ 145.5 (C), 134.6 (C), 128.3 (CH), 125.1 (CH), 126.2 (CH), 119.8 (CH), 68.2 (CH_2), 52.2 (C), 35.0 (CH_2), 26.0 (CH_3), 17.9 (CH_3). IR (KBr): 3547, 3442, 3435, 3087, 3057, 3026, 2967, 2925, 2914, 2882, 2859, 1599, 1496, 1444, 1377, 1065, 1038, 1024, 774, 756, 734, 699, 634, 615 cm^{-1}.



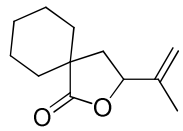
3,3-Diphenyl-5-(prop-1-en-2-yl)dihydrofuran-2(3*H*)-one (2a). A solution of $Pd(OAc)_2$ (1.1 mg, 0.005 mmol, 10 mol %) and (*P,R,R*)-*i*-Pr-SPRIX (2.8 mg, 0.0075 mmol, 15 mol %) in CH_2Cl_2 (0.25 mL) was stirred at 25 °C for 2 h. To this solution was added *p*-benzoquinone (10.8 mg, 0.10 mmol, 2 equiv) and **1a** (14.0 mg, 0.05 mmol) in CH_2Cl_2 (0.25 mL), and the mixture was stirred at 0 °C for 60 h. The reaction mixture was directly filtered through a short pad of silica gel, which was rinsed with EtOAc. The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 5/1, Rf 0.4) to afford **2a** (13.9 mg). >98% yield. Pale yellow wax. HRMS (ESI): calcd for $C_{19}H_{18}NaO_2$: *m/z* 301.1205 ($[M+H]^+$), found: *m/z* 301.1261. ^1H NMR (400 MHz, $CDCl_3$): δ 7.39–7.25 (m, 10H), 5.11 (s, 1H), 4.98 (s, 1H), 4.73 (dd, 1H, *J* = 11.0 Hz, *J* = 5.1 Hz), 3.06 (dd, 1H, *J* = 13.0 Hz, *J* = 5.1 Hz), 2.78 (dd, 1H, *J* = 13.0 Hz, *J* = 11.0 Hz), 1.80 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 176.9 (C=O), 141.9 (C), 141.3 (C), 139.5 (C), 129.0 (CH), 128.4 (CH), 127.8 (CH), 127.7 (CH), 127.4 (CH), 127.3 (CH), 113.3 (CH_2), 79.2 (CH), 58.3 (C), 42.5 (CH_2), 17.5 (CH_3). IR (KBr): 3451, 3065, 2938, 1761, 1645, 1496, 1446, 1386, 1327, 1175, 1047, 1010, 964, 924, 759, 699, 646, 495 cm^{-1}. The enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 40/1, flow rate = 0.5 mL/min, λ = 227 nm: 24.1 min, 29.4min) to be 82% ee. $[\alpha]_D^{15}$ +85.8 (*c* 0.70, $CHCl_3$).



3,3-Dibenzyl-5-(prop-1-en-2-yl)dihydrofuran-2(3*H*)-one (2b). A solution of $Pd(OAc)_2$ (1.1 mg, 0.005 mmol, 10 mol %) and (*P,R,R*)-*i*-Pr-SPRIX (2.8 mg, 0.0075 mmol, 15 mol %) in CH_2Cl_2 (0.25 mL) was stirred at 25 °C for 2 h. To this solution was added *p*-benzoquinone (10.8 mg, 0.10 mmol, 2 equiv) and **1b** (15.4 mg, 0.05 mmol) in CH_2Cl_2 (0.25 mL), and the mixture was stirred at 25 °C for 60 h. The reaction mixture was directly filtered through a short pad of silica gel, which was rinsed with EtOAc. The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 5/1, Rf 0.45) to afford **2b** (15.3 mg). >98% yield. White solid. Mp: 110–111 °C. HRMS (ESI): calcd for $C_{21}H_{22}NaO_2$: *m/z* 329.1517 ($[M+H]^+$), found: *m/z* 329.1509. ^1H NMR (400 MHz, $CDCl_3$): δ 7.33–7.19 (m, 10H), 4.63 (s, 1H), 4.60 (s, 1H), 3.56 (dd, 1H, *J* = 9.6 Hz, *J* = 7.4 Hz), 3.32 (d, 1H, *J* = 13.5 Hz), 3.20 (d, 1H, *J* = 13.2 Hz), 2.77 (d, 1H, *J* = 13.5 Hz), 2.76 (d, 1H, *J* = 13.2 Hz), 2.12 (dd, 1H, *J* = 7.4, *J* = 13.3 Hz), 2.02 (dd, 1H, *J* = 9.6, *J* = 13.3 Hz), 1.10 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 180.6 (C=O), 142.3 (C), 136.7 (C), 136.2 (C), 130.6 (CH), 129.9 (CH), 128.7 (CH), 128.5 (CH), 127.4 (CH), 127.0 (CH), 112.8 (CH_2), 79.8 (CH), 51.7 (C), 44.7 (CH_2), 43.4 (CH_2), 33.7 (CH_2), 15.7 (CH_3). IR (KBr): 3451, 3065, 2938, 1761, 1645, 1496, 1446, 1386, 1327, 1175, 1047, 1010, 964, 924, 759, 699, 646, 495 cm^{-1}. The enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column (Daicel Chiralpak AD-3, hexane/*i*-PrOH = 50/1, flow rate = 0.5 mL/min, λ = 217 nm: 16.1 min, 17.1 min) to be 48% ee. $[\alpha]_D^{16}$ −37.9 (*c* 0.28, $CHCl_3$).

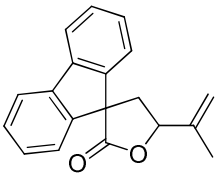


3,3-Dimethyl-5-(prop-1-en-2-yl)dihydrofuran-2(3*H*)-one (2c). A solution of $Pd(OAc)_2$ (1.1 mg, 0.005 mmol, 10 mol %) and (*P,R,R*)-*i*-Pr-SPRIX (2.8 mg, 0.0075 mmol, 15 mol %) in CH_2Cl_2 (0.25 mL) was stirred at 25 °C for 2 h. To this solution was added *p*-benzoquinone (10.8 mg, 0.10 mmol, 2 equiv) and **1c** (11.7 mg, 0.05 mmol) in CH_2Cl_2 (0.25 mL), and the mixture was stirred at 25 °C for 60 h. The reaction mixture was directly filtered through a short pad of silica gel, which was rinsed with EtOAc. The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 5/1, Rf 0.4) to afford **2c** (11.6 mg). >98% yield. Colorless liquid. HRMS (ESI): calcd for $C_9H_{14}NaO_2$: *m/z* 177.0891 ($[M+H]^+$), found: *m/z* 177.0883. ^1H NMR (400 MHz, $CDCl_3$): δ 5.09 (s, 1H), 4.94 (s, 1H), 4.82 (dd, 1H, *J* = 9.9 Hz, *J* = 6.5 Hz), 2.21 (dd, 1H, *J* = 12.6 Hz, *J* = 6.5 Hz), 1.92 (dd, 1H, *J* = 12.6 Hz, *J* = 9.9 Hz), 1.75 (s, 3H), 1.30 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 181.7 (C=O), 142.1 (C), 112.2 (CH_2), 78.9 (CH), 42.2 (CH_2), 40.4 (C), 25.0 (CH_3), 24.4 (CH_3), 17.4 (CH_3). IR (KBr): 2970, 2930, 1772, 1455, 1388, 1324, 1120, 1153, 1121, 1048, 996, 917, 503, 473, 440, 426, 414 cm^{-1}. The enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column (Daicel Chiralpak AD-3, hexane/*i*-PrOH = 50/1, flow rate = 0.5 mL/min, λ = 217 nm: 9.0 min, 9.7 min) to be 55% ee. $[\alpha]_D^{17}$ +2.4 (*c* 0.75, $CHCl_3$).

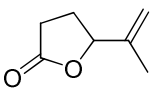


3-(Prop-1-en-2-yl)-2-oxaspiro-[4.5]decan-1-one (2d). A solution of $Pd(OAc)_2$ (1.1 mg, 0.005 mmol, 10 mol %) and (*P,R,R*)-*i*-Pr-SPRIX (2.8 mg, 0.0075 mmol, 15 mol %) in CH_2Cl_2 (0.25 mL) was stirred at 25 °C for 2 h. To this solution was added *p*-benzoquinone (10.8 mg, 0.10 mmol, 2 equiv) and **1d** (9.8 mg, 0.05 mmol) in CH_2Cl_2 (0.25 mL), and the mixture was stirred at 25 °C for 60 h. The reaction mixture was directly filtered through a short pad of silica gel, which was rinsed with EtOAc. The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 5/1, Rf 0.4) to afford **2d** (9.7 mg). >98% yield. White wax. HRMS (ESI): calcd for $C_{12}H_{18}NaO_2$: *m/z* 217.1204 ($[M+H]^+$), found: *m/z* 217.1196. ^1H NMR (400 MHz, $CDCl_3$): δ 5.08 (s, 1H), 4.93 (s, 1H), 4.80 (t, 1H, *J* = 9.2 Hz), 2.39 (dd, 1H, *J* =

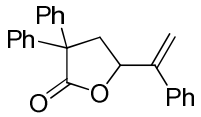
13.0 Hz, J = 6.8 Hz), 1.84–1.27 (m, 14H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 181.4 (C=O), 142.4 (C), 112.1 (CH_2), 79.3 (CH), 44.8 (CH_2), 38.2 (C), 34.1 (CH_2), 31.7 (CH_2), 25.3 (CH_2), 22.2 (CH_2), 22.2 (CH_2), 17.4 (CH_3). IR (KBr): 2933, 2858, 1766, 1656, 1450, 1377, 1326, 1282, 1264, 1191, 1164, 1135, 1109, 1095, 1063, 1034, 1005, 970, 939, 903, 467, 411, 404 cm^{-1}. The enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column (Daicel Chiralpak AD-3, hexane/*i*-PrOH = 50/1, flow rate = 0.5 mL/min, λ = 208 nm: 10.8 min, 11.4 min) to be 68% ee. $[\alpha]_D^{19}$ +6.3 (*c* 0.23, $CHCl_3$).



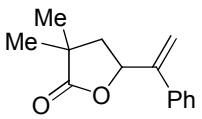
5'-(Prop-1-en-2-yl)-4',5'-dihydro-2'*H*-spiro[fluorene-9,3'-furan]-2'-one (2e). A solution of $Pd(OAc)_2$ (1.1 mg, 0.005 mmol, 10 mol %) and (*P,R,R*)-*i*-Pr-SPRIX (2.8 mg, 0.0075 mmol, 15 mol %) in CH_2Cl_2 (0.25 mL) was stirred at 25 °C for 2 h. To this solution was added *p*-benzoquinone (10.8 mg, 0.10 mmol, 2 equiv) and **1e** (13.9 mg, 0.05 mmol) in CH_2Cl_2 (0.25 mL), and the mixture was stirred at 25 °C for 60 h. The reaction mixture was directly filtered through a short pad of silica gel, which was rinsed with EtOAc. The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 5/1, Rf 0.5) to afford **2e** (13.8 mg). >98% yield. White wax. HRMS (ESI): calcd for $C_{19}H_{16}NaO_2$: *m/z* 299.1047 ($[M+H]^+$), found: *m/z* 299.1040. ^1H NMR (400 MHz, $CDCl_3$): δ 7.76 (m, 2H), 7.53–7.25 (m, 6H), 5.42 (t, 1H, J = 2.8 Hz), 5.29 (s, 1H), 5.10 (s, 1H), 2.81 (d, 2H, J = 8.0 Hz), 1.92 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 176.7 (C=O), 146.0 (C), 145.1 (C), 142.0 (C), 141.4 (C), 140.7 (C), 128.84 (CH), 128.79 (CH), 128.3 (CH), 128.0 (CH), 123.5 (CH), 122.8 (CH), 120.7 (CH), 120.4 (CH), 113.1 (CH_2), 80.3 (CH), 58.8 (C), 40.5 (CH_2), 17.4 (CH_3). IR (KBr): 3065, 2954, 2928, 1781, 1764, 1725, 1477, 1449, 1320, 1276, 1167, 1068, 1055, 1006, 970, 911, 769, 756, 733, 620, 423, 411 cm^{-1}. The enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column (Daicel Chiralpak AS-H, hexane/*i*-PrOH = 50/1, flow rate = 1.0 mL/min, λ = 267 nm: 59.8 min, 71.0 min) to be 78% ee. $[\alpha]_D^{17}$ −71.6 (*c* 0.34, $CHCl_3$).



5-(Prop-1-en-2-yl)dihydrofuran-2(3*H*)-one (2f). A solution of $Pd(OAc)_2$ (1.1 mg, 0.005 mmol, 10 mol %) and (*P,R,R*)-*i*-Pr-SPRIX (2.8 mg, 0.0075 mmol, 15 mol %) in CH_2Cl_2 (0.25 mL) was stirred at 25 °C for 2 h. To this solution was added *p*-benzoquinone (10.8 mg, 0.10 mmol, 2 equiv) and **1f** (6.4 mg, 0.05 mmol) in CH_2Cl_2 (0.25 mL), and the mixture was stirred at 25 °C for 60 h. The reaction mixture was directly filtered through a short pad of silica gel, which was rinsed with EtOAc. The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 5/1, Rf 0.3) to afford **2f** (6.3 mg). >98% yield. Colorless liquid. HRMS (ESI): calcd for $C_7H_{10}NaO_2$: *m/z* 149.0578 ($[M+H]^+$), found: *m/z* 149.0571. ^1H NMR (400 MHz, $CDCl_3$): δ 5.30 (s, 1H), 4.95 (s, 1H), 4.89 (t, 1H, J = 7.4 Hz), 2.58–2.54 (m, 2H), 2.41–2.36 (m, 1H), 2.07–2.02 (m, 1H), 1.77 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 177.0 (C=O), 142.0 (C), 112.4 (CH_2), 82.5 (CH), 28.5 (CH_2), 27.0 (CH_2), 17.5 (CH_3). IR (KBr): 2924, 1774, 1655, 1458, 1326, 1298, 1219, 1180, 1143, 1049, 1008, 980, 922, 683, 661, 522, 500, 194, 476, 467, 459, 451, 429, 414, 405 cm^{-1}. The enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column (Daicel Chiralpak AD-3, hexane/*i*-PrOH = 50/1, flow rate = 0.5 mL/min, λ = 211 nm: 16.3 min, 17.2 min) to be 18% ee.

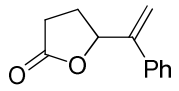


3,3-Diphenyl-5-(prop-1-en-2-yl)dihydrofuan-2(3*H*)-one (2g). A solution of $Pd(OAc)_2$ (1.1 mg, 0.005 mmol, 10 mol %) and (*P,R,R*)-*i*-Pr-SPRIX (2.8 mg, 0.0075 mmol, 15 mol %) in CH_2Cl_2 (0.25 mL) was stirred at 25 °C for 2 h. To this solution was added *p*-benzoquinone (10.8 mg, 0.10 mmol, 2 equiv) and **1g**(17.0 mg, 0.05 mmol) in CH_2Cl_2 (0.25 mL), and the mixture was stirred at 25 °C for 100 h. The reaction mixture was directly filtered through a short pad of silica gel, which was rinsed with EtOAc. The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 5/1, Rf 0.5) to afford **2g** (9.4 mg). 55% yield. Pale yellow solid. Mp: 142–144 °C. HRMS (ESI): calcd for $C_{24}H_{20}NaO_2$: *m/z* 360.1360 ($[M+H]^+$), found: *m/z* 363.1352. ^1H NMR (400 MHz, $CDCl_3$): δ 7.40–7.21 (m, 15H), 5.54 (s, 1H), 5.42 (s, 1H), 5.28 (dd, 1H, J = 10.2 Hz, J = 5.2 Hz), 3.14 (dd, 1H, J = 13.2 Hz, J = 5.2 Hz), 2.73 (dd, 1H, J = 13.2 Hz, J = 10.2 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 176.7 (C=O), 145.6 (C), 141.7 (C), 139.5 (C), 138.0 (C), 129.0 (CH), 128.7 (CH), 128.3 (CH), 128.2 (CH), 127.8 (CH), 127.7 (CH), 127.3 (CH), 127.2 (CH), 126.8 (CH), 114. 5 (CH_2), 77.4 (CH), 58.2 (C), 43.7 (CH_2). IR (KBr): 3058, 2927, 1770, 1727, 1599, 1495, 1447, 1324, 1285, 1054, 1021, 962, 911, 779, 768, 754, 725, 697, 670, 651, 613, 407 cm^{-1}. The enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column (Daicel Chiralpak AD-3, hexane/*i*-PrOH = 50/1, flow rate = 0.5 mL/min, λ = 221 nm: 23.4 min, 25.9 min) to be 67% ee. $[\alpha]_D^{19}$ −63.0 (*c* 0.33, $CHCl_3$).

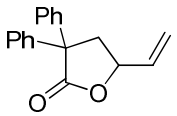


3,3-Dimethyl-5-(1-phenylvinyl)-dihydrofuran-2(3*H*)-one (2h). A solution of $Pd(OAc)_2$ (1.1 mg, 0.005 mmol, 10 mol %) and (*P,R,R*)-*i*-Pr-SPRIX (2.8 mg, 0.0075 mmol, 15 mol %) in CH_2Cl_2 (0.25 mL) was stirred at 25 °C for 2 h. To this solution was added *p*-benzoquinone (10.8 mg, 0.10 mmol, 2 equiv) and **1h** (10.9 mg, 0.05 mmol) in CH_2Cl_2 (0.25 mL), and the mixture was stirred at 25 °C for 100 h. The reaction mixture was directly filtered through a short pad of silica gel, which was rinsed with EtOAc. The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 5/1, Rf 0.4) to afford **2h** (5.9 mg). 55%

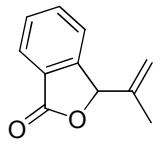
yield. Colorless liquid. HRMS (ESI): calcd for $C_{14}H_{16}NaO_2$: *m/z* 239.1047 ($[M+H]^+$), found: *m/z* 239.1040. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38–7.31 (m, 5H), 5.48 (s, 1H), 5.39 (s, 1H), 5.36 (dd, 1H, *J* = 9.1 Hz, *J* = 6.8 Hz), 2.26 (dd, 1H, *J* = 12.9 Hz, *J* = 6.8 Hz), 1.87 (dd, 1H, *J* = 12.9 Hz, *J* = 9.1 Hz), 1.31 (s, 3H), 1.24 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 181.7 (C=O), 146.6 (C), 138.1 (C), 128.6 (CH), 128.2 (CH), 126.8 (CH), 113.4 (CH_2), 77.0 (CH), 43.2 (CH_2), 40.2 (C), 25.1 (CH_3), 24.8 (CH_3). IR (KBr): 2969, 2930, 1772, 1496, 1457, 1388, 1326, 1250, 1228, 1201, 1153, 1122, 1039, 1006, 908, 779, 699, 607, 524, 513, 483, 474, 454, 436, 420 cm^{-1}. The enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 50/1, flow rate = 0.5 mL/min, λ = 234 nm: 22.8min, 24.5 min) to be 37% ee. $[\alpha]_D^{20}$ +18.8 (*c* 0.15, $CHCl_3$).



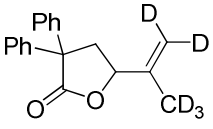
5-(1-Phenylvinyl)dihydrofuran-2(3*H*)-one (2i). A solution of $Pd(OAc)_2$ (1.1 mg, 0.005 mmol, 10 mol %) and (*P,R,R*)-*i*-Pr-SPRIX (2.8 mg, 0.0075 mmol, 15 mol %) in CH_2Cl_2 (0.25 mL) was stirred at 25 °C for 2 h. To this solution was added *p*-benzoquinone (10.8 mg, 0.10 mmol, 2 equiv) and **1i** (9.5 mg, 0.05 mmol) in CH_2Cl_2 (0.25 mL), and the mixture was stirred at 25 °C for 105 h. The reaction mixture was directly filtered through a short pad of silica gel, which was rinsed with EtOAc. The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 5/1, Rf 0.4) to afford **2i** (5.2 mg). 56% yield. Colorless liquid. HRMS (ESI): calcd for $C_{12}H_{12}NaO_2$: *m/z* 211.0734 ($[M+H]^+$), found: *m/z* 211.0726. ^{1}H NMR (400 MHz, CD_3OD): δ 7.32–7.22 (m, 5H), 5.47 (t, 1H, *J* = 7.1 Hz), 5.31 (s, 1H), 5.27 (s, 1H), 2.52–2.35 (m, 3H), 1.87–1.82 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, CD_3OD): δ 180.6 (C=O), 149.4 (C), 140.3 (C), 130.5 (CH), 130.1 (CH), 128.7 (CH), 114.1 (CH_2), 83.0 (CH), 29.83 (CH_2), 29.80 (CH_2). IR (KBr): 2958, 2926, 2855, 1784, 1728, 1461, 1262, 1178, 1122, 1098, 1073, 1039, 1028, 803, 472, 451, 412, 401 cm^{-1}. The enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column (Daicel Chiralpak AD-3, hexane/*i*-PrOH = 50/1, flow rate = 0.5 mL/min, λ = 236 nm: 25.8 min, 27.2min) to be 41% ee. $[\alpha]_D^{18}$ +3.3 (*c* 0.15, $CHCl_3$).



3,3-Diphenyl-5-vinyldihydrofuran-2(3*H*)-one (2j). A solution of $Pd(OAc)_2$ (1.1 mg, 0.005 mmol, 10 mol %) and (*P,R,R*)-*i*-Pr-SPRIX (2.8 mg, 0.0075 mmol, 15 mol %) in CH_2Cl_2 (0.25 mL) was stirred at 25 °C for 2 h. To this solution was added *p*-benzoquinone (10.8 mg, 0.10 mmol, 2 equiv) and **1j** (13.3 mg, 0.05 mmol) in CH_2Cl_2 (0.25 mL), and the mixture was stirred at 25 °C for 60 h. The reaction mixture was directly filtered through a short pad of silica gel, which was rinsed with EtOAc. The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 5/1, Rf 0.4) to afford **2j** (13.2 mg). >98% yield. Pale yellow wax. HRMS (ESI): calcd for $C_{18}H_{16}NaO_2$: *m/z* 287.1047 ($[M+H]^+$), found: *m/z* 287.1047. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.23 (m, 10H), 5.92 (m, 1H), 5.40 (d, 1H, *J* = 16.8 Hz), 5.30 (d, 1H, *J* = 10.7 Hz), 4.77 (m, 1H), 3.11 (dd, 1H, *J* = 13.0 Hz, *J* = 5.1 Hz), 2.75 (dd, 1H, *J* = 13.0 Hz, *J* = 10.5 Hz). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 176.8 (C=O), 141.7 (C), 139.6 (C), 134.9 (C), 129.0 (CH), 128.4 (CH), 127.8 (CH), 127.7 (CH), 127.3 (CH), 127.3 (CH), 118.9 (CH_2), 77.5 (CH), 58.1 (C), 43.8 (CH_2). IR (KBr): 3061, 3056, 2921, 1771, 1495, 1447, 1167, 697, 505, 458, 447, 441 cm^{-1}. The enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 50/1, flow rate = 0.5 mL/min, λ = 219 nm: 22.1 min, 28.6 min) to be 15% ee. $[\alpha]_D^{19}$ +38.6 (*c* 0.55, $CHCl_3$).

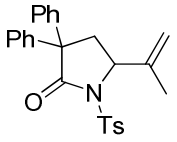


3-(Prop-1-en-2-yl)isobenzofuran-1(3*H*)-one (2l). A solution of $Pd(OAc)_2$ (1.1 mg, 0.005 mmol, 10 mol %) and (*P,R,R*)-*i*-Pr-SPRIX (2.8 mg, 0.0075 mmol, 15 mol %) in CH_2Cl_2 (0.25 mL) was stirred at 25 °C for 2 h. To this solution was added *p*-benzoquinone (10.8 mg, 0.10 mmol, 2 equiv) and **1h** (8.8 mg, 0.05 mmol) in CH_2Cl_2 (0.25 mL), and the mixture was stirred at 35 °C for 60 h. The reaction mixture was directly filtered through a short pad of silica gel, which was rinsed with EtOAc. The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 5/1, Rf 0.4) to afford **2h** (10.8 mg). >98% yield. White wax. HRMS (ESI): calcd for $C_{11}H_{10}NaO_2$: *m/z* 197.0578 ($[M+H]^+$), found: *m/z* 197.0572. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, 1H, *J* = 7.6 Hz), 7.68 (t, 1H, *J* = 7.6 Hz), 7.55 (t, 1H, *J* = 7.6 Hz), 7.40 (d, 1H, *J* = 7.6 Hz), 5.85 (s, 1H), 5.32 (s, 1H), 5.17 (s, 1H), 1.51 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 170.5 (C=O), 148.3 (C), 140.7 (C), 134.1 (CH), 129.4 (CH), 126.2 (C), 125.6 (CH), 122.3 (CH), 116.8 (CH_2), 85.0 (CH), 16.0 (CH_3). IR (KBr): 2979, 2799, 2157, 1943, 1749, 1716, 1506, 1327, 1087, 871, 669, 641, 499, 482, 456, 440 cm^{-1}. The enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column (Daicel Chiralpak AS-H, hexane/*i*-PrOH = 50/1, flow rate = 1.0 mL/min, λ = 227 nm: 30.9 min, 40.3 min) to be 40% ee. $[\alpha]_D^{17}$ +9.0 (*c* 0.18, $CHCl_3$).

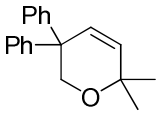


3,3-Diphenyl-5-(prop-1-en-2-yl)dihydrofuran-2(3*H*)-one-d_5 (2a-*d*). A solution of $Pd(OAc)_2$ (1.1 mg, 0.005 mmol, 10 mol %) and (*P,R,R*)-*i*-Pr-SPRIX (2.8 mg, 0.0075 mmol, 15 mol %) in CH_2Cl_2 (0.25 mL) was stirred at 25 °C for 2 h. To this solution was added *p*-benzoquinone (10.8 mg, 0.10 mmol, 2 equiv) and **1a-*d*** (14.7 mg, 0.05 mmol) in CH_2Cl_2 (0.25 mL), and the mixture was stirred at 25 °C for 60 h. The reaction mixture was directly filtered through a short pad of silica gel, which was rinsed with EtOAc. The filtrate was concentrated under reduced pressure and the residue was

purified by flash column chromatography on silica gel (hexane/EtOAc = 5/1, Rf 0.4) to afford **2a-*d*** (14.2 mg). >98% yield. Pale yellow wax. HRMS (ESI): calcd for $C_{19}H_{13}D_5NaO_2$: *m/z* 306.1518 ($[M+H]^+$), found: *m/z* 306.1507. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.24 (m, 10H), 4.74 (dd, 1H, *J* = 11.0 Hz, *J* = 5.0 Hz), 3.06 (dd, 1H, *J* = 12.9 Hz, *J* = 5.0 Hz), 2.78 (dd, 1H, *J* = 12.9 Hz, *J* = 11.0 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 176.9 (C=O), 141.9 (C), 141.0 (C), 139.5 (C), 129.0 (CH), 128.4 (CH), 127.8 (CH), 127.7 (CH), 127.4 (CH), 127.2 (CH), 79.2 (CH), 58.3 (C), 42.5 (CH_2) (signals of the deuterated carbons could not be detected). IR (KBr): 2958, 2925, 2872, 1766, 1496, 1457, 1447, 1321, 1278, 1172, 964, 766, 750, 698, 605, 562, 544, 524, 490, 466, 453, 446, 429, 415 cm^{-1}.



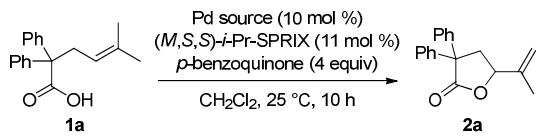
3,3-Diphenyl-5-(prop-1-en-2-yl)-1-tosylpyrrolidin-2-one (5). A solution of $Pd(OAc)_2$ (1.1 mg, 0.005 mmol, 10 mol %) and (*M,S,S*)-*i*-Pr-SPRIX (2.8 mg, 0.0075 mmol, 15 mol %) in CH_2Cl_2 (0.25 mL) was stirred at 25 °C for 2 h. To this solution was added *p*-benzoquinone (10.8 mg, 0.10 mmol, 2 equiv) and **4** (21.7mg, 0.05 mmol) in CH_2Cl_2 (0.25 mL), and the mixture was stirred at 35 °C for 48 h. The reaction mixture was directly filtered through a short pad of silica gel, which was rinsed with EtOAc. The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 5/1, Rf 0.4) to afford **5** (19.8 mg). 92% yield. Light yellow needle. Mp: 140–142 °C. HRMS (ESI): calcd for $C_{26}H_{25}NNaO_3S$: *m/z* 454.1542 ($[M+H]^+$), found: *m/z* 454.1442. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, 2H, *J* = 7.8 Hz), 7.25–7.10 (m, 10H), 6.96 (d, 2H, *J* = 7.8 Hz), 5.05 (s, 3H), 4.98 (s, 3H), 4.54 (dd, 1H, *J* = 9.1 Hz, *J* = 6.6 Hz), 2.95 (dd, 1H, *J* = 13.6 Hz, *J* = 6.6 Hz), 2.54 (dd, 1H, J = 13.6 Hz, *J* = 9.1 Hz), 2.41 (s, 3H), 1.84 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 174.6 (C=O), 144.9 (C), 143.5 (C), 141.9 (C), 139.1 (C), 134.3 (C), 129.1 (CH), 128.7 (CH), 128.5 (CH), 128.3 (CH), 127.8 (CH), 127.4 (CH), 127.3 (CH), 127.1 (CH), 113.6 (CH_2), 62.5 (CH), 58.0 (C), 40.1 (CH_2), 21.7 (CH_3), 17.5 (CH_3). IR (KBr): 3439, 2974, 2929, 1733, 1612, 1599, 1496, 1447, 1365, 1186, 1173, 1090, 645, 634, 622, 608 cm^{-1}.



6,6-Dimethyl-3,3-diphenyl-3,6-dihydro-2*H*-pyran (8). A solution of $Pd(OAc)_2$ (1.1 mg, 0.005 mmol, 10 mol %) and (*M,S,S*)-*i*-Pr-SPRIX (2.8 mg, 0.0075 mmol, 15 mol %) in CH_2Cl_2 (0.25 mL) was stirred at 25 °C for 2 h. To this solution was added *p*-benzoquinone (10.8 mg, 0.10 mmol, 2 equiv) and **6** (13.3 mg, 0.05 mmol) in CH_2Cl_2 (0.25 mL), and the mixture was stirred at 25 °C for 60 h. The reaction mixture was directly filtered through a short pad of silica gel, which was rinsed with EtOAc. The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 5/1, Rf 0.55) to afford **8** (7.9 mg). 95% yield. Colorless liquid. HRMS (ESI): calcd for $C_{19}H_{20}NaO_2$: *m/z* 287.1411 ($[M+H]^+$), found: *m/z* 287.1402. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32–7.16 (m, 10H), 6.18 (d, 1H, *J* = 8.0 Hz), 5.79 (d, 1H, *J* = 8.0 Hz), 4.15 (s, 2H), 1.27 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 146.0 (C), 134.0 (CH), 130.6 (CH), 128.2 (CH), 127.9 (CH) 126.2 (CH), 71.9 (C), 69.8 (CH_2), 47.6 (C), 26.9 (CH_3). IR (KBr): 2972, 2929, 2362, 1493, 1446, 1372, 1359, 1223, 1173, 1156, 1083, 1028, 1003, 789, 746, 716, 699, 500, 490, 474, 467, 438, 428, 418, 406 cm^{-1}.

Optimization of reaction conditions.

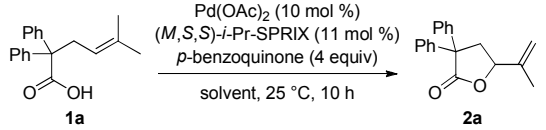
Table S1. Effect of Pd Source[a]



entry	Pd source	conv. (%)[b]	yield (%)[b]	ee (%)[c]
1	$Pd(OAc)_2$	100	>99	70
2	$Pd(hfacac)_2$	100	>99	8
3[d]	$Pd(OCOCF_3)_2$	47	28	18
4[d]	$[Pd(MeCN)_4](BF_4)_2$	46	11	2
5[d]	$PdCl_2(MeCN)_2$	1	0	—

[a] All reaction were carried out in the presence of 10 mol % of Pd, 11 mol % of (*M,S,S*)-*i*-Pr-SPRIX, and 4 equiv of *p*-benzoquinone at 25 °C for 10 h in CH_2Cl_2 (0.1 M) under a nitrogen atmosphere. [b] Determined by ^1H NMR. [c] Determined by HPLC analysis (Daicel Chiralpak AD-H). [d] 24 h. hfacac = hexafluoroacetylacetonato

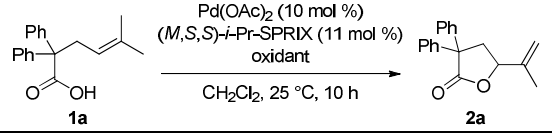
Table S2. Solvent Screening[a]



entry	solvent	conv. (%)[b]	yield (%)[b]	ee (%)[c]
1	CH_2Cl_2	100	>99	70
2	MeOH	100	93	*rac*
3	toluene	59	48	54
4	THF	22	21	*rac*
5	AcOH	23	11	–14
6	DMSO	7	7	31

[a] All reaction were carried out in the presence of 10 mol % of $Pd(OAc)_2$, 11 mol % of (*M,S,S*)-*i*-Pr-SPRIX, and 4 equiv of *p*-benzoquinone at 25 °C for 10 h in solvent (0.1 M) under a nitrogen atmosphere. [b] Determined by ^1H NMR. [c] Determined by HPLC analysis (Daicel Chiralpak AD-H).

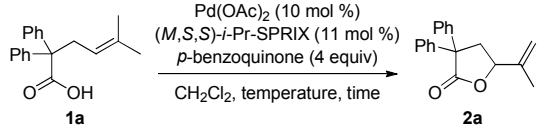
Table S3. Effect of Oxidant[a]



entry	oxidant	conv. (%)[b]	yield (%)[b]	ee (%)[c]
1	*p*-benzoquinone[d]	100	>99	70
2[e]	$PhI(OAc)_2$[f]	100	75	38
3[e]	$CuCl_2$, O_2[g]	23	2	37

[a] All reaction were carried out in the presence of 10 mol % of $Pd(OAc)_2$, 11 mol % of (*M,S,S*)-*i*-Pr-SPRIX, and oxidant at 25 °C for 10 h in CH_2Cl_2 (0.1 M) under a nitrogen atmosphere. [b] Determined by ^1H NMR. [c] Determined by HPLC analysis (Daicel Chiralpak AD-H). [d] 4 equiv. [e] 24 h. [f] 2 equiv. [g] 20 mol % of $CuCl_2$ under an oxygen atmosphere .

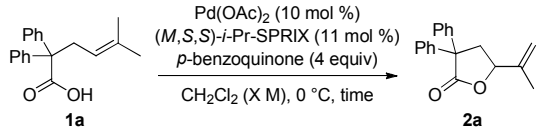
Table S4. Effect of Temperature[a]



entry	temperature (°C)	time (h)	yield (%)[b]	ee (%)[c]
1	25	10	>99	70
2	15	20	>99	73
3	0	48	>99	78
4	–20	216	90	80
5[d]	–40	120	15	59

[a] All reaction were carried out in the presence of 10 mol % of $Pd(OAc)_2$, 11 mol % of (*M,S,S*)-*i*-Pr-SPRIX, and 4 equiv of *p*-benzoquinone in CH_2Cl_2 (0.1 M) under a nitrogen atmosphere. [b] Determined by ^1H NMR. [c] Determined by HPLC analysis (Daicel Chiralpak AD-H). [d] Carried out in CH_2Cl_2 (0.3 M) using 20 mol % of $Pd(OAc)_2$ and 22 mol % of (*M,S,S*)-*i*-Pr-SPRIX.

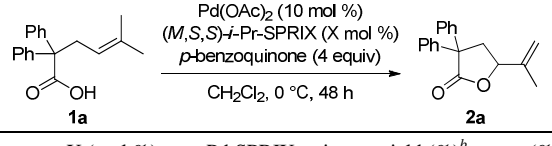
Table S5. Effect of Concentration[a]



entry	X (M)	time (h)	yield (%)[b]	ee (%)[c]
1	0.1	48	>99	78
2	0.2	36	>99	76
3	0.3	28	>99	74

[a] All reaction were carried out in the presence of 10 mol % of $Pd(OAc)_2$, 11 mol % of (*M,S,S*)-*i*-Pr-SPRIX, and 4 equiv of *p*-benzoquinone at 0 °C in CH_2Cl_2 under a nitrogen atmosphere. [b] Determined by ^1H NMR. [c] Determined by HPLC analysis (Daicel Chiralpak AD-H).

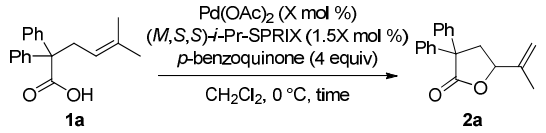
Table S6. Effect of Ratio of SPRIX Ligand to Pd[a]



entry	X (mol %)	Pd:SPRIX ratio	yield (%)[b]	ee (%)[c]
1	11	1 : 1.1	>99	78
2[d]	15	1 : 1.5	>99	83
3[d]	20	1 : 2	>99	79

[a] All reaction were carried out in the presence of 10 mol % of $Pd(OAc)_2$, the indicated amount of (*M,S,S*)-*i*-Pr-SPRIX, and 4 equiv of *p*-benzoquinone at 0 °C for 48 h in CH_2Cl_2 (0.1 M) under a nitrogen atmosphere. [b] Determined by ^1H NMR. [c] Determined by HPLC analysis (Daicel Chiralpak AD-H). [d] 60 h.

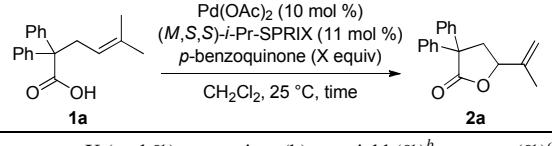
Table S7. Effect of Catalyst Loading[a]



entry	X (mol %)	time (h)	yield (%)[b]	ee (%)[c]
1	5	168	92	60
2	10	60	>99	83
3	20	30	>99	81

[a] All reaction were carried out in the presence of X mol % of $Pd(OAc)_2$, 1.5X mol % of (*M,S,S*)-*i*-Pr-SPRIX, and 4 equiv of *p*-benzoquinone at 0 °C in CH_2Cl_2 (0.1 M) under a nitrogen atmosphere. [b] Determined by ^1H NMR. [c] Determined by HPLC analysis (Daicel Chiralpak AD-H).

Table S8. Effect of Amount of *p*-Benzoquinone[a]



entry	X (mol %)	time (h)	yield (%)[b]	ee (%)[c]
1	1.1	10	>99	70
2	2	10	>99	76
3	4	10	>99	70
4	8	12	>99	70

[a] All reaction were carried out in the presence of 10 mol % of $Pd(OAc)_2$, 11 mol % of (*M,S,S*)-*i*-Pr-SPRIX, and the indicated amount of *p*-benzoquinone at 25 °C in CH_2Cl_2 (0.1 M) under a nitrogen atmosphere. [b] Determined by ^1H NMR. [c] Determined by HPLC analysis (Daicel Chiralpak AD-H).

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