Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Double γ-alkylation of allylic phosphorus ylides: a unique access to oxa-bicyclic[3.3.0] diene skeletons

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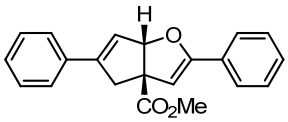
1. General Information All reactions were carried out under N_2 unless otherwise noted. All carbonyl compounds and solvents were purified according to standard methods unless otherwise noted. Cs_2CO_3 was purchased from Alfa Aesar, the purity of this reagent is 99.9% (metals basis).

^{1}H NMR spectra were recorded on a VARIAN Mercury 300 MHz or VARIAN Mercury 400 MHz spectrometer in chloroform-d. All signals are reported in ppm with the internal TMS signal at 0.0 ppm or chloroform signal at 7.26 ppm as a standard. The data are reported as (s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet or unresolved, coupling constant(s) in Hz, integration). ^{13}C NMR spectra were recorded on a VARIAN Mercury 75.5 MHz spectrometer in chloroform-d. All signals are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard. IR spectra were recorded on a Perkin–Elmer 983, Digital FT–IR spectrometer or Bruker–Tensor 27; frequencies are given in reciprocal centimeters (cm^{-1}) and only selected absorbance is reported; Mass spectra were determined on an Agilent 5973N MSD (EI) and Shimadzu LCMS-2010EV (ESI) mass spectrometer or Agilent G6100 LC/MSD (ESI) single Quand mass spectrometer. High resolution mass spectra were recorded on Waters Micromass GCT Premier (EI) and Bruker Daltonics, Inc. APEXIII 7.0 TESLA FTMS (ESI) mass spectrometers. Melting points (uncorrected) were determined with capillary melting point apparatus.

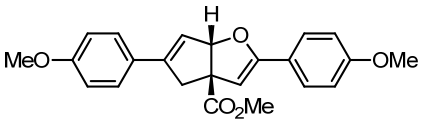
2. General procedure for synthesis of oxa-bicyclic[3.3.0] diene skeletons

In a Schlenk tube, to a stirred solution of phosphonium salt **1a** (176.4 mg, 0.4 mmol), $RCOCH_2Br$ (1.0 mmol) in dry CH_3CN (4.0 mL) under N_2 at room temperature was added Cs_2CO_3 (522.0 mg, 1.6 mmol) and dry CH_3CN (4.0 mL) to rinse the Schlenk tube. After the reaction was complete, the resulting mixture was filtered rapidly through a funnel with a thin layer of silica gel and eluted with DCM or EA. The filtrate was concentrated and the residue was purified by chromatography on silica gel to afford the desired products.



3a

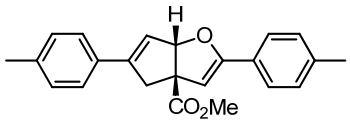
121.0 mg, 95% yield, white solid, mp 131-132 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.59-7.57 (m, 2H), 7.47-7.45 (m, 2H), 7.36-7.27 (m, 6H), 6.22 (dd, *J* = 2.0, 4.0 Hz, 1H), 6.14 (t, *J* = 1.6 Hz, 1H), 5.44 (s, 1H), 3.80 (s, 3H), 3.36 (dd, *J* =1.8, 16.6 Hz, 1H), 3.15 (dt, *J* = 1.8, 16.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 174.8, 155.5, 144.3, 134.5, 130.3, 128.8, 128.43, 128.41, 128.2, 126.2, 125.5, 122.8, 99.2, 93.1, 62.2, 52.5, 44.4; IR (neat) ν 1730 (s), 1237 (s), 1061 (s), 754 (s), 730 (s), 688 (s); MS (EI, m/z, rel. intensity) 318 (4.7, M^+), 286 (8.8), 258 (10.7), 241 (1.4), 229 (2.8), 212 (36.3), 181 (10.7), 153 (10.4), 128 (3.2), 115 (7.3), 105 (100), 91 (3.4), 77 (23.5), 59 (4.7), 51 (4.6); HRMS (EI) calcd for $C_{21}H_{18}O_3$ (M^+): 318.1256; Found: 318.1252.



3b

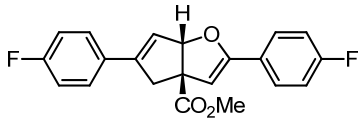
134.7 mg, 89% yield, white solid, mp 94-95 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.50 (d, *J* = 8.8 Hz, 2H), 7.38 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 6.8 Hz, 4H), 6.11 (s, 1H), 6.08 (s, 1H), 5.29 (s, 1H), 3.77 (s, 9H), 3.30 (d, *J* = 16.8 Hz, 1H), 3.09 (d, *J* = 16.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 175.0, 160.0, 159.7, 155.2, 143.7, 127.5, 127.2, 126.9, 123.0, 120.8, 113.7, 113.5, 97.4, 93.2, 62.1, 55.1, 52.3, 44.5; IR (neat) ν 2952 (m), 1727 (s), 1605 (m), 1510 (s), 1248 (s), 1174 (s), 1031 (m), 834 (m), 789 (m), 736 (m); MS (EI, m/z, rel. intensity) 380 (2.3, M^+), 349 (3.3), 320 (0.7), 281 (2.4), 230 (100), 215 (2.6), 198 (7.8), 187 (4.0), 171 (26.7), 150 (7.1), 135 (39.8), 115 (5.8), 107 (6.1), 92 (7.8),

77 (9.2), 64 (1.3), 51 (0.7); HRMS (EI) calcd for $C_{23}H_{22}O_5$ (M^+): 378.1467; Found: 378.1466.



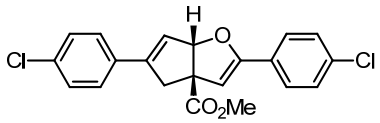
3c

131.6 mg, 95% yield, white solid, mp 72-73 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 7.6 Hz, 2H), 7.14-7.12 (m, 4H), 6.15 (s, 1H), 6.11 (s, 1H), 5.36 (s, 1H), 3.78 (s, 9H), 3.32 (d, *J* = 16.8 Hz, 1H), 3.11 (d, *J* = 16.0 Hz, 1H), 2.33 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 175.0, 155.6, 144.2, 138.8, 138.4, 131.8, 129.1, 128.9, 127.6, 126.2, 125.5, 122.0, 98.5, 93.1, 62.2, 52.4, 44.5, 21.3, 21.2; IR (neat) ν 2922 (m), 1732 (s), 1240 (m), 1062 (m), 949 (m), 789 (m), 738 (m); MS (EI, m/z, rel. intensity) 346 (2.5, M^+), 314 (3.7), 286 (3.6), 271 (0.83), 226 (13.6), 195 (3.0), 167 (3.7), 152 (4.3), 128 (3.3), 119 (100), 105 (1.6), 91 (14.6), 77 (0.55), 65 (2.1), 51 (0.39); HRMS (EI) calcd for $C_{23}H_{22}O_3$ (M^+): 346.1569; Found: 346.1566.



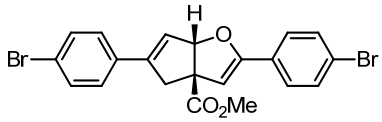
3d

136.1 mg, 96% yield, white paste, ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.57-7.54 (m, 2H), 7.44-7.41 (m, 2H), 7.04-6.99 (m, 4H), 6.14-6.12 (m, 2H), 5.37 (s, 1H), 3.80 (s, 3H), 3.33 (dd, *J* = 1.6, 16.4 Hz, 1H), 3.10 (dt, *J* = 1.6, 16.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 174.6, 164.5 (d, *J* = 17.9 Hz, 1C), 161.2 (d, *J* = 18.4 Hz, 1C), 154.6, 143.3, 130.7 (d, *J* = 3.4 Hz, 1C), 128.0 (d, *J* = 8.2 Hz, 1C), 127.4 (d, *J* = 8.3 Hz, 1C), 126.5 (d, *J* = 2.5 Hz, 1C), 122.5 (d, *J* = 2.0 Hz, 1C), 115.4 (d, *J* = 11.8 Hz, 1C), 115.1 (d, *J* = 11.4 Hz, 1C), 98.8 (d, *J* = 1.5 Hz, 1C), 93.2, 62.2, 52.5, 44.5; ^{19}F NMR ($CDCl_3$, 282 MHz) δ -112.2 - -112.3 (m. 1F), -113.0 - -113.1 (m, 1F); IR (neat) ν 2958 (m), 1731 (s), 1509 (s), 1231 (m), 1062 (m), 840 (m), 743 (m); MS (EI, m/z, rel. intensity) 354 (2.9, M^+), 322 (6.1), 294 (6.7), 265 (1.7), 251 (1.7), 230 (13.8), 199 (3.8), 171 (4.5), 152 (2.5), 133 (4.9), 123 (100), 109 (2.7), 95 (22.5), 75 (3.1), 65 (2.1), 59 (3.0); HRMS (EI) calcd for $C_{21}H_{16}F_2O_3$ (M^+): 354.1068; Found: 354.1069.



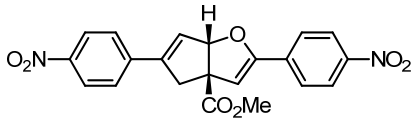
3e

151.8 mg, 98% yield, white solid, mp 126-127 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.52-7.48 (m, 2H), 7.39-7.36 (m, 2H), 7.32-7.29 (m, 4H), 6.18 (dd, *J* = 2.0, 4.0 Hz, 1H), 6.11 (t, *J* = 1.6 Hz, 1H), 5.42 (s, 1H), 3.80 (s, 3H), 3.32 (dd, *J* = 2.0, 16.8 Hz, 1H), 3.10 (dt, *J* = 2.0, 16.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 174.4, 154.6, 143.3, 134.7, 134.3, 132.9, 128.7, 128.6, 128.4, 127.5, 126.9, 123.3, 99.6, 93.2, 62.2, 52.6, 44.4; IR (neat) ν 2953 (m), 1729 (s), 1490 (m), 1196 (s), 1089 (m), 1058 (m), 1010 (s), 938 (m), 833 (m), 812 (s) 788 (m); MS (EI, m/z, rel. intensity) 386 (2.6, M^+), 354 (6.3), 327 (5.8), 291 (3.4), 264 (2.8), 246 (25.7), 228 (7.2), 215 (7.1), 203 (1.7), 188 (4.1), 167 (5.0), 152 (19.8), 141 (33.3), 139 (100), 113 (12.2), 111 (20.1), 101 (4.6), 89 (1.0), 75 (7.2), 59 (8.7), 51 (2.2); HRMS (EI) calcd for $C_{21}H_{16}Cl_2O_3$ (M^+): 386.0476; Found: 386.0480.



3f

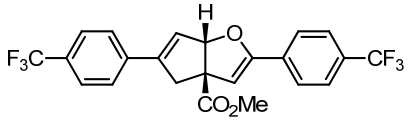
181.0 mg, 95% yield, white solid, mp 93-94 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.44-7.40 (m, 6H), 7.28 (d, *J* = 8.1 Hz, 2H), 6.18 (d, *J* = 0.9 Hz, 1H), 6.11 (s, 1H), 5.43 (s, 1H), 3.79 (s, 3H), 3.31 (d, *J* = 16.5 Hz, 1H), 3.08 (d, *J* = 16.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 174.3, 154.6, 143.3, 133.3, 131.5, 131.3, 129.1, 127.8, 127.1, 123.4, 122.9, 122.5, 99.7, 93.1, 62.2, 52.5, 44.2; IR (neat) ν 2950 (m), 1728 (s), 1487 (m), 1238 (m), 1060 (s), 1007 (s), 947 (m), 810 (m) 789 (m), 734 (s), 704 (m); MS (EI, m/z, rel. intensity) 476 (5.2, M^+), 444 (13.0), 416 (9.8), 399 (0.19), 335 (4.0), 308 (6.2), 292 (34.9), 259 (6.1), 228 (14.8), 212 (2.0), 183 (100), 168 (30.9), 152 (52.7), 128 (12.9), 114 (33.2), 101 (15.9), 88 (2.6), 76 (14.1), 59 (13.1), 50 (3.9); HRMS (EI) calcd for $C_{21}H_{16}Br_2O_3$ (M^+): 473.9466; Found: 473.9471.



3g

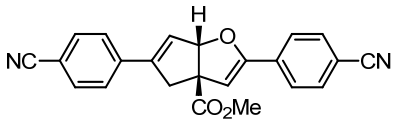
112.7 mg, 69% yield, light yellow solid, mp 174-175 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.23-8.19 (m, 4H), 7.73 (d, *J* = 8.7 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 6.40 (d, *J* = 1.5 Hz, 1H), 6.20 (s, 1H),

5.68 (s, 1H), 3.84 (s, 3H), 3.44 (d, J = 16.5 Hz, 1H), 3.20 (d, J = 16.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 173.6, 153.8, 147.6, 147.4, 142.8, 140.4, 136.0, 127.0, 126.8, 126.3, 123.8, 123.5, 103.1, 93.2, 62.4, 52.8, 44.2; IR (neat) ν 2955 (m), 1727 (s), 1595 (m), 1510 (s), 1341 (s), 1264 (m), 1060 (m), 1011 (m), 955 (m), 850 (m) 735 (s); MS (EI, m/z, rel. intensity) 408 (8.1, M^+), 376 (33.1), 348 (21.2), 302 (6.7), 281 (5.4), 258 (28.6), 242 (25.6), 226 (31.1), 215 (6.4), 207 (11.2), 183 (17.6), 168 (20.5), 151 (100), 134 (31.6), 120 (23.6), 104 (46.3), 92 (17.4), 76 (24.1), 59 (38.8), 50 (4.6); HRMS (EI) calcd for $C_{21}H_{16}N_2O_7$ (M^+): 408.0958; Found: 408.0954.



3h

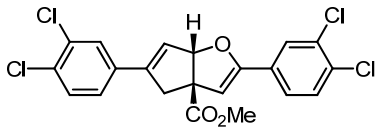
156.3 mg, 86% yield, colorless liquid, ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.69-7.67 (m, 2H), 7.60-7.54 (m, 6H), 6.30 (d, J = 1.6 Hz, 1H), 6.18 (s, 1H), 5.57 (s, 1H), 3.82 (s, 3H), 3.39 (dd, J = 1.6, 16.4 Hz, 1H), 3.16 (d, J = 16.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 174.2, 154.4, 143.3, 137.8 (q, J = 1.7 Hz, 1C), 133.5 (q, J = 1.2 Hz, 1C), 130.6 (q, J = 32.4 Hz, 1C), 130.3, 126.5, 125.8, 125.4 (q, J = 36.3 Hz, 1C), 125.33 (q, J = 180.1 Hz, 1C), 125.30 (q, J = 180.3 Hz, 1C), 125.2 (q, J = 38.3 Hz, 1C), 125.0, 110.3, 93.1, 62.3, 52.6, 44.2 ; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -62.72 (s, 3F), -62.75 (s, 3F); IR (neat) ν 2956 (m), 1731 (s), 1320 (s), 1241 (m), 1163 (m), 1108 (s), 1064 (s), 1013 (m), 952 (m), 846 (m), 727 (m); MS (EI, m/z, rel. intensity) 454 (5.7, M^+), 435 (8.4), 422 (15.6), 394 (20.8), 367 (1.5), 347 (1.7), 327 (6.2), 297 (5.2), 280 (53.1), 249 (21.1), 237 (4.1), 222 (5.0), 197 (13.2), 183 (4.8), 173 (100), 154 (2.2), 145 (44.5), 125 (5.8), 95 (7.7), 75 (3.0), 59 (18.0), 51 (1.2); HRMS (EI) calcd for $C_{23}H_{16}F_6O_3$ (M^+): 454.1004; Found: 454.1006.



3i

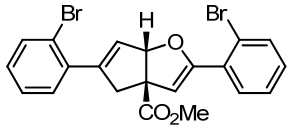
95.8 mg, 65% yield, white solid, mp 163-164 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.67-7.60 (m, 6H), 7.56-7.53 (m, 2H), 6.34 (d, J = 1.6 Hz, 1H), 6.18 (s, 1H), 5.62 (s, 1H), 3.83 (s, 3H), 3.39 (dd, J = 1.4, 16.6 Hz, 1H), 3.16 (dt, J = 1.6, 16.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.7, 153.9, 143.0, 138.5, 134.1, 132.2, 132.0, 126.7, 126.0, 118.47, 118.44, 112.1, 111.8, 102.3, 93.0, 62.2, 52.7, 44.0; IR (neat) ν 2953 (m), 2226 (m), 1729 (s), 1606 (m), 1262 (m), 1241 (m), 1062 (m), 1013 (m), 951

(m), 845 (m), 819 (m), 733 (s); HRMS (positive ESI) calcd for $C_{23}H_{17}N_2O_3^+$ ($[M+H]^+$): 369.1234; Found: 369.1227.



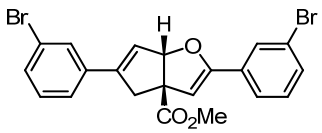
3j

135.0 mg, 74% yield, white solid, mp 118-119 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.65 (s, 1H), 7.50 (d, *J* = 1.2 Hz, 1H), 7.40-7.38 (m, 3H), 7.27 (d, *J* = 8.0 Hz, 1H), 6.20 (d, *J* = 1.2 Hz, 1H), 6.11 (s, 1H), 5.46 (s, 1H), 3.81 (s, 3H), 3.31 (d, *J* = 16.8 Hz, 1H), 3.07 (d, *J* = 16.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 174.0, 153.5, 142.4, 134.3, 132.7, 132.6, 132.5, 132.4, 130.3, 130.2, 130.1, 128.1, 127.4, 125.4, 124.8, 124.4, 100.6, 93.1, 62.2, 52.6, 44.2; IR (neat) ν 2949 (m), 1721 (s), 1471 (m), 1396 (m), 1261 (m), 1247 (m), 1064 (s), 1029 (m), 959 (m), 792(m), 749 (m), 676 (m); HRMS (positive ESI) calcd for $C_{21}H_{15}Cl_4O_3^+$ ($[M+H]^+$): 454.9770; Found: 454.9761.



3k

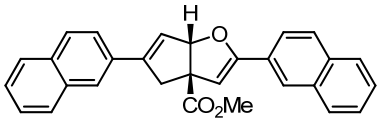
156.2 mg, 82% yield, white paste, ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.62-7.56 (m, 3H), 7.32-7.24 (m, 3H), 7.18-7.12 (m, 2H), 6.10 (s, 1H), 5.96 (d, *J* = 1.2 Hz, 1H), 5.70 (s, 1H), 3.81 (s, 3H), 3.40 (dd, *J* = 1.8, 16.6 Hz, 1H), 3.17 (dt, *J* = 1.6, 16.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 174.4, 153.4, 145.5, 137.4, 133.6, 133.1, 131.4, 130.1, 129.89, 129.86, 129.2, 128.2, 127.2, 127.0, 121.9, 121.7, 104.7, 92.3, 63.0, 52.5, 46.7; IR (neat) ν 2949 (m), 1729 (s), 1468 (m), 1432 (m), 1234 (m), 1067 (m), 1025 (m), 1007 (m), 954 (m), 742 (s); MS (EI, m/z, rel. intensity) 476 (10.9, M^+), 444 (17.8), 417 (7.2), 395 (1.4), 335 (14.2), 308 (3.4), 292 (27.7), 261 (7.8), 228 (21.6), 212 (1.8), 202 (4.5), 183 (100), 168 (17.0), 152 (58.8), 128 (17.0), 113 (34.5), 101 (21.2), 89 (4.4), 75 (12.6), 59 (12.4), 50 (4.3); HRMS (EI) calcd for $C_{21}H_{16}Br_2O_3$ (M^+): 473.9466; Found: 473.9465.



3l

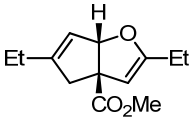
173.3, 91% yield, white solid, mp 117-118 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.72 (s, 1H), 7.58 (s,

1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.22-7.17 (m, 2H), 6.20 (s, 1H), 6.11 (s, 1H), 5.45 (s, 1H), 3.80 (s, 3H), 3.32 (d, *J* = 16.8 Hz, 1H), 3.09 (d, *J* = 16.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 174.2, 154.0, 143.0, 136.4, 132.1, 131.7, 131.3, 129.9, 129.7, 129.2, 128.4, 124.7, 124.0, 123.98, 122.6, 122.3, 100.3, 93.0, 62.0, 52.5, 44.1; IR (neat) ν 2950 (m), 1728 (s), 1559 (m), 1427 (m), 1236 (m), 1200 (m), 1061 (m), 1020 (m), 946 (m), 778 (s), 737 (s), 723 (s), 682 (m); MS (EI, m/z, rel. intensity) 476 (5.1, M^+), 444 (13.4), 416 (9.7), 336 (5.2), 308 (5.0), 292 (67.8), 261 (12.9), 228 (20.7), 212 (2.8), 202 (3.7), 183 (100), 168 (47.4), 152 (61.8), 128 (8.6), 114 (22.3), 101 (13.9), 88 (3.7), 76 (24.3), 59 (26.6), 50 (6.6); HRMS (EI) calcd for $C_{21}H_{16}Br_2O_3$ (M^+): 473.9466; Found: 473.9461.



3m

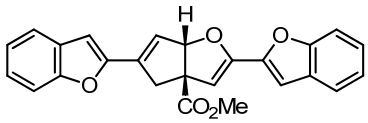
154.0 mg, 92% yield, white solid, mp 167-168 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.09 (s, 1H), 7.85-7.76 (m, 7H), 7.69-7.62 (m 2H), 7.47-7.45 (m, 4H), 6.39 (s, 1H), 6.26 (s, 1H), 5.61 (s, 1H), 3.83 (s, 3H), 3.51 (d, *J* = 16.8 Hz, 1H), 3.33 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 174.8, 155.6, 144.3, 133.4, 133.21, 133.20, 133.0, 131.9, 128.5, 128.2, 128.0, 127.8, 127.61, 127.56, 126.43, 126.36, 126.33, 125.7, 124.7, 124.1, 123.5, 123.4, 100.2, 93.2, 62.3, 52.6, 44.5; IR (neat) ν 2926 (m), 1728 (s), 1432 (m), 1246 (m), 1218 (m), 1060 (m), 1030 (m), 952 (m), 821 (m), 792 (m), 778 (m), 750 (s); MS (EI, m/z, rel. intensity) 418 (8.3, M^+), 386 (8.0), 358 (5.8), 341 (4.5), 327 (1.8), 316 (1.8), 302 (1.6), 281 (14.4), 262 (24.8), 231 (5.1), 221 (1.9), 207 (34.6), 191 (4.2), 178 (2.6), 155 (100), 127 (47.2), 115 (3.6), 104 (1.6), 96 (8.0), 73 (8.6), 59 (2.3), 44 (2.4); HRMS (EI) calcd for $C_{29}H_{22}O_3$ (M^+): 418.1569; Found: 418.1572.



3n

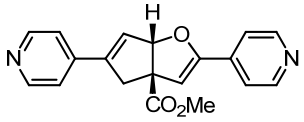
60.5 mg, 68% yield, colorless liquid, ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.74 (s, 1H), 5.36 (d, *J* = 1.2 Hz, 1H), 4.58 (s, 1H), 3.70 (s, 3H), 2.76 (d, *J* = 16.0 Hz, 1H), 2.47 (d, *J* = 16.8 Hz, 1H), 2.10-2.02 (m, 4H), 1.06-1.01 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 175.6, 160.1, 149.6, 121.3, 97.8, 93.2, 61.6, 52.1, 46.6, 23.8, 21.2, 11.8, 10.7; IR (neat) ν 2969 (m), 1734 (s), 1436 (m), 1249 (m), 1203 (m),

1058 (m); MS (EI, m/z, rel. intensity) 222 (12.7, M^+), 207 (1.3), 190 (15.0), 175 (8.2), 166 (46.7), 147 (30.3), 137 (53.7), 133 (81.4), 119 (27.7), 105 (72.5), 93 (100), 91 (64.1), 77 (25.9), 59 (20.6), 57 (38.0), 51 (7.0), 41 (6.8); HRMS (EI) calcd for $C_{13}H_{18}O_3$ (M^+): 222.1256; Found: 222.1252.



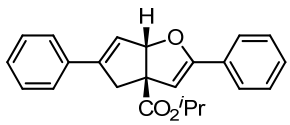
3o

62.2 mg, 39% yield, white solid, mp 132-133 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.54 (t, *J* = 7.6 Hz, 2H), 7.45-7.42 (m, 2H), 7.30-7.25 (m, 2H), 7.20 (t, *J* = 6.8 Hz, 2H), 6.88 (s, 1H), 6.67 (s, 1H), 6.38 (s, 1H), 6.20 (s, 1H), 5.64 (s, 1H), 3.82 (s, 3H), 3.39 (d, *J* = 16.4 Hz, 1H), 3.17 (d, *J* = 16.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.9, 155.02, 154.97, 151.6, 147.8, 147.3, 134.8, 128.3, 128.0, 125.24, 125.16, 124.1, 123.1, 122.9, 121.5, 121.2, 111.1, 105.6, 105.0, 101.8, 93.9, 62.4, 52.7, 43.0; IR (neat) ν 2952 (m), 1732 (s), 1448 (m), 1256 (s), 1197 (m), 1062 (m), 1028 (m), 953 (m), 930 (m), 792 (m), 745 (s); MS (EI, m/z, rel. intensity) 398 (37.0, M^+), 366 (22.3), 339 (18.2), 321 (5.2), 311 (7.5), 297 (5.1), 281 (15.6), 268 (2.9), 253 (100), 252 (73.2), 239 (5.8), 221 (32.9), 207 (15.8), 194 (36.5), 181 (44.3), 165 (48.7), 145 (86.4), 126 (20.6), 115 (19.7), 103 (7.3), 89 (42.4), 73 (6.0), 59 (15.7), 51 (2.5); HRMS (EI) calcd for $C_{25}H_{18}O_5$ (M^+): 398.1154; Found: 398.1157.



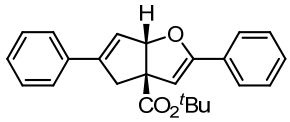
3p

58.9 mg, 46% yield, light yellow paste, ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.60 (d, *J* = 5.6 Hz, 4H), 7.44-7.42 (m, 2H), 7.32-7.30 (m, 2H), 6.42 (d, *J* = 1.6 Hz, 1H), 6.17 (s, 1H), 5.68 (s, 1H), 3.82 (s, 3H), 3.37 (dd, *J* = 1.4, 16.6 Hz, 1H), 3.15 (dt, *J* = 1.8, 16.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.7, 153.6, 150.0, 149.8, 142.5, 141.4, 137.2, 126.7, 120.6, 119.6, 102.9, 93.0, 62.1, 52.7, 43.6; IR (neat) ν 2952 (m), 1728 (s), 1595 (s), 1411 (m), 1246 (s), 1202 (s), 1063 (s), 951 (m), 792(m), 730 (m), 681 (m); HRMS (positive ESI) calcd for $C_{19}H_{17}N_2O_3^+$ ($[M+H]^+$): 321.1234; Found: 321.1232.



3r

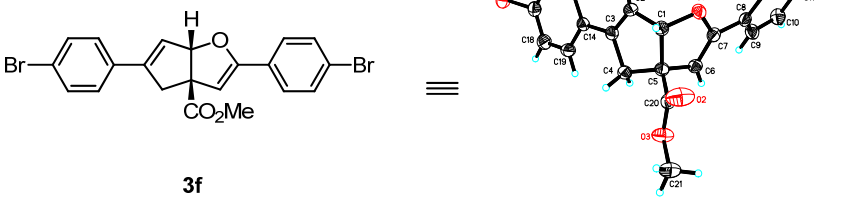
127.5 mg, 92% yield, white solid, mp 69-70 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.59-7.56 (m, 2H), 7.48-7.45 (m, 2H), 7.35-7.26 (m, 6H), 6.22 (dd, *J* = 1.8, 3.6 Hz, 1H), 6.14 (t, *J* = 1.8 Hz, 1H), 5.44 (s, 1H), 5.15-5.05 (m, 1H), 3.29 (dd, *J* = 1.6, 16.4 Hz, 1H), 3.14 (dt, *J* = 1.8, 16.8 Hz, 1H), 1.30-1.28 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.6, 155.2, 144.2, 134.6, 130.4, 128.7, 128.3, 128.1, 126.2, 125.5, 123.0, 99.3, 92.8, 68.5, 62.3, 44.5, 21.67, 21.66; IR (neat) ν 2924 (m), 1722 (s), 1448 (m), 1239 (m), 1104 (m), 1058 (m), 1012 (m), 945 (m), 753 (m), 728 (m), 690 (s); MS (EI, m/z, rel. intensity) 346 (6.4, M^+), 304 (0.82), 286 (14.6), 259 (17.6), 240 (44.9), 229 (5.4), 215 (13.5), 199 (23.7), 181 (20.2), 153 (22.6), 128 (7.9), 115 (14.6), 105 (100), 91 (2.7), 77 (23.2), 51 (5.1), 43 (37.5); HRMS (EI) calcd for $C_{23}H_{22}O_3$ (M^+): 346.1569; Found: 346.1567.



3s

139.8 mg, 97% yield, white solid, mp 124-125 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.59-7.57 (m, 2H), 7.48-7.46 (m, 2H), 7.35-7.26 (m, 6H), 6.22 (d, *J* = 1.6 Hz, 1H), 6.10 (s, 1H), 5.42 (s, 1H), 3.26 (dd, *J* = 1.4, 16.6 Hz, 1H), 3.12 (dt, *J* = 1.8, 16.4 Hz, 1H), 1.50 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.3, 155.0, 144.1, 134.6, 130.5, 128.6, 128.32, 128.29,128.1, 126.2, 125.5, 123.11, 99.6, 92.8, 81.1, 63.1, 44.6, 28.0; IR (neat) ν 2976 (m), 2929 (m), 1719 (s), 1447 (m), 1247 (m), 1155 (s), 1060 (m), 945 (m), 753 (s), 726 (s), 690 (s); HRMS (positive ESI) calcd for $C_{24}H_{25}O_3^+$ ($[M+H]^+$): 361.1798; Found: 361.1789.

X-Ray structure of 3f (CCDC 931337)



3f

Bond precision: C-C = 0.0043 A Wavelength=0.71073

Cell: a=7.8079(6) b=14.4168(11) c=16.8239(12)
alpha=90 beta=99.632(2) gamma=90

Temperature: 293 K

	Calculated	Reported
Volume	1867.1(2)	1867.1(2)
Space group	P 21/n	P2(1)/n
Hall group	-P 2yn	?
Moiety formula	C21 H16 Br2 O3	?
Sum formula	C21 H16 Br2 O3	C21 H16 Br2 O3
Mr	476.14	476.16
Dx,g cm-3	1.694	1.694
Z	4	4
Mu (mm-1)	4.359	4.360
F000	944.0	944.0
F000'	942.16	
h,k,lmax	9,17,20	9,17,20
Nref	3675	3673
Tmin,Tmax	0.352,0.531	0.384,1.000
Tmin'	0.227	

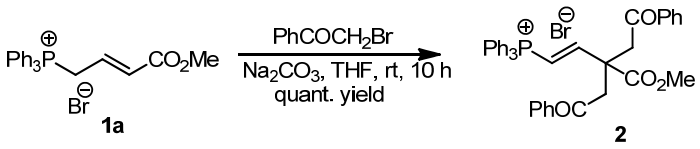
Correction method= EMPIRICAL

Data completeness= 0.999 Theta(max)= 26.000

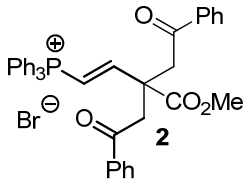
R(reflections)= 0.0401(2667) wR2(reflections)= 0.1066(3673)

S = 1.019 Npar= 236

3. General procedure for synthesis of vinyl phosphonium salt 2



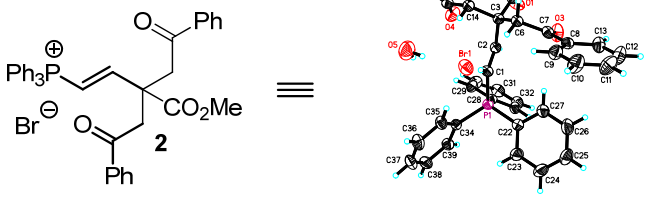
To a stirred suspension of phosphonium salt **1a** (441.0 mg, 1.0 mmol) and $PhCOCH_2Br$ (398.0 mg, 2.0 mmol) in dry THF (5.0 mL) under N_2 at room temperature was added Na_2CO_3 (424.0 mg, 4.0 mmol). Dry THF (5.0 mL) were added for washing the Schlenk tube and the resulting mixture was stirred at room temperature for 10 h. The resulting mixture was filtered rapidly through a funnel with a thin layer of celite and eluted with DCM. The filtrate was concentrated and the residue was purified by chromatography on silica gel to afford the desired vinyl phosphonium salt **2** as a white solid.



Quant. yield, white solid, ^1H NMR ($CDCl_3$, 300 MHz) δ 8.52 (dd, J = 17.4, 21.9 Hz, 1H), 8.32 (d, J = 7.8 Hz, 4H), 8.00 (dd, J = 17.7, 24.6 Hz, 1H), 7.74-7.69 (m, 3H), 7.59-7.47 (m, 14H), 7.40 (t, J = 7.5 Hz, 4H), 5.43 (d, J = 18.0 Hz, 2H), 3.86 (d, J = 17.7 Hz, 2H), 3.67 (s, 3H); ^{31}P NMR ($CDCl_3$, 121.4 MHz) δ 22.1. IR (neat) ν 1738 (s), 1680 (s), 1437 (m), 1211 (s), 1113 (m), 994 (m), 751 (m), 724 (m), 687 (s); HRMS (positive ESI) calcd for $C_{39}H_{34}O_4P^+$ ($[M\text{-}Br]^+$): 597.2189; Found: 597.2180.

This structure also determined by X-Ray analysis (CCDC 931342).

X-Ray structure of 2 (CCDC 931342)



Bond precision: C-C = 0.0048 A Wavelength=0.71073

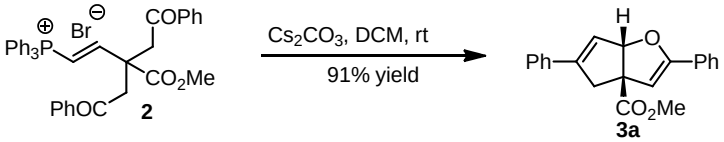
Cell: a=9.5869(5) b=35.5331(19) c=10.4715(6)
alpha=90 beta=104.270(1) gamma=90

Temperature: 293 K

	Calculated	Reported
Volume	3457.1(3)	3457.1(3)
Space group	P 21/c	P2(1)/c
Hall group	-P 2ybc	?
Moiety formula	2(C39 H34 O4 P), H2 O, 2(Br)	?
Sum formula	C78 H70 Br2 O9 P2	C39 H35 Br O4.50 P
Mr	1373.08	686.55
Dx,g cm-3	1.319	1.319
Z	2	4
Mu (mm-1)	1.276	1.276
F000	1420.0	1420.0
F000'	1419.82	
h,k,lmax	11,43,12	11,43,12
Nref	6782	6778
Tmin,Tmax	0.718,0.866	0.748,1.000
Tmin'	0.640	

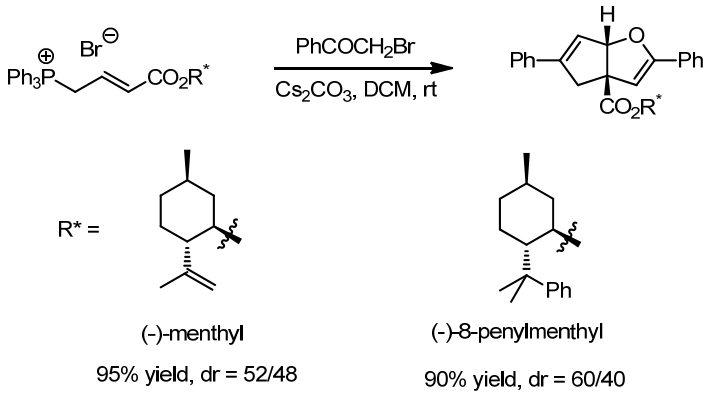
Correction method= EMPIRICAL
Data completeness= 0.999 Theta(max)= 25.990
R(reflections)= 0.0493(4782) wR2(reflections)= 0.1241(6778)
S = 1.023 Npar= 424

4. General procedure for transformation of intermediate 2

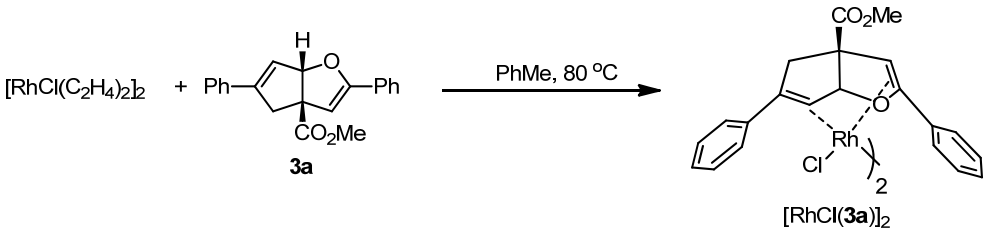


To a solution of vinyl phosphonium **2** (60.4 mg, 0.1 mmol) in dry DCM (2.0 mL) under N_2 at room temperature was added Cs_2CO_3 (98.9 mg, 0.3 mmol) and DCM (2.0 mL). The resulting mixture was stirred at room temperature for 18 hours, and then filtered rapidly through a funnel with a thin layer of silicon and eluted with DCM. The filtrate was concentrated and the residue was purified by chromatography on silica gel to afford the desired product **3a** (29.0 mg, 91% yield).

5. Asymmetric reactions with chiral esters.

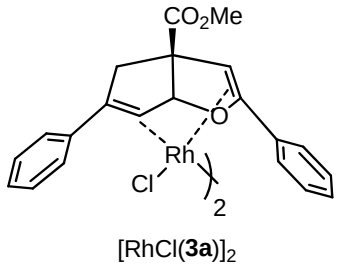


6. General procedure for synthesis of Rh-complex (CCDC 931343)



$[RhCl(CH_2{=}CH_2)]_2$ was synthesized according the literature.[1]

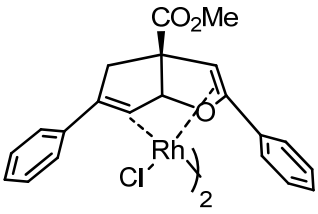
The solution of $[RhCl(CH_2{=}CH_2)]_2$ (116.7 mg, 0.3 mmol) and **3a** (190.8 mg, 0.6 mmol) in dry toluene (7.0 mL) was stirred at 80 ℃ for 12 hours. After the reaction was completed, the resulting solution was concentrated under vacuum, and then the solid was solvated in DCM and filtered rapidly through a funnel with a thin layer of celete and eluted with DCM under N_2. The final brick-red solution was concentrated and recystallized in DCM/Hexane to afford $[RhCl(7a)]_2$ as a maroon solid (261.0 mg, 95% yield).



95% yield, maroon solid, ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.79 (d, J = 7.2 Hz, 2H), 7.72 (d, J = 7.6 Hz, 2H), 7.57-7.21 (m, 16H), 4.47 (d, J = 24.4 Hz, 2H), 4.12 (s, 1H), 3.67-3.64 (m, 7H), 3.56 (s, 1H), 3.43 (dd, J = 3.0, 13.4 Hz, 2H), 3.32 (s, 1H), 2.25 (d, J = 12.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.92, 170.89, 139.27, 139.26, 134.81, 134.76, 130.6, 130.5, 130.3, 130.2, 129.8, 129.6, 128.8, 128.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.79, 127.75, 94.4, 94.3, 94.2, 94.1, 88.1, 88.0, 75.4, 75.3, 75.2, 75.1, 60.8, 60.7, 52.20, 52.18, 50.4, 50.3, 44.9; IR (neat) ν 2953 (m), 1729 (s), 1434 (m), 1305 (m), 1065 (m), 850 (s), 731 (s), 689 (s) 635 (m); Anal. Calcd for $C_{42}H_{36}Cl_2O_6Rh_2$: C, 55.22; H, 3.97; Found: C, 55.36; H, 4.24.

1 D. M. Haddleton, A. McCamley, R. N. Perutz, *J. Am. Chem. Soc.*, 1988, **110**, 1810–1817.

X-Ray structure of [RhCl(3a)]$_2$ (CCDC 931343)



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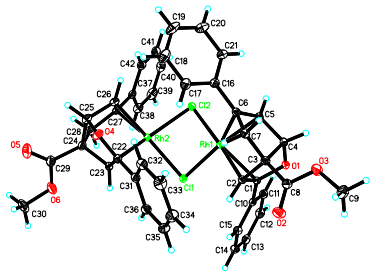

Bond precision: C-C = 0.0038 A Wavelength=0.71073

Cell: a=16.3366(13) b=14.6059(12) c=17.7679(14)

alpha=90 beta=105.468(1) gamma=90

Temperature: 143 K

	Calculated	Reported
Volume	4086.1(6)	4086.1(6)
Space group	P 21/c	P2(1)/c
Hall group	-P 2ybc	?
Moiety formula	C42 H36 Cl2 O6 Rh2, C4 H10 O	?
Sum formula	C46 H46 Cl2 O7 Rh2	C46 H46 Cl2 O7 Rh2
Mr	987.55	987.55
Dx,g cm-3	1.605	1.605
Z	4	4
Mu (mm-1)	0.991	0.991
F000	2008.0	2008.0
F000'	2000.98	
h,k,lmax	23,20,25	23,20,25
Nref	12429	12383
Tmin,Tmax	0.788,0.961	0.755,0.961
Tmin'	0.743	

Correction method= MULTI-SCAN

Data completeness= 0.996 Theta(max)= 30.470

R(reflections)= 0.0310(9877) wR2(reflections)= 0.0827(12383)

S = 1.024 Npar= 518