Advanced Synthesis & Catalysis

Supporting Information

Rh-BisbenzodioxanPhos Complex-catalyzed Homogeneous Enantioselective Pauson-Khand-type Cyclization in Alcoholic Solvents

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Supporting Information

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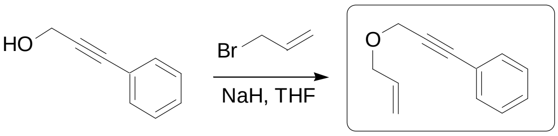
1. General considerations.

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. All air-sensitive reactions were performed in Rotaflo® (England) resealable screw cap Schlenk flask (approx. 10 mL volume) or Teflon-lined screw cap vials (approx. 2 mL volume) in the presence of Teflon-coated magnetic stirrer bar (3 mm × 10 mm). Toluene and tetrahydrofuran (THF) were distilled from sodium and sodium benzophenone ketyl under nitrogen, respectively.[1] Allylamine and triethylamine were distilled over CaH_2 prior to use. Aldehydes (liquid form at RT) were distilled under reduced pressure and stored in screw-capped vials. NaH (60% in mineral oil) was washed with dry hexane prior to use (*Caution*: This procedure should perform in a relatively dry atmosphere with adequate shielding). Shiny-orange $[Rh(COD)Cl]_2$ crystalline solid and (*S*)-BisbenzodioxanPhos (SYNPHOS®) were purchased from Strem Chemicals. Thin layer chromatography was performed on Merck precoated silica gel 60 F_{254} plates. Silica gel (Merck, 230-400 mesh) was used for flash column chromatography. Melting points were recorded on an uncorrected Büchi Melting Point B-545 instrument. ^1H NMR spectra were recorded on a Varian (500 MHz) spectrometer. Spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.26 ppm), or with tetramethylsilane (TMS, δ 0.00 ppm) as the internal standard. Commercially available $CDCl_3$ was stored under anhydrous K_2CO_3 granules with 4Å molecular sieves in desiccators. Chemical shifts (δ) were reported as part per million (ppm) in δ scale downfield from TMS. ^{13}C NMR spectra were recorded on a Varian 500 spectrometer and referenced to $CDCl_3$ (δ 77.0 ppm). Coupling constants (*J*) were reported in Hertz (Hz). Mass spectra (EIMS and FABMS) were recorded on a HP 5989B Mass Spectrometer. High-resolution mass spectra (HRMS) were obtained on a Brüker APEX 47e FT-ICR mass spectrometer (ESIMS). HPLC analyses were performed on a Waters™ 600 instrument using Chiralcel® AS-H, AD-H, and OD-H (0.46 cm diameter × 25 cm length) columns. Racemic bicyclic cyclopentenone products (for chiral HPLC analysis calibration) were obtained from the same PKR representative procedure except racemic ligand was used. GC-MS analysis was conducted on a HP G1800C GCD system using a HP5MS column (30 m × 0.25 mm).

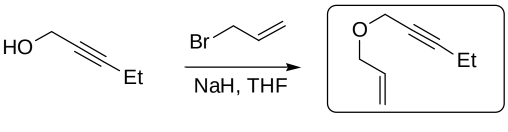
2. **Preparation of enyne substrates**

3-(Allyloxy)-1-phenyl-1-propyne[2]



General procedures of condensation of arylpropargyl alcohol with allyl bromide: To a solution of 3-phenyl-2-propyn-1-ol (5.28 g, 40 mmol) in freshly distilled THF (80 mL) was added NaH (1.44 g, 60 mmol, freshly pre-washed with dry hexane) portionwise under nitrogen atmosphere at 0 ºC. The white suspension was slowly warmed to room temperature and stirred for 2 hours. The reaction mixture was then cooled to 0 °C and allyl bromide (6.8 mL, 80 mmol) was added dropwise. After complete addition, the reaction was warmed to room temperature and further stirred for 2 hours. Water (~30 mL) was slowly added and the aqueous layer was extracted with diethyl ether (3 × ~100 mL). The combined organic layers were washed with water (~50 mL), brine (~50 mL) and dried over sodium sulfate. Solvent was removed by rotary evaporation and the light yellow crude product was purified by vacuum distillation (bp. 101-102 °C, 5 mmHg) to give title compound as a colorless liquid (6.53 g, 95% yield). R_f = 0.2 (hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.30-7.43 (m, 5H), 6.02 (tdd, *J* = 17.0 Hz, 10.0 Hz, 5.5 Hz, 1H), 5.38 (dd, *J* = 17.0 Hz, 2.0 Hz, 1H), 5.27 (dd, *J* = 10.0 Hz, 2.0 Hz, 1H), 4.39 (s, 2H), 4.17 (dd, *J* = 5.5 Hz, 1.5 Hz, 2H); IR (neat, cm^{-1}) 3080, 3019, 2982, 2938, 2849, 2237, 1954, 1881, 1647, 1598, 1571, 1489, 1442, 1424, 1354, 1256, 1124, 1081, 1027, 991, 964, 925, 757, 691, 626, 549, 585, 538, 525; MS(EI) *m/z* (relative intensity) 172 (M$^+$, 20), 131 (100).

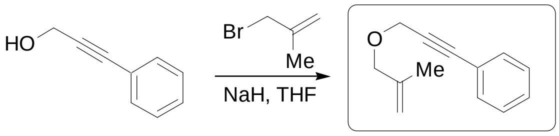
5-(Allyloxy)-3-pentyne[3]



The general procedures of C-O bond formation were followed: 3-Pentyn-1-ol (4.2 g, 50 mmol), NaH (1.8 g, 75 mmol, prewashed with dry hexane), allyl bromide (8.5 mL, 100 mmol) and freshly distilled THF (150 mL) were used to obtain the title compound as a colorless liquid

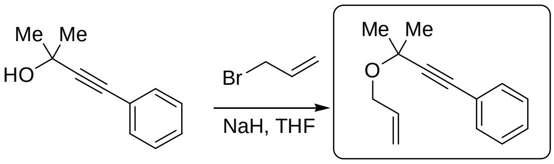
(5.3 g, 85% yield). Purification was conducted by distillation under reduced pressure (30-33 °C, 5 mmHg). $R_f = 0.2$ (hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.91 (tdd, *J* = 17.0 Hz, 10.0 Hz, 5.5 Hz, 1H), 5.31 (dd, *J* = 17.0 Hz, 2.0 Hz, 1H), 5.20 (dd, *J* = 10.0 Hz, 2.0 Hz, 1H), 4.12 (t, *J* = 2.5 Hz, 2H), 4.04 (d, *J* = 5.5 Hz, 2 H), 2.21-2.25 (m, 2H), 1.14 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 133.1, 117.6, 82.5, 75.1, 70.5, 57.7, 11.8, 9.5; IR (neat, cm^{-1}) 3078, 2978, 2938, 2851, 2289, 2223, 1649, 1454, 1424, 1357, 1316, 1137, 1084, 999, 926, 748, 650, 563; MS(EI) *m/z* (relative intensity) 125 (M$^+$, 15), 84 (100).

3-[(2-Methyl-2-propenyl)oxy]-1-phenyl-1-propyne[4]



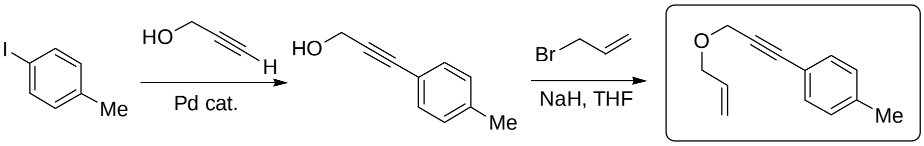
The general procedures of condensation of arylpropargyl alcohol with allyl bromide were followed: 3-Phenyl-2-propyn-1-ol (5.28 g, 40 mmol), NaH (1.44 g, 60 mmol, freshly pre-washed with dry hexane), 3-Bromo-2-methyl-1-propene (10.8 g, 80 mmol) and freshly distilled THF (100 mL) were used to afford the title compound as a colorless liquid (6.8 g, 92% yield). Purification was carried out using vacuum distillation (125-128 °C, 4 mmHg). $R_f = 0.2$ (hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.30-7.43 (m, 5H), 5.38 (d, *J* = 2.0 Hz, 1H), 5.27 (d, *J* = 2.0 Hz, 1H), 4.39 (s, 2H), 4.17 (s, 2H), 1.88 (s, 3H); IR (neat, cm^{-1}) 3452, 3078, 2980, 2914, 2842, 2233, 1946, 1885, 1798, 1654, 1593, 1489, 1443, 1356, 1250, 1086, 1034, 903, 757, 691, 594, 523; MS(EI) *m/z* (relative intensity) 186 (M$^+$, 20), 131 (100).

3-Methyl-3-(allyoxy)-1-phenyl-1-butyne[5]



The general procedures of condensation of arylpropargyl alcohol with allyl bromide were followed: 2-Methyl-4-Phenyl-3-butyn-1-ol (3.2 g, 20 mmol), NaH (0.72 g, 30 mmol, freshly pre-washed with dry hexane), allyl bromide (3.4 mL, 40 mmol) and freshly distilled THF (50 mL) were used to afford the title compound as a colorless liquid (3.4 g, 89% yield). R_f = 0.3 (hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.43-7.45 (m, 2H), 7.30-7.32 (m, 3H), 5.96-6.04 (m, 1H), 5.33 (dd, *J* = 17.0 Hz, 2.0 Hz, 1H), 5.17 (dd, *J* = 10.0 Hz, 2.0 Hz, 1H), 4.20 (d, *J* = 5.0 Hz, 2H), 1.59 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 135.5, 131.6, 128.2, 128.1, 122.8, 116.4, 91.3, 84.2, 70.7, 65.6, 28.9.

3-(Allyloxy)-1-(4-methylphenyl)-1-propyne

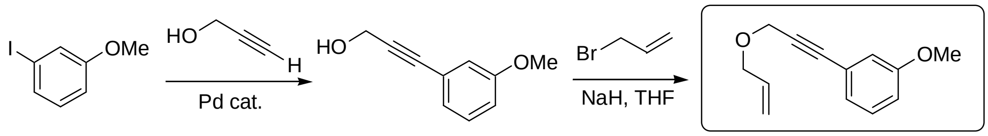


The procedure of Sonogashira coupling of propagyl alcohol with ArI were used: 4-Iodotoluene (10.9 g, 50 mmol), $Pd(PPh_3)_2Cl_2$ (3 mol%), CuI (6 mol%), piperidine (8.4 g, 100 mmol), propagyl alcohol (3.07 mL, 52 mmol) and freshly distilled toluene (50 mL) were charged into a round-bottom flask with Teflon inter-key under nitrogen. The resulting dark brown reaction mixture was stirred at 30-35 °C for 3 hours under nitrogen (ArI was completely consumed as judged by GC analysis). The 3-(4-methylphenyl)-2-propyn-1-ol[6] (5.26 g, 72% yield) was afforded as a light brown solid. Purification was conducted by filtered the reaction mixture over a silica pad (5 cm × 5 cm), and purified by flash column chromatography on silica gel using dichloromethane as eluent. R_f = 0.5 (dichloromethane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.33 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 4.49 (s, 2H), 3.23 (brs, 1H), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 138.2, 131.3, 128.6, 119.3, 86.5, 85.3, 51.2, 21.0; MS(EI) *m/z* (relative intensity) 146 (M^+, 100); HRMS cald. for $C_{10}H_{10}O$ 146.07316, found 146.07311.

The general procedures of condensation of arylpropargyl alcohol with allyl bromide were followed: 3-(4-Methylphenyl)-2-propyn-1-ol[6] (1.46 g, 10 mmol), NaH (360 mg, 15 mmol, prewashed with dry hexane), allyl bromide (1.7 mL, 20 mmol) and freshly distilled THF (20 mL) were used to afford 3-(allyloxy)-1-(4-methylphenyl)-1-propyne as a light yellow liquid (1.78 g, 96% yield). Purification was conducted by distillation under reduced pressure (130-133 °C, 3 mmHg). R_f = 0.2 (hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.35 (d, *J* = 8.5 Hz, 2H), 7.12 (d, *J* =

8.0 Hz, 2H), 5.92-6.00 (m, 1H), 5.33 (dd, *J* = 17.0 Hz, 1.0 Hz, 1H), 5.23 (dd, *J* = 17.5 Hz, 1.0 Hz, 1H), 4.38 (s, 2H), 4.13 (d, *J* = 5.0 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 137.5, 137.4, 132.0, 128.8, 119.3, 115.1, 89.4, 85.5, 72.2, 57.4, 20.1; IR (neat, cm^{-1}) 3080, 3028, 2982, 2921, 2851, 2243, 1910, 1649, 1509, 1442, 1424, 1354, 1260, 1123, 1080, 991, 926, 817, 666, 558, 526; MS(EI) *m/z* (relative intensity) 186 (M$^+$, 15), 145 (100); HRMS cald. for $C_{13}H_{14}O$ 186.10447, found 186.10451.

3-(Allyloxy)-1-(3-methoxyphenyl)-1-propyne

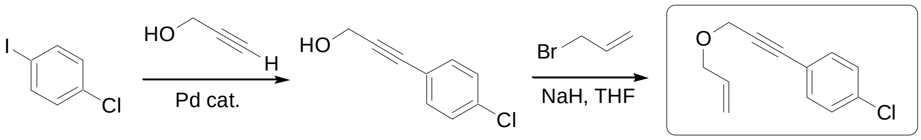


The general procedures for Sonogashira coupling of propagyl alcohol with ArI were used: 3-Iodoanisole (11.7 g, 50 mmol), $Pd(PPh_3)_2Cl_2$ (3 mol%), CuI (6 mol%), piperidine (8.4 g, 100 mmol), propagyl alcohol (3.07 mL, 52 mmol) and freshly distilled toluene (50 mL) were used to afford 3-(3-methoxyphenyl)-2-propyn-1-ol[7] (5.91 g, 73% yield) as a light yellow viscous liquid. Purification was conducted by filtered the reaction mixture over a silica pad (5 cm × 5 cm), and purified by flash column chromatography on silica gel using dichloromethane as eluent. R_f = 0.4 (dichloromethane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.22 (t, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 7.5 Hz, 1H), 6.97 (m, 1H), 6.89 (m, 1H), 4.50 (d, *J* = 6.5 Hz, 2H), 3.80 (s, 3H), 1.72 (t, *J* = 6.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 138.9, 131.1, 128.6, 119.6, 86.5, 85.3, 51.2, 44.8; MS(EI) *m/z* (relative intensity) 162 (M$^+$, 100); HRMS cald. for $C_{10}H_{10}O_2$ 162.06808, found 162.06829.

The general procedures of condensation of arylpropargyl alcohol with allyl bromide were followed: 3-(3-Methoxyphenyl)-2-propyn-1-ol[7] (1.0 g, 6.2 mmol), NaH (223 mg, 9.3 mmol, prewashed with dry hexane), allyl bromide (1.05 mL, 12.4 mmol) and freshly distilled THF (10 mL) were used to afford 3-(allyloxy)-1-(3-methoxyphenyl)-1-propyne as a light yellow liquid (1.16 g, 94% yield). Purification of crude product was conducted by filtered over a short silica pad followed by flash column chromatography on silica gel using hexane/ethyl acetate (10:1) as eluent. R_f = 0.5 (hexane/ethyl acetate = 10:1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.21 (t, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.96 (m, 1H), 6.89 (m, 1H), 5.94 (m, 1H), 5.32 (dd, *J* = 17.0

Hz, 1.0 Hz, 1H), 5.23 (dd, *J* = 17.5 Hz, 1.0 Hz, 1H), 4.37 (s, 2H), 4.13 (d, *J* = 5.0 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 159.7, 134.1, 133.2, 117.8, 114.7, 113.9, 86.2, 83.6, 70.6, 57.9, 55.2; IR (neat, cm^{-1}) 3077, 3004, 2939, 2911, 2840, 2228, 1644, 1600, 1572, 1483, 1419, 1353, 1318, 1289, 1204, 1165, 1124, 1046, 992, 927, 855, 784, 687, 584, 512; MS(EI) *m/z* (relative intensity) 202 (M^+, 10), 161 (100); HRMS cald. for $C_{13}H_{14}O_2$ 202.09938, found 202.09923.

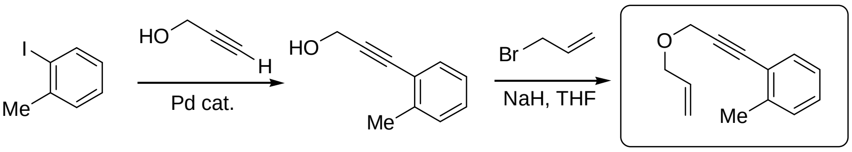
3-(Allyloxy)-1-(4-chlorophenyl)-1-propyne



The general procedures for Sonogashira coupling of propagyl alcohol with ArI were used: 3-Iodoanisole (11.9 g, 50 mmol), $Pd(PPh_3)_2Cl_2$ (3 mol%), CuI (6 mol%), piperidine (8.4 g, 100 mmol), propagyl alcohol (3.07 mL, 52 mmol) and freshly distilled toluene (50 mL) were used to afford 3-(4-chlorophenyl)-2-propyn-1-ol[8] (5.91 g, 73% yield) as a light yellow viscous liquid. Purification was conducted by filtered the reaction mixture over a silica pad (5 cm × 5 cm), and purified by flash column chromatography on silica gel using dichloromethane as eluent. R_f = 0.5 (dichloromethane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.36 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 4.45 (s, 2H), 1.98 (brs, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 133.2, 131.3, 128.2, 119.3, 86.5, 85.1, 51.2; MS(EI) *m/z* (relative intensity) 168 (M^+, 30), 166 (M^+, 100); HRMS cald. for C_9H_7ClO 166.01854, found 166.01850.

The general procedures of condensation of arylpropargyl alcohol with allyl bromide were followed: 3-(4-Chlorophenyl)-2-propyn-1-ol (1.67 g, 10 mmol), NaH (360 mg, 15 mmol, prewashed with dry hexane), allyl bromide (1.7 mL, 20 mmol) and freshly distilled THF (30 mL) were used to afford 3-(allyloxy)-1-(4-chlorophenyl)-1-propyne as a light yellow liquid (1.84 g, 89% yield). Purification of crude product was conducted by filtered over a short silica pad followed by flash column chromatography on silica gel using hexane/ethyl acetate (30:1) as eluent. R_f = 0.4 (hexane/ethyl acetate = 30:1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.38 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 5.94 (tdd, *J* = 17.0 Hz, 10.0 Hz, 5.5 Hz, 1H), 5.34 (dd, *J* = 17.0 Hz, 1.0 Hz, 1H), 5.24 (dd, *J* = 17.5 Hz, 1.0 Hz, 1H), 4.36 (s, 2H), 4.12 (d, *J* = 6.0 Hz); IR (neat, cm^{-1}) 3078, 3011, 2980, 2939, 2850, 2243, 1895, 1644, 1583, 1488, 1353, 1260, 1124, 1089, 1015, 991, 927, 828, 753, 526; MS(EI) *m/z* (relative intensity) 208 (M$^+$, 10), 206 (M$^+$, 40); 167 (30), 165 (100); HRMS cald. for $C_{12}H_{11}ClO$ 206.04984, found 206.04989.

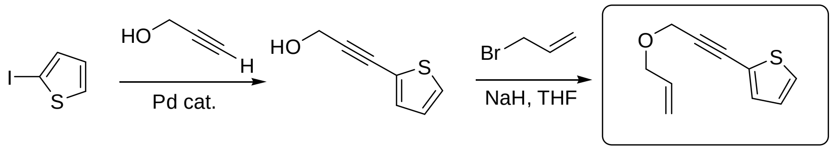
3-(Allyloxy)-1-(2-methylphenyl)-1-propyne



The general procedures for Sonogashira coupling of propagyl alcohol with ArI were used: 2-Iodotoluene (10.9 g, 50 mmol), $Pd(PPh_3)_2Cl_2$ (3 mol%), CuI (6 mol%), piperidine (8.4 g, 100 mmol), propagyl alcohol (3.07 mL, 52 mmol) and freshly distilled toluene (50 mL) were used to afford 3-(2-methylphenyl)-2-propyn-1-ol[7] (5.26 g, 72% yield) as a light brown solid. Purification was conducted by filtered the reaction mixture over a silica pad (5 cm × 5 cm), and purified by flash column chromatography on silica gel using dichloromethane as eluent. $R_f = 0.5$ (dichloromethane); Melting point: 43-44 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.41 (d, $J = 7.5$ Hz, 1H), 7.11-7.24 (m, 3H), 4.54 (d, $J = 6.0$ Hz), 2.43 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 138.2, 131.3, 128.6, 128.1, 119.3, 115.3, 86.5, 85.3, 51.2, 21.2; MS(EI) *m/z* (relative intensity) 146 (M$^+$, 100); HRMS cald. for $C_{10}H_{10}O$ 146.07316, found 146.07310.

The general procedures of condensation of arylpropargyl alcohol with allyl bromide were followed: 3-(2-Methylphenyl)-2-propyn-1-ol (1.46 g, 10 mmol), NaH (360 mg, 15 mmol, prewashed with dry hexane), allyl bromide (1.7 mL, 20 mmol) and freshly distilled THF (20 mL) were used to afford 3-(allyloxy)-1-(2-methylphenyl)-1-propyne as a light yellow liquid (1.73 g, 94% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.43 (d, $J = 8.0$ Hz, 1H), 7.12-7.25 (m, 3H), 5.95-6.01 (m, 1H), 5.36 (dd, $J = 17.0$ Hz, 1.0 Hz, 1H), 5.27 (dd, $J = 17.5$ Hz, 1.0 Hz, 1H), 4.44 (s, 2H), 4.16 (d, $J = 6.0$ Hz), 2.46 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 137.6, 137.4, 132.0, 128.8, 128.6, 119.6, 119.3, 115.1, 89.4, 85.5, 72.3, 57.4, 20.2; IR (neat, cm^{-1}) 3069, 3020, 2981, 2920, 2850, 2223, 1644, 1603, 1485, 1455, 1425, 1353, 1249, 1117, 1085, 926, 758, 716, 599, 452; HRMS cald. for $C_{13}H_{14}O$ 186.10447, found 186.10453.

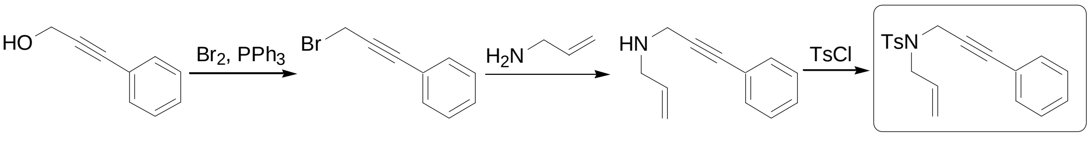
3-(Allyloxy)-1-(2-thiophenyl)-1-propyne



The general procedures for Sonogashira coupling of propagyl alcohol with ArI were used: 2-Iodothiophene (10.5 g, 50 mmol), $Pd(PPh_3)_2Cl_2$ (3 mol%), CuI (6 mol%), piperidine (8.4 g, 100 mmol), propagyl alcohol (3.07 mL, 52 mmol) and freshly distilled toluene (50 mL) were used to afford 3-(2-thiophenyl)-2-propyn-1-ol (5.03 g, 70% yield) as an orange-brown liquid. Purification was conducted by filtered the reaction mixture over a silica pad (5 cm × 5 cm), and purified by flash column chromatography on silica gel using dichloromethane as eluent. $R_f = 0.4$ (dichloromethane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.25 (d, 1H, $J = 5.0$ Hz), 7.21 (d, 1H, $J = 3.5$ Hz), 6.96 (t, 1H, $J = 5.0$ Hz), 4.50 (s, 2H), 2.41 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 132.7, 127.7, 127.2, 122.7, 91.5, 79.2, 51.8; MS(EI) *m/z* (relative intensity) 138 (M^+, 100), 121 (40), 109 (60).

The general procedures of condensation of arylpropargyl alcohol with allyl bromide were followed: 3-(2-thiophenyl)-2-propyn-1-ol (1.38 g, 10 mmol), NaH (360 mg, 15 mmol, prewashed with dry hexane), allyl bromide (1.7 mL, 20 mmol) and freshly distilled THF (20 mL) were used to afford 3-(allyloxy)-1-(2-thiophenyl)-1-propyne as a brown liquid (1.69 g, 91% yield). $R_f = 0.2$ (hexane/ethyl acetate = 100/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.25 (d, 1H, $J =$ 5.5 Hz), 7.22 (d, 1 H, $J = 3.5$ Hz), 6.97 (dd, 1H, $J = 4.0$ Hz, 5.0 Hz), 5.90-5.98 (m, 1H), 5.34 (dd, 1H, $J = 1.0$ Hz, 17.5 Hz), 5.24 (d, 1H, $J = 9.5$ Hz), 4.39 (s, 2H), 4.12 (d, 1H, $J = 6.0$ Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 133.9, 132.4, 127.3, 126.9, 122.5, 117.9, 89.1, 79.5, 70.7, 57.9; IR (neat, cm^{-1}) 3108, 3079, 3011, 2982, 2937, 2847, 2220, 1649, 1518, 1425, 1356, 1263, 1245, 1190, 1124, 1021, 927, 848, 703, 669, 589, 508; MS(EI) *m/z* (relative intensity) 178 (M^+, 5), 149 (40), 135 (65), 121 (100); HRMS cald. for $C_{10}H_{10}OS$ 178.04524, found 178.04514.

N-Allyl-*N*-(3-phenyl-2-propynyl)-4-tolylsulfonamide[9]

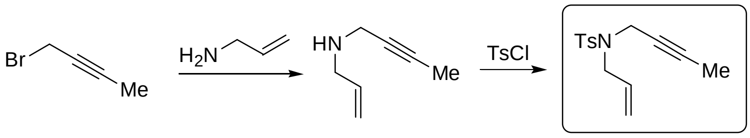


Triphenylphosphine (14.4 g, 55 mmol) was dissolved in dichloromethane (250 mL). Bromine (8.8 g, 2.82 mL, 55 mmol) was then added dropwise at 0 °C, and stirred for 30 mins. 3-Phenyl-2-propyn-1-ol was added at 0 °C and the reaction mixture were left to stir for 1 hour. Hexane (~800 mL) was added and the white suspension was passed through a short silica pad (5 cm width × 10 cm height) and washed with hexane. The crude product was concentrated and distilled under reduced pressure (88-90 °C, 1 mmHg) to afford 3-bromo-1-phenyl-1-propyne[10] (9.01 g, 92% yield) as a light yellow liquid. R_f = 0.4 (hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.44-7.46 (m, 2H), 7.32-7.36 (m, 3H), 4.17 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 132.1, 129.1, 128.6, 122.4, 87.0, 84.5, 15.6; MS(EI) *m/z* (relative intensity) 196 (M^+, 100), 194 (M^+, 100).

Allylamine (4.0 mL, 53 mmol) was charged into a 3-necked round bottom flask, followed by the addition of freshly distilled diethyl ether (10 mL) at room temperature under nitrogen. 3-Bromo-1-phenyl-1-propyne (1.0 g, 5.13 mmol) was added dropwise at 0 °C and the reaction mixtures were stirred at room temperature for 2 hours. The reaction was quenched with water and extracted with ethyl acetate (3 × ~50 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. The crude mixture was passed through a short silica pad (3 cm width x 10 cm height). Solvent was removed in *vacuo* and the *N*-allyl-*N*-(3-phenyl-2-propynyl)amine product was used in next step without further purification.

To a mixture of *N*-allyl-*N*-(3-phenyl-2-propynyl)amine (crude), triethylamine (0.9 mL), and dichloromethane (5 mL) was added a dichloromethane solution of *p*-toluenesulfonyl chloride (967 mg, 5.07 mmol) at 0 °C. The reaction mixture was slowly warmed to room temperature and stirred for 2 hours. Water (~50 mL) was added to quench the reaction, and the aqueous phase was extracted with chloroform (2 × ~50 mL). The combined organic layers were washed with brine and dried over sodium sulfate. Solvent was removed by rotary evaporation and the crude product was purified by column chromatography on silica gel using hexane/dichloromethane (2:1 → 1:1) to afford the title compound as a white solid (1.39 g, 83% yield in two steps). R_f = 0.3 (hexane/dichloromethane = 2:1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.78 (d, J = 8.0 Hz, 2H), 7.22-7.28 (m, 5H), 7.06 (d, J = 7.0 Hz, 2H), 5.77-5.83 (m, 1H), 5.33 (d, J = 17.5 Hz, 1H), 5.26 (d, J = 10.0 Hz, 1H), 4.31 (s, 2H), 3.89 (d, J = 6.0 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 143.5, 135.9, 132.0, 131.4, 129.5, 128.3, 128.1, 127.7, 122.2, 119.9, 85.6, 81.6, 49.2, 36.7, 21.4; IR (neat, cm^{-1}) 2904, 1460, 1376, 723; MS(EI) *m/z* (relative intensity) 325 (M$^+$, 5), 222 (20), 170 (80), 142 (70), 115 (100).

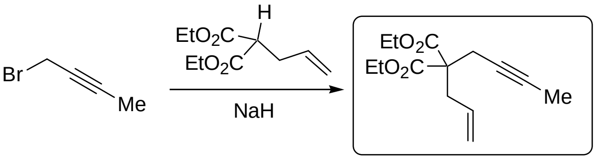
_N_-Allyl-_N_-(2-butynyl)-4-tolylsulfonamide



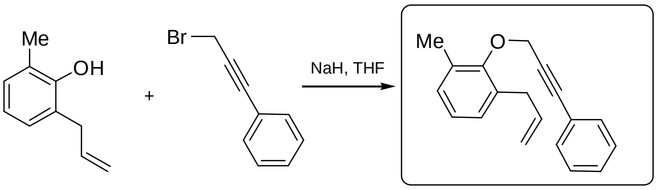
Allylamine (15.0 mL, 200 mmol) was charged into a 3-necked round bottom flask, followed by the addition of freshly distilled diethyl ether (50 mL) at room temperature under nitrogen. 1-Bromo-2-butyne (1.86 mL, 20 mmol) was added dropwise at 0 °C and the reaction mixtures were stirred at room temperature for 2 hours. The reaction was quenched with water and extracted with ethyl acetate (3 × ~100 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. The crude mixture was passed through a short silica pad (5 cm width × 10 cm height). Solvent was removed in *vacuo* and the *N*-allyl-*N*-(2-butynyl)amine product was used in next step without further purification.

To a mixture of *N*-allyl-*N*-(2-butynyl)amine (crude), triethylamine (4 mL), and dichloromethane (50 mL) was added a dichloromethane solution of *p*-toluenesulfonyl chloride (4 g, 22 mmol) at 0 °C. The reaction mixture was slowly warmed to room temperature and stirred for 2 hours. Water (~100 mL) was added to quench the reaction, and the aqueous phase was extracted with chloroform (2 × ~100 mL). The combined organic layers were washed with brine and dried over sodium sulfate. Solvent was removed by rotary evaporation and the crude product was purified by column chromatography on silica gel using hexane/dichloromethane (4:1) to afford the title compound as a colorless liquid (2.30 g, 44% yield in two steps). $R_f = 0.2$ (hexane/dichloromethane = 4:1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.70 (d, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 7.5 Hz, 2H), 5.67-5.73 (m, 1H), 5.25 (d, *J* = 17.0 Hz, 1H), 5.18 (d, *J* = 10.5 Hz, 1H), 3.98 (d, *J* = 2.0 Hz, 2H), 3.77 (d, *J* = 5.0 Hz, 2H), 2.39 (s, 3H), 1.51 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 143.5, 136.4, 132.4, 129.5, 128.1, 119.7, 81.8, 71.9, 49.2, 36.5, 21.7, 3.4; IR (neat, cm^{-1}) 3073, 3062, 2980, 2914, 2847, 2294, 2223, 1644, 1593, 1491, 1439, 1349, 1255, 1162, 1092, 1055, 899, 814, 735, 663, 572, 545; MS(EI) *m/z* (relative intensity) 263 (M$^+$, 5), 248 (10), 184 (40), 155 (60), 108 (100); HRMS cald. for $C_{14}H_{17}NO_2S$ 263.09800, found 263.09809.

Diethyl 7-octen-2-yne-5,5-dicarboxylate[11]



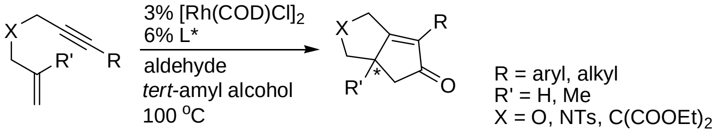
Diethyl 1-butene-4,4-dicarboxylate (2.0 g, 10 mmol) was charged to a 3-necked round bottom flask followed by the addition of dry THF (30 mL) under nitrogen at room temperature. NaH (360 mg, 15 mmol, prewashed with dry hexane) was added protionwise to the reaction mixture at 0 °C and stirred for 2 hours. White suspension was observed. 1-Bromo-2-butyne (1.86 mL, 20 mmol) was then added dropwise at 0 °C, and the reaction mixture was slowly warmed to room temperature with stirring for 3 hours. The reaction was quenched by water (~50 mL), and the aqueous phase was extracted by diethyl ether (3 × ~100 mL). The combined organic phase was washed with water, brine and dried over sodium sulfate. Solvent was removed by rotary evaporation, and the crude mixture was purified by distillation under reduced pressure to afford the title compound as a viscous colorless oil (2.31 g, 92% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.63 (m, 1H), 5.15 (d, *J* = 17.0 Hz, 1H), 5.09 (d, *J* = 10.0 Hz, 1H), 4.19 (q, *J* = 7.0 Hz, 4H), 2.78 (d, *J* = 7.5 Hz, 2H), 2.72 (q, *J* = 2.5 Hz, 2H), 1.75 (t, *J* = 2.5 Hz, 3H), 1.24 (t, *J* = 7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 169.9, 131.8, 119.3, 78.6, 73.2, 61.3, 56.8, 36.3, 22.7, 13.9, 3.3; IR (neat, cm^{-1}) 3646, 3472, 3083, 2982, 2929, 2233, 1739, 1639, 1465, 1441, 1325, 1292, 1218, 1136, 1096, 1036, 912, 855, 661, 574; MS(EI) *m/z* (relative intensity) 252 (M$^+$, 20), 194 (100).



3-Phenyl-1-(2-methyl-6-allyl-1-phenyoxy)propyne

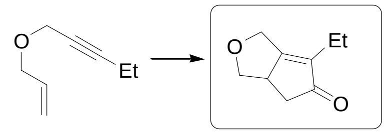
The general procedure for condensation was followed: viscous colorless liquid, R_f = 0.4 (hexane/ethyl acetate = 50/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.43-7.45 (m, 2H), 7.31-7.33 (m, 3H), 7.00-7.09 (m, 3H), 5.98-6.05 (m, 1H), 5.08-5.13 (m, 2H), 4.74 (s, 2H), 3.55 (d, 2H, *J* = 7.0 Hz), 2.39 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.3, 137.6, 133.6, 131.9, 131.7, 129.6, 128.8, 128.5, 128.3, 124.8, 122.8, 116.0, 87.0, 84.9, 61.5, 34.6, 16.9; IR (neat, cm^{-1}) 3078, 3062, 2975, 2914, 2852, 2233, 1639, 1539, 1485, 1465, 1364, 1256, 1184, 1086, 993, 906, 757, 691, 517; MS(EI) *m/z* (relative intensity) 178 (M$^+$, 5), 149 (40), 135 (65), 121 (100); HRMS cald. for $C_{19}H_{18}ONa$ 285.1255, found 285.1260.

3. General procedures for catalytic asymmetric Pauson-Khand cyclization reaction



General procedures for asymmetric Pauson-Khand-type cyclization of various enynes: $[Rh(COD)Cl]_2$ (4.4 mg, 9.0 μmol), (*S*)-BisBenzodioxanPhos (11.5 mg, 18.0 μmol), aldehyde (0.45 mmol, 1.5 equivalent with respected to enyne) and Teflon-coated magnetic stirrer bar (3 mm × 10 mm) were charged to a Teflon-lined screw-capped vials on bench-top at room temperature with continuous stirring. Enynes (0.3 mmol) was then added. These vials were evacuated and backfilled with nitrogen (3 cycles), followed by the addition of unpurified *tert*-amyl alcohol (0.2 mL, 1.5 M, from bench grade 4L bottle, prior bubbled with nitrogen for 2 mins). The reaction mixtures were magnetically stirred at a preheated 100 °C (± 3 °C) oil bath for 36 hours (reaction times were unoptimized for each substrate). The vials were allowed to reach room temperature. Diethyl ether or ethyl acetate (~2 mL) was added. The crude reaction mixtures were directly purified by column chromatography on silica gel using hexane/ethyl acetate as the eluent to afford chiral bicyclic cyclopentenones. The enantiomeric excess of the products were determined by chiral HPLC analysis using Chiralcel® columns.

4. Characterization data of PKR products

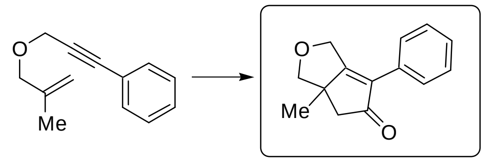


2-Ethyl-7-oxabicyclo[3.3.0]oct-1-en-3-one[3] **(Table 2, entry 1).**

Purified by column chromatography (2 cm diameter × ~20 cm height) on silica gel using hexane/ethyl acetate (3:1) as eluent to obtain the title compound as colorless oil. 61% yield; 96% *ee*; R_f = 0.3 (hexane/ethyl acetate = 2:1); ^{1}H NMR (CDCl$_3$, 500 MHz) δ 4.61 (q, *J* = 15.5 Hz, 2H), 4.30-4.34 (m, 1H), 3.19-3.23 (m, 2H), 2.64-2.71 (dd, *J* = 5.5 Hz, 18.0 Hz, 1H), 2.19-2.33 (m, 2H), 2.10-2.17 (dd, *J* = 2.5 Hz, 18.0 Hz, 1H), 1.12 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 208.0, 175.1, 138.6, 71.8, 64.8, 43.2, 38.6, 17.6, 16.3; MS(EI) *m/z* (relative intensity) 152 (M$^+$, 100), 123 (40), 105 (50).

Chiral HPLC conditions

Column:	Chiralcel AS-H
Solvent:	Hex:IPA = 9:1
Flow rate:	1.0 mL/ min
UV lamp:	210 nm
Retention time:	9.6, 11.7 min

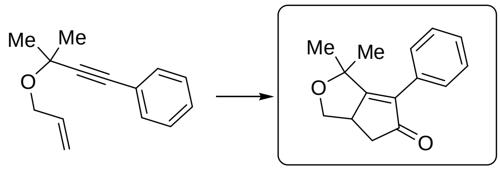


2-Phenyl-5-methyl-7-oxabicyclo[3.3.0]oct-1-en-3-one[12] **(Table 2, entry 2).**

Purified by column chromatography (2 cm diameter × ~20 cm height) on silica gel using hexane/ethyl acetate (3:1) as eluent to obtain the title compound as light yellow oil. 69% yield; 91% *ee*; R_f = 0.3 (hexane/ethyl acetate = 2:1); ^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.33-7.51 (m, 5H), 4.98 (d, *J* = 17.0 Hz, 1H), 4.60 (d, *J* = 17.0 Hz, 1H), 4.03 (d, *J* = 8.0 Hz, 1H), 3.43 (d, *J* = 8.0 Hz, 1H), 2.60 (d, *J* = 17.0 Hz, 1H), 2.54 (d, *J* = 17.0 Hz, 1H), 1.39 (s, 3H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 206.7, 180.6, 133.2, 130.5, 128.7, 128.6, 128.1, 76.5, 65.3, 48.7, 47.8, 24.7; MS(EI) *m/z* (relative intensity) 214 (M$^+$, 80), 184 (20), 169 (40), 141 (100), 115 (70).

Chiral HPLC conditions

Column:	Chiralcel AS-H
Solvent:	Hex:IPA = 9:1
Flow rate:	1.0 mL/ min
UV lamp:	254 nm
Retention time:	9.7, 10.8 min

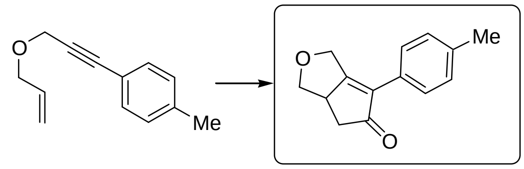


2-Phenyl-8,8-dimethyl-7-oxabicyclo[3.3.0]oct-1-en-3-one[5] (Table 2, entry 3).

Purified by column chromatography (2 cm diameter × ~20 cm height) on silica gel using hexane/ethyl acetate (3:1) as eluent to obtain the title compound as white solid. 78% yield; 91% *ee*; R_f = 0.3 (hexane/ethyl acetate = 3:1); Mp. = 96-98 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.33-7.41 (m, 3H), 7.27-7.29 (m, 2H), 4.32 (t, 1H, J = 8.0 Hz), 3.47-3.53 (m, 1H), 3.38 (dd, 1H, J = 8.0 Hz, 11.0 Hz), 2.28 (dd, 1H, J = 6.5 Hz, 17.5 Hz), 2.31 (dd, 1H, J = 3.5 Hz, 18.0 Hz), 1.65 (s, 3H), 1.13 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 201.1, 184.0, 136.2, 130.8, 129.0, 128.4, 128.3, 78.8, 69.9, 44.0, 39.2, 29.2, 24.1; MS(EI) *m/z* (relative intensity) 218 (M^+, 50), 213 (100), 200 (10), 185 (65), 171 (25), 157 (60).

Chiral HPLC conditions

Column:	Chiralcel AD-H
Solvent:	Hex:IPA = 9:1
Flow rate:	1.0 mL/ min
UV lamp:	254 nm
Retention time:	6.3, 7.0 min

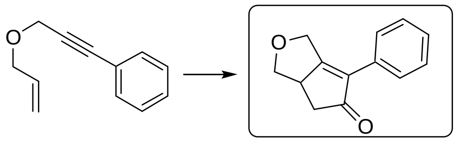


2-(4-Methylphenyl)-7-oxabicyclo[3.3.0]oct-1-en-3-one (Table 2, entry 4).

Purified by column chromatography (2 cm diameter × ~20 cm height) on silica gel using hexane/ethyl acetate (3:1) as eluent to obtain the title compound as white solid. 83% yield; 89% *ee*; R_f = 0.4 (hexane/ethyl acetate = 2:1); $[\alpha]^{25}_D$ = +55.9° (*c* = 0.10); Melting point: 49-51 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.42 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 1H), 4.93 (d, *J* = 16.0 Hz, 1H), 4.59 (d, *J* = 16.0 Hz, 1H), 4.37 (t, *J* = 7.5 Hz, 1H), 3.28-3.32 (m, 1H), 3.23 (dd, *J* = 8.0 Hz, 11.5 Hz, 1H), 2.84 (dd, *J* = 6.5 Hz, 17.5 Hz, 1H), 2.37 (s, 3H), 2.32 (dd, *J* = 3.5 Hz, 18.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 202.3, 175.2, 159.8, 134.1, 129.3, 123.2, 114.0, 71.3, 66.3, 43.1, 40.2, 23.8; IR (neat, cm^{-1}) 3020, 2397, 1747, 1511, 1419, 1215, 1040, 922, 756, 669; MS(EI) *m/z* (relative intensity) 214 (M^+, 100), 184 (30), 169 (40), 156 (45), 141 (70); HRMS cald. for $C_{14}H_{14}O_2$ 214.09938, found 214.09943.

Chiral HPLC conditions

Column:	Chiralcel AS-H
Solvent:	Hex:IPA = 9:1
Flow rate:	1.0 mL/ min
UV lamp:	254 nm
Retention time:	13.0, 18.5 min

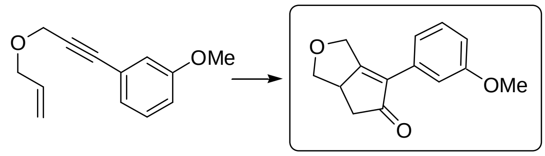


2-Phenyl-7-oxabicyclo[3.3.0]oct-1-en-3-one[13] (Table 2, entry 5).

Purified by column chromatography (2 cm diameter × ~20 cm height) on silica gel using hexane/ethyl acetate (3:1) as eluent to obtain the title compound as light yellow oil. 81% yield; 85% *ee* (*S* configuration); R_f = 0.3 (hexane/ethyl acetate = 2:1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.52 (d, *J* = 7.5 Hz, 2H), 7.39-7.42 (m, 2H), 7.33-7.37 (m, 1H), 4.93 (d, *J* = 16.5 Hz, 1H), 4.59 (d, *J* = 16.0 Hz, 1H), 4.38 (t, *J* = 8.0 Hz, 1H), 3.30-3.35 (m, 1H), 3.23 (dd, *J* = 8.0 Hz, 11.5 Hz, 1H), 2.85 (dd, *J* = 6.5 Hz, 18.5 Hz, 1H), 2.34 (dd, *J* = 4.0 Hz, 18.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 206.7, 177.3, 134.5, 130.5, 128.6, 128.5, 127.9, 71.2, 66.2, 43.2, 40.2; MS(EI) *m/z* (relative intensity) 200 (M^+, 70), 170 (40), 158 (50), 141 (100).

Chiral HPLC conditions

Column:	Chiralcel AD-H
Solvent:	Hex:IPA = 9:1
Flow rate:	1.0 mL/ min
UV lamp:	254 nm
Retention time:	12.8, 17.0 min

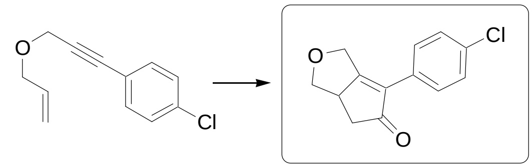


2-(3-Methoxyphenyl)-7-oxabicyclo[3.3.0]oct-1-en-3-one (Table 2, entry 6).

Purified by column chromatography (2 cm diameter × ~20 cm height) on silica gel using hexane/ethyl acetate (3:1) as eluent to obtain the title compound as light yellow viscous oil. 79% yield; 70% *ee*; R_f = 0.3 (hexane/ethyl acetate = 2:1); $[\alpha]^{25}_{D}$ = +17.2° (*c* = 0.11); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.31 (t, *J* = 7.5 Hz, 1H), 7.16 (s, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.90 (dd, *J* = 2.5 Hz, 8.0 Hz, 1H), 4.92 (d, *J* = 16.0 Hz, 1H), 4.59 (d, *J* = 16.0 Hz, 1H), 4.37 (t, *J* = 7.5 Hz, 1H), 3.82 (s, 3H), 3.29-3.33 (m, 1H), 3.23 (dd, *J* = 7.5 Hz, 11.5 Hz, 1H), 2.84 (dd, *J* = 6.5 Hz, 17.5 Hz, 1H), 2.33 (dd, *J* = 4.0 Hz, 17.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 206.7, 177.7, 159.6, 134.5, 131.8, 129.6, 120.5, 114.3, 113.4, 71.3, 66.3, 55.2, 43.3, 40.3; IR (neat, cm^{-1}) 3019, 2386, 1705, 1511, 1413, 1215, 1045, 1024, 922, 758, 669; MS(EI) *m/z* (relative intensity) 230 (M^+, 100), 213 (5), 199 (10), 185 (20), 171 (20), 159 (30); HRMS cald. for $C_{14}H_{14}O_3$ 230.09430, found 230.09422.

Chiral HPLC conditions

Column:	Chiralcel AS-H
Solvent:	Hex:IPA = 9:1
Flow rate:	1.0 mL/ min
UV lamp:	254 nm
Retention time:	21.9, 48.3 min

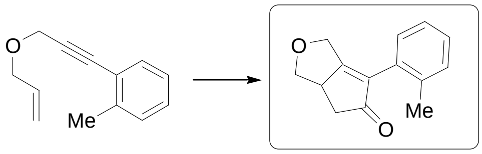


2-(4-Chlorophenyl)-7-oxabicyclo[3.3.0]oct-1-en-3-one[14] (Table 2, entry 7).

Purified by preparative TLC on silica gel using hexane/ethyl acetate (2:1) as eluent to obtain the title compound as light yellow oil. 72% yield; 49% *ee*; $R_f = 0.3$ (hexane/ethyl acetate = 2:1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.48 (d, *J* = 9.0 Hz, 2H), 7.38 (d, *J* = 9.0 Hz, 1H), 4.92 (d, *J* = 16.0 Hz, 1H), 4.57 (d, *J* = 16.0 Hz, 1H), 4.38 (t, *J* = 8.0 Hz, 1H), 3.30-3.37 (m, 1H), 3.25 (dd, *J* = 7.5 Hz, 11.0 Hz, 1H), 2.85 (dd, *J* = 6.0 Hz, 18.0 Hz, 1H), 2.33 (dd, *J* = 3.5 Hz, 18.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 205.3, 175.1, 159.7, 134.0, 129.3, 123.3, 114.1, 71.1, 66.3, 43.2, 40.2; MS(EI) *m/z* (relative intensity) 236 (M^+, 20), 234 (M^+, 60), 204 (15), 192 (25), 169 (95), 141 (100).

Chiral HPLC conditions

Column:	Chiralcel AS-H
Solvent:	Hex:IPA = 98:2
Flow rate:	1.0 mL/ min
UV lamp:	254 nm
Retention time:	26.1, 32.4 min

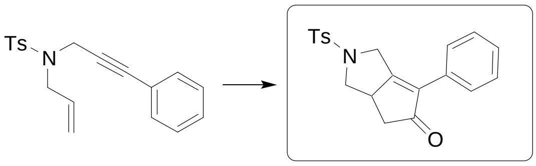


2-(2-Methylphenyl)-7-oxabicyclo[3.3.0]oct-1-en-3-one (Table 2, entry 8).

Purified by column chromatography (2 cm diameter × ~20 cm height) on silica gel using hexane/ethyl acetate (3:1) as eluent to obtain the title compound as colorless oil. 78% yield; 84% *ee*; $R_f = 0.4$ (hexane/ethyl acetate = 2:1); $[\alpha]^{25}_D = +39.1°$ ($c = 0.12$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.19-7.29 (m, 3H), 7.10 (d, *J* = 7.5 Hz, 1H), 4.63 (d, *J* = 16.0 Hz, 1H), 4.42 (t, *J* = 7.5 Hz, 1H), 4.36 (d, *J* = 15.5 Hz, 1H), 3.38-3.42 (m, 1H), 3.34 (dd, *J* = 7.0 Hz, 11.0 Hz, 1H), 2.85 (dd, *J* = 5.5 Hz, 17.5 Hz, 1H), 2.35 (dd, *J* = 3.5 Hz, 17.5 Hz, 1H); 2.18 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 202.3, 175.2, 159.8, 134.1, 129.3, 128.9, 123.2, 114.0, 111.3, 71.3, 66.3, 43.1, 40.2, 23.8; IR (neat, cm^{-1}) 3021, 2397, 1737, 1510, 1419, 1215, 1043, 922, 758, 669; MS(EI) *m/z* (relative intensity) 214 (M$^+$, 100), 199 (5), 183 (40), 169 (50), 154 (30), 141 (70); HRMS cald. for $C_{14}H_{14}O_2$ 214.09938, found 214.09946.

Chiral HPLC conditions

Column:	Chiralcel AD-H
Solvent:	Hex:IPA = 9:1
Flow rate:	1.0 mL/ min
UV lamp:	254 nm
Retention time:	11.7, 12.6 min

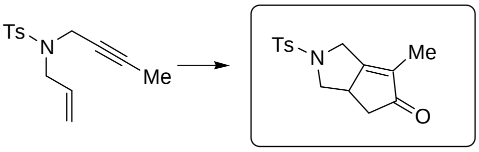


2-Phenyl-7-[(4-methylphenyl)sulfonyl]-7-azabicyclo[3.3.0]oct-1-en-3-one[15] (Table 2, entry 10)

Purified by column chromatography (2.0 cm diameter × ~20 cm height) on silica gel using hexane/ethyl acetate (2:1) as eluent to obtain the title compound as light yellow solid. 94% yield; 80% *ee*; R_f = 0.3 (hexane/ethyl acetate = 2:1); Melting point: 159-160 °C; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.36-7.46 (m, 5H), 7.30 (d, *J* = 8.0 Hz, 2H), 4.63 (dd, *J* = 2.0 Hz, 17.0 Hz, 1H), 4.04-4.09 (m, 2H), 3.18-3.23 (m, 1H), 2.78 (dd, *J* = 6.5 Hz, 17.5 Hz, 1H), 2.61 (dd, *J* = 9.0 Hz, 10.5 Hz, 1H), 2.40 (s, 3H), 2.25 (dd, *J* = 4.0 Hz, 18.0 Hz, 1H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 206.4, 171.9, 144.0, 136.0, 133.6, 130.0, 129.8, 128.9, 128.7, 128.2, 127.4, 52.0, 48.3, 41.8, 40.7, 21.5; MS(EI) *m/z* (relative intensity) 353 (M$^+$, 20), 198 (100), 171 (50), 141 (60), 128 (45).

Chiral HPLC conditions

Column:	Chiralcel AD-H
Solvent:	Hex:IPA = 9:1
Flow rate:	1.0 mL/ min
UV lamp:	254 nm
Retention time:	44.8, 53.9 min

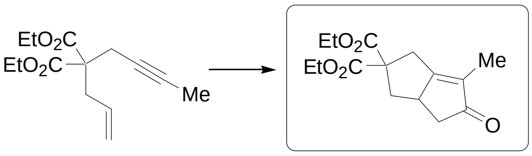


2-Methyl-7-[(4-methylphenyl)sulfonyl]-7-azabicyclo[3.3.0]oct-1-en-3-one[16] (Table 2, entry 11)

Purified by column chromatography (2.0 cm diameter × ~20 cm height) on silica gel using hexane/ethyl acetate (2:1) as eluent to obtain the title compound as white solid. 97% yield; 88% *ee*; R_f = 0.2 (hexane/ethyl acetate = 2:1); Melting point: 103-104 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.73 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 4.23 (d, *J* = 16.0 Hz, 1H), 3.96-4.00 (m, 2H), 2.96-3.06 (m, 1H), 2.54-2.62 (m, 2H), 2.44 (s, 3H), 2.03 (dd, *J* = 3.0 Hz, 17.5 Hz, 1H), 1.68 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 205.3, 171.0, 144.0, 134.1, 133.9, 129.9, 127.4, 52.6, 46.7, 41.6, 39.2, 21.5, 8.8; MS(EI) *m/z* (relative intensity) 291 (M^+, 30), 263 (5), 155 (10), 136 (100).

Chiral HPLC conditions

Column:	Chiralcel AD-H
Solvent:	Hex:IPA = 9:1
Flow rate:	1.0 mL/ min
UV lamp:	254 nm
Retention time:	34.2, 37.9 min



Diethyl 2-methyl-3-oxobicyclo[3.3.0]oct-1-ene-7,7-dicarboxylate[17] (Table 2, entry 12).

Purified by column chromatography (2 cm diameter × ~20 cm height) on silica gel using hexane/ethyl acetate (4:1) as eluent to obtain the title compound as light yellow viscous oil. 91% yield; 69% *ee* (*S* configuration); R_f = 0.3 (hexane/ethyl acetate = 4:1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.21 (q, *J* = 6.5 Hz, 2H), 4.17 (q, *J* = 6.5 Hz, 2H), 3.16 (q, *J* = 14.5 Hz, 2H), 2.94 (m, 1H), 2.74 (dd, *J* = 7.0 Hz, 12.5 Hz, 1H), 2.60 (dd, *J* = 6.0 Hz, 18.0 Hz, 1H), 2.04 (dd, *J* = 3.0 Hz, 18.5 Hz, 1H), 1.68 (s, 3H), 1.61 (t, *J* = 13.0 Hz, 3H), 1.24 (t, *J* = 7.0 Hz, 3H), 1.22 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 203.9, 177.7, 171.5, 170.9, 132.8, 61.9, 61.8, 60.8, 42.6, 41.3, 39.0, 33.9, 13.9 (overlapped), 8.4; MS(EI) *m/z* (relative intensity) 280 (M^+, 40), 235 (20), 206 (80), 178 (30), 133 (100).

Chiral HPLC conditions

Column:	Chiralcel AS-H
Solvent:	Hex:IPA = 9:1
Flow rate:	1.0 mL/ min
UV lamp:	254 nm
Retention time:	12.4, 15.6 min

5. References

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