Supplementary Material (ESI) for Chemical Communications

Supporting Information

Formate as CO Surrogate for Cascade Processes: Rh-Catalyzed Cooperative Decarbonylation and Asymmetric Pauson-Khand-type Cyclization Reactions

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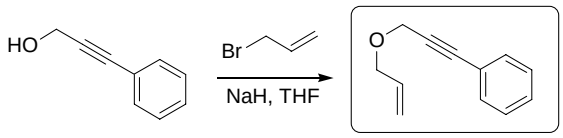
1. General considerations.

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further 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. Formates (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, (*S*)-BINAP, (*S*)-tol-BINAP, (*S*)-xyl-BINAP, (*S*)-SYNPHOS, (*S*)-P-Phos and (*R*,*R*)-Me-Duphos 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. ^{1}H 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 HP-1100 system 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 achiral ligand was used. GC-MS analysis was conducted on a HP 6890 system with a HP 5973N mass selective detector using a HP5MS column (30 m × 0.25 mm).

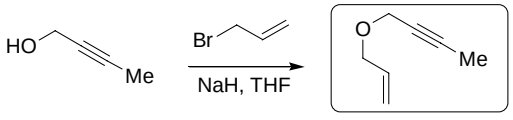
2. Preparation of enyne substrates

3-(Allyloxy)-1-phenyl-1-propyne (1a)[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).

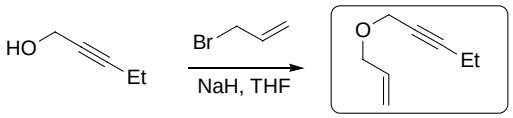
4-(Allyloxy)-2-butyne (1b)[3]



The general procedures of condensation of arylpropargyl alcohol with allyl bromide were followed: 2-Butyn-1-ol (4.0 g, 57.1 mmol), NaH (2.1 g, 87.5 mmol, prewashed with dry hexane), allyl bromide (9.7 mL, 115 mmol) and freshly distilled THF (200 mL) were used to obtain the

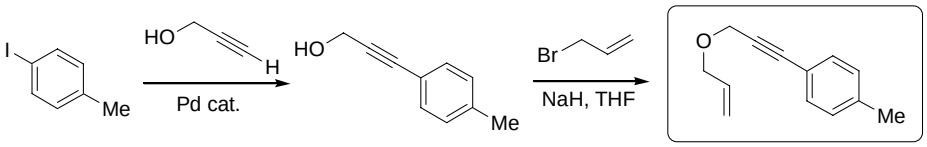
title compound as colorless liquid (5.5 g, 88% yield). General procedure workup and purified by vac-transfer. R_f = 0.2 (hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.90 (tdd, *J* = 17.0 Hz, 10.0 Hz, 5.5 Hz, 1H), 5.28 (dd, *J* = 17.0 Hz, 2.0 Hz, 1H), 5.19 (dd, *J* = 10.0 Hz, 2.0 Hz, 1H), 4.10 (q, *J* = 2.5 Hz, 2H), 4.04 (d, *J* = 5.5 Hz, 2H), 1.85 (t, *J* = 2.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 134.1, 117.5, 82.3, 75.0, 70.4, 57.6, 3.5; MS(EI) *m/z* (relative intensity) 110 (M^+, 10), 69 (100).

5-(Allyloxy)-3-pentyne (1c)[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-(Allyloxy)-1-(4-methylphenyl)-1-propyne (1d)

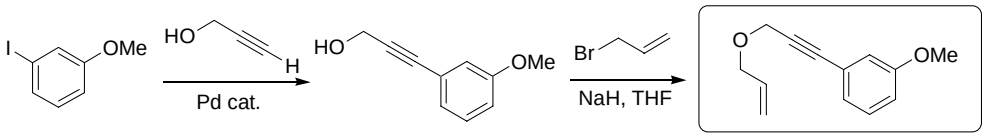


The procedure of Sonogashira coupling of propagyl alcohol with ArI were used: 4-Iodotoluene (10.9 g, 50 mmol), $Pd(PPh_3)_2Cl_2$ (3 mol%), CuI (6 mol%), piperidine (8.4 g, 100 mmol), propagyl alcohol (3.07 mL, 52 mmol) and freshly distilled toluene (50 mL) were charged into a round-bottom flask with 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[4] (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[4] (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 (1e)

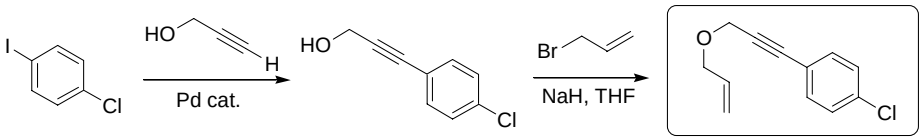


The general procedures for Sonogashira coupling of propagyl alcohol with ArI were used: 3-Iodoanisole (11.7 g, 50 mmol), $Pd(PPh_3)_2Cl_2$ (3 mol%), CuI (6 mol%), piperidine (8.4 g, 100 mmol), propagyl alcohol (3.07 mL, 52 mmol) and freshly distilled toluene (50 mL) were used to afford 3-(3-methoxyphenyl)-2-propyn-1-ol[5] (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[5] (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 (1f)

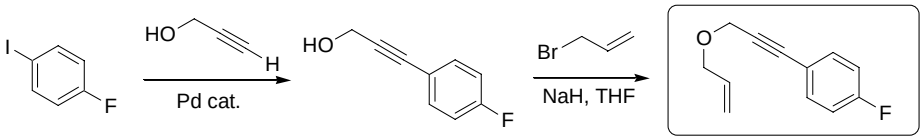


The general procedures for Sonogashira coupling of propagyl alcohol with ArI were used: 4-Chloroiodobenzene (11.9 g, 50 mmol), $Pd(PPh_3)_2Cl_2$ (3 mol%), CuI (6 mol%), piperidine (8.4 g, 100 mmol), propagyl alcohol (3.07 mL, 52 mmol) and freshly distilled toluene (50 mL) were used to afford 3-(4-chlorophenyl)-2-propyn-1-ol[6] (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-(4-fluorophenyl)-1-propyne (1g)

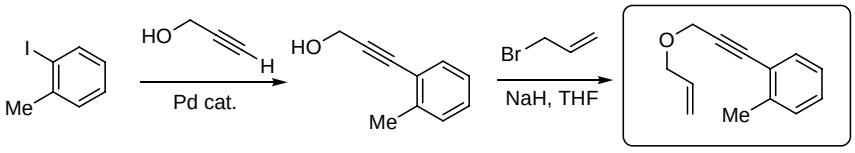


The general procedures for Sonogashira coupling of propagyl alcohol with ArI were used: 4-Iodoflurobenzene (11.1 g, 50 mmol), $Pd(PPh_3)_2Cl_2$ (3 mol%), CuI (6 mol%), piperidine (8.4 g, 100 mmol), propagyl alcohol (3.07 mL, 52 mmol) and freshly distilled toluene (50 mL) were used to afford 3-(4-fluorophenyl)-2-propyn-1-ol[7] (5.85 g, 78% yield) as 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 7.39 (d, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 8.5 Hz, 2H), 4.78 (s, 2H), 2.69 (brs, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 163.5, 161.5, 133.5 (d,

J_{CF} = 8.3 Hz), 118.5 (d, J_{CF} = 3.0 Hz), 115.5 (d, J_{CF} = 22.1 Hz), 86.9, 84.5, 51.3; MS(EI) *m/z* (relative intensity) 150 (M^+, 100); HRMS cald. for C_9H_7FO 150.04809, found 150.04820.

The general procedures of condensation of arylpropargyl alcohol with allyl bromide were followed: 3-(4-Fluorophenyl)-2-propyn-1-ol[7] (1.5 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-fluorophenyl)-1-propyne as colorless liquid (1.42 g, 75% yield). Purification was conducted by distillation under reduced pressure (89-90 °C, 2 mmHg). R_f = 0.2 (hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.41 (d, *J* = 8.5 Hz, 2H), 7.00 (t, *J* = 8.5 Hz), 5.95 (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), 4.13 (d, *J* = 6.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 163.5, 161.6, 134.0, 133.6 (d, J_{CF} = 8.4 Hz), 118.7, (d, J_{CF} = 3.0 Hz), 117.9, 115.5 (d, J_{CF} = 22.0 Hz), 85.1, 84.7, 70.7, 57.8; IR (neat, cm^{-1}) 3073, 3016, 2986, 2934, 2851, 2248, 1885, 1649, 1601, 1506, 1354, 1229, 1156, 1088, 992, 928, 837, 815, 563, 529; MS(EI) *m/z* (relative intensity) 190 (M^+, 10), 149 (100); HRMS cald. for $C_{12}H_{11}FO$ 190.07939, found 190.07923.

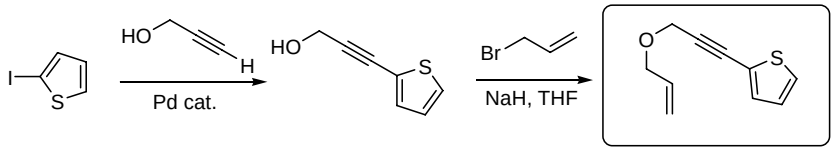
3-(Allyloxy)-1-(2-methylphenyl)-1-propyne (1i)



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[5] (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 (1j)

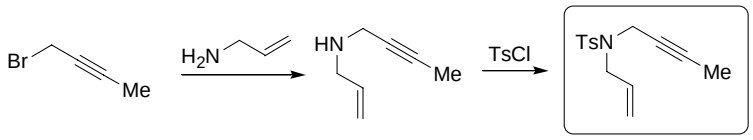


The general procedures for Sonogashira coupling of propagyl alcohol with ArI were used: 2-Iodothiophene (10.5 g, 50 mmol), $Pd(PPh_3)_2Cl_2$ (3 mol%), CuI (6 mol%), piperidine (8.4 g, 100 mmol), propagyl alcohol (3.07 mL, 52 mmol) and freshly distilled toluene (50 mL) were used to afford 3-(2-thiophenyl)-2-propyn-1-ol (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_-(2-butynyl)-4-tolylsulfonamide (1k)

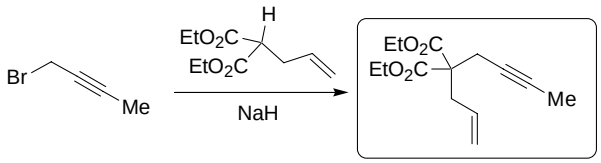


Allylamine (15.0 mL, 200 mmol) was charged into a 3-necked round bottom flask, followed by the addition of freshly distilled diethyl ether (50 mL) at room temperature under nitrogen. 1-Bromo-2-butyne (1.86 mL, 20 mmol) was added dropwise at 0 °C and the reaction mixtures were stirred at room temperature 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

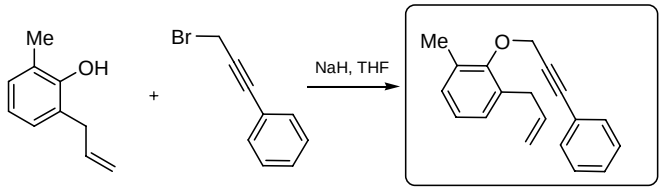
($CDCl_3$, 125 MHz) δ 143.5, 136.4, 132.4, 129.5, 128.1, 119.7, 81.8, 71.9, 49.2, 36.5, 21.7, 3.4; IR (neat, cm^{-1}) 3073, 3062, 2980, 2914, 2847, 2294, 2223, 1644, 1593, 1491, 1439, 1349, 1255, 1162, 1092, 1055, 899, 814, 735, 663, 572, 545; MS(EI) *m/z* (relative intensity) 263 (M^+, 5), 248 (10), 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 (1l)[8]



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). ^1H 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).

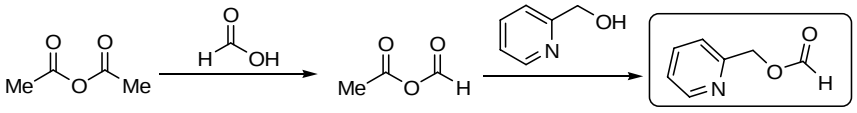
3-Phenyl-1-(2-methyl-6-allyl-1-phenyoxy)propyne (1m)



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.

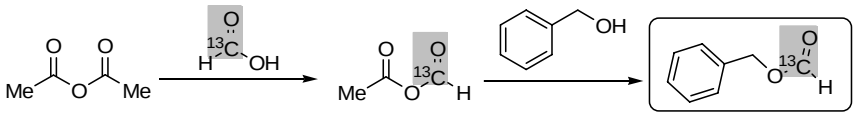
3. Preparation of pyridylmethyl formate and ^{13}C-labeled benzyl formate

2-Pyridylmethyl formate[9]

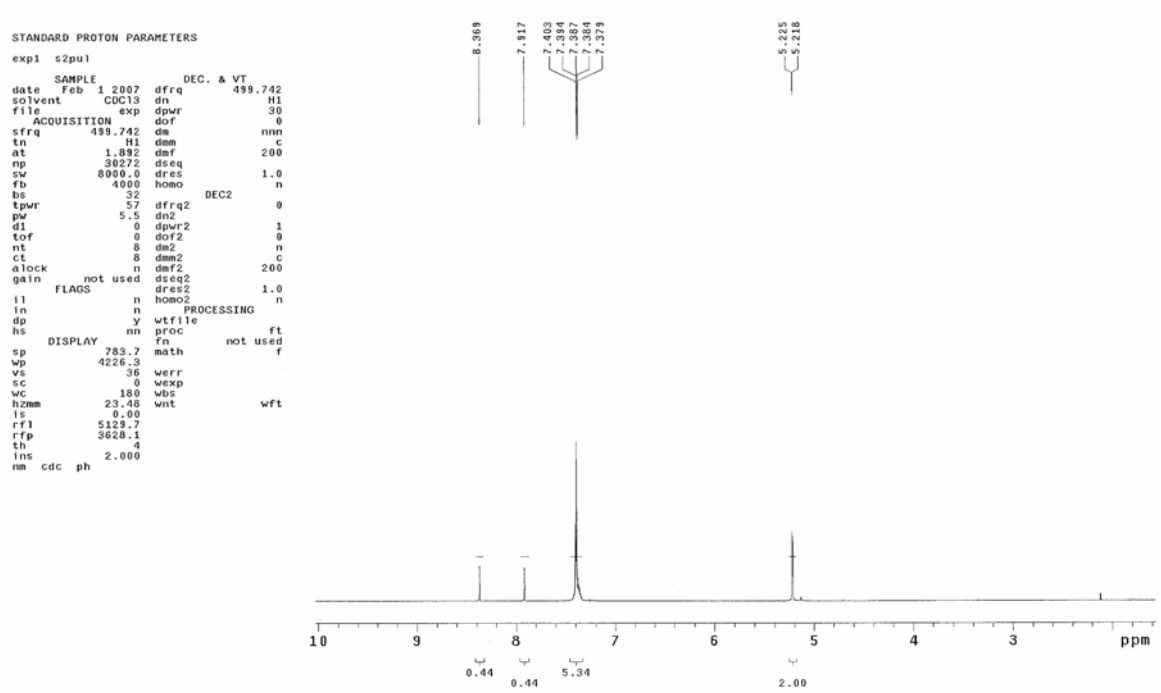


General procedure: To a stirring acetic anhydride (6.5 mL, 69 mmol) at 0 °C was added formic acid (2.6 mL, 99%, 69 mmol) dropwise. The reaction mixture was stirred at room temperature for 2 hours. The resulting formic acetic anhydride was cannulated to a stirring mixture of 2-pyridylmethanol (5 g, 46 mmol), $NaHCO_3$ (5.7 g, 69 mmol), and THF (25 mL). After stirring at RT for 1 hour, saturated aq. $NaHCO_3$ was added to the reaction mixture until gas evolution stopped. The resulting mixture was extracted with EtOAc (3 × ~50 mL). The organic layers were combined and washed with H_2O, saturated aq $NaHCO_3$, and brine, then were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel using 40% EtOAc in hexane as the eluent to give the desired product (6.1 g, 99%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (d, J = 4.0 Hz, 1H), 8.21 (s, 1H), 7.74 (dt, J = 1.5, 8.0 Hz, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.27 (dd, J = 5.0, 7.5 Hz, 1H), 5.3 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.4, 154.8, 149.4, 136.9, 123.1, 121.9, 65.9.

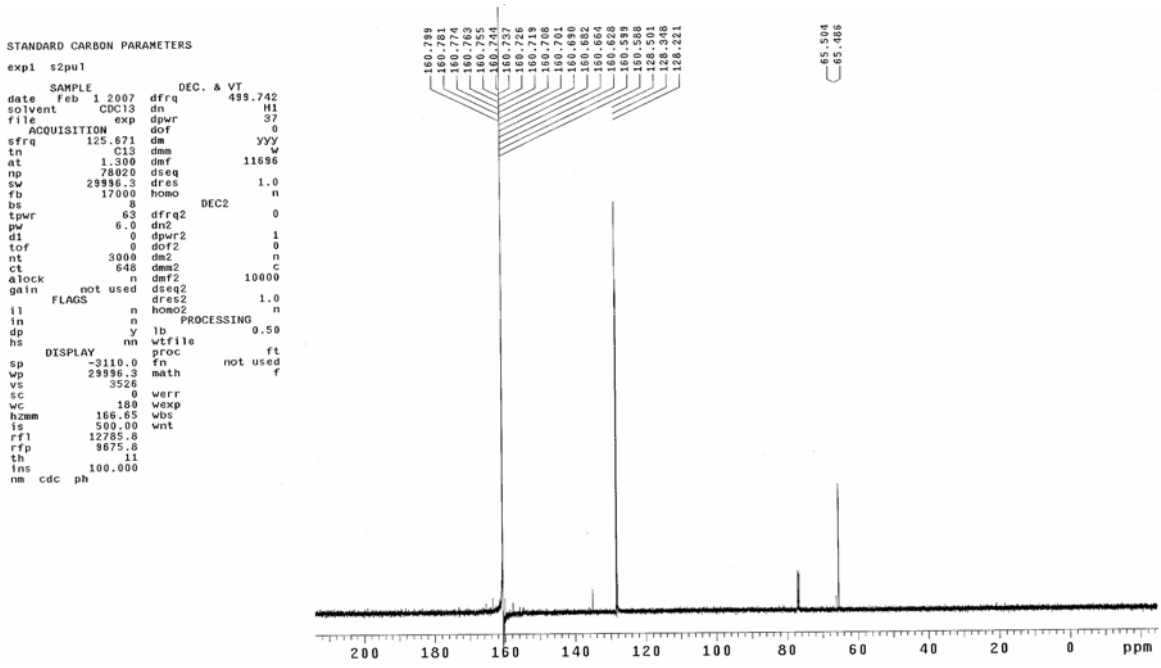
^{13}C-Enriched benzyl formate



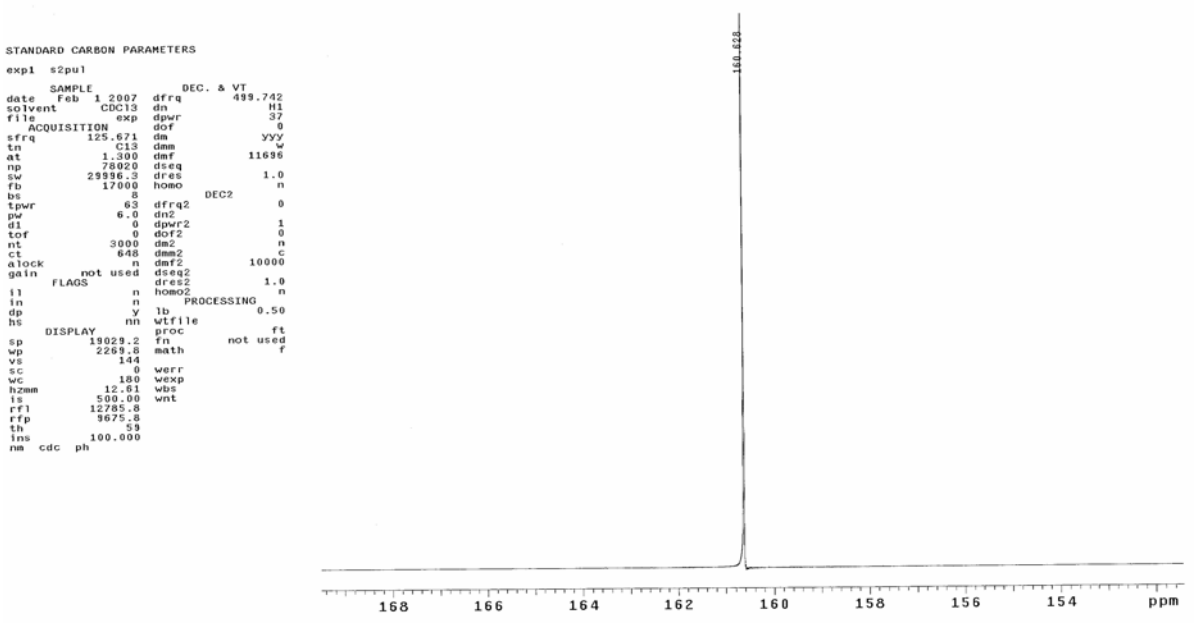
General procedures for the synthesis of 2-pyridylmethyl formate were used. Colorless liquid (90% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, J_{CH} = 226.0 Hz, 1 H), 7.38-7.40 (m, 5 H), 5.22 (d, J = 3.5 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.6, 135.1, 128.5, 128.3, 128.2, 65.5 (d, J_{CC} = 2.3 Hz); MS(EI) *m/z* (relative intensity) 137 (M^+, 80), 107 (40), 91 (100).



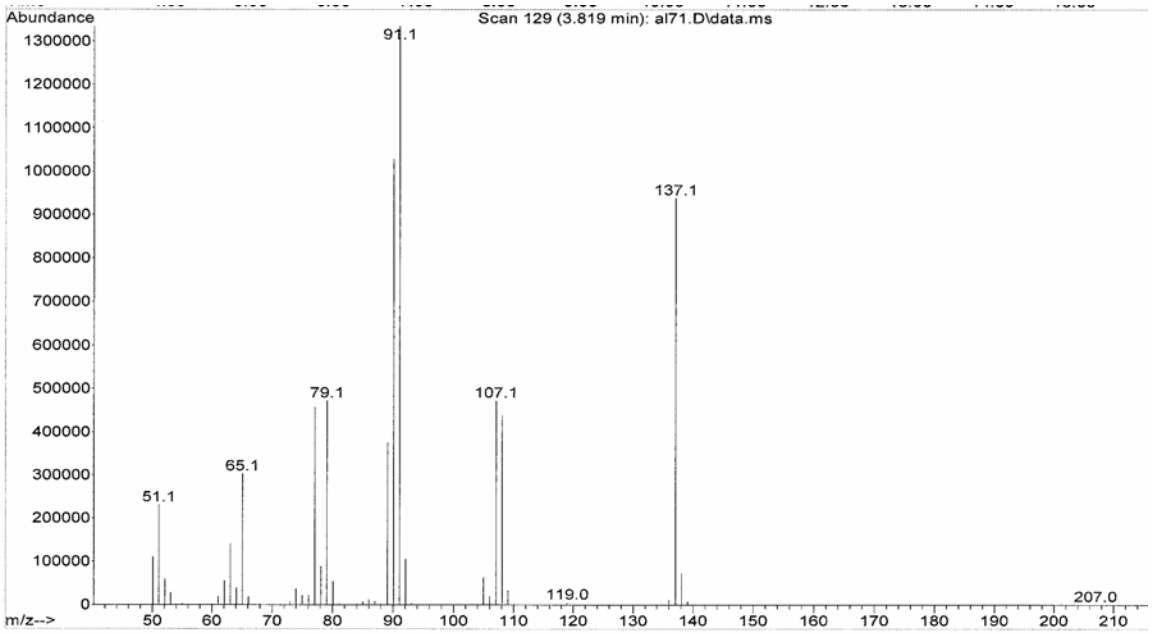
^{1}H NMR of ^{13}C-enriched benzyl formate



^{13}C NMR of ^{13}C-enriched benzyl formate

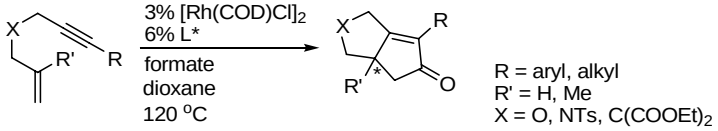


^{13}C NMR of ^{13}C-enriched benzyl formate (enlarged labeled region)



Mass spectrum of ^{13}C-enriched benzyl formate

4. General procedures for the cooperative decarbonylation–Pauson-Khand-type reaction using formate as CO surrogate

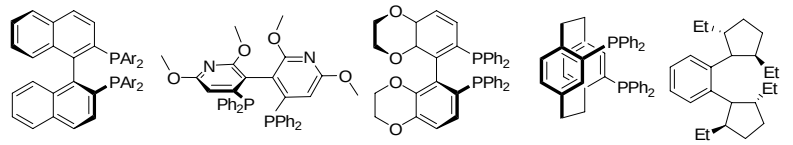


General procedures for asymmetric Pauson-Khand-type cyclization of various enynes: $[Rh(COD)Cl]_2$ (4.4 mg, 9.0 μmol), (*S*)-xyl-BINAP (16 mg, 18.0 μmol) and Teflon-coated magnetic stirrer bar (3 mm × 10 mm) were charged to a Teflon-lined screw-capped vials (or Schlenk flasks) on bench-top at room temperature. These vials were evacuated and backfilled with nitrogen (3 cycles), followed by the addition of anhydrous dioxane (0.5 mL) under nitrogen with continuous stirring for 30 mins. Enynes (0.3 mmol) and benzyl formate (1.5 mmol) were then added. The reaction mixtures were magnetically stirred at a preheated 120 °C (± 3 °C) oil bath for 3 days (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 (see details in Section 4).

Entry	Ligand	Rh-complex	Aldehyde	Solvent	%Yield	%*ee*
Ligand screening						
1	dppe	$[Rh(COD)Cl]_2$	2-pyridylmethyl formate	*t*-amylalcohol	23	/
2	dppp	$[Rh(COD)Cl]_2$	2-pyridylmethyl formate	*t*-amylalcohol	15	/
3	dppf	$[Rh(COD)Cl]_2$	2-pyridylmethyl formate	*t*-amylalcohol	32	/
4	(±)-BINAP	$[Rh(COD)Cl]_2$	2-pyridylmethyl formate	*t*-amylalcohol	38	/
Solvent screening						
5	(±)-BINAP	$[Rh(COD)Cl]_2$	2-pyridylmethyl formate	*t*-amylalcohol	38	/
6	(±)-BINAP	$[Rh(COD)Cl]_2$	2-pyridylmethyl formate	dioxane	47	/
7	(±)-BINAP	$[Rh(COD)Cl]_2$	2-pyridylmethyl formate	DMF	25	/
8	(±)-BINAP	$[Rh(COD)Cl]_2$	2-pyridylmethyl formate	toluene	37	/
Formate screening						
9	(±)-BINAP	$[Rh(COD)Cl]_2$	2-pyridylmethyl formate	dioxane	47	/
10	(±)-BINAP	$[Rh(COD)Cl]_2$	*n*-butyl formate	dioxane	20	/

11	(±)-BINAP	$[Rh(COD)Cl]_2$	*t*-butyl formate	dioxane	12	/
12	(±)-BINAP	$[Rh(COD)Cl]_2$	*n*-octyl formate	dioxane	23	/
13	(±)-BINAP	$[Rh(COD)Cl]_2$	benzyl formate	dioxane	42	/
14	(±)-BINAP	$[Rh(COD)Cl]_2$	*p*-chlorobenzyl formate	dioxane	60	/
Formate loading						
15	(±)-BINAP	$[Rh(COD)Cl]_2$	benzyl formate (1.0 eq.)	dioxane	18	/
16	(±)-BINAP	$[Rh(COD)Cl]_2$	benzyl formate (1.5 eq.)	dioxane	20	/
17	(±)-BINAP	$[Rh(COD)Cl]_2$	benzyl formate (5.0 eq.)	dioxane	42	/
18	(±)-BINAP	$[Rh(COD)Cl]_2$	benzyl formate (10.0 eq.)	dioxane	40	/

Chiral ligand screening for asymmetric PKR

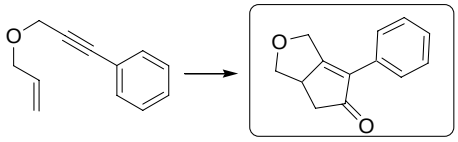


Ar = Ph, (*S*)-BINAP
Ar = *p*-tol, (*S*)-*p*-tol-BINAP
Ar = 3,5-xylyl, (*S*)-xyl-BINAP
(*S*)-P-Phos
(*S*)-BisbenzodioxanPhos
(*S*)-SYNPHOS
(*R*)-PHANEPHOS
(*R*,*R*)-Et-Duphos

19	(*S*)-BINAP	$[Rh(COD)Cl]_2$	benzyl formate	dioxane	45	70
20	(*S*)-tol-BINAP	$[Rh(COD)Cl]_2$	benzyl formate	dioxane	43	72
21	(*S*)-xyl-BINAP	$[Rh(COD)Cl]_2$	benzyl formate	dioxane	48	75
22	(*S*)-SYNPHOS	$[Rh(COD)Cl]_2$	benzyl formate	dioxane	38	41
23	(*S*)-P-Phos	$[Rh(COD)Cl]_2$	benzyl formate	dioxane	29	23
24	(*R*)-PHANEPHOS	$[Rh(COD)Cl]_2$	benzyl formate	dioxane	trace	n.d.
25	(*R*,*R*)-Et-Duphos	$[Rh(COD)Cl]_2$	benzyl formate	dioxane	33	10
Preliminary metal complex precursor screening						
26	(±)-BINAP	$Rh(COD)_2BF_4$	benzyl formate	dioxane	10	/
27	(±)-BINAP	$[Rh(COD)Cl]_2$/ $AgPF_6$	benzyl formate	dioxane	15	/
28	(±)-BINAP	$[Ir(COD)Cl]_2$	benzyl formate	dioxane	30	/
29	(±)-BINAP	$Ru_3(CO)_{12}$	benzyl formate	dioxane	15	/

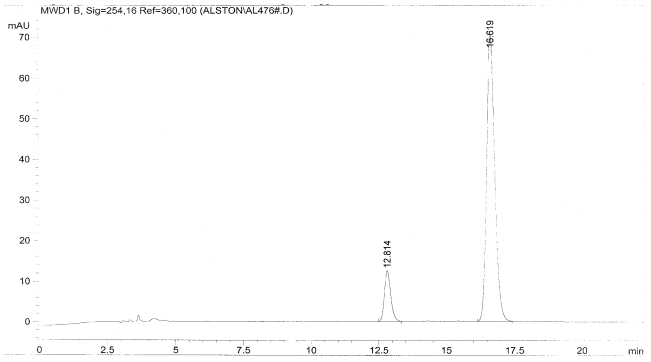
For all of the above preliminary optimizations, enyne **1a** was used. Reaction conditions were the same as the general procedures. Isolated yields were reported.

5. Characterization data of PKR products



2-Phenyl-7-oxabicyclo[3.3.0]oct-1-en-3-one[10] **(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 light yellow oil. 43% yield; 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).



Signal 1: MWD1 B, Sig=254,16 Ref=360,100

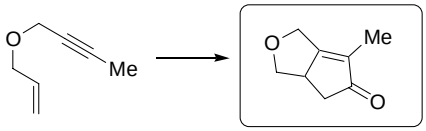
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.814	BB	0.2523	206.90604	12.55115	12.3344
2	16.619	BB	0.3218	1470.56140	70.36609	87.6656
Totals :				1677.46744	82.91724	

Results obtained with enhanced integrator!

*** End of Report ***

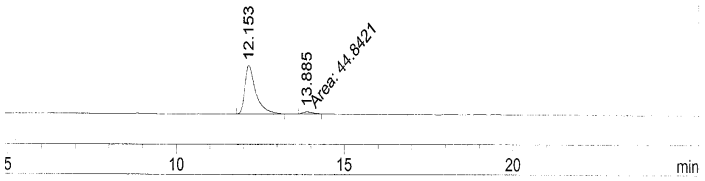
Chiral HPLC conditions

Column:	Chiralcel AD-H
Solvent:	Hex:IPA = 9:1
Flow rate:	1.0 mL/ min
UV lamp:	254 nm
Retention time:	12.8, 16.6 min



2-Methyl-7-oxabicyclo[3.3.0]oct-1-en-3-one[10] **(Table 2, entry 2).**

Purified by column chromatography (2 cm diameter × ~15 cm height) on silica gel using hexane/ethyl acetate (3:1) as eluent to obtain the title compound as colorless oil. 16% yield; R_f = 0.3 (hexane/ethyl acetate = 2:1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.54 (q, *J* = 15.0 Hz, 2H), 4.30-4.32 (m, 1H), 3.19-3.23 (m, 2H), 2.64-2.71 (dd, *J* = 5.5 Hz, 18.0 Hz, 1H), 2.09-2.17 (dd, *J* = 2.0 Hz, 18.0 Hz, 1H), 1.77 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 209.0, 176.1, 132.6, 71.8, 64.7, 43.2, 38.6, 8.9; MS(EI) *m/z* (relative intensity) 138 (M^+, 100), 123 (60), 105 (30).

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Signal 1: MWD1 E, Sig=210,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.153 BV    0.3366 1147.57092   50.22519  96.2394
   2  13.885 MM    0.3436   44.84212    2.17515   3.7606

Totals :                  1192.41305   52.40034

 Results obtained with enhanced integrator!
================================================================================
                          *** End of Report ***
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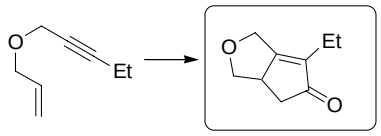
Chiral HPLC conditions

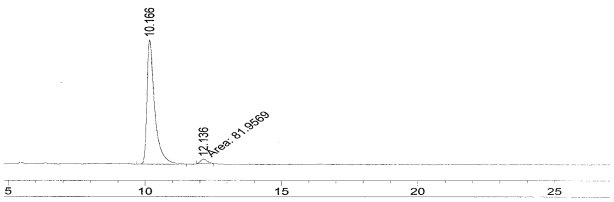
Column:	Chiralcel AS-H
Solvent:	Hex:IPA = 9:1
Flow rate:	1.0 mL/ min
UV lamp:	210 nm
Retention time:	12.2, 13.9 min



2-Ethyl-7-oxabicyclo[3.3.0]oct-1-en-3-oneError! Bookmark not defined. (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 colorless oil. 20% yield; 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).



Signal 1: MWD1 E, Sig=210,16 Ref=360,100

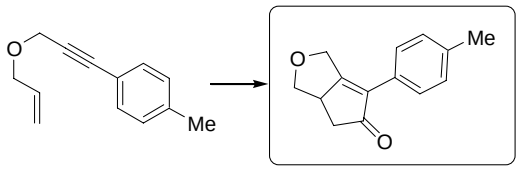
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.166	VB	0.2874	2619.79346	133.23909	96.9665
2	12.136	MM	0.2885	81.95692	4.73482	3.0335
Totals :				2701.75038	137.97391	

Results obtained with enhanced integrator!

*** End of Report ***

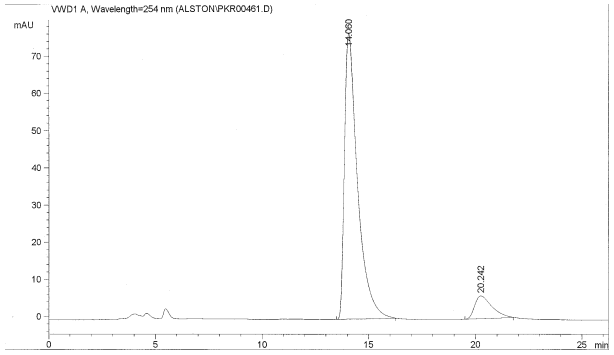
Chiral HPLC conditions

Column:	Chiralcel AS-H
Solvent:	Hex:IPA = 9:1
Flow rate:	1.0 mL/ min
UV lamp:	210 nm
Retention time:	10.2, 12.1 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. 44% yield; 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.



Signal 1: VWD1 A, Wavelength=254 nm

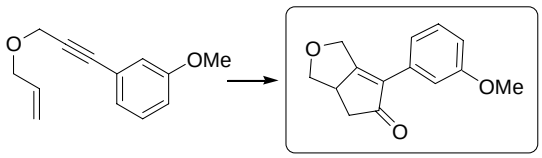
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.060	BB	0.6289	3264.54980	76.71992	90.5279
2	20.242	BB	0.8241	341.57483	6.08195	9.4721
Totals :				3606.12463	82.80187	

Results obtained with enhanced integrator!

*** End of Report ***

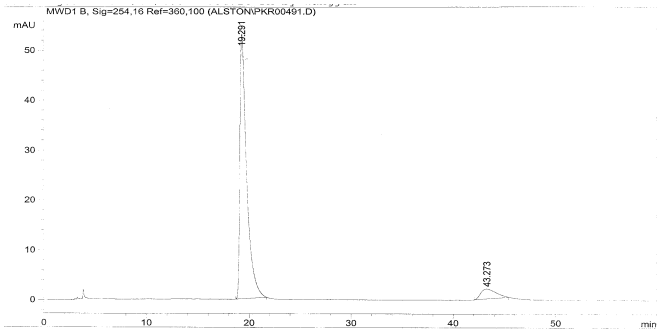
Chiral HPLC conditions

Column:	Chiralcel AS-H
Solvent:	Hex:IPA = 9:1
Flow rate:	1.0 mL/ min
UV lamp:	254 nm
Retention time:	14.1, 20.2 min



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

Purified by column chromatography (1.8 cm diameter × ~15 cm height) on silica gel using hexane/ethyl acetate (3:1) as eluent to obtain the title compound as light yellow viscous oil. 37% yield; R_f = 0.3 (hexane/ethyl acetate = 2:1); $[\alpha]^{25}_D$ = +21.4° (*c* = 0.011); ^{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.



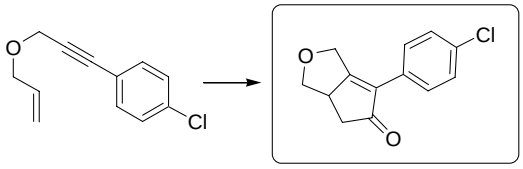
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.291	BB	0.6651	2439.30664	52.98916	92.1878
2	43.273	BB	1.2164	206.71307	1.99237	7.8122
Totals :				2646.01971	54.98152	

Results obtained with enhanced integrator!

*** End of Report ***

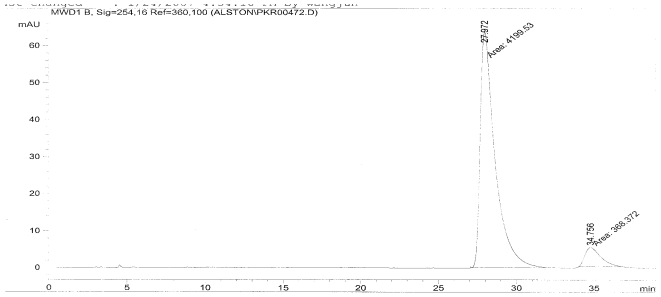
Chiral HPLC conditions

Column:	Chiralcel AS-H
Solvent:	Hex:IPA = 9:1
Flow rate:	1.0 mL/ min
UV lamp:	254 nm
Retention time:	19.3, 43.2 min



2-(4-Chlorophenyl)-7-oxabicyclo[3.3.0]oct-1-en-3-one[11] **(Table 2, entry 6).**

Purified by column chromatography (1.8 cm diameter × ~15 cm height) on silica gel using hexane/ethyl acetate (3:1) as eluent to obtain the title compound as light yellow oil. 65% yield; 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).



Signal 1: MWD1 B, Sig=254,16 Ref=360,100

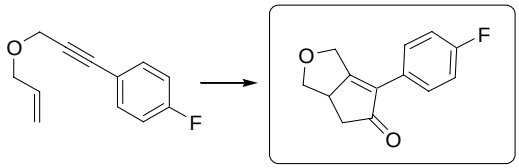
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.972	MM	1.1018	4199.52588	63.52272	91.9356
2	34.756	MM	1.1745	368.37219	5.22736	8.0644
Totals :				4567.89807	68.75008	

Results obtained with enhanced integrator!

*** End of Report ***

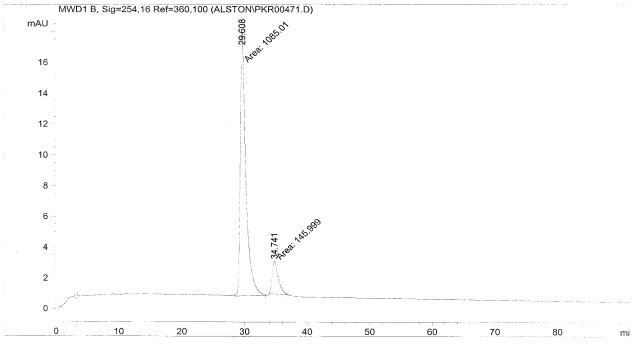
Chiral HPLC conditions

Column:	Chiralcel AS-H
Solvent:	Hex:IPA = 98:2
Flow rate:	1.0 mL/ min
UV lamp:	254 nm
Retention time:	28.0, 34.8 min



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

Purified by column chromatography (1.8 cm diameter × ~15 cm height) on silica gel using hexane/ethyl acetate (3:1) as eluent to obtain the title compound as light yellow oil. 61% yield; R_f = 0.3 (hexane/ethyl acetate = 2:1); $[\alpha]^{25}_D$ = +0.7° (*c* = 0.0083); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.52 (dd, *J* = 5.5 Hz, 8.0 Hz, 2H), 7.09 (t, *J* = 8.0 Hz, 2H), 4.91 (d, *J* = 16.5 Hz, 1H), 4.56 (d, *J* = 16.5 Hz, 1H), 4.37 (t, *J* = 7.5 Hz, 1H), 3.29-3.33 (m, 1H), 3.24 (dd, *J* = 7.5 Hz, 11.0 Hz, 1H), 2.84 (dd, *J* = 6.5 Hz, 18.0 Hz, 1H), 2.33 (dd, *J* = 3.5 Hz, 17.5 Hz, 1H), ^{13}C NMR ($CDCl_3$, 125 MHz) δ 204.1, 177.0, 161.7, 133.6, 129.8 (d, J_{CF} = 8.4 Hz), 126.7, 115.6 (d, J_{CF} = 22.0 Hz), 71.3, 66.2, 43.2, 40.1; IR (neat, cm^{-1}) 3021, 2392, 1701, 1506, 1215, 1029, 758, 669; MS(EI) *m/z* (relative intensity) 218 (M^+, 70), 188 (50), 176 (50), 159 (100), 146 (60); HRMS cald. for $C_{13}H_{11}FO_2$ 218.07431, found 218.07439.



Signal 1: MWD1 B, Sig=254,16 Ref=360,100

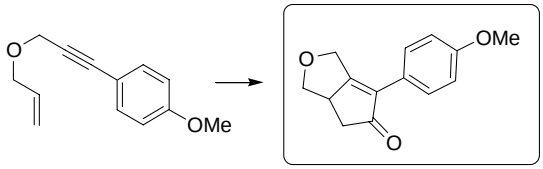
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.608	MM	1.0585	1085.00500	17.08397	88.1399
2	34.741	MM	1.1456	145.99861	2.12404	11.8601
Totals :				1231.00362	19.20801	

Results obtained with enhanced integrator!

*** End of Report ***

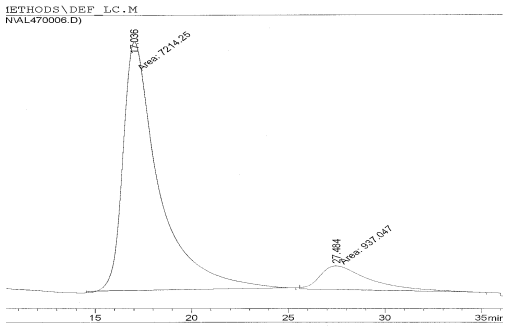
Chiral HPLC conditions

Column:	Chiralcel AS-H
Solvent:	Hex:IPA = 98:2
Flow rate:	1.0 mL/ min
UV lamp:	254 nm
Retention time:	29.6, 34.7 min



2-(4-Methoxyphenyl)-7-oxabicyclo[3.3.0]oct-1-en-3-one[11] **(Table 2, entry 8).**

Purified by column chromatography (1.8 cm diameter × ~15 cm height) on silica gel using hexane/ethyl acetate (2:1) as eluent to obtain the title compound as light yellow solid. 58% yield; R_f = 0.2 (hexane/ethyl acetate = 2:1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.48 (d, *J* = 9.0 Hz, 2H), 6.93 (d, *J* = 9.0 Hz, 1H), 4.89 (d, *J* = 16.0 Hz, 1H), 4.57 (d, *J* = 16.0 Hz, 1H), 4.35 (t, *J* = 8.0 Hz, 1H), 3.82 (s, 3H), 3.26-3.30 (m, 1H), 3.20 (dd, *J* = 7.5 Hz, 11.0 Hz, 1H), 2.81 (dd, *J* = 6.0 Hz, 17.5 Hz, 1H), 2.31 (dd, *J* = 3.0 Hz, 17.5 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, 55.2, 43.1, 40.2; MS(EI) *m/z* (relative intensity) 230 (M^+, 100), 201 (10), 189 (30), 172 (60).



Signal 1: VWD1 A, Wavelength=254 nm

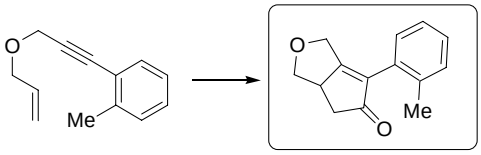
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.036	MM	2.1622	7214.25439	55.60995	88.5043
2	27.484	MM	2.9620	937.04688	5.27253	11.4957
Totals :				8151.30127	60.88247	

Results obtained with enhanced integrator!

*** End of Report ***

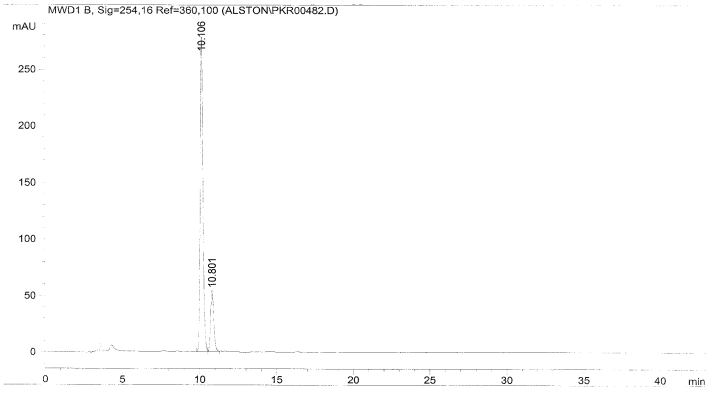
Chiral HPLC conditions

Column:	Chiralcel AS
Solvent:	Hex:IPA = 9:1
Flow rate:	1.0 mL/ min
UV lamp:	254 nm
Retention time:	17.0, 27.5 min



2-(2-Methylphenyl)-7-oxabicyclo[3.3.0]oct-1-en-3-one (Table 2, entry 9).

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. 11% yield; 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.



Signal 1: MWD1 B, Sig=254,16 Ref=360,100

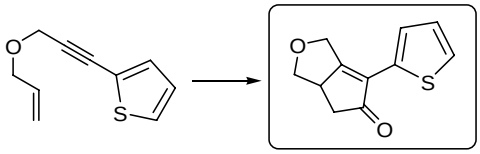
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.106	BV	0.2000	3619.47729	277.78891	82.6995
2	10.801	VB	0.2151	757.18298	54.16692	17.3005
Totals :				4376.66028	331.95583	

Results obtained with enhanced integrator!

*** End of Report ***

Chiral HPLC conditions

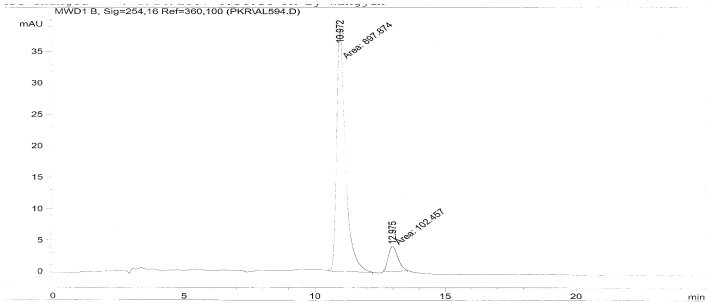
Column:	Chiralcel AD-H
Solvent:	Hex:IPA = 9:1
Flow rate:	1.0 mL/ min
UV lamp:	254 nm
Retention time:	10.1, 10.8 min



2-(2-Thiophenyl)-7-oxabicyclo[3.3.0]oct-1-en-3-one (Table 2, entry 10).

Purified by column chromatography (2 cm diameter × ~15 cm height) on silica gel using hexane/ethyl acetate (2:1) as eluent to obtain the title compound as yellow oil. 49% yield; R_f = 0.4 (hexane/ethyl acetate = 2:1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.44 (d, *J* = 3.5 Hz, 1H), 7.41 (d, *J* = 5 Hz, 1H), 7.11 (dd, *J* = 3.5 Hz, 4.7Hz, 1H), 4.87 (d, *J* = 16.5 Hz, 1H), 4.72 (d, *J* = 16.5 Hz, 1H), 4.37 (t, *J* = 7.5 Hz, 1H) 3.36-3.33 (m, 1H), 3.25 (dd, *J* = 7.5 Hz, 11Hz, 4.7Hz, 1H), 2.84 (dd, *J* = 6.5 Hz, 17.5 Hz, 1H), 2.31 (dd, J = 4 Hz, 17.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 205.4, 173.8, 132.2, 128.9, 127.4, 126.9, 126.6, 71.4, 66.3, 43.7, 39.4; MS(EI) *m/z* (relative intensity) 206 (M^+, 100), 176 (60), 164 (20). HRMS cald. for $C_{11}H_{10}O_2S$ 206.04015, found 206.04090.

Supporting Information



Signal 1: MWD1 B, Sig=254,16 Ref=360,100

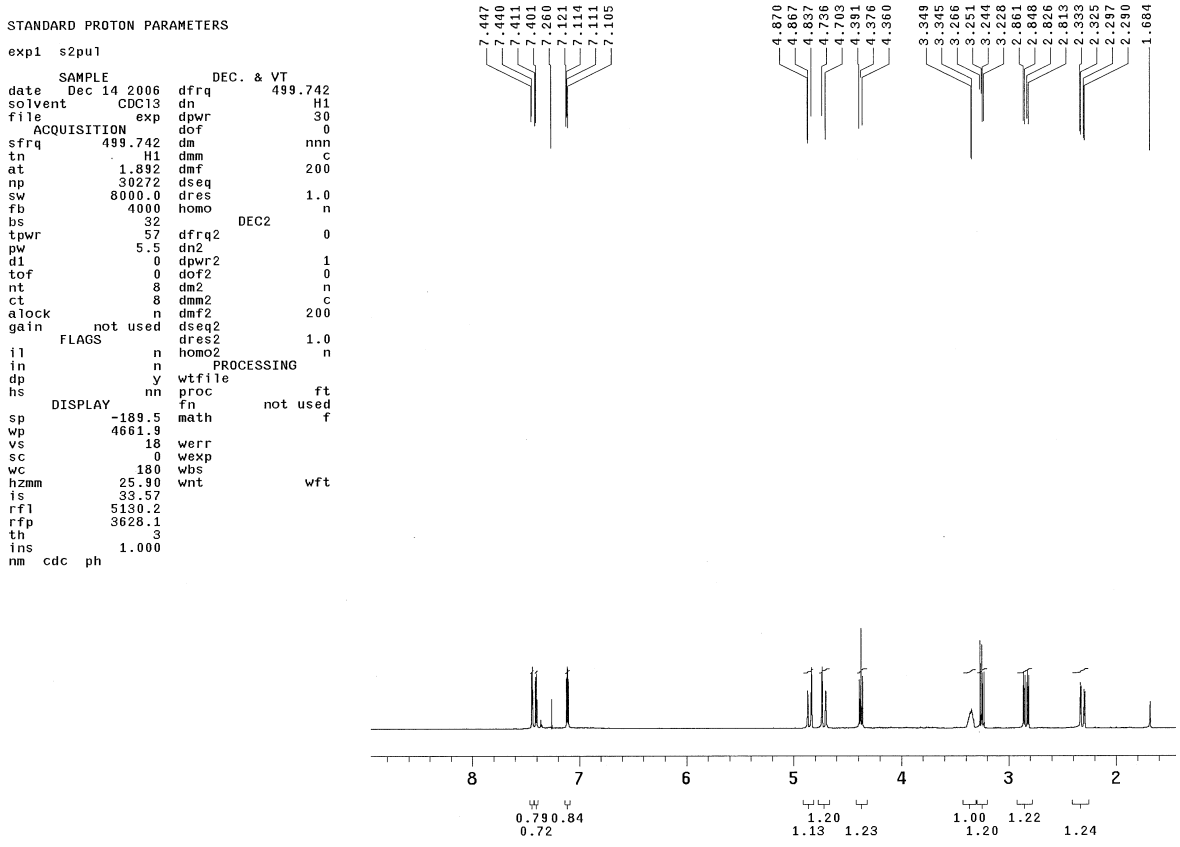
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.972	MM	0.3930	897.87360	38.07361	89.7577
2	12.975	MM	0.4274	102.45673	3.99507	10.2423
Totals :				1000.33032	42.06868	

Results obtained with enhanced integrator!

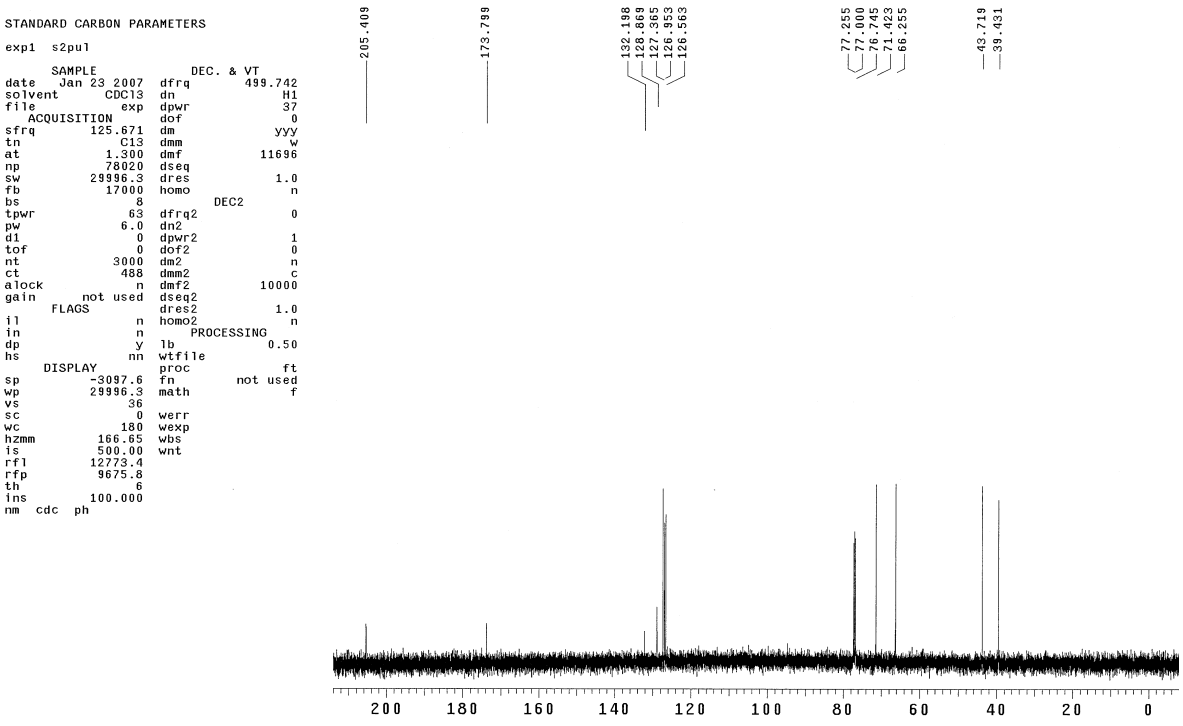
*** End of Report ***

Chiral HPLC conditions

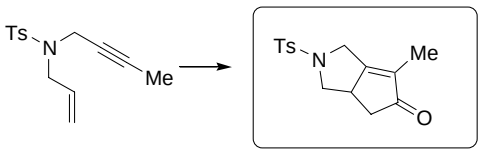
Column:	Chiralcel AS-H
Solvent:	Hex:IPA = 8:2
Flow rate:	1.0 mL/ min
UV lamp:	254 nm
Retention time:	11.0, 13.0 min



^{1}H NMR spectrum of new compound: 2-(2-thiophenyl)-7-oxabicyclo[3.3.0]oct-1-en-3-one

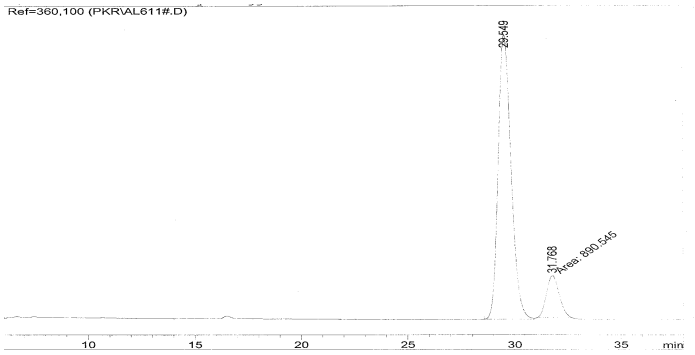


^{13}C NMR spectrum of new compound: 2-(2-thiophenyl)-7-oxabicyclo[3.3.0]oct-1-en-3-one



2-Methyl-7-[(4-methylphenyl)sulfonyl]-7-azabicyclo[3.3.0]oct-1-en-3-one[12] **(Table 2, entry 11)**

Purified by column chromatography (2.0 cm diameter × ~15 cm height) on silica gel using hexane/ethyl acetate (2:1) as eluent to obtain the title compound as white solid. 65% yield; 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).



Signal 1: MWD1 B, Sig=254,16 Ref=360,100

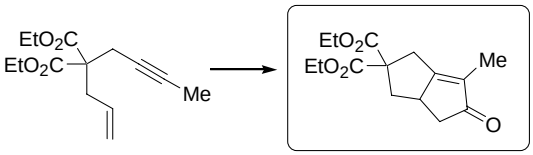
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.549	BB	0.6501	5998.62354	143.38464	87.0733
2	31.768	MM	0.6958	890.54547	21.33278	12.9267
Totals :				6889.16901	164.71743	

Results obtained with enhanced integrator!

*** End of Report ***

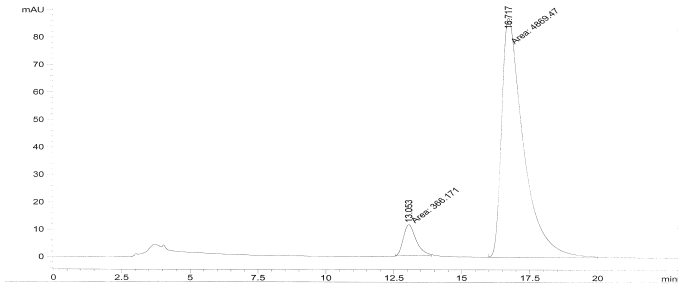
Chiral HPLC conditions

Column:	Chiralcel AD-H
Solvent:	Hex:IPA = 9:1
Flow rate:	1.0 mL/ min
UV lamp:	254 nm
Retention time:	29.5, 31.8 min



Diethyl 2-methyl-3-oxobicyclo[3.3.0]oct-1-ene-7,7-dicarboxylate[13] **(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. 40% yield; 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).



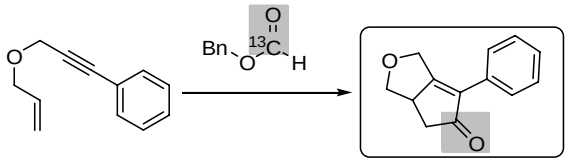
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.053	MM	0.5414	366.17145	11.27160	6.9938
2	16.717	MM	0.9317	4869.46680	87.10928	93.0062
Totals :				5235.63824	98.38089	

Results obtained with enhanced integrator!

*** End of Report ***

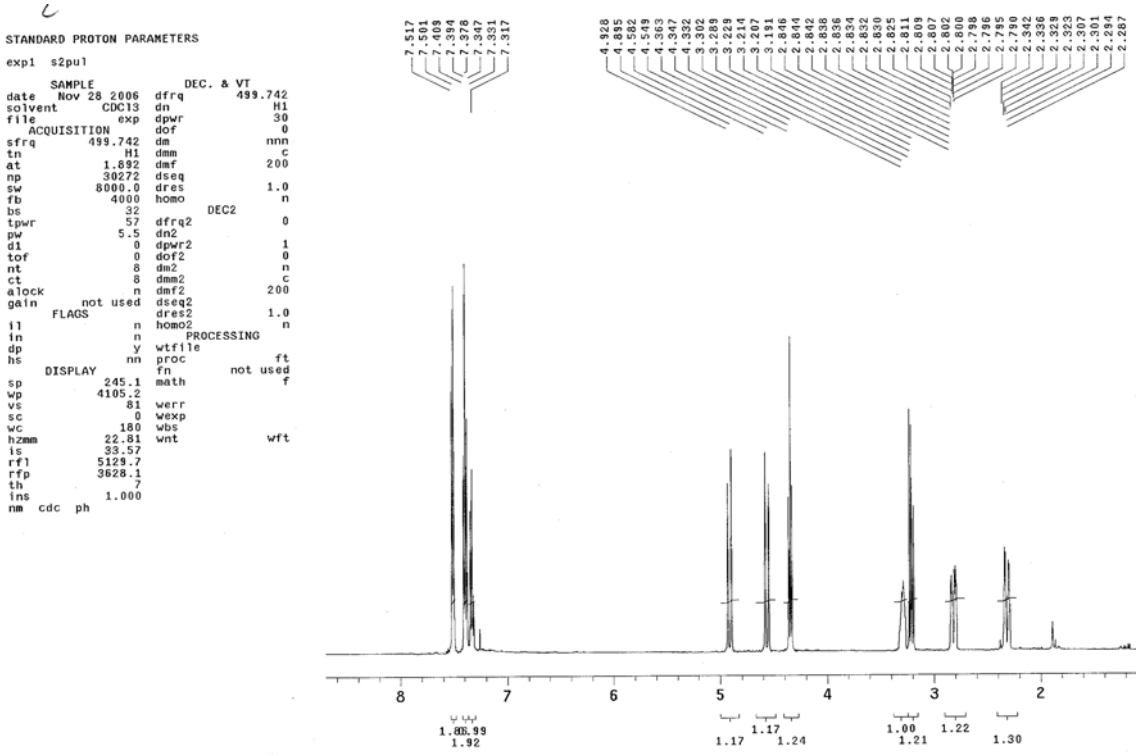
Chiral HPLC conditions

Column:	Chiralcel AS-H
Solvent:	Hex:IPA = 9:1
Flow rate:	1.0 mL/ min
UV lamp:	254 nm
Retention time:	13.1, 16.7 min

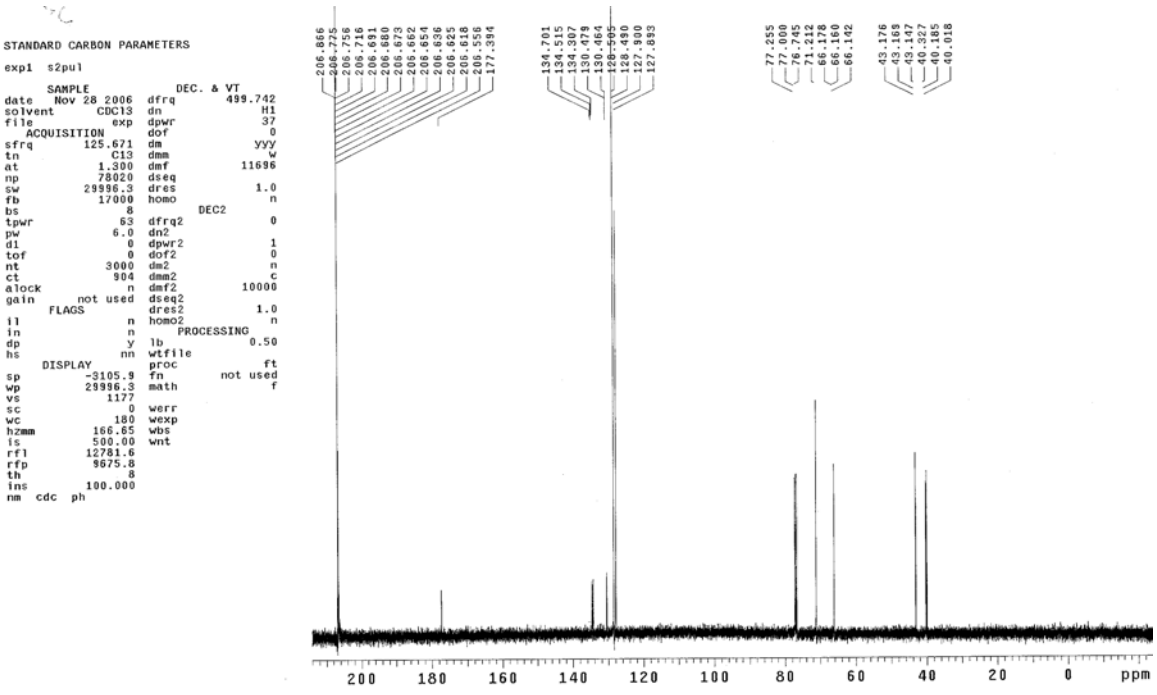


^{13}C-Enriched 2-phenyl-7-oxabicyclo[3.3.0]oct-1-en-3-one (Scheme 2)

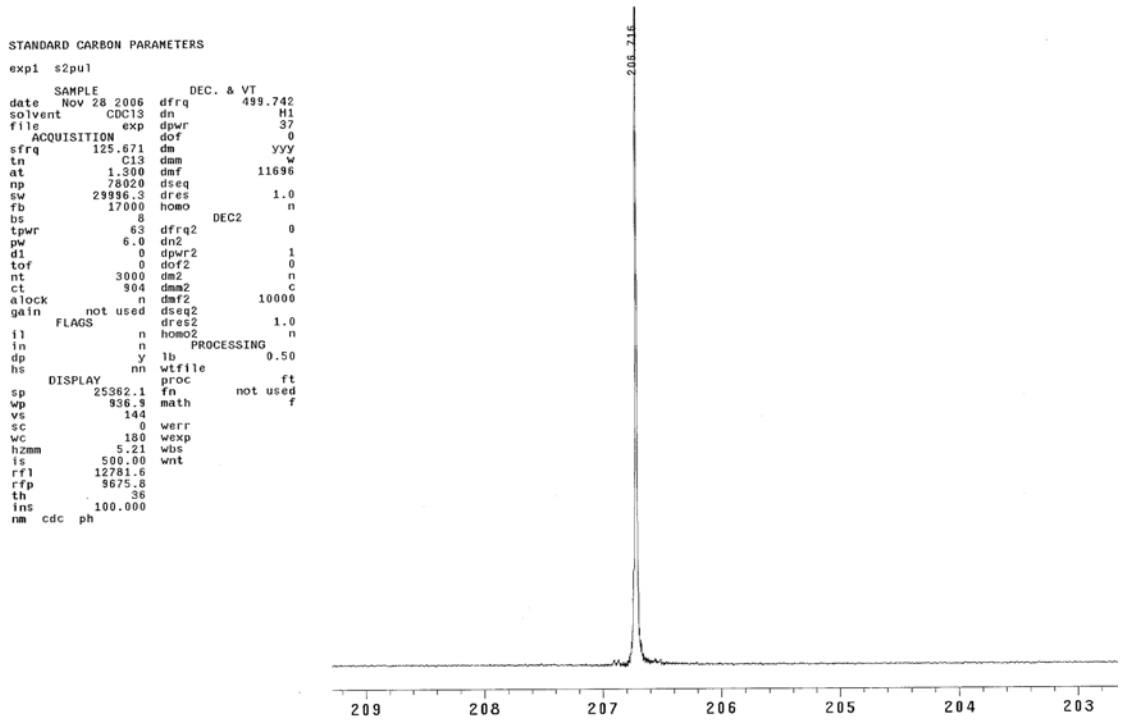
General procedures of PKR were used except ^{13}C-enriched benzyl formate was added instead of original benzyl formate. Purified by column chromatography (2 cm diameter × ~20 cm height) on silica gel using hexane/ethyl acetate (3:1) as eluent to obtain the title compound as light yellow oil. >99% ^{13}C-labeled.



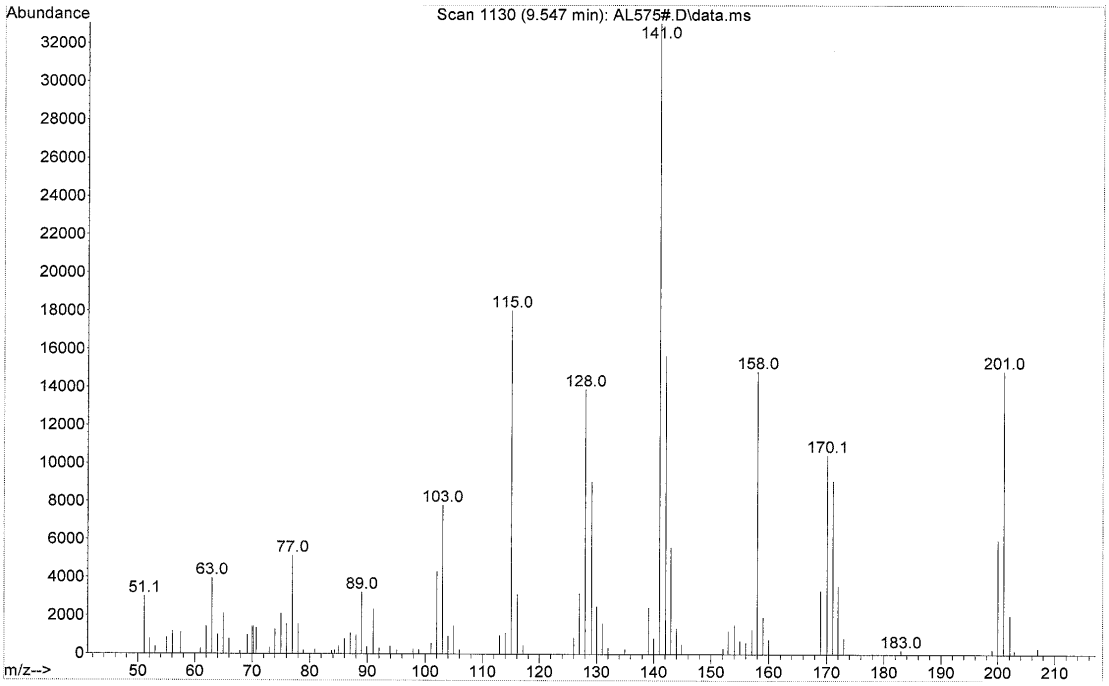
^{1}H NMR of ^{13}C-enriched 2-phenyl-7-oxabicyclo[3.3.0]oct-1-en-3-one



^{13}C NMR of ^{13}C-enriched 2-phenyl-7-oxabicyclo[3.3.0]oct-1-en-3-one



^{13}C NMR of ^{13}C-enriched 2-phenyl-7-oxabicyclo[3.3.0]oct-1-en-3-one (enlarged labeled region)



Mass spectrum of ^{13}C-enriched 2-phenyl-7-oxabicyclo[3.3.0]oct-1-en-3-one

6. References

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