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Iridium-catalyzed cascade decarbonylation/highly enantioselective Pauson–Khand-type cyclization reactions

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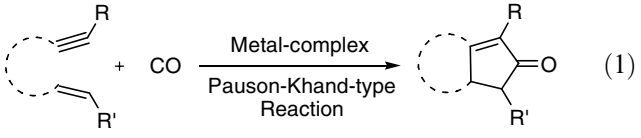
Abstract—An easily accessible chiral iridium-BINAP complex can effect the cooperative processes of decarbonylation of an aldehyde and cascaded enantioselective Pauson–Khand-type reaction. A survey of ligands revealed that atropisomeric aryl-diphosphine ligands were superior to chiral alkyl-diphosphines in this dual catalysis. Applying the reaction conditions of $[IrCl(COD)]_2$/(*S*)-BINAP complex with nonylaldehyde as a CO surrogate at 100 °C in anhydrous dioxane solvent, various 1,6-enynes were transformed to the corresponding optically active bicyclic cyclopentenones with excellent enantioselectivities (up to 98% ee).

1. Introduction

Transition-metal mediated [2+2+1] cyclization of an alkyne, alkene, and carbon monoxide was originally developed by Pauson and Khand in the early 1970s.[1,2] A stoichiometric amount of cobalt carbonyl complex was initially required in this carbonylative coupling reaction. This versatile transformation represents one of the most powerful protocols for the preparation of various pharmaceutically attractive and biologically active cyclopentenones.[3,4]



(1)

Recently, substantial advances have been achieved in the catalytic version of Pauson–Khand reaction (Eq. 1).[5] Instead of cobalt complexes,[6] other transition metal complexes were found to be suitable catalysts for Pauson–Khand-type cyclization in the presence of gaseous carbon monoxide.[7] In 1996, Buchwald and Hicks reported the first enantioselective Pauson–Khand-type reaction.[8] They pioneered in showing that chiral titanium complexes would transform various enynes into the corresponding optically active bicyclic cyclopentenones in high ee. Additionally, chiral cobalt,[9] rhodium,[10] and iridium complexes[11] are of significance to the recent developments of the asymmetric Pauson–Khand-type cyclization. An interesting alternative to CO gas for Pauson–Khand-type reaction is to use an aldehyde as CO surrogate (by in situ rhodium-catalyzed decarbonylation),[12] which was independently reported by Morimoto/Kakiuch[13] and Shibata et al.[14] Recently, we reported that a rhodium complex with a chiral atropisomeric dipyridyldiphosphine ligand was effective for the asymmetric Pauson–Khand-type cyclization in aqueous medium.[15] Apart from rhodium catalysts, we realized that iridium complexes such as $[Cp^*IrMe_2(DMSO)]$ would also be effective in decarbonylation of aldehydes to give iridium-carbonyl complexes.[16] However, the iridium-catalyzed enantioselective Pauson–Khand-type reaction remained only sporadically studied.[11] We were attracted by the capability of iridium-catalyzed decarbonylation (via a C–H activation or sigma-bond metathesis) of aldehydes. As a continuous study of the Pauson–Khand-type reaction,[10i,15] we were interested in exploring the applicability of a chiral iridium complex in the highly challenging cooperative decarbonylation/enantioselective cyclization sequential reactions.[11c] Shibata et al. has elegantly reported the results of iridium-catalyzed cascade/decarbonylation/highly enantioselective PKR.[11b]

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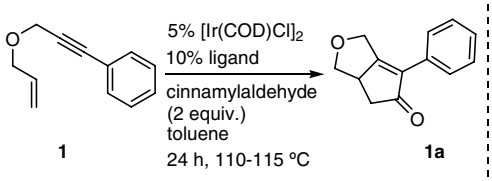
2. Results and discussion

2.1. Investigation of iridium-phosphine complex-catalyzed Pauson–Khand-type cyclization

Initial attempts to probe the feasibility of an Ir-catalyzed cooperative decarbonylation/Pauson–Khand-type reaction were performed with $[IrCl(COD)]_2$ complex (Scheme 1). Phosphine ligands were required for this catalytic transformation. Bidentate phosphines (e.g., dppb and *rac*-BINAP) provided significantly higher yields of the cyclopentenone **1a** triphenylphosphine.



Scheme 1. Feasibility of Ir-catalyzed decarbonylation/Pauson–Khand-type reaction.

With the promising initial results in hand (Scheme 1), we initiated a study of the capability of the enantioselective version of this dual catalysis. Several commercially available chiral diphosphine ligands were examined (Table 1). Easily accessible oxygen-tethered enyne **1** was used as the prototypical substrate for initial screening. (*S*)-BINAP provided the best results among the ligands screened (Table 1, entry 1). The sterically more demanding (*S*)-xylyl-BINAP had no beneficial effect on this [2+2+1] reaction (Table 1, entry 2).[17] Both atropisomeric dipyridyldiphosphine (*S*)-P-Phos[18] and (*S*)-BisbenzodioxanPhos[19] (SYNPHOS)[20] gave slightly lower ees of the product (Table 1, entries 3–5). Phospholane-type chiral alkylphosphine Duphos and Ferro-TANE showed significantly lower ees and yields of the bicyclic cyclopentenone (Table 1, entries 7–9). Moderate ees and poor yields of the product were observed when monodentate phosphoramidite ligand (*S*)-Monophos was applied (Table 1, entry 10). In addition to the ligand screening, the solvent effect was also investigated. Toluene as a solvent provided the highest ee of the product. We chose dioxane as the solvent for our study since it gave higher product yield with only slightly reduced enantioselectivity (Table 1, entry 12). Catalytic cooperative asymmetric Pauson–Khand-type reaction in ionic liquid remains unprecedented.[21] A good ee value but poor yield of the cyclopentenone product was observed when room temperature ionic liquid $[BMIM]NTf_2$ was used as solvent (Table 1, entry 15). Initial attempts at recycling the catalyst proved to be unsuccessful.

Table 1. Survey of chiral phosphine ligands and solvents in Ir-catalyzed asymmetric Pauson–Khand-type cyclization[a]

Entry	Chiral ligand	Solvent	% Yield[b]	% ee[c]
1	(*S*)-BINAP	Toluene	42	94
2	(*S*)-Xylyl-BINAP	Toluene	41	92
3	(*S*)-P-Phos	Toluene	39	90
4	(*S*)-Xylyl-P-Phos	Toluene	36	90
5	(*S*)-BisbenzodioxanPhos	Toluene	41	92
6	(*R*)-PHANEPHOS	Toluene	21	56
7[d]	(*R*,*R*)-Et-Duphos	Toluene	12	24
8[d]	(*R*,*R*)-Me-Duphos	Toluene	14	22
9[d]	(*R*,*R*)-Et-Ferro-TANE	Toluene	14	25
10[e]	(*S*)-*N*,*N*-DiMe-Monophos	Toluene	21	67
11	(*S*)-BINAP	DMF	26	89
12	(*S*)-BINAP	Dioxane	57	90
13	(*S*)-BINAP	DME	42	89
14	(*S*)-BINAP	THF	40	90
15	(*S*)-BINAP	$[BMIM]NTf_2$	11	81

[a] Reaction conditions: 5 mol % $[IrCl(COD)]_2$, 10 mol % L*, enyne **1** (0.3 mmol), cinnamylaldehyde (0.6 mmol), and anhydrous solvent (4.0 mL) were stirred at 100–105 °C for 48 h under nitrogen atmosphere.
[b] Isolated yield.
[c] Ee values were determined by chiral HPLC analysis using Daicel® Chiralcel AS column.
[d] A complex mixture of products was observed.
[e] 20 mol % ligand was used.

In order to increase the efficiency of the newly developed Ir-BINAP system, we examined different aldehydes as CO surrogates (Table 2). α,β-Unsaturated *trans*-cinnamylaldehyde gave good results in terms of both yield and enantioselectivity (Table 2, entry 1). The electrochemical nature of aromatic aldehydes was found to be responsible for both CO-transfer catalysis and the enantioselective carbonylative cyclization (Table 1, entries 2–4). Electron-poor *p*-chlorobenzaldehyde provided the CO moiety more effectively than the electron-rich *p*-methoxybenzaldehyde. The optimal aldehyde was *n*-nonylaldehyde (Table 2, entry 5). Notably, we showed for the first time that formate was capable of CO transfer/enantioselective Pauson–Khand-type dual catalysis (Table 2, entry 6). The aldehyde loading was found to be crucial to the product yield but the ee remained unaffected. The optimal yield was obtained when 5 equiv of aldehyde were used. The addition of a large excess of aldehyde was detrimental (Table 2, entries 8 and 9).

Table 2. Aldehyde screening for Ir-catalyzed enantioselective Pauson–Khand-type cyclization[a]

Entry	Aldehyde	Equiv	Yield[b] (%)	% ee[c]
1	*trans*-Cinnamylaldehyde	5	68	93
2	Benzaldehyde	5	35	92
3	*p*-Chlorobenzaldehyde	5	48	91
4	*p*-Methoxybenzaldehyde	5	21	90
5	*n*-Nonylaldehyde	5	74	94
6	2-Pyridylmethylformate	5	30	80
7	*n*-Nonylaldehyde	2	33	94
8	*n*-Nonylaldehyde	10	48	93
9	*n*-Nonylaldehyde	20	34	93

[a] Reaction conditions: 5 mol % $[Ir(COD)Cl]_2$, 10 mol % (*S*)-BINAP, enyne **1** (0.3 mmol), aldehyde (0.6–6.0 mmol), and anhydrous dioxane (4.0 mL) were stirred at 100–105 °C for 48 h under nitrogen atmosphere.
[b] Isolated yield.
[c] ee values were determined by chiral HPLC analysis using Daicel® Chiralcel AS column.

The relationship of the metal to ligand ratio was also investigated. No significant ee variations were observed when the ratio was varied from (*S*)-BINAP:Ir = 1:1 to 2:1. This result indicated that the catalytic complex with a ratio of

(*S*)-BINAP:Ir = 1:1 would be involved for the catalytic reaction. To investigate this further, the carbonylative cyclization of **1a** was performed using BINAP of varying ee. As shown in Figure 1, a linear correlation between the ee of the ligand and that of the product was observed, indicating that a 1:1 ligand-to-metal ratio is present in the catalytic complex.[22]

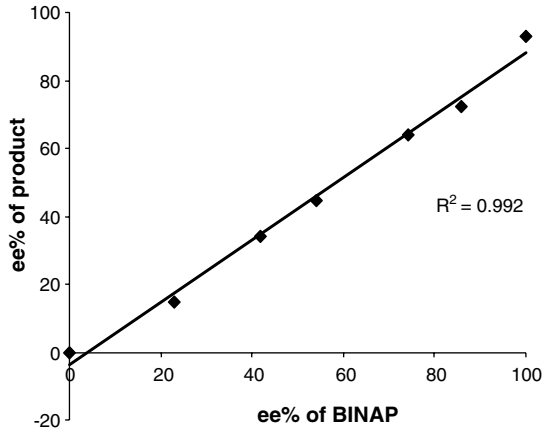


Figure 1. Ir-catalyzed asymmetric Pauson–Khand-type reaction of enyne **1** using BINAP of varying ee. Each data point is the average of two HPLC runs; the line corresponds to a least-squares linear regression of the data with $R^2 = 0.992$.

2.2. Scope and limitation of Ir-BINAP catalyzed asymmetric Pauson–Khand-type reaction

To test the effectiveness of the Ir-BINAP system, we examined various oxygen-tethered 1,6-enynes for the enantioselective Pauson–Khand-type cyclization (Table 3). Alkyl-substituted alkyne gave excellent enantioselectivity (95% ee) of the corresponding product (Table 3, entry 1). Enyne with a 1,1-disubstituted alkene reacted smoothly to give the stereogenic quaternary carbon center bicyclic cyclopentenone in good enantioselectivity (Table 3, entry 2). Remarkably, excellent enantioselectivity (98% ee) was attained for the reaction with enyne **7** (Table 3, entry 7). To the best of our knowledge, this is the highest ee value reported so far for cascade Pauson–Khand-type transformations.

Various new aromatic enynes possessing different electronic properties were prepared and subjected to carbonylative cyclizations (Table 3, entries 3–8). We have previously reported an electronic effect in the Rh-catalyzed asymmetric Pauson–Khand-type reaction.[15] A linear free energy relationship in a Hammett study was observed. Aromatic enynes with a larger Hammett constant σ usually provided higher enantioselectivity of the cyclopentenone. In contrast, no significant electronic relationship between the enyne substrates and the ee of the bicyclic cyclopentenones was observed in the Ir-BINAP catalyzed carbonylative cyclization. Aromatic enynes with different electronic properties generally provided enantioselectivites greater than 94% ee. Although the electronic effect was insignificant, the steric factor was found to play an important role. Sterically congested *ortho*-substituted enyne gave only a trace amount of product as indicated from GC analysis (Table 3, entry 9). The coordination of hindered enyne to iridium metal center seemed to be problematic and hence nearly no conversion was observed. A quantitative amount of starting material **9** was recovered after the reaction. Heterocyclic enynes with pyridyl or thiophenyl moiety were found to be unsuccessful (Table 3, entries 10 and 11). Presumably, the heteroatom bound to the metal center more tightly than π-interaction of the enyne and rendered the metal complex coordinatively saturated. The Ir-BINAP system was also applied to other nitrogen- and carbon-tethered enynes (Table 3, entries 12–14). Excellent enantioselectivities were obtained. We also attempted to extend the scope of this dual catalysis to 1,8-enyne, however, only a trace amount of product was observed from continuous GC-MS analysis after prolonged heating at higher temperature (120 °C).

3. Conclusion

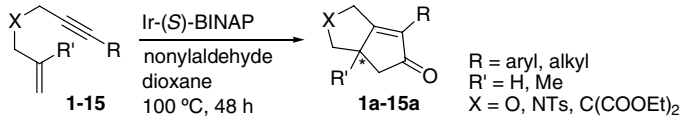
In conclusion, we have successfully demonstrated the Ir-diphosphine complex-catalyzed decarbonylation of aldehydes. This versatile reaction was found to be a suitable cooperative partner in the sequential decarbonylation and highly enantioselective [2+2+1] carbonylative cyclization. Additionally, apart from aldehydes, our initial result showed that formate was capable as the CO source in Ir-catalyzed asymmetric carbonylative cyclization, which opened up the opportunity to use other readily available carbonyl compounds as CO surrogates in iridium catalysis. In the presence of easily accessible chiral Ir-BINAP catalyst and nonylaldehyde, various 1,6-enynes were transformed into optically active bicyclic cyclopentenones with excellent enantioselectivities. It is noteworthy that, up to 98% ee was obtained with enyne **7** as the substrate, establishing the highest enantioselectivity accomplished so far for the cascade Pauson–Khand-type transformation.

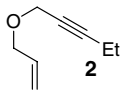
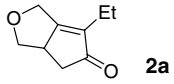
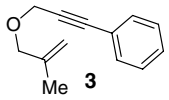
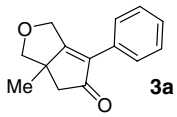
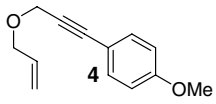
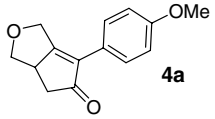
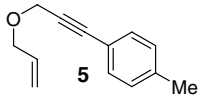
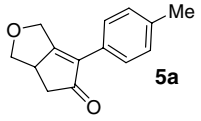
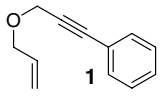
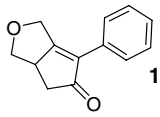
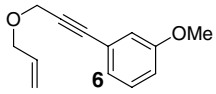
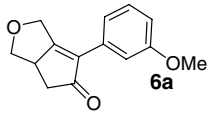
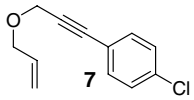
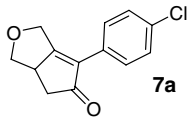
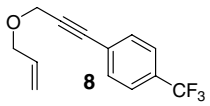
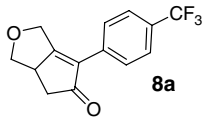
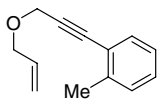
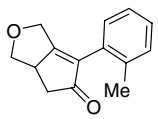
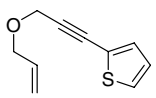
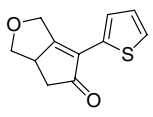
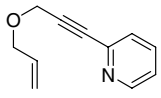
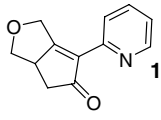
4. Experimental

4.1. General procedures for the Ir-catalyzed asymmetric Pauson–Khand-type cyclization of various enynes

$[IrCl(COD)]_2$ (10.0 mg, 0.015 mmol), (*S*)-BINAP (18.9 mg, 0.03 mmol), and a Teflon-coated magnetic stirrer bar (3 mm × 10 mm) were charged into a Rotaflo® (England) resealable screw-cap Schlenk flask on bench-top at rt. The flask was evacuated and backfilled with nitrogen (three cycles). Anhydrous dioxane (3.0 mL) was added under nitrogen atmosphere with continuous stirring for 10 min. Distilled aldehyde (1.5 mmol, 5 equiv with respected to enyne) and an enyne (0.3 mmol) were added sequentially via a micro-syringe. Additional dioxane (1.0 mL, total = 4.0 mL) was used to rinse the inner-wall of the Schlenk flask. The flask was resealed and the reaction mixtures were magnetically stirred in a preheated 100 °C (±3 °C) oil bath for 48 h (reaction times were unoptimized for each substrate). The flask was allowed to cool to rt. Diethyl ether or CH_2Cl_2 (~5 mL) was added (tiny amount of the aliquot was taken out for GC and TLC analysis) and then concentrated under reduced pressure. The crude reaction mixtures

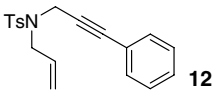
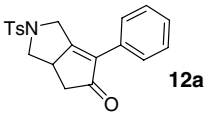
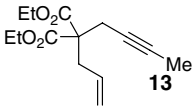
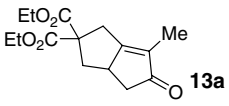
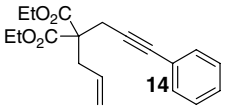
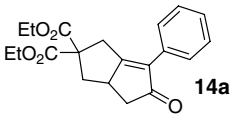
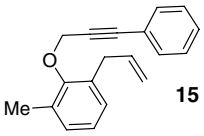
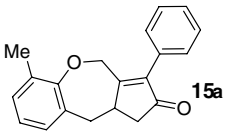
Table 3. Ir-BINAP catalyzed asymmetric Pauson–Khand-type cyclization of various enynes[a]



Entry	Substrate	Product	Yield[b] (%)	% ee[c]
1	 **2**	 **2a**	69	95
2	 **3**	 **3a**	41	96
3	 **4**	 **4a**	76	94
4	 **5**	 **5a**	75	95
5	 **1**	 **1a**	74	94
6	 **6**	 **6a**	24	94
7	 **7**	 **7a**	60	98
8	 **8**	 **8a**	42	96
9	 **9**	 **9a**	Trace	n.d.
10	 **10**	 **10a**	Trace	n.d.
11	 **11**	 **11a**	Trace	n.d.

(*continued on next page*)

Table 3 (*continued*)

Entry	Substrate	Product	Yield[b] (%)	% ee[c]
12	 **12**	 **12a**	31	95
13	 **13**	 **13a**	39	90
14	 **14**	 **14a**	35	90
15[d]	 **15**	 **15a**	Trace	n.d.

[a] Reaction conditions: 5 mol % $[IrCl(COD)]_2$, (Ir:BINAP = 1:1), enyne (0.3 mmol), aldehyde (1.5 mmol), and anhydrous dioxane (4.0 mL) were stirred at 100–105 °C for 48 h under nitrogen atmosphere.
[b] Isolated yield.
[c] ee values were determined by chiral HPLC analysis using Daicel® Chiralcel and Chiralpak columns.
[d] 100 °C, 96 h; 120 °C, 72 h.

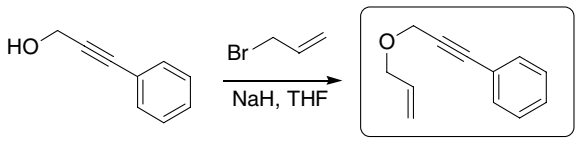
were directly purified by column chromatography on silica gel using hexane/ethyl acetate as the eluent to afford optically active bicyclic cyclopentenones. The enantiomer ratios were determined by chiral HPLC analysis.

4.2. 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 20 mL volume) in the presence of Teflon-coated magnetic stirrer bar (3 mm × 10 mm). Micro-syringes (50 μL to 5.0 mL) were purchased from Hammiton. Toluene and tetrahydrofuran (THF) were distilled from sodium and sodium benzophenone ketyl under nitrogen, respectively.[23] DMF was distilled from CaH_2 under reduced pressure. Anhydrous dioxane and DME were purchased from Aldrich®. 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 under nitrogen. 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 $[IrCl(COD)]_2$ crystalline solid and (*S*)-BINAP (and other chiral ligands for initial screening) were purchased from Strem Chemicals and stored under nitrogen. Thin layer chromatography was performed on Merck precoated silica gel 60 F_{254} plates. Silica gel (Merck or MN 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. Chemical shifts (δ) are 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 or HP 1100 instrument using Daicel® Chiralcel or Chiralpak 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 BINAP ligand was used. GC–MS analysis was conducted on a HP G1800C GCD system using a HP5MS column (30 m × 0.25 mm).

4.3. Preparation of enyne substrates

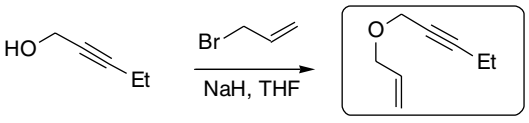
4.3.1. 3-(Allyloxy)-1-phenyl-1-propyne 1[24]



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

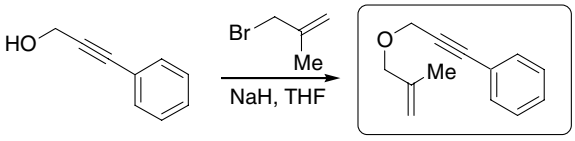
added NaH (1.44 g, 60 mmol, freshly pre-washed with dry hexane) portionwise under a nitrogen atmosphere at 0 °C. The white suspension was slowly warmed to room temperature and stirred for 2 h. The reaction mixture was then cooled to 0 °C and allyl bromide (6.8 mL, 80 mmol) was added dropwise. After complete addition, the reaction was warmed to room temperature and stirred further for 2 h. 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, $J = 17.0$, 10.0, 5.5 Hz, 1H), 5.38 (dd, $J = 17.0$, 2.0 Hz, 1H), 5.27 (dd, $J = 10.0$, 2.0 Hz, 1H), 4.39 (s, 2H), 4.17 (dd, $J = 5.5$, 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).

4.3.2. 5-(Allyloxy)-3-pentyne 2[25]



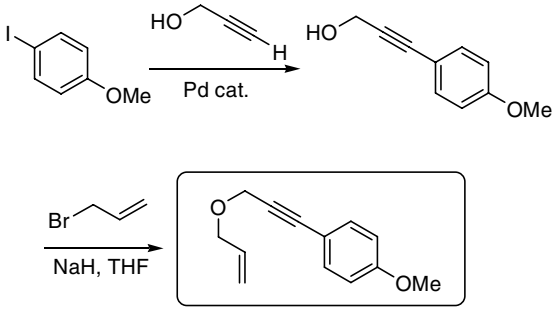
The general procedures of C–O bond formation were followed: 3-pentyn-1-ol (4.2 g, 50 mmol), NaH (1.8 g, 75 mmol, prewashed with dry hexane), allyl bromide (8.5 mL, 100 mmol), and freshly distilled THF (150 mL) were used to obtain the title compound as a colorless liquid (5.3 g, 85% yield). Purification 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, $J = 17.0$, 10.0, 5.5 Hz, 1H), 5.31 (dd, $J = 17.0$, 2.0 Hz, 1H), 5.20 (dd, $J = 10.0$, 2.0 Hz, 1H), 4.12 (t, $J = 2.5$ Hz, 2H), 4.04 (d, $J = 5.5$ Hz, 2H), 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).

4.3.3. 3-[(2-Methyl-2-propenyl)oxy]-1-phenyl-1-propyne 3[26]



The general procedures of condensation of arylpropargyl alcohol with allyl bromide was 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).

4.3.4. 3-(Allyloxy)-1-(4-methoxyphenyl)-1-propyne 4[27]

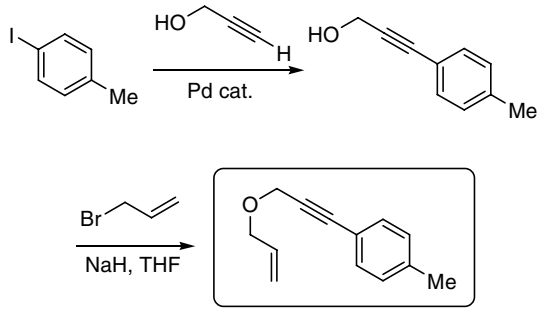


General procedure for Sonogashira coupling of propargyl alcohol with ArI: 4-Iodoanisole (11.7 g, 50 mmol), $Pd(PPh_3)_2Cl_2$ (3 mol %) and CuI (6 mol %) were dissolved in freshly distilled toluene (50 mL) under nitrogen at room temperature. Piperidine (8.4 g, 100 mmol) was added, followed by slow addition of propargyl alcohol (3.07 mL, 52 mmol) via syringe (*Caution*: exothermic reaction, when propargyl alcohol was added). The resulting dark brown reaction mixture was stirred at 30–35 °C for 3 h under nitrogen (ArI was completely consumed as judged by GC analysis). The reaction was allowed to reach room temperature and the dark brown crude product filtered over a silica pad (5 cm diameter × 5 cm height) and rinsed with dichloromethane (~200 mL). The solvent was removed by rotary evaporation to give a viscous brown liquid, which was purified by flash column chromatography on silica gel using dichloromethane as eluent to afford 3-(4-methoxyphenyl)-2-propyn-1-ol[28] as a yellow solid (6.07 g, 75% yield). $R_f = 0.4$ (dichloromethane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.37 (d, $J = 8.5$ Hz, 2H), 6.83 (d, $J = 8.5$ Hz, 2H), 4.47 (d, $J = 6.0$ Hz), 3.81 (s, 2H), 1.75 (t, $J = 5.5$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 138.8, 131.3, 128.8, 119.3, 86.5, 85.4, 51.2, 43.6; MS(EI) m/z (relative intensity) 162 (M^+, 100).

The general procedure for the condensation of arylpropargyl alcohol with allyl bromide was followed: 3-(4-methoxyphenyl)-2-propyn-1-ol[28] (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-(4-methoxyphenyl)-1-propyne as pale yellow liquid (1.18 g, 95% yield). Purification of the crude product was conducted by filtration 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 7.39 (d, $J = 8.5$ Hz, 2H), 6.84 (d, $J = 8.5$ Hz, 2H), 5.92–5.98 (m, 1H), 5.33 (dd, $J = 17.0$, 1.0 Hz, 1H), 5.23 (dd, $J = 17.5$, 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, 3039, 3006, 2935, 2901, 2839, 2541, 2235, 2049, 1967, 1885, 1648, 1606, 1568, 1509, 1462, 1442, 1354, 1291, 1251, 1175, 1085, 1032, 927, 833, 800, 675, 567, 536, 417; MS(EI) m/z (relative intensity) 202 (M^+, 10), 161 (100).

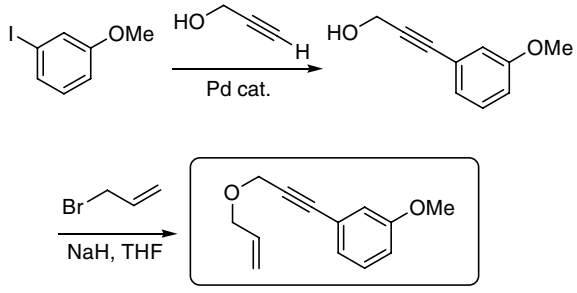
4.3.5. 3-(Allyloxy)-1-(4-methylphenyl)-1-propyne 5



The procedure of Sonogashira coupling of propargyl alcohol with ArI was used: 4-iodotoluene (10.9 g, 50 mmol), $Pd(PPh_3)_2Cl_2$ (3 mol %), CuI (6 mol %), piperidine (8.4 g, 100 mmol), propargyl alcohol (3.07 mL, 52 mmol), and freshly distilled toluene (50 mL) were charged into a round-bottomed flask with Teflon inter-key under nitrogen. The resulting dark brown reaction mixture was stirred at 30–35 °C for 3 h under nitrogen (ArI was completely consumed as judged by GC analysis). 3-(4-Methylphenyl)-2-propyn-1-ol[29] (5.26 g, 72% yield) was obtained as a light brown solid. Purification was conducted by filtering 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 (br s, 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 calcd for $C_{10}H_{10}O$ 146.07316, found 146.07311.

The general procedure of the condensation of arylpropargyl alcohol with allyl bromide was followed: 3-(4-methylphenyl)-2-propyn-1-ol[29] (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, $J = 17.0$, 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 calcd for $C_{13}H_{14}O$ 186.10447, found 186.10451.

4.3.6. 3-(Allyloxy)-1-(3-methoxyphenyl)-1-propyne 6

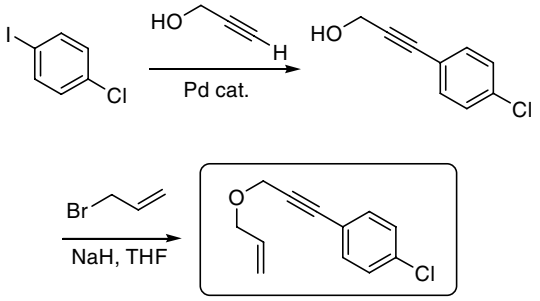


The general procedure for Sonogashira coupling of propargyl alcohol with ArI was used: 3-iodoanisole (11.7 g, 50 mmol), $Pd(PPh_3)_2Cl_2$ (3 mol %), CuI (6 mol %), piperidine (8.4 g, 100 mmol), propargyl alcohol (3.07 mL, 52 mmol), and freshly distilled toluene (50 mL) were used to afford 3-(3-methoxyphenyl)-2-propyn-1-ol[30] (5.91 g, 73% yield) as a light yellow viscous liquid. Purification was conducted by filtering 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 calcd for $C_{10}H_{10}O_2$ 162.06808, found 162.06829.

The general procedure of the condensation of arylpropargyl alcohol with allyl bromide was followed: 3-(3-methoxyphenyl)-2-propyn-1-ol[30] (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 the crude product was conducted by filtration 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, $J = 17.0$, 1.0 Hz, 1H), 5.23 (dd, $J = 17.5$, 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 calcd for $C_{13}H_{14}O_2$ 202.09938, found 202.09923.

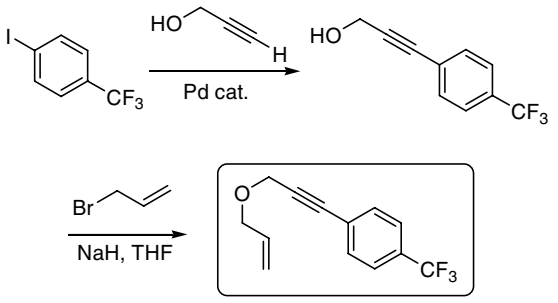
4.3.7. 3-(Allyloxy)-1-(4-chlorophenyl)-1-propyne 7



The general procedure for Sonogashira coupling of propargyl alcohol with ArI was used: 4-chloroiodobenzene (11.9 g, 50 mmol), $Pd(PPh_3)_2Cl_2$ (3 mol %), CuI (6 mol %), piperidine (8.4 g, 100 mmol), propargyl alcohol (3.07 mL, 52 mmol), and freshly distilled toluene (50 mL) were used to afford 3-(4-chlorophenyl)-2-propyn-1-ol[31] (5.91 g, 73% yield) as a light yellow viscous liquid. Purification was conducted by filtering 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); ^1H 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 (br s, 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 calcd for C_9H_7ClO 166.01854, found 166.01850.

The general procedure of the condensation of arylpropargyl alcohol with allyl bromide was 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 the crude product was conducted by filtering 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); ^1H 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, $J = 17.0$, 10.0, 5.5 Hz, 1H), 5.34 (dd, $J = 17.0$, 1.0 Hz, 1H), 5.24 (dd, $J = 17.5$, 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 calcd for $C_{12}H_{11}ClO$ 206.04984, found 206.04989.

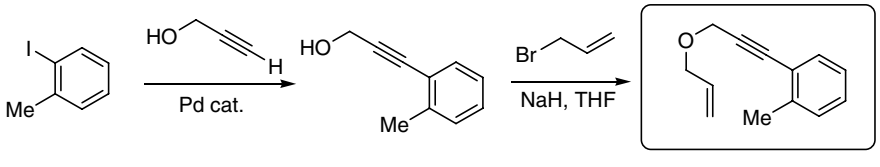
4.3.8. 3-(Allyloxy)-1-(4-trifluoromethylphenyl)-1-propyne 8



The general procedure for Sonogashira coupling of propargyl alcohol with ArI was used: 4-trifluoromethyliodobenzene (13.6 g, 50 mmol), $Pd(PPh_3)_2Cl_2$ (3 mol %), CuI (6 mol %), piperidine (8.4 g, 100 mmol), propargyl alcohol (3.07 mL, 52 mmol), and freshly distilled toluene (50 mL) were used to afford 3-(4-trifluoromethylphenyl)-2-propyn-1-ol (7.50 g, 75% yield) as a light yellow solid. Purification was conducted by filtering 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); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.56 (d, $J = 8.0$ Hz, 2H), 7.52 (d, $J = 8.0$ Hz, 2H), 4.52 (d, $J = 6.0$ Hz, 2H), 2.10 (t, $J = 6.0$ Hz, 1H); MS(EI) m/z (relative intensity) 200 (M^+, 100).

The general procedure of the condensation of arylpropargyl alcohol with allyl bromide was followed: 3-(4-trifluoromethylphenyl)-2-propyn-1-ol (2.0 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-trifluoromethylphenyl)-1-propyne as a colorless liquid (1.82 g, 91% yield). Purification of the crude product was conducted by filtering 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); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.56 (d, $J = 9.0$ Hz, 2H), 7.53 (d, $J = 8.0$ Hz, 2H), 5.37–5.97 (m, 1H), 5.35 (dd, $J = 17.0$, 1.0 Hz, 1H), 5.25 (dd, $J = 17.5$, 1.0 Hz, 1H), 4.39 (s, 2H), 4.13 (d, $J = 6.0$ Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 134.1, 132.2, 126.7, 125.4 (q, $J = 3.9$ Hz), 125.2, 123.0, 118.2, 87.9, 85.0, 71.1, 57.9; IR (neat, cm^{-1}) 3078, 3016, 2986, 2939, 2853, 1921, 1649, 1615, 1567, 1521, 1441, 1406, 1325, 1259, 1171, 1018, 928, 843, 716, 598; MS(EI) m/z (relative intensity) 240 (M^+, 100); HRMS calcd for $C_{13}H_{11}F_3O$ 240.07620, found 240.07690.

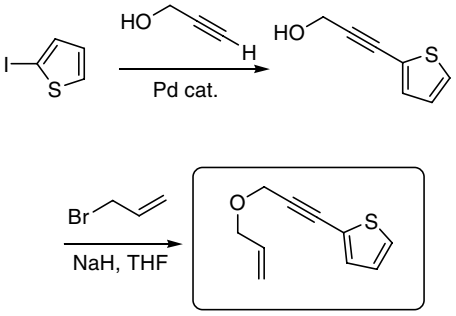
4.3.9. 3-(Allyloxy)-1-(2-methylphenyl)-1-propyne 9



The general procedure for Sonogashira coupling of propargyl alcohol with ArI was used: 2-Iodotoluene (10.9 g, 50 mmol), $Pd(PPh_3)_2Cl_2$ (3 mol %), CuI (6 mol %), piperidine (8.4 g, 100 mmol), propargyl alcohol (3.07 mL, 52 mmol), and freshly distilled toluene (50 mL) were used to afford 3-(2-methylphenyl)-2-propyn-1-ol[30] (5.26 g, 72% yield) as a light brown solid. Purification was conducted by filtration of 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 calcd for $C_{10}H_{10}O$ 146.07316, found 146.07310.

The general procedure of the condensation of arylpropargyl alcohol with allyl bromide was 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, $J = 17.0$, 1.0 Hz, 1H), 5.27 (dd, $J = 17.5$, 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 calcd for $C_{13}H_{14}O$ 186.10447, found 186.10453.

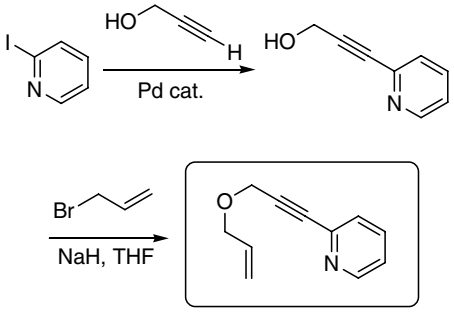
4.3.10. 3-(Allyloxy)-1-(2-thiophenyl)-1-propyne 10



The general procedure for Sonogashira coupling of propargyl alcohol with ArI was used: 2-iodothiophene (10.5 g, 50 mmol), $Pd(PPh_3)_2Cl_2$ (3 mol %), CuI (6 mol %), piperidine (8.4 g, 100 mmol), propargyl 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 filtering 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 procedure of the condensation of arylpropargyl alcohol with allyl bromide was 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, 1H, $J = 3.5$ Hz), 6.97 (dd, 1H, $J = 4.0$, 5.0 Hz), 5.90–5.98 (m, 1H), 5.34 (dd, 1H, $J = 1.0$, 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 calcd for $C_{10}H_{10}OS$ 178.04524, found 178.04514.

4.3.11. 3-(Allyloxy)-1-(2-pyridyl)-1-propyne 11

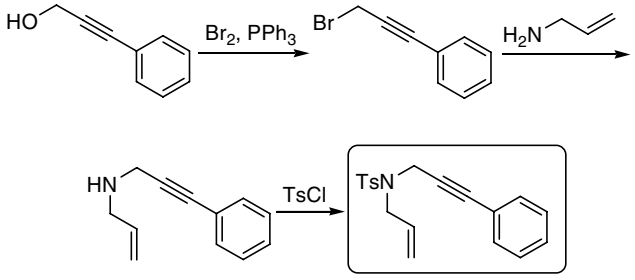


The general procedure for Sonogashira coupling of propargyl alcohol with ArI was used: 2-iodopyridine (10.25 g, 50 mmol), $Pd(PPh_3)_2Cl_2$ (3 mol %), CuI (6 mol %), piperidine (8.4 g, 100 mmol), propargyl alcohol (3.07 mL, 52 mmol), and freshly distilled toluene (50 mL) were used to afford 3-(2-pyridyl)-2-propyn-1-ol (4.59 g, 69% yield) as a brown solid. Purification was conducted by filtering the reaction mixture over a silica pad (5 cm × 5 cm), and purified by flash column chromatography on silica gel using dichloromethane as eluent. $R_f = 0.3$ (dichloromethane); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.56 (d, $J = 4.5$ Hz, 1H), 7.66 (dt, $J = 2.0$, 8.0 Hz, 1H), 7.43 (d, $J = 8.0$ Hz, 1H), 7.23–7.26 (m, 1H), 4.53 (s, 2H); MS(EI) m/z (relative intensity) 133 (M^+, 100), 126 (20).

The general procedure of the condensation of arylpropargyl alcohol with allyl bromide was followed: 3-(2-pyridyl)-2-propyn-1-ol (1.33 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-pyridyl)-1-propyne as a deep brown liquid (1.56 g, 90% yield). $R_f = 0.2$ (hexane/ethyl acetate = 100/1); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.55 (dd, $J = 1.0$, 5.0 Hz, 1H), 7.62 (dt, $J = 1.5$, 8.0 Hz, 1H), 7.41 (d, $J = 7.5$ Hz, 1H), 7.21 (dd, $J = 7.5$, 5.0 Hz, 1H), 5.86–5.94 (m, 1H), 5.32 (dd, $J = 1.0$, 16.5 Hz, 1H), 5.20 (dd, $J = 10.5$, 1.0 Hz, 1H), 4.38 (s, 2H), 4.12 (d, $J = 6.0$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 149.9, 142.7, 136.1, 133.8, 127.1, 123.0, 117.9, 85.4, 85.1, 70.7, 57.6; IR (neat, cm^{-1}) 3068, 3052, 3011, 2852, 1982, 1644, 1581, 1557, 1463, 1427, 1353, 1266, 1122, 1087, 994, 927, 780, 737, 630, 594, 528; MS(EI) m/z (relative intensity) 173 (M^+, 10), 132 (100); HRMS calcd for $C_{11}H_{12}N$ 174.0919, found 174.0912.

4.3.12. *N*-Allyl-*N*-(3-phenyl-2-propynyl)-4-tolylsulfonamide 12[32]

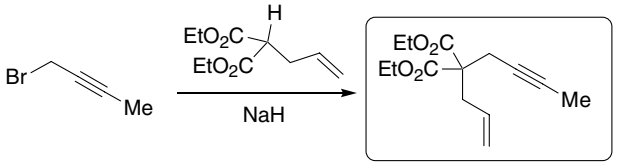


Triphenylphosphine (14.4 g, 55 mmol) was dissolved in dichloromethane (250 mL). Bromine (8.8 g, 2.82 mL, 55 mmol) was then added dropwise at 0 °C, and stirred for 30 min. 3-Phenyl-2-propyn-1-ol was added at 0 °C and the reaction mixture left to stir for 1 h. Hexane (~800 mL) was added and the white suspension 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[33] (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 three-necked round-bottomed 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 stirred at room temperature for 2 h. 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 × 10 cm height). Solvent was removed in vacuo and the *N*-allyl-*N*-(3-phenyl-2-propynyl)amine product used in next step without further purification.

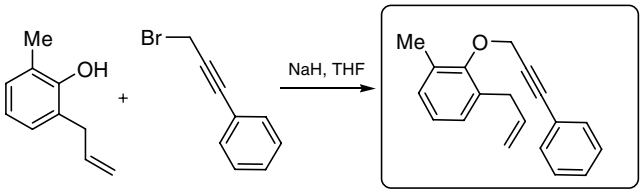
To a mixture of *N*-allyl-*N*-(3-phenyl-2-propynyl)amine (crude), triethylamine (0.9 mL), and dichloromethane (5 mL) was added a dichloromethane solution of *p*-toluenesulfonyl chloride (967 mg, 5.07 mmol) at 0 °C. The reaction mixture was slowly warmed to room temperature and stirred for 2 h. Water (~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).

4.3.13. Diethyl 7-octen-2-yne-5,5-dicarboxylate 13[34]



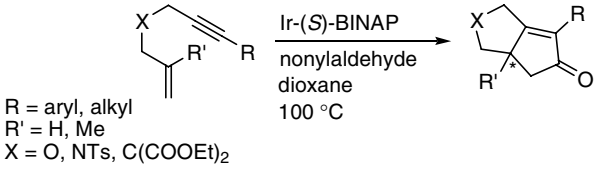
Diethyl 1-butene-4,4-dicarboxylate (2.0 g, 10 mmol) was charged to a three-necked round-bottomed flask followed by the addition of dry THF (30 mL) under nitrogen at room temperature. NaH (360 mg, 15 mmol, prewashed with dry hexane) was added portionwise to the reaction mixture at 0 °C and stirred for 2 h. 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 h. The reaction was quenched by water (~50 mL), and the aqueous phase extracted by diethyl ether (3 × ~100 mL). The combined organic phase was washed with water, brine and dried over sodium sulfate. The solvent was removed by rotary evaporation, and the crude mixture purified by distillation under reduced pressure to afford the title compound as 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).

4.3.14. 3-Phenyl-1-(2-methyl-6-allyl-1-phenyoxy)propyne 15



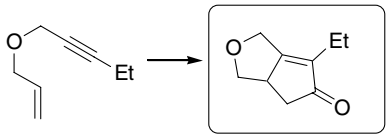
The general procedure for condensation was followed: viscous colorless liquid, $R_f = 0.4$ (hexane/ethyl acetate = 50:1); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.43–7.45 (m, 2H), 7.31–7.33 (m, 3H), 7.00–7.09 (m, 3H), 5.98–6.05 (m, 1H), 5.08–5.13 (m, 2H), 4.74 (s, 2H), 3.55 (d, 2H, $J = 7.0$ Hz), 2.39 (s, 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 calcd for $C_{19}H_{18}ONa$ 285.1255, found 285.1260.

4.4. General procedures for Ir-catalyzed asymmetric Pauson–Khand-type cyclization

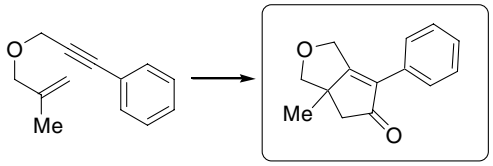


General procedures for Ir-catalyzed asymmetric Pauson–Khand-type cyclization of various enynes: $[Ir(COD)Cl]_2$ (10.0 mg, 0.015 mmol), (*S*)-BINAP (18.9 mg, 0.03 mmol) and Teflon-coated magnetic stirrer bar (3 mm × 10 mm) were charged into a Rotaflo® (England) resealable screw-cap Schlenk flask on bench-top at room temperature. The flask was evacuated and backfilled with nitrogen (three cycles). Anhydrous dioxane (3.0 mL) was added under nitrogen atmosphere with continuous stirring for 10 min. Distilled aldehyde (1.5 mmol, 5 equiv with respected to enyne) and enynes (0.3 mmol) were added sequentially via micro-syringe. Additional dioxane (1.0 mL, total = 4.0 mL) was used to rinse the inner-wall of the Schlenk flask. The flask was resealed and the reaction mixtures magnetically stirred in a preheated 100 °C (±3 °C) oil bath for 48 h (reaction times were unoptimized for each substrate). The flask was allowed to cool to room temperature. Diethyl ether or dichloromethane (~5 mL) was added and then concentrated under reduced pressure. The crude reaction mixtures were directly purified by column chromatography on silica gel using hexane/ethyl acetate as the eluent to afford optically active bicyclic cyclopentenones. The enantiomeric excess of the products were determined by chiral HPLC analysis using Daicel® Chiralcel and Chiralpak columns. Chiral HPLC conditions; Column: Chiralcel AS-H; Chiralcel AS; Chiralcel AD-H: Solvent; Hex–IPA = 9:1 or Hex–IPA = 98:2; flow rate: 1.0 mL/min.

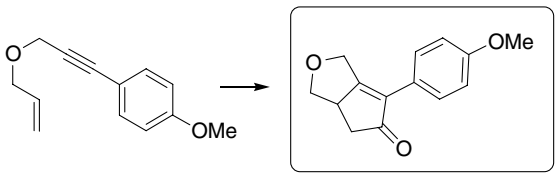
4.5. Characterization data of PKR products



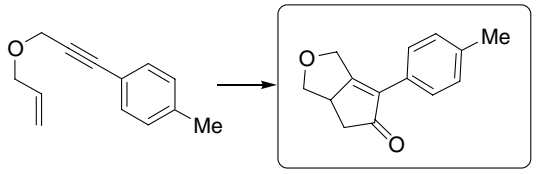
4.5.1. 2-Ethyl-7-oxabicyclo[3.3.0]oct-1-en-3-one[25] (Table 3, entry 1). Purified by column chromatography (2 cm diameter × ~20 cm height) on silica gel using hexane/ethyl acetate (3:1) as eluent to obtain the title compound as light yellow oil. Yield 69%; 95% ee; $R_f = 0.3$ (hexane/ethyl acetate = 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, $J = 5.5$, 18.0 Hz, 1H), 2.19–2.33 (m, 2H), 2.10–2.17 (dd, $J = 2.5$, 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 (30), 105 (50). Chiral HPLC conditions; UV lamp: 210 nm; retention time: 9.5 min (major), 11.4 min (minor).



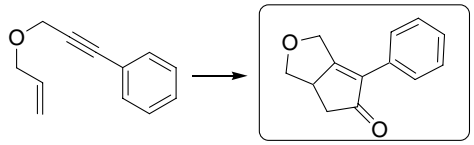
4.5.2. 2-Phenyl-5-methyl-7-oxabicyclo[3.3.0]oct-1-en-3-one[35] (Table 3, entry 2). Purified by column chromatography (2 cm diameter × ~20 cm height) on silica gel using hexane/ethyl acetate (3:1) as eluent to obtain the title compound as light yellow oil. Yield 41%; 96% ee; $R_f = 0.3$ (hexane/ethyl 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: UV lamp: 254 nm; retention time: 9.4 min (major), 11.3 min (minor).



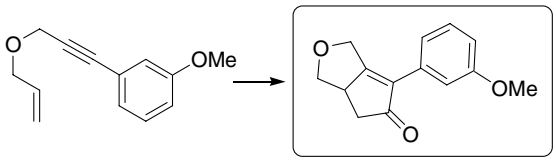
4.5.3. 2-(4-Methoxyphenyl)-7-oxabicyclo[3.3.0]oct-1-en-3-one[27] (Table 3, entry 3). Purified by column chromatography (2.0 cm diameter × ~20 cm height) on silica gel using hexane/ethyl acetate (2:1) as eluent to obtain the title compound as a light yellow solid. Yield 76%; 94% ee; $R_f = 0.2$ (hexane/ethyl 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, $J = 7.5$, 11.0 Hz, 1H), 2.81 (dd, $J = 6.0$, 17.5 Hz, 1H), 2.31 (dd, $J = 3.0$, 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). Chiral HPLC conditions: UV lamp: 254 nm; retention time: 17.1 min (major), 25.3 min (minor).



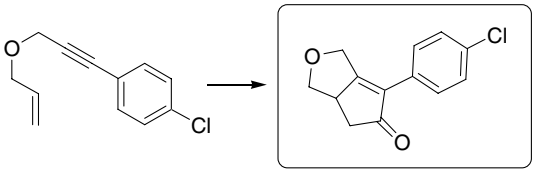
4.5.4. 2-(4-Methylphenyl)-7-oxabicyclo[3.3.0]oct-1-en-3-one (Table 3, entry 4). Purified by column chromatography (2 cm diameter × ~20 cm height) on silica gel using hexane/ethyl acetate (3:1) as eluent to obtain the title compound as a white solid. Yield 75%; 95% ee; $R_f = 0.4$ (hexane/ethyl acetate = 2:1); $[\alpha]_D^{25} = +60.9$ (c 0.10, CH_2Cl_2); 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, $J = 8.0$, 11.5 Hz, 1H), 2.84 (dd, $J = 6.5$, 17.5 Hz, 1H), 2.37 (s, 3H), 2.32 (dd, $J = 3.5$, 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 calcd for $C_{14}H_{14}O_2$ 214.09938, found 214.09943. Chiral HPLC conditions: UV lamp: 254 nm; retention time: 10.3 min (major), 13.2 min (minor).



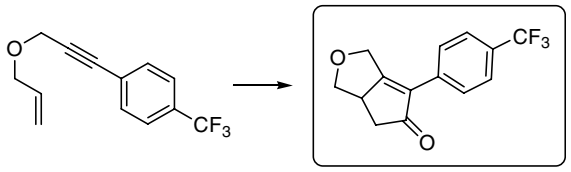
4.5.5. 2-Phenyl-7-oxabicyclo[3.3.0]oct-1-en-3-one[36] (Table 3, entry 5). Purified by column chromatography (2 cm diameter × ~20 cm height) on silica gel using hexane/ethyl acetate (3:1) as eluent to obtain the title compound as a light yellow oil. Yield 74%; 94% ee; $R_f = 0.3$ (hexane/ethyl acetate = 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, $J = 8.0$, 11.5 Hz, 1H), 2.85 (dd, $J = 6.5$, 18.5 Hz, 1H), 2.34 (dd, $J = 4.0$, 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: UV lamp: 254 nm; retention time: 12.0 min (minor), 15.7 min (major).



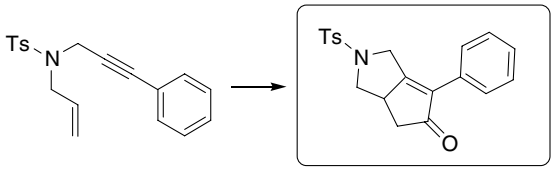
4.5.6. 2-(3-Methoxyphenyl)-7-oxabicyclo[3.3.0]oct-1-en-3-one (Table 3, entry 6). Purified by column chromatography (2 cm diameter × ~20 cm height) on silica gel using hexane/ethyl acetate (3:1) as eluent to obtain the title compound as a light yellow viscous oil. Yield 24%; 94% ee; $R_f = 0.3$ (hexane/ethyl acetate = 2:1); $[\alpha]_D^{25} = +26.3$ (c 0.11, CH_2Cl_2); ^{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, $J = 2.5$, 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, $J = 7.5$, 11.5 Hz, 1H), 2.84 (dd, $J = 6.5$, 17.5 Hz, 1H), 2.33 (dd, $J = 4.0$, 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 calcd for $C_{14}H_{14}O_3$ 230.09430, found 230.09422. Chiral HPLC conditions: UV lamp: 254 nm; retention time: 19.4 min (major), 42.2 min (minor).



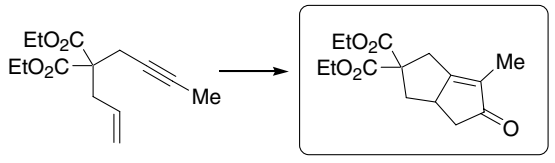
4.5.7. 2-(4-Chlorophenyl)-7-oxabicyclo[3.3.0]oct-1-en-3-one[37] (Table 3, entry 7). Purified by preparative TLC on silica gel using hexane/ethyl acetate (2:1) as eluent to obtain the title compound as a light yellow oil. Yield 60%; 98% ee; $R_f = 0.3$ (hexane/ethyl acetate = 2:1); ^{1}H NMR ($CDCl_3$, 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, $J = 7.5$, 11.0 Hz, 1H), 2.85 (dd, $J = 6.0$, 18.0 Hz, 1H), 2.33 (dd, $J = 3.5$, 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: UV lamp: 254 nm; retention time: 19.1 min (major), 22.9 min (minor).



4.5.8. 2-(4-Trifluoromethylphenyl)-7-oxabicyclo[3.3.0]oct-1-en-3-one (Table 3, entry 8). Purified by column chromatography on silica gel using hexane/ethyl acetate (3:1) as eluent to obtain the title compound as a light yellow oil. Yield 42%; 96% ee; $R_f = 0.3$ (hexane/ethyl acetate = 2:1); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.63–7.67 (m, 4H), 4.96 (d, $J = 16.0$ Hz, 1H), 4.59 (d, $J = 16.5$ Hz, 1H), 4.40 (t, $J = 8.0$ Hz, 1H), 3.36–3.38 (m, 1H), 3.26 (dd, $J = 7.5$, 11.0 Hz, 1H), 2.87 (dd, $J = 6.0$, 18.0 Hz, 1H), 2.36 (dd, $J = 3.5$, 18.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 179.6, 134.0, 133.5, 130.5, 130.2, 128.2, 125.5 (q, $J = 3.9$ Hz), 71.3, 66.2, 43.6, 40.2; IR (neat, cm^{-1}) 3023, 2346, 1715, 1527, 1443, 1202, 1040, 1026, 933, 758, 664; MS(EI) m/z (relative intensity) 268 (M^+, 20), 200 (100); HRMS calcd for $C_{14}H_{12}F_3O_2$ 269.0789, found 269.0787. Chiral HPLC conditions: UV lamp: 254 nm; retention time: 12.7 min (minor), 15.1 min (major).



4.5.9. 2-Phenyl-7-[(4-methylphenyl)sulfonyl]-7-azabicyclo-[3.3.0]oct-1-en-3-one[38] (Table 3, entry 12). 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 a light yellow solid. Yield 31%; 95% 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, $J = 2.0$, 17.0 Hz, 1H), 4.04–4.09 (m, 2H), 3.18–3.23 (m, 1H), 2.78 (dd, $J = 6.5$, 17.5 Hz, 1H), 2.61 (dd, $J = 9.0$, 10.5 Hz, 1H), 2.40 (s, 3H), 2.25 (dd, $J = 4.0$, 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: UV lamp: 254 nm; retention time: 40.4 min (minor), 44.5 min (major).



4.5.10. Diethyl 2-methyl-3-oxobicyclo[3.3.0]oct-1-ene-7,7-dicarboxylate[39] (Table 3, entry 13). 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 a light yellow viscous oil. Yield 39%; 90% ee; $R_f = 0.3$ (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, $J = 7.0$, 12.5 Hz, 1H), 2.60 (dd, $J = 6.0$, 18.0 Hz, 1H), 2.04 (dd, $J = 3.0$, 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: UV lamp: 254 nm; retention time: 12.4 min (minor), 15.6 min (major).

Acknowledgments

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