

Asymmetric Au-catalyzed cycloisomerization of 1,6-enynes: An entry to bicyclo[4.1.0]heptene

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Full Research Paper

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Abstract

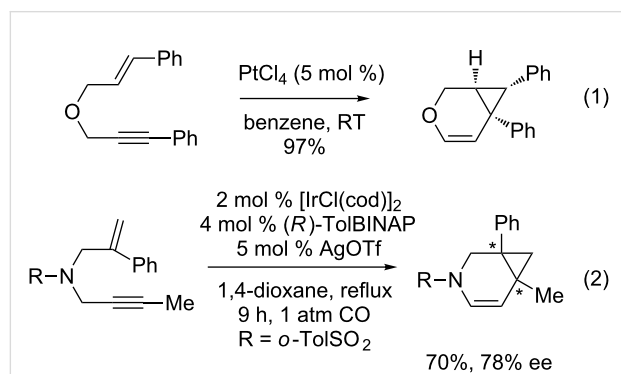
A comprehensive study on the asymmetric gold-catalyzed cycloisomerization reaction of heteroatom tethered 1,6-enynes is described. The cycloisomerization reactions were conducted in the presence of the chiral cationic Au(I) catalyst consisting of (*R*)-4-MeO-3,5-(*t*-Bu)₂-MeOBIPHEP-(AuCl)₂ complex and silver salts (AgOTf or AgNTf₂) in toluene under mild conditions to afford functionalized bicyclo[4.1.0]heptene derivatives. The reaction conditions were found to be highly substrate-dependent, the best results being obtained in the case of oxygen-tethered enynes. The formation of bicyclic derivatives, including cyclopropyl pentasubstituted ones, was reported in moderate to good yields and in enantiomeric excesses up to 99%.

Introduction

Metal-catalyzed cycloisomerization reactions of 1,*n*-enynes have emerged as efficient processes that contribute to sustainable development and atom economy concepts [1-8]. In the last ten years, they have provided extremely efficient access to cyclic skeletons with a broad range of functional moieties. Among them, the synthesis of oxa- and azabicyclo[4.1.0]heptenes starting from heteroatom-linked 1,6-enynes has been recently a field of high interest considering the fundamental skeleton rearrangement research of 1,*n*-enynes

[1-11] and the potential applications in biological active and natural products [12,13]. In 1995, Blum et al. described a novel PtCl₄-catalyzed cycloisomerization reaction of allyl propynyl ethers leading to oxabicyclo[4.1.0]heptenes [14] (Scheme 1, reaction 1). The group of Murai observed a similar reactivity in the presence of PtCl₂, although in a lower yield [15]. These seminal contributions were then followed by several comprehensive studies involving carbophilic complexes such as platinum or gold [16-22] that led to the formation of complex

bicyclic and tricyclic compounds [23–40]. The first asymmetric version was described by Shibata's group in 2005 in the presence of a chiral iridium catalyst [41] (Scheme 1, reaction 2). We and others recently pursued the improvement and development of this enantioselective process, by employing platinum [42–44], rhodium [45] or gold [46–48] complexes. Following our previous work with chiral gold catalysts [46], we report a comprehensive study on gold-catalyzed enantioselective synthesis of bicyclo[4.1.0]heptenes, focusing on the scope and limitations of such systems.



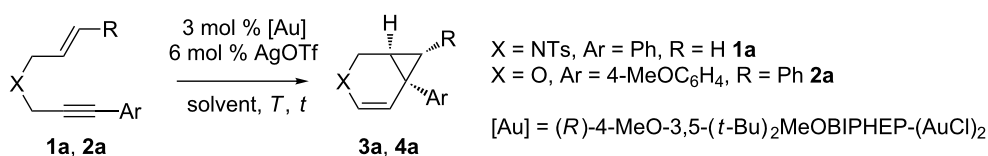
Scheme 1: First reports on the racemic and asymmetric synthesis of bicyclo[4.1.0]heptenes.

Results and Discussion

Optimization of the catalytic system

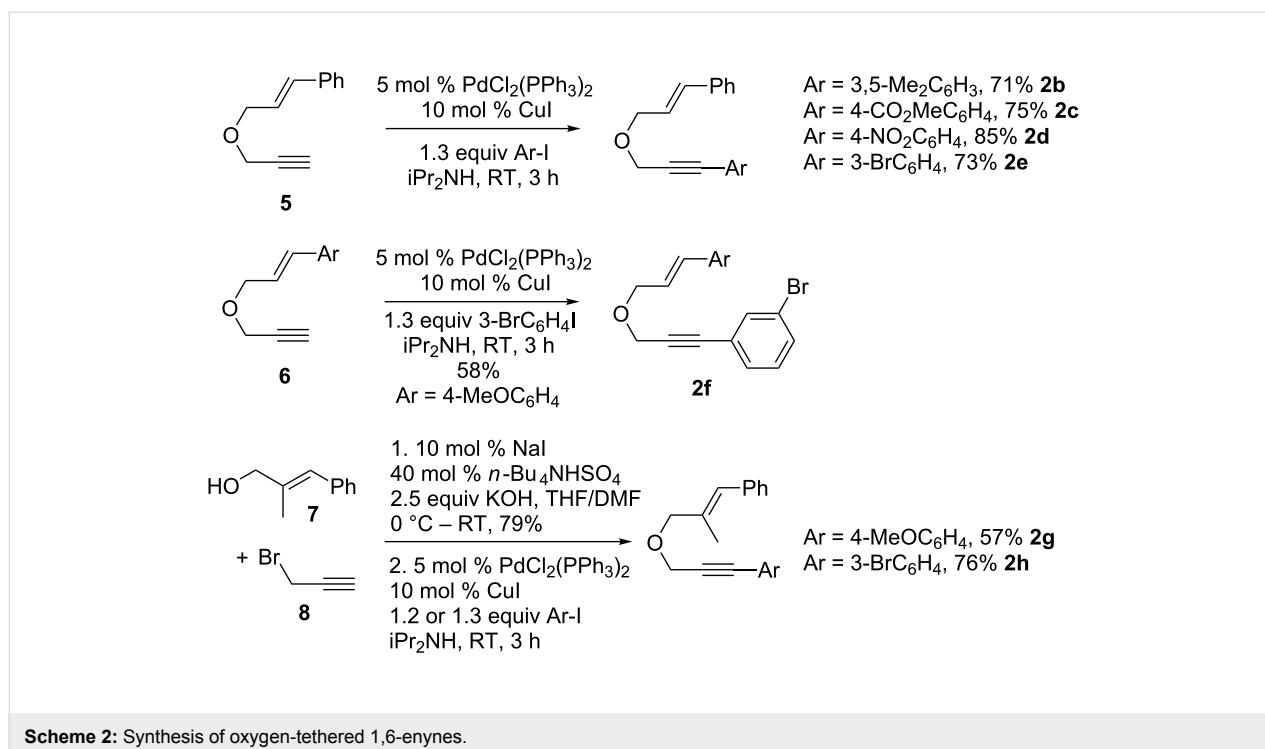
Based on our ongoing program on asymmetric gold catalysis [46,49–52], and on literature reports [53–55], we selected 4-MeO-3,5-*t*-Bu₂-MeOBIPHEP-(AuCl)₂ complex [56–58] as the best candidate for such a transformation. Initial experiments were performed using *N*-tosyl allyl substrate **1a** and oxygen-linked propargylic 1,6-enyne **2a** as model substrates (Table 1). The reaction of **1a** was evaluated in various solvents and proceeded smoothly leading to the desired alkene **3a** [59]. The reaction kinetics and stereoselectivity were found to be highly solvent-dependent, the enantiomeric excesses (ee) varying from 31% to 78% at room temperature (Table 1, entries 1–3). The reaction kinetic was very slow at room temperature in ether and toluene, but high ee's were obtained. Increasing the temperature to 40 °C in toluene or ether had a positive effect both on the conversion and on the ee's (Table 1, entries 4 and 5). The reaction was also conducted at 60 °C or 70 °C with good conversions and ee's (Table 1, entries 6–8), the best results being obtained in toluene. At 80 °C in toluene, a decrease in the stereoselectivity was observed as the ee dropped to 91% (Table 1, entry 9). The reactivity of oxygen-tethered enynes such as **2a** was different to that for **1a** as a complete conversion was observed at room temperature in toluene, dichloromethane, ether and tetrahydrofuran (Table 1, entries 10–13). A better ee

Table 1: Cycloisomerization reaction of nitrogen- and oxygen-linked 1,6-enynes **1a** and **2a**.



Entry	Substrate	Solvent	T [°C]	t [h]	Conv. (Yield) [%] ^a	Product	ee [%] ^b
1	1a	CH ₂ Cl ₂	RT	36	78	3a	31 (-)
2	1a	Et ₂ O	RT	39	17	3a	75 (-)
3	1a	toluene	RT	39	11	3a	78 (-)
4	1a	Et ₂ O	40	41	28	3a	90 (-)
5	1a	toluene	40	96	100 (47)	3a	98 (-)
6	1a	toluene	60	96	100 (74)	3a	98 (-)
7	1a	THF	60	96	69	3a	74 (-)
8	1a	toluene	70	96	100 (83)	3a	96 (-)
9	1a	toluene	80	48	66	3a	91 (-)
10	2a	toluene	RT	30	100 (57)	4a	92 (-)
11	2a	CH ₂ Cl ₂	RT	25	100 (26)	4a	70 (-)
12	2a	Et ₂ O	RT	25	100 (35)	4a	91 (-)
13	2a	THF	RT	25	100 (43)	4a	85 (-)
14	2a	toluene	0	120	100 (56)	4a	96 (-)

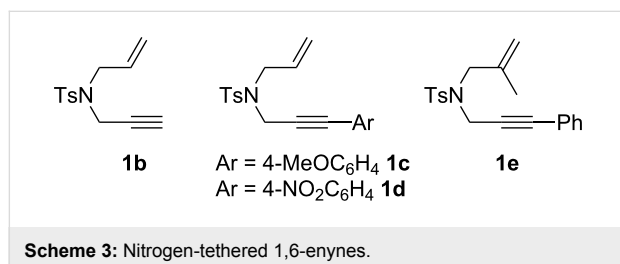
^aDetermined by ¹H NMR, ^bdetermined by HPLC.



was obtained in toluene compared to other solvents. Cyclopropyl alkene **4a** was isolated in 56% yield and 96% ee at 0 °C in toluene (Table 1, entry 14). Toluene was therefore chosen for further studies.

Synthesis of 1,6-enynes

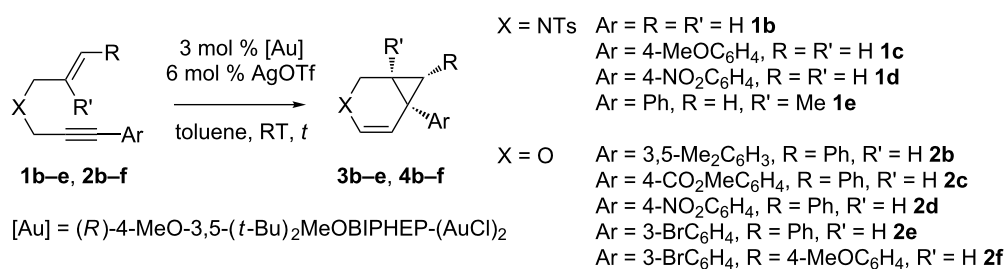
We prepared various oxygen-tethered 1,6-enynes according to classic methodologies employing a Williamson alkylation reaction and/or a Sonogashira cross-coupling [60,61] (Scheme 2 and Scheme 3). The known enyne **5** [62,63] was engaged in Pd-catalyzed coupling in the presence of diversely functionalized aryl iodides (Scheme 2). The corresponding substituted alkynes **2b–e** [46] were isolated in 71–85% yield. An analogous 1,6-enyne **6** [64] was also reacted with 3-bromiodobenzene under the same reaction conditions and led to the formation of substrate **2f** in 58% isolated yield. We also envisaged preparing two trisubstituted alkenes **2g** and **2h** by an alkylation/Sonogashira sequence starting from commercially available substrates **7** and **8**.



We also selected some nitrogen-tethered 1,6-enynes **1b–e** from the literature [23,41–44] and synthesized them to evaluate the efficiency of the gold chiral catalytic system (Scheme 3).

Scope and limitations of the catalytic system

The prepared heteroatom-linked 1,6-enynes were then engaged in the cycloisomerization process in the presence of Au(I) cationic catalyst generated by mixing (*R*)-4-MeO-3,5-(*t*-Bu)₂-MeOBIPHEP-(AuCl)₂ complex and silver salts (Table 2). Anticipating the moderate reactivity of nitrogen-tethered enynes **1**, the reactions were conducted at 60 °C in toluene (Table 2, entries 1–5). The substitution of the aromatic ring on the alkyne moiety led to a substantial decrease of both isolated yields and ee's, as the presence of several by-products was detected, presumably due to degradation or polymerization [15]. A good ee was achieved in the case of enyne **1c**, by using AgNTf₂ [65] instead of AgOTf (Table 2, entry 2 compared to entry 1). The substitution of the allylic side chain seemed to slow down the degradation process, as the cyclic alkene **3e** was isolated in 61% yield (Table 2, entry 4). In the case of non-substituted enyne **1b** (Table 2, entry 5), the bicyclic alkenyl derivative **3b** was isolated in low yield and ee: The synthesis of **3b** was accompanied by the formation of known 1,3- and 1,4-dienes (5% and 10% isolated yield respectively) resulting from 5-*exo*- and 6-*endo* cycloisomerization reactions [20,66]. Thus, the gold catalytic system cannot compete with the results obtained for the cyclizations of nitrogen-tethered enynes in the presence of iridium, platinum or rhodium catalysts [41–45]. The cyclois-

Table 2: Cycloisomerization reaction of nitrogen- and oxygen-linked 1,6-enynes.

Entry	Enyne		<i>t</i> [h]	Yield [%] ^a	Product	ee [%] ^b
1 ^c		1c	17	8		3c 77
2 ^{c,d}		1c	17	8		3c 89
3 ^c		1d	24	7		3d 35
4 ^c		1e	16	61		3e 13
5 ^c		1b	16	23		3b 22
6		2b	3.5	54		4b 93 (+)
7		2c	15	25		4c 94 (-)
8 ^d		2c	15	64		4c 94 (-)

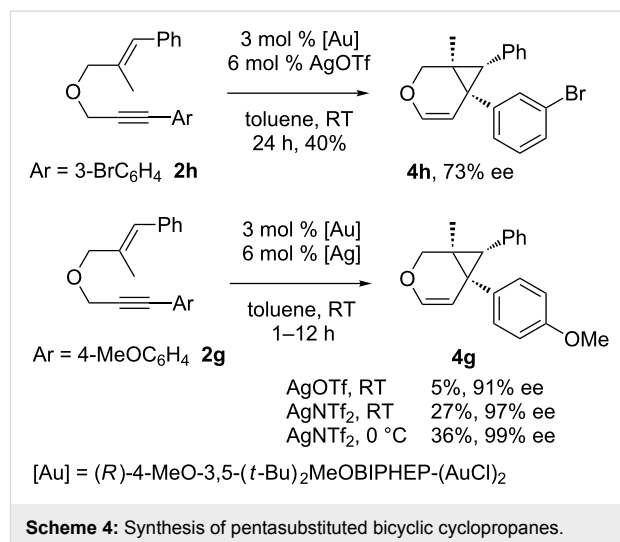
Table 2: Cycloisomerization reaction of nitrogen- and oxygen-linked 1,6-enynes. (continued)

9		2d	15	32		4d	96 (-)
10 ^d		2d	15	63		4d	98 (-)
11		2e	30	59		4e	95 (-)
12		2f	1	37		4f	95 (-)

^aIsolated yield, ^bdetermined by HPLC, ^c60 °C, ^dAgNTf₂.

merization process was found to be highly stereoselective in the case of oxygen-tethered enynes (Table 2, entries 6–12). In all cases, the ee's were greater than 90% and in one case as high as 98%. The stability of the resulting bicyclic alkenes **4** was generally only moderate, which led to low isolated yields. In the case of 1,6-enynes **2c** and **2d**, the low yields (25% and 32% respectively) could be improved by switching from AgOTf salt to AgNTf₂, presumably due to the experimentally observed lower hygroscopicity of bistriflimide complex (Table 2, entry 7 compared to 8 and 9 compared to 10). The functionalized derivatives **4c** and **4d** were obtained in 64% and 63% yields respectively and in excellent ee's (Table 2, entries 8 and 10). The compatibility with another functional group on the aromatic ring such as bromine (Table 2, entry 11), and with a different allylic side chain (Table 2, entry 12) was also evaluated: The corresponding bicyclic adducts **4e** and **4f** were isolated in modest to good yield and 95% ee.

Considering the observed highly stereoselective reactions of oxygen-tethered 1,6-enynes, we decided to study the challenging asymmetric synthesis of pentasubstituted cyclopropyl derivatives [67–70] (Scheme 4). The bicyclic derivative **4h** was obtained in moderate yield and 73% ee. Conducting the reaction at 0 °C and using AgNTf₂ as a chloride scavenger led to the formation of the alkenyl functionalized derivative **4g** in 36% isolated yield and excellent 99% ee.



Conclusion

In conclusion, we have contributed to the development of an asymmetric gold-catalyzed cycloisomerization reaction allowing the formation of oxa- and aza-bicyclo[4.1.0]heptene derivatives. The combination of chiral Au(I) complex (*R*)-4-MeO-3,5-(*t*-Bu)₂-MeOBIPHEP-(AuCl)₂ associated to silver salts promotes the enantioselective rearrangement of oxygen and nitrogen-tethered 1,6-enynes in toluene at room temperature or 60 °C. The cycloisomerization reactions were found to

be highly substrate-dependent as low yield and ee's were generally obtained in the case of nitrogen-tethered enynes. The enantiomerically enriched functionalized oxabicyclo[4.1.0]heptenes were isolated in moderate yields but with excellent ee values ranging from 73% to 99%. This methodology was successfully applied to the synthesis of pentasubstituted cyclopropyl heterobicycles.

Experimental

All reactions were carried out under an argon atmosphere. ^1H NMR and ^{13}C NMR were recorded on a Bruker AV 300 instrument. All signals were expressed as ppm (δ) and internally referenced to residual proton solvent signals. Coupling constants (J) are reported in Hz and refer to apparent peak multiplicities. Enantiomeric excesses were determined by high pressure liquid chromatography analyses (HPLC) on Waters instruments (Waters 486 detector, 717 autosampler equipped with Daicel Chiralcel OD-H, OJ and Chiralpak IA, AD, $\lambda = 215$ nm). Optical rotation measurements were conducted on a Perkin–Elmer 241 polarimeter at 589 nm. Enynes **5** [71], **2a** [72], **2b–e** [46], **1a** [73], **1b** [74], **1c,d** [75], **1e** [73], and **6** [64] were prepared according to published procedures. ^1H , ^{13}C NMR and mass spectrometry data for compounds **3a,b** [23], **3c,d** [75], **3e** [76] and **4a–e** [46] were described elsewhere.

(E)-1-Bromo-3-(3-(3-(4-methoxyphenyl)allyloxy)prop-1-ynyl)benzene (2f): CuI (46 mg, 0.1 equiv) and $\text{PdCl}_2(\text{PPh}_3)_2$ (86 mg, 0.05 equiv) were placed in a Schlenk tube under argon. Distilled diisopropylamine (3 mL) was added and the reaction mixture was stirred at RT for 5 min. 1-Bromo-3-iodobenzene (0.4 mL, 1.3 equiv) was added and the reaction mixture was stirred for 5 min. Enyne **6**, dissolved in 2 mL of distilled diisopropylamine was added and the reaction mixture stirred for 3 h at RT. After hydrolysis with sat. aq. NH_4Cl solution, the aqueous phase was extracted with EtOAc. The organic layer was successively washed with sat. aq. NH_4Cl solution and brine. The organic layer was then dried with MgSO_4 , filtered and the solvents were evaporated under reduced pressure. The crude product was purified by silica gel chromatography (cyclohexane/ethyl acetate 90:10) to give **2f** as a colorless oil (509 mg, 58%). TLC (cyclohexane/ethyl acetate 70:30) R_f 0.77; ^1H NMR (300 MHz, CDCl_3) δ 3.71 (s, 3H), 4.17 (dd, $J = 6.3, 1.2$ Hz, 2H), 4.30 (s, 2H), 6.08 (dt, $J = 15.9, 6.3$ Hz, 1H), 6.52 (d, $J = 15.9$ Hz, 1H), 6.76 (d, $J = 8.8$ Hz, 2H), 7.07 (t, $J = 7.9$ Hz, 1H), 7.16–7.33 (m, 3H), 7.36 (dt, $J = 8.0, 1.1$ Hz, 1H), 7.5 (t, $J = 1.6$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 55.6, 57.9, 71.0, 85.1, 87.1, 114.4 (2C), 122.4, 123.2, 125.1, 128.1 (2C), 129.7, 130.1, 130.7, 132.0, 133.6, 134.9, 159.8.

(E)-1-Methoxy-4-(3-(2-methyl-3-phenylallyloxy)prop-1-ynyl)benzene (2g): Following the same procedure as for the

synthesis of **2f**, in the presence of CuI (103 mg, 0.1 equiv) and $\text{PdCl}_2(\text{PPh}_3)_2$ (190 mg, 0.05 equiv), 1-methoxy-4-iodobenzene (1.52 g, 1.2 equiv) in distilled diisopropylamine (10 mL), (*E*)-(2-methyl-3-(prop-2-ynoxy)prop-1-enyl)benzene [77] (1 g, 1 equiv) was transformed to **2g** (896 mg) in 57% yield. TLC (cyclohexane/ethyl acetate 90:10) R_f 0.71; ^1H NMR (300 MHz, CDCl_3) δ 2.20 (d, $J = 1.2$ Hz, 3H), 4.07 (s, 3H), 4.44 (d, $J = 0.9$ Hz, 2H), 4.66 (s, 2H), 6.83 (s, 1H), 7.11 (m, 2H), 7.68–7.48 (m, 7H); ^{13}C NMR (75 MHz, CDCl_3) δ 15.7, 55.3, 57.8, 76.0, 83.8, 86.2, 113.9, 114.8, 126.5, 127.8, 128.1 (2C), 128.9 (2C), 133.3 (2C), 134.5, 137.4, 159.7.

(E)-1-Bromo-3-(3-(2-methyl-3-phenylallyloxy)prop-1-ynyl)benzene (2h): Following the same procedure as for the synthesis of **2f**, in the presence of CuI (62 mg, 0.1 equiv) and $\text{PdCl}_2(\text{PPh}_3)_2$ (115 mg, 0.05 equiv), 1-bromo-3-iodobenzene (0.53 mL, 1.3 equiv) in distilled diisopropylamine (6.8 mL), (*E*)-(2-methyl-3-(prop-2-ynoxy)prop-1-enyl)benzene [77] (611 mg, 1 equiv) was transformed to **2h** (851 mg) in 76% yield. TLC (cyclohexane/ethyl acetate 90:10) R_f 0.63; ^1H NMR (300 MHz, CDCl_3) δ 2.08 (d, $J = 1.3$ Hz, 3H), 4.31 (d, $J = 0.8$ Hz, 2H), 4.53 (s, 2H), 6.71 (d, $J = 1.0$ Hz, 1H), 7.30 (t, $J = 7.8$ Hz, 1H), 7.36–7.56 (m, 6H), 7.58 (dt, $J = 8.0, 0.8$ Hz, 1H), 7.75 (t, $J = 1.6$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 16.0, 58.0 (2C), 85.1, 87.1, 122.5, 125.1, 127.0, 128.3, 128.5 (2C), 129.3 (2C), 130.1, 130.7, 132.0, 134.7, 134.9, 137.7.

General procedure for Au(I)-catalyzed cycloisomerization reactions: A mixture of L-(AuCl)₂ (L = (*R*)-4-MeO-3,5-(*t*-Bu)₂MeOBIPHEP) (3 mol %) and AgOTf (or AgNTf₂) (6 mol %) in distilled toluene (0.5 M) was stirred under an argon atmosphere at room temperature for 30 min. Enyne (1 equiv) was then added and the mixture stirred until completion of the reaction. The mixture was then filtered through a short pad of silica to eliminate the catalyst (EtOAc) and the solvents were concentrated under reduced pressure. The crude product was purified by silica gel flash chromatography (petroleum ether/ethyl acetate 98:2 to 80:20 v/v) if necessary.

6-(3-Bromophenyl)-7-(4-methoxyphenyl)-3-oxabicyclo[4.1.0]hept-4-ene (4f): TLC (cyclohexane/ethyl acetate 80:20) R_f 0.70; ^1H NMR (300 MHz, CDCl_3) δ 2.29 (d, $J = 5.4$ Hz, 1H), 2.65 (d, $J = 6.0$ Hz, 1H), 3.61 (s, 3H), 3.96 (dd, $J = 10.6, 1.9$ Hz, 1H), 4.30 (d, $J = 10.6$ Hz, 1H), 5.21 (d, $J = 6.0$ Hz, 1H), 6.18 (d, $J = 6.0$ Hz, 1H), 6.52–6.65 (m, 4H), 6.86–6.92 (m, 2H), 7.12–7.19 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 29.9, 30.3, 37.3, 55.5, 61.6, 111.0, 113.7 (2C), 122.5, 128.7, 129.0 (2C), 129.4, 129.9, 130.1, 133.0, 141.2, 142.8, 158.2; HPLC (Chiralpak AD, hexane/propan-2-ol (97:3), flow rate 1.0 mL/min, $\lambda = 215$ nm): retention times 7 and 7.5 min, ee 95%; $[\alpha]_{\text{D}}^{23} -18.6$ (*c* 1, CHCl_3).

6-(4-Methoxyphenyl)-1-methyl-7-phenyl-3-oxabicyclo[4.1.0]hept-4-ene (4g): TLC (cyclohexane/ethyl acetate 90:10) R_f 0.66; ^1H NMR (300 MHz, CDCl_3) δ 1.18 (s, 3H), 2.84 (s, 1H), 3.73 (d, $J = 10.4$ Hz, 1H), 3.80 (s, 3H), 4.15 (d, $J = 10.4$ Hz, 1H), 5.19 (d, $J = 5.8$, 1 Hz, 1H), 6.21 (d, $J = 5.8$ Hz, 1H), 6.80–6.86 (m, 4H), 7.01–7.04 (m, 2H), 7.12–7.15 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 12.9, 31.6, 35.2, 38.2, 55.2, 67.8, 113.7, 114.5, 125.4, 127.5 (2C), 130.0 (2C), 130.7, 132.1 (2C), 137.5, 140.0, 158.1; HPLC (Chiralcel OJ, hexane/propan-2-ol (99/1), flow rate 1.0 mL/min, $\lambda = 215$ nm): retention times 20.3 and 27.1 min, ee 99%; $[\alpha]_{\text{D}}^{23} +26.1$ (c 1, CHCl_3).

6-(3-Bromophenyl)-1-methyl-7-phenyl-3-oxabicyclo[4.1.0]hept-4-ene (4h): TLC (cyclohexane/ethyl acetate 90:10) R_f 0.71; ^1H NMR (300 MHz, CDCl_3) δ 1.10 (s, 3H), 2.80 (s, 1H), 3.64 (d, $J = 10.5$ Hz, 1H), 4.07 (d, $J = 10.5$ Hz, 1H), 5.09 (d, $J = 5.8$ Hz, 1H), 6.16 (d, $J = 5.8$ Hz, 1H), 6.75 (d, $J = 2.1$ Hz, 1H), 6.78 (d, $J = 4.0$ Hz, 1H), 6.92 (dt, $J = 7.7$, 1.4 Hz, 1H), 7.00–7.20 (m, 5H), 7.29 (dt, $J = 7.8$, 1.2 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.4, 33.2, 36.5, 39.7, 68.9, 114.6, 123.5, 127.2, 129.0 (2C), 131.1 (2C), 131.2, 131.3 (2C), 135.3, 138.2, 142.0, 142.5; HPLC (Chiralpak IA, hexane/propan-2-ol (99.9:0.1), flow rate 0.5 mL/min, $\lambda = 215$ nm): retention times 11.8 and 12.6 min, ee 73%; $[\alpha]_{\text{D}}^{23} +11.7$ (c 1, CHCl_3).

Supporting Information

Supporting Information File 1

Spectral data.

[<http://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-7-116-S1.pdf>]

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