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Steric tuning of C_2-symmetric chiral *N*-heterocyclic carbene in gold-catalyzed asymmetric cyclization of 1,6-enynes

Ken-ichi Yamada [a,*], Yasumasa Matsumoto [a], Khalid B. Selim [b], Yasutomo Yamamoto [c], Kiyoshi Tomioka [c,*]

[a] *Graduate School of Pharmaceutical Sciences, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan*
[b] *Department of Pharmaceutical Organic Chemistry, Faculty of Pharmacy, Mansoura University, Mansoura 35516, Egypt*
[c] *Faculty of Pharmaceutical Sciences, Doshisha Women's College of Liberal Arts, Kodo, Kyotanabe 610-0395, Japan*

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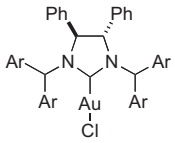
ABSTRACT

Steric tuning of C_2-symmetric chiral *N*-heterocyclic carbene (NHC) was performed in Au(I)-catalyzed asymmetric cyclization of 1,6-enyne. Higher enantioselectivity was realized when chiral NHC–AuCl/$AgSbF_6$ catalysts whose *N*-substituent on the NHC overlays the Au–Cl bond was utilized.

1. Introduction

Gold(I) complexes with phosphanes or *N*-heterocyclic carbenes (NHCs)[1] have emerged as attractive homogeneous catalysts that activate C–C multiple bonds.[2] Chiral phosphane–gold(I) complexes have been developed to catalyze asymmetric coupling of aldehydes with isocyanoacetate esters,[3] 1,6-enyne cyclization,[4] nucleophilic addition to allenes[5] and alkynes,[6] and cyclopropanation of alkenes.[7] In turn, NHCs are a growing class of ligands for transition metals, characterized by strong σ-donor and poor π-acceptor abilities, and have advantageous properties over phosphanes, such as tolerance to air.[8] Recently, we showed potential of a chiral NHC–gold(I) complex as a chiral catalyst for the first time,[9] applying a C_2-symmetric chiral NHC[10] as a chiral ligand for gold(I) and achieved moderate enantioselectivity in 1,6-enyne cyclization.[11] Although several chiral NHC–gold(I) complexes have been developed since then,[12] reactions catalyzed by chiral NHC–gold(I) complexes generally proceed with low to moderate enantioselectivity.[2e,13] To date, there is only one example of highly enantioselective transformation catalyzed by a carbene–gold(I) complex,[14] and thus development of a chiral NHC–gold(I) catalyzed asymmetric reaction is still important and challenging.

In our preliminary communication,[11] chiral NHC–gold(I) complexes **1a**–**c** (Fig. 1) were employed in asymmetric cyclization of 1,6-enyne.[15] All the cationic chiral NHC–gold(I) complexes, generated in situ from **1a**–**c** and silver hexafluoroantimonate, efficiently catalyzed cyclization of enyne **2a** in methanol at rt and gave **3a**[16] in high isolated yields; however, the enantioselectivity of the reaction was strongly dependent on the substituents on the NHC nitrogen atom (Table 1, entries 1–3). While complex **1a**, bearing diphenylmethyl groups, exhibited poor stereocontrolling ability (8% ee; entry 1), complex **1b**, bearing bis(2-methylphenyl)methyl groups, provided **3a** with 36% ee (entry 2). Furthermore, complex **1c**, having bis(2,5-dimethylphenyl)methyl groups, showed the best performance, and **3a** was obtained with 56% ee (entry 3). We speculated that one each of the aryl groups of the two *N*-substituents overlays the gold–chlorine bond, and the bulkiest 2,5-dimethylphenyl group of **1c** created the most effective chiral environment around the gold(I) coordination site among the complexes. We describe herein the correlation between the structure of the C_2-symmetric chiral NHC–gold(I) complex and enantioselectivity in the catalytic asymmetric cyclization of 1,6-enynes as well as the X-ray structures of the complexes, which validate our speculation. Additional information concerning effects of substituents on 1,6-enynes is also described.



1a Ar = Ph
1b Ar = 2-MeC_6H_4
1c Ar = 2,5-$Me_2C_6H_3$
1d Ar = 2,4-$Me_2C_6H_3$
1e Ar = 2,3-$Me_2C_6H_3$
1f Ar = 3,5-$Me_2C_6H_3$
1g Ar = 2-Me-5-PhC_6H_3
1h Ar = 3,5-*t*-$Bu_2C_6H_3$

Fig. 1. C_2-Symmetric chiral NHC–AuCl catalysts **1**.

2. Results and discussion

First, X-ray crystal analysis of **1a**–**c** was performed to gain structural information of the NHC–gold(I) complexes (Fig. 2). In complex **1a**, one of the phenyl groups of the *N*-substituents is overlapping the phenyl group of the ethylenediamine moiety,

* Corresponding authors. Tel.: +81 (0) 75 753 4573; fax: +81 (0) 75 753 4604 (K.-i.Y.); tel.: +81 (0) 774 65 8676; fax: +81 (0) 774 65 8658 (K.T.); e-mail addresses: yamak@pharm.kyoto-u.ac.jp (K.-ichi Yamada), tomioka@pharm.kyoto-u.ac.jp (K. Tomioka).

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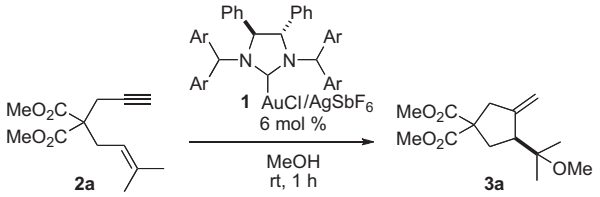
Table 1
Chiral NHC–Au(I) **1**-catalyzed cyclization of enyne **2a**



Entry	NHC–AuCl **1**	Yield (%)	ee (%)
1[a]	**1a**	95	8
2[a]	**1b**	95	32
3[a]	**1c**	95	56
4	**1d**	90	13
5	**1e**	95	47
6	**1f**	98	53
7	**1g**	99	54
8	**1h**	99	16[b]

[a] Ref. 11.
[b] The antipode was obtained.

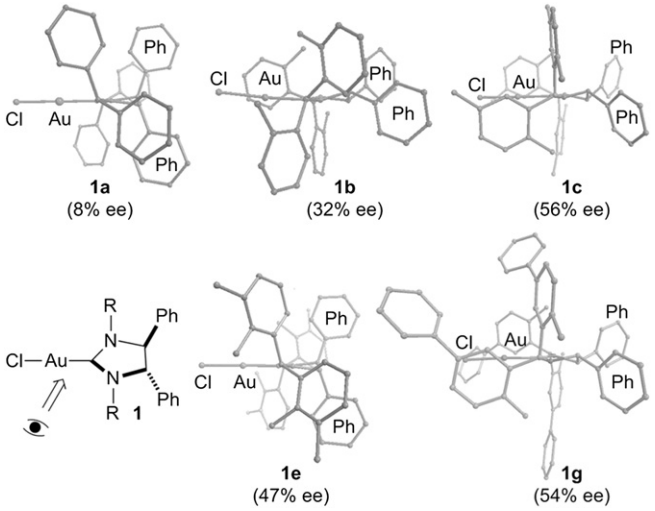


Fig. 2. Chem3D perspective view of X-ray structures of **1a**–**c**, **1e**, and **1g**. H atoms and solvent molecules (Et_2O, hexane, and THF for **1a**, **1c**, and **1g**, respectively) were omitted for clarity.

probably due to favorable π–π interaction, and the other phenyl group is almost perpendicular to the Au–Cl bond. Accordingly, the poor enantioselectivity observed using **1a** is attributable to the absence of a stereocontrolling group along with the Au–Cl bond. In complexes **1b** and **1c**, the aryl substituents of the *N*-substituents are overlying the Au–Cl bonds, and therefore, the stereocontrolling groups, the aryl substituents are close to the gold(I) coordination sites.

On the basis of these observations, complexes **1c**–**f**, bearing regioisomeric bis(dimethylphenyl)methyl groups as *N*-substituents, were compared in the reaction of **2a** to elucidate the best substitution positions on the phenyl groups (Table 1, entries 3–6). Although moderately good enantioselectivity (56% ee) was realized using 2,5-dimethylphenyl isomer **1c** (entry 3),[11] the selectivity was decreased to 13% ee with 2,4-dimethylphenyl isomer **1d** (entry 4). In contrast, 2,3-dimethylphenyl isomer **1e** showed comparable stereocontrolling ability to **1c** and gave **3a** with 47% ee in 95% yield (entry 5), and almost the same level of enantioselectivity (53% ee) as that with **1c** was observed when 3,5-dimethylphenyl isomer **1f** was used as a catalyst precursor (entry 6). Consequently, a 2,5- or 3,5-disubstituted phenyl group seemed to be the best aryl group for chiral environment around the gold(I) coordination site.

Next, complex **1g**, in which the 5-methyl group of **1c** was substituted by a bulkier phenyl group, was tested in the reaction. The enantioselectivity was, however, almost the same level (54% ee) as **1c** (56% ee) though **3a** was obtained in quantitative yield (entry 7). Replacing the methyl groups of **1f** by bulkier *tert*-butyl groups dramatically decreased the enantioselectivity; the enantiomer of **3a** with 16% ee was quantitatively obtained when **1h**, bearing 3,5-di-*tert*-butylphenyl groups, was used as a catalyst precursor (entry 8). Thus, newly developed complexes **1f** and **1g** were found to have comparable stereocontrolling ability to that of **1c**.

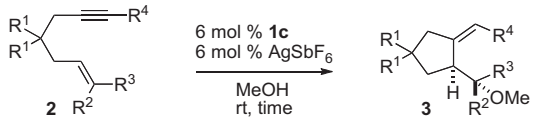
Among the new complexes **1d**–**h**, crystals suitable for X-ray analysis were obtained for **1e** and **1g** (Fig. 2). The relatively high enantioselectivities observed in the reactions of **2a** with **1e** and **1g** are explainable with the X-ray structures, in which the stereocontrolling groups, the aryl substituents are overlying the Au–Cl bond. These observations support our aforementioned speculation. In the X-ray structure of **1g**, the space occupied by the phenyl substituents of the diarylmethyl groups is far from the Au–Cl bond. This would be the reason why **1g** and **1c** showed almost the same stereocontrolling ability.

The effects of substituents on 1,6-enynes was further investigated using NHC–gold(I) complex **1c** (Table 2) in addition to the previously reported results (entries 1–3). First, enyne **2d**, bearing bissulfone and a phenylacetylene moiety, was applied to the reaction because high enantioselectivity (94% ee) was reported only for this particular substrate using a tol-BINAP–gold(I) complex, despite moderate enantioselectivity (2–53% ee) for other substrates.[4a] Although solubility of **2d** in methanol was quite low, the reaction proceeded smoothly in a 10:3 mixture of methanol and dichloromethane and produced **3d** with 49% ee in 61% yield (entry 4). The observed specific rotation value of **3d**, $[\alpha]_D^{25}$ +105 (*c* 0.59, $CHCl_3$), was significantly larger than that reported for the antipode with 94% ee, $[\alpha]_D^{25}$ −75.3 (*c* 0.6, $CHCl_3$)[4a] and smaller than that reported for 78% ee, $[\alpha]_D^{22}$ −218.1 (*c* 1.05, $CHCl_3$).[4d] Thus, the specific rotation was confirmed by measuring again after enantiomer enrichment by trituration in ether, and a reasonable value, $[\alpha]_D^{25}$ +162 (*c* 0.65, $CHCl_3$), was also observed for 73% ee.[17] The low yield of **3d** was attributed to intramolecular Friedel–Crafts reaction of the cationic intermediate of the enyne cyclization, for byproduct **4** with 17% ee was isolated in 37% yield. The reaction was then applied to **2e**, with expectation that the bulky ester moieties would improve the enantioselectivity. Although **3e** was formed in 95% yield within 1 h, the enantioselectivity was still moderate (42% ee; entry 5). Apparently, the bulkiness of the R^1 substituents of **2** has negative effect on enantioselectivity of the reaction (entries 1, 3, and 5).

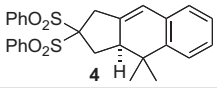
3. Conclusion

The C_2-symmetric chiral NHC–gold(I) catalyst **1c**, bearing *N*-bis(2,5-dimethylphenyl)methyl substituents to endow chiral environment around gold(I), showed the best selectivity in the 1,6-enyne cyclization among those tested, and **1f** and **1g**, bearing *N*-bis(3,5-dimethylphenyl)methyl substituents and *N*-bis(4-methylbiphenyl-3-yl)methyl substituents, respectively, also had comparable stereocontrolling ability. The X-ray crystal structures verified that the relatively high enantioselectivity was observed in the reaction with the NHC–gold (I) complexes whose *N*-substituents overlay the Au–Cl bond in the X-ray structures. Although X-ray structures do not directly reflect the reacting structures, these results would provide a basis for the design of much more efficient chiral NHC–gold(I) catalysts.

Table 2
Cyclization of enynes **2** catalyzed by NHC–Au(I) **1c**



Entry	2	R^1	R^2, R^3	R^4	Time/h	Yield (%)	ee (%)
1[a]	**2a**	CO_2Me	Me, Me	H	1	95	56
2[a]	**2b**	CO_2Me	H, Ph	H	11	91	59
3[a]	**2c**	SO_2Ph	Me, Me	H	1	93	52
4[b]	**2d**	SO_2Ph	Me, Me	Ph	3	61[c]	49
5	**2e**	CO_2CH (*i*-Pr)$_2$	Me, Me	H	1	95	42[d]



[a] Ref. 11.
[b] Solvent was MeOH/CH_2Cl_2 (10:3).
[c] Enyne cyclization-Friedel–Crafts product **4** with 17% ee was also obtained in 37% yield.
[d] The ee was determined after conversion to diol with $LiAlH_4$ reduction.

4. Experimental section

4.1. General

All melting points are uncorrected. Column chromatography was performed using silica gel. NMR (500 MHz for ^1H and 125 MHz for ^{13}C) was measured in $CDCl_3$ unless otherwise mentioned, and chemical shifts and coupling constants are presented in parts per million δ relative to Me_4Si and hertz, respectively. Abbreviations are as follows: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad. ^{13}C peak multiplicity assignments were made based on DEPT data. IR spectroscopy of oil and solid samples were measured as neat liquid films and KBr pellets, respectively. The wave numbers of maximum absorption peaks of IR spectroscopy are presented in cm^{-1}. Enynes **2a**,[18,19] **2b**,[19] **2c**,[20,21] and **2d**[22] were prepared according to the reported procedures. (1*S*,2*S*)-1,2-Diphenylethane-1,2-diamine was purchased and used as received. MeOH was distilled from CaH_2 before use. All the reactions were performed under argon atmosphere unless otherwise mentioned.

4.2. Synthesis of Au–NHC complexes

4.2.1. Synthesis of diarylmethylbromides.[23,24]

*4.2.1.1. 3,3′-(Bromomethylene)bis(4-methylbiphenyl) (**5g**).* A 1.0 M solution of (4-methylbiphenyl-3-yl)magnesium bromide in THF (50 mL, 50 mmol) was slowly added to a solution of HCO_2Et (1.6 g, 22 mmol) in THF (44 mL) at 0 °C. After 1 h, the reaction was quenched with satd NH_4Cl (50 mL), and then the whole was extracted with EtOAc (3×20 mL). The combined organic layers were washed with brine (2×20 mL), dried over Na_2SO_4, and then concentrated to give white solid. AcBr (7.1 mL, 97 mmol) was dropwise added to a solution of the white solid in benzene (41 mL) at 0 °C. After 3 h, the mixture was concentrated to give brown solids, whose recrystallization from hexane gave the titled compound as pale brown powder (3.5 g, 68%) of mp 122–124 °C. ^1H NMR: 2.38 (6H, s), 6.68 (1H, s), 7.22–7.24 (2H, m), 7.30–7.33 (2H, m), 7.38–7.45 (6H, m), 7.53–7.55 (4H, m), 7.81–7.83 (2H, m). ^{13}C NMR: 18.8 (CH_3), 50.9 (CH), 126.9 (CH), 127.0 (CH), 127.3 (CH), 128.4 (CH), 128.9 (CH), 131.1 (CH), 134.3 (C), 138.8 (C), 139.4 (C), 140.8 (C). IR: 3024, 1481, 1172, 756, 694. EIMS *m*/*z*: 347 (M–Br). Anal. Calcd for $C_{27}H_{23}Br$: C, 75.88; H, 5.42. Found: C, 75.74; H, 5.49.

*4.2.1.2. 5,5′-(Bromomethylene)bis(1,3-dimethylbenzene) (**5f**).* Synthesized from 3,5-$Me_2C_6H_3MgBr$ by the same procedure as **5g**. Recrystallization from hexane gave the titled compound as colorless blocks (4.5 g, 84%) of mp 80–82 °C. ^1H NMR: 2.30 (12H, s), 6.15 (1H, s), 6.90 (2H, s), 7.07 (4H, s). ^{13}C NMR: 21.2 (CH_3), 56.1 (CH), 126.2 (CH), 129.8 (CH), 138.1 (C), 141.1 (C). IR: 2916, 1597, 1458, 1178, 856, 727. EIMS *m*/*z*: 303 (M^+). Anal. Calcd for $C_{17}H_{19}Br\cdot 0.25H_2O$: C, 66.35; H, 6.39. Found: C, 66.56; H, 6.29.

*4.2.1.3. 5,5′-(Bromomethylene)bis(1,3-di-tert-butylbenzene) (**5h**).* Synthesized from 3,5-*t*-$Bu_2C_6H_3MgBr$ by the same procedure as **5g**. Recrystallization from hexane gave the titled compound as colorless powder (5.8 g, 68%) of mp 108–110 °C. ^1H NMR: 1.31 (36H, s), 6.33 (1H, s), 7.33 (6H, s). ^{13}C NMR: 31.4 (CH_3), 34.9 (C), 57.6 (CH), 122.1 (CH), 123.1 (CH), 140.3 (C), 150.8 (C). IR: 2954, 1597, 1364, 725. EIMS *m*/*z*: 391 (M–Br). Anal. Calcd for $C_{29}H_{43}Br$: C, 73.86; H, 9.19. Found: C, 73.91; H, 9.25.

4.2.2. Synthesis of diamines.

*4.2.2.1. (1S,2S)-N,N′-Bis(bis(4-methylbiphenyl-3-yl)methyl)-1,2-diphenylethane-1,2-diamine (**6g**).* Prepared by an analogous procedure to that reported.[25] A mixture of (1*S*,2*S*)-1,2-diphenylethane-1,2-diamine (1.1 g, 5.2 mmol), **5g** (4.7 g, 11 mmol), and Na_2CO_3 (2.1 g, 20 mmol) in DMPU (15 mL) was stirred for 2 h at 120 °C, and then 50 mL of water was added. The whole was extracted with EtOAc (3×30 mL). The combined organic layers were washed with water (2×50 mL) and brine (2×50 mL), dried over Na_2SO_4, and then concentrated to give pale yellow oil. Column chromatography (hexane/EtOAc=15/1) gave the titled compound as pale yellow amorphous solid (1.6 g, 54%) of mp 108–110 °C and $[\alpha]_D^{25}$ −30.4 (*c* 1.02, $CHCl_3$). ^1H NMR: 1.85 (6H, s), 2.05 (6H, s), 2.79 (2H, s), 3.98 (2H, s), 4.97 (2H, s), 7.00–7.02 (4H, m), 7.07–7.13 (10H, m), 7.17–7.20 (8H, m), 7.22–7.25 (4H, m), 7.32–7.34 (6H, m), 7.37–7.39 (2H, m), 7.43–7.47 (6H, m), 7.91 (2H, s). ^{13}C NMR: 18.8 (CH_3), 56.8 (CH), 65.9 (CH), 125.1 (CH), 125.4 (CH), 126.1 (CH), 126.67 (CH), 126.72 (CH), 126.75 (CH), 126.81 (CH), 127.1 (CH), 127.3 (CH), 127.9 (CH), 128.5 (CH), 128.6 (CH), 128.7 (CH), 131.0 (CH), 131.2 (CH), 135.6 (C), 135.7 (C), 138.5 (C), 138.6 (C), 140.0 (C), 141.0 (C), 141.1 (C), 141.3 (C). IR: 3325, 3024, 1481, 1450, 756, 694. EIMS *m*/*z*: 452 (M/2). Anal. Calcd for $C_{68}H_{60}N_2$: C, 90.22; H, 6.68; N, 3.09. Found: C, 90.22; H, 6.86; N, 3.03.

*4.2.2.2. (1S,2S)-N,N′-Bis(bis(3,5-dimethylphenyl)methyl)-1,2-diphenylethane-1,2-diamine (**6f**).* Synthesized from **5f** by the same procedure as **6g**. Column chromatography (hexane/EtOAc=20/1) gave the titled compound as colorless amorphous solid (2.5 g, 62%) of mp 75–76 °C and $[\alpha]_D^{25}$ +23.2 (*c* 1.04, $CHCl_3$). ^1H NMR: 2.22 (12H, s), 2.25 (12H, s), 2.67 (2H, s), 3.62 (2H, s), 4.38 (2H, s), 6.77 (4H, s), 6.80–6.82 (4H, m), 6.91 (4H, s), 6.97–7.01 (4H, m), 7.10–7.16 (6H, m). ^{13}C NMR: 21.35 (CH_3), 21.37 (CH_3), 63.2 (CH), 65.9 (CH), 124.9 (CH), 125.5 (CH), 126.8 (CH), 127.8 (CH), 128.2 (CH), 128.4 (CH), 128.5 (CH), 137.66 (C), 137.68 (C), 141.5 (C), 143.5 (C), 145.3 (C). IR: 3313, 2916, 1599, 1452, 853, 702. EIMS *m*/*z*: 328 (M/2). Anal. Calcd for $C_{48}H_{52}N_2$: C, 87.76; H, 7.98; N, 4.26. Found: C, 87.79; H, 8.04; N, 4.05.

*4.2.2.3. (1S,2S)-N,N′-Bis(bis(3,5-di-tert-butylphenyl)methyl)-1,2-diphenylethane-1,2-diamine (**6h**).* Synthesized from **5h** by the same procedure as **6g**. Column chromatography (hexane/EtOAc=40/1) gave the titled compound as colorless amorphous solid (505 mg, 51%) of mp 84–86 °C and $[\alpha]_{405}^{25}$ −14.1 (*c* 0.97, $CHCl_3$). ^1H NMR: 1.16 (36H, s), 1.23 (36H, s), 2.67 (2H, s), 3.64 (2H, s), 4.45 (2H, s), 6.97–6.99 (4H, m), 7.01–7.06 (8H, m), 7.15–7.19 (10H, m). ^{13}C NMR: 31.42 (CH_3), 31.44 (CH_3), 34.6 (C), 34.7 (C), 64.9 (CH), 65.9 (CH), 120.2 (CH), 120.6 (CH), 122.0 (CH), 122.3 (CH), 126.7 (CH), 127.7 (CH), 128.6 (CH), 141.8 (C), 142.0 (C), 144.3 (C), 150.1 (C), 150.2 (C). IR: 3336, 2951, 1599, 1477, 1248, 877, 698. EIMS *m*/*z*: 496 (M/2). Anal. Calcd for $C_{72}H_{100}N_2$: C, 87.04; H, 10.14; N, 2.82. Found: C, 86.97; H, 10.15; N, 2.78.

4.2.3. Synthesis of imidazolinium salts.

*4.2.3.1. (4S,5S)-1,3-Bis(bis(4-methylbiphenyl-3-yl)methyl)-4,5-diphenylimidazolinium tetrafluoroborate (**7g**).* Prepared from **6g** by the reported procedure.[26] Column chromatography ($CHCl_3$ then $CHCl_3$/EtOH=9/1) gave the titled compound as colorless amorphous solid (701 mg, 64% yield) of mp 280–282 °C and $[\alpha]_D^{25}$ −318 (*c* 1.04, $CHCl_3$). ^{1}H NMR: 1.91 (6H, s), 2.06 (6H, s), 5.26 (2H, s), 6.07 (2H, s), 7.12–7.19 (14H, m), 7.28–7.31 (6H, m), 7.32–7.38 (8H, m), 7.41 (1H, s), 7.43–7.46 (2H, m), 7.48–7.52 (6H, m), 7.61–7.63 (6H, m). ^{13}C NMR: 18.22 (CH_3), 18.26 (CH_3), 58.5 (CH), 73.3 (CH), 125.2 (CH), 126.8 (CH), 126.9 (CH), 127.0 (CH), 127.7 (CH), 127.9 (CH), 128.0 (CH), 128.1 (CH), 128.5 (CH), 128.9 (CH), 129.3 (CH), 129.9 (CH), 131.0 (CH), 132.2 (C), 132.4 (CH), 132.5 (C), 132.8 (CH), 133.5 (C), 135.8 (C), 136.0 (C), 139.7 (C), 139.9 (C), 140.0 (C), 140.1 (C), 155.2 (CH). IR: 3031, 1643, 1481, 1057, 702. FABMS *m*/*z*: 916 (M+H−BF_4). Anal. Calcd for $C_{69}H_{59}BF_4N_2$: C, 82.62; H, 5.93; N, 2.79. Found: C, 82.50; H, 6.07; N, 2.78.

*4.2.3.2. (4S,5S)-1,3-Bis(bis(3,5-dimethylphenyl)methyl)-4,5-diphenylimidazolinium tetrafluoroborate (**7f**).* Prepared from **6f** by the same procedure as **7g**. Recrystallization from EtOH gave the titled compound as colorless needles (1.0 g, 75%) of mp 260–262 °C and $[\alpha]_D^{25}$ −267 (*c* 0.50, $CHCl_3$). ^{1}H NMR: 2.25 (12H, s), 2.27 (12H, s), 4.97 (2H, s), 5.54 (2H, s), 6.82–6.84 (8H, m), 6.90 (4H, s), 7.18–7.20 (4H, m), 7.40–7.48 (6H, m), 7.52 (1H, s). ^{13}C NMR: 21.10 (CH_3), 21.15 (CH_3), 65.5 (CH), 73.8 (CH), 125.7 (CH), 126.3 (CH), 127.3 (CH), 129.9 (CH), 130.1 (CH), 130.7 (CH), 130.9 (CH), 134.3 (C), 135.1 (C), 135.2 (C), 139.1 (C), 139.4 (C), 156.4 (CH). IR: 2920, 1605, 1458, 1035, 719. FABMS *m*/*z*: 668 (M+H−BF_4). Anal. Calcd for $C_{49}H_{51}BF_4N_2$: C, 77.98; H, 6.81; N, 3.71. Found: C, 77.70; H, 6.95; N, 3.75.

*4.2.3.3. (4S,5S)-1,3-Bis(bis(3,5-di-tert-butylphenyl)methyl)-4,5-diphenylimidazolinium tetrafluoroborate (**7h**).* Prepared from **6h** by the same procedure as **7g**. Column chromatography (hexane/EtOAc=2/1) gave the titled compound as colorless amorphous solid (1.0 g, 94%) of mp 233–236 °C and $[\alpha]_D^{25}$ −243 (*c* 1.03, $CHCl_3$). ^{1}H NMR: 1.19 (36H, s), 1.31 (36H, s), 4.98 (2H, s), 5.55 (2H, s), 7.00–7.02 (8H, m), 7.13–7.15 (4H, m), 7.30 (2H, s), 7.35 (1H, s), 7.41–7.50 (8H, m). ^{13}C NMR: 31.2 (CH_3), 31.3 (CH_3), 34.8 (C), 34.9 (C), 66.6 (CH), 73.9 (CH), 122.2 (CH), 122.9 (CH), 123.2 (CH), 123.6 (CH), 127.6 (CH), 130.0 (CH), 130.7 (CH), 133.3 (C), 133.9 (C), 134.7 (C), 152.3 (C), 152.4 (C), 154.1 (CH). IR: 2964, 1628, 1213, 1064, 698. FABMS *m*/*z*: 1004 (M+H−BF_4). Anal. Calcd for $C_{73}H_{99}BF_4N_2\cdot 0.5H_2O$: C, 79.68; H, 9.16; N, 2.55. Found: C, 79.41; H, 9.11; N, 2.55.

4.2.4. Synthesis of Au–Carbene complexes.

*4.2.4.1. (4S,5S)-1,3-Dibenzhydryl-4,5-diphenylimidazolidin-2-ylidenegold(I) chloride (**1a**).* A mixture of the corresponding imidazolinium tetrafluoroborate[10c] (300 mg, 0.47 mmol), NaO*t*-Bu (46 mg, 0.47 mmol), and $Me_2S\cdot$AuCl (156 mg, 0.53 mmol) in THF (12 mL) was stirred at rt for 4.5 h and filtrated. The filtrate was concentrated, and the resulting residue was purified by column chromatography (hexane/EtOAc=3/1) to give the titled compound as colorless amorphous solid (200 mg, 54%) of mp 257–259 °C (dec) and $[\alpha]_D^{25}$ −188 (*c* 0.44, $CHCl_3$). ^{1}H NMR: 4.58 (2H, s), 5.84 (2H, s), 7.00–7.02 (4H, m), 7.08–7.10 (4H, m), 7.28–7.40 (22H, m). ^{13}C NMR: 66.5 (CH), 74.0 (CH), 127.4 (CH), 128.2 (CH), 128.4 (CH), 128.7 (CH), 128.8 (CH), 129.00 (CH), 129.04 (CH), 129.2 (CH), 129.3 (CH), 136.3 (C), 138.1 (C), 138.5 (C), 193.4 (C). IR: 3433, 3030, 1452, 1261, 750. FABMS *m*/*z*: 751 (M−Cl). Anal. Calcd for $C_{41}H_{34}AuClN_2\cdot 1.25H_2O$: C, 60.82; H, 4.54; N, 3.46. Found: C, 60.63; H, 4.27; N, 3.43. Single crystals suitable for X-ray diffraction were grown by placing a microtube of a THF solution of **1a** in a closed tube filled with Et_2O. The CIF file of the crystal structure (CCDC 864358) was deposited at the Cambridge Crystallographic Data Centre.

*4.2.4.2. (4S,5S)-1,3-Bis(di-o-tolylmethyl)-4,5-diphenylimidazolidin-2-ylidenegold(I) chloride (**1b**).* Prepared from the corresponding imidazolinium tetrafluoroborate[10c] by the same procedure as **1a**. Column chromatography (benzene) gave the titled compound as colorless amorphous solid (112 mg, 63%) of mp 91–93 °C and $[\alpha]_D^{25}$ −182 (*c* 0.56, $CHCl_3$). ^{1}H NMR: 1.88 (6H, s), 2.14 (6H, s), 4.80 (2H, s), 5.95 (2H, s), 6.84–6.86 (2H, m), 7.02–7.07 (8H, m), 7.10–7.12 (2H, m), 7.20–7.25 (6H, m), 7.28–7.33 (6H, m), 7.47 (2H, m). ^{13}C NMR: 18.8 (CH_3), 19.8 (CH_3), 60.6 (CH), 74.0 (CH), 126.38 (CH), 126.42 (CH), 127.8 (CH), 128.2 (CH), 128.45 (CH), 128.50 (CH), 128.8 (CH), 129.4 (CH), 130.2 (CH), 130.8 (CH), 131.1 (CH), 135.2 (C), 136.1 (C), 136.3 (C), 136.6 (C), 136.8 (C), 193.4 (C). IR: 3511, 2923, 1458, 1265, 748. FABMS *m*/*z*: 1650 (2M+H−Cl). Anal. Calcd for $C_{45}H_{42}AuClN_2\cdot 1.5H_2O$: C, 62.10; H, 5.21; N, 3.22. Found: C, 62.02; H, 5.09; N, 3.13. Single crystals suitable for X-ray diffraction were grown by placing a microtube of a THF solution of **1b** in a closed tube filled with hexane. The CIF file of the crystal structure (CCDC 864359) was deposited at the Cambridge Crystallographic Data Centre.

*4.2.4.3. (4S,5S)-1,3-Bis(bis(2,5-dimethylphenyl)methyl)-4,5-diphenylimidazolidin-2-ylidenegold(I) chloride (**1c**).* Prepared from the corresponding imidazolinium tetrafluoroborate[10d] by the same procedure as **1a**. Column chromatography (benzene) gave the titled compound as colorless amorphous solid (176 mg, 72%) of mp 135–138 °C and $[\alpha]_D^{25}$ −236 (*c* 0.96, $CHCl_3$). ^{1}H NMR: 1.82 (6H, s), 2.06 (6H, s), 2.14 (6H, s), 2.47 (6H, s), 4.77 (2H, s), 5.86 (2H, s), 6.58 (2H, s), 6.97–7.10 (12H, m), 7.27–7.35 (8H, m). ^{13}C NMR: 18.2 (CH_3), 19.3 (CH_3), 21.28 (CH_3), 21.31 (CH_3), 60.7 (CH), 73.7 (CH), 128.0 (CH), 128.7 (CH), 129.1 (CH), 129.4 (CH), 130.5 (CH), 131.1 (CH), 131.2 (CH), 133.5 (C), 133.6 (C), 135.2 (C), 135.5 (C), 135.6 (C), 136.0 (C), 136.6 (C), 192.9 (C). IR: 3495, 2916, 1450, 1211, 810. FABMS *m*/*z*: 1762 (2M+H−Cl). Anal. Calcd for $C_{49}H_{50}AuClN_2$: C, 65.44; H, 5.60; N, 3.11. Found: C, 65.26; H, 5.67; N, 3.16. Single crystals suitable for X-ray diffraction were grown by adding a benzene solution of **1c** to hexane. The CIF file of the crystal structure (CCDC 864360) was deposited at the Cambridge Crystallographic Data Centre.

*4.2.4.4. (4S,5S)-1,3-Bis(bis(2,4-dimethylphenyl)methyl)-4,5-diphenylimidazolidin-2-ylidenegold(I) chloride (**1d**).* Prepared from the corresponding imidazolinium tetrafluoroborate[10d] by the same procedure as **1a**. Column chromatography (benzene) gave the titled compound as colorless amorphous solid (157 mg, 65%) of mp 146–148 °C and $[\alpha]_D^{25}$ −171 (*c* 0.96, $CHCl_3$). ^{1}H NMR: 1.81 (6H, s), 2.10 (6H, s), 2.27 (6H, s), 2.31 (6H, s), 4.75 (2H, s), 5.88 (2H, s), 6.70 (2H, m), 6.82–6.85 (4H, m), 6.94 (2H, s), 7.01–7.03 (4H, m), 7.09 (2H, m), 7.24–7.32 (8H, m). ^{13}C NMR: 18.7 (CH_3), 19.7 (CH_3), 20.9 (CH_3), 21.0 (CH_3), 60.2 (CH), 73.9 (CH), 127.0 (CH), 127.1 (CH), 127.8 (CH), 128.4 (CH), 128.7 (CH), 129.2 (CH), 130.0 (CH), 131.6 (CH), 131.8 (CH), 132.3 (C), 133.4 (C), 136.3 (C), 136.5 (C), 136.6 (C), 137.7 (C), 138.4 (C), 194.7 (C). IR: 3517, 2916, 1450, 1265, 702. FABMS *m*/*z*: 1762 (2M+H−Cl). Anal. Calcd for $C_{49}H_{50}AuClN_2\cdot 0.5H_2O$: C, 64.79; H, 5.66; N, 3.08. Found: C, 64.55; H, 5.59; N, 3.08.

*4.2.4.5. (4S,5S)-1,3-Bis(bis(2,3-dimethylphenyl)methyl)-4,5-diphenylimidazolidin-2-ylidenegold(I) chloride (**1e**).* Prepared from the corresponding imidazolinium tetrafluoroborate[10d] by the same procedure as **1a**. Column chromatography (benzene) gave the titled compound as colorless amorphous solid (192 mg, 79%) of mp 146–149 °C and $[\alpha]_D^{25}$ −87.1 (*c* 0.98, $CHCl_3$). ^{1}H NMR: 1.89 (6H, s), 1.99 (6H, s), 2.10 (6H, s), 2.22 (6H, s), 4.79 (2H, s), 6.40 (2H, s), 6.88 (2H, m), 6.94–7.00 (8H, m), 7.05 (2H, m), 7.11 (2H, m), 7.16 (2H, m), 7.19–7.24 (6H, m). ^{13}C NMR: 14.8 (CH_3), 15.1 (CH_3), 20.5 (CH_3), 20.8 (CH_3), 61.5 (CH), 74.3 (CH), 125.3 (CH), 125.6 (CH), 126.4 (CH), 127.2 (CH), 127.8 (CH), 128.4 (CH), 128.8 (CH), 129.8 (CH), 129.9 (CH), 134.9 (C), 135.2 (C), 135.6 (C), 137.2 (C), 137.27 (C), 137.28 (C), 137.8 (C),

194.9 (C). IR: 3511, 2918, 1450, 1267, 731. FABMS *m/z*: 1762 (2M+H−Cl). Anal. Calcd for $C_{49}H_{50}AuClN_2$: C, 65.44; H, 5.60; N, 3.11. Found: C, 65.21; H, 5.78; N, 3.06. Single crystals suitable for X-ray diffraction were grown by placing a microtube of a THF solution of **1e** in a closed tube filled with hexane. The CIF file of the crystal structure (CCDC 864361) was deposited at the Cambridge Crystallographic Data Centre.

*4.2.4.6. (4S,5S)-1,3-Bis(bis(3,5-dimethylphenyl)methyl)-4,5-diphenylimidazolidin-2-ylidenegold(I) chloride (**1f**).* Prepared from **7f** by the same procedure as **1a**. Column chromatography (benzene) gave the titled compound as colorless amorphous solid (208 mg, 86%) of mp 99–102 °C and $[\alpha]_D^{25}$ −86.6 (*c* 0.43, $CHCl_3$). ^1H NMR: 2.20 (12H, s), 2.25 (12H, s), 4.57 (2H, s), 6.07 (2H, s), 6.73 (4H, s), 6.79 (2H, s), 6.84 (4H, s), 6.92 (2H, s), 7.01–7.04 (4H, m), 7.26–7.29 (6H, m). ^{13}C NMR: 21.2 (CH_3), 21.4 (CH_3), 67.1 (CH), 73.9 (CH), 126.7 (CH), 127.07 (CH), 127.08 (CH), 128.7 (CH), 128.9 (CH), 129.7 (CH), 136.6 (C), 137.9 (C), 138.1 (C), 138.9 (C), 139.1 (C), 194.7 (C). IR: 3529, 2916, 1602, 1458, 1265, 700. FABMS *m/z*: 1762 (2M+H−Cl). Anal. Calcd for $C_{49}H_{50}AuClN_2$: C, 65.44; H, 5.60; N, 3.11. Found: C, 65.71; H, 5.69; N, 3.03.

*4.2.4.7. (4S,5S)-1,3-Bis(bis(4-methylbiphenyl-3-yl)methyl)-4,5-diphenylimidazolidin-2-ylidenegold(I) chloride (**1g**).* Prepared from **7g** by the same procedure as **1a**. Column chromatography (benzene) gave the titled compound as colorless amorphous solid (128 mg, 56%) of mp 154–156 °C and $[\alpha]_D^{25}$ −143 (*c* 0.92, $CHCl_3$). ^1H NMR: 1.95 (6H, s), 2.03 (6H, s), 4.78 (2H, s), 6.22 (2H, s), 6.85–6.91 (8H, m), 6.99 (2H, m), 7.13 (2H, m), 7.19 (2H, m), 7.28 (2H, m), 7.32–7.49 (20H, m), 7.54–7.56 (4H, m), 7.68 (2H, m). ^{13}C NMR: 18.6 (CH_3), 19.5 (CH_3), 61.1 (CH), 74.8 (CH), 126.8 (CH), 127.0 (CH), 127.4 (CH), 127.6 (CH), 128.0 (CH), 128.4 (CH), 128.5 (CH), 128.7 (CH), 129.0 (CH), 131.4 (CH), 131.6 (CH), 135.2 (C), 135.8 (C), 136.1 (C), 137.2 (C), 137.3 (C), 139.2 (C), 139.6 (C), 140.7 (C), 141.6 (C), 194.5 (C). IR: 3488, 3032, 1481, 1265, 756. FABMS *m/z*: 2258 (2M+H−Cl). Anal. Calcd for $C_{69}H_{58}AuClN_2$: C, 72.21; H, 5.09; N, 2.44. Found: C, 72.04; H, 5.25; N, 2.44. Single crystals suitable for X-ray diffraction were grown by placing a microtube of a THF solution of **1g** in a closed tube filled with hexane. The CIF file of the crystal structure (CCDC 864362) was deposited at the Cambridge Crystallographic Data Centre.

*4.2.4.8. (4S,5S)-1,3-Bis(bis(3,5-di-tert-butylphenyl)methyl)-4,5-diphenylimidazolidin-2-ylidenegold(I) chloride (**1h**).* Prepared from **7h** by the same procedure as **1a**. Column chromatography (benzene) gave the titled compound as colorless amorphous solid (129 mg, 55%) of mp 106–109 °C and $[\alpha]_D^{25}$ −62.6 (*c* 1.03, $CHCl_3$). ^1H NMR: 1.20 (36H, s), 1.25 (36H, s), 4.63 (2H, s), 6.15 (2H, s), 6.86–6.89 (4H, m), 7.08–7.09 (4H, m), 7.14–7.21 (12H, m), 7.31–7.33 (2H, m). ^{13}C NMR: 31.39 (CH_3), 31.44 (CH_3), 34.70 (C), 34.77 (C), 68.8 (CH), 74.2 (CH), 121.90 (CH), 122.00 (CH), 123.4 (CH), 123.8 (CH), 126.8 (CH), 128.5 (CH), 129.0 (CH), 136.1 (C), 138.5 (C), 139.8 (C), 150.6 (C), 150.7 (C), 195.0 (C). IR: 2962, 1597, 1473, 1250, 702. FABMS *m/z*: 1234 (M^+). HRMS–FAB *m/z*: $[M]^+$ calcd for $C_{73}H_{98}N_2AuCl$, 1234.7084; found, 1234.7058.

4.3. Preparation of 2e

*4.3.1. Bis(1-isopropyl-2-methylpropyl)malonate (**8**).* Prepared by an analogous procedure to that reported.[27] A mixture of malonic acid (9.4 g, 90 mmol), 2,4-dimethyl-3-pentanol (44 g, 380 mmol), and *p*-TsOH·H_2O (1.7 g, 9.0 mmol) in toluene (180 mL) was stirred under reflux with a Dean–Stark trap for 14 h. The whole was washed with satd $NaHCO_3$ (3×30 mL) and brine (2×50 mL), dried over Na_2SO_4, and concentrated to give yellow oil (18 g). Distillation (122 °C/0.3 mmHg) gave the titled compound as colorless oil (14.1 g, 52%). ^1H NMR: 0.88 (12H, d, *J*=6.8), 0.90 (12H, d, *J*=7.0), 1.91 (4H, m), 3.43 (2H, s), 4.66 (2H, t, *J*=6.1). ^{13}C NMR: 17.1 (CH_3), 19.4 (CH_3), 29.3 (CH), 41.7 (CH_2), 84.1 (CH), 166.9 (C). IR: 2970, 1736, 1265. FABMS *m/z*: 301 (M+H). HRMS–FAB (*m/z*): $[M+H]^+$ calcd for $C_{17}H_{33}O_4$, 301.2379; found, 301.2378.

*4.3.2. Bis(1-isopropyl-2-methylpropyl)-2-(3-methylbut-2-enyl)-2-(prop-2-ynyl)malonate (**2e**).* Prepared by an analogous procedure to that reported.[19] To a suspension of NaH (60% in mineral oil, 133 mg, 3.3 mmol) in DMF (6 mL), was added a solution of malonate **8** (1.0 g, 3.3 mmol) in DMF (6 mL) and then prenyl bromide (0.40 mL, 3.3 mmol) at 0 °C. The mixture was stirred for 12 h at rt. The reaction was quenched by addition of H_2O (30 mL). After separation of the organic phase, the aqueous phase was extracted with EtOAc (3×20 mL). The combined organic layers were washed with brine (5×10 mL), dried over Na_2SO_4, and concentrated to give pale yellow oil (1.5 g). Column chromatography (Et_2O/hexane=1/19) gave pale yellow oil (1.1 g). To a suspension of NaH (60% in mineral oil, 125 mg, 3.0 mmol) in DMF (18 mL) was added a solution of the above oil (1.1 g) in DMF (8 mL) and then propargyl bromide (0.25 mL, 3.3 mmol) at 0 °C. The mixture was stirred for 13 h at rt. The reaction was quenched by addition of H_2O (30 mL). After separation of the organic phase, the aqueous phase was extracted with EtOAc (3×20 mL). The combined organic layers were washed with brine (6×10 mL), dried over Na_2SO_4, and concentrated to give orange oil (1.1 g). Column chromatography (EtOAc/hexane=1/30) gave colorless solids (1.1 g). Distillation (122 °C/0.3 mmHg) gave the titled compound as colorless cubes (830 mg, 60% in two steps) of mp 40–42 °C. ^1H NMR: 0.87–0.91 (24H, m), 1.68 (6H, s), 1.87–1.95 (4H, m), 1.98 (1H, t, *J*=2.5), 2.81–2.89 (4H, m), 4.66 (2H, dd, *J*=5.8, 6.1), 5.03 (1H, m). ^{13}C NMR: 17.2 (CH_3), 17.4 (CH_3), 18.1 (CH_3), 19.5 (CH_3), 19.6 (CH_3), 22.9 (CH_2), 26.0 (CH_3), 29.4 (CH), 29.6 (CH), 31.3 (CH_2), 58.3 (C), 71.5 (CH), 80.2 (C), 84.8 (CH), 118.0 (CH), 136.2 (C), 170.4 (C). IR: 2970, 1728, 1226. FABMS *m/z*: 407 (M+H). HRMS–FAB (*m/z*): $[M+H]^+$ calcd for $C_{25}H_{43}O_4$: 407.3161; found, 407.3145.

4.4. Asymmetric cyclization of 1,6-enynes

*4.4.1. Dimethyl (S)-3-(1-methoxy-1-methylethyl)-4-methylenecyclopentane-1,1-dicarboxylate (**3a**) (Table 2, entry 1).* A mixture of **1c** (27 mg, 0.03 mmol) and $AgSbF_6$ (10 mg, 0.03 mmol) in MeOH (2.5 mL) was stirred at rt for 15 min. To the mixture, was added enyne **2a** (119 mg, 0.5 mmol) in MeOH (2.5 mL) via cannula, and the whole mixture was stirred for 1 h at rt. The mixture was filtered through a Celite pad and concentrated. The resulting residue was purified by column chromatography (EtOAc/hexane=1/15) to give the titled compound[16] as colorless oil (128 mg, 95%) of $[\alpha]_D^{25}$ −13.4 (*c* 1.39, $CHCl_3$) with 56% ee (lit.[28] $[\alpha]_D^{22}$ +18.5 (*c* 0.14, $CHCl_3$) for the antipode with 50% ee). ^1H NMR: 1.12 (3H, s), 1.18 (3H, s), 2.00 (1H, dd, *J*=9.5, 13.5), 2.51 (1H, ddd, *J*=1.8, 8.5, 13.5), 2.83–2.93 (3H, m), 3.19 (3H, s), 3.72 (3H, s), 3.73 (3H, s), 4.98 (1H, s), 5.04 (1H, br s). ^{13}C NMR: 22.1 (CH_3), 22.6 (CH_3), 35.9 (CH_2), 43.3 (CH_2), 48.97 (CH_3), 49.05 (CH), 52.64 (CH_3), 52.68 (CH_3), 58.5 (C), 76.7 (C), 110.5 (CH_2), 148.2 (C), 172.0 (C), 172.1 (C). IR: 2978, 1736, 1434, 1234. FABMS *m/z*: 271 (M+H). Enantiomeric excess was determined by HPLC (DAICEL ChiralPack AD, *i*-PrOH/hexane=1/19, 0.5 mL/min, 220 nm, 9.0 min and 10.0 min for *S* and *R*, respectively).[4a] The absolute configuration was determined by the specific rotation.

*4.4.2. Dimethyl-3-(methoxy(phenyl)methyl)-4-methylenecyclopentane-1,1-dicarboxylate (**3b**) (Table 2, entry 2).*[16] Colorless oil (145 mg, 91%) of $[\alpha]_D^{25}$ −51.4 (*c* 1.0, $CHCl_3$) with 59% ee. ^1H NMR: 2.34 (1H, dd, *J*=8.8, 13.4), 2.43 (1H, dd, *J*=8.8, 13.4), 2.88–3.00 (3H, m), 3.20 (3H, s), 3.67 (3H, s), 3.74 (3H, s), 4.17 (1H, d, *J*=5.8), 4.51 (1H, s), 4.93 (1H, s), 7.26–7.35 (5H, m). ^{13}C NMR: 35.3

(CH_2), 42.0 (CH_2), 49.3 (CH), 52.6 (CH_3), 57.2 (CH_3), 58.6 (C), 85.7 (CH), 108.5 (CH_2), 127.3 (CH), 127.6 (CH), 128.3 (CH), 140.7 (C), 148.6 (C), 172.1 (C), 172.2 (C). IR: 2954, 1735, 1265. FABMS *m*/*z*: 319 (M+H). Enantiomeric excess was determined by HPLC (DAICEL ChiralPack AD-H, *i*-PrOH/hexane=1/30, 0.5 mL/min, 254 nm, 11.7 min and 13.0 min for major and minor, respectively). Relative configuration was determined by the comparison of spectra with those reported.[16] The absolute configuration was tentatively assigned by analogy.

*4.4.3. (S)-1,1-Bis(phenylsulfonyl)-3-(1-methoxy-1-methylethyl)-4-methylenecyclopentane (**3c**) (Table 2, entry 3).*[16,29] Colorless powder (202 mg, 93%) of mp 70–73 °C and $[\alpha]_D^{25}$ −20.5 (*c* 0.97, $CHCl_3$) with 52% ee (lit.[4a] $[\alpha]^{25}$ +21.2 (*c* 0.4, $CHCl_3$) for the antipode with 53% ee). ^{1}H NMR: 1.10 (3H, s), 1.19 (3H, s), 2.65 (1H, m), 2.70–2.79 (2H, m), 3.02 (1H, m), 3.14 (3H, s), 3.46 (1H, m), 4.99 (1H, s), 5.01 (1H, s), 7.56–7.62 (4H, m), 7.70–7.73 (2H, m), 8.04–8.08 (4H, m). ^{13}C NMR: 22.1 (CH_3), 22.4 (CH_3), 33.2 (CH_2), 40.5 (CH_2), 49.1 (CH_3), 50.2 (CH), 76.7 (C), 91.8 (C), 111.1 (CH_2), 128.66 (CH), 128.71 (CH), 131.1 (CH), 134.47 (CH), 134.65 (CH), 136.0 (C), 137.2 (C), 146.5 (C). IR: 2939, 1327, 1150, 756. FABMS *m*/*z*: 435 (M+H). Enantiomeric excess was determined by HPLC (DAICEL ChiralPack AD, *i*-PrOH/hexane=1/9, 0.7 mL/min, 254 nm, 28.3 min and 34.9 min for major and minor, respectively).[4a] The absolute configuration was determined by the specific rotation.

*4.4.4. (S)-(Z)-1,1-Bis(phenylsulfonyl)-4-(1-methoxy-1-methylethyl)-3-phenylmethylidenecyclopentane (**3d**) (Table 2, entry 4).*[16,29] Colorless powder (156 mg, 61%) of mp 162–164 °C and $[\alpha]_D^{25}$ +105 (*c* 0.59, $CHCl_3$) with 49% ee (lit. $[\alpha]_D^{25}$ −75.3 (*c* 0.6, $CHCl_3$)[4a] and $[\alpha]_D^{22}$ −218.1 (*c* 1.05, $CHCl_3$)[4d] for the antipode with 94 and 78% ee, respectively). ^{1}H NMR: 0.80 (3H, s), 0.89 (3H, s), 2.55 (1H, d, *J*=15.9), 2.78 (1H, m), 2.87 (1H, m), 2.94 (3H, s), 3.67 (1H, m), 3.76 (1H, m), 6.41 (1H, s), 7.22 (1H, m), 7.31–7.34 (4H, m), 7.53–7.57 (2H, m), 7.60–7.63 (2H, m), 7.67–7.73 (2H, m), 8.10–8.14 (4H, m). ^{13}C NMR: 22.4 (CH_3), 23.7 (CH_3), 32.4 (CH_2), 42.1 (CH_2), 47.1 (CH), 49.1 (CH_3), 78.2 (C), 91.8 (C), 126.3 (CH), 126.8 (CH), 128.3 (CH), 128.5 (CH), 128.6 (CH), 128.7 (CH), 131.1 (CH), 131.2 (CH), 134.4 (CH), 134.6 (CH), 135.9 (C), 137.4 (C), 138.6 (C), 140.6 (C). IR: 2977, 1319, 1150. FABMS *m*/*z*: 511 (M+H). Enantiomeric excess was determined by HPLC (DAICEL ChiralPack AS-H, *i*-PrOH/hexane=1/20, 1 mL/min, 254 nm, 34.9 min and 50.0 min for minor and major, respectively).[4a] The absolute configuration was determined by the specific rotation. Trituration of the obtained powder in Et_2O followed by filtration gave enantiomerically enriched **3d** (73% ee) as colorless powder with $[\alpha]_D^{25}$ +162 (*c* 0.65, $CHCl_3$).

*4.4.5. 4,4-Dimethyl-2,2-bis(phenylsulfonyl)-2,3,3a,4-tetrahydro-1H-cyclopenta[b]naphthalene (**4**) (Table 2, entry 4).* Colorless powder (90 mg, 37%) of mp 210–214 °C (dec) and $[\alpha]_D^{25}$ +1.76 (c 0.54, CD_2Cl_2). ^{1}H NMR (CD_2Cl_2): 0.84 (3H, s), 1.34 (3H, s), 2.53 (1H, dd, *J*=8.3, 14.7), 2.77 (1H, dd, *J*=12.2, 14.7), 2.93 (1H, m), 3.47 (1H, d, *J*=19.9), 3.55 (1H, ddd, *J*=2.5, 2.8, 19.9), 6.36 (1H, m), 7.02 (1H, m), 7.13–7.18 (2H, m), 7.27 (1H, m), 7.59–7.67 (4H, m), 7.73–7.78 (2H, m), 8.02–8.08 (4H, m). ^{13}C NMR (CD_2Cl_2): 21.1 (CH_3), 24.9 (CH_3), 32.0 (CH_2), 36.3 (CH_2), 36.6 (C), 48.8 (CH), 92.2 (C), 119.7 (CH), 123.2 (CH), 126.1 (CH), 126.2 (CH), 127.1 (CH), 128.60 (CH), 128.64 (CH), 130.75 (CH), 130.79 (CH), 133.1 (C), 134.4 (CH), 134.6 (CH), 135.8 (C), 136.8 (C), 140.5 (C), 143.3 (C). IR: 2962, 1327, 1150. FABMS *m*/*z*: 479 (M+H). HRMS–FAB (*m*/*z*): $[M+H]^+$ calcd for $C_{27}H_{27}O_4S_2$, 479.1351; found, 479.1347. Enantiomeric excess was determined to be 17% by HPLC (DAICEL ChiralPack AD-H, *i*-PrOH/hexane=1/10, 1 mL/min, 254 nm, 41.8 min and 45.9 min for minor and major, respectively). The absolute configuration was tentatively assigned by analogy.

*4.4.6. Bis(1-isopropyl-2-methylpropyl) (S)-3-(1-methoxy-1-methylethyl)-4-methylenecyclopentane-1,1-dicarboxylate (**3e**) (Table 2, entry 5).* Colorless oil (208 mg, 95%) of $[\alpha]_D^{25}$ −9.4 (*c* 1.2, $CHCl_3$). ^{1}H NMR: 0.87–0.90 (24H, m), 1.13 (3H, s), 1.19 (3H, s), 1.85–1.94 (4H, m), 2.04 (1H, dd, *J*=9.8, 13.4), 2.61 (1H, m), 2.88–2.95 (3H, m), 3.19 (3H, s), 4.62–4.67 (2H, m), 4.99 (1H, s), 5.04 (1H, s). ^{13}C NMR: 17.0 (CH_3), 17.1 (CH_3), 17.3 (CH_3), 17.5 (CH_3), 19.47 (CH_3), 19.52 (CH_3), 19.59 (CH_3), 22.1 (CH_3), 22.7 (CH_3), 29.4 (CH), 29.5 (CH), 29.6 (CH), 36.6 (CH_2), 44.0 (CH_2), 48.89 (CH), 48.95 (CH_3), 59.9 (C), 76.9 (C), 84.0 (CH), 84.2 (CH), 110.6 (CH_2), 148.6 (C), 171.8 (C). IR: 2970, 1736, 1466, 1234. FABMS *m*/*z*: 439 (M+H). HRMS–FAB (*m*/*z*): $[M+H]^+$ calcd for $C_{26}H_{47}O_5$, 439.3423; found, 439.3452. The absolute configuration and enantiomeric excess were determined at the stage of the corresponding diol by comparison of specific rotation and gas chromatography with those of the authentic sample prepared from (*S*)-**3a** (see below).

4.5. Determination of ee and absolute configuration of 3e

*4.5.1. 3-(1-Methoxy-1-methylethyl)-4-methylenecyclopentane-1,1-dimethanol (**9**). From (S)-**3e**.* To a suspension of $LiAlH_4$ (20 mg, 0.54 mmol) in Et_2O (1 mL), was added a solution of (*S*)-**3e** (40 mg, 0.09 mmol) in Et_2O (1 mL) at rt and stirred for 1 h. Then to the reaction mixture, cooled in an ice-water bath, were added 0.5 mL of H_2O, 0.5 mL of 15% NaOH, and then 1.5 mL of H_2O. The whole mixture was extracted with Et_2O (3×5 mL). The combined organic layers were dried over Na_2SO_4, and concentrated. The resulting residue was purified by column chromatography (EtOAc/hexane=2/1) to give the titled compound with 42% ee as colorless oil (18 mg, 93%) of $[\alpha]_D^{25}$ −34.5 (*c* 0.85, $CHCl_3$): ^{1}H NMR: 1.12 (3H, s), 1.18 (3H, s), 1.45 (1H, dd, *J*=8.9, 13.7), 1.79 (1H, dd, *J*=9.3, 13.7), 2.15–2.19 (3H, m), 2.28 (1H, d, *J*=15.3), 2.75 (1H, dd, *J*=8.9, 9.3), 3.20 (3H, s), 3.56 (2H, d, *J*=4.5), 3.71 (2H, d, *J*=4.3), 4.99 (1H, s), 5.02 (1H, s). ^{13}C NMR: 22.1 (CH_3), 22.6 (CH_3), 33.2 (CH_2), 41.3 (CH_2), 46.3 (C), 48.88 (CH_3), 48.92 (CH), 67.4 (CH_2), 71.2 (CH_2), 77.2 (C), 110.3 (CH_2), 150.7 (C). IR: 3379, 2939, 1381, 1041. FABMS *m*/*z*: 215 (M+H). HRMS–FAB (*m*/*z*): $[M+H]^+$ calcd for $C_{12}H_{23}O_3$, 215.1647; found, 215.1638. Enantiomeric excess was determined by gas chromatography (BETA DEXTM 120; 150 °C for 30 min, then 3 °C/min to 220 °C; 42.2 min and 42.5 min for major and minor, respectively).

*4.5.2. From (S)-**3a** with 34% ee.* The same procedure above was followed using $LiAlH_4$ (19 mg, 0.51 mmol) and (*S*)-**3a** (23 mg, 0.085 mmol, 34% ee) to give the titled compound as colorless oil (17 mg, 93%) of $[\alpha]_D^{25}$ −26.1 (*c* 0.85, $CHCl_3$). The enantiomeric excess was verified to be 38% ee by gas chromatography (see above).

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Supplementary data

NMR spectra of the new compounds, and HPLC or GC traces for the determination of the enantiomeric excesses. Supplementary data related to this article can be found online at doi:10.1016/j.tet.2012.03.107.

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