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Asymmetric Dearomatization of 1-Aminonaphthalene Derivatives through C–C Bond Formation with Electron-Rich Heterocycles as Nucleophiles

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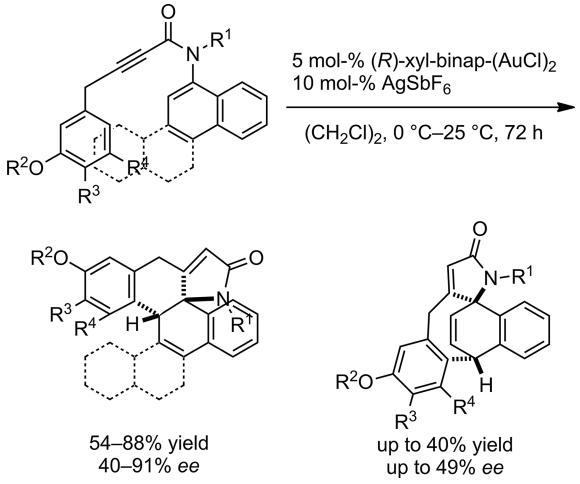
A cationic gold(I)/axially chiral biaryl bis(phosphine) complex has been employed to catalyze the asymmetric dearomatization reactions of 1-aminonaphthalene derivatives through a C–C bond-forming reaction with electron-rich heterocycles as the nucleophiles. These reactions afford pentacyclic heterocycles in good yields with moderate enantiomeric excess (*ee*) values.

Introduction

The catalytic asymmetric C–C bond-forming dearomatization of arenes is an attractive method for the synthesis of chiral carbocycles.[1] A number of transition-metal-catalyzed[2–4] and organocatalytic[5] asymmetric dearomatizations that occur through an oxidative single C–C bond-forming reaction at the *ortho*- or *para*-position of a substituent have been reported for the synthesis of chiral cyclohexadiene derivatives. However, our group recently reported the gold(I)-catalyzed asymmetric dearomatization reactions of 3-benzyl-substituted propiolic acid 1-naphthylamides (Scheme 1) and *N*-benzyl-substituted propiolic acid 1-naphthylamide (Scheme 2) through redox-neutral double C–C bond formation at the *ipso*- and *ortho*- or *para*-positions of the amino substituent[6–9] to give chiral dihydronaphthalene derivatives.[10–12] The former reactions afforded the corresponding dearomatization products with moderate to high enantiomeric excess (*ee*) values (Scheme 1), whereas the latter reaction afforded the corresponding dearomatization product with a low *ee* value (Scheme 2).[10] In these reactions, alkoxy-substituted electron-rich benzenes were employed as nucleophiles. Herein, we disclose the asymmetric dearomatization of 1-aminonaphthalene derivatives, which proceeds through C–C bond-forming reactions with electron-rich heterocycles as the nucleophiles.



Scheme 1. Gold-catalyzed asymmetric dearomatization of 3-benzyl-substituted propiolic acid 1-naphthylamides {(*R*)-xyl-binap = (*R*)-2,2′-bis[di(3,5-xylyl)phosphino]-1,1′-binaphthyl}.

Scheme 2. Gold-catalyzed asymmetric dearomatization of *N*-benzyl-substituted propiolic acid 1-naphthylamide {(*R*)-H_8-binap = (*R*)-2,2′-bis(diphenylphosphino)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl}.

Results and Discussion

We first examined the reaction of *N*-(3-furanylmethylene)-substituted propiolic acid 1-naphthylamide **1a** as

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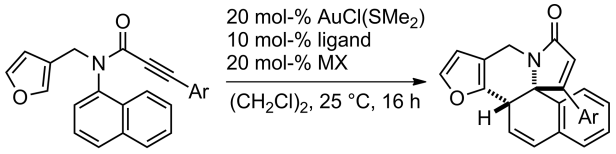
shown in Table 1. The use of the cationic gold(I)/(*R*)-H_8-binap catalyst (20 mol-% Au), which was the optimal catalyst when *N*-benzyl-substituted propiolic acid 1-naphthylamide was the substrate (Scheme 2),[10] afforded the desired dearomatization product **2a** in excellent yield with an *ee* value of 43% (Table 1, Entry 1). Although this reaction proceeded with moderate enantioselectivity, the *ee* value is higher than that of the example in Scheme 2, which employed an electron-rich benzene as the nucleophile. The screening of axially chiral biaryl bis(phosphine) ligands (Figure 1, Table 1, Entries 1–7) revealed that (*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl [(*R*)-binap] afforded **2a** in high yield in combination with a high *ee* value (Table 1, Entry 2). We then screened the silver salts (Table 1, Entries 2 and 8–12) and found that $AgBF_4$ and AgOTf (OTf = trifluoromethanesulfonate) afforded **2a** with the highest *ee* values (Table 1, Entries 8 and 9). AgOTf (Table 1, Entry 13) performed better than $AgBF_4$ (Table 1, Entry 14) when the catalyst loading was decreased to 5 mol-%. Lowering the reaction temperature (0 °C) and employing the isolated chiral gold(I) catalyst (*R*)-binap-$(AuCl)_2$ significantly decreased the product yields and *ee* values (Table 1, Entries 15 and 16, respectively). Thus, the details provided in Entry 13 were selected as the optimal reaction conditions.

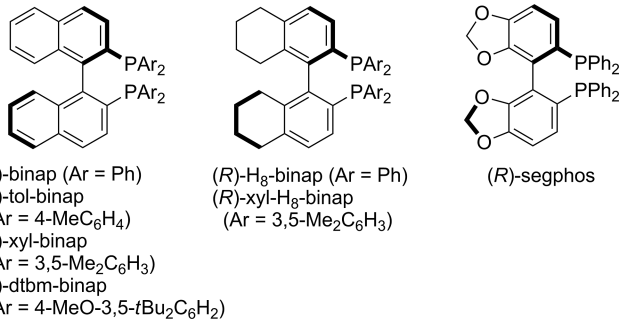
Table 1. Gold-catalyzed asymmetric dearomatization of 1-aminonaphthalene derivative **1a**.[a]



1a (Ar = 2-MeOC$_6$H$_4$) **2a**

Entry	Ligand	MX	% Conv.	% Yield **2a**[b] [% *ee*]
1	(*R*)-H_8-binap	$AgSbF_6$	100	>99 (43)
2	(*R*)-binap	$AgSbF_6$	100	>99 (46)
3	(*R*)-segphos[c]	$AgSbF_6$	100	>99 (13)
4	(*R*)-tol-binap[c]	$AgSbF_6$	100	80 (47)
5	(*R*)-xyl-binap	$AgSbF_6$	100	57 (43)
6	(*S*)-dtbm-binap[c]	$AgSbF_6$	64	49 (14)
7	(*S*)-xyl-H_8-binap[c]	$AgSbF_6$	100	61 (34)
8	(*R*)-binap	$AgBF_4$	100	>99 (48)
9	(*R*)-binap	AgOTf	100	>99 (48)
10	(*R*)-binap	$AgNTf_2$	100	93 (40)
11	(*R*)-binap	AgOTs[c]	12	–
12	(*R*)-binap	$NaBArF_4$	53	–
13[d]	(*R*)-binap	AgOTf	100	99 (47)
14[d]	(*R*)-binap	$AgBF_4$	100	81 (47)
15[e]	(*R*)-binap	AgOTf	34	30 (27)
16[f]	(*R*)-binap	AgOTf	65	30 (12)

[a] $AuCl(SMe_2)$ (0.010 mmol), ligand (0.0050 mmol), MX (0.010 mmol), **1a** (0.05 mmol), and $(CH_2Cl)_2$ (2.0 mL) were used. The relative configuration is shown for **2a**. [b] Isolated yield. [c] (*R*)-segphos = (*R*)-5,5′-bis(diphenylphosphino)-4,4′-bi-1,3-benzodioxole, (*R*)-tol-binap = (*R*)-2,2′-bis(di-*p*-tolylphosphino)-1,1′-binaphthyl, (*S*)-dtbm-binap = (*S*)-2,2′-bis[di-(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphino]-1,1′-binaphthyl, (*S*)-xyl-H_8-binap = (*S*)-2,2′-bis[di(3,5-xylyl)phosphino]-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl, and OTs *para*-toluenesulfonate. [d] $AuCl(SMe_2)$ (0.010 mmol), (*R*)-binap (0.0050 mmol), AgOTf or $AgBF_4$ (0.010 mmol), **1a** (0.20 mmol), and $(CH_2Cl)_2$ (2.0 mL) were used. [e] The reaction was conducted at 0 °C. [f] Isolated (*R*)-binap-$(AuCl)_2$ (0.010 mmol), AgOTf (0.020 mmol), **1a** (0.050 mmol), and $(CH_2Cl)_2$ (2.0 mL) were used.



(*R*)-binap (Ar = Ph)
(*R*)-tol-binap (Ar = 4-MeC$_6$H$_4$)
(*R*)-xyl-binap (Ar = 3,5-Me$_2$C$_6$H$_3$)
(*R*)-dtbm-binap (Ar = 4-MeO-3,5-*t*Bu$_2$C$_6$H$_2$)

(*R*)-H_8-binap (Ar = Ph)
(*R*)-xyl-H_8-binap (Ar = 3,5-Me$_2$C$_6$H$_3$)

(*R*)-segphos

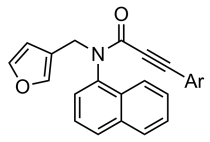
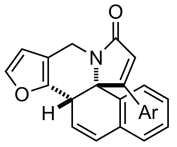
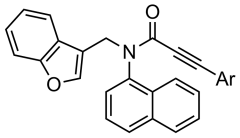
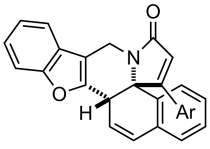
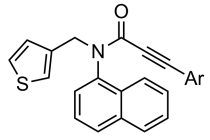
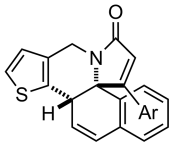
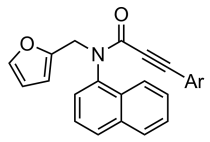
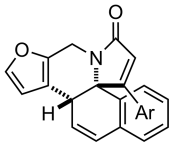
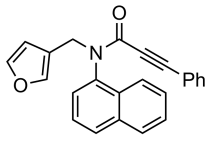
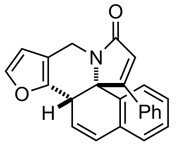
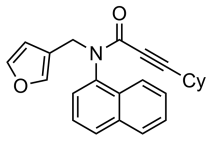
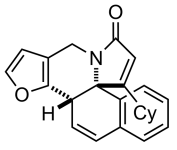
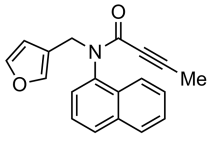
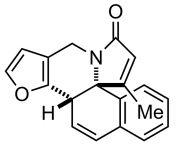
Figure 1. Structures of axially chiral biaryl bis(phosphine) ligands.

With the optimized conditions in hand, the substrate scope was examined (Table 2). Not only the furan moiety of **1a** (Table 2, Entry 1) but also the benzofuran unit of **1b** (Table 2, Entry 2), and the thiophene of **1c** (Table 2, Entry 3) were employed as nucleophiles to give the corresponding dearomatization products **2a**, **2b**, and **2c** in high yields with moderate *ee* values. However higher catalyst loadings were required in the latter two cases.[13] Importantly, the C–C bond formation between naphthalene and the highly nucleophilic 2-position of furan **1a** proceeded in high yield (Table 2, Entry 1), whereas that between naphthalene and the less nucleophilic 3-position of furan **1d** did not proceed at all (Table 2, Entry 4). With regard to substituents, we successfully incorporated the phenyl, cyclohexyl, and alkyl groups at the alkyne terminus in high yields, but the *ee* values of these products were significantly lower (Table 2, Entries 5–7).

The structure of the dearomatization product was unambiguously confirmed by the X-ray crystallographic analysis of compound (±)-**2f** (Figure 2).[14]

We next examined the reaction of 3-(3-furanylmethylene)-substituted propiolic acid 1-naphthylamide **3a** (Table 3). The cationic gold(I)/(*R*)-H_8-binap complex (20 mol-% Au) catalyzed the double C–C bond formation not only at the *ipso*- and *ortho*-positions but also at the *ipso*- and *para*-positions to give **4a** in 88% yield with 49% *ee* and eight-membered ring product **5a** in 12% yield (Table 3, Entry 1). Compound **5a**, however, could not be isolated in pure form because of its instablity. Screening the axially chiral biaryl bis(phosphine) ligands (Table 3, Entries 1–6) revealed that (*R*)-xyl-binap afforded **4a** with the highest *ee* value (Table 3, Entry 5). Screening the silver salts (Table 3, Entries 5 and 7–11) revealed that $AgSbF_6$ afforded **4a** in high yield in combination with a high *ee* value (Table 3, Entry 5). Lowering the reaction temperature (0 °C) and employing the isolated chiral gold(I) catalyst (*R*)-xyl-binap-$(AuCl)_2$ resulted in a decreased product yield (Table 3, Entries 12 and 13). Lowering the catalyst loading to 10 mol-% Au maintained the product yield and *ee* value (Table 3, Entry 14), but further decreasing the catalyst loading to 5 mol-% Au significantly lowered both the product yield

Table 2. Gold-catalyzed asymmetric dearomatization of 1-aminonaphthalene derivative **1a**–**1g**.[a]

Entry	**1** (catalyst loading, time)	**2a** / yield,[b] *ee*
1	 **1a** (5 mol-%) (16 h)	
	(Ar = 2-MeOC$_6$H$_4$)	(–)-**2a** / 99% yield, 47% *ee*
2[c,d]	 **1b** (20 mol-%) (72 h)	
	(Ar = 2-MeOC$_6$H$_4$)	(–)-**2b** / 84% yield, 44% *ee*
3[d]	 **1c** (10 mol-%) (16 h)	
	(Ar = 2-MeOC$_6$H$_4$)	(–)-**2c** / 88% yield, 54% *ee*
4	 **1d** (20 mol-%) (16 h)	
	(Ar = 2-MeOC$_6$H$_4$)	**2d** / 0% yield
5	 **1e** (20 mol-%) (72 h)	
		(–)-**2e** / 91% yield, 13% *ee*
6	 **1f** (20 mol-%) (72 h)	
		(–)-**2f** / >99% yield, 14% *ee*
7	 **1g** (5 mol-%) (16 h)	
		(–)-**2g** / 86% yield, 12% *ee*

[a] The reactions were conducted by using AuCl(SMe$_2$) (0.010–0.040 mmol), (*R*)-binap (0.0050–0.020 mmol), AgOTf (0.010–0.040 mmol), **1** (0.20 mmol), and $(CH_2Cl)_2$ (2.0 mL) at 25 °C. The relative configurations are shown for **2**. [b] Isolated yield. [c] At 80 °C. [d] **1** (0.10 mmol) was used.

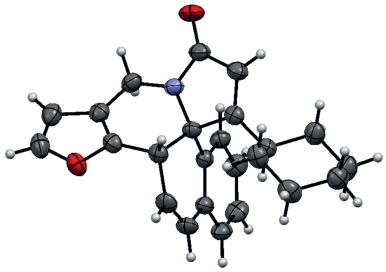
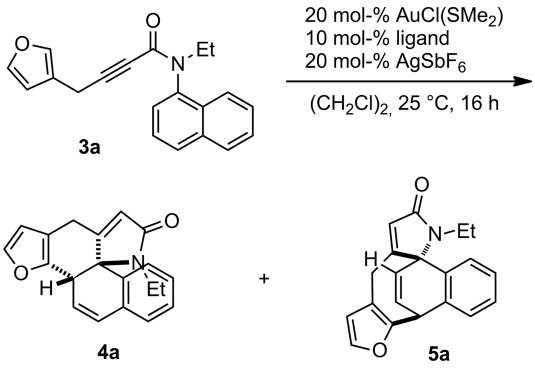


Figure 2. ORTEP diagram of (±)-**2f** with ellipsoids at 50% probability.

Table 3. Gold-catalyzed enantioselective dearomatization of 1-aminonaphthalene derivative **3a**.[a]



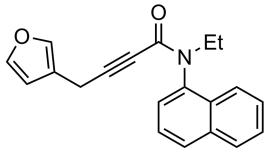
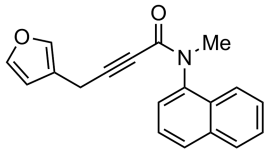
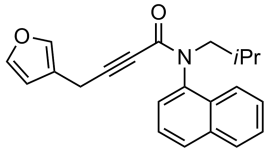
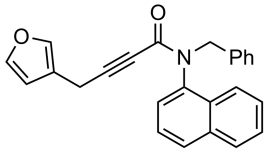
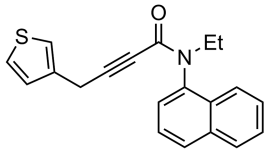
Entry	Ligand	MX	% Conv.	% Yield[b] **4a** [% *ee*]	**5a**
1	(*R*)-H$_8$-binap	AgSbF$_6$	100	88 (49)	12
2	(*R*)-binap	AgSbF$_6$	100	77 (41)	19
3	(*R*)-segphos	AgSbF$_6$	100	72 (48)	26
4	(*R*)-tol-binap	AgSbF$_6$	100	80 (51)	20
5	(*R*)-xyl-binap	AgSbF$_6$	100	78 (61)	22
6	(*S*)-dtbm- binap	AgSbF$_6$	59	39 (30)	9
7	(*R*)-xyl-H$_8$-binap	AgSbF$_6$	100	74 (53)	10
8	(*R*)-xyl-binap	AgBF$_4$	86	55 (59)	14
9	(*R*)-xyl-binap	AgOTf	49	54 (63)	13
10	(*R*)-xyl-binap	AgNTf$_2$	100	80 (59)	16
11	(*R*)-xyl-binap	NaBArF$_4$	22	19 (62)	2
12[c]	(*R*)-xyl-binap	AgSbF$_6$	71	53 (62)	18
13[d]	(*R*)-xyl-binap	AgSbF$_6$	68	53 (63)	8
14[e]	(*R*)-xyl-binap	AgSbF$_6$	100	74 (60)	15
15[f]	(*R*)-xyl-binap	AgSbF$_6$	69	53 (50)	9

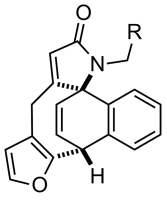
[a] AuCl(SMe$_2$) (0.010 mmol), ligand (0.0050 mmol), MX (0.010 mmol), **3a** (0.05 mmol), and $(CH_2Cl)_2$ (2.0 mL) were used. Relative configurations are shown for **4a** and **5a**. [b] Determined by ^{1}H NMR spectroscopic analysis. [c] The reactions were conducted at 0 °C. [d] Isolated (*R*)-xyl-binap-(AuCl)$_2$ (0.010 mmol), AgSbF$_6$ (0.020 mmol), **3a** (0.050 mmol), and $(CH_2Cl)_2$ (2.0 mL) were used. [e] The reaction was conducted with AuCl(SMe$_2$) (0.010 mmol), (*R*)-xyl-binap (0.0050 mmol), AgSbF$_6$ (0.010 mmol), **3a** (0.10 mmol), and $(CH_2Cl)_2$ (2.0 mL) at 25 °C for 72 h. [f] The reaction was conducted with AuCl(SMe$_2$) (0.010 mmol), (*R*)-xyl-binap (0.0050 mmol), AgSbF$_6$ (0.010 mmol), **3a** (0.20 mmol), and $(CH_2Cl)_2$ (2.0 mL) at 25 °C for 72 h.

and *ee* value (Table 3, Entry 15). Thus, the details provided in Entry 14 were selected as the optimal reaction conditions.

With the optimized conditions in hand, the scope of substrates was examined (Table 4). Taking the substituent on the nitrogen into consideration, we found that not only an ethyl group (i.e., **3a**, Table 4, Entry 1) but also a methyl (i.e., **3b**, Table 4, Entry 2), isobutyl (i.e., **3c**, Table 4, Entry 3), and benzyl group (i.e., **3d**, Table 4, Entry 4) could be employed to give the corresponding dearomatization products **4a**–**4d** in good to high yields with moderate *ee* values. In

Table 4. Gold-catalyzed enantioselective dearomatization of 1-aminonaphthalene derivatives **3a**–**3e**.[a]

Entry	3	4 / yield,[b] *ee*
1	 **3a**	**4a** and **5a** / 89% (**4a**/**5a** = 83:17)[c] (+)-**4a** / 60% *ee*
2	 **3b**	**4b** and **5b** / 89% (**4b**/**5b** = 88:12)[c] (+)-**4b** / 61% *ee*
3	 **3c**	(+)-**4c** / 74%, 53% *ee*
4	 **3d**	(+)-**4d** / 66%, 52% *ee*
5	 **3e**	(+)-**4e** / 59%, 43% *ee*

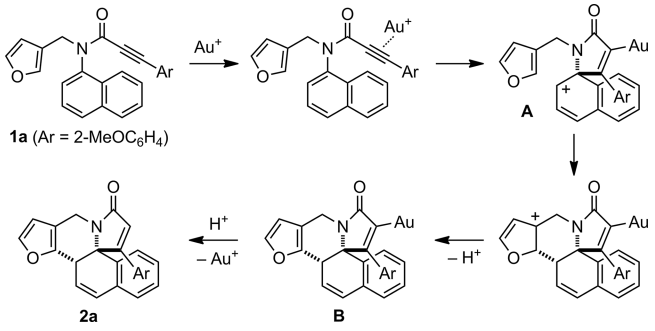


5a (R = Me), **5b** (R = H), **5c** (R = *i*Pr), **5d** (R = Ph)

[a] The reactions were conducted by using $AuCl(SMe_2)$ (0.010 mmol), (*R*)-xyl-binap (0.0050 mmol), $AgSbF_6$ (0.010 mmol), **3** (0.10 mmol), and $(CH_2Cl)_2$ (2.0 mL) at 25 °C for 72 h. Relative configurations are shown for **4** and **5**. [b] Isolated yield. [c] Mixtures of **4** and **5** were isolated. Ratios of **4**/**5** were determined by ^1H NMR spectroscopic analysis.

addition, both electron-rich furan as well as thiophene (i.e., **3e**, Table 4, Entry 5) could be employed in this reaction. In reactions of highly nucleophilic furan derivatives, eight-membered ring byproducts **5a**–**5d** were generated but could not be isolated in pure form because of their instability.

A possible mechanism for the conversion of **1a** into **2a** is depicted in Scheme 3. The coordination of the cationic gold(I) complex to the alkyne triple bond of **1a** induces the *ipso*-cyclization to generate cationic intermediate **A**. A Friedel–Crafts type reaction followed by deprotonation gives intermediate **B**, and protonation of **B** affords **2a** and regenerates the cationic gold(I) catalyst.



Scheme 3. Possible mechanism for the formation of **2a** from **1a**.

A possible mechanism for the formation of **4a** and **5a** from **3a** is shown in Scheme 4, which is similar to that for **2a** (Scheme 3). An *ipso*-cyclization through the coordination of a cationic gold(I) complex to the alkyne triple bond of **3a** affords cationic intermediate **C**. A Friedel–Crafts-type reaction at the *ortho*- and *para*-positions followed by deprotonation gives intermediate **D** and **E**, respectively. Protonation of **D** and **E** then affords **4a** and **5a**, respectively, and regenerates the cationic gold(I) catalyst.

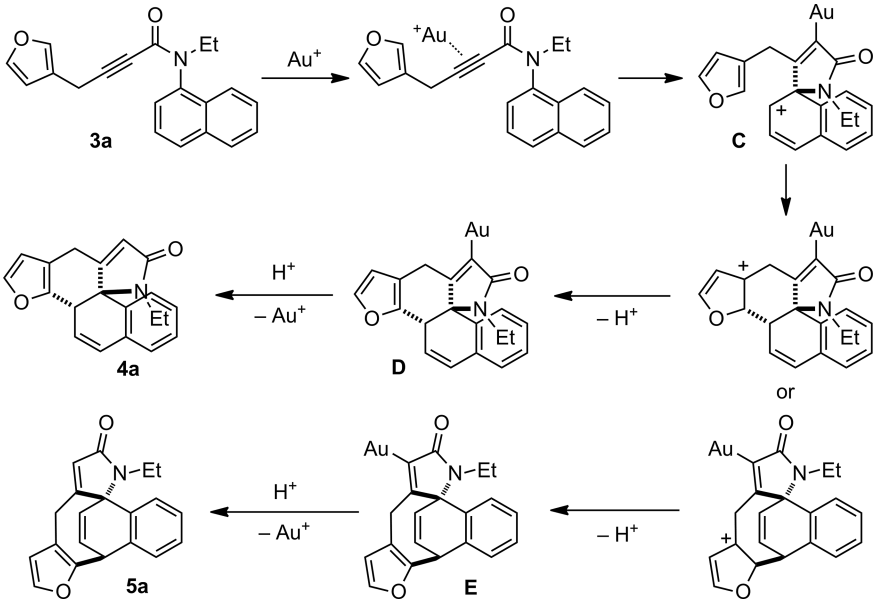
Conclusions

In summary, we have established that a cationic gold(I)/axially chiral biaryl bis(phosphine) complex catalyzes asymmetric dearomatization reactions of 1-aminonaphthalene derivatives through a C–C bond-forming reaction with electron-rich heterocycles as nucleophiles. These reactions afford pentacyclic heterocycles in good yields with moderate *ee* values.

Experimental Section

General Methods: The ^1H and ^{13}C NMR spectroscopic data were recorded with JEOL AL-300 (300 MHz) and JEOL JNM-ECA500 (500 MHz) spectrometers at ambient temperature. HRMS data were obtained on a Bruker micrOTOF Focus II mass spectrometer. Anhydrous $(CH_2Cl)_2$ (no. 28,450–5) and CH_3CN (no. 27,100-4) were obtained from Aldrich and used as received. Solvents that were used for the preparation of the substrates were dried over molecular sieves (4 Å, Wako) prior to use. H_8-binap and segphos derivatives were obtained from Takasago International Corporation. All other reagents were obtained from commercial sources and used as received. All reactions were carried out under argon or nitrogen in oven-dried glassware with magnetic stirring.

***N*-[(Furan-3-yl)methyl]-3-(2-methoxyphenyl)-*N*-(naphthalen-1-yl)-propynamide (1a):** To a stirred solution of 3-(2-methoxyphenyl) prop-2-ynoic acid[15] (0.706 g, 4.00 mmol) and 4-methylmorpholine (0.607 g, 6.00 mmol) in tetrahydrofuran (THF, 20 mL) was added isobutyl chloroformate (0.656 g, 4.80 mmol) in THF (3 mL) at 0 °C, and the mixture was stirred at 0 °C for 0.5 h. 1-Naphth-



Scheme 4. Possible mechanism for the formation of **4a** and **5a** from **3a**.

ylamine (0.687 g, 4.80 mmol) in THF (2 mL) was added at 0 °C, and the mixture was then stirred at 0 °C for 1 h and at room temperature for 16 h. The reaction was quenched with water, and the resulting mixture was extracted with CH_2Cl_2. The organic layer was washed with brine, dried with Na_2SO_4, and concentrated to furnish the corresponding crude 3-(2-methoxyphenyl)-*N*-(naphthalen-1-yl)-propiolamide[11a] (1.055 g). A mixture of (furan-3-yl)methanol (0.294 g, 3.00 mmol), PPh_3 (1.023 g, 3.90 mmol), and carbon tetrabromide (1.193 g, 3.60 mmol) in CH_2Cl_2 (15 mL) was stirred at room temperature for 3 h. The mixture was then poured into hexane (200 mL), and the resulting precipitate was removed by vacuum filtration through a pad of Celite. The filtrate was concentrated, and any additional precipitate was removed by filtration. The filtrate, which contained the 3-(bromomethyl)furan, was used without further purification. To a suspension of 55% sodium hydride (96 mg, 2.2 mmol) in THF (10 mL) was added a portion of the above crude 3-(2-methoxyphenyl)-*N*-(naphthalen-1-yl)propiolamide (0.602 g) in THF (10 mL) at 0 °C, and the mixture was then stirred at 0 °C for 0.5 h. The above 3-(bromomethyl)furan in THF (5 mL) was added at 0 °C, and the mixture was stirred at room temperature for 16 h. The reaction was quenched with water, and the resulting solution was extracted with EtOAc (3×). The yellow layer was washed with brine and dried with Na_2SO_4. The resulting solution was concentrated and purified by a silica gel column chromatography (hexane/EtOAc, 3:1), to furnish **1a** [0.505 g, 1.32 mmol, 58% yield from 3-(2-methoxyphenyl)-prop-2-ynoic acid] as a pale yellow, sticky oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.99–7.84 (m, 3 H), 7.82 (d, J = 8.2 Hz, 0.2 H), 7.78–7.73 (m, 0.2 H), 7.62 (dd, J = 7.6, 1.7 Hz, 0.2 H), 7.55–7.50 (m, 2 H), 7.50–7.46 (m, 0.2 H), 7.45–7.39 (m, 1 H), 7.36–7.31 (m, 0.8 H), 7.26 (d, J = 8.4 Hz, 0.2 H), 7.24–7.20 (m, 1.6 H), 7.15–7.11 (m, 0.8 H), 6.98 (t, J = 7.5 Hz, 0.2 H), 6.92 (d, J = 8.4 Hz, 0.2 H), 6.68 (dd, J = 7.6, 1.8 Hz, 0.8 H), 6.65–6.60 (m, 0.8 H), 6.57 (d, J = 8.4 Hz, 0.8 H), 6.47 (d, J = 1.7 Hz, 0.2 H), 6.41 (d, J = 1.7 Hz, 0.8 H), 5.60 (d, J = 15.3 Hz, 0.2 H), 5.40 (d, J = 14.4 Hz, 0.8 H), 4.75 (d, J = 15.3 Hz, 0.2 H), 4.35 (d, J = 14.4 Hz, 0.8 H), 3.84 (s, 0.6 H), 3.39 (s, 2.4 H) ppm. ^{13}C NMR (125 Hz, $CDCl_3$): δ = 160.7, 155.0, 142.8, 141.4, 137.3, 134.3, 134.1, 131.3, 130.7, 128.7, 128.1, 127.5, 126.9, 126.3, 125.2, 122.6, 120.5, 119.8, 111.2, 110.3, 109.1, 87.4, 86.3, 55.0, 42.7 ppm. HRMS (ESI): calcd. for $C_{25}H_{19}NNaO_3$ $[M + Na]^+$ 404.1263; found 404.1264.

***N*-[(Benzofuran-3-yl)methyl]-3-(2-methoxyphenyl)-*N*-(naphthalen-1-yl)propynamide (1b):** By following the procedure used to prepare **1a**, 3-(2-methoxyphenyl)-*N*-(naphthalen-1-yl)propiolamide and 3-(bromomethyl)benzofuran[16] afforded **1b** [53% yield from 3-(2-methoxyphenyl)prop-2-ynoic acid] as a pale orange, sticky oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.94–7.86 (m, 2.4 H), 7.85–7.80 (m, 0.8 H), 7.74–7.69 (m, 0.2 H), 7.63 (dd, J = 7.6, 1.7 Hz, 0.2 H), 7.55–7.50 (m, 1.8 H), 7.49–7.46 (m, 0.2 H), 7.43–7.37 (m, 1 H), 7.23–7.20 (m, 0.8 H), 7.17–7.09 (m, 2 H), 7.07 (dd, J = 5.0, 1.3 Hz, 0.8 H), 7.04–7.01 (m, 1 H), 6.99 (td, J = 7.6, 0.9 Hz, 0.2 H), 6.93 (d, J = 8.4 Hz, 0.2 H), 6.68 (dd, J = 7.6, 1.9 Hz, 0.8 H), 6.66–6.61 (m, 0.8 H), 6.58 (d, J = 8.4 Hz, 0.8 H), 5.76 (d, J = 15.1 Hz, 0.2 H), 5.58 (d, J = 14.2 Hz, 0.8 H), 4.91 (d, J = 15.1 Hz, 0.2 H), 4.51 (d, J = 14.2 Hz, 0.8 H), 3.82 (s, 0.6 H), 3.42 (s, 2.4 H) ppm. ^{13}C NMR (125 Hz, $CDCl_3$): δ = 160.7, 155.0, 137.4, 137.2, 134.3, 134.1, 131.3, 130.7, 128.7, 128.5, 128.1, 127.5, 127.0, 126.2, 125.6, 125.2, 124.3, 122.5, 119.9, 110.3, 109.2, 87.5, 86.3, 55.1, 46.7 ppm. HRMS (ESI): calcd. for $C_{25}H_{19}NNaO_2S$ $[M + Na]^+$ 420.1034; found 420.1033.

3-(2-Methoxyphenyl)-*N*-(naphthalen-1-yl)-*N*-[(thiophen-3-yl)methyl]propynoic Acid amide (1c): By following the procedure used to prepare **1a**, 3-(2-methoxyphenyl)-*N*-(naphthalen-1-yl)propiolamide and 3-(bromomethyl)thiophene[17] afforded **1b** [73% yield from 3-(2-methoxyphenyl)prop-2-ynoic acid as a pale orange, sticky oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.94–7.86 (m, 2.4 H), 7.85–7.80 (m, 0.8 H), 7.74–7.69 (m, 0.2 H), 7.63 (dd, J = 7.6, 1.7 Hz, 0.2 H), 7.55–7.50 (m, 1.8 H), 7.49–7.46 (m, 0.2 H), 7.43–7.37 (m, 1 H), 7.23–7.20 (m, 0.8 H), 7.17–7.09 (m, 2 H), 7.07 (dd, J = 5.0, 1.3 Hz, 0.8 H), 7.04–7.01 (m, 1 H), 6.99 (td, J = 7.6, 0.9 Hz, 0.2 H), 6.93 (d, J = 8.4 Hz, 0.2 H), 6.68 (dd, J = 7.6, 1.9 Hz, 0.8 H), 6.66–6.61 (m, 0.8 H), 6.58 (d, J = 8.4 Hz, 0.8 H), 5.76 (d, J = 15.1 Hz, 0.2 H), 5.58 (d, J = 14.2 Hz, 0.8 H), 4.91 (d, J = 15.1 Hz, 0.2 H), 4.51 (d, J = 14.2 Hz, 0.8 H), 3.82 (s, 0.6 H), 3.42 (s, 2.4 H) ppm. ^{13}C NMR (125 Hz, $CDCl_3$): δ = 160.7, 155.0, 137.4, 137.2, 134.3, 134.1, 131.3, 130.7, 128.7, 128.5, 128.1, 127.5, 127.0, 126.2, 125.6, 125.2, 124.3, 122.5, 119.9, 110.3, 109.2, 87.5, 86.3, 55.1, 46.7 ppm. HRMS

(ESI): calcd. for $C_{25}H_{19}NNaO_2S$ [M + Na]$^+$ 420.1034; found 420.1033.

***N*-[(Furan-2-yl)methyl]-3-(2-Methoxyphenyl)-*N*-(naphthalen-1-yl)-propynamide (1d):** By following the procedure used to prepare **1a**, 3-(2-methoxyphenyl)-*N*-(naphthalen-1-yl)propiolamide and 2-(bromomethyl)furan[18] afforded **1d** [32% yield from 3-(2-methoxyphenyl)prop-2-ynoic acid] as a pale yellow, sticky oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.94–7.85 (m, 2 H), 7.83 (d, J = 8.6 Hz, 0.2 H), 7.82–7.77 (m, 1 H), 7.68 (s, 0.2 H), 7.63 (dd, J = 7.7, 1.4 Hz, 0.2 H), 7.52 (td, J = 6.6, 3.2 Hz, 1.6 H), 7.49–7.40 (m, 1 H), 7.33–7.28 (m, 1 H), 7.27–7.21 (m, 1 H), 7.19–7.12 (m, 1 H), 6.99 (dd, J = 8.6, 7.4 Hz, 0.2 H), 6.94 (d, J = 8.6 Hz, 0.2 H), 6.72–6.62 (m, 1.8 H), 6.60 (d, J = 8.6 Hz, 0.8 H), 6.27–6.22 (m, 1 H), 6.17 (d, J = 3.4 Hz, 0.8 H), 5.66 (d, J = 15.8 Hz, 0.2 H), 5.47 (d, J = 14.9 Hz, 0.8 H), 5.01 (d, J = 15.8 Hz, 0.2 H), 4.67 (d, J = 14.9 Hz, 0.8 H), 3.87 (s, 0.6 H), 3.43 (s, 2.4 H) ppm. ^{13}C NMR (125 Hz, $CDCl_3$): δ = 160.8, 155.1, 150.0, 142.2, 137.5, 134.3, 131.4, 131.1, 128.8, 128.2, 127.4, 127.0, 126.3, 125.4, 122.6, 120.0, 110.42, 110.37, 109.6, 109.4, 87.7, 86.3, 55.2, 44.5 ppm. HRMS (ESI): calcd. for $C_{25}H_{19}NNaO_3$ [M + Na]$^+$ 404.1263; found 404.1275.

***N*-[(Furan-3-yl)methyl]-*N*-(naphthalen-1-yl)-3-phenylpropynamide (1e):** By following the procedure used to prepare **1a**, phenylpropiolic acid, 1-naphthylamine, and 3-(bromomethyl)furan afforded **1e** [39% yield from phenylpropiolic acid] as a pale orange, sticky oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.96–7.82 (m, 3 H), 7.78–7.73 (m, 0.1 H), 7.68–7.64 (m, 0.2 H), 7.58–7.50 (m, 2 H), 7.49–7.40 (m, 1.3 H), 7.38 (t, J = 1.7 Hz, 0.1 H), 7.37–7.33 (m, 0.9 H), 7.25–7.17 (m, 2.7 H), 7.13 (dd, J = 7.3, 1.1 Hz, 0.1 H), 7.11–7.03 (m, 1.8 H), 6.79–6.70 (m, 1.8 H), 6.48 (dd, J = 1.8, 0.8 Hz, 0.1 H), 6.41 (dd, J = 1.8, 0.8 Hz, 0.9 H), 5.49 (d, J = 15.5 Hz, 0.1 H), 5.38 (d, J = 14.4 Hz, 0.9 H), 4.71 (d, J = 15.5 Hz, 0.9 H), 4.42 (d, J = 14.5 Hz, 0.1 H) ppm. ^{13}C NMR (125 Hz, $CDCl_3$): δ = 155.0, 143.1, 141.6, 137.5, 134.4, 132.3, 130.8, 129.8, 129.1, 128.4, 128.1, 127.6, 127.2, 126.5, 125.3, 122.6, 120.5, 120.0, 111.3, 90.6, 82.5, 42.8 ppm. HRMS (ESI): calcd. for $C_{24}H_{17}NNaO_2$ [M + Na]$^+$ 374.1157; found 374.1151.

3-Cyclohexyl-*N*-[(furan-3-yl)methyl]-*N*-(naphthalen-1-yl)propynamide (1f): By following the procedure used to prepare **1a**, 3-cyclohexylprop-2-ynoic acid,[11a] 1-naphthylamine, and 3-(bromomethyl)furan afforded **1f** [54% yield from 3-cyclohexylprop-2-ynoic acid] as an orange solid; m.p. 68.5–70.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.91–7.86 (m, 1 H), 7.84 (d, J = 8.6 Hz, 0.8 H), 7.82–7.75 (m, 1 H), 7.69 (t, J = 4.9 Hz, 0.2 H), 7.59–7.44 (m, 2 H), 7.40 (t, J = 7.7 Hz, 0.8 H), 7.37 (q, J = 1.7 Hz, 0.2 H), 7.32 (t, J = 1.7 Hz, 0.8 H), 7.20 (s, 0.8 H), 7.14 (dd, J = 6.9, 1.1 Hz, 0.8 H), 7.05 (dd, J = 7.4, 1.1 Hz, 0.2 H), 6.46–6.31 (m, 1 H), 5.40 (d, J = 14.9 Hz, 0.2 H), 5.29 (d, J = 14.9 Hz, 0.8 H), 4.60 (d, J = 15.5 Hz, 0.2 H), 4.36 (d, J = 14.3 Hz, 0.8 H), 2.14 (s, 0.8 H), 2.01–1.90 (s, 0.2 H), 1.77 (s, 0.2 H), 1.61 (s, 0.2 H), 1.39 (t, J = 8.6 Hz, 0.4 H), 1.31–1.19 (m, 0.2 H), 1.18–1.00 (m, 3.2 H), 0.96–0.75 (m, 4.8 H) ppm. ^{13}C NMR (125 Hz, $CDCl_3$): δ = 155.3, 143.0, 141.5, 137.9, 134.5, 130.9, 128.8, 128.2, 127.3, 127.0, 126.4, 125.2, 122.8, 120.7, 111.4, 97.1, 75.2, 42.7, 30.6, 28.1, 25.4, 23.3 ppm. HRMS (ESI): calcd. for $C_{24}H_{23}NNaO_2$ [M + Na]$^+$ 380.1626; found 380.1621.

***N*-[(Furan-3-yl)methyl]-*N*-(naphthalen-1-yl)but-2-ynamide (1g):** By following the procedure used to prepare **1a**, 2-butynoic acid, 1-naphthylamine, and 3-(bromomethyl)furan afforded **1g** [36% yield from 2-butynoic acid] as a black oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.93–7.88 (m, 1 H), 7.88–7.84 (m, 0.9 H), 7.83–7.75 (m, 1 H), 7.71–7.65 (m, 0.1 H), 7.58–7.51 (m, 2 H), 7.50–7.47 (m, 0.2 H), 7.41 (dd, J = 8.3, 7.2 Hz, 0.9 H), 7.38–7.35 (m, 0.1 H), 7.32 (t, J = 1.7 Hz, 0.9 H), 7.17 (q, J = 0.7 Hz, 0.9 H), 7.14 (d, J = 0.8 Hz, 0.1 H), 7.12 (dd, J = 7.2, 1.1 Hz, 0.9 H), 7.06 (dd, J = 7.2, 1.1 Hz, 0.1 H), 6.41 (dd, J = 1.8, 0.8 Hz, 0.1 H), 6.34 (dd, J = 1.8, 0.8 Hz, 0.9 H), 5.39 (d, J = 15.4 Hz, 0.1 H), 5.35 (d, J = 14.4 Hz, 0.9 H), 4.60 (d, J = 15.4 Hz, 0.1 H), 4.25 (d, J = 14.4 Hz, 0.9 H), 2.16 (s, 0.3 H), 1.49 (s, 2.7 H) ppm. ^{13}C NMR (125 Hz, $CDCl_3$): δ = 155.0, 143.0, 141.5, 137.4, 134.4, 130.6, 128.9, 128.4, 127.5, 127.1, 126.4, 125.2, 122.6, 120.5, 111.3, 89.7, 74.0, 42.7, 3.7 ppm. HRMS (ESI): calcd. for $C_{19}H_{15}NNaO_2$ [M + Na]$^+$ 312.1000; found 312.1005.

Representative Procedure for Gold-Catalyzed Asymmetric Dearomatization: (Table 2) $AuCl(SMe_2)$ (2.9 mg, 0.010 mmol), (*R*)-binap (3.1 mg, 0.0050 mmol), and AgOTf (2.6 mg, 0.010 mmol) were dissolved in $(CH_2Cl)_2$ (1.5 mL). The resulting mixture was added to a solution of **1a** (76.2 mg, 0.200 mmol) in $(CH_2Cl)_2$ (0.5 mL) at room temperature and then stirred at 25 °C for 16 h. The resulting solution was concentrated, and the residue was purified by preparative TLC (hexane/EtOAc/toluene/CH_2Cl_2/CH_3Cl, 1:1:1:1:1) to furnish (–)-**2a** (75.2 mg, 0.197 mmol, 99% yield, 47%*ee*).

(–)-5-(2-Methoxyphenyl)-9,12b-dihydro-7*H*-benzo[*h*]furo[3,2-*c*]pyrrolo[2,1-*j*]quinolin-7-one [(–)-2a]: Pale yellow solid (75.2 mg, 99% yield, 47%*ee*); m.p. 62.3–62.5 °C. $[a]_D^{25}$ = –116 (c = 1.50, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.28–7.18 (m, 4 H), 7.15 (dd, J = 7.5, 1.3 Hz, 1 H), 6.87 (dd, J = 7.3, 1.3 Hz, 1 H), 6.80 (d, J = 8.3 Hz, 1 H), 6.59 (td, J = 7.5, 0.9 Hz, 1 H), 6.17 (d, J = 1.9 Hz, 1 H), 6.00–5.95 (m, 3 H), 5.91 (s, 1 H), 5.10 (dd, J = 16.0, 2.0 Hz, 1 H), 4.05 (s, 1 H), 3.93 (dd, J = 16.0, 2.6 Hz, 1 H), 3.69 (s, 3 H) ppm. ^{13}C NMR (125 Hz, $CDCl_3$): δ = 170.1, 162.5, 156.3, 147.0, 142.4, 134.0, 129.7, 129.3, 128.7, 128.6, 127.3, 124.3, 124.0, 122.7, 122.3, 119.5, 114.6, 110.0, 107.9, 70.3, 55.3, 37.3, 35.0 ppm. HPLC (CHIRALPAK AD-H; hexane/2-PrOH, 90:10; 1.0 mL min^{-1}): t_R = 19.3 min (major isomer) and t_R = 27.6 min (minor isomer). HRMS (ESI): calcd. for $C_{25}H_{19}NNaO_3$ [M + Na]$^+$ 404.1263; found 404.1261.

(–)-7-(2-Methoxyphenyl)-11,16b-dihydro-9*H*-benzo[*h*]benzofuro[3,2-*c*]pyrrolo[2,1-*j*]quinolin-9-one [(–)-2b]: Pale yellow solid (36.1 mg, 84% yield, 44%*ee*); m.p. 72.5–74.0 °C. $[a]_D^{25}$ = –213 (c = 1.00, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.33 (m, 2 H), 7.29–7.26 (m, 1 H), 7.25–7.14 (m, 4 H), 6.86 (dd, J = 7.4, 1.0 Hz, 1 H), 6.83 (dd, J = 8.4, 0.7 Hz, 1 H), 6.62 (td, J = 7.4, 1.0 Hz, 1 H), 6.09–5.99 (m, 3 H), 5.98 (s, 1 H), 5.36 (dd, J = 16.0, 2.2 Hz, 1 H), 4.26–4.21 (m, 1 H), 4.15 (dd, J = 16.0, 2.8 Hz, 1 H), 3.73 (s, 3 H) ppm. ^{13}C NMR (125 Hz, $CDCl_3$): δ = 170.1, 162.7, 156.4, 155.2, 150.1, 134.0, 129.8, 129.7, 129.3, 128.8, 128.7, 127.8, 127.4, 125.7, 124.3, 123.9, 123.5, 122.8, 122.7, 122.2, 119.5, 118.6, 111.2, 110.7, 110.1, 70.3, 55.4, 37.9, 34.2 ppm. HPLC (CHIRALPAK AD-H; hexane/2-PrOH, 90:10; 1.0 mL min^{-1}): t_R = 24.6 min (minor isomer) and t_R = 28.7 min (major isomer). HRMS (ESI): calcd. for $C_{29}H_{21}NNaO_3$ [M + Na]$^+$ 454.1414; found 454.1411.

(–)-5-(2-Methoxyphenyl)-9,12b-dihydro-7*H*-benzo[*h*]pyrrolo[2,1-*j*]-thieno[3,2-*c*]quinolin-7-one [(–)-2c]: Pale yellow solid (35.0 mg, 88% yield, 54%*ee*); m.p. 56.5–57.6 °C. $[a]_D^{25}$ = –124 (c = 0.67, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.27–7.22 (m, 2 H), 7.22–7.15 (m, 2 H), 7.09 (dd, J = 5.2, 1.0 Hz, 1 H), 6.86 (dd, J = 7.4, 0.9 Hz, 1 H), 6.80 (d, J = 8.2 Hz, 1 H), 6.70 (d, J = 5.2 Hz, 1 H), 6.59 (td, J = 7.4, 0.9 Hz, 1 H), 6.03 (dd, J = 9.7, 6.2 Hz, 1 H), 5.99–5.90 (m, 3 H), 5.28 (dd, J = 16.5, 1.7 Hz, 1 H), 4.11 (dd, J = 16.5, 2.3 Hz, 1 H), 4.06 (d, J = 6.2 Hz, 1 H), 3.69 (s, 3 H) ppm. ^{13}C NMR (125 Hz, $CDCl_3$): δ = 170.0, 162.8, 156.3, 135.2, 134.1, 131.9, 130.1, 129.6, 129.3, 128.7, 128.6, 127.4, 127.2, 124.3, 123.8, 122.9, 122.6, 119.4, 110.0, 70.0, 55.4, 39.0, 37.8 ppm. HPLC (CHIRALPAK AD-H; hexane/2-PrOH, 97:3; 1.0 mL min^{-1}): t_R = 103.0 min (minor isomer) and t_R = 111.4 min (major isomer).

HRMS (ESI): calcd. for $C_{25}H_{19}NNaO_2S$ [M + Na]$^+$ 420.1034; found 420.1029.

(–)-5-Phenyl-9,12b-dihydro-7*H*-benzo[*h*]furo[3,2-*c*]pyrrolo[2,1-*j*]quinolin-7-one [(–)-2e]: Orange solid (63.8 mg, 91% yield, 13%*ee*); m.p. 143.2–144.0 °C. $[\alpha]_D^{25}$ = –43.7 (*c* = 2.80, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.33–7.26 (m, 3 H), 7.24–7.19 (m, 2 H), 7.19–7.14 (m, 2 H), 7.02–6.97 (m, 1 H), 6.72–6.67 (m, 2 H), 6.16 (d, *J* = 1.9 Hz, 1 H), 6.10 (d, *J* = 9.8 Hz, 1 H), 5.99–5.95 (m, 1 H), 5.95 (s, 1 H), 5.10 (dd, *J* = 16.0, 2.0 Hz, 1 H), 3.88 (dd, *J* = 16.0, 2.5 Hz, 1 H), 3.78–3.72 (m, 1 H) ppm. ^{13}C NMR (125 Hz, $CDCl_3$): δ = 169.6, 165.8, 146.8, 142.6, 134.2, 133.2, 129.1, 129.0, 128.8, 127.74, 127.72, 127.6, 124.7, 124.0, 121.1, 115.0, 107.8, 69.4, 38.2, 34.7 ppm. HPLC (CHIRALPAK AD-H; hexane/2-PrOH, 90:10; 1.0 mL min^{-1}): t_R = 21.1 min (minor isomer) and t_R = 24.9 min (major isomer). HRMS (ESI): calcd. for $C_{24}H_{17}NNaO_2$ [M + Na]$^+$ 374.1157; found 374.1158.

(–)-5-Cyclohexyl-9,12b-dihydro-7*H*-benzo[*h*]furo[3,2-*c*]pyrrolo[2,1-*j*]-quinolin-7-one [(–)-2f]: White solid (71.5 mg, >99% yield, 14%*ee*); m.p. 204.5–206.2 °C. $[\alpha]_D^{25}$ = –57.6 (*c* = 2.90, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.23 (dd, *J* = 1.9, 1.1 Hz, 1 H), 7.22–7.19 (m, 1 H), 7.19–7.15 (m, 1 H), 7.09 (dd, *J* = 7.2, 1.5 Hz, 1 H), 6.99–6.94 (m, 1 H), 6.56 (d, *J* = 9.8 Hz, 1 H), 6.41 (dd, *J* = 9.8, 6.1 Hz, 1 H), 6.14 (d, *J* = 1.9 Hz, 1 H), 5.75 (d, *J* = 0.5 Hz, 1 H), 4.99 (dd, *J* = 16.0, 2.0 Hz, 1 H), 3.77 (dd, *J* = 16.0, 2.5 Hz, 1 H), 3.72–3.64 (m, 1 H), 2.37–2.30 (m, 1 H), 1.91–1.86 (m, 1 H), 1.78–1.73 (m, 1 H), 1.63–1.58 (m, 1 H), 1.55–1.48 (m, 1 H), 1.30–1.08 (m, 3 H), 1.02–0.86 (m, 3 H) ppm. ^{13}C NMR (125 Hz, $CDCl_3$): δ = 174.6, 170.7, 146.9, 142.5, 133.1, 130.3, 129.0, 128.7, 128.3, 127.8, 124.8, 124.6, 116.8, 115.0, 107.8, 68.5, 38.1, 36.9, 34.4, 34.3, 34.1, 26.5, 26.4, 25.7 ppm. HPLC (CHIRALPAK AD-H, EtOH, 1.0 mL min^{-1}): t_R = 23.2 min (minor isomer) and t_R = 51.1 min (major isomer). HRMS (ESI): calcd. for $C_{24}H_{23}NNaO_2$ [M + Na]$^+$ 380.1626; found 380.1621.

(–)-5-Methyl-9,12b-dihydro-7*H*-benzo[*h*]furo[3,2-*c*]pyrrolo[2,1-*j*]-quinolin-7-one [(–)-2g]: Pale yellow solid (50.0 mg, 86% yield, 12%*ee*); m.p. 173.4–175.0 °C. $[\alpha]_D^{25}$ = –99.1 (*c* = 1.68, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.24–7.16 (m, 3 H), 7.09 (dd, *J* = 7.1, 1.8 Hz, 1 H), 7.01–6.96 (m, 1 H), 6.55 (d, *J* = 9.8 Hz, 1 H), 6.36 (dd, *J* = 9.8, 6.2 Hz, 1 H), 6.15 (d, *J* = 1.9 Hz, 1 H), 5.69 (q, *J* = 1.5 Hz, 1 H), 5.01 (dd, *J* = 16.0, 2.1 Hz, 1 H), 3.83 (dd, *J* = 16.0, 2.5 Hz, 1 H), 3.59 (m, 1 H), 1.90 (d, *J* = 1.5 Hz, 3 H) ppm. ^{13}C NMR (125 Hz, $CDCl_3$): δ = 170.4, 164.4, 146.5, 142.5, 132.9, 130.6, 129.0, 128.6, 128.5, 127.8, 124.3, 124.1, 118.9, 115.1, 107.9, 68.6, 37.8, 34.7, 13.7 ppm. HPLC (CHIRALPAK AD-H; hexane/2-PrOH, 90:10; 1.0 mL min^{-1}): t_R = 18.6 min (minor isomer) and t_R = 27.4 min (major isomer). HRMS (ESI): calcd. for $C_{19}H_{15}NNaO_2$ [M + Na]$^+$ 312.1000; found 312.0995.

***N*-Ethyl-4-(furan-3-yl)-*N*-(naphthalen-1-yl)but-2-ynamide (3a):** *N*-Ethyl-*N*-(naphthalen-1-yl)propiolamide[10] (0.670 g, 3.00 mmol) was added to a mixture of 3-(bromomethyl)furan (0.483 g, 3.00 mmol), copper(I) iodide (0.628 g, 3.33 mmol), potassium carbonate (0.456 g, 3.33 mmol), and tetrabutylammonium iodide (1.219 g, 3.33 mmol) in dry acetonitrile (40 mL). The resulting slurry was stirred at 40 °C for 2 d and then diluted with saturated aqueous ammonium chloride. The resulting mixture was extracted with diethyl ether (2×). The combined organic layers were dried with Na_2SO_4 and passed through a filter to remove the drying agent. The filtrate was concentrated, and the residue was purified by silica gel column chromatography (hexane/EtOAc/toluene, 3:1:3) to afford **3a** (0.119 g, 0.330 mmol, 11% yield) as an orange solid; m.p. 50.3–50.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.97–7.81 (m, 3 H), 7.60–7.54 (m, 2 H), 7.50 (dd, *J* = 8.2, 7.2 Hz, 1 H), 7.40 (dd, *J* = 7.2, 1.2 Hz, 1 H), 7.10 (t, *J* = 1.7 Hz, 1 H), 6.25–6.21 (m, 1 H), 5.62–5.61 (m, 1 H), 4.25 (dq, *J* = 7.2, 14.3 Hz, 1 H), 3.62–3.49 (dq, *J* = 7.2, 14.3 Hz, 1 H), 3.07 (t, *J* = 1.3 Hz, 2 H), 1.19 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.6, 142.7, 139.2, 137.7, 134.6, 131.0, 129.0, 128.4, 127.3, 127.2, 126.6, 125.4, 122.7, 118.2, 109.9, 89.4, 75.7, 43.5, 15.3, 13.2 ppm. HRMS (ESI): calcd. for $C_{20}H_{17}O_2NNa$ [M + Na]$^+$ 326.1151; found 326.1151.

4-(Furan-3-yl)-*N*-methyl-*N*-(naphthalen-1-yl)but-2-ynamide (3b): By following the procedure used to prepare **3a**, *N*-methyl-*N*-(naphthalen-1-yl)propiolamide[10] and 3-(bromomethyl)furan afforded **3b** (32% yield) as an orange solid; m.p. 52.0–53.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.96–7.87 (m, 2 H), 7.86–7.79 (m, 1 H), 7.61–7.53 (m, 2 H), 7.52–7.47 (m, 1 H), 7.43 (dd, *J* = 7.2, 1.1 Hz, 1 H), 7.10 (t, *J* = 1.7 Hz, 1 H), 6.25–6.24 (m, 1 H), 5.62–5.61 (m, 1 H), 3.42 (s, 3 H), 3.08 (s, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.9, 142.7, 139.4, 139.2, 134.5, 130.5, 128.9, 128.5, 127.4, 126.7, 126.1, 125.6, 122.4, 118.2, 109.9, 89.7, 75.4, 36.5, 15.2 ppm. HRMS (ESI): calcd. for $C_{19}H_{15}O_2NNa$ [M + Na]$^+$ 312.1000; found 312.1005.

4-(Furan-3-yl)-*N*-isobutyl-*N*-(naphthylen-1-yl)but-2-ynamide (3c): By following the procedure used to prepare **3a**, *N*-isobutyl-*N*-(naphthalen-1-yl)propiolamide[10] and 3-(bromomethyl)furan afforded **3c** (44% yield) as an orange sticky oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.98–7.92 (m, 1 H), 7.90 (d, *J* = 8.2 Hz, 1 H), 7.87–7.80 (m, 1 H), 7.60–7.53 (m, 2 H), 7.51–7.46 (m, 1 H), 7.42 (dd, *J* = 7.2, 1.2 Hz, 1 H), 7.10 (t, *J* = 1.7 Hz, 1 H), 6.25–6.24 (m, 1 H), 5.62–5.61 (m, 1 H), 4.22 (dd, *J* = 13.3, 9.3 Hz, 1 H), 3.17 (dd, *J* = 13.3, 5.6 Hz, 1 H), 3.07 (s, 2 H), 1.90–1.82 (m, 1 H), 1.03 (d, *J* = 6.7 Hz, 3 H), 0.90 (d, *J* = 6.7 Hz, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.3, 142.7, 139.2, 138.2, 134.6, 130.7, 128.9, 128.5, 127.3, 126.6, 125.3, 122.6, 118.2, 109.9, 89.8, 75.6, 55.2, 27.5, 20.3, 20.1, 15.3 ppm. HRMS (ESI): calcd. for $C_{22}H_{21}O_2NNa$ [M + Na]$^+$ 354.1465; found 354.1474.

***N*-Benzyl-4-(furan-3-yll)-*N*-(naphthalen-1-yl)but-2-ynamide (3d):** By following the procedure used to prepare **3a**, *N*-benzyl-*N*-(naphthalen-1-yl)propiolamide[10] and 3-(bromomethyl)furan afforded **3d** (>99% yield) as a yellow sticky oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.96–7.75 (m, 3 H), 7.57–7.51 (m, 2 H), 7.33 (dd, *J* = 8.3, 7.3 Hz, 1 H), 7.27–7.17 (m, 5 H), 7.08 (t, *J* = 1.7 Hz, 1 H), 7.00 (dd, *J* = 7.3, 1.1 Hz, 1 H), 6.23–6.20 (m, 1 H), 5.65 (d, *J* = 14.1 Hz, 1 H), 5.61–5.57 (m, 1 H), 4.35 (d, *J* = 14.1 Hz, 1 H), 5.60–5.59 (m, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.9, 142.7, 139.2, 137.4, 136.7, 134.5, 130.7, 129.3 (2 C), 129.0, 128.5, 128.4, 127.7, 127.6, 127.3, 126.5, 125.3, 122.5, 118.1, 109.9, 90.1, 75.4, 52.0, 15.3 ppm. HRMS (ESI): calcd. for $C_{25}H_{19}O_2NNa$ [M + Na]$^+$ 388.1308; found 388.1322.

***N*-Ethyl-*N*-(naphthalen-1-yl)-4-(thiophen-3-yl)but-2-ynamide (3e):** By following the procedure used to prepare **3a**, *N*-ethyl-*N*-(naphthalen-1-yl)propiolamide[10] and 3-(bromomethyl)thiophene[17] afforded **3e** (23% yield) as an orange sticky oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.00–7.79 (m, 3 H), 7.61–7.53 (m, 2 H), 7.49 (dd, *J* = 8.2, 7.2 Hz, 1 H), 7.41 (dd, *J* = 7.2, 1.2 Hz, 1 H), 6.99 (dd, *J* = 4.9, 3.0 Hz, 1 H), 6.25 (dd, *J* = 4.9, 1.3 Hz, 1 H), 5.86–5.84 (m, 1 H), 4.25 (dq, *J* = 14.4, 7.2 Hz, 1 H), 3.58 (dq, *J* = 14.4, 7.2 Hz, 1 H), 3.31–3.26 (m, 2 H), 1.20 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.6, 137.7, 134.6, 134.0, 131.1, 129.0, 128.5, 127.4, 127.2, 126.8, 126.6, 125.5, 125.5, 122.7, 121.0, 89.8, 76.4, 43.5, 20.1, 13.2 ppm. HRMS (ESI): calcd. for $C_{20}H_{17}NOSNa$ [M + Na]$^+$ 342.0929; found 342.0939.

Representative Procedure for Gold-Catalyzed Asymmetric Dearomatization: (Table 4)**:** $AuCl(SMe_2)$ (2.9 mg, 0.010 mmol), (*R*)-xylbinap (3.7 mg, 0.0050 mol), and $AgSbF_6$ (3.4 mg, 0.010 mmol)

were dissolved in $(CH_2Cl)_2$ (1.0 mL) and then added to a solution of **3a** (35.9 mg, 0.10 mmol) in $(CH_2Cl)_2$ (1.0 mL) at room temperature. The mixture was stirred at 25 °C for 72 h. The resulting solution was concentrated, and the residue was purified by preparative TLC (hexane/EtOAc, 1:1) to furnish a mixture of (+)-**4a** (60%*ee*) and **5a** (31.9 mg, 89% yield, **4a**/**5a** = 83:17).

(+)-5-Ethyl-8,11b-dihydrofuro[3,2-*f*]naphtho[2,1-*h*]indol-6(5*H*)-one [(+)-4a]: The solid mixture of **4a** and **5a** was washed with Et_2O and filtered to give pure **4a** (95% *ee*) as an orange solid; m.p. 212.2–213.5 °C. $[\alpha]_D^{25}$ = +444 (*c* = 0.18, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.28 (td, *J* = 7.4, 1.1 Hz, 1 H), 7.25–7.23 (m, 1 H), 7.20 (td, *J* = 7.4, 1.5 Hz, 1 H), 7.15 (dd, *J* = 7.4, 1.1 Hz, 1 H), 7.01 (d, *J* = 7.4 Hz, 1 H), 6.69 (d, *J* = 9.7 Hz, 1 H), 6.52 (dd, *J* = 9.5, 6.0 Hz, 1 H), 6.26 (d, *J* = 1.7 Hz, 1 H), 6.11 (d, *J* = 1.7 Hz, 1 H), 3.72–3.65 (m, 1 H), 3.60 (dd, *J* = 17.5, 1.4 Hz, 1 H), 3.41–3.28 (m, 2 H), 3.00 (dq, *J* = 14.3, 7.1 Hz, 1 H), 0.85 (t, *J* = 7.1 Hz, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.0, 160.0, 147.5, 142.8, 133.0, 130.0, 129.2, 129.1, 127.9, 127.6, 126.0, 125.1, 123.5, 115.0, 109.3, 66.7, 42.2, 35.4, 23.7, 14.4 ppm. HRMS (ESI): calcd. for $C_{20}H_{17}O_2NNa$ $[M + Na]^+$ 326.1151; found 326.1151. HPLC (CHIRALPAK IE-3; hexane/2-PrOH, 90:10; 0.6 mL min^{-1}): t_R = 89.6 min (major isomer) and t_R = 100.2 min (minor isomer).

(+)-5-Methyl-8,11b-dihydrofuro[3,2-*f*]naphtho[2,1-*h*]indol-6(5*H*)-one [(+)-4b]: Following the representative procedure above afforded a mixture of (+)-**4b** (24.0 mg, 84% yield, 61%*ee*) and **5b** (27.4 mg). Leaving the mixture of **4b** and **5b** under Ar for 3 d followed by preparative TLC afforded pure **4b** as an orange solid; m.p. 154.3–155.2 °C. $[\alpha]_D^{25}$ = +349 (*c* = 0.45, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.28 (td, *J* = 7.6, 1.3 Hz, 1 H), 7.24 (dd, *J* = 1.9, 1.3 Hz, 1 H), 7.21 (td, *J* = 7.6, 1.3 Hz, 1 H), 7.15 (dd, *J* = 7.6, 1.3 Hz, 1 H), 6.99 (d, *J* = 7.6 Hz, 1 H), 6.67 (d, *J* = 9.7 Hz, 1 H), 6.49 (dd, *J* = 9.7, 6.1 Hz, 1 H), 6.28 (d, *J* = 1.9 Hz, 1 H), 6.12 (d, *J* = 1.9 Hz, 1 H), 3.62 (dd, *J* = 13.1, 1.3 Hz, 1 H), 3.60 (s, 1 H), 3.40–3.33 (m, 1 H), 3.65 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.7, 160.0, 147.3, 142.9, 133.0, 129.5, 129.2, 129.1, 127.8, 127.5, 126.0, 124.7, 123.4, 115.2, 109.3, 66.7, 41.6, 25.4, 23.8 ppm. HRMS (ESI): calcd. for $C_{19}H_{15}O_2NNa$ $[M + Na]^+$ 312.0995; found 312.1006. HPLC (CHIRALPAK IA; hexane/$CHCl_3$, 60:40; 0.4 mL min^{-1}): t_R = 34.0 min (major isomer) and t_R = 52.9 min (minor isomer).

(+)-5-Isobutyl-8,11b-dihydrofuro[3,2-*f*]naphtho[2,1-*h*]indol-6(5*H*)-one [(+)-4c]: Following the representative procedure above afforded **4c** (52.1 mg, 0.0741 mmol, 74% yield, 53%*ee*) as an orange solid; m.p. 158.3–160.0 °C. $[\alpha]_D^{25}$ = +231 (*c* = 1.57, $CDCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.27 (td, *J* = 7.5, 1.4 Hz, 1 H), 7.23 (dd, *J* = 1.9, 1.2 Hz, 1 H), 7.19 (td, *J* = 7.5, 1.4 Hz, 1 H), 7.12 (dd, *J* = 7.5, 1.2 Hz, 1 H), 7.01 (d, *J* = 7.5 Hz, 1 H), 6.64 (d, *J* = 10.3 Hz, 1 H), 6.49 (dd, *J* = 9.6, 6.1 Hz, 1 H), 6.26 (d, *J* = 1.9 Hz, 1 H), 6.10 (d, *J* = 1.9 Hz, 1 H), 3.75–3.63 (m, 1 H), 3.59 (dd, *J* = 17.8, 1.6 Hz, 1 H), 3.31 (dt, *J* = 17.8, 2.5 Hz, 1 H), 3.06 (dd, *J* = 14.1, 8.2 Hz, 1 H), 2.75 (dd, *J* = 14.1, 7.1 Hz, 1 H), 1.57–1.43 (m, 1 H), 0.73 (d, *J* = 6.6 Hz, 3 H), 0.66 (d, *J* = 6.6 Hz, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.8, 159.8, 147.5, 142.7, 133.0, 130.1, 129.1, 128.9, 127.4, 127.3, 126.0, 125.4, 123.2, 114.9, 109.2, 66.9, 48.0, 41.9, 28.2, 23.7, 20.3, 20.0 ppm. HRMS (ESI): calcd. for $C_{22}H_{21}O_2NNa$ $[M + Na]^+$ 354.1465; found 354.1462. HPLC (CHIRALPAK AD-H; hexane/2-PrOH, 80:20; 1.0 mL min^{-1}): t_R = 7.0 min (major isomer) and t_R = 8.2 min (minor isomer).

(+)-5-Benzyl-8,11b-dihydrofuro[3,2-*f*]naphtho[2,1-*h*]indol-6(5*H*)-one [(+)-4d]: Following the representative procedure above afforded **4d** (23.9 mg, 0.0654 mmol, 66% yield, 52%*ee*) as a colorless solid; m.p. 99.2–101.0. $[\alpha]_D^{25}$ = +144 (*c* = 1.25, $CDCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.23 (td, *J* = 7.4, 1.3 Hz, 1 H), 7.20–7.13 (m, 5 H), 7.12–7.08 (m, 2 H), 7.07 (dd, *J* = 7.4, 1.3 Hz, 1 H), 7.02 (d, *J* = 7.4 Hz, 1 H), 6.56 (d, *J* = 9.6 Hz, 1 H), 6.38 (d, *J* = 1.9 Hz, 1 H), 6.08 (d, *J* = 1.9 Hz, 1 H), 5.97 (dd, *J* = 9.6, 6.2 Hz, 1 H), 4.73 (d, *J* = 15.8 Hz, 1 H), 3.76 (d, *J* = 15.8 Hz, 1 H), 3.62 (dd, *J* = 17.9, 1.6 Hz, 1 H), 3.47–3.41 (m, 1 H), 3.35 (dt, *J* = 17.9, 2.5 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.8, 160.6, 147.4, 142.7, 138.1, 133.2, 129.2, 128.9, 127.8, 127.7, 127.4, 127.3, 126.7, 125.9, 125.5, 114.7, 109.2, 67.0, 43.4, 41.6, 23.8 ppm. HRMS (ESI): calcd. for $C_{25}H_{19}O_2NNa$ $[M + Na]^+$ 388.1308; found 388.1304. HPLC (CHIRALPAK AD-H; hexane/2-PrOH, 90:10; 1.0 mL min^{-1}): t_R = 20.0 min (major isomer) and t_R = 25.2 min (minor isomer).

(+)-5-Ethyl-8,11b-dihydronaphtho[2,1-*h*]thieno[3,2-*f*]indol-6(5*H*)-one [(+)-4e]: Following the representative procedure above afforded **4e** (37.8 mg, 59% yield, 43%*ee*) as an orange solid; m.p. 171.4–173.2 °C. $[\alpha]_D^{25}$ = +222 (*c* = 1.57, $CDCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.27 (td, *J* = 7.5, 1.4 Hz, 1 H), 7.20 (td, *J* = 7.5, 1.4 Hz, 1 H), 7.14 (dd, *J* = 7.5, 1.0 Hz, 1 H), 7.11 (dd, *J* = 5.2, 1.0 Hz, 1 H), 7.01 (d, *J* = 7.5 Hz, 1 H), 6.69 (d, *J* = 9.5 Hz, 1 H), 6.64 (d, *J* = 5.2 Hz, 1 H), 6.58 (dd, *J* = 9.5, 6.2 Hz, 1 H), 6.26 (d, *J* = 2.3 Hz, 1 H), 3.84 (dd, *J* = 18.1, 1.0 Hz, 1 H), 3.76–3.65 (m, 1 H), 3.52 (dt, *J* = 18.1, 2.3 Hz, 1 H), 3.37 (dq, *J* = 14.2, 7.1 Hz, 1 H), 3.00 (dq, *J* = 14.2, 7.1 Hz, 1 H), 0.87 (t, *J* = 7.1 Hz, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.2, 159.6, 136.1, 133.2, 132.3, 130.2, 129.2, 129.1, 128.4, 128.0, 127.5, 126.1, 125.4, 124.9, 123.2, 66.6, 43.8, 35.4, 27.3, 14.5 ppm. HRMS (ESI): calcd. for $C_{20}H_{17}NOSNa$ $[M + Na]^+$ 342.0923; found 342.0923. HPLC (CHIRALPAK AD-H; hexane/2-PrOH, 80:20; 1.0 mL min^{-1}): t_R = 8.5 min (major isomer) and t_R = 12.2 min (minor isomer).

Supporting Information (see footnote on the first page of this article): Chiral HPLC chromatograms and ^{1}H and ^{13}C NMR spectra.

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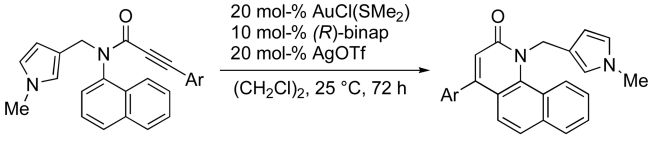

1h (Ar = 2-MeOC$_6$H$_4$) **6**

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