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Regioselective Hydration of Terminal Alkynes Catalyzed by a Neutral Gold(I) Complex [(IPr)AuCl] and One-Pot Synthesis of Optically Active Secondary Alcohols from Terminal Alkynes by the Combination of [(IPr)AuCl] and Cp*RhCl[(*R*,*R*)-TsDPEN]

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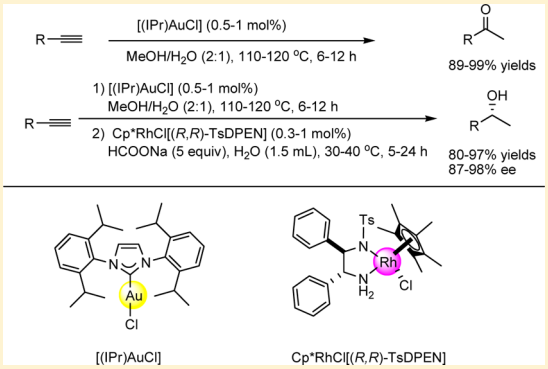
Supporting Information

ABSTRACT: A neutral gold(I) complex [(IPr)AuCl] (IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene) was found to be a highly effective catalyst for the hydration of terminal alkynes, including aromatic alkynes and aliphatic alkynes. The desired methyl ketones were obtained in high yields with complete regioselectivities. Furthermore, a series of optically active secondary alcohols could be obtained in high yield with good to excellent enatioselectivities via one-pot sequential hydration/asymmetric transfer hydrogenation (ATH) from terminal alkynes by the combination of of [(IPr)AuCl] and Cp*RhCl[(*R*,*R*)-TsDPEN] (Cp* = pentamethylcyclopentadienyl, TsDPEN = *N*-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine). Notably, this research exhibited the potential of the direct use of neutral gold(I) complexes instead of cationic ones as catalysts for the activation of multiple bonds for organic synthesis.



INTRODUCTION

The regioselective hydration of terminal alkynes to methyl ketones represents one of the most important C−O bond-forming reactions in organic synthesis because of the wide availability of alkynyl substrates, the fundamental importance of the carbonyl motif, and the complete atom efficiency of the reaction.[1] Traditionally, this transformation is performed in the presence of a large amount of concentrated sulfuric acid (typically ≥ stoichiometric amount) and/or highly toxic mercury reagents.[2] Over the past several decades, various metal complexes such as Pt,[3] Fe,[4] Pd,[5] Ir,[6] Ag,[7] Co,[8] and Au[9] have been developed as catalysts for such transformations. Recently, cationic gold(I) species $[Au(L)]^+$ (L = phosphine or *N*-heterocyclic carbene) have emerged as one of the most promising catalysts for the regioselective hydration of terminal alkynes because of high reactivity and regioselectivity.[9f−s] Generally, cationic gold(I) species were generated via reactions of neutral gold(I) complexes [Au(L)Cl] with silver salts (AgX, X = OTf, BF_4, SbF_6, NTf_2, etc.) (Scheme 1, **A**). However, these procedures have some drawbacks, such as high price and the light sensitivity of silver salts. In addition, silver salts have themselves also catalytic activities for the hydration of akynes.[10] More recently, several silver salt-free protocols for the generation of cationic gold(I) species have been developed, including a protic acid (methanesulfonic acid) activation of $[Au(CH_3)(PPh_3)]$ complex (Scheme 1, **B**),[11] a Brønsted acid activation of [(IPr)Au(OH)] (Scheme 1, **C**),[12] the use of the silylium salt $[(Tol)SiEt_3][B(C_6F_5)_4]$ to activate [(IPr)AuCl] (Scheme 1, **D**),[13] the use of $Cu(OTf)_2$ to acivate $[(PPh_3)AuCl]$ (Scheme 1, **E**),[14] and the use of a Brønsted acid/Lewis acid to $[(PPh_3)Au(Pht)]$ (Scheme 1, **F**).[15] Despite these advances, the direct use of a neutral gold(I) complex [Au(L)Cl] as an efficient catalyst for the regioselective hydration of terminal alkynes to methyl ketons is apparently highly desirable from both synthetic and environmental points of view.

We have reported a series of catalytic transformations with alcohols as electrophiles catalyzed by an iridium complex.[16] We also described the combination of cationic gold(I) and iridium catalysts for the synthesis of α-alkylated ketones[17a] and α-alkylated amides.[17b] As part of our continuing interest in this field of research, we herein demonstrate the direct use of a neutral gold(I) complex as a general and highly effective catalyst for the regioselective hydration of terminal alkynes. Furthermore, one-pot synthesis of optically active secondary alcohols via hydration/asymmetric transfer hydrogenation (ATH) from terminal alkynes by the combination of [(IPr)AuCl] and Cp*RhCl[(*R*,*R*)-Tsdpen] (Cp* = pentamethylcyclopentadienyl, Tsdpen = *N*-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine) was demonstrated.

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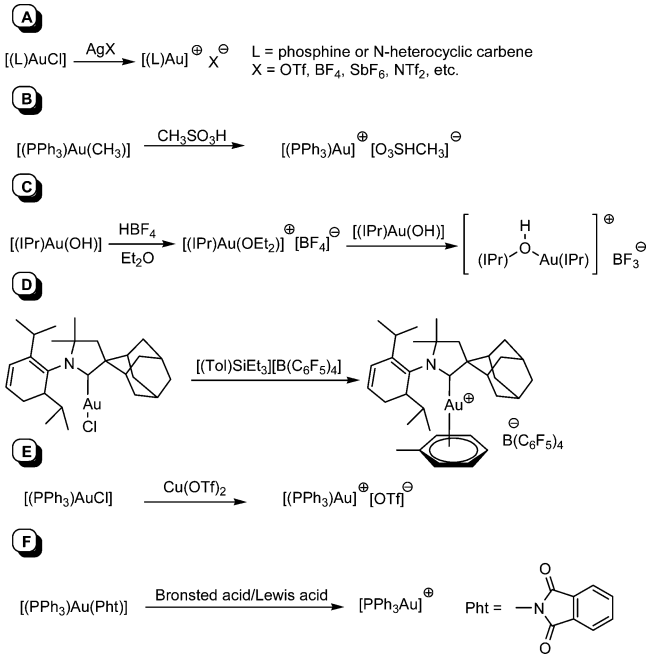
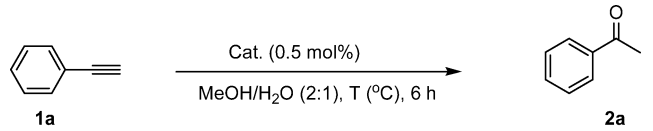
Scheme 1. Advances in the Generation of Cationic Gold(I) Species



RESULTS AND DISCUSSION

Initially, the hydration of phenylacetylene (**1a**) was chosen as a model reaction. The reaction of **1a** was carried out in the presence of [(IPr)AuCl] (IPr = 1,3-bis(diisopropylphenyl)-imidazol-2-ylidene) (0.5 mol %) in MeOH/H_2O (2:1) at 80 °C for 6 h to afford acetophenone (**2a**) in 88% yield with complete regioselectivity. It was observed that the product **2a** could be obtained in 99% yield when the temperature of reaction was enhanced to 110 °C. When [(Ph_3P)AuCl] was used as an alternative catalyst under same reaction conditions, this reaction gave the product **2a** in 51% yield (Scheme 2).

Scheme 2. Hydration of Phenylacetylene (1a)



Having established the optimized conditions, the hydration of a variety of alkynes **1** was conducted, and the results are shown in Table 1. Reactions of phenylacetylenes bearing one or two halogen atoms, such as 3-fluoro (**1b**), 4-fluoro (**1c**), 4-chloro (**1d**), 3-bromo (**1e**), and 4-bromo (**1f**), gave the corresponding products **2b–f** in 93–97% yields (Table 1, entries 1–5). Phenylacetylenes bearing a serious electron-withdrawing group, such as 4-nitro (**1g**), 4-(trifluoromethyl) (**1h**), and 4-cyano (**1i**), could be converted to the desired products **2g–i** in 91%–94% yields, although relatively long reaction time was required (Table 1, entries 6–8). When phenylacetylenes bearing an electron-donating group, such as 3-methyl (**1j**), 4-methyl (**1k**), 4-ethyl (**1l**), 4-propyl (**1m**), 4-methoxy (**1n**), and 4-amino (**1o**), were used as substrates, the corresponding products **2j–o** were obtained in 89–96% yields (Table 1, entries 9–14). Transformations of other arylalkynes, such as 2-ethynylnaphthalene (**1p**) and 2-ethynylthiophene (**1q**), also afforded the desired products **2p** and **2q** in 94% and 93% yields, respectively (Table 1, entries 15 and 16). In the case of bisalkyne, such as 1,3-diethynylbenzene (**1r**) and 1,4-diethynylbenzene (**1s**), the corresponding bisketones **2r** and **2s** were isolated in 90% and 92% yields, respectively (Table 1, entries 17 and 18). Aliphatic alkynes, such as 3,3-dimethyl-1-butyne (**1t**), ethynylcyclopropane (**1u**), 1-hexyne (**1v**), 3-butynol (**1w**), and propargyl acetate (**1x**), were proven to be suitable substrates, and reactions gave the corresponding products **2t–x** in >99% NMR yields (Table 1, entries 19–23). However, no reaction occurred when nonterminal alkyne 1,2-diphenylethyne (**1y**) was used as a substrate under the same reaction conditions (Table 1, entry 24).

It noteworthy that apart from the desired methyl ketones, none of isomer byproducts (aldehydes) were observed in all cases. Clearly, the hydration of terminal alkynes catalyzed by [(IPr)AuCl] exhibited complete regioselectivities.

To demonstrate the practicality and safety of this protocol, the hydration of alkyne on a multigram scale was investigated (Scheme 3). In a sealed 250 mL Schlenk tube, the reaction of **1a** (5.1 g, 50 mmol) was carried out in the presence of [(IPr)AuCl] (0.2 mol %) in MeOH/H_2O (2:1) at 110 °C for 12 h to give the product in 90% yield. This experiment is safe under the present reaction conditions without safety precautions.

A possible reacion mechansm is proposed to account for the hydration of alkynes catalyzed by [(IPr)AuCl] (Scheme 4). The initial step of the reaction involved the formation of cationic species **A** by the dissociation of [(IPr)AuCl] in a polar H_2O/MeOH mixture.[18] The resulting species **A** was coordinated with an alkyne as a two-electron ligand to give species **B**. Furthermore, species **B** underwent nucleophilic attack of water to afford species **C**, which could be converted to species **D** via keto–enol equilibrium. Finally, the reaction of species **D** and H^+ occurred to release methyl ketones as the product accompanied by the regeneration of catalytic species **A**.

As shown in Figure 1, the addition of NaCl (10 mol %) has obvious influence on the reaction rate. Apparently, the presence of a large excess of chloride resulted in a left shift of equilibrium in Scheme 5, and thus, the reaction rate for the hydration of **1a** is reduced. This result strongly supported the proposed reaction mechanism in Scheme 4 where $[(IPr)Au]^+$ is the catalytic active species.

In recent years, one-pot syntheses have received great attention as an alternative to traditional multistep synthetic procedures for the rapid assembly of biologically active and complex chiral molecules from simple substrates because they minimize the use of chemicals, energy, and waste production.[19] Herzon and co-workers demonstrated a one-pot syntheis of racemic secondary alcohols involving cationic gold(I)-catalyzed regioselective hydration of alkynes.[9m] Very recently, Lei, Sun, and co-workers described the synthesis of optical active secondary alcohols via one-pot sequential hydration/asymmetric-transfer hydrogenation (ATH) from terminal alkynes catalyzed by the combination of Salen–Co^{3+} catalyst and chiral ruthenium catalyst.[8b] However, the addition of H_2SO_4 (2 mol %) is necessary for the hydration of terminal alkynes. In addition, the scope of reaction is also limited and Salen–Co^{3+} catalyst is not effective for the hydration of phenylacetylenes bearing a serious electron-withdrawing group. As a result, we

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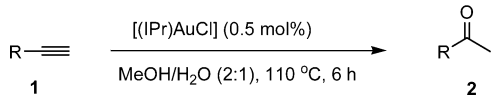
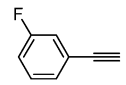
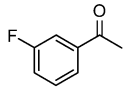
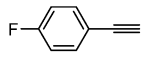
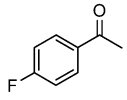
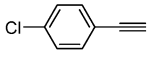
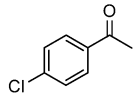
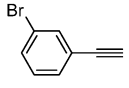
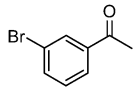
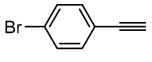
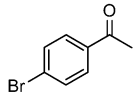
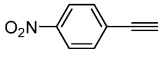
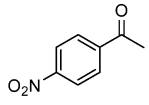
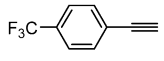
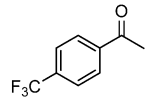
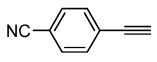
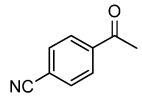
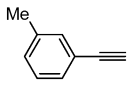
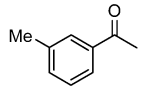
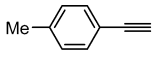
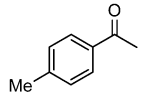
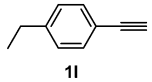
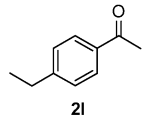
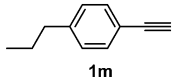
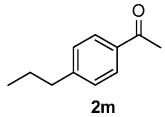
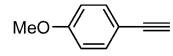
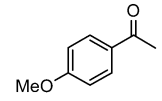
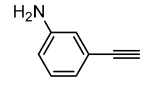
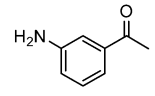
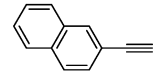
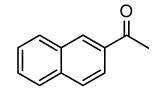
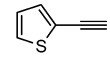
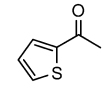
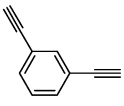
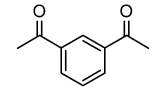
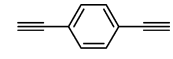
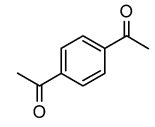
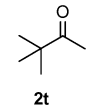
Table 1. Hydration of a Variety of Alkynes 1 to Methyl Ketones Catalyzed by [(IPr)AuCl][a]



Entry	Alkyne	Product	Yield (%)
1	 **1b**	 **2b**	97
2	 **1c**	 **2c**	96
3	 **1d**	 **2d**	94
4	 **1e**	 **2e**	93[b]
5	 **1f**	 **2f**	95
6	 **1g**	 **2g**	94[c]
7	 **1h**	 **2h**	91[c]
8	 **1i**	 **2i**	92[c]
9	 **1j**	 **2j**	96
10	 **1k**	 **2k**	95
11	 **1l**	 **2l**	93
12	 **1m**	 **2m**	89

Entry	Alkyne	Product	Yield (%)
13	 **1n**	 **2n**	92
14	 **1o**	 **2o**	90
15	 **1p**	 **2p**	94[d]
16	 **1q**	 **2q**	93
17	 **1r**	 **2r**	90
18	 **1s**	 **2s**	92
19	 **1t**	 **2t**	>99[e]
20	 **1u**	**2u**	>99[e]
21	**1v**	**2v**	>99[e]
22	**1w**	**2w**	>99[e]
23	**1x**	**2x**	>99[e]
24	**1y**	**2y**	0

[a]Reaction conditions: **1** (1 mmol), [(IPr)AuCl] (0.5 mol %), MeOH (1 mL), H_2O (0.5 mL), 110 °C, 6 h. [b][(IPr)AuCl] (1 mol %). [c][(IPr)AuCl] (1 mol %), 120 °C. [d]12 h. [e]Determined by ^1H NMR spectroscopy.

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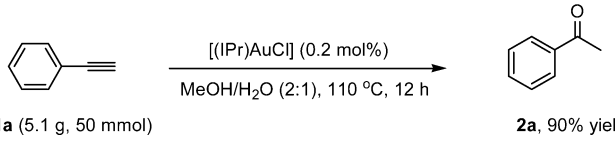
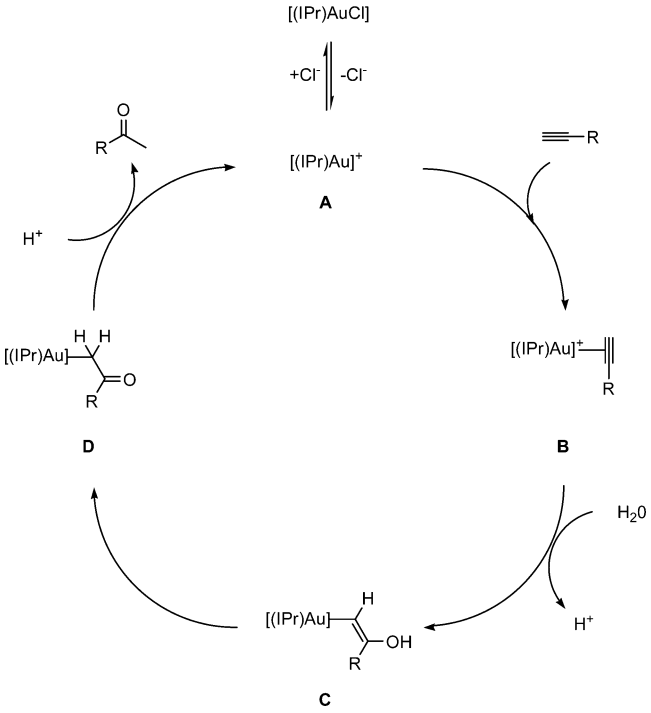
J. Org. Chem. 2015, 80, 3538−3546

Scheme 3. Hydration of Phenylacetylene (1a) on a Multigram Scale



Scheme 4. Proposed Reaction Mechanism



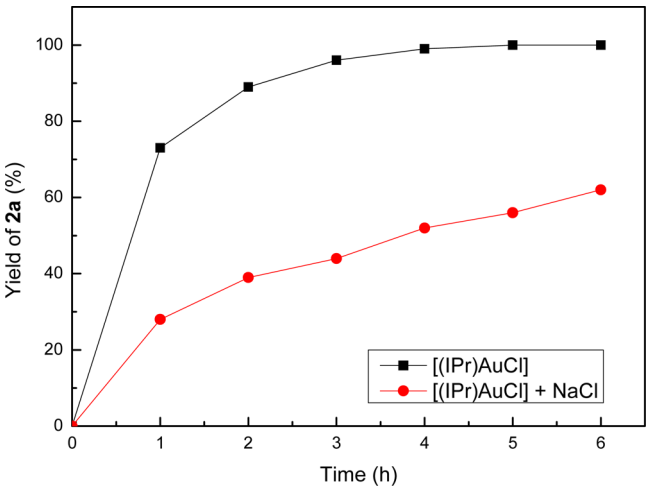
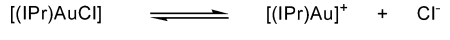


Figure 1. Time-Course of the Hydration of **1a**. Reaction conditions for black course are described in Scheme 2. The red course indicates the addition of NaCl (10 mol %).

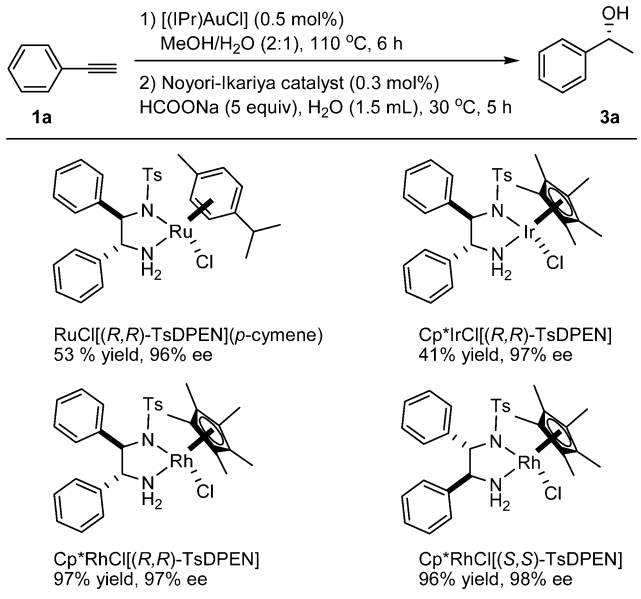
Scheme 5. Dissociation Equilibrium of [(IPr)AuCl]



are interested in exploring the combination of [(IPr)AuCl] and Noyori–Ikariya catalysts[20] for one-pot synthesis of optically active secondary alcohols from terminal alkynes.

As shown in Scheme 6, a series of Noyori–Ikariya catalysts (0.3 mol %), including RuCl[(*R*,*R*)-TsDPEN](*p*-cymene), Cp*IrCl[(*R*,*R*)-TsDPEN], and Cp*RhCl[(*R*,*R*)-TsDPEN], were selected as a catalyst, and HCOONa (5 equiv) was used as a hydrogen source for the asymmetric-transfer hydrogenation (ATH) of acetophenone (**2a**), which resulted from the regioselective hydration of phenylacetylene (**1a**) catalyzed by [(IPr)AuCl]. Among them, Cp*RhCl[(*R*,*R*)-TsDPEN] exhibited the highest reactivity and enatioselectivity, and this cascade reaction afforded (*R*)-1-phenylethanol (**3a**) in 97% yield with 97% ee. When Cp*RhCl[(*S*,*S*)-TsDPEN] was used as an alternative catalyst, the product (*S*)-1-phenylethanol (**4a**) was obtained in 96% yield with 98% ee.

Scheme 6. One-Pot Synthesis of Optically Active 1-Phenylethanol (3a) from Phenylacetylene (1a)



To expend the scope of this one-pot sequential reaction, a range of alkynes were investigated, and these results are outlined in Table 2. Transformations of phenylacetylenes bearing a halide atom (**1b–f**) afforded the corresponding products **3b–f** in 89–95% yields with 90–97% ee (Table 2, entries 1–5). Furthermore, phenylacetylenes bearing a serious electron-withdrawing group, such as nitro (**1g**), trifluoromethyl (**1h**), and cyano (**1i**), could be converted to the desired products **3g–i** in 88–90% yields with 87–95% ee (Table 2, entries 6–8). This catalytic system was also successfully applied to phenylacetylenes bearing an electron-donating group, such as methyl (**1j,k**), ethyl (**1l**), propyl (**1m**), methoxy (**1n**), and amino (**1o**), affording the desired products **3j–o** in 80–93% yield with 93–98% ee, although a longer time (24 h) is required (Table 2, entries 9–14). For 2-ethynylnaphthalene (**1p**) and 2-ethynylthiophene (**1q**), reactions proceeded smoothly to give the corresponding products **3p** and **3q** in 92% yield with 92% ee and in 91% yield with 98% ee, respectively (Table 2, entries 15 and 16).

CONCLUSION

In summary, we have demonstrated that a neutral gold(I) complex [(IPr)AuCl] is a general and highly effective catalyst for the regioselective hydration of terminal alkynes, including aromatic alkynes and aliphatic alkynes. A series of methyl

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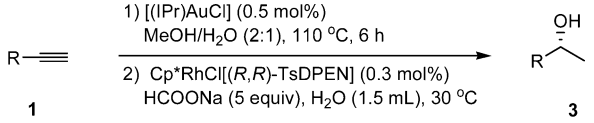
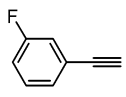
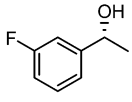
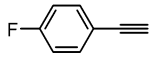
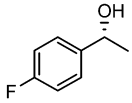
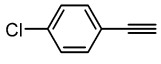
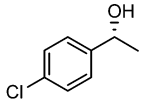
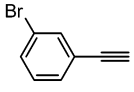
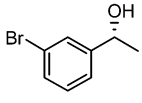
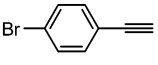
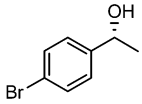
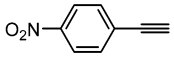
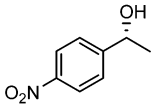
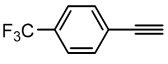
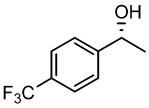
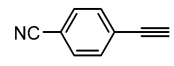
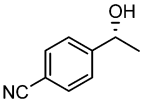
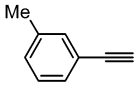
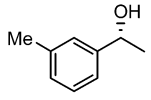
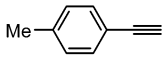
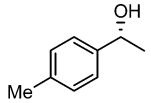
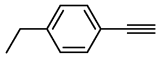
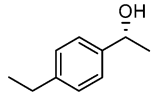
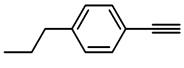
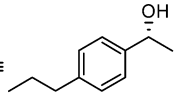
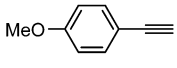
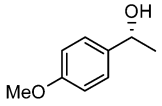
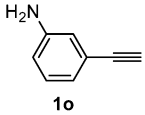
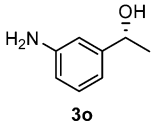
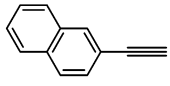
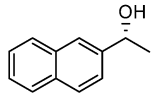
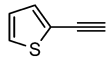
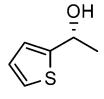
Table 2. One-Pot Synthesis of Optically Active Alcohols from Terminal Alkynes 1 by the Combination of [(IPr)AuCl] and Cp*RhCl[(*R*,*R*)-TsDPEN].[a]



Entry	Alkyne	Product	Time (h)	Yield (%)	e.e (%)[b]
1	 **1b**	 **3b**	5	95	97
2	 **1c**	 **3c**	5	93	95
3	 **1d**	 **3d**	5	94	95
4	 **1e**	 **3e**	5	89	90[c]
5	 **1f**	 **3f**	5	94	96
6	 **1g**	 **3g**	5	90	87[d]
7	 **1h**	 **3h**	5	88	95[e]
8	 **1i**	 **3i**	24	90	92[e]
9	 **1j**	 **3j**	24	93	97
10	 **1k**	 **3k**	24	91	96
11	 **1l**	 **3l**	24	90	97
12	 **1m**	 **3m**	24	87	98
13	 **1n**	 **3n**	24	84	98
14	 **1o**	 **3o**	24	80	93
15	 **1p**	 **3p**	24	92	92[f]
16	 **1q**	 **3q**	24	91	98

[a]Reaction conditions: (1) **1a** (1 mmol), [(IPr)AuCl] (0.5 mol %), MeOH (1 mL), H_2O (0.5 mL), 110 °C, 6 h; (2) [Cp*RhCl[(*R*,*R*)-TsDPEN] (0.3 mol %), HCOONa (5 equiv), H_2O (1.5 mL), 30 °C, 5 h. [b]Determined by chiral GC or HPLC analysis. [c]In the first step, [(IPr)AuCl] (1 mol %). [d]In the first step, [(IPr)AuCl] (1 mol %), 120 °C; in the second step, [Cp*RhCl[(*R*,*R*)-TsDPEN] (1 mol %), 40 °C. [e]In the first step, [(IPr)AuCl] (1 mol %), 120 °C. f In the first step, 12 h.

ketones were obtained in high yields with complete regioselectivities. Furthermore, a range of optically active secondary alcohols could be obtained in high yields with good to excellent enatioselectivities from terminal alkynes via a one-pot sequential hydration/asymmetric-transfer hydrogenation (ATH) by the combination of of [(IPr)AuCl] and Cp*RhCl[(*R*,*R*)-TsDPEN]. Notably, this research exhibited the potential of the direct use of neutral gold(I) complexes instead of cationic ones as catalysts for the activation of of multiple bonds for organic synthesis.

EXPERIMENTAL SECTION

Experimental Details. Melting points were measured on a micromelting apparatus. ^{1}H NMR spectra were recorded at 500 MHz. Chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from tetramethylsilane or ppm relative to the center of the singlet at 7.26 ppm for $CDCl_3$. Coupling constants (J) are reported in hertz (Hz), and the splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; b, broad. $^{13}C\{^1H\}$ NMR spectra were recorded at 125 MHz with broadband ^{1}H decoupling. Chemical shifts are reported in δ, ppm relative to the center of the triplet at 77.0 ppm for $CDCl_3$. ^{19}F NMR spectra were recorded at 470 MHz. Analytical thin-layer chromatography (TLC)

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was carried out using 0.2 mm commercial silica gel plates. Optical rotations were measured on a polarimeter. The enantiomeric excess of the compounds was determined by chiral GC or HPLC using racemic compounds as references.

[(IPr)AuCl],[21,22] RuCl[(*R*,*R*)-TsDPEN](*p*-cymene),[23] Cp*IrCl-[(*R*,*R*)-TsDPEN],[24] Cp*RhCl[(*R*,*R*)-TsDPEN],[25] and Cp*RhCl-[(*S*,*S*)-TsDPEN][25] were synthesized according the previous reports.

General Procedure for Hydration of Alkynes Catalyzed by [(IPr)AuCl] (Table 1). To a 25 mL Schlenk tube were added alkyne **1** (1 mmol), [(IPr)AuCl] (3.1 mg, 0.5 mol %), MeOH (1 mL), and H_2O (0.5 mL). The mixture was heated at 110 °C for 6 h and was then allowed to cool to ambient temperature. The reaction was concetrated in vacuo and purified by flash column chromatography with hexanes/ethyl acetate to afford the corresponding product.

*Acetophenone (**2a**):*[26] light yellow oil; 99% yield (119 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99−7.94 (m, 2H), 7.59−7.54 (m, 1H), 7.46 (t, J = 7.7 Hz, 2H), 2.61 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 198.0, 136.9, 133.0, 128.4, 128.1, 26.4.

*1-(3-Fluorophenyl)ethanone (**2b**):*[26] colorless oil; 97% yield (134 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, J = 7.1 Hz, 1H), 7.63 (d, J = 8.9 Hz, 1H), 7.45 (q, J = 7.1 Hz, 1H), 7.30−7.24 (m, 1H), 2.60 (d, J = 0.9 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 196.5, 162.6 (d, J_{C-F} = 245.7 Hz), 139.0 (d, J_{C-F} = 5.8 Hz), 130.6 (d, J_{C-F} = 7.5 Hz), 123.9, 119.8 (d, J_{C-F} = 22.0 Hz), 114.6 (d, J_{C-F} = 22.6 Hz), 26.35; ^{19}F NMR (470 MHz, CDCl3) δ −111.9.

*1-(4-Fluorophenyl)ethanone (**2c**):*[27] colorless oil; 96% yield (133 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01−7.96 (m, 2H), 7.13 (t, J = 8.5 Hz, 2H), 2.59 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 196.4, 165.7 (d, J_{C-F} = 252.5 Hz), 133.5, 130.9 (d, J_{C-F} = 9.1 Hz), 115.6 (d, J_{C-F} = 22.2 Hz), 26.40; ^{19}F NMR (470 MHz, $CDCl_3$) δ −105.3.

*1-(4-Chlorophenyl)ethanone (**2d**):*[28] colorless oil; 94% yield (145 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (dt, J = 8.5 and 2.2 Hz, 2H), 7.44 (dt, J = 8.6 and 2.1 Hz, 2H), 2.59 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 196.7, 139.4, 135.3, 129.6, 128.8, 26.4.

*1-(3-Bromophenyl)ethanone (**2e**):*[28] colorless oil; 93% yield (186 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.88 (d, J = 8.0 Hz, 1H), 769 (d, J = 8.0 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 2.59 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 196.5, 138.7, 135.8, 131.3, 130.1, 126.8, 122.9, 26.5.

*1-(4-Bromophenyl)ethanone (**2f**):*[27] yellow solid; 95% yield (189 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (dt, J = 8.6 and 2.1 Hz, 2H), 7.60 (dt, J = 8.6 and 2.1 Hz, 2H), 2.58 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 196.8, 135.7, 131.7, 129.7, 128.1, 26.4.

*1-(4-Nitrophenyl)ethanone (**2g**):*[29] yellow solid; 94% yield (156 mg); m.p 82−83 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, J = 9.3 Hz, 2H), 8.11 (d, J = 9.3 Hz, 2H), 2.68 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 196.2, 150.3, 141.3, 129.2, 123.7, 26.9.

*1-(4-(Trifluoromethyl)phenyl)ethanone (**2h**):*[30] yellow oil; 91% yield (171 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, J = 8.3 Hz, 2H), 7.74 (d, J = 8.3 Hz, 2H), 2.65 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 196.7, 139.6, 134.2 (q, J_{C-F} = 32.4 Hz), 128.5, 125.6 (d, J_{C-F} = 3.4 Hz), 123.5 (q, J_{C-F} = 270.6 Hz), 26.41; ^{19}F NMR (470 MHz, $CDCl_3$) δ −63.1.

*4-Acetylbenzonitrile (**2i**):*[31] white solid; 92% yield (133 mg); m.p 60−61 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, J = 8.2 Hz, 2H), 7.78 (d, J = 7.8 Hz, 2H), 2.65 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 196.4, 139.8, 132.4, 128.6, 117.8, 116.3, 26.7.

*1-m-Tolylethanone (**2j**:.*[32] colorless oil; 96% yield (129 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78−7.73 (m, 2H), 7.40−7.33 (m, 2H), 2.59 (s, 3H), 2.41 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 198.3, 138.2, 137.1, 133.7, 128.7, 128.3, 125.5, 26.5, 21.2.

*1-p-Tolylethanone (**2k**):*[32] colorless oil; 95% yield (127 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 2.57 (s, 3H), 2.40 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 197.6, 143.7, 134.5, 129.0, 128.2, 26.2, 21.4.

*1-(4-Ethylphenyl)ethanone (**2l**):*[32] colorless oil; 93% yield (137 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, J = 8.5 Hz, 2H), 7.28 (d, J = 8.5 Hz, 2H), 2.71 (q, J = 7.8 Hz, 2H), 2.58 (s, 3H), 1.25 (t, J = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 197.8, 150.0, 134.9, 128.5, 128.0, 28.8, 26.4, 15.1.

*1-(4-Propylphenyl)ethanone (**2m**):*[31] colorless oil; 89% yield (144 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, J = 7.9 Hz, 2H), 7.26 (d, J = 7.9 Hz, 2H), 2.64 (t, J = 7.9 Hz, 2H), 2.58 (s, 3H), 1.66 (sext, J = 7.6 Hz, 2H), 0.94 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 197.7, 148.4, 134.9, 128.5, 128.3, 37.9, 26.4, 24.1, 13.6.

*1-(4-Methoxyphenyl)ethanone (**2n**):*[26] colorless oil; 92% yield (138 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, J = 9.0 Hz, 2H), 6.93 (d, J = 8.6 Hz, 2H), 3.87 (s, 3H), 2.55 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 196.7, 163.4, 130.5, 130.2, 113.6, 55.4, 26.2.

*1-(3-Aminophenyl)ethanone (**2o**):*[32] yellow solid; 90% yield (122 mg); mp 98−99 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, J = 7.5 Hz, 1H), 7.28−7.21 (m, 2H), 6.89−6.85 (m, 1H), 3.81 (br s, 2H), 2.56 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 198.5, 146.7, 138.1, 129.3, 119.6, 118.6, 113. 9, 26.5.

*1-(Naphthalen-2-yl)ethanone (**2p**):*[27] white solid; 95% yield (161 mg); m.p 58−59 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.04 (d, J = 8.8 Hz, 1H), 7.97 (d, J = 7.2 Hz, 1H), 7.89 (t, J = 8.0 Hz, 1H), 7.63−7.53 (m, 2H), 2.73 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 197.8, 135.3, 134.2, 132.3, 130.0, 129.3, 128.2, 128.2, 127.5, 126.5, 123.6, 26.4.

*1-(Thiophene-2-yl)ethanone (**2q**):*[31] colorless oil; 93% yield (117 mg); ^{1}HNMR (500 MHz, $CDCl_3$) δ 7.71−7.69 (m, 1H), 7.64 (d, J = 4.8 Hz, 1H), 7.15−7.11 (m, 1H), 2.57 (d, J = 2.1 Hz), $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 190.4, 144.1, 133.5, 132.3, 127.8, 26.5.

*1,3-Diacetylbenzene (**2r**):*[33] white solid; 90% yield (145 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.16 (dd, J = 1.3 and 7.8 Hz, 2H), 7.59 (t, J = 7.7 Hz, 1H), 2.67 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 197.2, 137.3, 132.4, 128.9, 127.9, 26.6.

*1,4-Diacetylbenzene (**2s**):*[31] white solid; 92% yield (150 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (s, 4H), 2.65 (s, 6H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 197.4, 140.0, 128.4, 26.8.

*3,3-Dimethylbutan-2-one (**2t**):*[26] colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.16−2.13 (m, 3H), 1.16−1.13 (m, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 214.0, 44.1, 26.2, 24.5.

*1-Cyclopropylethanone (**2u**):*[34] colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.25−2.23 (m, 3H), 1.98−1.91 (m, 1H), 1.05−1.00 (m, 2H), 0.92−0.86 (m, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 208.6, 29.8, 20.9, 10.4.

*Hexan-2-one (**2v**):*[35] colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.43 (t, J = 7.7 Hz, 2H), 2.14 (s, 3H), 1.60−1.51 (m, 2H), 1.37−1.27 (m, 2H), 0.90 (td, J = 7.4 and 1.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 209.3, 43.4, 29.7, 25.9, 22.2, 13.7.

*4-Hydroxybutan-2-one (**2w**):*[36] colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.84 (q, J = 4.9 Hz, 2H), 2.79 (br s, 1H), 2.73−2.67 (m, 2H), 2.21−2.18 (m, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 209.5, 57.6, 45.3, 30.4.

*2-Oxopropyl acetate (**2x**):*[37] pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.66 (s, 2H), 2.17 (s, 3H), 2.16 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 201.5, 170.1, 68.2, 25.9, 20.3.

Procedure for the Hydration of 1a on a Multigram Scale (Scheme 3). To a 250 mL Schlenk tube were added alkyne **1a** (5.1 g, 50 mmol), [(IPr)AuCl] (62 mg, 0.2 mol %), MeOH (20 mL), and H_2O (10 mL). The mixture was heated at 110 °C for 12 h and was then allowed to cool to ambient temperature. The reaction mixture was concetrated in vacuo and purified by flash column chromatography with hexanes/ethyl acetate to afford the corresponding product **2a** in 90% yield (5.371 g).

Cascade Synthesis of Optically Active Secondary Alcohols Catalyzed by the Combination of [(IPr)AuCl] and Cp*RhCl-[(*R*,*R*)-TsDPEN] (Table 2). To a 25 mL Schlenk tube were added alkyne **1** (1 mmol), [(IPr)AuCl] (3.1 mg, 0.5 mol %), MeOH (1 mL), and H_2O (0.5 mL). The mixture was heated at 110 °C for 6 h and was then allowed to cool to ambient temperature. Cp*RhCl[(*R*,*R*)-TsDPEN] (1.9 mg, 0.3 mol %), HCOONa (340 mg, 5 mmol, 5 equiv), and water (1.5 mL) were added, and the mixture was further stirred at 30 °C for another 5 h. The reaction mixture was cooled to ambient temperature, concentrated in vacuo, and purified by flash column chromatography with hexanes/ethyl acetate to afford the corresponding product.

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J. Org. Chem. 2015, 80, 3538−3546

*(R)-1-Phenylethanol (**3a**):*[38] yellow oil; 97% yield (118 mg); $[\alpha]^{26}_{D}$ +72.4 (*c* 1, $CHCl_3$, 97% ee) (lit.[38] $[\alpha]^{23}_{D}$ +55.9 (*c* 0.78, $CHCl_3$, 94.9% ee); ^{1}HNMR (500 MHz, $CDCl_3$) δ 7.39−7.32 (m, 4H), 7.29−7.24 (m, 1H), 4.88 (q, *J* = 5.0 Hz, 1H), 1.92 (br s, 1H), 1.49 (dd, *J* = 1.20 and 6.45 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 145.8, 128.3, 127.2, 125.3, 70.1, 25.0.

GC analysis: CP-Chirasil-DEX CB column (25 m × 0.32 mm); carrier gas: N_2; flow rate 2 mL/min; injector temp = 230 °C; detector temp (FID) = 280 °C; column temp: 1 min at 70 °C, heating at 20 °C/min to 130 °C, keeping at 130 °C for 5 min; t_R = 6.60 min, t_S = 6.86 min

*(R)-1-(3-Fluorophenyl)ethanol (**3b**):*[39] light yellow oil; 95% yield (133 mg); $[\alpha]^{26}_{D}$ +49.7 (*c* 1, $CHCl_3$, 97% ee) (lit.[39] $[\alpha]^{20}_{D}$ +42.4 (*c* 1, $CHCl_3$, 96% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33−7.28 (m, 1H), 7.15−7.08 (m, 2H), 6.95 (m, 1H), 4.94−4.87 (m, 1H), 1.85 (d, *J* = 3.4 Hz, 1H), 1.49 (d, *J* = 6.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 162.9 (d, J_{C-F} = 244.3 Hz), 148.5 (d, J_{C-F} = 6.7 Hz), 129.9 (d, J_{C-F} = 7.7 Hz), 120.9 (d, J_{C-F} = 2.8 Hz), 114.2 (d, J_{C-F} = 20.8 Hz), 112.3 (d, J_{C-F} = 21.8 Hz), 69.7, 25.2; ^{19}F NMR (470 MHz, $CDCl_3$) δ −112.9.

GC analysis: CP-Chirasil-DEX CB column (25 m × 0.32 mm); carrier gas: N_2; flow rate 2 mL/min; injector temp = 250 °C; detector temp (FID) = 300 °C; column temp: 1 min at 70 °C, heating at 20 °C/min to 140 °C, keeping at 140 °C for 9 min; t_R = 6.26 min, t_S = 6.49 min.

*(R)-1-(4-Fluorophenyl)ethanol (**3c**):*[38] light yellow oil; 93% yield (130 mg); $[\alpha]^{26}_{D}$ +66.4 (*c* 1, $CHCl_3$, 95% ee) (lit.[38] $[\alpha]^{23}_{D}$ +43.1 (*c* 0.73, $CHCl_3$, 92.3% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36−7.32 (m, 2H), 7.02 (t, *J* = 8.7 Hz, 2H), 4.88 (q, *J* = 6.3 Hz, 1H), 1.89 (br s, 1H), 1.47 (d, *J* = 6.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 162.0 (d, J_{C-F} = 244.0 Hz), 141.8 (d, J_{C-F} = 2.6 Hz), 127.0 (d, J_{C-F} = 7.5 Hz), 115.1 (d, J_{C-F} = 20.9 Hz), 69.6, 25.2; ^{19}F NMR (470 MHz, $CDCl_3$) δ −115.3.

GC analysis: CP-Chirasil-DEX CB column (25 m × 0.32 mm); carrier gas: N_2; flow rate 2 mL/min; injector temp = 230 °C; detector temp (FID) = 280 °C; column temp: 1 min at 70 °C, heating at 20 °C/min to 130 °C, keeping at 130 °C for 5 min; t_R = 7.18 min, t_S = 7.61 min.

*(R)-1-(4-Chlorophenyl)ethanol (**3d**):*[40] light yellow oil; 94% yield (146 mg); $[\alpha]^{26}_{D}$ +56.4 (*c* 1, $CHCl_3$, 95% ee) (lit.[40] $[\alpha]^{21}_{D}$ +41.3 (*c* 1.1, Et_2O, 91% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (s, 4H), 4.88 (q, *J* = 6.4 Hz, 1H), 1.83 (br s, 1H), 1.47 (d, *J* = 6.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 144.2, 132.9, 128.5, 126.7, 69.6, 25.2.

GC analysis: CP-Chirasil-DEX CB column (25 m × 0.32 mm); carrier gas: N_2; flow rate 2 mL/min; injector temp = 250 °C; detector temp (FID) = 300 °C; column temp: 1 min at 70 °C, heating at 20 °C/min to 140 °C, keeping at 140 °C for 9 min; t_R = 10.32 min, t_S = 11.10 min.

*(R)-1-(3-Bromophenyl)ethanol (**3e**):*[41] yellow oil; 89% yield (178 mg); $[\alpha]^{26}_{D}$ +46.75 (*c* 1, $CHCl_3$, 89% ee) (lit.[41] $[\alpha]_{D}$ +45.0 (*c* 1, $CHCl_3$, 96% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 7.8 Hz, 1H), 7.20 (t, *J* = 7.9 Hz, 1H), 4.84 (q, *J* = 6.3 Hz, 1H), 2.11 (br s, 1H), 1.47 (d, *J* = 6.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 148.1, 130.4, 130.1, 128.5, 124.0, 122.6, 69.7, 25.2.

HPLC analysis: Chiralpak IA column, UV detection at 254 nm, flow 1.0 mL/min, *n*-hexane/*i*-PrOH = 96:4, t_R = 7.84 min, t_S = 8.31 min.

*(R)-1-(4-Bromophenyl)ethanol (**3f**):*[42] colorless oil; 94% yield (188 mg); $[\alpha]^{26}_{D}$ +49.2 (*c* 1, $CHCl_3$, 96% ee) (lit.[42] $[\alpha]^{20}_{D}$ +36.0 (*c* 1.7, CH_2Cl_2, 95% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.6 Hz, 2H), 4.86 (q, *J* = 7.2 Hz, 1H), 1.85 (s, 1H), 1.47 (d, *J* = 6.9 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 144.8, 131.6, 127.1, 121.2, 69.8, 25.2.

GC analysis: CP-Chirasil-DEX CB column (25 m × 0.32 mm); carrier gas: N_2; 15 psi; injector temp = 250 °C; detector temp (FID) = 300 °C; column temp: 1 min at 70 °C, heating at 20 °C/min to 170 °C, keeping at 170 °C for 6 min; t_R = 7.06 min, t_S = 7.20 min.

*(R)-1-(4-Nitrophenyl)ethanol (**3g**):*[38] yellow oil; 90% yield (151 mg); $[\alpha]^{26}_{D}$ +26.3 (*c* 1, $CHCl_3$, 87% ee), (lit.[38] $[\alpha]^{23}_{D}$ +35.1 (*c* 1.46, $CHCl_3$, 88.4% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.5 Hz, 2H), 7.54 (d, *J* = 8.6 Hz, 2H), 5.06−4.99 (m, 1H), 2.20 (br s, 1H), 1.52 (d, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 153.1, 147.1, 126.1, 123.7, 69.5, 25.5.

GC analysis: CP-Chirasil-DEX CB column (25 m × 0.32 mm); carrier gas: N_2; 30 psi; injector temp = 250 °C; detector temp (FID) = 300 °C; column temp = 170 °C; t_R = 3.56 min, t_S = 3.88 min.

*(R)-1-(4-(Trifluoromethyl)phenyl)ethanol (**3h**):*[43] yellow oil; 88% yield (167 mg); $[\alpha]^{26}_{D}$ +43.5 (*c* 1, $CHCl_3$, 95% ee) (lit.[43] $[\alpha]^{25}_{D}$ +35.0 (*c* 0.3, $CHCl_3$, 91% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 4.96 (q, *J* = 9.8 Hz, 1H), 2.05 (br s, 1H), 1.50 (d, *J* = 6.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 149.7, 129.5 (q, J_{C-F} = 32.4 Hz), 124.1 (q, J_{C-F} = 270.4 Hz), 125.6, 125.3 (d, J_{C-F} = 3.5 Hz), 69.6, 25.1; ^{19}F NMR (470 MHz, $CDCl_3$) δ −62.4.

GC analysis: CP-Chirasil-DEX CB column (25 m × 0.32 mm); carrier gas: N_2; 7 psi; injector temp = 250 °C; detector temp (FID) = 300 °C; column temp: 1 min at 70 °C, heating at 20 °C/min to 170 °C, keeping at 170 °C for 6 min; t_R = 6.75 min, t_S = 6.91 min.

*(R)-4-(1-Hydroxyethyl)benzonitrile (**3i**):*[44] yellow oil; 90% yield (133 mg); $[\alpha]^{26}_{D}$ +52.78 (*c* 1, $CHCl_3$, 92% ee) (lit.[44] $[\alpha]^{20}_{D}$ +77.1 (*c* 0.7, $CHCl_3$, 92% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66−7.60 (m, 2H), 7.49 (d, *J* = 7.8 Hz, 2H), 5.00−4.94 (m, 1H), 2.18 (br s, 1H), 1.49 (d, *J* = 6.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 151.1, 132.3, 126.0, 118.8, 111.0, 69.6.

GC analysis: CP-Chirasil-DEX CB column (25 m × 0.32 mm); carrier gas: N_2; 30 psi; injector temp = 250 °C; detector temp (FID) = 300 °C; column temp = 170 °C; t_R = 2.14 min, t_S = 2.33 min.

*(R)-1-m-Tolylethanol (**3j**):*[39] yellow oil; 93% yield (126 mg); $[\alpha]^{26}_{D}$ +56.0 (*c* 1, $CHCl_3$, 97% ee) (lit.[39] $[\alpha]^{20}_{D}$ +64.2 (*c* 1, $CHCl_3$, 97% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26−7.22 (m, 1H), 7.19 (s, 1H), 7.18−7.14 (d, *J* = 7.9 Hz, 1H), 7.10−7.07 (d, *J* = 7.4 Hz, 1H), 4.85 (q, *J* = 6.4 Hz, 1H), 2.36 (s, 3H), 1.86 (br s, 1H), 1.48 (d, *J* = 6.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 145.8, 138.1, 128.4, 128.2, 126.1, 122.4, 70.4, 25.1, 21.4.

GC analysis: CP-Chirasil-DEX CB column (25 m × 0.32 mm); carrier gas: N_2; flow rate 2 mL/min; injector temp = 250 °C; detector temp (FID) = 300 °C; column temp: 1 min at 70 °C, heating at 20 °C/min to 140 °C, keeping at 140 °C for 9 min; t_R = 6.88 min, t_S = 7.06 min.

*(R)-1-p-Tolylethanol (**3k**):*[38] yellow oil; 91% yield (124 mg); $[\alpha]^{26}_{D}$ +56.0 (*c* 1, $CHCl_3$, 96% ee) (lit.[38] $[\alpha]^{23}_{D}$ +52.2 (*c* 0.96, $CHCl_3$, 93.7% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28−7.24 (d, *J* = 7.8 Hz, 2H), 7.18−7.14 (d, *J* = 8.2 Hz, 2H), 4.86 (m, 1H), 2.34 (s, 3H), 1.83 (br s, 1H), 1.47 (d, *J* = 6.5, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 142.9, 137.1, 129.1, 125.3, 70.2, 25.1, 21.1;

GC analysis: CP-Chirasil-DEX CB column (25 m × 0.32 mm); carrier gas: N_2; flow rate 2 mL/min; injector temp = 250 °C; detector temp (FID) = 300 °C; column temp: 1 min at 70 °C, heating at 20 °C/min to 140 °C, keeping at 140 °C for 9 min; t_R = 6.64 min, t_S = 6.90 min.

*(R)-1-(4-Ethylphenyl)ethanol (**3l**):*[45] yellow oil; 90% yield (135 mg); $[\alpha]^{26}_{D}$ +47.5 (*c* 1, $CHCl_3$, 97% ee) (lit.[45] $[\alpha]^{23}_{D}$ +32.6 (c 0.62, $CHCl_3$, 97% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.7 Hz, 2H), 7.18 (d, *J* = 7.7 Hz, 2H), 4.86 (q, *J* = 7.2 Hz, 1H), 2.64 (q, *J* = 7.7 Hz, 2H), 1.85 (d, *J* = 19.1 Hz, 1H), 1.48 (d, *J* = 7.0 Hz, 3H), 1.23 (t, *J* = 7.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 143.5, 143.1, 128.0, 125.4, 70.3, 28.5, 25.0, 15.6;

GC analysis: CP-Chirasil-DEX CB column (25 m × 0.32 mm); carrier gas: N_2; flow rate 2 mL/min; injector temp = 250 °C; detector temp (FID) = 300 °C; column temp: 1 min at 70 °C, heating at 20 °C/min to 140 °C, keeping at 140 °C for 9 min; t_R = 8.16 min, t_S = 8.47 min.

*(R)-1-(4-Propylphenyl)ethanol (**3m**):*[46] Yellow oil; 87% yield (143 mg); $[\alpha]^{26}_{D}$ +47.9 (*c* 1, $CHCl_3$, 98% ee) (lit.[46] $[\alpha]^{20}_{D}$ +33.2 (c 2.2, MeOH, 93% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.6 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 4.87 (q, *J* = 6.8 Hz, 1H), 2.57 (t, *J* = 7.7 Hz, 2H), 1.79 (br s, 1H), 1.68−1.58 (m, 2H), 1.49 (d, *J* = 6.1 Hz, 3H), 0.94 (t, *J* = 7.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 143.0, 142.0, 128.6, 125.3, 70.3, 37.7, 25.0, 24.6, 13.8.

GC analysis: CP-Chirasil-DEX CB column (25 m × 0.32 mm); carrier gas: N_2; flow rate 2 mL/min; injector temp = 250 °C; detector

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J. Org. Chem. 2015, 80, 3538−3546

temp (FID) = 300 °C; column temp: 1 min at 70 °C, heating at 20 °C/min to 140 °C, keeping at 140 °C for 9 min; t_R = 10.40 min, t_S = 10.90 min.

*(R)-1-(4-Methoxyphenyl)ethanol (**3n**):*[40] yellow oil; 84% yield (127 mg); $[\alpha]^{26}_D$ +51.8 (*c* 1, $CHCl_3$, 98% ee) (lit.[40] $[\alpha]^{25}_D$ +53.5 (*c* 1.7, $CHCl_3$, 94% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 4.85 (q, *J* = 6.5 Hz, 1H), 3.82 (s, 3H), 2.15 (br s, 1H), 1.49 (d, *J* = 6.3 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.9, 138.0, 126.6, 113.8, 69.8, 55.2, 24.9;

GC analysis: CP-Chirasil-DEX CB column (25 m × 0.32 mm); carrier gas: N_2; flow rate 2 mL/min; injector temp = 250 °C; detector temp (FID) = 300 °C; column temp: 1 min at 70 °C, heating at 20 °C/min to 140 °C, keeping at 140 °C for 9 min; t_R = 10.20 min, t_S = 10.60 min.

*(R)-1-(3-Aminophenyl)ethanol (**3o**):*[47] brown oil; 80% yield (110 mg); mp 64−65 °C; $[\alpha]^{26}_D$ +45.7 (*c* 1.2, $CHCl_3$, 93% ee) (lit.[47] $[\alpha]^{25}_D$ +45.6 (*c* 1.2, $CHCl_3$, 95% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (t, *J* = 7.8 Hz, 1H), 6.72 (d, *J* = 7.3 Hz, 1H), 6.66 (s, 1H), 6.56 (d, *J* = 8.3 Hz, 1H), 4.75 (q, *J* = 9.8 Hz, 1H), 3.67 (s, 2H), 2.43 (br s, 1H), 1.43 (d, *J* = 6.8 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 147.2, 129.4, 115.6, 114.2, 112.0, 70.4, 25.0.

HPLC analysis: Chiralpak IA column, UV detection at 254 nm, flow 1.0 mL/min, hexane/EtOH = 90:10, t_R = 15.35 min, t_S = 16.72 min.

*(R)-1-(Naphthalen-2-yl)ethanol (**3p**):*[38] white solid; 92% yield (159 mg); mp 69−70 °C; $[\alpha]^{26}_D$ +53.7 (*c* 1, $CHCl_3$, 92% ee) (lit.[38] $[\alpha]^{23}_D$ +46.7 (c 1.04, $CHCl_3$, 92% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86−7.80 (m, 4H), 7.52−7.44 (m, 3H), 5.06 (q, *J* = 6.9 Hz, 1H), 1.95 (br s, 1H), 1.58 (d, *J* = 5.8 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 143.2, 133.3, 132.8, 128.2, 127.9, 127.6, 126.1, 125.7, 123.8, 123.7, 70.4, 25.1.

HPLC analysis: Chiralpak IA column, UV detection at 254 nm, flow 1.0 mL/min, *n*-hexane/EtOH = 98:2, t_R = 14.63 min, t_S = 15.61 min.

*(R)-1-(Thiophene-2-yl)ethanol (**3q**):*[38] yellow oil; 91% yield (116 mg); $[\alpha]^{26}_D$ +39.9 (*c* 1, $CHCl_3$, 98% ee) (lit.[38] $[\alpha]^{23}_D$ +20.4 (*c* 0.56, $CHCl_3$, 94.7% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 1.6 and 1.5 Hz, 1H), 6.99−6.95 (m, 2H), 5.12 (q, *J* = 6.4 Hz, 1H), 2.10 (br s, 1H), 1.60 (d, *J* = 6.4 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 149.8, 126.4, 124.1, 123.0, 65.8, 25.0.

GC analysis: CP-Chirasil-DEX CB column (25 m × 0.32 mm); carrier gas: N_2; 7 psi; injector temp = 250 °C; detector temp (FID) = 300 °C; column temp: 1 min at 70 °C, heating at 20 °C/min to 170 °C, keeping at 170 °C for 6 min; t_R = 6.33 min, t_S = 6.41 min.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra of products; chiral GC and HPLC chromatograms of chiral products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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