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Article

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Enantioselective Alkynylation of Aromatic Aldehydes Catalyzed by a Sterically Highly Demanding Chiral-at-Rhodium Lewis Acid

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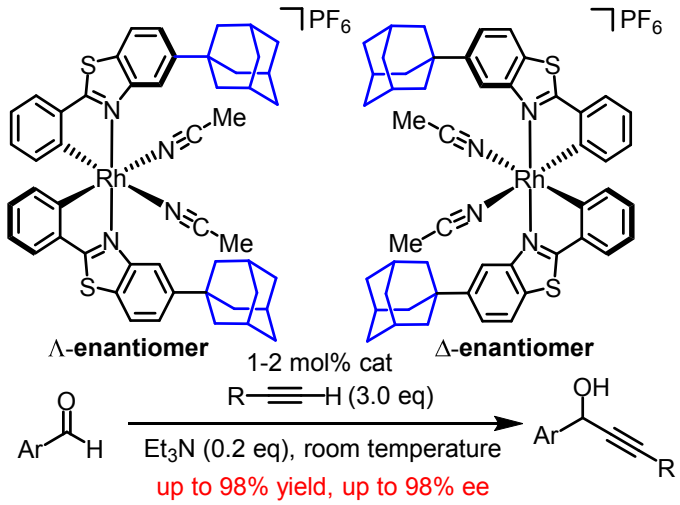
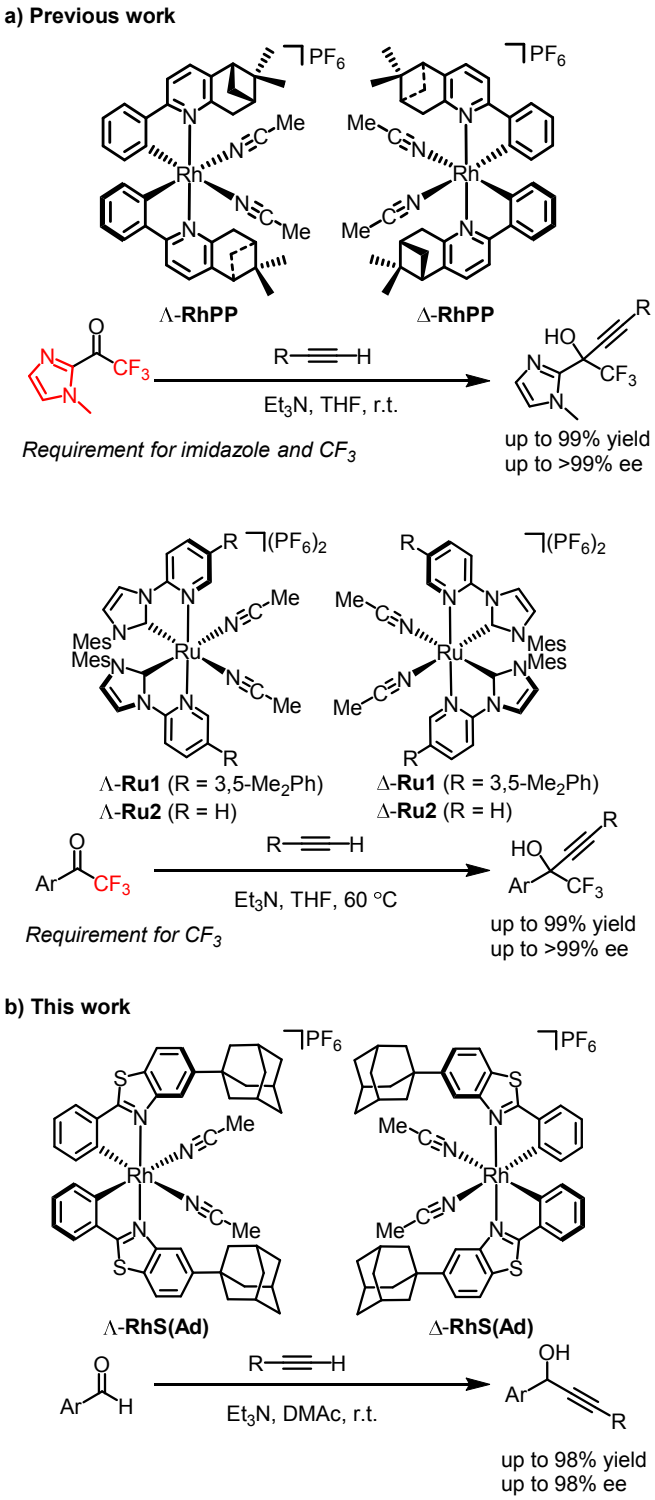
Abstract: The enantioselective catalytic alkynylation of aromatic aldehydes is reported using a sterically highly hindered bis-cyclometalated rhodium-based Lewis acid catalyst featuring the octahedral metal as the only stereogenic center. Yields of 58-98% with 79-98% enantiomeric excess were achieved using 1-2 mol% of catalyst. This work complements previous work from our laboratory on the enantioselective alkynylation of 2-trifluoroacetyl imidazoles (*Chem. Eur. J.* **2016**, *22*, 11977-11981) and trifluoromethyl ketones (*J. Am. Chem. Soc.* **2017**, *139*, 4322-4325) using catalysts with octahedral metal-centered chirality.

TOC graphic:



Introduction

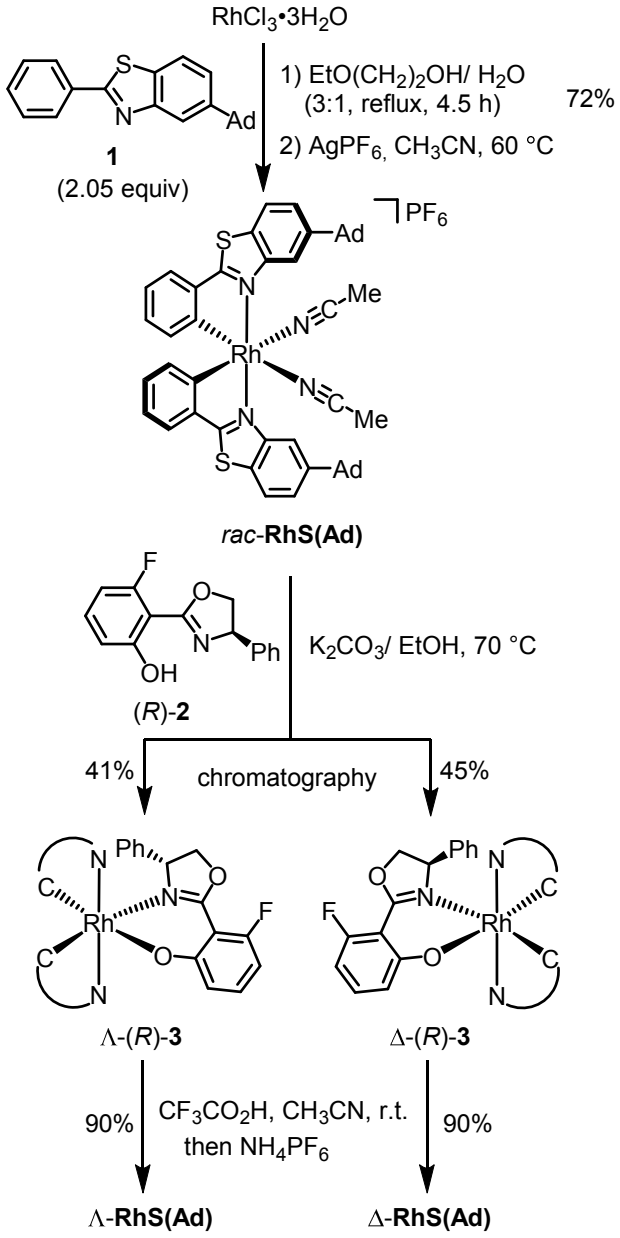
Enantioenriched propargylic alcohols are versatile chiral building blocks in organic synthesis since both hydroxyl group and triple bond can be subjected to further reactions, including etherifications, nucleophilic propargylic substitutions, a variety of 1,2-additions, coupling reactions, cyclizations, isomerizations, and reduction of the alkyne to the corresponding alkene or alkane, among others.[1] The enantioselective addition of alkyne nucleophiles to aldehydes or ketones constitutes one of the most direct methods for the preparation of enantioenriched propargylic alcohols.[2] We recently contributed to this area of research by applying chiral-at-metal[3] Lewis acids to the catalytic enantioselective alkynylation of carbonyl compounds.[4] The chiral diastereomeric rhodium complexes Λ-**RhPP** and Δ-**RhPP** containing two metallocyclic 2-phenyl-5,6-(*S*,*S*)-pinenopyridine ligands showed excellent results for the enantioselective alkynylation of 2-trifluoroacetyl imidazoles,[5] whereas the chiral-at-ruthenium complexes Λ/Δ-**Ru1**,**2** containing two *N*-(2-pyridyl)-substituted *N*-heterocyclic carbene chelate ligands catalyzed the alkynylation of trifluoromethyl ketones with very high enantioselectivity at catalysts loadings down to 0.2 mol% (Scheme 1a).[6] However, both catalysts featured limitations as they appear to be restricted to trifluoromethyl ketone substrates. Here, we report that a sterically highly hindered chiral-at-rhodium Lewis acid Λ/Δ-**RhS(Ad)** catalyzes the alkynylation of aromatic aldehydes with high enantioselectivity at room temperature only requiring catalytic amounts of a base such as triethylamine (Scheme 1b).



Scheme 1. Enantioselective alkynylations of ketones and aldehydes with chiral-at-metal Lewis acid catalysts.

Results and Discussion

Catalyst synthesis. The synthesis of enantiopure Λ- and Δ-**RhS(Ad)** is shown in Scheme 2 and follows the synthesis of related bis-cyclometalated chiral-at-rhodium catalysts developed in our laboratory.[7,8] Accordingly, rhodium trichloride hydrate was first converted into the corresponding racemic bis-cyclometalated catalyst in a yield of 72% by reacting with 2.05 equivalents 5-(1-adamantyl)-2-phenylbenzothiazole (**1**) at reflux for 4.5 hours, followed by treatment with 2.5 equivalents of $AgPF_6$ in MeCN at 60 °C for 16 hours. Afterwards, the racemic catalyst was reacted with the chiral salicyloxazoline auxiliary (*R*)-**2** to afford a diastereomeric mixture of the complexes Λ-(*R*)-**3** and Δ-(*R*)-**3**, which could be resolved by silica gel chromatography. Finally, starting from the individual pure diastereoisomers Λ-(*R*)-**3** (41% yield) or Δ-(*R*)-**3** (45% yield), the coordinated auxiliary ligands were removed by treatment with trifluoroacetic acid in MeCN to generate the individual enantiomers Λ-**RhS(Ad)** (90% yield) and Δ-**RhS(Ad)** (90% yield). The structure of Λ-**RhS(Ad)** including the absolute configuration was confirmed by X-ray crystallography (Figure 1).



Scheme 2. Auxiliary mediated synthesis of Λ- and Δ-**RhS(Ad)**.

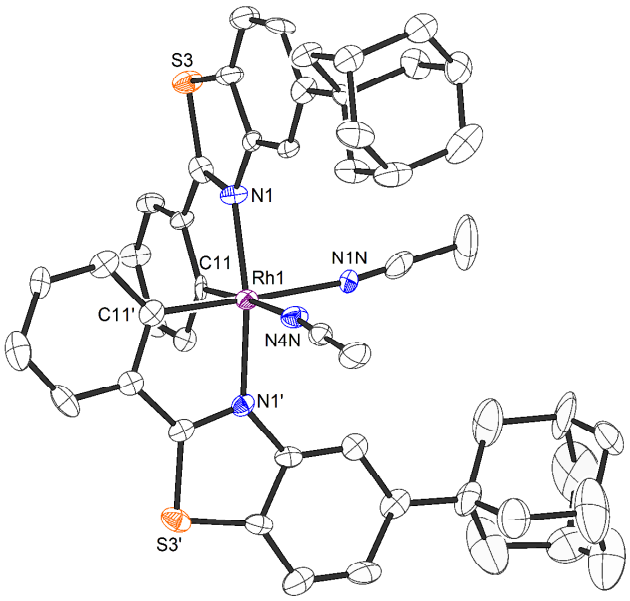
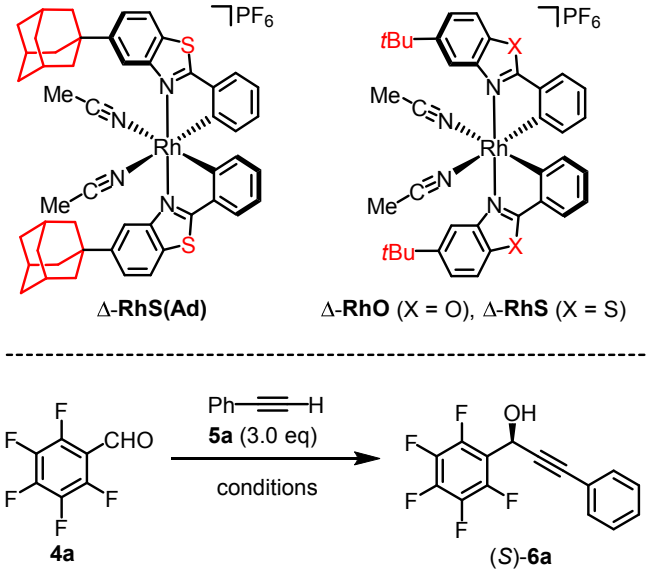


Figure 1. Crystal structure of the catalyst Λ-**RhS(Ad)** (CCDC number 1552828). ORTEP drawing with 50% thermal ellipsoids.

Initial Catalysis Experiments. We chose the alkynylation of the electron-deficient pentafluorobenzaldehyde (**4a**) with phenylacetylene (**5a**) to provide the propargylic alcohol **6a** as our model reaction. Our previously reported catalyst Δ-**RhPP** at a catalyst loading of 4.0 mol% using an excess of 3 equivalents of phenylacetylene and Et_3N (0.2 equivalents) as the base afforded the propargylic alcohol (*S*)-**6a** at room temperature after 16 hours with a yield of 51% but disappointing 25% ee (Table 1, entry 1). The previously reported chiral-at-ruthenium catalyst Δ-**Ru1** provided under the same conditions (*S*)-**6a** with 88% yield and 48% ee (entry 2). Further improvements were observed when the chiral-at-rhodium catalysts Δ-**RhO** and Δ-**RhS** were examined, providing (*S*)-**6a** with yields of 92% and 71% ee respectively 89% ee (entries 3 and 4).

We next envisioned to improve the effectivity of the asymmetric induction by increasing the steric hindrance of the chiral Lewis acid. Gratifyingly, when we replaced the *tert*-butyl groups of the catalyst Δ-**RhS** with adamantyl substituents, providing the catalyst Δ-**RhS(Ad)**, the enantioselectivity could be raised significantly to 92% ee (entry 5). Next, after having identified a suitable catalyst, we focused on optimizing the reaction conditions. We found that the catalyst loading could be reduced to 2.0 mol% (entry 6) and even 1.0 mol% (entry 7) without affecting enantioselectivity. Screening different solvents (entries 8-11 and Supporting Information) resulted in the identification of *N*,*N*-dimethylacetamide (DMAc) as the solvent of choice, reaching 95% yield and 96% ee after 24 hours at room temperature by just using 1.0 mol% of the catalyst Δ-**RhS(Ad)** (entry 11). Interesting for practical reasons, the catalytic reaction can be performed under air without affecting the enantioselectivity although the yield decreased somewhat (entry 12), and the reaction is not sensitive to the addition of water (10 equivalents based on pentafluorobenzaldehyde) (entry 13). Control experiments confirm that both the base[9] and the catalyst are essential for this reaction (entries 14 and 15).

Table 1. Initial experiments and optimizations.



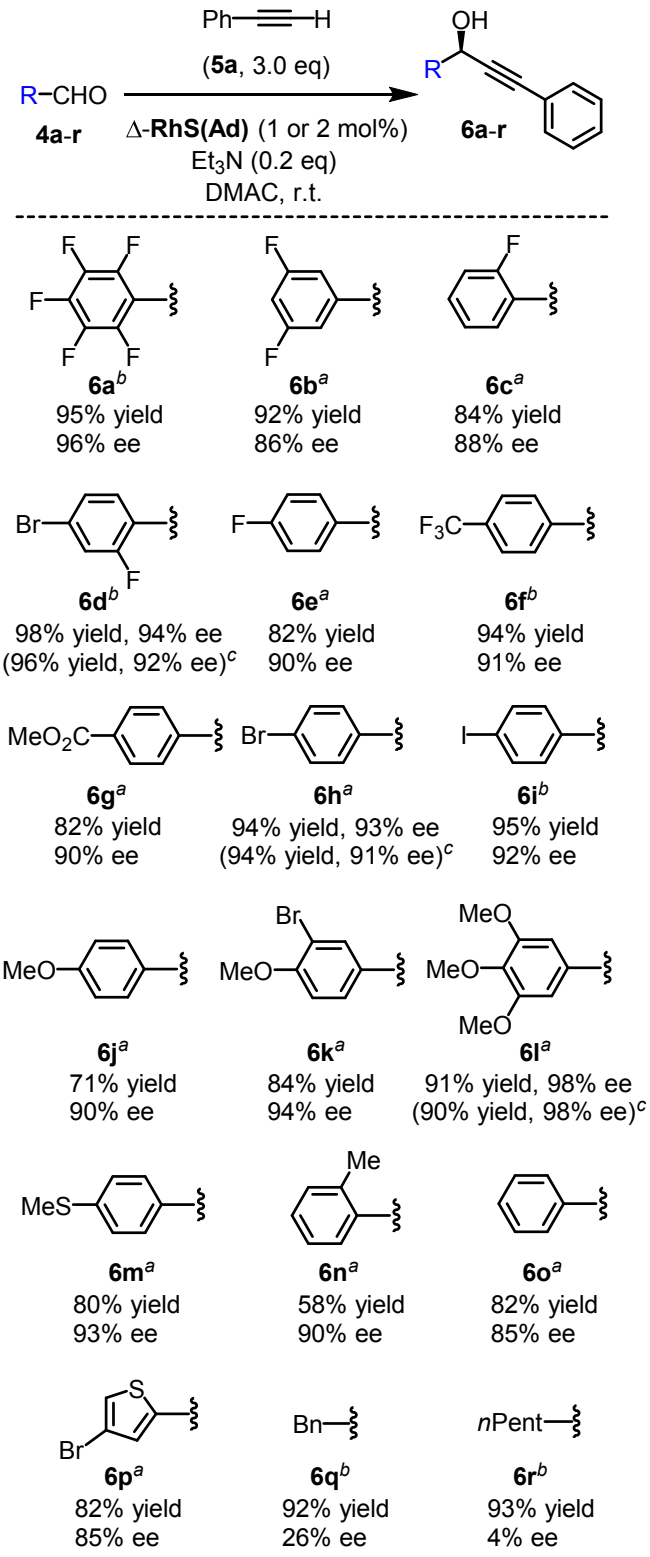
Entry	Catalyst	Conditions[a]	Time (h)	Solvent	Yield (%)[b]	*Ee* (%)[c]
1	Δ-**RhPP** (4.0 mol%)	standard	16	THF	51	25
2	Δ-**Ru1** (4.0 mol%)	standard	16	THF	88	48
3	Δ-**RhO** (4.0 mol%)	standard	16	THF	92	71
4	Δ-**RhS** (4.0 mol%)	standard	16	THF	92	89
5	Δ-**RhS(Ad)** (4.0 mol%)	standard	16	THF	92	92
6	Δ-**RhS(Ad)** (2.0 mol%)	standard	16	THF	92	92
7	Δ-**RhS(Ad)** (1.0 mol%)	standard	24	THF	91	92
8	Δ-**RhS(Ad)** (1.0 mol%)	standard	48	CH_3CN	25	95
9	Δ-**RhS(Ad)** (1.0 mol%)	standard	24	DCM	92	93
10	Δ-**RhS(Ad)** (1.0 mol%)	standard	24	DMF	81	94
11	Δ-**RhS(Ad)** (1.0 mol%)	standard	24	DMAc	95	96
12	Δ-**RhS(Ad)** (1.0 mol%)	under air	24	DMAc	83	96
13	Δ-**RhS(Ad)** (1.0 mol%)	added water[d]	24	DMAc	95	96
14	Δ-**RhS(Ad)** (1.0 mol%)	1.2 eq of **5a**	24	DMAc	82	94
15	Δ-**RhS(Ad)** (1.0 mol%)	2.0 eq of **5a**	24	DMAc	90	96
16	Δ-**RhS(Ad)** (1.0 mol%)	no base	24	DMAc	0	n.a.[e]
17	none	standard	24	DMAc	0	n.a.

[a] Standard conditions: Pentafluorobenzaldehyde (0.2 mmol), phenylacetylene (0.6 mmol), Et_3N (0.04 mmol), in 0.4 mL solvent was stirred at room temperature under an atmosphere of molecular nitrogen. [b] Isolated yield. [c] Determined by HPLC on a chiral stationary phase. [d] Presence of 2.0 mmol of H_2O. [e] n.a. = not applicable.

Substrates scope. First, we investigated the substrate scope with respect to aldehydes (Scheme 3). The reaction of phenylacetylene (**5a**) with a range of benzaldehydes bearing one or more electron-withdrawing or electron-donating substituents (F, Br, I, CF_3, CO_2Me, SMe, OMe, Me) in the phenyl moiety were examined under optimized reaction conditions (1-2 mol% Δ-**RhS(Ad)**, 0.2 equiv. Et_3N, DMAc, r.t., 24-48 hours) and provided the corresponding propargylic alcohols **6a**-**6n** in 58-98% yield and with 86-98% ee. For example, 4-bromo-2-fluorobenzaldehyde afforded the propargylic alcohol **6d** in 98% yield and with 94% ee, whereas 3,4,5-trimethoxylbenzaldehyde provided the propargylic alcohol **6l** in 91% yield and with excellent 98% ee. It is noticeable that for all these examples, enantioselectivities are higher compared to benzaldehyde itself, which leads to propargylic alcohol **6o** in 82% yield with only 85% ee. The heteroaromatic aldehyde 4-bromothiophene-2-carboxaldehyde provided the propargylic alcohol **6p** also with 82% yield and 85% ee. However, the aliphatic aldehydes phenylacetaldehyde and hexanal yielded the corresponding propargylic alcohols **6q** and **6r** only with very low enantioselectivity. We propose that the requirement for aromatic aldehydes stems for a π-π stacking between the substrate and one cyclometalated ligands of the catalyst. Finally, we compared **RhS(Ad)** and **RhS** for three additional randomly selected aldehydes (products **6d**, **6h**, and **6l**) which confirmed that **RhS(Ad)** is the catalyst of choice over **RhS** for this reaction (Scheme 3). While the two catalysts provide **6l** with identical enantiomeric excess, **RhS(Ad)** provides ee values that are 2% higher for the propargylic alcohols **6d** and **6h**.

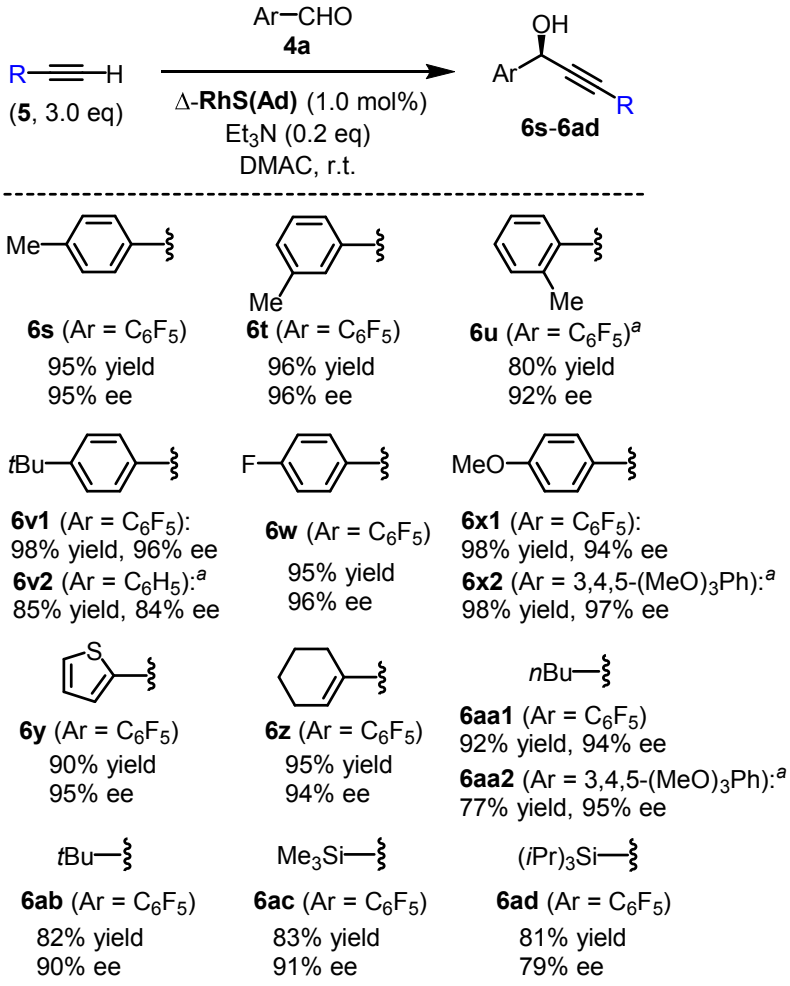
Next, we evaluated the substrate scope with respect to different terminal alkynes using the reaction with pentafluorobenzaldehyde under our standard conditions. Gratifyingly, the substrate

scope appears to be broad as shown in Scheme 4. Phenylacetylenes with alkyl, electron-donating, and electron-accepting substituents provide the corresponding propargylic alcohols **6s**-**6x** in 80-98% yields and 92-96% ee. 2-Ethynylthiophene gave the propargyl alcohol **6y** in 90% yield and 95% ee. A propargyl alcohol with a conjugated alkene **6z** was synthesized with 95% yield and 94% ee. Furthermore, aliphatic substituents (*n*Bu and *t*Bu) and a trimethylsilyl group are also well accommodated and afford the propargylic alcohols **6aa1** (94% ee), **6ab** (90% ee), and **6ac** (91% ee) with satisfactory enantioselectivities. Alone the highly bulky $(i\text{Pr})_3\text{Si}$ group reduces the enantiomeric excess to 79% ee (product **6ad**). Typically, 1 mol% of Δ-**RhS(Ad)** was sufficient for most substrates, with the only exception of *o*-methylphenylacetylene which reacted more sluggishly and needed an increased catalysts loading of 2 mol% in order to achieve satisfactory results. We also reacted 3,4,5-trimethoxybenzaldehyde with *p*-methoxyphenylacetylene and 1-hexyne under standard conditions and obtained the corresponding propargyl alcohols in 98% yield with 97% ee (**6x2**) and 77% yield with 95% ee (**6aa2**), respectively. Furthermore, the reaction of benzaldehyde with 4-*tert*-butylbenzaldehyde under standard conditions afforded the expected propargyl alcohol in 85% yield with 84% ee (**6v2**). These results are consistent with the trends obtained with pentafluorobenzaldehyde.



Scheme 3. Substrate scope with respect to aldehydes. [a] 2.0 mol% catalyst loading was used. [b] 1.0

mol% catalyst loading was used. [c] Reaction performed with Λ-**RhS** instead for comparison.



Scheme 4. Substrate scope with respect to terminal alkynes. [a] 2.0 mol% catalyst loading instead.

Comparison with other catalysts. Many laboratories have contributed to the catalytic enantioselective alkynylation of aldehydes and excellent methods exist.[2,10-14] Much efforts have been dedicated to alkylzinc-mediated enantioselective alkynylations in the presence of chiral ligands such as ephedrine derivatives, or chiral catalysts.[10] The most attractive methods rely on a "soft metalation strategy"[2] in which terminal alkynes are metalated in situ using catalytic amounts

of zinc(II),[11] indium(III),[12] or copper(I)[13] salts in the presence of a base and a chiral ligand. Furthermore, a ruthenium-Phebox-catalyzed enantioselective alkynylation has been developed.[14] Our rhodium-catalyzed method contributes to the soft-metalation strategy. We are convinced that this method will find applications as it is characterized by a combination of low catalyst loadings (1-2 mol%), modest amounts of base (e.g. 20 mol% Et_3N), room temperature conditions, little influence by air, and no effect by small amounts of water.

It is striking that the here introduced rhodium complex **RhS(Ad)** and the previously reported sterically less demanding congener **RhS** are capable of catalyzing the enantioselective alkynylation of aromatic aldehydes, whereas the complexes **RhPP** and **Ru1** –which follow a quite similar structural blueprint– only provide inferior results with respect to both catalytic activity and enantioselectivity (Table 1, entries 1 and 2). Interestingly, likewise **RhS(Ad)** is not suitable for the catalytic enantioselective alkynylation of trifluoroacetyl imidazoles (preferred substrates for **RhPP**) and trifluoroacetophenones (preferred substrates for **Ru1**) (see Supporting Information for details). The reasons for this distinct reactivity pattern is unclear but it demonstrates that even allegedly small structural changes in these propeller-type chiral-at-metal complexes results in significantly modified catalytic properties.

Conclusions

In summary, we here reported the enantioselective alkynylation of aromatic aldehydes employing a sterically highly demanding rhodium(III)-based chiral-at-metal Lewis acid catalyst. The new catalyst expands our family of bis-cyclometalated iridium(III) and rhodium(III) catalysts relying

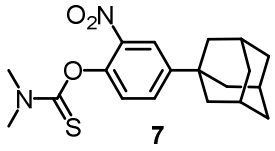
exclusively on metal-centered chirality for the asymmetric induction. Δ-**RhS(Ad)** at catalyst loadings of 1-2 mol% converts aromatic aldehydes and terminal alkynes into their corresponding chiral propargylic alcohols in 58-98% yields and with 79-98% ee at room temperature. Whereas the enantioselectivity with aromatic aldehydes significantly varies with the nature of the substituents and the substitution pattern, a broad scope exist with respect to terminal alkynes. This method nicely complements previously developed catalytic enantioselective alkynylations of 2-trifluoroacetylimidazoles and aromatic trifluoromethylketones with chiral-at-metal catalysts. The application of catalytic enantioselective alkynylations to the efficient synthesis of drugs and drug candidates is ongoing in our laboratory.

Experimental Section

General Methods and Materials. All reactions were carried out under an atmosphere of nitrogen with magnetic stirring. Catalytic reactions were performed in Schlenk tubes (10 mL). Solvents were freshly distilled under nitrogen from calcium hydride (CH_3CN and CH_2Cl_2) or sodium/benzophenone (THF). All aldehydes were purchased with highest purity or were freshly distilled. Oother reagents from commercial suppliers were used without further purification. Flash column chromatography was performed with silica gel 60 M from Macherey-Nagel (irreg. shaped, 230-400 mesh, pH 6.8, pore volume: 0.81 mL × g^{-1}, mean pore size: 66 Å, specific surface: 492 m^2 × g^{-1}, particle size distribution: 0.5% < 25 μm and 1.7% > 71 μm, water content: 1.6%). ^{1}H NMR, proton-decoupled ^{13}C NMR spectra, and proton-coupled ^{19}F NMR spectra were recorded on Bruker Avance 300 (300 MHz) or 500 (500 MHz) spectrometers at ambient temperature. NMR standards

were used as follows: ^{1}H NMR spectroscopy: δ = 7.26 ppm ($CDCl_3$), δ = 5.32 ppm (CD_2Cl_2). ^{13}C NMR spectroscopy: δ = 77.0 ppm ($CDCl_3$), δ = 54.0 ppm (CD_2Cl_2). All ^{13}C NMR signals are singlets unless noted otherwise. IR spectra were recorded on a Bruker Alpha FT-IR spectrophotometer. CD spectra were recorded on a JASCO J-810 CD spectropolarimeter (200-600 nm, 1 nm bandwidth, 50 nm/min scanning speed, accumulation of 3 scans). High-resolution mass spectra were recorded either on an HR-ESI-MS from Bruker En Apex Ultra 7.0 TFT-MS instrument (FT-ICR analyzer) or HR-FD-MS from AccuTOF GCv 4G (JEOL) Time of Flight (TOF analyzer). HPLC chromatography on chiral stationary phase was performed with Agilent 1200 or 1260 HPLC systems. Optical rotations were measured on a Perkin-Elmer 241 polarimeter with $[\alpha]_D^{22}$ values reported in degrees with concentrations reported in g/100 mL.

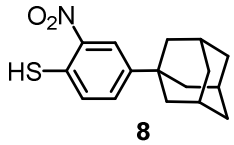
Synthesis of the benzothiazole ligand 1



7

O-(4-(Adamantan-1-yl)-2-nitrophenyl) dimethylcarbamothioate (7). To a suspension of NaH (60% in mineral oil, 600 mg, 15.0 mmol) in DMF (40.0 mL) at 0 °C were added 4-(adamantan-1-yl)-2-nitrophenol[15] (1.37 g, 5.0 mmol) in DMF (5 mL) dropwise under an atmosphere of nitrogen. After being stirred for 30 minutes at 0 °C, dimethylcarbamothioic chloride (1.23 g, 10 mmol) in DMF (5 mL) was added dropwise. The reaction mixture was warmed to 90 °C and stirred at that temperature for 2 hours. The reaction mixture was cooled to 0 °C and quenched with a solution of aqueous saturated NH_4Cl (50 mL) dropwise, and then diluted with H_2O (200 mL). The mixture was extracted with EtOAc (3 × 50 mL), the combined organic layers were

washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (R_f = 0.2, EtOAc/ *n*-hexane = 1:20) to give compound **7** (1.26 g, 3.5 mmol, yield: 70%) as a pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, J = 2.4 Hz, 1H), 7.65 (dd, J =8.6, 2.4 Hz, 1H), 7.18 (d, J = 8.6 Hz, 1H), 3.46 (s, 3H), 3.38 (s, 3H), 2.18-2.08 (m, 3H), 1.97-1.89 (m, 6H), 1.87-1.65 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.2, 150.4, 144.8, 141.6, 131.2, 125.9, 122.3, 43.5, 42.9, 39.0, 36.44, 36.38, 28.7. IR (film): v (cm^{-1}) 2900, 2845, 2533, 1490, 1450, 1395, 1343, 1288, 1229, 1178, 1133, 1083, 1053, 837, 717, 760, 516, 453. HRMS (ESI, m/z) calcd for $C_{19}H_{25}N_2O_3S$ $[M+H]^+$: 361.1580, found: 361.1581.



8

*4-(Adamantan-1-yl)-2-nitrobenzenethiol (**8**).* Compound **7** (1.38 g, 4.0 mmol) was heated without solvent and stirred at 200 °C for 3 hours at an atmosphere of nitrogen. Thereafter, the reaction mixture was cooled to room temperature, KOH (448 mg, 8.0 mmol) in MeOH/THF (1/1, 40 mL) was added and stirred for 3 hours at room temperature. Then, the reaction mixture was cooled to 0 °C and HCl aqueous (1 mol/L) was added dropwise until pH = 2.0. The mixture was diluted with water (100 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was recrystallized from EtOAc/ *n*-hexane to give compound **8** (948 mg, 82%) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, J = 2.1 Hz, 1H), 7.45 (dd, J =8.4, 2.1 Hz, 1H), 7.36 (d, J = 8.4 Hz, 1H), 3.96 (s, 1H), 2.18-2.08 (m, 3H), 1.94-1.86 (m, 6H),

1.86-1.68 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.1, 145.3, 131.7, 131.0, 129.9, 122.6, 42.8, 36.4, 36.1, 28.7. IR (film): ν (cm^{-1}) 2907, 2874, 2849, 2549, 1514, 1475, 1449, 1335, 1303, 1278, 1124, 1052, 978, 885, 834, 809, 751, 679, 572, 455. HRMS (ESI, *m*/*z*) calcd for $C_{16}H_{18}NO_2S$ $[M-H]^-$: 288.1064, found: 288.1062.

*5-(Adamantan-1-yl)-2-phenylbenzo[d]thiazole (**1**).* Under an atmosphere of nitrogen, to a mixture of compound **8** (578 mg, 2.0 mmol) and metal indium powder (460 mg, 4.0 mmol) in anhydrous toluene (20.0 mL) were added acetic acid (1.14 mL, 20 mmol) and (trimethoxymethyl)benzene (0.687 mL, 4.0 mmol) in one portion. The mixture was warmed to 100 °C and stirred for 24 hours at the same temperature. The reaction mixture was cooled to room temperature and the solid was filtered, then a solution of saturated NH_4Cl (25 mL) was added and the reaction mixture was diluted with water (50 mL). The mixture was extracted with EtOAc (3 × 20 mL) and the combined organic layers were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (R_f = 0.2, EtOAc/ *n*-hexane = 1:50) to provide benzothiazole ligand **1** (304 mg, 0.88 mmol, 44%) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16-8.04 (m, 3H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.57-7.43 (m, 4H), 2.20-2.10 (m, 3H), 2.08-1.96 (m, 6H), 1.88-1.74 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.0, 154.6, 150.4, 133.8, 132.0, 130.8, 129.0, 127.5, 122.9, 121.0, 119.5, 43.4, 36.8, 36.4, 29.0. IR (film): ν (cm^{-1}) 2900, 1845, 1600, 1541, 1477, 1448, 1313, 1241, 962, 921, 878, 828, 801, 761, 689, 652, 481. HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{24}NS$ $[M+H]^+$: 346.1624, found: 346.1625.

Synthesis of *rac*-RhS(Ad). The racemic rhodium catalyst was synthesized according to a route

reported in our laboratory with some modifications.[8] Benzothiazole ligand **1** (362 mg, 1.05 mmol) was added to $RhCl_3•3H_2O$ (131 mg, 0.50 mmol) in a solvent mixture of 2-ethoxyethanol and water (v/v = 3/1, 10 mL). The reaction mixture was heated at 120 °C for 4.5 hours under an atmosphere of nitrogen, then it was concentrated by reduced pressure to give a brown black solid. The solid was used in the next step without further purification. To the brown black solid in CH_3CN (10 mL) was added $AgPF_6$ (316 mg, 1.25 mmol) in one portion and stirred at 60 °C overnight under an atmosphere of nitrogen. After being cooled to room temperature, the mixture was filtered and the filtrate was collected, evaporated to dryness, and purified by column chromatography on silica gel (R_f = 0.2, 100% CH_2Cl_2 to CH_2Cl_2/CH_3CN = 20:1) to provide *rac*-**RhS(Ad)** (366 mg, 0.36 mmol, 72% yield over two steps) as a pale yellow solid. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.43 (d, J = 1.0 Hz, 2H), 8.03 (d, J = 8.6 Hz, 2H), 7.76-7.64 (m, 4H), 7.03 (t, J = 7.4 Hz, 2H), 6.88-6.78 (m, 2H), 6.20 (d, J = 7.8 Hz, 2H), 2.18 (s, 6H), 2.17-2.09 (m, 6H), 2.08-1.98 (m, 12H), 1.90-1.74 (m, 12H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 176.94, 176.89, 161.1, 160.7, 153.1, 150.4, 140.6, 133.6, 131.4, 129.31, 129.30, 126.4, 125.2, 124.7, 123.1, 122.3, 117.0, 44.0, 37.4, 37.1, 29.6, 3.8. IR (film): ν (cm^{-1}) 2903, 2847, 1578, 1444, 1416, 1302, 1236, 1184, 1127, 984, 879, 753, 724, 659, 522, 477, 446. HRMS (ESI, *m*/*z*) calcd for $C_{46}H_{44}N_2RhS_2$ $[M\text{-}2CH_3CN\text{-}PF_6]^+$: 791.1995, found: 791.2001.

Synthesis of Enantiomerically Pure Rhodium Catalysts. ***Λ*-(*R*)-3 and *Δ*-(*R*)-3.** To a mixture of *rac*-**RhS(Ad)** (305 mg, 0.30 mmol) and K_2CO_3 (124 mg, 0.60 mmol) in absolute ethanol (6.0 mL) was added (*R*)-3-fluoro-2-(4-phenyl-4,5-dihydrooxazol-2-yl)phenol ((*R*)-**2**, 91 mg, 0.33 mmol) in one portion. After being stirred at 70 °C for 16 hours under an atmosphere of nitrogen, the reaction mixture was cooled to room temperature and concentrated to dryness. The residue was subjected to

flash chromatography on silica gel (R_f = 0.1, CH_2Cl_2/ *n*-hexane = 1/20 to 5:1) providing Δ-(*R*)-**3** (142 mg, 45% yield) as a yellow solid and Λ-(*R*)-**3** (132 mg, 41% yield) as a yellow solid (for Λ-(*R*)-**3**, a second flash chromatography is necessary to get the pure product), respectively. Δ-(*R*)-**3**: CD (MeOH): λ, nm (Δε, $M^{-1}cm^{-1}$) 418 (+22), 347 (–30), 300 (+36), 272 (–6), 249 (–7), 235 (+6). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.87 (d, J = 1.7 Hz, 1H), 7.95 (d, J = 1.7 Hz, 1H), 7.83 (d, J = 8.6 Hz, 1H), 7.64-7.56 (m, 2H), 7.53 (dd, J = 8.6, 1.9 Hz, 1H), 7.45 (dd, J = 8.6, 1.9 Hz, 1H), 7.37-7.33 (m, 1H), 6.99-6.77 (m, 6H), 6.74-6.68 (m, 2H), 6.43 (dd, J = 8.8, 1.0 Hz, 1H), 6.27 (d, J = 7.2 Hz, 2H), 5.88-5.82 (m, 2H), 4.90-4.84 (m, 2H), 4.01-3.95 (m, 1H), 2.20-2.12 (m, 3H), 2.04-1.94 (m, 9H), 1.92-1.75 (m, 12H), 1.75-1.64 (m, 6H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ 177.6, 177.5, 175.92, 175.90, 175.08, 175.05, 170.3, 170.0, 168.6, 168.3, 166.22, 166.19, 164.0 (d, J = 257.3 Hz), 152.1, 152.0, 151.9, 151.6, 142.0, 141.60, 141.57, 135.4, 133.4, 133.0, 132.9, 130.2, 129.8, 129.7, 129.1, 128.2, 127.7, 126.1, 126.0, 123.8, 123.4, 123.2, 122.60, 122.57, 121.5, 121.02, 121.00, 119.8, 116.4, 101.1 (d, J = 6.2 Hz), 98.7 (d, J = 24.0 Hz), 75.8, 69.7, 43.8, 43.7, 37.15 (2C), 37.07, 37.02, 29.64, 29.61. IR (film): ν (cm^{-1}) 3055, 2913, 1849, 1735, 1615, 1583, 1527, 1443, 1373, 1316, 1290, 1218, 1158, 1095, 1032, 988, 941, 793, 753, 727, 694, 664, 609, 579, 530, 454. HRMS (ESI, *m*/*z*) calcd for $C_{61}H_{56}FN_3O_2RhS_2$ $[M+H]^+$: 1048.2848, found: 1048.2844. Λ-(*R*)-**3**: CD (MeOH): λ, nm (Δε, $M^{-1}cm^{-1}$) 420 (–23), 376 (+16), 298 (–24), 274 (+14), 249 (+17), 226 (+6). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.97 (d, J = 1.6 Hz, 1H), 8.22 (d, J = 1.6 Hz, 1H), 7.93 (d, J = 8.6 Hz, 1H), 7.81 (d, J = 8.6 Hz, 1H), 7.61-7.57 (m, 1H), 7.56-7.48 (m, 2H), 7.29 (dd, J = 7.6, 1.0 Hz, 1H), 8.96-6.74 (m, 8H), 6.60 (td, J = 7.3, 1.0 Hz, 1H), 6.36-6.28 (m, 3H), 6.03 (d, J = 7.8 Hz, 1H), 5.91 (qd, J = 7.8, 1.0 Hz, 1H), 4.23 (dd, J = 9.3, 8.4 Hz, 1H), 4.03 (dd, J = 11.1, 9.3 Hz, 1H), 3.93 (dd, J = 11.1, 8.4 Hz, 1H),

2.12-2.06 (m, 3H), 2.00-1.86 (m, 9H), 1.84-1.72 (m, 12H), 1.70-1.56 (m, 6H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ 176.8, 176.7, 176.53, 176.50, 174.69, 174.67, 169.9, 169.6, 168.8, 168.6, 167.3, 163.6 (d, J = 254.4 Hz), 153.0, 151.7, 151.6, 151.3, 141.3, 140.6, 139.7, 135.5, 133.6, 133.1, 133.0, 130.4, 129.8, 129.0, 128.9, 128.4, 127.7, 127.6, 126.0, 125.8, 124.0, 123.8, 123.1, 122.5, 122.2, 122.1, 120.26, 120.25, 119.1, 117.8, 117.0, 103.2 (d, J = 6.6 Hz), 98.7 (d, J = 23.0 Hz), 75.0, 70.2, 43.7, 43.6, 37.19, 37.15, 37.10, 37.07, 29.6. IR (film): v (cm^{-1}) 3054, 2900, 2846, 1617, 1579, 1530, 1442, 1372, 1317, 1291, 1264, 1221, 1095, 1031, 986, 792, 753, 726, 696, 665, 582, 529, 453. HRMS (ESI, m/z) calcd for $C_{61}H_{56}FN_3O_2RhS_2$ $[M+H]^+$: 1048.2848, found: 1048.2844.

Λ-RhS(Ad) *and* ***Δ-RhS(Ad)***. To a suspension of Λ-(*R*)-**3** (210 mg, 0.20 mmol) or Δ-(*R*)-**3** (210 mg, 0.20 mmol) in CH_3CN (5 mL) was added TFA (88 μL, 1.2 mmol) in one portion and then stirred at room temperature for 0.5 hours in the dark. The color of the mixture changed to colorless. The reaction mixture was evaporated to dryness, then subjected to the flash chromatography on silica gel (100% CH_2Cl_2 to CH_2Cl_2/ CH_3CN = 20:1) to remove the auxiliary carefully, followed by the addition of excess NH_4PF_6 (30 equiv) on the top of the silica gel in the column, and an eluent (CH_2Cl_2/CH_3CN = 10:1 to 5:1) was used to exchange the counter ion. The obtained pale yellow filtrate was concentrated, providing the enantiopure catalysts Λ-**RhS(Ad)** (183 mg, 0.18 mmol, 90% yield) or Δ-**RhS(Ad)** (183 mg, 0.18 mmol, 90% yield) as yellow solids. CD (CH_3OH) for Λ-**RhS(Ad)**: λ, nm (Δε, M^{-1}cm^{-1}) 407 (–42), 366 (+76), 358 (+66), 299 (–60), 259 (+29), 245 (+38). CD (CH_3OH) for Δ- **RhS(Ad)**: λ, nm (Δε, M^{-1}cm^{-1}) 406 (+44), 365 (–66), 358 (–58), 298 (+69), 260 (–20), 244 (–25).

General Procedure for the Alkynylation of Aromatic Aldehydes. A dried 10 mL Schlenk

tube was charged with the rhodium catalyst Δ-**RhS(Ad)** (1-2 mol%) and the corresponding aldehydes (0.20 mmol, 1.0 eq). The tube was purged with nitrogen, DMAc (0.4 mL) and Et_3N (5.6 μL, 0.2 eq, Merck) were added via syringe, followed by adding the corresponding alkynes (0.60 mmol, 3.0 eq). The vial was sealed and the reaction was stirred at room temperature for 24-48 hours under an atmosphere of nitrogen. Then, the reaction mixture was diluted with CH_2Cl_2 (2 mL) and silica (200 mg) was added. The solvent was removed under reduce pressure and the residue was purified by flash chromatography on silica gel to afford the corresponding propargylic alcohols. Racemic reference products were obtained using *rac*-**RhS(Ad)**.

*(S)-1-(Perfluorophenyl)-3-phenylprop-2-yn-1-ol (**6a**).*[10f] Starting from pentafluorobenzaldehyde (39.2 mg, 0.20 mmol), phenylacetylene (61.3 mg, 0.60 mmol) and Δ-**RhS(Ad)** (2.0 mg, 0.002 mmol), according to the general procedure, reacting at room temperature for 24 hours to give **6a** as a white solid (56.6 mg, 0.190 mmol, yield: 95%). R_f = 0.3 (10% ethyl acetate in *n*-hexane). Enantiomeric excess was established by HPLC analysis using a Daicel Chiralcel AS-H column, ee = 96% (HPLC: AS-H, 254 nm, *n*-hexane/ isopropanol = 95:5, flow rate 1.0 mL/min, 25 °C, t_r (major) = 8.3 min, t_r (minor) = 12.4 min). $[\alpha]_D^{22}$ = –10.2° (*c* 1.0, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49-7.41 (m, 2H), 7.37-7.29 (m, 3H), 5.98 (d, *J* = 7.8 Hz, 1H), 2.71 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.9, 129.2, 128.4, 121.5, 86.7, 85.5, 55.5. IR: 3209, 2921, 2188, 1499, 1332, 1294, 1120, 1032, 987, 799, 855, 692, 632, 570, 478. ^{19}F NMR (282 MHz, $CDCl_3$) –144.18 - –144.36 (m, 2F), –154.44 - –154.66 (m, 1F), –161.98 - –161.26 (m, 2F). HRMS (FD, *m*/*z*) calcd for $C_{15}H_7F_5O$ $[M]^+$: 298.0412, found: 298.0410.

*(R)-1-(3,5-Difluorophenyl)-3-phenylprop-2-yn-1-ol (**6b**).*[11b] Starting from 3,5-difluorobenzalde-

hyde (28.4 mg, 0.20 mmol), phenylacetylene (61.3 mg, 0.60 mmol) and Δ-**RhS(Ad)** (4.1 mg, 0.004 mmol), according to the general procedure, reacting at room temperature for 24 hours to give **6b** as a white solid (44.9 mg, 0.184 mmol, yield: 92%). R_f = 0.3 (10% ethyl acetate in *n*-hexane). Enantiomeric excess established by HPLC analysis using a Daicel Chiralcel AS-H column, ee = 86% (HPLC: AS-H, 254 nm, *n*-hexane/ isopropanol = 96:4, flow rate 1.0 mL/min, 25 °C, t_r (major) = 12.2 min, t_r (minor) = 14.0 min). $[\alpha]_D^{22}$ = +9.4° (*c* 1.0, EtOH). Lit.[11b]: $[\alpha]_D^{25}$ = +11° (*c* 1.0, EtOH, 99.8% ee for *R*-configuration). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55-7.43 (m, 2H), 7.41-7.29 (m, 3H), 7.22-7.10 (m, 2H), 6.85-6.73 (m, 1H), 5.67 (d, *J* = 5.6 Hz, 1H), 2.46 (d, *J* = 5.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.0 (dd, *J* = 249.1, 12.5 Hz), 161.4 (t, *J* = 8.8 Hz), 131.8, 129.0, 128.4, 121.8, 109.6 (dd, *J* = 17.6, 8.4 Hz), 103.6 (t, *J* = 5.4 Hz), 87.4, 87.2, 63.0 (t, *J* = 2.2 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ –63.36. IR (film): ν (cm^{-1}) 3326, 2924, 2854, 2227, 1621, 1595, 1443, 1317, 1116, 1035, 978, 917, 857, 753, 685, 635, 572, 515, 428. HRMS (ESI, *m*/*z*) calcd for $C_{15}H_9F_2O$ $[M-H]^-$: 243.0627, found: 243.0626.

(S)-1-(2-Fluorophenyl)-3-phenylprop-2-yn-1-ol ***(6c)***.[16] Starting from 2-fluorobenzaldehyde (24.8 mg, 0.20 mmol), phenylacetylene (61.3 mg, 0.60 mmol) and Δ-**RhS(Ad)** (4.1 mg, 0.004 mmol), according to the general procedure, reacting at room temperature for 48 hours to give **6c** as a pale yellow oil (38.0 mg, 0.168 mmol, yield: 84%). R_f = 0.3 (20% ethyl acetate in *n*-hexane). Enantiomeric excess established by HPLC analysis using a Daicel Chiralcel OD-H column, ee = 88% (HPLC: OD-H, 254 nm, *n*-hexane/ isopropanol = 90:10, flow rate 1.0 mL/min, 25 °C, t_r (major) = 9.5 min, t_r (minor) = 12.5 min). $[\alpha]_D^{22}$ = –4.8° (*c* 1.0, $CHCl_3$). Lit.[16]: $[\alpha]_D^{25}$ = +6.5° (*c* 0.71, $CHCl_3$, 94% ee for *R*-configuration). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80-7.70 (m, 1H), 7.53-7.45

(m, 2H), 7.41-7.29 (m, 4H), 7.24-7.05 (m, 2H), 5.98 (s, 1H), 2.58 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.2 (d, J = 248.4 Hz), 131.8, 130.2 (d, J = 8.3 Hz), 128.6, 128.4 (d, J = 3.5 Hz), 128.3, 127.9 (d, J = 13.2 Hz), 124.4 (d, J = 3.5 Hz), 122.2, 115.6 (d, J = 21.2 Hz), 87.6, 86.6, 59.6 (d, J = 5.0 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ –119.88. IR (film): ν (cm^{-1}) 3347, 2907, 2851, 2238, 2851, 1602, 1504, 1440, 1416, 1291, 1224, 1156, 1096, 1020, 961, 835, 754, 664, 555, 515. HRMS (ESI, m/z) calcd for $C_{15}H_{10}F$ $[M+H–H_2O]^+$: 209.0761, found: 209.0762.

(S)-1-(4-Bromo-2-fluorophenyl)-3-phenylprop-2-yn-1-ol ***(6d)***. Starting from 4-bromo-2-fluorobenzaldehyde (46.4 mg, 0.20 mmol), phenylacetylene (61.3 mg, 0.60 mmol) and Δ-**RhS(Ad)** (2.0 mg, 0.002 mmol), according to the general procedure, reacting at room temperature for 24 hours to give **6d** as a white solid (59.8 mg, 0.196 mmol, yield: 98%). R_f = 0.3 (20% ethyl acetate in *n*-hexane). Enantiomeric excess established by HPLC analysis using a Daicel Chiralcel AS-H column, ee = 94% (HPLC: AS-H, 254 nm, *n*-hexane/ isopropanol = 96:4, flow rate 1.0 mL/min, 25 °C, t_r (major) = 18.7 min, t_r (minor) = 21.0 min). $[\alpha]_D^{22}$ = –12.8° (*c* 1.0, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, J = 8.0 Hz, 1H), 7.49-7.43 (m, 2H), 7.38-7.26 (m, 5H), 5.92 (d, J = 5.8 Hz, 1H), 2.41 (d, J = 5.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.9 (d, J = 253.2 Hz), 131.8, 129.6 (d, J = 4.2 Hz), 128.8, 128.3, 127.7 (d, J = 3.6 Hz), 127.1 (d, J = 13.2 Hz), 122.7 (d, J = 9.6 Hz), 122.0, 119.3 (d, J = 14.6 Hz), 87.0, 86.9, 59.1 (d, J = 4.6 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ –117.08. IR (film): ν (cm^{-1}) 3322, 3087, 2220, 1602, 1576, 1479, 1396, 1245, 1217, 1042, 963, 872, 827, 752, 683, 662, 586, 539, 509, 473. HRMS (ESI, m/z) calcd for $C_{15}H_{11}BrFO$ $[M+H]^+$: 304.9972, found: 304.9975.

(R)-1-(4-Fluorophenyl)-3-phenylprop-2-yn-1-ol ***(6e)***.[16] Starting from 4-fluorobenzaldehyde

(24.8 mg, 0.20 mmol), phenylacetylene (61.3 mg, 0.60 mmol) and Δ-**RhS(Ad)** (4.1 mg, 0.004 mmol), according to the general procedure, reacting at room temperature for 48 hours to give **6e** as a pale yellow oil (37.1 mg, 0.164 mmol, yield: 82%). R_f = 0.3 (20% ethyl acetate in *n*-hexane). Enantiomeric excess established by HPLC analysis using a Daicel Chiralcel OD-H column, ee = 90% (HPLC: OD-H, 254 nm, *n*-hexane/ isopropanol = 90:10, flow rate 1.0 mL/min, 25 °C, t_r (major) = 9.5 min, t_r (minor) = 25.8 min). $[\alpha]_D^{22}$ = +6.0° (*c* 1.0, $CHCl_3$). Lit.[16]: $[\alpha]_D^{25}$ = –6.3° (*c* 0.78, $CHCl_3$, 94% ee for *S*-configuration). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64-7.56 (m, 2H), 7.51-7.45 (m, 2H), 7.37-7.29 (m, 3H), 7.14-7.04 (m, 2H), 5.68 (s, 1H), 2.47 (s, 1H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.6 (d, *J* = 247.9 Hz), 136.5 (d, *J* = 3.1 Hz), 131.7, 128.7, 128. 6 (d, *J* = 8.3 Hz), 128.3, 122.2, 115.5 (d, *J* = 21.8 Hz), 88.5, 86.9, 64.4. ^{19}F NMR (282 MHz, $CDCl_3$) δ –114.12. IR (film): ν (cm^{-1}) 3309, 2928, 2209, 1589, 1488, 1452, 1225, 1177, 1022, 961, 834, 751, 689, 630, 582, 530, 498. HRMS (ESI, *m*/*z*) calcd for $C_{15}H_{11}FONa$ $[M+Na]^+$: 249.0686, found: 249.0687.

(R)-3-Phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-yn-1-ol ***(6f)***.[14] Starting from 4-(trifluoromethyl)benzaldehyde (34.2 mg, 0.20 mmol), phenylacetylene (61.3 mg, 0.60 mmol) and Δ-**RhS(Ad)** (2.0 mg, 0.002 mmol), according to the general procedure, reacting at room temperature for 24 hours to give **6f** as a white solid (51.9 mg, 0.188 mmol, yield: 94%). R_f = 0.3 (20% ethyl acetate in *n*-hexane). Enantiomeric excess established by HPLC analysis using a Daicel Chiralcel OD-H column, ee = 91% (HPLC: OD-H, 254 nm, *n*-hexane/ isopropanol = 90: 10, flow rate 1.0 mL/min, 25 °C, t_r (major) = 8.0 min, t_r (minor) = 25.0 min). $[\alpha]_D^{22}$ = +11.8° (*c* 1.0, EtOH). Lit.[14]: $[\alpha]_D^{20}$ = +10.9° (*c* 1.0, EtOH, 90% ee for *R*-configuration). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.51-7.43 (m, 2H), 7.39-7.29 (m, 3H), 5.76 (s,

1H), 2.41 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.4, 131.8, 130.5 (q, J = 32.5 Hz), 128.9, 128.4, 127.0, 125.6 (q, J = 3.8 Hz), 124.0 (q, J = 272.5 Hz), 122.0, 87.9, 87.3, 64.4. ^{19}F NMR (282 MHz, $CDCl_3$) δ –63.36 (3H). IR (film): ν (cm^{-1}) 3367, 2225, 1619, 1489, 1418, 1323, 1163, 1117, 1064, 1017, 962, 922, 842, 754, 689, 660, 604, 533, 475, 442. HRMS (ESI, m/z) calcd for $C_{16}H_{10}F_3O$ $[M-H]^-$: 275.0689, found: 275.0691.

(R)-Methyl-4-(1-hydroxy-3-phenylprop-2-yn-1-yl)benzoate ***(6g)***.[17] Starting from methyl 4-formyl benzoate (32.8 mg, 0.20 mmol), phenylacetylene (61.3 mg, 0.60 mmol) and Δ-**RhS(Ad)** (4.1 mg, 0.004 mmol), according to the general procedure, reacting at room temperature for 48 hours to give **6g** as a pale yellow oil (43.7 mg, 0.164 mmol, yield: 82%). R_f = 0.3 (20% ethyl acetate in *n*-hexane). Enantiomeric excess established by HPLC analysis using a Daicel Chiralcel OD-H column, ee = 90% (HPLC: OD-H, 254 nm, *n*-hexane/ isopropanol =90:10, flow rate 1.0 mL/min, 25 °C, t_r (major) = 15.7 min, t_r (minor) = 47.2 min). $[\alpha]_D^{22}$ = +6.4° (*c* 1.0, $CHCl_3$). Lit.[17]: $[\alpha]_D^{23}$ = +7.56° (*c* 1.5, $CHCl_3$, 97% ee for *R*-configuration). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10-8.04 (m, 2H), 7.72-7.04 (m, 2H), 7.50-7.44 (m, 2H), 7.37-7.29 (m, 3H), 5.74 (d, J = 5.6 Hz, 1H), 3.93 (s, 3H), 2.58 (d, J = 5.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 145.4, 131.7, 130.1, 129.9, 128.8, 128.3, 126.6, 122.1, 88.1, 87.1, 64.6, 52.2. IR (film): ν (cm^{-1}) 3340, 2949, 2922, 2230, 1714, 1607, 1487, 1429, 1282, 1186, 1107, 1039, 1019, 960, 862, 838, 803, 756, 732, 689, 611, 552, 522, 480. HRMS (ESI, m/z) calcd for $C_{17}H_{14}O_3Na$ $[M+Na]^+$: 289.0835, found: 289.0836.

(R)-1-(4-Bromophenyl)-3-phenylprop-2-yn-1-ol ***(6h)***.[14] Starting from 4-bromobenzaldehyde (37.0 mg, 0.20 mmol), phenylacetylene (61.3 mg, 0.60 mmol) and Δ-**RhS(Ad)** (4.1 mg, 0.004 mmol), according to the general procedure, reacting at room temperature for 24 hours to give **6h** as

a white solid (54.0 mg, 0.188 mmol, yield: 94%). R_f = 0.3 (20% ethyl acetate in *n*-hexane). Enantiomeric excess established by HPLC analysis using a Daicel Chiralcel OD-H column, ee = 93% (HPLC: OD-H, 254 nm, *n*-hexane/ isopropanol = 90:10, flow rate 1.0 mL/min, 25 °C, t_r (major) = 9.7 min, t_r (minor) = 22.6 min). $[\alpha]_D^{22}$ = +7.6° (*c* 1.0, $CHCl_3$). Lit.[14]: $[\alpha]_D^{20}$ = +7.9° (*c* 0.76, $CHCl_3$, 93% ee for *R*-configuration), and Daicel Chiralcel OD-H column, 254 nm, *n*-hexane/ isopropanol = 80:20, flow rate 1.0 mL/min, 25 °C. t_r (major) = 6.7 min, t_r (minor) = 21.2 min. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51-7.43 (m, 6H), 7.37-7.29 (m, 3H), 5.66 (d, *J* = 6.0 Hz, 1H), 2.35 (d, *J* = 6.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.6, 131.7 (2C), 128.8, 128.41, 128.35, 122.4, 122.1, 88.1, 87.0, 64.4. IR (film): ν (cm^{-1}) 3332, 2929, 2229, 1483, 1399, 1285, 1237, 1175, 1070, 1006, 951, 841, 794, 749, 686, 580, 531, 499, 471, 409. HRMS (ESI, *m*/*z*) calcd for $C_{15}H_{10}BrO$ $[M-H]^-$: 284.9921, found: 284.9921.

(R)-1-(4-Iodophenyl)-3-phenylprop-2-yn-1-ol ***(6i)***.[18] Starting from 4-Iodobenzaldehyde (46.4 mg, 0.20 mmol), phenylacetylene (61.3 mg, 0.60 mmol) and Δ-**RhS(Ad)** (4.1 mg, 0.004 mmol), according to the general procedure, reacting at room temperature for 24 hours to give **6i** as a brown solid (63.5 mg, 0.19 mmol, yield: 95%). R_f = 0.3 (20% ethyl acetate in *n*-hexane). Enantiomeric excess established by HPLC analysis using a Daicel Chiralcel OD-H column, ee = 92% (HPLC: OD-H, 254 nm, *n*-hexane/ isopropanol = 90:10, flow rate 1.0 mL/min, 25 °C, t_r (major) = 11.2 min, t_r (minor) = 35.9 min). $[\alpha]_D^{22}$ = +11.6° (*c* 1.0, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77-7.69 (m, 2H), 7.49-7.43 (m, 2H), 7.41-7.29 (m, 5H), 5.64 (d, *J* = 6.0 Hz, 1H), 2.36 (d, *J* = 6.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.3, 137.7, 131.7, 128.8, 128.6, 128.3, 122.1, 94.1, 88.1, 87.0, 64.5. IR (film): ν (cm^{-1}) 3318, 3055, 2230, 1483, 1399, 1285, 1237, 1175, 1069, 1006, 951, 841, 794, 749,

686, 580, 531, 499, 471, 409. HRMS (ESI, *m*/*z*) calcd for $C_{15}H_{10}IO$ $[M-H]^-$: 332.9782, found: 332.9783.

*(R)-1-(4-Methoxyphenyl)-3-phenylprop-2-yn-1-ol (**6j**).*[16] Starting from 4-methoxybenzaldehyde (30.4 mg, 0.20 mmol), phenylacetylene (61.3 mg, 0.60 mmol) and Δ-**RhS(Ad)** (4.1 mg, 0.004 mmol), according to the general procedure, reacting at room temperature for 48 hours to give **6j** as a pale yellow oil (33.8 mg, 0.142 mmol, yield: 71%). R_f = 0.3 (20% ethyl acetate in *n*-hexane). Enantiomeric excess established by HPLC analysis using a Daicel Chiralcel OD-H column, ee = 90% (HPLC: OD-H, 254 nm, *n*-hexane/ isopropanol = 90:10, flow rate 1.0 mL/min, 25 °C, t_r (major) = 16.3 min, t_r (minor) = 30.0 min). $[\alpha]_D^{22}$ = +4.4° (*c* 1.0, $CHCl_3$). Lit.[16]: $[\alpha]_D^{20}$ = -5.4° (*c* 0.78, $CHCl_3$, 93% ee for *S*-configuration). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59-7.57 (m, 2H), 7.50-7.44 (m, 2H), 7.37-7.29 (m, 3H), 6.97-6.29 (m, 2H), 5.65 (d, *J* = 5.6 Hz, 1H), 3.82 (s, 3H), 2.23 (d, *J* = 5.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.8, 133.0, 131.7, 128.5, 128.3, 128.2, 122.5, 114.0, 88.9, 86.5, 64.8, 55.3. IR (film): ν (cm^{-1}) 3352, 2922, 2854, 2221, 1596, 1490, 1283, 1261, 1179, 1084, 1029, 955, 751, 685, 549, 463. HRMS (FD, *m*/*z*) calcd for $C_{16}H_{14}O_2$ $[M]^+$: 238.0994, found: 238.0977.

*(R)-1-(3-Bromo-4-methoxyphenyl)-3-phenylprop-2-yn-1-ol (**6k**).* Starting from 3-bromo-4-methoxybenzaldehyde (43.0 mg, 0.20 mmol), phenylacetylene (61.3 mg, 0.60 mmol) and Δ-**RhS(Ad)** (4.1 mg, 0.004 mmol), according to the general procedure, reacting at room temperature for 48 hours to give **6k** as a pale yellow oil (53.3 mg, 0.168 mmol, yield: 84%). R_f = 0.3 (20% ethyl acetate in *n*-hexane). Enantiomeric excess established by HPLC analysis using a Daicel Chiralpak AS-H column, ee = 94% (HPLC: AS-H, 254 nm, *n*-hexane/ isopropanol = 90:10,

flow rate 1.0 mL/min, 25 °C, t_r (major) = 16.4 min, t_r (minor) = 17.6 min). $[\alpha]_D^{22}$ = +7.0° (*c* 1.0, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, *J* = 2.1 Hz, 1H), 7.55-7.43 (m, 3H), 7.37-7.29 (m, 3H), 6.91 (d, *J* = 8.4 Hz, 1H), 5.62 (s, 1H), 3.90 (s, 3H), 2.39 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.9, 134.3, 131.8, 131.7, 128.7, 128.3, 127.0, 122.2, 111.8, 111.7, 88.3, 86.9, 64.0, 56.3. IR (film): ν (cm^{-1}) 3360, 2839, 2200, 1596, 1491, 1442, 1402, 1257, 1183, 1150, 1050, 1018, 965, 890, 858, 814, 753, 683, 618, 569, 524, 471, 434. HRMS (ESI, *m*/*z*) calcd for $C_{16}H_{12}BrO$ $[M+H-H_2O]^+$: 299.0066, found: 299.0067.

(R)-3-Phenyl-1-(3,4,5-trimethoxyphenyl)prop-2-yn-1-ol ***(6l)***.[10n] Starting from 3,4,5-trimethoxybenzaldehyde (39.2 mg, 0.20 mmol), phenylacetylene (61.3 mg, 0.60 mmol) and Δ-**RhS(Ad)** (4.1 mg, 0.004 mmol), according to the general procedure, reacting at room temperature for 24 hours to give **6l** as a white solid (54.3 mg, 0.182 mmol, yield: 91%). R_f = 0.3 (30% ethyl acetate in *n*-hexane). Enantiomeric excess established by HPLC analysis using a Daicel Chiralcel AS-H column, ee = 98% (HPLC: AS-H, 254 nm, *n*-hexane/ isopropanol = 80:20, flow rate 1.0 mL/min, 25 °C, t_r (major) = 14.3 min, t_r (minor) = 15.6 min). $[\alpha]_D^{22}$ = +8.8° (*c* 1.0, $CHCl_3$). Lit.[10n]: $[\alpha]_D^{19}$ = –6.1° (*c* 1.3, $CHCl_3$, 82% ee for *S*-configuration). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51-7.43 (m, 2H), 7.37-7.31 (m, 3H), 6.86 (s, 2H), 5.64 (d, *J* = 5.9 Hz, 1H), 3.89 (s, 6H), 3.86 (s, 3H), 2.39 (d, *J* = 5.9 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.4, 138.1, 136.3, 131.7, 128.7, 128.4, 122.3, 103.8, 88.6, 86.7, 65.2, 60.8, 56.2. IR (film): ν (cm^{-1}) 3311, 2931, 2839, 2219, 1592, 1502, 1458, 1416, 1325, 1239, 1187, 1070, 1035, 998, 917, 841, 754, 687, 529, 487. HRMS (ESI, *m*/*z*) calcd for $C_{18}H_{18}O_4Na$ $[M+Na]^+$: 321.1097, found: 321.1097.

(R)-1-(4-(Methylthio)phenyl)-3-phenylprop-2-yn-1-ol ***(6m)***. Starting from 4-(methylthio)

benzaldehyde (30.4 mg, 0.20 mmol), phenylacetylene (61.3 mg, 0.60 mmol) and Δ-**RhS(Ad)** (4.1 mg, 0.004 mmol), according to the general procedure, reacting at room temperature for 48 hours to give **6m** as a pale yellow oil (40.7 mg, 0.16 mmol, yield: 80%); R_f = 0.3 (20% ethyl acetate in *n*-hexane). Enantiomeric excess established by HPLC analysis using a Daicel Chiralcel AS-H column, ee = 93% (HPLC: AS-H, 254 nm, *n*-hexane/ isopropanol = 90:10, flow rate 1.0 mL/min, 25 °C, t_r (major) = 20.3 min, t_r (minor) = 22.4 min). $[\alpha]_D^{22}$ = +5.0° (*c* 1.0, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53-7.47 (m, 2H), 7.46-7.39 (m, 2H), 7.33-7.21 (m, 5H), 5.61 (d, *J* = 5.2 Hz, 1H), 2.46 (s, 3H), 2.36 (d, *J* = 5.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.9, 137.5, 131.7, 128.6, 128.3, 127.3, 126.7, 122.4, 88.6, 86.7, 64.7, 15.8. IR (film): *v* (cm^{-1}) 3355, 2917, 2850, 2224, 1594, 1486, 1414, 1288, 1263, 1183, 1090, 1019, 957, 815 750, 685, 599, 549, 518, 467. HRMS (ESI, *m*/*z*) calcd for $C_{16}H_{13}S$ $[M+H-H_2O]^+$: 237.0372, found: 237.0373.

*(S)-3-Phenyl-1-(o-tolyl)prop-2-yn-1-ol (**6n**).*[16] Starting from 2-methylbenzaldehyde (24.0 mg, 0.20 mmol), phenylacetylene (61.3 mg, 0.60 mmol) and Δ-**RhS(Ad)** (4.1 mg, 0.004 mmol), according to the general procedure, reacting at room temperature for 48 hours to give **6n** as a pale yellow oil (25.7 mg, 0.116 mmol, yield: 58%). R_f = 0.3 (20% ethyl acetate in *n*-hexane). Enantiomeric excess established by HPLC analysis using a Daicel Chiralcel OD-H column, ee = 90% (HPLC: OD-H, 254 nm, *n*-hexane/ isopropanol = 90:10, flow rate 1.0 mL/min, 25 °C, t_r (major) = 10.0 min, t_r (minor) = 20.2 min). $[\alpha]_D^{22}$ = –9.8° (*c* 1.0, $CHCl_3$). Lit.[16]: $[\alpha]_D^{20}$ = +11.9° (*c* 1.0, $CHCl_3$, 95% ee for *R*-configuration). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67-7.59 (m, 2H), 7.51-7.43 (m, 2H), 7.39-7.25 (m, 6H), 5.85 (d, *J* = 5.2 Hz, 1H), 2.51 (s, 3H), 2.18 (d, *J* = 5.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.4, 136.0, 131.7, 130.8, 128.53, 128.46, 128.3, 126.6, 126.3, 122.5,

88.5, 86.5, 63.0, 19.0. IR (film): ν (cm^{-1}) 3058, 2904, 2228, 1488, 1444, 1185, 1028, 959, 911, 755, 721, 690, 641, 576, 547, 521. HRMS (FD, *m*/*z*) calcd for $C_{16}H_{14}O[M]^+$:222.1045, found: 222.1045.

*(R)-1,3-Diphenylprop-2-yn-1-ol (**6o**).*[14] Starting from benzaldehyde (21.2 mg, 0.20 mmol), phenylacetylene (61.3 mg, 0.60 mmol) and Δ-**RhS(Ad)** (4.1 mg, 0.004 mmol), according to the general procedure, reacting at room temperature for 48 hours to give **6o** as a pale yellow oil (34.1 mg, 0.164 mmol, yield: 82%). R_f = 0.3 (20% ethyl acetate in *n*-hexane). Enantiomeric excess established by HPLC analysis using a Daicel Chiralcel AS-H column, ee = 85% (HPLC: AS-H, 254 nm, *n*-hexane/ isopropanol = 92:8, flow rate 1.0 mL/min, 25 °C, t_r (major) = 14.1 min, t_r (minor) = 15.0 min). $[\alpha]_D^{22}$ = +4.8° (*c* 1.0, EtOH). Lit.[14]: $[\alpha]_D^{20}$ = +7.5° (*c* 1.0, EtOH, 93% ee for *R*-configuration). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67-7.59 (m, 2H), 7.55-7.31 (m, 8H), 5.71 (d, *J* = 5.8 Hz, 1H), 2.37 (d, *J* = 5.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.6, 131.7, 128.7, 128.6, 128.4, 128.3, 126.7, 122.4, 88.7, 86.7, 65.1. IR (film): ν (cm^{-1}) 3059, 2904, 2233, 1489, 1447, 1185, 1022, 959, 915, 754, 723, 690, 638, 577, 547, 521. HRMS (ESI, *m*/*z*) calcd for $C_{15}H_{11}$ $[M+H-H_2O]^+$:191.0855, found: 191.0855.

*(S)-1-(4-Bromothiophen-2-yl)-3-phenylprop-2-yn-1-ol (**6p**).* Starting from benzaldehyde (21.2 mg, 0.20 mmol), phenylacetylene (61.3 mg, 0.60 mmol) and Δ-**RhS(Ad)** (4.1 mg, 0.004 mmol), according to the general procedure, reacting at room temperature for 48 hours to give **6p** as a brown oil (48.1 mg, 0.164 mmol, yield: 82%). R_f = 0.3 (20% ethyl acetate in *n*-hexane). Enantiomeric excess established by HPLC analysis using a Daicel Chiralcel AS-H column, ee = 85% (HPLC: AS-H, 254 nm, *n*-hexane/ isopropanol = 90:10, flow rate 1.0 mL/min, 25 °C, t_r (major) = 10.7 min, t_r (minor) = 11.9 min). $[\alpha]_D^{25}$ = –12.2° (*c* 1.0, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52-7.44 (m,

2H), 7.41-7.29 (m, 3H), 7.24-7.14 (m, 2H), 5.83 (s, 1H), 2.71 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.8, 131.8, 129.0, 128.4, 128.1, 123.2, 121.7, 109.3, 87.1, 86.6, 60.5. IR (film): ν (cm^{-1}) 3544, 3059, 3031, 2222, 1489, 1448, 1185, 1022, 959, 916, 754, 723, 690, 638, 577, 547, 521. HRMS (FD, *m*/*z*) calcd for $C_{13}H_9BrOS$ $[M]^+$: 291.9557, found: 291.9539.

*(R)-1,4-Diphenylbut-3-yn-2-ol (**6q**).*[19] Starting from phenylacetaldehyde (24.0 mg, 0.20 mmol), phenylacetylene (61.3 mg, 0.60 mmol) and Δ-**RhS(Ad)** (2.0 mg, 0.002 mmol), according to the general procedure, reacting at room temperature for 24 hours to give **6q** as a pale yellow oil (40.9 mg, 0.184 mmol, yield: 92%). R_f = 0.3 (10% ethyl acetate in *n*-hexane). Enantiomeric excess established by HPLC analysis using a Daicel Chiralcel AS-H column, ee = 26% (HPLC: AS-H, 254 nm, *n*-hexane/ isopropanol = 95:5, flow rate 1.0 mL/min, 25 °C, t_r (major) = 14.4 min, t_r (minor) = 13.5 min). $[\alpha]_D^{22}$ = +4.0° (*c* 1.0, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44-7.38 (m, 2H), 7.37-7.27 (m, 8H), 4.82 (q, *J* = 6.1, 1H), 3.14 (dd, *J* = 15.2, 6.1 Hz, 1H), 3.09 (dd, *J* = 15.2, 6.5 Hz, 1H), 1.96 (d, *J* = 6.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.5, 131.6, 129.9, 128.5, 128.4, 128.3, 127.0, 122.5, 89.4, 85.8, 63.7, 44.2. IR (film): ν (cm^{-1}) 3362, 3028, 2923, 2219, 1598, 1490, 1446, 1386, 1336, 1256, 1025, 968, 914, 752, 692, 615, 543, 473. HRMS (ESI, *m*/*z*) calcd for $C_{16}H_{14}ONa$ $[M+Na]^+$: 245.0937, found: 245.0938.

*(R)-1-Phenyloct-1-yn-3-ol (**6r**).*[17] Starting from hexanal (20.0 mg, 0.20 mmol), phenylacetylene (61.3 mg, 0.60 mmol) and Δ-**RhS(Ad)** (2.0 mg, 0.002 mmol), according to the general procedure, reacting at room temperature for 24 hours to give **6p** as a pale yellow oil (37.6 mg, 0.186 mmol, yield: 93%). R_f = 0.3 (5% ethyl acetate in *n*-hexane). Enantiomeric excess established by HPLC analysis using a Daicel Chiralcel AD-H column, ee = 4% (HPLC: AD-H, 254 nm, *n*-hexane/

isopropanol = 99:1, flow rate 1.0 mL/min, 25 °C, t_r (minor) = 44.7 min, t_r (major) = 57.8 min). $[\alpha]_D^{22}$ = –1.2° (*c* 1.0, $CHCl_3$). Lit.[17]: $[\alpha]_D^{23}$ = –4.8° (*c* 2.1, $CHCl_3$, 96% ee for *R*-configuration). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47-7.39 (m, 2H), 7.34-7.28 (m, 3H), 4.65-4.55 (m, 1H), 1.97 (d, J = 4.4 Hz, 1H), 1.86-1.78 (m, 2H), 1.59-1.45 (m, 2H), 1.43-1.29 (m, 4H), 0.92 (t, J = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.6, 128.3, 128.2, 122.7, 90.3, 84.8, 63.0, 37.9, 31.5, 24.9, 22.6, 14.0. IR (film): ν (cm^{-1}) 3356, 2928, 2861, 2214, 1598, 1490, 1449, 1060, 1023, 754, 690, 556, 523. HRMS (FD, *m*/*z*) calcd for $C_{14}H_{18}O$ $[M]^+$: 202.1358, found: 202.1332.

*(S)-1-(Perfluorophenyl)-3-(p-tolyl)prop-2-yn-1-ol (**6s**).* Starting from pentafluorobenzaldehyde (39.2 mg, 0.20 mmol), 4-ethynyltoluene (69.7 mg, 0.60 mmol) and Δ-**RhS(Ad)** (2.0 mg, 0.002 mmol), according to the general procedure, reacting at room temperature for 24 hours to give **6s** as a white solid (59.3 mg, 0.19 mmol, yield: 95%). R_f = 0.3 (10% ethyl acetate in *n*-hexane). Enantiomeric excess established by HPLC analysis using a Daicel Chiralcel AS-H column, ee = 95% (HPLC: AS-H, 254 nm, *n*-hexane/ isopropanol = 95:5, flow rate 1.0 mL/min, 25 °C, t_r (major) = 7.3 min, t_r (minor) = 9.1 min). $[\alpha]_D^{22}$ = –11.2° (*c* 1.0, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37-7.29 (m, 2H), 7.17-7.09 (m, 2H), 5.96 (d, J = 7.9 Hz, 1H), 2.68 (d, J = 7.9 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.4, 131.8, 129.2, 118.4, 87.0, 84.8, 55.5, 21.5. ^{19}F NMR (282 MHz, $CDCl_3$) δ –143.44 - –143.56 (m, 2F), –153.78 - –153.98 (m, 1F), –161.18 - –161.46 (m, 2F). IR: 8183, 2218, 1651, 1498, 1292, 1118, 1041, 985, 912, 814, 789, 652, 553, 526, 411. HRMS (ESI, *m*/*z*) calcd for $C_{16}H_8F_5$ $[M+H-H_2O]^+$: 295.0541, found: 295.0542.

*(S)-1-(Perfluorophenyl)-3-(m-tolyl)prop-2-yn-1-ol (**6t**).* Starting from pentafluorobenzaldehyde (39.2 mg, 0.20 mmol), 3-ethynyltoluene (69.7 mg, 0.60 mmol) and Δ-**RhS(Ad)** (2.0 mg, 0.002

mmol), according to the general procedure, reacting at room temperature for 24 hours to give **6t** as a white solid (59.9 mg, 0.192 mmol, yield: 96%). R_f = 0.3 (10% ethyl acetate in *n*-hexane). Enantiomeric excess established by HPLC analysis using a Daicel Chiralcel AS-H column, ee = 96% (HPLC: AS-H, 254 nm, *n*-hexane/ isopropanol = 95:5, flow rate 1.0 mL/min, 25 °C, t_r (major) = 7.1 min, t_r (minor) = 13.1 min). $[\alpha]_D^{22}$ = –7.0° (*c* 1.0, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.17 (m, 4H), 6.02 (d, *J* = 8.0 Hz, 1H), 2.76 (d, *J* = 8.0 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.2, 132.4, 130.0, 128.9, 128.3, 121.3, 86.9, 85.1, 55.5, 21.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ –143.38 - –143.56 (m, 2F), –153.62 - –153.88 (m, 1F), –161.16 - –161.44 (m, 2F). IR (film): *v* (cm^{-1}) 3299, 2929, 2218, 1651, 1506, 1422 1120, 991, 930, 783, 689, 648, 484. HRMS (ESI, *m*/*z*) calcd for $C_{16}H_8F_5$ $[M+H-H_2O]^+$: 295.0541, found: 295.0542.

*(S)-1-(Perfluorophenyl)-3-(o-tolyl)prop-2-yn-1-ol (**6u**)*. Starting from pentafluorobenzaldehyde (39.2 mg, 0.20 mmol), 2-ethynyltoluene (69.7 mg, 0.60 mmol) and Δ-**RhS(Ad)** (4.0 mg, 0.004 mmol), according to the general procedure, reacting at room temperature for 24 hours to give **6u** as a white solid (49.9 mg, 0.16 mmol, yield: 80%). R_f = 0.3 (10% ethyl acetate in *n*-hexane). Enantiomeric excess established by HPLC analysis using a Daicel Chiralcel AS-H column, ee = 92% (HPLC: AS-H, 254 nm, *n*-hexane/ isopropanol = 95:5, flow rate 1.0 mL/min, 25 °C, t_r (major) = 6.5 min, t_r (minor) = 9.8 min). $[\alpha]_D^{22}$ = –6.4° (*c* 1.0, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43-7.37 (m, 1H), 7.29-7.11 (m, 3H), 6.02 (d, *J* = 8.0 Hz, 1H), 2.71 (d, *J* = 8.0 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.7, 132.3, 129.6, 129.2, 125.6, 121.3, 89.3, 85.8, 55.5, 20.5. ^{19}F NMR (282 MHz, $CDCl_3$) δ –143.28 - –143.46 (m, 2F), –153.56 - –153.68 (m, 1F), –161.06 - –161.32 (m, 2F). IR (film): *v* (cm^{-1}) 3343, 2958, 2232, 1652, 1504, 1456, 1423, 1335, 1283, 1120,

1021, 990, 917, 816, 754, 711, 649, 553, 452. HRMS (ESI, *m*/*z*) calcd for $C_{16}H_8F_5$ $[M+H-H_2O]^+$: 295.0541, found: 295.0542.

*(S)-3-(4-(tert-Butyl)phenyl)-1-(perfluorophenyl)prop-2-yn-1-ol (**6v1**).* Starting from pentafluoro benzaldehyde (39.2 mg, 0.20 mmol), 4-*tert*-butylphenylacetylene (94.9 mg, 0.60 mmol) and Δ-**RhS(Ad)** (2.0 mg, 0.002 mmol), according to the general procedure, reacting at room temperature for 24 hours to give **6v1** as a white solid (69.4 mg, 0.196 mmol, yield: 98%). R_f = 0.3 (10% ethyl acetate in *n*-hexane). Enantiomeric excess established by HPLC analysis using a Daicel Chiralcel AS-H column, ee = 96% (HPLC: AS-H, 254 nm, *n*-hexane/ isopropanol = 95:5, flow rate 1.0 mL/min, 25 °C, t_r (major) = 5.8 min, t_r (minor) = 8.6 min). $[\alpha]_D^{22}$ = –21.4° (*c* 1.0, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.30 (m, 4H), 5.97 (d, *J* = 8.0 Hz, 1H), 2.71 (d, *J* = 8.0 Hz, 1H), 1.31 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.6, 131.6, 125.4, 118.5, 87.0, 84.9, 55.5, 34.8, 31.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ –143.40 - –143.58 (m, 2F), –153.78 - –154.00 (m, 1F), –161.18 - –161.52 (m, 2F). IR (film): *v* (cm^{-1}) 3375, 2964, 2870, 2234, 1652, 1500, 1419, 1296, 1118, 1035, 987, 915, 835, 799, 667, 640, 565, 478. HRMS (ESI, *m*/*z*) calcd for $C_{19}H_{14}F_5$ $[M+H-H_2O]^+$: 337.1010, found: 337.1012.

*(R)-3-(4-(tert-Butyl)phenyl)-1-phenylprop-2-yn-1-ol (**6v2**).* Starting from benzaldehyde (21.2 mg, 0.20 mmol), 4-*tert*-butylphenylacetylene (94.9 mg, 0.60 mmol) and Δ-**RhS(Ad)** (4.1 mg, 0.004 mmol), according to the general procedure, reacting at room temperature for 48 hours to give **6v2** as a pale yellow oil (44.5 mg, 0.17 mmol, yield: 85%). R_f = 0.3 (10% ethyl acetate in *n*-hexane). Enantiomeric excess established by HPLC analysis using a Daicel Chiralcel OD-H column, ee = 84% (HPLC: OD-H, 254 nm, *n*-hexane/ isopropanol = 90:10, flow rate 1.0 mL/min, 25 °C, t_r (major)

= 9.6 min, t_r (minor) = 7.5 min). $[\alpha]_D^{22}$ = +3.4° (*c* 1.0, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66-7.59 (m, 2H), 7.44-7.36 (m, 7H), 5.70 (d, *J* = 6.0 Hz, 1H), 2.71 (d, *J* = 6.0 Hz, 1H), 1.32 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.9, 140.8, 131.5, 128.6, 128.4, 126.8, 125.3, 119.4, 88.0, 86.9, 65.2, 84.8, 31.1. IR (film): *v* (cm^{-1}) 3346, 2961, 2868, 2230, 1648, 1419, 1296, 1256, 1028, 968, 914, 752, 692, 615, 541, 475. HRMS (ESI, *m*/*z*) calcd for $C_{19}H_{20}ONa$ $[M+Na]^+$: 287.1406, found: 287.1411.

*(S)-3-(4-Fluorophenyl)-1-(perfluorophenyl)prop-2-yn-1-ol (**6w**).* Starting from pentafluoro benzaldehyde (39.2 mg, 0.20 mmol), 4-fluorophenylacetylene (72.1 mg, 0.60 mmol) and Δ-**RhS(Ad)** (2.0 mg, 0.002 mmol), according to the general procedure, reacting at room temperature for 24 hours to give **6w** as a white solid (60.1 mg, 0.190 mmol, yield: 95%). R_f = 0.3 (10% ethyl acetate in *n*-hexane). Enantiomeric excess established by HPLC analysis using a Daicel Chiralcel AS-H column, ee = 96% (HPLC: AS-H, 254 nm, *n*-hexane/ isopropanol = 95:5, flow rate 1.0 mL/min, 25 °C, t_r (major) = 9.9 min, t_r (minor) = 13.9 min). $[\alpha]_D^{22}$ = –8.6° (*c* 1.0, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49-7.39 (m, 2H), 7.09-6.97 (m, 2H), 5.96 (d, *J* = 8.0 Hz, 1H), 2.74 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.0 (d, *J* = 251.0 Hz), 133.9 (d, *J* = 8.5 Hz), 117.6 (d, *J* = 3.5 Hz, 1H), 115.8 (d, *J* = 2.3 Hz, 1H), 85.6, 85.3, 55.3. ^{19}F NMR (282 MHz, $CDCl_3$) δ –109.36 (1F), –143.36 - –143.58 (m, 2F), –153.44 - –153.66 (m, 1F), –161.06 - –161.32 (m, 2F). IR (film): *v* (cm^{-1}) 3200, 2219, 1653, 1599, 1499, 1421, 1337, 1296, 1229, 1151, 1121, 1032, 985, 913, 836, 791, 747, 654, 553, 464. HRMS (FD, *m*/*z*) calcd for $C_{15}H_6F_6O$ $[M]^+$: 316.0323, found: 316.0319.

*(S)-3-(4-Methoxyphenyl)-1-(perfluorophenyl)prop-2-yn-1-ol (**6x1**).*[20] Starting from pentafluoro

benzaldehyde (39.2 mg, 0.20 mmol), 4-methoxylphenylacetylene (79.3 mg, 0.60 mmol) and Δ-**RhS(Ad)** (2.0 mg, 0.002 mmol), according to the general procedure, reacting at room temperature for 24 hours to give **6x1** as a white solid (64.3 mg, 0.196 mmol, yield: 98%). R_f = 0.3 (30% ethyl acetate in *n*-hexane). Enantiomeric excess established by HPLC analysis using a Daicel Chiralcel AS-H column, ee = 94% (HPLC: AS-H, 254 nm, *n*-hexane/ isopropanol = 92:8, flow rate 1.0 mL/min, 25 °C, t_r (major) = 11.8 min, t_r (minor) = 10.5 min). $[\alpha]_D^{22}$ = –7.8° (*c* 1.0, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.34 (m, 2H), 6.87-6.81 (m, 2H), 5.95 (d, *J* = 8.0 Hz, 1H), 3.81 (s, 3H), 2.74 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.2, 133.4, 114.0, 113.5, 86.8, 84.3, 55.5, 55.3. ^{19}F NMR (282 MHz, $CDCl_3$) δ –143.34 - –143.52 (m, 2F), –153.78 - –154.02 (m, 1F), –161.18 - –161.44 (m, 2F). IR (film): ν (cm^{-1}) 3299, 2230, 1654, 1504, 1503, 1416, 1331, 1294, 1250, 1176, 1120, 1028, 990, 910, 830, 785, 646, 535, 481, 444. HRMS (ESI, *m*/*z*) calcd for $C_{16}H_8F_5O$ $[M+H-H_2O]^+$: 311.0490, found: 311.0490.

(R)-3-(4-Methoxyphenyl)-1-(3,4,5-trimethoxyphenyl)prop-2-yn-1-ol ***(6x2)***. Starting from 3,4,5-trimethoxybenzaldehyde (39.2 mg, 0.20 mmol), 4-methoxylphenylacetylene (79.3 mg, 0.60 mmol) and Δ-**RhS(Ad)** (4.1 mg, 0.004 mmol), according to the general procedure, reacting at room temperature for 48 hours to give **6x2** as a white solid (64.3 mg, 0.196 mmol, yield: 98%). R_f = 0.3 (40% ethyl acetate in *n*-hexane). Enantiomeric excess established by HPLC analysis using a Daicel Chiralcel AS-H column, ee = 97% (HPLC: AS-H, 254 nm, *n*-hexane/ isopropanol =80:20, flow rate 1.0 mL/min, 25 °C, t_r (major) = 17.3 min, t_r (minor) = 14.7 min). $[\alpha]_D^{22}$ = +2.4° (*c* 1.0, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45-7.37 (m, 2H), 6.87-6.79 (m, 4H), 5.61 (s, 1H), 3.89 (s, 6H), 3.85 (s, 3H), 3.81 (s, 3H), 2.50 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.9, 153.3, 138.0, 1365, 133.2,

114.4, 114.0, 103.8, 87.3, 86.6, 65.2, 60.8, 56.1, 55.3. IR (film): ν (cm^{-1}) 2928, 2832, 2228, 1596, 1503, 1457, 1328, 1290, 1241, 1180, 1121, 1038, 1001, 834, 725, 646, 534. HRMS (ESI, *m*/*z*) calcd for $C_{19}H_{20}O_5Na$ $[M+Na]^+$: 351.1203, found: 351.1203.

*(S)-1-(Perfluorophenyl)-3-(thiophen-3-yl)prop-2-yn-1-ol (**6y**).* Starting from pentafluoro benzaldehyde (39.2 mg, 0.20 mmol), 3-ethynylthiophene (64.9 mg, 0.60 mmol) and Δ-**RhS(Ad)** (2.0 mg, 0.002 mmol), according to the general procedure, reacting at room temperature for 24 hours to give **6y** as a white solid (54.7 mg, 0.18 mmol, yield: 90%). R_f = 0.3 (10% ethyl acetate in *n*-hexane). Enantiomeric excess established by HPLC analysis using a Daicel Chiralcel AS-H column, ee = 95% (HPLC: AS-H, 254 nm, *n*-hexane/ isopropanol = 95:5, flow rate 1.0 mL/min, 25 °C, t_r (major) = 11.9 min, t_r (minor) = 18.7 min). $[\alpha]_D^{22}$ = –6.8° (*c* 1.0, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53-7.45 (m, 1H), 7.29-7.23 (m, 1H), 7.13-7.07 (m, 1H), 5.95 (d, *J* = 7.0 Hz, 1H), 2.70 (d, *J* = 7.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 130.1, 129.7, 125.6, 120.6, 85.2, 82.0, 55.5. ^{19}F NMR (282 MHz, $CDCl_3$) δ –143.38 - –143.56 (m, 2F), –153.58 - –153.86 (m, 1F), –161.08 - –161.42 (m, 2F). IR (film): ν (cm^{-1}) 3169, 2238, 1653, 1499, 1421, 1389, 1333, 1287, 1181, 1119, 1047, 986, 936, 887, 824, 783, 739, 693, 627, 572, 482. HRMS (FD, *m*/*z*) calcd for $C_{13}H_5F_5OS$ $[M]^+$: 303.9976, found: 303.9981.

*(S)-3-(Cyclohex-1-en-1-yl)-1-(perfluorophenyl)prop-2-yn-1-ol (**6z**).* Starting from pentafluoro benzaldehyde (39.2 mg, 0.20 mmol), 1-ethynylcyclohex-1-ene (63.7 mg, 0.60 mmol) and Δ-**RhS(Ad)** (2.0 mg, 0.002 mmol), according to the general procedure, reacting at room temperature for 24 hours to give **6z** as a white solid (57.4 mg, 0.19 mmol, yield: 95%). R_f = 0.3 (10% ethyl acetate in *n*-hexane). Enantiomeric excess established by HPLC analysis using a Daicel

Chiralcel AS-H column, ee = 94% (HPLC: AS-H, 254 nm, *n*-hexane/ isopropanol = 95:5, flow rate 1.0 mL/min, 25 °C, t_r (major) = 7.5 min, t_r (minor) = 14.2 min). $[\alpha]_D^{22}$ = –6.2° (*c* 1.0, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.21-6.13 (m, 1H), 5.85 (s, 1H), 2.58 (s, 1H), 2.13-2.05 (m, 4H), 1.69-1.51 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.1, 119.5, 88.6, 82.9, 55.4, 28.7, 25.6, 22.1, 21.3. ^{19}F NMR (282 MHz, $CDCl_3$) δ –143.56 - –143.78 (m, 2F), –154.14 - –154.38 (m, 1F), –161.40 - –161.72 (m, 2F). IR (film): ν (cm^{-1}) 3206, 2930, 2861, 2225, 1652, 1500, 1338, 1288, 1207, 1117, 1042, 989, 851, 846, 794, 755, 725, 642, 577, 457. HRMS (ESI, *m*/*z*) calcd for $C_{15}H_{10}F_5$ $[M+H-H_2O]^+$: 285.0697, found: 285.0698.

*(S)-1-(Perfluorophenyl)hept-2-yn-1-ol (**6aa1**).* Starting from pentafluorobenzaldehyde (39.2 mg, 0.20 mmol), 1-hexyne (49.3 mg, 0.60 mmol) and Δ-**RhS(Ad)** (2.0 mg, 0.002 mmol), according to the general procedure, reacting at room temperature for 24 hours to give **6aa1** as a white solid (51.2 mg, 0.184 mmol, yield: 92%). R_f = 0.3 (5% ethyl acetate in *n*-hexane). Enantiomeric excess established by HPLC analysis using a Daicel Chiralpak AS-H column, ee = 94% (HPLC: AS-H, 254 nm, *n*-hexane/ isopropanol = 98:2, flow rate 1.0 mL/min, 25 °C, t_r (major) = 7.0 min, t_r (minor) = 7.9 min). $[\alpha]_D^{22}$ = +6.0° (*c* 1.0, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.77-5.68 (m, 1H), 2.56 (d, *J* = 7.9 Hz, 1H), 2.22 (td, *J* = 7.0, 2.0 Hz, 2H), 1.56-1.32 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.3 (m), 142.9 (m), 139.3 (m), 136.0 (m), 115.7 (m), 88.2 (2C), 55.2, 30.3, 21.9, 18.4, 13.4. ^{19}F NMR (282 MHz, $CDCl_3$) δ –143.80 - –143.98 (m, 2F), –154.36 - –154.58 (m, 1F), –161.52 - –161.86 (m, 2F). IR (film): ν (cm^{-1}) 3342, 2961, 2936, 2870, 2232, 1652, 1502, 1424, 1387, 1301, 1147, 1115, 1023, 990, 936, 809, 722, 659, 639, 575, 491. HRMS (FD, *m*/*z*) calcd for $C_{13}H_{10}F_5O$ $[M+H-H_2O]^+$: 261.0703, found: 261.0694.

(R)-1-(3,4,5-Trimethoxyphenyl)hept-2-yn-1-ol ***(6aa2)***. Starting from 3,4,5-trimethoxybenzaldehyde (39.2 mg, 0.20 mmol), 1-hexyne (49.3 mg, 0.60 mmol) and Δ-**RhS(Ad)** (4.1 mg, 0.004 mmol), according to the general procedure, reacting at room temperature for 48 hours to give **6aa2** as a white solid (42.8 mg, 0.154 mmol, yield: 77%). R_f = 0.3 (25% ethyl acetate in *n*-hexane). Enantiomeric excess established by HPLC analysis using a Daicel Chiralpak IA column, ee = 95% (HPLC: IA, 254 nm, *n*-hexane/ isopropanol = 85:15, flow rate 1.0 mL/min, 25 °C, t_r (major) = 9.7 min, t_r (minor) = 9.2 min). $[\alpha]_D^{22}$ = +3.6° (*c* 1.0, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.79 (s, 2H), 5.38 (d, *J* = 5.8 Hz, 1H), 3.87 (s, 6H), 3.83 (s, 3H), 2.90 (td, 7.0, 2.0 Hz, 2H), 2.20 (d, *J* = 5.8 Hz, 1H), 1.59-1.33 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.2, 137.8, 136.9, 103.7, 87.7, 79.9, 64.9, 60.8, 56.1, 30.6, 21.9, 18.5, 13.5. IR (film): *v* (cm^{-1}) 3329, 2943, 2922, 2224, 1658, 1501, 1438, 1391, 1144, 1025, 996, 812, 732, 659, 577, 493. HRMS (ESI, *m*/*z*) calcd for $C_{16}H_{21}O_3$ $[M+H-H_2O]^+$: 261.1485, found: 261.1486.

(S)-4,4-Dimethyl-1-(perfluorophenyl)pent-2-yn-1-ol ***(6ab)***. Starting from pentafluorobenzaldehyde (39.2 mg, 0.20 mmol), 3,3-dimethylbut-1-yne (49.3 mg, 0.60 mmol) and Δ-**RhS(Ad)** (2.0 mg, 0.002 mmol), according to the general procedure, reacting at room temperature for 24 hours to give **6ab** as a white solid (45.6 mg, 0.164 mmol, yield: 82%). R_f = 0.3 (5% ethyl acetate in *n*-hexane). Enantiomeric excess established by HPLC analysis using a Daicel Chiralpak OD-H column, ee = 90% (HPLC: OD-H, 254 nm, *n*-hexane/ isopropanol = 99:1, flow rate 1.0 mL/min, 25 °C, t_r (major) = 6.7 min, t_r (minor) = 6.1 min). $[\alpha]_D^{22}$ = +4.2° (*c* 1.0, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.71 (d, *J* = 7.8 Hz, 1H), 2.51 (d, *J* = 7.8 Hz, 1H), 1.21 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 96.0, 75.7, 55.1, 30.6, 27.5. ^{19}F NMR (282 MHz, $CDCl_3$) δ –143.74 -

–143.86 (m, 2F), –154.35 - –154.50 (m, 1F), –161.59 - –161.79 (m, 2F). IR (film): ν (cm^{-1}) 3321, 2958, 2922, 2876, 2230, 1648, 1501, 1416, 1309, 1113, 1029, 991, 814, 720, 659, 577, 490. HRMS (FD, *m*/*z*) calcd for $C_{13}H_{11}F_5O$ $[M]^+$: 278.0730, found: 278.0731.

(R)-1-(Perfluorophenyl)-3-(trimethylsilyl)prop-2-yn-1-ol ***(6ac)***. Starting from pentafluoro benzaldehyde (39.2 mg, 0.20 mmol), ethynyltrimethylsilane (58.9 mg, 0.60 mmol) and Δ-**RhS(Ad)** (2.0 mg, 0.002 mmol), according to the general procedure, reacting at room temperature for 24 hours to give **6ac** as a white solid (48.7 mg, 0.166 mmol, yield: 83%). R_f = 0.3 (5% ethyl acetate in *n*-hexane). Enantiomeric excess established by HPLC analysis using a Daicel Chiralcel AS-H column, ee = 91% (HPLC: AS-H, 254 nm, *n*-hexane/ isopropanol = 95:5, flow rate 1.0 mL/min, 25 °C, t_r (major) = 5.0 min, t_r (minor) = 5.4 min). $[\alpha]_D^{22}$ = +1.8° (*c* 1.0, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.72 (d, *J* = 7.8 Hz, 1H), 2.57 (d, *J* = 7.8 Hz, 1H). 0.18 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 101.3, 92.4, 55.3, 0.5. ^{19}F NMR (282 MHz, $CDCl_3$) δ –143.26 - –143.48 (m, 2F), –153.66 - –153.88 (m, 1F), –161.12 - –161.56 (m, 2F). IR (film): ν (cm^{-1}) 2928, 2218, 1708, 1653, 1505, 1422, 1333, 1304, 1252, 1123, 1053, 993, 914, 841, 793, 702, 648, 613. HRMS (FD, *m*/*z*) calcd for $C_{13}H_{11}F_3O$ $[M+H-H_2O]^+$: 277.0446, found: 277.0456.

(R)-1-(Perfluorophenyl)-3-(triisopropylsilyl)prop-2-yn-1-ol ***(6ad)***. Starting from pentafluoro benzaldehyde (39.2 mg, 0.20 mmol), ethynyltriisopropylsilane (109 mg, 0.60 mmol) and Δ-**RhS(Ad)** (2.0 mg, 0.002 mmol), according to the general procedure, reacting at room temperature for 24 hours to give **6ac** as pale yellow oil (61.2 mg, 0.162 mmol, yield: 81%). R_f = 0.3 (5% ethyl acetate in *n*-hexane). Enantiomeric excess established by HPLC analysis using a Daicel Chiralcel OD-H column, ee = 79% (HPLC: OD-H, 254 nm, *n*-hexane/ isopropanol = 99.5:0.5, flow rate 1.0 mL/min,

25 °C, t_r (major) = 16.7 min, t_r (minor) = 14.6 min). $[\alpha]_D^{22}$ = +3.2° (*c* 1.0, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.75 (d, J = 7.8 Hz, 1H), 2.57 (d, J = 7.8 Hz, 1H). 1.06 (s, 21H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 103.4, 89.2, 55.3, 18.4, 11.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ –143.36 - –143.50 (m, 2F), –153.66 - –153.86 (m, 1F), –161.30 - –161.52 (m, 2F). IR (film): ν (cm^{-1}) 2929, 2220, 1708, 1651, 1507, 1421, 1338, 1304, 1250, 1125, 1055, 991, 914, 845, 792, 708, 641, 577, 491. HRMS (FD, *m*/*z*) calcd for $C_{18}H_{23}F_5OSi$ $[M]^+$: 378.1438, found: 378.1421.

■ASSOCIATED CONTENT

^{1}H and ^{13}C NMR spectra of all compounds, HPLC traces, CD spectra of chiral rhodium complexes, crystallographic data of Λ-**RhS(Ad)**, and some additional reactions (PDF)

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Notes

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Hessen, Germany.

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