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Monomeric Cobalt Oxazoline Palladacycles (COP). Useful Catalysts for Catalytic Asymmetric Rearrangement of Allylic Trichloroacetimidates

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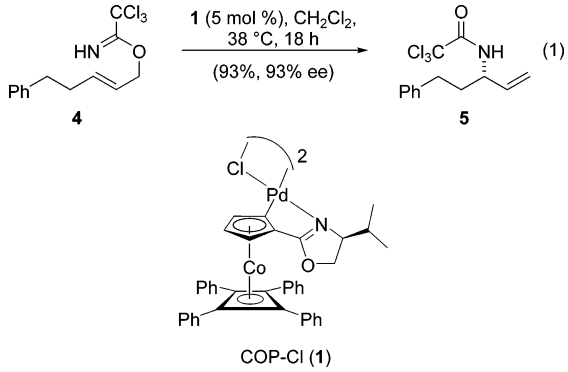
Abstract: Cobalt oxazoline palladacycles (COP) containing acetylacetonate and hexafluoroacetylacetonate ligands were prepared as catalysts for the asymmetric rearrangement of allylic trichloroacetimidates. These monomeric catalysts are more soluble than the previously described chloride-bridged dimer COP-Cl (**1**). COP-hfacac (**2**) provides rearranged allylic trichloroacetamides with high enantiomeric purities (91−98% ee) in solvents of widely varying polarities: cyclohexane, toluene, 1,2-dichloroethane, ethyl acetate, acetone, acetonitrile, and THF. The first single-crystal X-ray structure of a COP catalyst is also reported.

The rearrangement of allylic trichloroacetimidates to allylic trichloroacetamides is a widely used method for transforming readily available allylic alcohols to less available allylic amines.[1] This method has been employed as a central step in the synthesis of a variety of nitrogen-containing compounds, including alkaloids, antibiotics, amino sugars, and unnatural amino acids.[2] The rearrangement can be accomplished at elevated temperatures or at room temperature in the presence of some Hg(II)[1] or Pd(II) complexes.[3] Since the first report in 1997,[4] various Pd(II) complexes have been shown to catalyze the asymmetric rearrangement of prochiral *N*-arylimidates to chiral allylic *N*-arylamides.[4−6] Unfortunately, cleavage of these amides to deliver the parent allylic amines is typically not high-yielding.

We recently reported that the cobalt oxazoline palladacycle catalyst COP-Cl (**1**)[7] is an excellent catalyst for asymmetric rearrangement of allylic *N*-(*p*-methoxyphenyl)trifluoroacetimidates[8] and allylic trichloroacetimidates (eq 1).[9] This latter transformation is of particular



importance as the trichloroacetyl group can be removed in high yield from allylic trichloroacetamide products under basic, acidic, or reductive conditions.[1,2] However, the chloride-bridged dimer COP-Cl has limited solubility in solvents other than CH_2Cl_2. We disclose herein the synthesis of two new monomeric 2-(η^5-cyclopentadienyl)-(η^4-tetraphenylcyclobutadiene)cobalt oxazoline palladacycle catalysts **2** and **3**, which are soluble in a variety of solvents and perform well in transforming prochiral (*E*)-allylic trichloroacetimidates into transposed allylic trichloroacetamides of high enantiopurities. We also report the first single-crystal X-ray structure of a COP catalyst.

The starting material for preparing COP-hfacac (**2**) and COP-acac (**3**) is the acetate-bridged COP dimer **6**, which is available on a multigram scale from sodium cyclopentadienide, tris(triphenylphosphine)cobalt chloride, and diphenylacetylene using a modification[10] of a procedure originally reported by Stevens and Richards (Scheme 1).[11]

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(2) More than 180 publications report use of this rearrangement to prepare allylic amines and their analogues. (a) For a brief review, see: Ritter, K. Formation of C−N Bonds by Sigmatropic Rearrangements. In *Methods of Organic Chemistry (Houben-Weyl) Stereoselective Synthesis*, ed. 21; Helmchen, G., Hoffmann, R. W., Mulzer, J., Schaumann, E., Eds.; Georg Thieme: Stuttgart, 1996; Vol. 9, pp 5677−5689. Recent examples include: (b) Kim, S.; Lee, T.; Lee, E.; Lee, Ja.; Fan, G.-J.; Lee, S. K.; Kim, D. *J. Org. Chem.* **2004**, *69*, 3144−3149. (c) Jamieson, A. G.; Sutherland, A.; Willis, C. L. *Org. Biomol. Chem.* **2004**, *2*, 808−809. (d) Lurain, A. E.; Walsh, P. J. *J. Am. Chem. Soc.* **2003**, *125*, 10677−10683. (e) Reilly, M.; Anthony, D. R.; Gallagher, C. *Tetrahedron Lett.* **2003**, *44*, 2927−2930.

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(6) For a recent review, see: Nubbemeyer, U. *Synthesis* **2003**, 961−1008.

(7) Available from Aldrich Chemical Co.

(8) Overman, L. E.; Owen, C. E.; Pavan, M. M.; Richards, C. J. *Org. Lett.* **2003**, *5*, 1809−1812.

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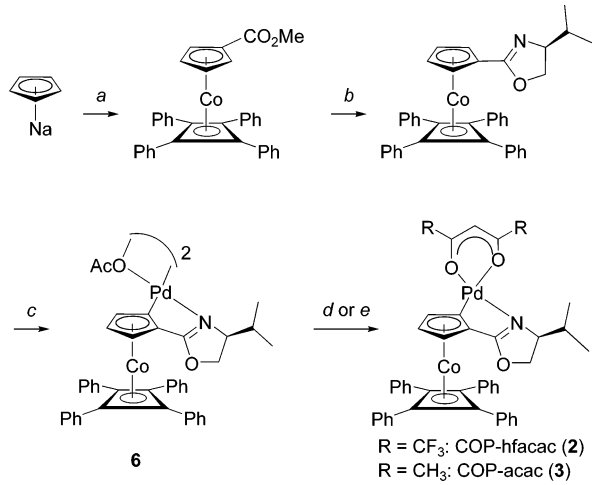
SCHEME 1. Synthesis of COP Catalysts 2 and 3[a]



[a] Reagents and conditions: (a) $C(O)(OMe)_2$, THF, reflux; then $CoCl(PPh_3)_3$, PhC≡CPh, PhMe, reflux, 68%; (b) (i) LiI, reflux (2,4,6-collidine), (ii) $(ClCO)_2$, cat. DMF, CH_2Cl_2, rt, (iii) (*S*)-valinol·HCl, Et_3N, CH_2Cl_2, rt; then MsCl, rt, 87%; (c) $Pd(OAc)_2$, HOAc, reflux, 95 °C; (d) $[CF_3COCH{=}C(O^-)CF_3]Na^+$, acetone/water, rt, 91%; (e) $[CH_3COCH{=}C(O^-)CH_3]Na^+$, acetone/water, rt, 98%.

Simple anion exchange of **6** by reaction with sodium hexafluoroacetylacetonate at room temperature in acetone/water gives the enantiopure monomeric hexafluoroacetylacetonate complex, (*S*)-COP-hfacac (**2**), in 91% yield. Similar treatment of **6** with sodium acetylacetonate yields (*S*)-COP-acac (**3**) in 98% yield. Catalysts **2** and **3** are obtained by simple collection of the orange precipitate and subsequent drying under vacuum. These complexes were used without further purification in the rearrangement reactions reported herein unless otherwise indicated.[12] COP-hfacac (**2**) and COP-acac (**3**) can be stored at room temperature for several months without diminishing their catalytic activity; moisture should be excluded because of their slight hygroscopicity.

The single-crystal X-ray model of COP-hfacac (**2**) is shown in Figure 1.[13] This structure confirms the expected monomeric nature of the complex and coordination of the oxazoline nitrogen to palladium. It rigorously establishes the proposed *pR* configuration of **6** and the positioning of the isopropyl group away from the tetraphenylcyclobutadiene moiety.[11] The *i*-Pr group is oriented in the expected sense with the methine hydrogen directed at the hexafluoroacetylacetonate ligand. The phenyl substituents of the (η^4-tetraphenylcyclobutadiene)cobalt moiety are geared, as is observed in X-ray structures of other complexes having this fragment.[14]

Rearrangement of allylic trichloroacetimidate **4**[15,16] to allylic trichloroacetamide **5** in the presence of COP catalysts **2** and **3** (10 mol %) was examined initially under reaction conditions employed previously[9] for rearrangements catalyzed by COP-Cl (**1**) (Table 1, entries 1−3). Under these conditions, COP-Cl (**1**) is slightly superior in terms of rate and yield. Because of their higher solubility, COP catalysts **2** and **3** can be used at higher substrate concentrations and in solvents other than CH_2Cl_2. Exposure of imidate **4** (2.6 M) to 5 mol % of **2** at 38 °C in CH_2Cl_2 provided trichloroacetamide **5** in 96% ee and in an improved yield of 85% after 18 h (entry 4). In THF under identical conditions, allylic trichloroacetamide **5** was formed in 95% yield and 97% ee after 18 h (entry 5). Increasing the reaction temperature to 50 °C led to the anticipated increase in reaction rate with little or no erosion of enantioselectivity (entries 6 and 7).[17]

As summarized in Table 1, the conversion of **4** to (*S*)-**5** can be accomplished in high enantioselectivity in a variety of solvents under notably practical conditions:

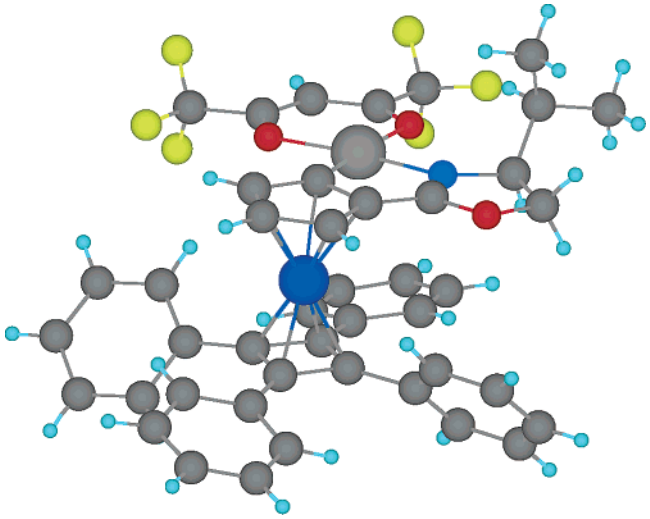


FIGURE 1. X-ray model of **2**.

TABLE 1. Enantioselective Conversion of 4 to (*S*)-5[a]

entry	catalyst	solvent	time [h]	temp [°C]	yield [%][b]	ee [%][c]
1[d]	**1**	CH_2Cl_2	18	38	93	93
2[d]	**2**	CH_2Cl_2	18	38	79	97
3[d]	**3**	CH_2Cl_2	43	38	77	95
4	**2**	CH_2Cl_2	18	38	85	96
5	**2**	THF	18	38	95	97
6	**2**	THF	6	50	93	96
7	**3**	THF	6	50	98	96
8	**2**	cyclohexane[e]	12	50	88	95
9	**2**	toluene[e]	15	50	85	97
10	**2**	acetone	9	50	93	92
11	**3**	acetone	9	50	95	96
12	**2**	MeCN	9	50	93	92
13	**3**	MeCN	9	50	93	96

[a] Conditions: 5 mol % catalyst, [substrate] = 2.6 M. [b] Yield after column chromatography. [c] Determined by GC analysis. [d] 10 mol % catalyst, [substrate] = 0.6 M. [e] **2** was purified by filtration through a short column of silica gel.

(12) Additional purification by simple filtration through silica using dichloromethane as eluent gives **2** in analytical purity.

(13) Crystallographic data for **2** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-245754. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033. E-mail: deposit@ccdc.cam.ac.uk).

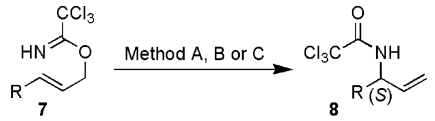
(14) The Cambridge Crystallographic Database includes 14 complexes having a (η^5-cyclopentadienyl)(η^4-tetraphenylcyclobutadiene)-cobalt part structure.

(15) Allylic trichloroacetimidates employed in this study were prepared in 68−99% yield by DBU-catalyzed addition of allylic alcohols to trichloroacetonitrile.[16]

(16) Numata, M.; Sugimoto, M.; Koike, K.; Ogawa, T. *Carbohydr. Res.* **1987**, *163*, 209−225.

(17) A control experiment demonstrated that the palladium(II) catalyst is required: stirring a solution of allylic imidate **4** in THF in the absence of **2** produced no detectable amounts of allylic amide **5** after 24 h at 50 °C.

TABLE 2. Enantioselective Synthesis of Allylic Trichloroacetamides 8 from (*E*)-Allylic Trichloroacetimidates 7



Method A: 5 mol % COP-hfacac (**2**), 50 °C, THF (2.6 M)
Method B: 1 mol % COP-hfacac (**2**), 50 °C, MeCN (2.6 M)
Method C: 5 mol % COP-acac (**3**), 50 °C, THF (2.6 M)

entry	substrate R =	method	time [h]	yield[a] [%]	ee[b] [%]
1	Me	A	5	93	91[c]
2		B	20	82	92[c]
3		C	7	93	91[c]
4	*n*-Pr	A	8	94	91
5		B	22	91	91
6		C	8	91	95
7	*i*-Bu	A	8	99	98
8		B	29	95	95
9	$AcOCH_2CH_2CH_2$	A	8	95	92
10		B	24	93	93
11	$Bn_2N(CH_2)_9$	A	9	98	92[c]
12	$(CH_2O)_2CH(CH_2)_2$	A	9	80	91[c]
13		B	29	86	93[c]

[a] Isolated yield after column chromatography. [b] Determined by chiral GC analysis after purification unless otherwise indicated. [c] Determined by chiral HPLC analysis after purification.

substrate concentration of 2.6 M, catalyst loading of 5 mol %, 50 °C, reaction times 6−29 h (entries 6−13).[18] Rearrangement of (*E*)-allylic trichloroacetimidate **4** with COP catalyst **2** in nonpolar solvents such as cyclohexane and toluene (entries 8 and 9) provides the corresponding trichloroacetamide in high yields and enantiomeric purities, although the catalysis rate was somewhat depressed. The rearrangement catalyzed by COP-acac (**3**) was impractically slow when carried out in cyclohexane or toluene. Reactions in toluene and cyclohexane require anhydrous conditions; in these solvents, it was crucial to filter catalyst **2** through silica gel to remove water and trace impurities prior to use. Further optimization showed that as little as 1 mol % of complex **2** was sufficient to effect rearrangement at 50 °C using acetonitrile as solvent.[19] For example, the rearranged trichloroacetamide **5** was obtained from **4** in 90% yield and high enantiomeric purity (95% ee) after 24 h.

From this preliminary survey, three particularly useful reaction conditions were identified: 5 mol % COP-hfacac (**2**), THF, 50 °C (Method A); 1 mol % COP-hfacac (**2**), MeCN, 50 °C (Method B); and 5 mol % COP-acac (**3**), THF, 50 °C (Method C). Results obtained from catalytic rearrangements of various prochiral (*E*)-allylic trichloroacetimidates using these conditions are summarized in Table 2. As with COP-Cl, enantioselectivity is highest with imidates having branching at C5 (entries 7 and 8). Although not extensively examined at this point, functionalities such as tertiary amine (entry 11), ester (entries 9 and 10), and acetal (entries 12 and 13) are well tolerated. In reactions performed in THF (Methods A or C), anhydrous conditions are not required to obtain the rearranged products in excellent yields and enantiomeric purities. For example, the conversion of **4** to **5** catalyzed by 5 mol % of **2** takes place in wet THF (1% water) at 50 °C giving a 72% conversion after 7 h.[20] As observed with COP-Cl, this catalytic method is limited to (*E*)-allylic trichloroacetimidates; Z stereoisomers rearrange at impractically slow rates with COP catalysts **2** and **3**.

In conclusion, the new monomeric palladacycles **2** and **3** were prepared and shown to catalyze the asymmetric rearrangement of allylic trichloroacetimidates to transposed allylic trichloroacetamides in good yields and with high asymmetric induction (>90% ee). In CH_2Cl_2, yields and enantioselectivities are slightly inferior to those realized with COP-Cl.[9] However, these more soluble catalysts can be used in a much wider variety of solvents. Moreover, this enhanced solubility allows reactions to be conducted at high substrate concentrations (e.g., 2.6 M) with practical catalytic rates being achieved in acetonitrile using as little as 1 mol % of COP-hfacac (**2**).

Experimental Section

Hexafluoroacetylacetonate[(η^5-(*S*)-(*pR*)-2-(2′-(4′-methylethyl)oxazolinyl)cyclopentadienyl,1-*C*, 3′-*N*)(η^4-tetraphenylcyclobutadiene)cobalt]palladium (2). To a mixture of COP-OAc (**6**)[10,11] (1.0 g, 0.66 mmol) in acetone (6.6 mL) and water (3.3 mL) was added sodium hexafluoroacetylacetonate (1.6 g, 6.8 mmol). The reaction mixture was stirred vigorously at room temperature for 9 h. The product was collected by filtration, washed with water (10 mL), and dried over P_2O_5 under vacuum to provide 1.1 g (1.2 mmol, 91%) of COP-hfacac (**2**) as an orange solid. COP-hfacac (**2**) thus prepared was sufficiently pure to effect allylic imidate rearrangements by Methods A and B. An analytically pure sample of COP-hfacac (**2**) was obtained by filtration through a plug of silica gel using CH_2Cl_2 as eluent: R_f = 0.63 (hexanes−EtOAc, 80:20); $[\alpha]^{28}_D$ = +271.2, $[\alpha]^{28}_{577}$ = +277.6, $[\alpha]^{28}_{546}$ = +214.8, $[\alpha]^{28}_{435}$ = −57.7, $[\alpha]^{28}_{405}$ = −86.8 (*c* = 1.02, $CHCl_3$); mp 108−110 °C (decomp); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54−7.56 (m, 8 H), 7.19−7.29 (m, 12 H), 5.95 (s, 1 H), 4.68 (d, *J* = 2.3 Hz, 1 H), 4.90 (d, *J* = 2.3 Hz, 1 H), 4.53 (t, *J* = 2.3 Hz, 1 H), 4.33 (dd, *J* = 8.6, 5.3 Hz, 1 H), 3.72 (t, *J* = 9.4 Hz, 1 H), 3.45 (td, *J* = 9.4, 5.1 Hz, 1 H), 2.05−2.08 (m, 1 H), 0.83 (d, *J* = 7.0 Hz, 3 H), 0.79 (d, *J* = 6.9 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.0, 173.7, 173.3, 135.5, 128.9, 127.9, 126.5, 118.2, 118.1, 97.6, 90.1, 87.7, 84.8, 84.1, 78.9, 76.7, 72.3, 65.3, 29.3, 18.4, 14.9; IR (neat) cm^{-1} 3061, 2964, 1629, 1598, 1509, 1475, 1258, 1208, 1150. Anal. Calcd for $C_{44}H_{34}CoF_6NO_3Pd$: C, 58.45; H, 3.79; N, 1.55. Found: C, 58.81; H, 3.74; N, 1.54.

Acetylacetonate[(η^5-(*S*)-(*pR*)-2-(2′-(4′-methylethyl)oxazolinyl)cyclopentadienyl,1-*C*,3′-*N*)(η^4-tetraphenylcyclobutadiene)cobalt]palladium (3). A mixture of COP-OAc[10,11] (1.0 g, 0.66 mmol), sodium acetylacetonate monohydrate (954 mg, 6.8 mmol), acetone (6.6 mL), and water (3.3 mL) was vigorously stirred for 24 h. The mixture was then extracted with CH_2Cl_2 (10 mL). The organic layer was dried (Na_2SO_4), filtered, and concentrated to give 1.0 g (quantitative yield) of COP-acac as an orange solid. COP-acac thus prepared was sufficiently pure to effect allylic imidate rearrangements by Method C: R_f = 0.59 (hexanes−EtOAc, 80:20); $[\alpha]^{28}_D$ = +246.1, $[\alpha]^{28}_{577}$ = +250.2, $[\alpha]^{28}_{546}$ = +175.5, $[\alpha]^{28}_{435}$ = −59.8, $[\alpha]^{28}_{405}$ = −91.4 (*c* = 1.00, $CHCl_3$); mp 100−104 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.6 Hz, 8 H), 7.20−7.30 (m, 12 H), 5.26 (s, 1 H), 5.17 (s, 1 H), 4.89 (d, *J* = 1.6 Hz, 1 H), 4.47 (s, 1 H), 4.27 (dd, *J* = 8.4, 5.6 Hz, 1 H), 3.67 (t, *J* = 9.0 Hz, 1 H), 3.29−3.31 (m, 1

(18) COP complex **2** (5 mol %) catalyzed the rearrangement of **4** also in 1,2-dichloroethane or ethyl acetate, providing **5** in 93% yield and 91% ee after 29 h (1,2-dichloroethane) or 90% yield and 92% ee after 29 h (EtOAc). In 1,4-dioxane or *tert*-butyl methyl ether, formation of **5** under similar conditions with catalyst **2** was not observed. The use of DMSO led to catalyst decomposition.

(19) Heating **2** in THF at 50°C for times longer than 10 h results in some decomposition of the catalyst; reactions employing 1 mol % of catalyst should not be performed in THF.

(20) Higher amounts of water slow the reaction significantly.

H), 2.26−2.27 (m, 1 H), 2.00 (s, 3 H), 1.94 (s, 3 H), 0.84 (d, J = 7.6 Hz, 3 H), 0.82 (d, J = 8.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.3, 184.9, 172.0, 136.0, 129.2, 128.1, 127.8, 126.0, 99.4, 86.3, 85.8, 85.1, 80.0, 76.0, 71.6, 65.1, 29.0, 27.6, 27.2, 18.6, 14.8; IR (neat) cm^{-1} 3058, 2960, 1597, 1579, 1508, 1399, 1265, 1183, 1067. Anal. Calcd for $C_{44}H_{40}CoNO_3Pd$: C, 66.38; H, 5.06; N, 1.76. Found: C, 66.20; H, 5.02; N, 1.84.

Representative Procedure for Allylic Trichloroacetimidate Rearrangement Catalyzed by COP-hfacac in THF (Method A). COP-hfacac (**2**; 5 mol %, 0.0065 mmol, 5.8 mg) was added to a solution of trichloroacetimidate **4** (40 mg, 0.13 mmol) in THF (0.05 mL), and the reaction vial was sealed, protected from light, and maintained at 50 °C. After 6 h, the orange solution was concentrated under reduced pressure. Purification of the residue by flash chromatography on silica with 9:1 hexanes−EtOAc as eluent gave allylic trichloroacetamide **5**[9] as a colorless solid (37 mg, 0.12 mmol; 93%). Chiral GC (Chiraldex γ cyclodextrin trifluoroacetyl, 20 m × 0.25 mm; initial temperature 50 °C (1 min), final temperature 150 °C, 5 °C/min) showed that **5** had been formed in 96% ee. Characterization data for **5**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.93−2.07 (m, 2 H), 2.71 (t, J = 8.2 Hz, 2 H), 4.44−4.52 (m, 1 H), 5.25 (ddd, J = 10.4, 1.5, 0.8 Hz, 1 H), 5.27 (ddd, J = 17.2, 1.6, 0.8 Hz, 1 H), 5.84 (ddd, J = 17.2, 10.4, 5.6 Hz, 1 H), 6.53 (broad s, 1 H), 7.17−7.24 (m, 3 H), 7.28−7.32 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.8, 35.9, 53.3, 92.7, 116.5, 126.3, 128.3, 128.6, 136.3, 140.8, 161.2.

Representative Procedure for Rearrangement Catalyzed by COP-hfacac in Acetonitrile (Method B). COP-hfacac (**2**; 1 mol %, 0.0013 mmol, 1.2 mg) was added to a solution of trichloroacetimidate **4** (40 mg, 0.13 mmol) in acetonitrile (0.05 mL), and the reaction vial was sealed, protected from light, and maintained at 50 °C. After 6 h, the solution was concentrated under reduced pressure. Purification of the residue by flash chromatography on silica with 9:1 hexanes−EtOAc as eluent gave allylic trichloroacetamide **5**[9] as a colorless solid (36 mg, 0.12 mmol; 90%). Chiral GC (Chiraldex γ cyclodextrin trifluoroacetyl, 20 m × 0.25 mm; initial temperature 50 °C (1 min), final temperature 150 °C, 5 °C/min) showed that **5** had been formed in 95% ee.

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Supporting Information Available: HPLC and GC traces used to determine enantiopurity of rearrangement products; ^{1}H and ^{13}C NMR spectra for allylic trichloroacetamide products; and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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