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Tris(1,2-diphenylethylenediamine)cobalt(III) Complexes: Chiral Hydrogen Bond Donor Catalysts for Enantioselective α-Aminations of 1,3-Dicarbonyl Compounds

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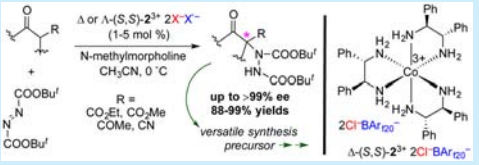
Supporting Information

ABSTRACT: The enantiopure salt Δ-$[Co((S,S)\text{-dpen})_3]^{3+}2Cl^-B(C_6F_5)_4^-$ is an effective hydrogen bond donor catalyst for additions of 1,3-dicarbonyl compounds to di-*tert*-butyl azodicarboxylate in the presence of *N*-methylmorpholine (1.0:1.0:0.10) in CH_3CN at 0 °C, as illustrated with educts derived from five- or six-membered ring ketones (99−88% yields, >99−91% ee) and cycloheptanone (94%, 72% ee) as well as 2-cyanocyclopentanone (92%, 45% ee) and an acyclic system (98%, >99% ee).



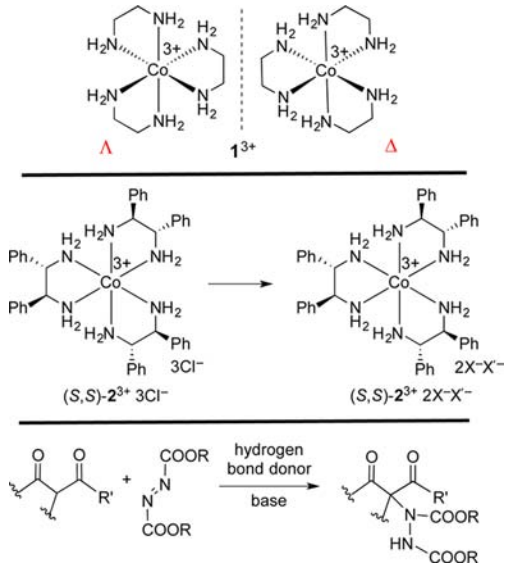
The last 15 years have witnessed an extensive development of small molecule hydrogen bond donor catalysts for enantioselective organic synthesis.[1] During this period, many types of catalyst-based stereogenic elements have been evaluated. We have sought to (1) expand the chiral pool to include inorganic or organometallic molecules that exhibit chiralty motifs not commonly encountered in organic systems[2] and (2) explore the utility of NH hydrogen bond donor groups that are either ligated to the metal[3] or positioned at remote sites.[4,5] Related themes have been of interest in the Meggers group.[5,6]

In particular, our attention has been attracted to helically chiral Werner complexes, for which the D_3 symmetric trication $[Co(en)_3)]^{3+}$ ($\mathbf{1}^{3+}$; en = 1,2-ethylenediamine) is the prototype.[3] The mirror images of $\mathbf{1}^{3+}$, depicted in Scheme 1 (top), have commonly been designated Λ and Δ. Salts of these trications were among the first inorganic compounds separated into enantiomers.[7] However, the solubilities of such species are generally restricted to water or other protic media, which can inhibit the binding of substrates to NH donor sites.

In previous work, we prepared a series of salts of a related trication with (*S*,*S*)-1,2-diphenylethylenediamine ligands ((*S*,*S*)-dpen) as shown in Scheme 1 (middle).[3b] The starting trichloride $[Co((S,S)\text{-dpen})_3]^{3+}3Cl^-$ ((*S*,*S*)-$\mathbf{2}^{3+}3Cl^-$) was easily obtained as the Λ or Δ diastereomer, and the exchange of one chloride for the lipophilic anion BAr_f^- ($B(3,5\text{-}C_6H_3(CF_3)_2)_4^-$) gave salts with high solubilities in aprotic media. This in turn facilitated the formation of a number of mixed salts of the formula Λ- or Δ-(*S*,*S*)-$\mathbf{2}^{3+}2X^-X'^-$ as well as analogues with three lipophilic anions (Λ- or Δ-(*S*,*S*)-$\mathbf{2}^{3+}3X''^-$). Many of these gave high levels of enantioselection as catalysts for Michael additions of malonate esters to nitroalkenes.[3b]

In order to demonstrate the applicability of such catalysts to a broader palette of transformations, we began to investigate additions of 1,3-dicarbonyl and related compounds to azo linkages, a reaction type shown in Scheme 1 (bottom). Such additions, often termed aminations, have been demonstrated

Scheme 1. Chiral Cobalt(III) Trication Originally Separated into Enantiomers by Werner (Top); General Catalyst Family (Middle); Reaction to Be Investigated (Bottom)



with other hydrogen bond donor catalysts,[8] and yield nitrogen functionalized systems that can be elaborated to α-amino acids.[9] In this paper, we report that salts derived from the trication (*S*,*S*)-$\mathbf{2}^{3+}$ also effect additions of activated methylene compounds to azo species in very high enantioselectivities. Four unoptimized reactions were briefly described in a previous communication.[3b]

The trichloride salt (*S*,*S*)-$\mathbf{2}^{3+}3Cl^-$ was prepared as reported previously as a 83:17 mixture of Δ/Λ diastereomers.[3b] Catalysts were then synthesized as shown in Scheme 2. First, (*S*,*S*)-

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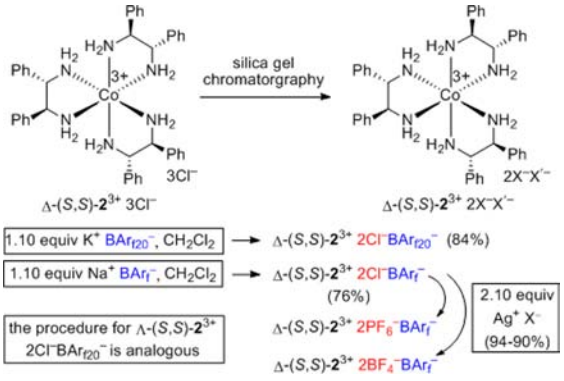
Scheme 2. Syntheses of New Lipophilic Werner Salts



$\mathbf{2}^{3+}3Cl^-$ (83:17 Δ/Λ) was treated with the perfluorinated tetraarylborate salt $K^+BAr_{f20}^-$ ($K^+B(C_6F_5)_4^-$; 1.1 equiv) in CH_2Cl_2/CH_3OH. Silica gel chromatography gave the diastereomerically pure hydrate Δ-(*S*,*S*)-$\mathbf{2}^{3+}2Cl^-BAr_{f20}^-\cdot 3H_2O$ as an orange solid in 58% yield (84% of theory). An analogous procedure with the opposite diastereomer, Λ-(*S*,*S*)-$\mathbf{2}^{3+}3Cl^-$, gave Λ-(*S*,*S*)-$\mathbf{2}^{3+}2Cl^-BAr_{f20}^-\cdot 3H_2O$ in 87% yield. Both salts were soluble in CH_2Cl_2 and acetone.

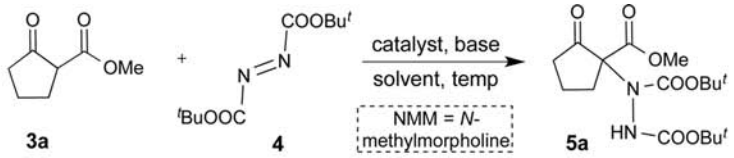
Next, the chloride ions of the previously reported salt Δ-(*S*,*S*)-$\mathbf{2}^{3+}2Cl^-BAr_f^-\cdot 3H_2O$[3b] were metathesized via procedures described for the diastereomers. As shown in Scheme 2, additions of the silver salts $Ag^+BF_4^-$ and $Ag^+PF_6^-$ gave the hydrates Δ-(*S*,*S*)-$\mathbf{2}^{3+}2BF_4^-BAr_f^-\cdot 3H_2O$ and Δ-(*S*,*S*)-$\mathbf{2}^{3+}2PF_6^-BAr_f^-\cdot 2H_2O$ in 94−90% yields after workups. All of these new salts were characterized by NMR (^1H, ^{13}C) and microanalyses, as summarized in the Supporting Information.

As shown in Scheme 3, catalysts were screened at 5 mol % loadings using the β-keto ester **3a** and di-*tert*-butyl azodicarboxylate (**4**). The first experiments used the base *N*-methylmorpholine and were carried out in CD_2Cl_2 in NMR tubes at room temperature. Entries 1 and 2, which involve the previously reported diastereomeric mixed bis(chloride) salts Λ- and Δ-(*S*,*S*)-$\mathbf{2}^{3+}2Cl^-BAr_f^-$, gave opposite enantiomers of the addition product **5a** in 76% and 79% ee, respectively, roughly on same time scale. Hence, the cobalt configuration is the main determinant of the product configuration.

The corresponding bis(tetrafluoroborate) and bis(hexafluorophosphate) salts gave diminished enantioselectivities (entries 3−6, 70−56% ee). However, the perfluorotetraphenylborate salts Δ- and Λ-(*S*,*S*)-$\mathbf{2}^{3+}2Cl^-BAr_{f20}^-$ gave equal or better results (entries 7 and 8), with the improvement more pronounced in the Δ series (84% ee). Hence, this catalyst was selected for solvent, temperature, and base optimization.

For Δ-(*S*,*S*)-$\mathbf{2}^{3+}2Cl^-BAr_{f20}^-$, enantioselectivities increased slightly in acetone-d_6 (87% ee, entry 9) and still more in CD_3CN (89% ee, entry 10). Next, reactions were conducted in CD_3CN at lower temperatures (entries 11 and 12). Interest-

Scheme 3. Optimization of Catalysts and Conditions



entry[a]	catalyst (mol %)	solvent	base (equiv)	temp	time (min)	conversion (%)[b]	ee (%) (config)[c]
1	Λ-(*S*,*S*)-$\mathbf{2}^{3+}$ $2Cl^-BAr_f^-$ (5)	CD_2Cl_2	NMM (1.0)	rt	20	99	76 (*S*)
2	Δ-(*S*,*S*)-$\mathbf{2}^{3+}$ $2Cl^-BAr_f^-$ (5)	CD_2Cl_2	NMM (1.0)	rt	20	99	79 (*R*)
3	Λ-(*S*,*S*)-$\mathbf{2}^{3+}$ $2BF_4^-BAr_f^-$ (5)	CD_2Cl_2	NMM (1.0)	rt	20	99	70 (*S*)
4	Δ-(*S*,*S*)-$\mathbf{2}^{3+}$ $2BF_4^-BAr_f^-$ (5)	CD_2Cl_2	NMM (1.0)	rt	20	99	56 (*R*)
5	Λ-(*S*,*S*)-$\mathbf{2}^{3+}$ $2PF_6^-BAr_f^-$ (5)	CD_2Cl_2	NMM (1.0)	rt	20	99	60 (*S*)
6	Δ-(*S*,*S*)-$\mathbf{2}^{3+}$ 2 $PF_6^-BAr_f^-$ (5)	CD_2Cl_2	NMM (1.0)	rt	20	99	68 (*R*)
7	Λ-(*S*,*S*)-$\mathbf{2}^{3+}$ $2Cl^-BAr_{f20}^-$ (5)	CD_2Cl_2	NMM (1.0)	rt	20	99	77 (*S*)
8	Δ-(*S*,*S*)-$\mathbf{2}^{3+}$ $2Cl^-BAr_{f20}^-$ (5)	CD_2Cl_2	NMM (1.0)	rt	20	99	84 (*R*)
9	Δ-(*S*,*S*)-$\mathbf{2}^{3+}$ $2Cl^-BAr_{f20}^-$ (5)	acetone-d_6	NMM (1.0)	rt	20	99	87 (*R*)
10	Δ-(*S*,*S*)-$\mathbf{2}^{3+}$ $2Cl^-BAr_{f20}^-$ (5)	CD_3CN	NMM (1.0)	rt	20	99	89 (*R*)
11	Δ-(*S*,*S*)-$\mathbf{2}^{3+}$ $2Cl^-BAr_{f20}^-$ (5)	CD_3CN	NMM (1.0)	0 °C	20	99	91 (*R*)
12	Δ-(*S*,*S*)-$\mathbf{2}^{3+}$ $2Cl^-BAr_{f20}^-$ (5)	CD_3CN	NMM (1.0)	−35 °C	20	99	84 (*R*)
13	Δ-(*S*,*S*)-$\mathbf{2}^{3+}$ $2Cl^-BAr_{f20}^-$ (5)	CD_3CN	Et_3N (1.0)	0 °C	20	99	81 (*R*)
14	Δ-(*S*,*S*)-$\mathbf{2}^{3+}$ $2Cl^-BAr_{f20}^-$ (5)	CD_3CN	DABCO (1.0)	0 °C	20	99	77 (*R*)
15	Δ-(*S*,*S*)-$\mathbf{2}^{3+}$ $2Cl^-BAr_{f20}^-$ (5)	CD_3CN	DBU (1.0)	0 °C	20	99	80 (*R*)
16	Δ-(*S*,*S*)-$\mathbf{2}^{3+}$ $2Cl^-BAr_{f20}^-$ (5)	CD_3CN	DMAP (1.0)	0 °C	20	99	80 (*R*)
17	Δ-(*S*,*S*)-$\mathbf{2}^{3+}$ $2Cl^-BAr_{f20}^-$ (1)	CD_3CN	NMM (1.0)	0 °C	480	99	70 (*R*)
18	Δ-(*S*,*S*)-$\mathbf{2}^{3+}$ $2Cl^-BAr_{f20}^-$ (2)	CD_3CN	NMM (1.0)	0 °C	240	99	84 (*R*)
19	Δ-(*S*,*S*)-$\mathbf{2}^{3+}$ $2Cl^-BAr_{f20}^-$ (10)	CD_3CN	NMM (1.0)	0 °C	20	99	91 (*R*)
20	Δ-(*S*,*S*)-$\mathbf{2}^{3+}$ $2Cl^-BAr_{f20}^-$ (5)	CD_3CN	NMM (0.50)	0 °C	35	99	91 (*R*)
21	Δ-(*S*,*S*)-$\mathbf{2}^{3+}$ $2Cl^-BAr_{f20}^-$ (5)	CD_3CN	NMM (0.10)	0 °C	360	99	91 (*R*)

[a]Reactions were carried out with 0.050 mmol each of **3a** and **4** in 0.50 mL of solvent. [b]The conversion was determined by ^1H NMR integration of the $CHCO_2Me$ proton of **3a** versus the standard Ph_2SiMe_2. [c]Enantioselectivities were determined by chiral HPLC analyses.

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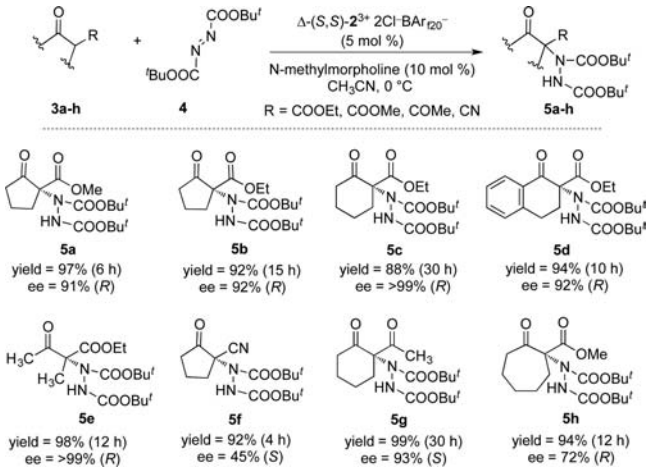
ingly, the ee values first increased (91% ee, 0 °C) but diminished with further cooling (84% ee, −35 °C). Thus, four additional bases were evaluated at 0 °C (Et_3N, DABCO, DBU, DMAP), but the ee values decreased to 81−77% ee (entries 13−16). Next, the catalyst charge was varied. At 1 and 2 mol % loadings (entries 17 and 18), enantioselectivities decreased (70% and 84% ee), presumably due to increased competition from the background reaction or catalysis. However, 10% loadings gave no improvement (entry 19). Finally the amount of base was decreased from 1.0 equiv to 0.50−0.10 equiv (entries 20 and 21). Reactions times increased, but enantioselectivities were maintained.

Next, the optimal conditions from Scheme 3 were applied to additional substrates, giving the results summarized in Scheme 4. Five different cyclic β-ketoesters were examined, providing

Scheme 4. Substrate Scope under Optimized Conditions[a−c]



[a]All reactions were carried out with 0.1 mmol of **3** and 0.1 mmol of **4** in 1.0 mL of CH_3CN. [b]Yields are for isolated products. [c]Enantioselectivities were determined by chiral HPLC analyses.

products **5a−d,h** in 88−97% yields. The carboethoxy cyclohexanone **5c** formed somewhat more slowly than the others, whereas the carbomethoxy cyclopentanone **5a** formed somewhat faster. Within this group, the ee values were excellent for the five- and six-membered ring keto esters (**5a−d**; >99−91% ee). However, the seven-membered ring keto ester formed with lower enantioselectivity (5 h; 72% ee).

An acyclic β-keto ester also underwent amination in high yield (98%) and enantioselectivity (>99% ee) to give **5e**. A cyclic 1,3 diketone was also efficiently derivatized to give **5g** in 99% yield and 93% ee. Finally, when α-cyanocyclopentanone was employed, **5f** was obtained in 92% yield, but the ee value dropped to 45%. Importantly, the dominant product configurations were, in a relative sense, the same in each case.

Naturally, it is by no means assured that the screening results in Scheme 3 reflect the optimum conditions for all of the substrates in Scheme 4. Thus, for the reactions yielding **5e** and **5g**, additional catalysts were investigated, as summarized in Table 1. These data confirm that the best overall catalyst is Δ-(*S*,*S*)-$\mathbf{2}^{3+}$2Cl$^-$BAr$_{f20}^-$. For the acyclic substrate yielding **5e**, the Δ diastereomer gives significantly higher enantioselectivity than the Λ diastereomer (entries 1 vs 2, >99% vs 84% ee). However, for the diketone **5g**, these two catalysts give comparable enantioselectivities (entries 4 vs 5, 93−92% ee). We note in

Table 1. Variation of the Catalyst used for 5e and 5g under Optimized Conditions[a]

entry	product	catalyst	time (h)	yield (%)	ee (%) (config)
1	**5e**	Δ-(*S*,*S*)-$\mathbf{2}^{3+}$ 2Cl$^-$BAr$_{f20}^-$	12	94	>99 (*R*)
2	**5e**	Λ-(*S*,*S*)-$\mathbf{2}^{3+}$ 2Cl$^-$BAr$_{f20}^-$	15	97	84 (*S*)
3	**5e**	Δ-(*S*,*S*)-$\mathbf{2}^{3+}$ 2Cl$^-$BAr$_f^-$	13	93	84 (*R*)
4	**5g**	Δ-(*S*,*S*)-$\mathbf{2}^{3+}$ 2Cl$^-$BAr$_{f20}^-$	30	98	93 (*R*)
5	**5g**	Λ-(*S*,*S*)-$\mathbf{2}^{3+}$ 2Cl$^-$BAr$_{f20}^-$	28	97	92 (*S*)
6	**5g**	Δ-(*S*,*S*)-$\mathbf{2}^{3+}$ 2Cl$^-$BAr$_f^-$	32	94	70 (*R*)

[a]All reactions were carried out with 0.10 mmol each of **3** and **4** in 1.0 mL of CH_3CN at 0 °C in the presence of *N*-methylmorpholine (0.10 equiv).

passing that these would be excellent test systems for multivariate reaction parameter analyses.[10]

As summarized in Scheme 2, this study has expanded the palette of tris(1,2-diphenylethylenediamine)cobalt(III) salts applied earlier as catalysts for Et_3N promoted additions of malonate esters to nitroalkenes to BAr$_{f20}^-$ anions.[3b] At least one lipophilic tetraarylborate anion, BAr$_f^-$ or BAr$_{f20}^-$, is necessary to solubilize these salts in aprotic organic solvents, with the former being slightly more effective.

Scheme 3 shows that all of the cobalt(III) salts prepared catalyze the title reaction with appreciable enantioselectivities. Curiously, the Δ diastereomers always afford slightly greater enantioselectivities. This is in stark contrast to the malonate/nitroalkene additions,[3b] for which the Λ diastereomers are distinctly superior; current evidence suggests that these proceed via a C_3 face of the trication, where three NH bonds are directed in a roughly synperiplanar fashion. As shown in Scheme 5 (top), the three NH protons on each C_3 face of the trichloride salt Δ-(*S*,*S*)-$\mathbf{2}^{3+}$3Cl$^-$ are directed in a more divergent fashion than those of Λ-(*S*,*S*)-$\mathbf{2}^{3+}$3Cl$^-$, and the C_2 face is much more congested.[3b] While it borders on pure speculation to propose transition-state assemblies for the reactions in Schemes 3 and 4 at this time, we offer (in response to requests of two reviewers) the model **I** (Scheme 5, middle) as a starting point. Note the possibility that the educts may also simultaneously bind to one or more NH units associated with a C_2 face.

Although it is difficult to quantitatively compare the effectiveness of different families of enantioselective catalysts, the ee values in Scheme 4 usually rank with the best in the literature. For products **5a,b,d**, the current "records" are 96% ee (vs 91%),[8g] 98% ee (vs 92%),[8e] and 97% ee (vs 92%),[8e] respectively. For **5c,e,g**, our data are superior (>99% ee vs 98%;[8e] 99% ee vs 85%;[8e] 93% vs no previous reports). With the products **5f,h**, our data are inferior (45% ee vs 90%;[8g] 72% ee vs 94%[8g]). The catalysts that feature in these comparisons are depicted in Scheme 5 (**A**, **B**; bottom), together with other representative examples (**C**, **D**). Importantly, **A** and **B** were effective at somewhat lower loadings than (*S*,*S*)-$\mathbf{2}^{3+}$2Cl$^-$BAr$_{f20}^-$ (2−0.5 vs 5 mol %). This may be due, at least in part, to their bifuncational nature, obviating the need for an external base.

In summary, this study has expanded the applicability of chiral Werner complexes based upon ethylenediamine chelates as hydrogen bond donor catalysts for enantioselective organic reactions. The anion effects evident in Scheme 3 furthermore raise the possibility of additional types of controlling interactions. These will be probed in future efforts, together with bifunctional catalysts that incorporate tertiary amines[11] and

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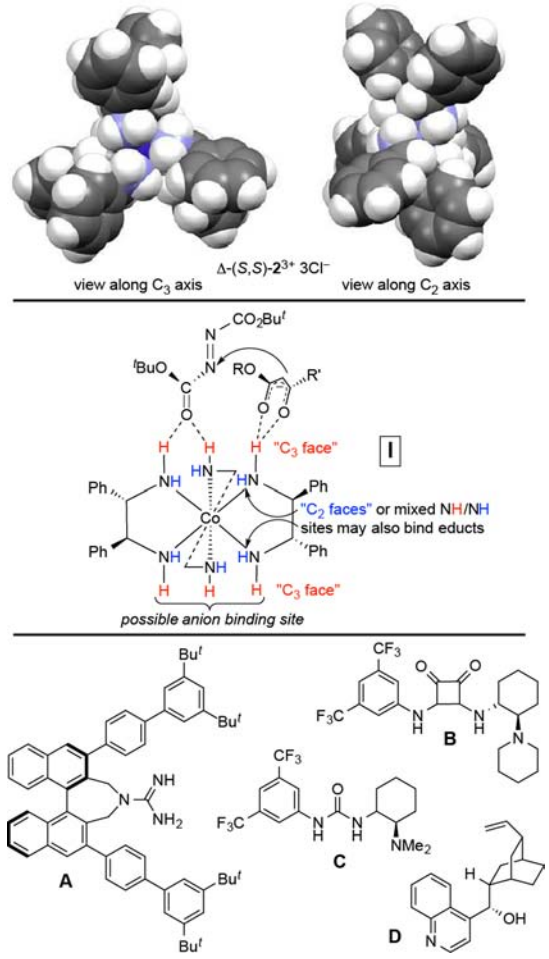
Scheme 5. Views of the C_3 and C_2 faces of the Trication of Λ-(*S*,*S*)-$2^{3+}3Cl^-$ (top),[3b] A Possible Transition State Assembly (middle), Other Chiral Hydrogen Bond Donor Catalysts Employed for the Title Reaction (bottom)



transformations that cannot be effected with existing hydrogen bond donor catalysts.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b00023.

Data involving starting materials, instrumentation, catalyst synthesis, catalytic reactions, and product characterization (PDF)

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Notes

The authors declare no competing financial interest.

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