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Synthesis of (*R*)-BINOL-Derived (Cyclopentadienone)iron Complexes and Their Application in the Catalytic Asymmetric Hydrogenation of Ketones

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A family of chiral (cyclopentadienone)iron complexes, featuring an (*R*)-BINOL-derived backbone, and their application in the asymmetric hydrogenation of ketones are described. The complexes differ from each other in the substituents at the 3,3′-positions of the binaphthyl residue (H, OH, OR, OCOR, OSO_2R) or at the 2,5-positions of the cyclopentadienone ring [trimethylsilyl (TMS) or Ph]. Remarkably, eight precatalysts with different 3,3′-binaphthyl substitution [(*R*)-**1c**–**1j**] were synthesized from a common parent complex [(*R*)-**1b**] through direct functional group interconversion reactions of the complexes. The 3,3′-(bis)methoxy-substituted precatalyst (*R*)-**1b** gave the best catalytic performance, and its application scope was assessed in the hydrogenation of several ketones. The observed *ee* values (up to 77 %) are much higher than those previously reported for other chiral (cyclopentadienone)iron complexes.

Introduction

The development of homogeneous catalytic methodologies based on first-row transition metals is becoming an industrially relevant task, owing to the high price and limited stock of noble metals. Indeed, first-row transition metals such as Fe, Co, Ni and Cu are far more abundant and, generally, less toxic than their second- and third-row counterparts, which have been employed intensely in homogeneous catalysis. In particular, Fe is readily available (second most abundant metal in the earth's crust) and has a lower toxicity than those of most other transition metals. As such, Fe has been employed widely in heterogeneous catalysis (e.g., in the Haber process for the synthesis of ammonia).[1] On the contrary, the use of Fe in homogeneous catalysis has been relatively limited,[2] possibly because of its tendency to engage in radical reactions rather than in two-electron processes. However, the use of "noninnocent" ligands [i.e., those able to modify the redox properties of the metal and/or to interact with the reactant(s)] may "force" the Fe catalyst to follow reactivity patterns different from the more common ones.[3] This approach has been applied extensively to Fe-catalyzed reductions[4] such as hydrogenation (of olefins,[5] ketones,[6] imines,[6c] esters[4a,7] and carbon dioxide/sodium hydrogen carbonate)[8] and transfer hydrogenation (of ketones[9] and imines).[9c,10] (Cyclopentadienone)iron complexes **A**[11] (Scheme 1) perhaps represent the most impressive application of this concept.[12] Analogously to what is reported for the Shvo Ru catalyst,[13] the shuttling of the ligand between its two cyclopentadienone/hydroxycyclopentadienyl forms enables a Fe^0/Fe^{II} catalytic cycle (Scheme 1, Cycle I), which is uncharacteristic of more classical Fe complexes. The active cyclopentadienone(iron) complexes **act-A** are able to split H_2 and, thus, catalyze the hydrogenation of carbonyl compounds through a concerted outer-sphere mechanism, in which the ligand is involved again through its OH group.[14]

This catalytic Cycle I (Scheme 1) can be accessed either from the cyclopentadienone(iron) complexes **act-A**, generated in situ from complexes **A** by creation of a vacant coordination site (by reaction with Me_3NO[15] or UV light),[16] or from the (hydroxycyclopentadienyl)iron complexes **B**. The latter can be either preisolated (as in the seminal work of Casey and Guan)[17] or generated in situ by reaction of **A** with an aqueous base.[18] The in situ activation protocols have the advantage of employing the stable complexes **A** (which can be handled in air) and avoid the direct manipulation of the highly air- and moisture-sensitive compounds

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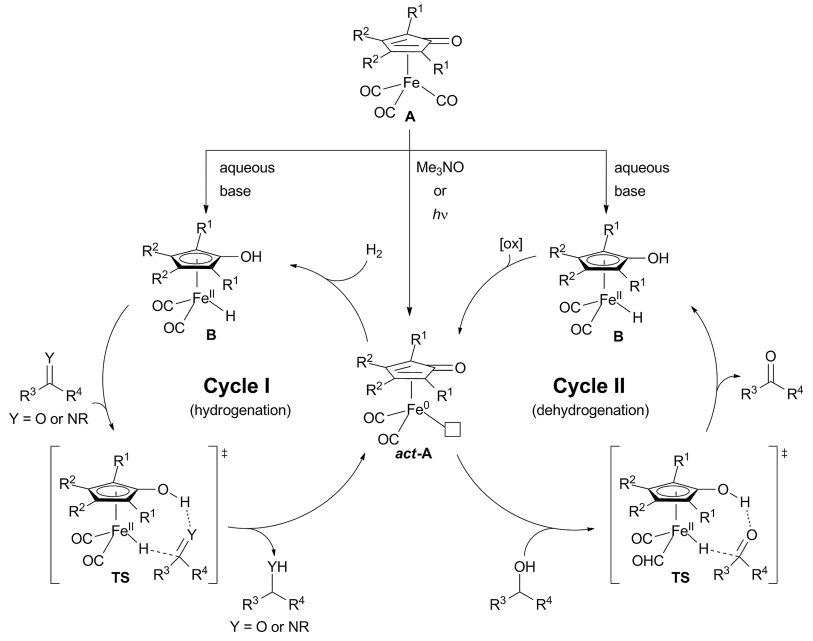


Scheme 1. Catalytic pathways of (i) hydrogenation of C=O and C=N double bonds (Cycle I) and (ii) Oppenauer-type alcohol oxidation (Cycle II) catalyzed by cyclopentadienone complexes **act-A**.

B. Owing to their easy preparation and interesting catalytic properties, complexes **A** and **B** have become the object of increasing interest among organic chemists: they have been employed successfully to promote the hydrogenation of C=O[15a,15e,18,19a] and C=N bonds[15b,15c,15e,19b,19c] as well as the transfer hydrogenation of ketones.[15d,20] Moreover, through the same mechanism (Scheme 1, Cycle II) they also catalyze the Oppenauer-type dehydrogenation of alcohols to carbonyl compounds[21] as well as the amination of alcohols through a "hydrogen-borrowing" reaction.[22]

Despite this burgeoning interest, the applications of complexes **A** and **B** in enantioselective reductions remain scarce; the most successful example was the cooperative iron–Brønsted acid catalysis developed by Beller and co-workers for the hydrogenation of imines[19c] and quinoxalines.[19b] However, in the latter case, an achiral **B**-type complex was used, and the enantiodiscrimination stems from chiral phosphoric acid derivatives.[23] Chiral **A**-type complexes were developed by Berkessel et al. (Figure 1, a)[16] and Wills et al. (Figure 1, b),[15d] but their use in ketone reduction led only to modest enantioselectivities (up to 31% *ee*).

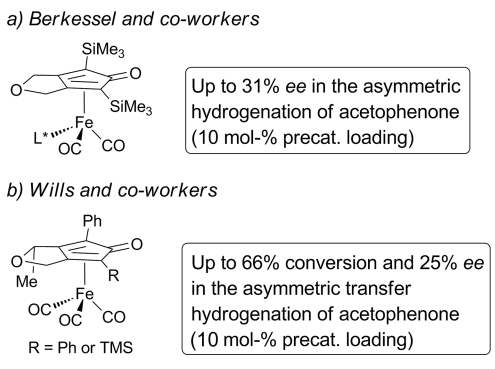


Figure 1. Previously reported methods for the enantioselective reduction of ketones catalyzed by chiral **A**-type complexes.

To fill this gap, our research group has recently developed a new class of **A**-type complexes featuring a chiral backbone derived from (*R*)-BINOL.[24] In this paper, we present a full account of the synthesis of 11 members of this family of chiral complexes. Their use as precatalysts for the asymmetric hydrogenation (AH) of ketones allowed us to obtain the highest *ee* ever reported with (cyclopentadienone)iron complexes.

Results and Discussion

We selected (*R*)-BINOL as a cheap and readily available chiral building block for the synthesis of our (cyclopentadienone)iron complexes **1** (Figure 2, a). In the pericyclic transition state commonly accepted for ketone hydrogenation (Figure 2, b),[14,17b] the substrate is located at a remarkable distance from the binaphthyl stereoaxis. For this reason, we expected that the substituents at the 3,3′-positions of the binaphthyl moiety[25] and at the 2,5-positions of the cyclopentadienone ring would influence the transfer

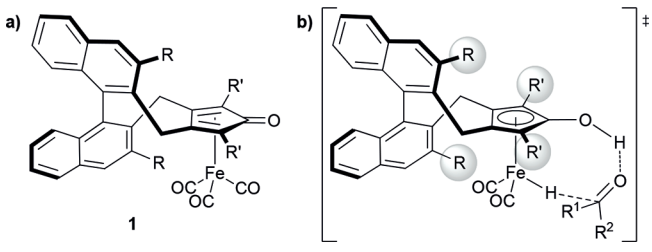
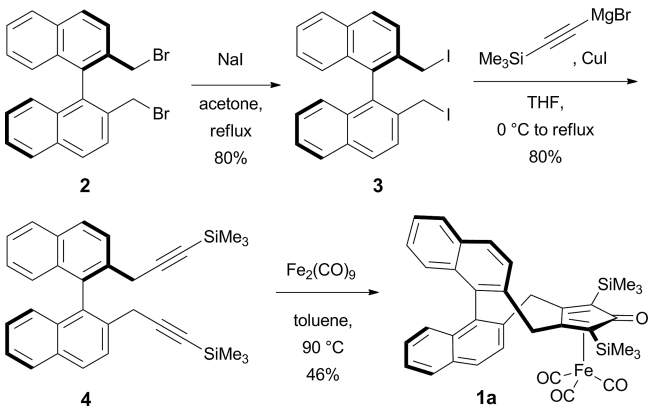


Figure 2. (a) General structure of chiral precatalysts **1** and (b) expected importance of the binaphthyl 3,3′-substituents and cyclopentadienone 2,5-substituents in AH.

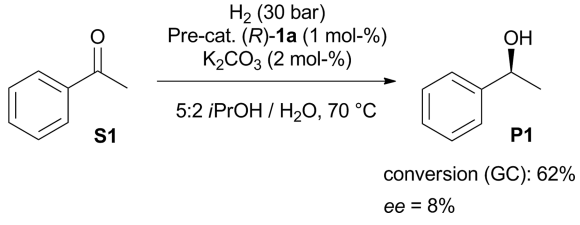
of stereochemical information. Thus, we synthesized several derivatives, each differing in the substituents at these "crucial" positions.

Firstly, the 3,3′-unsubstituted complex (*R*)-**1a** was synthesized in three steps from the commercially available compound (*R*)-**2** according to the procedure shown in Scheme 2.[24]



Scheme 2. Synthesis of the precatalyst (*R*)-**1a**.[24]

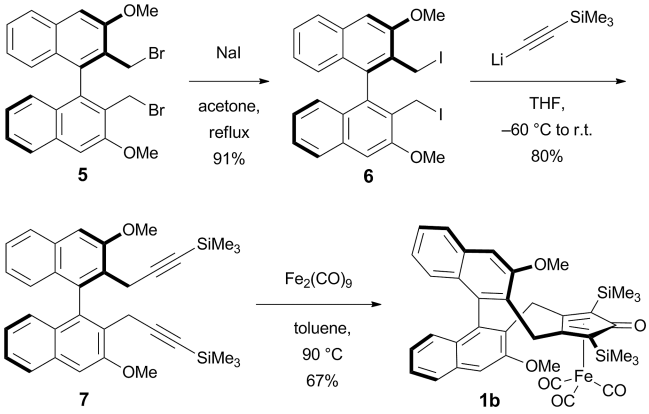
Precatalyst (*R*)-**1a** was tested in the AH of acetophenone (**S1**, Scheme 3) under the conditions reported by Beller and co-workers[18] for the in situ activation of (cyclopentadienone)iron complexes. A conversion of 62% into 1-phenylethanol (**P1**) was observed, along with a very low enantioselectivity (8% *ee*) in favor of the *S* enantiomer.[24]



Scheme 3. Test of precatalyst (*R*)-**1a** in the AH of acetophenone (**S1**).[24]

We attributed this low enantiomeric excess to a poor transfer of stereochemical information owing to the remote position of the stereoaxis with respect to the substrate in the reaction transition state (Figure 2, b). Consequently, we set out to synthesize the 3,3′-bis(methoxy) derivative (*R*)-**1b** from (*R*)-**5**, the preparation of which was described by Cramer and co-workers.[26] The synthesis was carried out in three steps, as shown in Scheme 4.[24]

The double alkynylation of bis(iodide) **6** did not occur under the conditions used for the synthesis of **4** (copper-catalyzed reaction of the alkynyl Grignard, see Scheme 2) but proceeded smoothly with the lithium acetylide (80% yield). On the contrary, the latter reaction was not successful with bis(iodide) **3**, which suggests that the assistance of the 3,3′-OMe groups is required for the nucleophilic substitution by the lithium acetylide. Complex (*R*)-**1b** was tested in the AH of **S1** and showed a substantially increased enantioselectivity compared to that with (*R*)-**1a** (50 vs. 8% *ee*). The optimization of the reaction parameters in the



Scheme 4. Synthesis of the 3,3′-disubstituted precatalyst (*R*)-**1b**.[24]

presence of (*R*)-**1b** allowed the identification of the optimal conditions for AH, and these conditions were adopted for the substrate screening (Table 1).[24] Notably, the use of Me_3NO for precatalyst activation led to higher and more reproducible conversions than those obtained with the initially used K_2CO_3[18] (84% instead of 54% conversion with 1 mol-% catalyst).

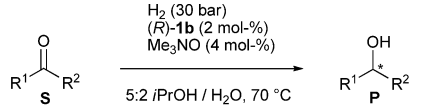
As can be seen in Table 1, the application scope of the precatalyst (*R*)-**1b** is quite broad and ranges from acetophenones to aliphatic and cyclic ketones. As a general trend, a larger difference in size between the substituents of the carbonyl group leads to a higher enantiomeric excess, which ranges from fair to good (up to 77%).

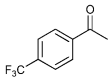
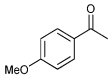
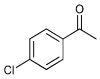
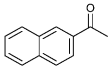
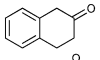
The improved enantioselectivity obtained with (*R*)-**1b** stimulated us to prepare other precatalysts substituted at the 3,3′-positions of the binaphthyl system. To this end, rather than opting for a costly and time-consuming parallel synthesis of each new precatalyst, we decided to directly derivatize (*R*)-**1b**. Like other (cyclopentadienone)iron derivatives **A**, this iron complex possesses a stability uncommonly high among metal complexes. Complexes **1** are stable in air and moisture, do not decompose in column chromatography (silica), and are also compatible with the experimental conditions required for the transformation of unreactive functional groups. Remarkably, the conversion of (*R*)-**1b** into (*R*)-**1c** (Scheme 5) involved treatment with BBr_3 and Bu_4NI at 85 °C in 1,2-dichloroethane (DCE) for 70 h. Despite these harsh conditions, the yield of the desired product was 80%, and no appreciable degradation of the metal complex was observed.[24]

Compound (*R*)-**1c** was characterized by single-crystal X-ray diffraction analysis, and the structure is shown in Figure 3. CCDC-1037376 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.[24]

It was decided to use (*R*)-**1c** as a scaffold for the preparation of new compounds by exploiting its 3,3′-hydroxy groups for the following transformations (Scheme 5): (a) esterification, (b) etherification, (c) sulfonylation, possibly followed by (d) cross-coupling to form the 3,3′-substituted derivatives. In this way, our synthetic efforts to obtain

Table 1. Substrate screening[a] for the **act**-(*R*)-**1b**-catalyzed AH.[24]



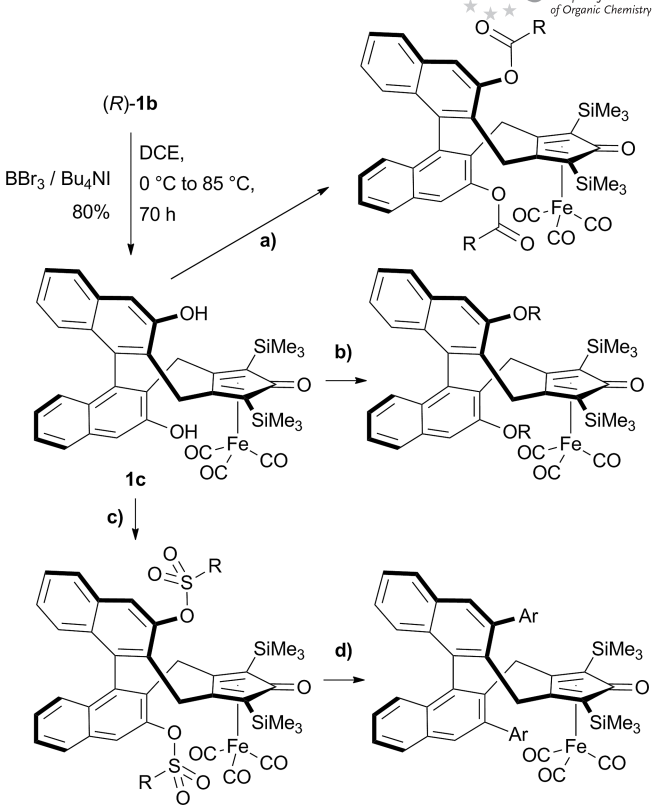
Entry	Substrate		Conv. (%)[b]	*ee* (%),[c] absol. config.[d]
1		**S1**	100	50, *S*
2		**S2**	100	46, *S*
3		**S3**	64	50, *S*
4		**S4**	100	51, *S*
5		**S5**	43	68, *S*
6		**S6**	99	51, *S*
7		**S7**	35	50, *S*
8		**S8**	97	57, *S*
9[e]		**S9**	25	77, *S*
10		**S10**	100	13, *R*
11		**S11**	78	59, *R*
12		**S12**	89	61, *S*
13		**S13**	76	0
14		**S14**	22	77, *S*

[a] Reaction conditions: substrate/(*R*)-**1b**/Me_3NO 100:2:4, P_{H_2} = 30 bar, solvent: 5:2 *i*PrOH/H_2O, c_0(substrate) = 1.43 M, T = 70 °C, reaction time: 18 h. [b] Determined by GC with a chiral capillary column (see Supporting Information). [c] Determined by GC or HPLC with a chiral capillary column (see Supporting Information). [d] Assigned by comparison of the sign of the optical rotation with the literature data (see Supporting Information). [e] Substrate/(*R*)-**1b**/Me_3NO 100:5:10.

(*R*)-**1c** [12 steps and three chromatographic purifications from (*R*)-BINOL] were leveraged towards the preparation of several new precatalysts in just one or two steps from the same advanced precursor.

The esterification of (*R*)-**1c** proceeded smoothly under classical conditions [acyl chloride, triethylamine (TEA), and catalytic 4-(dimethylamino)pyridine (DMAP) in tetrahydrofuran (THF) under reflux] to provide diesters (*R*)-**1d** and (*R*)-**1e** in high yields (Scheme 6).

The etherification of (*R*)-**1c** was more problematic, as only the bis(benzyl ether) (*R*)-**1f** could be prepared in a synthetically meaningful yield (Scheme 7). Attempts to prepare



Scheme 5. General synthetic strategy for the preparation of 3,3′-substituted (cyclopentadienone)iron complexes **1**: (a) esterification, (b) etherification, (c) sulfonylation, and (d) cross-coupling.

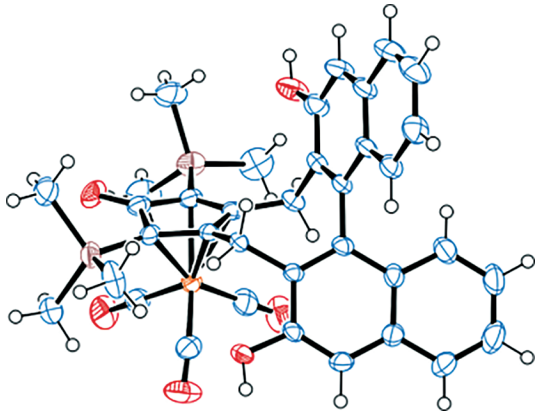
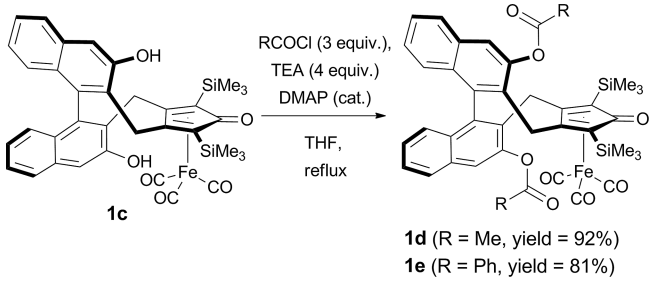
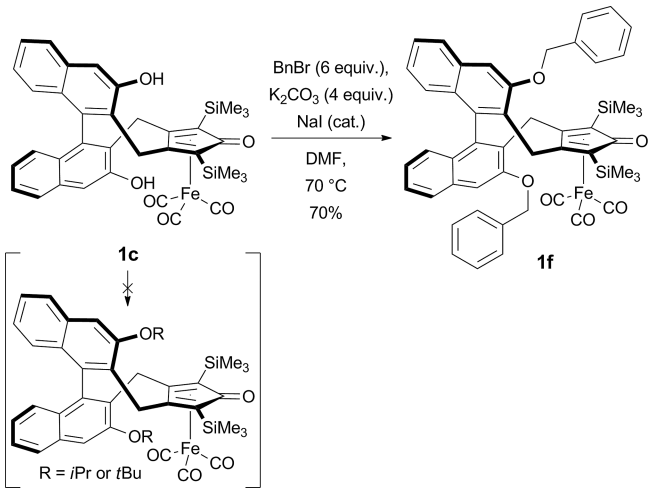


Figure 3. ORTEP diagram (CCDC-1037376) of the molecular structure of (*R*)-**1c** (thermal ellipsoids set at the 50% probability level). Cocrystallized solvent molecules are omitted for clarity.[24]



Scheme 6. Synthesis of esters (*R*)-**1d** and (*R*)-**1e**.

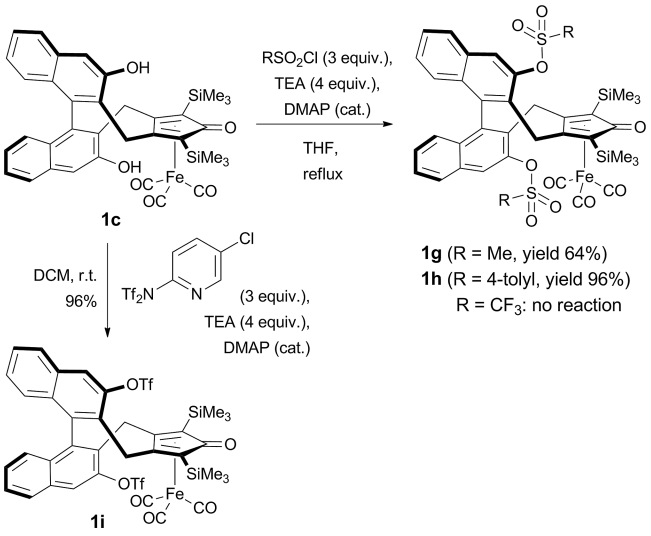
the bis(isopropyl ether) under similar reaction conditions failed, as did the preparation of the bis(*tert*-butyl ether) by reaction of (*R*)-**1c** with isobutene or $(t\text{BuO})_2\text{CHNMe}_2$.



Scheme 7. Synthesis of (*R*)-**1c** and attempted preparation of other 3,3′-bis(ether) derivatives.

Complex (*R*)-**1c** showed a good reactivity with methanesulfonyl chloride (MsCl) and *p*-toluenesulfonyl chloride (TsCl), which, in the presence of TEA and catalytic DMAP, allowed us to obtain (*R*)-**1g** and (*R*)-**1h**, respectively, in good yields (Scheme 8). To our surprise, (*R*)-**1c** did not react with trifluoromethanesulfonyl chloride (TfCl) or trifluoromethanesulfonic anhydride (Tf_2O) under the same conditions. However, the synthesis of the 3,3′-bis(triflate) (*R*)-**1i** could be realized with good yield (Scheme 8) by reaction of (*R*)-**1c** with the Comins reagent [*N*-(5-chloro-2-pyridyl)bis(trifluoromethanesulfonimide)].[27]

According to our general synthetic strategy (Scheme 5, d), we tried to exploit the triflate groups of (*R*)-**1i** for the installation of aryl groups through cross-coupling reaction. The Suzuki–Miyaura cross-coupling of (*R*)-**1i** with phenylboronic acid under typical conditions for aryl triflates[28]

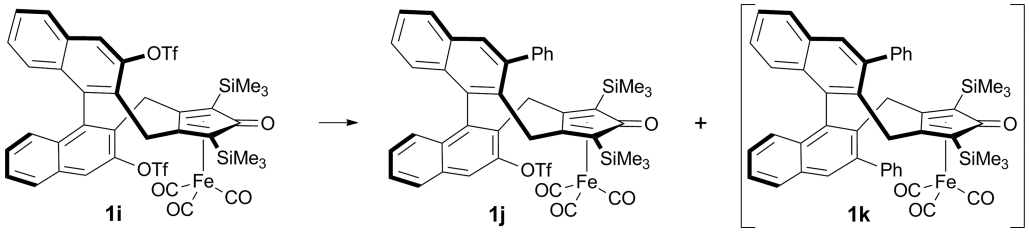


Scheme 8. Synthesis of sulfonyl esters (*R*)-**1g**–**1i**.

led to almost quantitative formation of the monosubstituted product (*R*)-**1j** (Table 2, Entries 1 and 2), without any trace of the desired product (*R*)-**1k**. Other conditions for the Suzuki–Miyaura reaction[30,31] were screened without success (Table 2, Entries 3–6). In particular, the use of relatively strong bases, the presence of water, or both caused the decomposition of the iron complex, probably through a Hieber base reaction to form the sensitive **B**-type (hydroxycyclopentadienyl)iron complex.[29] Several other Pd- and Ni-catalyzed cross-coupling reactions were screened (see Supporting Information for the full set of employed methodologies), but (*R*)-**1k** could not be formed.

NMR spectroscopy analysis showed that (*R*)-**1j** (see Scheme Table 2) is a single species, not a mixture of the two possible monosubstitution products. However, as we could not grow crystals of (*R*)-**1j**, we could not ascertain which of the two diastereotopic OTf groups of (*R*)-**1i** was replaced. We speculate that the OTf group of (*R*)-**1i** that did not react

Table 2. Arylation of bis-triflate (*R*)-**1i** by Suzuki–Miyaura cross-coupling.

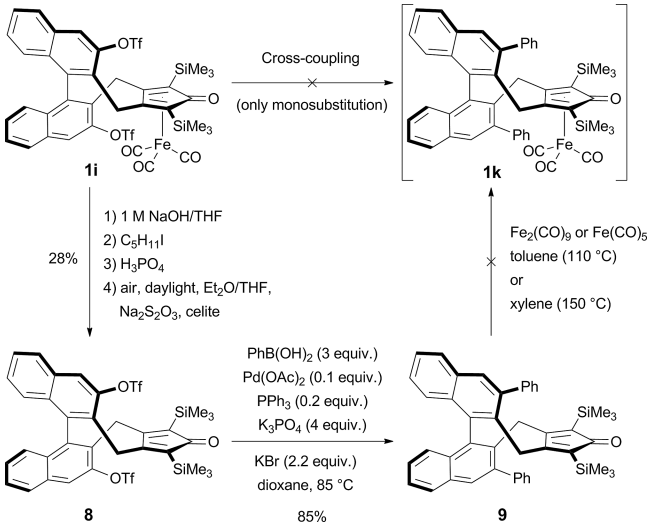


Entry	Conditions	NMR ratio[a]		
		1i [%]	**1j** [%]	**1k** [%]
1[28]	$PhB(OH)_2$ (2.5 equiv.), $[Pd(PPh_3)_4]$ (0.1 equiv.), K_3PO_4 (3 equiv.), KBr (2.2 equiv.), dioxane, 85 °C	5	95 (74)	0
2	$PhB(OH)_2$ (2.5 equiv.), $Pd(OAc)_2$ (0.2 equiv.), PPh_3 (0.4 equiv.), K_3PO_4 (3 equiv.), KBr (2.2 equiv.), dioxane, 85 °C	2	98 (80)	0
3[30]	$PhB(OH)_2$ (2.5 equiv.), $Pd(OAc)_2$ (0.15 equiv.), PCy_3 (0.18 equiv.), KF (3.3 equiv.), THF, 60 °C	97	3	0
4[31]	$PhB(OH)_2$ (5 equiv.), $[Pd(PPh_3)_4]$ (0.1 equiv.), $Ba(OH)_2{\cdot}8H_2O$, DME/H_2O, 85 °C		decomposition	

[a] Conversion determined by NMR spectroscopy; isolated yields are indicated in parentheses.

is probably the one close the $Fe(CO)_3$ group, which is sterically more hindered than the one that is more distant from the metal center.

To achieve substitution of both OTf groups, we decided to perform the Suzuki–Miyaura reaction of the cyclopentadienone ligand **8** (Scheme 9), obtained by decomplexation of (*R*)-**1i** according to the methodology reported by Knölker and co-workers.[29] As expected, both of the homotopic OTf groups of **8** reacted smoothly under Suzuki–Miyaura conditions[28] to yield the 3,3′-bis(phenyl)-substituted cyclopentadienone **9** (Scheme 9). This result lends credit to our hypothesis that the unreactive OTf group of complex (*R*)-**1i** is the one close to the $Fe(CO)_3$ group. We then tried to prepare complex (*R*)-**1k** by reaction of **9** with $Fe_2(CO)_9$ or $Fe(CO)_5$ in hot toluene or xylene (Scheme 6),[32] but no reaction occurred.

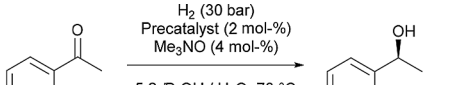


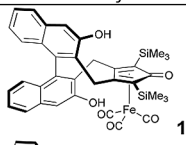
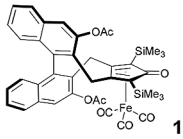
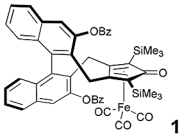
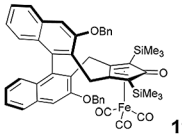
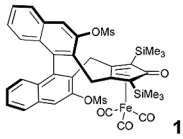
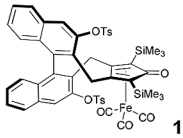
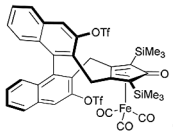
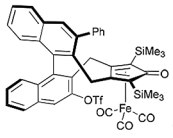
Scheme 9. Attempted synthesis of (*R*)-**1k** from (*R*)-**1i** by a decomplexation/cross-coupling/recomplexation sequence.

The newly synthesized complexes (*R*)-**1c**–**1j** were screened in the AH of acetophenone under the optimized conditions used with (*R*)-**1b**,[24] and the results are shown in Table 3. All complexes (*R*)-**1c**–**1j** (Table 3) were less active and induced lower enantioselectivity that the parent complex (*R*)-**1b** (Table 1, Entry 1). An incomplete conversion of the starting material was observed in all cases, and the best conversion (63%) was obtained with (*R*)-**1c** (Table 3, Entry 1). Moreover, only (*R*)-**1j** (Table 3, Entry 8) led to the same level of enantioselectivity as that obtained with (*R*)-**1b**, and all of the other precatalysts gave lower *ee* values (Table 3, Entries 1–7). Although a slight decrease of enantioselectivity was expected for (*R*)-**1c** owing to the smaller size of its OH substituents compared with OMe groups, we do not have a straightforward explanation for the low *ee* values observed with (*R*)-**1d**–**1i**, which bear 3,3′-substituents bulkier than OMe.

To assess the influence of the 2,5-substituents of the cyclopentadienone ring on the catalytic performance, we decided to replace the trimethylsilyl (TMS) groups of (*R*)-**1b** with triisopropylsilyl (TIPS), Ph, or H. The results of

Table 3. Screening of precatalysts (*R*)-**1c**–**1j** in the AH of acetophenone.[a]

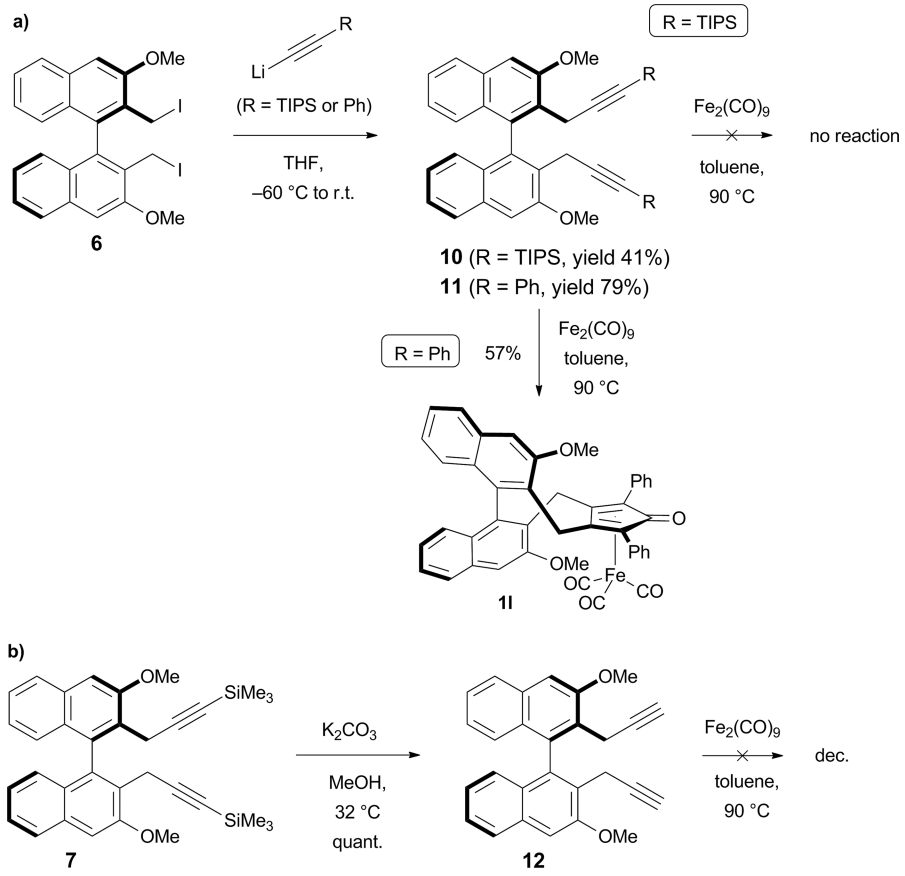


Entry	Precatalyst	Conv. (%)[b]	*ee* (%)[b,c]
1	 **1c**	63	46
2	 **1d**	3	46
3	 **1e**	16	38
4	 **1f**	38	39
5	 **1g**	14	39
6	 **1h**	20	37
7	 **1i**	7	35
8	 **1j**	22	52

[a] Reaction conditions: substrate/(*R*)-**1b**/Me_3NO 100:2:4, P_{H_2} = 30 bar, solvent: 5:2 *i*PrOH/H_2O, c_0(substrate) = 1.43 M, T = 70 °C, reaction time: 18 h. [b] Determined by GC with a chiral capillary column (MEGADEX DACTBSβ, diacetyl-*tert*-butylsilyl-β-cyclodextrin). [c] Absolute configuration: *S* in all cases (assigned by comparison of the optical rotation sign with literature data).[24]

our synthetic efforts towards these modified analogs of (*R*)-**1b** are shown in Scheme 10. The precursor diynes (*R*)-**10** and (*R*)-**11** were prepared by the reactions of the bis(iodide) (*R*)-**6** with [(triisopropylsilyl)ethynyl]lithium and [(phenyl)-ethynyl]lithium, respectively (Scheme 10, a).

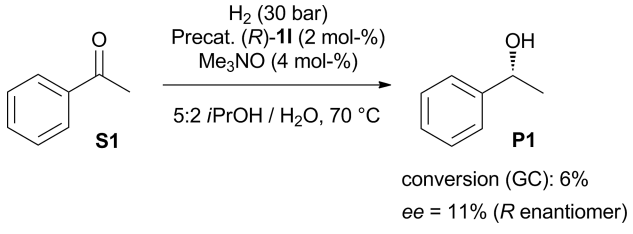
Diyne (*R*)-**12** was synthesized in 90% yield by desilylation of (*R*)-**7** in the presence of K_2CO_3 in MeOH (Scheme 10, b). The cyclization of the diynes to give the corresponding (cyclopentadienone)iron complexes was suc-



Scheme 10. Synthesis of (*R*)-**1b** analogs modified at the 2,5-positions of the cyclopentadienone ring.

cessful only for (*R*)-**11**, which yielded the corresponding bis-(phenyl)-substituted complex (*R*)-**1l**. Diyne (*R*)-**10** did not cyclize, probably owing to the excessive steric bulk of the TIPS groups, whereas the unprotected diyne **12** underwent complete degradation under cyclization conditions.

The new precatalyst (*R*)-**1l** was tested in the AH of acetophenone under the conditions optimized for (*R*)-**1b** (Scheme 11).



Scheme 11. Test of precatalyst (*R*)-**1l** in the AH of acetophenone under the optimized conditions [substrate/(*R*)-**1l**/Me_3NO 100:2:4, P_{H_2} = 30 bar, solvent = 5:2 *i*PrOH/H_2O, c_0(substrate) = 1.43 M, T = 70 °C, reaction time: 18 h].

Precatalyst (*R*)-**1l** gave very low conversion (6%). A possible explanation for such low activity is that the phenyl groups on the cyclopentadienone ring are not bulky enough to prevent dimerization of the (*R*)-**1l**-derived **B**-type complex followed by decomposition, as pointed out by Guan and co-workers for a related achiral complex.[21a] A modest enantiomeric excess (11%) was observed in favor of the *R* enantiomer of **P1**, in sharp contrast with the bis(trimethylsilyl)-substituted precatalyst (*R*)-**1b**, which forms (*S*)-**P1** preferentially. This inversion in the stereochemical preference demonstrates that the cyclopentadienone 2,5-substituents play an important role in the transmission of the stereochemical information to the substrate, which is no less important than that of the binaphthyl 3,3′-substituents.

Overall, the outcome of the AH promoted by precatalysts (*R*)-**1a**–**1l** depends on a subtle interplay between the binaphthyl 3,3′-substituents and the adjacent cyclopentadienone 2,5-substituents, and the optimal balance (in terms of both activity and enantiodiscrimination) was reached with the 3,3′-bis(methoxy)- and 2,5-bis(trimethylsilyl)-substituted complex (*R*)-**1b**. Future work will be devoted to rationalize this interplay to develop more-efficient second-generation precatalysts.

Conclusions

We have presented a new family of chiral (cyclopentadienone)iron complexes [(*R*)-**1a**–**1j** and (*R*)-**1l**], which feature a backbone derived from (*R*)-BINOL, and their use as precatalysts for the AH of ketones. The 3,3′-(bis)methoxy-substituted complex (*R*)-**1b** provided the best conversion and *ee* with acetophenone; thus, (*R*)-**1b** was employed in substrate screening and provided up to 77% *ee*. These *ee* values are the highest obtained to date with chiral (cyclo-

pentadienone/hydroxycyclopentdienyl)iron catalysts.[15d,16] Like other previously reported (cyclopentadienone)iron complexes, the new compounds are highly stable and tolerate the conditions required for several functional-group interconversion reactions. Taking advantage of this feature, we prepared seven complexes with different substituents at the 3,3′-positions of the binaphthyl moiety [(*R*)-**1d**–**1j**] from the common precursor (*R*)-**1c**, which in turn was prepared by demethylation of (*R*)-**1b**.[24] Substitution at the 3,3′-positions of the binaphthyl system affected both the activity and the enantioselectivity in an unclear manner, and (*R*)-**1b** remained the best precatalyst. The synthesis of analogs of (*R*)-**1b** featuring different substituents at the 2,5-positions of the cyclopentadienone ring was then undertaken, and the 2,5-bis(phenyl)-substituted compound (*R*)-**1l** was prepared. Compared to (*R*)-**1b**, the latter complex showed low catalytic activity and the opposite stereochemical preference in the AH of acetophenone. This finding suggests that both the binaphthyl 3,3′-substituents and the cyclopentadienone 2,5-substituents of the new catalysts play a role in the transmission of the stereochemical information.

Experimental Section

General Remarks: All reactions were performed in flame-dried glassware with magnetic stirring under an inert atmosphere (nitrogen or argon), unless otherwise stated. The solvents for the reactions were distilled from the following drying agents and transferred under nitrogen: CH_2Cl_2 (CaH_2), MeOH (CaH_2), THF (Na), dioxane (Na), toluene (Na), Et_3N (CaH_2). Dry dichloroethane, *N*,*N*-dimethylformamide (DMF), dimethoxyethane, 2-propanol, ethanol, acetone, and $CHCl_3$ (over molecular sieves in bottles with crown caps) were purchased from Sigma–Aldrich and stored under nitrogen. The reactions were monitored by analytical thin-layer chromatography (TLC) with silica gel 60 F254 precoated glass plates (0.25 mm thickness). Visualization was accomplished by irradiation with a UV lamp, staining with a potassium permanganate alkaline solution, or both. Flash column chromatography was performed with silica gel (60 Å, particle size 40–64 μm) as the stationary phase by following the procedure of Still and co-workers.[33] The ^{1}H NMR spectra were recorded with a spectrometer operating at 400.13 MHz. The ^{1}H chemical shifts (δ) are reported in ppm with the solvent signal relative to tetramethylsilane employed as the internal standard ($CDCl_3$ δ = 7.26 ppm, CD_2Cl_2 δ = 5.32 ppm, $[D]_6$acetone δ = 2.05 ppm). The following abbreviations are used to describe spin multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad signal, dd = doublet of doublets, ddd = doublet of doublets- of doublets, td = triplet of doublets. The ^{13}C NMR spectra were recorded with a 400 MHz spectrometer operating at 100.56 MHz with complete proton decoupling. The ^{13}C chemical shifts are reported in ppm (δ) relative to tetramethylsilane with the respective solvent resonance as the internal standard ($CDCl_3$ δ = 77.16 ppm, CD_2Cl_2 δ = 54.00 ppm, $[D]_6$acetone δ = 29.84, 206.26 ppm). The ^{19}F NMR spectra were recorded with a 300 MHz spectrometer operating at 282 MHz. The ^{19}F NMR chemical shifts are reported in ppm relative to external $CFCl_3$ at δ = 0 ppm (positive values downfield). The coupling constants are given in Hz. The infrared spectra were recorded with a standard FTIR spectrometer. The optical rotation values were measured with an automatic polarimeter with a 1 dm cell at the sodium D line (λ = 589 nm) or with a Hg lamp at λ = 436 nm. Gas chromatography was performed with a GC instrument equipped with a flame ionization detector and a chiral capillary column. High-resolution mass spectrometry (HRMS) was performed with a Fourier transform ion cyclotron resonance (FTICR) Mass Spectrometer APEX II with a 4.7 T Magnet (Magnex) and an ESI source at CIGA (Centro Interdipartimentale Grandi Apparecchiature) c/o Università degli Studi di Milano; the Xmass software (Bruker Daltonics) was used. Elemental analyses were performed with a Perkin–Elmer Series II CHNS/O Analyzer 2000. The X-ray intensity data were collected with a Bruker Apex II CCD area detector by using graphite-monochromated Mo-K_α radiation.

General Procedure for the Asymmetric Hydrogenation: Hydrogenations were performed in a 450 mL Parr autoclave equipped with a removable aluminum block that can accommodate up to fifteen magnetically stirred 7 mL glass vials. The catalyst (0.01 mmol, 2 mol-%) was weighed into glass vials, which were accommodated in the aluminum block after the addition of magnetic stir bars to each of them. The block was placed in a Schlenk tube, which was then subjected to three vacuum–nitrogen cycles. *i*PrOH (0.25 mL) was added to each vial, and stirring was started. Me_3NO (0.02 mmol, 4 mol-%) was added to each vial as an H_2O solution (0.1 mL). The mixtures were stirred at room temperature under nitrogen for 10 min, and then the substrate (0.5 mmol) was added. Each vial was capped with a Teflon septum pierced by a needle, the block was transferred into the autoclave, and stirring was started. After four purges with hydrogen at the selected pressure, heating was started. The reaction mixtures were stirred under hydrogen pressure overnight and then analyzed for conversion and *ee* determination.

Complex (*R*)-1a: Diyne **4** (0.510 g, 1.07 mmol, 1 equiv.) and $Fe_2(CO)_9$ (0.781 g, 2.14 mmol, 2 equiv.) were dissolved in toluene (9 mL) and heated to 90 °C for 4 h. After cooling to room temperature, the reaction mixture was filtered through a pad of Celite [rinsed with dichloromethane (DCM)]. The filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography (8:2 hexane/DCM) to afford (*R*)-**1a** as a pale yellow solid, yield 0.320 g (46%); m.p. 209 °C (dec.). $[\alpha]_D^{19}$ = –32.24 (*c* = 0.9, DCM). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.04 [d, ^3J(H,H) = 8.5 Hz, 2 H], 7.99 [d, ^3J(H,H) = 8.8 Hz, 1 H], 7.97 [d, ^3J(H,H) = 8.8 Hz, 1 H], 7.68 [d, ^3J(H,H) = 8.5 Hz, 1 H], 7.55 [d, ^3J(H,H) = 8.5 Hz, 1 H], 7.52–7.45 (m, 2 H), 7.30 [td, ^3J(H,H) = 8.5, ^4J(H,H) = 1.1 Hz, 1 H], 7.25 [td, ^3J(H,H) = 8.5, ^4J(H,H) = 1.1 Hz, 1 H], 7.20 [d, ^3J(H,H) = 8.5 Hz, 1 H], 7.09 [d, ^3J(H,H) = 8.5 Hz, 1 H], 3.76 [d, ^2J(H,H) = 15.7 Hz, 1 H], 3.67 [d, ^2J(H,H) = 14.1 Hz, 1 H], 3.45 [d, ^2J(H,H) = 15.7 Hz, 1 H], 3.38 [d, ^2J(H,H) = 14.1 Hz, 1 H], 0.41 (s, 9 H), 0.26 (s, 9 H) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 209.8, 181.4, 137.0, 135.6, 135.0, 134.6, 133.4, 132.5, 130.0, 129.7, 128.9, 128.7, 127.5, 127.3, 127.1, 127.0, 126.9, 126.5, 113.1, 111.5, 76.0, 74.0, 34.8, 32.8, 0.9, 0.5 ppm. IR (film): $\tilde{\nu}$ = 3054.69, 2953.93, 2060.1, 2005.1, 1985.4, 1626.2, 1507.6, 1429.5, 1264.1, 1248.7 cm^{-1}. HRMS (ESI+): calcd. for $C_{36}H_{35}O_4Si_2Fe$ $[M + H]^+$ 643.14294; found 643.14164.

Complex (*R*)-1b: Diyne **7** (3.27 g, 6.11 mmol, 1 equiv.) and $Fe_2(CO)_9$ (4.55 g, 12.5 mmol, 2 equiv.) were dissolved in toluene (45 mL) and heated to 90 °C for 4.5 h. After cooling to room temperature, the reaction mixture was filtered through a pad of Celite (rinsed with DCM). The filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography (93:7 hexane/AcOEt) to afford (*R*)-**1b** as a pale yellow solid, yield 2.88 g (67% yield); m.p. 233–237 °C (dec.). $[\alpha]_D^{23}$ = –129.38 (*c* = 0.41, DCM). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (m, 2 H), 7.42 [t, ^3J(H,H) = 7.2 Hz, 2 H], 7.33 (s, 1 H), 7.30 (s, 1 H), 7.11–7.03 (m, 2 H), 6.92 [d,

^3J(H,H) = 8.4 Hz, 2 H], 4.37 [d, ^2J(H,H) = 15.5 Hz, 1 H], 4.15 [d, ^2J(H,H) = 13.7 Hz, 1 H], 4.04 (s, 3 H), 3.94 (s, 3 H), 3.26 [d, ^2J(H,H) = 13.7 Hz, 1 H], 3.12 [d, ^2J(H,H) = 15.5 Hz, 1 H], 0.43 (s, 9 H), 0.32 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.7, 181.1, 155.1, 154.8, 138.6, 137.2, 133.9, 133.8, 127.4, 127.2, 127.1, 127.0, 126.9, 126.8, 126.6, 126.5, 126.4, 124.3, 124.1, 115.4, 107.8, 106.3, 105.7, 75.2, 74.9, 55.6, 54.8, 26.3, 26.2, 0.7, 0.2 ppm. IR (film): $\tilde{\nu}$ = 3059.5, 2960.2, 2169.0, 2059.6, 2004.2, 1987.3, 1620.4, 1598.7, 1454.1, 1246.3, 1111.3 cm^{-1}. HRMS (ESI+): calcd. for $C_{38}H_{39}O_6Si_2Fe$ [M + H]$^+$ 703.16410; found 703.16264.

Complex (*R*)-1c: In a Schlenk tube fitted with a Teflon screw cap, BBr_3 (1 M DCM solution, 14.0 mL, 14.0 mmol, 10 equiv.) was added dropwise to a stirred solution of (*R*)-**1b** (0.99 g, 1.41 mmol, 1 equiv.) and Bu_4NI (1.30 g, 3.52 mmol, 2.5 equiv.) in DCE (40 mL) at 0 °C. The Schlenk tube was sealed, and the mixture was heated to 84 °C and stirred for 3 d. After this time, the reaction mixture was cooled to 0 °C, and ice-cold H_2O (50 mL) was added. The mixture was extracted with DCM (3 × 20 mL), washed with brine (30 mL), and then dried with Na_2SO_4. Filtration of the DCM solution through a short pad of silica allowed the removal of the ammonium salts (which eluted before the product), and then complex (*R*)-**1c** was obtained as a pale yellow solid after purification by flash column chromatography (83:17 to 77:23 hexane/AcOEt), yield 0.762 g (80%); m.p. 187–195 °C (dec.). $[\alpha]_D^{23}$ = –115.07 (*c* = 0.515, DCM). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 [d, ^3J(H,H) = 8.2 Hz, 2 H], 7.39–7.35 (m, 3 H), 7.31 (s, 1 H), 7.06 [t, ^3J(H,H) = 7.5 Hz, 2 H], 6.98 [dd, ^3J(H,H) = 8.3, ^4J(H,H) = 2.3 Hz, 2 H], 6.32 (br s, 2 H), 4.34 [d, ^2J(H,H) = 15.6 Hz, 1 H], 4.14 [d, ^2J(H,H) = 13.8 Hz, 1 H], 3.24 [d, ^2J(H,H) = 13.8 Hz, 1 H], 3.11 [d, ^2J(H,H) = 15.5 Hz, 1 H], 0.41 (s, 9 H), 0.31 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.4, 180.3, 152.3, 152.2, 138.9, 137.7, 134.0, 133.9, 127.3, 127.3, 127.1, 126.4, 126.1, 125.5, 123.8, 123.6, 114.7, 110.4, 109.5, 76.3, 75.4, 29.8, 26.4, 0.9, 0.5 ppm. IR (film): $\tilde{\nu}$ = 3236.0, 2953.4, 2852.7, 2065.9, 2010.4, 1996.9, 1575.1, 1342.2, 1248.2 cm^{-1}. HRMS (ESI+): calcd. for $C_{36}H_{35}O_6Si_2Fe$ [M + H]$^+$ 675.13277; found 675.13152.

Complex (*R*)-1d: Acetyl chloride (32 μL, 0.44 mmol, 3 equiv.) was added slowly to a stirred solution of (*R*)-**1c** (100 mg, 0.15 mmol, 1 equiv.), Et_3N (83 μL, 0.59 mmol, 4 equiv.), and DMAP (1.6 mg, 0.015 mmol, 0.1 equiv.) in THF (2 mL), and the mixture was heated under reflux for 3 h. After this time, the mixture was diluted with DCM and washed with 0.5 M HCl (2 × 5 mL), saturated aqueous $NaHCO_3$ (5 mL), and brine (5 mL). The organic phase was then dried with Na_2SO_4. Complex (*R*)-**1d** was obtained as a pale yellow solid after purification by flash column chromatography (90:10 to 85:15 hexane/AcOEt), yield 103.3 g (92%); m.p. 162–166 °C. $[\alpha]_D^{22}$ = + 19.37 (*c* = 0.51, DCM). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 [d, ^3J(H,H) = 8.2 Hz, 1 H], 7.87 [d, ^3J(H,H) = 8.2 Hz, 1 H], 7.80 (s, 1 H), 7.73 (s, 1 H), 7.52–7.43 (m, 2 H), 7.25–7.17 (m, 2 H), 6.99 [d, ^3J(H,H) = 8.4 Hz, 1 H], 6.85 [d, ^3J(H,H) = 8.4 Hz, 1 H], 4.00 [d, ^2J(H,H) = 16.0 Hz, 1 H], 3.89 [d, ^2J(H,H) = 14.3 Hz, 1 H], 3.36 [d, ^2J(H,H) = 14.3 Hz, 1 H], 3.34 [d, ^2J(H,H) = 16.0 Hz, 1 H], 2.45 (s, 3 H), 2.39 (s, 3 H), 0.45 (s, 9 H), 0.32 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.2, 181.0, 170.1, 169.8, 146.1, 138.8, 137.5, 133.0, 132.9, 130.2, 130.1, 128.7, 127.9, 127.8, 127.5, 127.0, 126.8, 126.7, 126.6, 121.6, 121.1, 112.0, 110.2, 74.9, 74.6, 27.5, 26.6, 22.3, 21.9, 0.9, 0.5 ppm. IR (film): $\tilde{\nu}$ = 3062.4, 2953.9, 2923.6, 2903.3, 2852.7, 2062.5, 2007.5, 1989.7, 1768.4, 1624.25, 1189.4, 1155.6, 1087.7, 849.0 cm^{-1}. HRMS (ESI+): calcd. for $C_{50}H_{43}O_8Si_2Fe$ [M + H]$^+$ 759.15395; found 759.15207.

Complex (*R*)-1e: Benzoyl chloride (26 μL, 0.22 mmol, 3 equiv.) was added slowly to stirred solution of (*R*)-**1c** (50 mg, 0.07 mmol, 1 equiv.), Et_3N (41 μL, 0.3 mmol, 4 equiv.), and DMAP (0.8 mg, 0.007 mmol, 0.1 equiv.) in THF (1 mL), and the mixture was heated under reflux for 4 h. After this time, the mixture was diluted with DCM and washed with 0.5 M HCl (2 × 5 mL), saturated aqueous $NaHCO_3$ (5 mL), and brine (5 mL). The organic phase was then dried with Na_2SO_4. After concentration, the pure complex (*R*)-**1e** was obtained as a pale yellow solid after purification by flash column chromatography (95:5 to 9:1 hexane/AcOEt), yield 53 mg (81%); m.p. 176 °C (dec.). $[\alpha]_{436}^{27}$ = –108.6 (*c* = 0.25 in DCM). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.26 (m, 1 H), 8.24 (m, 1 H), 8.21 (m, 1 H), 8.19 (m, 1 H), 7.92 [d, ^3J(H,H) = 4.7 Hz, 1 H], 7.90 [d, ^3J(H,H) = 4.6 Hz, 1 H], 7.83 (s, 1 H), 7.82 (s, 1 H), 7.72–7.64 (m, 2 H), 7.59–7.46 (m, 6 H), 7.31–7.26 (m, 2 H), 7.01 [dd, ^3J(H,H) = 8.4, ^4J(H,H) = 0.6 Hz, 1 H], 6.97 [dd, ^3J(H,H) = 8.5, ^4J(H,H) = 0.6 Hz, 1 H], 4.01 [d, ^2J(H,H) = 14.5 Hz, 1 H], 3.98 [d, ^2J(H,H) = 16.1 Hz, 1 H], 3.58 [d, ^2J(H,H) = 14.6 Hz, 1 H], 3.49 [d, ^2J(H,H) = 16.1 Hz, 1 H], 0.10 (s, 9 H), 0.03 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.1, 181.0, 167.0, 166.6, 147.3, 147.1, 139.0, 137.8, 134.2, 134.1, 133.3, 131.1, 130.7, 129.7, 129.7, 129.5, 129.2, 128.7, 127.8, 127.1, 126.9, 126.7, 121.1, 120.7, 113.2, 109.1, 75.7, 74.8, 27.7, 27.2, 0.7, 0.3 ppm. IR (film): $\tilde{\nu}$ = 3062.9, 2953.9, 2897.5, 2062.0, 2007.5, 1990.2, 1740.4, 1624.7, 1266.0, 1246.3, 1090.1, 1022.1, 847.1, 711.1 cm^{-1}. HRMS (ESI+): calcd. for $C_{50}H_{43}O_8Si_2Fe$ [M + H]$^+$ 883.18537; found 883.187411.

Complex (*R*)-1f: Benzyl bromide (53 μL, 0.45 mmol, 6 equiv.) was added slowly to a stirred solution of (*R*)-**1c** (50 mg, 0.07 mmol, 1 equiv.) and K_2CO_3 (41 mg, 0.30 mmol, 4 equiv.) in DMF (0.37 mL), and the mixture was stirred at 70 °C overnight. After this time, the reaction mixture was cooled to room temp. and diluted with Et_2O (8 mL). The mixture was washed with H_2O (3 × 5 mL), and the organic phase was dried with Na_2SO_4. Complex (*R*)-**1f** was obtained as a pale yellow solid after purification by flash column chromatography (9:1 DCM/hexane), yield 42 mg (70%); m.p. 155 °C (dec.). $[\alpha]_D^{32}$ = –20.6 (*c* = 0.92, DCM). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 [d, ^3J(H,H) = 8.1 Hz, 1 H], 7.71 [d, ^3J(H,H) = 8.1 Hz, 1 H], 7.46–7.23 (m, 14 H), 7.11–7.03 (m, 2 H), 6.91–6.84 (m, 2 H), 5.51 [d, ^2J(H,H) = 13.5 Hz, 1 H], 5.46 [d, ^2J(H,H) = 13.5 Hz, 1 H], 5.26 [d, ^2J(H,H) = 11.3 Hz, 1 H], 5.17 [d, ^2J(H,H) = 11.3 Hz, 1 H], 4.38 [d, ^2J(H,H) = 15.6 Hz, 1 H], 4.29 [d, ^2J(H,H) = 13.8 Hz, 1 H], 3.35 [d, ^2J(H,H) = 13.8 Hz, 1 H], 3.15 [d, ^2J(H,H) = 15.6 Hz, 1 H], 0.32 (s, 9 H), 0.08 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.6, 181.1, 154.1, 153.6, 139.0, 137.6, 136.7, 136.1, 133.8, 133.6, 129.1, 128.9, 128.7, 128.5, 128.1, 127.4, 127.4, 127.2, 127.1, 127.1, 127.0, 126.9, 126.9, 126.6, 126.4, 124.3, 124.3, 114.8, 108.7, 108.6, 107.3, 75.8, 75.1, 70.5, 70.1, 26.4, 26.2, 0.8, 0.2 ppm. IR (film): $\tilde{\nu}$ = 3063.4, 3034.4, 2953.0, 2899.0, 2060.1, 2004.2, 1987.3, 1757.3, 1620.9, 1596.8, 1246.3, 1105.5, 850.5, 738.1 cm^{-1}. HRMS (ESI+): calcd. for $C_{50}H_{47}O_6Si_2Fe$ [M + H]$^+$ 855.22685; found 855.22583.

Complex (*R*)-1g: Methanesulfonyl chloride (17 μL, 0.22 mmol, 3 equiv.) was added slowly to a stirred solution of (*R*)-**1c** (50 mg, 0.07 mmol, 1 equiv.), Et_3N (41 μL, 0.30 mmol, 4 equiv.), and DMAP (0.8 mg, 0.007 mmol, 0.1 equiv.) in THF (1 mL), and the mixture was heated under reflux for 5 h. After this time, the reaction mixture was cooled to room temp., diluted with AcOEt (5 mL), and washed with 0.5 M HCl (2 × 5 mL), saturated aqueous $NaHCO_3$ (5 mL), and brine (5 mL). The organic phase was dried with Na_2SO_4. After concentration, the pure complex (*R*)-**1g** was obtained as a pale yellow solid, yield 40 mg (65%); m.p. 172 °C (dec.). $[\alpha]_D^{27}$ = –6.8 (*c* = 1.4 in DCM). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (s, 1 H), 8.09 (s, 1 H), 7.99 [d, ^3J(H,H) = 8.3 Hz, 1 H], 7.96 [d, ^3J(H,H) = 8.3 Hz, 1 H], 7.56 [dd, ^3J(H,H) = 8.3, ^3J(H,H) = 7.0 Hz, 1 H], 7.53 [dd, ^3J(H,H) = 8.3, ^3J(H,H) = 6.9 Hz, 1 H],

7.33 [dd, ^3J(H,H) = 8.4, ^3J(H,H) = 7.0 Hz, 1 H], 7.28 [dd, ^3J(H,H) = 8.5, ^3J(H,H) = 6.9 Hz, 1 H], 6.99 [d, ^3J(H,H) = 8.4 Hz, 1 H], 6.85 [d, ^3J(H,H) = 8.5 Hz, 1 H], 4.25 [d, ^2J(H,H) = 16.2 Hz, 1 H], 4.15 [d, ^2J(H,H) = 14.4 Hz, 1 H], 3.35 [d, ^2J(H,H) = 14.4 Hz, 1 H], 3.33 [d, ^2J(H,H) = 16.2 Hz, 1 H], 3.31 (s, 3 H), 3.29 (s, 3 H), 0.45 (s, 9 H), 0.33 (m, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.2, 181.4, 144.4, 143.5, 139.3, 138.0, 132.8, 132.7, 130.5, 130.5, 128.8, 128.5, 128.4, 128.2, 128.0, 127.8, 127.8, 127.7, 126.6, 126.3, 121.9, 121.4, 111.1, 110.1, 75.5, 75.1, 38.8, 38.6, 27.7, 26.7, 0.7, 0.5 ppm. IR (film): $\tilde{\nu}$ = 3054.2, 2986.7, 2066.4, 2010.4, 1994.5, 1617.5, 1265.6, 739.1, 705.3 cm^{-1}. HRMS (ESI+): calcd. for $C_{38}H_{38}O_{10}S_2Si_2FeNa$ [M + Na]$^+$ 853.06985; found 853.06820.

Complex (*R*)-1h: *p*-Toluenesulfonyl chloride (43 mg, 0.22 mmol, 3 equiv.) was added slowly to a stirred solution of (*R*)-**1c** (50 mg, 0.07 mmol, 1 equiv.), Et_3N (41 μL, 0.03 mmol, 4 equiv.), and DMAP (0.8 mg, 0.007 mmol, 0.1 equiv.) in THF (1 mL), and the mixture was heated under reflux overnight. The reaction mixture was cooled to room temp., diluted with AcOEt (5 mL), and washed with 0.5 M HCl (2× 5 mL), saturated aqueous $NaHCO_3$ (5 mL), and brine (5 mL). The organic phase was dried with Na_2SO_4. After concentration, the pure complex (*R*)-**1h** was obtained as a pale yellow solid, yield 63 mg (96%); m.p. 166–168 °C (dec.). $[\alpha]_D^{23}$ = + 168.6 (*c* = 1.2, DCM). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 (s, 1 H), 7.85 [d, ^3J(H,H) = 8.3 Hz, 1 H], 7.82 [d, ^3J(H,H) = 8.3 Hz, 1 H], 7.79 (s, 1 H), 7.70 [d, ^3J(H,H) = 8.0 Hz, 2 H], 7.65 [d, ^3J(H,H) = 8.0 Hz, 2 H], 7.51 [t, ^3J(H,H) = 7.5 Hz, 2 H], 7.29–7.19 (m, 6 H), 6.65 [d, ^3J(H,H) = 8.4 Hz, 1 H], 6.54 [d, ^3J(H,H) = 8.5 Hz, 1 H], 3.93 [d, ^2J(H,H) = 16.1 Hz, 1 H], 3.92 [d, ^2J(H,H) = 14.3 Hz, 1 H], 3.01 [d, ^2J(H,H) = 14.3 Hz, 1 H], 2.86 [d, ^2J(H,H) = 16.1 Hz, 1 H], 2.40 (s, 3 H), 2.37 (s, 3 H), 0.43 (s, 9 H), 0.27 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.0, 181.3, 145.9, 145.9, 145.0, 145.0, 138.8, 137.3, 132.7, 132.5, 132.4, 130.2, 130.1, 130.0, 129.9, 129.3, 128.9, 128.8, 128.5, 128.4, 128.3, 127.4, 127.3, 127.3, 126.2, 126.1, 121.2, 121.2, 111.5, 108.6, 75.3, 74.9, 27.3, 26.4, 21.9, 21.9, 0.6, 0.6 ppm. IR (film): $\tilde{\nu}$ = 3054.2, 2986.7, 2916.8, 2066.4, 2010.9, 1422.2, 1265.6, 895.8, 740.5, 705.3 cm^{-1}. HRMS (ESI+): calcd. for $C_{50}H_{47}O_{10}S_2Si_2Fe$ [M + H]$^+$ 983.15069; found 983.14923.

Complex (*R*)-1i: *N*-(5-Chloro-2-pyridyl)bis(trifluoromethanesulfonimide) (1.2 g, 3.0 mmol, 3 equiv.) was added to a stirred solution of (*R*)-**1c** (670 mg, 1.0 mmol, 1 equiv.), Et_3N (550 μL, 4.0 mmol, 4 equiv.), and DMAP (12 mg, 0.1 mmol, 0.1 equiv.) in DCM (30 mL), and the mixture was stirred at room temp. overnight. The reaction was diluted with DCM (30 mL) and washed with 0.5 M HCl (2× 50 mL), 0.5 M NaOH (2× 50 mL), and brine (50 mL). The organic phase was then dried with Na_2SO_4. Complex (*R*)-**1i** was obtained as a pale yellow solid after purification by flash column chromatography (10:1 hexane/AcOEt), yield 882 mg (94%); m.p. 142–143 °C (dec.). $[\alpha]_D^{24}$ = + 43.9 (*c* = 1.9, DCM). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (s, 1 H), 8.12 (s, 1 H), 8.03 [d, ^3J(H,H) = 8.5 Hz, 1 H], 8.01 [d, ^3J(H,H) = 8.3 Hz, 1 H], 7.62 [t, ^3J(H,H) = 7.5 Hz, 1 H], 7.61 [t, ^3J(H,H) = 7.5 Hz, 1 H], 7.40 [t, ^3J(H,H) = 8.2 Hz, 1 H], 7.38 [t, ^3J(H,H) = 8.1 Hz, 1 H], 6.90 [d, ^3J(H,H) = 8.5 Hz, 1 H], 6.84 [d, ^3J(H,H) = 8.5 Hz, 1 H], 4.18 [d, ^2J(H,H) = 16.2 Hz, 1 H], 4.13 [d, ^2J(H,H) = 14.6 Hz, 1 H], 3.40 [d, ^2J(H,H) = 14.7 Hz, 1 H], 3.35 [d, ^2J(H,H) = 16.2 Hz, 1 H], 0.41 (s, 9 H), 0.31 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.9, 181.3, 145.2, 144.9, 139.4, 137.9, 132.7, 132.6, 130.8, 130.7, 128.9, 128.8, 128.8, 128.7, 128.4, 128.3, 127.8, 127.1, 126.2, 126.0, 120.9, 120.8, 119.0 [q, ^1J(C,F) = 324.5 Hz], 118.9 [q, ^1J(C,F) = 324.5 Hz], 110.7, 108.7, 75.5, 75.5, 27.6, 26.8, 0.5, 0.4 ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –71.7, –72.7 ppm. IR (film): $\tilde{\nu}$ = 3066.7, 2954.9, 2925.5, 2903.3, 2852.7, 2065.4, 2011.9, 1993.6, 1629.1, 1427.6, 1245.8, 1212.5, 1138.3, 915.5, 883.2, 844.7, 822.0 cm^{-1}. HRMS (ESI+): calcd. for $C_{38}H_{32}O_{10}F_6S_2Si_2FeNa$ [M + Na]$^+$ 961.01332; found 961.01272.

Complex (*R*)-1j: Complex (*R*)-**1i** (100 mg, 0.1 mmol, 1 equiv.), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 0.2 equiv.), PPh_3 (10.5 mg, 0.04 mmol, 0.4 equiv.), K_3PO_4 (63 mg, 0.3 mmol, 3 equiv.), KBr (26 mg, 0.22 mmol, 2.2 equiv.), and phenylboronic acid (30.5 mg, 0.25 mmol, 2.5 equiv.) were dissolved in dioxane (2.5 mL). The reaction mixture was heated to 85 °C and stirred overnight. The mixture was diluted with DCM (5 mL), washed with 1 M NaOH (5 mL), H_2O (5 mL), and brine (5 mL), and then dried with Na_2SO_4. Complex (*R*)-**1j** was obtained as a yellow solid after purification by flash column chromatography (6:4 to 8:2 DCM/hexane), yield 69 mg (80%); m.p. 157–158 °C (dec.). $[\alpha]_D^{21}$ = + 88.3 (*c* = 0.6, DCM). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10 (s, 1 H), 8.01 [d, ^3J(H,H) = 8.2 Hz, 1 H], 7.93 [d, ^3J(H,H) = 8.2 Hz, 1 H], 7.90 (s, 1 H), 7.63–7.31 (m, 8 H), 7.26 [dd, ^3J(H,H) = 8.5, ^3J(H,H) = 7.3 Hz, 1 H], 7.02 [d, ^3J(H,H) = 8.5 Hz, 1 H], 6.70 [d, ^3J(H,H) = 8.5 Hz, 1 H], 4.27 [d, ^2J(H,H) = 14.8 Hz, 1 H], 4.11 [d, ^2J(H,H) = 15.8 Hz, 1 H], 3.58 [d, ^2J(H,H) = 14.8 Hz, 1 H], 3.50 [d, ^2J(H,H) = 15.8 Hz, 1 H], 0.33 (s, 9 H), –0.15 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.1, 180.8, 144.9, 141.6, 141.3, 139.4, 136.1, 132.7, 132.5, 132.5, 132.1, 131.1, 130.9, 128.6, 128.3, 128.1, 127.9, 127.6, 127.4, 127.0, 126.4, 125.7, 120.0, 118.9 [q, ^1J(C,F) = 321.3 Hz], 111.8, 111.2, 75.9, 75.5, 29.5, 27.5, 0.5, 0.4 ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –72.1 ppm. IR (film): $\tilde{\nu}$ = 3054.7, 2987.2, 2065.4, 2009.5, 1639.7, 1421.8, 1265.6, 744.4, 705.3 cm^{-1}. HRMS (ESI+): calcd. for $C_{43}H_{37}O_7F_3S_1Si_2FeNa$ [M + Na]$^+$ 889.10049; found 889.10212.

Complex (*R*)-1l: Diyne **11** (271 mg, 0.50 mmol, 1 equiv.) and $Fe_2(CO)_9$ (455 mg, 1.25 mmol, 2.5 equiv.) were dissolved in toluene (6 mL), and the mixture was stirred at 90 °C overnight. After cooling to room temperature, the reaction mixture was filtered through a pad of Celite (rinsed with DCM). The filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography (8:2 hexane/DCM) to afford (*R*)-**1l** as a pale yellow solid, yield 201 mg (57% yield); m.p. 156–158 °C. $[\alpha]_D^{17}$ = –92.1 (*c* = 0.4, DCM). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 [d, ^3J(H,H) = 8.2 Hz, 1 H], 7.80 [d, ^3J(H,H) = 8.2 Hz, 1 H], 7.46–7.30 (m, 5 H), 7.30 (s, 1 H), 7.26 (s, 1 H), 7.21–7.01 (m, 9 H), 6.91 (m, 1 H), 6.81 (m, 1 H), 3.97 [d, ^2J(H,H) = 15.2 Hz, 1 H], 3.96 (s, 3 H), 3.86 [d, ^2J(H,H) = 14.3 Hz, 1 H], 3.80 (s, 3 H), 3.08 [d, ^2J(H,H) = 15.1 Hz, 1 H], 2.99 [d, ^2J(H,H) = 14.3 Hz, 1 H] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.8, 212.2, 205.9, 204.7, 183.1, 167.3, 155.6, 155.1, 148.7, 148.6, 138.6, 138.4, 134.0, 133.8, 132.7, 129.8, 128.6, 128.2, 128.0, 127.5, 127.2, 127.0, 127.0, 127.0, 126.9, 126.6, 126.5, 126.4, 126.4, 126.3, 124.1, 123.9, 105.9, 105.6, 55.1, 54.8, 30.2, 29.3 ppm. IR (film): $\tilde{\nu}$ = 3055.7, 2919.7, 2858.0, 2061.5, 1985.4, 2024.9, 1599.6, 1451.2, 1111.8, 1025.9 cm^{-1}. HRMS (ESI+): calcd. for $C_{40}H_{30}O_2Na$ [M + Na]$^+$ 733.12972; found 733.13041.

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