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Microstructure Analysis of a CO_2 Copolymer from Styrene Oxide at the Diad Level

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Abstract: A large amount of interesting information on the alternating copolymerization of CO_2 with terminal epoxides has already been reported, such as the regiochemistry of epoxide ring-opening and the stereochemistry of the carbonate unit sequence in the polymer chain. Moreover, the microstructures of CO_2 copolymers from propylene oxide and cyclohexene oxide have also been well-studied. However, the microstructure of the CO_2 copolymer from styrene oxide (SO), an epoxide that contains an electron-withdrawing group, has not yet been investigated. Herein, we focus on the spectroscopic assignment of the CO_2 copolymer from styrene oxide at the diad level by using three kinds of model dimer compounds, that is, **T-T**, **H-T**, and **H-H**. By comparing the signals in the carbonyl region, we concluded that the signals at $\delta = 154.3$, 153.8, and 153.3 ppm in the ^{13}C NMR spectrum of poly(styrene carbonate) were due to tail-to-tail, head-to-tail, and head-to-head carbonate linkages, respectively. Moreover, various isotactic and syndiotactic model compounds based on **T-T**, **H-T**, and **H-H** (dimers (*R*,*R*)-**T-T**, (*S*,*S*)-**T-T**, and (*R*,*S*)-**T-T**; (*R*,*R*)-**H-T**, (*S*,*S*)-**H-T**, and (*R*,*S*)-**H-T**; (*R*,*R*)-**H-H**, (*S*,*S*)-**H-H**, and (*R*,*S*)-**H-H**) were synthesized for the further spectroscopic assignment of stereospecific poly(styrene carbonate)s. We found that the carbonate carbon signals were sensitive towards the stereocenters on adjacent styrene oxide ring-opening units. These discoveries were found to be well-matched to the microstructures of the stereoregular poly(styrene carbonate)s that were prepared by using a multichiral Co^{III}-based catalyst system.

Keywords: copolymerization · NMR spectroscopy · poylmers · stereochemistry · styrene oxide

Introduction

The control of polymer microstructure is one of the most-important goals in the area of stereoselective polymerization catalysis,[1] because the physical properties of a polymer are mainly determined by the relative stereochemistry of adjacent locations in the polymeric chain (that is, the spatial arrangement of atoms or groups in a polymeric unit). Importantly, the regio- and/or stereochemistry of a polymer preserves the traces of the reaction pathway, which is beneficial for understanding the polymerization mechanism.[2] Therefore, the assignment of the stereo- and/or regiochemistry information of a polymer is one of the most-important tasks in the field of stereospecific polymerization catalysis.[3,4]

In the alternating copolymerization of CO_2 with terminal epoxides,[5] there are also considerations of regiochemistry of the epoxide ring-opening and stereochemistry of the carbonate unit sequence in the resulting polymer chain.[6] In 2004, Chisholm and co-workers synthesized a series of oligoether carbonates, $R(PO)_nOCO_2(PO)_nR$ (R = Me, Et, or H; PO = propylene oxide ring-opened unit; and $n = 1$, 2, 3, 4, 10), as potential models for the microstructural assignment of poly(propylene carbonate) chains by NMR spectroscopy (Scheme 1).[7] In a recent study, Rieger and co-workers studied the microstructure and enantioselective ring-opening mechanism of poly(propylene carbonate) by using chiral GC and high-resolution NMR spectrometry.[8] $^{13}C\{^1H\}$ NMR investigations revealed that the carbon signals in the carbonate unit had both regio- and stereosensitivity towards its adjacent epoxide ring-opened units. These studies greatly contributed to the understanding of various regio- and stereospecific poly(propylene carbonate)s, as well as boosting the development of stereospecific catalyst systems for the copolymerization of CO_2 with aliphatic terminal epoxides.[9] More recently, we synthesized poly(propylene carbonate) with >99% head-to-tail content by using multichiral cobalt complexes.[10] We found that the highly isotactic poly(propylene carbonate) had a T_g of 47 °C, which was 10–12 °C higher than that of its corresponding irregular polycarbonate. New stereogradient poly(propylene carbonate)s, which possessed high thermal-decomposition temperatures, were synthesized by Nozaki and co-workers.[11] In the copolymerization of CO_2 with *meso*-epoxides, two structure patterns (isotactic and syndiotactic microstructures) can be

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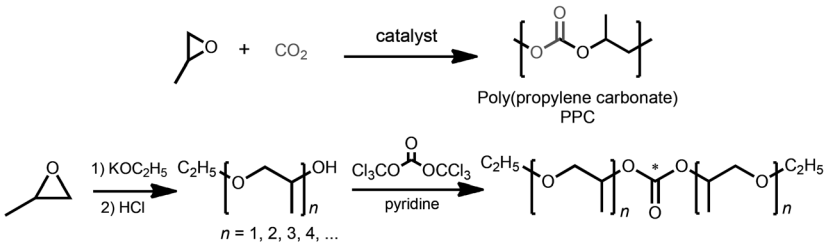
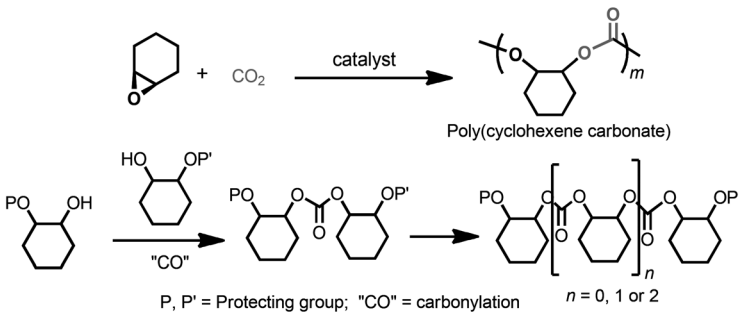


Scheme 1. Copolymerization of CO_2 with propylene oxide and the synthesis of model compounds for studying the microstructure of poly(propylene carbonate) by Chisholm and co-workers.[7]

formed.[12] In 2001, Nozaki and co-workers completed the spectroscopic assignment of poly(cyclohexene carbonate) on the basis of the spectroscopic analysis of various isotactic and syndiotactic model dimers and tetramers (Scheme 2).[13] The determination of various isotactic-enriched or syndio-



Scheme 2. Copolymerization of CO_2 with cyclohexene oxide and the synthesis of a model compound for studying the microstructure of poly(cyclohexene carbonate) by Nozaki and co-workers.[13]

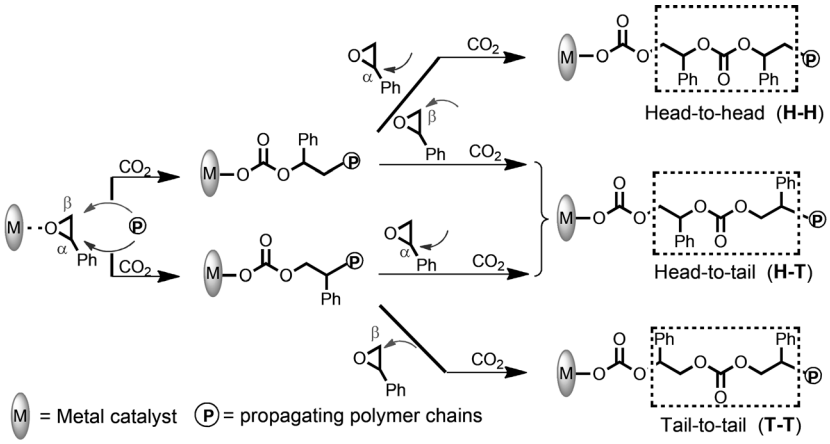
tactic-enriched poly(cyclohexene carbonate)s in subsequent experiments was realized on the basis of previous spectroscopic assignments.[14] More recent, highly stereoregular poly(cyclohexene carbonate)s with a high melting point (T_m) of about 215–230 °C were synthesized and their unique crystallization behavior was revealed.[12b,15]

Nevertheless, these investigations on CO_2 copolymers have been associated with the use of aliphatic terminal epoxides or cyclohexene oxide and its derivatives. The synthesis of copolymers from CO_2 and epoxides that contain electron-withdrawing substituents, such as styrene oxide (SO), have only rarely been reported.[16] Recently, we reported the completely alternating copolymerization of styrene oxide and CO_2 by using cobalt(III) catalyst systems, in which the resultant polycarbonate exhibited excellent thermal stability (thermolysis temperature >300 °C) and had a relatively high glass-transition temperature of 80 °C.[17] In addition, the electron-withdrawing group on the benzene ring of styrene oxide causes significant differences in catalyst activity, polymer selectivity, and stereochemistry control,[18] in comparison with propylene oxide, during the copolymerization with CO_2. Unfortunately, the microstructure of the resultant poly(styrene carbonate) remains unclear. The purpose of this study is to synthesize some model compounds of various poly(styrene carbonate)s and further identify their microstructures.

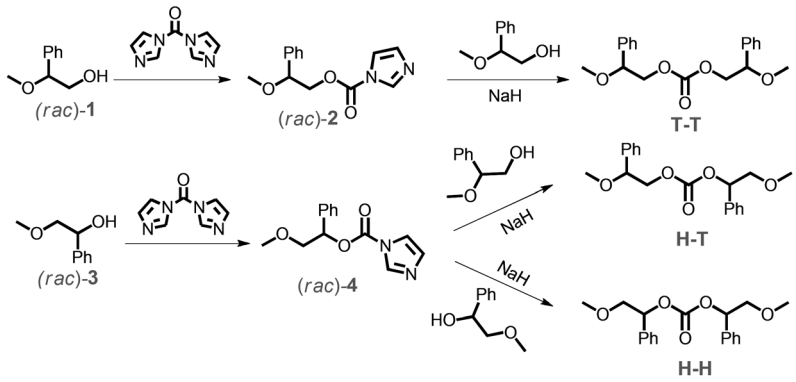
Results and Discussion

In the CO_2 copolymers from styrene oxide, there are three possible linkages for neighboring carbonate units, which are dependent on the regioselectivity of the epoxide ring-opening. The head-to-tail carbonate linkage is produced by successive epoxide ring-opening at either the methylene C_β–O or methine C_α–O bonds, whilst the formation of head-to-head or tail-to-tail linkages involves alternating ring-opening at the methylene C_β–O bond of one epoxide and the methine C_α–O bond of the following epoxide (Scheme 3). To assign the carbonate signals of the poly(styrene carbonate) microstructure, we first synthesized three model compounds (**T-T**, **H-T**, and **H-H**) to simulate three carbonate linkages in this CO_2 copolymer, including tail-to-tail, head-to-tail, and head-to-head linkages (Scheme 4). Notably, the successful synthesis of a model compound with head-to-tail linkages should show an ultraviolet absorption of the aromatic structure, which would make the purification of resulting intermediate and the final product by column chromatography very convenient. As shown in Scheme 4, the treatment of 2-methoxy-2-phenylethanol ((*rac*)-**1**) with 1,1′-(carbonyl diimidazole) (Im_2CO) in a 1:1 molar ratio produced imidazole-1-carboxylic ester ((*rac*)-**2**). After purification, this product was allowed to react with one equivalent of (*rac*)-**1** in the presence of NaH, thus affording the **T-T** dimer in about 95% total yield. In a similar manner, the **H-H** dimer was easily synthesized from 2-methoxy-1-phenylethanol ((*rac*)-**3**) in 92% total yield. Slightly different from the **T-T** and **H-H** dimers, dimer **H-T** was synthesized by an alternative treat-

Abstract in Chinese:
摘要：本文设计合成了 CO_2 和氧化苯乙烯（SO）交替共聚物的三种模式二元寡聚物 **T-T**, **H-T** 和 **H-H**，证明了在该聚合物 ^{13}C NMR 图上的 154.3, 153.8 和 153.3 ppm 分别属于尾-尾、头-尾和头-头碳酸酯连接方式。在此基础上又分别合成了三种模式化合物的间同和全同结构二聚体，用于研究聚碳酸苯乙烯酯的微结构。发现环氧烷烃开环方式和立体构型对碳酸酯碳信号均有影响。全同和间同结构对这些模式化合物的碳酸酯碳信号的影响与我们先前合成的立构规整性聚碳酸苯乙烯酯一致。



Scheme 3. Regiochemistry in poly(styrene carbonate)s that are derived from the alternating copolymerization of CO_2 and styrene oxide.

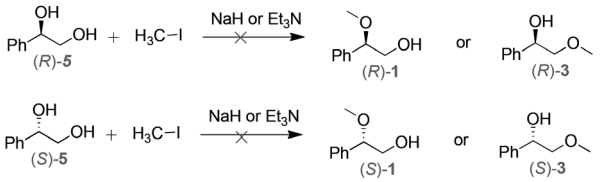


Scheme 4. Synthetic strategies for model dimer oligomers **T-T**, **H-T**, and **H-H** to simulate poly(styrene carbonate)s.

ment of 2-methoxy-2-phenylethanol and 2-methoxy-1-phenylethanol.

As shown in Figure 1 A–C, the carbonyl resonance in the ^{13}C NMR spectra of the three model compounds **T-T**, **H-T**, and **H-H** appears at $\delta = 154.9$, 154.4, and 153.9 ppm, respectively. Figure 1 D shows the carbonyl region in the ^{13}C NMR spectrum of an equimolar mixture of the three model compounds. By comparing Figure 1 D and E, the three groups of signals at $\delta = 154.3$, 153.8, and 153.3 ppm, which are observed in atactic poly(styrene carbonate) ($M_n = 12000$, $M_w/M_n = 1.09$), could be attributed to tail-to-tail, head-to-tail, and head-to-head linkages, respectively. In addition, it should be noted that the small chemical-shift differences ($\delta = 0.6$ ppm) between the model dimer compound ($\delta =$ 154.9, 154.4, and 153.9 ppm) and the SO/CO_2 copolymer ($\delta = 154.3$, 153.8, and 153.3 ppm) are probably due to the terminal methyl groups, which do not exist in the main chain of the copolymer. Further examining the three carbonate linkages of the SO/CO_2 copolymer (Figure 1 E) shows that there are more than two resonances in each group of tail-to-tail, head-to-tail, and head-to-head regions, thus indicating that the carbonate carbon atom should be sensitive to the configuration of the stereocenters on the polymer chain. As is evident from an inspection of the dimer model **H-T** and **T-T** oligomers in the ^{13}C NMR spectrum (Figure 1 D), the carbonate carbon resonance splits into two peaks. To identify the influence of adjacent stereocenters on the carbonyl group, we synthesized a series of syndiotactic and isotactic dimers based on **T-T**, **H-T**, and **H-H** model compounds ((*R*,*R*)-**T-T**, (*S*,*S*)-**T-T**, and (*R*,*S*)-**T-T**; (*R*,*R*)-**H-T**, (*S*,*S*)-**H-T**, and (*R*,*S*)-**H-T**; (*R*,*R*)-**H-H**, (*S*,*S*)-**H-H**, and (*R*,*S*)-**H-H**) and measured their ^{13}C NMR spectra in the carbonate carbon region.

To synthesize syndiotactic and isotactic dimers, four kinds of monoprotected 1-phenylethane-1,2-diols with different chirality that is, (*R*)-**1**, (*S*)-**1**, (*R*)-**3**, and (*S*)-**3**, are required (Scheme 5 and Scheme 6). In the presence of an acid-binding agent, the treatment of 1-phenylethane-1,2-diol with one equivalent of methyl iodide



Scheme 5. Unsuccessful route towards chiral compounds **1** and **3** by using methyl iodide.

predominantly produces the corresponding dihydroxymethyl product (Scheme 5), because the mono-hydroxymethyl intermediates are much more reactive than the parent diol. The increased reactivity is probably due to the strong intramolecular hydrogen bonding of the diol group. For synthesizing a monoprotected primary alcohol derivative, such as (*R*)-**1** and (*R*)-**2**, we adopted an indirect approach,[19] as shown in Scheme 6. Our synthetic route began with the hydrolytic kinetic resolution of (*rac*)-SO by using Jacobsen′s catalyst, followed by selective protection of the primary hydroxy group as its *tert*-butyldimethylsilyl (TBDMS) ether ((*R*)-**6** and (*S*)-**6**). Then, further reaction with an equimolar amount of iodomethane in the presence of NaH gave com-

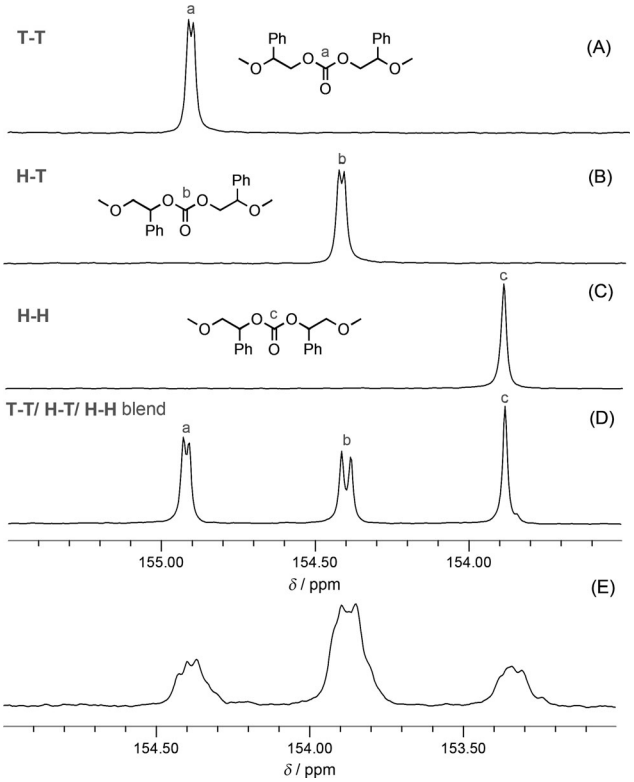
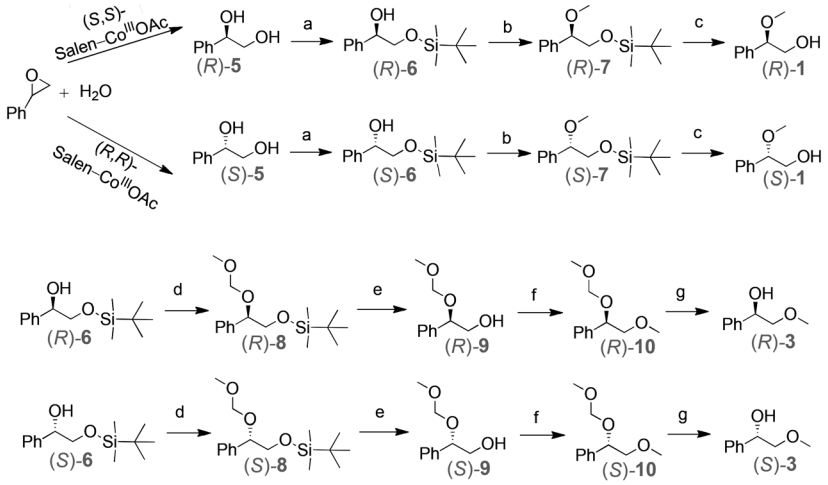


Figure 1. Carbonyl region in the ^{13}C NMR spectra of A) **T-T**; B) **H-T**; C) **H-H**; D) an equimolar mixture of **T-T**, **H-T**, and **H-H**; and E) atactic poly(styrene carbonate).



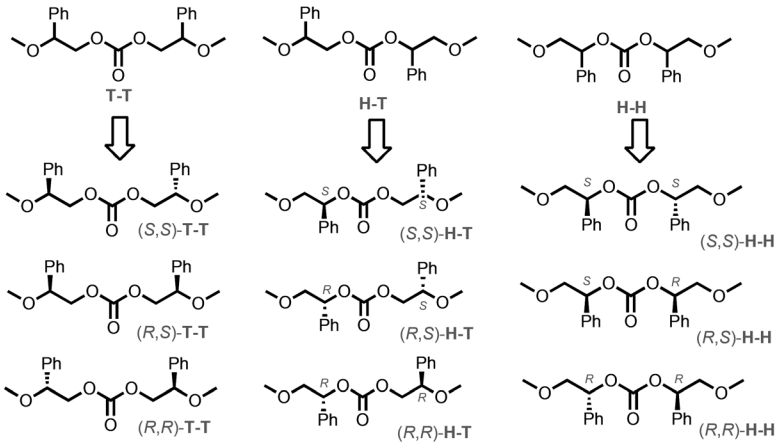
Scheme 6. Successful route towards chiral compounds **1** and **3**. Reaction conditions: a) TBDMSCl, Et_3N, DMAP, CH_2Cl_2; b) MeI, NaH, THF; c) TBAF, CH_3CN; d) DIPEA, MOMCl, CH_2Cl_2; e) TBAF, CH_3CN; f) MeI, NaH, THF; g) HCl, THF.

pounds (*R*)-**7** and (*S*)-**7**, respectively. Finally, the selective deprotection of the primary alcohol group with tetrabutylammonium fluoride (TBAF) in MeCN yielded the corresponding chiral methoxyalcohols ((*R*)-**1** and (*S*)-**1**) in excellent yields.

Based on these above-mentioned synthetic steps for compounds (*R*)-**1** and (*S*)-**1**, next, we devised an indirect approach for the synthesis of monoprotected alcohol derivatives (*R*)-**3** and (*S*)-**3**, as shown in Scheme 6. The reaction of one equivalent of methoxymethyl chloride with compounds (*R*)-**6** or (*S*)-**6** in the presence of diisopropylethylamine (DIPEA) gave intermediates (*R*)-**8** and (*S*)-**8**, which were treated with TBAF for desilication to give compounds (*R*)-**9** and (*S*)-**9**, respectively. The methylation of intermediates (*R*)-**9** and (*S*)-**9** and subsequent deprotection by using dilute hydrochloric acid afforded compounds (*R*)-**3** and (*S*)-**3** in moderate overall yields, respectively.

By using the same method for the synthesis of model dimer compounds **T-T**, **H-T**, and **H-H** (Scheme 4), three kinds of syndiotactic and isotactic dimers in each class were also prepared with (*R*)-**1**, (*S*)-**1**, (*R*)-**3**, and (*S*)-**3** as starting materials (Scheme 7). Three isomers of model compounds **T-T** and **H-T** are assigned in Figure 2. For the three isomers of model **T-T** with different stereosequences, the carbonate carbon signal of isotactic dimers (*R*,*R*)-**T-T** and (*S*,*S*)-**T-T** both appeared at $\delta = 154.93$ ppm in the ^{13}C NMR spectrum; the carbonate carbon signal of syndiotactic dimer (*R*,*S*)-**T-T** ($\delta = 154.91$ ppm) appeared at a slightly higher field than the isotactic dimers ($\delta = 154.93$ ppm). Similarly, the small difference between the isotactic and syndiotactic isomers of model **H-T** can also be unequivocally identified in Figure 2b. Isotactic dimers (*R*,*R*)-**H-T** and (*S*,*S*)-**H-T** showed a signal at $\delta = 154.38$ ppm, which was at higher field than syndiotactic dimer (*R*,*S*)-**H-T** ($\delta = 154.41$ ppm). Three kinds of isomers with different stereosequences of model **H-H** ((*R*,*R*)-**H-H**, (*S*,*S*)-**H-H**, and (*R*,*S*)-**H-H**) were also well-prepared. Disappointingly, the ^{13}C NMR signal of the carbonate carbon atom did not show resolution between its isotactic and syndiotactic dimers, which were all found at $\delta =$ 153.88 ppm. It is probable that the distance between the chiral centers and the carbonate carbon atom is too close to be resolved by ^{13}C NMR spectroscopy. These results clearly indicate that the stereosequence of the model dimer has a significant impact on the ^{13}C NMR signal of the carbonate carbon atom. Accordingly, we can conclude that the multi-response signals at $\delta = 154.3$, 153.8, 153.3 ppm in the SO/CO_2 copolymer are attributed to the stereosequences that are associated with the adjacent styrene oxide ring-opening units.

In a recent publication, we reported a new catalyst system based on unsymmetrical (*S*,*S*,*S*)-salen−Co^{III} complexes that contained a derived chiral-BINOL unit (BINOL = 1,1′-bi-2-naphthol) for the asymmetric copolymerization of CO_2 and racemic propylene oxide under mild conditions.[20] Both the



Scheme 7. Corresponding isotactic and syndiotactic dimers of compounds **T-T**, **H-T**, and **H-H**.

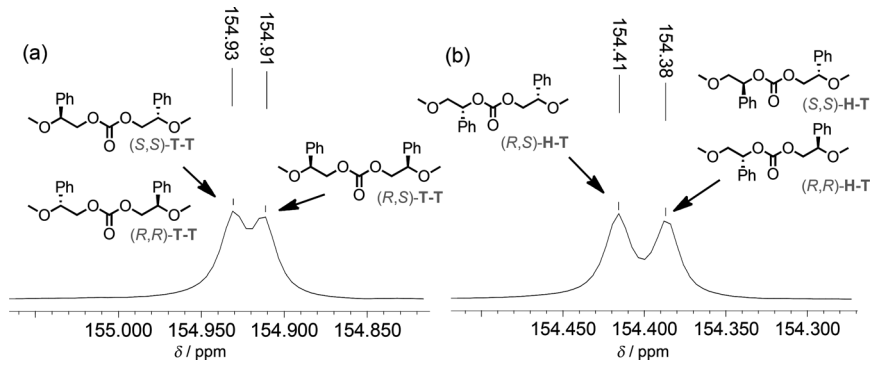


Figure 2. Assignment of the carbonate signals in the ^{13}C NMR spectra of isotactic and syndiotactic model compounds a) **T-T** and b) **H′-T** at the diad level.

chiral diaminocyclohexane backbone and the *S*-configured 2′-isopropyloxy-1,1′-binaphthyl ligand cooperatively provide a chiral environment around the central metal ion for this reaction. When the unsymmetrical (*S*,*S*,*S*)-salen–Co^{III} complex with PPNY (PPN = bis(triphenylphosphine)iminium, Y = 2,4-dinitrophenoxide) were tested in the copolymerization of CO_2 and (*R*)-SO (Figure 3), 92% enantioselectivity for the *R* configuration was observed. This result indicates that the stereochemistry of the methine carbon atom of (*R*)-styrene oxide was retained up to 96% during the copolymerization with CO_2.[18b] Accordingly, the isotactic signals should dominate the microstructure of the resulting copolymer. The ^{13}C NMR spectrum of the resulted copolymer is shown in Figure 3, from which two peaks (δ = 153.94 and 153.85 ppm) were observed in part of head-to-tail carbonate linkage. By comparing the integral-area ratio of the two peaks, the signal at δ = 153.94 ppm can be assigned to syndiotactic sensitivity and the large peak at δ = 153.85 ppm is ascribed to the isotactic sensitivity that is caused by the adjacent styrene oxide ring-opening units. This result is consistent with our assignment of the model diad compounds, in which the peak of isotactic diad appears at higher field than the syndiotactic diad, as shown in Figure 2.

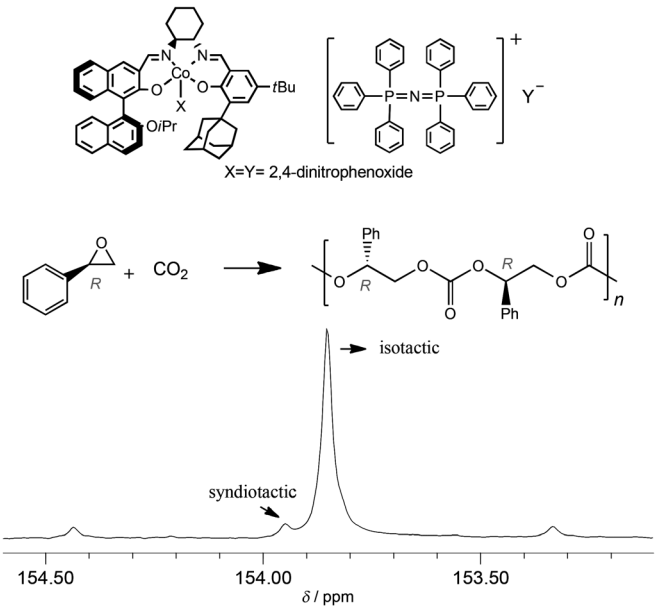


Figure 3. Binary catalyst system of an unsymmetrical (*S*,*S*,*S*)-salen–Co^{III} complex and PPNY (PPN = bis(triphenylphosphine)iminium, Y = 2,4-dinitrophenoxide) for the copolymerization of CO_2 with (*R*)-styrene oxide and the carbonyl region of the ^{13}C NMR spectrum of the resulting copolymer.

Conclusions

Three kinds of model compounds, that is, **T-T**, **H-T**, and **H-H**, were synthesized for the microstructural assignment of poly(styrene carbonate) by NMR spectroscopy. Furthermore, one syndiotactic *R*,*S* dimer and two isotactic dimers (*R*,*R* and *S*,*S*) in each model linkage unit were also prepared to study the stereosensitivity at the diad level. ^{13}C NMR investigations of these compounds revealed that the carbonate carbon signals showed both regio- and stereosensitivity at the diad level towards the adjacent epoxide ring-opened unit and we concluded that the signals of poly(styrene carbonate) at δ = 154.3, 153.8, and 153.3 ppm were attributed to tail-to-tail, head-to-tail, and head-to-head carbonate linkages, respectively. The syndiotactic and isotatic diads matched well with the microstructures of the stereoregular poly(styrene carbonate)s in our previous studies.[18]

Experimental Section

General Methods

All of the manipulations that involved air- and/or water-sensitive compounds were performed under an argon atmosphere with standard Schlenk techniques. All of the solvents were distilled under an argon atmosphere after drying over an appropriate drying reagent. Gel C-200 was used for column chromatography on silica gel. ^{1}H and ^{13}C NMR spectra were recorded on Varian INOVA-400 MHz and Bruker 500 MHz (^{13}C: 125 MHz) spectrometers, respectively. ^{1}H NMR shifts were referenced to an internal standard (TMS, $\delta = 0$ ppm) and to the solvent; ^{13}C NMR shifts were referenced to $CDCl_3$ ($\delta = 77.0$ ppm).

*2-Methoxy-2-phenylethyl-1 H-imidazole-1-carboxylate ((rac)-**2**)*

To a stirring solution of 2-methoxy-2-phenylethanol ((*rac*)-**1**; 1.52 g, 10.00 mmol) in dry THF (50 mL) was slowly added carbonyl diimidazole (4.86 g, 30.00 mmol). After the addition was complete, the reaction was stirred for 12 h at RT. Then, the reaction mixture was diluted with Et_2O (100 mL) and washed with water (3×50 mL). The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to afford 1-imidazolecarboxylate as a white solid (2.41 g, 98% yield). ^{1}H NMR ($CDCl_3$): $\delta = 3.27$ (s, 3H), 4.41–4.53 (m, 3H), 7.03 (s, 1H), 7.32–7.39 (m, 6H), 8.09 ppm (s, 1H).

*Bis(2-methoxy-2-phenylethyl) Carbonate (**T-T**)*

To a stirring solution of 2-methoxy-2-phenylethanol ((*rac*)-**1**; 0.456 g, 3.00 mmol) in THF (20 mL) was added NaH (72 mg, 3.00 mmol). After the resultant solution had been stirred for 1 h at RT, a solution of (*rac*)-**2** (0.74 g, 3.00 mmol) in THF (10 mL) was slowly added. After 4 h, the reaction mixture was diluted with Et_2O (50 mL) and washed with water (3×30 mL). The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 5:1) to obtain compound **T-T** as a colorless oil (0.94 g, 95% yield). $R_f = 0.45$ (petroleum ether/EtOAc, 5:1); ^{1}H NMR ($CDCl_3$): $\delta = 3.28$ (s, 6H), 4.16–4.19 (m, 2H), 4.28 (q, 2H), 4.44–4.48 (m, 2H), 7.25–7.39 ppm (m, 10H); ^{13}C NMR ($CDCl_3$): $\delta = 154.93$, 154.91 (1C), 137.45, 137.41 (2C), 128.48 (4CH), 128.25 (2CH), 126.85 (4CH), 81.32, 81.30 (2CH), 71.00, 70.95 ($2CH_2$), 56.86 ppm ($2CH_3$).

*2-Methoxy-1-phenylethyl-1 H-imidazole-1-carboxylate ((rac)-**4**)*

To a stirring solution of 2-methoxy-1-phenylethanol ((*rac*)-**3**; 1.52 g, 10.00 mmol) in dry THF (50 mL) was slowly added carbonyl diimidazole (4.86 g, 30.00 mmol). After the addition was complete, the reaction was stirred for 12 h at RT. Then, the reaction mixture was diluted with Et_2O (100 mL) and washed with water (50×3 mL). The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to afford 1-imidazolecarboxylate as a white solid (2.31 g, 94% yield). ^{1}H NMR ($CDCl_3$): $\delta = 3.43$ (s, 3H), 3.68 (d, $J = 1.60$, 3.20 Hz, 1H), 3.88 (d, $J = 8.40$ Hz, 1H), 6.13–6.16 (q, 1H), 7.07 (s, 1H), 7.3–7.47 (m, 6H), 8.13 ppm (s, 1H).

*2-Methoxy-1-phenylethyl(2-methoxy-2-phenylethyl) Carbonate (**H-T**)*

To a stirring solution of 2-methoxy-2-phenylethanol ((*rac*)-**1**; 0.456 g, 3.00 mmol) in THF (20 mL) was added NaH (72 mg, 3.00 mmol) and the solution was stirred for 1 h at RT. Then, a solution of (*rac*)-**4** (0.74 g, 3.00 mmol) in THF (10 mL) was slowly added. After 4 h, the reaction mixture was diluted with Et_2O (50 mL) and washed with water (3×30 mL). The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 5:1) to obtain **H-T** as a colorless oil (0.94 g, 95% yield). $R_f = 0.45$ (petroleum ether/EtOAc, 5:1); ^{1}H NMR ($CDCl_3$): $\delta = 3.26$ (s, 3H), 3.40 (s, 3H), 3.55–3.59 (m, 1H), 3.72–3.77 (m, 1H), 4.13–4.27 (m, 2H), 4.41–4.47 (m, 1H), 5.78 (q, 1H), 7.30–7.37 ppm (m, 10H); ^{13}C NMR ($CDCl_3$): $\delta = 154.41$, 154.38 (1C), 137.39 (1C), 136.70 (1C), 128.45 (2CH), 128.38 (2CH), 128.21 (2H), 126.81 (2CH), 126.50 (2CH), 81.26, 81.24 (1CH), 78.40, 78.36 (1CH), 75.08, 75.04 ($1CH_2$), 70.97 ($1CH_2$), 59.01 ($1CH_3$), 56.85 ppm ($1CH_3$).

*Bis(2-methoxy-1-phenylethyl) Carbonate (**H-H**)*

To a stirring solution of 2-methoxy-1-phenylethanol ((*rac*)-**3**; 0.456 g, 3.00 mmol) in THF (20 mL) was added NaH (72 mg, 3.00 mmol) and the solution was stirred for 1 h at RT. Then, a solution of (*rac*)-**4** (0.74 g, 3.00 mmol) in THF (10 mL) was slowly added. After 4 h, the reaction mixture was diluted with Et_2O (50 mL) and washed with water (3×30 mL). The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 5:1) to obtain **H-H** as a colorless oil (0.89 g, 90% yield). $R_f = 0.45$ (petroleum ether/EtOAc, 5:1); ^{1}H NMR ($CDCl_3$): $\delta = 3.39$ (s, 6H), 3.56–3.59 (m, 2H), 3.72–3.77 (m, 2H), 5.77 (q, 2H), 7.27–7.33 ppm (m, 10H); ^{13}C NMR ($CDCl_3$): $\delta = 153.88$ (1C), 136.78 (2C), 128.31 (2CH), 128.23 (4CH), 126.38 (4CH), 78.28 (2CH), 75.06 ($2CH_2$), 58.98 ppm ($2CH_3$).

*(R)-2-((tert-Butyldimethylsilyl)oxy)-1-phenylethanol ((R)-**6**)*

(*R*)-1-Phenylethane-1,2-diol ((*R*)-**5**; 0.68 g, 5 mmol)[21] and 4-dimethylaminopyridine (DMAP; 0.061 g, 0.5 mmol) were dissolved in dry CH_2Cl_2 (30 mL) under a N_2 atmosphere. Then, Et_3N (1.1 mL, 7.5 mmol) and TBDMSCl (1.13 g, 7.5 mmol in CH_2Cl_2) were added dropwise. The reaction mixture was stirred for 4 h, after which a saturated aqueous solution of NH_4Cl (20 mL) was added. The aqueous layer was extracted with CH_2Cl_2 (3×20 mL) and the combined organic layers were dried over anhydrous Na_2SO_4. The solvent was removed by rotary evaporation and the resulting oil was purified by column chromatography on silica gel (petroleum ether/EtOAc, 20:1) to afford compound (*R*)-**6** as a colorless oil (1.23 g, 98% yield). $[\alpha]_D^{20} = -30.3°$ ($c = 0.1$, $CHCl_3$); ^{1}H NMR ($CDCl_3$): $\delta = 7.27–7.38$ (m, 5H), 4.73–4.77 (m, 1H), 3.75–3.78 (d, $J = 4.0$ Hz, 1H), 3.52–3.3.57 (d, $J = 8.0$ Hz, 1H), 2.95–2.96 (d, $J = 4.0$ Hz, 1H), 0.91 (s, 9H), 0.07 (s, 3H), 0.06 ppm (s, 3H).

*(S)-2-((tert-Butyldimethylsilyl)oxy)-1-phenylethanol ((S)-**6**)*

All of the synthesis steps for compound (*S*)-**6** were the same as for (*R*)-**6** (see above), except for the replacement of compound (*R*)-**5** with (*S*)-**5**. $[\alpha]_D^{20} = 30.0°$ ($c = 0.1$, $CHCl_3$); ^{1}H NMR ($CDCl_3$): $\delta = 7.27–7.38$ (m, 5H), 4.73–4.77 (m, 1H), 3.75–3.78 (d, $J = 4.0$ Hz, 1H), 3.52–3.3.57 (d, $J = 8.0$ Hz, 1H), 2.95–2.96 (d, $J = 4.0$ Hz, 1H), 0.91 (s, 9H), 0.07 (s, 3H), 0.06 ppm (s, 3H).

*(R)-tert-Butyl(2-methoxy-2-phenylethoxy)dimethylsilane ((R)-**7**)*

Compound (*R*)-**6** (1.8 g, 7 mmol) was dissolved in THF (30 mL) and NaH (0.34 g, 14 mmol) was added. After about 1 h, a solution of MeI (1.2 g, 8.4 mmol) in THF was added dropwise. The reaction mixture was stirred in the dark overnight and a saturated aqueous solution of NaCl (20 mL) was added. The crude reaction was extracted with EtOAc (3×20 mL) and the combined organic layers were dried over anhydrous Na_2SO_4. The solvent was removed under vacuum and the resulting oil was purified by column chromatography on silica gel (petroleum ether/EtOAc, 20:1) to afford compound (*R*)-**7** as a colorless oil (1.7 g, 90% yield). $[\alpha]_D^{20} = -58.2°$ ($c = 0.2$, $CHCl_3$); ^{1}H NMR ($CDCl_3$): $\delta = 7.30–7.40$ (m, 5H), 4.26–4.29 (t, 1H), 3.82–3.88 (m, 1H), 3.672–3.711 (m, 1H), 3.35 (s, 3H), 0.90 (s, 9H), 0.037 (s, 3H), 0.00 ppm (s, 3H).

*(S)-tert-Butyl(2-methoxy-2-phenylethoxy)dimethylsilane ((S)-**7**)*

All of the synthesis steps for compound (*S*)-**7** were the same as for (*R*)-**7** (see above), except for the replacement of compound (*R*)-**6** with (*S*)-**6**. $[\alpha]_D^{20} = 60.1°$ ($c = 0.2$, $CHCl_3$); ^{1}H NMR ($CDCl_3$): $\delta = 7.30–7.40$ (m, 5H), 4.26–4.29 (t, 1H), 3.82–3.88 (m, 1H), 3.672–3.711 (m, 1H), 3.35 (s, 3H), 0.90 (s, 9H), 0.037 (s, 3H), 0.00 ppm (s, 3H).

*(R)-2-Methoxy-2-phenylethanol ((R)-**1**)*

Compound (*R*)-**7** (0.53 g, 2 mmol) was dissolved in MeCN (2 mL) and TBAF (1.04 g, 4 mmol) was added. The reaction mixture was stirred overnight and the solvent was removed under vacuum. The resulting oil was purified by column chromatography on silica gel (petroleum ether/

EtOAc, 1:1) to afford compound (*R*)-**1** as a colorless oil (0.22 g, 73% yield). $[\alpha]_D^{20} = -105.1°$ ($c = 0.1$, $CHCl_3$); ^1H NMR ($CDCl_3$): $\delta = 7.30–7.37$ (m, 5H), 4.30–4.31 (d, $J = 4.8$ Hz, 1H), 3.62–3.70 (q, 2H), 3.31 (s, 3H), 2.30–2.32 ppm (d, $J = 7.6$ Hz).

*(S)-2-Methoxy-2-phenylethanol ((S)-**1**)*

All of the synthesis steps for (*S*)-**1** were the same as for (*R*)-**1** (see above), except for the replacement of compound (*R*)-**7** with (*S*)-**7**. $[\alpha]_D^{20} = 108.0°$ ($c = 0.1$, $CHCl_3$); ^1H NMR ($CDCl_3$): $\delta = 7.30–7.37$ (m, 5H), 4.30–4.31 (d, $J = 4.8$ Hz, 1H), 3.62–3.70 (q, 2H), 3.31 (s, 3H), 2.30–2.32 ppm (d, $J = 7.6$ Hz).

*(R)-8,8,9,9-tetramethyl-5-phenyl-2,4,7-trioxa-8-siladecane ((R)-**8**)*

A solution of compound (*R*)-**6** (1 g, 4 mmol) and DIPEA (2.8 mL, 16 mmol) in CH_2Cl_2 (30 mL) was stirred for 1 h, chloromethyl methyl ether (MOMCl; 0.5 mL, 6 mmol) was added dropwise, and the mixture was stirred for a further 2 h at RT. Then, water was added and the mixture was extracted with CH_2Cl_2 (3×20 mL). The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The resulting residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 20:1) to obtain compound (*R*)-**8** as a colorless oil (0.93 g, 80% yield. $[\alpha]_D^{20} = -89.7°$ ($c = 1.05$, CH_2Cl_2); ^1H NMR ($CDCl_3$): $\delta = 7.27–7.35$ (m, 5H), 4.69–4.72 (d, $J = 4.4$ Hz, 2H), 4.61–4.68 (t, 1H), 3.81–3.3.85 (d, $J = 7.6$ Hz, 1H), 3.68–3.3.72 (d, $J = 4.4$ Hz, 1H), 3.39 (s, 3H), 0.89 (s, 9H), 0.032 (s, 3H), 0.022 ppm (s, 3H).

*(S)-8,8,9,9-tetramethyl-5-phenyl-2,4,7-trioxa-8-siladecane ((S)-**8**)*

All of the synthesis steps for compound (*S*)-**8** were the same as for (*R*)-**8** (see above), except for the replacement of compound (*R*)-**6** with (*S*)-**6**. $[\alpha]_D^{20} = +96.5°$ ($c = 1.13$, CH_2Cl_2); ^1H NMR ($CDCl_3$): $\delta = 7.27–7.35$ (m, 5H), 4.69–4.72 (d, $J = 4.4$ Hz, 2H), 4.61–4.68 (t, 1H), 3.81–3.3.85 (d, $J = 7.6$ Hz, 1H), 3.68–3.3.72 (d, $J = 4.4$ Hz, 1H), 3.39 (s, 3H), 0.89 (s, 9H), 0.032 (s, 3H), 0.022 ppm (s, 3H).

*(R)-2-(Methoxymethoxy)-2-phenylethanol ((R)-**9**)*

Compound (*R*)-**8** (0.96 g, 3 mmol) was dissolved in MeCN (30 mL) and TBAF (1.56 g, 6 mmol) was added. Then, the reaction was stirred overnight and the solvent was removed under vacuum. The resulting oil was purified by column chromatography on silica gel (petroleum ether/EtOAc, 1:1) to afford compound (*R*)-**9** as a colorless oil (0.51 g, 87% yield). $[\alpha]_D^{20} = -82.3°$ ($c = 1.85$, CH_2Cl_2); ^1H NMR ($CDCl_3$): $\delta = 7.28–7.37$ (m, 5H), 4.70–4.73 (d, $J = 3.6$ Hz, 2H), 4.64–4.68 (t, 1H), 3.66–3.78 (m, 2H), 3.41 ppm (s, 3H).

*(S)-2-(Methoxymethoxy)-2-phenylethanol ((S)-**9**)*

All of the synthesis steps for compound (*S*)-**9** were the same as for (*R*)-**9** (see above), except for the replacement of compound (*R*)-**8** with (*S*)-**8**. $[\alpha]_D^{20} = +81.6°$ ($c = 1.81$, CH_2Cl_2); ^1H NMR ($CDCl_3$): $\delta = 7.28–7.37$ (m, 5H), 4.70–4.73 (d, $J = 3.6$ Hz, 2H), 4.64–4.68 (t, 1H), 3.66–3.78 (m, 2H), 3.41 ppm (s, 3H).

*(R)-(2-Methoxy-1-(methoxymethoxy)ethyl)benzene ((R)-**10**)*

Compound (*R*)-**9** (1.6 g, 9 mmol) was dissolved in THF (30 mL) and NaH (0.24 g, 9.9 mmol) was added. After about 1 h, a solution of MeI (1.41 g, 9.9 mmol) in THF was added dropwise. The reaction mixture was stirred in the dark overnight and a saturated aqueous solution of NaCl (20 mL) was added. The crude mixture was extracted with EtOAc ($3 \times$ 20 mL) and the combined organic layers were dried over anhydrous Na_2SO_4. The solvent was removed under vacuum and the resulting oil was purified by column chromatography on silica gel (petroleum ether/EtOAc, 5:1) to afford compound (*R*)-**10** as a colorless oil (1.51 g, 86% yield). $[\alpha]_D^{20} = -177.1°$ ($c = 1.91$, CH_2Cl_2); ^1H NMR ($CDCl_3$): $\delta = 7.28–7.35$ (m, 5H), 4.81–4.83 (d, $J = 3.6$, Hz, 1H), 4.58–4.65 (q, 2H), 3.62–3.67 (d, $J = 8.0$ Hz, 1H), 3.47–3.50 (d, $J = 3.6$ Hz, 1H), 3.39 (s, 3H), 3.37 ppm (s, 3H).

*(S)-(2-Methoxy-1-(methoxymethoxy)ethyl)benzene ((S)-**10**)*

All of the synthesis steps for compound (*S*)-**10** were the same as for (*R*)-**10** (see above), except for the replacement of compound (*R*)-**9** with (*S*)-**9**. $[\alpha]_D^{20} = +171.9°$ ($c = 2.3$, CH_2Cl_2); ^1H NMR ($CDCl_3$): $\delta = 7.28–7.35$ (m, 5H), 4.81–4.83 (d, $J = 3.6$, Hz, 1H), 4.58–4.65 (q, 2H), 3.62–3.67 (d, $J = 8.0$ Hz, 1H), 3.47–3.50 (d, $J = 3.6$ Hz, 1H), 3.39 (s, 3H), 3.37 ppm (s, 3H).

*(R)-2-Methoxy-1-phenylethanol ((R)-**3**)*

Compound (*R*)-**10** (0.19 g, 1 mmol) was dissolved in THF (1.7 mL) and 6 M HCl (1.7 mL, 10 mmol) was added dropwise. Then, the reaction mixture was stirred for 4 h, after which time a saturated aqueous solution of $NaHCO_3$ solution was added. The crude reaction was extracted with EtOAc (10×3 mL) and the combined organic layers were dried over anhydrous Na_2SO_4. The solvent was removed under vacuum and the resulting oil was purified by column chromatography on silica gel (petroleum ether/EtOAc, 1:1) to afford compound (*R*)-**3** as a colorless oil (0.12 g, 79% yield). $[\alpha]_D^{20} = -56.3°$ ($c = 1.1$, $CHCl_3$). ^1H NMR ($CDCl_3$): $\delta = 7.25–7.39$ (m, 5H), 4.87–4.89 (d, $J = 8.8$ Hz, 1H), 3.54–3.55 (q, 1H), 3.52–3.53 (q, 1H), 3.42 ppm (s, 3H).

*(S)-2-Methoxy-1-phenylethanol ((S)-**3**)*

All of the synthesis steps for compound (*S*)-**3** were the same as for (*R*)-**3** (see above), except for the replacement of compound (*R*)-**10** by (*S*)-**10**. $[\alpha]_D^{20} = 54.3°$ ($c = 1.1$, $CHCl_3$); ^1H NMR ($CDCl_3$): $\delta = 7.25–7.39$ (m, 5H), 4.87–4.89 (d, $J = 8.8$ Hz, 1H), 3.54–3.55 (q, 1H), 3.52–3.53 (q, 1H), 3.42 ppm (s, 3H).

*(R)-2-Methoxy-2-phenylethyl-1 H-imidazole-1-carboxylate ((R)-**2**)*

All of the synthesis steps for compound (*R*)-**2** were the same as for (*rac*)-**2** (see above), except for the replacement of compound (*rac*)-**1** with (*R*)-**1**. $[\alpha]_D^{20} = -70.4°$ ($c = 1.15$, CH_2Cl_2); ^1H NMR ($CDCl_3$): $\delta = 3.27$ (s, 3H), 4.41–4.53 (m, 3H), 7.03 (s, 1H), 7.32–7.39 (m, 6H), 8.09 ppm (s, 1H).

*(S)-2-Methoxy-2-phenylethyl-1 H-imidazole-1-carboxylate ((S)-**2**)*

All of the synthesis steps for compound (*S*)-**2** were the same as for (*rac*)-**2** (see above), except for the replacement of compound (*rac*)-**1** with (*S*)-**1**. $[\alpha]_D^{20} = +64.6°$ ($c = 1.70$, CH_2Cl_2); ^1H NMR ($CDCl_3$): $\delta = 3.27$ (s, 3H), 4.41–4.53 (m, 3H), 7.03 (s, 1H), 7.32–7.39 (m, 6H), 8.09 ppm (s, 1H).

*(R)-2-Methoxy-1-phenylethyl-1 H-imidazole-1-carboxylate ((R)-**4**)*

All of the synthesis steps for compound (*R*)-**4** were the same as for (*rac*)-**4** (see above), except for the replacement of compound (*rac*)-**3** with (*R*)-**3**. $[\alpha]_D^{20} = -34.2°$ ($c = 1.41$, CH_2Cl_2); ^1H NMR ($CDCl_3$): $\delta = 3.43$ (s, 3H), 3.68 (d, $J = 3.20$ Hz, 1H), 3.88 (d, $J = 8.40$ Hz, 1H), 6.13–6.16 (q, 1H), 7.07 (s, 1H), 7.3–7.47 (m, 6H), 8.13 ppm (s, 1H).

*(S)-2-Methoxy-1-phenylethyl-1 H-imidazole-1-carboxylate ((S)-**4**)*

All of the synthesis steps for compound (*S*)-**4** were the same as for (*rac*)-**4** (see above), except for the replacement of compound (*rac*)-**3** with (*S*)-**3**. $[\alpha]_D^{20} = +31.7°$ ($c = 1.35$, CH_2Cl_2); ^1H NMR ($CDCl_3$): $\delta = 3.43$ (s, 3H), 3.68 (d, $J = 3.20$ Hz, 1H), 3.88 (d, $J = 8.40$ Hz, 1H), 6.13–6.16 (q, 1H), 7.07 (s, 1H), 7.3–7.47 (m, 6H), 8.13 ppm (s, 1H).

*Bis((S)-2-methoxy-2-phenylethyl) Carbonate ((S,S)-**T-T**)*

To a stirring solution of (*S*)-2-methoxy-2-phenylethanol ((*S*)-**1**, 0.456 g, 3.00 mmol) in THF (20 mL) was added NaH (72 mg, 3.00 mmol) and the solution was stirred for 1 h at RT. Then, a solution of compound (*S*)-**2** (0.74 g, 3.00 mmol) in THF (10 mL) was slowly added. After 4 h, the reaction mixture was diluted with Et_2O (50 mL) and washed with water (3×30 mL). The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 5:1) to obtain compound (*S,S*)-**T-T** as a colorless oil (0.94 g, 95% yield). $R_f = 0.45$ (petroleum ether/EtOAc, 5:1); $[\alpha]_D^{20} = +98.7°$ ($c = 1.87$, CH_2Cl_2); ^1H NMR ($CDCl_3$): $\delta = 7.25–7.39$ (m, 10H), 4.44–4.48 (m, 2H), 4.28 (q, 2H), 4.16–4.19 (m, 2H), 3.28 ppm (s, 6H); ^{13}C NMR ($CDCl_3$): $\delta = 154.93$, 154.91 (1C), 137.45 (2C), 128.48 (4CH), 128.25 (2CH), 126.85 (4CH),

81.32 (2CH), 71.00 ($2CH_2$), 56.86 ppm ($2CH_3$); elemental analysis calcd (%) for $C_{19}H_{22}O_5$: C 69.07, H 6.71; found: C 69.07, H 6.74.

*Bis((R)-2-methoxy-2-phenylethyl) Carbonate ((R,R)-**T-T**)*

All of the synthesis steps for (*R*,*R*)-**T-T** were the same as for (*S*,*S*)-**T-T** (see above), except for the replacement of compounds (*S*)-**1** and (*S*)-**2** with (*R*)-**1** and (*R*)-**2**, respectively. $[\alpha]_D^{20} = -99.5°$ ($c = 1.01$, CH_2Cl_2); ^1H NMR ($CDCl_3$): $\delta = 7.25–7.39$ (m, 10H), 4.44–4.48 (m, 2H), 4.28 (q, 2H), 4.16–4.19 (m, 2H), 3.28 ppm (s, 6H); ^{13}C NMR ($CDCl_3$): $\delta = 154.93$, 154.91 (1C), 137.45 (2C), 128.48 (4CH), 128.25 (2CH), 126.85 (4CH), 81.32 (2CH), 71.00 ($2CH_2$), 56.86 ppm ($2CH_3$); elemental analysis calcd (%) for $C_{19}H_{22}O_5$: C 69.07, H 6.71; found: C 69.13, H 6.85.

*(R)-2-Methoxy-2-phenylethyl((S)-2-methoxy-2-phenylethyl) Carbonate ((R,S)-**T-T**)*

All of the synthesis steps for (*R*,*S*)-**T-T** were the same as for (*R*,*R*)-**T-T** (see above), except for the replacement of compound (*R*)-**2** with (*S*)-**2**. $[\alpha]_D^{20} = 0.2°$ ($c = 1.0$, $CHCl_3$); ^1H NMR ($CDCl_3$): $\delta = 7.25–7.39$ (m, 10H), 4.44–4.48 (m, 2H), 4.28 (q, 2H), 4.16–4.19 (m, 2H), 3.28 ppm (s, 6H); ^{13}C NMR ($CDCl_3$): $\delta = 154.91$ (1C), 137.41 (2C), 128.48 (4CH), 128.25 (2CH), 126.85 (4CH), 81.32 (2CH), 70.95 ($2CH_2$), 56.86 ppm ($2CH_3$); elemental analysis calcd (%) for $C_{19}H_{22}O_5$: C 69.07, H 6.71; found: C 69.13, H 6.82.

*(S)-2-Methoxy-1-phenylethyl((S)-2-methoxy-2-phenylethyl) Carbonate ((S,S)-**H-T**)*

To a stirring solution of (*S*)-2-methoxy-2-phenylethanol ((*S*)-**1**; 0.456 g, 3.00 mmol) in THF (20 mL) was added NaH (72 mg, 3.00 mmol) and the solution was stirred for 1 h at RT. Then, a solution of compound (*S*)-**4** (0.74 g, 3.00 mmol) in THF (10 mL) was slowly added. After 4 h, the reaction mixture was diluted with Et_2O (50 mL) and washed with water (3×30 mL). The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 5:1) to obtain compound (*S*,*S*)-**H-T** as a colorless oil (0.94 g, 95% yield). R_f = 0.45 (petroleum ether/EtOAc, 5:1); $[\alpha]_D^{20} = +109.9°$ ($c = 1.62$, CH_2Cl_2). ^1H NMR ($CDCl_3$): $\delta = 7.30–7.37$ (m, 10H), 5.78 (q, 1H), 4.41–4.47 (m, 1H), 4.13–4.27 (m, 2H), 3.72–3.77 (m, 1H), 3.55–3.59 (m, 1H), 3.40 (s, 3H), 3.26 ppm (s, 3H); ^{13}C NMR ($CDCl_3$): $\delta = 154.38$ (1C), 137.39 (1C), 136.70 (1C), 128.45 (2CH), 128.38 (2CH), 128.21 (2H), 126.81 (2CH), 126.50 (2CH), 81.26 (1CH), 78.40 (1CH), 75.08 ($1CH_2$), 70.97 ($1CH_2$), 59.01 ($1CH_3$), 56.85 ppm ($1CH_3$); elemental analysis calcd (%) for $C_{19}H_{22}O_5$: C 69.07, H 6.71; found: C 69.09, H 6.75.

*(R)-2-Methoxy-1-phenylethyl((R)-2-methoxy-2-phenylethyl) Carbonate ((R,R)-**H-T**)*

All of the synthesis steps for (*R*,*R*)-**H-T** were the same as for (*S*,*S*)-**H-T** (see above), except for the replacement of compounds (*S*)-**1** and (*S*)-**4** with (*R*)-**1** and (*R*)-**4**, respectively. $[\alpha]_D^{20} = -113.6°$ ($c = 1.02$, CH_2Cl_2); ^1H NMR ($CDCl_3$): $\delta = 7.30–7.37$ (m, 10H), 5.78 (q, 1H), 4.41–4.47 (m, 1H), 4.13–4.27 (m, 2H), 3.72–3.77 (m, 1H), 3.55–3.59 (m, 1H), 3.40 (s, 3H), 3.26 ppm (s, 3H); ^{13}C NMR ($CDCl_3$): $\delta = 154.38$ (1C), 137.39 (1C), 136.70 (1C), 128.45 (2CH), 128.38 (2CH), 128.21 (2H), 126.81 (2CH), 126.50 (2CH), 81.26 (1CH), 78.40 (1CH), 75.08 ($1CH_2$), 70.97 ($1CH_2$), 59.01 ($1CH_3$), 56.85 ppm ($1CH_3$); elemental analysis calcd (%) for $C_{19}H_{22}O_5$: C 69.07, H 6.71; found: C 69.10, H 6.83.

*(R)-2-Methoxy-1-phenylethyl((S)-2-methoxy-2-phenylethyl) Carbonate ((R,S)-**H-T**)*

All of the synthesis steps for compound (*R*,*S*)-**H-T** were the same as for (*R*,*R*)-**H-T** (see above), except for the replacement of compound (*R*)-**4** with (*S*)-**4**. $[\alpha]_D^{20} = -22.9°$ ($c = 1.20$, CH_2Cl_2); ^1H NMR ($CDCl_3$): $\delta = 7.30–7.37$ (m, 10H), 5.78 (q, 1H), 4.41–4.47 (m, 1H), 4.13–4.27 (m, 2H), 3.72–3.77 (m, 1H), 3.55–3.59 (m, 1H), 3.40 (s, 3H), 3.26 ppm (s, 3H); ^{13}C NMR ($CDCl_3$): $\delta = 154.41$ (1C), 137.39 (1C), 136.70 (1C), 128.45 (2CH), 128.38 (2CH), 128.21 (2H), 126.81 (2CH), 126.50 (2CH), 81.24 (1CH), 78.36 (1CH), 75.08, 75.04 ($1CH_2$), 70.97 ($1CH_2$), 59.01 ($1CH_3$), 56.85 ppm ($1CH_3$); elemental analysis calcd (%) for $C_{19}H_{22}O_5$: C 69.07, H 6.71; found: C 69.20, H 6.75.

*Bis((S)-2-methoxy-1-phenylethyl) Carbonate ((S,S)-**H-H**)*

To a stirring solution of (*S*)-2-methoxy-1-phenylethanol ((*S*)-**3**; 0.456 g, 3.00 mmol) in THF (20 mL) was added NaH (72 mg, 3.00 mmol) and the solution was stirred for 1 h at RT. Then, a solution of compound (*S*)-**4** (0.74 g, 3.00 mmol) in THF (10 mL) was slowly added. After 4 h, the reaction mixture was diluted with Et_2O (50 mL) and washed with water (3×30 mL). The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 5:1) to obtain compound (*S*,*S*)-**H-H** as a colorless oil (0.89 g, 90% yield). R_f = 0.45 (petroleum ether/EtOAc, 5:1); $[\alpha]_D^{20} = +110°$ ($c = 1.75$, CH_2Cl_2); ^1H NMR ($CDCl_3$): $\delta = 7.27–7.33$ (m, 10H), 5.77 (q, 2H), 3.72–3.77 (m, 2H), 3.56–3.59 (m, 2H), 3.39 ppm (s, 6H); ^{13}C NMR ($CDCl_3$): $\delta = 153.88$ (1C), 136.78 (2C), 128.31 (2CH), 128.23 (4CH), 126.38 (4CH), 78.28 (2CH), 75.06 ($2CH_2$), 58.98 ppm ($2CH_3$); elemental analysis calcd (%) for $C_{19}H_{22}O_5$: C 69.07, H 6.71; found: C 69.14, H 6.79.

*Bis((R)-2-methoxy-1-phenylethyl) Carbonate ((R,R)-**H-H**)*

All of the synthesis steps for compound (*R*,*R*)-**H-H** were the same as for (*S*,*S*)-**H-H** (see above), except for the replacement of compounds (*S*)-**3** and (*S*)-**4** with (*R*)-**3** and (*R*)-**4**, respectively. $[\alpha]_D^{20} = -112.3°$ ($c = 0.99$, CH_2Cl_2); ^1H NMR ($CDCl_3$): $\delta = 7.27–7.33$ (m, 10H), 5.77 (q, 2H), 3.72–3.77 (m, 2H), 3.56–3.59 (m, 2H), 3.39 ppm (s, 6H); ^{13}C NMR ($CDCl_3$): $\delta = 153.88$ (1C), 136.78 (2C), 128.31 (2CH), 128.23 (4CH), 126.38 (4CH), 78.28 (2CH), 75.06 ($2CH_2$), 58.98 ppm ($2CH_3$); elemental analysis calcd (%) for $C_{19}H_{22}O_5$: C 69.07, H 6.71; found: C 69.13, H 6.85.

*(R)-2-Methoxy-1-phenylethyl((S)-2-methoxy-1-phenylethyl) Carbonate ((R,S)-**H-H**)*

All of the synthesis steps for compound (*R*,*S*)-**H-H** were the same as for (*R*,*R*)-**H-H** (see above), except for the replacement of compound (*R*)-**3** with (*S*)-**3**. $[\alpha]_D^{20} = 0.1°$ ($c = 0.1$, $CHCl_3$); ^1H NMR ($CDCl_3$): $\delta = 7.27–7.33$ (m, 10H), 5.77 (q, 2H), 3.72–3.77 (m, 2H), 3.56–3.59 (m, 2H), 3.39 ppm (s, 6H); ^{13}C NMR ($CDCl_3$): $\delta = 153.88$ (1C), 136.78 (2C), 128.31 (2CH), 128.23 (4CH), 126.38 (4CH), 78.28 (2CH), 75.06 ($2CH_2$), 58.98 ppm ($2CH_3$); elemental analysis calcd (%) for $C_{19}H_{22}O_5$: C 69.07, H 6.71; found: C 69.12, H 6.83.

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