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Synthesis and Application of Diphenyl Sulfide Linked Bis(imidazoline) Ligands: Dramatic Electronic Effect of Ligands on Catalytic Behavior

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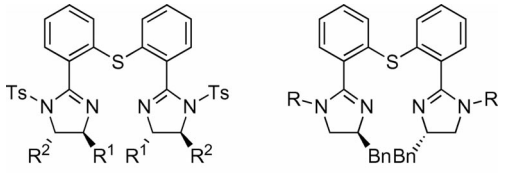
Diphenyl sulfide linked bis(imidazoline) ligands with electron-withdrawing *N*-Ts substitution and electron-donating *N*-alkyl or *N*-H substitutions were synthesized through different routes. The electronic effects of the ligands were tuned rationally, and dramatic variation in their catalytic behavior was observed. *N*-Alkyl and *N*-H ligands demonstrated much higher catalytic activity and improved enantioselectivity than *N*-Ts ligands in Pd-catalyzed asymmetric allylic alkylation reactions.

Introduction

The development of efficient asymmetric methodologies for providing enantiomerically pure products is of great value, due to the increasing demands for chiral compounds in the development of pharmaceuticals, agrochemicals, and materials. In order to develop efficient and highly enantioselective metal-catalyzed asymmetric reactions, the design and synthesis of chiral ligands and catalysts is a challenging task. As an important aspect of ligand structure modification, the tuning of electronic effects has attracted the attention of scientists from coordination chemistry and catalysis. In order to realize the structure–reactivity relationship and to optimize the ligand structure with a designated scaffold, both electron-withdrawing groups and electron-donating groups are introduced into the ligands at proper sites. Variation in the ligand electron density can be transferred to the metal cation through coordination bonds and affects the crucial properties of the complex, such as the positive charge density of the metal, the redox potential, the length of the coordination bonds, and the stability of the complex. During the past two decades, electronic effects of chiral ligands have been investigated by several groups.[1,2] Compared with the variation of the ligand scaffold, the catalytic activity and stereoselectivity (including enantioselectivity and diastereoselectivity) of the catalysts were tuned finely. Dramatic electronic effects such as inversion of diastereoselectivity were observed only in some cases.[2i,2j]

Since the first report of pyridine-derived imidazoline ligands in rhodium-catalyzed asymmetric hydrosilylation of ketones in 1989,[3] chiral imidazoline ligands with diverse scaffolds have been developed and applied in a variety of asymmetric transformations.[4] Compared with the corresponding oxazoline and thiazoline ligands, the introduction of substituents at the N-1 site of the imidazoline ring provides the opportunity to fine-tune the electronic effects orthogonally to steric effects.[2f,5] As part of our project on the development of diphenylamine-linked and diphenyl sulfide linked chiral ligands,[6] we developed diphenylamine-linked bis(imidazoline) ligands.[6h] Compared with diphenylamine-linked bis(oxazoline) and bis(thiazoline) ligands,[6e] the bis(imidazoline) ligands with electron-withdrawing *N*-Ts substitution gave better enantioselectivity and lower catalytic activity in the asymmetric Friedel–Crafts alkylation. Inspired by these results, we designed diphenyl sulfide linked bis(imidazoline) ligands **1** (Figure 1) to realize their electronic effects in palladium-catalyzed asymmetric allylic alkylations. Herein, we would like to document our recent progress.



1a R^1 = Ph, R^2 = H
1b R^1 = Bn, R^2 = H
1c R^1 = *i*Pr, R^2 = H
1d R^1 = *t*Bu, R^2 = H
1e R^1 = R^2 = Ph
1f R^1 = R^2 = $(CH_2)_4$

1g R = H
1h R = Me
1i R = *i*Pr

Figure 1. Diphenyl sulfide linked bis(imidazoline) ligands.

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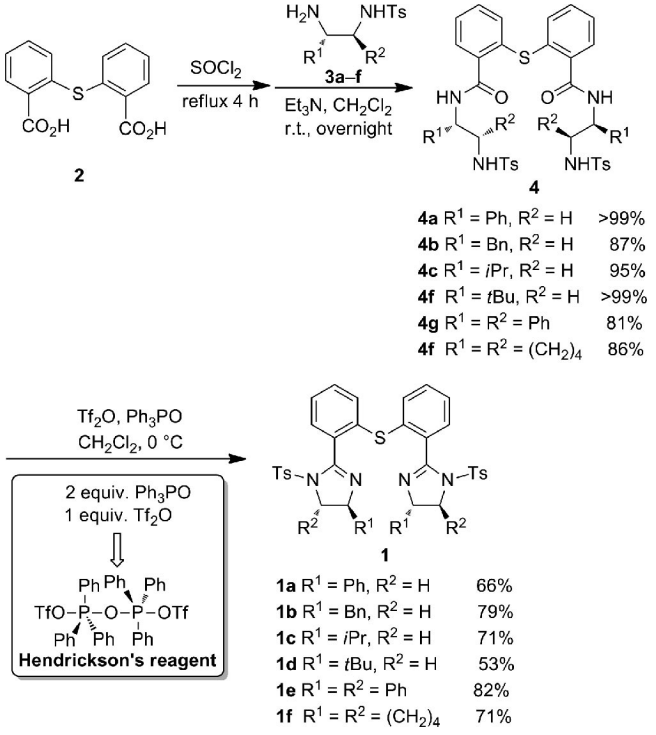
Results and Discussion

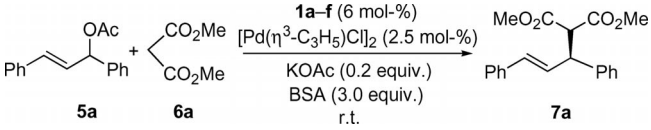
After obtaining the encouraging results with the use of bis(imidazoline) ligands in catalyzed asymmetric Friedel–Crafts alkylations,[6h] we designed *N*-Ts ligands **1a**–**f**. The ligands were synthesized from 2-(2-carboxyphenyl)sulfanylbenzoic acid (**2**), as illustrated in Scheme 1. Mono- and bis-substituted *N*-tosyl chiral ethylene diamines **3a**–**f** were synthesized from the corresponding amino alcohols or diamines, as we reported before.[6h] Precursors **4a**–**f** were obtained in good yields. Some of the products can precipitate from the reaction mixture and be isolated in pure form through filtration as a result of their poor solubility in CH_2Cl_2. The desired ligands were obtained in moderate to good yields through imidazoline formation by using the Hendrickson's reagent.[7]



Scheme 1. Synthesis of *N*-Ts-substituted diphenyl sulfide linked bis(imidazoline) ligands.

With the desired ligands **1a**–**f** in hand, we tested their catalytic activity in palladium-catalyzed asymmetric allylic alkylation reactions by using racemic (*E*)-1,3-diphenylprop-2-en-1-yl acetate (**5a**) and dimethyl malonate (**6a**) as model substrates; the catalysts were used at a loading of 5 mol-%. As summarized in Table 1, ligand **1b** gave the highest enantioselectivity with 85%*ee* (Table 1, Entry 2). The enantioselectivity is comparable to the optimized result using bis(oxazoline) ligands, whereas the catalytic activity of the bis(imidazoline) ligands is much lower. In most cases, up to 14 d were needed to observe notable conversion (Table 1, Entries 1–5). For ligand **1f** with less bulky substitution on the imidazoline ring, though the reaction rate was higher, only 6%*ee* was obtained (Table 1, Entry 6). Such low activity could not be improved in other solvents (Table 1, Entries 7–10). When the catalyst loading was raised to 8 and 10 mol-%, the reaction time could be shortened to 5 d with ca. 50% conversion, but the enantioselectivity was not affected significantly.

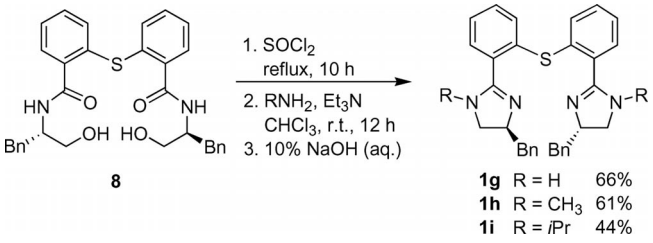
Table 1. Screening of ligands **1a**–**f**, solvents, and catalyst loading in asymmetric allylic alkylation reactions.[a]



Entry	Ligand	Solvent	Time [d]	Yield [%][b]	*ee* [%][c]
1	**1a**	CH_2Cl_2	14	30	59
2	**1b**	CH_2Cl_2	9	55	85
3	**1c**	CH_2Cl_2	14	16	41
4	**1d**	CH_2Cl_2	14	37	77
5	**1e**	CH_2Cl_2	14	7	63
6	**1f**	CH_2Cl_2	8	99	6
7	**1b**	toluene	9	15	75
8	**1b**	THF	9	37	73
9	**1b**	CH_3CN	9	73	79
10	**1b**	Et_2O	9	14	78
11[d]	**1b**	CH_2Cl_2	5	42	80
12[e]	**1b**	CH_2Cl_2	5	53	89

[a] The reaction was conducted with **5a** (0.5 mmol) and **6a** (1.5 mmol) in solvent (3 mL) at room temperature. [b] Isolated yield. [c] Determined by HPLC by using a Chiralcel IA column with *n*-hexane/2-propanol (90:10) as eluent. [d] The catalyst loading was 8 mol-%. [e] The catalyst loading was 10 mol-%.

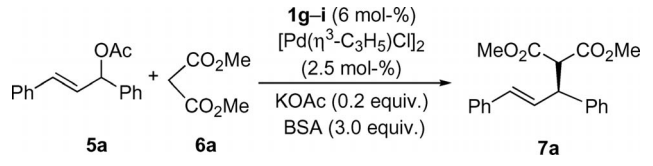
Considering the mechanism of allylic alkylation, such a significant but discouraging electronic effect can be attributed to the electron-withdrawing nature of the *N*-Ts substituent. The introduction of *N*-Ts groups reduces the electron density at the N-3 sites and the metal center relative to that of the corresponding bis(oxazoline) ligands. Thus, the rate of the oxidative addition of the allyl substrate to Pd^0 species is slower. On the basis of this analysis, we concluded that bis(imidazoline) ligands with electron-donating substituents at the N-1 position should give enhanced catalytic activity. To further test our hypothesis of electronic effect, novel ligands **1g**–**i** were designed by using optimized **1b** as a leading structure. In this case, the Hendrickson reagent cannot be used for the nucleophiles of the corresponding diamines (instead of the sulfonamides in **4**), as they may destroy the reagent. Finally, desired ligands **1g**–**i** with electron-donating substituents were synthesized following Casey's procedure[8] by using bis(β-hydroxy amide) **8** as precursor (Scheme 2), which was the intermediate in our bis(oxazoline) preparation.[6i] Only primary amines with low molecular weights can be successfully used in this transformation. It is feasible to use large excess amounts of the amines to suppress the side reactions. When we tried to use a slight excess amount of benzylamine or 4-methylaniline in this reaction, only inseparable mixtures without major components were obtained. Other routes toward **1g**–**i** did not give fruitful results.[9]



Scheme 2. Synthesis of bis(imidazoline) ligands through chlorination/substitution.

Ligands **1g**–**i** were tested in the model asymmetric allylic alkylation by using 5 mol-% of the catalysts. As we expected, the catalytic activity increased dramatically. As summarized in Table 2, full conversion was achieved within 1 d at room temperature (Table 2, Entries 1–3). To our surprise, ligand **1h** with an *N*-CH_3 substituent was so active that the product was obtained in 96% yield with 93%*ee* within only 1 h (Table 2, Entry 2). In contrast, the optimized bis(oxazoline) ligand reported previously[6i] gave 84% yield and 89%*ee* after 48 h. When the temperature was further reduced to 0 °C, no improvement in the enantioselectivity and a decreased yield were observed (Table 2, Entry 4).

Table 2. Catalytic behavior of ligands **1g**–**i** in the model asymmetric allylic alkylation reaction.[a]

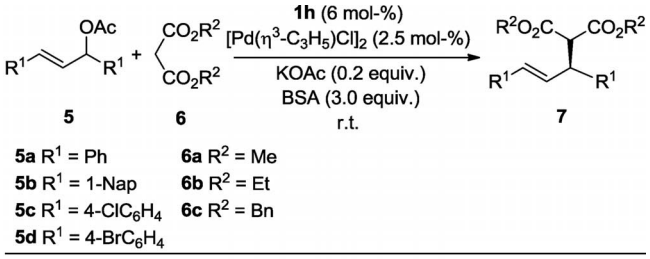


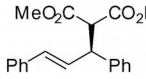
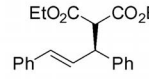
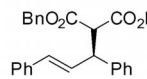
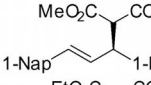
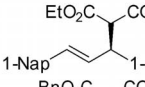
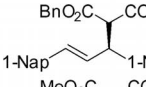
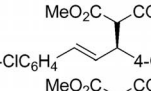
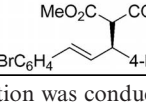
Entry	Ligand	*T* [°C]	Time [h]	Yield [%][b]	*ee* [%][c]
1	**1g**	25	16	99	87
2	**1h**	25	1	96	93
3	**1i**	25	17	94	86
4	**1h**	0	24	59	93

[a] The reaction was conducted with **5a** (0.5 mmol) and **6a** (1.5 mmol) in solvent (3 mL) at room temperature. [b] Isolated yield. [c] Determined by HPLC by using a Chiralcel IA column with *n*-hexane/2-propanol (90:10) as eluent.

To illustrate the generality of the high reactivity of ligand **1h**, other substrates were tested under the optimized condition (Table 3). For the phenyl-containing model substrate, diethyl and dibenzyl malonates gave comparable activity to dimethyl malonate, whereas the enantioselectivity was 91 and 90%, respectively (Table 3, Entries 2 and 3). When bulky 1,3-bis(1-naphthyl)prop-2-en-1-yl acetate[10] was used, full conversion was achieved within 1 h for all three malonates (Table 3, Entries 4–6). When substrates with electron-withdrawing groups were tested,[10] comparable activity but lower enantioselectivities were obtained (Table 3, Entries 7 and 8). In all the cases, ligand **1h** gave much higher reactivity and comparable enantioselectivity than those reported for the optimized bis(oxazoline) ligand (data in parentheses in Table 3).[6i] The absolute configurations of the products were determined to be *S* by comparison of the optical rotations of the products and their retention times on HPLC with literature data. We used other substrates, such as indole, benzyl alcohol, and morpholine, but they did not work in our reaction. A simple catalytic enantioselectivity comparison between our bis(oxazoline)s and bis(imidazoline)s may not be appropriate, because the best ligand, bis(oxazoline), contains a 4-*tert*-butyl group in the oxazoline ring, whereas the best bis(imidazoline) ligand contains a 4-benzyl group. The scientific value of this research is the direct observation of a dramatic electronic effect in the bis(imidazoline) ligands on the catalytic behavior.

Table 3. Scope of substrates for Pd-**1h**- catalyzed asymmetric allylic alkylations.[a]



Entry	Product		Yield [%][b,e]	*ee* [%][c,e]
1		**7aa**	96 (84)	93 (89)
2		**7ab**	99 (98)	91 (91)
3[d]		**7ac**	99	90
4		**7ba**	99 (98)	99 (94)
5		**7bb**	95 (80)	90 (94)
6[d]		**7bc**	99	91
7		**7ca**	99	86
8		**7da**	84	89

[a] The reaction was conducted with allyl acetate **5** (0.5 mmol) and nucleophile **6** (1.5 mmol) in CH_2Cl_2 (3 mL) at room temperature using **1h** (6 mol-%) and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (2.5 mol-%) as catalyst. [b] Isolated yield. [c] Determined by HPLC by using a Chiralcel IA column. [d] Dibenzyl malonate (1.0 mmol) was used. [e] The data in parentheses were obtained by using the optimized bis(oxazoline) ligand with a *tert*-butyl group on the oxazoline ring.

On the basis of the absolute configurations of the products, a transition-state model of the asymmetric allylic alkylation reaction was proposed (Figure 2). Considering the coordination number of the Pd center and the results obtained by Schulz by using sulfur-containing monooxazoline ligands[11] and Gomez by using diphenyl ether linked bis(oxazoline) ligands,[12] we envisioned that chelation of the S

and N atoms to Pd with one imidazoline free is not a favorable transition state, because bis(oxazoline) is more powerful than monooxazoline in Schulz's report.[11] The weak interaction between the sulfur atom and Pd cannot be exclusively abandoned. The sulfur atom may function as an additional chelation point to stabilize the complex. The nucleophile attacks the η^3-allyl complex as illustrated in Figure 2 to release the steric hindrance and gives the *S* configured product. Electron-poor substrates **5c** and **5d** will give looser complexes with larger bond lengths between the η^3-allyl ligands and the Pd^{II} center, which will lead to weaker stereochemical information transfer and lower enantioselectivities.

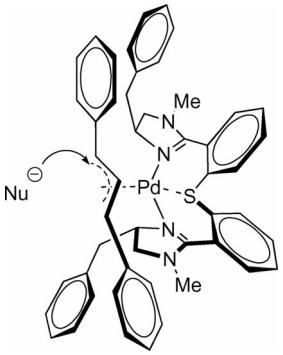


Figure 2. Proposed transition-state model.

Conclusions

In conclusion, we designed and synthesized diphenyl sulfide linked bis(imidazoline) ligands **1a**–**f** having electron-withdrawing *N*-Ts substituents. According to their low catalytic activity in asymmetric allylic alkylation reactions, we rationally designed and synthesized bis(imidazoline)s **1g**–**i** with benzyl groups on the imidazoline rings. These ligands demonstrated much higher catalytic activity than ligands **1a**–**f** and the corresponding bis(oxazoline) ligands we reported before, as well as significantly improved enantioselectivity in some cases. Further application of these ligands in other asymmetric transformations is under way in our laboratory.

Experimental Section

General Remarks: Commercially available compounds were used without further purification. Solvents were dried according to standard procedures. Column chromatography was carried out by using silica gel (200–300 mesh). Melting points were measured with a XT-4 melting point apparatus. ^{1}H NMR spectra were recorded with a Mercury 300 MHz spectrometer, whereas ^{13}C NMR spectra were recorded at 75 MHz. Infrared spectra were obtained with a Nicolet AVATAR 330 FTIR spectrometer. ESI mass spectra were obtained with a Thermo Finnigan LCQ Deca XP Plus mass spectrometer. Optical rotations were measured with a Perkin–Elmer 341 LC or WZZ-3 spectrometer. The enantiomeric excess values of the products were determined by chiral HPLC by using an Agilent HP 1200 instrument on a Chiralpak IA column.

2,2′-Bis{*N*-[(*S*)-1-phenyl-2-(4-methylbenzenesulfonamido)ethyl]carbamoyl}diphenyl Sulfide (4a): To a round-bottomed flask was added **2** (1.151 g, 4.2 mmol) and $SOCl_2$ (10 mL). The mixture was heated at reflux for 4 h, and the excess amount of $SOCl_2$ was removed under vacuum. The diacyl chloride residue was dissolved in CH_2Cl_2 (10 mL). To a round-bottomed flask was added **3a** (2.436 g, 8.4 mmol), Et_3N (3.0 mL, 21 mmol), and CH_2Cl_2 (20 mL). The mixture was cooled to 0 °C, and the solution of the diacyl chloride was added dropwise. After completion of the addition, the mixture was stirred at room temperature overnight. During the reaction the product precipitated from the mixture. The reaction was quenched with saturated NH_4Cl (aq.), and the white precipitate was filtered and washed thoroughly with water. After being dried by lamp heating, the desired product (3.43 g, >99% yield) was obtained as a white powder. M.p. 269–271 °C. $[\alpha]_D^{20}$ = +4.74 (*c* = 0.49, DMSO). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.34 (s, 6 H, CH_3), 3.01–3.11 (m, 4 H, CH_2), 3.34–3.37 (m, 2 H, NH), 5.05–5.09 (m, 2 H, CH), 7.11–7.14 (m, 2 H, ArH), 7.20–7.28 (m, 6 H, ArH), 7.32–7.35 (m, 10 H, ArH), 7.55–7.58 (m, 2 H, ArH), 7.64 (d, *J* = 8.1 Hz, 4 H, ArH), 7.73 (t, *J* = 6.0 Hz, 2 H, ArH), 8.77 (d, *J* = 8.4 Hz, 2 H, NH) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 20.9, 47.3, 52.9, 126.4, 126.8, 126.9, 127.0, 128.0, 128.1, 129.6, 130.3, 132.6, 134.7, 137.1, 138.4, 140.3, 142.6, 166.9 ppm. IR (neat): $\tilde{\nu}$ = 3315, 3269, 1634, 1512, 1330, 1160, 1092, 928, 810 cm^{-1}. HRMS (ESI): calcd. for $C_{44}H_{42}N_4NaO_6S_3$ $[M + Na]^+$ 841.21587; found 841.21373.

2,2′-Bis{*N*-[(*S*)-1-(4-methylbenzenesulfonamido)-3-phenylprop-2-yl]carbamoyl}diphenyl Sulfide (4b): Compound **4b** was prepared following the procedure outlined for **4a** from **2** (419 mg, 1.53 mmol) and **3b** (1.003 g, 3.3 mmol). The desired product was obtained as a white solid (1.125 g, 87% yield). M.p. 155–158 °C. $[\alpha]_D^{20}$ = –52.6 (*c* = 0.41, DMSO). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.34 (s, 6 H, CH_3), 2.70 (dd, *J* = 13.7, 8.9 Hz, 2 H, CH), 2.86–2.92 (m, 6 H, CH), 3.34 (d, *J* = 7.2 Hz, 2 H, NH), 4.12 (br., 2 H, CH), 7.05–7.08 (m, 2 H, ArH), 7.13–7.24 (m, 10 H, ArH), 7.26–7.36 (m, 8 H, ArH), 7.65–7.68 (m, 4 H, ArH), 7.73–7.74 (m, 2 H, ArH), 8.25 (d, *J* = 8.4 Hz, 2 H, NH) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 20.9, 36.6, 45.5, 50.4, 126.0, 126.4, 126.6, 127.6, 128.0, 129.0, 129.6, 130.1, 132.6, 134.7, 137.4, 138.4, 138.9, 142.6, 167.2 ppm. IR (neat): $\tilde{\nu}$ = 3295, 2979, 2603, 2498, 1639, 1526, 1334, 1157, 1096, 869, 851 cm^{-1}. HRMS (ESI): calcd. for $C_{46}H_{47}N_4O_6S_3$ $[M + H]^+$ 847.26522; found 847.26394.

2,2′-Bis{*N*-[(*S*)-1-(4-methylbenzenesulfonamido)-3-methylbut-2-yl]carbamoyl}diphenyl Sulfide (4c): Compound **4c** was prepared following the procedure outlined for **4a** from **2** (685 mg, 2.5 mmol) and **3c** (1.280 g, 5.0 mmol). The crude product was purified by silica gel column chromatography (CH_2Cl_2/MeOH, 20:1). The desired product was obtained as a white solid (1.710 g, 95% yield). M.p. 103–106 °C. $[\alpha]_D^{20}$ = –10.9 (*c* = 0.40, CH_2Cl_2). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 0.81 (d, *J* = 6.6 Hz, 6 H, CH_3), 0.85 (d, *J* = 6.9 Hz, 6 H, CH_3), 1.79–1.90 (m, 2 H, CH), 2.37 (s, 6 H, CH_3), 2.78–2.86 (m, 4 H, CH), 3.36–3.39 (m, 2 H, NH), 3.79–3.89 (m, 2 H, CH), 7.14–7.19 (m, 2 H, ArH), 7.29–7.34 (m, 4 H, ArH), 7.37–7.40 (m, 4 H, ArH), 7.48–7.51 (m, 2 H, ArH), 7.69 (d, *J* = 8.1 Hz, 4 H, ArH), 8.10 (d, *J* = 9 Hz, 2 H, NH) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 17.6, 19.5, 21.0, 28.7, 43.9, 53.6, 126.5, 126.8, 127.9, 129.6, 130.0, 132.7, 134.3, 137.3, 139.5, 142.6, 167.6 ppm. IR (neat): $\tilde{\nu}$ = 3275, 2961, 1636, 1534, 1464, 1326, 1158, 1093, 841 cm^{-1}. HRMS (ESI): calcd. for $C_{38}H_{47}N_4O_6S_3$ $[M + H]^+$ 751.26522; found 751.26480.

2,2′-Bis{*N*-[(*S*)-1-(4-methylbenzenesulfonamido)-3,3-dimethylbut-2-yl]carbamoyl}diphenyl Sulfide (4d): Compound **4d** was prepared following the procedure outlined for **4a** from **2** (548 mg, 2.0 mmol)

and **3d** (1.141 g, 4.2 mmol). The crude product was purified by silica gel column chromatography (CH_2Cl_2/MeOH, 20:1). The desired product was obtained as a white solid (1.55 g, >99% yield). M.p. 130–131 °C. $[a]_D^{20}$ = –12.3 (*c* = 0.90, CH_2Cl_2). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 0.86 (s, 18 H, CH_3), 2.38 (s, 6 H, CH_3), 2.77–2.85 (m, 2 H, CH), 2.94–2.98 (m, 2 H, CH), 3.36–3.40 (m, 2 H, NH), 3.85–3.91 (m, 2 H, CH), 7.21–7.22 (m, 2 H, ArH), 7.31–7.34 (m, 4 H, ArH), 7.38–7.41 (m, 4 H, ArH), 7.57–7.61 (m, 2 H, ArH), 7.72 (d, *J* = 8.1 Hz, 4 H, ArH), 8.15 (d, *J* = 9.6 Hz, 2 H, NH) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 20.9, 26.6, 34.1, 43.2, 57.2, 126.5, 128.1, 129.6, 129.9, 132.9, 134.6, 137.55, 137.63, 140.0, 142.5, 168.0 ppm. IR (neat): $\tilde{\nu}$ = 3260, 2962, 1638, 1534, 1466, 1327, 1157, 1092, 1025, 952, 814 cm^{-1}. HRMS (ESI): calcd. for $C_{40}H_{51}N_4O_6S_3$ [M + H]$^+$ 779.29652; found 779.29607.

2,2′-Bis{*N*-[(1*S*,2*S*)-1,2-diphenyl-2-(4-methylbenzenesulfonamido)-ethyl]carbamoyl}diphenyl Sulfide (4e): Compound **4e** was prepared following the procedure outlined for **4a** from **2** (822 mg, 3.0 mmol) and **3e** (2.206 g, 6.0 mmol). The desired product was obtained as a white solid (2.360 g, 81% yield). M.p. 290–292 °C. $[a]_D^{20}$ = +20.2 (*c* = 0.66, DMSO). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.23 (s, 6 H, CH_3), 3.34 (d, *J* = 6.9 Hz, 2 H, NH), 4.83 (d, *J* = 5.4 Hz, 2 H, CH), 5.32–5.37 (m, 2 H, CH), 6.96–6.99 (m, 4 H, ArH), 7.03–7.05 (m, 12 H, ArH), 7.13–7.19 (m, 8 H, ArH), 7.26 (br., 4 H, ArH), 7.33 (br., 6 H, ArH), 8.24 (d, *J* = 9.6 Hz, 2 H, ArH), 8.68 (d, *J* = 9.0 Hz, 2 H, NH) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 20.8, 57.7, 61.7, 125.9, 126.6, 127.1, 127.5, 127.7, 128.8, 130.3, 132.6, 134.7, 138.3, 138.5, 139.1, 139.5, 141.6, 166.7 ppm. IR (neat): $\tilde{\nu}$ = 3320, 3279, 1636, 1526, 1322, 1159, 1085, 920 cm^{-1}. HRMS (ESI): calcd. for $C_{56}H_{51}N_4O_6S_3$ [M + H]$^+$ 971.29652; found 971.29576.

2,2′-Bis{*N*-[(1*S*,2*S*)-2-(4-methylbenzenesulfonamido)cyclohexan-1-yl]carbamoyl}diphenyl Sulfide (4f): Compound **4f** was prepared following the procedure outlined for **4a** from **2** (822 mg, 3.0 mmol) and **3f** (1.779 g, 6.6 mmol). The desired product was obtained as a white solid (2.050 g, 86% yield). M.p. 240–241 °C. $[a]_D^{20}$ = –43.2 (*c* = 0.48, DMSO). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 0.97–1.32 (m, 8 H, CH_2), 1.42–1.53 (m, 6 H, CH_2), 1.74–1.78 (m, 2 H, CH_2), 2.36 (s, 6 H, CH_3), 3.02 (d, *J* = 8.1 Hz, 2 H, CH), 3.35 (d, *J* = 6.9 Hz, 2 H, NH), 3.66 (d, *J* = 6.3 Hz, 2 H, CH), 7.15 (d, *J* = 7.2 Hz, 2 H, ArH), 7.33 (m, 8 H, ArH), 7.47 (d, *J* = 6.6 Hz, 2 H, ArH), 7.70 (d, *J* = 7.8 Hz, 4 H, ArH), 8.02 (d, *J* = 8.1 Hz, 2 H, NH) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 20.9, 23.9, 24.1, 31.3, 31.9, 51.8, 56.1, 126.2, 126.5, 127.9, 129.4, 130.0, 132.2, 134.5, 138.8, 139.6, 142.1, 167.1 ppm. IR (neat): $\tilde{\nu}$ = 3285, 2936, 2856, 1635, 1534, 1325, 1158, 1089, 816 cm^{-1}. HRMS (ESI): calcd. for $C_{40}H_{47}N_4O_6S_3$ [M + H]$^+$ 775.26522; found 775.26498.

2,2′-Bis[(*S*)-1-(4-methylbenzenesulfonyl)-4-phenylimidazolin-2-yl]-diphenyl Sulfide (1a): To a flame-dried Schlenk tube was added triphenylphosphane oxide (1.668 g, 6.0 mmol) and CH_2Cl_2 (15 mL). The solution was cooled to 0 °C, and trifluoromethanesulfonic anhydride (0.5 mL, 3.0 mmol) was added in one portion. The mixture was stirred at 0 °C for 0.5 h, then **4a** (818 mg, 1.0 mmol) was added in several portions. After completion of the addition, the mixture was stirred at 0 °C for 2 h. The reaction was quenched with saturated $NaHCO_3$ (aq.). The organic phase was separated, and the water phase was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic phase was dried with anhydrous Na_2SO_4, and the solvent was removed under vacuum. The residue was purified by silica gel (buffered with Et_3N) column chromatography (CH_2Cl_2). The desired product was obtained as a white solid (517 mg, 66% yield). M.p. 107–110 °C. $[a]_D^{20}$ = –40.7 (*c* = 0.72, CH_2Cl_2). IR (neat): $\tilde{\nu}$ = 3094, 2925, 1633, 1494, 1362, 1167, 1092, 1017, 814 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.37 (s, 6 H, CH_3), 3.79 (t, *J* = 9.0 Hz, 2 H, CH), 4.37 (t, *J* = 10.2 Hz, 2 H, CH), 5.21 (t, *J* = 9.0 Hz, 2 H, CH), 7.17–7.20 (m, 12 H, ArH), 7.25–7.34 (m, 6 H, ArH), 7.38–7.41 (m, 2 H, ArH), 7.46–7.48 (m, 2 H, ArH), 7.59 (d, *J* = 7.8 Hz, 4 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.6, 55.8, 68.4, 126.4, 126.6, 127.3, 127.7, 128.6, 129.8, 130.0, 130.9, 132.7, 132.8, 134.7, 137.2, 141.5, 144.5, 157.2 ppm. HRMS (ESI): calcd. for $C_{44}H_{39}N_4O_4S_3$ [M + H]$^+$ 783.21279; found 783.21175.

2,2′-Bis[(*S*)-1-(4-methylbenzenesulfonyl)-4-benzylimidazolin-2-yl]-diphenyl Sulfide (1b): Compound **1b** was prepared following the procedure outlined for **1a** from **4b** (874 mg, 1.03 mmol). The desired product was obtained as a pale yellow oil (663 mg, 79% yield). $[a]_D^{20}$ = –45.8 (*c* = 0.56, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.40 (s, 6 H, CH_3), 2.47 (dd, *J* = 13.7, 8.9 Hz, 2 H, CH_2), 3.03 (dd, *J* = 13.8, 6.0 Hz, 2 H, CH_2), 3.64 (dd, *J* = 12.0, 6.6 Hz, 2 H, CH), 3.86 (t, *J* = 9.9 Hz, 2 H), 4.33–4.43 (m, 2 H, CH), 7.06–7.09 (m, 4 H, ArH), 7.15–7.38 (m, 18 H, ArH), 7.57 (d, *J* = 8.4 Hz, 4 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.6, 41.4, 52.2, 66.5, 126.3, 126.4, 127.7, 128.4, 129.2, 129.7, 130.7, 131.8, 132.6, 132.9, 135.2, 137.0, 137.5, 144.4, 156.0 ppm. IR (neat): $\tilde{\nu}$ = 3062, 2922, 1636, 1493, 1361, 1167, 1099, 1030, 814 cm^{-1}. HRMS (ESI): calcd. for $C_{46}H_{43}N_4O_4S_3$ [M + H]$^+$ 811.24409; found 811.24302.

2,2′-Bis[(*S*)-1-(4-methylbenzenesulfonyl)-4-isopropylimidazolin-2-yl]diphenyl Sulfide (1c): Compound **1c** was prepared following the procedure outlined for **1a** from **4c** (750 mg, 1.0 mmol). The desired product was obtained as a colorless oil (510 mg, 71% yield). $[a]_D^{20}$ = –53.3 (*c* = 1.08, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.81 (d, *J* = 6.6 Hz, 6 H, CH_3), 0.90 (d, *J* = 6.6 Hz, 6 H, CH_3), 1.62–1.68 (m, 2 H, CH), 2.41 (s, 6 H, CH_3), 3.54–3.63 (m, 2 H, CH), 3.86–3.95 (m, 4 H, CH), 7.24–7.38 (m, 12 H, ArH), 7.62 (d, *J* = 8.1 Hz, 4 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.3, 18.8, 21.6, 32.8, 50.7, 71.4, 126.2, 127.8, 129.7, 129.8, 130.6, 132.5, 133.0, 135.2, 137.2, 144.3, 155.4 ppm. IR (neat): $\tilde{\nu}$ = 2958, 2927, 1638, 1597, 1467, 1361, 1168, 1092, 1025 cm^{-1}. HRMS (ESI): calcd. for $C_{38}H_{43}N_4O_4S_3$ [M + H]$^+$ 715.24409; found 715.24392.

2,2′-Bis[(*S*)-1-(4-methylbenzenesulfonyl)-4-*tert*-butylimidazolin-2-yl-]diphenyl Sulfide (1d): Compound **1d** was prepared following the procedure outlined for **1a** from **4d** (778 mg, 1.0 mmol). The desired product was obtained as a white solid (394 mg, 53% yield). M.p. 176–180 °C. $[a]_D^{20}$ = –54.6 (*c* = 0.47, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.83 (s, 18 H, CH_3), 2.40 (s, 6 H, CH_3), 3.61 (t, *J* = 7.7 Hz, 2 H, CH), 3.82–3.95 (m, 4 H, CH), 7.22–7.32 (m, 8 H, ArH), 7.35–7.38 (m, 2 H, ArH), 7.42–7.45 (m, 2 H, ArH), 7.64 (d, *J* = 8.1 Hz, 4 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.6, 25.9, 34.0, 49.1, 74.9, 126.1, 127.8, 129.7, 129.9, 130.5, 132.5, 132.9, 134.8, 137.3, 144.4, 155.4 ppm. IR (neat): $\tilde{\nu}$ = 2957, 2869, 1638, 1477, 1362, 1186, 1109, 1042 cm^{-1}. HRMS (ESI): calcd. for $C_{40}H_{47}N_4O_4S_3$ [M + H]$^+$ 743.27539; found 743.27481.

2,2′-Bis[(4*S*,5*S*)-1-(4-methylbenzenesulfonyl)-4,5-diphenylimidazolin-2-yl]diphenyl Sulfide (1e): Compound **1e** was prepared following the procedure outlined for **1a** from **4e** (649 mg, 0.67 mmol). The desired product was obtained as a white solid (512 mg, 82% yield). M.p. 115–117 °C. $[a]_D^{20}$ = +11.4 (*c* = 0.25, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.30 (s, 6 H, CH_3), 5.03 (d, *J* = 5.4 Hz, 2 H, CH), 5.14–5.29 (m, 2 H, CH), 6.98–7.58 (m, 36 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.4, 72.1, 79.0, 126.1, 126.5, 127.2, 127.8, 128.5, 128.9, 129.3, 130.2, 130.8, 134.5, 141.3, 141.6, 144.3, 157.1 ppm. IR (neat): $\tilde{\nu}$ = 3061, 2923, 1632, 1494, 1365, 1135, 1000 cm^{-1}. HRMS (ESI): calcd. for $C_{56}H_{47}N_4O_4S_3$ [M + H]$^+$ 935.27539; found 935.27392.

2,2′-Bis[(4*S*,5*S*)-4,5-butylidenyl-1-(4-methylbenzenesulfonyl)imidazolin-2-yl]diphenyl Sulfide (1f): Compound **1f** was prepared following the procedure outlined for **1a** from **4f** (433 mg, 0.50 mmol). The desired product was obtained as a white solid (260 mg, 71% yield). M.p. 125–127 °C. $[\alpha]_D^{20} = -41.0$ ($c = 0.30$, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.25–1.37 (m, 4 H, CH_2), 1.41–1.48 (m, 2 H, CH_2), 1.58–1.62 (m, 2 H, CH_2), 1.83–1.91 (m, 4 H, CH_2), 2.30–2.34 (m, 2 H, CH_2), 2.42 (s, 6 H, CH_3), 2.46–2.51 (m, 2 H, CH_2), 3.33 (br., 4 H, CH), 7.19–7.31 (m, 12 H, ArH), 7.57 (d, J = 7.8 Hz, 4 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.6, 24.5, 25.0, 30.1, 30.5, 69.3, 71.1, 126.2, 127.7, 129.0, 129.5, 130.3, 132.7, 134.4, 136.0, 136.8, 144.1, 158.5 ppm. IR (neat): $\tilde{\nu}$ = 2931, 2857, 1621, 1466, 1363, 1264, 1168, 1047, 1079, 1025 cm^{-1}. HRMS (ESI): calcd. for $C_{40}H_{43}N_4O_4S_3$ $[M + H]^+$ 739.24409; found 739.24395.

2,2′-Bis[(*S*)-4-benzylimidazolin-2-yl]diphenyl Sulfide (1g): To a round-bottomed flask was added **8**[6i] (270 mg, 0.5 mmol) and $SOCl_2$ (2 mL). The mixture was heated at reflux for 10 h, and the excess amount of $SOCl_2$ was removed under vacuum. The residue was dissolved in $CHCl_3$ (10 mL). Et_3N (0.6 mL, 4.2 mmol) was added, followed by a saturated solution of ammonia in $CHCl_3$ (30 mL). The mixture was stirred at room temperature overnight and then was treated with 10% NaOH (aq.) (10 mL) for 1 h. The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (3× 50 mL). The combined organic phase was dried with anhydrous $NaSO_4$. The solvent was removed under vacuum, and the residue was purified by silica gel (buffered with Et_3N) column chromatography (CH_2Cl_2/MeOH, 20:1). The desired product was obtained as a pale yellow oil (166 mg, 66% yield). $[\alpha]_D^{20} = -63.1$ ($c = 0.69$, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.59 (dd, J = 13.5, 7.2 Hz, 2 H, CH), 2.84 (dd, J = 13.5, 6.6 Hz, 2 H, CH), 3.38 (dd, J = 12.0, 7.2 Hz, 2 H, CH), 3.61 (t, J = 11.0 Hz, 2 H, CH), 4.03–4.14 (m, 2 H, CH), 5.29 (br., 2 H, NH), 7.12–7.30 (m, 16 H, ArH), 7.64–7.67 (m, 2 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 41.8, 55.7, 62.3, 126.2, 127.3, 128.4, 129.0, 130.2, 130.5, 131.9, 132.5, 134.2, 138.3, 163.2 ppm. IR (neat): $\tilde{\nu}$ = 3169, 2919, 2849, 1726, 1603, 1583, 1494, 1453, 1287, 1121, 977 cm^{-1}. HRMS (ESI): calcd. for $C_{32}H_{31}N_4S$ $[M + H]^+$ 503.22639; found 503.22680.

2,2′-Bis[(*S*)-1-methyl-4-benzylimidazolin-2-yl]diphenyl Sulfide (1h): Compound **1h** was prepared following the procedure outlined for **1g** from **8** (270 mg, 0.5 mmol) and a saturated solution of methylamine in $CHCl_3$ (5 mL). The desired product was obtained as a pale yellow oil (161 mg, 61% yield). $[\alpha]_D^{20} = -63.9$ ($c = 0.41$, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.66 (s, 6 H, CH_3), 2.72 (dd, J = 13.5, 8.7 Hz, 2 H, CH), 3.11 (dd, J = 13.7, 5.0 Hz, 2 H, CH), 3.27 (t, J = 8.9 Hz, 2 H, CH), 3.50 (t, J = 9.9 Hz, 2 H, CH), 4.18–4.29 (m, 2 H, CH), 7.18–7.31 (m, 10 H, ArH), 7.33–7.43 (m, 8 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 34.1, 41.4, 56.6, 63.3, 126.3, 127.7, 128.3, 129.4, 130.0, 130.7, 131.1, 132.5, 134.0, 137.7, 164.5 ppm. IR (neat): $\tilde{\nu}$ = 3061, 2922, 1610, 1580, 1493, 1453, 1388, 1291, 1250, 1291, 1044 cm^{-1}. HRMS (ESI): calcd. for $C_{34}H_{35}N_4S$ $[M + H]^+$ 531.25769; found 531.25783.

2,2′-Bis[(*S*)-1-(1-methylethyl)-4-benzylimidazolin-2-yl]diphenyl Sulfide (1i): Compound **1i** was prepared following the procedure outlined for **1g** from **8** (270 mg, 0.5 mmol) and isopropylamine (1.18 g, 20 mmol). The desired product was obtained as a pale yellow oil (130 mg, 44% yield). $[\alpha]_D^{20} = -56.3$ ($c = 0.39$, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.95 (d, J = 5.1 Hz, 6 H, CH_3), 1.01 (d, J = 6.6 Hz, 6 H, CH_3), 2.74 (dd, J = 13.5, 8.7 Hz, 2 H, CH), 3.12–3.18 (m, 4 H, CH), 3.34–3.45 (m, 4 H, CH), 4.31–4.42 (m, 2 H, CH), 7.18–7.31 (m, 18 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.0, 20.5, 42.2, 46.2, 46.7, 65.0, 125.9, 126.8, 128.1, 129.1, 129.4, 129.7, 131.8, 133.7, 135.3, 138.7, 163.3 ppm. IR (neat): $\tilde{\nu}$ = 3091, 2966, 2931, 2871, 1726, 1603, 1580, 1453, 1406, 1364, 1287, 1121, 1073, 1046 cm^{-1}. HRMS (ESI): calcd. for $C_{38}H_{43}N_4S_3$ $[M + H]^+$ 587.32029; found 587.32031.

(*S*)-Dimethyl 2-[(*E*)-1,3-Diphenylprop-2-en-1-yl]malonate (7aa): To a flame-dried Schlenk tube was added $[Pd(allyl)Cl]_2$ (4.6 mg, 0.0125 mmol) and ligand **1h** (15.9 mg, 0.03 mmol) under an argon atmosphere, followed by the addition of CH_2Cl_2 (2.0 mL). The solution was stirred at room temperature for 0.5 h. Then, a solution of **5a** (126 mg, 0.50 mmol) in CH_2Cl_2 (1 mL) was added, and the mixture was stirred for 10 min before the addition of **6a** (0.17 mL, 1.5 mmol), *N*,*O*-bis(trimethylsilyl)acetamide (BSA; 0.37 mL, 1.5 mmol) and anhydrous KOAc (10 mg, 0.10 mmol). After being stirred for 1 h (full conversion of the substrate was monitored by TLC), water (10 mL) was added, and the mixture was extracted with EtOAc (2 × 20 mL). The combined organic phase was dried with anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by silica gel flash chromatography (petroleum ether/ethyl acetate, 20:1). The desired product was obtained as a colorless oil (155 mg, 96% yield). The *ee* was determined by chiral HPLC. HPLC (Daicel Chiralpak IA column, *n*-hexane/2-propanol = 90:10, 0.5 mL/min, 254 nm): t_{minor} = 15.2 min, t_{major} = 18.3 min. $[\alpha]_D^{20} = -13.7$ ($c = 1.8$, CH_2Cl_2; 93%*ee*) {ref.[13] $[\alpha]_D^{20} = -11.2$; $c = 1.04$, $CHCl_3$; 86%*ee*}. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.51 (s, 3 H, CH_3), 3.69 (s, 3 H, CH_3), 3.96 (d, J = 10.8 Hz, 1 H, CH), 4.27 (dd, J = 10.8, 8.4 Hz, 1 H, CH), 6.33 (dd, J = 15.6, 8.4 Hz, 1 H, =CH), 6.48 (d, J = 15.6 Hz, 1 H, =CH), 7.19–7.30 (m, 10 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 49.1, 52.4, 52.6, 57.6, 126.3, 127.1, 127.5, 127.8, 128.4, 128.7, 129.1, 131.8, 136.8, 140.1, 167.7, 168.1 ppm.

(*S*)-Diethyl 2-[(*E*)-1,3-Diphenylprop-2-en-1-yl]malonate (7ab): Compound **7ab** was prepared according to the procedure outlined for **7aa** by using **5a** (126 mg, 0.50 mmol) and **6b** (240 mg, 1.5 mmol). The desired product was obtained as a colorless oil (174 mg, 99% yield). The *ee* was determined by chiral HPLC. HPLC (Daicel Chiralcel IA column, *n*-hexane/2-propanol = 90:10, 0.5 mL/min, 254 nm): t_{minor} = 14.1 min, t_{major} = 16.9 min. $[\alpha]_D^{20} = -7.9$ ($c = 2.3$, CH_2Cl_2; 91%*ee*) {ref.[14] $[\alpha]_D^{25} = -17.2$; $c = 1.02$, $CHCl_3$; 97%*ee*}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.00 (t, J = 7.2 Hz, 3 H, CH_3), 1.20 (t, J = 7.2 Hz, 3 H, CH_3), 3.92 (d, J = 9.0 Hz, 1 H, CH), 3.96 (q, J = 7.2 Hz, 2 H, CH_2), 4.16 (q, J = 7.2 Hz, 2 H, CH_2), 4.27 (dd, J = 10.8, 8.7 Hz, 1 H, CH), 6.34 (dd, J = 15.6, 8.1 Hz, 1 H, =CH), 6.48 (d, J = 15.6 Hz, 1 H, =CH), 7.16–7.31 (m, 10 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.7, 14.0, 49.2, 57.7, 61.3, 61.5, 126.3, 127.0, 127.4, 127.9, 128.4, 128.6, 129.3, 131.6, 136.8, 140.3, 167.3, 167.8 ppm.

(*S*)-Dibenzyl 2-[(*E*)-1,3-Diphenylprop-2-en-1-yl]malonate (7ac): Compound **7ac** was prepared according to the procedure outlined for **7aa** by using **5a** (126 mg, 0.50 mmol) and **6c** (284 mg, 1.0 mmol). The desired product was obtained as a colorless oil (236 mg, 99% yield). The *ee* was determined by chiral HPLC. HPLC (Daicel Chiralcel IA column, *n*-hexane/2-propanol = 95:5, 1.0 mL/min, 254 nm): t_{minor} = 19.8 min, t_{major} = 23.0 min. $[\alpha]_D^{20} = -6.7$ ($c = 3.0$, CH_2Cl_2; 90%*ee*) {ref.[10] $[\alpha]_D^{25} = -7.1$; $c = 1.0$, $CHCl_3$; 95%*ee*}. ^1H NMR (300 MHz, $CDCl_3$): δ = 4.05 (d, J = 11.1 Hz, 1 H, CH), 4.30 (dd, J = 10.8, 8.1 Hz, 1 H, CH), 4.92 (ABq, J = 12 Hz, 2 H), 5.10 (ABq, J = 12 Hz, 2 H), 6.30 (dd, J = 15.9, 8.1 Hz, 1 H, =CH), 6.42 (d, J = 15.9 Hz, 1 H, =CH), 7.02–7.05 (m, 2 H, ArH), 7.20–7.28 (m, 18 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 49.2, 57.7, 67.1, 67.3, 126.4, 127.1, 127.5, 127.9, 128.0, 128.1, 128.2, 128.31, 128.35, 128.43, 128.7, 128.9, 131.8, 135.01, 135.05, 136.6, 140.0, 167.1, 167.5 ppm.

(*S*)-Dimethyl 2-[(*E*)-1,3-Bis(1-naphthyl)prop-2-en-1-yl]malonate (7ba): Compound **7ba** was prepared according to the procedure outlined for **7aa** by using **5b** (176 mg, 0.50 mmol) and **6a** (0.17 mL, 1.5 mmol). The desired product was obtained as a yellowish oil (240 mg, 99% yield). The *ee* was determined by chiral HPLC. HPLC (Daicel Chiralpak IA column, *n*-hexane/2-propanol = 80:20, 1.0 mL/min, 254 nm): t_{minor} = 9.2 min, t_{major} = 13.5 min. $[\alpha]_D^{20}$ = +41.2 (*c* = 1.5, CH_2Cl_2; 99%*ee*) {ref.[6i] $[\alpha]_D^{20}$ = +46.9; *c* = 0.6, CH_2Cl_2; 94%*ee*}. ^{1}H NMR (300 Hz, $CDCl_3$): δ = 3.40 (s, 3 H, CH_3), 3.71 (s, 3 H, CH_3), 4.33 (d, *J* = 10.5 Hz, 1 H, CH), 5.34 (t, *J* = 9.6 Hz, 1 H, CH), 6.42 (dd, *J* = 15.6, 8.7 Hz, 1 H, =CH), 7.27–7.58 (m, 9 H, ArH, =CH), 7.66 (d, *J* = 8.1 Hz, 1 H, ArH), 7.71–7.75 (m, 2 H, ArH), 7.82 (d, *J* = 8.1 Hz, 1 H, ArH), 7.95 (d, *J* = 7.5 Hz, 1 H, ArH), 8.40 (d, *J* = 8.7 Hz, 1 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 44.1, 52.4, 52.6, 57.2, 123.2, 123.6, 123.9, 124.2, 125.3, 125.4, 125.6, 125.9, 126.3, 127.77, 127.83, 128.3, 128.9, 129.8, 131.0, 131.3, 132.2, 133.3, 134.1, 134.5, 136.1, 167.7, 168.5 ppm.

(*S*)-Diethyl 2-[(*E*)-1,3-Bis(1-naphthyl)prop-2-en-1-yl]malonate (7bb): Compound **7bb** was prepared according to the formerly described procedure outlined for **7aa** by using **5b** (176 mg, 0.50 mmol) and **6b** (240 mg, 1.5 mmol). The desired product was obtained as a colorless oil (215 mg, 95% yield). The *ee* was determined by chiral HPLC. HPLC (Daicel Chiralcel IA column, *n*-hexane/2-propanol = 85:15, 0.8 mL/min, 254 nm): t_{minor} = 7.9 min, t_{major} = 10.4 min. $[\alpha]_D^{20}$ = +39.2 (*c* = 2.6, CH_2Cl_2; 90%*ee*) {ref.[6i] $[\alpha]_D^{20}$ = +33.6; *c* = 0.8, CH_2Cl_2; 94%*ee*}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.80 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.19 (t, *J* = 7.2 Hz, 3 H, CH_3), 3.85 (q, *J* = 7.2 Hz, 2 H, CH_2), 4.21 (qd, *J* = 7.2, 2.1 Hz, 2 H, CH_2), 4.29 (d, *J* = 10.8 Hz, 1 H, CH), 5.34 (t, *J* = 9.6 Hz, 1 H, CH), 6.45 (dd, *J* = 15.6, 8.4 Hz, 1 H, =CH), 7.29–7.59 (m, 9 H, ArH, =CH), 7.66 (d, *J* = 8.1 Hz, 1 H, ArH), 7.71–7.75 (m, 2 H, ArH), 7.82 (d, *J* = 8.1 Hz, 1 H, ArH), 7.96 (d, *J* = 7.5 Hz, 1 H, ArH), 8.42 (d, *J* = 8.7 Hz, 1 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.4, 14.0, 44.0, 57.6, 61.3, 61.6, 123.4, 123.6, 123.8, 124.4, 125.2, 125.4, 125.6, 125.9, 126.2, 127.6, 127.8, 128.3, 128.8, 129.5, 131.0, 131.4, 132.4, 133.4, 124.0, 134.5, 136.3, 167.3, 168.1 ppm.

(*S*)-Dibenzyl 2-[(*E*)-1,3-Bis(1-naphthyl)prop-2-en-1-yl]malonate (7bc): Compound **7bc** was prepared according to the procedure outlined for **7aa** by using **5b** (176 mg, 0.50 mmol) and **6c** (284 mg, 1.0 mmol). The desired product was obtained as a colorless oil (284 mg, 99% yield). The *ee* was determined by chiral HPLC. HPLC (Daicel Chiralcel IA column, *n*-hexane/2-propanol = 95:5, 1.0 mL/min, 254 nm): t_{minor} = 19.0 min, t_{major} = 28.3 min. $[\alpha]_D^{20}$ = +24.5 (*c* = 2.6, CH_2Cl_2; 91%*ee*). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.41 (d, *J* = 10.8 Hz, 1 H, CH), 4.83 (ABq, *J* = 12.3 Hz, 2 H, CH), 5.15 (s, 2 H, CH), 5.35 (t, *J* = 9.6 Hz, 1 H, CH), 6.40 (dd, *J* = 15.3, 8.4 Hz, 1 H, =CH), 6.89 (d, *J* = 6.6 Hz, 2 H, =CH), 7.09–7.23 (m, 8 H, ArH), 7.28–7.56 (m, 9 H, ArH), 7.68–7.79 (m, 3 H, ArH), 7.83–7.92 (m, 2 H, ArH), 8.35 (d, *J* = 8.4 Hz, 1 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 44.2, 57.5, 67.2, 67.4, 123.3, 123.7, 123.9, 124.4, 125.3, 125.4, 125.6, 125.7, 126.0, 126.3, 127.8, 127.9, 128.0, 128.25, 128.34, 128.4, 128.9, 129.8, 131.0, 131.4, 132.0, 133.4, 134.1, 134.4, 134.8, 135.0, 136.1, 167.1, 167.9 ppm. IR (neat): $\tilde{\nu}$ = 3061, 1754, 1735, 1597, 1510, 1456, 1376, 1264, 1218, 1152, 1003, 968, 908 cm^{-1}. HRMS (ESI): calcd. for $C_{40}H_{32}O_4Na$ $[M + Na]^+$ 599.21928; found 599.21904.

(*S*)-Dimethyl 2-[(*E*)-1,3-Bis(4-chlorophenyl)prop-2-en-1-yl]malonate (7ca): Compound **7ca** was prepared according to the procedure outlined for **7aa** by using **5c** (160 mg, 0.50 mmol) and **6a** (0.17 mL, 1.5 mmol). The desired product was obtained as a colorless oil (194 mg, 99% yield). The *ee* was determined by chiral HPLC. HPLC (Daicel Chiralcel IA column, *n*-hexane/2-propanol = 85:15, 1.0 mL/min, 254 nm): t_{minor} = 9.9 min, t_{major} = 13.6 min. $[\alpha]_D^{20}$ = +1.5 (*c* = 2.0, CH_2Cl_2; 86%*ee*) {ref.[10] $[\alpha]_D^{25}$ = –3.1; *c* = 1.0, $CHCl_3$; 97%*ee*}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.54 (s, 3 H, CH_3), 3.70 (s, 3 H, CH_3), 3.92 (d, *J* = 10.8 Hz, 1 H, CH), 4.25 (dd, *J* = 10.5, 8.4 Hz, 1 H, CH), 6.29 (dd, *J* = 15.9, 8.4 Hz, 1 H, =CH), 6.42 (d, *J* = 15.9 Hz, 1 H, =CH), 7.17–7.34 (m, 8 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 48.3, 52.4, 52.6, 57.2, 127.5, 128.5, 128.8, 129.08, 129.13, 130.9, 132.9, 133.2, 134.9, 138.4, 167.4, 167.8 ppm.

(*S*)-Dimethyl 2-[(*E*)-1,3-Bis(4-bromophenyl)prop-2-en-1-yl]malonate (7da): Compound **7da** was prepared according to the procedure outlined for **7aa** by using **5d** (205 mg, 0.50 mmol) and **6a** (0.17 mL, 1.5 mmol). The desired product was obtained as a colorless oil (202 mg, 84% yield). The *ee* was determined by chiral HPLC. HPLC (Daicel Chiralcel IA column, *n*-hexane/2-propanol = 85:15, 1.0 mL/min, 254 nm): t_{minor} = 11.6 min, t_{major} = 15.9 min. $[\alpha]_D^{20}$ = +7.2 (*c* = 3.5, CH_2Cl_2; 89%*ee*) {ref.[10] $[\alpha]_D^{25}$ = +3.1; *c* = 1.0, $CHCl_3$; 97%*ee*}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.55 (s, 3 H, CH_3), 3.70 (s, 3 H, CH_3), 3.91 (d, *J* = 10.8 Hz, 1 H, CH), 4.23 (dd, *J* = 10.8, 8.4 Hz, 1 H, CH), 6.29 (dd, *J* = 15.9, 8.1 Hz, 1 H, =CH), 6.40 (d, *J* = 15.6 Hz, 1 H, =CH), 7.17 (d, *J* = 6.9 Hz, 4 H, ArH), 7.39 (d, *J* = 8.4 Hz, 2 H, ArH), 7.45 (d, *J* = 8.4 Hz, 2 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 48.3, 52.5, 52.6, 57.1, 121.0, 121.4, 127.8, 129.1, 129.5, 131.0, 131.5, 131.8, 135.3, 138.9, 167.4, 167.8 ppm.

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra of new compounds and HPLC diagrams of the alkylation products.

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