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PAPER

New multifunctional chiral phosphines and BINOL derivatives co-catalyzed enantioselective aza-Morita–Baylis–Hillman reaction of 5,5-disubstituted cyclopent-2-enone and *N*-sulfonated imines†

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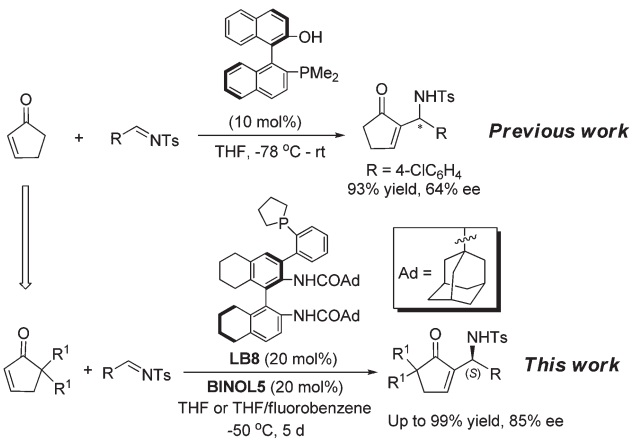
New multifunctional chiral phosphine (phosphine-amide type) **LB8** and BINOL derivative co-catalyzed asymmetric aza-MBH reaction of 5,5-disubstituted cyclopent-2-enones **1** with *N*-sulfonated imines **2** afforded the corresponding optically active adducts **3** in good to outstanding yields with moderate to good ee's under mild conditions. The steric hindrance environment of BINOL derivatives as well as the nucleophilicity of the phosphorus center and the acidity of free OH which could significantly affect the stereochemical and chemical outcomes had been discussed, indicating the co-catalyzed system is very important to this particular asymmetric aza-MBH reaction.

Introduction

Morita–Baylis–Hillman (MBH)/aza-MBH reaction, as one of the most important carbon–carbon or carbon–heteroatom bond formation and atom economic reactions, has been widely investigated during the past few decades.[1] Meanwhile, great progress in asymmetric MBH or aza-MBH processes in the presence of chiral organocatalysts has been made.[2] However, in contrast to traditional highly active α,β-unsaturated ketones such as MVK (methyl vinyl ketone) and EVK (ethyl vinyl ketone), the investigations of 2-cyclopenten-1-one were limited due to its low reactivity.[3] Recently, an aza-MBH reaction of 2-cyclopenten-1-one with *N*-sulfonated imines has attracted much attention and satisfied outcomes were obtained.[4] Nevertheless, a catalytic asymmetric aza-MBH reaction was still a challenge.[5] To the best of our knowledge, hydrogen-bonding plays an essential role in a wide range of organocatalytic reactions.[6] In particular, the utilization of chiral diols as promoters has been widely delivered.[3h,7] Recently, Sasai and co-workers have developed the novel bifunctional amine and phosphine diol catalysts which were applied in asymmetric aza-MBH reations.[8] Herein, on the basis of our previous work, we wish to report a new multifunctional chiral phosphine combined with BINOL derivative co-catalyzed asymmetric aza-MBH reaction using 5,5-disubstituted 2-cyclopenten-1-ones as the Michael acceptors which affords the corresponding aza-MBH adducts in high yields with good enantioselectivities (up to 85% ee) (Scheme 1).



Scheme 1

Results and discussion

Previously, we reported a chiral bifunctional phosphine catalyzed aza-MBH reaction of 2-cyclopenten-1-one and *N*-tosyl aldimines which gave the aza-MBH adducts in high yields, however, with low to moderate enantioselectivities (up to 62% ee value).[2p,5b] Recently, our group has developed a series of new chiral

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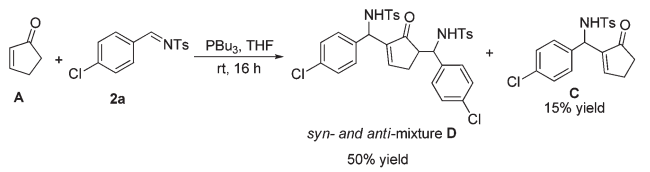
multifunctional phosphine catalysts **LB1–LB8**. This encouraged us to test their performance in the aza-MBH reaction of 2-cyclopenten-1-one and *N*-tosyl aldimines for improving the enantioselectivity. For this purpose, we initiated our screening using 2-cyclopenten-1-one **A** and *N*-(4-chlorobenzylidene)-4-methylbenzenesulfonamide **2a** as model substrates. The results are summarized in the ESI.† On preparing the racemic MBH adduct **C**, we found that the MBH–aldol reaction byproduct **D** was formed as a diastereomeric mixture, in which the structure of the major diastereomer was determined by X-ray analysis (Scheme 2).[9] Meanwhile, in order to explore the scope of the reaction, further experiments were conducted using different chiral Lewis bases (**LB1–LB9**) and additives (chiral binols) in THF or MTBE (*tert*-butyl methyl ether) (Fig. 1). The results are summarized in Table S1 in the ESI.† Unfortunately, we found that the reaction conducted at room temperature for 24 h in the presence of chiral phosphine catalyst **LB8** with BINOL derivative **BINOL1** with the optimized conditions, afforded adduct **C** in 80% yield, but with only 41% ee value (Table S1,† entry 10).



Scheme 2 aza-Morita–Baylis–Hillman reaction of 2-cyclopenten-1-one **A** (1.0 equiv) with *N*-(4-chlorobenzylidene)-4-methylbenzenesulfonamide **2a** (1.0 equiv) in the presence of PBu_3 (20 mol%).

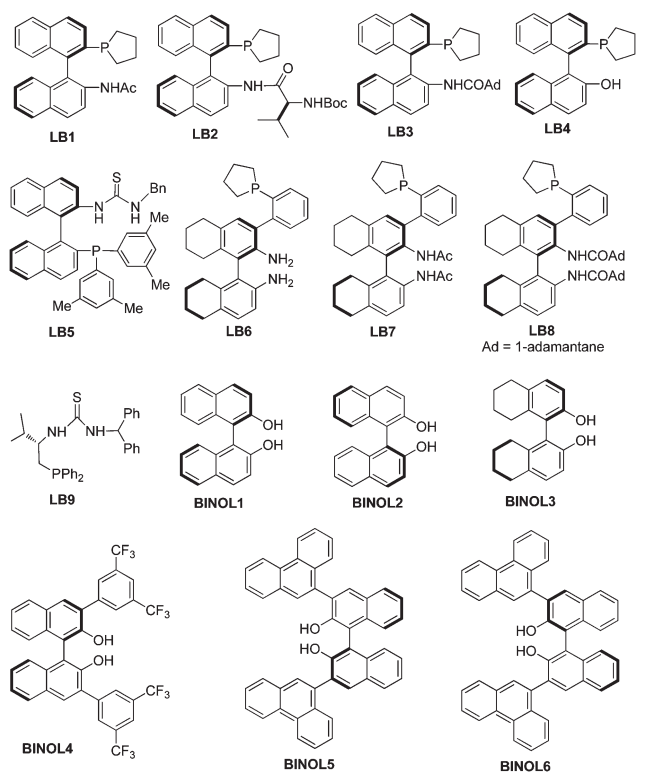


Fig. 1 Tested multifunctional chiral phosphines and BINOL derivatives for asymmetric aza-MBH reactions.

Based on the above results, we attempted to replace the 5,5-hydrogen atoms of 2-cyclopenten-1-one with phenyl groups as a new model substrate to investigate this reaction again. The results are summarized in Table 1. Firstly, we found that the corresponding aza-MBH adduct **3a** was produced in poor chemical yields and enantioselectivities in the presence of **LB4** or **LB7** without additives (Table 1, entries 1 and 3). Upon using catalyst **LB5**,[10] the reaction could not proceed. Only **LB8** gave better results, affording **3a** in 51% yield and 37% ee than those of **LB4** and **LB7**. Next, we attempted to apply the different additives combined with the chiral catalyst **LB8** to this reaction system. To our delight, moderate yields and ee values of **3a** were obtained (Table 1, entries 5–8). **BINOL1** (*R*-configuration) gave a slightly better ee value than that of **BINOL2** (*S*-configuration) under identical conditions (Table 1, entries 5 *vs.* 6). However, **BINOL3** and **BINOL4** gave better ee values and lower yields compared with those of **BINOL1** and **BINOL2** (Table 1, entries 7 and 8).

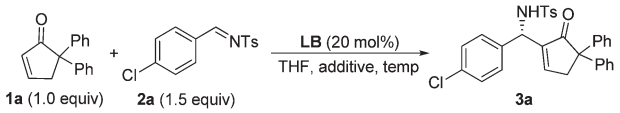
Then, we screened the effect of temperature in the presence of **BINOL4** and **LB8** and found that lower temperatures caused the reaction to proceed slowly with increasing ee values and diminishing yields of product **3a** (Table 1, entries 9, 11, 12). While at −30 °C, this co-catalytic system afforded **3a** in 70% yield and 80% ee (Table 1, entry 10).

Furthermore, we were pleased to find that enhancing the 3,3′-substituents' steric hindrance of the 1,10-binaphthyl framework of diol proved to be a valuable approach to increase the yields and enantioselectivities (Table 1, entries 13, 14). Meanwhile, if the temperature was reduced to −78 °C, the yield was only 46% and the ee retained (Table 1, entry 16). **BINOL5** (*R*-configuration) again gave a slightly better ee value and higher yield than that of **BINOL6** under identical conditions (Table 1, entries 14 *vs.* 15). The reaction catalyzed by **$PPhMe_2$** and **BINOL4** also went well, but the product was racemic (Table 1, entry 19). These investigations revealed that the chirality of the product was controlled by the chiral phosphine catalyst and the chiral BINOL derivative only played a role in activating the *N*-sulfonated imine and subsequently offered the steric environment. However, the additives had a positive influence on the yields (Table 1, entry 11 *vs.* 14).

Other than BINAP-derived multifunctional phosphine catalysts, we also tested chiral phosphine catalysts based on an amino acid skeleton **LB9**.[11] Regardless of addition of an additive, **LB9** could not catalyze the reaction, probably due to its lower nucleophilicity (Table 1, entries 17 and 18). Our investigations revealed that strong nucleophilicity of the phosphine Lewis base was essential in this reaction, otherwise the reaction could not proceed smoothly. In this interesting asymmetric aza-MBH reaction, the steric hindrance environment of the BINOL derivative as well as the nucleophilicity of the phosphorus center and the acidity of free OH could significantly affect the stereochemical and chemical outcomes. The best results were found to be to carry out the reaction for 5 days in the presence of chiral phosphine catalyst **LB8** with BINOL derivative **BINOL5** and 4 Å MS at −50 °C, furnishing **3a** in 92% yield and 81% ee.

In order to improve the results, we then embarked on further optimization of the reaction conditions. The solvent effects were investigated, using substrates **1a** and **2a** and **LB8** and **BINOL5** as the catalytic system. The results are summarized in Table 2

Table 1 Multifunctional chiral phosphines and BINOL derivatives co-catalyzed aza-MBH reaction: 5,5-diphenylcyclopent-2-enone **1a** with *N*-(4-chlorobenzylidene)-4-methylbenzenesulfonamide **2a** in THF

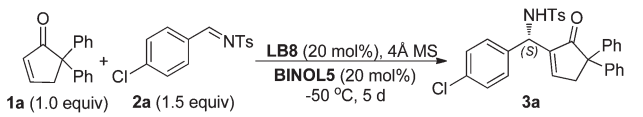


1a (1.0 equiv) **2a** (1.5 equiv) **3a**

Entry	Catalyst	Additive	Temperature (°C)	Time	Yield[a] (%)	ee[b] (%)
1	**LB4**	—	rt	1 d	19	15
2	**LB5**	—	rt	1 d	—	—
3	**LB7**	—	rt	1 d	41	28
4	**LB8**	—	rt	1 d	51	37
5	**LB8**	**BINOL1**	rt	1 d	77	61
6	**LB8**	**BINOL2**	rt	1 d	83	56
7	**LB8**	**BINOL3**	rt	1 d	60	65
8	**LB8**	**BINOL4**	rt	1 d	58	64
9[c]	**LB8**	**BINOL4**	−10	2 d	56	75
10[c]	**LB8**	**BINOL4**	−30	2 d	70	80
11[c]	**LB8**	**BINOL4**	−50	5 d	53	80
12[c]	**LB8**	**BINOL4**	−78	5 d	31	73
13[c]	**LB8**	**BINOL5**	−30	2 d	85	81
14[c]	**LB8**	**BINOL5**	−50	5 d	92	81
15[c]	**LB8**	**BINOL6**	−50	5 d	81	75
16[c]	**LB8**	**BINOL5**	−78	5 d	46	75
17[c]	**LB9**	—	−30	2 d	NR	—
18[c]	**LB9**	**BINOL4**	−30	2 d	NR	—
19[c]	$PhPMe_2$	**BINOL4**	−30	2 d	77	Race

[a] Isolated yield. [b] Determined by chiral HPLC. [c] 4 Å MS was used.

Table 2 Screening of solvent effects on the aza-MBH reaction of **1a** with **2a** in the presence of **LB8**



1a (1.0 equiv) **2a** (1.5 equiv) **3a**

Entry	Solvent	Yield[a] (%)	ee[b] (%)
1	DCM	92	50
2	Toluene	85	82
3	$CHCl_3$	81	43
4	Et_2O	—	—
5	DMF	54	51
6	THF	92	81
7[c]	Fluorobenzene	92	64
8	Toluene–THF = 1 : 1	58	62
9	Fluorobenzene–THF = 1 : 1	90	82
10	$CHCl_3$–THF = 1 : 1	81	62
11	Fluorobenzene–THF = 1 : 4	92	78
12[d]	THF	69	70

[a] Isolated yield. [b] Determined by chiral HPLC. Unless otherwise specified, **1a** (0.05 mmol), **2a** (0.075 mmol), **LB8** (0.01 mmol), **BINOL5** (0.01 mmol) and 50 mg 4 Å MS were used. [c] The reaction was conducted at −40 °C. [d] The catalyst and additive loadings were reduced by half (10 mol%).

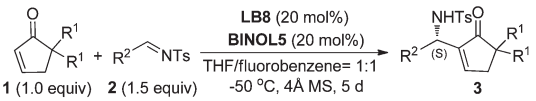
and Table S2,† respectively. We found that THF or THF–fluorobenzene was the solvent of choice (Table 2, entries 6, 9), while other solvents such as DCM, $CHCl_3$, Et_2O, DMF and fluorobenzene gave low enantioselectivities or yields (Table 2, entries 1, 3, 4, 5, 7; Table S2,† entries 8–13). The reaction in toluene went well and offered the product in 85% yield and 82% ee (Table 2, entry 2). Next, we switched from single solvents to mixed solvents. THF–fluorobenzene (1 : 1), out of all kinds of mixed solvents, afforded the best results (Table 2, entries 8–10; Table S2,† entries 19–25). When the catalyst and additive loadings were reduced to 10 mol% respectively, we found the yield and ee value of **3a** decreased remarkably (Table 2, entry 12).

Under these optimized conditions, we next examined the generality of this reaction using 5,5-disubstituted cyclopent-2-enone **1a**, **1b** (R^1 = 4-FC_6H_4), **1c** (R^1 = 4-$CF_3C_6H_4$) and *N*-sulfonated imines **2**. The results are presented in Table 3. The corresponding products **3** were obtained in high yields and good ee's, regardless of the electron-donating or the electron-withdrawing group in *meta* or *para* position of R^2 (Table 3, entries 1, 2, 4, 6–9) in spite of the poor reaction outcomes if R^2 were 2-furyl and 2-naphthyl groups (Table 3, entries 5, 10). Moreover, if R^2 was 2-thienyl, it worked well to furnish the corresponding adduct **3d** in 94% yield and 76% ee (Table 3, entry 3). Outstanding ee's (73%–85%) and yields (88%–99%) were also attained for **1b** and **1c** with **2** when substituents were in *para* position of R^2 (Table 3, entries 11–15).

The constitutions and absolute configurations of **3** have been determined as *S*-configurations by X-ray diffraction of **3c** bearing a bromine atom on the *meta* position of the benzene ring.[12] The CIF data for **3c** are presented in the ESI.†[9]

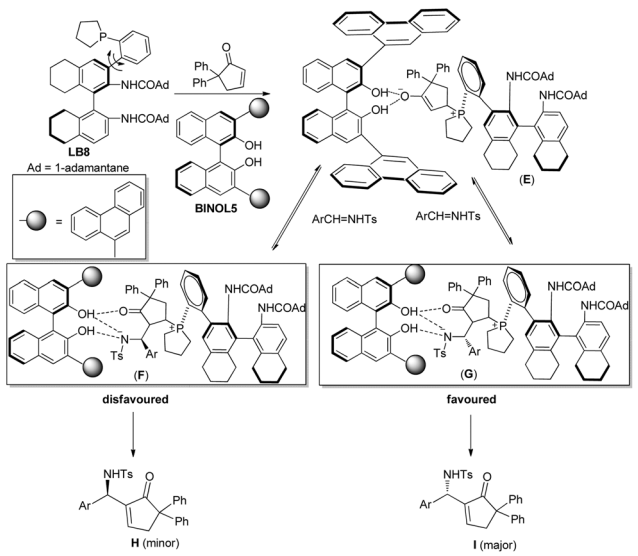
A plausible mechanism for this asymmetric aza-MBH reaction is outlined in Scheme 3. First, 5,5-disubstituted cyclopent-2-enone reacts with **LB8** to form a phosphonium enolate **E**,[2g,13] which is stabilized by intermolecular hydrogen bonding with **BINOL5**. In addition, the intermolecular hydrogen bonding between the chiral binolic OH and the nitrogen anion stabilized by sulfonyl group and oxygen atom of carbonyl group can

Table 3 Multifunctional chiral phosphine **LB8**-catalyzed aza-MBH reaction: 5,5-disubstituted cyclopent-2-enones **1** with *N*-sulfonated imines **2**



Entry	R^1	R^2	Yield[a] (%)	ee[b] (%)	Absolute configuration
1	Ph (**1a**)	4-$NO_2C_6H_4$	99 (**3b**)	85	*S*
2	Ph (**1a**)	3-BrC_6H_4	96 (**3c**)	79 (88)[d]	*S*
3	Ph (**1a**)	2-Thienyl	94 (**3d**)	76	*S*
4	Ph (**1a**)	3-$MeOC_6H_4$	90 (**3e**)	75	*S*
5	Ph (**1a**)	2-Furyl	61 (**3f**)	68	*S*
6	Ph (**1a**)	4-BrC_6H_4	96 (**3g**)	84	*S*
7	Ph (**1a**)	4-$CF_3C_6H_4$	99 (**3h**)	80	*S*
8	Ph (**1a**)	4-$CF_3C_6H_4$	84 (**3i**)	84	*S*
9	Ph (**1a**)	3-$NO_2C_6H_4$	99 (**3j**)	82	*S*
10	Ph (**1a**)	2-Naphthyl	44 (**3k**)	60	*S*
11	4-FC_6H_4 (**1b**)	4-$NO_2C_6H_4$	99 (**3l**)	82	*S*
12[c]	4-FC_6H_4 (**1b**)	4-$CH_3C_6H_4$	91 (**3m**)	84	*S*
13[c]	4-FC_6H_4 (**1b**)	4-ClC_6H_4	89 (**3n**)	75	*S*
14[c]	4-$CF_3C_6H_4$ (**1c**)	4-$NO_2C_6H_4$	99 (**3o**)	73	*S*
15[c]	4-$CF_3C_6H_4$ (**1c**)	4-$CH_3C_6H_4$	88 (**3p**)	85	*S*

[a] Isolated yields. [b] Determined by chiral HPLC. [c] The reaction was carried out in THF. [d] The ee of **3c** after recrystallization.



Scheme 3 A plausible reaction mechanism.

produce relatively stable intermediates **F** and **G**. While, intermediate **F** is less stable than **G** due to that the steric repulsions between Ar in *N*-sulfonated imine and phenyl in phosphonium enolate **E**. Meanwhile, the fact that the yield of **3k** is low when Ar is 2-naphthyl can also prove the effect of large sterically hindered substituents. Therefore, the favoured intermediate **G** undergoes β-elimination to give the target product **I** with (***S***)-enriched configuration instead of **H**.

In conclusion, we have established a new multifunctional chiral strong nucleophilic phosphine (phosphine-amides) **LB8** combined with BINOL derivative **BINOL5** co-catalyzed aza-MBH reaction of 5,5-disubstituted cyclopent-2-enone **1** with *N*-sulfonated imines **2** to provide easy access to optically active adducts **3** under mild conditions. Good to excellent yields and ee's have been achieved. Multifunctional phosphines and large sterically hindered chiral binols are required to get good results. Further efforts are in progress regarding the reaction scope and mechanistic details.

Experimental section

General remarks

^{1}H NMR spectra were recorded on a Bruker AM-300 or AM-400 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as internal standard; *J*-values are in Hz. Mass spectra were recorded with a HP-5989 instrument. All of the compounds reported in this paper gave satisfactory HRMS analytic data. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. Optical rotations were determined at 589 nm (sodium D line) by using a Perkin-Elmer-341 MC digital polarimeter; $[\alpha]_D$-values are given in unit of 10 deg^{-1} cm^2 g^{-1}. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Chiral HPLC was performed on a SHIMADZU SPD-10A vp series with chiral columns (Chiralpak AD-H, IC-H columns 4.6 × 250 mm, (Daicel Chemical Ind., Ltd.)). THF, toluene and Et_2O were distilled from sodium (Na) under argon (Ar) atmosphere. CH_3CN, 1,2-dichloroethane and dichloromethane were distilled from CaH_2 under an argon (Ar) atmosphere. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF254 silica gel coated plates. Flash column chromatography was carried out using 300–400 mesh silica gel at increased pressure.

Reaction procedure for the preparation of catalysts

Reaction procedures for the preparation of **LB1–LB4**, **LB6**, **LB7**, and **LB8** have been summarized in the ESI† and the spectroscopic data are shown below.

Amine precursor of **LB1**: (*R*)-2′-(phospholan-1-yl)-1,1′-binaphthyl-2-amine

(*R*)-2′-(Phospholan-1-yl)-1,1′-binaphthyl-2-amine. Procedure: This compound was prepared according to the previous literature.[10] A white solid. m.p. 178–180 °C; $[\alpha]_D^{20} = -92.9$ (*c* 0.6, CH_2Cl_2). IR (CH_2Cl_2) *ν* 3378, 3050, 2927, 2855, 1618, 1511, 1471, 1431, 1379, 1351, 1262, 1211, 1144, 1094, 1022, 963, 933, 810, 773, 734 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): *δ* 7.92 (1H, d, *J* = 8.4 Hz), 7.89 (1H, d, *J* = 8.0 Hz), 7.82 (1H, d, *J* = 8.8 Hz), 7.77 (1H, d, *J* = 8.0 Hz), 7.67 (1H, d, *J* = 8.4 Hz), 7.45 (1H, qu, *J* = 8.4 Hz), 7.25 (1H, s), 7.24 (1H, s), 7.22–7.18 (1H, m), 7.16–7.14 (1H, m), 7.11 (1H, d, *J* = 9.2 Hz), 6.82 (1H, d, *J* = 8.4 Hz), 3.56 (2H, brs), 2.17–2.11 (1H, m), 1.87–1.29 (7H, m); ^{31}P NMR (162 MHz, $CDCl_3$, 85% H_3PO_4): *δ* −22.0; MS (ESI) *m/z* (%) 356.1 [M^+ + H]; HRMS (ESI) Calcd for $C_{24}H_{23}NP^{+1}$ [M^+ + H] requires 356.1490, Found 356.1488.

LB1: (*R*)-*N*-(2′-(phospholan-1-yl)-1,1′-binaphthyl-2-yl)acetamide. Procedure: This compound was prepared according to the previous literature.[10] A white solid. m.p. 102–104 °C; $[\alpha]_D^{20} = -81.0$ (*c* 0.3, CH_2Cl_2). IR (CH_2Cl_2) *ν* 3411, 3064, 2959, 2925, 2857, 1693, 1596, 1496, 1424, 1263, 1096, 1016, 867, 798, 733 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): *δ* 8.57 (1H, d, *J* = 9.2 Hz), 8.01 (2H, t, *J* = 9.2 Hz), 7.91 (2H, t, *J* = 8.8 Hz), 7.70 (1H, d, *J* = 8.8 Hz), 7.49 (1H, t, *J* = 8.0 Hz), 7.39 (1H, t, *J* = 7.8 Hz), 7.26 (1H, t, *J* = 7.8 Hz), 7.21 (1H, t, *J* = 7.8 Hz), 7.10 (1H, d, *J* = 7.2 Hz), 6.88 (1H, d, *J* = 8.4 Hz), 6.82 (1H, s), 2.06–2.02 (1H, m), 1.86–1.68 (4H, m), 1.82 (3H, s), 1.57–1.50 (2H, m), 1.30–1.23 (1H, m); ^{31}P NMR (162 MHz, $CDCl_3$, 85% H_3PO_4): *δ* −21.7; MS (ESI) *m/z* (%) 398.2 [M^+ + H]; HRMS (ESI) Calcd for $C_{26}H_{25}NOP^{+1}$ [M^+ + H] requires 398.1596, Found 398.1595.

LB2: *tert*-Butyl (*R*)-3-methyl-1-oxo-1-((*R*)-2′-(phospholan-1-yl)-1,1′-binaphthyl-2-ylamino)butan-2-ylcarbamate. Procedure: This compound was prepared according to the previous literature.[14] A white solid. m.p. 98–100 °C; $[\alpha]_D^{20} = +12$ (*c* 0.3, CH_2Cl_2). IR (CH_2Cl_2) *ν* 3402, 3369, 3054, 2960, 2931, 2871, 1691, 1500, 1427, 1366, 1331, 1264, 1168, 1019, 895, 736 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): *δ* (rotamer: major/minor = 5/1) 8.50 (1H, d, *J* = 8.8 Hz), 8.03 (1H, d, *J* = 9.2 Hz), 7.98 (1H, d, *J* = 8.4 Hz), 7.90 (2H, t, *J* = 7.2 Hz), 7.69 (1H, dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz), 7.49–7.39 (2H, m), 7.27–7.19 (3H, m), 7.05 (1H, d, *J* = 8.4 Hz), 6.98 (1H, d, *J* = 8.4 Hz), 4.88 (0.68H, d, *J* = 8.4 Hz), 4.34 (0.14H, d, *J* = 8.4 Hz), 3.83–3.77 (0.15H, m), 3.73–3.70 (0.74H, m), 2.16–2.09 (1H, m), 1.89–1.42 (7H, m), 1.35–1.13 (10H, m), 0.46 (3H, d, *J* = 7.8 Hz), 0.40 (3H, d, *J* = 7.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$, 85% H_3PO_4): *δ* −22.2, −22.6; MS (ESI) *m/z* (%) 555.3 [M^+ + H]; HRMS (ESI) Calcd for $C_{34}H_{40}N_2O_3P^{+1}$ [M^+ + H] requires 555.2689, Found 555.2701.

LB3: (*R*)-*N*-(2′-(Phospholan-1-yl)-1,1′-binaphthyl-2-yl)adamantanecarboxamide. Procedure: This compound was prepared according to the previous literature.[15] A white solid. m.p. 187–190 °C; $[\alpha]_D^{20} = -147.9$ (*c* 0.5, CH_2Cl_2). IR (CH_2Cl_2) *ν* 3417, 3055, 2924, 2851, 1727, 1683, 1620, 1594, 1499, 1453, 1426, 1376, 1332, 1263, 1219, 1103, 937, 814, 736 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): *δ* 8.63 (1H, d, *J* = 8.8 Hz), 8.01 (2H, t, *J* = 8.8 Hz), 7.91 (2H, t, *J* = 8.8 Hz), 7.71 (1H, dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz), 7.48 (1H, t, *J* = 7.2 Hz), 7.39 (1H, t, *J* = 7.2 Hz), 7.26–7.25 (1H, m), 7.10 (2H, t, *J* = 10.0 Hz), 7.03 (1H, s), 1.97–1.90 (1H, m), 1.83–1.69 (7H, m), 1.82 (3H, s), 1.62–1.54 (6H, m), 1.41–1.30 (10H, m); ^{31}P NMR (162 MHz, $CDCl_3$, 85% H_3PO_4): *δ* −22.0; MS (ESI) *m/z* (%) 518.3 [M^+ + H]; HRMS (ESI) Calcd for $C_{35}H_{37}NOP^{+1}$ [M^+ + H] requires 518.2535, Found 518.2537.

LB4: (*R*)-2′-(Phospholan-1-yl)-1,1′-binaphthyl-2-ol. Procedure: This compound was prepared according to the previous literature.[2p,15] A white solid. m.p. 188–200 °C; $[\alpha]_D^{20} = -120.6$ (*c* 1.0, $CHCl_3$). IR (KBr): *ν* 3506, 3425, 3054, 2933, 2856, 1619, 1594, 1514, 1501, 1345, 1265, 1203, 1143, 866, 812, 735, 683 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): *δ* 7.98 (1H, d, *J* = 8.8 Hz), 7.95 (1H, d, *J* = 8.8 Hz), 7.92 (1H, d, *J* = 8.0 Hz), 7.87 (1H, d, *J* = 8.0 Hz), 7.70 (1H, dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz), 7.48 (1H, dt, J_1 = 8.0 Hz, J_2 = 1.2 Hz), 7.36 (1H, d, *J* = 8.8 Hz), 7.34–7.26 (2H, m), 7.25–7.20 (2H, m), 6.92 (1H, d, *J* = 8.4 Hz), 4.84 (1H, s, OH), 2.10–2.01 (1H, m), 1.89–1.64 (5H, m), 1.44–1.25 (2H, m); ^{31}P NMR ($CDCl_3$, 121.5 MHz, 85% H_3PO_4): *δ* −21.69, −21.71; MS (EI) *m/z* (%): 356 (34.94) [M^+], 355 (18.83), 340 (27.25), 399 (100), 281 (14.69), 268 (29.67), 252 (17.67), 239 (20.96); HRMS (EI) Calcd For $C_{24}H_{21}PO^{+1}$ (M^+) requires 356.1330, Found: 356.1324.

LB6: (*R*)-3-(2-(Phospholan-1-yl)phenyl)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2,2′-diamine. Procedure: Compound **VI** (2.52 g, 4.5 mmol) was dissolved in 85 mL of EtOH, and then 85 mL 50% potassium hydroxide aqueous solution was added into the mixture. The resulting solution was heated to 120 °C overnight and the reaction was quenched by addition of saturated 10% HCl solution, washed with water, extracted by CH_2Cl_2 twice, dried by anhydrous Na_2SO_4. The solution was concentrated for the next step without further purification (quantitative yield). Triphenylphosphine (5.98 g, 22.8 mmol) in toluene (50 mL) was added into this product mixture (2.12 g, 4.57 mmol) and then trichlorosilane (2.31 mL, 22.8 mmol) was added. The resulting mixture was heated at 110 °C for three days. After being cooled to room temperature, the product mixture was diluted with dichloromethane, quenched with a small amount of saturated $NaHCO_3$ solution. The resulting suspension was filtered through Celite, and washed with dichloromethane. The combined extracts were dried over anhydrous Na_2SO_4, and the residue was chromatographed on silica gel (PE–EA = 8 : 1 as eluent) to provide compound **LB6** as white solid (1.56 g, 75% yield). m.p. 171–172 °C; $[\alpha]_D^{20} = +76$ (*c* 0.5, CH_2Cl_2). IR (CH_2Cl_2) *ν* 3458, 3363, 2926, 2854, 2833, 1606, 1482, 1447, 1422, 1353, 1302, 1286, 1262, 1219, 1106, 1028, 943, 872, 811, 767, 743 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): *δ* 7.45–7.41 (1H, m), 7.33–7.25 (3H, m), 6.91 (1H, d, *J* = 8.4 Hz), 6.87 (1H, d, *J* = 12.0 Hz), 6.62 (1H, dd, J_1 = 8.0 Hz, J_2 = 3.6 Hz), 3.25 (4H, brs), 2.77–2.71 (4H, m), 2.40–2.23 (4H, m), 1.96–1.60 (16H, m); ^{31}P NMR (162 MHz, $CDCl_3$, 85% H_3PO_4): *δ* −19.9, −21.1; MS (ESI) *m/z* (%) 455.3 [M^+ + H]; HRMS (ESI) Calcd for $C_{30}H_{36}N_2P^{+1}$ [M^+ + H] requires 455.2604, Found 455.2611.

LB7: (*R*)-*N*,*N*′-(3-(2-(Phospholan-1-yl)phenyl)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2,2′-diyl)diacetamide. Procedure: This compound was prepared according to the previous literature.[16]

A white solid (70% yield). m.p. 144–146 °C; $[\alpha]_D^{20}$ = −236.5 (*c* 1.0, CH_2Cl_2). IR (CH_2Cl_2) *ν* 3287, 3256, 2929, 2856, 1688, 1665, 1592, 1524, 1434, 1401, 1366, 1292, 1263, 1092, 1060, 1015, 799 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): *δ* 8.30 (0.5H, s), 7.56–7.27 (5.5H, m), 7.09–7.04 (2H, m), 2.86–2.76 (4H, m), 2.31–2.25 (2H, m), 2.05–1.94 (5H, m), 1.86–1.41 (15H, m), 1.32–1.27 (4H, m); ^{31}P NMR (162 MHz, $CDCl_3$, 85% H_3PO_4): *δ* −16.0; MS (ESI) *m/z* (%) 539.3 [M^+ + H]; HRMS (ESI) Calcd for $C_{34}H_{40}N_2O_2P^{+1}$ [M^+ + H] requires 539.2812, Found 539.2822.

LB8: (*R*)-*N*,*N*′-(3-(2-(Phospholan-1-yl)phenyl)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2,2′-diyl)diadamantanecarboxamide. Procedure: This compound was prepared according to the previous literature.[17] To a solution of resolved **LB6** (454 mg, 1.0 mmol) and pyridine (320 mg, 4.0 mmol) in toluene (10 mL) was added 1-adamantanecarboxylic acid chloride (794 mg, 4.0 mmol) in one portion. The reaction mixture was stirred at 90 °C for 12 h. The reaction mixture was cooled to room temperature and the toluene was removed under high vacuum. The remaining residue was chromatographed on silica gel (PE–EA = 8 : 1 as eluent) to provide compound **LB8** as white solid (355 mg, 45% yield). m.p. >320 °C; $[\alpha]_D^{20}$ = −193.6 (*c* 0.5, CH_2Cl_2). IR (CH_2Cl_2) *ν* 3312, 2905, 2850, 1725, 1700, 1661, 1590, 1486, 1452, 1344, 1264, 1180, 1102, 1079, 975, 802, 764, 739 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): *δ* 8.06 (1H, s), 7.38 (1H, d, *J* = 8.4 Hz), 7.34–7.25 (4H, m), 7.18–7.15 (1H, m), 7.04 (1H, d, *J* = 8.4Hz), 7.01 (1H, s), 2.82–2.77 (4H, m), 2.37–2.18 (5H, m), 1.98 (3H, s), 1.87–1.41 (36H, m), 1.57 (6H, s); ^{31}P NMR (162 MHz, $CDCl_3$, 85% H_3PO_4): *δ* −15.9, −23.9; MS (ESI) *m/z* (%) 779.7 [M^+ + H]; HRMS (ESI) Calcd for $C_{52}H_{64}N_2O_2P^{+1}$ [M^+ + H] requires 779.4695, Found 779.4699.

Typical procedure for the preparation of Boc-protected Morita–Baylis–Hillman adducts

The reaction procedure for the preparation of 5,5-disubstituted cyclopent-2-enones has been summarized in the ESI† and their spectroscopic data are shown below.

Compound 1a: 5,5-Diphenylcyclopent-2-enone. Procedure: This is a known compound. A white solid. ^1H NMR (400 MHz, $CDCl_3$, TMS): *δ* 7.86–7.83 (1H, m), 7.32–7.20 (10H, m), 6.29–6.26 (1H, m), 3.51 (2H, t, *J* = 2.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 208.8, 162.3, 143.1, 132.7, 128.4, 127.9, 126.7, 59.9, 47.8.

Compound 1b: 5,5-Bis(4-fluorophenyl)cyclopent-2-enone. Procedure: This compound was prepared according to the previous literature.[18] A yellow solid. m.p. 64–66 °C; IR (CH_2Cl_2) *ν* 3074, 2919, 1702, 1597, 1505, 1436, 1407, 1342, 1229, 1162, 1108, 1015, 951, 830, 738 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): *δ* 7.86–7.83 (1H, m), 7.26–7.14 (4H, m), 7.01–6.96 (4H, m), 6.28–6.26 (1H, m), 3.46 (2H, t, *J* = 2.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 208.4, 162.3, 160.5 (d, J_{C-F} = 244.6 Hz), 138.7 (d, J_{C-F} = 2.6 Hz), 132.5, 129.4 (d, J_{C-F} = 7.8 Hz), 115.2 (d, J_{C-F} = 21.2 Hz), 58.5, 47.6; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): *δ* −115.8; (EI) *m/z* (%) 270 (100) [M^+], 241 (33.37), 227 (18.15), 201 (43.45), 175 (20.67), 146 (31.31), 133 (13.27), 120 (17.11), 109 (64.97); HRMS (EI) Calcd for $C_{17}H_{12}OF_2$ [M^+] requires 270.0856, Found 270.0860.

Compound 1c: 5,5-Bis(4-(trifluoromethyl)phenyl)cyclopent-2-enone. Procedure: This compound was prepared according to the previous literature.[19,20] A mixture of **5** and **5′** (400 mg, 0.8 mmol) was dissolved in 15 mL toluene and potassium carbonate (336 mg, 2.4 mmol) was added. The resulting solution was heated to reflux for three hours. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (EtOAc–PE = 1 : 4 as eluent) to furnish product **1c** as white solid (150 mg, 51% yield). m.p. 97–99 °C; IR (CH_2Cl_2) *ν* 2926, 1707, 1616, 1595, 1410, 1320, 1261, 1163, 1112, 1017, 958, 936, 831, 802, 766 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): *δ* 7.93–7.90 (1H, m), 7.58 (4H, d, *J* = 8.4 Hz), 7.32 (4H, d, *J* = 8.4 Hz), 6.33–6.31 (1H, m), 3.53 (2H, d, *J* = 2.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 207.0, 162.4 (d, J_{C-F} = 1.5 Hz), 146.3 (d, J_{C-F} = 1.1 Hz), 132.7, 129.4 (q, J_{C-F} = 32.4 Hz), 128.3, 125.6 (q, J_{C-F} = 3.7 Hz), 123.9 (q, J_{C-F} = 270.3 Hz), 59.6, 46.9; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): *δ* −62.7; (EI) *m/z* (%) 370 (100.00) [M^+], 351 (17.56), 301 (33.68), 273 (40.35), 225 (40.90), 202 (14.32), 183 (11.08), 177 (16.41), 159 (34.82); HRMS (EI) Calcd for $C_{19}H_{12}OF_6$ [M^+] requires 370.0792, Found 370.0786.

General procedure for the preparation of 3 from the reaction of 1a with 2a using 3a as an example in the presence of LB8

To a mixture of **1a** (0.075 mmol, 18 mg), **2a** (0.1125 mmol, 33 mg), catalyst **LB8** (10 mg, 0.015 mmol), **BINOL5** (12 mg, 0.015 mmol) and 50 mg 4 Å MS was added 1.0 mL of THF–fluorobenzene (1 : 1) at −50 °C under argon. The reaction solution was stirred for about 5 days and monitored by TLC. After the reaction completed, the solution was concentrated under reduced pressure and the residue was further purified by silica gel column chromatography (EtOAc–PE = 1 : 4) to give the target product **3a**.

(*S*)-*N*-((4-Chlorophenyl)(5-oxo-4,4-diphenylcyclopent-1-enyl)-methyl)-4-methylbenzenesulfonamide 3a. Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3a** (36 mg, 90% yield). A white solid. m.p. for racemic **3a** = 206–208 °C; m.p. for **3a** = 169–170 °C; $[\alpha]_D^{20}$ = +18.0 (*c* 0.3, CH_2Cl_2). IR (CH_2Cl_2): *ν* 3277, 3057, 2923, 2585, 1694, 1634, 1596, 1490, 1328, 1157, 1088, 1034, 1013, 919, 883, 812, 756, 734 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): *δ* 7.58 (2H, d, *J* = 8.0 Hz), 7.47 (1H, s), 7.26–7.21 (6H, m), 7.11–6.99 (10H, m), 6.05 (1H, d, *J* = 8.4 Hz), 5.32 (1H, d, *J* = 8.4 Hz), 3.32 (1H, d, *J* = 19.2 Hz), 3.14 (1H, d, *J* = 19.2 Hz), 2.31 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 206.9, 158.0, 143.4, 142.3, 142.2, 141.4, 137.2, 136.8, 133.7, 129.6, 128.6, 128.5, 128.4, 128.1, 127.8, 127.6, 127.1, 127.0, 126.9, 61.0, 54.5, 45.4, 21.4; MS (ESI) *m/e* 550.0 (M^+ + Na); HRMS (ESI) for $C_{31}H_{26}ClNO_3SNa^{+1}$ (M^+ + Na): 550.1223, Found: 550.1214. The ee of the **3a** was determined to be 82% [determined by HPLC, Chiralpak AD-H, *n*-hexane–isopropanol = 70 : 30, 0.5 mL min^{-1}, *λ* = 214 nm, *t* (major) = 25.55 min, *t* (minor) = 34.47 min].

(*S*)-4-Methyl-*N*-((4-nitrophenyl)(5-oxo-4,4-diphenylcyclopent-1-enyl)methyl)benzenesulfonamide 3b. Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3b** (40 mg, 99% yield).

A white solid. m.p. for racemic **3b** = 160–162 °C; m.p. for **3b** = 145–148 °C; $[\alpha]_D^{20}$ = +13.6 (*c* 0.6, CH_2Cl_2). IR (CH_2Cl_2): *v* 3279, 3058, 2923, 2583, 1697, 1634, 1597, 1492, 1444, 1345, 1159, 1089, 1034, 1015, 927, 883, 814, 757, 734 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.98 (2H, d, *J* = 8.4 Hz), 7.60 (2H, d, *J* = 8.0 Hz), 7.52 (1H, s), 7.30–7.20 (8H, m), 7.08 (2H, d, *J* = 8.0 Hz), 7.01–6.97 (4H, m), 6.25 (1H, d, *J* = 9.2 Hz), 5.46 (1H, d, *J* = 8.8 Hz), 3.35 (1H, d, *J* = 18.0 Hz), 3.14 (1H, d, *J* = 17.2 Hz), 2.30 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 206.7, 158.6, 147.3, 145.4, 143.8, 142.0, 141.8, 140.5, 137.0, 129.7, 128.6, 128.5, 127.7, 127.6, 127.5, 127.2, 127.1, 123.6, 60.9, 54.3, 45.5, 21.4; MS (ESI) *m/e* 561.0 (M^+ + Na); HRMS (ESI) for $C_{31}H_{26}N_2O_5SNa^{+1}$ (M^+ + Na): 561.1460, Found: 561.1454. The ee of the **3b** was determined to be 85% [determined by HPLC, Chiralpak AD-H, *n*-hexane–isopropanol = 70 : 30, 0.5 mL min^{-1}, λ = 214 nm, *t* (major) = 51.21 min, *t* (minor) = 56.76 min].

(*S*)-*N*-((3-Bromophenyl)(5-oxo-4,4-diphenylcyclopent-1-enyl)-methyl)-4-methylbenzenesulfonamide 3c. Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3c** (41 mg, 96% yield). A white solid. m.p. for racemic **3c** = 146–148 °C; m.p. for **3c** = 150–152 °C; $[\alpha]_D^{20}$ = +22.0 (*c* 0.3, CH_2Cl_2). IR (CH_2Cl_2): *v* 3273, 3058, 2961, 2923, 2846, 1698, 1634, 1595, 1492, 1473, 1443, 1330, 1259, 1158, 1090, 1018, 931, 797, 759 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.58 (2H, d, *J* = 6.8 Hz), 7.49 (1H, s), 7.29–7.20 (7H, m), 7.15 (1H, s), 7.08–7.02 (8H, m), 6.06 (1H, d, *J* = 8.8 Hz), 5.33 (1H, d, *J* = 8.4 Hz), 3.35–3.31 (1H, m), 3.16 (1H, dd, J_1 = 19.6 Hz, J_2 = 2.0 Hz), 2.30 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 206.8, 158.2, 143.5, 142.3, 142.2, 141.1, 140.4, 137.1, 130.9, 130.1, 129.7, 129.6, 128.53, 128.50, 127.8, 127.5, 127.1, 127.0, 126.9, 125.4, 122.6, 60.9, 54.4, 45.5, 21.4; MS (ESI) *m/e* 594.0 (M^+ + Na); HRMS (ESI) for $C_{31}H_{26}NO_3SBrNa^{+1}$ (M^+ + Na): 594.0715, Found: 594.0709. The ee of the **3c** was determined to be 79% [determined by HPLC, Chiralpak AD-H, *n*-hexane–isopropanol = 70 : 30, 0.5 mL min^{-1}, λ = 214 nm, *t* (major) = 19.96 min, *t* (minor) = 12.36 min].

(*S*)-4-Methyl-*N*-((5-oxo-4,4-diphenylcyclopent-1-enyl)(thiophen-2-yl)methyl)benzenesulfonamide 3d. Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3d** (35 mg, 94% yield). A white solid. m.p. for racemic **3d** = 185–187 °C; m.p. for **3d** = 182–184 °C; $[\alpha]_D^{20}$ = +51.6 (*c* 0.4, CH_2Cl_2). IR (CH_2Cl_2): *v* 3275, 3060, 2923, 2852, 1697, 1635, 1597, 1492, 1443, 1331, 1304, 1259, 1106, 1089, 921, 814, 758 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.63 (2H, d, *J* = 8.4 Hz), 7.55 (1H, t, *J* = 2.4 Hz), 7.30–7.21 (6H, m), 7.12–7.05 (7H, m), 6.77 (1H, dd, J_1 = 5.2 Hz, J_2 = 3.6 Hz), 6.65–6.64 (1H, m), 6.04 (1H, d, *J* = 8.8 Hz), 5.60 (1H, d, *J* = 8.8 Hz), 3.38–3.32 (1H, m), 3.17 (1H, dd, J_1 = 19.6 Hz, J_2 = 2.4 Hz), 2.29 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 206.6, 157.9, 143.4, 142.4, 142.3, 142.1, 141.4, 137.2, 129.6, 128.44, 128.42, 127.8, 127.7, 127.1, 126.9, 126.8, 125.7, 125.4, 60.9, 51.1, 45.5, 21.5; MS (ESI) *m/z* 522.0 (M^+ + Na); HRMS (ESI) for $C_{29}H_{25}NO_3S_2Na^{+1}$ (M^+ + Na): 522.1174, Found: 522.1186. The ee of the **3d** was determined to be 76% [determined by HPLC, Chiralpak AD-H, *n*-hexane–isopropanol = 70 : 30, 0.5 mL min^{-1}, λ = 214 nm, *t* (major) = 30.22 min, *t* (minor) = 26.58 min].

(*S*)-*N*-((3-Methoxyphenyl)(5-oxo-4,4-diphenylcyclopent-1-enyl)-methyl)-4-methylbenzenesulfonamide 3e. Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3e** (35 mg, 90% yield). A white solid. m.p. for racemic **3e** = 153–154 °C; m.p. for **3e** = 141–143 °C; $[\alpha]_D^{20}$ = +27.3 (*c* 0.4, CH_2Cl_2). IR (CH_2Cl_2): *v* 3277, 2923, 2853, 1700, 1599, 1492, 1444, 1331, 1262, 1160, 1091, 1036, 917, 814, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.60 (2H, d, *J* = 8.0 Hz), 7.50 (1H, s), 7.26–7.20 (6H, m), 7.09–7.01 (7H, m), 6.71 (1H, dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz), 6.66 (1H, d, *J* = 6.8 Hz), 6.61 (1H, s), 5.95 (1H, d, *J* = 8.4 Hz), 5.32 (1H, d, *J* = 8.4 Hz), 3.60 (3H, s), 3.36–3.31 (1H, m), 3.17 (1H, dd, J_1 = 19.6 Hz, J_2 = 2.8 Hz), 2.30 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 206.9, 159.7, 157.9, 143.2, 142.5, 141.9, 139.8, 137.3, 129.6, 129.5, 128.4, 127.8, 127.6, 127.2, 126.9, 118.9, 113.9, 111.8, 60.9, 55.0, 45.5, 21.4; MS (ESI) *m/z* 546.0 (M^+ + Na); HRMS (ESI) for $C_{32}H_{29}NO_4SNa^{+1}$ (M^+ + Na): 546.1711, Found: 546.1710. The ee of the **3e** was determined to be 75% [determined by HPLC, Chiralpak AD-H, *n*-hexane–isopropanol = 70 : 30, 0.5 mL min^{-1}, λ = 214 nm, *t* (major) = 31.59 min, *t* (minor) = 27.87 min].

(*S*)-*N*-(Furan-2-yl(5-oxo-4,4-diphenylcyclopent-1-enyl)methyl)-4-methylbenzenesulfonamide 3f. Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3f** (23 mg, 61% yield). A white solid. m.p. for racemic **3f** = 160–163 °C; m.p. for **3f** = 167–168 °C; $[\alpha]_D^{20}$ = +22.0 (*c* 0.8, CH_2Cl_2). IR (CH_2Cl_2): *v* 3278, 3059, 1701, 1638, 1597, 1493, 1444, 1332, 1184, 1106, 1090, 1012, 917, 753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.63 (2H, d, *J* = 8.0 Hz), 7.56 (1H, s), 7.30–7.18 (7H, m), 7.10–7.04 (6H, m), 6.16–6.15 (1H, m), 5.95 (1H, d, *J* = 3.2 Hz), 5.88 (1H, d, *J* = 8.8 Hz), 5.45 (1H, d, *J* = 8.8 Hz), 3.34 (1H, dd, J_1 = 19.6 Hz, J_2 = 2.0 Hz), 3.19 (1H, dd, J_1 = 19.6 Hz, J_2 = 2.4 Hz), 2.30 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 206.5, 158.2, 150.4, 143.3, 142.6, 142.4, 139.9, 137.2, 129.5, 128.4, 127.9, 127.6, 127.1, 126.9, 110.5, 107.7, 60.9, 49.2, 45.6, 21.5; MS (ESI) *m/z* 506.0 (M^+ + Na); HRMS (ESI) for $C_{29}H_{25}NO_4SNa^{+1}$ (M^+ + Na): 506.1396, Found: 506.1397. The ee of the **3f** was determined to be 68% [determined by HPLC, Chiralpak AD-H, *n*-hexane–isopropanol = 70 : 30, 0.5 mL min^{-1}, λ = 214 nm, *t* (major) = 29.53 min, *t* (minor) = 25.44 min].

(*S*)-*N*-((4-Bromophenyl)(5-oxo-4,4-diphenylcyclopent-1-enyl)-methyl)-4-methylbenzenesulfonamide 3g. Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3g** (41 mg, 96% yield). A white solid. m.p. for racemic **3g** = 200–201 °C; m.p. for **3g** = 183–185 °C; $[\alpha]_D^{20}$ = +30.8 (*c* 0.8, CH_2Cl_2). IR (CH_2Cl_2): *v* 3280, 3059, 2923, 2853, 1701, 1635, 1597, 1491, 1444, 1331, 1262, 1184, 1160, 1090, 1010, 755 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.58 (2H, d, *J* = 8.4 Hz), 7.47 (1H, s), 7.30–7.20 (8H, m), 7.08 (2H, d, *J* = 8.4 Hz), 7.04–7.00 (4H, m), 6.96 (2H, d, *J* = 8.4 Hz), 6.05 (1H, d, *J* = 8.4 Hz), 5.30 (1H, d, *J* = 8.8 Hz), 3.37–3.31 (1H, m), 3.15 (1H, dd, J_1 = 19.6 Hz, J_2 = 2.4 Hz), 2.32 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ

206.9, 158.0, 143.4, 142.3, 142.2, 141.3, 137.3, 137.2, 131.6, 130.0, 128.5, 128.4, 127.8, 127.6, 127.1, 127.0, 126.9, 121.9, 61.0, 54.6, 45.4, 21.5; MS (ESI) *m/z* 594.0 (M^+ + Na); HRMS (ESI) for $C_{31}H_{26}NO_3SBrNa^{+1}$ (M^+ + Na): 594.0700, Found: 594.0709. The ee of the **3g** was determined to be 84% [determined by HPLC, Chiralpak AD-H, *n*-hexane–isopropanol = 70 : 30, 0.5 mL min^{-1}, λ = 214 nm, *t* (major) = 40.85 min, *t* (minor) = 28.32 min].

(*S*)-4-Methyl-*N*-((5-oxo-4,4-diphenylcyclopent-1-enyl)(4-(trifluoromethyl)phenyl)methyl)benzenesulfonamide 3h. Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3h** (42 mg, 99% yield). A white solid. m.p. for racemic **3h** = 96–98 °C; m.p. for **3h** = 116–118 °C; $[\alpha]_D^{20}$ = +20.2 (*c* 0.5, CH_2Cl_2). IR (CH_2Cl_2): *v* 3279, 2962, 1695, 1617, 1596, 1493, 1444, 1324, 1260, 1160, 1090, 1017, 798 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.56 (2H, d, *J* = 8.0 Hz), 7.52 (1H, s), 7.37 (2H, d, *J* = 8.0 Hz), 7.25–7.20 (8H, m), 7.05–7.00 (6H, m), 6.29 (1H, d, *J* = 8.8 Hz), 5.43 (1H, d, *J* = 8.8 Hz), 3.32 (1H, d, *J* = 19.2 Hz), 3.17 (1H, dd, J_1 = 19.6 Hz, J_2 = 2.0 Hz), 2.29 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 206.8, 158.1, 143.5, 142.2, 142.1, 141.2, 137.1, 129.9 (q, J_{C-F} = 32.4 Hz), 129.5, 128.5, 128.4, 127.7, 127.5, 127.1, 127.03, 127.00, 126.9, 125.3 (q, J_{C-F} = 3.7 Hz), 123.4 (q, J_{C-F} = 270.7 Hz), 60.9, 54.6, 45.5, 21.3; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ −62.7; MS (ESI) *m/z* 584.0 (M^+ + Na); HRMS (ESI) for $C_{32}H_{26}NO_3SF_3Na^{+1}$ (M^+ + Na): 584.1479, Found: 584.1478. The ee of the **3h** was determined to be 80% [determined by HPLC, Chiralpak AD-H, *n*-hexane–isopropanol = 70 : 30, 0.5 mL min^{-1}, λ = 214 nm, *t* (major) = 27.69 min, *t* (minor) = 21.37 min].

(*S*)-4-Methyl-*N*-((5-oxo-4,4-diphenylcyclopent-1-enyl)(*p*-tolyl)methyl)benzenesulfonamide 3i. Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3i** (32 mg, 84% yield). A white solid. m.p. for racemic **3i** = 223–224 °C; m.p. for **3i** = 220–222 °C; $[\alpha]_D^{20}$ = +24.5 (*c* 0.5, CH_2Cl_2). IR (CH_2Cl_2): *v* 3289, 2923, 1693, 1615, 1592, 1498, 1444, 1335, 1288, 1157, 1100, 1035, 1018, 931, 863, 813, 754 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.60 (2H, d, *J* = 8.4 Hz), 7.49 (1H, t, *J* = 2.4 Hz), 7.28–7.20 (6H, m), 7.08–7.02 (6H, m), 7.00 (4H, s), 5.86 (1H, d, *J* = 8.4 Hz), 5.29 (1H, d, *J* = 8.4 Hz), 3.36–3.31 (1H, m), 3.16 (1H, dd, J_1 = 19.6 Hz, J_2 = 2.0 Hz), 2.31 (3H, s), 2.26 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 206.8, 157.7, 143.2, 142.5, 142.0, 137.6, 137.2, 135.3, 129.5, 129.2, 128.4, 128.3, 127.9, 127.6, 127.2, 126.83, 126.81, 126.6, 60.9, 54.8, 45.4, 21.4, 20.1; MS (ESI) *m/z* 530.0 (M^+ + Na); HRMS (ESI) for $C_{32}H_{29}NO_3SNa^{+1}$ (M^+ + Na): 530.1761, Found: 530.1760. The ee of the **3i** was determined to be 84% [determined by HPLC, Chiralpak AD-H, *n*-hexane–isopropanol = 70 : 30, 0.5 mL min^{-1}, λ = 214 nm, *t* (major) = 24.68 min, *t* (minor) = 27.06 min].

(*S*)-4-Methyl-*N*-((3-nitrophenyl)(5-oxo-4,4-diphenylcyclopent-1-enyl)methyl)benzenesulfonamide 3j. Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3j** (40 mg, 99% yield). A white solid. m.p. for racemic **3j** = 153–155 °C; m.p. for **3j** = 172–174 °C; $[\alpha]_D^{20}$ = +31.3 (*c* 1.0, CH_2Cl_2). IR (CH_2Cl_2): *v* 3273, 3060, 2923, 1700, 1636, 1529, 1493, 1444, 1347, 1265, 1159, 1089, 1018, 912, 781, 732 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.99 (1H, dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz), 7.87 (1H, t, *J* = 1.6 Hz), 7.60 (1H, s), 7.58–7.56 (3H, m), 7.33 (1H, t, *J* = 8.0 Hz), 7.28–7.18 (6H, m), 7.06–6.98 (6H, m), 6.35 (1H, d, *J* = 9.2 Hz), 5.47 (1H, d, *J* = 8.8 Hz), 3.37–3.31 (1H, m), 3.15 (1H, dd, J_1 = 19.6 Hz, J_2 = 2.4 Hz), 2.27 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 206.6, 158.8, 148.0, 143.7, 142.0, 141.8, 140.6, 140.3, 136.9, 133.0, 129.7, 129.5, 128.5, 128.4, 127.7, 127.4, 127.0, 126.3, 122.7, 121.5, 60.8, 54.1, 45.7, 21.4; MS (ESI) *m/z* 561.1 (M^+ + Na); HRMS (ESI) for $C_{31}H_{26}N_2O_5SNa^{+1}$ (M^+ + Na): 561.1453, Found: 561.1455. The ee of the **3j** was determined to be 82% [determined by HPLC, Chiralpak AD-H, *n*-hexane–isopropanol = 60 : 40, 0.5 mL min^{-1}, λ = 230 nm, *t* (major) = 27.18 min, *t* (minor) = 17.87 min].

(*S*)-4-Methyl-*N*-(naphthalen-2-yl(5-oxo-4,4-diphenylcyclopent-1-enyl)methyl)benzenesulfonamide 3k. Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3k** (18 mg, 44% yield). A white solid. m.p. for racemic **3k** = 214–216 °C; m.p. for **3k** = 227–229 °C; $[\alpha]_D^{20}$ = +7.0 (*c* 0.2, CH_2Cl_2). IR (CH_2Cl_2): *v* 3278, 2962, 1699, 1635, 1598, 1493, 1444, 1330, 1260, 1160, 1091, 1018, 860, 798, 756 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.74 (1H, d, *J* = 8.4 Hz), 7.65 (1H, d, *J* = 8.4 Hz), 7.60 (1H, d, *J* = 8.0 Hz), 7.54–7.50 (2H, m), 7.45–7.39 (2H, m), 7.37 (1H, s), 7.27–7.21 (7H, m), 7.06–7.03 (4H, m), 7.00 (2H, d, *J* = 8.4 Hz), 6.13 (1H, d, *J* = 8.8 Hz), 5.52 (1H, d, *J* = 8.8 Hz), 3.39–3.33 (1H, m), 3.16 (1H, dd, J_1 = 19.6 Hz, J_2 = 2.4 Hz), 2.30 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 207.0, 158.1, 143.3, 142.5, 142.3, 141.5, 137.2, 135.4, 132.9, 132.7, 129.7, 129.5, 128.5, 128.4, 127.9, 127.8, 127.7, 127.4, 127.1, 127.0, 126.9, 126.4, 126.2, 125.6, 124.7, 61.1, 55.0, 45.4, 21.4; MS (ESI) *m/z* 566.1 (M^+ + Na); HRMS (ESI) for $C_{35}H_{29}NO_3SNa^{+1}$ (M^+ + Na): 566.1868, Found: 566.1853. The ee of the **3k** was determined to be 60% [determined by HPLC, Chiralpak AD-H, *n*-hexane–isopropanol = 60 : 40, 0.5 mL min^{-1}, λ = 230 nm, *t* (major) = 48.73 min, *t* (minor) = 55.92 min].

(*S*)-*N*-((4,4-Bis(4-fluorophenyl)-5-oxocyclopent-1-enyl)(4-nitrophenyl)methyl)-4-methylbenzenesulfonamide 3l. Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3l** (43 mg, 99% yield). A white solid. m.p. for racemic **3l** = 95–98 °C; m.p. for **3l** = 77–80 °C; $[\alpha]_D^{20}$ = +15.0 (*c* 0.3, CH_2Cl_2). IR (CH_2Cl_2): *v* 3281, 2924, 1701, 1635, 1598, 1520, 1507, 1434, 1233, 1184, 1161, 1091, 1015, 817, 735 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.97 (2H, d, *J* = 8.8 Hz), 7.60 (3H, d, *J* = 8.0 Hz), 7.28 (2H, d, *J* = 8.8 Hz), 7.10 (2H, d, *J* = 8.4 Hz), 6.97–6.88 (8H, m), 6.40 (1H, d, *J* = 8.4 Hz), 5.46 (1H, d, *J* = 8.0 Hz), 3.33–3.28 (1H, m), 3.15 (1H, dd, J_1 = 19.6 Hz, J_2 = 2.4 Hz), 2.31 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 206.1, 161.6 (dd, J_{1C-F} = 245.7 Hz, J_{2C-F} = 2.6 Hz), 158.5, 147.3, 145.3, 143.9, 140.9, 137.6 (dd, J_{1C-F} = 16.7 Hz, J_{2C-F} = 3.7 Hz), 136.8, 129.2 (dd, J_{1C-F} = 12.6 Hz, J_{2C-F} = 7.8 Hz), 127.6, 127.0, 123.6, 115.4 (dd, J_{1C-F} = 21.2 Hz, J_{2C-F} = 3.0 Hz), 59.5, 54.0, 45.5, 21.4; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ −114.8 to −114.9 (m); MS (ESI) *m/z* 597.0 (M^+ + Na); HRMS (ESI) for $C_{31}H_{24}N_2O_5SF_2Na^{+1}$ (M^+ + Na): 597.1251, Found: 597.1266.

The ee of the **3l** was determined to be 82% [determined by HPLC, Chiralpak AD-H, *n*-hexane–isopropanol = 70 : 30, 0.5 mL min^{-1}, λ = 214 nm, *t* (major) = 45.42 min, *t* (minor) = 52.19 min].

(*S*)-*N*-((4,4-Bis(4-fluorophenyl)-5-oxocyclopent-1-enyl)(*p*-tolyl)-methyl)-4-methylbenzenesulfonamide 3m. Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3m** (37 mg, 91% yield). A white solid. m.p. for racemic **3m** = 182–184 °C; m.p. for **3m** = 181–183 °C; $[\alpha]_D^{20}$ = +19.8 (*c* 0.4, CH_2Cl_2). IR (CH_2Cl_2): ν 3248, 2961, 2923, 1702, 1633, 1598, 1506, 1439, 1326, 1259, 1186, 1160, 1092, 1016, 804, 740 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.60 (2H, d, *J* = 8.0 Hz), 7.56–7.55 (1H, m), 7.09 (2H, d, *J* = 8.4 Hz), 7.00–6.89 (12H, m), 5.92 (1H, d, *J* = 8.4 Hz), 5.28 (1H, d, *J* = 8.0 Hz), 3.30–3.24 (1H, s), 3.17–3.11 (1H, m), 2.32 (3H, s), 2.25 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 206.3, 161.6 (dd, J_{1C-F} = 245.0 Hz, J_{2C-F} = 3.0 Hz), 157.3, 143.3, 142.5, 138.2 (d, J_{1C-F} = 3.3 Hz), 137.7, 137.1, 135.1, 129.4 (dd, J_{1C-F} = 13.4 Hz, J_{2C-F} = 5.6 Hz), 129.24, 129.21, 127.1, 126.5, 115.2 (dd, J_{1C-F} = 21.6 Hz, J_{2C-F} = 1.5 Hz), 60.0, 54.5, 45.4, 21.4, 20.9; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ −115.4 to −115.5 (m); MS (ESI) *m*/*z* 566.1 (M^+ + Na); HRMS (ESI) for $C_{32}H_{27}NO_3SF_2Na^{+1}$ (M^+ + Na): 566.1561, Found: 566.1571. The ee of the **3m** was determined to be 84% [determined by HPLC, Chiralpak AD-H, *n*-hexane–isopropanol = 80 : 20, 0.5 mL min^{-1}, λ = 214 nm, *t* (major) = 38.68 min, *t* (minor) = 41.74 min].

(*S*)-*N*-((4,4-Bis(4-fluorophenyl)-5-oxocyclopent-1-enyl)(4-chlorophenyl)methyl)-4-methylbenzenesulfonamide 3n. Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3n** (38 mg, 89% yield). A white solid. m.p. for racemic **3n** = 198–201 °C; m.p. for **3n** = 179–181 °C; $[\alpha]_D^{20}$ = +10.0 (*c* 0.3, CH_2Cl_2). IR (CH_2Cl_2): ν 3278, 2961, 1701, 1634, 1598, 1506, 1434, 1328, 1260, 1233, 1184, 1160, 1089, 1014, 806, 736 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.58 (2H, d, *J* = 8.0 Hz), 7.55–7.54 (1H, m) 7.12–7.09 (4H, m), 7.00–6.89 (10H, m), 6.05 (1H, d, *J* = 8.4 Hz), 5.31 (1H, d, *J* = 8.4 Hz), 3.31–3.26 (1H, m), 3.17–3.12 (1H, m), 2.33 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 206.4, 161.7 (dd, J_{1C-F} = 245.4 Hz, J_{2C-F} = 2.6 Hz), 157.8, 143.6, 141.8, 137.9 (dd, J_{1C-F} = 17.1 Hz, J_{2C-F} = 3.4 Hz), 137.0, 136.6, 133.9, 129.6, 129.3 (dd, J_{1C-F} = 15.2 Hz, J_{2C-F} = 7.8 Hz), 128.7, 128.0, 127.1, 115.4 (dd, J_{1C-F} = 21.6 Hz, J_{2C-F} = 2.6 Hz), 60.0, 54.3, 45.5, 21.5; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ −115.1 to −115.2 (m); MS (ESI) *m*/*z* 586.0 (M^+ + Na); HRMS (ESI) for $C_{31}H_{24}NO_3SF_2ClNa^{+1}$ (M^+ + Na): 586.1033, Found: 586.1025. The ee of the **3n** was determined to be 75% [determined by HPLC, Chiralpak AD-H, *n*-hexane–isopropanol = 70 : 30, 0.5 mL min^{-1}, λ = 214 nm, *t* (major) = 21.53 min, *t* (minor) = 27.05 min].

(*S*)-4-Methyl-*N*-((4-nitrophenyl)(5-oxo-4,4-bis(4-(trifluoromethyl)-phenyl)cyclopent-1-enyl)methyl)benzenesulfonamide 3o. Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3o** (50 mg, 99% yield). A white solid. m.p. for racemic **3o** = 110–113 °C; m.p. for **3o** = 70–73 °C; $[\alpha]_D^{20}$ = +6.3 (*c* 0.9, CH_2Cl_2). IR (CH_2Cl_2): ν 3283, 2926, 1704, 1615, 1522, 1410, 1348, 1324, 1161, 1118, 1092, 1070, 1017, 833 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.98 (2H, d, *J* = 8.8 Hz), 7.71–7.70 (1H, m), 7.60 (2H, d, *J* = 8.4 Hz), 7.51 (4H, dd, J_1 = 8.4 Hz, J_2 = 5.6 Hz), 7.29 (2H, d, *J* = 8.8 Hz), 7.11 (6H, t, *J* = 8.8 Hz), 6.38 (1H, d, *J* = 6.0 Hz), 5.47 (1H, d, *J* = 4.4 Hz), 3.42–3.37 (1H, s), 3.24 (1H, dd, J_1 = 19.6 Hz, J_2 = 2.0 Hz), 2.31 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 204.8, 158.7, 147.4, 145.3 (dd, J_{1C-F} = 8.5 Hz, J_{2C-F} = 1.1 Hz), 145.0, 144.1, 141.5, 136.7, 129.67, 129.65 (dq, J_{1C-F} = 32.7 Hz, J_{2C-F} = 3.7 Hz), 128.0, 127.9, 127.6, 127.0, 125.6 (dq, J_{1C-F} = 3.8 Hz, J_{2C-F} = 2.6 Hz), 123.8, 123.7 (dq, J_{1C-F} = 270.6 Hz, J_{2C-F} = 1.5 Hz), 60.5, 53.9, 44.9, 21.3; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ −62.7; MS (ESI) *m*/*e* 697.0 (M^+ + Na); HRMS (ESI) for $C_{33}H_{24}N_2O_5SF_6Na^{+1}$ (M^+ + Na): 697.1202, Found: 697.1202. The ee of the **3o** was determined to be 73% [determined by HPLC, Chiralpak AD-H, *n*-hexane–isopropanol = 80 : 20, 0.5 mL min^{-1}, λ = 214 nm, *t* (major) = 40.71 min, *t* (minor) = 46.40 min].

(*S*)-4-Methyl-*N*-((5-oxo-4,4-bis(4-(trifluoromethyl)phenyl)-cyclopent-1-enyl)(*p*-tolyl)methyl)benzenesulfonamide 3p. Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3p** (42 mg, 88% yield). A white solid. m.p. for racemic **3p** = 203–204 °C; m.p. for **3p** = 186–188 °C; $[\alpha]_D^{20}$ = +18.7 (*c* 0.4, CH_2Cl_2). IR (CH_2Cl_2): ν 3282, 2960, 2925, 1701, 1615, 1513, 1410, 1323, 1261, 1160, 1117, 1070, 1017, 813, 737 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.69 (1H, t, *J* = 2.8 Hz), 7.61 (2H, d, *J* = 7.6 Hz), 7.50 (4H, d, *J* = 8.4 Hz), 7.14 (6H, q, *J* = 8.4 Hz), 6.96 (2H, d, *J* = 8.4 Hz), 6.90 (2H, d, *J* = 7.2 Hz), 5.80 (1H, d, *J* = 7.8 Hz), 5.27 (1H, d, *J* = 7.2 Hz), 3.40–3.34 (1H, m), 3.27–3.22 (1H, m), 2.32 (3H, s), 2.25 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 205.0, 157.4 (d, J_{C-F} = 3.0 Hz), 145.8, 143.5 (d, J_{C-F} = 0.8 Hz), 143.1 (t, J_{C-F} = 1.1 Hz), 138.0, 137.0 (t, J_{C-F} = 2.2 Hz), 134.8 (d, J_{C-F} = 1.1 Hz), 129.5, 129.4 (q, J_{C-F} = 32.4 Hz), 129.38, 128.2, 128.1, 127.1, 126.5, 125.5 (dq, J_{1C-F} = 3.7 Hz, J_{2C-F} = 1.5 Hz), 123.4 (q, J_{C-F} = 270.0 Hz), 60.7, 54.5, 45.8, 21.4 (d, J_{C-F} = 1.2 Hz), 21.0 (d, J_{C-F} = 1.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ −62.7; MS (ESI) *m*/*z* 666.0 (M^+ + Na); HRMS (ESI) for $C_{34}H_{27}NO_3SF_6Na^{+1}$ (M^+ + Na): 666.1496, Found: 666.1508. The ee of the **3p** was determined to be 85% [determined by HPLC, Chiralpak AD-H, *n*-hexane–isopropanol = 80 : 20, 0.5 mL min^{-1}, λ = 214 nm, *t* (major) = 25.86 min, *t* (minor) = 23.99 min].

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