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Enantioselective synthesis of spirocyclic cyclopentenes: asymmetric [3+2] annulation of 2-arylideneindane-1,3-diones with MBH carbonates derivatives catalyzed by multifunctional thiourea–phosphines

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ABSTRACT

The [3+2] annulation reactions of 2-arylideneindane-1,3-diones with Morita–Baylis–Hillman (MBH) carbonates proceeded smoothly in the presence of multifunctional thiourea–phosphines to produce the corresponding quaternary carbon centered spirocyclic cyclopentenes in moderate yields, with high diastereoselectivities and enantioselectivities under mild conditions. The plausible reaction has been also discussed on the basis of previous literature.

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1. Introduction

1,3-Indanedione and its derivatives constitute a unique group of compounds and attracted much attention of organic chemists and biologists due to their characteristic features.[1] Thus far, they have been widely employed in the synthesis of drugs,[2] in forensic chemistry for fingerprint detection,[3] in dyes and pigments,[4] and in semi- and photo-semiconductors,[5] proving that 1,3-indanedione and its derivatives are versatile starting materials for the synthesis of potentially important compounds.

Mortia–Baylis–Hillman (MBH) adducts have been also proven to be suitable precursors for the synthesis of multifunctional cyclic compounds, because the in situ generated phosphorus ylides from MBH carbonates in the presence of tertiary phosphines are very reactive 1,3-dipoles in a variety of annulations.[6] In this field, Lu and his co-workers first reported a series of intra- and intermolecular [3+*n*] annulations (*n*=2, 4, 6) using MBH carbonates as 1,3-dipoles with various electron-deficient olefins catalyzed by a tertiary phosphine, affording the corresponding cycloadducts in good yields and high regioselectivities under mild conditions.[7] More recently, Zhang, Huang and He as well as their co-workers have also developed several MBH adducts involved in [4+1] annulations to give the cycloaddition products in high yields, respectively.[8]

To the best of our knowledge, there are few reports about asymmetric version of this reaction. The first report on the asymmetric intermolecular [3+2] cycloaddition of MBH carbonates with methyleneindolinones was disclosed by Barbas and his co-workers, providing the corresponding spirocyclopentane–oxindoles in good yields and high ee values.[9] Then, Lu's group developed L-threonine-derived chiral phosphines and indicated that these chiral catalysts were effective promoters in the asymmetric [3+2] annulation of MBH carbonates with isatylidenemalononitriles to deliver the optically active cyclic products in high yields with high enantioselectivities.[10] With regard to the intramolecular [3+2] annulation of MBH carbonates with electron-deficient olefins, Tang and his co-workers first utilized spirobiindane-based chiral phosphines as catalysts to produce the corresponding intramolecular [3+2] cyclic adducts in good yields along with high ee values.[11] Moreover, our group has designed and synthesized a series of chiral multifunctional thiourea–phosphine catalysts derived from an axially chiral binaphthyl scaffold and has also demonstrated that these chiral phosphines were very effective catalysts in the asymmetric aza-MBH reaction and asymmetric allylic substitution of MBH adducts, giving the corresponding products in good yields and excellent enantioselectivities as well as in the asymmetric [3+2] annulations of MBH carbonates with isatylidenemalononitriles, giving the desired cycloadducts in good yields along with moderate enantioselectivities.[12–14] Recently, we have further developed a series of multifunctional thiourea–phosphine catalysts derived from natural amino acid and applied them in asymmetric [3+2] annulation of MBH carbonates with trifluoroethylidenemalonates to give corresponding highly functionalized trifluoromethyl or pentafluoroethyl-bearing cyclopentenes in excellent yields (upto >99%), high diastereoselectivities (upto 99:1) and enantioselectivities (upto 96%) under mild conditions.[15] Herein as a part of

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our continuing interest in asymmetric annulation catalyzed by multifunctional thiourea–phosphines, we wish to report the asymmetric annulation of 2-arylideneindane-1,3-diones **1** with MBH carbonates **2** catalyzed by multifunctional thiourea–phosphines to afford the corresponding quaternary carbon centered spirocyclic cyclopentenes in moderate yields, high diastereoselectivities, and enantioselectivities under mild conditions.[16]

2. Results and discussion

Initially, we examined the reaction of 2-(4-nitrobenzylidene) indan-1,3-dione **1a** (0.1 mmol, 1.0 equiv) with MBH carbonate **2a** (0.2 mmol, 2.0 equiv) catalyzed by PPh_3 in THF (2 mL) at room temperature, the *C*-1 addition product **3a** was obtained in 74% yield along with excellent diastereoselectivities (upto >99% dr) within 24 h. Based on the preliminary investigation on [3+2] annulation of 2-(4-nitro-benzylidene)-indan-1,3-dione **1a** with MBH carbonate **2a**, asymmetric version of this reaction was subsequently exploited. Primarily, we utilized bifunctional chiral phosphine derived from an axially chiral binaphthyl scaffold **TP1** as a catalyst for the [3+2] annulation of electron-deficient alkene **1a** with MBH carbonate **2a** in toluene, giving the product **3a** in 39% yield along with 19% ee (Table 1, entry 1). In order to improve the yield and enantioselectivity, other multifunctional thiourea–phosphines **TPs**, derived from natural amino acids were further tested for this [3+2] annulation. To our delight, **TP2** derived from L-valine was used to catalyze the reaction in toluene (2 mL) within 24 h at room temperature, furnishing **3a** in 59% yield and 65% ee (Table 1, entry 2). We continued examining multifunctional thiourea–phosphines with more sterically hindered substituents **TP3**–**TP6**. **TP3** could promote the reaction very well, producing **3a** in 94% yield along with 75% ee value and **TP4** is the best catalyst in terms of enantioselectivity, affording **3a** in 88% yield along with 78% ee value (Table 1, entries 3 and 4). However, increasing the steric hindrance of thiourea moiety did not further increase the enantioselectivities (Table 1, entries 5 and 6). In order to obtain better result, we synthesized multifunctional squaramide–phosphines **TP7**–**TP9** derived from natural amino acid according to the previous literature[13s] to catalyze the [3+2] annulation, however, furnishing **3a** in moderate yield along with low ee value (Table 1, entries 7–9).

Having identified the best catalyst, we subsequently optimized the reaction conditions, such as temperature, solvent, and additive using **TP3** as catalyst, **1a** and **2a** as substrates. Initially we carried out the reaction of **1a** (0.1 mmol, 1.0 equiv) with **2a** (0.2 mmol, 2.0 equiv) in toluene (2.0 mL) at room temperature using 4 Å MS as additive, affording **3a** in 99% yield and 73% ee value, suggesting that 4 Å MS could promote the yield, but slightly decrease the ee value (Table 2, entry 1). We next examined the reaction at 0 °C, producing **3a** in 30% yield along with 85% ee within 144 h (Table 2, entry 2). We believed that the poor solubility of **1a** in toluene decreased the yield remarkably at low reaction temperature. Other solvents, such as DCM (dichloromethane), chloroform, and *o*-xylene were examined under the same conditions, but these solvents could not improve reaction outcomes (Table 2, entries 3–5). In order to increase the solubility of **1a** in toluene at 0 °C, the reaction was conducted in 10 mL of toluene, affording **3a** in 70% yield along with 89% ee (Table 2, entry 6) and increasing the employed amount of **1a** or **2a** decrease the ee value (Table 2, entries 7 and 8). We subsequently used **TP4** as catalyst to further examine the [3+2] annulation under the standard conditions, indicating that **TP4** could also facilitate the [3+2] annulation to give **3a** in 80% yield and 88% ee value (Table 2, entry 9). Decreasing the temperature to −10 °C or increasing the temperature to 5 °C was detrimental to the ee value of **3a**, affording **3a** in 86% ee value and 82% ee value, respectively (Table 2, entries 10 and 11). Next, we attempted to add some additives to improve the reaction outcome, it was found that adding organic base, such as triethylamine or 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP) could not improve the reaction outcome (Table 2, entries 12 and 13). If the [3+2] annulation was conducted using Brønsted acid, such as benzoic acid or acetic acid as additives, the reaction could not occur, suggesting that proton acid could destroy the formation of the in situ generated phosphorus ylides from MBH carbonates in the presence of tertiary phosphines (Table 2, entries 14 and 15). The solvent effects have been also examined using **TP3** as the catalyst in chlorobenzene, (trifluoromethyl)benzene, and mixed solvent (toluene/chloroform), but the ee value and yield of **3a** decreased remarkably (Table 2, entries 16–18). Therefore, the best reaction conditions have been determined as that **TP3** (20 mol %) should be used as the catalyst and the reaction should be carried out in toluene at 0 °C without any additives.

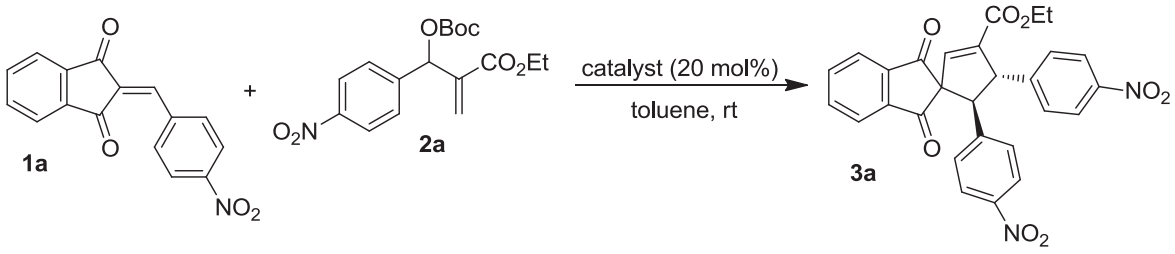
Having determined the optimal reaction conditions, we next turned our attention to the scope of the asymmetric [3+2] annulation of 2-arylideneindane-1,3-diones **1** with MBH carbonates **2** and the results are summarized in Table 3. Substrates with an electron-withdrawing substituent on the aromatic ring of MBH carbonates afforded the corresponding annulation adducts in moderate yields with excellent diastereo- and enantioseletivities using **TP3** or **TP4** (Table 3, entries 1–9). As for substrates **2f** and **2g**, in which the substituents at the *ortho* position of the aromatic ring of MBH carbonates, the corresponding products were acquired with high ee upto 97%, respectively (Table 3, entries 5 and 6). When two electron-withdrawing substituents were introduced to the aromatic ring of MBH carbonates, the reaction could proceed smoothly to give the annulation adducts in moderate yields and good ee values (Table 3, entries 10–14). Especially when the substituents were introduced at 2, 3- or 2, 4-position of the aromatic ring of MBH carbonates, the corresponding annulation adducts were obtained in 96% ee and 98% ee, respectively (Table 3, entries 10 and 11). While when the substituents were introduced at 2, 6-position, the yield and ee value decreased remarkably due to the steric hindrance (Table 3, entry 13). Owing to the lower activities at 0 °C, substrate with electron-donating substituent on the aromatic ring of MBH carbonate afforded the trace product (Table 3, entry 15). We next examined R^1 moiety of electron-deficient olefins derived from 1,3-indanedione. Whether an aryl or alkyl group was introduced, the reaction could proceed smoothly to give the corresponding cycloadducts **3p**–**3s** in moderate yields and ee values within 48 h using **TP3** or **TP4** (Table 3, entries 16–19).

Their structures have been determined by ^1H and ^{13}C NMR spectroscopic data, MS, and HRMS analyses. The absolute configuration of **3k** has been unambiguously determined by X-ray diffraction. The ORTEP drawing of **3k** is shown in Fig. 1 and its CIF data are presented in the Supplementary data (for details see Supplementary data).

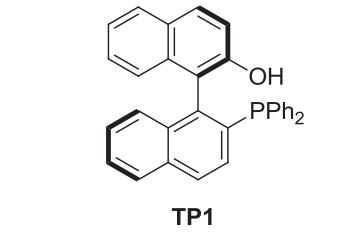
The mechanism of this interesting [3+2] reaction is proposed in Scheme 1 on the basis of previous literature.[7a,14e,17] Initially the multifunctional thiourea–phosphine **TP3** attacks from β position of MBH carbonates to take off carbon dioxide and *tert*-butyl alcohol, producing phosphorus ylide **A**, which undergoes the nucleophilic attack with the *C*-1 carbon center to the electron-deficient olifin **1** to give the corresponding intermediate **B**. Subsequent Michael addition produces cyclic intermediate **C**, which produces **3** and regenerates **TP3** via elimination of multifunctional thiourea–phosphine **TP3**. The high regio-, diastereo-, and enantioselectivity of this reaction are probably controlled by steric hindrance between benzyl group and benzhydryl group on the catalyst with 2-arylideneindane-1,3-dione **1** as shown in Scheme 1.

In conclusion, a fairly efficient [3+2] annulation reaction of 2-arylideneindane-1,3-diones with MBH carbonates catalyzed by multifunctional thiourea–phosphine has been developed, which provides an easy access to the synthesis of the corresponding

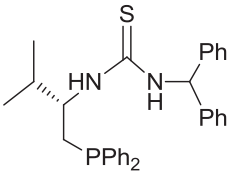
Table 1
Screening of catalysts for the asymmetric [3+2] annulation



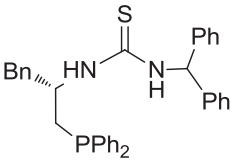
Entry[a]	Catalyst	Time (h)	Yield of **3a** (%)[b]	ee of **3a** (%)[c]
1	**TP1**	24	39	19
2	**TP2**	24	59	65
3	**TP3**	24	94	75
4	**TP4**	24	88	78
5	**TP5**	24	92	70
6	**TP6**	24	80	74
7	**TP7**	24	71[d]	25
8	**TP8**	24	39[d]	40
9	**TP9**	24	53[d]	−32



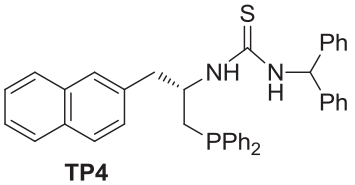
TP1



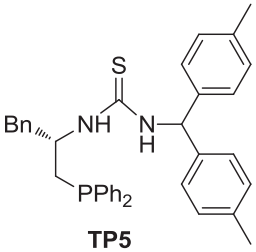
TP2



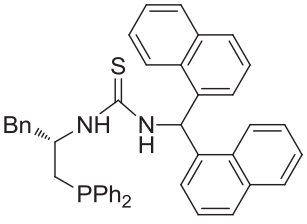
TP3



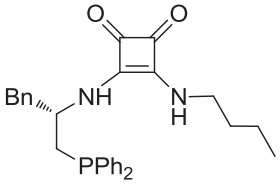
TP4



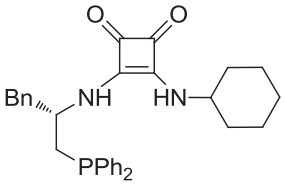
TP5



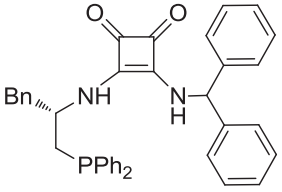
TP6



TP7



TP8



TP9

[a] The reaction was carried out using **1a** (0.1 mmol), **2a** (0.2 mmol) and catalyst (0.02 mmol) in toluene (2.0 mL).
[b] Isolated yield with a dr (diastereoselective ratio) value>99:1 if not otherwise specified.
[c] Determined by chiral HPLC analysis.
[d] The reaction was carried out in chloroform (5.0 mL).

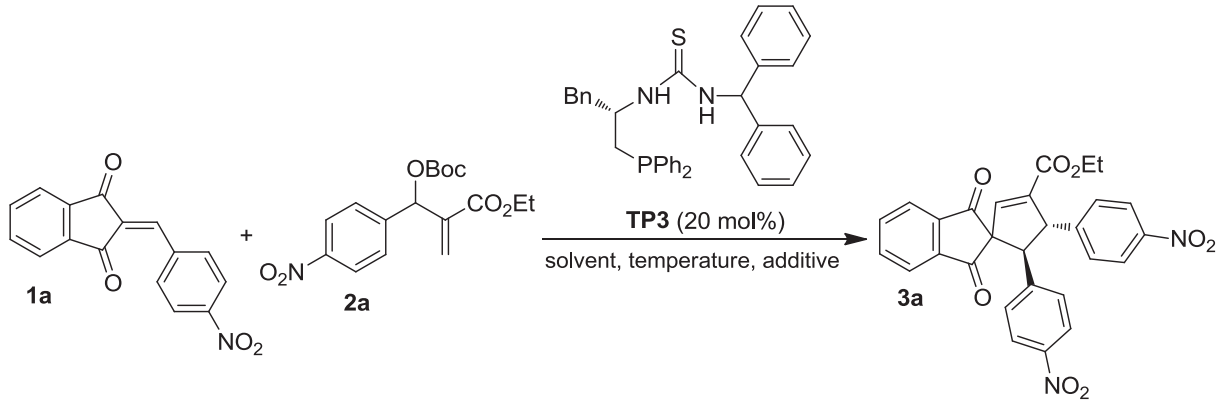
quaternary carbon centered spirocyclic cyclopentenes under mild reaction conditions in moderate to good yields (upto 75%), with high diastereoselectivities (upto >99:1) and enantioselectivities (upto 98%). Efforts are in progress to elucidate the mechanistic details of this reaction and use the multifunctional thiourea–phosphines in other asymmetric reactions.

3. Experimental section

3.1. General remarks

Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. Optical rotations were

Table 2
Optimization of reaction conditions for the asymmetric [3+2] annulation



Entry[a]	Solvent	Temperature (°C)	Additive	Yield of **3a** (%)[b]	ee of **3a** (%)[c]
1[d]	Toluene	25	4 A MS	99	73
2[d]	Toluene	0	/	30	85
3[d]	$CHCl_3$	0	/	40	78
4[d]	DCM	0	/	78	62
5[d]	*o*-Xylene	0	/	67	69
6	Toluene	0	/	70	89
7[e]	Toluene	0	/	78	86
8[f]	Toluene	0	/	78	84
9[g]	Toluene	0	/	80	88
10	Toluene	−10	/	47	86
11	Toluene	5	/	75	82
12	Toluene	0	Et_3N	67	82
13	Toluene	0	HFIP	65	89
14	Toluene	0	4-Nitrophenol	Trace	—[h]
15	Toluene	0	Benzoic acid	Trace	—[h]
16	Chlorobenzene	0	/	60	70
17	(Trifluoromethyl)benzene	0	/	45	75
18	Toluene/$CHCl_3$ (10/1)	0	/	47	60

[a] The reaction was carried out by employing **1a** (0.1 mmol), **2a** (0.2 mmol) and solvent (10 mL) at 0 °C within 144 h.
[b] Isolated yield.
[c] Determined by Chiral HPLC.
[d] The reaction was conducted in 2 mL solvent.
[e] **2a** (3.0 equiv) was used.
[f] **1a** (0.2 mmol) and **2a** (0.1 mmol) were used.
[g] Catalyst **TP4** was used.
[h] Not determined.

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} ^1H NMR spectra were recorded on a Varian Mercury-300 and 400 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard; coupling constants *J* are given in Hertz. ^{13}C NMR spectra were recorded on a Varian Mercury-300 and 400 spectrophotometers (75 or 100 MHz) with complete proton decoupling spectrophotometers ($CDCl_3$: 77.0 ppm). Infrared spectra were recorded on a Perkin–Elmer PE-983 spectrometer with absorption in cm^{-1}. Flash column chromatography was performed using 300–400 mesh silica gel. For thin-layer chromatography (TLC), silica gel plates (Huanghai GF254) were used. Chiral HPLC was performed on a SHIMADZU SPD-10A vp series with chiral columns (Chiralpak AD-H, OD-H, and IC-H columns 4.6×250 mm, (Daicel Chemical Ind., Ltd.)) and chiral column (Phenomenex Lux 5μ Amylose-2 column 4.6×250 mm (PA-2), Phenomenex Lux 5μ Cellulose-2 column 4.6×250 mm (PC-2), (Phenomenex Ind., Ltd.)). Mass spectra were recorded by EI, ESI, MALDI, and HRMS was measured on a HP-5989 instrument.

3.2. General procedure for the asymmetric [3+2] annulation reaction of MBH carbonates with 2-arylidene-indane-1,3-dione

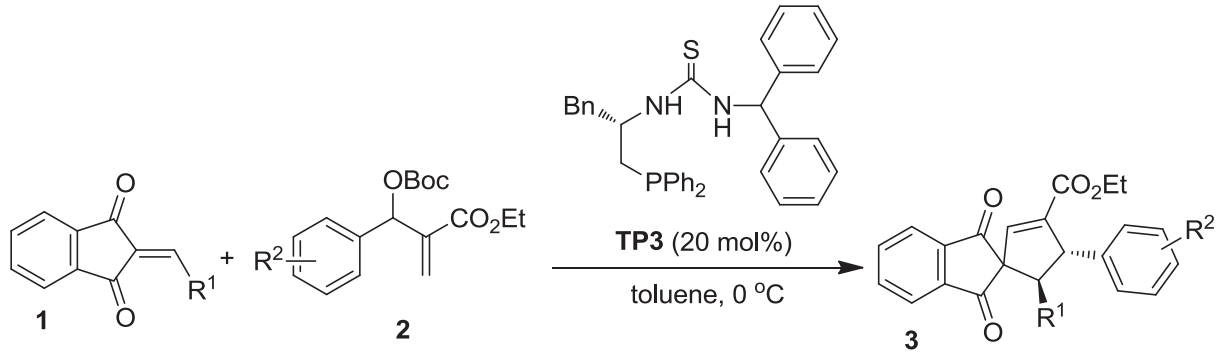
Into a 25 mL oven-dried reaction flask under Ar gas protection were added, 2-benzylidene-1*H*-indene-1,3(2*H*)-dione (0.1 mmol), MBH carbonates (0.2 mmol), catalyst (0.02 mmol), and toluene (10 mL). The reaction mixture was stirred at 0 °C for 144 h, then the solvent was removed under reduced pressure and the residue was purified by flash column chromatography.

Catalysts **TP1**, **TP2**, **TP3**, **TP4**, and **TP5** were synthesized according to the previous literature[15] and the preparation of new catalysts **TB6**, **TB7**, and **TB8** can be found in the Supplementary data.

*3.2.1. (S)-3-(Butylamino)-4-((1-(diphenylphosphino)-3-phenylpropan-2-yl)amino)cyclobut-3-ene-1,2-dione (**TP7**).* A white solid, Mp: 251–252 °C. ^1H NMR (DMSO-d_6, 400 MHz, TMS) δ 0.89 (t, *J*=7.2 Hz, 3H, CH_3), 1.25–1.31 (m, 2H, CH_2), 1.44 (br, 2H, CH_2), 2.35–2.42 (m, 1H, CH), 2.50–2.53 (m, 1H, CH), 2.90–3.02 (m, 2H, CH_2), 3.34–3.43 (m, 4H), 4.20 (br, 1H, CH), 7.10–7.43 (m, 15H, Ar). ^{31}P NMR (161.93 MHz, DMSO-d_6, 85% H_3PO_4): δ −18.68. IR (CH_2Cl_2) ν 1026, 1091, 1231, 1352, 1431, 1475, 1560, 1636, 1802, 2875, 2928 cm^{-1}. MS (ESI) *m/e* 471.1 (M^++1). HRMS (ESI) calcd for $C_{29}H_{31}N_2O_2P$: 470.2123. Found: 470.2118.

*3.2.2. (S)-3-(Cyclohexylamino)-4-((1-(diphenylphosphino)-3-phenylpropan-2-yl)amino)cyclobut-3-ene-1,2-dione (**TP8**).* A white solid, Mp:285–286 °C. ^1H NMR (DMSO-d_6, 400 MHz, TMS) δ 1.12–1.32 (m, 6H, CH_2), 1.52–1.56 (m, 1H, CH), 1.65 (br, 2H, CH_2), 1.82–1.84 (m, 2H, CH_2), 2.32–2.44 (m, 2H, CH_2), 2.90–3.04 (m, 2H, CH_2), 3.35 (s, 2H), 3.67 (br, 1H, NH), 4.21 (br, 1H, CH), 7.14–7.34 (m,

Table 3
Substrate scope for the asymmetric [3+2] annulation



Entry[a]	R^1	R^2	Yield (%)[b]	ee (%)[c]
1	**1a**, 4-$NO_2C_6H_4$	**2b**, 4-Cl	**3b**, 52	88[d]
2	**1a**, 4-$NO_2C_6H_4$	**2c**, 4-Br	**3c**, 51	92
3	**1a**, 4-$NO_2C_6H_4$	**2d**, 4-CN	**3d**, 65	91[d]
4	**1a**, 4-$NO_2C_6H_4$	**2e**, 4-CF_3	**3e**, 50	91
5	**1a**, 4-$NO_2C_6H_4$	**2f**, 2-Cl	**3f**, 68	97
6	**1a**, 4-$NO_2C_6H_4$	**2g**, 2-Br	**3g**, 50	97
7	**1a**, 4-$NO_2C_6H_4$	**2h**, 3-NO_2	**3h**, 75	87
8	**1a**, 4-$NO_2C_6H_4$	**2i**, 3-Cl	**3i**, 60	91
9	**1a**, 4-$NO_2C_6H_4$	**2j**, 3-Br	**3j**, 51	90[d]
10	**1a**, 4-$NO_2C_6H_4$	**2k**, 2,4-Cl_2	**3k**, 62	96
11	**1a**, 4-$NO_2C_6H_4$	**2l**, 2,3-Cl_2	**3l**, 67	98
12	**1a**, 4-$NO_2C_6H_4$	**2m**, 3,4-Cl_2	**3m**, 54	92
13	**1a**, 4-$NO_2C_6H_4$	**2n**, 2,6-Cl_2	**3n**, 30	92
14	**1a**, 4-$NO_2C_6H_4$	**2o**, 4-F, 3-Br	**3o**, 50	90
15	**1a**, 4-$NO_2C_6H_4$	**2p**, 4-CH_3	Trace	—[f]
16	**1b**, C_6H_5	**2a**, 4-NO_2	**3p**, 75[e]	66[d]
17	**1c**, 3-BrC_6H_4	**2a**, 4-NO_2	**3q**, 64[e]	67[d]
18	**1d**, 4-BrC_6H_4	**2a**, 4-NO_2	**3r**, 75[e]	65
19	**1e**, Cyclohexyl	**2a**, 4-NO_2	**3s**, 68[e]	−67

[a] The reaction was carried out by employing **1** (0.1 mmol), **2** (0.2 mmol) and toluene (10 mL) at 0 °C within 144 h.
[b] Isolated yield.
[c] Determined by Chiral HPLC.
[d] Catalyst **TP4** was used.
[e] The reaction was carried out within 48 h.
[f] Not determined.

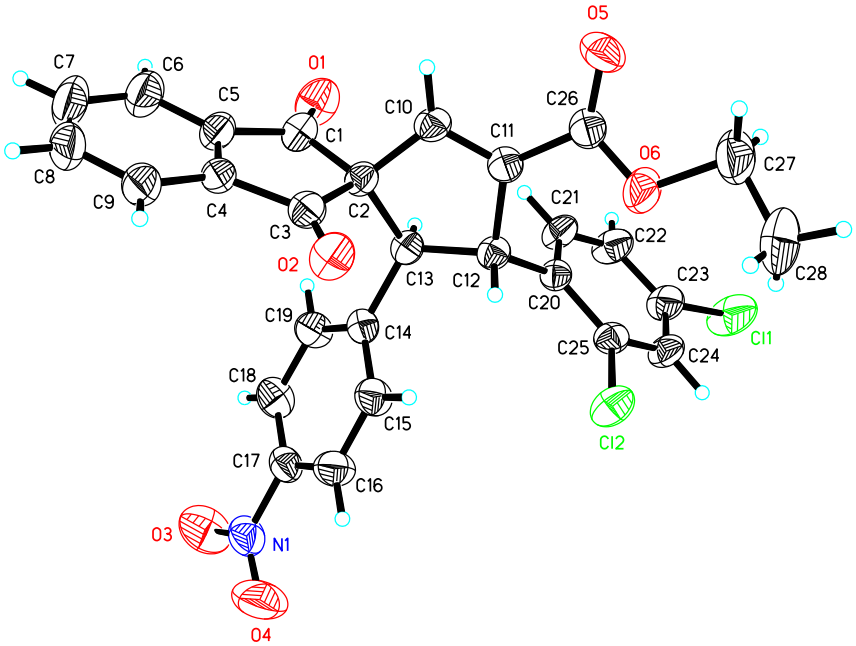
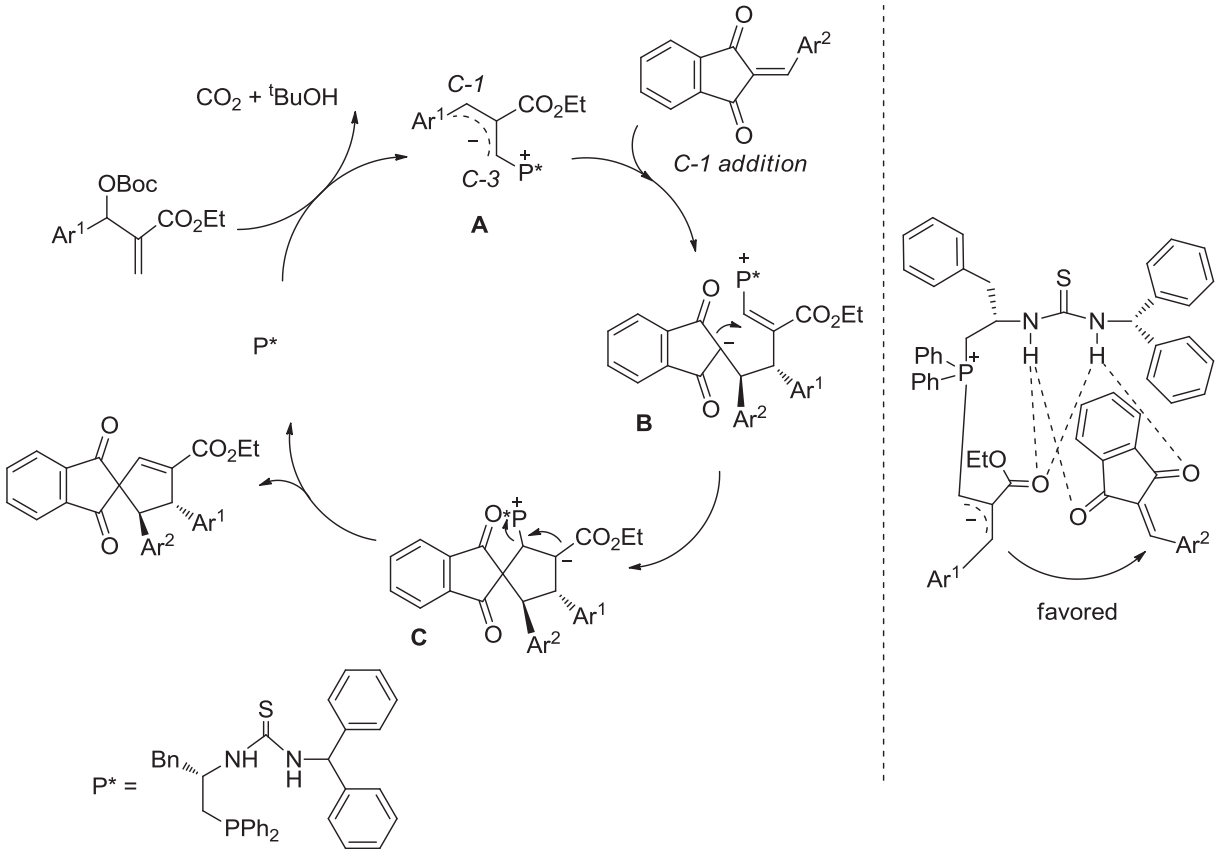


Fig. 1. X-ray crystal structure of **3k**.



Scheme 1. A proposed mechanism.

15H, Ar). ^{31}P NMR (161.93 MHz, DMSO-d_6, 85% H_3PO_4): δ −18.84. IR (CH_2Cl_2) ν 1030, 1242, 1372, 1433, 1471, 1553, 1637, 1790, 2842, 2932 cm^{-1}. MS (ESI) *m*/*e* 497.1 (M^++1). HRMS (ESI) calcd for $C_{31}H_{33}N_2O_2P$: 496.2280. Found: 496.2271.

*3.2.3. (S)-3-(Benzhydrylamino)-4-((1-(diphenylphosphino)-3-phenylpropan-2-yl)amino)cyclobut-3-ene-1,2-dione (**TP9**).* A white solid, Mp: 297–298 °C. ^{1}H NMR (DMSO-d_6, 400 MHz, TMS) δ 2.36–2.43 (m, 1H, CH), 2.54–2.57 (m, 1H, CH), 2.89–2.94 (m, 1H, CH), 3.02–3.07 (m, 1H, CH), 4.25 (br, 1H, CH), 6.32 (s, 1H, CH), 7.14–7.41 (m, 25H, Ar), 8.02 (br, 1H, NH). ^{31}P NMR (161.93 MHz, DMSO-d_6, 85% H_3PO_4): δ −18.63. IR (CH_2Cl_2) ν 1006, 1009, 1201, 1358, 1434, 1455, 1548, 1638, 1799, 3021, 3143 cm^{-1}. MS (ESI) *m*/*e* 581.2 (M^++1). HRMS (ESI) calcd for $C_{38}H_{33}N_2O_2P$: 580.2280. Found: 580.2277.

*3.2.4. Compound **3a**.* A white solid, Mp: 225–226 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.11 (t, *J*=7.2 Hz, 3H, CH_3), 4.03–4.15 (m, 2H, CH_2), 4.23 (d, *J*=10.2 Hz, 1H, CH), 5.14 (dd, *J*=10.2 Hz, *J*=1.2 Hz, 1H, CH), 6.68 (d, *J*=1.2 Hz, 1H,=CH), 7.33 (d, *J*=8.7 Hz, 2H, Ar), 7.43 (d, *J*=8.7 Hz, 2H, Ar), 7.80–7.90 (m, 3H, Ar), 7.97 (d, *J*=8.7 Hz, 2H, Ar), 8.03 (d, *J*=7.2 Hz, 1H, Ar), 8.15 (d, *J*=8.7 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.9, 54.1, 61.1, 61.2, 71.5, 123.7, 123.8, 124.0, 128.3, 129.9, 136.7, 136.8, 139.2, 141.5, 141.6, 141.7, 143.8, 147.2, 147.4, 148.7, 162.6, 197.5, 198.9. IR (CH_2Cl_2) ν 911, 1012, 1100, 1168, 1233, 1270, 1343, 1515, 1599, 1701, 1721, 2850, 2927 cm^{-1}. MS (ESI) *m*/*e* 535.0 (M^++Na). HRMS (ESI) calcd for $C_{28}H_{20}N_2NaO_8$: 535.1112. Found: 535.1110; Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column [λ=230 nm; eluent: Hexane/Isopropanol=60/40; Flow rate: 0.50 mL/min; t_{major}=37.67 min, t_{minor}=58.60 min; ee%=89%; $[\alpha]_D^{20}$=+206.7 (*c* 1.0, CH_2Cl_2)].

*3.2.5. Compound **3b**.* A white solid, Mp: 86–87 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.09 (t, *J*=7.2 Hz, 3H, CH_3), 4.04 (dq, *J*=11.2 Hz, *J*=7.2 Hz 1H, CH_2), 4.13 (dq, *J*=11.2 Hz, *J*=7.2 Hz, 1H, CH_2), 4.23 (d, *J*=10.4 Hz, 1H, CH), 4.99 (dd, *J*=10.4 Hz, *J*=2.4 Hz, 1H, CH), 6.60 (d, *J*=2.4 Hz, 1H,=CH), 7.12–7.14 (m, 1H, Ar), 7.16–7.23 (m, 3H, Ar), 7.31 (d, *J*=8.8 Hz, 2H, Ar), 7.50–7.81 (m, 2H, Ar), 7.83–7.94 (m, 1H, Ar), 7.96 (d, *J*=8.8 Hz, 2H, Ar), 8.01 (d, *J*=7.2 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.9, 53.8, 60.9, 61.5, 71.5, 123.6, 123.7, 128.8, 128.9, 129.9, 133.1, 136.5, 136.7, 138.1, 139.5, 141.5, 141.7, 142.4, 144.7, 147.3, 163.0, 197.9, 199.2. IR (CH_2Cl_2) ν 909, 1014, 1095, 1168, 1231, 1344, 1492, 1518, 1597, 1702, 2875, 2978 cm^{-1}. MS (ESI) *m*/*e* 502.0 (M^++1). HRMS (MALDI) calcd for $C_{28}H_{20}NO_6ClNa$: 524.0880. Found: 524.0871; Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column [λ=230 nm; eluent: Hexane/Isopropanol=60/40; Flow rate: 0.50 mL/min; t_{major}=31.13 min, t_{minor}=40.67 min; ee%=88%; $[\alpha]_D^{20}$=+183.4 (*c* 1.0, CH_2Cl_2)].

*3.2.6. Compound **3c**.* A white solid, Mp: 168–169 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.10 (t, *J*=7.2 Hz, 3H, CH_3), 4.05 (dq, *J*=11.2 Hz, *J*=7.2 Hz, 1H, CH), 4.12 (dq, *J*=11.2 Hz, *J*=7.2 Hz, 1H, CH), 4.19 (d, *J*=10.4 Hz, 1H, CH), 4.99 (dd, *J*=10.4 Hz, *J*=2.8 Hz, 1H, CH), 6.59 (d, *J*=2.8 Hz, 1H,=CH), 7.12 (d, *J*=8.8 Hz, 2H, Ar), 7.30 (d, *J*=8.8 Hz, 2H, Ar), 7.39 (d, *J*=8.8 Hz, 2H, Ar), 7.75–7.81 (m, 2H, Ar), 7.83–7.87 (m, 1H, Ar), 7.95 (d, *J*=8.8 Hz, 2H, Ar), 8.01 (d, *J*=7.6 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.9, 53.9, 60.9, 61.4, 71.4, 121.2, 123.5, 123.7, 129.1, 129.9, 131.8, 136.5, 136.6, 138.2, 140.1, 141.5, 141.7, 142.4, 144.6, 147.3, 163.0, 197.8, 199.2. IR (CH_2Cl_2) ν 908, 1010, 1168, 1232, 1269, 1344, 1488, 1519, 1597, 1703, 1744, 2870, 2958 cm^{-1}. MS (ESI) *m*/*e* 546.0 (M^++1). HRMS (MALDI) calcd for $C_{28}H_{20}NO_6BrNa$: 568.0379. Found: 568.0366; Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column [λ=230 nm; eluent: Hexane/Isopropanol=60/40; Flow rate: 0.50 mL/min;

t_{major}=39.58 min, t_{minor}=51.38 min; ee%=93%; $[\alpha]_D^{20}$=+198.5 (*c* 1.0, CH_2Cl_2)].

3.2.7. Compound ***3d***. A white solid, Mp: 135–136 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.10 (t, *J*=7.2 Hz, 3H, CH_3), 4.01–4.16 (m, 2H, CH_2), 4.20 (d, *J*=10.0 Hz, 1H, CH), 5.08 (dd, *J*=10.0 Hz, *J*=2.0 Hz, 1H, CH), 6.66 (d, *J*=2.0 Hz, 1H,=CH), 7.31 (d, *J*=8.4 Hz, 2H, Ar), 7.37 (d, *J*=8.4 Hz, 2H, Ar), 7.58 (d, *J*=8.4 Hz, 2H, Ar), 7.77–7.83 (m, 2H, Ar), 7.85–7.89 (m, 1H, Ar), 7.97 (d, *J*=8.4 Hz, 2H, Ar), 8.02 (d, *J*=7.6 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.8, 54.3, 61.0, 61.2, 71.5, 111.2, 118.5, 123.6, 123.8, 128.2, 129.8, 132.5, 136.6, 136.8, 139.0, 141.4, 141.6, 141.8, 143.9, 146.6, 147.4, 162.6, 197.5, 198.9. IR (CH_2Cl_2) ν 1015, 1095, 1144, 1168, 1233, 1271, 1345, 1519, 1596, 1703, 2868, 2934 cm^{-1}. MS (ESI) *m*/*e* 493.0 (M^++1). HRMS (MALDI) calcd for $C_{29}H_{20}N_2NaO_6$: 515.1208. Found: 515.1214; Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column [λ=230 nm; eluent: Hexane/Isopropanol=60/40; Flow rate: 0.50 mL/min; t_{major}=56.47 min, t_{minor}=88.75 min; ee%=91%; $[\alpha]_D^{20}$=+200.3 (*c* 1.0, CH_2Cl_2)].

3.2.8. Compound ***3e***. A white solid, Mp: 184–185 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.08 (t, *J*=7.2 Hz, 3H, CH_3), 4.04 (dq, *J*=10.8 Hz, *J*=7.2 Hz, 1H, CH), 4.12 (dq, *J*=10.8 Hz, *J*=7.2 Hz, 1H, CH), 4.23 (d, *J*=10.4 Hz, 1H, CH), 5.09 (dd, *J*=10.4 Hz, *J*=2.0 Hz, 1H, CH), 6.64 (d, *J*=2.0 Hz, 1H,=CH), 7.32 (d, *J*=8.4 Hz, 2H, Ar), 7.37 (d, *J*=8.0 Hz, 2H, Ar), 7.53 (d, *J*=8.0 Hz, 2H, Ar), 7.76–7.82 (m, 2H, Ar), 7.84–7.88 (m, 1H, Ar), 7.96 (d, *J*=8.4 Hz, 2H, Ar), 8.02 (d, *J*=7.6 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.8, 54.1, 60.9, 61.4, 71.5, 123.6, 123.8, 124.0 (q, *J*=270.2 Hz), 125.7 (d, *J*=3.8 Hz), 127.8, 129.5 (q, *J*=32.4 Hz), 129.9, 136.6, 137.7, 138.6, 141.5, 141.7, 142.2, 144.3, 145.2, 147.3, 162.8, 197.7, 199.1. ^{19}F NMR (376 MHz, $CFCl_3$) δ −62.6. IR (CH_2Cl_2) ν 835, 1019, 1069, 1112, 1156, 1234, 1323, 1370, 1520, 1597, 1705, 2850, 2930 cm^{-1}. MS (ESI) *m*/*e* 536.0 (M^++1). HRMS (MALDI) calcd for $C_{29}H_{20}NO_6F_3Na$: 558.1141. Found: 558.1135; Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column [λ=230 nm; eluent: Hexane/Isopropanol=60/40; Flow rate: 0.50 mL/min; t_{major}=31.74 min, t_{minor}=40.70 min; ee%=90%; $[\alpha]_D^{20}$=+197.0 (*c* 1.0, CH_2Cl_2)].

3.2.9. Compound ***3f***. A white solid, Mp: 106–107 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.04 (t, *J*=7.2 Hz, 3H, CH_3), 3.99–4.11 (m, 2H, CH_2), 4.30 (d, *J*=7.2 Hz, 1H, CH), 5.72 (d, *J*=7.2 Hz, 1H, CH), 6.61 (s, 1H,=CH), 7.12–7.16 (m, 1H, Ar), 7.26–7.28 (m, 2H, Ar), 7.37 (d, *J*=8.8 Hz, 2H, Ar), 7.49 (d, *J*=6.4 Hz, 1H, Ar), 7.75–7.81 (m, 2H, Ar), 7.83–7.86 (m, 1H, Ar), 7.93 (d, *J*=8.8 Hz, 2H, Ar), 8.01 (d, *J*=7.2 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.7, 49.2, 60.8, 61.7, 71.6, 123.2, 123.66, 123.7, 127.5, 128.1, 128.3, 129.4, 130.1, 134.1, 136.4, 136.6, 137.9, 139.2, 141.6, 141.7, 142.4, 145.3, 147.3, 162.8, 197.7, 199.4. IR (CH_2Cl_2) ν 856, 908, 1034, 1096, 1233, 1269, 1345, 1475, 1519, 1597, 1704, 1744, 2852, 2924 cm^{-1}. MS (ESI) *m*/*e* 524.0 (M^++Na). HRMS (ESI) calcd for $C_{28}H_{20}ClNNaO_6$: 524.0871. Found: 524.0872; Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column [λ=230 nm; eluent: Hexane/Isopropanol=60/40; Flow rate: 0.50 mL/min; t_{major}=30.87 min, t_{minor}=37.24 min; ee%=97%; $[\alpha]_D^{20}$=+243.8 (*c* 1.0, CH_2Cl_2)].

3.2.10. Compound ***3g***. A white solid, Mp: 119–120 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.04 (t, *J*=6.9 Hz, 3H, CH_3), 3.98–4.14 (m, 2H, CH_2), 4.30 (d, *J*=9.6 Hz, 1H, CH), 5.70 (d, *J*=9.6 Hz, 1H, CH), 6.62 (s, 1H,=CH), 7.04–7.10 (m, 1H, Ar), 7.32–7.51 (m, 5H, Ar), 7.76–7.88 (m, 3H, Ar), 7.94 (d, *J*=8.4 Hz, 2H, Ar), 8.02 (d, *J*=7.5 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.7, 52.2, 60.8, 62.0, 71.7, 123.2, 123.7, 123.8, 125.0, 128.1, 128.3, 128.7, 130.4, 132.8, 136.4, 136.6, 137.8, 141.0, 141.7, 142.3, 145.5, 147.3, 162.8, 197.7, 199.4. IR (CH_2Cl_2) ν 1235, 1268, 1322, 1346, 1521, 1706, 1744, 2972, 3040 cm^{-1}. MS (ESI) *m*/*e* 546.0 (M^++1). HRMS (MALDI) calcd for $C_{28}H_{20}NO_6BrNa$: 568.0362. Found: 568.0366; Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column [λ=230 nm; eluent: Hexane/Isopropanol=60/40; Flow rate: 0.50 mL/min; t_{major}=44.42 min, t_{minor}=56.46 min; ee%=97%; $[\alpha]_D^{20}$=+229.8 (*c* 1.0, CH_2Cl_2)].

3.2.11. Compound ***3h***. A white solid, Mp: 116–117 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.10 (t, *J*=7.2 Hz, 3H, CH_3), 4.01–4.16 (m, 2H, CH_2), 4.25 (d, *J*=8.4 Hz, 1H, CH), 5.15 (dd, *J*=8.4 Hz, *J*=2.0 Hz, 1H, CH), 6.68 (d, *J*=2.0 Hz, 1H,=CH), 7.34 (d, *J*=8.8 Hz, 2H, Ar), 7.46–7.50 (m, 1H, Ar), 7.61 (d, *J*=7.6 Hz, 1H, Ar), 7.77–7.83 (m, 2H, Ar), 7.85–7.89 (m, 1H, Ar), 7.97 (d, *J*=8.8 Hz, 2H, Ar), 8.03 (d, *J*=7.6 Hz, 1H, Ar), 8.08–8.12 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.9, 53.9, 61.0, 61.2, 71.4, 122.47, 122.5, 123.7, 123.8, 129.7, 129.9, 133.7, 136.6, 136.8, 139.2, 141.5, 141.7, 141.8, 143.2, 143.8, 144.6, 147.4, 148.4, 162.6, 197.5, 198.8. IR (CH_2Cl_2) ν 908, 1012, 1093, 1170, 1231, 1268, 1344, 1520, 1595, 1702, 1741, 2857, 2929 cm^{-1}. MS (ESI) *m*/*e* 535.0 (M^++Na). HRMS (ESI) calcd for $C_{28}H_{20}N_2O_8Na$: 535.1112. Found: 535.1099; Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column [λ=230 nm; eluent: Hexane/Isopropanol=60/40; Flow rate: 0.50 mL/min; t_{major}=41.67 min, t_{minor}=63.17 min; ee%=87%; $[\alpha]_D^{20}$=+210.2 (*c* 1.0, CH_2Cl_2)].

3.2.12. Compound ***3i***. A white solid, Mp: 115–116 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.09 (t, *J*=7.2 Hz, 3H, CH_3), 4.00–4.08 (m, 1H, CH_2), 4.09–4.17 (m, 1H, CH_2), 4.23 (d, *J*=10.0 Hz, 1H, CH), 4.99 (d, *J*=10.0 Hz, 1H, CH), 6.61 (s, 1H,=CH), 7.13–7.27 (m, 4H, Ar), 7.31 (d, *J*=8.4 Hz, 2H, Ar), 7.75–7.81 (m, 2H, Ar), 7.83–7.87 (m, 1H, Ar), 7.96 (d, *J*=8.4 Hz, 2H, Ar), 8.02 (d, *J*=7.6 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.8, 53.9, 60.8, 61.3, 71.5, 123.6, 123.7, 125.8, 127.5, 127.6, 129.87, 129.9, 134.5, 136.5, 136.6, 138.2, 141.5, 141.7, 142.3, 143.1, 144.5, 147.3, 162.9, 197.8, 199.1. IR (CH_2Cl_2) ν 910, 1016, 1094, 1170, 1233, 1343, 1495, 1520, 1599, 1703, 2876, 2980 cm^{-1}. MS (ESI) *m*/*e* 524.0 (M^++Na). HRMS (MALDI) calcd for $C_{28}H_{20}NO_6ClNa$: 524.0882. Found: 524.0871; Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column [λ=230 nm; eluent: Hexane/Isopropanol=60/40; Flow rate: 0.50 mL/min; t_{major}=32.60 min, t_{minor}=45.33 min; ee%=91%; $[\alpha]_D^{20}$=+214.2 (*c* 1.0, CH_2Cl_2)].

3.2.13. Compound ***3j***. A white solid, Mp: 104–105 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.09 (t, *J*=7.2 Hz, 3H, CH_3), 4.04 (dq, *J*=11.2 Hz, *J*=7.2 Hz, 1H, CH), 4.14 (dq, *J*=11.2 Hz, *J*=7.2 Hz, 1H, CH), 4.23 (d, *J*=10.4 Hz, 1H, CH), 5.14 (dd, *J*=10.4 Hz, *J*=2.0 Hz, 1H, CH), 6.68 (d, *J*=2.0 Hz, 1H,=CH), 7.12–7.19 (m, 2H, Ar), 7.31 (d, *J*=8.8 Hz, 2H, Ar), 7.33–7.35 (m, 1H, Ar), 7.38–7.39 (m, 1H, Ar), 7.75–7.81 (m, 2H, Ar), 7.83–7.87 (m, 1H, Ar), 7.96 (d, *J*=8.8 Hz, 2H, Ar), 8.02 (d, *J*=7.2 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.8, 53.9, 60.9, 61.3, 71.5, 122.7, 123.6, 123.7, 126.3, 129.9, 130.2, 130.5, 136.5, 136.6, 138.2, 141.5, 141.7, 142.3, 143.3, 144.5, 147.3, 162.9, 197.8, 199.1. IR (CH_2Cl_2) ν 905, 1010, 1096, 1231, 1268, 1345, 1490, 1518, 1598, 1702. 2930 cm^{-1}. MS (ESI) *m*/*e* 568.0 (M^++Na). HRMS (MALDI) calcd for $C_{28}H_{20}NO_6BrNa$: 568.0369. Found: 568.0366; Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column [λ=230 nm; eluent: Hexane/Isopropanol=60/40; Flow rate: 0.50 mL/min; t_{major}=40.66 min, t_{minor}=55.19 min; ee%=90%; $[\alpha]_D^{20}$=+186.3 (*c* 1.0, CH_2Cl_2)].

3.2.14. Compound ***3k***. A white solid, Mp: 184–185 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.10 (t, *J*=7.2 Hz, 3H, CH_3), 4.02–4.22 (m, 2H, CH_2), 4.23 (d, *J*=9.0 Hz, 1H, CH), 5.66 (d, *J*=9.0 Hz, 1H, CH), 6.62 (s, 1H,=CH), 7.27–7.29 (m, 2H, Ar), 7.36 (d, *J*=8.4 Hz, 2H, Ar), 7.43 (d, *J*=7.8 Hz, 1H, Ar), 7.76–7.88 (m, 3H, Ar), 7.94 (d, *J*=8.4 Hz, 2H, Ar), 8.02 (d, *J*=7.2 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.8, 49.0, 60.9, 61.6, 71.5, 123.3, 123.7, 123.8, 127.9, 128.9, 129.2, 130.1, 133.4, 134.7, 136.5, 136.7, 137.9, 138.4, 141.6, 142.0, 144.7, 147.4, 162.6, 197.5, 199.2. IR (CH_2Cl_2) ν 742, 846, 1017, 1100, 1234, 1345, 1475, 1519, 1588, 1702, 2853, 2963 cm^{-1}. MS (ESI) *m*/*e* 558.0 (M^++Na).

HRMS (MALDI) calcd for $C_{28}H_{19}NO_6Cl_2Na$: 558.0482. Found: 558.0477; Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column [λ=230 nm; eluent: Hexane/Isopropanol=60/40; Flow rate: 0.50 mL/min; t_{major}=33.73 min, t_{minor}=42.43 min; ee%=96%; $[\alpha]_D^{20}$=+255.7 (*c* 1.0, CH_2Cl_2)].

3.2.15. Compound ***3l***. A white solid, Mp: 109–110 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.06 (t, *J*=7.2 Hz, 3H, CH_3), 3.98–4.13 (m, 2H, CH_2), 4.27 (d, *J*=7.2 Hz, 1H, CH), 5.77 (d, *J*=7.2 Hz, 1H, CH), 6.63 (s, 1H,=CH), 7.22–7.27 (m, 1H, Ar), 7.32–7.39 (m, 1H, Ar), 7.37 (d, *J*=8.4 Hz, 2H, Ar), 7.42 (d, *J*=7.6 Hz, 1H, Ar), 7.76–7.81 (m, 2H, Ar), 7.83–7.87 (m, 1H, Ar), 7.94 (d, *J*=8.4 Hz, 2H, Ar), 8.01 (d, *J*=8.0 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.7, 50.2, 60.9, 61.7, 71.6, 123.3, 123.7, 123.8, 126.2, 127.7, 129.3, 130.1, 132.5, 133.2, 136.5, 136.7, 138.2, 141.6, 141.8, 142.1, 145.0, 147.4, 162.6, 197.5, 199.2. IR (CH_2Cl_2) ν 848, 902, 1015, 1095, 1167, 1232, 1269, 1344, 1519, 1597, 1705, 1743, 2925, 2957 cm^{-1}. MS (ESI) *m*/*e* 535.9 (M^++1). HRMS (MALDI) calcd for $C_{28}H_{19}NO_6Cl_2Na$: 558.0478. Found: 558.0482; Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column [λ=230 nm; eluent: Hexane/Isopropanol=60/40; Flow rate: 0.50 mL/min; t_{major}=34.78 min, t_{minor}=42.96 min; ee%=98%; $[\alpha]_D^{20}$=+198.8 (*c* 1.0, CH_2Cl_2)].

3.2.16. Compound ***3m***. A white solid, Mp: 199–200 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.13 (t, *J*=7.2 Hz, 3H, CH_3), 4.07 (dq, *J*=11.2, Hz *J*=7.2 Hz, 1H, CH_2), 4.14 (dq, *J*=11.2, Hz *J*=7.2 Hz, 1H, CH_2), 4.19 (d, *J*=10.4 Hz, 1H, CH), 4.97 (dd, *J*=10.4 Hz, *J*=2.4 Hz, 1H, CH), 6.62 (d, *J*=2.4 Hz, 1H,=CH), 7.10 (dd, *J*=8.4 Hz, *J*=2.4 Hz, 1H, Ar), 7.31 (d, *J*=8.8 Hz, 2H, Ar), 7.32–7.35 (m, 2H, Ar), 7.75–7.82 (m, 2H, Ar), 7.84–7.88 (m, 1H, Ar), 7.97 (d, *J*=8.8 Hz, 2H, Ar), 8.02 (d, *J*=8.0 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.9, 53.5, 61.0, 61.2, 71.4, 123.6, 123.8, 126.9, 129.4, 129.9, 130.7, 131.4, 132.8, 136.6, 136.7, 138.6, 141.3, 141.5, 141.7, 142.0, 144.1, 147.4, 162.7, 197.6, 199.0. IR (CH_2Cl_2) ν 849, 1030, 1078, 1144, 1231, 1269, 1348, 1470, 1523, 1595, 1705, 1742, 2852, 2922 cm^{-1}. MS (ESI) *m*/*e* 535.9 (M^++1). HRMS (MALDI) calcd for $C_{28}H_{19}NO_6Cl_2Na$: 558.0475. Found: 558.0482; Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column [λ=230 nm; eluent: Hexane/Isopropanol=60/40; Flow rate: 0.50 mL/min; t_{major}=34.95 min, t_{minor}=51.14 min; ee%=92%; $[\alpha]_D^{20}$=+189.5 (*c* 1.0, CH_2Cl_2)].

3.2.17. Compound ***3n***. A white solid, Mp: 122–123 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.07 (t, *J*=7.2 Hz, 3H, CH_3), 4.03–4.17 (m, 2H, CH_2), 5.16 (d, *J*=11.1 Hz, 1H, CH), 6.04 (dd, *J*=11.1 Hz, *J*=1.5 Hz, 1H, CH), 6.59 (d, *J*=1.5 Hz, 1H,=CH), 7.04–7.09 (m, 1H, Ar), 7.22 (d, *J*=7.8 Hz, 2H, Ar), 7.48 (d, *J*=8.4 Hz, 2H, Ar), 7.79–7.85 (m, 3H, Ar), 7.93 (d, *J*=8.4 Hz, 2H, Ar), 7.99 (d, *J*=7.2 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.8, 49.9, 56.6, 60.8, 71.5, 123.2, 123.6, 123.7, 128.6, 128.8, 130.0, 130.7, 134.0, 135.2, 136.3, 136.4, 136.5, 141.5, 141.9, 142.3, 144.8, 147.6, 163.2, 198.2, 199.1. IR (CH_2Cl_2) ν 847, 1017, 1100, 1169, 1236, 1346, 1518, 1588, 1701, 2923, 2963 cm^{-1}. MS (ESI) *m*/*e* 536.0 (M^++1). HRMS (MALDI) calcd for $C_{28}H_{19}NaO_6Cl_2Na$: 558.0484. Found: 558.0482; Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column [λ=230 nm; eluent: Hexane/Isopropanol=60/40; Flow rate: 0.50 mL/min; t_{major}=47.54 min, t_{minor}=55.01 min; ee%=69%; $[\alpha]_D^{20}$=+145.3 (*c* 1.0, CH_2Cl_2)].

3.2.18. Compound ***3o***. A white solid, Mp: 223–224 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.12 (t, *J*=7.2 Hz, 3H, CH_3), 4.06 (dq, *J*=11.2 Hz, *J*=7.2 Hz, 1H, CH), 4.14 (dq, *J*=11.2 Hz, *J*=7.2 Hz, 1H, CH), 4.19 (d, *J*=10.0 Hz, 1H, CH), 4.97 (dd, *J*=10.0 Hz, *J*=2.8 Hz, 1H, CH), 6.60 (d, *J*=2.8 Hz, 1H,=CH), 7.00–7.05 (m, 1H, Ar), 7.15–7.19 (m, 1H, Ar), 7.31 (d, *J*=9.2 Hz, 2H, Ar), 7.44 (dd, *J*=6.8 Hz, *J*=2.4 Hz, 1H, Ar), 7.75–7.82 (m, 2H, Ar), 7.84–7.88 (m, 1H, Ar), 7.97 (d, *J*=9.2 Hz, 2H, Ar), 8.02 (d, *J*=7.6 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.9, 53.4, 61.0, 61.3, 71.4, 109.3 (d, *J*=21.4 Hz), 116.4 (d, *J*=22.4 Hz), 123.6, 123.8, 128.1 (d, *J*=7.1 Hz), 129.9, 136.6, 136.7, 138.4, 138.5 (d, *J*=3.7 Hz), 141.5, 141.7, 142.1, 144.3, 147.4, 158.3 (d, *J*=246.1 Hz), 162.8, 197.7, 199.1. ^{19}F NMR (376 MHz, $CFCl_3$) δ −109.16–109.11 (m). IR (CH_2Cl_2) ν 908, 1014, 1088, 1145, 1235, 1349, 1493, 1519, 1598, 1705, 2853, 2930 cm^{-1}. MS (ESI) *m*/*e* 586.0 (M^++Na). HRMS (MALDI) calcd for $C_{28}H_{19}NO_6FBrNa$: 586.0265. Found: 586.0272; Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column [λ=230 nm; eluent: Hexane/Isopropanol=60/40; Flow rate: 0.50 mL/min; t_{major}=36.21 min, t_{minor}=54.41 min; ee%=90%; $[\alpha]_D^{20}$=+181.8 (*c* 1.0, CH_2Cl_2)].

3.2.19. Compound ***3p***. A white solid, Mp: 145–146 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.11 (t, *J*=7.2 Hz, 3H, CH_3), 4.02–4.16 (m, 2H, CH_2), 4.09 (d, *J*=10.4 Hz, 1H, CH), 5.10 (dd, *J*=10.4 Hz, *J*=2.0 Hz, 1H, CH), 6.68 (d, *J*=2.0 Hz, 1H,=CH), 7.03–7.08 (m, 5H, Ar), 7.23 (d, *J*=8.8 Hz, 2H, Ar), 7.71–7.76 (m, 2H, Ar), 7.78–7.82 (m, 1H, Ar), 7.98 (d, *J*=7.2 Hz, 1H, Ar), 8.11 (d, *J*=8.8 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.9, 53.8, 60.9, 62.9, 71.7, 123.4, 123.5, 123.8, 127.9, 128.4, 128.7, 133.8, 136.1, 136.3, 139.4, 141.8, 141.9, 144.3, 146.9, 149.6, 163.0, 198.0, 199.8. IR (CH_2Cl_2) ν 842, 1016, 1106, 1166, 1233, 1514, 1599, 1699, 1724, 2915, 2955 cm^{-1}. MS (ESI) *m*/*e* 468.0 (M^++1). HRMS (MALDI) calcd for $C_{28}H_{21}NO_6Na$: 490.1244. Found: 490.1261; Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column [λ=230 nm; eluent: Hexane/Isopropanol=60/40; Flow rate: 0.50 mL/min; t_{major}=43.13 min, t_{minor}=51.44 min; ee%=66%; $[\alpha]_D^{20}$=+149.2 (*c* 1.0, CH_2Cl_2)].

3.2.20. Compound ***3q***. A white solid, Mp: 245–246 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.10 (t, *J*=7.2 Hz, 3H, CH_3), 4.04 (d, *J*=10.4 Hz, 1H, CH), 4.03–4.13 (m, 2H, CH_2), 5.05 (dd, *J*=10.4 Hz, *J*=2.0 Hz, 1H, CH), 6.67 (d, *J*=2.0 Hz, 1H,=CH), 6.96–7.00 (m, 1H, Ar), 7.08 (d, *J*=8.0 Hz, 1H, Ar), 7.20 (d, *J*=8.0 Hz, 1H, Ar), 7.21 (s, 1H, Ar), 7.41 (d, *J*=8.4 Hz, 2H, Ar), 7.78–7.86 (m, 3H, Ar), 8.01 (d, *J*=7.6 Hz, 1H, Ar), 8.13 (d, *J*=8.4 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.9, 54.0, 60.9, 61.8, 71.6, 122.5, 123.6, 123.7, 123.9, 127.4, 128.4, 130.0, 131.1, 131.9, 136.3, 136.4, 136.5, 139.3, 141.7, 141.8, 144.0, 147.1, 149.1, 162.8, 197.7, 199.3. IR (CH_2Cl_2) ν 1013, 1083, 1229, 1268, 1343, 1512, 1594, 1704, 1743, 2852, 2922 cm^{-1}. MS (ESI) *m*/*e* 545.9 (M^++1). HRMS (MALDI) calcd for $C_{28}H_{20}NO_6BrNa$: 568.0361. Found: 568.0366; Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column [λ=230 nm; eluent: Hexane/Isopropanol=60/40; Flow rate: 0.40 mL/min; t_{major}=30.48 min, t_{minor}=53.03 min; ee%=67%; $[\alpha]_D^{20}$=+150.6 (*c* 1.0, CH_2Cl_2)].

3.2.21. Compound ***3r***. A white solid, Mp: 128–129 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.10 (t, *J*=7.2 Hz, 3H, CH_3), 4.05 (d, *J*=10.4 Hz, 1H, CH), 4.04–4.13 (m, 2H, CH_2), 5.04 (dd, *J*=10.4 Hz, *J*=1.6 Hz, 1H, CH), 6.66 (d, *J*=1.6 Hz, 1H,=CH), 6.98 (d, *J*=8.4 Hz, 2H, Ar), 7.22 (d, *J*=8.4 Hz, 2H, Ar), 7.39 (d, *J*=8.4 Hz, 2H, Ar), 7.79–7.86 (m, 3H, Ar), 7.99 (d, *J*=7.2 Hz, 1H, Ar), 8.13 (d, *J*=8.4 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.9, 54.1, 61.0, 61.8, 71.4, 122.0, 123.6, 123.7, 123.9, 128.4, 130.5, 131.7, 133.0, 136.4, 136.5, 139.3, 141.7, 141.8, 144.1, 147.0, 149.2, 162.8, 197.9, 199.5. IR (CH_2Cl_2) ν 848, 1237, 1269, 1325, 1347, 1523, 1707, 1744, 2973, 3041 cm^{-1} MS (ESI) *m*/*e* 546.0 (M^++1). HRMS (MALDI) calcd for $C_{28}H_{20}NO_6BrNa$: 568.0352. Found: 568.0366; Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column [λ=230 nm; eluent: Hexane/Isopropanol=60/40; Flow rate: 0.50 mL/min; t_{major}=48.82 min, t_{minor}=72.04 min; ee%=65%; $[\alpha]_D^{20}$=+147.2 (*c* 1.0, CH_2Cl_2)].

3.2.22. Compound ***3s***. A white solid, Mp: 168–169 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.37–0.46 (m, 1H, CH), 0.56–0.64 (m, 1H, CH_2), 0.83–0.89 (m, 3H, CH_2), 1.05 (t, *J*=7.2 Hz, 3H, CH_3), 1.32–1.33 (m, 2H, CH_2), 1.43–1.50 (m, 2H, CH_2), 1.68–1.72 (m, 1H, CH_2), 1.89–1.97 (m, 1H, CH), 3.10 (dd, *J*=10.4 Hz, *J*=8.4 Hz, 1H, CH), 3.90–4.46 (m, 2H, CH), 4.46 (dd, *J*=8.4 Hz, *J*=1.2 Hz, 1H, CH), 6.38 (d,

J=1.2 Hz, 1H,=CH), 7.62 (d, J=8.4 Hz, 2H, Ar), 7.93–7.96 (m, 2H, Ar), 8.04–8.10 (m, 2H, Ar), 8.20 (d, J=8.4 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.8, 25.5, 25.6, 32.4, 33.1, 39.0, 55.0, 60.2, 60.6, 70.4, 123.5, 123.7, 124.2, 129.7, 136.3, 139.0, 140.5, 141.2, 143.3, 146.6, 152.4, 162.8, 198.4, 199.7. IR (CH_2Cl_2) ν 1105, 1142, 1160, 1233, 1342, 1509, 1593, 1701, 2842, 2933 cm^{-1}. MS (ESI) m/e 474.1 (M^++1). HRMS (MALDI) calcd for $C_{28}H_{27}NO_6Na$: 496.1729. Found: 496.1731; Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column [λ=230 nm; eluent: Hexane/Isopropanol=60/40; Flow rate: 0.50 mL/min; t_{major}=31.90 min, t_{minor}=28.90 min; ee%=67%; $[\alpha]_D^{20}$=−91.1 (c 1.0, CH_2Cl_2)].

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Supplementary data

Detailed description of experimental procedures, spectral charts, and analytical data for new compounds shown in schemes and figures, CIF files, and X-ray crystal data of **3k** (CCDC 872832). This material is available free of charge from authors or via the internet. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tet.2012.07.013.

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