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Enantioselective Allylic Amination of Morita–Baylis–Hillman Carbonates Catalysed by Modified Cinchona Alkaloids

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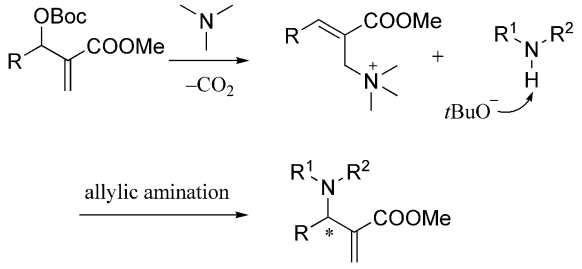
An efficient procedure for the asymmetric allylic amination of Morita–Baylis–Hillman carbonates with cyclic imides catalysed by commercially available cinchona alkaloids is reported. It proves to be a facile protocol that affords α-methylene β-amino esters with good-to-excellent enantioselectivities (up to 94 % *ee*) and in high yields (up to 97 %).

Introduction

β-Amino carbonyl compounds containing an α-alkylidene group are widely used in the synthesis of medicinal reagents and natural products.[1] Therefore, the development of protocols for the synthesis of these multifunctional compounds has triggered increasing interest over the past few decades. Apparently, the aza-Morita–Baylis–Hillman (aza-MBH) reaction provides the most efficient approach to these materials.[2] Since Perlmutter and Teo reported the aza-MBH reaction between a preformed *N*-tosylimine and methyl acrylate,[3] many groups have focused on the asymmetric aza-MBH reaction of *N*-sulfonyl imines and various activated olefins catalysed by diverse chiral tertiary phosphane, amine or bifunctional organocatalysts.[4] Raheem and Jacobsen have also employed chiral thiourea derivatives to catalyse the aza-MBH reaction between methyl acrylate and *N*-nosylarylimines and high enantioselectivities and fair yields were obtained.[5] Furthermore, Balan and Adolfsson have reported a three-component reaction with aryl aldehyde, pTsNH$_2$, and methyl acrylate using the combined Ti(O*i*Pr)$_4$ and β-ICD catalyst system.[6] However, the reported methods were generally limited to specialized imines bearing electron-withdrawing sulfonyl groups, which might restrict their applications in organic synthesis. Thus, some alternative processes for the preparation of α-alkylidene-β-amino derivatives have been explored.[7] We have reported an asymmetric tandem Mannich-type Wittig reaction that affords highly enantioenriched *N*-Boc-protected α-methylene β-amino esters.[8] In addition, the Lewis base catalysed direct asymmetric allylic amination of Morita–Baylis–Hillman adducts is also a very attractive strategy, however, only low-to-moderate enantioselectivities have been obtained to date.[9]

Recently, we presented the results of some asymmetric allylic alkylation reactions of Morita–Baylis–Hillman carbonates catalysed by cinchona alkaloid based tertiary amines.[10] We then turned our attention to the development of a highly enantioselective allylic amination reaction of MBH carbonates operating through the same catalytic mechanism that would be an effective process for producing chiral α-methylene β-amino ester derivatives (Scheme 1).



Scheme 1. Allylic amination of MBH carbonates to access chiral α-methylene β-amino esters.

Results and Discussion

In an initial study, a variety of nitrogen nucleophiles **1** (Figure 1)[11] were screened in the reaction with MBH carbonate **2a** catalysed by quinidine in DCE (1,2-dichloroethane) at room temperature. The results are summarized in Table 1. Although all the tested nitrogen nucleophiles exhibited good reactivity (Table 1, entries 1–8), in general, better enantioselectivity was obtained when cyclic imide-

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type nitrogen sources **1d–h** were used (entries 4–8).[9] Subsequently, some modified cinchona alkaloids were tested in the reaction of phthalimide **1d** with MBH carbonate **2a** (entries 9–11). To our gratification, of these alkaloids, $(DHQD)_2PYR$ exhibited the best enantiocontrol (entry 11). Moreover, an even higher *ee* was observed when 1,8-naphthalimide **1h** was used (entry 12). $(DHQ)_2PYR$ gave the product with the opposite configuration with a moderate enantioselectivity (entry 13). It was also pleasing that the reaction could be more effectively conducted at 35 °C without affecting the enantioselectivity (entry 14). Although the reaction time could be greatly shortened at 50 °C, the enantioselectivity was also reduced (entry 15). When the reaction was performed in a number of other solvents, similar data were obtained (entries 16–19).

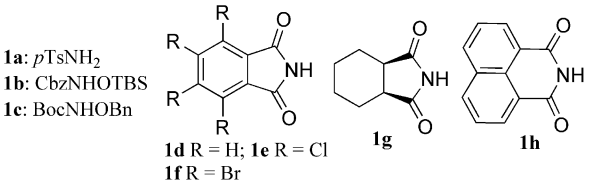
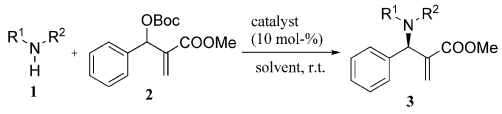


Figure 1. The structures of various nitrogen nucleophiles.

Table 1. Screening studies of nitrogen nucleophiles in the allylic amination of MBH carbonates.[a]

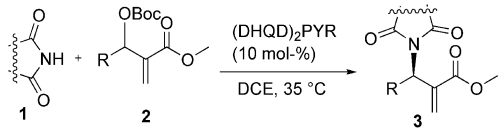


Entry	NuH	Catalyst	Solvent	*t* [h]	Yield[b] [%]	*ee*[c] [%]
1	**1a**	quinidine	DCE	69	71	22
2	**1b**	quinidine	DCE	106	87	12
3	**1c**	quinidine	DCE	85	50	30
4	**1d**	quinidine	DCE	28	40	51
5	**1e**	quinidine	DCE	39	83	47
6	**1f**	quinidine	DCE	59	66	50
7	**1g**	quinidine	DCE	35	61	50
8	**1h**	quinidine	DCE	48	65	40
9	**1d**	$(DHQD)_2AQN$	DCE	42	81	60
10	**1d**	$(DHQD)_2PHAL$	DCE	42	59	14
11	**1d**	$(DHQD)_2PYR$	DCE	84	91	85
12	**1h**	$(DHQD)_2PYR$	DCE	95	92	90
13	**1h**	$(DHQ)_2PYR$	DCE	95	92	–72
14[d]	**1h**	$(DHQD)_2PYR$	DCE	70	94	90
15[e]	**1h**	$(DHQD)_2PYR$	DCE	24	94	84
16[d]	**1h**	$(DHQD)_2PYR$	$CHCl_3$	71	92	85
17[d]	**1h**	$(DHQD)_2PYR$	THF	98	92	91
18[d]	**1h**	$(DHQD)_2PYR$	dioxane	105	86	90
19[d]	**1h**	$(DHQD)_2PYR$	toluene	92	86	88

[a] Unless otherwise noted, the reactions were performed with 0.1 mmol of **1**, 0.2 mmol of **2a** and 0.01 mmol of catalyst in 1 mL of solvent at room temp. [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] At 35 °C. [e] At 50 °C.

Having established the optimal reaction conditions, the scope and limitation of the asymmetric allylic amination reaction were investigated with a variety of cyclic imides and MBH carbonates **2** in DCE catalysed by 10 mol-% of $(DHQD)_2PYR$ at 35 °C. The results are summarized in Table 2. For naphthaline-1,8-dicarboximide **1h**, good-to-excellent enantioselectivities and high yields were generally achieved with MBH carbonates bearing diverse electron-withdrawing or -donating aryl and heteroaryl groups (Table 2, entries 1–13). On the other hand, phthalimides **1d**, **1e** and **1f** were also tested with a few MBH carbonates and good results were delivered (entries 14–20). Nevertheless, MBH carbonates bearing a β-alkyl substituent failed to afford the desired allylic amination products.

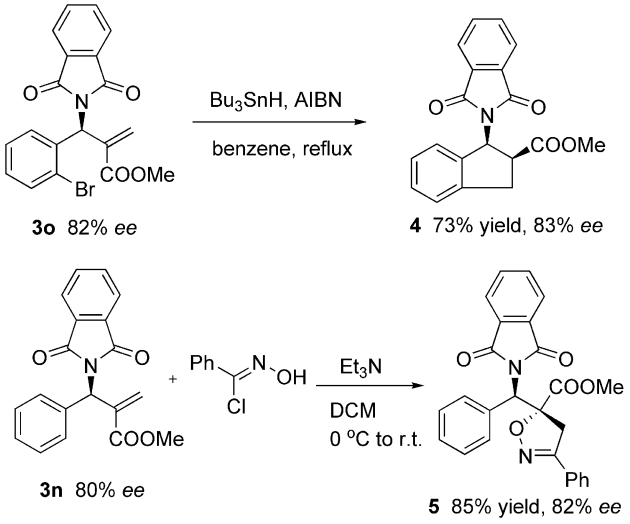
Table 2. Asymmetric allylic amination reaction of imides **1** with MBH carbonates **2**.[a]



Entry	R	**1**	*t* [h]	**3**	Yield[b] [%]	*ee*[c] [%]
1	Ph	**1h**	70	**3a**	92	90
2	1-naphthyl	**1h**	22	**3b**	97	94
3	*p*-ClC_6H_4	**1h**	67	**3c**	94	91
4	*m*-ClC_6H_4	**1h**	60	**3d**	96	89
5[d]	*o*-ClC_6H_4	**1h**	48	**3e**	94	91
6	*p*-FC_6H_4	**1h**	92	**3f**	95	93
7	*o*-BrC_6H_4	**1h**	25	**3g**	96	93
8	*o*-$O_2NC_6H_4$	**1h**	23	**3h**	89	90
9	3,4-$Cl_2C_6H_3$	**1h**	69	**3i**	95	90
10	*p*-$MeOC_6H_4$	**1h**	106	**3j**	95	93
11	*m*-MeC_6H_4	**1h**	83	**3k**	96	90
12	*p*-MeC_6H_4	**1h**	83	**3l**	92	88
13	2-thienyl	**1h**	40	**3m**	90	82
14[e]	Ph	**1d**	47 (84)	**3n**	90 (91)	80 (85)
15[e]	*o*-BrC_6H_4	**1d**	29 (52)	**3o**	92 (93)	82 (87)
16	1-naphthyl	**1d**	18	**3p**	91	89
17	Ph	**1e**	28	**3q**	91	89
18	*o*-ClC_6H_4	**1e**	30	**3r**	92	90
19	*o*-BrC_6H_4	**1e**	26	**3s**	92	90
20	Ph	**1f**	30	**3t**	86	87

[a] Unless otherwise noted, reactions were performed with 0.1 mmol of **1**, 0.2 mmol of **2** and 0.01 mmol of $(DHQD)_2PYR$ in 1 mL of DCE at 35 °C. [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] The absolute configuration of **3e** was determined by X-ray analysis.[12] The other products were assigned by analogy. [e] The data in parentheses were obtained at room temp.

As outlined in Scheme 2, the allylic products could be smoothly transformed into more complex compounds. For example, intramolecular radical cyclization of the product **3o** proceeded efficiently in the presence of Bu_3SnH and AIBN with no impact on the enantiopurity of the reaction and is thus a facile route to the interesting β-amino ester **4**. Also, the 1,3-dipolar cycloaddition reaction of the allylic amination product **3n** with chlorobenzaldoxime was performed in DCM and the diastereomerically pure product **5** was isolated in high yield and with the *ee* value retained.[10b,13]



Scheme 2. Transformations of the allylic amination products.

Conclusions

We have developed an efficient and enantioselective allylic amination of MBH carbonates catalysed by modified cinchona alkaloids. A range of α-methylene β-amino esters have been obtained with good-to-excellent enantioselectivities (up to 94% *ee*) and high yields (up to 97%). The allylic products could be smoothly transformed into more complex compounds in good yields without any racemization. Further studies on cinchona alkaloid catalysed asymmetric allylic alkylation reactions are under way in our laboratory.

Experimental Section

General: ^{1}H NMR spectra were recorded at 400 or 300 MHz (Varian) and ^{13}C NMR spectra at 50 or 100 MHz (Varian) with tetramethylsilane as the internal standard. Chemical shifts are reported in ppm downfield from $CDCl_3$ (δ = 7.27 ppm) for ^{1}H NMR and relative to the central $CDCl_3$ resonance (δ = 77.0 ppm) for ^{13}C NMR spectroscopy. Coupling constants are given in Hz. Optical rotations were measured at 589 nm at 20 °C. Enantiomeric excesses were determined by HPLC analysis using Chiralpak AD and Chiralcel OD columns. DCE was distilled from CaH_2. All other chemicals were used as commercially available without further purification. Cinchona alkaloid catalysts $(DHQD)_2PHAL$, $(DHQD)_2PYR$, $(DHQD)_2AQN$ and $(DHQ)_2PYR$ were purchased from Aldrich Chemical Company. Morita–Baylis–Hillman carbonates were prepared according to the literature procedure.[14]

General Procedure for the Catalytic Allylic Amination of Morita–Baylis–Hillman Carbonates: A mixture of cyclic imide **1** (0.1 mmol), Morita–Baylis–Hillman carbonate **2** (0.2 mmol) and catalyst $(DHQD)_2PYR$ (8.8 mg, 0.01 mmol) in anhydrous DCE (1 mL) was stirred at 35 °C for a specified reaction time. Then the solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to give the product **3**.

Methyl (*R*)-2-{[1,3-Dioxo-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl](phenyl)methyl}acrylate (3a): R_f = 0.3 (petroleum ether/EtOAc = 10:1); 92% yield. $[\alpha]_D^{20}$ = 111.4 (c = 0.30, $CHCl_3$); 90% *ee*, determined by HPLC analysis [Daicel chiralpak AD, *n*-hexane/*i*PrOH = 90:10, 1.0 mL/min, λ = 220 nm, t(major) = 28.32, t(minor) = 24.49 min]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.58 (dd, J = 7.2, 1.2 Hz, 2 H), 8.19 (dd, J = 8.2, 1.0 Hz, 2 H), 7.75–7.71 (m, 2 H), 7.58–7.55 (m, 2 H), 7.36–7.28 (m, 3 H), 7.19 (t, J = 1.8 Hz, 1 H), 6.47 (d, J = 2.0 Hz, 1 H), 5.60 (d, J = 2.0 Hz, 1 H), 3.67 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.6, 164.3, 139.1, 137.7, 133.9, 131.5, 129.2, 128.5, 128.3, 127.8, 126.9, 122.8, 56.7, 52.0 ppm. HRMS (ESI): calcd. for $C_{23}H_{18}NO_4$ + H 372.1236; found 372.1247.

Methyl (*R*)-2-{[1,3-Dioxo-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl](1-naphthyl)methyl}acrylate (3b): R_f = 0.3 (petroleum ether/EtOAc = 6:1); 97% yield. $[\alpha]_D^{20}$ = 125.5 (c = 0.44, $CHCl_3$); 94% *ee*, determined by HPLC analysis [Daicel chiralpak AD, *n*-hexane/*i*PrOH = 70:30, 1.0 mL/min, λ = 220 nm, t(major) = 15.15, t(minor) = 12.40 min]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.58 (d, J = 7.6 Hz, 2 H), 8.20 (d, J = 8.4 Hz, 2 H), 8.02 (d, J = 8.4 Hz, 1 H), 7.97 (s, 1 H), 7.86 (d, J = 7.6 Hz, 1 H), 7.81 (d, J = 8.4 Hz, 1 H), 7.76–7.72 (m, 3 H), 7.51–7.43 (m, 3 H), 6.53 (s, 1 H), 5.53 (s, 1 H), 3.70 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 166.6, 164.6, 138.4, 134.0, 133.8, 133.2, 131.7, 131.5, 131.4, 129.0, 128.7, 128.4, 127.8, 127.4, 127.0, 126.6, 125.5, 125.2, 123.2, 122.8, 54.0, 52.2 ppm. HRMS (ESI): calcd. for $C_{27}H_{19}NO_4$ + Na 444.1212; found 444.1176.

Methyl (*R*)-2-{(4-Chlorophenyl)[1,3-dioxo-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl]methyl}acrylate (3c): R_f = 0.4 (petroleum ether/EtOAc = 8:1); 94% yield. $[\alpha]_D^{20}$ = 79.1 (c = 0.38, $CHCl_3$); 91% *ee*, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*PrOH = 70:30, 1.0 mL/min, λ = 220 nm, t(major) = 11.55, t(minor) = 13.62 min]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.58 (dd, J = 7.2, 0.8 Hz, 2 H), 8.21 (dd, J = 8.4, 1.2 Hz, 2 H), 7.74 (dd, J = 8.4, 0.8 Hz, 2 H), 7.52–7.49 (m, 2 H), 7.32–7.30 (m, 2 H), 7.18 (t, J = 2.0 Hz, 1 H), 6.48 (d, J = 2.0 Hz, 1 H), 5.60 (d, J = 2.0 Hz, 1 H), 3.68 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.4, 164.3, 138.5, 136.3, 134.1, 133.7, 131.6, 131.5, 130.7, 128.6, 128.3, 128.0, 127.0, 122.7, 56.0, 52.1 ppm. HRMS (ESI): calcd. for $C_{23}H_{16}ClNO_4$ + Na 428.0666; found 428.0634.

Methyl (*R*)-2-{(3-Chlorophenyl)[1,3-dioxo-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl]methyl}acrylate (3d): R_f = 0.3 (petroleum ether/EtOAc = 8:1); 96% yield. $[\alpha]_D^{20}$ = 84.8 (c = 0.44, $CHCl_3$); 89% *ee*, determined by HPLC analysis [Daicel chiralpak AD, *n*-hexane/*i*PrOH = 90:10, 1.0 mL/min, λ = 220 nm, t(major) = 25.79, t(minor) = 24.20 min]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.58 (dd, J = 7.4, 1.0 Hz, 2 H), 8.21 (dd, J = 8.4, 0.8 Hz, 2 H), 7.74 (dd, J = 8.0, 0.8 Hz, 2 H), 7.55–7.54 (m, 1 H), 7.45–7.43 (m, 1 H), 7.30–7.26 (m, 2 H), 7.18 (t, J = 1.8 Hz, 1 H), 6.50 (d, J = 2.0 Hz, 1 H), 5.63 (d, J = 2.0 Hz, 1 H), 3.68 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 166.3, 164.3, 139.8, 138.3, 134.3, 134.1, 131.7, 129.7, 129.3, 128.5, 128.3, 128.0, 127.5, 127.4, 127.0, 122.6, 56.0, 52.2 ppm. HRMS (ESI): calcd. for $C_{23}H_{16}ClNO_4$ + Na 428.0666; found 428.0658.

Methyl (*S*)-2-{(2-Chlorophenyl)[1,3-dioxo-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl]methyl}acrylate (3e): R_f = 0.3 (petroleum ether/EtOAc = 8:1); 94% yield. $[\alpha]_D^{20}$ = –44.9 (c = 0.50, $CHCl_3$); 93% *ee*, determined by HPLC analysis [Daicel chiralpak AD, *n*-hexane/*i*PrOH = 70:30, 1.0 mL/min, λ = 254 nm, t(major) = 11.45, t(minor) = 8.84 min]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.57 (d, J = 7.2 Hz, 2 H), 8.22 (d, J = 8.0 Hz, 2 H), 7.74 (t, J = 7.8 Hz, 2 H), 7.60–7.57 (m, 1 H), 7.42–7.35 (m, 2 H), 7.27–7.23 (m, 2 H), 6.54 (s, 1 H), 5.60 (s, 1 H), 3.70 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 166.2, 164.3, 137.2, 135.5, 134.0, 133.8, 131.7, 131.0, 129.6, 129.1, 128.4, 127.2, 127.0, 126.6, 122.7, 54.9, 52.2 ppm. HRMS (ESI): calcd. for $C_{23}H_{16}ClNO_4$ + Na 428.0666; found 428.0677.

Methyl (*R*)-2-{[1,3-Dioxo-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl](4-fluorophenyl)methyl}acrylate (3f): R_f = 0.3 (petroleum ether/EtOAc = 8:1); 95% yield. $[\alpha]_D^{20}$ = 123.4 (*c* = 0.40, $CHCl_3$); 93% *ee*, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*PrOH = 70:30, 1.0 mL/min, λ = 254 nm, *t*(major) = 10.71, *t*(minor) = 14.35 min]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.58 (dd, *J* = 7.2, 1.2 Hz, 2 H), 8.21 (dd, *J* = 8.2, 1.0 Hz, 2 H), 7.74 (t, *J* = 7.8 Hz, 2 H), 7.59–7.55 (m, 2 H), 7.17 (t, *J* = 2.0 Hz, 1 H), 7.05–7.00 (m, 2 H), 6.46 (d, *J* = 2.0 Hz, 1 H), 5.58 (d, *J* = 2.0 Hz, 1 H), 3.67 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 166.5, 164.7, 164.3, 159.8, 139.0, 134.0, 133.6, 133.5, 131.6, 131.3, 131.1, 128.3, 127.0, 126.7, 122.7, 115.6, 115.2, 56.1, 52.1 ppm. HRMS (ESI): calcd. for $C_{23}H_{16}FNO_4$ + Na 412.0961; found 412.0959.

Methyl (*S*)-2-{(2-Bromophenyl)[1,3-dioxo-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl]methyl}acrylate (3g): R_f = 0.3 (petroleum ether/EtOAc = 8:1); 96% yield. $[\alpha]_D^{20}$ = –35.1 (*c* = 0.42, $CHCl_3$); 93% *ee*, determined by HPLC analysis [Daicel chiralpak AD, *n*-hexane/*i*PrOH = 70:30, 1.0 mL/min, λ = 220 nm, *t*(major) = 13.60, *t*(minor) = 9.00 min]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.58 (dd, *J* = 7.4, 1.0 Hz, 2 H), 8.20 (dd, *J* = 8.4, 0.8 Hz, 2 H), 7.76–7.72 (m, 2 H), 7.59–7.55 (m, 2 H), 7.17–7.00 (m, 3 H), 6.46 (d, *J* = 2.0 Hz, 1 H), 5.58 (d, *J* = 2.0 Hz, 1 H), 3.67 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 166.1, 164.3, 137.3, 137.1, 134.0, 133.0, 131.7, 131.1, 129.3, 128.4, 127.2, 127.0, 124.1, 122.7, 57.4, 52.2 ppm. HRMS (ESI): calcd. for $C_{23}H_{16}BrNO_4$ + Na 472.0160; found 472.0192.

Methyl (*R*)-2-{[1,3-Dioxo-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl](2-nitrophenyl)methyl}acrylate (3h): R_f = 0.4 (petroleum ether/EtOAc = 5:1); 89% yield. $[\alpha]_D^{20}$ = 125.0 (*c* = 0.35, $CHCl_3$); 90% *ee*, determined by HPLC analysis [Daicel chiralpak AD, *n*-hexane/*i*PrOH = 70:30, 1.0 mL/min, λ = 220 nm, *t*(major) = 16.49, *t*(minor) = 12.28 min]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.56 (d, *J* = 7.6 Hz, 2 H), 8.21 (d, *J* = 8.4 Hz, 2 H), 7.95 (d, *J* = 8.0 Hz, 1 H), 7.78–7.67 (m, 4 H), 7.57 (t, *J* = 7.6 Hz, 1 H), 7.45 (t, *J* = 7.6 Hz, 1 H), 6.54 (s, 1 H), 5.61 (d, *J* = 1.2 Hz, 1 H), 3.69 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 165.9, 164.4, 149.2, 137.3, 134.2, 132.9, 132.7, 131.8, 131.5, 131.3, 128.7, 128.4, 127.4, 127.0, 124.7, 122.4, 53.2, 52.3 ppm. HRMS (ESI): calcd. for $C_{23}H_{16}N_2O_6$ + Na 439.0906; found 439.0905.

Methyl (*R*)-2-{(3,4-Dichlorophenyl)[1,3-dioxo-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl]methyl}acrylate (3i): R_f = 0.3 (petroleum ether/EtOAc = 8:1); 95% yield. $[\alpha]_D^{20}$ = 30.3 (*c* = 0.40, $CHCl_3$); 90% *ee*, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*PrOH = 80:20, 1.0 mL/min, λ = 220 nm, *t*(major) = 13.24, *t*(minor) = 17.52 min]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.59 (dd, *J* = 7.2, 1.2 Hz, 2 H), 8.23 (dd, *J* = 8.0, 0.8 Hz, 2 H), 7.76 (dd, *J* = 8.0, 0.8 Hz, 2 H), 7.64 (s, 1 H), 7.41 (d, *J* = 1.2 Hz, 2 H), 7.18 (t, *J* = 1.8 Hz, 1 H), 6.51 (d, *J* = 2.0 Hz, 1 H), 5.64 (d, *J* = 2.0 Hz, 1 H), 3.69 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 166.2, 164.2, 138.1, 137.9, 134.2, 132.5, 131.8, 131.6, 131.2, 130.3, 128.8, 127.5, 127.1, 122.5, 55.5, 52.2 ppm. HRMS (ESI): calcd. for $C_{23}H_{15}Cl_2NO_4$ + Na 462.0276; found 462.0222.

Methyl (*R*)-2-{[1,3-Dioxo-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl](4-methoxyphenyl]methyl}acrylate (3j): R_f = 0.3 (petroleum ether/EtOAc = 10:1); 95% yield. $[\alpha]_D^{20}$ = 112.6 (*c* = 0.45, $CHCl_3$); 93% *ee*, determined by HPLC analysis [Daicel chiralpak AD, *n*-hexane/*i*PrOH = 80:20, 1.0 mL/min, λ = 220 nm, *t*(major) = 23.20, *t*(minor) = 21.44 min]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.57 (dd, *J* = 7.6, 1.2 Hz, 2 H), 8.18 (dd, *J* = 8.4, 1.2 Hz, 2 H), 7.72 (dd, *J* = 8.0, 0.8 Hz, 2 H), 7.54–7.52 (m, 2 H), 7.13 (t, *J* = 2.2 Hz, 1 H), 6.88–6.86 (m, 2 H), 6.43 (d, *J* = 2.0 Hz, 1 H), 5.59 (d, *J* = 2.0 Hz, 1 H), 3.78 (s, 3 H), 3.66 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 166.6, 164.3, 159.1, 139.5, 133.9, 131.5, 130.8, 129.9, 128.3, 126.9, 126.4, 122.8, 113.9, 56.3, 55.2, 52.0 ppm. HRMS (ESI): calcd. for $C_{24}H_{19}NO_5$ + Na 424.1161; found 424.1160.

Methyl (*R*)-2-{[1,3-Dioxo-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl](*m*-tolyl)methyl}acrylate (3k): R_f = 0.4 (petroleum ether/EtOAc = 10:1); 96% yield. $[\alpha]_D^{20}$ = 18.1 (*c* = 0.95, $CHCl_3$); 90% *ee*, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*PrOH = 70:30, 1.0 mL/min, λ = 220 nm, *t*(major) = 14.14, *t*(minor) = 26.56 min]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.58 (dd, *J* = 7.4, 1.0 Hz, 2 H), 8.18 (dd, *J* = 8.4, 0.8 Hz, 2 H), 7.75–7.71 (m, 2 H), 7.38–7.35 (m, 2 H), 7.23 (t, *J* = 7.8 Hz, 1 H), 7.14 (s, 1 H), 7.09 (d, *J* = 7.6 Hz, 1 H), 6.45 (d, *J* = 2.0 Hz, 1 H), 5.59 (d, *J* = 2.0 Hz, 1 H), 3.67 (s, 3 H), 2.32 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 166.6, 164.3, 139.2, 138.1, 137.6, 133.8, 131.5, 129.8, 128.6, 128.3, 126.9, 126.8, 126.3, 122.8, 56.8, 52.0, 21.5 ppm. HRMS (ESI): calcd. for $C_{24}H_{19}NO_4$ + Na 408.1212; found 408.1187.

Methyl (*R*)-2-{[1,3-Dioxo-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl](*p*-tolyl)methyl}acrylate (3l): R_f = 0.3 (petroleum ether/EtOAc = 10:1); 92% yield. $[\alpha]_D^{20}$ = 120.0 (*c* = 0.28, $CHCl_3$); 88% *ee*, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*PrOH = 70:30, 1.0 mL/min, λ = 220 nm, *t*(major) = 20.82, *t*(minor) = 13.84 min]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.57 (dd, *J* = 7.2, 1.2 Hz, 2 H), 8.18 (dd, *J* = 8.2, 1.0 Hz, 2 H), 7.72 (dd, *J* = 8.0, 0.8 Hz, 2 H), 7.46 (d, *J* = 8.4 Hz, 2 H), 7.15–7.14 (m, 3 H), 6.45 (d, *J* = 1.6 Hz, 1 H), 5.60 (d, *J* = 1.6 Hz, 1 H), 3.67 (s, 3 H), 2.32 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 166.6, 164.3, 139.2, 137.4, 134.7, 133.8, 131.5, 129.2, 129.1, 128.2, 126.9, 126.6, 122.8, 56.5, 52.0, 21.1 ppm. HRMS (ESI): calcd. for $C_{24}H_{19}NO_4$ + Na 408.1212; found 408.1212.

Methyl (*S*)-2-{[1,3-Dioxo-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl](thiophen-2-yl)methyl}acrylate (3m): R_f = 0.3 (petroleum ether/EtOAc = 8:1); 90% yield. $[\alpha]_D^{20}$ = 330.8 (*c* = 0.85, $CHCl_3$); 82% *ee*, determined by HPLC analysis [Daicel chiralpak AD, *n*-hexane/*i*PrOH = 70:30, 1.0 mL/min, λ = 220 nm, *t*(major) = 13.19, *t*(minor) = 15.08 min]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.60 (dd, *J* = 7.2, 1.2 Hz, 2 H), 8.18 (dd, *J* = 8.4, 0.8 Hz, 2 H), 7.73 (dd, *J* = 8.0, 0.8 Hz, 2 H), 7.55 (t, *J* = 2.0 Hz, 1 H), 7.32–7.28 (m, 2 H), 7.00–6.98 (m, 1 H), 6.50 (d, *J* = 2.4 Hz, 1 H), 5.90 (d, *J* = 2.0 Hz, 1 H), 3.64 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.1, 163.8, 139.1, 133.9, 131.5, 129.1, 128.2, 127.7, 126.9, 126.7, 126.2, 122.6, 52.0, 51.7 ppm. HRMS (ESI): calcd. for $C_{21}H_{15}NO_4S$ + Na 400.0619; found 400.0628.

Methyl (*R*)-2-[(1,3-Dioxoisoindolin-2-yl)(phenyl)methyl]acrylate (3n): R_f = 0.4 (petroleum ether/EtOAc = 10:1); 91% yield. $[\alpha]_D^{20}$ = 118.2 (*c* = 0.64, $CHCl_3$); 85% *ee*, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*PrOH = 70:30, 1.0 mL/min, λ = 254 nm, *t*(major) = 6.85, *t*(minor) = 10.23 min]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85–7.82 (m, 2 H), 7.72–7.70 (m, 2 H), 7.45–7.30 (m, 5 H), 6.57 (s, 1 H), 6.40 (s, 1 H), 5.63 (s, 1 H), 3.71 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 167.9, 166.1, 137.6, 137.0, 134.1, 131.9, 129.7, 128.7, 128.1, 123.4, 54.7, 52.2 ppm. HRMS (ESI): calcd. for $C_{19}H_{15}NO_4$ + Na 344.0899; found 344.0928.

Methyl (*S*)-2-[(2-Bromophenyl)(1,3-dioxoisoindolin-2-yl)methyl]-acrylate (3o): R_f = 0.4 (petroleum ether/EtOAc = 10:1); 93% yield. $[\alpha]_D^{20}$ = 13.9 (*c* = 0.22, $CHCl_3$); 87% *ee*, determined by HPLC analysis [Daicel chiralpak AD, *n*-hexane/*i*PrOH = 90:10, 1.0 mL/min, λ = 220 nm, *t*(major) = 21.19, *t*(minor) = 17.76 min]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85–7.82 (m, 2 H), 7.75–7.72 (m, 2 H), 7.59–7.50 (m, 2 H), 7.36–7.29 (m, 1 H), 7.20–7.16 (m, 1 H), 6.71 (s, 1 H), 6.59 (d, *J* = 1.2 Hz, 1 H), 5.58 (d, *J* = 2.0 Hz, 1 H), 3.71 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 167.7, 165.7, 136.3, 136.1, 134.2, 133.1, 131.7, 130.5, 129.7, 129.0, 127.4, 124.0, 123.5,

54.6, 52.3 ppm. HRMS (ESI): calcd. for $C_{19}H_{14}NO_4$ + Na 422.0004; found 422.0002.

Methyl (*R*)-2-[(1,3-Dioxoisoindolin-2-yl)(1-naphthyl)methyl]acrylate (3p): R_f = 0.4 (petroleum ether/EtOAc = 8:1); 91% yield. $[\alpha]_D^{20}$ = 52.5 (*c* = 0.20, $CHCl_3$); 89% *ee*, determined by HPLC analysis [Daicel chiralpak AD, *n*-hexane/*i*PrOH = 90:10, 1.0 mL/min, λ = 220 nm, *t*(major) = 27.63, *t*(minor) = 26.16 min]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00–7.81 (m, 5 H), 7.73–7.63 (m, 3 H), 7.55–7.44 (m, 3 H), 7.23 (s, 1 H), 6.59 (d, *J* = 1.2 Hz, 1 H), 5.63 (d, *J* = 1.6 Hz, 1 H), 3.71 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 168.0, 166.1, 137.1, 134.2, 133.9, 132.1, 131.7, 130.9, 129.4, 129.0, 127.3, 126.9, 126.8, 125.7, 125.1, 123.5, 123.0, 52.3, 51.3 ppm. HRMS (ESI): calcd. for $C_{23}H_{17}NO_4$ + Na 394.1055; found 394.1008.

Methyl (*R*)-2-[Phenyl(4,5,6,7-tetrachloro-1,3-dioxoisoindolin-2-yl)-methyl]acrylate (3q): R_f = 0.3 (petroleum ether/EtOAc = 20:1); 91% yield. $[\alpha]_D^{20}$ = 144.6 (*c* = 0.38, $CHCl_3$); 89% *ee*, determined by HPLC analysis [Daicel chiralpak AD, *n*-hexane/*i*PrOH = 90:10, 1.0 mL/min, λ = 254 nm, *t*(major) = 12.17, *t*(minor) = 10.90 min]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.42 (m, 2 H), 7.39–7.33 (m, 3 H), 6.59 (d, *J* = 1.6 Hz, 1 H), 6.33 (s, 1 H), 5.62 (d, *J* = 1.6 Hz, 1 H), 3.73 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 166.0, 163.2, 159.5, 140.3, 136.7, 136.2, 130.6, 128.9, 128.7, 128.5, 127.3, 55.6, 52.3 ppm. HRMS (ESI): calcd. for $C_{19}H_{11}Cl_4NO_4$ + Na 479.9340; found 479.9358.

Methyl (*S*)-2-[(2-Chlorophenyl)(4,5,6,7-tetrachloro-1,3-dioxoisoindolin-2-yl)methyl]acrylate (3r): R_f = 0.3 (petroleum ether/EtOAc = 20:1); 92% yield. $[\alpha]_D^{20}$ = 69.9 (*c* = 0.24, $CHCl_3$); 90% *ee*, determined by HPLC analysis [Daicel chiralpak AD, *n*-hexane/*i*PrOH = 90:10, 1.0 mL/min, λ = 220 nm, *t*(major) = 10.22, *t*(minor) = 8.81 min]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48–7.46 (m, 1 H), 7.42–7.39 (m, 1 H), 7.30–7.27 (m, 2 H), 6.76 (s, 1 H), 6.60 (d, *J* = 1.2 Hz, 1 H), 5.57 (d, *J* = 2.0 Hz, 1 H), 3.73 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 165.6, 163.1, 135.5, 133.7, 130.1, 129.9, 129.8, 129.6, 127.1, 52.7, 52.4 ppm. HRMS (ESI): calcd. for $C_{19}H_{10}Cl_5NO_4$ + Na 513.8950; found 513.8951.

Methyl (*S*)-2-[(2-Bromophenyl)(4,5,6,7-tetrachloro-1,3-dioxoisoindolin-2-yl)methyl]acrylate (3s): R_f = 0.3 (petroleum ether/EtOAc = 20:1); 92% yield. $[\alpha]_D^{20}$ = 63.3 (*c* = 1.00, $CHCl_3$); 90% *ee*, determined by HPLC analysis [Daicel chiralpak AD, *n*-hexane/*i*PrOH = 90:10, 1.0 mL/min, λ = 220 nm, *t*(major) = 11.12, *t*(minor) = 9.20 min]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (dd, *J* = 7.8, 1.4 Hz, 1 H), 7.47 (dd, *J* = 7.8, 1.8 Hz, 1 H), 7.32 (td, *J* = 7.4, 1.3 Hz, 1 H), 7.21 (td, *J* = 7.7, 1.5 Hz, 1 H), 6.71 (s, 1 H), 6.61 (d, *J* = 1.2 Hz, 1 H), 5.55 (d, *J* = 1.6 Hz, 1 H) 3.73 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 165.5, 163.1, 140.5, 135.5, 135.4, 133.3, 130.2, 130.1, 129.7, 127.7, 127.2, 124.0, 55.3, 52.4 ppm. HRMS (ESI): calcd. for $C_{19}H_{10}BrCl_4NO_4$ + Na 557.8445; found 557.8467.

Methyl (*R*)-2-[Phenyl(4,5,6,7-tetrabromo-1,3-dioxoisoindolin-2-yl)-methyl]acrylate (3t): R_f = 0.4 (petroleum ether/EtOAc = 10:1); 86% yield. $[\alpha]_D^{20}$ = 112.0 (*c* = 0.28, $CHCl_3$); 87% *ee*, determined by HPLC analysis [Daicel chiralpak AD, *n*-hexane/*i*PrOH = 90:10, 1.0 mL/min, λ = 254 nm, *t*(major) = 14.90, *t*(minor) = 12.76 min]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.41 (m, 2 H), 7.38–7.32 (m, 3 H), 6.58 (d, *J* = 2.0 Hz, 1 H), 6.33 (s, 1 H), 5.61 (d, *J* = 2.0 Hz, 1 H), 3.72 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 168.9, 166.0, 163.4, 137.8, 136.8, 136.2, 130.5, 128.9, 128.7, 128.5, 121.5, 55.7, 52.3 ppm. HRMS (ESI): calcd. for $C_{19}H_{11}Br_4NO_4$ + Na 655.7319; found 655.7359.

Methyl (1*S*,2*S*)-1-(1,3-Dioxoisoindolin-2-yl)-2,3-dihydro-1*H*-indene-2-carboxylate (4): Bu_3SnH (19.6 mg, 0.0675 mmol) was added to a solution of compound **3o** (18 mg, 0.045 mmol) and AIBN (1.5 mg, 0.009 mmol) in benzene . The solution was stirred at 90 °C for about 6 h. Then the solvent was removed and the residue was purified by column chromatography (petroleum ether/ethyl acetate = 20:1) to afford the product **4** as a white solid (10.5 mg, 73%). R_f = 0.3 (petroleum ether/EtOAc = 10:1). $[\alpha]_D^{20}$ = –73.9 (*c* = 0.25, $CHCl_3$); 83% *ee*, determined by HPLC analysis [Daicel chiralpak AD, *n*-hexane/*i*PrOH = 70:30, 1.0 mL/min, λ = 220 nm, *t*(major) = 9.54, *t*(minor) = 15.51 min]. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.78–7.67 (m, 4 H), 7.33–7.19 (m, 4 H), 6.05 (d, *J* = 9.2 Hz, 1 H), 3.93 (dd, *J* = 15.5, 9.3 Hz, 1 H), 3.79–3.70 (m, 1 H), 3.55 (s, 3 H), 3.28 (dd, *J* = 15.7, 8.6 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 171.7, 167.7, 143.5, 138.1, 134.0, 131.9, 129.0, 127.1, 124.6, 124.5, 123.3, 54.4, 51.9, 46.2, 35.0 ppm. HRMS (ESI): calcd. for $C_{19}H_{15}NO_4$ + Na 344.0899; found 344.0907. The relative configuration of compound **4** was established by NOE analysis.

Methyl (*R*)-5-[(*R*)-(1,3-Dioxoisoindolin-2-yl)(phenyl)methyl]-3-phenyl-4,5-dihydroisoxazole-5-carboxylate (5): TEA (43.4 μL, 0.31 mmol) was added to a solution of chlorobenzaldoxime (48.5 mg, 0.31 mmol) in anhydrous CH_2Cl_2 (1 mL) at 0 °C. After stirring for 10 min a solution of **3n** (50 mg, 0.16 mmol) in anhydrous CH_2Cl_2 was added dropwise. The mixture was stirred at room temperature for 36 h. Then the reaction was quenched with water (5 mL) and the organic layer was separated. The aqueous layer was extracted with EtOAc (2 × 5 mL). The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated. Flash chromatography on silica gel (petroleum ether/ethyl acetate = 15:1) afforded the diastereomerically pure product **5** as a white solid (58.3 mg, 85%). R_f = 0.3 (petroleum ether/EtOAc = 5:1). $[\alpha]_D^{20}$ = 87.2 (*c* = 0.86, $CHCl_3$); 82% *ee*, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*PrOH = 70:30, 1.0 mL/min, λ = 254 nm, *t*(major) = 8.20, *t*(minor) = 10.71 min]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91–7.86 (m, 2 H), 7.79–7.75 (m, 2 H), 7.58–7.51 (m, 4 H), 7.38–7.22 (m, 6 H), 6.22 (s, 1 H), 4.19 (d, *J* = 18.4 Hz, 1 H), 3.74 (d, *J* = 18.4 Hz, 1 H), 3.66 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 169.9, 167.9, 158.1, 134.5, 134.3, 131.4, 130.3, 128.6, 126.8, 123.7, 91.1, 56.8, 53.2, 41.0 ppm. HRMS (ESI): calcd. for $C_{26}H_{20}N_2O_5$ + H 441.1450; found 441.1450. The relative configuration of compound **5** was established by NOE analysis and by analogy to the previous report.[10b]

Supporting Information (see also the footnote on the first page of this article): NMR spectra and HPLC chromatograms of the products **3a**–**3t**, **4** and **5** and crystal data of enantiopure **3e**.

Acknowledgments

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