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Enantioselective Synthesis of Quaternary Carbon Stereogenic Centers through the Primary Amine-Catalyzed Michael Addition Reaction of α-Substituted Cyclic Ketones at High Pressure[‡]

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The enantioselective Michael addition reaction of α-substituted cyclic ketones with acrylates was efficiently promoted by a primary amine chiral catalyst under high-pressure conditions (1.0 GPa) in tetrahydrofuran. This method was highly successful for the construction of an all-carbon-substituted quaternary-carbon stereogenic center at the α-position of cyclic ketones in high enantiomeric excess, and could be conveniently applied to the formal synthesis of (+)-aspidospermidine.

Introduction

There is a strong demand for the catalytic asymmetric synthesis of quaternary carbon stereogenic centers, particularly all-carbon-substituted centers, because of their widespread distribution as pivotal structural units in complex biologically active natural products.[1] Among several approaches, considerable attention has recently been focused on organocatalytic asymmetric transformation as an efficient and convenient methodology owing to its environmentally friendly characteristics,[2] and asymmetric Michael addition reactions are generally accepted as the most convenient and reliable of these transformations.[2] In our ongoing studies in this area,[3] we recently found that a primary amine-thiourea conjugate bifunctional organocatalyst, e.g. catalyst **A**, strongly supported the asymmetric Michael addition reactions of α,β-unsaturated ketones with malonates under atmospheric or high-pressure conditions.[4] As an extension of this chemistry, we were particularly interested in its application to α-substituted cyclic ketones as Michael donors, because the whole process would constitute an expeditious route for the construction of an all-carbon-substituted quaternary-carbon stereogenic center at the α-position of cyclic ketones in an enantio-controlled manner.

With regard to this synthetic endeavor, various approaches that use a chiral auxiliary or palladium-catalyzed technique have been developed.[5,6] Several years ago, Pfau, d'Angelo and others reported an efficient strategy based on the asymmetric alkylation reaction of α-substituted cyclic ketones through an imine-enamine activation process by using 1-phenylethylamine as a chiral auxiliary.[5,7] On the other hand, the palladium-catalyzed asymmetric decarboxylative allylic alkylation reaction of allyl carboxylates has also been shown to have substantial utility in this area.[6] As an organocatalytic version, Kang and Carter reported primary amine-thiourea-catalyzed asymmetric Michael addition reactions for the enantioselective synthesis of α,α-disubstituted cyclic ketones.[8]

Very recently, Maruoka and co-workers presented a new method for the asymmetric alkylation of 2-arylcyclohexanones under chiral phase-transfer conditions.[9] In this paper, we describe our own approach based on the primary amine-catalyzed asymmetric Michael addition reaction of α-substituted cyclic ketones with acrylates.

Results and Discussion

To find the optimum reaction conditions, the Michael addition reaction of 2-methylcyclohexanone (**1a**) with methyl acrylate (**2a**; 3.0 equiv.) was carried out in the presence of a variety of primary amine-based chiral organocatalysts (Figure 1). The results are summarized in Table 1.

Under our previously established conditions with 10 mol-% of catalyst **A** in toluene as a solvent, the reaction proceeded sluggishly even at elevated temperatures. As expected, increased pressure dramatically accelerated the reaction[10] and desired adduct **3a** was obtained in excellent enantioselectivity, albeit along with a large amount of regioisomer **4a** (Table 1, Entries 1 and 2). The formation of the latter isomer suggests that the imine-enamine equilibrium between **1a** and catalyst **A** might be shifted to some extent to the less-congested α′-side. We next turned our at-

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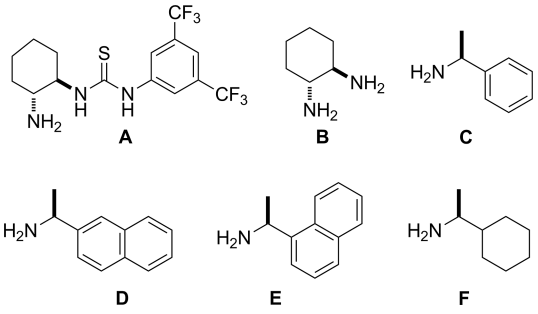
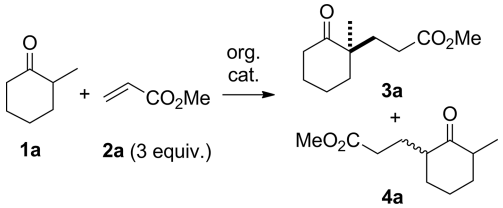


Figure 1. Catalysts screened.

Table 1. Optimization of the Michael addition reaction between 2-methylcyclohexanone (**1a**) and methyl acrylate (**2**).

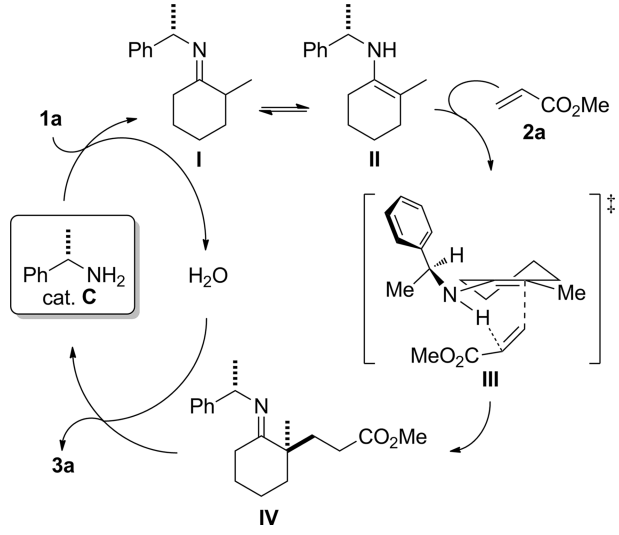


Entry	Catalyst [mol-%]	Conditions	Yield[a] [%]	**3a/4a**[b]	*ee*[c] [%]
1	**A** [10]	toluene, 1 atm, 75 °C, 48 h	8	89:11	98
2	**A** [10]	toluene, 1.0 GPa, 25 °C, 48 h	64	62:38	98
3	**B** [30]	THF, 1.0 GPa, 25 °C, 48 h	75	87:13	74
4	**C** [30]	THF, 1.0 GPa, 25 °C, 48 h	96	95:5	98
5	**C** [20]	THF, 1.0 GPa, 25 °C, 48 h	76	96:4	98
6	**C** [10]	THF, 1.0 GPa, 25 °C, 48 h	69	96:4	96
7	**C** [5]	THF, 1.0 GPa, 25 °C, 48 h	20	96:4	98
8	**C** [30]	THF, 0.8 GPa, 25 °C, 48 h	74	97:3	98
9	**C** [30]	THF, 0.6 GPa, 25 °C, 48 h	34	96:4	87
10	**C** [30]	toluene, 1.0 GPa, 25 °C, 48 h	41	96:4	86
11	**C** [30]	CH_2Cl_2, 1.0 GPa, 25 °C, 48 h	12	95:5	93
12	**C** [30]	MeCN, 1.0 GPa, 25 °C, 48 h	36	97:3	92
13	**D** [30]	THF, 1.0 GPa, 25 °C. 48 h	95	84:16	98
14	**E** [30]	THF, 1.0 GPa, 25 °C, 48 h	97	86:14	98
15	**F** [30]	THF, 1.0 GPa, 25 °C, 48 h	55	98:2	86
16	**–C** [30]	THF, 1.0 GPa, 25 °C, 48 h	96	95:5	–98

[a] Isolated yields. [b] Determined by ^{1}H NMR spectroscopic analysis of the crude reaction mixture. [c] After conversion to the corresponding benzyl ester, determined by chiral HPLC analysis by using a Chiralpak AS-H.

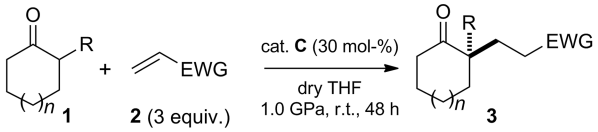
tention to the use of smaller primary amine-based chiral organocatalysts such as catalysts **B**–**F**; in every case, (*R*)-enantiomer **3a** was obtained predominantly. After several experiments, we found that the use of 30 mol-% of catalyst **C** gave the best results in terms of efficiency and feasibility (Table 1, Entry 4 versus Entries 3 and 13–15). Consistent with previous observations by d'Angelo et al.,[5,11] phenylamines **C**–**E** were more favorable than cyclohexyl congeners **B** and **F** (Table 1, Entries 4, 13, and 14 versus Entries 3 and 15). Furthermore, we found that the yields decreased at lower pressures and with lower catalyst loadings (Table 1, Entry 4 versus Entries 5–9). We briefly examined the solvent effect in this Michael addition reaction: toluene, dichloromethane, and MeCN resulted in incomplete conversion of the reaction (Table 1, Entry 4 versus Entries 10–12). These results suggest that, in tetrahydrofuran (THF), the initial stage of forming a chiral imine from **1a** and catalyst **C** took place smoothly. As expected, the replacement of catalyst **C** with its (*R*)-antipode led to complete reversal of configuration of the product (Table 1, Entry 16).

The stereochemical outcome of this highly enantioselective Michael addition process could be rationalized by an imine-enamine activation mode, as proposed by d'Angelo et al. (Scheme 1).[5,11,12] Compound **1a** could be condensed with catalyst **C** to form imine compound **I** as an initial product. After spontaneous equilibrium to enamine tautomer **II**, methyl acrylate (**2a**) could be attacked from the less-hindered side opposite a rather bulky phenyl ring (transition structure **III**), after hydrolysis of **IV**, to give final product **3a** with regeneration of catalyst **C**.[13] Importantly, in this synthetic sequence the interaction between the enamine donor and methyl acrylate (**2a**) as the Michael acceptor and C–C bond-forming processes are both favorable under high-pressure conditions, and the whole process should be efficiently accelerated under these conditions.[12] As a result of the unavoidable side reaction that leads to the hetero-Michael adduct from methyl acrylate (**2a**) and primary amine catalysts,[14] we conclude that at least 3 equiv. of acceptor and 30 mol-% of catalyst are necessary to attain satisfactory results.[15]



Scheme 1. Plausible mechanism through an imine–enamine equilibrium process.

Table 2. The Michael addition reaction between cyclic ketones **1** and acrylates (**2**) is a general one.

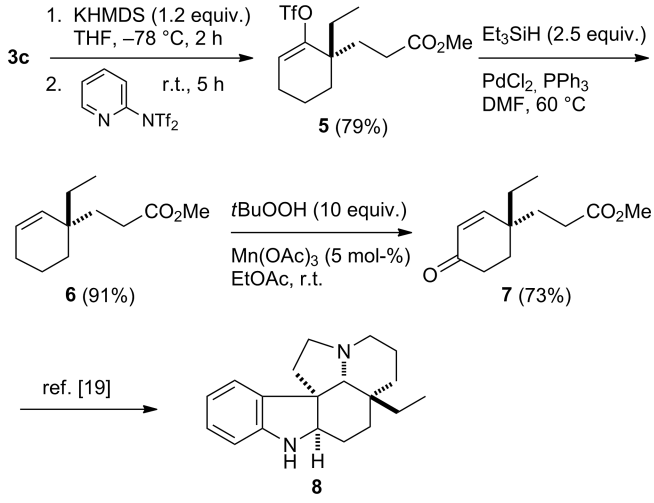


Entry	Donor [1]	Product [3]	Yield [%][a] (ratio)[b]	*ee*[c] [%]
1	**1a**	**3b**	77 (92 : 8)	95
2[d]	**1b**	**3c**	90 (96 : 4)	99
3	**1b**	**3d**[e]	81 (96 : 4)	91
4	**1c**	**3e**[e]	60 (>99 : 1)	98
5	**1d**	**3f**[e]	61 (>99 : 1)	99
6	**1e**	**3g**[e]	26 (89 : 11)	99
7	**1f**	**3h**	<5	---
8	**1g**	**3i**	75 (>99 : 1)	93
9	**1g**	**3j**	61 (>99 : 1)	88
10	**1h**	**3k**[e]	46 (95 : 5)	95

[a] Isolated yields. [b] Determined by ^{1}H NMR spectroscopic analysis of the crude reaction mixture. [c] After conversion to the corresponding benzyl ester, determined by chiral HPLC. [d] The antipode of catalyst **C** was used. [e] The absolute configuration of the products was surmised by analogy with **3a**.

With the optimized reaction conditions in hand, we investigated the general scope of this chemistry by using a variety of cyclic ketones with acrylates (Table 2).[16] Several cyclohexanones, such as **1a**–**1d**, efficiently reacted with methyl acrylate (**2a**) or acrylonitrile (**2b**) to give the desired adducts in good to excellent yields with high enantioselectivity (Table 2, Entries 1–5). The procedure is highly sensitive to steric and electronic effects. The reactions that use 2-benzylcyclohexanone (**1e**) and 2-methylthiopyranone (**1f**) as Michael donors are very sluggish even at high pressure (Table 2, Entries 6 and 7).[17] Finally, cyclopentanone analogs, such as **1g** and **1h**, were used as moderately reactive Michael donors, and smooth reactions with **2a** and **2b** were observed (Table 2, Entries 8–10).[18]

To demonstrate the synthetic value of this efficient organocatalytic asymmetric transformation, (+)-aspidospermidine (**8**), a well-known aspidosperma alkaloid, was targeted (Scheme 2).[19,20] Treatment of **3c** with potassium hexamethyldisilazide (1.2 equiv.) followed by exposure to *N*-(2-pyridyl)bis(trifluoromethanesulfonamide) gave corresponding enol triflate **5** in 79% yield. This compound was subjected to palladium-catalyzed reduction under our previously established conditions (91%),[21] and resulting cyclohexene **6** was oxidized by reaction with manganese triacetate/*tert*-butyl hydroperoxide[22] to give cyclohexenone **7** in 73% yield. This can be converted into (+)-aspidospermidine (**8**) as described in the literature,[23] and hence the formal synthesis of this natural product has been completed.[24]



Scheme 2. Formal total synthesis of (+)-aspidospermidine (**8**).

Conclusions

In conclusion, we have developed a new efficient method for constructing complex molecules that bear a quaternary carbon stereogenic center at the α-position of cyclic ketones. The reaction is performed by catalysis with chiral 1-phenylethylamine at high pressure and, depending on the substrate, high to excellent yields can be attained. Because this organocatalyst is commercially available in both (*S*)-

and (*R*)-forms and the process does not require the preparation of imine precursors and this method provides a highly useful synthetic pathway in modern organic synthesis. Finally, the utility of this method was exemplified by its application to the formal synthesis of (+)-aspidospermidine (**8**). Further studies to extend the scope of this method are now in progress in our laboratory.

Experimental Section

General Remarks: ^{1}H and ^{13}C NMR spectra were recorded with a JEOL JNM-ECA-500 spectrometer (500 MHz and 125.8 MHz, respectively) for solutions in $CDCl_3$. Chemical shifts are reported relative to residual $CHCl_3$ (7.27 for ^{1}H and 77.20 for ^{13}C) as an internal reference. IR spectra were measured with a JASCO FT/IR-460 plus Fourier Transform Infrared spectrophotometer. High-pressure reactions were performed in a Hikari-koatsu HR-15-B3 apparatus, which is designed for pressures up to 1.0 GPa. The silica gel used for flash chromatography was 230–400 mesh. All reagents were of reagent grade and used as received or distilled prior to use. All solvents were dried according to standard procedures and freshly distilled prior to use.

Typical Procedure for the Michael Addition Reaction of 2-Methylcyclohexanone (1a) with Methyl Acrylate (2a): A mixture of **1a** (1.0 mmol), **2a** (3.0 mmol), and (*S*)-1-phenylethylamine (catalyst **C**, 0.3 mmol) in THF (1.4 mL) was placed in a Teflon® reaction vessel and allowed to react at 1.0 GPa and room temp. After 2 d, the mixture was concentrated and purified by silica gel column chromatography (eluted with hexane/acetone = 10:1) to give the desired adduct. In general, the *ee* value was determined by chiral HPLC analysis after conversion to the corresponding benzyl ester (5.2 equiv. of $PhCH_2OH$, cat. dry *p*TsOH, microwave, 100 °C, 0.5 h, 84% yield).

Methyl (*R*)-3-(1-Methyl-2-oxocyclohexyl)propanoate (3a):[5a,8] Colorless oil. $[\alpha]_D^{23}$ = +30.5 (*c* = 2.95, EtOH, 98% *ee*) {ref.[8] $[\alpha]_D^{20}$ = +30.0 (*c* = 2.95, EtOH, 98% *ee*)}. FTIR (neat): $\tilde{\nu}$ = 1739, 1705 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.07 (s, 3 H), 1.57–1.65 (m, 1 H), 1.67–1.91 (m, 6 H), 2.04 (ddd, *J* = 14.0, 11.5, 5.0 Hz, 1 H), 2.16 (ddd, *J* = 16.0, 11.0, 5.0 Hz, 1 H), 2.32 (ddd, *J* = 16.0, 11.0, 5.0 Hz, 1 H), 2.37–2.44 (m, 2 H), 3.66 (s, 3 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 20.97, 22.37, 27.42, 28.99, 32.48, 38.70, 39.23, 47.90, 51.67, 174.04, 215.19 ppm. *ee* of the corresponding benzyl ester was determined by chiral HPLC analysis with a Chiralpak AS-H column (0.46 × 25 cm, hexane/2-propanol = 99:1, flow rate 0.15 cm^3/min, λ = 254 nm), t_R (*S*-isomer) = 76.2 min and t_R (*R*-isomer) = 82.1 min.

Methyl 3-(3-Methyl-2-oxocyclohexyl)propanoate (4a):[12c] Colorless oil. FTIR (neat): $\tilde{\nu}$ = 1738, 1709 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.00 (d, *J* = 7.0 Hz, 3 H), 1.32 (dd, *J* = 13.5, 4.0 Hz, 1 H), 1.36 (dd, *J* = 13.5, 4.0 Hz, 1 H), 1.48–1.55 (m, 1 H), 1.75 (tq, *J* = 13.5, 4.0 Hz, 1 H), 1.81–1.87 (m, 1 H), 2.03–2.15 (m, 3 H), 2.29–2.45 (m, 4 H), 3.66 (s, 3 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 14.47, 24.71, 25.50, 31.71, 35.29, 37.40, 45.68, 49.77, 51.50, 174.14, 213.60 ppm.

(*R*)-3-(1-Methyl-2-oxocyclohexyl)propionitrile (3b):[8] Colorless oil. $[\alpha]_D^{24}$ = –8.48 (*c* = 17.5, EtOH, 95% *ee*) {ref.[8] $[\alpha]_D^{20}$ = –3.4 (*c* = 26, EtOH, 85% *ee*)}. FTIR (neat): $\tilde{\nu}$ = 2246, 1703 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.16 (s, 3 H), 1.69–1.99 (m, 8 H), 2.28–2.40 (m, 3 H), 2.45–2.51 (m, 1 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 12.44, 20.87, 22.33, 27.24, 33.70, 38.57, 38.60, 47.73, 120.07, 214.34 ppm. The *ee* value was determined by chiral HPLC analysis as described in **3a** after conversion to the corresponding benzyl ester (80 equiv. of $PhCH_2OH$, 100 equiv. of conc. HCl, microwave, 150 °C, 2.0 h, 60–70% yield).

Methyl (*S*)-3-(1-Ethyl-2-oxocyclohexyl)propanoate (3c):[25] Colorless oil. $[\alpha]_D^{23}$ = +13.33 (*c* = 1.00, $CHCl_3$, 99% *ee*) {ref.[25] for (*R*)-isomer: $[\alpha]_D^{23}$ = –9.45 (*c* = 0.995, $CHCl_3$, 87% *ee*)}. FTIR (neat): $\tilde{\nu}$ = 1739, 1703 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.77 (t, *J* = 7.0 Hz, 3 H), 1.48 (sextet, *J* = 7.5 Hz, 1 H), 1.65–1.87 (m, 8 H), 1.92 (ddd, *J* = 14.0, 11.5, 5.0 Hz, 1 H), 2.12 (ddd, *J* = 16.0, 11.5, 5.0 Hz, 1 H), 2.27 (ddd, *J* = 16.0, 11.5, 5.0 Hz, 1 H), 2.33–2.42 (m, 2 H), 3.66 (s, 3 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 7.67, 20.68, 27.06, 28.72, 28.95, 35.77, 39.08, 50.98, 51.66 (× 2), 174.23, 214.85 ppm. *ee* of the corresponding benzyl ester was determined by chiral HPLC analysis with a Chiralpak AS-H column (0.46 × 25 cm, hexane/2-propanol = 99:1, flow rate 0.15 cm^3/min, λ = 254 nm), t_R (major) = 60.11 min and t_R (minor) = 64.35 min.

Methyl 3-(3-Ethyl-2-oxocyclohexyl)propanoate (4c): Colorless oil. FTIR (neat): $\tilde{\nu}$ = 1739, 1709 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.5 Hz, 3 H), 1.20 (sextet, *J* = 7.0 Hz, 1 H), 1.25–1.38 (m, 2 H), 1.48–1.55 (m, 1 H), 1.68–1.89 (m, 3 H), 2.06 (sextet, *J* = 7.0 Hz, 1 H), 2.11–2.21 (m, 3 H), 2.28–2.44 (m, 3 H), 3.66 (s, 3 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 11.81, 22.05, 24.66, 25.51, 31.70, 34.96, 35.53, 50.11, 51.52, 52.78, 174.15, 213.43 ppm. HRMS: calcd. for $C_{12}H_{20}O_3$ 212.1412; found 212.1416.

(*R*)-3-(1-Ethyl-2-oxocyclohexyl)propionitrile (3d): Colorless oil. $[\alpha]_D^{23}$ = –62.88 (*c* = 1.02, EtOH, 91% *ee*). FTIR (neat): $\tilde{\nu}$ = 2247, 1702 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.79 (t, *J* = 7.5 Hz, 3 H), 1.53 (sextet, *J* = 7.5 Hz, 1 H), 1.62–1.83 (m, 8 H), 1.98 (ddd, *J* = 14.5, 9.5, 5.5 Hz, 1 H), 2.21–2.37 (m, 3 H), 2.44 (ddd, *J* = 14.5, 12.0, 6.0 Hz, 1 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 7.54, 12.14, 20.50, 26.91, 27.15, 29.96, 35.28, 38.90, 51.08, 120.20, 214.02 ppm. HRMS: calcd. for $C_{11}H_{17}NO$ + H 180.1388; found 180.1391. The *ee* value was determined by chiral HPLC analysis as described in **3c** after conversion to the corresponding benzyl ester (80 equiv. of $PhCH_2OH$, 100 equiv. of conc. HCl, microwave, 150 °C, 2.0 h, 60–70% yield).

Methyl (*R*)-3-(2-Oxo-1,5,5-trimethylcyclohexyl)propanoate (3e): Colorless oil. $[\alpha]_D^{19}$ = +16.8 (*c* = 1.02, $CHCl_3$, 98% *ee*). FTIR (neat): $\tilde{\nu}$ = 1739, 1705, 1437 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.08 (s, 3 H), 1.10 (s, 6 H), 1.51 (d, *J* = 14.5 Hz, 1 H), 1.64 (t, *J* = 14.5 Hz, 1 H), 1.79 (t, *J* = 5.0 Hz, 1 H), 1.81 (ddd, *J* = 14.5, 11.0, 5.0 Hz, 1 H), 1.94 (ddd, *J* = 14.5, 11.0, 5.0 Hz, 1 H), 2.21 (ddd, *J* = 16.0, 11.0, 5.0 Hz, 1 H), 2.31 (ddd, *J* = 16.0, 11.0, 5.0 Hz, 1 H), 2.44 (t, *J* = 7.0 Hz, 1 H), 3.66 (s, 3 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 25.08, 29.23, 29.98, 30.34, 30.47, 34.45, 35.38, 37.98, 46.63, 50.59, 51.65, 174.03, 216.30 ppm. HRMS: calcd. for $C_{13}H_{22}O_3$ 226.1569; found 226.1571. *ee* of the corresponding benzyl ester was determined by chiral HPLC analysis with a Chiralpak AS-H column (0.46 × 25 cm, hexane/2-propanol = 99:1, flow rate 0.15 cm^3/min, λ = 254 nm), t_R (major) = 75.0 min and t_R (minor) = 78.9 min.

Methyl (*S*)-3-(7-Methyl-8-oxo-1,4-dioxaspiro[4.5]decan-7-yl)-propanoate (3f):[26] Colorless oil. $[\alpha]_D^{20}$ = +14.11 (*c* = 1.07, $CHCl_3$, 99% *ee*). FTIR (neat): $\tilde{\nu}$ = 1738, 1709 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.13 (s, 3 H), 1.81–1.89 (m, 2 H), 1.98–2.01 (m, 2 H), 2.09–2.19 (m, 3 H), 2.31 (ddd, *J* = 16.0, 10.5, 4.5 Hz, 1 H), 2.54 (dt, *J* = 15.0, 7.0 Hz, 1 H), 2.61 (ddd, *J* = 15.0, 8.5, 6.0 Hz, 1 H), 3.66 (s, 3 H), 3.97–4.05 (m, 4 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 23.47, 29.09, 33.17, 34.45, 35.63, 45.14, 46.99, 51.65, 64.33, 64.49, 107.28, 173.91, 213.77 ppm. HRMS: calcd. for $C_{13}H_{20}O_5$ 256.1311; found 256.1319. The *ee* value was determined

by chiral HPLC analysis with a Chiralpak AS-H column (0.46 × 25 cm, hexane/2-propanol = 99:1, flow rate 0.15 cm^3/min, λ = 210 nm), t_R (major) = 24.9 min and t_R (minor) = 42.9 min.

Methyl (*R*)-3-(1-Benzyl-2-oxocyclohexyl)propanoate (3g):[27] Colorless oil. $[\alpha]_D^{23}$ = +6.91 (*c* = 1.04, EtOH, 99% *ee*). FTIR (neat): $\tilde{\nu}$ = 1738, 1703 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.60–1.89 (m, 7 H), 1.97 (ddd, *J* = 15.5, 11.5, 5.0 Hz, 1 H), 2.12 (ddd, *J* = 15.5, 11.5, 5.0 Hz, 1 H), 2.39–2.47 (m, 3 H), 2.88 (ABq, J_{AB} = 13.5 Hz, 2 H), 3.66 (s, 3 H), 7.09 (d, *J* = 7.0 Hz, 2 H), 7.19–7.27 (m, 3 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 20.71, 26.74, 28.90, 29.69, 35.75, 39.41, 40.47, 51.69, 51.91, 126.42, 128.08 (× 2), 130.51 (× 2), 137.15, 173.83, 214.15 ppm. HRMS: calcd. for $C_{17}H_{22}O_3$ + H 275.1647; found 275.1644. The *ee* value was determined by chiral HPLC analysis with a Chiralpak AS-H column (0.46 × 25 cm, hexane/2-propanol = 99:1, flow rate 0.2 cm^3/min, λ = 254 nm), t_R (minor) = 43.19 min and t_R (major) = 86.89 min.

Methyl 3-(3-Benzyl-2-oxocyclohexyl)propanoate (4g): Colorless oil. FTIR (neat): $\tilde{\nu}$ = 1736, 1707 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.30 (dt, *J* = 13.5, 3.5 Hz, 1 H), 1.38 (dt, *J* = 13.5, 3.5 Hz, 1 H), 1.51–1.60 (m, 1 H), 1.64 (tq, *J* = 13.5, 3.5 Hz, 1 H), 1.80–1.83 (m, 1 H), 2.04–2.15 (m, 3 H), 2.27–2.46 (m, 4 H), 2.52–2.58 (m, 1 H), 3.20 (dd, *J* = 13.5, 4.5 Hz, 1 H), 3.66 (s, 3 H), 7.13–7.19 (m, 3 H), 7.25–7.28 (m, 2 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 24.67, 25.35, 31.65, 34.78, 35.36, 35.44, 50.06, 51.53, 52.83, 125.88, 128.24 (× 2), 129.09 (× 2), 140.47, 174.07, 212.77 ppm. HRMS: calcd. for $C_{17}H_{22}O_3$ + H 275.1647; found 275.1634.

Methyl (*R*)-3-(1-Methyl-2-oxocyclopentyl)propanoate (3i):[8] Colorless oil. $[\alpha]_D^{23}$ = +40.43 (*c* = 1.04, $CHCl_3$, 93% *ee*) {ref.[8] $[\alpha]_D^{20}$ = +33.0 (*c* = 1.68, EtOH, 99% *ee*)}; FTIR (neat): $\tilde{\nu}$ = 1737 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.01 (s, 3 H), 1.69–1.98 (m, 6 H), 2.19–2.40 (m, 4 H), 3.66 (s, 3 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 18.56, 21.31, 29.25, 31.33, 35.99, 37.46, 47.50, 51.67, 173.87, 222.47 ppm. *ee* of the corresponding benzyl ester was determined by chiral HPLC analysis with a Chiralpak AS-H column (0.46 × 25 cm, hexane/2-propanol = 99:1, flow rate 0.15 cm^3/min, λ = 254 nm), t_R (major) = 99.2 min and t_R (minor) = 108.8 min.

(*R*)-3-(1-Methyl-2-oxocyclopentyl)propionitrile (3j):[8] Colorless oil. $[\alpha]_D^{24}$ = +36.16 (*c* = 1.01, EtOH, 88% *ee*) {ref.[8] $[\alpha]_D^{20}$ = +26.5 (*c* = 1.0, EtOH, 72% *ee*)}. FTIR (neat): $\tilde{\nu}$ = 2247, 1734 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.05 (s, 3 H), 1.76–2.00 (m, 6 H), 2.20–2.46 (m, 4 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 12.54, 18.50, 20.96, 32.07, 35.88, 37.25, 47.32, 119.70, 221.48 ppm. The *ee* value was determined by chiral HPLC analysis as described in **3i** after conversion to the corresponding benzyl ester (80 equiv. of $PhCH_2OH$, 100 equiv. of conc. HCl, microwave, 150 °C, 2.0 h, 60–70% yield).

Benzyl (*R*)-3-(2-Methyl-3-oxotetrahydrofuran-2-yl)propanoate (3k):[28] Colorless oil. $[\alpha]_D^{19}$ = +36.86 (*c* = 1.03, $CHCl_3$, 95% *ee*). FTIR (neat): $\tilde{\nu}$ = 1752, 1736 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.18 (s, 3 H), 1.92 (ddd, *J* = 14.5, 9.0, 6.5 Hz, 1 H), 1.99 (ddd, *J* = 14.5, 9.0, 6.5 Hz, 1 H), 2.34 (ddd, *J* = 16.0, 9.0, 6.5 Hz, 1 H), 2.45 (ddd, *J* = 16.0, 9.0, 6.5 Hz, 1 H), 2.52 (dt, *J* = 8.0, 3.0 Hz, 2 H), 4.09 (sextet, *J* = 8.0 Hz, 2 H), 5.11 (ABq, J_{AB} = 12.5 Hz, 2 H), 7.32–7.38 (m, 5 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 20.30, 28.76, 30.67, 36.24, 61.64, 66.37, 80.53, 128.24, 128.27 (× 2), 128.54 (× 2), 135.84, 172.88, 217.07 ppm. HRMS: calcd. for $C_{15}H_{18}O_4$ + H 263.1283; found 263.1289. The *ee* value was determined by chiral HPLC analysis with a Chiralpak AS-H column (0.46 × 25 cm, hexane/2-propanol = 99:1, flow rate 0.5 cm^3/min, λ = 254 nm), t_R (major) = 37.8 min and t_R (minor) = 46.8 min.

Benzyl 3-(2-Methyl-3-oxotetrahydrofuran-5-yl)propanoate (4k): Colorless oil. FTIR (neat): $\tilde{\nu}$ = 1754, 1735 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.31 (d, *J* = 7.0 Hz, 3 H), 1.74 (sextet, *J* = 8.0 Hz, 1 H), 2.08 (sextet, *J* = 6.5 Hz, 1 H), 2.43–2.57 (m, 3 H), 3.64 (t, *J* = 10.0 Hz, 1 H), 3.76 (q, *J* = 7.0 Hz, 1 H), 4.42 (t, *J* = 10.0 Hz, 1 H), 5.12 (s, 2 H), 7.33–7.39 (m, 5 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 15.98, 22.59, 31.81, 45.79, 66.47, 69.97, 76.89, 128.30 (× 2), 128.35, 128.60 (× 2), 135.68, 172.51, 217.40 ppm. HRMS: calcd. for $C_{15}H_{18}O_4$ 262.1205; found 262.1215.

Methyl (*S*)-3-(1-Ethyl-2-trifluoromethylsulfonyloxy-2-cyclohexen-1-yl)propanoate (5): To a solution of **3c** (1.34 g, 6.3 mmol) in dry THF (9 mL) at –78 °C was added slowly potassium hexamethyldisilazide (0.5 M in toluene, 15.2 mL, 7.6 mmol), and the mixture was stirred at this temperature for 2 h. Then a THF (9 mL) solution of *N*-(2-pyridyl)bis(trifluoromethanesulfonimide) (2.72 g, 7.6 mmol) was added dropwise, and the mixture was warmed to room temperature and stirred for 5 h. After dilution with hexane, the mixture was quenched by addition of cold aq. HCl (5%), washed with aq. NaOH (5%) and brine, dried ($MgSO_4$), and concentrated. The crude product was purified by silica gel column chromatography (eluted with hexane/EtOAc = 4:1) to give **5** (1.71 g, 79%). Colorless oil. $[\alpha]_D^{21}$ = +14.05 (*c* = 1.13, $CHCl_3$). FTIR (neat): $\tilde{\nu}$ = 1742, 1674 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.5 Hz, 3 H), 1.45–1.73 (m, 6 H), 1.76–1.87 (m, 2 H), 2.15–2.19 (m, 2 H), 2.32 (t, *J* = 8.0 Hz, 2 H), 3.68 (s, 3 H), 5.84 (t, *J* = 4.0 Hz, 1 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 8.22, 18.37, 24.57, 29.25, 29.61, 30.92, 31.63, 40.86, 51.74, 118.25, 153.56, 173.96 ppm. HRMS: calcd. for $C_{13}H_{19}F_3O_5S$ + H 345.0984; found 345.0972.

Methyl (*S*)-3-(1-Ethyl-2-cyclohexen-1-yl)propanoate (6): To a mixture of enol triflate **5** (1.58 g, 4.6 mmol), $Pd(OAc)_2$ (20 mg, 0.09 mmol), and PPh_3 (47 mg, 0.18 mmol) in dry dimethylformamide (23 mL) at 60 °C was added Et_3SiH (1.84 mL, 11.5 mmol). At this time the solution color changed sharply from light yellow to deep brown. The mixture was stirred for 2 d, and additional Et_3SiH (1.0 mL, 6.3 mmol) was introduced and stirred until completion of the reaction (8 h). After dilution with Et_2O, the mixture was washed with H_2O, satd. $NaHCO_3$, and brine, dried (Na_2SO_4), and concentrated. The crude product was purified by silica gel column chromatography (eluted with hexane/EtOAc = 6:1) to give **6** (820 mg, 91%). Colorless oil. $[\alpha]_D^{21}$ = +30.75 (*c* = 1.17, $CHCl_3$). FTIR (neat): $\tilde{\nu}$ = 1741 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.82 (t, *J* = 7.5 Hz, 3 H), 1.26–1.47 (m, 4 H), 1.57–1.66 (m, 4 H), 1.90–1.95 (m, 2 H), 2.24–2.27 (m, 2 H), 3.66 (s, 3 H), 5.35 (d, *J* = 10.5 Hz, 1 H), 5.68 (dt, *J* = 10.5, 4.0 Hz, 1 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 8.04, 18.98, 25.08, 29.22, 31.52, 32.13, 33.94, 36.39, 51.46, 127.17, 134.26, 174.78 ppm. HRMS: calcd. for $C_{12}H_{20}O_2$ + H 197.1542; found 197.1558.

Methyl (*S*)-3-(1-Ethyl-4-oxo-2-cyclohexen-1-yl)propanoate (7): To a solution of cyclohexene **6** (20 mg, 0.1 mmol) in dry EtOAc (0.7 mL) were added *t*BuOOH (2.38 M in toluene, 0.5 mL, 1.0 mmol) and powdered MS 4A (20 mg), and the mixture was stirred at 18 °C for 30 min. Then $Mn(OAc)_3 \cdot 2H_2O$ (3.6 mg, 0.005 mmol) was added in one portion, and the mixture was stirred at this temperature for 16 h. The insoluble substance was removed by filtration through Celite, and the mixture was concentrated. The crude product was purified by silica gel column chromatography (eluted with hexane/EtOAc = 2:1) to give **7** (15.4 mg, 73%). Colorless oil. $[\alpha]_D^{20}$ = +45.57 (*c* = 1.10, EtOH, > 99% *ee*) {ref.[23b] for (*R*)-isomer: $[\alpha]_D^{21}$ = –40.4 (*c* = 1.73, EtOH)}. FTIR (neat): $\tilde{\nu}$ = 1738, 1682 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 7.5 Hz, 3 H), 1.46–1.57 (m, 2 H), 1.78–1.90 (m, 4 H), 2.30 (ddd, *J* = 9.5, 7.0, 3.5 Hz, 2 H), 2.44 (t, *J* = 7.0 Hz, 2 H), 3.67 (s, 3 H), 5.93 (d, *J* = 10.0 Hz, 1 H), 6.64 (d, *J* = 10.0 Hz, 1 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 8.27, 29.03, 30.17, 30.25, 32.02, 33.74, 37.88, 51.72, 128.71, 157.06,

173.67, 199.09 ppm. The *ee* value was determined by chiral HPLC analysis with a Chiralpak AS-H column (0.46 × 25 cm, hexane/2-propanol = 99:1, flow rate 0.5 cm^3/min, λ = 210 nm), t_R (major) = 30.22 min.

Supporting Information (see footnote on the first page of this article): NMR spectra and HPLC chromatogram for all adducts.

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