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Enantioselective Michael additions of β-keto esters to α,β-unsaturated carbonyl compounds catalyzed by a chiral biquinoline *N*,*N*′-dioxide–scandium trifluoromethanesulfonate complex

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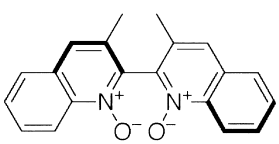
Abstract—A catalytic, enantioselective Michael addition of β-keto esters to α,β-unsaturated carbonyl compounds was achieved by using a chiral biquinoline *N*,*N*′-dioxide–scandium trifluoromethanesulfonate complex as a catalyst. The corresponding Michael adducts were obtained in high yields and with enantioselectivities up to 84% ee.

1. Introduction

Catalytic, enantioselective Michael additions are fundamental carbon–carbon bond formation reactions in organic synthesis because the products are versatile chiral building blocks.[1] Michael additions of prochiral β-keto esters to α,β-unsaturated carbonyl compounds generate quaternary stereogenic centers, which are still challenging for synthetic organic chemists. Various chiral catalysts have been developed for this type of Michael addition including cinchona alkaloids,[2a–c] chiral alkoxide complexes,[2d] chiral crown ether–metal alkoxide complexes,[2e] chiral transition metal complexes,[2f–k] and chiral bimetallic lanthanoid complexes.[1b]



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Although *N*-oxide is a functional group possessing a unique electron-donating property, which allows it to form complexes with a variety of metals,[3] there are a limited reports using *N*-oxides as chiral ligands.[4] In our pursuit to develop *N*-oxide-mediated reactions,[5] herein we describe the details of a chiral biquinoline *N*,*N*′-dioxide–scandium trifluoromethanesulfonate complex catalyzed enantioselective Michael addition of β-keto esters to α,β-unsaturated carbonyl compounds.[6]

2. Results and discussion

We have recently reported enantioselective conjugate additions of thiols to cyclic enones and acyclic enals catalyzed by a complex of chiral *N*-oxide **1** and cadmium iodide.[7] Some effective catalysts for enantioselective conjugate addition of thiols also catalyze enantioselective Michael addition of α,β-unsaturated carbonyl compounds to enones.[1b,2a,b] This prompted us to investigate the Michael addition of dibenzyl malonate to cyclohexenone employing the **1**–cadmium complex. According to the procedure for the above conjugate addition,[7] dibenzyl malonate was added to a solution of cyclohexenone, *N*-oxide **1** (5 mol%) and cadmium iodide (5 mol%) in toluene, but the Michael adduct was not obtained at all. Then the Michael addition of methyl 1-oxoindan-2-carboxylate (**2a**) to methyl vinyl ketone (Eq. (1)), a reaction[2] frequently investigated as a probe for the enantioselective Michael addition was examined. The reaction proceeded smoothly with **1**–cadmium iodide complex in dichloromethane, but the observed enantiomeric excess of the adduct was low (Table 1, entry 1). Table 1 also shows other representative results using various metal salts that resulted in a high yield

Keywords: enantioselectivities; α,β-unsaturated carbonyl compounds; chiral biquinoline; enantioselection; catalyst; Michael addition; *N*-oxide; scandium trifluoromethanesulfonate.
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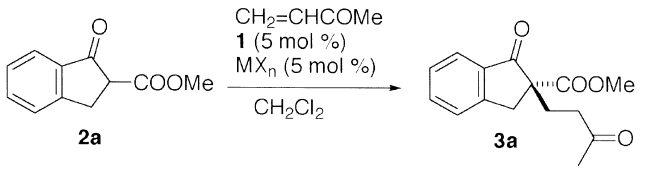

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Table 1. Enantioselective Michael addition of **2a** to MVK catalyed by 1-metal complex

Entry	MX_n	Time (h)	Yield (%)[a]	ee (%)[b]
1	CdI_2	48	75	13
2	$Yb(OTf)_3$	24	98	9
3	$Hf(OTf)_4$	24	82	18
4	$Sc(OTf)_3$	1	98	39
5	$ScCl_3$	24	83	9

Catalyst concentration: 0.5 mM.
[a] Isolated yield.
[b] Determined by Chiral HPLC (Daicel Chiralpak AD).

of the Michael adduct **3a** with observable enantioselectivities. Among the surveyed metal salts, we found that scandium trifluoromethanesulfonate[8,9] gave **3a** in a quantitative yield with a moderate enantioselectivity of 39% ee (entry 4).

Although scandium trifluoromethanesulfonate is insoluble in dichloromethane, its complex with **1** and **2a** dissolves in dichloromethane to give a yellow solution. Other solvents

Table 2. Enantioselective Michael addition of **2a** to MVK catalyzed by **1**–$Sc(OTf)_3$ complex

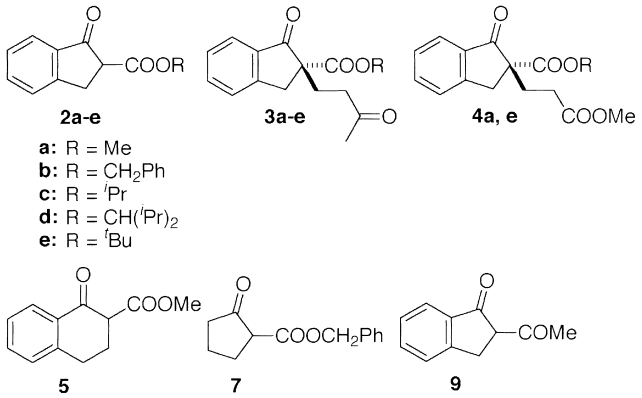
Entry	**1**/$Sc(OTf)_3$	mM[a]	Solvent	Time (h)	Yield (%)[b]	ee (%)[c]
1	1	0.5	CH_2Cl_2	1	98	39
2	1	0.5	Toluene	5	96	8
3	1	0.5	THF	24	97	10
4	1	0.5	EtCN	1	97	19
5	0.1	0.5	CH_2Cl_2	1	94	30
6	2.5	0.5	CH_2Cl_2	2	98	9
7	1	0.1	CH_2Cl_2	1	85	35
8	1	2.5	CH_2Cl_2	0.2	93	6

[a] Concentration of catalyst.
[b] Isolated yield.
[c] Determined by Chiral HPLC (Daicel Chiralpak AD).

examined for the Michael addition afforded the product in lower enantiomeric excess than dichloromethane (Table 2, entries 2–4 vs. entry 1).[10] The enantioselectivity was strongly dependent on the ratio of *N*-oxide to scandium (entries 5, 6 vs. entry 1) and the catalyst concentration (entries 7, 8 vs. entry 1). These observations suggest a variety of aggregation states for the scandium and *N*-oxide complexes, but the details are unclear.

The Michael addition of **2a** with various α,β-unsaturated carbonyl compounds was investigated. Chalcone generated a complex mixture of products, while a reaction was not observed using methyl acrylate as an acceptor. The mild reaction conditions allowed acrolein to react with **2a**, which generated the corresponding adduct with a similar enantioselectivity (isolated as methyl ester **4a**, 75% yield, 30% ee).

Various β-keto esters were then evaluated as Michael donors employing methyl vinyl ketone as an acceptor. Reactions of methyl 1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (**5**), (10 h, 81%), benzyl 2-oxocyclopentane-carboxylate (**7**), (3 h, 98%), and 2-acetyl-2-indanone (**9**) (0.5 h, 86%) yielded racemic mixtures, which suggests that indan-2-carboxylate skeleton is important in directing the enantiocontrol.



Enantioselective Michael additions of various esters of 1-oxoindan-2-carboxylic acid to methyl vinyl ketone were then investigated. The bulkiness of the ester substituent of 1-oxoindan-2-carboxylate had a pronounced effect on the observed enantioselectivity. As shown in Table 3, the enantioselectivities increased with the bulkiness of the ester. *tert*-Butyl ester **2e** gave the highest enantioselectivity of 84% ee (Table 3, entry 5)[11]. The addition of acrolein to **2e** affirmed the beneficial effect of *tert*-butyl ester (entry 6) and is a rare example of the catalytic enantioselective Michael addition of β-keto ester to α,β-unsaturated aldehyde.[2a,12]

The transition state model shown in Figure 1, in which scandium trifluoromethanesulfonate forms a complex with *N*-oxide **1** and β-keto ester **2a**, may explain the predominant formation of (*R*)-**3e**. In order to avoid steric repulsion with the quinoline moiety, the bulky *tert*-butyl ester moiety should be located on the *si*-face of the keto ester plane which causes the methyl vinyl ketone to preferentially attack the *re*-face.

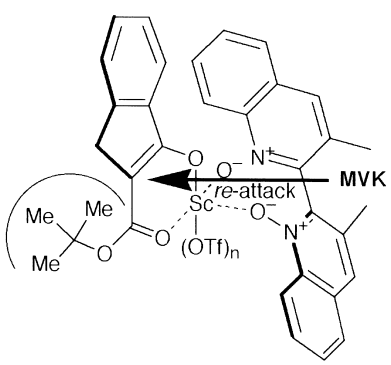


Figure 1. Proposed model for the enantioselective Micheal addition catalyzed by **1**–$Sc(OTf)_3$ complex.

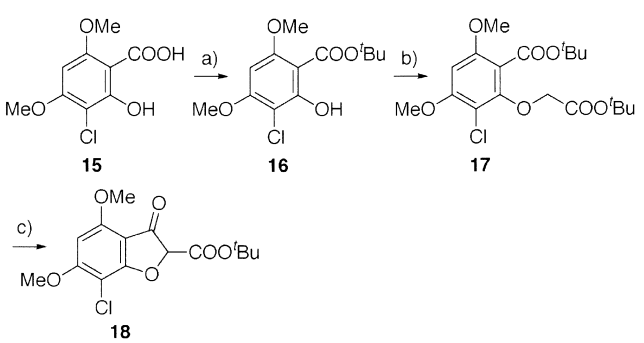
Table 3. Enantioselective Michael addition of β-keto ester **2** catalyzed by **1**–$Sc(OTf)_3$ complex

Entry	Donor	R	Acceptor	Adduct	Yield (%)	ee (%)[a]	Configuration	$[\alpha]_D^{25}$ (Benzene)
1	**2a**	Me	CH_2=CHCOMe	**3a**	98	39	*R*[b]	+27.1
2	**2b**	CH_2Ph	CH_2=CHCOMe	**3b**	85	38	*R*[c]	+17.5
3	**2c**	^{i}Pr	CH_2=CHCOMe	**3c**	94	47	*R*[d]	+31.9
4	**2d**	$CH(^iPr)_2$	CH_2=CHCOMe	**3d**	98	69	*R*[d]	+20.4
5[e]	**2e**	^{i}Bu	CH_2=CHCOMe	**3e**	89	84	*R*[f]	+47.1
6	**2e**	^{i}Bu	CH_2=CHCHO	**4e**	73[g]	75[g]	*R*[d]	+38.3[h]

Catalyst concentration: 0.5 mM.
[a] Determined by HPLC analysis employing Daicel Chiralpak AD or Chiralcel OJ.
[b] Assigned by optical rotation.
[c] Assigned by optical rotation of **3b** prepared from **3a**.
[d] Assigned by analogy.
[e] Catalyst concentration: 0.1 mM.
[f] Assigned by optical rotation after conversion to **3a**.
[g] Determined after conversion of aldehyde into methyl ester **4e**.
[h] Optical rotation of diester **4e**.

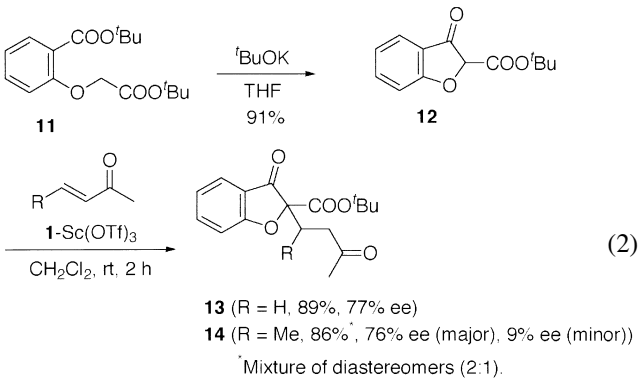
Next, the present Michael addition was applied to the enantioselective synthesis of biologically active compounds. Griseofulvin[13] is an antifungal agent that is used to treat dermatomycoses in animals and humans. To date only Pirrung,[14] who applied an asymmetric sigmatropic rearrangement of oxonium ylide for the construction of spirocyclic structure, has reported the enantioselective synthesis of griseofulvin. We plan to apply the present Michael addition to the enantioselective synthesis of griseofulvin.

As a model for synthesizing griseofulvin, the Michael addition of *tert*-butyl 3-oxobenzo[*b*]furan-2-carboxylate **12**, an oxygen analogue of **2e** was investigated. The reaction of **12** to methyl vinyl ketone proceeded smoothly to afford the Michael adduct in 77% ee (Eq. (2)). Although the diastereoselectivity was modest, the reaction of 3-penten-2-one also proceeded smoothly to give a diastereomeric mixture with a 76% ee of the major isomer, but the stereochemistries of the newly formed chiral centers were not determined. Encouraged by these findings, *tert*-butyl oxofurancarboxylate **18** was synthesized from chlorodimethoxysalicylic acid **15** via a Dieckmann condensation shown in Scheme 1 and the enantioselective Michael addition of **18** was studied. The reaction proceeded smoothly, but neither diastereoselectivity nor enantioselectivity were observed (Eq. (3)). This dramatic drop in selectivities may be due to the steric repulsion of the methoxy group of the substrate and the quinoline ring of **1** in Figure 1, though details are unclear.



Scheme 1. Preparation of Micheal donor **18**. *Reagents and condition*: (a) $Me_2NCH(O^tBu)_2$, benzene, reflux, 2 h, 82%. (b) $BrCH_2COO^tBu$, K_2CO_3, 2-butanone, reflux, 6 h, 97%. (c) ^{t}BuOK, THF, room temperature, 15 min, 98%.

griseofulvin



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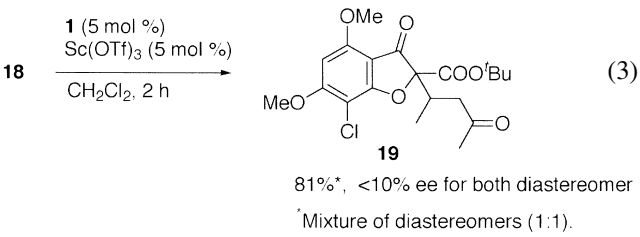

(3)

3. Conclusion

In conclusion, the potential of a chiral biquinoline *N*,*N*′-dioxide–scandium trifluoromethanesulfonate complex to catalyze enantioselective Michael additions of β-keto esters to methyl vinyl ketone or acrolein was demonstrated. 1-Oxoindan-2-carboxylate skeleton is essential for the enantiocontrol. The present reaction provides a rare example of a catalytic enantioselective Michael addition to α,β-unsaturated aldehyde.

4. Experimental

4.1. General

Melting points were measured using a Büchi 535 melting point apparatus and were not corrected. Optical rotations were obtained on a JASCO P-1030 digital polarimeter. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL EX-270 (^{1}H, 270 MHz; ^{13}C, 68 MHz) spectrometer in deuteriochloroform. The chemical shift values are in ppm relative to internal tetramethylsilane. The coupling constants (J) are in Hertz (Hz). Abbreviations are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, br, broad. Infrared spectra (IR) were recorded on a JASCO FT/IR-5300 spectrometer. Mass spectra were obtained on a JEOL JMS-FABmate spectrometer by electron impact (EI) with an ionization voltage of 70 eV. Michael donors **2a**,[2b] **2b**,[15] **5**,[16] **7**,[17] and **9**[18] were prepared by literature methods. Esters **2c**–**2e** were prepared from **2a** with transesterification catalyzed by dibutyltin oxide.[19]

4.2. A representative procedure for the synthesis of Michael donor by transesterification

A solution of **2a** (1.0 mmol), dibutyltin oxide (0.10 mmol) and the corresponding alcohol (10 mmol) in toluene (10 ml) was refluxed for 2 h. Evaporation of the solvent and chromatography (silica gel 10 g, hexane/AcOEt=20:1) afforded the corresponding ester.

4.2.1. Isopropyl 1-oxoindan-2-carboxylate (2c). Yield 68%. Colorless needles of mp 41–42°C. IR ($CHCl_3$): ν 1713, 1732 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.28 (3H, d, J=6.6 Hz), 1.29 (3H, d, J=6.6 Hz), 3.36 (1H, dd, J=8.6, 17.3 Hz), 3.53 (1H, dd, J=4.0, 17.3 Hz), 3.68 (1H, dd, J=4.0, 8.6 Hz), 5.09 (1H, sept, J=5.9 Hz), 7.30–7.80 (4H, m). ^{13}C NMR ($CDCl_3$): δ 21.7, 30.2, 53.4, 69.2, 124.6, 126.7, 127.7, 129.2, 135.2, 153.6, 168.7, 199.6. MS (EI): m/z 218 (M^+), 176. HRMS: calcd for $C_{13}H_{14}O_3$ 218.0943 found 218.0950.

4.2.2. 2,4-Dimethyl-3-pentyl 1-oxoindan-2-carboxylate (2d). Yield 31%. Colorless needles of mp 62–63°C. IR ($CHCl_3$): ν 1713, 1731 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.82–0.93 (12H, m), 1.86–1.99 (1H, m), 3.39 (1H, dd, J=8.4, 17.0 Hz), 3.58 (1H, dd, J=4.1, 17.0 Hz), 3.75 (1H, dd, J=4.1, 8.4 Hz), 4.67 (1H, t, J=6.5 Hz), 7.30–7.80 (4H, m). ^{13}C NMR ($CDCl_3$): δ 16.9, 17.3, 19.4, 19.5, 29.4, 29.5, 30.5, 53.6, 84.2, 124.6, 126.5, 127.7, 135.2, 135.4, 153.5, 169.1, 199.6. MS (EI): m/z 274 (M^+), 176. HRMS: calcd for $C_{17}H_{22}O_3$ 274.1569 found 274.1546.

4.2.3. *tert*-Butyl 1-oxoindan-2-carboxylate (2e). Yield 52%. Colorless needles of mp 44–46°C. IR ($CHCl_3$): ν 1711, 1731 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.47 (9H, s), 3.30 (1H, dd, J=8.6, 17.3 Hz), 3.47 (1H, dd, J=4.0, 17.3 Hz), 3.59 (1H, dd, J=4.0, 8.6 Hz), 7.33–7.55 (4H, m). ^{13}C NMR ($CDCl_3$): δ 28.0, 30.3, 54.4, 82.0, 124.5, 126.6, 127.6, 135.2, 135.5, 153.7, 168.3, 200.0. MS (EI): m/z 232 (M^+), 176. HRMS: calcd for $C_{14}H_{16}O_3$ 232.1099 found 232.1094.

4.3. A representative procedure for the enantioselective Michael addition catalyzed by a scandium trifluoromethanesulfonate–1 complex

A mixture of N,N'-dioxide **1** (0.026 mmol), scandium trifluoromethanesulfonate (0.026 mmol) and β-keto ester **2e** (0.52 mmol) in dichloromethane (5 ml) was sonicated for 5 min, resulting in a yellow solution. An α,β-unsaturated carbonyl compound (2.6 mmol) was added to the solution and the mixture was stirred at room temperature for 0.5 h. The reaction mixture was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography (silica gel 5 g, hexane/AcOEt=5:1) to yield the corresponding Michael adduct. N,N'-Dioxide **1** was recovered by eluding with 10% ethanol in dichloromethane without losing of optical purity. The enantiomeric excess of the adduct was determined by chiral HPLC.

4.3.1. Methyl 1-oxo-2-(3-oxobutyl)indan-2-carboxylate (3a).[2a] HPLC: Daicel Chiralpak AD, hexane/2-propanol=9:1, 1 ml/min, t_R: 16 (S) and 18 (R) min. $[\alpha]_D^{25}$=+27.1, $[\alpha]_{577}^{25}$=+29.8 (c 1.24, benzene) for 39% ee {lit. $[\alpha]_{578}^{rt}$=−77 (c 2, benzene) for (S)-isomer}. IR ($CHCl_3$): ν 1742, 1715 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.12 (3H, s), 2.19–2.27 (2H, m), 2.45–2.76 (2H, m), 3.04 (1H, d, J=17.8 Hz), 3.67 (1H, d, J=17.8 Hz), 3.70 (3H, s), 7.39–7.79 (4H, m). ^{13}C NMR ($CDCl_3$): δ 28.6, 29.8, 37.8, 38.7, 52.7, 59.1, 124.8, 126.4, 127.9, 135.0, 135.5, 152.5, 171.5, 202.2, 207.3. MS (EI): m/z 260 (M^+), 190.

4.3.2. Benzyl 1-oxo-2-(3-oxobutyl)indan-2-carboxylate (3b). HPLC: Daicel Chiralpak AD, hexane/2-propanol=9:1, 1 ml/min, t_R: 19 (S) and 22 (R) min. $[\alpha]_D^{25}$=+17.5 (c 0.66, benzene) for 38% ee. IR ($CHCl_3$): ν 1714 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.08 (3H, s), 2.20–2.28 (2H, m), 2.48–2.66 (2H, m), 3.03 (1H, d, J=17.2 Hz), 3.66 (1H, d, J=17.2 Hz), 5.15 (2H, s), 7.23–7.79 (9H, m); ^{13}C NMR ($CDCl_3$): δ 28.7, 29.9, 37.8, 38.8, 59.2, 67.1, 124.8, 126.3, 127.7, 127.9, 128.1, 128.4, 134.9, 135.3, 135.4, 152.3, 170.7, 201.9, 207.3. MS (EI): m/z 336 (M^+), 266, 149. HRMS: calcd for $C_{21}H_{20}O_4$ (M^+) 336.1361, found 336.1368. Anal. calcd for $C_{21}H_{20}O_4$: C, 74.98; H, 5.99. Found: C, 74.52; H, 6.38. The absolute configuration was determined by the optical rotation of **3b** ($[\alpha]_D^{25}$=+18.4 (c 0.65, benzene)) prepared from **3a** ($[\alpha]_D^{25}$=+27.1 (c 1.24, benzene)) by transesterification with dibutyltin oxide and benzyl alcohol.

4.3.3. Isopropyl 1-oxo-2-(3-oxobutyl)indan-2-carboxylate (3c). HPLC: Daicel Chiralcel OJ, hexane/2-propanol=9:1, 1 ml/min, t_R: 17 (S) and 25 (R) min. $[\alpha]_D^{25}$=+31.9 (c 1.21, benzene) for 47% ee. IR ($CHCl_3$): ν 1712 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.17 (6H, d, J=5.9 Hz, 6H), 2.11 (3H, s), 2.17–2.23 (2H, m), 2.43–2.68 (2H, m), 3.01 (1H, d, J=17.2 Hz), 3.63 (1H, d, J=17.2 Hz), 5.01 (1H, sept, J=5.9 Hz), 7.37–7.77 (4H, m, 4H). ^{13}C NMR ($CDCl_3$): δ 21.5, 21.6, 28.5, 30.0, 37.9, 38.9, 59.3, 69.2, 124.7, 126.3, 127.8, 135.0, 135.3, 152.5, 170.4, 202.3, 207.5. MS (EI): m/z 288 (M^+), 218, 176. HRMS: calcd for $C_{17}H_{20}O_4$ 288.1361, found 288.1370. Anal. calcd for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found: C, 70.87; H, 7.14.

4.3.4. 2,4-Dimethyl-3-pentyl 1-oxo-2-(3-oxobutyl)indan-2-carboxylate (3d). HPLC: Daicel Chiralcel OJ, hexane/2-propanol=9:1, 1 ml/min, t_R: 9 (*S*) and 24 (*R*) min. $[\alpha]_D^{24}$=+20.4 (*c* 1.17, benzene) for 69% ee. IR ($CHCl_3$): ν 1711 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.71 (6H, d, *J*=4.6 Hz), 0.82 (6H, d, *J*=3.3 Hz), 1.73–1.87 (2H, m), 2.13 (3H, s), 2.27 (2H, t, *J*=7.6 Hz), 2.46–2.74 (2H, m), 3.07 (1H, d, *J*=17.2 Hz), 3.64 (1H, d, *J*=17.2 Hz), 4.58 (1H, t, *J*=5.9 Hz), 7.38–7.79 (4H, m). ^{13}C NMR ($CDCl_3$): δ 17.0, 17.2, 19.5, 19.6, 28.2, 29.4, 29.5, 30.0, 38.2, 38.8, 59.5, 84.1, 124.6, 126.2, 127.8, 135.2, 135.5, 152.4, 171.0, 202.4, 207.6. MS (EI): *m/z* 344 (M^+), 229, 176; HRMS: calcd for $C_{21}H_{28}O_4$ 344.1987, found 344.1991. Anal. calcd for $C_{21}H_{28}O_4$: C, 73.23; H, 8.19. Found: C, 73.21; H, 8.20.

4.3.5. *tert*-Butyl 1-oxo-2-(3-oxobutyl)indan-2-carboxylate (3e). HPLC: Daicel Chiralpak OJ, hexane/2-propanol=9:1, 1 ml/min, t_R: 10 (*S*) and 16 (*R*) min. $[\alpha]_D^{25}$=+47.1 (*c* 1.03, benzene) for 84% ee. IR ($CHCl_3$): ν 1712, 1370, 1154 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.39 (9H, s), 2.13 (3H, s), 2.15–2.21 (2H, m), 2.44–2.69 (2H, m), 3.00 (1H, d, *J*=17.2 Hz), 3.60 (1H, d, *J*=17.2 Hz), 7.37–7.77 (4H, m, 4H). ^{13}C NMR ($CDCl_3$): δ 27.9, 28.5, 30.0, 38.0, 38.9, 59.9, 82.0, 124.6, 126.2, 127.7, 135.1, 135.2, 152.5, 170.0, 202.6, 207.0. MS (EI): *m/z* 246 ($M^+-{}^t$Bu), 200, 176, 157. HRMS: calcd for $C_{14}H_{14}O_4$ ($M^+-{}^t$Bu) 246.0892, found 246.0886. Anal. calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.51; H, 7.42. The absolute configuration was determined by the optical rotation of **3a** ($[\alpha]_D^{25}$=+72.0 (*c* 0.49, benzene)) from **3e** ($[\alpha]_D^{25}$=+44.7 (*c* 1.23, benzene)) by treating with trifluoroacetic acid and then diazomethane.

4.3.6. Methyl 2-(methoxycarbonylethyl)-1-oxoindan-2-carboxylate (4a). To the crude Michael adduct (from 92 mg of **2a**) in MeOH–water (9:1, 1 ml) was added $NaHCO_3$ (0.81 g, 9.6 mmol). To this mixture, bromine (0.1 ml, 1.9 mmol) was added over 30 min with vigorous stirring at room temperature.[20] After stirring for 2 h, the excess bromine was decomposed with solid $Na_2S_2O_3$. The mixture was filtered and the filtrate was extracted with AcOEt. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography (silica gel 10 g, hexane/AcOEt=5:1) to give **4a** as a yellow oil (87 mg, 65%). HPLC: Daicel Chiralpak AD, hexane/2-propanol=9:1, 1 ml/min, t_R: 16 (*S*) and 18 (*R*) min. IR (neat): ν 1741, 1712 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.20–2.49 (4H, m), 3.07 (1H, d, *J*=17.2 Hz), 3.65 (3H, s), 3.70 (3H, s), 3.70 (1H, d, *J*=17.2 Hz), 7.41–7.79 (4H, m). ^{13}C NMR ($CDCl_3$): δ 29.6, 29.7, 37.2, 51.7, 52.8, 59.4, 124.9, 126.4, 128.0, 135.0, 135.5, 152.5, 171.2, 173.1, 201.8. MS (EI): *m/z* 276 (M^+), 244. HRMS: calcd for $C_{15}H_{16}O_5$ 276.0997, found 276.1004.

4.3.7. *tert*-Butyl 2-(methoxycarbonylethyl)-1-oxoindan-2-carboxylate (4e). HPLC: Daicel Chiralpak AD, hexane/2-propanol=9:1, 1 ml/min, t_R: 9.0 (*S*) and 9.8 (*R*) min. $[\alpha]_D^{22}$=+38.3 (*c* 0.69, benzene) for 75% ee. IR (neat): ν 1742, 1709 cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.38 (9H, s), 2.13–2.46 (4H, m), 3.01 (1H, d, *J*=17.2 Hz), 3.62 (1H, d, *J*=17.2 Hz), 3.63 (3H, s), 7.33–7.78 (4H, m). ^{13}C NMR ($CDCl_3$): δ 27.8, 29.4, 29.7, 37.0, 51.8, 52.5, 59.9, 125.0, 126.3, 128.6, 135.4, 135.8, 152.5, 171.0, 173.0, 201.5. MS (EI): *m/z* 318 (M^+), 262. HRMS: calcd for $C_{18}H_{22}O_5$ 318.1467, found 318.1460.

4.3.8. Methyl 1-oxo-2-(3-oxobutyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (6).[21] HPLC: Daicel Chiralpak AD, hexane/2-propanol=9:1, 1 ml/min, t_R: 11 and 13 min. IR ($CHCl_3$): ν 1730, 1688 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.97–2.18 (2H, m), 2.08 (3H, s), 2.44–2.51 (4H, m), 2.91–2.93 (2H, m), 3.61 (3H, s), 7.13–7.98 (4H, m). ^{13}C NMR ($CDCl_3$): δ 25.8, 27.6, 29.9, 31.6, 39.0, 52.4, 56.6, 126.8, 128.0, 128.7, 131.8, 133.6, 142.8, 172.3, 195.3, 207.6. MS (EI): *m/z* 274 (M^+), 204. HRMS: calcd for $C_{16}H_{18}O_4$ 274.1205, found 274.1194.

4.3.9. Benzyl 2-oxo-1-(3-oxobutyl)cyclopentanecarboxylate (8).[17] HPLC: Daicel Chiralpak AD, hexane/2-propanol=9:1, 1 ml/min, t_R: 10 and 11 min. IR ($CHCl_3$): ν 1740, 1722 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.82–2.00 (4H, m), 2.08 (3H, s), 2.10–2.18 (1H, m), 2.30–2.49 (4H, m), 2.58–2.71 (1H, m), 5.15 (2H, s), 7.32–7.40 (5H, m). ^{13}C NMR ($CDCl_3$): δ 19.5, 27.1, 29.8, 34.3, 37.9, 38.7, 59.0, 67.0, 128.0, 128.3, 128.6, 135.5, 171.1, 207.6, 214.5.

4.3.10. 2-Acetyl-2-(3-oxobutyl)-1-indanone (10). HPLC: Daicel Chiralcel OJ, hexane/2-propanol=9:1, 1 ml/min, t_R: 36 and 44 min. IR ($CHCl_3$): ν 1716, 1701 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.12 (3H, s), 2.23 (3H, s), 2.24–2.31 (2H, m), 2.39–2.42 (2H, m), 2.86 (1H, d, *J*=17.8 Hz), 3.77 (1H, d, *J*=17.8 Hz), 7.37–7.76 (4H, m). ^{13}C NMR ($CDCl_3$): δ 26.1, 26.2, 28.5, 30.0, 38.6, 67.3, 124.5, 126.4, 127.8, 135.1, 135.5, 152.7, 203.0, 203.8, 206.9. MS (EI): *m/z* 244 (M^+), 201, 145. HRMS: calcd for $C_{15}H_{16}O_3$ 244.1099, found 244.1085. Anal. calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.18; H, 6.98.

4.3.11. *tert*-Butyl 2-(2-*tert*-butoxy-2-oxoethyl)benzoate (11). To a solution of *tert*-butyl salicylate (400 mg, 2.06 mmol) and potassium carbonate (300 mg, 2.16 mmol) in 2-butanone (1 ml) was added *tert*-butyl bromoacetate (442 mg, 2.16 mmol) and the mixture was refluxed for 2 h. The reaction was quenched with water and the whole mixture was extracted with chloroform. The organic layer was washed with 5% NaOH aq and brine successively and dried over Na_2SO_4. Evaporation of the solvent and chromatography (silica gel 20 g, hexane/AcOEt=20:1) afforded **11** (585 mg, 92%) as a pale yellow oil. IR ($CHCl_3$): ν 1719, 1753 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.44 (9H, s), 1.56 (9H, s), 4.56 (2H, s), 6.82 (1H, d *J*=7.6 Hz), 6.97 (1H, m), 7.36 (1H, m), 7.70 (1H, d *J*=7.9 Hz). ^{13}C NMR ($CDCl_3$): δ 27.8, 28.1, 66.8, 80.9, 81.9, 113.9, 121.0, 123.0, 131.2, 132.3, 157.2, 165.1, 167.4. MS (EI): *m/z* 308 (M^+), 251. HRMS: calcd for $C_{17}H_{24}O_5$ 308.1624, found 308.1622.

4.3.12. *tert*-Butyl 3-oxo-2,3-dihydrobenzo[*b*]furan-2-carboxylate (12). To a suspension of potassium *tert*-butoxide (218 mg, 1.95 mmol) in toluene (10 ml) was added **11** (300 mg, 0.974 mmol) and the mixture was stirred for 30 min at room temperature. The reaction was quenched with NH_4Cl satd aq. and the whole was extracted with AcOEt. The organic layer was washed with brine and dried over Na_2SO_4. Evaporation and chromatography (silica gel 10 g, hexane/AcOEt=30:1) afforded **12** (208 mg, 91%) as a

pale yellow viscous oil. IR ($CHCl_3$): ν 1659, 1744 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.66 (9H, s), 7.45 (2H, d, J=7.1 Hz), 7.72 (2H, d, J=7.1 Hz), 8.20 (1H, brs); ^{13}C NMR ($CDCl_3$): δ 27.6, 83.0, 97.9, 112.5, 120.3, 122.8, 126.8, 128.8, 150.3, 153.2, 162.1. MS (EI): m/z 234 (M^+), 178. HRMS: calcd for $C_{13}H_{14}O_4$ 234.0892, found 234.0891.

4.3.13. *tert*-Butyl 3-oxo-2-(3-oxobutyl)-2,3-dihydrobenzo[*b*]furan-2-carboxylate (13). A mixture of *N*,*N*′-dioxide **1** (4.7 mg, 0.015 mmol), scandium trifluoromethanesulfonate (9.0 mg, 0.015 mmol) and β-keto ester **18** (70 mg, 0.30 mmol) in dichloromethane (10 ml) was sonicated for 5 min to give a yellow solution. Methyl vinyl ketone (0.1 ml, 1.3 mmol) were added to the solution and the mixture was stirred at room temperature for 1 h. The reaction mixture was washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography (silica gel 5 g, hexane/AcOEt=10:1) to give **13** (82 mg, 89%) as a viscous oil. HPLC: Daicel Chiralpak AD, hexane/2-propanol=40:1, 1 ml/min, t_R: 21.4 (min) and 23.3 (maj) min. IR ($CHCl_3$): ν 1720, 1745 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.36 (9H, s), 2.04 (3H, s), 2.2–2.6 (4H, m), 7.0–7.2 (2H, m), 7.5–7.6 (2H, m). ^{13}C NMR ($CDCl_3$): δ 27.0, 27.6, 37.1, 83.8, 90.8, 113.3, 119.6, 122.5, 124.8, 138.3, 138.4, 164.3, 172.1, 196.0, 206.3. MS (EI): m/z 304 (M^+), 248. HRMS: calcd for $C_{17}H_{20}O_5$ 304.1310 found 304.1325.

4.3.14. *tert*-Butyl 3-oxo-2-(1-methyl-3-oxobutyl)-2,3-dihydrobenzo[*b*]furan-2-carboxylate (14). A mixture of *N*,*N*′-dioxide **1** (4.4 mg, 0.014 mmol), scandium trifluoromethanesulfonate (8.4 mg, 0.014 mmol) and β-keto ester **13** (65 mg, 0.28 mmol) in dichloromethane (10 ml) was sonicated for 5 min, resulting in a yellow solution. 3-Penten-2-one[22] (0.1 ml, 1.3 mmol) was added to the solution and the mixture was stirred at room temperature for 1 h. The reaction mixture was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography (silica gel 5 g, hexane/AcOEt=10:1) to give **14** (76 mg, 86%) as a inseparable mixture of diastereomers. HPLC: Daicel Chiralcel OD, hexane/2-propanol=100:1, 1 ml/min, t_R: 17.1 (minor enantiomer of major diastereomer), 18.4 (minor enantiomer of minor diastereomer), 21.9 (major enantiomer of major diastereomer), 24.6 (major enantiomer of minor diastereomer). IR ($CHCl_3$): ν 1720, 1745 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.79 (3H×1/3, d J=7.0 Hz), 1.12 (3H×2/3, d J=7.0 Hz), 1.44 (9H×1/3, s), 1.46 (9H×2/3, s), 2.06 (3H×2/3, s), 2.18 (3H×1/3, s), 2.3–2.7 (2H, m), 3.1–3.3 (H, m), 7.0–7.2 2, m), 7.6–7.7 (2H, m). ^{13}C NMR ($CDCl_3$): δ 13.7, 14.2, 14.6, 21.0, 27.7, 29.0, 30.1, 30.2, 33.9, 34.0, 43.9, 45.4, 60.4, 84.0, 94.8, 113.2, 113.4, 120.2, 120.3, 122.4, 122.5, 124.7, 124.8, 138.4, 138.6, 171.1, 172.5, 172.7, 195.7, 206.0, 206.3. MS (EI): m/z 318 (M^+). HRMS calcd for $C_{18}H_{22}O_5$ 318.1467, found 318.1451.

4.3.15. *tert*-Butyl 5-chloro-2,6-dimethoxy-6-hydroxybenzoate (16). A solution of 3-chloro-4,6-dimethoxysalicylic acid **15**[23] (106 mg, 0.456 mmol) and *N*,*N*-dimethylformamide di-*tert*-butyl acetal[24] (0.50 ml, 2.09 mmol) in benzene (2 ml) was refluxed for 2 h. The mixture was diluted with AcOEt and then successively washed with water, $NaHCO_3$ satd aq., and brine. Drying over Na_2SO_4, evaporation of the solvent and chromatography (silica gel 5 g, hexane/AcOEt=5:1) afforded **16** (108 mg, 82%) as colorless prisms of mp 56°C. IR ($CHCl_3$): ν 1601, 1649, 2980 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.90 (9H, s), 3.85 (3H, s), 3.94 (3H, s), 6.04 (1H, s), 12.62 (1H, s). ^{13}C NMR ($CDCl_3$): δ 28.2, 55.9, 56.0, 82.9, 87.8, 98.9, 101.7, 159.6, 159.9, 160.8, 170.1. MS (EI): m/z 288 (M^+), 232. HRMS: calcd for $C_{13}H_{17}ClO_5$ 288.0764 found 288.0760. Anal. calcd for $C_{13}H_{17}ClO_5$ C, 54.08; H, 5.93 found C, 54.09; H, 6.02.

4.3.16. *tert*-Butyl 6-(2-*tert*-butoxy-2-oxoethoxy)-3-chloro-2,4-dimethoxybenzoate (17). To a suspension of **16** (800 mg, 2.77 mmol) and potassium carbonate (402 mg, 2.91 mmol) in 2-butanone (2 ml) was added *tert*-butyl bromoacetate (595 mg, 3.05 mmol) and the mixture was refluxed for 6 h. The reaction was quenched with water and the whole mixture was extracted with chloroform. The organic layer was washed with 5% NaOH aq. and brine successively and dried over Na_2SO_4. Evaporation of the solvent and chromatography (silica gel 50 g, hexane/AcOEt=20:1) afforded **17** (1.08 g, 97%) as colorless needles of mp 160–161°C. IR ($CHCl_3$): ν 1718, 1753 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.51 (9H, s), 1.54 (9H, s), 3.83 (3H, s), 3.91 (3H, s), 4.51 (2H, s), 6.31 (1H, s). ^{13}C NMR ($CDCl_3$): δ 28.0, 28.7, 56.2, 56.3, 70.4, 81.8, 82.1, 93.0, 108.2, 114.1, 152.4, 156.1, 157.0, 164.0, 166.9. MS (FAB): m/z 425 (M^++Na), 402. HRMS: calcd for $C_{19}H_{27}ClO_7$−Na 425.1343, found 425.1336. Anal. calcd for $C_{19}H_{27}ClO_7$ C, 56.64; H, 6.77, found C, 56.60; H, 6.81.

4.3.17. *tert*-Butyl 7-chloro-4,6-dimethoxy-3-oxo-2,3-dihydrobenzo[*b*]furan-2-carboxylate (18). To a solution of potassium *tert*-butoxide (168 mg, 1.50 mmol) in tetrahydrofuran (10 ml) was added **17** (300 mg, 0.745 mmol) and the mixture was stirred for 1 h at room temperature. The reaction was quenched with NH_4Cl sat aq and the whole was extracted with AcOEt. The organic layer was washed with brine and dried over Na_2SO_4. Evaporation and chromatography (silica gel 10 g, hexane/AcOEt=2:1) afforded **18** (240 mg, 98%) as a pale yellow viscous oil. IR ($CHCl_3$): ν 1709, 1741 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.49 (9H, s), 3.95 (3H, s), 3.99 (3H, s), 5.05 (1H, s), 6.10 (1H, s). ^{13}C NMR ($CDCl_3$): δ 27.7, 56.2, 56.8, 83.8, 89.7, 91.3, 97.4, 103.7, 157.8, 162.6, 164.3, 169.3, 188.0. MS (FAB): m/z 328 (M^+), 272 ($M^+-{}^t$Bu). HRMS: calcd for $C_{15}H_{17}ClO_6$ 328.0713 found 328.1711.

4.3.18. *tert*-Butyl 7-chloro-4,6-dimethoxy-3-oxo-2-(1-methyl-3-oxobutyl)-2,3-dihydrobenzo[*b*]furan-2-carboxylate (19). A mixture of *N*,*N*′-dioxide **1** (4.3 mg, 0.014 mmol), scandium trifluoromethanesulfonate (8.2 mg, 0.014 mmol) and β-keto ester **18** (90 mg, 0.27 mmol) in dichloromethane (10 ml) was sonicated for 5 min, resulting in a yellow solution. 3-Penten-2-one[22] (0.1 ml, 1.3 mmol) was added to the solution and the mixture was stirred at room temperature for 1 h. The reaction mixture was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography (silica gel 8 g, hexane/AcOEt=25:1) to give **19** (92 mg, 81%) as an inseparable mixture of diastereomers. HPLC: Daicel Chiralcel OD, hexane/2-propanol=100:1, 1 ml/min, t_R: 16.0, 19.3, 24.0, 25.3 min. IR ($CHCl_3$): ν 1720,

1745 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.82 (3H×1/2, d, J=6.6 Hz), 1.13 (3H×1/2, d, J=6.6 Hz), 1.45 (9H×1/2, s), 1.14 (9H×1/2, s), 2.07 (3H×1/2, s), 2.18 (3H×1/2, s), 2.2–2.3 (1H, m), 2.6–2.7 (1H, m), 3.2–3.3 (1H, m), 3.96 (3H×1/2, s), 3.98 (3H×1/2, s), 4.01 (3H, s), 6.10 (1H×1/2, s), 6.11 (1H×1/2, s). ^{13}C NMR ($CDCl_3$): δ 13.5, 14.4, 27.7, 30.2, 33.7, 43.8, 45.4, 56.3, 56.9, 75.9, 83.9, 89.2, 89.5, 95.9, 96.1, 104.6, 104.7, 157.5, 157.7, 164.0, 164.3, 168.9, 169.1, 190.2, 190.4, 194.4, 206.0, 206.3. MS (FAB): *m/z* 412 (M^+). HRMS: calcd for $C_{20}H_{25}ClO_7$ 412.1289, found 412.1276.

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