Supporting Information

An asymmetric vinylogous Mukaiyama-Michael reaction of α , β -unsaturated 2-acyl imidazoles catalyzed by chiral Sc(III)- or Er(III)- pybox complexes

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1. General. All reactions were carried out under an atmosphere of nitrogen in oven dried glassware with magnetic stirring. ¹H and ¹³C NMR spectra were recorded on Jeol (500 MHz and 400 MHz) spectrometers in CDCl₃. Chemical shifts are reported in delta (δ) units, in parts per million (ppm). Tetramethylsilane and CDCl₃ were used as internal standard for ¹H and ¹³C NMR respectively. Coupling constants were reported in Hz. Splitting patterns are designated as s for singlet; d for doublet; t for triplet; q for quartet; dd for doublet of doublet; m for multiplet. IR spectra were measured with PerkinElmer FT-IR Spectrum Two spectrometer. Mass spectrometric analysis was done on waters Q Tof Premier Micromass (ESI). Routine monitoring of reactions were performed using precoated silicagel TLC plates from E-Merck. All the chromatographic separations were carried out by using silica gel (Acme's, 100–200 mesh). Enantiomeric excess was determined by HPLC analysis on Daicel chiral columns using *iso*-propanol and *n*-hexane as eluent at 25°C. Optical rotations were measured on a commercially available automatic polarimeter. Melting points were recorded on a digital melting point apparatus.

2. Materials:



Ligands **2a-c** were synthesized according to procedure known in literature.¹ Ligands **2d-g** were commercially available. α , β -unsaturated 2-acyl imidazoles were prepared according to literature known procedure.² Silyloxyfuran **3a** was commercially available and silyloxyfuran **3b** was prepared according to reported method.³ HFIP (1, 1, 1, 3, 3, 3-Hexafluoro-2-propanol) and all the metal triflates were commercially available. Methyl cinnamate **11** was prepared according to literature known method.⁴

3. General procedure for asymmetric vinylogous Mukaiyama-Michael reaction and the details of scale-up of reaction:

(a) General procedure for the reaction of **3a** with α , β -unsaturated 2-acyl imidazoles catalyzed by Sc(III)-**2g** complex.

A solution of a ligand **2g** (0.024 mmol) and Sc(OTf)₃ (0.02 mmol) in dry chloroform (2 mL) was stirred at room temperature for 3 hours under nitrogen atmosphere. α , β -Unsaturated 2-acyl imidazoles (0.20 mmol) were added and

the whole mixture was stirred for an additional 15 minute at rt. HFIP (0.20 mmol) was then added to the mixture and the resulting reaction mixture was again stirred for 15 minute at rt. Then silyloxyfuran 3a (0.40 mmol) was added and the reaction mixture was allowed for stirring at room temperature until the completion of the reaction (monitored by TLC). The mixture was concentrated in vacuo and purified over silica gel by column chromatography (20-60% ethyl acetate in hexane) to afford the products.

Details of scale-up of reaction

Scheme S1 Scale-up of reaction.



General Procedure: A solution of a ligand **2g** (0.283 mmol) and Sc(OTf)₃ (0.236 mmol) in dry chloroform (12 mL) was stirred at room temperature for 3 hours under nitrogen atmosphere. α,β -Unsaturated 2-acyl imidazole **4a** (2.36 mmol) was added and the whole mixture was stirred for an additional 15 minute at rt. HFIP (2.36 mmol) was then added to the mixture and the resulting reaction mixture was again stirred for 15 minute at rt. Then silyloxyfuran **3a** (4.72 mmol) was added and the reaction mixture was allowed for stirring at room temperature for 50 min. The mixture was concentrated in vacuo and purified over silica gel by column chromatography (20-60% ethyl acetate in hexane) to afford the product **5a** in 89% yield with >20:1 *d.r.* and 96% *ee*.

(b) General procedure for the reaction of **3b** with α , β -unsaturated 2-acyl imidazoles catalyzed by Sc(III)-**2g** complex.

A solution of a ligand 2g (0.024 mmol) and Sc(OTf)₃ (0.02 mmol) in dry chloroform (1.6 mL) was stirred at room temperature for 3 hours under nitrogen atmosphere. α , β -Unsaturated 2-acyl imidazoles (0.20 mmol) were added and the whole mixture was stirred for an additional 15 minute at rt. HFIP (0.20 mmol) was then added and the resulting mixture was again stirred for 15 minute more at rt. Then silyloxyfuran **3b** (0.30 mmol in 0.4 mL chloroform) was added and the reaction mixture was allowed for stirring at room temperature until the completion of the reaction (monitored by TLC). The mixture was concentrated in vacuo and purified over silica gel by column chromatography (20-60% ethyl acetate in hexane) to afford the products.

(c) General procedure for the reaction of **3a** with α , β -unsaturated 2-acyl imidazoles catalyzed by Er(III)-**2g** complex.

A solution of a ligand **2g** (0.024 mmol) and Er(OTf)₃ (0.02 mmol) in dry chloroform (2 mL) was stirred at room temperature for 3 hour under nitrogen atmosphere. α_{β} -Unsaturated 2-acyl imidazoles (0.20 mmol) were added and

the whole mixture was stirred for an additional 15 minute at rt. 4Å molecular sieve (20 mg) was added and the mixture was cooled to -20 °C and stirred for 15 minute at same temperature. Then HFIP (0.20 mmol) was added and the resulting mixture was again allowed to stir for additional 15 minute at -20 °C. The silyloxyfuran **3a** (0.40 mmol) was added and the reaction mixture was allowed for stirring at -20 °C until the completion of the reaction (monitored by TLC). The mixture was concentrated in vacuo and purified over silica gel by column chromatography (20-60% ethyl acetate in hexane) to afford the products.

(d) General procedure for the reaction of **3b** with α , β -unsaturated 2-acyl imidazoles catalyzed by Er(III)-**2g** complex.

A solution of a ligand **2g** (0.024 mmol) and Er(OTf)₃ (0.02 mmol) in dry chloroform (1.6 mL) was stirred at room temperature for 3 hour under nitrogen atmosphere. α , β -Unsaturated 2-acyl imidazoles (0.20 mmol) was added and the whole mixture was stirred for an additional 15 minute at rt. 4Å molecular sieve (20 mg) was added and the mixture was cooled to -40 °C and stirred for 15 minute at same temperature. Then HFIP (0.20 mmol) was added and the resulting mixture was again allowed to stir for additional 15 minute. The silyloxyfuran **3b** (0.30 mmol in 0.4 mL chloroform) was added and the reaction mixture was concentrated in vacuo and purified over silica gel by column chromatography (20-60% ethyl acetate in hexane) to afford the products.

OSiMe ₃	Ph N Sc	; (12 mol %) (OTf) ₃ (10 mol %) Solvent, rt	0 Ph	
3a	4a		5a	~~~
Entry	Solvent	Time	Yield ^b	ee^d
			(%)	(%)
1	CH_2Cl_2	1 h	86	80
2	CHCl ₃	1 h	86	91
3	DCE	1 h	85	91
4	THF	2 h	87	90
5	1,4-Dioxane	2 h	85	84
6	Toluene	10 h	68	52
7^e	CHCl ₃	45 min	90	88
8 ^f	CHCl ₃	2 h	86	89
9^g	CHCl ₃	1 h	85	91
10^{h}	CHCl ₃	45 min	90	96
$11^{h,i}$	CHCl ₃	25 min	84	81
$12^{h,i,j}$	CHCl ₃	45 min	83	85
$13^{h,i,k}$	CHCl ₃	1.5 h	82	86
$14^{h,i,k,l}$	CHCl ₃	1.5 h	88	91

4. Optimization of vinylogous Mukaiyama-Michael reaction:

Table S1 Studies of reaction conditions^{*a,c*}

^{*a*} Reaction conditions: **4a** (0.1 mmol), **3a** (0.2 mmol), **2g** (0.012 mmol), Sc(OTf)₃ (0.01 mmol), Solvent (1.0 mL), rt. ^{*b*} Isolated yield. ^{*c*} dr in all cases is determined to be >20:1 from ¹H NMR of crude reaction mixture. ^{*d*} Determined by chiral HPLC. ^{*e*} 15 mol % catalyst loading. ^{*f*} 5 mol % catalyst loading. ^{*f*} Reaction at -5 °C. ^{*h*} 1 equiv. of HFIP. ^{*i*} **2g**-Er(OTf)₃ complex. ^{*j*} Reaction at 5 °C. ^{*k*} A molecular sieve.

5. Characterization data of vinylogous Michael products 5 and 7:



¹H NMR (500 MHz, CHLOROFORM-D) δ 7.26 – 7.16 (m, 6H), 7.06 (s, 1H), 6.93 (s, 1H), 5.97 (dd, J = 5.7, 1.7 Hz, 1H), 5.12 (d, J = 8.1 Hz, 1H), 3.83 (s, 3H), 3.72 – 3.63 (m, 2H), 3.55 (td, J = 8.2, 6.0 Hz, 1H). ¹³C NMR (125 MHz, CHLOROFORM-D) δ 189.78, 172.60, 155.16, 142.88, 138.81, 129.10, 128.93, 128.40, 127.78, 127.21, 122.30, 86.03, 45.03, 41.24, 36.18. IR (thin film): v = 3110, 3031, 2924, 2854, 1756, 1677, 1600, 1411, 1291, 1160, 1102, 1086 cm⁻¹. HRMS (ES+): Exact mass calcd for

C₁₇H₁₇N₂O₃ [M+H]⁺: 297.1239. Found: 297.1239.

For Sc(III)-2g: The compound 5a was isolated as white semisolid in 90% yield with >20:1 *d.r.* and 96% *ee.* $[\alpha]_D^{25} =$ + 72.7 (*c* 0.71, CHCl₃). The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IC-3 column, *n*-hexane/2-propanol (70:30) as eluent, flow rate = 1.0 mL/min. t_R (major) = 36.77 min, t_R (minor) = 41.67 min.

For Er(III)-2g: The compound 5a was isolated as white semisolid in 88% yield with >20:1 *d.r.* and 91% *ee.* $[\alpha]_D^{25} =$ + 54.3 (*c* 0.59, CHCl₃). The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IC-3 column, *n*-hexane/2-propanol (70:30) as eluent, flow rate = 1.0 mL/min. *t*_R (major) = 37.66 min, *t*_R (minor) = 42.74 min.



The compound **5b** was isolated as white semisolid in 91% yield with >20:1 *d.r.* and 92% *ee.* $[\alpha]_D^{25} = +57.1$ (*c* 0.72, CHCl₃). The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IC-3 column, *n*-hexane/2-propanol (70:30) as eluent, Flow rate: 1.0 mL/min. t_R (major) = 27.94 min, t_R (minor) = 32.89 min. ¹H NMR (500 MHz, CHLOROFORM-D) δ 7.40 (d, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 5.5 Hz, 1H), 7.21 – 7.17 (m, 1H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.06 (s, 1H), 6.94 (s, 1H),

6.03 (d, J = 4.2 Hz, 1H), 5.17 (d, J = 6.4 Hz, 1H), 4.22 (d, J = 6.7 Hz, 1H), 3.84 (s, 3H), 3.63 (d, J = 6.1 Hz, 2H). ¹³C NMR (125 MHz, CHLOROFORM-D) δ 189.42, 172.58, 155.15, 142.68, 136.95, 134.16, 130.11, 129.31, 129.17, 128.84, 127.49, 127.25, 122.35, 85.32, 40.13, 39.65, 36.19. IR (thin film): v = 3112, 2958, 2924, 1757, 1678, 1600, 1476, 1411, 1291, 1160, 1103, 1039 cm⁻¹. HRMS (ES+): Exact mass calcd for C₁₇H₁₆ClN₂O₃ [M+H]⁺: 331.0849. Found: 331.0843.



¹H NMR (500 MHz, CHLOROFORM-D) δ 7.22 – 7.17 (m, 5H), 7.06 (s, 1H), 6.94 (s, 1H), 6.01 – 5.99 (m, 1H), 5.11 (d, *J* = 6.4 Hz, 1H), 3.84 (s, 3H), 3.68 (td, *J* = 10.3, 4.5 Hz, 1H), 3.61 – 3.54 (m, 2H). ¹³C NMR (125 MHz, CHLOROFORM-D) δ 189.44, 172.37, 154.63, 142.75, 137.28, 133.63, 129.85, 129.24, 129.07, 127.39, 122.70, 85.58, 44.18, 40.69, 36.20. IR (thin film): v = 3112, 2924, 2853, 1757, 1677, 1599, 1493, 1411,

1244, 1160, 1095, 1036 cm⁻¹. HRMS (ES+): Exact mass calcd for $C_{17}H_{16}ClN_2O_3$ [M+H]⁺: 331.0849. Found: 331.0844.

For Sc(III)-2g: The compound 5c was isolated as white semisolid in 92% yield with >20:1 *d.r.* and 96% *ee.* $[\alpha]_D^{25} =$ + 80.3 (*c* 0.35, CHCl₃). The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IC-3 column, *n*-hexane/2-propanol (70:30) as eluent, flow rate: 1.0 mL/min. *t*_R (major) = 26.40min, *t*_R (minor) = 29.11 min.

For Er(III)-2g: The compound 5c was isolated as white semisolid in 85% yield with >20:1 *d.r.* and 93% *ee.* The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IC-3 column, *n*-hexane/2-propanol (70:30) as eluent, flow rate: 1.0 mL/min. t_R (major) = 26.43min, t_R (minor) = 29.08 min.



The compound **5d** was isolated as white semisolid in 91% yield with >20:1 *d.r.* and 93% *ee.* $[\alpha]_D^{25} = +$ 48.8 (*c* 1.31, CHCl₃). The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IC-3 column, *n*-hexane/2-propanol (70:30) as eluent, flow rate: 1.0 mL/min. t_R (major) = 29.47 min, t_R (minor) = 34.13 min. ¹H NMR (500 MHz, CHLOROFORM-D) δ 7.52 (d, *J* = 7.8 Hz, 1H), 7.40 (d, *J* = 7.1 Hz, 1H), 7.27 – 7.20 (m, 2H), 7.13 – 6.98 (m, 2H), 6.94 (s, 1H), 6.04 (dd, *J* = 5.6, 1.7 Hz, 1H),

5.15 (d, J = 5.4 Hz, 1H), 4.23 (d, J = 6.5 Hz, 1H), 3.84 (s, 3H), 3.61 (d, J = 6.8 Hz, 2H). ¹³C NMR (125 MHz, CHLOROFORM-D) δ 189.35, 172.59, 155.17, 142.64, 138.63, 133.43, 129.34, 129.14, 128.13, 127.26, 125.03, 122.33, 85.42, 42.59, 39.72, 36.20. IR (thin film): v = 3111, 2957, 2924, 2854, 1757, 1677, 1600, 1472, 1411, 1291, 1159, 1103, 1081 cm⁻¹. HRMS (ES+): mass calcd for C₁₇H₁₆BrN₂O₃ [M+H]⁺: 375.0344. Found: 375.0341.



The compound **5e** was isolated as white semisolid in 93% yield with >20:1 *d.r.* and 97% *ee*. $[\alpha]_D^{25} = +$ 63.2 (*c* 1.12, CHCl₃). The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IC-3 column, *n*-hexane/2-propanol (70:30) as eluent, flow rate: 1.0 mL/min. *t*_R (major) = 26.15 min, *t*_R (minor) = 29.90 min. ¹H NMR (500 MHz, CHLOROFORM-D) δ 7.39 (s, 1H), 7.32 (d, *J* = 7.9 Hz, 1H), 7.21 – 7.19 (m, 2H), 7.12 (t, *J* = 7.8 Hz, 1H), 7.07 (s, 1H), 6.95 (s, 1H), 6.01 (dd, *J* = 5.7, 1.7 Hz, 1H), 5.12

(d, J = 7.4 Hz, 1H), 3.85 (s, 3H), 3.68 – 3.54 (m, 3H). ¹³C NMR (125 MHz, CHLOROFORM-D) δ 189.26, 172.34, 154.66, 142.64, 141.25, 131.46, 130.99, 130.48, 129.17, 127.37, 127.22, 122.92, 122.68, 85.50, 44.43, 40.76, 36.22. IR (thin film): v = 3112, 2958, 2925, 2854, 1756, 1677, 1596, 1476, 1411, 1291, 1160, 1097, 1036 cm⁻¹. HRMS (ES+): Exact mass calcd for C₁₇H₁₆BrN₂O₃ [M+H]⁺: 375.0344. Found: 375.0340.



¹H NMR (500 MHz, CHLOROFORM-D) δ 7.37 (d, *J* = 8.4 Hz, 2H), 7.20 (dd, *J* = 4.1, 1.2 Hz, 1H), 7.13 (d, *J* = 8.3 Hz, 2H), 7.07 (s, 1H), 6.95 (s, 1H), 6.01 (dd, *J* = 5.7, 1.8 Hz, 1H), 5.11 (d, *J* = 7.2 Hz, 1H), 3.85 (s, 3H), 3.67 (dd, *J* = 12.5, 5.9 Hz, 1H), 3.61 – 3.56 (m, 2H). ¹³C NMR (125 MHz, CHLOROFORM-D) δ 189.40, 172.34, 154.59, 142.71, 137.80, 132.07, 130.22, 129.16, 127.40, 122.76, 121.80, 85.52, 44.38, 40.75, 36.26. IR (thin film): v = 3110, 2924, 1757, 1676, 1600, 1489, 1411, 1243, 1160, 1102,

1074 cm⁻¹. HRMS (ES+): Exact mass calcd for C₁₇H₁₆BrN₂O₃ [M+H]⁺: 375.0344. Found: 375.0346.

For Sc(III)-2g: The compound 5f was isolated as white semisolid in 90% yield with >20:1 *d.r.* and 97% *ee.* $[\alpha]_D^{25} =$ + 78.8 (*c* 0.59, CHCl₃). The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IC-3 column, *n*-hexane/2-propanol (80:20) as eluent, Flow rate: 1.0 mL/min. *t*_R (major) = 57.19 min, *t*_R (minor) = 64.09 min.

For Er(III)-2g: The compound 5f was isolated as white semisolid in 83% yield with >20:1 *d.r.* and 93% *ee.* The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IC-3 column, *n*-hexane/2-propanol (80:20) as eluent, Flow rate: 1.0 mL/min. $t_{\rm R}$ (major) = 58.64 min, $t_{\rm R}$ (minor) = 65.59 min.



¹H NMR (500 MHz, CHLOROFORM-D) δ 7.22 – 7.19 (m, 3H), 7.06 (s, 1H), 6.94 – 6.91 (m, 3H), 6.00 (dd, J = 5.7, 1.7 Hz, 1H), 5.11 (d, J = 7.0 Hz, 1H), 3.84 (s, 3H), 3.69 – 3.55 (m, 3H). ¹³C NMR (125 MHz, CHLOROFORM-D) δ 189.58, 172.45, 162.23 (d, $J_{C-F} = 246.3$), 154.75, 142.80, 134.48, 130.06 (d, $J_{C-F} = 8$), 129.22, 127.35, 122.63, 115.79 (d, $J_{C-F} = 21.4$), 85.79, 44.07, 40.93, 36.20. IR (thin film): v = 3114, 2960, 2924, 1757, 1677, 1604, 1511, 1411, 1225, 1160, 1100, 1081 cm⁻¹. HRMS (ES+): Exact mass

calcd for C₁₇H₁₆FN₂O₃ [M+H]⁺: 315.1145. Found: 315.1149.

For Sc(III)-2g: The compound 5g was isolated as white semisolid in 91% yield with >20:1 *d.r.* and 98% *ee.* $[\alpha]_D^{25} =$ + 68.9 (*c* 0.37, CHCl₃). The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IC-3 column, *n*-hexane/2-propanol (70:30) as eluent, Flow rate 1.0 mL/min. t_R (major) = 27.23 min, t_R (minor) = 30.75 min.

For Er(III)-2g: The compound 5g was isolated as white semisolid in 85% yield with >20:1 *d.r.* and 96% *ee.* The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IC-3 column, *n*-hexane/2-propanol (70:30) as eluent, Flow rate 1.0 mL/min. t_R (major) = 27.48 min, t_R (minor) = 30.96 min.



The compound **5h** was isolated as yellowish semisolid in 90% yield with >20:1 *d.r.* and 94% *ee.* $[\alpha]_D^{25} = +55.6$ (*c* 0.79, CHCl₃). The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IC-3 column, *n*-hexane/2-propanol (60:40) as eluent, flow rate: 1.0 mL/ min, t_R (major) = 52.62 min, t_R (minor) = 58.90 min. ¹H NMR (500 MHz, CHLOROFORM-D) δ 8.17 – 8.09 (m, 2H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.50 (t, *J* = 7.9 Hz, 1H), 7.37 (dd, *J* = 5.7, 1.2 Hz, 1H), 7.14 (s, 1H), 7.03 (s, 1H), 6.10

(dd, J = 5.8, 2.0 Hz, 1H), 5.29 – 5.26 (m, 1H), 3.94 – 3.87 (m, 4H), 3.78 (dd, J = 17.6, 8.5 Hz, 1H), 3.67 (dd, J = 17.6, 5.7 Hz, 1H). ¹³C NMR (125 MHz, CHLOROFORM-D) δ 188.80, 175.51, 172.07, 154.01, 148.45, 142.36, 140.93, 135.04, 129.85, 129.29, 127.58, 123.29, 122.86, 84.98, 43.91, 39.92, 36.25. IR (thin film): v = 3091, 2927, 1755, 1677, 1600, 1530, 1411, 1291, 1350, 1160, 1101, 1032 cm⁻¹. HRMS (ES+): Exact mass calcd for C₁₇H₁₆N₃O₅ [M+H]⁺: 342.1090. Found: 342.1098.



The compound **5i** was isolated as white solid in 91% yield with >20:1 *d.r.* and 94% *ee.* mp 146 – 148 °C; $[\alpha]_D^{25} = +$ 69.6 (*c* 0.6, CHCl₃). The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IC-3 column, *n*-hexane/2-propanol (60:40) as eluent, flow rate: 1.0 mL/min. t_R (major) = 32.76 min, t_R (minor) = 52.05 min. ¹H NMR (500 MHz, CHLOROFORM-D) δ 8.17 – 8.14 (m, 2H), 7.52 – 7.50 (m, 2H), 7.33 (dd, *J* = 5.7, 1.5 Hz, 1H), 7.13 (s, 1H), 7.03 (s, 1H), 6.10 (dd, *J* = 5.8, 2.0 Hz, 1H),

5.25 (dt, J = 6.3, 1.6 Hz, 1H), 3.92 – 3.85 (m, 4H), 3.80 (dd, J = 17.3, 8.8 Hz, 1H), 3.62 (dd, J = 17.2, 5.2 Hz, 1H). ¹³C NMR (125 MHz, CHLOROFORM-D) δ 188.83, 171.99, 153.94, 147.54, 146.35, 142.46, 129.62, 129.39, 127.64, 123.99, 123.26, 84.86, 44.13, 39.84, 36.22. IR (neat): v = 3112, 2924, 1757, 1676, 1599, 1520, 1411, 1348, 1290, 1160, 1104, 1081 cm⁻¹. HRMS (ES+): Exact mass calcd for C₁₇H₁₆N₃O₅ [M+H]⁺: 342.1090. Found: 342.1097.



The compound **5j** was isolated as white semisolid in 92% yield with >20:1 *d.r.* and 98% *ee*. $[\alpha]_D^{25} = +$ 79.5 (*c* 0.61, CHCl₃). The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IC-3 column, *n*-hexane/2-propanol (80:20) as eluent, flow rate: 1.0 mL/min. t_R (major) = 68.13 min, t_R (minor) = 73.52 min. ¹H NMR (500 MHz, CHLOROFORM-D) δ 7.23 (d, *J* = 5.0 Hz, 1H), 7.19 – 7.10 (m, 5H), 6.99 (s, 1H), 6.04 (dd, *J* = 5.6, 1.6 Hz, 1H), 5.16 (d, *J* = 8.2 Hz, 1H), 3.91 (s, 3H), 3.78 –

3.68 (m, 2H), 3.58 (dd, J = 14.2, 8.1 Hz, 1H), 2.30 (s, 3H). ¹³C NMR (125 MHz, CHLOROFORM-D) δ 189.92, 172.69, 155.28, 142.94, 137.45, 135.72, 129.63, 129.11, 128.25, 127.17, 122.25, 86.19, 44.72, 41.40, 36.21, 21.17. IR (thin film): v = 3111, 2923, 1757, 1676, 1600, 1515, 1410, 1291, 1160, 1102, 1080 cm⁻¹. HRMS (ES+): Exact mass calcd for C₁₈H₁₉N₂O₃ [M+H]⁺: 311.1396. Found: 311.1391.



The compound **5k** was isolated as white semisolid in 89% yield with >20:1 *d.r.* and 98% *ee*. $[\alpha]_D^{25} = +$ 62.0 (*c* 0.92, CHCl₃). The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IC-3 column, *n*-hexane/2-propanol (70:30) as eluent, flow rate: 1.0 mL/min. t_R (major) = 48.55 min. t_R (minor) = 52.72 min. ¹H NMR (500 MHz, CHLOROFORM-D) δ 7.22 – 7.13 (m, 3H), 7.04 (s, 1H), 6.91 (s, 1H), 6.83 (dd, J = 16.2, 8.0 Hz, 2H), 5.95 (dd, J = 5.7, 1.8 Hz, 1H), 5.33 – 5.31 (m, 1H), 3.87 –

3.83 (m, 4H), 3.78 (s, 3H), 3.69 (d, J = 6.9 Hz, 2H). ¹³C NMR (125 MHz, CHLOROFORM-D) δ 190.45, 172.96, 157.26, 156.16, 143.09, 129.86, 129.02, 128.81, 127.24, 126.98, 121.54, 121.04, 111.11, 85.43, 55.60, 40.23, 40.12, 36.13. IR (thin film): v = 2923, 1755, 1675, 1600, 1493, 1409, 1244, 1159, 1103, 1080, 1028 cm⁻¹. HRMS (ES+): Exact mass calcd for C₁₈H₁₉N₂O₄ [M+H]⁺: 327.1345. Found: 327.1346.



The compound **51** was isolated as light yellow semisolid in 88% yield with >20:1 *d.r.* and 94% *ee.* $[\alpha]_D^{25} = +$ 81.2 (*c* 1.01, CHCl₃). The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralcel OJ-H column, *n*-hexane/2 propanol (60:40) as eluent, flow rate: 1.0 mL/min. *t*_R (minor) = 16.90 min, *t*_R (major) = 33.11 min. ¹H NMR (500 MHz, CHLOROFORM-D) δ 7.19 – 7.14 (m, 3H), 7.09 (s, 1H), 6.95 (s, 1H), 6.77

(d, J = 8.6 Hz, 2H), 5.97 (dd, J = 5.7, 1.8 Hz, 1H), 5.09 (d, J = 8.3 Hz, 1H), 3.85 (s, 3H), 3.70 (s, 3H), 3.64 (dd, J = 7.0, 4.9 Hz, 2H), 3.50 (dd, J = 14.2, 8.2 Hz, 1H). ¹³C NMR (125 MHz, CHLOROFORM-D) δ 189.69, 172.66, 159.12, 155.27, 142.64, 130.62, 129.43, 128.71, 127.20, 122.28, 114.34, 86.24, 55.36, 44.42, 41.54, 36.32. IR (thin film): v = 3112, 2924, 2852, 1755, 1677, 1611, 1514, 1410, 1290, 1251, 1161, 1102, 1080, 1031 cm⁻¹. HRMS (ES+): Exact mass calcd for C₁₈H₁₉N₂O₄ [M+H]⁺: 327.1345. Found: 327.1340.



The compound **5m** was isolated as white semisolid in 92% yield with >20:1 *d.r.* and 95% *ee.* mp 126 – 128 °C; $[\alpha]_D^{25} = +$ 87.8 (*c* 0.66, CHCl₃). The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IB-3 column, *n*-hexane/2-propanol (80:20) as eluent, flow rate: 1.0 mL/min. t_R (major) = 22.17 min, t_R (minor) = 27.50 min. ¹H NMR (500 MHz, CHLOROFORM-D) δ 7.75 – 7.71 (m, 4H), 7.40 – 7.36 (m, 3H), 7.19 – 7.16 (m, 1H), 7.07 (s, 1H), 6.91 (s, 1H), 5.98 (dd, *J* = 5.7, 1.7 Hz, 1H), 5.22

(d, J = 7.9 Hz, 1H), 3.87 - 3.82 (m, 4H), 3.77 - 3.67 (m, 2H). ¹³C NMR (125 MHz, CHLOROFORM-D) δ 189.71, 172.58, 155.16, 142.85, 136.33, 133.51, 132.95, 129.06, 128.77, 128.00, 127.78, 127.31, 127.25, 126.48, 126.40, 126.23, 122.38, 86.08, 45.31, 41.41, 36.23. IR (thin film): v = 2959, 2926, 1754, 1676, 1600, 1508, 1411, 1290, 1160, 1101, 1080, 1033 cm⁻¹. HRMS (ES+): Exact mass calcd for C₂₁H₁₉N₂O₃ [M+H]⁺: 347.1396. Found: 347.1390.



The compound **5n** was isolated as brown semisolid in 90% yield with >20:1 *d.r.* and 93% *ee*. $[\alpha]_D^{25} = +106.7$ (*c* 0.25, CHCl₃). The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IC-3 column, *n*-hexane/2-propanol (70:30) as eluent, flow rate: 1.0 mL/min. t_R (major) = 44.36 min, t_R (minor) = 51.55 min. ¹H NMR (500 MHz, CHLOROFORM-D) δ 7.28 (d, *J* = 5.1 Hz, 1H), 7.10 (d, *J* = 4.4 Hz, 1H), 7.07 (s, 1H), 6.96 (s, 1H), 6.90 (s, 1H), 6.86 (s, 1H), 6.00 (d, *J* = 4.5 Hz, 1H), 5.14 (d, *J*

= 7.1 Hz, 1H), 3.96 - 3.87 (m, 4H), 3.73 - 3.62 (m, 2H). ¹³C NMR (125 MHz, CHLOROFORM-D) δ 189.18, 172.34, 154.65, 142.83, 141.14, 129.31, 127.38, 127.12, 126.08, 124.68, 122.65, 85.46, 42.21, 40.00, 36.18. IR (thin film): v = 3102, 2922, 1756, 1675, 1600, 1410, 1292, 1156, 1102, 1080, 1019 cm⁻¹. HRMS (ES+): Exact mass calcd for C₁₅H₁₅N₂O₃S [M+H]⁺: 303.0803. Found: 303.0804.



The compound **50** was isolated as colorless semisolid in 92% yield with >20:1 *d.r.* and 92% *ee.* $[\alpha]_D^{25} = +75.9$ (*c* 0.66, CHCl₃). The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IC-3 column, *n*-hexane/2-propanol (85:15) as eluent, flow rate: 1.0 mL/min. t_R (major) = 105.09 min, t_R (minor) = 117.62 min. ¹H NMR (500 MHz, CHLOROFORM-D) δ 7.46 (d, *J* = 5.7 Hz, 1H), 7.06 (s, 1H), 6.98 (s, 1H), 6.07 (dd, *J* = 5.7, 1.2 Hz, 1H), 4.98 (d, *J* = 1.2 Hz, 1H), 3.93 (s, 3H), 3.20 - 3.15

(m, 1H), 3.07 - 3.02 (m, 1H), 2.66 - 2.58 (m, 1H), 0.98 (dd, J = 6.9, 0.7 Hz, 3H). ¹³C NMR (125 MHz, CHLOROFORM-D) δ 190.89, 172.82, 154.64, 143.03, 129.25, 127.37, 122.70, 86.49, 41.30, 36.29, 32.88, 15.84. IR (thin film): v = 3109, 2966, 1751, 1674, 1460, 1408, 1291, 1163, 1096, 1019 cm⁻¹. HRMS (ES+): Exact mass calcd for C₁₂H₁₅N₂O₃ [M+H]⁺: 235.1083. Found: 235.1082.



The compound **5p** was isolated as white solid in 91% yield with >20:1 *d.r.* and 93% *ee.* mp 102 – 104 °C; $[\alpha]_D^{25} = +$ 4.4 (*c* 0.45, CHCl₃). The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IC-3 column, *n*-hexane/2-propanol (70:30) as eluent, flow rate: 1.0 mL/min. t_R (minor) = 25.82 min, t_R (major) = 36.60 min. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.30 (d, *J* = 5.7 Hz, 1H), 7.27 – 7.15 (m, 5H), 7.04 (s, 1H), 6.91 (s, 1H), 5.93 (d, *J* = 5.6 Hz, 1H), 3.78 (s, 3H), 3.75 – 3.62 (m,

2H), 3.40 (dd, J = 16.5, 4.1 Hz, 1H), 1.30 (s, 3H). ¹³C NMR (100 MHz, CHLOROFORM-D) δ 190.03, 172.30, 160.59, 142.88, 138.72, 129.57, 129.22, 128.52, 127.56, 127.19, 120.91, 90.40, 47.87, 39.69, 36.14, 22.04. IR (neat): v = 3115, 3026, 2924, 1747, 1681, 1601, 1494, 1454, 1414, 1293, 1279, 1219, 1104, 1045 cm⁻¹. HRMS (ES+): Exact mass calcd for C₁₈H₁₉N₂O₃ [M+H]⁺: 311.1396. Found: 311.1399.



The compound **5q** was isolated white solid in 92% yield with >20:1 *d.r.* and 90% *ee.* mp 164 – 166 °C; $[\alpha]_D^{25} = -8.4$ (*c* 0.44, CHCl₃). The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IC-3 column, *n*-hexane/2-propanol (70:30) as eluent, flow rate: 1.0 mL/min. t_R (minor) = 22.01 min, t_R (major) = 24.87 min. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.59 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.46 (d, *J* = 5.6 Hz, 1H), 7.36 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.28 – 7.15 (m, 2H),

7.09 (d, J = 0.8 Hz, 1H), 6.97 (s, 1H), 6.04 (d, J = 5.6 Hz, 1H), 4.47 (dd, J = 8.5, 5.4 Hz, 1H), 3.86 (s, 3H), 3.58 (dd, J = 17.5, 8.5 Hz, 1H), 3.44 (dd, J = 17.5, 5.4 Hz, 1H), 1.35 (s, 3H). ¹³C NMR (100 MHz, CHLOROFORM-D) δ 189.73, 172.37, 160.70, 142.70, 136.88, 135.07, 130.47, 129.56, 129.33, 128.66, 127.44, 127.25, 121.01, 90.37, 41.72, 40.09, 36.16, 22.35. IR (neat): v = 3112, 2982, 1751, 1680, 1475, 1410, 1287, 1236, 1102, 1035 cm⁻¹. HRMS (ES+): Exact mass calcd for C₁₈H₁₈ClN₂O₃ [M+H]⁺: 345.1006. Found: 345.1003.



The compound **5r** was isolated as white solid in 90% yield with >20:1 *d.r.* and 86% *ee.* mp 148 – 150 °C; $[\alpha]_D^{25} = +$ 13.1 (*c* 0.75, CHCl₃). The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IC-3 column, *n*-hexane/2-propanol (70:30) as eluent, flow rate: 1.0 mL/min. t_R (minor) = 23.19 min, t_R (major) = 26.09 min. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.55 (d, *J* = 7.7 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 5.5 Hz, 1H), 7.28 – 6.99 (m, 3H), 6.91 (s, 1H), 5.97 (d, *J* = 5.5 Hz, 1H), 7.28 – 6.99 (m, 3H), 6.91 (s, 1H), 5.97 (d, *J* = 5.5 Hz, 1H), 7.28 – 6.99 (m, 3H), 6.91 (s, 1H), 5.97 (d, *J* = 5.5 Hz, 1H), 7.28 – 6.99 (m, 3H), 6.91 (s, 1H), 5.97 (d, *J* = 5.5 Hz, 1H), 7.28 – 6.99 (m, 3H), 6.91 (s, 1H), 5.97 (d, *J* = 5.5 Hz, 1H), 7.28 – 6.99 (m, 3H), 6.91 (s, 1H), 5.97 (d, *J* = 5.5 Hz, 1H), 7.28 – 6.99 (m, 3H), 6.91 (s, 1H), 5.97 (d, *J* = 5.5 Hz, 1H), 7.28 – 6.99 (m, 3H), 6.91 (s, 1H), 5.97 (d, *J* = 5.5 Hz, 1H), 7.28 – 6.99 (m, 3H), 6.91 (s, 1H), 5.97 (d, *J* = 5.5 Hz, 1H), 7.28 – 6.99 (m, 3H), 6.91 (s, 1H), 5.97 (d, *J* = 5.5 Hz, 1H), 7.28 – 6.99 (m, 3H), 6.91 (s, 1H), 5.97 (d, *J* = 5.5 Hz, 1H), 7.28 – 6.99 (m, 3H), 6.91 (s, 1H), 5.97 (d, *J* = 5.5 Hz, 1H), 7.28 – 6.99 (m, 3H), 6.91 (s, 1H), 5.97 (d, *J* = 5.5 Hz, 1H), 7.28 – 6.99 (m, 3H), 6.91 (s, 1H), 5.97 (d, *J* = 5.5 Hz, 1H), 7.8 – 6.99 (m, 3H), 6.91 (s, 1H), 5.97 (d, *J* = 5.5 Hz, 1H), 7.8 – 6.99 (m, 3H), 6.91 (s, 1H), 5.97 (d, *J* = 5.5 Hz, 1H), 7.8 – 6.99 (m, 3H), 6.91 (s, 1H), 5.97 (s,

1H), 4.40 (dd, J = 7.7, 5.8 Hz, 1H), 3.80 (s, 3H), 3.46 (dd, J = 17.3, 8.1 Hz, 1H), 3.38 (dd, J = 17.3, 5.5 Hz, 1H), 1.29 (s, 3H). ¹³C NMR (100 MHz, CHLOROFORM-D) δ 189.72, 172.37, 160.74, 142.69, 138.63, 132.93, 130.65, 129.35, 128.98, 128.10, 127.24, 126.27, 121.00, 90.40, 44.65, 40.32, 36.16, 22.50. IR (neat): v = 3110, 2983, 2932, 1753, 1676, 1603, 1471, 1409, 1287, 1254, 1147, 1101, 1023 cm⁻¹. HRMS (ES+): Exact mass calcd for C₁₈H₁₈BrN₂O₃ [M+H]⁺: 389.0501. Found: 389.0501.



¹H NMR (400 MHz, CHLOROFORM-D) δ 7.43 – 7.39 (m, 2H), 7.38 (d, *J* = 5.6 Hz, 1H), 7.23 – 7.19 (m, 2H), 7.10 (d, *J* = 0.9 Hz, 1H), 6.98 (s, 1H), 6.02 (d, *J* = 5.6 Hz, 1H), 3.86 (s, 3H), 3.76 – 3.66 (m, 2H), 3.36 (dd, *J* = 15.1, 2.5 Hz, 1H), 1.35 (s, 3H). ¹³C

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NMR (100 MHz, CHLOROFORM-D) δ 189.70, 172.10, 160.07, 142.74, 137.78, 131.66, 131.33, 129.36, 127.38, 121.62, 121.34, 90.00, 47.27, 39.60, 36.20, 22.50. IR (neat): v = 3128, 3111, 3075, 2976, 2929, 1749, 1679, 1600, 1490, 1413, 1282, 1146, 1100, 1012 cm⁻¹. HRMS (ES+): Exact mass calcd for C₁₈H₁₈BrN₂O₃ [M+H]⁺: 389.0501. Found: 389.0502.

For Sc(III)-2g: The compound 5s was isolated as light yellow semisolid in 92% yield with >20:1 *d.r.* and 93% *ee.* mp 174 – 176 °C; $[\alpha]_D^{25} = -5.6$ (*c* 1.08, CHCl₃). The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IC-3 column, *n*-hexane/2-propanol (70:30) as eluent, flow rate: 1.0 mL/min. t_R (minor) = 22.20 min, t_R (major) = 27.39 min.

For Er(III)-2g: The compound 5s was isolated as light yellow semisolid in 85% yield with >20:1 *d.r.* and 87% *ee.* mp 174 – 176 °C; The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IC-3 column, *n*-hexane/2-propanol (70:30) as eluent, flow rate: 1.0 mL/min. t_R (minor) = 22.26 min, t_R (major) = 27.42 min.



¹H NMR (400 MHz, CHLOROFORM-D) δ 7.38 (d, J = 5.6 Hz, 1H), 7.31 – 7.25 (m, 2H), 7.10 (d, J = 0.6 Hz, 1H), 6.99 – 6.95 (m, 3H), 6.01 (d, J = 5.6 Hz, 1H), 3.86 (s, 3H), 3.76 – 3.68 (m, 2H), 3.38 (dt, J = 13.6, 8.4 Hz, 1H), 1.35 (s, 3H). ¹³C NMR (100 MHz, CHLOROFORM-D) δ 189.89, 172.18, 163.41, 160.22, 142.81, 134.43, 131.16 (d, $J_{C-F} = 7.9$ Hz), 129.34, 127.33, 121.25, 115.41 (d, $J_{C-F} = 21.2$ Hz), 90.24, 47.06, 39.84, 36.18, 22.46. IR (neat): v = 3131, 3117, 3075, 2980, 2929, 1743, 1683, 1604,

1511, 1416, 1335, 1239, 1222, 1108, 1044 cm⁻¹. HRMS (ES+): Exact mass calcd for $C_{18}H_{18}FN_2O_3$ [M+H]⁺: 329.1301. Found: 329.1307.

For Sc(III)-2g: The compound 5t was isolated as white solid in 93% yield with >20:1 *d.r.* and 93% *ee.* mp 165 – 167 °C; $[\alpha]_D^{25} = +$ 14.9 (*c* 0.71, CHCl₃). The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IC-3 column, *n*-hexane/2-propanol (70:30) as eluent, flow rate: 1.0 mL/min. t_R (minor) = 20.29 min, t_R (major) = 27.13 min.

For Er(III)-2g: The compound 5t was isolated as white solid in 88% yield with >20:1 *d.r.* and 83% *ee.* mp 165 – 167 °C; $[\alpha]_D^{25} = +$ 6.4 (*c* 0.70, CHCl₃). The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IC-3 column, *n*-hexane/2-propanol (70:30) as eluent, flow rate: 1.0 mL/min. t_R (minor) = 20.25 min, t_R (major) = 26.92 min.



The compound **5u** was isolated as white solid in 91% yield with >20:1 *d.r.* and 94% *ee.* mp 134 – 136 °C; $[\alpha]_D^{25} = +$ 16.4 (*c* 1.73, CHCl₃). The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralcel AD-H column, *n*-hexane/2-propanol (70:30) as eluent, flow rate: 1.0 mL/min. t_R (major) = 10.49 min, t_R (minor) = 13.81 min. ¹H NMR (400 MHz, CHLOROFORM-D) δ 8.15 – 8.09 (m, 2H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 5.6 Hz, 1H), 7.11 (d, *J* = 0.7 Hz, 1H), 7.00 (s,

1H), 6.06 (d, J = 5.6 Hz, 1H), 3.90 – 3.86 (m, 4H), 3.72 (dd, J = 17.5, 9.2 Hz, 1H), 3.44 (dd, J = 17.5, 4.7 Hz, 1H), 1.38 (s, 3H). ¹³C NMR (100 MHz, CHLOROFORM-D) δ 189.13, 171.76, 159.42, 148.11, 142.51, 140.99, 135.91, 129.65, 129.55, 127.59, 124.57, 122.78, 121.89, 89.61, 47.34, 39.68, 36.20, 23.17. IR (neat): v = 3088, 3927, 1756, 1676, 1529, 1409, 1348, 1281, 1154, 1102, 1032 cm⁻¹. HRMS (ES+): Exact mass calcd for C₁₈H₁₈N₃O₅ [M+H]⁺: 356.1246. Found: 356.1248.



The compound **5v** was isolated as white semisolid in 88% yield with >20:1 *d.r.* and 90% *ee*. $[\alpha]_D^{25} = +6.5$ (*c* 0.78, CHCl₃). The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IC-3 column, *n*-hexane/2-propanol (60:40) as eluent, flow rate: 1.0 mL/min. t_R (minor) = 24.17 min, t_R (major) = 50.41 min. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.36 (d, *J* = 5.6 Hz, 1H), 7.22 (d, *J* = 8.6 Hz, 2H), 7.09 (s, 1H), 6.96 (s, 1H), 6.80 (d, *J* = 8.5 Hz, 2H), 5.98 (d, *J* = 5.6 Hz, 1H), 3.84 (s, 3H), 3.77 –

3.64 (m, 5H), 3.40 (dd, J = 16.6, 4.2 Hz, 1H), 1.36 (s, 3H). ¹³C NMR (100 MHz, CHLOROFORM-D) δ 190.13, 172.37, 160.67, 158.86, 142.89, 130.60, 130.54, 129.17, 127.19, 120.88, 113.83, 90.64, 55.28, 47.13, 39.76, 36.16, 21.95. IR (thin film): v = 3110, 2928, 2853, 1755, 1676, 1611, 1513, 1463, 1410, 1293, 1249, 1180, 1104, 1033 cm⁻¹. HRMS (ES+): Exact mass calcd for C₁₉H₂₁N₂O₄ [M+H]⁺: 341.1501. Found: 341.1503



¹H NMR (400 MHz, CHLOROFORM-D) δ 7.81 – 7.78 (m, 4H), 7.51 – 7.44 (m, 3H), 7.40 (d, J = 5.6 Hz, 1H), 7.11 (d, J = 0.8 Hz, 1H), 6.95 (s, 1H), 6.03 (d, J = 5.6 Hz, 1H), 3.96 – 3.87 (m, 2H), 3.82 (s, 3H), 3.52 (dd, J = 14.9, 2.2 Hz, 1H), 1.41 (s, 3H). ¹³C NMR (100 MHz, CHLOROFORM-D) δ 189.99, 172.35, 160.63, 142.90, 136.36, 133.28, 132.82, 129.28, 128.41, 128.26, 128.05, 127.70, 127.26, 126.25, 126.09, 121.02, 90.55, 48.00, 39.75, 36.15, 22.20. IR (neat): v = 3057, 2981, 2931, 1754, 1675,

1600, 1508, 1409, 1279, 1155, 1104, 1078 cm⁻¹. HRMS (ES+): Exact mass calcd for $C_{22}H_{21}N_2O_3$ [M+H]⁺: 361.1552. Found: 361.1556.

For Sc(III)-2g: The compound 5w was isolated as white solid in 90% yield with >20:1 *d.r.* and 92% *ee.* mp 168 – 170 °C; $[\alpha]_D^{25} = +$ 139.0 (*c* 0.52, CHCl₃). The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IC-3 column, *n*-hexane/2-propanol (70:30) as eluent, flow rate: 1.0 mL/min. t_R (minor) = 33.57 min, t_R (major) = 40.77 min.

For Er(III)-2g: The compound 5w was isolated as white solid in 80% yield with >20:1 *d.r.* and 80% *ee.* mp 168 – 170 °C; The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IC-3 column, *n*-hexane/2-propanol (70:30) as eluent, flow rate: 1.0 mL/min. t_R (minor) = 33.55 min, t_R (major) = 40.70 min.



The compound **5x** was isolated as white solid in 91% yield with >20:1 *d.r.* and 92% *ee.* mp 113 – 115 °C; $[\alpha]_D^{25} = +$ 33.1 (*c* 0.97, CHCl₃). The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IC-3 column, *n*-hexane/2-propanol (70:30) as eluent, flow rate: 1.0 mL/min. t_R (minor) = 32.57 min, t_R (major) = 47.53 min.

¹H NMR (400 MHz, CHLOROFORM-D) δ 7.42 (d, J = 5.6 Hz, 1H), 7.17 (dd, J = 5.1, 1.1 Hz, 1H), 7.12 (d, J = 0.9 Hz, 1H), 7.00 (s, 1H), 6.97 (dd, J = 3.5, 0.8 Hz, 1H), 6.92 (dd, J = 5.1, 3.5 Hz, 1H), 6.01 (d, J = 5.6 Hz, 1H), 4.03 (dd, J = 9.4, 4.6 Hz, 1H), 3.89 (s, 3H), 3.78 (dd, J = 17.2, 9.4 Hz, 1H), 3.49 (dd, J = 17.2, 4.6 Hz, 1H), 1.48 (s, 3H). ¹³C NMR (100 MHz, CHLOROFORM-D) δ 189.35, 172.07, 160.15, 142.80, 141.31, 129.34, 127.30, 127.07, 126.92, 124.83, 121.13, 89.94, 43.34, 41.15, 36.19, 21.58. IR (neat): v = 3108, 2982, 2931, 1756, 1675, 1602, 1510, 1409, 1277, 1243, 1154, 1104, 1080 cm⁻¹. HRMS (ES+): Exact mass calcd for C₁₆H₁₇N₂O₃S [M+H]⁺: 317.0960. Found: 317.0964.



The compound **7a** was isolated as brown semisolid in 90% yield with >20:1 *d.r.* and 94% *ee*. $[\alpha]_D^{25} = +$ 127.8 (*c* 1.01, CHCl₃). The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IC-3 column, *n*-hexane/2-propanol (70:30) as eluent, flow rate: 1.0 mL/min. t_R (major) = 40.40 min, t_R (minor) = 46.42 min. ¹H NMR (500 MHz, CHLOROFORM-D) δ 7.40 (d, *J* = 5.7 Hz, 1H), 7.31 (d, *J* = 1.2 Hz, 1H), 7.14 (s, 1H), 7.03 (s, 1H), 6.27 (dd, *J* = 2.8, 1.9 Hz, 1H), 6.21 (d, *J* = 3.1 Hz, 1H), 6.07

(dd, J = 5.7, 1.8 Hz, 1H), 5.22 (d, J = 7.1 Hz, 1H), 3.95 (s, 3H), 3.85 – 3.75 (m, 2H), 3.62 (dd, J = 16.8, 5.2 Hz, 1H). ¹³C NMR (125 MHz, CHLOROFORM-D) δ 189.36, 172.43, 154.85, 152.00, 142.84, 142.16, 129.39, 127.38, 122.29, 110.57, 107.87, 84.19, 39.00, 38.42, 36.19. IR (thin film): v = 3314, 2923, 2853, 1756, 1676, 1600, 1505, 1411, 1291, 1160, 1103, 1083, 1014 cm⁻¹. HRMS (ES+): Exact mass calcd for C₁₅H₁₅N₂O₄ [M+H]⁺: 287.1032. Found: 287.1037.



The compound **7b** was isolated as light brown semisolid in 91% yield with >20:1 *d.r.* and 95% *ee.* $[\alpha]_D^{25}$ + 102.0 (*c* 2.04, CHCl₃). The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IC-3 column, *n*-hexane/2-propanol (70:30) as eluent, flow rate: 1.0 mL/min. t_R (major) = 27.55 min, t_R (minor) = 35.92 min. ¹H NMR (500 MHz, CHLOROFORM-D) δ 7.45 (dd, J = 5.8, 1.3 Hz, 1H), 7.13 (s, 1H), 7.04 (s, 1H), 6.21 (d, J = 3.2 Hz, 1H), 6.18 (d, J = 3.2 Hz, 1H), 6.09 (dd, J = 5.7, 1.9 Hz, 1H),

5.22 (d, J = 6.9 Hz, 1H), 3.96 (s, 3H), 3.82 (dd, J = 13.8, 7.0 Hz, 1H), 3.70 (dd, J = 17.3, 8.0 Hz, 1H), 3.59 (dd, J = 17.4, 5.9 Hz, 1H). ¹³C NMR (125 MHz, CHLOROFORM-D) δ 188.94, 172.23, 154.46, 154.09, 142.63, 129.39, 127.49, 122.55, 121.15, 112.29, 110.88, 83.68, 38.39, 38.34, 36.20. IR (thin film): v = 3113, 2923, 1758, 1676, 1505, 1411, 1291, 1158, 1122, 1080 cm⁻¹. HRMS (ES+): Exact mass calcd for C₁₅H₁₄BrN₂O₄ [M+H]⁺: 365.0137. Found: 365.0134.



The compound **7c** was isolated as brown semisolid in 92% yield with >20:1 *d.r.* and 95% *ee.* $[\alpha]_D^{25} = +$ 115.2 (*c* 0.4, CHCl₃). The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IC-3 column, *n*-hexane/2-propanol (70:30) as eluent, flow rate: 1.0 mL/min. t_R (major) = 32.23 min, t_R (minor) = 41.06 min. ¹H NMR (500 MHz, CHLOROFORM-D) δ 7.42 (dd, J = 5.7, 1.1 Hz, 1H), 7.13 (s, 1H), 7.02 (s, 1H), 6.07 – 6.06 (m, 2H), 5.83 (d, J = 1.9 Hz, 1H), 5.19 (d, J = 7.1 Hz, 1H), 3.96 (s,

3H), 3.76 – 3.70 (m, 2H), 3.64 – 3.58 (m, 1H), 2.21 (s, 3H). ¹³C NMR (125 MHz, CHLOROFORM-D) δ 189.55,

172.54, 155.15, 151.81, 150.11, 142.91, 129.31, 127.30, 122.11, 108.52, 106.40, 84.38, 39.14, 38.52, 36.20, 13.62. IR (thin film): v = 3109, 2922, 1757, 1676, 1562, 1411, 1291, 1158, 1102, 1082, 1024. cm⁻¹. HRMS (ES+): Exact mass calcd for C₁₆H₁₇N₂O₄ [M+H]⁺: 301.1188. Found: 301.1189.



The compound **7d** was isolated as brown solid in 91% yield with >20:1 *d.r.* and 91% *ee.* mp 146 – 148 °C; $[\alpha]_D^{25} = +$ 76.7 (*c* 0.61, CHCl₃). The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IC-3 column, *n*-hexane/2-propanol (60:40) as eluent, flow rate: 1.0 mL/min. t_R (major) = 22.58 min, t_R (minor) = 25.86 min. ¹H NMR (500 MHz, CHLOROFORM-D) δ 7.48 – 7.42 (m, 5H), 7.15 (s, 1H), 7.04 (s,

1H), 6.53 (d, J = 3.3 Hz, 1H), 6.31 (d, J = 3.3 Hz, 1H), 6.10 (dd, J = 5.7, 1.8 Hz, 1H), 5.28 (d, J = 6.9 Hz, 1H), 3.96 – 3.90 (m, 4H), 3.83 (dd, J = 17.1, 8.2 Hz, 1H), 3.64 (dd, J = 17.1, 5.6 Hz, 1H). ¹³C NMR (125 MHz, CHLOROFORM-D) δ 189.23, 172.34, 154.55, 152.58, 151.98, 142.83, 131.94, 129.54, 129.50, 127.50, 125.24, 122.57, 121.27, 110.29, 106.54, 84.03, 38.65, 38.53, 36.23. IR (thin film): v = 3113, 2923, 1757, 1676, 1541, 1478, 1408, 1290, 1158, 1102, 1073, 1024 cm⁻¹. HRMS (ES+): Exact mass calcd for C₂₁H₁₈BrN₂O₄ [M+H]⁺: 441.0450. Found: 441.0457.



The compound **7e** was isolated as yellow solid in 90% yield with 13:1 *d.r.* and 92% *ee.* mp 105 – 107 °C; $[\alpha]_D^{25} = +$ 91.0 (*c* 0.49, CHCl₃). The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IC-3 column, *n*-hexane/2-propanol (70:30) as eluent, flow rate: 1.0 mL/min. t_R (minor) = 37.99 min, t_R (major) = 43.90 min. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.45 (d, *J* = 5.7 Hz, 1H), 7.32 (d, *J* = 1.1 Hz, 1H), 7.14 (d, *J* = 0.6 Hz, 1H), 7.02 (s, 1H), 6.29 – 6.22 (m, 2H), 6.00 (d, *J* = 5.7 Hz, 2H)

1H), 3.92 - 3.85 (m, 4H), 3.80 (dd, J = 9.8, 3.8 Hz, 1H), 3.50 (dd, J = 16.9, 3.8 Hz, 1H), 1.44 (s, 3H). ¹³C NMR (100 MHz, CHLOROFORM-D) δ 189.40, 172.09, 160.48, 152.54, 142.84, 142.02, 129.33, 127.33, 120.57, 110.61, 108.37, 89.51, 42.03, 37.91, 36.23, 20.68. IR (neat): v = 3109, 2919, 2849, 1759, 1677, 1604, 1559, 1411, 1284, 1109, 1024 cm⁻¹. HRMS (ES+): Exact mass calcd for C₁₆H₁₇N₂O₄ [M+H]⁺: 301.1188. Found: 301.1180.



The compound **7f** was isolated as light yellow semisolid in 93% yield with 6:1 *d.r.* and 90% *ee*. $[\alpha]_D^{25} = +$ 68.1 (*c* 0.84, CHCl₃). The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IC-3 column, *n*-hexane/2-propanol (70:30) as eluent, flow rate: 1.0 mL/min. *t*_R (minor) = 21.75 min, *t*_R (major) = 27.57 min. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.47 (d, *J* = 5.7 Hz, 1H), 7.14 (d, *J* = 0.7 Hz, 1H), 7.03 (s, 1H), 6.21 (dd, *J* = 12.9, 3.3 Hz, 2H), 6.02 (d, *J* = 5.7 Hz, 1H), 3.93 (s, 3H), 3.83

-3.76 (m, 2H), 3.53 - 3.45(m, 1H), 1.45 (s, 3H). ¹³C NMR (100 MHz, CHLOROFORM-D) δ 189.00, 171.92, 160.07, 154.65, 142.67, 129.39, 127.45, 120.97, 120.85, 112.37, 111.31, 89.12, 42.04, 37.66, 36.25, 20.89. IR (thin film): v = 3113, 2956, 2926, 2854, 1760, 1677, 1603, 1500, 1412, 1208, 1124, 1015 cm⁻¹. HRMS (ES+): Exact mass calcd for C₁₆H₁₆BrN₂O₄ [M+H]⁺: 379.0293. Found: 379.0293.



The compound **7g** was isolated as white semisolid in 91% yield with 9:1 *d.r.* and 82% *ee.* $[\alpha]_D^{25} = +$ 22.1 (*c* 0.28, CHCl₃). The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IC-3 column, *n*-hexane/2-propanol (70:30) as eluent, flow rate: 1.0 mL/min. t_R (minor) = 25.71 min, t_R (major) = 34.22 min. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.48 (d, *J* = 5.6 Hz, 1H), 7.14 (s, 1H), 7.01 (s, 1H), 6.07 (d, *J* = 3.0 Hz, 1H), 6.00 (d, *J* = 5.7 Hz, 1H), 5.84 (d, *J* = 3.0 Hz, 1H), 3.93 (s, 3H), 3.85

(dd, J = 17.1, 9.6 Hz, 1H), 3.72 (dd, J = 9.6, 4.2 Hz, 1H), 3.49 (dd, J = 17.2, 4.4 Hz, 1H), 2.22 (s, 3H), 1.43 (s, 3H). ¹³C NMR (100 MHz, CHLOROFORM-D) δ 189.56, 172.22, 160.88, 151.67, 150.62, 142.91, 129.25, 127.27, 120.31, 109.03, 106.45, 89.62, 42.07, 37.86, 36.25, 20.41, 13.73. IR (thin film): v = 3109, 2919, 2849, 1759, 1677, 1604, 1559, 1411, 1284, 1109, 1024 cm⁻¹. HRMS (ES+): Exact mass calcd for C₁₇H₁₉N₂O₄ [M+H]⁺: 315.1345. Found: 315.1342.

6. General procedure and characterization of 9:

To a solution of diethylmalonate (1.0 mmol) in dry THF (2 mL) at 0 °C, NaH (1.0 mmol) was added. The mixture was allowed to stir for 30 min. Then, a solution of **5** (0.2 mmol) in dry THF (1.0 mL) and TMSCl (0.6 mmol) were added. The resulting reaction mixture was stirred for 1.5 h at 0 °C. It was then quenched with saturated NH₄Cl (4.0 mL) and extracted with EtOAc (3x12 mL). The mixture was dried over Na₂SO₄ and concentrated in vacuo and purified over silica gel by column chromatography (20-60% ethyl acetate in hexane) to afford the products.



The compound **9a** was isolated as colorless semisolid in 75% yield with >20:1 *d.r.* and 92% *ee.* $[\alpha]_D^{25} = -4.4$ (*c* 0.98, CHCl₃). The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IA-3 column, *n*-hexane/2-propanol (70:30) as eluent, flow rate: 1.0 mL/min. t_R (minor) = 13.54 min, t_R (major) = 24.26 min. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.26 – 7.17 (m, 5H), 7.05 (s, 1H), 6.92 (s, 1H), 4.53 (dd, *J* = 7.6, 3.7 Hz, 1H), 4.10 – 4.05 (m, 2H), 4.03 – 3.91 (m, 2H), 3.84 (s, 3H), 3.67 – 3.56

(m, 3H), 2.96 (d, J = 6.8 Hz, 1H), 2.85 – 2.79 (m, 1H), 2.52 – 2.39 (m, 2H), 1.16 (t, J = 7.1 Hz, 3H), 1.10 (t, J = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CHLOROFORM-D) δ 190.13, 175.38, 167.47, 167.41, 143.08, 138.78, 129.19, 129.11, 128.73, 127.85, 127.15, 84.79, 62.04, 53.65, 45.42, 41.21, 37.62, 36.20, 32.03, 14.08, 14.00. IR (thin film): v = 2983, 1783, 1729, 1677, 1454, 1412, 1369, 1267, 1179, 1155, 1027 cm⁻¹. HRMS (ES+): Exact mass calcd for C₂₄H₂₉N₂O₇ [M+H]⁺: 457.1975. Found: 457.1975.



The compound **9b** was isolated as colorless semisolid in 61% yield with 10:1 *d.r.* and 97% *ee.* $[\alpha]_D^{25} = -3.8$ (*c* 0.66, CHCl₃). The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IA-3 column, *n*-hexane/2-propanol (70:30) as eluent, flow rate: 1.0 mL/min. t_R (minor) = 20.00 min, t_R (major) = 34.53 min. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.39 – 7.36 (m, 2H), 7.17 – 7.12 (m, 2H), 7.05 (s, 1H), 6.93 (s, 1H), 4.51 (dd, J = 7.4, 3.6 Hz, 1H), 4.12 – 4.07 (m, 2H), 4.03 – 3.95 (m, 2H),

3.84 (s, 3H), 3.59 (d, J = 2.3 Hz, 3H), 3.08 (d, J = 6.9 Hz, 1H), 2.83 – 2.77 (m, 1H), 2.52 (dd, J = 18.5, 9.2 Hz, 1H),

2.42 (dd, J = 18.5, 4.6 Hz, 1H), 1.17 – 1.11 (m, 6H). ¹³C NMR (100 MHz, CHLOROFORM-D) δ 189.74, 175.21, 167.42, 167.33, 142.87, 137.96, 132.19, 130.45, 129.28, 127.34, 121.80, 84.47, 62.21, 62.18, 53.82, 44.70, 40.69, 37.39, 36.26, 32.09, 14.09, 14.02. IR (thin film): v = 2959, 2925, 2854, 1783, 1730, 1677, 1489, 1413, 1369, 1291, 1178, 1157, 1074, 1028 cm⁻¹. HRMS (ES+): Exact mass calcd for C₂₄H₂₈BrN₂O₇ [M+H]⁺: 535.1080. Found: 535.1081.



The compound **9c** was isolated as colorless semisolid in 63% yield with 20:1 *d.r.* and 90% *ee*. $[\alpha]_D^{25} = +4.1$ (*c* 0.60, CHCl₃). The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IA-3 column, *n*-hexane/2-propanol (70:30) as eluent, flow rate: 1.0 mL/min. t_R (minor) = 15.16 min, t_R (major) = 24.81 min. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.32 - 7.27 (m, 2H), 7.12 (s, 1H), 7.03 - 6.99 (m, 3H), 4.60 - 4.53 (m, 1H), 4.15 (dd, J = 7.1,

1.9 Hz, 2H), 4.07 (dd, J = 12.4, 7.1 Hz, 2H), 3.91 (s, 3H), 3.70 – 3.62 (m, 3H), 3.09 (d, J = 6.9 Hz, 1H), 2.90 – 2.83 (m, 1H), 2.56 (dd, J = 18.5, 9.0 Hz, 1H), 2.49 (dd, J = 18.5, 5.0 Hz, 1H), 1.23 (t, J = 7.1 Hz, 3H), 1.18 (t, J = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CHLOROFORM-D) δ 189.84, 175.26, 167.43, 167.37, 162.25 (d, $J_{C-F} = 246.5$ Hz), 142.84, 134.58, 134.55, 130.29 (d, $J_{C-F} = 7.9$ Hz), 129.13, 127.28, 116.01 (d, $J_{C-F} = 21.2$ Hz), 84.67, 62.15, 53.71, 44.57, 41.05, 37.44, 36.28, 32.05, 14.08, 14.01. IR (thin film): v = 2925, 2854, 1782, 1729, 1677, 1605, 1511, 1411, 1369, 1291, 1224, 1159, 1095, 1027 cm⁻¹. HRMS (ES+): Exact mass calcd for C₂₄H₂₈FN₂O₇ [M+H]⁺: 475.1881. Found: 475.1880.



The compound **9d** was isolated as colorless semisolid in 71% yield with 15:1 *d.r.* and 96% *ee*. $[\alpha]_D^{25} = +$ 6.8 (*c* 1.21, CHCl₃). The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IA-3 column, *n*-hexane/2-propanol (70:30) as eluent, flow rate: 1.0 mL/min. t_R (minor) = 15.00 min, t_R (major) = 26.83 min. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.20 (dd, J = 5.1, 1.0 Hz, 1H), 7.12 (s, 1H), 7.00 (d, J = 3.8 Hz, 2H), 6.95 (dd, J = 5.1, 3.4 Hz, 1H), 4.60 (dd, J = 7.3, 3.4 Hz, 1H), 4.18 – 4.09 (m,

4H), 4.03 (d, J = 7.2 Hz, 1H), 3.93 (s, 3H), 3.69 (d, J = 7.0 Hz, 2H), 3.16 (d, J = 6.7 Hz, 1H), 3.01 – 2.95 (m, 1H), 2.48 (dd, J = 18.5, 4.6 Hz, 1H), 2.40 (dd, J = 18.5, 9.3 Hz, 1H), 1.24 – 1.19 (m, 6H). ¹³C NMR (100MHz, CHLOROFORM-D) δ 189.38, 175.43, 167.51, 142.87, 141.06, 129.29, 127.44, 127.29, 126.52, 125.14, 84.32, 62.14, 62.12, 53.83, 42.03, 40.63, 37.38, 36.26, 32.00, 14.08, 14.04. IR (thin film): v = 3111, 2983, 2918, 2850, 1783, 1729, 1678, 1465, 1412, 1370, 1266, 1178, 1095, 1016 cm⁻¹. HRMS (ES+): Exact mass calcd for C₂₂H₂₇N₂O₇S [M+H]⁺: 463.1539. Found: 463.1531.

7. General procedure and characterization of 10:

To a solution of compound **5** (0.15 mmol) in dry CH₃CN (1.5 ml) at 35 °C, was added 4Å molecular sieve (50 mg) and MeOTf (0.19 mmol) under N₂ atmosphere. After stirring for 5 hours at 35 °C, MeOH (375 μ L) and DBU (0.19

mmol) was added. The resulting mixture was allowed to stir for 30 min at 35 °C and the reaction mixture was purified purified over silica gel by column chromatography (10-30% ethyl acetate in hexane) to afford the products.



The compound **10a** was isolated as colorless semisolid in 75% yield and 92% *ee*. $[\alpha]_D^{25}$ = - 52.9 (*c* 0.73, CHCl₃). The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IC-3 column, *n*-hexane/2-propanol (70:30) as eluent, flow rate: 0.8 mL/min. t_R (minor) = 17.303 min, t_R (major) = 20.785 min. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.30 (d, *J* = 5.7 Hz, 1H), 7.27 – 7.20 (m, 5H), 5.99 (d, *J* = 5.7 Hz, 1H), 3.47 (s, 3H), 3.41 – 3.37 (m, 1H), 2.66 – 2.63 (m, 2H), 1.23 (s, 3H). ¹³C NMR (100

MHz, CHLOROFORM-D) δ 172.34, 172.27, 160.58, 138.36, 129.33, 128.71, 127.85, 120.88, 90.03, 51.94, 48.67, 35.33, 22.37. IR (thin film): ν = 3087, 2952, 2921, 2850, 1753, 1738, 1602, 1494, 1454, 1436, 1376, 1292, 1264, 1168, 1103 cm⁻¹. HRMS (ES+): Exact mass calcd for C₁₅H₁₇O₄ [M+H]⁺: 261.1127. Found: 261.1129.



The compound **10b** was isolated as colorless semisolid in 82% yield and 80% *ee*. $[\alpha]_D^{25}$ = - 71.1 (*c* 0.40, CHCl₃). The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IC-3 column, *n*-hexane/2-propanol (70:30) as eluent, flow rate: 0.8 mL/min. *t*_R (minor) = 18.980 min, *t*_R (major) = 23.516 min. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.85 – 7.81 (m, 3H), 7.75 (s, 1H), 7.50 – 7.45 (m, 3H), 7.41 (dd, *J* = 5.7, 1.0 Hz, 1H), 6.09 (d, *J* = 5.7 Hz, 1H), 3.65 – 3.61 (m, 1H), 3.51 (s, 3H), 2.81 –

2.79 (m, 2H), 1.32 (s, 3H). ¹³C NMR (100 MHz, CHLOROFORM-D) δ 172.41, 172.27, 160.64, 135.96, 133.37, 132.97, 128.52, 128.38, 128.08, 127.77, 127.12, 126.42, 126.28, 121.00, 90.19, 51.99, 48.79, 35.42, 22.56. IR (neat): v = 2923, 2852, 1759, 1738, 1600, 1508, 1436, 1285, 1168, 1103 cm⁻¹. HRMS (ES+): Exact mass calcd for C₁₉H₁₈NaO₄ [M+Na]⁺: 333.1103. Found: 333.1107.

8. General procedure for the treatment of methyl cinnamate 11 with silyloxyfurans 3a-b:

Scheme S2 Treatment of methyl cinnamate 11 with silyloxyfurans 3a-b.



(a) General procedure for the reaction of **3a** with methyl cinnamate **11** catalyzed by Sc(III)-**2g** complex.

A solution of a ligand 2g (0.024 mmol) and Sc(OTf)₃ (0.02 mmol) in dry chloroform (1.8 mL) was stirred at room temperature for 3 hours under nitrogen atmosphere. Methyl cinnamate **11** (0.20 mmol in 0.2 mL) was added and the whole mixture was stirred for an additional 15 minute at rt. HFIP (0.20 mmol) was then added to the mixture and the resulting reaction mixture was again stirred for 15 minute at rt. Then silyloxyfuran **3a** (0.40 mmol) was added and the reaction mixture was allowed for stirring at room temperature for 48 hours. No product formation was observed.

(b) General procedure for the reaction of **3b** with methyl cinnamate **11** catalyzed by Sc(III)-**2g** complex.

A solution of a ligand 2g (0.024 mmol) and Sc(OTf)₃ (0.02 mmol) in dry chloroform (1.6 mL) was stirred at room temperature for 3 hours under nitrogen atmosphere. Methyl cinnamate **11** (0.20 mmol 0.2) was added and the whole mixture was stirred for an additional 15 minute at rt. HFIP (0.20 mmol) was then added and the resulting mixture was again stirred for 15 minute more at rt. Then silyloxyfuran **3b** (0.30 mmol in 0.3 mL chloroform) was added and the reaction mixture was allowed for stirring at room temperature for 48 hours. No product formation was observed.

9. X-ray crystal structures of 5q, 5x and 7d:



5q (CCDC 1526457)





(R)

^(Z) 7d

Br

0=

5x (CCDC 1526458)



7d (CCDC 1526459)

10. Crystallographic Data and Pertinent Refinement Parameters of 5q, 5x and 7d:

Parameters	5q	5x	7d
Empirical formula	$C_{18}H_{17}ClN_2O_3$	$C_{16}H_{16}N_2O_3S$	$C_{21}H_{17}BrN_2O_4$
Formula weight	344.79	316.37	441.27
Temperature	100	100	100
Crystal system, space group	Orthorhombic, $P2_12_12_1$	Orthorhombic, $P2_12_12_1$	Monoclinic, $P2_1$
Unit cell dimensions	a = 10.8555(4)	a = 7.683(5)	a = 12.610(5)
(Å, deg)	<i>b</i> = 12.1442(5)	b = 10.196(5)	<i>b</i> = 5.974(5)
	c = 12.5528(5)	c = 19.340(5)	c = 12.888(5)
	$\alpha = 90$	$\alpha = 90$	$\alpha = 90$
	$\beta = 90$	$\beta = 90$	$\beta = 106.487(5)$
	$\gamma = 90$	$\gamma = 90$	$\gamma = 90$
Volume/Å ³	1654.85(11)	1515.0(13)	931.0(9)
Z, $\rho_{\rm c}$ g/cm ³	4, 1.384	4, 1.387	2, 1.574
Absorption coefficient	0.250 mm ⁻¹	0.228 mm ⁻¹	2.239 mm ⁻¹
F(000)	720.0	664.0	448.0
Crystal size (mm ³)	$0.02 \times 0.02 \times 0.02$	$0.02\times0.02\times0.02$	$0.02 \times 0.02 \times 0.02$
2θ range for data collection (deg)	4.96 to 56.628	4.212 to 50.09	5.34 to 50.234
Limiting indices	$-14 \le h \le 14,$	$-9 \le h \le 9$	$-15 \le h \le 15$
	$-16 \le k \le 16$	$-12 \le k \le 12$	$-7 \le k \le 7$
	$-16 \le l \le 16$	$-22 \le 1 \le 22$	$-15 \le l \le 15$
Reflections collected	25291	12101	10915
Completeness to θ (%)	100	100	100
Data / restraints / paraparameters	4126/0/219	2671/1/196	3246/1/254
Goodness-of-fit on F^2	1.053	1.030	1.037
Final R indices [I	$R_1 = 0.0349$	$R_1 = 0.0635$	$R_1 = 0.0242$
>2o(I)]	$wR_2 = 0.0765$	$wR_2 = 0.1796$	$wR_2 = 0.0551$
R indices (all data)	$R_1 = 0.0415$	$R_1 = 0.0671$	$R_1 = 0.0273$
	$wR_2 = 0.0789$	$wR_2 = 0.1839$	$wR_2 = 0.0560$
Largest diff. peak and hole $(e \cdot A^{-3})$	0.23/-0.22	1.46/-0.66	0.25/-0.26
Flack parameter	0.00(2)	0.08(3)	0.076(5)

11. Proposed transition state

It is proposed that the two-point coordination of α , β -unsaturated 2-acyl imidazole with catalyst {**2g**/Sc(OTf)₃} takes place to give a octahedral complex (Fig. S1). The attack of silyloxy furan takes place from the sterically less demanding *Re* face as *Si* face is hindered by the aryl group of the ligand, leading to the formation of product with (*R*, *R*) configuration.



12. References:

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13. NMR spectra:











125 MHz 13 C NMR spectra of compound 5c in CDCl₃















125 MHz ^{13}C NMR spectra of compound 5g in CDCl_3











125 MHz ^{13}C NMR spectra of compound 5j in CDCl_3



125 MHz ^{13}C NMR spectra of compound 5k in CDCl_3







125 MHz ^{13}C NMR spectra of compound 5m in CDCl_3







125 MHz ^{13}C NMR spectra of compound 50 in CDCl_3














100 MHz ^{13}C NMR spectra of compound 5s in CDCl_3







100 MHz ¹³C NMR spectra of compound **5u** in CDCl₃



100 MHz ^{13}C NMR spectra of compound 5v in CDCl_3

















125 MHz ¹³C NMR spectra of compound **7b** in CDCl₃



125 MHz ^{13}C NMR spectra of compound 7c in CDCl_3









100 MHz ¹³C NMR spectra of compound **7f** in CDCl₃







400 MHz ¹H NMR spectra of compound **9a** in CDCl₃



100 MHz ¹³C NMR spectra of compound **9a** in CDCl₃



100 MHz ¹³C NMR spectra of compound **9b** in CDCl₃



100 MHz ¹³C NMR spectra of compound **9c** in CDCl₃









100 MHz ¹³C NMR spectra of compound **10a** in CDCl₃



100 MHz ^{13}C NMR spectra of compound 10b in CDCl_3



HPLC graph of enantioenriched 5a [For Er(III)-2g]



HPLC graph of enantioenriched 5b







S61



DEFAULT REPORT

Peak	Component	Time	Area	Height	Area	Norm. Area
#	Name	[min]	[uV*sec]	[uV]	[%]	[%]
1		28.560	23840193.35	368963.88	49.75	49.75
2		32.733	24082610.71	354583.69	50.25	50.25
			47922804.05	723547.57	100.00	100.00





HPLC graph of enantioenriched 5d











HPLC graph of enantioenriched 5f [For Er(III)-2g]



HPLC graph of enantioenriched $5g\ [For\ Sc(III)\mathchar`-2g]$



HPLC graph of enantioenriched 5g [For Er(III)-2g]









HPLC graph of enantioenriched 5j



				וט	⊏г≁	AUL I	
Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	
1 2		69.610 73.350	9380965.66 10691518.62	98166.02 94835.18	46.74 53.26	46.74 53.26	
			20072484.29	193001.20	100.00	100.00	

DEFAULT REPORT





HPLC graph of enantioenriched $\mathbf{5k}$







HPLC graph of enantioenriched 5m



HPLC graph of enantioenriched 5n














HPLC graph of enantioenriched 5r



HPLC graph of enantioenriched $5s\ [For\ Er(III)\mathchar`-2g]$



HPLC graph of enantioenriched $5t\ [For\ Er(III)\mathchar`-2g]$

HPLC graph of enantioenriched 5u



HPLC graph of racemic 5u

				D	REPORT		
Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	
1 2		10.698 14.228	15295218.36 15018484.58	216430.48 162944.78	50.46 49.54	50.46 49.54	
			30313702.94	379375.27	100.00	100.00	







HPLC graph of enantioenriched $\mathbf{5v}$



HPLC graph of enantioenriched 5w [For Er(III)-2g]













HPLC graph of enantioenriched 7b



HPLC graph of enantioenriched 7c







HPLC graph of enantioenriched 7e







S88







HPLC graph of enantioenriched 9a



HPLC graph of enantioenriched $\mathbf{9b}$







HPLC graph of enantioenriched 9d



S94

