

Supporting Information

Phase-Transfer-Catalysed, Enantioselective Vinylogous Conjugate Addition–Cyclization of Olefinic Azlactones to Access Multi-Functionalized Chiral Cyclohexenones

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1. General information:

General procedures and methods

Experiments involving moisture and/or air sensitive components were performed under a positive pressure of nitrogen in oven-dried glassware equipped with a rubber septum inlet. Dried solvents and liquid reagents were transferred by oven-dried syringes or hypodermic syringe cooled to ambient temperature in a desiccator. Reactions mixtures were stirred in 4 mL sample vial with Teflon-coated magnetic stirring bars unless otherwise stated. Moisture in non-volatile reagents/compounds was removed in high *vacuo* by means of an oil pump and subsequent purging with nitrogen. Solvents were removed in *vacuo* under ~30 mmHg and heated with a water bath at 30–40 °C using rotary evaporator with aspirator. The condenser was cooled with running water at 0 °C.

All experiments were monitored by analytical thin layer chromatography (TLC). TLC was performed on pre-coated plates, 60 F₂₅₄. After elution, plate was visualized under UV illumination at 254 nm for UV active material. Further visualization was achieved by staining KMnO₄, ceric molybdate, or anisaldehyde solution. For those using the aqueous stains, the TLC plates were heated on a hot plate.

Columns for flash chromatography (FC) contained silica gel 200–300 mesh. Columns were packed as slurry of silica gel in petroleum ether and equilibrated solution using the appropriate solvent system. The elution was assisted by applying pressure of about 2 atm with an air pump.

Instrumentations

Proton nuclear magnetic resonance (¹H NMR), carbon NMR (¹³C NMR), and fluorous (¹⁹F NMR) spectra were recorded in CDCl₃ otherwise stated. ¹H (400 MHz) and ¹³C (100 MHz), ¹H (600 MHz) and ¹³C (150 MHz) were performed on the 400 MHz or 600 MHz spectrometer. Chemical shifts are reported in parts per million (ppm), using the residual solvent signal as an internal standard: CDCl₃ (¹H NMR: δ 7.26, singlet; ¹³C NMR: δ 77.0, triplet). Multiplicities were given as: *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), *quintet*, *m* (multiplets), *dd* (doublet of doublets), *dt* (doublet of triplets), and *br* (broad). Coupling constants (*J*) were recorded in Hertz (Hz). The number of proton atoms (*n*) for a given resonance was indicated by *nH*. The number of carbon atoms (*n*) for a given resonance was indicated by *nC*. HRMS

was reported in units of mass of charge ratio (m/z). Mass samples were dissolved in DCM and MeOH (HPLC Grade) unless otherwise stated. Optical rotations were recorded on a polarimeter with a sodium lamp of wavelength 589 nm and reported as follows; $[\alpha]_{\lambda}^{T^{\circ}C}$ ($c =$ g/100 mL, solvent). Melting points were determined on a melting point apparatus. Enantiomeric excesses were determined by chiral High Performance Liquid Chromatography (HPLC) analysis. UV detection was monitored at 254 nm, 230 nm and 210 nm at the same time. HPLC samples were dissolved in HPLC grade isopropanol (IPA) unless otherwise stated.

Materials

All commercial reagents were purchased with the highest purity grade. They were used without further purification unless specified. All solvents used, mainly petroleum ether (PE) and ethyl acetate (EtOAc), were distilled. Anhydrous CH₂Cl₂, CHCl₃ and CPME were freshly distilled from CaH₂ and stored under N₂ atmosphere. THF, Et₂O, and toluene were freshly distilled from sodium/benzophenone before use. All compounds synthesized were stored in a -20 °C freezer and light-sensitive compounds were protected with aluminium foil.

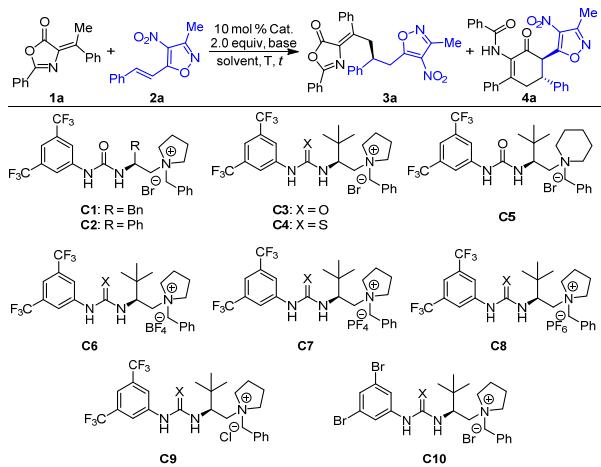
The following compounds were synthesized according to previous reported procedures:
alkenylisoxazoles¹, quaternary ammonium salt catalysts².

(1) Motaleb, R. M. A.; Bakeer, H. M.; Tamam, G. H.; Arafa, W. A. A. *J. Heterocyclic Chem.* **2012**, *49*, 1071-1076.

(2) Duan, S.; Li, S.; Ye, X.; Du, N.; Tan, C.; Jiang, Z. *J. Org. Chem.* **2015**, *80*, 7770-7778.

2. Optimization for the reaction conditions

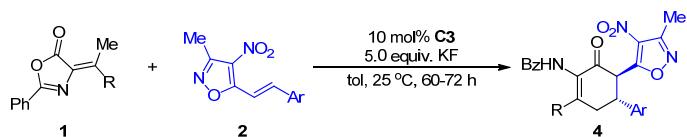
Table S1. Condition optimization^a



entry	cat.	base	solvent	T (°C)	t (h)	3a:4a^b	4a Yield (%) ^c	ee (%)^d
1	TEA	--	Tol	25	60	n.d	n.d	n.d
2	TMG	--	Tol	25	60	1:1	26	--
3	C1	K ₂ HPO ₄	Tol	25	60	1:3	32	52
4	C2	K ₂ HPO ₄	Tol	25	60	1:4	41	30
5	C3	K ₂ HPO ₄	Tol	25	60	1:15	56	92
6	C4	K ₂ HPO ₄	Tol	25	60	n.d	n.d	n.d
7	C5	K ₂ HPO ₄	Tol	25	60	1:7	47	91
8	C6	K ₂ HPO ₄	Tol	25	60	1:15	69	91
9	C7	K ₂ HPO ₄	Tol	25	60	1:13	45	89
10	C8	K ₂ HPO ₄	Tol	25	60	1:14	48	91
11	C9	K ₂ HPO ₄	Tol	25	60	1:12	25	82
12	C10	K ₂ HPO ₄	Tol	25	60	1:13	42	85
13 ^e	C3	K ₂ HPO ₄	DCM	25	60	2:1	15	83
14	C3	K ₂ HPO ₄	Et ₂ O	25	60	n.d	n.d	n.d
15	C3	K ₂ HPO ₄	THF	25	60	n.d	n.d	n.d
16	C3	K ₂ HPO ₄	C ₆ F ₅ H	25	60	1:6	60	86
17	C3	K ₂ HPO ₄	mesitylene	25	60	1:6	38	92
15	C3	K ₂ HPO ₄	m-Xylene	25	60	1:1	13	93
16	C3	K ₂ HPO ₄	o-Xylene	25	60	1:8	46	92
17	C3	K ₃ PO ₄	Tol	25	60	1:15	62	90
18	C3	K ₂ CO ₃	Tol	25	60	1:3	36	93
19	C3	Na ₂ CO ₃	Tol	25	60	1:2	29	93
20	C3	Cs ₂ CO ₃	Tol	25	60	1:17	75	84
21	C3	CsF	Tol	25	60	1:17	72	81
22	C3	KF	Tol	25	60	1:16	63	93
23	C3	KF	Tol	25	60	1:16	63	93
24 ^f	C3	KF	Tol	25	60	1:16	91	93

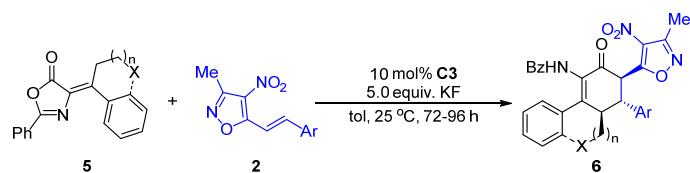
^a Reaction conditions: **1a** (0.05 mmol), **2a** (0.05 mmol), catalyst (0.005 mmol), base (0.1mmol), solvent (0.5 mL). ^b Determined by ¹H NMR analysis. ^c Yield was isolated by flash column. ^d Determined by HPLC analysis on a chiral stationary phase. ^e **3a**: 36% yield, *Z/E* > 19:1, 83% *ee*. ^f 0.1 mmol of **1a** and KF (0.25 mmol) were used and in 0.25 mL solvent.

3. General experimental procedure for the reactions of olefinic azlactones **1 with alkenylisoxazoles **2****



Olefinic azlactones **1** (0.2 mmol, 2.0 equiv.), KF (29.05 mg, 0.5 mmol, 5.0 equiv.), catalyst **C3** (5.97 mg, 0.01 mmol, 0.1 equiv.) were dissolved in toluene (0.5 mL) and stirred at 25 °C for 15 min. Then, 3-methyl-4-nitro-alkenylisoxazoles **2** (0.1 mmol, 1.0 equiv.) was added. The reaction mixture was stirred at 25 °C and monitored by TLC. Upon complete consumption of 3-methyl-4-nitro-alkenylisoxazoles **2** (60–72 h), the reaction mixture was directly loaded onto a short *silica gel* column, followed by flash chromatography by gradient elution with PE/EtOAc/DCM (10/1/1–3/1/1). Removing the solvent *in vacuo*, afforded products **4**.

4. General experimental procedure for the reactions of olefinic azlactones **5 with alkenylisoxazoles **2****



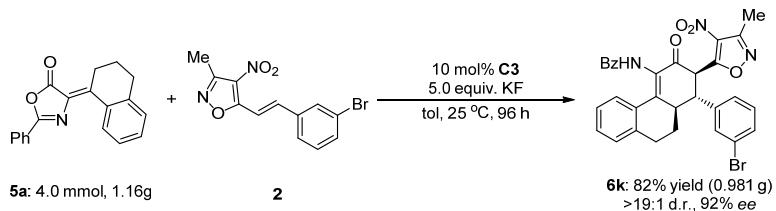
Olefinic azlactones **5** (0.2 mmol, 2.0 equiv.), KF (29.05 mg, 0.5 mmol, 5.0 equiv.), catalyst **C3** (5.97 mg, 0.01 mmol, 0.1 equiv.) were dissolved in toluene (0.5 mL) and stirred at 25 °C for 15 min. Then, 3-methyl-4-nitro-alkenylisoxazoles **2** (0.1 mmol, 1.0 equiv.) was added. The reaction mixture was stirred at 25 °C and monitored by TLC. Upon complete consumption of 3-methyl-4-nitro-alkenylisoxazoles **2** (72–96 h), the reaction mixture was directly loaded onto a short *silica gel* column, followed by flash chromatography by gradient elution with PE/EtOAc/DCM (10/1/1–3/1/1). Removing the solvent *in vacuo*, afforded products **6**.

5. Control experiment for *rac*-**3a** to **3a** and **4a**



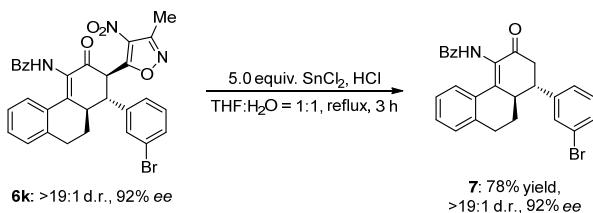
The racemic conjugate addition adduct **rac-3a** ($Z/E = 4:1$) (49.3 mg, 0.1 mmol, 2.0 equiv.), KF (29.05 mg, 0.5 mmol, 5.0 equiv.), catalyst **C3** (5.97 mg, 0.01 mmol, 0.1 equiv.) were dissolved in toluene (0.5 mL) and stirred at 25 °C for 46 hours. the reaction mixture was directly loaded onto a short *silica gel* column, followed by flash chromatography by gradient elution with PE/EtOAc/DCM (10/1/1–3/1/1). Removing the solvent *in vacuo*, afforded the cycloadditon product **4a** in 66% yield (32.5 mg) with 5% *ee* and the conjugate addition adduct **3a** in 31% yield (15.3 mg) with 22% *ee*.

6. Experimental procedure for gram-scale preparation of **6k**

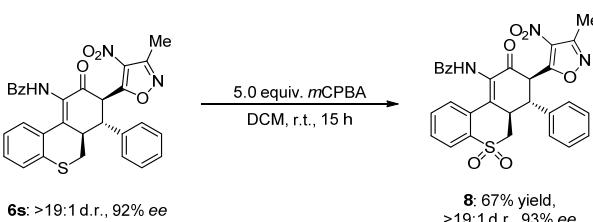


Olefinic azlactone **5a** (1.16 g, 4.0 mmol, 2.0 equiv.), KF (581.0 mg, 10 mmol, 5.0 equiv.), catalyst **C3** (119.4 mg, 0.2 mmol, 0.1 equiv.) were dissolved in toluene (10.0 mL) and stirred at 25 °C for 15 min. Then, 3-methyl-4-nitro-alkenylisoxazoles **2** (616.0 g, 2 mmol, 1.0 equiv.) was added. The reaction mixture was stirred at 25 °C for 96 hours. The reaction mixture was directly loaded onto a short *silica gel* column, followed by flash chromatography by gradient elution with PE/EtOAc/DCM (10/1/1–3/1/1). Removing the solvent *in vacuo*, afforded products **6k** in 82% yield (981.0 mg) and 92% *ee*.

7. Experimental procedures for transformations



To the solution of compound **6k** (0.31 mmol, 185.2 mg) in THF/water (14 mL, 1:1) was added $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (1.55 mmol, 349.8 mg), and 36% HCl (0.35 mL). The reaction mixture was refluxed for 3 h and then cooled to room temperature. THF was evaporated off and the aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by silica gel column chromatography with PE/EtOAc (10/1–3/1) to afford the product **7** in 78% yield (113.9 mg) and 92% *ee*.



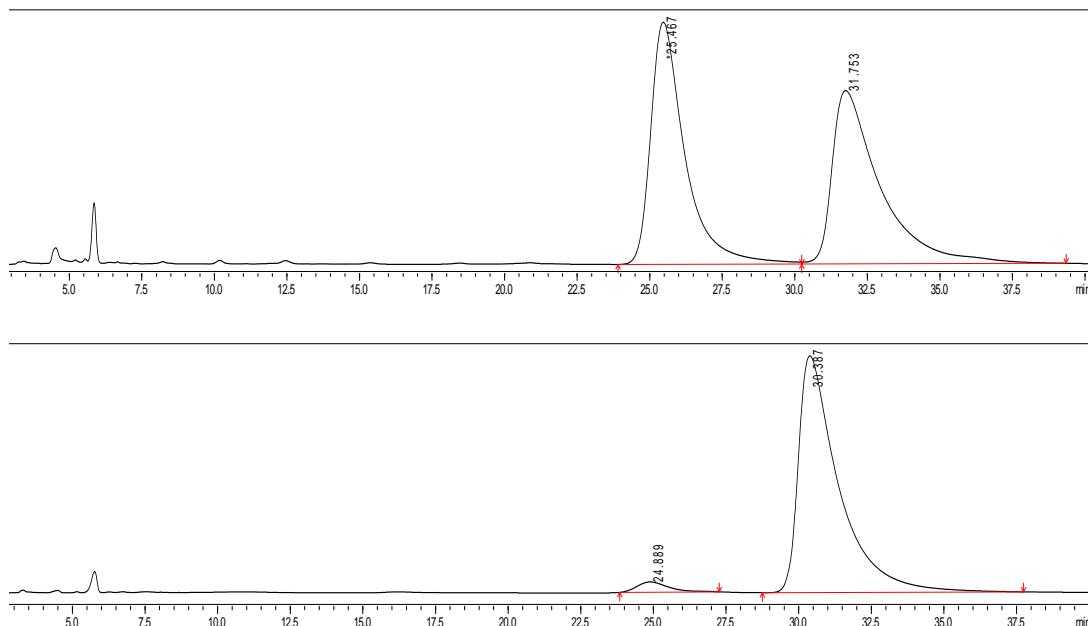
To a cooled CH_2Cl_2 (4.0 mL) solution of **6s** (83.4 mg, 0.155 mmol) was added *m*-CPBA (0.134 mg, 0.776 mmol) and stirred from 0 °C to 25 °C for 15 hours. The reaction was quenched with aqueous NaHCO_3 and the aqueous layer was extracted with DCM. The combined organic extracts were washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated in *vacuo*. The crude product was purified by column chromatography using PE/EtOAc/DCM (10/1/1–3/1/1) to afford the product **8** in 67% yield (59.1 mg) and 93% *ee*.

8. Characterization of adducts

4a: Ar = Ph

Pale yellow solid, Mp 168.4–169.6 °C; 91% yield (46.9 mg); 93% ee; $[\alpha]_D^{24} = -38.3$ (*c* 0.49), ^1H NMR (600 MHz, CDCl_3) δ 7.72 (s, 1H), 7.66 (d, *J* = 7.3 Hz, 2H), 7.50 (d, *J* = 7.3 Hz, 2H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.34 (t, *J* = 7.2 Hz, 4H), 7.31–7.27 (m, 5H), 7.24–7.23 (m, 1H), 5.43 (d, *J* = 10.8 Hz, 1H), 4.27–4.22 (m, 1H), 3.31 (d, *J* = 10.8 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 189.0, 170.0, 165.2, 155.3, 151.4, 139.3, 138.3, 133.8, 132.3, 131.9, 129.4, 129.1, 128.5, 128.0, 127.9, 127.2, 126.9, 126.7, 51.8, 43.5, 40.2, 11.5; HRMS (ESI) *m/z* 516.1519 ($\text{M}+\text{Na}^+$), calc. for $\text{C}_{29}\text{H}_{23}\text{N}_3\text{O}_5\text{Na}$ 516.1530.

The ee was determined by HPLC analysis. CHIRALPAK INC (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM = 89.5/10/0.5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 24.9 min (minor) and 30.4 min (major).

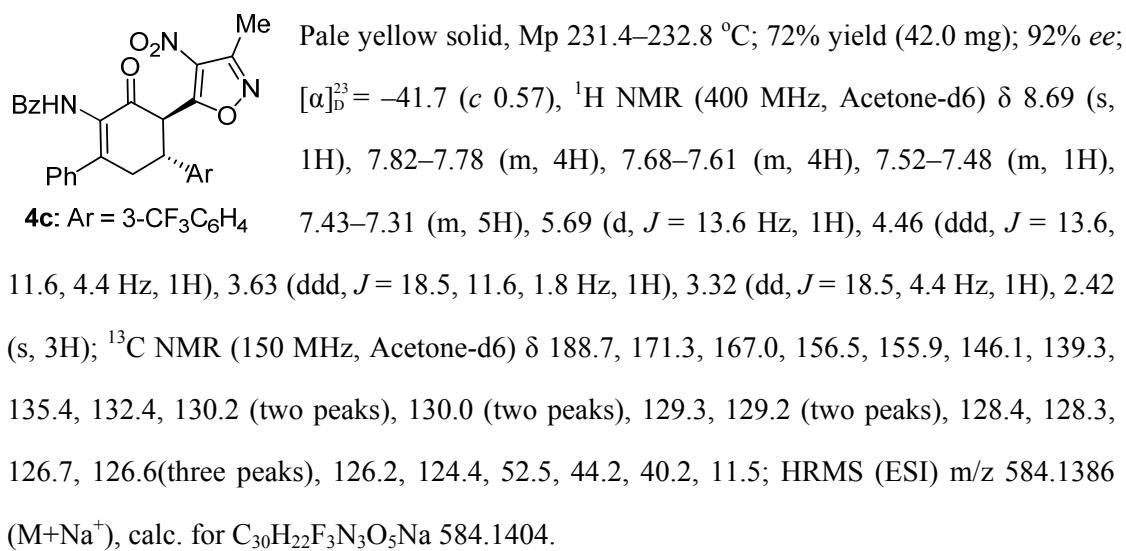
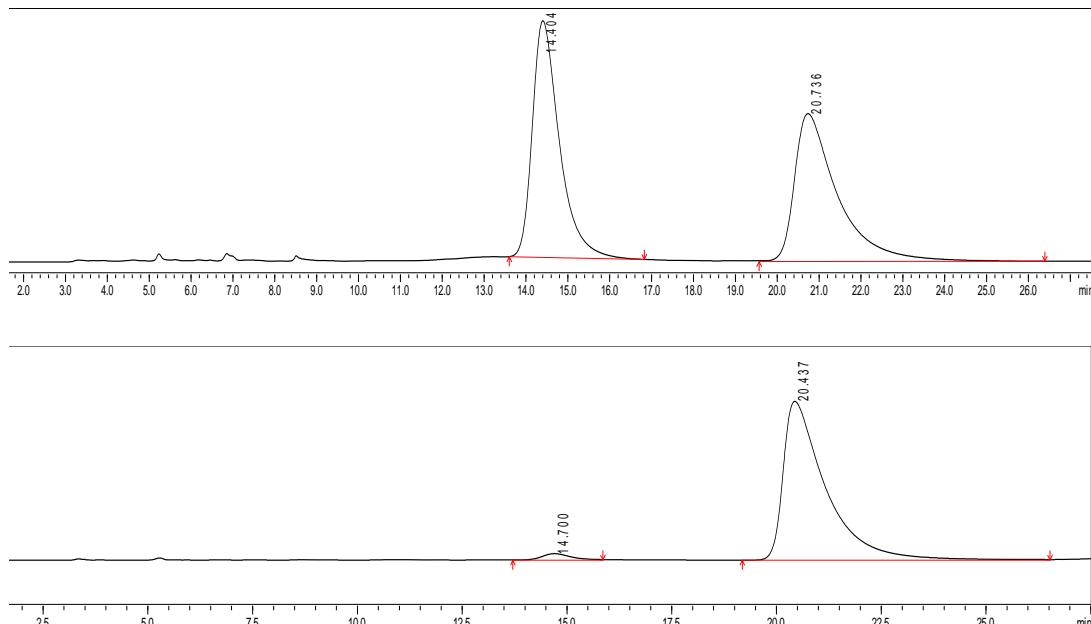


4b: Ar = 4-CF₃C₆H₄

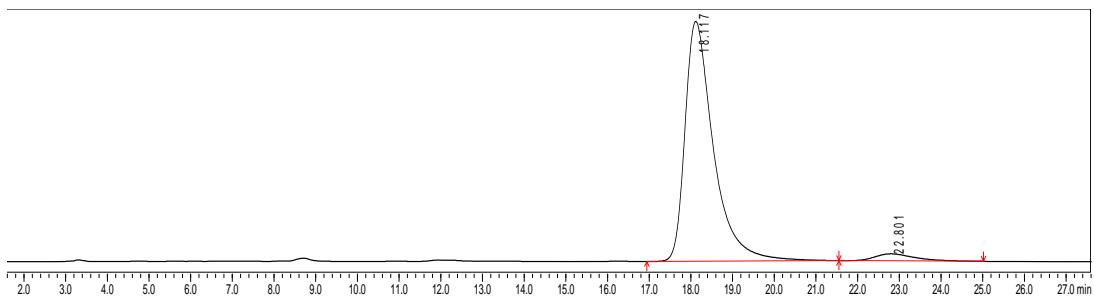
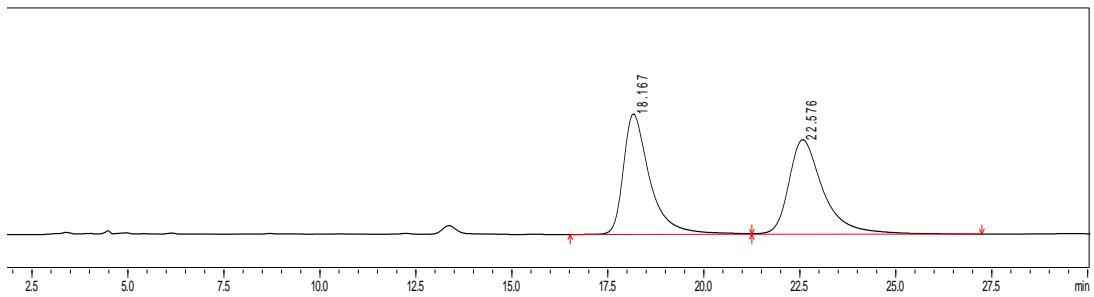
Yellow solid, Mp 129.8–130.3 °C; 93% yield (54.3 mg); 94% ee; $[\alpha]_D^{23} = -36.1$ (*c* 0.37), ^1H NMR (400 MHz, CDCl_3) δ 7.74 (s, 1H), 7.64 (d, *J* = 7.4 Hz, 2H), 7.56 (s, 1H), 7.53–7.42 (m, 6H), 7.37–7.28 (m, 5H), 5.45 (d, *J* = 13.8 Hz, 1H), 4.34 (dt, *J* = 13.8, 8.0 Hz, 1H), 3.32 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 188.5, 169.4, 165.3, 155.4, 151.4, 140.4, 138.1, 133.6, 132.4, 131.9, 130.3, 129.7, 129.5, 128.7, 128.5, 128.1, 127.2,

126.7, 125.0, 123.9, 51.4, 43.1, 39.9, 11.4; HRMS (ESI) m/z 584.1392 ($M+Na^+$), calc. for $C_{30}H_{22}F_3N_3O_5Na$ 584.1404.

The ee was determined by HPLC analysis. CHIRALPAK INC (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM = 89.5/10/0.5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 14.7 min (minor) and 20.4 min (major).

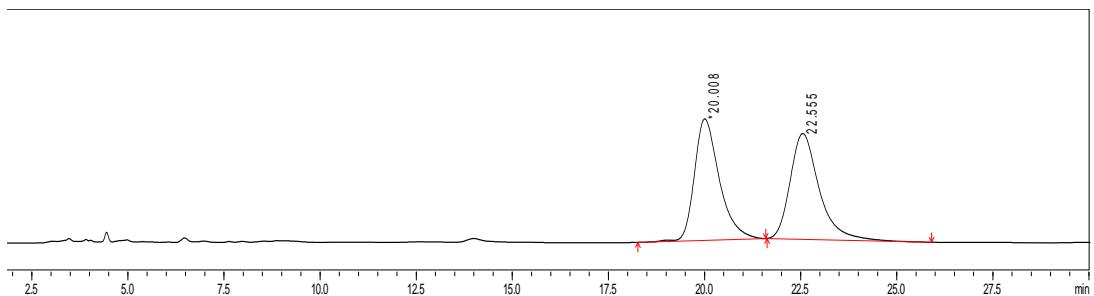


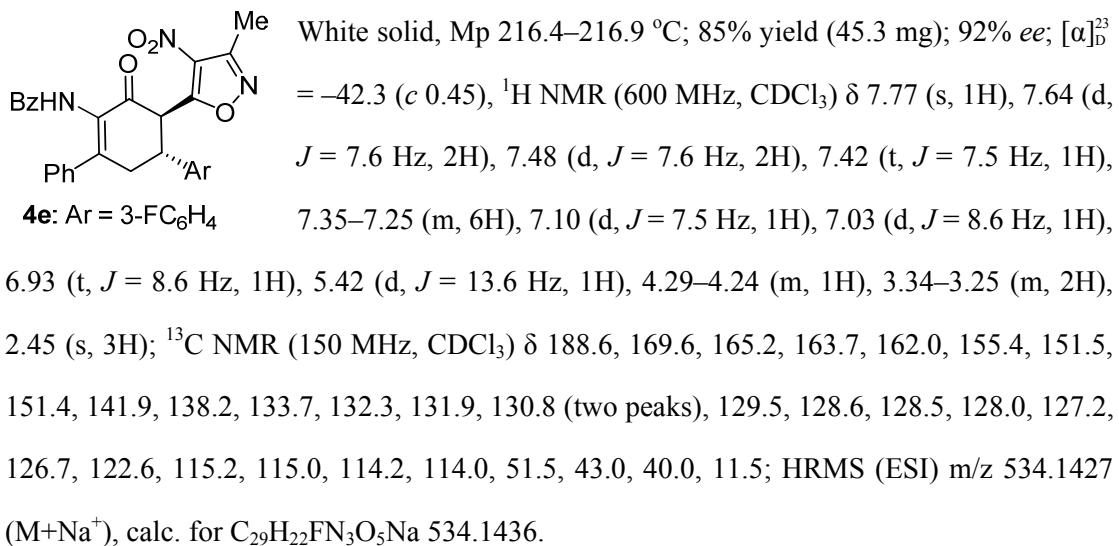
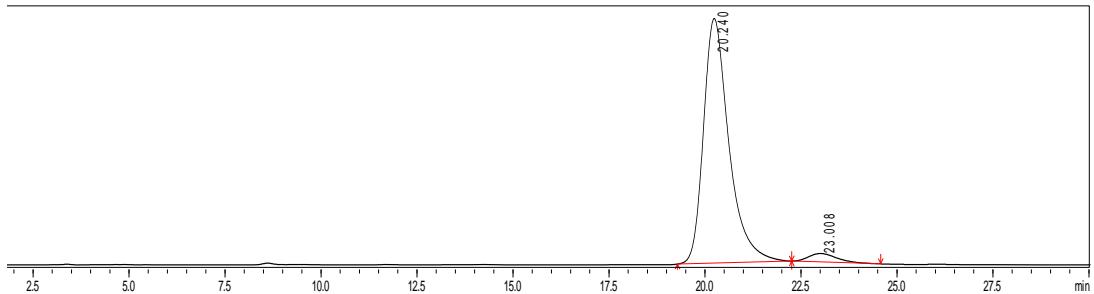
The ee was determined by HPLC analysis. CHIRALPAK INC (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM = 89.5/10/0.5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 18.1 min (major) and 22.8 min (minor).



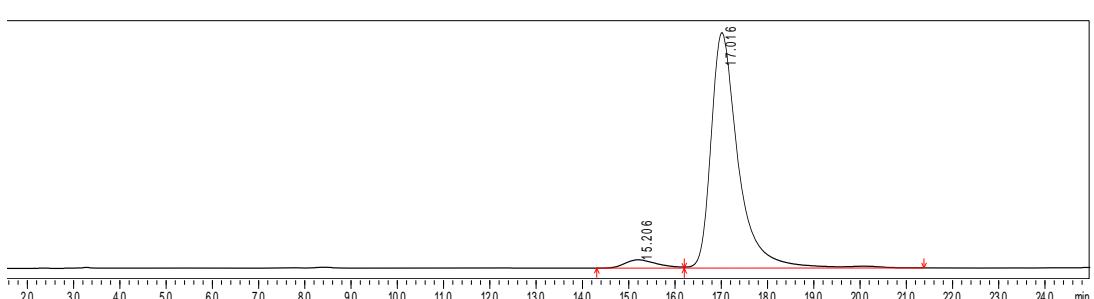
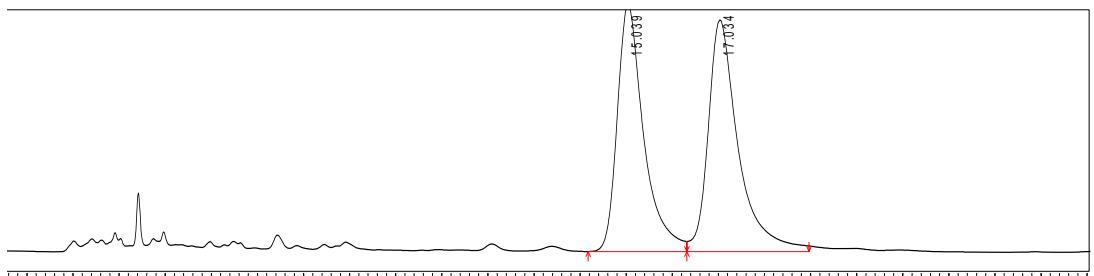
4d: Ar = 4-FC₆H₄ White solid, Mp 183.7–184.1 °C; 85% yield (45.4 mg); 93% ee; $[\alpha]_D^{23}$ = −36.8 (*c* 0.41), ¹H NMR (600 MHz, CDCl₃) δ 7.76 (s, 1H), 7.64 (d, *J* = 7.7 Hz, 2H), 7.48 (d, *J* = 7.7 Hz, 2H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.36–7.28 (m, 7H), 6.98 (t, *J* = 7.8 Hz, 2H), 5.41 (d, *J* = 10.6 Hz, 1H), 4.27–4.22 (m, 1H), 3.28 (d, *J* = 10.6 Hz, 2H), 2.44 (s, 3H); ¹³C NMR (150 MHz, Acetone-d6) δ 189.0, 171.6, 167.0, 163.7, 162.1, 156.4, 156.1, 139.4, 137.6, 135.4, 132.4, 130.4, 130.3, 130.2, 130.0, 129.2 (two peaks), 128.4, 128.2, 116.5, 116.3, 53.2, 44.0, 40.6, 11.5; HRMS (ESI) m/z 534.1426 (M+Na⁺), calc. for C₂₉H₂₂FN₃O₅Na 534.1436.

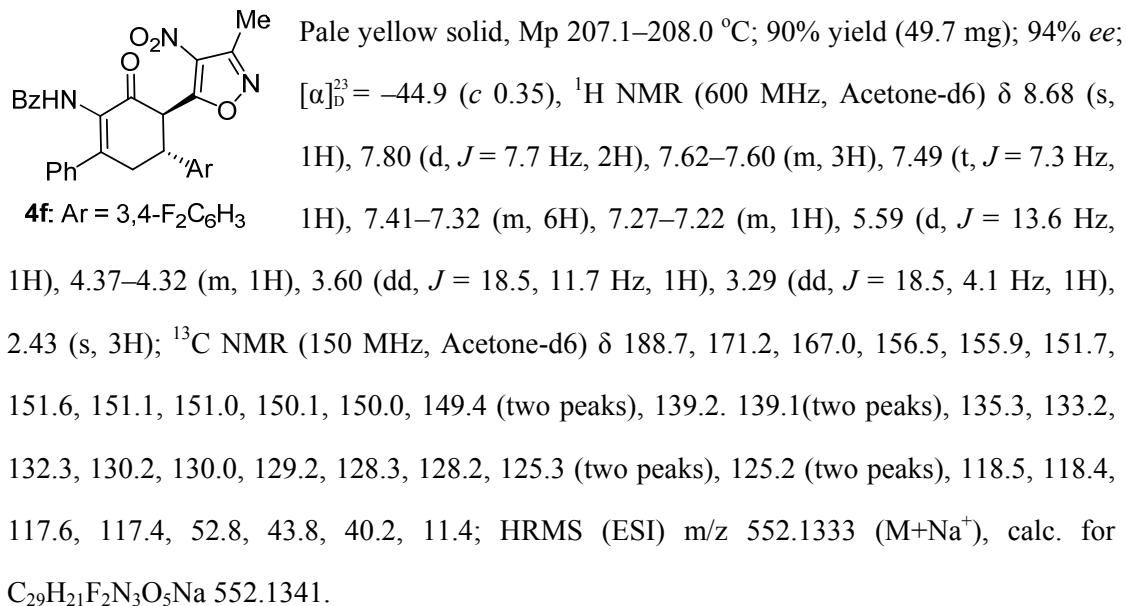
The ee was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM = 79/20/1; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 20.2 min (major) and 23.0 min (minor).



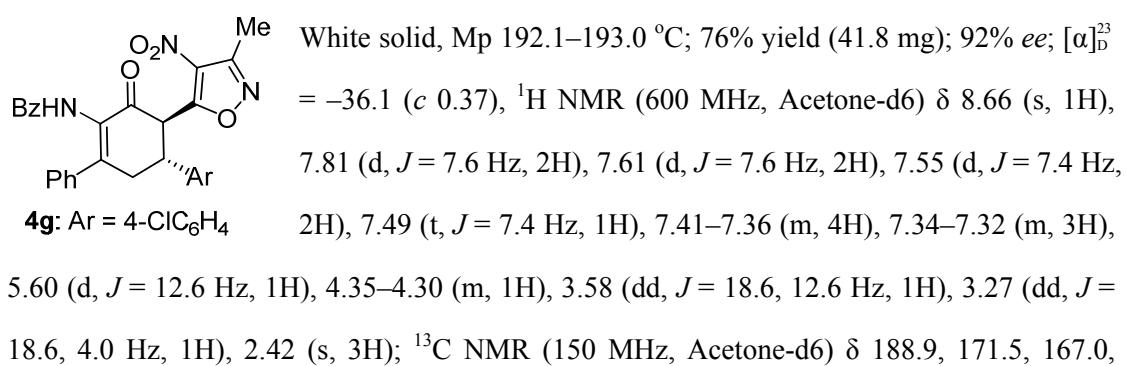
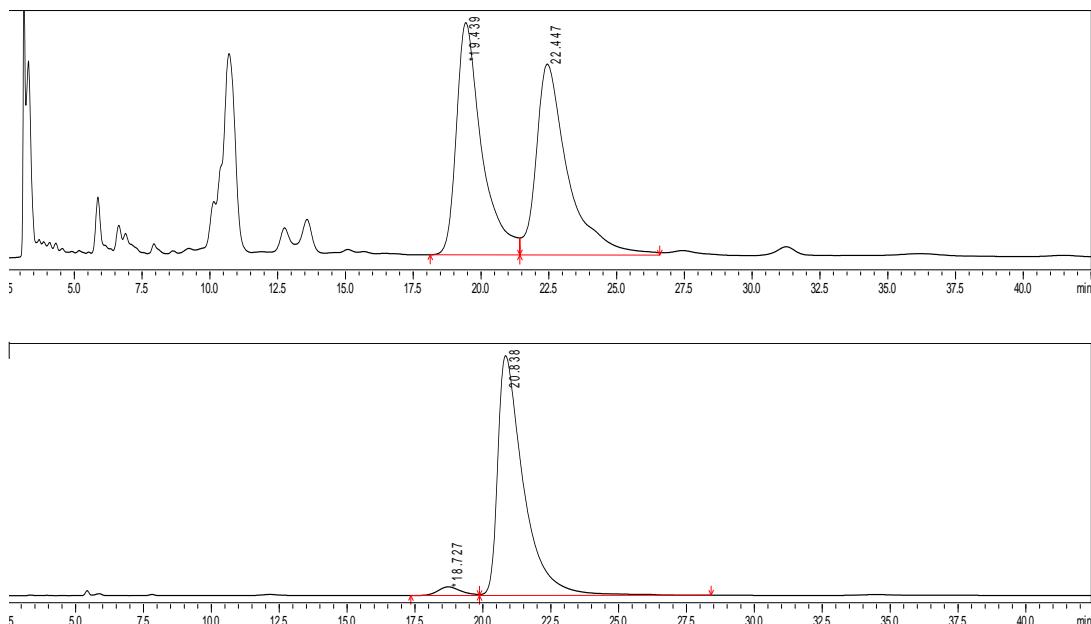


The ee was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM = 79/20/1; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 15.2 min (minor) and 17.0 min (major).



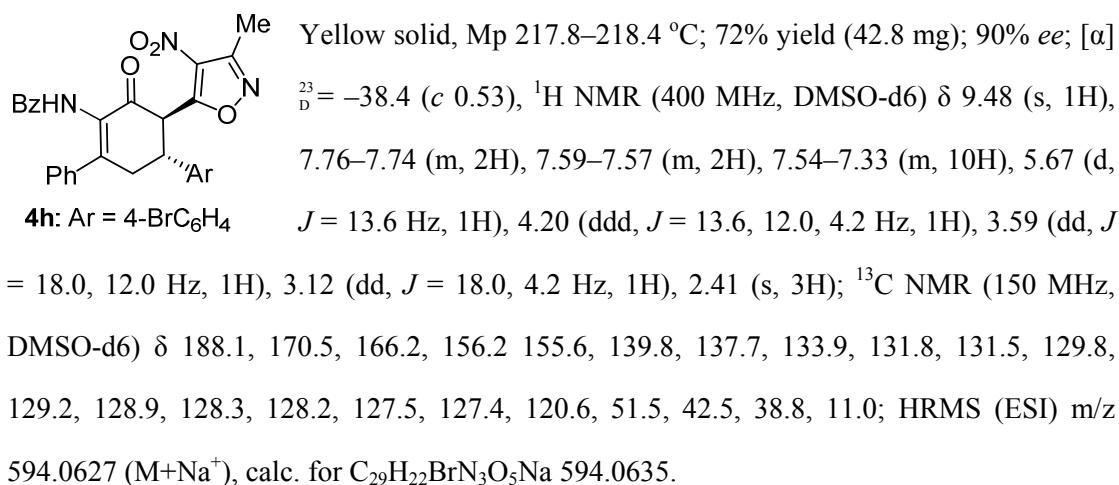
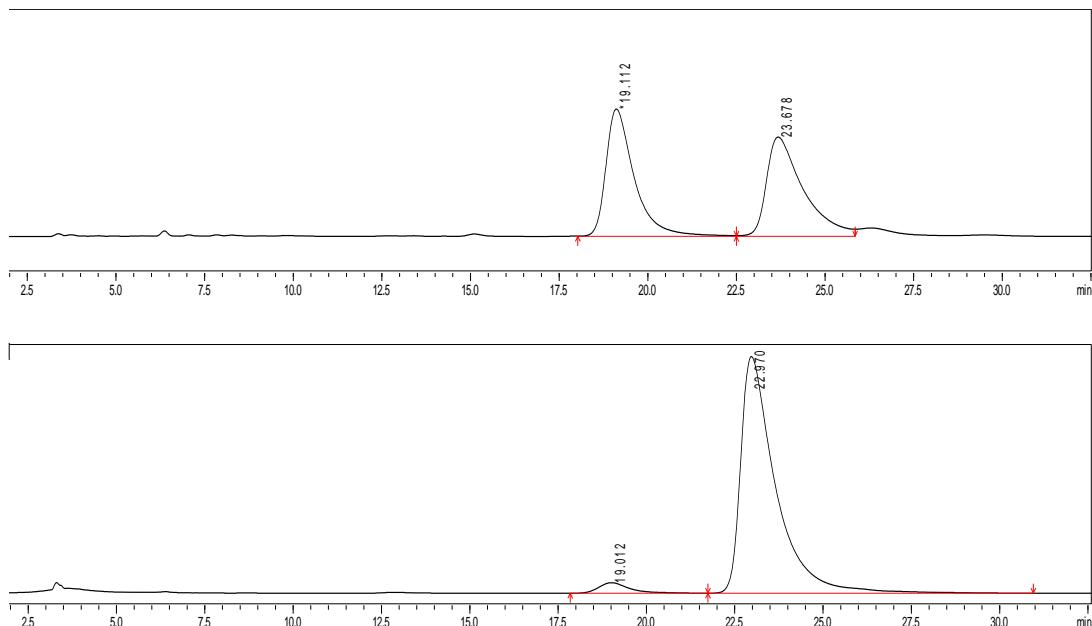


The ee was determined by HPLC analysis. CHIRALPAK INC (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM = 89.5/20/0.5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 18.7 min (minor) and 20.8 min (major).

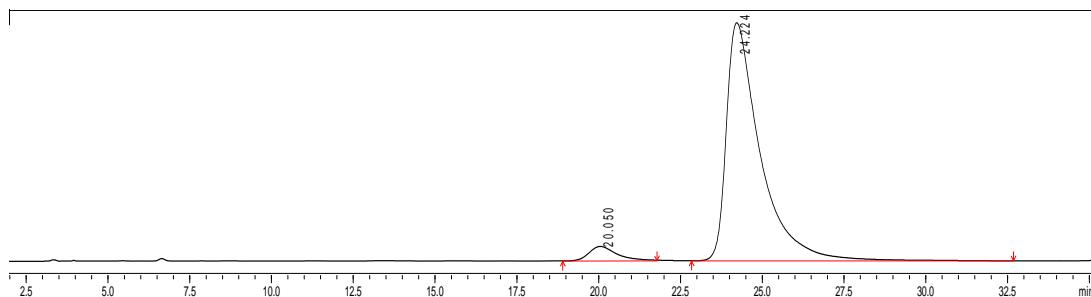
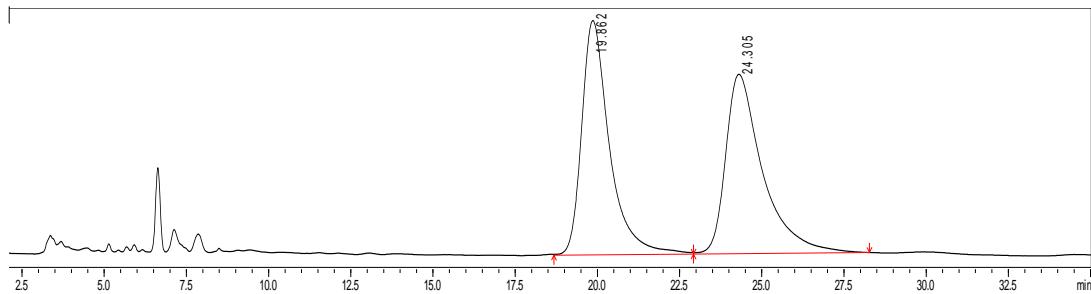


156.5, 156.0, 140.4, 139.3, 135.4, 133.8, 133.2, 132.4, 130.2, 129.8, 129.2(two peaks), 128.4, 128.3, 52.9, 44.0, 40.4, 11.5; HRMS (ESI) m/z 550.1123 ($M+Na^+$), calc. for $C_{29}H_{22}N_3O_5ClNa$ 550.1140.

The ee was determined by HPLC analysis. CHIRALPAK INC (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM = 89.5/10/0.5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 19.0 min (minor) and 23.0 min (major).



The ee was determined by HPLC analysis. CHIRALPAK INC (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM = 89.5/10/0.5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 20.0 min (minor) and 24.2 min (major).

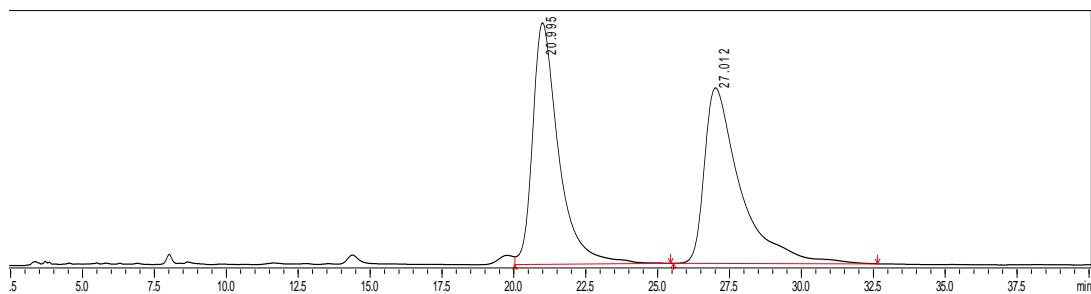


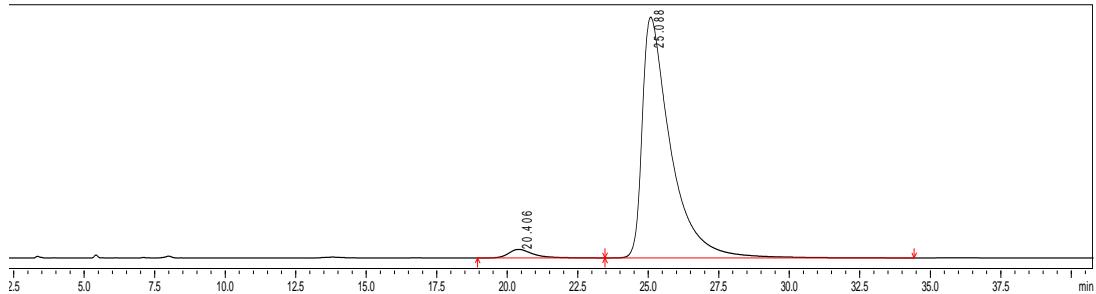
4i: Ar = 3-BrC₆H₄

Chemical Structure:

White solid, Mp 152.5–153.7 °C; 93% yield (55.2 mg); 94% ee; $[\alpha]_{D}^{23}$ = –42.4 (*c* 0.52), ¹H NMR (600 MHz, CDCl₃) δ 7.77 (s, 1H), 7.62 (d, *J* = 7.5 Hz, 2H), 7.47 (s, 3H), 7.42–7.25 (m, 8H), 7.16 (t, *J* = 7.5 Hz, 1H), 5.42 (d, *J* = 13.6 Hz, 1H), 4.25–4.20 (m, 1H), 3.30–3.24 (m, 2H), 2.44 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 188.6, 169.6, 165.2, 155.4, 151.8, 141.7, 138.0, 133.5, 132.3, 131.8, 131.2, 130.7, 130.3, 129.5, 128.68, 128.5, 128.0, 127.2, 126.7, 125.5, 123.0, 51.4, 42.8, 40.0, 11.5; HRMS (ESI) m/z 594.0625 (M+Na⁺), calc. for C₂₉H₂₂BrN₃O₅Na 594.0635.

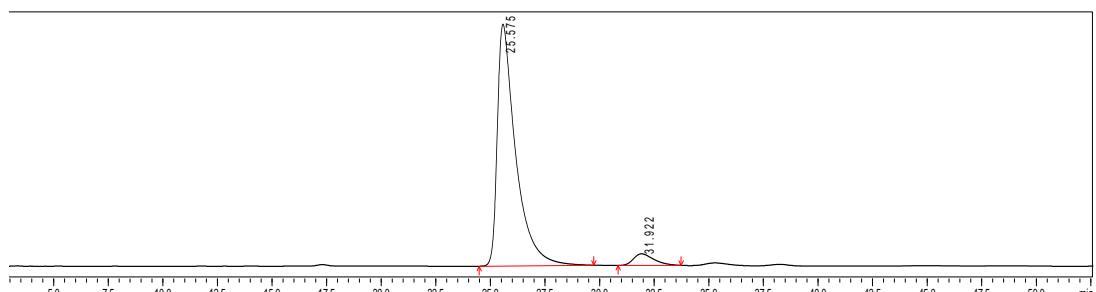
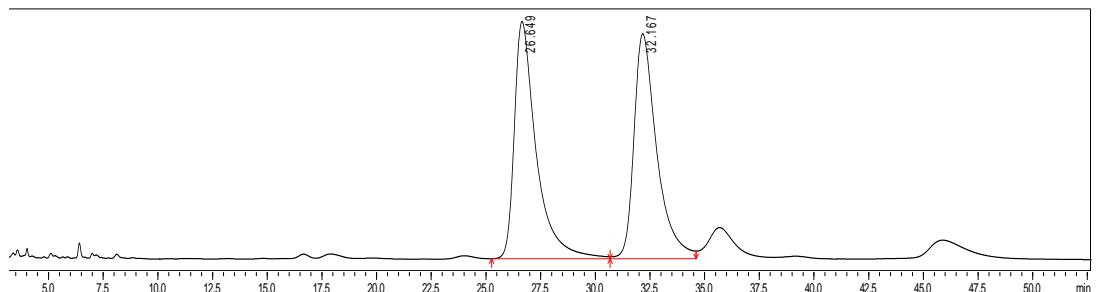
The ee was determined by HPLC analysis. CHIRALPAK INC (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM = 89.5/10/0.5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 20.4 min (major) and 25.1 min (minor).





4j: Ar = 2-BrC₆H₄ Pale yellow solid, Mp 130.2–131.1 °C; 88% yield (52.3 mg); 90% ee;
 $[\alpha]_D^{23} = -20.6$ (*c* 1.07), ¹H NMR (400 MHz, CDCl₃) δ 7.68–7.66 (m, 3H), 7.54–7.40 (m, 5H), 7.36–7.28 (m, 6H), 7.13–7.07 (m, 1H), 5.43 (s, 1H), 4.89 (s, 1H), 3.38–3.34 (m, 1H), 3.10 (s, 1H), 2.46 (s, 3H);
¹³C NMR (100 MHz, CDCl₃) δ 188.6, 169.7, 165.4, 155.5, 151.4, 138.4, 138.2, 133.7, 132.2, 131.9, 129.5, 129.3, 128.6, 128.5, 128.2, 127.9, 127.2, 126.8, 126.7, 124.3, 50.8, 41.3, 39.0, 11.6; HRMS (ESI) m/z 594.0621 (M+Na⁺), calc. for C₂₉H₂₂BrN₃O₅Na 594.0635.

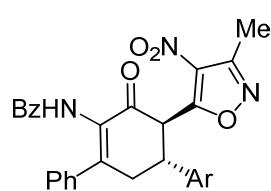
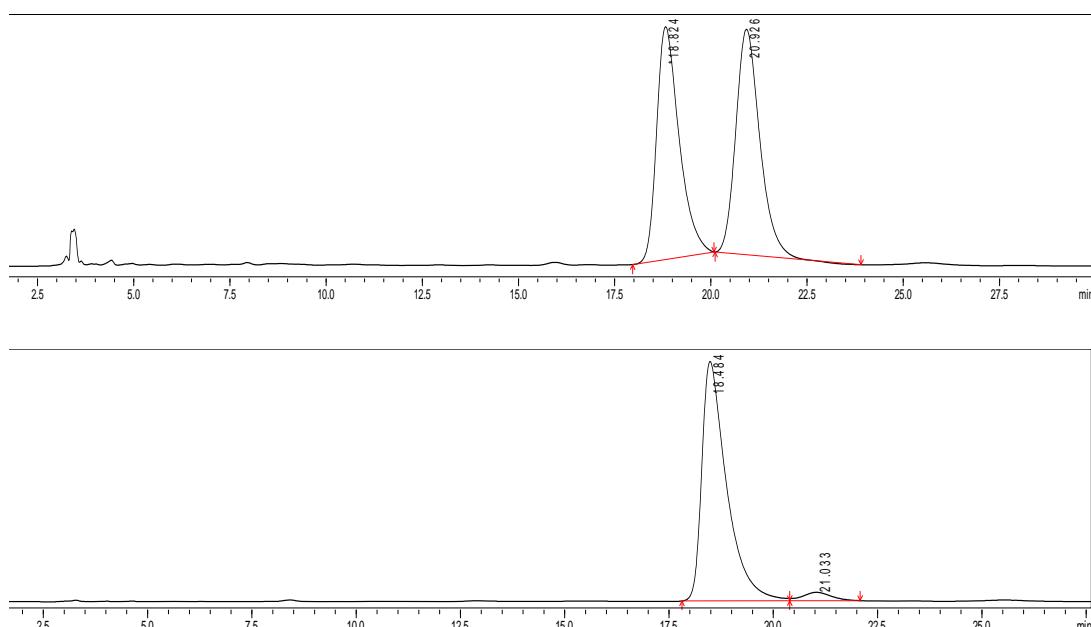
The ee was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM = 89.5/10/0.5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 25.6 min (major) and 31.9 min (minor).



4k: Ar = 4-MeC₆H₄ Pale yellow solid, Mp 188.0–188.8 °C; 93% yield (49.3 mg); 92% ee;
 $[\alpha]_D^{23} = -34.9$ (*c* 0.58), ¹H NMR (400 MHz, CDCl₃) δ 7.79 (s, 1H), 7.64 (d, *J* = 7.1 Hz, 2H), 7.48 (d, *J* = 7.1 Hz, 2H), 7.41 (t, *J* = 7.4 Hz,

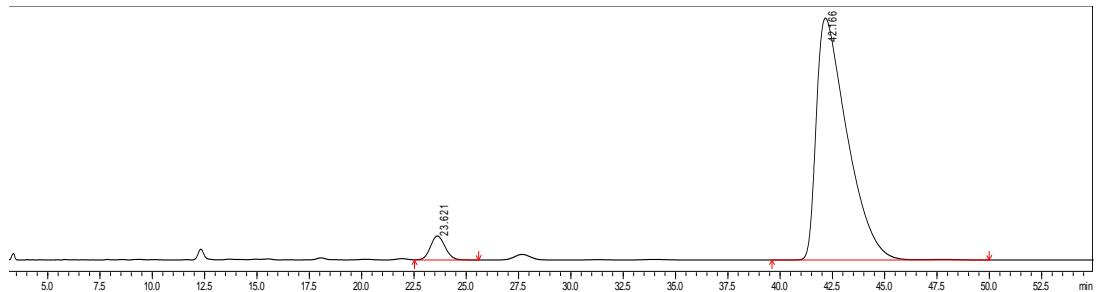
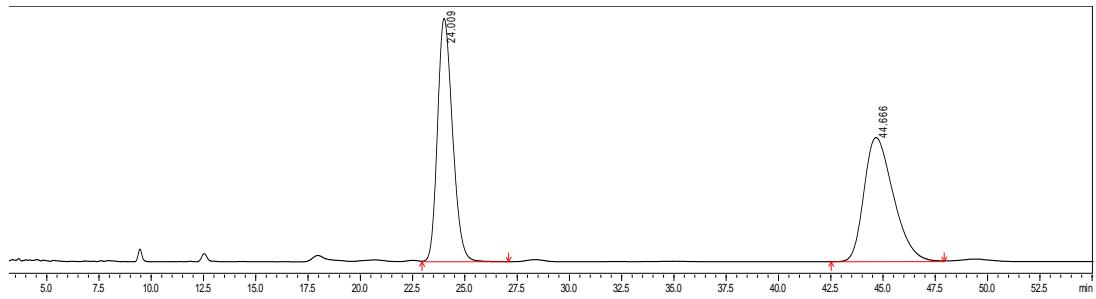
1H), 7.35–7.28 (m, 5H), 7.19 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 5.44 (d, J = 13.8 Hz, 1H), 4.26–4.19 (m, 1H), 3.35–3.24 (m, 2H), 2.42 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 189.4, 170.3, 165.4, 155.4, 152.3, 138.4, 137.8, 136.5, 133.8, 132.3, 131.9, 129.8, 129.4, 128.6, 128.5, 128.0, 127.2, 126.9, 126.8, 52.0, 43.1, 40.4, 21.1, 11.6; HRMS (ESI) m/z 530.1672 ($\text{M}+\text{Na}^+$), calc. for $\text{C}_{30}\text{H}_{25}\text{N}_3\text{O}_5\text{Na}$ 530.1686.

The ee was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM = 79/20/1; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 18.5 min (major) and 21.0 min (minor).



4l: Ar = 3-MeC₆H₄ Pale yellow solid, Mp 138.6–139.6 °C; 94% yield (49.8 mg); 91% ee; $[\alpha]_D^{23} = -35.4$ (c 0.74), ^1H NMR (400 MHz, CDCl_3) δ 7.79–7.78 (m, 1H), 7.66–7.64 (m, 2H), 7.50–7.48 (m, 2H), 7.44–7.40 (m, 1H), 7.36–7.28 (m, 5H), 7.18–7.02 (m, 4H), 5.45 (d, J = 13.8 Hz, 1H), 4.21 (ddd, J = 13.8, 9.1, 6.9 Hz, 1H), 3.36–3.24 (m, 2H), 2.42 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 189.2, 170.1, 165.3, 155.3, 152.0, 139.3, 138.7, 138.3, 133.7, 132.3, 131.8, 129.3, 128.9, 128.7, 128.5, 128.4, 127.9, 127.7, 127.2, 126.7, 123.8, 51.7, 43.3, 40.3, 21.3, 11.5; HRMS (ESI) m/z 530.1668 ($\text{M}+\text{Na}^+$), calc. for $\text{C}_{30}\text{H}_{25}\text{N}_3\text{O}_5\text{Na}$ 530.1686.

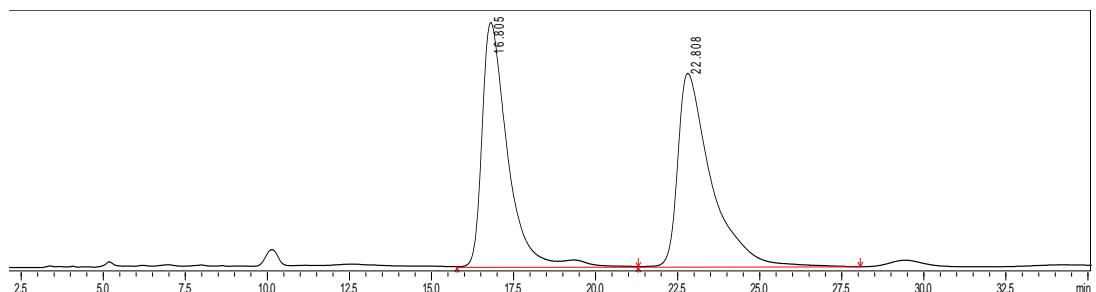
The ee was determined by HPLC analysis. CHIRALPAK IE (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM = 65/30/5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 23.6 min (minor) and 42.2 min (major).

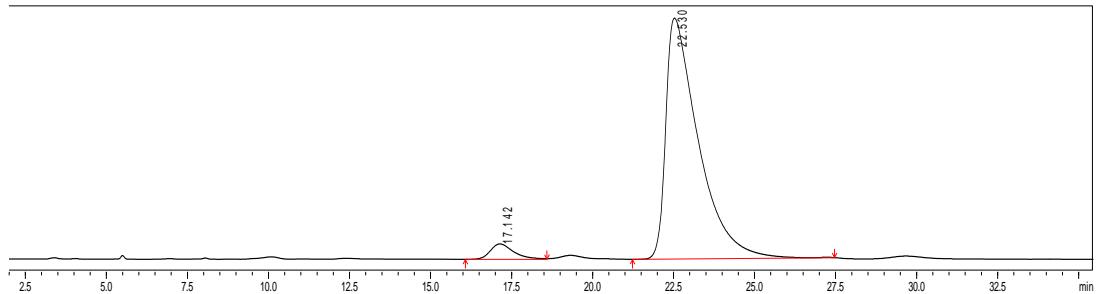


4m: Ar = 2-MeC₆H₄

Yellow solid, Mp 154.3–154.7 °C; 91% yield (48.2 mg); 91% ee; [α]
²³D = -25.4 (c 1.00), ¹H NMR (400 MHz, CDCl₃) δ 7.86 (s, 1H), 7.65–7.64 (m, 2H), 7.49–7.47 (m, 2H), 7.42–7.27 (m, 7H), 7.18–7.09 (m, 3H), 5.62 (d, J = 13.8 Hz, 1H), 4.61–4.55 (m, 1H), 3.29–3.14 (m, 2H), 2.43 (s, 3H), 2.41 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 189.6, 170.2, 165.2, 155.4, 151.9, 138.3, 137.6, 135.8, 133.6, 132.3, 131.8, 131.1, 129.4, 128.6, 128.5, 127.7, 127.5, 127.1, 126.7, 126.6, 125.2, 51.2, 39.8, 38.0, 19.5, 11.5; HRMS (ESI) m/z 530.1677 (M+Na⁺), calc. for C₃₀H₂₅N₃O₅Na 530.1686.

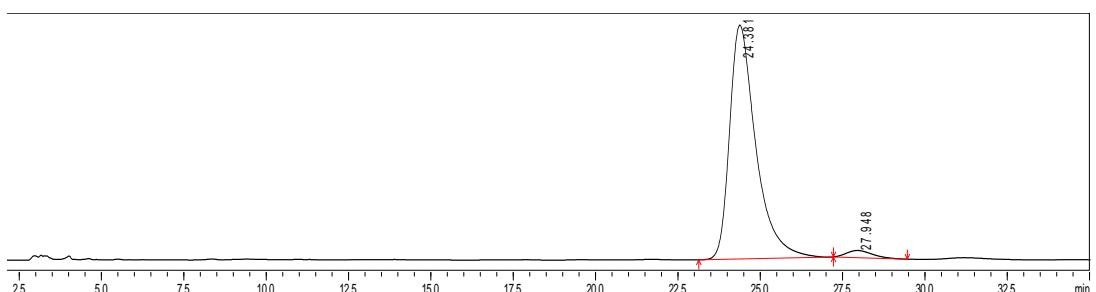
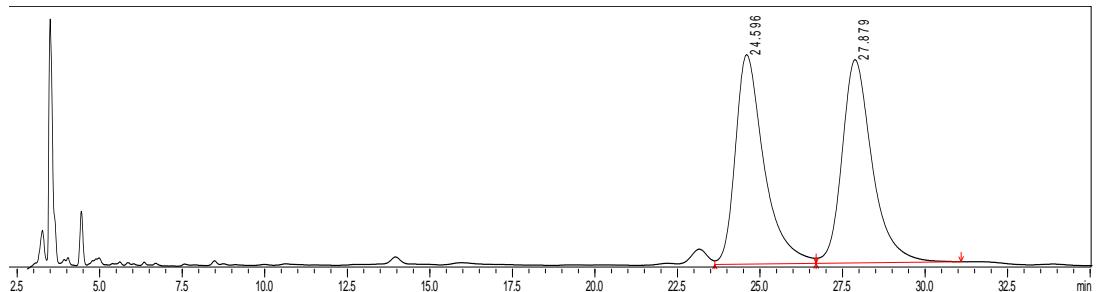
The ee was determined by HPLC analysis. CHIRALPAK INC (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM = 89.5/10/0.5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 17.1 min (minor) and 22.5 min (major).

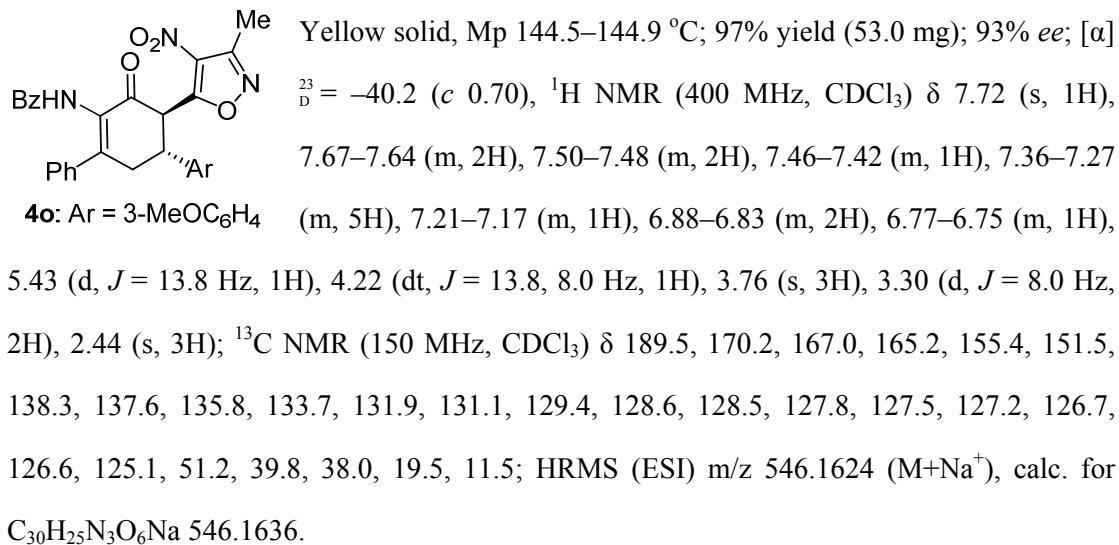




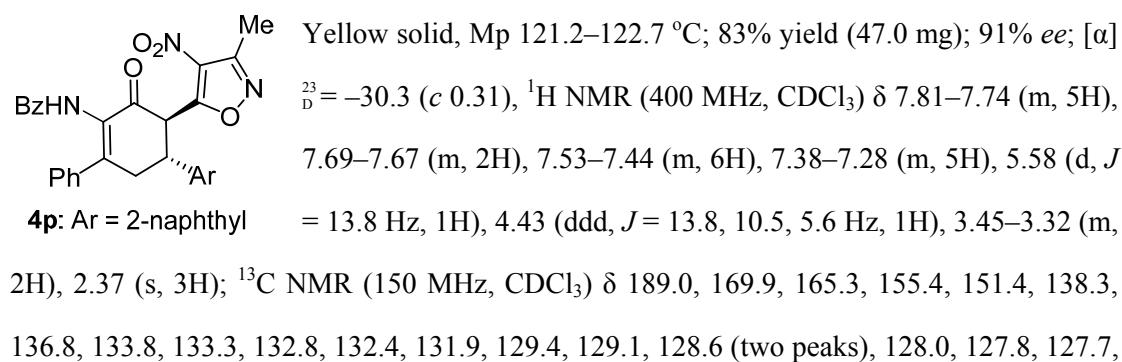
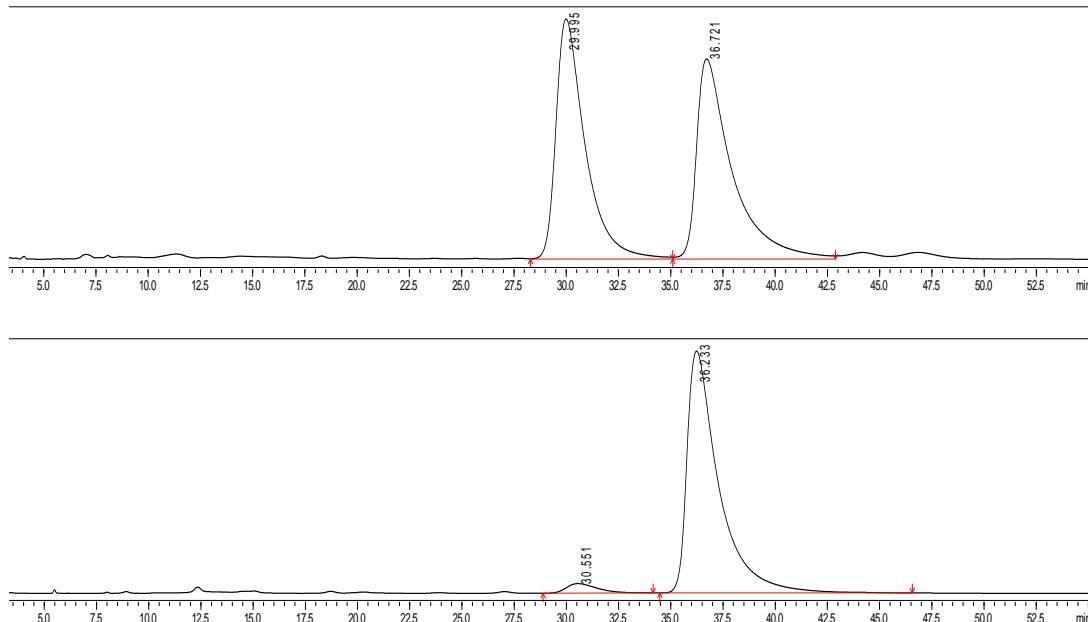
Pale yellow solid, Mp 224.5–225.7 °C; 92% yield (50.2 mg); 94% ee;
 $[\alpha]_D^{23} = -31.5$ (*c* 0.44), ^1H NMR (600 MHz, CDCl_3) δ 7.78 (s, 1H), 7.64 (d, *J* = 7.7 Hz, 2H), 7.48 (d, *J* = 7.7 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.32–7.27 (m, 5H), 7.22 (d, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 8.4 Hz, 2H), 5.41 (d, *J* = 13.6 Hz, 1H), 4.22–4.17 (m, 1H), 3.75 (s, 3H), 3.28 (d, *J* = 7.9 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 189.2, 170.2, 165.3, 159.0, 155.3, 152.0, 138.3, 133.7, 132.3, 131.8, 131.4, 129.3, 128.6, 128.5, 128.0, 127.2, 126.7, 114.4, 55.2, 52.1, 42.7, 40.4, 11.5; HRMS (ESI) *m/z* 546.1627 ($\text{M}+\text{Na}^+$), calc. for $\text{C}_{30}\text{H}_{25}\text{N}_3\text{O}_6\text{Na}$ 546.1636.

The ee was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM = 79/20/1; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 24.4 min (major) and 27.9 min (minor).



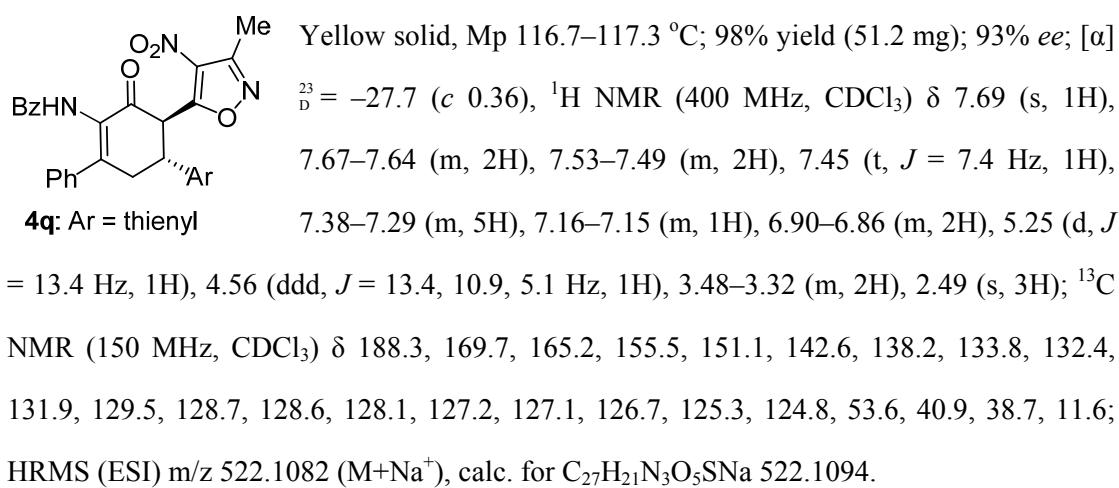
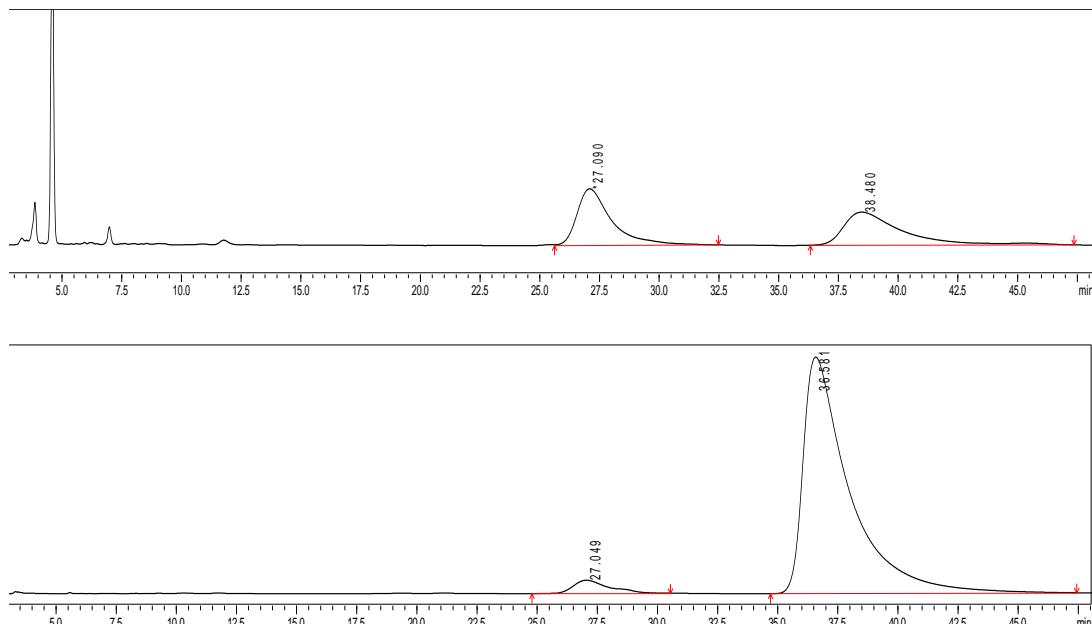


The ee was determined by HPLC analysis. CHIRALPAK INC (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM = 89.5/10/0.5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 30.6 min (minor) and 36.2 min (major).

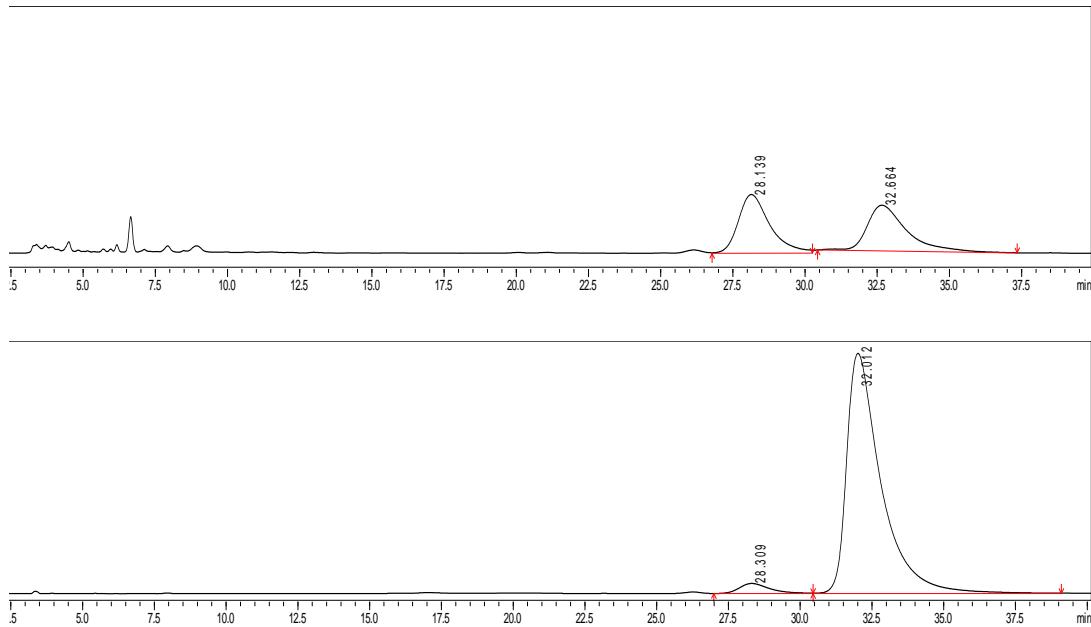


127.2, 126.7, 126.5, 126.3 (two peaks) 124.3, 51.6, 43.6, 40.3, 11.5; HRMS (ESI) m/z 566.1671 ($M+Na^+$), calc. for $C_{33}H_{25}N_3O_5Na$ 566.1686.

The ee was determined by HPLC analysis. CHIRALPAK INC (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM = 89.5/10/0.5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 27.0 min (minor) and 36.6 min (major).

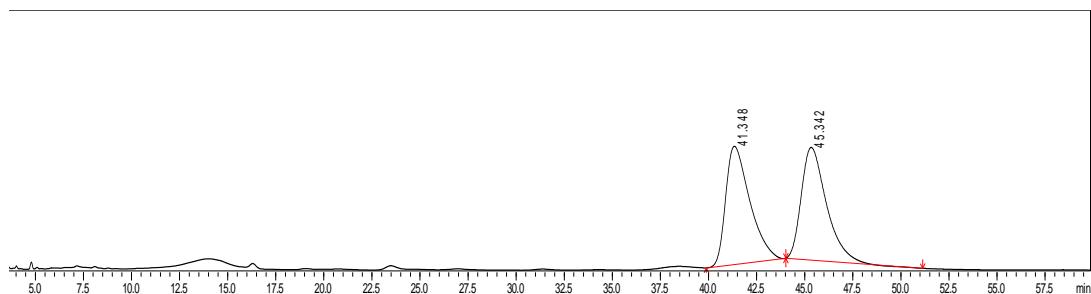


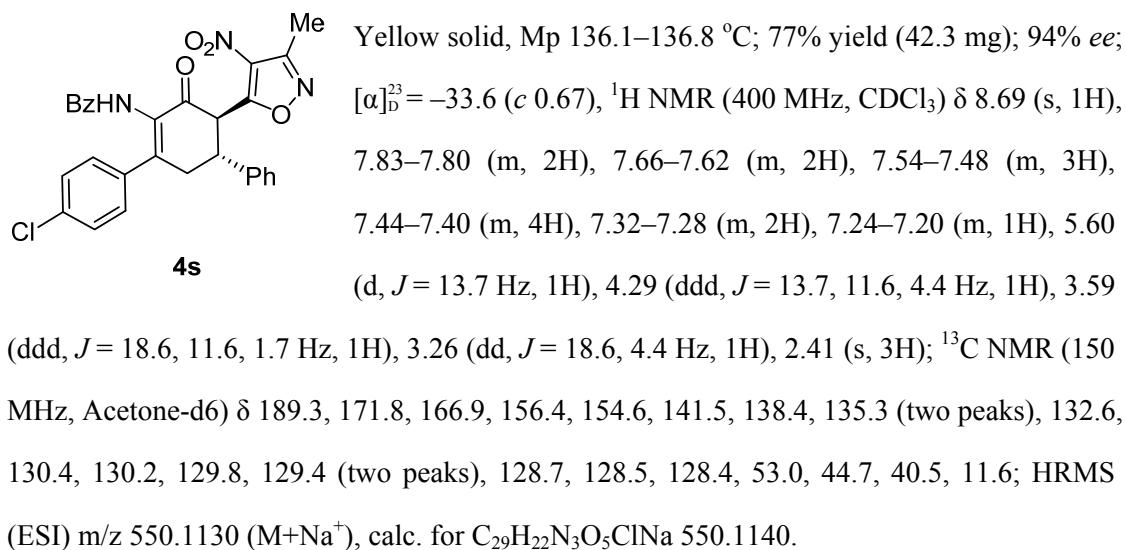
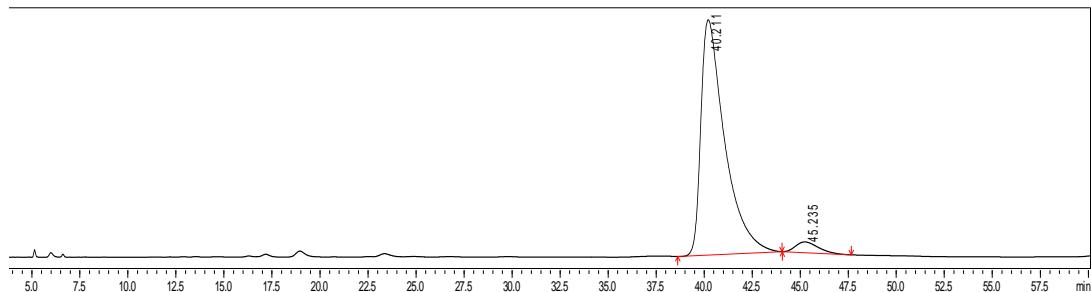
The ee was determined by HPLC analysis. CHIRALPAK INC (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM = 79.5/20/0.5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 28.3 min (major) and 32.0 min (minor).



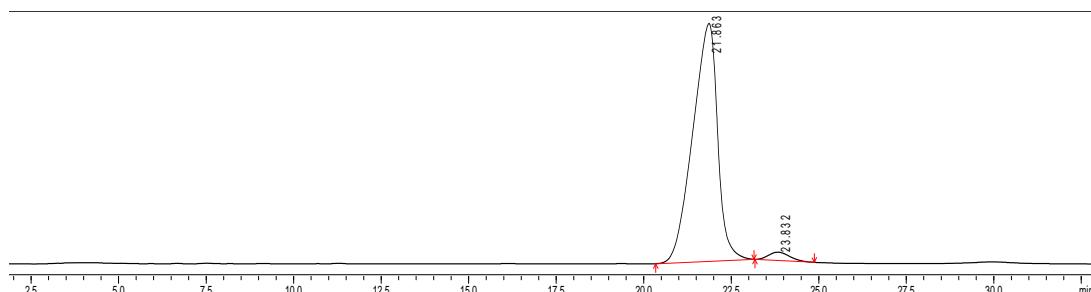
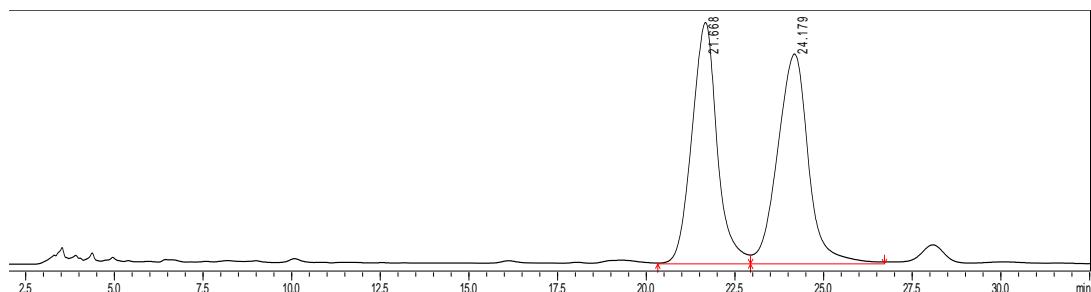
4r: Ar = furyl Yellow solid, Mp 135.4–136.2 °C; 83% yield (42.0 mg); 92% ee; $[\alpha]$
 $^{23}_{\text{D}} = -27.4$ (*c* 0.37), ^1H NMR (400 MHz, CDCl_3) δ 7.66–7.64 (m, 3H),
 7.51–7.44 (m, 3H), 7.39–7.28 (m, 6H), 6.22 (dd, *J* = 3.2, 1.9 Hz, 1H),
 6.10 (d, *J* = 3.2 Hz, 1H), 5.23 (d, *J* = 13.3 Hz, 1H), 4.37 (ddd, *J* =
 13.3, 11.4, 4.7 Hz, 1H), 3.46–3.28 (m, 2H), 2.52 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ
 188.2, 169.9, 165.2, 155.5, 152.3, 151.1, 142.4, 138.4, 133.8, 131.9, 129.4, 128.6 (two peaks),
 128.0, 127.2, 126.7, 110.3, 106.9, 50.7, 37.0, 36.8, 11.6; HRMS (ESI) *m/z* 506.1313 ($\text{M}+\text{Na}^+$),
 calc. for $\text{C}_{27}\text{H}_{21}\text{N}_3\text{O}_6\text{Na}$ 506.1323.

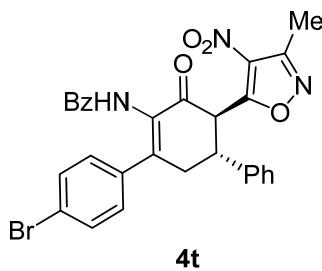
The ee was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm);
 Hexane/2-propanol/DCM = 89.5/10/0.5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time:
 40.2 min (major) and 45.2 min (minor).





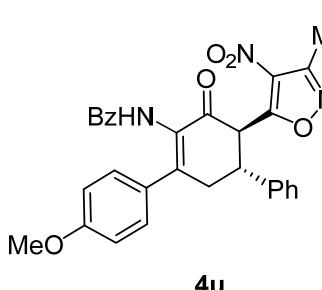
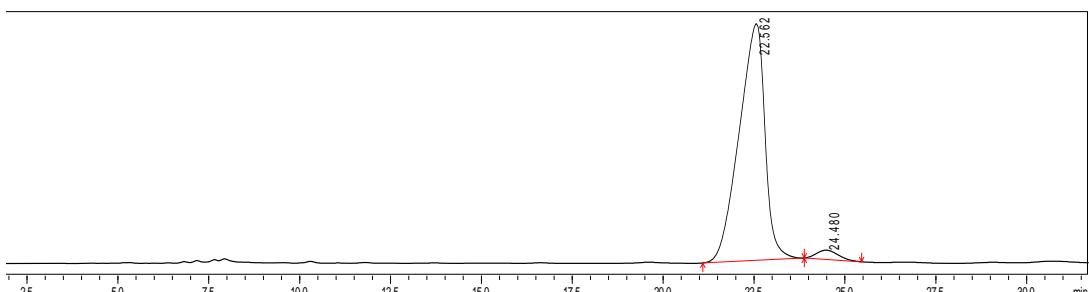
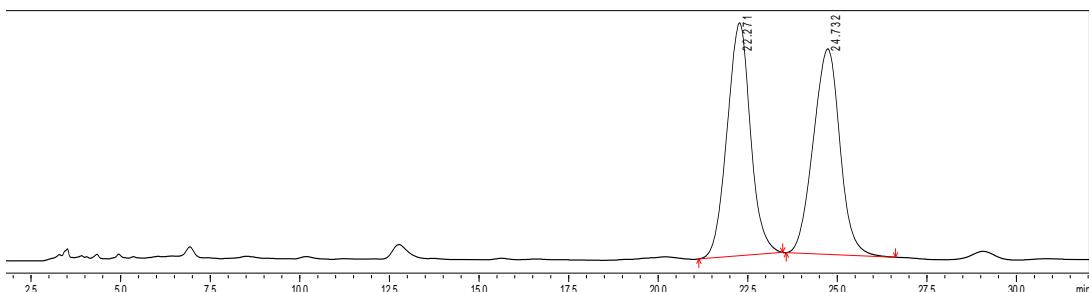
The ee was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM = 79/20/1; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 21.9 min (major) and 23.8 min (minor).





Pale yellow solid, Mp 145.9–146.6 °C; 76% yield (45.1 mg); 94% ee; $[\alpha]_D^{23} = -37.3$ (c 0.57), ^1H NMR (400 MHz, Acetone-d6) δ 8.69 (s, 1H), 7.83–7.80 (m, 2H), 7.59–7.48 (m, 8H), 7.44–7.40 (m, 2H), 7.31–7.28 (m, 2H), 7.24–7.20 (m, 1H), 5.60 (d, J = 13.7 Hz, 1H), 4.29 (ddd, J = 13.7, 11.6, 4.5 Hz, 1H), 3.59 (ddd, J = 18.6, 11.6, 1.8 Hz, 1H), 3.25 (dd, J = 18.6, 4.5 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (150 MHz, CDCl₃) δ 189.2, 171.6, 166.8, 156.3, 154.4, 141.3, 138.6, 135.2, 133.0, 132.2, 130.3, 130.2, 129.6, 129.3, 129.2, 128.3 (two peaks), 128.2, 123.5, 52.9, 44.5, 40.3, 11.4; HRMS (ESI) m/z 594.0616 (M+Na⁺), calc. for C₂₉H₂₂N₃O₅BrNa 594.0635.

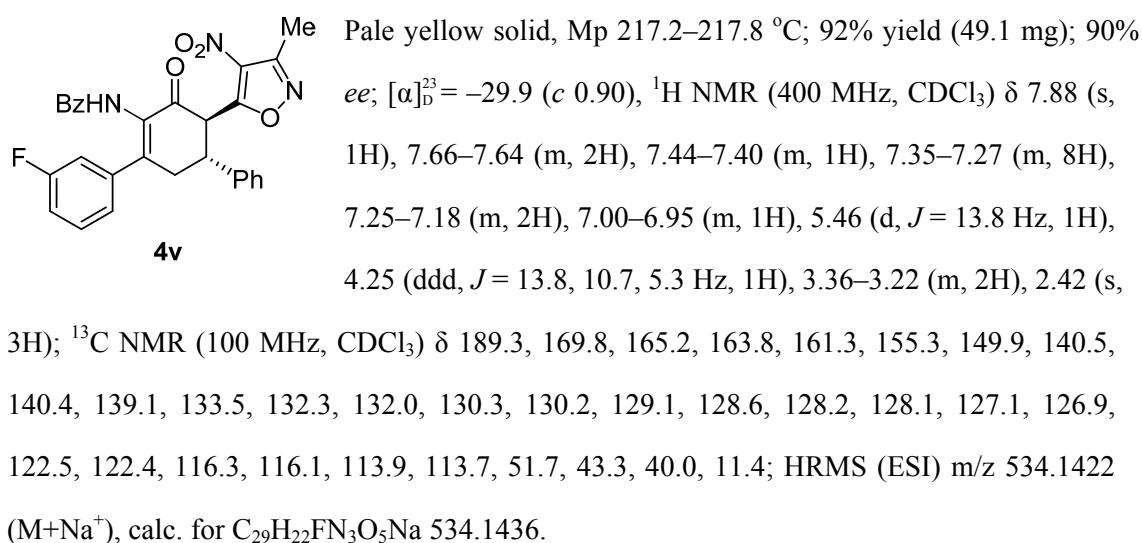
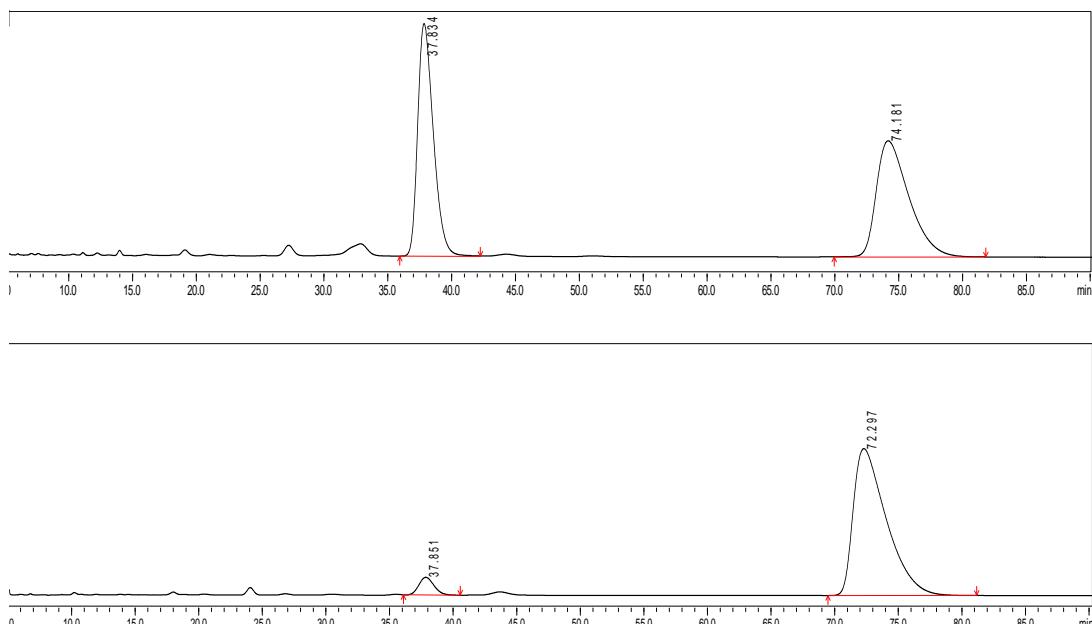
The ee was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM = 79/20/1; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 22.6 min (major) and 24.5 min (minor).



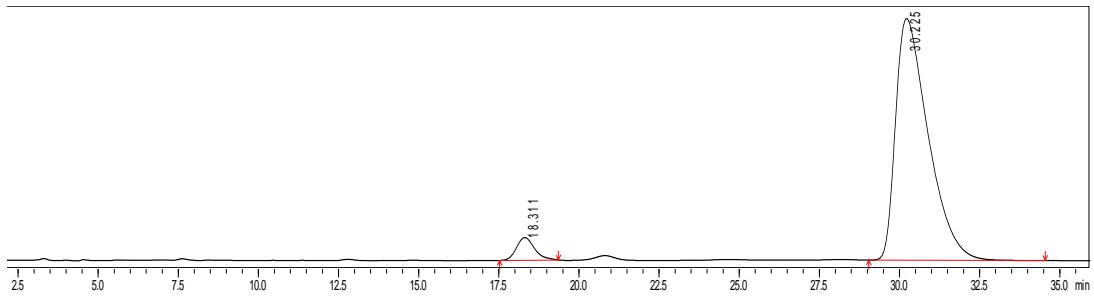
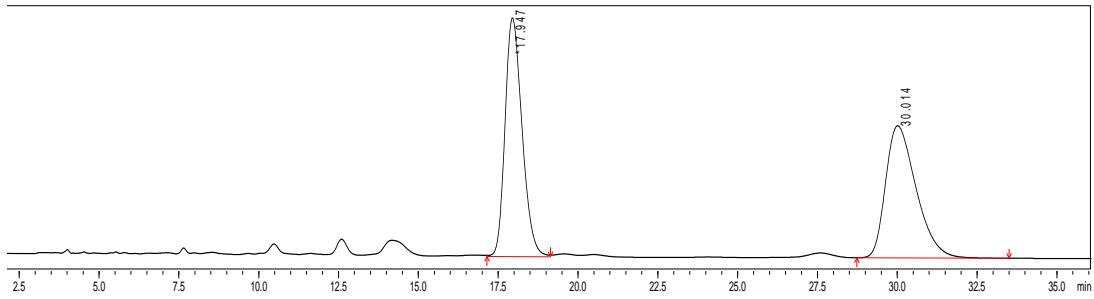
Yellow solid, Mp 165.8–166.0 °C; 92% yield (50.2 mg); 90% ee; $[\alpha]_D^{23} = -58.4$ (c 0.87), ^1H NMR (400 MHz, CDCl₃) δ 7.88–7.86 (m, 1H), 7.69–7.67 (m, 2H), 7.49–7.46 (m, 2H), 7.43–7.39 (m, 1H), 7.36–7.28 (m, 6H), 7.24–7.20 (m, 1H), 6.85–6.82 (m, 2H), 5.45 (d, J = 13.8 Hz, 1H), 4.22 (ddd, J = 13.8, 10.7, 5.3 Hz, 1H), 3.75 (s, 3H), 3.36–3.22 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, CDCl₃) δ 189.1, 170.2, 165.3, 160.4, 155.2, 151.7, 139.5, 133.7, 132.2, 131.8, 130.2, 129.0,

128.5, 128.4, 127.9, 127.2, 126.9, 114.0, 55.1, 51.6, 43.11, 40.0, 11.4; HRMS (ESI) m/z 546.1626 ($M+Na^+$), calc. for $C_{30}H_{25}N_3O_6Na$ 546.1636.

The ee was determined by HPLC analysis. CHIRALPAK IE (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM = 65/30/5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 37.8 min (minor) and 72.3 min (major).



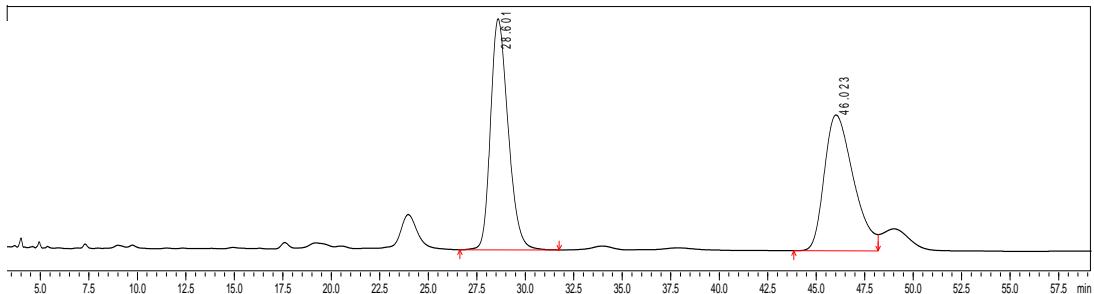
The ee was determined by HPLC analysis. CHIRALPAK IE (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM = 65/30/5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 18.3 min (minor) and 30.2 min (major).

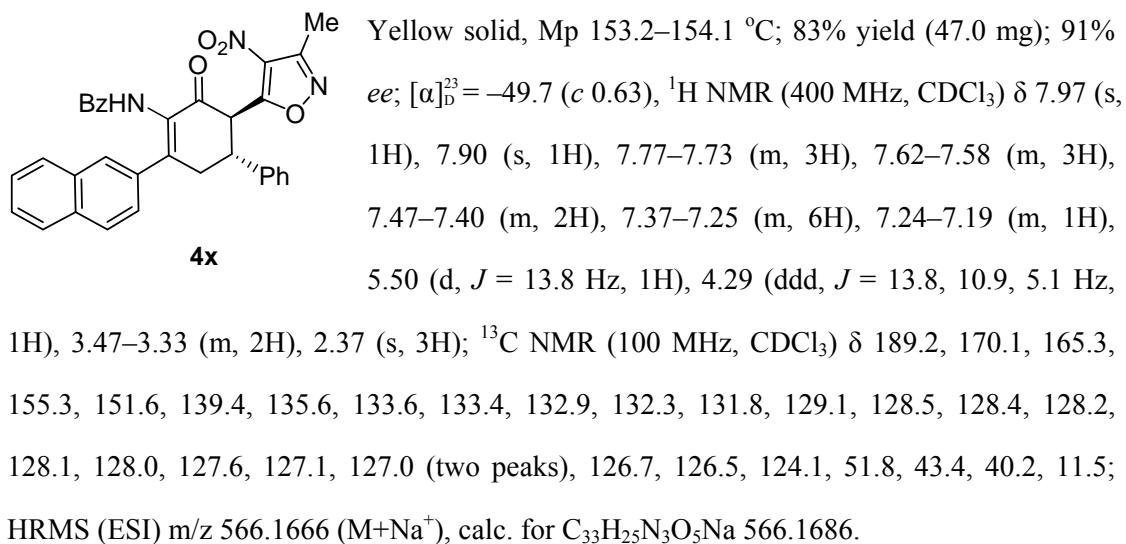
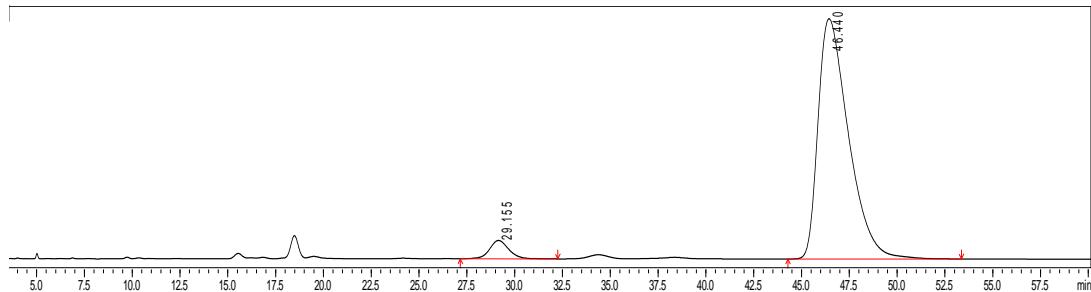


4w

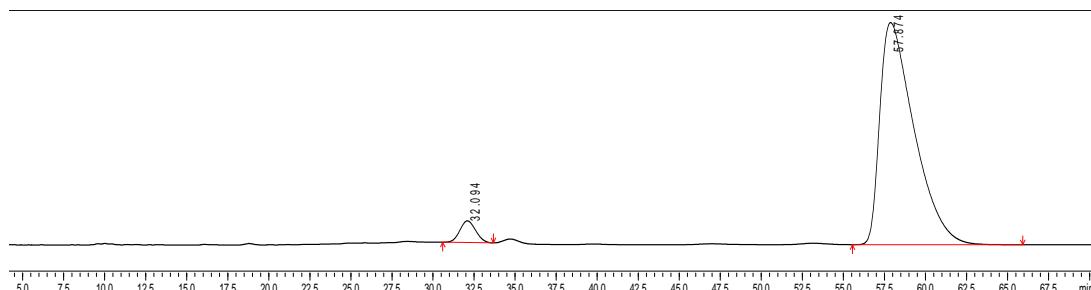
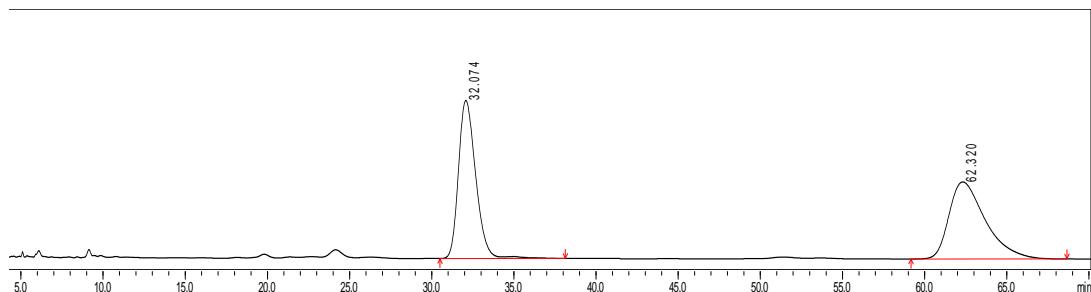
Pale yellow solid, Mp 222.1–222.4 °C; 99% yield (54.1 mg); 91% ee; $[\alpha]_D^{23} = -41.7$ (c 0.99), ^1H NMR (400 MHz, CDCl_3) δ 7.79 (s, 1H), 7.66–7.64 (m, 2H), 7.42–7.38 (m, 1H), 7.31–7.19 (m, 8H), 7.07–7.02 (m, 2H), 6.83–6.80 (m, 1H), 5.46 (d, $J = 13.8$ Hz, 1H), 4.24 (ddd, $J = 13.8, 9.9, 6.2$ Hz, 1H), 3.68 (s, 3H), 3.36–3.25 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 189.1, 170.0, 165.5, 159.4, 155.3, 152.1, 139.4 (two peaks), 133.6, 132.2, 131.8, 129.6, 129.0, 128.5, 128.0 (two peaks), 127.2, 126.9, 119.1, 115.2, 112.2, 55.1, 51.7, 43.3, 40.2, 11.4; HRMS (ESI) m/z 546.1620 ($\text{M}+\text{Na}^+$), calc. for $\text{C}_{30}\text{H}_{25}\text{N}_3\text{O}_6\text{Na}$ 546.1636.

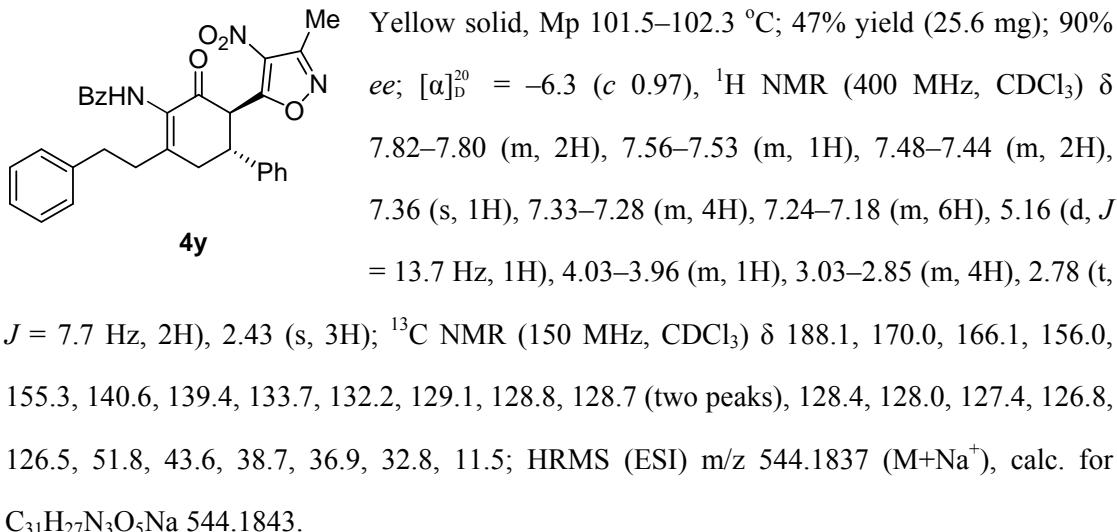
The ee was determined by HPLC analysis. CHIRALPAK IE (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM = 65/30/5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 29.2 min (minor) and 46.4 min (major).



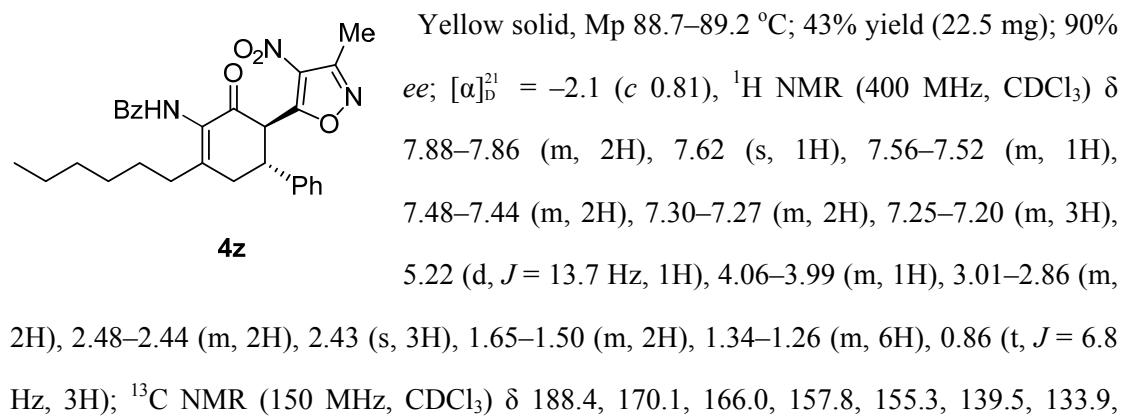
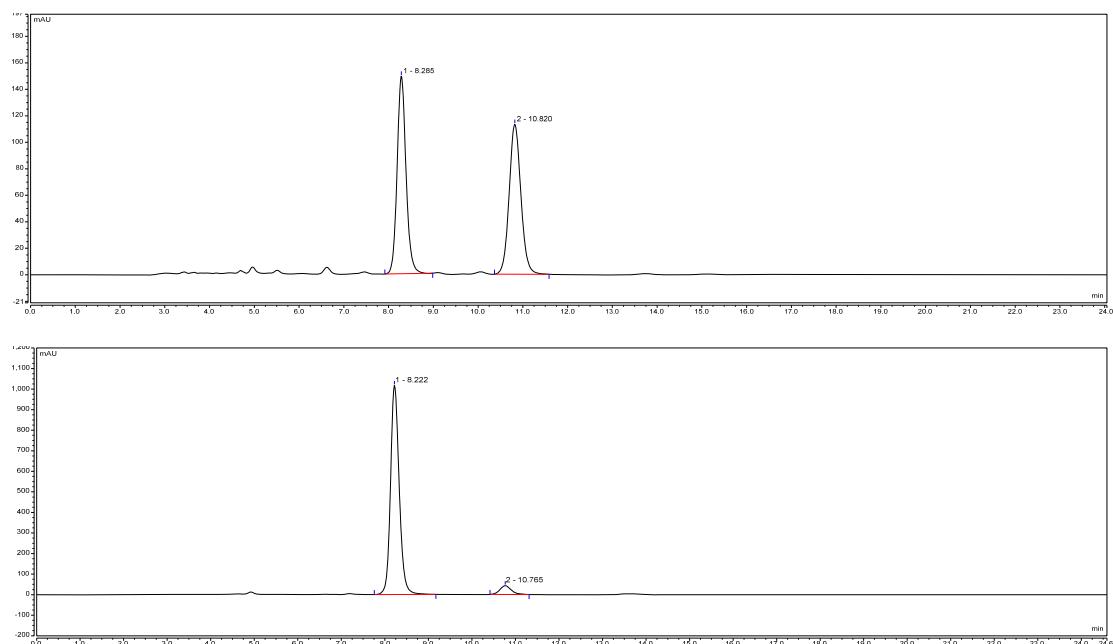


The ee was determined by HPLC analysis. CHIRALPAK IE (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM = 65/30/5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 32.1 min (minor) and 57.9 min (major).



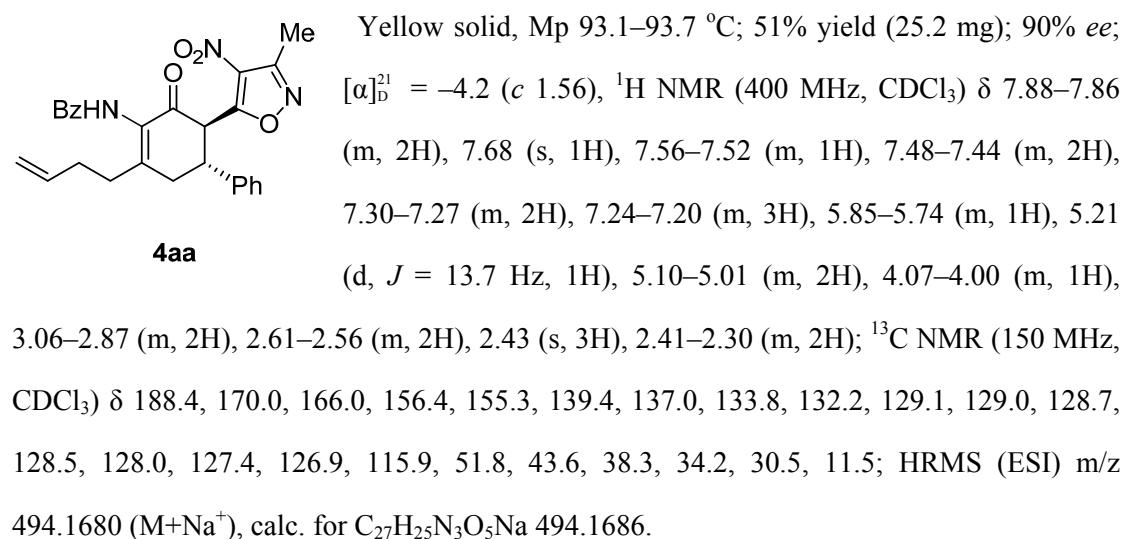
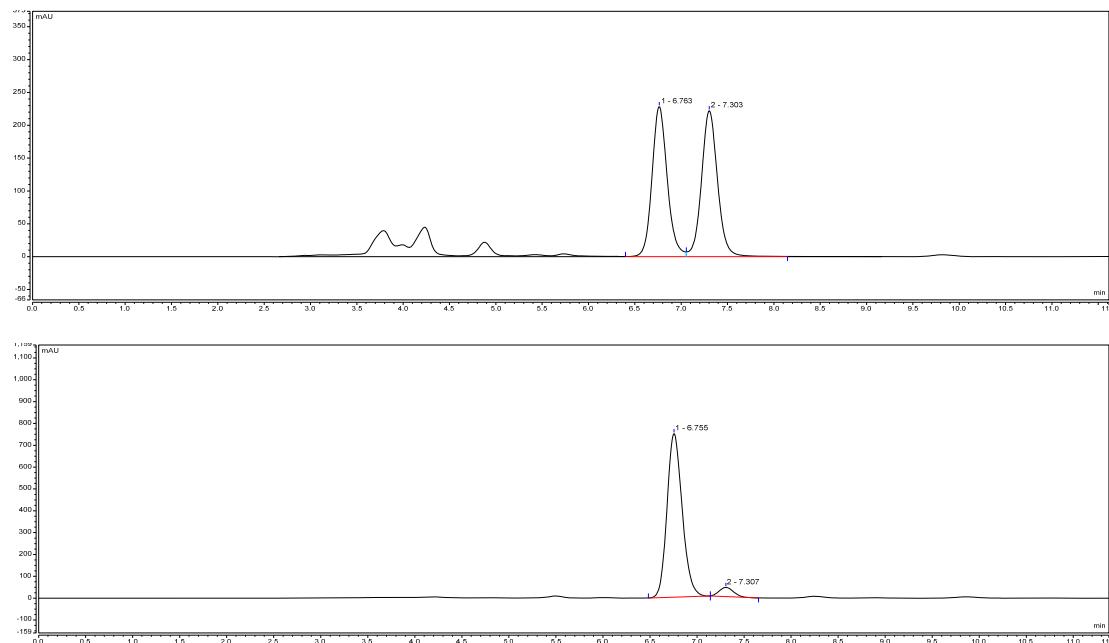


The ee was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM = 65/30/5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 8.2 min (major) and 10.8 min (minor).

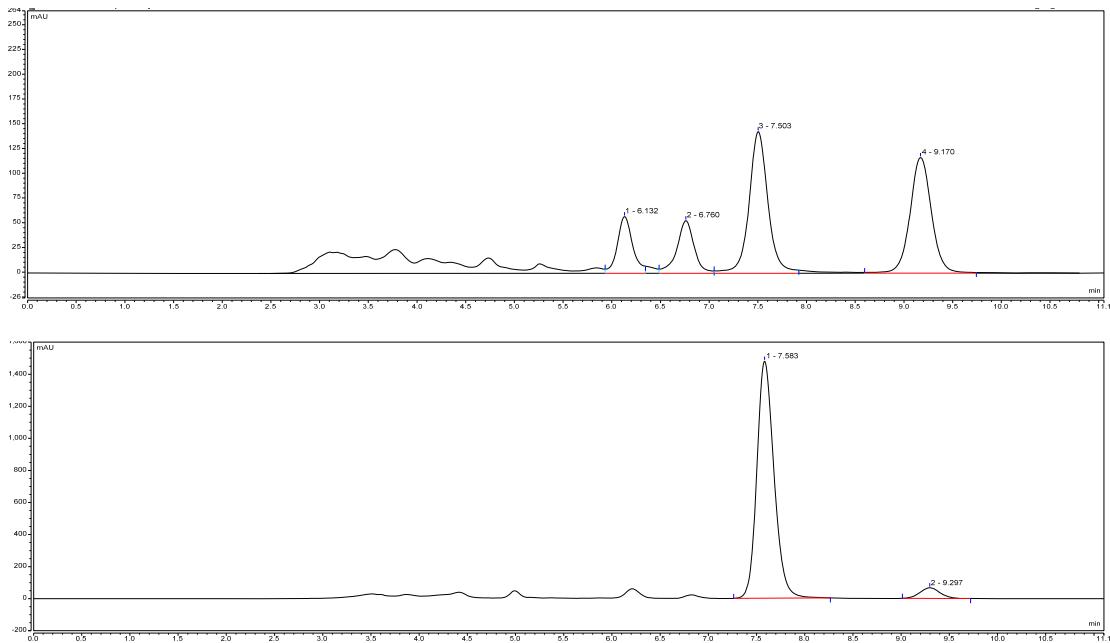


132.1, 129.1, 128.7, 128.0 (two peaks), 127.4, 126.9, 51.8, 43.7, 38.4, 35.1, 31.5, 29.5, 26.6, 22.4, 14.0, 11.5; HRMS (ESI) m/z 524.2160 ($M+Na^+$), calc. for $C_{29}H_{31}N_3O_5Na$ 524.2156.

The ee was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM = 65/30/5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 6.8 min (major) and 7.3 min (minor).

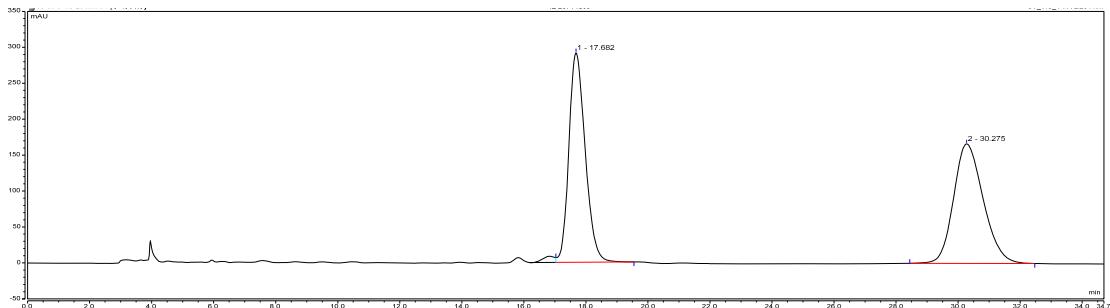


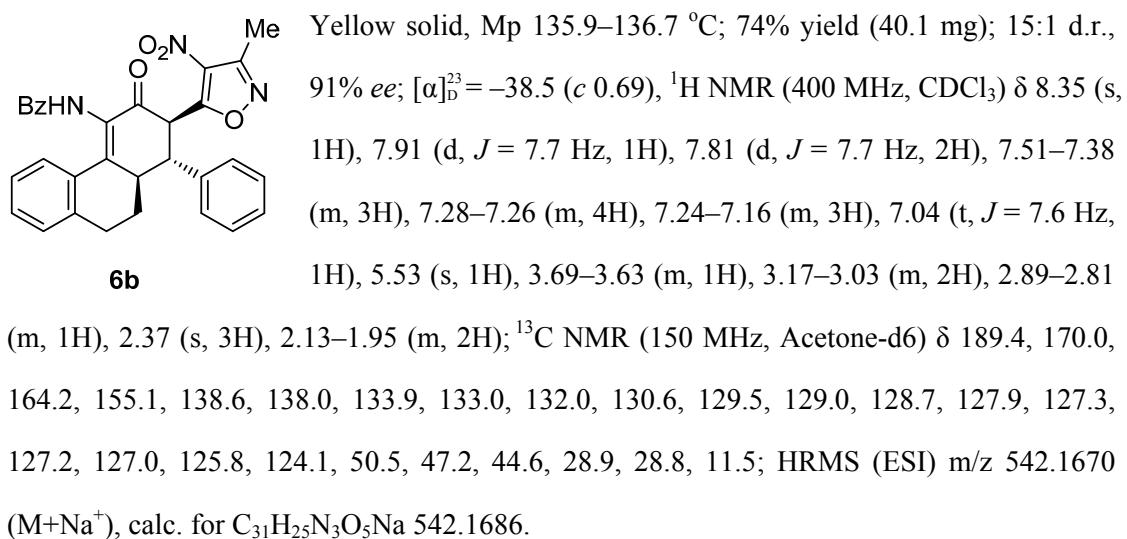
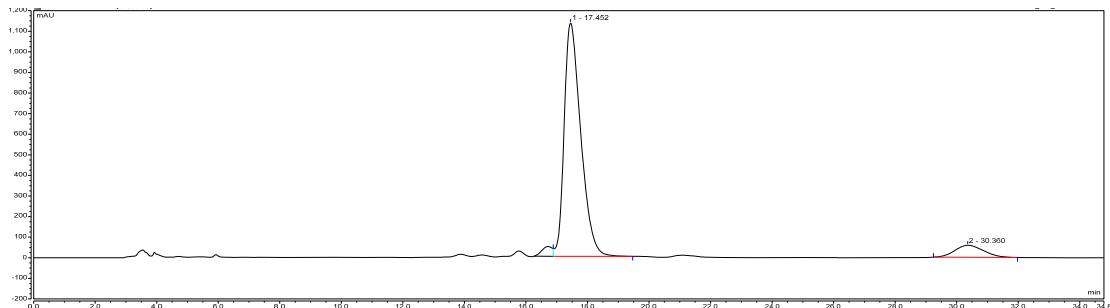
The ee was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM = 65/30/5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 7.6 min (major) and 9.3 min (minor).



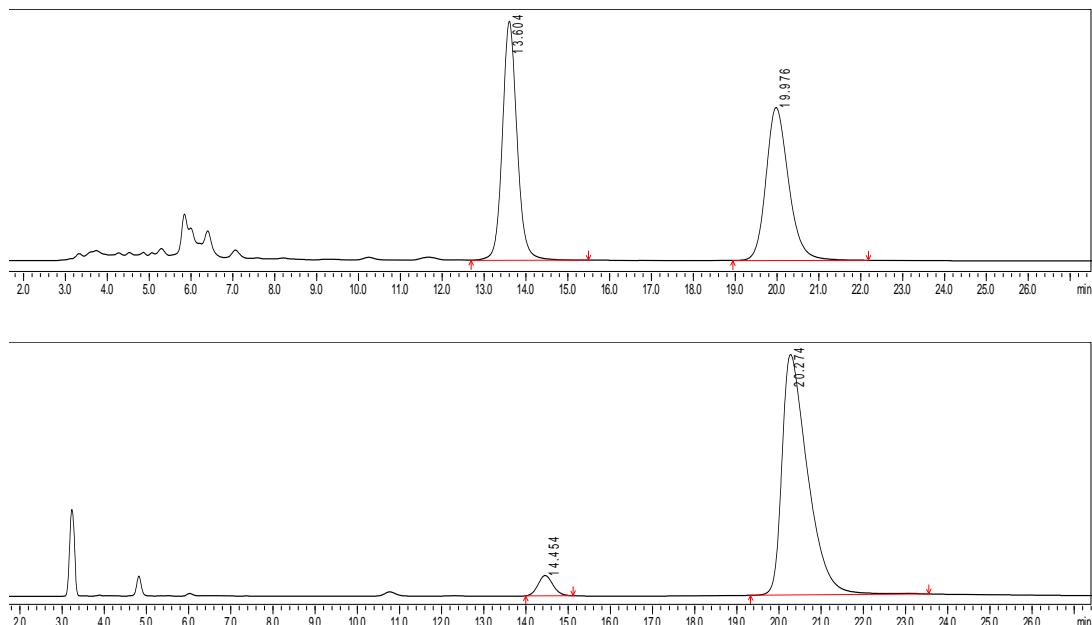
Yellow solid, Mp 205.2–205.8 °C; 35% yield (19.1 mg); >19:1 d.r., 84% ee; $[\alpha]_D^{17} = 75.4$ (*c* 0.32), ^1H NMR (400 MHz, CDCl_3) δ 7.52–7.50 (m, 2H), 7.35 (t, J = 7.4 Hz, 1H), 7.23 (d, J = 7.4 Hz, 2H), 7.26–7.22 (m, 4H), 7.16–7.07 (m, 6H), 5.39 (d, J = 13.7 Hz, 1H), 3.75 (dd, J = 13.7, 10.2 Hz, 1H), 3.43–3.39 (m, 1H), 2.32 (s, 3H), 2.22 (s, 3H), 0.76 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 188.1, 170.1, 166.3, 159.9, 155.2, 138.7, 138.3, 133.8, 133.7, 132.0, 131.7, 129.1, 129.0, 128.9, 128.4, 128.0, 127.6, 127.2, 126.4, 52.4, 51.1, 41.4, 21.2, 18.2, 11.5; HRMS (ESI) m/z 544.1836 ($\text{M}+\text{Na}^+$), calc. for $\text{C}_{31}\text{H}_{27}\text{N}_3\text{O}_5\text{Na}$ 544.1843.

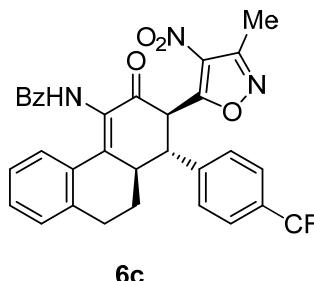
The ee was determined by HPLC analysis. CHIRALPAK IE (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM = 65/30/5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 17.5 min (major) and 30.4 min (minor).





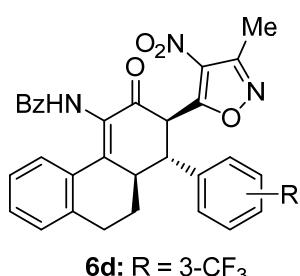
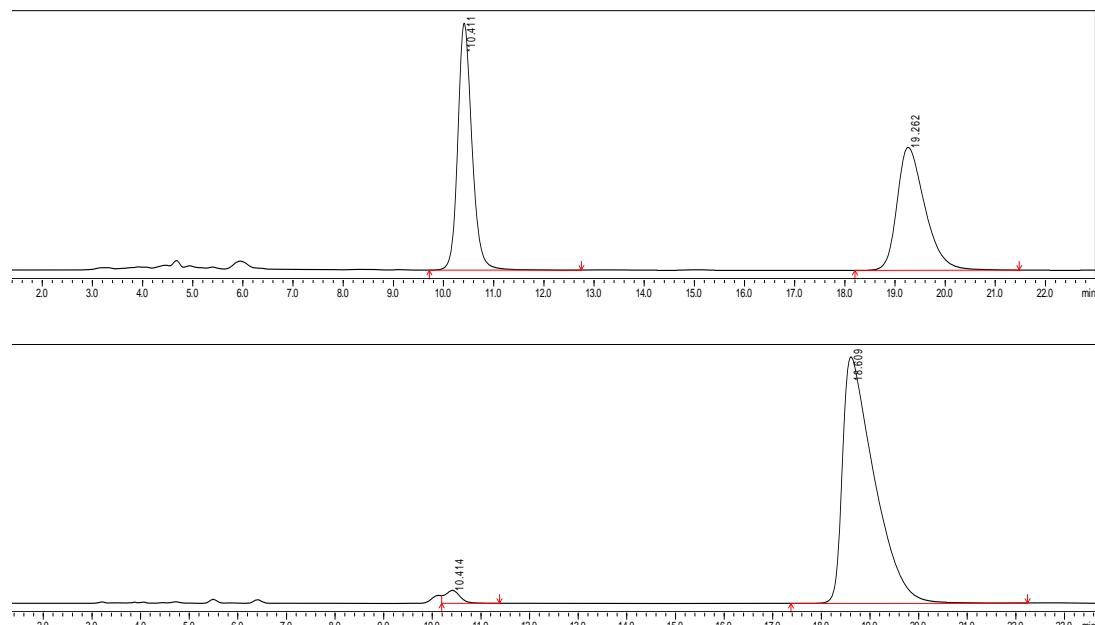
The ee was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM/DCM = 65/30/5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 14.4 min (minor) and 20.3 min (major).





Yellow solid, Mp 198.5–199.5 °C; 98% yield (59.8 mg); >19:1 d.r., 95% ee; $[\alpha]_D^{23} = -39.5$ (c 0.81), ^1H NMR (400 MHz, CDCl_3) δ 8.33 (s, 1H), 7.90 (d, J = 7.8 Hz, 1H), 7.80 (d, J = 7.8 Hz, 2H), 7.55–7.38 (m, 7H), 7.27–7.23 (m, 1H), 7.18 (d, J = 7.6 Hz, 1H), 7.05 (t, J = 7.6 Hz, 1H), 5.51 (s, 1H), 3.78–3.72 (m, 1H), 3.19–3.05 (m, 2H), 2.92–2.83 (m, 1H), 2.38 (s, 3H), 2.05–2.01 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 188.7, 169.3, 164.4, 155.3, 148.1, 139.3, 138.4, 133.8, 132.9, 132.4, 132.1, 131.9, 131.6, 131.2, 130.9, 130.7, 129.6, 129.5, 128.7, 127.7, 127.3, 127.1, 126.0, 125.0 (two peaks), 124.7, 124.3, 122.3, 119.6, 50.4, 47.1, 44.4, 28.9, 28.8, 11.4; HRMS (ESI) m/z 610.1561 ($M+\text{Na}^+$), calc. for $\text{C}_{32}\text{H}_{24}\text{F}_3\text{N}_3\text{O}_5\text{Na}$ 610.1560.

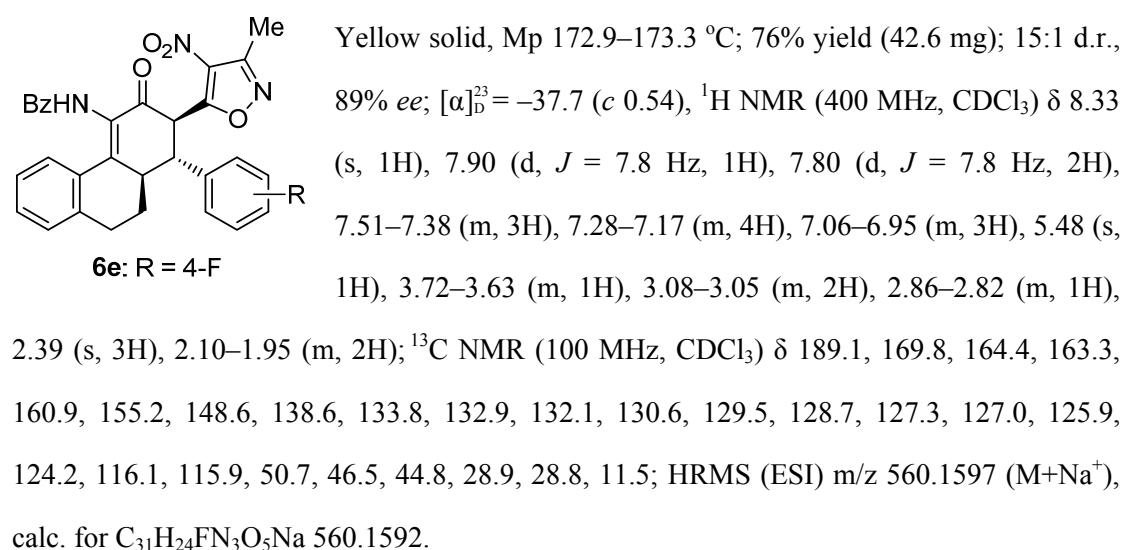
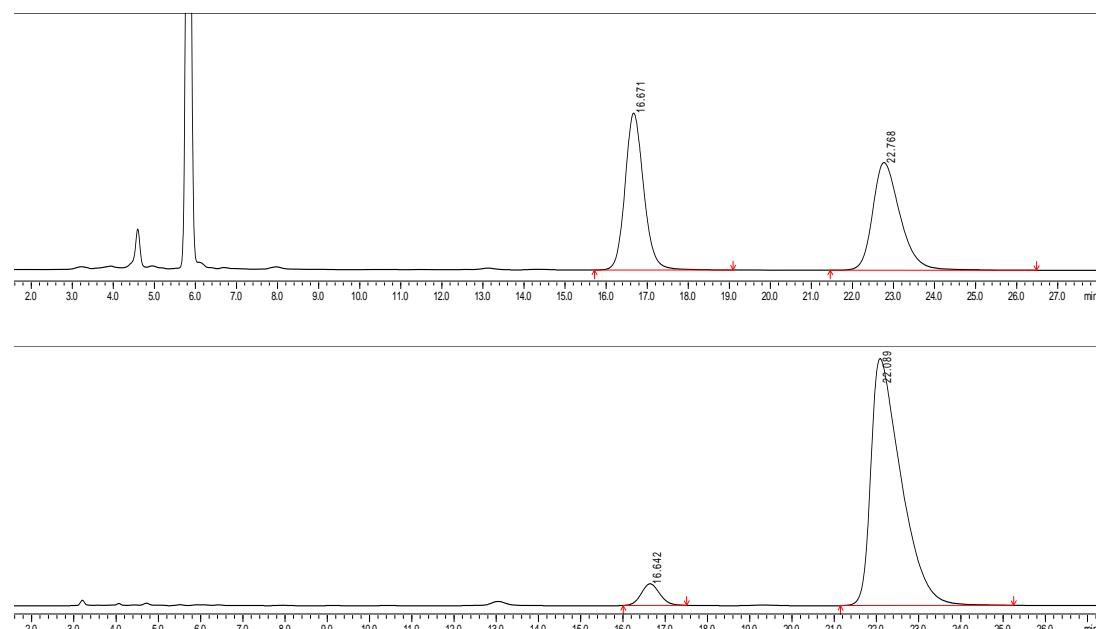
The ee was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM/DCM = 65/30/5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 10.4 min (minor) and 18.6 min (major).



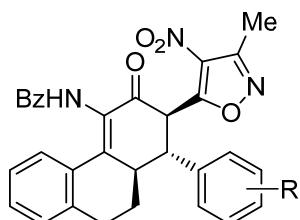
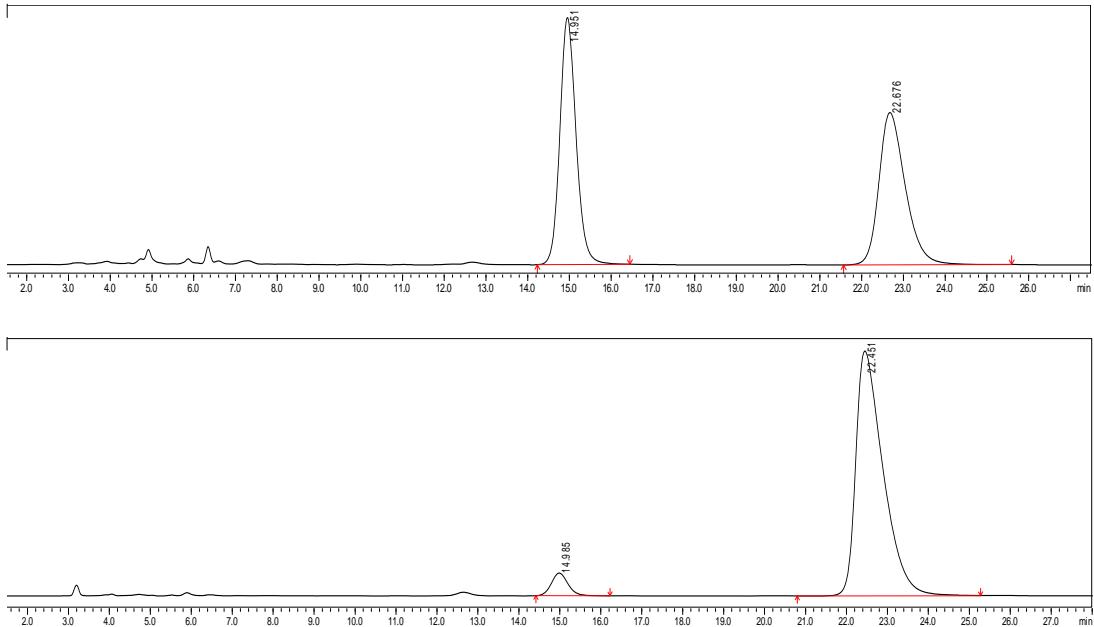
Yellow solid, Mp 191.9–192.6 °C; 96% yield (58.6 mg); 19:1 d.r., 90% ee; $[\alpha]_D^{23} = -38.2$ (c 0.60), ^1H NMR (400 MHz, CDCl_3) δ 8.37 (s, 1H), 7.89 (d, J = 7.8 Hz, 1H), 7.79 (d, J = 7.8 Hz, 1H), 7.58–7.56 (m, 2H), 7.49–7.41 (m, 2H), 7.37 (t, J = 7.6 Hz, 3H), 7.27–7.23 (m, 2H), 7.18 (d, J = 7.6 Hz, 1H), 7.03 (t, J = 7.5 Hz, 1H), 5.57 (s, 1H), 3.79–3.04 (m, 1H), 3.17–3.04 (m, 2H), 2.90–2.82 (m, 1H), 2.37 (s, 3H),

2.04–2.01 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 188.9, 169.4, 164.4, 155.3, 148.8, 142.3, 138.5, 133.7, 132.8, 132.1, 130.8, 130.4, 130.1, 129.8, 129.5, 128.7, 128.5, 127.3, 127.2, 127.0, 126.1, 126.0, 125.9, 125.1, 124.2, 122.4, 50.2, 46.8, 44.6, 28.8, 28.8, 11.5; HRMS (ESI) m/z 610.1551 ($\text{M}+\text{Na}^+$), calc. for $\text{C}_{32}\text{H}_{24}\text{F}_3\text{N}_3\text{O}_5\text{Na}$ 610.1560.

The ee was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM/DCM = 65/30/5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 16.6 min (minor) and 22.1 min (major).

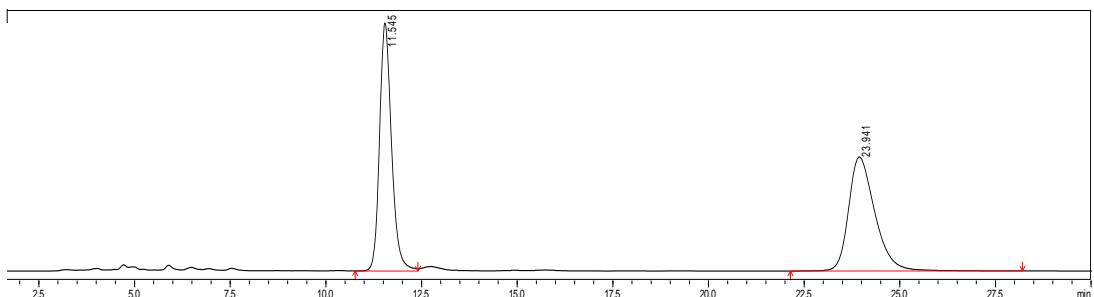


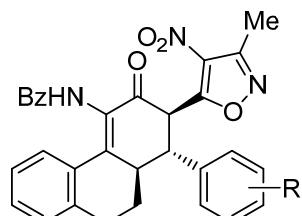
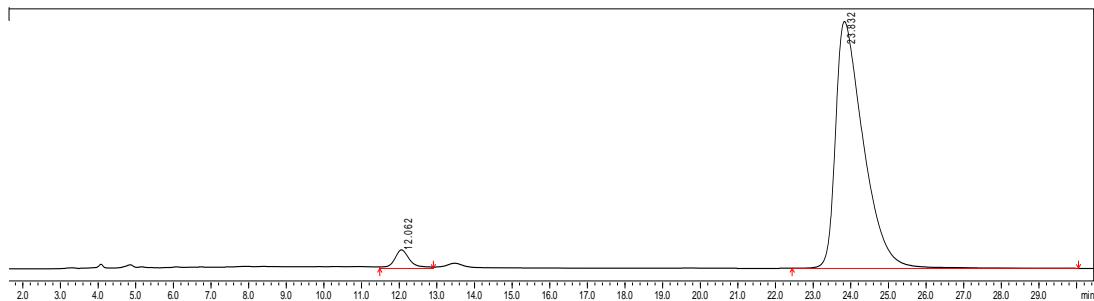
The ee was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM/DCM = 89.5/10/0.5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 15.0 min (minor) and 22.4 min (major).



Yellow solid, Mp 186.1–187.0 °C; 75% yield (43.3 mg); 19:1 d.r., 92% ee; $[\alpha]_{\text{D}}^{23} = -45.8$ (c 0.71), ^1H NMR (400 MHz, CDCl_3) δ 8.40 (s, 1H), 7.86 (d, $J = 7.8$ Hz, 1H), 7.76 (d, $J = 7.8$ Hz, 2H), 7.43 (t, $J = 7.0$ Hz, 1H), 7.31 (t, $J = 7.0$ Hz, 2H), 7.25–7.22 (m, 1H), 7.18–6.99 (m, 5H), 5.51 (s, 1H), 3.67–3.62 (m, 1H), 3.09–3.04 (m, 2H), 2.91–2.83 (m, 1H), 2.35 (s, 3H), 2.10–1.95 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 189.0, 169.5, 164.4, 155.3, 151.6, 151.5, 151.0, 150.9, 149.1, 149.0, 148.6, 148.4, 138.6, 135.3, 133.6, 132.7, 132.4, 132.0, 130.7, 129.5, 128.6, 127.3, 127.2, 127.0, 125.9, 124.2, 118.0, 117.8, 116.8, 50.5, 46.2, 44.6, 28.8, 11.4; HRMS (ESI) m/z 578.1482 ($\text{M}+\text{Na}^+$), calc. for $\text{C}_{31}\text{H}_{23}\text{F}_2\text{N}_3\text{O}_5\text{Na}$ 578.1482.

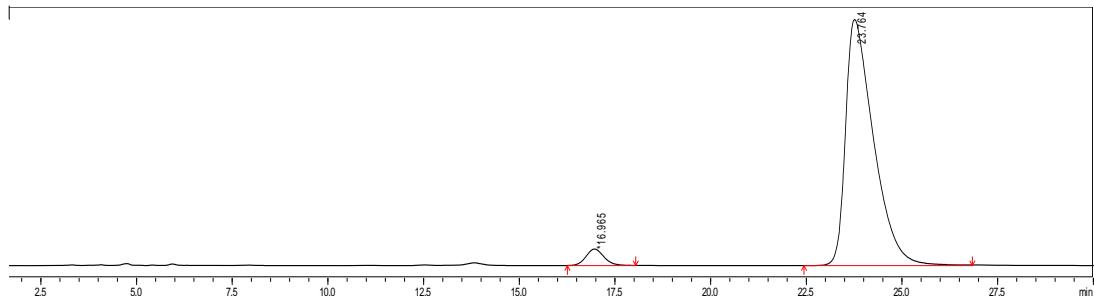
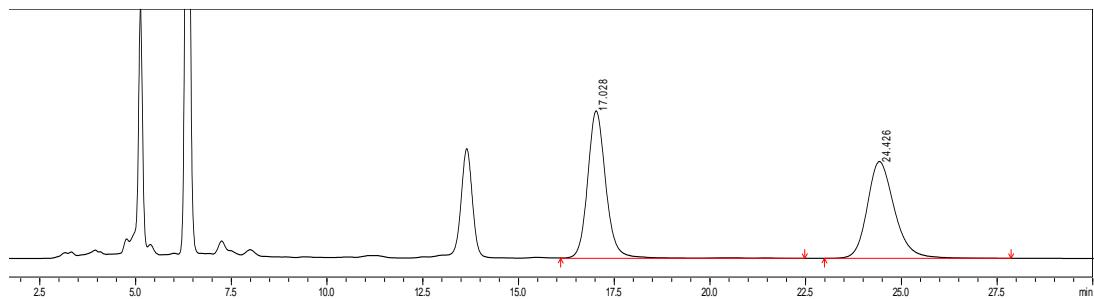
The ee was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM/DCM = 65/30/5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 12.1 min (minor) and 23.8 min (major).

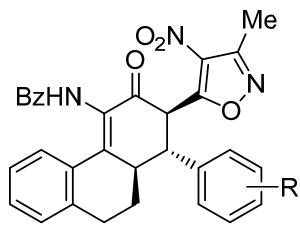




Yellow solid, Mp 198.5–199.5 °C; 60% yield (34.6 mg); >19:1 d.r., 92% ee; $[\alpha]_D^{23} = -44.1$ (*c* 0.45), ^1H NMR (400 MHz, CDCl_3) δ 8.37 (s, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.28–7.16 (m, 5H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 5.53 (s, 1H), 3.73–3.63 (m, 1H), 3.12–3.03 (m, 2H), 2.90–2.81 (m, 1H), 2.37 (s, 3H), 2.10–1.95 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 189.1, 169.7, 164.4, 155.3, 148.9, 138.6, 136.7, 133.8, 132.8, 132.0, 130.7, 129.5, 129.4, 129.2, 128.6, 127.3, 127.2, 127.0, 125.9, 124.2, 50.4, 46.5, 44.7, 28.8, 28.8, 11.5; HRMS (ESI) *m/z* 576.1277 ($\text{M}+\text{Na}^+$), calc. for $\text{C}_{31}\text{H}_{24}\text{ClN}_3\text{O}_5\text{Na}$ 576.1297.

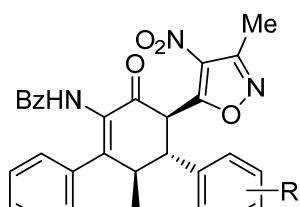
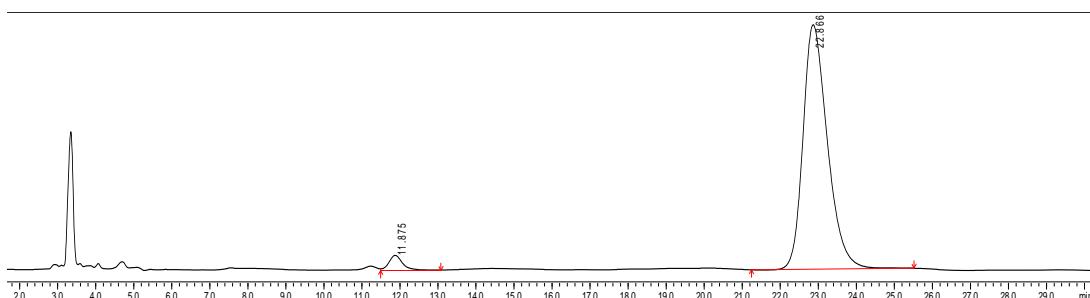
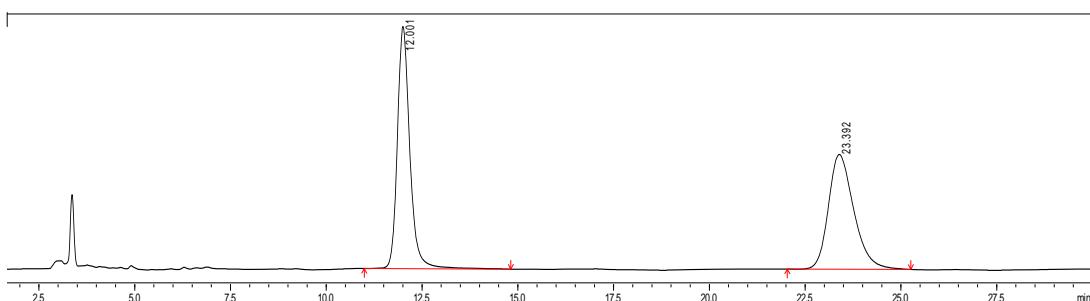
The ee was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM/DCM = 65/30/5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 17.0 min (minor) and 23.8 min (major).





6h: R = 3-Cl

Yellow solid, Mp 243.9–244.5 °C; 96% yield (55.3 mg); >19:1 d.r., 93% ee; $[\alpha]_D^{23} = -30.0$ (*c* 0.82), ^1H NMR (400 MHz, CDCl_3) δ 8.38 (s, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 7.8 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.35–7.30 (m, 3H), 7.25–7.10 (m, 4H), 7.16 (d, *J* = 7.4 Hz, 1H), 7.01 (t, *J* = 7.4 Hz, 1H), 5.53 (s, 1H), 3.67–3.62 (m, 1H), 3.13–3.02 (m, 2H), 2.91–2.82 (m, 1H), 2.35 (s, 3H), 2.11–1.96 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 189.0, 169.6, 164.4, 155.2, 149.1, 140.3, 138.6, 134.8, 133.7, 132.8, 132.0, 130.6, 130.3, 129.4, 128.6, 128.2, 127.2, 127.0, 126.2, 125.8, 124.2, 50.4, 46.7, 44.5, 28.8 (two peaks), 11.4; HRMS (ESI) m/z 576.1282 ($M+\text{Na}^+$), calc. for $\text{C}_{31}\text{H}_{24}\text{ClN}_3\text{O}_5\text{Na}$ 576.1297. The ee was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM/DCM = 65/30/5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 11.9 min (minor) and 22.9 min (major).

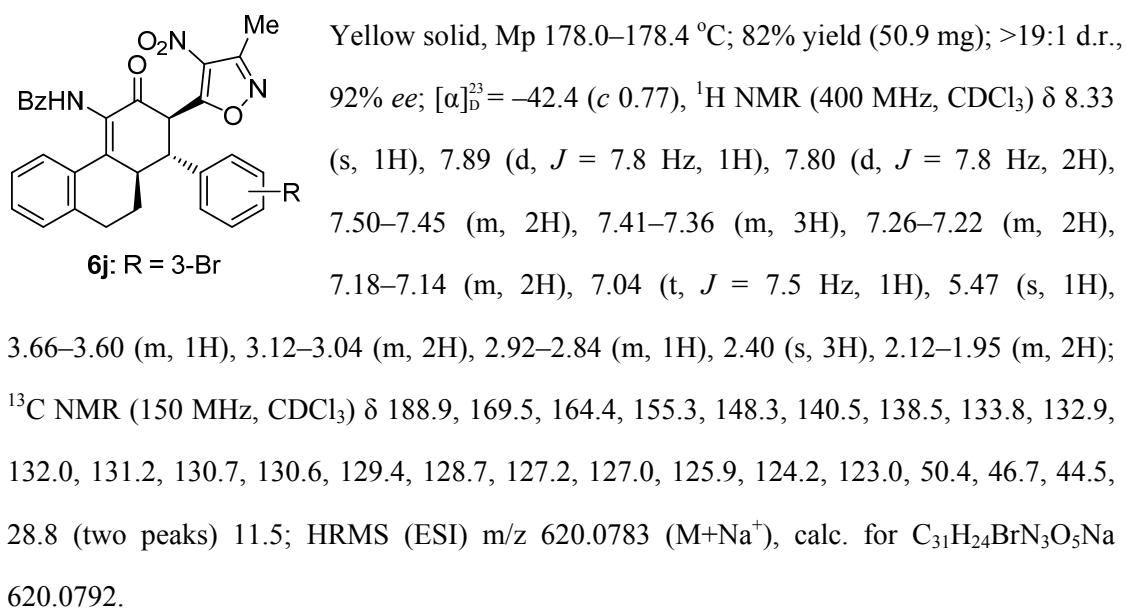
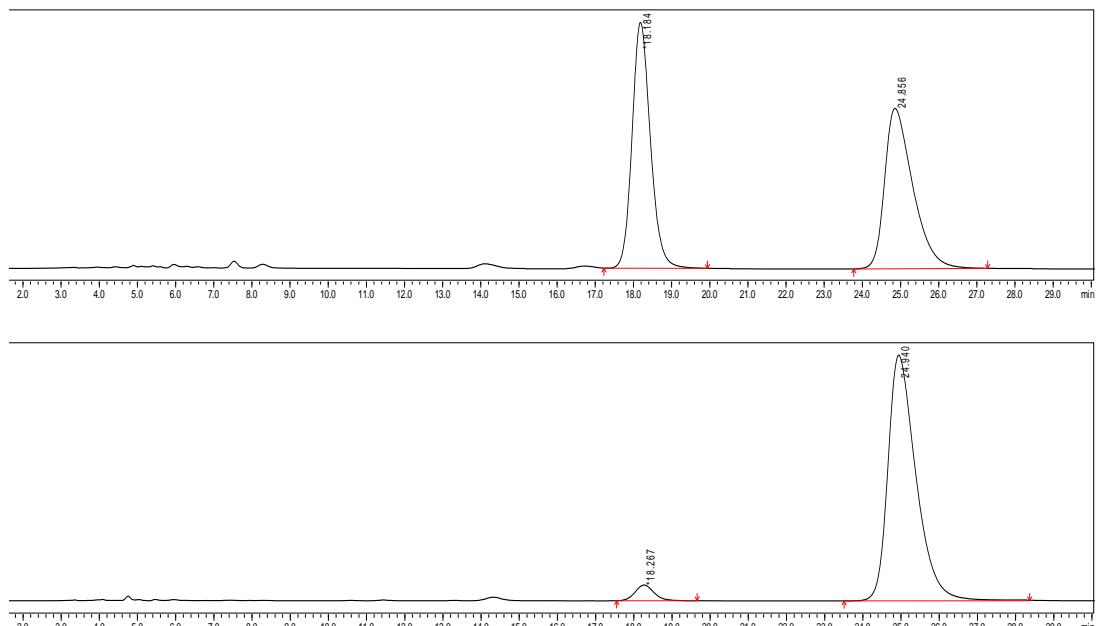


6i: R = 4-Br

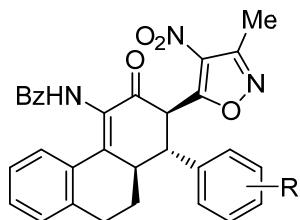
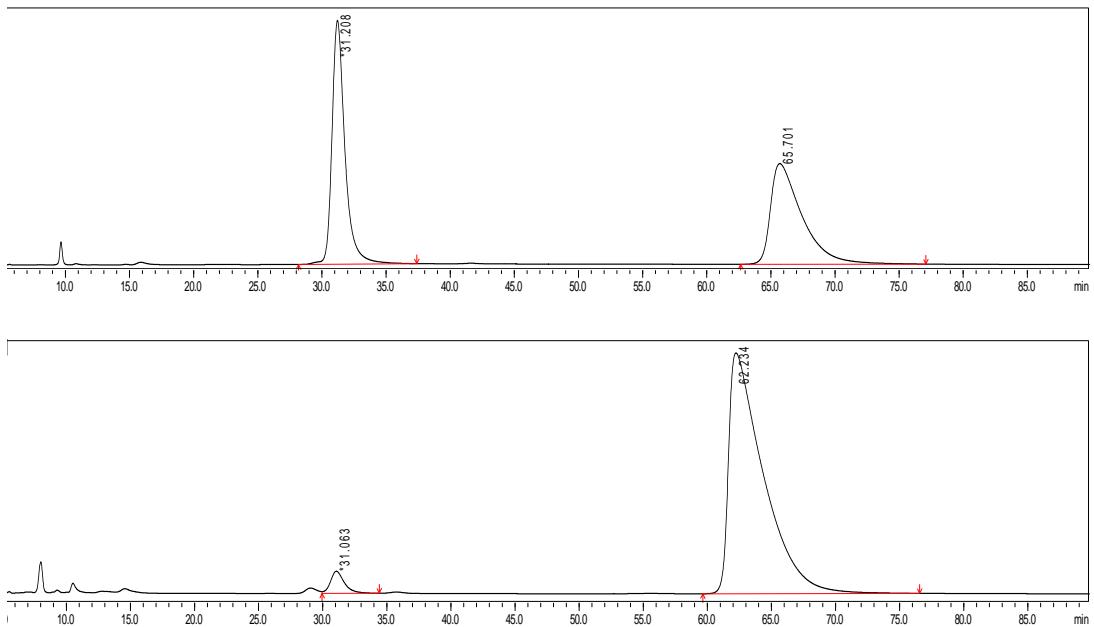
Yellow solid, Mp 197.2–197.6 °C; 62% yield (38.4 mg); 15:1 d.r., 92% ee; $[\alpha]_D^{23} = -39.4$ (*c* 0.35), ^1H NMR (400 MHz, CDCl_3) δ 8.33 (s, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.80 (d, *J* = 7.8 Hz, 2H), 7.50–7.36 (m, 5H), 7.23–7.17 (m, 4H), 7.03 (t, *J* = 7.5 Hz, 1H), 5.49 (s, 1H), 3.68–3.62 (m, 1H), 3.09–3.04 (m, 2H), 2.85–2.81 (m, 1H), 2.40 (s, 3H), 2.09–1.94 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 188.9, 169.6, 164.4, 155.3, 145.0, 138.4, 137.2, 133.8, 132.9, 132.2, 132.1, 130.7, 129.7, 129.5, 128.7, 127.2,

127.0, 125.9, 124.2, 121.9, 50.2, 46.6, 44.6, 28.8, 28.8, 11.5; HRMS (ESI) m/z 620.0783 ($M+Na^+$), calc. for $C_{31}H_{24}BrN_3O_5Na$ 620.0792.

The ee was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM/DCM = 65/30/5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 18.3 min (minor) and 24.9 min (major).

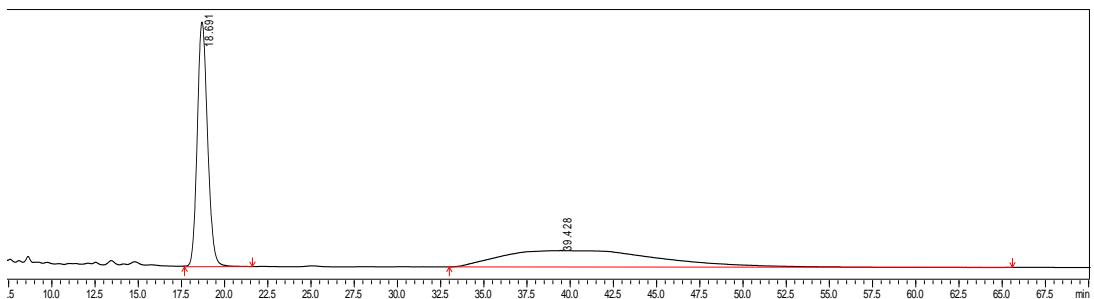


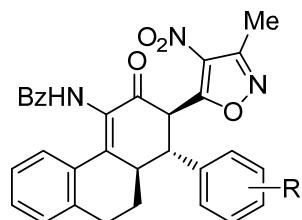
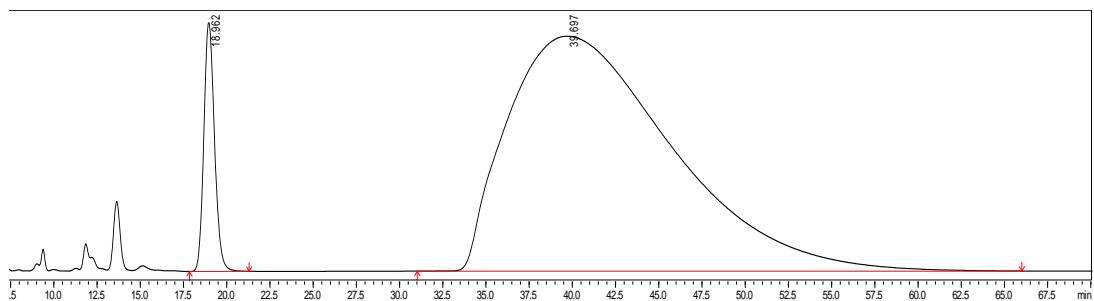
The ee was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM/DCM = 79/20/1; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 31.1 min (minor) and 62.2 min (major).



6k: R = 2-Br
Yellow solid, Mp 225.5–226.3 °C; 83% yield (51.5 mg); 11:1 d.r., 87% ee; $[\alpha]_D^{23} = -41.6$ (*c* 0.47), ¹H NMR (400 MHz, CDCl₃) δ 8.40 (s, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 7.8 Hz, 2H), 7.55–7.46 (m, 3H), 7.41–7.36 (m, 2H), 7.31–7.28 (m, 1H), 7.24–7.22 (m, 1H), 7.18–7.16 (m, 1H), 7.11–7.01 (m, 2H), 5.47 (s, 1H), 4.55–4.49 (m, 1H), 3.14–3.05 (m, 2H), 2.88–2.80 (m, 1H), 2.37 (s, 3H), 2.21–2.09 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 188.8, 169.7, 164.5, 155.3, 138.6, 138.1, 135.2, 133.9, 133.4, 132.9, 132.0, 130.6, 129.8, 129.4, 129.2, 128.8, 128.2, 127.8, 127.4, 127.2, 126.3, 125.9, 124.5, 50.6, 45.8, 44.4, 29.0, 28.5, 11.6; HRMS (ESI) m/z 620.0773 (M+Na⁺), calc. for C₃₁H₂₄BrN₃O₅Na 620.0792.

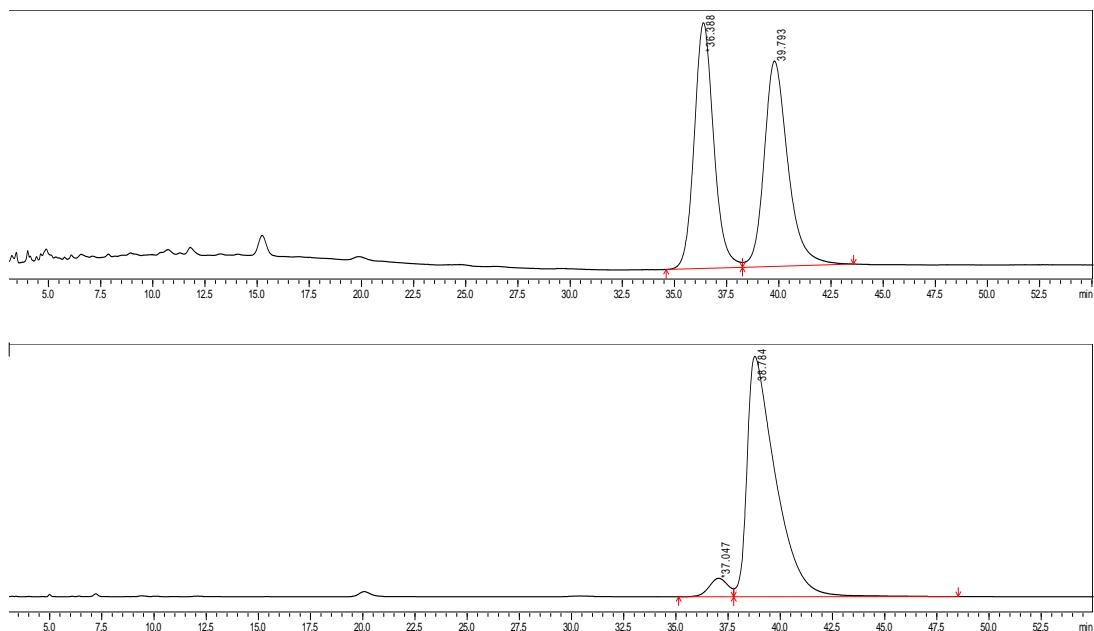
The ee was determined by HPLC analysis. CHIRALPAK IE (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM/DCM = 55/40/5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 19.0 min (minor) and 39.7 min (major).

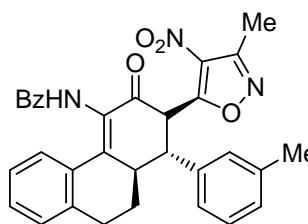




Yellow solid, Mp 116.5–117.2 °C; 98% yield (54.5 mg); 16:1 d.r., 90% ee; $[\alpha]_D^{23} = -36.9$ (*c* 0.86), ^1H NMR (400 MHz, CDCl_3) δ 8.32 (s, 1H), 7.91 (d, *J* = 7.7 Hz, 1H), 7.81 (d, *J* = 7.7 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.24–7.14 (m, 4H), 7.07–7.02 (m, 3H), 5.48 (s, 1H), 3.64–3.59 (m, 1H), 3.12–3.02 (m, 2H), 2.89–2.80 (m, 1H), 2.39 (s, 3H), 2.28 (s, 3H), 2.13–1.93 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 189.4, 170.2, 164.5, 155.1, 138.7, 137.6, 134.9, 134.0, 133.1, 132.0, 130.5, 129.7, 129.4, 128.7, 127.8, 127.3, 127.1, 125.8, 124.2, 50.8, 46.8, 44.8, 28.9, 28.8, 21.0, 11.5; HRMS (ESI) *m/z* 556.1831 ($\text{M}+\text{Na}^+$), calc. for $\text{C}_{32}\text{H}_{27}\text{N}_3\text{O}_5\text{Na}$ 556.1843.

The ee was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM/DCM = 78/20/2; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 37.0 min (minor) and 38.8 min (major).

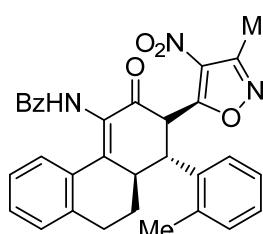
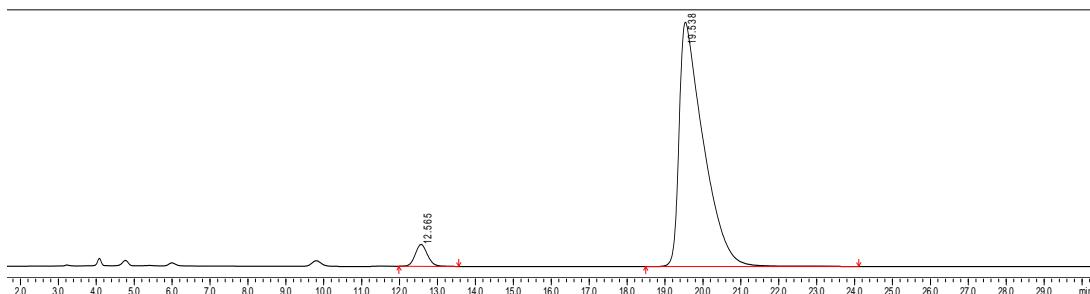
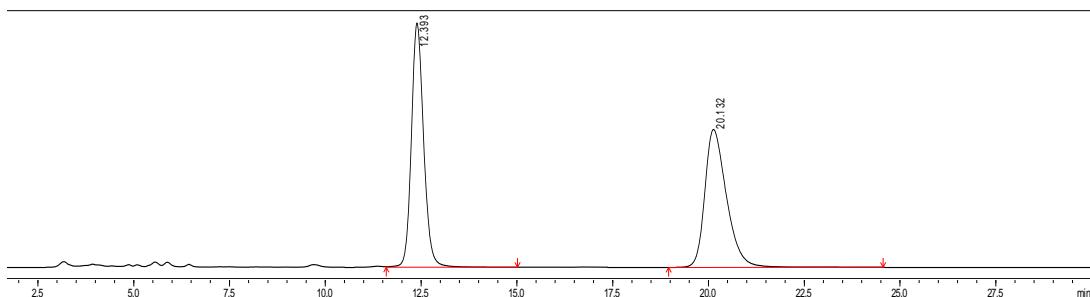




6m

Yellow solid, Mp 144.5–145.3 °C; 73% yield (40.6 mg); 17:1 d.r., 91% ee; $[\alpha]_D^{23} = -36.7$ (*c* 0.84), ^1H NMR (400 MHz, CDCl_3) δ 8.36 (s, 1H), 7.90 (d, *J* = 7.7 Hz, 1H), 7.81 (d, *J* = 7.7 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.26–7.22 (m, 1H), 7.18–7.13 (m, 2H), 7.08–7.02 (dd, *J* = 15.7, 9.1 Hz, 4H), 5.52 (s, 1H), 3.64–3.58 (m, 1H), 3.14–3.03 (m, 2H), 2.90–2.82 (m, 1H), 2.37 (s, 3H), 2.29 (s, 3H), 2.14–1.94 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 189.4, 170.1, 164.4, 155.1, 148.7, 138.7, 138.6, 137.9, 133.9, 133.0, 132.0, 130.5, 129.4, 128.8, 128.7, 128.7, 127.2, 127.0, 125.8, 125.0, 124.2, 50.7, 47.2, 44.6, 28.9, 28.8, 21.4, 11.5; HRMS (ESI) *m/z* 556.1834 ($\text{M}+\text{Na}^+$), calc. for $\text{C}_{32}\text{H}_{27}\text{N}_3\text{O}_5\text{Na}$ 556.1843.

The ee was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM/DCM = 65/30/5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 12.6 min (minor) and 19.5 min (major).

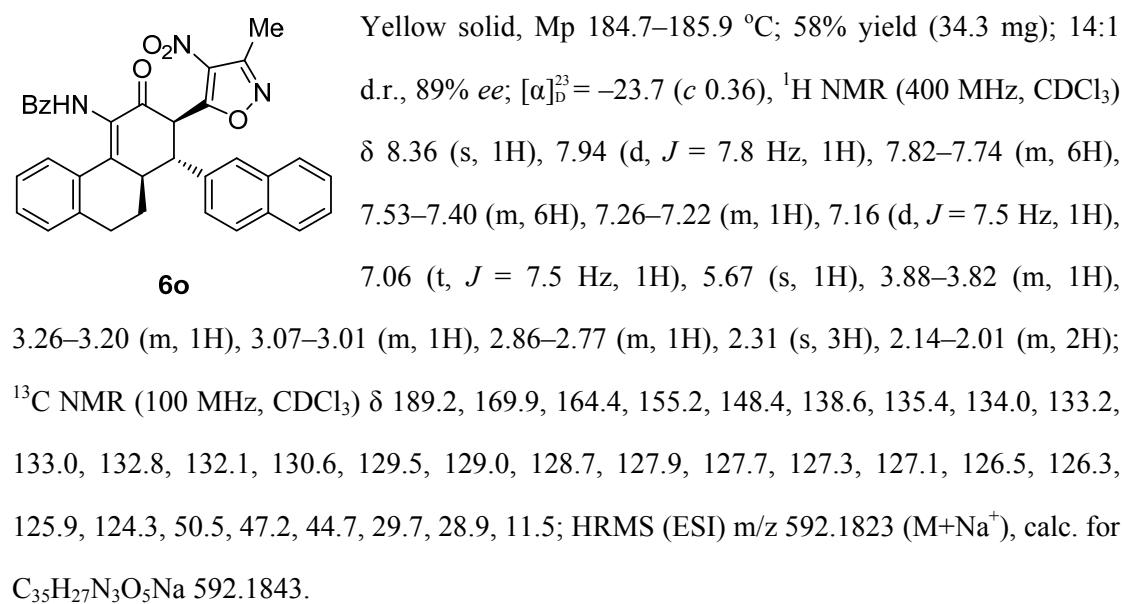
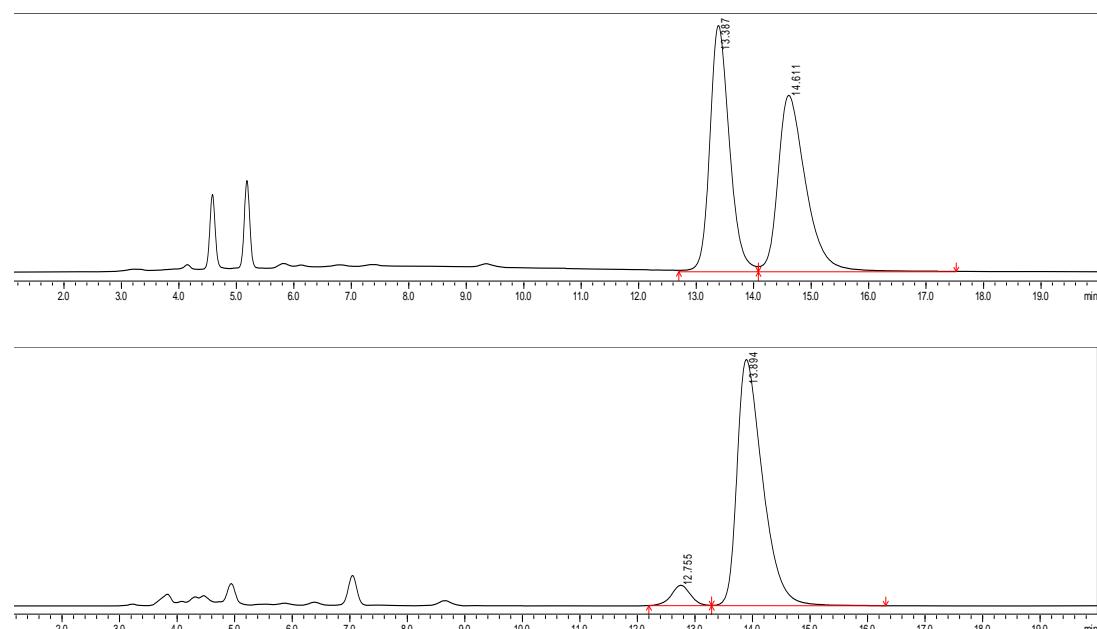


6n

Yellow solid, Mp 145.1–146.0 °C; 56% yield (31.2 mg); >19:1 d.r., 88% ee; $[\alpha]_D^{23} = -34.5$ (*c* 0.87), ^1H NMR (400 MHz, CDCl_3) δ 8.40 (s, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 2H), 7.50–7.47 (m, 1H), 7.41–7.36 (m, 3H), 7.24–7.22 (m, 1H), 7.18–7.01 (m, 5H), 5.58 (s, 1H), 4.06–4.00 (m, 1H), 3.16–3.02 (m, 2H), 2.89–2.80 (m, 1H), 2.40 (s, 3H), 2.36 (s, 3H), 2.04–1.99 (m, 2H); ^{13}C NMR (100

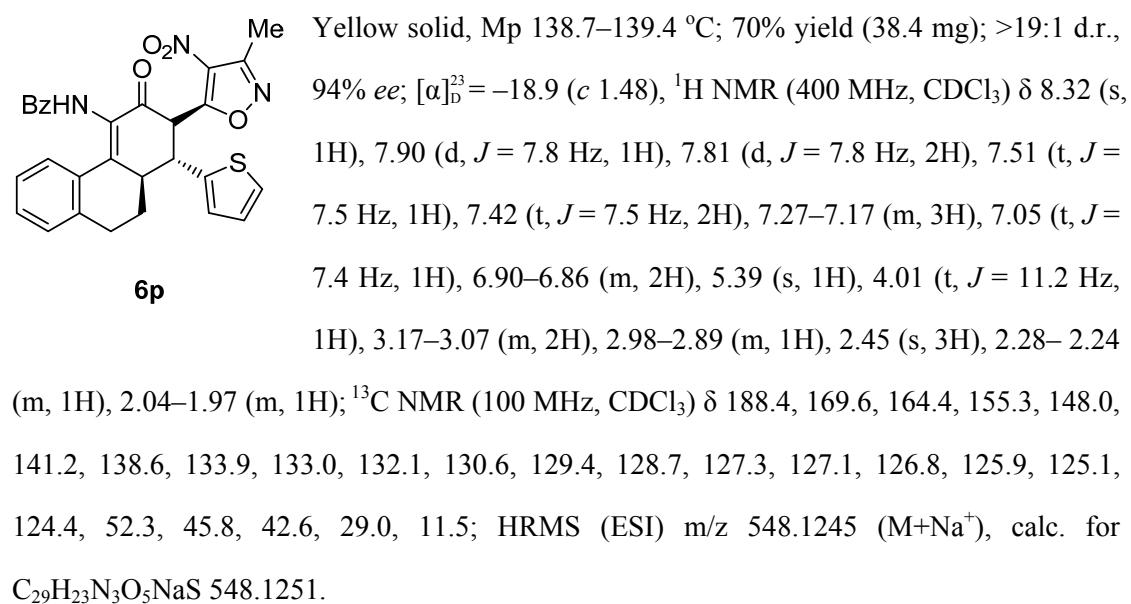
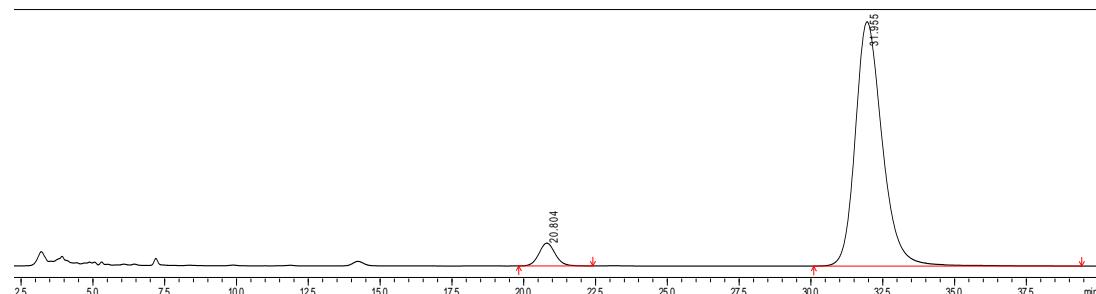
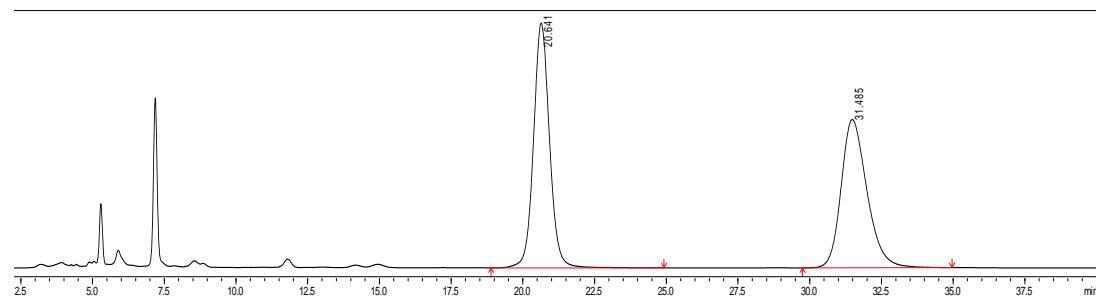
MHz, CDCl₃) δ 189.7, 170.2, 164.4, 155.2, 148.7, 138.5, 137.3, 136.8, 133.9, 132.9, 132.1, 130.8, 130.6, 129.5, 128.7, 127.4, 127.3, 127.0, 126.8, 125.8, 125.7, 124.1, 50.6, 46.2, 41.1, 29.0, 28.5, 20.0, 11.5; HRMS (ESI) m/z 556.1832 (M+Na⁺), calc. for C₃₂H₂₇N₃O₅Na 556.1843.

The ee was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM/DCM = 65/30/5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 12.8 min (minor) and 13.9 min (major).

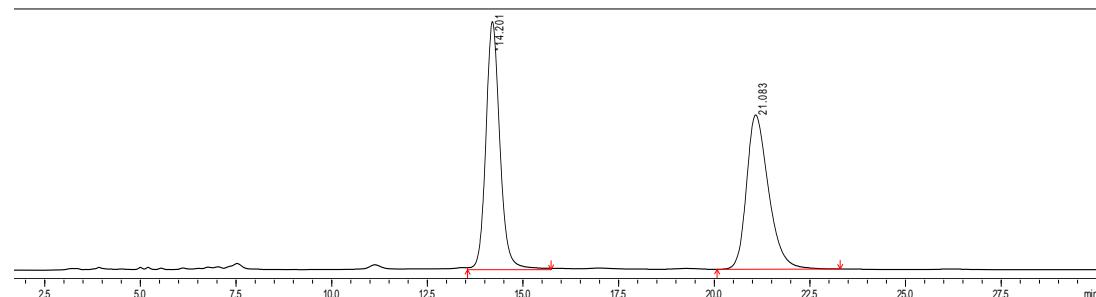


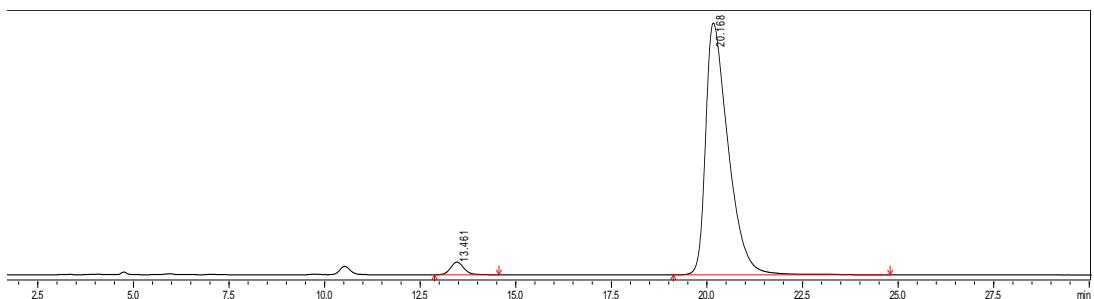
The ee was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM/DCM = 65/30/5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention

time: 20.6 min (minor) and 31.5 min (major).



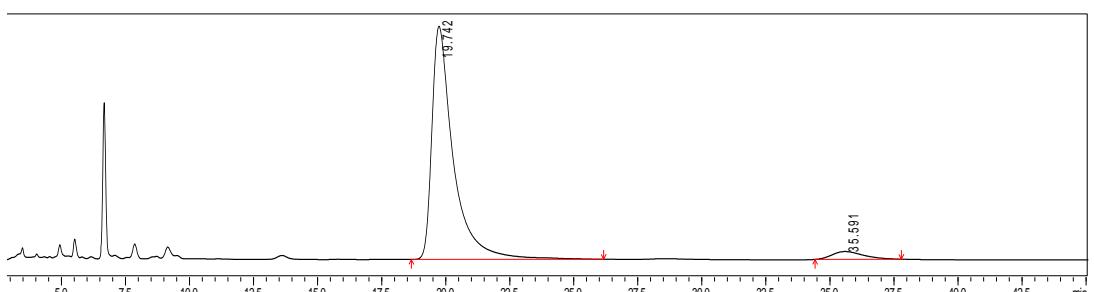
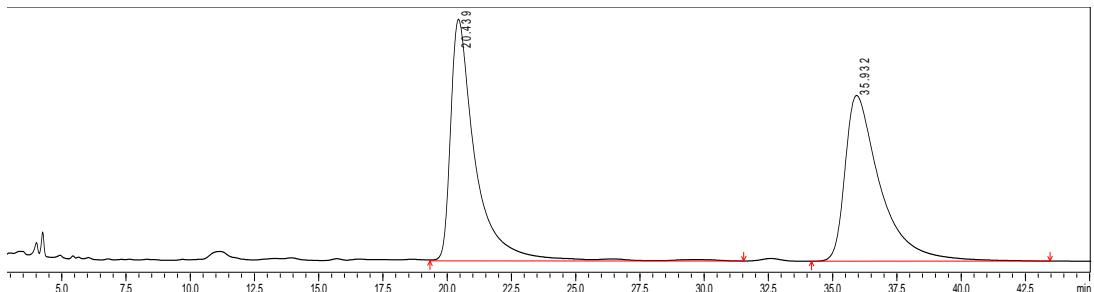
The ee was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM/DCM = 65/30/5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 13.5 min (minor) and 20.2 min (major).

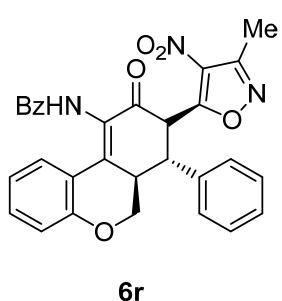




6q Yellow solid, Mp 135.2–135.9 °C; 46% yield (24.3 mg); 7:1 d.r., 91% ee; $[\alpha]_D^{23} = -40.2$ (c 0.57), ^1H NMR (400 MHz, CDCl_3) δ 8.00–7.95 (m, 3H), 7.57–7.54 (m, 2H), 7.50–7.45 (m, 2H), 7.41–7.37 (m, 1H), 7.33–7.26 (m, 6H), 7.26–7.23 (m, 2H), 5.36–5.35 (m, 1H), 4.05–3.95 (m, 2H), 2.96–2.85 (m, 2H), 2.36 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 189.3, 170.3, 166.4, 155.3, 148.4, 138.1, 136.9, 133.6, 132.2 (two peaks), 129.2, 128.8, 128.2, 127.8, 127.6 (two peaks), 127.2, 125.0, 122.9, 53.4, 50.4, 48.3, 36.0, 11.4; HRMS (ESI) m/z 528.1524 ($\text{M}+\text{Na}^+$), calc. for $\text{C}_{30}\text{H}_{23}\text{N}_3\text{O}_5\text{Na}$ 528.1530.

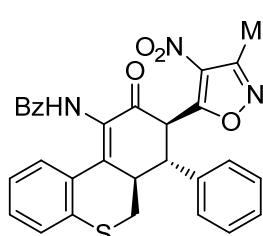
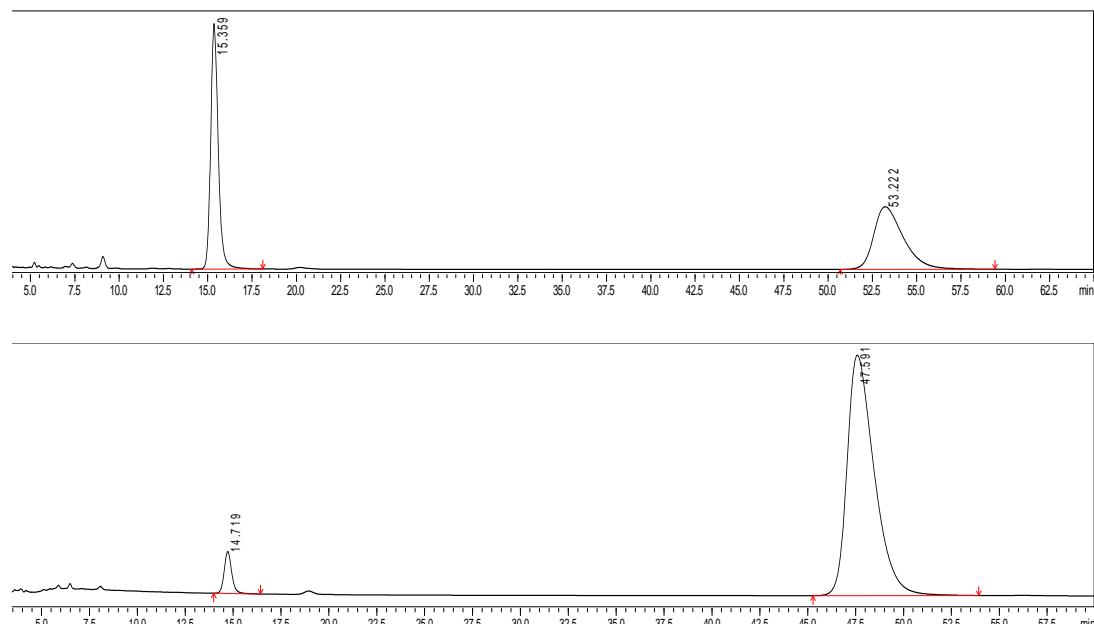
The ee was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM/DCM = 79/20/1; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 19.7 min (major) and 35.6 min (minor).





Yellow solid, Mp 194.8–195.3 °C; 59% yield (32.1 mg); 14:1 d.r., 91% ee; $[\alpha]_D^{23} = -54.1$ (*c* 0.51), ^1H NMR (400 MHz, CDCl_3) δ 8.40 (s, 1H), 7.88–7.85 (m, 3H), 7.54–7.40 (m, 3H), 7.31–7.22 (m, 6H), 6.85 (d, *J* = 7.6 Hz, 1H), 6.78 (t, *J* = 7.63 Hz, 1H), 5.53 (s, 1H), 4.24–4.14 (m, 2H), 3.63–3.46 (m, 2H), 2.36 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 188.4, 169.3, 164.5, 155.3, 136.5, 133.5, 133.1, 132.3, 129.3, 128.8 (two peaks), 128.5, 127.4 (two peaks), 120.8, 118.7, 117.6, 67.8, 50.8, 43.9, 41.1, 11.5; HRMS (ESI) *m/z* 544.1458 ($\text{M}+\text{Na}^+$), calc. for $\text{C}_{30}\text{H}_{23}\text{N}_3\text{O}_6\text{Na}$ 544.1479.

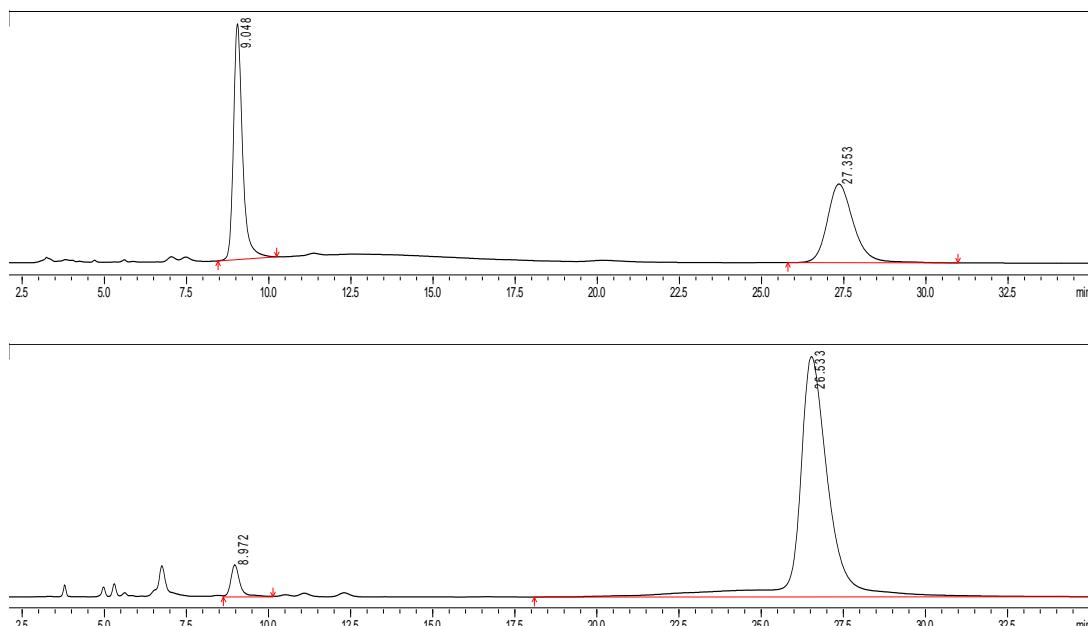
The ee was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM/DCM = 65/30/5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 14.7 min (minor) and 47.6 min (major).



Yellow solid, Mp 185.8–186.3 °C; 92% yield (51.5 mg); 15:1 d.r., 92% ee; $[\alpha]_D^{23} = -169.6$ (*c* 0.30), ^1H NMR (400 MHz, CDCl_3) δ 8.31 (s, 1H), 7.82–7.77 (m, 3H), 7.50–7.47 (m, 1H), 7.43–7.36 (m, 2H), 7.32–7.22 (m, 5H), 7.17–7.12 (m, 2H), 6.92–6.88 (m, 1H), 5.53 (s, 1H), 3.67–3.61 (m, 1H), 3.50–3.42 (m, 1H), 3.28–3.22 (m, 1H), 3.00–2.96 (m, 1H), 2.37 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 188.7, 169.3, 164.2, 155.2, 144.9, 136.8, 135.6, 133.7, 132.1, 130.8, 130.6, 129.3, 128.7, 128.4, 128.3, 128.0, 127.3,

127.2, 124.1, 50.4, 46.8, 43.7, 30.3, 11.4; HRMS (ESI) m/z 560.1238 ($M+Na^+$), calc. for $C_{30}H_{23}N_3O_5NaS$ 560.1251.

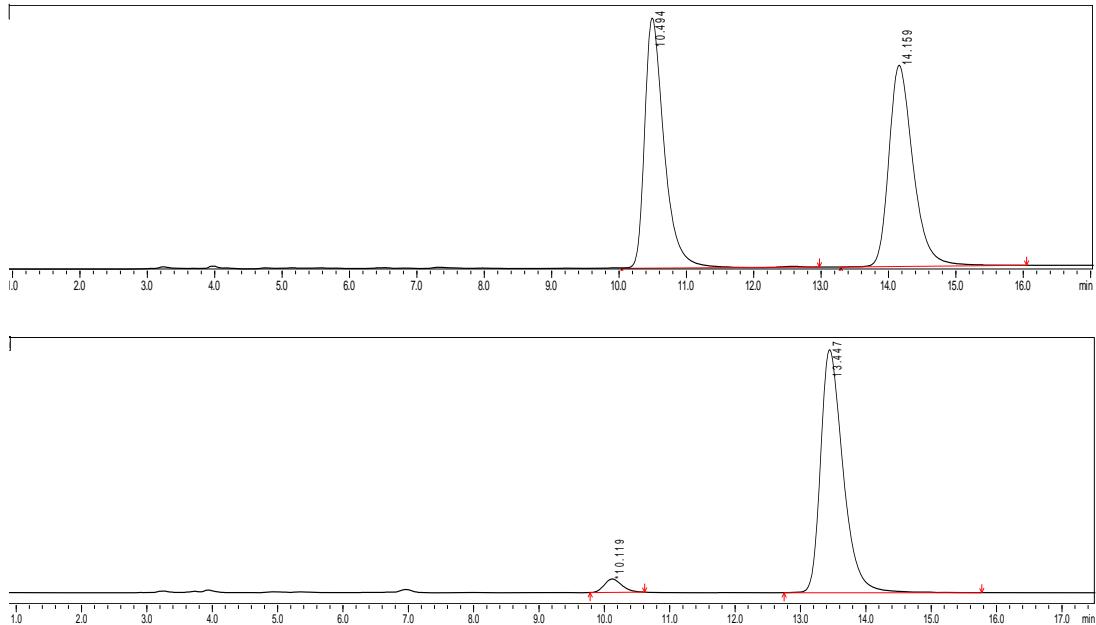
The ee was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM/DCM = 65/30/5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 9.0 min (minor) and 26.5 min (major).



7

Yellow solid, Mp 124.1–125.2 °C; 78% yield (113.9 mg, 0.31 mmol); >19:1 d.r., 92% ee; $[\alpha]_D^{23} = -6.5$ (c 0.66), 1H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.88–7.84 (m, 3H), 7.56–7.43 (m, 5H), 7.27–7.15 (m, 4H), 7.02 (t, J = 7.5 Hz, 1H), 3.05–2.98 (m, 2H), 2.93–2.84 (m, 3H), 2.75–2.70 (m, 1H), 2.06–2.03 (m, 1H), 1.90–1.80 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.5, 164.4, 145.8, 144.0, 138.4, 134.3, 133.7, 132.0, 130.8, 130.4 (two peaks), 130.0, 129.3, 128.7, 127.4, 127.0, 126.7, 125.7, 125.1, 122.9, 44.4, 44.0, 42.9, 29.0, 28.9; HRMS (ESI) m/z 494.0720 ($M+Na^+$), calc. for $C_{27}H_{22}BrNO_2Na$ 494.0726.

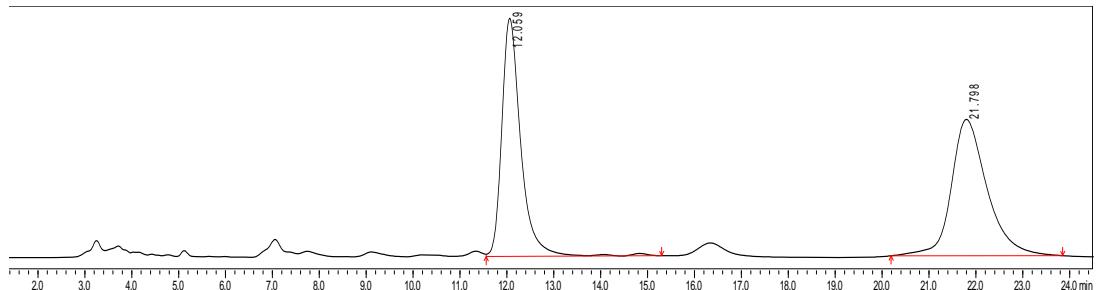
The ee was determined by HPLC analysis. CHIRALPAK IF (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM/DCM = 65/30/5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 10.5 min (minor) and 14.2 min (major).

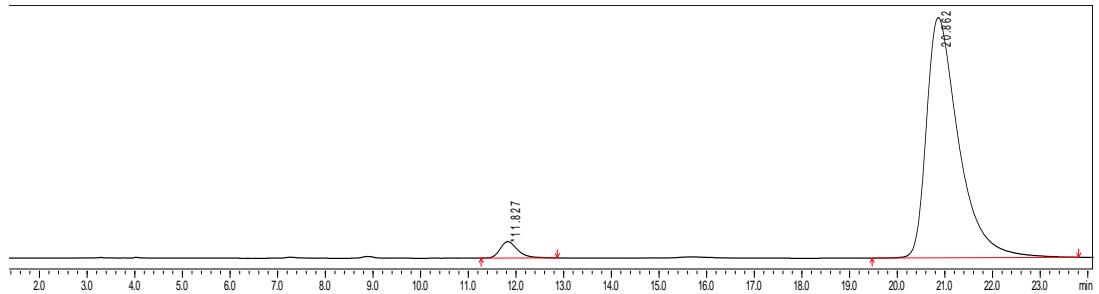


8

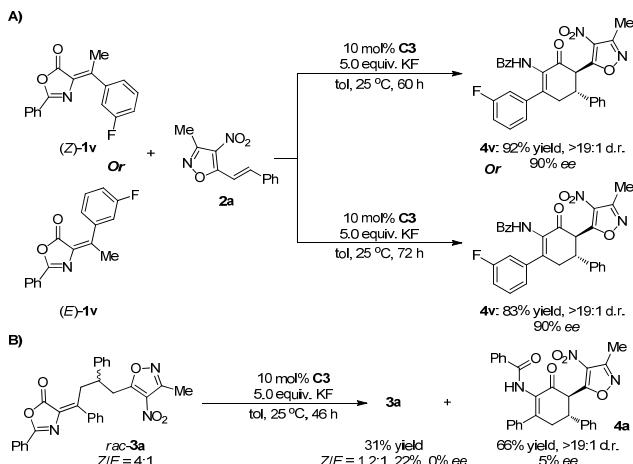
Yellow solid, Mp 178.1–178.9 °C; 67% yield (59.1 mg, 0.155 mmol); >19:1 d.r., 93% ee; $[\alpha]_D^{23} = -26.4$ (c 0.15), ^1H NMR (400 MHz, CDCl_3) δ 8.22 (s, 1H), 8.01 (d, J = 7.9, 1H), 7.93 (d, J = 7.9 Hz, 1H), 7.77 (d, J = 7.4 Hz, 2H), 7.56 (t, J = 7.4 Hz, 2H), 7.49–7.44 (m, 3H), 7.37–7.27 (m, 5H), 5.51 (s, 1H), 4.06–3.98 (m, 2H), 3.47–3.39 (m, 1H), 3.35–3.27 (m, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 187.6, 168.4, 164.8, 162.4, 155.3, 139.2, 138.2, 135.2, 133.1, 133.0, 132.6, 131.2, 129.9, 129.8, 129.1, 128.9, 127.9, 127.7, 127.4, 124.3, 52.5, 47.6, 43.1, 29.3, 11.5; HRMS (ESI) m/z 592.1133 ($M+\text{Na}^+$), calc. for $\text{C}_{30}\text{H}_{23}\text{N}_3\text{O}_7\text{NaS}$ 592.1149.

The ee was determined by HPLC analysis. CHIRALPAK IF (4.6 mm i.d. x 250 mm); Hexane/2-propanol/DCM/DCM = 65/30/5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 11.8 min (minor) and 20.9 min (major).



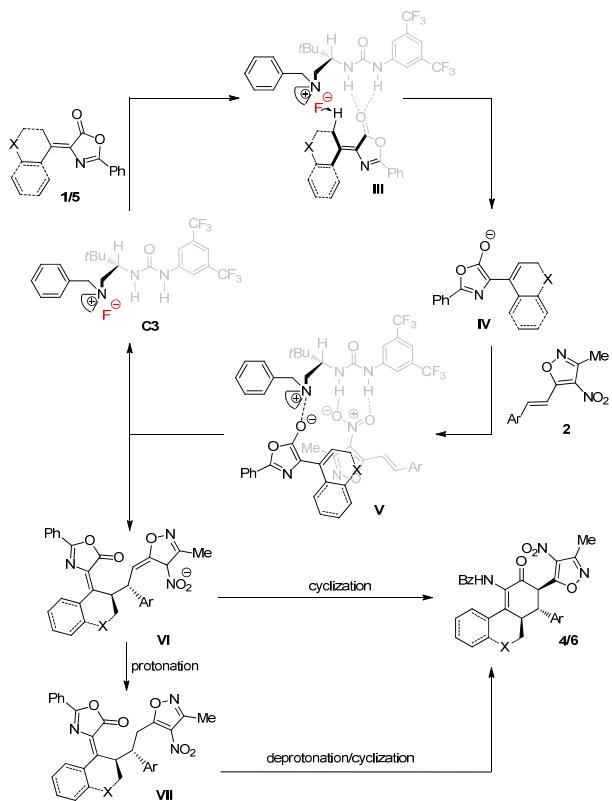


9. Control experiments and plausible mechanism



To elucidate the mechanism of this reaction, several control experiments were carried out. First, a pair of *E/Z* isomers of an olefinic azlactone, i.e., (*Z*)-**1v** and (*E*)-**1v**, were subjected to the reaction with **2a** under the standard reaction conditions (Eqn. A). Both transformations afforded product **4v** with the same enantioselectivity and diastereoselectivity. Notably, (*Z*)-**1v** was slightly more reactive than (*E*)-**1v** based on the yield and reaction time. The results suggest that the reaction proceeds through a stepwise conjugate addition–vinyllogous cyclization cascade and is not a concerted [4+2] cycloaddition. To understand the formation of the three stereocentres, *rac*-**3a** with a 4:1 *Z/E* ratio was evaluated (Eqn. 2). After 46 h, **3a** was recovered in 31% yield with a 1.2:1 *Z/E* ratio, and the *ee* values of *Z*-**3a** and *E*-**3a** were determined to be 22% and 0%, respectively. Meanwhile, product **4a** was generated in 66% yield with 5% *ee* and >19:1 d.r. Thus, the vinyllogous conjugate addition is responsible for the enantiopurity of the final product.

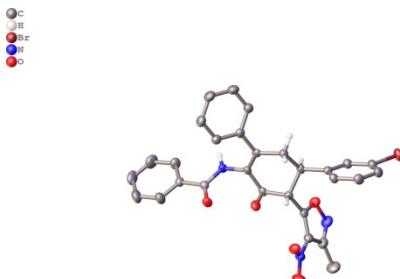
Based on our previous investigations (see reference 14 in the manuscript) on bifunctional phase-transfer catalysis and the experimental observations in this work, a plausible mechanism has been proposed and is depicted. With the H-bonding interactions (**III**) between the carbonyls of olefinic azlactones **1/5** and the urea moiety of catalyst **C3**, dienolate intermediates **IV** can be generated after deprotonation. The results shown in entries 5 and 6 and footnote *g* in Table 1 as well as Eqn. A (see above) provide evidence for this activation mode. The steric hindrance of **C3** is also crucial to obtaining the dienolates with a high *Z/E* ratio. Subsequently, the electrostatic interaction between the N cation of the ammonium of **C3** with the O anion of the dienolate and the H-bonding interactions between the urea of **C3** and



the nitro group of 4-nitro-isoxazole **2** would facilitate the vinylogous addition and provide the stereocontrol (see **V**). The results of the reactions of olefinic azlactones **5** support this cooperative catalysis. With respect to the generation of products **4/6** from anion intermediates **VI**, both the direct vinylogous cyclization and protonation to form **VII** and the deprotonation–cyclization are possible.

10. Determination of the absolute configuration

(1) The absolute configurations of the amination adducts **4** were assigned based on the structure of **4i** as solved by single crystal X-ray diffraction(CCDC 1874522)

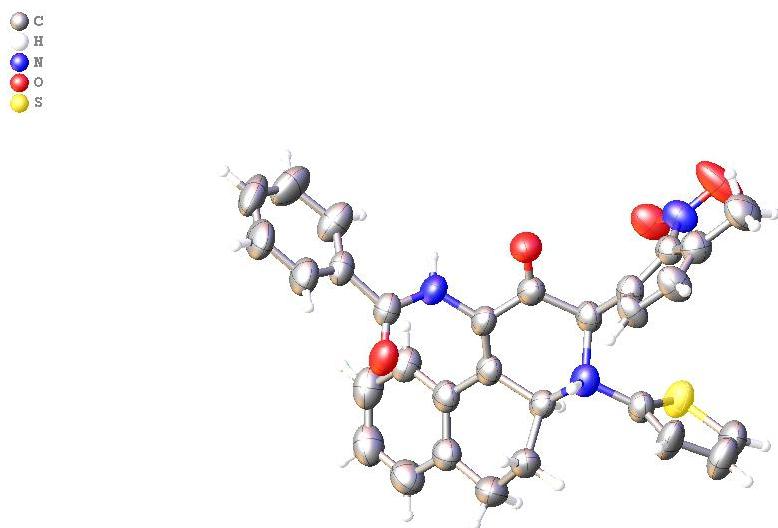


Crystal data and structure refinement for 20180615C1_1.

Identification code	20180615C1_1
Empirical formula	C ₃₀ H ₂₆ BrN ₃ O ₆
Formula weight	604.45
Temperature/K	149.93(11)
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	13.46870(10)
b/Å	16.9916(2)
c/Å	24.6770(2)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	5647.45(9)
Z	8
ρ _{calcg/cm³}	1.422
μ/mm ⁻¹	2.388
F(000)	2480.0
Crystal size/mm ³	0.35 × 0.29 × 0.08
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	6.316 to 124.996
Index ranges	-15 ≤ h ≤ 8, -19 ≤ k ≤ 14, -28 ≤ l ≤ 27
Reflections collected	17276
Independent reflections	8403 [R _{int} = 0.0236, R _{sigma} = 0.0294]
Data/restraints/parameters	8403/0/727
Goodness-of-fit on F ²	1.043
Final R indexes [I>=2σ (I)]	R ₁ = 0.0241, wR ₂ = 0.0619
Final R indexes [all data]	R ₁ = 0.0248, wR ₂ = 0.0623

Largest diff. peak/hole / e Å ⁻³	0.28/-0.58
Flack parameter	-0.023(5)

(2) The absolute configurations of the aldol adducts **6** and **7–8** were based on the *X*-ray structure analysis of **6p** (CCDC 1874533)



Crystal data and structure refinement for zb-3064a_sq.

Identification code	zb-3064a_sq
Empirical formula	C ₂₉ H ₂₃ N ₃ O ₅ S
Formula weight	525.56
Temperature/K	296.8(3)
Crystal system	monoclinic
Space group	P2 ₁
a/Å	13.2464(4)
b/Å	7.5853(2)
c/Å	15.4082(7)
α/°	90
β/°	106.395(3)
γ/°	90
Volume/Å ³	1485.23(9)
Z	2
ρ _{calc} g/cm ³	1.175
μ/mm ⁻¹	1.297
F(000)	548.0
Crystal size/mm ³	0.38 × 0.26 × 0.15
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.956 to 170.392
Index ranges	-16 ≤ h ≤ 16, -9 ≤ k ≤ 9, -19 ≤ l ≤ 19
Reflections collected	41882
Independent reflections	5842 [R _{int} = 0.0376, R _{sigma} = 0.0201]
Data/restraints/parameters	5842/1/344

Goodness-of-fit on F^2	1.062
Final R indexes [$I \geq 2\sigma$ (I)]	$R_I = 0.0400, wR_2 = 0.1062$
Final R indexes [all data]	$R_I = 0.0441, wR_2 = 0.1114$
Largest diff. peak/hole / e \AA^{-3}	0.19/-0.23
Flack parameter	0.023(7)

11. Copies of NMR spectra

