

Electronic Supplementary Information

Asymmetric Direct Vinylogous Michael Addition of 3-Alkylidene Oxindoles to Chalcones Catalyzed by a Chiral Ytterbium(III)-*N,N'*-Dioxide Complex

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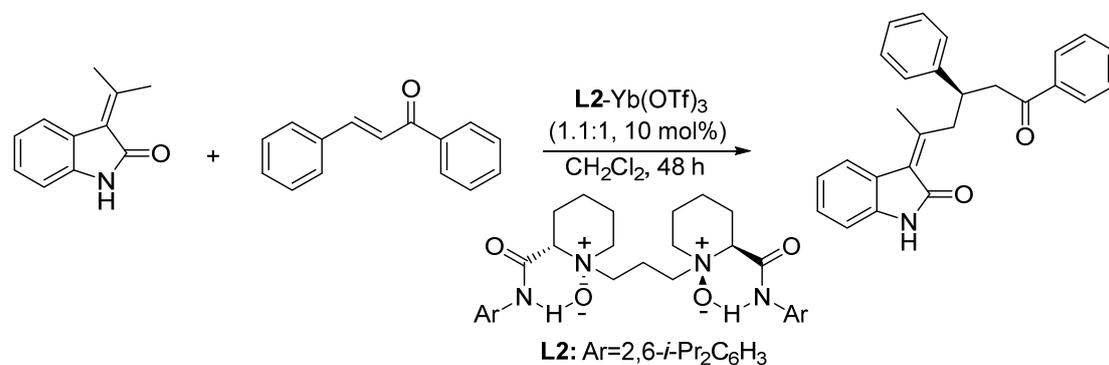
Contents:

1. General remarks.....	S2
2. Typical experimental procedure for the catalytic asymmetric direct vinylogous Michael reaction	S2
3. Typical experimental procedure for the scale-up reaction	S3
4. Characterization of the product 3	S3
5. Determination of Absolute Configurations of the Products 3a	S20
6. CD spectra of the products 3	S21
7. References.....	S23
8. Copy of ¹ H NMR and ¹³ C NMR spectra for products.....	S23

1. General remarks

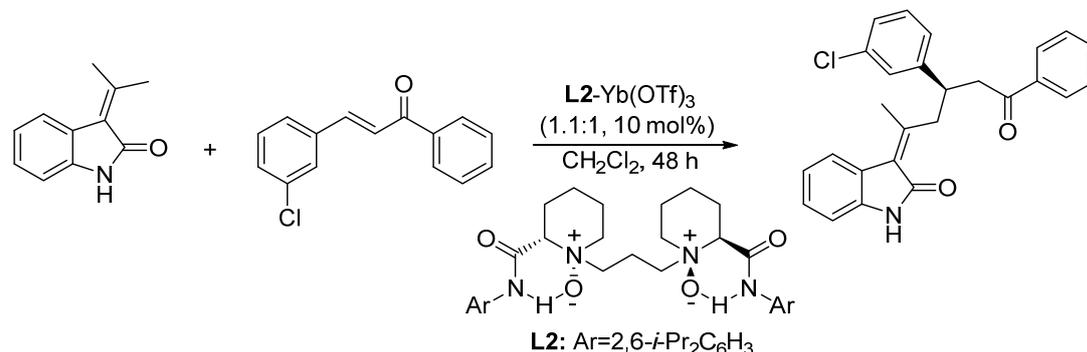
^1H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl_3 , $\delta = 7.26$). Spectra are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration, and assignment. ^{13}C NMR spectra were collected on commercial instruments (100 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard (CDCl_3 , $\delta = 77.16$). The enantiomeric excess was determined by HPLC analysis on commercial chiral columns. Optical rotations were measured on a commercial polarimeter and reported as follows: $[\alpha]_D^T$ (c = g/100 mL, solvent). HR-ESIMS spectra were recorded using a commercial apparatus and methanol or acetonitrile was used to dissolve the sample. Unless otherwise indicated, reagents obtained from commercial sources were used without further purification. Solvents were dried and distilled prior to use according to the standard methods. 4 Å MS was powdered <50 μm , which was activated at 400 °C for 3 hours and stored under nitrogen. Unless noted, commercial reagents were used without further purification. 3-alkylidene oxindoles were prepared according to the literature and references therein.^[1] Chalcones were prepared according to the literature.^[2] The N,N' -dioxdes were prepared according to the methods reported in the literature.^[3] The racemic products of the catalytic asymmetric direct vinylogous Michael reactions were prepared with the $\text{Yb}(\text{OTf})_3$ -racemic ligand-DMAP complex.

2. Typical experimental procedure for the catalytic asymmetric direct vinylogous Michael reaction



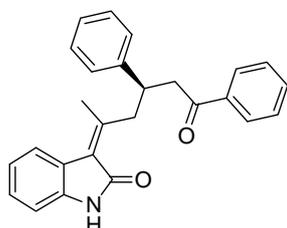
N,N' -dioxide **L2** (7.2 mg, 0.011 mmol, 11 mol%), ytterbium triflate (6.2 mg, 0.010 mmol, 10 mol%), 4 Å molecular sieves (20 mg), and chalcone **2a** (0.1 mmol, 20.8 mg) were stirred in a dry reaction tube under nitrogen, then CH_2Cl_2 (0.5 mL) was added, and the reaction was stirred at 30 °C under nitrogen. After 0.5 h, 3-allylidene oxindole **1a** (0.12 mmol, 20.7 mg), and DMAP (7.32 mg, 0.6 mmol) were added and the mixture was stirred at 0 °C for 48 h. The Z/E ratio was determined by ^1H NMR analysis. Separation by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1-3:1) afforded the desired product Z/E -**3a**, the pure Z -isomer could be separated. The enantiomeric excess (ee) of product Z -**3a** was determined by high-performance liquid chromatography (HPLC).

3. Typical procedure for the scale-up reaction with 10 mol% catalyst loading:

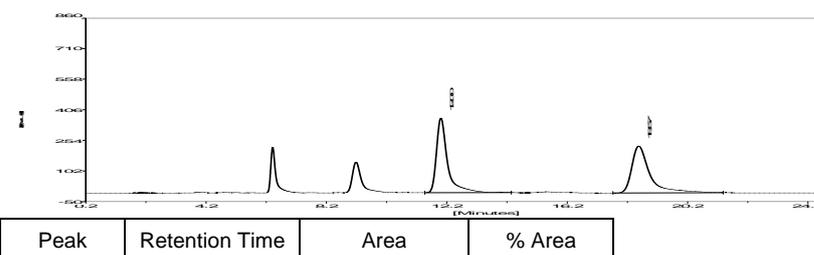


N,N'-dioxide **L2** (218.0 mg, 0.33 mmol, 11 mol%), ytterbium triflate (186.0 mg, 0.30 mmol, 10 mol%), 4 Å molecular sieves (600 mg), and chalcone **2h** (3.0 mmol, 726.0 mg) were stirred in a dry reaction boiling flask under nitrogen, then CH₂Cl₂ (15.0 mL) was added, and the reaction was stirred at 0 °C under nitrogen. After 0.5 h, 3-allylidene oxindole **1a** (3.6 mmol, 623.0 mg), and DMAP (2196.0 mg, 18.0 mmol) were added and the mixture was stirred at 0 °C for 48 h. The *Z/E* ratio was determined by ¹H NMR analysis. Separation by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1-3:1) afforded the desired product *Z/E*-**3h**, the pure *Z*-isomer could be separated. The enantiomeric excess (*ee*) of product *Z*-**3h** was determined by high-performance liquid chromatography (HPLC).

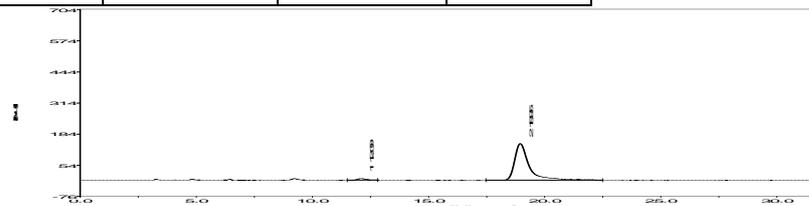
4. Characterization of the product 3



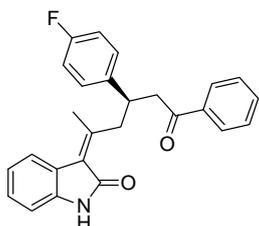
(*R,Z*)-3a (Table 1, entry 1): A yellow solid, 88% isolated yield of *Z/E* products. The *ee* was determined by HPLC analysis [Chiralpak IA, 70:30 *n*-hexane/*i*PrOH, 1.0 mL/min; *t_r* (major) = 18.95 min, *t_r* (minor) = 12.09 min]. [α]_D²⁵ = -3.846 (c = 0.31 in CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ = 2.29 (s, 3H), 3.14 - 3.18 (dd, *J* = 12.0, 7.2 Hz, 1H), 3.28 - 3.34 (dd, *J* = 16.8, 6.8 Hz, 1H), 3.50 - 3.56 (dd, *J* = 16.8, 6.8 Hz, 1H), 3.84 - 3.92 (m, 1H), 4.01 - 4.07 (m, 1H), 6.76 - 6.78 (d, *J* = 7.6, 1H), 6.95 - 6.99 (t, *J* = 7.6, 1H), 7.12 - 7.18 (dd, *J* = 16.0, 7.6 Hz, 2H), 7.25 - 7.31 (m, 4H), 7.39 - 7.45 (m, 4H), 7.79 - 7.81 (d, *J* = 7.2, 2H), 8.27 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ = 199.1, 169.5, 157.6, 144.6, 139.4, 137.1, 132.9, 128.4, 128.1, 128.0, 127.7, 126.7, 124.7, 124.3, 121.8, 109.3, 44.4, 41.6, 40.8, 23.6 ppm. ESI-HRMS: calcd for C₂₆H₂₃NO₂Na⁺, ([M + Na]⁺) 404.1621, found 404.1628.



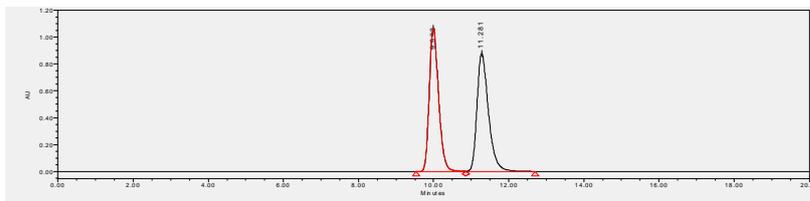
1	12.00	9589.02	49.7646
2	18.57	9679.74	50.2354



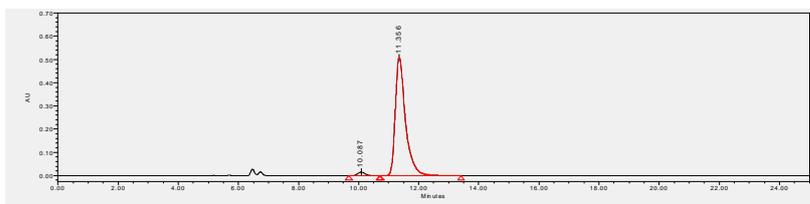
Peak	Retention Time	Area	% Area
1	12.09	144.47	2.1497
2	18.95	6576.03	97.8503



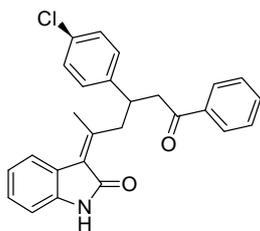
(R, Z)-3b (Table 1, entry 2): A yellow solid, 83% isolated yield of *Z/E* products. The ee was determined by HPLC analysis [Chiralpak IE, 70:30 *n*-hexane/*i*PrOH, 1.0 mL/min; t_r (major) = 11.35 min, t_r (minor) = 10.08 min]. $[\alpha]_D^{25} = -3.883$ ($c = 0.41$ in CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) $\delta = 2.29$ (s, 3H), 3.22 - 3.33 (m, 2H), 3.46 - 3.52 (dd, $J = 16.8, 6.0$ Hz, 1H), 3.84 - 3.93 (m, 2H), 6.75 - 6.77 (d, $J = 7.6$, 1H), 6.92 - 7.00 (m, 3H), 7.14 - 7.17 (t, $J = 7.6$, 1H), 7.30 - 7.36 (m, 4H), 7.41 - 7.48 (m, 2H), 7.80 - 7.82 (d, $J = 7.6$, 2H), 7.93 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3) $\delta = 198.9, 169.2, 162.8, 160.4, 157.1, 140.1, 139.3, 137.1, 133.0, 129.2, 129.1, 128.5, 128.1, 124.7, 124.4, 124.2, 121.9, 115.5, 115.2, 109.2, 44.6, 41.5, 40.0, 23.5$ ppm. ESI-HRMS: calcd for $\text{C}_{26}\text{H}_{22}\text{NO}_5\text{FNa}^+$, ($[\text{M} + \text{Na}]^+$) 422.1527, found 422.1533.



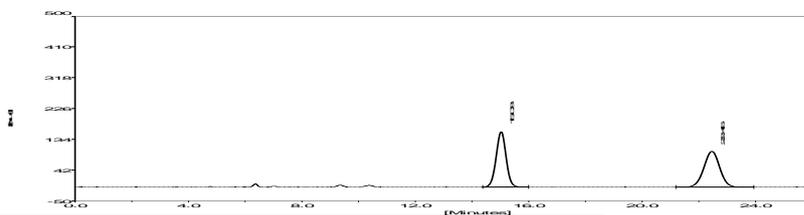
Peak	Retention Time	Area	% Area
1	9.993	18444018	49.62
2	11.281	18724117	50.38



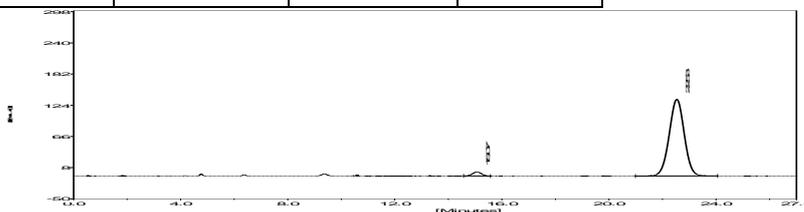
Peak	Retention Time	Area	% Area
1	10.087	278832	2.28
2	11.356	11971286	97.72



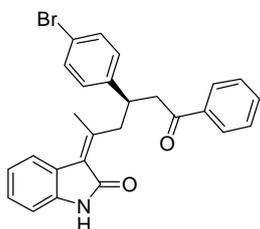
(R, Z)-3c (Table 1, entry 3): A yellow solid, 81% isolated yield of *Z/E* products. The ee was determined by HPLC analysis [Chiralpak IA, 70:30 *n*-hexane/*i*PrOH, 1.0 mL/min; t_r (major) = 22.53 min, t_r (minor) = 15.07 min]. $[\alpha]_D^{25} = -3.755$ ($c = 0.36$ in CH_2Cl_2). $^1\text{H NMR}$ (400 MHz, CDCl_3) $\delta = 2.28$ (s, 3H), 3.21 - 3.33 (m, 2H), 3.46 - 3.52 (dd, $J = 16.8, 6.0$ Hz, 1H), 3.82 - 3.94 (m, 2H), 6.76 - 6.78 (d, $J = 8.0$ Hz, 1H), 6.96 - 7.00 (t, $J = 7.6$ Hz, 1H), 7.14 - 7.17 (t, $J = 7.6$ Hz, 1H), 7.21 - 7.23 (m, 2H), 7.30 - 7.34 (m, 4H), 7.41 - 7.47 (m, 2H), 7.80 - 7.82 (d, $J = 8.0$ Hz, 2H), 8.12 (s, 1H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3) $\delta = 198.7, 169.4, 156.8, 143.0, 139.4, 137.0, 133.1, 132.3, 129.2, 128.5, 128.1, 124.6, 124.4, 124.2, 121.9, 109.3, 44.4, 41.4, 40.2, 23.7$ ppm. ESI-HRMS: calcd for $\text{C}_{26}\text{H}_{22}\text{NO}_5^{34.9689}\text{ClNa}^+$, ($[\text{M} + \text{Na}]^+$) 438.1231, found 438.1237, $\text{C}_{26}\text{H}_{22}\text{NO}_5^{36.9659}\text{ClNaS}^+$, ($[\text{M} + \text{Na}]^+$) 440.1202, found 440.1207.



Peak	Retention Time	Area	% Area
1	15.03	4006.89	49.2522
2	22.46	4128.57	50.7478

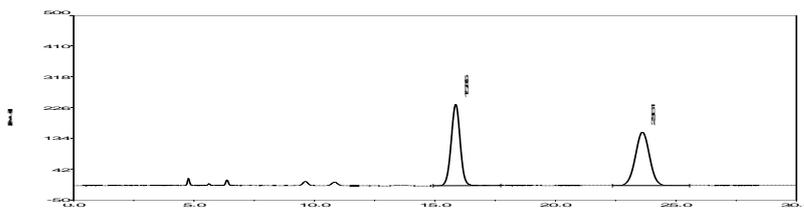


Peak	Retention Time	Area	% Area
1	15.07	174.87	3.0486
2	22.53	5561.20	96.9514

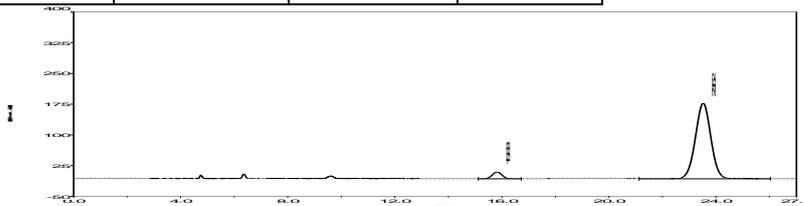


(R, Z)-3d (Table 1, entry 4): A yellow solid, 82% isolated yield of *Z/E* products. The ee was determined by HPLC analysis [Chiralpak IA, 70:30 *n*-hexane/*i*PrOH, 1.0 mL/min; t_r (major) = 23.52 min, t_r (minor) = 15.83 min]. $[\alpha]_D^{25} = -2.564$ ($c = 0.31$ in CH_2Cl_2). $^1\text{H NMR}$ (400 MHz, CDCl_3) $\delta = 2.29$ (s, 3H), 3.21 - 3.32 (m, 2H), 3.46 - 3.51 (dd, $J = 17.2, 6.0$ Hz, 1H), 3.82 - 3.92 (m, 2H), 6.75 - 6.77 (d, $J = 7.6$, 1H), 6.97 - 7.00 (t, $J = 8.0$, 1H), 7.14 - 7.18 (t, $J = 7.6$, 1H), 7.26 - 7.33 (m, 4H), 7.36 - 7.39 (m, 2H), 7.41 - 7.49 (m, 2H), 7.71 (s, 1H), 7.80 - 7.82 (d, $J = 7.6$, 2H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3) $\delta = 198.7, 169.1, 156.9, 143.6, 139.2, 137.0, 133.1, 131.7, 129.7, 128.5, 128.1, 124.7, 124.4, 124.2, 121.9, 120.4, 109.2, 100.1, 44.4, 41.2, 40.1, 23.5$ ppm. ESI-HRMS: calcd for $\text{C}_{26}\text{H}_{22}\text{NO}_5^{78.9183}\text{BrNa}^+$, ($[\text{M} + \text{Na}]^+$) 482.0726, found 482.0732,

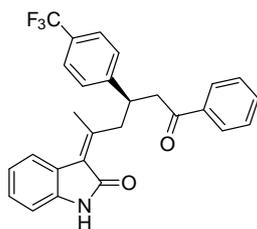
$C_{26}H_{22}NO_5^{80.9163}BrNa^+$, $([M + Na]^+)$ 484.0706, found 484.0724.



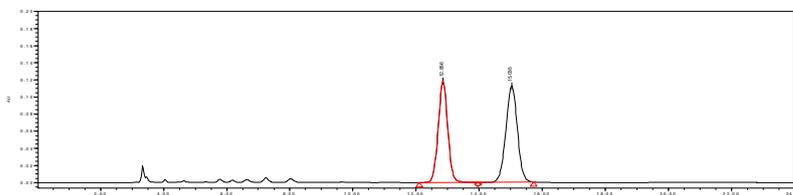
Peak	Retention Time	Area	% Area
1	15.86	6302.48	49.0509
2	23.61	6546.37	50.9491



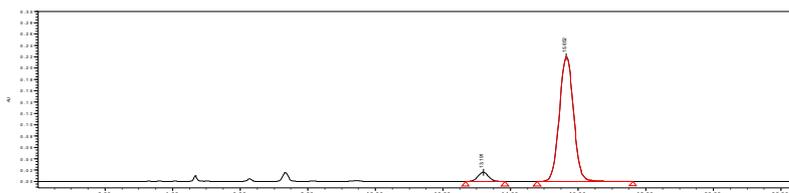
Peak	Retention Time	Area	% Area
1	15.83	382.46	4.8930
2	23.52	7434.08	95.1070



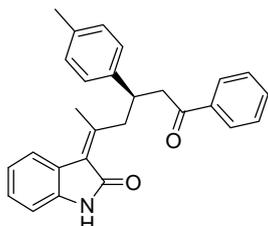
(*R, Z*)-3e (Table 1, entry 5): A yellow solid, 88% isolated yield of *Z/E* products. The ee was determined by HPLC analysis [Chiralpak IA, 70:30 *n*-hexane/*i*PrOH, 1.0 mL/min; t_r (major) = 15.65 min, t_r (minor) = 13.19 min]. $[\alpha]_D^{25} = -8.163$ ($c = 0.29$ in CH_2Cl_2). 1H NMR (400 MHz, $CDCl_3$) $\delta = 2.30$ (s, 3H), 3.20 - 3.24 (dd, $J = 10.6, 5.6$ Hz, 1H), 3.32 - 3.38 (m, 1H), 3.51 - 3.57 (m, 1H), 3.91 - 4.01 (m, 2H), 6.76 - 6.78 (d, $J = 8.0$, 1H), 6.97 - 7.01 (t, $J = 7.6$, 1H), 7.14 - 7.18 (t, $J = 7.6$, 1H), 7.42 - 7.46 (m, 2H), 7.53 (s, 4H), 7.80 - 7.82 (d, $J = 7.6$, 2H), 8.03 - 8.15 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 198.5, 169.3, 156.4, 148.7, 139.4, 136.9, 133.1, 129.1, 128.7, 128.6, 128.2, 128.1, 128.0, 125.6, 124.9, 124.4, 124.1, 123.0, 121.9, 109.3, 44.1, 41.2, 40.4, 23.6$ ppm. ESI-HRMS: calcd for $C_{27}H_{22}NO_2F_3Na^+$, $([M + Na]^+)$ 472.1495, found 472.1498.



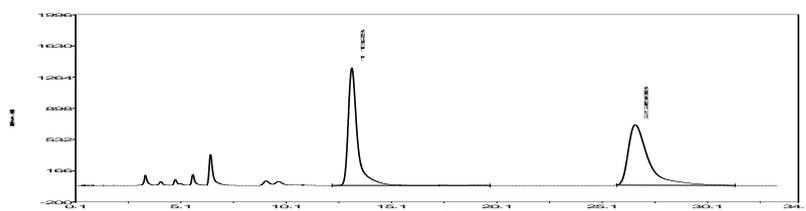
Peak	Retention Time	Area	% Area
1	12.856	2501879	48.38
2	15.035	2668964	51.62



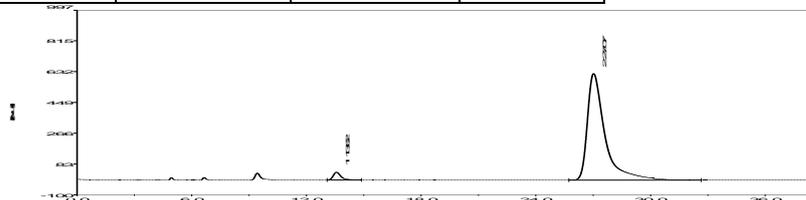
Peak	Retention Time	Area	% Area
1	13.191	358534	5.25
2	15.652	6464706	94.75



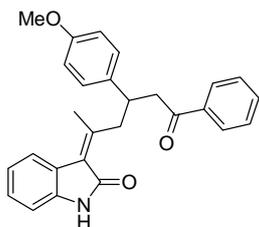
(*R, Z*)-3f (Table 1, entry 6): A yellow solid, 91% isolated yield of *Z/E* products. The ee was determined by HPLC analysis [Chiralpak IA, 70:30 *n*-hexane/*i*PrOH, 1.0 mL/min; t_r (major) = 27.07 min, t_r (minor) = 13.62 min]. $[\alpha]_D^{25} = -7.865$ ($c = 0.18$ in CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) $\delta = 2.28$ (s, 3H), 2.29 (s, 3H), 3.12 - 3.16 (dd, $J = 12.0, 7.2$ Hz, 1H), 3.25 - 3.31 (dd, $J = 16.8, 7.6$ Hz, 1H), 3.48 - 3.54 (dd, $J = 12.0, 7.2$ Hz, 1H), 3.81 - 3.85 (m, 1H), 4.00 - 4.05 (m, 1H), 6.75-6.77 (d, $J = 7.6$, 1H), 6.95 - 6.99 (t, $J = 7.6$, 1H), 7.07 - 7.09 (d, $J = 7.6$, 2H), 7.12 - 7.16 (t, $J = 7.6$, 1H), 7.26 - 7.30 (m, 4H), 7.41 - 7.43 (m, 2H), 7.79 - 7.80 (d, $J = 12.0, 7.2$ Hz, 2H), 8.21 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3) $\delta = 199.1, 169.5, 157.9, 164.3, 157.6, 141.6, 139.4, 137.2, 136.1, 132.8, 129.3, 128.4, 128.1, 127.9, 127.6, 124.6, 124.3, 121.8, 115.3, 109.2, 44.6, 41.7, 40.4, 23.6, 21.2$ ppm. ESI-HRMS: calcd for $\text{C}_{27}\text{H}_{25}\text{NO}_2\text{Na}^+$, ($[\text{M} + \text{Na}]^+$) 418.1778, found 418.1786.



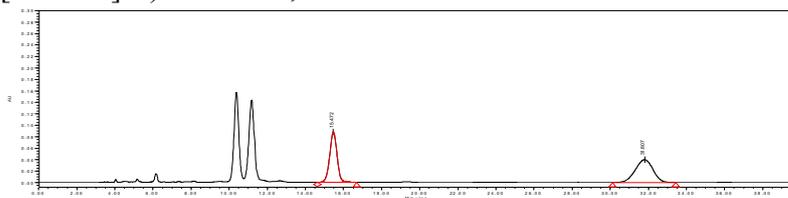
Peak	Retention Time	Area	% Area
1	13.23	41928.07	46.9522
2	26.68	47371.44	53.0478



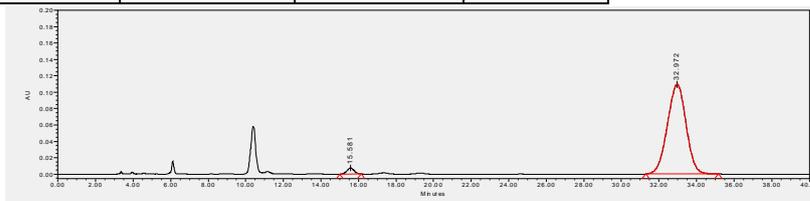
Peak	Retention Time	Area	% Area
1	13.62	1289.03	3.0842
2	27.07	40505.64	96.9158



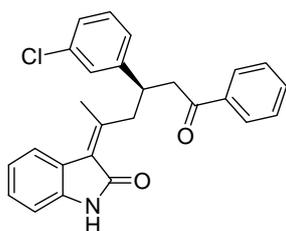
(Z)-3g (Table 1, entry 7): A yellow solid, 86% isolated yield of *Z/E* products. The ee was determined by HPLC analysis [Chiralpak IA, 70:30 *n*-hexane/*i*PrOH, 1.0 mL/min; t_r (major) = 32.97 min, t_r (minor) = 15.83 min]. ^1H NMR (400 MHz, CDCl_3) δ = 2.28 (s, 3H), 3.17 - 3.30 (m, 2H), 3.44 - 3.51 (m, 1H), 3.75 (s, 3H), 3.79 - 3.84 (m, 1H), 3.92 - 3.97 (m, 1H), 6.74 - 6.81 (m, 3H), 6.95 - 7.00 (m, 1H), 7.13 - 7.19 (m, 1H), 7.26 - 7.33 (m, 4H), 7.41 - 7.47 (m, 2H), 7.66 (s, 1H), 7.80 - 7.82 (d, 2H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ = 199.2, 169.1, 158.3, 157.9, 139.2, 137.2, 136.6, 132.9, 128.7, 128.5, 128.1, 127.9, 124.4, 121.8, 113.9, 109.1, 100.0, 55.3, 44.8, 41.7, 40.0, 23.6 ppm. ESI-HRMS: calcd for $\text{C}_{27}\text{H}_{25}\text{NO}_3\text{Na}^+$, ($[\text{M} + \text{Na}]^+$) 434.1727, found 434.1737.



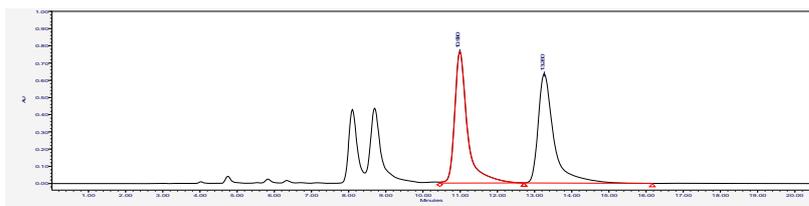
Peak	Retention Time	Area	% Area
1	15.472	2360673	48.05
2	31.807	2551932	51.95



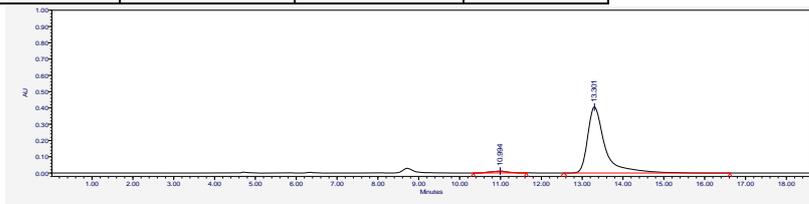
Peak	Retention Time	Area	% Area
1	15.581	196066	2.53
2	32.972	7545259	97.47



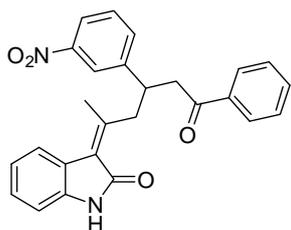
(R, Z)-3h (Table 1, entry 8): A yellow solid, 96% isolated yield of *Z/E* products. The ee was determined by HPLC analysis [Chiralpak IA, 70:30 *n*-hexane/*i*PrOH, 1.0 mL/min; t_r (major) = 13.30 min, t_r (minor) = 10.99 min]. $[\alpha]_D^{25} = -1.596$ ($c = 0.37$ in CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ = 2.30 (s, 3H), 3.12 - 3.17 (dd, $J = 12.0, 7.2$ Hz, 1H), 3.26 - 3.32 (dd, $J = 17.2, 7.2$ Hz, 1H), 3.49 - 3.55 (dd, $J = 17.2, 7.2$ Hz, 1H), 3.83 - 3.88 (m, 1H), 3.98 - 4.03 (m, 1H), 6.77 - 6.79 (d, $J = 7.6$, 1H), 6.96 - 7.00 (t, $J = 7.6$, 1H), 7.13 - 7.20 (m, 3H), 7.29 - 7.33 (m, 3H), 7.42 - 7.46 (m, 3H), 7.79 - 7.81 (d, $J = 7.6$, 2H), 8.26 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ = 198.9, 169.2, 162.8, 160.4, 157.1, 140.1, 139.3, 137.1, 133.0, 129.2, 129.1, 128.5, 128.1, 124.6, 124.4, 124.2, 121.9, 115.5, 115.2, 109.2, 44.6, 41.5, 40.0, 23.5 ppm. ESI-HRMS: calcd for $\text{C}_{26}\text{H}_{22}\text{NO}_5^{34.9689}\text{ClNa}^+$, ($[\text{M} + \text{Na}]^+$) 438.1231, found 438.1243, $\text{C}_{26}\text{H}_{22}\text{NO}_2^{36.9659}\text{ClNaS}^+$, ($[\text{M} + \text{Na}]^+$) 440.1202, found 440.1224.



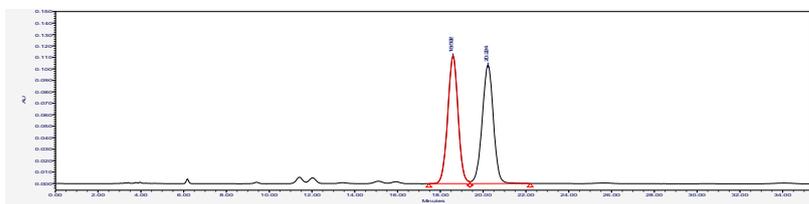
Peak	Retention Time	Area	% Area
1	10.990	18208126	49.45
2	13.260	18612084	50.55



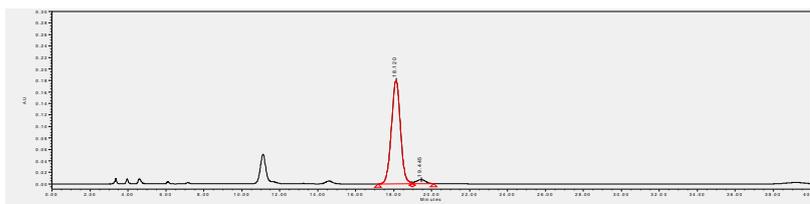
Peak	Retention Time	Area	% Area
1	10.994	326238	2.64
2	13.301	12012001	97.36



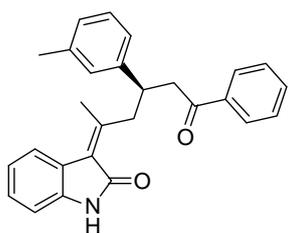
(Z)-3i (Table 1, entry 9): A yellow solid, 81% isolated yield of *Z/E* products. The ee was determined by HPLC analysis [Chiralpak IA, 70:30 *n*-hexane/*i*PrOH, 1.0 mL/min; t_r (major) = 18.12 min, t_r (minor) = 19.44 min]. ^1H NMR (400 MHz, CDCl_3) δ = 2.32 (s, 3H), 3.34 - 3.43 (m, 2H), 3.54 - 3.60 (m, 1H), 3.85 - 3.90 (m, 1H), 4.00 - 4.04 (m, 1H), 6.76 - 6.78 (m, 1H), 6.97 - 7.00 (m, 1H), 7.12 - 7.19 (m, 1H), 7.33 - 7.37 (t, 2H), 7.41 - 7.48 (m, 3H), 7.72 - 7.77 (m, 2H), 7.82 - 7.84 (m, 2H), 8.02 - 8.04 (d, 1H), 8.29 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ = 198.2, 169.0, 155.6, 148.4, 146.6, 139.3, 136.8, 134.3, 133.3, 129.5, 128.9, 128.6, 128.4, 128.1, 125.1, 124.5, 124.0, 122.8, 122.0, 121.9, 109.3, 44.0, 41.1, 40.3, 23.5 ppm. ESI-HRMS: calcd for $\text{C}_{26}\text{H}_{22}\text{N}_2\text{O}_4\text{Na}^+$, ($[\text{M} + \text{Na}]^+$) 449.1472, found 449.1476.



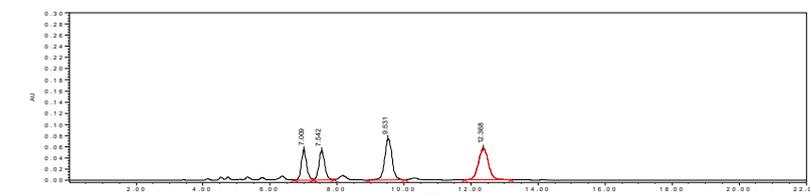
Peak	Retention Time	Area	% Area
1	18.592	3761555	49.92
2	20.224	3773316	50.08



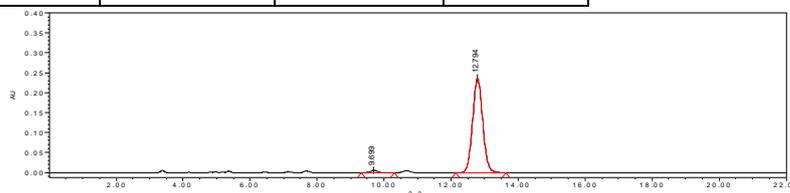
Peak	Retention Time	Area	% Area
1	18.120	5983152	95.99
2	19.445	250237	4.01



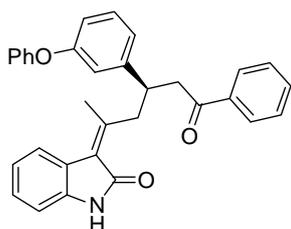
(*R*, *Z*)-3j (Table 1, entry 10): A yellow solid, 91% isolated yield of *Z/E* products. The ee was determined by HPLC analysis [Chiralpak IA, 70:30 *n*-hexane/*i*PrOH, 1.0 mL/min; t_r (major) = 12.79 min, t_r (minor) = 9.69 min]. $[\alpha]_D^{25} = -3.755$ ($c = 0.51$ in CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ = 2.30 (s, 3H), 2.31 (s, 3H), 3.04 - 3.08 (dd, $J = 12.0, 6.8$ Hz, 1H), 3.24 - 3.30 (dd, $J = 16.8, 6.8$ Hz, 1H), 3.50 - 3.56 (dd, $J = 16.8, 6.8$ Hz, 1H), 3.82 - 3.89 (m, 1H), 4.08 - 4.13 (dd, $J = 12.0, 8.8$ Hz, 1H), 6.74-6.76 (d, $J = 7.6$, 1H), 6.95 - 6.99 (t, $J = 7.6$, 2H), 7.12 - 7.21 (m, 4H), 7.26 - 7.30 (m, 2H), 7.40 - 7.44 (t, $J = 7.2$, 2H), 7.78 - 7.80 (d, $J = 7.6$, 2H), 8.09 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ = 199.3, 169.5, 157.6, 144.6, 143.6, 139.3, 138.1, 137.2, 128.5, 128.5, 128.4, 128.1, 127.9, 127.4, 124.7, 124.6, 124.4, 124.3, 121.8, 109.4, 44.4, 41.7, 40.7, 23.6, 21.7 ppm. ESI-HRMS: calcd for $\text{C}_{27}\text{H}_{25}\text{NO}_2\text{Na}^+$, ($[\text{M} + \text{Na}]^+$) 418.1778, found 418.1788.



Peak	Retention Time	Area	% Area
1	9.531	1136003	49.20
2	12.368	1172869	50.80

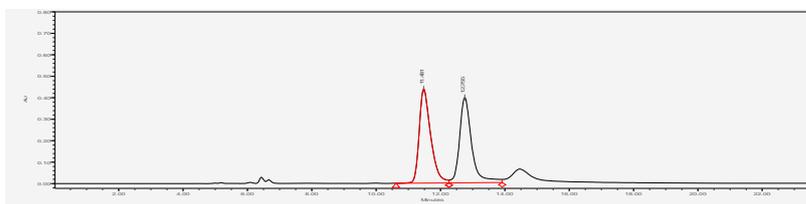


Peak	Retention Time	Area	% Area
1	9.699	93511	1.83
2	12.794	5010399	98.17

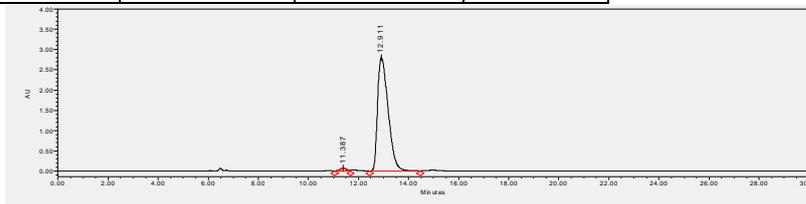


(R, Z)-3k (Table 1, entry 11): A yellow solid, 88% isolated yield of *Z/E* products. The ee was determined by HPLC analysis [Chiralpak IA, 70:30 *n*-hexane/*i*PrOH, 1.0 mL/min; t_r (major) = 12.91 min, t_r (minor) = 11.38 min]. $[\alpha]_D^{25} = -17.018$ ($c = 0.47$ in CH_2Cl_2). $^1\text{H NMR}$ (400 MHz, CDCl_3)

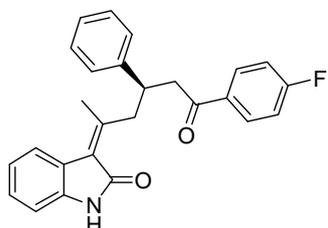
$\delta = 2.29$ (s, 3H), 3.26 - 3.36 (m, 2H), 3.47 - 3.53 (dd, $J = 16.8, 6.0$ Hz, 1H), 3.81 - 3.92 (m, 2H), 6.76 - 6.80 (t, $J = 16.8, 2\text{H}$), 6.85-6.87 (d, $J = 8.0, 2\text{H}$), 6.96 - 7.04 (m, 2H), 7.07 (s, 1H), 7.12 - 7.25 (m, 5H), 7.29 - 7.33 (m, 2H), 7.41 - 7.46 (m, 2H), 7.80 - 7.82 (m, 2H), 8.42 (s, 1H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3) $\delta = 198.9, 169.5, 157.6, 157.1, 157.0, 146.6, 143.6, 139.5, 137.1, 133.0, 129.9, 129.7, 128.0, 124.8, 124.3, 124.2, 122.9, 121.8, 118.7, 118.5, 117.4, 109.4, 44.4, 41.4, 40.7, 23.6$ ppm. ESI-HRMS: calcd for $\text{C}_{32}\text{H}_{27}\text{NO}_3\text{Na}^+$, ($[\text{M} + \text{Na}]^+$) 496.1883, found 496.1885.



Peak	Retention Time	Area	% Area
1	11.481	10870509	51.05
2	12.755	10423169	48.95



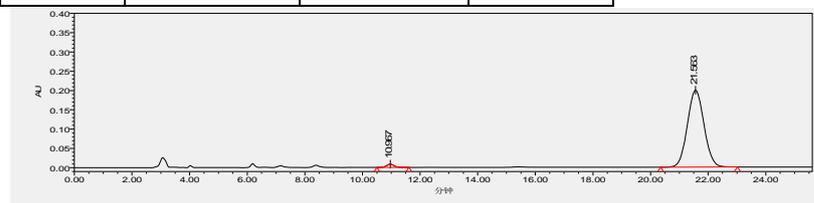
Peak	Retention Time	Area	% Area
1	11.387	1374684	1.64
2	12.911	82304860	98.36



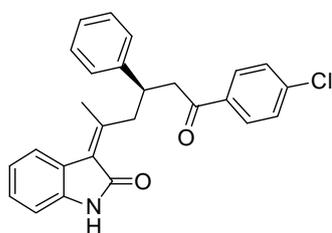
(R, Z)-3l (Table 1, entry 12): A yellow solid, 96% isolated yield of *Z/E* products. The ee was determined by HPLC analysis [Chiralpak IA, 70:30 *n*-hexane/*i*PrOH, 1.0 mL/min; t_r (major) = 21.56 min, t_r (minor) = 10.96 min]. $[\alpha]_D^{25} = -3.883$ ($c = 0.41$ in CH_2Cl_2). $^1\text{H NMR}$ (400 MHz, CDCl_3) $\delta = 2.28$ (s, 3H), 3.05 - 3.10 (dd, $J = 12.0, 7.2$ Hz, 1H), 3.21 - 3.26 (dd, $J = 16.8, 6.8$ Hz, 1H), 3.49 - 3.55 (dd, $J = 16.8, 6.8$ Hz, 1H), 3.83 - 3.91 (m, 1H), 4.09 - 4.14 (m, 1H), 6.76 - 6.78 (d, $J = 7.6$ Hz, 1H), 6.91 - 6.99 (m, 2H), 7.13 - 7.19 (dd, $J = 16.4, 7.6$ Hz, 2H), 7.26 - 7.30 (m, 2H), 7.38 - 7.42 (m, 3H), 7.78 - 7.82 (m, 2H), 8.37 (s, 1H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3) $\delta = 197.4, 169.6, 166.9, 164.3, 157.6, 144.6, 139.4, 130.7, 124.7, 121.8, 115.3, 109.2, 44.2, 41.7, 41.0$.

23.7 ppm. ESI-HRMS: calcd for $C_{26}H_{22}NO_2FNa^+$, $([M + Na]^+)$ 422.1527, found 422.1539.

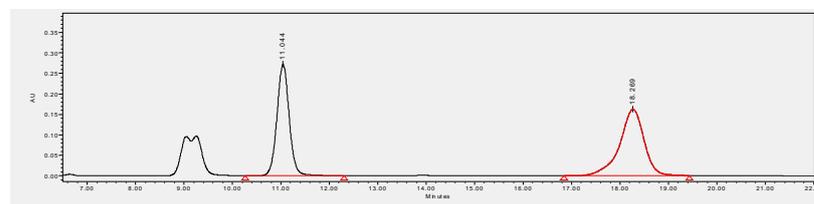
Peak	Retention Time	Area	% Area
1	10.888	6416106	48.79
2	21.146	6734385	51.21



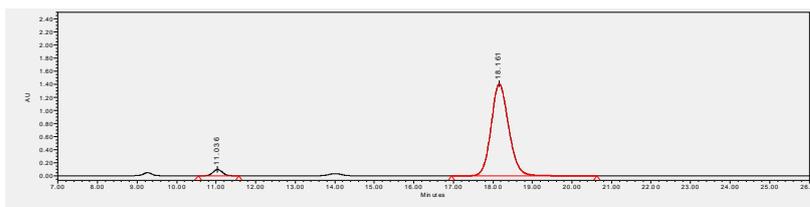
Peak	Retention Time	Area	% Area
1	10.967	148488	1.83
2	21.563	7984898	98.17



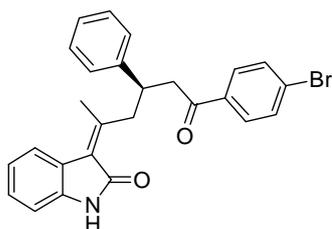
(R, Z)-3m (Table 1, entry 13): A yellow solid, 83% isolated yield of *Z/E* products. The ee was determined by HPLC analysis [Chiralpak IA, 70:30 *n*-hexane/*i*PrOH, 1.0 mL/min; t_r (major) = 18.16 min, t_r (minor) = 11.03 min]. $[\alpha]_D^{25} = -1.750$ ($c = 0.40$ in CH_2Cl_2). 1H NMR (400 MHz, $CDCl_3$) $\delta = 2.27$ (s, 3H), 3.00 - 3.21 (dd, $J = 12.0, 6.8$ Hz, 1H), 3.17 - 3.23 (dd, $J = 16.8, 6.8$ Hz, 1H), 3.51 - 3.57 (dd, $J = 16.8, 6.8$ Hz, 1H), 3.82 - 3.90 (m, 1H), 4.11 - 4.16 (dd, $J = 12.0, 8.8$ Hz, 1H), 6.75 - 6.77 (d, $J = 7.6$, 1H), 6.96 - 7.00 (t, $J = 7.6$, 1H), 7.14 - 7.20 (dd, $J = 16.0, 7.6$, 2H), 7.22 - 7.30 (m, 4H), 7.38 - 7.42 (m, 3H), 7.69 - 7.71 (d, $J = 8.4$, 2H), 7.97 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 197.8, 169.3, 157.6, 144.5, 139.2, 135.4, 129.5, 128.7, 127.3, 126.8, 124.7, 124.4, 124.2, 121.9, 109.2, 44.2, 41.7, 41.0, 23.7$ ppm. ESI-HRMS: calcd for $C_{26}H_{22}NO_2^{34.9689}CINaS^+$, $([M + Na]^+)$ 438.1231, found 438.1238, $C_{26}H_{22}NO_2^{36.9659}CINaS^+$, $([M + Na]^+)$ 4440.1202, found 440.1218.



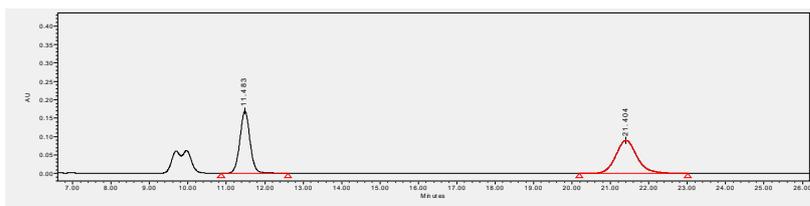
Peak	Retention Time	Area	% Area
1	11.044	4779938	47.16
2	18.269	5355852	52.84



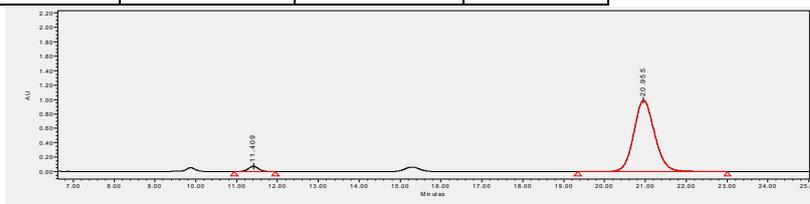
Peak	Retention Time	Area	% Area
1	11.036	1613336	3.59
2	18.161	43309887	96.41



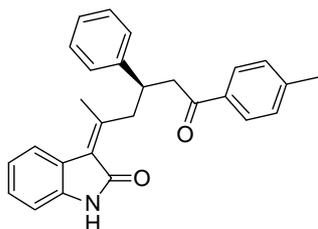
(*R, Z*)-3n (Table 1, entry 14): A yellow solid, 73% isolated yield of *Z/E* products. The ee was determined by HPLC analysis [Chiralpak IA, 70:30 *n*-hexane/*i*PrOH, 1.0 mL/min; t_r (major) = 20.95 min, t_r (minor) = 11.40 min]. $[\alpha]_D^{25} = -2.222$ ($c = 0.27$ in CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) $\delta = 2.27$ (s, 3H), 2.98 - 3.03 (dd, $J = 12.4, 6.8$ Hz, 1H), 3.15 - 3.21 (dd, $J = 16.4, 6.4$ Hz, 1H), 3.51 - 3.57 (dd, $J = 16.4, 7.2$ Hz, 1H), 3.82 - 3.90 (m, 1H), 4.11 - 4.16 (dd, $J = 12.0, 8.8$ Hz, 1H), 6.74 - 6.76 (d, $J = 8.0$ Hz, 1H), 6.96 - 7.00 (t, $J = 7.6$ Hz, 1H), 7.14 - 7.20 (dd, $J = 15.6, 7.6$ Hz, 2H), 7.26 - 7.30 (m, 2H), 7.38 - 7.41 (m, 5H), 7.61 - 7.63 (d, $J = 8.8$ Hz, 2H), 7.84 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3) $\delta = 198.0, 169.2, 157.6, 144.5, 139.2, 135.8, 131.6, 129.6, 128.7, 127.7, 126.8, 124.7, 124.4, 124.2, 121.9, 109.2, 44.2, 41.8, 41.0, 23.7$ ppm. ESI-HRMS: calcd for $\text{C}_{26}\text{H}_{22}\text{NO}_2^{78,9183}\text{BrNa}^+$, ($[\text{M} + \text{Na}]^+$) 482.0726, found 482.0737, $\text{C}_{26}\text{H}_{22}\text{NO}_5^{80,9163}\text{BrNa}^+$, ($[\text{M} + \text{Na}]^+$) 484.0706, found 484.0725.



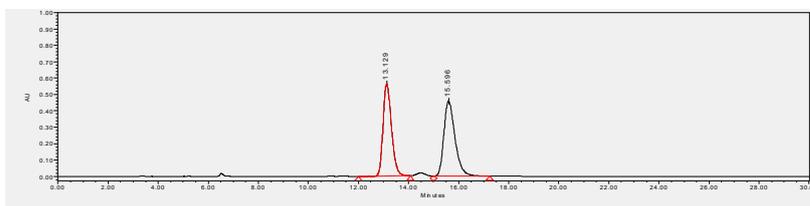
Peak	Retention Time	Area	% Area
1	11.483	3128504	47.48
2	21.404	3460021	52.52



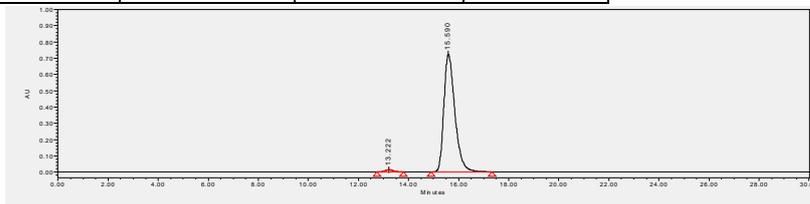
Peak	Retention Time	Area	% Area
1	11.409	1257735	3.48
2	20.955	34836487	96.52



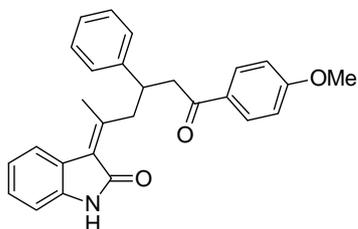
(R, Z)-3o (Table 1, entry 15): A yellow solid, 67% isolated yield of *Z/E* products. The ee was determined by HPLC analysis [Chiralpak IE, 70:30 *n*-hexane/*i*PrOH, 1.0 mL/min; t_r (major) = 15.59 min, t_r (minor) = 13.22 min]. $[\alpha]_D^{25} = -2.837$ ($c = 0.28$ in CH_2Cl_2). $^1\text{H NMR}$ (400 MHz, CDCl_3) $\delta = 2.29$ (s, 3H), 2.32 (s, 3H), 3.19 - 3.31 (m, 2H), 3.46 - 3.52 (dd, $J = 16.8, 6.7$ Hz, 1H), 3.83 - 3.91 (m, 1H), 3.96 - 4.01 (dd, $J = 12.4, 6.8$ Hz, 1H), 6.75-6.77 (d, $J = 7.6$, 1H), 6.95 - 6.98 (t, $J = 7.6$, 1H), 7.08 - 7.18 (m, 4H), 7.24 - 7.28 (m, 2H), 7.38 - 7.42 (m, 3H), 7.70 - 7.72 (d, $J = 8.0$, 2H), 8.02 (s, 1H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3) $\delta = 198.7, 169.3, 157.6, 144.7, 143.6, 139.3, 134.7, 129.1, 128.6, 128.2, 127.9, 127.7, 126.3, 124.6, 124.4, 124.3, 121.8, 109.1, 44.4, 41.5, 40.8, 23.6, 21.7$ ppm. ESI-HRMS: calcd for $\text{C}_{27}\text{H}_{25}\text{NO}_2\text{Na}^+$, ($[\text{M} + \text{Na}]^+$) 418.1778, found 418.1788.



Peak	Retention Time	Area	% Area
1	13.129	13192082	48.10
2	15.596	14234631	51.90

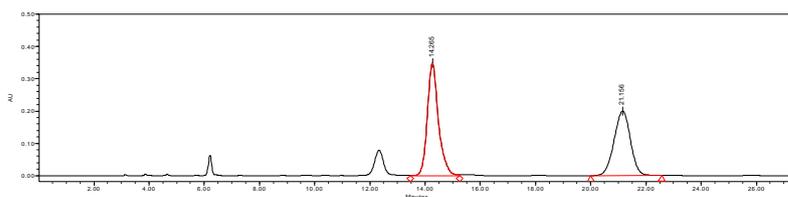


Peak	Retention Time	Area	% Area
1	13.222	312151	1.39
2	15.590	22166699	98.61

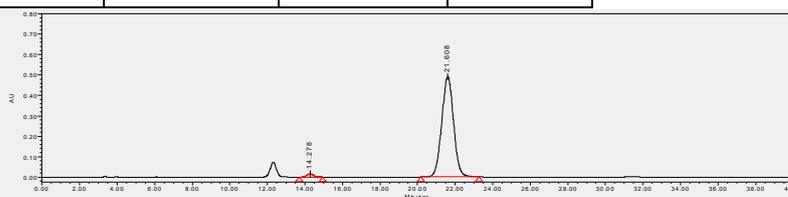


(Z)-3p (Table 1, entry 16): A yellow solid, 66% isolated yield of *Z/E* products. The ee was determined by HPLC analysis [Chiralpak IA, 70:30 *n*-hexane/*i*PrOH, 1.0 mL/min; t_r (major) = 21.60 min, t_r (minor) = 14.27 min]. $^1\text{H NMR}$ (400 MHz, CDCl_3) $\delta = 2.29$ (s, 3H), 3.14 - 3.26 (m, 2H), 3.45 - 3.51 (m, 1H), 3.77 (s, 3H), 3.83 - 3.91 (m, 1H), 4.01 - 4.06 (m, 1H), 6.73 - 6.78 (m, 3H), 6.94 - 7.00 (m, 1H), 7.12 - 7.17 (m, 2H), 7.24 - 7.28 (m, 3H), 7.39 - 7.42 (m, 2H), 7.77 - 7.79 (d, 2H), 8.47 (s, 1H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3) $\delta = 197.6, 169.6, 163.3, 157.7, 144.7, 139.5, 130.5, 130.3, 127.9, 127.6, 126.6, 124.7, 124.3, 121.7, 113.8, 113.5, 109.3, 55.5, 44.1, 41.6, 40.9, 23.6$ ppm. ESI-HRMS: calcd for $\text{C}_{27}\text{H}_{25}\text{NO}_3\text{Na}^+$,

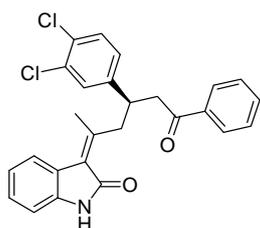
$([M + Na]^+)$ 434.1727, found 434.1726.



Peak	Retention Time	Area	% Area
1	14.265	8964696	51.89
2	21.156	8311059	48.11

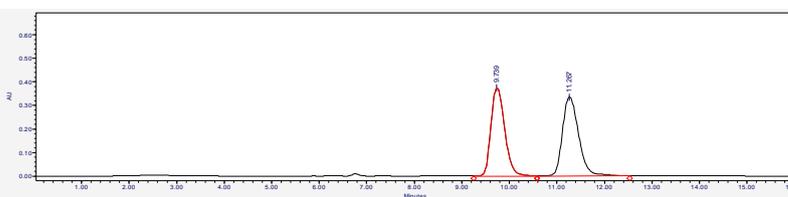


Peak	Retention Time	Area	% Area
1	14.278	406744	1.85
2	21.608	21533119	98.15

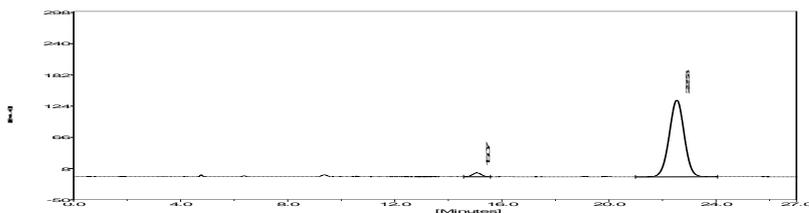


(*R*, *Z*)-3q (Table 1, entry 17): A yellow solid, 81% isolated yield of *Z/E* products. The ee was determined by HPLC analysis [Chiralpak IA, 70:30 *n*-hexane/*i*PrOH, 1.0 mL/min; t_r (major) = 11.15 min, t_r (minor) = 9.68 min]. $[\alpha]_D^{25} = -32.022$ ($c = 0.20$ in CH_2Cl_2). 1H NMR (400 MHz, $CDCl_3$) $\delta = 2.30$ (s,

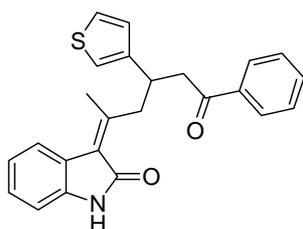
3H), 3.20 - 3.33 (m, 2H), 3.47 - 3.52 (dd, $J = 17.2, 6.0$ Hz, 1H), 3.83 - 3.93 (m, 2H), 6.78 - 6.80 (d, $J = 7.6$, 1H), 6.96 - 7.01 (t, $J = 7.6$, 1H), 7.14 - 7.18 (t, $J = 7.6$, 1H), 7.24 - 7.27 (m, 1H), 7.30 - 7.34 (m, 3H), 7.42 - 7.48 (m, 2H), 7.51 - 7.52 (m, 1H), 7.80 - 7.82 (m, 2H), 8.39 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 198.3, 169.5, 156.1, 144.9, 139.5, 136.8, 133.2, 132.5, 130.5, 129.8, 128.0, 127.3, 125.1, 124.4, 124.1, 121.9, 109.4, 44.1, 41.1, 39.9, 23.5$ ppm. ESI-HRMS: calcd for $C_{26}H_{21}NO_2^{34.9689}Cl_2Na^+$, $([M + Na]^+)$ 472.0842, found 472.0845, $C_{26}H_{21}NO_2^{36.9659}Cl_2Na^+$, $([M + Na]^+)$ 476.0783, found 476.0812.



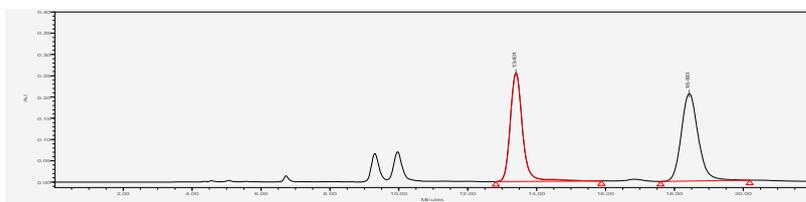
Peak	Retention Time	Area	% Area
1	9.739	7522802	48.56
2	11.267	7970374	51.44



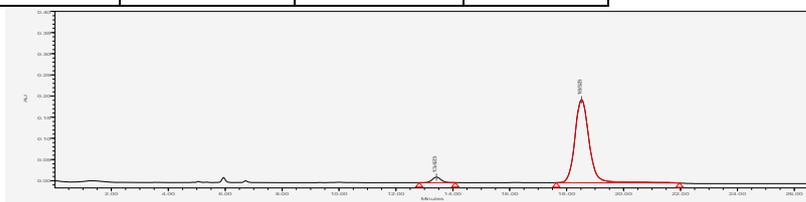
Peak	Retention Time	Area	% Area
1	9.685	773491	8.16
2	11.150	8709973	91.84



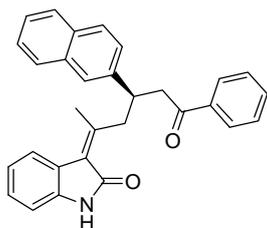
(Z)-3r (Table 1, entry 18): A yellow solid, 77% isolated yield of *Z/E* products. The ee was determined by HPLC analysis [Chiralpak IA, 70:30 *n*-hexane/*i*PrOH, 1.0 mL/min; t_r (major) = 18.52 min, t_r (minor) = 13.42 min]. $[\alpha]_D^{25} = -20.805$ ($c = 0.60$ in CH_2Cl_2). $^1\text{H NMR}$ (400 MHz, CDCl_3) $\delta = 2.32$ (s, 3H), 3.23 - 3.28 (m, 1H), 3.35 - 3.41 (m, 1H), 3.50 - 3.56 (m, 1H), 4.01 - 4.06 (m, 1H), 4.19 - 4.22 (m, 1H), 6.77 - 6.79 (d, $J = 7.6$ Hz, 1H), 6.86 - 6.89 (m, 1H), 6.95 - 7.00 (m, 2H), 7.09 - 7.11 (m, 1H), 7.13 - 7.17 (t, $J = 8.0$ Hz, 1H), 7.29 - 7.33 (t, $J = 7.6$ Hz, 2H), 7.43 - 7.47 (m, 2H), 7.82 - 7.84 (m, 2H), 8.36 (s, 1H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3) $\delta = 198.5, 169.4, 156.7, 148.2, 139.6, 137.0, 133.0, 128.5, 128.5, 128.1, 126.8, 124.9, 124.4, 124.2, 124.1, 123.3, 121.8, 109.4, 45.6, 42.5, 37.0, 23.5$ ppm. ESI-HRMS: calcd for $\text{C}_{24}\text{H}_{21}\text{NO}_2\text{SNa}^+$, ($[\text{M} + \text{Na}]^+$) 410.1185, found 410.1190.



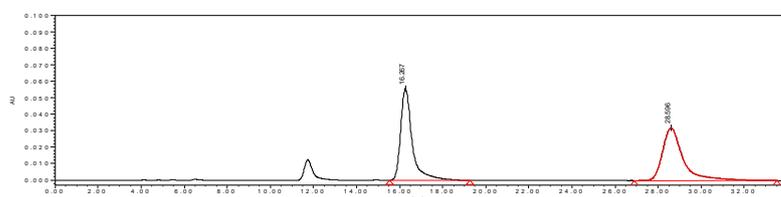
Peak	Retention Time	Area	% Area
1	13.401	6342157	47.41
2	18.433	7034758	52.59



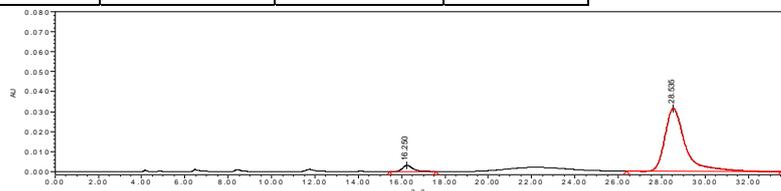
Peak	Retention Time	Area	% Area
1	13.423	280923	3.90
2	18.523	6918863	96.10



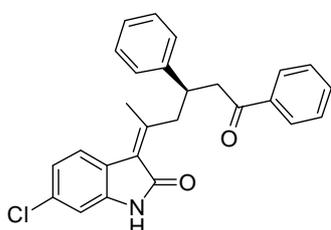
(R, Z)-3s (Table 1, entry 19): A yellow solid, 88% isolated yield of *Z/E* products. The ee was determined by HPLC analysis [Chiralpak IA, 70:30 *n*-hexane/*i*PrOH, 1.0 mL/min; t_r (major) = 28.53 min, t_r (minor) = 16.25 min]. $[\alpha]_D^{25} = -14.706$ ($c = 0.22$ in CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) $\delta = 2.31$ (s, 3H), 3.24 - 3.28 (dd, $J = 12.0, 6.8$ Hz, 1H), 3.37 - 3.43 (dd, $J = 16.8, 6.8$ Hz, 1H), 3.59 - 3.65 (dd, $J = 16.8, 6.8$ Hz, 1H), 4.05 - 4.16 (m, 2H), 6.76 - 6.75 (d, $J = 7.6$, 1H), 6.94 - 6.97 (t, $J = 7.6$, 1H), 7.11 - 7.15 (t, $J = 7.6$, 1H), 7.27 - 7.31 (t, $J = 7.6$, 2H), 7.40 - 7.44 (m, 4H), 7.58 - 7.61 (dd, $J = 8.4, 1.8$ Hz, 1H), 7.77 - 7.81 (m, 6H), 7.91 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3) $\delta = 197.0, 169.3, 157.5, 142.2, 139.3, 137.1, 133.6, 132.9, 132.5, 128.3, 128.0, 127.7, 126.2, 124.3, 121.6, 109.2, 44.5, 41.5, 40.9, 23.7$ ppm. ESI-HRMS: calcd for $\text{C}_{30}\text{H}_{25}\text{NO}_2\text{Na}^+$, ($[\text{M} + \text{Na}]^+$) 454.1778, found 454.1781.



Peak	Retention Time	Area	% Area
1	16.267	2070556	49.40
2	28.596	2121236	50.60

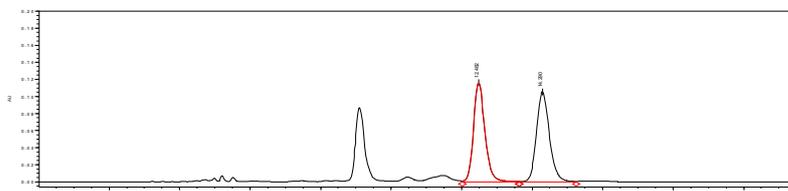


Peak	Retention Time	Area	% Area
1	16.250	98151	4.53
2	28.535	2068299	95.47

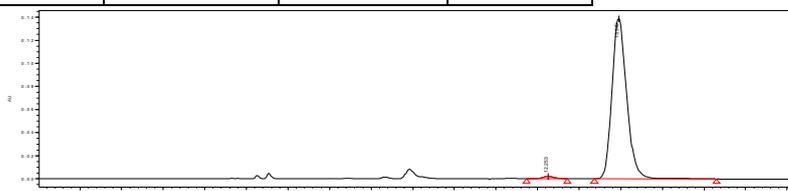


(R, Z)-3t (Table 1, entry 20): A yellow solid, 88% isolated yield of *Z/E* products. The ee was determined by HPLC analysis [Chiralpak IA, 70:30 *n*-hexane/*i*PrOH, 1.0 mL/min; t_r (major) = 13.94 min, t_r (minor) = 12.25 min]. $[\alpha]_D^{25} = -4.348$ ($c = 0.20$ in CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) $\delta = 2.30$ (s, 3H), 3.20 - 3.24 (m, 1H), 3.31 - 3.37 (dd, $J = 17.2, 5.2$ Hz, 1H), 3.51 - 3.56 (dd, $J = 17.2, 5.2$ Hz, 1H), 3.91 - 4.01 (m, 2H), 6.76 - 6.78 (d, $J = 7.6$, 1H), 6.97 - 7.01 (t, $J = 7.6$, 1H), 7.14 - 7.18 (t, $J = 7.6$, 1H), 7.31 - 7.34 (t, $J = 7.6$, 2H), 7.42 - 7.48 (m, 2H), 7.52 (s, 4H), 7.80 - 7.82 (d, $J = 7.6$, 2H), 7.98 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3) $\delta = 198.5, 168.9, 156.4, 148.7, 143.0, 139.3, 136.9, 133.1, 128.8, 128.6, 128.2, 128.1, 125.6, 124.9, 124.4, 124.1, 121.9, 109.3, 44.1, 41.2,$

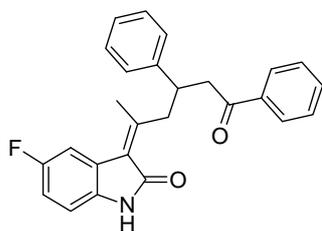
40.4, 23.5 ppm. ESI-HRMS: calcd for $C_{26}H_{22}NO_2^{34.9689}ClNa^+$, ($[M + Na]^+$) 438.1231, found 438.1230, $C_{26}H_{22}NO_2^{36.9659}ClNa^+$, ($[M + Na]^+$) 440.1202, found 440.1227.



Peak	Retention Time	Area	% Area
1	12.482	2613701	49.17
2	14.290	2702127	50.83

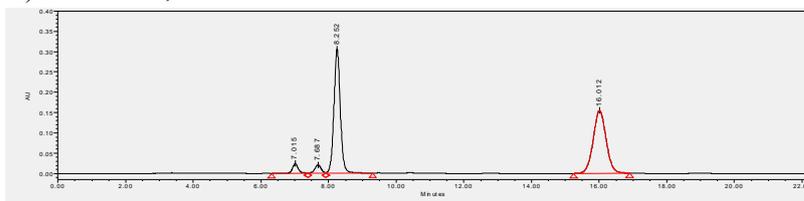


Peak	Retention Time	Area	% Area
1	12.253	42445	1.23
2	13.949	3420723	98.77

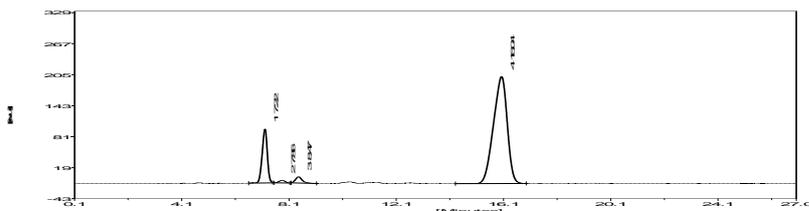


(Z)-3u (Table 1, entry 21): A yellow solid, 84% isolated yield of *Z/E* products. The ee was determined by HPLC analysis [Chiralpak IA, 70:30 *n*-hexane/*i*PrOH, 1.0 mL/min; t_r (major) = 16.04 min, t_r (minor) = 8.47 min]. $[\alpha]_D^{25} = -1.200$ (c = 0.46 in CH_2Cl_2). 1H NMR (400 MHz, $CDCl_3$) $\delta = 2.26$ (s, 3H), 3.17 - 3.22 (m, 1H), 3.25 - 3.31 (m, 1H), 3.53 - 3.59 (m, 1H), 3.87 - 3.91 (m, 1H), 3.98 - 4.03 (m, 1H), 6.65 - 6.68 (m, 1H), 6.83 - 6.87 (m, 1H), 7.13 - 7.19 (m, 2H), 7.26 - 7.32 (m, 5H), 7.38 - 7.44 (m, 3H), 7.80 - 7.82 (d, 2H), 8.40 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 198.9, 169.6, 159.7, 159.5, 157.4, 144.5, 137.1, 135.4, 133.0, 128.7, 128.0, 126.8, 125.1, 124.6, 114.2, 114.0, 111.8, 109.5, 109.4, 44.5, 41.7, 40.8, 23.6$ ppm. ESI-HRMS: calcd for $C_{26}H_{22}NO_2FNa^+$, ($[M + Na]^+$) 422.1527, found 422.1533.

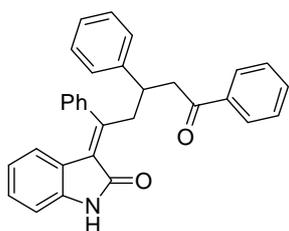
1H NMR (400 MHz, $CDCl_3$) $\delta = 2.26$ (s, 3H), 3.17 - 3.22 (m, 1H), 3.25 - 3.31 (m, 1H), 3.53 - 3.59 (m, 1H), 3.87 - 3.91 (m, 1H), 3.98 - 4.03 (m, 1H), 6.65 - 6.68 (m, 1H), 6.83 - 6.87 (m, 1H), 7.13 - 7.19 (m, 2H), 7.26 - 7.32 (m, 5H), 7.38 - 7.44 (m, 3H), 7.80 - 7.82 (d, 2H), 8.40 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 198.9, 169.6, 159.7, 159.5, 157.4, 144.5, 137.1, 135.4, 133.0, 128.7, 128.0, 126.8, 125.1, 124.6, 114.2, 114.0, 111.8, 109.5, 109.4, 44.5, 41.7, 40.8, 23.6$ ppm. ESI-HRMS: calcd for $C_{26}H_{22}NO_2FNa^+$, ($[M + Na]^+$) 422.1527, found 422.1533.



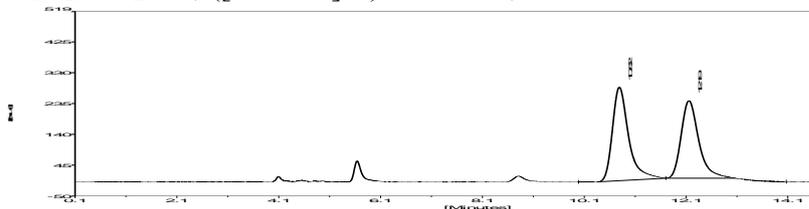
Peak	Retention Time	Area	% Area
1	7.015	289315	3.33
2	7.687	268782	3.09
3	8.252	4042197	46.50
4	16.012	4093498	47.09



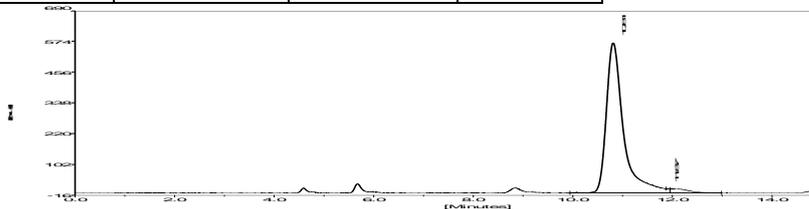
Peak	Retention Time	Area	% Area
1	7.22	1433.99	15.3334
2	7.86	80.74	0.8633
3	8.47	216.05	2.3102
4	16.04	7621.25	81.4930



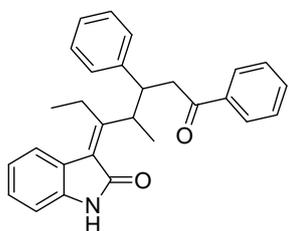
(Z)-3v (Table 1, entry 22): A yellow solid, 84% isolated yield of *Z/E* products. The ee was determined by HPLC analysis [Chiralpak IA, 70:30 *n*-hexane/*i*PrOH, 1.0 mL/min; t_r (major) = 11.87 min, t_r (minor) = 10.81 min]. $[\alpha]_D^{25} = 48.024$ ($c = 0.65$ in CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) $\delta = 3.33 - 3.56$ (m, 3H), 3.93 - 3.95 (m, 2H), 5.99 - 6.01 (d, $J = 7.6$ Hz, 1H), 6.53 - 6.57 (t, $J = 7.6$ Hz, 1H), 6.76 - 6.78 (d, $J = 7.6$ Hz, 1H), 6.96 - 7.04 (m, 2H), 7.09 - 7.13 (m, 1H), 7.18 - 7.21 (m, 2H), 7.24 - 7.27 (m, 2H), 7.32 - 7.34 (m, 2H), 7.40 - 7.48 (m, 4H), 7.81 - 7.83 (d, $J = 7.6$ Hz, 2H), 8.74 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3) $\delta = 199.1, 170.1, 158.0, 144.1, 139.7, 137.2, 133.0, 128.5, 128.1, 128.0, 127.3, 127.2, 126.6, 125.4, 123.5, 121.5, 109.3, 45.3, 39.8, 39.2$ ppm. ESI-HRMS: calcd for $\text{C}_{31}\text{H}_{25}\text{NO}_2\text{Na}^+$, ($[\text{M} + \text{Na}]^+$) 466.1778, found 466.1786.



Peak	Retention Time	Area	% Area
1	10.82	10870509	51.05
2	12.19	10423169	48.95

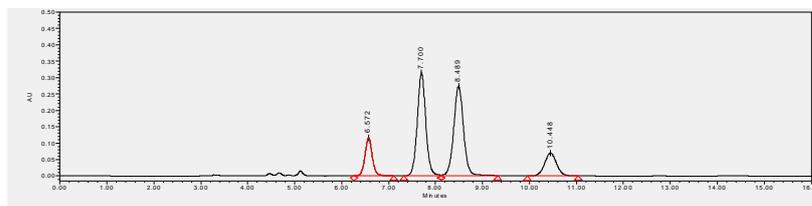


Peak	Retention Time	Area	% Area
1	10.81	13642.91	96.8661
2	11.87	441.39	3.1339

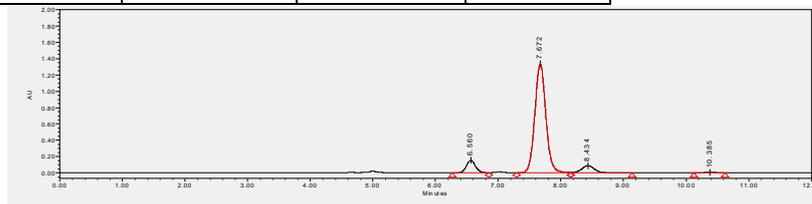


(Z)-3w (Table 1, entry 23): A yellow solid, 71% isolated yield of *Z/E* products. The ee was determined by HPLC

analysis [Chiralpak IA, 70:30 *n*-hexane/*i*PrOH, 1.0 mL/min; t_r (major) = 7.67 min, t_r (minor) = 8.43 min]. $[\alpha]_D^{25} = 53.807$ ($c = 0.40$ in CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) $\delta = 1.13 - 1.17$ (t, $J = 7.6$ Hz, 3H), 1.32 - 1.34 (d, $J = 6.8$ Hz 3H), 2.41 - 2.48 (m, 1H), 2.58 - 2.64 (m, 1H), 3.39 - 3.51 (m, 2H), 3.68 - 3.74 (m, 1H), 5.48 - 5.56 (m, 1H), 6.77 - 6.79 (d, $J = 8.0$ Hz, 1H), 6.90 - 6.96 (d, 2H), 7.02 - 7.06 (t, $J = 7.2$ Hz, 2H), 7.10 - 7.13 (t, $J = 7.2$ Hz, 1H), 7.24 - 7.26 (m, 3H), 7.37 - 7.40 (t, $J = 8.0$ Hz, 2H), 7.48 - 7.51 (t, $J = 7.6$ Hz, 1H), 7.84 - 7.86 (d, $J = 7.2$ Hz, 2H), 8.17 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3) $\delta = 199.4, 169.8, 168.8, 143.6, 137.4, 133.0, 128.5, 128.2, 128.1, 127.7, 126.4, 124.3, 123.6, 123.3, 121.8, 109.1, 45.4, 44.4, 38.7, 23.8, 17.6, 13.4$ ppm. ESI-HRMS: calcd for $\text{C}_{28}\text{H}_{27}\text{NO}_2\text{Na}^+$, ($[\text{M} + \text{Na}]^+$) 432.1934, found 432.1940.

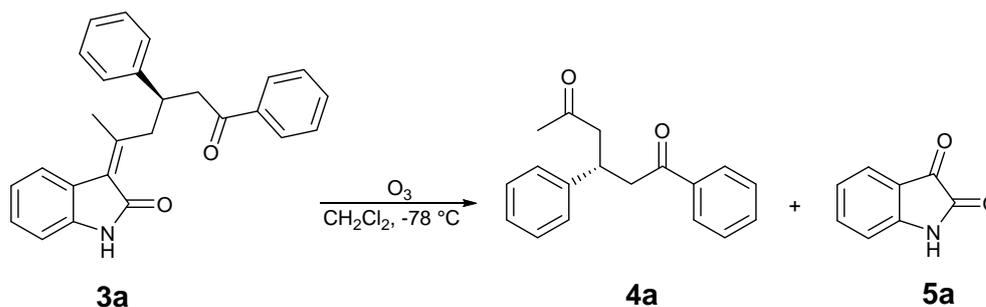


Peak	Retention Time	Area	% Area
1	6.572	1255275	11.99
2	7.700	3985548	38.08
3	8.489	3989355	38.12
4	10.448	1235879	11.81



Peak	Retention Time	Area	% Area
1	6.560	1594200	8.30
2	7.672	16335267	85.00
3	8.434	1197072	6.23
4	10.385	90802	0.47

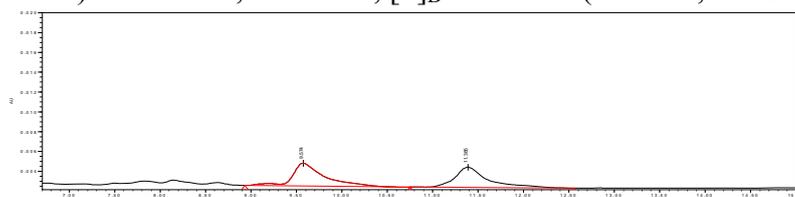
5. Determination of Absolute Configurations of the Products **3a**



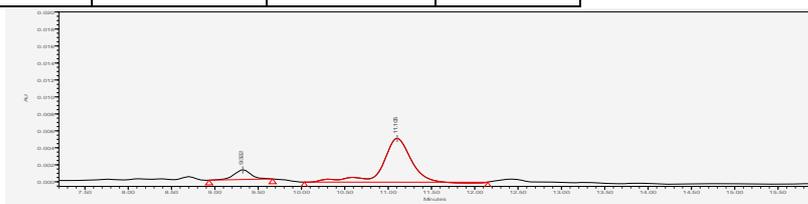
To a stirred solution of **3a** (19.1 mg, 0.05 mmol) in dichloromethane (10 mL) under

ozone atmosphere. The reaction mixture was stirred for indicated time at $-78\text{ }^{\circ}\text{C}$. After completion of the reaction, added PPh_3 to quench the reaction, the resulting solution was concentrated in vacuo and the obtained residue was purified by flash chromatography (petroleum ether/ethyl acetate, 8:1) to afford adduct **4a** with 73% yield.

The ^1H NMR spectrum of **4a** was consistent with the literature data. [4] The enantiomers of **4a** were analyzed by chiral phase HPLC using IC column at 254 nm (2-propanol : hexane = 20 : 80), flow rate = 1.0 mL/min, t_r (major) = 11.11 min, t_r (minor) = 9.32 min, $ee = 85\%$, $[\alpha]_{\text{D}}^{27} = -12.54$ ($c = 0.27$, in CHCl_3). (literature 4 : IC column at 254 nm (2-propanol : hexane = 20 : 80), 1.0 mL/min, t_r (major) = 12.5 min, t_r (minor) = 11.6 min, $ee = 95\%$, $[\alpha]_{\text{D}}^{25} = -10.3$ ($c = 1.00$, in CHCl_3) .

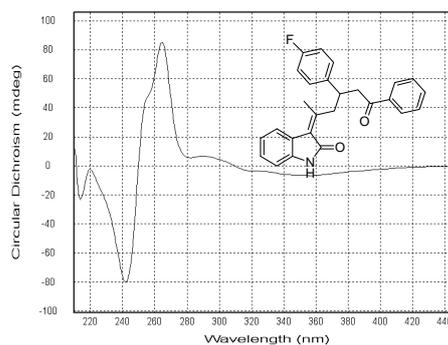
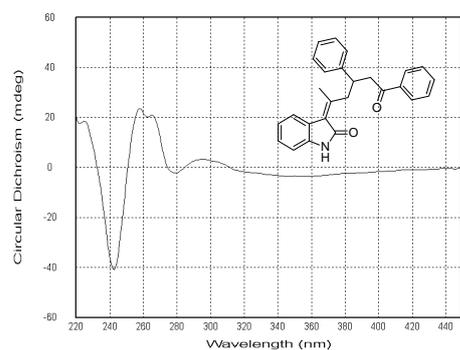


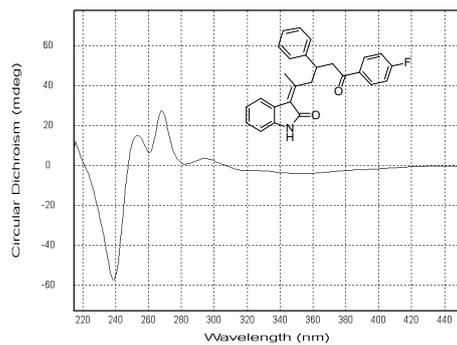
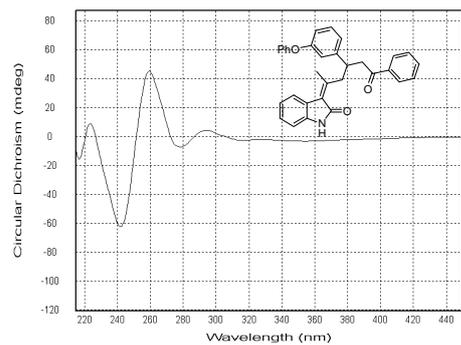
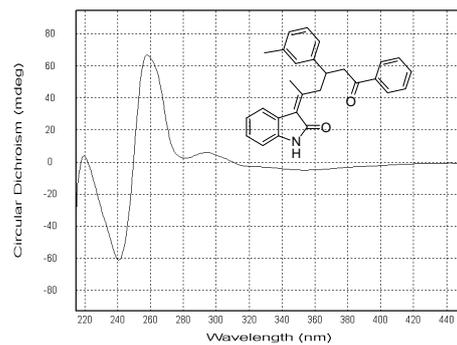
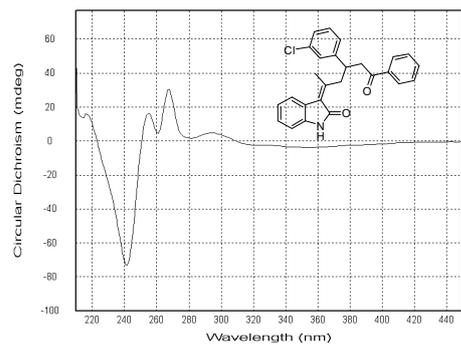
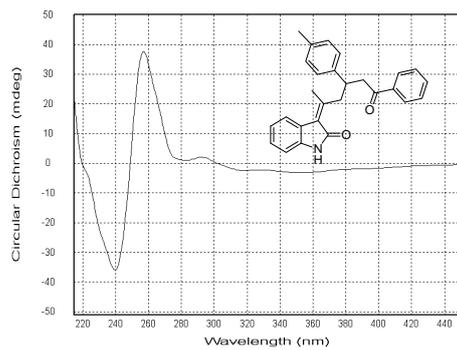
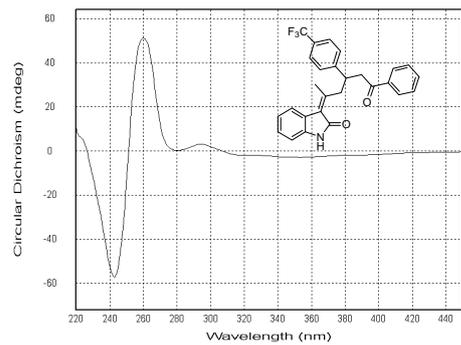
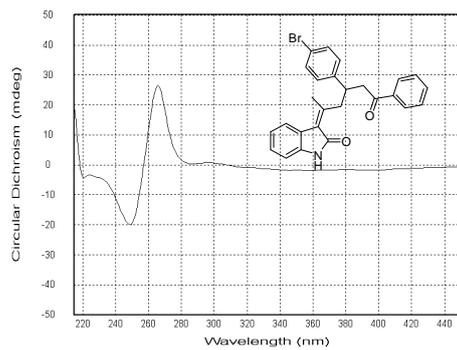
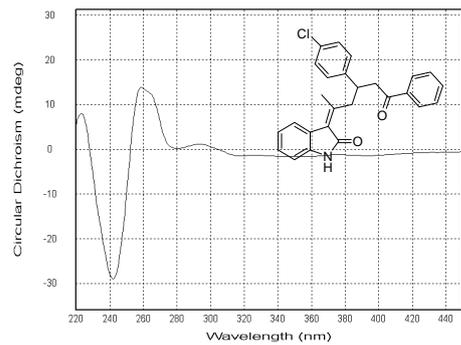
Peak	Retention Time	Area	% Area
1	9.574	57944	53.05
2	11.385	51277	46.95

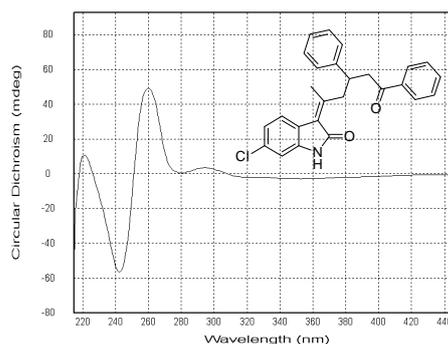
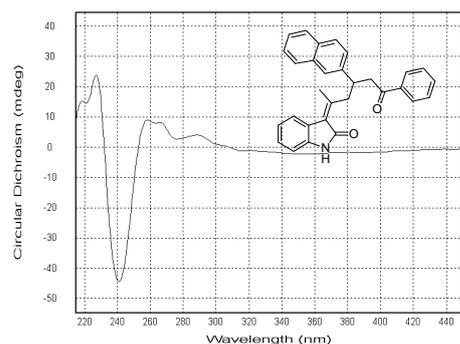
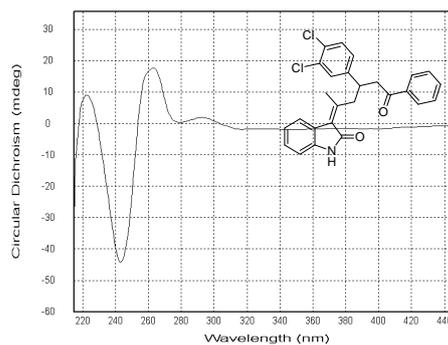
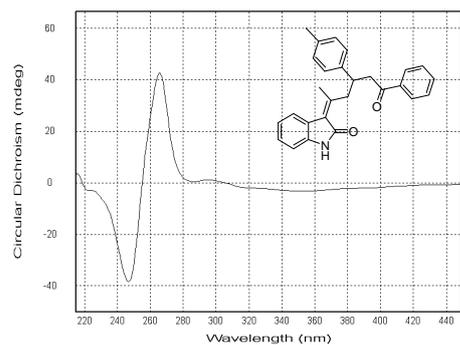
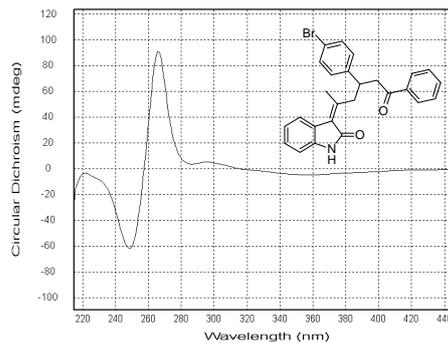
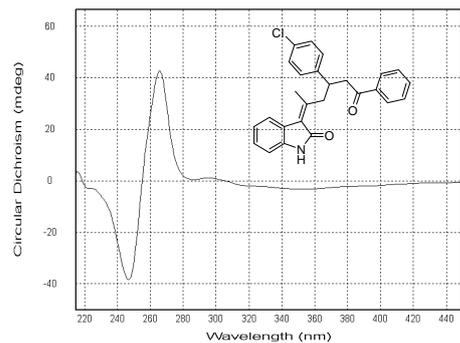


Peak	Retention Time	Area	% Area
1	9.322	9823	7.43
2	11.105	122375	92.57

6. CD spectra of the products 3







6. References:

1. C. Curti, G. Rassu, V. Zambrano, L. Pinna, A. Sartori, L. Battistini, F. Zanardi, G. Casiraghi, *Angew. Chem. Int. Ed.* 2012, **51**, 6200-6204.
2. D. H. Chen, Z. L. Chen, X. Xiao, Z. G. Yang, X. H. Liu, L. L. Lin, X. M. Feng, *Chem. Eur. J.* 2009, **12**, 6807-6810.
3. (a) Y. H. Wen, X. Huang, J. L. Huang, Y. Xiong, B. Qin, X. M. Feng, *Synlett* 2005, 2445-2448.
(b) J. L. Huang, J. Wang, X. H. Chen, Y. H. Wen, X. H. Liu, X. M. Feng, *Adv. Synth. Catal.* 2008, **350**, 287-294.
4. Y. K. Kang, H. J. Lee, H. W. Moon, D. Y. Kim, Y. K. Yang, H. J. Lee, *RSC Adv.* 2013, **3**, 1332-1335.

7. Copy of ^1H NMR and ^{13}C NMR spectra for products:

