Electronic Supplementary Material (ESI) for Chemical Communications.

Catalytic Asymmetric Desymmetrization of *N*-Arylmaleimides: Efficient Construction of Both Atom Chirality and Axial Chirality †

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Supporting Information

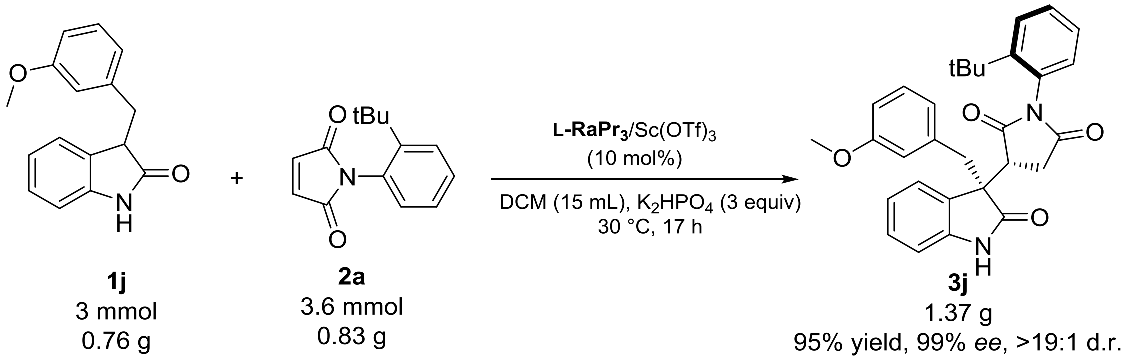
1. General remarks.

^1H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz), integration. ^{13}C NMR 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. Enantiomeric excesses were determined by chiral HPLC analysis on Daicel Chiralcel ODH, ASH, ID, in comparison with the authentic racemates. Optical rotations were reported as follows: $[\alpha]_D^T$ (c: g/100 mL, in solvent). HRMS was recorded on a commercial apparatus (ESI Source). All the solvents were purified by usual methods before use. CD spectra were determined by commercial instruments (DCM as the solvent). The *N,N'*-dioxide ligands were synthesized by the same procedure in the literature.[1]

2. General procedure for asymmetric Michael addition/ desymmetrization reaction.

In a test tube, a mixture of **L-RaPr$_3$** and $Sc(OTf)_3$ (10 mol%, 1:1), **1a** (0.1 mmol, 22.3 mg) in DCM (1 mL) were stirred at 30 ℃ for 0.5 hour. Then **2a** (0.12 mmol, 27.5 mg) and K_2HPO_4 (0.3 mmol, 51.2 mg) were added. The reaction mixture was stirred at 30 ℃ for 17h. After flash column chromatography (eluent: EtOAc/pet = 1/3), the pure product **3a** was obtained.

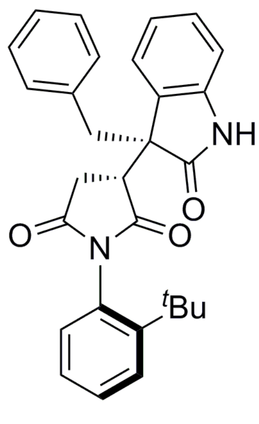
3. Experimental procedure for the gram-scale synthesis of 3j.



A mixture of **L-RaPr$_3$** (235.0 mg, 0.3 mmol), Sc(OTf)$_3$ (148.0 mg, 0.3 mmol) and **3j** (0.76 g, 3.0 mmol) in 15.0 mL DCM were stirred at 30 ℃ for 0.5 hour. Then **2a** (0.83 g, 3.6 mmol) was added, and the reaction continued stirring at 30 ℃ for 17 h. The product (1.37 g, 95% yield, 99% *ee*, >19:1 d.r.) was obtained as white solid after purification by flash chromatography on silica gel (EtOAc : pet = 1:3)

4. The analytical and spectral characterization data of the products.

(*M*)-(*R*)-3-((*R*)-3-benzyl-2-oxoindolin-3-yl)-1-(2-(tert-butyl)phenyl)pyrrolidine-2,5-dione



3a

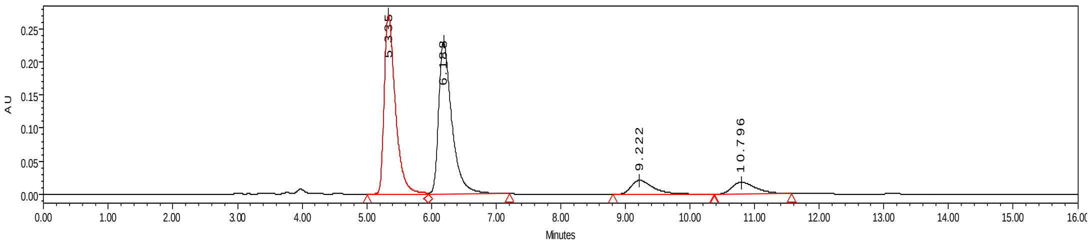
($C_{29}H_{28}N_2O_3$) colorless oil; 99% yield, 97% *ee*, >19:1 d.r. $[\alpha]_D^{20.7} = -12.36$ (c 0.696, CH_2Cl_2, 97% *ee*).

HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.335 min, 6.188 min, 9.222 min, 10.796 min.

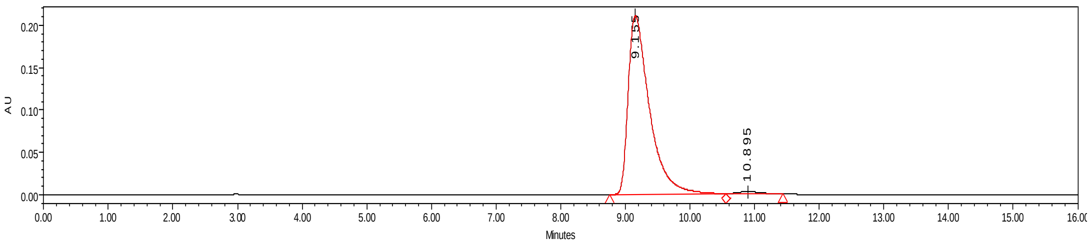
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.23 (m, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.33 – 7.27 (m, 1H), 7.23 (m, 1H), 7.15 – 7.01 (m, 6H), 6.94 (m, 2H), 6.51 (d, *J* = 4.0 Hz, 1H), 6.27 (s, 1H), 3.68 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.44 (d, *J* = 16.0 Hz, 1H), 3.38 (dd, *J* = 48.0, 16.0 Hz, 1H), 3.02 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.81 (d, *J* = 20.0 Hz, 1H), 1.27 (s, 9H).

^{13}C NMR (100 MHz, CDCl$_3$) δ = 178.53, 176.71, 176.09, 147.88, 141.56, 134.46, 130.46, 130.31, 130.14, 129.69, 129.22, 128.55, 128.33, 127.83, 127.47, 126.89, 123.61, 122.33, 110.60, 55.74, 45.23, 40.99, 35.62, 32.20, 31.66.

HRMS (ESI-TOF) calcd for $C_{29}H_{28}N_2O_3$ ([M+Na$^+$]) = 475.1992. Found 475.1992.

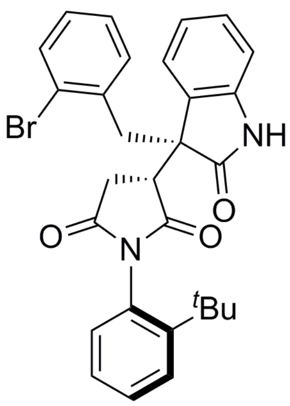


	Retention Time	Area	% Area
1	5.335	3248235	43.48
2	6.188	3263534	43.68
3	9.222	505447	6.77
4	10.796	453857	6.07



	Retention Time	Area	% Area
1	9.155	4870758	98.41
2	10.895	78691	1.59

(*M*)-(*R*)-3-((*R*)-3-(2-bromobenzyl)-2-oxoindolin-3-yl)-1-(2-(tert-butyl)phenyl)pyrrolidine-2,5-dione



3b

($C_{29}H_{27}BrN_2O_3$) colorless oil; 99% yield, 96% *ee*, >19:1 d.r. $[\alpha]_D^{20.6}$ = +50.30 (c 0.672, CH_2Cl_2, 96% *ee*).

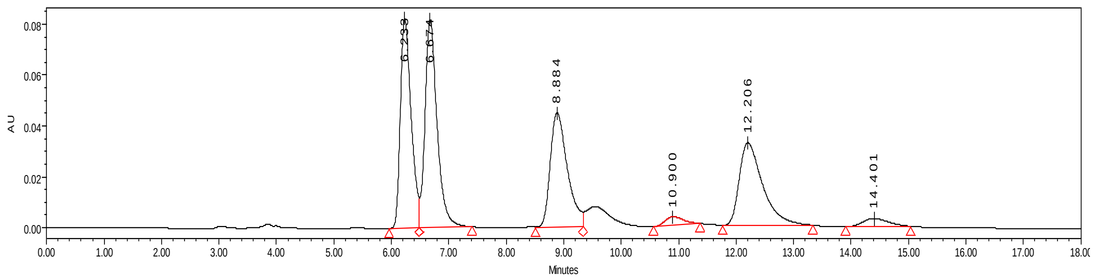
HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 6.233 min, 6.674 min, 8.884 min,10.900 min, 12.206 min, 14.401min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.35 (m, 2H), 7.29 (m, 3H), 7.13 – 7.00 (m, 3H), 6.98 – 6.89 (m, 2H), 6.47 (d,

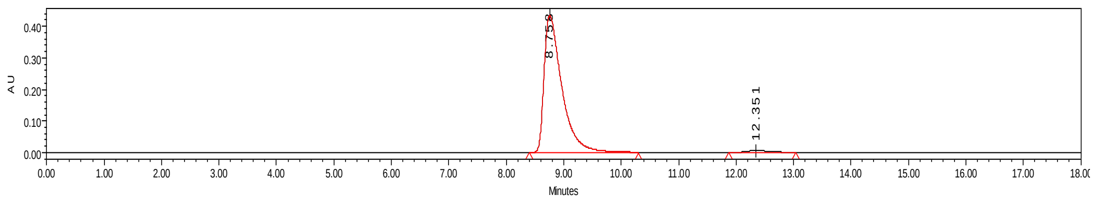
J = 8.0 Hz, 1H), 6.09 (s, 1H), 3.82 (d, J = 16.0 Hz, 1H), 3.74 (dd, J = 8.0, 4.0 Hz, 1H), 3.54 (d, J = 12.0 Hz, 1H), 3.05 (m, 2H), 1.26 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 179.00, 176.60, 175.97, 147.86, 141.34, 134.85, 132.77, 131.14, 130.35, 130.06, 129.70, 129.32, 128.67, 128.53, 127.44, 127.34, 125.89, 124.53, 122.15, 110.43, 55.55, 45.50, 39.26, 35.61, 32.37, 31.65.

HRMS (ESI-TOF) calcd for $C_{29}H_{27}Br^{78.9183}N_2O_3$ ($[M+Na^+]$) = 553.1097, Found 553.1108; $C_{29}H_{27}Br^{80.9163}N_2O_3$ ($[M+Na^+]$) = 555.1077, Found 555.1096.

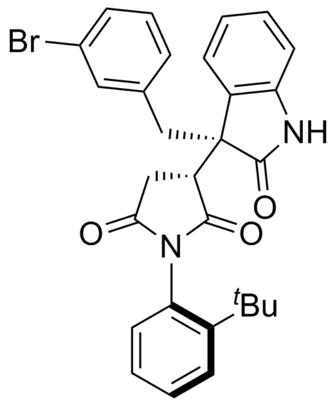


	Retention Time	Area	% Area
1	6.233	1076355	25.08
2	6.674	1188236	27.68
3	8.884	932757	21.73
4	10.900	75551	1.76
5	12.206	920046	21.43
6	14.401	99561	2.32



	Retention Time	Area	% Area
1	8.758	9286609	98.18
2	12.351	171817	1.82

(*M*)-(*R*)-3-((*R*)-3-(3-bromobenzyl)-2-oxoindolin-3-yl)-1-(2-(tert-butyl)phenyl)pyrrolidine-2,5-dione



3c

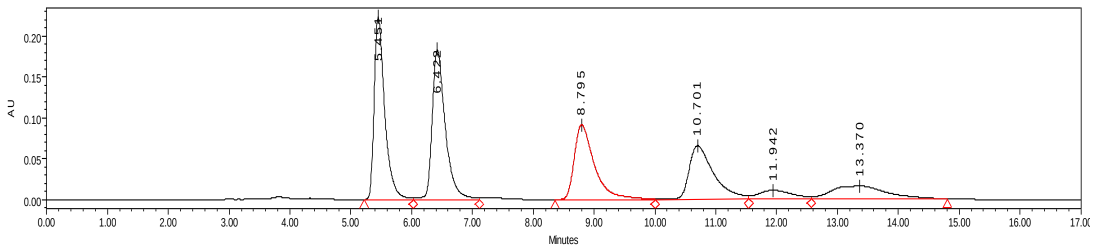
($C_{29}H_{27}BrN_2O_3$) colorless oil; 98% yield, 98% *ee*, >19:1 d.r. $[\alpha]_D^{20.6}$ = +0.34 (c 0.882, CH_2Cl_2, 98% *ee*).

HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.451 min, 6.422 min, 8.795 min, 10.701 min, 11.942 min, 13.370 min.

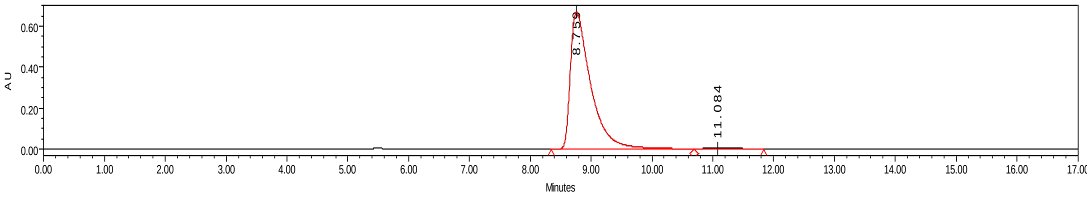
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (m, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.32 (m, 1H), 7.25 – 7.20 (m, 2H), 7.17 (t, *J* = 8.0 Hz, 1H), 7.13 – 7.03 (m, 3H), 6.97 – 6.85 (m, 2H), 6.56 (d, *J* = 8.0 Hz, 1H), 6.34 (s, 1H), 3.64 (dd, *J* = 12.0, 4.0 Hz, 1H), 3.42 (d, *J* = 12.0 Hz, 1H), 3.29 (d, *J* = 16.0 Hz, 1H), 3.00 (dd, *J* = 20.0, 8.0 Hz, 1H), 2.73 (m, 1H), 1.27 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 178.15, 176.62, 175.93, 147.87, 141.43, 136.83, 133.19, 130.45, 130.10, 130.06, 129.75, 129.51, 129.41, 129.00, 128.59, 127.98, 127.51, 123.55, 122.56, 121.74, 110.75, 55.62, 44.96, 40.47, 35.62, 32.18, 31.65.

HRMS (ESI-TOF) calcd for $C_{29}H_{27}Br^{78.9183}N_2O_3$ ($[M+Na^+]$) = 553.1097, Found 553.1105; $C_{29}H_{27}Br^{80.9163}N_2O_3$ ($[M+Na^+]$) = 555.1077, Found 555.1091.

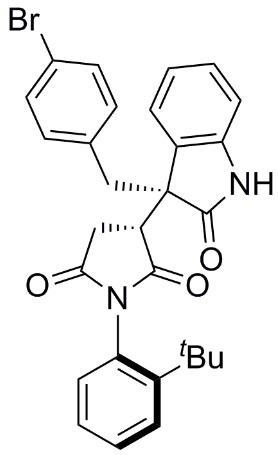


	Retention Time	Area	% Area
1	5.451	2684760	24.75
2	6.422	2739814	25.26
3	8.795	2119287	19.54
4	10.701	1854522	17.10
5	11.942	432998	3.99
6	13.370	1014074	9.35



	Retention Time	Area	% Area
1	8.759	15549173	98.75
2	11.084	196992	1.25

(*M*)-(*R*)-3-((*R*)-3-(4-bromobenzyl)-2-oxoindolin-3-yl)-1-(2-(tert-butyl)phenyl)pyrrolidine-2,5-dione



3d

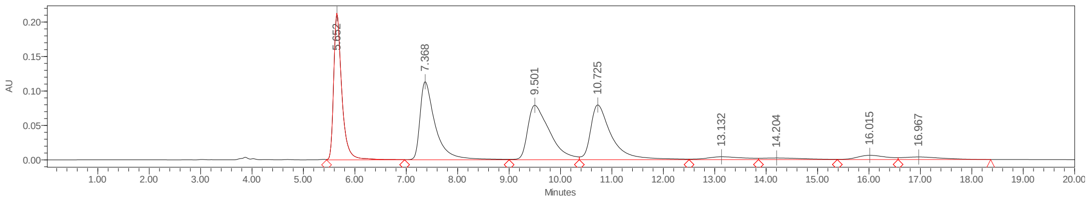
($C_{29}H_{27}BrN_2O_3$) colorless oil; 99% yield, 96% *ee*, >19:1 d.r. $[\alpha]_D^{20.6}$ = –11.65 (c 0.824, CH_2Cl_2, 96% *ee*).

HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.652 min, 7.368 min, 9.501 min, 10.725 min, 13.132 min, 14.204 min, 16.015 min, 16.967 min.

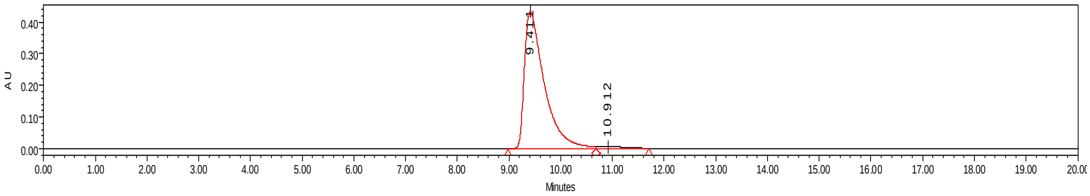
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (m, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.35 – 7.28 (m, 1H), 7.24 (m, 1H), 7.15 (m, 3H), 7.12 – 7.02 (m, 2H), 6.79 (d, *J* = 8.0 Hz, 2H), 6.51 (d, *J* = 8.0 Hz, 1H), 6.28 (s, 1H), 3.64 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.42 (d, *J* = 16.0 Hz, 1H), 3.25 (d, *J* = 12.0 Hz, 1H), 3.01 (dd, *J* = 20.0, 8.0 Hz, 1H), 2.77 (m, 1H), 1.26 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 178.14, 176.62, 175.94, 147.87, 141.48, 133.44, 131.97, 130.95, 130.40, 130.05, 129.75, 129.45, 128.59, 128.00, 127.48, 123.44, 122.52, 121.09, 110.76, 55.58, 45.19, 40.32, 35.62, 32.13, 31.64.

HRMS (ESI-TOF) calcd for $C_{29}H_{27}Br^{78.9183}N_2O_3$ ([M+Na$^+$]) = 553.1097, Found 553.1102; $C_{29}H_{27}Br^{80.9163}N_2O_3$ ([M+Na$^+$]) = 555.1077, Found 555.1093.

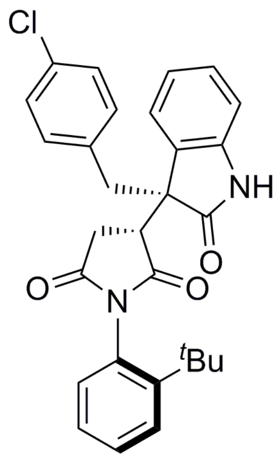


	Retention Time	Area	% Area
1	5.652	2343049	23.30
2	7.368	2339482	23.26
3	9.501	2337933	23.25
4	10.725	2244418	22.32
5	13.132	210296	2.09
6	14.204	137339	1.37
7	16.015	245200	2.44
8	16.967	198128	1.97



	Retention Time	Area	% Area
1	9.411	11530306	98.17
2	10.912	214639	1.83

(*M*)-(*R*)-1-(2-(tert-butyl)phenyl)-3-((*R*)-3-(4-chlorobenzyl)-2-oxoindolin-3-yl)pyrrolidine-2,5-dione



3e

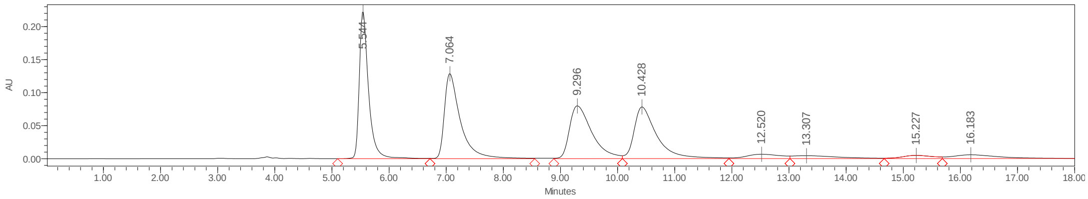
(**$C_{29}H_{27}ClN_2O_3$**) colorless oil; 99% yield, 96% *ee*, >19:1d.r. $[\alpha]_D^{17.8}$ = –10.17 (c 0.718, CH_2Cl_2, 96% *ee*).

HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.544 min, 7.064 min, 9.296 min, 10.428 min, 12.520 min, 13.307 min, 15.227 min, 16.183 min.

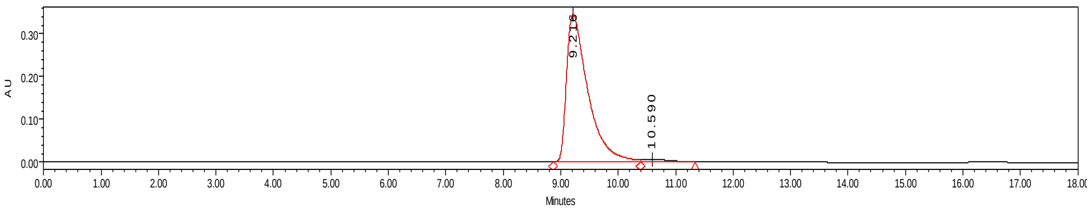
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.04 (m, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.34 – 7.28 (m, 1H), 7.24 (m, 1H), 7.15 (t, *J* = 8.0 Hz, 1H), 7.11 – 7.00 (m, 4H), 6.84 (d, *J* = 8.0 Hz, 2H), 6.51 (d, *J* = 8.0 Hz, 1H), 6.28 (s, 1H), 3.65 (dd, *J* = 12.0, 4.0 Hz, 1H), 3.44 (d, *J* = 16.0 Hz, 1H), 3.27 (d, *J* = 12.0 Hz, 1H), 3.02 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.78 (d, *J* = 20.0 Hz, 1H), 1.26 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 178.16, 176.61, 175.94, 147.87, 141.48, 132.92, 132.87, 131.59, 130.40, 130.05, 129.74, 129.43, 128.59, 128.00, 127.48, 123.44, 122.51, 110.73, 55.65, 45.19, 40.27, 35.62, 32.13, 31.64.

HRMS (ESI-TOF) calcd for $C_{29}H_{27}Cl^{34.9689}N_2O_3$ ($[M+Na^+]$) = 509.1602, Found 509.1612; $C_{29}H_{27}Cl^{36.9659}N_2O_3$ ($[M+Na^+]$) = 511.1573, Found 511.1597.



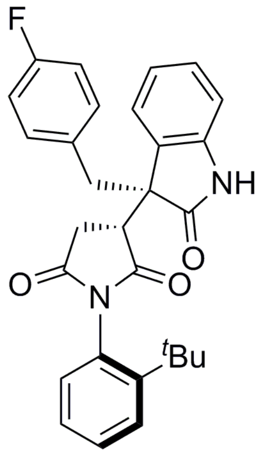
	Retention Time	Area	% Area
1	5.544	2519216	24.25
2	7.064	2513204	24.19
3	9.296	2172430	20.91
4	10.428	2159791	20.79
5	12.520	275200	2.65
6	13.307	245333	2.36
7	15.227	178885	1.72
8	16.183	324149	3.12



	Retention Time	Area	% Area
1	9.216	8939033	97.96

2	10.590	186614	2.04

(M)-(R)-1-(2-(tert-butyl)phenyl)-3-((R)-3-(4-fluorobenzyl)-2-oxoindolin-3-yl)pyrrolidine-2,5-dione



3f

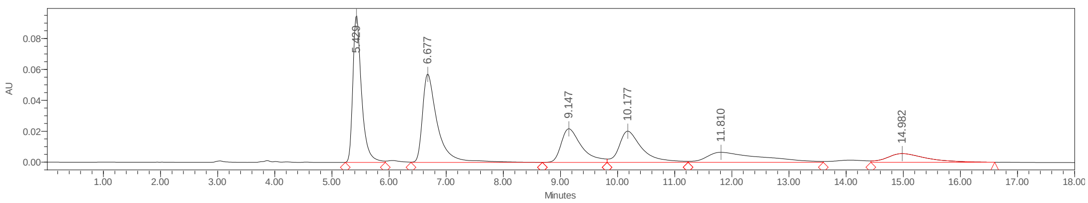
($C_{29}H_{27}FN_2O_3$) colorless oil; 87% yield, 95% *ee*, >19:1d.r. $[\alpha]_D^{20.5}$ = –4.02 (c 0.522, CH_2Cl_2, 95% *ee*).

HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.429 min, 6.677 min, 9.147 min, 10.177 min, 11.810 min, 14.982 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (m, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.31 (m, 1H), 7.24 (m, 1H), 7.15 (t, *J* = 8.0 Hz, 1H), 7.07 (m, 2H), 6.87 (m, 2H), 6.73 (m, 2H), 6.52 (d, *J* = 8.0 Hz, 1H), 6.28 (s, 1H), 3.65 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.45 (d, *J* = 12.0 Hz, 1H), 3.27 (d, *J* = 16.0 Hz, 1H), 3.02 (dd, *J* = 20.0, 8.0 Hz, 1H), 2.79 (d, *J* = 8.0 Hz, 1H), 1.26 (s, 9H).

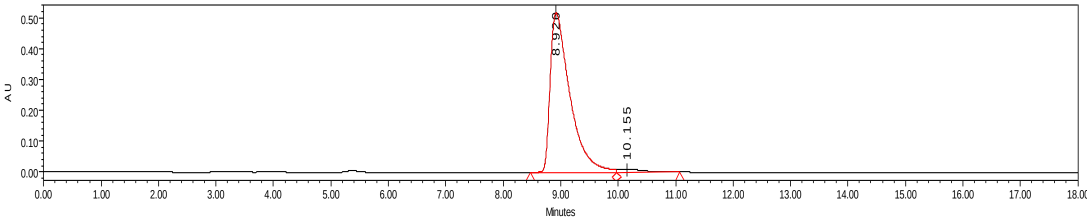
^{13}C NMR (100 MHz, $CDCl_3$) δ = 178.26, 176.63, 175.96, 163.08, 160.64, 147.87, 141.49, 131.80, 131.72, 130.41, 130.11, 130.06, 129.73, 129.37, 128.58, 128.13, 127.48, 123.46, 122.48, 114.80, 114.58, 110.64, 99.99, 55.75, 45.19, 40.15, 35.62, 32.14, 31.63.

HRMS (ESI-TOF) calcd for $C_{29}H_{27}FN_2O_3$ ([M+Na$^+$]) = 493.1898, Found 493.1904.



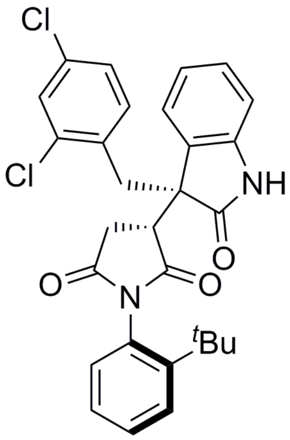
	Retention Time	Area	% Area
1	5.429	1007839	26.11
2	6.677	1043155	27.03
3	9.147	544563	14.11
4	10.177	562805	14.58
5	11.810	434251	11.25

6	14.982	267085	6.92



	Retention Time	Area	% Area
1	8.920	12342962	97.58
2	10.155	305510	2.42

(*M*)-(*R*)-1-(2-(tert-butyl)phenyl)-3-((*R*)-3-(2,4-dichlorobenzyl)-2-oxoindolin-3-yl) pyrrolidine-2,5-dione



3g

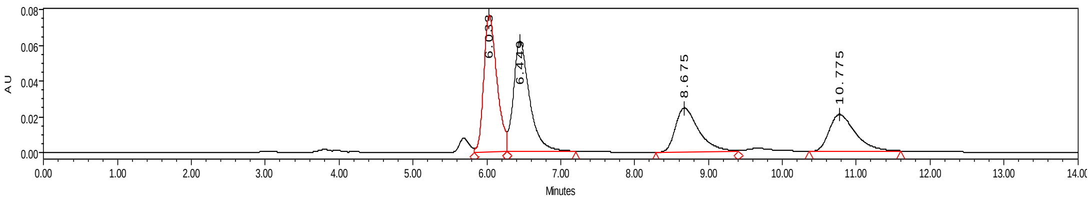
($C_{29}H_{26}Cl_2N_2O_3$) colorless oil; 99% yield, 97% *ee*, >19:1 d.r. $[\alpha]_D^{20.7}$ = +33.13 (c 0.830, CH_2Cl_2, 97% *ee*).

HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 6.033 min, 6.449 min, 8.675 min, 10.775 min.

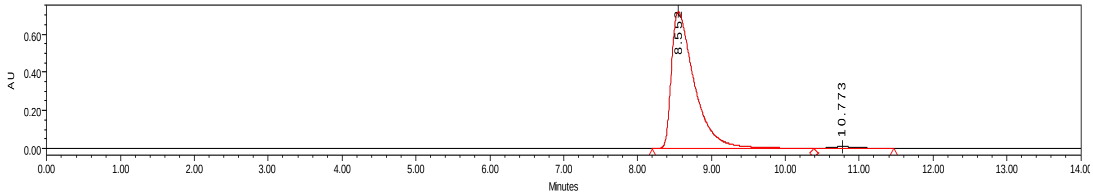
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (m, 1H), 7.50 (d, *J* = 8.0, 1H), 7.29 (m, 3H), 7.15 (m, 1H), 7.12 – 7.01 (m, 3H), 6.96 (m, 1H), 6.44 (m, 1H), 6.11 (s, 1H), 3.71 (m, 2H), 3.49 (d, *J* = 12.0 Hz, 1H), 3.19 – 2.73 (m, 2H), 1.25 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 178.66, 176.56, 175.84, 147.86, 141.28, 135.26, 133.43, 132.13, 131.64, 130.31, 129.99, 129.74, 129.51, 129.13, 128.58, 127.46, 127.01, 124.21, 122.29, 110.55, 55.42, 45.58, 36.20, 35.61, 32.27, 31.63.

HRMS (ESI-TOF) calcd for $C_{29}H_{26}Cl_2^{34.9689}N_2O_3$ ($[M+Na^+]$) = 543.1213, Found 543.1219; $C_{29}H_{26}Cl_2^{36.9659}N_2O_3$ ($[M+Na^+]$) = 545.1183, Found 545.1209.

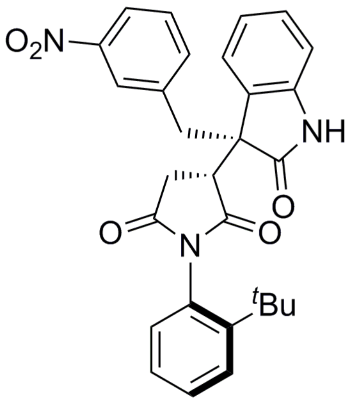


	Retention Time	Area	% Area
1	6.033	942877	32.23
2	6.449	939725	32.12
3	8.675	535371	18.30
4	10.775	507557	17.35



	Retention Time	Area	% Area
1	8.552	15493314	98.58
2	10.773	223048	1.42

(*M*)-(*R*)-1-(2-(tert-butyl)phenyl)-3-((*R*)-3-(3-nitrobenzyl)-2-oxoindolin-3-yl)pyrrolidine-2,5-dione



3h

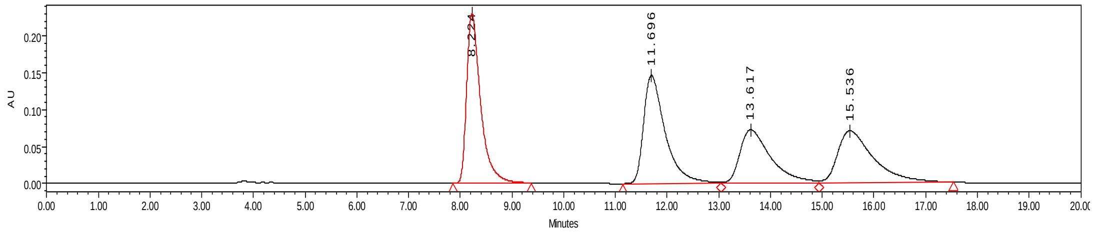
($C_{30}H_{27}N_3O_5$) white solid; 99% yield, 97% *ee*, >19:1 d.r. $[\alpha]_D^{18.3}$ = +28.13 (c 0.718, CH_2Cl_2, 97% *ee*).

HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 8.224 min, 11.696 min, 13.617 min, 15.536 min.

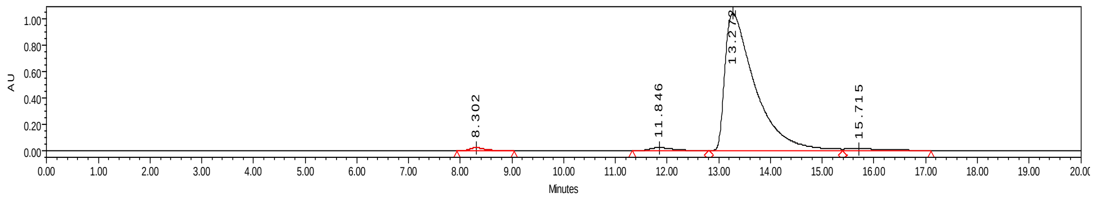
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 – 8.12 (m, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.70 (s, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 7.3 Hz, 3H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.19 – 7.05 (m, 3H), 6.49 (m, 1H), 6.34 (s, 1H), 3.74 – 3.58 (m, 2H), 3.39 (d, *J* = 16.0 Hz, 1H), 3.02 (dd, *J* = 20.0, 8.0 Hz, 1H), 2.88 – 2.55 (m, 1H), 1.25 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 177.85, 176.56, 175.80, 147.87, 147.60, 141.29, 136.57, 136.47, 130.39, 130.01, 129.80, 128.87, 128.63, 127.50, 124.99, 123.44, 122.92, 122.08, 110.83, 55.63, 45.08, 40.45, 35.61, 32.11, 31.62.

HRMS (ESI-TOF) calcd for $C_{30}H_{27}N_3O_5$ ([M+Na$^+$]) = 520.1843. Found 520.1856.

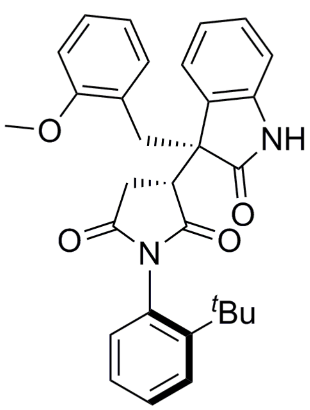


	Retention Time	Area	% Area
1	8.224	4326961	28.94
2	11.696	4247705	28.41
3	13.617	2989819	20.00
4	15.536	3386449	22.65



	Retention Time	Area	% Area
1	8.302	463320	1.05
2	11.846	704230	1.60
3	13.272	42183191	95.89
4	15.715	638423	1.45

(*M*)-(*R*)-1-(2-(tert-butyl)phenyl)-3-((*R*)-3-(2-methoxybenzyl)-2-oxoindolin-3-yl)pyrrolidine-2,5-dione



3i

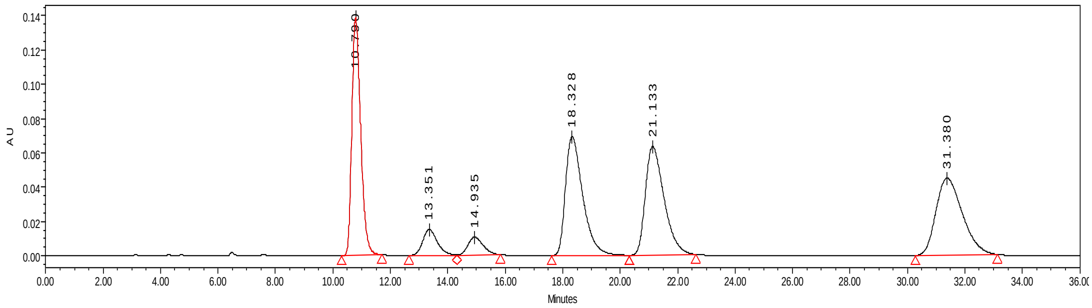
($C_{30}H_{30}N_2O_4$) colorless oil; 99% yield, 99% *ee*, >19:1 d.r. $[\alpha]_D^{17.2}$= +22.21 (c 0.716, CH_2Cl_2, 99% *ee*).

HPLC DAICEL CHIRALCEL IE, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 10.790 min, 13.351 min, 14.935 min, 18.328 min, 21.133 min, 31.380 min.

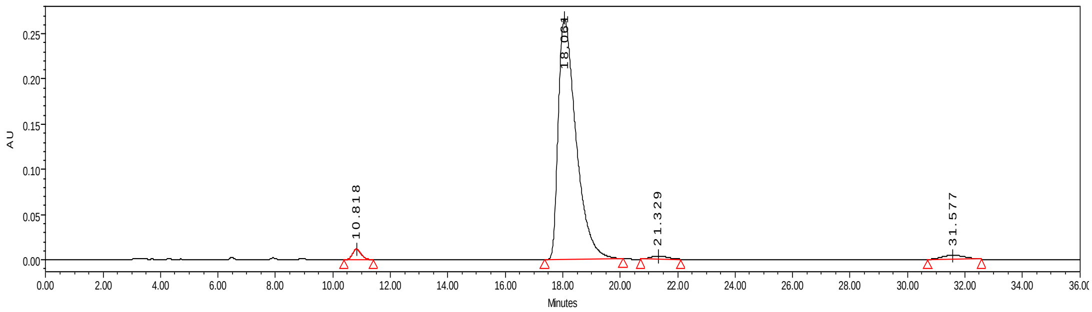
^1H NMR (400 MHz, $CDCl_3$) δ 8.23 (m, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.20 (m, 2H), 7.03 (m, 3H), 6.90 (m, 1H), 6.75 (m, 1H), 6.58 (d, J = 8.0 Hz, 1H), 6.46 (d, J = 8.0 Hz, 1H), 5.96 (s, 1H), 3.71 (m, 2H), 3.56 (s, 3H), 3.25 (d, J = 12.0 Hz, 1H), 3.15 – 2.90 (m, 2H), 1.25 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 179.26, 176.72, 176.33, 157.10, 147.86, 141.48, 131.30, 130.34, 130.12, 129.60, 128.83, 128.46, 128.30, 128.03, 127.39, 124.27, 123.44, 121.41, 120.17, 110.13, 109.83, 55.38, 54.68, 45.91, 35.59, 33.73, 32.33, 31.63.

HRMS (ESI-TOF) calcd for $C_{30}H_{30}N_2O_4$ ($[M+Na^+]$) = 505.2098. Found 505.2106.



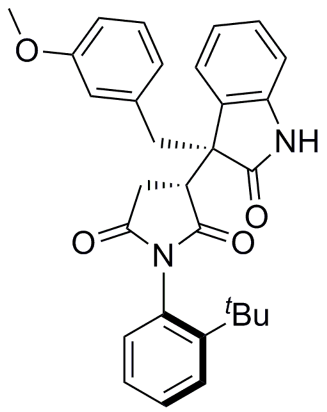
	Retention Time	Area	% Area
1	10.790	2961850	23.62
2	13.351	540992	4.31
3	14.935	382097	3.05
4	18.328	2908983	23.20
5	21.133	2861099	22.82
6	31.380	2884548	23.00



	Retention Time	Area	% Area
1	10.818	245928	2.04

2	18.061	11428388	94.59
3	21.329	149726	1.24
4	31.577	257503	2.13

(*M*)-(*R*)-1-(2-(tert-butyl)phenyl)-3-((*R*)-3-(3-methoxybenzyl)-2-oxoindolin-3-yl)pyrrolidine-2,5-dione



3j

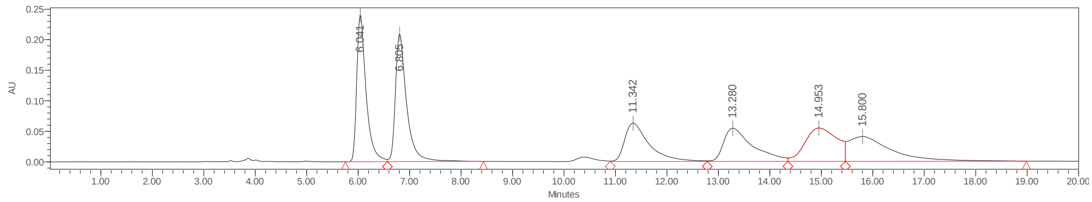
($C_{30}H_{30}N_2O_4$) white solid, 94% yield, 97% *ee*, >19:1 d.r. $[\alpha]_D^{20.6}$ = –2.47 (c 1.296, CH_2Cl_2, 97% *ee*).

HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 6.041 min, 6.805 min, 11.342 min, 13.280 min, 14.953 min, 15.800 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.34 – 7.28 (m, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.15 (t, *J* = 8.0 Hz, 1H), 7.13 – 7.02 (m, 2H), 6.98 (t, *J* = 8.0 Hz, 1H), 6.65 (m, 2.1 Hz, 1H), 6.57 (t, *J* = 8.0 Hz, 2H), 6.46 (s, 1H), 6.34 (m, 1H), 3.70 – 3.62 (m, 1H), 3.57 (s, 3H), 3.41 (d, *J* = 12.0 Hz, 1H), 3.33 (d, *J* = 16.0 Hz, 1H),3.00 (dd, *J* = 16.0, 12.0 Hz, 1H), 2.76 (m, 1H), 1.27 (s, 9H).

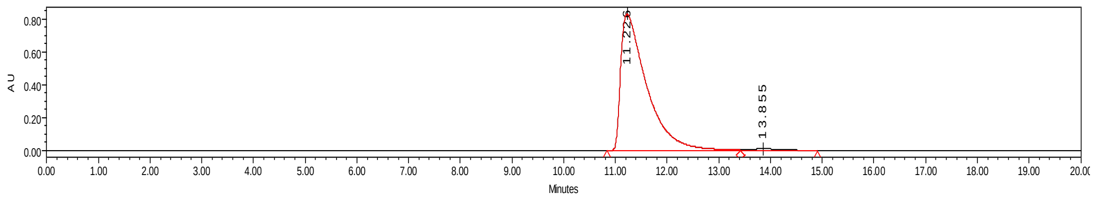
^{13}C NMR (100 MHz, $CDCl_3$) δ = 178.46, 176.67, 176.02, 158.94, 147.85, 141.62, 135.96, 130.48, 130.15, 129.70, 129.26, 128.81, 128.54, 127.49, 123.67, 122.86, 122.32, 115.14, 113.23, 110.62, 69.62, 55.67, 55.02, 53.80, 45.06, 41.01, 35.62, 32.21, 31.76, 31.64, 29.27.

HRMS (ESI-TOF) calcd for $C_{30}H_{30}N_2O_4$ ($[M+Na^+]$) = 505.2098. Found 505.2107.



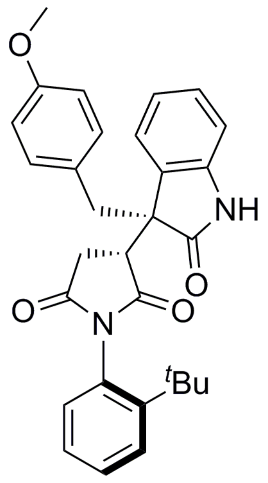
	Retention Time	Area	% Area
1	6.041	3040662	20.10
2	6.805	3158252	20.88
3	11.342	2075048	13.72

4	13.280	2146219	14.19
5	14.953	2358908	15.59
6	15.800	2349513	15.53



	Retention Time	Area	% Area
1	11.226	28959292	98.58
2	13.855	415788	1.42

(*M*)-(*R*)-1-(2-(tert-butyl)phenyl)-3-((*R*)-3-(4-methoxybenzyl)-2-oxoindolin-3-yl)pyrrolidine-2,5-dione



3k

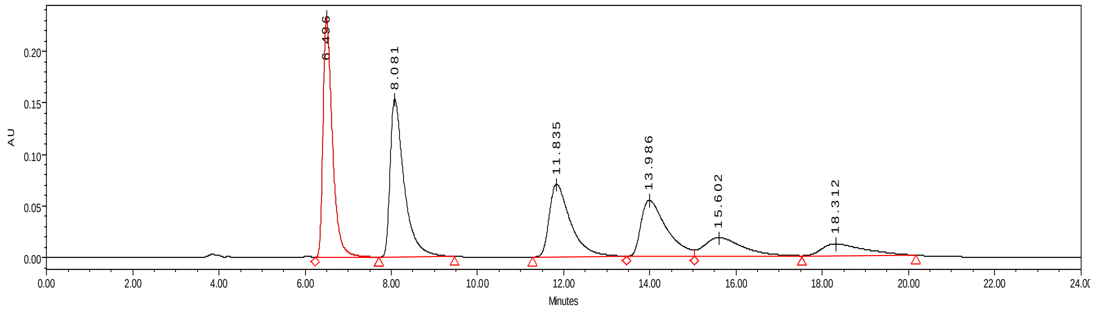
($C_{30}H_{30}N_2O_4$) colorless oil; 99% yield, 97% *ee*, >19:1 d.r. $[\alpha]_D^{18.4}$= –24.43 (c 0.700, CH_2Cl_2, 97% *ee*).

HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 6.496 min, 8.081 min, 11.835 min, 13.986 min, 15.602 min, 18.312 min.

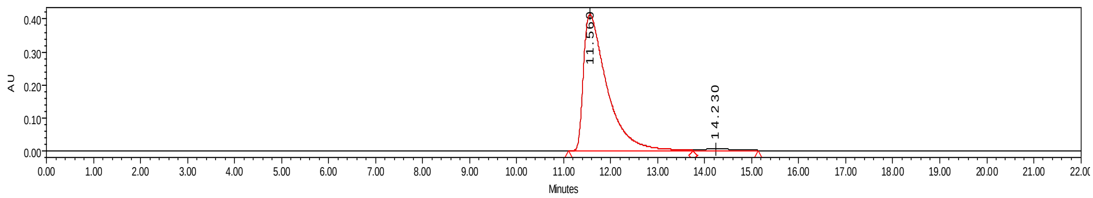
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (m, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.30 (t, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.15 (m,, 1H), 7.06 (dt, *J* = 16.0, 8.0 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 6.57 (dd, *J* = 20.0, 8.0 Hz, 3H), 6.26 (s, 1H), 3.68 (s, 3H), 3.67 – 3.61 (m, 1H), 3.37 (d, *J* = 12.0 Hz, 1H), 3.27 (d, *J* = 12.0 Hz, 1H), 3.01 (dd, *J* = 20.0, 12.0 Hz, 1H), 2.79 (d, *J* = 20.0 Hz, 1H), 1.26 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 178.53, 176.70, 176.08, 158.43, 147.86, 141.53, 131.33, 130.45, 130.13, 129.68, 129.19, 128.53, 127.46, 126.42, 123.56, 122.34, 113.22, 110.58, 55.79, 55.07, 45.14, 40.18, 35.62, 32.18, 31.65.

HRMS (ESI-TOF) calcd for $C_{30}H_{30}N_2O_4$ ($[M+Na^+]$) = 505.2098. Found 505.2098.

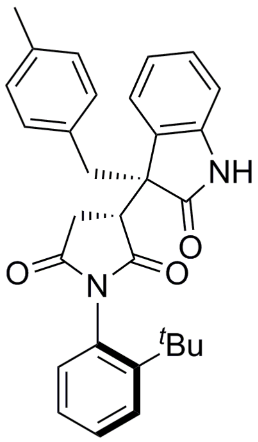


	Retention Time	Area	% Area
1	6.496	3515418	25.96
2	8.081	3464058	25.58
3	11.835	2419732	17.87
4	13.986	2249041	16.61
5	15.602	1102365	8.14
6	18.312	789167	5.83



	Retention Time	Area	% Area
1	11.560	14360229	98.46
2	14.230	223936	1.54

(*M*)-(*R*)-1-(2-(tert-butyl)phenyl)-3-((*R*)-3-(4-methylbenzyl)-2-oxoindolin-3-yl)pyrrolidine-2,5-dione



3l

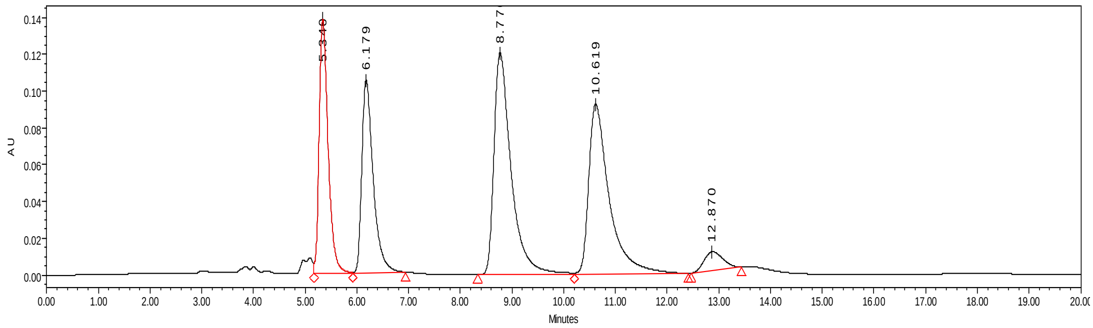
($C_{30}H_{30}N_2O_3$) colorless oil; 99% yield, 97% *ee*, >19:1 d.r. $[\alpha]_D^{20.6}$ = –21.01 (c 0.790, CH_2Cl_2, 97% *ee*).

HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.340 min, 6.179 min, 8.770 min, 10.619 min, 12.870 min.

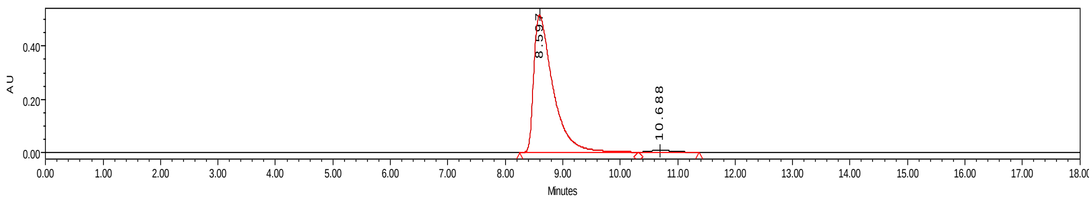
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (m, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.34 – 7.27 (m, 1H), 7.23 (m, 1H), 7.15 (t, *J* = 8.0 Hz, 1H), 7.06 (dt, *J* = 16.0, 8.0 Hz, 2H), 6.85 (dd, *J* = 24.0, 8.0 Hz, 4H), 6.55 (d, *J* = 8.0 Hz, 1H), 6.27 (s, 1H), 3.67 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.40 (d, *J* = 16.0 Hz, 1H), 3.30 (d, *J* = 12.0 Hz, 1H), 3.01 (dd, *J* = 20.0, 12.0 Hz, 1H), 2.80 (d, *J* = 16.0 Hz, 1H), 2.21 (s, 3H), 1.27 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 178.48, 176.68, 176.06, 147.86, 141.51, 136.43, 131.29, 130.46, 130.19, 130.14, 129.67, 129.17, 128.56, 128.53, 127.46, 123.61, 122.32, 110.55, 55.71, 45.22, 40.62, 35.62, 32.20, 31.65, 21.04.

HRMS (ESI-TOF) calcd for $C_{30}H_{30}N_2O_3$ ($[M+Na^+]$) = 489.2149, Found 489.2150.

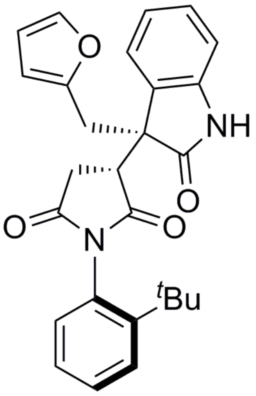


	Retention Time	Area	% Area
1	5.340	1653922	18.76
2	6.179	1595401	18.10
3	8.770	2773638	31.46
4	10.619	2536058	28.77
5	12.870	257431	2.92



	Retention Time	Area	% Area
1	8.597	11997550	98.33
2	10.688	203458	1.67

M)-(*R*)-1-(2-(tert-butyl)phenyl)-3-((*R*)-3-(furan-2-ylmethyl)-2-oxoindolin-3-yl)pyrrolidine-2,5-dione



3m

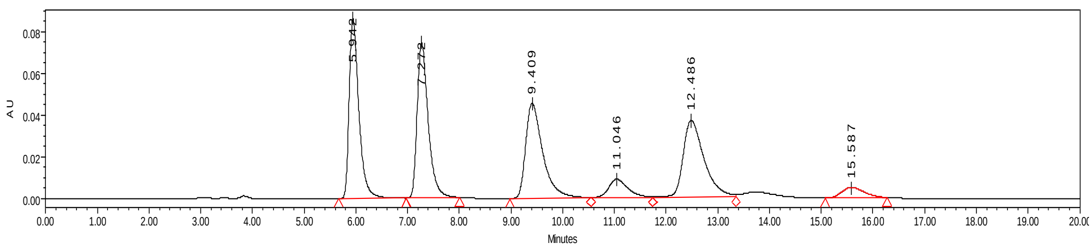
($C_{27}H_{26}N_2O_4$) colorless oil; 95% yield, 94% *ee*, >19:1 d.r. $[\alpha]_D^{15.0}$= +39.81 (c 0.422, CH_2Cl_2, 94% *ee*).

HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.942 min, 7.272 min, 9.409 min, 11.046 min, 12.486 min, 15.587 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 – 8.25 (m, 1H), 7.51 (d, *J* = 8.0, 1H), 7.34 – 7.28 (m, 1H), 7.19 (m, 2H), 7.14 – 7.07 (m, 2H), 7.02 (m, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 6.37 (s, 1H), 6.17 (m, 1H), 6.00 (d, *J* = 4.0 Hz, 1H), 3.65 (dd, *J* = 12.0, 4.0 Hz, 1H), 3.50 (d, *J* = 16.0 Hz, 1H), 3.41 (d, *J* = 12.0 Hz, 1H), 2.95 (dd, *J* = 20.0, 4.0 Hz, 1H), 2.72 – 2.56 (m, 1H), 1.27 (s, 9H).

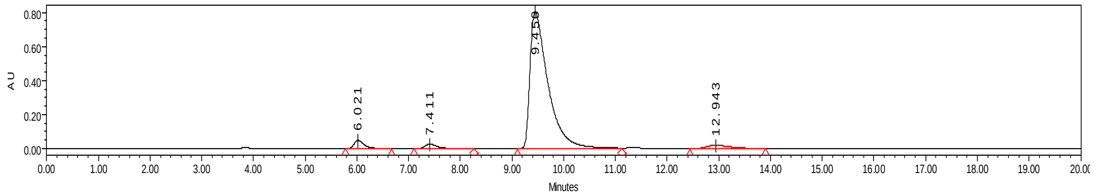
^{13}C NMR (100 MHz, $CDCl_3$) δ = 178.47, 176.52, 175.93, 149.59, 147.84, 141.76, 141.30, 130.53, 130.17, 129.70, 129.31, 128.69, 128.53, 127.49, 123.68, 122.61, 110.60, 110.43, 108.82, 54.08, 44.50, 35.62, 33.55, 32.06, 31.64, 29.71.

HRMS (ESI-TOF) calcd for $C_{27}H_{26}N_2O_4$ ([M+Na$^+$]) = 465.1785, Found 465.1795.



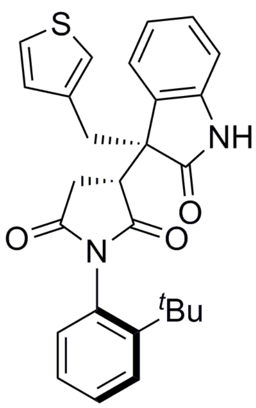
	Retention Time	Area	% Area

1	5.942	1126389	23.86
2	7.272	1105064	23.41
3	9.409	1054170	22.33
4	11.046	236463	5.01
5	12.486	1047838	22.19
6	15.587	151392	3.21



	Retention Time	Area	% Area
1	6.021	657283	3.12
2	7.411	424197	2.01
3	9.450	19417598	92.07
4	12.943	591417	2.80

(*M*)-(*R*)-1-(2-(tert-butyl)phenyl)-3-((*R*)-2-oxo-3-(thiophen-3-ylmethyl)indolin-3-yl)pyrrolidine-2,5-dione



3n

($C_{27}H_{26}N_2O_3S$) colorless oil; 93% yield, 95% *ee*, >19:1 d.r. $[\alpha]_D^{18.0}$ = +18.84 (c 0.674, CH_2Cl_2, 95% *ee*).

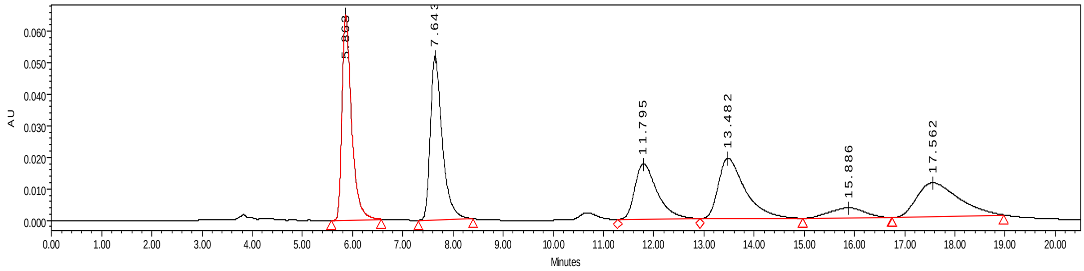
HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.863 min, 7.643 min, 11.795 min, 13.482 min, 15.886 min, 17.562 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (m, 1H), 7.52 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.36 – 7.28 (m, 1H), 7.22 (m, 2H), 7.09 (m, 2H), 7.00 (m, 1H), 6.77 (dd, *J* = 8.0, 4.0 Hz, 1H), 6.67 (m, 2H), 6.37 (s, 1H), 3.71 (d, *J* = 16.0 Hz, 1H), 3.66

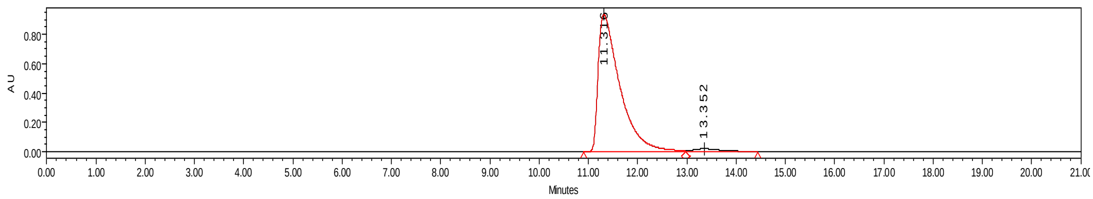
(dd, J = 12.0, 4.0 Hz, 1H), 3.56 (d, J = 16.0 Hz, 1H), 2.98 (dd, J = 20.0, 8.0 Hz, 1H), 2.70 (m, 1H), 1.27 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 178.32, 176.49, 175.89, 147.86, 141.82, 135.95, 130.51, 130.13, 129.73, 129.55, 128.56, 128.46, 127.93, 127.51, 126.46, 124.95, 123.62, 122.66, 110.72, 55.47, 44.76, 35.63, 35.25, 32.11, 31.66.

HRMS (ESI-TOF) calcd for $C_{27}H_{26}N_2O_3S$ ([M+Na$^+$]) = 481.1556, Found 481.1561.

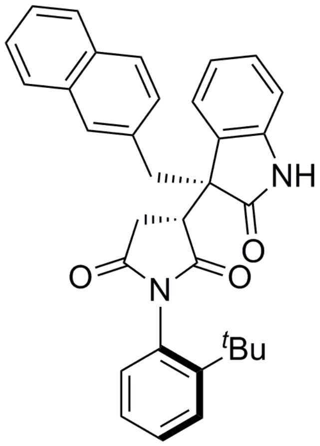


	Retention Time	Area	% Area
1	5.863	858038	22.89
2	7.643	855407	22.82
3	11.795	549612	14.66
4	13.482	713704	19.04
5	15.886	156364	4.17
6	17.562	615769	16.43



	Retention Time	Area	% Area
1	11.316	28541578	97.61
2	13.352	698406	2.39

(*M*)-(*R*)-1-(2-(tert-butyl)phenyl)-3-((*R*)-3-(naphthalen-2-ylmethyl)-2-oxoindolin-3-yl)pyrrolidine-2,5-dione



3o

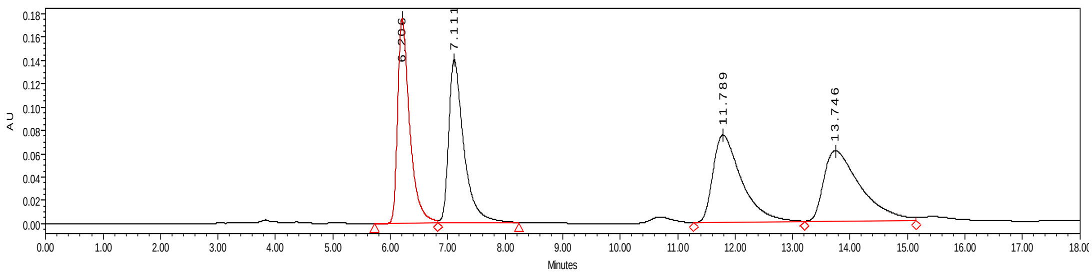
($C_{33}H_{30}N_2O_3$) colorless oil; 99% yield, 97% *ee*, >19:1 d.r. $[\alpha]_D^{18.0}$ = −26.52 (c 0.690, CH_2Cl_2, 97% *ee*).

HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 6.206 min, 7.111 min, 11.789 min, 13.746 min.

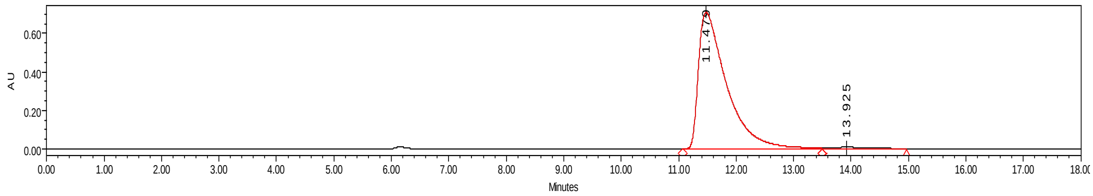
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.66 (m, 2H), 7.56 – 7.45 (m, 3H), 7.38 (m, 2H), 7.34 – 7.27 (m, 2H), 7.16 – 6.98 (m, 4H), 6.47 (d, *J* = 8.0 Hz, 1H), 6.33 (s, 1H), 3.71 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.60 (d, *J* = 12.0 Hz, 1H), 3.48 (d, *J* = 12.0 Hz, 1H), 3.01 (dd, *J* = 20.0, 12.0 Hz, 1H), 2.80 (m, 1H), 1.27 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 178.34, 176.67, 176.02, 147.86, 141.46, 133.04, 132.29, 132.11, 130.49, 130.15, 129.70, 129.30, 128.55, 128.48, 128.41, 127.80, 127.49, 127.46, 127.22, 125.81, 125.69, 123.67, 122.41, 110.62, 55.81, 45.16, 41.09, 35.62, 32.24, 31.65.

HRMS (ESI-TOF) calcd for $C_{33}H_{30}N_2O_3$ ($[M+Na^+]$) = 525.2149, Found 525.2155.

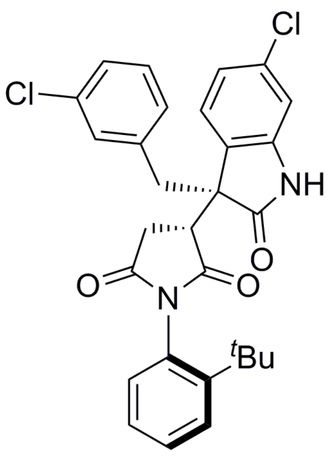


	Retention Time	Area	% Area
1	6.206	2564387	24.56
2	7.111	2573298	24.64
3	11.789	2601175	24.91
4	13.746	2703028	25.89



	Retention Time	Area	% Area
1	11.479	24114118	98.61
2	13.925	341055	1.39

(*M*)-(*R*)-1-(2-(tert-butyl)phenyl)-3-((*R*)-6-chloro-3-(3-chlorobenzyl)-2-oxoindolin-3-yl)pyrrolidine-2,5-dione



3p

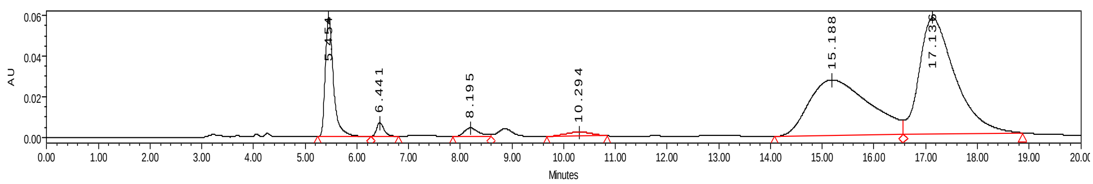
($C_{29}H_{26}Cl_2N_2O_3$) colorless oil; 95% yield, 99% *ee*, >19:1 d.r. $[\alpha]_D^{18.5}$ = –12.97 (c 0.794, CH_2Cl_2, 99% *ee*).

HPLC DAICEL CHIRALCEL IE, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.454 min, 6.441min, 8.195 min, 10.294 min, 15.188 min, 17.136 min.

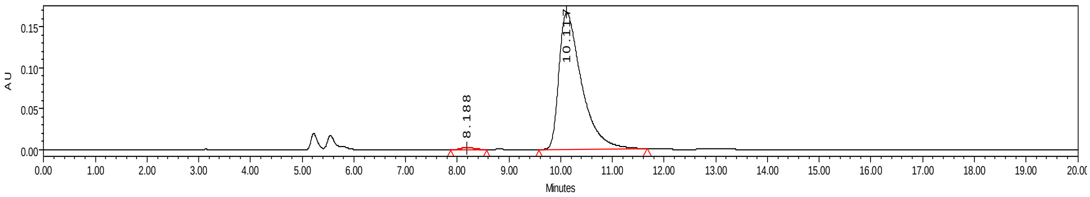
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.33 (m, 1H), 7.12 (m, 3H), 7.06 – 7.00 (m, 2H), 6.94 (m, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.58 (m, 1H), 6.33 (s, 1H), 3.63 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.39 (d, *J* = 12.0 Hz, 1H), 3.28 (d, *J* = 12.0 Hz, 1H), 3.02 (dd, *J* = 20.0, 12.0 Hz, 1H), 2.83 – 2.62 (m, 1H), 1.26 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 178.19, 176.45, 175.67, 147.80, 142.63, 136.14, 135.30, 133.74, 130.26, 129.92, 129.87, 129.75, 129.29, 128.75, 128.45, 127.61, 127.40, 126.37, 124.48, 122.49, 111.38, 55.25, 45.01, 40.38, 35.62, 32.03, 31.64.

HRMS (ESI-TOF) calcd for $C_{29}H_{26}Cl_2^{34.9689}N_2O_3$ ([M+Na$^+$]) = 543.1213, Found 543.1216; $C_{29}H_{26}Cl_2^{36.9659}N_2O_3$ ([M+Na$^+$]) = 545.1183, Found 545.1199.

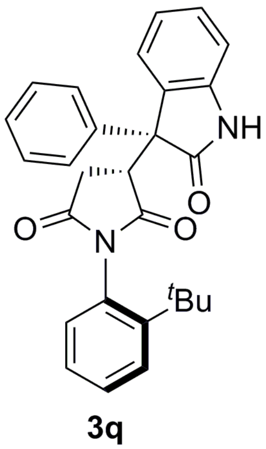


	Retention Time	Area	% Area
1	5.454	652479	11.09
2	6.441	68578	1.17
3	8.195	84266	1.43
4	10.294	73668	1.25
5	15.188	2240207	38.08
6	17.136	2763690	46.98



	Retention Time	Area	% Area
1	8.188	45389	0.89
2	10.117	5069198	99.11

(*M*)-(*R*)-1-(2-(tert-butyl)phenyl)-3-((*S*)-2-oxo-3-phenylindolin-3-yl)pyrrolidine-2,5-dione



3q

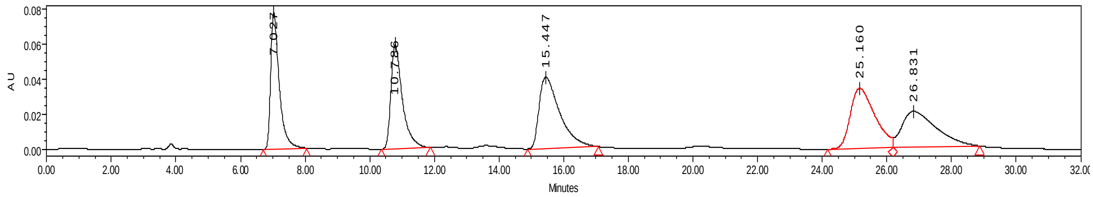
($C_{28}H_{26}N_2O_3$) colorless oil; 96% yield, 89% *ee*, 9:1 d.r. $[\alpha]_D^{17.4} = -158.50$ (c 0.906, THF, 89% *ee*).

HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 7.027 min, 10.786 min, 15.447 min, 25.160 min, 26.831 min.

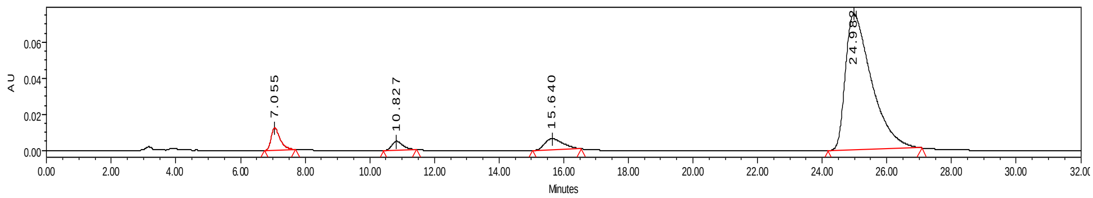
^{1}H NMR (400 MHz, DMSO) δ 10.62 (s, 1H), 7.62 – 7.20 (m, 10H), 7.16 – 6.93 (m, 3H), 5.70 (s, 1H), 4.48 (d, *J* =8.0 Hz, 0.9 H), 4.03 (d, *J* = 8.0 Hz, 0.1H), 2.73 (d, *J* = 20.0 Hz, 1H), 1.19 (s, 9H).

^{13}C NMR (100 MHz, DMSO) δ = 177.15, 176.47, 176.15, 147.74, 143.42, 137.99, 130.49, 130.03, 129.43, 129.34, 128.68, 128.26, 127.59, 127.33, 126.83, 124.59, 121.74, 110.43, 79.15, 57.14, 45.65, 35.08, 32.53, 31.24, 30.69, 29.57.

HRMS (ESI-TOF) calcd for $C_{28}H_{26}N_2O_3$ ([M+Na$^+$]) = 461.1836, Found 461.1836.

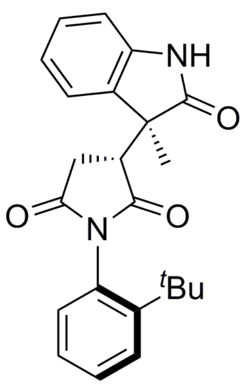


	Retention Time	Area	% Area
1	7.027	1437146	17.80
2	10.786	1471927	18.23
3	15.447	1806787	22.38
4	25.160	1819707	22.54
5	26.831	1537681	19.05



	Retention Time	Area	% Area
1	7.055	237674	4.92
2	10.827	118306	2.45
3	15.640	247536	5.13
4	24.982	4223681	87.50

(*M*)-(*R*)-1-(2-(tert-butyl)phenyl)-3-((*R*)-3-methyl-2-oxoindolin-3-yl)pyrrolidine-2,5-dione



3r

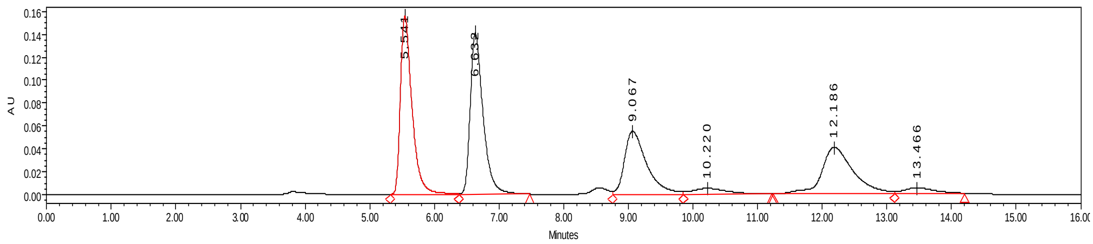
($C_{23}H_{24}N_2O_3$) white solid; 99% yield, 88% *ee*, 80:20 d.r.

HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.541 min, 6.632 min, 9.067 min, 10.220 min, 12.186 min, 13.466 min.

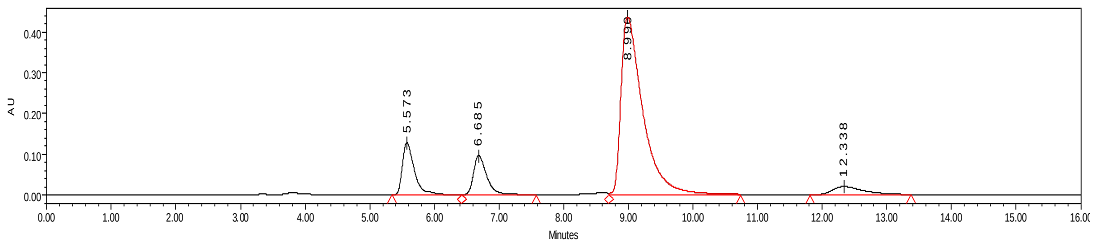
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 – 8.62 (m, 1H), 7.58 (d, *J* = 8.0 Hz, 0.3H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 0.3H), 7.31 – 7.27 (m, 1H), 7.25 – 7.18 (m, 2H), 7.05 (t, *J* = 8.0 Hz, 2H), 6.81 (t, *J* = 8.0 Hz, 0.3H), 6.73 (d, *J* = 8.0 Hz, 1H), 6.68 (dd, *J* = 8.0, 4.0 Hz, 0.3H), 6.05 (d, *J* = 8.0 Hz, 1H), 3.57 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.52 – 3.46 (m, 0.3H), 3.06 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.91 – 2.83 (m, 1H), 1.82 (s, 0.8H), 1.60 (s, 3H), 1.30 (s, 2H), 1.25 (m, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 180.15, 177.54, 176.73, 176.10, 175.52, 148.00, 147.90, 141.14, 140.92, 130.67, 130.58, 130.31, 130.04, 129.90, 129.70, 129.35, 129.19, 129.06, 128.55, 127.50, 127.43, 124.07, 123.28, 122.68, 110.93, 110.71, 49.80, 49.59, 46.24, 44.73, 35.75, 35.59, 31.92, 31.66, 31.62, 21.85.

HRMS (ESI-TOF) calcd for $C_{23}H_{24}N_2O_3$ ([M+Na$^+$]) = 399.1679, Found 399.1686.



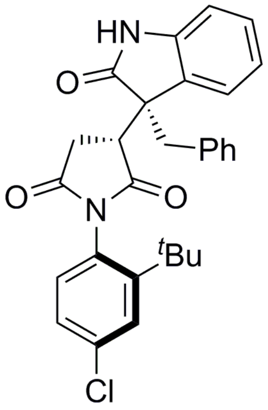
	Retention Time	Area	% Area
1	5.541	1955510	28.25
2	6.632	1942366	28.06
3	9.067	1301944	18.81
4	10.220	185950	2.69
5	12.186	1376481	19.89
6	13.466	159888	2.31



	Retention Time	Area	% Area

1	5.573	1657208	11.95
2	6.685	1356011	9.78
3	8.990	10201623	73.57
4	12.338	652310	4.70

(*M*)-(*R*)-3-((*R*)-3-benzyl-2-oxoindolin-3-yl)-1-(2-(tert-butyl)-4-chlorophenyl)pyrrolidine-2,5-dione



3s

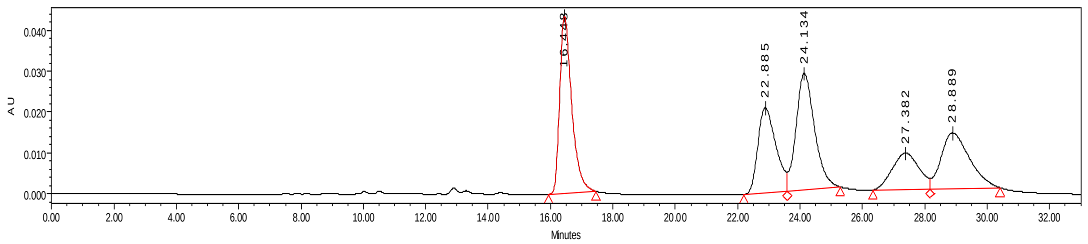
($C_{29}H_{27}ClN_2O_3$) colorless oil; 99% yield, 98% *ee*, >19:1 d.r. $[\alpha]_D^{13.1}$ = +4.16 (c 0.672, CH_2Cl_2, 98% *ee*).

HPLC DAICEL CHIRALCEL IB combined with IE, *n*-hexane/2-propanol = 80/20, flow rate = 0.8 mL/min, λ = 254 nm, retention time: 16.448 min, 22.885 min, 24.134 min, 27.382 min, 28.889 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.05 (m, 1H), 7.48 (s, 1H), 7.24 – 7.13 (m, 2H), 7.13 – 6.99 (m, 5H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.53 (d, *J* = 4.0 Hz, 1H), 6.27 (s, 1H), 3.67 (d, *J* = 8.0 Hz, 1H), 3.46 (d, *J* = 12.0 Hz, 1H), 3.32 (d, *J* = 12.0 Hz, 1H), 3.00 (m, 1H), 2.76 (m, 1H), 1.26 (s, 9H).

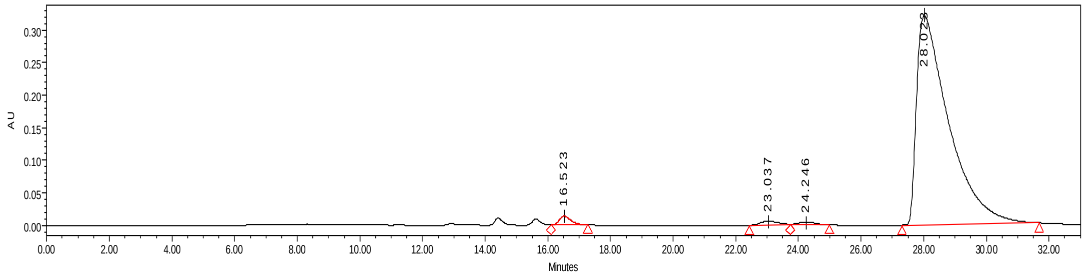
^{13}C NMR (100 MHz, $CDCl_3$) δ = 178.44, 176.53, 175.84, 149.99, 141.44, 135.65, 134.35, 131.92, 130.30, 129.30, 128.90, 128.83, 128.31, 127.87, 127.71, 126.95, 123.62, 122.46, 110.56, 55.89, 45.06, 40.94, 35.81, 32.24, 31.41.

HRMS (ESI-TOF) calcd for $C_{29}H_{27}Cl^{34.9689}N_2O_3$ ($[M+Na^+]$) = 509.1602, Found 509.1604; $C_{29}H_{27}Cl^{36.9659}N_2O_3$ ($[M+Na^+]$) = 511.1573, Found 511.1599.



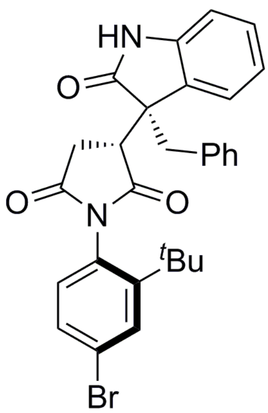
	Retention Time	Area	% Area
1	16.448	1159573	25.36
2	22.885	835120	18.26
3	24.134	1178672	25.77

4	27.382	532688	11.65
5	28.889	866911	18.96



	Retention Time	Area	% Area
1	16.523	358395	1.51
2	23.037	256884	1.08
3	24.246	177985	0.75
4	28.023	22942489	96.66

(*M*)-(*R*)-3-((*R*)-3-benzyl-2-oxoindolin-3-yl)-1-(4-bromo-2-(tert-butyl)phenyl)pyrrolidine-2,5-dione



3t

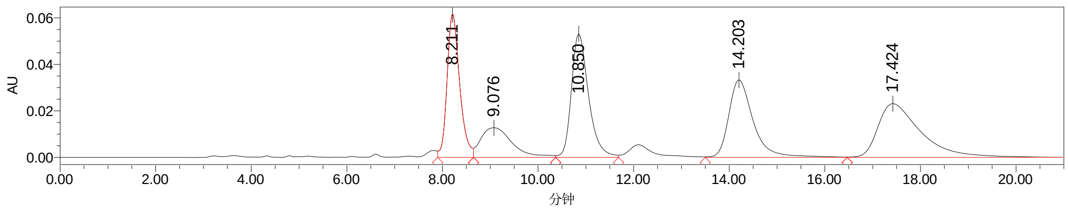
($C_{29}H_{27}BrN_2O_3$) colorless oil; 92% yield, 98% *ee*, >19:1 d.r. $[\alpha]_D^{13.3}$ = +3.41 (c 0.734, CH_2Cl_2, 98% *ee*).

HPLC DAICEL CHIRALCEL IE, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 8.211 min, 9.076 min, 10.850 min, 14.203 min, 17.424 min.

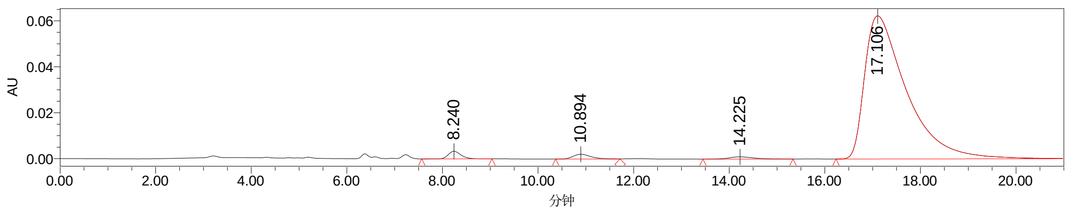
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (m, 1H), 7.63 (d, *J* = 4.0 Hz, 1H), 7.26 – 7.14 (m, 3H), 7.13 – 7.01 (m, 4H), 6.92 (m, 2H), 6.62 – 6.50 (m, 1H), 6.21 (s, 1H), 3.66 (dd, *J* = 12.0, 4.0 Hz, 1H), 3.47 (d, *J* = 12.0 Hz, 1H), 3.32 (d, *J* = 12.0 Hz, 1H), 3.00 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.75 (m, 1H), 1.25 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 178.29, 176.44, 175.75, 150.26, 141.41, 134.33, 132.18, 131.85, 130.73, 130.29, 129.39, 129.33, 128.32, 127.87, 126.96, 124.09, 123.63, 122.48, 110.54, 55.88, 45.06, 40.96, 35.80, 32.25, 31.43.

HRMS (ESI-TOF) calcd for $C_{29}H_{27}Br^{78.9183}N_2O_3$ ([M+Na$^+$]) = 553.1097, Found 553.1103; $C_{29}H_{27}Br^{80.9163}N_2O_3$ ([M+Na$^+$]) = 555.1077, Found 555.1090.

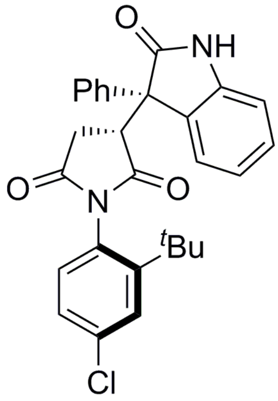


	Retention Time	Area	% Area
1	8.211	1131516	19.96
2	9.076	581934	10.27
3	10.850	1326106	23.40
4	14.203	1185132	20.91
5	17.424	1443577	25.47



	Retention Time	Area	% Area
1	8.240	62390	1.58
2	10.894	55014	1.39
3	14.225	33702	0.85
4	17.106	3797843	96.17

(*M*)-(*R*)-1-(2-(tert-butyl)-4-chlorophenyl)-3-((*S*)-2-oxo-3-phenylindolin-3-yl)pyrrolidine-2,5-dione



3u

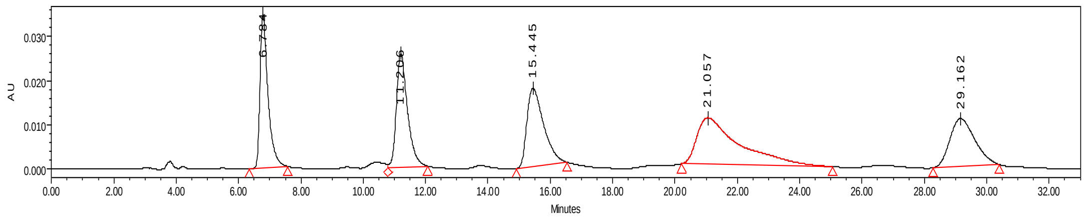
($C_{28}H_{25}ClN_2O_3$) colorless oil; 99% yield, 84% *ee*, 9:1 d.r. $[\alpha]_D^{13.4}$ = −215.50 (c 0.596, CH_2Cl_2, 84% *ee*).

HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 6.784 min, 11.206 min, 15.445 min, 21.057 min, 29.162 min.

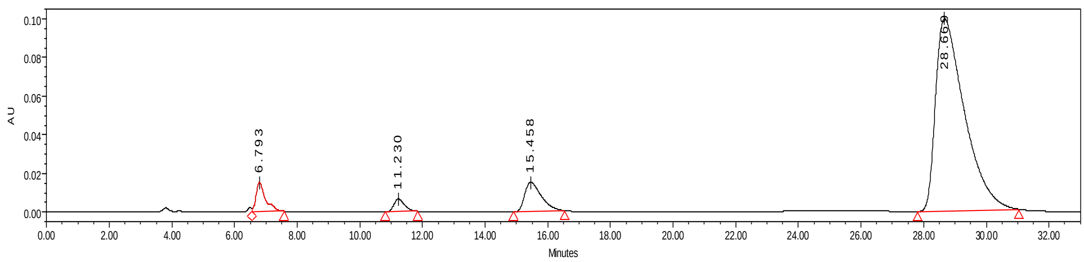
[1]H NMR (400 MHz, $CDCl_3$) δ 8.73 – 8.52 (m, 1H), 7.43 (m, 1H), 7.39 – 7.28 (m, 6H), 7.24 (m, 1H), 7.12 (t, *J* = 8.0 Hz, 1H), 6.95 (dd, *J* = 8.0, 4.0 Hz, 1H), 6.67 (m, 1H), 5.55 (m, 1H), 4.37 (dd, *J* = 12.0, 4.0 Hz, 1H), 3.10 (dd, *J* = 20.0, 12.0 Hz, 1H), 3.01 – 2.89 (m, 0.08H), 2.82 (dd, *J* = 20.0, 8.0 Hz, 1H), 1.26 – 1.19 (m, 9H).

[13]C NMR (100 MHz, $CDCl_3$) δ = 177.61, 176.31, 175.91, 150.03, 142.70, 136.61, 135.63, 131.45, 129.88, 129.13, 128.88, 128.55, 128.35, 127.56, 127.54, 127.48, 124.53, 122.39, 111.62, 57.28, 47.14, 35.76, 32.94, 31.38.

HRMS (ESI-TOF) calcd for $C_{28}H_{25}Cl^{34.9689}N_2O_3$ ($[M+Na^+]$) = 495.1446, Found 509.1458; $C_{28}H_{25}Cl^{36.9659}N_2O_3$ ($[M+Na^+]$) = 497.1416, Found 497.1441.



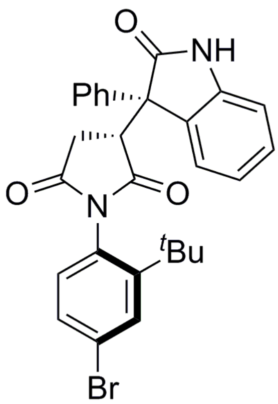
	Retention Time	Area	% Area
1	6.784	618279	17.59
2	11.206	636267	18.10
3	15.445	658895	18.74
4	21.057	1000054	28.45
5	29.162	601915	17.12



	Retention Time	Area	% Area

1	6.793	318861	4.30
2	11.230	154839	2.09
3	15.458	559399	7.55
4	28.669	6378514	86.06

(M)-(*R*)-1-(4-bromo-2-(tert-butyl)phenyl)-3-((*S*)-2-oxo-3-phenylindolin-3-yl)pyrrolidine-2,5-dione



3v

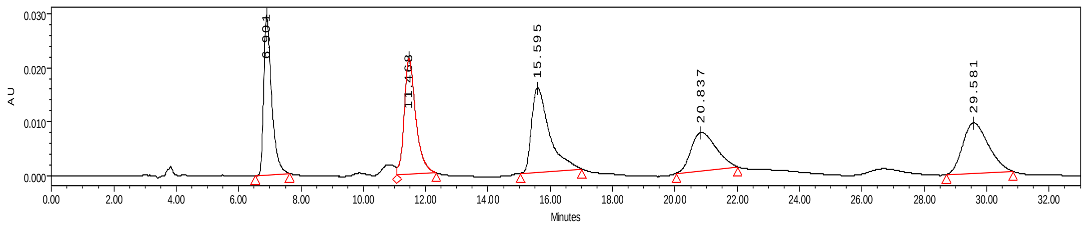
($C_{28}H_{25}BrN_2O_3$) colorless oil; 99% yield, 84% *ee*, 9:1 d.r. $[\alpha]_D^{13.7}$ = −143.47 (c 0.812, CH_2Cl_2, 84% *ee*).

HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 6.901 min, 11.468 min, 15.595 min, 20.837 min, 29.581 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 – 8.47 (m, 1H), 7.58 (m, 1H), 7.39 – 7.28 (m, 6H), 7.27 (m, 1H), 7.18 – 7.05 (m, 2H), 6.68 (m, 5.47 (m, 1H), 4.36 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.10 (dd, *J* = 16.0, 8.0 Hz, 1H), 3.02 – 2.89 (m, 0.04 H), 2.82 (dd, *J* = 20.0, 4.0 Hz, 1H), 1.22 (m, 9H).

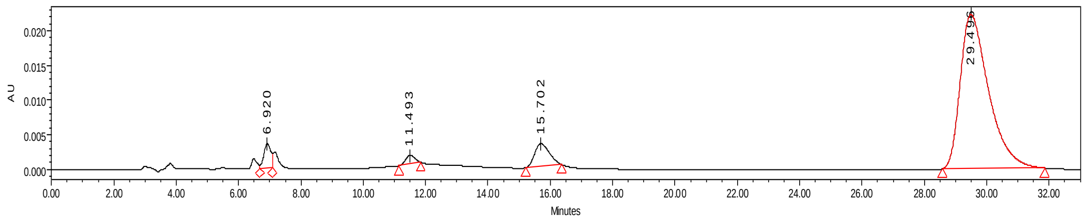
^{13}C NMR (100 MHz, $CDCl_3$) δ = 177.57, 176.23, 175.84, 150.31, 142.68, 136.60, 131.84, 131.70, 130.56, 129.92, 129.13, 128.36, 127.56, 127.47, 124.56, 124.06, 122.40, 111.57, 57.26, 47.16, 35.76, 32.95, 31.40.

HRMS (ESI-TOF) calcd for $C_{28}H_{25}Br^{78.9183}N_2O_3$ ($[M+Na^+]$) = 539.0941, Found 539.0971; $C_{28}H_{25}Br^{80.9163}N_2O_3$ ($[M+Na^+]$) = 541.0920, Found 555.0943.



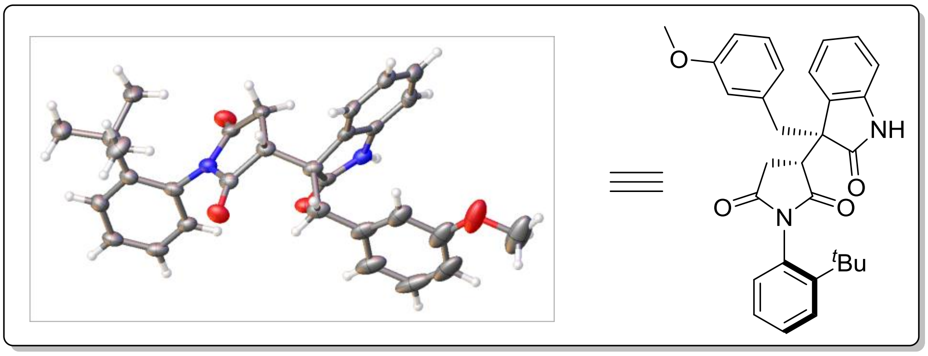
	Retention Time	Area	% Area
1	6.901	517710	19.93
2	11.468	545581	21.00

3	15.595	614456	23.66
4	20.837	389662	15.00
5	29.581	529984	20.40



	Retention Time	Area	% Area
1	6.920	55682	3.49
2	11.493	25209	1.58
3	15.702	108483	6.79
4	29.496	1407745	88.14

5. The X-ray data for 3j.



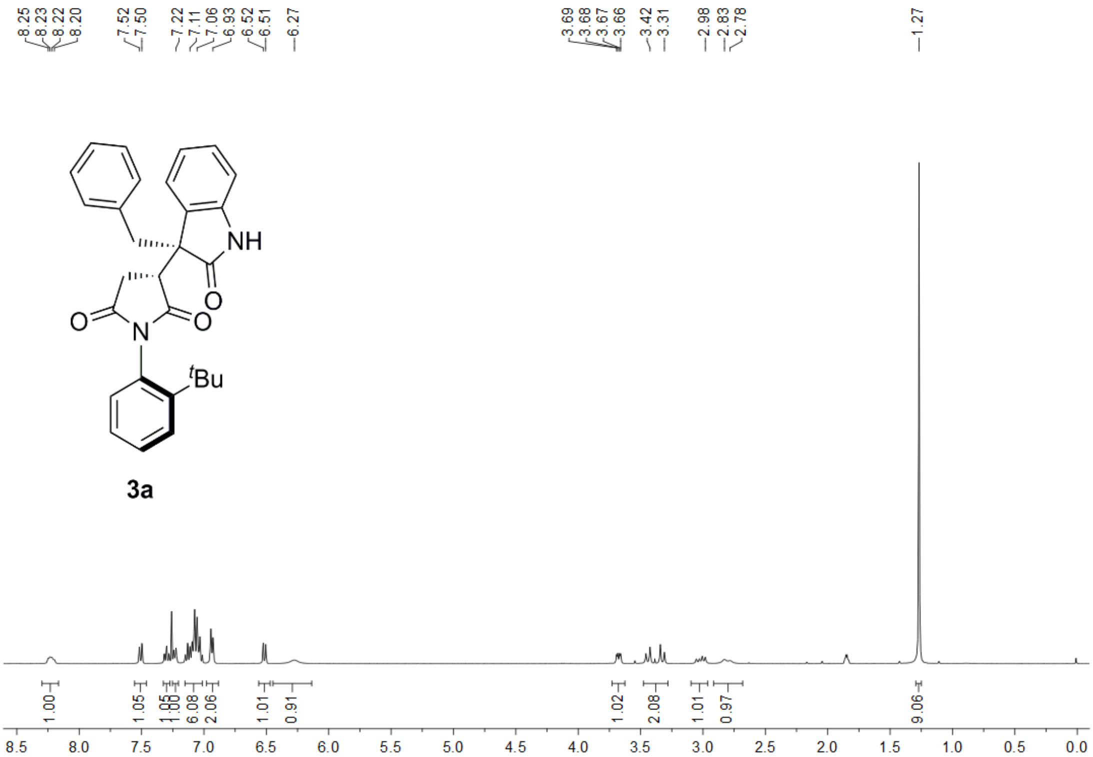
The product **3j** was recrystallized from EtOH and Pet.

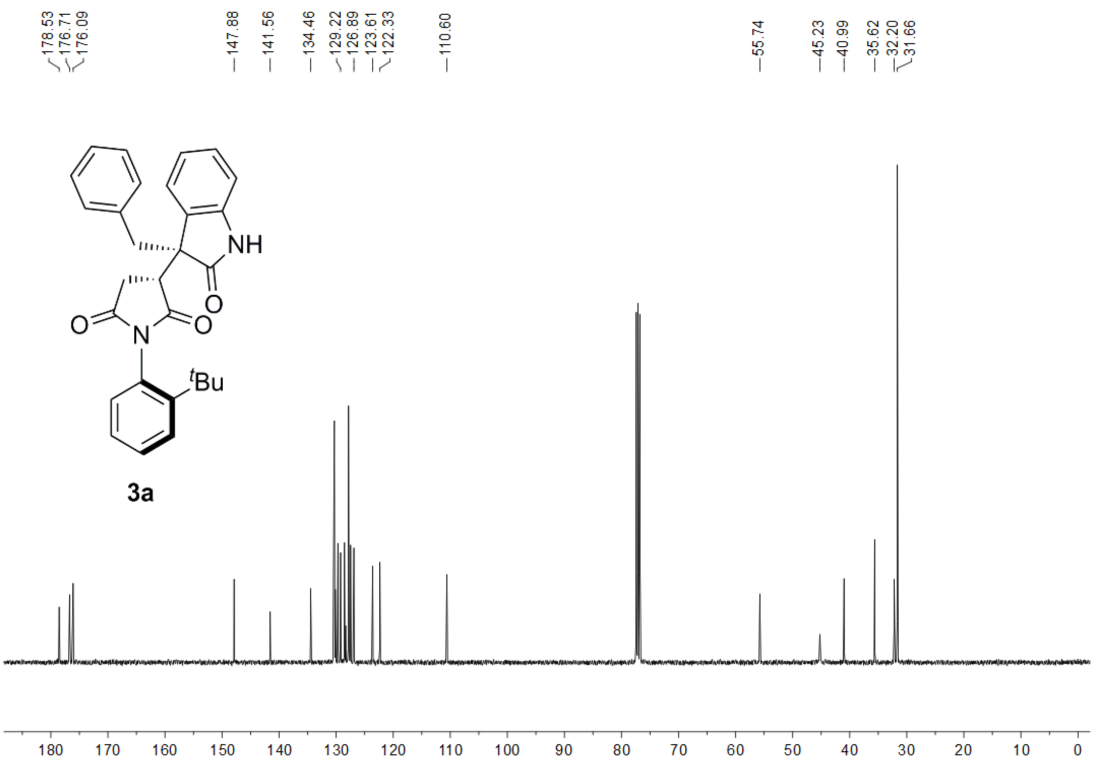
CCDC-1037298 (**3j**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk./ data_request/cif.

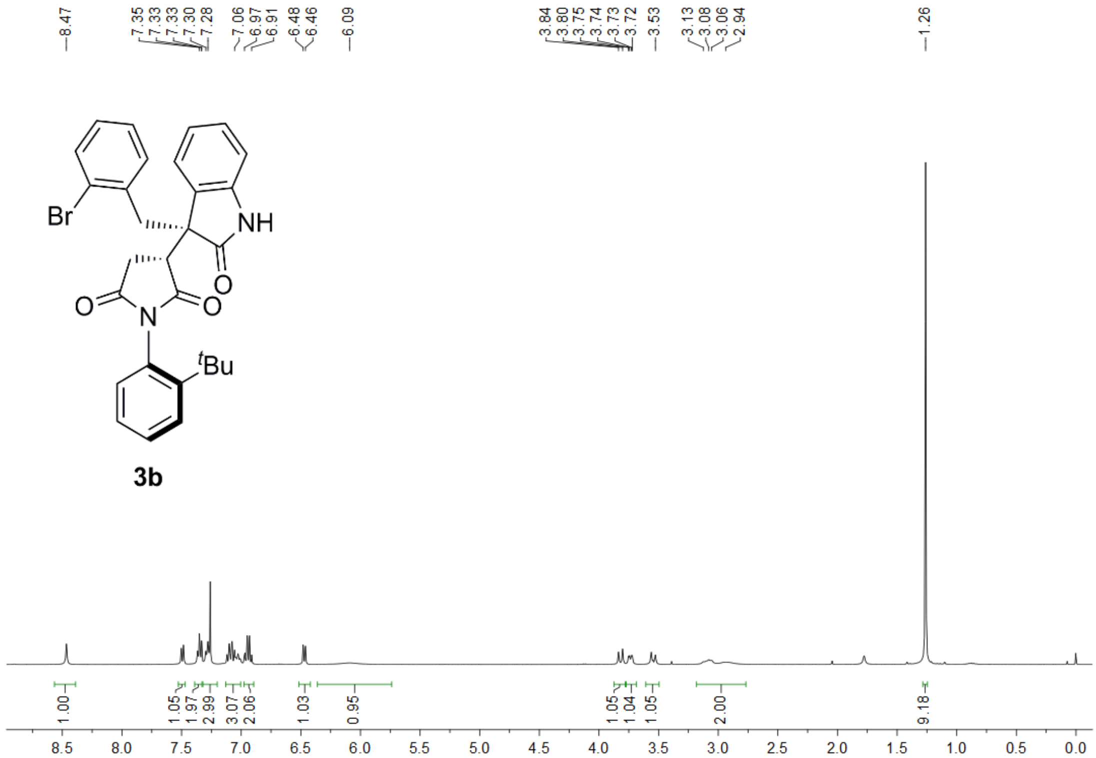
6. References.

(1) *a*) Y. H. Wen, X. Huang, J. L. Huang, Y. Xiong, B. Qin, X. M. Feng, *Synlett* **2005**, 2445; *b*) Z. P. Yu, X. H. Liu, Z. H. Dong, M. S. Xie, X. M. Feng, *Angew. Chem.* **2008**, *120*, 1328-1331; *Angew. Chem. Int. Ed.* **2008**, *47*, 1308-1311; *c*) K. Zheng, B. Qin, X. H. Liu, X. M. Feng, *J. Org. Chem.* **2007**, *72*, 8478; *d*) X. Zhang, D. H. Chen, X. H. Liu, X. M. Feng, *J. Org. Chem.* **2007**, *72*, 5227; *e*) X. Zhou, D. J. Shang, Q. Zhang, L. L. Lin, X. H. Liu, X. M. Feng, *Org. Lett.* **2009**, *11*, 1401.

7. NMR spectrum.







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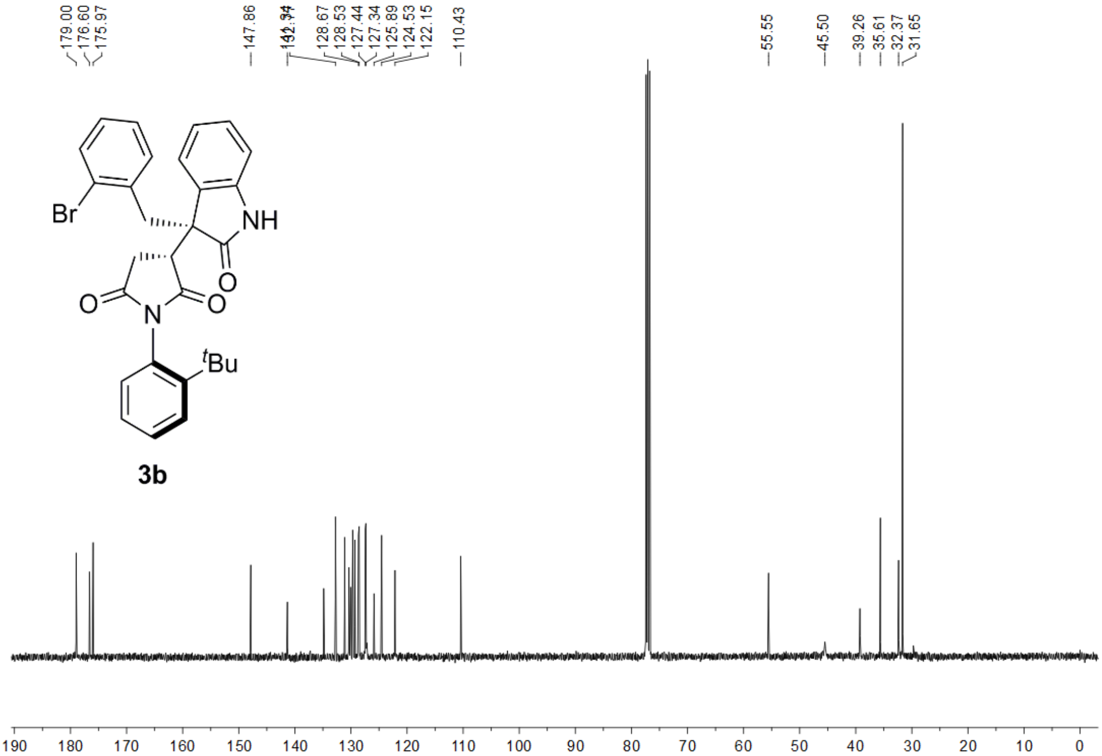

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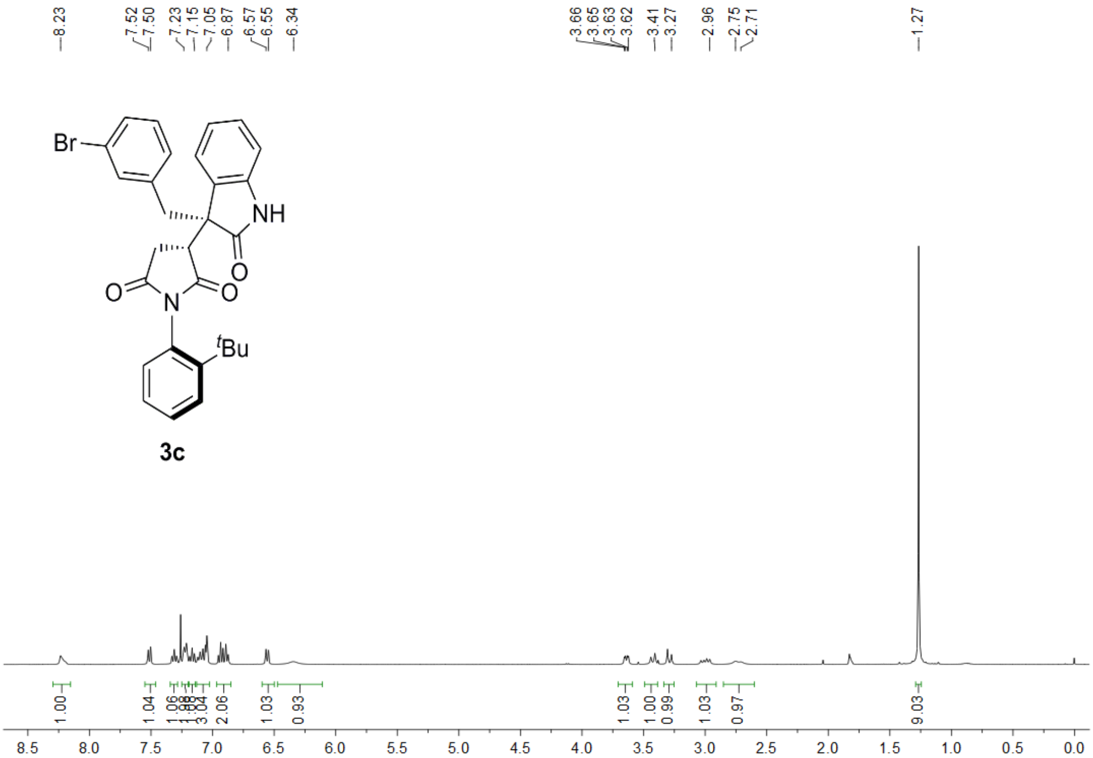

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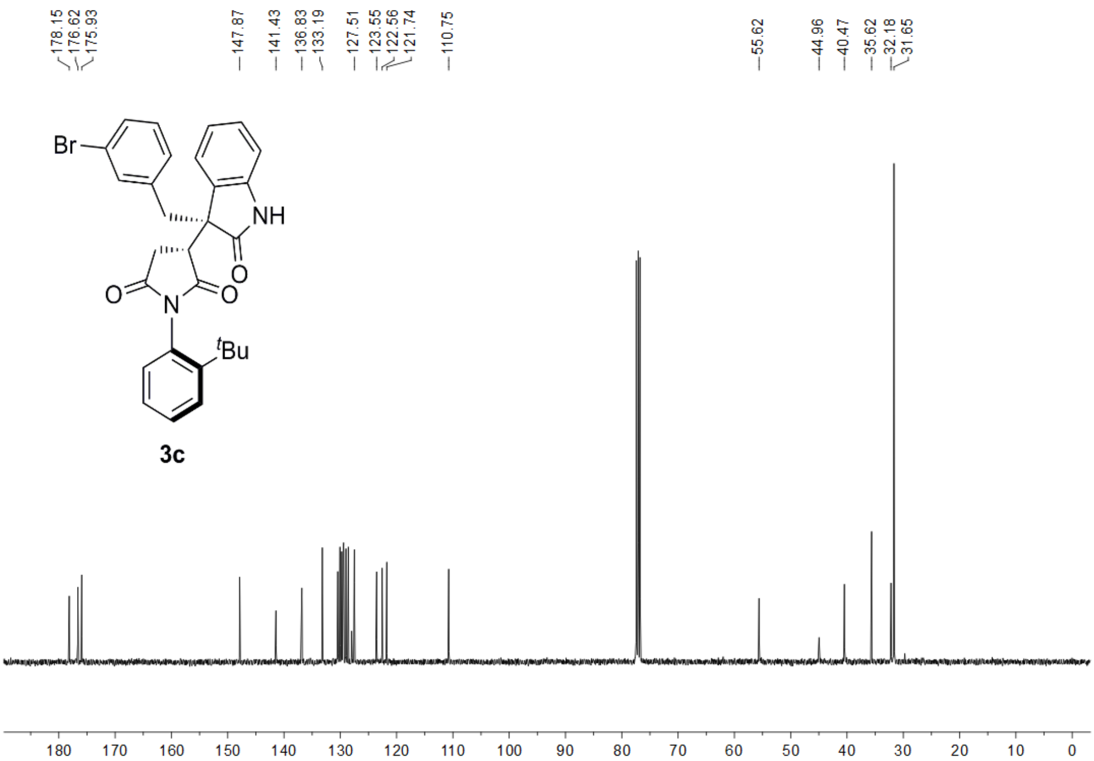

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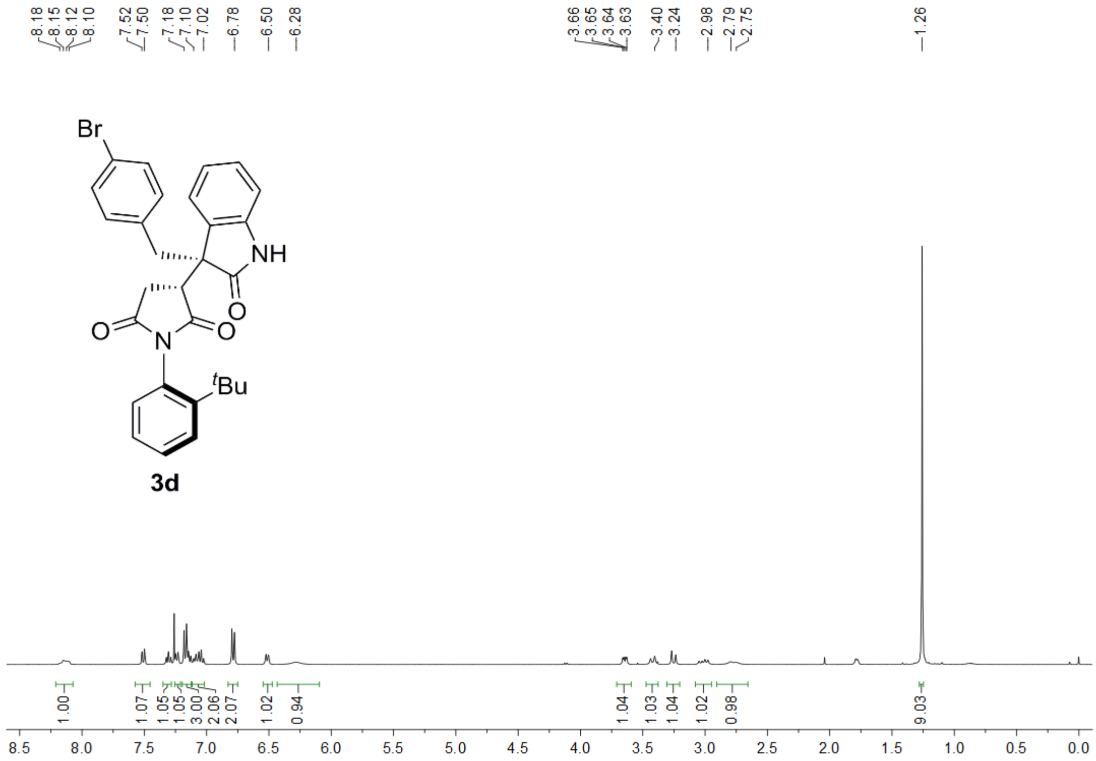

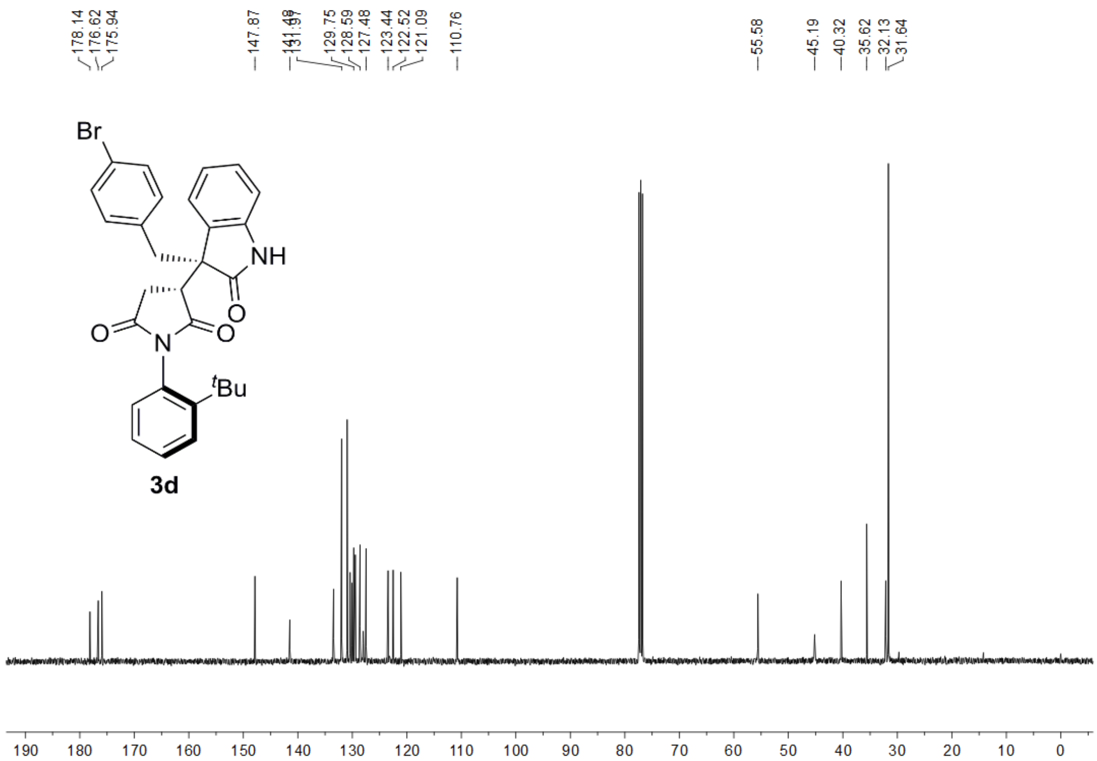

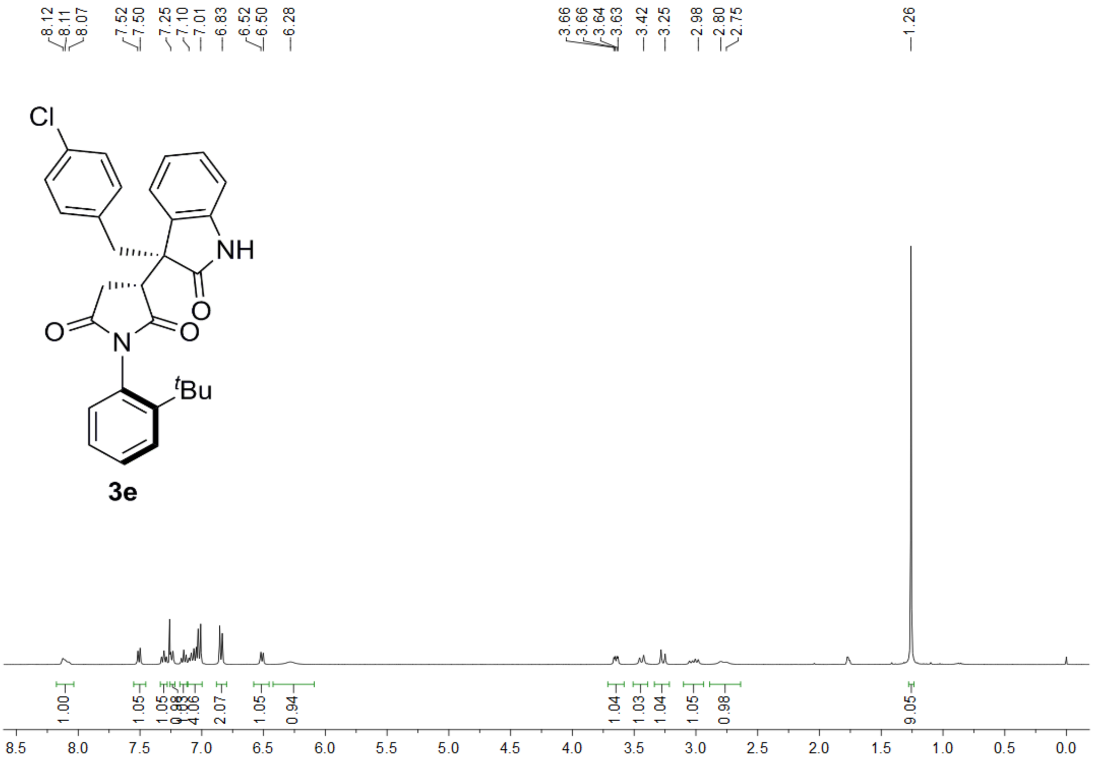
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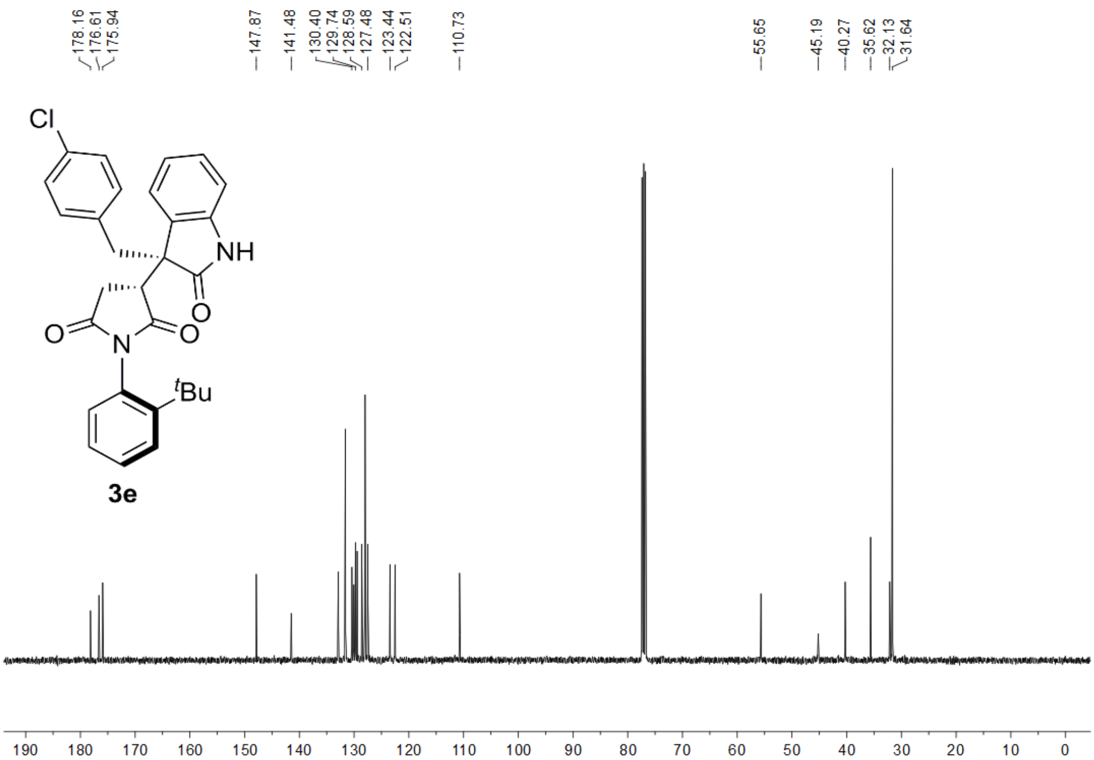
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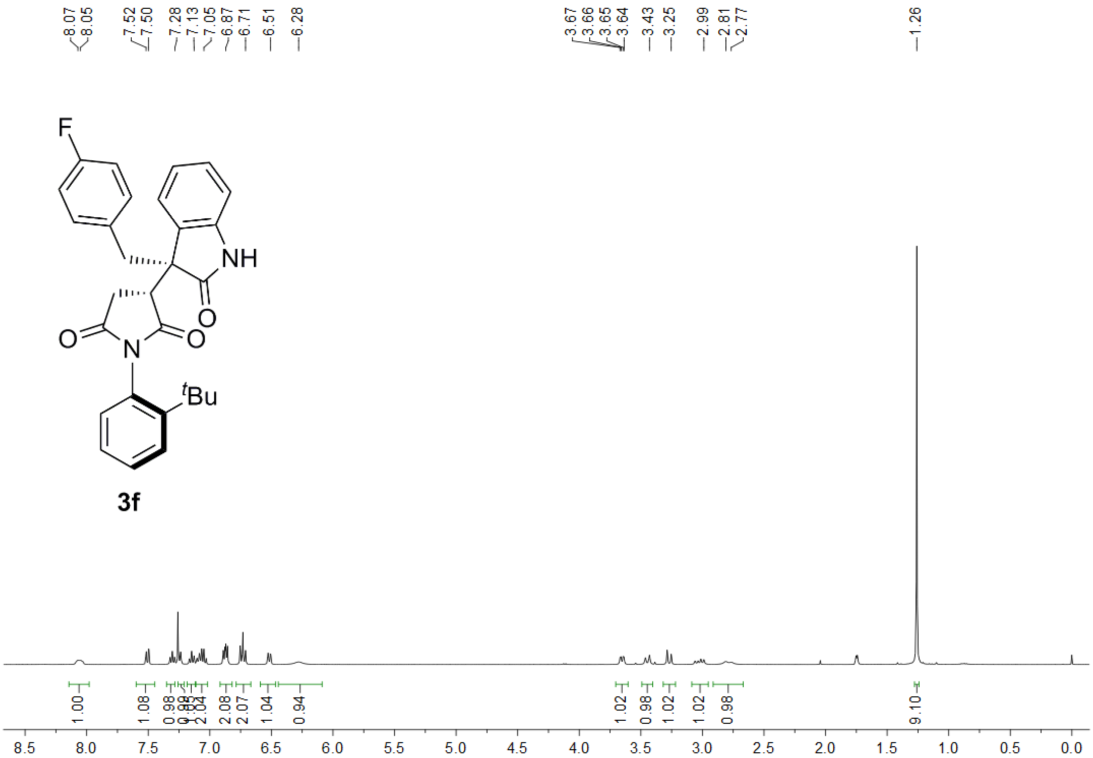
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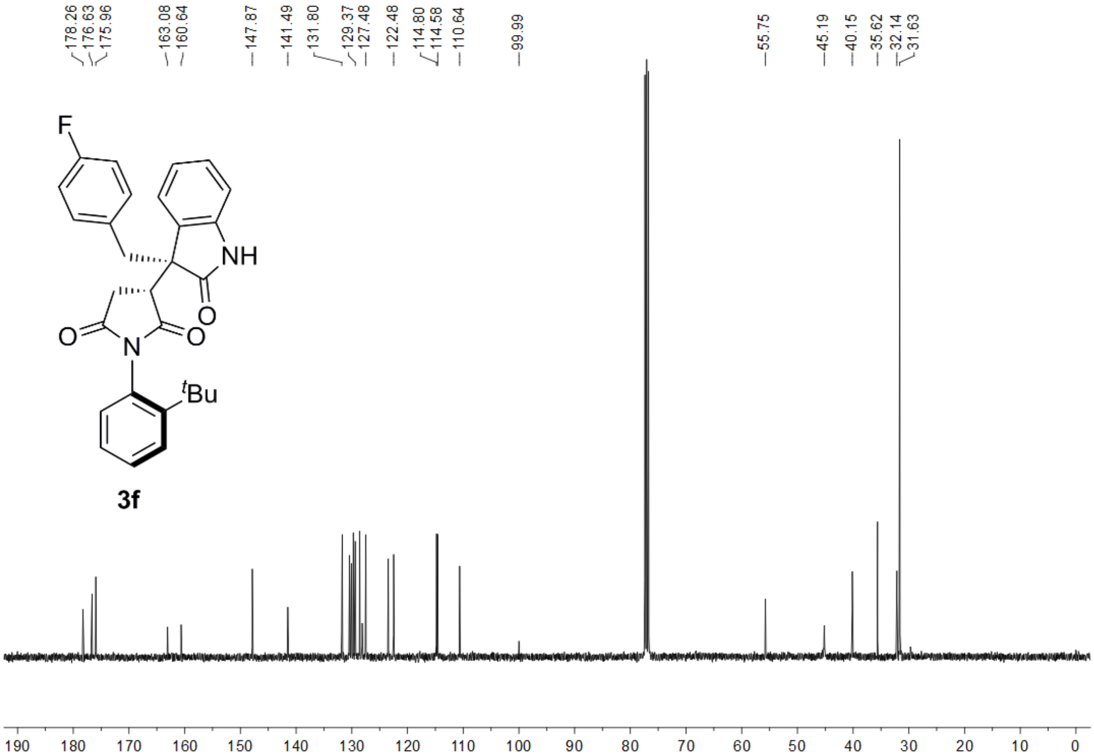
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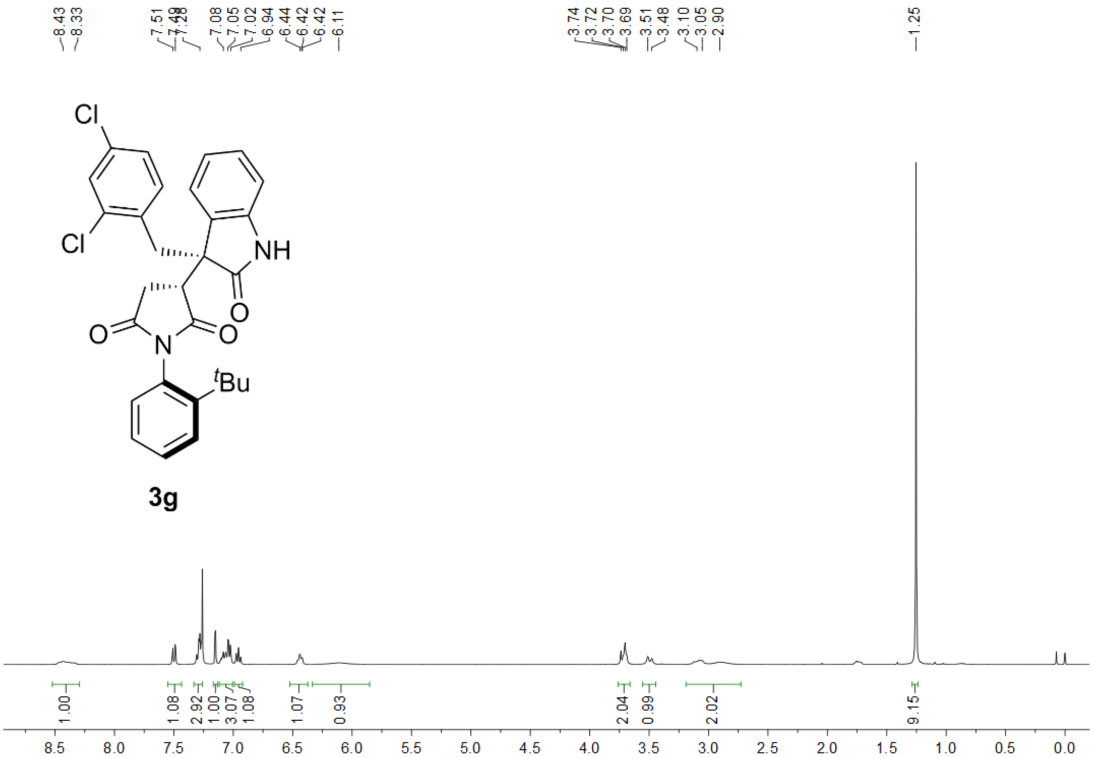
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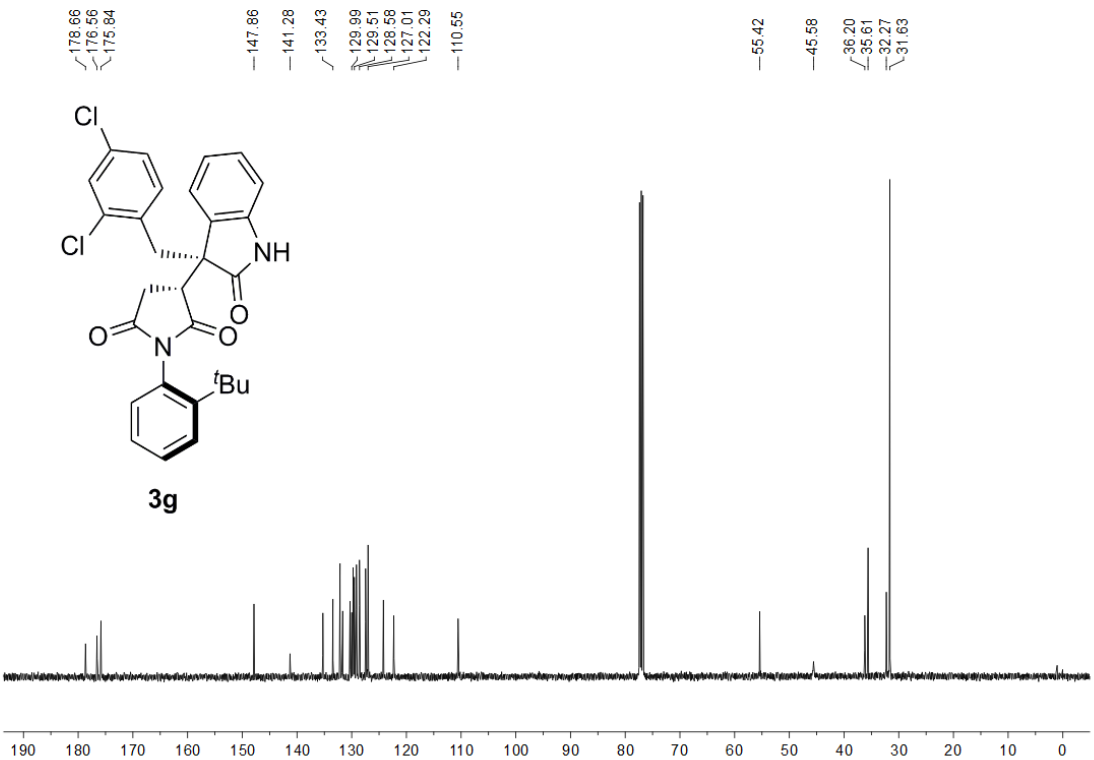
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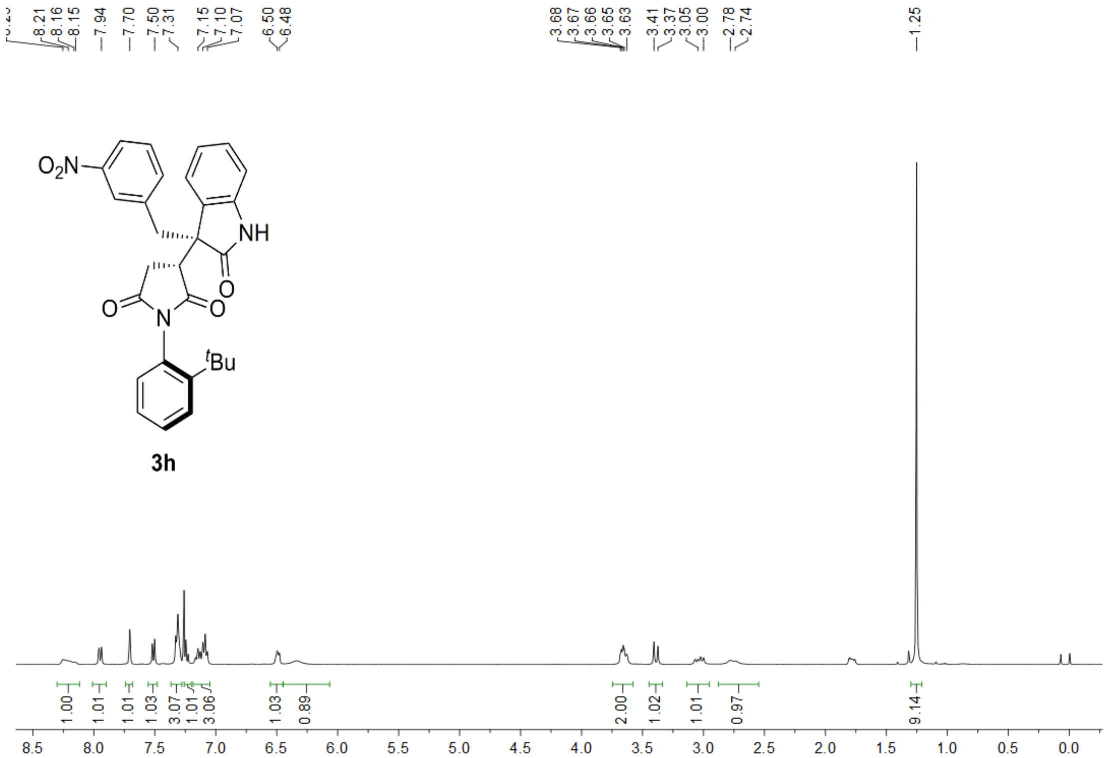
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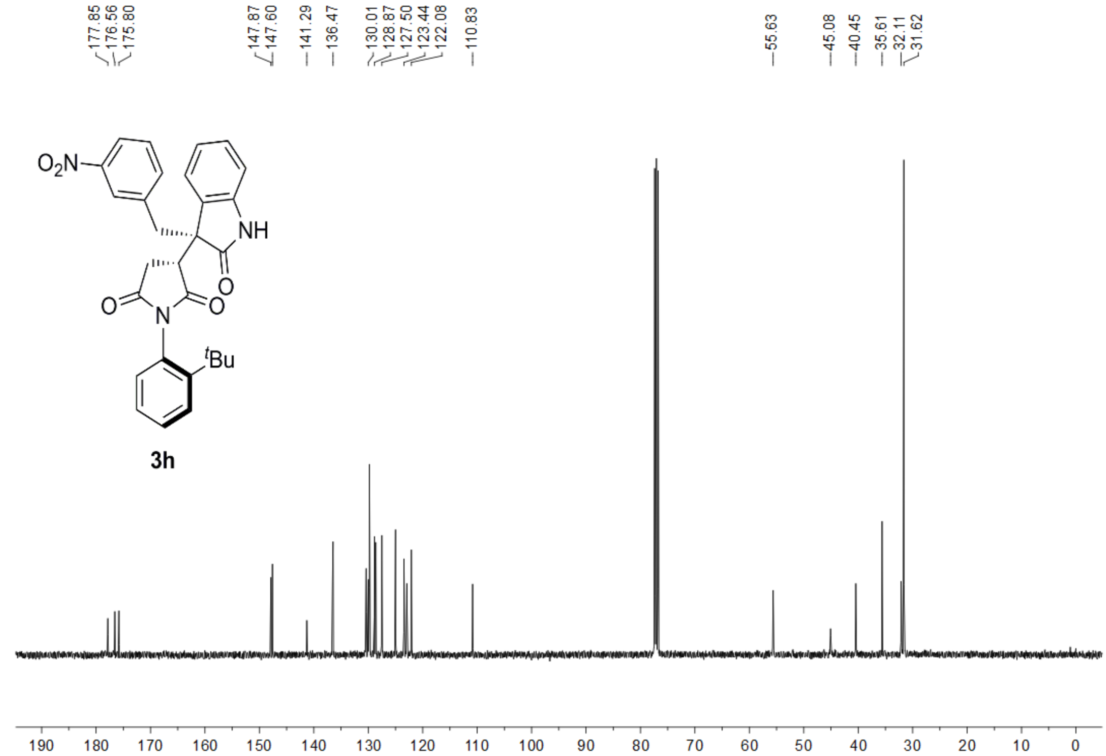
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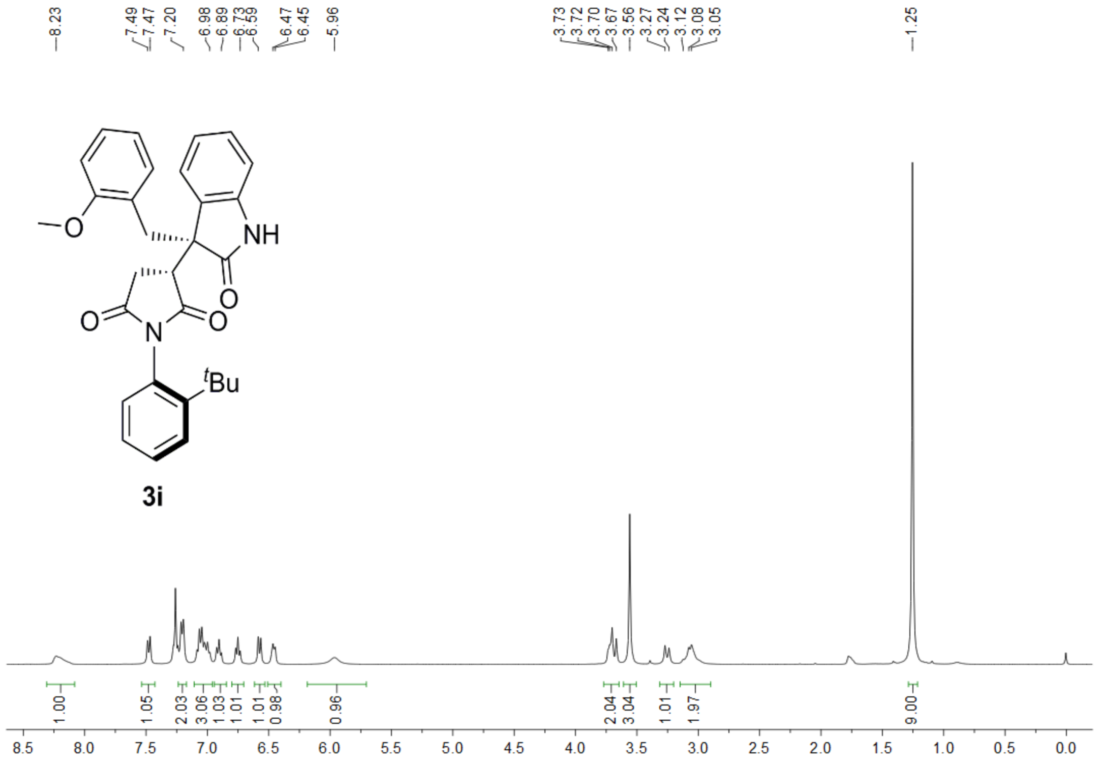

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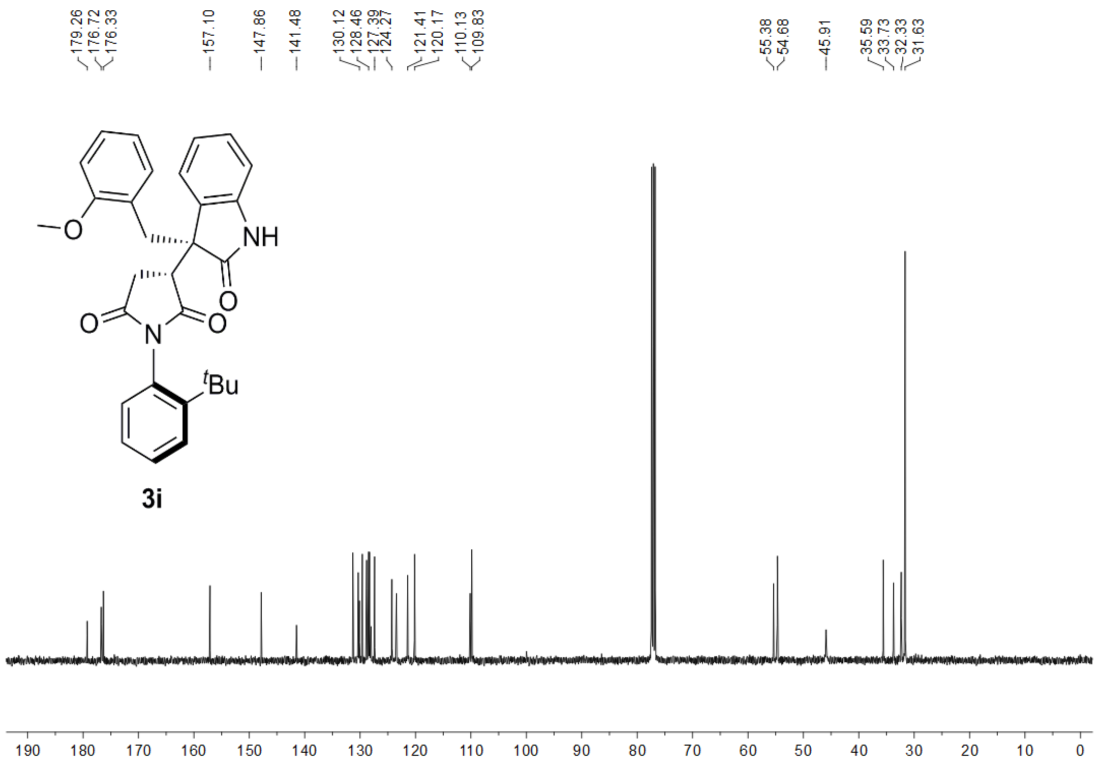

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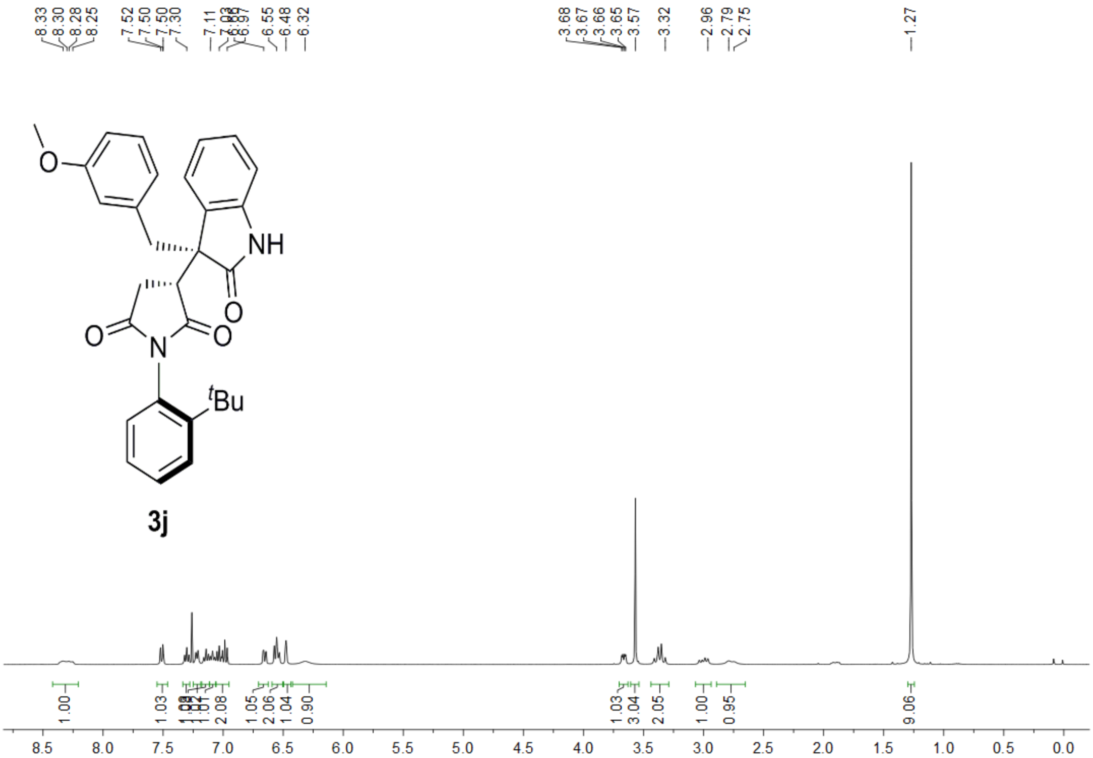
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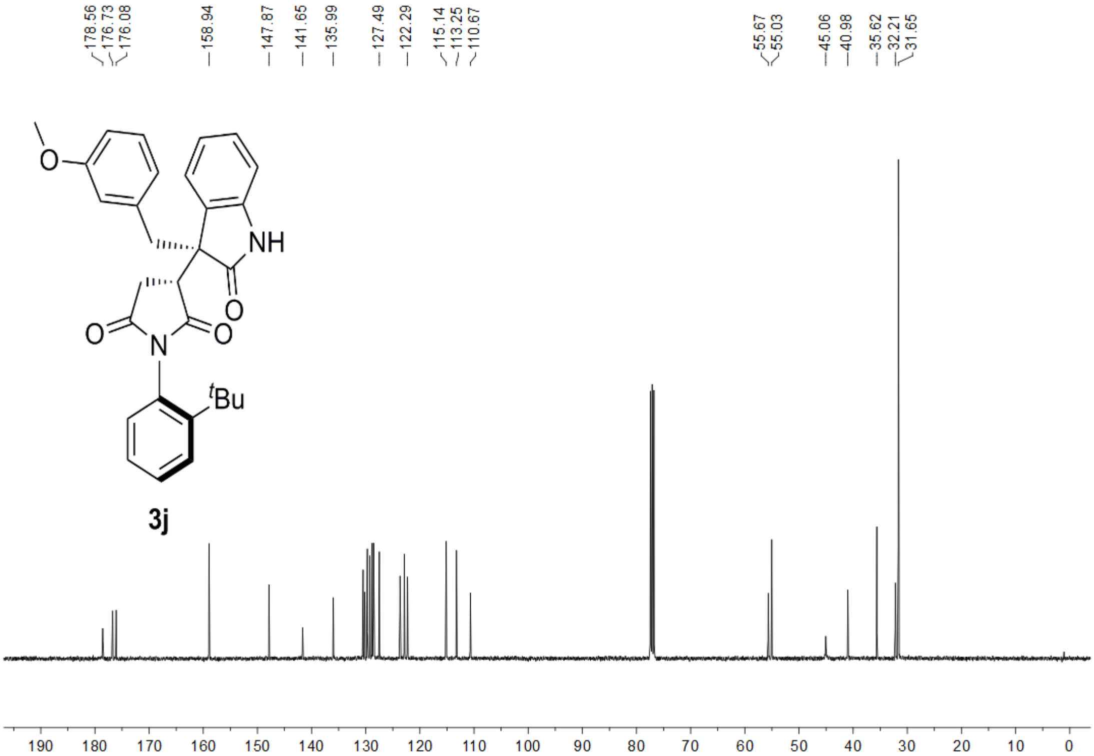
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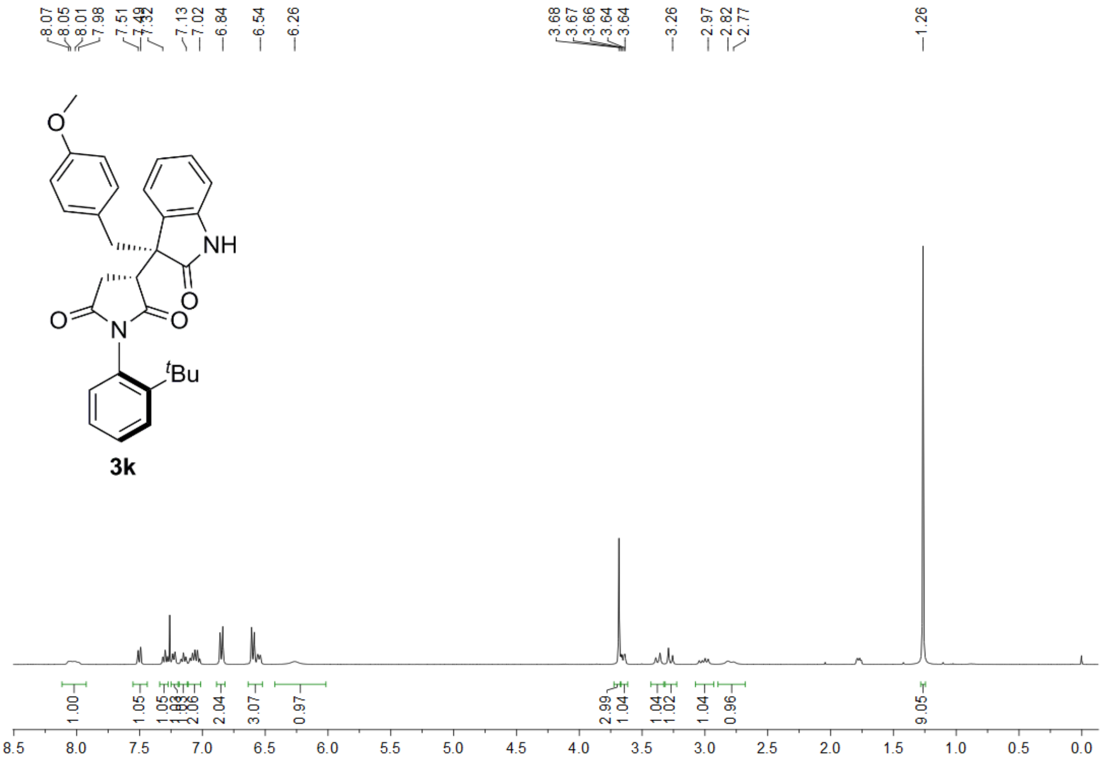
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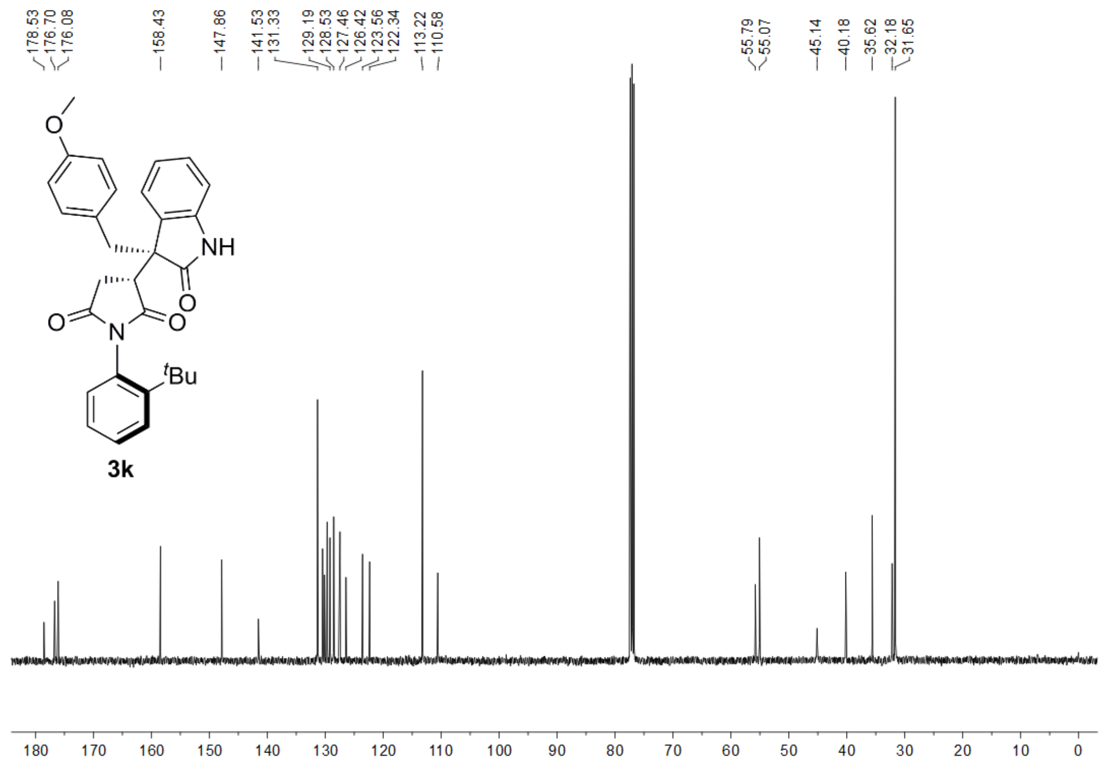
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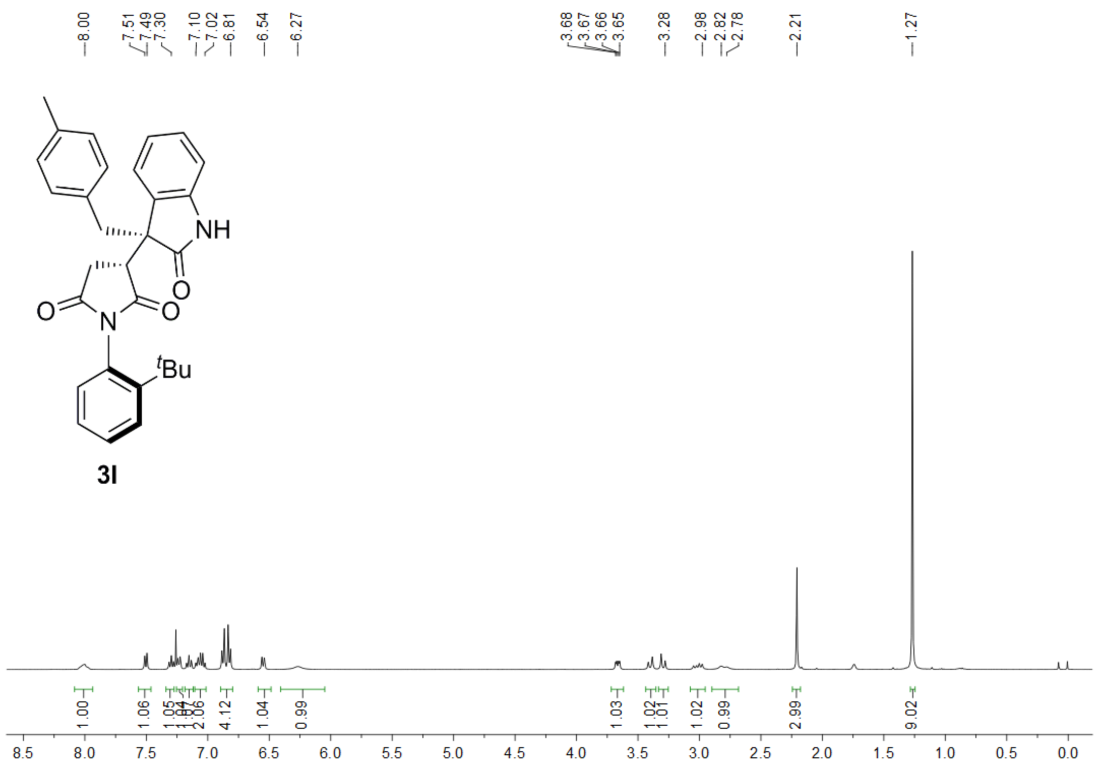

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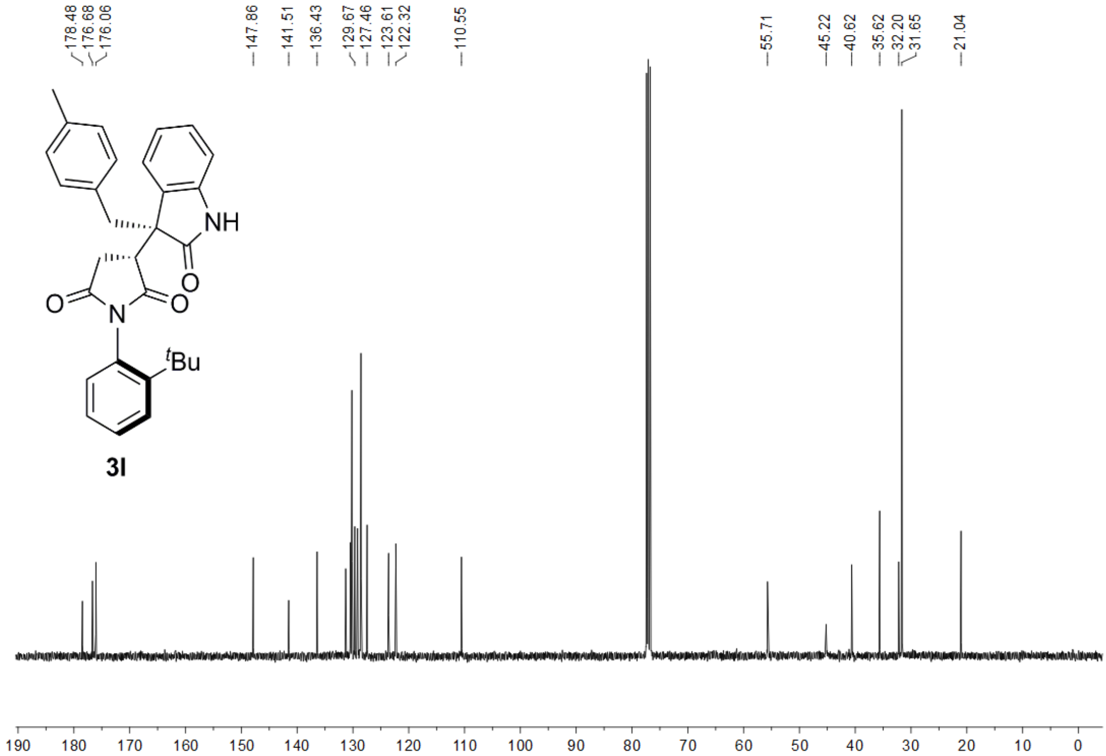

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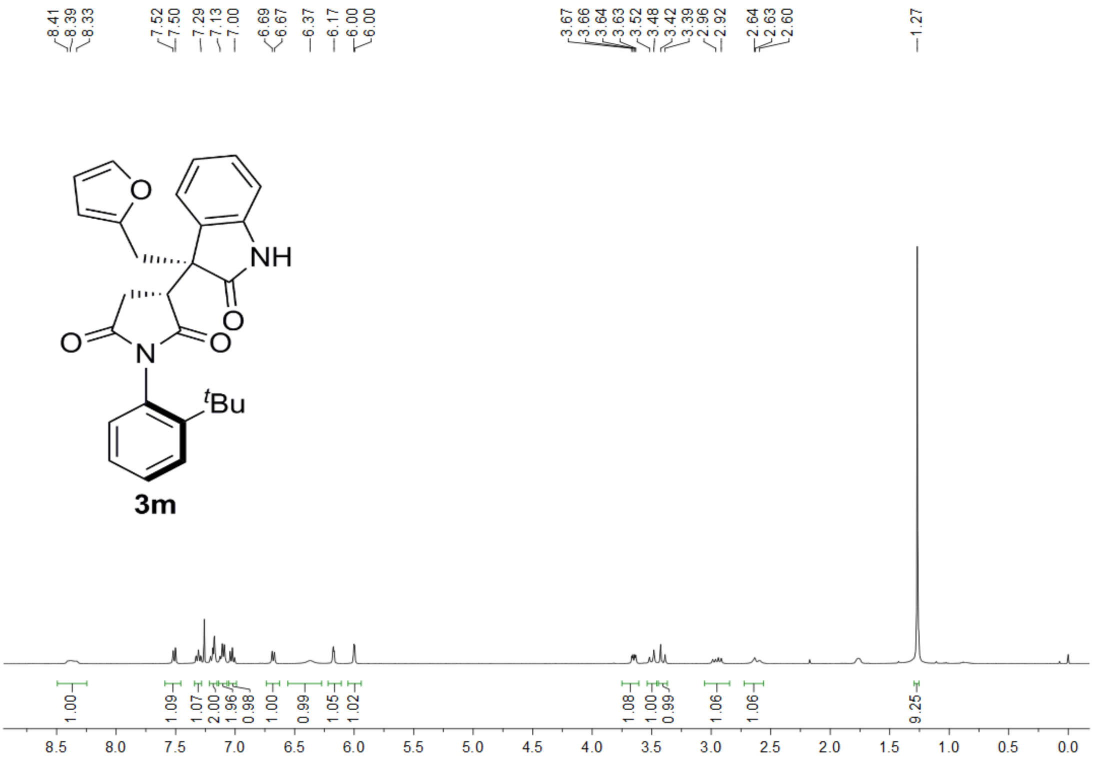
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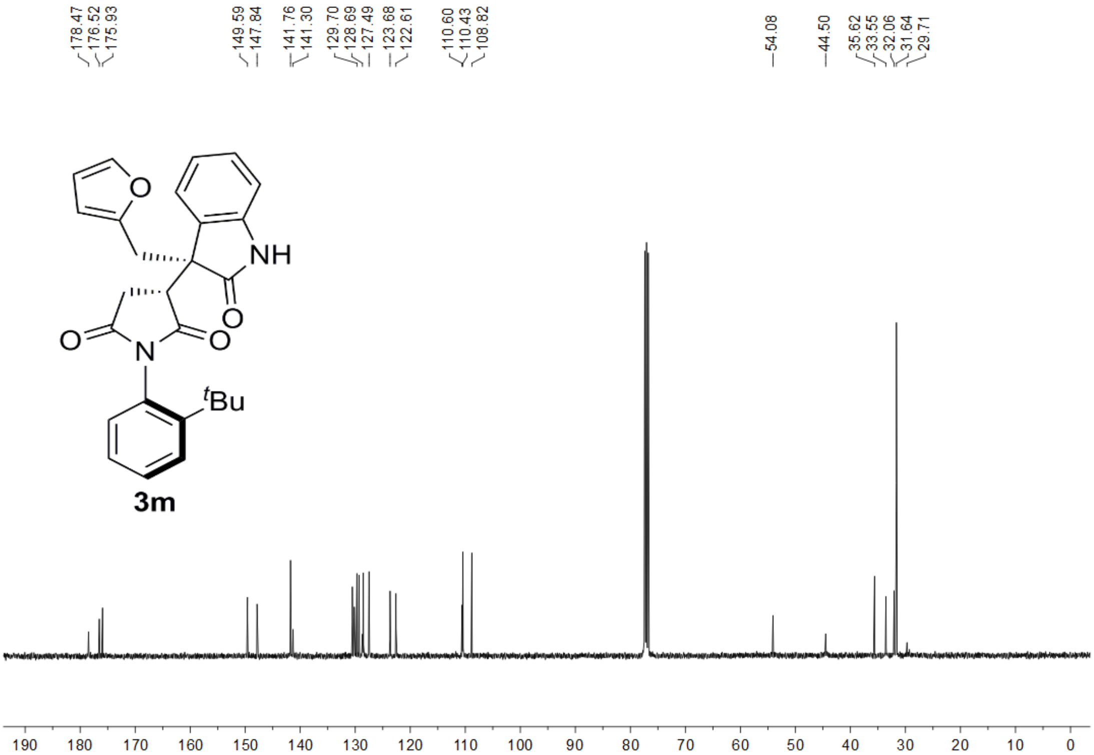
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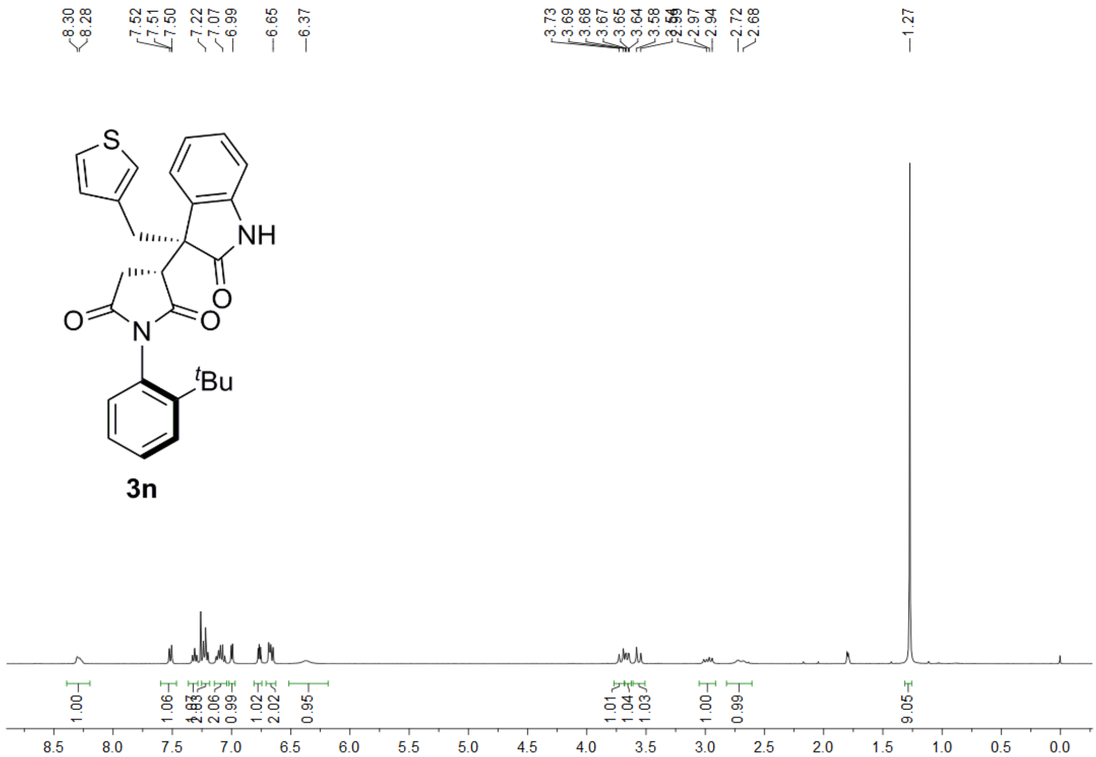
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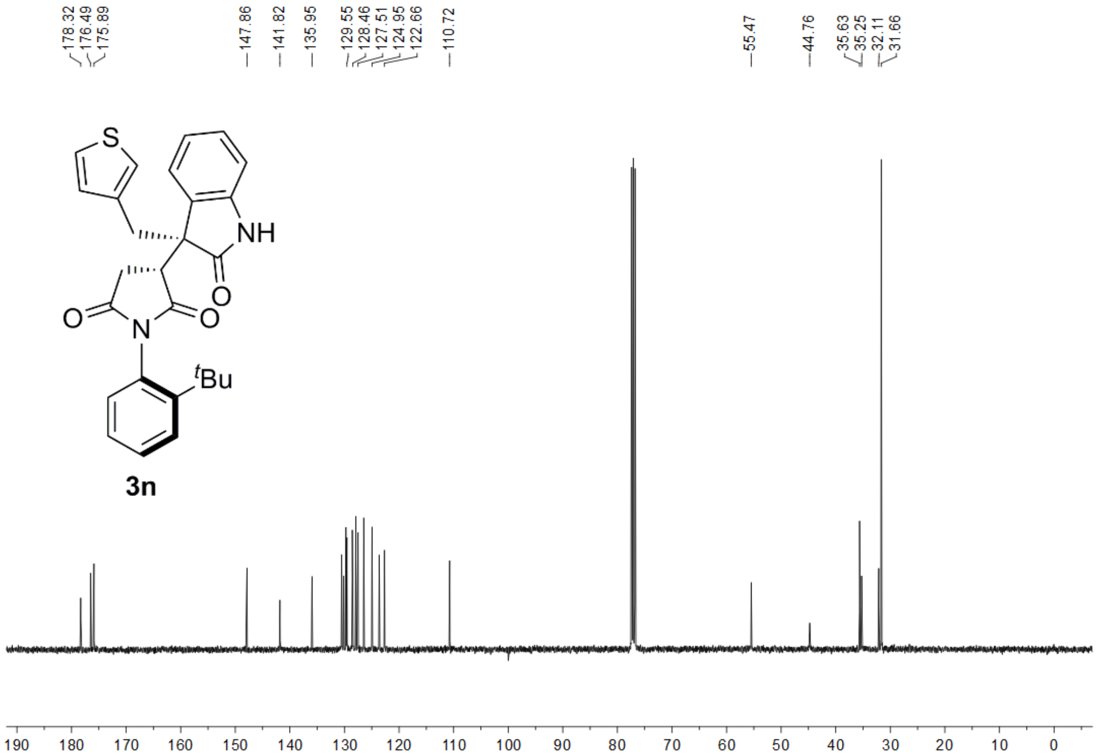
7.52
7.51
7.50
7.22
7.07
6.99
6.65
6.37
3.73
3.69
3.68
3.67
3.65
3.64
3.58
3.54
2.99
2.97
2.94
2.72
2.68
1.27
S
NH
O
N
tBu
1.00
1.06
1.03
2.06
0.99
1.02
2.02
0.95
1.01
1.04
1.03
1.00
0.99
9.05

3n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176.49
175.89
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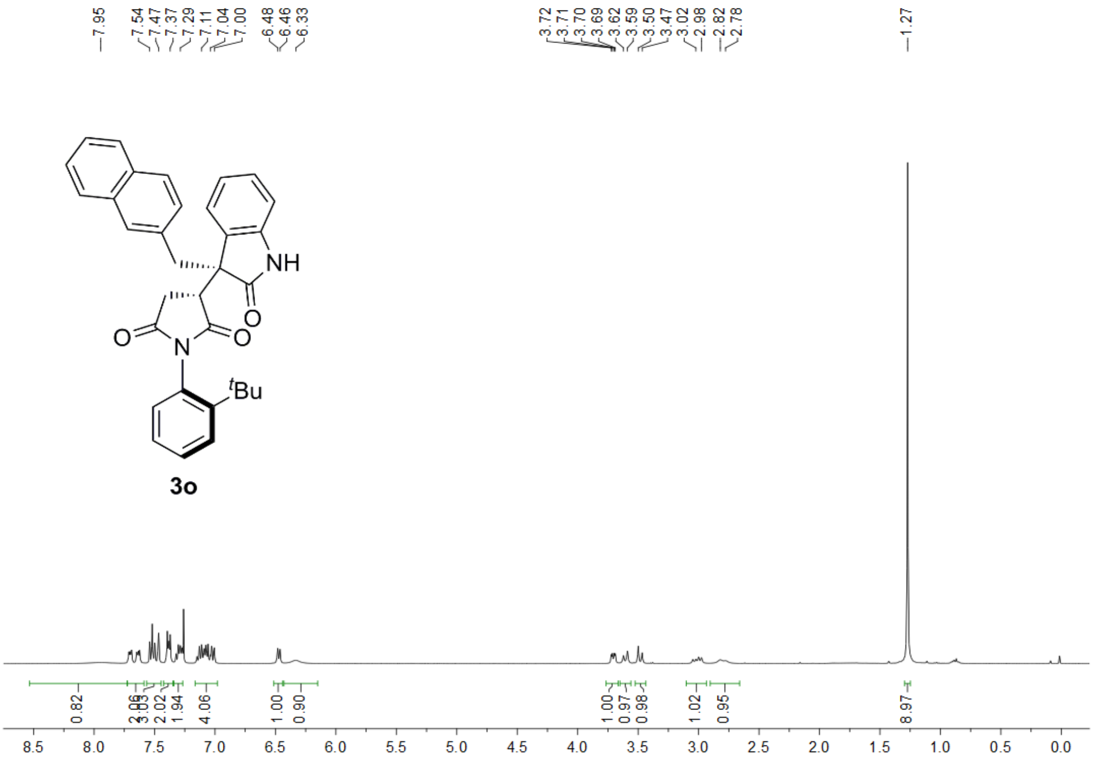
141.82
135.95
129.55
128.46
127.51
124.95
122.66
110.72
55.47
44.76
35.63
35.25
32.11
31.66
S
NH
O
N
tBu

3n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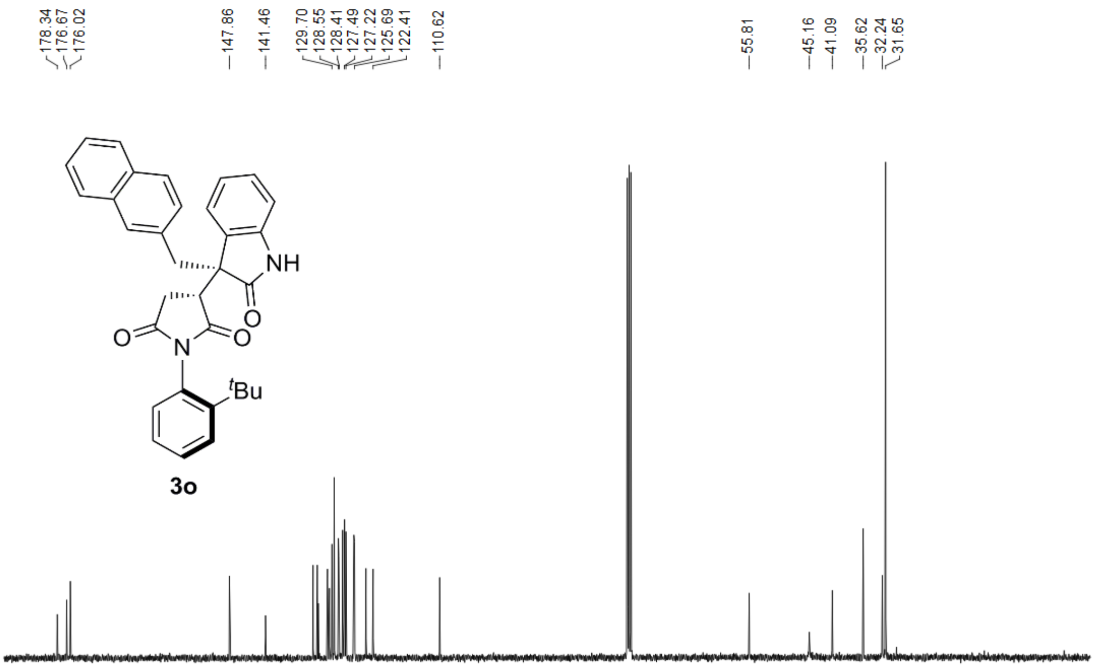
7.54
7.47
7.37
7.29
7.11
7.04
7.00
6.48
6.46
6.33
3.72
3.71
3.70
3.69
3.62
3.59
3.50
3.47
3.02
2.98
2.82
2.78
1.27
NH
O
N
^{t}Bu
0.82
2.06
3.03
2.02
1.94
4.06
1.00
0.90
1.00
0.97
0.98
1.02
0.95
8.97
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

3o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176.67
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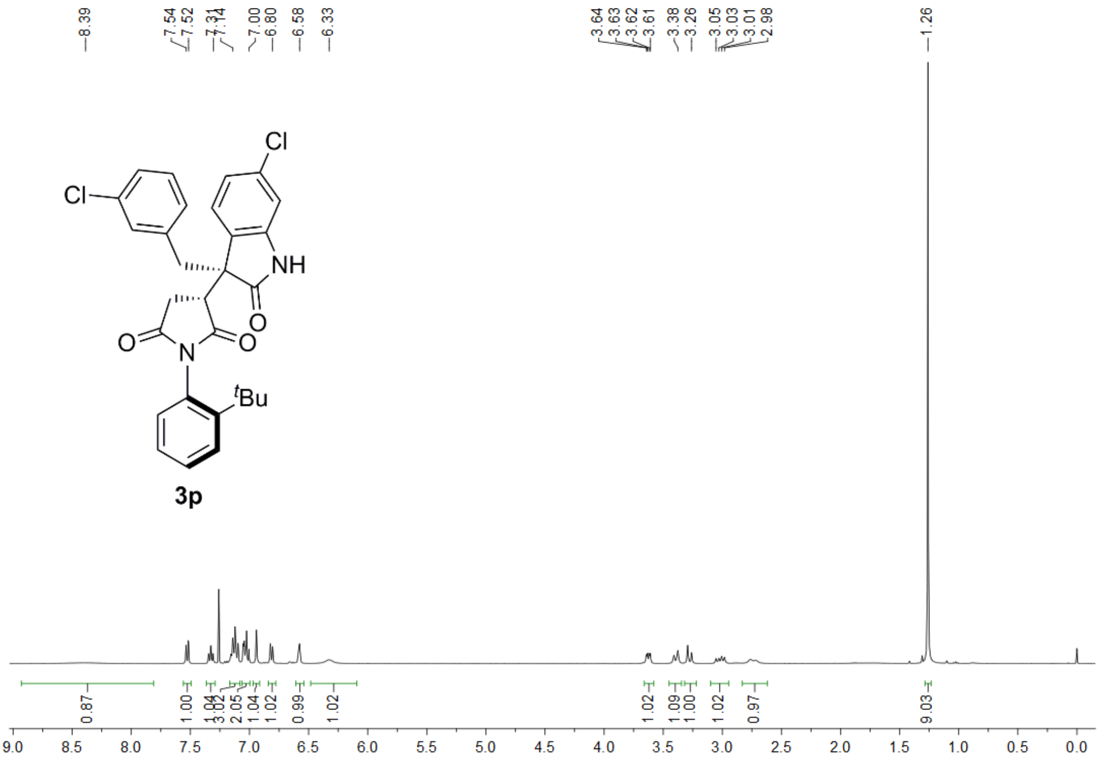
147.86
141.46
129.70
128.55
128.41
127.49
127.22
125.69
122.41
110.62
55.81
45.16
41.09
35.62
32.24
31.65
NH
O
N
^{t}Bu
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

3o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7.31
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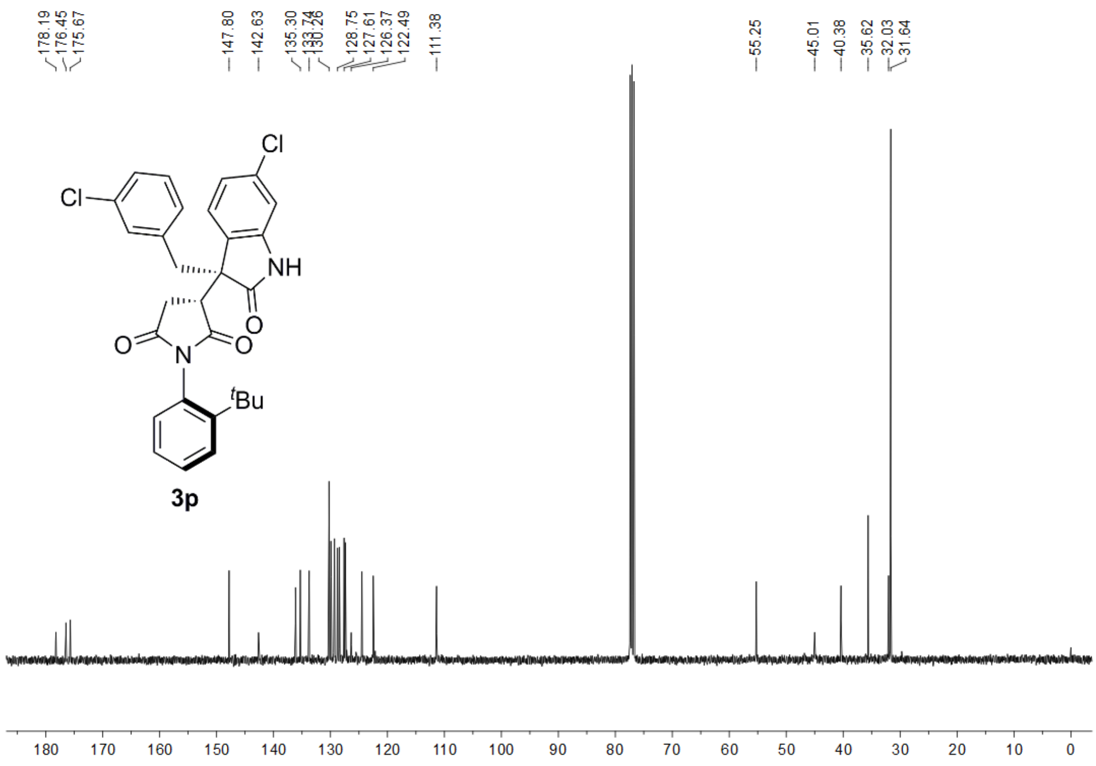
7.00
6.80
6.58
6.33
3.64
3.63
3.62
3.61
3.38
3.26
3.05
3.03
3.01
2.98
1.26
Cl
Cl
NH
O
O
O
N
tBu
3p
0.87
1.00
1.04
3.02
2.05
1.04
1.02
0.99
1.02
1.02
1.09
1.00
1.02
0.97
9.03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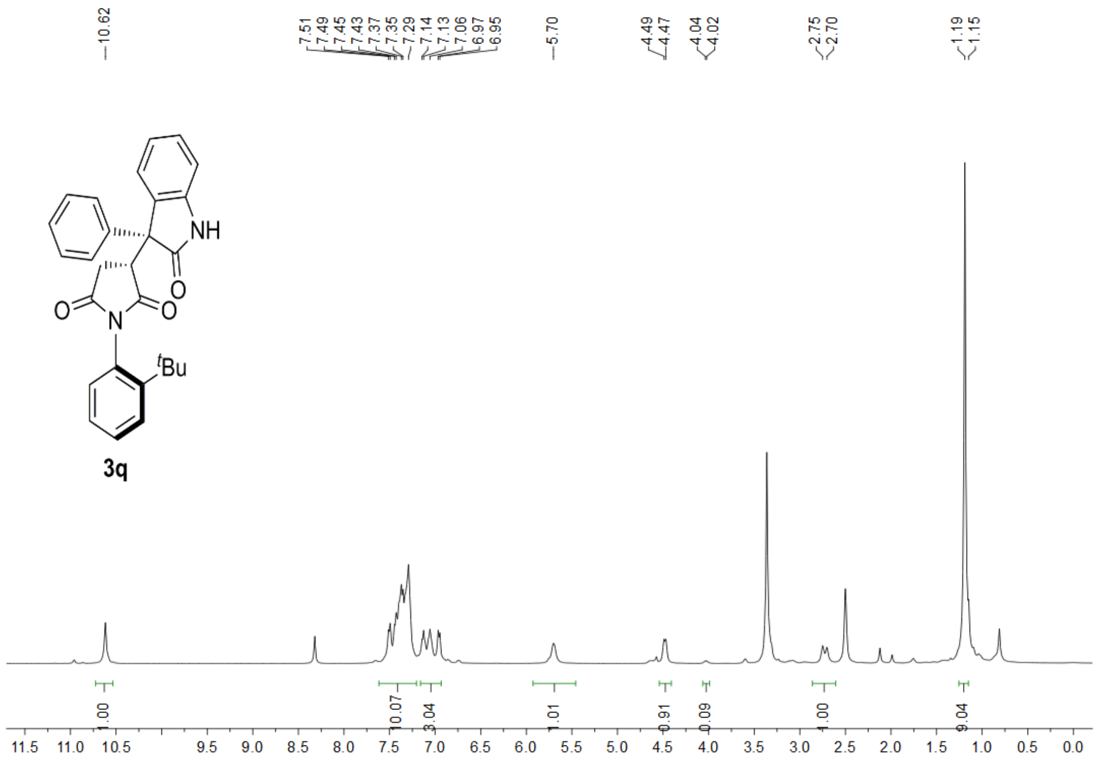
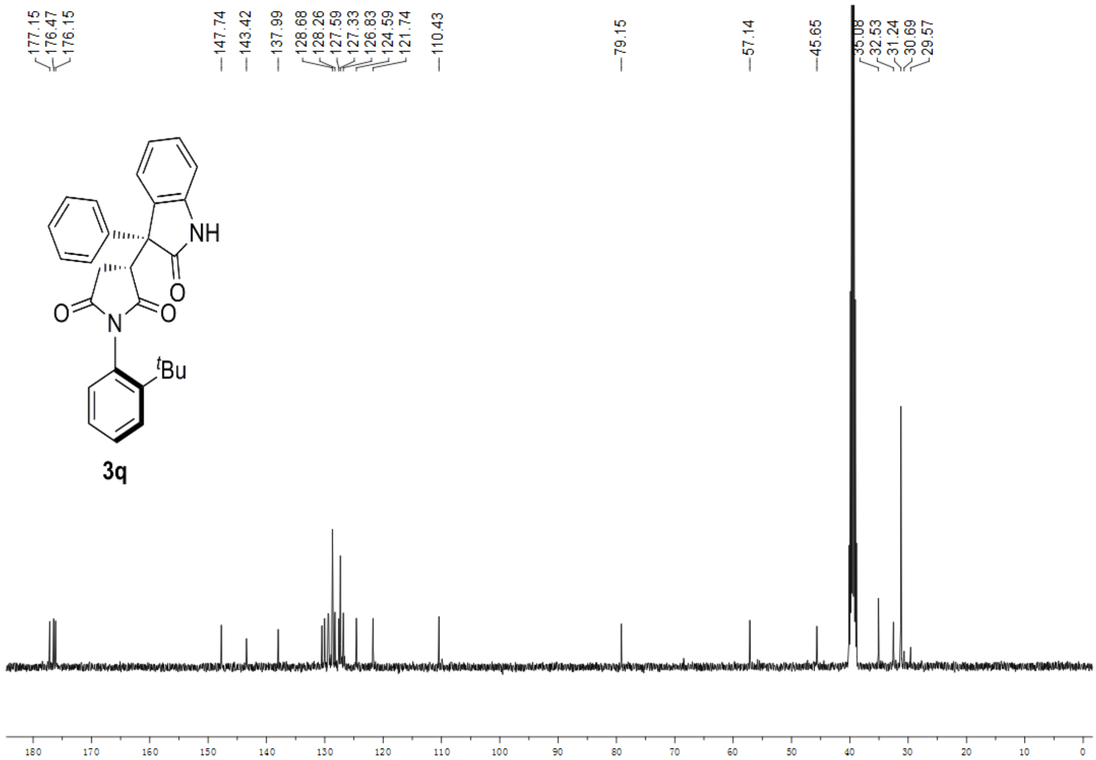
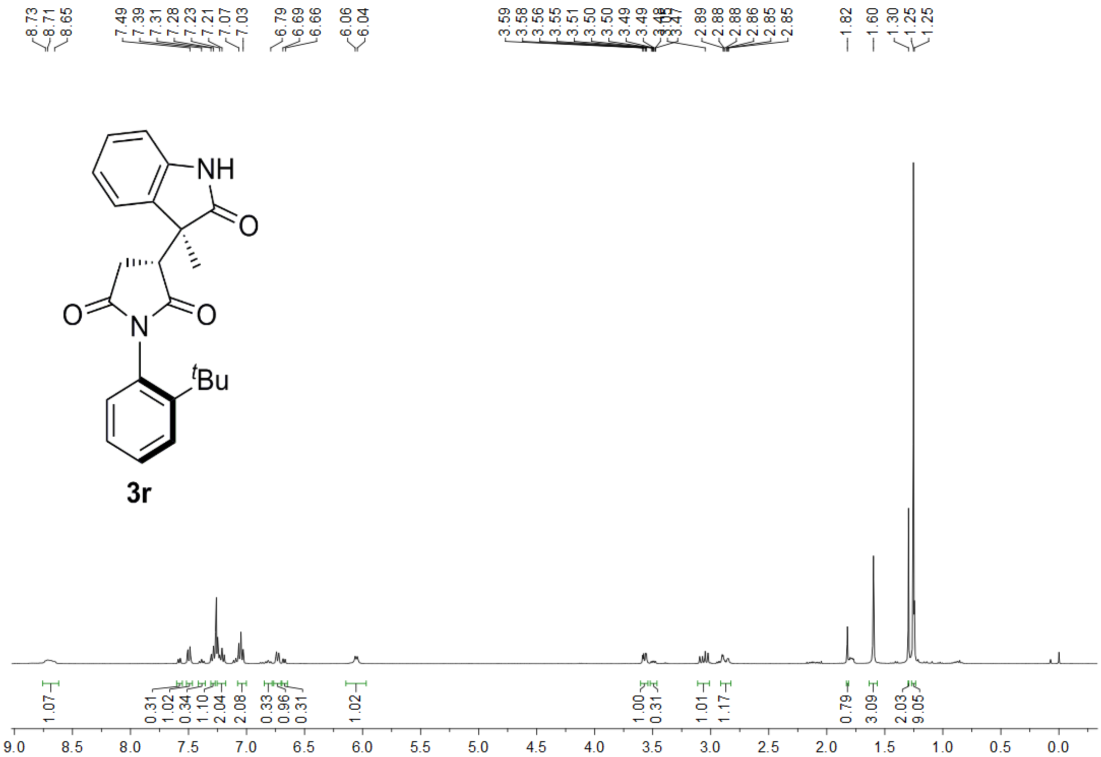
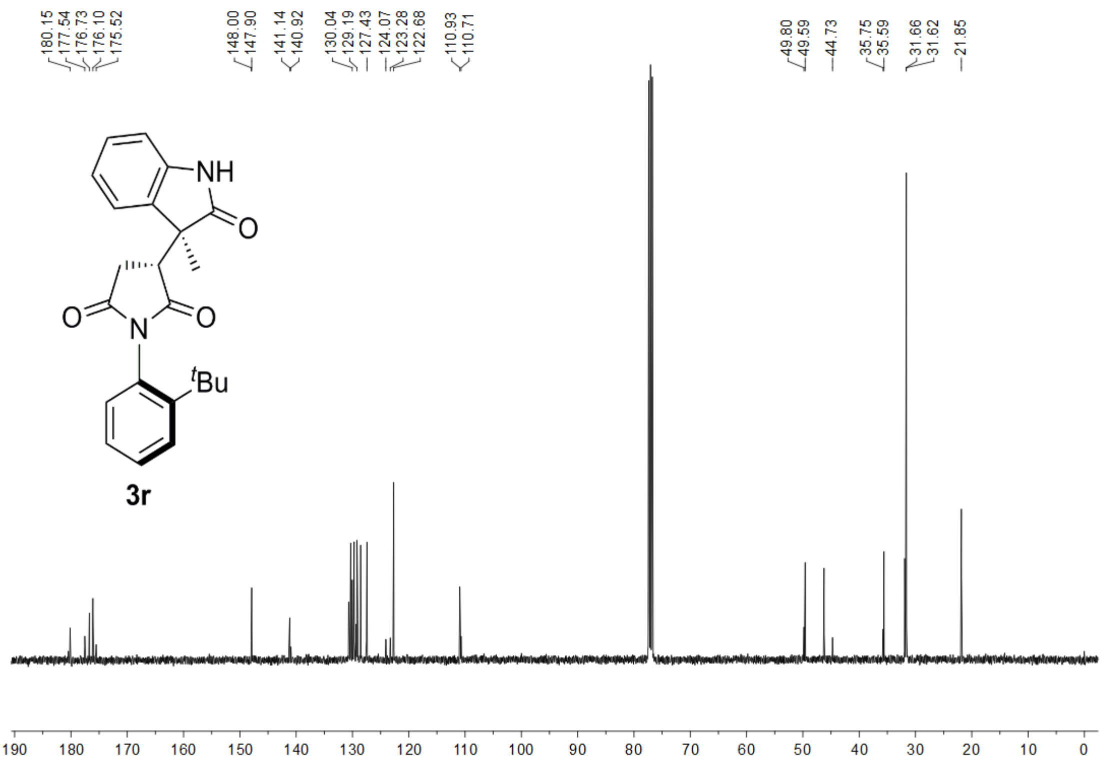
135.30
133.74
130.26
128.75
127.61
126.37
122.49
111.38
55.25
45.01
40.38
35.62
32.03
31.64
Cl
Cl
NH
O
O
O
N
tBu
3p



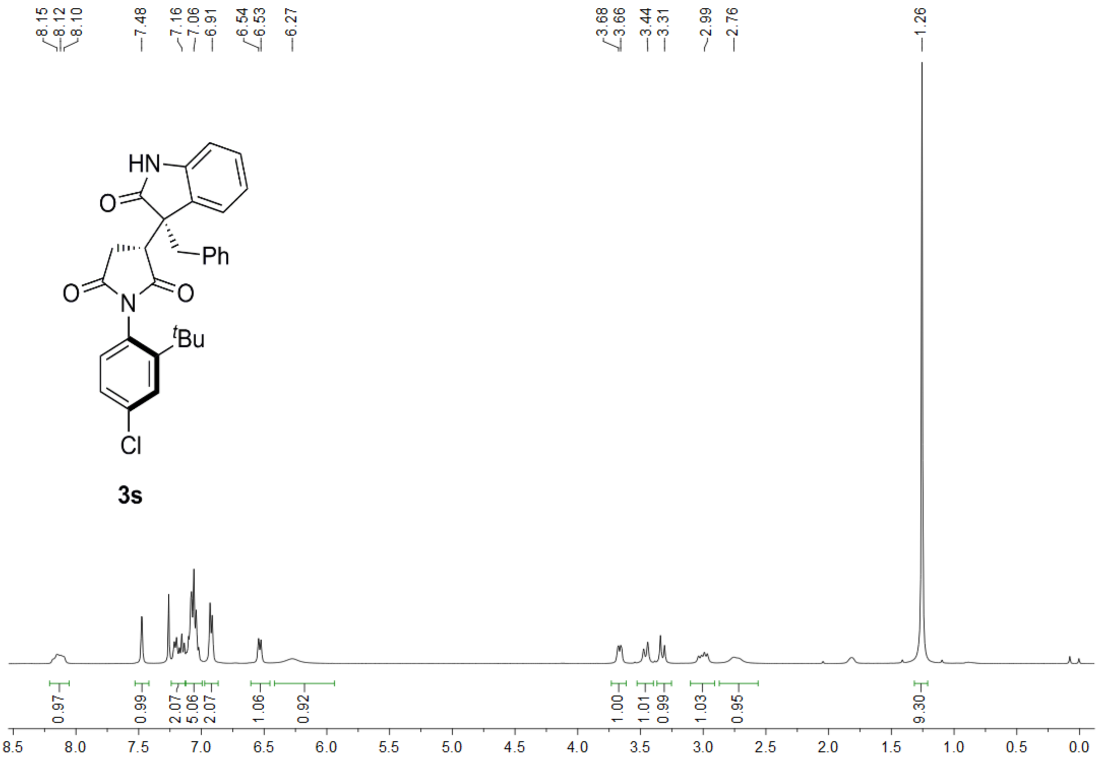




3r



3r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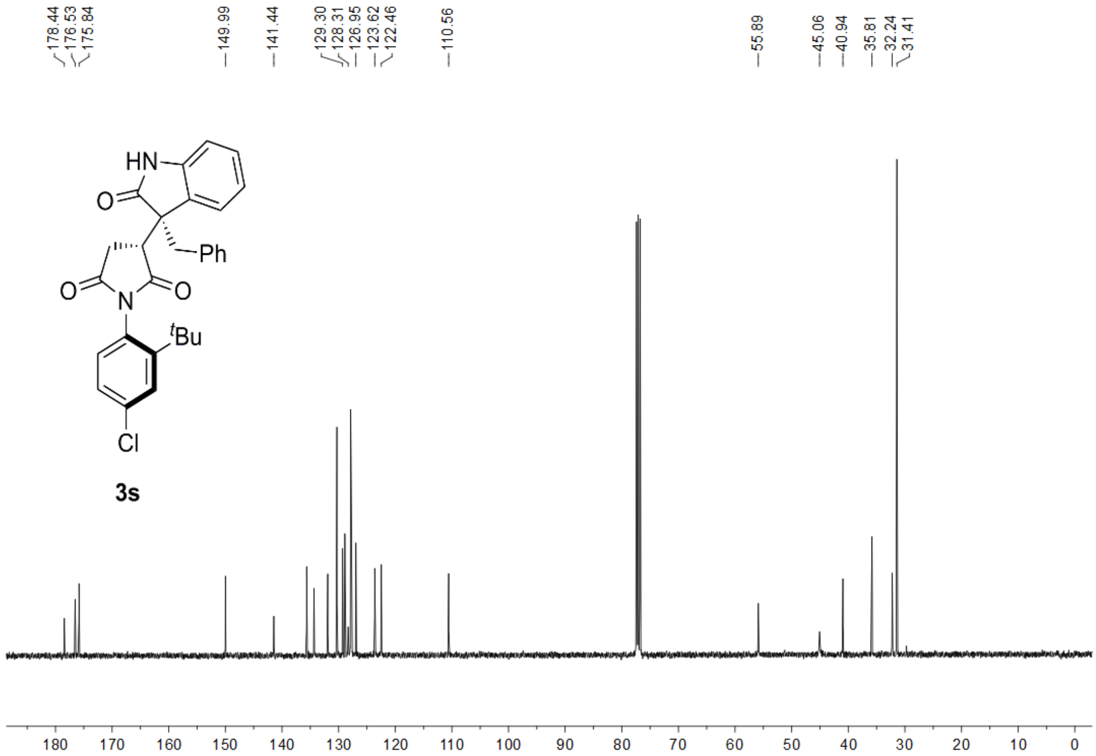
8.10
7.48
7.16
7.06
6.91
6.54
6.53
6.27
3.68
3.66
3.44
3.31
2.99
2.76
1.26
HN
O
Ph
O
N
O
tBu
Cl
3s
0.97
0.99
2.07
5.06
2.07
1.06
0.92
1.00
1.01
0.99
1.03
0.95
9.30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141.44
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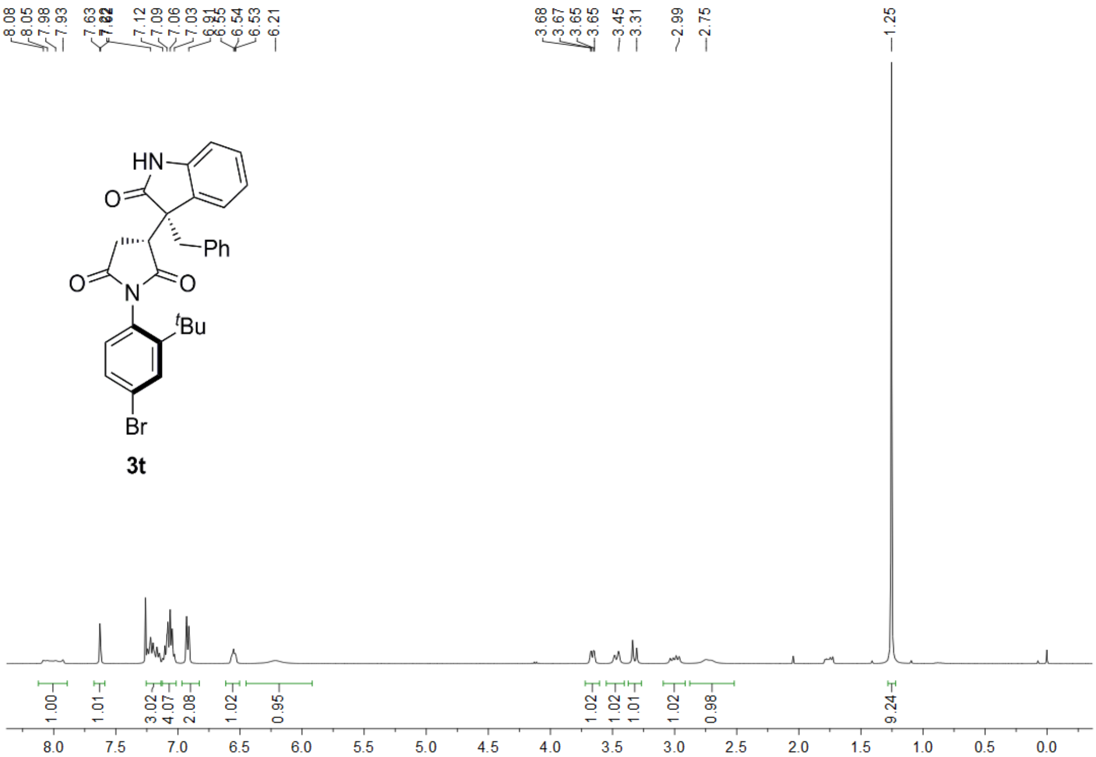
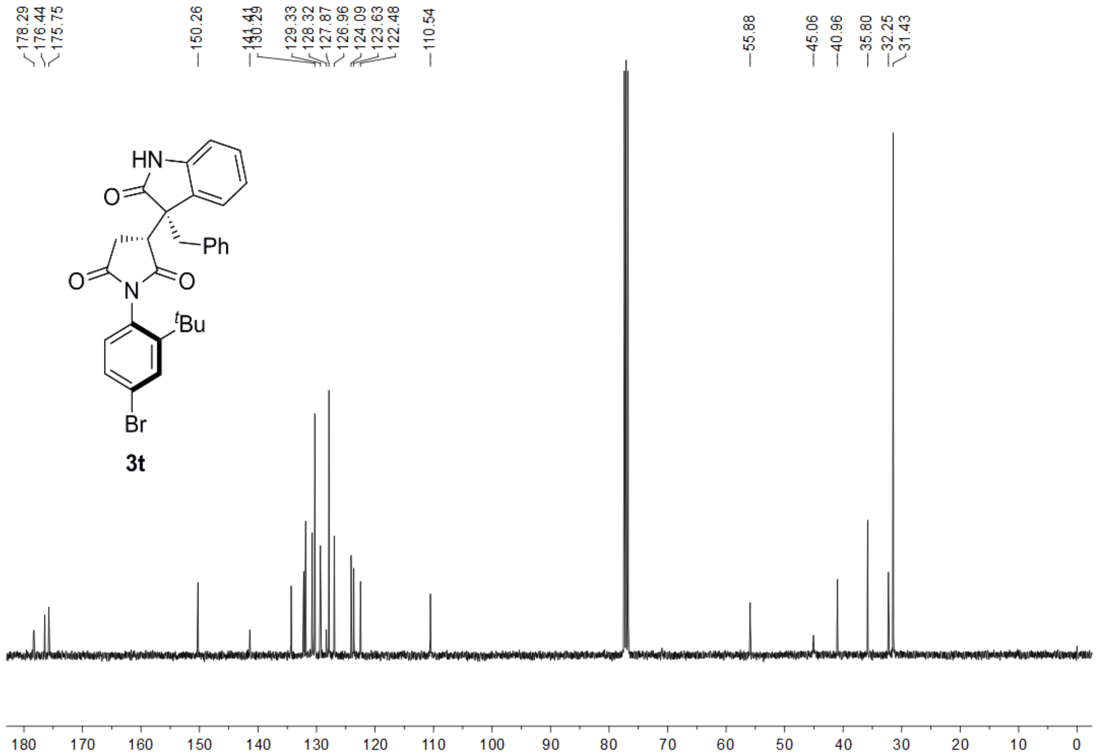
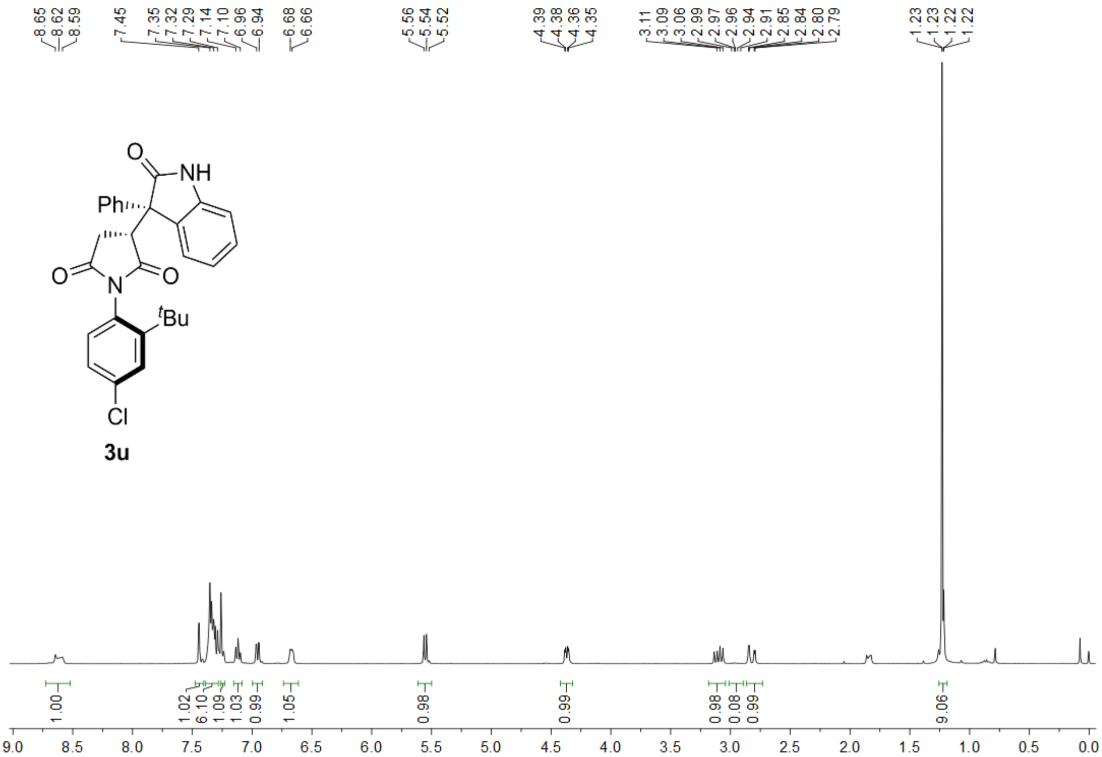
128.31
126.95
123.62
122.46
110.56
55.89
45.06
40.94
35.81
32.24
31.41
HN
O
Ph
O
N
O
tBu
Cl
3s



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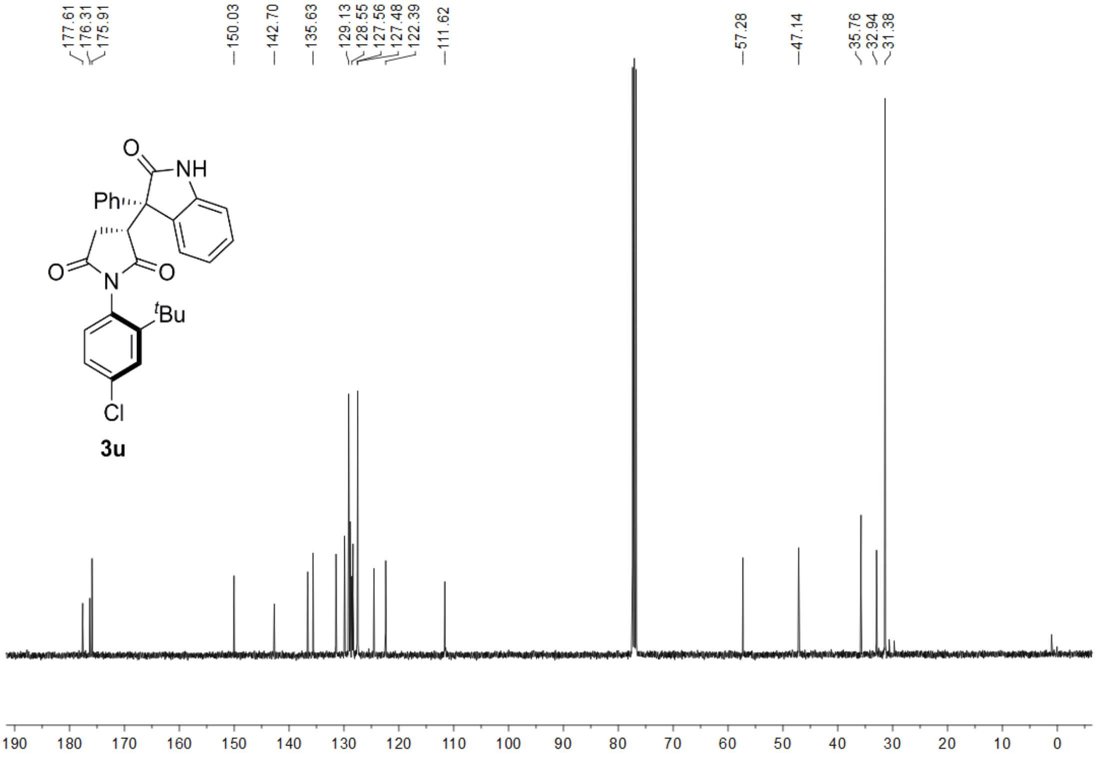
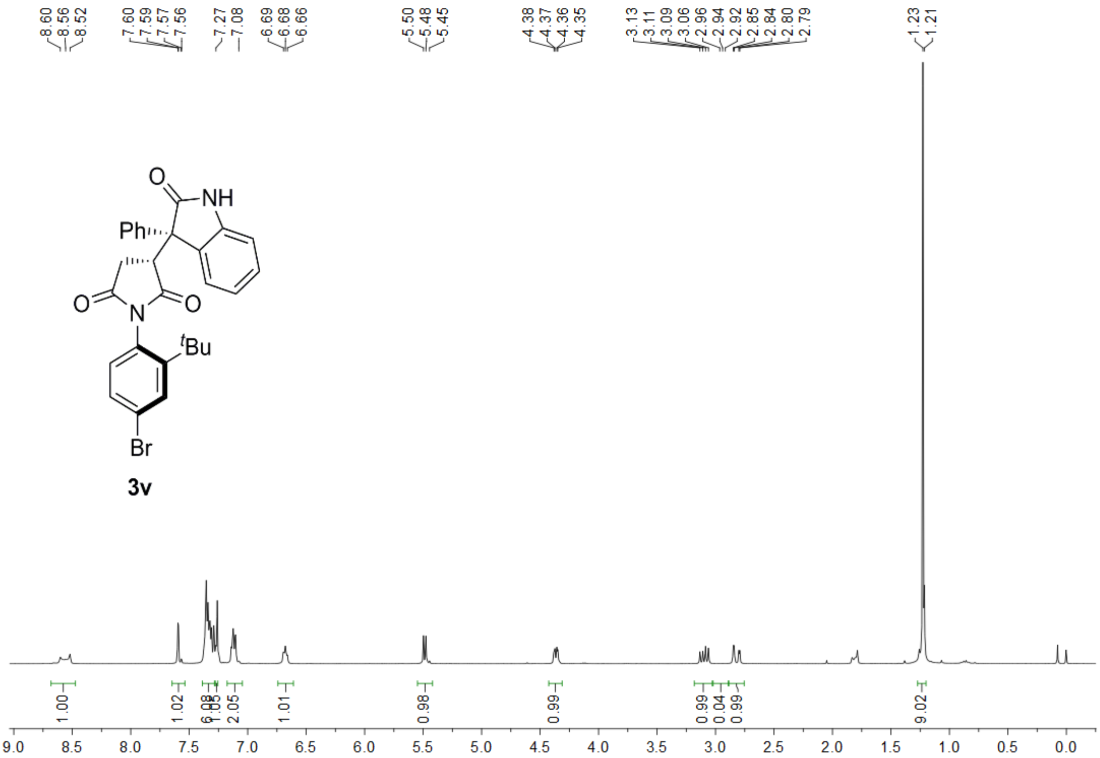
8.62
8.59
7.45
7.35
7.32
7.29
7.14
7.10
6.96
6.94
6.68
6.66
5.56
5.54
5.52
4.39
4.38
4.36
4.35
3.11
3.09
3.06
2.99
2.97
2.96
2.94
2.91
2.85
2.84
2.80
2.79
1.23
1.23
1.22
1.22
O
NH
Ph
N
O
O
^{t}Bu
Cl
3u
1.00
1.02
6.10
1.09
1.03
0.99
1.05
0.98
0.99
0.98
0.08
0.99
9.06
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


177.61
176.31
175.91
150.03
142.70
135.63
129.13
128.55
127.56
127.48
122.39
111.62
57.28
47.14
35.76
32.94
31.38
O
NH
Ph
N
O
O
^{t}Bu
Cl
3u
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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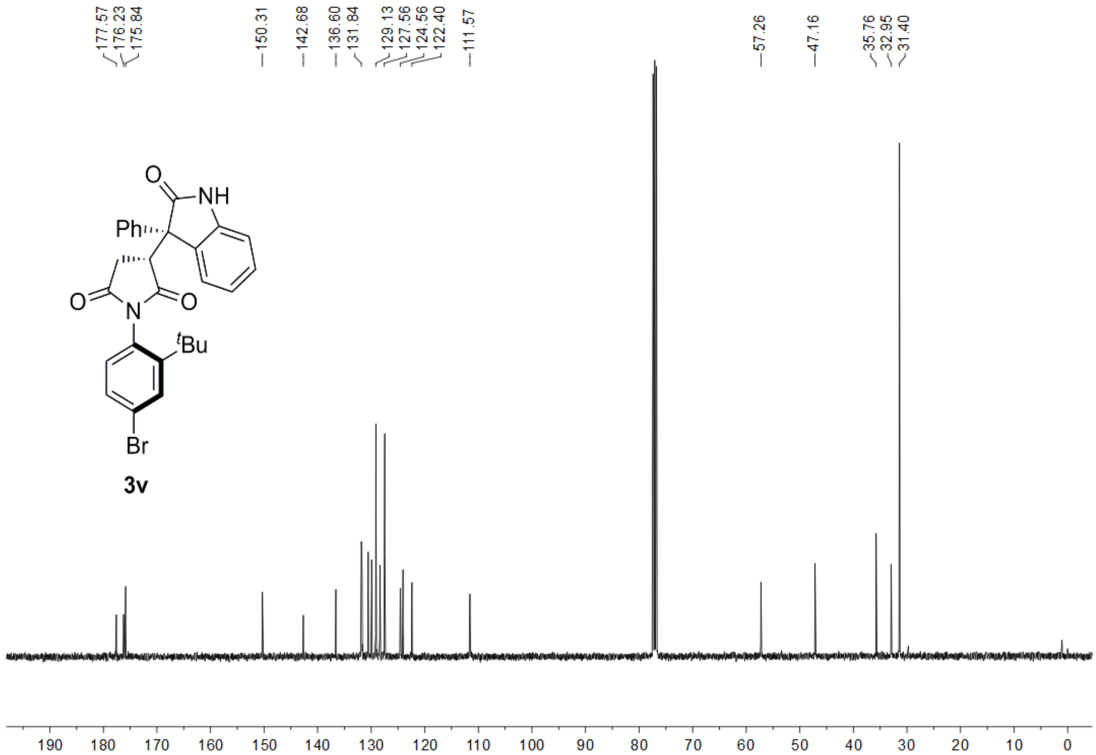
8.56
8.52
7.60
7.59
7.57
7.56
7.27
7.08
6.69
6.68
6.66
5.50
5.48
5.45
4.38
4.37
4.36
4.35
3.13
3.11
3.09
3.06
2.96
2.94
2.92
2.85
2.84
2.80
2.79
1.23
1.21
O
NH
Ph
O
N
O
tBu
Br
3v
1.00
1.02
6.08
1.05
2.05
1.01
0.98
0.99
0.99
0.04
0.99
9.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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176.23
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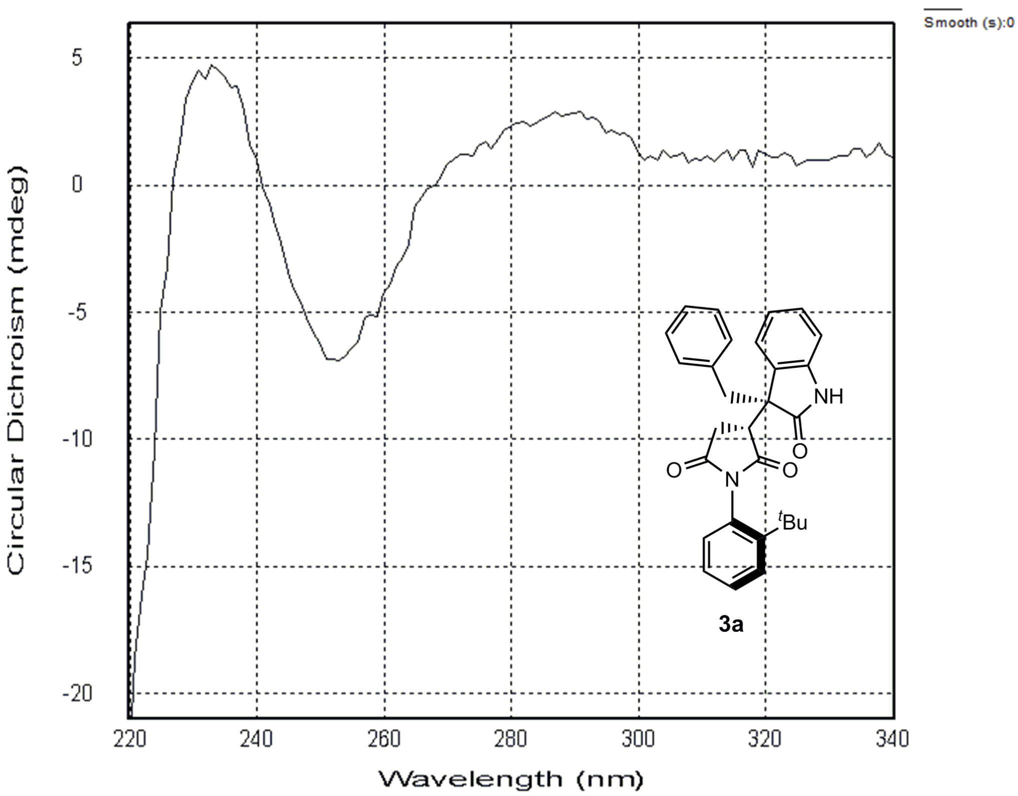
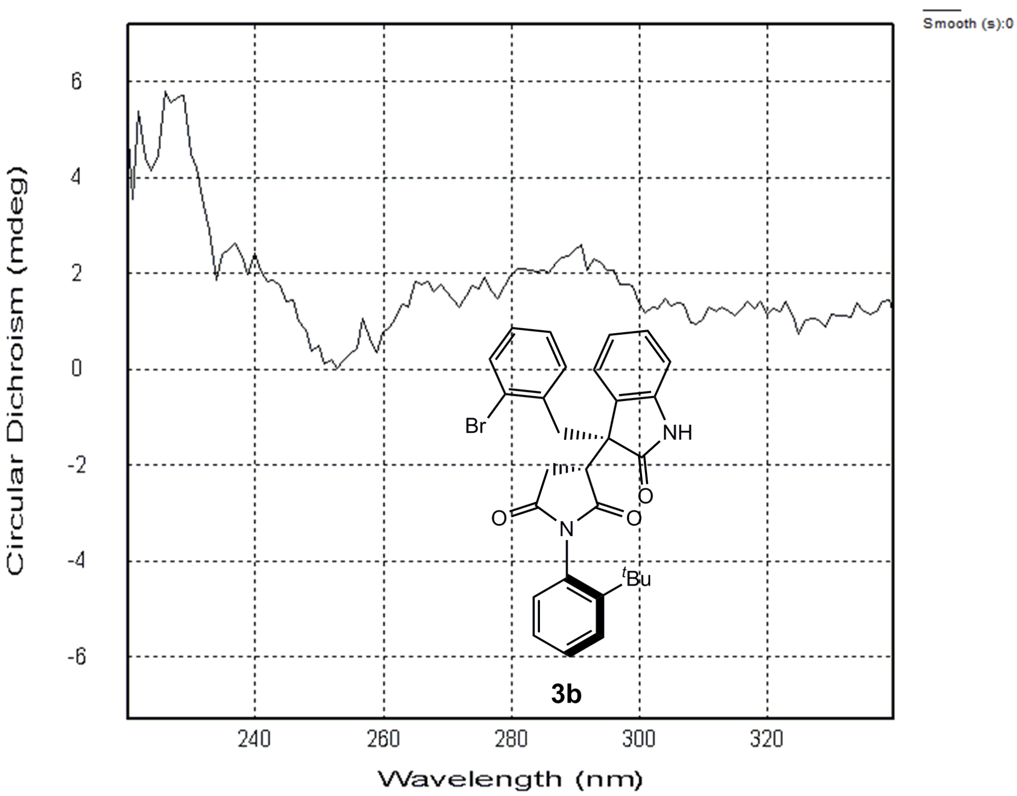
150.31
142.68
136.60
131.84
129.13
127.56
124.56
122.40
111.57
57.26
47.16
35.76
32.95
31.40
O
NH
Ph
O
N
O
tBu
Br
3v
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

8. CD spectrum

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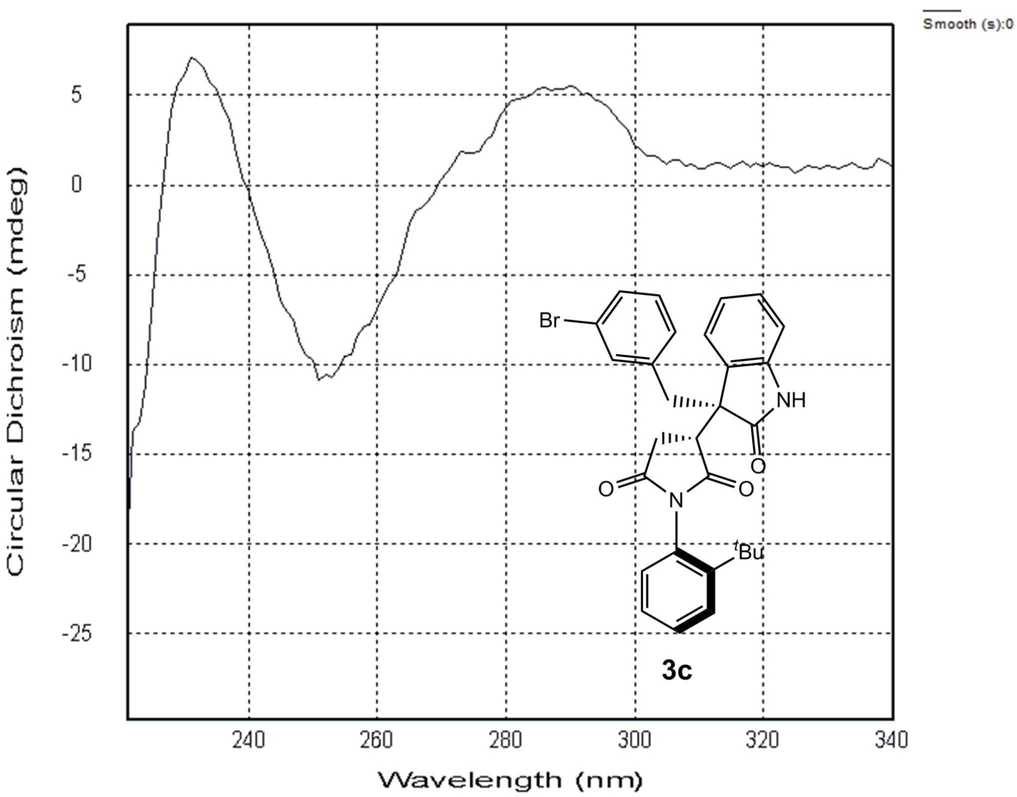
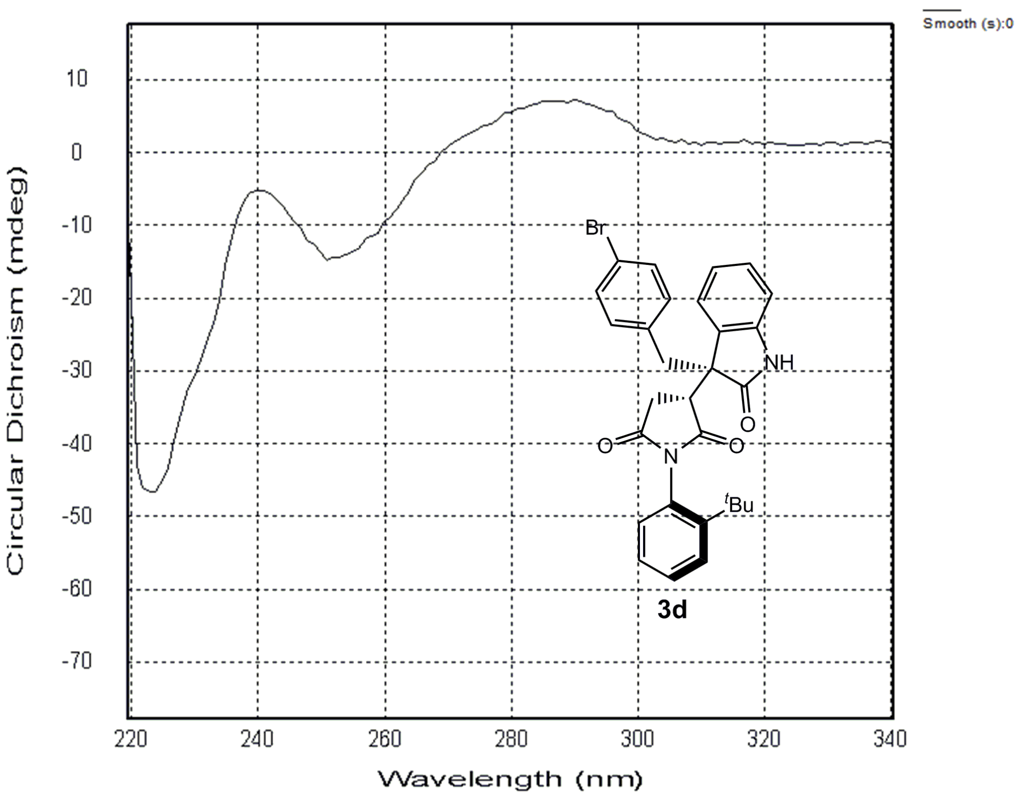
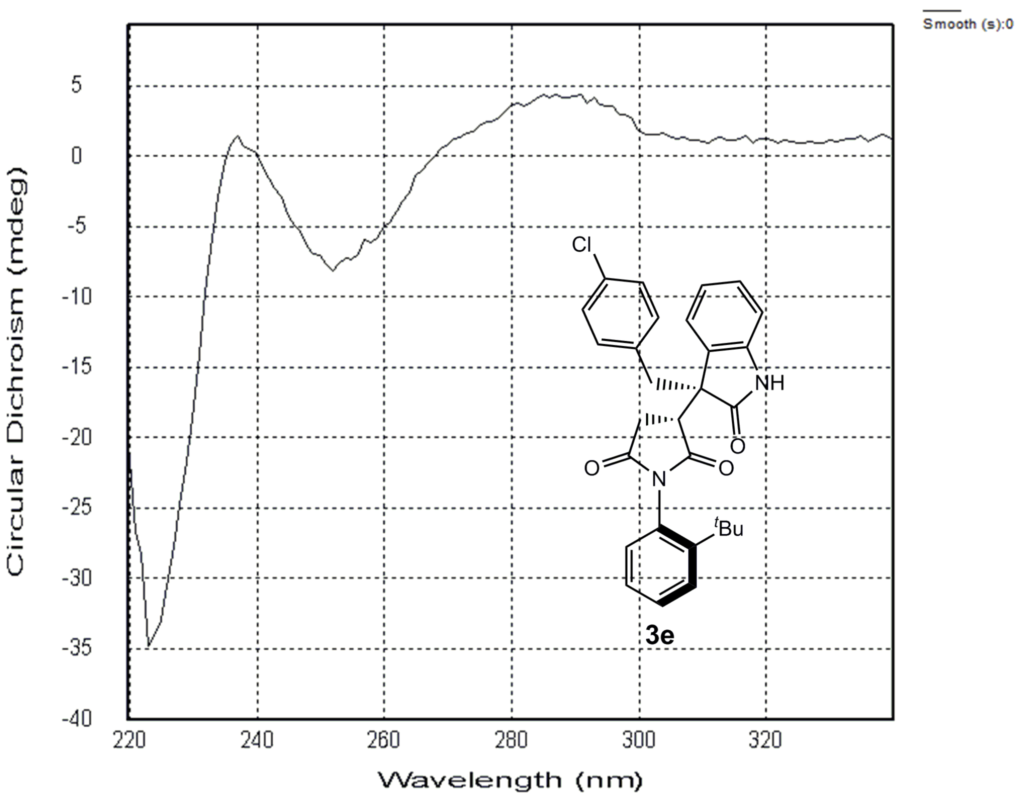
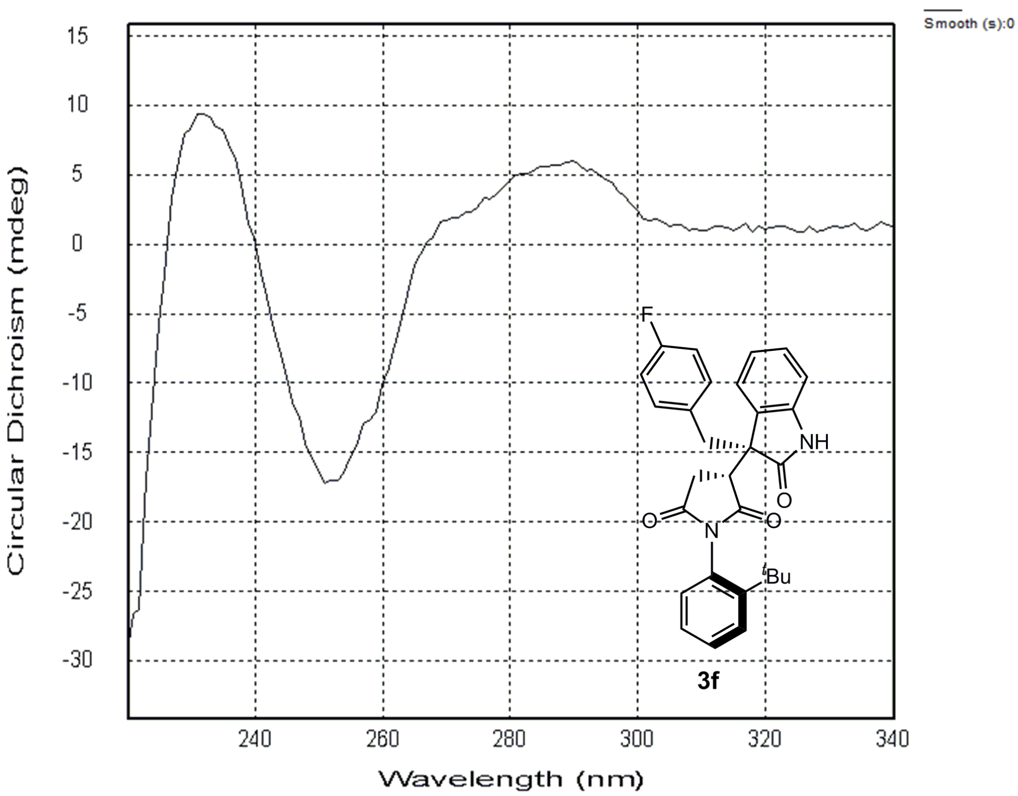
Circular Dichroism (mdeg)
Wavelength (nm)
Br
NH
O
N
tBu
3b


Smooth (s):0
Circular Dichroism (mdeg)
Wavelength (nm)
Br
NH
O
N
tBu
3c


Smooth (s):0
10
0
-10
-20
-30
-40
-50
-60
-70
Circular Dichroism (mdeg)
220
240
260
280
300
320
340
Wavelength (nm)
Br
NH
O
O
N
O
tBu
3d


Smooth (s):0
5
0
-5
-10
-15
-20
-25
-30
-35
-40
Circular Dichroism (mdeg)
220
240
260
280
300
320
Wavelength (nm)
Cl
NH
O
O
N
O
tBu
3e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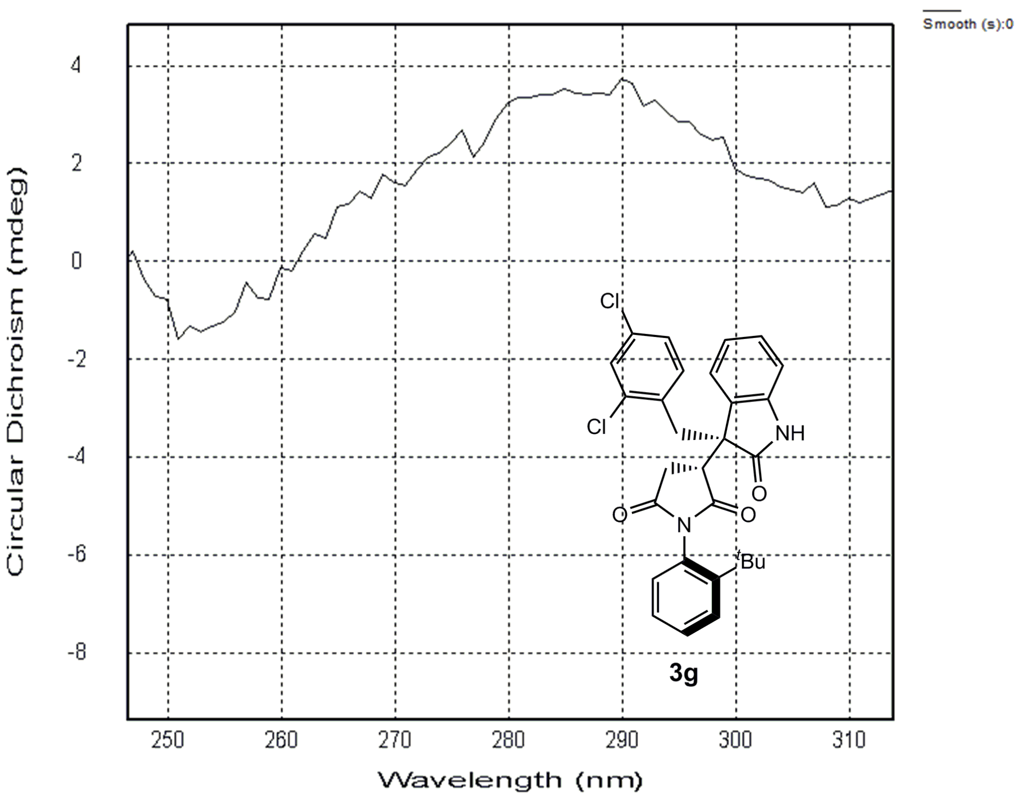
15
10
5
0
-5
-10
-15
-20
-25
-30
Circular Dichroism (mdeg)
240
260
280
300
320
340
Wavelength (nm)
F
NH
O
O
O
N
^{t}Bu

3f


Smooth (s):0
4
2
0
-2
-4
-6
-8
Circular Dichroism (mdeg)
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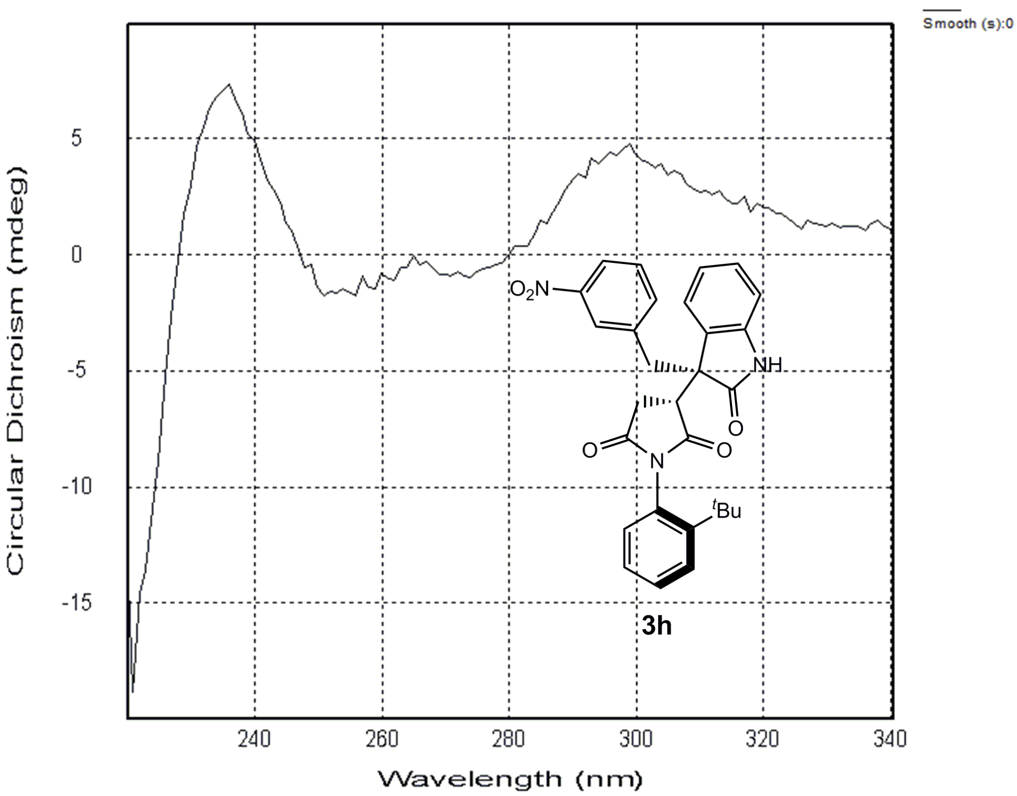
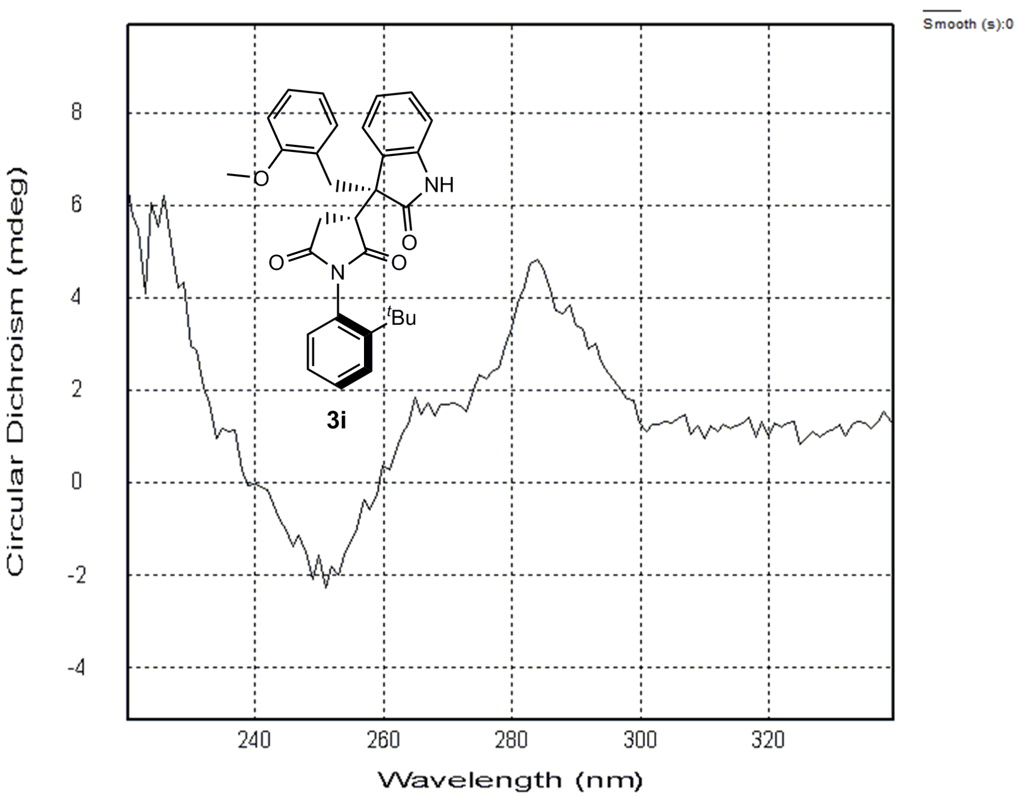
260
270
280
290
300
310
Wavelength (nm)
Cl
Cl
NH
O
O
O
N
^{t}Bu

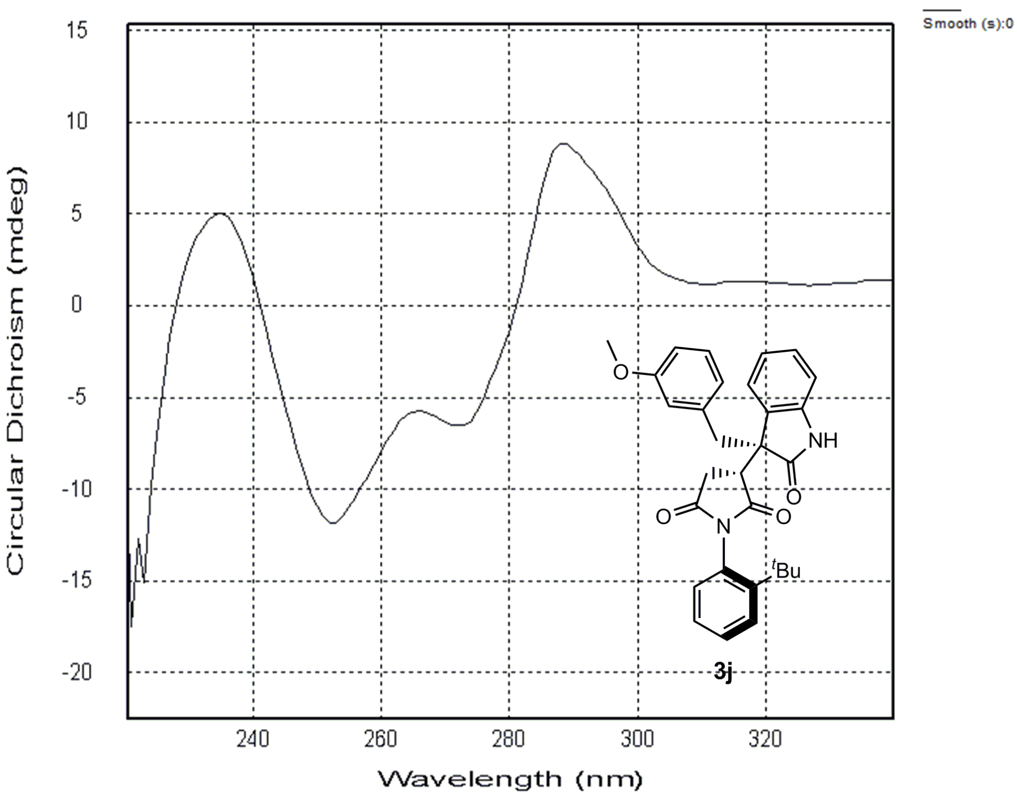
3g



Smooth (s):0
Circular Dichroism (mdeg)
5
0
-5
-10
-15
240
260
280
300
320
340
Wavelength (nm)
O2N
NH
O
O
N
O
tBu
3h



Smooth (s):0
Circular Dichroism (mdeg)
8
6
4
2
0
-2
-4
240
260
280
300
320
Wavelength (nm)
O
NH
O
O
N
O
tBu
3i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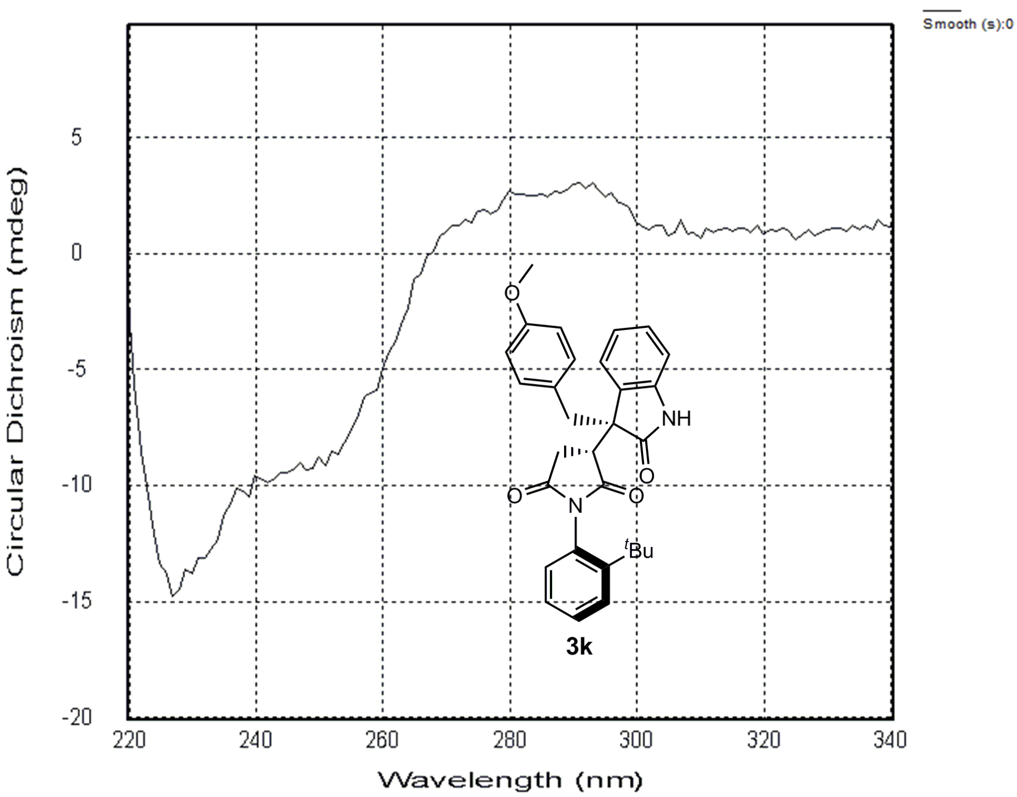
Circular Dichroism (mdeg)
Wavelength (nm)
NH
O
O
O
N
O
tBu
3j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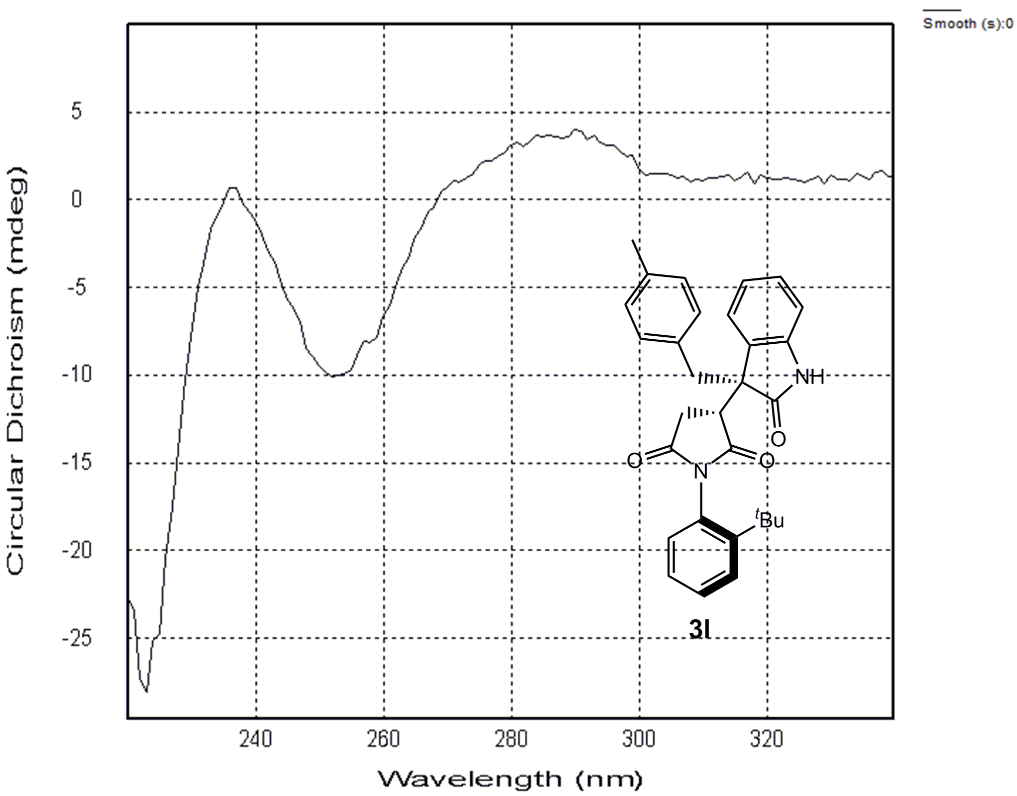
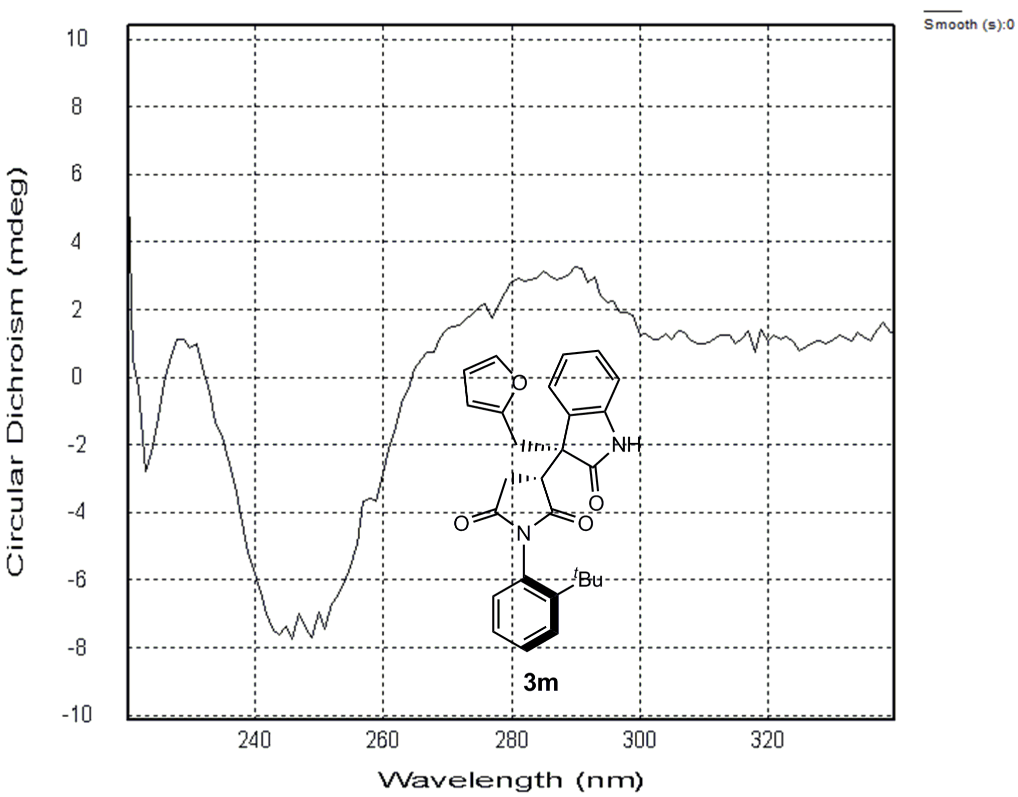
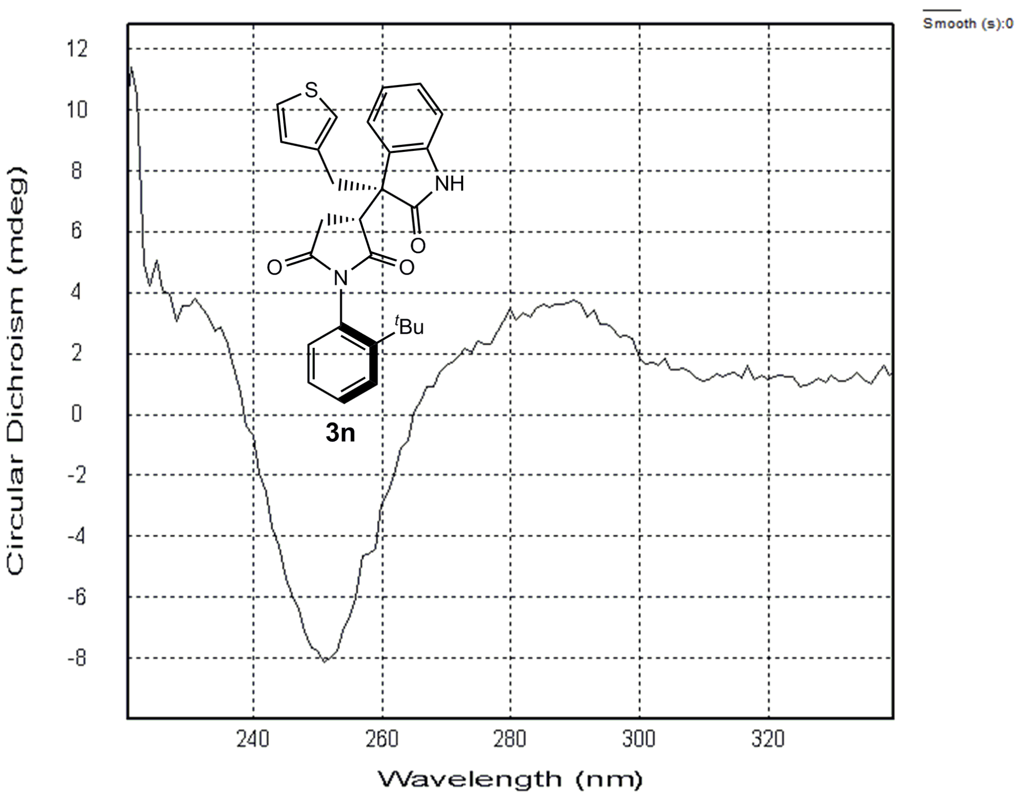
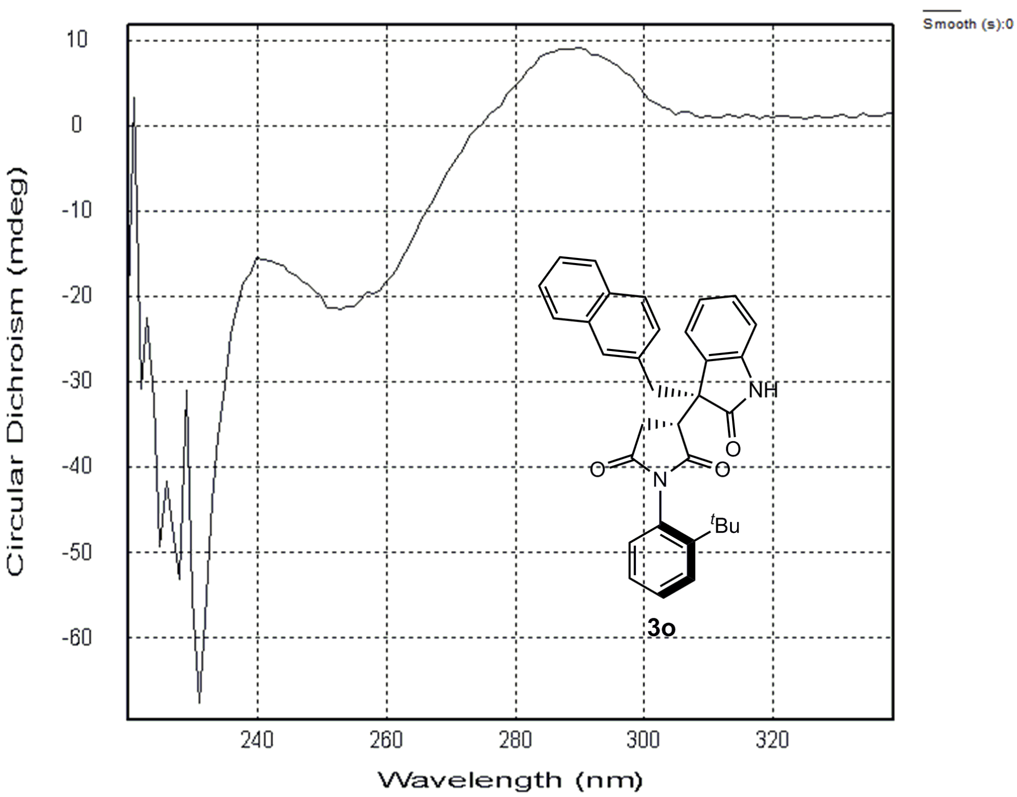
Circular Dichroism (mdeg)
Wavelength (nm)
NH
O
O
O
N
O
tBu
3k


Smooth (s):0
5
0
-5
-10
-15
-20
-25
Circular Dichroism (mdeg)
240
260
280
300
320
Wavelength (nm)
NH
O
O
N
O
^{t}Bu
3l


Smooth (s):0
10
8
6
4
2
0
-2
-4
-6
-8
-10
Circular Dichroism (mdeg)
240
260
280
300
320
Wavelength (nm)
O
NH
O
O
N
O
^{t}Bu
3m


Smooth (s):0
12
10
8
6
4
2
0
-2
-4
-6
-8
Circular Dichroism (mdeg)
240
260
280
300
320
Wavelength (nm)
S
NH
O
O
N
O
tBu
3n


Smooth (s):0
10
0
-10
-20
-30
-40
-50
-60
Circular Dichroism (mdeg)
240
260
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320
Wavelength (nm)
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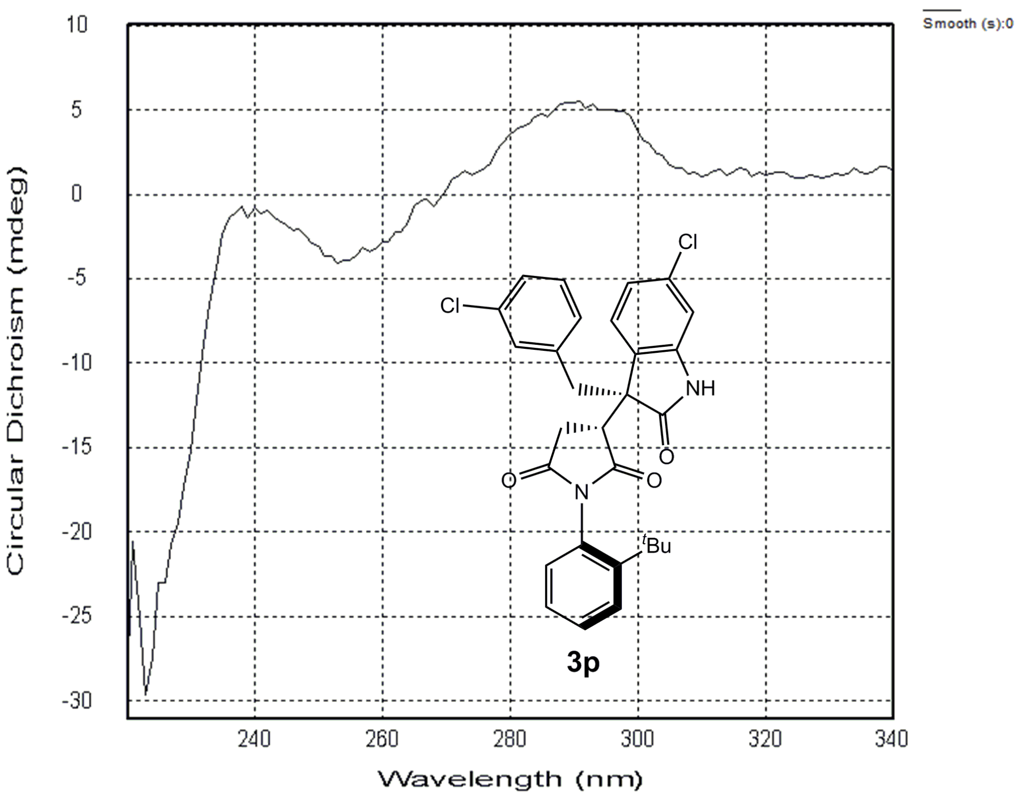
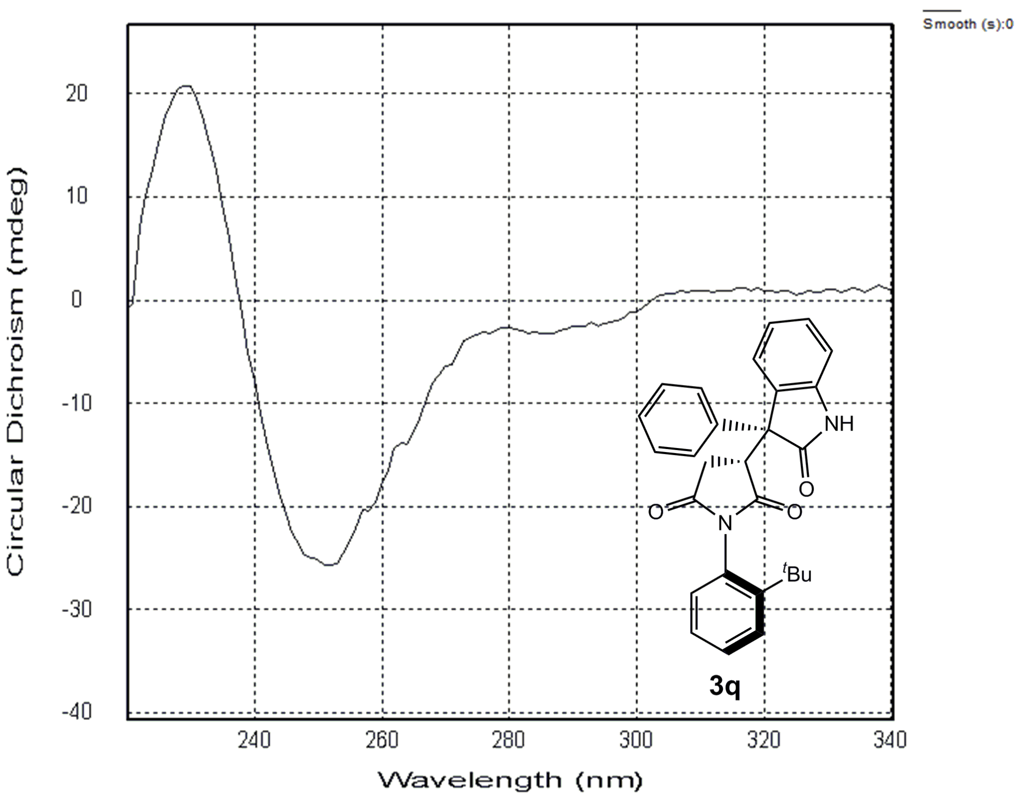
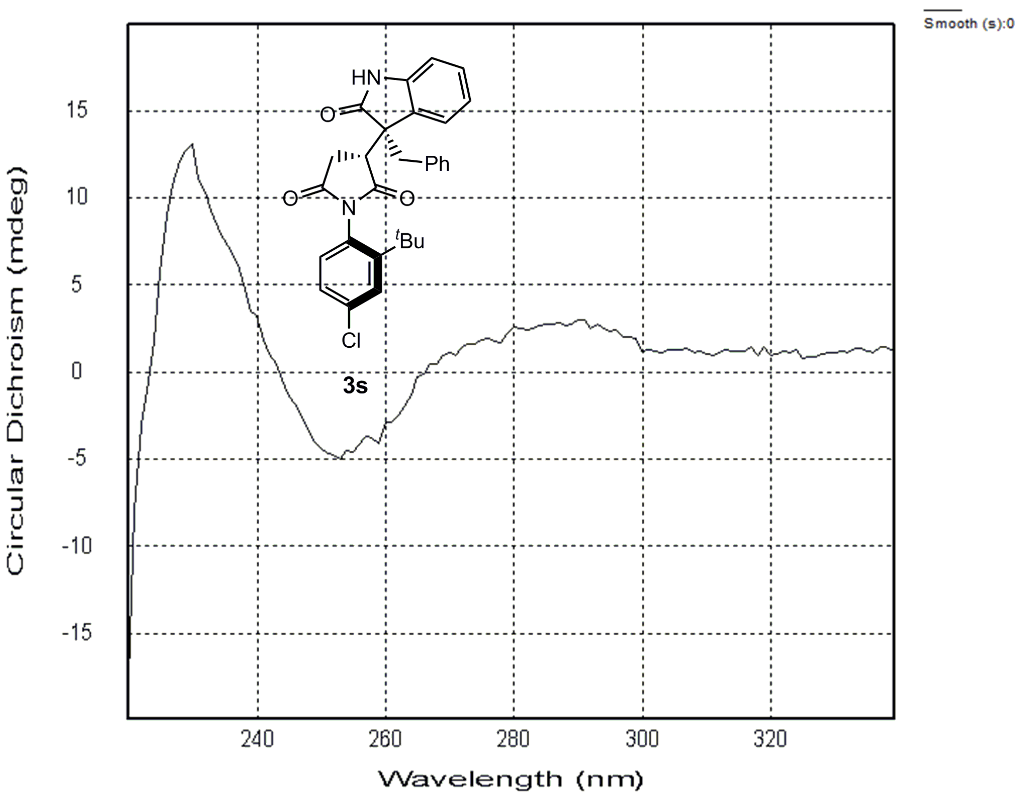
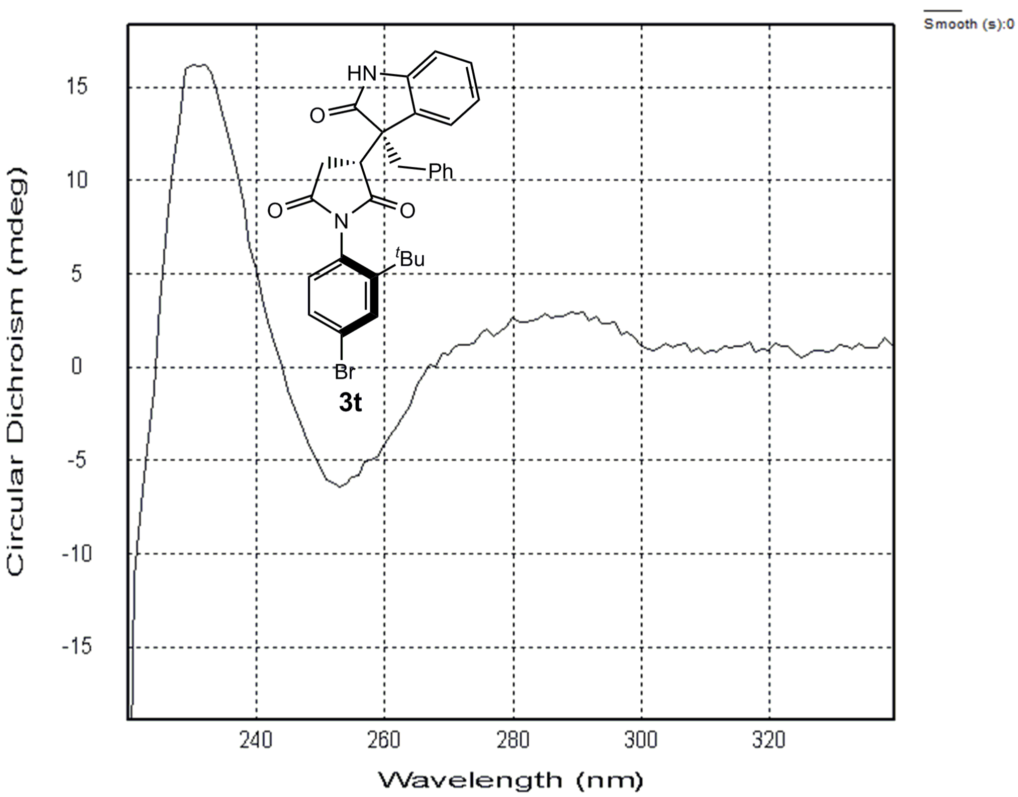
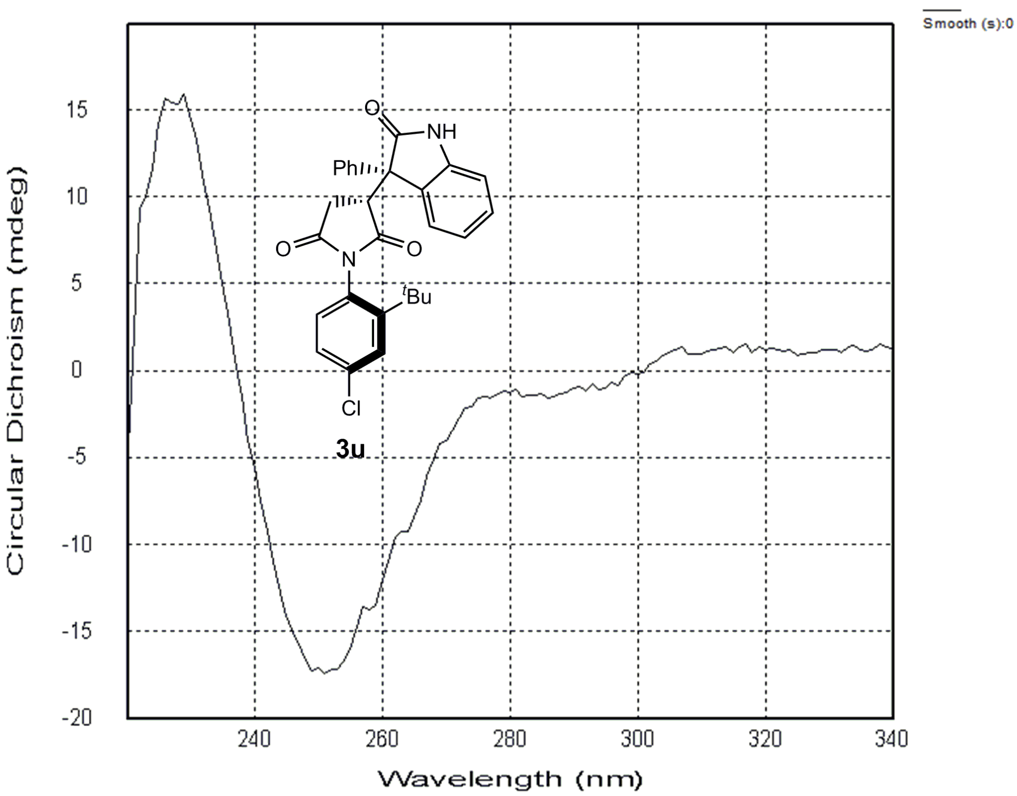
O
N
O
tBu
3o

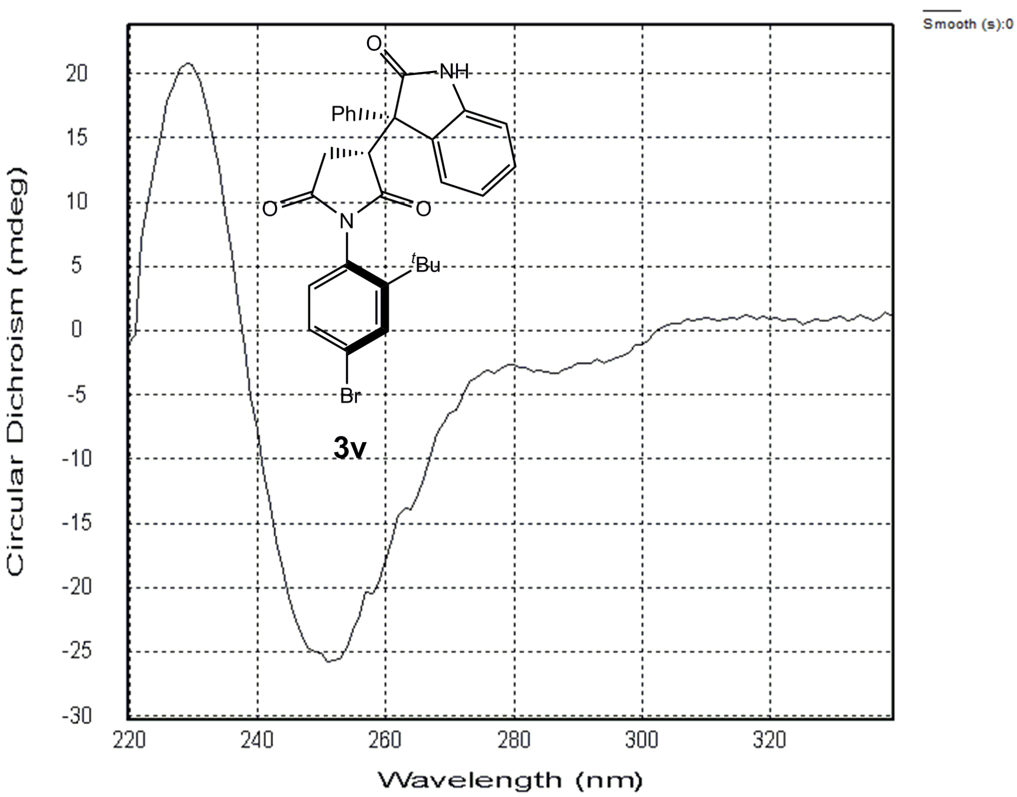

Smooth (s):0
Circular Dichroism (mdeg)
10
5
0
-5
-10
-15
-20
-25
-30
240
260
280
300
320
340
Wavelength (nm)
Cl
Cl
NH
O
O
N
O
tBu
3p


Smooth (s):0
Circular Dichroism (mdeg)
20
10
0
-10
-20
-30
-40
240
260
280
300
320
340
Wavelength (nm)
NH
O
O
N
O
tBu
3q


Smooth (s):0
Circular Dichroism (mdeg)
15
10
5
0
-5
-10
-15
240
260
280
300
320
Wavelength (nm)
HN
O
Ph
O
N
O
^{t}Bu
Cl
3s


Smooth (s):0
Circular Dichroism (mdeg)
15
10
5
0
-5
-10
-15
240
260
280
300
320
Wavelength (nm)
HN
O
Ph
O
N
O
^{t}Bu
Br
3t


Smooth (s):0
Circular Dichroism (mdeg)
Wavelength (nm)
Ph
NH
O
N
^{t}Bu
Cl
3u


Smooth (s):0
Circular Dichroism (mdeg)
Wavelength (nm)
Ph
NH
O
N
^{t}Bu
Br
3v