

Efficient Synthesis of Carbazolespirooxindole Skeletons via Asymmetric Diels–Alder Reaction of 3-Vinyliindoles and Methyleneindolinones†

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1. General information

^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 were 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 , $\delta = 77.0$).

Enantiomeric excesses (*ee*) were determined by HPLC analysis using the corresponding commercial chiralpak column as stated in the experimental procedures at 23 °C.

Optical rotations were reported as follows: $[\alpha]_{\text{D}}^{28}$ (c: g/100 mL, in solvent).

HRMS was recorded on a commercial apparatus (ESI Source).

All catalytic reactions were run in dried glassware. THF, toluene and diethyl ether (Et_2O) were distilled from sodium benzophenone ketyl. CH_2Cl_2 was distilled over CaH_2 .

2. Optimization of the reaction conditions

Table 1: Screening of the metals

Entry ^[a]	Metal	Yield [%] ^[b]	dr ^[c]	ee [%] ^[d]
1	Sc(OTf) ₃	17	>99:1	-11
2	Yb(OTf) ₃	67	>99:1	-20
3	Cu(OTf) ₂	71	>99:1	17
4	Zn(OTf) ₂	78	>99:1	69
5	Co(ClO ₄) ₂ · 6H ₂ O	56	>99:1	80
6	Mg(OTf) ₂	78	>99:1	80
7	Ni(OTf) ₂	93	>99:1	85

[a] Unless otherwise noted, the reactions were performed with **L1**-metal (10 mol%, 1:1), **2a** (0.1 mmol) in CH_2Cl_2 (1.0 mL) at 30 °C for 30 min. After cooled to 0 °C, **1a** (0.15 mmol, 1.5 equiv) in CH_2Cl_2 (0.2 mL) was added in one-portion. The mixture was reacted at 0 °C for 30 min. [b] Isolated yield. [c] Determined by HPLC and ^1H NMR analysis of the product **3a**. [d] Determined by HPLC analysis (Chiralcel OD-H).

Table 2. Screening of the counter ion the metal precursors

Entry ^[a]	Metal	Yield [%] ^[b]	dr ^[c]	ee [%] ^[d]
1	Ni(BF ₄) ₂ 6H ₂ O	95	>99:1	74
2	Ni(ClO ₄) ₂ 6H ₂ O	95	>99:1	74
3	NiBr ₂	94	>99:1	82

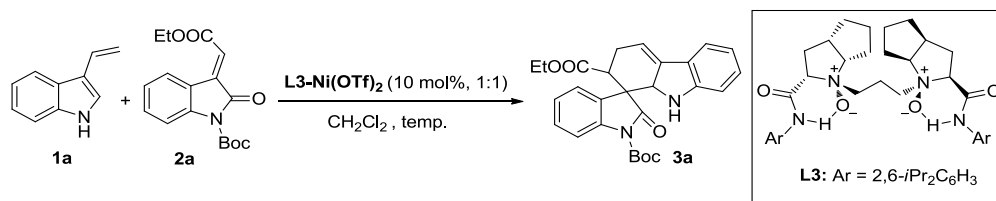
[a] Unless otherwise noted, the reactions were performed with **L3**-metal (10 mol%, 1:1), **2a** (0.1 mmol) in CH₂Cl₂ (1.0 mL) at 30 °C for 30 min. After cooled to 0 °C, **1a** (0.15 mmol, 1.5 equiv) in CH₂Cl₂ (0.2 mL) was added in one-portion. The mixture was reacted at 0 °C for 30 min. [b] Isolated yield. [c] Determined by HPLC and ¹H NMR analysis of the product **3a**. [d] Determined by HPLC analysis (Chiralcel OD-H).

Table 3. Screening of the solvents

Entry ^[a]	Solvent	Yield [%] ^[b]	dr ^[c]	ee [%] ^[d]
1	CH ₂ Cl ₂	95	>99:1	96
2	THF	70	>99:1	10
3	Et ₂ O	88	>99:1	74
4	Toluene	78	>99:1	70
5	hexane	92	>99:1	6
6	CHCl ₃	86	>99:1	96
7	Cl ₂ CHCHCl ₂	92	>99:1	94
8	ClCH ₂ CH ₂ Cl	97	>99:1	95
9	ClCH ₂ CHClCH ₃	95	>99:1	93
10	ClCHCH ₂ CH ₂ CHCl	95	>99:1	93

[a] Unless otherwise noted, the reactions were performed with **L3**-Ni(OTf)₂ (10 mol%, 1:1), **2a** (0.1 mmol) in the corresponding solvent (1.0 mL) at 30 °C for 30 min. After cooled to 0 °C, **1a** (0.15 mmol, 1.5 equiv) in the solvent (0.2 mL) was added in one-portion. The mixture was stirred at 0 °C for 30 min. [b] Isolated yield. [c] Determined by HPLC and ¹H NMR analysis of the product **3a**. [d] Determined by HPLC analysis (Chiralcel OD-H).

Table 4. Screening of the reaction temperature

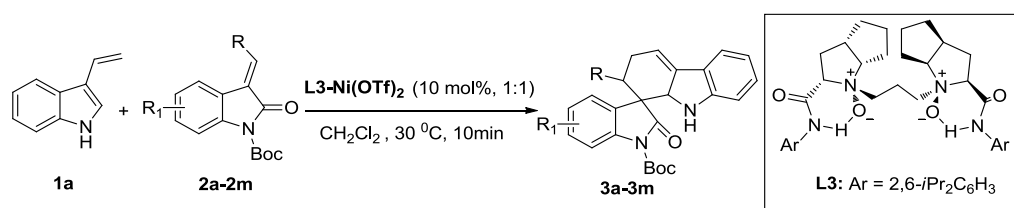


Entry ^[a]	Temp. (°C)	Yield [%] ^[b]	dr ^[c]	ee [%] ^[d]
1	35	95	>99:1	90
2	30	96	>99:1	96
3	0	95	>99:1	96
4	-20	95	>99:1	93

[a] Unless otherwise noted, the reactions were performed with **L3-Ni(OTf)₂** (10 mol%, 1:1), **2a** (0.1 mmol) in CH₂Cl₂ (1.0 mL) at 30 °C for 30 min. Then **1a** (0.15 mmol, 1.5 equiv) in CH₂Cl₂ (0.2 mL) was added at the corresponding temperature in one-portion. The mixture was stirred for a few minutes (<30 min). [b] Isolated yield. [c] Determined by HPLC and ¹H NMR analysis of the product **3a**. [d] Determined by HPLC analysis (Chiralcel OD-H).

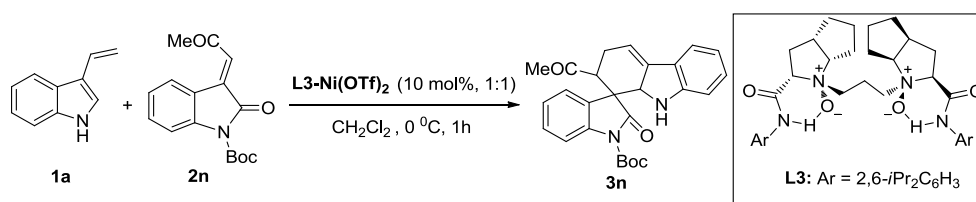
3. General Procedure for the Diels-Alder reaction with different methyleneindolinones (2a-2z)

General procedure A for the reaction of methyleneindolinones **2a-2m**:



In a test tube with a magnetic stirring bar, *N,N'*-dioxide **L3** (0.01 mmol, 7.0 mg), Ni(OTf)₂ (0.01 mmol, 3.6 mg), and the methyleneindolinones (**2a-2m**) (0.1 mmol) in CHCl₃ (1.0 mL) were stirred at 30 °C for 30 min, then 3-vinylindole **1a** (0.15 mmol, 1.5 eq) dissolved in CH₂Cl₂ (0.2 mL) was added in one-portion. The mixture was stirred at 30 °C for a few minutes (<10 min), the yellow color of the solution disappeared, and the reaction mixture was further detected by TLC. After completion, flash column chromatography provided the desired product (**3a-3m**) with almost quantitative yield and the product was directed for HPLC and NMR analysis.

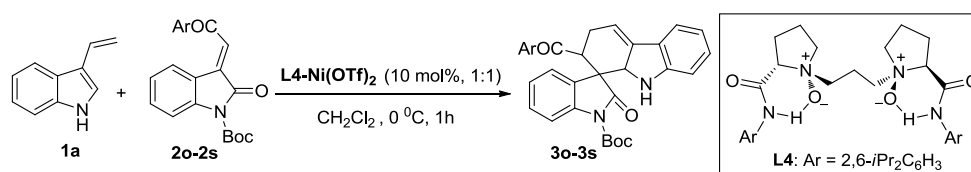
General procedure B for the reaction of methyleneindolinone **2n**:



In a test tube with a magnetic stirring bar, *N,N'*-dioxide **L3** (0.01 mmol, 7.0 mg), Ni(OTf)₂ (0.01 mmol, 3.6 mg), and the methyleneindolinone (**2n**) (0.1 mmol) in CHCl₂ (1.0 mL) were stirred at 30 °C for 30 min. Then it was cooled to 0 °C, and 3-vinylindole **1a** (0.15 mmol, 1.5 equiv) dissolved in CHCl₂ (0.2 mL) was added in one-portion. The mixture was stirred at 0 °C until the yellow color of the solution disappeared, and the reaction mixture was further detected by TLC.

After completion (<60 min), the reaction mixture was treated with 6 M HCl (0.2 mL) at room temperature for 15 minutes, and then quenched with saturated aqueous NaHCO₃ solution, extracted with DCM, dried over anhydrous Na₂SO₄, filtered, and concentrated *in vacuo*. Flash column chromatography provided the desired product **3n** which was directed for HPLC and NMR analysis.

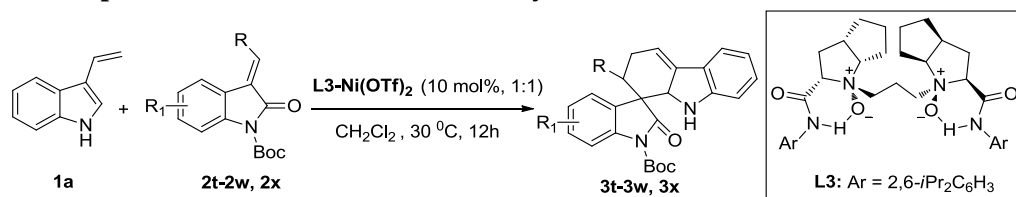
General procedure C for the reaction of methyleneindolinones **2o-2s**:



In a test tube with a magnetic stirring bar, *N,N'*-dioxide **L4** (0.01 mmol, 6.1 mg), Ni(OTf)₂ (0.01 mmol, 3.6 mg), and the methyleneindolinones (**2o-2s**) (0.1 mmol) in CH₂Cl₂ (1.0 mL) were stirred at 30 °C for 30 min. Then it was cooled to 0 °C, and 3-vinylindole **1a** (0.15 mmol, 1.5 equiv) dissolved in CH₂Cl₂ (0.2 mL) was added in one-portion. The mixture was stirred at 0 °C for 60 min, until the yellow color of solution disappeared, and the reaction mixture was further detected by TLC.

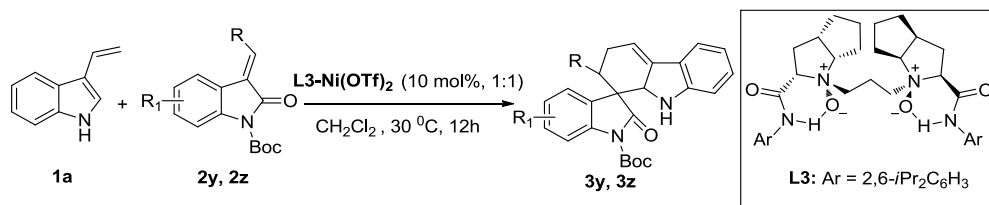
The reaction mixture was treated with 6 M HCl (0.2 mL). After stirring at room temperature for 15 minutes, the mixture was quenched with saturated aqueous NaHCO₃ solution, extracted with DCM, dried over anhydrous Na₂SO₄, filtered, and concentrated *in vacuo*. Flash column chromatography provided the desired product (**4o-4s**) which was directed for HPLC and NMR analysis.

General procedure D for the reaction of methyleneindolinones **2t-2w** and **2x**:



In a test tube with a magnetic stirring bar, *N,N'*-dioxide **L3** (0.01 mmol, 7.0 mg), Ni(OTf)₂ (0.01 mmol, 3.6 mg), and the methyleneindolinones (**2t-2w**, **2x**) (0.1 mmol) in CHCl₂ (1.0 mL) were stirred at 30 °C for 30 min, then 3-vinylindole **1a** (0.15 mmol, 1.5 equiv) dissolved in CHCl₂ (0.2 mL) was added in one-portion. The mixture was stirred at 30 °C for 12h until the yellow color in solution disappeared. The reaction mixture was further detected by TLC. After completion, flash column chromatography provided the desired product (**3t-3w**, **3x**) which was directed for HPLC and NMR analysis.

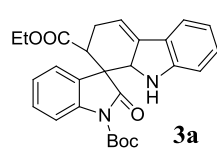
General procedure for the reaction of methyleneindolinones **2y** and **2z**:



In a test tube with a magnetic stirring bar, *N,N'*-dioxide **L3** (0.01 mmol, 7.0 mg), Ni(OTf)₂ (0.01 mmol, 3.6 mg), and the methyleneindolinones (**2y**, **2z**) (0.1 mmol) in CHCl₂ (1.0 mL) were stirred at 30 °C for 30 min, then the mixture was cooled to 0 °C, and 3-vinylindole **1a** (0.15 mmol, 1.5 equiv) dissolved in CHCl₂ (0.2 mL) was added in one-portion. The mixture was stirred at 30 °C for 12 h until the yellow color of the solution disappeared. The reaction mixture was further detected by TLC.

The reaction mixture was treated with 6 M HCl (0.2 mL). After stirring at room temperature for 15 minutes, the mixture was quenched with saturated aqueous NaHCO₃ solution, extracted with DCM, dried over anhydrous Na₂SO₄, filtered, and concentrated *in vacuo*. Flash column chromatography provided the desired products (**4y**, **4z**) which were directed for HPLC and NMR analysis.

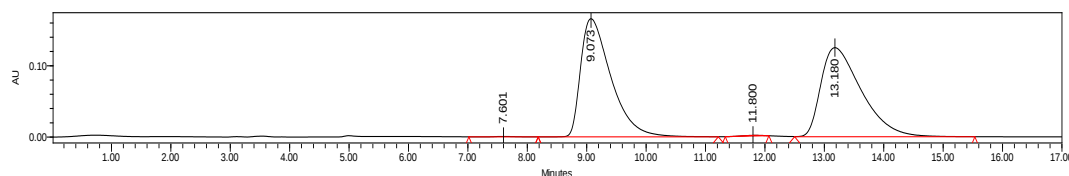
4. The analytical and spectral characterization data of the products (3a-3z)



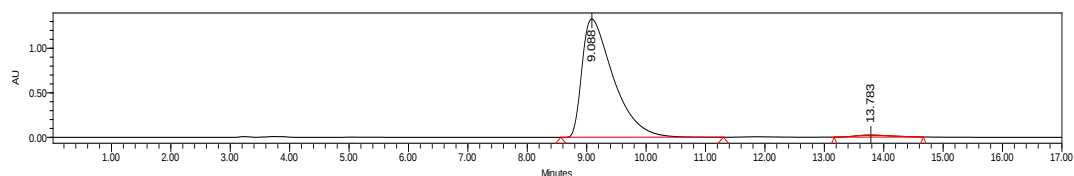
1'-tert-butyl 2-ethyl 2'-oxo-2,3,9,9a-tetrahydrospiro
[carbazole-1,3'-indoline]-1',2-dicarboxylate (**3a**)

General procedure A; White solid; 96% yield, 96% ee, >99:1dr; [α]_D²⁸ = 310 (c 0.97, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak ODH, n-hexane/*i*-PrOH = 93/7, 1.0 mL/min, λ = 254 nm, t (major) = 9.08 min, t (minor) = 13.78 min];

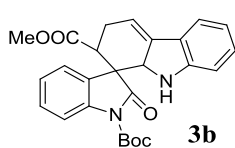
¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.27 – 7.20 (m, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 6.95 (t, *J* = 7.6 Hz, 2H), 6.70 (t, *J* = 7.6 Hz, 1H), 6.42 (d, *J* = 8.0 Hz, 1H), 6.09 (dd, *J* = 7.2, 3.6 Hz, 1H), 4.95–4.91 (m, 1H), 3.93 – 3.85 (m, 2H), 3.81 (d, *J* = 5.2 Hz, 1H), 3.57 (t, *J* = 9.6 Hz, 1H), 2.98–2.94 (m, 2H), 1.68 (s, 9H), 1.01 (t, *J* = 7.2 Hz, 3H);



	Retention Time	Area	% Area
	7.601	12695	0.11
	9.073	5880827	49.71
	11.800	21634	0.18
	13.180	5915145	50.00



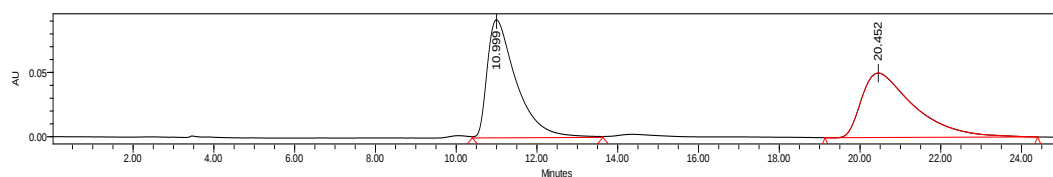
	Retention Time	Area	% Area
	9.088	48891602	98.21
	13.783	890043	1.79



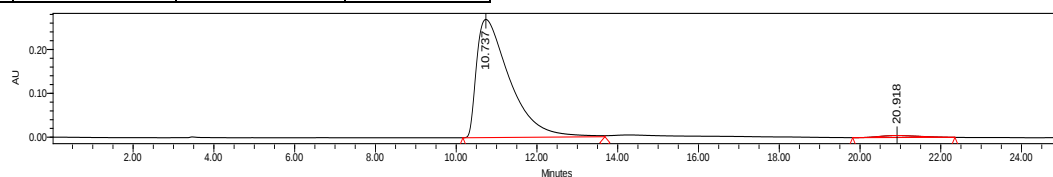
1'-tert-butyl 2-methyl 2'-oxo-2,3,9,9a-tetrahydrospiro[carbazole-1,3'-indoline]-1',2-dicarboxylate (**3b**)

General procedure A; White solid; 95% yield, 96% ee, >99:1dr; $[\alpha]_D^{28} = 280$ (c 0.96, CH_2Cl_2); Determined by HPLC analysis [Daicel chiralpak ODH, n-hexane/i-PrOH = 93/7, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 10.73 min, t (minor) = 20.91 min];

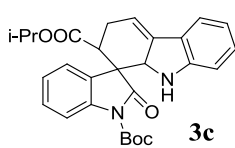
^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, $J = 8.4$ Hz, 1H), 7.31 (d, $J = 7.2$ Hz, 1H), 7.26 – 7.21 (m, 1H), 7.18 (d, $J = 7.6$ Hz, 1H), 6.99 – 6.94 (m, 2H), 6.72 (t, $J = 7.6$ Hz, 1H), 6.45 (d, $J = 8.0$ Hz, 1H), 6.08 (dd, $J = 7.2, 3.6$ Hz, 1H), 4.96 (d, $J = 2.4$ Hz, 1H), 3.78 (s, 1H), 3.60 (dd, $J = 10.4, 8.0$ Hz, 1H), 3.48 (s, 3H), 3.05 – 2.85 (m, 2H), 1.69 (s, 9H);



	Retention Time	Area	% Area
	10.999	4586262	50.11
	20.452	4566285	49.89



	Retention Time	Area	% Area
	10.737	15361300	98.06
	20.918	304129	1.94

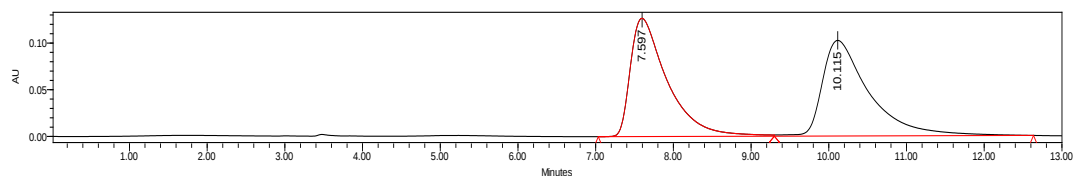


1'-tert-butyl 2-isopropyl 2'-oxo-2,3,9,9a-tetrahydrospiro[carbazole-1,3'-indoline]-1',2-dicarboxylate (**3c**)

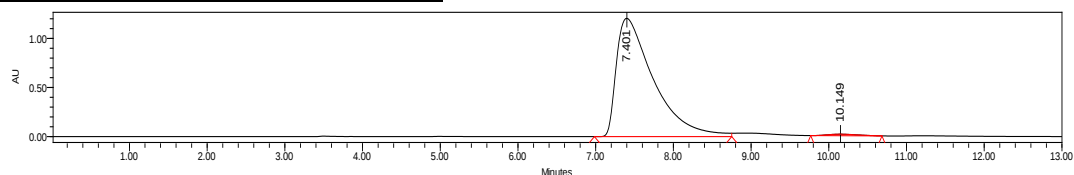
General procedure A; White solid; 97% yield, 98% ee, >99:1dr; $[\alpha]_D^{28} = 300$ (c 1.05, CH_2Cl_2); Determined by HPLC analysis [Daicel chiralpak

ODH, n-hexane/i-PrOH = 93/7, 1.0 mL/min, λ = 254 nm, t (major) = 7.40 min, t (minor) = 10.14 min];

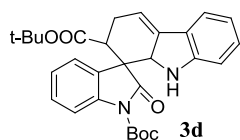
^1H NMR (400 MHz, CDCl_3) δ 7.80 (d, J = 8.0 Hz, 1H), 7.22 (d, J = 7.2 Hz, 1H), 7.18 – 7.12 (m, 1H), 7.08 (d, J = 7.2 Hz, 1H), 6.88 (t, J = 7.6 Hz, 2H), 6.63 (t, J = 7.6 Hz, 1H), 6.35 (d, J = 8.0 Hz, 1H), 6.02 (dd, J = 7.6, 3.6 Hz, 1H), 4.85 (s, 1H), 4.73 – 4.62 (m, 1H), 3.75 (s, 1H), 3.47 (t, J = 9.2 Hz, 1H), 2.94 – 2.83 (m, 2H), 1.61 (s, 9H), 1.00 (d, J = 6.0 Hz, 3H), 0.72 (d, J = 6.0 Hz, 3H).



	Retention Time	Area	% Area
	7.597	4179105	49.40
	10.115	4279933	50.60



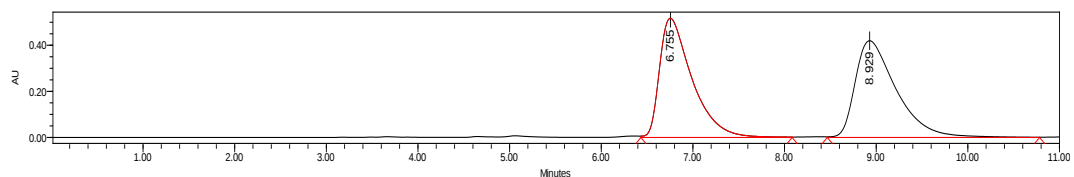
	Retention Time	Area	% Area
	7.401	40076505	98.99
	10.149	408994	1.01



di-tert-butyl 2'-oxo-2,3,9a-tetrahydrospiro [carbazole-1,3'-indoline]-1',2-dicarboxylate (**3d**)

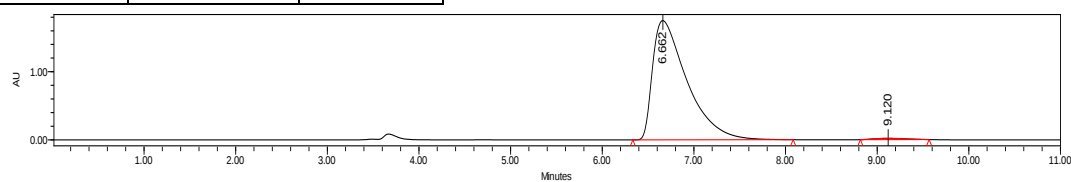
General procedure A; White solid; 97% yield, 98.0% ee, >99:1dr; $[\alpha]_{\text{D}}^{27}$ = 290 (c 1.13, CH_2Cl_2); Determined by HPLC analysis [Daicel chiralpak ODH, n-hexane/i-PrOH = 93/7, 1.0 mL/min, λ = 254 nm, t (major) = 6.66 min, t (minor) = 9.12 min];

^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, J = 8.0 Hz, 1H), 7.29 (d, J = 7.6 Hz, 1H), 7.23 – 7.21 (m, 1H), 7.14 (d, J = 7.6 Hz, 1H), 6.97 – 6.91 (m, 2H), 6.69 (t, J = 7.4 Hz, 1H), 6.40 (d, J = 8.0 Hz, 1H), 6.10 (dd, J = 8.0, 4.0 Hz, 1H), 4.90 – 4.88 (m, 1H), 3.83 (d, J = 5.8 Hz, 1H), 3.50 (t, J = 8.8 Hz, 1H), 3.06 – 2.97 (m, 1H), 2.89 – 2.81 (m, 1H), 1.67 (s, 9H), 1.12 (s, 9H).

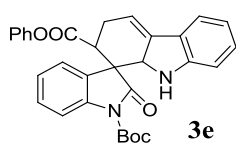


	Retention Time	Area	% Area
	6.755	12732154	49.35

	8.929	13065284	50.65
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	Retention Time	Area	% Area
	6.662	45604542	99.04
	9.120	442729	0.96



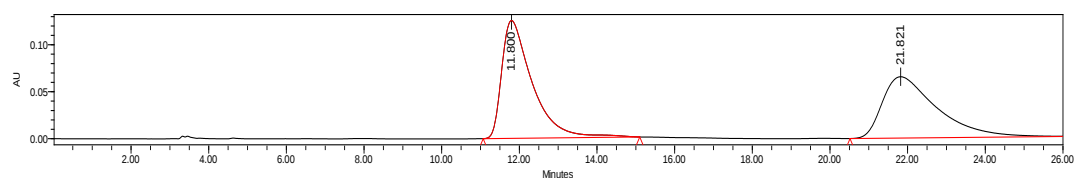
1'-tert-butyl 2-phenyl 2'-oxo-2,3,9a-tetrahydrospiro [carbazole-1,3'-indoline]-1',2-dicarboxylate (**3e**)

General procedure A; White solid; 95% yield, 96% ee, >99:1dr; $[\alpha]_D^{28} = 250$ (c 1.08, CH_2Cl_2); Determined by HPLC analysis [Daicel chiralpak ODH, n-hexane/i-PrOH = 93/7, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 11.55 min, t (minor) = 21.93 min];

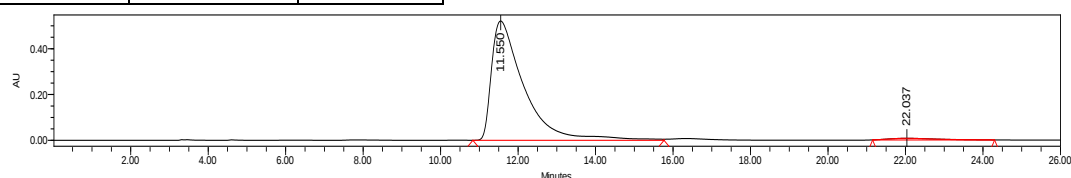
^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, $J = 7.6$ Hz, 1H), 7.34 (d, $J = 7.6$ Hz, 1H), 7.28 – 7.21 (m, 4H), 7.12 (t, $J = 7.2$ Hz, 1H), 7.01 – 6.94 (m, 2H), 6.75 – 6.67 (m, 3H), 6.43 (d, $J = 8.0$ Hz, 1H), 6.13 (dd, $J = 7.6, 3.6$ Hz, 1H), 5.04 – 5.02 (m, 1H), 3.86 – 3.82 (m, 2H), 3.17 – 3.00 (m, 2H), 1.52 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 178.05, 169.66, 152.68, 150.04, 149.04, 140.57, 137.68, 129.44, 128.62, 126.26, 126.00, 125.72, 124.72, 121.15, 120.56, 119.60, 114.78, 112.92, 111.33, 84.41, 67.42, 51.77, 45.21, 28.00, 26.38.

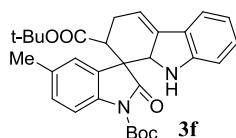
HRMS (ESI) calcd for $[\text{M}+\text{Na}]^+ \text{C}_{31}\text{H}_{28}\text{N}_2\text{O}_5\text{Na}$, m/z: 531.1896, observed: 531.1896.



	Retention Time	Area	% Area
	11.800	6832333	51.75
	21.821	6369210	48.25



	Retention Time	Area	% Area
	11.550	30319306	98.08
	22.037	594736	1.92



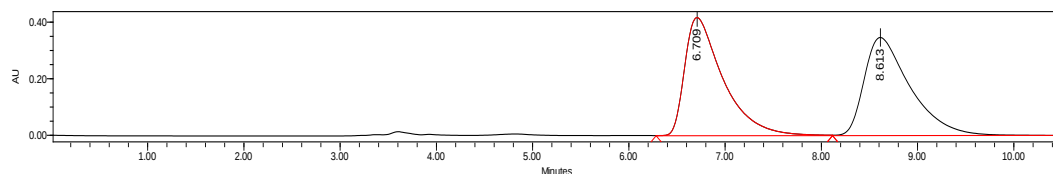
di-tert-butyl 5'-methyl-2'-oxo-2,3,9,9a-tetrahydrospiro
[carbazole-1,3'-indoline]-1',2-dicarboxylate (**3f**)

General procedure A; White solid; 98% yield, 98% ee, >99:1dr; $[\alpha]_D^{29} = 320$ (c 0.97, CH_2Cl_2); Determined by HPLC analysis [Daicel chiralpak ODH, n-hexane/i-PrOH = 93/7, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 6.62 min, t (minor) = 8.68 min];

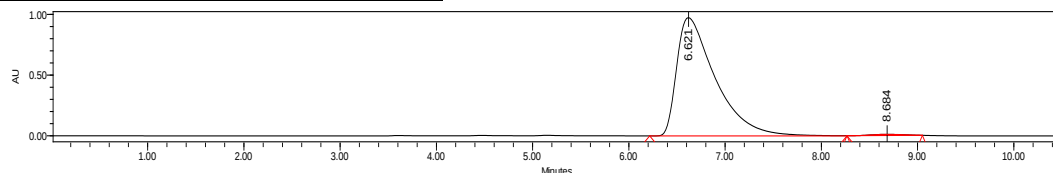
^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, $J = 8.4$ Hz, 1H), 7.30 (d, $J = 7.6$ Hz, 1H), 7.01 (dd, $J = 7.6, 0.8$ Hz, 1H), 6.96 – 6.91 (m, 2H), 6.70 (t, $J = 7.2$ Hz, 1H), 6.40 (d, $J = 8.0$ Hz, 1H), 6.09 (dd, $J = 7.6, 3.6$ Hz, 1H), 4.87 (d, $J = 3.6$ Hz, 1H), 3.86 (s, 1H), 3.48 (dd, $J = 9.6, 7.6$ Hz, 1H), 3.10 – 2.95 (m, 1H), 2.91 – 2.78 (m, 1H), 2.16 (s, 3H), 1.67 (s, 9H), 1.12 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 178.28, 170.22, 152.75, 149.36, 138.08, 137.09, 133.94, 129.21, 128.77, 126.42, 126.03, 120.48, 119.35, 114.19, 113.28, 111.18, 84.20, 81.93, 67.85, 52.10, 44.81, 28.19, 27.40, 26.24, 21.27.

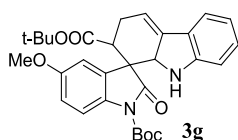
HRMS (ESI) calcd for $[\text{M}+\text{Na}]^+ \text{C}_{30}\text{H}_{34}\text{N}_2\text{O}_5\text{Na}$, m/z: 525.2365, observed: 525.2368.



	Retention Time	Area	% Area
	6.709	11602675	50.21
	8.613	11507179	49.79



	Retention Time	Area	% Area
	6.621	27182195	99.20
	8.684	220019	0.80



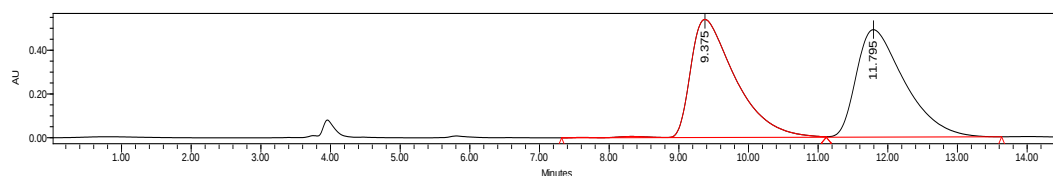
di-tert-butyl 5'-methoxy-2'-oxo-2,3,9,9a-tetrahydrospiro
[carbazole-1,3'-indoline]-1',2-dicarboxylate (**3g**)

General procedure A; White solid; 94% yield, 98% ee, >99:1dr; $[\alpha]_D^{29} = 310$ (c 0.98, CH_2Cl_2) Determined by HPLC analysis [Daicel chiralpak ODH, n-hexane/i-PrOH = 93/7, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 9.09 min, t (minor) = 11.75 min];

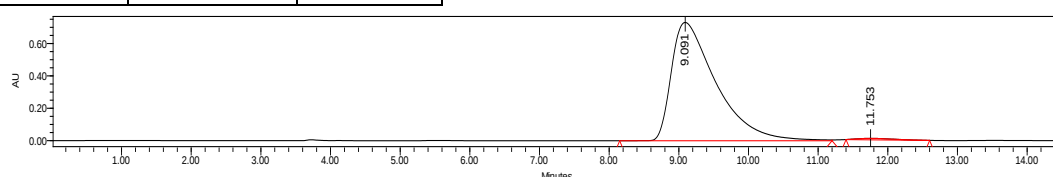
^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, $J = 8.8$ Hz, 1H), 7.28 (d, $J = 7.2$ Hz, 1H), 6.96 – 6.92 (m, 1H), 6.75 – 6.67 (m, 3H), 6.40 (d, $J = 8.0$ Hz, 1H), 6.09 (dd, $J = 7.6, 4.0$ Hz, 1H), 4.88 (s, 1H), 3.86 (s, 1H), 3.62 (s, 3H), 3.48 (t, $J = 9.2$ Hz, 1H), 3.00 – 2.96 (m, 1H), 2.87 – 2.81 (m, 1H), 1.66 (s, 9H), 1.14 (s, 9H);

^{13}C NMR (101 MHz, CDCl_3) δ 178.08, 170.06, 156.50, 152.66, 149.35, 137.23, 134.02, 129.27, 127.98, 126.31, 120.48, 119.45, 115.02, 113.23, 112.83, 111.79, 111.13, 84.16, 81.95, 67.79, 55.38, 52.21, 44.85, 28.19, 27.44, 26.27;

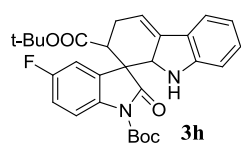
HRMS (ESI) calcd for $[\text{M}+\text{Na}]^+ \text{C}_{30}\text{H}_{34}\text{N}_2\text{O}_6\text{Na}$, m/z : 541.2315, observed: 541.2316.



	Retention Time	Area	% Area
	9.375	24175437	50.57
	11.795	23629989	49.43



	Retention Time	Area	% Area
	9.091	3246296	99.02
	11.753	320438	0.98



di-tert-butyl 5'-fluoro-2'-oxo-2,3,9,9a-tetrahydrospiro

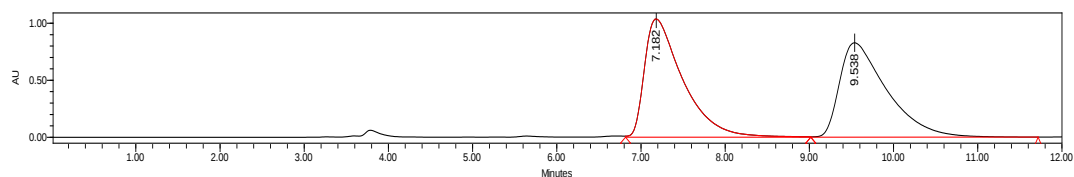
[carbazole-1,3'-indoline]-1',2-dicarboxylate (**3h**)

General procedure A; White solid; 95% yield, 97% ee, >99:1dr; $[\alpha]_{\text{D}}^{29} = 340$ (c 0.88, CH_2Cl_2); Determined by HPLC analysis [Daicel chiralpak ODH, n-hexane/i-PrOH = 93/7, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 7.10 min, t (minor) = 9.60 min];

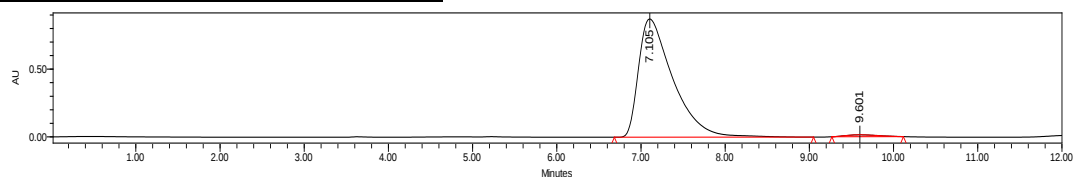
^1H NMR (400 MHz, CDCl_3) δ 7.88 (dd, $J = 8.8, 4.4$ Hz, 1H), 7.30 (d, $J = 7.2$ Hz, 1H), 7.00 – 6.84 (m, 3H), 6.72 (t, $J = 7.6$ Hz, 1H), 6.37 (d, $J = 8.0$ Hz, 1H), 6.09 (dd, $J = 7.6, 4.0$ Hz, 1H), 4.86 (d, $J = 3.2$ Hz, 1H), 3.87 (s, 1H), 3.49 (t, $J = 9.2$ Hz, 1H), 3.06 – 2.79 (m, 2H), 1.66 (s, 9H), 1.15 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 177.69, 169.86, 160.91, 158.50, 152.51, 149.24, 137.12, 136.58, 129.47, 128.49, 126.18, 120.60, 119.69, 115.50, 114.69, 114.46, 113.32, 113.05, 111.19, 84.57, 82.12, 67.77, 52.20, 44.89, 28.16, 27.46, 26.25.

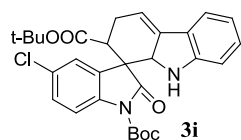
HRMS (ESI) calcd for $[\text{M}+\text{Na}]^+ \text{C}_{29}\text{H}_{31}\text{FN}_2\text{O}_5\text{Na}$, m/z : 529.2114, observed: 529.2120.



	Retention Time	Area	% Area
	7.182	32932419	50.53
	9.538	32239225	49.47



	Retention Time	Area	% Area
	7.105	24763171	98.50
	9.601	376979	1.50



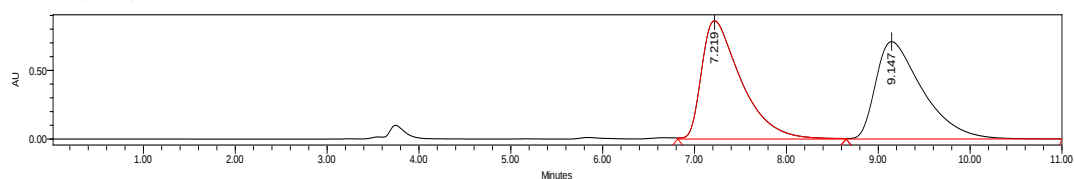
di-tert-butyl 5-chloro-2'-oxo-2,3,9,9a-tetrahydrospiro[carbazole-1,3'-indoline]-1',2-dicarboxylate (**3i**)

General procedure A; White solid; 95% yield, 98% ee, >99:1dr; $[\alpha]_D^{29} = 280$ (c 0.94, CH_2Cl_2); Determined by HPLC analysis [Daicel chiralpak ODH, n-hexane/i-PrOH = 93/7, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 7.28 min, t (minor) = 9.31 min];

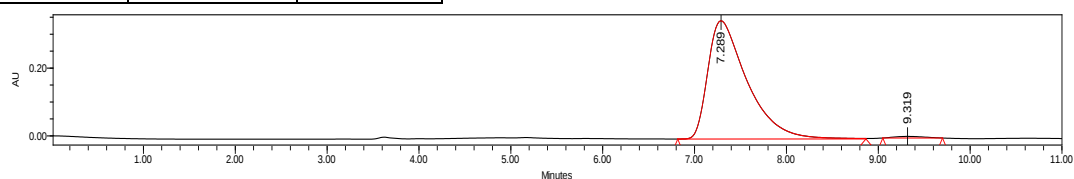
^1H NMR (400 MHz, CDCl_3) δ 7.85 (d, $J = 8.8$ Hz, 1H), 7.31 (d, $J = 7.6$ Hz, 1H), 7.20 (dd, $J = 8.8, 2.4$ Hz, 1H), 7.09 (d, $J = 2.4$ Hz, 1H), 6.97 (t, $J = 7.6$ Hz, 1H), 6.73 (t, $J = 7.2$ Hz, 1H), 6.44 (d, $J = 7.6$ Hz, 1H), 6.10 (dd, $J = 7.2, 3.6$ Hz, 1H), 4.95 – 4.82 (m, 1H), 3.82 (d, $J = 4.0$ Hz, 1H), 3.49 (t, $J = 8.8$ Hz, 1H), 3.02 – 2.81 (m, 2H), 1.66 (s, 9H), 1.15 (s, 9H);

^{13}C NMR (101 MHz, CDCl_3) δ 177.46, 169.82, 152.50, 149.10, 139.17, 137.03, 129.81, 129.46, 128.50, 128.27, 126.16, 125.50, 120.68, 119.73, 115.57, 113.33, 111.22, 84.75, 82.17, 67.86, 52.07, 44.89, 28.13, 27.46, 26.25;

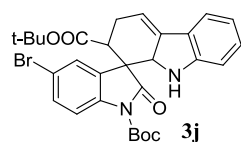
HRMS (ESI) calcd for $[\text{M}+\text{Na}]^+$ $\text{C}_{29}\text{H}_{31}\text{ClN}_2\text{O}_5\text{Na}$, m/z: 545.1818, observed: 545.1818.



	Retention Time	Area	% Area
	7.219	25750237	50.68
	9.147	25061513	49.32



	Retention Time	Area	% Area
	7.289	10356924	99.01
	9.319	103687	0.99



di-tert-butyl 5'-bromo-2'-oxo-2,3,9,9a-tetrahydrospiro

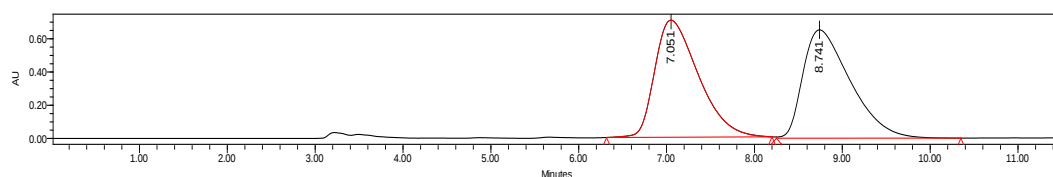
[carbazole-1,3'-indoline]-1',2-dicarboxylate (**3j**)

General procedure A; White solid; 93% yield, 97% ee, >99:1dr; $[\alpha]_D^{28} = 220$ (c 0.86, CH_2Cl_2); Determined by HPLC analysis [Daicel chiralpak ODH, n-hexane/i-PrOH = 93/7, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 7.04 min, t (minor) = 9.06 min];

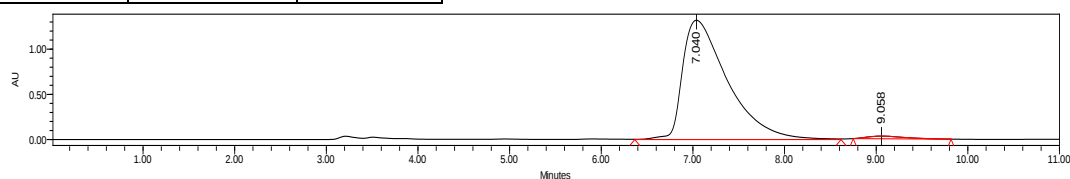
^1H NMR (400 MHz, CDCl_3) δ 7.80 (d, $J = 8.8$ Hz, 1H), 7.37 (dd, $J = 8.8, 2.4$ Hz, 1H), 7.32 (d, $J = 7.2$ Hz, 1H), 7.22 (d, $J = 2.0$ Hz, 1H), 6.99 (t, $J = 7.6$ Hz, 1H), 6.74 (t, $J = 7.6$ Hz, 1H), 6.45 (d, $J = 8.0$ Hz, 1H), 6.10 (dd, $J = 7.6, 3.6$ Hz, 1H), 4.88 (s, 1H), 3.82 (s, 1H), 3.49 (t, $J = 8.8$ Hz, 1H), 2.96 – 2.86 (m, 2H), 1.66 (s, 9H), 1.15 (s, 9H);

^{13}C NMR (101 MHz, CDCl_3) δ 177.33, 169.80, 152.50, 149.08, 139.68, 137.02, 131.23, 129.46, 128.88, 128.23, 126.14, 120.69, 119.74, 117.50, 116.00, 113.30, 111.22, 84.78, 82.18, 67.89, 52.02, 44.91, 28.13, 27.45, 26.24;

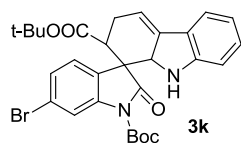
HRMS (ESI) calcd for $[\text{M}+\text{Na}]^+ \text{C}_{29}\text{H}_{31}\text{BrN}_2\text{O}_5\text{Na}$, m/z: 589.1314, observed: 589.1318.



	Retention Time	Area	% Area
	7.051	24313716	49.88
	8.741	24426584	50.12



	Retention Time	Area	% Area
	7.040	45101404	98.17
	9.058	840500	1.83



di-tert-butyl 6'-bromo-2'-oxo-2,3,9,9a-tetrahydrospiro

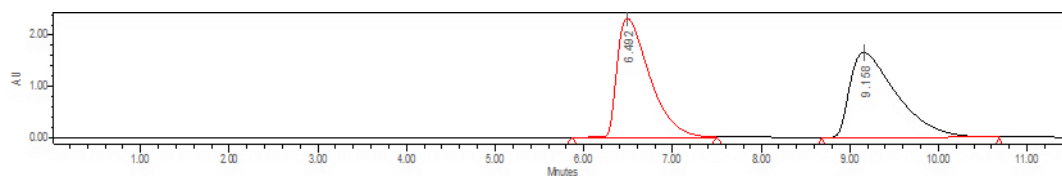
[carbazole-1,3'-indoline]-1',2-dicarboxylate (**3k**)

General procedure A; White solid; 94% yield, 96% ee, >99:1dr; $[\alpha]_D^{28} = 280$ (c 1.12, CH_2Cl_2); Determined by HPLC analysis [Daicel chiralpak ODH, n-hexane/i-PrOH = 93/7, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 6.44 min, t (minor) = 9.53 min];

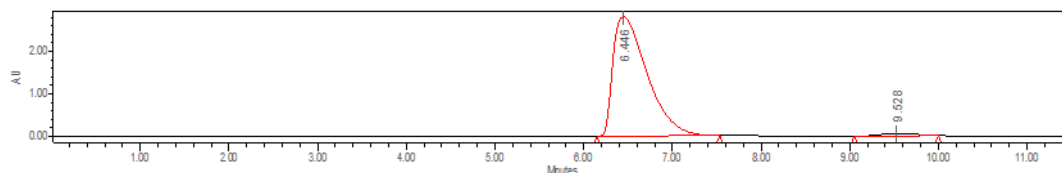
^1H NMR (400 MHz, CDCl_3) δ 8.12 (d, J = 1.6 Hz, 1H), 7.29 (d, J = 7.6 Hz, 1H), 7.10 (dd, J = 8.0, 1.6 Hz, 1H), 6.98 (dd, J = 14.0, 8.0 Hz, 2H), 6.72 (t, J = 7.2 Hz, 1H), 6.42 (dd, J = 7.6, 3.6 Hz, 1H), 6.10 (dd, J = 7.6, 3.6 Hz, 1H), 4.85 (s, 1H), 3.83 (s, 1H), 3.48 (t, J = 8.8 Hz, 1H), 2.99 – 2.82 (m, 2H), 1.67 (s, 9H), 1.16 (s, 9H);

^{13}C NMR (101 MHz, CDCl_3) δ 177.57, 169.92, 152.49, 149.03, 141.59, 137.17, 129.47, 127.45, 126.59, 126.18, 125.60, 122.07, 120.50, 119.67, 118.01, 113.43, 111.26, 84.93, 82.19, 67.64, 52.01, 44.84, 28.13, 27.49, 26.29;

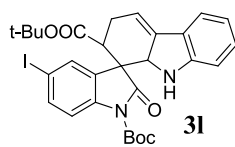
HRMS (ESI) calcd for $[\text{M}+\text{Na}]^+ \text{C}_{29}\text{H}_{31}\text{BrN}_2\text{O}_5\text{Na}$, m/z : 589.1314, observed: 589.1318.



	Retention Time	Area	% Area
	6.492	59759609	49.80
	9.158	60235332	50.20



	Retention Time	Area	% Area
	6.446	74718633	98.03
	9.530	1502984	1.97



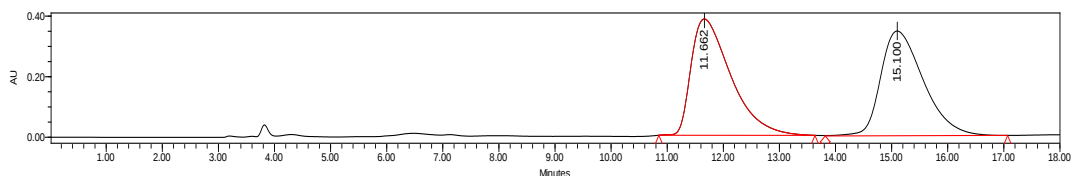
di-tert-butyl 5'-iodo-2'-oxo-2,3,9,9a-tetrahydrospiro
[carbazole-1,3'-indoline]-1',2-dicarboxylate (**3I**)

General procedure A; White solid; 96% yield, 96% ee, >99:1dr; $[\alpha]_{\text{D}}^{28}$ = 190 (c 1.02, CH_2Cl_2); Determined by HPLC analysis [Daicel chiralpak ODH, n-hexane/i-PrOH = 93/7, 1.0 mL/min, λ = 254 nm, t (minor) = 15.54 min, t (major) = 11.73 min];

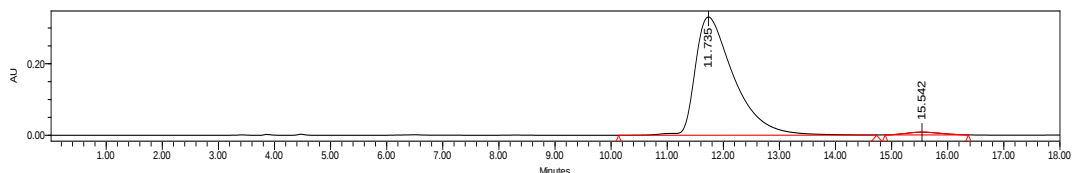
^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, J = 8.4 Hz, 1H), 7.57 (dd, J = 8.8, 2.0 Hz, 1H), 7.38 (d, J = 2.0 Hz, 1H), 7.31 (d, J = 7.2 Hz, 1H), 6.99 (t, J = 7.2 Hz, 1H), 6.74 (t, J = 7.6 Hz, 1H), 6.47 (d, J = 7.6 Hz, 1H), 6.10 (dd, J = 7.6, 4.0 Hz, 1H), 4.87 (s, 1H), 3.81 (s, 1H), 3.47 (t, J = 8.8 Hz, 1H), 3.01 – 2.83 (m, 2H), 1.66 (s, 9H), 1.14 (s, 9H);

^{13}C NMR (101 MHz, CDCl_3) δ 177.22, 169.83, 152.53, 149.06, 140.42, 137.31, 137.04, 133.88, 129.46, 129.18, 126.17, 120.71, 119.76, 116.48, 113.28, 111.25, 88.15, 84.81, 82.20, 67.92, 51.90, 44.91, 28.14, 27.46, 26.24, 22.35;

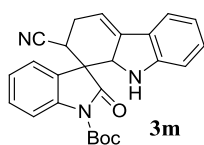
HRMS (ESI) calcd for $[\text{M}+\text{Na}]^+ \text{C}_{29}\text{H}_{31}\text{IN}_2\text{O}_5\text{Na}$, m/z : 637.1175, observed: 637.1188.



Retention Time	Area	% Area
11.662	18942532	50.87
15.100	18294061	49.13



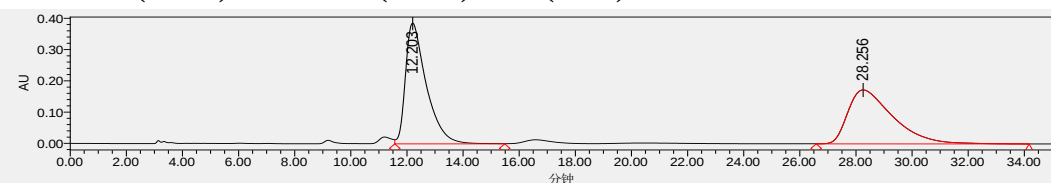
Retention Time	Area	% Area
11.735	15849800	98.00
15.542	323853	2.00



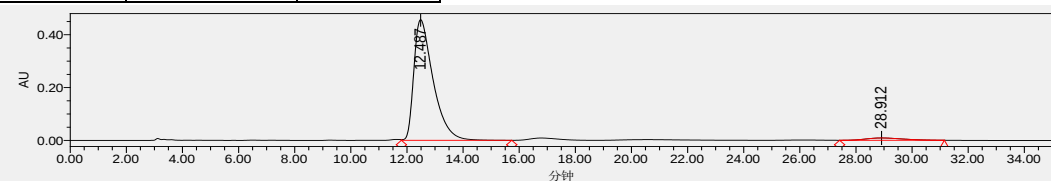
tert-butyl 2-cyano-2'-oxo-2,3,9,9a-tetrahydrospiro
[carbazole-1,3'-indoline]-1'-carboxylate (**3m**)

General procedure A; White solid; 95% yield, 93% ee, >99:1dr; $[\alpha]_D^{28} = 210$ (c 1.04, CH_2Cl_2); Determined by HPLC analysis [Daicel chiralpak ODH, n-hexane/i-PrOH = 90/10, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 12.48 min, t (minor) = 28.91 min];

^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, $J = 8.0$ Hz, 1H), 7.32 – 7.27 (m, 2H), 7.23 (d, $J = 6.4$ Hz, 1H), 6.98 (t, $J = 8.0$ Hz, 2H), 6.74 (t, $J = 7.2$ Hz, 1H), 6.38 (d, $J = 7.6$ Hz, 1H), 5.99 (dd, $J = 7.2, 3.6$ Hz, 1H), 4.79 (s, 1H), 3.90 (d, $J = 5.2$ Hz, 1H), 3.57 (dd, $J = 10.8, 6.8$ Hz, 1H), 3.04 – 2.96 (m, 1H), 2.90 – 2.88 (m, 1H), 1.66 (s, 9H);

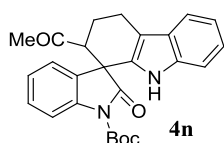
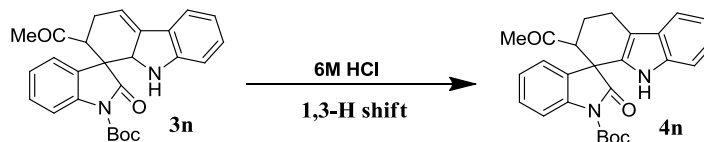


Retention Time	Area	% Area
12.203	19906717	50.85
28.256	19239181	49.15



	Retention Time	Area	% Area
	12.487	21787293	96.53
	28.912	782106	3.47

tert-butyl 2-acetyl-2'-oxo-2,3,9a-tetrahydrospiro
[carbazole-1,3'-indoline]-1'-carboxylate (**3n**)



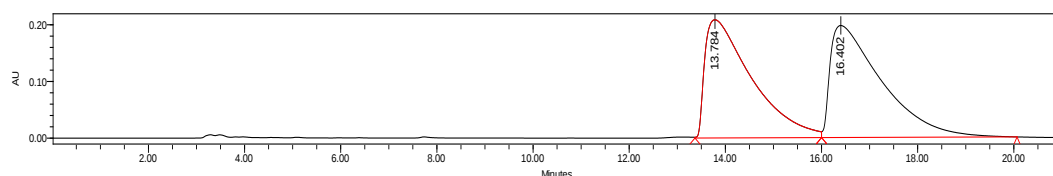
tert-butyl 2-acetyl-2'-oxo-2,3,4,9-tetrahydrospiro
[carbazole-1,3'-indoline]-1'-carboxylate (**4n**)

General procedure B; White solid; 93% yield, 88% ee, >99:1dr; $[\alpha]_D^{23} = 130$ (c 0.30, CH_2Cl_2); Determined by HPLC analysis [Daicel chiralpak IB, n-hexane/i-PrOH = 95/5, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 7.62 min, t (minor) = 37.00 min];

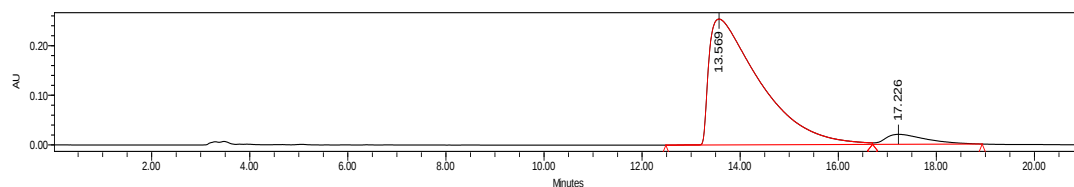
^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, $J = 8.0$ Hz, 1H), 7.52 (d, $J = 7.6$ Hz, 1H), 7.41 (s, 1H), 7.31 – 7.27 (m, 1H), 7.13 – 7.01 (m, 5H), 3.63 (dd, $J = 12.8, 3.2$ Hz, 1H), 3.15 – 3.09 (m, 1H), 3.00 – 2.92 (m, 1H), 2.58 – 2.54 (m, 1H), 2.48 – 2.37 (m, 1H), 2.00 (s, 3H), 1.67 (s, 9H);

^{13}C NMR (101 MHz, CDCl_3) δ 176.16, 149.30, 139.30, 136.71, 131.05, 129.77, 128.97, 126.51, 124.73, 124.45, 122.71, 119.65, 118.57, 115.32, 112.66, 111.13, 84.93, 57.28, 51.68, 29.12, 28.17, 22.93, 20.40;

HRMS (ESI) calcd for $[\text{M}+\text{Na}]^+ \text{C}_{26}\text{H}_{26}\text{N}_2\text{O}_4\text{Na}$, m/z: 453.1790, observed: 453.1793.

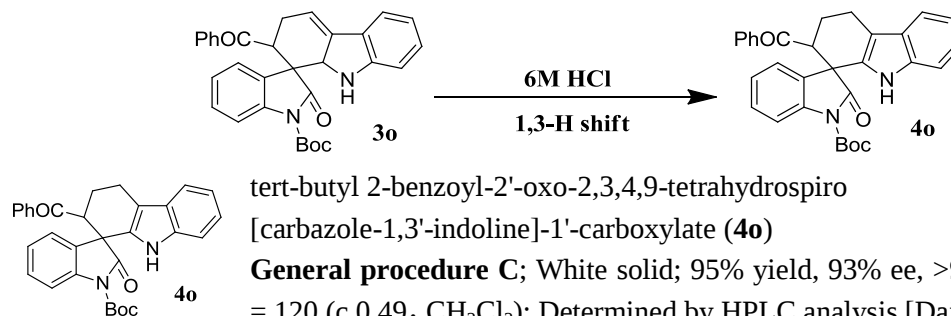


	Retention Time	Area	% Area
	13.784	14139510	48.98
	16.402	14726181	51.02



	Retention Time	Area	% Area
	13.569	18365235	94.04
	17.226	1163179	5.96

tert-butyl 2-benzoyl-2'-oxo-2,3,9,9a-tetrahydrospiro
[carbazole-1,3'-indoline]-1'-carboxylate (**3o**)

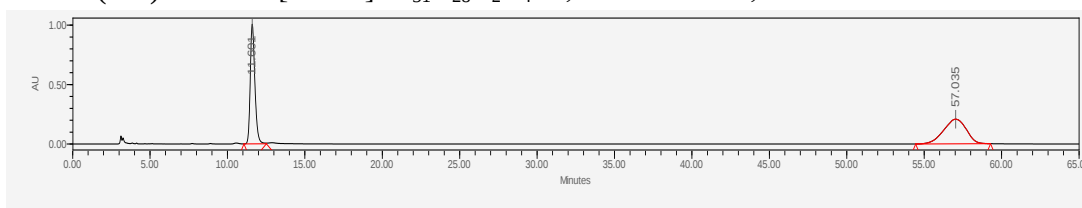


General procedure C; White solid; 95% yield, 93% ee, >99:1dr; $[\alpha]_D^{28}$ = 120 (c 0.49, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IA, n-hexane/i-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 11.34 min, t (minor) = 55.65 min];

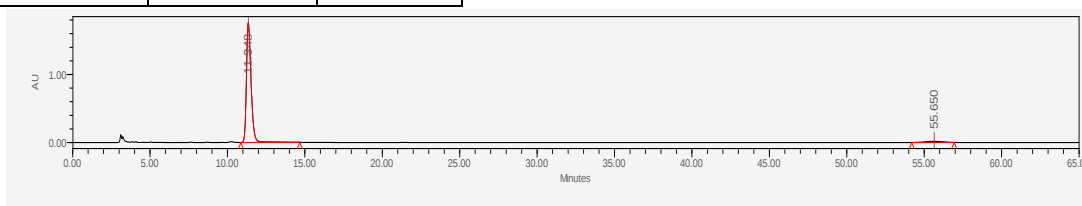
¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, *J* = 8.0 Hz, 1H), 7.56 – 7.54 (m, 1H), 7.50 – 7.44 (m, 3H), 7.36 – 7.30 (m, 4H), 7.28 – 7.23 (m, 1H), 7.17 – 7.06 (m, 5H), 4.51 (dd, *J* = 12.0, 3.2 Hz, 1H), 3.18 – 3.12 (m, 1H), 3.04 – 2.96 (m, 1H), 2.58 – 2.47 (m, 1H), 2.43 – 2.38 (m, 1H), 1.50 (s, 9H);

¹³C NMR (101 MHz, CDCl₃) δ 200.60, 176.06, 148.46, 138.72, 137.34, 136.73, 132.97, 130.62, 129.12, 128.83, 128.32, 126.62, 125.72, 124.87, 122.68, 119.63, 118.66, 114.82, 113.79, 111.09, 84.54, , 52.53, 51.26, 27.99, 23.70, 19.93;

HRMS (ESI) calcd for [M+Na]⁺ C₃₁H₂₈N₂O₄Na, m/z: 515.1947, observed: 515.1948.

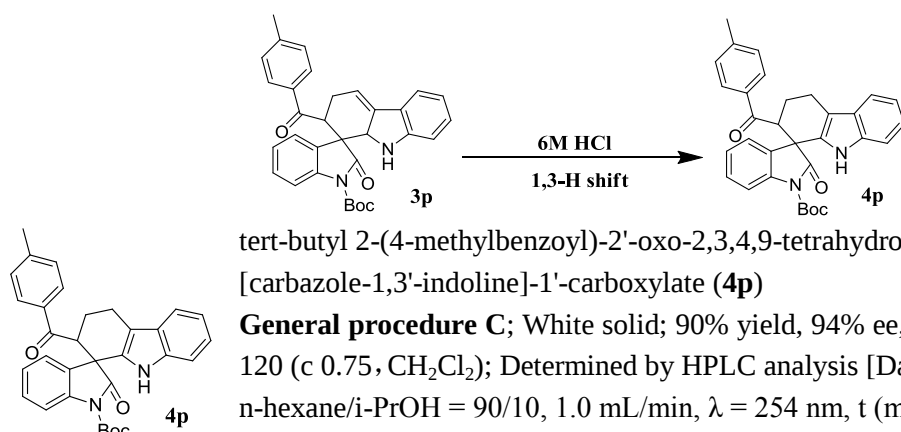


	Retention Time	Area	% Area
	11.601	20884077	49.79
	57.035	21056811	50.21



	Retention Time	Area	% Area
	11.348	36665921	96.60
	55.650	1289128	3.40

tert-butyl 2-(4-methylbenzoyl)-2'-oxo-2,3,9,9a-tetrahydrospiro
[carbazole-1,3'-indoline]-1'-carboxylate (**3p**)



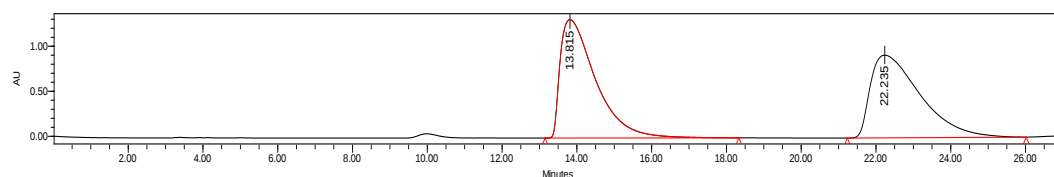
tert-butyl 2-(4-methylbenzoyl)-2'-oxo-2,3,4,9-tetrahydrospiro
[carbazole-1,3'-indoline]-1'-carboxylate (**4p**)

General procedure C; White solid; 90% yield, 94% ee, >99:1dr; $[\alpha]_D^{28} = 120$ (c 0.75, CH_2Cl_2); Determined by HPLC analysis [Daicel chiralpak IC, n-hexane/i-PrOH = 90/10, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 13.63 min, t (minor) = 22.84 min];

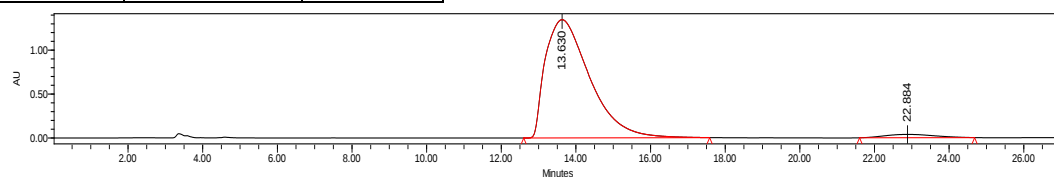
^1H NMR (400 MHz, CDCl_3) δ 7.69 (d, $J = 8.4$ Hz, 1H), 7.56 (d, $J = 7.2$ Hz, 1H), 7.44 (d, $J = 8.0$ Hz, 2H), 7.30 – 7.24 (m, 2H), 7.20 – 7.05 (m, 7H), 4.49 (dd, $J = 12.4, 2.8$ Hz, 1H), 3.23 – 3.08 (m, 1H), 3.07 – 2.94 (m, 1H), 2.63 – 2.47 (m, 1H), 2.44 – 2.37 (m, 1H), 2.35 (s, 3H), 1.51 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 199.91, 176.09, 148.45, 143.62, 138.67, 136.71, 134.74, 130.64, 129.11, 129.04, 128.89, 128.37, 126.65, 125.77, 124.82, 122.67, 119.63, 118.65, 114.79, 113.87, 111.04, 84.37, 52.62, 51.00, 27.93, 23.72, 21.62, 19.93;

HRMS (ESI) calcd for $[\text{M}+\text{Na}]^+ \text{C}_{26}\text{H}_{26}\text{N}_2\text{O}_4\text{Na}$, m/z : 453.1790, observed: 453.1793.

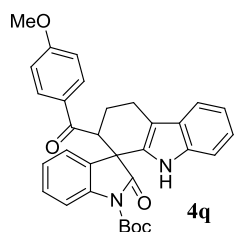


	Retention Time	Area	% Area
	13.815	86527410	50.43
	22.235	85034850	49.57



	Retention Time	Area	% Area
	13.630	111051443	96.97
	22.884	3464522	3.03

tert-butyl 2-(4-methoxybenzoyl)-2'-oxo-2,3,9a-tetrahydrospiro
[carbazole-1,3'-indoline]-1'-carboxylate (**3q**)



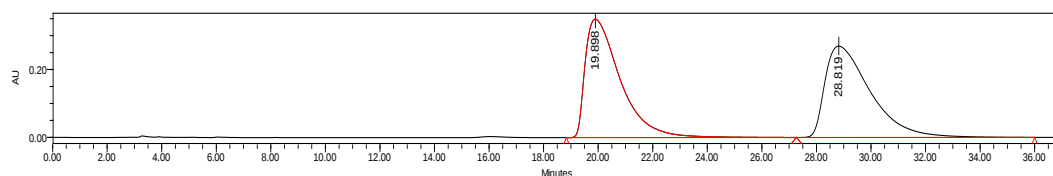
tert-butyl 2-(4-methoxybenzoyl)-2'-oxo-2,3,4,9-tetrahydrospiro
[carbazole-1,3'-indoline]-1'-carboxylate (**4q**)

General procedure C; White solid; 90% yield, 92% ee, >99:1dr; $[\alpha]_D^{28}$
= 130 (c 0.85, CH_2Cl_2); Determined by HPLC analysis [Daicel
chiralpak IC, n-hexane/i-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t
(major) = 19.20 min, t (minor) = 29.28 min];

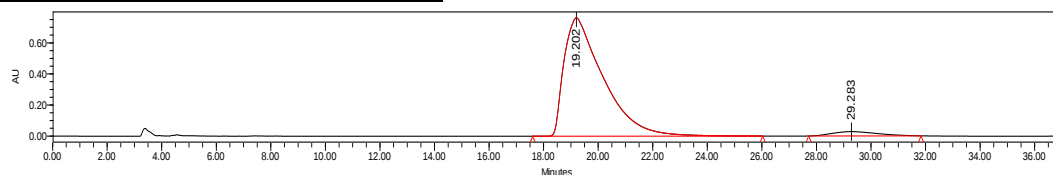
^1H NMR (400 MHz, CDCl_3) δ 7.67 (d, J = 7.6 Hz, 1H), 7.60 – 7.52 (m, 3H), 7.37 (s, 1H),
7.30 – 7.24 (m, 1H), 7.17 (dd, J = 7.6, 1.2 Hz, 1H), 7.16 – 7.06 (m, 4H), 6.85 – 6.78 (m, 2H),
4.46 (dd, J = 12.0, 2.8 Hz, 1H), 3.81 (s, 3H), 3.15 (ddd, J = 15.8, 5.2, 2.2 Hz, 1H), 3.09 – 2.94
(m, 1H), 2.60 – 2.49 (m, 1H), 2.38 – 2.33 (m, 1H), 1.50 (s, 9H);

^{13}C NMR (101 MHz, CDCl_3) δ 200.60, 176.06, 148.46, 138.72, 137.34, 136.73, 132.97,
130.62, 129.12, 128.83, 128.32, 126.62, 125.72, 124.87, 122.68, 119.63, 118.66, 114.82,
113.79, 111.09, 84.54, 52.53, 51.26, 27.99, 23.70, 19.93;

HRMS (ESI) calcd for $[\text{M}+\text{Na}]^+$ $\text{C}_{32}\text{H}_{30}\text{N}_2\text{O}_5\text{Na}$, m/z: 545.2052, observed: 545.2060.

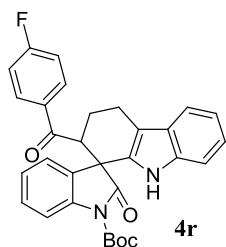
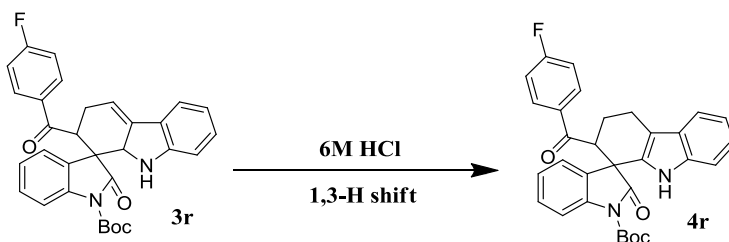


	Retention Time	Area	% Area
	19.898	31199453	50.10
	28.819	31070392	49.90



	Retention Time	Area	% Area
	19.202	75908250	96.00
	29.283	3161611	4.00

tert-butyl 2-(4-fluorobenzoyl)-2'-oxo-2,3,9,9a-tetrahydrospiro
[carbazole-1,3'-indoline]-1'-carboxylate (**3r**)



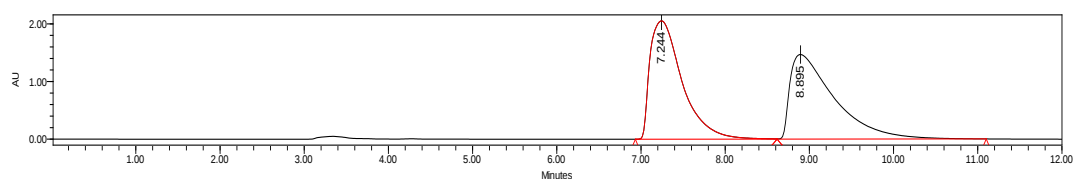
tert-butyl 2-(4-fluorobenzoyl)-2'-oxo-2,3,4,9-tetrahydrospiro
[carbazole-1,3'-indoline]-1'-carboxylate (**4r**)

General procedure C; White solid; 90% yield, 90% ee, >99:1dr; $[\alpha]_{\text{D}}^{30} = 110$ (c 0.85, CH_2Cl_2); Determined by HPLC analysis [Daicel chiralpak IB, n-hexane/i-PrOH = 90/10, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 8.83 min, t (minor) = 7.48 min];

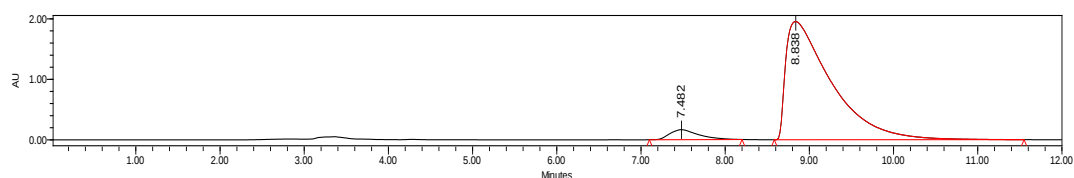
^1H NMR (400 MHz, CDCl_3) δ 7.67 (d, $J = 8.4$ Hz, 1H), 7.59 – 7.49 (m, 3H), 7.30 – 7.24 (m, 2H), 7.19 – 7.07 (m, 5H), 7.00 (t, $J = 8.4$ Hz, 2H), 4.46 (dd, $J = 12.4, 2.8$ Hz, 1H), 3.19 – 3.13 (m, 1H), 3.06 – 2.93 (m, 1H), 2.62 – 2.47 (m, 1H), 2.41 – 2.36 (m, 1H), 1.53 (s, 9H);

^{13}C NMR (101 MHz, CDCl_3) δ 199.02, 176.06, 166.81, 164.27, 148.32, 138.57, 136.73, 133.72, 130.91, 130.35, 129.22, 128.57, 126.57, 125.79, 124.94, 122.78, 119.70, 118.67, 115.64, 115.42, 114.77, 113.91, 111.06, 84.77, 52.62, 51.22, 27.93, 23.60, 19.86;

HRMS (ESI) calcd for $[\text{M}+\text{Na}]^+$ $\text{C}_{31}\text{H}_{27}\text{FN}_2\text{O}_4\text{Na}$, m/z: 533.1852, observed: 533.1853.

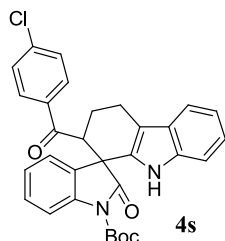
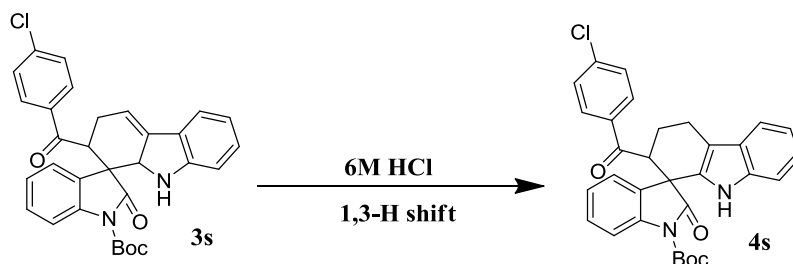


	Retention Time	Area	% Area
	7.244	54552984	50.38
	8.895	53724574	49.62



	Retention Time	Area	% Area
	7.482	3884947	5.00
	8.838	73753371	95.00

tert-butyl 2-(4-chlorobenzoyl)-2'-oxo-2,3,9a-tetrahydrospir
[carbazole-1,3'-indoline]-1'-carboxylate (**3s**)



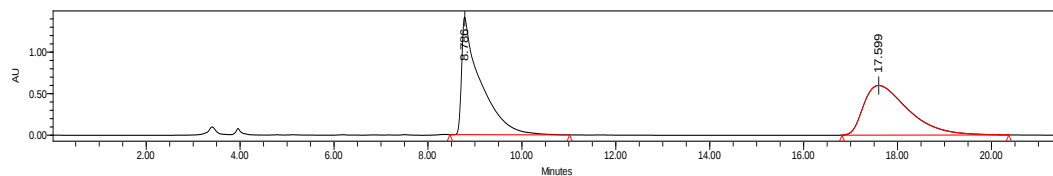
tert-butyl 2-(4-chlorobenzoyl)-2'-oxo-2,3,4,9-tetrahydrospiro[carbazole-1,3'-indoline]-1'-carboxylate (**4s**)

General procedure C; White solid; 94% yield, 90% ee, >99:1dr; $[\alpha]_D^{30} = 140$ (c 0.76, CH_2Cl_2); Determined by HPLC analysis [Daicel chiralpak IC, n-hexane/i-PrOH = 90/10, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 8.91 min, t (minor) = 18.07 min];

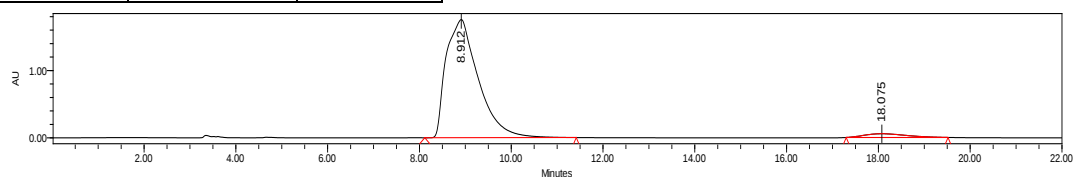
^1H NMR (400 MHz, CDCl_3) δ 7.67 (d, $J = 8.4$ Hz, 1H), 7.57 (d, $J = 7.2$ Hz, 1H), 7.43 (d, $J = 8.4$ Hz, 2H), 7.34 – 7.25 (m, 4H), 7.18 – 7.06 (m, 5H), 4.45 (dd, $J = 12.4, 2.8$ Hz, 1H), 3.22 – 3.11 (m, 1H), 3.06 – 2.93 (m, 1H), 2.61 – 2.47 (m, 1H), 2.43 – 2.33 (m, 1H), 1.54 (s, 9H);

^{13}C NMR (101 MHz, CDCl_3) δ 199.40, 175.98, 148.31, 139.39, 138.56, 136.73, 135.65, 130.29, 129.65, 129.26, 128.71, 128.49, 126.55, 125.77, 124.96, 122.80, 119.71, 118.68, 114.78, 113.92, 111.07, 84.83, 52.60, 51.22, 27.95, 23.55, 19.84;

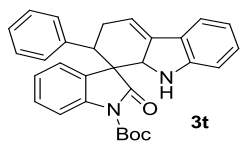
HRMS (ESI) calcd for $[\text{M}+\text{Na}]^+$ $\text{C}_{31}\text{H}_{27}\text{ClN}_2\text{O}_4\text{Na}$, m/z : 521.1608, observed: 521.1612.



	Retention Time	Area	% Area
	8.786	39457573	50.03
	17.599	39414098	49.97



	Retention Time	Area	% Area
	8.912	85414278	96.07
	18.075	3490272	3.93



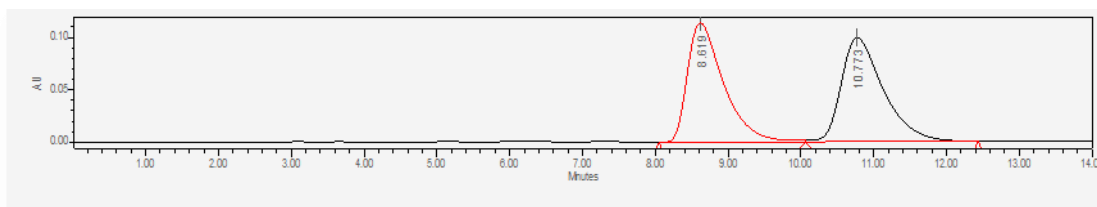
tert-butyl 2'-oxo-2-phenyl-2,3,9,9a-tetrahydrospiro

[carbazole-1,3'-indoline]-1'-carboxylate (**3t**)

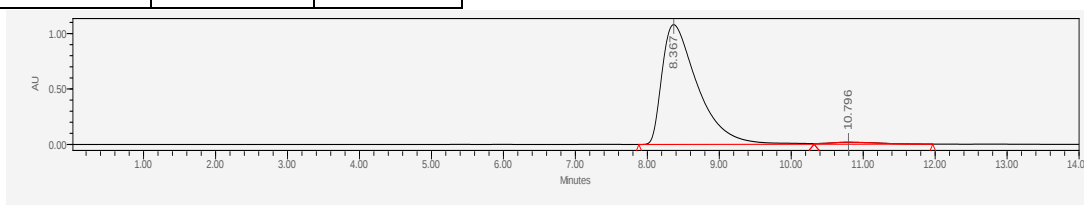
General procedure D; White solid; 89.0% yield, 95.0% ee, >99:1dr; $[\alpha]_D^{28} = 500$ (c 0.12, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak ODH, n-hexane/i-PrOH = 93/7, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 8.36 min, t (minor) = 10.79 min];

¹H NMR (400 MHz, CDCl₃) δ 7.59 (d, $J = 8.0$ Hz, 1H), 7.51 (dd, $J = 3.6, 1.2$ Hz, 1H), 7.39 (d, $J = 7.2$ Hz, 1H), 7.27 – 7.22 (m, 1H), 7.14 – 7.07 (m, 2H), 7.06 – 6.98 (m, 3H), 6.79 – 6.75 (m, 1H), 6.70 – 6.63 (m, 2H), 6.53 (d, $J = 8.0$ Hz, 1H), 6.15 (dd, $J = 7.2, 3.6$ Hz, 1H), 5.26 (m, 1H), 3.80 (d, $J = 4.8$ Hz, 1H), 3.67 (dd, $J = 11.2, 6.4$ Hz, 1H), 2.97 – 2.70 (m, 2H), 1.47 (s, 9H);

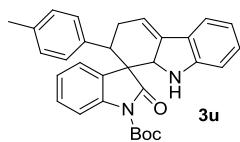
¹³C NMR (101 MHz, CDCl₃) δ 176.48, 151.98, 147.30, 139.38, 136.70, 128.28, 127.19, 126.78, 126.41, 125.81, 124.98, 123.32, 119.51, 118.48, 113.96, 113.62, 110.28, 82.75, 64.79, 54.36, 47.14, 29.91, 26.90;



	Retention Time	Area	% Area
	8.619	3929115	49.82
	10.773	3957136	50.18



	Retention Time	Area	% Area
	8.367	37195171	97.71
	10.796	870087	2.29



tert-butyl 2'-oxo-2-(p-tolyl)-2,3,9,9a-tetrahydrospiro

[carbazole-1,3'-indoline]-1'-carboxylate (**3u**)

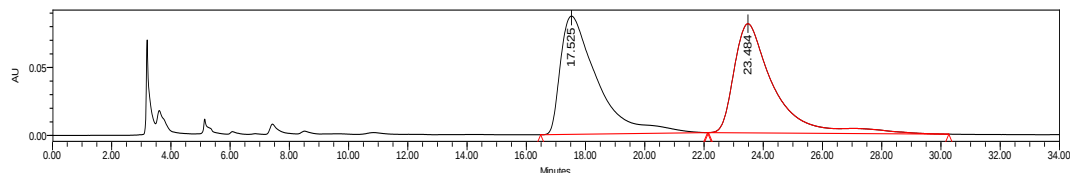
General procedure D; White solid; 85.0% yield, 97.0% ee, >99:1dr; $[\alpha]_D^{28} = 510$ (c 0.06, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak ODH, n-hexane/i-PrOH = 98/2, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 16.48 min, t (minor) = 24.00 min];

¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, $J = 8.0$ Hz, 1H), 7.49 (dd, $J = 7.2, 0.8$ Hz, 1H), 7.38 (d, $J = 7.6$ Hz, 1H), 7.27 – 7.22 (m, 1H), 7.06 – 7.10 (m, 1H), 7.04 – 6.98 (m, 1H), 6.83 (d, $J = 8.0$ Hz, 2H), 6.78 – 6.75 (m, 1H), 6.53 (t, $J = 8.0$ Hz, 3H), 6.13 (dd, $J = 7.2, 3.6$ Hz,

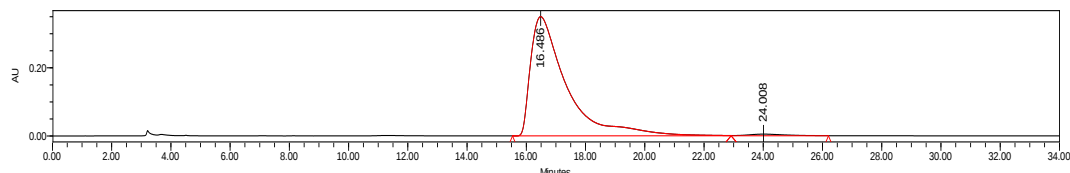
1H), 5.24 (s, 1H), 3.79 (s, 1H), 3.63 (dd, $J = 11.6, 6.4$ Hz, 1H), 2.93 – 2.67 (m, 2H), 2.19 (s, 3H), 1.47 (s, 9H);

^{13}C NMR (101 MHz, CDCl_3) δ 177.61, 153.03, 148.38, 140.45, 137.81, 136.95, 134.59, 129.29, 128.48, 128.12, 126.88, 126.05, 124.33, 120.53, 119.48, 115.13, 114.68, 111.30, 83.68, 65.79, 55.46, 47.88, 31.03, 27.90, 20.92 ;

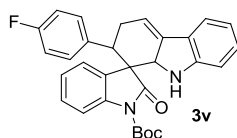
HRMS (ESI) calcd for $[\text{M}+\text{Na}]^+ \text{C}_{31}\text{H}_{30}\text{N}_2\text{O}_3\text{Na}$, m/z : 501.2154, observed: 501.2157.



	Retention Time	Area	% Area
	17.525	7481774	49.98
	23.484	7488995	50.02



	Retention Time	Area	% Area
	16.486	29359136	98.65
	24.008	402250	1.35



tert-butyl 2-(4-fluorophenyl)-2'-oxo-2,3,9,9a-

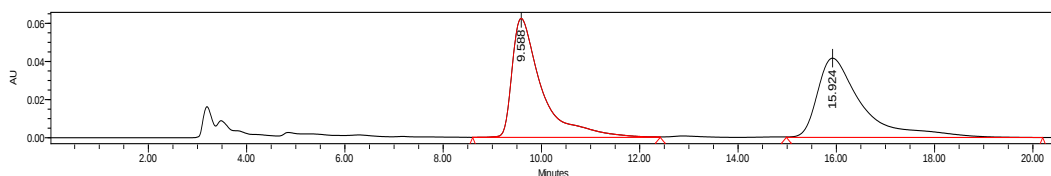
tetrahydrospiro[carbazole-1,3'-indoline]-1'-carboxylate (**3v**)

General procedure D; White solid; 86.0% yield, 94.0% ee, >99:1dr; $[\alpha]_{\text{D}}^{28} = 490$ (c 0.05, CH_2Cl_2); Determined by HPLC analysis [Daicel chiralpak ODH, n-hexane/i-PrOH = 93/7, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 9.30 min, t (minor) = 15.85 min];

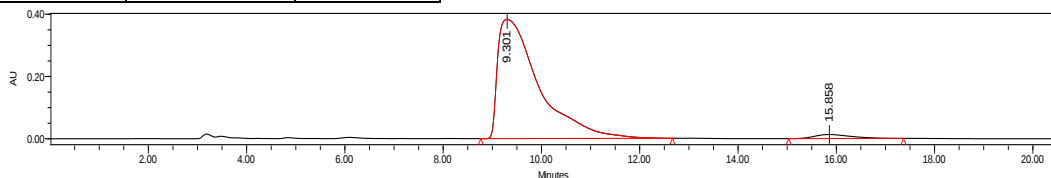
^1H NMR (400 MHz, CDCl_3) δ 7.60 (d, $J = 8.0$ Hz, 1H), 7.49 (dd, $J = 7.6, 0.8$ Hz, 1H), 7.39 (d, $J = 7.6$ Hz, 1H), 7.30 – 7.23 (m, 1H), 7.10 (m, 1H), 7.02 (t, $J = 7.6$ Hz, 1H), 6.78 (t, $J = 7.6$ Hz, 1H), 6.72 (t, $J = 8.8$ Hz, 2H), 6.66 – 6.59 (m, 2H), 6.53 (d, $J = 7.6$ Hz, 1H), 6.13 (dd, $J = 7.2, 3.6$ Hz, 1H), 5.28 – 5.19 (m, 1H), 3.80 (d, $J = 4.8$ Hz, 1H), 3.66 (dd, $J = 10.8, 6.4$ Hz, 1H), 2.91 – 2.69 (m, 2H), 1.49 (s, 9H);

^{13}C NMR (101 MHz, CDCl_3) δ 176.43, 162.28, 159.84, 151.95, 147.20, 139.32, 136.88, 132.42, 128.70, 128.35, 127.39, 125.71, 125.01, 124.69, 123.42, 119.53, 118.52, 113.67, 113.46, 110.30, 83.00, 64.73, 54.36, 46.31, 30.04, 26.89 ;

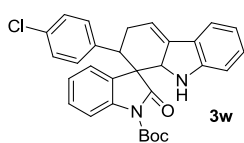
HRMS (ESI) calcd for $[\text{M}+\text{Na}]^+ \text{C}_{30}\text{H}_{27}\text{FN}_2\text{O}_3\text{Na}$, m/z : 505.1906, observed: 505.1906.



	Retention Time	Area	% Area
	9.588	2617236	49.96
	15.924	2620976	50.04



	Retention Time	Area	% Area
	9.301	22236539	97.11
	15.858	661809	2.89



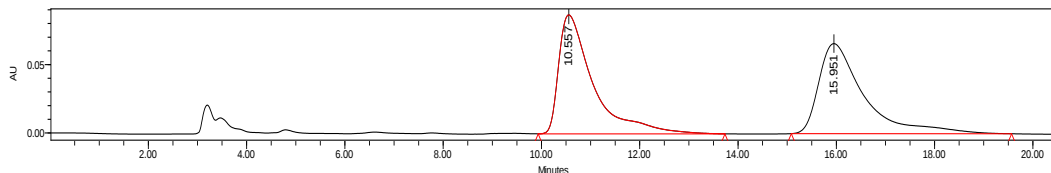
tert-butyl 2-(4-chlorophenyl)-2'-oxo-2,3,9,9a-tetrahydrospiro[carbazole-1,3'-indoline]-1'-carboxylate (**3w**)

General procedure D; White solid; 85.0% yield, 93.0% ee, >99:1dr; $[\alpha]_D^{28} = 460$ (c 0.05, CH_2Cl_2); Determined by HPLC analysis [Daicel chiralpak ODH, n-hexane/i-PrOH = 93/7, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 10.27 min, t (minor) = 15.98 min];

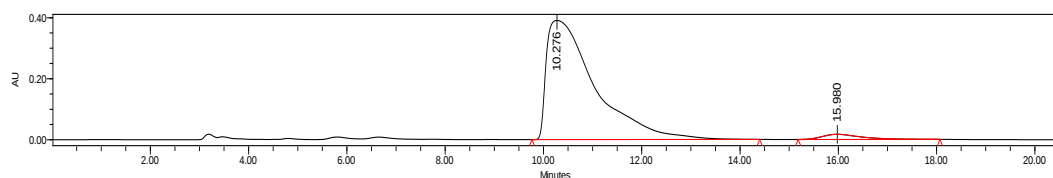
^1H NMR (400 MHz, CDCl_3) δ 7.60 (d, $J = 8.0$ Hz, 1H), 7.48 (d, $J = 6.4$ Hz, 1H), 7.39 (d, $J = 7.6$ Hz, 1H), 7.30 – 7.23 (m, 1H), 7.09 (m, 1H), 7.05 – 6.97 (m, 3H), 6.78 (t, $J = 7.2$ Hz, 1H), 6.59 (d, $J = 8.4$ Hz, 2H), 6.52 (d, $J = 8.0$ Hz, 1H), 6.12 (dd, $J = 7.2, 3.6$ Hz, 1H), 5.27 – 5.18 (m, 1H), 3.79 (d, $J = 5.2$ Hz, 1H), 3.64 (dd, $J = 10.8, 6.4$ Hz, 1H), 2.89 – 2.68 (m, 2H), 1.50 (s, 9H);

^{13}C NMR (101 MHz, CDCl_3) δ 176.33, 151.94, 147.14, 139.32, 136.91, 135.21, 132.21, 128.44, 127.43, 126.90, 125.67, 125.00, 124.55, 123.45, 119.54, 118.53, 113.64, 110.31, 83.08, 64.67, 54.24, 46.48, 29.83, 26.88;

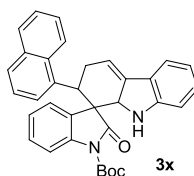
HRMS (ESI) calcd for $[\text{M}+\text{Na}]^+ \text{C}_{30}\text{H}_{27}\text{ClN}_2\text{O}_3\text{Na}$, m/z: 525.2365, observed: 525.2368.



	Retention Time	Area	% Area
	10.557	4235914	50.22
	15.951	4198344	49.78



	Retention Time	Area	% Area
	10.276	26802451	96.67
	15.980	922529	3.33



tert-butyl 2-(naphthalen-1-yl)-2'-oxo-2,3,9,9a-tetrahydrospiro[carbazole-1,3'-indoline]-1'-carboxylate (**3x**)

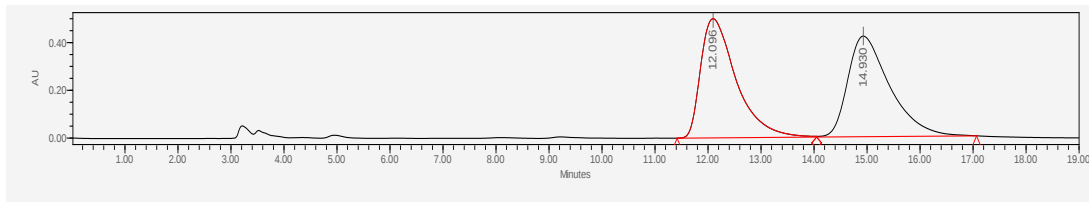
General procedure D; White solid; 86.0% yield, 92.0% ee, >99:1dr; $[\alpha]_D^{28} = 520$ (c 0.06, CH_2Cl_2); Determined by HPLC analysis [Daicel chiralpak ODH, n-hexane/i-PrOH = 93/7, 1.0 mL/min, $\lambda = 254$ nm, t

(major) = 12.03 min, t (minor) = 15.06 min];

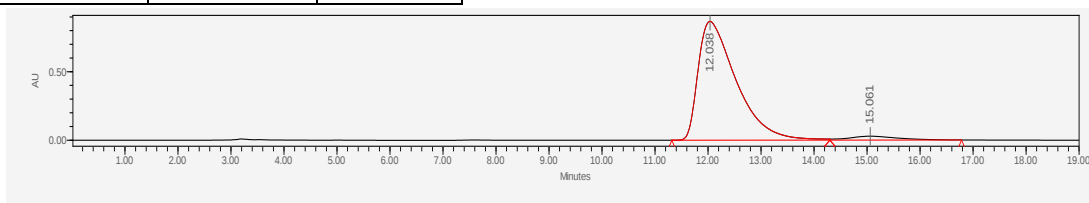
^1H NMR (400 MHz, CDCl_3) δ 7.65 – 7.68 (m, 1H), 7.59 – 7.56 (m, 2H), 7.51 (d, $J = 8.4$ Hz, 1H), 7.45 (d, $J = 8.8$ Hz, 1H), 7.41 (d, $J = 7.6$ Hz, 1H), 7.36 (dd, $J = 6.4, 3.2$ Hz, 2H), 7.27 – 7.22 (m, 2H), 7.14 (t, $J = 7.6$ Hz, 1H), 7.03 (t, $J = 7.6$ Hz, 1H), 6.79 (t, $J = 7.6$ Hz, 1H), 6.61 (d, $J = 8.4$ Hz, 1H), 6.54 (d, $J = 7.6$ Hz, 1H), 6.17 (dd, $J = 7.2, 3.6$ Hz, 1H), 5.31 (s, 1H), 3.83 (dd, $J = 11.6, 5.6$ Hz, 2H), 2.93 – 3.03 (m, 1H), 2.89 – 2.75 (m, 1H), 1.19 (s, 9H);

^{13}C NMR (101 MHz, CDCl_3) δ 177.53, 153.04, 148.10, 140.48, 137.92, 135.21, 132.99, 132.77, 129.37, 128.86, 128.35, 127.83, 127.26, 126.86, 126.06, 125.89 – 125.37, 124.42, 120.59, 119.54, 114.97, 114.72, 111.35, 83.64, 65.73, 55.56, 48.47, 31.04, 27.55;

HRMS (ESI) calcd for $[\text{M}+\text{Na}]^+$ $\text{C}_{34}\text{H}_{30}\text{N}_2\text{O}_3\text{Na}$, m/z: 537.2154, observed: 537.2153.

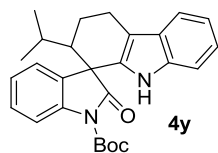
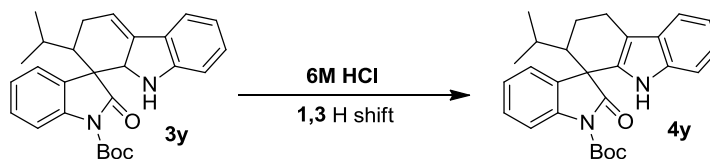


	Retention Time	Area	% Area
	12.096	23238835	50.07
	14.930	23172894	49.93



	Retention Time	Area	% Area
	12.038	43234641	96.04
	15.061	1783828	3.96

tert-butyl 2-isopropyl-2'-oxo-2,3,9,9a-tetrahydrospiro
[carbazole-1,3'-indoline]-1'-carboxylate (**3y**)



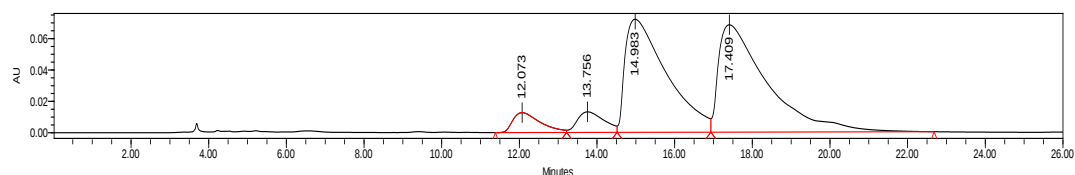
tert-butyl 2-isopropyl-2'-oxo-2,3,4,9-tetrahydrospiro
[carbazole-1,3'-indoline]-1'-carboxylate (**4y**)

General procedure E; White solid; 90% yield, 92.0% ee, >99:1dr; $[\alpha]_D^{20}$ =190 (c 0.15, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IB, n-hexane/i-PrOH = 99/1, 1.0 mL/min, λ = 254 nm, t (major) =14.29 min, t (minor) =18.02 min,];

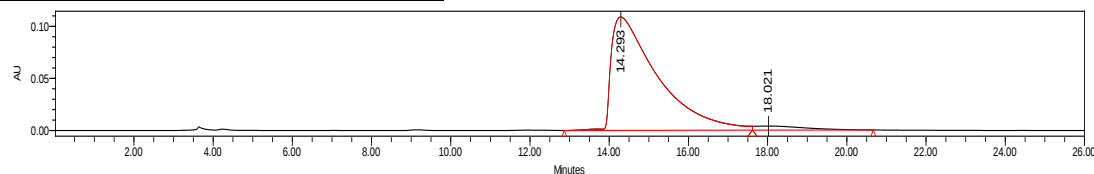
¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, J = 8.4 Hz, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 7.25 (s, 1H), 7.19 – 7.01 (m, 5H), 3.08 (dd, J = 16.0, 3.6 Hz, 1H), 2.94 – 2.76 (m, 1H), 2.63 – 2.48 (m, 1H), 2.20 – 2.08 (m, 1H), 2.04 – 1.93 (m, 1H), 1.68 (s, 9H), 1.59 – 1.50 (m, 1H), 0.88 (d, J = 6.8 Hz, 3H), 0.44 (d, J = 6.4 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 177.40, 149.24, 138.93, 136.64, 132.24, 130.48, 128.73, 126.78, 125.99, 124.46, 122.33, 119.40, 118.49, 115.08, 113.54, 110.97, 84.91, 54.75, 50.39, 28.47, 28.18, 23.48, 21.16, 18.27;

HRMS (ESI) calcd for [M+Na]⁺ C₂₇H₃₀N₂O₃Na, m/z: 453.2154, observed: 453.2152.

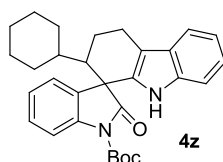
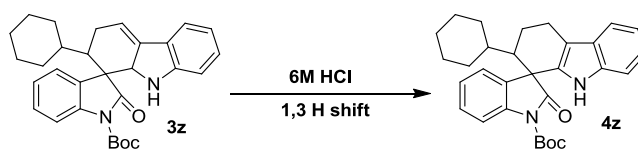


	Retention Time	Area	% Area
	12.073	621407	4.95
	13.756	626292	4.99
	14.983	5369675	42.75
	17.409	5943417	47.32



	Retention Time	Area	% Area
	14.293	8865164	96.20
	18.021	350114	3.80

tert-butyl 2-cyclohexyl-2'-oxo-2,3,9,9a-tetrahydrospiro
[carbazole-1,3'-indoline]-1'-carboxylate (**3z**)



tert-butyl 2-cyclohexyl-2'-oxo-2,3,4,9-tetrahydrospiro
[carbazole-1,3'-indoline]-1'-carboxylate (**4z**)

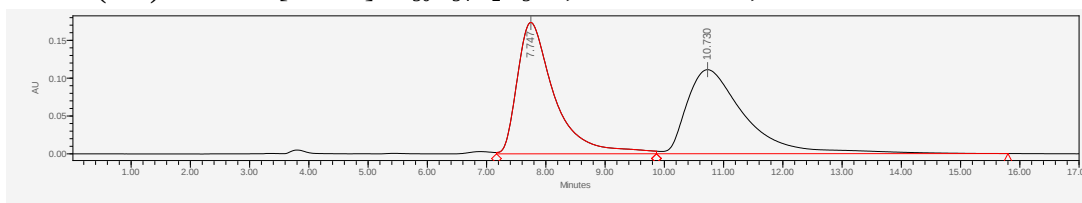
General procedure E; White solid; 80% yield, 90.0% ee, >99:1dr;
[α]_D²⁸ = 130 (c 0.11, CH₂Cl₂); Determined by HPLC analysis [Daicel
chiralpak ODH, n-hexane/i-PrOH = 98/2, 1.0 mL/min, λ = 254 nm, t

(major) = 7.28 min, t (minor) = 10.61 min];

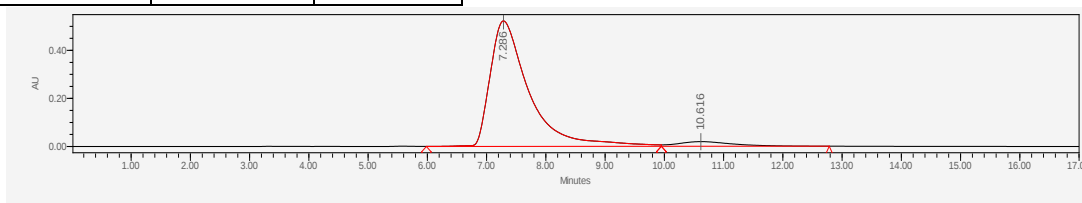
¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, J = 8.4 Hz, 1H), 7.52 (d, J = 7.6 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 7.23 (s, 1H), 7.08 (m, 5H), 3.06 (dd, J = 16.0, 4.4 Hz, 1H), 2.92 – 2.76 (m, 1H), 2.50 (d, J = 11.2 Hz, 1H), 2.16 – 2.13 (m, 1H), 2.01 (m, 1H), 1.68 (s, 9H), 1.44 (d, J = 7.0 Hz, 2H), 1.28 – 0.67 (m, 9H);

¹³C NMR (101 MHz, CDCl₃) δ 177.47, 149.21, 138.90, 136.62, 132.13, 130.66, 128.71, 126.80, 125.88, 124.44, 122.31, 119.38, 118.47, 115.01, 113.53, 110.96, 84.84, 54.72, 50.63, 39.02, 33.45, 28.96, 28.18, 26.97, 26.56, 26.30, 21.90, 21.27;

HRMS (ESI) calcd for [M+Na]⁺ C₃₀H₃₄N₂O₃Na, m/z: 493.2467, observed: 493.2466.

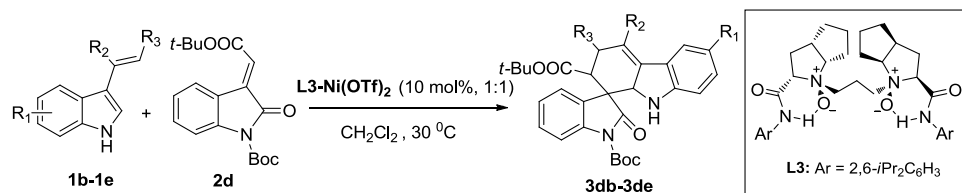


	Retention Time	Area	% Area
	7.747	7552153	49.94
	10.730	7569608	50.06



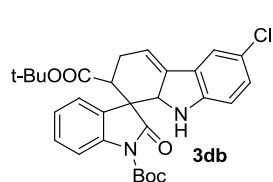
	Retention Time	Area	% Area
	7.286	23691502	95.04
	10.616	1236031	4.96

5. General procedure for the Diels-Alder reaction with different 3-vinylindoles (1b-1e)



In a test tube with a magnetic stirring bar, *N,N'*-dioxide **L3** (0.01 mmol, 7.0 mg), $\text{Ni}(\text{OTf})_2$ (0.01 mmol, 3.6 mg), the methyleneindolinone (**2d**) (0.1 mmol) in CH_2Cl_2 (1.0 mL) were stirred at 30 °C for 30 min, then 3-vinylindoles (**1b-1e**) (0.15 mmol, 1.5 equiv) dissolved in CH_2Cl_2 (0.2 mL) was added in one-portion. The mixture was stirred at 30 °C for a few minutes until the yellow color of the solution disappeared. The reaction mixture was further detected by TLC. After completion, flash column chromatography was carried out to provide the desired product **3db-3de** with almost quantitative yield. The product was directed for HPLC and NMR analysis.

6. The analytical and spectral characterization data of the products (3db-3de)



di-tert-butyl 6-chloro-2'-oxo-2,3,9,9a-tetrahydrospiro

[carbazole-1,3'-indoline]-1',2-dicarboxylate(**3db**)

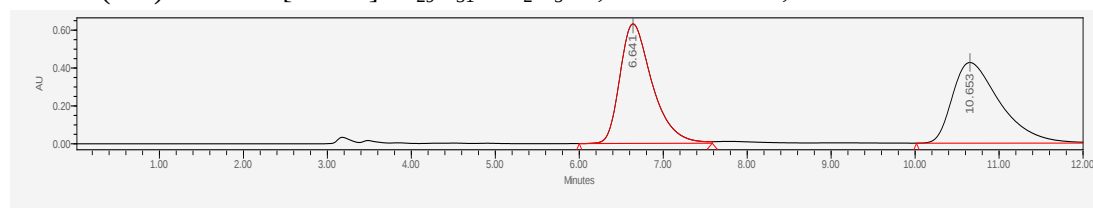
White solid; 95% yield, 96.0% ee, >99:1dr; $[\alpha]_{\text{D}}^{28} = 370$ (c 0.13, CH_2Cl_2); Determined by HPLC analysis [Daicel chiralpak ODH, n-hexane/i-PrOH = 93/7, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 6.59

min, t (minor) = 10.79 min];

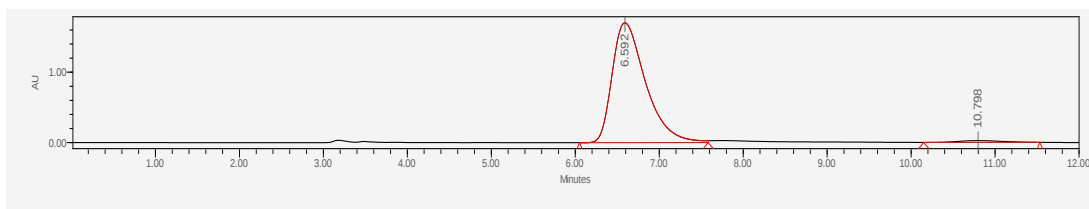
^1H NMR (400 MHz, CDCl_3) δ 7.89 (d, $J = 8.0$ Hz, 1H), 7.28 – 7.20 (m, 2H), 7.10 (dd, $J = 7.6, 1.2$ Hz, 1H), 6.97 (t, $J = 7.6$ Hz, 1H), 6.88 (dd, $J = 8.4, 2.4$ Hz, 1H), 6.31 (d, $J = 8.4$ Hz, 1H), 6.12 (dd, $J = 7.6, 3.6$ Hz, 1H), 4.98 – 4.85 (m, 1H), 3.84 (d, $J = 4.0$ Hz, 1H), 3.48 (t, $J = 8.8$ Hz, 1H), 3.11 – 2.97 (m, 1H), 2.93 – 2.80 (m, 1H), 1.67 (s, 9H), 1.12 (s, 9H);

^{13}C NMR (101 MHz, CDCl_3) δ 177.91, 169.92, 151.04, 149.24, 140.49, 136.23, 128.96, 128.34, 127.93, 126.33, 125.28, 124.46, 120.47, 114.99, 114.47, 111.94, 84.48, 82.08, 68.08, 52.07, 44.68, 28.16, 27.38, 26.29;

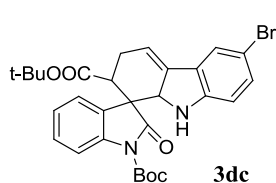
HRMS (ESI) calcd for $[\text{M}+\text{Na}]^+ \text{C}_{29}\text{H}_{31}\text{ClN}_2\text{O}_5\text{Na}$, m/z: 545.1819, observed: 545.1826.



	Retention Time	Area	% Area
	6.641	16862995	50.05
	10.653	16831215	49.95



	Retention Time	Area	% Area
	6.641	16862995	50.05
	10.653	16831215	49.95



1'-tert-butyl 2-tert-butyl-6-bromo 2'-oxo-2,3,9,9a-tetrahydrospiro [carbazole-1,3'-indoline]-1',2-dicarboxylate(**3dc**)

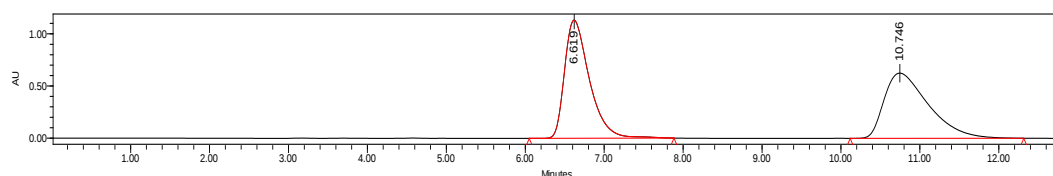
White solid; 95% yield, 96% ee, >99:1dr; $[\alpha]_D^{28} = 350$ (c 1.14, CH_2Cl_2); Determined by HPLC analysis [Daicel chiralpak ODH, n-hexane/i-PrOH = 93/7, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 6.64

min, t (minor) = 11.03 min];

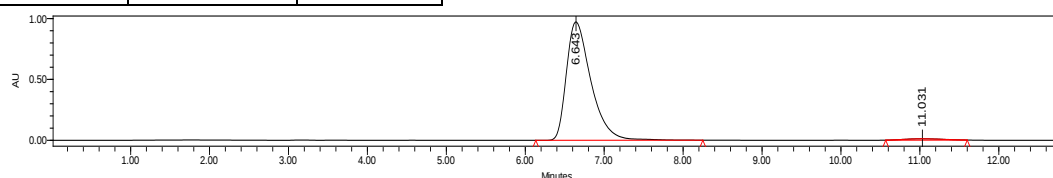
^1H NMR (400 MHz, CDCl_3) δ 7.89 (d, $J = 8.4$ Hz, 1H), 7.37 (d, $J = 1.6$ Hz, 1H), 7.26 – 7.20 (m, 1H), 7.10 (d, $J = 3.6$ Hz, 1H), 7.04 – 6.95 (m, 2H), 6.29 (d, $J = 8.4$ Hz, 1H), 6.11 (dd, $J = 7.6$, 4.0 Hz, 1H), 4.95 – 4.85 (m, 1H), 3.85 (d, $J = 4.8$ Hz, 1H), 3.48 (t, $J = 8.8$ Hz, 1H), 3.10 – 2.97 (m, 1H), 2.92 – 2.80 (m, 1H), 1.67 (s, 9H), 1.11 (s, 9H);

^{13}C NMR (101 MHz, CDCl_3) δ 177.91, 169.91, 151.47, 149.23, 140.47, 136.06, 131.77, 128.40, 126.31, 125.29, 124.57, 123.38, 115.06, 114.47, 112.44, 111.44, 84.50, 82.09, 68.00, 52.04, 44.66, 28.16, 27.38, 26.29;

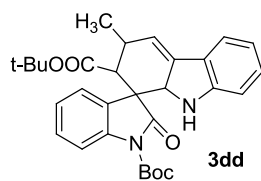
HRMS (ESI) calcd for $[\text{M}+\text{Na}]^+ \text{C}_{29}\text{H}_{31}\text{BrN}_2\text{O}_5\text{Na}$, m/z: 589.1314, observed: 589.1314.



	Retention Time	Area	% Area
	6.619	24853100	50.54
	10.746	24326225	49.46



	Retention Time	Area	% Area
	6.643	20955579	98.29
	11.031	364757	1.71



di-tert-butyl 3-methyl-2'-oxo-2,3,9,9a-tetrahydrospiro

[carbazole-1,3'-indoline]-1',2-dicarboxylate(**3dd**)

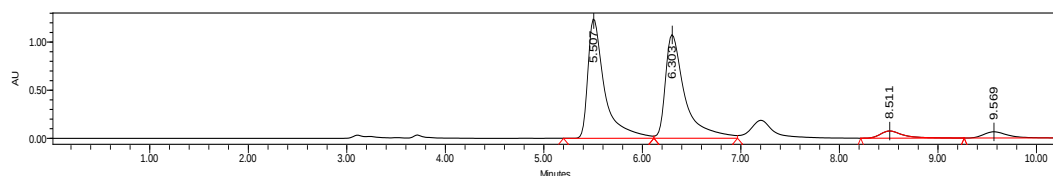
White solid; 98% yield, 98.0% ee, >99:1dr; $[\alpha]_D^{28} = 430$ (c 0.18, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IA, n-hexane/i-PrOH = 90/10, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 5.51

min, t (major) = 6.22 min];

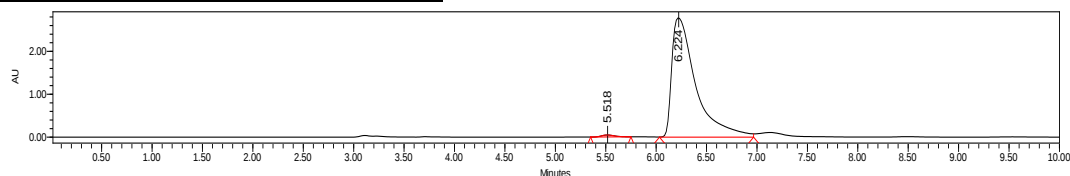
¹H NMR (400 MHz, CDCl₃) δ 7.90 – 7.83 (m, 1H), 7.30 (d, $J = 7.6$ Hz, 1H), 7.25 – 7.19 (m, 2H), 6.99 – 6.93 (m, 2H), 6.75 – 6.68 (m, 1H), 6.45 (d, $J = 8.0$ Hz, 1H), 6.01 (t, $J = 4.0$ Hz, 1H), 4.95 – 4.91 (m, 1H), 3.82 (d, $J = 5.6$ Hz, 1H), 3.33 – 3.26 (m, 1H), 3.06 (d, $J = 8.4$ Hz, 1H), 1.67 (s, 9H), 1.29 (d, $J = 6.8$ Hz, 3H), 1.13 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 177.56, 169.58, 152.84, 149.23, 140.17, 135.75, 129.31, 128.31, 126.28, 125.75, 124.55, 120.50, 119.52, 114.43, 111.17, 84.40, 81.76, 66.87, 54.46, 53.16, 32.14, 28.16, 27.38, 21.46;

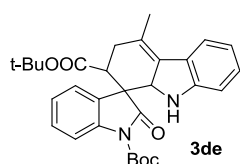
HRMS (ESI) calcd for $[M+Na]^+$ C₃₀H₃₄N₂O₅Na, m/z: 525.2365, observed: 525.2371.



	Retention Time	Area	% Area
	5.507	14678894	46.18
	6.303	14802597	46.57
	8.511	1199175	3.77
	9.569	1107294	3.48



	Retention Time	Area	% Area
	5.518	415308	0.89
	6.224	46040887	99.11



di-tert-butyl 4-methyl-2'-oxo-2,3,9,9a-tetrahydrospiro

[carbazole-1,3'-indoline]-1',2-dicarboxylate(**3de**)

White solid; 96% yield, 98.0% ee, >99:1dr; $[\alpha]_D^{27} = 290$ (c 0.07, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak IB, n-hexane/i-PrOH = 98/2, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 15.07

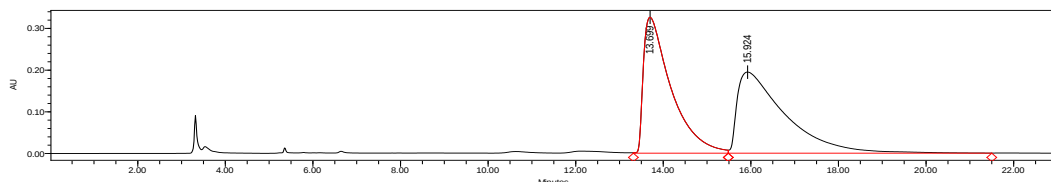
min, t (minor) = 13.93 min];

¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, $J = 8.0$ Hz, 1H), 7.41 (d, $J = 7.6$ Hz, 1H), 7.25 – 7.20 (m, 1H), 7.00 – 6.89 (m, 3H), 6.71 (t, $J = 7.6$ Hz, 1H), 6.44 (d, $J = 7.6$ Hz, 1H), 4.91 (d,

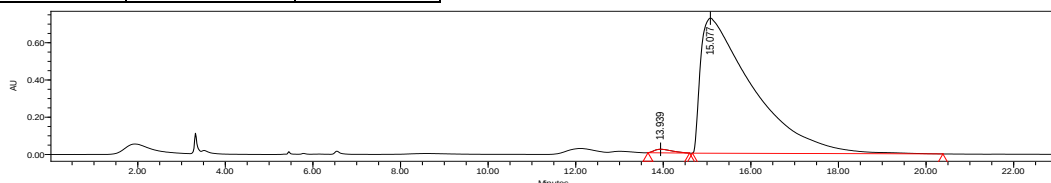
$J = 2.0$ Hz, 1H), 3.81 (d, $J = 4.8$ Hz, 1H), 3.46 (t, $J = 8.8$ Hz, 1H), 2.87 – 2.82 (m, 2H), 2.20 – 2.10 (m, 3H), 1.68 (s, 9H), 1.12 (s, 9H);

^{13}C NMR (101 MHz, CDCl_3) δ 178.20, 170.22, 153.11, 149.29, 140.46, 129.78, 128.24, 127.09, 126.73, 125.25, 124.44, 123.62, 119.12, 114.42, 110.61, 84.36, 81.93, 68.64, 52.61, 44.98, 33.11, 28.18, 27.39, 18.77;

HRMS (ESI) calcd for $[\text{M}+\text{Na}]^+ \text{C}_{30}\text{H}_{34}\text{N}_2\text{O}_5\text{Na}$, m/z : 525.2365, observed: 525.2369.

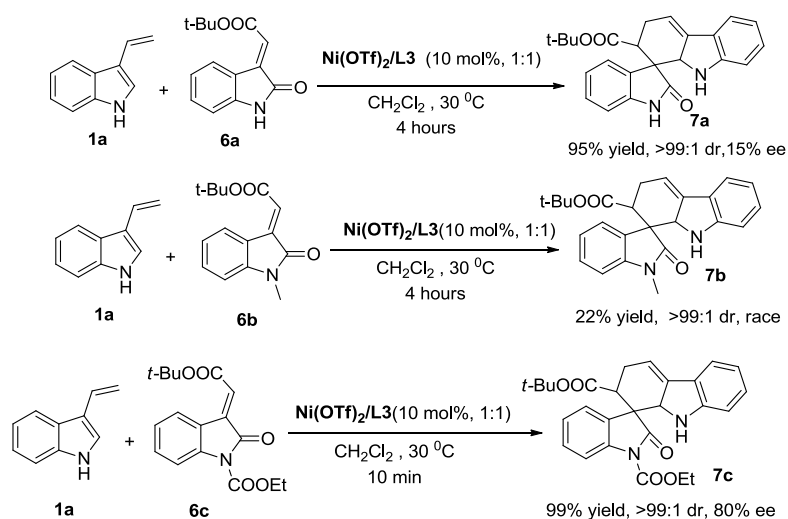


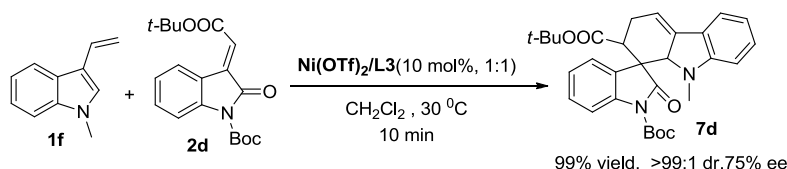
	Retention Time	Area	% Area
	13.699	14268001	49.31
	15.924	14666613	50.69



	Retention Time	Area	% Area
	13.939	538632	0.89
	15.077	60323275	99.11

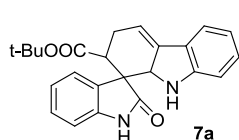
7. Control experiments





In a test tube with a magnetic stirring bar, *N,N'*-dioxide **L3** (0.01 mmol, 7.0 mg), Ni(OTf)_2 (0.01 mmol, 3.6 mg), and the methyleneindolinones (**6a-6c**, **2d**) (0.1 mmol) in CHCl_3 (1.0 mL) were stirred at 30 °C for 30 min, then 3-vinylindole (**1a,1f**) (0.15 mmol, 1.5 equiv) dissolved in CHCl_3 (0.2 mL) was added in one-portion. The mixture was stirred at 30 °C for 10 min, then the reaction mixture was detected by TLC. After completion, flash column chromatography was carried out to provide the desired product (**7a-7d**). The product was directed for HPLC and NMR analysis.

8. The analytical and spectral characterization data of the products (7a-7d)



tert-butyl 2'-oxo-2,3,9,9a-tetrahydrospiro
[carbazole-1,3'-indoline]-2-carboxylate (**7a**)

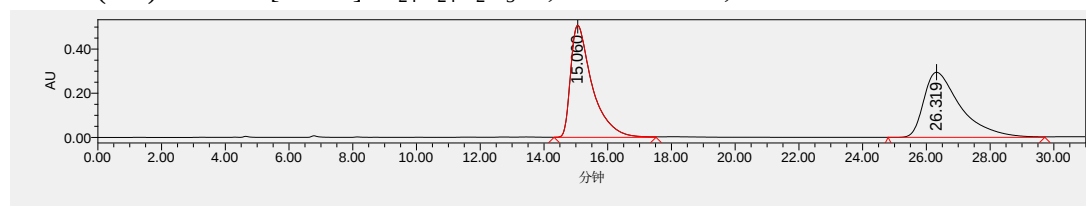
White solid; 95% yield, 15.0% ee, >99:1dr; Determined by HPLC analysis [Daicel chiralpak IC, n-hexane/i-PrOH = 90/10, 1.0 mL/min,

$\lambda = 254\text{ nm}$, $t(\text{major}) = 26.71\text{ min}$, $t(\text{minor}) = 15.28\text{ min}$];

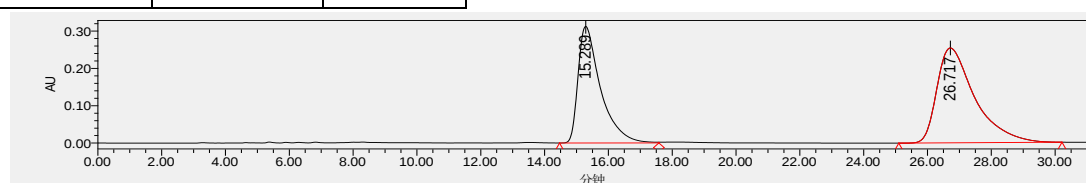
^1H NMR (400 MHz, CDCl_3) δ 8.27 (s, 1H), 7.22 (d, $J = 7.6\text{ Hz}$, 1H), 7.09 – 7.02 (m, 2H), 6.87 – 6.82 (m, 1H), 6.78 (t, $J = 7.6\text{ Hz}$, 2H), 6.62 (t, $J = 7.6\text{ Hz}$, 1H), 6.30 (dd, $J = 16.4, 8.0\text{ Hz}$, 1H), 6.02 (dd, $J = 7.2, 3.6\text{ Hz}$, 1H), 4.81 (s, 1H), 3.79 (s, 1H), 3.44 – 3.33 (m, 1H), 2.91 (m, 1H), 2.87 – 2.73 (m, 1H), 1.11 (s, 9H);

^{13}C NMR (101 MHz, CDCl_3) δ 181.10, 170.42, 152.70, 141.40, 137.46, 129.21, 127.99, 126.48, 126.12, 122.60, 120.35, 119.28, 113.34, 111.12, 109.33, 81.65, 66.93, 52.30, 44.48, 27.54, 26.51;

HRMS (ESI) calcd for $[\text{M}+\text{Na}]^+ \text{C}_{24}\text{H}_{24}\text{N}_2\text{O}_3\text{Na}$, m/z : 411.1685, observed: 411.1680.

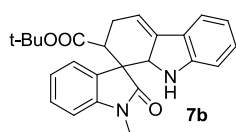


Retention Time	Area	% Area
15.060	23787091	50.11
26.319	23682534	49.89



Retention Time	Area	% Area
15.283		
26.717		

	15.289	15260757	42.21
	26.717	20895368	57.79



tert-butyl 1'-methyl-2'-oxo-2,3,9,9a-tetrahydrospiro

[carbazole-1,3'-indoline]-2-carboxylate (**7b**)

White solid; 22.1% yield, race, >99:1dr; Determined by HPLC analysis

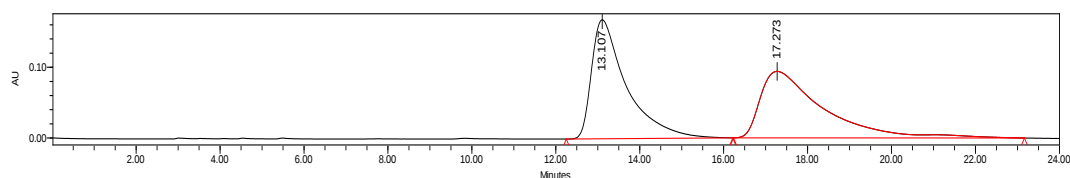
[Daicel chiralpak ODH, n-hexane/i-PrOH = 90/10, 1.0 mL/min, λ =

254 nm, t_1 = 13.55 min, t_2 = 17.72 min];

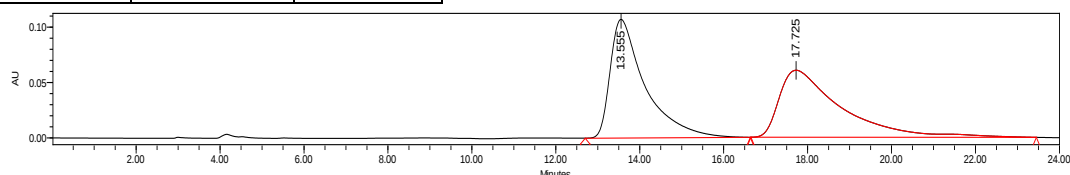
^1H NMR (400 MHz, CDCl_3) δ 7.40 – 7.29 (m, 3H), 7.07 – 6.97 (m, 2H), 6.86 (d, J = 7.6 Hz, 1H), 6.76 – 6.70 (m, 1H), 6.54 (d, J = 7.6 Hz, 1H), 6.29 – 6.25 (m, 1H), 4.86 (s, 1H), 3.89 – 3.74 (m, 1H), 3.18 (s, 3H), 2.98 – 2.89 (m, 2H), 2.48 – 2.35 (m, 1H), 1.08 (s, 9H);

^{13}C NMR (101 MHz, CDCl_3) δ 177.04, 172.06, 152.33, 144.62, 138.47, 131.60, 128.94, 128.57, 126.60, 123.81, 122.42, 120.96, 119.34, 113.14, 110.85, 107.64, 80.79, 65.30, 53.19, 46.25, 27.54, 26.42;

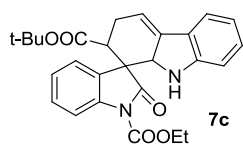
HRMS (ESI) calcd for $[\text{M}+\text{Na}]^+$ $\text{C}_{25}\text{H}_{26}\text{N}_2\text{O}_3\text{Na}$, m/z : 425.1841, observed: 425.1835.



	Retention Time	Area	% Area
	13.107	9711014	49.94
	17.273	9733026	50.06



	Retention Time	Area	% Area
	13.555	6167615	50.00
	17.725	6168685	50.00



2-tert-butyl 1'-ethyl 2'-oxo-2,3,9,9a-tetrahydrospiro

[carbazole-1,3'-indoline]-1',2-dicarboxylate (**7c**)

White solid; 99% yield, 80%ee, >99:1dr; Determined by HPLC

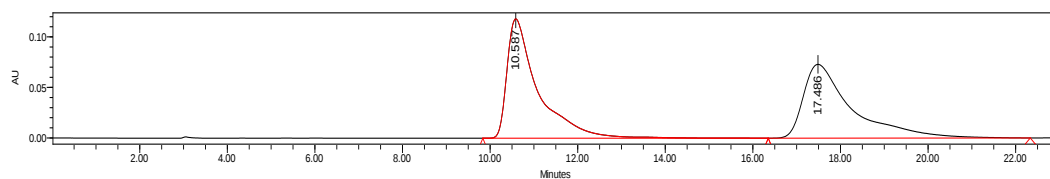
analysis [Daicel chiralpak ODH, n-hexane/i-PrOH = 93/7, 1.0 mL/min,

λ = 254 nm, t (minor) = 17.55 min, t (major) = 10.42 min];

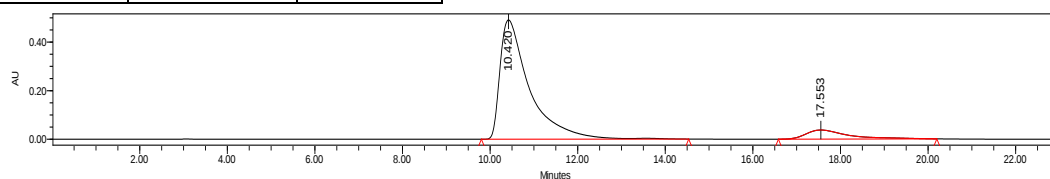
^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, J = 8.0 Hz, 1H), 7.30 (d, J = 7.6 Hz, 1H), 7.27 – 7.21 (m, 1H), 7.16 (d, J = 7.2 Hz, 1H), 7.02 – 6.91 (m, 2H), 6.70 (t, J = 7.2 Hz, 1H), 6.43 (d, J = 8.0 Hz, 1H), 6.10 (dd, J = 7.2, 3.6 Hz, 1H), 4.92 (d, J = 3.6 Hz, 1H), 4.59 – 4.41 (m, 2H), 3.94 (d, J = 4.8 Hz, 1H), 3.51 (t, J = 8.8 Hz, 1H), 3.08 – 2.96 (m, 1H), 2.94 – 2.83 (m, 1H), 1.46 (t, J = 7.2 Hz, 3H), 1.11 (s, 9H);

^{13}C NMR (101 MHz, CDCl_3) δ 177.04, 169.02, 151.69, 149.95, 139.18, 136.17, 128.28, 127.27, 125.60, 125.27, 124.43, 123.75, 119.40, 118.40, 113.50, 112.38, 110.12, 80.99, 66.84, 62.36, 51.19, 43.95, 26.35, 25.28, 13.30;

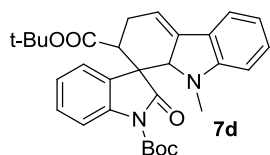
HRMS (ESI) calcd for $[\text{M}+\text{Na}]^+ \text{C}_{27}\text{H}_{28}\text{N}_2\text{O}_5\text{Na}$, m/z : 483.1896, observed: 483.1897.



	Retention Time	Area	% Area
	10.587	5808801	50.88
	17.486	5608915	49.12



	Retention Time	Area	% Area
	10.420	22961482	90.15
	17.553	2508932	9.85

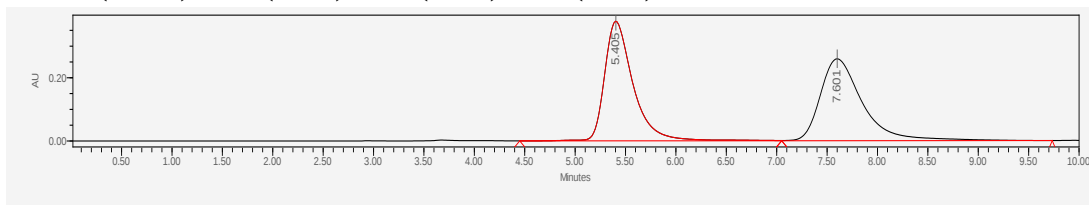


di-tert-butyl 9-methyl-2'-oxo-2,3,9,9a-tetrahydrospiro[carbazole-1,3'-indoline]-1',2-dicarboxylate (**7d**)

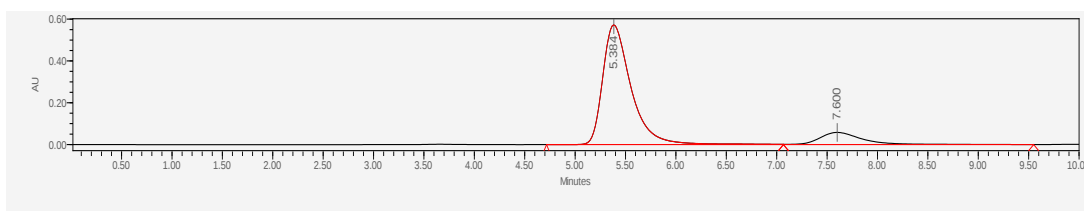
White solid; 90% yield, 75%ee, >99:1dr; Determined by HPLC analysis [Daicel chiralpak ODH, n-hexane/i-PrOH = 93/7, 1.0

mL/min, λ = 254 nm, t (major) = 5.38 min, t (minor) = 7.60 min];

^1H NMR (400 MHz, CDCl_3) δ 7.86 (d, J = 8.4 Hz, 1H), 7.32 – 7.20 (m, 2H), 7.12 (d, J = 7.6 Hz, 1H), 7.02 (t, J = 7.6 Hz, 1H), 6.95 (t, J = 7.6 Hz, 1H), 6.68 (t, J = 7.6 Hz, 1H), 6.35 (d, J = 7.6 Hz, 1H), 6.12 (d, J = 3.6 Hz, 1H), 4.44 (d, J = 3.6 Hz, 1H), 3.52 (t, J = 8.8 Hz, 1H), 3.05 – 2.79 (m, 2H), 2.62 (s, 3H), 1.66 (s, 9H), 1.13 (s, 9H).

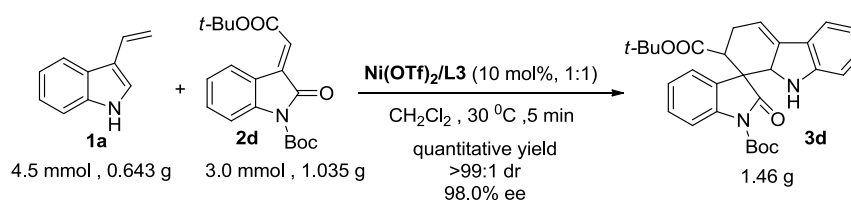


	Retention Time	Area	% Area
	5.405	7428248	49.80
	7.601	7487353	50.20



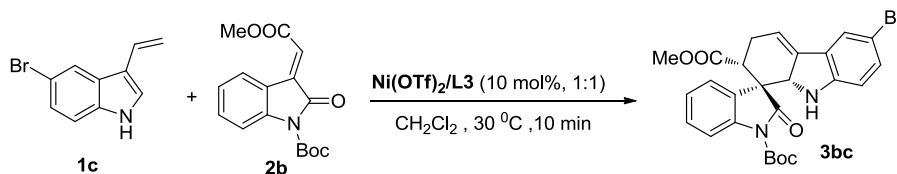
	Retention Time	Area	% Area
	5.384	11199862	86.66
	7.600	1723541	13.34

9. Gram scale experiment



In a test tube with a magnetic stirring bar, *N,N'*-dioxide **L3** (0.3 mmol, 211.5 mg), Ni(OTf)_2 (0.3 mmol, 107.05 mg), and the methyleneindolinone (**2d**) (3.0 mmol, 1.035 g) in CHCl_2 (30.0 mL) were stirred at 30 °C for 30 min, then 3-vinylindole **1a** (4.5 mmol, 0.643 g, 1.5 equiv) dissolved in CHCl_2 (6.0 mL) was added in one-portion. The mixture was stirred at 30 °C for 5 minutes until the yellow color of the solution disappeared. The reaction mixture was further detected by TLC. After completion, flash column chromatography was carried out to provide the desired product (**3d**) with quantitative yield. The product was directed for HPLC analysis. (99% yield, >99:1 dr, 98% ee)

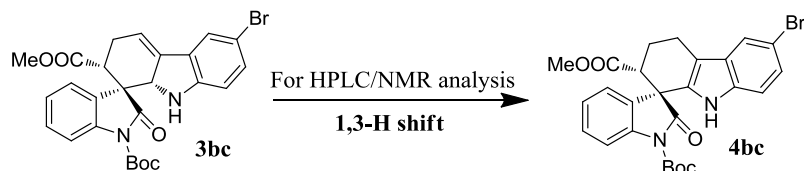
10. Determination of the absolute configuration of 3bc by the x-ray crystal structure



In a test tube with a magnetic stirring bar, *N,N'*-dioxide **L3** (0.01 mmol, 7.0 mg), Ni(OTf)_2 (0.01 mmol, 3.6 mg), and the methyleneindolinones (**2b**) (0.1 mmol) in CHCl_2 (1.0 mL) were stirred at 30 °C for 30 min, then 3-vinylindole **1c** (0.15 mmol, 1.5 equiv) dissolved in CHCl_2 (0.2 mL) was added in one-portion. The mixture was stirred at 30 °C for a few

minutes (<10 min) until the yellow color of the solution disappeared. The reaction mixture was further detected by TLC.

After completion, the reaction mixture was treated with 6 M HCl (0.2 mL) at 0 °C. After stirred for 30 minutes, the mixture was quenched with saturated aqueous NaHCO₃ solution, extracted with DCM, dried over anhydrous Na₂SO₄, filtered, and concentrated *in vacuo*. Flash column chromatography provided the desired product (**4bc**) which was directed for HPLC and NMR analysis.

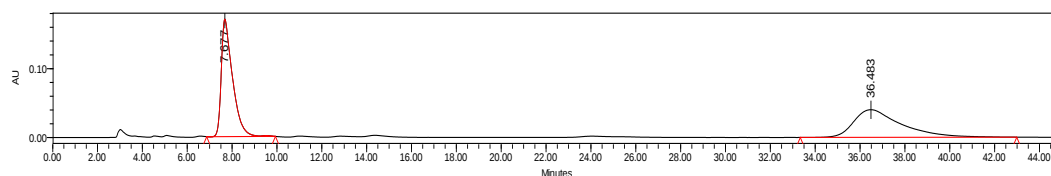


(1R, 2R)-1'-tert-butyl 2-methyl 6-bromo-2'-oxo-2,3,4,9-tetrahydrospiro[carbazole-1,3'-indoline]-1',2-dicarboxylate (**4bc**)

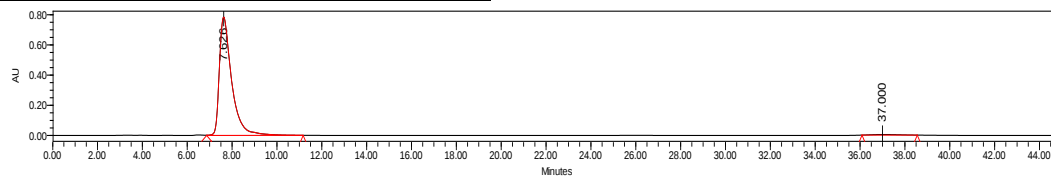
White solid; 99% yield, 98% ee, >99:1dr; $[\alpha]_D^{23} = +70.65$ (c = 0.092 in CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak AD, n-hexane/i-PrOH = 90/10, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 37.00 min, t (major) = 7.62 min];

¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 1.6 Hz, 1H), 7.47 (s, 1H), 7.38 – 7.30 (m, 1H), 7.23 – 7.12 (m, 2H), 7.07 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 1H), 3.63 (dd, *J* = 13.2, 4.0 Hz, 1H), 3.33 (s, 3H), 3.08 – 2.98 (m, 1H), 2.91 – 2.79 (m, 1H), 2.59 – 2.49 (m, 1H), 2.38 – 2.27 (m, 1H), 1.67 (s, 9H);

HRMS (ESI) calcd for $[M+Na]^+$ C₂₆H₂₅BrN₂O₅Na, m/z: 547.0845, observed: 547.0840.

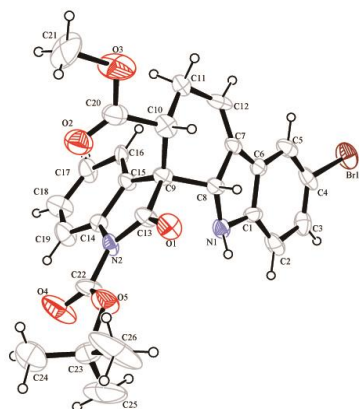


	Retention Time	Area	% Area
	7.677	5941007	50.14
	36.483	5906928	49.86

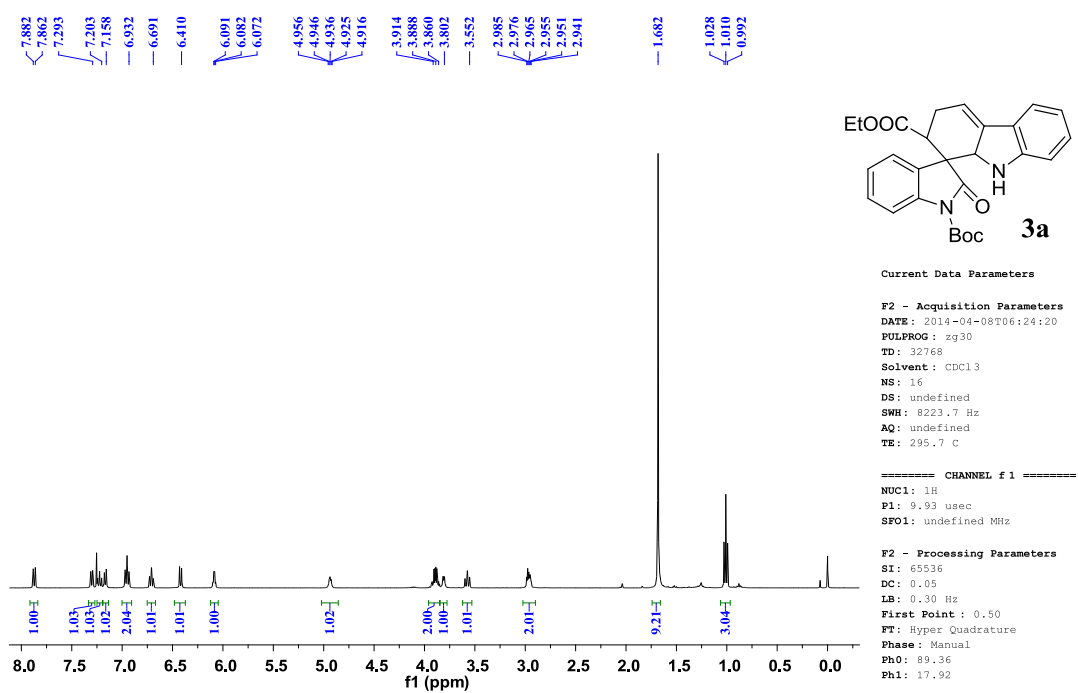


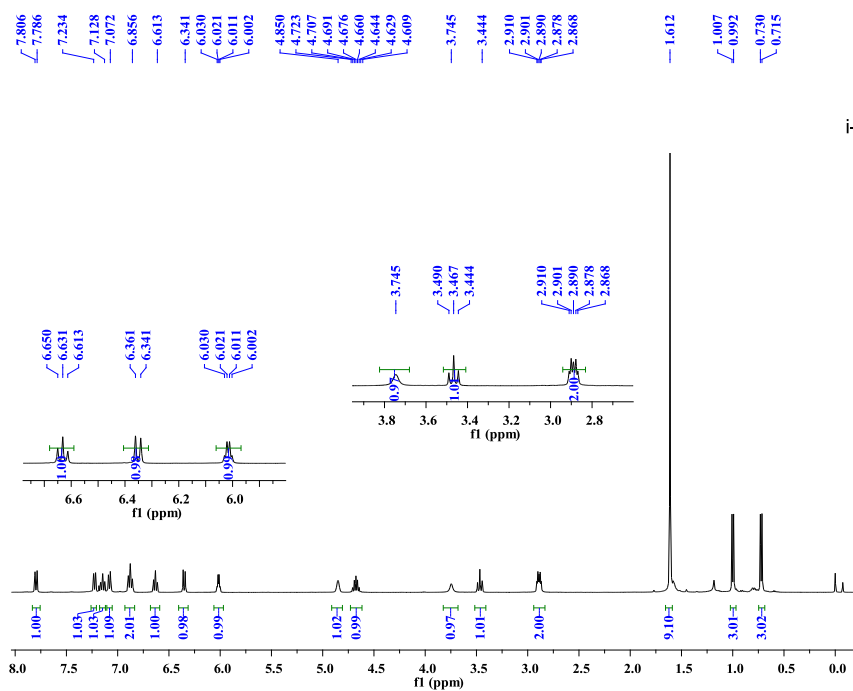
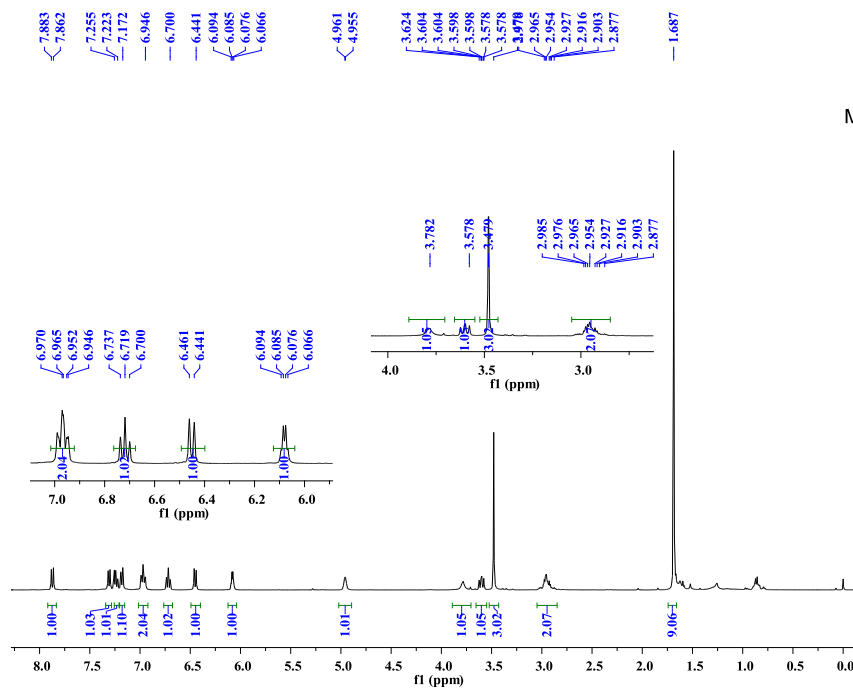
	Retention Time	Area	% Area
	7.626	29793322	98.93
	37.000	323550	1.07

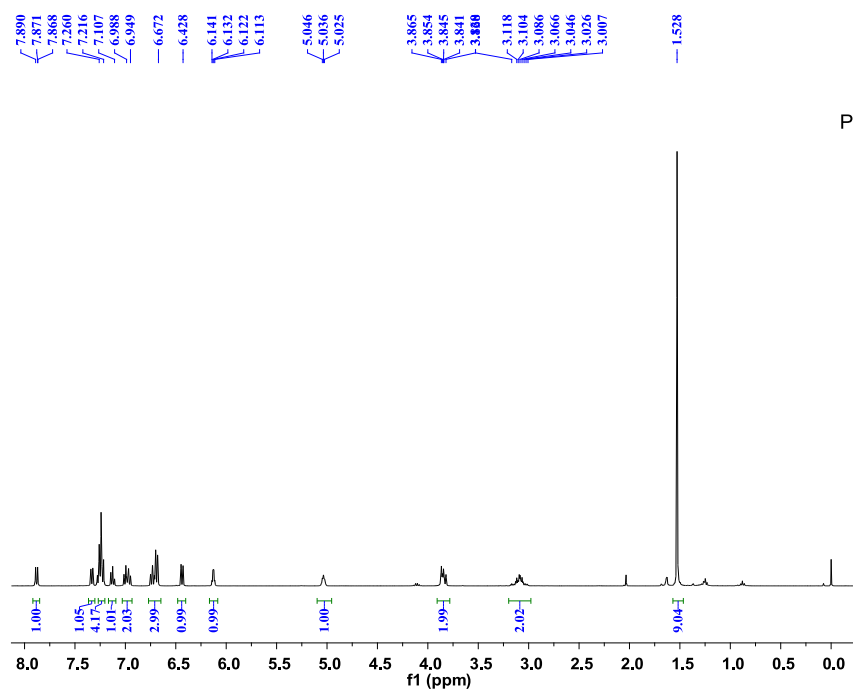
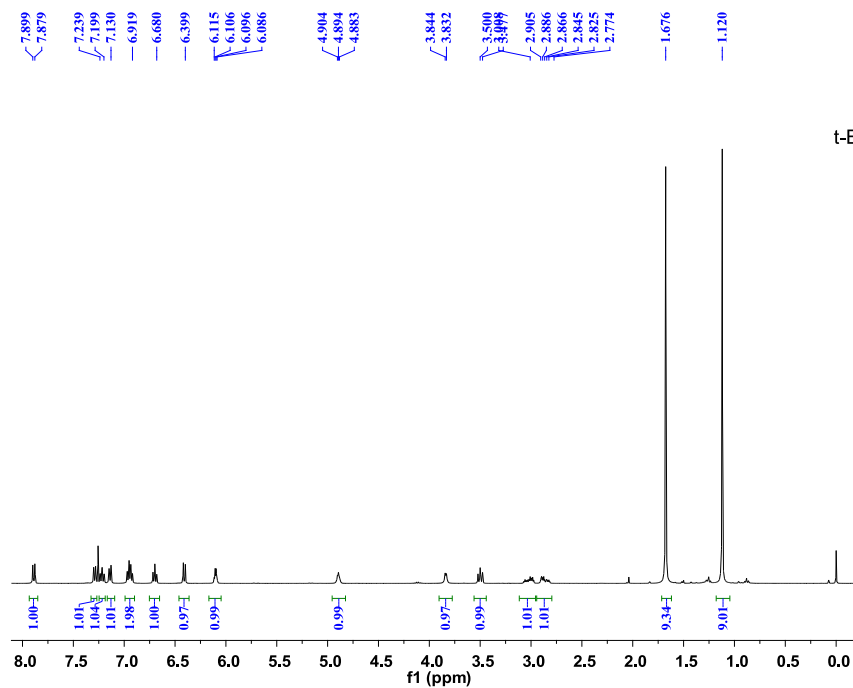
X-ray crystal structure of product 3bc:

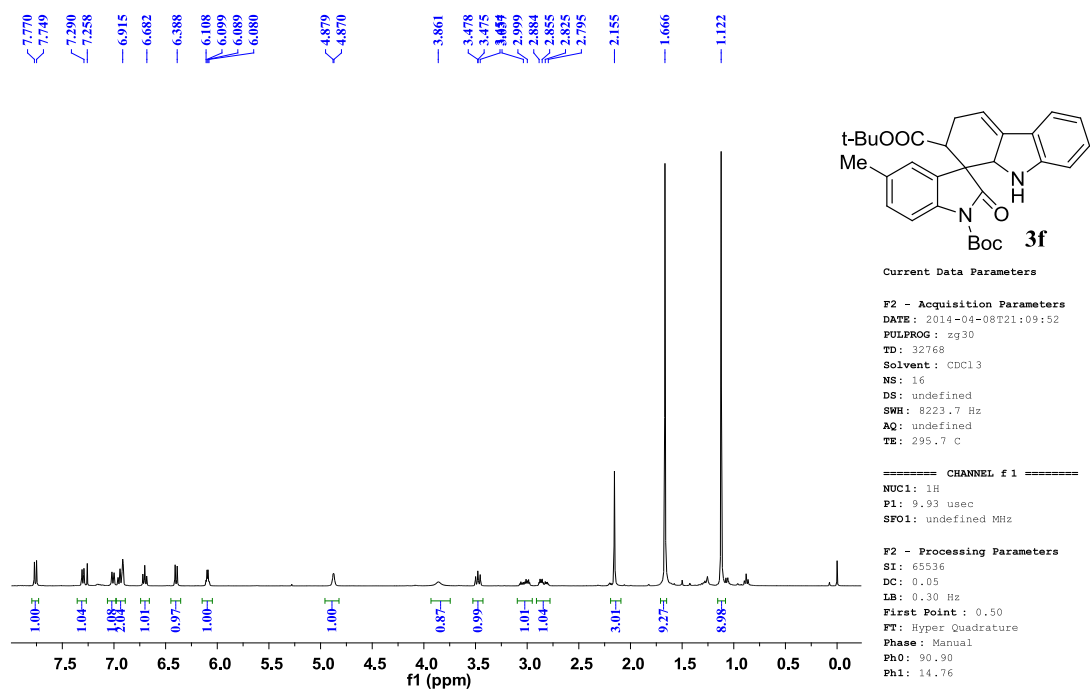
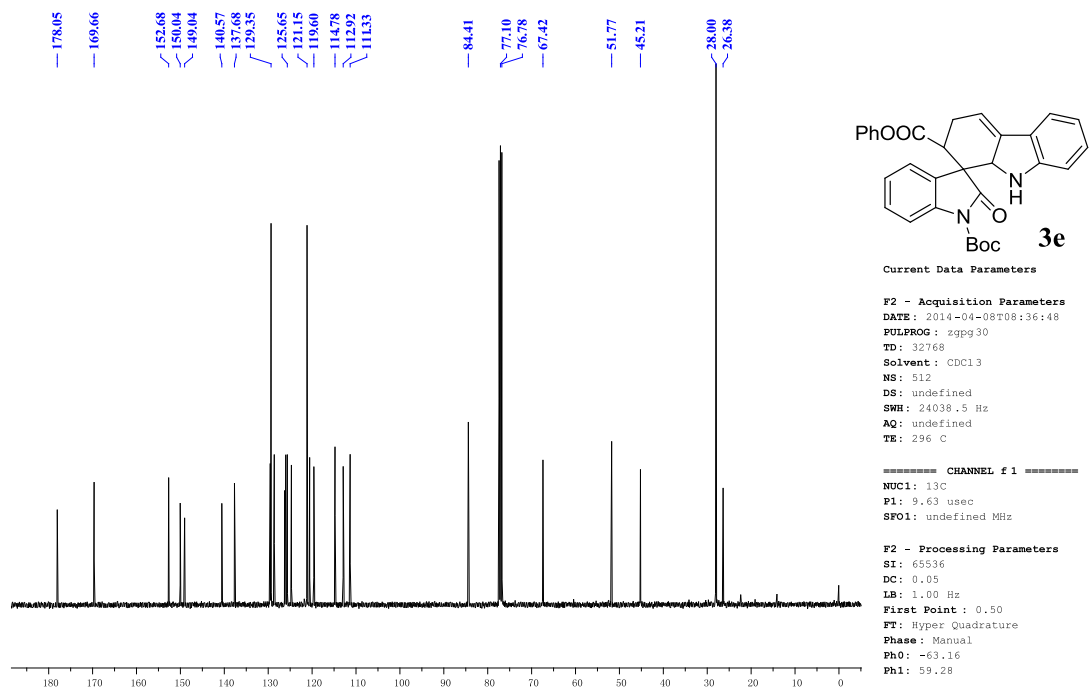


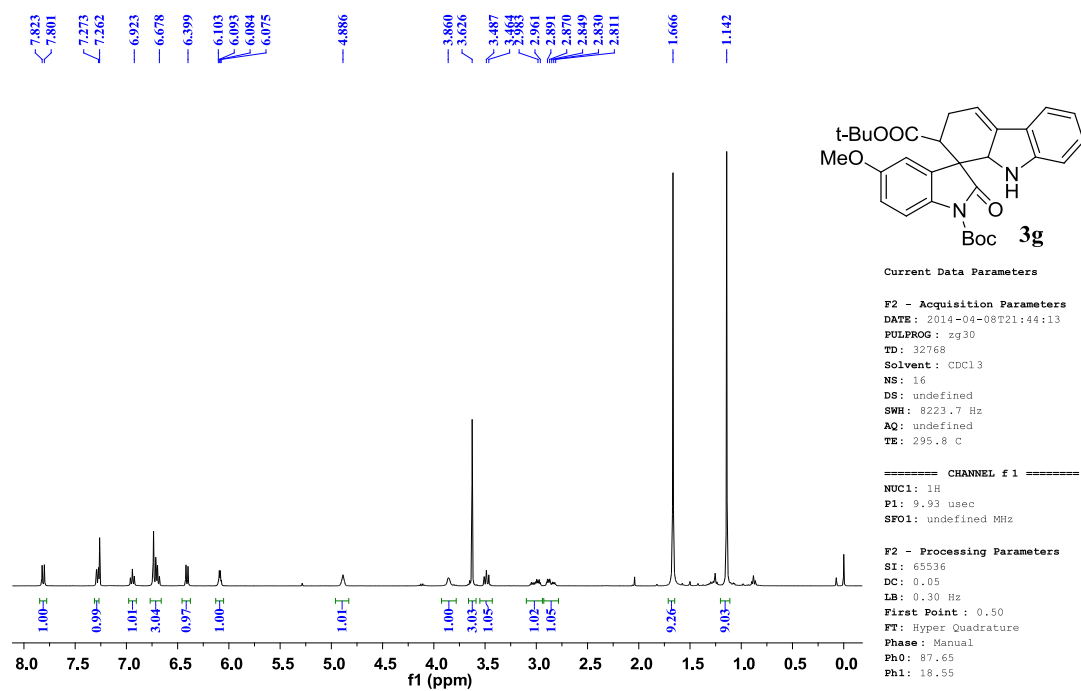
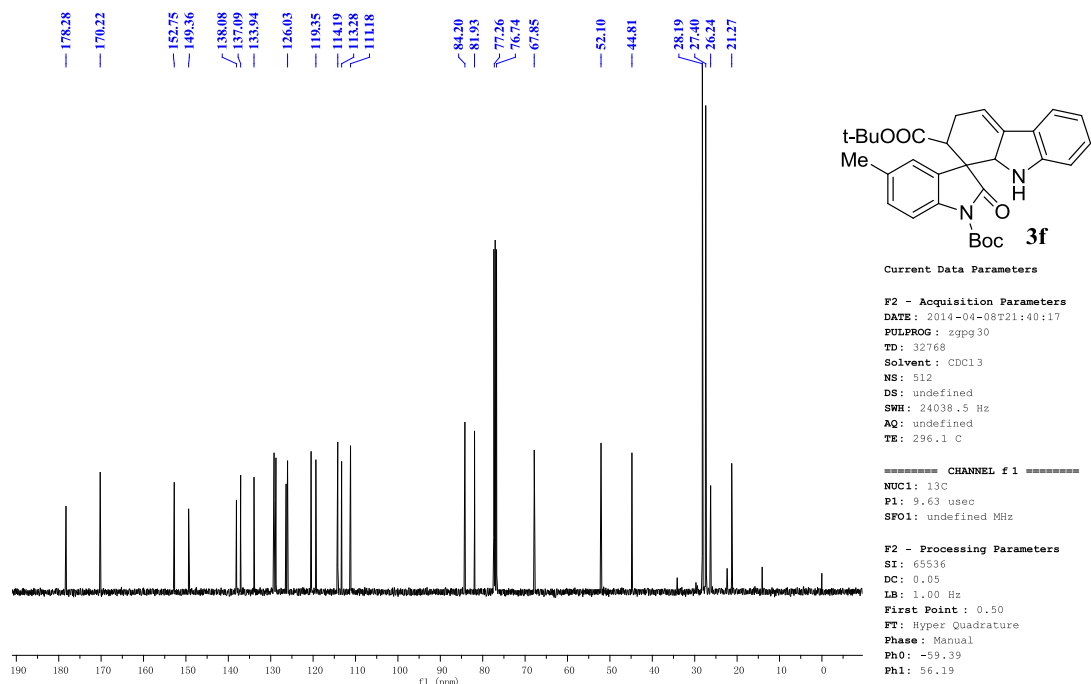
11.NMR spectra

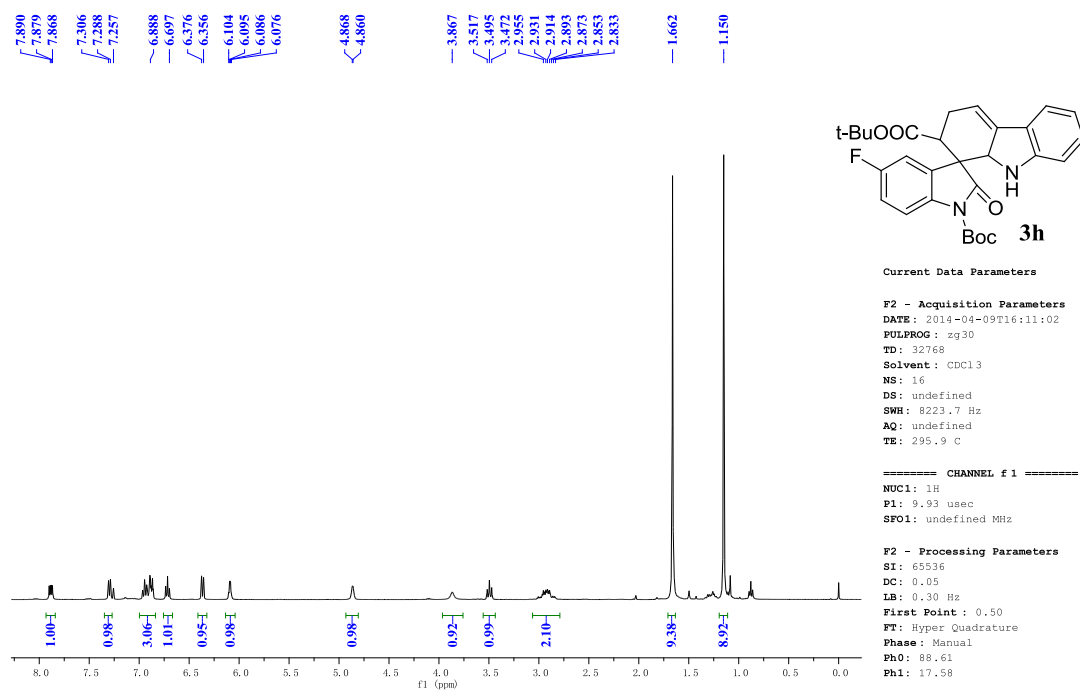
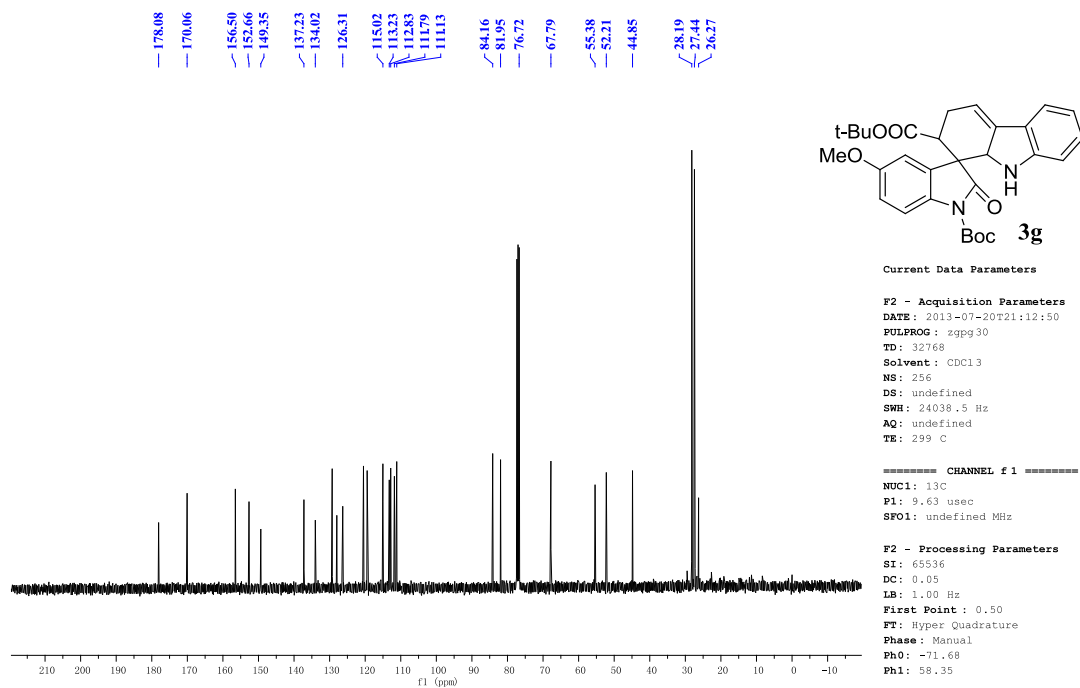


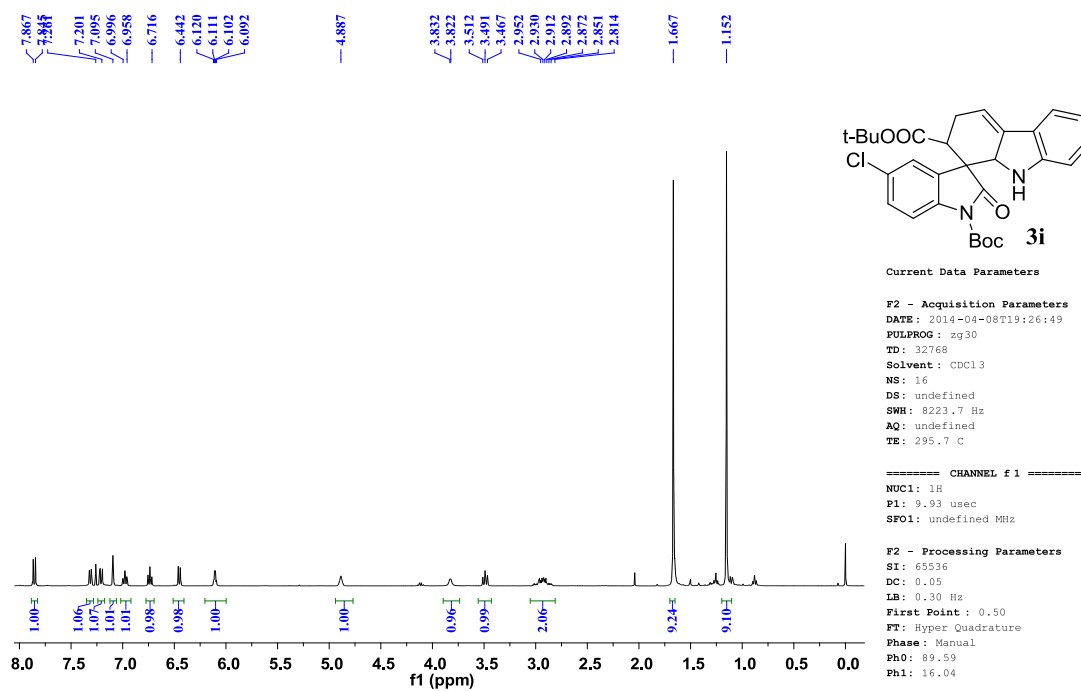
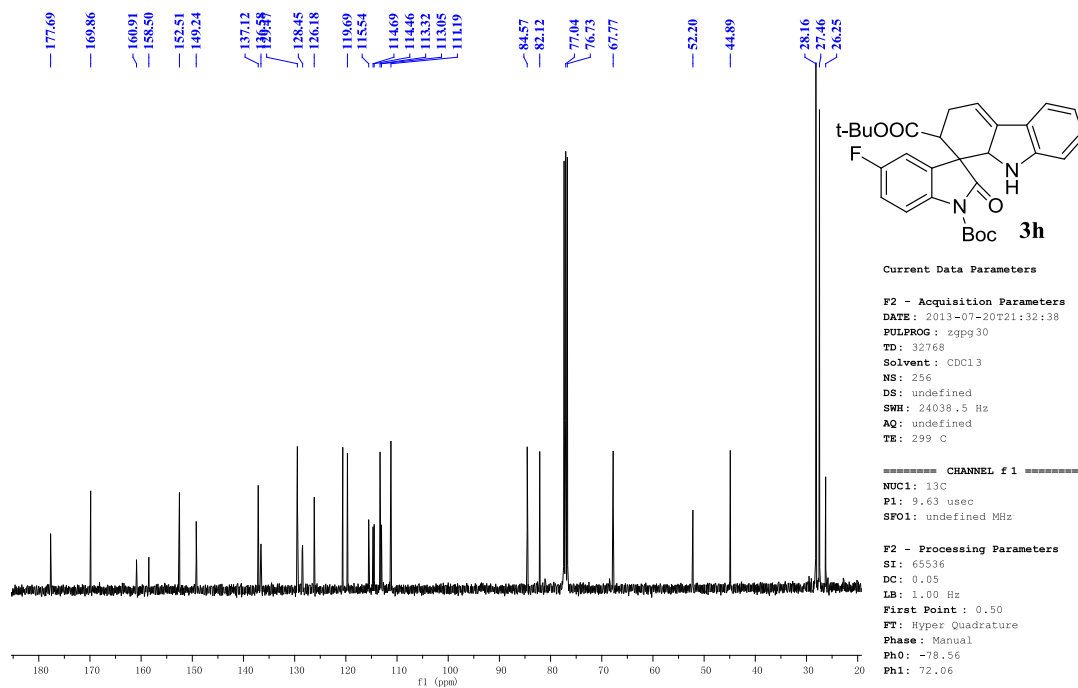


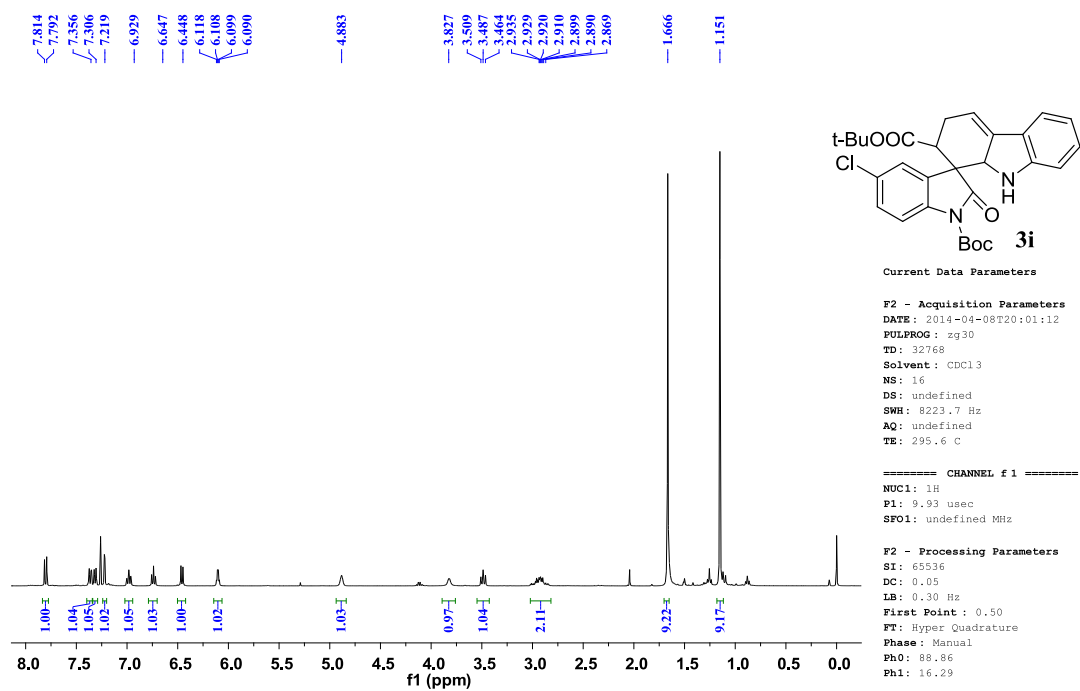
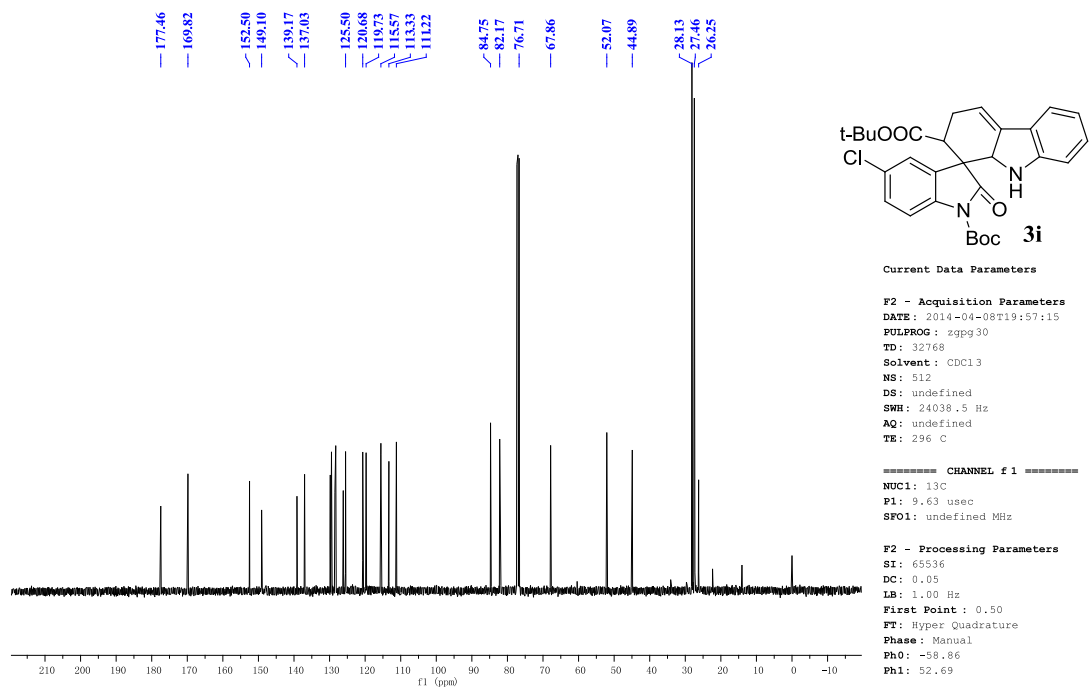


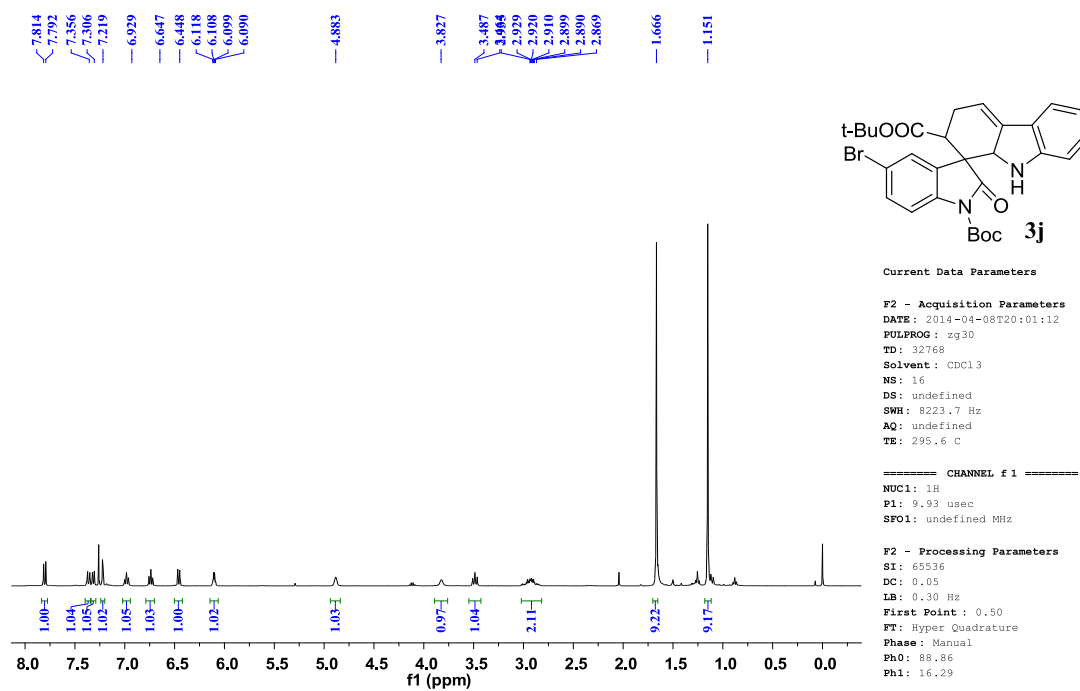
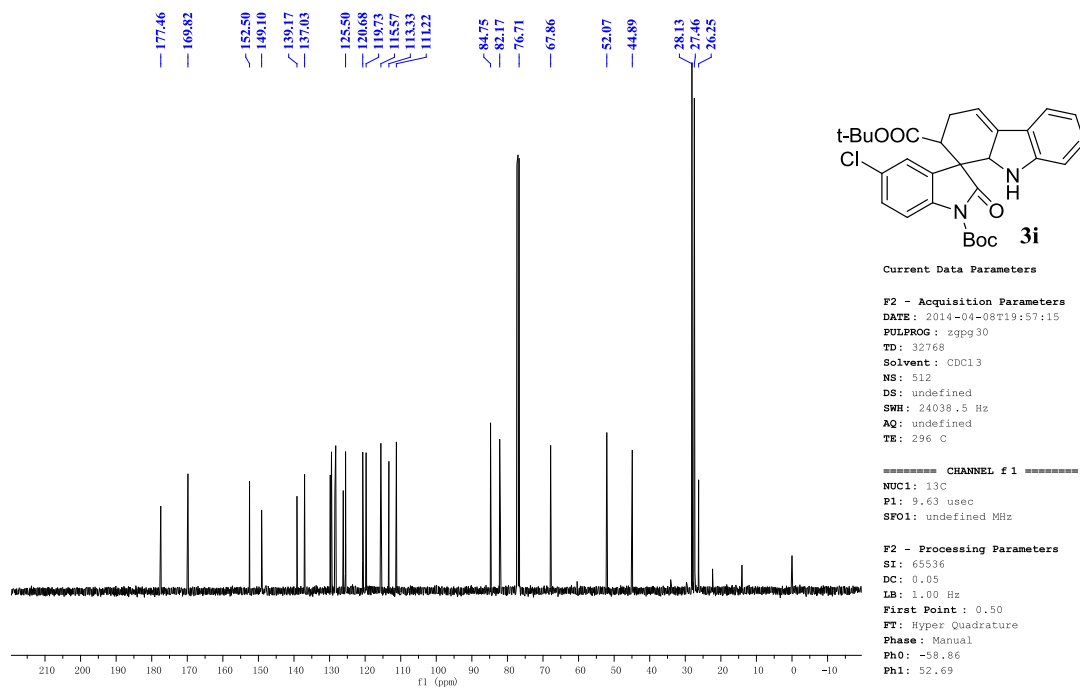


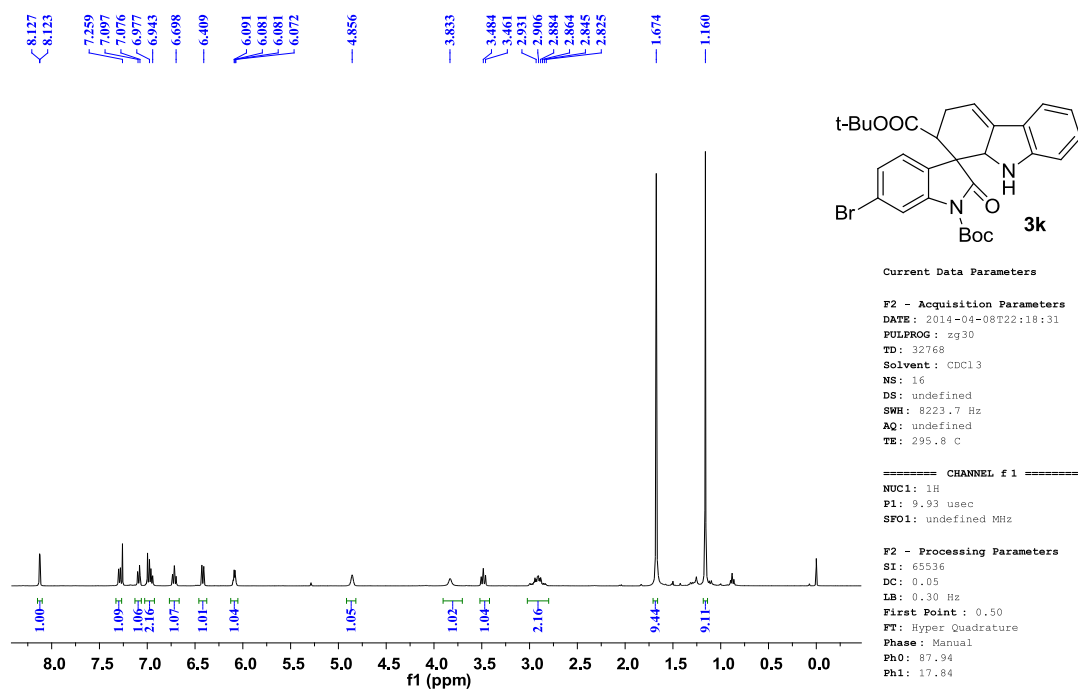
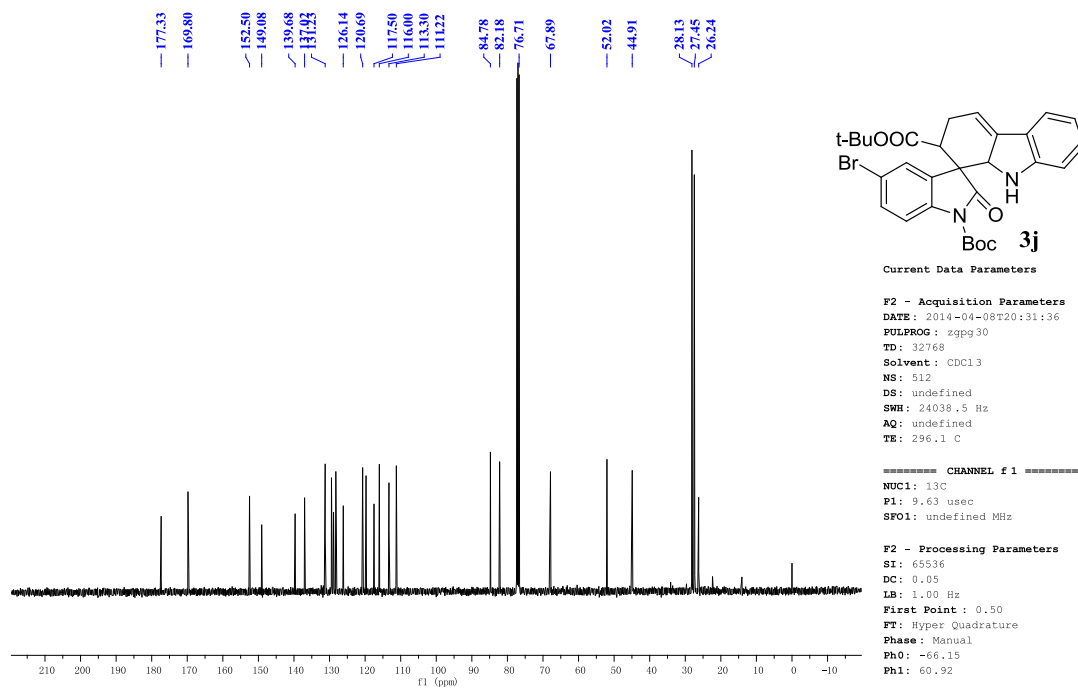


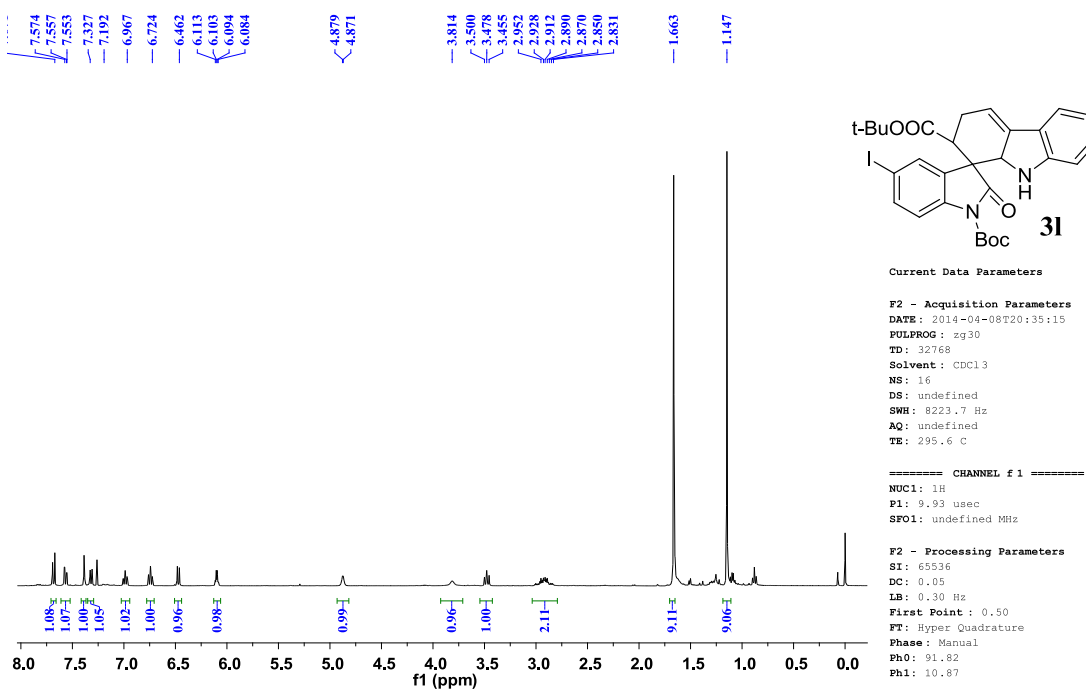
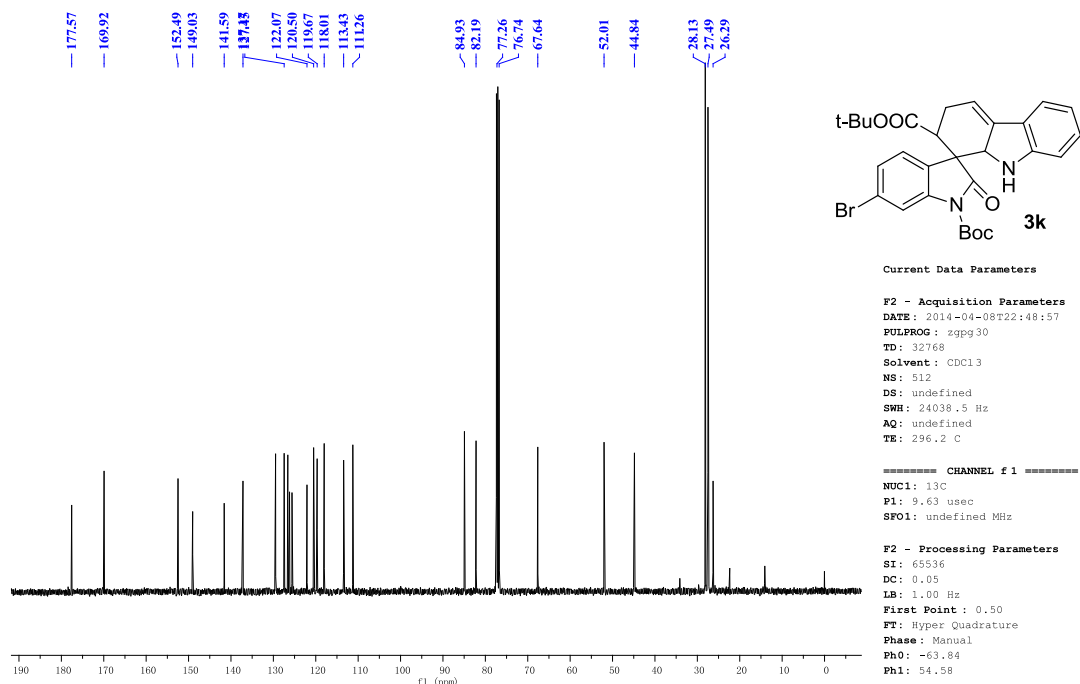


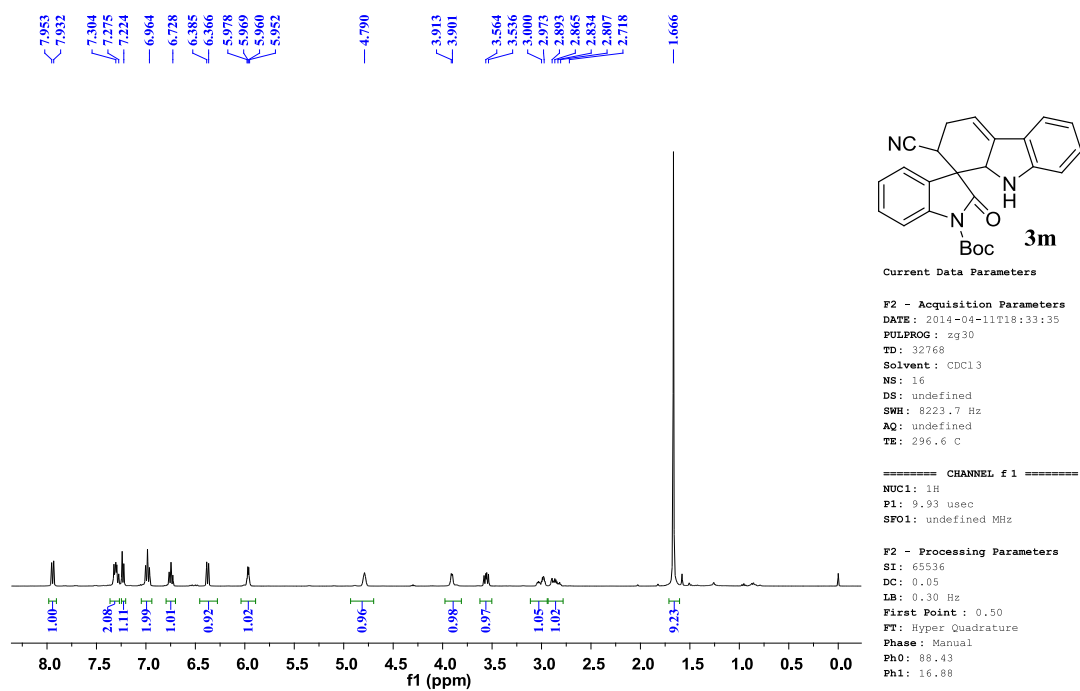
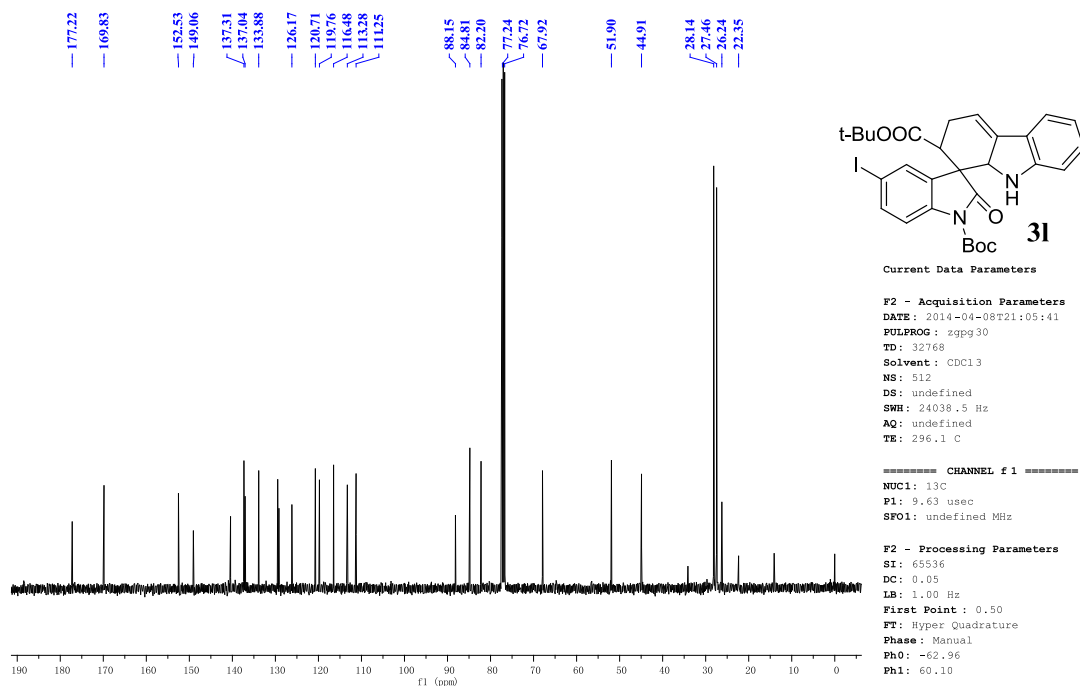


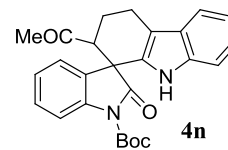
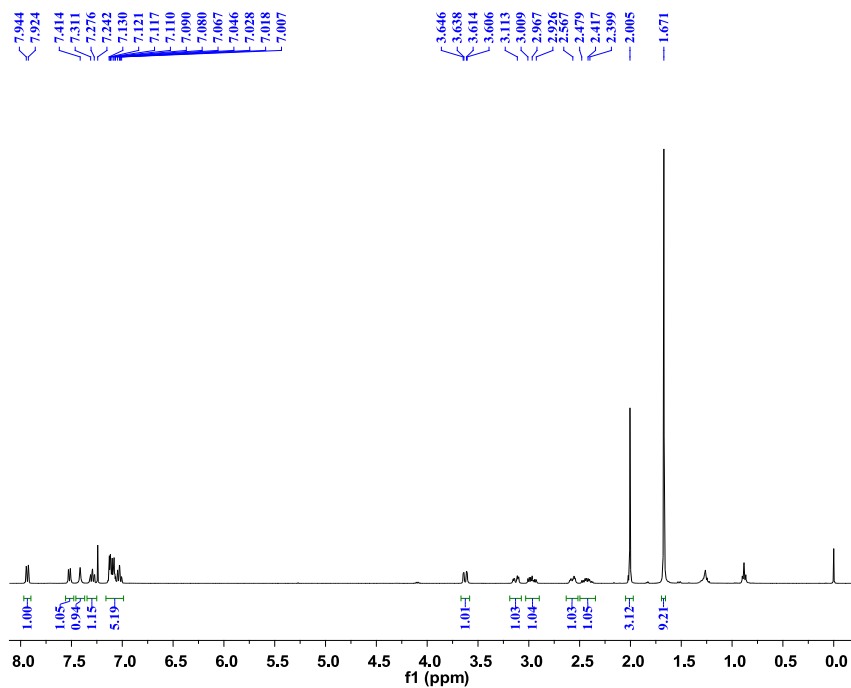










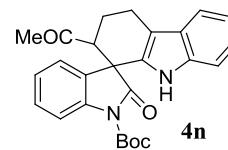
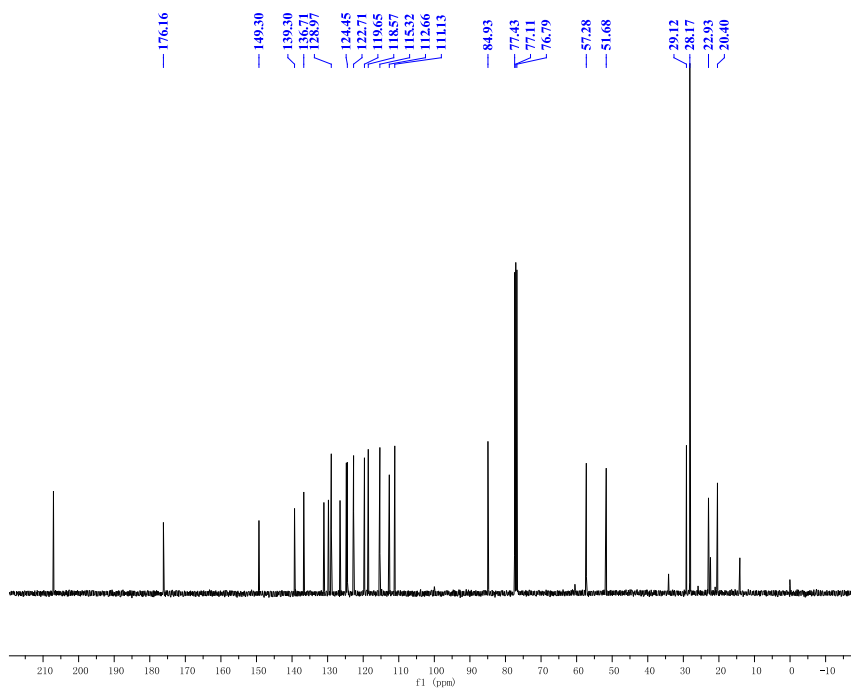


Current Data Parameters

F2 - Acquisition Parameters
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 FULPROG: zg30
 TD: 32768
 Solvent: CDCl3
 NS: 16
 DS: undefined
 SWH: 8223.7 Hz
 AQ: undefined
 TE: 296.7 C

===== CHANNEL f1 =====
 NUC1: 1H
 P1: 9.93 usec
 SFO1: undefined MHz

F2 - Processing Parameters
 SI: 65536
 DC: 0.05
 LB: 0.30 Hz
 First Point: 0.50
 FT: Hyper Quadrature
 Phase: Manual
 Ph0: 87.76
 Ph1: 20.57

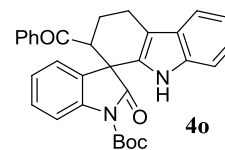
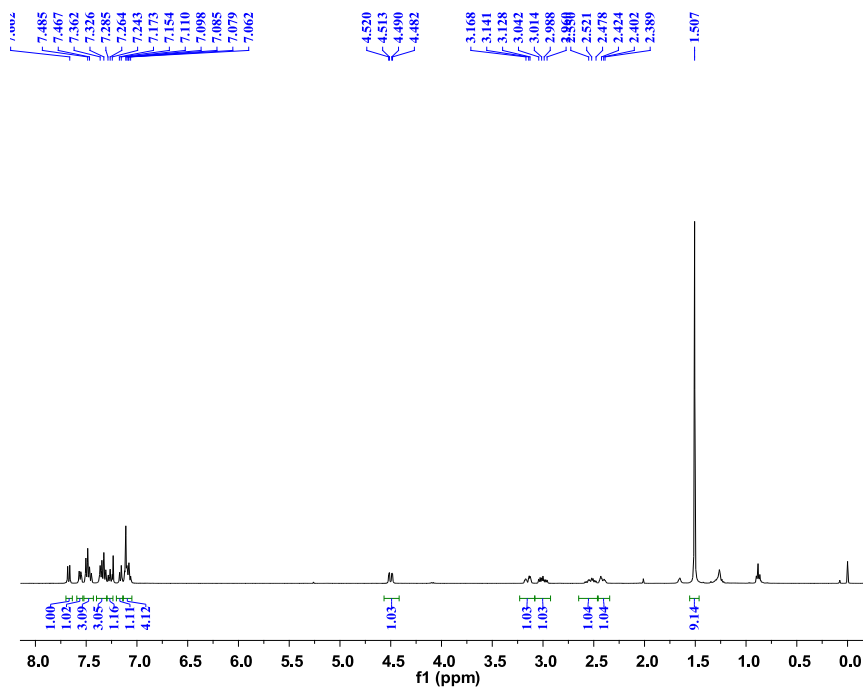


Current Data Parameters

F2 - Acquisition Parameters
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 Solvent: CDCl3
 NS: 256
 DS: undefined
 SWH: 24038.5 Hz
 AQ: undefined
 TE: 297 C

===== CHANNEL f1 =====
 NUC1: 13C
 P1: 9.63 usec
 SFO1: undefined MHz

F2 - Processing Parameters
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 LB: 1.00 Hz
 First Point: 0.50
 FT: Hyper Quadrature
 Phase: Manual
 Ph0: -66.80
 Ph1: 68.62

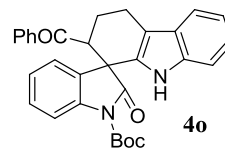
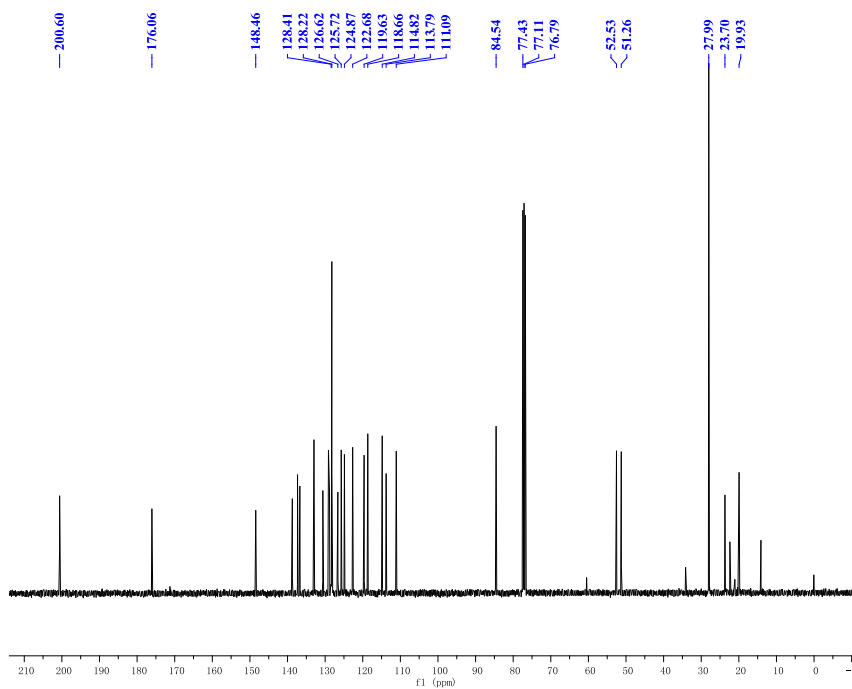


Current Data Parameters

F2 - Acquisition Parameters
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 Solvent: CDCl3
 NS: 16
 DS: undefined
 SWH: 8223.7 Hz
 AQ: undefined
 TE: 296.7 C

===== CHANNEL f1 =====
 NUC1: 1H
 P1: 9.93 usec
 SFO1: undefined MHz

F2 - Processing Parameters
 SI: 65536
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 LB: 0.30 Hz
 First Point: 0.50
 FT: Hyper Quadrature
 Phase: Manual
 Phi0: 88.53
 Phi1: 19.20

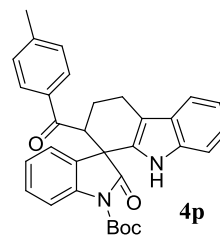
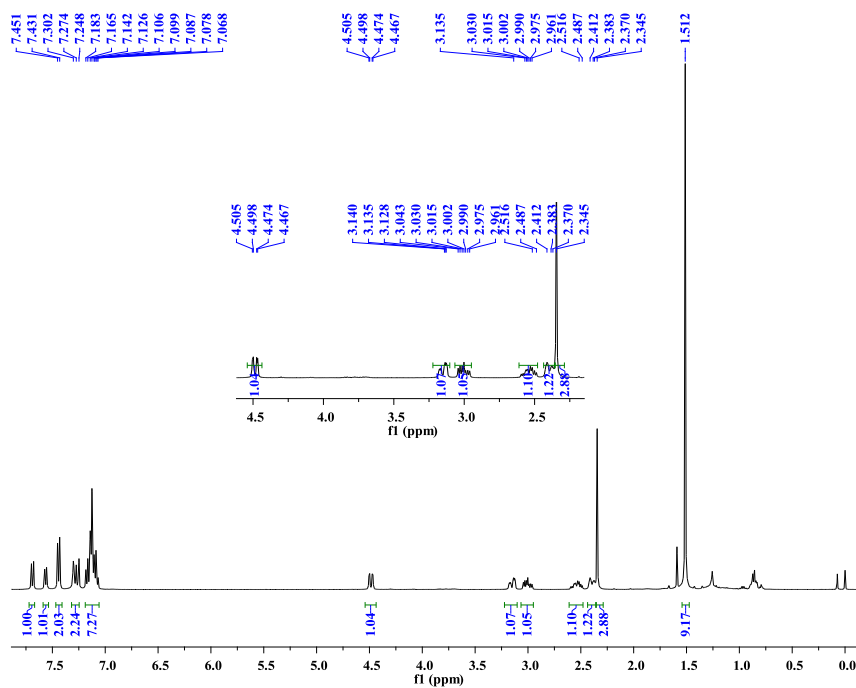


Current Data Parameters

F2 - Acquisition Parameters
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 FULPROG: zgpg30
 TD: 32768
 Solvent: CDCl3
 NS: 256
 DS: undefined
 SWH: 24038.5 Hz
 AQ: undefined
 TE: 296.9 C

===== CHANNEL f1 =====
 NUC1: 13C
 P1: 9.63 usec
 SFO1: undefined MHz

F2 - Processing Parameters
 SI: 65536
 DC: 0.05
 LB: 1.00 Hz
 First Point: 0.50
 FT: Hyper Quadrature
 Phase: Manual
 Phi0: -60.75
 Phi1: 55.64



Current Data Parameters

F2 - Acquisition Parameters

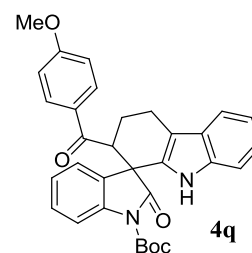
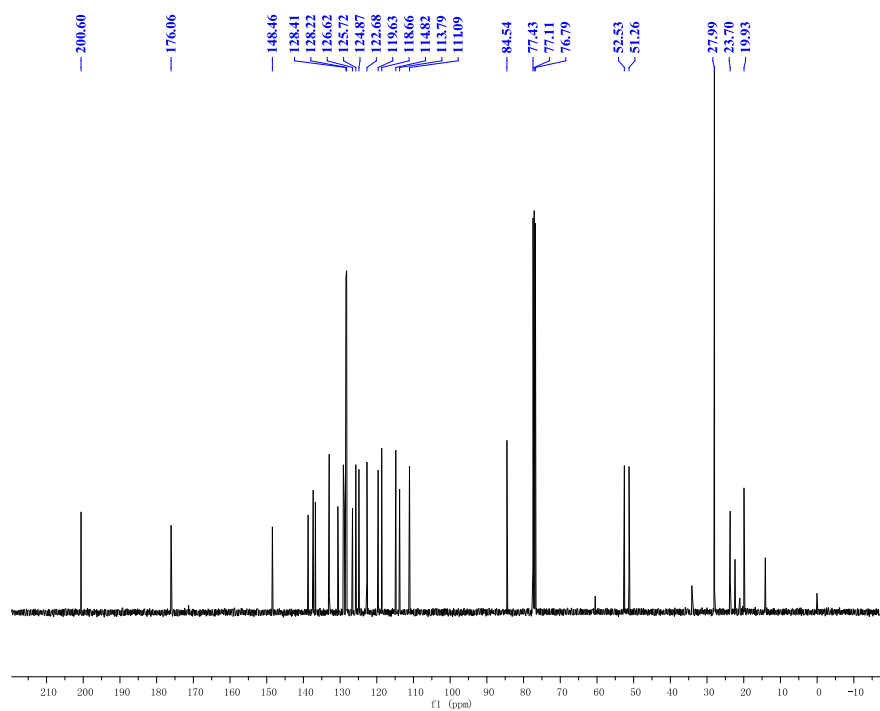
DATE: 2013-07-30T19:17:43
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 299.1 C

===== CHANNEL f1 =====

NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters

SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Phi0: 84.17
Phi1: 19.90



Current Data Parameters

F2 - Acquisition Parameters

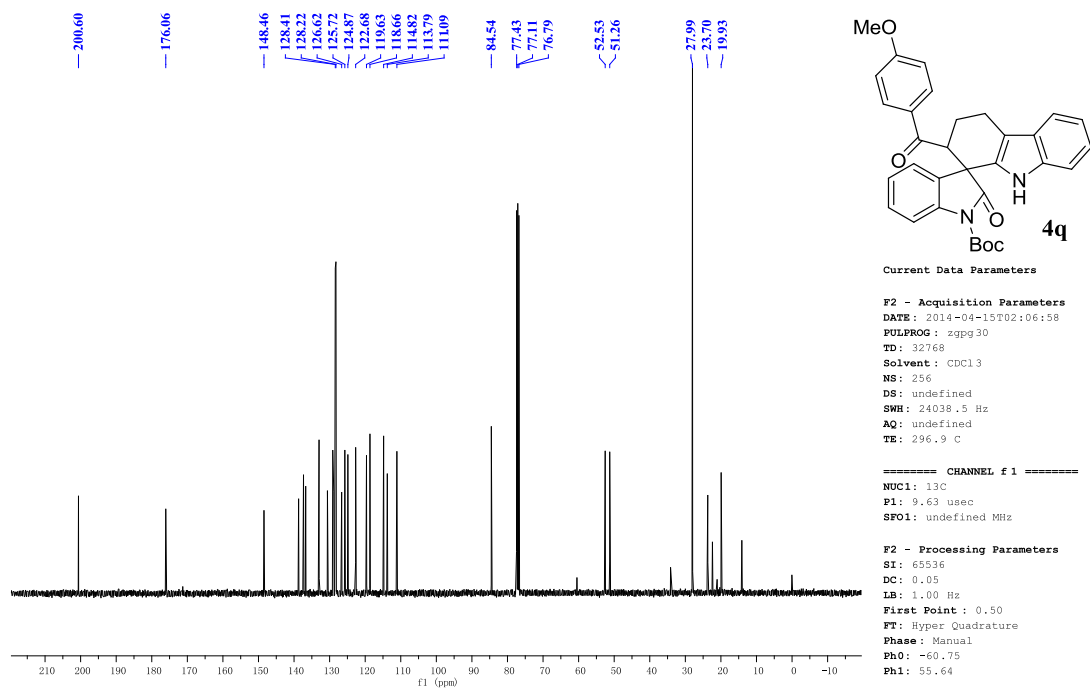
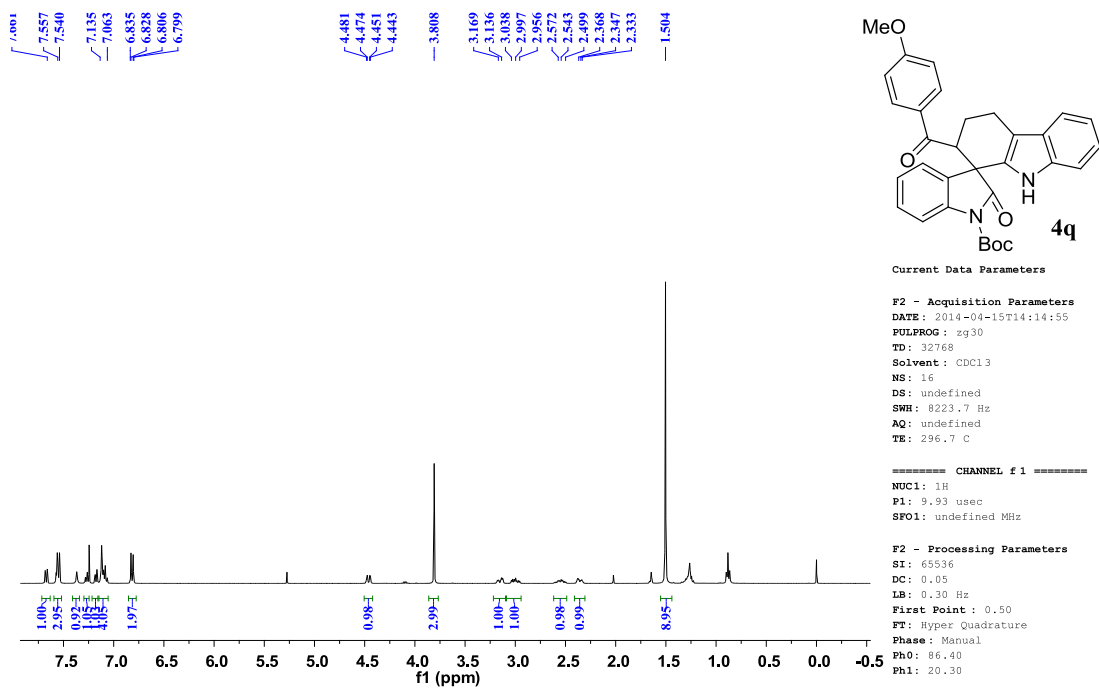
DATE: 2014-04-15T02:06:58
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 296.9 C

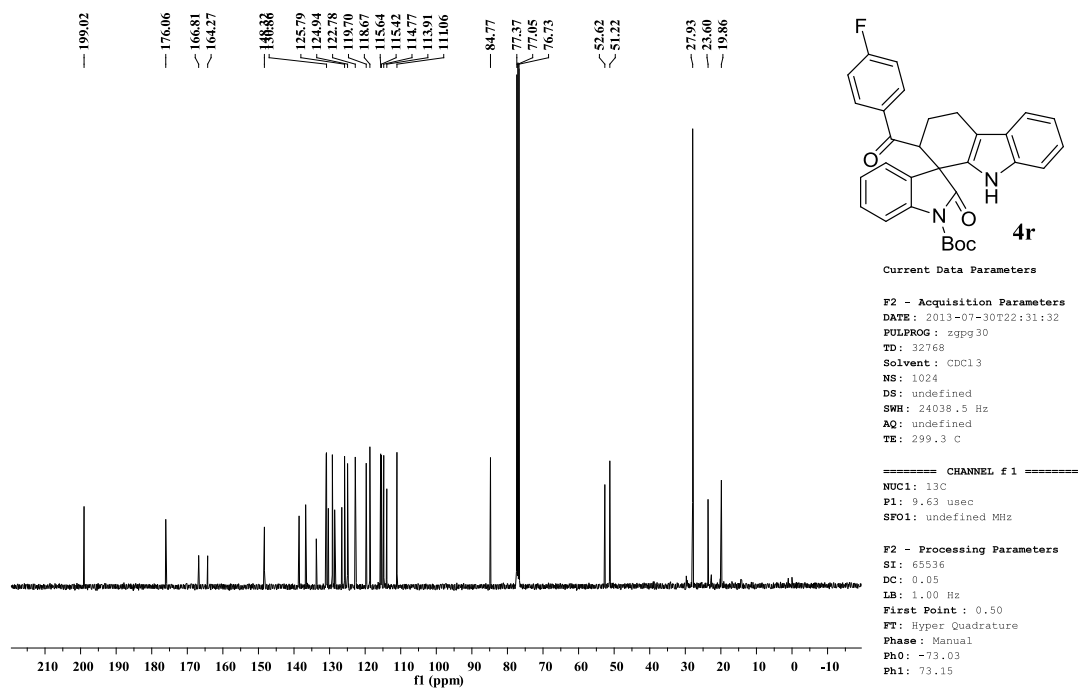
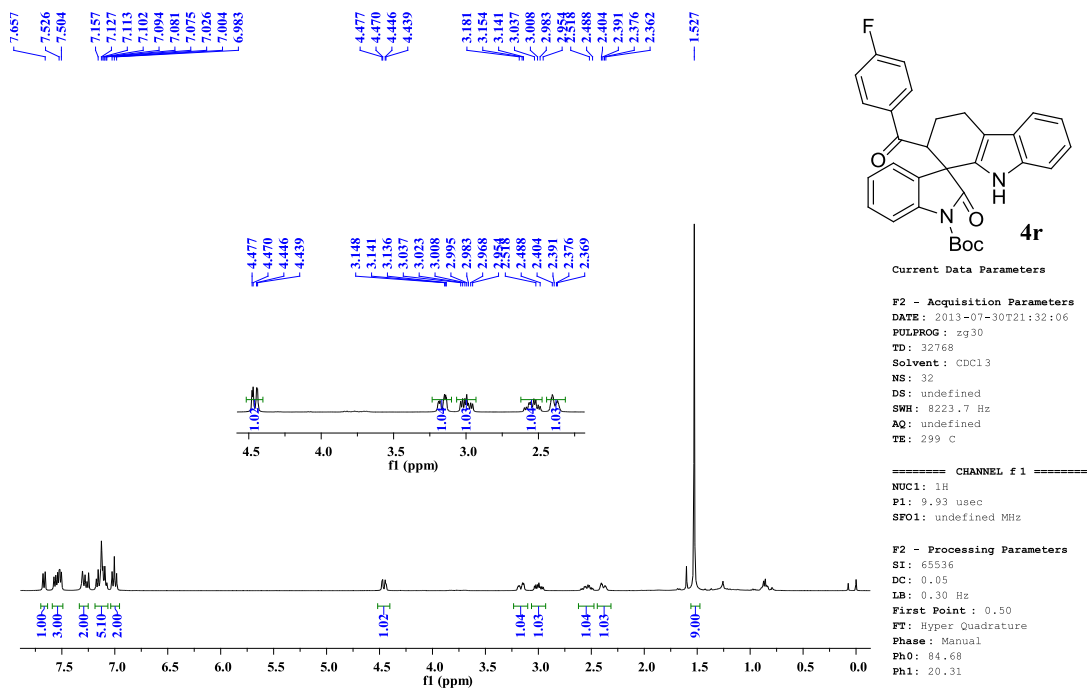
===== CHANNEL f1 =====

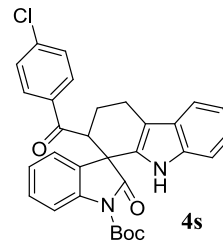
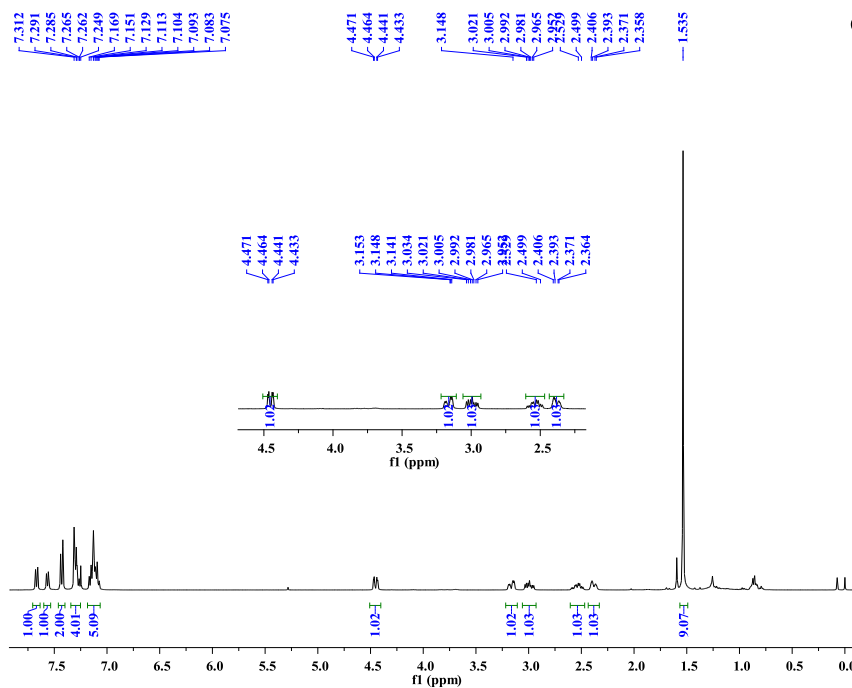
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters

SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Phi0: -60.75
Phi1: 55.64





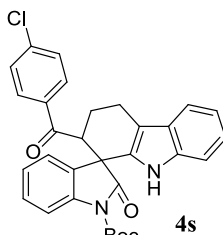
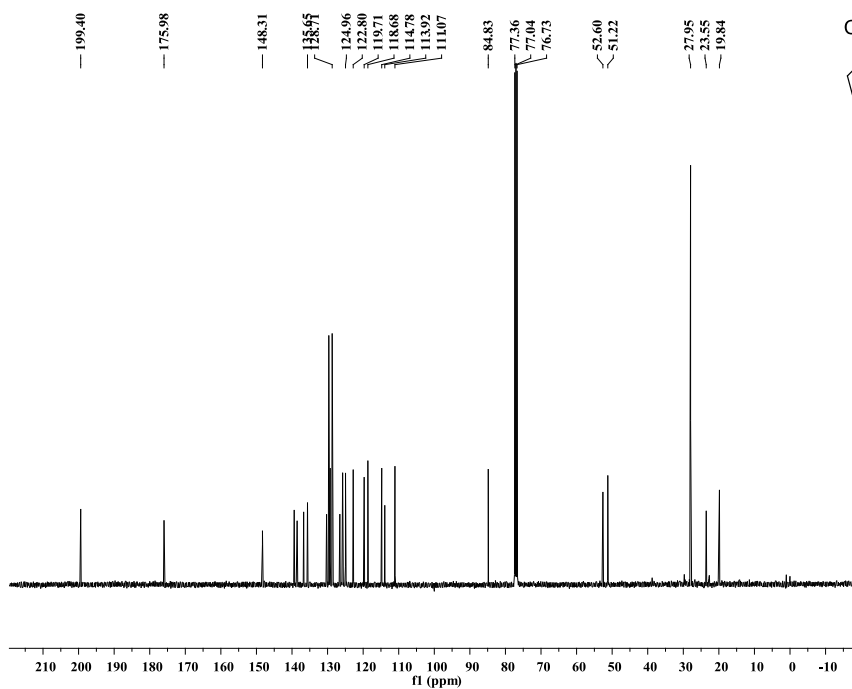


Current Data Parameters

F2 - Acquisition Parameters
 DATE: 2013-07-30T18:13:54
 FULPROG: zg30
 TD: 32768
 Solvent: CDCl3
 NS: 16
 DS: undefined
 SWH: 8223.7 Hz
 AQ: undefined
 TE: 299.1 C

===== CHANNEL f1 =====
 NUC1: 1H
 P1: 9.93 usec
 SFO1: undefined MHz

F2 - Processing Parameters
 SI: 65536
 DC: 0.05
 LB: 0.30 Hz
 First Point: 0.50
 FT: Hyper Quadrature
 Phase: Manual
 Ph0: 84.02
 Ph1: 19.42

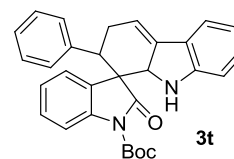


Current Data Parameters

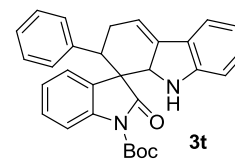
F2 - Acquisition Parameters
 DATE: 2013-07-30T19:13:34
 FULPROG: zgpg30
 TD: 32768
 Solvent: CDCl3
 NS: 1024
 DS: undefined
 SWH: 24038.5 Hz
 AQ: undefined
 TE: 299.4 C

===== CHANNEL f1 =====
 NUC1: 13C
 P1: 9.63 usec
 SFO1: undefined MHz

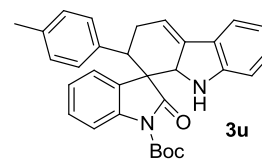
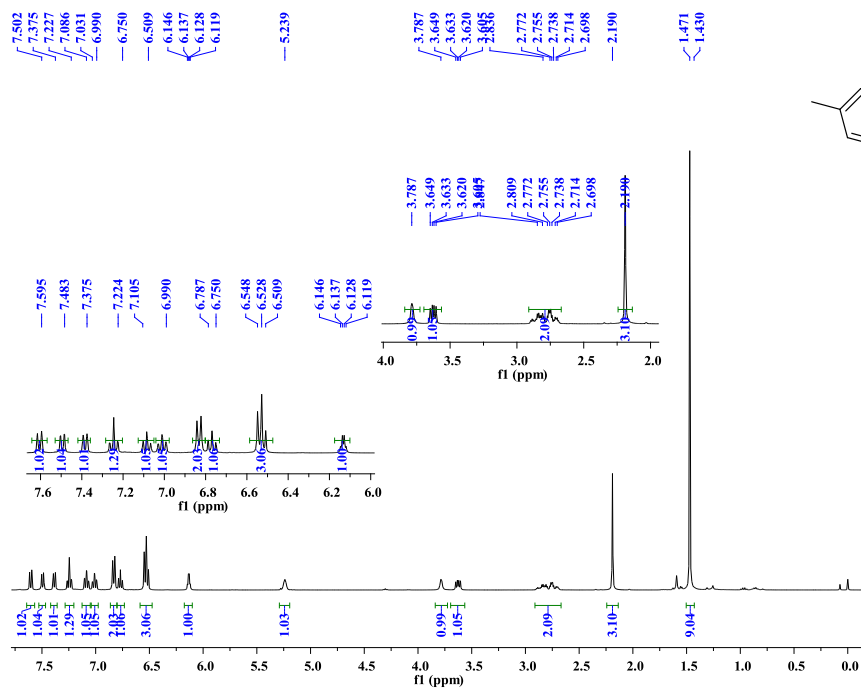
F2 - Processing Parameters
 SI: 65536
 DC: 0.05
 LB: 1.00 Hz
 First Point: 0.50
 FT: Hyper Quadrature
 Phase: Manual
 Ph0: -61.67
 Ph1: 54.51



F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point : 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 80.64
Ph1: 13.42



```
F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point : 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -77.60
Ph1: 72.27
```



Current Data Parameters

F2 - Acquisition Parameters

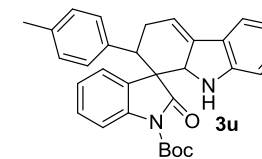
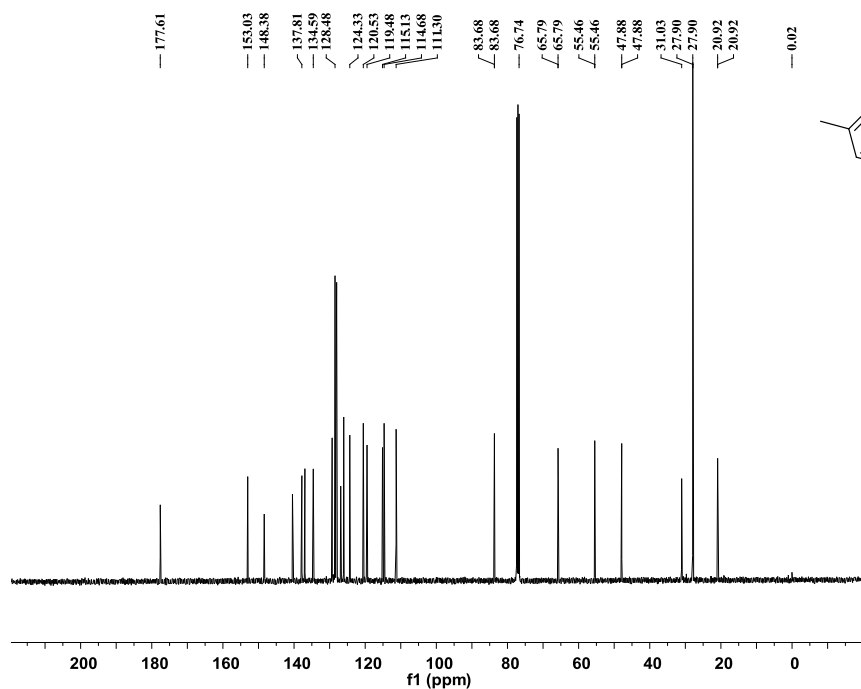
DATE: 2013-09-04T13:17:41
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 298.2 C

CHANNEL f1

NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters

SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 83.48
Ph1: 16.74



Current Data Parameters

F2 - Acquisition Parameters

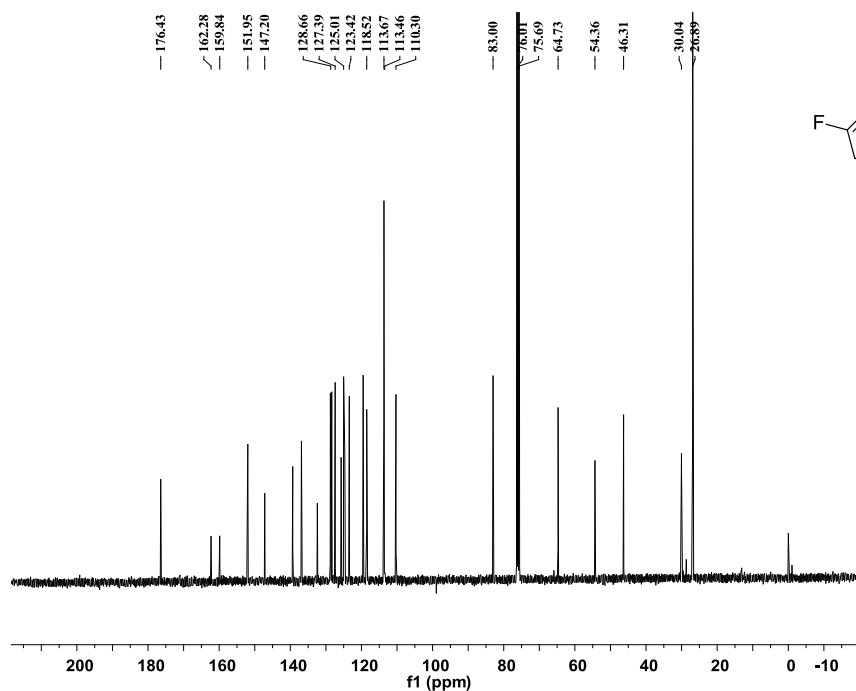
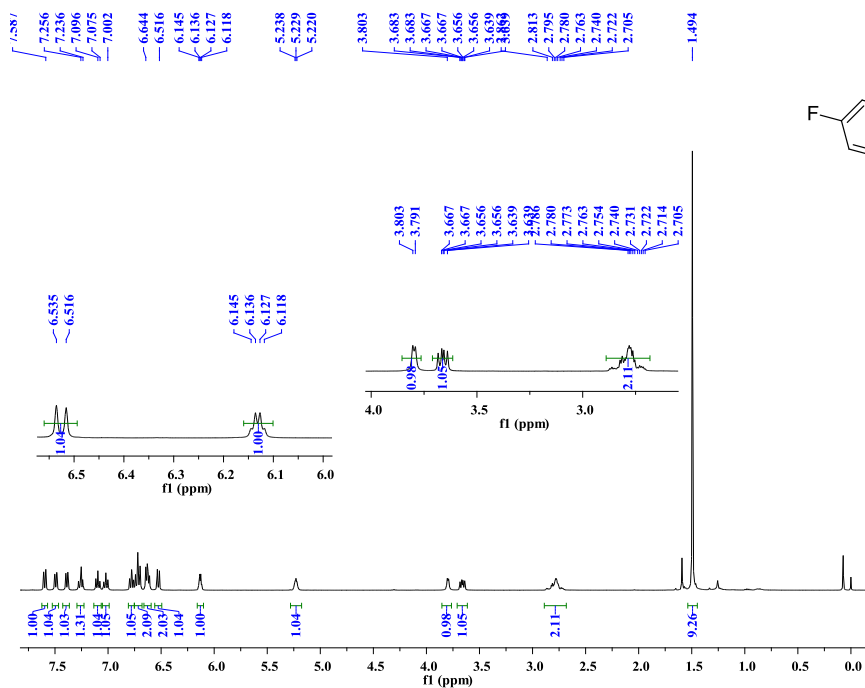
DATE: 2013-09-04T14:17:21
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 1024
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 298.6 C

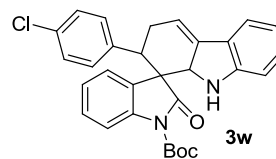
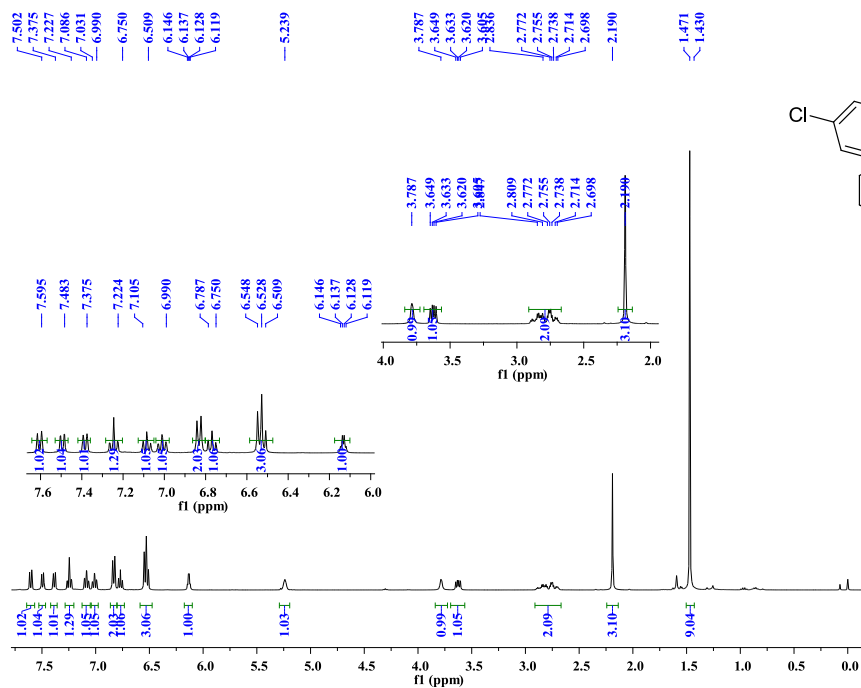
CHANNEL f1

NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters

SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -68.76
Ph1: 62.31



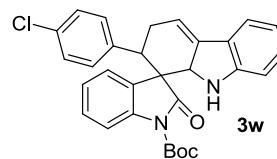
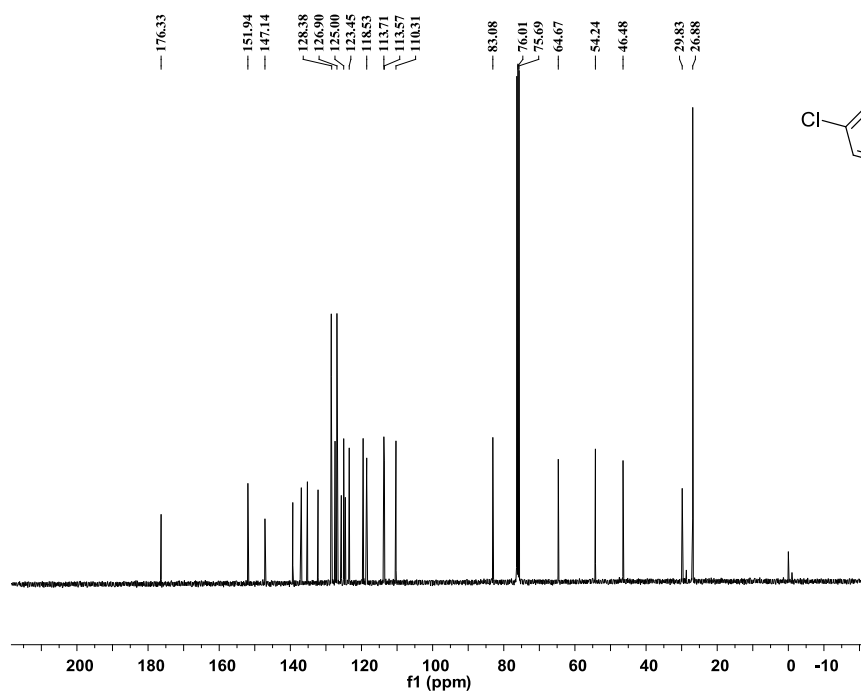


Current Data Parameters

F2 - Acquisition Parameters
 DATE: 2013-09-04T13:17:41
 PULPROG: zg30
 TD: 32768
 Solvent: CDCl3
 NS: 16
 DS: undefined
 SWH: 8223.7 Hz
 AQ: undefined
 TE: 298.2 C

===== CHANNEL f1 =====
 NUC1: 1H
 P1: 9.93 usec
 SFO1: undefined MHz

F2 - Processing Parameters
 SI: 65536
 DC: 0.05
 LB: 0.30 Hz
 First Point: 0.50
 FT: Hyper Quadrature
 Phase: Manual
 Ph0: 83.48
 Ph1: 16.74

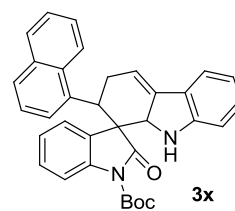
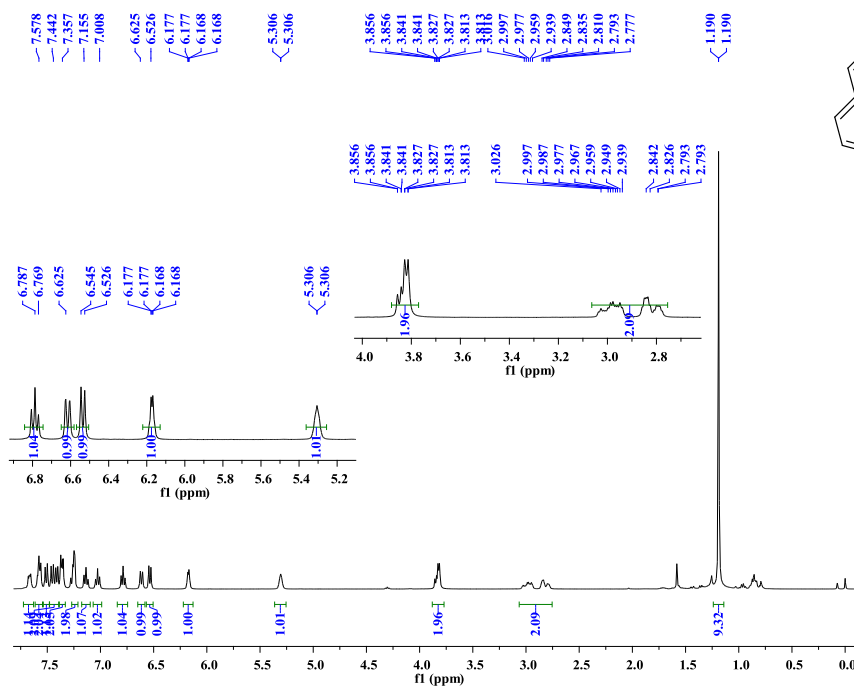


Current Data Parameters

F2 - Acquisition Parameters
 DATE: 2013-09-02T16:26:16
 PULPROG: zgpg30
 TD: 32768
 Solvent: CDCl3
 NS: 1024
 DS: undefined
 SWH: 24038.5 Hz
 AQ: undefined
 TE: 299 C

===== CHANNEL f1 =====
 NUC1: 13C
 P1: 9.63 usec
 SFO1: undefined MHz

F2 - Processing Parameters
 SI: 65536
 DC: 0.05
 LB: 1.00 Hz
 First Point: 0.50
 FT: Hyper Quadrature
 Phase: Manual
 Ph0: -77.85
 Ph1: 70.48

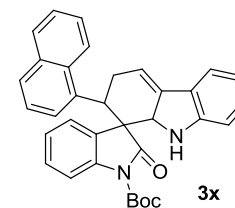
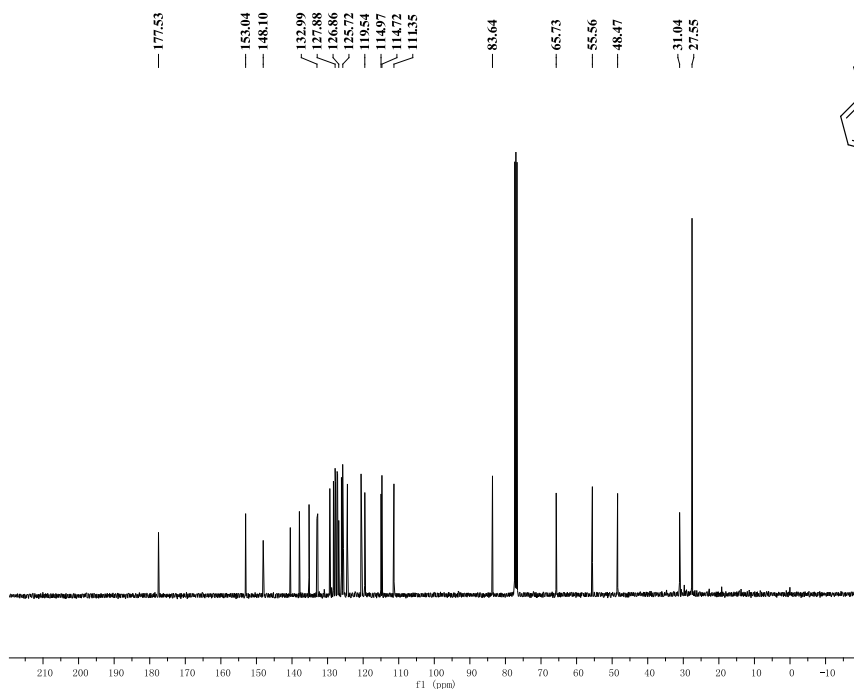


Current Data Parameters

F2 - Acquisition Parameters
 DATE: 2013-09-04T12:13:49
 PULPROG: zg30
 TD: 32768
 Solvent: CDCl3
 NS: 16
 DS: undefined
 SWH: 8223.7 Hz
 AQ: undefined
 TE: 298.2 C

===== CHANNEL f1 =====
 NUC1: 1H
 P1: 9.93 usec
 SFO1: undefined MHz

F2 - Processing Parameters
 SI: 65536
 DC: 0.05
 LB: 0.30 Hz
 First Point: 0.50
 FT: Hyper Quadrature
 Phase: Manual
 Ph0: 83.37
 Ph1: 18.40

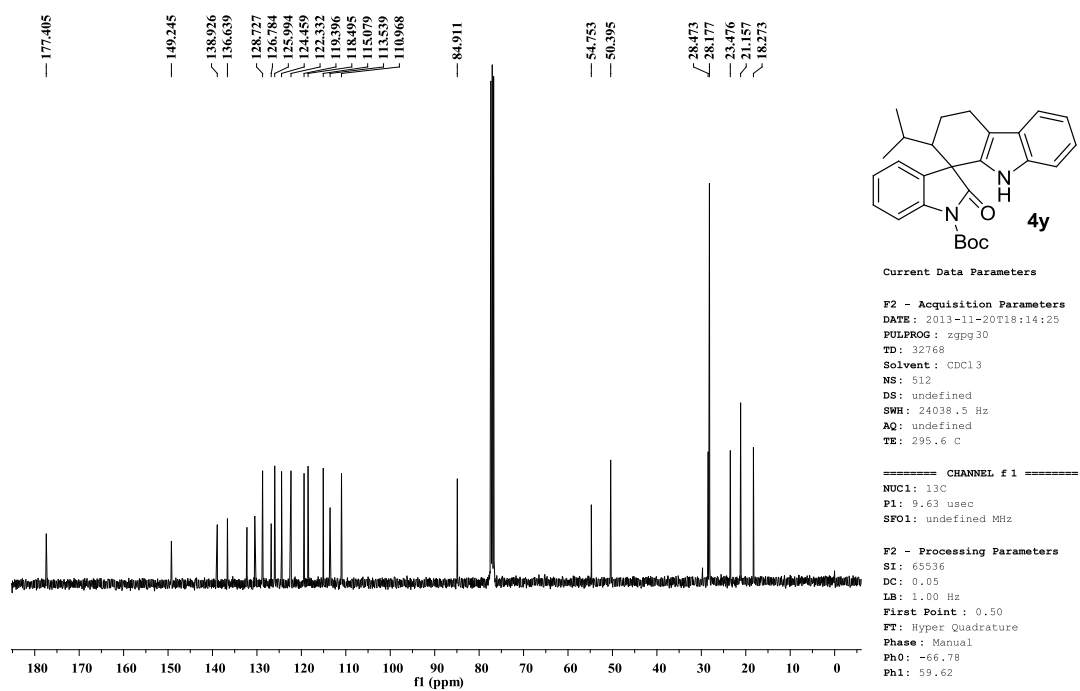
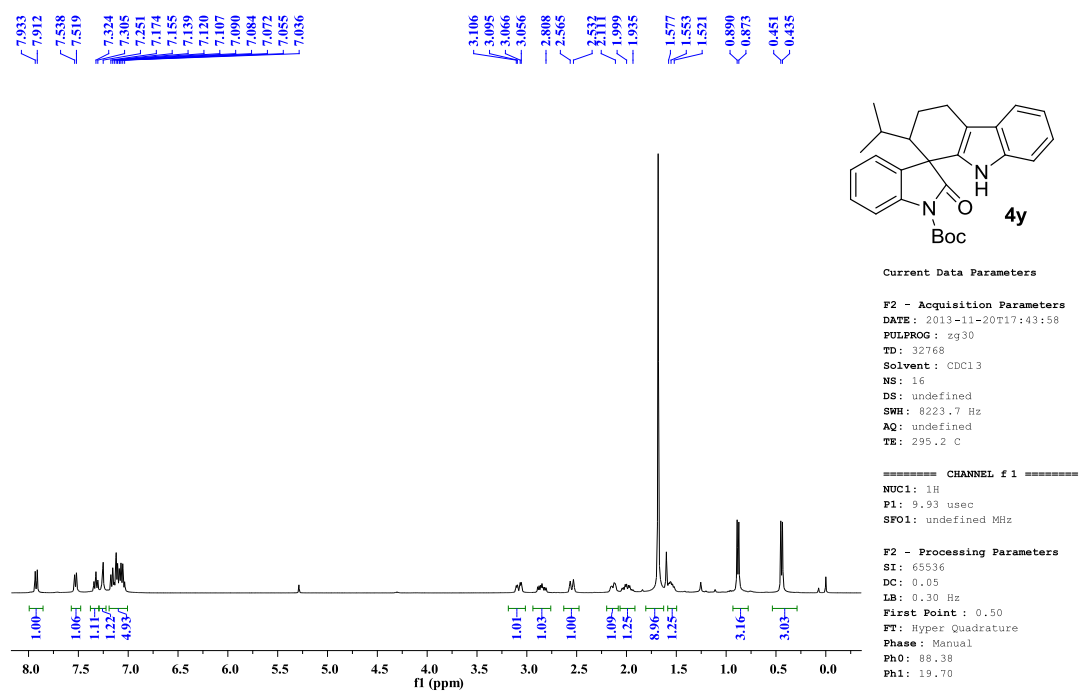


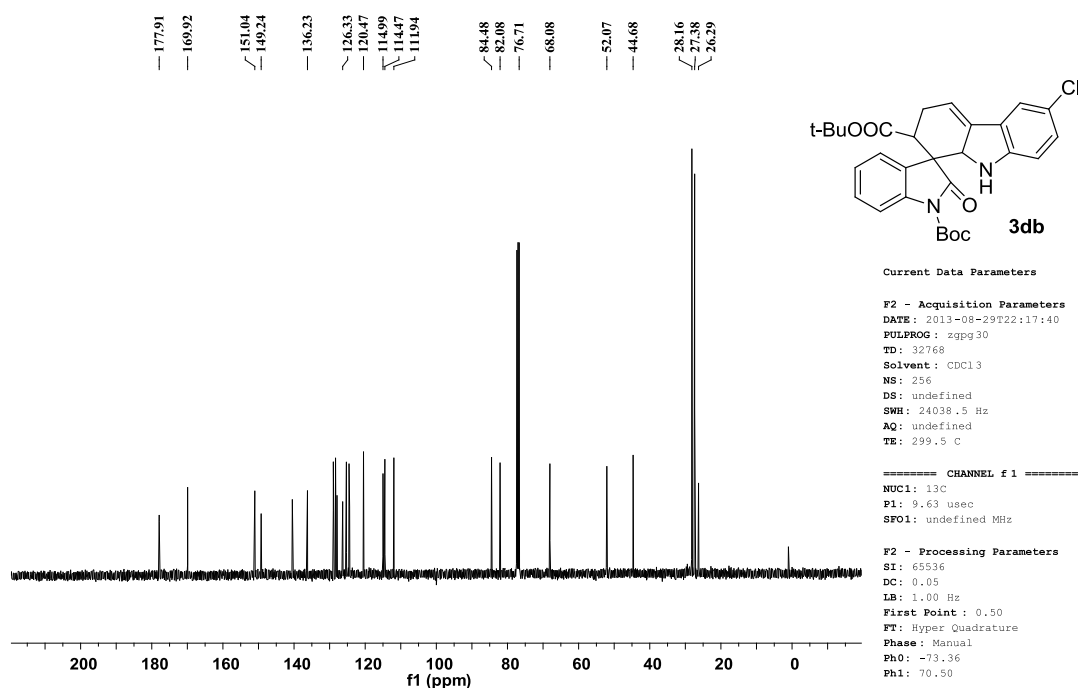
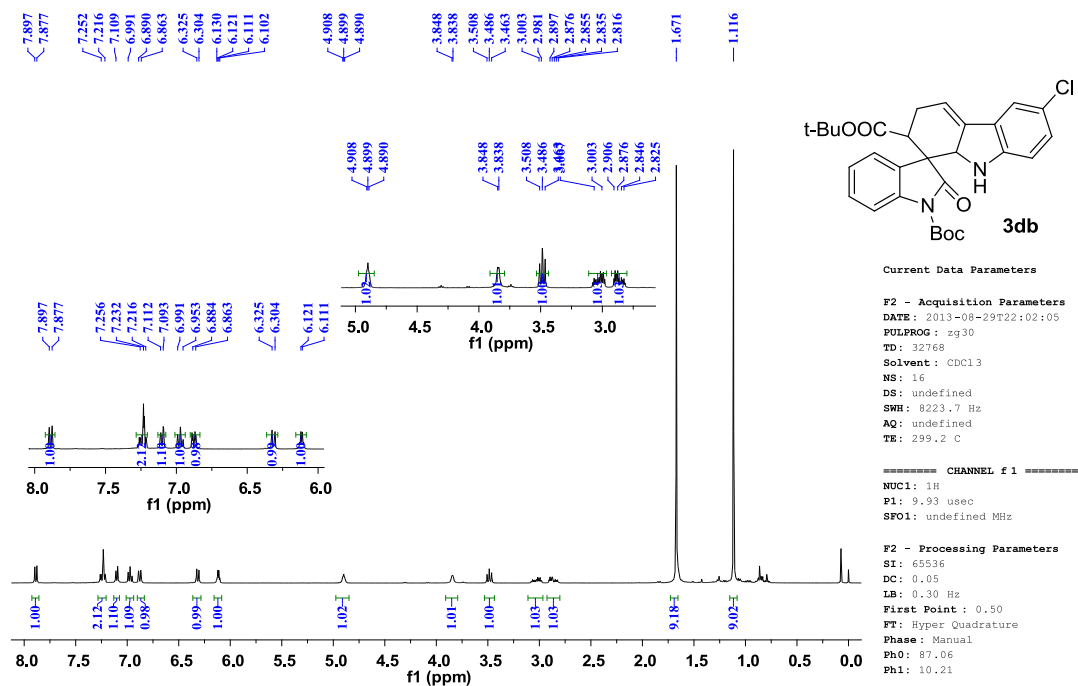
Current Data Parameters

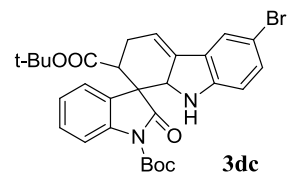
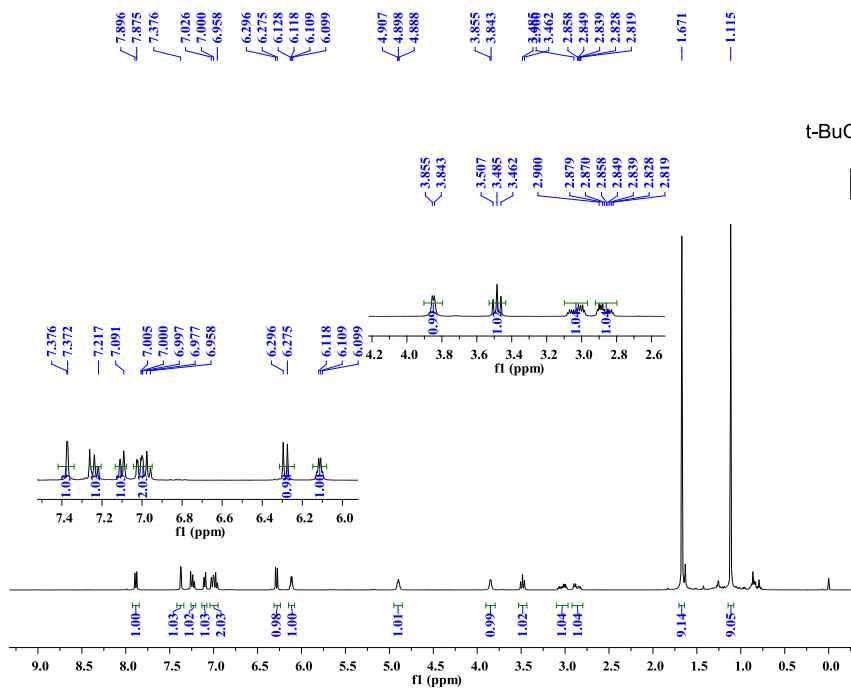
F2 - Acquisition Parameters
 DATE: 2013-09-04T13:13:29
 PULPROG: zgpg30
 TD: 32768
 Solvent: CDCl3
 NS: 1024
 DS: undefined
 SWH: 24038.5 Hz
 AQ: undefined
 TE: 298.6 C

===== CHANNEL f1 =====
 NUC1: 13C
 P1: 9.63 usec
 SFO1: undefined MHz

F2 - Processing Parameters
 SI: 65536
 DC: 0.05
 LB: 1.00 Hz
 First Point: 0.50
 FT: Hyper Quadrature
 Phase: Manual
 Ph0: -75.16
 Ph1: 71.56







Current Data Parameters

F2 - Acquisition Parameters

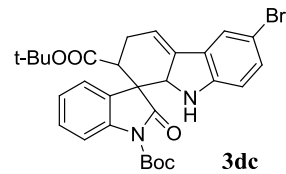
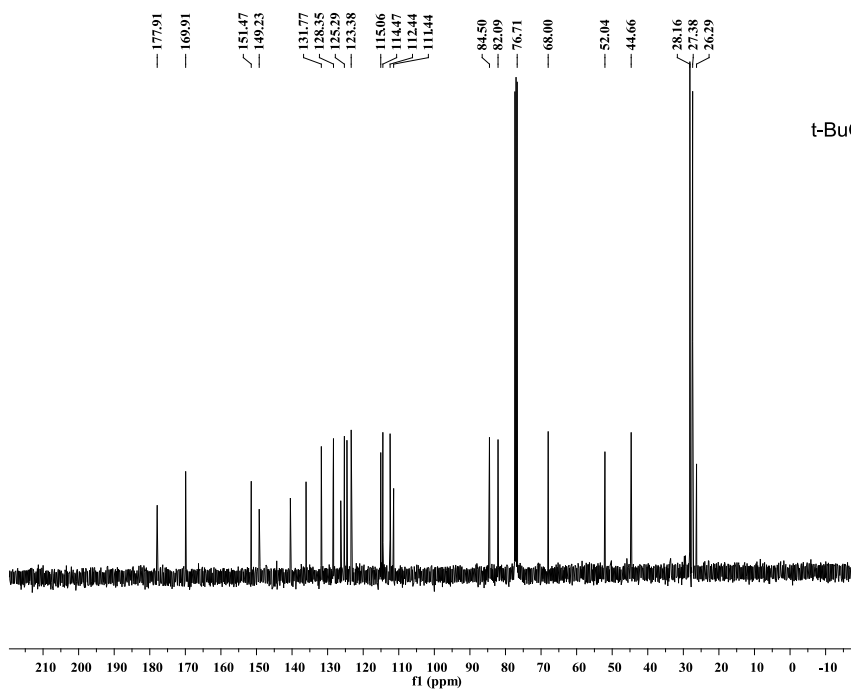
DATE: 2013-07-16T18:11:57
 FULPROG: zg30
 TD: 32768
 Solvent: CDCl3
 NS: 16
 DS: undefined
 SWH: 8223.7 Hz
 AQ: undefined
 TE: 298.6 C

===== CHANNEL f1 =====

NUC1: 1H
 P1: 9.93 usec
 SFO1: undefined MHz

F2 - Processing Parameters

SI: 65536
 DC: 0.05
 LB: 0.30 Hz
 First Point: 0.50
 FT: Hyper Quadrature
 Phase: Manual
 Ph0: 76.63
 Ph1: 21.51



Current Data Parameters

F2 - Acquisition Parameters

DATE: 2013-07-17T12:49:36
 FULPROG: zgpg30
 TD: 32768
 Solvent: CDCl3
 NS: 256
 DS: undefined
 SWH: 24038.5 Hz
 AQ: undefined
 TE: 299.1 C

===== CHANNEL f1 =====

NUC1: 13C
 P1: 9.63 usec
 SFO1: undefined MHz

F2 - Processing Parameters

SI: 65536
 DC: 0.05
 LB: 1.00 Hz
 First Point: 0.50
 FT: Hyper Quadrature
 Phase: Manual
 Ph0: -82.09
 Ph1: 77.52

