Supporting information

Magnesium (II)-Catalyzed Hetero–Diels–Alder Reaction of Brassard's Dienes with Isatins

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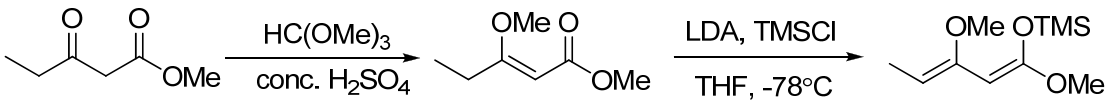
1. General remarks

^{1}H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts are recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26). Spectra are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz), integration and assignment. ^{13}C NMR data 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 ($CDCl_3$, δ = 77.0). Enantiomeric excesses (ee) were determined by chiral HPLC analysis on Daicel Chiralcel IA, IB, ADH and ODH in comparison with the authentic racemates. Optical rotations were reported as follows: $[\alpha]_D^T$ (c: g/100 mL, in solvent). HRMS was recorded on a commercial apparatus (ESI Source). All the solvents were purified by usual methods before use. All isatins were prepared according to the literature.[1] Brassard's dienes **1**, **2** were prepared from methyl 3-oxopentanoate and methyl 3-oxobutanoate according to a literature procedure.[2] CD spectra (MeOH as the solvent) were determined by Chirascan CD which was purchased from Applied photophysics Ltd. Silica gel for Thin-layer chromatography (HG/T2354-92) made in Qingdao Haiyang Chemical Co., Ltd.

2. General procedure for preparation of Brassard's diene

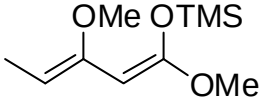


Preparation of Brassard type diene **1**: 1) To a 150 mL round bottom flask with calcium chloride tube, methyl 3-oxopentanoate (150 mmol, 19.5 mL),

trimethoxymethane (250 mmol, 26.5 mL) were added. The mixture was kept at 0 ^{o}C and conc. sulfuric acid (0.25 mL) was added to the reaction mixture, The reaction was allowed to warm to room temperature and detected by TLC. After 24 h, The mixture was concentrated and purified by distillation under reduced pressure to afford the methyl 3-methoxypent-2-enoate with 64% yield.

2) To a 250 mL three round bottom flask with constant pressure funnel, the device was filled with N_2 gas. Lithium diisopropylamide (75 mmol, 38 mL), dry tetrahydrofuran (30 mL) were added, keep the device at -78 ^{o}C, 3-methoxypent-2-enoate (50 mmol, 7.2 mL), dry tetrahydrofuran (15 mL) were added to the constant pressure funnel, competing the drops within half an hour, then dry tetrahydrofuran (5 mL) was added to wash the funnel. The reaction mixture continues stiring 1 hour, then dry trimethylchlorosilane (125 mmol, 15.6 mL) was added, After competing the drops within half an hour and keeping the reaction mixture stirring half an hour, the reaction was allowed to warm to room temperature to stir overnight. Removing the salts by filtration and the reaction mixture was purified by distillation under reduced pressure to afford the (1,3-dimethoxypent-3-enyloxy) trimethylsilane in 40% yield.

1,3-dimethoxypent-3-enyloxy trimethylsilane 1

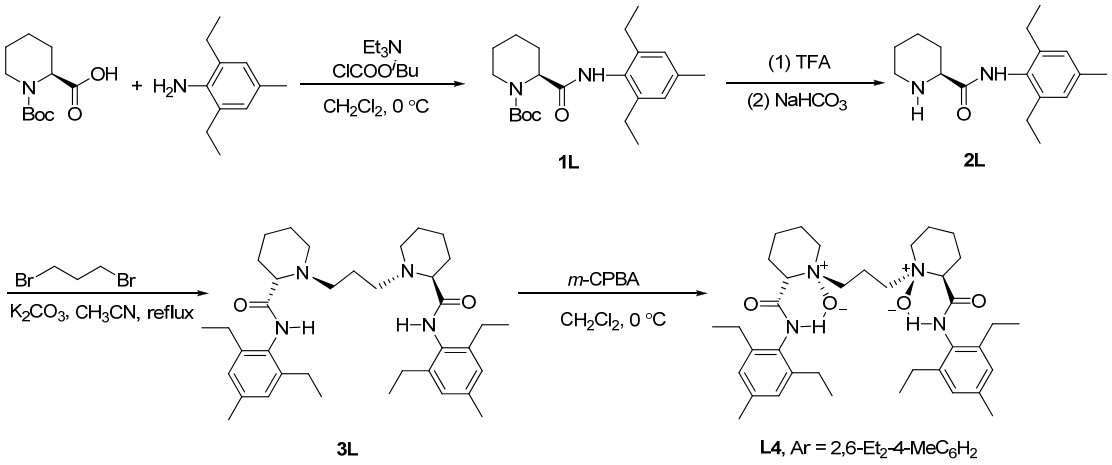


^{1}H NMR (400 MHz, $CDCl_3$) δ 4.62 (q, J = 6.9 Hz, 1H), 3.77 (s, 1H), 3.32 (s, 3H), 3.27 (s, 3H), 1.40 (d, J = 6.9 Hz, 3H), -0.00

(s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.47, 151.07, 103.98, 74.03, 57.03, 54.60, 10.03, 0.00.

3. General procedure for *N, N'*-dioxide preparation

The *N, N'*-dioxide ligands **L1**–**L6** were synthesized by the same procedure in the literature.[3]



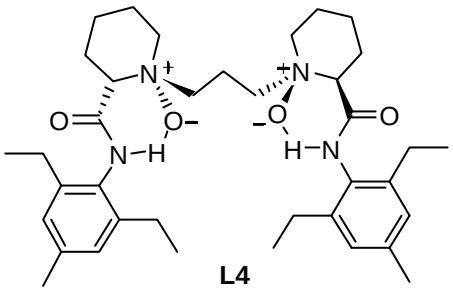
To a solution of (*S*)-1-*N*-Boc-piperidine-2-carboxylic acid (2.29 g, 10 mmol) in CH_2Cl_2 (20 mL) was added Et_3N (1.55 mL, 11 mmol), isobutyl chloroformate (1.50 g, 11 mmol) at 0 °C under stirring. After 30 min, 2,6-diethyl-4-methylaniline (1.95 g, 12 mmol) was added. The reaction was allowed to warm to room temperature and detected by TLC. After 24 h, the mixture was washed with 1 M $KHSO_4$, saturated $NaHCO_3$, brine, dried over anhydrous $MgSO_4$ and concentrated and purified through flash chromatograph to give **1L** (3.76 g, up to 99% isolate yield).

The white solid of **1L** in CH_2Cl_2 (8 mL) was added TFA (10 mL) at 0 °C and stirred until the reaction was finished (2 h). Then, the solvent was evaporated, and H_2O (10 mL) was added. The pH value of the mixture was brought into the range of 10–12 by

the addition of solid K_2CO_3 and saturated $NaHCO_3$. The aqueous phase was extracted with CH_2Cl_2 (5 × 20 mL). The combined organic phase was washed with brine, dried over anhydrous $MgSO_4$ and evaporated in vacuo. The residue was directly used for next step without further purification.

To a solution of **2L** (2.74 g, 10 mmol) in CH_3CN (8 mL) was added K_2CO_3 (2.76 g, 20 mmol) and 1,3-dibromopropane (510 μL, 5 mmol) under stirring. It was kept stirring at 80 °C, and monitored by TLC. Then, K_2CO_3 was removed by filtration and washed by CH_2Cl_2. The filtrate was concentrated and purified by silica gel column chromatography to give **3L** (2.35 g, 80% isolate yield).

The *N, N'*-dioxide **L4** was prepared through oxidation of **3L** by m-CPBA (1.38 g, 8 mmol) in CH_2Cl_2 (20 mL) at 0 °C for 1 h and purified through flash chromatograph to give a white foam solid. Then it was dissolved in CH_2Cl_2 and filtration through Celite to remove the silicon gel, concentrate to get a kind white foam **L4** (2.23 g, 90% isolated yield). For other ligands, the synthesis method could be found in reference.



L4

L4: white solid; m. p. 120–122 °C; $[\alpha]_D^{27.6}$ = −25.2 (c = 0.20 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.86 (s, 2H), 6.91 (s, 4H), 3.63 (d, *J* = 11.7 Hz, 4H), 3.56 (d, *J* = 11.0 Hz, 2H), 3.40 (dd, *J* = 19.3, 8.3 Hz, 2H), 2.95 (t, *J* = 11.6 Hz, 2H), 2.83 – 2.71 (m, 2H), 2.70 – 2.60 (m, 2H), 2.52 (dd, *J* = 14.4, 7.1 Hz, 8H), 2.43 – 2.35 (m, 2H), 2.29 (s, 6H), 2.14 (d, *J* = 13.1 Hz, 2H), 1.92 (d, *J* = 12.9 Hz, 2H), 1.69 (d, *J* = 14.0 Hz, 2H), 1.44 (dd, *J* = 25.9,

12.9 Hz, 2H), 1.17 (t, J = 7.5 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.63, 140.37, 137.30, 129.60, 127.45, 64.10, 64.92, 26.72, 25.37, 22.48, 21.25, 20.32, 16.28, 15.01.

4. General procedure for the catalytic asymmetric hetero-Diels–Alder reaction

For Brassard type diene **1**:

In a test tube, isatin **3e** (0.10 mmol, 31.6 mg), ligand **L4** (0.01 mmol, 6.2 mg), $Mg(ClO_4)_2$ (0.01 mmol, 2.3 mg) were added. The tube was filled with N_2 gas, and 0.5 mL of CH_2Cl_2 was added. The reaction was stirred at 30 °C for 0.5 h, then the Brassard type diene **1** (1.5 equiv, 40 μL) was added at 35 °C and the reaction mixture was stirred for 1 h until isatin **3e** was consumed (determined by TLC). Then TFA (30 μL) was added to the reaction mixture at room temperature, and the solution kept stirring for 2 h. Next, saturated $NaHCO_3$ (4 mL) was added, and the solution was stirred for 5 min. After diluted with 4 mL of CH_2Cl_2, the mixture was filtered through a plug of celite. The layers were separated. The acquired aqueous layer was extracted with CH_2Cl_2 (2 × 5 mL), and then the combined organic layers were washed with brine and dried over anhydrous $MgSO_4$ and concentrated. The crude oil was purified by flash chromatography (petroleum : CH_2Cl_2 : EtOAc = 3 : 1 : 0.5) to afford the product **4e.**

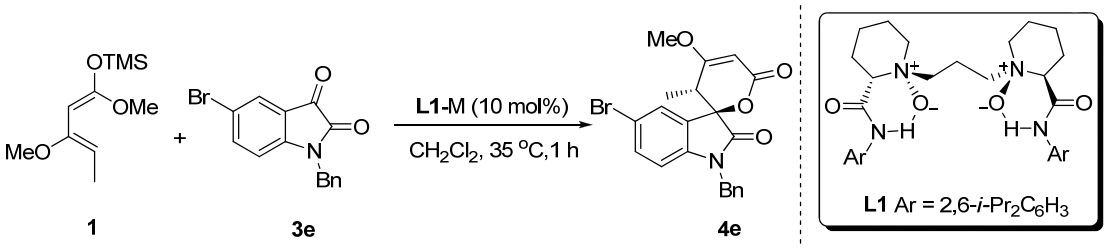
For Brassard's diene **2**:

In a test tube, isatin **3a** (0.1 mmol, 23.7 mg), ligand **L4** (0.01 mmol, 6.20 mg), and $Mg(OTf)_2$ (0.011 mmol, 3.6 mg) were added. The tube was filled with N_2 gas, and 0.5 mL of CH_2Cl_2 was added. The reaction was stirred at 30 °C for 0.5 h, then the

Brassard's diene **2** (1.5 equiv, 40 μL) was added at 35 °C and the reaction mixture kept stirring for 1 h (determined by TLC). The crude mixture was purified by flash chromatography (petroleum : CH_2Cl_2 : EtOAc = 3 : 1 : 0.5) to afford the product **5a.**

5. Optimization of other conditions

5.1 Screening of other metals

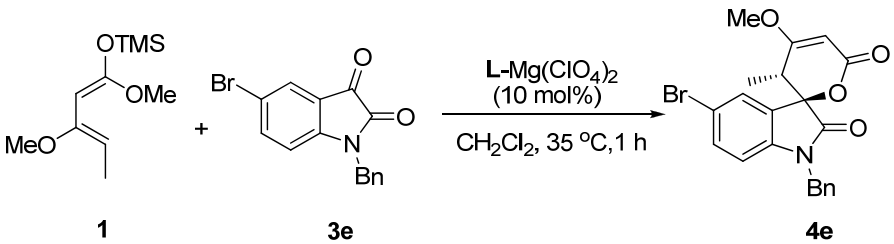


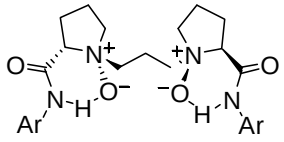
Entry[a]	Metal	Yield[b] (%)	dr[c]	ee[c] (%)
1	$Er(OTf)_3$	0	-	-
2	$Zn(OTf)_2$	29	51:49	13
3	$Fe(acac)_2$	32	12:88	15
4	$Ni(BF_4)_2{\cdot}6H_2O$	21	28:72	15

[a] Unless specified, all reactions were performed with L–metal (10 mol %, 1:1), **1** (0.15 mmol), **3e** (0.10 mmol), at 35 °C for 1 h. [b] Isolated yield. [c] Determined by HPLC analysis (Chiralcel IB).

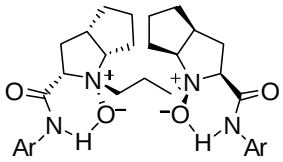
Table 5.1 showed that other metals, such as $Er(OTf)_3$, $Zn(OTf)_2$, $Fe(acac)_2$, $Ni(BF_4)_2{\cdot}6H_2O$, gave poor results.

5.2 Screening of the other ligands





L5: Ar = 2,6-Et_2-4-MeC_6H_2



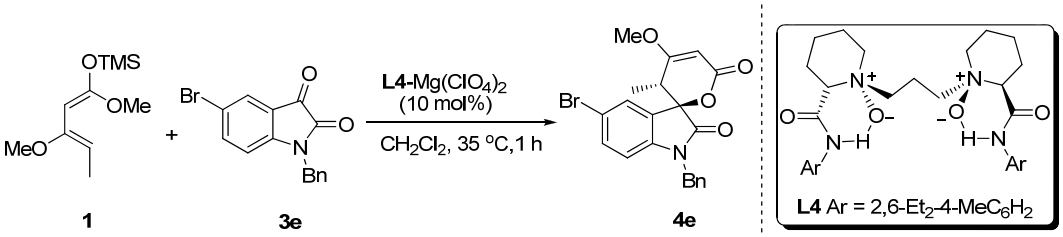
L6: Ar = 2,6-Et_2-4-MeC_6H_2

Entry[a]	Ligand	Yield[b] (%)	dr[c]	ee[c] (%)
1	**L5**	25	70:30	60
2	**L6**	60	70:30	15

[a] Unless specified, all reactions were performed with L–metal (10 mol %, 1:1), **1** (0.15 mmol), **3e** (0.10 mmol), at 35 °C for 1 h. [b] Isolated yield. [c] Determined by HPLC analysis (Chiralcel IB).

Table 5.2 showed that the amino acid backbone of the ligand also affected the reactivity and selectivity of the reaction greatly.

5.3 Optimization of the concentration of reaction

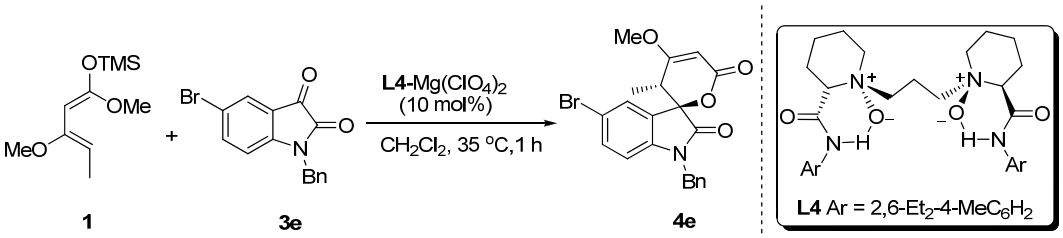


1 **3e** **4e**

Entry[a]	Concentration (mol/L)	Yield[b] (%)	dr[c]	ee[c] (%)
1	0.5	54	95:5	93
2	0.25	54	97:3	95
3	0.2	70	95:5	96
4	0.17	61	92:8	93
5	0.12	23	78:22	80

[a] Unless specified, all reactions were performed with L–metal (10 mol %, 1:1), **1** (0.15 mmol), **3e** (0.10 mmol), at 35 °C for 1 h. [b] Isolated yield. [c] Determined by HPLC analysis (Chiralcel IB).

5.4 Optimization of the additives of the reaction



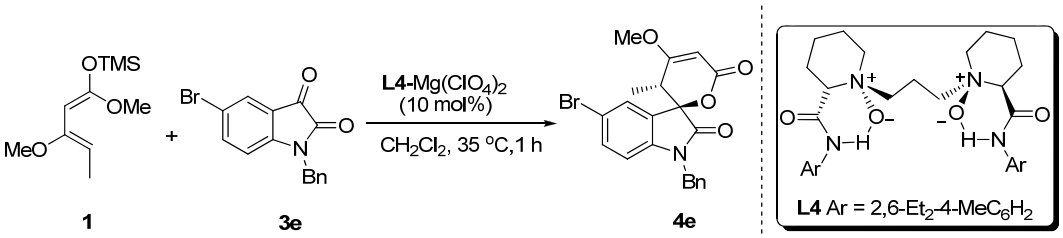
1 3e 4e

Entry[a]	Additive	Yield[b] (%)	dr[c]	ee[c] (%)
1	-	70	95:5	96
2	3Å MS	45	82:18	93
3	4Å MS	50	95:5	96
4	5Å MS	47	92:8	96
5	$MgSO_4$	28	84:16	83
6	Na_2SO_4	23	78:22	80

[a] Unless specified, all reactions were performed with L–metal (10 mol %, 1:1), Additives (30 mg), **1** (0.15 mmol), **3e** (0.10 mmol), at 35 °C for 1 h. [b] Isolated yield. [c] Determined by HPLC analysis (Chiralcel IB).

Table 5.4 showed molecular sieves and desiccants decreased the yield of the reaction obviously in the present catalyst system.

5.5 Optimization of the ratio of metal to ligand



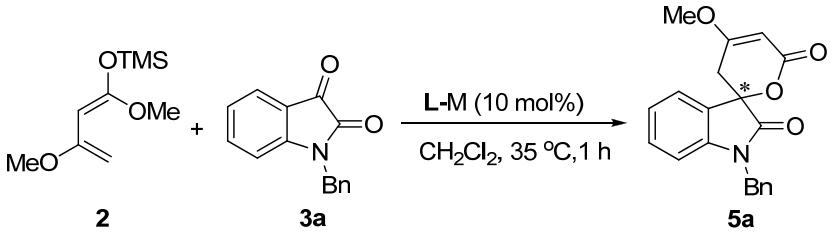
1 3e 4e

Entry[a]	M : L	Yield[b] (%)	dr[c]	ee[c] (%)
1	1:1	70	95:5	96
2	1.2:1	57	94:6	92
3	1:1.2	38	95:5	96
4[d]	1:1	31	90:10	89
5[e]	1:1	93	95:5	96

[a] Unless specified, all reactions were performed with L–metal (10 mol %), **1** (0.15 mmol), **3e** (0.1 mmol), at 35 °C for 1 h. [b] Isolated yield. [c] Determined by HPLC analysis (Chiralcel IB). [d] the reaction was exposed in air. [e] After 1 h, TFA (30 μL) was added to the reaction mixture, then stirred for 2 h at room temperature.

Table 5.5, entries 1-4 showed that the molar ratio of **L4** to $Mg(ClO_4)_2$ also affected the reactivity of the reaction. The yield of the reaction decreased in the presence of a excess of Ligand or Metal in the reaction. Entry 5 showed that TFA could improve the yield by promoting the transformation of Aldol product to the cycloaddition product.

5.6 Optimization of the reaction conditions of Brassard's diene **2** with isatin **3a**



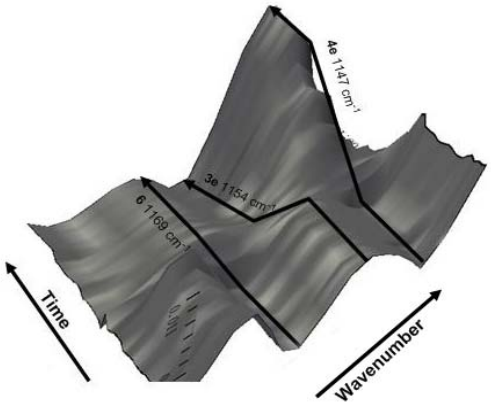
2 **3a** **5a**

Entry[a]	Metal	Ligand	M : L	Yield[b] (%)	ee[c] (%)
1	$Mg(ClO_4)_2$	**L4**	1:1	60	81
2	$Mg(OTf)_2$	**L4**	1:1	80	90
3	$Mg(OTf)_2$	**L1**	1:1	80	90
4	$Mg(OTf)_2$	**L2**	1:1	38	90
5	$Mg(OTf)_2$	**L3**	1:1	59	91
6	$Mg(OTf)_2$	**L4**	1.1:1	82	93
7[d]	$Mg(OTf)_2$	**L4**	1.1:1	82	93

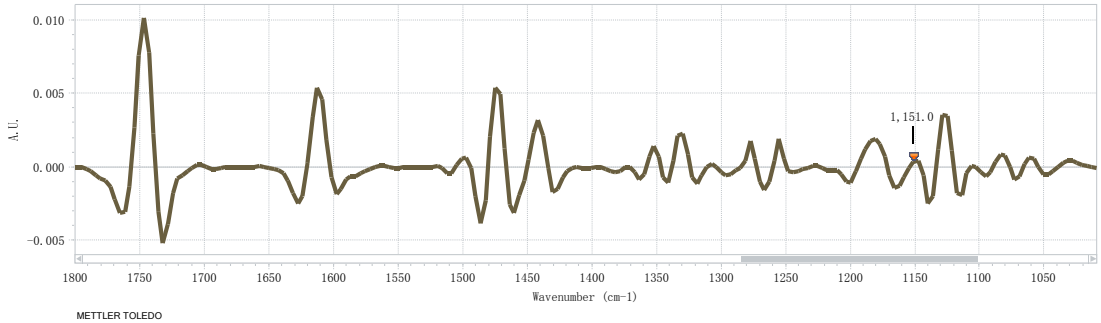
[a] Unless specified, all reactions were performed with L–metal (10 mol %), **2** (0.15 mmol), **3a** (0.1 mmol), at 35 °C for 1 h. [b] Isolated yield. [c] Determined by HPLC analysis (Chiralcel ODH). [d] After 1 h, TFA (30 μL) was added to the reaction mixture, then stirred for 2 h at room temperature.

For the reaction of Brassard's diene **2** with isatin, as shown in Table 5.6, entries 1-2 showed that when **L4**-$Mg(OTf)_2$ instead of **L4**-$Mg(ClO_4)_2$ was applied to the reaction, the yield and ee could be improved to 80% and 90%, respectively. Further surveying the ratio of metal to ligand, the best result was obtained in the presence of **L4**: $Mg(OTf)_2$ =1:1.1 (entry 6). Entry 7 shows that TFA couldn't improve the yield of the reaction because of trace amount of Aldol product.

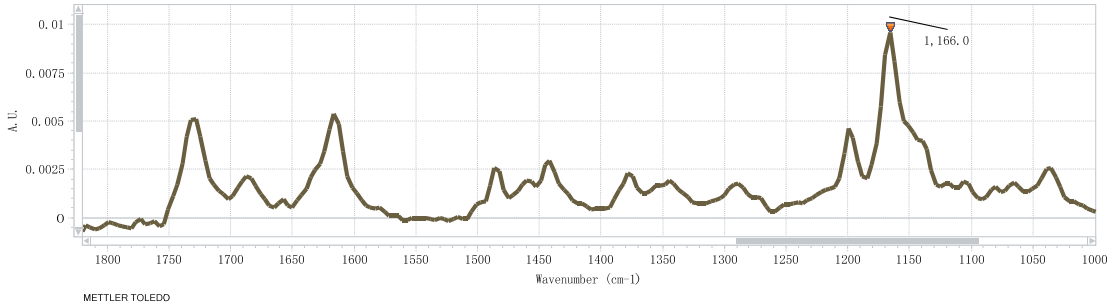
6. The operando IR experiments of the reaction



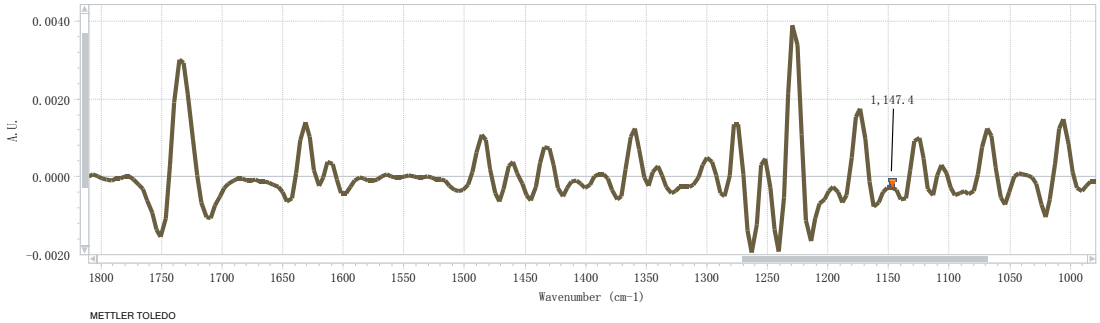
The 3D ATR-FTIR profile of the reaction



The IR spectrum of isatin **3e**



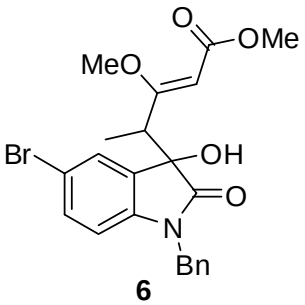
The IR spectrum of Aldol product **6**



The IR spectrum of **4e**

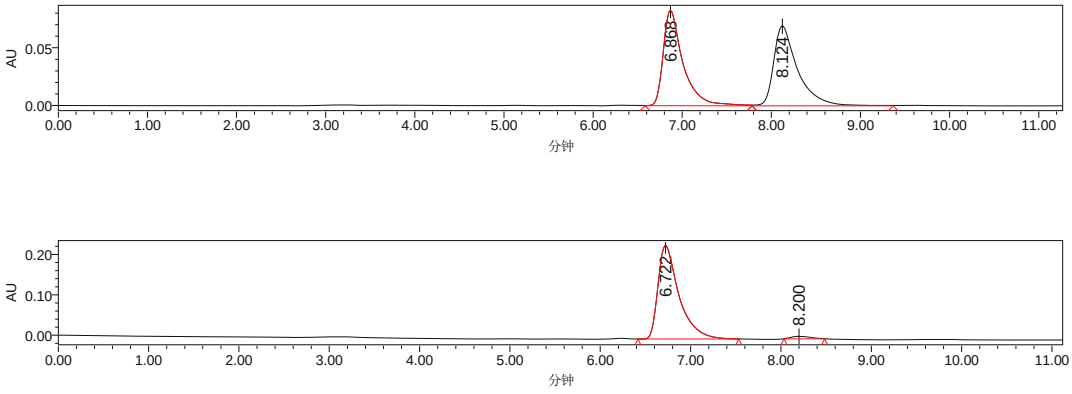
7. The analytical and spectral characterization data of the aldol product 6

(Z)-methyl-4-(1-benzyl-5-bromo-3-hydroxy-2-oxoindolin-3-yl)-3-methoxypent-2-enoate **6**



6

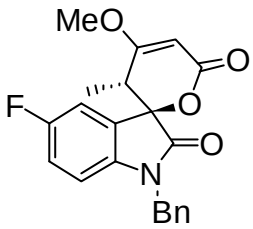
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 1.9 Hz, 1H), 7.35 – 7.29 (m, 3H), 7.29 – 7.21 (m, 3H), 6.54 (d, *J* = 8.3 Hz, 1H), 5.24 (s, 1H), 5.22 (s, 1H), 5.00 (d, *J* = 15.7 Hz, 1H), 4.67 (d, *J* = 15.7 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 1H), 3.73 (s, 3H), 3.63 (s, 3H), 1.02 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.32, 173.71, 170.34, 141.81, 135.38, 133.3, 132.06, 128.82, 127.77, 127.41, 126.72, 115.66, 110.51, 93.61, 78.50, 55.88, 51.67, 43.99, 42.27, 11.77. HRMS (SEI-TOF) calcd for $C_{22}H_{22}Br^{80.9163}NNaO_5$ ([M+Na$^+$]) = 482.0579, Found 482.0579.



	Retention Time	Area %
1	6.72	97.76
2	8.20	2.24

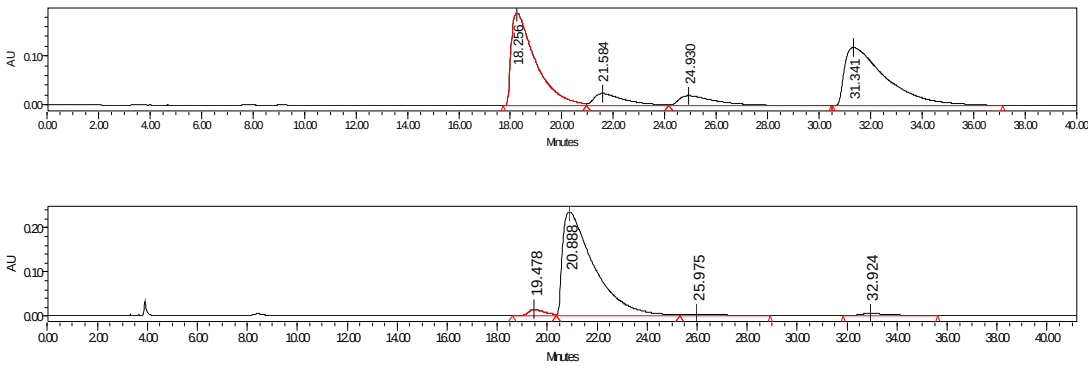
8. The analytical and spectral characterization data of the products

(2′*R*,3′*R*)-1-benzyl-5-fluoro-4'-methoxy-3'-methylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione **4b**



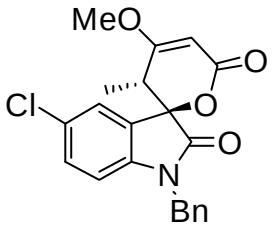
4b

White solid; m. p. 108-110 °C ; HPLC (Chiralcel IB, hexane/*i*-PrOH = 80/20, flow rate = 1.0 ml/min, λ = 254 nm), retention time: t_{r1} = 19.48 min, t_{r2} = 20.89 min, t_{r3} = 25.98 min, t_{r4} = 32.92 min, ee = 96%, d.r. = 95:5. $[\alpha]_D^{16.7}$ = +50.0 (c = 0.55 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 3H), 7.26 (d, *J* = 4.9 Hz, 2H), 7.16 (dd, *J* = 7.4, 2.4 Hz, 1H), 6.97 (m, *J* = 8.8, 2.5 Hz, 1H), 6.69 – 6.59 (m, 1H), 5.37 (s, 1H), 4.97 (d, *J* = 16.0 Hz, 1H), 4.70 (d, *J* = 16.0 Hz, 1H), 3.84 (s, 3H), 3.30 (dd, *J* = 7.1 Hz, 1H), 1.02 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.90, 171.48, 164.79, 160.65, 158.23, 139.07, 134.78, 129.00, 128.01, 127.33, 117.31 (d, *J*=23.5 Hz), 112.38 (d, *J*=25.2 Hz), 110.40 (d, *J*=7.9 Hz), 90.05, 82.33, 56.57, 44.13, 37.55, 10.07. HRMS (SEI-TOF) calcd for $C_{21}H_{18}FNNaO_4$ ([M+Na$^+$]) = 390.1118, Found 390.1117.



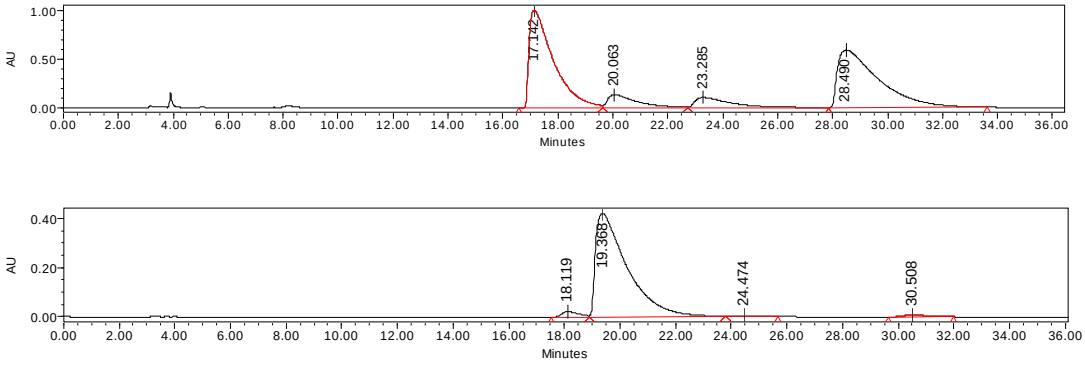
	Retention Time	% Area
1	19.48	3.06
2	20.89	93.23
3	25.98	1.85
4	32.92	1.86

(2'*R*,3'*R*)-1-benzyl-5-chloro-4'-methoxy-3'-methylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione **4c**



4c

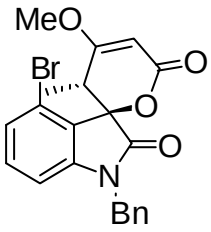
White solid; m. p. 130-132 °C ; HPLC (Chiralcel IB, hexane/*i*-PrOH = 80/20, flow rate = 1.0 ml/min, λ = 254 nm), rentention time: t_{r1} = 18.12 min, t_{r2} = 19.37 min, t_{r3} = 24.47 min, t_{r4} = 30.51 min, ee = 98%, d.r. = 96:4. $[\alpha]_D^{15.7}$ = +66.7 (c = 0.25 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 1.9 Hz, 1H), 7.34 – 7.28 (m, 3H), 7.26 – 7.22 (m, 3H), 6.64 (d, *J* = 8.4 Hz, 1H), 5.36 (s, 1H), 4.96 (d, *J* = 15.7 Hz, 1H), 4.70 (d, *J* = 15.7 Hz, 1H), 3.83 (s, 3H), 3.31 (dd, *J* = 7.1 Hz, 1H), 1.01 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.74, 171.47, 164.73, 141.69, 134.65, 130.88, 129.01, 128.94, 128.23, 128.05, 127.33, 124.75, 110.66, 90.01, 82.19, 56.59, 44.09, 37.46, 10.07. HRMS (SEI-TOF) calcd for $C_{21}H_{18}Cl^{34.9689}NNaO_4$ ([M+Na$^+$]) = 406.0822, Found 406.0822.



	Retention Time	% Area
1	18.12	2.63
2	19.37	95.43
3	24.47	0.69

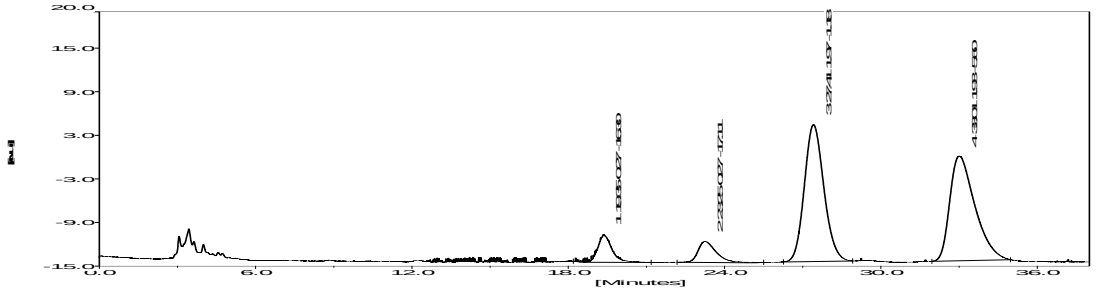
4	30.51	1.26

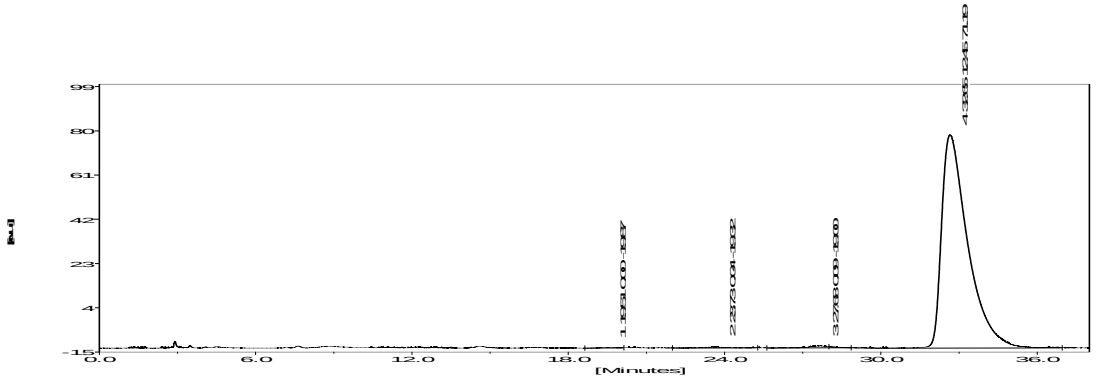
(*2'R,3'R*)-1-benzyl-4-bromo-4'-methoxy-3'-methylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione **4d**



4d

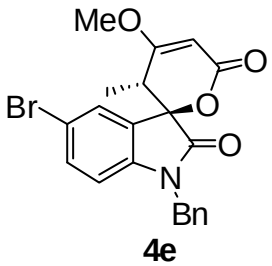
White solid; m. p. 182-184 °C ; HPLC (Chiralcel ADH, hexane/*i*-PrOH = 80/20, flow rate = 1.0 ml/min, λ = 254 nm), retention time: t_{r1} = 19.51 min, t_{r2} = 23.73 min, t_{r3} = 27.68 min t_{r4} = 32.65 min, ee = 99%, d.r. = 99:1. $[\alpha]_D^{17.8}$ = +78.8 (c = 0.66 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.21 (m, 3H), 7.20 – 7.18 (m, 2H), 7.12 (d, *J* = 8.2 Hz, 1H), 7.07 (t, *J* = 7.9 Hz, 1H), 6.61 (d, *J* = 7.8 Hz, 1H), 5.27 (s, 1H), 4.91 (d, *J* = 15.6 Hz, 1H), 4.63 (d, *J* = 15.6 Hz, 1H), 4.11 (dd, *J* = 7.1 Hz, 1H), 3.76 (s, 3H), 0.91 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.80, 171.24, 164.97, 145.25, 134.67, 132.17, 128.98, 128.04, 127.91, 127.37, 123.92, 119.95, 108.64, 89.63, 83.66, 56.48, 44.07, 33.54, 9.93. HRMS (SEI-TOF) calcd for $C_{21}H_{18}Br^{80.9163}NKO_4$ ([M+K$^+$]) = 468.0036, Found 468.0031.





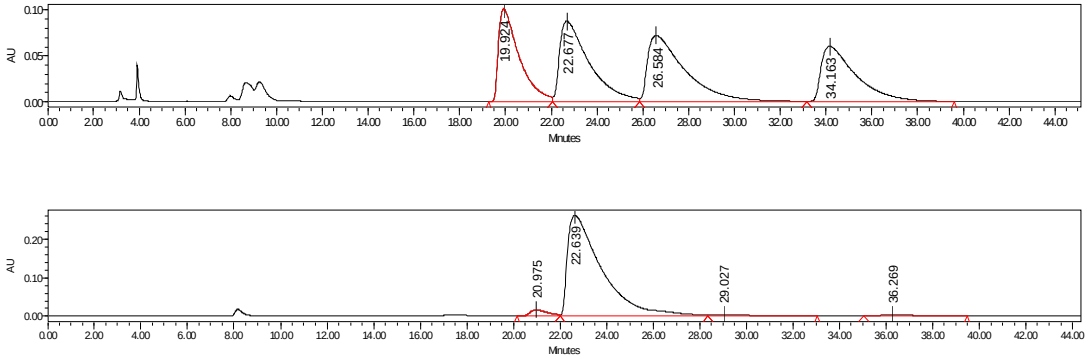
	Retention Time	% Area
1	19.51	0.04
2	23.73	0.25
3	27.68	0.77
4	32.65	98.94

(2′*R*,3′*R*)-1-benzyl-5-bromo-4'-methoxy-3'-methylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione **4e**



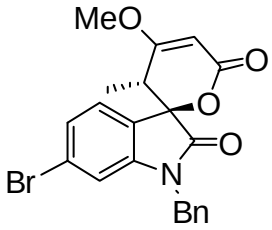
4e

White solid; m. p. 156-158 °C; HPLC (Chiralcel IB, hexane/*i*-PrOH = 80/20, flow rate = 1.0 ml/min, λ = 254 nm), retention time: t_{r1} = 20.98 min, t_{r2} = 22.64 min, t_{r3} = 29.03 min, t_{r4} = 36.27 min, ee = 95%, d.r. = 95:5. $[\alpha]_D^{17.2}$ = +61.3 (c = 0.80 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 1.4 Hz, 1H), 7.38 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.31 (dd, *J* = 12.8, 5.6 Hz, 3H), 7.24 (s, 2H), 6.59 (d, *J* = 8.3 Hz, 1H), 5.36 (s, 1H), 4.96 (d, *J* = 15.6 Hz, 1H), 4.70 (d, *J* = 15.6 Hz, 1H), 3.83 (s, 3H), 3.32 (dd, *J* = 7.1 Hz, 1H), 1.00 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.63, 171.46, 164.72, 142.19, 134.62, 133.79, 129.02, 128.55, 127.51, 127.32, 116.10, 111.12, 90.00, 82.13, 76.77, 56.60, 44.06, 37.44, 10.07. HRMS (SEI-TOF) calcd for $C_{21}H_{18}Br^{80.9163}NNaO_4$ ([M+Na^+]) = 452.0296, Found 452.0296.



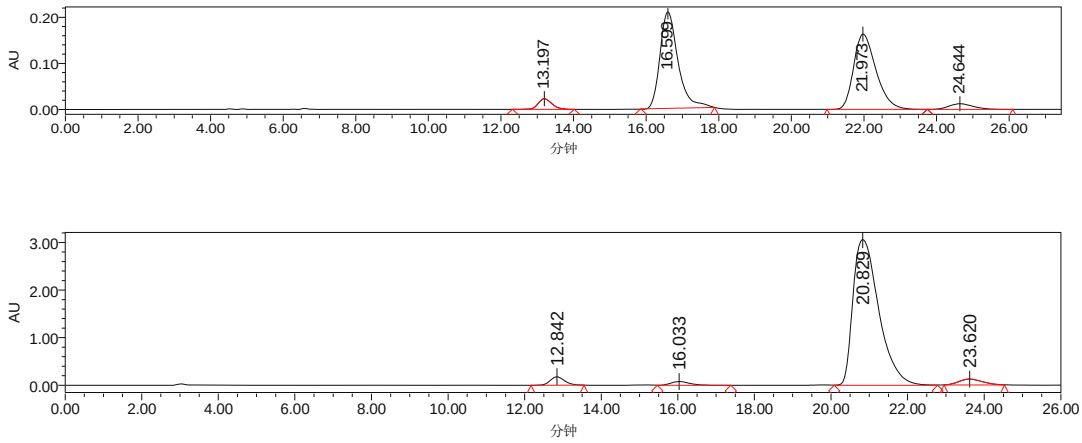
	Retention Time	% Area
1	20.98	3.17
2	22.64	93.82
3	29.03	1.60
4	36.27	1.41

(2′*R*,3′*R*)-1-benzyl-6-bromo-4'-methoxy-3'-methylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione **4f**



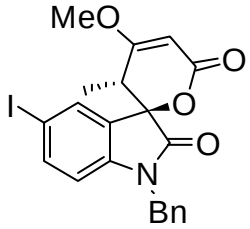
4f

White solid; m. p. 150-152 °C; HPLC (Chiralcel ADH, hexane/*i*-PrOH = 80/20, flow rate = 1.0 ml/min, λ = 254 nm), retention time: t_{r1} = 12.84 min, t_{r2} = 16.03 min, t_{r3} = 20.83 min t_{r4} = 23.62 min, ee = 98%, d.r. = 94:6. $[\alpha]_D^{15.7}$ = +45.0 (c = 0.76 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 2H), 7.24 – 7.21 (m, 1H), 7.19 (dd, *J* = 4.5, 2.7 Hz, 3H), 7.15 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.81 (dd, *J* = 12.5, 1.5 Hz, 1H), 5.28 (s, 1H), 4.88 (d, *J* = 15.7 Hz, 1H), 4.59 (d, *J* = 15.7 Hz, 1H), 3.75 (s, 3H), 3.23 (q, *J* = 7.1 Hz, 1H), 0.91 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.99, 171.48, 164.89, 144.49, 134.57, 129.07, 128.11, 127.32, 126.47, 125.59, 125.46, 124.76, 112.95, 90.02, 81.99, 56.57, 44.09, 37.43, 10.02. HRMS (SEI-TOF) calcd for $C_{21}H_{18}Br^{80.9163}NNaO_4$ ([M+Na^+]) = 452.0296, Found 452.0297.



	Retention Time	% Area
1	12.84	2.98
2	16.03	1.70
3	20.83	91.97
4	23.62	3.35

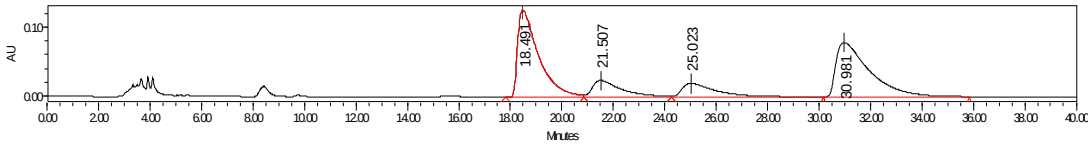
(2′*R*,3′*R*)-1-benzyl-5-iodo-4'-methoxy-3'-methylspiro[indoline-3,2'-pyran]-2,6'(3'H)-di one **4h**

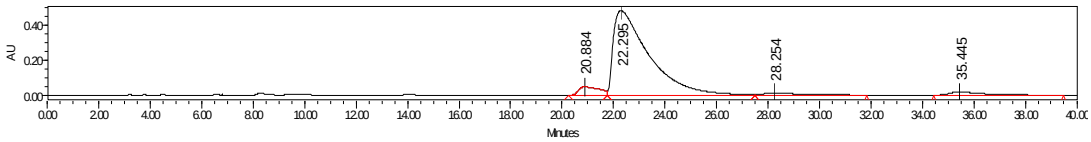


4h

White solid; m. p. 156-158 °C ; HPLC (Chiralcel IB, hexane/*i*-PrOH = 80/20, flow rate = 1.0 ml/min, λ = 254 nm), rentention time: t_{r1} = 20.88 min, t_{r2} = 22.30 min, t_{r3} = 28.25 min, t_{r4} = 35.45 min, ee = 96%, d.r. = 92:8. $[\alpha]_D^{18.1}$ = +70.8 (c = 0.70 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.58 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.31 (dd, *J* = 12.7, 5.4 Hz, 3H), 7.24 (d, *J* = 7.8 Hz, 2H), 6.51 (dd, *J* = 13.9, 8.3 Hz, 1H), 5.36 (s, 1H), 4.94 (d, *J* = 15.7 Hz, 1H), 4.69 (d, *J* = 15.6 Hz, 1H), 3.83 (s, 3H), 3.32 (dd, *J* = 7.1 Hz, 1H), 1.00 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.47, 171.45, 164.73, 142.89, 139.72, 134.62, 133.04, 129.01,

128.80, 128.06, 127.33, 111.61, 89.99, 85.82, 82.00, 56.60, 44.01, 37.40, 10.05. HRMS (SEI-TOF) calcd for $C_{21}H_{18}INNaO_4$ ([M+Na$^+$]) = 498.0178, Found 498.0176.

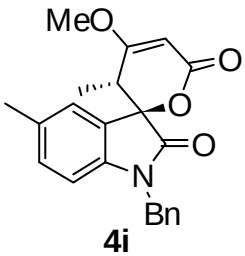




	Retention Time	% Area
1	20.88	5.07
2	22.30	90.39
3	28.25	1.87
4	35.45	2.68

(2′*R*,3′*R*)-1-benzyl-4'-methoxy-3',5-dimethylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione

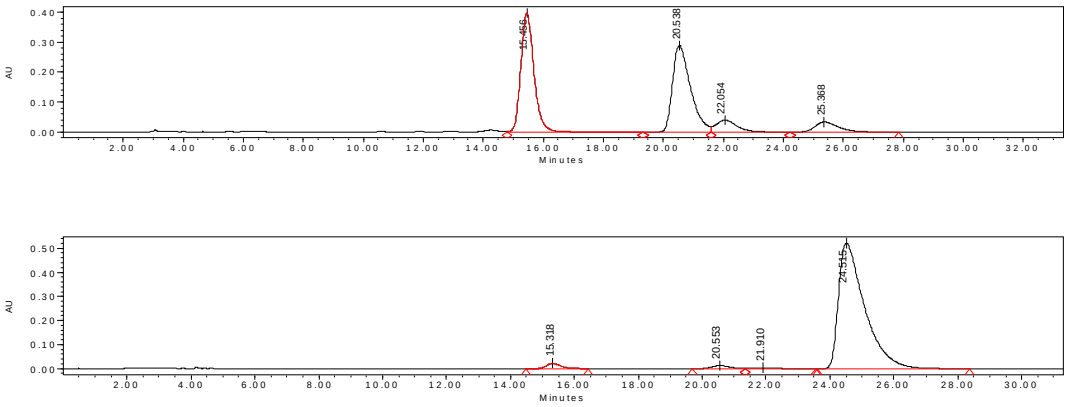
4i



4i

White solid; m. p. 110-112 °C; HPLC (Chiralcel ADH, hexane/*i*-PrOH = 80/20, flow rate = 1.0 ml/min, λ = 254 nm), rentention time: t_{r1} = 15.32 min, t_{r2} = 20.55 min, t_{r3} = 21.91 min, t_{r4} = 24.52 min, ee = 98%, d.r. = 96:4. $[\alpha]_D^{13.9}$ = +50.7 (c = 0.68 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 2H), 7.40 (d, *J* = 4.4 Hz 3H), 7.35 (s, 1H), 7.18 (d, *J* = 7.9 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 5.49 (s, 1H), 5.08 (d, *J* = 15.6 Hz, 1H), 4.81 (d, *J* = 15.6 Hz, 1H), 3.95 (s, 3H), 3.46 (dd, *J* = 7.2 Hz, 1H), 2.43 (s, 3H), 1.11 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.11, 171.72,

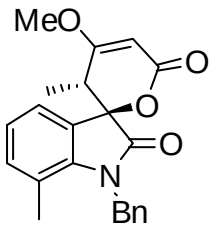
165.31, 140.76, 135.27, 133.21, 131.16, 128.86, 127.80, 127.37, 126.61, 124.86, 109.32, 90.04, 82.61, 56.48, 43.96, 37.51, 21.06, 10.06. HRMS (SEI-TOF) calcd for $C_{22}H_{21}NKO_4$ ([M+K^+]) = 402.1108, Found 402.1103.



	Retention Time	% Area
1	15.32	2.25
2	20.55	1.66
3	21.91	0.65
4	24.52	95.43

(2′*R*,3′*R*)-1-benzyl-4'-methoxy-3',7-dimethylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione

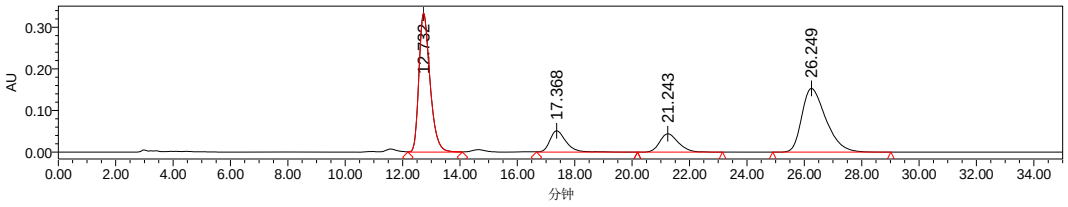
4j

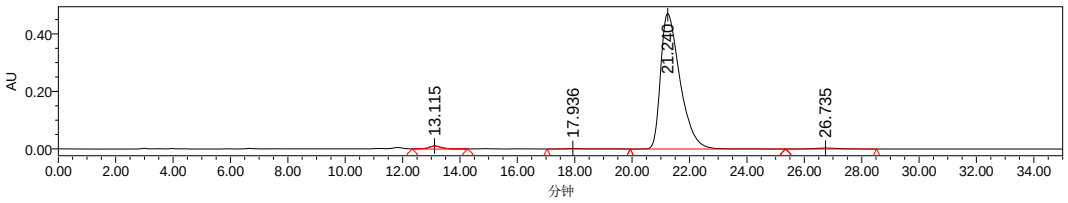


4j

White solid; m. p. 128-130 °C ; HPLC (Chiralcel ADH, hexane/*i*-PrOH =70/30, flow rate = 1.0 mL/min, λ = 254 nm), retention time: t_{r1} = 13.12 min, t_{r2} = 17.94 min, t_{r3} = 21.24 min t_{r4} = 26.74 min, ee = 99%, d.r. = 98:2. $[\alpha]_D^{14.8}$ = +50.2 (c = 0.43 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 3H), 7.24 (d, *J* = 7.3 Hz, 1H), 7.16 (d, *J* = 7.2 Hz, 2H), 7.07 – 6.99 (m, 2H), 5.35 (s, 1H), 5.11 (s, 2H), 3.81 (s, 3H), 3.36 (dd, *J* = 7.1 Hz, 1H), 2.26 (s, 3H), 1.01 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz,

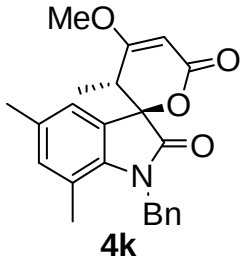
$CDCl_3$) δ 173.24, 171.61, 165.35, 141.31, 136.93, 134.92, 128.95, 127.39, 125.74, 123.63, 122.13, 120.28, 99.99, 90.10, 81.91, 56.46, 45.20, 37.64, 18.72, 10.11. HRMS (SEI-TOF) calcd for $C_{22}H_{21}NNaO_4$ ([M+Na^+]) = 386.1368, Found 386.1370.





Retention Time	% Area
13.12	1.41
17.94	0.34
21.24	97.48
26.74	0.77

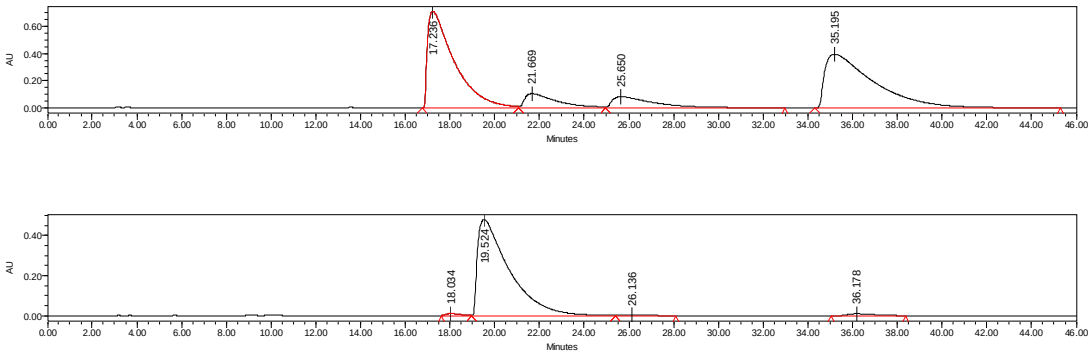
(2′*R*,3′*R*)-1-benzyl-4'-methoxy-3',5,7-trimethylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione **4k**



4k

White solid; m. p. 179-181 °C ; HPLC (Chiralcel IB, hexane/*i*-PrOH = 80/20, flow rate = 1.0 ml/min, λ = 254 nm), retention time: t_{r1} = 18.03 min, t_{r2} = 19.52 min, t_{r3} = 26.14 min, t_{r4} = 36.18 min, ee = 98%, d.r. = 98:2. $[\alpha]_D^{15.6}$ = +14.8 (c = 0.56 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.3 Hz, 2H), 7.25 – 7.20 (m, 1H), 7.15 (d, *J* = 7.3 Hz, 2H), 7.10 (s, 1H), 6.84 (s, 1H), 5.34 (s, 1H), 5.08 (s, 2H),

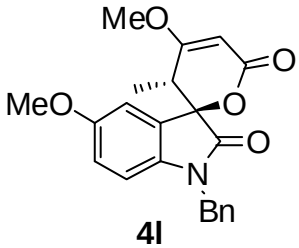
3.80 (s, 3H), 3.35 (dd, J = 7.1 Hz, 1H), 2.28 (s, 3H), 2.20 (s, 3H), 1.02 (d, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.21, 171.65, 165.40, 138.81, 137.01, 135.30, 133.23, 128.91, 127.40, 127.33, 125.76, 122.82, 119.98, 90.06, 82.11, 56.45, 45.12, 37.60, 20.74, 18.55, 10.12. HRMS (SEI-TOF) calcd for $C_{23}H_{23}NNaO_4$ ([M+Na$^+$]) = 400.1525, Found 400.1521.



	Retention Time	% Area
1	18.03	1.20
2	19.52	96.06
3	26.14	0.79
4	36.18	1.94

(2′*R*,3′*R*)-1-benzyl-4',5-dimethoxy-3'-methylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione

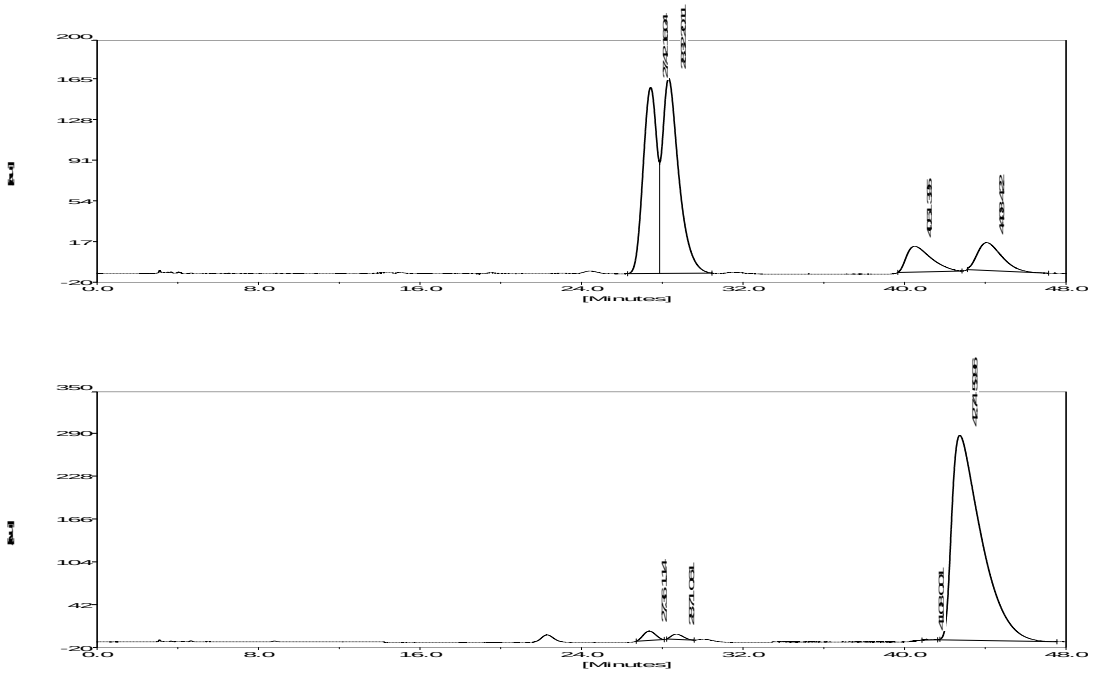
4l



4l

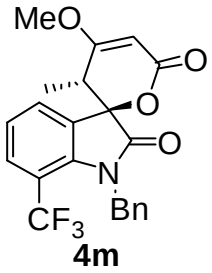
White solid; m. p. 122-124 °C; HPLC (Chiralcel ADH, hexane/*i*-PrOH = 80/20, flow rate = 1.0 ml/min, λ = 254 nm), retention time: t_{r1} = 27.36 min, t_{r2} = 28.71 min, t_{r3} = 41.08 min t_{r4} = 42.74 min, ee = 99%, d.r. = 97:3. $[\alpha]_D^{17.1}$ = +65.7 (c = 0.40 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (dt, J = 11.8, 6.1 Hz, 5H), 7.01

(d, *J* = 2.4 Hz, 1H), 6.78 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.61 (d, *J* = 8.6 Hz, 1H), 5.36 (s, 1H), 4.95 (d, *J* = 15.6 Hz, 1H), 4.68 (d, *J* = 15.6 Hz, 1H), 3.82 (s, 3H), 3.75 (s, 3H), 3.32 (dd, *J* = 7.1 Hz, 1H), 1.00 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.93, 171.64, 165.22, 156.50, 136.39, 135.22, 128.89, 127.83, 127.77, 127.37, 115.42, 111.18, 110.17, 90.04, 82.75, 56.49, 55.85, 44.04, 37.65, 10.03. HRMS (SEI-TOF) calcd for $C_{22}H_{22}NO_5$ ([M+H$^+$]) = 380.1498, Found 380.1494.



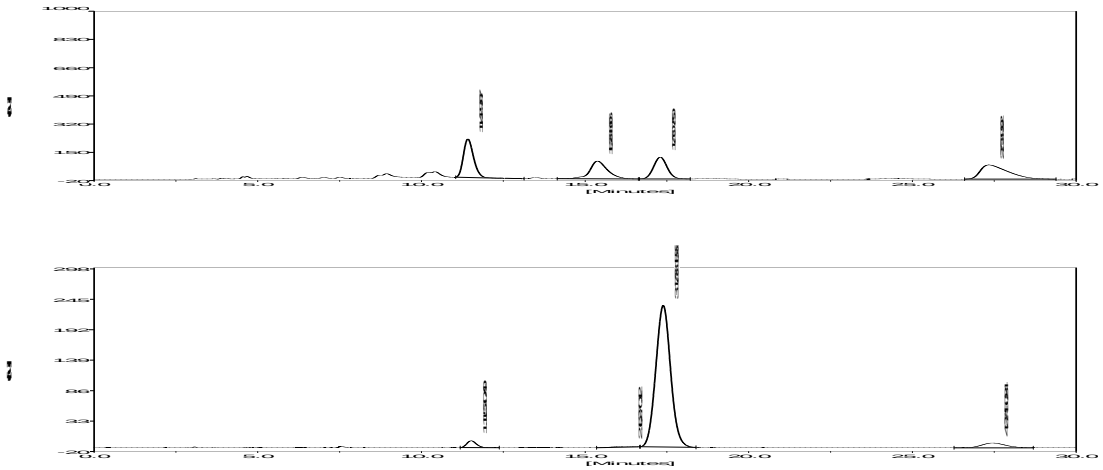
	Retention Time	% Area
1	27.36	1.84
2	28.71	0.98
3	41.08	0.22
4	42.74	96.96

(2′*R*,3′*R*)-1-benzyl-4'-methoxy-3'-methyl-7-(trifluoromethyl)spiro[indoline-3,2'-pyran]-2,6'(3'H)-dione **4m**



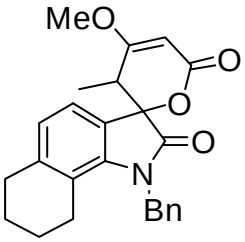
4m

White solid; m. p. 120-122 °C ; HPLC (Chiralcel ADH, hexane/*i*-PrOH = 80/20, flow rate = 1.0 ml/min, λ = 254 nm), retention time: t_{r1} = 11.53 min, t_{r2} = 16.27 min, t_{r3} = 17.38 min， t_{r4} = 27.45 min, ee = 98%, d.r. = 92:8. $[\alpha]_D^{15.4}$ = +51.1 (c = 0.80 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (t, *J* = 8.2 Hz, 2H), 7.29 – 7.12 (m, 6H), 5.34 (s, 1H), 5.17 (d, *J* = 16.8 Hz, 1H), 5.06 (d, *J* = 16.8 Hz, 1H), 3.79 (s, 3H), 3.36 (dd, *J* = 7.0 Hz, 1H), 0.95 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.53, 171.16, 164.68, 141.76, 135.52, 129.53, 129.18, 129.12, 128.48, 128.00, 127.17, 125.94, 123.24, 113.34, 90.03, 80.28, 56.59, 46.01, 37.65, 9.85. HRMS (SEI-TOF) calcd for $C_{22}H_{18}F_3NNaO_4$ ([M+Na^+]) = 440.1086, Found 440.1089.



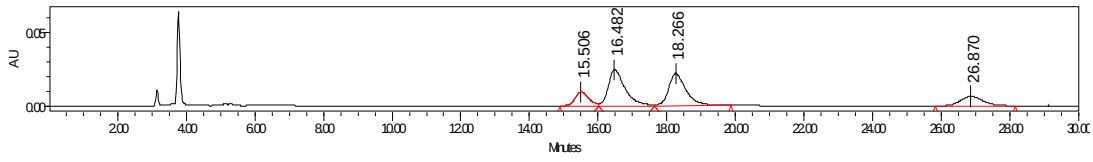
	Retention Time	% Area
1	11.53	2.90
2	16.27	0.71
3	17.38	91.46
4	27.45	4.93

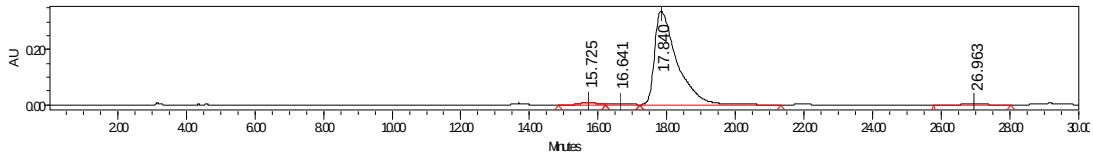
1-benzyl-4'-methoxy-3'-methyl-6,7,8,9-tetrahydrospiro[benzo[g]indole-3,2'-pyran]-2,6'(1H,3'H)-dione **4n**



4n

White solid; m. p. 109-111 °C; HPLC (Chiralcel ADH, hexane/*i*-PrOH = 80/20, flow rate = 1.0 ml/min, λ = 254 nm), retention time: t_{r1} = 15.73 min, t_{r2} = 16.64 min, t_{r3} = 17.84 min, t_{r4} = 26.96 min, ee = 96%, d.r. = 96:4. $[\alpha]_D^{19.9}$ = +11.6 (c = 0.81 in CH_2Cl_2), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (t, *J* = 7.3 Hz, 2H), 7.18-7.14 (m, 1H), 7.09 (t, *J* = 7.0 Hz, 3H), 6.79 (d, *J* = 7.7 Hz, 1H), 5.26 (s, 1H), 5.06 (s, 2H), 3.72 (s, 3H), 3.26 (dd, *J* = 7.1 Hz, 1H), 2.74 – 2.60 (m, 4H), 1.66 – 1.47 (m, 4H), 0.95 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.86, 171.73, 165.54, 141.76, 141.40, 137.28, 128.90, 127.27, 125.71, 124.91, 124.38, 121.22, 121.06, 90.09, 81.84, 56.42, 45.86, 37.57, 30.61, 24.90, 22.72, 21.94, 10.19. HRMS (SEI-TOF) calcd for $C_{25}H_{25}NNaO_4$ ([M+Na$^+$]) = 426.1681, Found 426.1683.

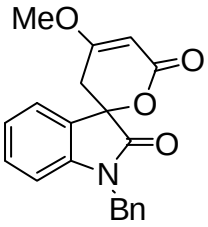




	Retention Time	% Area
1	15.73	1.93
2	16.64	1.21
3	17.84	95.76

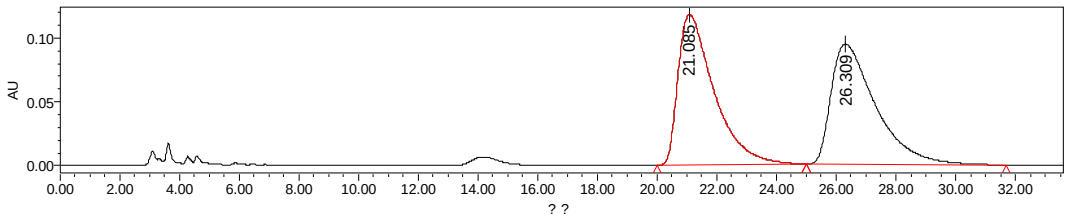
4	26.96	1.11

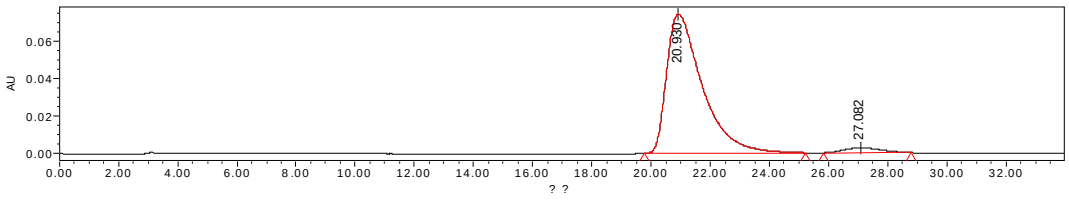
1-benzyl-4'-methoxyspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione **5a**



5a

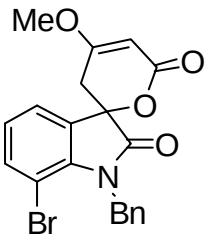
White solid; m. p. 126-128 °C ; HPLC (Chiralcel ODH, hexane/*i*-PrOH= 75/25, flow rate = 1.0 ml/min, λ = 254 nm), retention time: t_{r1} = 20.93 min, t_{r2} = 27.08 min, ee = 93%, $[\alpha]_D^{22.0}$ = +33.8 (c = 0.55 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.4 Hz, 1H), 7.31 (dt, *J* = 15.6, 7.7 Hz, 5H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 7.9 Hz, 1H), 5.42 (s, 1H), 4.88 (s, 2H), 3.86 (s, 3H), 3.08 (d, *J* = 17.4 Hz, 1H), 2.78 (d, *J* = 17.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.55, 169.92, 164.97, 142.25, 134.83, 131.02, 128.98, 127.94, 127.63, 127.27, 124.05, 123.48, 110.01, 90.66, 78.36, 56.43, 44.02, 33.58. HRMS (SEI-TOF) calcd for $C_{20}H_{17}NNaO_4$ ([M+Na$^+$]) = 358.1055, Found 358.1053.





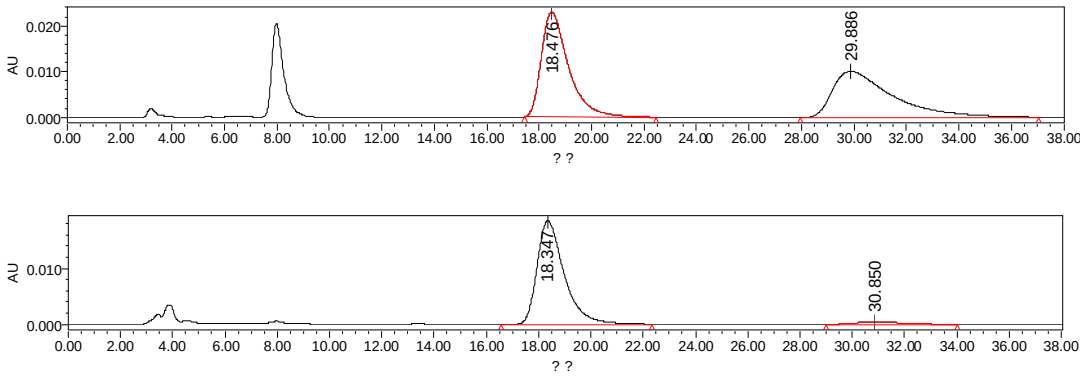
	Retention Time	% Area
1	20.93	96.51
2	27.08	3.49

1-benzyl-7-bromo-4'-methoxyspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione **5g**



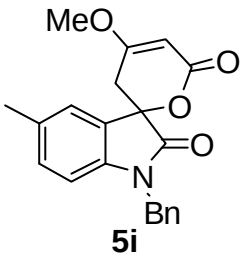
5g

White solid; m. p. 119-121 °C ; HPLC (Chiralcel ODH, hexane/*i*-PrOH = 70/30, flow rate = 1.0 ml/min, λ = 254 nm), retention time: t_{r1} = 18.35 min, t_{r2} = 30.85 min, ee = 90%, $[\alpha]_D^{23.9}$ = +10.0 (c = 0.75 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.39 (m, 2H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.28 – 7.22 (m, 1H), 7.19 (d, *J* = 7.3 Hz, 2H), 6.94 (t, *J* = 7.8 Hz, 1H), 5.44 – 5.28 (m, 3H), 3.84 (s, 3H), 2.98 (d, *J* = 17.5 Hz, 1H), 2.83 (d, *J* = 17.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.57, 169.45, 164.59, 139.87, 136.94, 136.41, 130.80, 128.74, 127.38, 126.26, 124.87, 123.33, 103.21, 90.63, 56.48, 44.75, 33.77. HRMS (SEI-TOF) calcd for $C_{20}H_{16}Br^{78.9163}NNaO_4$ ([M+Na^+]) = 436.0160, Found 436.0161.



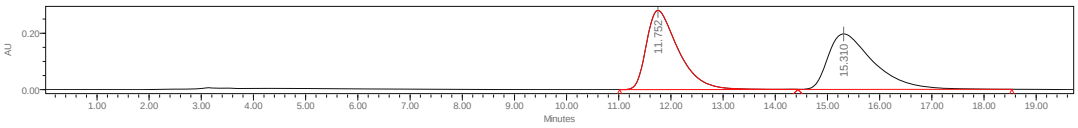
	Retention Time	% Area
1	18.35	95.41
2	30.85	4.59

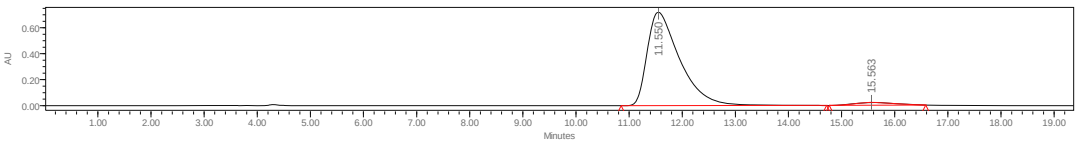
1-benzyl-4'-methoxy-5-methylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione **5i**



5i

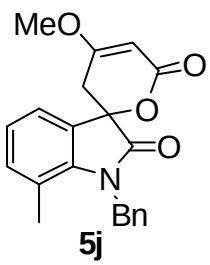
White solid; m. p. 129-131 °C ; HPLC (Chiralcel ODH, hexane/*i*-PrOH= 70/30, flow rate=1.0 ml/min, λ = 254 nm), retention time: t_{r1} = 11.55 min, t_{r2} = 15.56 min, ee = 93%, $[\alpha]_D^{21.3}$ = +14.8 (c = 0.54 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.23 (m, 6H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 5.42 (s, 1H), 4.86 (s, 2H), 3.86 (s, 3H), 3.07 (d, *J* = 17.4 Hz, 1H), 2.77 (d, *J* = 17.4 Hz, 1H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.54, 169.97, 165.08, 139.77, 134.96, 133.21, 131.23, 128.93, 127.87, 127.65, 127.25, 124.76, 109.79, 90.66, 78.53, 56.43, 44.00, 33.59, 21.05. HRMS (SEI-TOF) calcd for $C_{21}H_{19}NNaO_4$ ([M+Na^+]) = 372.1212, Found 372.1212.





	Retention Time	% Area
1	11.55	96.53
2	15.56	3.47

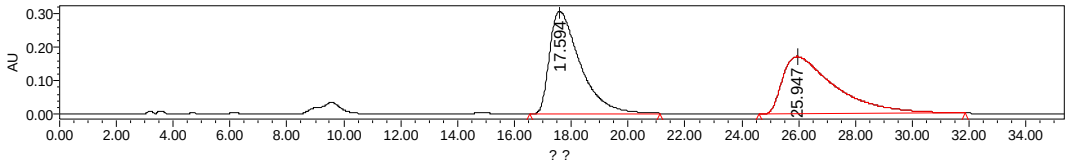
1-benzyl-4'-methoxy-7-methylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione **5j**

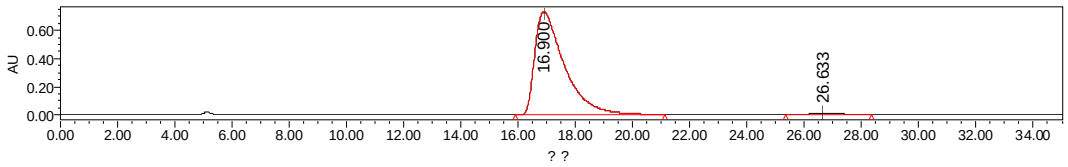


5j

White solid; m. p. 138-140 °C ; HPLC (Chiralcel ODH, hexane/*i*-PrOH = 70/30, flow rate = 1.0 ml/min, λ = 254 nm), t_{r1} = 16.90 min, t_{r2} = 26.63 min, ee = 97%. $[\alpha]_D^{23.0}$ = +23.2 (c = 0.64 in

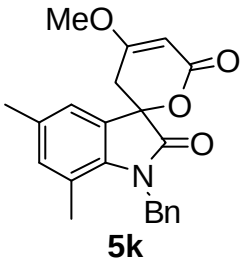
CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 16.4, 7.7 Hz, 3H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 7.4 Hz, 2H), 7.03 (d, *J* = 7.5 Hz, 1H), 6.96 (dd, *J* = 4.6 Hz, 1H), 5.41 (s, 1H), 5.14 (q, *J* = 16.8 Hz, 2H), 3.84 (s, 3H), 3.02 (d, *J* = 17.4 Hz, 1H), 2.84 (d, *J* = 17.4 Hz, 1H), 2.24 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 173.81, 169.75, 165.10, 140.22, 136.63, 134.95, 129.04, 128.42, 127.47, 125.59, 123.65, 122.03, 120.80, 90.68, 77.76, 56.38, 45.20, 33.91, 18.75. HRMS (SEI-TOF) calcd for $C_{21}H_{19}NNaO_4$ ([M+Na^+]) = 372.1212 Found 372.1213.





	Retention Time	% Area
1	16.90	98.69
2	26.63	1.31

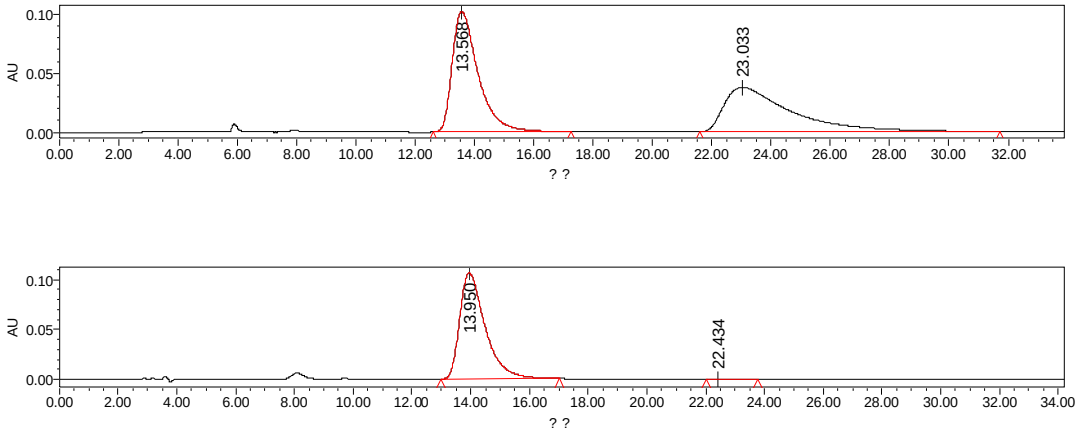
1-benzyl-4'-methoxy-5,7-dimethylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione **5k**



5k

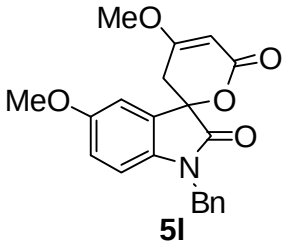
White solid; m. p. 160-162 °C; HPLC (Chiralcel ODH, hexane/*i*-PrOH = 70/30, flow rate = 1.0 ml/min, λ = 254 nm), t_{r1} = 13.95 min, t_{r2} = 22.43 min, ee = 99%. $[\alpha]_D^{24.2}$ = +27.1 (c = 0.62 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.3 Hz, 2H), 7.24 (d, *J* = 7.4 Hz, 1H), 7.19 – 7.07 (m, 3H), 6.83 (s, 1H), 5.41 (s, 1H), 5.12 (q, *J* = 16.8 Hz, 2H), 3.85 (s, 3H), 3.01 (d, *J* = 15.6 Hz, 1H), 2.84 (d, *J* = 15.6 Hz, 1H),

2.25 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.80, 169.79, 165.20, 137.70, 136.70, 135.33, 133.29, 129.00, 128.48, 127.42, 125.60, 122.68, 120.50, 90.68, 77.93, 56.38, 45.14, 33.92, 20.73, 18.59. HRMS (SEI-TOF) calcd for $C_{22}H_{21}NNaO_4$ ([M+Na$^+$]) = 386.1368, Found 386.1370.



	Retention Time	% Area
1	13.95	99.97
2	22.43	0.03

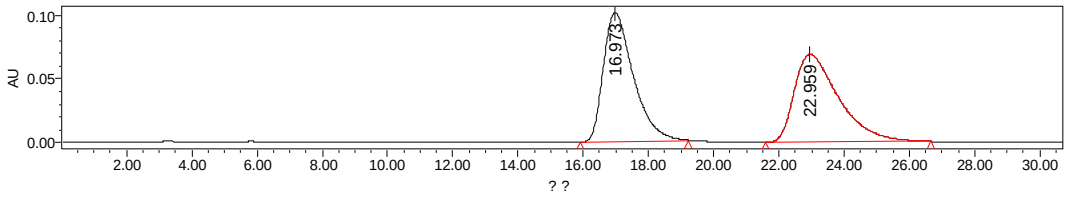
1-benzyl-4',5-dimethoxyspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione **5l**

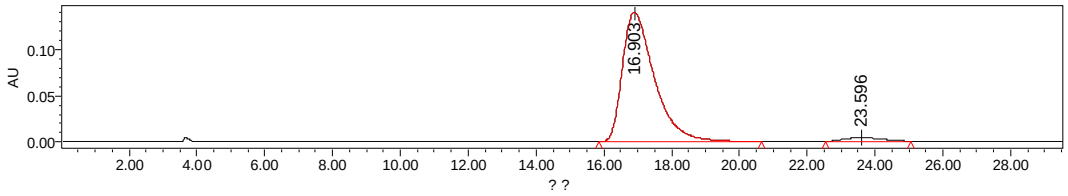


5l

White solid; m. p. 116-118 °C; HPLC (Chiralcel ODH, hexane/*i*-PrOH = 70/30, flow rate = 1.0 ml/min, λ = 254 nm), retention time: t_{r1} = 16.90 min, t_{r2} = 23.60 min, ee = 93%, $[\alpha]_D^{22.6}$ = +33.7 (c = 0.44 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 10.1, 4.2 Hz, 2H), 7.28 (s, 2H), 7.27 (s, 1H), 7.07 (d, *J* = 2.5 Hz, 1H), 6.76 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.62 (d, *J* = 8.6 Hz, 1H), 5.41 (s, 1H), 4.85 (s, 2H), 3.85 (s, 3H), 3.73 (s, 3H), 3.07 (d, *J* = 17.4 Hz, 1H), 2.76 (d, *J* = 17.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.34, 169.89, 164.91, 156.35, 135.41, 134.92,

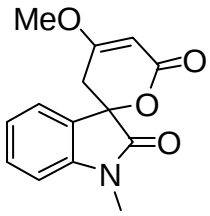
128.95, 128.77, 127.90, 127.25, 114.90, 111.72, 110.53, 90.61, 78.63, 56.43, 55.87, 44.07, 33.63. HRMS (SEI-TOF) calcd for $C_{21}H_{19}NNaO_4$ ([M+Na$^+$]) = 388.1161, Found 388.1154.





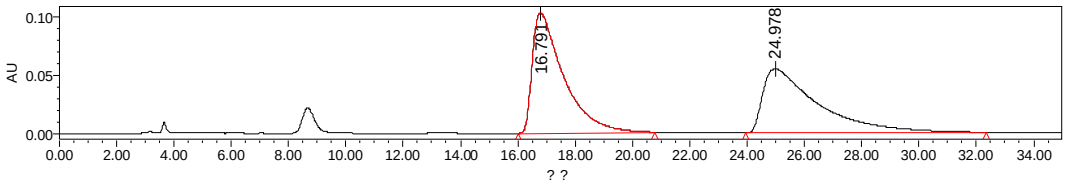
	Retention Time	% Area
1	16.90	96.71
2	23.60	3.29

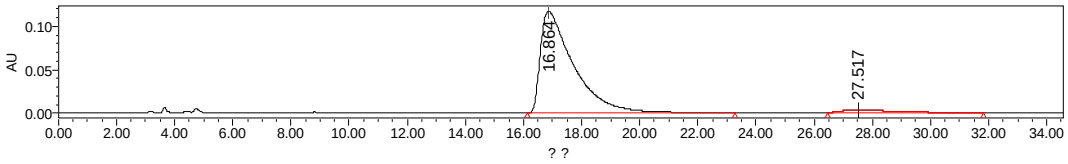
4'-methoxy-1-methylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione **5o**



5o

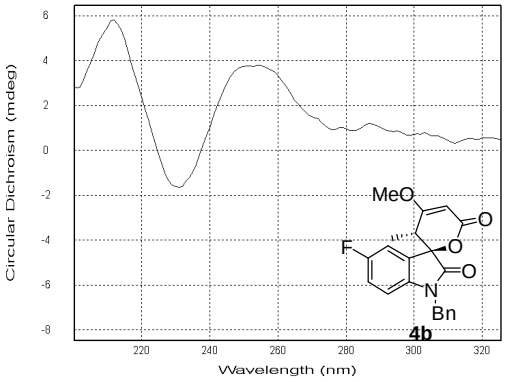
White solid; m. p. 139-141 ^{o}C ; HPLC (Chiralcel ODH, hexane/*i*-PrOH= 70/30, flow rate = 1.0 ml/min, λ = 254 nm), retention time: t_{r1} = 16.86 min, t_{r2} = 27.52 min, ee = 91%. $[\alpha]_D^{22.1}$ = +24.8 (c = 0.31 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 5.39 (s, 1H), 3.85 (s, 3H), 3.20 (s, 3H), 3.02 (d, *J* = 17.4 Hz, 1H), 2.72 (d, *J* = 17.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.32, 169.99, 164.93, 143.18, 131.14, 127.59, 123.95, 123.45, 108.95, 90.61, 78.31, 56.39, 33.35, 26.46. HRMS (SEI-TOF) calcd for $C_{14}H_{13}NNaO_4$ ([M+Na$^+$]) = 282.0742, Found 282.0747.

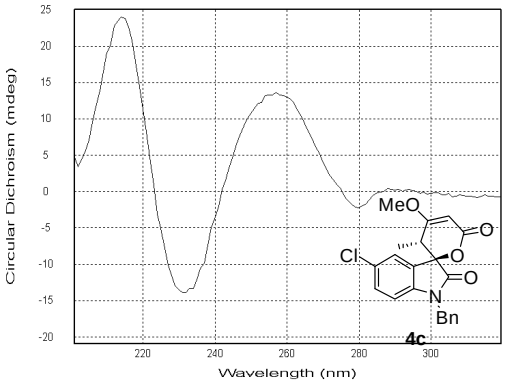


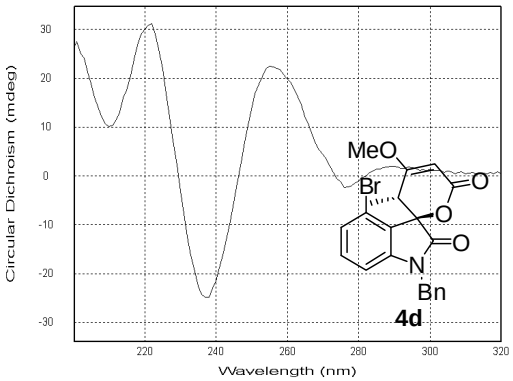


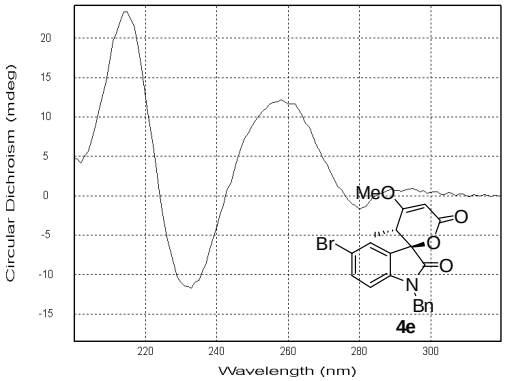
	Retention Time	% Area
1	16.86	95.63
2	27.52	4.37

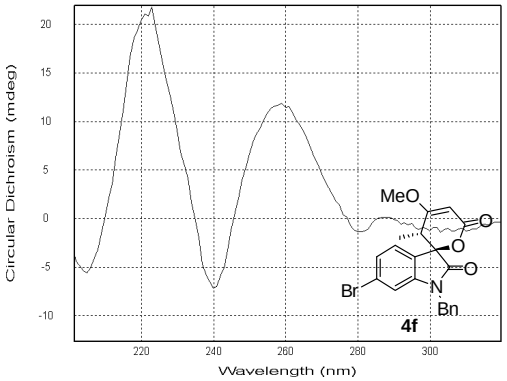
9. Copies of CD spectras for products

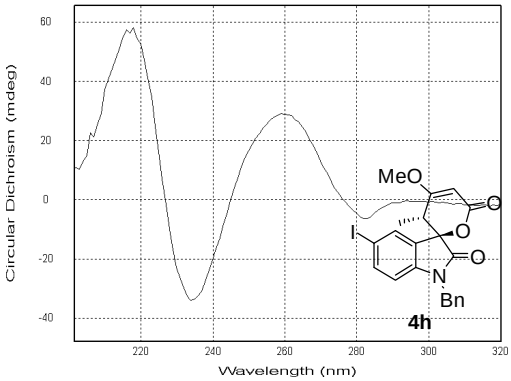


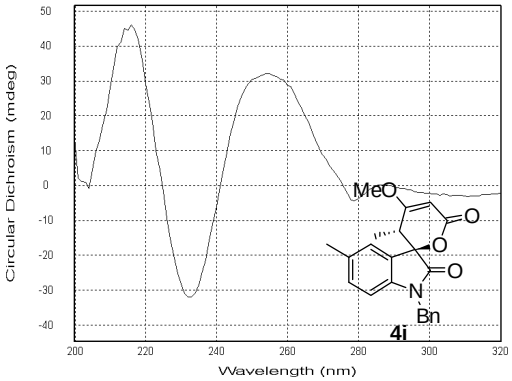


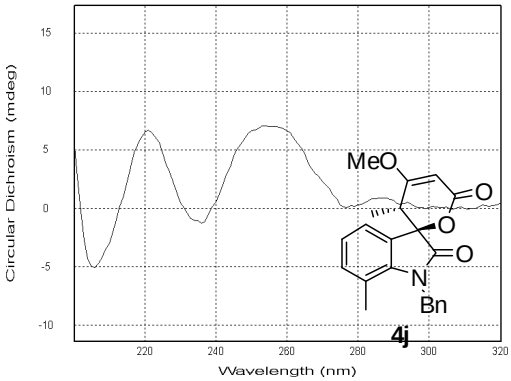


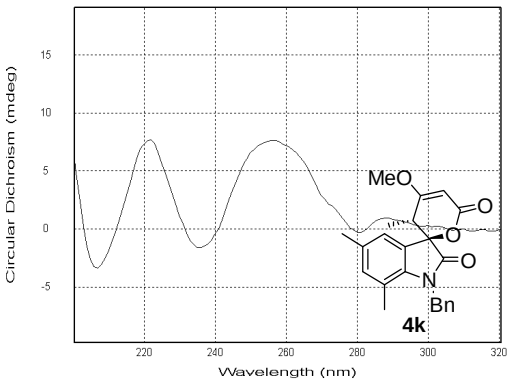


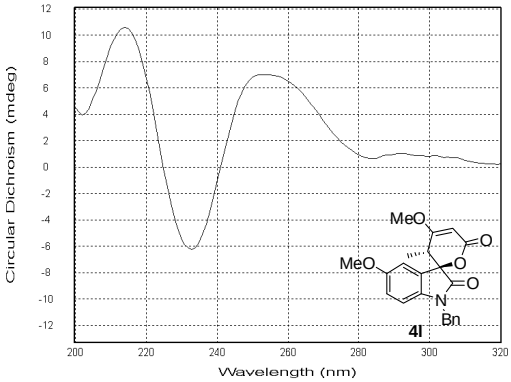

Circular Dichroism (mdeg)
Wavelength (nm)
MeO
Br
Bn
4f

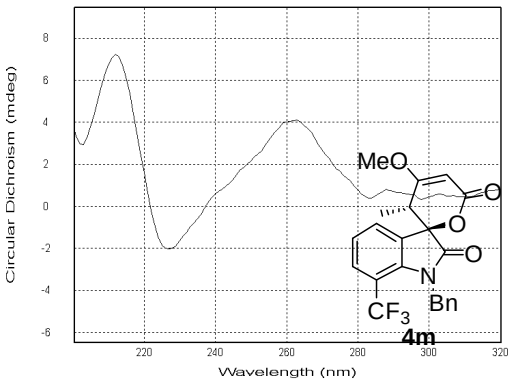

Circular Dichroism (mdeg)
Wavelength (nm)
MeO
I
Bn
4h


Circular Dichroism (mdeg)
Wavelength (nm)
MeO
Bn
4i


Circular Dichroism (mdeg)
Wavelength (nm)
MeO
Bn
4j


Circular Dichroism (mdeg)
Wavelength (nm)
MeO
Bn
4k


Circular Dichroism (mdeg)
Wavelength (nm)
MeO
MeO
Bn
4l


Circular Dichroism (mdeg)
Wavelength (nm)
MeO
CF3
Bn
4m

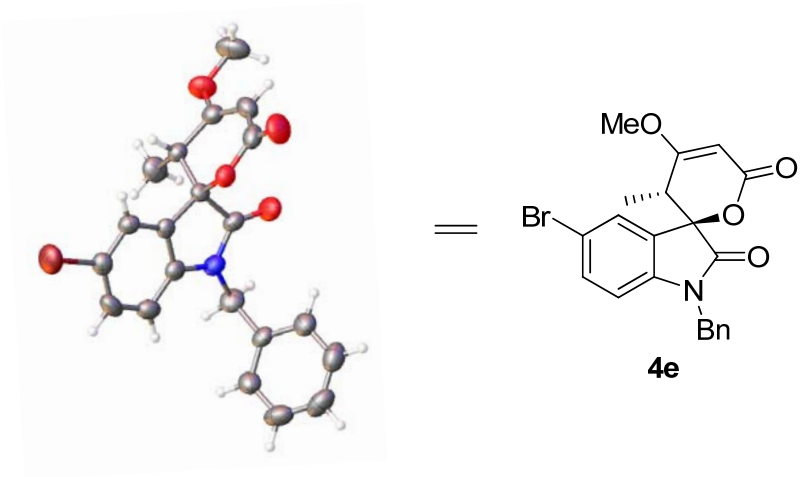
10. Reference

1 (*a*) T. J. Rauls, K. C. Rice, *J. Med. Chem.* 1976, **19**, 887； (*b*) K. Janz, A. Huang, N. Kalia, *J. Med. Chem.* 2007, **50**, 40; (*c*) L. Somogyi, *Bull. Chem. Soc. Jpn.* 2001, **74**, 873; (*d*) K. A. Mamari, H, Ennajih, E. M. Essasi, *Tetrahedron. Lett.* 2012, **53**, 2328.

2 (*a*) J. Savard, P. Brassard, *Tetrahedron. Lett.* 1979, **20**, 4911; b) L. L. Lin, Y. L. Kuang, X. H. Liu, X. M. Feng, *Org. Lett.* 2011, **13**, 3868.

3 J. L. Huang, J. Wang, X. H. Chen, Y. H. Wen, X. H. Liu, X. M. Feng, *Adv. Synth. Catal.* 2008, **350**, 287.

11. The absolute configuration of 4e

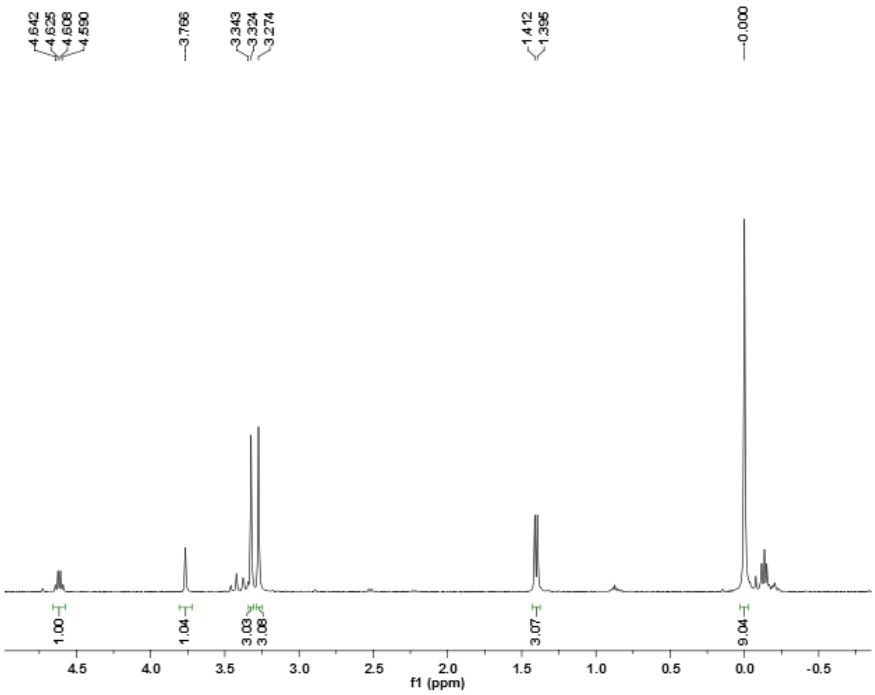


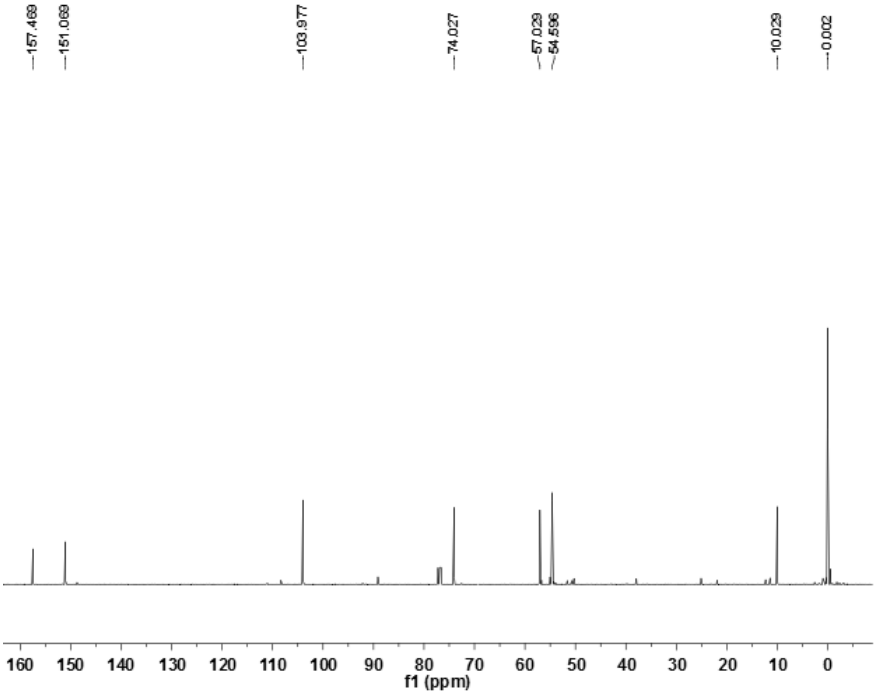
4e

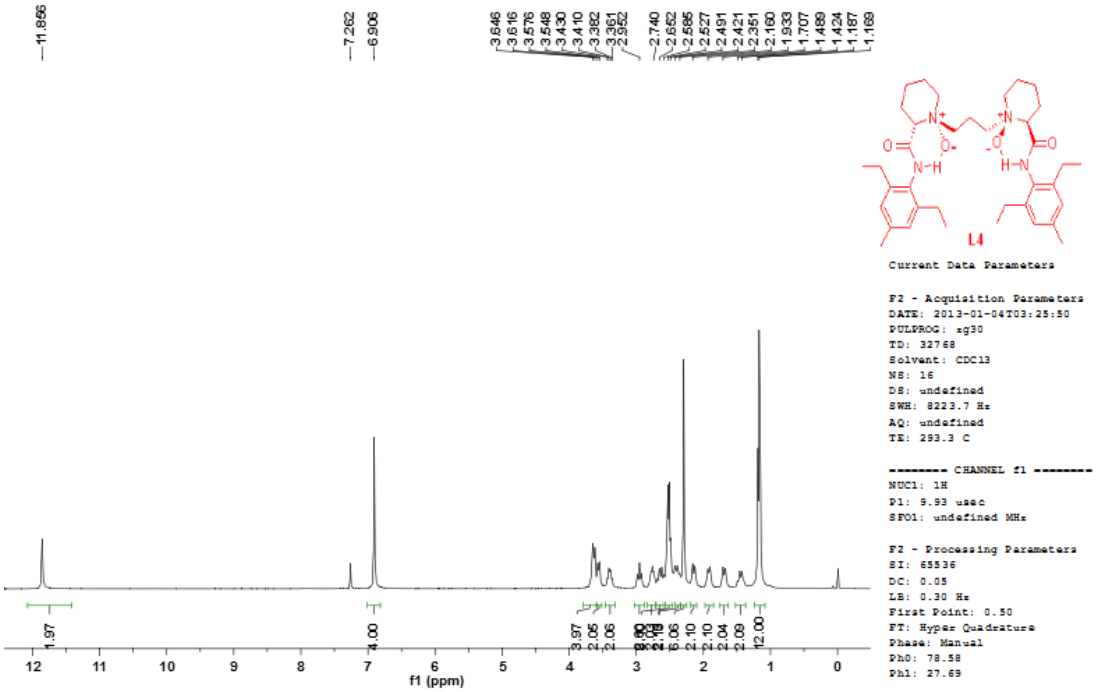
The cycloadduct **4e** was recrystallized from EtOAc and Pet.

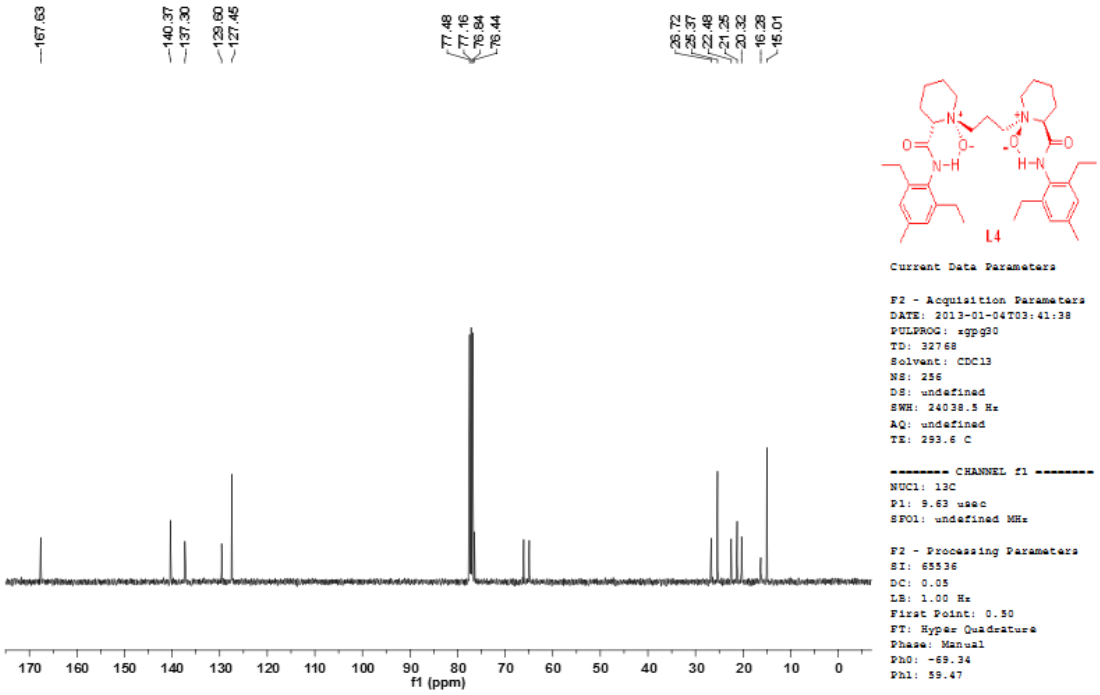
CCDC-959984(**4e**) contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk./ data_request/cif.

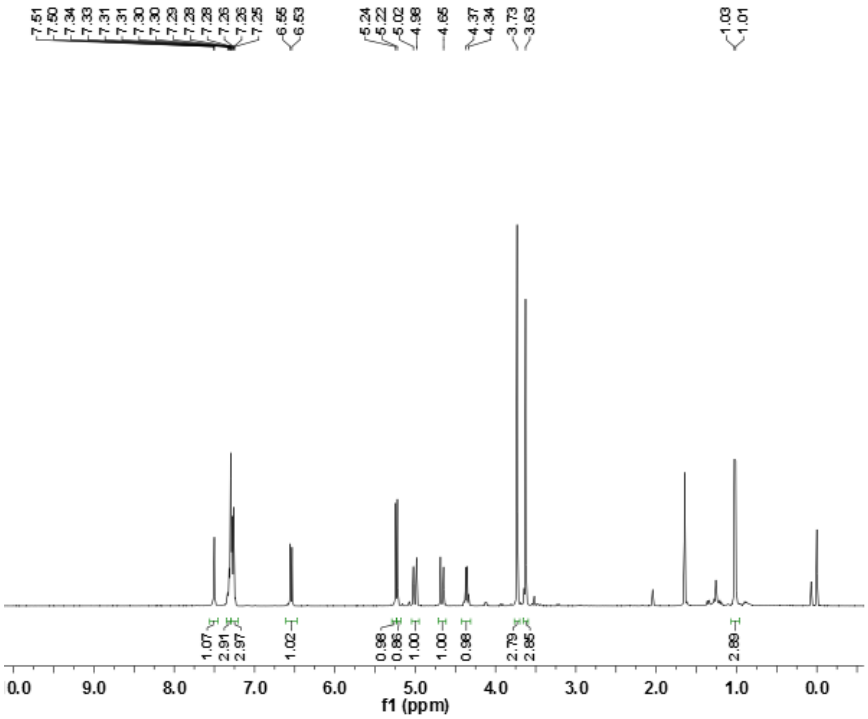
12. Copies of NMR specture


4.642
4.625
4.608
4.590
3.766
3.343
3.324
3.274
1.412
1.395
0.000
OMeOTMS
OMe
1
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2013-02-28T18:46:20
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 293.6 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: 74.27
Ph1: 18.36
1.00
1.04
3.03
3.08
3.07
9.04
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


157.469
151.069
103.977
74.027
57.029
54.596
10.029
0.002
OMeOTMS
OMe
1
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2013-06-26T16:44:42
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
Ph0: -62.89
Ph1: 62.26
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


11.856
7.262
6.906
3.646
3.616
3.576
3.548
3.430
3.410
3.382
3.361
2.952
2.740
2.652
2.586
2.527
2.491
2.421
2.351
2.160
1.933
1.707
1.489
1.424
1.187
1.169
L4
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2013-01-04T03:25:50
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 293.3 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: 78.58
Ph1: 27.69
1.97
4.00
3.97
2.05
2.21
2.06
2.08
2.06
2.10
2.10
2.04
2.09
12.00
f1 (ppm)


167.63
140.37
137.30
129.60
127.45
77.48
77.16
76.84
76.44
26.72
26.37
22.48
21.25
20.32
16.28
15.01
L4
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2013-01-04T03:41:38
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 293.6 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: -69.34
Ph1: 59.47
f1 (ppm)



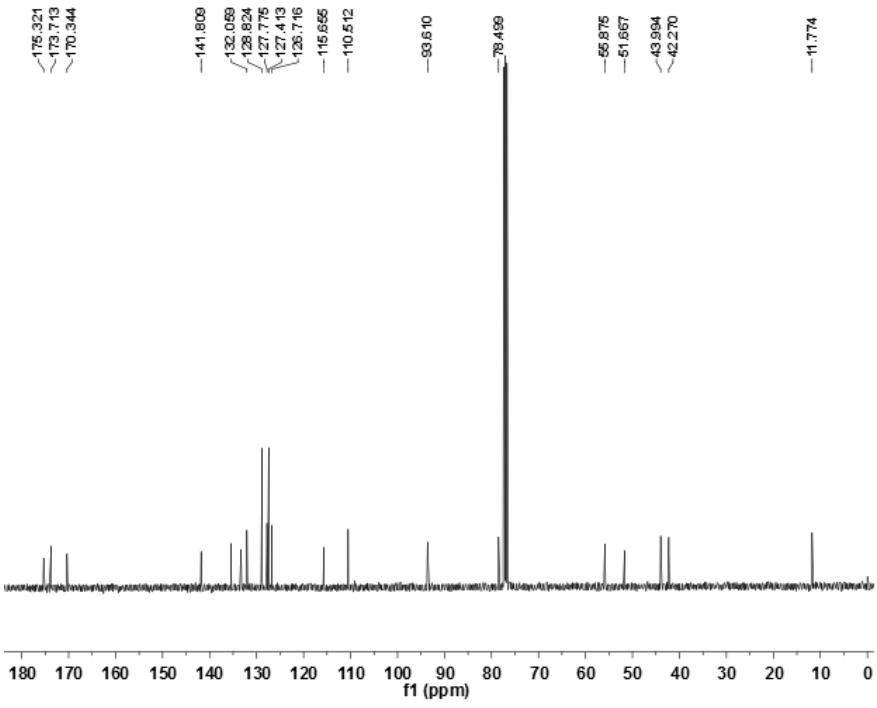
6

Current Data Parameters

F2 - Acquisition Parameters
DATE: 2013-08-31T16:35:25
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 298.7 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: 87.61
Ph1: 11.86



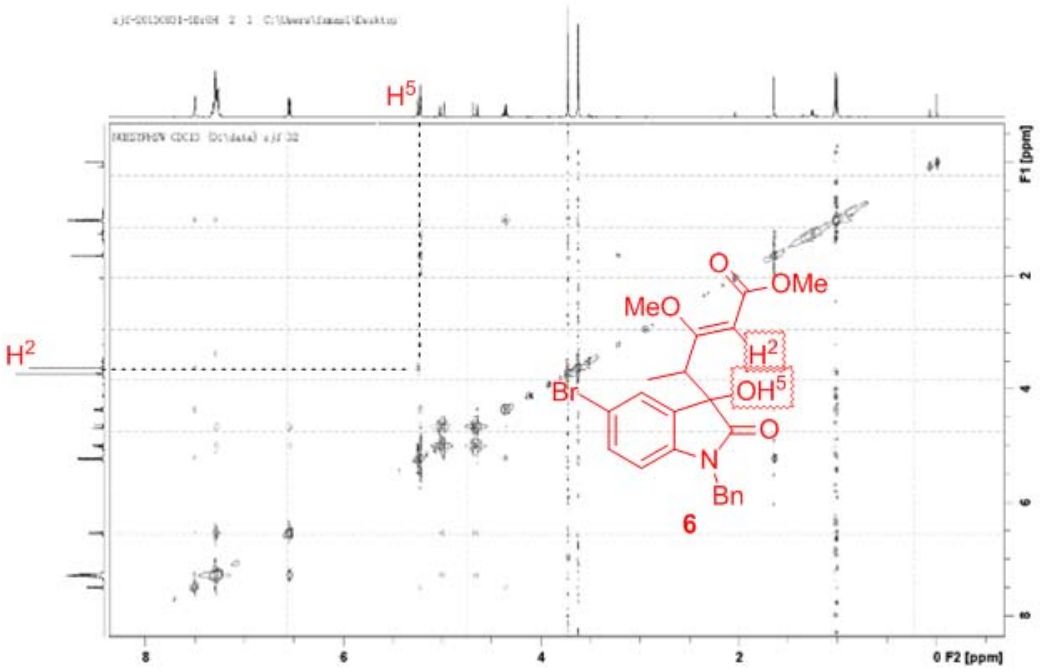
6

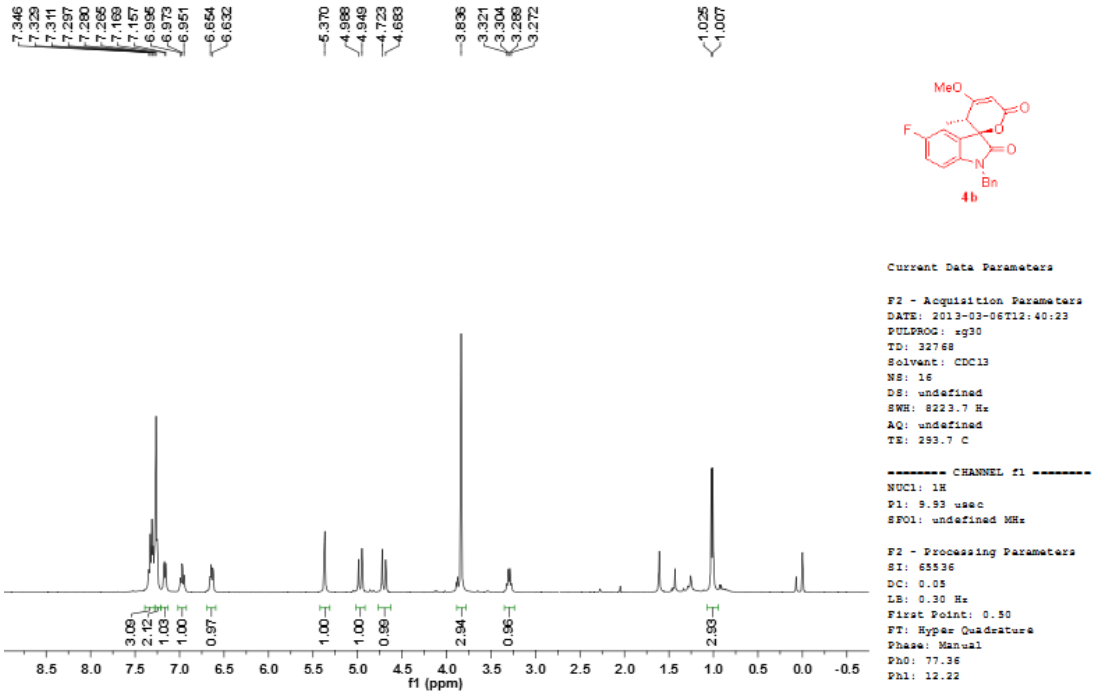
Current Data Parameters

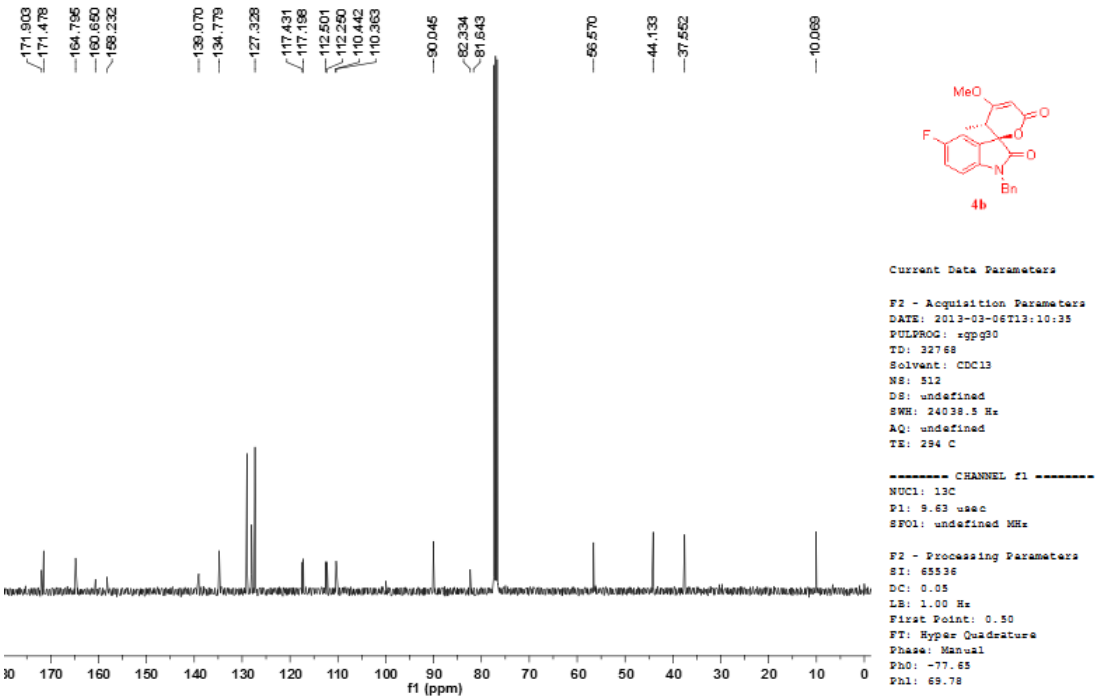
F2 - Acquisition Parameters
DATE: 2013-08-31T17:58:47
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 299 C

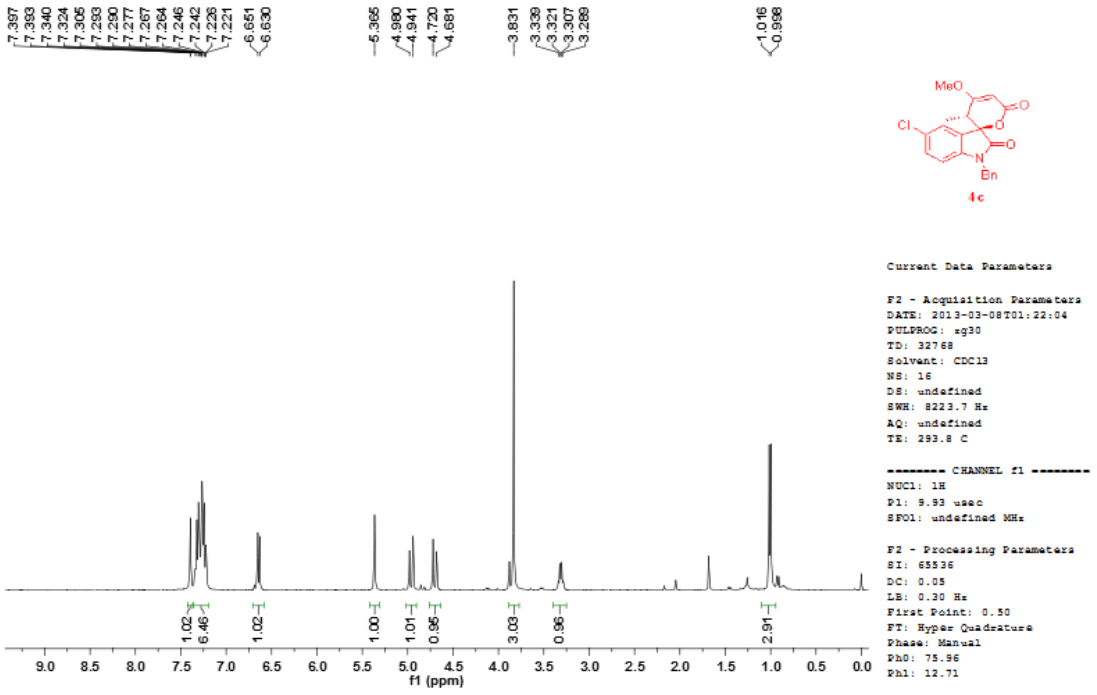
======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

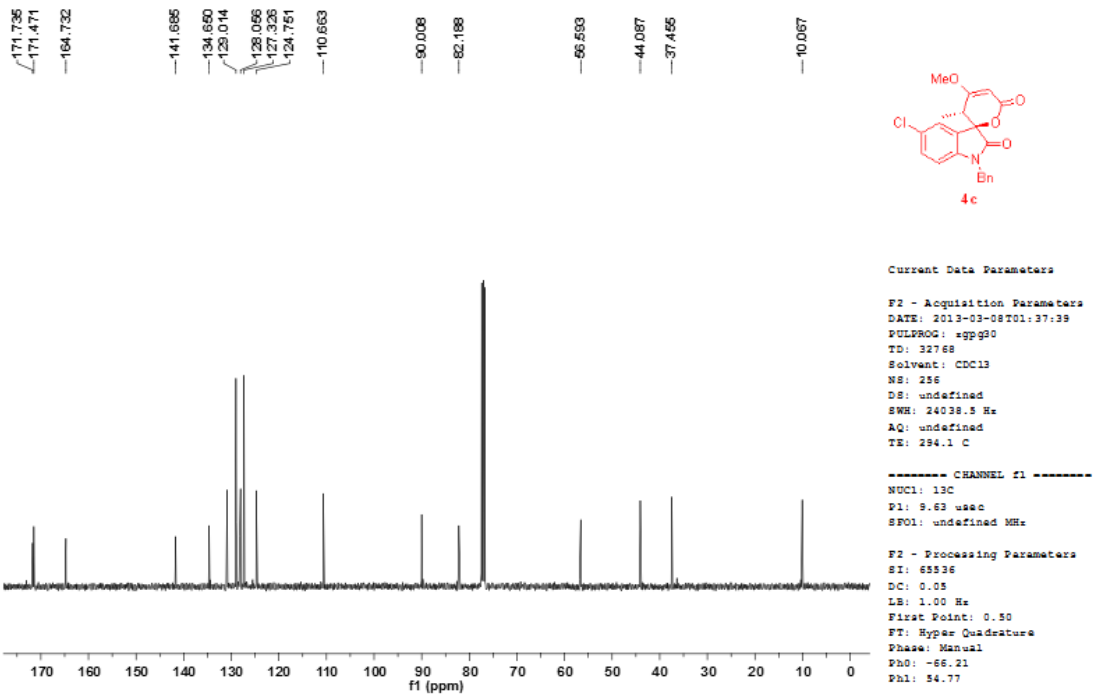
F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -52.64
Ph1: 33.81

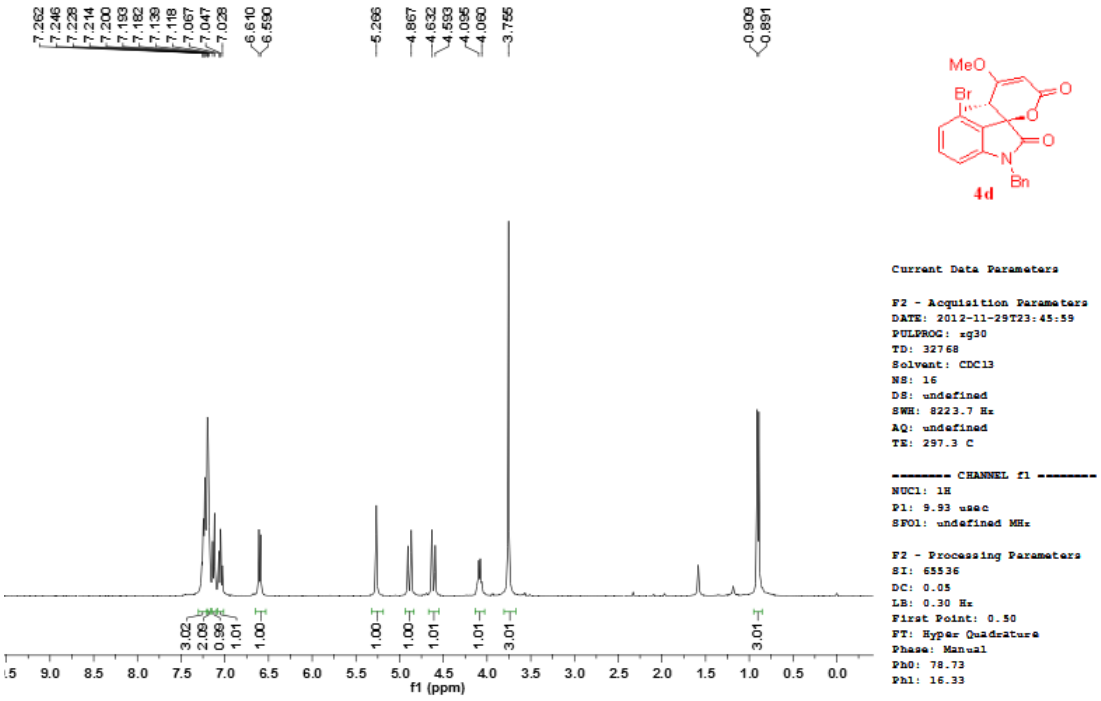

H5
H2
F1 [ppm]
F2 [ppm]
O
OMe
MeO
H2
Br
OH5
O
N
Bn
6

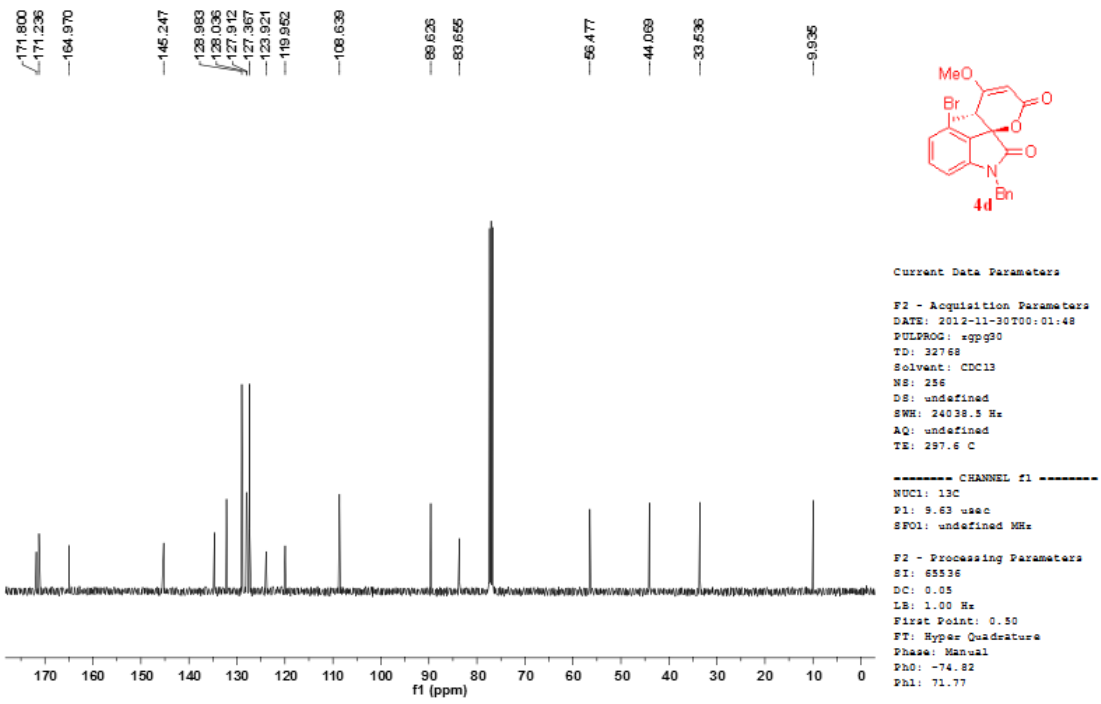

7.346
7.329
7.311
7.297
7.280
7.266
7.169
7.157
6.995
6.973
6.951
6.654
6.632
5.370
4.988
4.949
4.723
4.683
3.836
3.321
3.304
3.289
3.272
1.025
1.007
MeO
F
O
O
N
Bn
4b
3.09
2.12
1.03
1.00
0.97
1.00
1.00
0.99
2.94
0.96
2.93
f1 (ppm)
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2013-03-06T12:40:23
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 293.7 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: 77.36
Ph1: 12.22

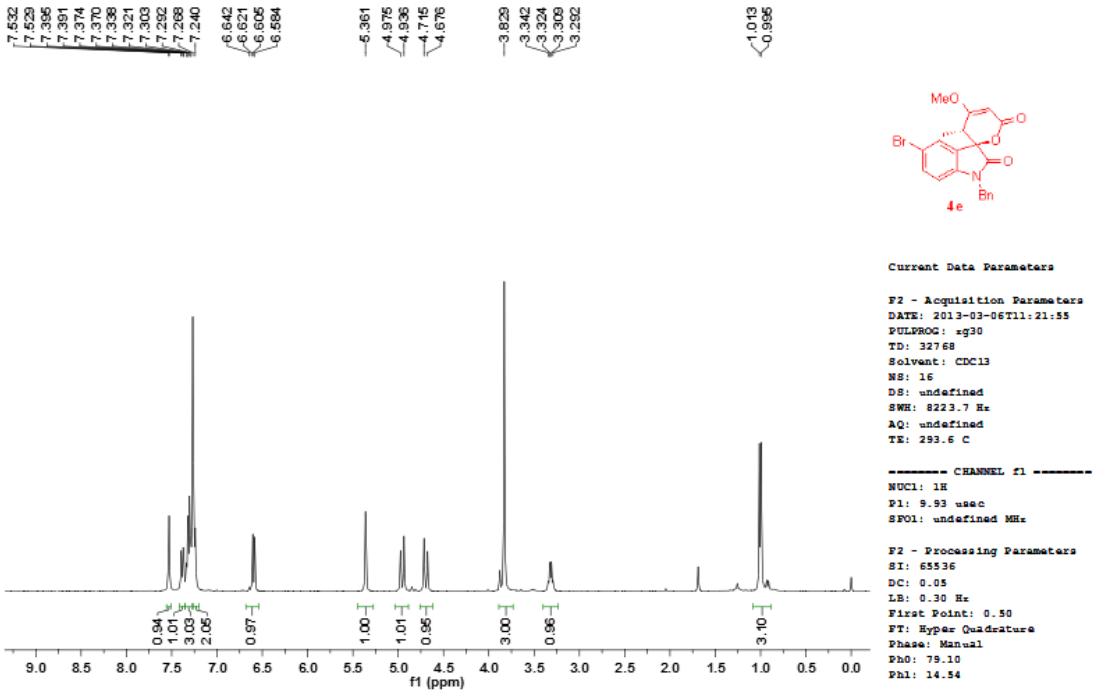

171.903
171.478
164.795
160.650
158.232
139.070
134.779
127.328
117.431
117.198
112.501
112.250
110.442
110.363
90.045
82.334
81.643
66.570
44.133
37.552
10.069
MeO
F
O
O
N
Bn
4b
f1 (ppm)
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2013-03-06T13:10:35
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 294 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: -77.65
Ph1: 69.78

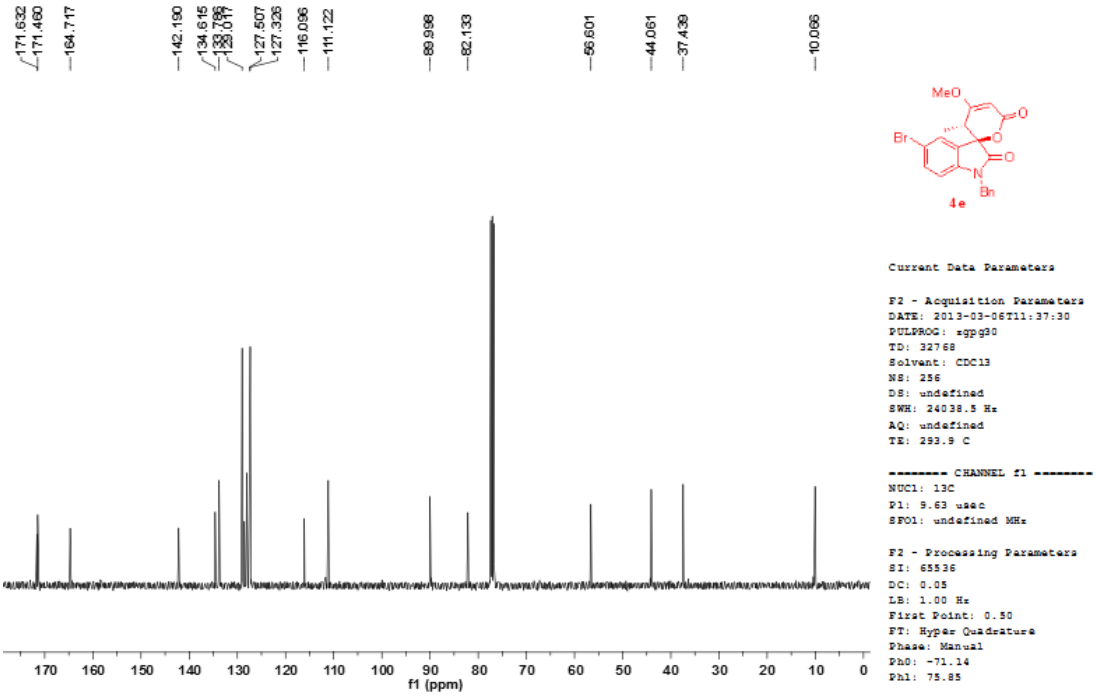

7.397
7.393
7.340
7.324
7.305
7.293
7.290
7.277
7.267
7.264
7.246
7.242
7.226
7.221
6.651
6.630
5.365
4.990
4.941
4.720
4.681
3.831
3.339
3.321
3.307
3.289
1.016
0.998
MeO
Cl
O
O
O
N
Bn
4c
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2013-03-08T01:22:04
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 293.8 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: 75.96
Ph1: 12.71
1.02
6.46
1.02
1.00
1.01
0.95
3.03
0.96
2.91
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

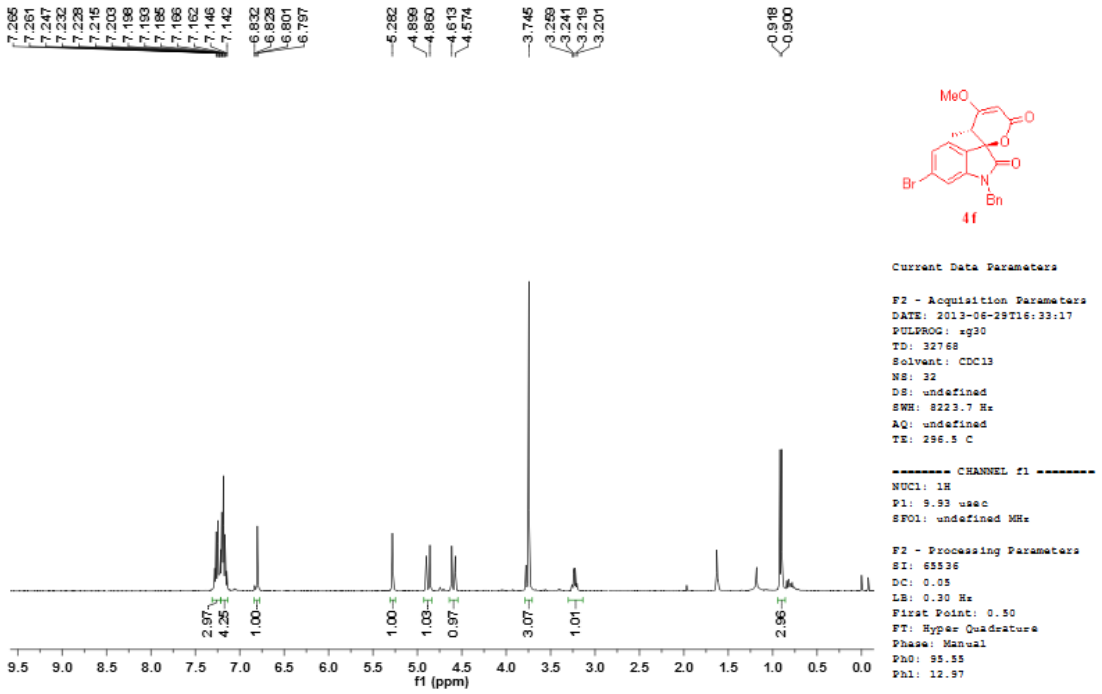

171.735
171.471
164.732
141.685
134.650
129.014
128.056
127.326
124.751
110.663
90.008
82.188
66.593
44.087
37.455
10.067
MeO
Cl
O
O
O
N
Bn
4c
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2013-03-08T01:37:39
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 294.1 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: -66.21
Ph1: 54.77
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

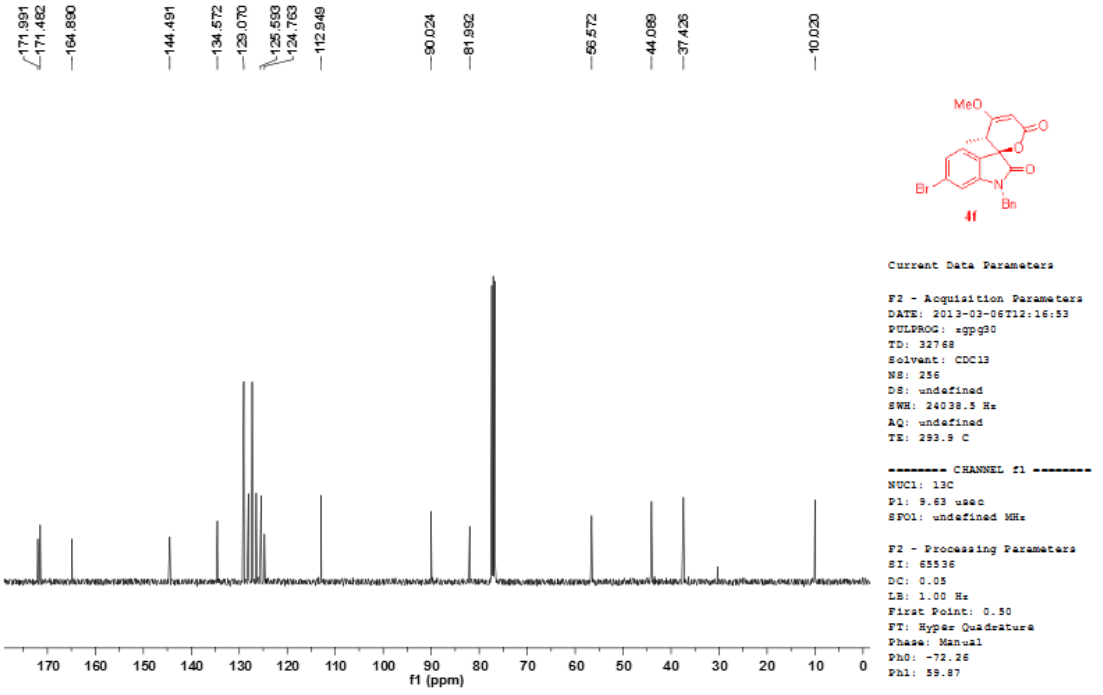

7.262
7.246
7.228
7.214
7.200
7.193
7.182
7.139
7.118
7.067
7.047
7.028
6.610
6.590
5.266
4.867
4.632
4.593
4.095
4.060
3.755
0.909
0.891
MeO
Br
O
O
O
N
Bn
4d
3.02
2.09
0.99
1.01
1.00
1.00
1.00
1.01
1.01
3.01
3.01
f1 (ppm)
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2012-11-29T23:45:59
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 297.3 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: 78.73
Ph1: 16.33

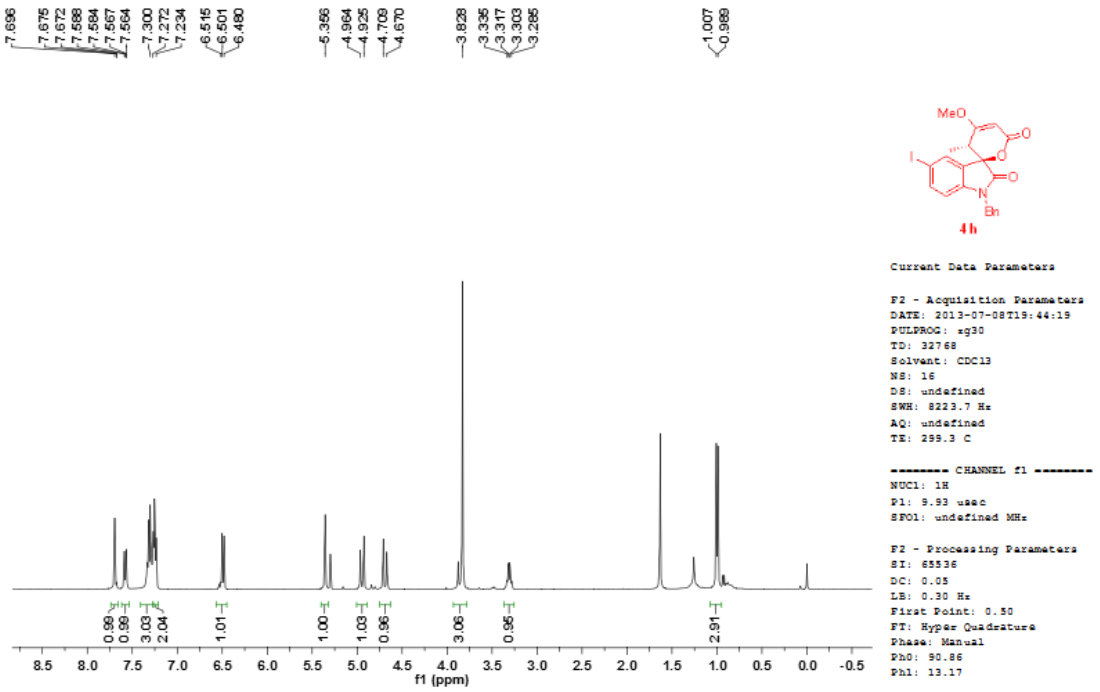

171.800
171.236
164.970
145.247
129.983
128.036
127.912
127.367
123.921
119.952
108.639
89.626
83.655
66.477
44.069
33.536
9.935
MeO
Br
O
O
O
N
Bn
4d
f1 (ppm)
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2012-11-30T00:01:48
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 297.6 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: -74.82
Ph1: 71.77

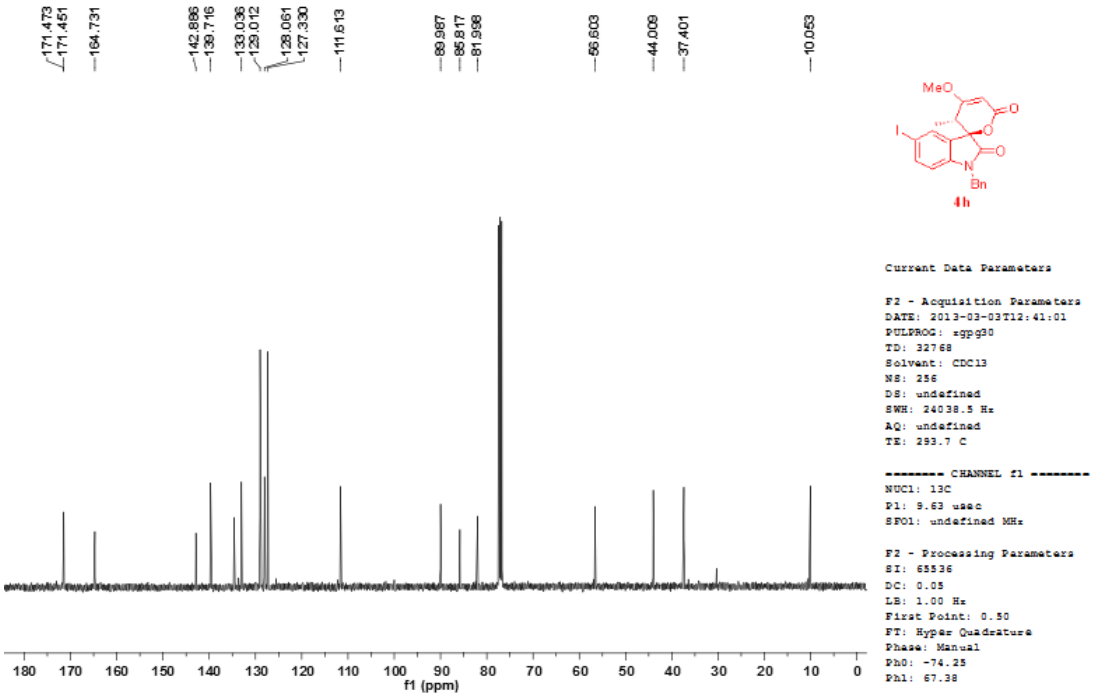

7.532
7.529
7.395
7.391
7.374
7.370
7.338
7.321
7.303
7.292
7.268
7.240
6.642
6.621
6.605
6.584
5.361
4.975
4.936
4.715
4.676
3.829
3.342
3.324
3.309
3.292
1.013
0.995
MeO
Br
O
O
N
Bn
4e
0.94
1.01
3.03
2.05
0.97
1.00
1.01
0.95
3.00
0.96
3.10
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2013-03-06T11:21:55
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 293.6 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: 79.10
Ph1: 14.54

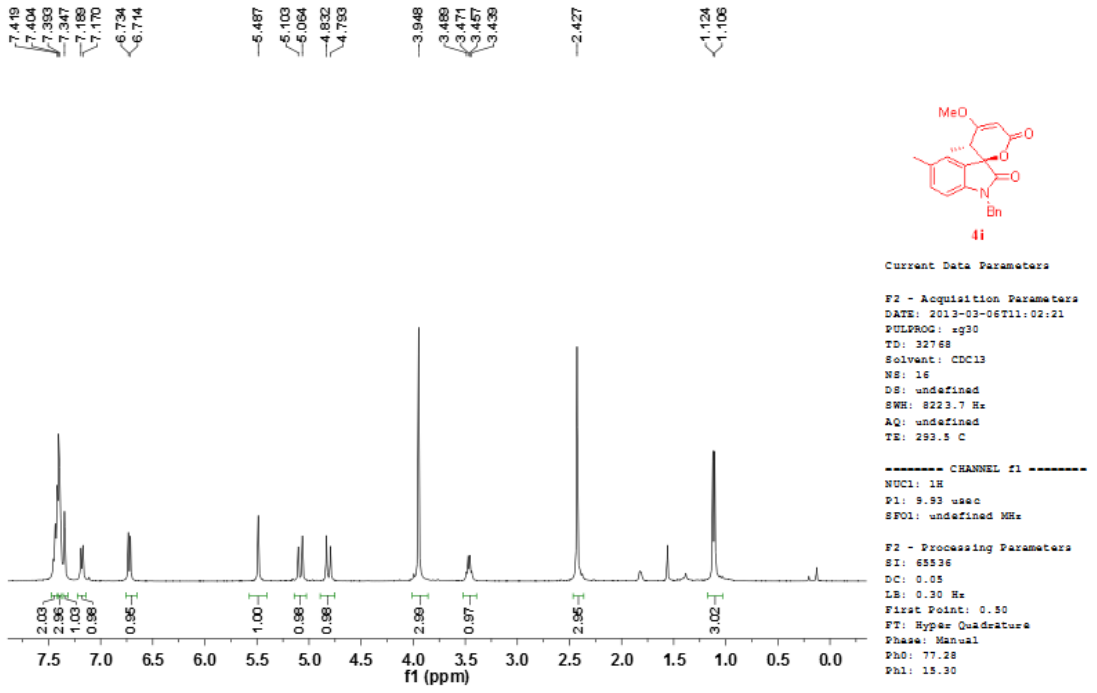

171.632
171.460
164.717
142.190
134.615
133.786
133.017
127.507
127.326
116.096
111.122
89.998
82.133
56.601
44.061
37.439
10.066
MeO
Br
O
O
N
Bn
4e
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2013-03-06T11:37:30
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 293.9 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
Ph0: -71.14
Ph1: 75.85

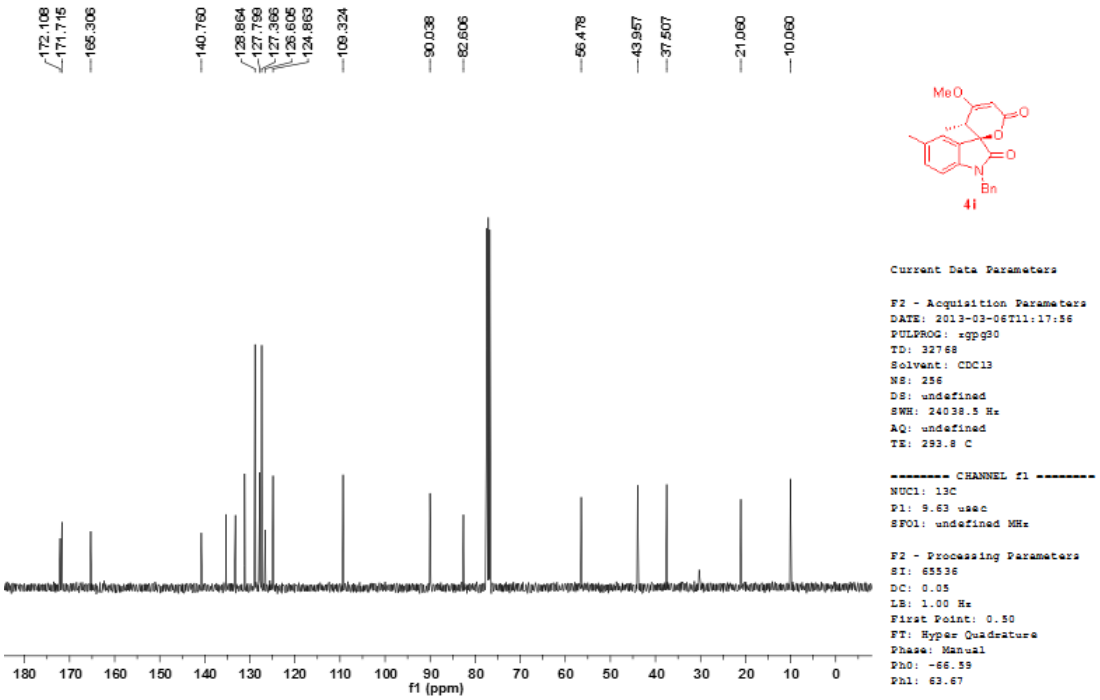

7.265
7.261
7.247
7.232
7.228
7.215
7.203
7.198
7.193
7.185
7.166
7.162
7.146
7.142
6.832
6.828
6.801
6.797
5.282
4.899
4.880
4.613
4.574
3.745
3.259
3.241
3.219
3.201
0.918
0.900
MeO
O
O
O
Br
N
Bn
4f
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2013-06-29T16:33:17
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 32
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 296.5 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: 95.55
Ph1: 12.97
2.97
4.25
1.00
1.00
1.03
0.97
3.07
1.01
2.96
f1 (ppm)

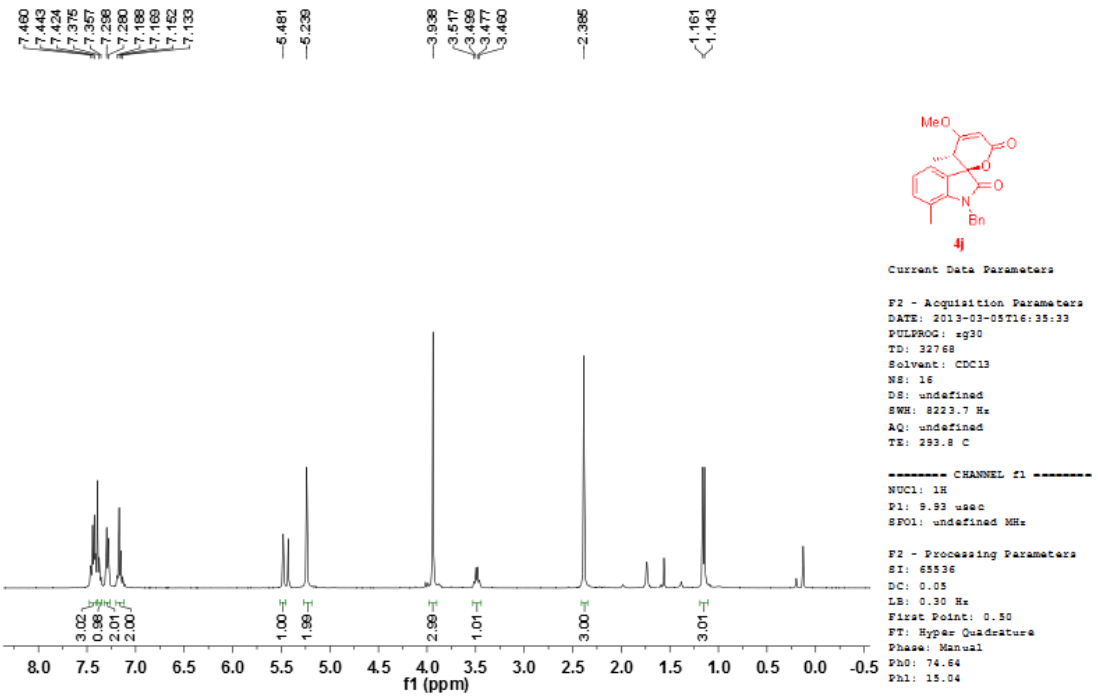

171.991
171.482
164.890
144.491
134.572
129.070
125.593
124.763
112.949
90.024
81.992
56.572
44.089
37.426
10.020
MeO
O
O
O
Br
N
Bn
4f
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2013-03-06T12:16:53
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 293.9 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
Ph0: -72.26
Ph1: 59.87
f1 (ppm)

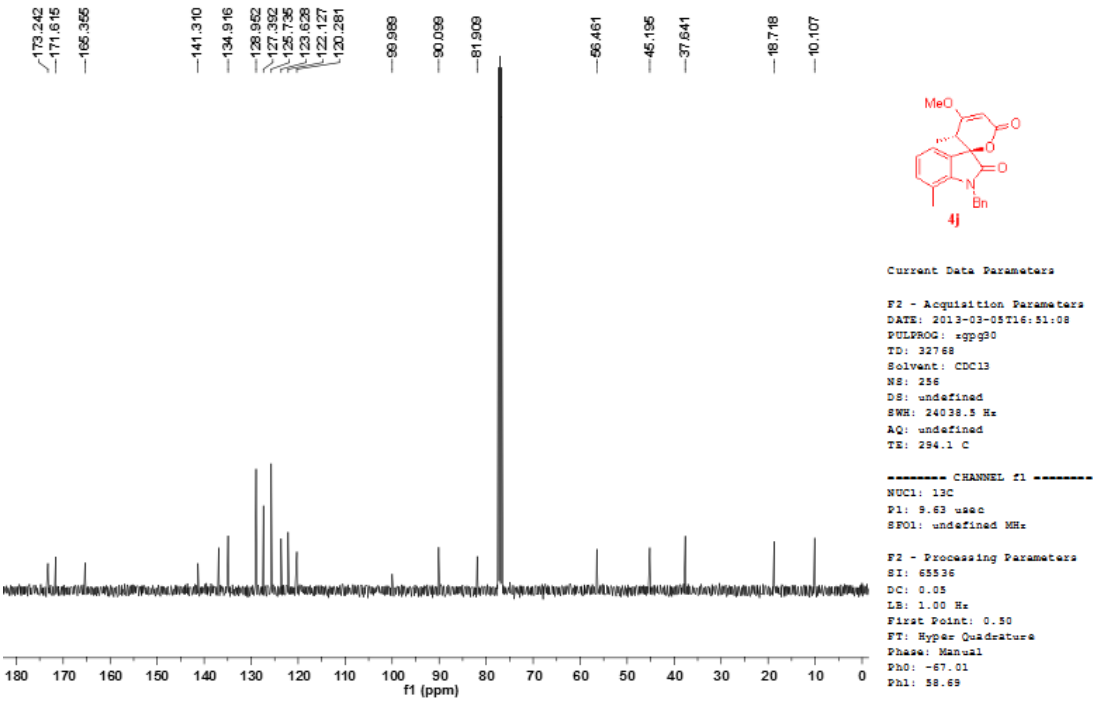

7.696
7.675
7.672
7.588
7.584
7.567
7.564
7.300
7.272
7.234
6.515
6.501
6.480
5.356
4.964
4.925
4.709
4.670
3.828
3.335
3.317
3.303
3.285
1.007
0.989
MeO
I
N
Bn
4h
0.99
0.99
3.03
2.04
1.01
1.00
1.03
0.96
3.06
0.95
2.91
f1 (ppm)
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2013-07-08T19:44:19
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 299.3 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: 90.86
Ph1: 13.17

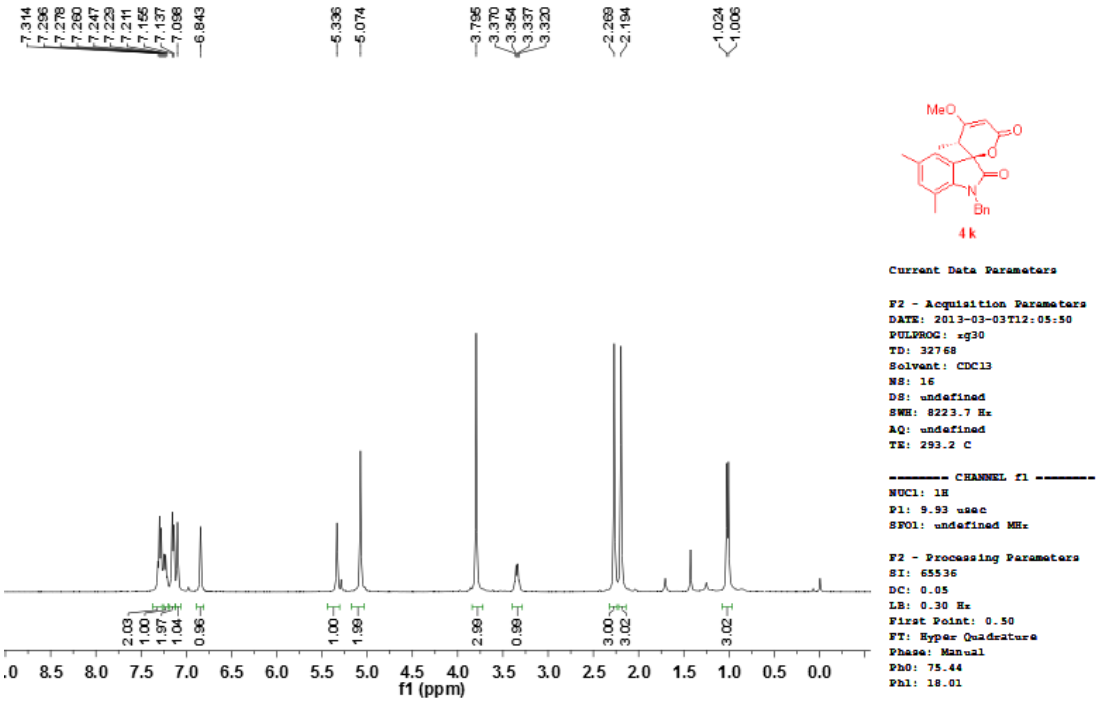

171.473
171.451
164.731
142.886
139.716
133.036
129.012
128.061
127.330
111.613
89.987
86.817
81.998
56.603
44.009
37.401
10.053
MeO
I
N
Bn
4h
f1 (ppm)
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2013-03-03T12:41:01
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 293.7 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: -74.25
Ph1: 67.38

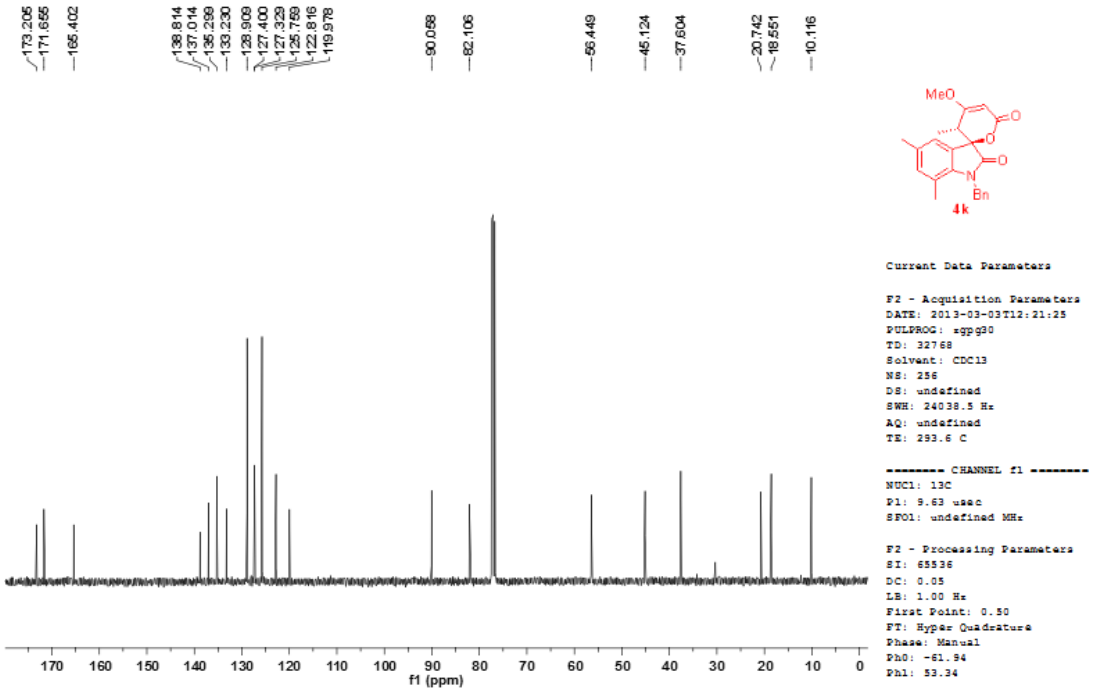

7.419
7.404
7.393
7.347
7.189
7.170
6.734
6.714
5.487
5.103
5.064
4.832
4.793
3.948
3.489
3.471
3.457
3.439
2.427
1.124
1.106
MeO
O
O
O
N
Bn
4i
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2013-03-06T11:02:21
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 293.5 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: 77.28
Ph1: 15.30
2.03
2.96
1.03
0.98
0.95
1.00
0.98
0.98
2.99
0.97
2.95
3.02
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

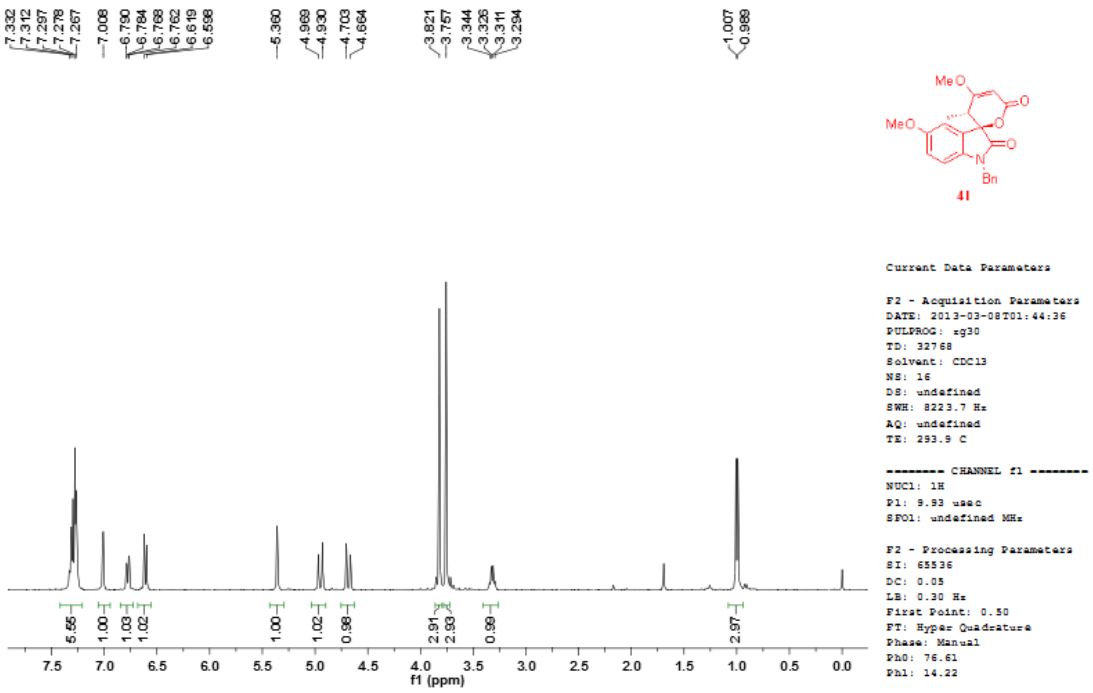

172.108
171.715
165.306
140.760
129.864
127.799
127.366
126.605
124.863
109.324
90.038
82.606
66.478
43.957
37.507
21.060
10.060
MeO
O
O
O
N
Bn
4i
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2013-03-06T11:17:56
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 293.8 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: -66.59
Ph1: 63.67
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

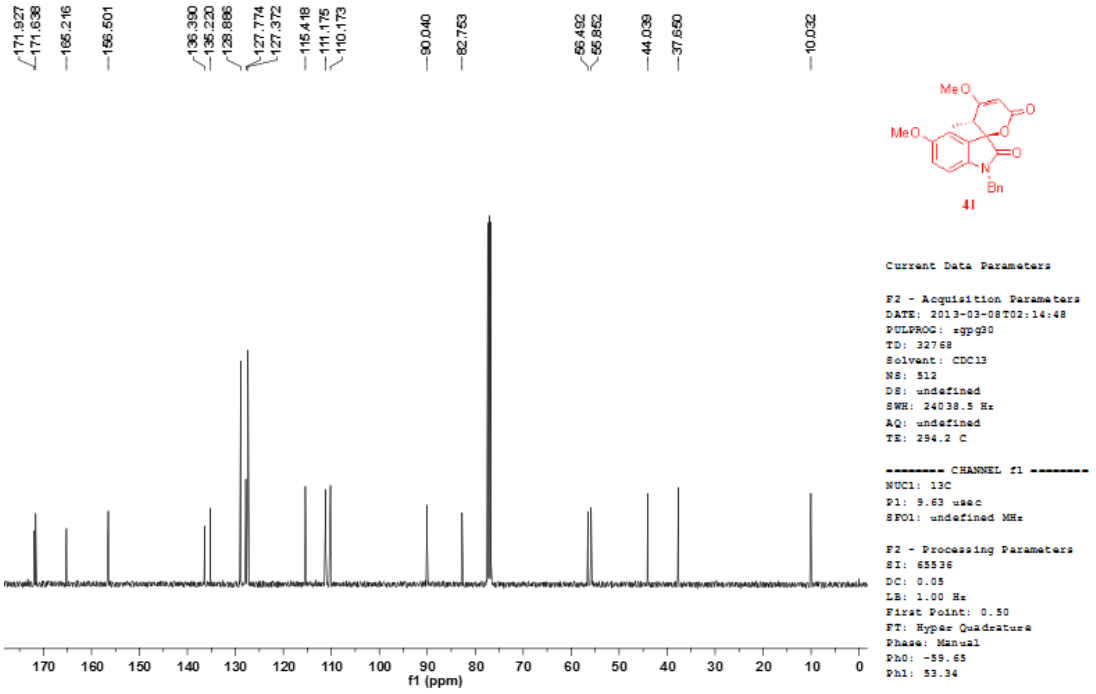

7.460
7.443
7.424
7.375
7.357
7.298
7.280
7.188
7.169
7.152
7.133
5.481
5.239
3.936
3.517
3.499
3.477
3.460
2.385
1.161
1.143
MeO
O
O
O
N
Bn
4j
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2013-03-05T16:35:33
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 293.8 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: 74.64
Ph1: 15.04
3.02
0.98
2.01
2.00
1.00
1.99
2.99
1.01
3.00
3.01
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

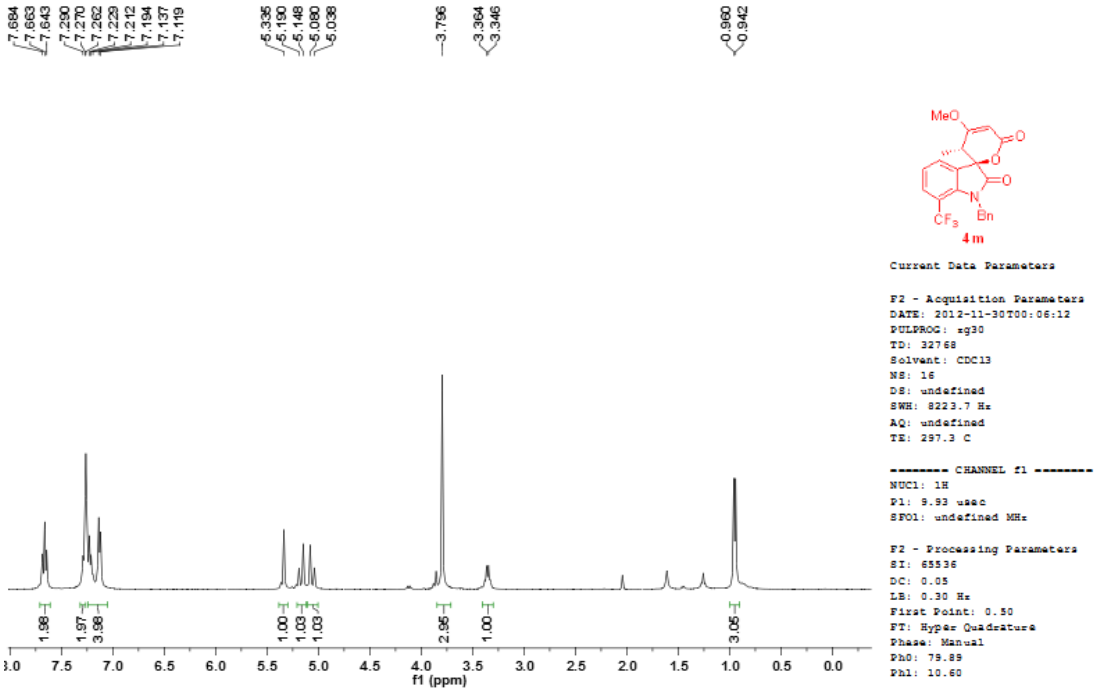

173.242
171.615
165.365
141.310
134.916
128.952
127.392
125.736
123.628
122.127
120.281
99.989
90.099
81.909
55.461
45.195
37.641
18.718
10.107
MeO
O
O
O
N
Bn
4j
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2013-03-05T16:51:08
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 294.1 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: -67.01
Ph1: 58.69
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

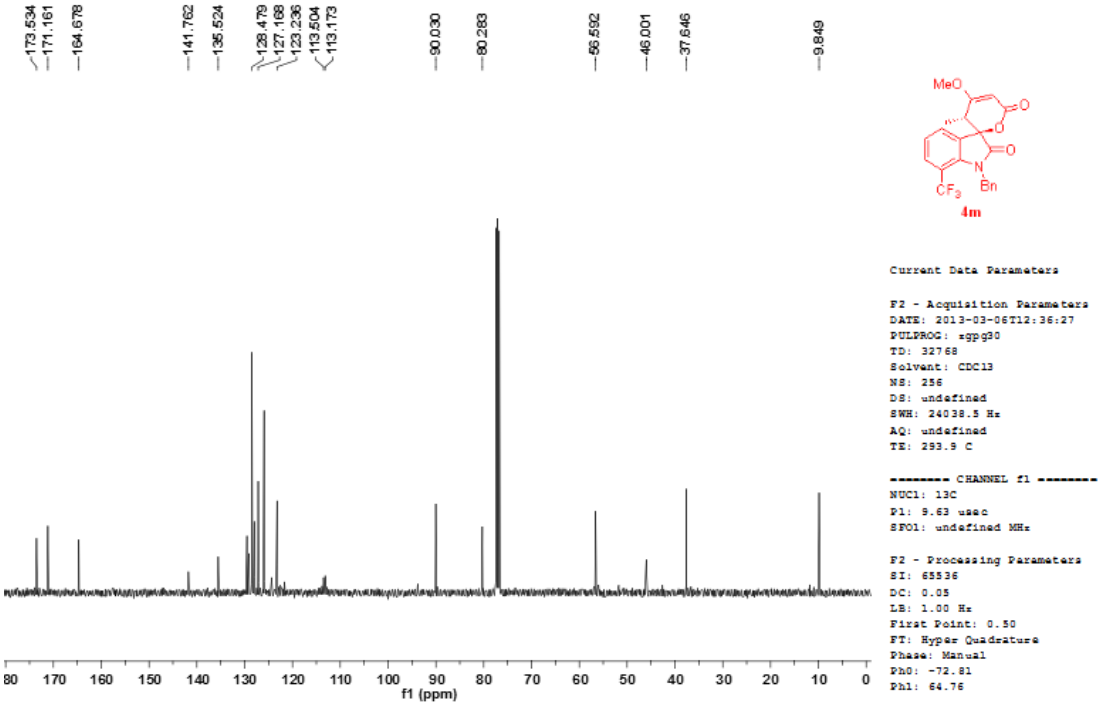

7.314
7.296
7.278
7.260
7.247
7.229
7.211
7.155
7.137
7.098
6.843
5.336
5.074
3.795
3.370
3.354
3.337
3.320
2.269
2.194
1.024
1.006
MeO
O
O
O
N
Bn
4k
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2013-03-03T12:05:50
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 293.2 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: 75.44
Ph1: 18.01
2.03
1.00
1.97
1.04
0.96
1.00
1.99
2.99
0.99
3.00
3.02
3.02
f1 (ppm)

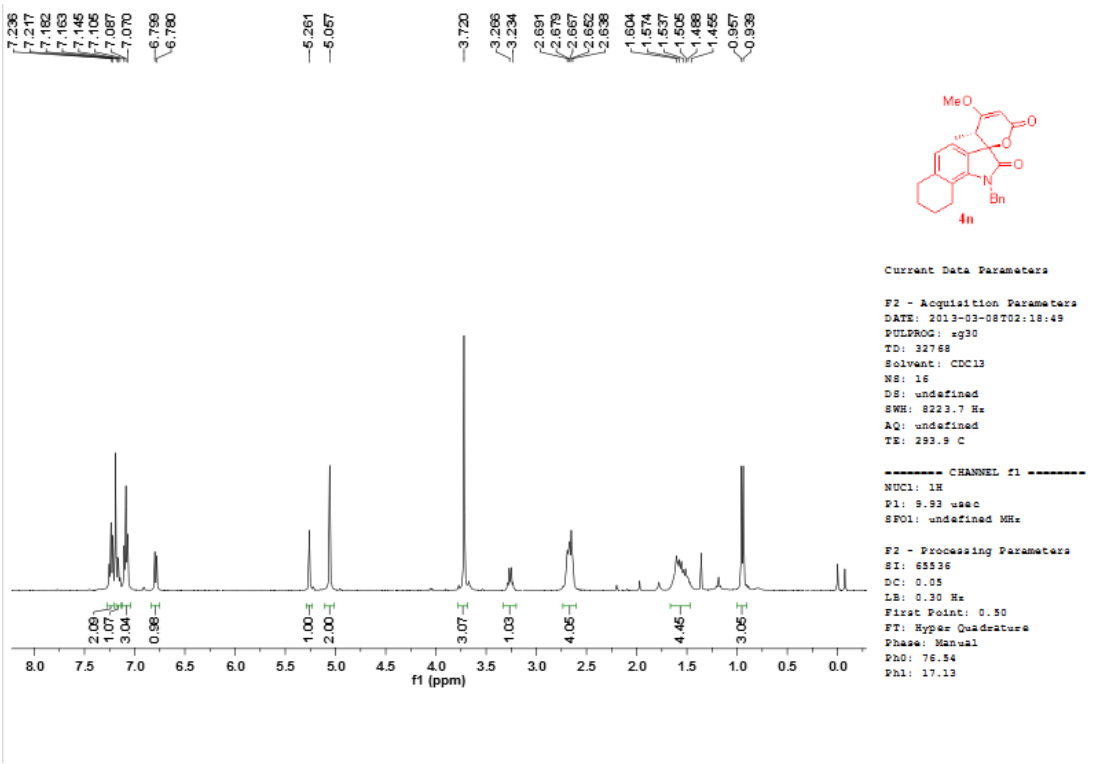

173.205
171.655
165.402
138.814
137.014
136.299
133.230
129.909
127.400
127.329
126.769
122.816
119.978
90.058
82.106
56.449
45.124
37.604
20.742
18.551
10.116
MeO
O
O
O
N
Bn
4k
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2013-03-03T12:21:25
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 293.6 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: -61.94
Ph1: 53.34
f1 (ppm)

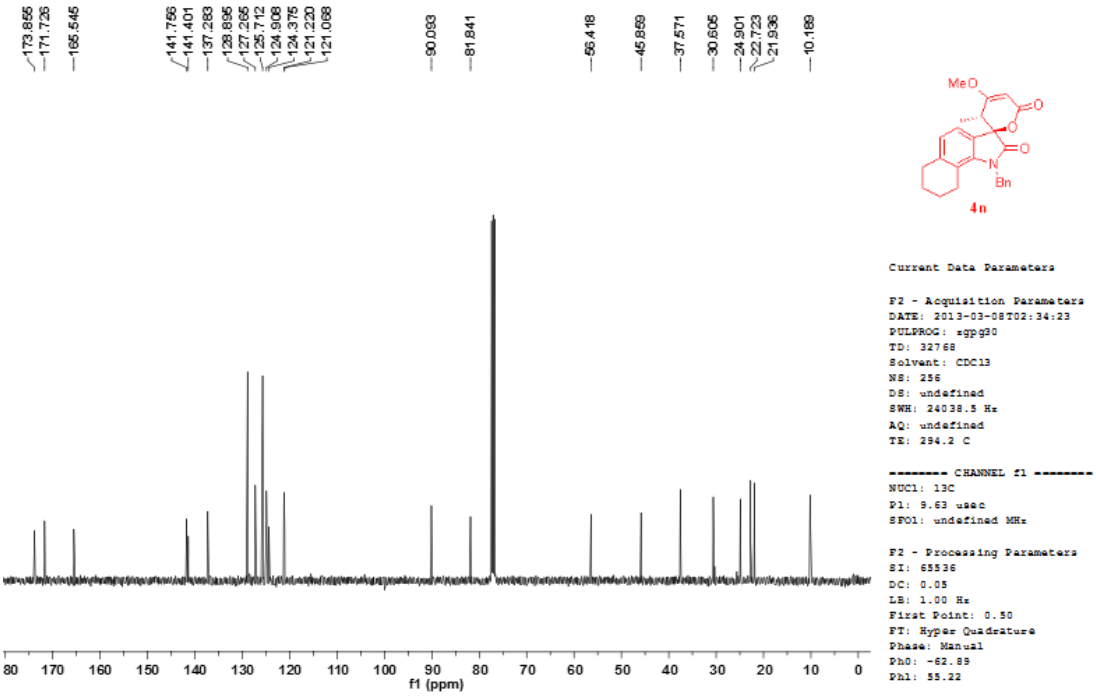

7.332
7.312
7.297
7.278
7.267
7.008
6.790
6.784
6.768
6.762
6.619
6.598
5.360
4.969
4.930
4.703
4.664
3.821
3.757
3.344
3.326
3.311
3.294
1.007
0.989
MeO
MeO
O
O
O
N
Bn
41
5.55
1.00
1.03
1.02
1.00
1.02
0.98
2.91
2.93
0.99
2.97
f1 (ppm)
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2013-03-08T01:44:36
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 293.9 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: 76.61
Ph1: 14.22

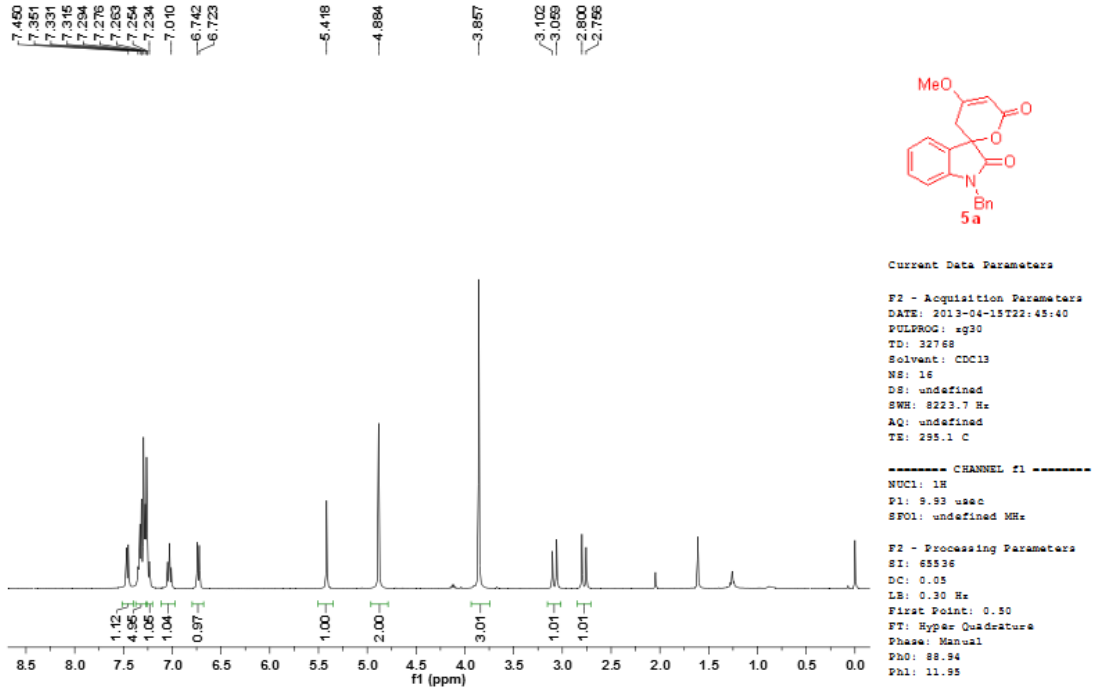

171.927
171.638
165.216
155.501
136.390
135.220
128.886
127.774
127.372
115.418
111.175
110.173
90.040
82.753
55.492
55.852
44.039
37.650
10.032
MeO
MeO
O
O
O
N
Bn
41
f1 (ppm)
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2013-03-08T02:14:48
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 294.2 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: -59.65
Ph1: 53.34

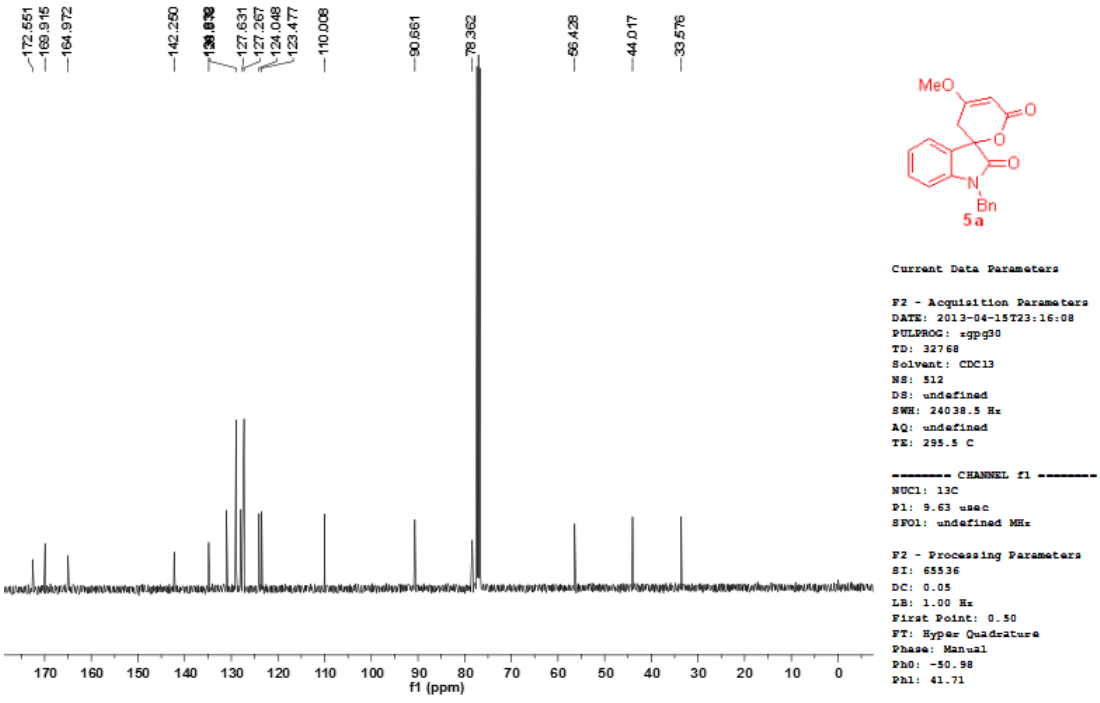

7.684
7.663
7.643
7.290
7.270
7.262
7.229
7.212
7.194
7.137
7.119
5.335
5.190
5.148
5.080
5.038
3.796
3.364
3.346
0.960
0.942
1.98
1.97
3.98
1.00
1.03
1.03
2.95
1.00
3.05
f1 (ppm)
MeO
O
O
O
N
Bn
CF3
4m
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2012-11-30T00:06:12
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 297.3 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: 79.89
Ph1: 10.60

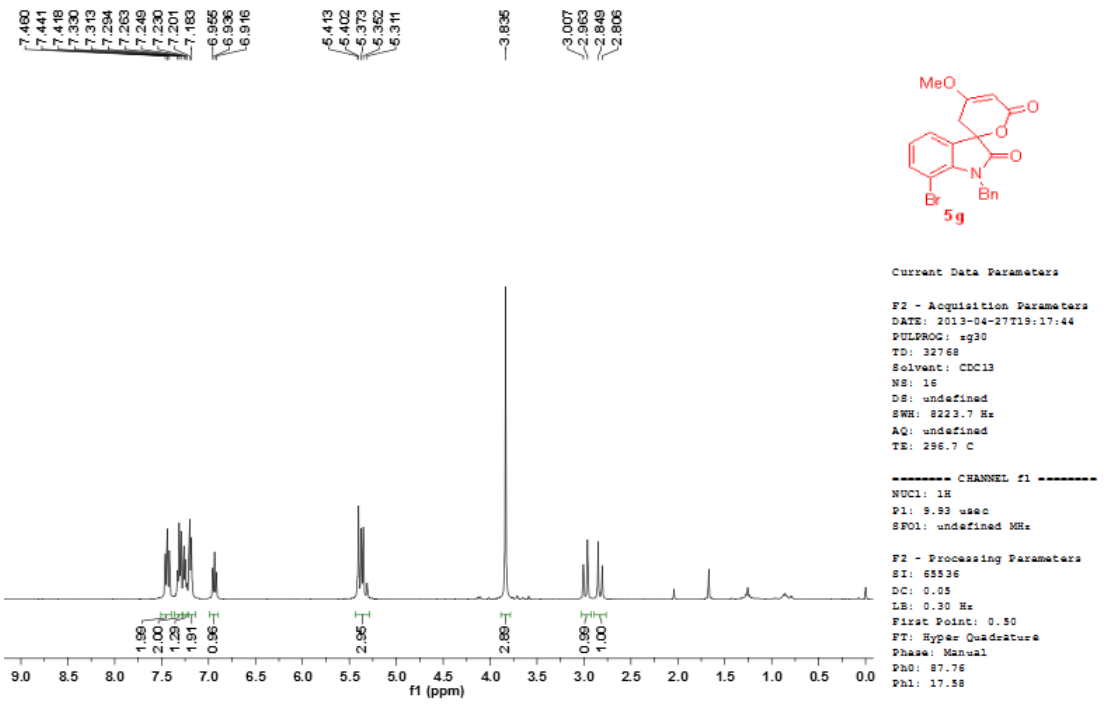

173.534
171.161
164.678
141.762
135.524
128.479
127.168
123.236
113.504
113.173
90.030
80.283
56.592
46.001
37.646
9.849
f1 (ppm)
MeO
O
O
O
N
Bn
CF3
4m
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2013-03-06T12:36:27
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 293.9 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
Ph0: -72.81
Ph1: 64.76

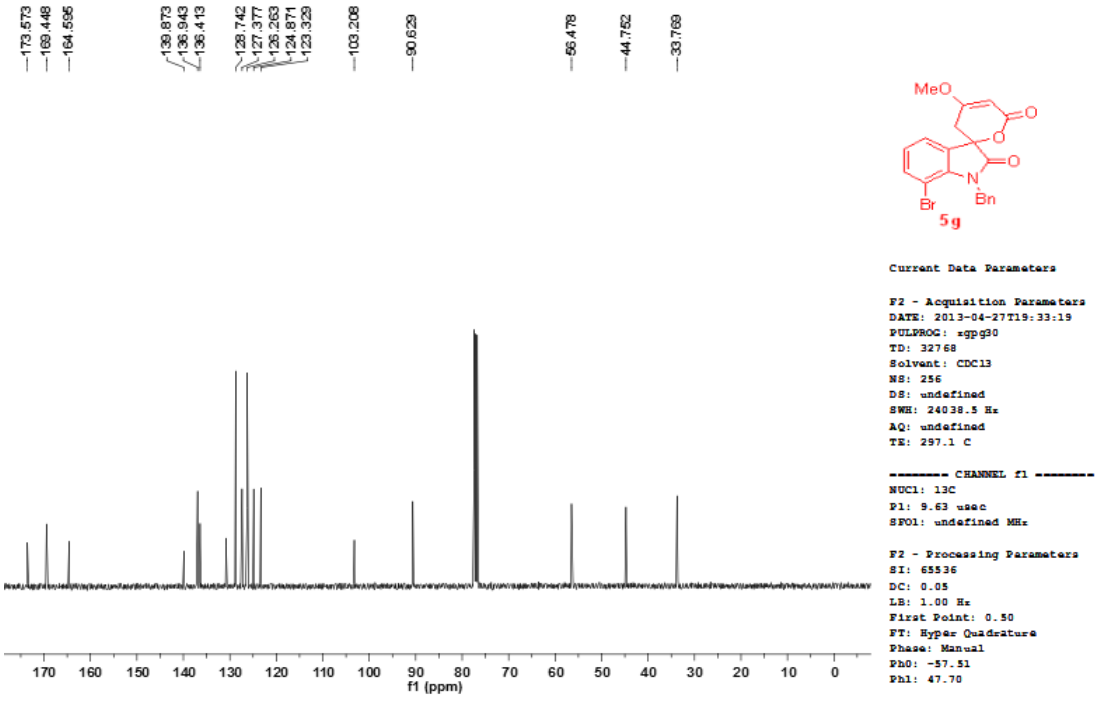

7.236
7.217
7.182
7.163
7.145
7.105
7.087
7.070
6.799
6.780
5.261
5.057
3.720
3.266
3.234
2.691
2.679
2.667
2.652
2.638
1.604
1.574
1.537
1.505
1.488
1.455
0.957
0.939
MeO
O
O
O
N
Bn
4n
2.09
1.07
3.04
0.98
1.00
2.00
3.07
1.03
4.05
4.45
3.05
f1 (ppm)
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2013-03-08T02:18:49
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 293.9 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: 76.54
Ph1: 17.13

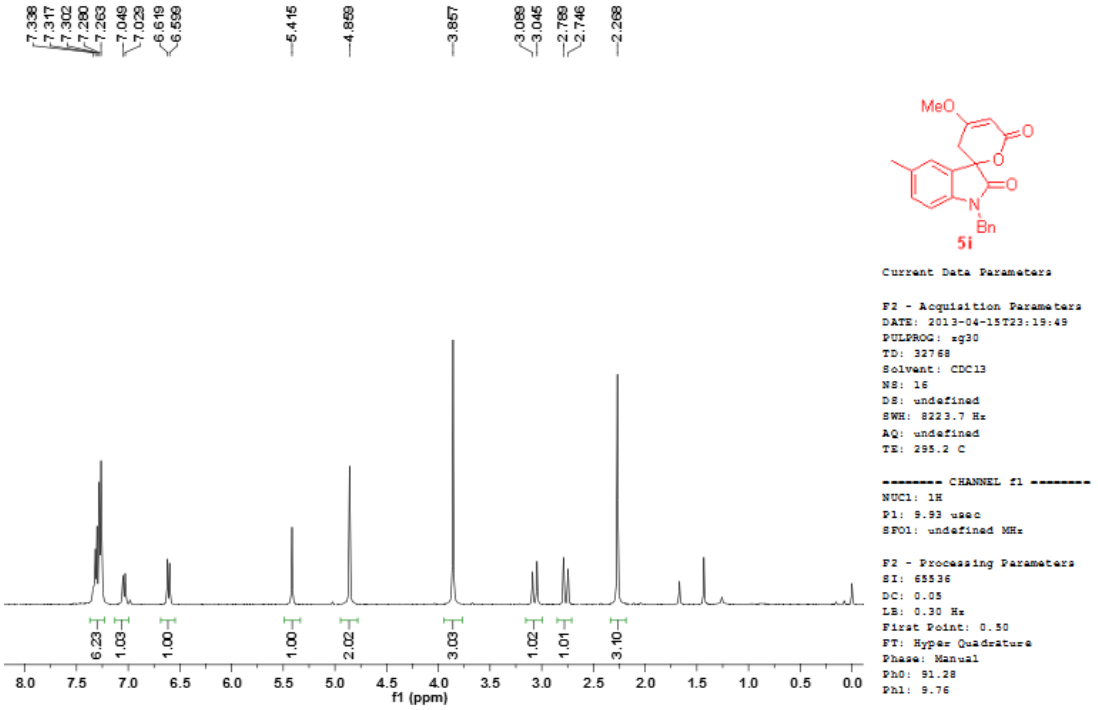

173.855
171.725
165.545
141.756
141.401
137.283
128.895
127.265
125.712
124.908
124.375
121.220
121.068
90.093
81.841
56.418
45.859
37.571
30.605
24.901
22.723
21.936
10.189
MeO
O
O
O
N
Bn
4n
f1 (ppm)
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2013-03-08T02:34:23
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 294.2 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: -62.89
Ph1: 55.22

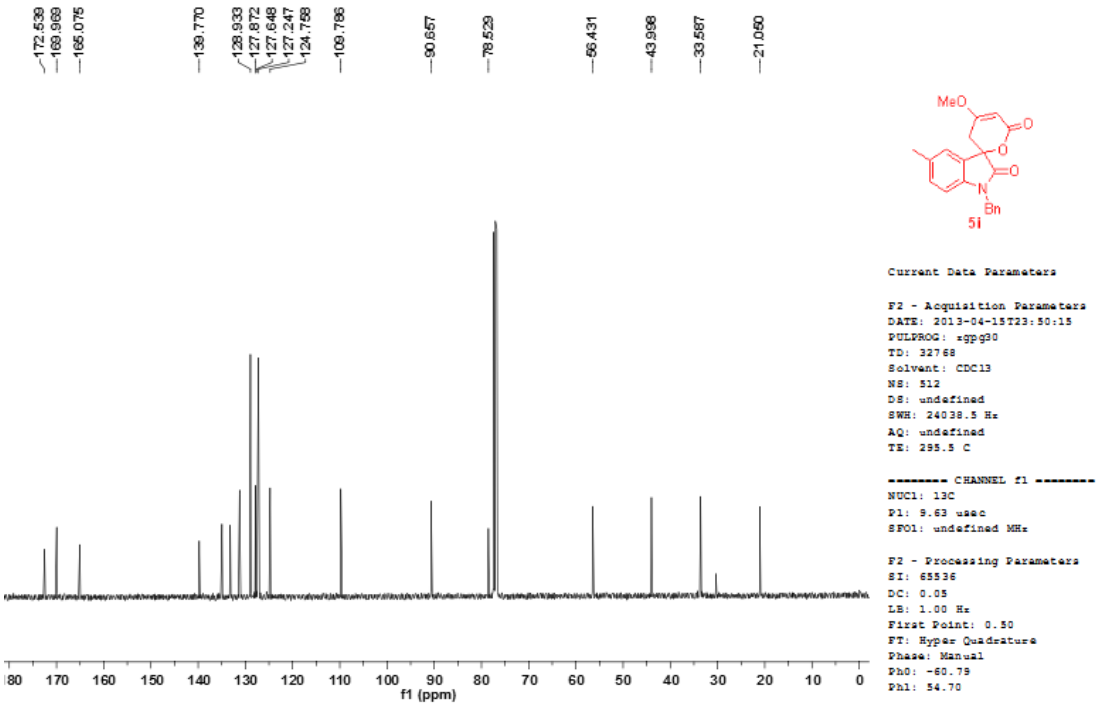

7.450
7.351
7.331
7.315
7.294
7.276
7.263
7.254
7.234
7.010
6.742
6.723
5.418
4.884
3.857
3.102
3.059
2.800
2.766
MeO
O
O
O
N
Bn
5a
1.12
4.95
1.05
1.04
0.97
1.00
2.00
3.01
1.01
1.01
f1 (ppm)
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2013-04-15T22:45:40
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 295.1 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: 88.94
Ph1: 11.95

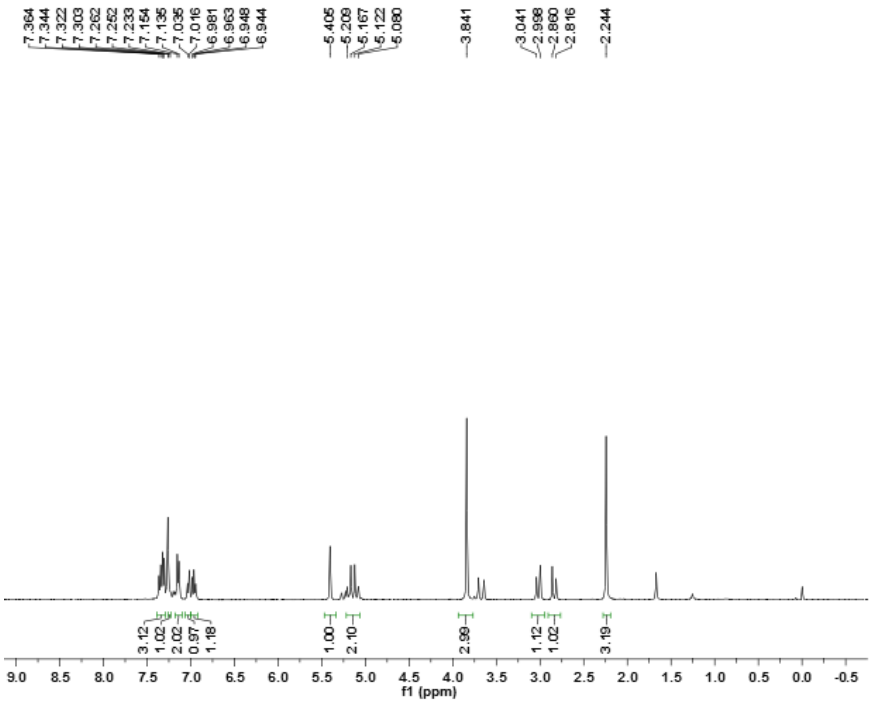

172.551
169.915
164.972
142.250
127.631
127.267
124.048
123.477
110.008
90.661
78.362
66.428
44.017
33.576
MeO
O
O
O
N
Bn
5a
f1 (ppm)
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2013-04-15T23:16:08
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 295.5 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: -50.98
Ph1: 41.71


7.460
7.441
7.418
7.330
7.313
7.294
7.263
7.249
7.230
7.201
7.183
6.956
6.936
6.916
5.413
5.402
5.373
5.352
5.311
3.835
3.007
2.963
2.849
2.806
MeO
O
O
O
N
Bn
Br
5g
1.99
2.00
1.29
1.91
0.96
2.95
2.89
0.99
1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2013-04-27T19:17:44
PULPROG: 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: 17.58


173.573
169.448
164.595
139.873
136.943
136.413
128.742
127.377
126.263
124.871
123.329
103.208
90.629
56.478
44.752
33.769
MeO
O
O
O
N
Bn
Br
5g
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2013-04-27T19:33:19
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 297.1 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: -57.51
Ph1: 47.70


7.338
7.317
7.302
7.290
7.263
7.049
7.029
6.619
6.599
5.415
4.859
3.857
3.089
3.045
2.789
2.746
2.268
MeO
O
O
O
N
Bn
5i
6.23
1.03
1.00
1.00
2.02
3.03
1.02
1.01
3.10
f1 (ppm)
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2013-04-15T23:19:49
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 295.2 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: 91.28
Ph1: 9.76


172.539
169.969
165.075
139.770
128.933
127.872
127.648
127.247
124.758
109.786
90.657
79.529
66.431
43.998
33.587
21.060
MeO
O
O
O
N
Bn
5i
f1 (ppm)
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2013-04-15T23:50:15
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 295.5 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: -60.79
Ph1: 54.70



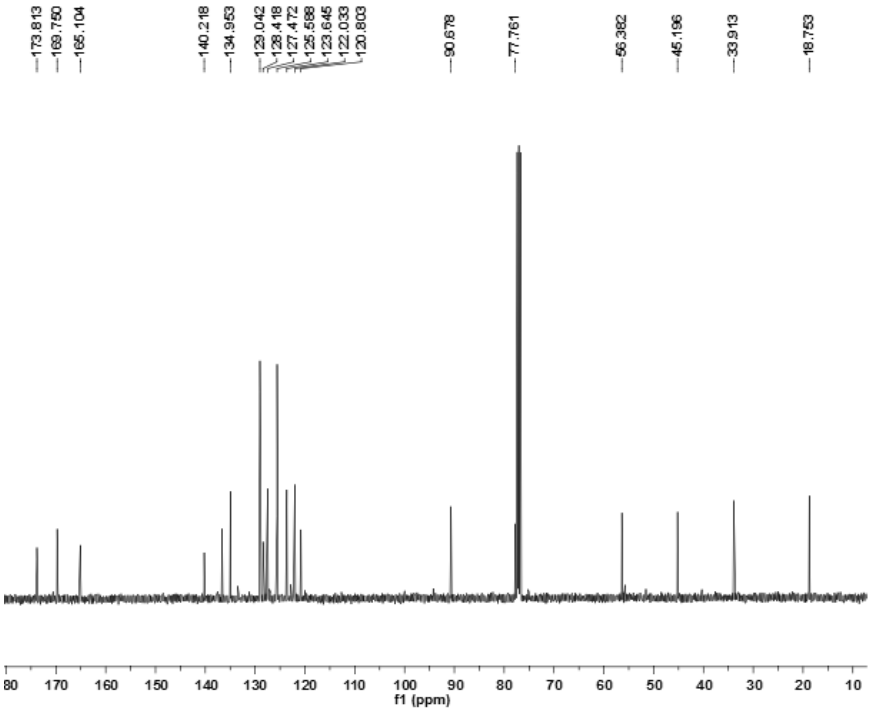
5j

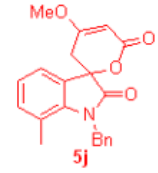
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2013-04-24T14:39:34
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 296.6 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: 94.34
Ph1: 7.44





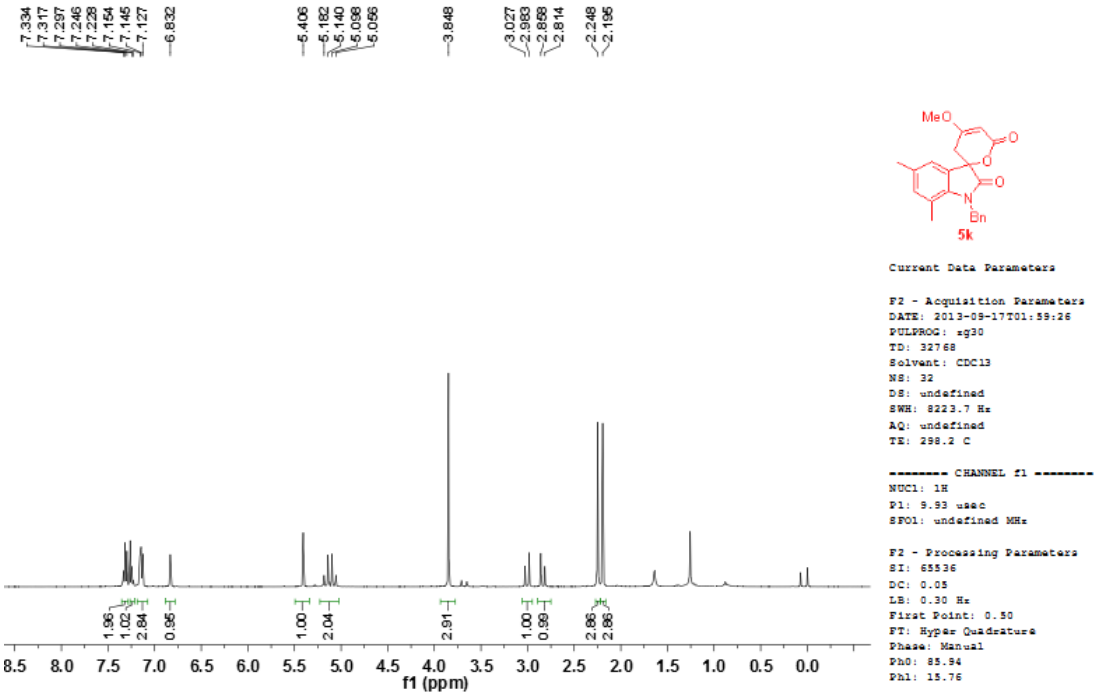
5j

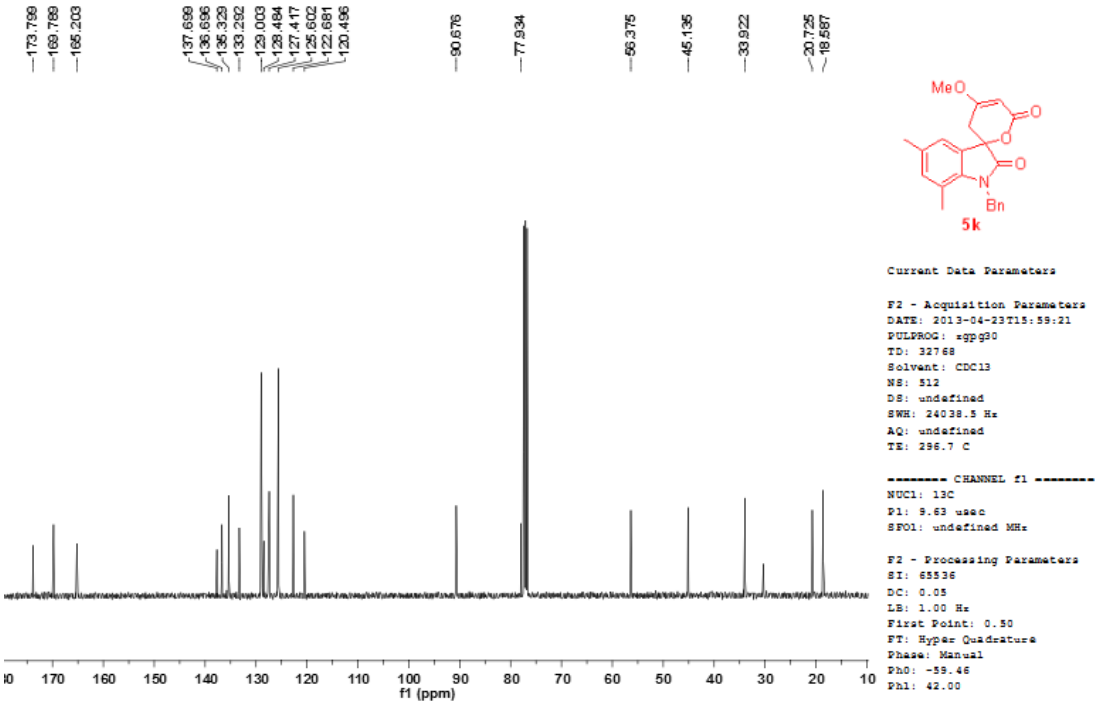
Current Data Parameters

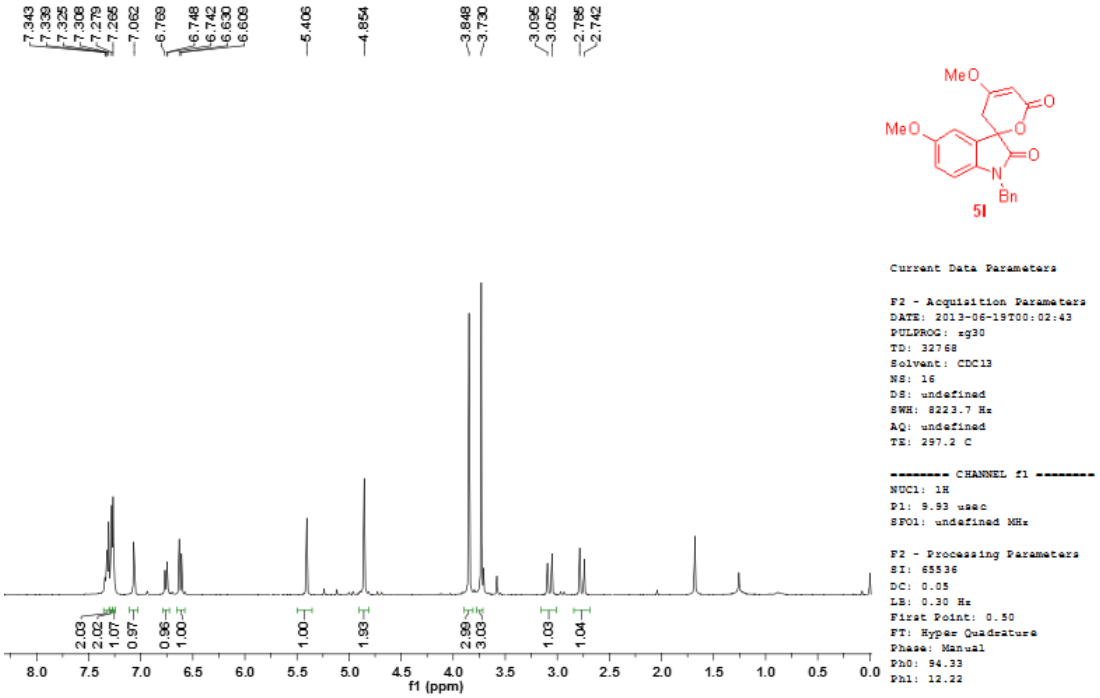
F2 - Acquisition Parameters
DATE: 2013-04-24T14:55:09
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 296.9 C

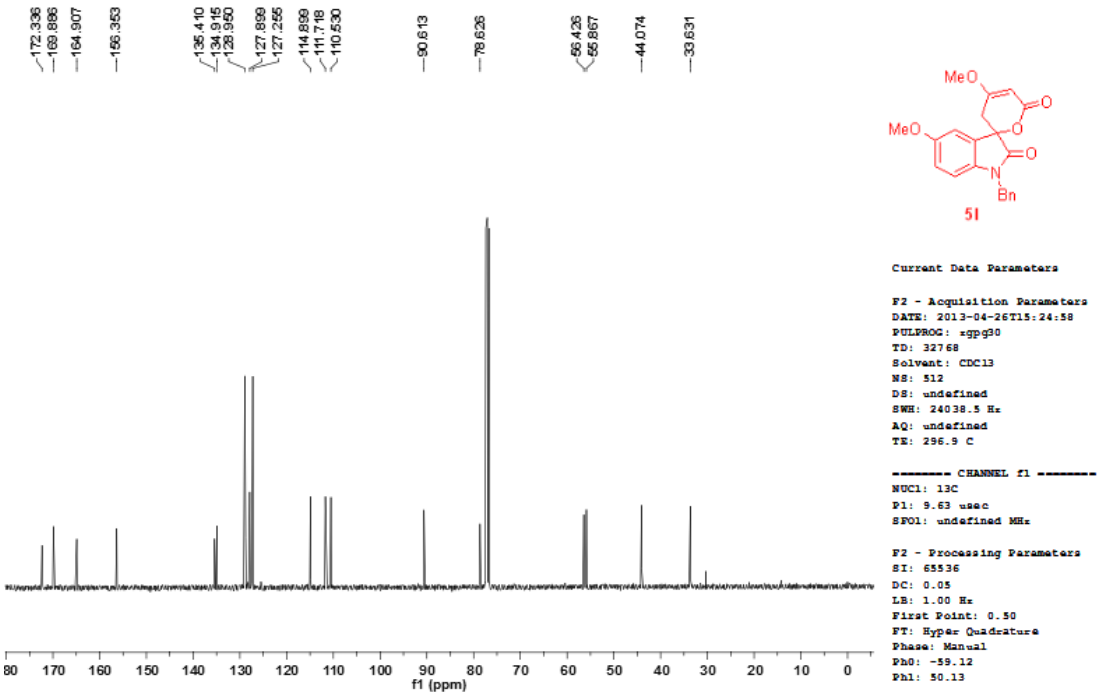
-------- CHANNEL f1 --------
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

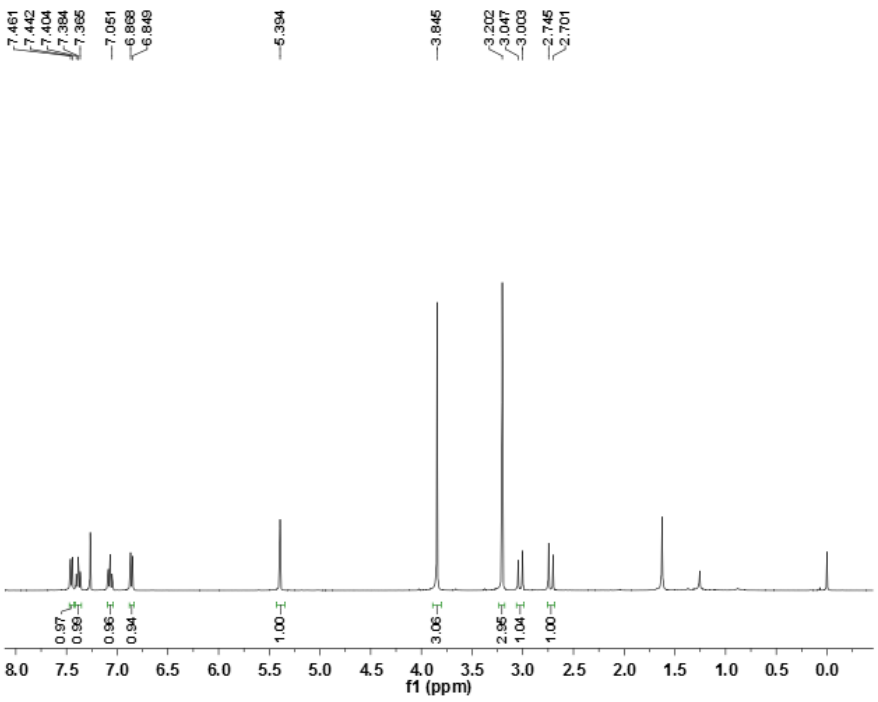
F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -60.98
Ph1: 63.02

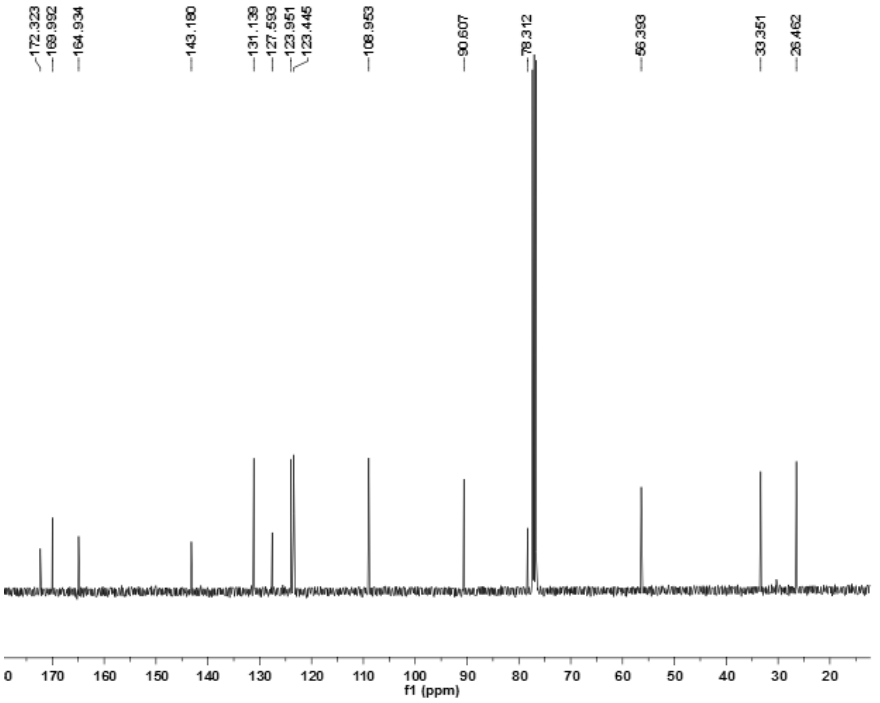

7.334
7.317
7.297
7.246
7.229
7.154
7.145
7.127
6.832
5.406
5.182
5.140
5.098
5.056
3.848
3.027
2.983
2.869
2.814
2.248
2.195
MeO
O
O
O
N
Bn
5k
1.96
1.02
2.84
0.95
1.00
2.04
2.91
1.00
0.99
2.86
2.86
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2013-09-17T01:59:26
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 32
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: 85.94
Ph1: 15.76


173.799
169.789
165.203
137.699
136.696
135.329
133.292
129.003
128.484
127.417
125.602
122.681
120.496
90.676
77.934
66.375
45.135
33.922
20.725
18.587
MeO
O
O
O
N
Bn
5k
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2013-04-23T15:59:21
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 296.7 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: -59.46
Ph1: 42.00


7.343
7.339
7.325
7.308
7.279
7.265
7.062
6.769
6.748
6.742
6.630
6.609
5.406
4.854
3.848
3.730
3.095
3.062
2.785
2.742
MeO
MeO
O
O
O
N
Bn
5l
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2013-06-19T00:02:43
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 297.2 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: 94.33
Ph1: 12.22
2.03
2.02
1.07
0.97
0.96
1.00
1.00
1.93
2.99
3.03
1.03
1.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


172.336
169.886
164.907
156.353
135.410
134.915
128.950
127.899
127.255
114.899
111.718
110.530
90.613
78.626
56.426
55.867
44.074
33.631
MeO
MeO
O
O
O
N
Bn
5l
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2013-04-26T15:24:58
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
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
Ph0: -59.12
Ph1: 50.13
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.461
7.442
7.404
7.384
7.365
7.051
6.868
6.849
5.394
3.845
3.202
3.047
3.003
2.745
2.701
MeO
O
O
O
N
5o
0.97
0.99
0.96
0.94
1.00
3.06
2.95
1.04
1.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2013-09-18T14:37:37
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 32
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 298.3 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: 86.56
Ph1: 12.43


172.323
169.992
164.934
143.180
131.139
127.593
123.951
123.445
108.953
90.607
78.312
56.393
33.351
26.462
MeO
O
O
O
N
5o
0 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2013-04-17T11:56:17
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 295.9 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
Ph0: -66.67
Ph1: 64.85