Electronic Supplementary Material (ESI) for Chemical Communications

Organocatalytic Michael-aldol cascade: formal [3+2] annulation to construct enantioenriched spirocyclic oxindole derivatives

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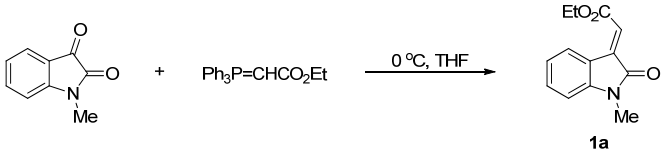
Contents

1. General Information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to general methods. Flash column chromatography was performed using 200-300 mesh silica gel. ^{1}H NMR spectra were recorded on 400/600 MHz spectrophotometers. Chemical shifts (δ) are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on 100/150 MHz with complete proton decoupling spectrophotometers ($CDCl_3$: 77.0 ppm). Mass spectra were measured on a MS spectrometer. Elemental analysis was taken on an elementary analysis instrument. Enantiomeric ratios were determined by chiral HPLC with chiral columns (chiralpak AS-H column, chiralpak AD-H column, chiralpak OJ-H column or chiralcel OD-H column) with hexane and i-PrOH as solvents. Optical rotations were measured with a polarimeter.

2. Preparation and Spectral Data of Substrates

2.1 General preparation procedure of 3-ylideneoxindoles.



1a

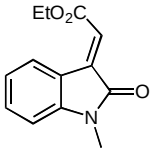
To a stirred solution of ethyl 2-(triphenylphosphoranylidene) acetate (22 mmol, 1.1 eq.) in anhydrous THF (50 mL), the N-methylindoline-2, 3-dione[1] (20 mmol, 1.0 eq.) was added at 0 °C. The mixture was stirred at the same temperature until the reaction was completed monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ ethyl acetate 5:1). Compound **1a** was obtained as a red solid (1.74 g, 87% yield).

The other 3-ylideneoxindoles were prepared according to the above procedure.

Reference: [1] Trost, B. M.; Zhang, Y. *J. Am. Chem. Soc.* **2007**, *129*, 14548.

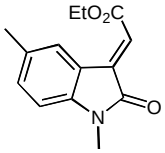
2.2 Spectral Data of Substrates

***(E)*-Ethyl 2-(1-methyl-2-oxoindolin-3-ylidene)acetate (1a)**



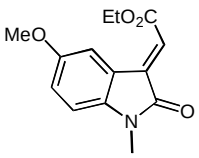
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.54 (1 H, d, *J* = 7.7Hz), 7.36 (1 H, t, *J* = 7.7Hz), 7.05 (1 H, t, *J* = 7.7Hz), 6.88 (1 H, s), 6.77 (1 H, d, *J* = 7.8Hz), 4.32 (2 H, q, *J* = 7.1Hz), 3.21 (3 H, s), 1.37 (3 H, t, *J* = 7.1Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.39, 165.54, 145.85, 137.74, 132.30, 128.62, 122.69, 122.31, 119.72, 108.00, 61.07, 26.12, 14.10. MS: m/z = 231.14 ($[M]^+$).

***(E)*-Ethyl 2-(1,5-dimethyl-2-oxoindolin-3-ylidene)acetate (1b)**



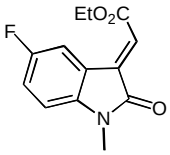
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.35 (1H, s), 7.15 (1H, d, *J* = 8Hz), 6.85 (1H, s), 6.65 (1H, d, *J* = 8Hz), 4.33 (2H, q, *J* = 7.1Hz), 3.18 (3H, s), 2.34 (3H, s), 1.38 (3H, t, *J* = 7Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.38, 165.63, 143.65, 138.06, 132.65, 132.11, 129.23, 121.89, 119.68, 107.71, 61.02, 26.10, 21.03, 14.10. MS: m/z = 245.17 ($[M]^+$).

***(E)*-Ethyl 2-(5-methoxy-1-methyl-2-oxoindolin-3-ylidene)acetate (1c)**



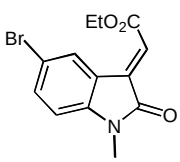
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.23 (1 H, d, *J* = 2.4Hz), 6.91-6.88 (1 H, m), 6.85 (1 H, s), 6.65 (1 H, d, *J* = 8.5Hz), 4.32 (2 H, q, *J* = 7.1Hz), 3.82 (3 H, s), 3.17 (3 H, s), 1.37 (3 H, t, *J* = 7.1Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.17, 165.45, 155.64, 139.69, 138.24, 122.40, 120.31, 118.07, 114.41, 108.35, 61.05, 55.73, 26.11, 14.08. MS: m/z = 261.10 ($[M]^+$).

***(E)*-Ethyl 2-(5-fluoro-1-methyl-2-oxoindolin-3-ylidene)acetate (1d)**



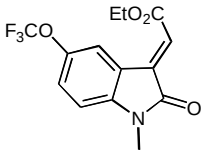
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.36-8.33 (1H, m), 7.09-7.05 (1H, m), 6.90 (1H, s), 6.71-6.68 (1H, m), 4.33 (2H, q, *J* = 7Hz), 3.21 (3H, s), 1.38 (3H, t, *J* = 7Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.11, 165.26, 160.03, 157.65, 141.97, 137.40, 123.65, 120.62, 120.52, 118.63, 118.39, 116.49, 116.22, 108.40, 108.32, 61.33, 26.25, 14.08. MS: m/z = 249.04 ($[M]^+$).

***(E)*-Ethyl 2-(5-bromo-1-methyl-2-oxoindolin-3-ylidene)acetate (1e)**



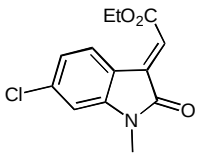
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.70 (1 H, s), 7.48 (1 H, d, *J* = 8.2Hz), 6.90 (1 H, s), 6.67 (1 H, d, *J* = 8.3Hz), 4.34 (2 H, q, *J* = 7.1Hz), 3.21 (3 H, s), 1.39 (3 H, t, *J* = 7.1Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.87, 165.22, 144.74, 136.67, 134.81, 131.48, 123.89, 121.28, 115.43, 109.43, 61.43, 26.29, 14.13. MS: m/z = 310.98 ($[M]^+$).

***(E)*-Ethyl 2-(1-methyl-2-oxo-5-(trifluoromethoxy)indolin-3-ylidene)acetate (1f)**



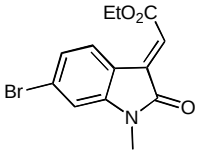
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.53 (1 H, s), 7.25 (1 H, d, *J* = 8.4Hz), 6.95 (1 H, d, *J* = 1.6Hz), 6.78 (1 H, d, *J* = 8.5Hz), 4.35 (2 H, q, *J* = 7.1Hz), 3.23 (3 H, s), 1.38 (3 H, t, *J* = 7.1Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.18, 165.20, 144.56, 144.43, 136.86, 125.23, 124.22, 122.55, 121.80, 120.59, 119.25, 108.39, 61.46, 26.30, 14.05. MS: m/z = 315.03 ($[M]^+$).

***(E)*-Ethyl 2-(6-chloro-1-methyl-2-oxoindolin-3-ylidene)acetate (1g)**



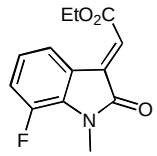
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.48 (1 H, d, *J* = 8.3Hz), 7.00-6.98 (1 H, m), 6.85 (1 H, s), 6.75 (1 H, d, *J* = 1.6Hz), 4.31 (2 H, q, *J* = 7.1Hz), 3.19 (3 H, s), 1.37 (3 H, t, *J* = 7.1Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.35, 165.40, 146.92, 138.23, 136.70, 129.70, 122.65, 122.55, 118.13, 108.74, 61.22, 26.23, 14.09. MS: m/z = 265.09 ($[M]^+$).

***(E)*-Ethyl 2-(6-bromo-1-methyl-2-oxoindolin-3-ylidene)acetate (1h)**



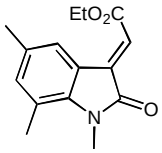
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.40 (1 H, d, *J* = 8.3Hz), 7.17-7.14 (1 H, m), 6.91 (1H, d, *J* = 1.4Hz), 6.87 (s, 1H), 4.31 (2 H, q, *J* = 7.1Hz), 3.19 (3 H, s), 1.37 (3 H, t, *J* = 7.1Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.18, 165.39, 146.84, 136.76, 129.83, 126.57, 125.54, 122.88, 118.52, 111.55, 61.23, 26.22, 14.08. MS: m/z = 310.94 ($[M]^+$).

***(E)*-Ethyl 2-(7-fluoro-1-methyl-2-oxoindolin-3-ylidene)acetate (1i)**



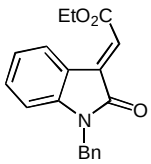
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.36 (1 H, d, *J* = 7.7Hz), 7.14 – 7.03 (1 H, m), 7.02 – 6.88 (2 H, m), 4.32 (2 H, q, *J* = 7.1Hz), 3.44 (3 H, s), 1.37 (3 H, t, *J* = 7.1Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.04, 165.24, 148.67, 146.26, 136.87, 132.29, 124.54, 123.78, 123.08, 123.01, 122.35, 120.22, 120.03, 61.25, 28.81, 28.75, 14.08. MS: m/z = 249.11 ($[M]^+$).

***(E)*-Ethyl 2-(1,5,7-trimethyl-2-oxoindolin-3-ylidene)acetate (1j)**



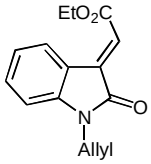
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.28 (1 H, s), 6.91 (1 H, s), 6.85 (1 H, s), 4.32 (2 H, q, *J* = 7.1Hz), 3.48 (3 H, s), 2.50 (3 H, s), 2.29 (3 H, s), 1.37 (3 H, t, *J* = 7.1Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 168.10, 165.60, 141.19, 137.63, 136.76, 131.84, 126.98, 121.43, 120.33, 119.11, 60.93, 29.54, 20.68, 18.81, 14.09. MS: m/z =259.10 ($[M]^+$).

(*E*)-Ethyl 2-(1-benzyl-2-oxoindolin-3-ylidene)acetate (1k)



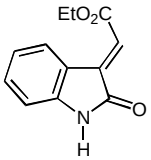
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.57 (1 H, d, *J* = 7.7 Hz), 7.42 – 7.18 (6 H, m), 7.01 (2 H, m), 6.68 (1 H, d, *J* = 7.8Hz), 4.93 (2 H, s), 4.33 (2 H, q, *J* = 7.1Hz), 1.37 (3 H, t, *J* = 7.1Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.61, 165.57, 145.01, 137.60, 135.35, 132.29, 128.75, 127.67, 127.16, 122.76, 119.90, 109.08, 61.16, 43.76, 14.14. MS: m/z =307.11 ($[M]^+$).

(*E*)-Ethyl 2-(1-allyl-2-oxoindolin-3-ylidene)acetate (1l)



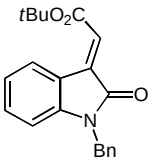
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.56 (1 H, d, *J* = 7.7Hz), 7.33 (1 H, t, *J* = 7.7Hz), 7.05 (1 H, t, *J* = 7.7Hz), 6.92 (1 H, s), 6.78 (1 H, d, *J* = 7.9Hz), 5.88-5.79 (1 H, m), 5.25 (1H, d, *J* = 7.4Hz), 5.21 (1H, s), 4.41 – 4.29 (4 H, m), 1.37 (3 H, t, *J* = 7.1Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.16, 165.55, 145.08, 137.60, 132.25, 130.97, 128.71, 122.69, 122.52, 119.82, 117.62, 108.93, 61.11, 42.30, 14.12. MS: m/z = 257.14($[M]^+$).

(*E*)-Ethyl 2-(2-oxoindolin-3-ylidene)acetate (1m)



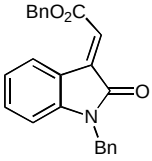
^{1}H NMR (600 MHz, DMSO) δ（ppm）10.82 (s, 1H), 8.36 (1H, d, *J* = 7.7 Hz), 7.37 (1H, t, *J* = 7.7 Hz), 7.02 (1H, t, *J* = 7.6 Hz), 6.89 (1H, d, *J* = 7.7 Hz), 6.60 (s, 1H), 4.28 (2H, q, *J* = 7.1 Hz), 1.31 (3H, t, *J* = 7.1 Hz). ^{13}C NMR (150 MHz, DMSO) δ 167.79, 165.10, 145.04, 138.26, 133.00, 128.09, 121.87, 120.71, 119.56, 110.33, 60.99, 14.01. MS: m/z = 217.0 (M^+).

(*E*)-*tert*-Butyl 2-(1-benzyl-2-oxoindolin-3-ylidene)acetate (1n)



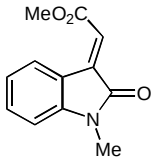
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (1 H, d, *J* = 7.6Hz), 7.38 – 7.17 (7 H, m), 7.03 (1 H, t, *J* = 7.6Hz), 6.93 (1 H, s), 6.68 (1 H, d, *J* = 7.7Hz), 4.94 (2 H, s), 1.58 (10 H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.79, 164.86, 144.73, 136.49, 135.38, 131.96, 128.72, 128.54, 127.62, 127.12, 125.07, 122.71, 119.95, 109.01, 81.85, 43.67, 28.02. MS: m/z = 335.24 (M^+).

(*E*)-Benzyl 2-(1-benzyl-2-oxoindolin-3-ylidene)acetate (1o)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (1 H, d, *J* = 7.7Hz), 7.49 – 7.34 (5 H, m), 7.32 – 7.21 (7 H, m), 7.08 – 6.94 (2 H, m), 6.69 (1 H, d, *J* = 7.8Hz), 5.32 (2 H, s), 4.93 (2 H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.46, 165.28, 145.01, 138.07, 135.24, 132.43, 128.83, 128.73, 128.57, 128.36, 128.20, 127.65, 127.12, 122.79, 122.16, 119.76, 109.09, 66.84, 43.71. MS: m/z = 369.17 (M^+).

(*E*)-Methyl 2-(1-methyl-2-oxoindolin-3-ylidene)acetate (1p)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (1 H, d, *J* = 7.7Hz), 7.38 (1 H, t, *J* = 7.7Hz), 7.07 (1 H, t, *J* = 7.6Hz), 6.91 (1 H, s), 6.80 (1 H, d, *J* = 7.8Hz), 3.88 (3 H, s), 3.24 (3 H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.33, 165.97, 145.84, 138.01, 132.42, 128.62, 122.74, 121.69, 119.61, 108.06, 52.08, 26.13. MS: m/z = 217.09 (M^+).

3. Detailed optimization of reaction conditions

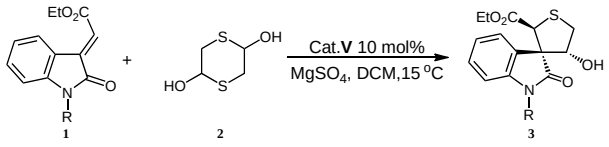
3.1 Optimization of the protection group on the N atom of the oxindole.

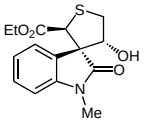
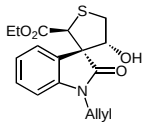
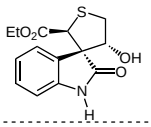
In order to examine the effect of the protection group on the N atom, we prepared the corresponding substrates according to the general procedure. The results are listed in Table S1.

3.2 Optimization of the ester group in the oxindole.

The corresponding substrates were prepared according to the general procedure . The results are listed in Table S2.

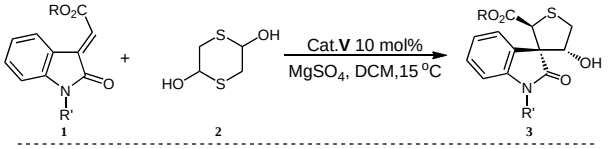
Table S1 Optimization of the protection group on the N atom[a]

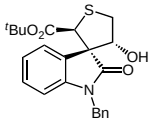
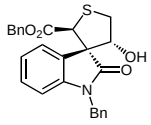
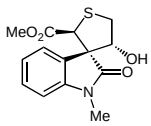


Entry	product		time	yield[b]	ee[c]
1		**3a**	50 min	90%	80
2		**3l**	60 min	96 %	82
3[d]		**3m**	5 h	32%	-38

[a] Unless otherwise specified, all reactions were carried out with **1** (0.3 mmol), **2** (0.18 mmol), **V** (10 mol%), $MgSO_4$ (36 mg) in DCM (1 mL) at 15 °C. [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] The reaction was conducted with 10 mol% of **VI**.

Table S2 Optimization of the ester group[a]

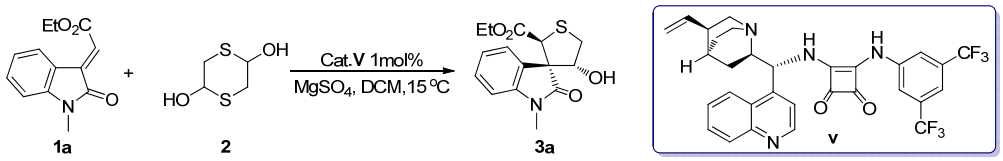


Entry	product		time	yield[b]	ee[c]
1		**3n**	5 h	96%	81
2		**3o**	40 min	92 %	79
3		**3p**	50 min	78%	78

[a] Unless otherwise specified, all reactions were carried out with **1** (0.3 mmol), **2** (0.18 mmol), **V** (10 mol%), $MgSO_4$ (36 mg) in DCM (1 mL) at 15 °C. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

4. General Procedure and Spectral Data of Products

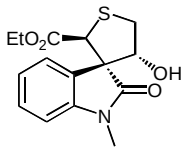
4.1 General Procedure



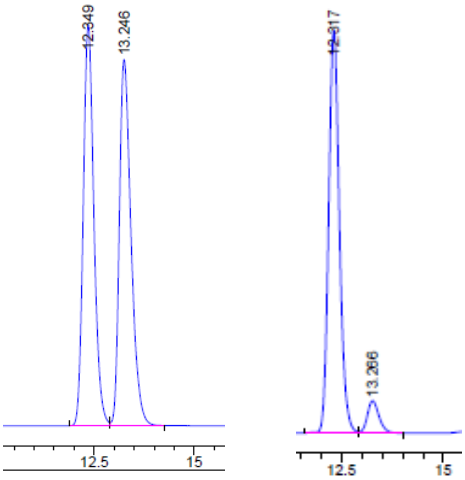
A mixture of *(E)*-ethyl 2-(1-methyl-2-oxoindolin-3-ylidene)acetate **1a** (0.5 mmol, 115.6 mg), $MgSO_4$ (60 mg) and cat. **V** (0.005 mmol, 3.0 mg) in DCM (10 mL) was stirred at 15°C for 30 min followed by addition of **2** (0.3 mmol, 45.7 mg). The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 5:1~3:1) to give the desired product **3a** as a white solid.

4.2 Spectral Data of Products

(2'S,3R,4'R)-Ethyl 4'-hydroxy-1-methyl-2-oxo-4',5'-dihydro-2'H-spiro[indoline-3,3'-thiophene]-2'-carboxylate(3a)

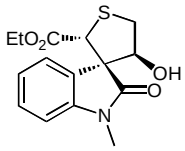


Prepared according to the general procedure from **1a** (0.5 mmol, 115.6 mg), **2** (0.3 mmol, 45.7 mg), $MgSO_4$ (60 mg) and cat.**V** (0.005mol, 3.0 mg) in disted. DCM (10 mL) at 15 °C for 7 h to provide the title compound as a white solid (92% yield, mp:126-128 °C, 84% ee, >19:1 d.r.). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.60 (1 H, d, *J* = 7.4Hz), 7.37 (1 H, t, *J* = 7.8Hz), 7.12 (1 H, t, *J* = 7.6Hz), 6.93 (1 H, d, *J* = 7.8Hz), 5.02 (1 H, s), 4.60 (1 H, s), 4.30 (1 H, d, *J* = 3.2Hz), 3.91 – 3.69 (2 H, m), 3.47 (1 H, dd, *J* = 11.7Hz, 3.2Hz), 3.32 (3 H, s), 3.22 (1 H, d, *J* = 11.7Hz), 0.79 (3 H, t, *J* = 7.1Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 176.15, 168.23, 143.25, 129.39, 126.00, 124.71, 123.36, 108.36, 79.68, 61.28, 54.75, 54.71, 38.40, 26.57, 13.42. MS: m/z = 307.00 ($[M]^+$). Anal. calcd for ($C_{15}H_{17}NO_4S$): C, 58.61; H, 5.57; N, 4.56; S, 10.43. found: C, 58.67; H, 5.30; N, 4.38; S, 10.69. $[\alpha]_D^{19}$= 99.17 (C = 1.00, CH_2Cl_2). HPLC (Chiralpak AD-H column, hexane/2-propanol = 80:20, 1.0 mL/min; 254 nm, 25 °C, t_1 = 12.35 min, t_2 = 13.25 min).

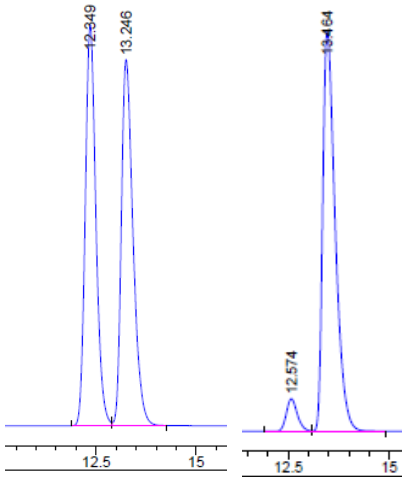


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.317	BV	0.2817	1.23544e4	675.69775	91.9714
2	13.266	VB	0.3046	1078.47693	54.28935	8.0286

(2'R,3S,4'S)-Ethyl 4'-hydroxy-1-methyl-2-oxo-4',5'-dihydro-2'H-spiro[indoline-3,3'-thiophene]-2'-carboxylate(ent-3a)

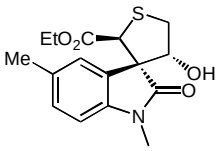


Prepared according to the general procedure from **1a** (0.5 mmol, 115.6 mg), **2** (0.3 mmol, 45.7 mg), $MgSO_4$ (60 mg) and cat.**VI** (0.005mol, 3.2 mg) in disted. DCM (10 mL) at 15 ^oC for 12 h to provide the title compound as a white solid (96% yield, -87% ee, >19:1 d.r.). $[\alpha]_D^{17}$= -91.87 (C = 0.99, CH_2Cl_2).

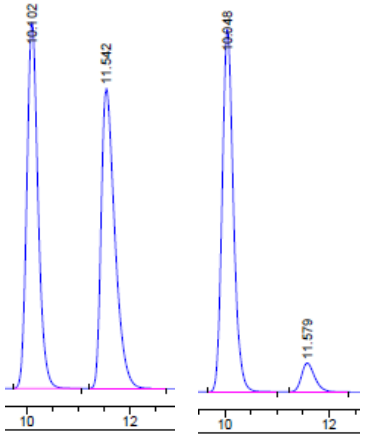


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.574	BV	0.2917	1428.83704	75.16361	6.7289
2	13.464	VB	0.3271	1.98056e4	924.47528	93.2711

(2'S,3R,4'R)-Ethyl 4'-hydroxy-1,5-dimethyl-2-oxo-4',5'-dihydro-2'H-spiro[indoline-3,3'-thiophene]-2'-carboxylate(3b)

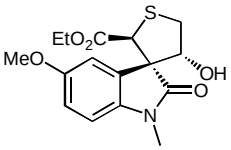


Prepared according to the general procedure from **1b** (0.5 mmol, 122.6 mg), **2** (0.3 mmol, 45.7 mg), $MgSO_4$ (60 mg) and cat.**V** (0.005mol, 3.0 mg) in disted. DCM (10 mL) at 15 ^oC for 12 h to provide the title compound as a white solid (96% yield, mp:109-112 ^oC, 83% ee, 17:1 d.r.). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.39 (1 H, s), 7.16 (1 H, d, *J* = 7.9Hz), 6.82 (1 H, d, *J* = 7.9Hz), 5.01 (1 H, s), 4.67 (1 H, s), 4.28 (1 H, d, *J* = 3.1Hz), 3.93 – 3.69 (2 H, m), 3.49 (1 H, d, *J* = 11.6Hz), 3.30 (3 H, s), 3.22 (1 H, d, *J* = 11.7Hz), 2.35 (3 H, s), 0.80 (3 H, t, *J* = 7.1Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 176.06, 168.27, 140.87, 133.02, 129.61, 126.02, 125.41, 108.09, 79.74, 61.37, 61.25, 54.77, 38.45, 26.59, 21.12, 13.44. MS: m/z = 321.01 ($[M]^+$). Anal. calcd for ($C_{16}H_{19}NO_4S$): C, 59.79; H, 5.96; N, 4.36; S, 9.98. found: C, 59.88; H, 5.79; N, 4.15; S 10.02. $[\alpha]_D^{21}$= 70.29 (C = 1.00, CH_2Cl_2). HPLC (Chiralpak AD-H column, hexane/2-propanol = 80:20, 1.0 mL/min; 254 nm, 25 ^oC, t_1 = 10.10 min, t_2 = 11.54 min).

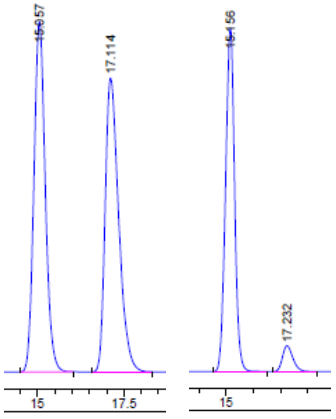


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.048	BB	0.2303	1.35067e4	900.71259	91.3772
2	11.579	BB	0.2729	1274.56689	71.69286	8.6228

(2'S,3R,4'R)-Ethyl 4'-hydroxy-5-methoxy-1-methyl-2-oxo-4',5'-dihydro-2'H-spiro[indoline-3,3'-thiophene]-2'-carboxylate(3c)

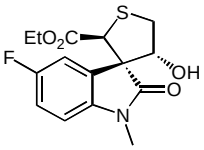


Prepared according to the general procedure from **1c** (0.5 mmol, 130.6 mg), **2** (0.3 mmol, 45.7 mg), $MgSO_4$ (60 mg) and cat.**V** (0.005mol, 3.0 mg) in disted. DCM (10 mL) at 15 ^oC for 10 h to provide the title compound as a white solid (96% yield, mp:128-130 ^oC, 84% ee, 13:1 d.r.). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.25 (1 H, d, J = 2.2Hz), 6.90 – 6.82 (2 H, m), 5.02 (1 H, s), 4.67 (1 H, s), 4.29 (1 H, d, J = 3.1Hz), 3.94 – 3.72 (5 H, m), 3.47 (1 H, d, J = 11.5Hz), 3.30 (3 H, s), 3.21 (1 H, d, J = 11.8Hz), 0.84 (3 H, t, J = 7.1Hz) ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 175.63, 168.11, 156.26, 136.60, 127.27, 112.98, 112.44, 108.56, 79.60, 61.47, 61.20, 55.63, 54.53, 38.11, 26.58, 13.41. MS: m/z = 337.01 ($[M]^+$). Anal. calcd for ($C_{16}H_{19}NO_5S$): C, 56.96; H, 5.68; N, 4.15; S, 9.50. found: C, 56.94; H, 5.45; N, 4.02; S, 9.60. $[\alpha]_D^{20}$= 60.05 (C = 0.98, CH_2Cl_2). HPLC (Chiralpak AD-H column, hexane/2-propanol = 80:20, 1.0 mL/min; 254 nm, 25 ^oC, t_1 = 15.06 min, t_2 = 17.11 min).

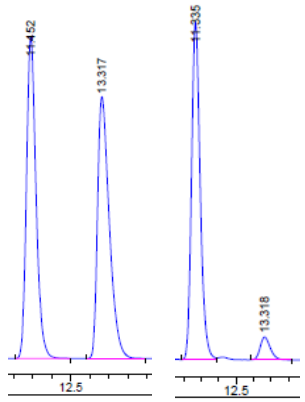


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.156	BB	0.3552	1.71589e4	747.48737	91.9521
2	17.232	BB	0.4101	1501.79175	56.32570	8.0479

(2'S,3R,4'R)-Ethyl 5-fluoro-4'-hydroxy-1-methyl-2-oxo-4',5'-dihydro-2'H-spiro[indoline-3,3'-thiophene]-2'-carboxylate(3d)

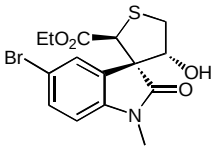


Prepared according to the general procedure from **1d** (0.5 mmol, 124.6 mg), **2** (0.3 mmol, 45.7 mg), $MgSO_4$ (60 mg) and cat.**V** (0.005mol, 3.0 mg) in disted. DCM (10 mL) at 15 ^oC for 4 h to provide the title compound as a white solid (92% yield, mp:146-149 ^oC, 85% ee, 11:1 d.r.). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.40 (1 H, dd, J = 8.2Hz, 2.5Hz), 7.11 – 7.06 (1 H, m), 6.86 (1 H, dd, J = 8.5Hz, 4.2Hz), 5.03 (1 H, s), 4.54 (1 H, s), 4.30 (1 H, d, J = 3.2Hz), 3.96 – 3.75 (2 H, m), 3.47 – 3.39 (1 H, m), 3.31 (3 H, s), 3.24 (1 H, d, J = 11.9Hz), 0.88 (3 H, t, J = 7.1Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 175.76, 168.02, 160.49, 158.09, 139.30, 127.65, 127.56, 115.69, 115.45, 113.21, 112.95, 108.89, 108.81, 79.44, 61.44, 54.43, 54.39, 38.11, 26.72, 13.49. MS: m/z = 325.01 ($[M]^+$). Anal. calcd for ($C_{15}H_{16}FNO_4S$): C, 55.37; H, 4.96; N, 4.31; S, 9.86. found: C, 55.36; H, 4.76; N, 4.18; S, 9.73. $[\alpha]_D^{20}$= 74.86 (C = 1.01, CH_2Cl_2). HPLC (Chiralpak AD-H column, hexane/2-propanol = 80:20, 1.0 mL/min; 254 nm, 25 ^oC, t_1 = 11.45 min, t_2 = 13.32 min).

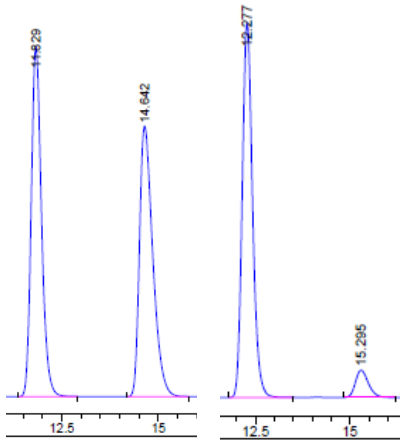


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.335	VV	0.2642	1.40417e4	812.71832	92.6271
2	13.318	BB	0.3096	1117.69067	55.06048	7.3729

(2'S,3R,4'R)-Ethyl 5-bromo-4'-hydroxy-1-methyl-2-oxo-4',5'-dihydro-2'H-spiro[indoline-3,3'-thiophene]-2'-carboxylate(3e)

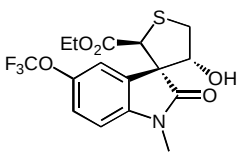


Prepared according to the general procedure from **1e** (0.5 mmol, 155.1 mg), **2** (0.3 mmol, 45.7 mg), $MgSO_4$ (60 mg) and cat.**V** (0.005mol, 3.0 mg) in disted. DCM (10 mL) at 15 ^oC for 3 h to provide the title compound as a white solid (83% yield, mp:122-124 ^oC, 83% ee, 4:1 d.r.). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.72 (1 H, d, *J* = 2.7Hz), 7.52 (1 H, d, *J* = 8.2Hz), 6.82 (1 H, d, *J* = 8.3Hz), 5.02 (1 H, d, *J* = 5.2Hz), 4.46 (1 H, s), 4.29 (1 H, s), 4.02 – 3.74 (2 H, m), 3.44 (1 H, d, *J* = 11.8Hz), 3.31 (3 H, d, *J* = 2.9Hz), 3.24 (1 H, dd, *J* = 11.8Hz, 4.6Hz), 0.90 (3 H, t, *J* = 7.0Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 175.61, 168.02, 142.43, 132.23, 128.22, 127.74, 116.06, 109.77, 79.48, 61.56, 61.34, 54.43, 38.32, 26.73, 13.57. MS: m/z = 384.88 ($[M]^+$). Anal. calcd for ($C_{15}H_{16}BrNO_4S$): C, 46.64; H, 4.18; N, 3.63; S, 8.30. found: C,46.65; H, 4.28; N, 3.49; S, 8.33. $[\alpha]_D^{17}$= 50.84 (C = 0.98, CH_2Cl_2). HPLC (Chiralpak AD-H column, hexane/2-propanol = 80:20, 1.0 mL/min; 254 nm, 25 ^oC, t_1 = 11.83 min, t_2 = 14.64 min).



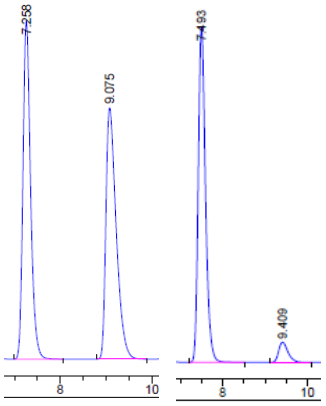
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.277	BB	0.2911	1.76707e4	931.85284	91.5892
2	15.295	BB	0.3676	1622.74426	68.25755	8.4108

(2'S,3R,4'R)-ethyl 4'-hydroxy-1-methyl-2-oxo-5-(trifluoromethoxy)-4',5'-dihydro-2'H-spiro[indoline-3,3'-thiophene]-2'-carboxylate (3f)



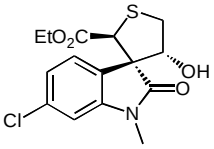
Prepared according to the general procedure from **1f** (0.5 mmol, 157.6 mg), **2** (0.3 mmol, 45.7 mg), $MgSO_4$ (60 mg) and cat.**V** (0.005mol, 3.0 mg) in disted. DCM (10 mL) at 15 ^oC for 10 h to provide the title compound as a white solid (74% yield, mp:127-129 ^oC, 86% ee, 6:1 d.r.). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.53 (1 H, s), 7.27 (1 H, d, *J* =

3.9Hz), 6.93 (1 H, d, *J* = 8.5Hz), 5.03 (1 H, s), 4.44 (1 H, s), 4.31 (1 H, d, *J* = 3.2 Hz), 3.98 – 3.75 (2 H, m), 3.41 (1 H, d, *J* = 11.9 Hz), 3.33 (3 H, s), 3.25 (1 H, d, *J* = 11.8 Hz), 0.88 (3 H, t, *J* = 7.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 175.89, 168.05, 144.94, 142.10, 127.73, 122.45, 121.58, 118.95, 108.79, 79.42, 61.56, 61.45, 54.31, 38.14, 26.74, 13.51. MS: m/z = 391.00 ($[M]^+$). Anal. calcd for ($C_{16}H_{16}F_3NO_5S$): C, 49.10; H, 4.12; N, 3.58; S, 8.19. found: C,49.06; H, 3.90; N, 3.56; S, 8.46. $[\alpha]_D^{16}$= 64.79 (C = 1.01, CH_2Cl_2). HPLC (Chiralpak AD-H column, hexane/2-propanol = 80:20, 1.0 mL/min; 254 nm, 25 °C, t_1 = 7.26 min, t_2 = 9.08 min).

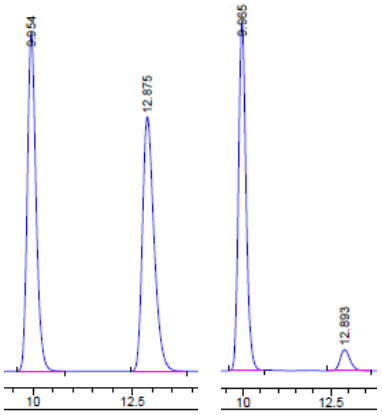


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.493	BB	0.1823	1.72354e4	1451.07397	92.8058
2	9.409	BB	0.2334	1336.07556	87.53539	7.1942

(2'S,3R,4'R)-Ethyl 6-chloro-4'-hydroxy-1-methyl-2-oxo-4',5'-dihydro-2'H-spiro[indoline-3,3'-thiophene]-2'-carboxylate(3g)

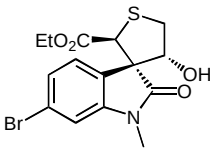


Prepared according to the general procedure from **1g** (0.5 mmol, 132.8 mg), **2** (0.3 mmol, 45.7 mg), $MgSO_4$ (60 mg) and cat.**V** (0.005mol, 3.0 mg) in disted. DCM (10 mL) at 15 °C for 4 h to provide the title compound as a white solid (87% yield, mp:136-139 °C, 85% ee, 8:1 d.r.). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.52 (1 H, d, *J* = 8.0Hz), 7.09 (1 H, dd, *J* = 8.0Hz, 1.6Hz), 6.93 (1 H, d, *J* = 1.6Hz), 5.01 (1 H, s), 4.43 (1 H, s), 4.27 (1 H, d, *J* = 3.2Hz), 4.00 – 3.70 (2 H, m), 3.46 – 3.36 (1 H, m), 3.30 (3 H, s), 3.23 (1 H, d, *J* = 11.8Hz), 0.89 (3 H, t, *J* = 7.1Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 176.11, 168.10, 144.55, 135.27, 125.69, 124.51, 123.09, 109.14, 79.51, 61.51, 61.04, 54.48, 38.31, 26.72, 13.58. MS: m/z = 341.04 ($[M]^+$). Anal. calcd for ($C_{15}H_{16}ClNO_4S$): C, 52.71; H, 4.72; N, 4.10; S, 9.38. found: C, 52.93; H, 4.65; N, 4.07; S, 9.36. $[\alpha]_D^{22}$= 93.33 (C = 0.99, CH_2Cl_2). HPLC (Chiralpak AD-H column, hexane/2-propanol = 80:20, 1.0 mL/min; 254 nm, 25 °C, t_1 = 9.95 min, t_2 = 12.88 min).

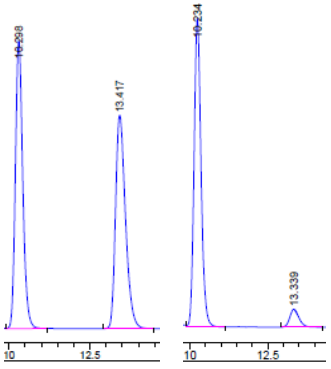


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.965	BV	0.2305	1.31808e4	877.82440	92.6004
2	12.893	VB	0.3017	1053.25610	53.67213	7.3996

(2'S,3R,4'R)-Ethyl 6-bromo-4'-hydroxy-1-methyl-2-oxo-4',5'-dihydro-2'H-spiro[indoline-3,3'-thiophene]-2'-carboxylate(3h)

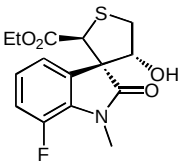


Prepared according to the general procedure from **1h** (0.5 mmol, 155.1 mg), **2** (0.3 mmol, 45.7 mg), $MgSO_4$ (60 mg) and cat.**V** (0.005mol, 3.0 mg) in disted. DCM (10 mL) at 15 ^oC for 5 h to provide the title compound as a white solid (89% yield, mp:146-149 ^oC, 86% ee, 7:1 d.r.). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.47 (1 H, d, *J* = 8.0Hz), 7.25 (1 H, dd, *J* = 8.0Hz, 1.5Hz), 7.08 (1 H, d, *J* = 1.3Hz), 5.01 (1 H, s), 4.42 (1 H, s), 4.27 (1 H, d, *J* = 3.2Hz), 3.96 – 3.76 (2 H, m), 3.40 (1 H, d, *J* = 11.8Hz), 3.30 (3 H, s), 3.23 (1 H, d, *J* = 11.8Hz), 0.89 (3 H, t, *J* = 7.1Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 175.97, 168.09, 144.63, 126.05, 126.00, 125.07, 123.07, 111.90, 79.46, 61.52, 61.09, 54.42, 38.31, 26.71, 13.58. MS: m/z = 384.81 ($[M]^+$). Anal. calcd for ($C_{15}H_{16}BrNO_4S$): C, 46.64; H, 4.18; N, 3.63; S, 8.30. found: C, 46.37; H, 4.04; N, 3.62; S, 8.10. $[\alpha]_D^{21}$= 77.59 (C = 0.99, CH_2Cl_2). HPLC (Chiralpak AD-H column, hexane/2-propanol = 80:20, 1.0 mL/min; 254 nm, 25 ^oC, t_1 = 10.30 min, t_2 = 13.42 min).

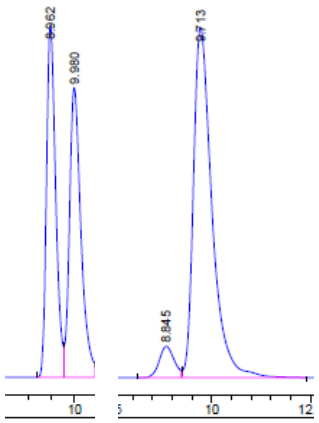


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.234	VB	0.2387	1.09004e4	699.07599	92.8033
2	13.339	BB	0.3204	845.30688	40.78711	7.1967

(2'S,3R,4'R)-Ethyl 7-fluoro-4'-hydroxy-1-methyl-2-oxo-4',5'-dihydro-2'H-spiro[indoline-3,3'-thiophene]-2'-carboxylate(3i)

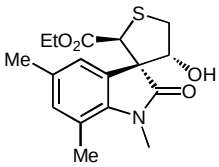


Prepared according to the general procedure from **1i** (0.5 mmol, 124.6 mg), **2** (0.3 mmol, 45.7 mg), $MgSO_4$ (60 mg) and cat.**V** (0.005mol, 3.0 mg) in disted. DCM (10 mL) at 15 ^oC for 10 h to provide the title compound as a white solid (81% yield, mp:116-118 ^oC, 87% ee, 5:1 d.r.). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.41 (1 H, d, *J* = 7.3Hz), 7.16 – 7.00 (2 H, m), 5.02 (1 H, s), 4.51 (1 H, s), 4.30 (1 H, d, *J* = 3.3Hz), 4.00 – 3.72 (2 H, m), 3.53 (3 H, d, *J* = 2.8Hz), 3.49 – 3.40 (1 H, m), 3.23 (1 H, d, *J* = 11.8Hz), 0.88 (3 H, t, *J* = 7.1Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 175.74, 168.08, 148.89, 146.46, 129.99, 128.98, 124.00, 123.93, 120.52, 117.44, 117.25, 79.66, 61.41, 54.77, 54.74, 38.28, 29.09, 13.49. MS: m/z = 325.02 ($[M]^+$). Anal. calcd for ($C_{15}H_{16}FNO_4S$): C, 55.37; H, 4.96; N, 4.31; S, 9.86. found: C, 55.40; H, 4.74; N, 4.31; S, 9.92. $[\alpha]_D^{16}$= 92.82 (C = 1.02, CH_2Cl_2). HPLC (Chiralpak OJ-H column, hexane/2-propanol = 80:20, 1.0 mL/min; 254 nm, 25 ^oC, t_1 = 8.96 min, t_2 = 9.98 min).

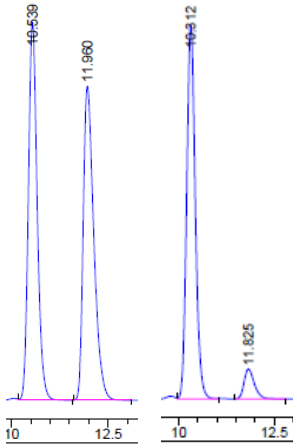


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.845	BV	0.4048	1233.50488	46.84075	6.7539
2	9.713	VB	0.4919	1.70300e4	523.18903	93.2461

(2'S,3R,4'R)-Ethyl 4'-hydroxy-1,5,7-trimethyl-2-oxo-4',5'-dihydro-2'H-spiro[indoline-3,3'-thiophene]-2'-carboxylate(3j)

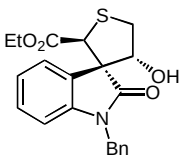


Prepared according to the general procedure from **1j** (0.5 mmol, 129.7 mg), **2** (0.3 mmol, 45.7 mg), $MgSO_4$ (60 mg) and cat.**V** (0.005mol, 3.0 mg) in disted. DCM (10 mL) at 15 ^oC for 10 h to provide the title compound as a white solid (94% yield, mp:145-149 ^oC, 83% ee, 15:1 d.r.). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.25 (1 H, s), 6.89 (1 H, s), 4.99 (1 H, s), 4.75 (1 H, s), 4.23 (1 H, d, *J* = 2.9Hz), 3.97 – 3.70 (2 H, m), 3.57 (3 H, s), 3.48 (1 H, d, *J* = 11.7Hz), 3.20 (1 H, d, *J* = 11.7Hz), 2.55 (3 H, s), 2.29 (3 H, s), 0.83 (3 H, t, *J* = 7.1Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 176.69, 168.23, 138.41, 133.45, 132.66, 126.66, 122.96, 119.50, 79.88, 61.08, 60.68, 54.86, 38.37, 29.88, 20.70, 18.78, 13.45. MS: m/z = 335.01 ($[M]^+$). Anal. calcd for ($C_{17}H_{21}NO_4S$): C, 60.87; H, 6.31; N, 4.18; S, 9.56. found: C, 61.07; H, 6.18; N, 4.03; S, 9.85. $[\alpha]_D^{21}$= 82.82 (C = 0.98, CH_2Cl_2). HPLC (Chiralpak AD-H column, hexane/2-propanol = 80:20, 1..0 mL/min; 254 nm, 25 ^oC, t_1 = 10.54 min, t_2 = 11.96 min).



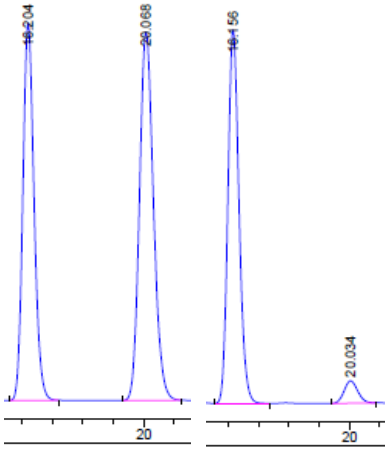
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.312	VB	0.2414	1.76776e4	1126.12451	91.2576
2	11.825	BB	0.2872	1693.50098	90.30971	8.7424

(2'S,3R,4'R)-Ethyl 1-benzyl-4'-hydroxy-2-oxo-4',5'-dihydro-2'H-spiro[indoline-3,3'-thiophene]-2'-carboxylate(3k)



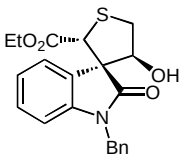
Prepared according to the general procedure from **1k** (0.5 mmol, 153.7 mg), **2** (0.3 mmol, 45.7 mg), $MgSO_4$ (60 mg) and cat.**V** (0.005mol, 3.0 mg) in disted. DCM (10 mL) at 15 ^oC for 6 h to provide the title compound as a white solid (95% yield, mp:104-107 ^oC, 86% ee, >19:1 d.r.). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.60 (1 H, d, *J* = 7.5Hz), 7.39-7.29 (5 H, m), 7.27-

7.24 (1 H, m), 7.07 (1 H, t, *J* = 7.6Hz), 6.85 (1 H, d, *J* = 7.9Hz), 5.08 (1 H, s), 5.00 (2 H, dd, *J* = 39.7Hz, 15.6Hz), 4.63 (1 H, s), 4.33 (1 H, d, *J* = 2.9Hz), 3.94 – 3.57 (2 H, m), 3.48 (1 H, d, *J* = 11.5Hz), 3.24 (1 H, d, *J* = 11.7Hz), 0.59 (3 H, t, *J* = 7.0Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 176.35, 168.26, 142.35, 134.99, 129.24, 128.72, 127.86, 127.45, 126.20, 124.77, 123.38, 109.39, 80.16, 61.42, 61.37, 54.61, 44.19, 38.28, 13.21. MS: m/z = 383.02 ([M]$^+$). Anal. calcd for ($C_{21}H_{21}NO_4S$): C, 65.78; H, 5.52; N, 3.65; S, 8.36. found: C, 65.57; H, 5.37; N, 3.55; S, 8.52. $[\alpha]_D^{21}$= 67.91 (C = 0.99, CH_2Cl_2). HPLC (Chiralpak AD-H column, hexane/2-propanol = 80:20, 1.0 mL/min; 254 nm, 25 °C, t_1 = 16.20 min, t_2 = 20.07 min).

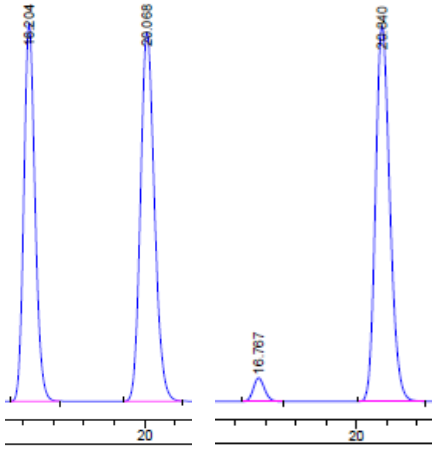


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.156	VB	0.3928	1.36641e4	537.33417	93.0827
2	20.034	PB	0.4865	1015.42084	32.40254	6.9173

(2'R,3S,4'S)-Ethyl 1-benzyl-4'-hydroxy-2-oxo-4',5'-dihydro-2'H-spiro[indoline-3,3'-thiophene]-2'-carboxylate(ent-3k)

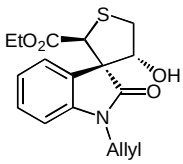


Prepared according to the general procedure from **1k** (0.5 mmol, 153.6 mg), **2** (0.3 mmol, 45.7 mg), $MgSO_4$ (60 mg) and cat.**VI** (0.005mol, 3.2 mg) in disted. DCM (10 mL) at 15 °C for 11 h to provide the title compound as a white solid (94% yield, -90% ee, >19:1 d.r.). $[\alpha]_D^{17}$= -71.20 (C = 1.01, CH_2Cl_2).



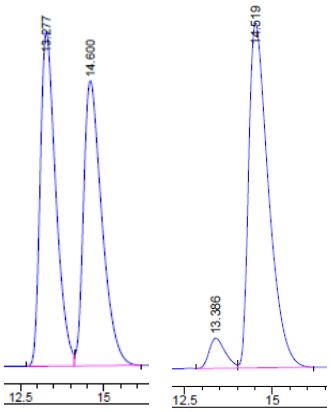
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.767	BB	0.3994	801.58215	31.13420	4.7003
2	20.840	BB	0.5085	1.62523e4	494.68558	95.2997

(2'S,3R,4'R)-Ethyl 1-allyl-4'-hydroxy-2-oxo-4',5'-dihydro-2'H-spiro[indoline-3,3'-thiophene]-2'-carboxylate(3l)



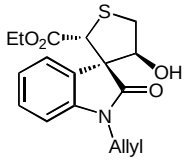
Prepared according to the general procedure from **1l** (0.5 mmol, 128.6 mg), **2** (0.3 mmol, 45.7 mg), $MgSO_4$ (60 mg) and cat.**V** (0.005mol, 3.0 mg) in disted. DCM (10 mL) at 15 °C

for 6 h to provide the title compound as a white solid (94% yield, mp: 90-92 °C, 87% ee, >19:1 d.r.). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.61 (1 H, d, *J* = 7.5Hz), 7.33 (1 H, t, *J* = 7.7Hz), 7.11 (1 H, t, *J* = 7.6Hz), 6.93 (1 H, d, *J* = 7.8Hz), 5.90 – 5.83 (1 H, m), 5.31 (2 H, dd, *J* = 18.1Hz, 13.8Hz), 5.04 (1 H, s), 4.57 (1 H, d, *J* = 1.8Hz), 4.44 (2 H, d, *J* = 2.4Hz), 4.30 (1 H, d, *J* = 3.2Hz), 3.93 – 3.75 (2 H, m), 3.50 – 3.46 (1 H, m), 3.23 (1 H, d, *J* = 11.7Hz), 0.79 (3 H, t, *J* = 7.1Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 175.94, 168.24, 142.40, 130.49, 129.23, 126.14, 124.73, 123.29, 118.14, 109.25, 79.94, 61.42, 61.24, 54.57, 42.69, 38.29, 13.41. MS: m/z = 333.03 ($[M]^+$). Anal. calcd for ($C_{17}H_{19}NO_4S$): C, 61.24; H, 5.74; N, 4.20; S, 9.62. found: C, 61.48; H, 5.47; N, 3.94; S, 9.71. $[\alpha]_D^{20}$= 87.05 (C = 0.99, CH_2Cl_2). HPLC (Chiralpak OD-H column, hexane/2-propanol = 90:10, 1.0 mL/min; 254 nm, 25 °C, t_1 = 13.28 min, t_2 = 14.60 min).

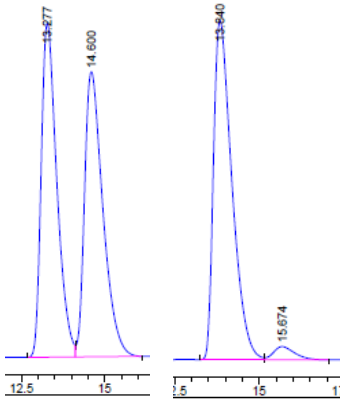


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.386	VV	0.4846	1051.37268	33.05771	6.6647
2	14.519	VB	0.5950	1.47238e4	374.92966	93.3353

(2'R,3S,4'S)-Ethyl 1-allyl-4'-hydroxy-2-oxo-4',5'-dihydro-2'H-spiro[indoline-3,3'-thiophene]-2'-carboxylate(ent-3l)

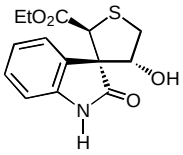


Prepared according to the general procedure from **1l** (0.5 mmol, 128.6 mg), **2** (0.3 mmol, 45.7 mg), $MgSO_4$ (60 mg) and cat.**VI** (0.005mol, 3.2 mg) in disted. DCM (10 mL) at 15 °C for 11 h to provide the title compound as a white solid (93% yield, -91% ee, >19:1 d.r.). $[\alpha]_D^{18}$= -88.61 (C = 1.00, CH_2Cl_2).

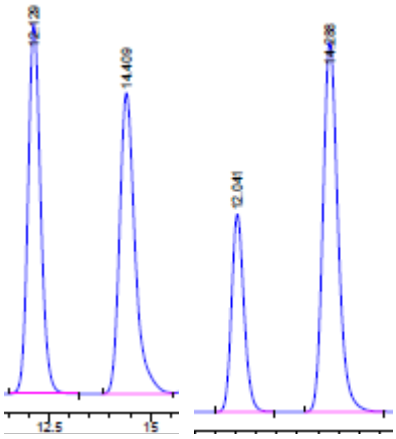


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.840	VV	0.5733	1.86725e4	494.15768	95.6771
2	15.674	VB	0.6397	843.65753	19.29388	4.3229

ethyl 4'-hydroxy-2-oxo-4',5'-dihydro-2'H-spiro[indoline-3,3'-thiophene]-2'-carboxylate (3m)

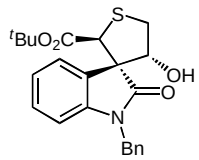


white solid (mp:151-154 °C) ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.50 (1 H, s), 7.58 (1 H, d, *J* = 7.4 Hz), 7.31 (1 H, t, *J* = 7.8 Hz), 7.09 (1 H, t, *J* = 7.5 Hz), 7.02 (1 H, d, *J* = 7.7 Hz), 5.03 (1 H, s), 4.58 (1 H, s), 4.40 (1 H, s), 3.95-3.78 (2 H, m), 3.60 – 3.42 (1 H, m), 3.24 (1 H, d, *J* = 11.7 Hz), 0.83 (3 H, t, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 178.77, 168.57, 140.62, 129.45, 126.58, 125.03, 123.32, 110.44, 79.89, 62.15, 61.71, 54.48, 38.40, 13.39. MS: m/z = 293.19 ($[M]^+$). Anal. calcd for ($C_{14}H_{15}NO_4S$): C, 57.32; H, 5.15; N, 4.77; S, 10.93. found: C, 57.39; H, 5.01; N, 4.88; S, 10.67. HPLC (Chiralpak AD-H column, hexane/2-propanol = 80:20, 1.0 mL/min; 254 nm, 25 °C, t_1 = 12.04 min, t_2 = 14.29 min).

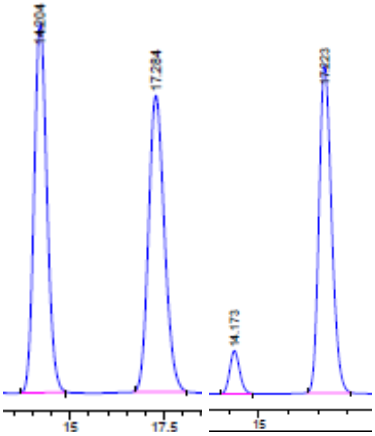


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.041	BB	0.3252	3996.53052	190.25113	30.8498
2	14.288	BB	0.3862	8958.27734	356.71005	69.1502

***tert*-butyl 1-benzyl-4'-hydroxy-2-oxo-4',5'-dihydro-2'H-spiro[indoline-3,3'-thiophene]-2'-carboxylate (3n)**

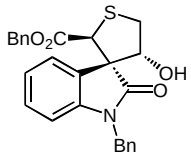


white solid (mp: 91-92 °C) ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.65 (1 H, d, *J* = 7.4Hz), 7.36 – 7.25 (7 H, m), 7.09 (1 H, t, *J* = 7.6Hz), 6.86 (1 H, d, *J* = 7.8Hz), 5.38 (1 H, d, *J* = 15.5Hz), 5.03 (1 H, s), 4.65 (1 H, s), 4.58 (1 H, d, *J* = 15.5Hz), 4.33 (1 H, d, *J* = 2.8Hz), 3.46 (1 H, dd, *J* = 11.5Hz, 3.0Hz), 3.22 (1 H, d, *J* = 11.7Hz), 1.00 (9 H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 176.64, 167.30, 142.41, 134.86, 129.27, 128.85, 127.86, 127.15, 126.51, 124.94, 123.41, 109.24, 82.26, 80.29, 61.53, 55.65, 44.04, 38.23, 27.08. MS: m/z = 411.25 ($[M]^+$). Anal. calcd for ($C_{23}H_{25}NO_4S$): C, 67.13; H, 6.12; N, 3.40; S, 7.79. found: C, 67.10; H, 6.10; N, 3.20; S, 7.77. HPLC (Chiralpak AD-H column, hexane/2-propanol = 80:20, 1.0 mL/min; 254 nm, 25 °C, t_1 = 14.20 min, t_2 = 17.28 min).

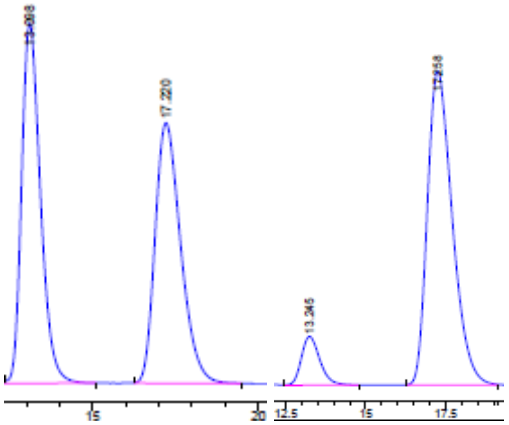


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.173	BB	0.3607	940.96271	40.37455	9.3602
2	17.223	BB	0.4575	9111.87598	309.09109	90.6398

benzyl 1-benzyl-4'-hydroxy-2-oxo-4',5'-dihydro-2'H-spiro[indoline-3,3'-thiophene]-2'-carboxylate (3o)

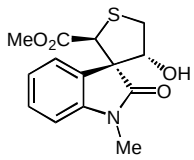


white solid (mp: 105-107 °C) ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.58 (1 H, d, *J* = 7.4Hz), 7.35 – 7.20 (9 H, m), 7.18 (1 H, d, *J* = 7.7Hz), 7.03 (1 H, t, *J* = 7.5Hz), 6.89 (2 H, d, *J* = 7.1Hz), 6.61 (1 H, d, *J* = 7.8Hz), 5.13 (1 H, s), 4.91 (1 H, d, *J* = 15.7Hz), 4.74 (2 H, dd, *J* = 46.2Hz, 12.0Hz), 4.62 (1 H, s), 4.30 (2 H, dd, *J* = 9.2Hz, 6.3Hz), 3.46 (1 H, d, *J* = 11.5Hz), 3.23 (1 H, d, *J* = 11.7Hz). ^{13}C NMR 176.25, 168.23, 142.15, 134.97, 134.57, 129.19, 128.74, 128.13, 127.76, 127.12, 125.87, 124.64, 123.38, 109.66, 80.05, 67.23, 61.29, 54.57, 43.78, 38.25. MS: m/z = 445.35 ([M]$^+$). Anal. calcd for ($C_{26}H_{23}NO_4S$): C, 70.09; H, 5.20; N, 3.14; S, 7.20. found: C, 70.19; H, 5.14; N, 3.22; S, 7.06. HPLC (Chiralpak OD-H column, hexane/2-propanol = 80:20, 1.0 mL/min; 254 nm, 25 °C, t_1 = 13.10 min, t_2 = 17.22 min).

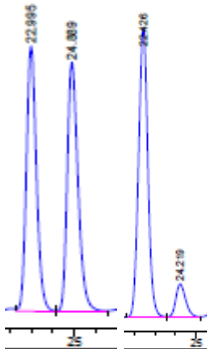


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.245	VB	0.6214	940.52930	23.34769	10.3469
2	17.258	BB	0.8369	8149.41162	150.18855	89.6531

benzyl 1-benzyl-4'-hydroxy-2-oxo-4',5'-dihydro-2'H-spiro[indoline-3,3'-thiophene]-2'-carboxylate (3p)

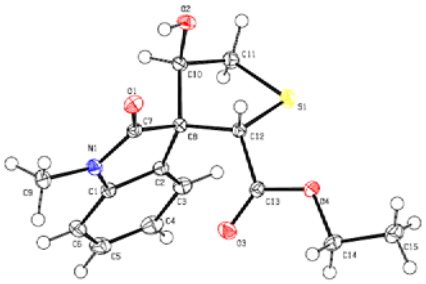


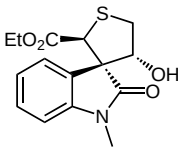
white solid (mp: 147-150 °C) ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.58 (1 H, d, *J* = 7.5Hz), 7.38 (1 H, t, *J* = 7.7Hz), 7.12 (1 H, t, *J* = 7.6Hz), 6.94 (1 H, d, *J* = 7.8Hz), 5.03 (1 H, s), 4.60 (1 H, s), 4.29 (1 H, d, *J* = 2.7Hz), 3.49 (1 H, dd, *J* = 11.7Hz, 3.1Hz), 3.37 (3 H, s), 3.33 (3 H, s), 3.24 (1 H, d, *J* = 11.7Hz). ^{13}C NMR 176.09, 168.83, 143.22, 129.42, 126.03, 124.70, 123.40, 108.48, 79.48, 61.32, 54.39, 52.48, 38.55, 26.65. MS: m/z = 293.27 ([M]$^+$). Anal. calcd for ($C_{14}H_{15}NO_4S$): C, 57.32; H, 5.15; N, 4.77; S, 10.93. found: C, 57.52; H, 5.39; N, 4.71; S, 10.68. HPLC (Chiralpak AD-H column, hexane/2-propanol = 90:10, 1.0 mL/min; 266 nm, 25 °C, t_1 = 23.00 min, t_2 = 24.89 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.426	BV	0.4888	1.45538e4	461.44934	89.1677
2	24.219	VB	0.5151	1768.03430	52.90700	10.8323

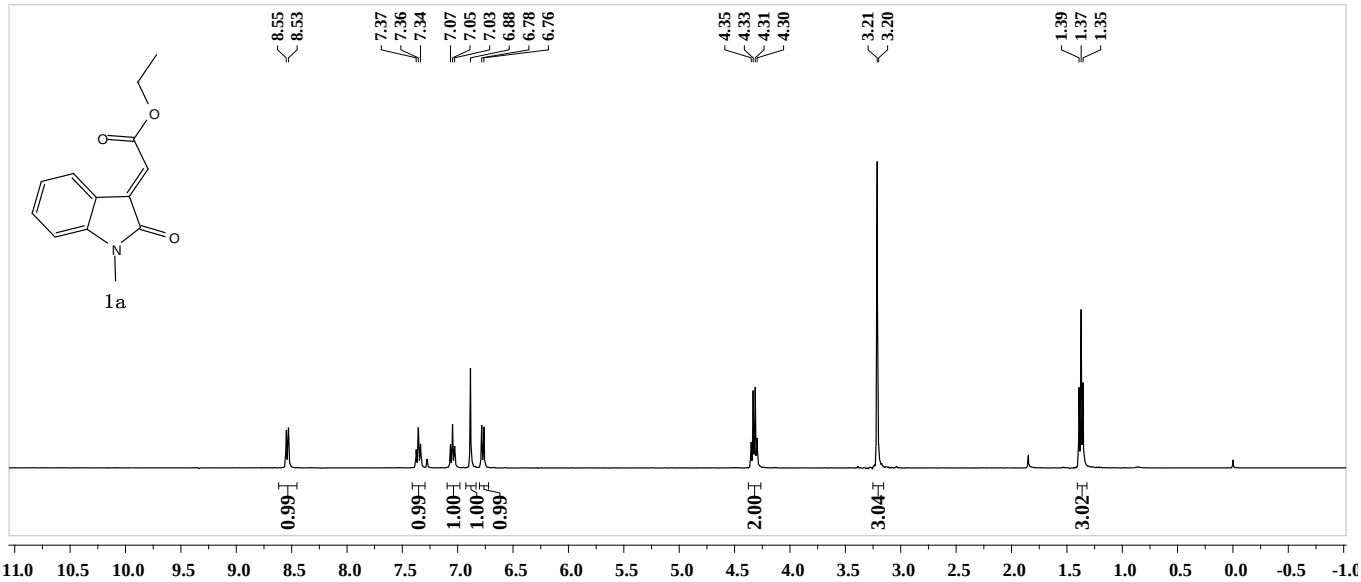
5. X-Ray structure of 3a (CCDC 861216).

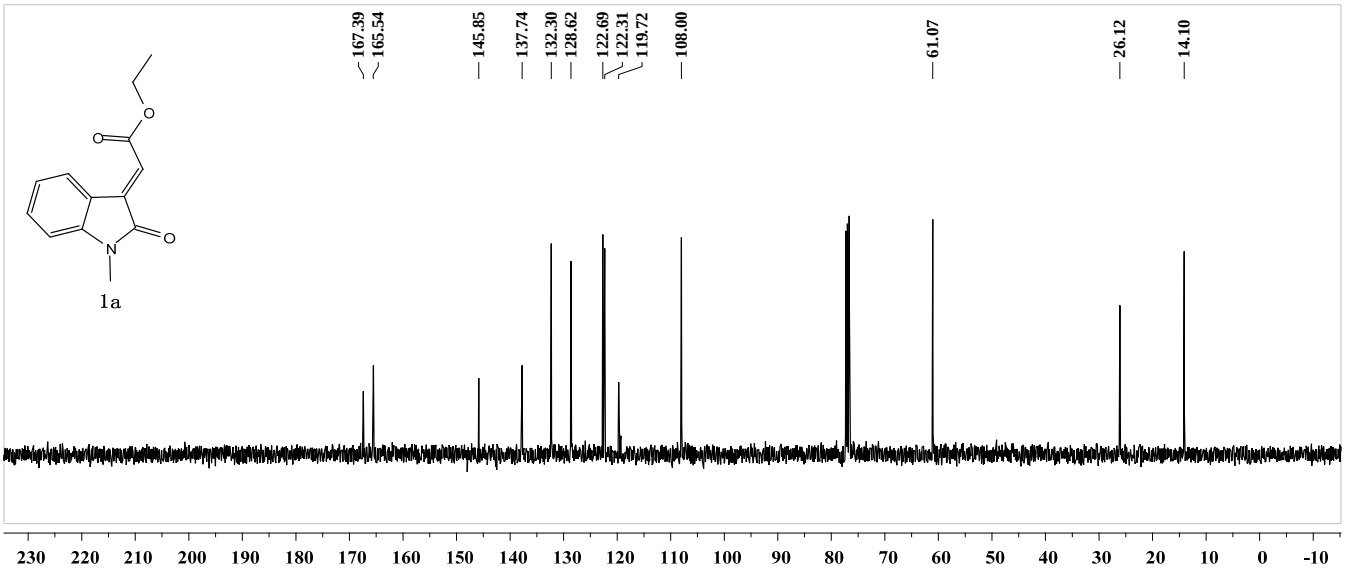


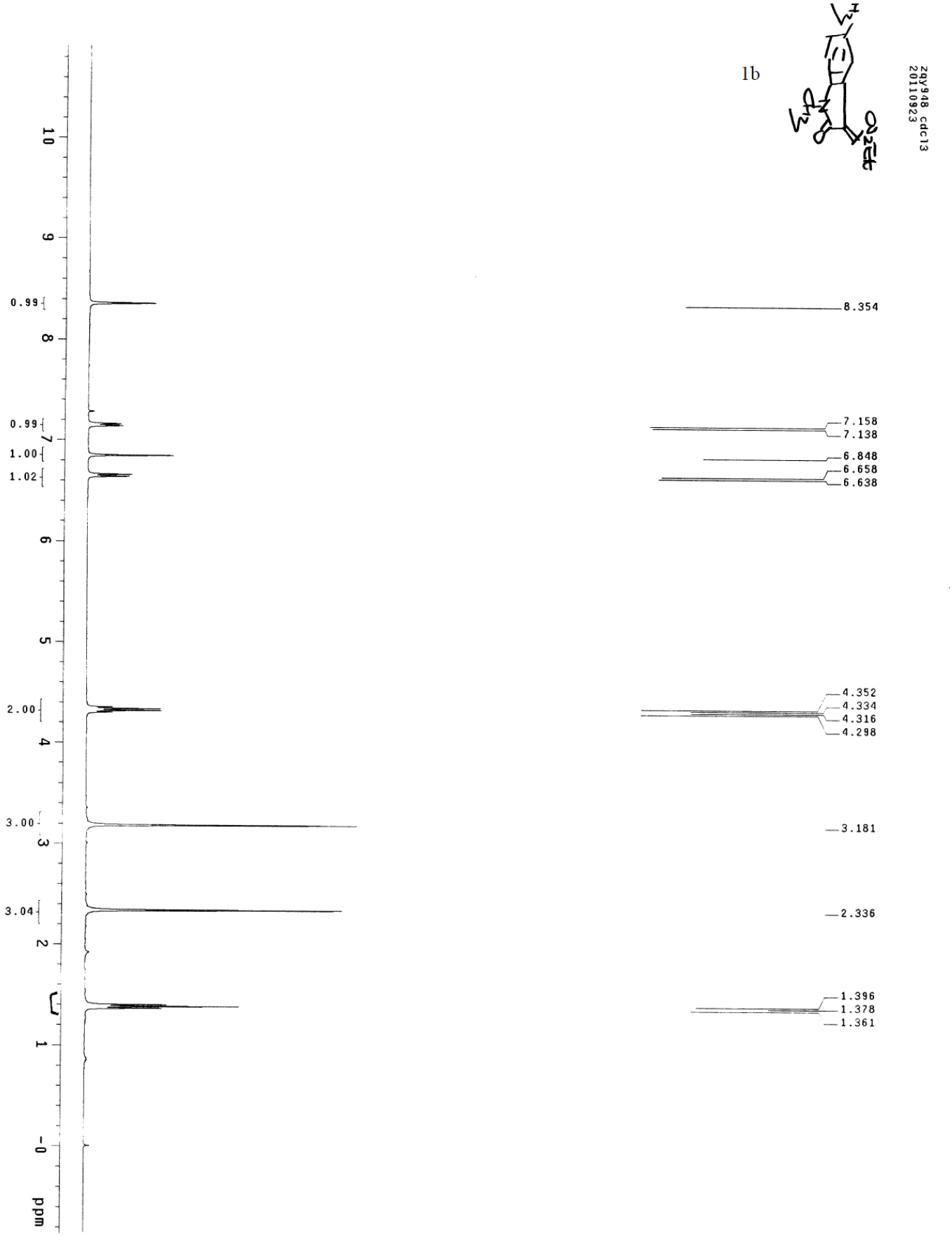


3a

6. Copies of NMR, MS and Elemental Analysis Spectra



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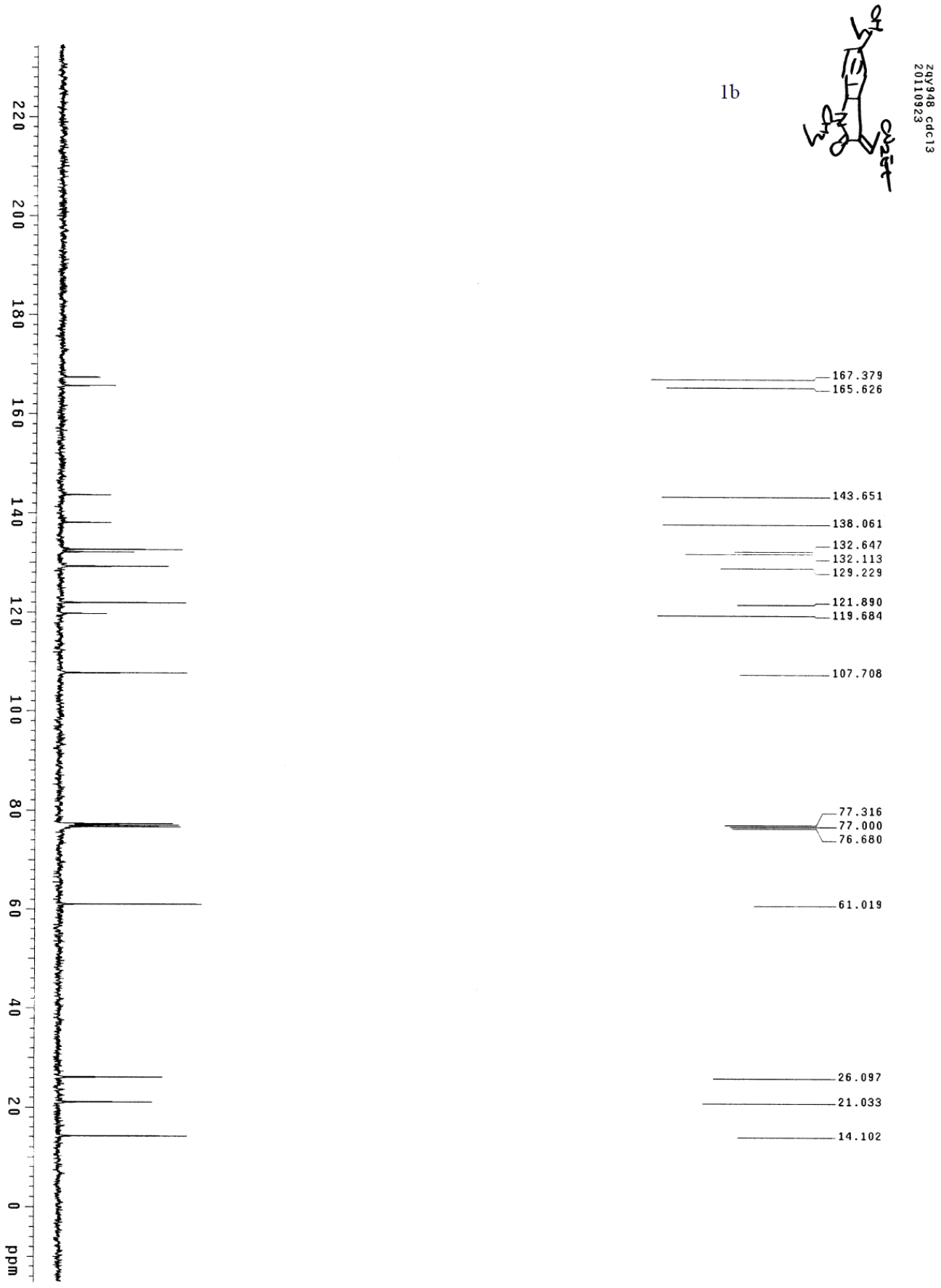
7.138
6.848
6.658
6.638
4.352
4.334
4.316
4.298
3.181
2.336
1.396
1.378
1.361
0.99
0.99
1.00
1.02
2.00
3.00
3.04
ppm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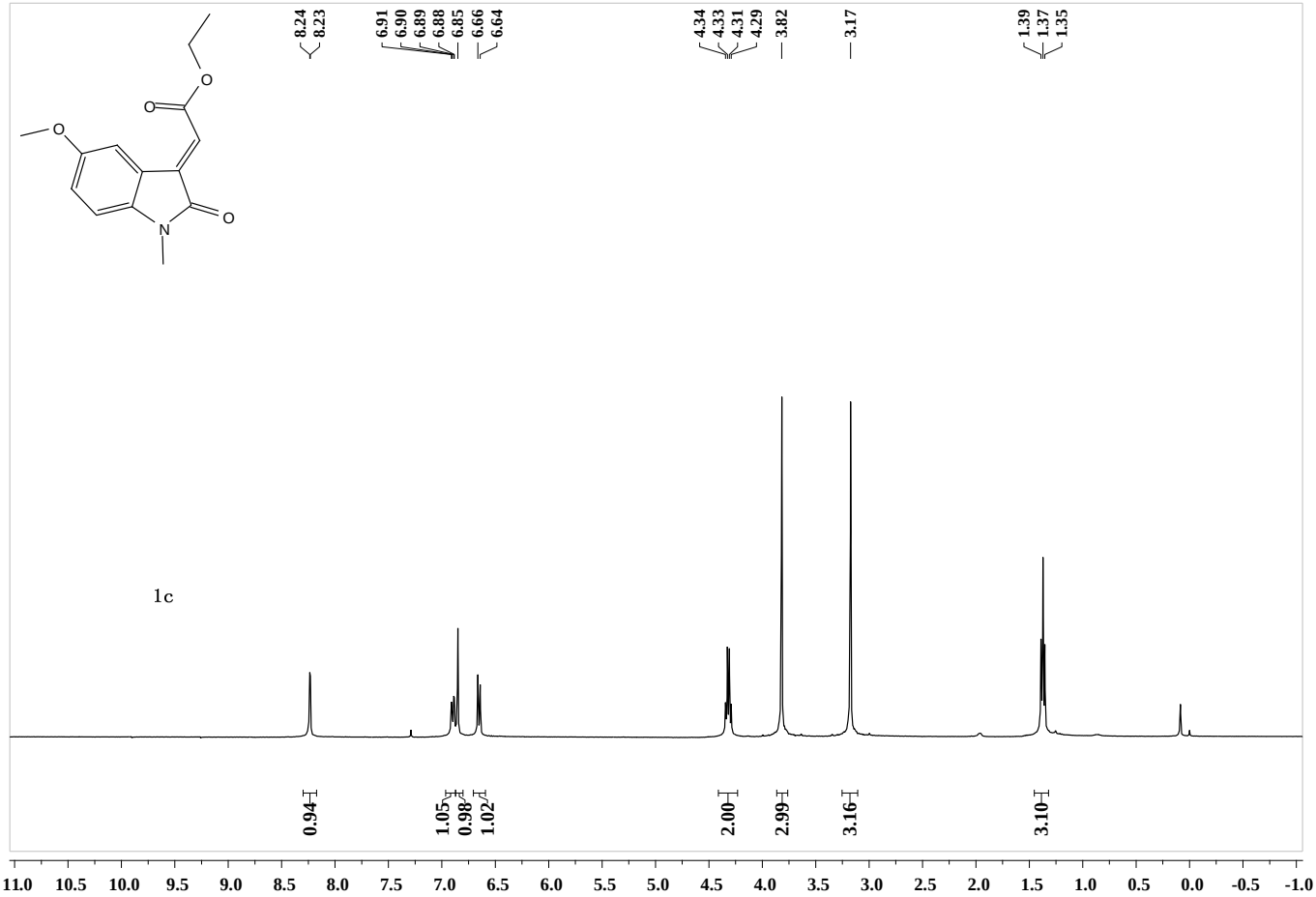
132.113
129.229
121.890
119.684
107.708
77.316
77.000
76.680
61.019
26.097
21.033
14.102
220
200
180
160
140
120
100
80
60
40
20
0
ppm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6.90
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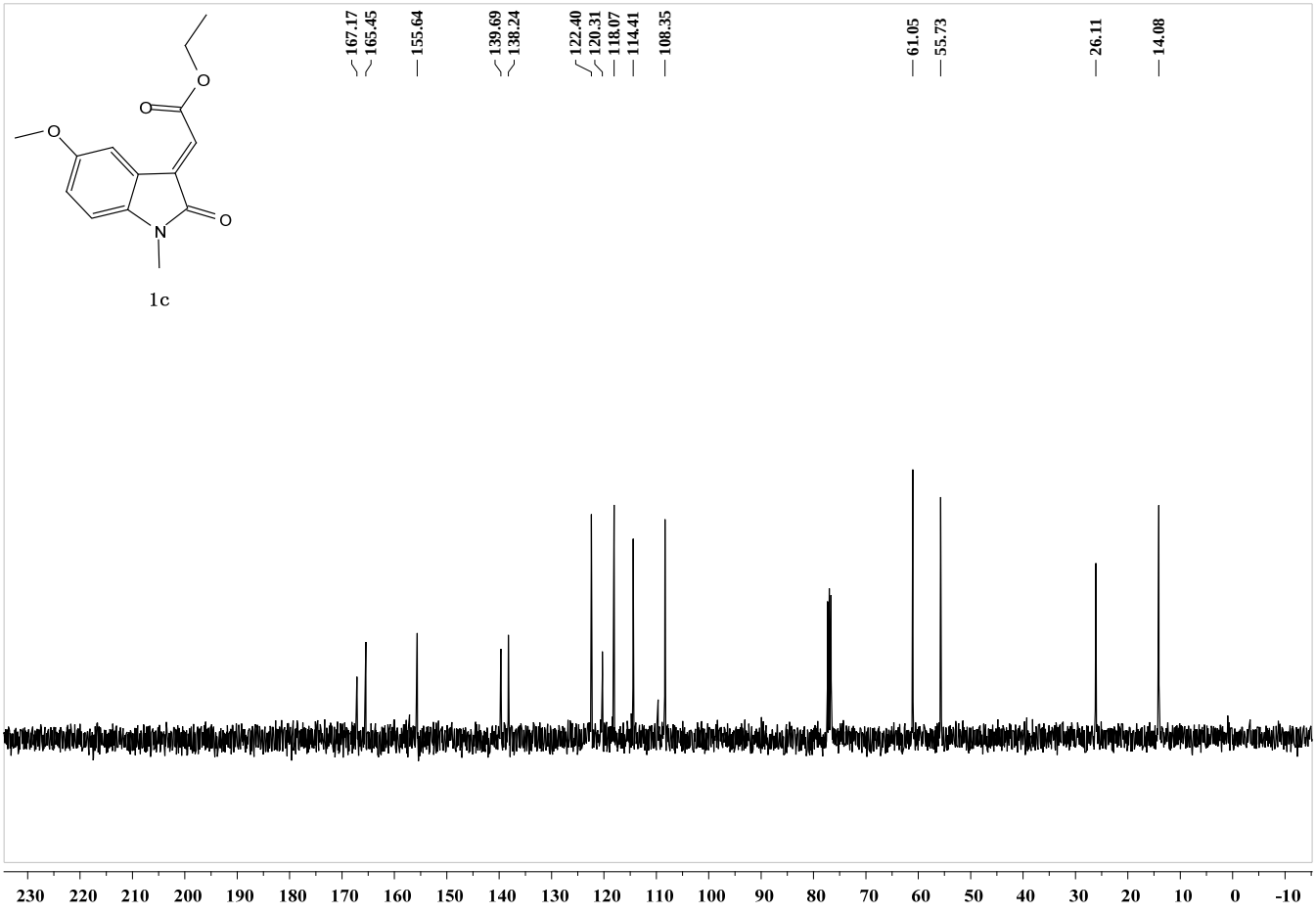
6.88
6.85
6.66
6.64
4.34
4.33
4.31
4.29
3.82
3.17
1.39
1.37
1.35
1c
0.94
1.05
0.98
1.02
2.00
2.99
3.16
3.10
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0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155.64
139.69
138.24
122.40
120.31
118.07
114.41
108.35
61.05
55.73
26.11
14.08
1c
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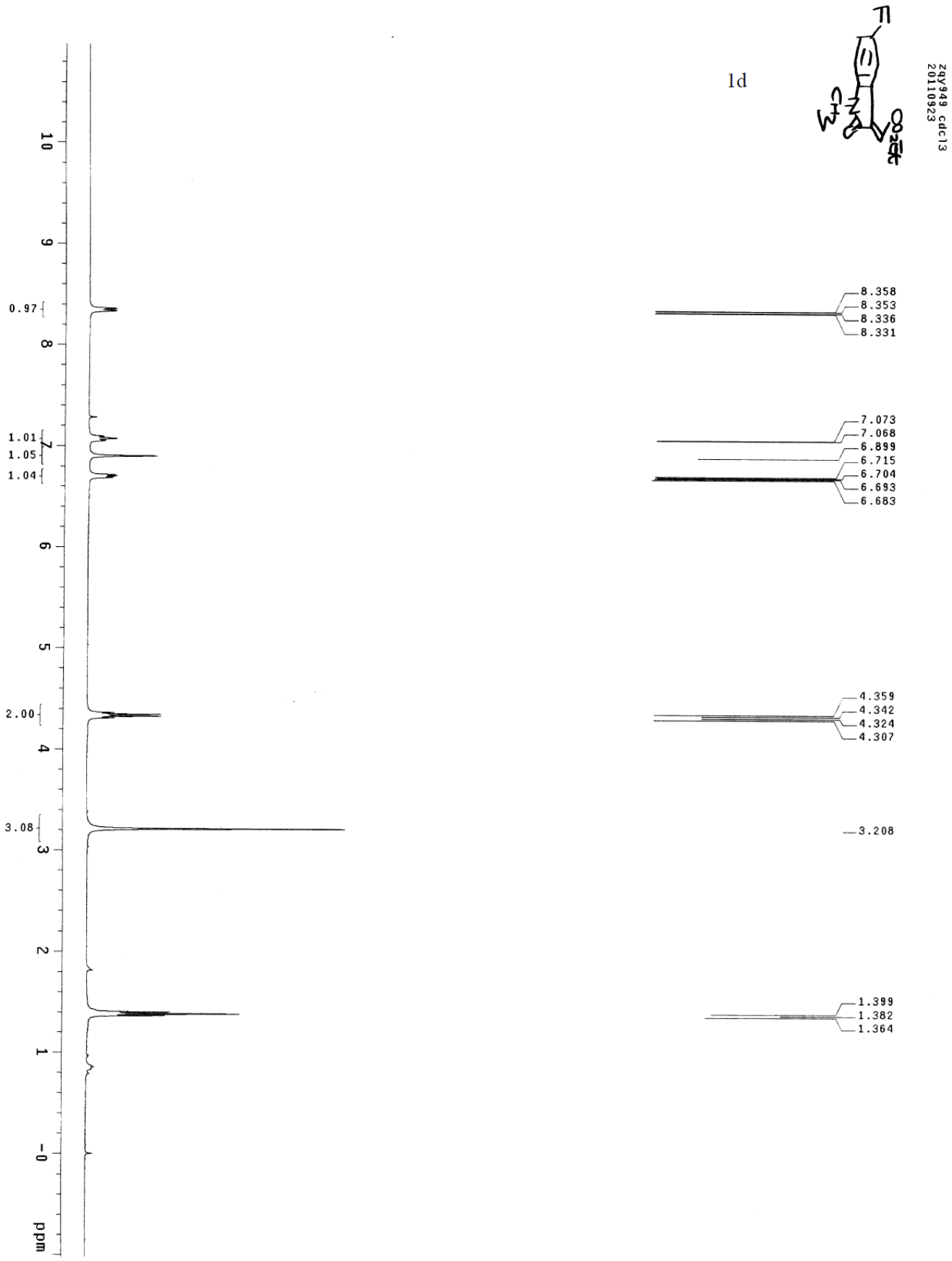
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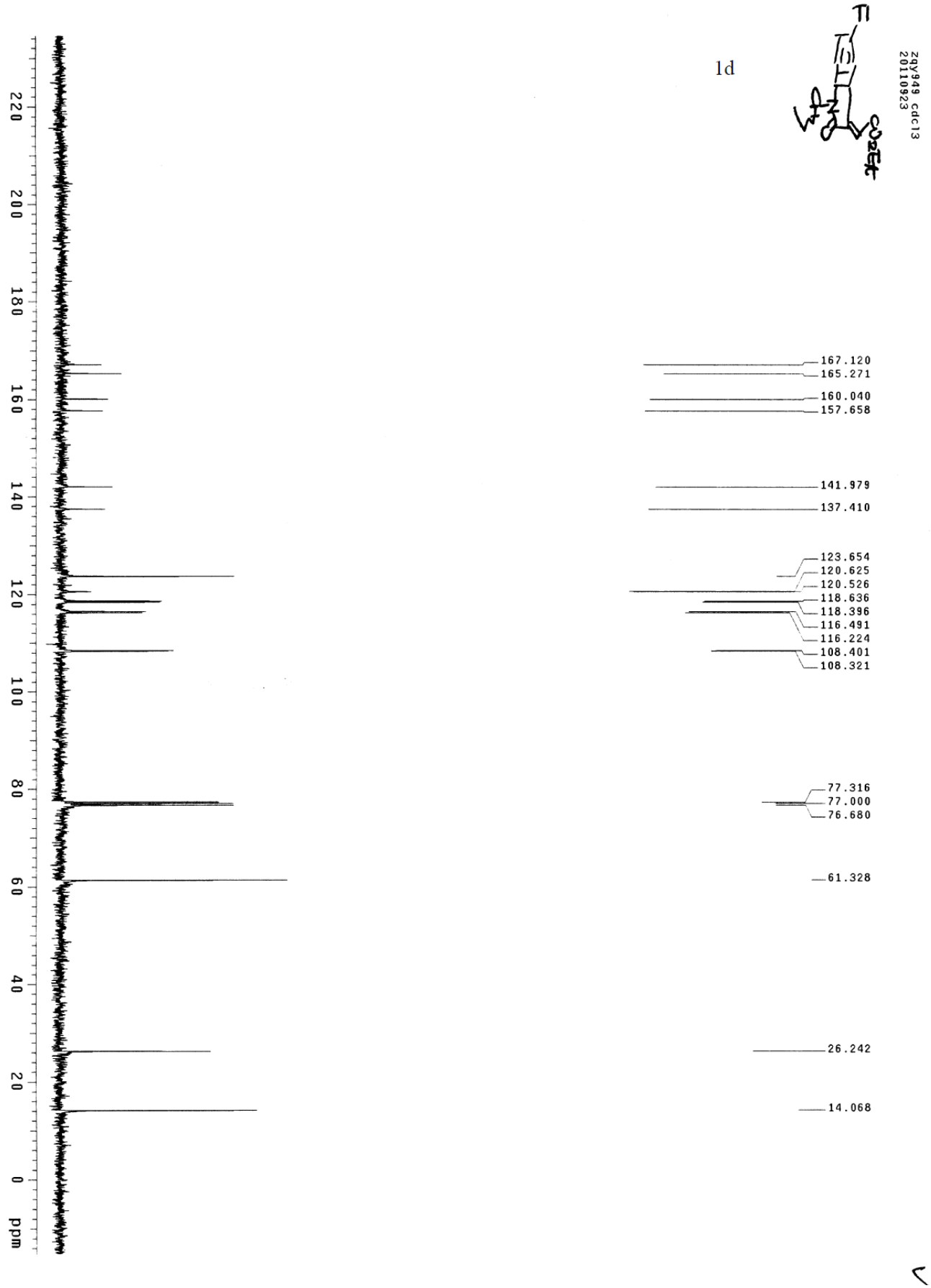
8.331
7.073
7.068
6.899
6.715
6.704
6.693
6.683
4.359
4.342
4.324
4.307
3.208
1.399
1.382
1.364
0.97
1.01
1.05
1.04
2.00
3.08
ppm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160.040
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141.979
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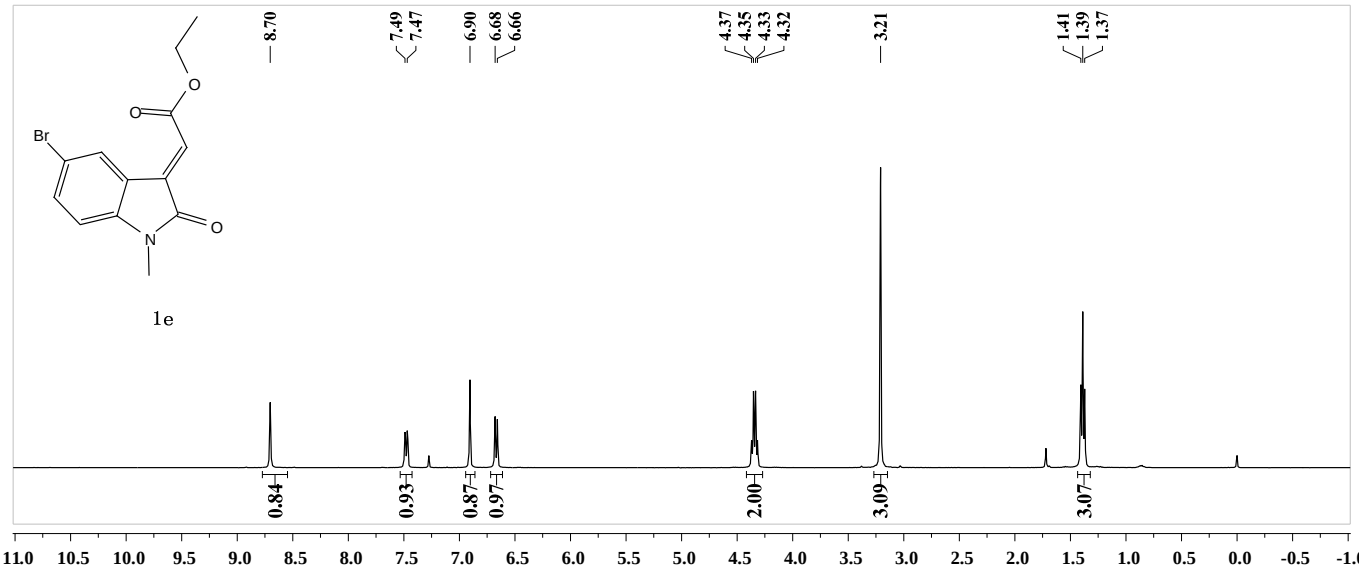
120.526
118.636
118.396
116.491
116.224
108.401
108.321
77.316
77.000
76.680
61.328
26.242
14.068
220
200
180
160
140
120
100
80
60
40
20
0
ppm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6.66
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4.32
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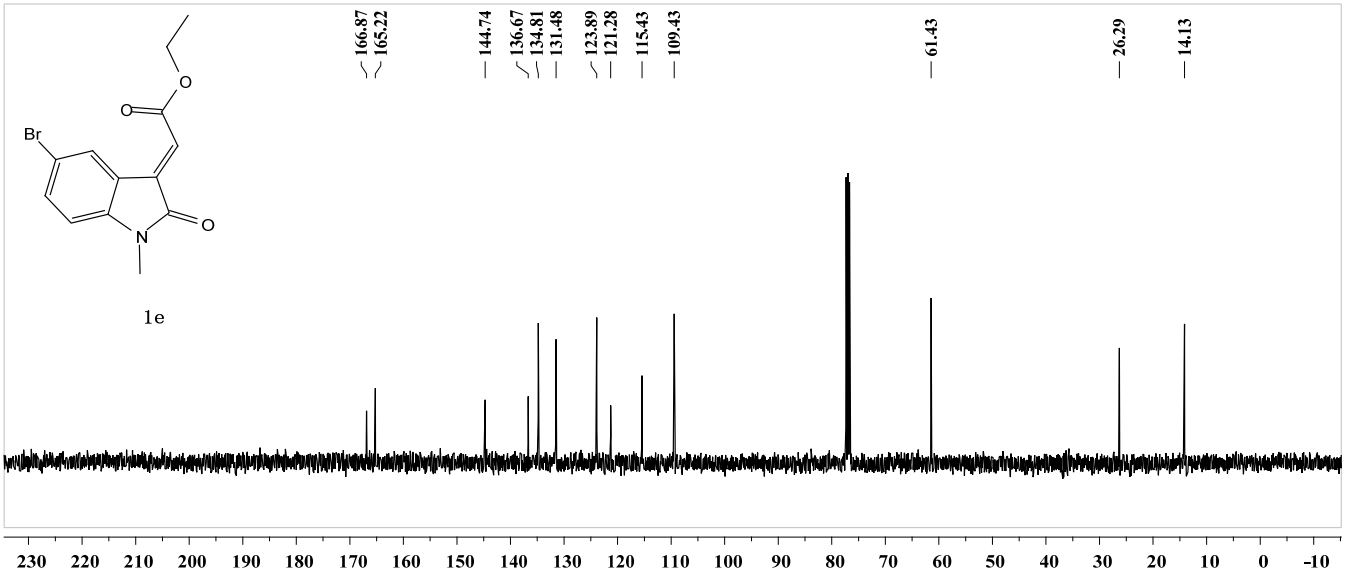
1.39
1.37
Br
O
O
N
O
1e
0.84
0.93
0.87
0.97
2.00
3.09
3.07
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0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131.48
123.89
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115.43
109.43
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26.29
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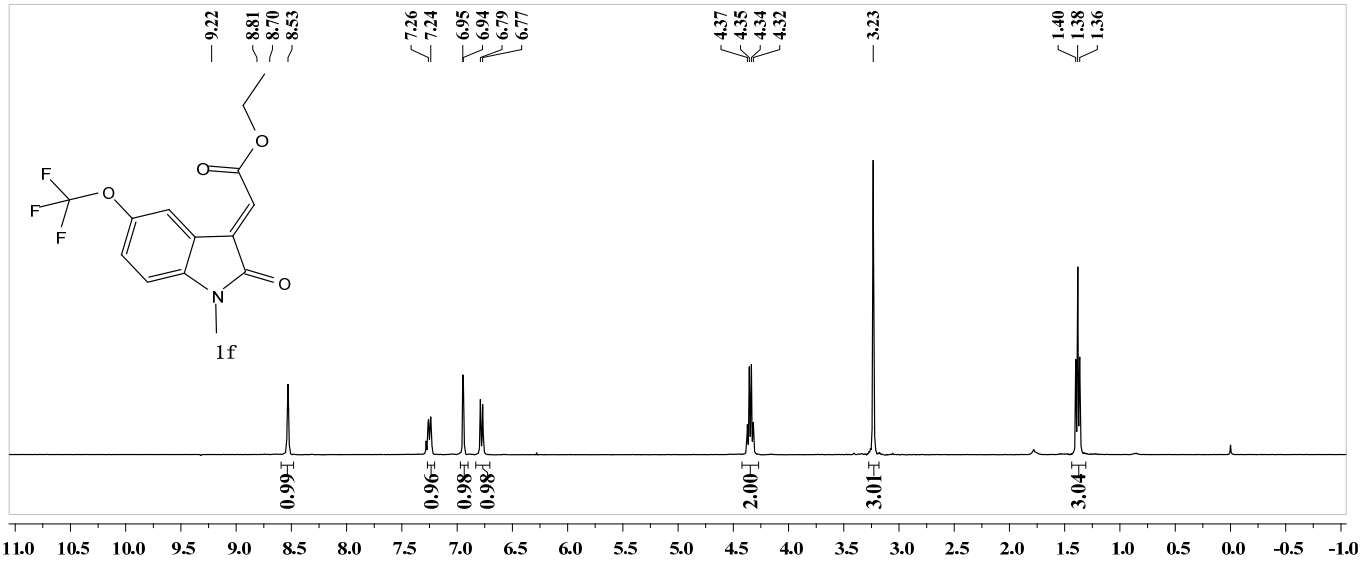
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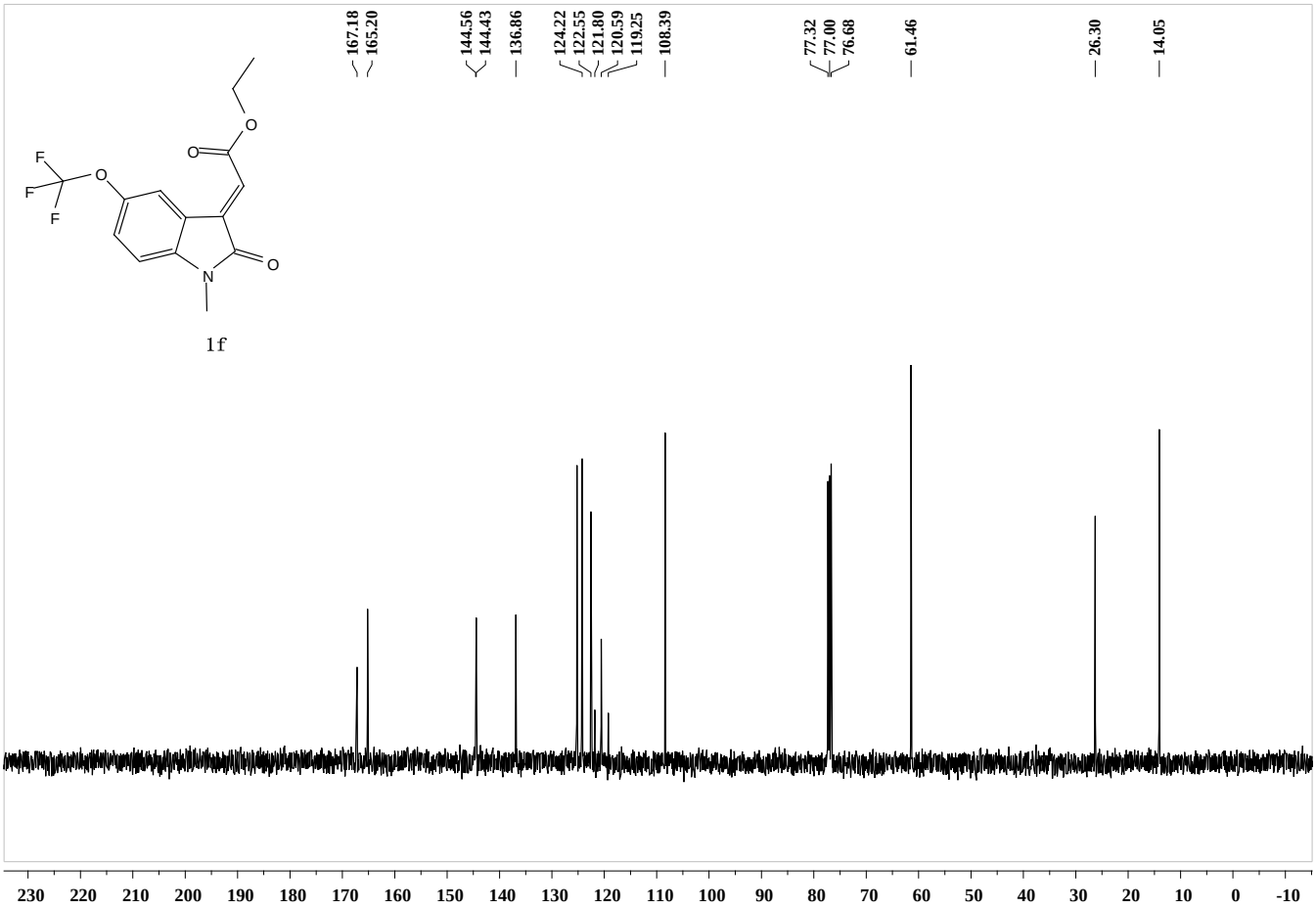
3.23
1.40
1.38
1.36
F
F
F
O
O
O
N
O
1f
0.99
0.96
0.98
0.98
2.00
3.01
3.04
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0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26.30
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O
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N
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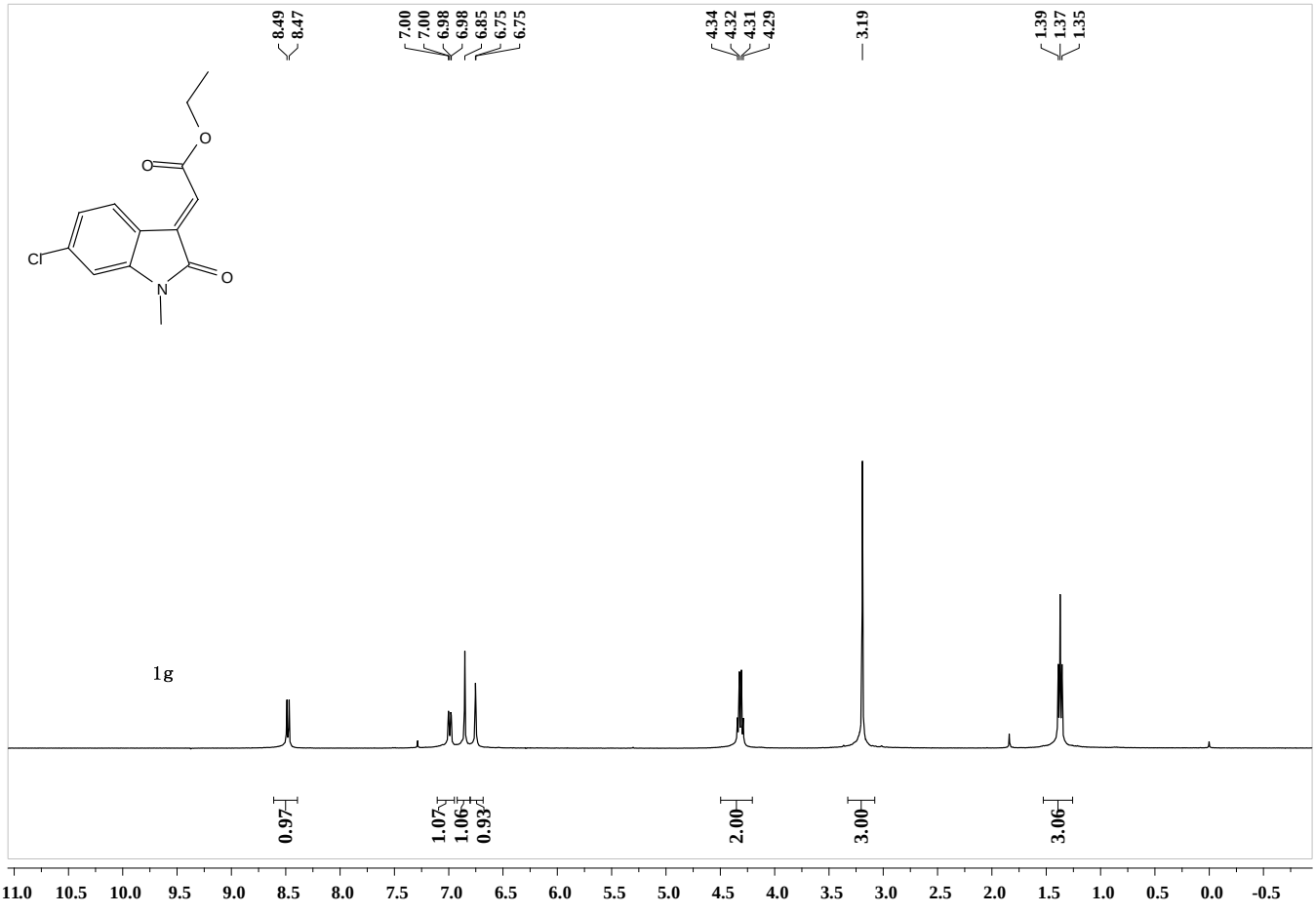
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1.35
Cl
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O
N
O
1g
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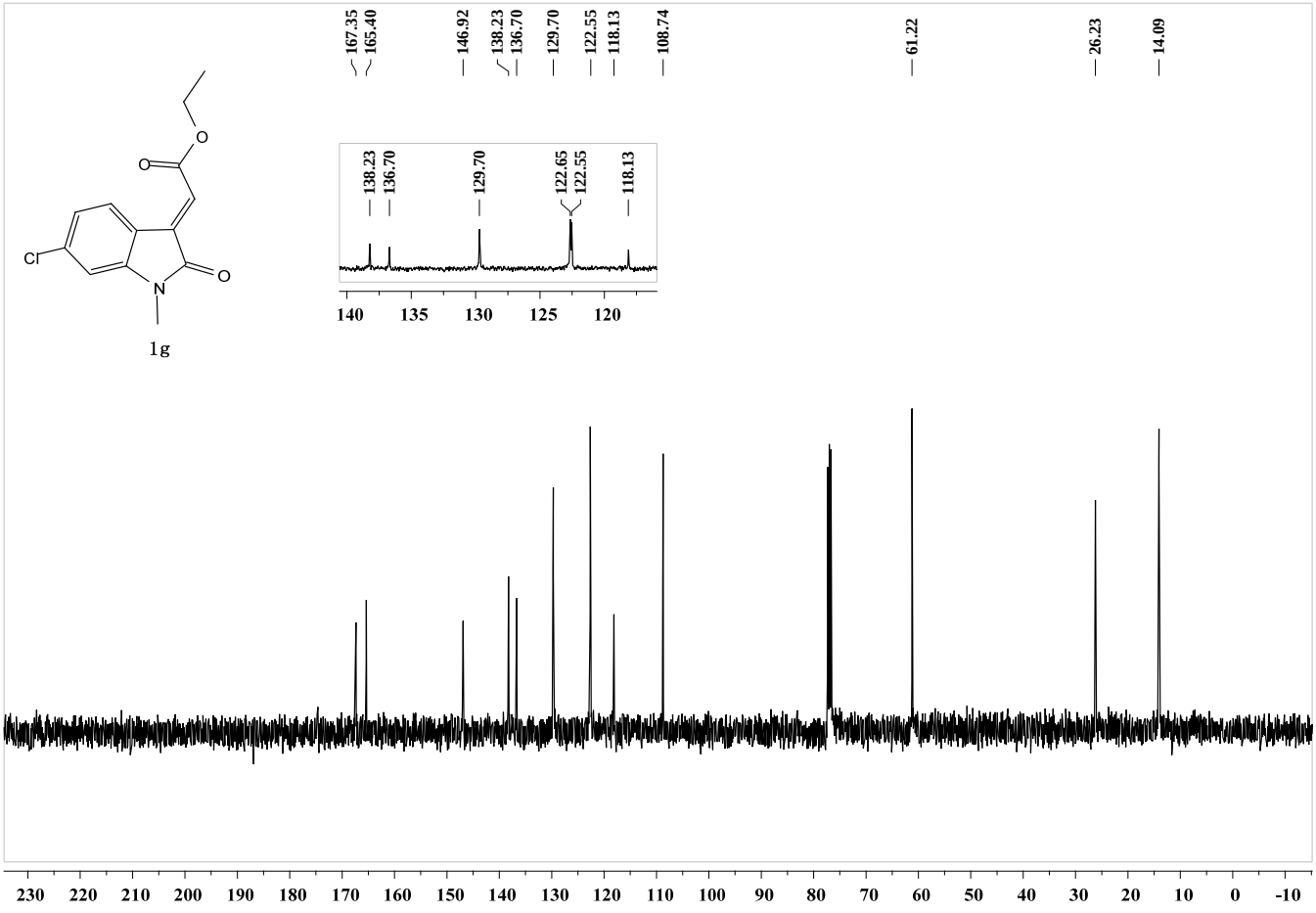
1.07
1.06
0.93
2.00
3.00
3.06
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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122.55
118.13
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130
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N
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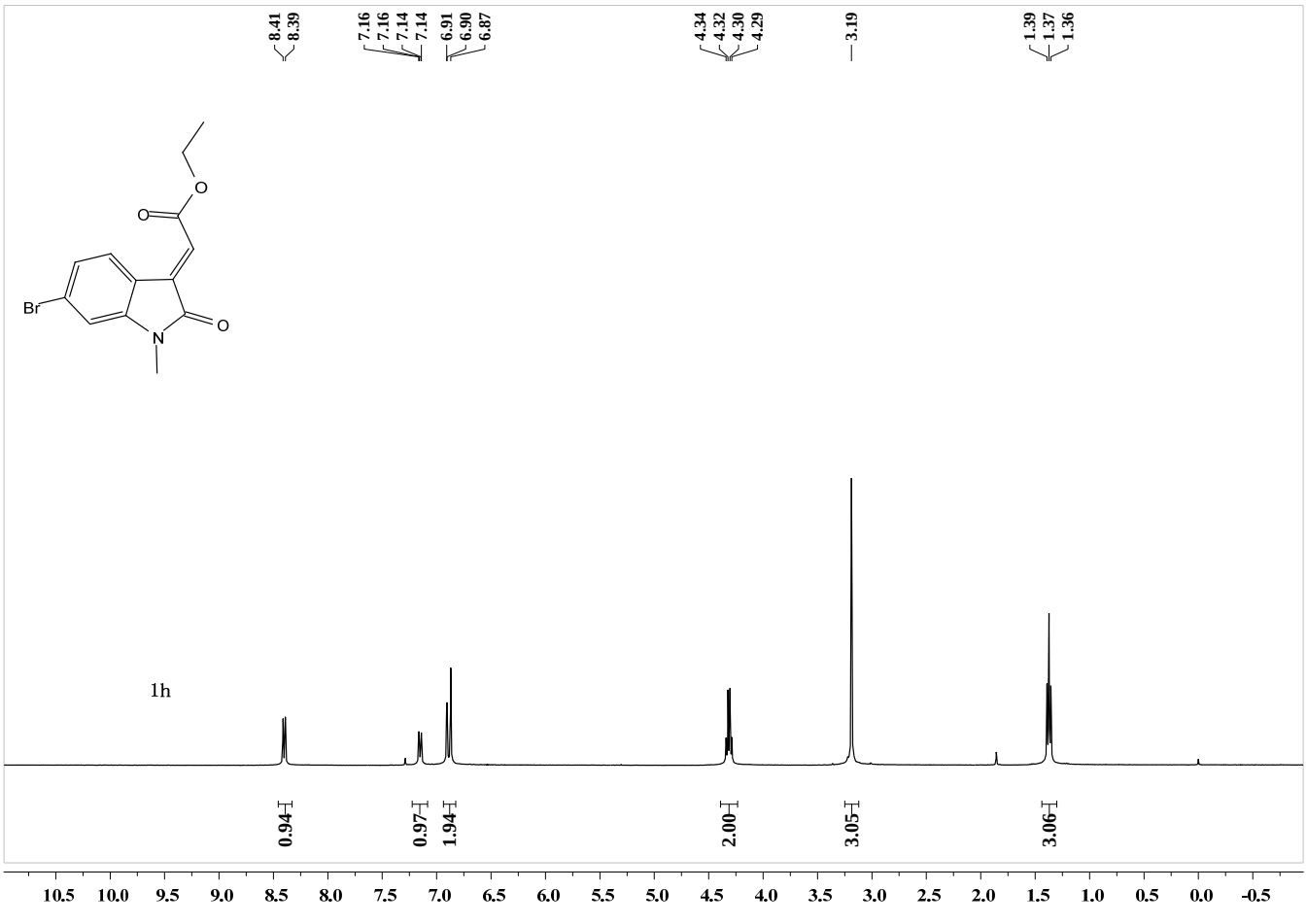
1g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1.36
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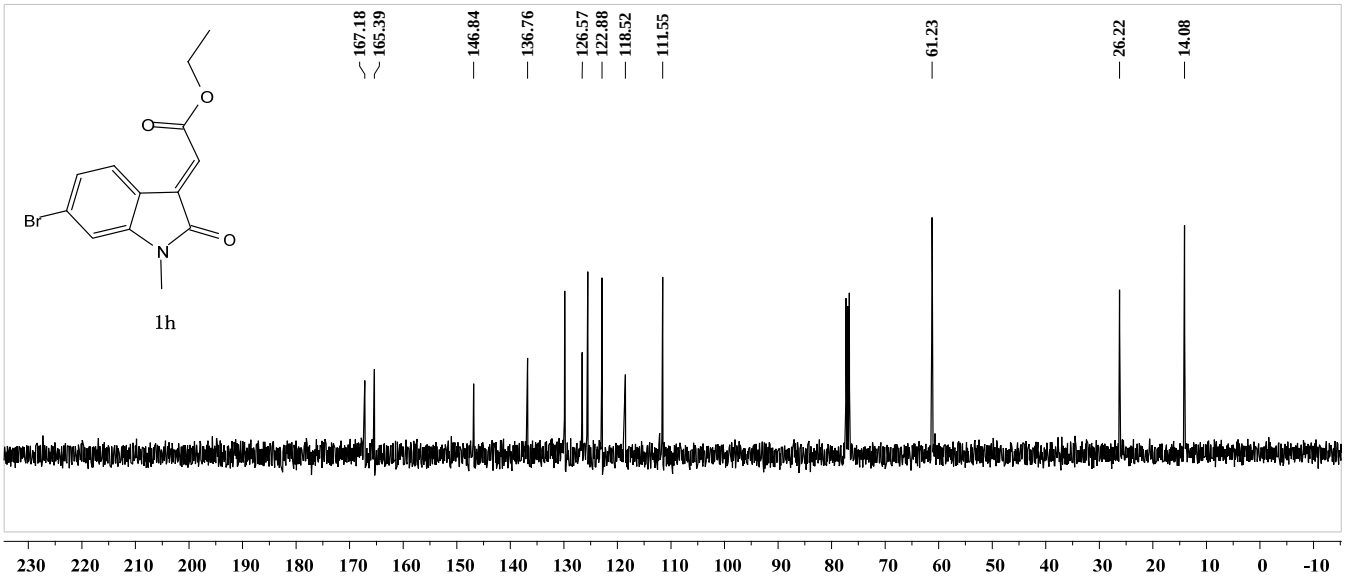
0.97
1.94
2.00
3.05
3.06
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

1h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N
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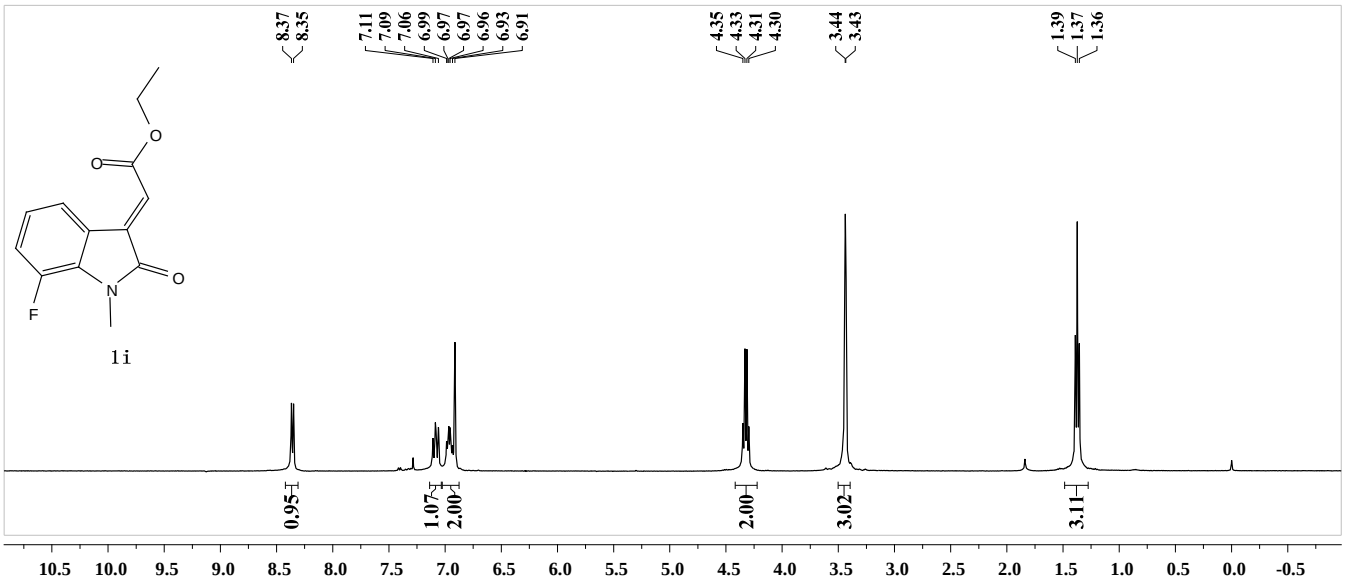
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2.00
2.00
3.02
3.11
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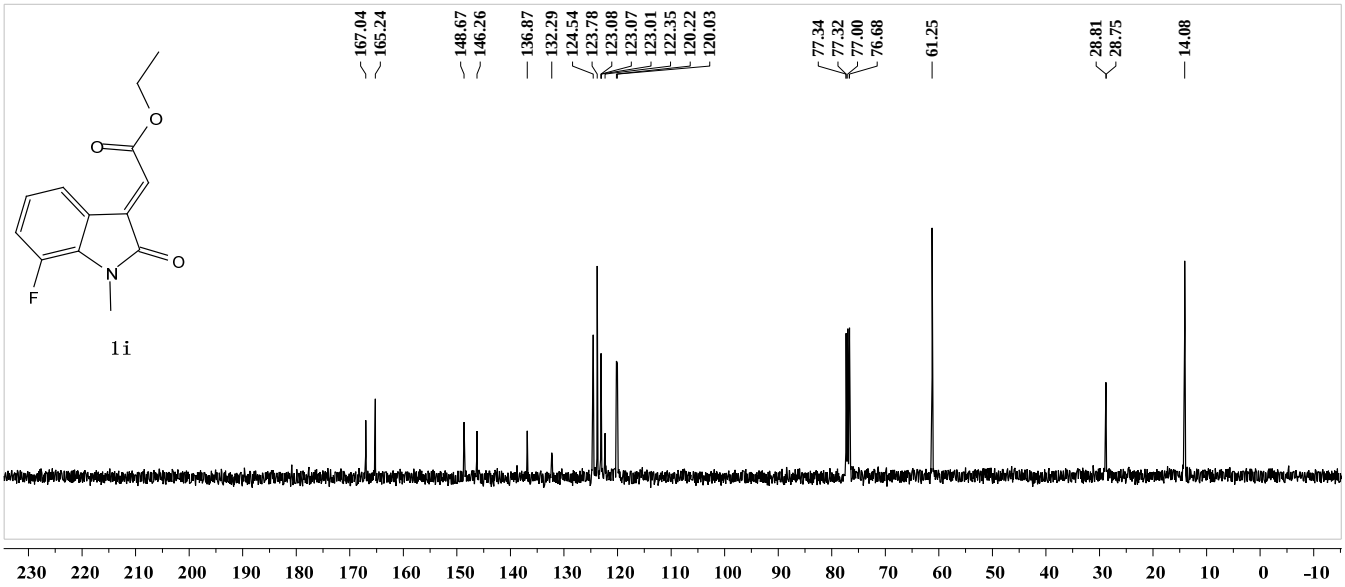
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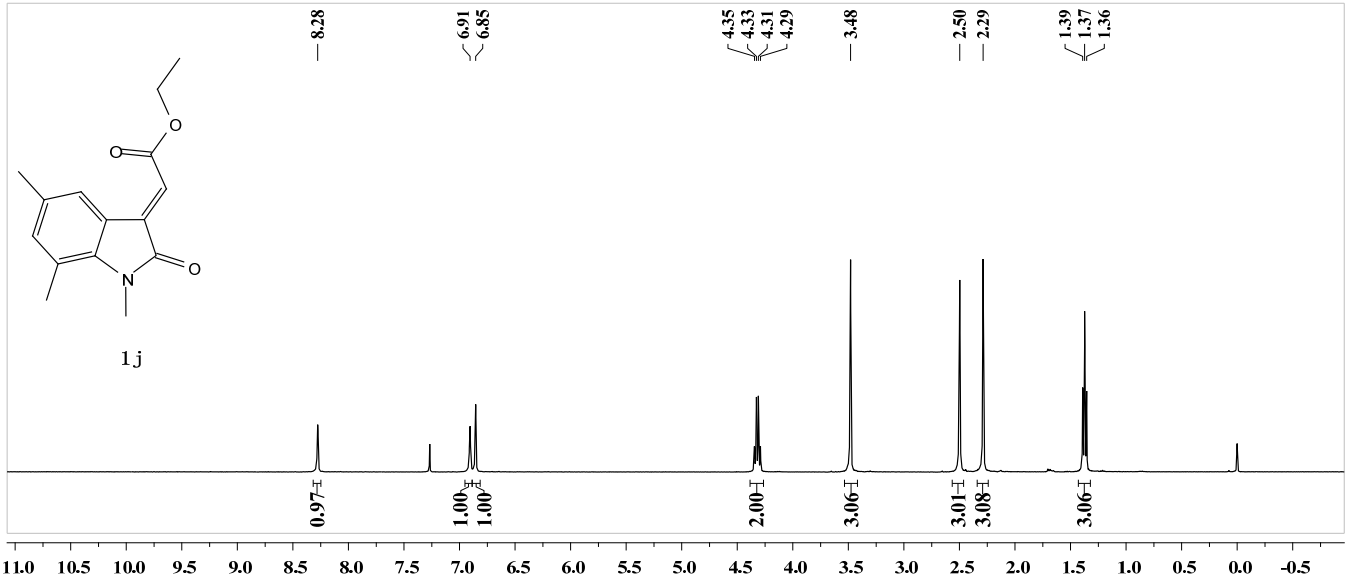
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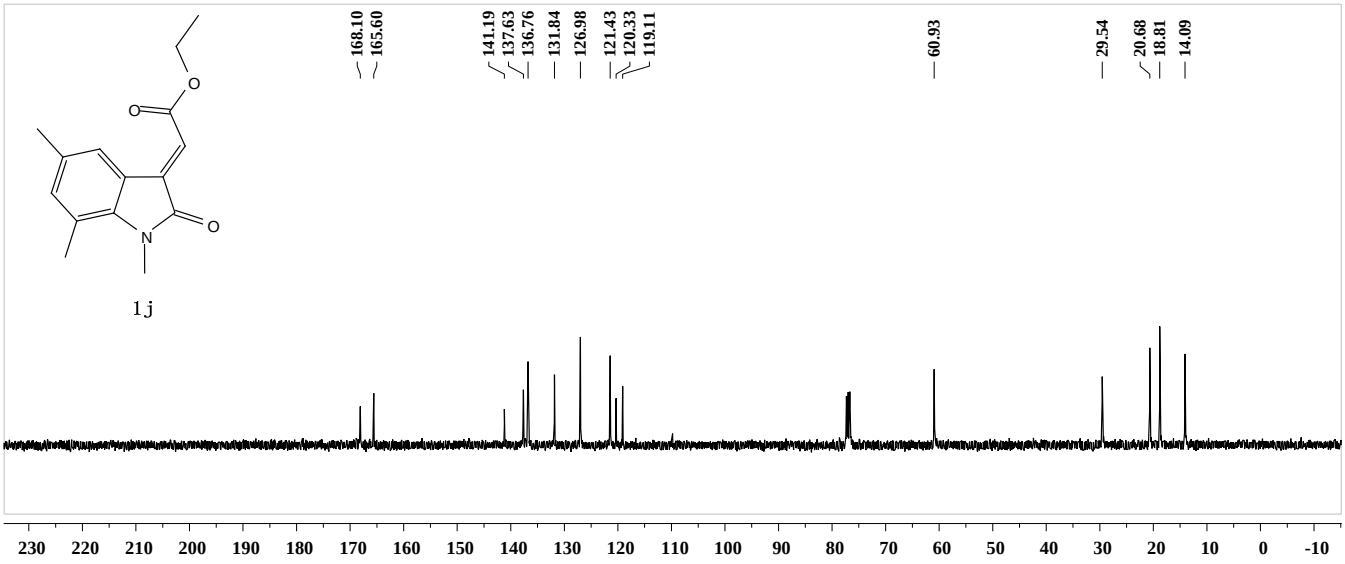
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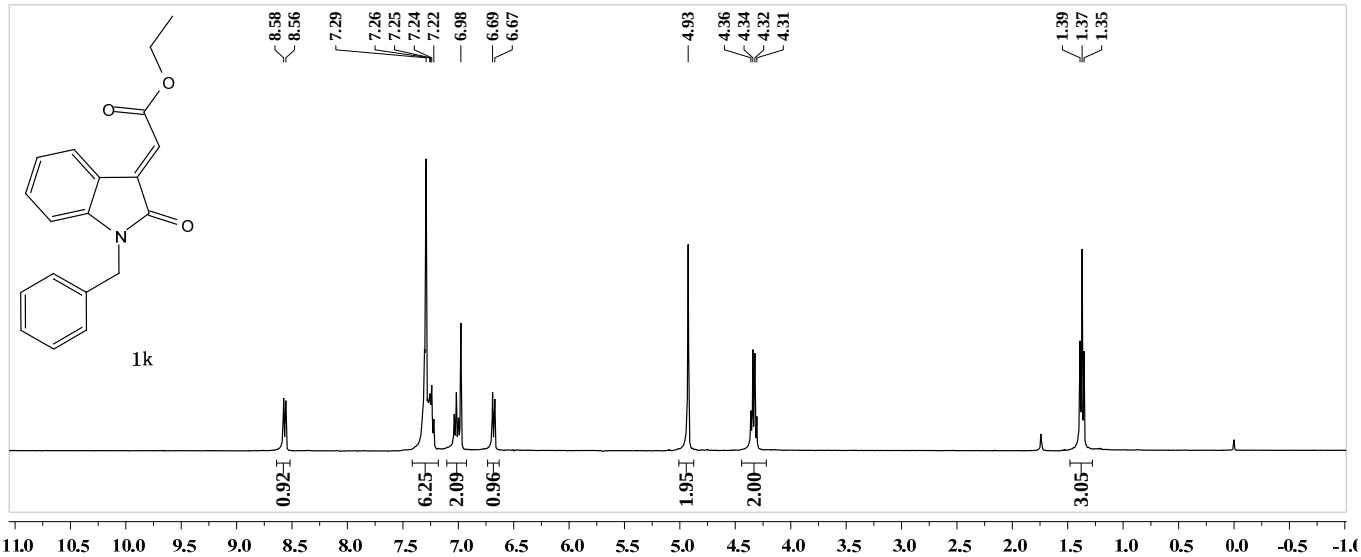
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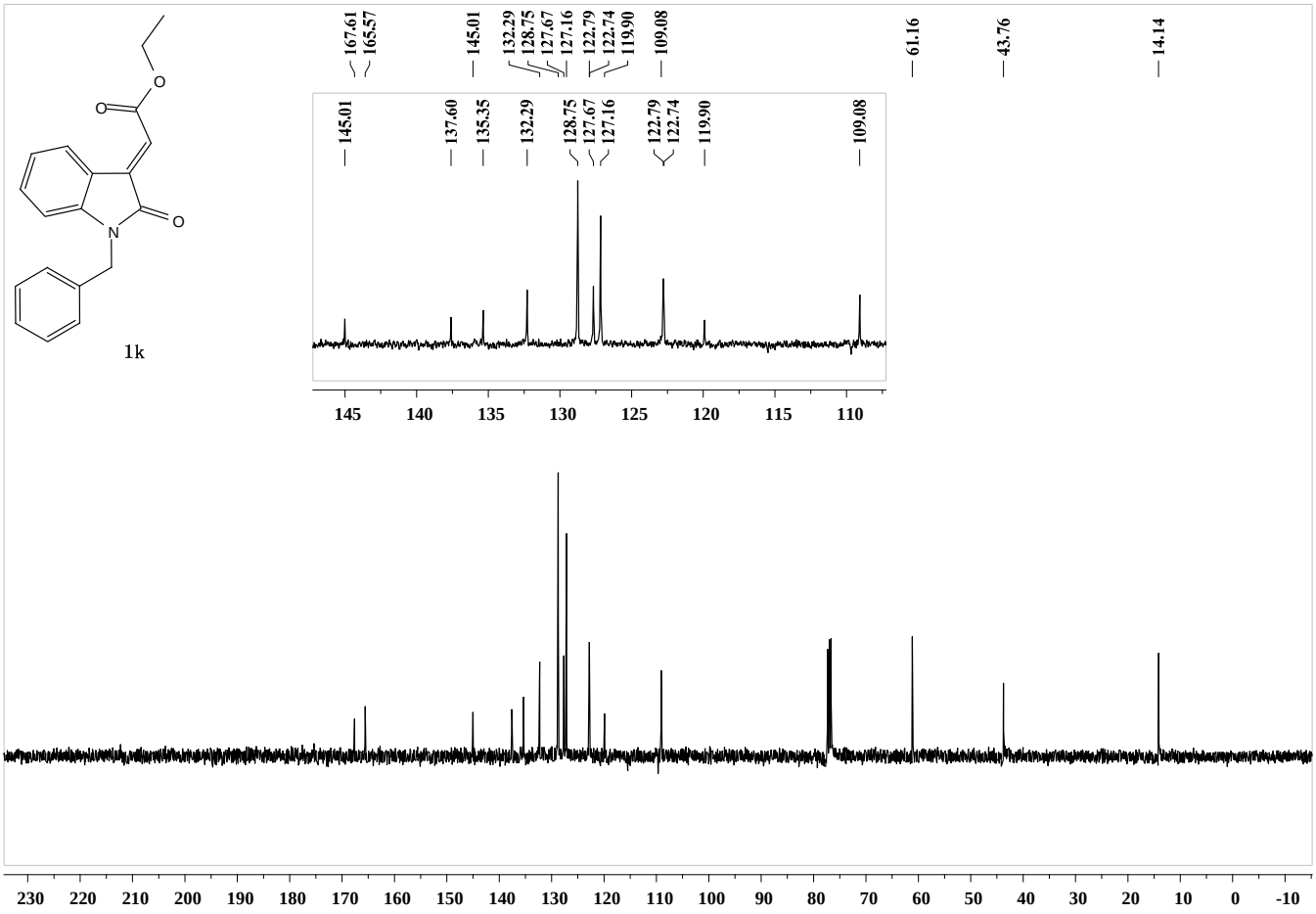
1k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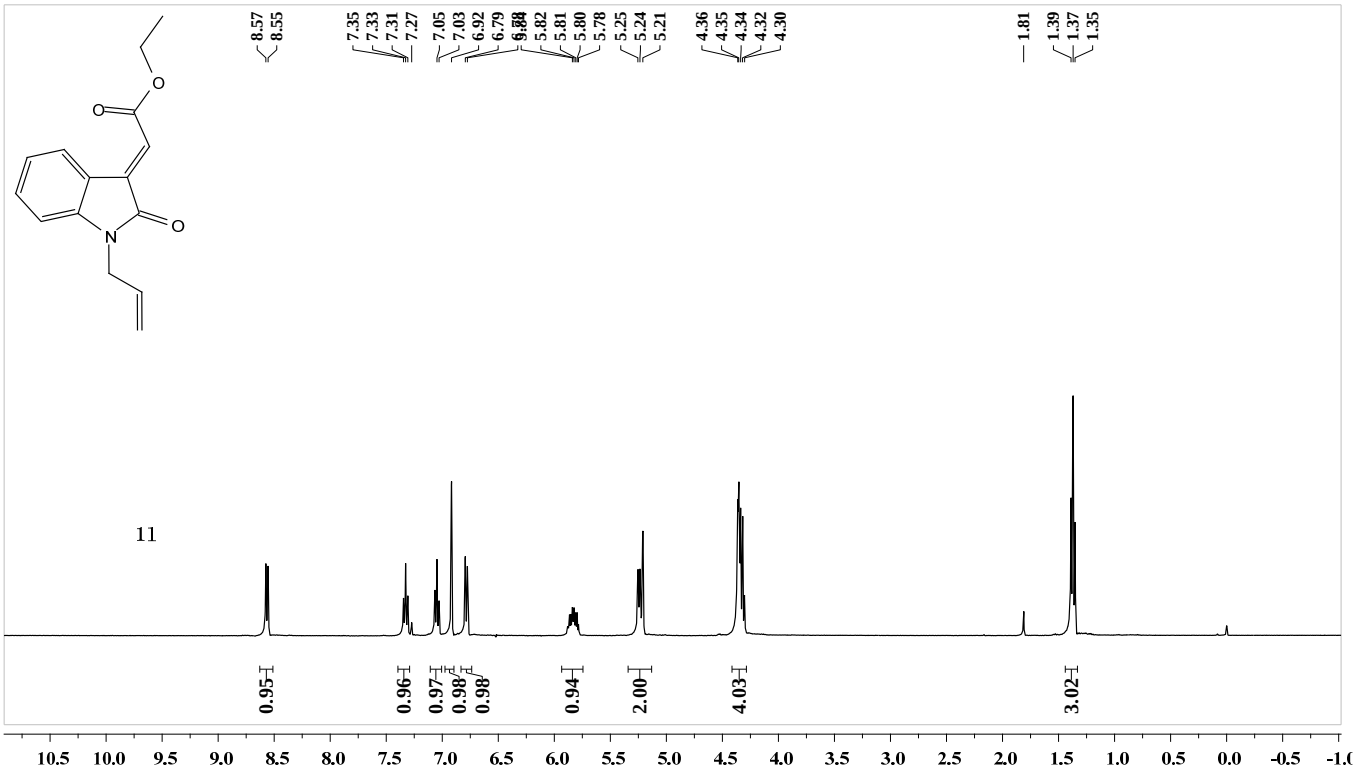
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7.03
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6.79
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5.80
5.78
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4.35
4.34
4.32
4.30
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1.39
1.37
1.35
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0.96
0.97
0.98
0.98
0.94
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4.03
3.02
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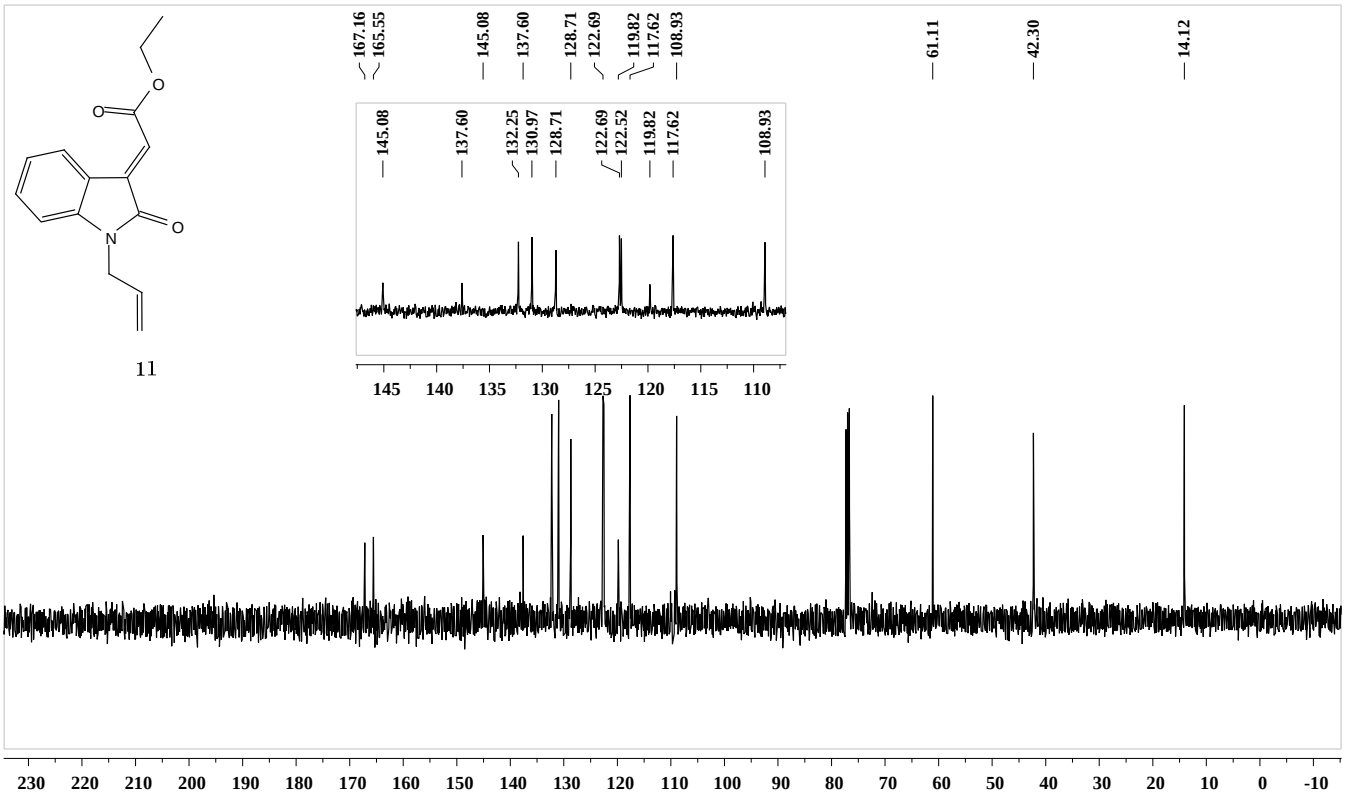
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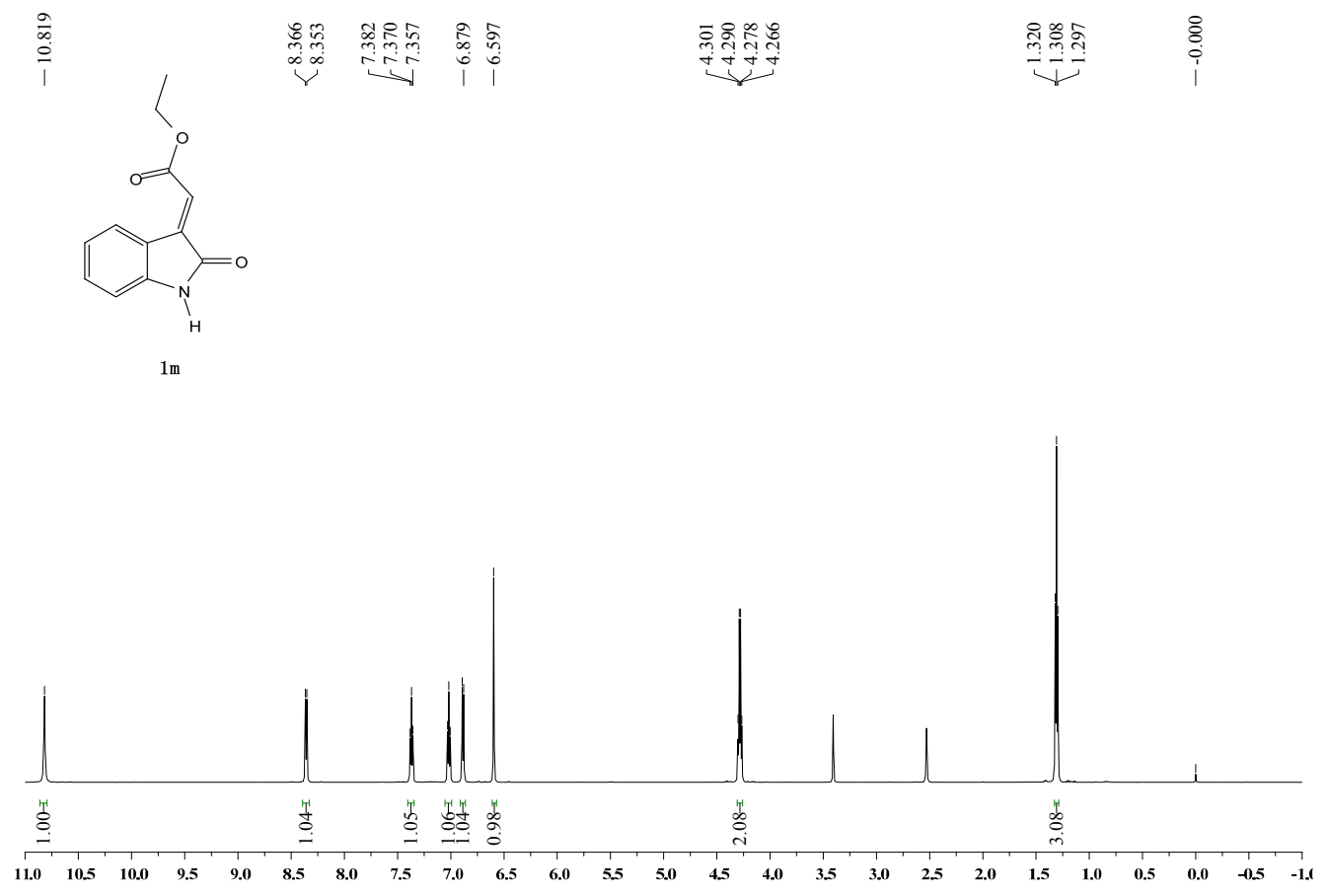
11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1.297
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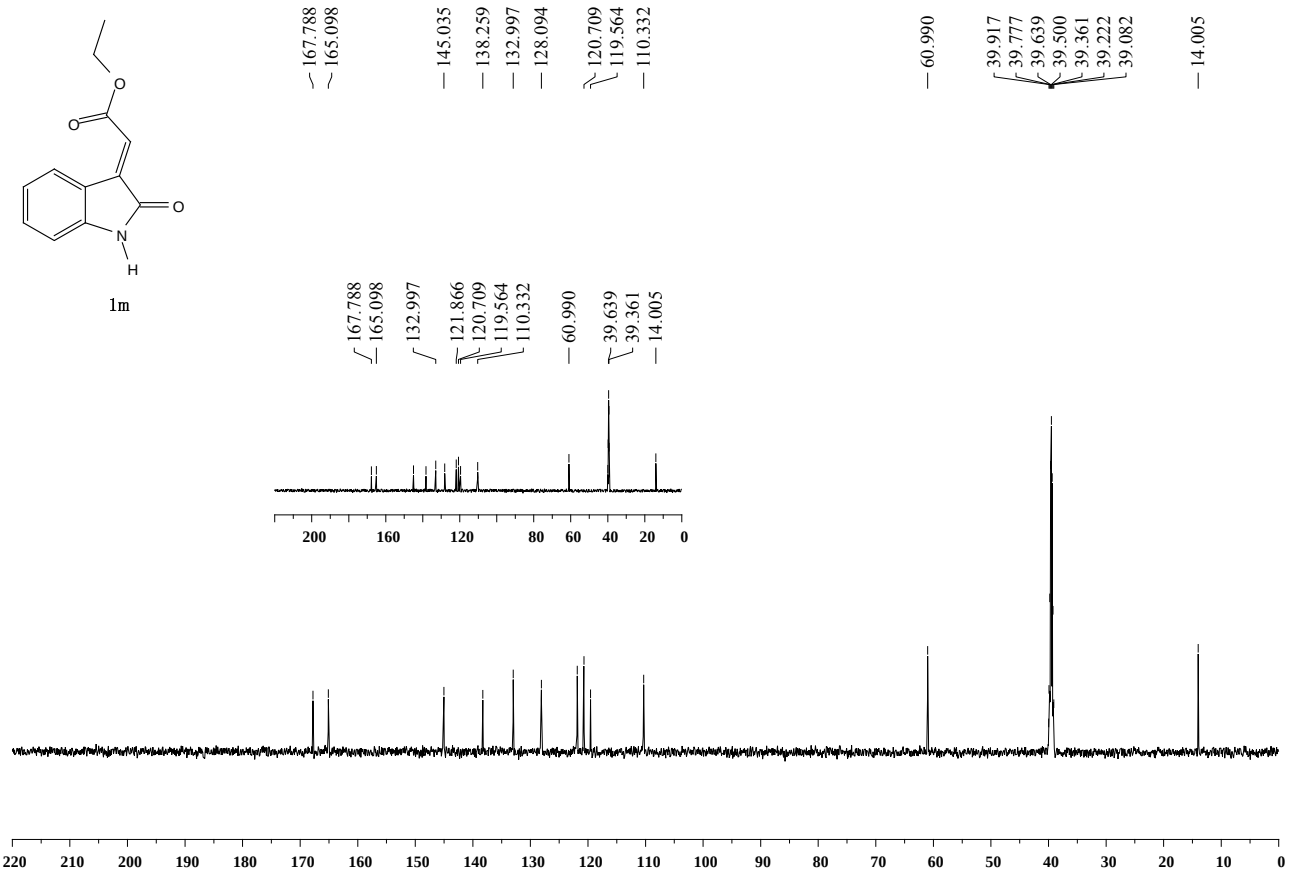
1.04
1.05
1.06
1.04
0.98
2.08
3.08
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

1m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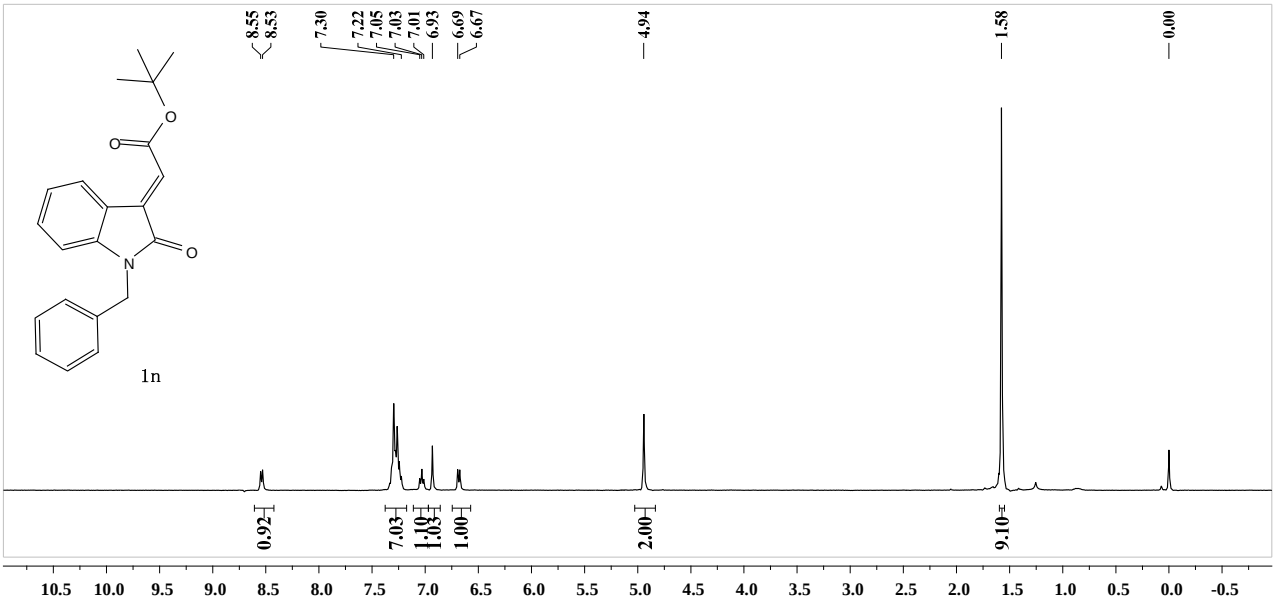
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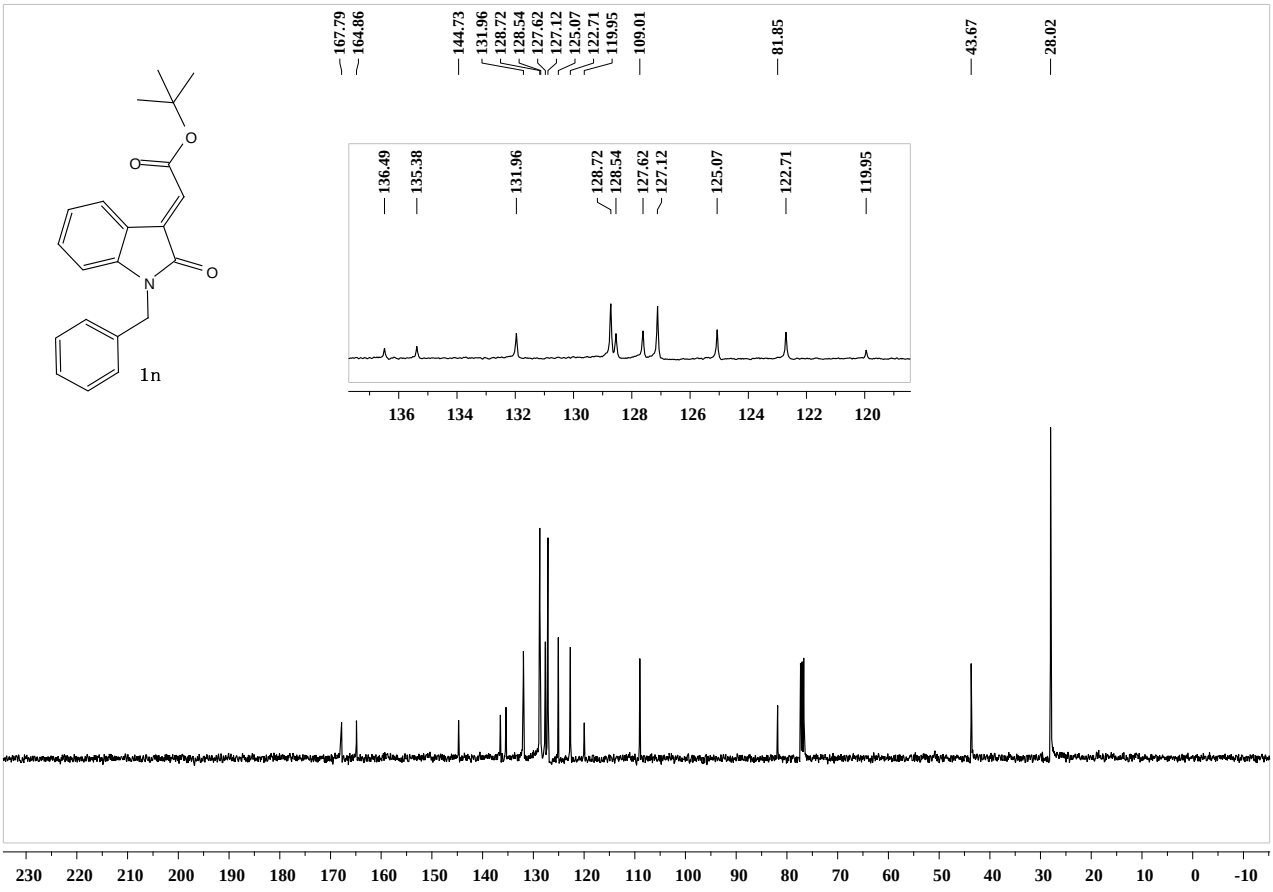
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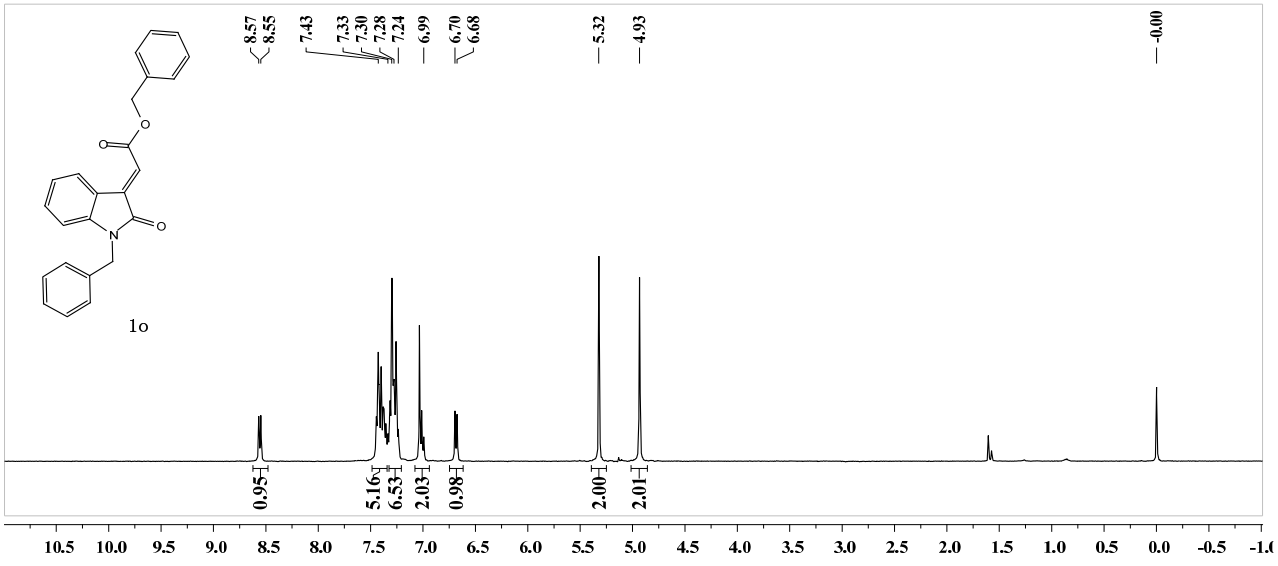
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6.53
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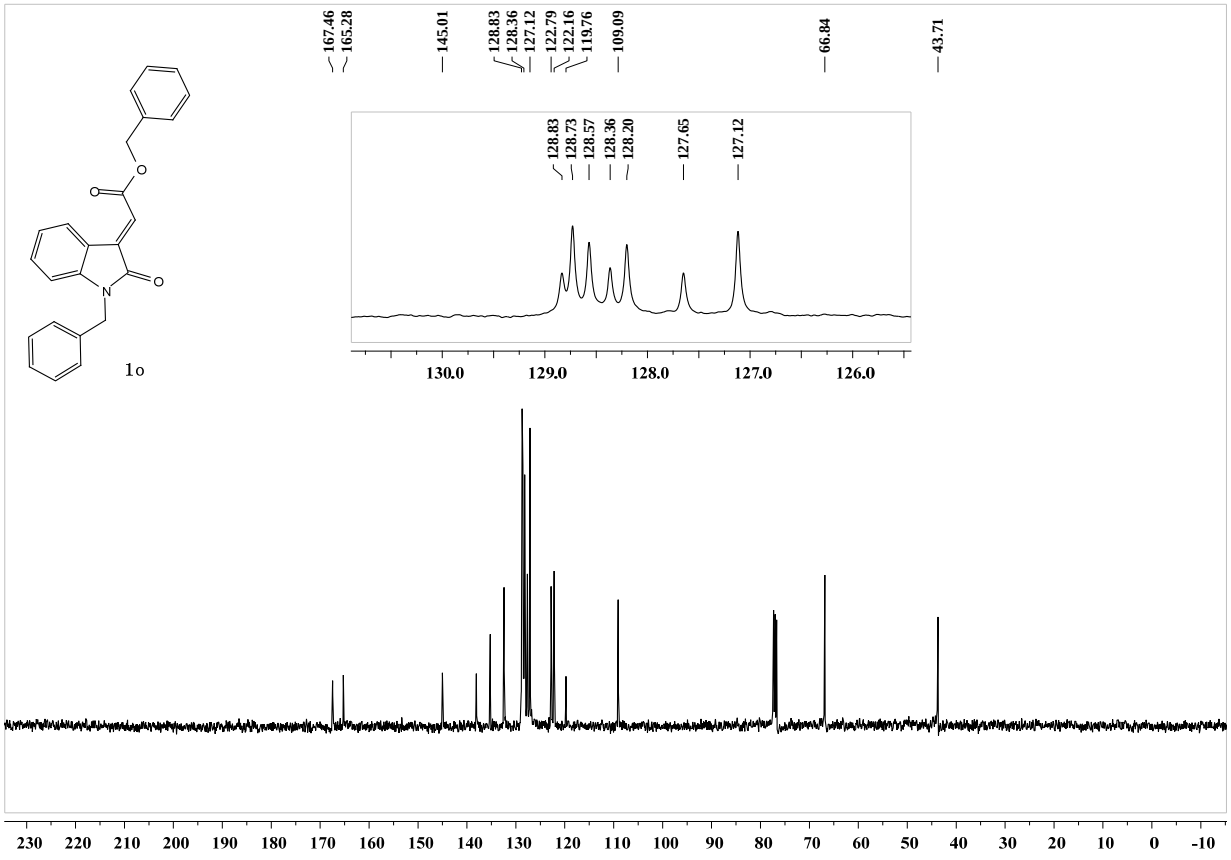
2.01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128.73
128.57
128.36
128.20
127.65
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127.0
126.0
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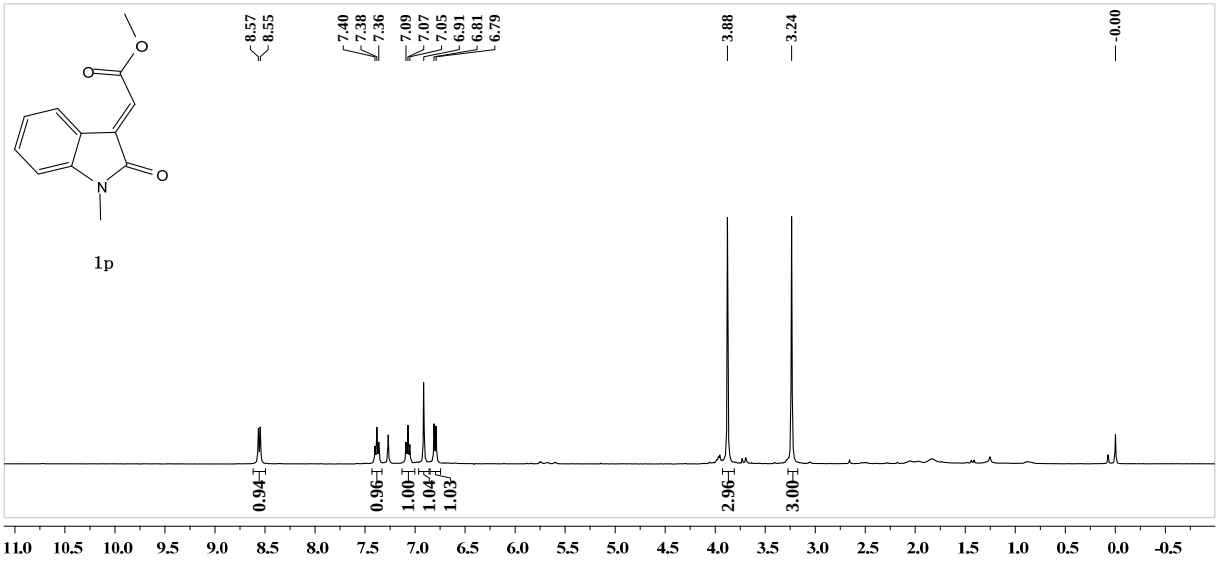
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6.81
6.79
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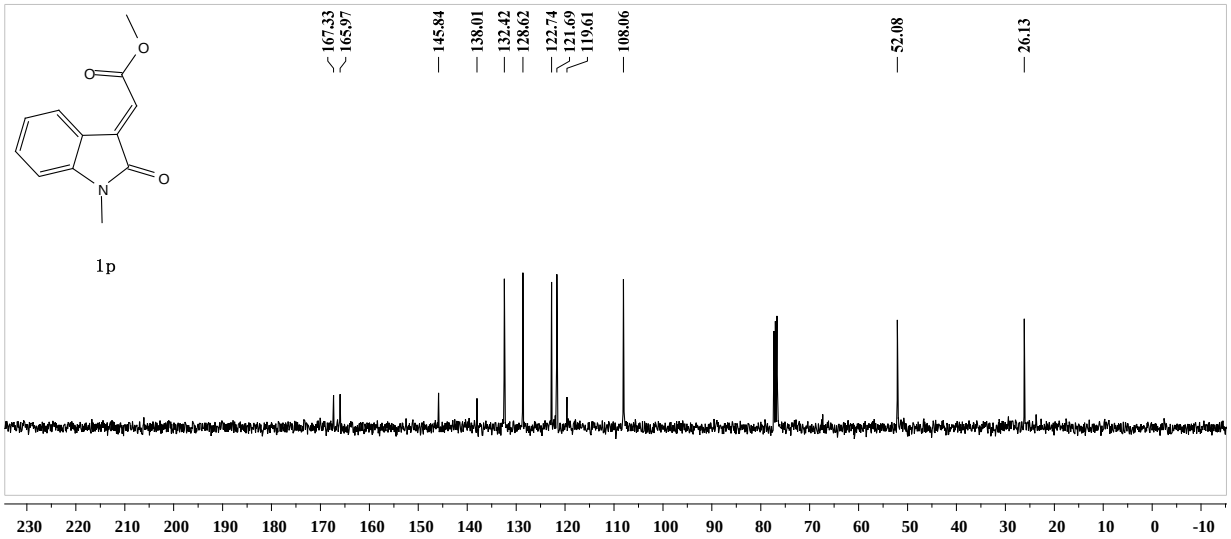
3.24
-0.00
0.94
0.96
1.00
1.04
1.03
2.96
3.00
1p
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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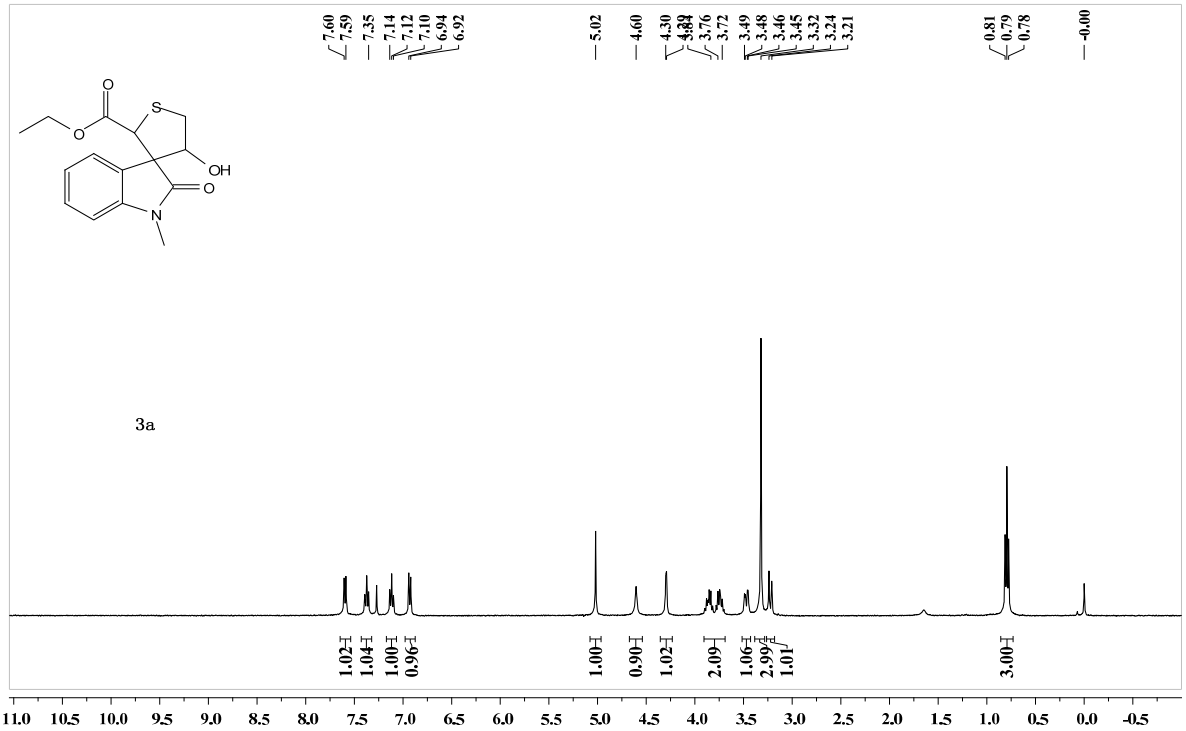
26.13
1p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7.10
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6.92
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4.60
4.30
3.76
3.72
3.49
3.48
3.46
3.45
3.32
3.24
3.21
0.81
0.79
0.78
-0.00
3a
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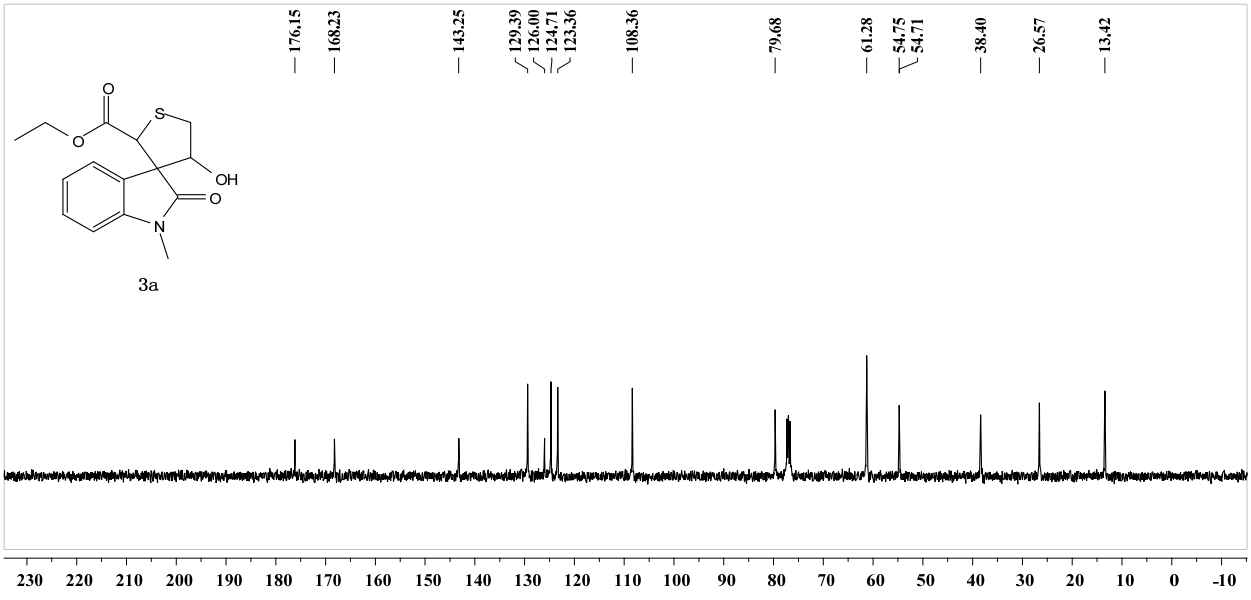
1.02
2.09
1.06
2.99
1.01
3.00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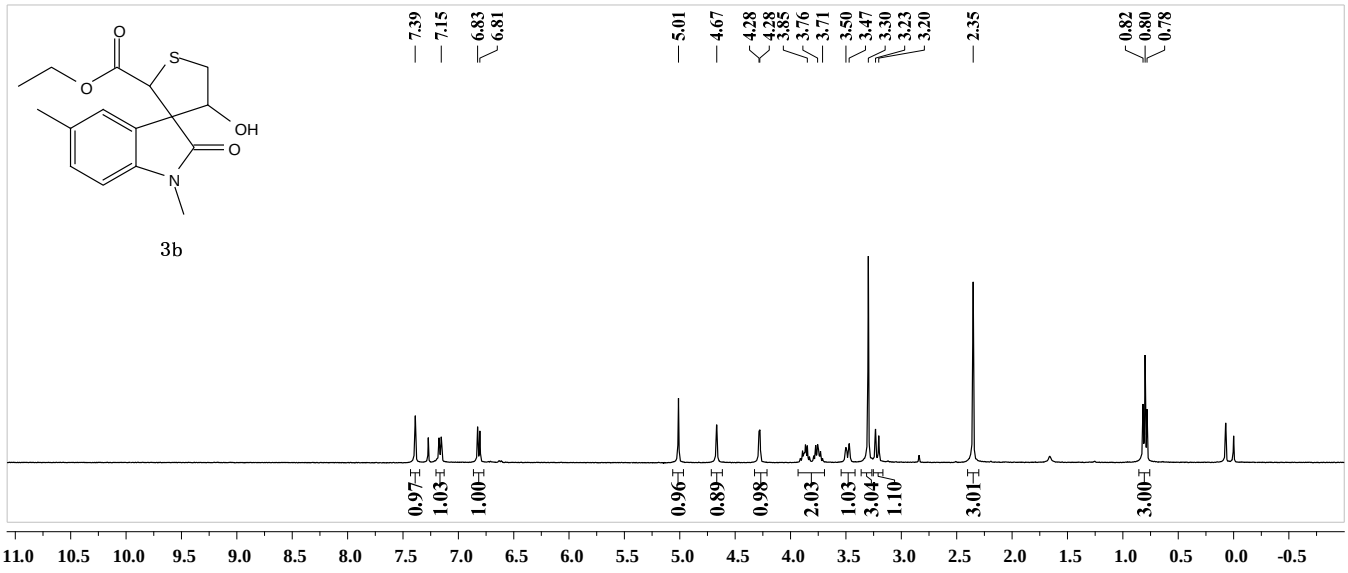
13.42
3a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3.47
3.30
3.23
3.20
2.35
0.82
0.80
0.78
0.97
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3.04
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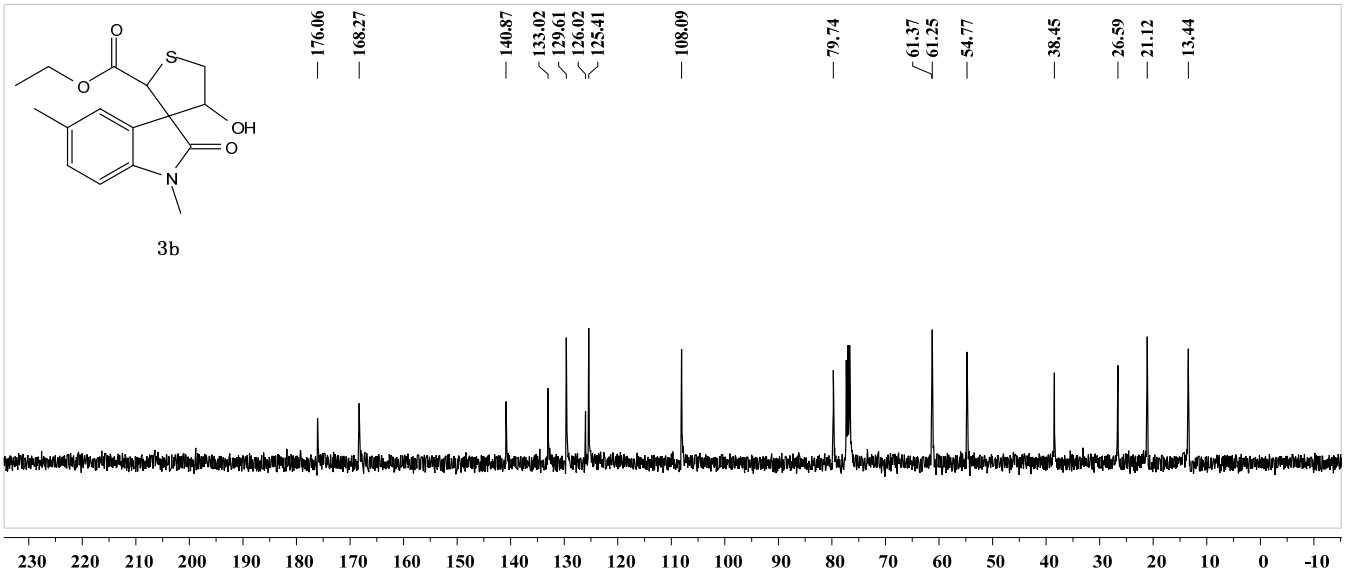
3.01
3.00
3b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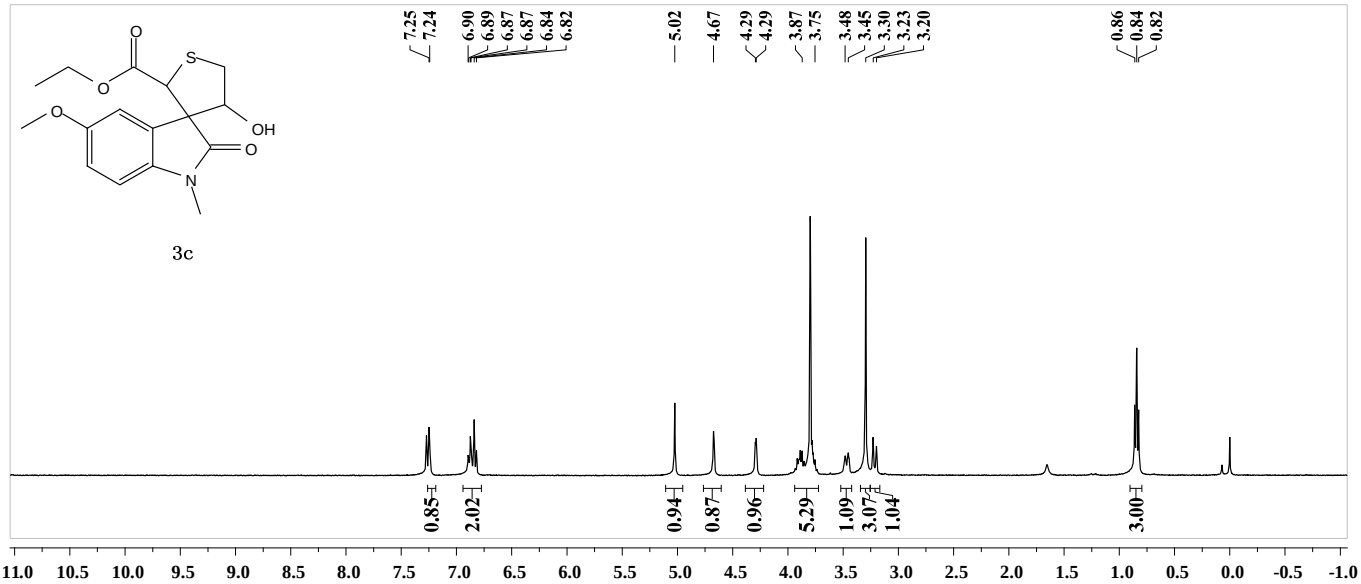
3b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6.82
5.02
4.67
4.29
4.29
3.87
3.75
3.48
3.45
3.30
3.23
3.20
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0.84
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0.87
0.96
5.29
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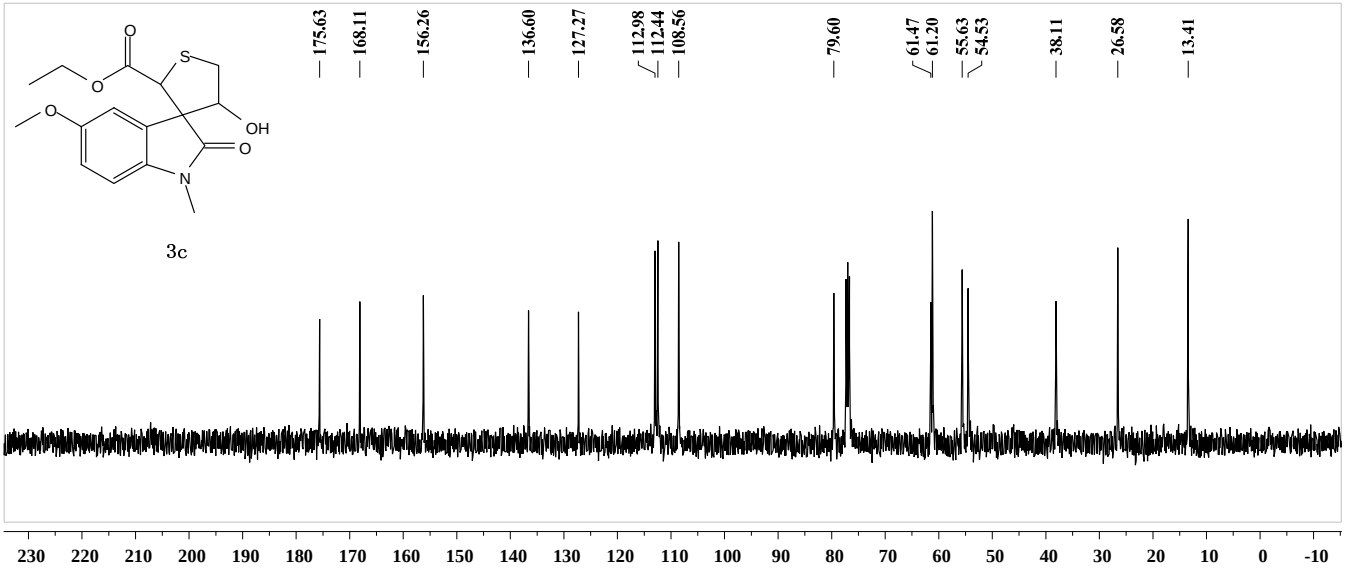
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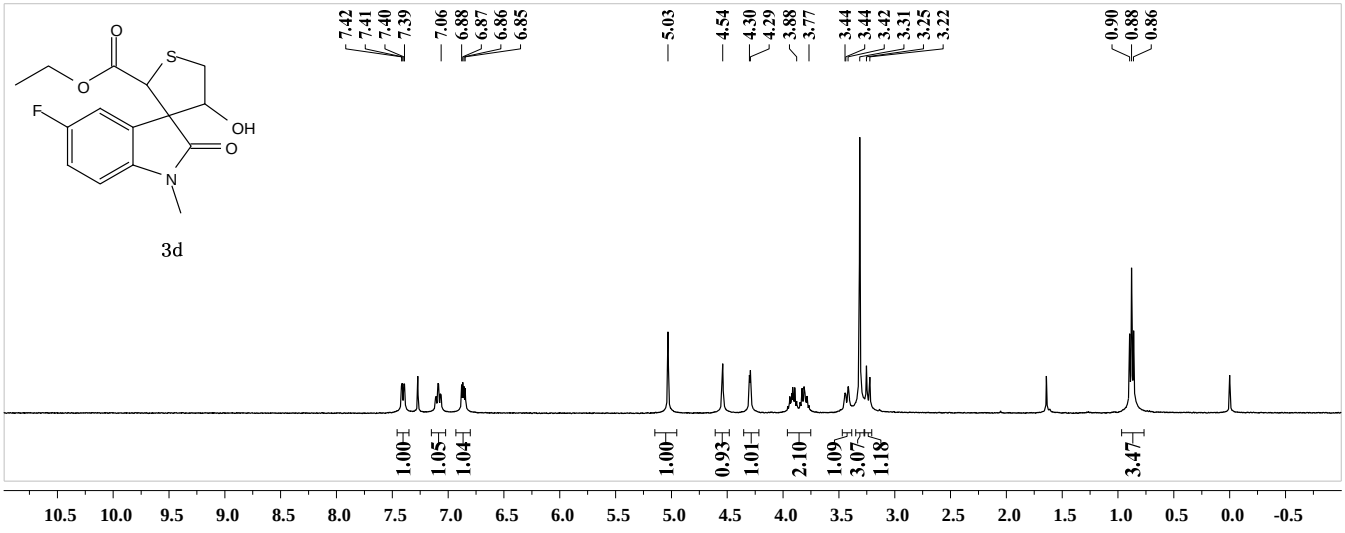
13.41
3c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4.29
3.88
3.77
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3.44
3.42
3.31
3.25
3.22
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0.88
0.86
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1.04
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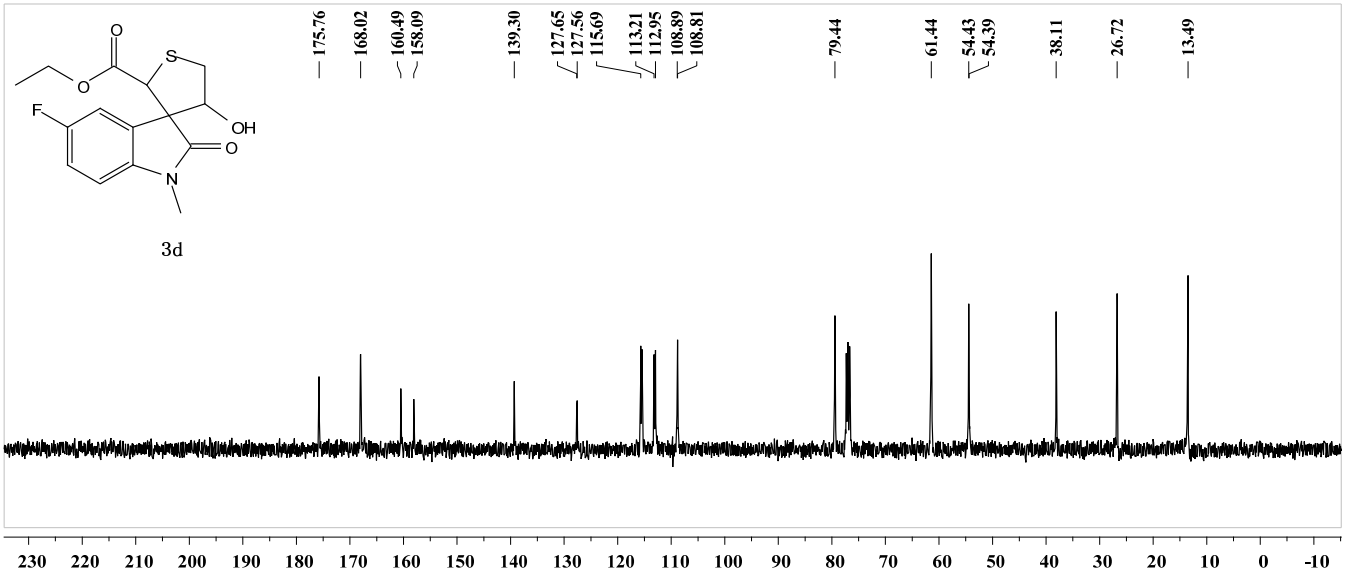
3d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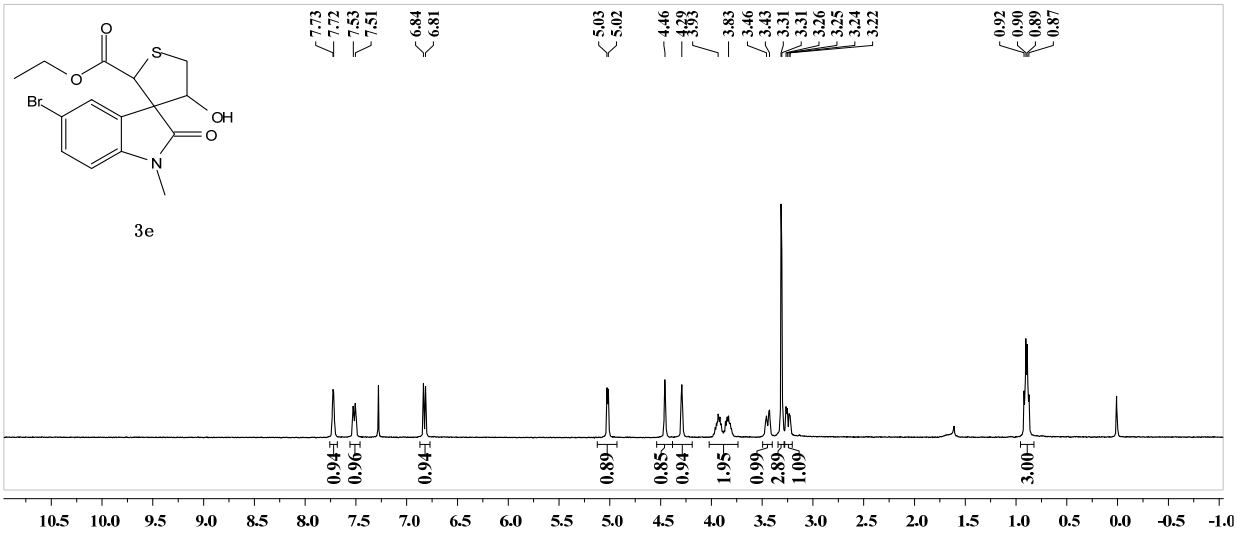
3d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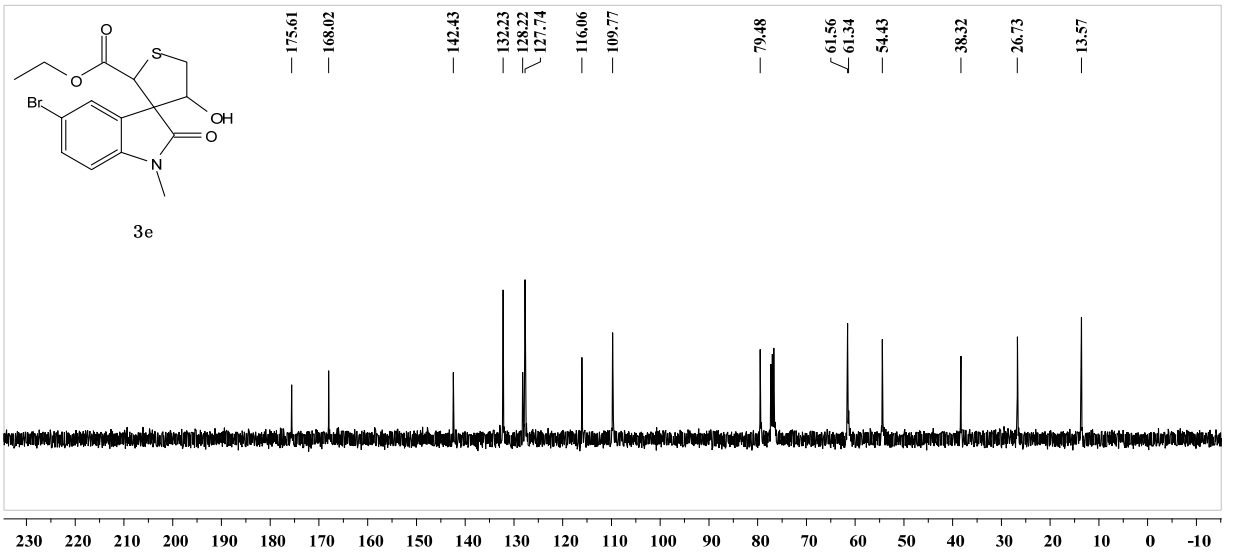
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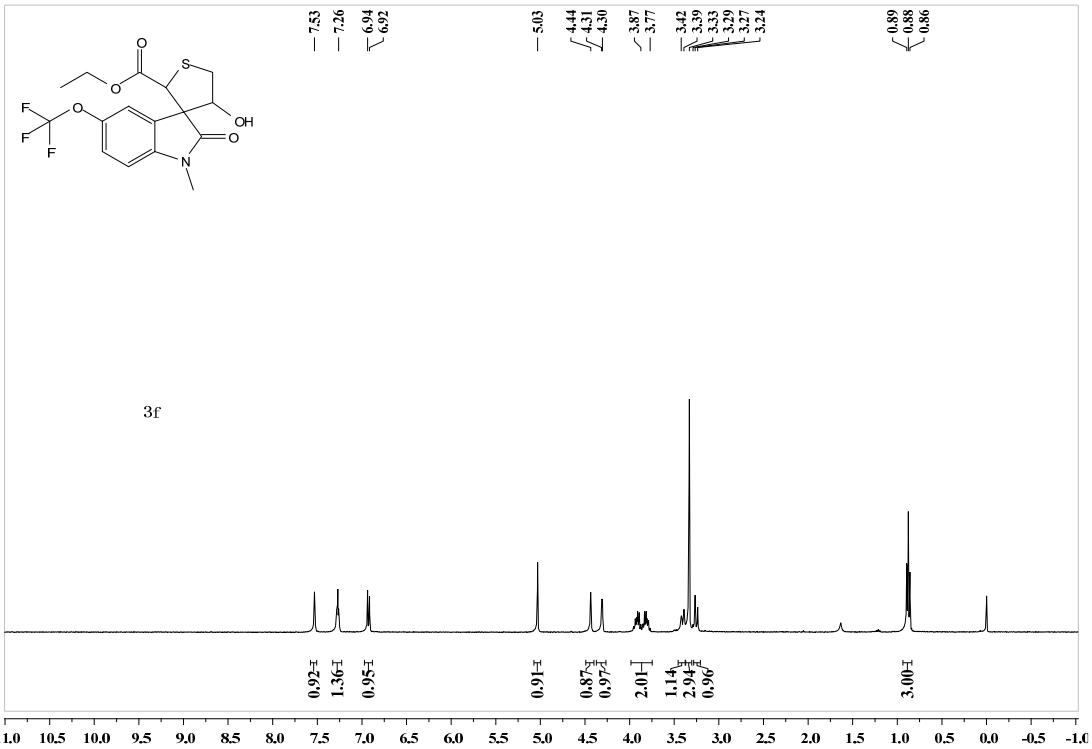
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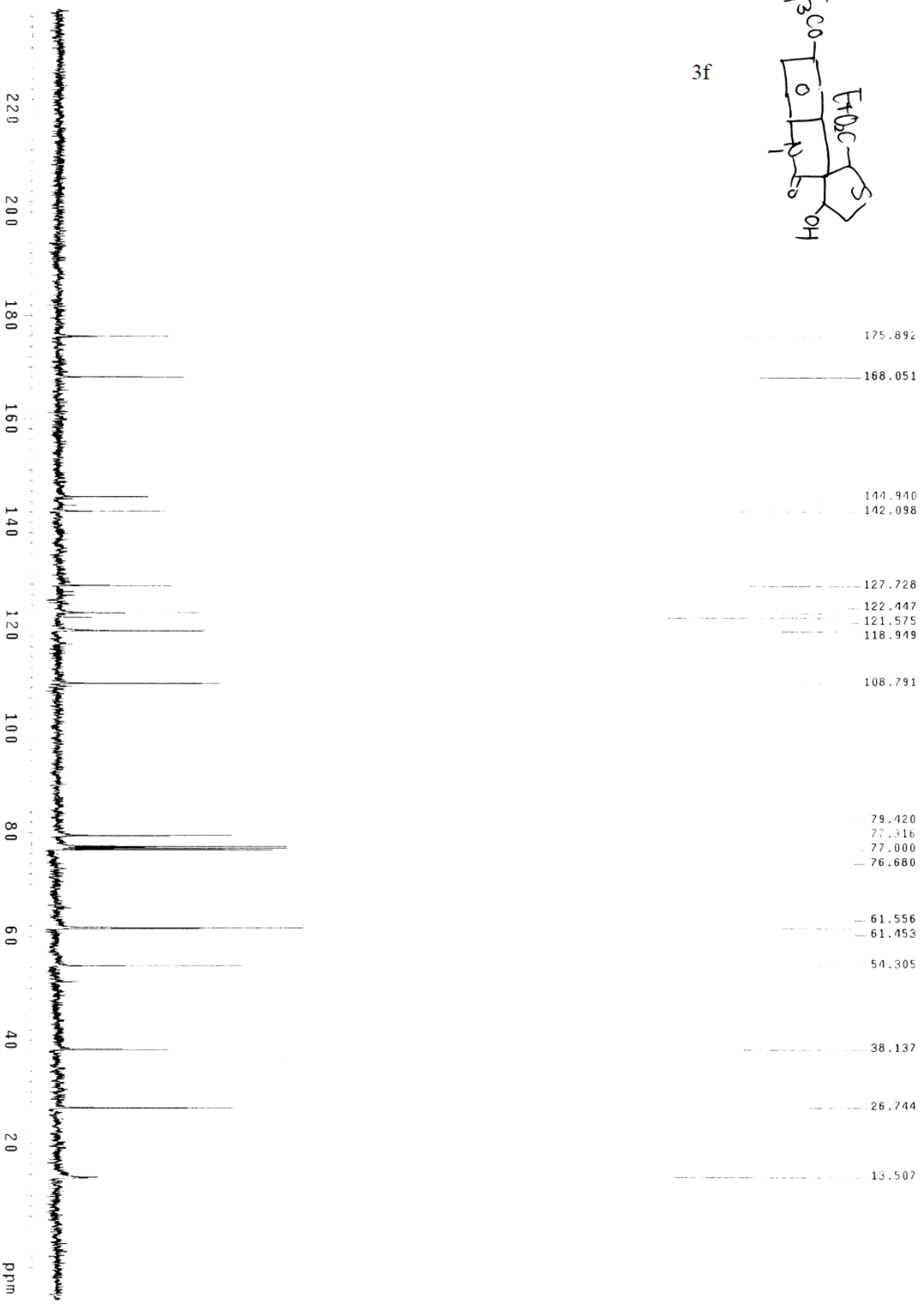
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61.556
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140
120
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60
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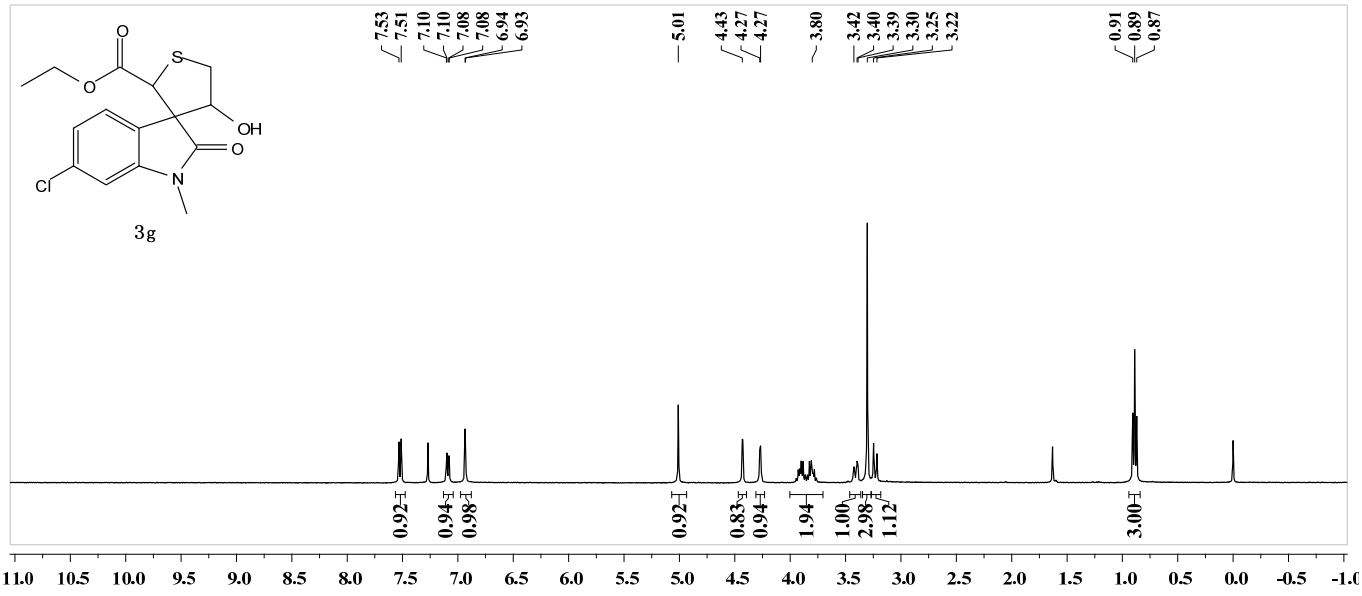
20
ppm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4.27
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3.42
3.40
3.39
3.30
3.25
3.22
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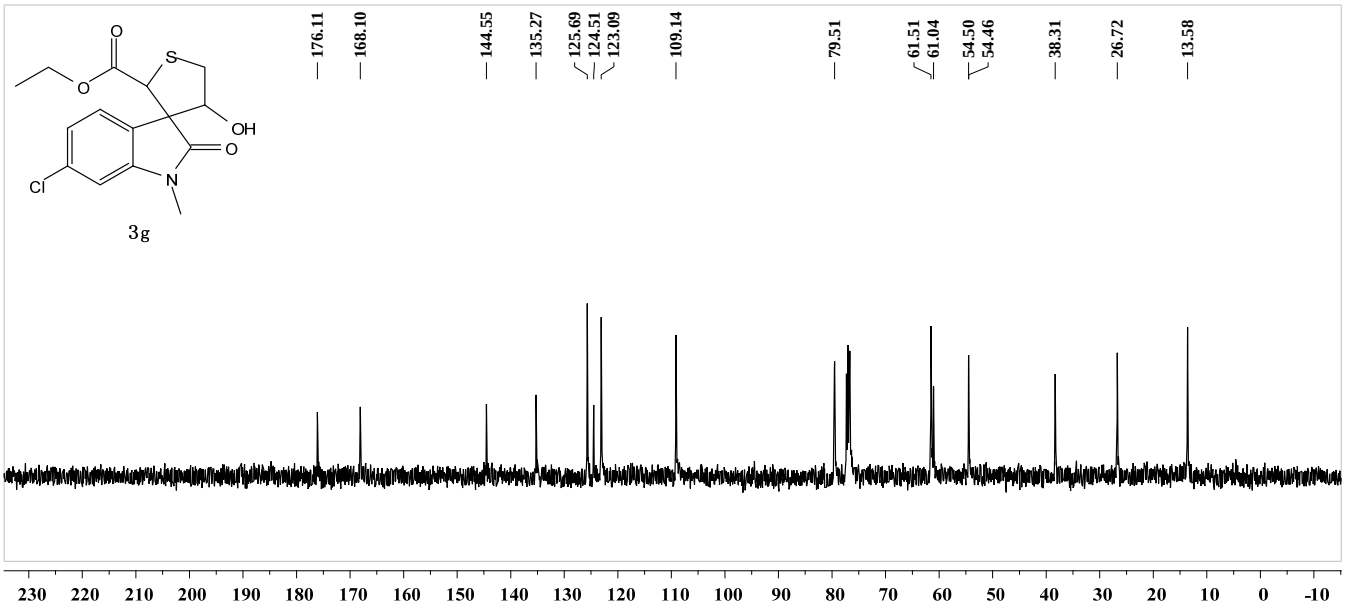
0.89
0.87
0.92
0.94
0.98
0.92
0.83
0.94
1.94
1.00
2.98
1.12
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0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54.46
38.31
26.72
13.58
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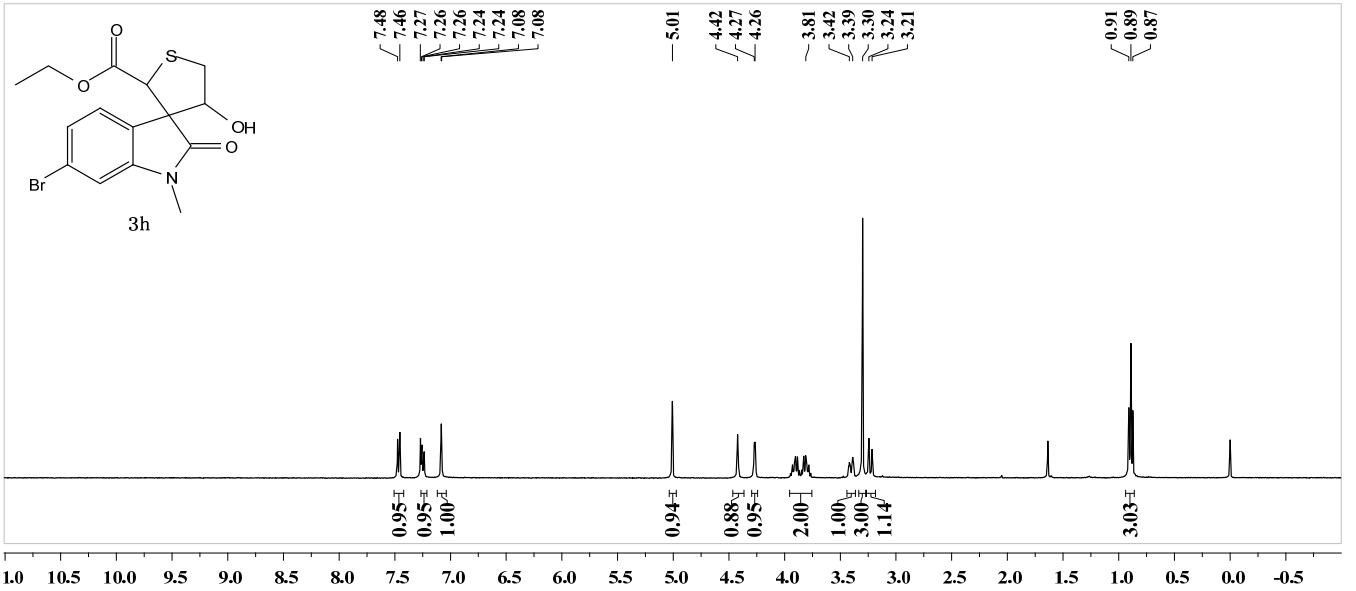
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3.39
3.30
3.24
3.21
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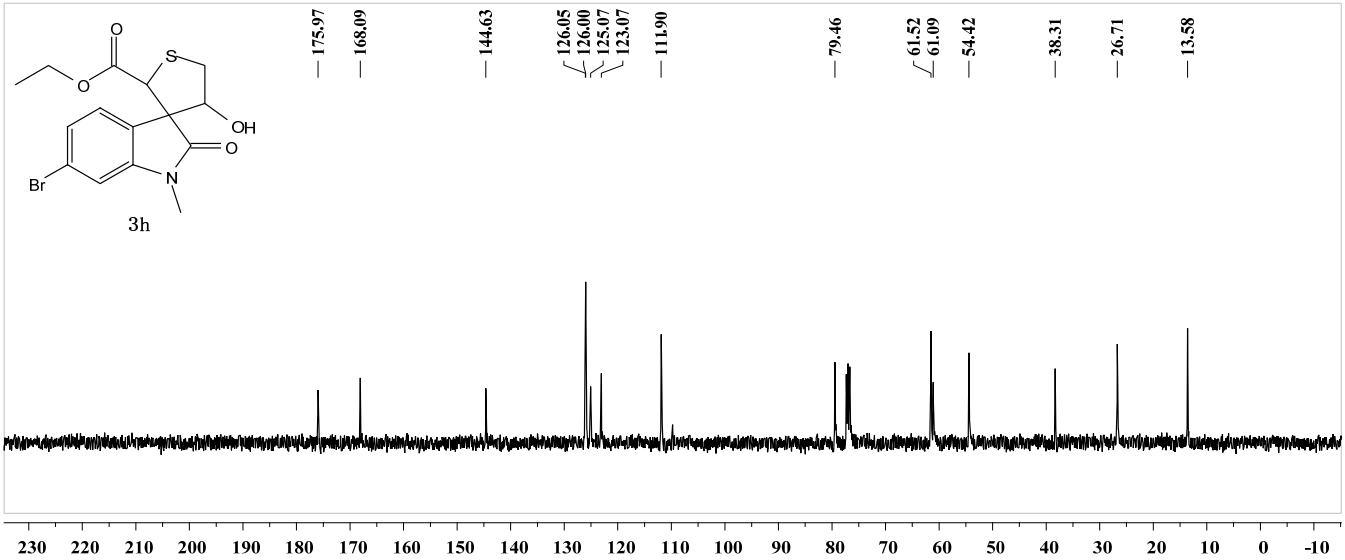
0.89
0.87
0.95
0.95
1.00
0.94
0.88
0.95
2.00
1.00
3.00
1.14
3.03
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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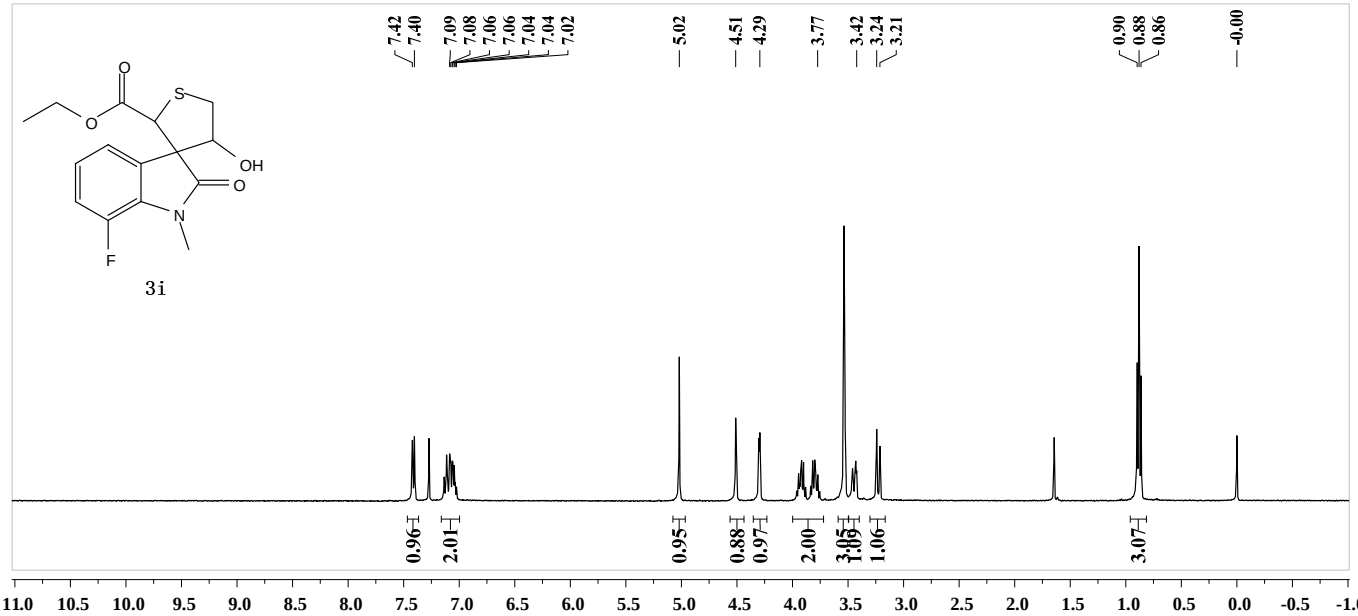
13.58
Br
OH
O
S
N
3h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5.02
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3.42
3.24
3.21
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0.88
0.86
-0.00
0.96
2.01
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2.00
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1.09
1.06
3.07
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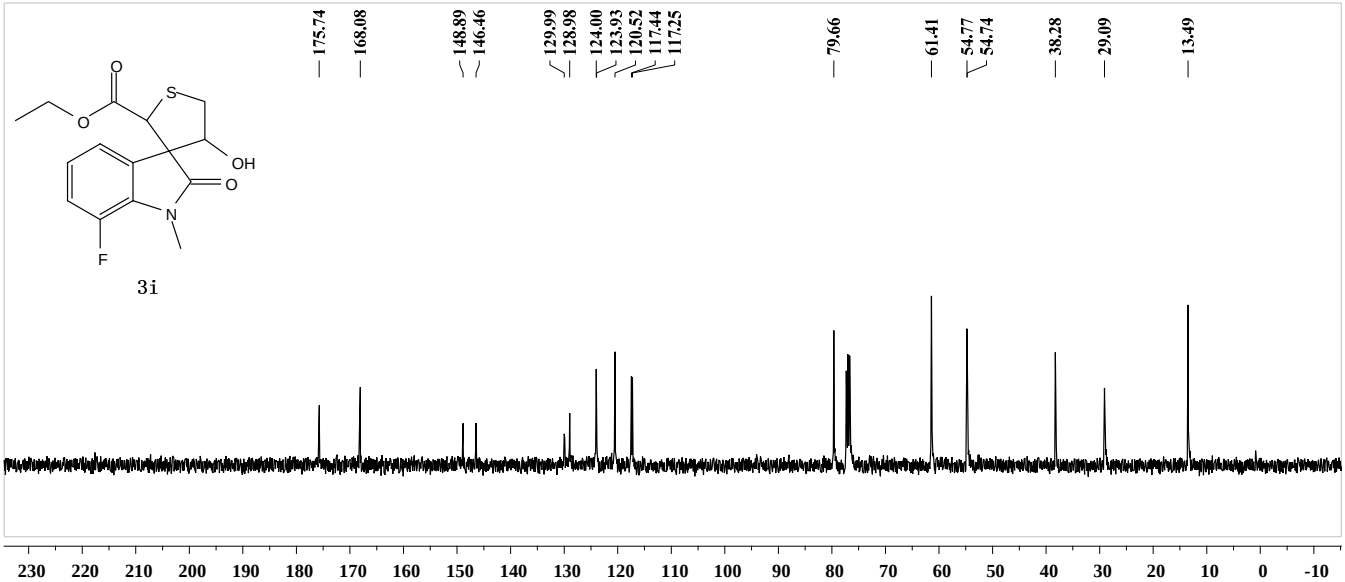
OH
O
S
N
3i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OH
O
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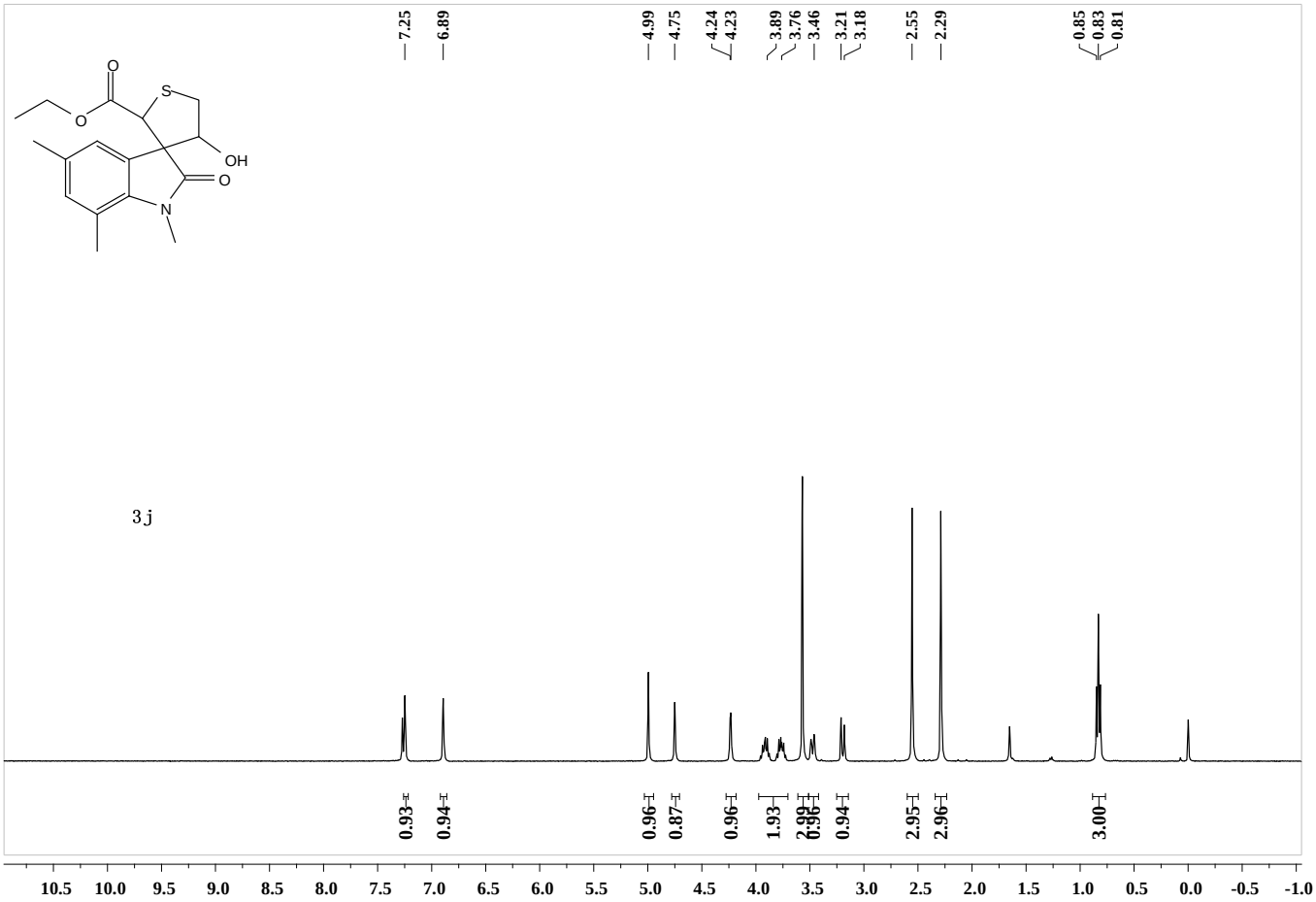
N
3i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0.83
0.81
3j
O
S
O
OH
O
N
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0.94
0.96
0.87
0.96
1.93
2.99
0.96
0.94
2.95
2.96
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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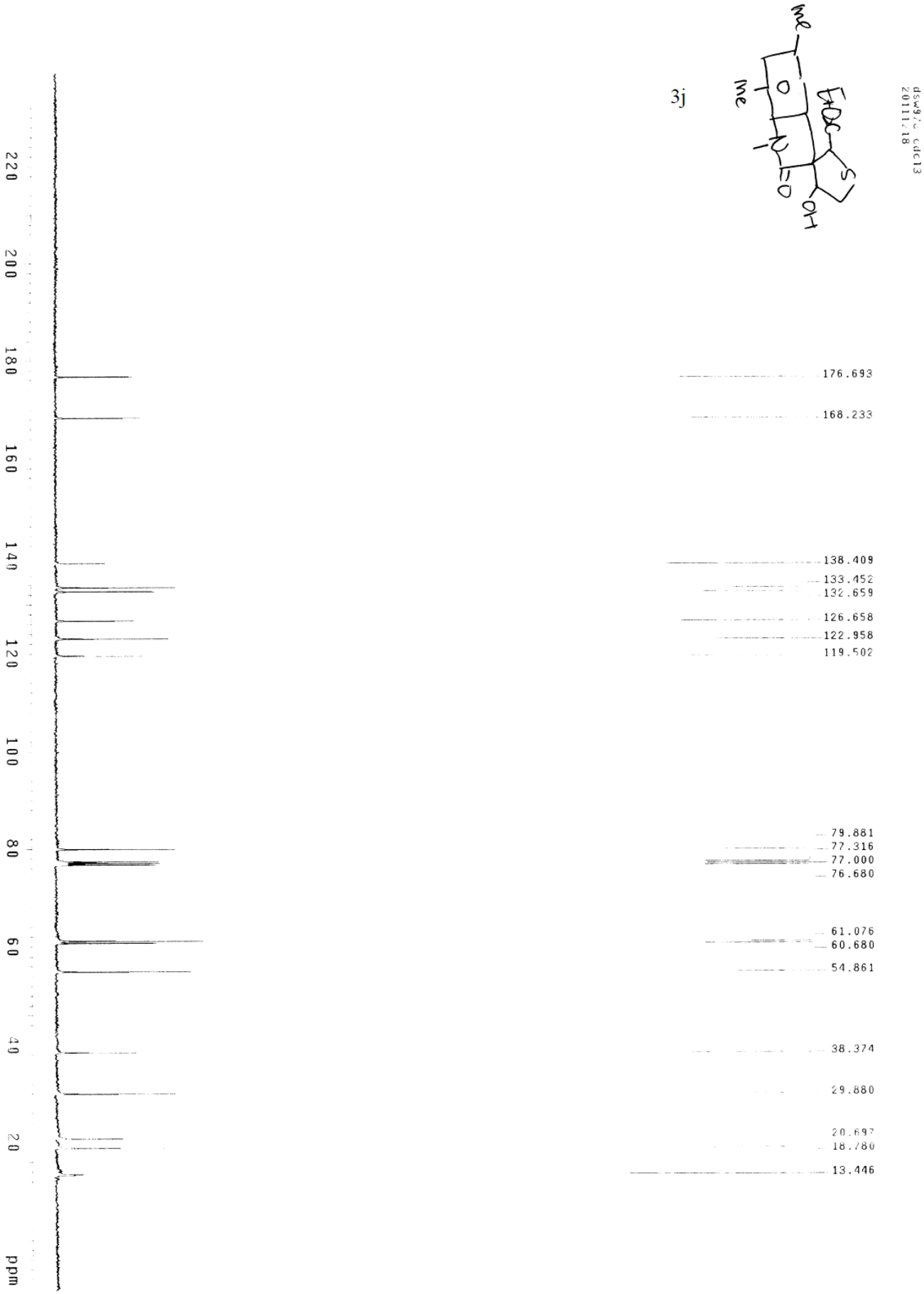
-1.0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54.861
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140
120
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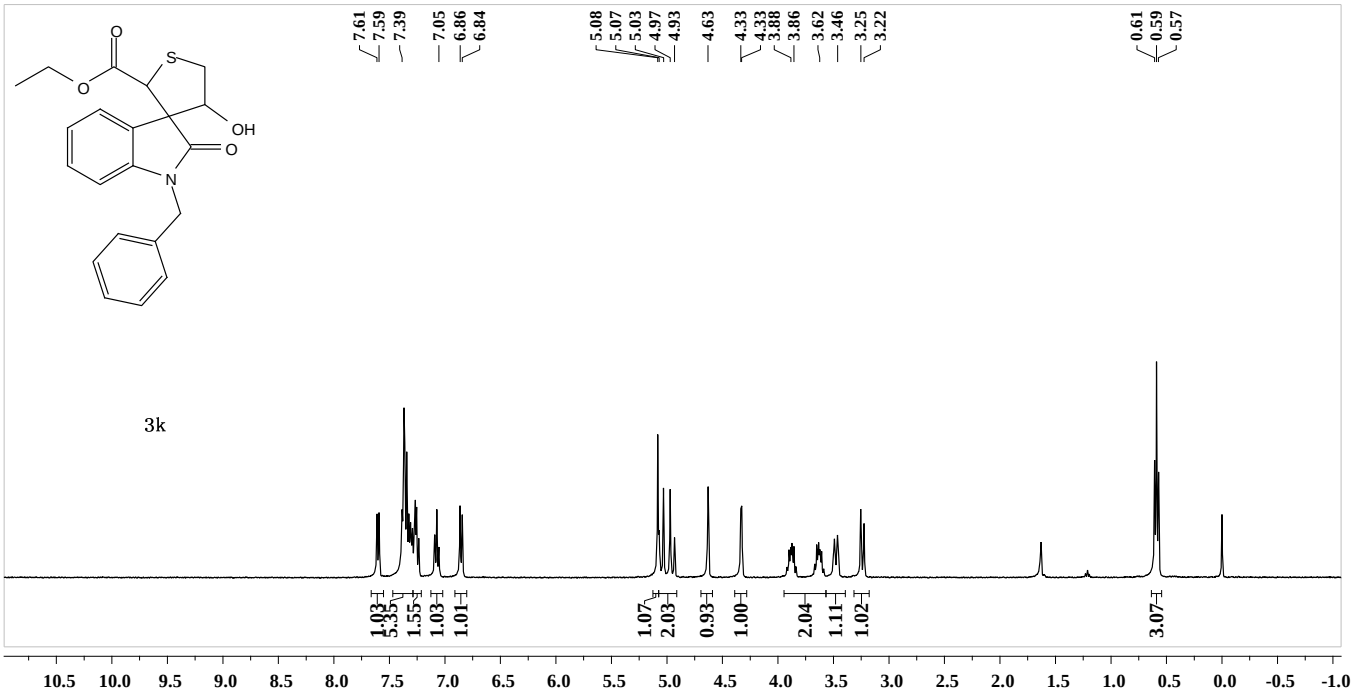
80
60
40
20
ppm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3.88
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3.62
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3.25
3.22
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0.59
0.57
3k
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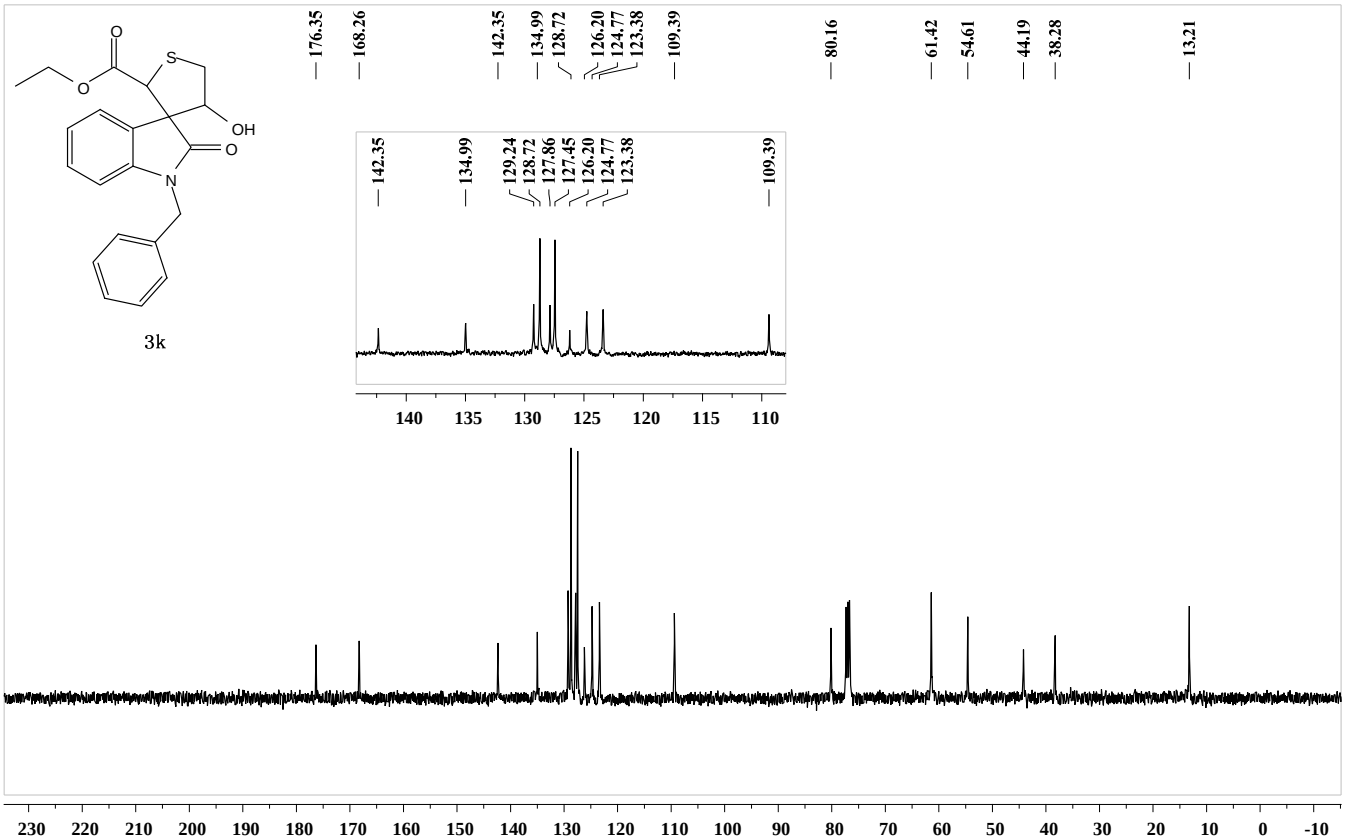
5.35
1.55
1.03
1.01
1.07
2.03
0.93
1.00
2.04
1.11
1.02
3.07
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0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123.38
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61.42
54.61
44.19
38.28
13.21
3k
142.35
134.99
129.24
128.72
127.86
127.45
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123.38
109.39
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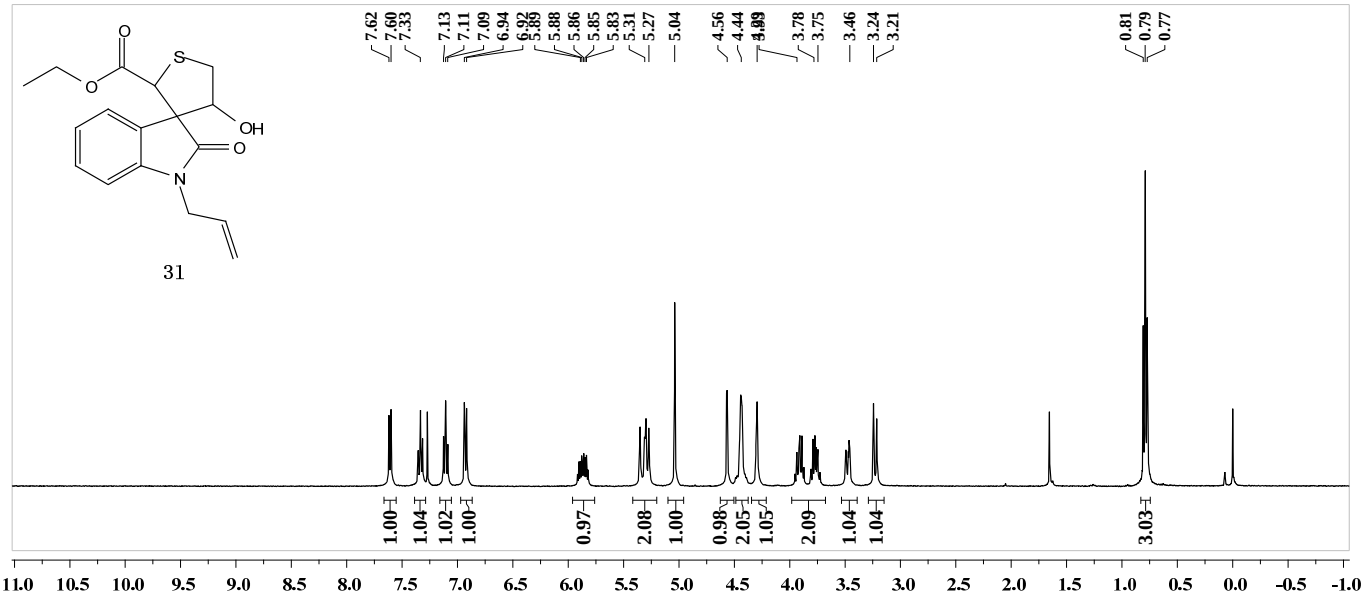
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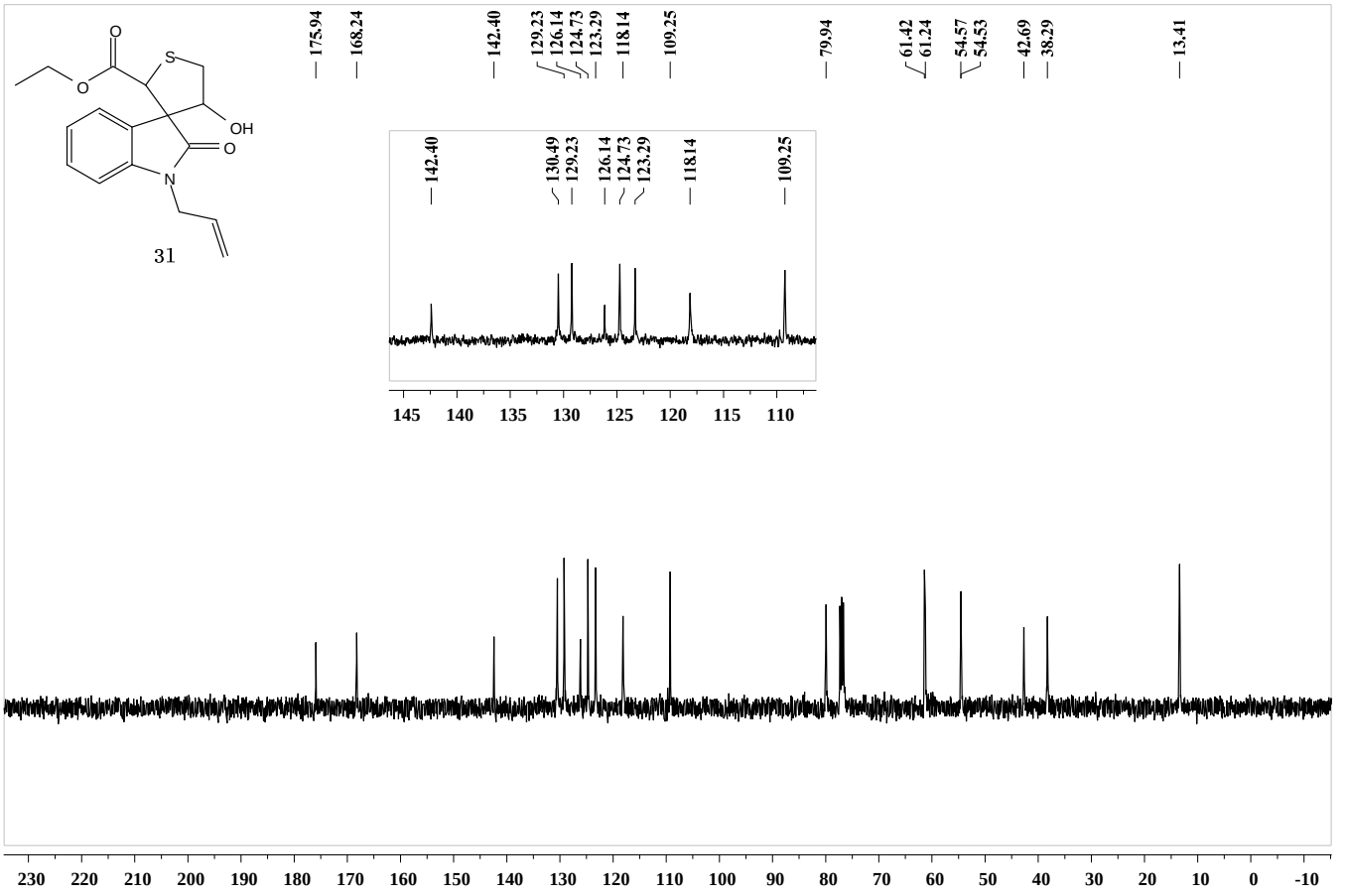
5.31
5.27
5.04
4.56
4.44
3.78
3.75
3.46
3.24
3.21
0.81
0.79
0.77
1.00
1.04
1.02
1.00
0.97
2.08
1.00
0.98
2.05
1.05
2.09
1.04
1.04
3.03
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0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61.24
54.57
54.53
42.69
38.29
13.41
142.40
130.49
129.23
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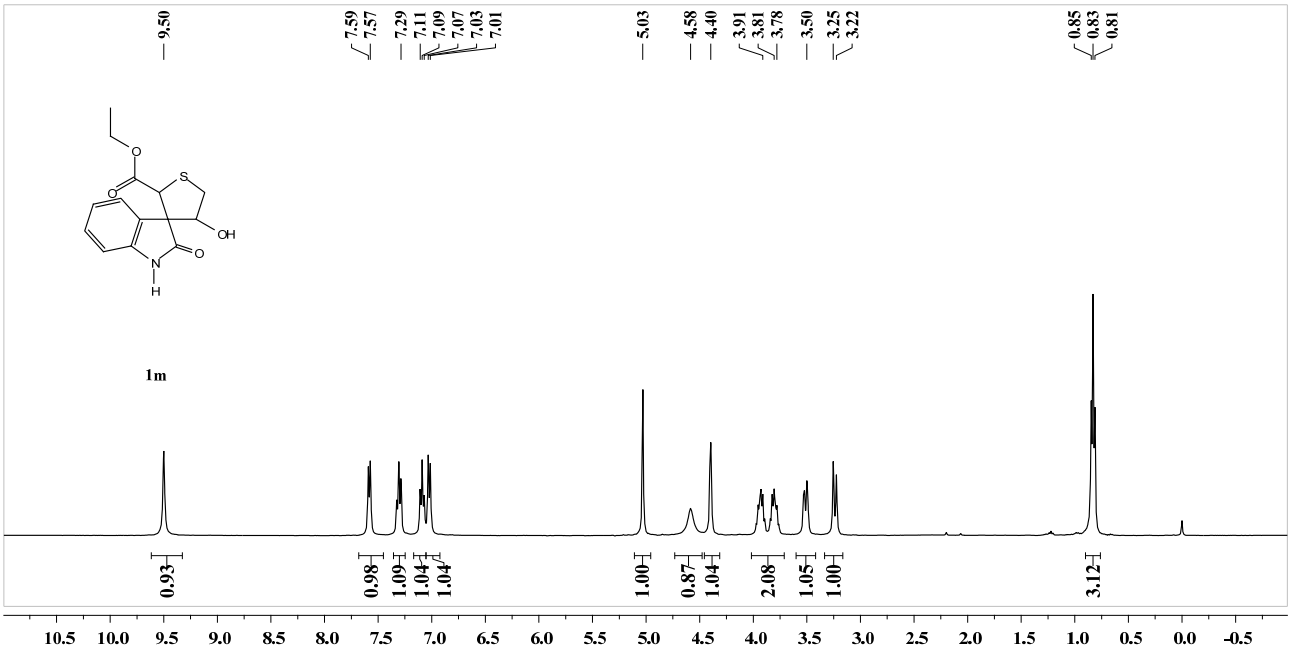
118.14
109.25
145 140 135 130 125 120 115 110
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10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7.07
7.03
7.01
5.03
4.58
4.40
3.91
3.81
3.78
3.50
3.25
3.22
0.85
0.83
0.81
1m
0.93
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1.04
1.04
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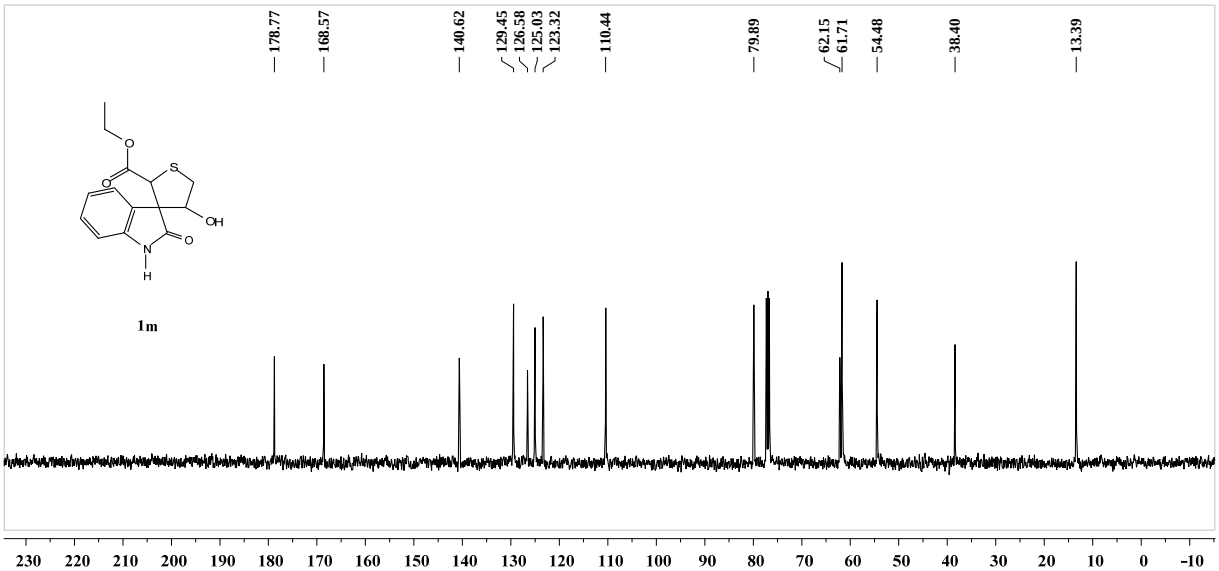
1.04
2.08
1.05
1.00
3.12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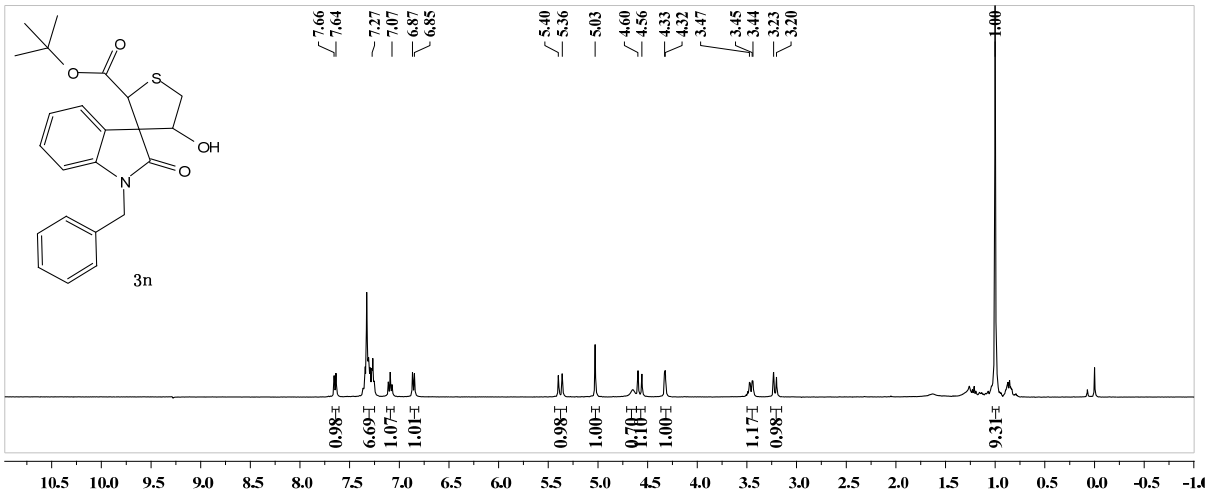
1m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4.56
4.33
4.32
3.47
3.45
3.44
3.23
3.20
1.00
3n
0.98
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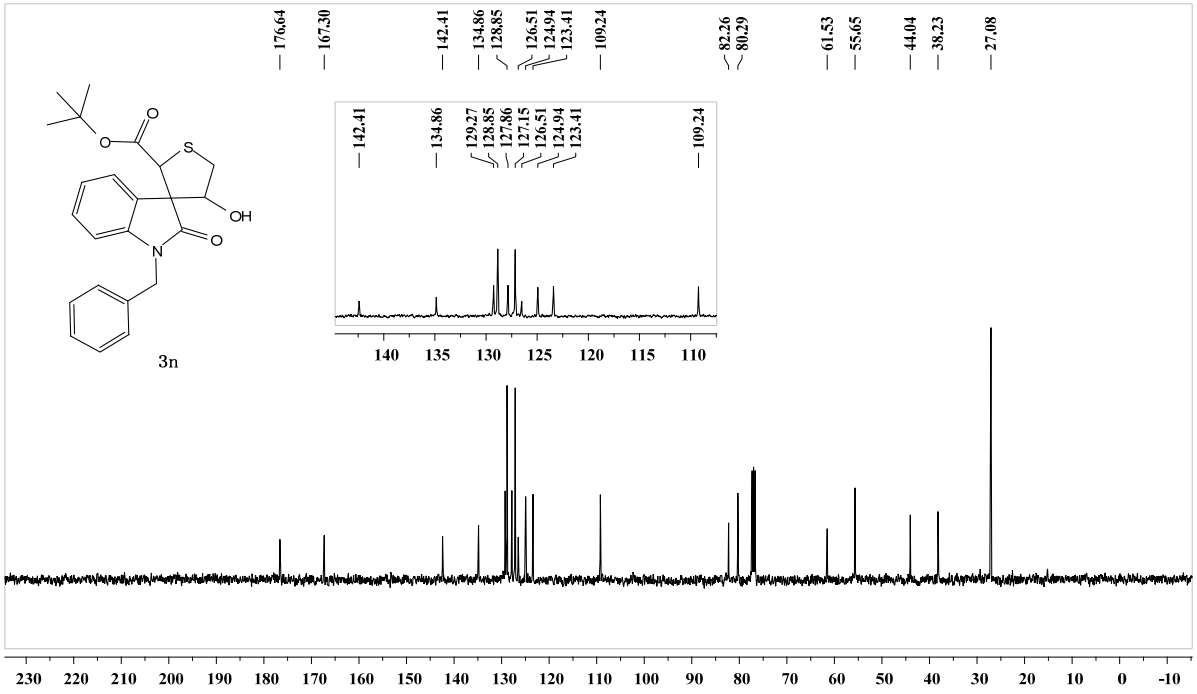
1.10
1.00
1.17
0.98
9.31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55.65
44.04
38.23
27.08
O
O
S
OH
N
O
3n
142.41
134.86
129.27
128.85
127.86
127.15
126.51
124.94
123.41
109.24
140
135
130
125
120
115
110
230
220
210
200
190
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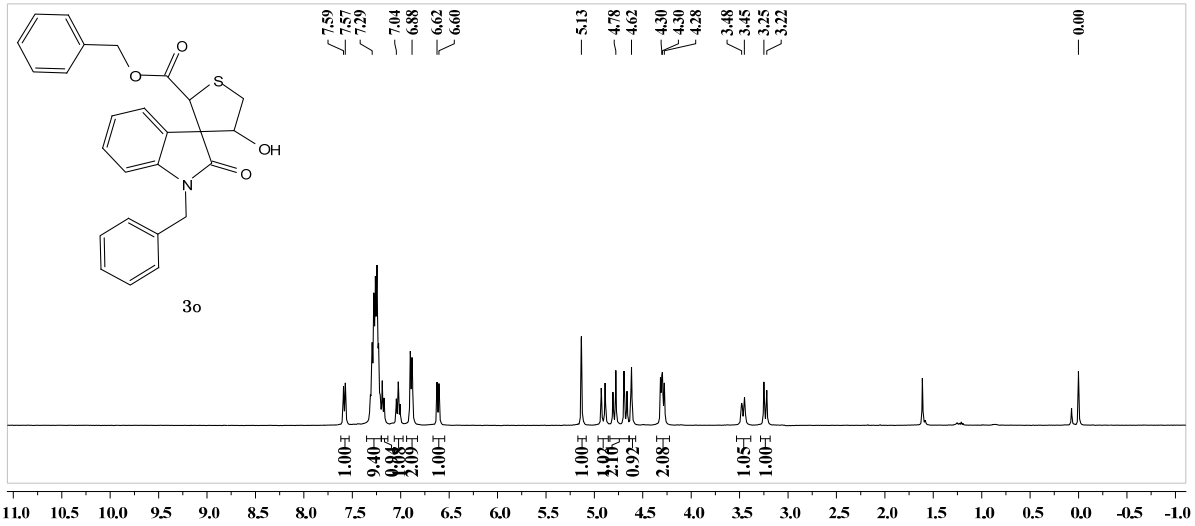
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5.13
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4.30
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4.28
3.48
3.45
3.25
3.22
0.00
O
O
S
OH
N
O
3o
1.00
9.40
2.00
1.00
1.00
2.10
0.92
2.08
1.05
1.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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5.0
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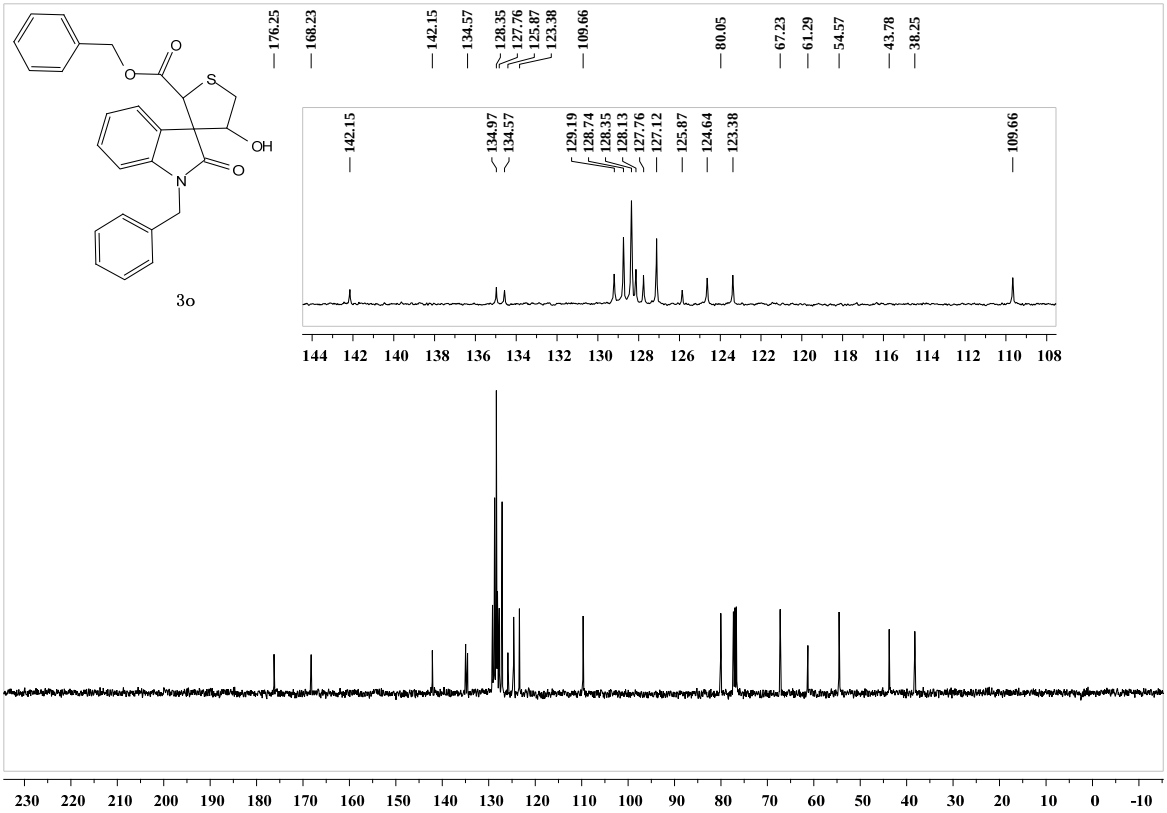
-1.0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54.57
43.78
38.25
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O
S
N
3o
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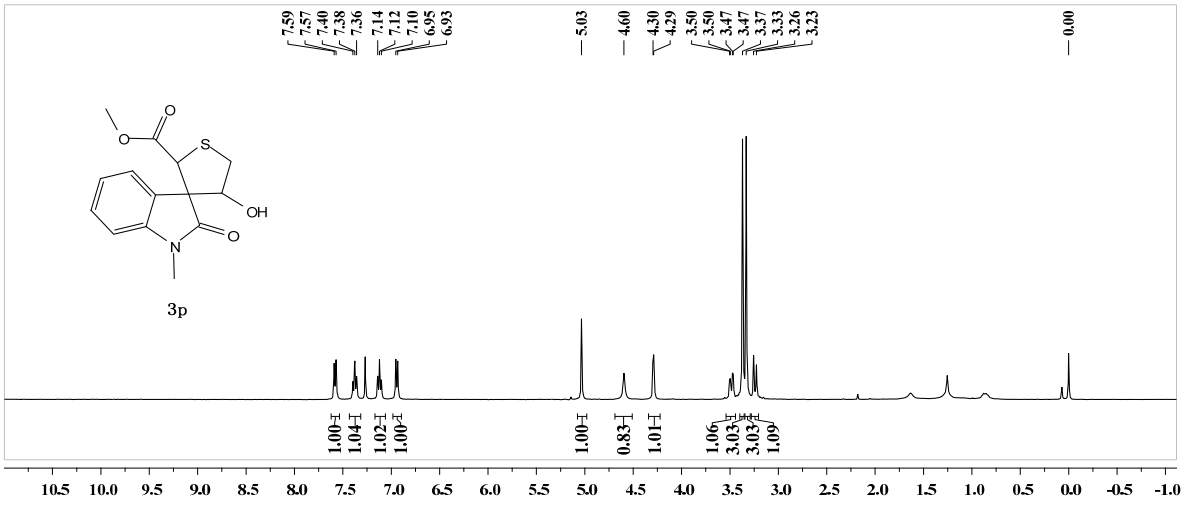
124.64
123.38
109.66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3.33
3.26
3.23
0.00
OH
O
S
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1.00
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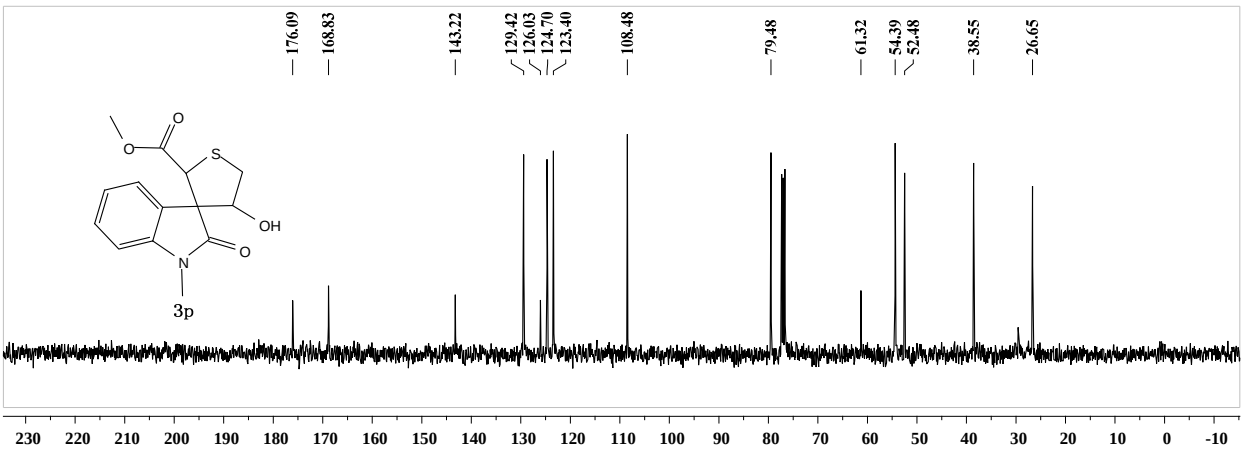
3.03
3.03
1.09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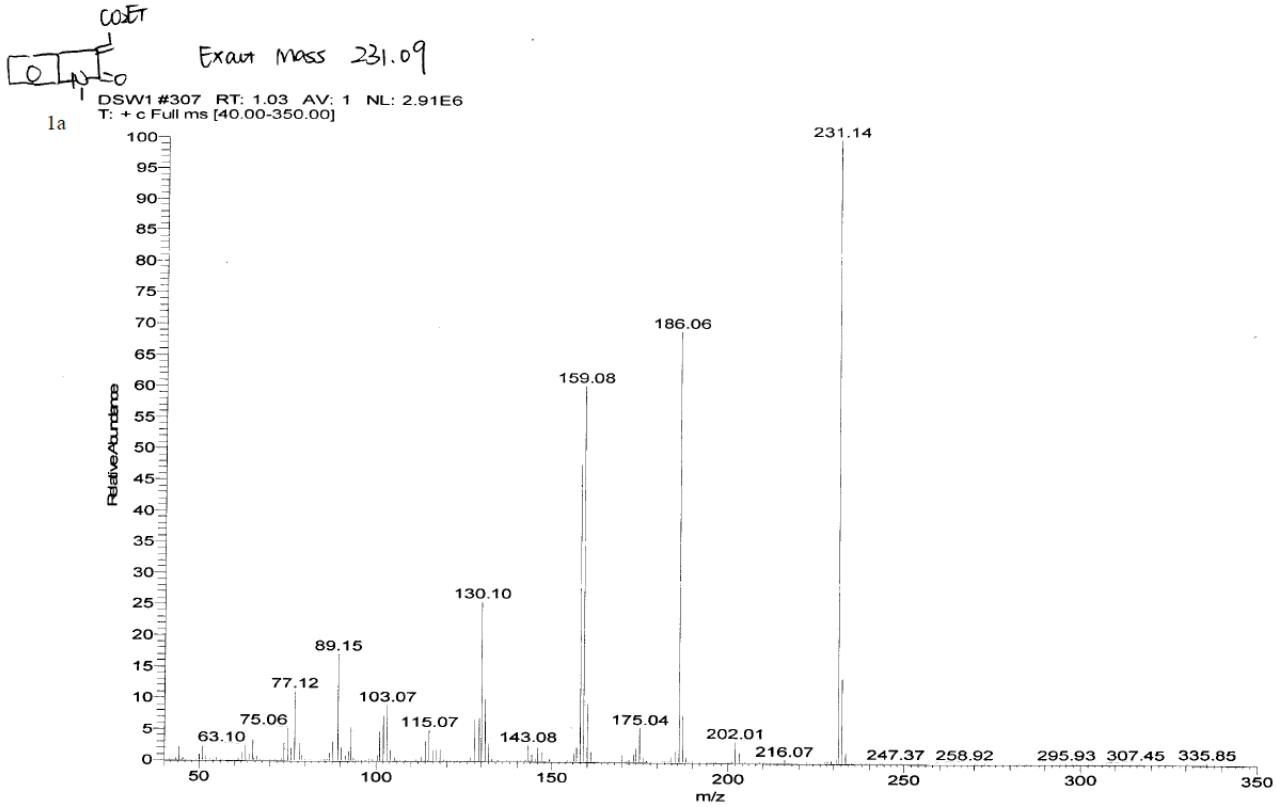
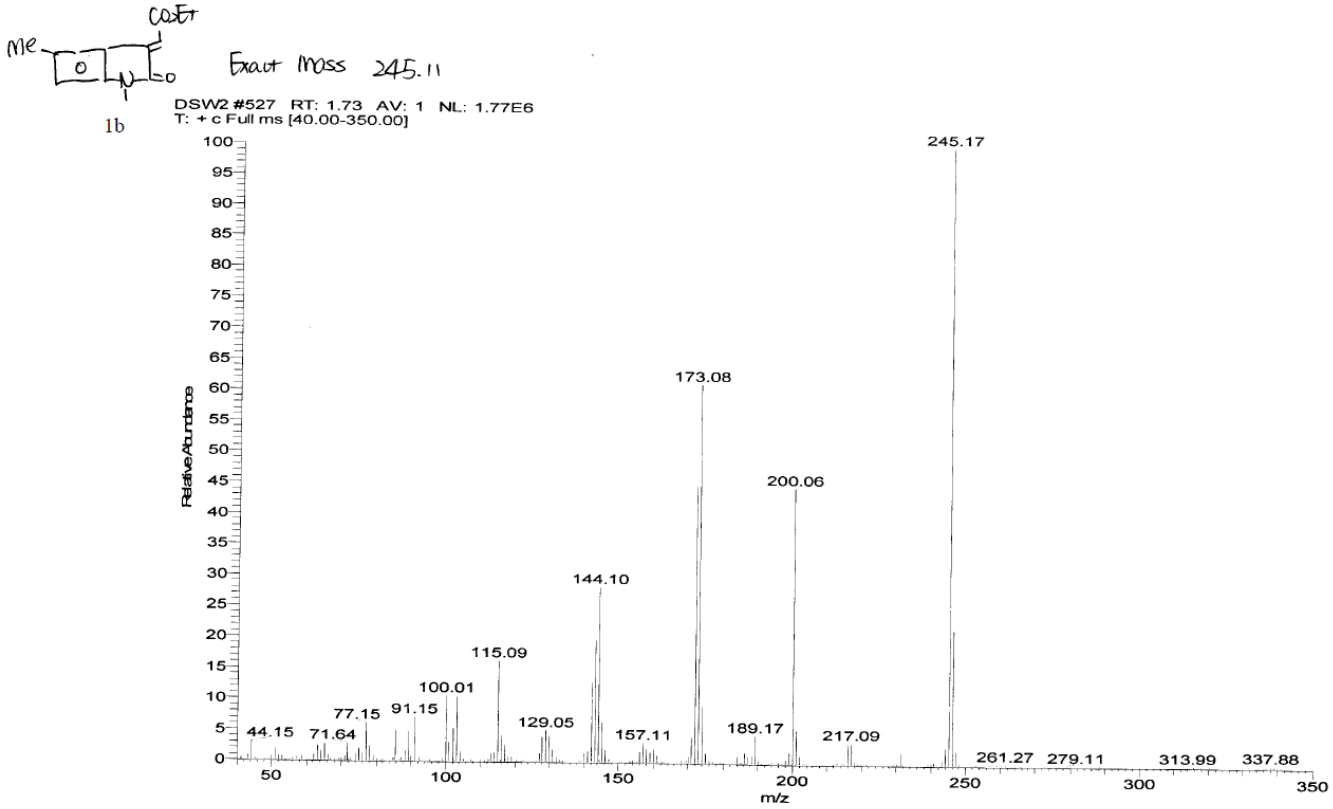
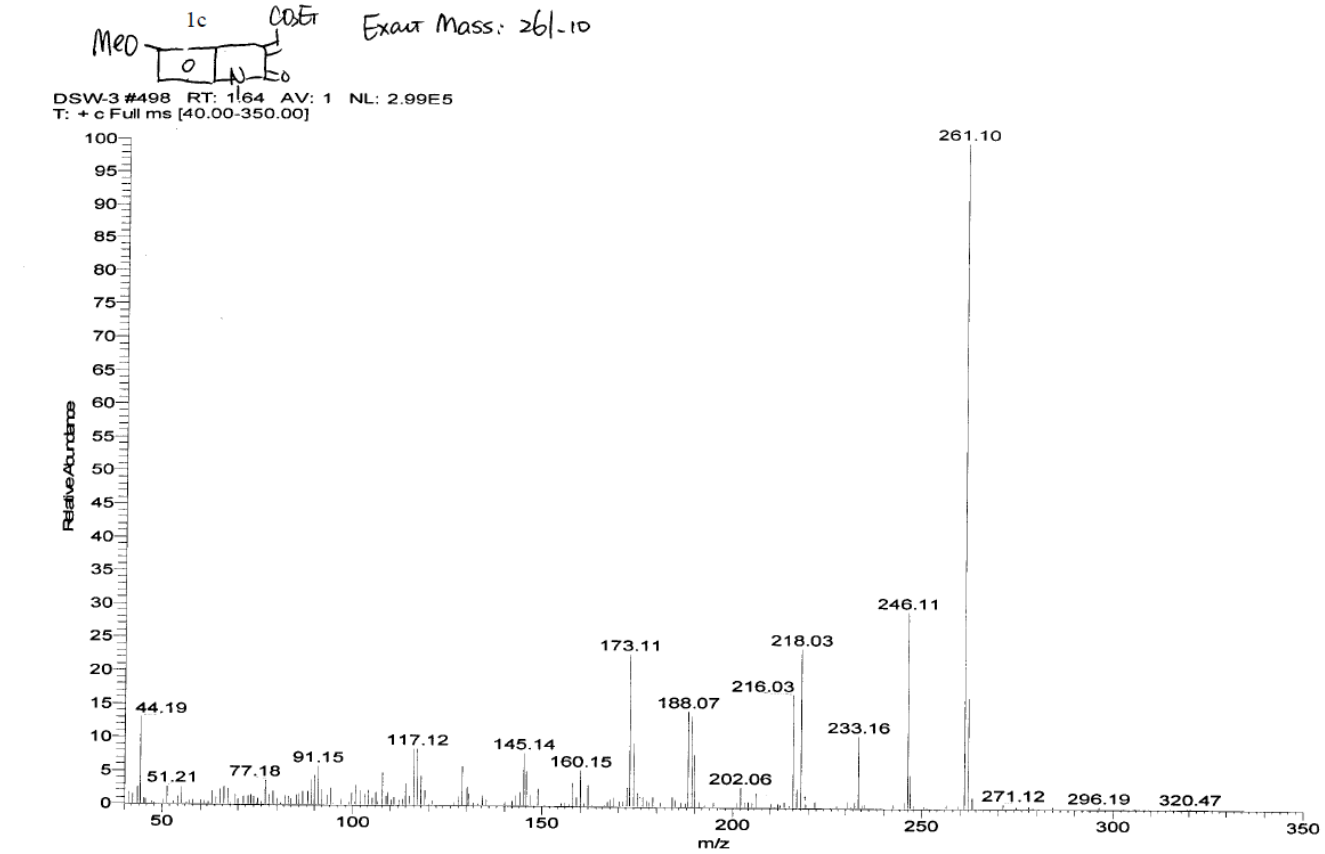
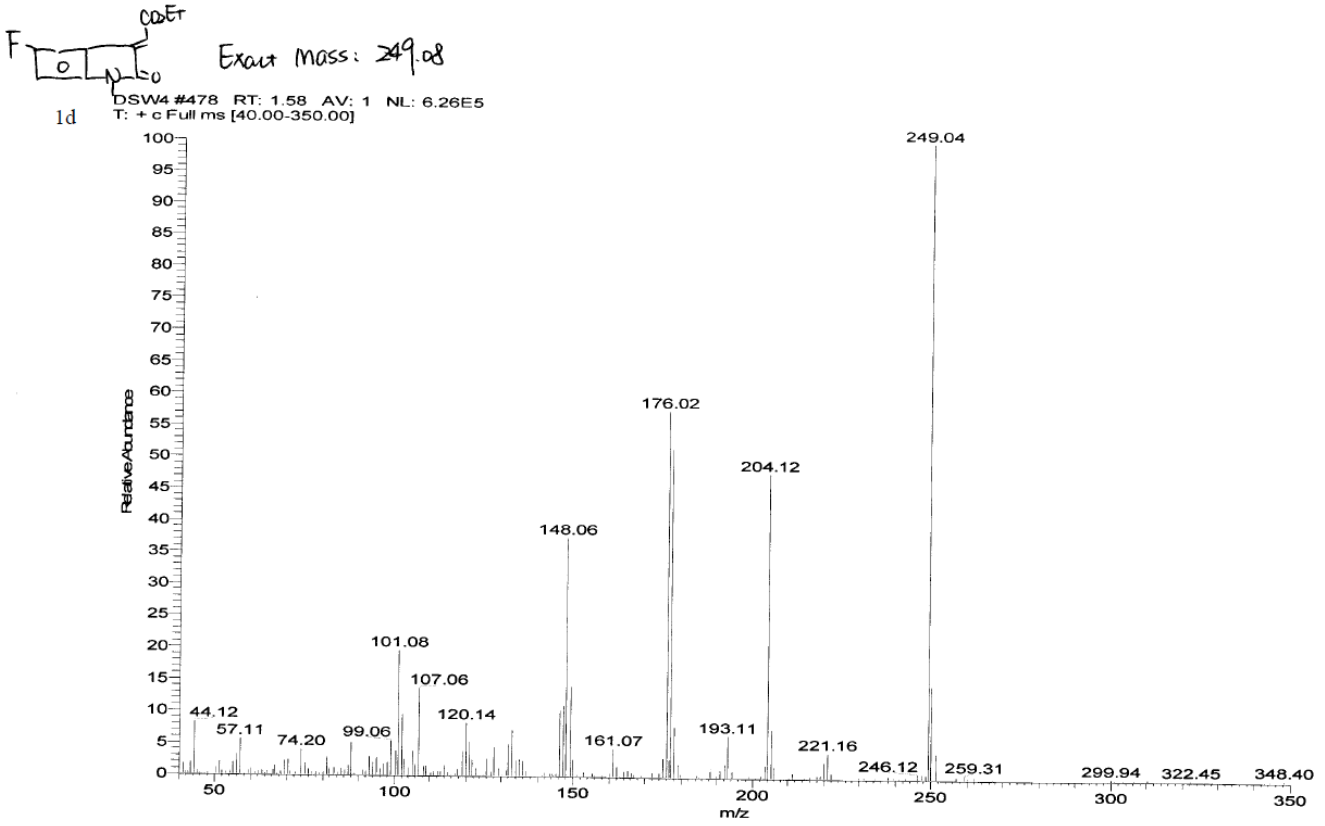
126.03
124.70
123.40
108.48
79.48
61.32
54.39
52.48
38.55
26.65
OH
O
S
N
3p

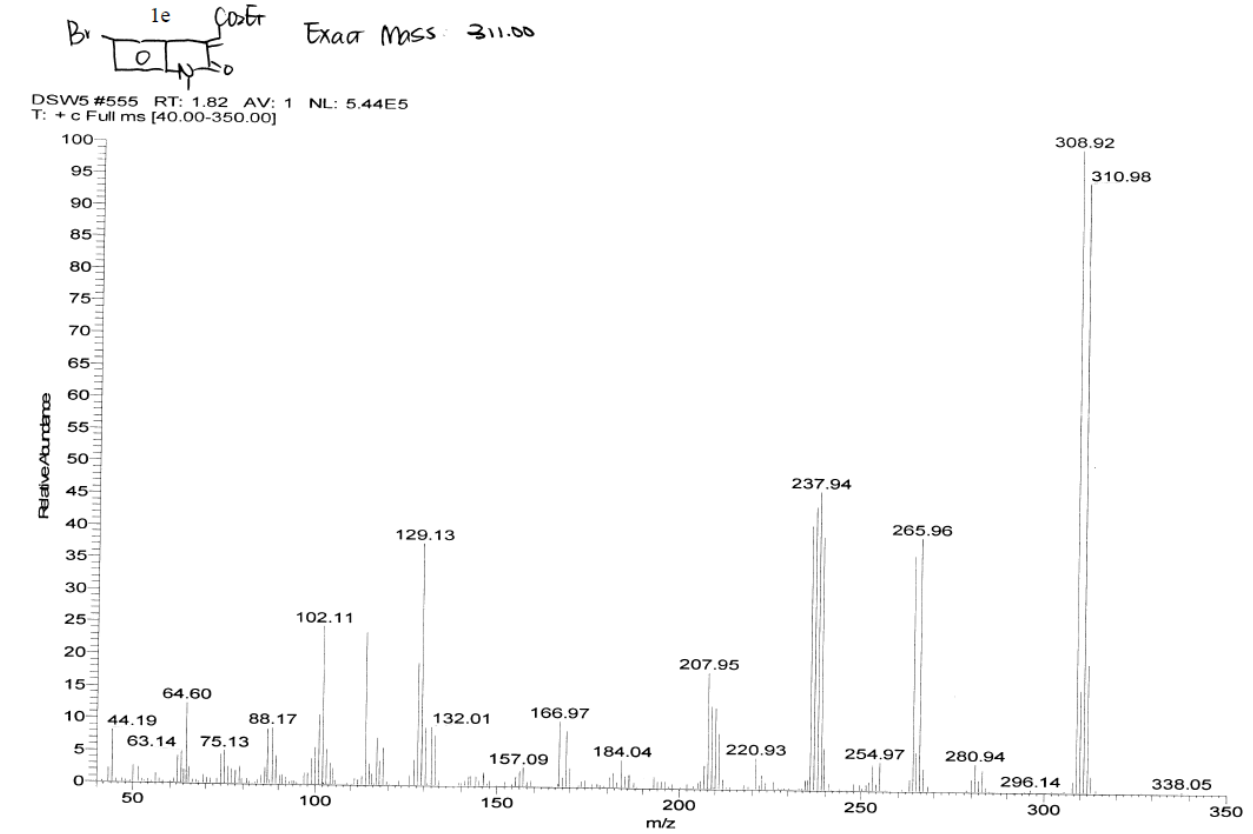
7. Copies of MS and elemental analysis Spectra






1c
MeO
CO2Et
Exact Mass: 261.10
DSW-3 #498 RT: 1.64 AV: 1 NL: 2.99E5
T: + c Full ms [40.00-350.00]
Relative Abundance
m/z
261.10
246.11
173.11
218.03
216.03
188.07
233.16
44.19
117.12
145.14
91.15
160.15
77.18
51.21
202.06
271.12
296.19
320.47


1d
F
CO2Et
Exact Mass: 249.08
DSW4 #478 RT: 1.58 AV: 1 NL: 6.26E5
T: + c Full ms [40.00-350.00]
Relative Abundance
m/z
249.04
176.02
204.12
148.06
101.08
107.06
120.14
44.12
57.11
74.20
99.06
161.07
193.11
221.16
246.12
259.31
299.94
322.45
348.40


1e
Exact Mass: 311.00
DSW5 #555 RT: 1.82 AV: 1 NL: 5.44E5
T: + c Full ms [40.00-350.00]
Relative Abundance
m/z
308.92
310.98
237.94
265.96
129.13
102.11
207.95
64.60
44.19
63.14
75.13
88.17
132.01
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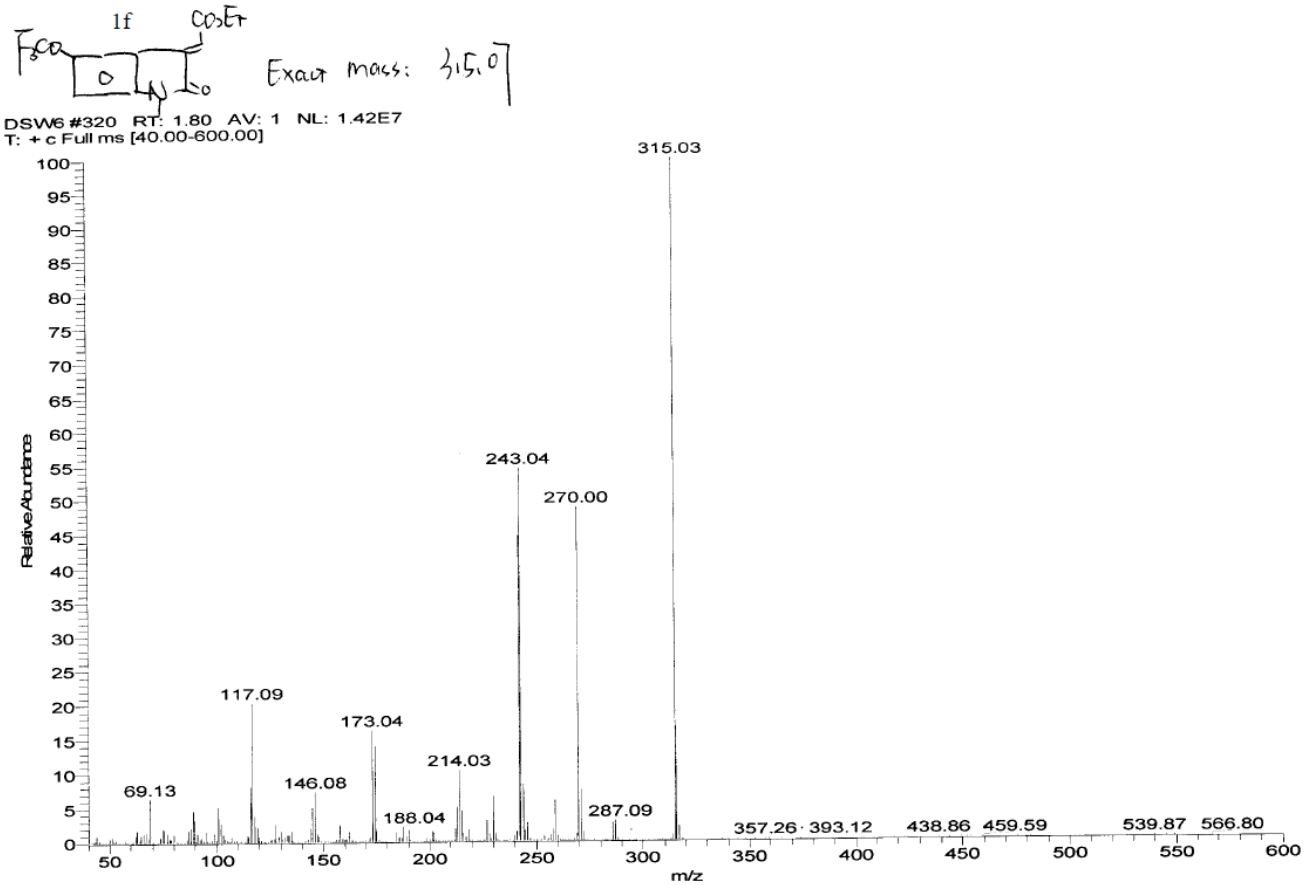
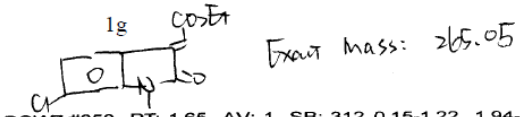
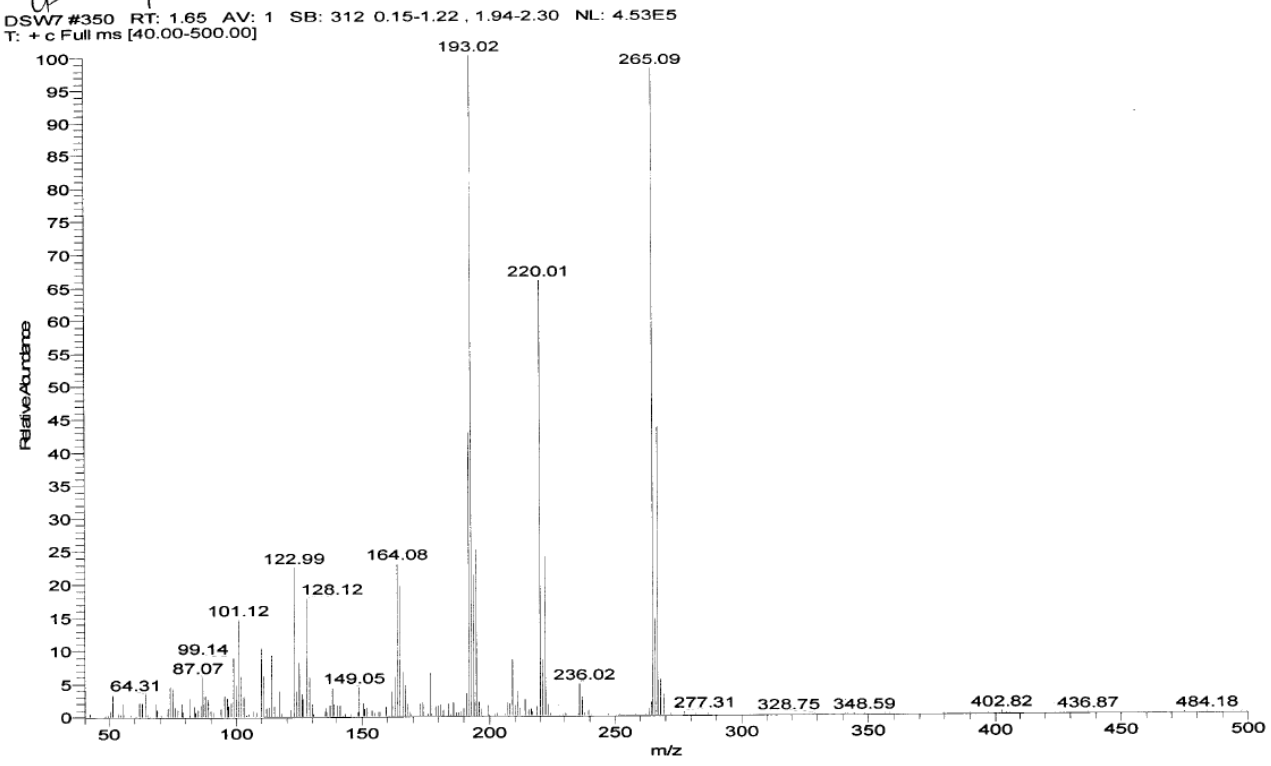
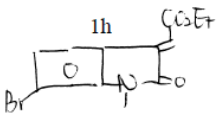
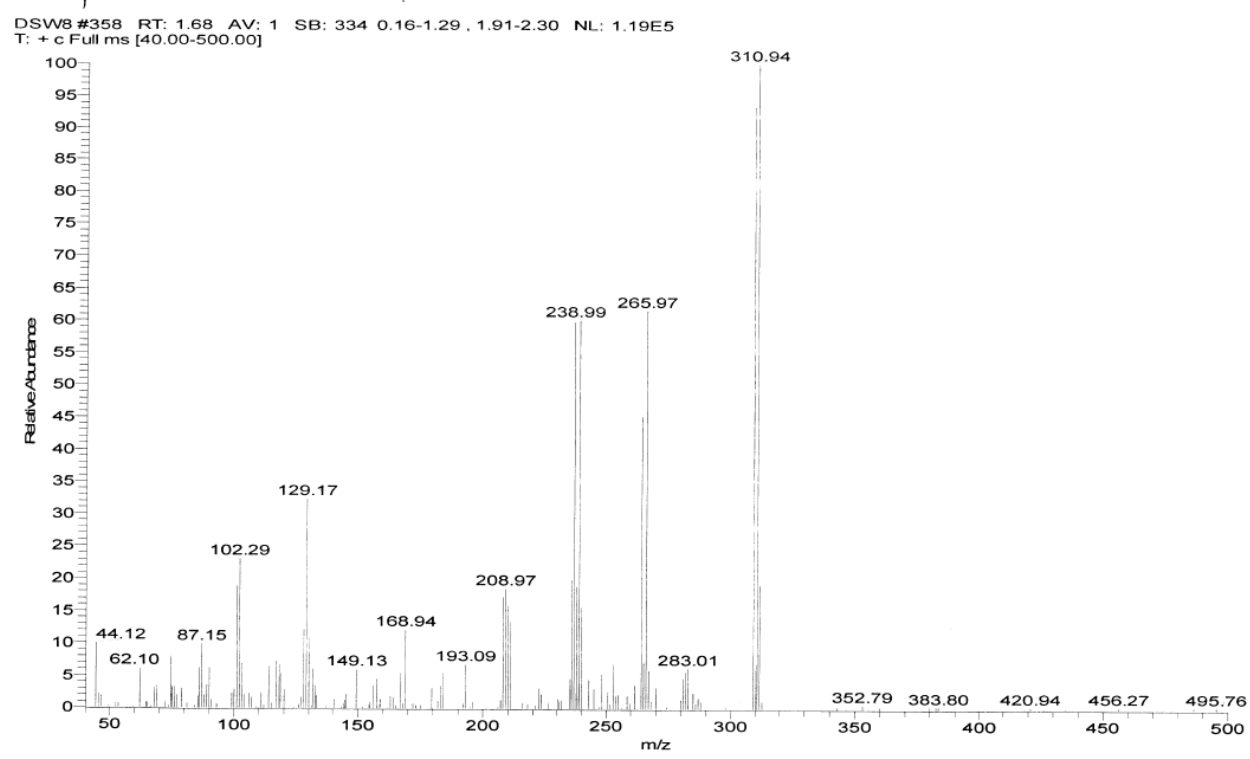
184.04
220.93
254.97
280.94
296.14
338.05

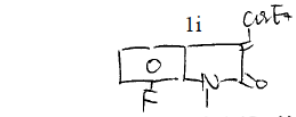

1f
Exact mass: 315.07
DSW6 #320 RT: 1.80 AV: 1 NL: 1.42E7
T: + c Full ms [40.00-600.00]
Relative Abundance
m/z
315.03
243.04
270.00
117.09
173.04
214.03
146.08
69.13
188.04
287.09
357.26
393.12
438.86
459.59
539.87
566.80


1g
CO2Et
Exact mass: 265.05

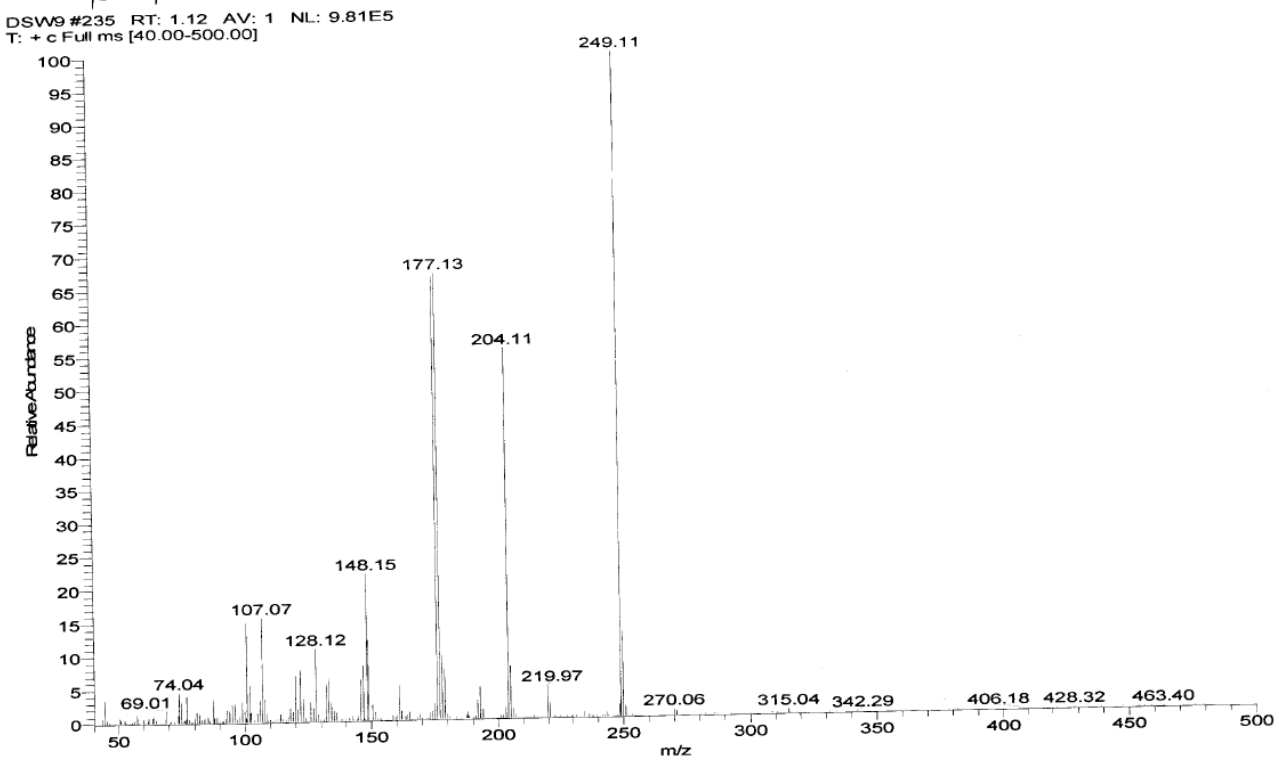

DSW7 #350 RT: 1.65 AV: 1 SB: 312 0.15-1.22 , 1.94-2.30 NL: 4.53E5
T: + c Full ms [40.00-500.00]
Relative Abundance
m/z
193.02
265.09
220.01
122.99
164.08
128.12
101.12
99.14
87.07
64.31
149.05
236.02
277.31
328.75
348.59
402.82
436.87
484.18

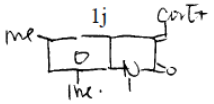

1h
CO2Et
Br
Exact mass. 311.00


DSW8 #358 RT: 1.68 AV: 1 SB: 334 0.16-1.29 , 1.91-2.30 NL: 1.19E5
T: + c Full ms [40.00-500.00]
Relative Abundance
m/z
310.94
238.99
265.97
129.17
102.29
208.97
168.94
44.12
87.15
62.10
149.13
193.09
283.01
352.79
383.80
420.94
456.27
495.76

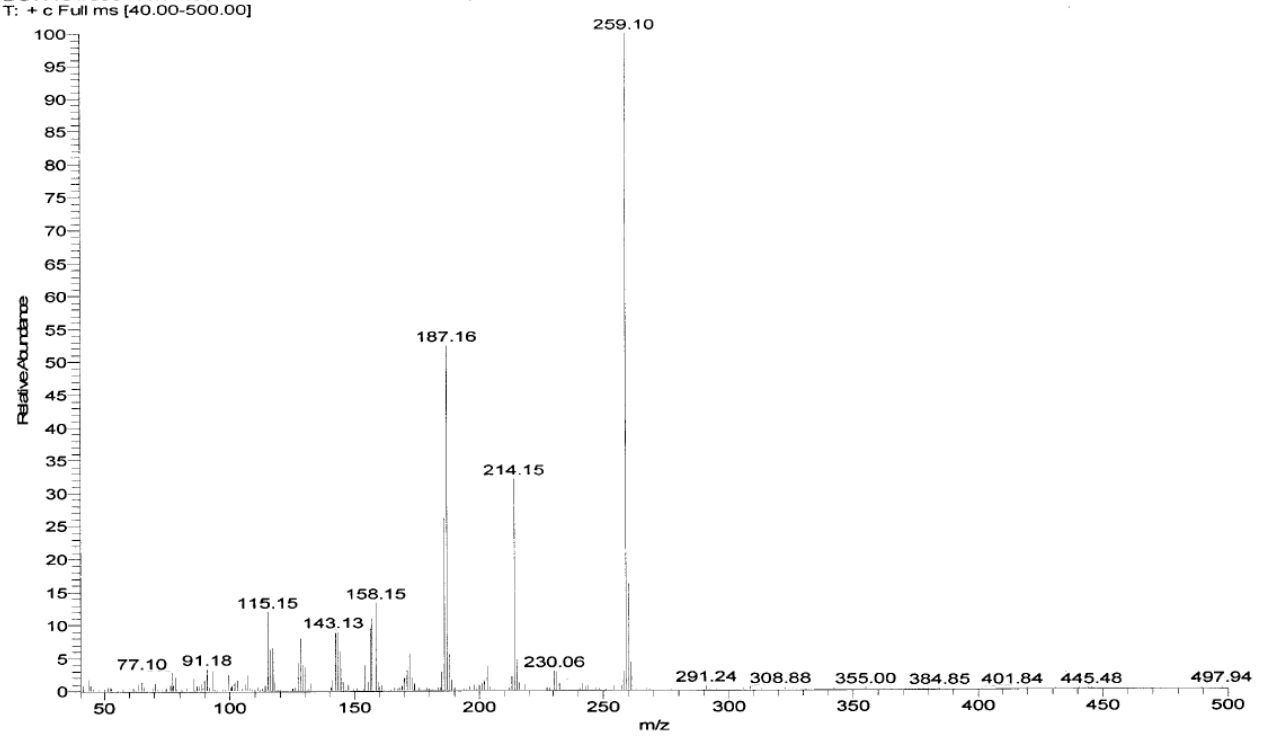


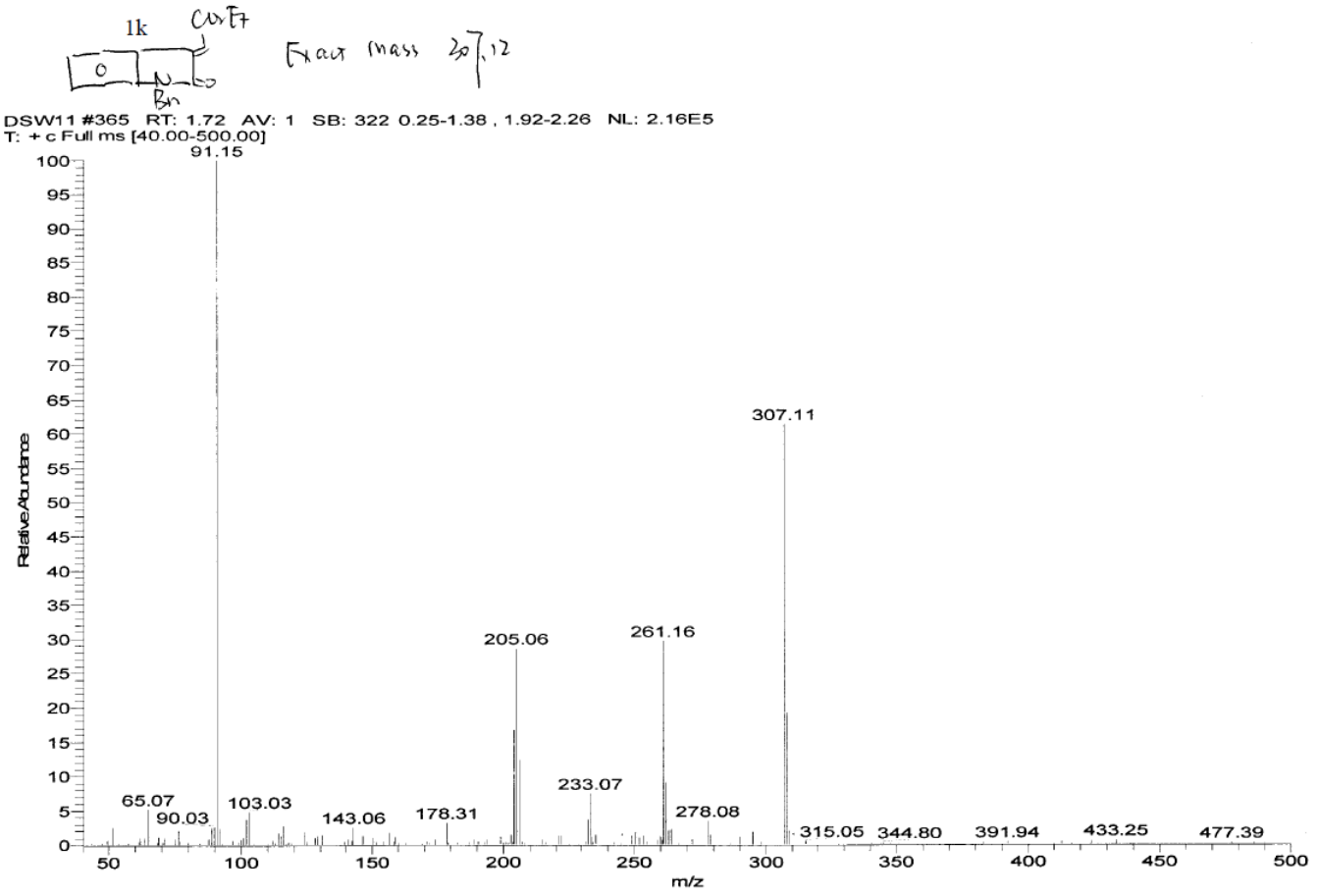
Exact mass 249.08

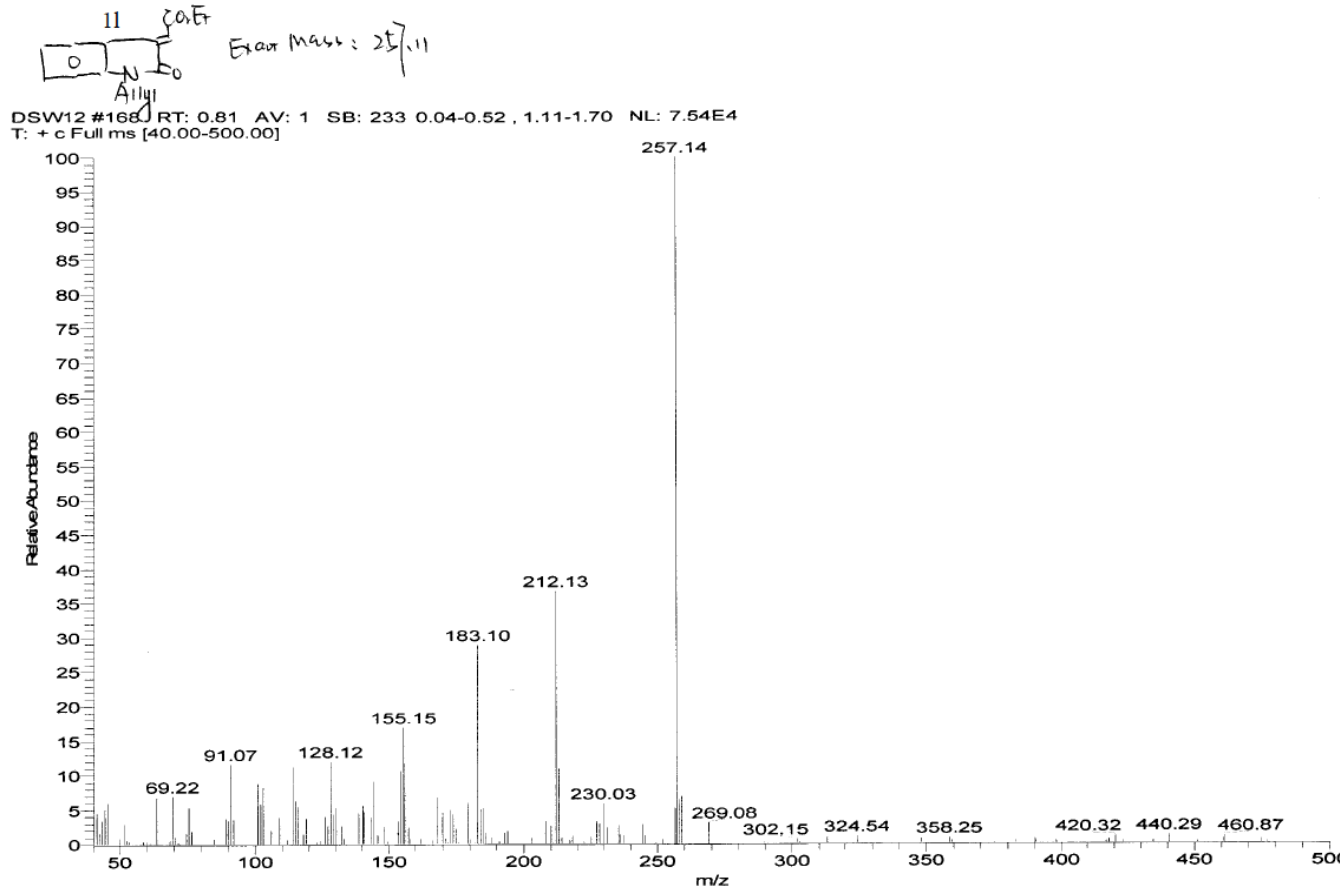


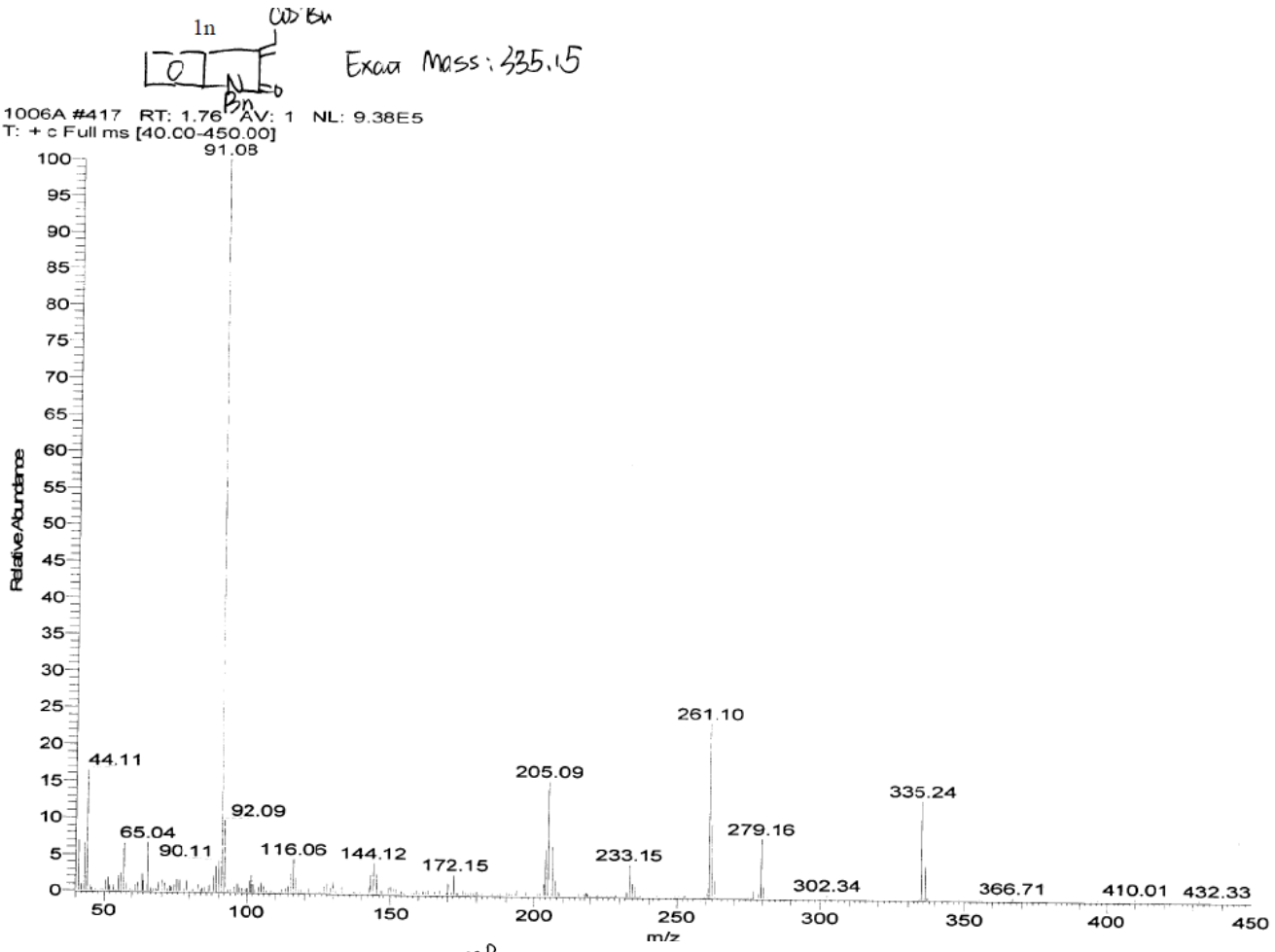


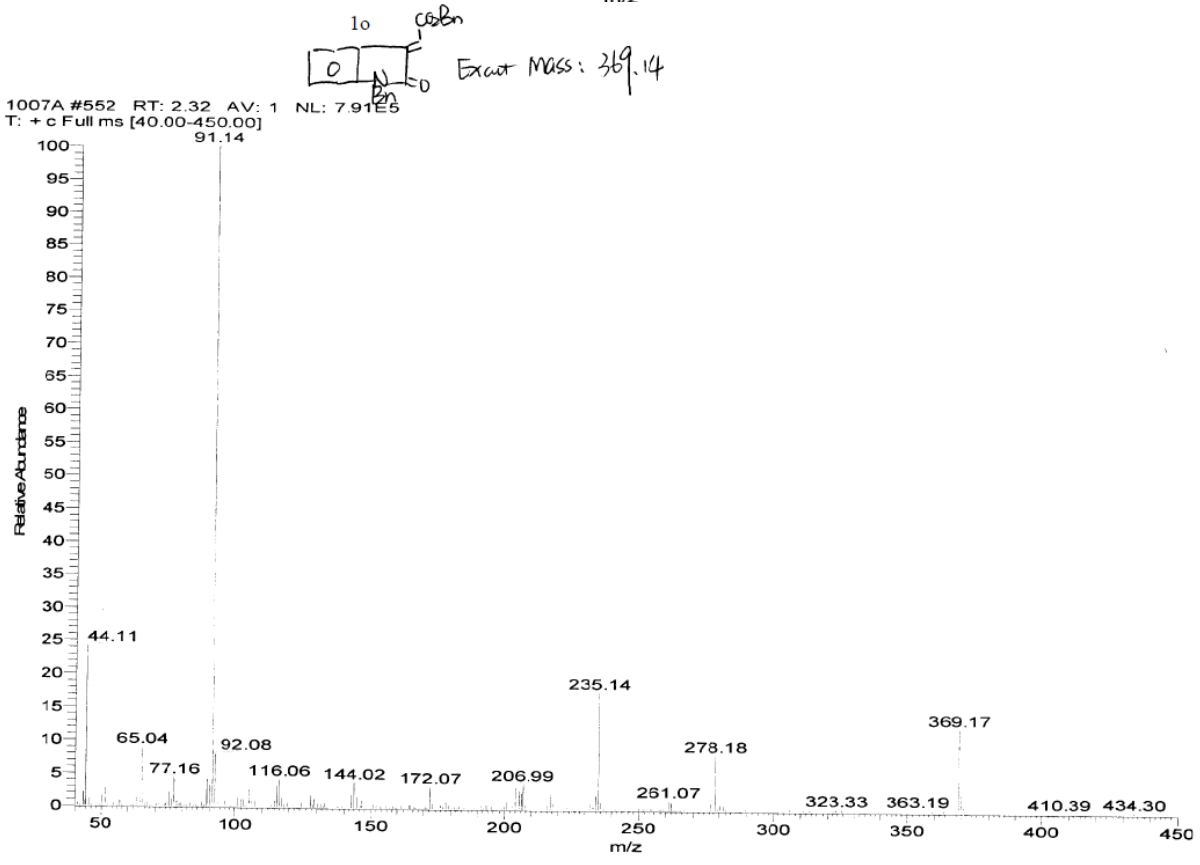
Exact mass: 259.12

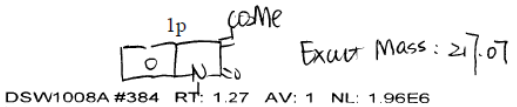



1k
CO2Et
Bn
Exact mass 307.12
DSW11 #365 RT: 1.72 AV: 1 SB: 322 0.25-1.38 , 1.92-2.26 NL: 2.16E5
T: + c Full ms [40.00-500.00]
Relative Abundance
m/z
91.15
307.11
205.06
261.16
233.07
65.07
90.03
103.03
143.06
178.31
278.08
315.05
344.80
391.94
433.25
477.39

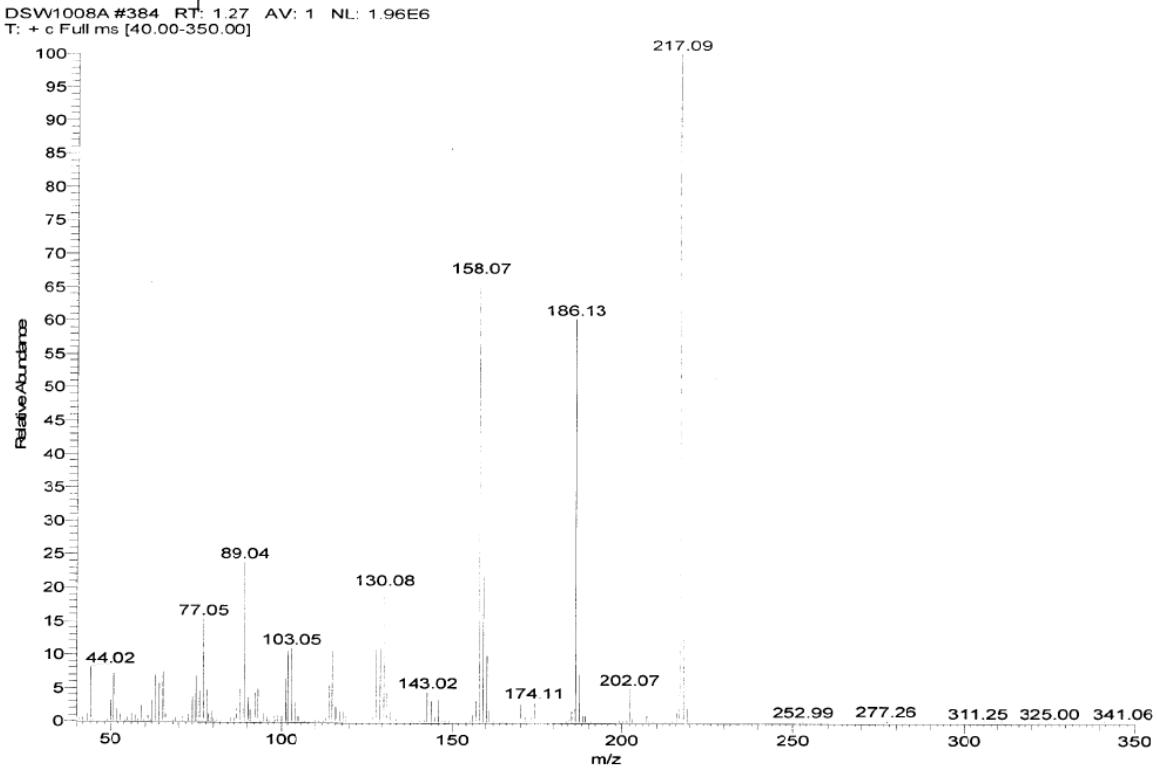

11
CO2Et
Allyl
Exact mass : 257.11
DSW12 #168 RT: 0.81 AV: 1 SB: 233 0.04-0.52 , 1.11-1.70 NL: 7.54E4
T: + c Full ms [40.00-500.00]
Relative Abundance
m/z
257.14
212.13
183.10
155.15
91.07
128.12
69.22
230.03
269.08
302.15
324.54
358.25
420.32
440.29
460.87

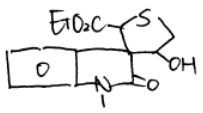

1n
Exact Mass: 335.15
1006A #417 RT: 1.76 AV: 1 NL: 9.38E5
T: + c Full ms [40.00-450.00]
Relative Abundance
m/z
91.08
44.11
65.04
90.11
92.09
116.06
144.12
172.15
205.09
233.15
261.10
279.16
302.34
335.24
366.71
410.01
432.33


1o
Exact Mass: 369.14
1007A #552 RT: 2.32 AV: 1 NL: 7.91E5
T: + c Full ms [40.00-450.00]
Relative Abundance
m/z
91.14
44.11
65.04
77.16
92.08
116.06
144.02
172.07
206.99
235.14
261.07
278.18
323.33
363.19
369.17
410.39
434.30

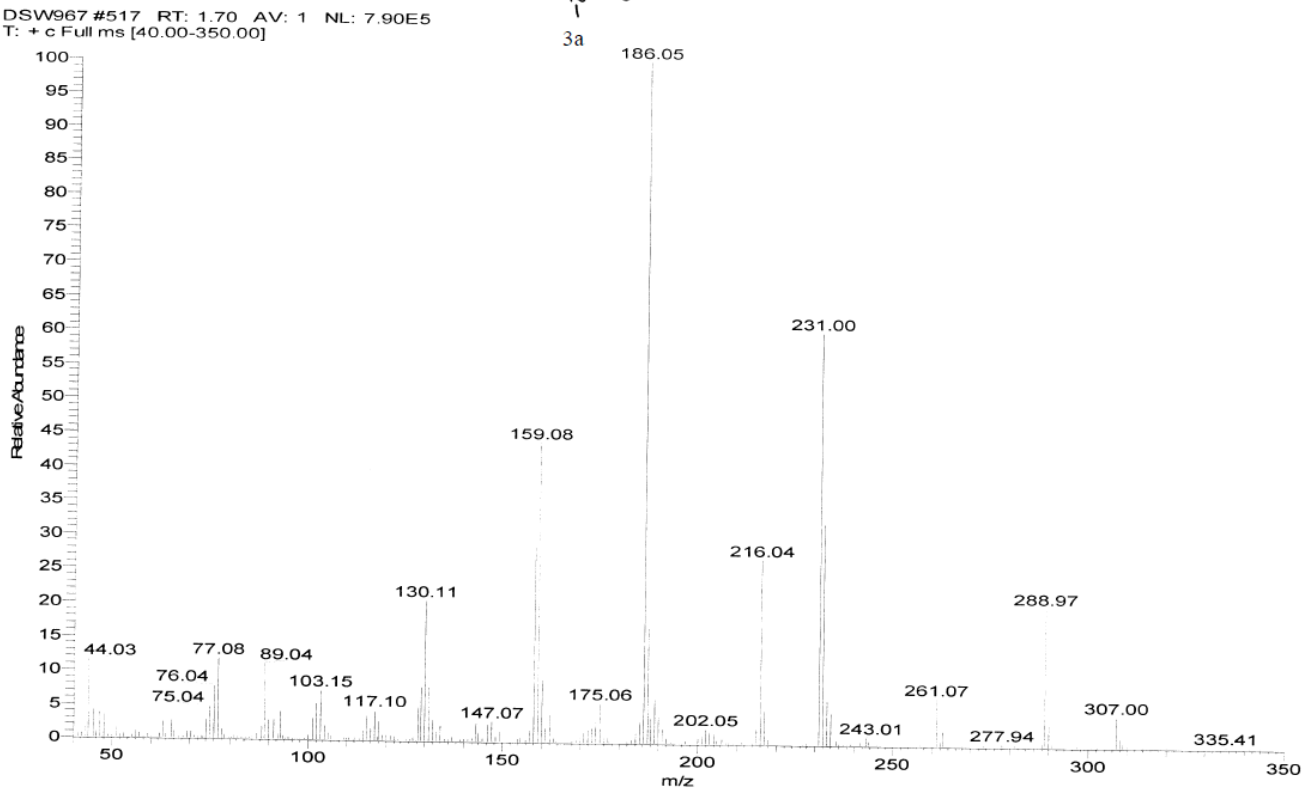


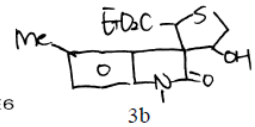
Exact Mass: 217.07





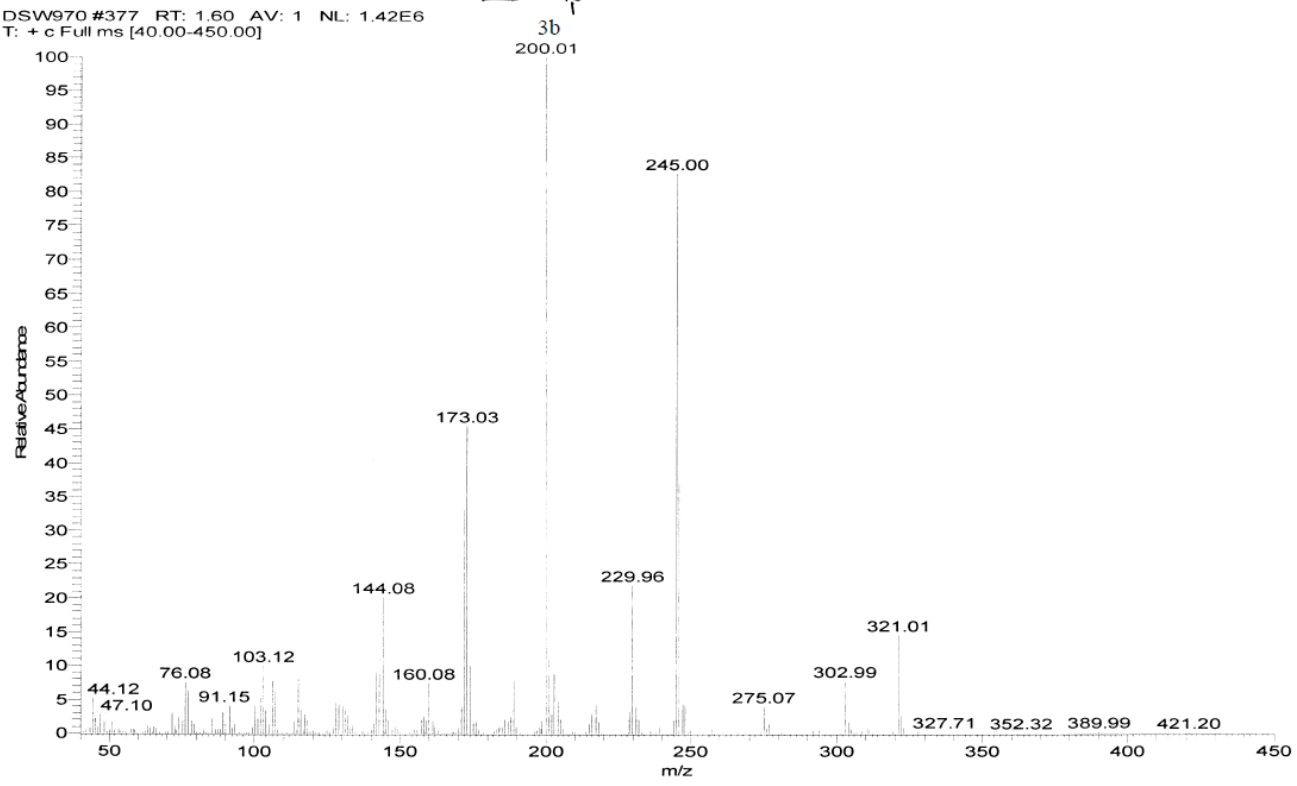
Exact Mass: 307.09

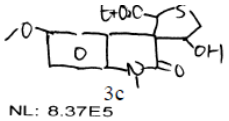




Exact Mass 321.10

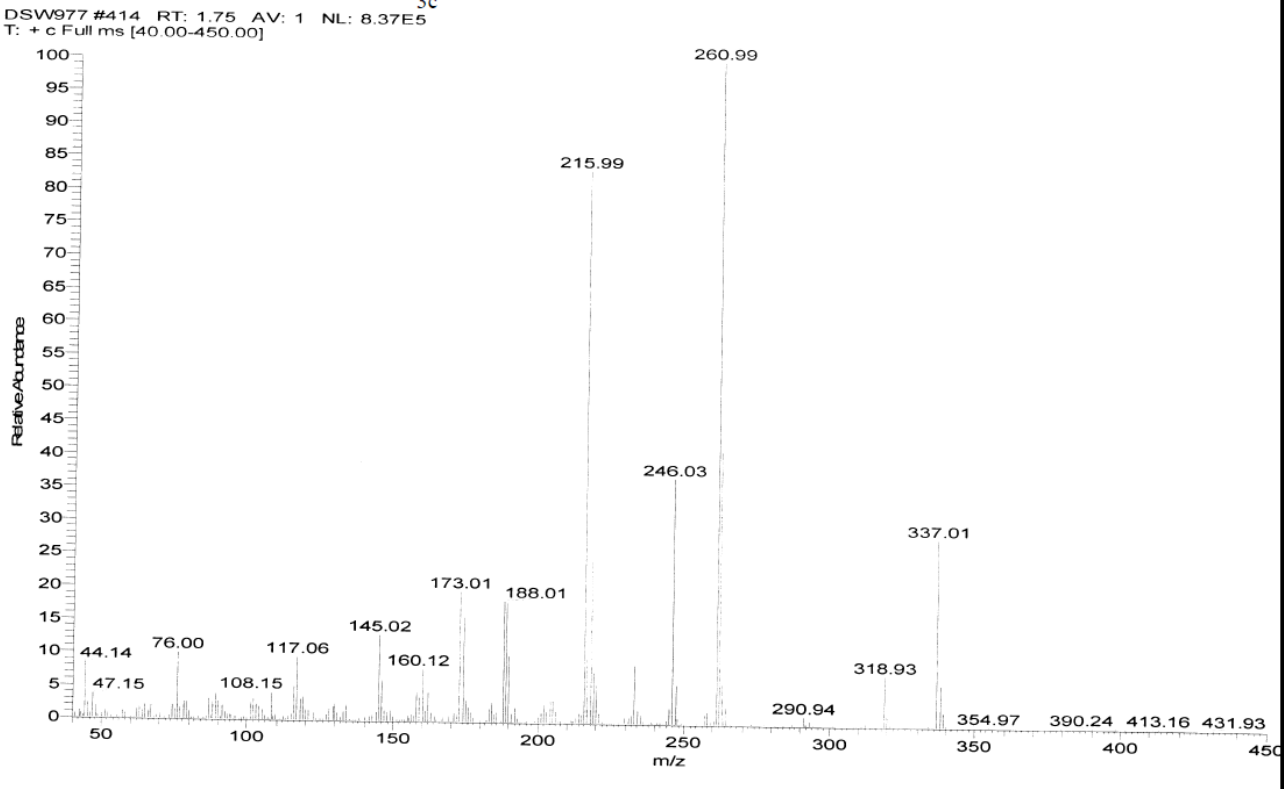
3b

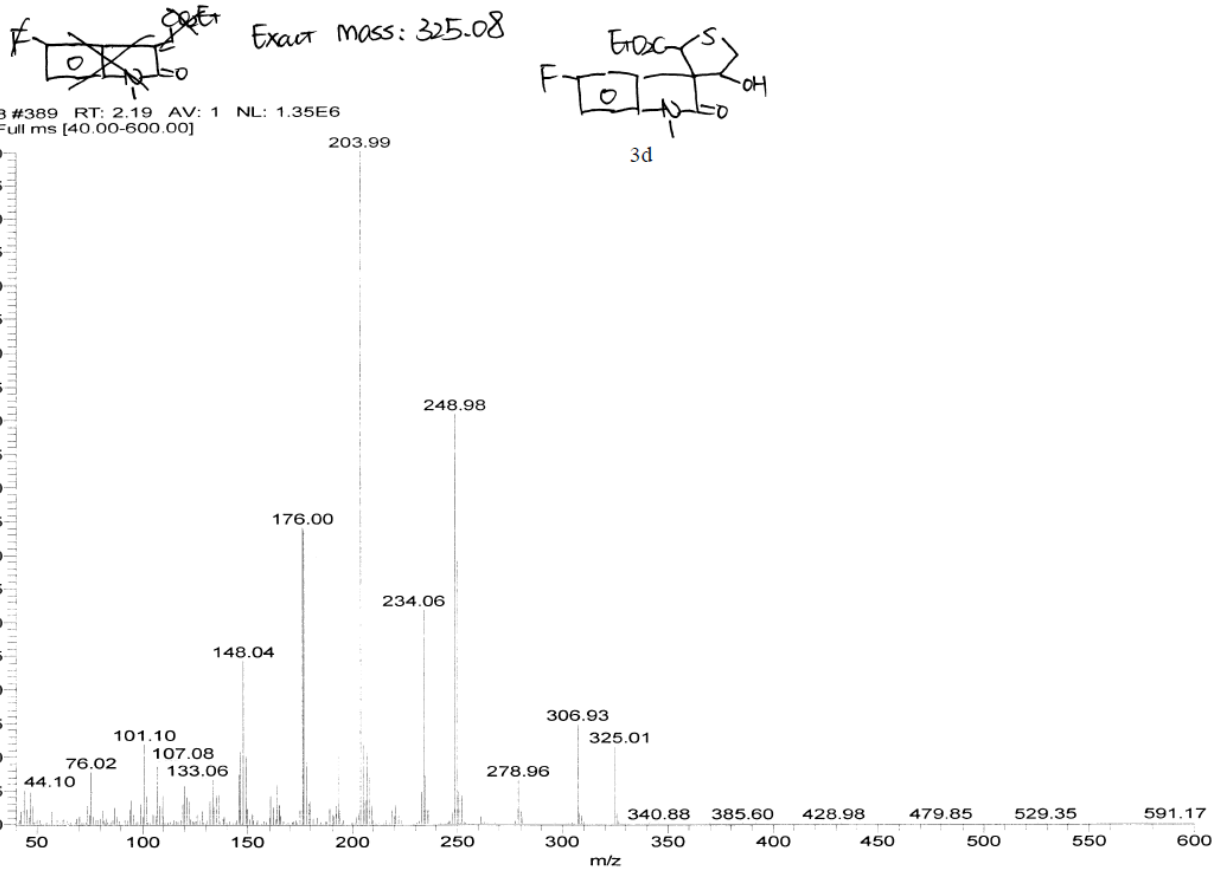


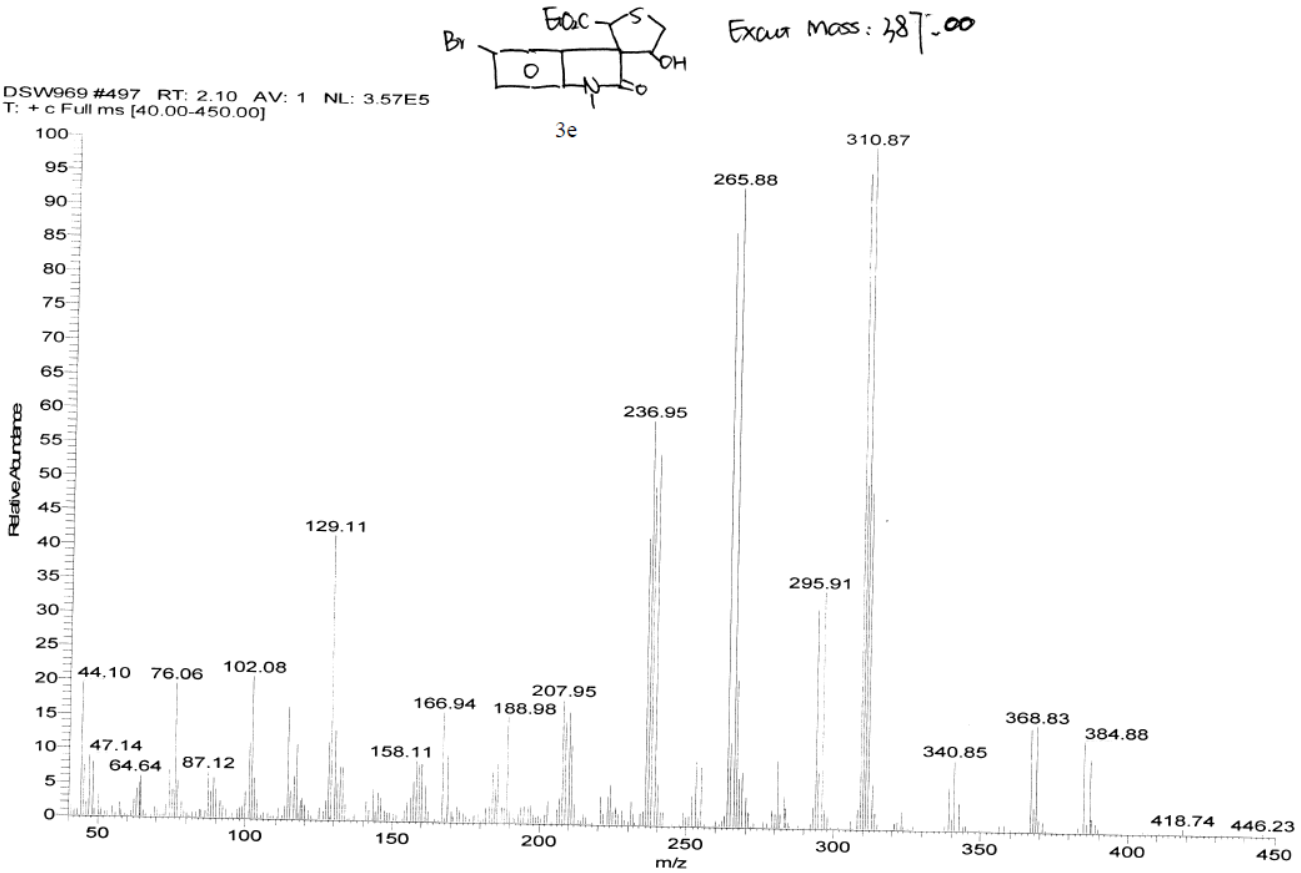


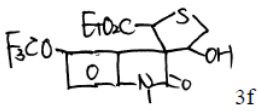
Exact Mass : 337.10

3c




Exact mass: 325.08
3d
DW968 #389 RT: 2.19 AV: 1 NL: 1.35E6
T: + c Full ms [40.00-600.00]
RelativeAbundance
m/z
203.99
248.98
176.00
234.06
148.04
306.93
325.01
101.10
107.08
76.02
133.06
44.10
278.96
340.88
385.60
428.98
479.85
529.35
591.17

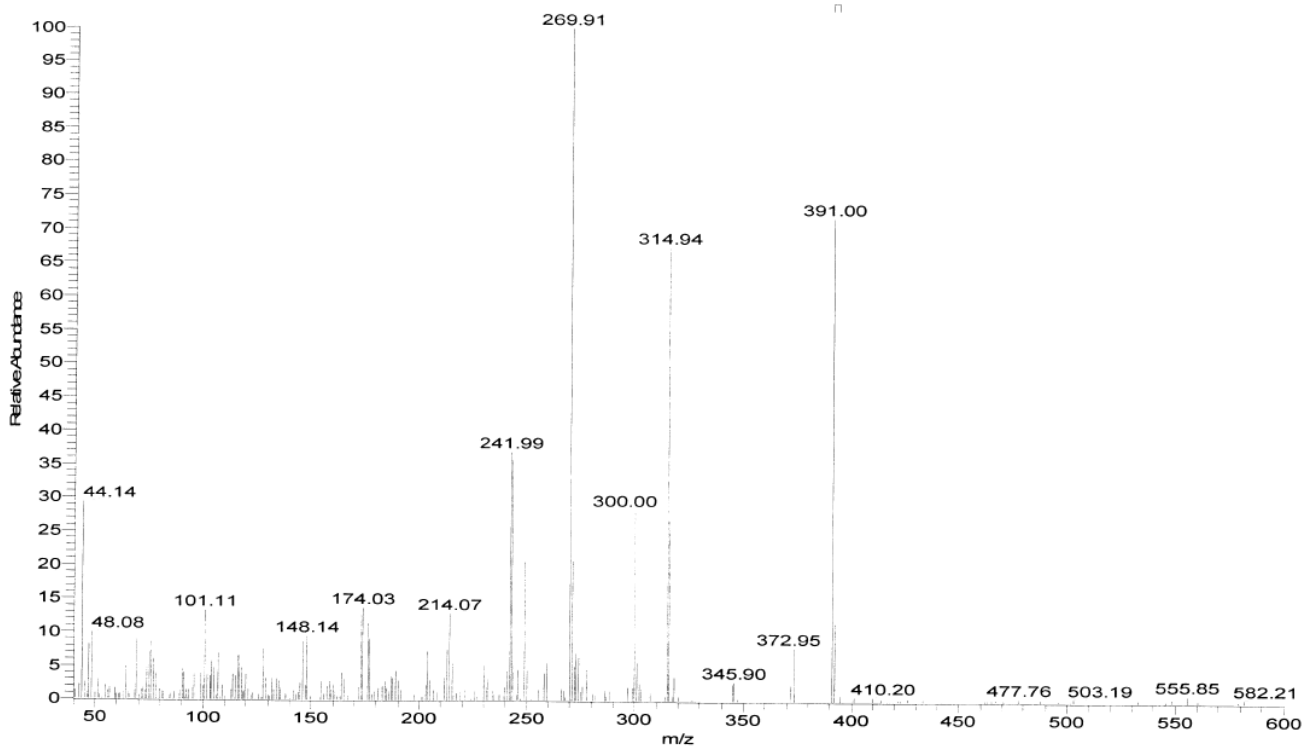

Exact mass: 387.00
3e
DSW969 #497 RT: 2.10 AV: 1 NL: 3.57E5
T: + c Full ms [40.00-450.00]
RelativeAbundance
m/z
310.87
265.88
236.95
129.11
295.91
44.10
76.06
102.08
207.95
166.94
188.98
47.14
64.64
87.12
158.11
340.85
368.83
384.88
418.74
446.23

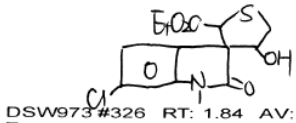


Exact mass: 391.07

3f

DSW975 #254 RT: 1.44 AV: 1 NL: 1.41E5
T: + c Full ms [40.00-600.00]

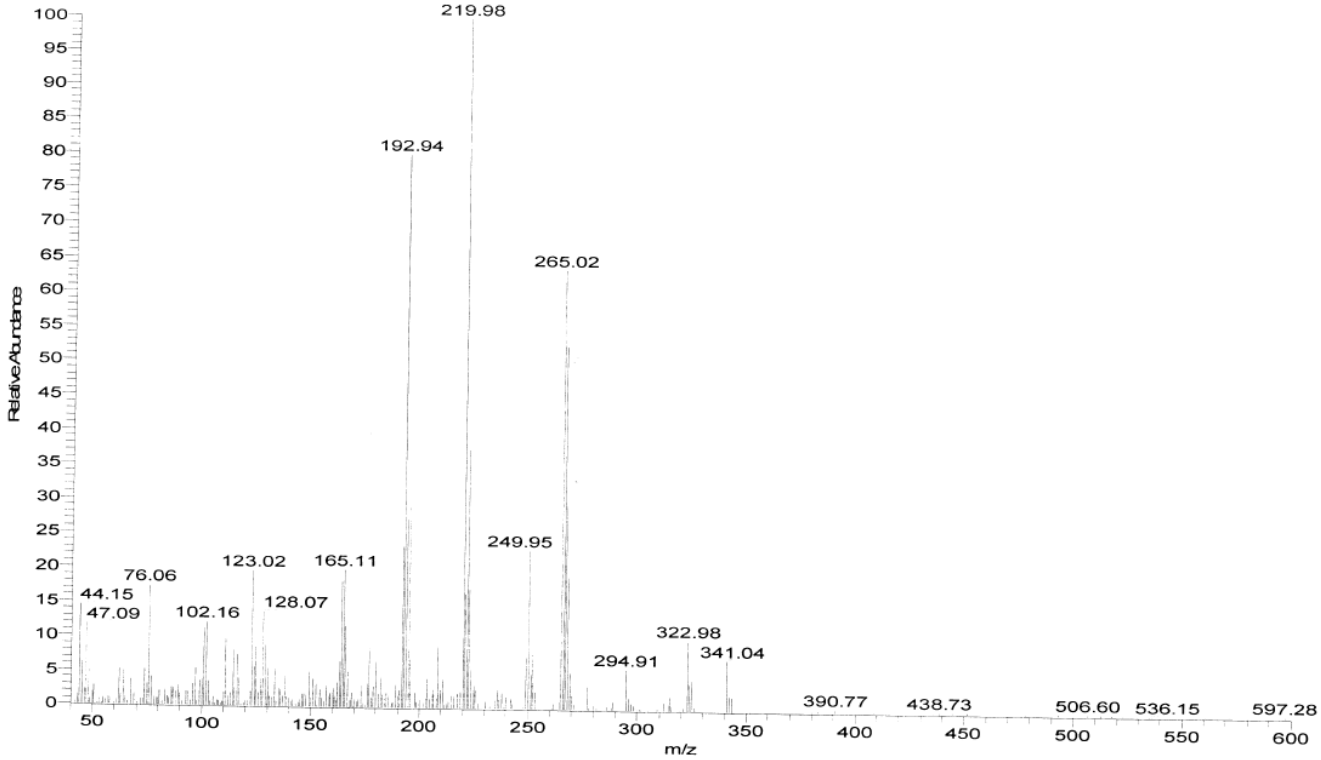


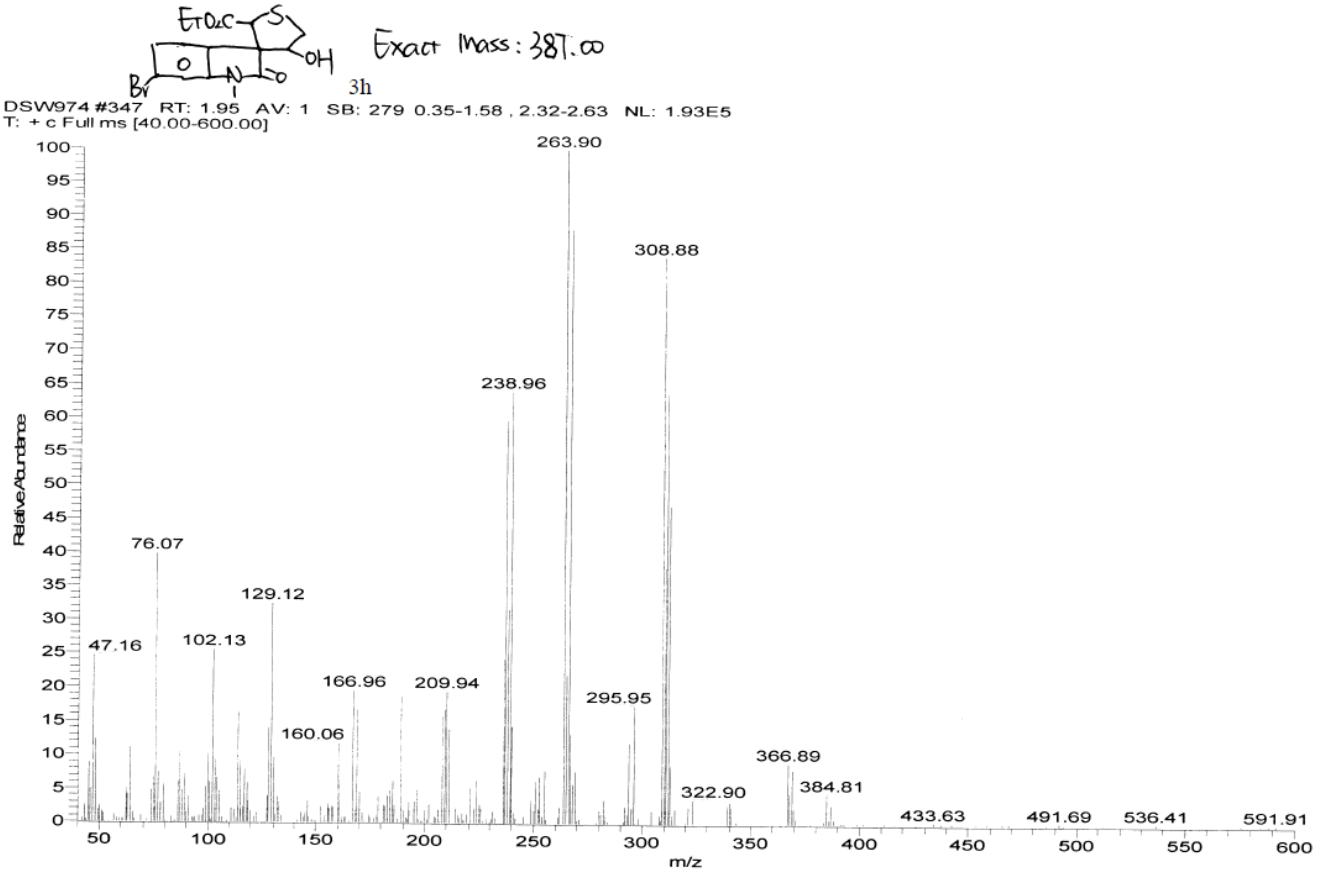


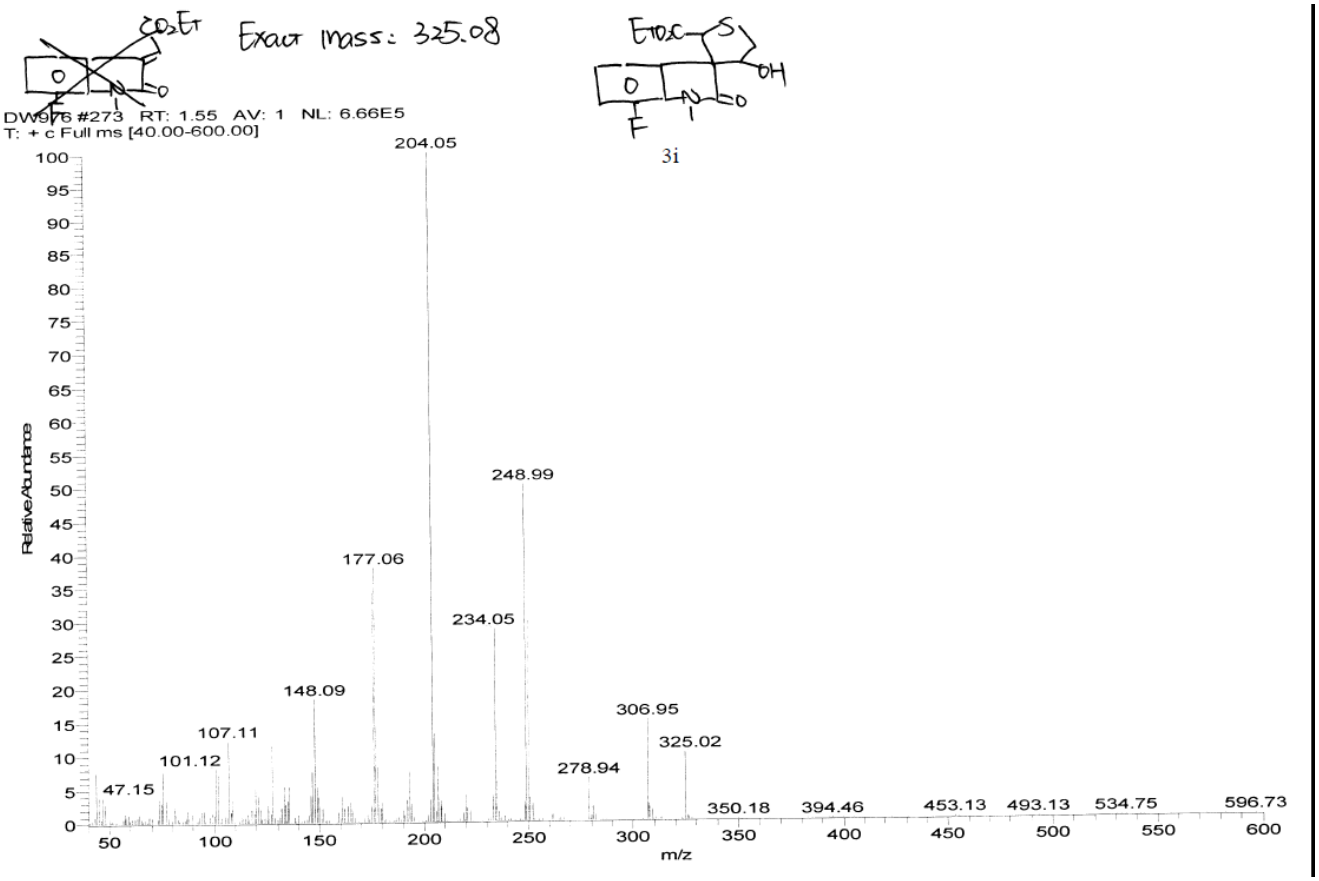
Exact mass: 341.05

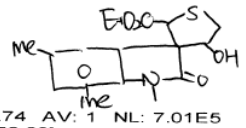
3g

DSW973 #326 RT: 1.84 AV: 1 NL: 3.30E5
T: + c Full ms [40.00-600.00]



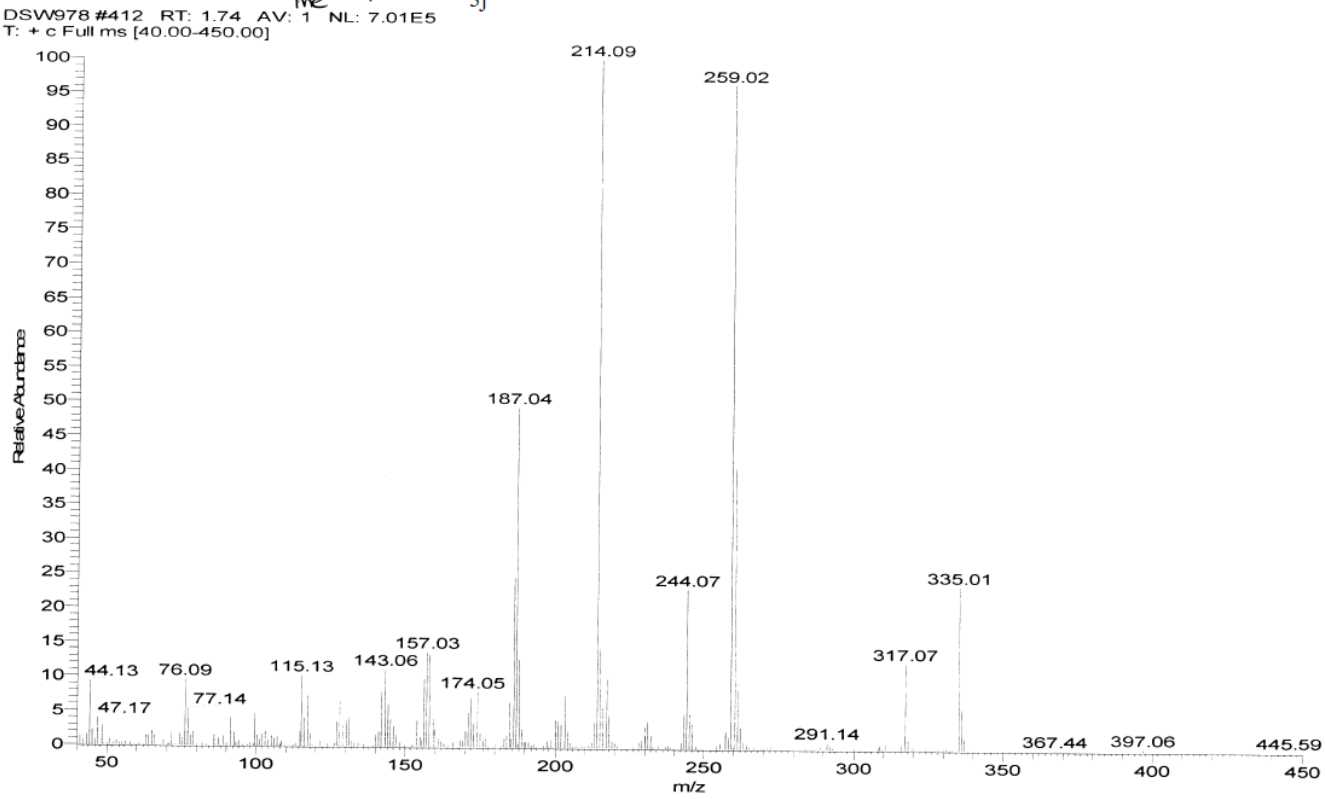

Exact Mass: 387.00
3h
DSW974 #347 RT: 1.95 AV: 1 SB: 279 0.35-1.58 , 2.32-2.63 NL: 1.93E5
T: + c Full ms [40.00-600.00]
Relative Abundance
m/z
263.90
308.88
238.96
76.07
129.12
47.16
102.13
166.96
209.94
295.95
160.06
366.89
322.90
384.81
433.63
491.69
536.41
591.91

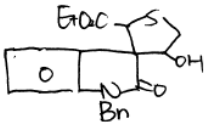

Exact mass: 325.08
3i
DW976 #273 RT: 1.55 AV: 1 NL: 6.66E5
T: + c Full ms [40.00-600.00]
Relative Abundance
m/z
204.05
248.99
177.06
234.05
148.09
306.95
325.02
107.11
101.12
278.94
47.15
350.18
394.46
453.13
493.13
534.75
596.73



Exact Mass: 335.12

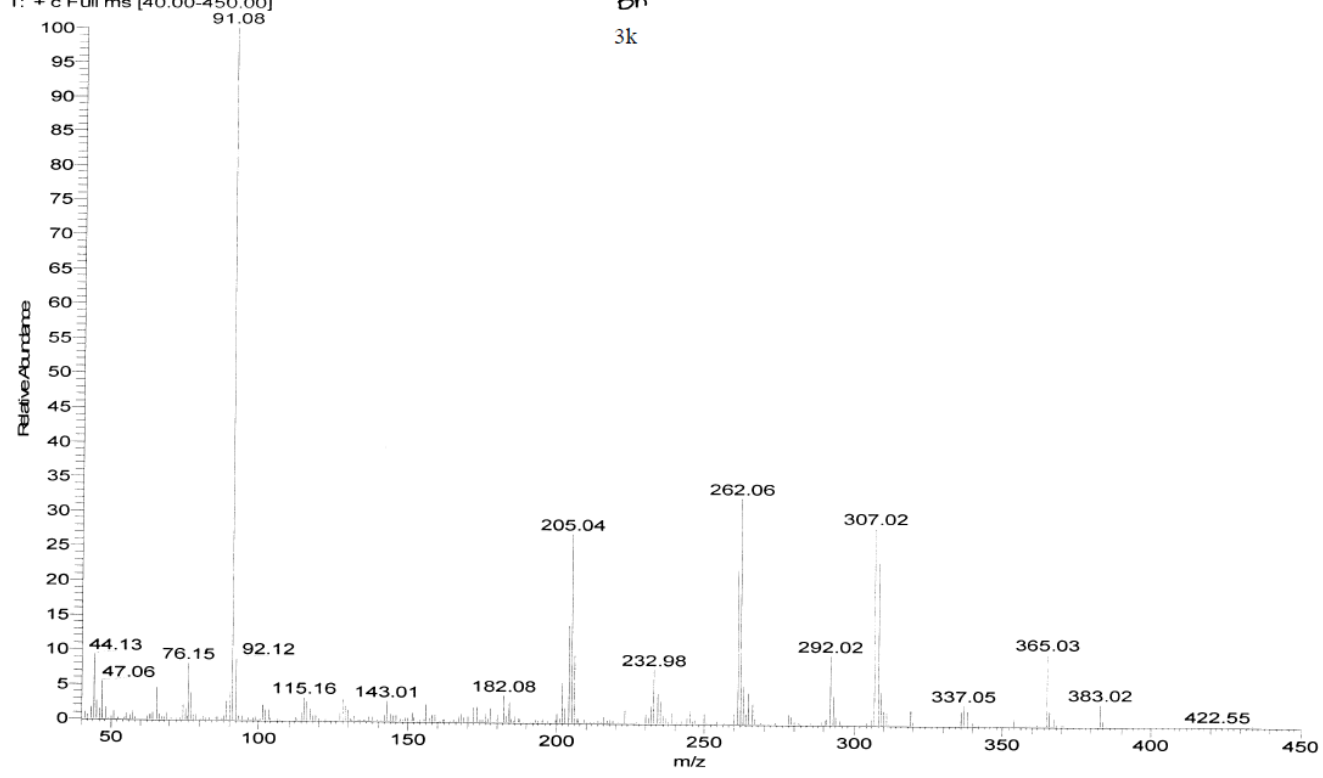
3j

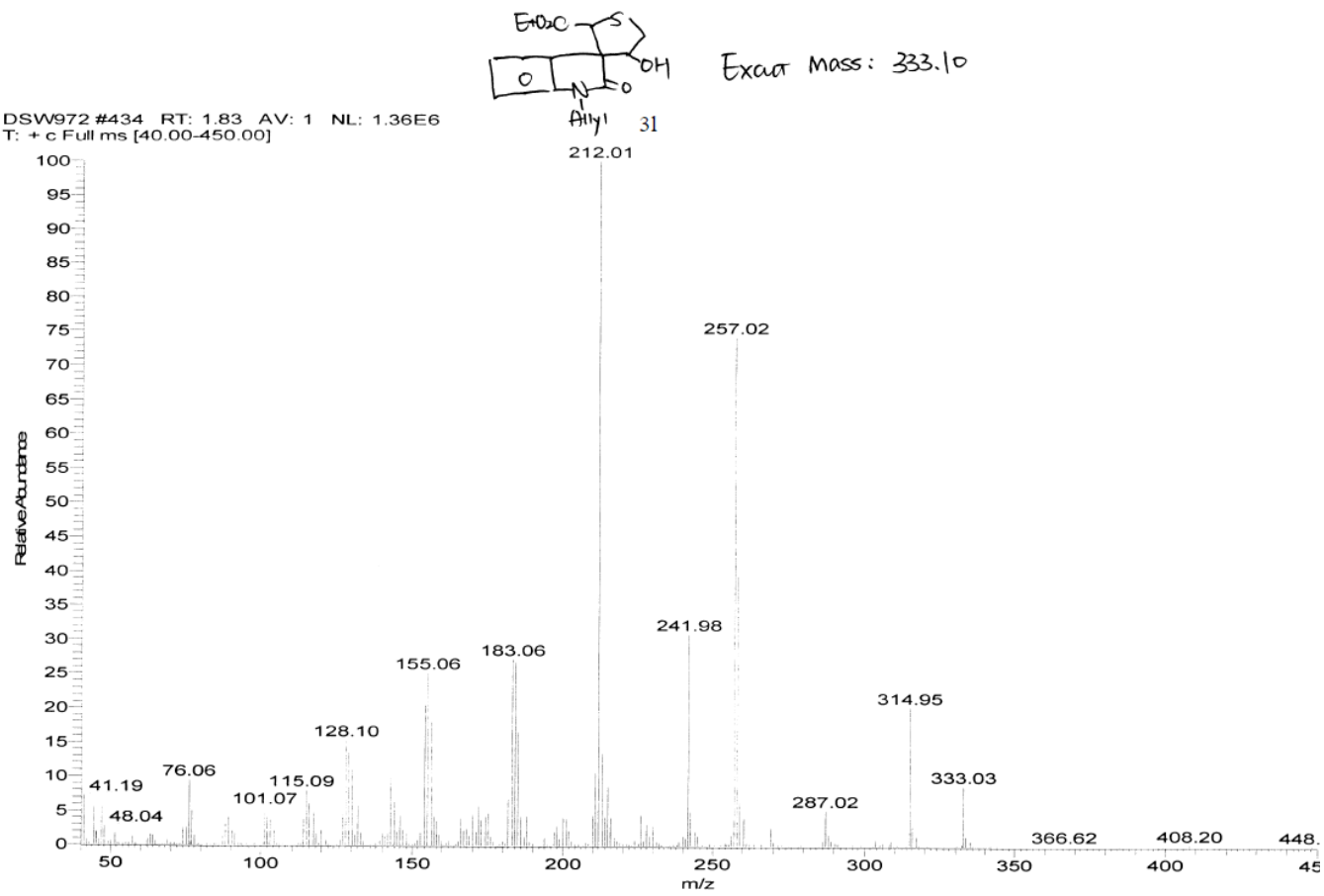


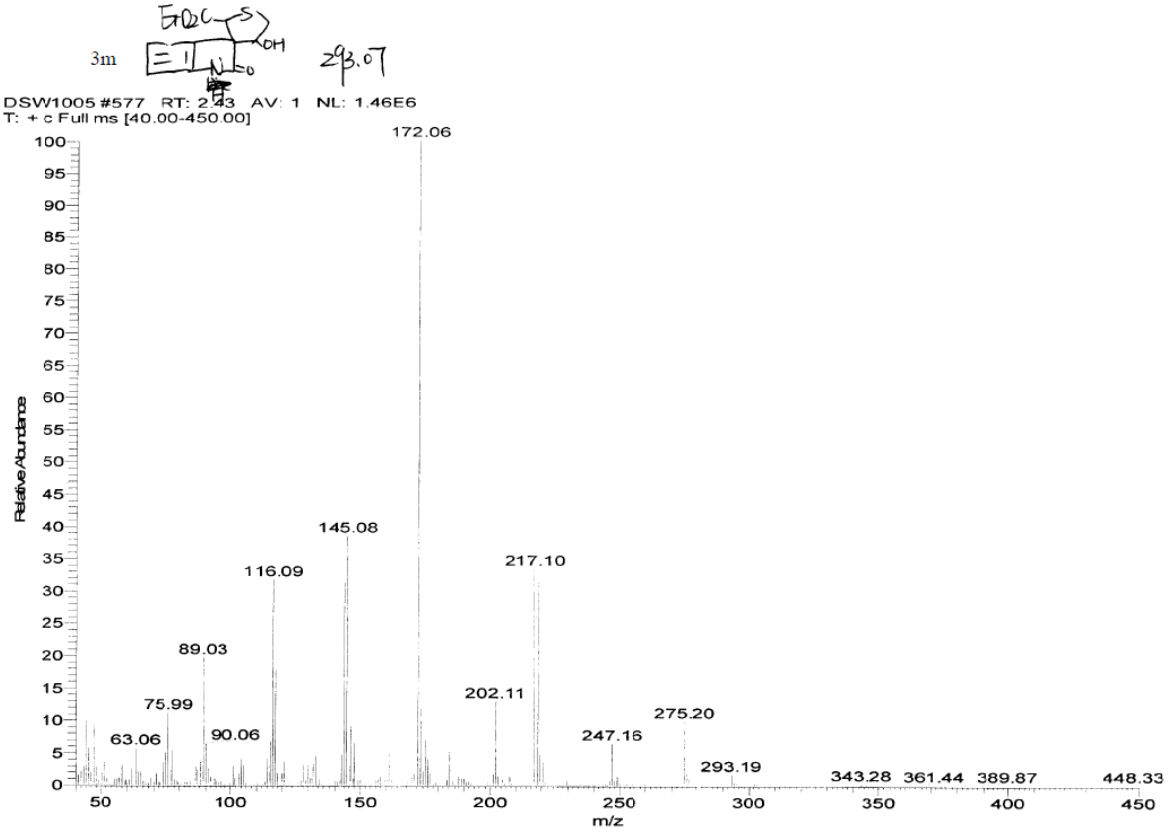


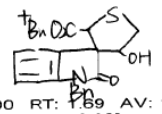
Exact Mass: 383.12

3k



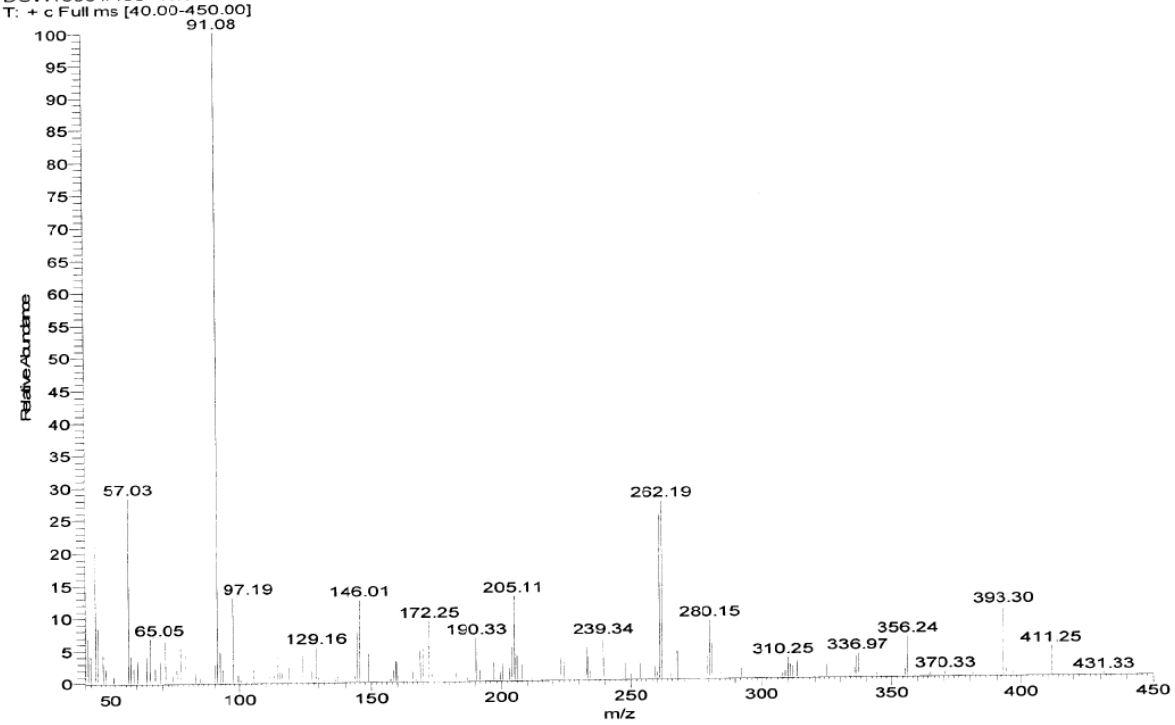

EtO2C
S
OH
O
N
O
Allyl
31
Exact mass: 333.10
DSW972 #434 RT: 1.83 AV: 1 NL: 1.36E6
T: + c Full ms [40.00-450.00]
Relative Abundance
m/z
212.01
257.02
241.98
183.06
155.06
314.95
128.10
333.03
76.06
115.09
41.19
101.07
48.04
287.02
366.62
408.20
448.

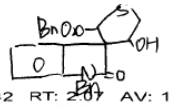

EtO2C
S
OH
N
O
3m
293.07
DSW1005 #577 RT: 2.43 AV: 1 NL: 1.46E6
T: + c Full ms [40.00-450.00]
Relative Abundance
m/z
172.06
145.08
116.09
217.10
89.03
202.11
75.99
275.20
63.06
90.06
247.16
293.19
343.28
361.44
389.87
448.33

3n 

411.15

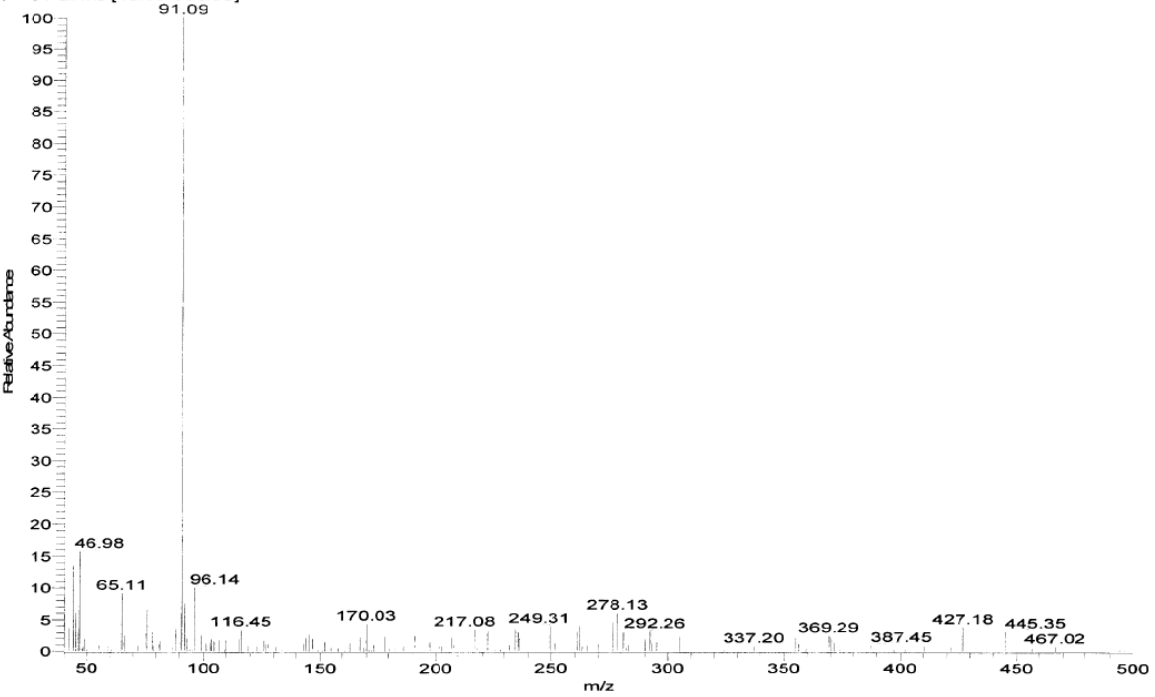
DSW1006 #400 RT: 1.69 AV: 1 SB: 447 0.04-1.69 , 2.44-2.63 NL: 6.79E4
T: + c Full ms [40.00-450.00]

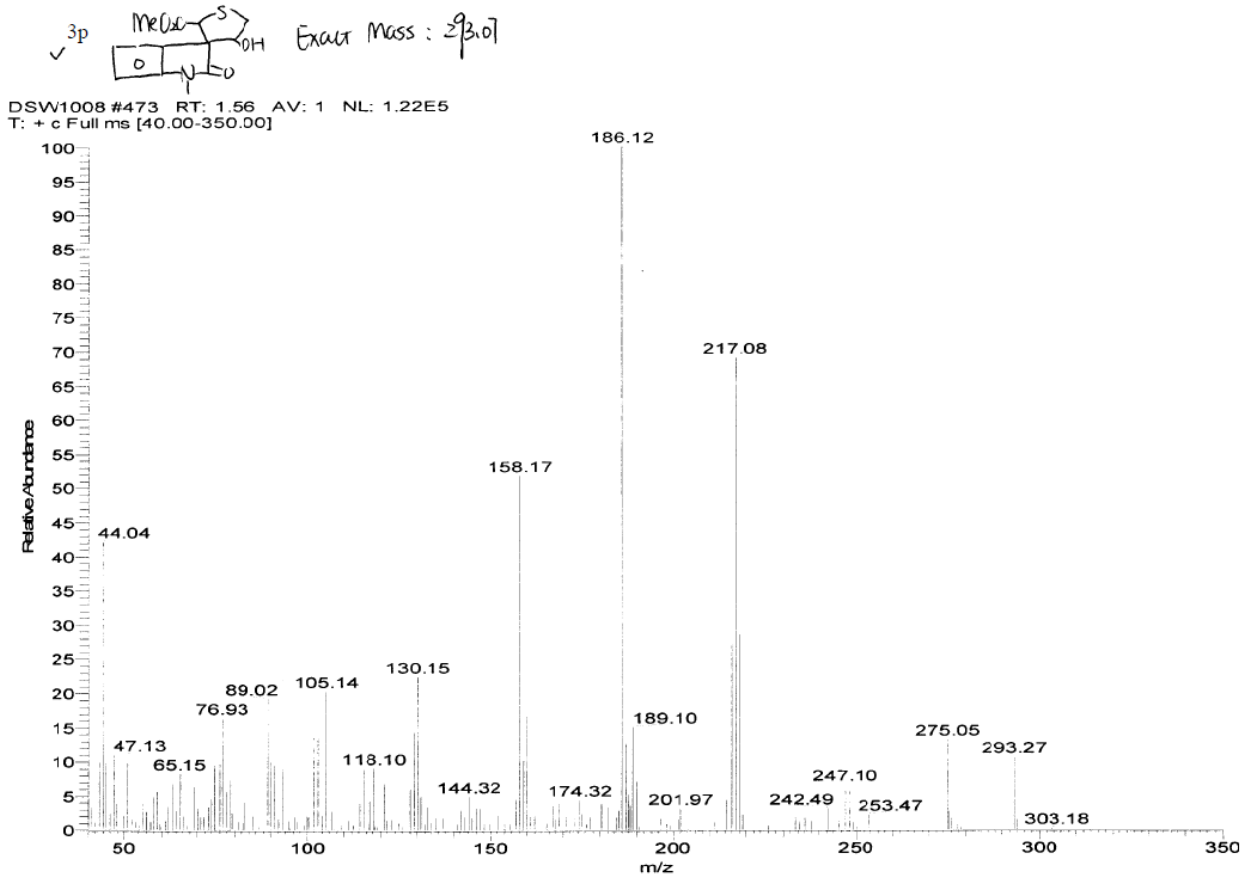


3o 

445.13

DSW1007 #442 RT: 2.07 AV: 1 SB: 467 0.04-1.95 , 2.80-3.03 NL: 1.10E5
T: + c Full ms [40.00-500.00]

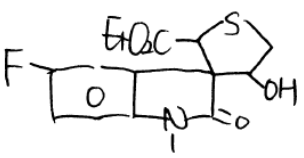



3p
Exact Mass : 293.07
DSW1008 #473 RT: 1.56 AV: 1 NL: 1.22E5
T: + c Full ms [40.00-350.00]
Relative Abundance
m/z
186.12
217.08
158.17
44.04
130.15
89.02
105.14
76.93
189.10
275.05
293.27
47.13
65.15
118.10
144.32
174.32
201.97
247.10
242.49
253.47
303.18

analytic functional testing 27.12.11
VarioEL III CHNS
serial number 11033032

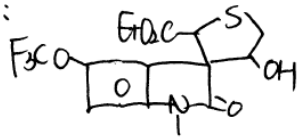
No.	Name	Weight [mg]		Content [%]	Peak Area
53	DSW001	1.2640	N:	4.183	1803
			C:	55.36	17211
			S:	9.728	1307
			H:	4.755	4268
54	DSW002	1.2190	N:	3.557	1472
			C:	49.06	14685
			S:	8.456	1086
			H:	3.902	3202
55	DSW003	1.2220	N:	4.072	1695
			C:	52.93	15895
			S:	9.363	1212
			H:	4.649	3988
56	DSW004	1.1920	N:	3.615	1463
			C:	46.37	13558
			S:	8.104	1014
			H:	4.042	3254
57	DSW005	1.1740	N:	4.312	1725
			C:	55.40	15985
			S:	9.922	1235
			H:	4.736	3885

DSW001



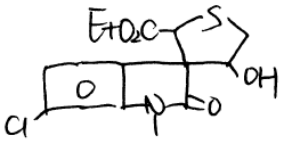
3d

DSW002:



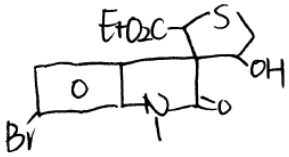
3f

DSW003:



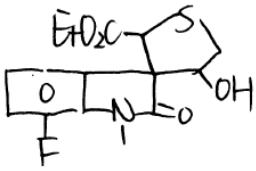
3g

DSW004:



3h

DSW005:

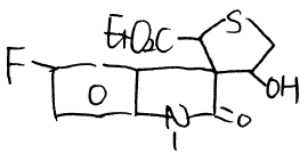


3i

analytic functional testing 27.12.11
VarioEL III CHNS
serial number 11033032

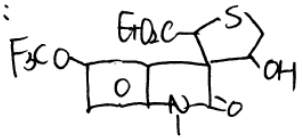
No.	Name	Weight [mg]		Content [%]	Peak Area
53	DSW001	1.2640	N:	4.183	1803
			C:	55.36	17211
			S:	9.728	1307
			H:	4.755	4268
54	DSW002	1.2190	N:	3.557	1472
			C:	49.06	14685
			S:	8.456	1086
			H:	3.902	3202
55	DSW003	1.2220	N:	4.072	1695
			C:	52.93	15895
			S:	9.363	1212
			H:	4.649	3988
56	DSW004	1.1920	N:	3.615	1463
			C:	46.37	13558
			S:	8.104	1014
			H:	4.042	3254
57	DSW005	1.1740	N:	4.312	1725
			C:	55.40	15985
			S:	9.922	1235
			H:	4.736	3885

DSW001



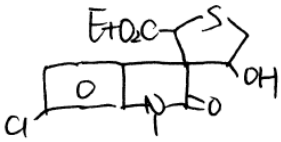
3d

DSW002:



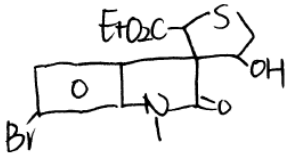
3f

DSW003:



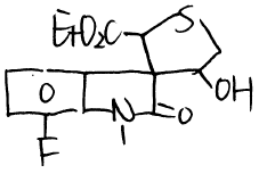
3g

DSW004:



3h

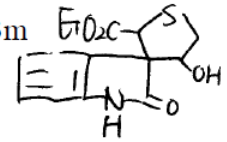
DSW005:

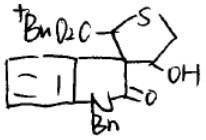


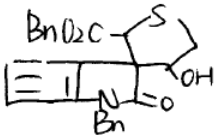
3i

VarioEL III CHNS
serial number 11033032

No.	Name	Weight [mg]	Content [%]	
124	DSW1005	1.1210	N:	4.882
			C:	57.39
			S:	10.67
			H:	5.012
126	DSW1006	1.2130	N:	3.204
			C:	67.10
			S:	7.768
			H:	6.101
127	DSW1007	1.2270	N:	3.215
			C:	70.19
			S:	7.059
			H:	5.141
128	DSW1008	1.2570	N:	4.710
			C:	57.52
			S:	10.68
			H:	5.389

DSW1005: compound 3m 

DSW1006: compound: 3n 

DSW1007: compound 3o 

DSW1008: compound: 3p