Supplementary Information

Oxidative N-Heterocyclic Carbene Catalyzed Stereoselective Annulation of Simple Aldehydes and 5-Alkenyl Thiazolones

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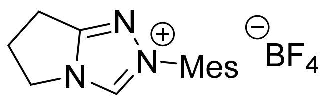
General methods:

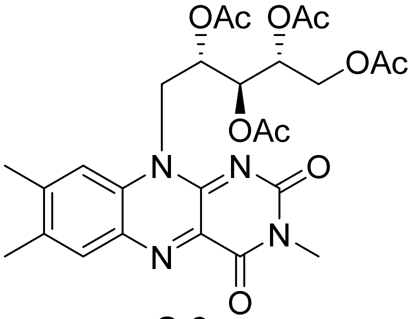
All reactions were monitored by thin layer chromatography (TLC), column chromatography purifications were carried out using silica gel. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 300M Bruker® instrument (300 MHz and 75 MHz, respectively) using tetramethylsilane as internal reference. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet or unresolved, coupling constant(s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). Optical rotations were reported as follows: $[\alpha]_D^{22}$ (c: g/100 mL, in solvent). HRMS was measured with a Bruker®maXis 4G mass spectrometer. As the diastereomers of the product cannot be separated via TLC or silica column, the ee and d.r. value of the product were determined by chiral HPLC analysis.after a micro separation via TLC. The ee as well as d.r. determination was carried out using chiral HPLC with Daicel Chiracel IA column on Waters® with a 996 UV-detector, flow rate = 1.0 mL/min.

Materials:

Pre-catalysts **NHC-5**, **NHC-6**, **NHC-7**, **NHC-8**, and Oxidant **O-1** were all commercially available. **NHC-1**, [1] **NHC-2**, [2] **NHC-3**,[2] **NHC-4**,[1] **NHC$_S$**,[2] and Riboflavin tetra acetate (**O-2**)[3] were synthesized following the literature's procedure.



NHC$_S$

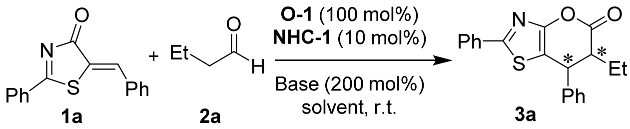


O-2

All solvents were purified according to the standard procedures. Racemic product was prepared and catalyzed by pre-catalyst **NHC$_S$** for the HPLC analysis.

[1] J. R. Struble, J. W. Bode, *Org. Synth.* **2010**, *87*, 362-376.
[2] M. S. Kerr, J. R. Alaniz, T. Rovis, *J. Org. Chem.* **2005**, *70*, 5725–5728.
[3] H. Schmaderer, P. Hilgers, R. Lechner, B. König, *Adv. Synth. Catal.* **2009**, *351*, 163-174.

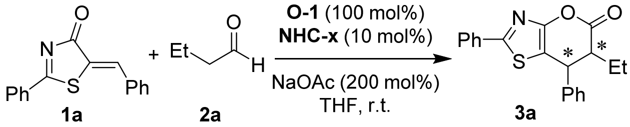
Table S1. Base and solvent screening studies in the model reaction.[a]



entry	base	solvent[b]	yield%[c]	ee%[d]	d.r. [d]
1	NaH	THF	trace	ND[e]	ND[e]
2	K_2CO_3	THF	79	73	3:1
3	KOH	THF	75	71	5:1
4	DBU	THF	trace	ND[e]	ND[e]
5	DIPEA	THF	75	91	15:1
6	Et_3N	THF	85	92	>20:1
7	NaOAc	THF	74	95	>20:1
8	NaOAc	Tol	70	96	>20:1
9	NaOAc	DCM	72	97	>20:1
10	NaOAc	DCE	74	97	>20:1
11	NaOAc	MeCN	53	95	>20:1

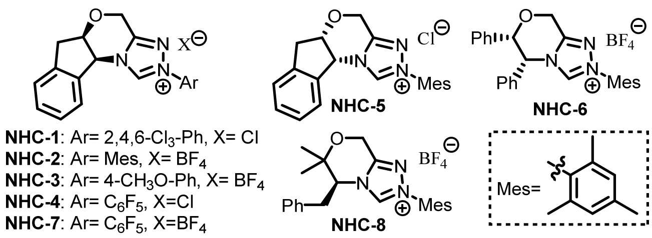
[a] All the reactions were carried out with **1a** (0.2 mmol), **2a** (0.4 mmol), Base (0.4 mmol), **O-1** (0.2 mmol), and **NHC-1** (0.02 mmol) at room temperature. [b] Freshly distilled before using (2.0 mL). [c] Isolated yield. [d] Determined by HPLC analysis. [e] Not determined.

Table S2. Screening studies on different NHC pre-catalyst..[a]

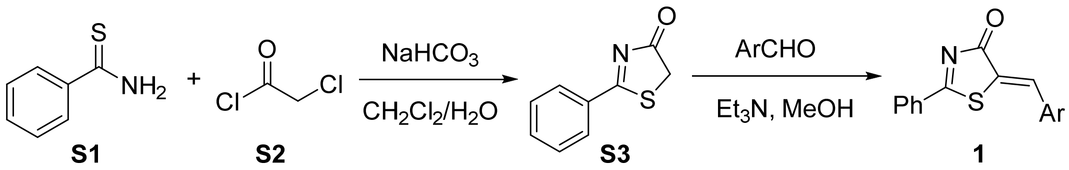


entry	pre-catalyst	yield%[b]	ee%[c]	d.r. [c]
1	**NHC-1**	74	95	>20:1
2	**NHC-2**	**80**	**>99**	**>20:1**
3	**NHC-3**	Trace	ND[d]	ND[d]
4	**NHC-4**	Trace	ND[d]	ND[d]
5	**NHC-5**	**82**	**>-99[e]**	**>20:1**
6	**NHC-6**	48	>99	>20:1
7	**NHC-7**	Trace	ND[d]	ND[d]
8	**NHC-8**	51	>99	>20:1
9[f]	**NHC-2**	71	96	>20:1

[a] In freshly distilled THF, all the reactions were carried out with **1a** (0.2 mmol), **2a** (0.4 mmol), NaOAc (0.4 mmol), **O-1** (0.2 mmol), and **NHC** (0.02 mmol) at room temperature. [b] Isolated yield. [c] Determined by HPLC analysis. [d] Not determined. [e] ee refers to **3a'**, enantiomer of **3a**. [f] Riboflavin tetra acetate (**O-2**) was used instead of **O-1**.



General procedure for the synthesis of 5-alkenyl thiazolone 1:[4-5]



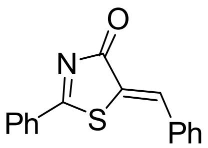
The solution of $NaHCO_3$ (20 mmol in 20 mL water) was added to a CH_2Cl_2 (40 mL) solution of thiobenzamide **S1** (10 mmol). After cooling to 0^{o}C with ice-water bath, chloroacetyl chloride (**S2** 10 mmol) was added drop-wise to the stirred solution. Then reaction mixture was then stirred overnight at room temperature. The organic phase of the reaction mixture was separated, aqueous phase was extracted with CH_2Cl_2 (50 mL x 2). The combined organic phase was washed with H_2O (40 mL x 2), dried with anhydrous Na_2SO_4, and evaporated to dryness. The solid residue was washed with EtOH and filtered to give **S3** (yiled 70%).[4]

Compound **S3** (1 mmol), benzaldehyde (1.1 mmol), and Et_3N (2 mmol) were dissolved in 20 mL of MeOH, and heated to reflux at 65℃ for 3h, during which some precipitate appear gradually. After cooling to room temperature, the precipitate was filtered, and washed with another 20 mL of cold MeOH. The 5-alkenyl thiazolone **1** was obtained as a solid.[5]

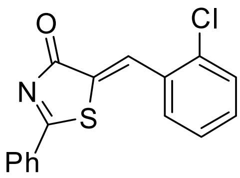
Following the similar procedure, substrate **1r** was synthesized starting from 4-chloro thiobenzamide, and then condensed with benzaldehyde.

[4] T. Okawara, H. Kashihara, M. Furukawa, *Chem. Pharm. Bull.* **1985**, *33*, 3479-3483.
[5] B. Hofmann, S. Barzen, C. B. Rödl, A. Kiehl, J. Borig, A. Živković, H. Stark, G. Schneider, D. Steinhilber, *J. Med. Chem.* **2011**, *54*, 1943-1947.

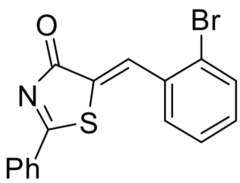
Characterization of 5-alkenyl thiazolone 1:



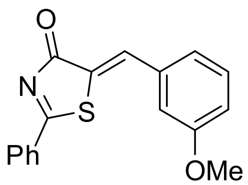
1a: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.25-8.21 (m, 2H), 8.09 (s, 1H), 7.70 (d, *J*=7.5 Hz, 3H), 7.66-7.46 (m, 5H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 187.37, 183.29, 138.64, 135.19, 133.75, 131.76, 131.13, 130.72, 129.30, 129.26, 128.88, 128.47, 126.32;
HRMS (ESI): C16H12NOS $[M+ H]^+$, Calc: 266.0634, Found: : 266.0636**.**



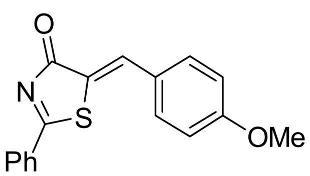
1b: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.19 (d, *J* = 7.5 Hz, 2H), 7.77 – 7.68 (m, 2H), 7.59 – 7.48 (m, 3H), 7.45-7.39 m, 2H); **^{13}C NMR** (75MHz, $CDCl_3$) δ 187.5, 182.55, 136.65, 135.38, 134.25, 132.41, 131.77, 131.62, 130.54, 129.37, 129.28, 128.92, 127.32;
HRMS (ESI): C16H11ClN OS $[M+ H]^+$, Calc: 300.0244, found: 300.0247.



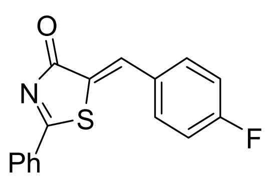
1c: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.20 (d, *J* = 7.8 Hz, 2H), 7.77 – 7.69 (m, 3H), 7.57 (t, *J* = 7.5 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.30 (dd, *J* = 15.3, 7.8 Hz, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 187.68, 182.43, 136.92, 135.37, 134.32, 133.85, 131.84, 131.68, 129.60, 129.54, 129.29, 128.92, 127.92, 126.99;
HRMS (ESI): C16H11BrNOS $[M+ H]^+$, Calc: 343.9739, found: 343.9752.



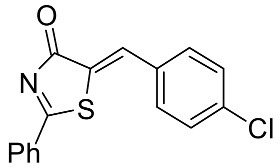
1d: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.5 Hz, 2H), 8.03 (s, 1H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 2H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.30 (s, 1H), 7.19 (s, 1H), 7.03 (dd, *J* = 8.4, 2.1 Hz, 1H), 3.89 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 187.37, 183.23, 160.05, 138.56, 135.21, 135.08, 131.75, 130.29, 129.25, 128.90, 126.67, 123.28, 116.85, 115.63, 55.46;
HRMS (ESI): C17H14NO2S $[M+ H]^+$, Calc: 296.0740, found: 296.0742.



1e: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.23 – 8.19 (m, 2H), 8.03 (s, 1H), 7.70 – 7.63 (m, 3H), 7.56 (dd, *J* = 15.3 Hz, 8.1 Hz, 2H), 7.05 –7.00 (m, 2H), 3.89 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 186.60, 183.53, 162.08, 138.72, 134.92, 132.87, 131.91, 129.20, 128.74, 126.43, 123.51, 114.86, 55.58;
HRMS (ESI): C17H14NO2S $[M+ H]^+$, Calc: 296.0740, found: 296.0744.

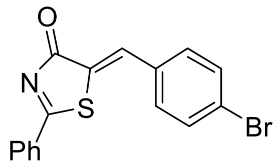


1f: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.22 (d, *J* =7.8 Hz, 2H), 8.03 (s, 1H), 7.74– 7.66 (m, 3H), 7.58 (t, *J* = 7.2 Hz, 2H), 7.23 (dd, *J* = 16.2, 7.8 Hz, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 187.13, 183.18, 162.38, 137.24, 135.27, 132.86, 132.75, 131.68, 130.11, 130.07, 129.28, 128.89, 126.05, 116.80, 116.50;
HRMS (ESI): C16H11FNOS $[M+ H]^+$, Calc: 284.0540, found: 284.0543.



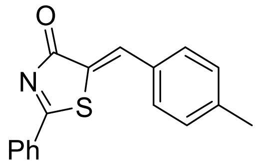
1g: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.21 (d, *J* = 7.8 Hz, 2H), 7.99 (s, 1H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.58 (dd, *J* = 13.5, 7.5 Hz, 4H), 7.48 (d, *J* = 8.1 Hz, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 187.06, 183.11, 137.20, 136.93, 135.35, 132.21, 131.75, 131.59, 129.61, 129.29, 128.94, 126.86;

HRMS (ESI): C16H11ClNOS $[M+ H]^+$, Calc: 300.0244, found: 300.0247.



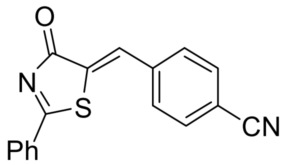
1h: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.23 – 8.19 (m, 2H), 7.98 (s, 1H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.66-7.60 (m, 3H), 7.55 (t, *J* = 8.7 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 187.07, 183.12, 137.00, 135.36, 132.63, 132.58, 131.88, 131.59, 129.30, 128.96, 127.01, 125.71;

HRMS (ESI): C16H11BrNOS $[M+ H]^+$, Calc: 343.9739, found: 343.9743.



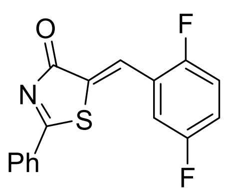
1i: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.5 Hz, 2H), 8.00 (s, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.57-7.51 (m, 4H), 7.29 (d, *J* = 7.8 Hz, 2H), 2.41 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 186.98, 183.39, 142.09, 138.78, 135.05, 131.76, 130.93, 130.82, 130.06, 129.20, 128.79, 125.09, 21.71;

HRMS (ESI): C17H14NOS $[M+ H]^+$, Calc: 280.0791, found: 280.0794



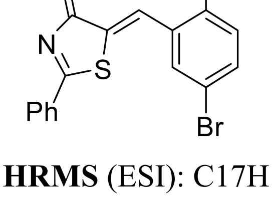
1j: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.23 (d, *J* = 7.8 Hz, 2H), 8.02 (s, 1H), 7.83-7.72 (m, 5H), 7.60 (t, *J* = 7.5 Hz, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 187.32, 182.73, 137.99, 135.76, 135.30, 132.86, 131.35, 130.69, 129.96, 129.41, 129.13, 118.14, 113.77;

HRMS (ESI): C17H10N2NaOS $[M+ Na]^+$, Calc: 313.0406, found: 313.0413.



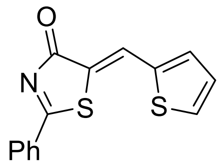
1k: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.23 (d, *J* = 6.6 Hz, 3H), 7.74 (t, *J* = 7.2 Hz, 1H), 7.59 (t, *J* = 7.8 Hz, 2H), 7.43 (t, *J* = 6.9 Hz, 1H), 7.17 (t, *J* = 6.0 Hz, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 187.12, 182.63, 135.57, 131.44, 129.67 – 129.45 (m), 129.21 (d, *J*= 20.7 Hz), 128.53, 119.47, 117.74, 115.01;

HRMS (ESI): C16H9 F2N NaOS $[M+ H]^+$, Calc: 324.0265; found: 324.0272

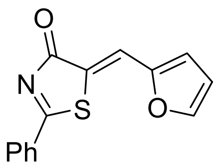


1l: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.22 (d, *J* = 7.5 Hz, 2H), 7.10 (dd, *J* = 2.1, 7.8 Hz, 2H), 7.60-7.48 (m, 3H), 6.84 (d, *J* = 9.0 Hz, 1H), 3.90 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 187.13, 183.00, 158.09, 135.21, 135.06, 131.86, 131.71, 131.59, 129.24, 128.93, 127.38, 124.99, 113.17, 112.95, 55.96;

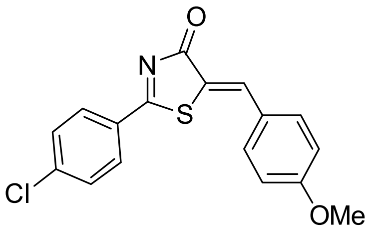
HRMS (ESI): C17H13BrNO2S $[M+ H]^+$, Calc: 373.9845, found: 373.9847



1m: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.22 (s, 1H), 8.20 (s, 2H), 7.71-7.66(m, 2H), 7.59 – 7.50 (m, 3H), 7.22 (dd, *J* = 4.8, 3.6 Hz, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 185.99, 182.95, 139.16, 135.06, 134.68, 132.72, 131.75, 130.67, 129.23, 129.00, 128.86, 124.88;
HRMS (ESI): C14H10NOS2 $[M+H]^+$, Calc: 272.0198, found: 272.0201

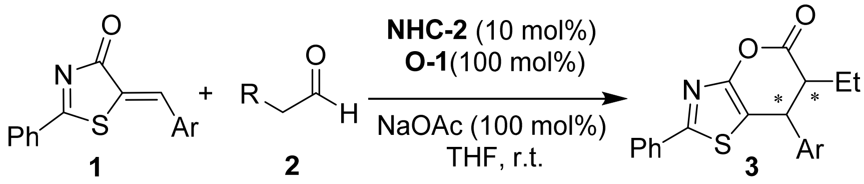


1n: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.5 Hz, 2H), 7.78 (s, 1H), 7.69 (dd, *J* = 15.0, 7.8 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 2H), 6.91 (d, *J* = 3.6 Hz, 1H), 6.63 (t, *J* = 1.5 Hz, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 187.69, 183.10, 150.26, 146.97, 134.90, 131.97, 129.17, 128.67, 124.36, 123.48, 119.34, 113.70;
HRMS (ESI): C14H10NO2S $[M+H]^+$, Calc: 256.0427, found: 256.0431.



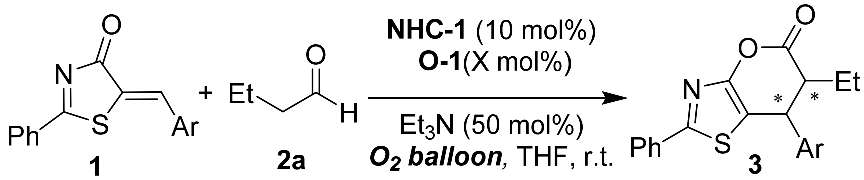
1r: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.12(d, *J* = 8.4Hz, 2H), 8.00 (s, 1H), 7.61(d, *J* = 8.7Hz, 2H), 7.52(d, *J* = 8.7Hz, 2H), 7.01(d, *J* = 8.7Hz, 2H), 3.89 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 185.13, 183.21, 162.20, 141.33, 139.08, 132.90, 130.32, 129.84, 129.57, 126.27, 123.25, 114.89, 55.57;
HRMS (ESI): C17H13ClNO2S $[M+H]^+$, Calc: 330.0350, found: 330.0352.

Typical experimental procedure using stoichiometric amount of O-1:



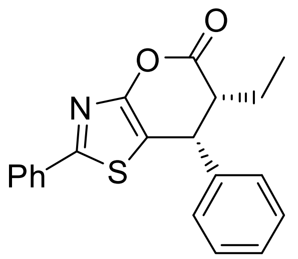
To a dry round bottom flask containing a magnetic stir bar, the pre-catalyst triazolium salt **NHC-2** (0.02 mmol) and NaOAc (0.2 mmol) were added. After adding 2.0 mL of dry THF, the suspension was stirred for one half hour to generate the real carbene catalyst via deprotonating of **NHC-2.** The 5-alkenyl thiazolone (0.2 mmol) and aliphatic aldehyde (0.4 mmol) were added in one portion and stirred for 10 minutes. Oxidant quinone **O-1** (0.2 mmol) was then added in one-portion at room temperature. The reaction was stirred until the disappearance of the substrate **1** (monitored by TLC). After a TLC separation, the ee and d.r. value of the product were determined by chiral HPLC analysis. The reaction mixture was then concentrated under reduced pressure to give a brown residue, which was purified by silica gel column chromatography (petroleum ether/ethyl acetate 10:1), and afforded the desired chiral thiazolo pyrone **3**.

Typical experimental procedure using catalytic amount of O-1 in presenct of O_2:

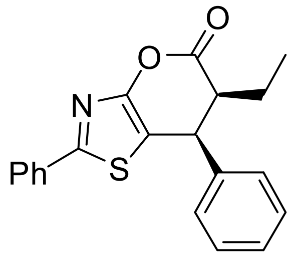


To a dry round bottom flask containing a magnetic stir bar, the pre-catalyst triazolium salt **NHC-1** (0.02 mmol) and Et_3N (0.1 mmol) were added. After adding 2.0 mL of dry THF, the suspension was stirred for one half hour. The 5-alkenyl thiazolone (0.2 mmol) and butanal (0.4 mmol) were added in one portion and stirred for 10 minutes. Catalytic amount of oxidant quinone **O-1** was then added at room temperature. An oxygen balloon was used to make sure the reaction proceeded under oxygen atmosphere. The reaction mixture was stirred vigorously till accomplishment (monitored by TLC). After a TLC separation, the ee and d.r. value of the product were determined by chiral HPLC analysis. The reaction mixture was then concentrated under reduced pressure to give a brown residue, which was purified by silica gel column chromatography (petroleum ether/ethyl acetate 10:1), and afforded the related chiral thiazolo pyrone **3**.

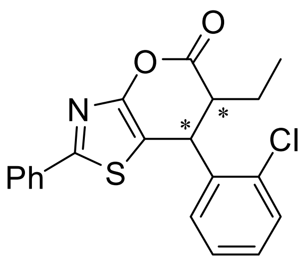
Characterization of the chiral chiral thiazolo pyrones:



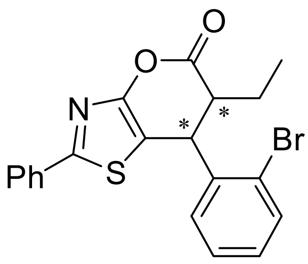
3a: white solid.
Yield: 80%.
ee: ≥99%; Dr: ≥20:1
HPLC: IA, Hexane/iPrOH = 90/10, t_{major} = 13.4, t_{minor} = 25.2.
$[\alpha]_D^{22}$ = +85 (c = 1.0, $CHCl_3$)
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 5.7, 2.1 Hz, 2H), 7.43 (dd, *J* = 6.3, 3.6Hz, 3H), 7.36 – 7.26 (m, 3H), 7.13 (dd, *J* = 7.8, 1.8 Hz, 2H), 4.38 (d, *J* = 6.9 Hz, 1H), 3.07 (dd, *J* = 13.8, 6.6 Hz, 1H), 1.94 – 1.79 (m, 1H), 1.39-1.22 (m, 1H), 1.06 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 168.72, 165.22, 156.00, 137.77, 132.87, 130.64, 129.19, 129.02, 128.17, 127.50, 125.82, 110.98, 47.17, 39.97.20.44.11.94; **HRMS** (ESI): C20H18NO2S $[M+ H]^+$, Calc: 336.1053, found: 336.1057.



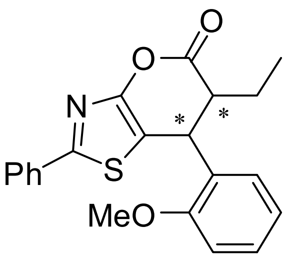
3a': white solid.
Yield: 82%.
ee: ≥-99%; Dr: ≥20:1
HPLC: IA, Hexane/iPrOH = 90/10, t_{minor} = 14.7, t_{major} = 24.2.
$[\alpha]_D^{22}$ = -87 (c = 1.0, $CHCl_3$)
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 – 7.76 (m, 2H), 7.41 (d, *J* = 1.8 Hz, 3H), 7.35 – 7.21 (m, 3H), 7.12 (d, *J* = 6.4 Hz, 2H), 4.37 (d, *J* = 6.7 Hz, 1H), 3.05 (q, *J* = 6.8 Hz, 1H), 1.98 – 1.75 (m, 1H), 1.31 (tt, *J* = 14.3, 7.1 Hz, 1H), 1.05 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ168.66, 165.11, 155.91, 137.72, 132.78, 130.55, 129.10, 128.93, 128.07, 127.42, 125.72, 110.95, 47.05, 39.87, 20.38, 11.86; **HRMS** (ESI): C20H18NO2S $[M+ H]^+$, Calc: 336.1053, found: 336.1059.



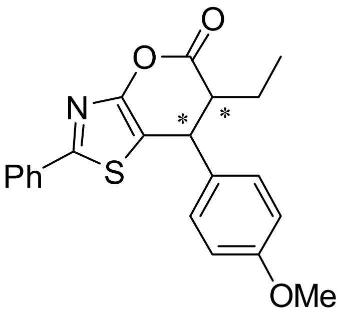
3b: light yellow solid.
Yield: 72%.
ee: 99%; Dr: ≥20:1
HPLC: IA, Hexane/iPrOH = 90/10, t_{major} = 10.6, t_{minor} = 13.6.
$[\alpha]_D^{22}$ = +61 (c = 1.0, $CHCl_3$).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 – 7.84 (m, 2H), 7.42 (s, 4H), 7.23 (dd, *J* = 15.0, 9.9 Hz, 2H), 7.13 – 7.09 (m, 1H), 5.08 (d, *J* = 6.9 Hz, 1H), 3.15 (q, *J* = 7.2 Hz, 1H), 2.05 – 1.86(m, 1H), 1.51 – 1.38 (m, 1H), 1.02 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 169.02, 165.26, 155.87, 135.78, 133.18, 132.77, 130.69, 130.15, 129.23, 129.02, 127.96, 125.82, 110.01, 45.85, 35.43, 20.30.11.98; **HRMS** (ESI): C20H17Cl N O2S $[M+ H]^+$, Calc: 370.0663, found: 370.0668.



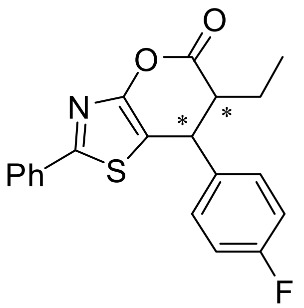
3c: light yellow oil.
Yield: 80%.
ee: 99%; Dr: ≥20:1
HPLC: IA, Hexane/iPrOH = 90/10, t_{major} = 11.0, t_{minor} = 14.7.
$[\alpha]_D^{22}$ = +69 (c = 1.0, $CHCl_3$).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88-7.85 (m, 2H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.41 (t, *J* = 4.5 Hz, 3H), 7.24 (s, 1H), 7.13 (dd, *J* = 10.5, 8.4 Hz, 2H), 5.07 (d, *J* = 7.2 Hz, 1H), 3.14 (q, *J* = 6.9 Hz, 1H), 2.02-1.84(m, 1H), 1.54 – 1.39 (m, 1H), 1.02 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 169.05, 165.21, 155.75, 137.52, 133.48, 132.79, 130.68, 129.51, 129.01, 128.62, 128.13, 125.84, 123.94, 110.00, 45.77, 38.34, 20.32, 11.95; **HRMS** (ESI): C20H17BrNO2S $[M+ H]^+$414.0158, found: 414.0176



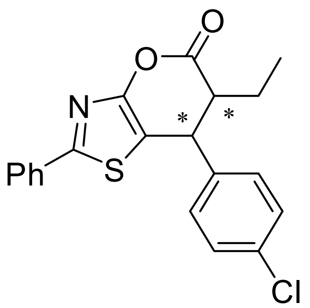
3d: white solid.
Yield: 82%.
ee: ≥99%; Dr: ≥20:1
HPLC: IA, Hexane/iPrOH = 90/10, t_{major} = 19.1, t_{minor} = 24.0.
$[\alpha]_D^{22}$ = +27 (c = 1.0, $CHCl_3$).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90-7.86 (m, 2H), 7.43(dd, *J* = 6.3, 3.6 Hz, 3H), 7.22 (d, *J* = 7.8 Hz, 1H), 6.81 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.71 (d, *J* = 7.5 Hz, 1H), 6.66 (t, *J* = 2.1 Hz, 1H), 4.34 (d, *J* = 6.6 Hz, 1H), 3.77 (s, 3H), 3.05 (dd, *J* = 13.8, 6.6 Hz, 1H), 1.96 – 1.78 (m, 1H), 1.43 – 1.25 (m, 1H), 1.06 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 168.71，165.21，160.02，155.99，139.33, 132.87，130.64，130.27，129.02，125.82, 119.66, 113.50, 113.07, 110.83, 55.22, 47.10, 39.98, 20.44, 11.99; **HRMS** (ESI): C21H20NO3S $[M+ H]^+$, Calc: 366.1158, found: 366.1162



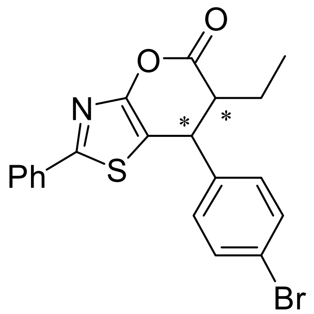
3e: white solid.
Yield: 76%.
ee: ≥99%; Dr: ≥20:1
HPLC: IA, Hexane/iPrOH = 90/10, t_{major} = 17.1, t_{minor} = 32.4.
$[\alpha]_D^{22}$ = +88 (c = 1.0, $CHCl_3$)
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (t, *J* = 3.6 Hz, 2H), 7.44 -7.41(m, 3H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 4.34 (d, *J* = 6.9 Hz, 1H), 3.77 (s, 3H), 3.03 (q, *J* = 6.6 Hz, 1H), 1.94-1.79 (*m*, 1H), 1.43– 1.26 (m, 1H), 1.06 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 168.83, 165.09, 159.31, 155.88, 132.90, 130.60, 129.68, 129.01, 128.60, 125.81, 114.48, 111.37, 55.28, 47.37, 39.18, 20.40, 11.92; **HRMS** (ESI): C21H20NO3S $[M+ H]^+$, Calc: 366.1158, found: 366.1163



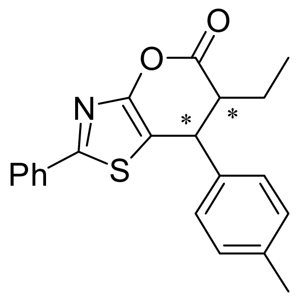
3f: light yellow solid.
Yield: 78%.
ee: ≥99%; Dr: ≥20:1
HPLC: IA, Hexane/iPrOH = 90/10, t_{major} = 11.9, t_{minor} = 20.8.
$[\alpha]_D^{22}$ = +83 (c = 1.0, $CHCl_3$).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (dd, *J* =5.7, 2.1 Hz, 2H), 7.44 – 7.42 (m, 3H), 7.10 (dd, *J* = 8.7, 5.7 Hz, 2H), 7.01 (t, *J* = 8.4 Hz, 2H), 4.38 (d, *J* = 6.6 Hz, 1H), 3.06 (q, *J* = 6.6 Hz, 1H), 1.94 – 1.78 (m, 1H), 1.40 – 1.25 (m, 1H), 1.06 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 168.52, 165.45, 156.00, 133.55, 133.50, 132.78, 130.75, 129.21, 129.10, 129.05, 125.84, 116.32, 116.03, 110.72, 47.21, 39.24, 20.44, 11.92; **HRMS** (ESI): $C20H17FNO_2S$ $[M+ H]^+$, Calc: 354.0959, found: 354.0970.



3g: white solid.
Yield: 82%.
ee: ≥-99%; Dr: ≥20:1
HPLC: IA, Hexane/iPrOH = 90/10, t_{major} = 12.8, t_{minor} = 23.4.
$[\alpha]_D^{22}$ = +64 (c = 1.0, $CHCl_3$).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (dd, *J* =5.7, 3.6 Hz, 2H), 7.46 –7.40 (m, 3H), 7.32 – 7.27 (m, 2H), 7.08 – 7.04(m, 2H), 4.37 (d, *J* = 6.9 Hz, 1H), 3.07 (dd, *J* =13.8Hz, *J* = 6.6 Hz, 1H), 1.94 – 1.79(m, 1H), 143 – 1.25 (m, 1H), 1.06 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 168.40, 165.56, 156.06, 136.26, 134.10, 132.74, 130.78, 129.40, 129.06, 128.86, 125.85, 110.35, 47.04, 39.38.20.45.11.91; **HRMS** (ESI): C20H17ClNO2S $[M+ H]^+$, Calc: 370.0663, found: 370.0667.



3h: light yellow oil.
Yield: 81%.
ee: ≥99%; Dr: ≥20:1
HPLC: IA, Hexane/iPrOH = 90/10, t_{major} = 13.1, t_{minor} = 24.8.
$[\alpha]_D^{22}$ = +35 (c = 1.0, $CHCl_3$).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (t, *J* = 3.6 Hz, 2H), 7.47-7.42 (m, 5H), 7.00 (d, *J* = 8.1 Hz, 2H), 4.35 (d, *J* = 6.6 Hz, 1H), 3.06 (q, *J* = 6.9 Hz, 1H), 1.92–1.82 (m, 1H), 1.35 – 1.27 (m, 1H), 1.06 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 168.37, 165.58, 156.08, 136.79, 132.74, 132.36, 130.79, 129.19, 129.06, 125.86, 122.20, 110.24, 46.97, 39.46, 20.46, 11.92; **HRMS** (ESI): $C20H_{17}BrNO_2S$ $[M+ H]^+$, Calc: 414.0158, found: 414.0163.



3i: white solid.

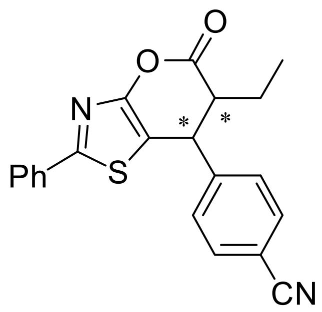
Yield: 81%.

ee: ≥99%; Dr: ≥20:1

HPLC: IA, Hexane/iPrOH = 90/10, t_{major} = 12.0, t_{minor} = 18.8.

$[\alpha]_D^{22}$ = +73 (c = 1.0, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 6.0, 2.1 Hz, 2H), 7.43-7.40 (m, 3H), 7.12 (d, *J* =8.1 Hz, 2H), 7.01 (d, *J* = 8.1 Hz, 2H), 4.34 (d, *J* = 6.6 Hz, 1H), 3.04 (q, *J* = 6.9 Hz, 1H), 2.31 (s, 3H), 1.94-1.73 (m, 1H), 1.37-1.26 (m, 1H), 1.05 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 168.83, 165.09, 155.92, 137.98, 134.73, 132.91, 130.59, 129.85, 129.01, 127.36, 125.80, 111.25, 47.19, 39.58, 26.91, 21.08, 20.41, 11.92; **HRMS** (ESI): C21H20NO2S $[M+ H]^+$, Calc: 350.1209, found: 350.1215.



3j: white solid.

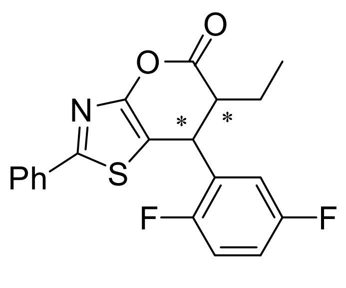
Yield: 86%.

ee: 99%; Dr: 10:1

HPLC: IA, Hexane/iPrOH = 75/25, t_{major} = 17.2, t_{minor} = 39.0.

$[\alpha]_D^{22}$ = +24 (c = 1.0, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90-7.86 (m, 2H), 7.64 (d, *J* =7.1Hz, 2H), 7.44 (d, *J* = 7.1 Hz, 3H), 7.24(s, 1H), 4.44 (d, *J* = 6.9 Hz, 1H), 3.13 (q, *J* = 6.9 Hz, 1H), 1.95–1.79 (m, 1H), 1.32 – 1.19 (m, 1H), 1.06 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 167.97, 166.07, 156.30, 143.16, 133.03, 132.59, 130.98, 129.10, 128.41, 125.90, 118.18, 112.32, 109.23, 46.83, 39.97, 20.57, 11.95; **HRMS** (ESI): C21H17N2O2S $[M+ H]^+$, Calc: 361.1005, found: 361.1015.



3k: white solid.

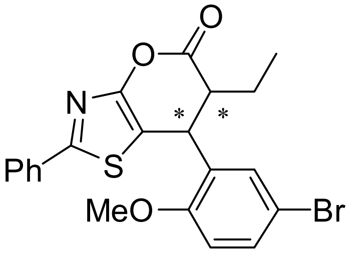
Yield: 74%.

ee: ≥99%; Dr: ≥20:1

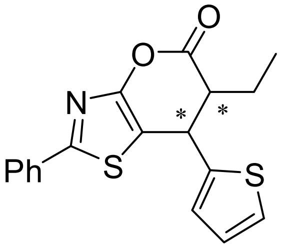
HPLC: IA, Hexane/iPrOH = 90/10, t_{major} = 15.5, t_{minor} = 18.3.

$[\alpha]_D^{22}$ = +80 (c = 1.0, $CHCl_3$).

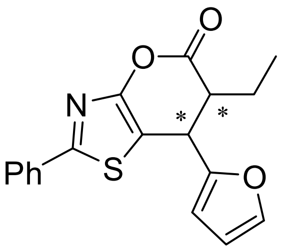
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 5.4, 2.1 Hz, 2H), 7.45– 7.39 (m, 3H), 7.10-7.02 (m, 1H), 7.01-6.80(m, 1H), 6.80-6.76(m, 1H), 4.75 (d, *J* = 6.9 Hz, 1H), 3.10 (q, *J* = 7.2 Hz, 1H), 2.08– 1.84(m, 1H), 1.47 – 1.32 (m, 1H), 1.07 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 168.06, 165.84, 156.40, 132.70, 130.85, 129.06, 126.53 (d, *J* = 17.1 Hz), 125.88, 117.16 (dd, *J* = 25.6, 8.4 Hz), 116.71 – 116.22 (m), 115.95 – 115.55 (m), 115.32 (d, *J* = 24.6 Hz), 108.54, 46.18, 33.22, 20.43, 11.97; **HRMS** (ESI): C20H16F2NO2S $[M+ H]^+$, Calc: 372.0864, found: 372.0869.



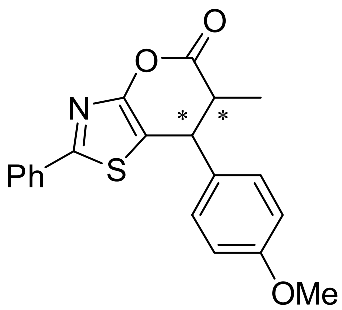
3l: white solid.
Yield: 72%.
ee: 99%; Dr: 10:1
HPLC: IA, Hexane/iPrOH = 90/10, t_{major} = 11.8, t_{minor} = 37.6.
$[\alpha]_D^{22}$ = +75 (c = 1.0, $CHCl_3$).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 –7.83 (m, 2H), 7.43–7.35 (m, 4H), 7.30 (s, 1H), 6.70 (d, *J* =8.7 Hz, 1H), 4.42 – 4.38 (m, 1H), 3.69 (s, 3H), 2.93 (dd, *J* = 10.8Hz, 8.1Hz, 1H), 2.08 – 1.96 (m, 1H), 1.34 – 1.20 (m, 1H), 1.00 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 168.24, 164.76, 156.49, 155.91, 132.92, 132.12, 130.51, 128.96, 128.54, 125.76, 112.92, 112.55, 54.52, 44.49, 29.71, 20.58, 12.09; **HRMS** (ESI): C21H19Br NO3S $[M+ H]^+$, Calc: 444.0264, found: 444.0265



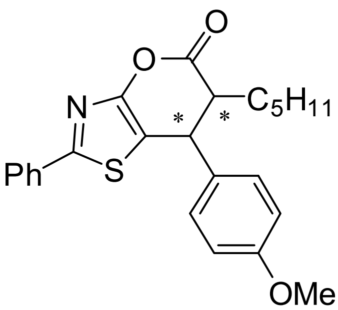
3m: white solid.
Yield: 76%.
ee: ≥99%; Dr: ≥20:1
HPLC: IA, Hexane/iPrOH = 90/10, t_{major} = 15.0, t_{minor} = 25.0.
$[\alpha]_D^{22}$ = +41 (c = 1.0, $CHCl_3$).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92– 7.87 (m, 2H), 7.46 – 7.40 (m, 3H), 7.22 (dd, *J* = 5.1, 0.9 Hz, 1H), 6.95 (dd, *J* =4.8, 3.3 Hz, 1H), 6.87 – 6.85 (m, 1H), 4.70 (d, *J* = 6.3 Hz, 1H), 3.08-3.01 (m, 1H), 2.06 – 1.90 (m, 1H), 1.55 – 1.39 (m, 1H), 1.10 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 168.21, 165.36, 155.83, 140.23, 132.79, 130.75, 129.04, 127.36, 125.88, 125.69, 125.35, 110.75, 47.80, 34.85, 20.44, 11.87; **HRMS** (ESI): C18H16NO2S2 $[M+ H]^+$, Calc: 342.0617, found: 342.0624.



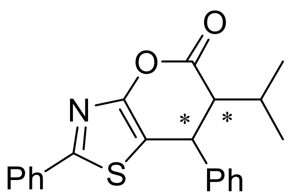
3n: white solid.
Yield: 70%.
ee: ≥99%; Dr: ≥20:1
HPLC: IA, Hexane/iPrOH = 90/10, t_{major} = 12.0, t_{minor} = 21.3.
$[\alpha]_D^{22}$ = +19 (c = 1.0, $CHCl_3$).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 – 7.87 (m, 2H), 7.46 – 7.41 (m, 3H), 7.33 (d, *J* = 1.2 Hz, 1H), 6.29 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.17 (d, *J* = 3.3 Hz, 1H), 4.52 (d, *J* = 6.3 Hz, 1H), 3.04-2.96 (m, 1H), 2.05 – 1.93 (m, 1H), 1.43-1.32 (m, 1H), 1.08 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 168.28, 165.19, 156.41, 150.65, 142.93, 132.84, 130.68, 129.02, 125.86, 110.36, 107.76, 107.70, 46.12, 33.34, 20.54, 11.75; **HRMS** (ESI): C18H16NO3S $[M+ H]^+$, Calc: 326.0845, found: 326.0853.



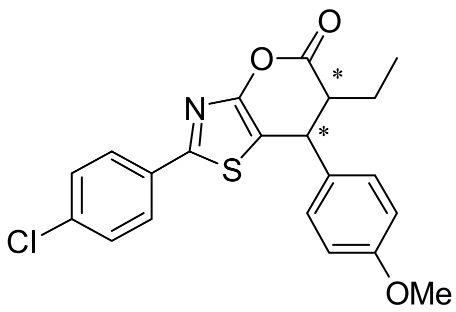
3o: white solid.
Yield: 72%.
ee: ≥99%; Dr: 15:1
HPLC: IA, Hexane/iPrOH = 90/10, t_{major} = 17.3, t_{minor} = 26.5.
$[\alpha]_D^{22}$ = +86 (c = 1.0, $CHCl_3$).
¹H NMR (300 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 6.0, 2.4 Hz, 2H), 7.43 (dd, *J* = 6.6, 3.9Hz, 3H), 7.00 (d, *J* = 8.7 Hz, 2H), 6.87-6.82 (m, 2H), 4.24(d, *J* = 6.9 Hz, 1H), 3.77 (s, 3H), 3.23 (t, *J* = 6.6 Hz, 1H), 1.15 (d, *J* = 6.9 Hz, 3H); **¹³C NMR** (75 MHz, $CDCl_3$) δ 169.40, 165.27, 159.36, 156.08, 132.87, 130.64, 129.45, 129.02, 128.75, 125.81, 114.45, 111.05, 55.29, 41.20, 40.48, 13.22; **HRMS** (ESI): C20H18NO3S $[M+ H]^+$, Calc: 352.1002, found: 352.1002**.**



3p: white solid.
Yield: 77%.
ee: ≥99%; Dr: ≥20:1
HPLC: IA, Hexane/iPrOH = 90/10, t_{major} = 25.5, t_{minor} = 38.6.
$[\alpha]_D^{22}$ = +28 (c = 1.0, $CHCl_3$).
¹H NMR (300 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 5.7, 2.1 Hz, 2H), 7.44 – 7.41 (m, 3H), 7.03 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 4.31 (d, *J* = 6.6 Hz, 1H), 3.78 (s, 3H), 3.11 (q, *J* = 6.9 Hz, 1H), 1.82-1.76(m, 1H), 1.45 – 1.42(m, 2H), 1.33 – 1.25 (m, 5H), 0.87 (t, *J* = 6.3 Hz, 3H); **¹³C NMR** (75 MHz, $CDCl_3$) δ 168.98, 165.07, 159.29, 155.88, 132.91, 130.59, 129.73, 129.01, 128.60, 125.81, 114.47, 111.41, 55.28, 45.71, 39.43, 31.58, 26.99, 26.86, 22.44, 14.01; **HRMS** (ESI): C24H26NO3S $[M+ H]^+$, Calc: 408.1628, found: 408.1625.



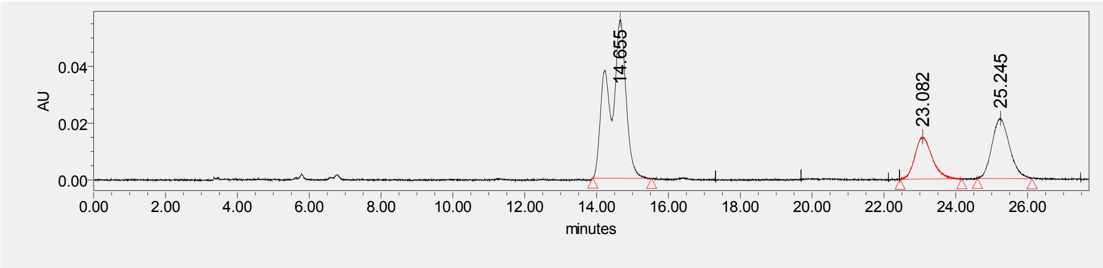
3q: white solid.
Yield: 71%.
ee: ≥99%; Dr: ≥20:1
HPLC: IA, Hexane/iPrOH = 90/10, t_{major} = 14.5, t_{minor} = 26.0.
$[\alpha]_D^{22}$ = +40 (c = 1.0, $CHCl_3$).
¹H NMR (300 MHz, $CDCl_3$) δ 7.87 – 7.84 (m, 2H), 7.41 (d, *J* = 4.5 Hz, 3H), 7.31 (d, *J* = 7.2 Hz, 3H), 7.22 (d, *J* = 7.5 Hz, 2H), 4.46 (d, *J* = 6.3 Hz, 1H), 2.93 (t, *J* = 7.5 Hz, 1H), 2.07-1.93 (m, 1H), 1.13 (d, *J* = 6.6 Hz, 3H), 0.96 (d, *J* = 6.9 Hz, 3H); **¹³C NMR** (75 MHz, $CDCl_3$) δ 168.31, 164.94, 155.61, 138.57, 132.89, 130.58, 129.24, 128.99, 128.06, 127.44, 125.80, 111.77, 51.74, 39.47, 26.53, 21.78, 20.49; **HRMS** (ESI): C21H20NO2S $[M+ H]^+$, Calc: 350.1209, found: 350.1209.



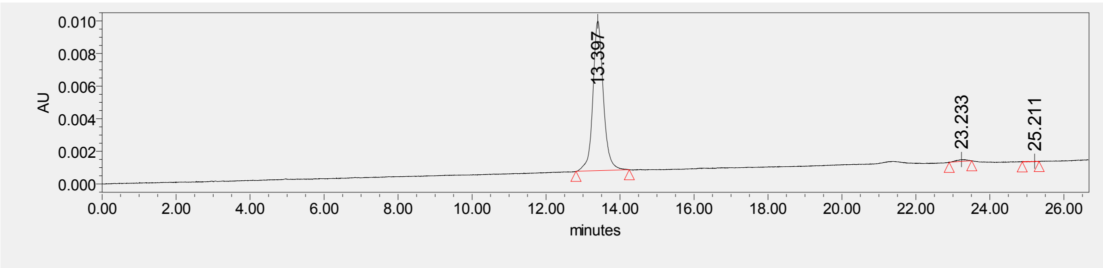
3r: white solid.
Yield: 82%.
ee: ≥-99%; Dr: ≥20:1
HPLC: IA, Hexane/iPrOH = 90/10, t_{major} = 20.4, t_{minor} = 36.4.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4, 2H), 7.38 (d, *J* = 8.4, 2H), 7.03 (d, *J* = 8.5, 2H), 6.84 (d, *J* = 8.5, 2H), 4.34 (d, *J* = 6.6, 1H), 3.77 (s, 3H), 3.03 (q, *J* = 13.6, 6.8, 1H), 1.95 – 1.75 (m, 1H), 1.40 – 1.26 (m, 1H), 1.05 (t, *J* = 7.3, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 168.69, 163.66, 159.36, 155.97, 136.54, 131.41, 129.56, 129.26, 128.57, 128.35, 126.99, 114.65, 114.52, 111.84, 55.28, 47.29, 39.19, 20.40, 11.89; **HRMS** (ESI): C21H19ClNO3S $[M+ H]^+$, Calc: 400.0769, found: 400.0781.

HPLC condition and spectra:

3a: IA, Hexane/iPrOH = 90/10.
Racemic:

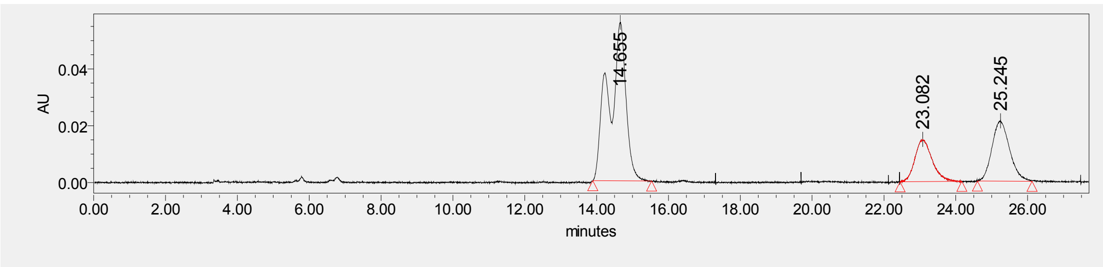


	Retention Time	Area	% Area	Hight
1	14.655	1843265	60.26	55873
2	23.082	493589	16.14	14899
3	25.245	722146	23.61	21208

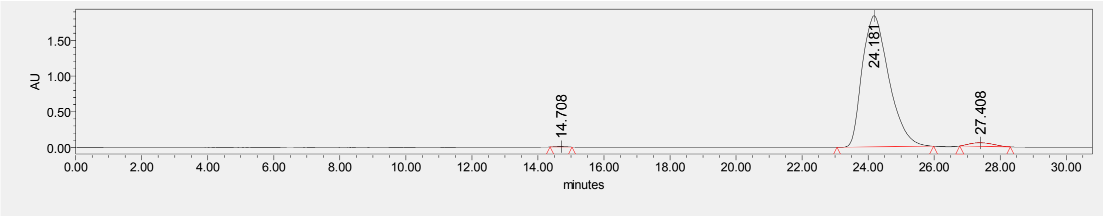


	Retention Time	Area	% Area	Hight
1	13.397	180078	98.77	9191
2	23.233	2124	1.16	113
3	25.211	124	0.07	26

3a': IA, Hexane/iPrOH = 90/10.
Racemic:

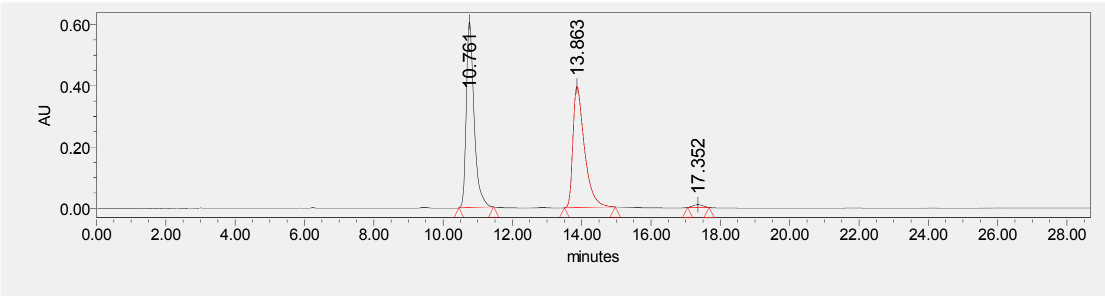


	Retention Time	Area	% Area	Hight
1	14.655	1843265	60.26	55873
2	23.082	493589	16.14	14899
3	25.245	722146	23.61	21208

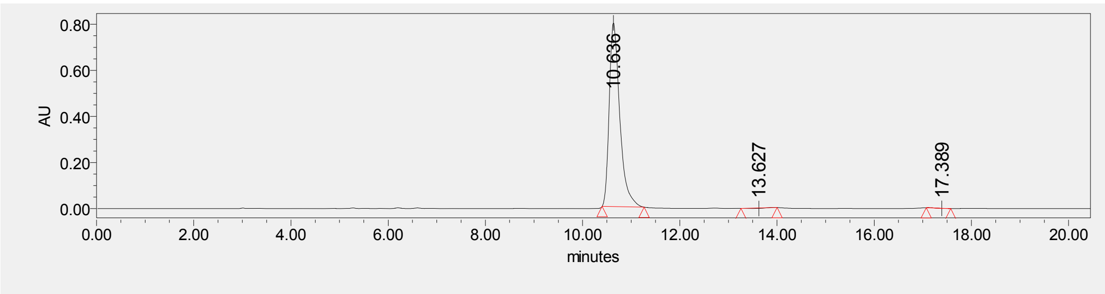


	Retention Time	Area	% Area	Hight
1	14.708	123231	0.12	4907
2	24.181	103084033	97.48	1838665
3	27.408	2544818	2.41	49525

3b: IA, Hexane/iPrOH = 90/10.
Racemic:



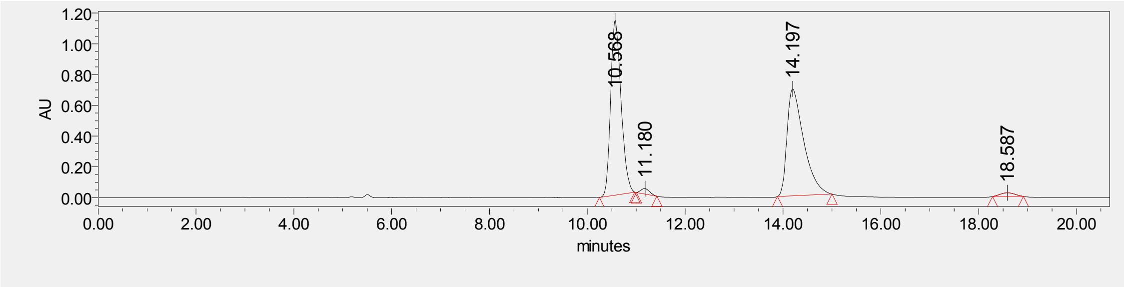
	Retention Time	Area	% Area	Hight
1	10.761	9503659	50.58	606208
2	13.863	9102580	48.45	396784
3	17.352	182395	0.97	9137



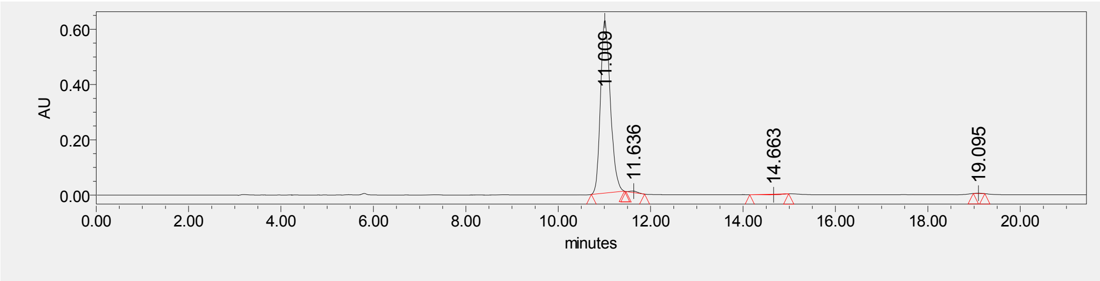
	Retention Time	Area	% Area	Hight
1	10.636	12030151	99.51	796958
2	13.627	48051	0.40	-2136
3	17.389	11319	0.09	-615

3c: IA, Hexane/iPrOH = 90/10.

Racemic:



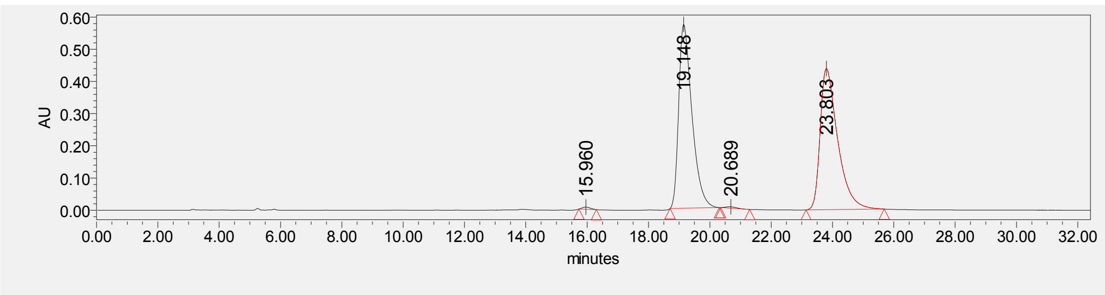
	Retention Time	Area	% Area	Hight
1	10.568	16822476	49.06	1136253
2	11.180	434409	1.27	35233
3	14.197	16529514	48.20	694994
4	18.587	505417	1.47	24153



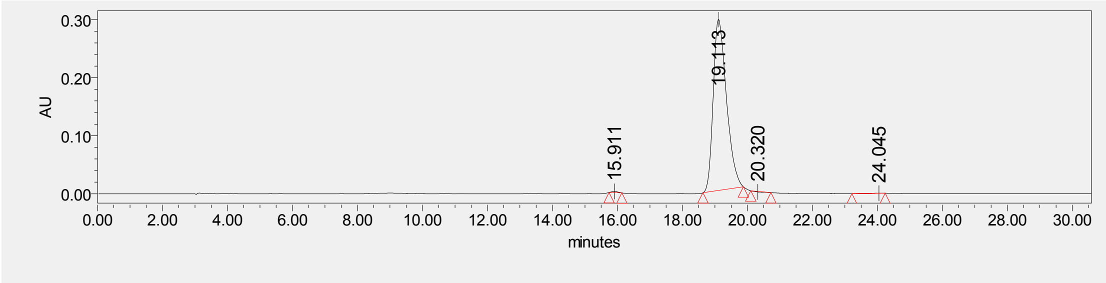
	Retention Time	Area	% Area	Hight
1	11.009	9255567	98.53	624626
2	11.636	61245	0.65	5513
3	14.663	64042	0.68	-2313
4	19.095	12550	0.13	1301

3d: IA, Hexane/iPrOH = 90/10.

Racemic:

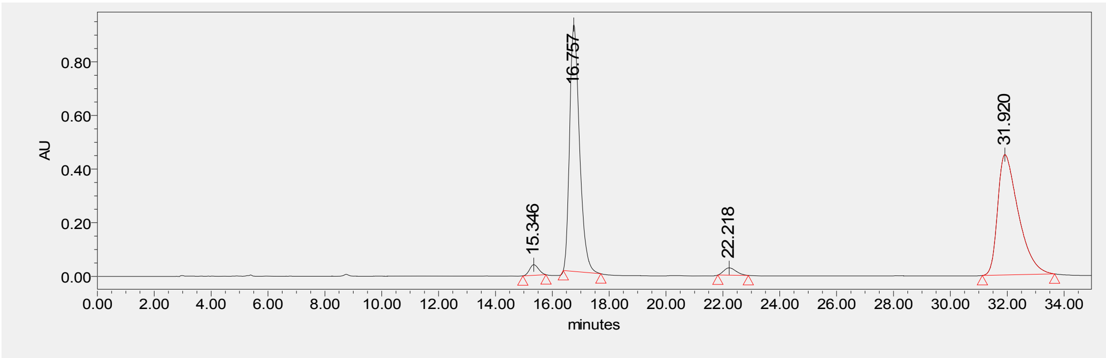


	Retention Time	Area	% Area	Hight
1	15.960	127981	0.37	6996
2	19.148	17130358	49.27	571171
3	20.689	106730	0.31	4401
4	23.803	17402530	50.05	438609

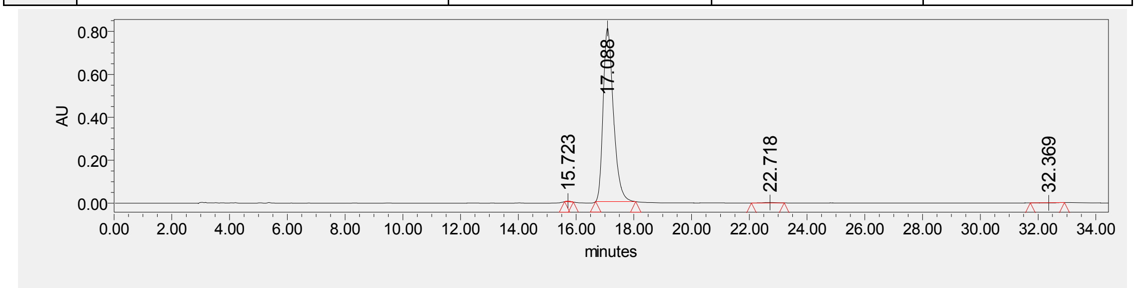


	Retention Time	Area	% Area	Hight
1	15.911	28786	0.34	2014
2	19.113	8348500	99.33	294301
3	20.320	20341	0.24	-934
4	24.045	7057	0.08	212

3e: IA, Hexane/iPrOH = 90/10.
Racemic:



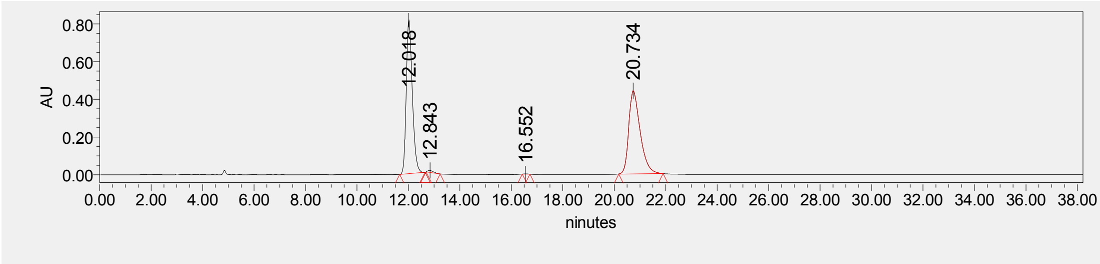
	Retention Time	Area	% Area	Hight
1	15.346	878234	1.88	39674
2	16.757	22225404	47.65	920617
3	22.218	816465	1.75	27273
4	31.920	22726223	48.72	449100



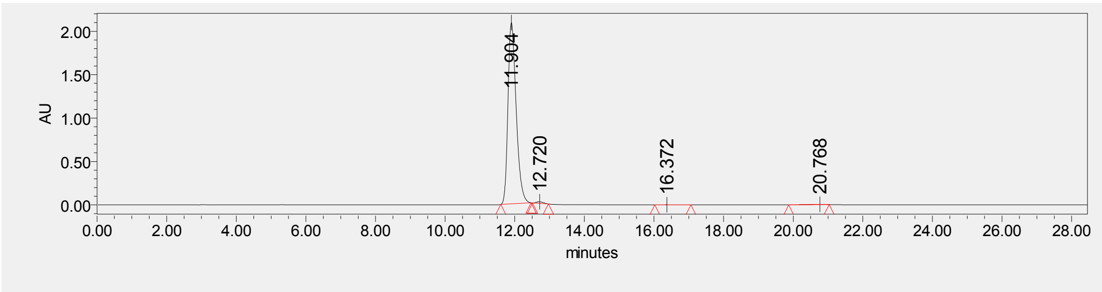
	Retention Time	Area	% Area	Hight
1	15.723	33459	0.17	2915
2	17.088	19928062	99.31	807609
3	22.718	64804	0.32	2119
4	32.369	39608	0.20	-976

3f: IA, Hexane/iPrOH = 90/10.

Racemic:



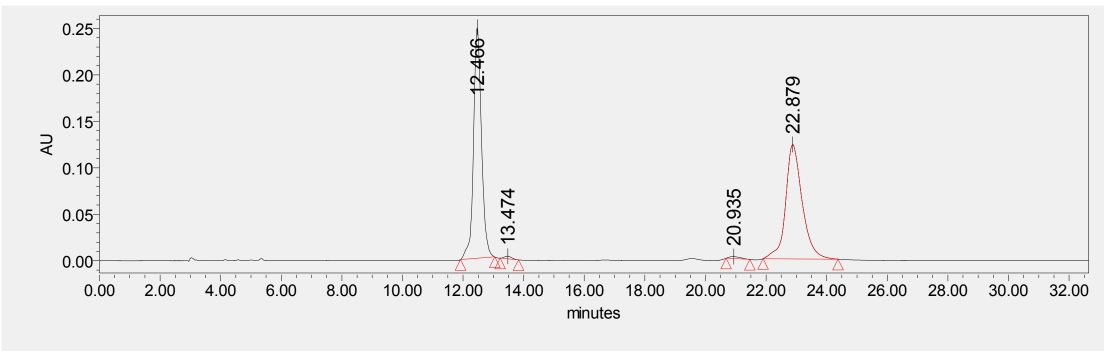
	Retention Time	Area	% Area	Hight
1	12.018	13344868	49.23	818954
2	12.843	154305	0.57	10297
3	16.552	12857	0.05	1176
4	20.734	13597775	50.16	441761



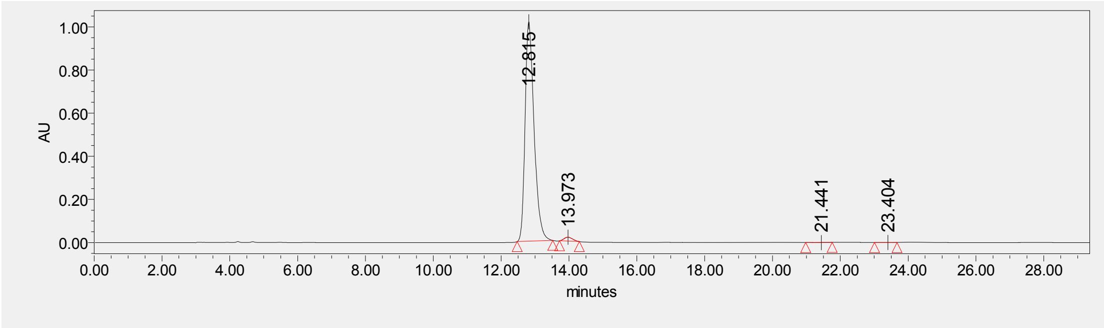
	Retention Time	Area	% Area	Hight
1	11.904	34151375	98.89	2088901
2	12.720	270134	0.78	19675
3	16.372	14235	0.04	584
4	20.768	99714	0.29	3817

3g: IA, Hexane/iPrOH = 90/10.

Racemic:

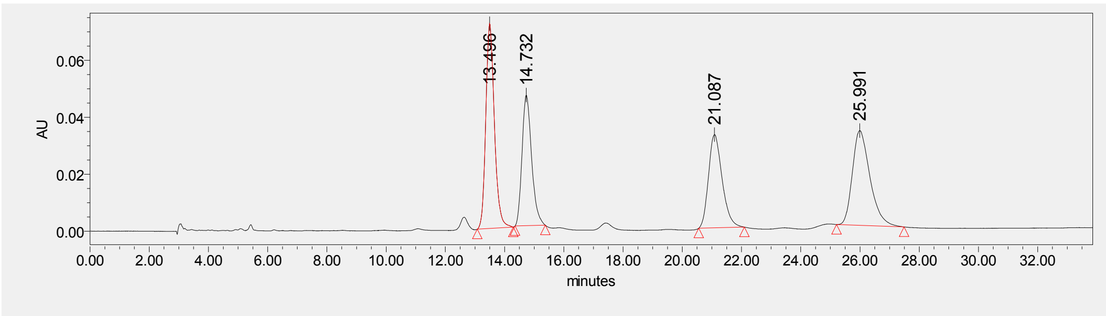


	Retention Time	Area	% Area	Hight
1	12.466	4517918	48.54	248457
2	13.474	48674	0.52	2896
3	20.935	56256	0.60	2175
4	22.879	4683973	50.33	123202

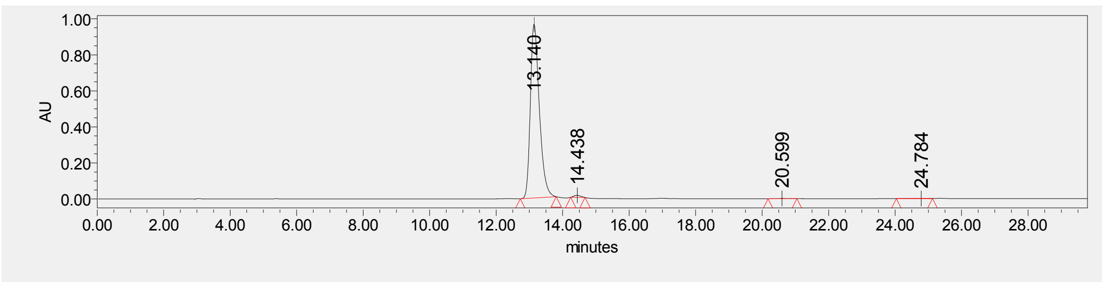


	Retention Time	Area	% Area	Hight
1	12.815	18719531	98.23	1017607
2	13.973	319454	1.68	18261
3	21.441	12668	0.07	-444
4	23.404	5543	0.03	-228

3h: IA, Hexane/iPrOH = 90/10.
Racemic:

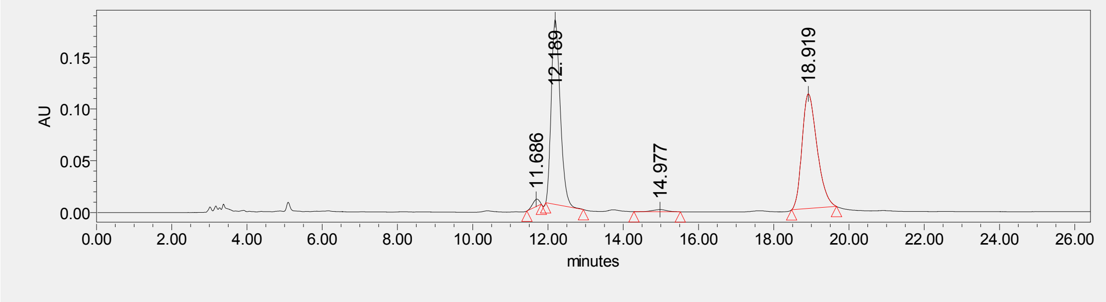


	Retention Time	Area	% Area	Hight
1	13.496	1447532	29.56	71899
2	14.732	1028564	21.00	45822
3	21.087	1048106	21.40	32789
4	25.991	1372734	28.03	33318

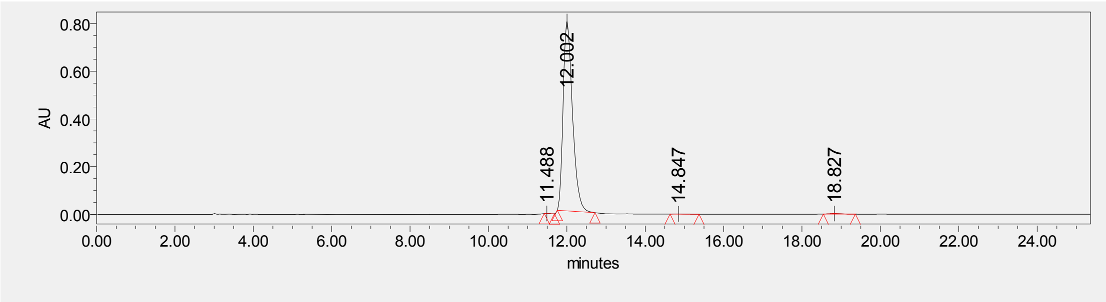


	Retention Time	Area	% Area	Hight
1	13.140	18130123	98.76	963640
2	14.438	166042	0.90	11125
3	20.599	31793	0.17	1222
4	24.784	30596	0.17	-770

3i: IA, Hexane/iPrOH = 90/10.
Racemic:

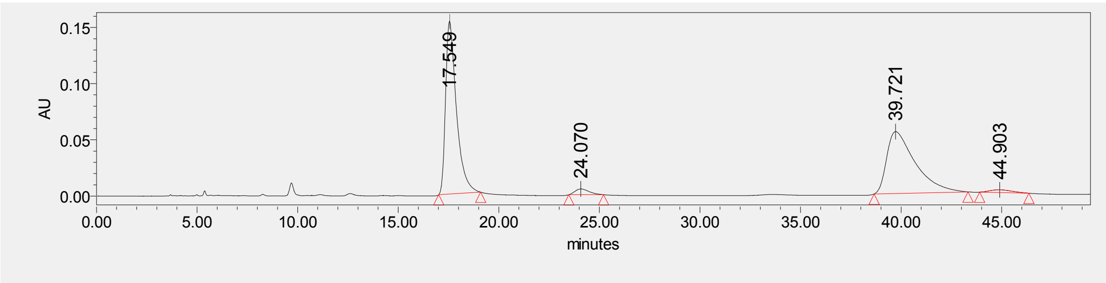


	Retention Time	Area	% Area	Hight
1	11.686	83525	1.35	7018
2	12.189	2958505	47.89	178210
3	14.977	56820	0.92	2141
4	18.919	3078322	49.83	110637

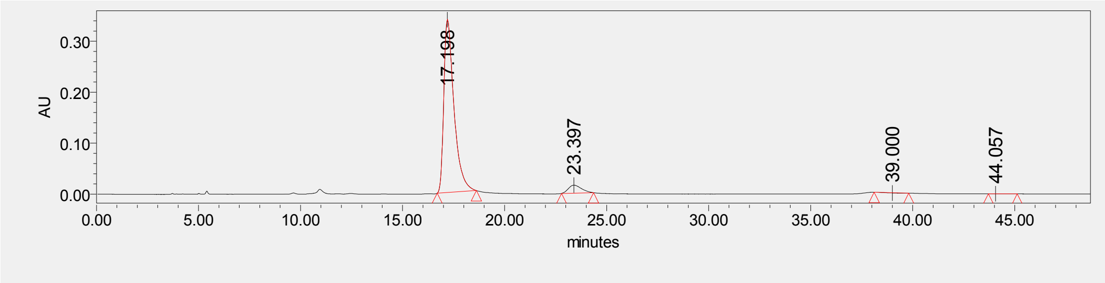


	Retention Time	Area	% Area	Hight
1	11.488	7729	0.06	804
2	12.002	13178868	99.46	792992
3	14.847	10114	0.08	602
4	18.827	54357	0.41	2243

3j: IA, Hexane/iPrOH = 90/10.
Racemic:

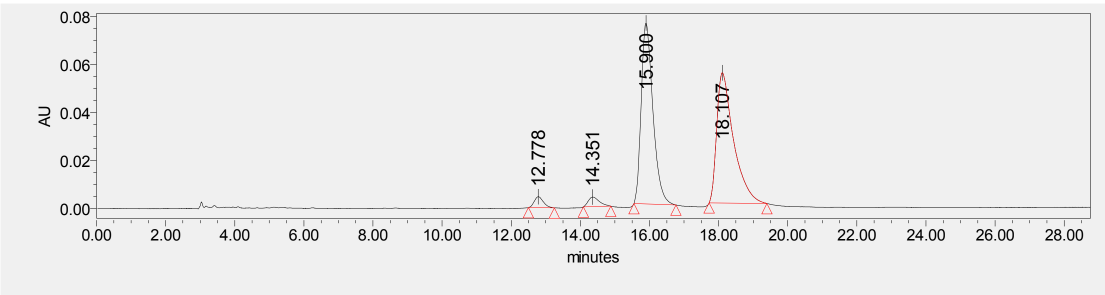


	Retention Time	Area	% Area	Hight
1	17.549	5750655	49.46	153717
2	24.070	251063	2.16	5176
3	39.721	5434880	46.74	55061
4	44.903	190173	1.64	2493

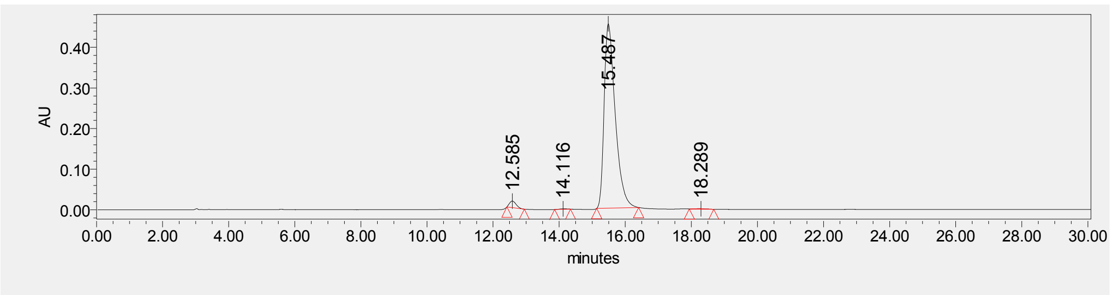


	Retention Time	Area	% Area	Hight
1	17.198	11701658	94.20	339256
2	23.397	692820	5.58	15659
3	39.000	25979	0.21	-519
4	44.057	1724	0.01	57

3k: IA, Hexane/iPrOH = 90/10.
Racemic:

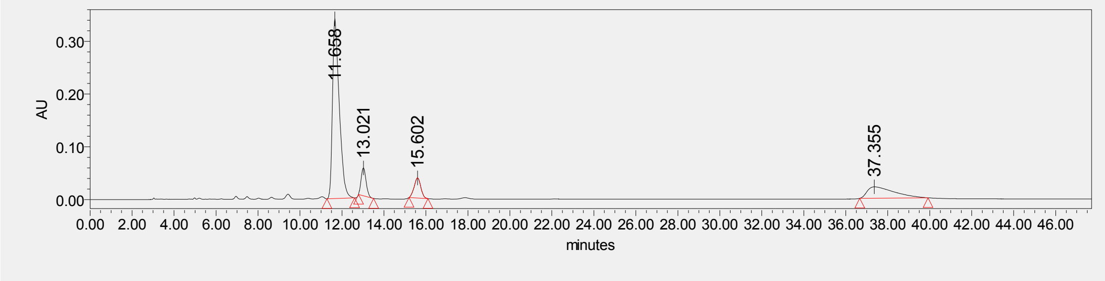


	Retention Time	Area	% Area	Hight
1	12.778	83778	2.21	4574
2	14.351	88305	2.33	3983
3	15.900	1780228	47.03	75405
4	18.107	1832664	48.42	54248

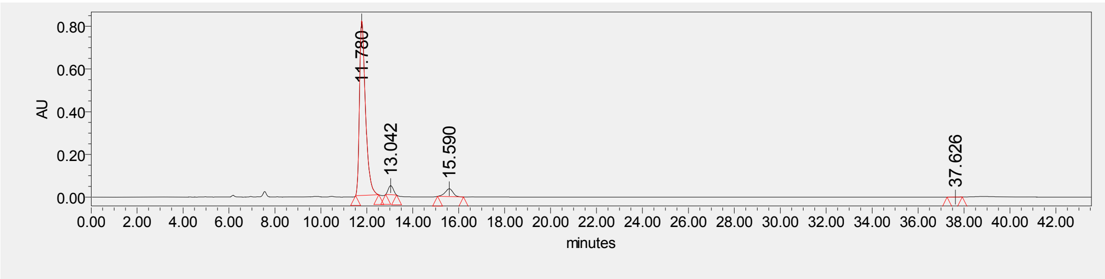


	Retention Time	Area	% Area	Hight
1	12.585	223073	2.06	16121
2	14.116	18329	0.17	1183
3	15.487	10545664	97.61	453462
4	18.289	17057	0.16	742

3l: IA, Hexane/iPrOH = 90/10.
Racemic:

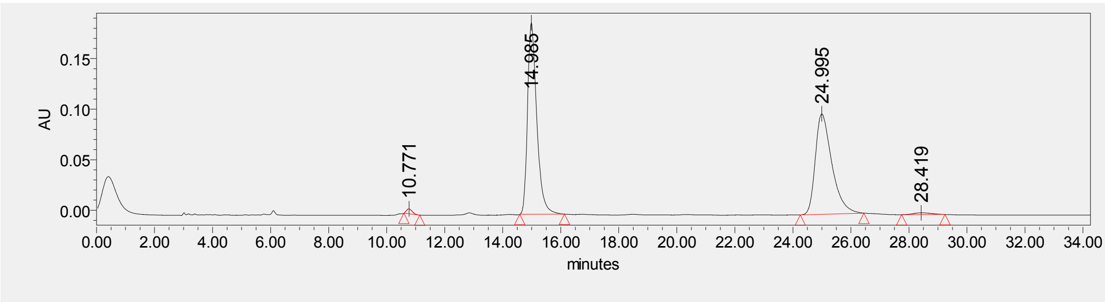


	Retention Time	Area	% Area	Hight
1	11.658	7599640	67.67	340796
2	13.021	861321	7.67	52786
3	15.602	842999	7.51	38068
4	37.355	1927161	17.16	21629

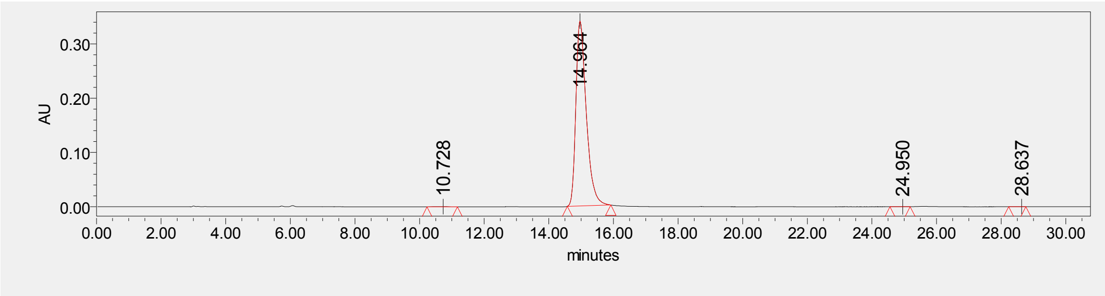


	Retention Time	Area	% Area	Hight
1	11.780	14870368	90.78	817791
2	13.042	637628	3.89	42565
3	15.590	868885	5.30	36783
4	37.626	3210	0.02	-144

3m: IA, Hexane/iPrOH = 90/10.
Racemic:

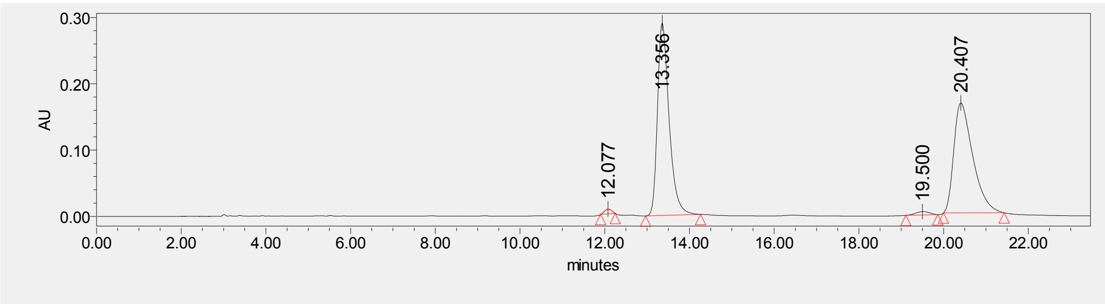


	Retention Time	Area	% Area	Hight
1	10.771	67218	0.81	4913
2	14.985	4187246	50.66	189416
3	24.995	3931926	47.57	99363
4	28.419	79177	0.96	1794

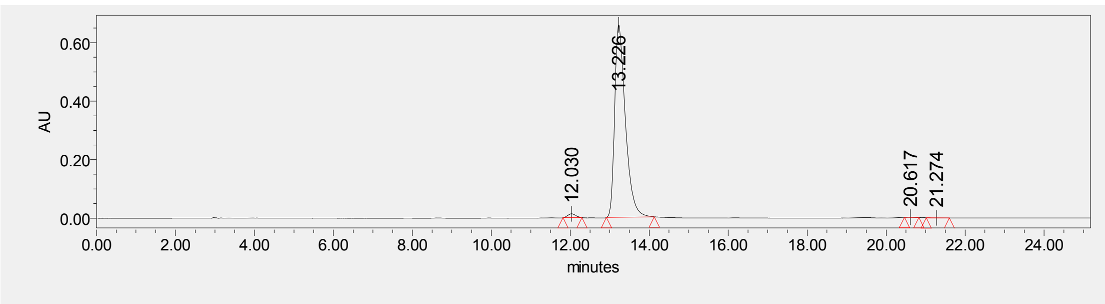


	Retention Time	Area	% Area	Hight
1	10.728	8484	0.11	372
2	14.964	7571624	99.85	340254
3	24.950	2244	0.03	-102
4	28.637	571	0.01	50

3n: IA, Hexane/iPrOH = 90/10.
Racemic:

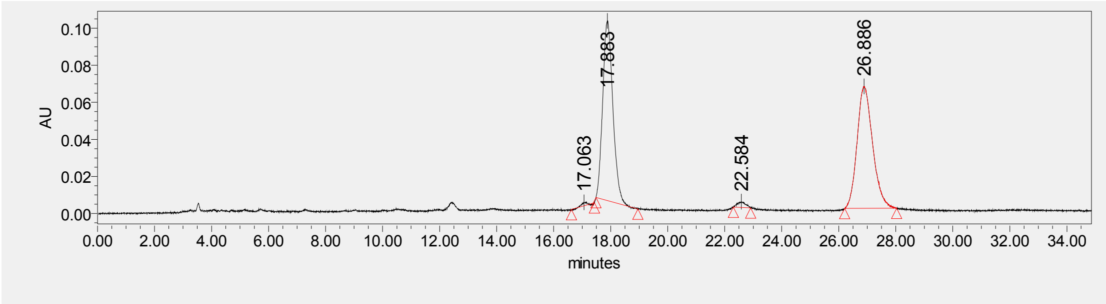


	Retention Time	Area	% Area	Hight
1	12.077	85018	0.78	7248
2	13.356	5528687	50.80	290149
3	19.500	115385	1.06	5125
4	20.407	5153938	47.36	165824

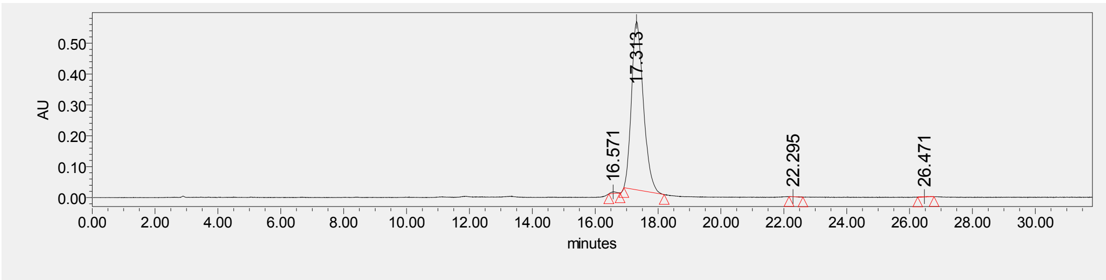


	Retention Time	Area	% Area	Hight
1	12.030	184529	1.46	13075
2	13.226	12440997	98.43	657827
3	20.617	8702	0.07	640
4	21.274	5058	0.04	-243

3o: IA, Hexane/iPrOH = 90/10.
Racemic:

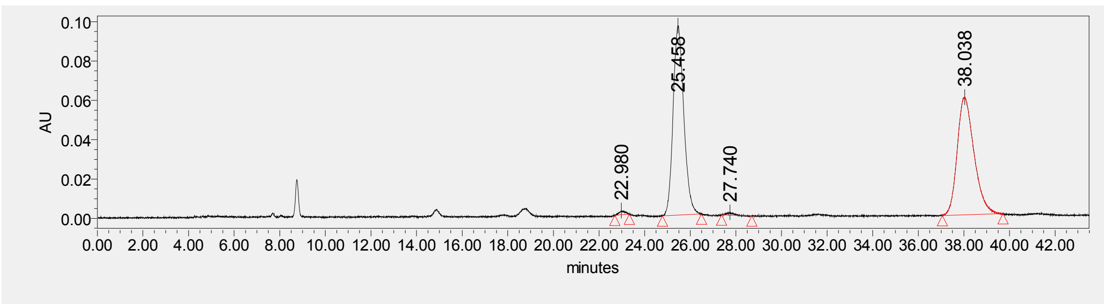


	Retention Time	Area	% Area	Hight
1	17.063	32029	0.64	1893
2	17.883	2401678	48.13	97019
3	22.584	61798	1.24	3130
4	26.886	2494481	49.99	65825

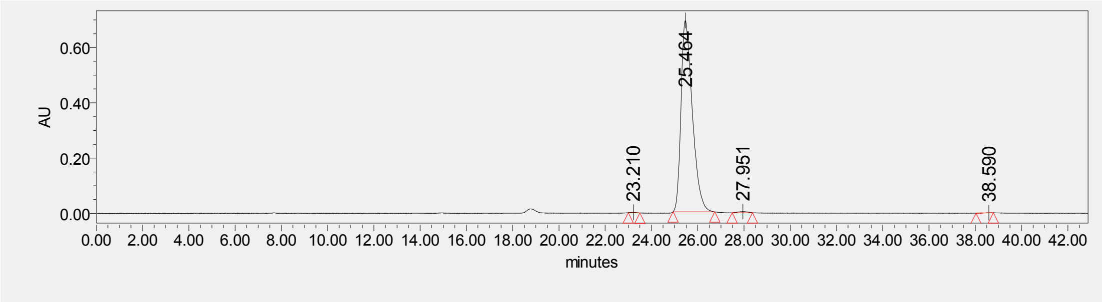


	Retention Time	Area	% Area	Hight
1	16.571	64005	0.45	5421
2	17.313	14270785	99.48	545316
3	22.295	3338	0.02	443
4	26.471	7400	0.05	805

3p: IA, Hexane/iPrOH = 90/10.
Racemic:

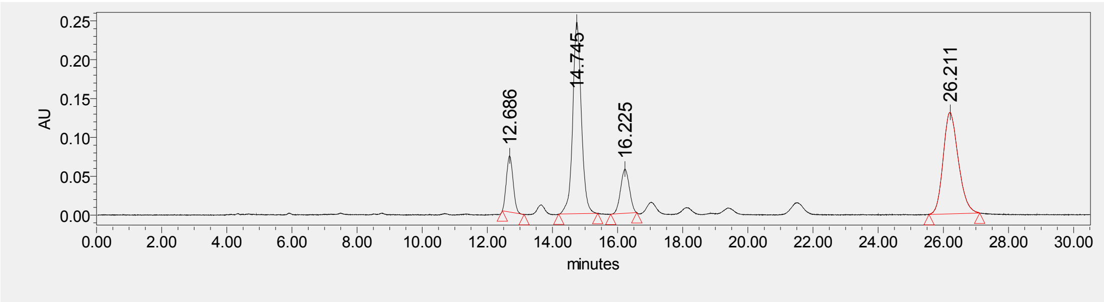


	Retention Time	Area	% Area	Hight
1	22.980	34632	0.55	2110
2	25.458	3133277	49.99	96288
3	27.740	30232	0.48	1476
4	38.038	3070017	48.98	59799

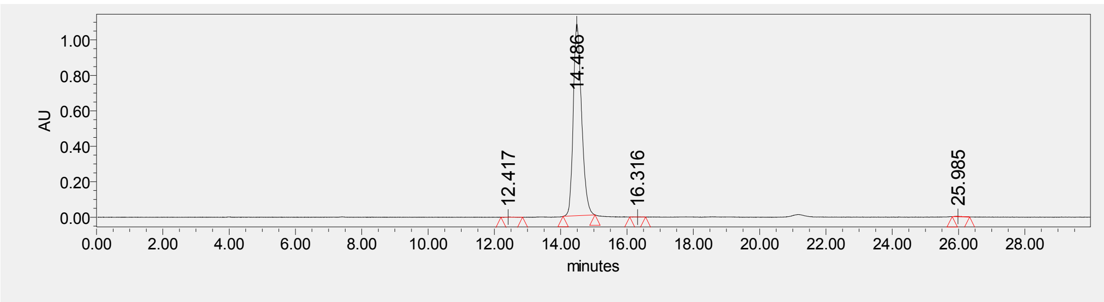


	Retention Time	Area	% Area	Hight
1	23.210	31033	0.13	1949
2	25.464	23525574	99.33	692150
3	27.951	117587	0.50	4255
4	38.590	10132	0.04	775

3q: IA, Hexane/iPrOH = 90/10.
Racemic:

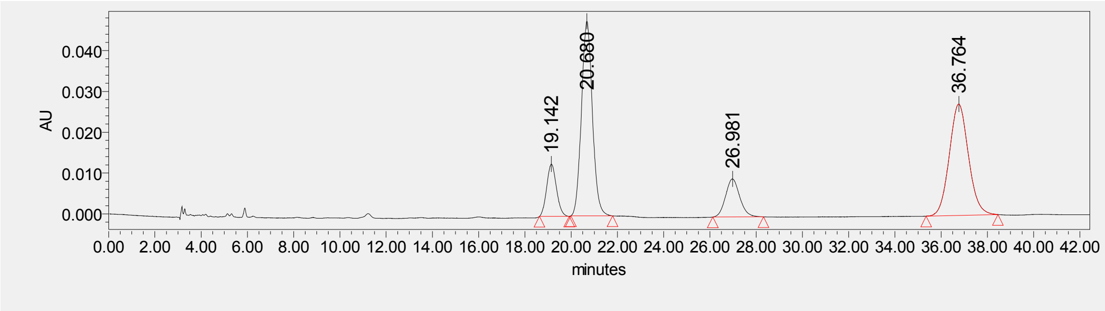


	Retention Time	Area	% Area	Hight
1	12.686	1030258	9.52	72443
2	14.745	4506087	41.63	246635
3	16.225	1065515	9.84	57031
4	26.211	4223062	39.01	130659

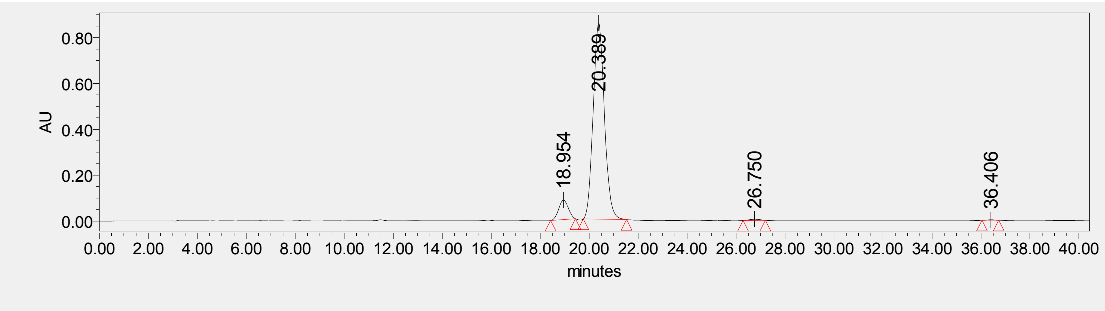


	Retention Time	Area	% Area	Hight
1	12.417	12585	0.07	849
2	14.486	18835273	99.77	1081932
3	16.316	4572	0.02	-615
4	25.985	25339	0.13	1879

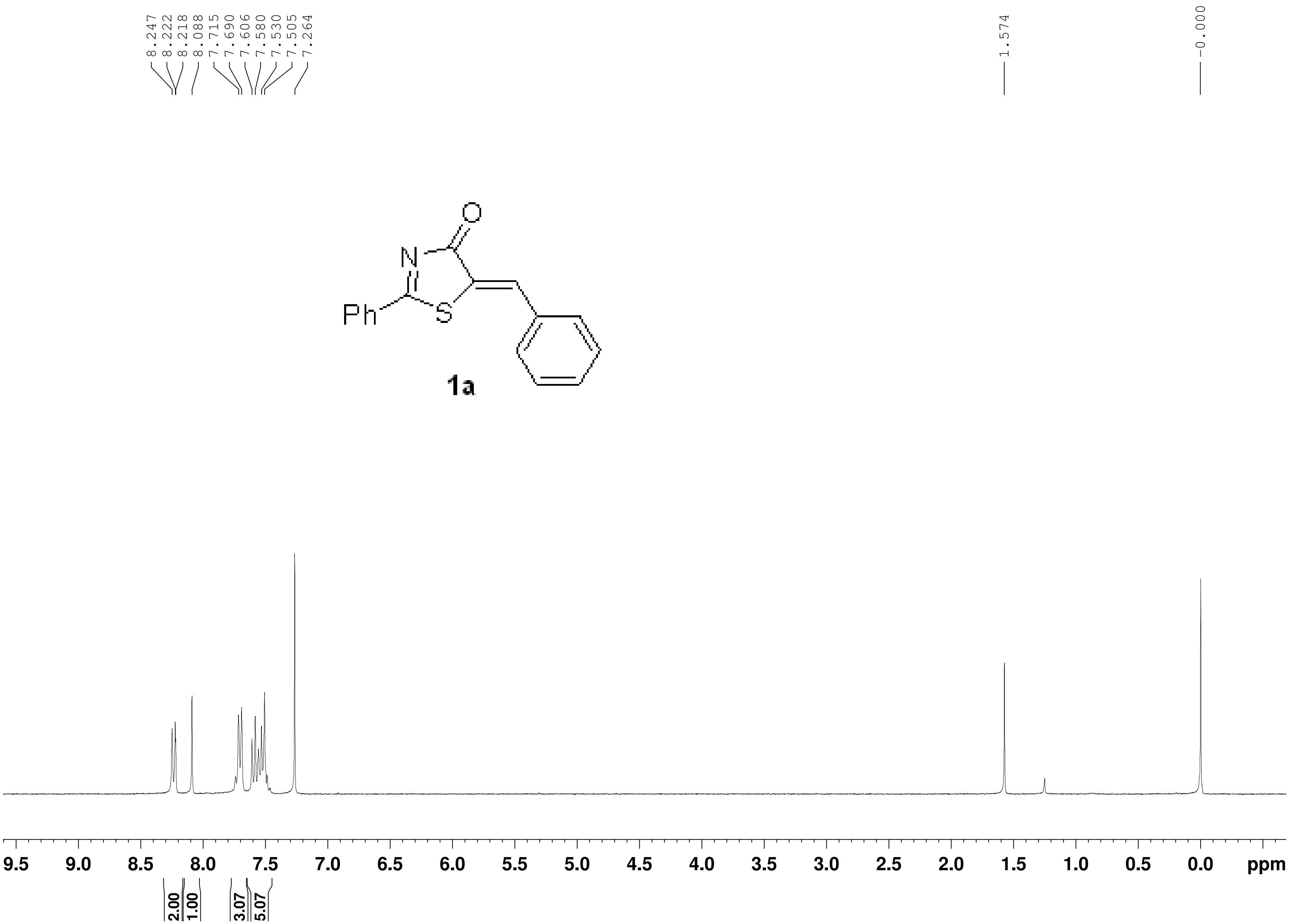
3r: IA, Hexane/iPrOH = 90/10.
Racemic:

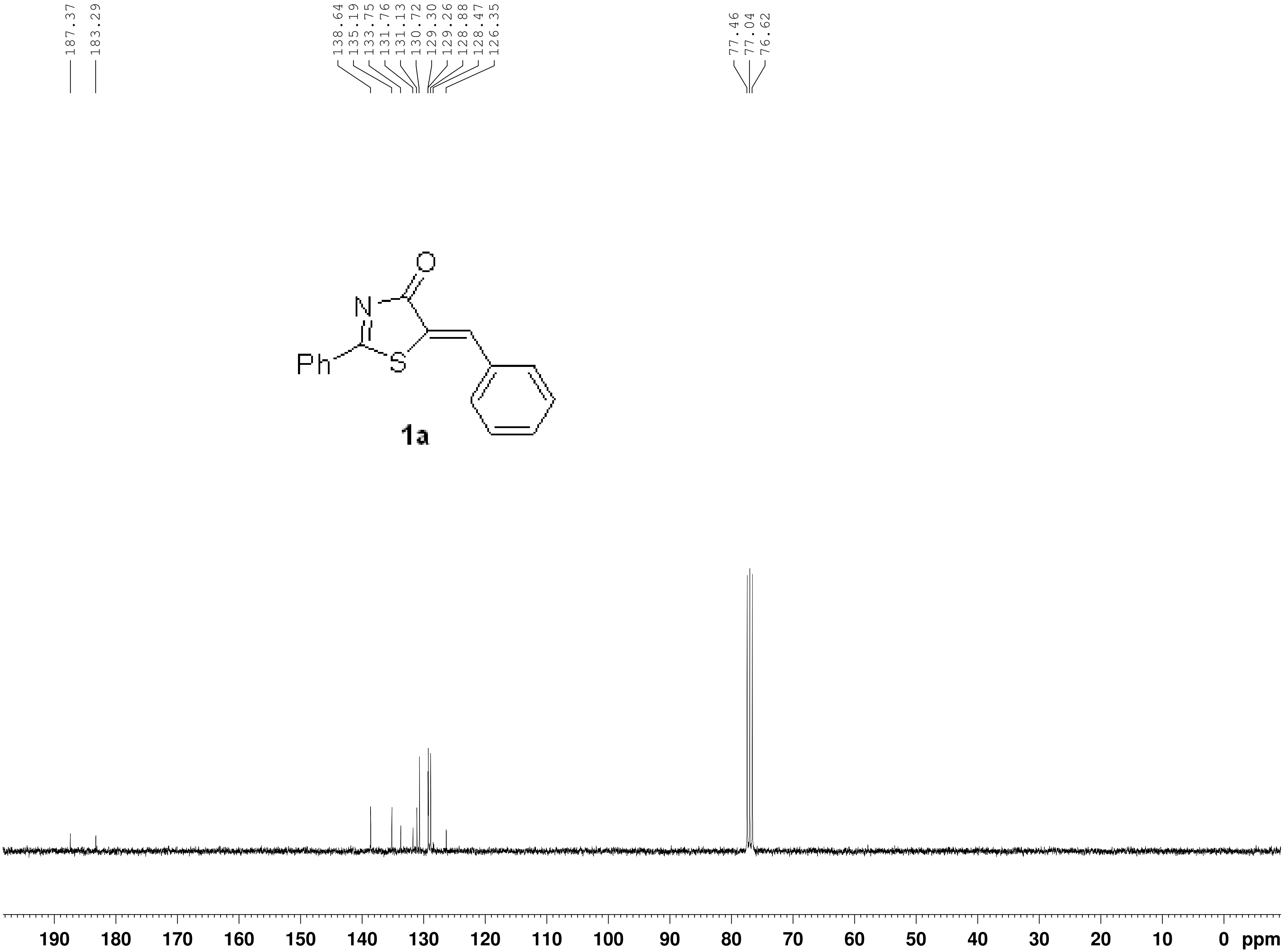


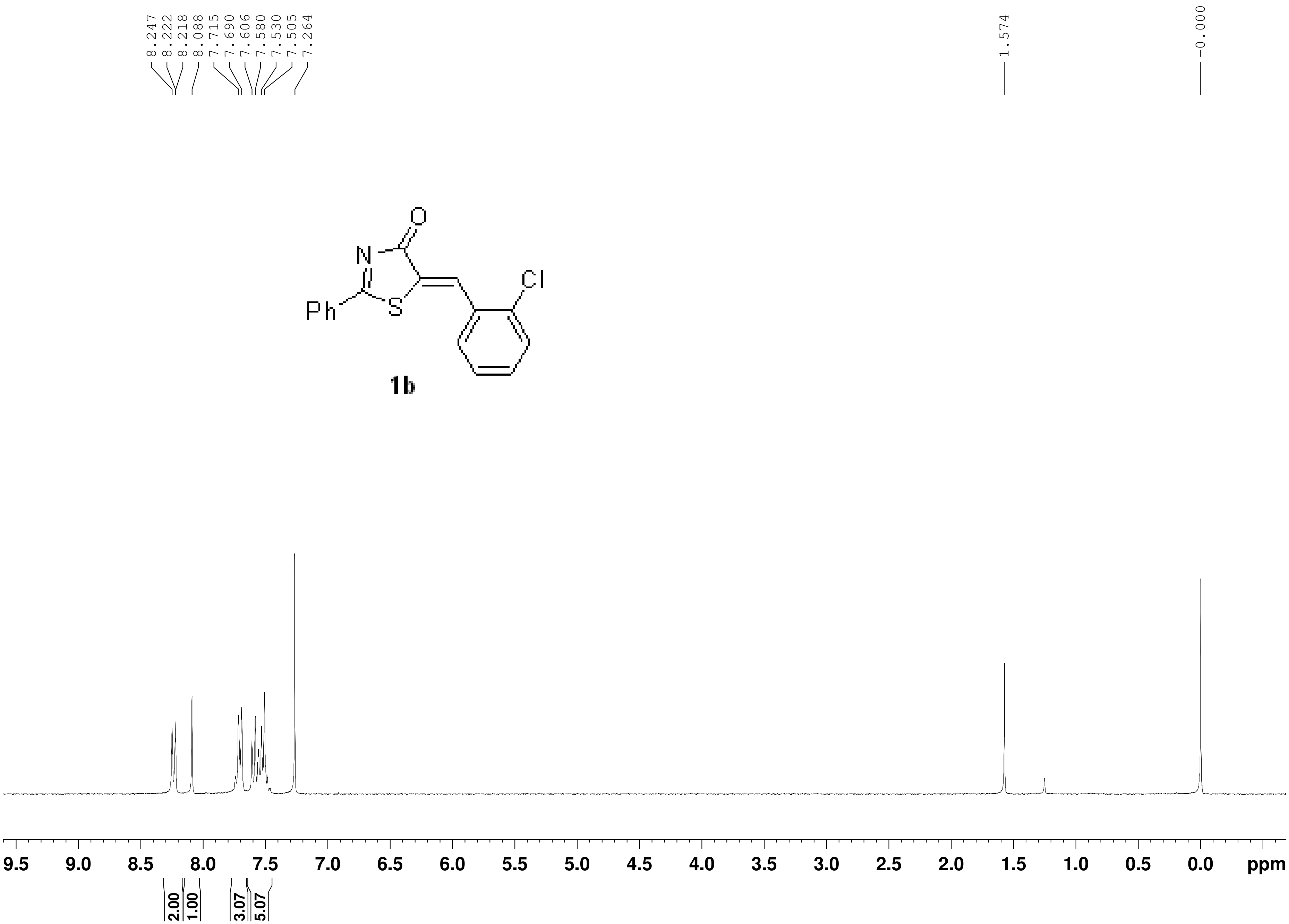
	Retention Time	Area	% Area	Hight
1	19.142	375074	9.58	12812
2	20.680	1566927	40.03	47646
3	26.981	397485	10.15	9322
4	36.764	1574742	40.23	27273

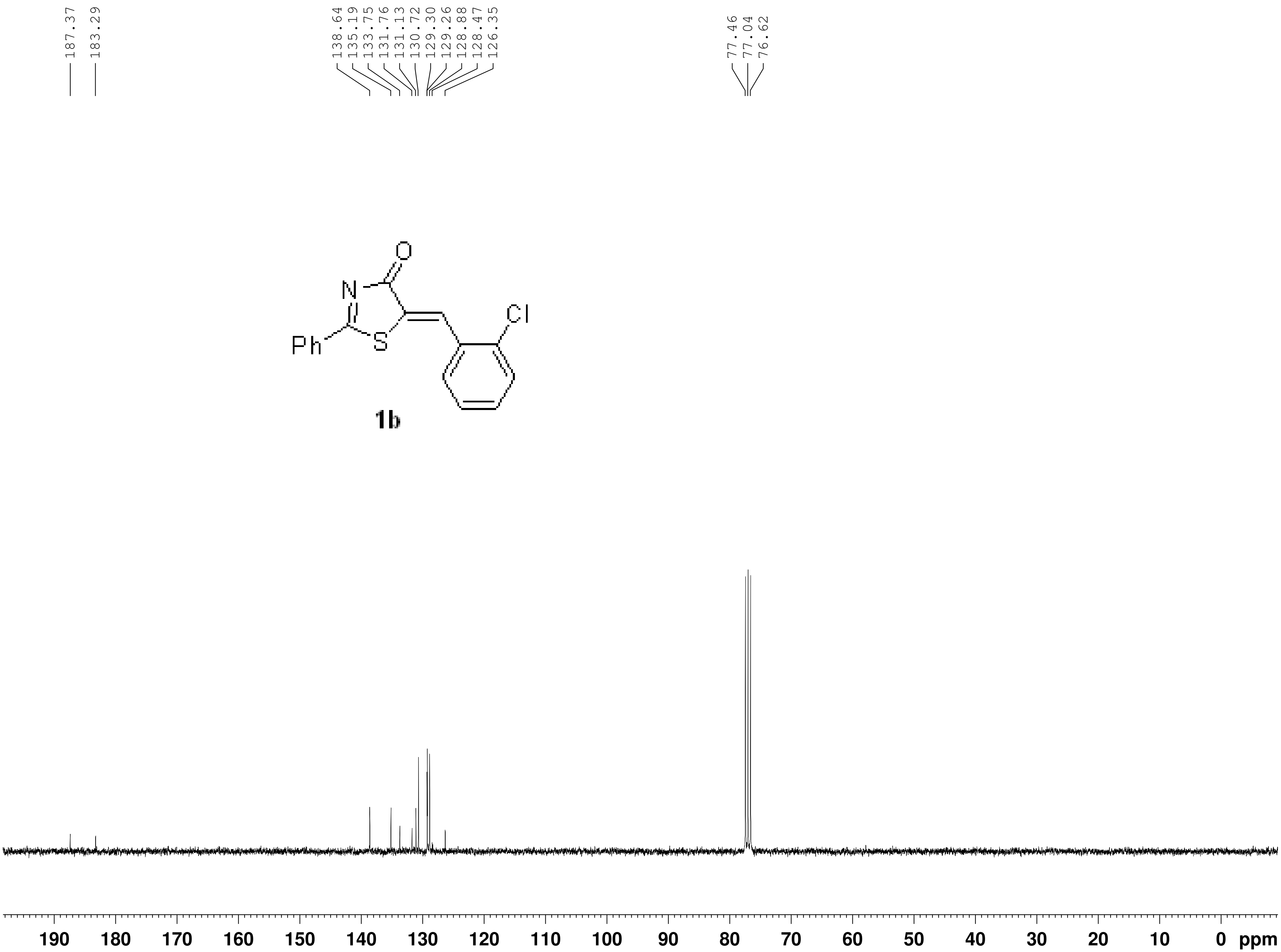


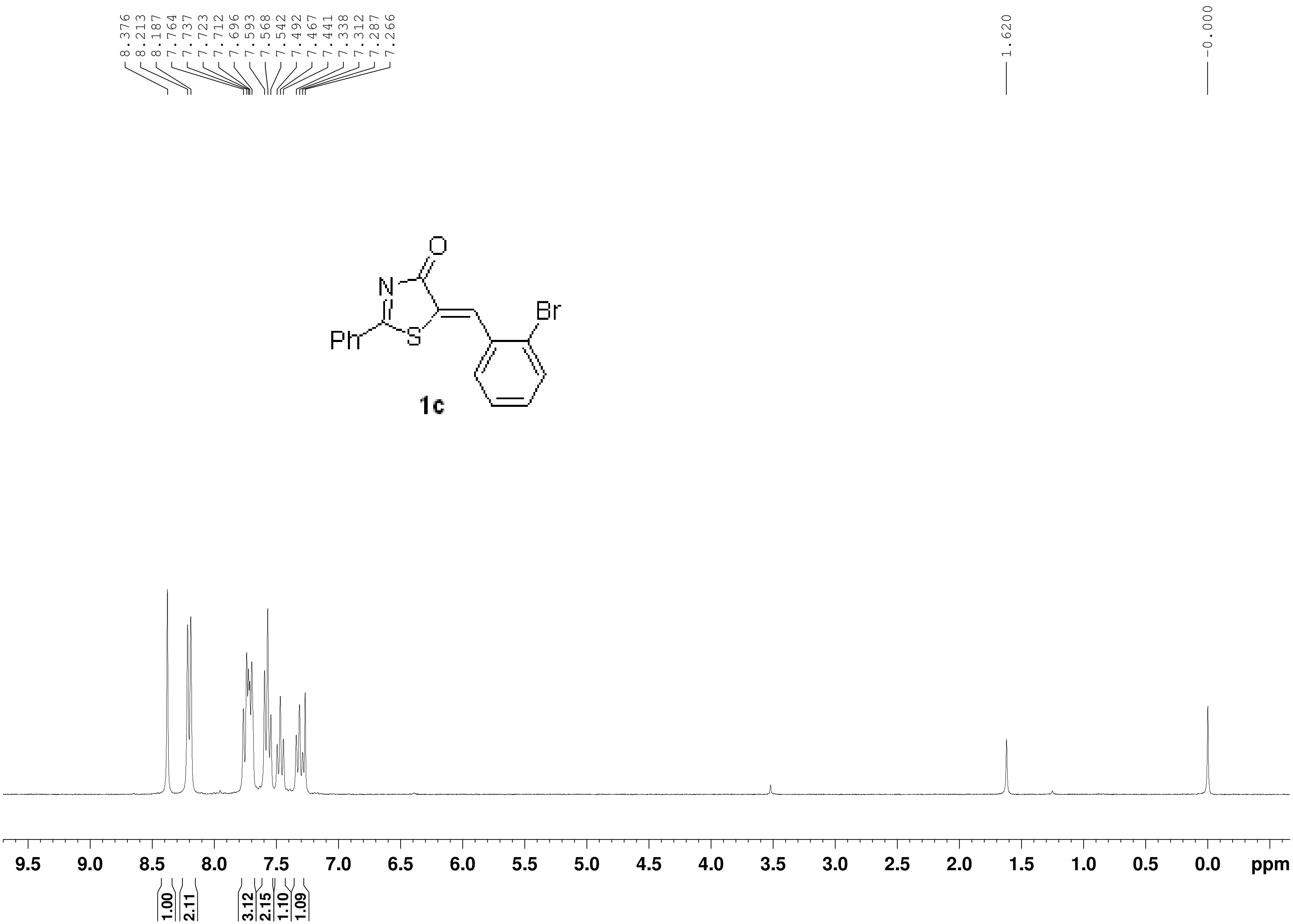
	Retention Time	Area	% Area	Hight
1	18.954	2315741	7.78	85201
2	20.389	27279967	91.62	855839
3	26.750	146379	0.49	4732
4	36.406	32356	0.11	1242

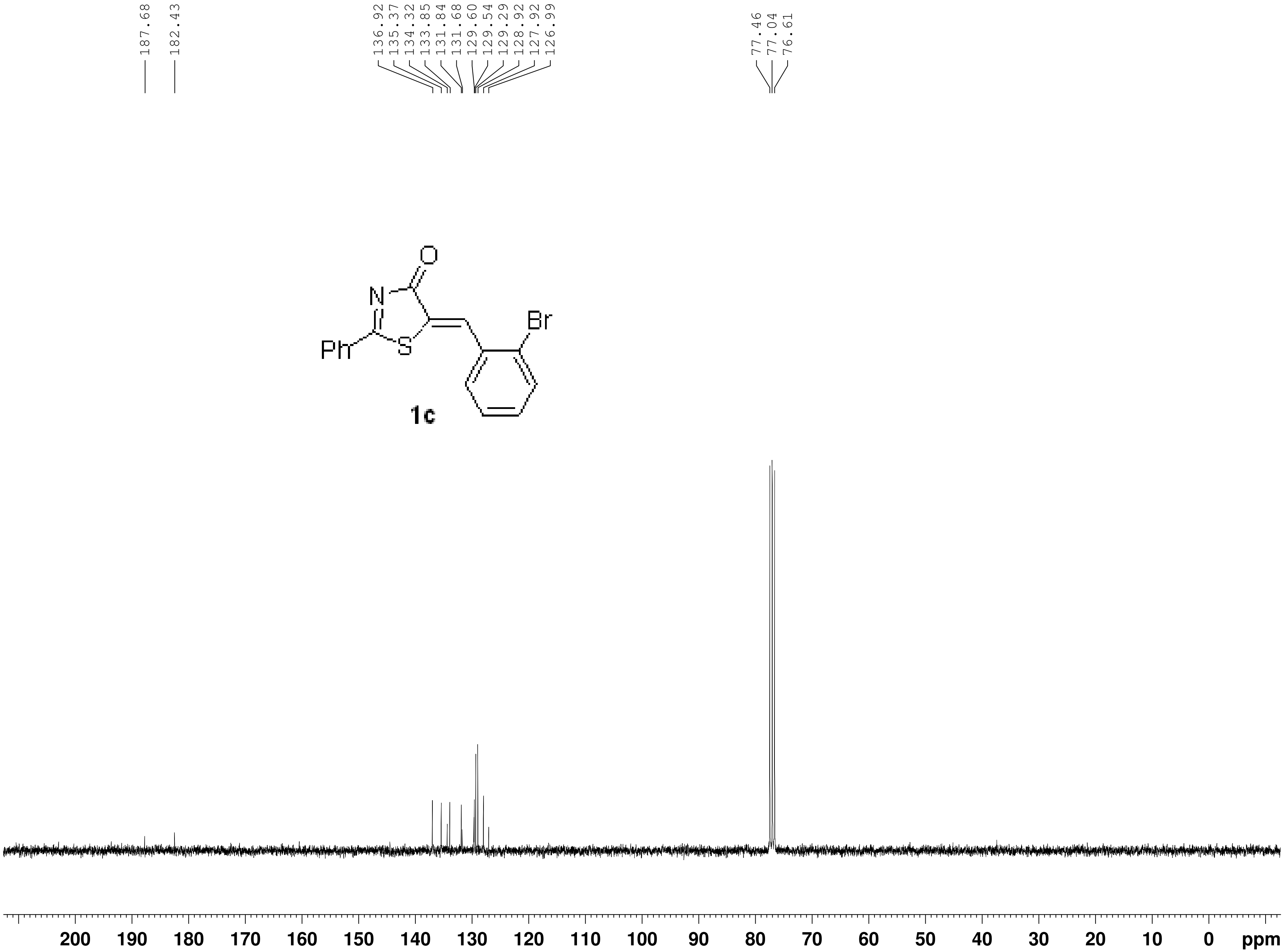

8.247
8.222
8.218
8.088
7.715
7.690
7.606
7.580
7.530
7.505
7.264
1.574
-0.000
O
N
Ph
S
1a
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.00
1.00
3.07
5.07

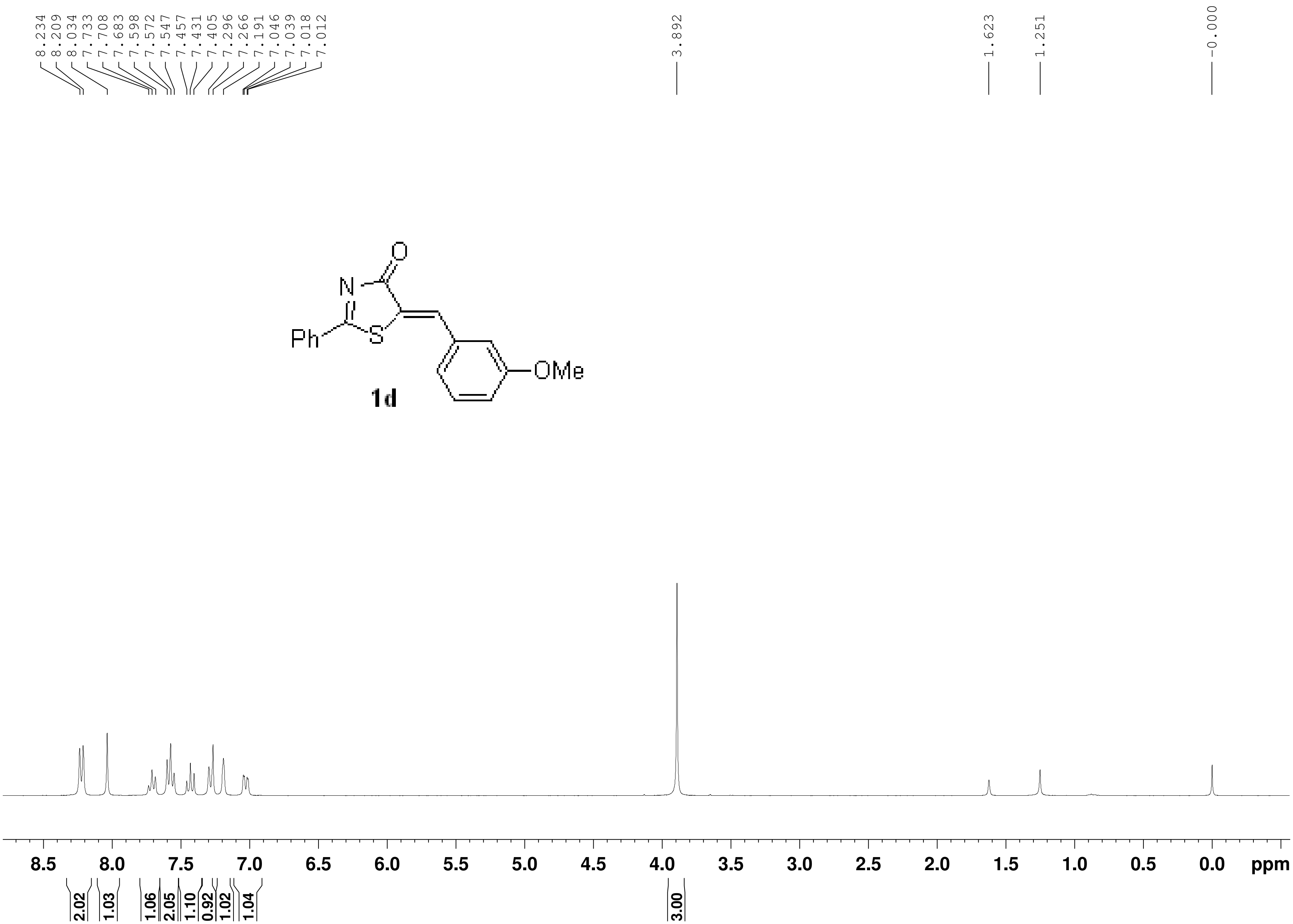

187.37
183.29
138.64
135.19
133.75
131.76
131.13
130.72
129.30
129.26
128.88
128.47
126.35
77.46
77.04
76.62
O
N
S
Ph
1a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

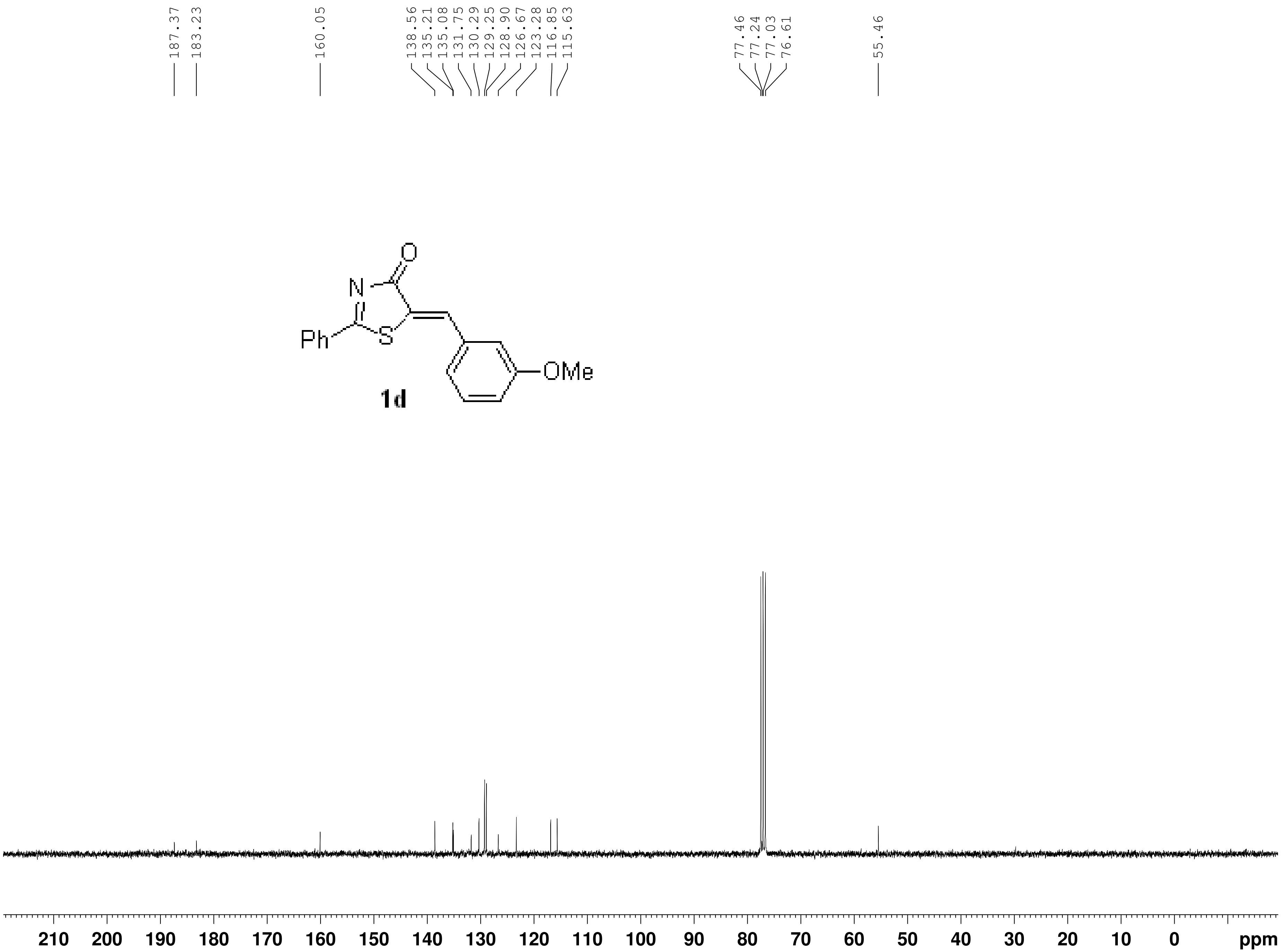

8.247
8.222
8.218
8.088
7.715
7.690
7.606
7.580
7.530
7.505
7.264
1.574
-0.000
O
N
S
Ph
Cl
1b
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.00
1.00
3.07
5.07


187.37
183.29
138.64
135.19
133.75
131.76
131.13
130.72
129.30
129.26
128.88
128.47
126.35
77.46
77.04
76.62
1b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.376
8.213
8.187
7.764
7.737
7.723
7.712
7.696
7.593
7.568
7.542
7.492
7.467
7.441
7.338
7.312
7.287
7.266
1.620
-0.000
O
N
S
Ph
Br
1c
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 ppm
1.00
2.11
3.12
2.15
1.10
1.09


187.68
182.43
136.92
135.37
134.32
133.85
131.84
131.68
129.60
129.54
129.29
129.29
128.92
127.92
126.99
77.46
77.04
76.61
O
N
Br
Ph
S
1c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


8.234
8.209
8.034
7.733
7.708
7.683
7.598
7.572
7.547
7.457
7.431
7.405
7.296
7.266
7.191
7.046
7.039
7.018
7.012
3.892
1.623
1.251
-0.000
O
N
Ph
S
OMe
1d
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
ppm
2.02
1.03
1.06
2.05
1.10
0.92
1.02
1.04
3.00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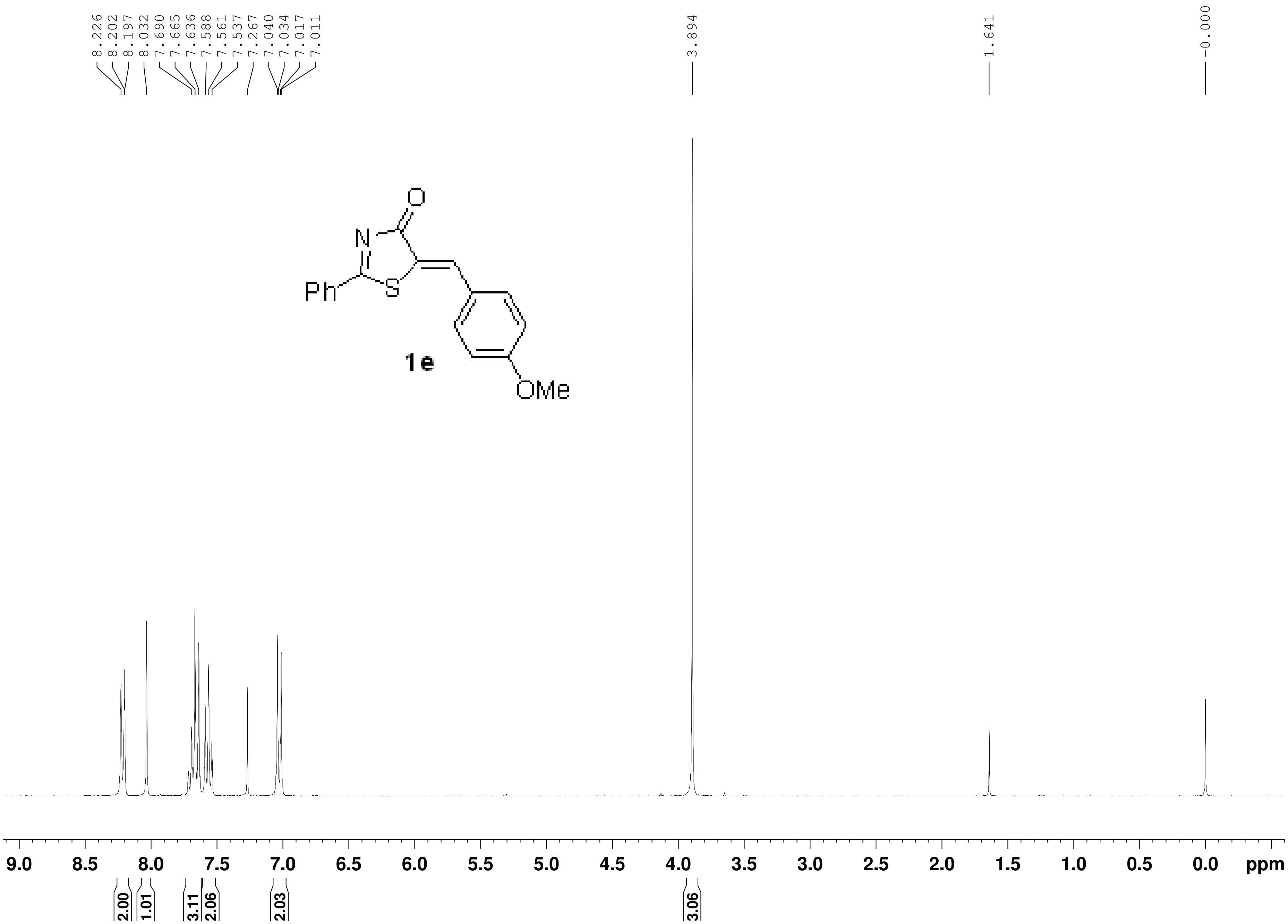
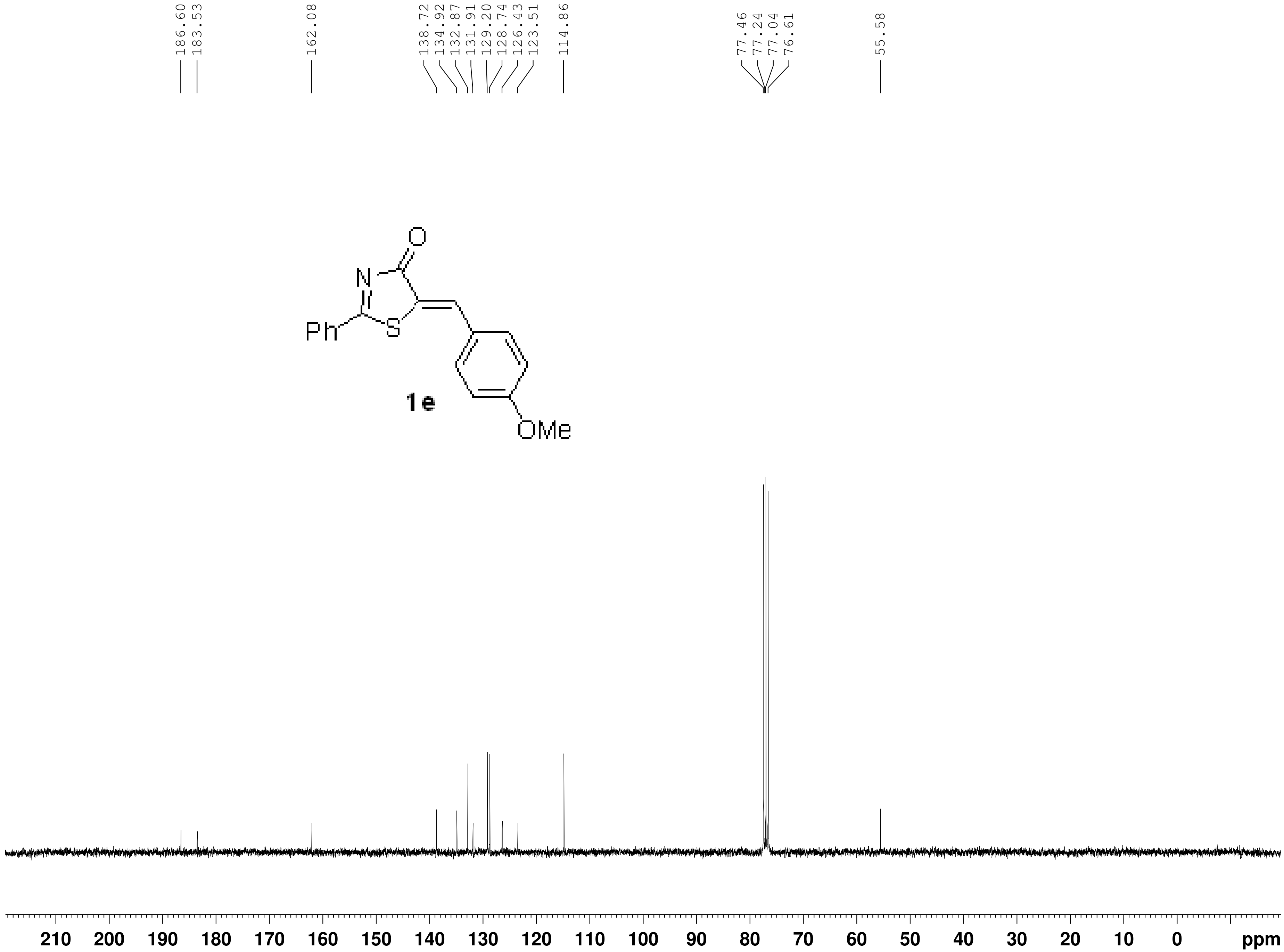
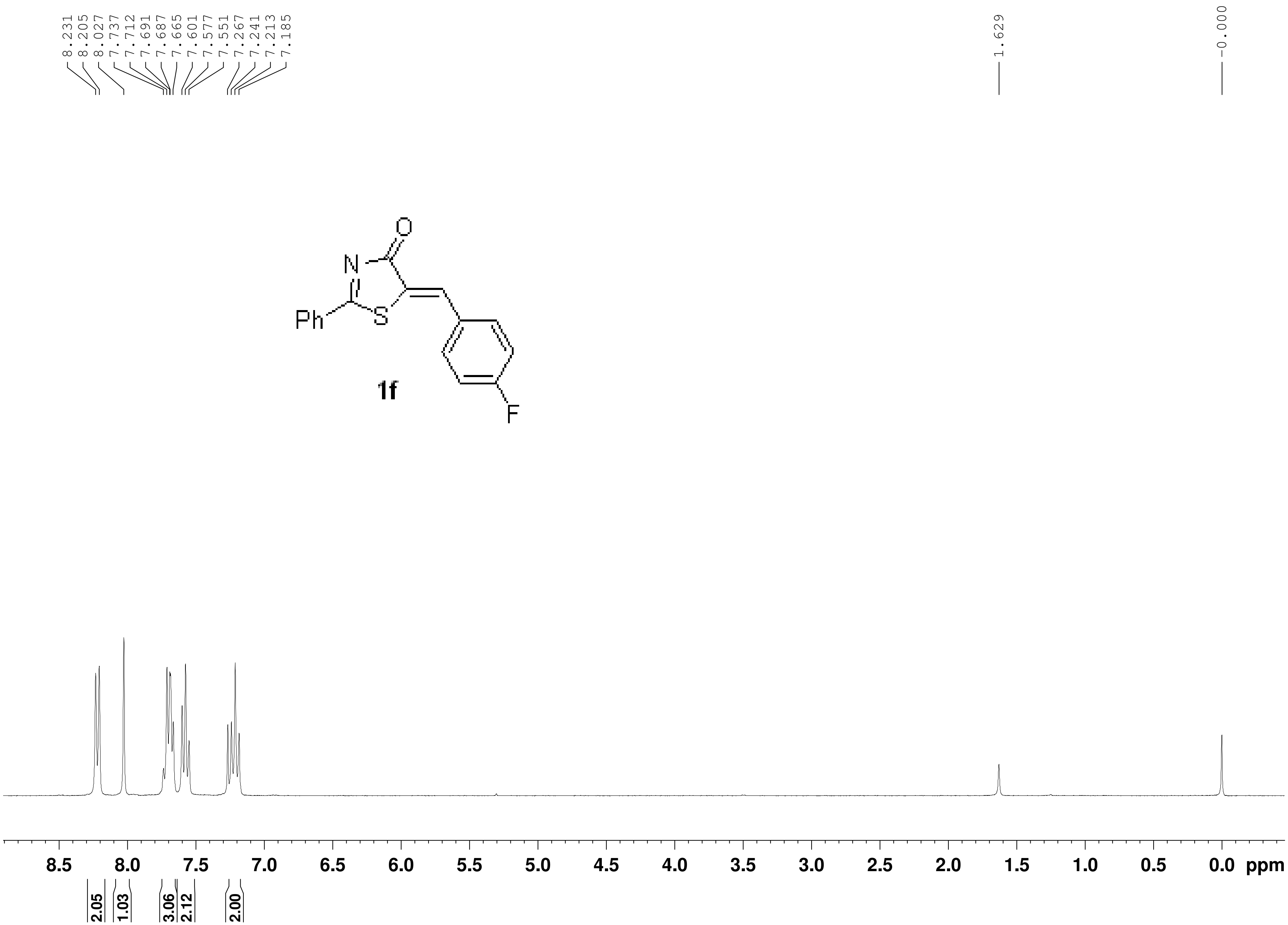
183.23
160.05
138.56
135.21
135.08
131.75
130.29
129.25
128.90
126.67
123.28
116.85
115.63
77.46
77.24
77.03
76.61
55.46
N
O
S
Ph
OMe
1d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

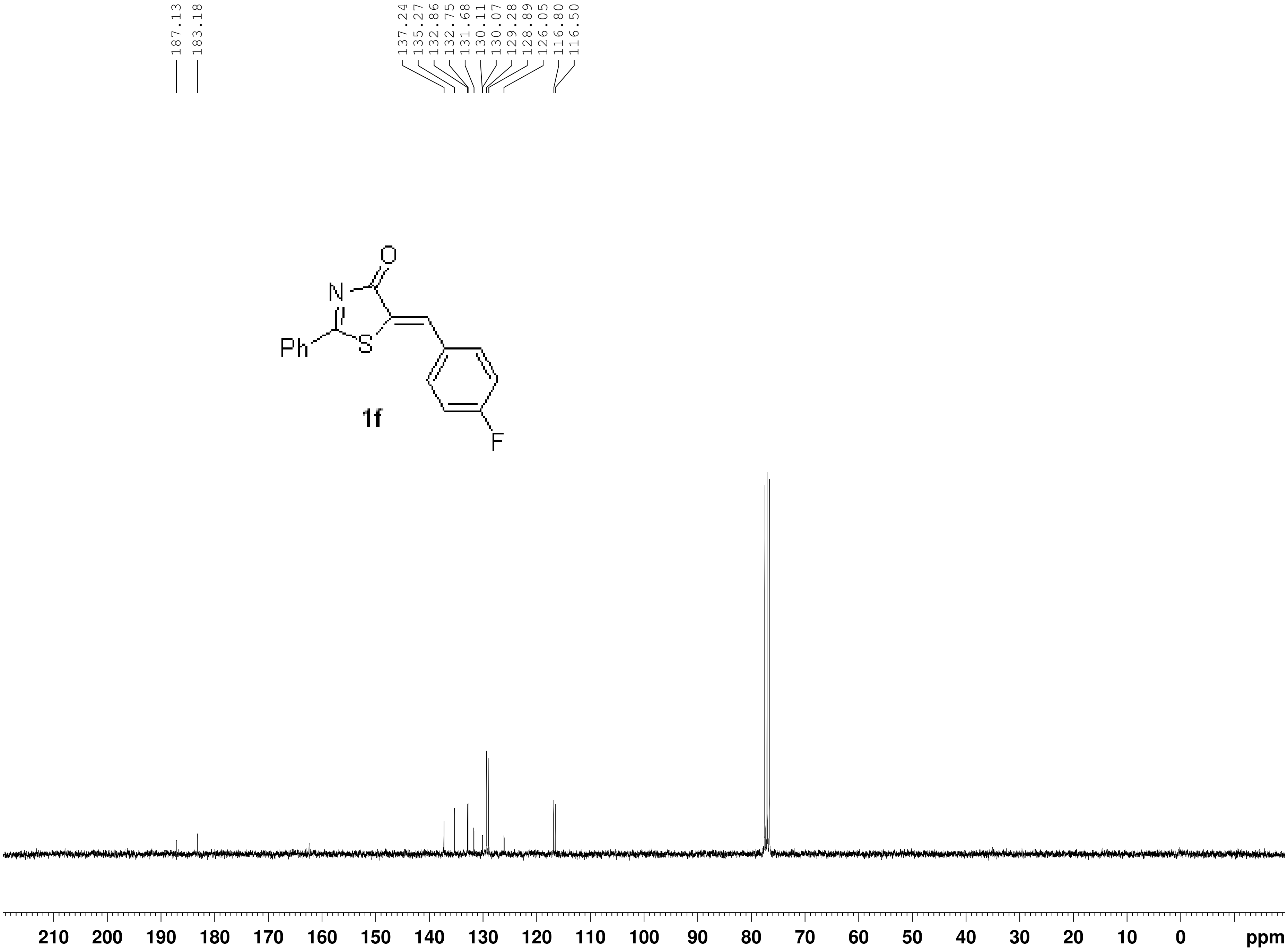

8.226
8.202
8.197
8.032
7.690
7.665
7.636
7.588
7.561
7.537
7.267
7.040
7.034
7.017
7.011
3.894
1.641
-0.000
O
N
Ph
S
1e
OMe
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.00
1.01
3.11
2.06
2.03
3.06


186.60
183.53
162.08
138.72
134.92
132.87
131.91
129.20
128.74
126.43
123.51
114.86
77.46
77.24
77.04
76.61
55.58
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

1e



8.231
8.205
8.027
7.737
7.712
7.691
7.687
7.665
7.601
7.577
7.551
7.267
7.241
7.213
7.185
1.629
-0.000
O
N
Ph
S
F
1f
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 ppm
2.05
1.03
3.06
2.12
2.00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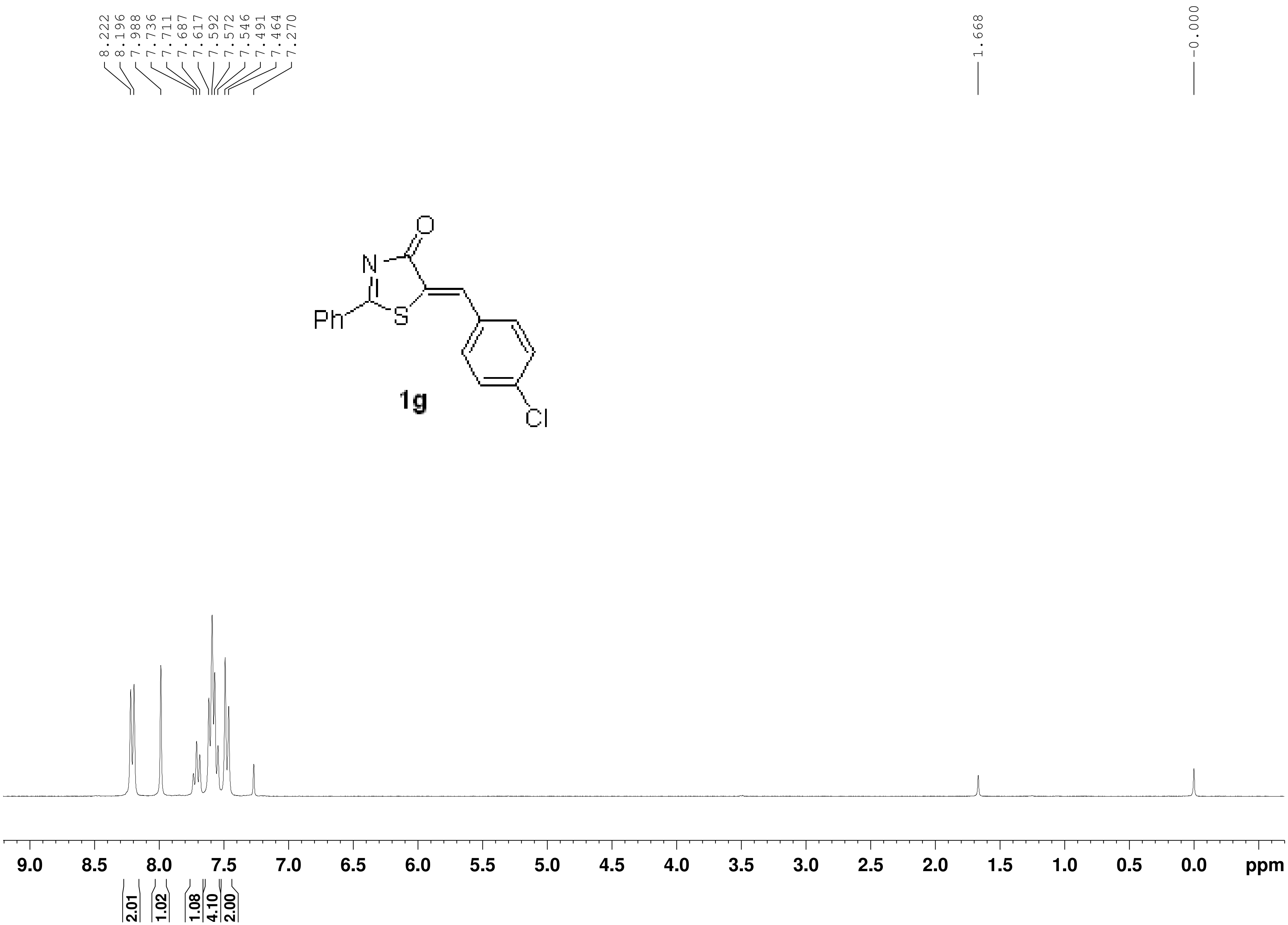
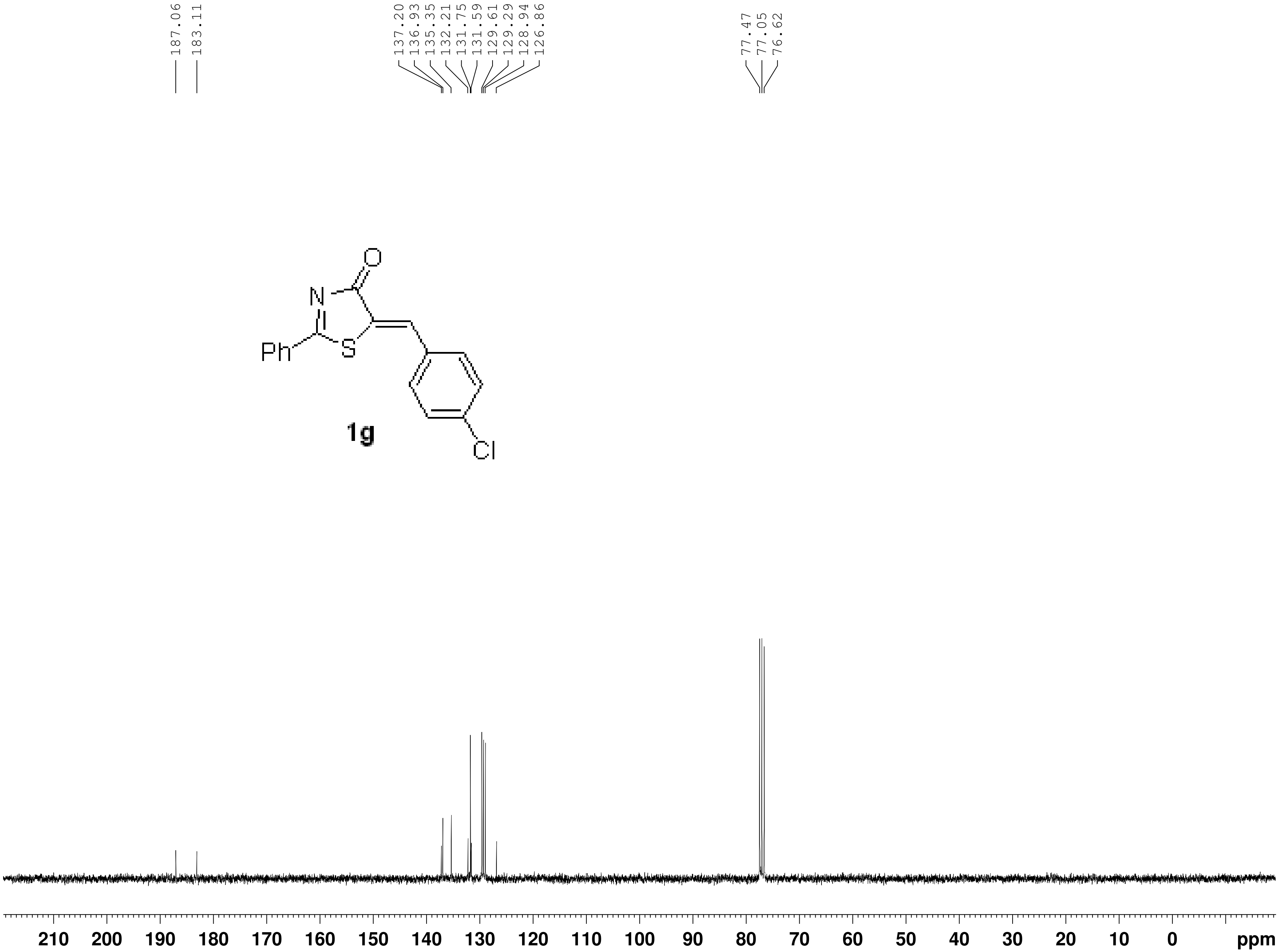
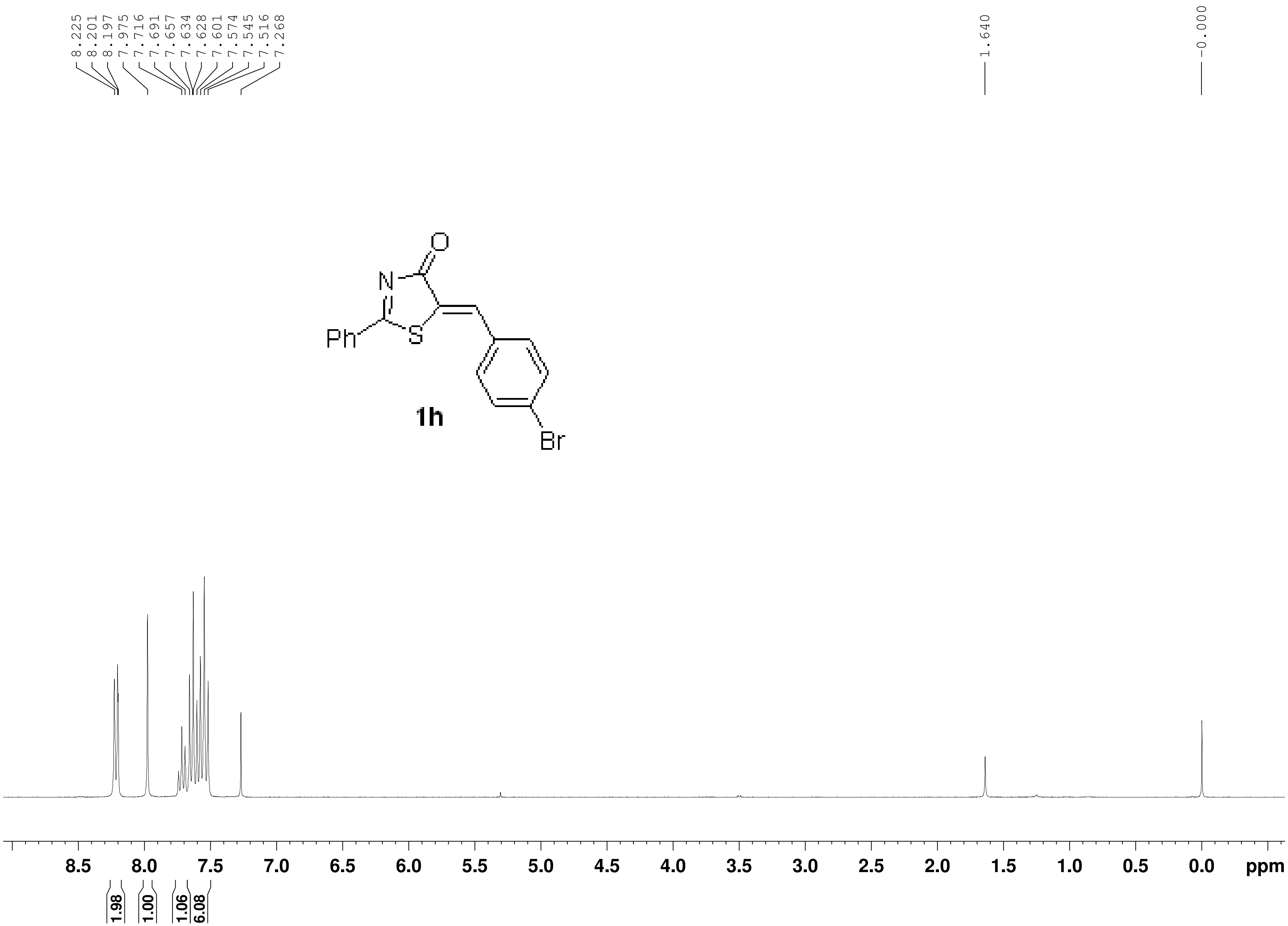
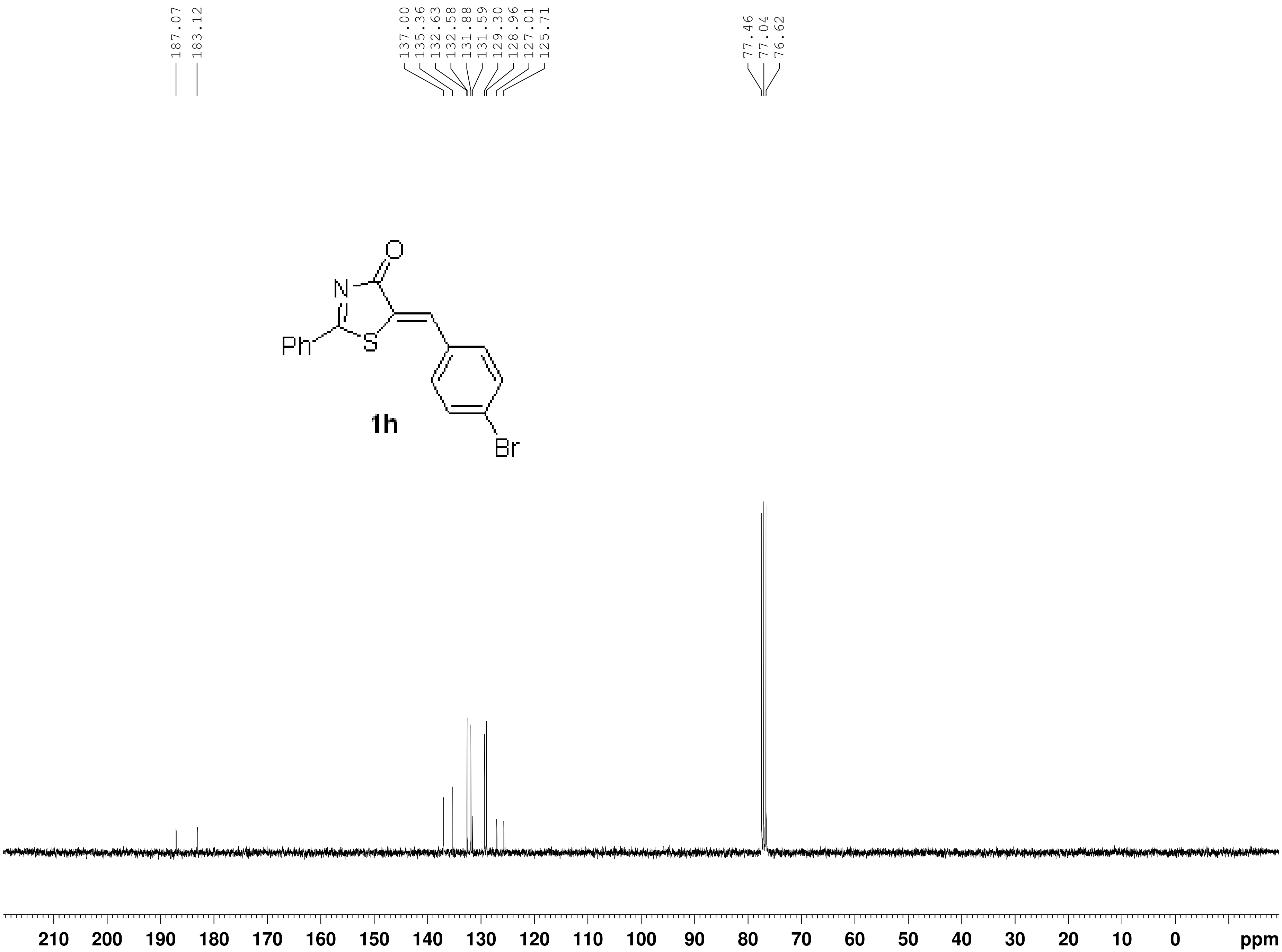
183.18
137.24
135.27
132.86
132.75
131.68
130.11
130.07
129.28
128.89
126.05
116.80
116.50
O
N
Ph
S
F
1f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.222
8.196
7.988
7.736
7.711
7.687
7.617
7.592
7.572
7.546
7.491
7.464
7.270
1.668
-0.000
O
N
Ph
S
Cl
1g
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 ppm
2.01
1.02
1.08
4.10
2.00


187.06
183.11
137.20
136.93
135.35
132.21
131.75
131.59
129.61
129.29
128.94
126.86
77.47
77.05
76.62
O
N
Ph
S
Cl
1g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.225
8.201
8.197
7.975
7.716
7.691
7.657
7.634
7.628
7.601
7.574
7.545
7.516
7.268
1.640
-0.000
O
N
Ph
S
Br
1h
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
ppm
1.98
1.00
1.06
6.08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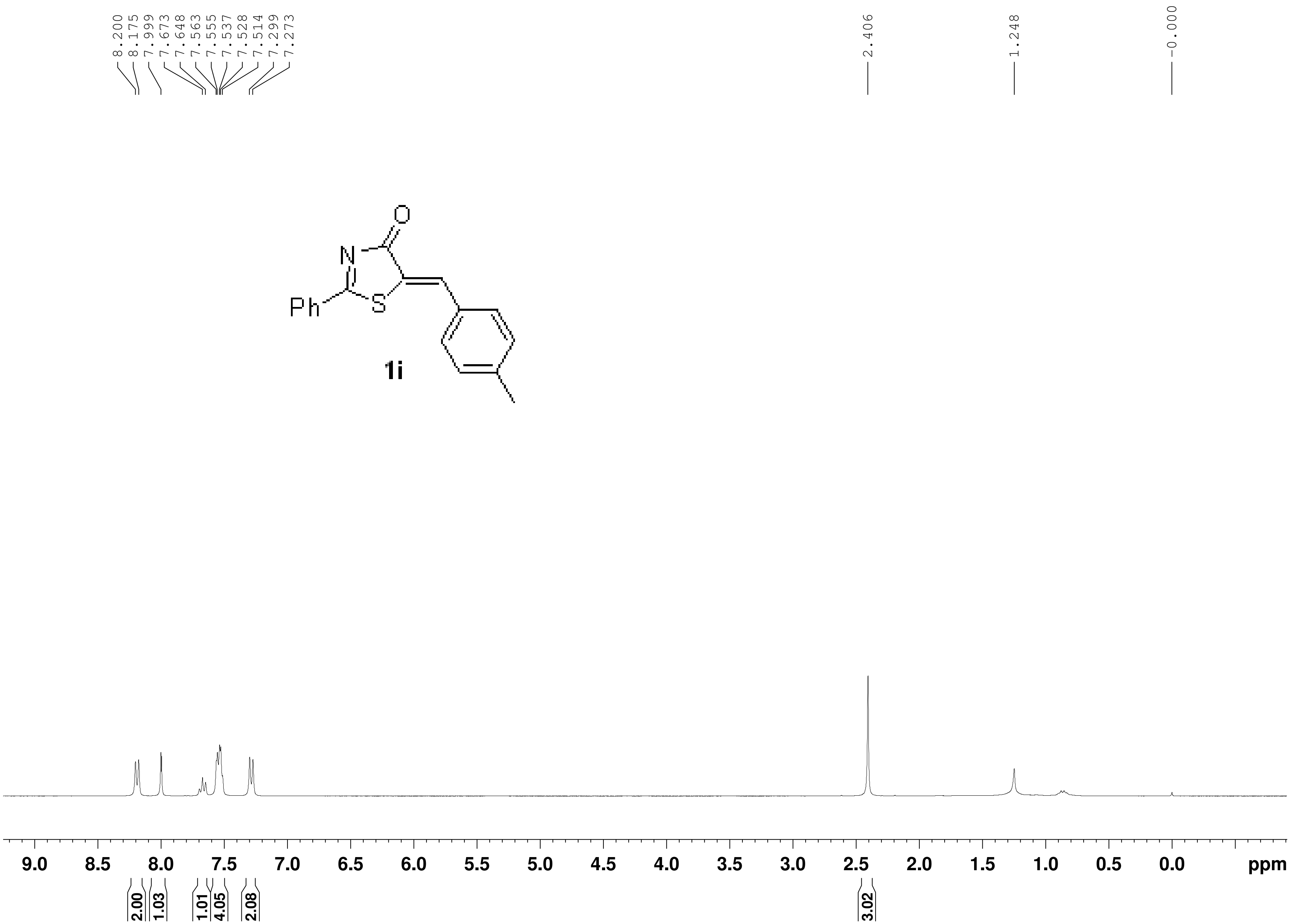
183.12
137.00
135.36
132.63
132.58
131.88
131.59
129.30
128.96
127.01
125.71
77.46
77.04
76.62
O
N
S
Ph
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

1h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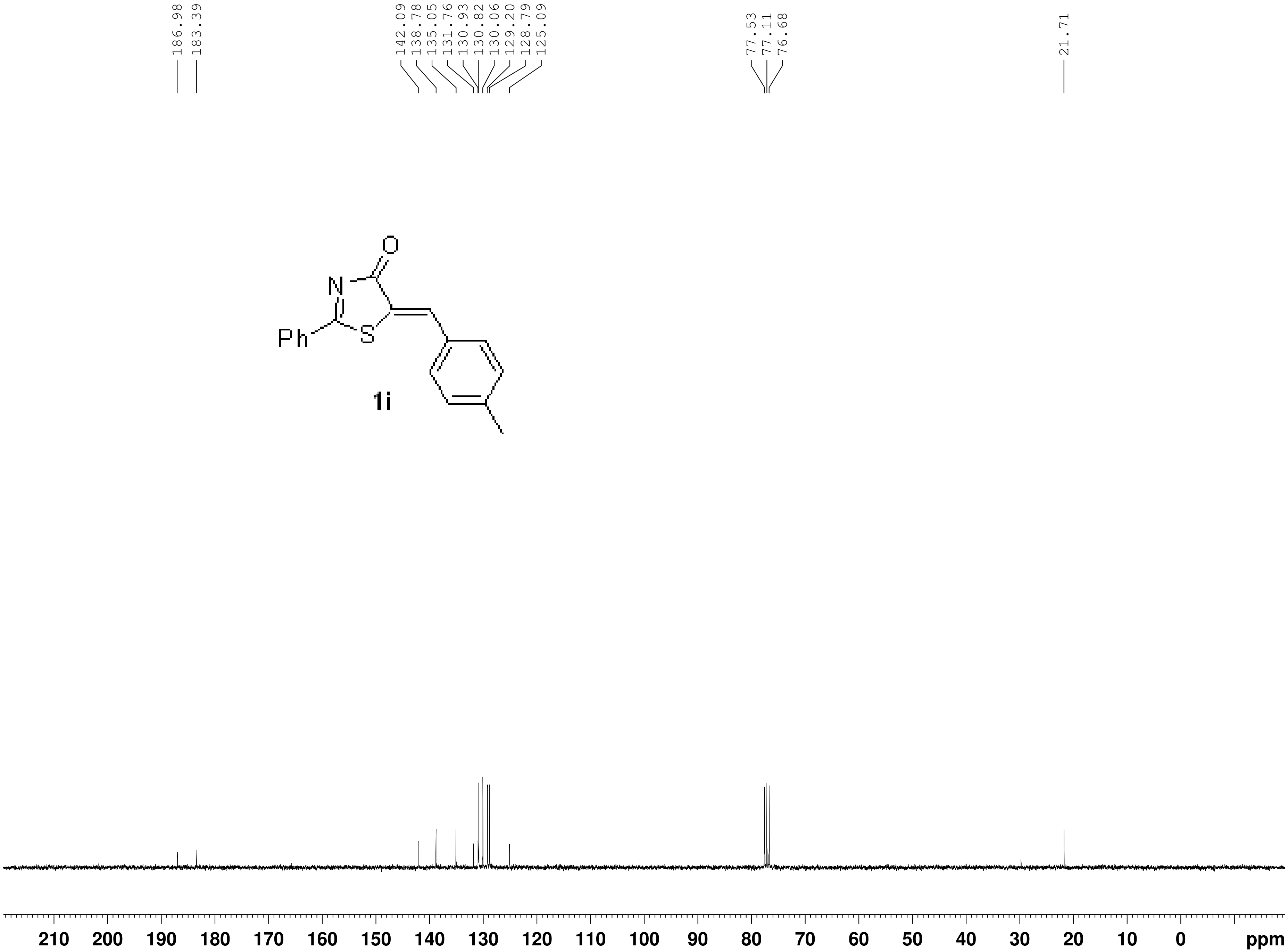
8.175
7.999
7.673
7.648
7.563
7.555
7.537
7.528
7.514
7.299
7.273
2.406
1.248
-0.000
O
N
Ph
S
1i
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.00
1.03
1.01
4.05
2.08
3.02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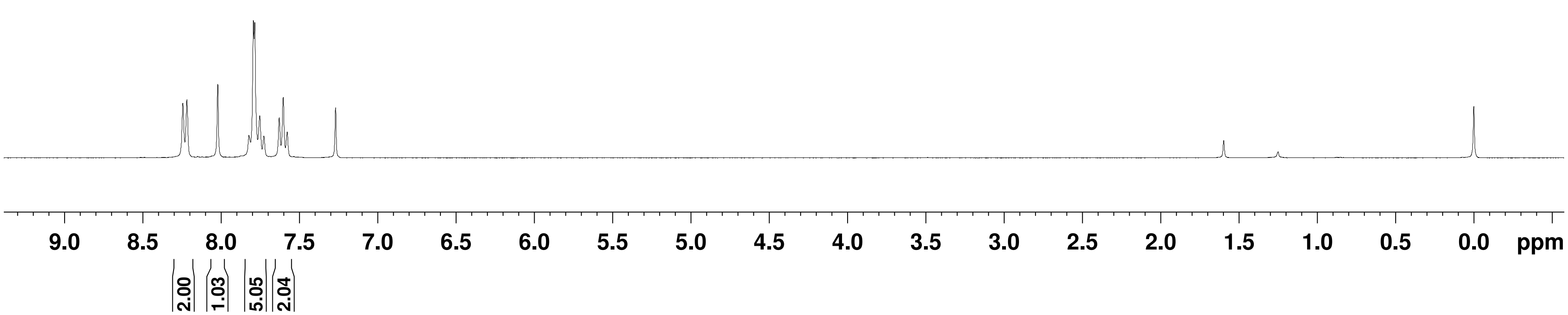
142.09
138.78
135.05
131.76
130.93
130.82
130.06
129.20
128.79
125.09
77.53
77.11
76.68
21.71
O
N
Ph
S
1i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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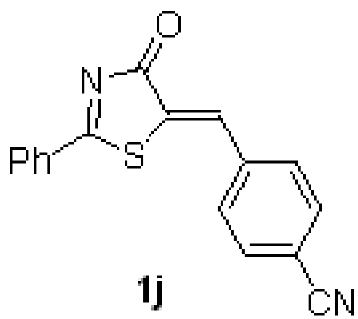
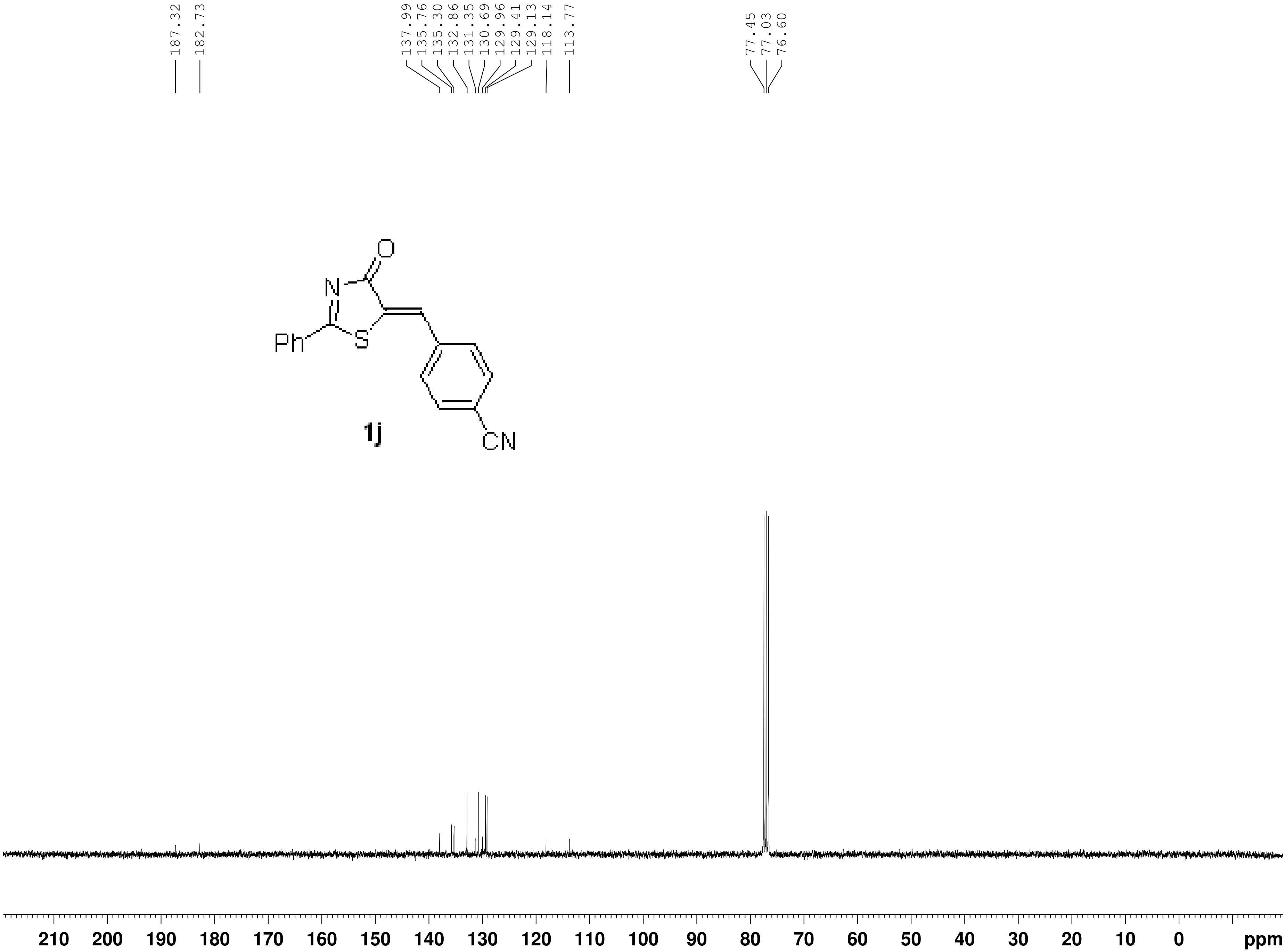
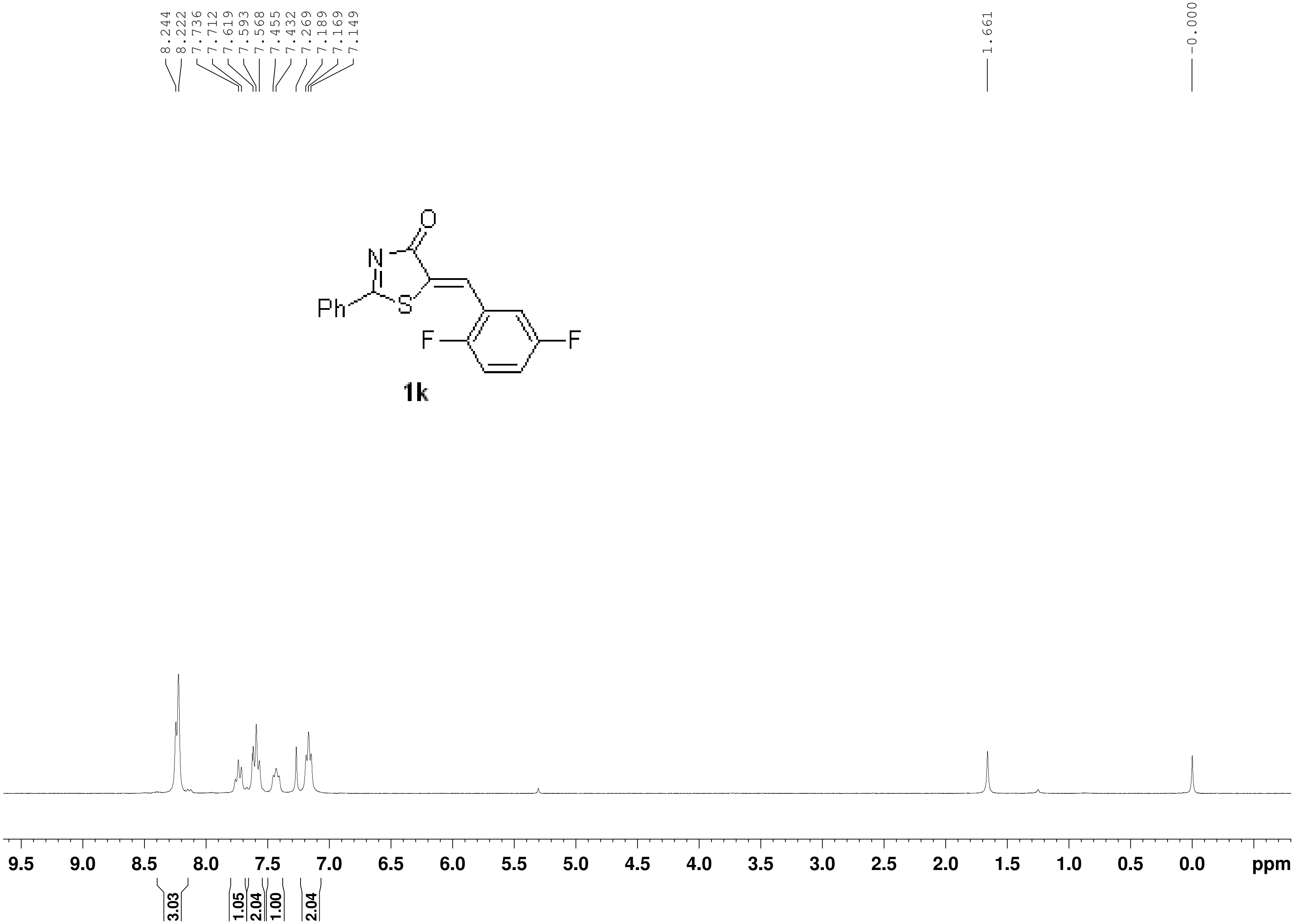
8.217
8.020
7.821
7.792
7.784
7.752
7.725
7.627
7.602
7.576
7.267
1.597
-0.000
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.00
1.03
5.05
2.04


O
N
Ph
S
CN

1j



187.32
182.73
137.99
135.76
135.30
132.86
131.35
130.69
129.96
129.41
129.13
118.14
113.77
77.45
77.03
76.60
O
N
S
Ph
CN
1j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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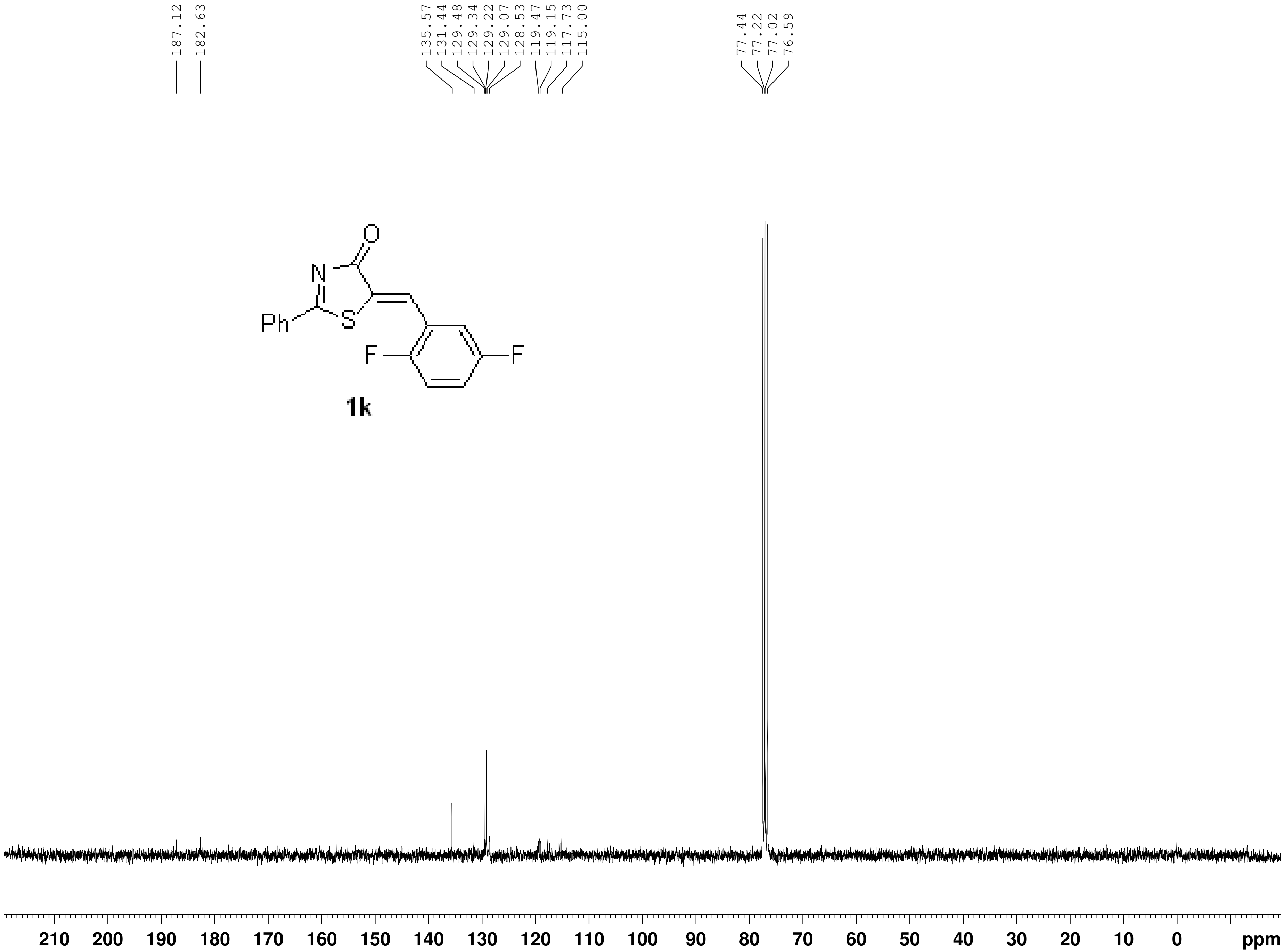
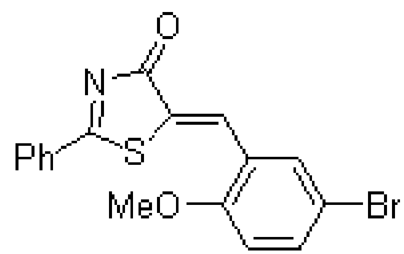
8.222
7.736
7.712
7.619
7.593
7.568
7.455
7.432
7.269
7.189
7.169
7.149
1.661
-0.000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
3.03
1.05
2.04
1.00
2.04

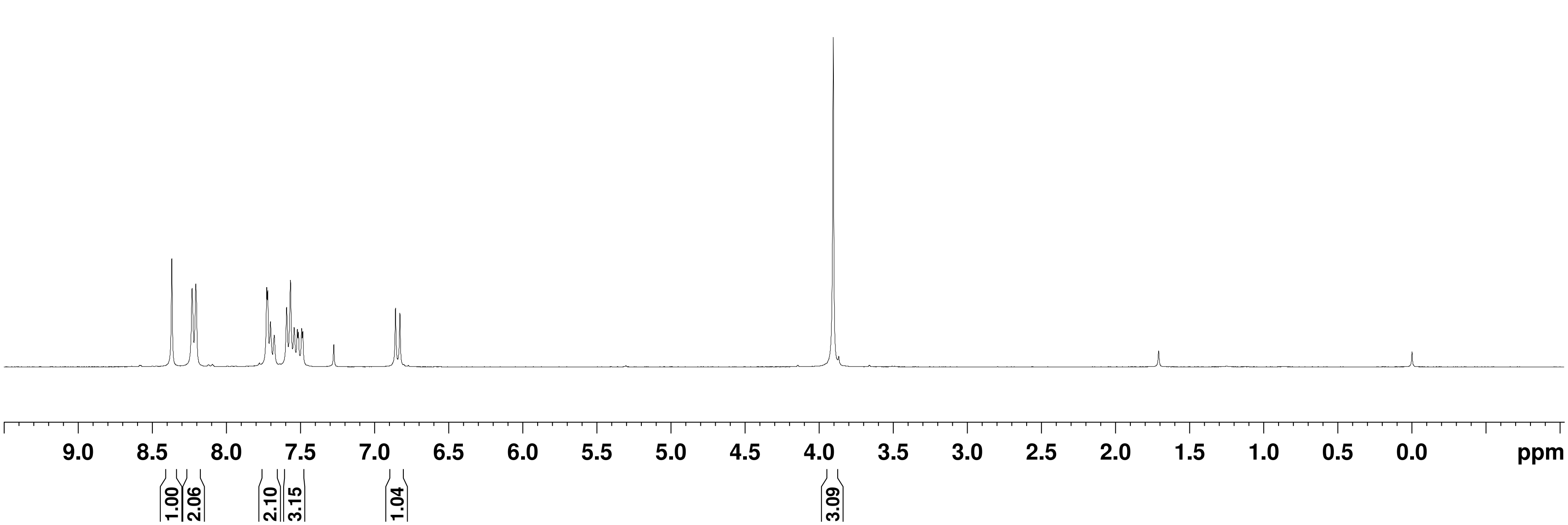
1k


187.12
182.63
135.57
131.44
129.48
129.34
129.22
129.07
128.53
119.47
119.15
117.73
115.00
77.44
77.22
77.02
76.59
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
O
N
S
Ph
F
F

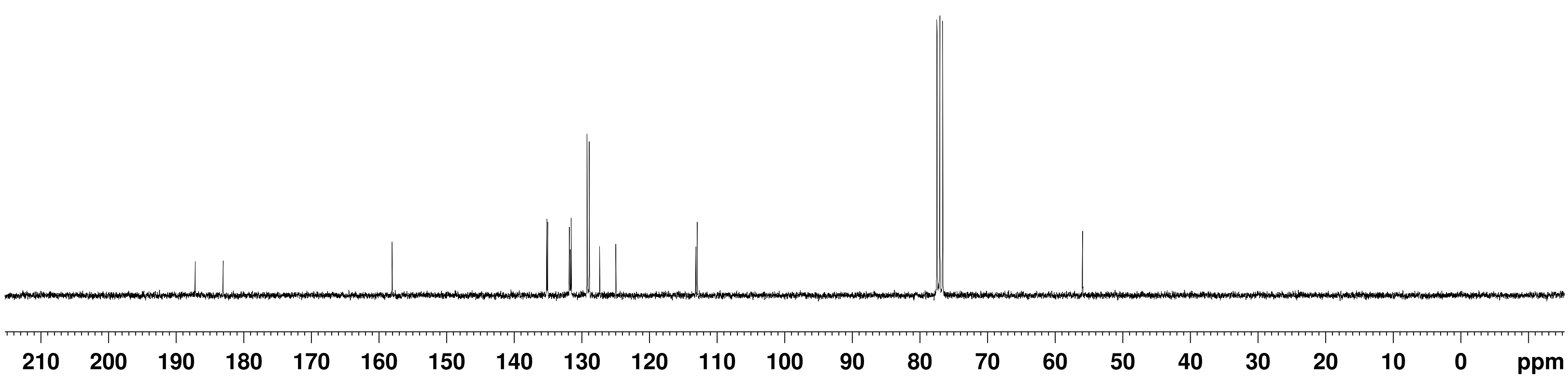
1k



1l



8.367
8.230
8.205
7.726
7.719
7.700
7.676
7.592
7.566
7.541
7.520
7.512
7.490
7.483
7.273
6.857
6.827
3.903
1.710
-0.000
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
ppm
1.00
2.06
2.10
3.15
1.04
3.09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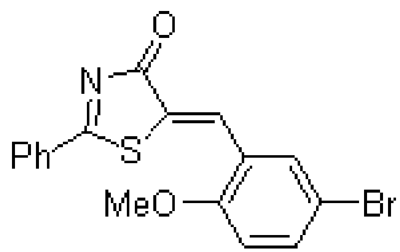
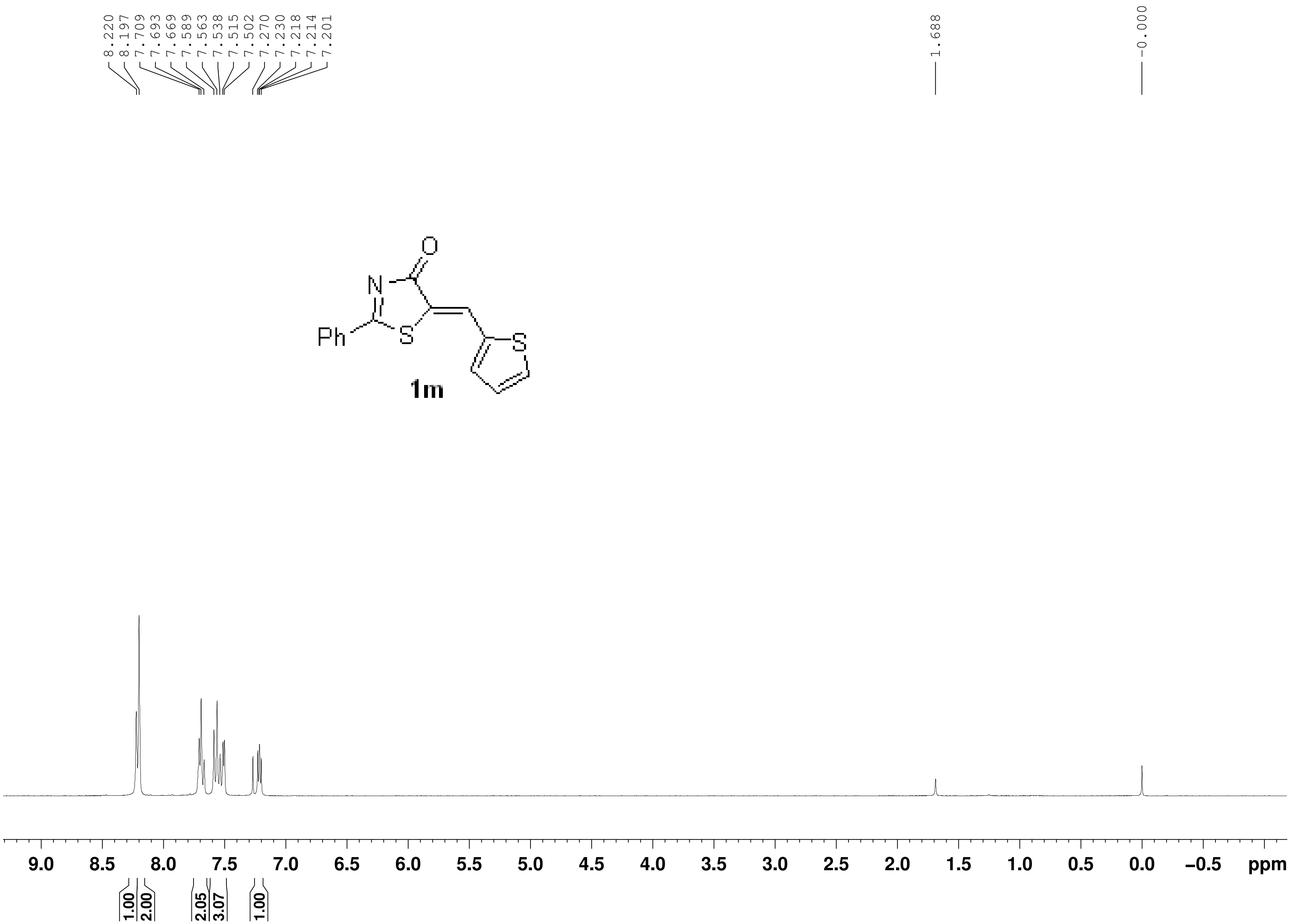
183.00
158.09
135.21
135.06
131.86
131.71
131.59
129.24
128.93
127.38
124.99
113.17
112.95
77.49
77.07
76.64
55.96
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


O
N
S
Ph
MeO
Br

1l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8.197
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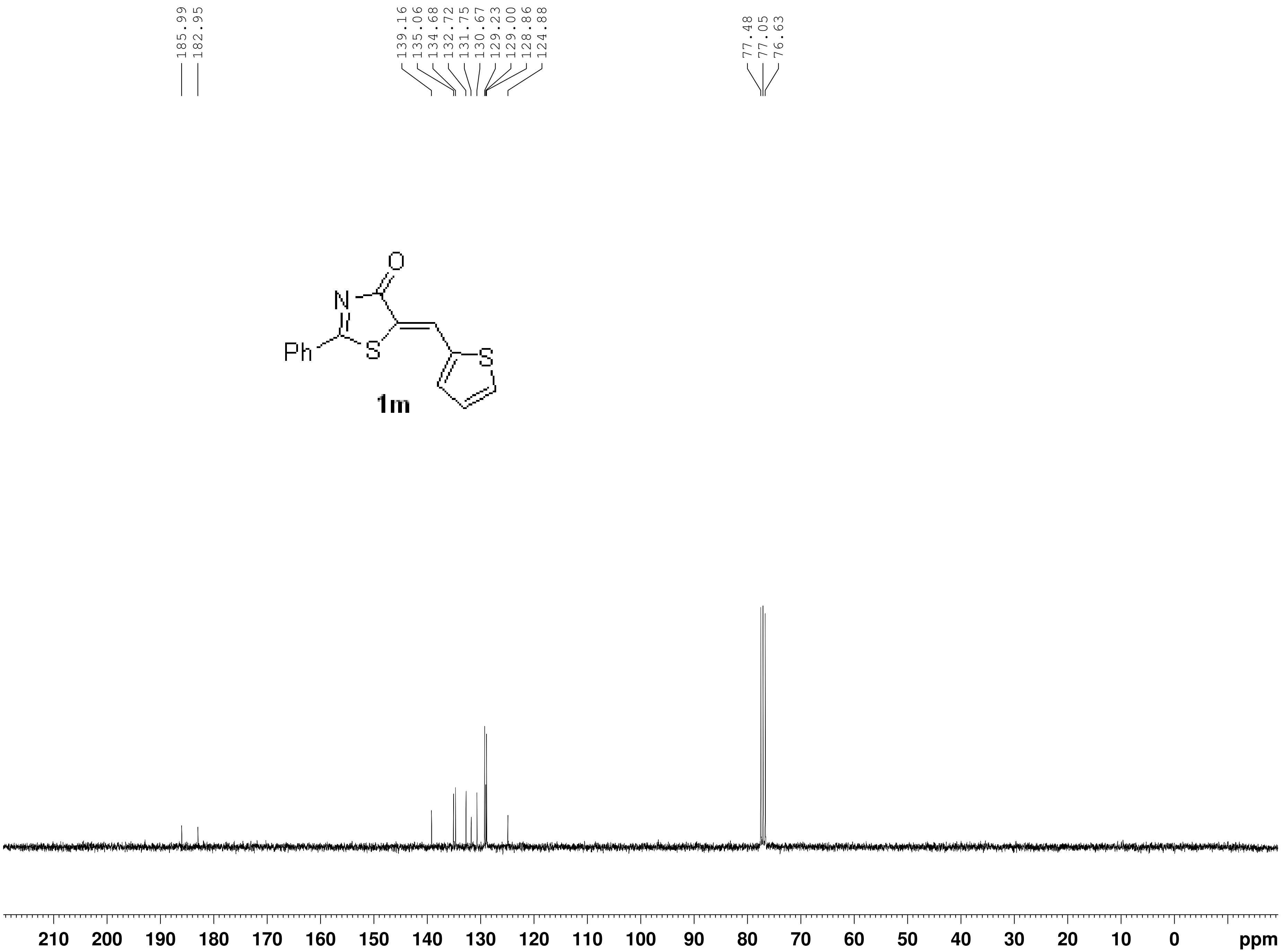
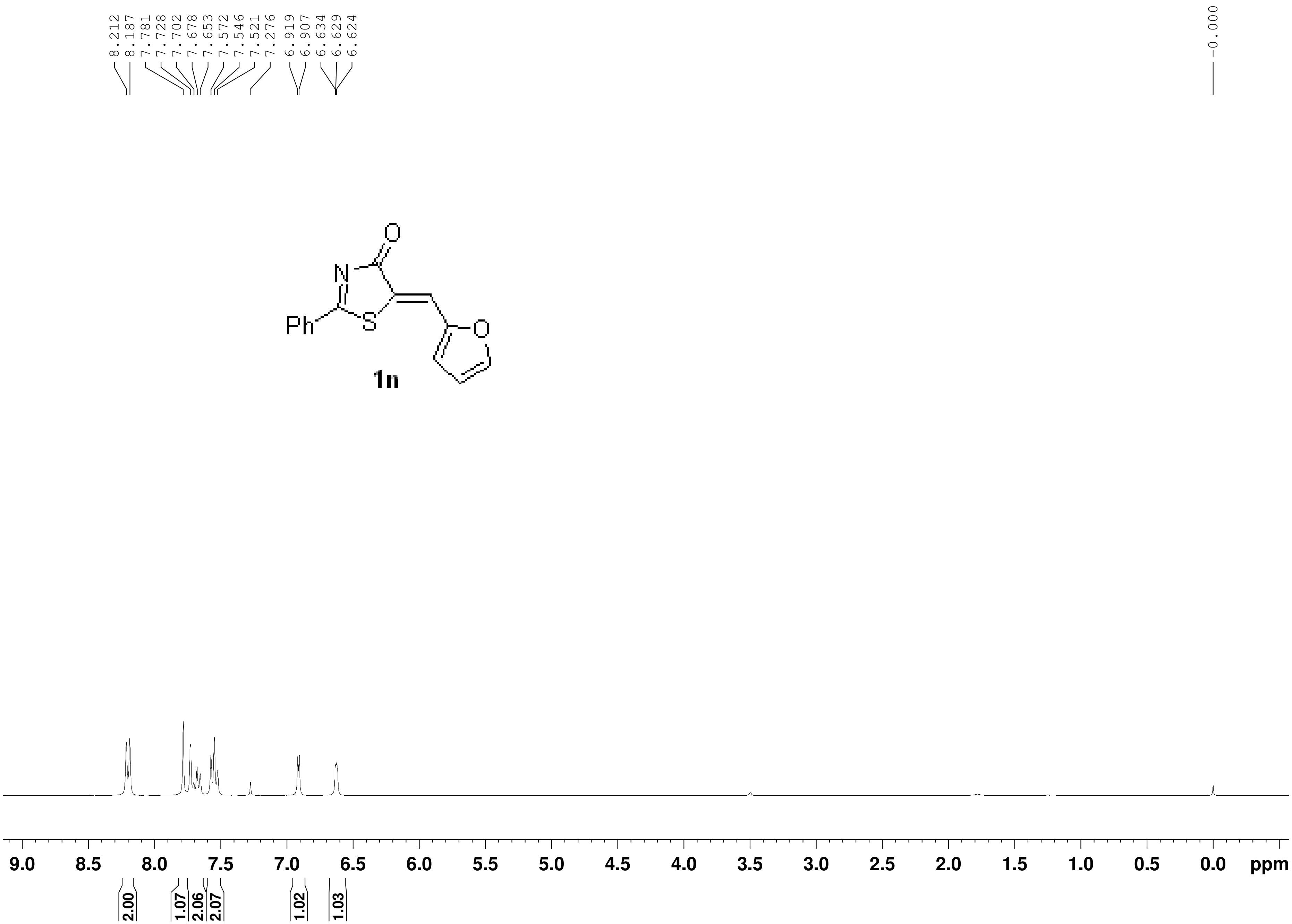
7.693
7.669
7.589
7.563
7.538
7.515
7.502
7.270
7.230
7.218
7.214
7.201
1.688
0.000
O
N
S
Ph
S
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
–0.5
ppm
1.00
2.00
2.05
3.07
1.00

1m


185.99
182.95
139.16
135.06
134.68
132.72
131.75
130.67
129.23
129.00
128.86
124.88
77.48
77.05
76.63
O
N
Ph
S
S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

1m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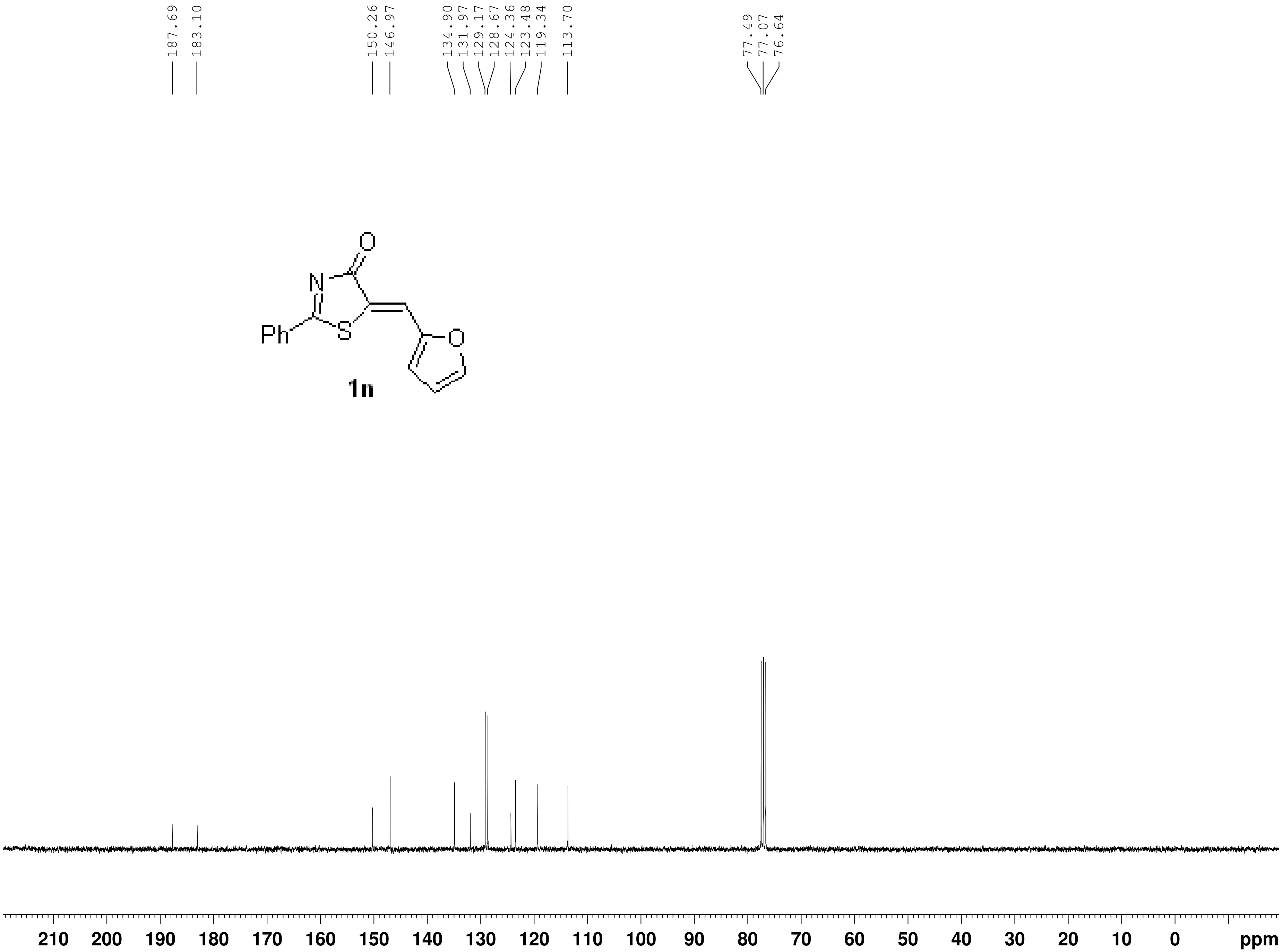
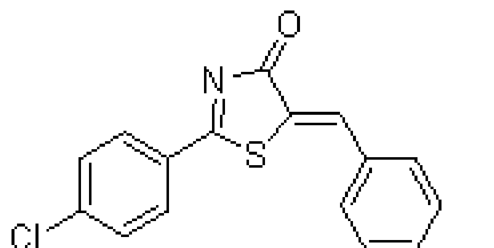
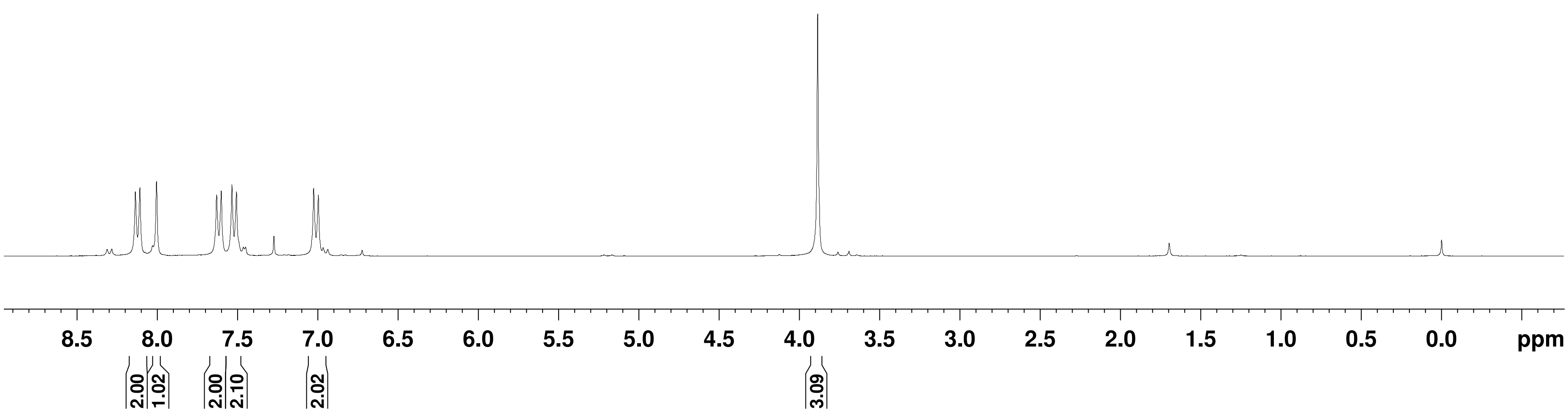
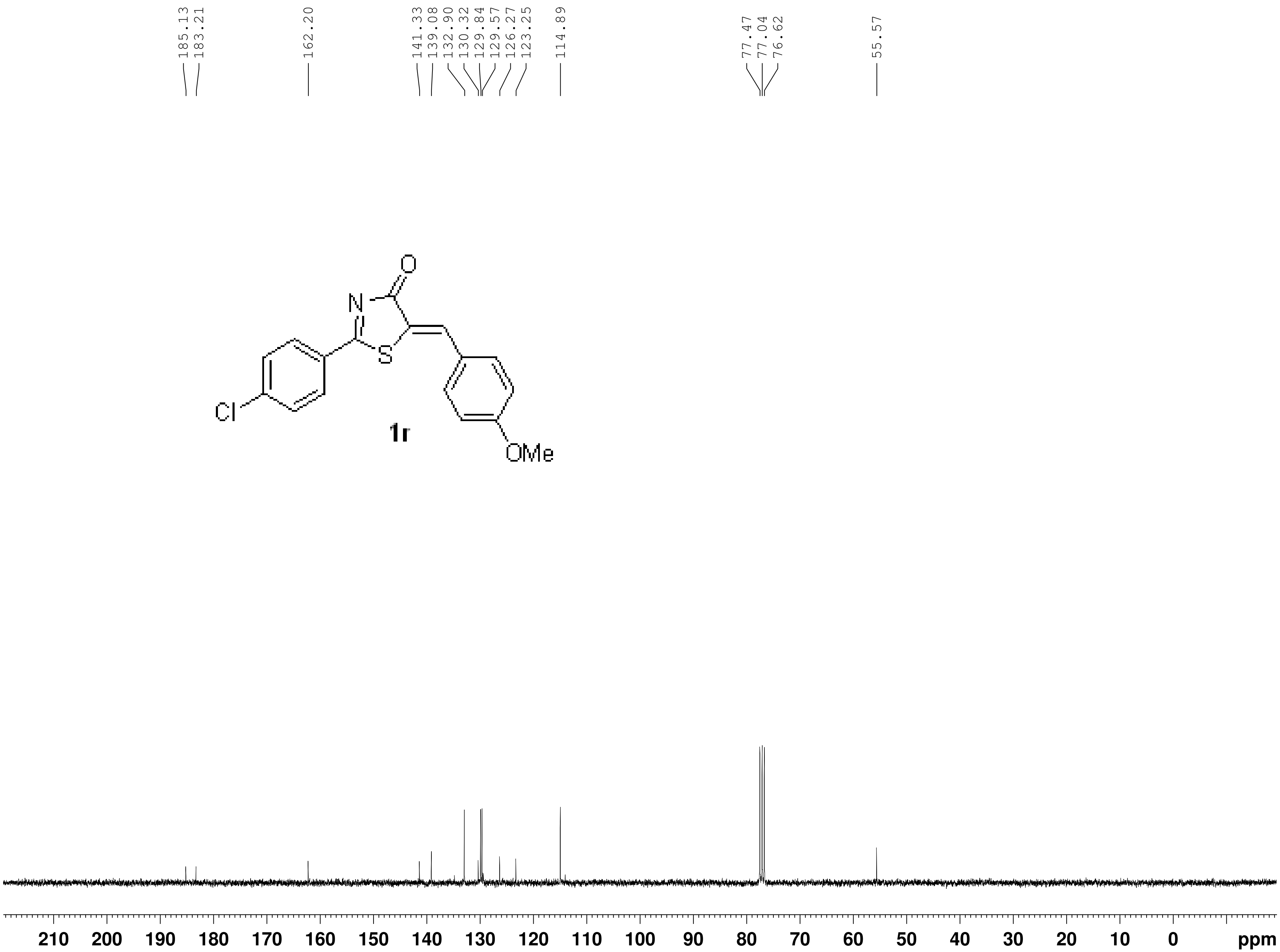
8.187
7.781
7.728
7.702
7.678
7.653
7.572
7.546
7.521
7.276
6.919
6.907
6.634
6.629
6.624
-0.000
O
N
S
O
Ph
1n
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.00
1.07
2.06
2.07
1.02
1.03


187.69
183.10
150.26
146.97
134.90
131.97
129.17
128.67
124.36
123.48
119.34
113.70
77.49
77.07
76.64
O
N
S
O
Ph
1n
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

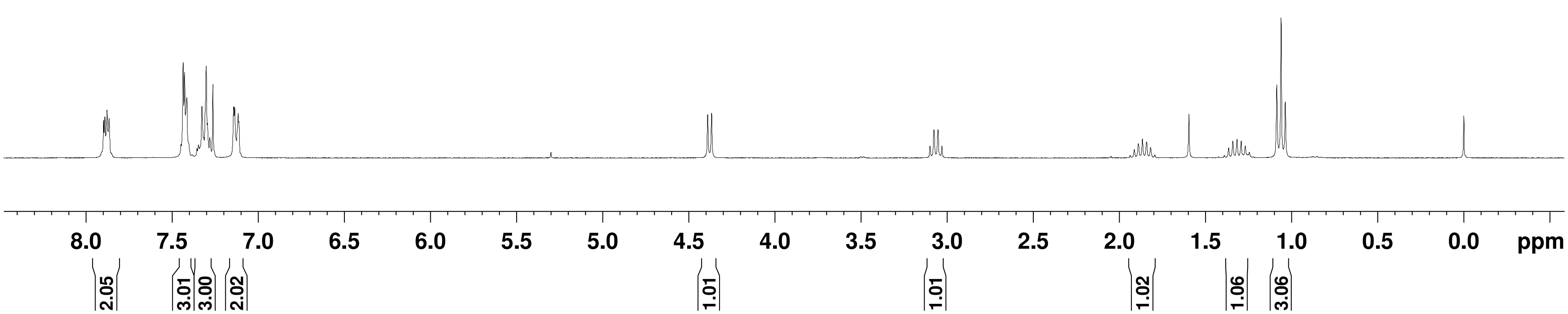

O
N
S
Cl
OMe

1r


8.135
8.107
8.003
7.629
7.600
7.534
7.505
7.272
7.024
6.995
3.887
1.697
-0.000
2.00
1.02
2.00
2.10
2.02
3.09
ppm



185.13
183.21
162.20
141.33
139.08
132.90
130.32
129.84
129.57
126.27
123.25
114.89
77.47
77.04
76.62
55.57
O
N
S
Cl
OMe
1r
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



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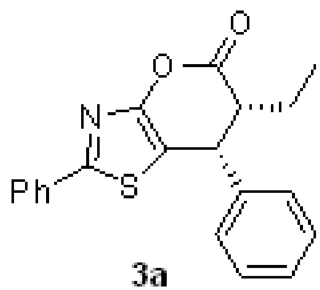
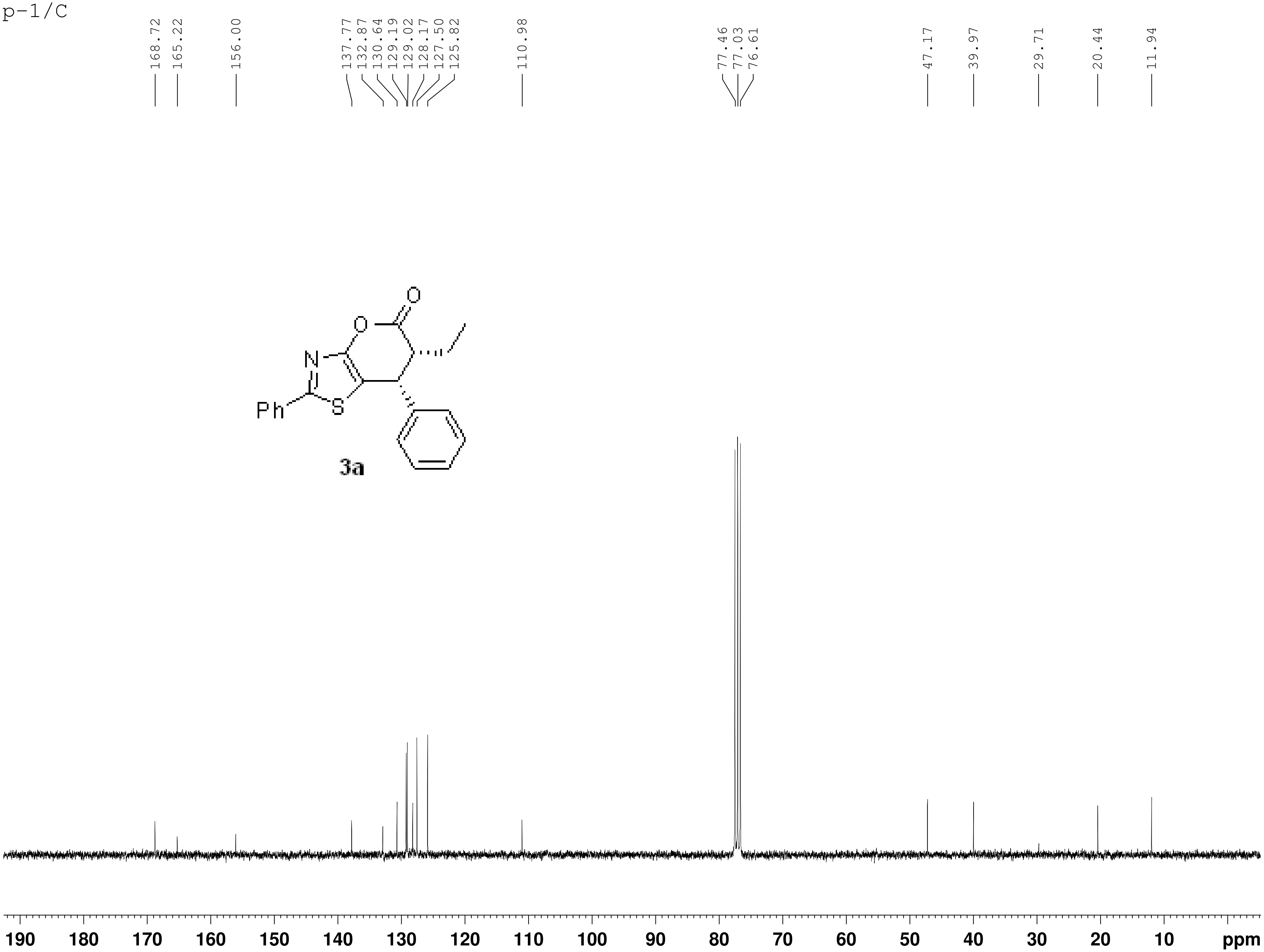
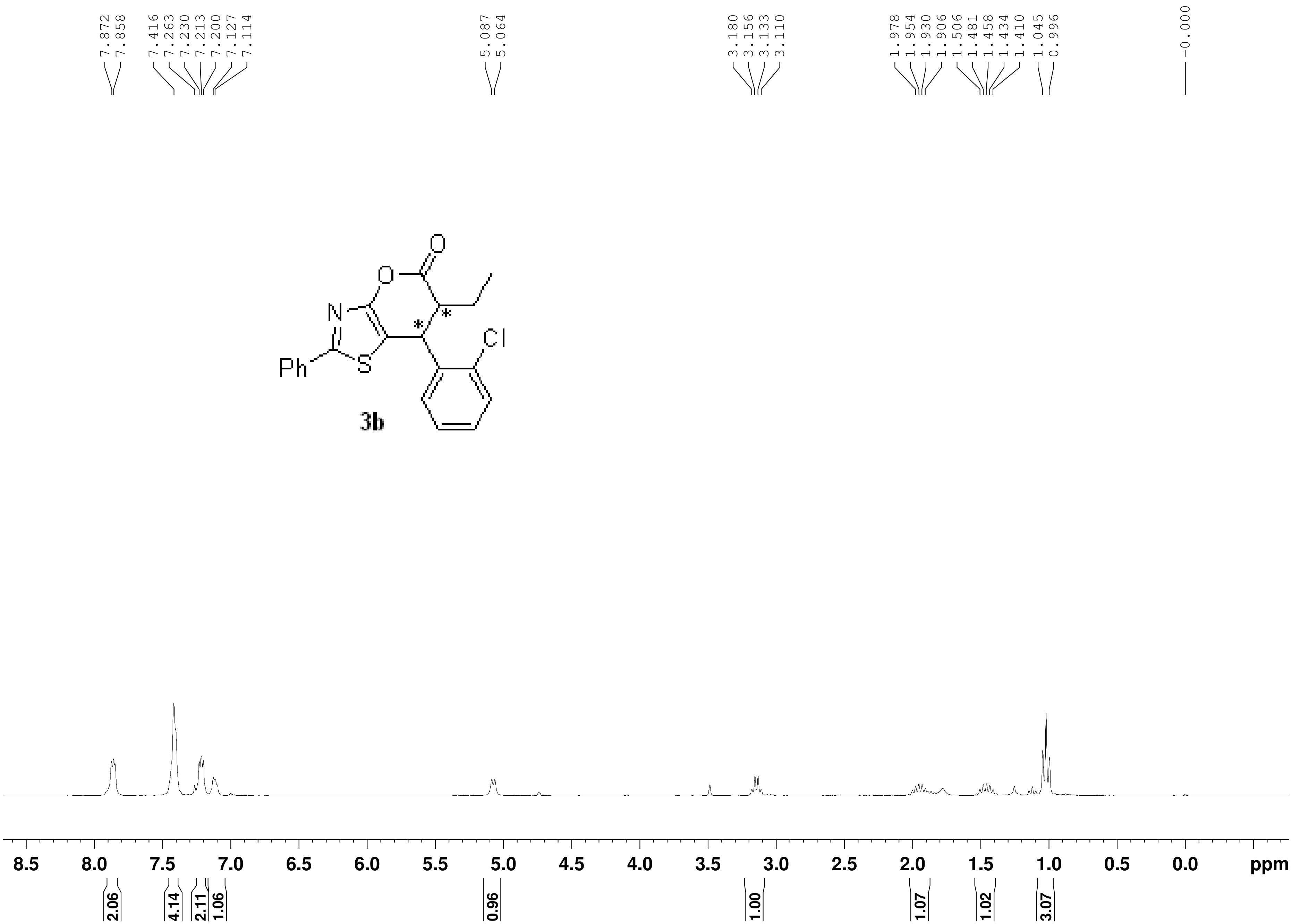
7.889
7.877
7.864
7.435
7.426
7.413
7.325
7.315
7.300
7.293
7.280
7.262
7.141
7.135
7.115
7.111
4.391
4.368
3.099
3.077
3.053
3.031
1.913
1.890
1.866
1.842
1.819
1.596
1.365
1.341
1.317
1.293
1.268
1.085
1.061
1.036
-0.000
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.05
3.01
3.00
2.02
1.01
1.01
1.02
1.06
3.06

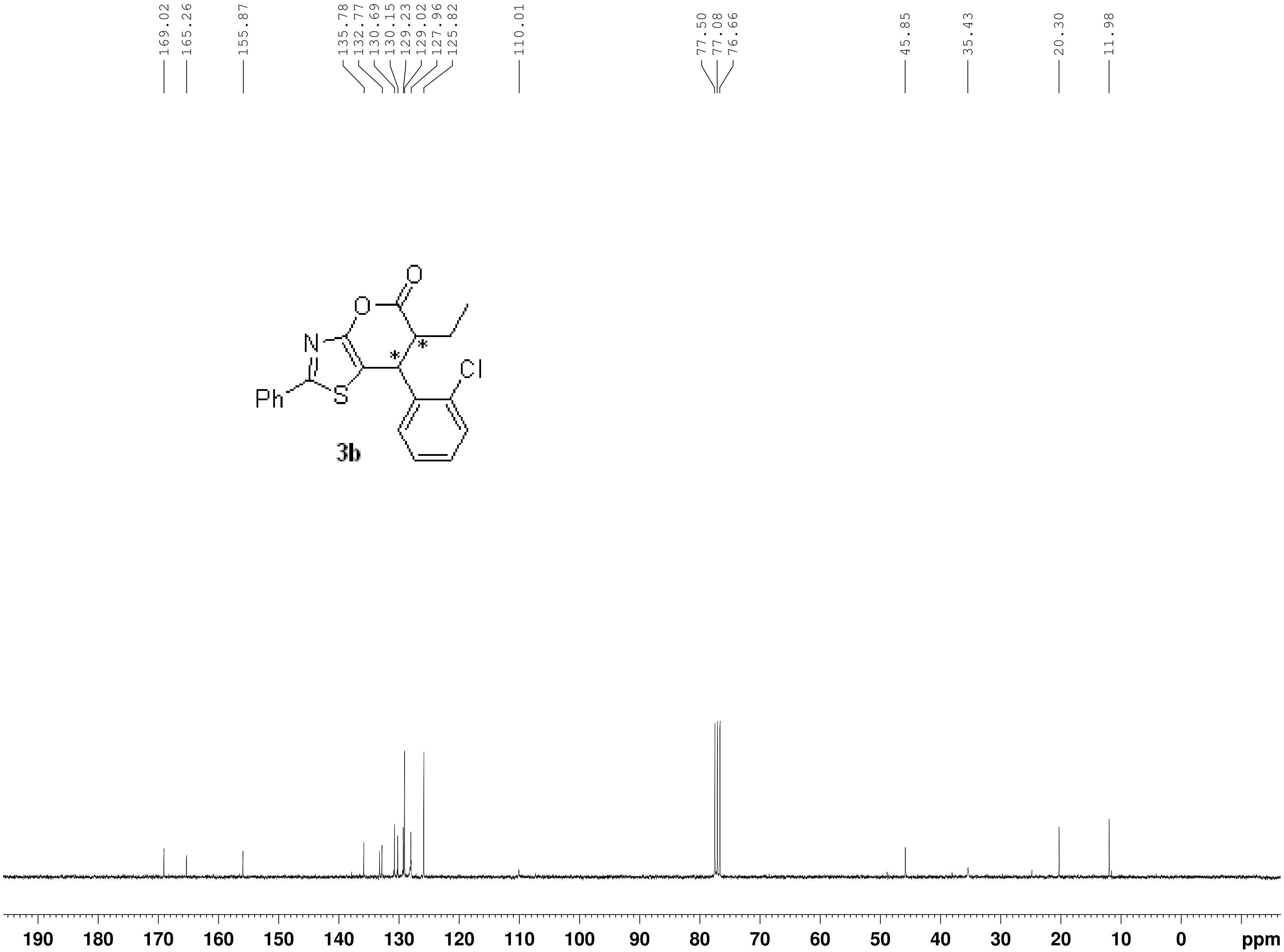


O
O
N
S
Ph

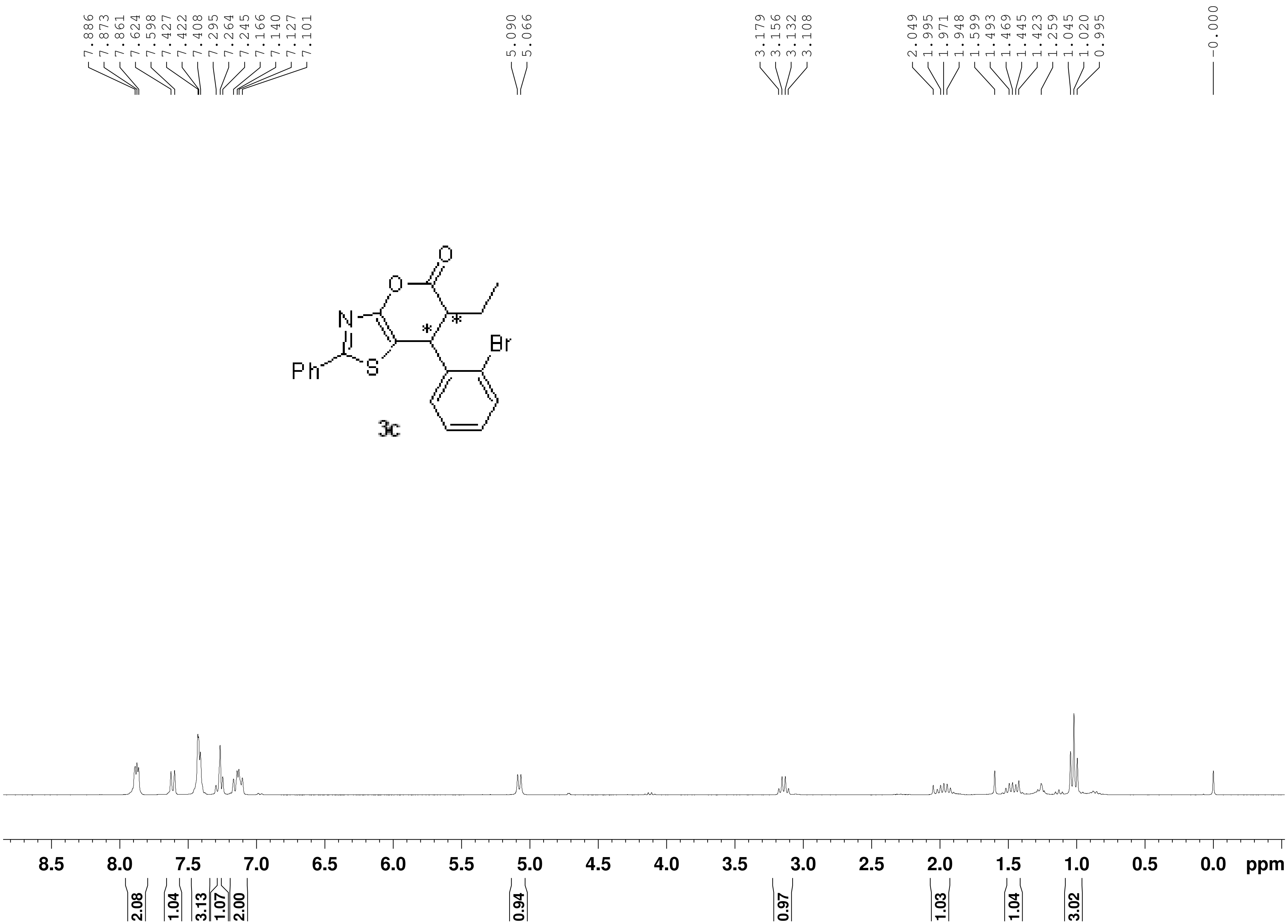
3a


p-1/C
168.72
165.22
156.00
137.77
132.87
130.64
129.19
129.02
128.17
127.50
125.82
110.98
77.46
77.03
76.61
47.17
39.97
29.71
20.44
11.94
O
O
N
S
Ph
3a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.872
7.858
7.416
7.263
7.230
7.213
7.200
7.127
7.114
5.087
5.064
3.180
3.156
3.133
3.110
1.978
1.954
1.930
1.906
1.506
1.481
1.458
1.434
1.410
1.045
0.996
-0.000
O
O
N
S
Ph
Cl
*
*
3b
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
ppm
2.06
4.14
2.11
1.06
0.96
1.00
1.07
1.02
3.07


169.02
165.26
155.87
135.78
132.77
130.69
130.15
129.23
129.02
127.96
125.82
110.01
77.50
77.08
76.66
45.85
35.43
20.30
11.98
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
O
O
N
S
Ph
Cl
*
*

3b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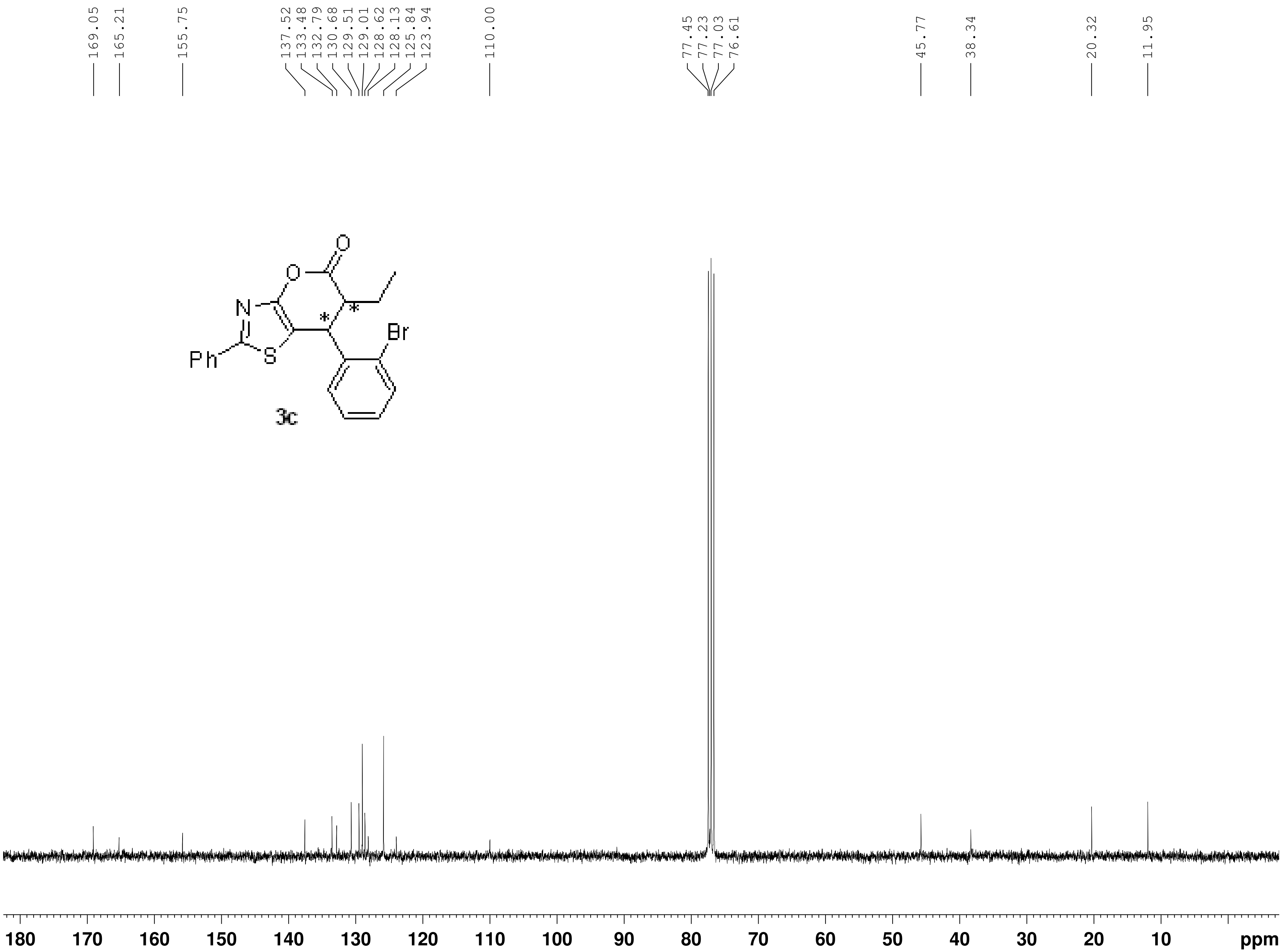
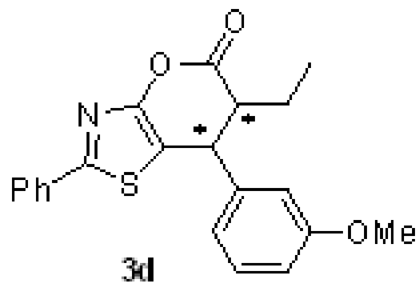
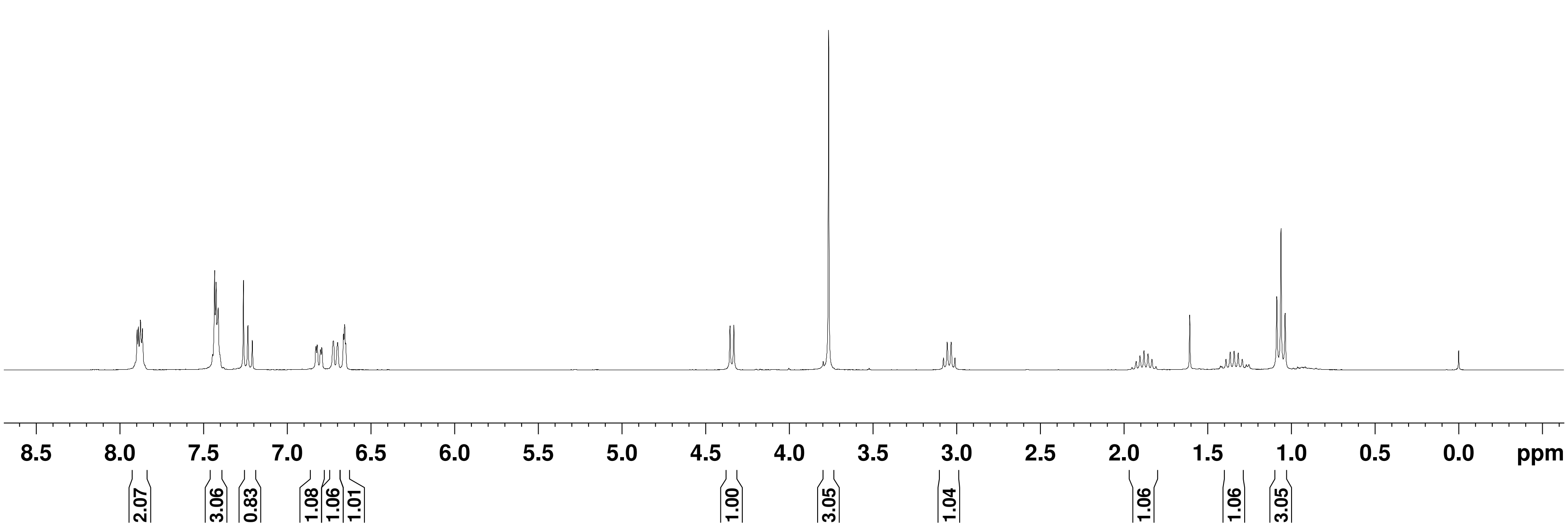
7.873
7.861
7.624
7.598
7.427
7.422
7.408
7.295
7.264
7.245
7.166
7.140
7.127
7.101
5.090
5.066
3.179
3.156
3.132
3.108
2.049
1.995
1.971
1.948
1.599
1.493
1.469
1.445
1.423
1.259
1.045
1.020
0.995
-0.000
O
O
N
S
Ph
Br
3c
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.08
1.04
3.13
1.07
2.00
0.94
0.97
1.03
1.04
3.02


169.05
165.21
155.75
137.52
133.48
132.79
130.68
129.51
129.01
128.62
128.13
125.84
123.94
110.00
77.45
77.23
77.03
76.61
45.77
38.34
20.32
11.95
O
O
N
S
Ph
Br
3c
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

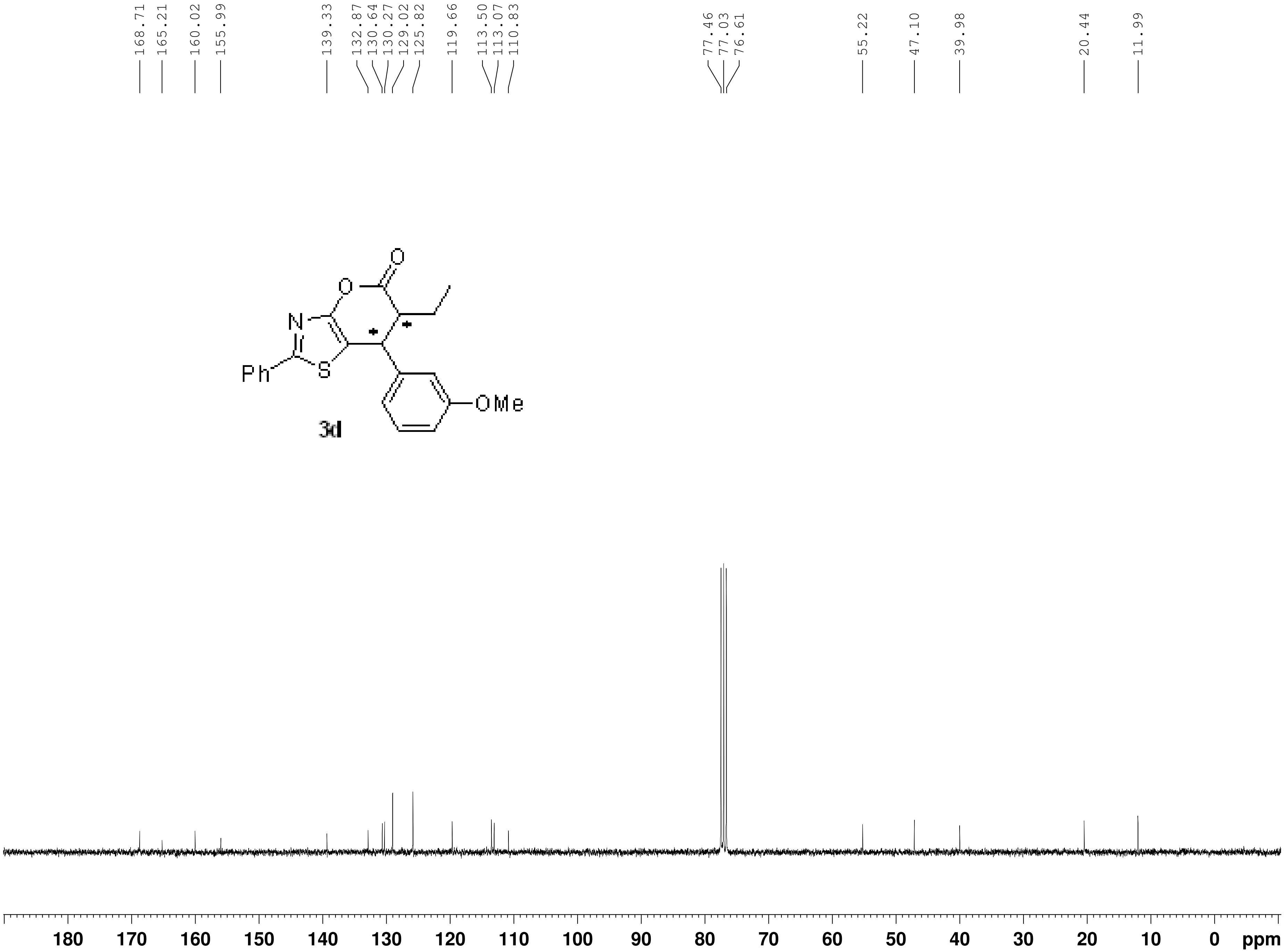


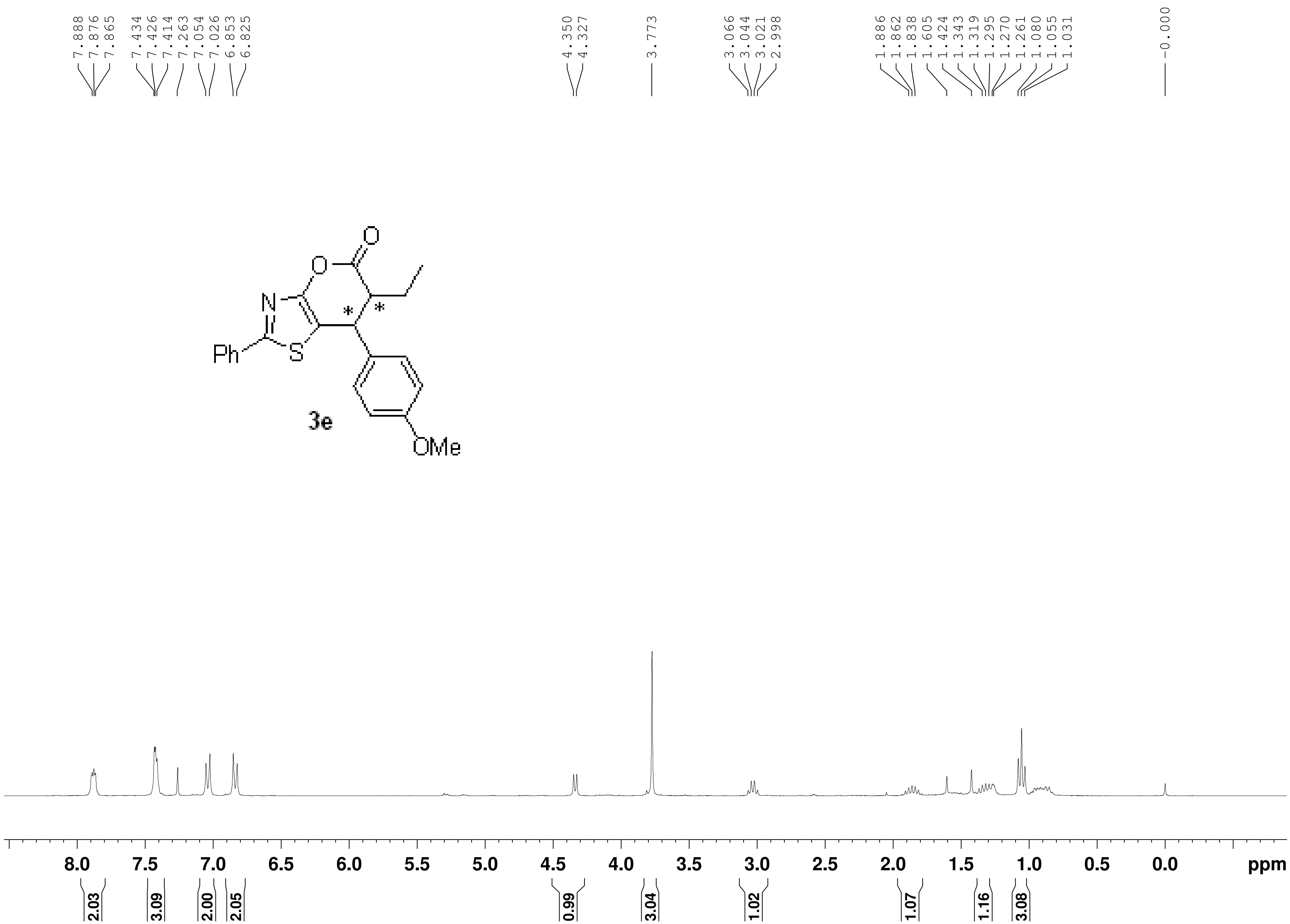
O
O
N
S
Ph
OMe

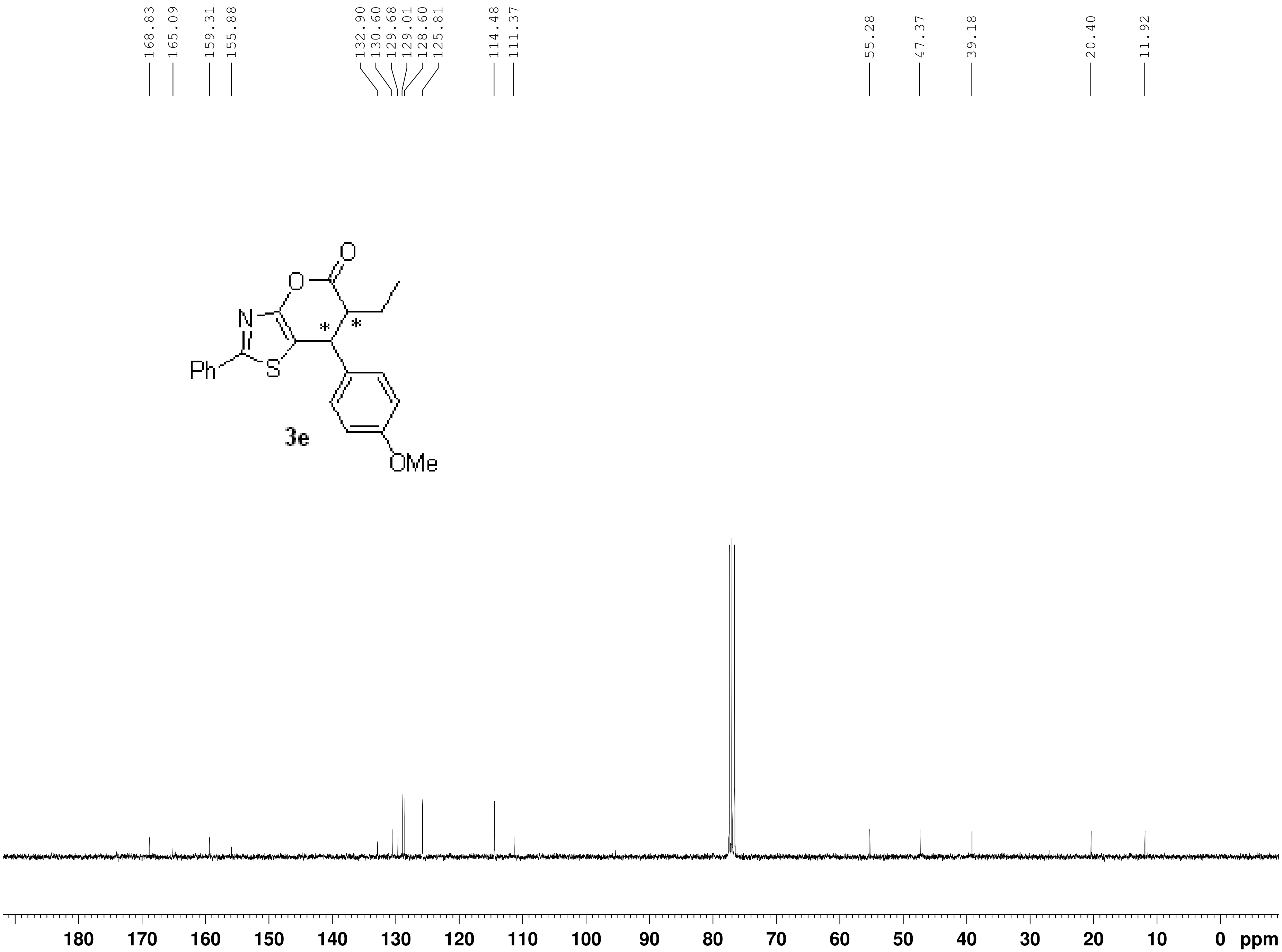
3d

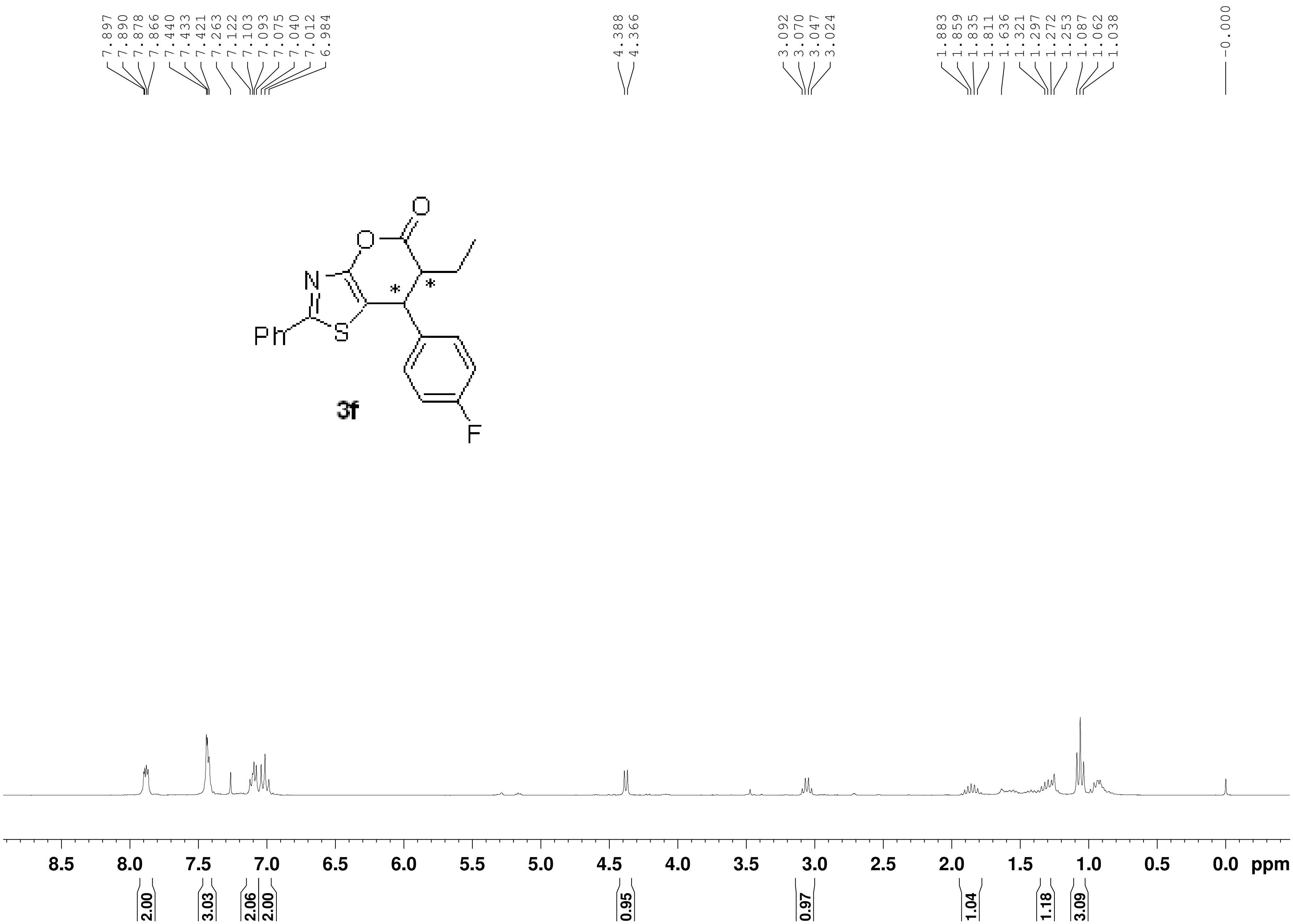


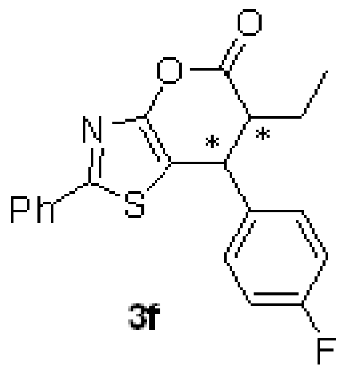
7.896
7.888
7.879
7.875
7.863
7.435
7.426
7.413
7.262
7.236
7.210
6.829
6.822
6.801
6.795
6.725
6.700
6.665
6.658
6.652
4.354
4.332
3.765
3.079
3.057
3.033
3.010
1.905
1.880
1.856
1.833
1.607
1.390
1.365
1.341
1.317
1.293
1.086
1.062
1.037
-0.000
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.07
3.06
0.83
1.08
1.06
1.01
1.00
3.05
1.04
1.06
1.06
3.05


168.71
165.21
160.02
155.99
139.33
132.87
130.64
130.27
129.02
125.82
119.66
113.50
113.07
110.83
77.46
77.03
76.61
55.22
47.10
39.98
20.44
11.99
O
O
N
S
Ph
OMe
3d
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

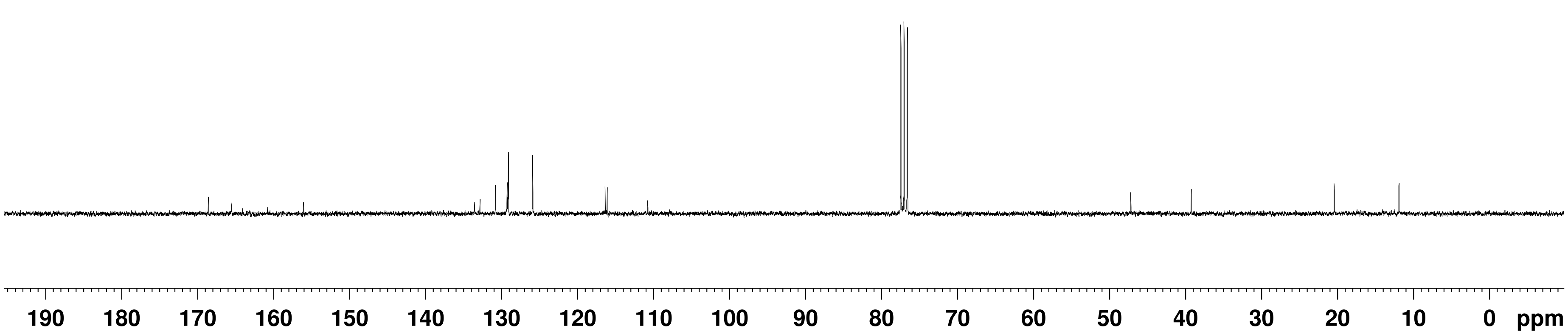



168.83
165.09
159.31
155.88
132.90
130.60
129.68
129.01
128.60
125.81
114.48
111.37
55.28
47.37
39.18
20.40
11.92
O
O
N
Ph
S
OMe
3e
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.897
7.890
7.878
7.866
7.440
7.433
7.421
7.263
7.122
7.103
7.093
7.075
7.040
7.012
6.984
4.388
4.366
3.092
3.070
3.047
3.024
1.883
1.859
1.835
1.811
1.636
1.321
1.297
1.272
1.253
1.087
1.062
1.038
-0.000
O
N
S
Ph
F
*
*
3f
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 ppm
2.00
3.03
2.06
2.00
0.95
0.97
1.04
1.18
3.09


O
O
N
S
Ph
F

3f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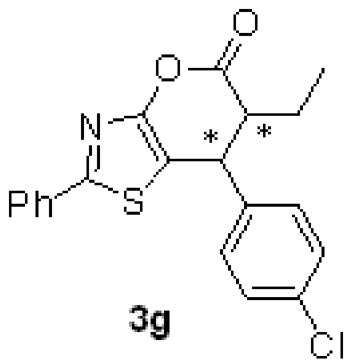
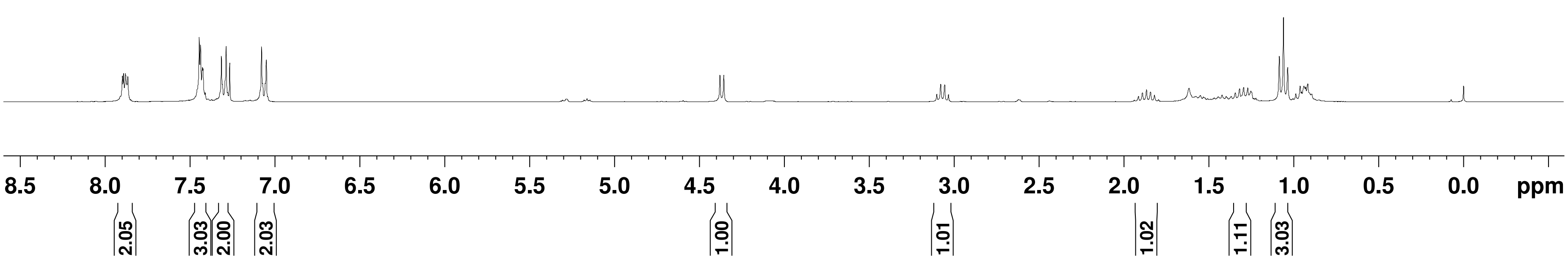
133.50
132.78
130.75
129.21
129.10
129.05
125.84
116.32
116.03
110.72
77.46
77.04
76.61
47.21
39.24
20.44
11.92
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


O
O
N
S
Ph
Cl
*
*

3g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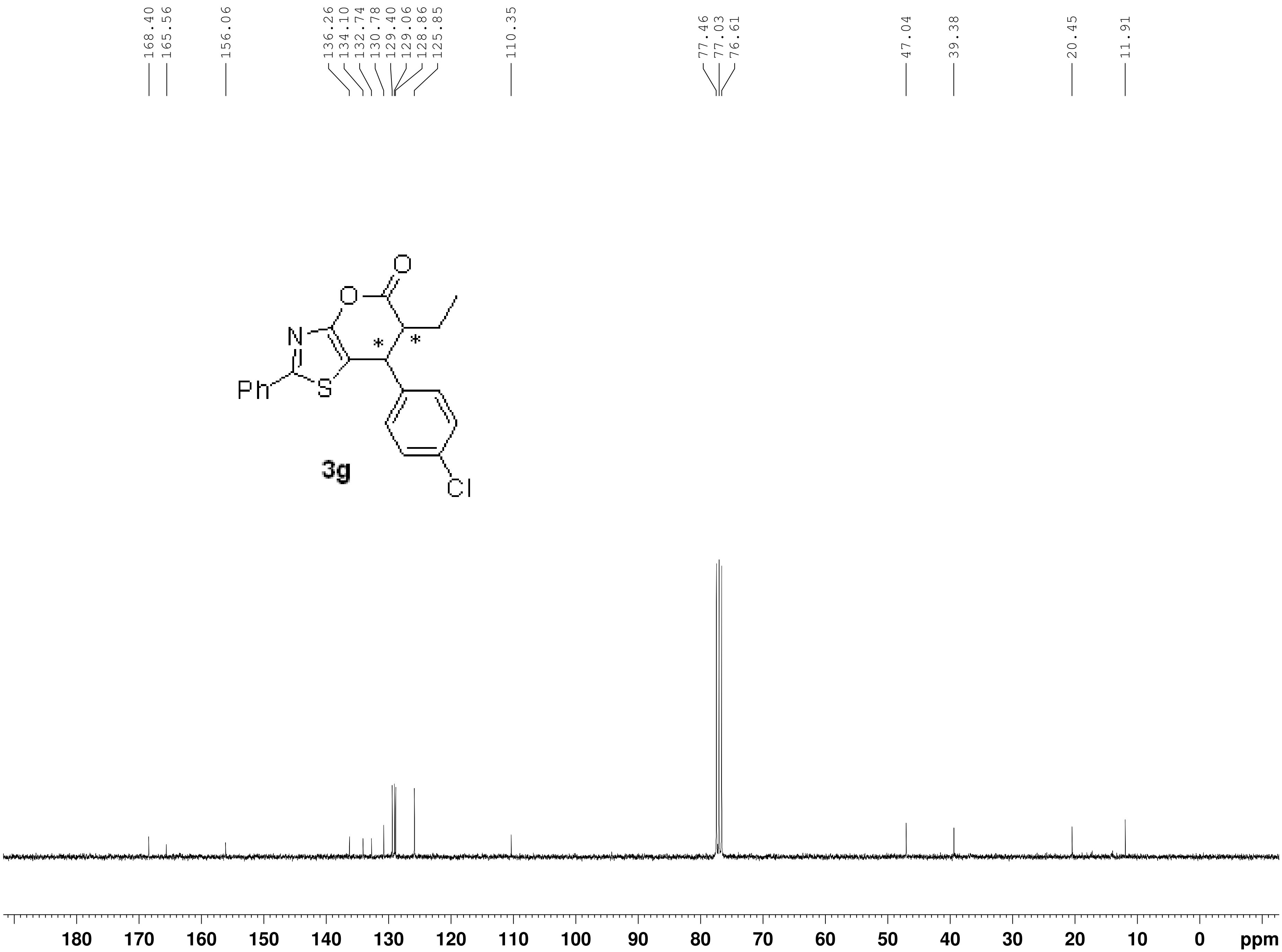
7.889
7.878
7.864
7.443
7.436
7.425
7.421
7.313
7.291
7.285
7.264
7.076
7.070
7.054
7.048
4.377
4.354
3.099
3.077
3.053
3.031
1.892
1.867
1.843
1.617
1.344
1.319
1.295
1.271
1.252
1.085
1.060
1.036
0.000
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.05
3.03
2.00
2.03
1.00
1.01
1.02
1.11
3.03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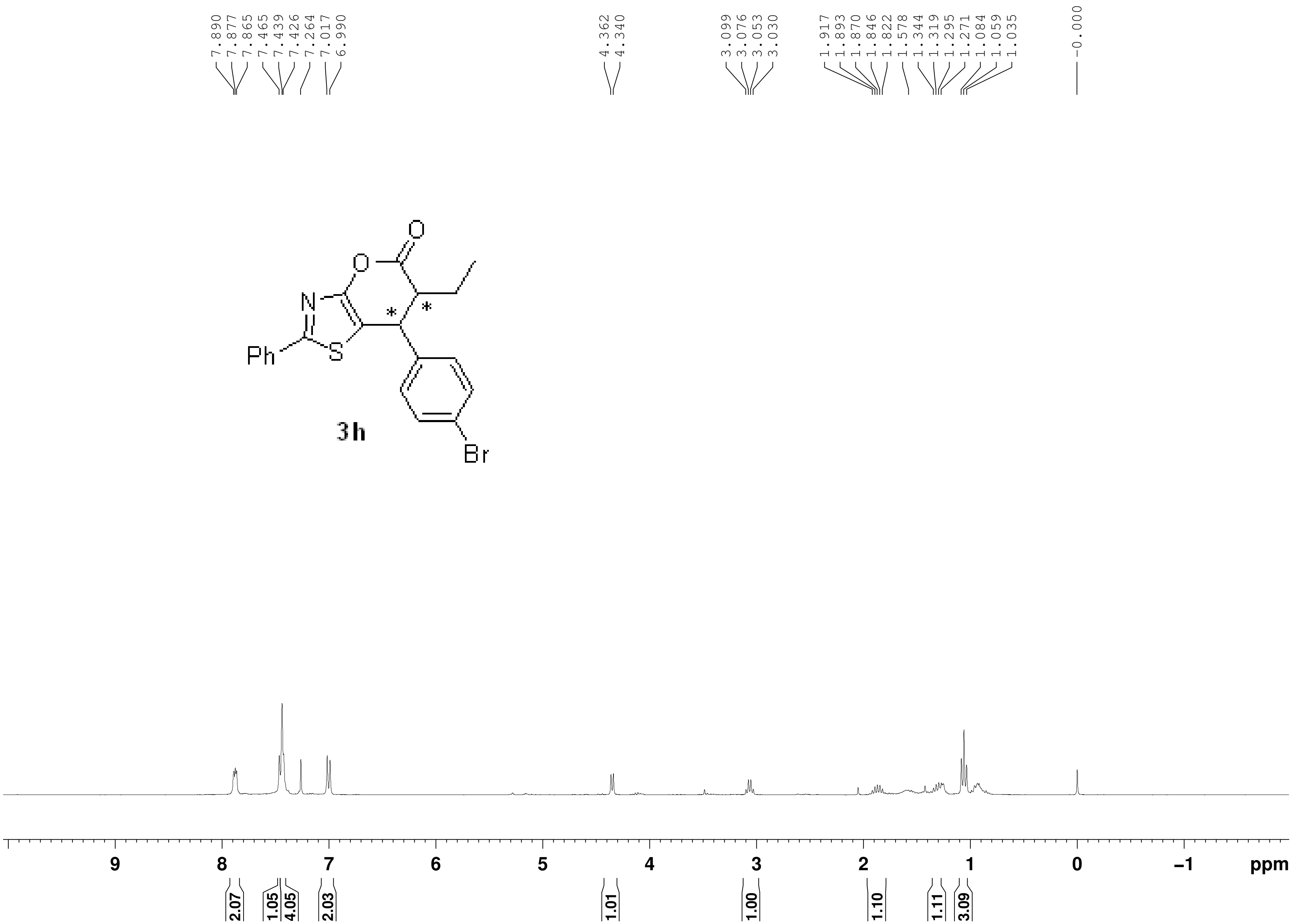
165.56
156.06
136.26
134.10
132.74
130.78
129.40
129.06
128.86
125.85
110.35
77.46
77.03
76.61
47.04
39.38
20.45
11.91
O
O
N
S
Ph
Cl
3g
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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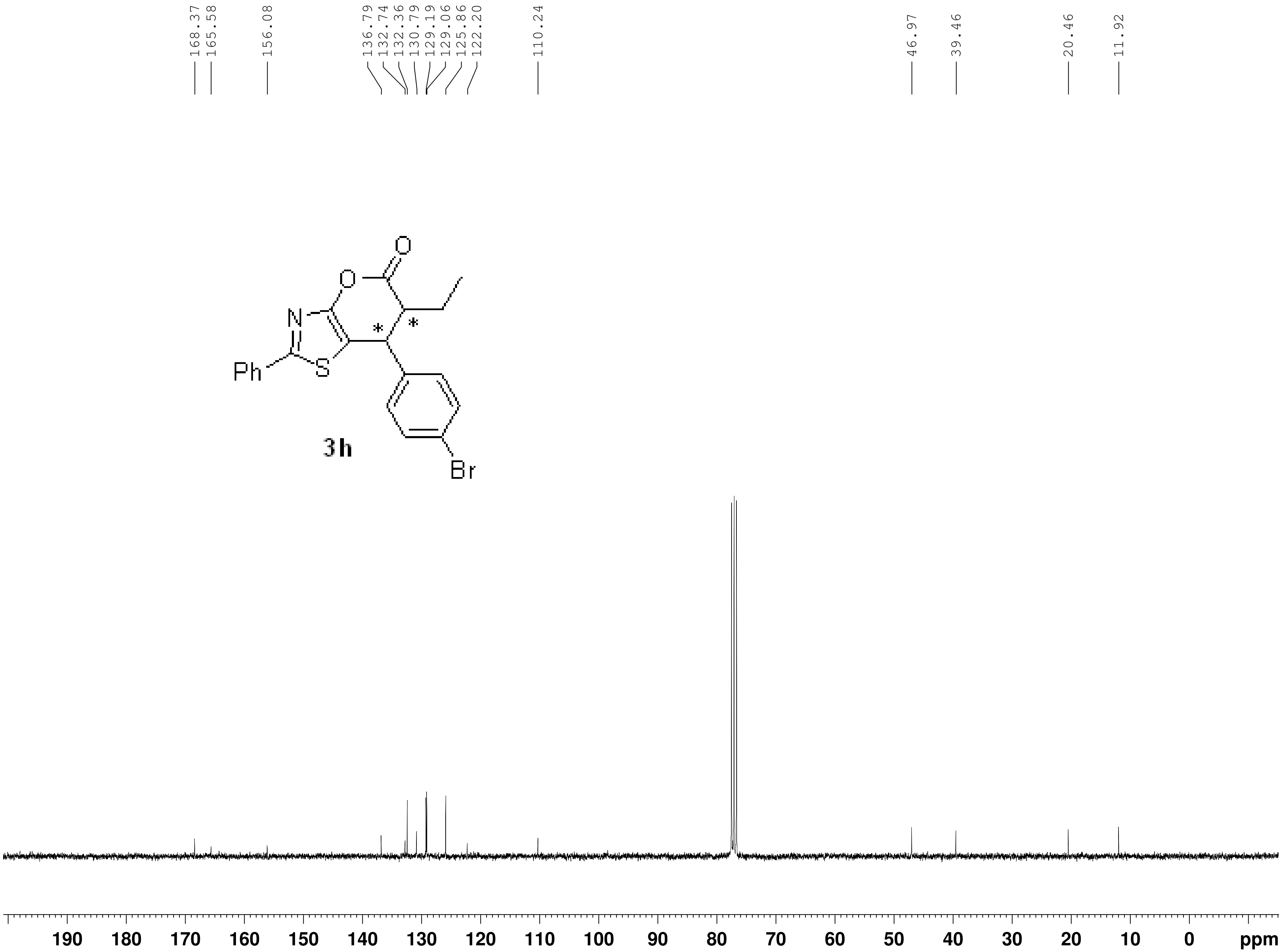
7.865
7.465
7.439
7.426
7.264
7.017
6.990
4.362
4.340
3.099
3.076
3.053
3.030
1.917
1.893
1.870
1.846
1.822
1.578
1.344
1.319
1.295
1.271
1.084
1.059
1.035
-0.000
O
O
N
S
Ph
Br
*
*
3h
9
8
7
6
5
4
3
2
1
0
–1
ppm
2.07
1.05
4.05
2.03
1.01
1.00
1.10
1.11
3.09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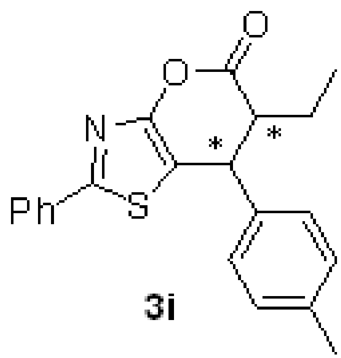
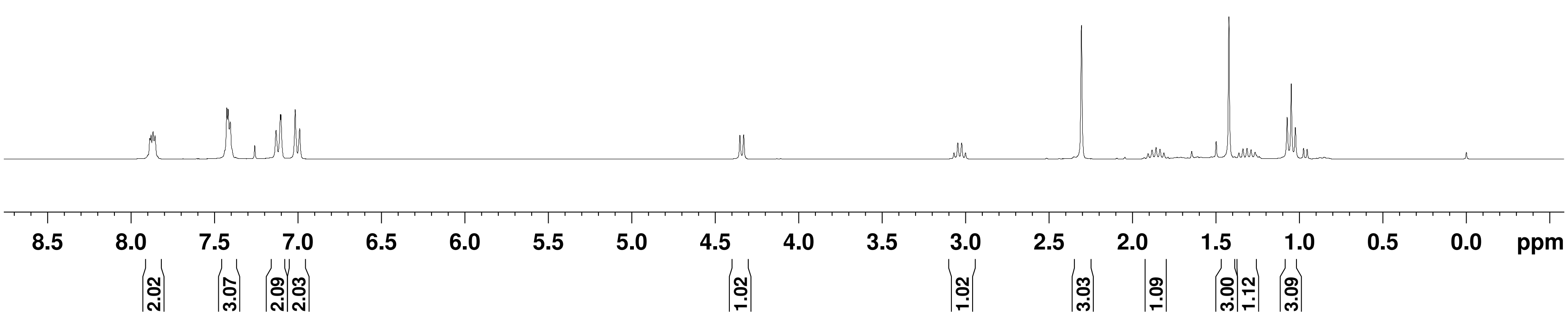
165.58
156.08
136.79
132.74
132.36
130.79
129.19
129.06
125.86
122.20
110.24
46.97
39.46
20.46
11.92
O
O
N
S
Ph
Br
*
*
3h
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



3i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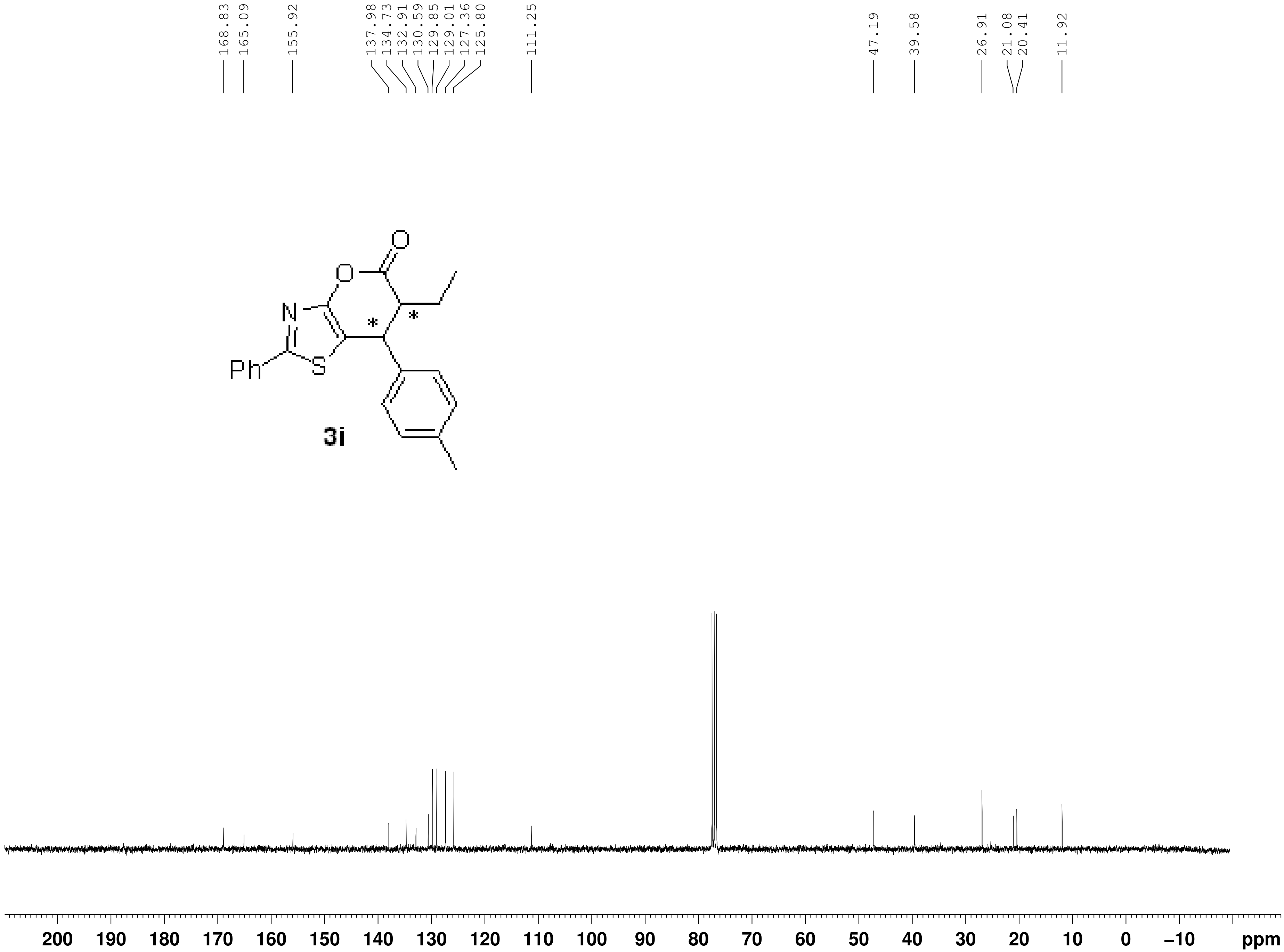
7.879
7.866
7.854
7.425
7.416
7.404
7.257
7.130
7.103
7.018
6.991
4.352
4.330
3.070
3.047
3.024
3.001
2.306
1.906
1.883
1.859
1.835
1.812
1.499
1.422
1.363
1.338
1.314
1.290
1.266
1.073
1.049
1.024
-0.000
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.02
3.07
2.09
2.03
1.02
1.02
3.03
1.09
3.00
1.12
3.09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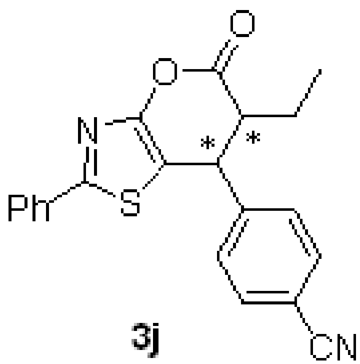
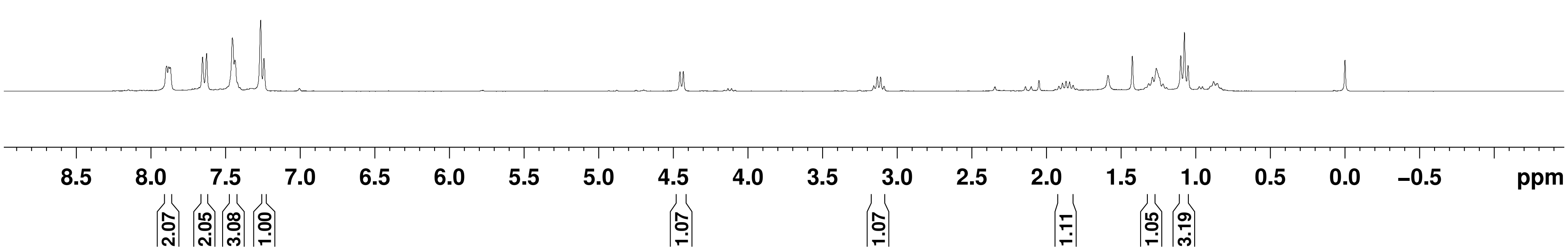
165.09
155.92
137.98
134.73
132.91
130.59
129.85
129.01
127.36
125.80
111.25
47.19
39.58
26.91
21.08
20.41
11.92
O
O
N
Ph
S
3i
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 ppm


O
O
N
S
Ph
*
*
CN

3j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7.868
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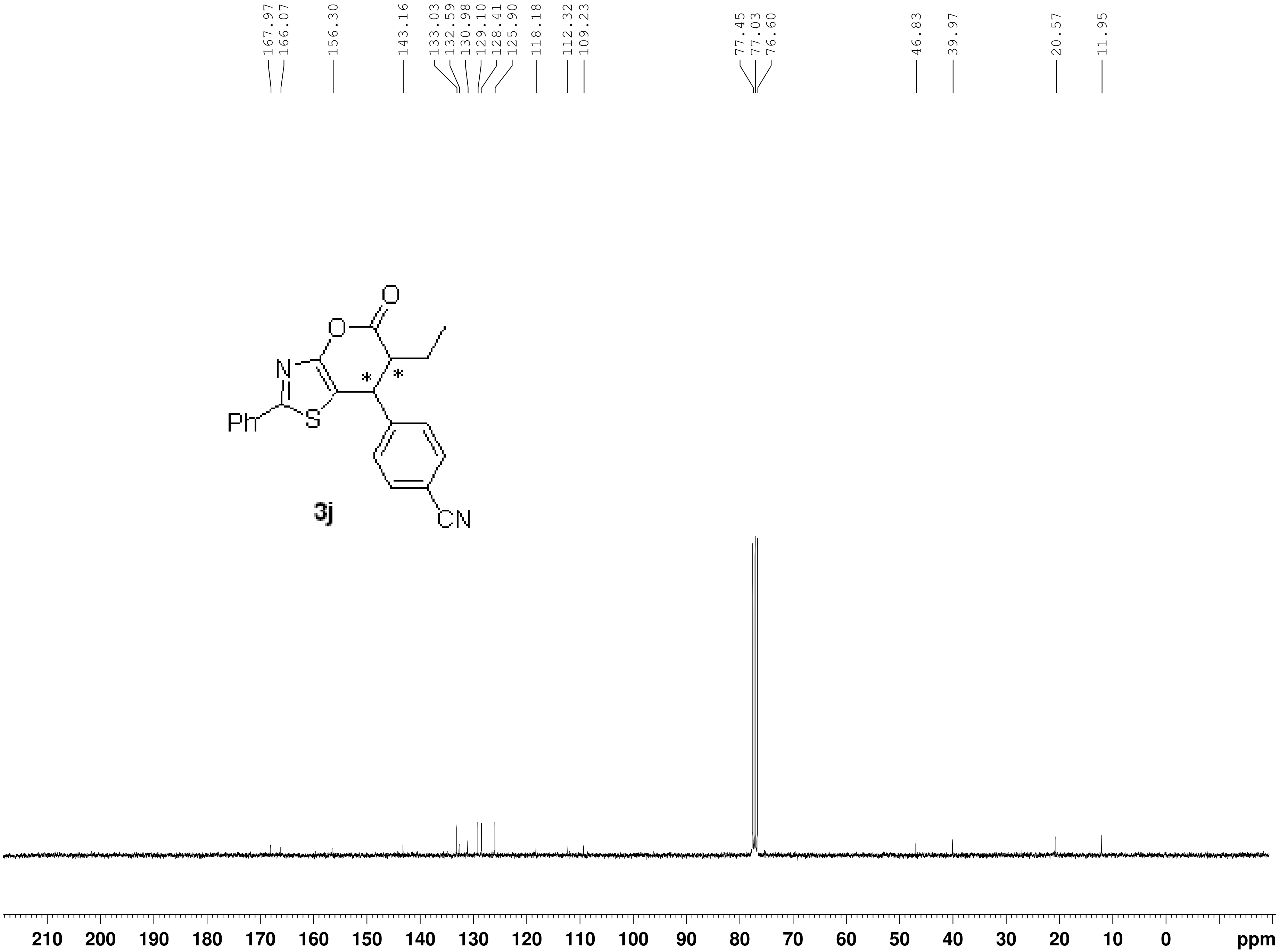
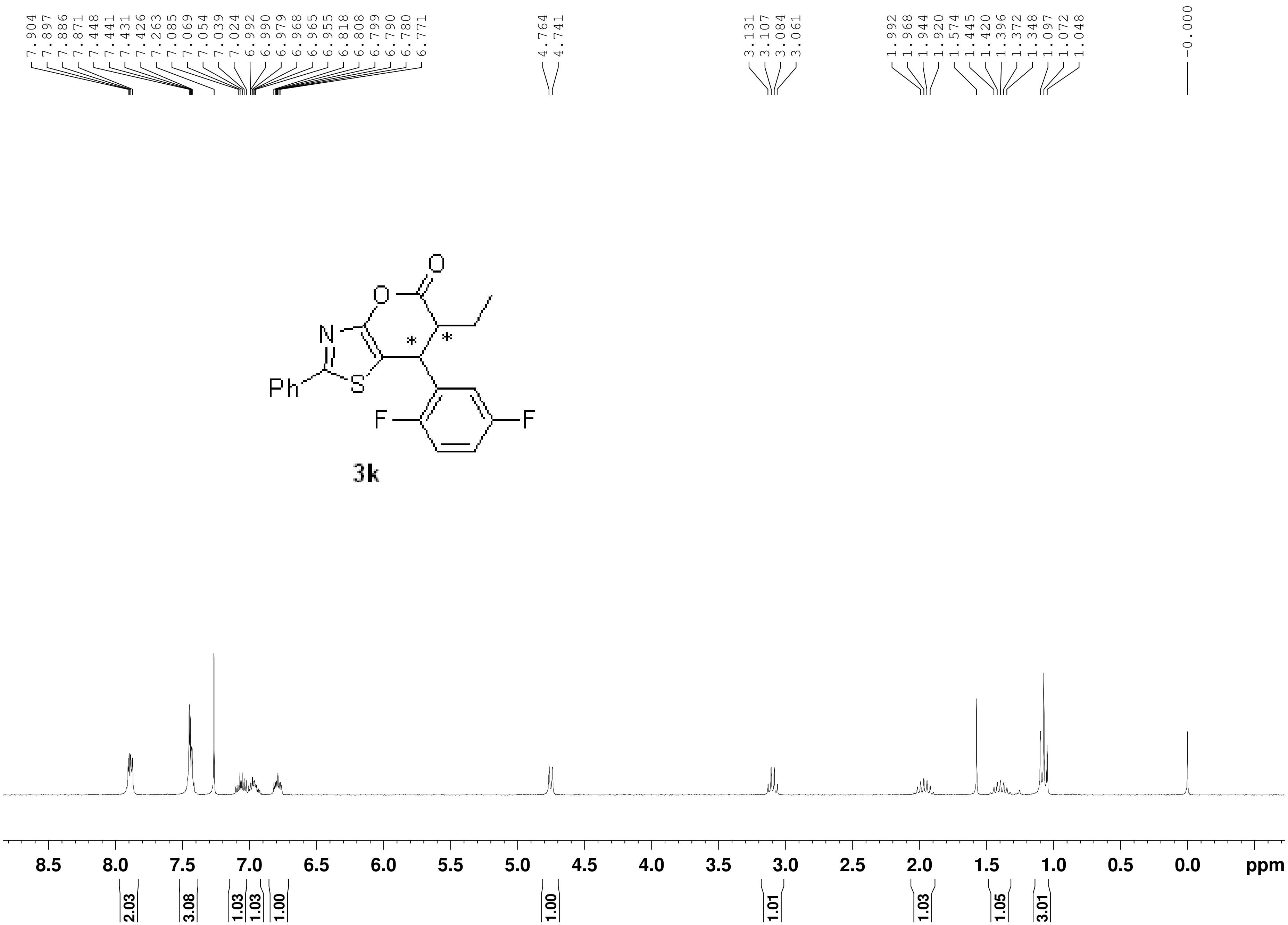
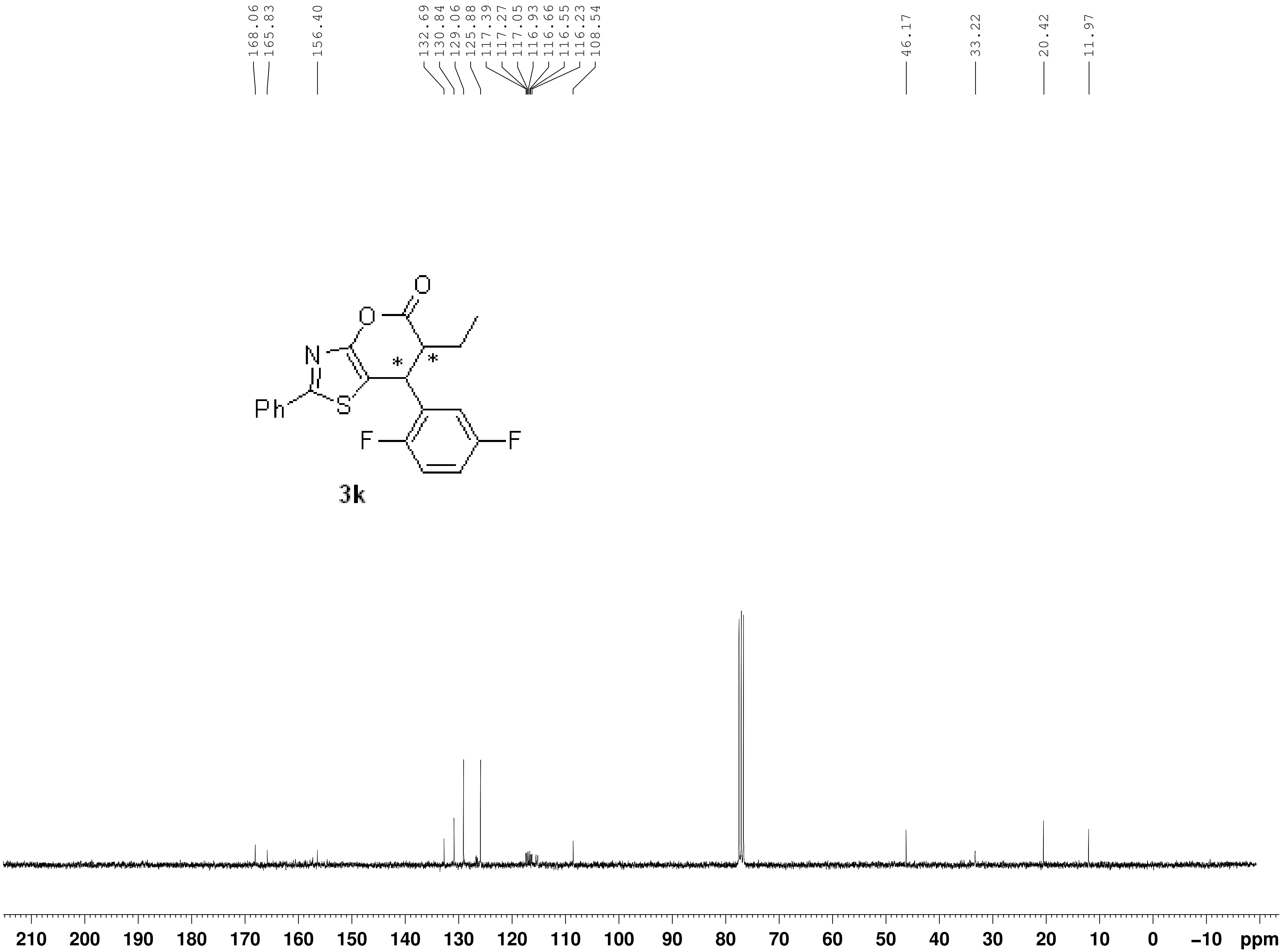
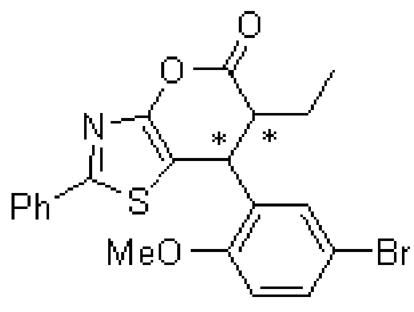
7.625
7.452
7.435
7.266
7.243
4.456
4.433
3.157
3.134
3.111
3.088
1.892
1.869
1.845
1.587
1.425
1.315
1.289
1.264
1.219
1.100
1.076
1.051
-0.000
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
–0.5
ppm
2.07
2.05
3.08
1.00
1.07
1.07
1.11
1.05
3.19


167.97
166.07
156.30
143.16
133.03
132.59
130.98
129.10
128.41
125.90
118.18
112.32
109.23
77.45
77.03
76.60
46.83
39.97
20.57
11.95
O
O
N
Ph
S
*
*
CN
3j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.904
7.897
7.886
7.871
7.448
7.441
7.431
7.426
7.263
7.085
7.069
7.054
7.039
7.024
6.992
6.990
6.979
6.968
6.965
6.955
6.818
6.808
6.799
6.790
6.780
6.771
4.764
4.741
3.131
3.107
3.084
3.061
1.992
1.968
1.944
1.920
1.574
1.445
1.420
1.396
1.372
1.348
1.097
1.072
1.048
0.000
3k
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 ppm
2.03
3.08
1.03
1.03
1.00
1.00
1.01
1.03
1.05
3.01

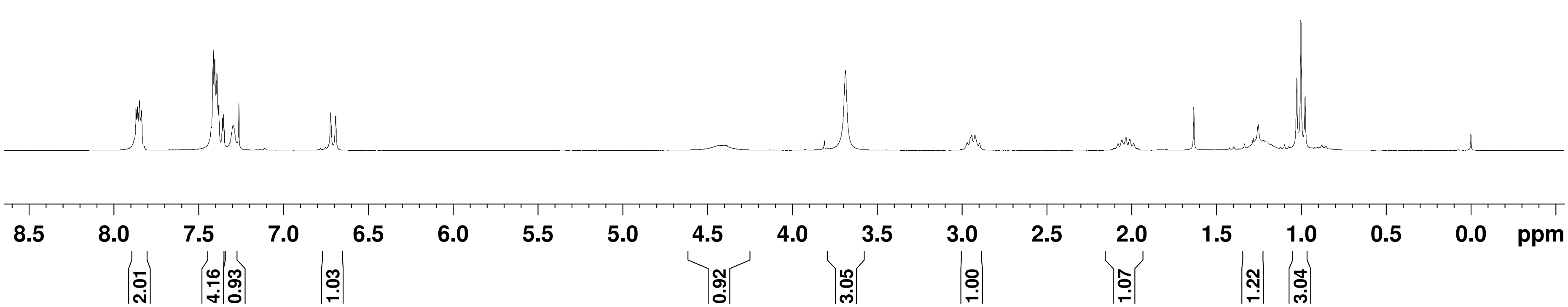

168.06
165.83
156.40
132.69
130.84
129.06
125.88
117.39
117.27
117.05
116.93
116.66
116.55
116.23
108.54
46.17
33.22
20.42
11.97
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 –10 ppm
O
O
N
S
Ph
F
F
*
*

3k

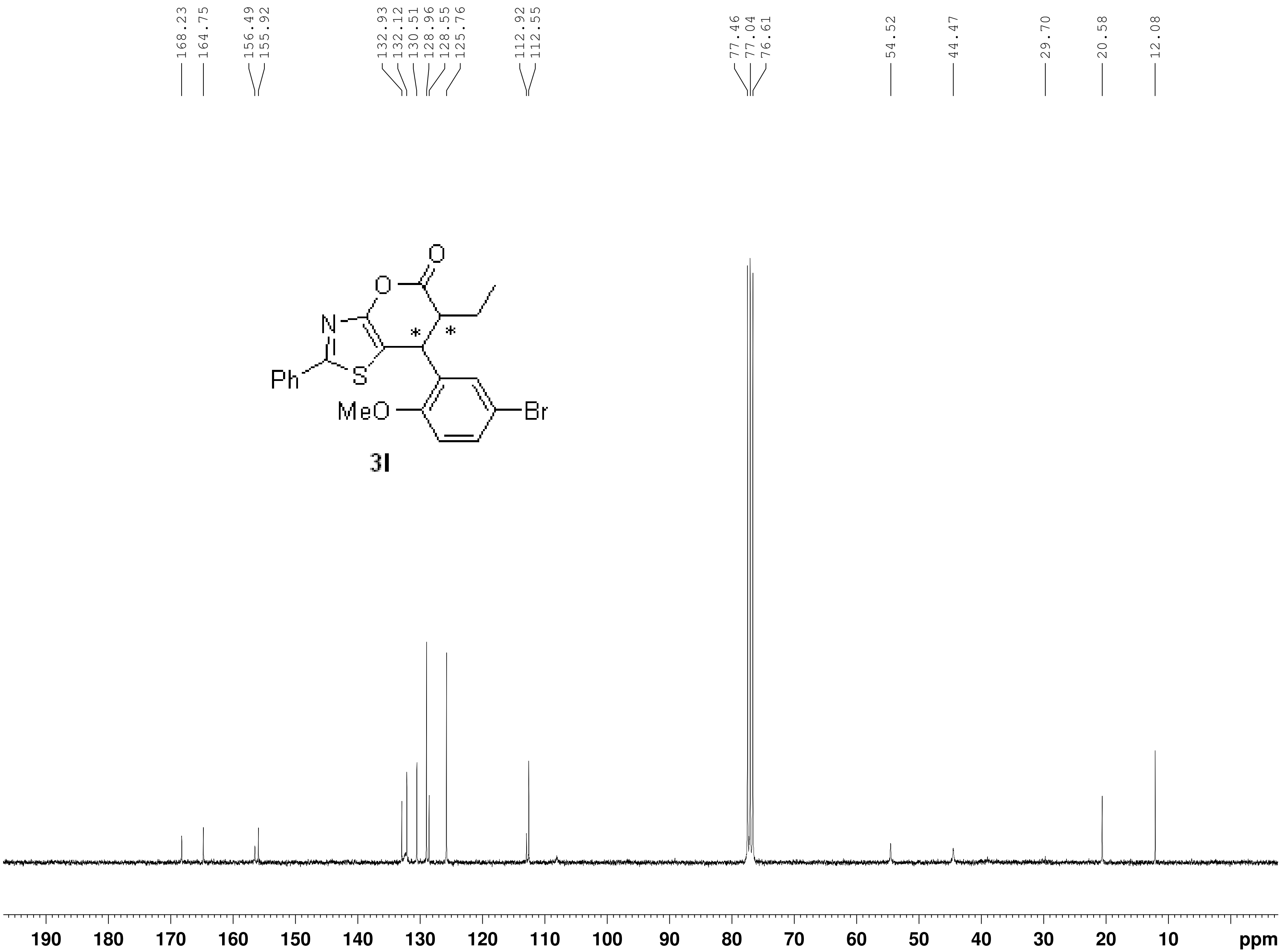


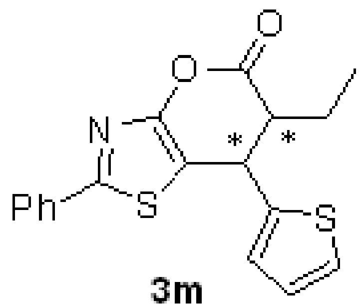
O
O
N
S
Ph
MeO
Br
*
*

3l

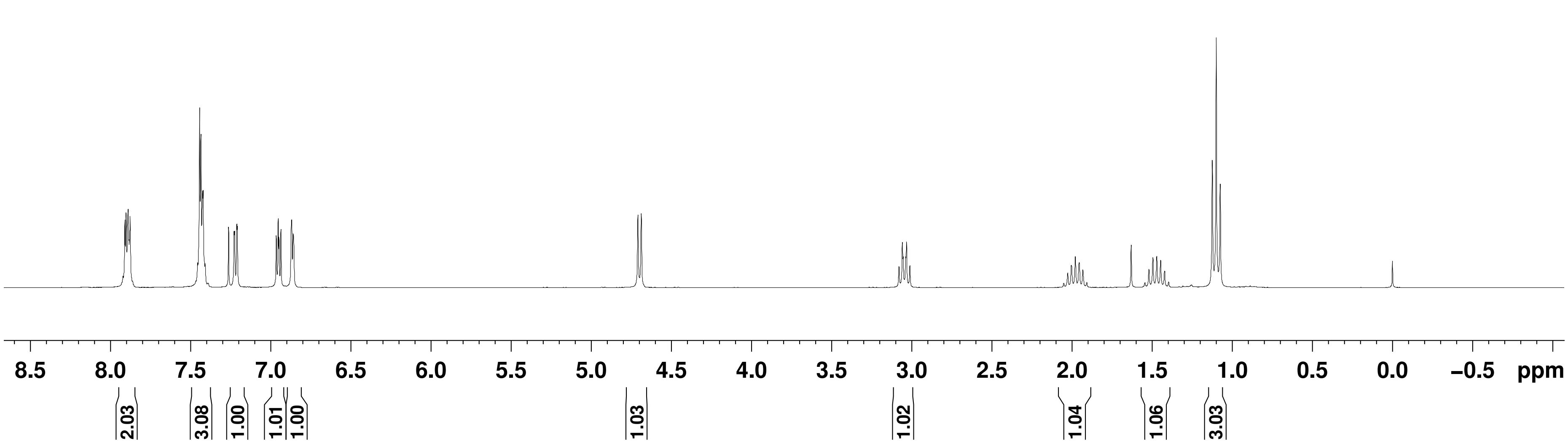


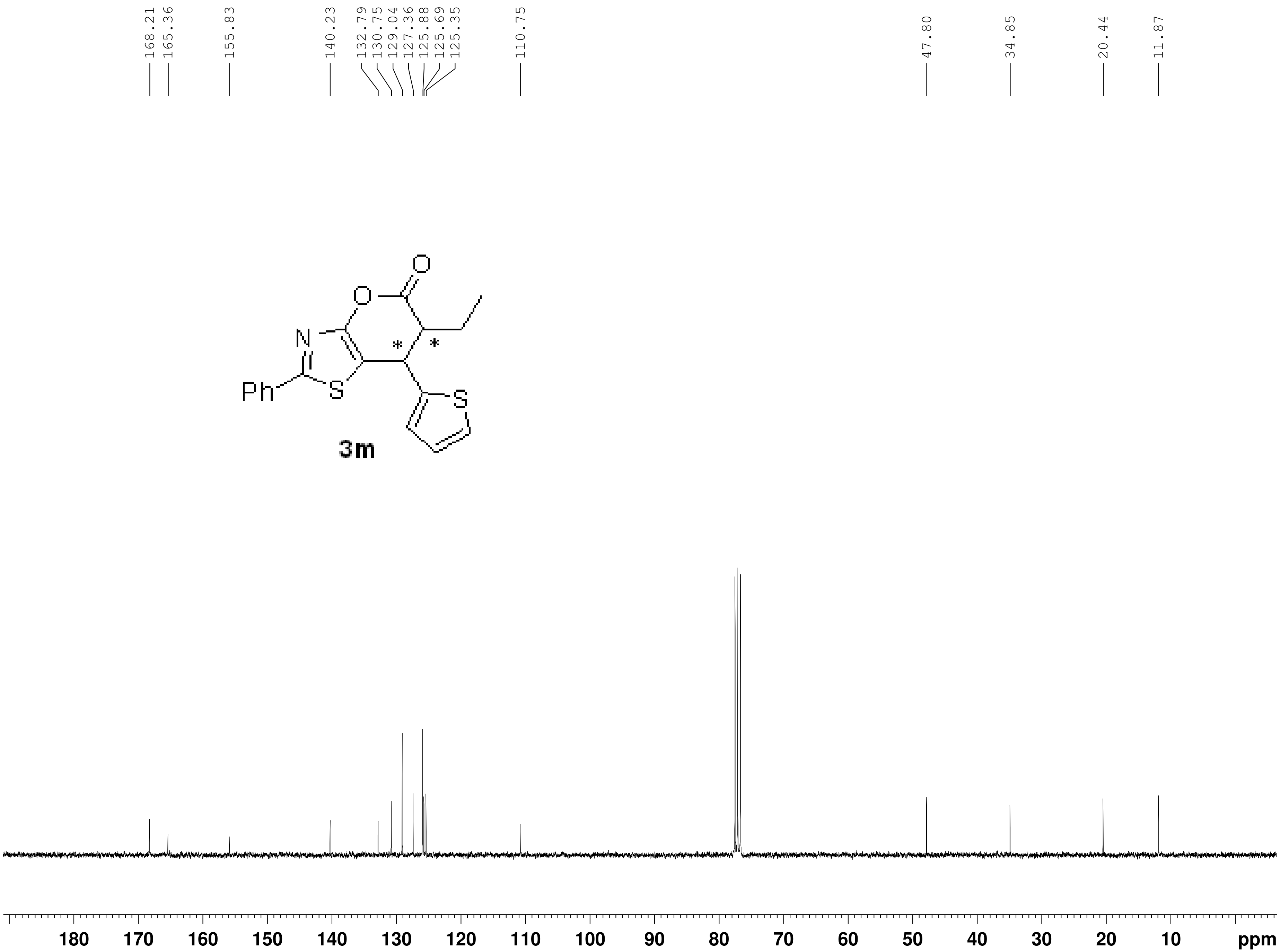
7.870
7.862
7.854
7.850
7.838
7.427
7.415
7.406
7.393
7.382
7.361
7.353
7.298
7.264
6.722
6.693
4.420
4.396
4.387
3.687
2.970
2.943
2.924
2.897
2.080
2.057
2.034
2.012
1.989
1.964
1.633
1.335
1.284
1.254
1.222
1.203
1.027
1.002
0.977
-0.000
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.01
4.16
0.93
1.03
0.92
3.05
1.00
1.07
1.22
3.04

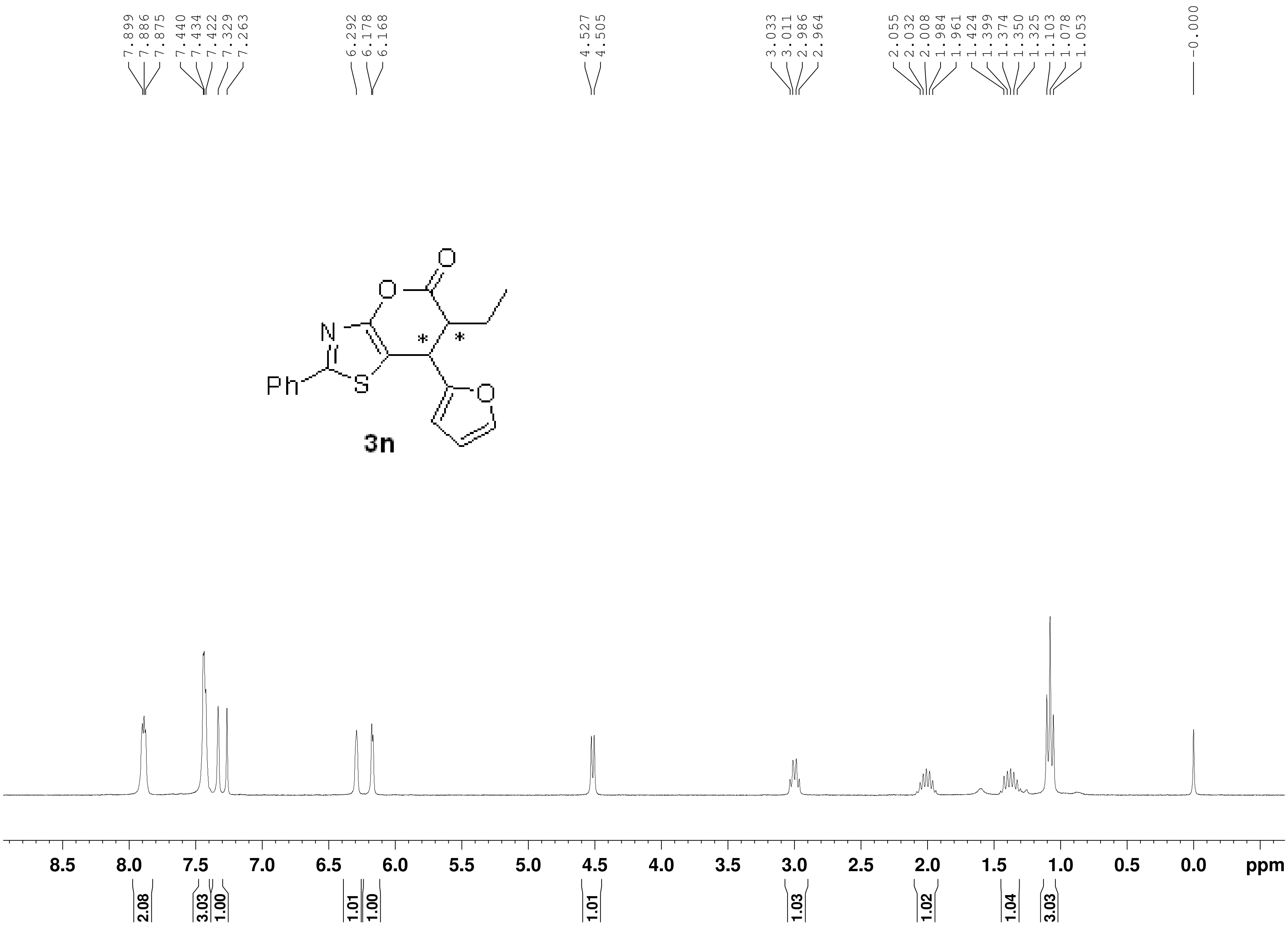

168.23
164.75
156.49
155.92
132.93
132.12
130.51
128.96
128.55
125.76
112.92
112.55
77.46
77.04
76.61
54.52
44.47
29.70
20.58
12.08
O
O
N
S
Ph
MeO
Br
*
*
3l
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

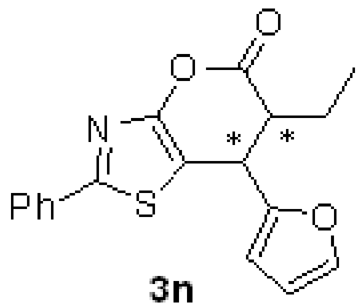

Ph
N
S
O
O
S
*
*

3m

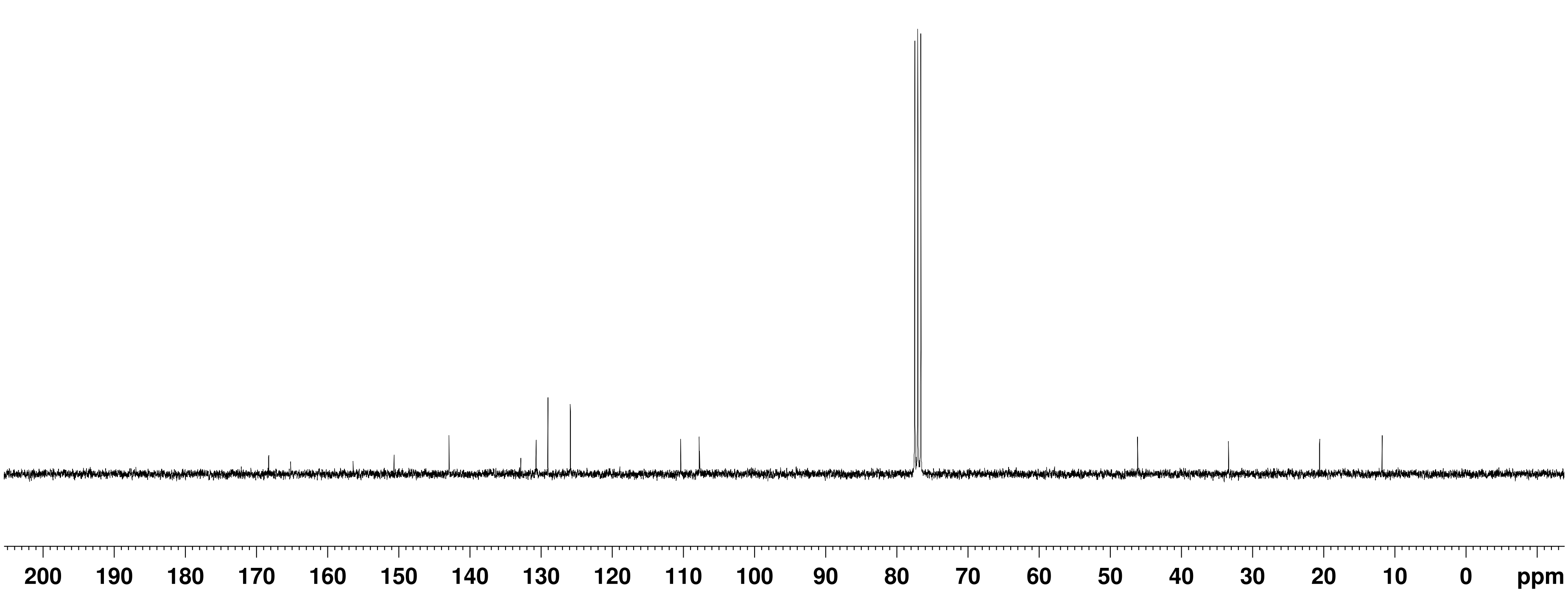

7.908
7.901
7.888
7.876
7.442
7.434
7.423
7.420
7.261
7.227
7.224
7.210
7.207
6.963
6.952
6.947
6.935
6.869
6.867
6.857
4.709
4.688
3.080
3.059
3.054
3.037
3.033
3.012
2.026
2.004
1.979
1.955
1.932
1.631
1.520
1.495
1.471
1.446
1.422
1.124
1.099
1.075
-0.000
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
–0.5
ppm
2.03
3.08
1.00
1.01
1.00
1.03
1.02
1.04
1.06
3.03

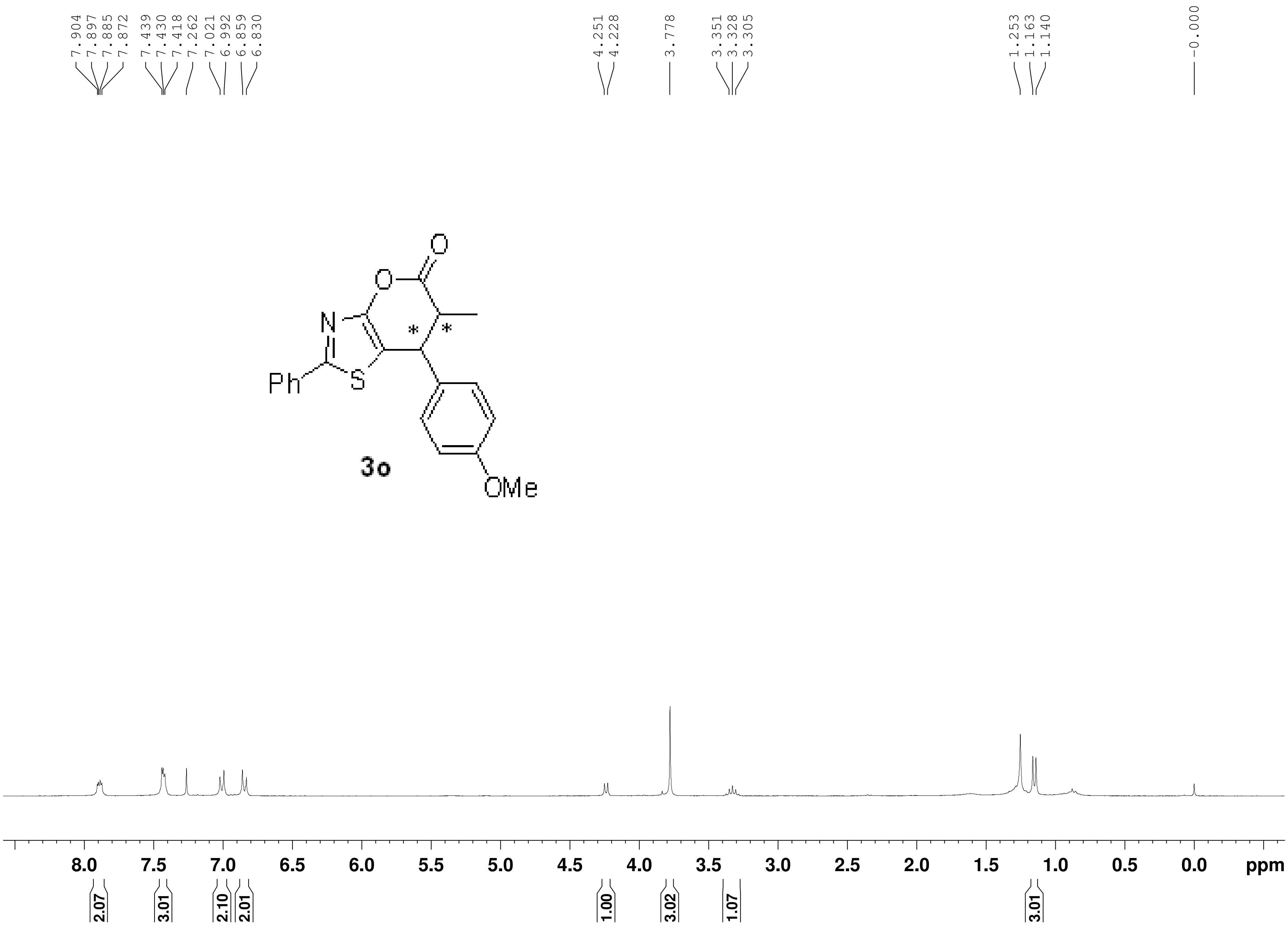

168.21
165.36
155.83
140.23
132.79
130.75
129.04
127.36
125.88
125.69
125.35
110.75
47.80
34.85
20.44
11.87
O
O
N
S
S
Ph
*
*
3m
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

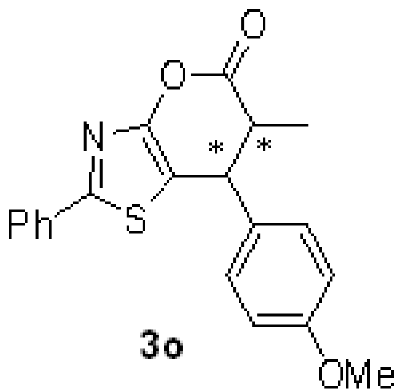

7.899
7.886
7.875
7.440
7.434
7.422
7.329
7.263
6.292
6.178
6.168
4.527
4.505
3.033
3.011
2.986
2.964
2.055
2.032
2.008
1.984
1.961
1.424
1.399
1.374
1.350
1.325
1.103
1.078
1.053
-0.000
O
O
N
S
Ph
*
*
O
3n
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.08
3.03
1.00
1.01
1.00
1.01
1.03
1.02
1.04
3.03



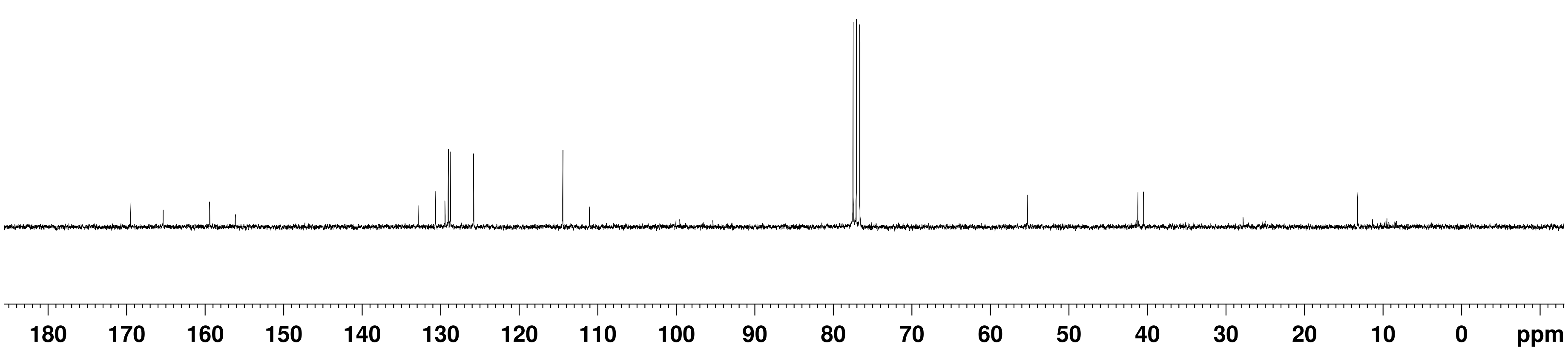
3n

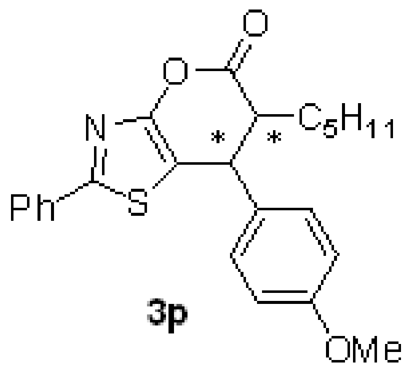

168.28
165.19
156.41
150.65
142.93
132.84
130.68
129.02
125.86
110.36
107.76
107.70
77.45
77.03
76.60
46.12
33.34
20.54
11.75
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.904
7.897
7.885
7.872
7.439
7.430
7.418
7.262
7.021
6.992
6.859
6.830
4.251
4.228
3.778
3.351
3.328
3.305
1.253
1.163
1.140
-0.000
O
O
N
*
*
Ph
S
OMe
3o
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
ppm
2.07
3.01
2.10
2.01
1.00
3.02
1.07
3.01

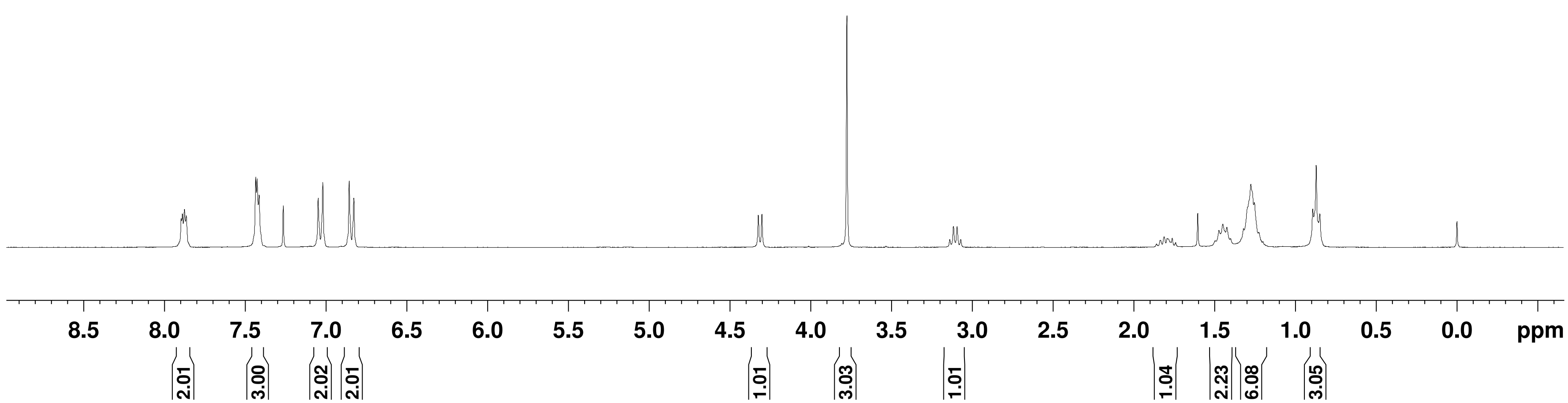


3o

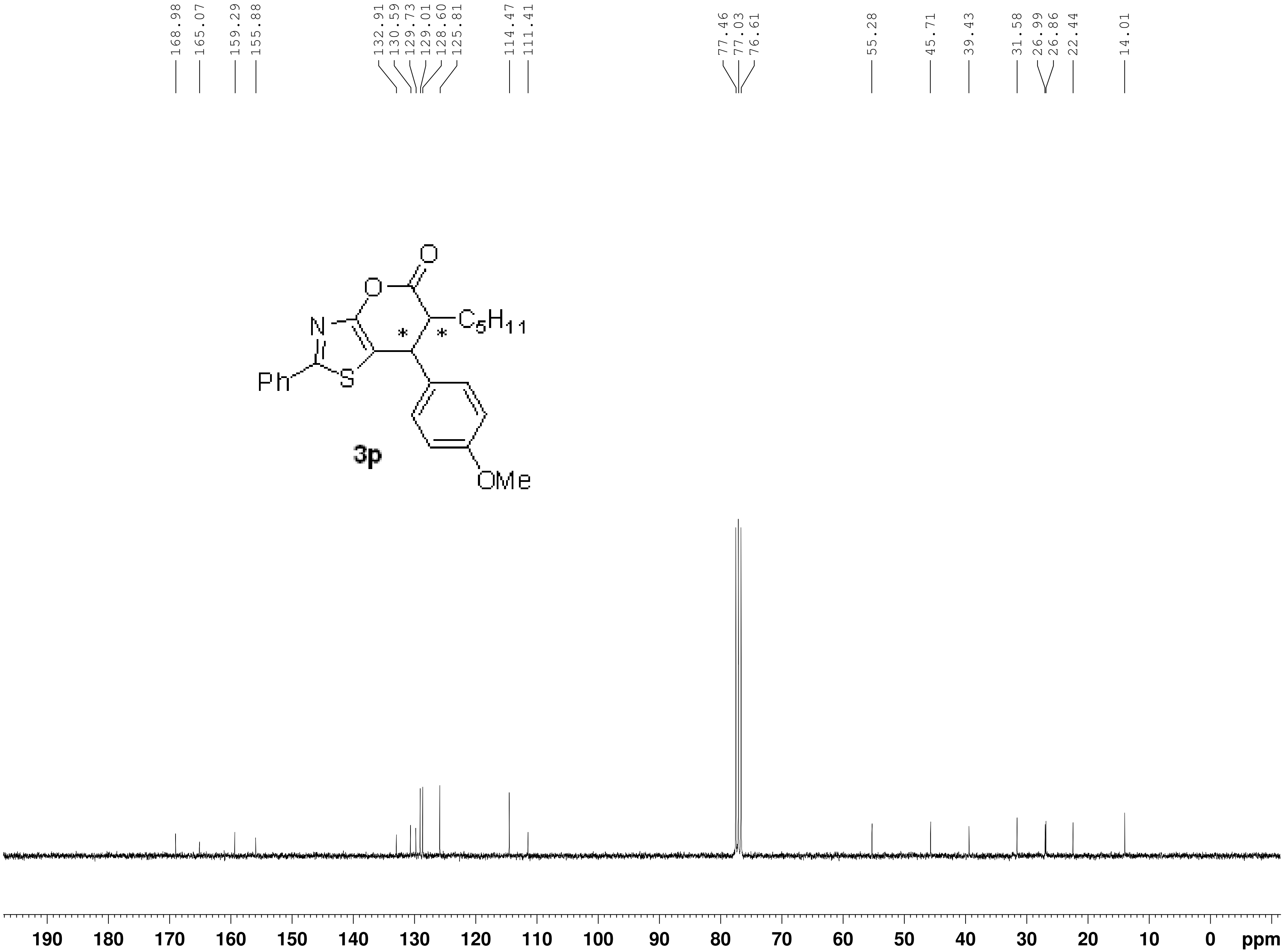

169.40
165.27
159.36
156.08
132.87
130.64
129.45
129.02
128.75
125.81
114.45
111.05
77.47
77.05
76.62
55.29
41.20
40.48
13.22
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



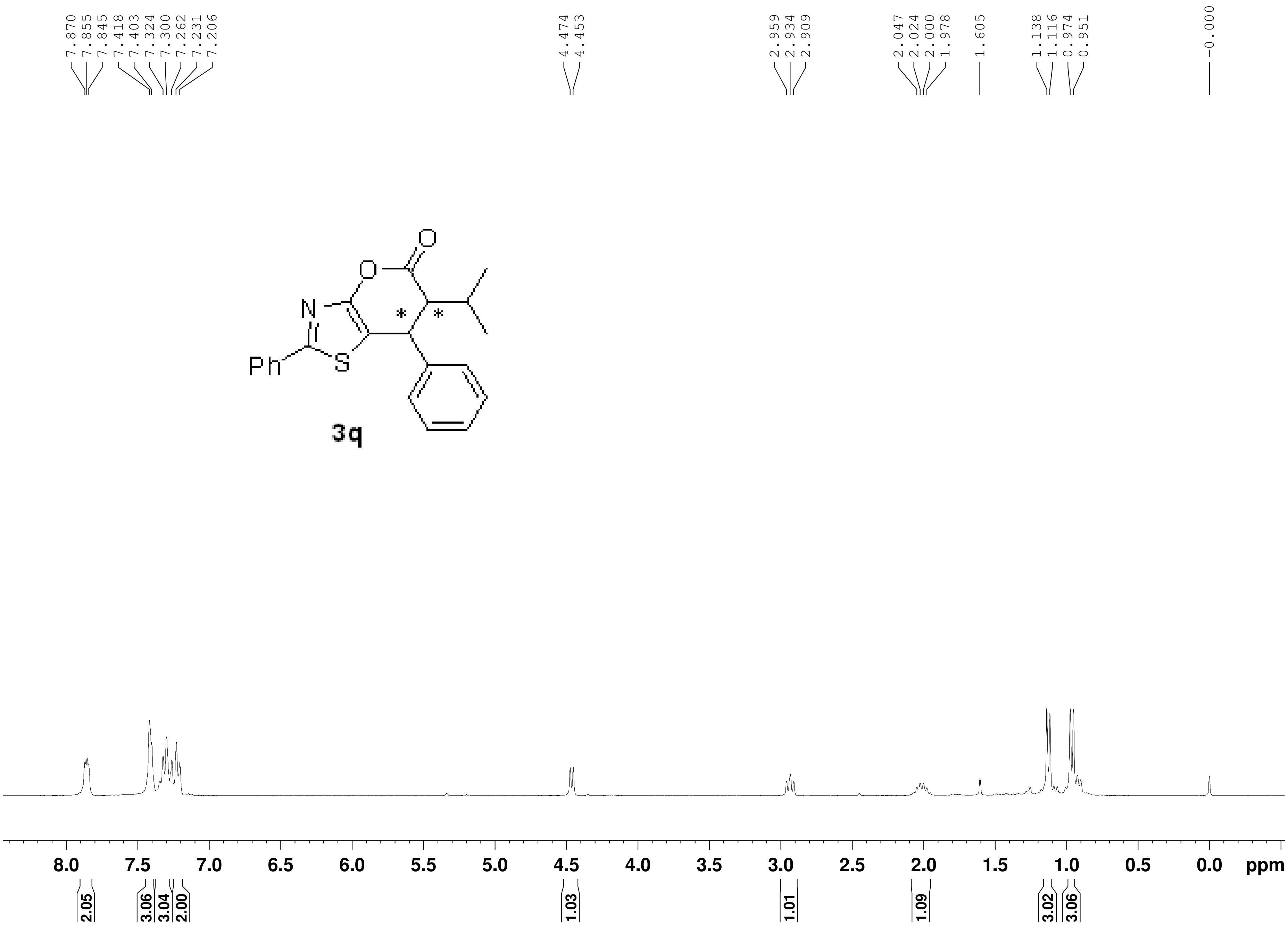
3p

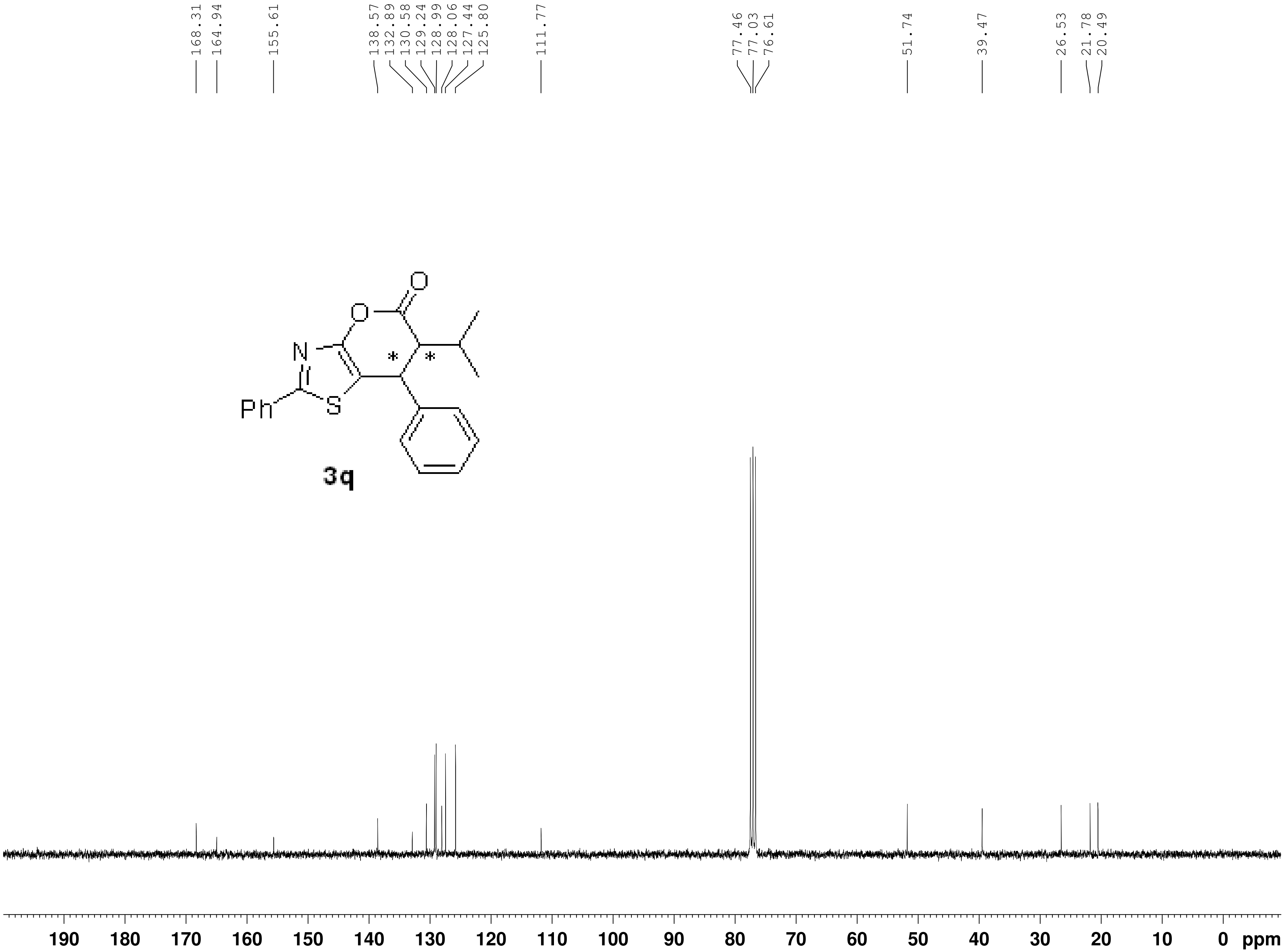


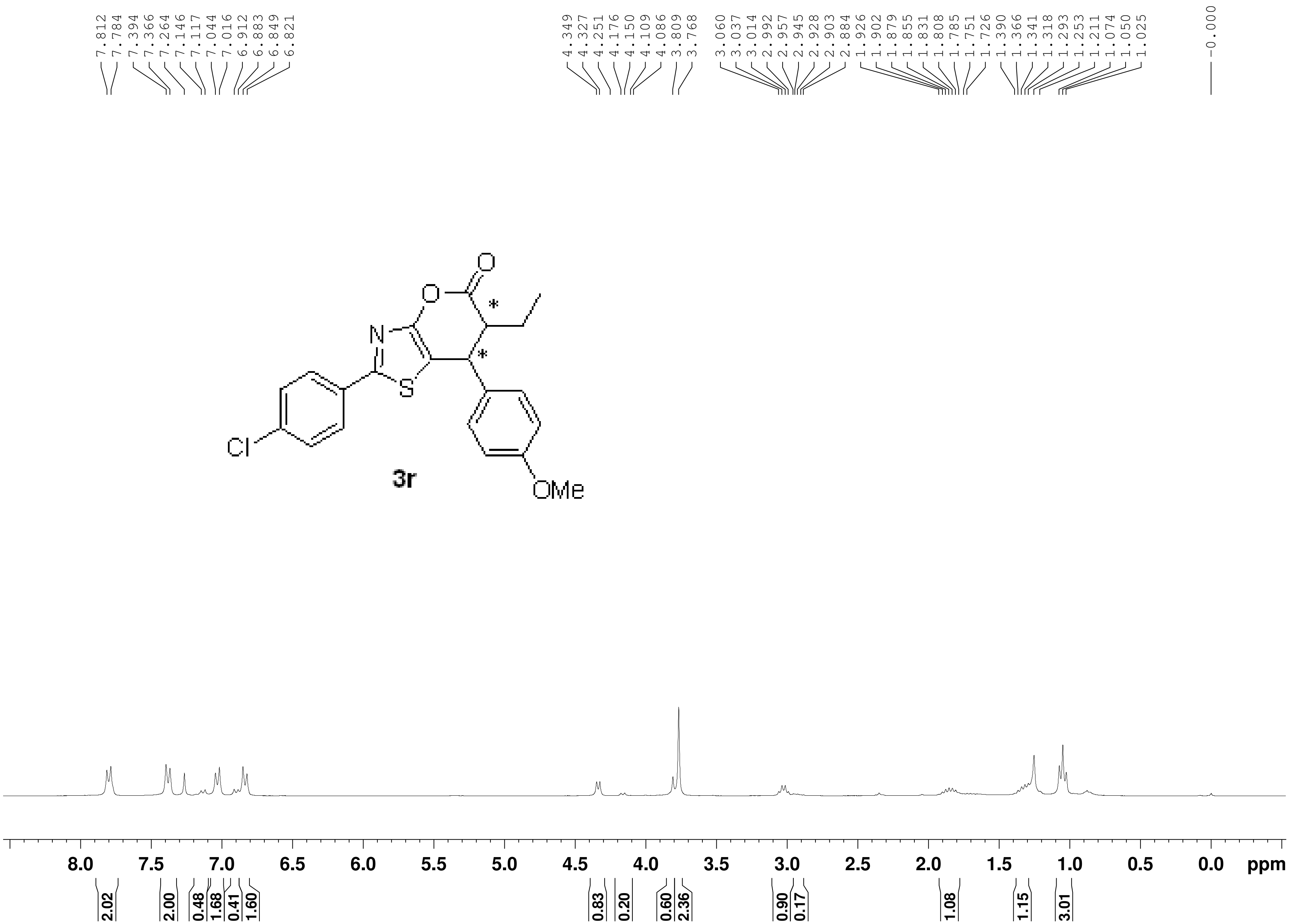
7.893
7.886
7.874
7.862
7.432
7.424
7.412
7.262
7.046
7.017
6.854
6.825
4.324
4.302
3.776
3.139
3.116
3.094
3.071
1.813
1.794
1.787
1.762
1.605
1.449
1.424
1.321
1.296
1.276
1.254
0.892
0.871
0.849
-0.000
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.01
3.00
2.02
2.01
1.01
3.03
1.01
1.04
2.23
6.08
3.05

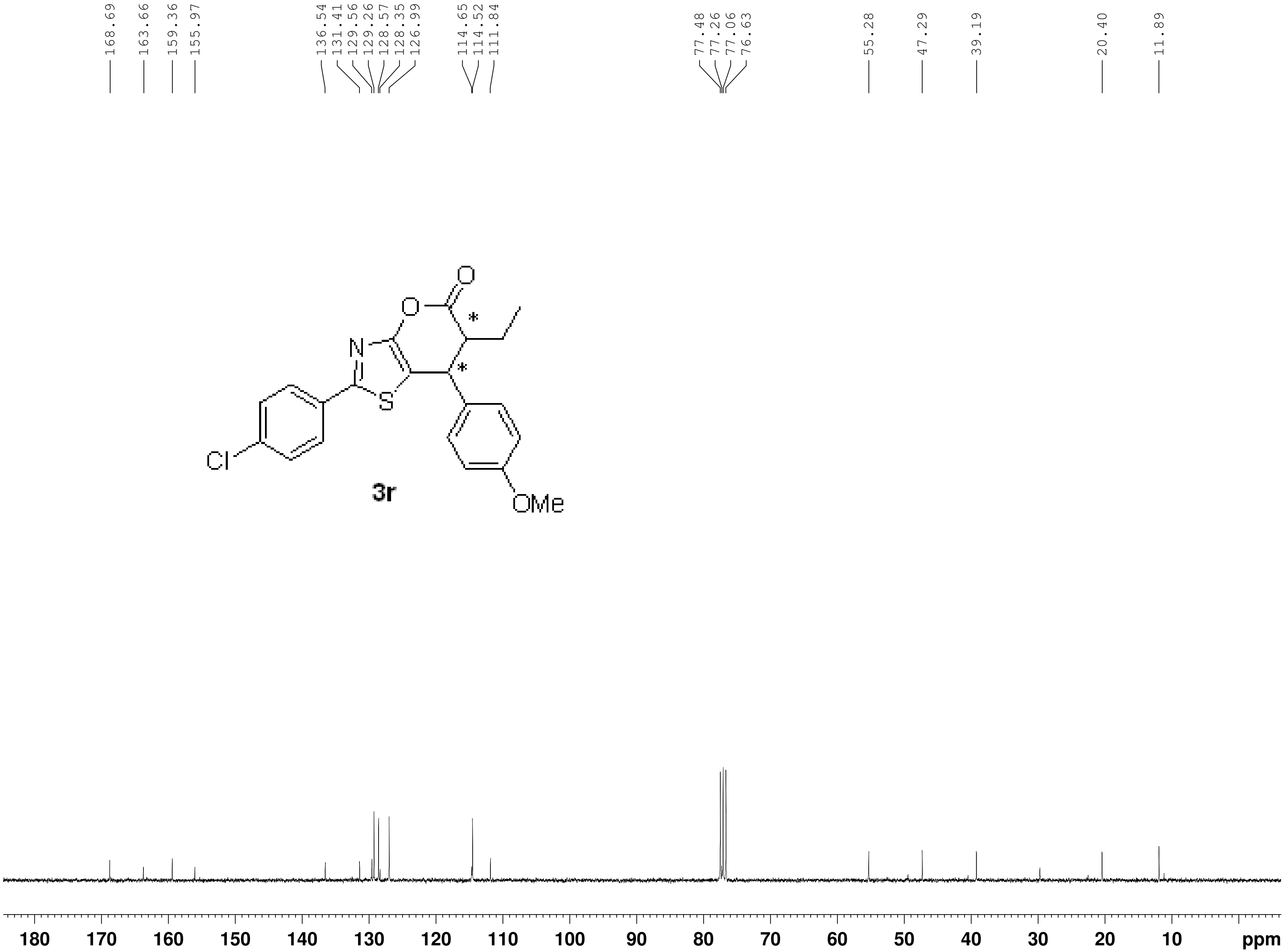


168.98
165.07
159.29
155.88
132.91
130.59
129.73
129.01
128.60
125.81
114.47
111.41
77.46
77.03
76.61
55.28
45.71
39.43
31.58
26.99
26.86
22.44
14.01
O
O
N
S
Ph
C_5H_{11}
OMe
3p
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.870 7.855 7.845 7.418 7.403 7.324 7.300 7.262 7.231 7.206
4.474 4.453
2.959 2.934 2.909
2.047 2.024 2.000 1.978
1.605
1.138 1.116 0.974 0.951
-0.000
Ph
N
O
S
3q
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 ppm
2.05 3.06 3.04 2.00 1.03 1.01 1.09 3.02 3.06


168.31
164.94
155.61
138.57
132.89
130.58
129.24
128.99
128.06
127.44
125.80
111.77
77.46
77.03
76.61
51.74
39.47
26.53
21.78
20.49
O
O
N
S
Ph
*
*
3q
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.812 7.784 7.394 7.366 7.264 7.146 7.117 7.044 7.016 6.912 6.883 6.849 6.821
4.349 4.327 4.251 4.176 4.150 4.109 4.086 3.809 3.768
3.060 3.037 3.014 2.992 2.957 2.945 2.928 2.903 2.884 1.926 1.902 1.879 1.855 1.831 1.808 1.785 1.751 1.726
1.390 1.366 1.341 1.318 1.293 1.253 1.211 1.074 1.050 1.025
-0.000
O
O
N
S
Cl
OMe
*
*
3r
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 ppm
2.02 2.00 0.48 1.68 0.41 1.60 0.83 0.20 0.60 2.36 0.90 0.17 1.08 1.15 3.01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163.66
159.36
155.97
136.54
131.41
129.56
129.26
128.57
128.35
126.99
114.65
114.52
111.84
77.48
77.26
77.06
76.63
55.28
47.29
39.19
20.40
11.89
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
Cl
N
S
O
O
*
*
OMe

3r