Supporting Information

Photochemical Regioselective C(sp^3)–H Amination of Amides Using *N*-haloimides

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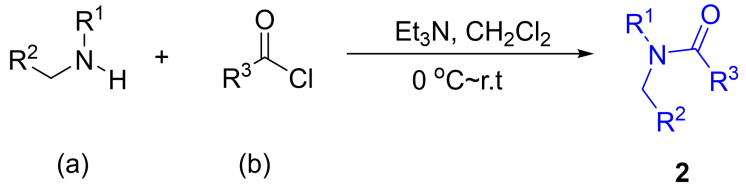
General Information

All the solvents and commercially available reagents were purchased from commercial sources (Acros Organics,TCI, Alfa Aesar, Sigma-Aldrich, Oakwood) and used directly. Thin layer chromatography (TLC) was performed on EMD precoated plates (silica gel 60 F254, Art 5715) and visualized by fluorescence quenching under UV light or stains for TLC Plates. Column chromatography was performed on EMD Silica Gel 60 (200–300 Mesh) using a forced flow of 0.5–1.0 bar. The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AVANCE III-400 spectrometer. ^{1}H NMR data was reported as: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. ^{13}C NMR data was reported in terms of chemical shift (δ ppm), multiplicity, and coupling constant (Hz). High Resolution Mass Spectrometry (HRMS) analysis was obtained using Agilent Technologies 6520 Accurate-Mass Q-TOF LC/MS system. UV-Vis was obtained using GENESYS™ 10S UV-Vis Spectrophotometer and fisherbrand macro quartz cuvettes (cat. No. 14-958-112). Melting point was obtained using MPA160 Melting Point Apparatus. A Kessil broadband Blue LED lamp 34W (No. BL-20,391) was used for this light-promoted reaction. The vial was placed approximately 4 cm away from the Blue LED, with the LED shining directly at the side of the vial. 10ml microwave reaction vial secured by 20mm aluminum seals with 0.125-inch thick, blue PTFE / white silicone septa was used for the reaction.

Procedure for Preparation of Starting Materials

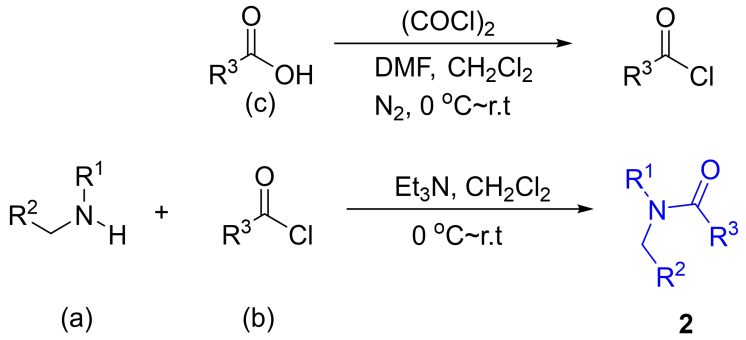
1. The General Procedure for the Preparation of Amides 2:[1]

Procedure A:



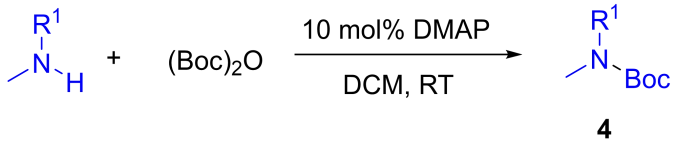
To a stirred solution of amine (a) (6 mmol) in dichloromethane (18 mL) were added triethylamine (6.6 mmol) and acyl chloride (b) (1.0 mmol) dropwisely under 0 °C. Then the mixture was stirred at r.t. overnight. Then the reaction mixture was poured into a separatory funnel and washed with saturated $NaHCO_3$ (aq) and extracted with 3*40 mL CH_2Cl_2. The combined organic phases were dried over anhydrous Na_2SO_4, concentrated under reduced pressure and purified by column chromatography to afford products **2**.

Procedure B:



To a solution of carboxylic acid (c) (6 mmol, 1.0 equiv) and DMF (4 drops) in CH_2Cl_2 (18 mL) at 0 °C was added $(COCl)_2$ (2 equiv) dropwise. After completion of addition, the solution was stirred for 5 minutes at 0 °C and then stirred at rt for 1 h. The solution was concentrated in vacuo to obtain the crude acyl chloride (b), which will be used without purification. To a mixture of amine (a) (6 mmol) (1.0 equiv) and triethylamine (2.0 equiv) in CH_2Cl_2 (18 mL) at 0 °C was added the solution of crude acyl chloride (b) in CH_2Cl_2 dropwise. After stirred for 5 minutes at 0 °C, the mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched with a saturated $NaHCO_3$ solution and extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column to give compounds **2**.

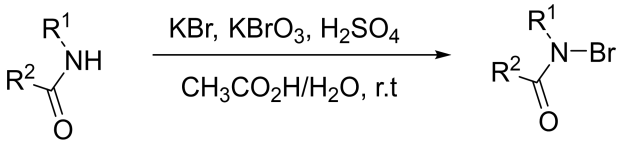
2. The General Procedure for the Preparation of *N*-Boc amines 4:[2]



According to literature, the *N*-Boc amines can be synthesized by the condensation of corresponding amines with di-*tert*-butyl dicarbonate. The corresponding amines (1.0 equiv.) and

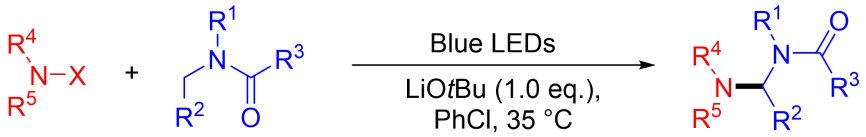
4-dimethylaminopyridine (10 mol %) were mixed in a flask with a magnetic stirring bar. DCM was added as solvent. Then a solution of di-*tert*-butyl dicarbonate (1.1 equiv.) in DCM was added slowly under ice bath conditions. The mixture was stirred 10 min at 0 °C and then 24 h at rt. The solution was washed with water and brine, then dried over $MgSO_4$ and concentrated. The crude product was purified by flash column chromatography, and corresponding *N*-Boc amines were obtained.

3. Synthesis of *N*-haloimides.[3]



To a mixture of imides (8 mmol), $KBrO_3$ (4 mmol) and sulphuric acid (97%, 0.33 mL, 7.58 g, 6 mmol) in aqueous acetic acid (70%, 5.6 mL), KBr(0.637g 5.4 mmol) was added portionwise at room temperature. The reaction mixture was stirred at room temperature overnight, the precipitate was filtered off, washed with water and dried to afford the crude product. The crude product was crystallized from acetic acid/water to get pure product which was thoroughly vacuum-dried at room temperature.

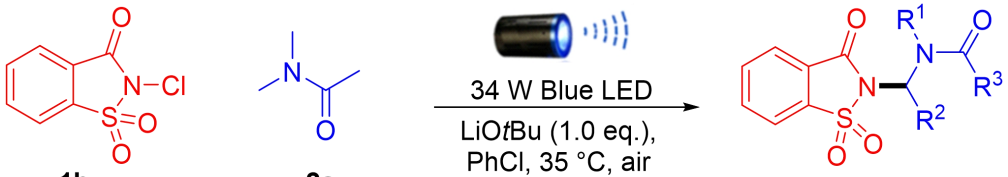
General Procedure for the Synthesis of 3 or 5.



1 **2 or 4** **3 or 5**

A 10 mL microwave vial was charged with *N*-halo saccharins or *N*-halo phthalimides or other nitrogen sources (0.2 mmol), Li*O*t*B*u (16 mg, 0.2 mmol), 1.0 ml PhCl. Then amides (1 mmol) was added into the tube and capped with 20 mm microwave crimp caps with septa. The reaction mixture was stirred vigorously at room temperature for 3 mins and then put the vial approximately 4 cm away from the Blue LED lamp and then stirred overnight. After the completion of reaction, the product was determined by thin layer chromatography (TLC). The solvent was removed under vacuo, then the residue was purified by flash chromatography on silica gel to yield the desired product **3 or 5**.

1 mmol scale detailed method included for one-step transformations



1b **2a** **3ba**

A 10 mL microwave vial was charged with *N*-chlorosaccharin (218 mg, 1 mmol) , Li*O*t*B*u (80 mg, 1 mmol), 3.0 ml PhCl. Then *N*,*N*-dimethylacetamide (435 mg, 5 mmol) was added into the tube and capped with 20 mm microwave crimp caps with septa. The reaction mixture was stirred vigorously at room temperature for 3 mins and then put the vial approximately 4 cm away from the Blue LED lamp and stirred 24h. After the completion of reaction, the product was determined by thin layer

chromatography (TLC). The solvent was removed under vacuo, then the residue was purified by flash chromatography (ethyl acetate/dichloromethane=1/10 to 1/5) on silica gel to yield the desired product **3ba** (164 mg, 61 %).

Full Table of Reaction Optimization

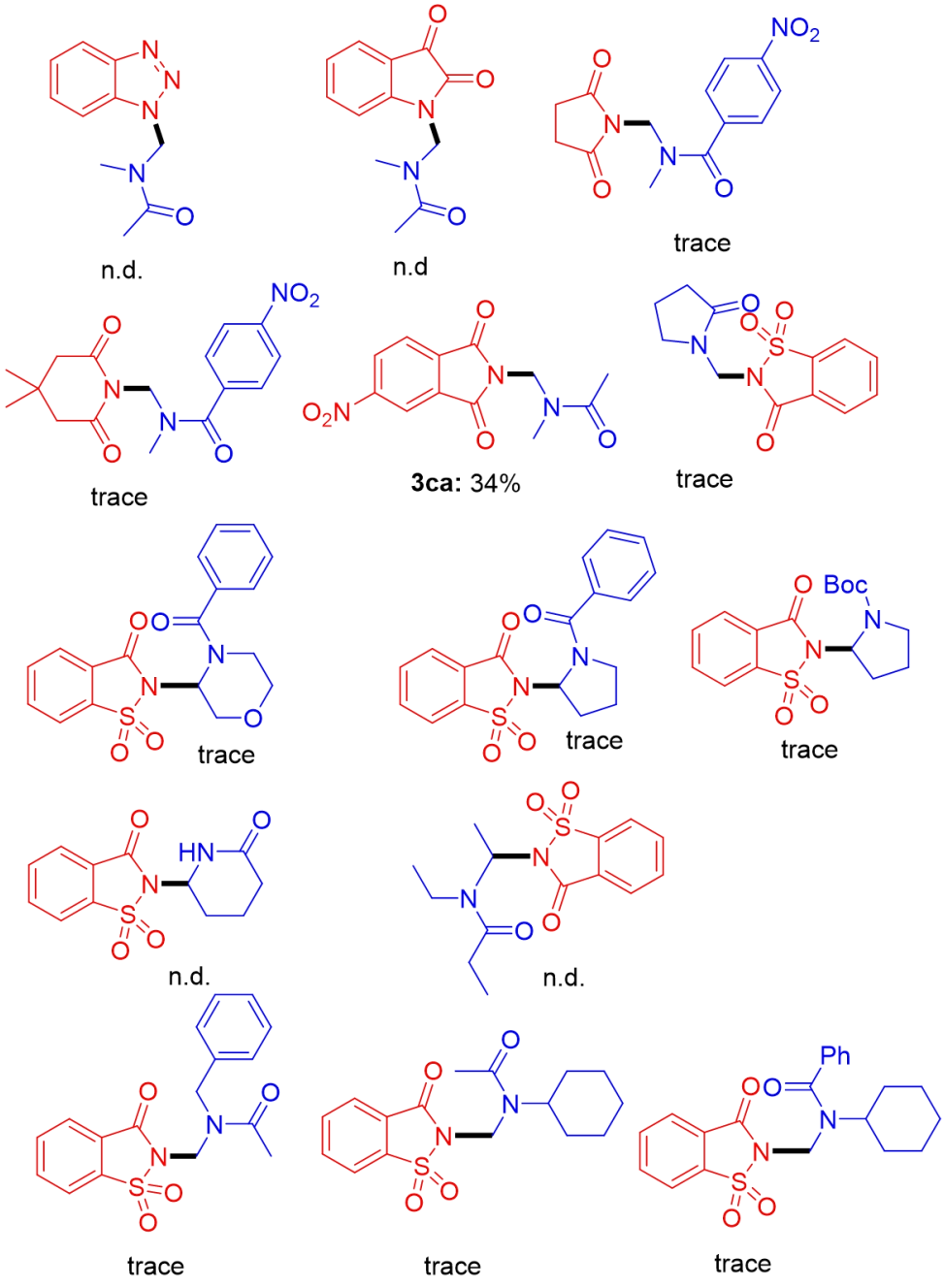
1a ***2a*** ***3aa***

Entry	Base (*equiv.*)	Solvent (*mL*)	Yield (%)[b]
1	LiO*t*Bu (1.0)	$PhCF_3$ (1.0)	42
2	LiO*t*Bu (1.0)	PhCl (1.0)	67 (65)[c]
3	LiO*t*Bu (1.0)	Ch_3CN (1.0)	10
4	LiO*t*Bu (1.0)	PhH (1.0)	49
5	NaO*t*Bu (1.0)	PhCl (1.0)	24
6	KO*t*Bu (1.0)	PhCl (1.0)	2
7	DBU (1.0)	PhCl (1.0)	8
8	LiO*t*Bu(1.0)	PhCl (0.5)	53
9	LiO*t*Bu (1.0)	PhCl (0.75)	57
10	LiO*t*Bu (1.0)	PhCl (1.5)	62
11	LiO*t*Bu (1.0)	PhCl (2.0)	59
12	LiO*t*Bu (1.0)	PhCl (2.5)	54
13	LiO*t*Bu (1.0)	PhCl (3.0)	47
14	-	PhCl (1.0)	-
15	LiO*t*Bu (0.75)	PhCl (1.0)	45
16	LiO*t*Bu (1.25)	PhCl (1.0)	63
17	LiO*t*Bu (1.5)	PhCl (1.0)	35
18	LiO*t*Bu (2.0)	PhCl (1.0)	15
19[d]	LiO*t*Bu(1.0)	PhCl (1.0)	7
20[e]	LiO*t*Bu (1.0)	PhCl (1.0)	44
21[f]	LiO*t*Bu (1.0)	PhCl (1.0)	60
22[g]	LiO*t*Bu (1.0)	PhCl (1.0)	16

a. Reaction conditions: ***1a*** (0.2 mmol, 1 eq.), ***2a*** (1.0 mmol, 5 eq.), base (1 eq.), solvent (1 mL), room temperature around reaction flask was 35 °C (heating caused by the LED lamp), reaction flask capped, overnight. *b.* ^{1}H-NMR yields using dibromomethane as internal standard. *c.* Isolated yield. *d.* The reaction performed at 60 °C without light. *e.* ***2a*** (2.5 eq.) was used instead of 5 eq. *f.* ***2a*** (4 eq.) was used intead of 5 eq. *g.* The reaction was performed by adding 20 μL of H_2O.

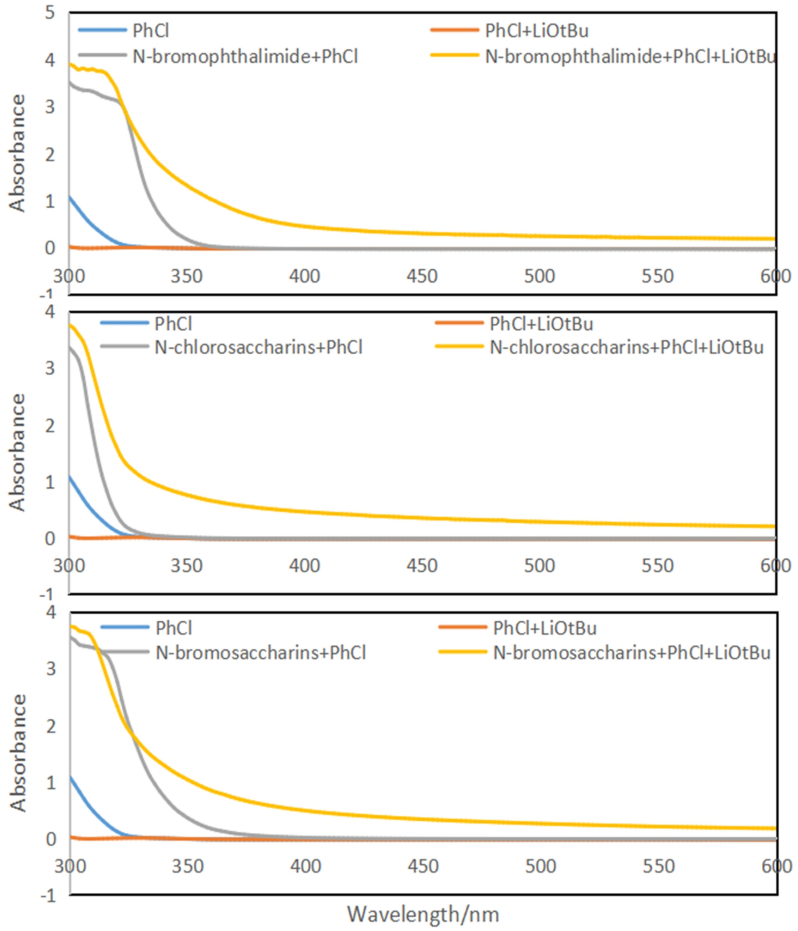
Additional Substrate Scope Explored for the Transformation

1 **2** **3**



[a] Reaction conditions: **1** (0.2 mmol), **2** (1.0 mmol), LiO*t*Bu (0.2 mmol), 1.0 ml PhCl, 35 °C (Heating caused by the LED lamp.), overnight. [b] Isolated yields. n.d means no detected in TLC and NMR

UV-vis Spectra

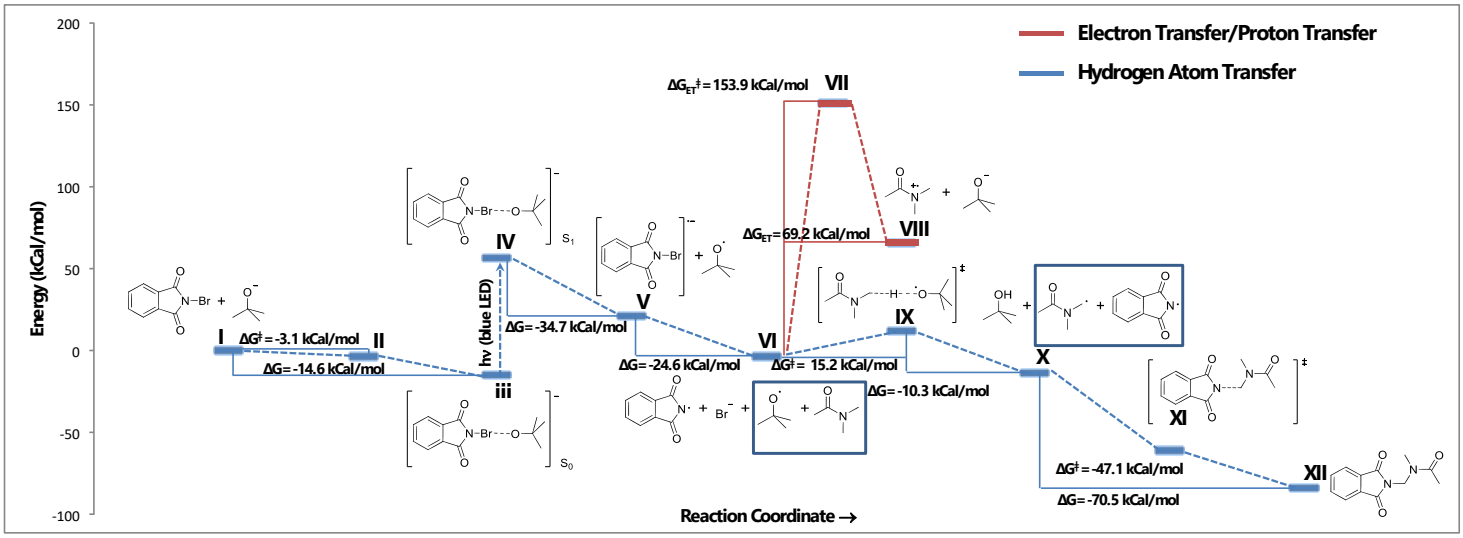


UV-vis spectroscopic measurements on various combination of ***1a***, ***1b*** and lithium *tert*-butoxide in PhCl. Spectra taken with 0.04mmol of substrate in 2mL of PhCl; concentration 0.02mmol/mL.

To further understand the role played by Li*O*t*Bu*, we performed a series of UV−vis spectroscopic measurements on various combinations of ***1a***, ***1b*** and lithium *tert*-butoxide in PhCl (Figure above). The combination of *N*-haloimides, Li*O*t*Bu* and PhCl (yellow line) showed an increased in absorption throughout all waves lengths, but also shows that this combination can absorb blue light (380–500 nm) while the other combinations of reagents (blue, red, and grey lines) do not show significant light absorbing property in the blue light wavelength in this test. This indicates that Li*O*t*Bu* is interacting with the *N*-haloimide, possibly via halogen bonding,[1] and generates a halogen-bonded adduct capable of absorbing blue light to initiate the radical reaction.

1 Weinberger, C.; Hines, R.; Zeller, M.; Rosokha, S. V. Continuum of Covalent to Intermolecular Bonding in the Halogen Bonded Complexes of 1,4-Diazabicyclo [2.2.2]octane with Bromine Containing Electrophiles. *Chem. Commun.* **2018**, *54*, 8060−8063.

Calculated Energy Reaction Pathway

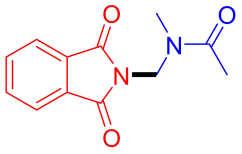


Energy reaction pathways (kCal/mol) of *N*-bromophthalimide ***1a*** with *tert*-butoxide through computational simulations using B3LYP/6-311+G(d,p)/MWB28 (Br) level of theory.

To further understand the process in which the reaction takes place, the energetic profile of the mechanism was explored through quantum calculations (Figure above, computational details can be found in S60). The formation of an electron-donor-acceptor (EDA) complex presents an exergonic energy profile (-14.6 kCal/mol), denoting that its formation is favored (**I→III**). The decomposition of the EDA complex to yield the radical anion is an endergonic process (36.1 kCal/mol) through conventional synthetic processes. However, through electronic excitation of the EDA complex (**III→IV**) this pathway becomes accessible, yielding *t*-BuO• and the radical anion **B** (**IV→V**) (see SI, S59). The latter is not stable and further decomposes to give the imidyl radical **D** and Br^- (**V→VI**). On the other hand, the generation of *N,N*-dimethylacetamide radical (**C**) can follow two possible mechanistic pathways, hydrogen atom transfer (HAT) and electron transfer/proton transfer (ET/PT). The first one can be categorized as the synchronized abstraction of a proton and an electron in a one-step reaction, while the second one refers to a sequential process in which first occurs a single electron transfer to give a radical cation as intermediary followed by a posterior proton transfer.[1] Exploration of both mechanistic pathways reveals that the reaction follows a classic HAT mechanism (**VI→X**) since the ET/PT pathway (**VI→VIII**) is energetically hindered. Lastly, the radical-radical coupling between **D** and **C** to yield the desired product (***3aa***) displays an exergonic outline (**X→XII**).

1 Hancock, A.N.; Tanko, J.M. Radical cation/anion and neutral radicals: a comparison. In *Encyclopedia of Radicals in Chemistry, Biology and Materials*, John Wiley & Sons, Chinchester, UK **2012**.

Analytical Data of Compounds



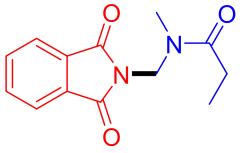
3aa

N-((1,3-dioxoisoindolin-2-yl)methyl)-*N*-methylacetamide (**3aa**)[4] (mixture of rotamers)

Conditions: *N*-bromophthalimide (45 mg, 0.2 mmol), LiO*t*Bu (16 mg, 0.2 mmol), 1.0 ml PhCl, *N*,*N*-dimethylacetamide (87 mg, 1 mmol), overnight. The product was isolated by flash chromatography (ethyl acetate/hexane= 1/1 to 3/1) as a white solid (30.2 mg, 65%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.57 (m, 4H), 5.19 (d, *J* = 36.1 Hz, 2H), 2.95 (d, *J* = 64.3 Hz, 3H), 2.18 (d, *J* = 147.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1 (s), 171.0(s), 167.8 (s), 167.6(s), 134.6 (s), 134.2 (s), 131.8 (s), 131.5 (s), 123.7 (s), 123.5 (s), 52.7 (s), 49.4 (s), 35.8 (s), 32.5 (s), 21.8 (s), 21.4 (s).



3ab

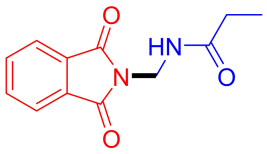
N-((1,3-dioxoisoindolin-2-yl)methyl)-*N*-methylpropionamide (**3ab**)[4] (mixture of rotamers)

Conditions: *N*-bromophthalimide (45 mg, 0.2 mmol), LiO*t*Bu (16 mg, 0.2 mmol), 1.0 ml PhCl, *N*,*N*-dimethylpropionamide (101 mg, 1 mmol), overnight.

The product was isolated by flash chromatography (ethyl acetate/hexane= 1/1 to 3/1) as a colorless oil (32.5 mg, 66%).

^{1}H NMR (400 MHz, CDCl3) δ 7.91 – 7.81 (m, 2H), 7.80 – 7.67 (m, 2H), 5.27 (d, *J* = 34.7 Hz, 2H), 3.03 (d, J = 56.3 Hz, 3H), 2.55 (dq, *J* = 197.5, 7.3 Hz, 2H), 1.15 (dt, *J* = 28.9, 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.4 (s),174.2 (s), 167.9 (s), 167.7(s), 134.6 (s), 134.2 (s), 131.9 (s), 131.6 (s), 123.8 (s), 123.6 (s), 51.8 (s), 50.1 (s), 35.2 (s), 32.8 (s), 26.8 (s), 26.0 (s), 9.4 (s), 8.8 (s).



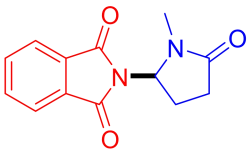
3ac

N-((1,3-dioxoisoindolin-2-yl)methyl)propionamide (**3ac**)[5] (mixture of rotamers)

Conditions: *N*-bromophthalimide (45 mg, 0.2 mmol), LiO*t*Bu (16 mg, 0.2 mmol), 1.0 ml PhCl, *N*-methylpropionamide (87 mg, 1 mmol), overnight. The product was isolated by flash chromatography (ethyl acetate/hexane= 1/1 to 3/1) as a white solid (20.9 mg, 45%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.70 (dd, *J* = 5.4, 3.1 Hz, 2H), 6.54 (s, 1H), 5.18 (d, *J* = 6.5 Hz, 2H), 2.20 (q, *J* = 7.6 Hz, 2H), 1.11 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4 (s), 167.5 (s), 134.3 (s), 131.9 (s), 123.6 (s), 42.5 (s), 29.3 (s), 9.3 (s).



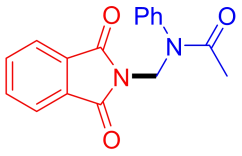
3ad

2-(1-methyl-5-oxopyrrolidin-2-yl)isoindoline-1,3-dione (**3ad**)[4] (mixture of rotamers)

Conditions: *N*-bromophthalimide (45 mg, 0.2 mmol), LiO*t*Bu (16 mg, 0.2 mmol), 1.0 ml PhCl, 1-methylpyrrolidin-2-one (99 mg, 1 mmol), overnight. The product was isolated by flash chromatography (ethyl acetate/hexane= 1/1 to 3/1) as a white solid (25.9 mg, 53%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.67 (m, 4H), 5.78 (dd, *J* = 8.9, 1.5 Hz, 1H), 3.04 – 2.90 (m, 1H), 2.70 (s, 3H), 2.59 – 2.37 (m, 2H), 2.27 (ddd, *J* = 13.1, 7.7, 2.1 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.3 (s), 167.4 (s), 134.6 (s), 131.5 (s), 123.7 (s), 65.7 (s), 29.6 (s), 27.1 (s), 23.2 (s).



3ae

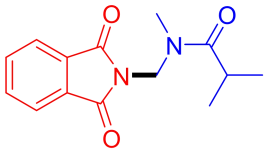
N-((1,3-dioxoisoindolin-2-yl)methyl)-*N*-phenylacetamide (**3ae**) (mixture of rotamers)

Conditions: *N*-bromophthalimide (45 mg, 0.2 mmol), LiO*t*Bu (16 mg, 0.2 mmol), 1.0 ml PhCl, *N*-methyl-*N*-phenylacetamide (149 mg, 1 mmol), overnight. The product was isolated by flash chromatography (ethyl acetate/hexane= 1/1 to 3/1) as a white solid (27.7 mg, 47%). m.p：143-146 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (m, 2H), 7.73 – 7.64 (m, 2H), 7.37 – 7.28 (m, 3H), 7.15 (d, *J* = 6.6 Hz, 2H), 5.66 (s, 2H), 1.83 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5 (s), 167.1 (s), 140.4 (s), 134.2 (s), 131.6 (s), 129.8 (s), 128.6 (2C), 123.6 (s), 49.7 (s), 22.8 (s).

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{15}N_2O_3$ 295.1077 ; found 295.1077.



3af

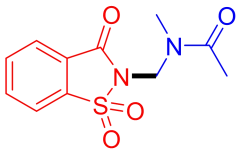
N-((1,3-dioxoisoindolin-2-yl)methyl)-*N*-methylisobutyramide (**3af**) (mixture of rotamers)

Conditions: *N*-bromophthalimide (45 mg, 0.2 mmol), LiO*t*Bu (16 mg, 0.2 mmol), 1.0 ml PhCl, *N*,*N*-dimethylisobutyramide (115 mg, 1 mmol), overnight. The product was isolated by flash chromatography (ethyl acetate/hexane= 1/1 to 3/1) as a pale yellow solid (25.0 mg, 48%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.65 (m, 4H), 5.27 (d, *J* = 14.6 Hz, 2H), 3.54 – 2.61 (dt, *J* = 13.1, 6.5 Hz, 1H), 3.04 (d, *J* = 79.8 Hz, 3H), 1.12 (dd, *J* = 33.6, 6.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.0 (s), 177.4 (s), 167.9(s),167.6 (s), 134.6 (s), 134.2 (s), 131.9 (s), 131.6 (s), 123.8 (s), 123.6 (s), 51.7 (s), 50.47 (s), 35.2 (s), 33.1 (s), 30.7 (s), 29.9 (s), 19.9 (s), 19.0 (s).

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{14}H_{16}N_2NaO_3$ 283.1053; found 283.1041.



3ba

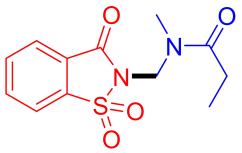
N-((1,1-dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)methyl)-*N*-methylacetamide (**3ba**) (mixture of rotamers)

Conditions: *N*-chlorosaccharin (44 mg, 0.2 mmol) or *N*-bromosaccharin(52 mg,0.2 mmol), Li*O*t*Bu* (16mg, 0.2 mmol), 1.0 ml PhCl, *N*,*N*-dimethylacetamide (87 mg, 1 mmol), overnight. The product was isolated by flash chromatography (ethyl acetate/dichloromethane=1/10 to 1/3) as a colorless oil (33.8 mg, 63% (X=Cl), 27.4 mg, 51%(X=Br)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.99 (m, 1H), 7.96 – 7.76 (m, 3H), 5.40 (d, *J* = 51.6 Hz, 2H), 3.03 (d, *J* = 38.3 Hz, 3H), 2.23 (d, *J* = 108.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8 (s), 169.9 (s), 158.3 (s), 158.1 (s), 136.9 (s), 136.4 (s), 134.6 (s), 134.3 (s), 133.8 (s), 133.4 (s), 125.6 (s), 124.6 (s), 124.4 (s), 120.3 (s), 120.1 (s), 53.7 (s), 49.2 (s), 34.1 (s), 31.7 (s), 20.7 (s), 20.5 (s).

HRMS (ESI) m/z: $[M+K]^+$ calcd for $C_{11}H_{12}KN_2O_4S$ 307.0149; found 307.0142.



3bb

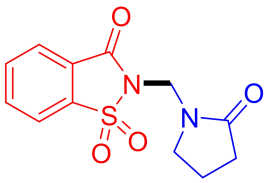
N-((1,1-dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)methyl)-*N*-methylpropionamide (**3bb**) (mixture of rotamers)

Conditions: *N*-chlorosaccharin (44 mg, 0.2 mmol) or *N*-bromosaccharin(52 mg,0.2 mmol), Li*O*t*Bu* (16mg, 0.2 mmol), 1.0 ml PhCl, *N*,*N*-dimethylpropionamide (101 mg, 1 mmol), overnight. The product was isolated by flash chromatography (ethyl acetate/dichloromethane=1/10 to 1/3) as a pale yellow oil (40.66 mg, 72%(X=Cl), 28.8 mg, 51%(X=Br)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.02 (m, 1H), 7.97 – 7.79 (m, 3H), 5.43 (d, *J* = 52.7 Hz, 2H), 3.06 (d, *J* = 29.9 Hz, 3H), 2.52 (dq, *J* = 136.3, 7.3 Hz, 2H), 1.23 – 1.04 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8 (s), 173.1 (s), 158.2 (s), 158.1 (s), 136.9 (s), 136.5 (s), 134.5 (s), 134.2 (s), 133.8 (s), 133.4 (s), 125.7 (s), 124.6 (s), 124.4 (s), 120.2 (s), 120.0 (s), 52.8 (s), 49.7 (s), 33.4 (s), 32.0 (s), 25.65 (s), 25.2 (s), 8.4 (s), 7.8 (s).

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{15}N_2O_4S$ 283.0747; found 283.0752.



3bd'

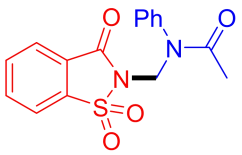
2-((2-oxopyrrolidin-1-yl)methyl)benzo[d]isothiazol-3(2H)-one 1,1-dioxide (**3bd'**) (mixture of rotamers)

Conditions: *N*-chlorosaccharin (44 mg, 0.2 mmol) or *N*-bromosaccharin(52 mg, 0.2 mmol), LiO*t*Bu (16mg, 0.2 mmol), 1.0 ml PhCl, 1-methylpyrrolidin-2-one (99 mg, 1 mmol), overnight. The product was isolated by flash chromatography (ethyl acetate/dichloromethane=1/10 to 1/3) as a yellow oil (5.0 mg, 9%(X=Cl), 5.6 mg, 10%(X=Br)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.3 Hz, 1H), 7.96 – 7.81 (m, 3H), 5.36 (s, 2H), 3.50 (t, *J* = 7.0 Hz, 2H), 2.40 (t, *J* = 8.1 Hz, 2H), 2.09 – 1.97 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.8 (s), 158.2 (s), 137.8 (s), 135.4 (s), 134.5 (s), 126.7 (s), 125.5 (s), 121.2 (s), 46.0 (s), 45.9 (s), 30.4 (s), 17.9 (s).

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{13}N_2O_4S$ 281.0591; found 281.0597.



3be

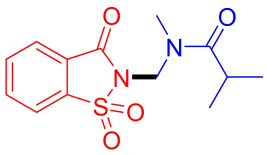
N-((1,1-dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)methyl)-*N*-phenylacetamide (**3be**) (mixture of rotamers)

Conditions: *N*-chlorosaccharin (44 mg, 0.2 mmol) or *N*-bromosaccharin(52 mg, 0.2 mmol), LiO*t*Bu (16mg, 0.2 mmol), 1.0 ml PhCl, *N*-methyl-*N*-phenylacetamide (149 mg, 1 mmol), overnight. The product was isolated by flash chromatography (ethyl acetate/dichloromethane=1/10 to 1/3) as a white solid (42.3 mg, 64%(X=Cl), 27.8 mg, 42%(X=Br)). m.p：182-185 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.68 (m, 4H), 7.36 – 7.16 (m, 5H), 5.76 (s, 2H), 1.83 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1 (s), 158.4 (s), 140.5 (s), 138.0 (s), 135.2 (s), 134.3 (s), 129.9 (s), 128.8 (s), 128.5 (s), 126.4 (s), 125.5 (s), 121.1 (s), 50.3 (s), 22.5 (s).

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{15}N_2O_4S$ 331.0747; found 331.0747.



3bf

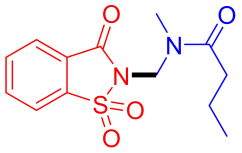
N-((1,1-dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)methyl)-*N*-methylisobutyramide (**3bf**) (mixture of rotamers)

Conditions: *N*-chlorosaccharin (44 mg, 0.2 mmol) or *N*-bromosaccharin(52 mg, 0.2 mmol), LiO*t*Bu (16mg, 0.2 mmol), 1.0 ml PhCl, *N*,*N*-dimethylisobutyramide (115 mg, 1 mmol), overnight. The product was isolated by flash chromatography (ethyl acetate/dichloromethane=1/10 to 1/3) as a pale yellow oil (40.9 mg, 69%(X=Cl), 31.4 mg, 53%(X=Br)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.03 (m, 1H), 7.99 – 7.75 (m, 3H), 5.47 (d, *J* = 41.4 Hz, 2H), 3.30-2.80 (dt, *J* = 13.4, 6.7 Hz, 1H), 3.10 (d, *J* = 52.1 Hz, 3H), 1.18 (dd, *J* = 22.9, 6.5 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.97 (s), 159.24 (s), 138.00 (s), 135.50 (s), 135.18 (s), 134.72 (s), 134.31 (s), 126.74 (s), 125.66 (s), 125.44 (s), 121.20 (s), 121.02 (s), 53.70 (s), 50.94 (s), 34.37 (s), 33.18 (s), 30.51 (s), 29.69 (s), 19.76 (s), 18.84 (s).

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{17}N_2O_4S$ 297.0904; found 297.0889.



3bg

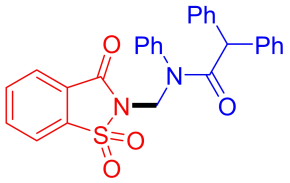
N-((1,1-dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)methyl)-*N*-methylbutyramide (**3bg**) (mixture of rotamers)

Conditions: *N*-chlorosaccharin (44 mg, 0.2 mmol) or *N*-bromosaccharin(52 mg, 0.2 mmol), LiO*t*Bu (16mg, 0.2 mmol), 1.0 ml PhCl, *N*,*N*-dimethylbutyramide (1 mmol), overnight. The product was isolated by flash chromatography (ethyl acetate/dichloromethane=1/10 to 1/3) as a pale yellow solid (37.3 mg, 63%(X=Cl), 36.1 mg, 61%(X=Br)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.03 (m, 1H), 7.97 – 7.79 (m, 3H), 5.45 (d, *J* = 51.7 Hz, 2H), 3.20 – 2.95 (m, 3H), 2.48 (dt, *J* = 134.7, 7.4 Hz, 2H), 1.70 (dp, *J* = 14.8, 7.5 Hz, 2H), 0.97 (dt, *J* = 14.9, 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0 (s), 172.3 (s), 158.3 (s), 158.1 (s), 137.0 (s), 136.5 (s), 134.5 (s), 134.2 (s), 133.7 (s), 133.3 (s), 130.5 (s), 128.2 (s), 125.7 (s), 124.6 (s), 124.4 (s), 120.2 (s), 120.0 (s), 34.2 (s), 33.7 (s), 33.5 (s), 31.9 (s), 17.6 (s), 17.0 (s), 12.9 (s), 128.8 (s).

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{17}N_2O_4S$ 297.0904; found 297.0889.



3bh

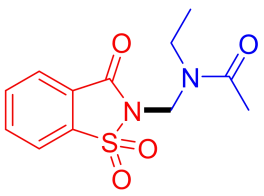
N-((1,1-dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)methyl)-*N*,2,2-triphenylacetamide (**3bh**) (mixture of rotamers)

Conditions: *N*-chlorosaccharin (44 mg, 0.2 mmol) or *N*-bromosaccharin(52 mg, 0.2 mmol), LiO*t*Bu (16mg, 0.2 mmol), 1.0 ml PhCl, *N*-methyl-*N*,2,2-triphenylacetamide (301 mg, 1 mmol), overnight. The product was isolated by flash chromatography (ethyl acetate/dichloromethane=1/10 to 1/3) as a white solid (47.2 mg, 49%(X=Cl), 31.8 mg, 33%(X=Br)). m.p：156-159 ºC

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.62 (m, 4H), 7.32 – 7.20 (m, 3H), 7.19 – 7.01 (m, 12H), 5.77 (s, 2H), 4.83 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4 (s), 158.5 (s), 139.7 (s), 139.1 (s), 138.0 (s), 135.2 (s), 134.3 (s), 129.8 (s), 129.1 (s), 129.0 (s), 129.0 (s), 128.4 (s), 127.0 (s), 126.4 (s), 125.5 (s), 121.1 (s), 54.7 (s), 50.9 (s).

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{23}N_2O_4S$ 483.1373; found 483.1373.



3bi

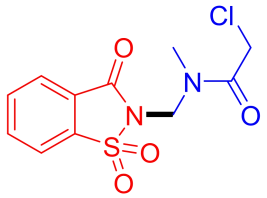
N-((1,1-dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)methyl)-*N*-ethylacetamide (**3bi**) (mixture of rotamers)

Conditions: *N*-chlorosaccharin (44 mg, 0.2 mmol) or *N*-bromosaccharin(52 mg, 0.2 mmol), LiO*t*Bu (16mg, 0.2 mmol), 1.0 ml PhCl, *N*-ethyl-*N*-methylacetamide (101 mg, 1 mmol), overnight. The product was isolated by flash chromatography (ethyl acetate/dichloromethane=1/10 to 1/3) as a pale yellow oil (25.4 mg, 45%(X=Cl), 20.9 mg, 37%(X=Br)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.02 (m, 1H), 7.88 (m, 3H), 5.42 (d, *J* = 60.3 Hz, 2H), 3.50 (dq, *J* = 21.4, 7.1 Hz, 2H), 2.27 (d, *J* = 93.8 Hz, 3H), 1.20 (dt, *J* = 38.8, 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3 (s), 170.3 (s), 159.5 (s), 159.2 (s), 138.1 (s), 137.6 (s), 135.5 (s), 135.3 (s), 134.8 (s), 134.3 (s), 126.6 (s), 126.6 (s), 125.6 (s), 125.4 (s), 121.3 (s), 125.1 (s), 52.6 (s), 48.0 (s), 42.2 (s), 39.7 (s), 21.9 (s), 21.2 (s), 14.00 (s), 12.6 (s).

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{15}N_2O_4S$ 283.0747; found 283.0752.



3bj

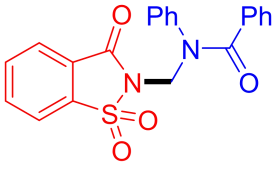
2-chloro-*N*-((1,1-dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)methyl)-*N*-methylacetamide (**3bj**) (mixture of rotamers)

Conditions: *N*-chlorosaccharin (44 mg, 0.2 mmol) or *N*-bromosaccharin(52 mg, 0.2 mmol), LiO*t*Bu (16mg, 0.2 mmol), 1.0 ml PhCl, 2-chloro-*N*,*N*-dimethylacetamide (122 mg, 1 mmol), overnight. The product was isolated by flash chromatography (ethyl acetate/dichloromethane=1/10 to 1/3) as a pale yellow solid (24.8 mg, 41%(X=Cl), 26.0 mg, 43%(X=Br)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.06 (m, 1H), 8.02 – 7.81 (m, 3H), 5.47 (d, *J* = 38.8 Hz, 2H), 4.31 (d, *J* = 153.9 Hz, 2H), 3.15 (d, *J* = 49.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4 (s), 159.2 (s), 137.9 (s), 137.4 (s), 135.7 (s), 135.4 (s), 134.9 (s), 134.5 (s), 126.6 (s), 125.8 (s), 125.6 (s), 121.4 (s), 121.2 (s), 54.03.95 (s), 50.8 (s), 41.0 (s), 40.9 (s), 34.7 (s), 33.6 (s).

HRMS (ESI) m/z: $[M+K]^+$ calcd for $C_{11}H_{11}ClKN_2O_4S$ 340.9760; found 340.9764.



3bk

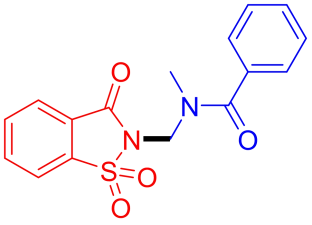
N-((1,1-dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)methyl)-*N*-phenylbenzamide (**3bk**) (mixture of rotamers)

Conditions: *N*-chlorosaccharin (44 mg, 0.2 mmol) or *N*-bromosaccharin(52 mg, 0.2 mmol), LiO*t*Bu (16mg, 0.2 mmol), 1.0 ml PhCl, *N*-methyl-*N*-phenylbenzamide (211mg, 1 mmol), overnight. The product was isolated by flash chromatography (ethyl acetate/dichloromethane=1/10 to 1/3) as a pale yellow solid (33.0 mg, 42%(X=Cl), 10.2 mg, 13%(X=Br)). m.p：205-208 ºC

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.8 Hz, 2H), 7.86 (t, *J* = 7.6 Hz, 1H), 7.78 (t, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 7.3 Hz, 2H), 7.19 (m, 8H), 6.04 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0 (s), 158.5 (s), 141.0 (s), 138.0 (s), 135.2 (s), 134.8 (s), 134.2 (s), 130.1 (s), 129.3 (s), 128.9 (s), 128.3 (s), 127.7 (s), 127.6 (s), 126.4 (s), 125.5 (s), 121.0 (s), 52.0 (s).

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{16}N_2NaO_4S$ 415.0723; found 415.0726.



3bl

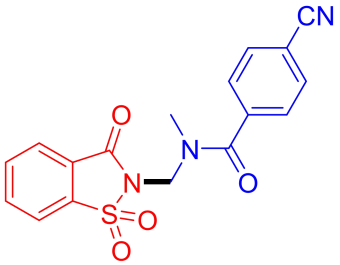
N-((1,1-dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)methyl)-*N*-methylbenzamide (**3bl**) (mixture of rotamers)

Conditions: *N*-chlorosaccharin (44 mg, 0.2 mmol) or *N*-bromosaccharin(52 mg, 0.2 mmol), Li*O*t*B*u (16mg, 0.2 mmol), 1.0 ml PhCl, *N*,*N*-dimethylbenzamide (149 mg, 1 mmol), overnight. The product was isolated by flash chromatography (ethyl acetate/dichloromethane=1/10 to 1/3) as a pale yellow oil (41.6 mg, 63%(X=Cl), 33.7 mg, 51%(X=Br)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.0 Hz, 1H), 7.96 – 7.78 (m, 3H), 7.45 (d, *J* = 30.7 Hz, 5H), 5.55 (d, *J* = 101.1 Hz, 2H), 3.06 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3 (s), 159.1 (s), 137.8 (s), 135.5 (s), 135.1 (s), 134.6 (s), 130.2 (s), 128.5 (s), 127.3 (s), 126.6 (s), 125.5 (s), 121.1 (s), 50.6 (s), 36.5 (s).

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{15}N_2O_4S$ 331.0747; found 331.0747.



3bm

4-cyano-*N*-((1,1-dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)methyl)-*N*-methylbenzamide (**3bm**) (mixture of rotamers)

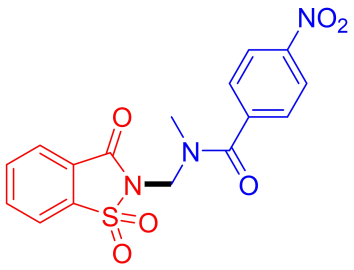
Conditions: *N*-chlorosaccharin (44 mg, 0.2 mmol) or *N*-bromosaccharin(52 mg, 0.2 mmol), Li*O*t*B*u (16mg, 0.2 mmol), 1.0 ml PhCl, 4-cyano-*N*,*N*-dimethylbenzamide (174 mg, 1 mmol), overnight.

The product was isolated by flash chromatography (ethyl acetate/dichloromethane=1/10 to 1/3) as a white solid (39.1 mg, 55%(X=Cl), 45.5 mg, 64%(X=Br)). m.p：179-181 ºC

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 7.39 (m, 8H), 5.44 (d, *J* = 157.9 Hz, 2H), 3.01 (d, *J* = 45.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3 (s), 159.0 (s), 139.4 (s), 137.8 (s), 135.5 (s), 134.7 (s), 132.4 (s), 127.8 (s), 126.5 (s), 125.7 (s), 121.2 (s), 118.1 (s), 114.0 (s), 50.2 (s), 36.3 (s).

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{14}N_3O_4S$ 356.0700; found 356.0699.



3bn

N-((1,1-dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)methyl)-*N*-methyl-4-nitrobenzamide (**3bn**) (mixture of rotamers)

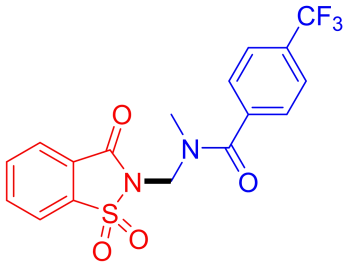
Conditions: *N*-chlorosaccharin (44 mg, 0.2 mmol) or *N*-bromosaccharin(52 mg, 0.2 mmol), LiO*t*Bu (16mg, 0.2 mmol), 1.0 ml PhCl, *N*,*N*-dimethyl-4-nitrobenzamide (194 mg, 1 mmol), overnight.

The product was isolated by flash chromatography (ethyl acetate/dichloromethane=1/10 to 1/3) as a white solid (54.1 mg, 72%(X=Cl), 47.3 mg, 63%(X=Br)). m.p：127-129 ºC

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 – 7.54 (m, 8H), 5.50 (d, *J* = 156.1 Hz, 2H), 3.07 (d, *J* = 49.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0 (s), 159.0 (s), 148.7 (s), 141.2 (s), 137.8 (s), 135.6 (s), 134.7 (s), 128.9 (s), 128.1 (s), 126.5 (s), 125.7 (s), 123.9 (s), 121.2 (s), 54.6 (s), 50.1 (s), 36.3 (s), 32.2 (s).

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{14}N_3O_6S$ 376.0598; found 376.0585.



3bo

N-((1,1-dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)methyl)-*N*-methyl-4-(trifluoromethyl)benzamide (**3bo**) (mixture of rotamers)

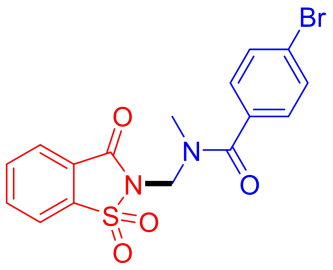
Conditions: *N*-chlorosaccharin (44 mg, 0.2 mmol) or *N*-bromosaccharin(52 mg, 0.2 mmol), LiO*t*Bu (16mg, 0.2 mmol), 1.0 ml PhCl, *N*,*N*-dimethyl-4-(trifluoromethyl)benzamide (217 mg, 1 mmol), overnight. The product was isolated by flash chromatography (ethyl acetate/dichloromethane=1/10 to 1/3) as a white solid (59.8 mg, 75%(X=Cl), 64.6 mg, 81%(X=Br)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.99 – 7.81 (m, 3H), 7.64 (d, *J* = 27.8 Hz, 4H), 5.52 (d, *J* = 146.0 Hz, 2H), 3.02 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.84 (s), 159.03 (s), 138.66 (s), 137.75 (s), 135.50 (s), 134.61 (s), 132.00 (q, *J* = 32.7 Hz), 127.87 – 127.34 (m), 126.52 (s), 125.61 (s), 125.56 (s), 123.71 (q, *J* = 271 Hz), 121.15 (s), 54.76 (s), 50.22 (s), 36.32 (s), 31.89 (s).

^{19}F NMR (377 MHz, $CDCl_3$) δ -62.91 (s).

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{14}F_3N_2O_4S$ 399.0621; found 399.0609.



3bp

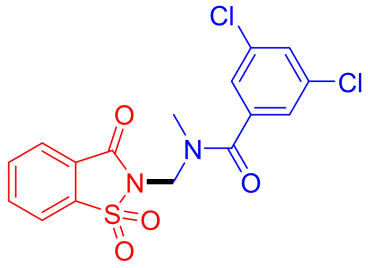
4-bromo-*N*-((1,1-dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)methyl)-*N*-methylbenzamide (**3bp**) (mixture of rotamers)

Conditions: *N*-chlorosaccharin (44 mg, 0.2 mmol) or *N*-bromosaccharin(52 mg, 0.2 mmol), LiO*t*Bu (16mg, 0.2 mmol), 1.0 ml PhCl, 4-bromo-*N*,*N*-dimethylbenzamide (228 mg, 1 mmol), overnight. The product was isolated by flash chromatography (ethyl acetate/dichloromethane=1/10 to 1/3) as a white solid (59.8 mg, 73%(X=Cl), 41.7 mg, 51%(X=Br)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.2 Hz, 1H), 7.99 – 7.79 (m, 3H), 7.56 (d, *J* = 6.8 Hz, 2H), 7.39 (s, 2H), 5.66 (s, 2H), 3.06 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3 (s), 159.0 (s), 137.8 (s), 135.4 (s), 134.6 (s), 133.9 (s), 131.7 (s), 129.1 (s), 126.6 (s), 125.6 (s), 124.6 (s), 121.1 (s), 50.4 (s), 36.5 (s).

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{14}BrN_2O_4S$ 408.9852; found 408.9857.



3bq

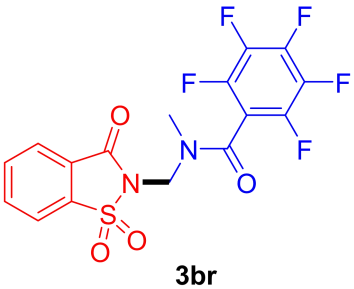
3,5-dichloro-*N*-((1,1-dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)methyl)-*N*-methylbenzamide (**3bq**) (mixture of rotamers)

Conditions: *N*-chlorosaccharin (44 mg, 0.2 mmol) or *N*-bromosaccharin(52 mg, 0.2 mmol), LiO*t*Bu (16mg, 0.2 mmol), 1.0 ml PhCl, 3,5-dichloro-*N*,*N*-dimethylbenzamide (218 mg, 1 mmol), overnight. The product was isolated by flash chromatography (ethyl acetate/dichloromethane=1/10 to 1/3) as a white solid (62.3 mg, 78%(X=Cl), 39.9 mg, 50%(X=Br)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.0 Hz, 1H), 8.00 – 7.83 (m, 3H), 7.39 (d, *J* = 26.1 Hz, 3H), 5.51 (d, *J* = 126.2 Hz, 2H), 3.05 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3 (s), 159.0 (s), 137.8 (s), 135.5 (s), 135.4 (s), 134.6 (s), 130.2 (s), 126.5 (s), 125.7 (s), 121.2 (s), 54.7 (s), 50.1 (s), 36.3 (s), 31.6 (s).

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{13}Cl_2N_2O_4S$ 398.9968; found 398.9979.



3br

N-((1,1-dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)methyl)-2,3,4,5,6-pentafluoro-*N*-methylbenzamide (**3br**) (mixture of rotamers)

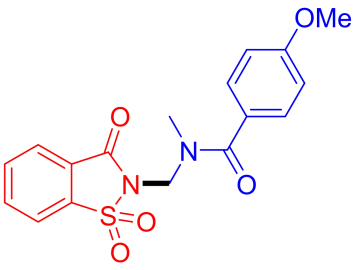
Conditions: *N*-chlorosaccharin (44 mg, 0.2 mmol) or *N*-bromosaccharin(52 mg, 0.2 mmol), LiO*t*Bu (16mg, 0.2 mmol), 1.0 ml PhCl, 2,3,4,5,6-pentafluoro-*N*,*N*-dimethylbenzamide (239 mg, 1 mmol), overnight. The product was isolated by flash chromatography (ethyl acetate/dichloromethane=1/10 to 1/3) as a white solid (44.6 mg, 53%(X=Cl), 59.7 mg, 71%(X=Br)). m.p：129-132 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 21.1, 7.5 Hz, 1H), 8.00 – 7.83 (m, 3H), 5.44 (d, *J* = 160.6 Hz, 2H), 3.16 (d, *J* = 80.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4 (d, *J* = 75 Hz), 159.2 (s), 159.0 (s), 144.8 (ddd, *J* = 12.8, 8.0, 3.9 Hz), 144.3 (ddd, *J* = 12.1, 8.2, 4.1 Hz), 142.5 – 142.1 (m), 141.8 (qd, *J* = 8.4, 3.9 Hz), 139.2 – 138.7 (m), 137.9 (s), 137.4 (s), 136.8 – 136.2 (m), 135.7 (s), 135.5(s), 134.9 (s), 134.6 (s), 126.5 (s), 126.3 (s), 125.8 (s), 125.6 (s), 121.3 (s), 121.3 (s), 110.3 (dd, *J* = 42.0, 20.2 Hz), 54.2 (s), 49.4 (s), 34.9 (s), 33.0 (s).

^{19}F NMR (377 MHz, $CDCl_3$) δ -139.01 (tdd, *J* = 8.7, 5.8, 2.8 Hz), -139.94 (ddd, *J* = 11.6, 7.4, 3.4 Hz), -150.56 – -150.72 (m), -150.98 (tt, *J* = 20.6, 2.1 Hz), -159.62 (tt, *J* = 20.6, 5.8 Hz), -159.82 (ddd, *J* = 20.7, 16.1, 5.9 Hz).

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{10}F_5N_2O_4S$ 421.0276; found 421.0282.



3bs

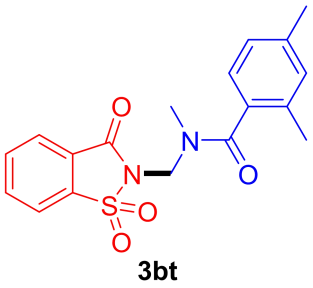
N-((1,1-dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)methyl)-4-methoxy-*N*-methylbenzamide (**3bs**) (mixture of rotamers)

Conditions: *N*-chlorosaccharin (44 mg, 0.2 mmol) or *N*-bromosaccharin(52 mg, 0.2 mmol), LiO*t*Bu (16mg, 0.2 mmol), 1.0 ml PhCl, 4-methoxy-*N*,*N*-dimethylbenzamide (179 mg, 1 mmol), overnight. The product was isolated by flash chromatography (ethyl acetate/dichloromethane=1/10 to 1/3) as a white solid (31.7 mg, 44%(X=Cl), 25.9 mg, 36%(X=Br)). m.p：223-227 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.4 Hz, 1H), 7.97 – 7.80 (m, 3H), 7.50 (d, *J* = 8.6 Hz, 2H), 6.92 (d, *J* = 8.5 Hz, 2H), 5.60 (s, 2H), 3.83 (s, 3H), 3.10 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2 (s), 161.2 (s), 159.1 (s), 137.9 (s), 135.3 (s), 134.5 (s), 129.6 (s), 127.2 (s), 126.7 (s), 125.5 (s), 121.1 (s), 113.7 (s), 55.4 (s), 53.4 (s), 31.6 (s).

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{16}N_2NaO_5S$ 383.0672; found, 383.0669.



3bt

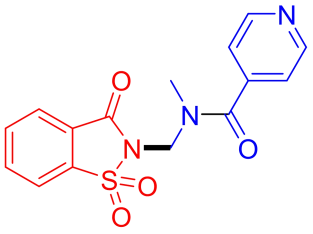
N-((1,1-dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)methyl)-*N*,2,4-trimethylbenzamide (**3bt**) (mixture of rotamers)

Conditions: *N*-chlorosaccharin (44 mg, 0.2 mmol) or *N*-bromosaccharin(52 mg, 0.2 mmol), Li*O*t*Bu* (16mg, 0.2 mmol), 1.0 ml PhCl, *N*,*N*,2,4-tetramethylbenzamide (177 mg, 1 mmol), overnight. The product was isolated by flash chromatography (ethyl acetate/dichloromethane=1/10 to 1/3) as a pale yellow solid (22.9 mg, 32%(X=Cl), 20.0 mg, 28%(X=Br)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 18.5, 7.3 Hz, 1H), 7.98 – 7.80 (m, 3H), 7.35 – 6.93 (m, 3H), 5.71 (s, 2H), 3.03 (d, *J* = 98.2 Hz, 3H), 2.42 – 2.24 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4 (s), 172.0 (s), 159.3 (s), 158.9 (s), 139.6 (s), 139.1 (s), 138.0 (s), 137.(s), 135.5 (s), 134.4 (s), 134.6 (s), 134.6 (s),134.5 (s), 132.4 (s), 131.8 (s), 131.9 (s), 131.5 (s), 131.2 (s), 127.3 (s), 126.7 (s), 126.4 (s), 126.0 (s), 125.5 (s), 121.1 (s), 54.5 (s), 49.7 (s), 35.4 (s), 31.1 (s), 21.2 (s), 19.1 (s), 18.8 (s).

HRMS (ESI) m/z: $[M+K]^+$ calcd for $C_{18}H_{18}N_2KO_4S$ 397.0619; found, 397.0609.



3bu

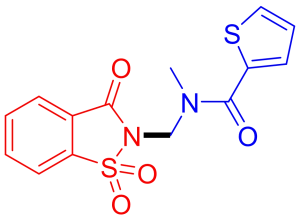
N-((1,1-dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)methyl)-*N*-methylisonicotinamide (**3bu**) (mixture of rotamers)

Conditions: *N*-chlorosaccharin (44 mg, 0.2 mmol) or *N*-bromosaccharin(52 mg, 0.2 mmol), Li*O*t*Bu* (16mg, 0.2 mmol), 1.0 ml PhCl, *N*,*N*-dimethylisonicotinamide (150 mg, 1 mmol), overnight. The product was isolated by flash chromatography (ethyl acetate/dichloromethane=1/10 to 1/3) as a pale yellow oil (23.2 mg, 35%(X=Cl), 34.5 mg, 52%(X=Br)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 18.7 Hz, 2H), 8.10 (s, 1H), 8.01 – 7.82 (m, 3H), 7.41 (d, *J* = 42.4 Hz, 2H), 5.50 (d, *J* = 156.8 Hz, 2H), 3.08 (d, *J* = 55.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7 (s), 159.0 (s), 150.3 (s), 142.7 (s), 137.8 (s), 135.5 (s), 134.6 (s), 126.6 (s), 125.7 (s), 121.8 (s), 121.7 (s), 121.0 (s), 54.6 (s), 49.9 (s), 36.1 (s), 31.8 (s).

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{15}H_{14}N_3NaO_4S$ 354.0519; found, 354.0515.



3bv

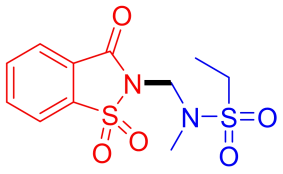
N-((1,1-dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)methyl)-*N*-methylthiophene-2-carboxamide (**3bv**) (mixture of rotamers)

Conditions: *N*-chlorosaccharin (44 mg, 0.2 mmol) or *N*-bromosaccharin(52 mg, 0.2 mmol), LiO*t*Bu (16mg, 0.2 mmol), 1.0 ml PhCl, *N*,*N*-dimethylthiophene-2-carboxamide (155 mg, 1 mmol), overnight. The product was isolated by flash chromatography (ethyl acetate/dichloromethane=1/10 to 1/3) as a white solid (21.5 mg, 32%(X=Cl), 36.3 mg, 54%(X=Br)). m.p：124-127 ºC

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.3 Hz, 1H), 7.97 – 7.80 (m, 3H), 7.50 (dd, *J* = 6.5, 4.4 Hz, 2H), 7.07 (dd, *J* = 4.8, 3.9 Hz, 1H), 5.67 (s, 2H), 3.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2 (s), 159.2 (s), 137.9 (s), 136.5 (s), 135.4 (s), 134.5 (s), 130.4 (s), 130.0 (s), 126.9 (s), 126.6 (s), 125.6 (s), 121.1 (s), 52.7 (s), 35.9 (s).

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{13}N_2O_4S_2$ 337.0311; found 337.0319.



3bw

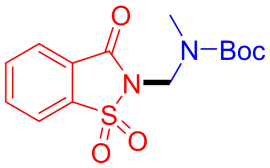
N-((1,1-dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)methyl)-*N*-methylethanesulfonamide (**3bw**) (mixture of rotamers)

Conditions: *N*-chlorosaccharin (44 mg, 0.2 mmol) or *N*-bromosaccharin(52 mg, 0.2 mmol), LiO*t*Bu (16mg, 0.2 mmol), 1.0 ml PhCl, *N*,*N*-dimethylethanesulfonamide (137 mg, 1 mmol), overnight. The product was isolated by flash chromatography (ethyl acetate/dichloromethane=1/10 to 1/3) as a white solid (34.4 mg, 54%(X=Cl),35.7 mg, 56%(X=Br)). m.p：144-147 ºC

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.5 Hz, 1H), 8.00 – 7.79 (m, 3H), 5.32 (s, 2H), 3.16 (q, *J* = 7.4 Hz, 2H), 3.07 (s, 3H), 1.34 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6 (s), 137.6 (s), 135.7 (s), 134.8 (s), 126.5 (s), 125.7 (s), 121.3 (s), 53.8 (s), 46.9 (s), 34.8 (s), 7.9 (s).

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{11}H_{14}N_2NaO_5S_2$ 341.0236; found 341.0240.



5ba

tert-butyl ((1,1-dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)methyl)(methyl)carbamate (**5ba**) (mixture of rotamers)

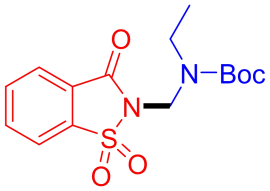
Conditions: *N*-chlorosaccharin (44 mg, 0.2 mmol) or *N*-bromosaccharin(52 mg, 0.2 mmol), LiO*t*Bu

(16mg, 0.2 mmol), 1.0 ml PhCl, *tert*-butyl dimethylcarbamate (145 mg, 1 mmol), overnight. The product was isolated by flash chromatography (ethyl acetate/dichloromethane=1/10 to 1/3) as a pale yellow oil (52.2 mg, 80%(X=Cl), 55.5 mg, 85%(X=Br)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 7.4 Hz, 1H), 7.81 (m, 3H), 5.32 (d, J = 18.4 Hz, 2H), 2.90 (s, 3H), 1.45 (d, J = 25.2 Hz, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3 (s), 154.4 (s), 138.1 (s), 135.3 (s), 134.3 (s), 126.7 (s), 125.4 (s), 121.0 (s), 81.6 (s), 81.0 (s), 53.0 (s), 52.8 (s), 33.7 (s), 33.3 (s), 28.1 (s).

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{14}H_{18}N_2NaO_5S$ 349.0829; found 349.0840.



5bb

tert-butyl ((1,1-dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)methyl)(ethyl)carbamate (**5bb**) (mixture of rotamers)

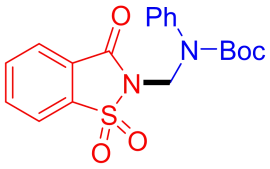
Conditions: *N*-chlorosaccharin (44 mg, 0.2 mmol) or *N*-bromosaccharin(52 mg, 0.2 mmol), Li*O*t*B*u (16mg, 0.2 mmol), 1.0 ml PhCl, *tert*-butyl ethyl(methyl)carbamate (159 mg, 1 mmol), overnight.

The product was isolated by flash chromatography (ethyl acetate/dichloromethane=1/10 to 1/3) as a pale yellow oil (30.6 mg, 45%(X=Cl), 17.7 mg, 26%(X=Br)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 7.4 Hz, 1H), 7.94 – 7.78 (m, 3H), 5.37 (s, 2H), 3.41 (d, J = 6.7 Hz, 2H), 1.52 (d, J = 22.5 Hz, 9H), 1.17 (t, J = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4 (s), 153.9 (s), 138.2 (s), 135.2 (s), 134.3 (s), 126.6 (s), 125.4 (s), 120.9 (s), 81.6 (s), 51.1 (s), 41.6 (s), 40.8 (s), 28.2 (s), 13.8 (s), 13.2 (s).

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{15}H_{20}N_2NaO_5S$ 363.0985; found 363.0977.



5bc

tert-butyl ((1,1-dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)methyl)(phenyl)carbamate (5bc) (mixture of rotamers)

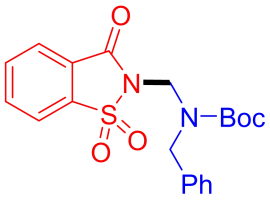
Conditions: *N*-chlorosaccharin (44 mg, 0.2 mmol) or *N*-bromosaccharin(52 mg, 0.2 mmol), Li*O*t*B*u (16mg, 0.2 mmol), 1.0 ml PhCl, *tert*-butyl methyl(phenyl)carbamate (207 mg, 1 mmol), overnight.

The product was isolated by flash chromatography (ethyl acetate/dichloromethane=1/10 to 1/3) as a pale yellow oil (24.1 mg, 31%(X=Cl), 10.1 mg, 13%(X=Br)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.74 (m, 4H), 7.37 – 7.23 (m, 5H), 5.76 (d, J = 10.1 Hz, 2H), 1.53 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3 (s), 154.0 (s), 139.8 (s), 138.1 (s), 135.1 (s), 134.2 (s), 129.1 (s), 127.9 (s), 127.4 (s), 126.5 (s), 125.5 (s), 120.9 (s), 82.2 (s), 53.2 (s), 28.2 (s).

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{21}N_2O_5S$ 389.1166; found 389.1167.



5bd

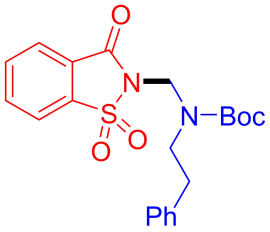
tert-butyl benzyl((1,1-dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)methyl)carbamate (**5bd**) (mixture of rotamers)

Conditions: *N*-chlorosaccharin (44 mg, 0.2 mmol) or *N*-bromosaccharin(52 mg, 0.2 mmol), LiO*t*Bu (16mg, 0.2 mmol), 1.0 ml PhCl, *tert*-butyl benzyl(methyl)carbamate (221 mg, 1 mmol), overnight. The product was isolated by flash chromatography (ethyl acetate/dichloromethane=1/10 to 1/3) as a white solid (36.2 mg, 45%(X=Cl), 8.0 mg, 10%(X=Br)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 7.4 Hz, 1H), 7.87 – 7.72 (m, 3H), 7.37 – 7.15 (m, 5H), 5.29 (d, J = 39.7 Hz, 2H), 4.49 (d, J = 9.5 Hz, 2H), 1.48 (d, J = 43.8 Hz, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5 (s), 154.5 (s), 138.2 (s), 137.5 (s), 135.2 (s), 134.3 (s), 128.5 (s), 128.4 (s), 127.5 (s), 125.4 (s), 120.9 (s), 82.0 (s), 50.6 (s), 48.6 (s), 28.2 (s).

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{23}N_2O_5S$ 403.1322; found 403.1322.



5be

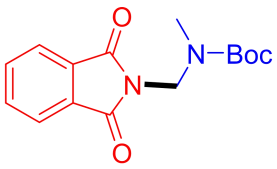
tert-butyl ((1,1-dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)methyl)(phenethyl)carbamate (**5be**) (mixture of rotamers)

Conditions: *N*-chlorosaccharin (44 mg, 0.2 mmol) or *N*-bromosaccharin(52 mg, 0.2 mmol), LiO*t*Bu (16mg, 0.2 mmol), 1.0 ml PhCl, *tert*-butyl methyl(phenethyl)carbamate (235 mg, 1 mmol), overnight. The product was isolated by flash chromatography (ethyl acetate/dichloromethane=1/10 to 1/3) as a pale yellow oil (20.0 mg, 24%(X=Cl), 10.0 mg, 12%(X=Br)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 7.3 Hz, 1H), 7.93 – 7.79 (m, 3H), 7.32 – 7.13 (m, 5H), 5.27 (d, J = 29.0 Hz, 2H), 3.58 (dt, J = 14.7, 7.4 Hz, 2H), 2.91 (dd, J = 14.5, 7.2 Hz, 2H), 1.54 (d, J = 30.6 Hz, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.546 (s), 154.0 (s), 138.9 (s), 138.2 (s), 135.2(s), 134.3 (s), 132.0 (s), 130.2 (s), 129.9 (s), 129.1 (s), 128.5 (s), 128.4 (s), 126.6 (s), 126.4 (s), 126.3 (s), 125.4 (s), 81.8 (s), 81.1 (s), 51.8 (s), 51.5 (s), 48.656 (s), 48.2 (s), 35.2 (s), 34.4 (s), 28.2 (s).

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{25}N_2O_5S$ 417.1479; found 417.1467.



5aa

tert-butyl ((1,3-dioxoisoindolin-2-yl)methyl)(methyl)carbamate (**5aa**) (mixture of rotamers)

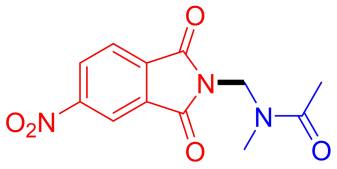
Conditions: *N*-bromophthalimide (45 mg, 0.2 mmol), LiO*t*Bu (16mg, 0.2 mmol), 1.0 ml PhCl, *tert*-butyl dimethylcarbamate (145 mg, 1 mmol), overnight.

The product was isolated by flash chromatography (ethyl acetate/dichloromethane=1/10 to 1/3) as a white solid (13.4 mg, 23%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.74 (dd, *J* = 5.4, 3.1 Hz, 2H), 5.22 (s, 2H), 2.96 (s, 3H), 1.51 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8 (s), 155.0 (s), 134.2 (s), 131.9 (s), 123.6 (s), 80.7 (s), 51.4 (s), 33.9 (s), 28.3 (s).

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{15}H_{18}N_2NaO_4$ 313.1159; found 313.1165.



3ca

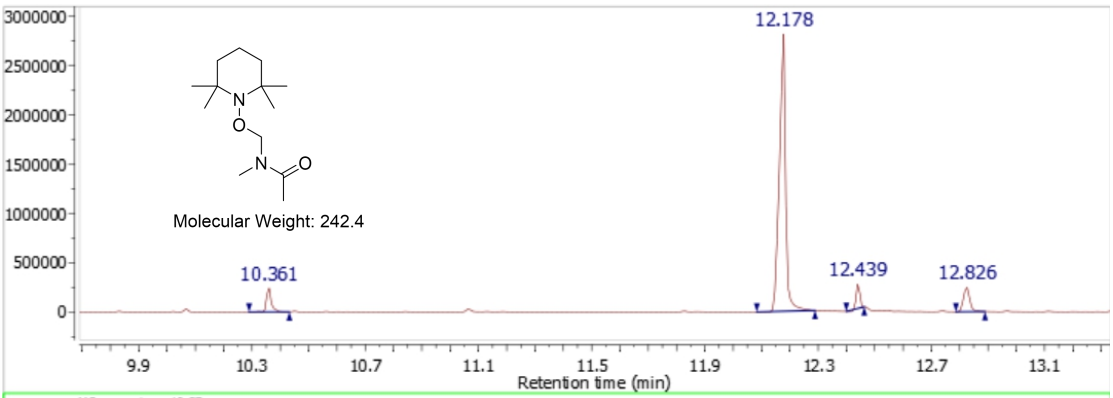
N-methyl-*N*-((5-nitro-1,3-dioxoisoindolin-2-yl)methyl)acetamide (**3ca**)[4] (mixture of rotamers)

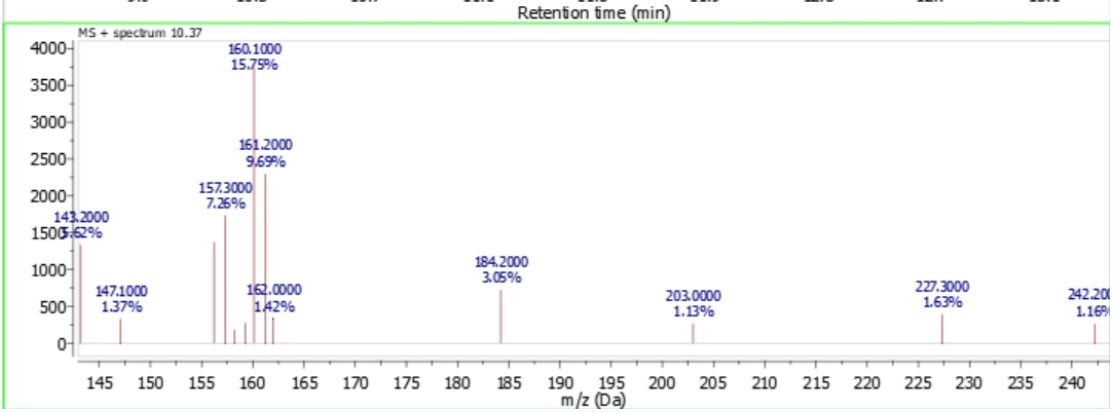
Conditions: 2-bromo-5-nitroisoindoline-1,3-dione (54 mg, 0.2 mmol), LiO*t*Bu (16mg, 0.2 mmol), 1.0 ml PhCl, *N*,*N*-dimethylacetamide (87 mg, 1 mmol), overnight. The product was isolated by flash chromatography (ethyl acetate/dichloromethane=1/10 to 1/3) as a yellow solid (18.9 mg, 34%). m.p：175-178 °C

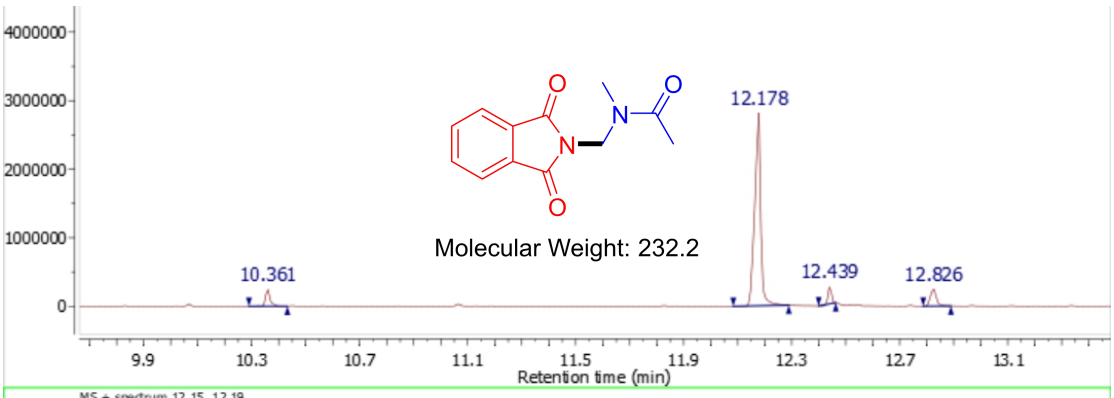
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 – 8.54 (m, 2H), 8.08 (dd, *J* = 17.2, 8.1 Hz, 1H), 5.30 (d, *J* = 18.7 Hz, 2H), 3.06 (d, *J* = 82.5 Hz, 3H), 2.26 (d, *J* = 145.0 Hz, 3H).

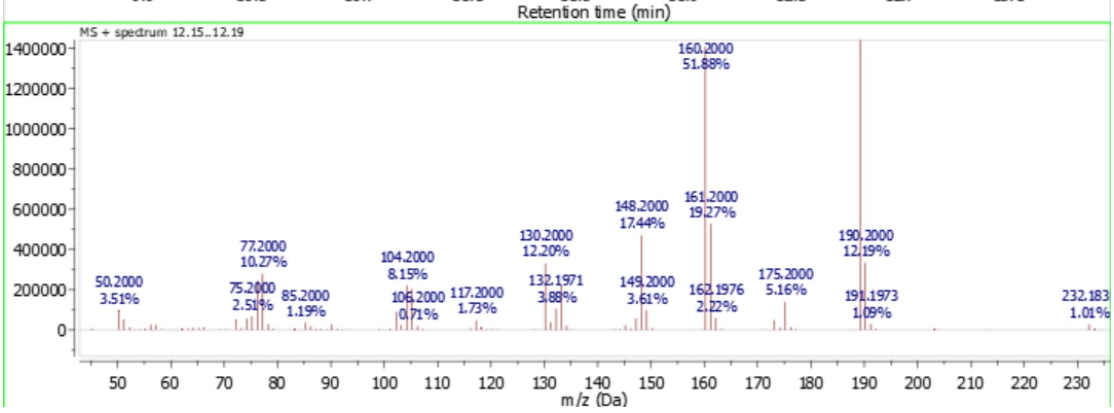
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3 (s), 171.1 (s), 165.8 (s), 165.5 (s), 165.5 (s), 165.4 (s), 152.1 (s), 151.9 (s), 136.2 (s), 135.9 (s), 133.2 (s), 133.0 (s), 129.8 (s), 129.5 (s), 125.2 (s), 124.9 (s), 119.3 (s), 119.0 (s), 53.3 (s), 50.7 (s), 36.6 (s), 32.8 (s), 21.8 (s), 21.4 (s).

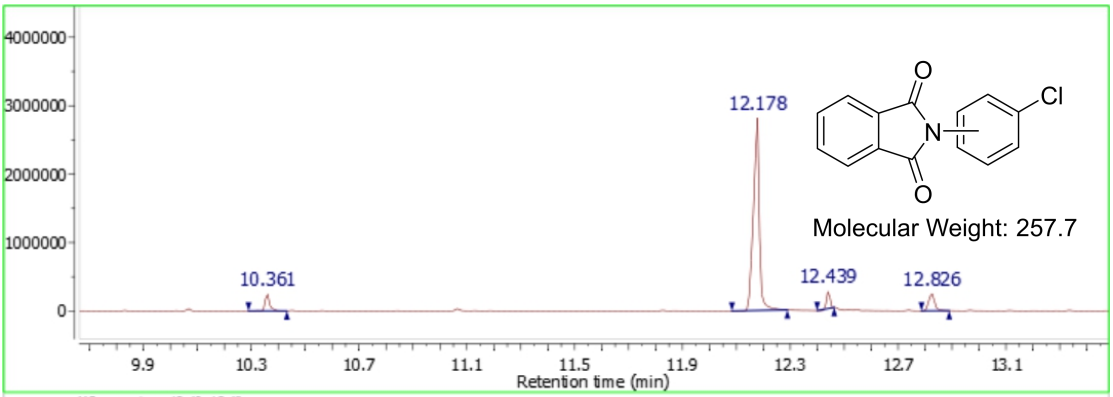
GC-MS Spectra from Radical Trapping Experiment







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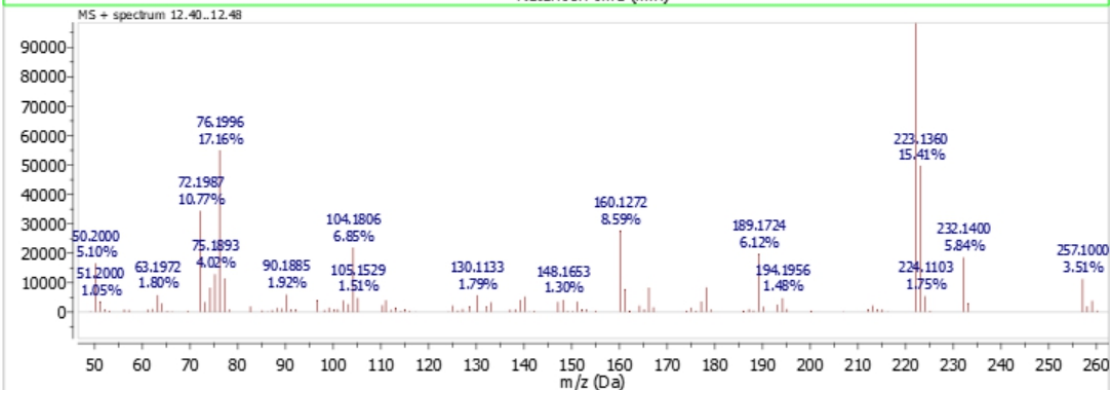
10.361
12.439
12.826
Molecular Weight: 257.7
Retention time (min)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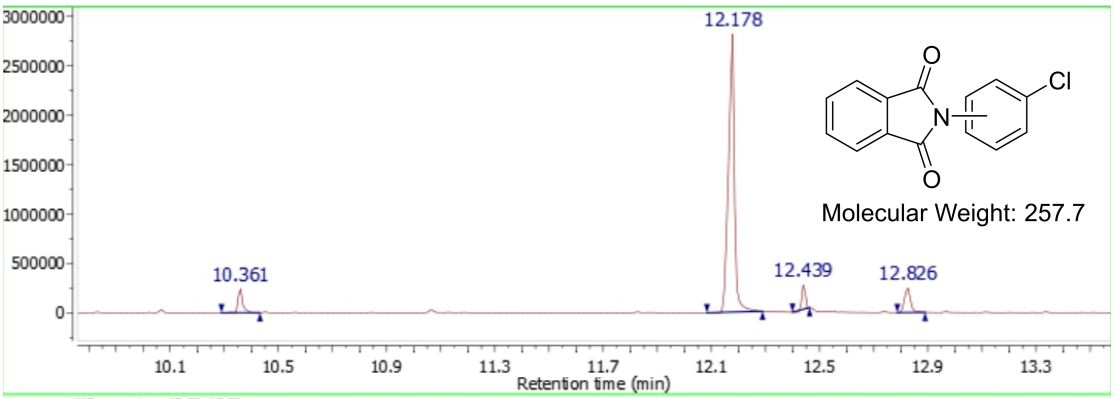
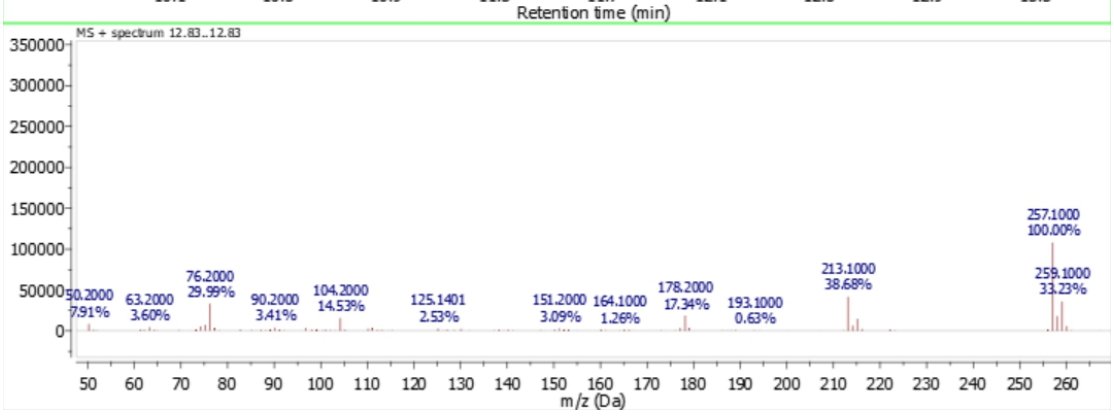
76.1996 17.16%
72.1987 10.77%
223.1360 15.41%
160.1272 8.59%
104.1806 6.85%
189.1724 6.12%
232.1400 5.84%
257.1000 3.51%
m/z (Da)


12.178
10.361
12.439
12.826
Molecular Weight: 257.7
Retention time (min)


MS + spectrum 12.83..12.83
257.1000 100.00%
76.2000 29.99%
213.1000 38.68%
259.1000 33.23%
m/z (Da)

Supplementary References

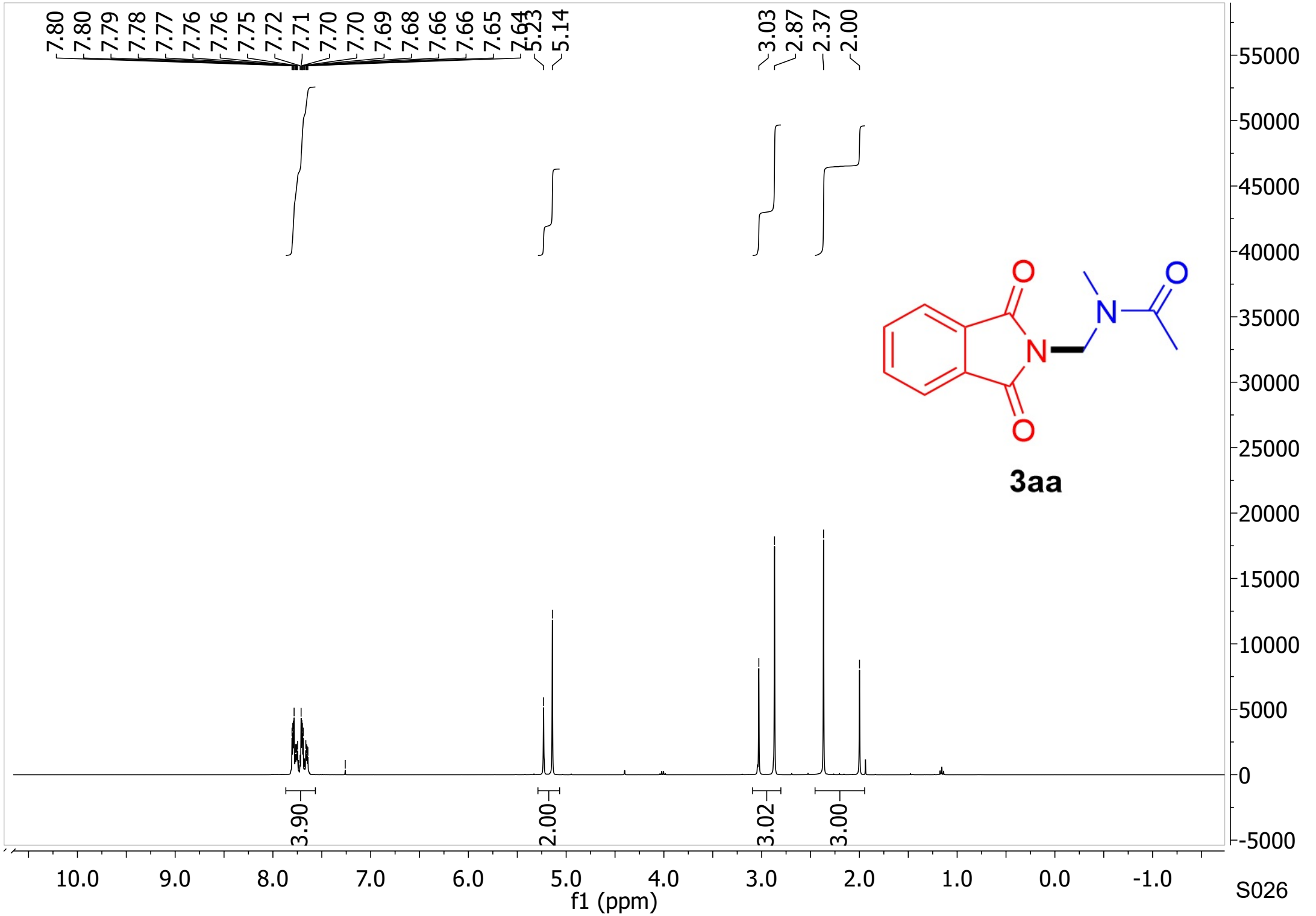
(1) (a) John, J. M.; Loorthuraja, R.; Antoniuk, E.; Bergens, S. H. Catalytic hydrogenation of functionalized amides under basic and neutral conditions. Catal. Sci. Technol. **2015**, 5, 1181−1186. (b) Lu, K.; Han, X.-W.; Yao, W.-W.; Luan, Y.-X.; Wang, Y.-X.; Chen, H.; Xu, X.-T.; Zhang, K.; Ye, M. DMF-Promoted Redox-Neutral Ni-Catalyzed Intramolecular Hydroarylation of Alkene with Simple Arene. *ACS Catal*. **2018**, *8*, 3913-3917.

(2) Dong, J.- Y.; Xia, Q.; Lv, X.-L.; Yan, C.-C.; Song, H.-J.; Liu, Y.-X.; Wang, Q.-M. Photoredox-Mediated Direct Cross-Dehydrogenative Coupling of Heteroarenes and Amines. *Org. Lett*. **2018** , *20*, 5661-5665.

(3) Song, L.; Zhang, L.; Luo, S.; Cheng, J. Visible‐Light Promoted Catalyst‐Free Imidation of Arenes and Heteroarenes. *Chem. - Eur. J*. **2014** , *20*, 14231-14234.

(4) Lao, Z.-Q.; Zhong, W.-H.; Lou, Q.-H.; Li, Z.-J.; Meng, X.-B. KI-catalyzed imidation of sp^3C‐H bond adjacent to amidenitrogen atom. *Org. Biomol. Chem*. **2012**, *10*, 7869-7871.

(5) Unterhalt, B. Preparation of N-phthalimidomethyl- and N-benzosulfimidomethyl-N-acyl amines. Archiv der Pharmazie und Berichte der Deutschen Pharmazeutischen Gesellschaft, **1967**, *300*(3), 247-249.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7.65
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2.00
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O
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40000
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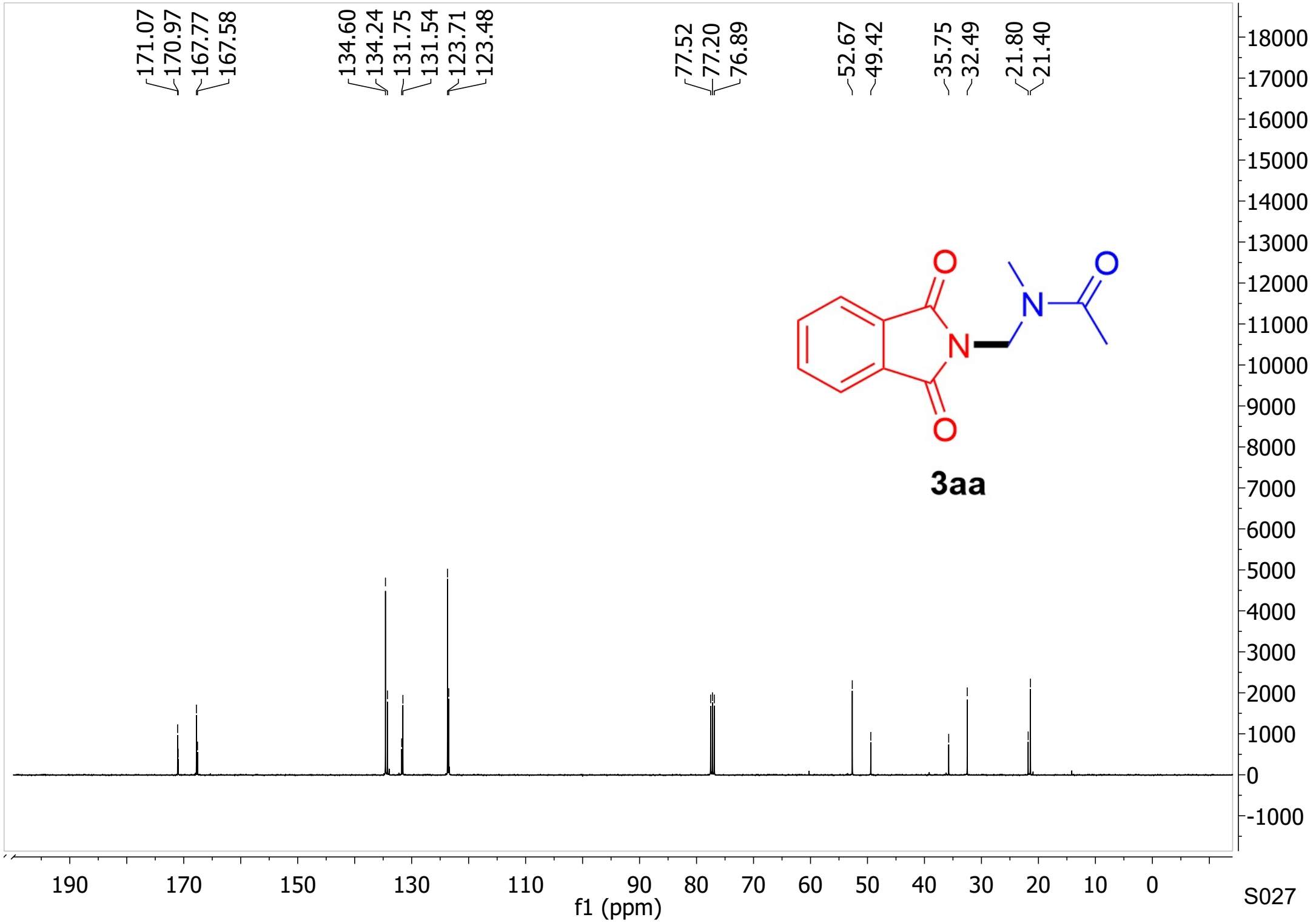
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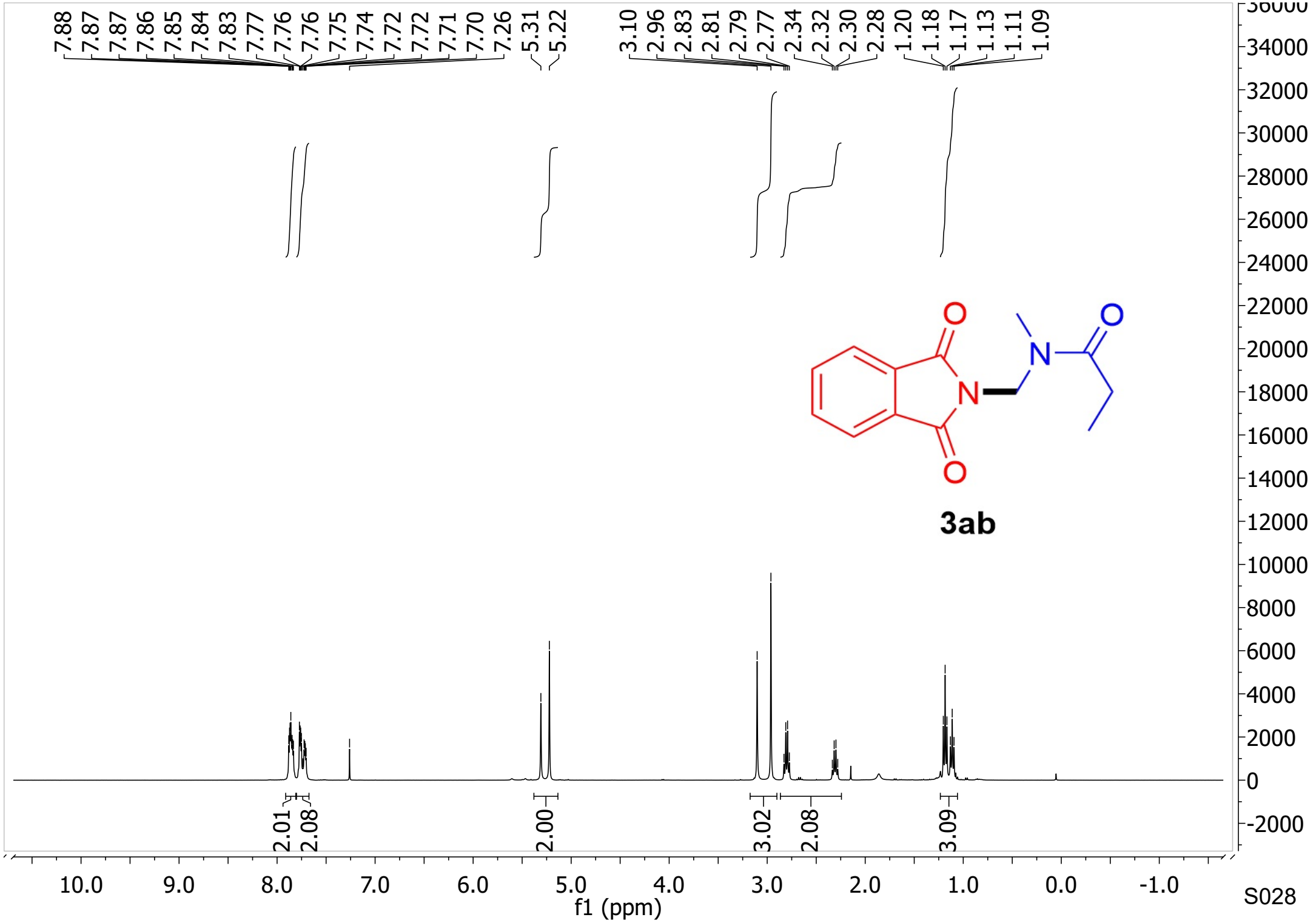
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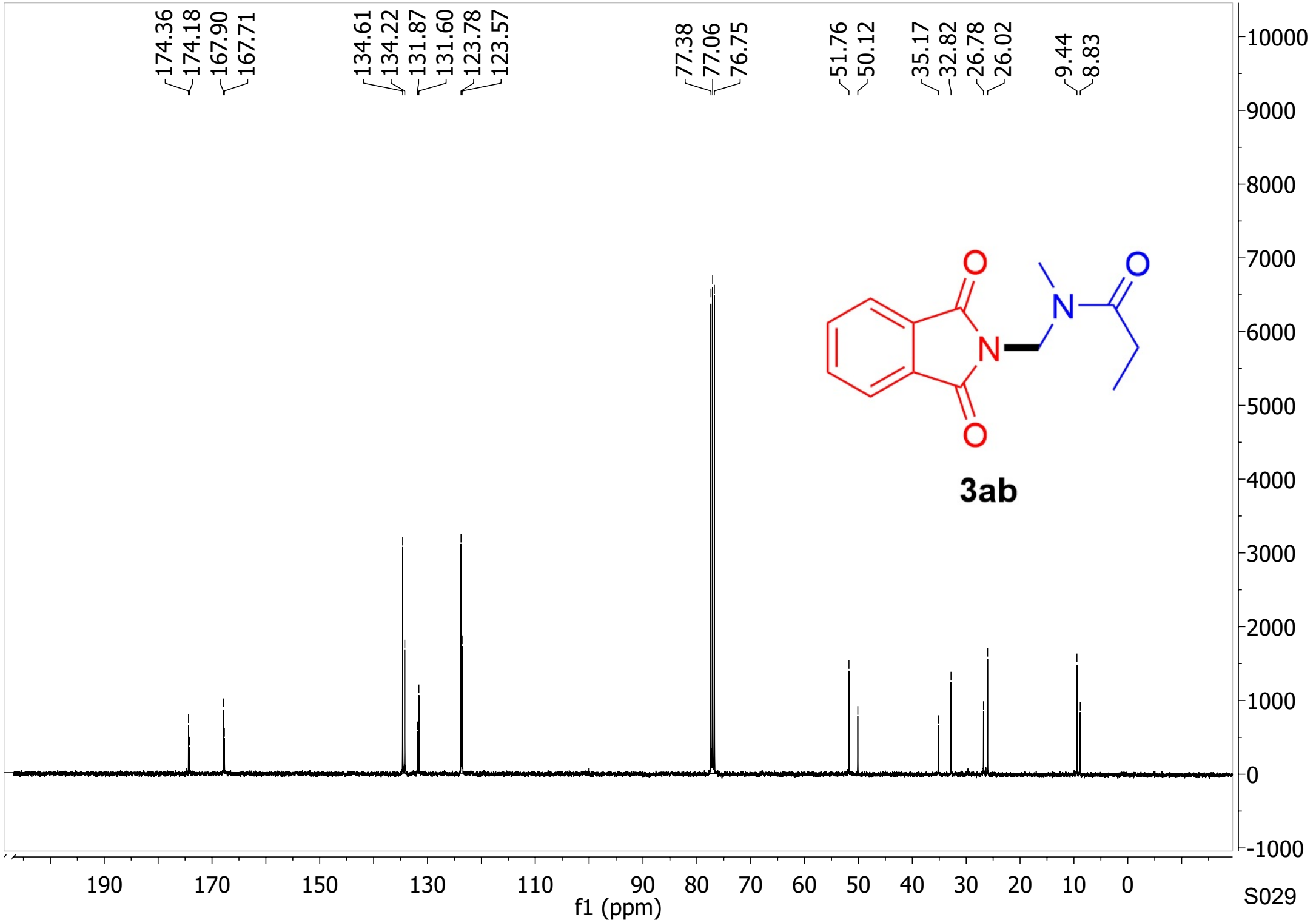
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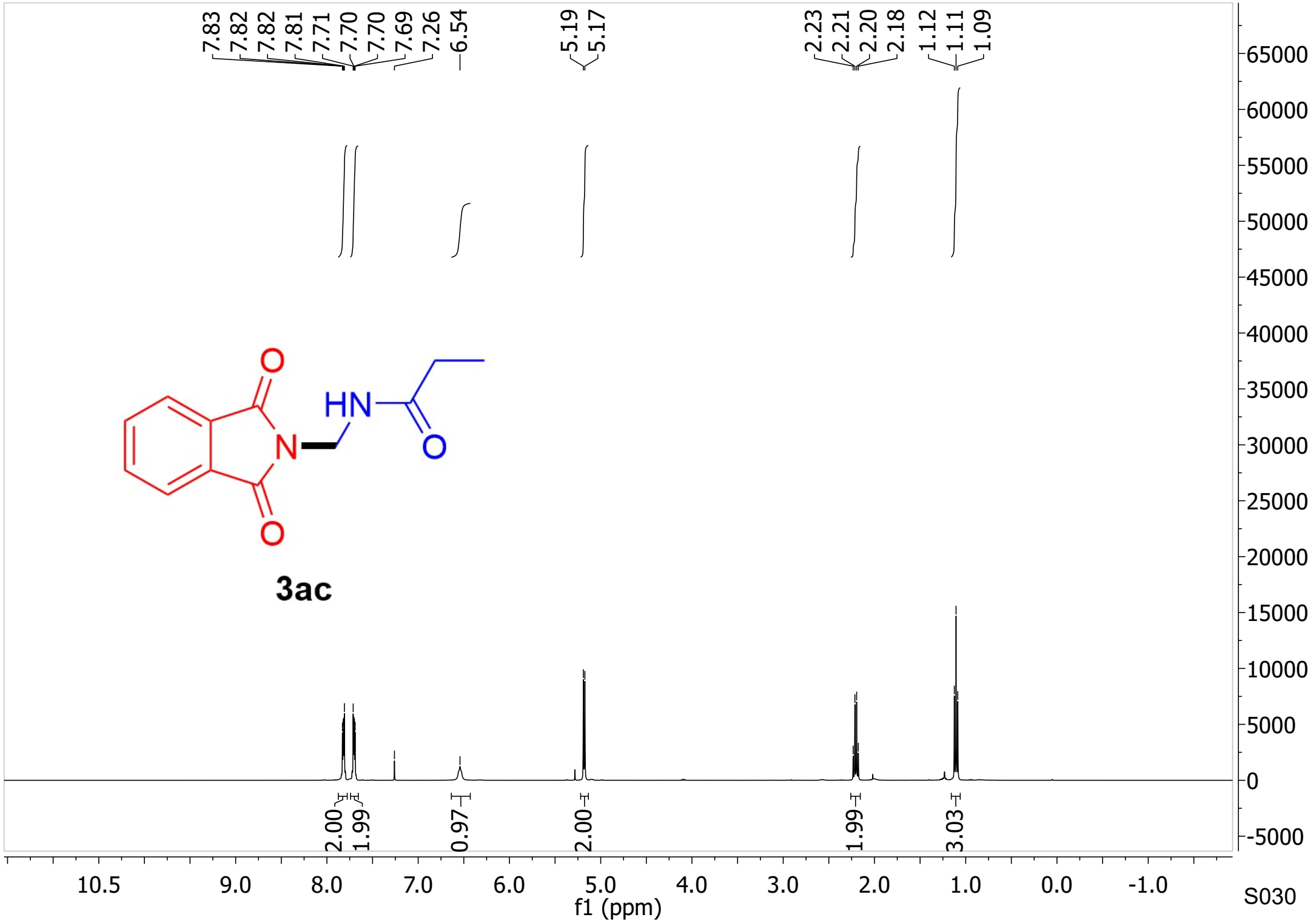
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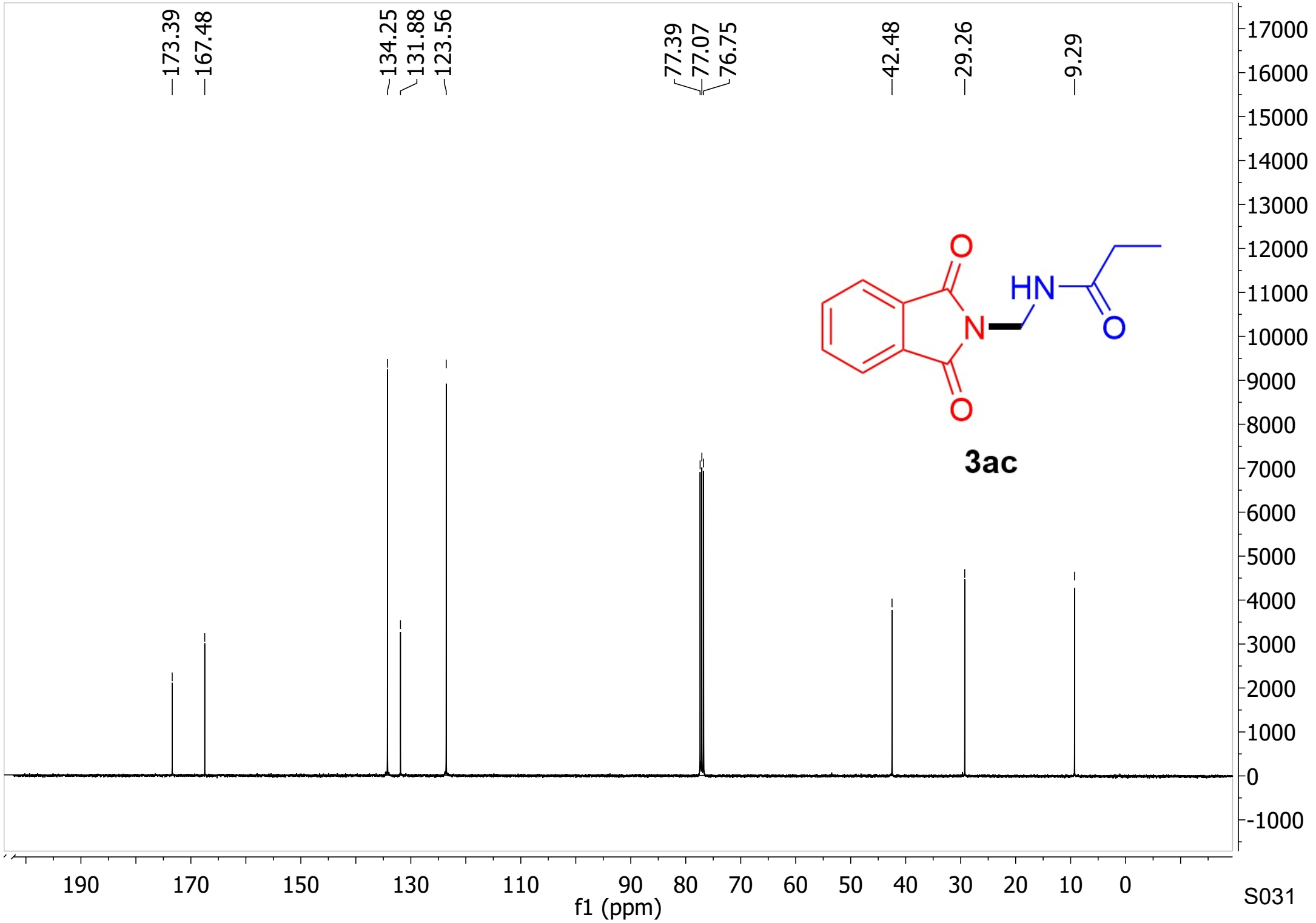
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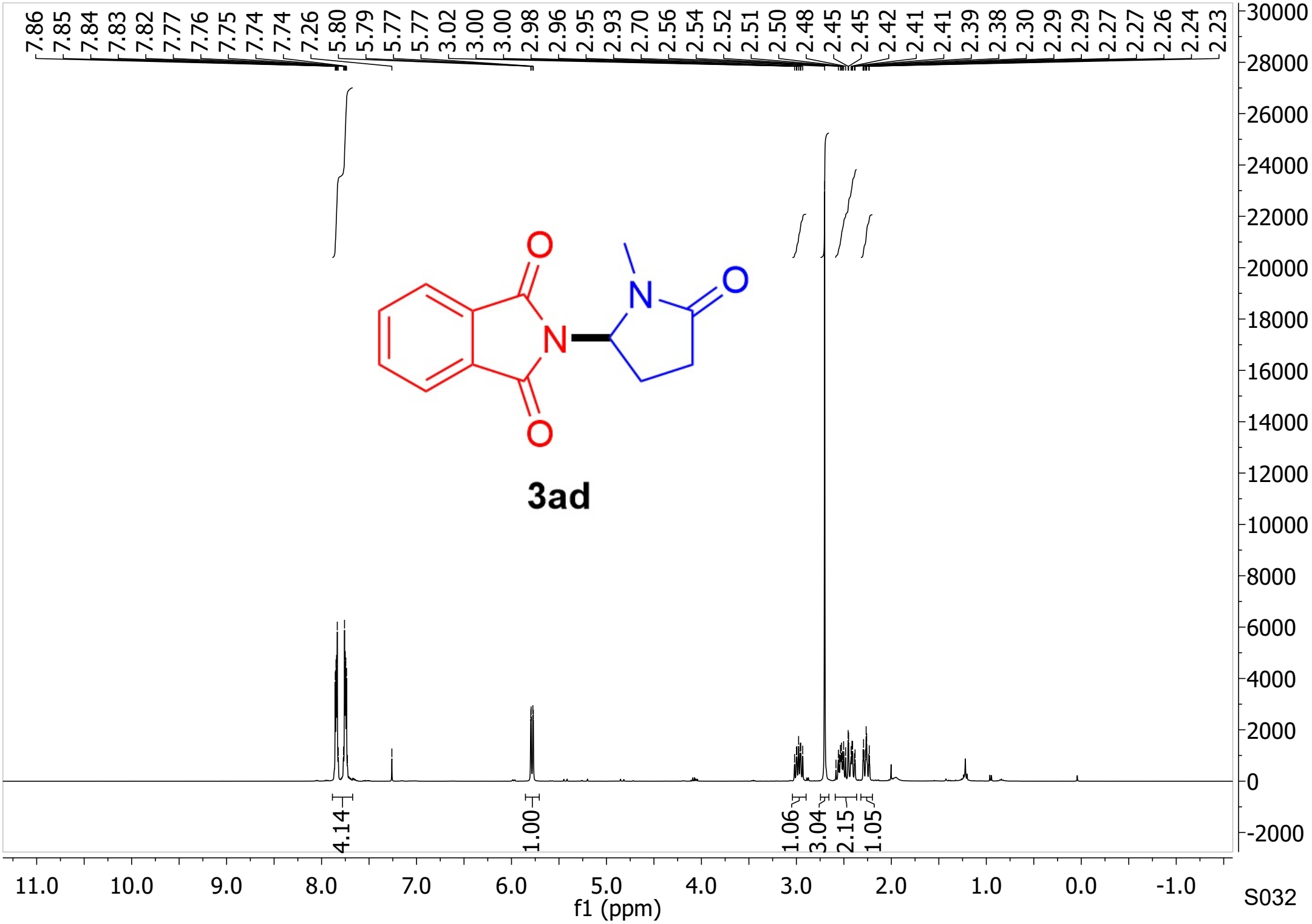
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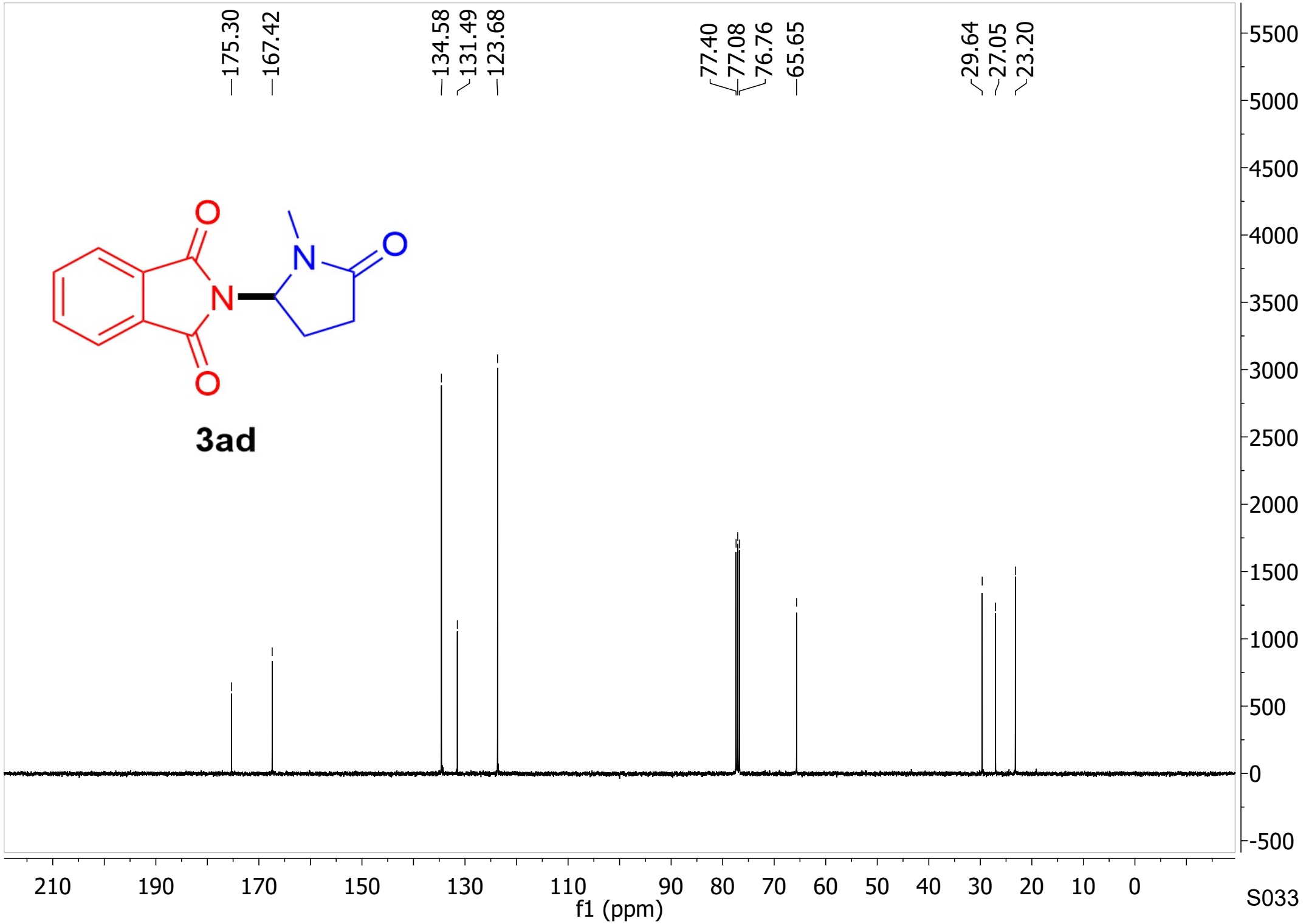
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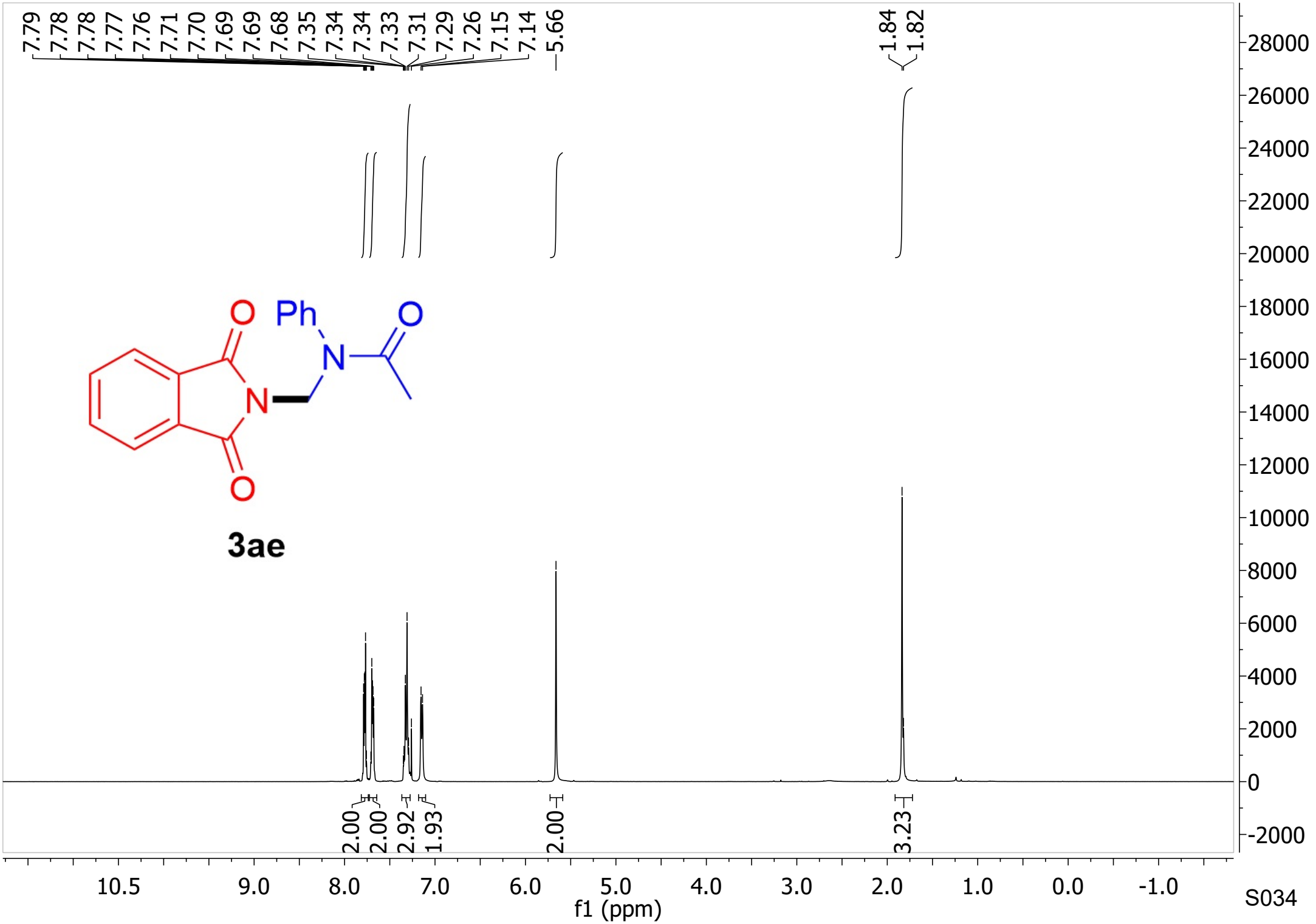
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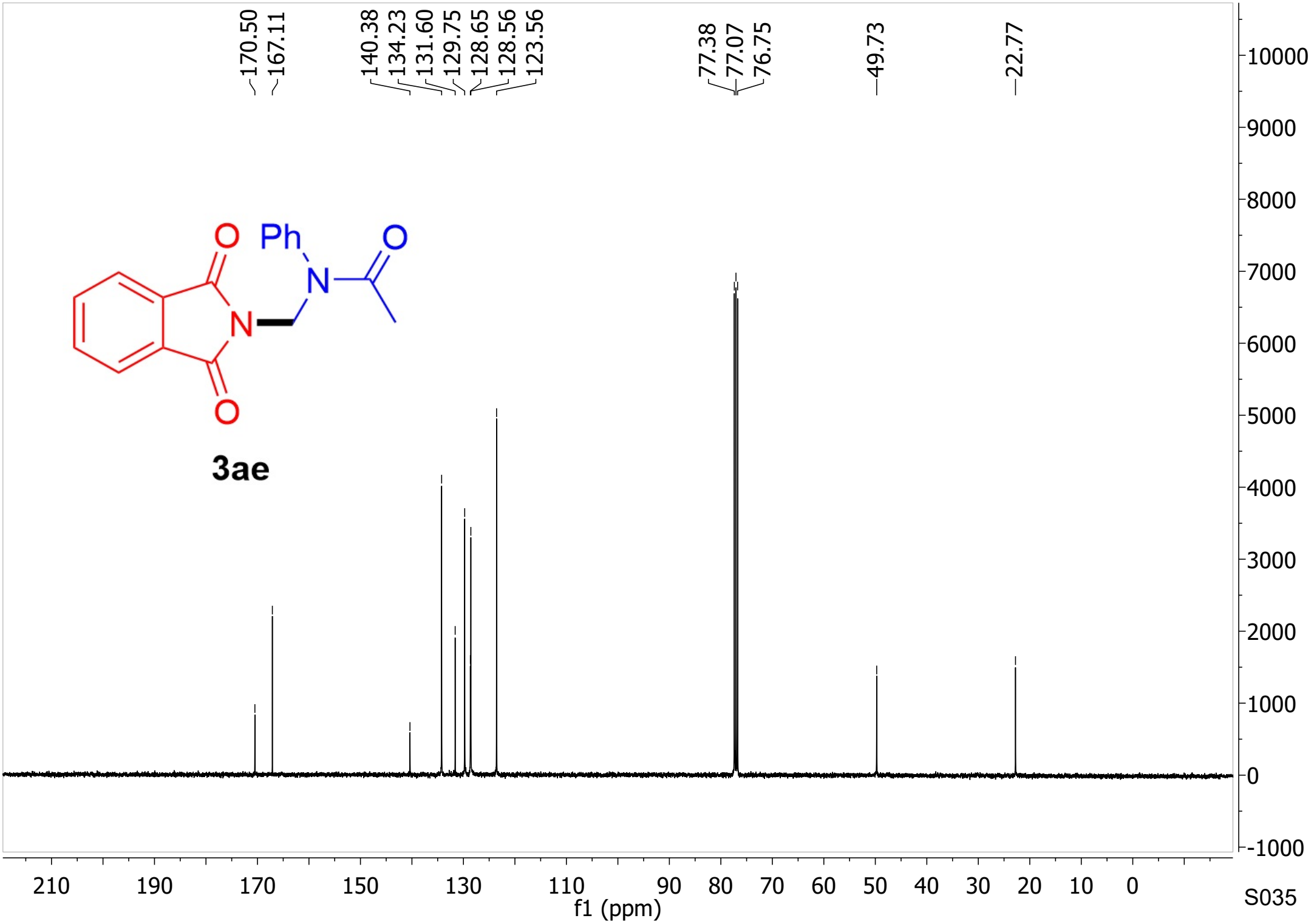
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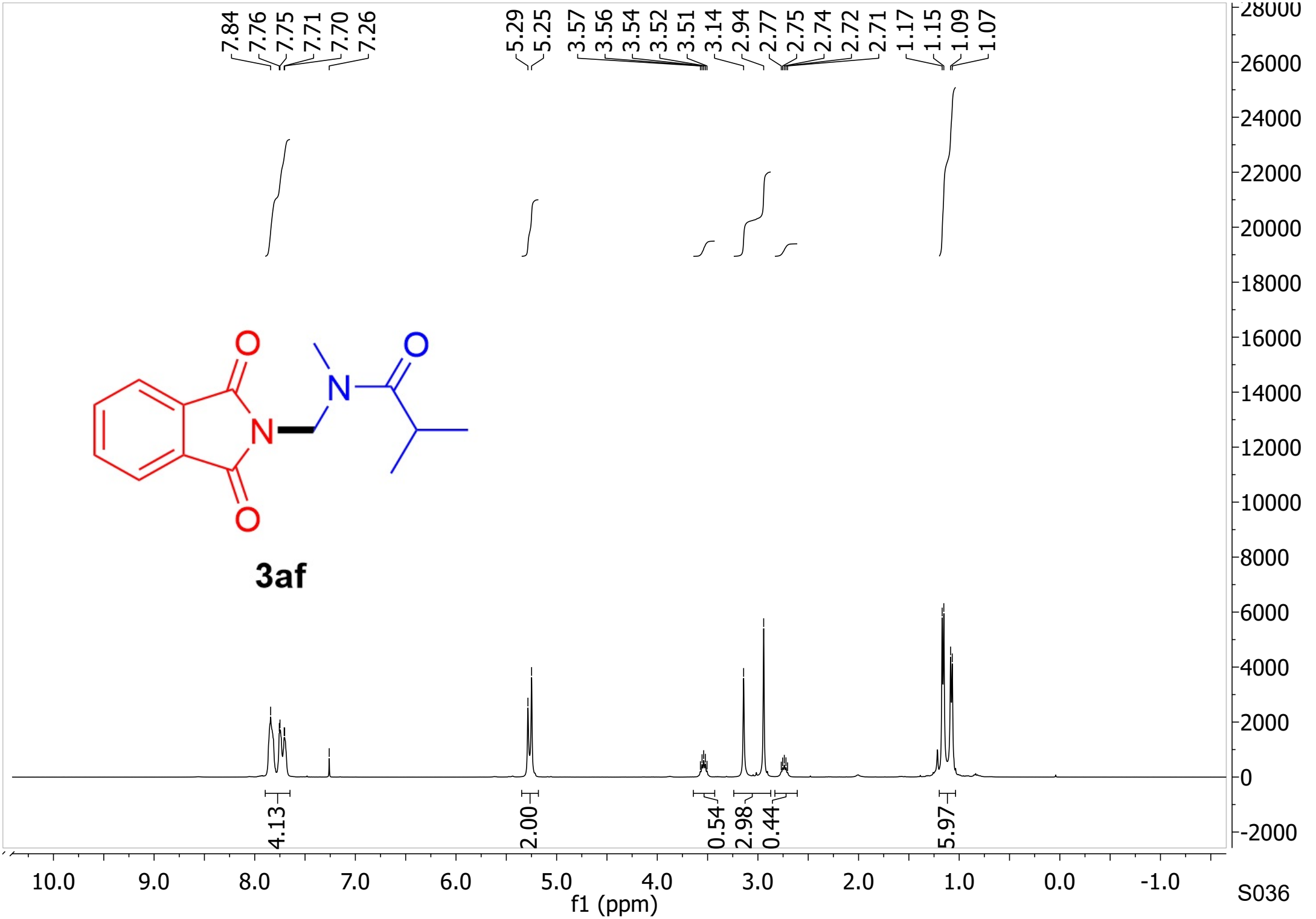
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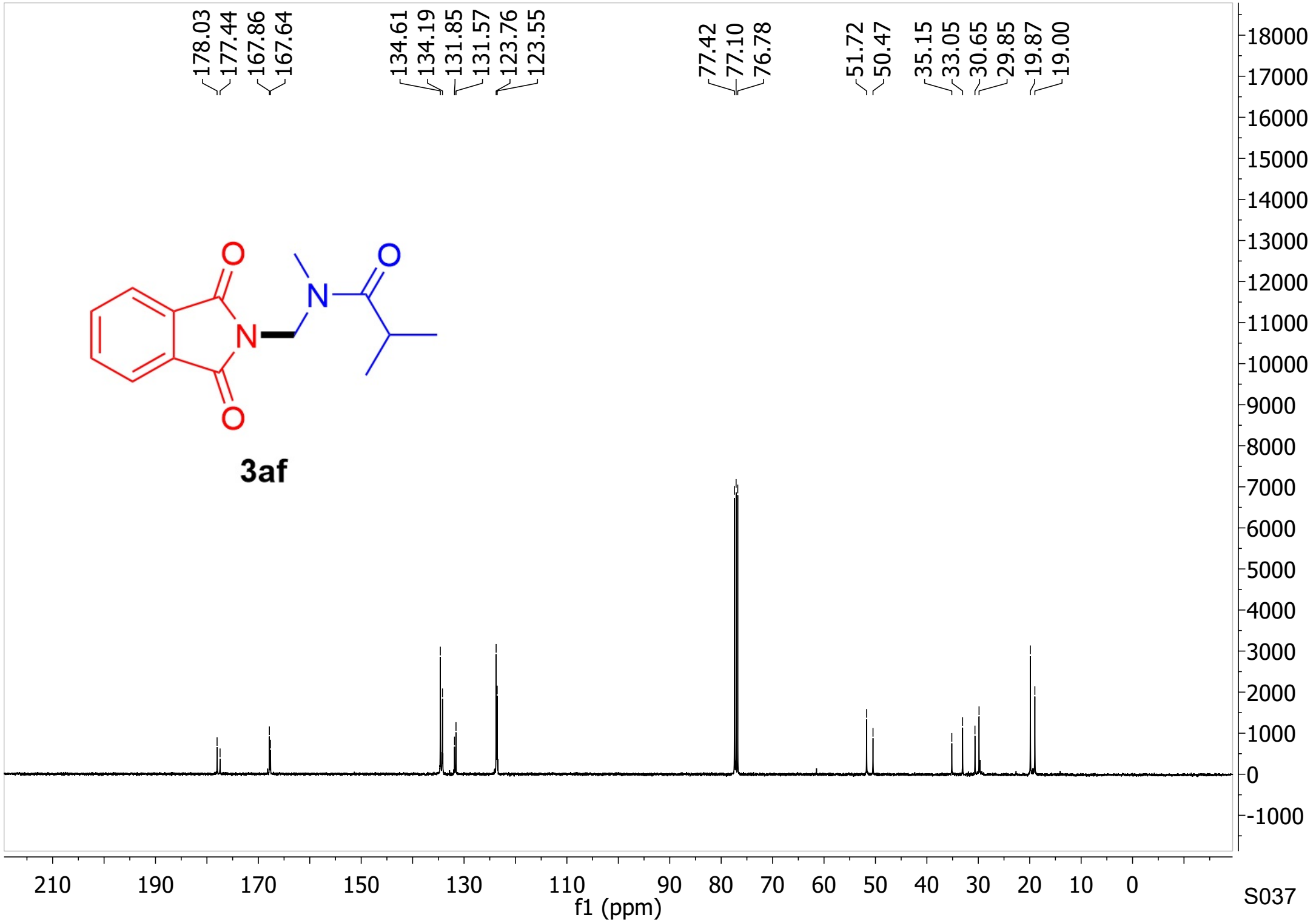
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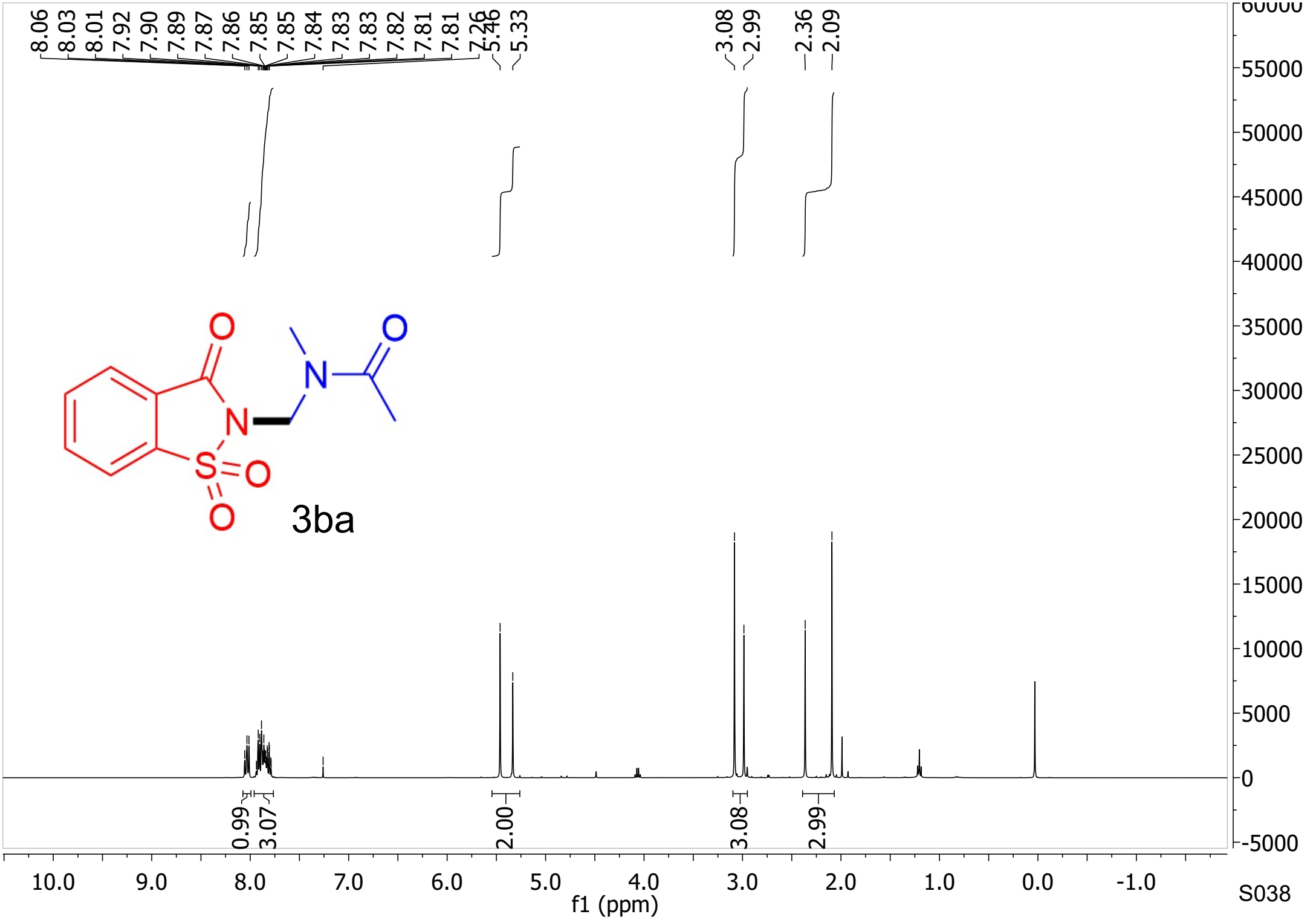
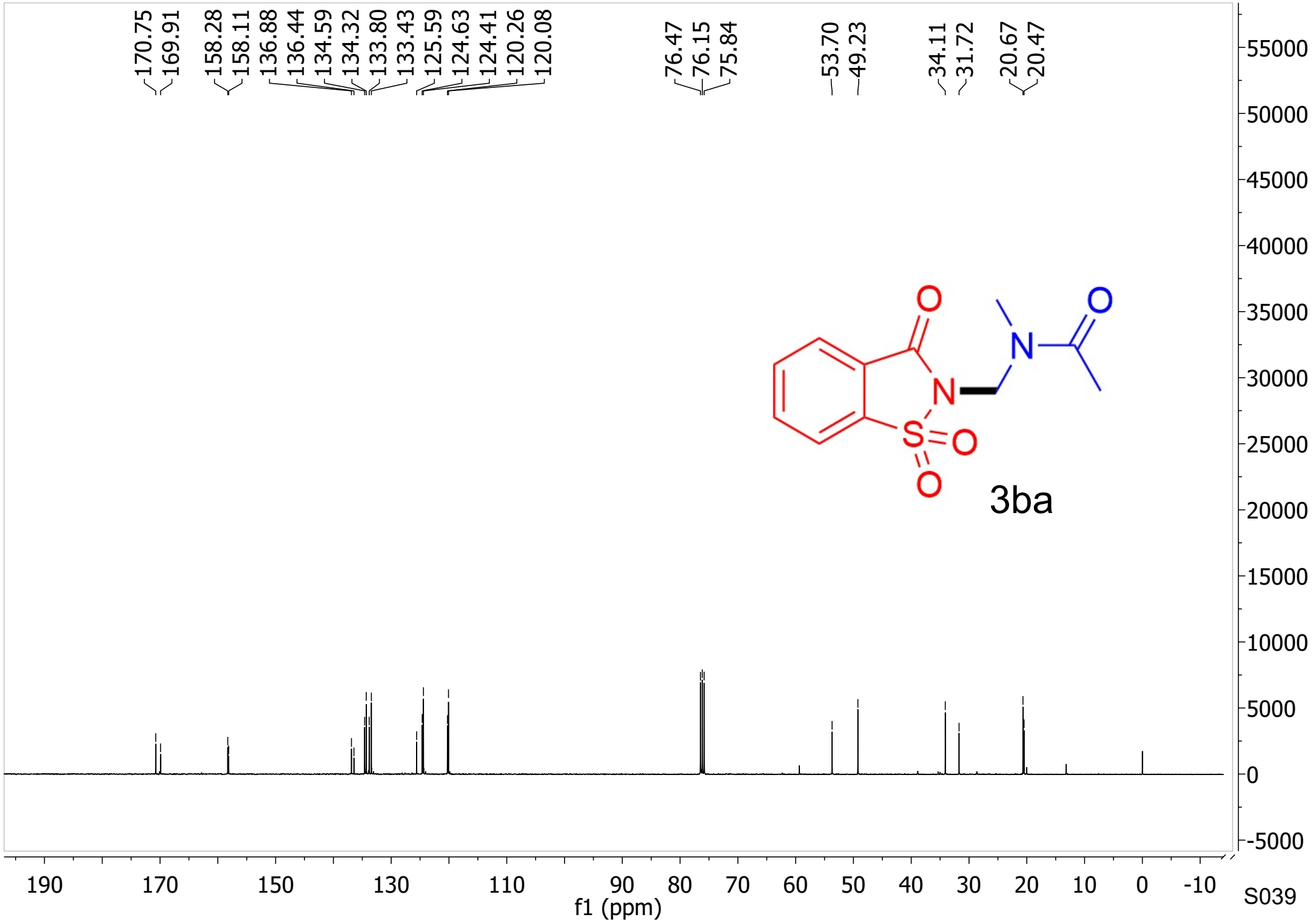
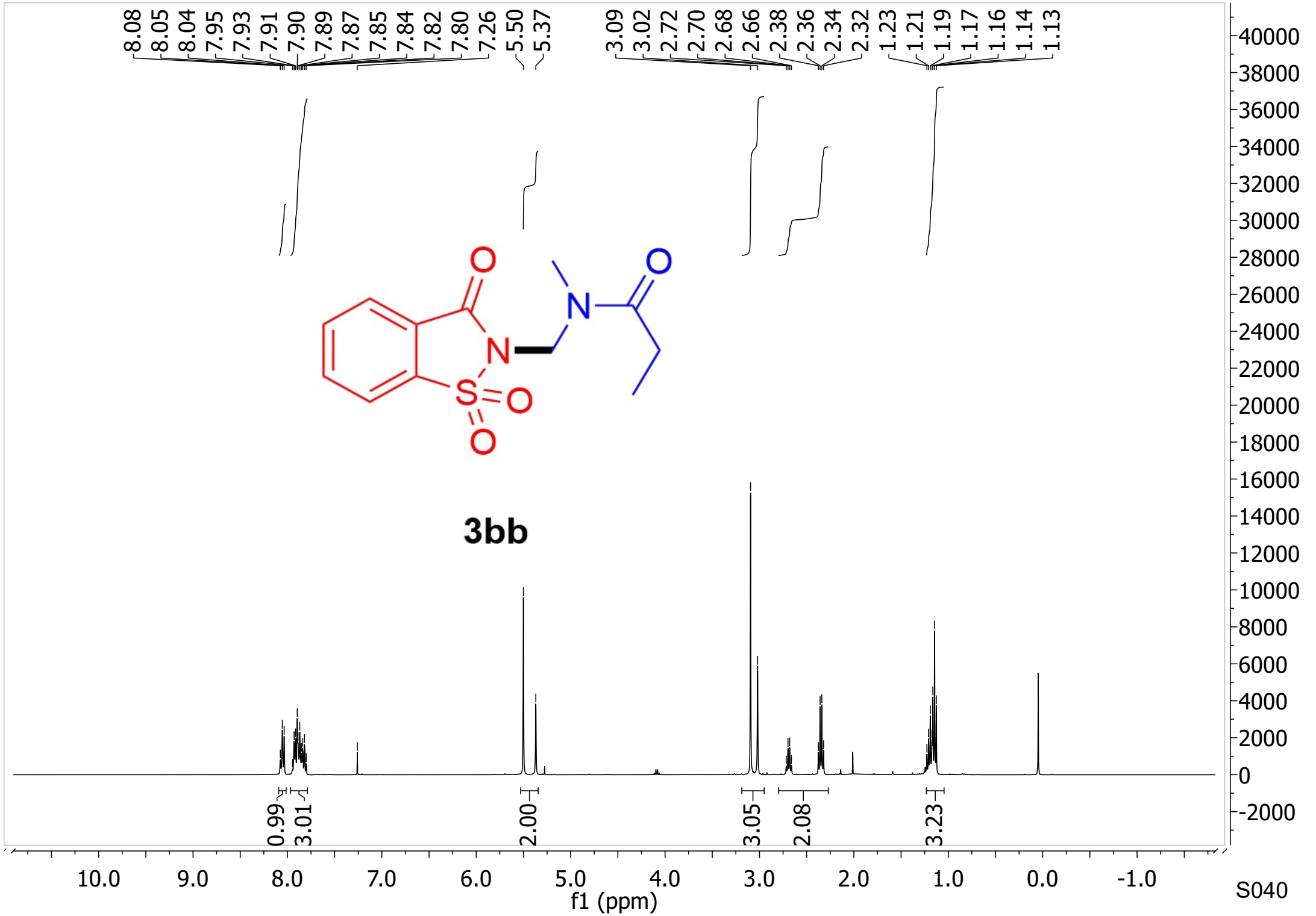
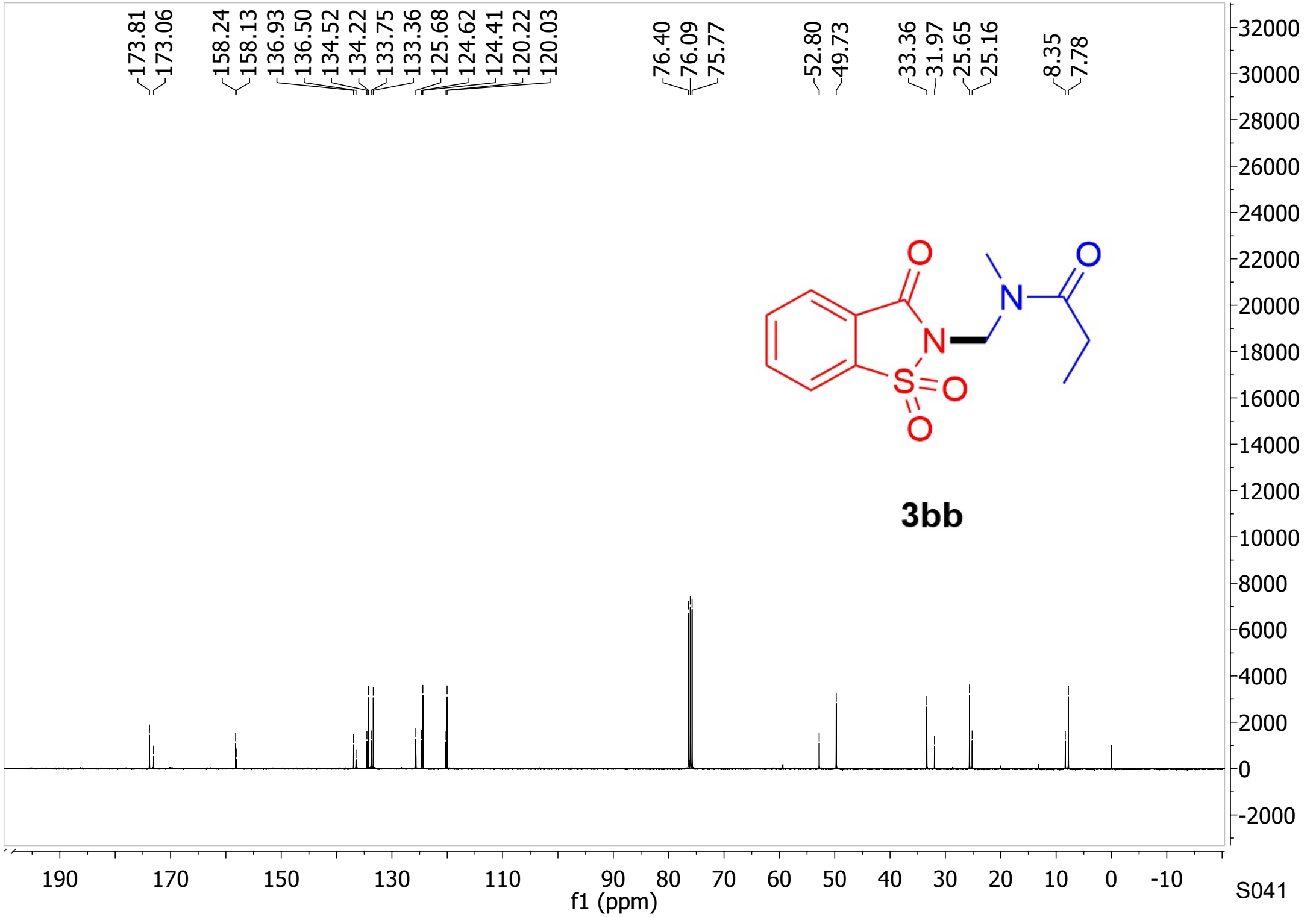
f1 (ppm)
S037

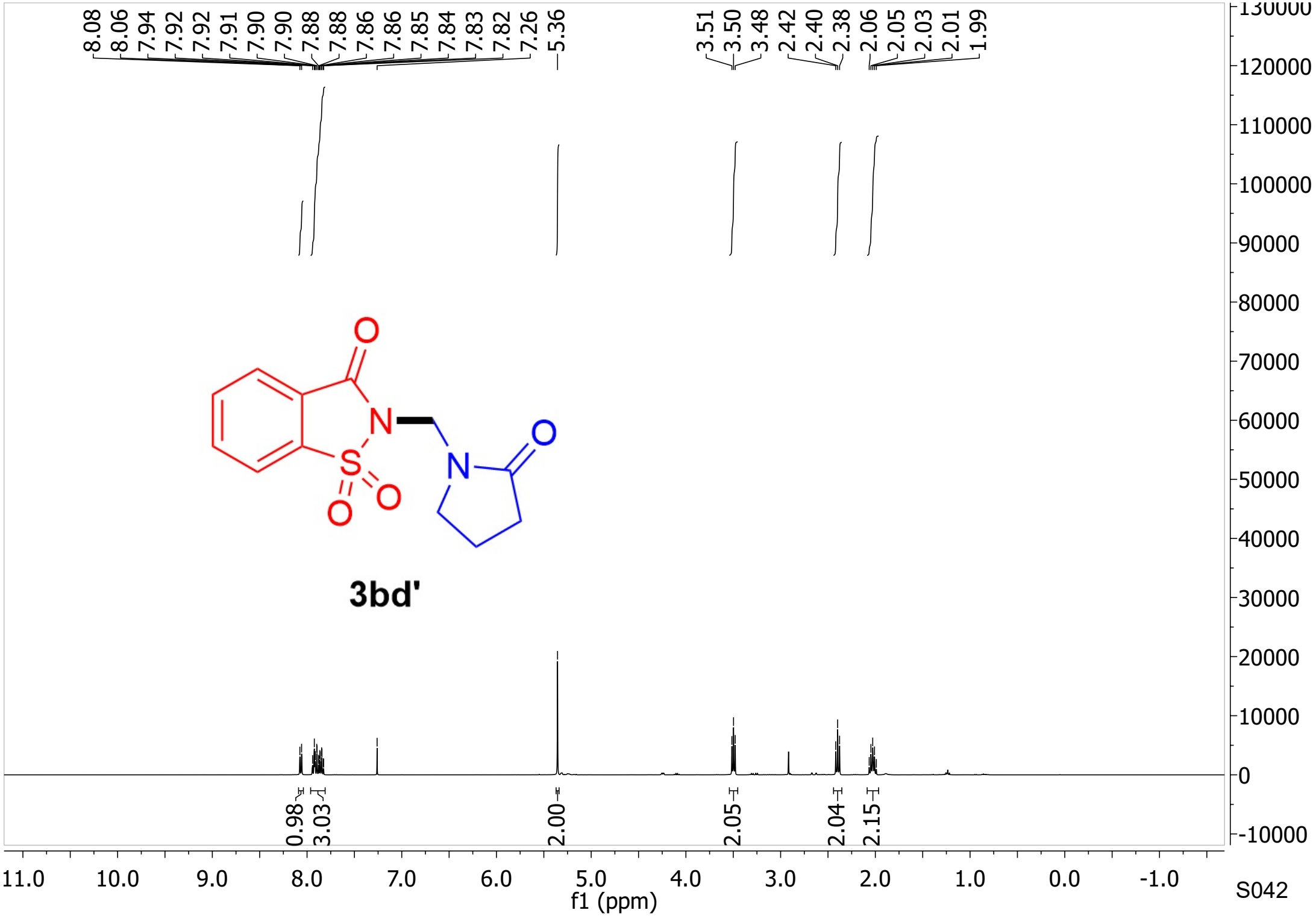

8.06
8.03
8.01
7.92
7.90
7.89
7.87
7.86
7.85
7.85
7.84
7.83
7.83
7.82
7.81
7.81
7.26
5.46
5.33
3.08
2.99
2.36
2.09
3ba
0.99
3.07
2.00
3.08
2.99
f1 (ppm)
S038

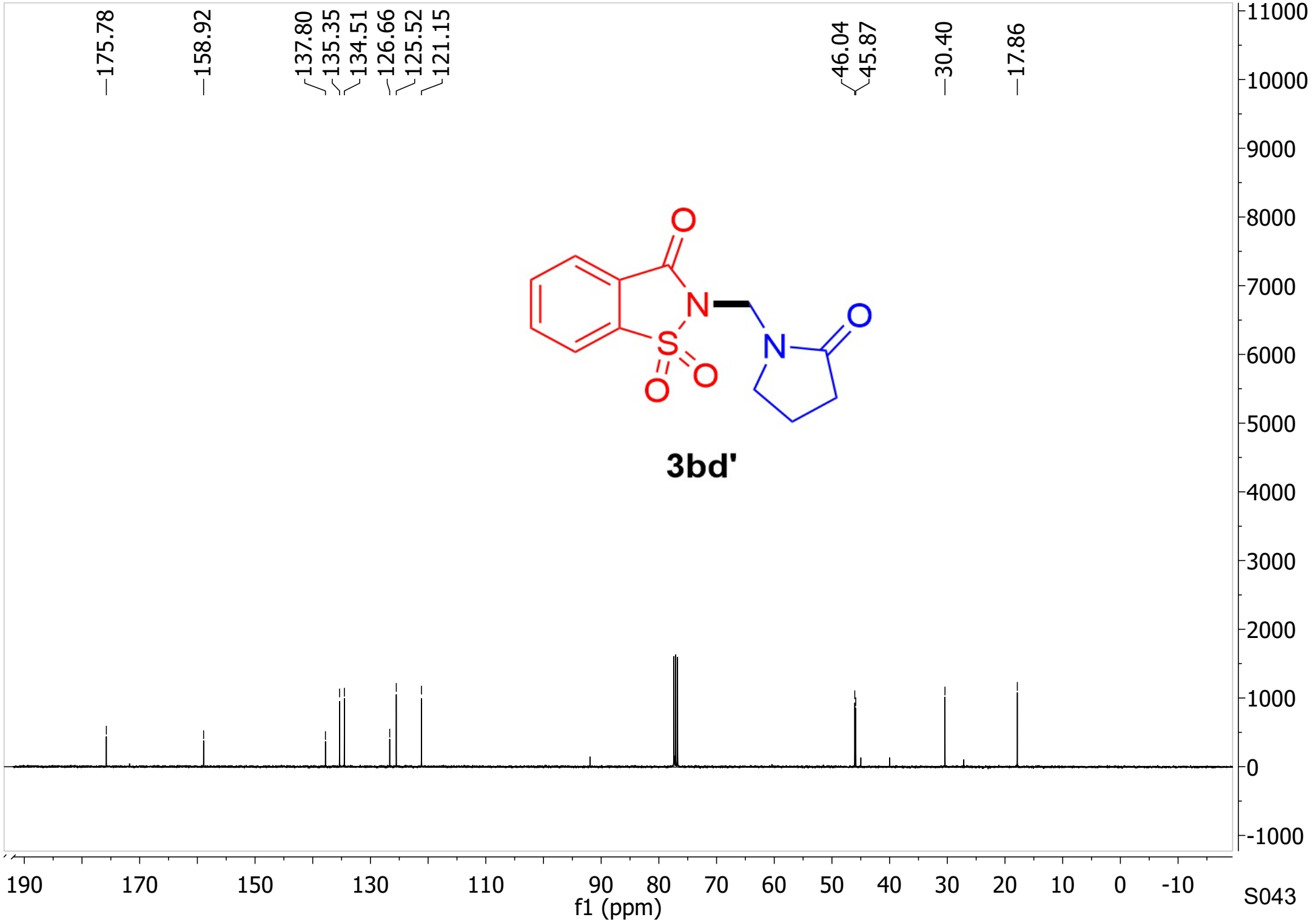

170.75
169.91
158.28
158.11
136.88
136.44
134.59
134.32
133.80
133.43
125.59
124.63
124.41
120.26
120.08
76.47
76.15
75.84
53.70
49.23
34.11
31.72
20.67
20.47
O
O
N
N
S
O
O
3ba
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
S039

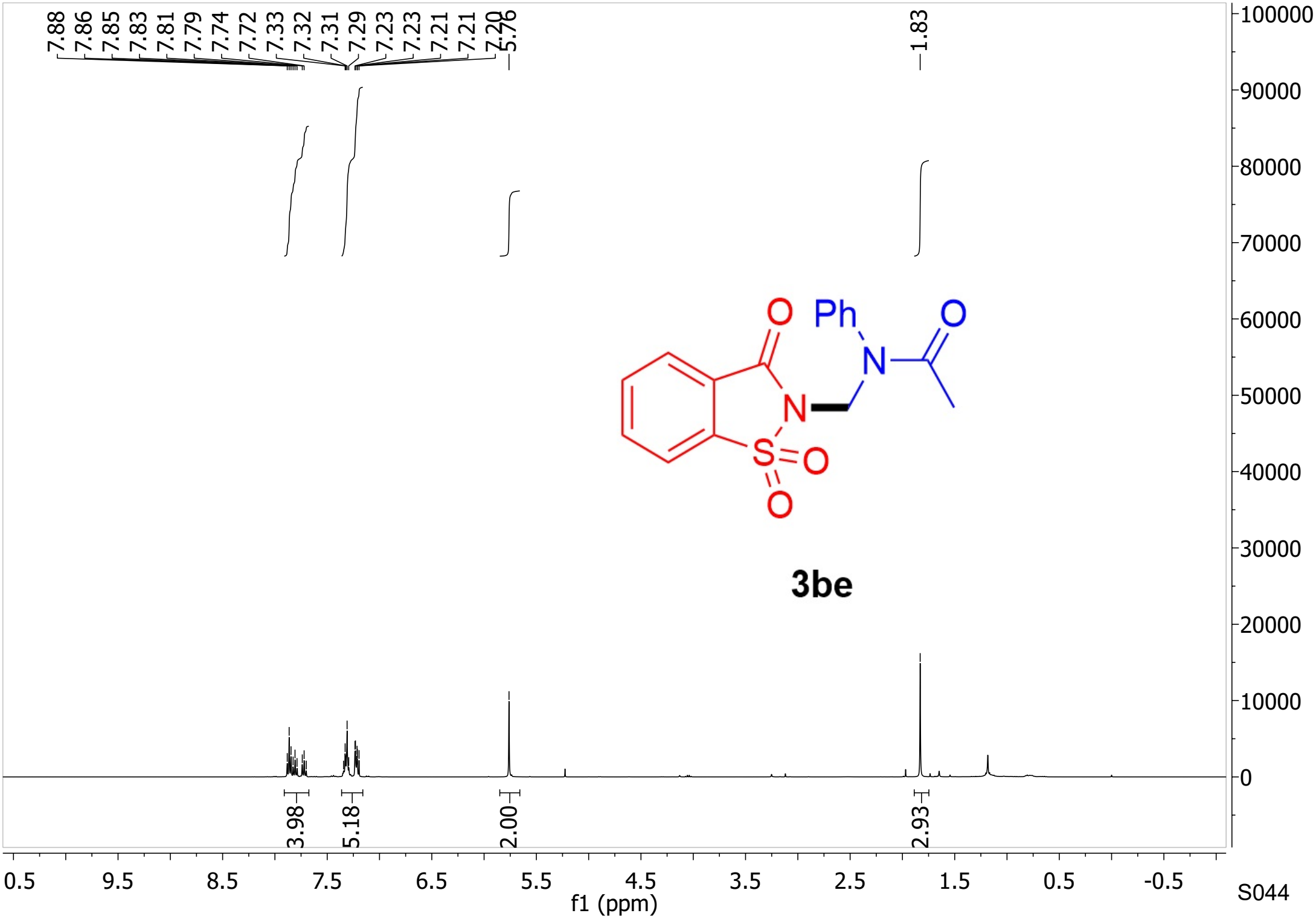

8.08
8.05
8.04
7.95
7.93
7.91
7.90
7.89
7.87
7.85
7.84
7.82
7.80
7.26
5.50
5.37
3.09
3.02
2.72
2.70
2.68
2.66
2.38
2.36
2.34
2.32
1.23
1.21
1.19
1.17
1.16
1.14
1.13
O
N
O
N
S
O
O
3bb
0.99
3.01
2.00
3.05
2.08
3.23
40000
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

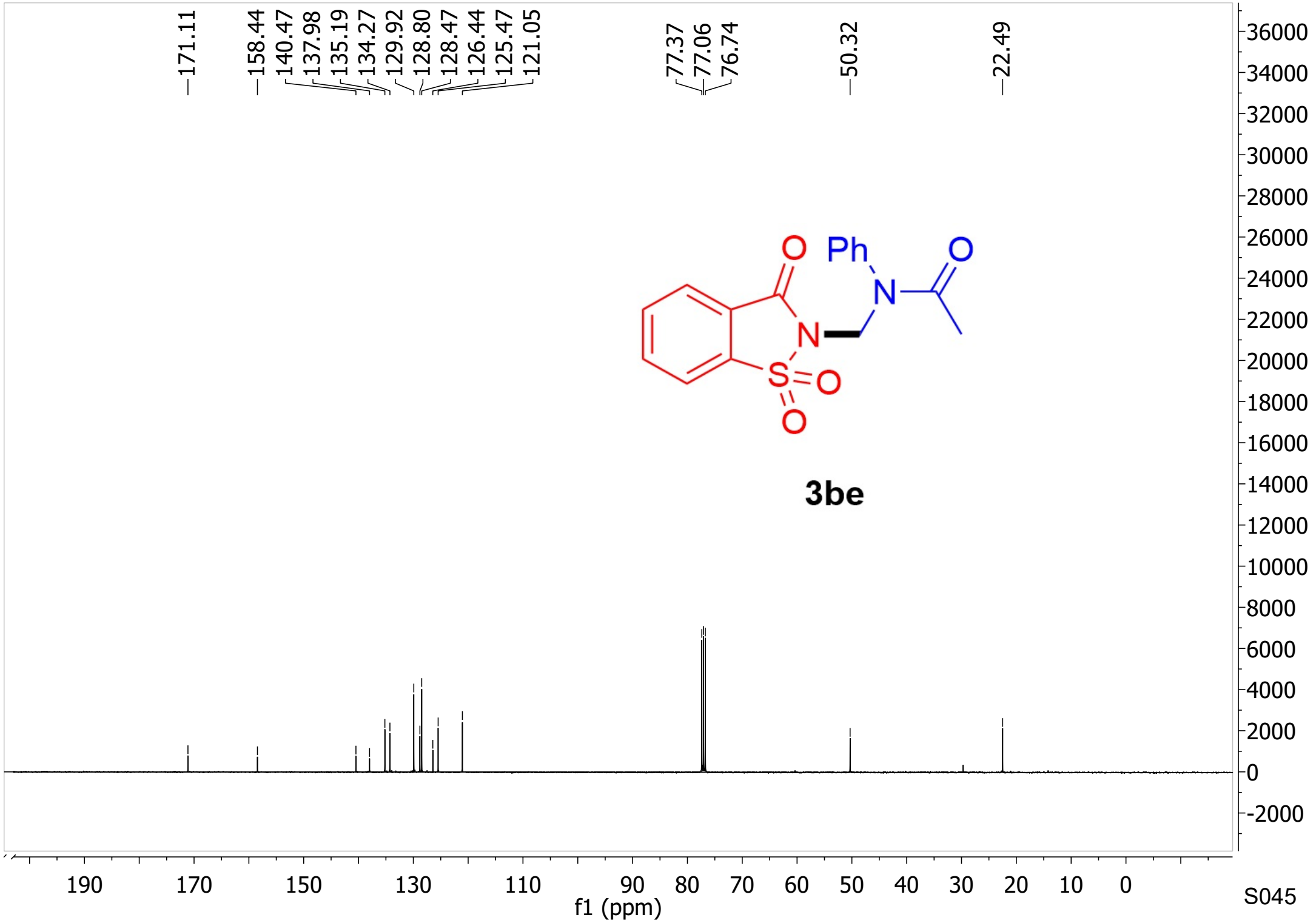
S040

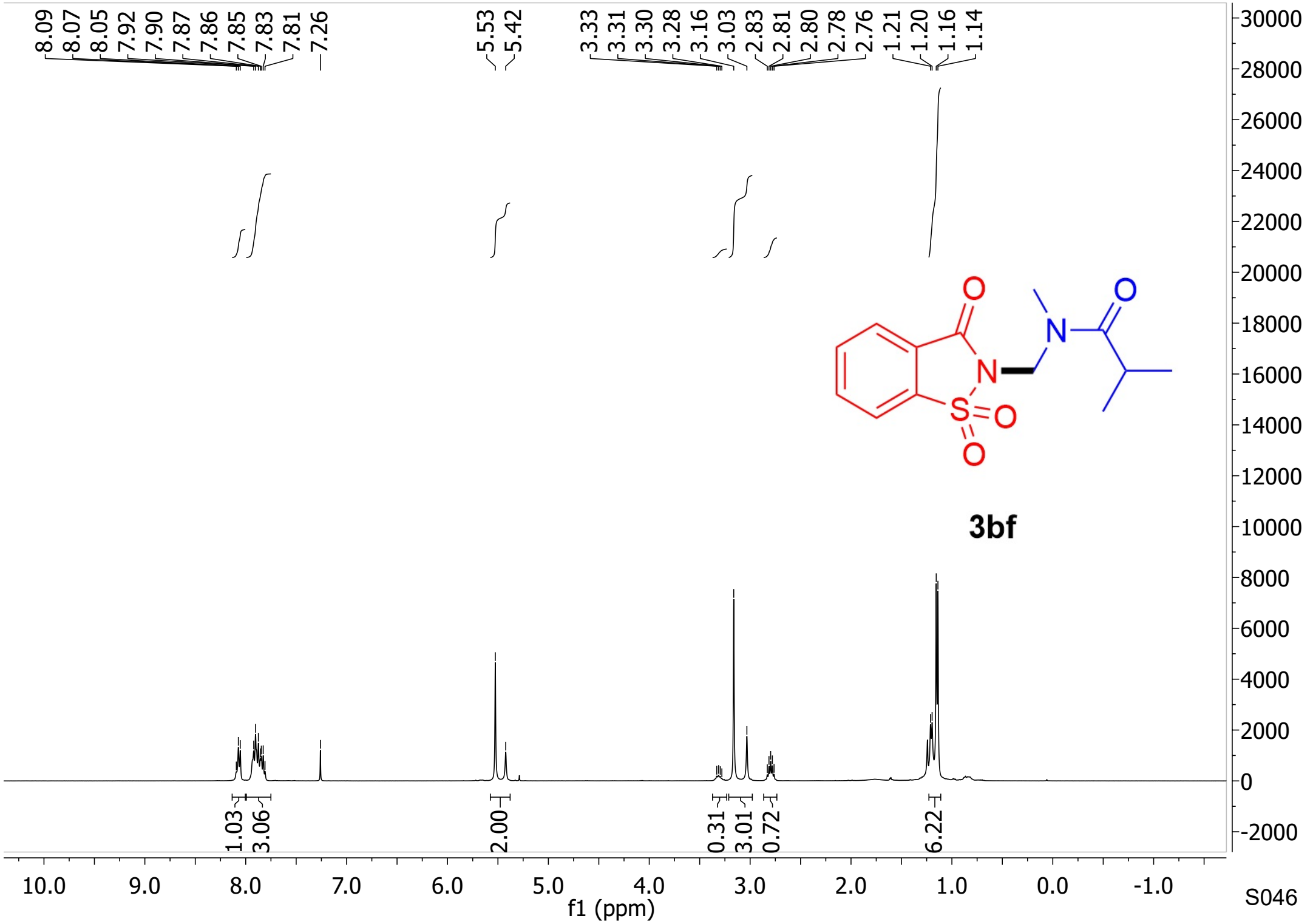

173.81
173.06
158.24
158.13
136.93
136.50
134.52
134.22
133.75
133.36
125.68
124.62
124.41
120.22
120.03
76.40
76.09
75.77
52.80
49.73
33.36
31.97
25.65
25.16
8.35
7.78
O
O
N
N
S
O
O
3bb
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
S041

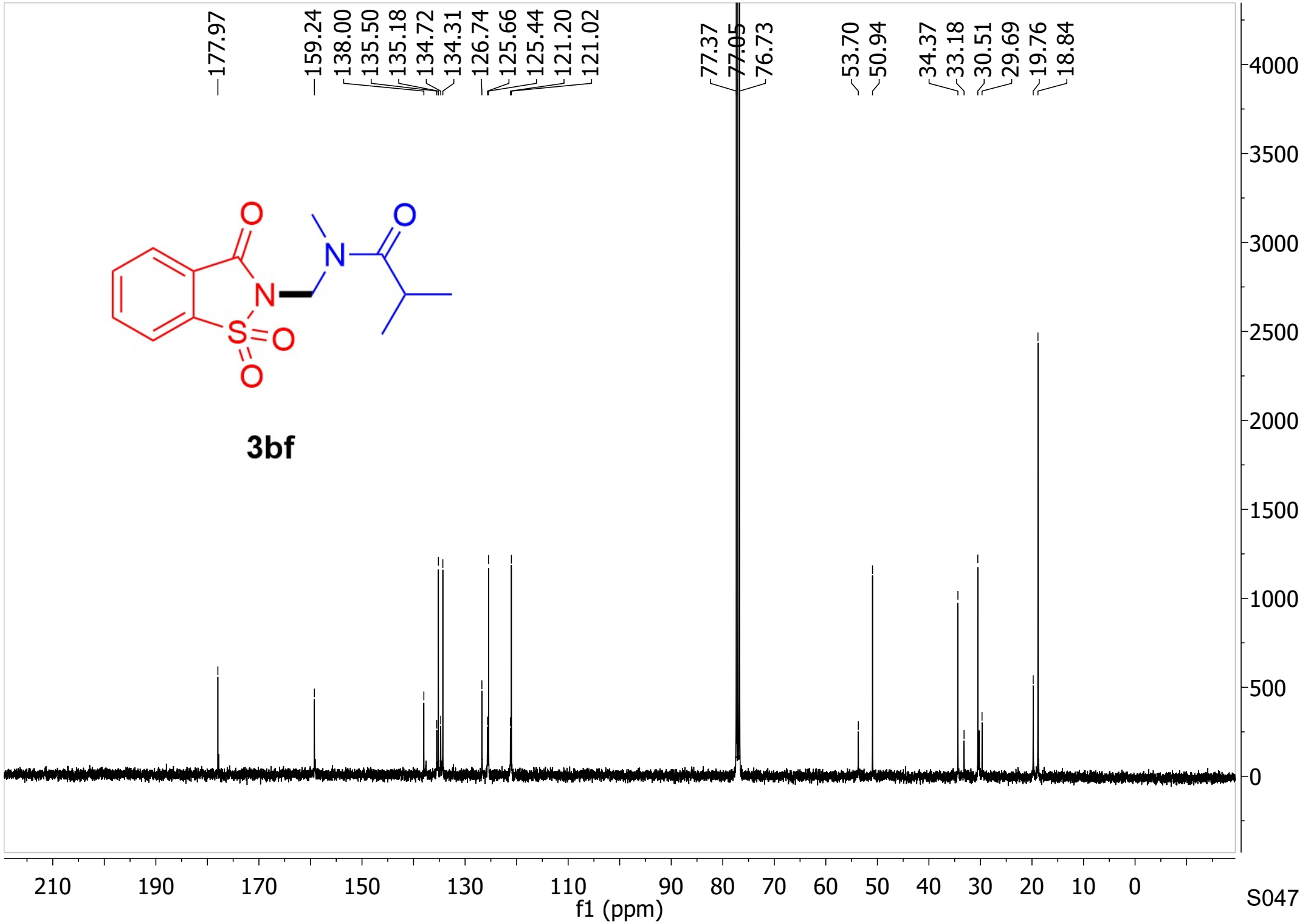

8.08
8.06
7.94
7.92
7.92
7.91
7.90
7.90
7.88
7.88
7.86
7.86
7.85
7.84
7.83
7.82
7.26
5.36
3.51
3.50
3.48
2.42
2.40
2.38
2.06
2.05
2.03
2.01
1.99
O
N
S
O
O
N
O
3bd'
0.98
3.03
2.00
2.05
2.04
2.15
f1 (ppm)
S042

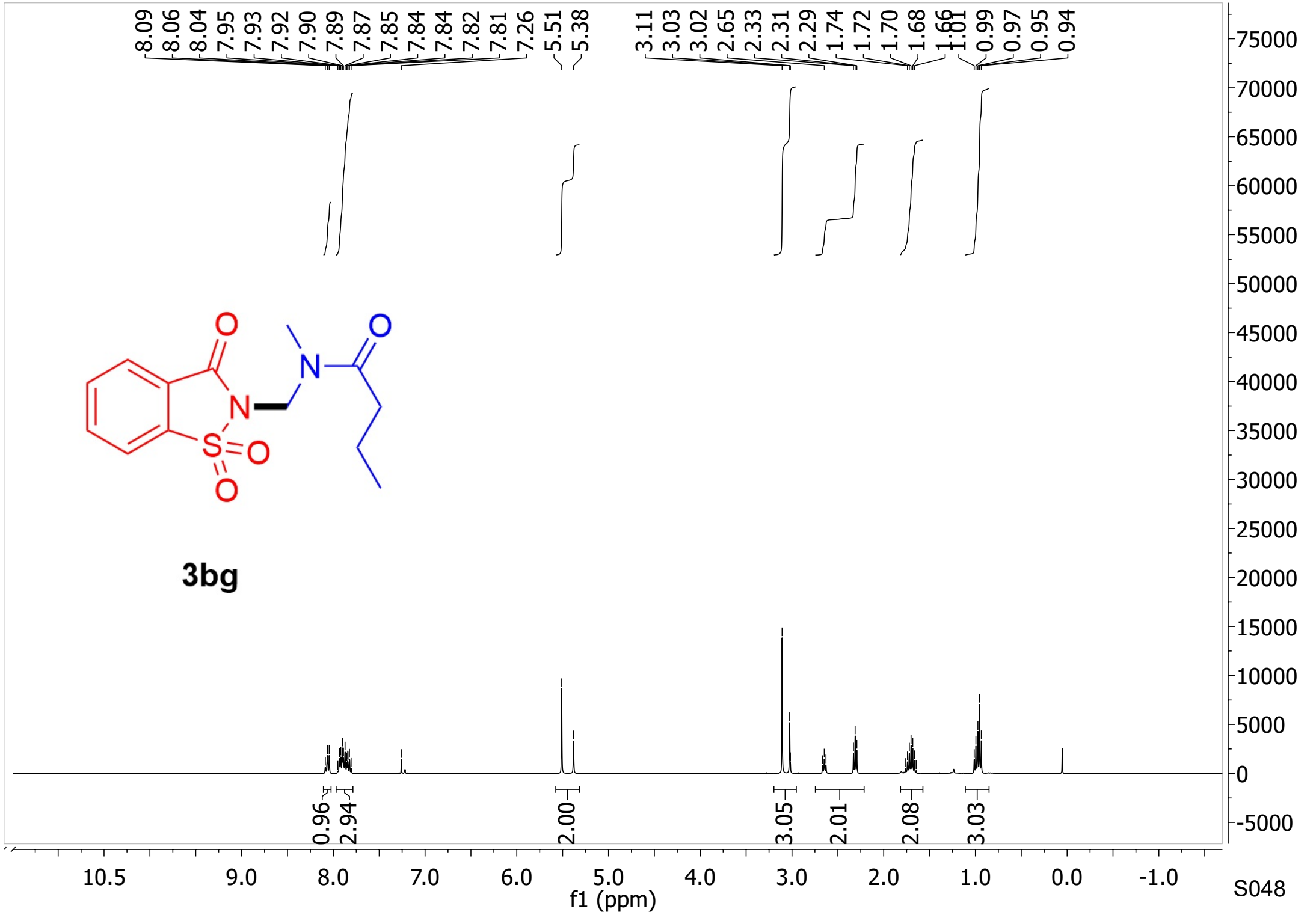

175.78
158.92
137.80
135.35
134.51
126.66
125.52
121.15
46.04
45.87
30.40
17.86
O
N
S
O
O
N
O
3bd'
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
S043

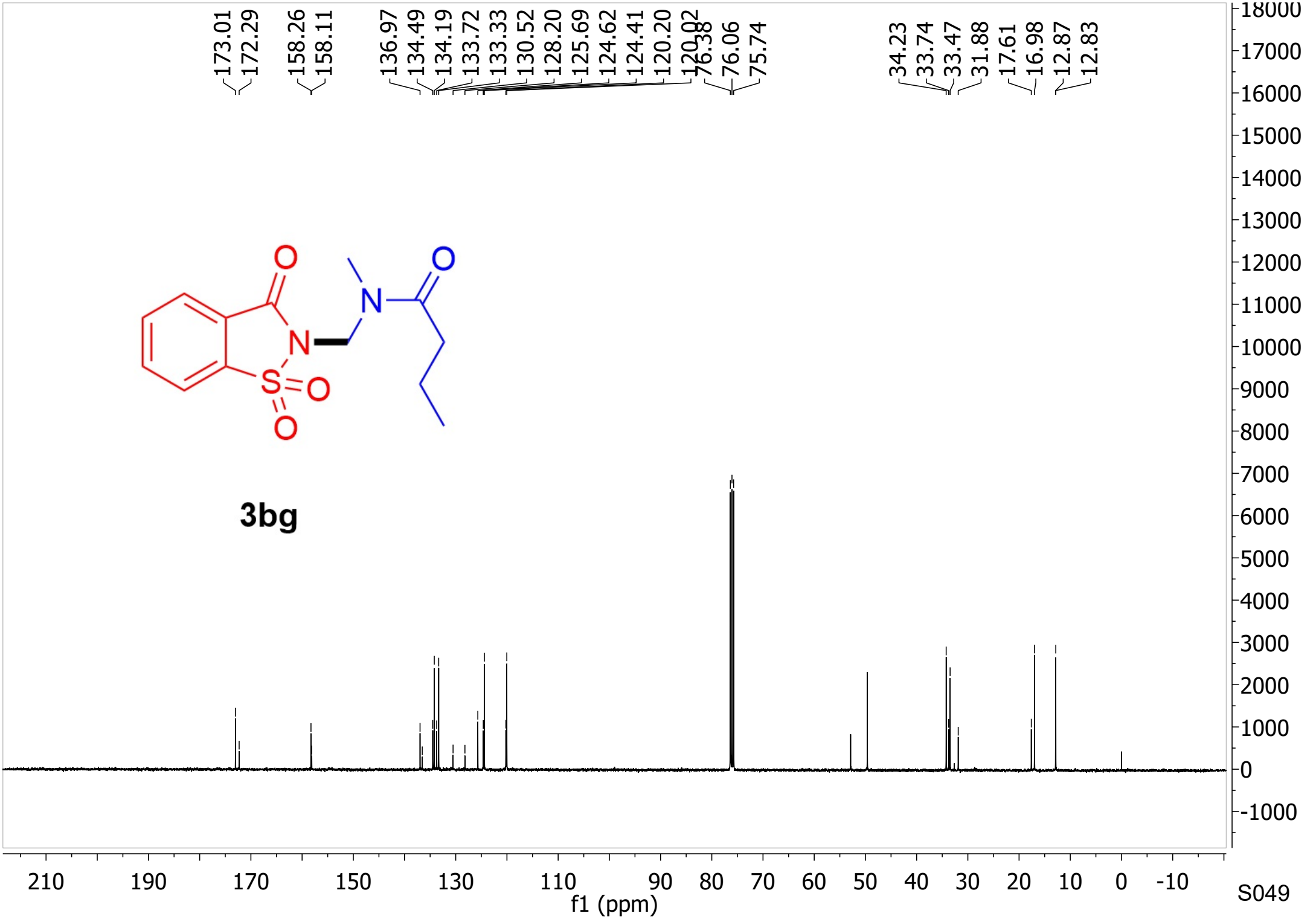

7.88
7.86
7.85
7.83
7.81
7.79
7.74
7.72
7.33
7.32
7.31
7.29
7.23
7.23
7.21
7.21
7.20
5.76
1.83
O
Ph
O
N
N
S
O
O
3be
3.98
5.18
2.00
2.93
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
0.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)
S044

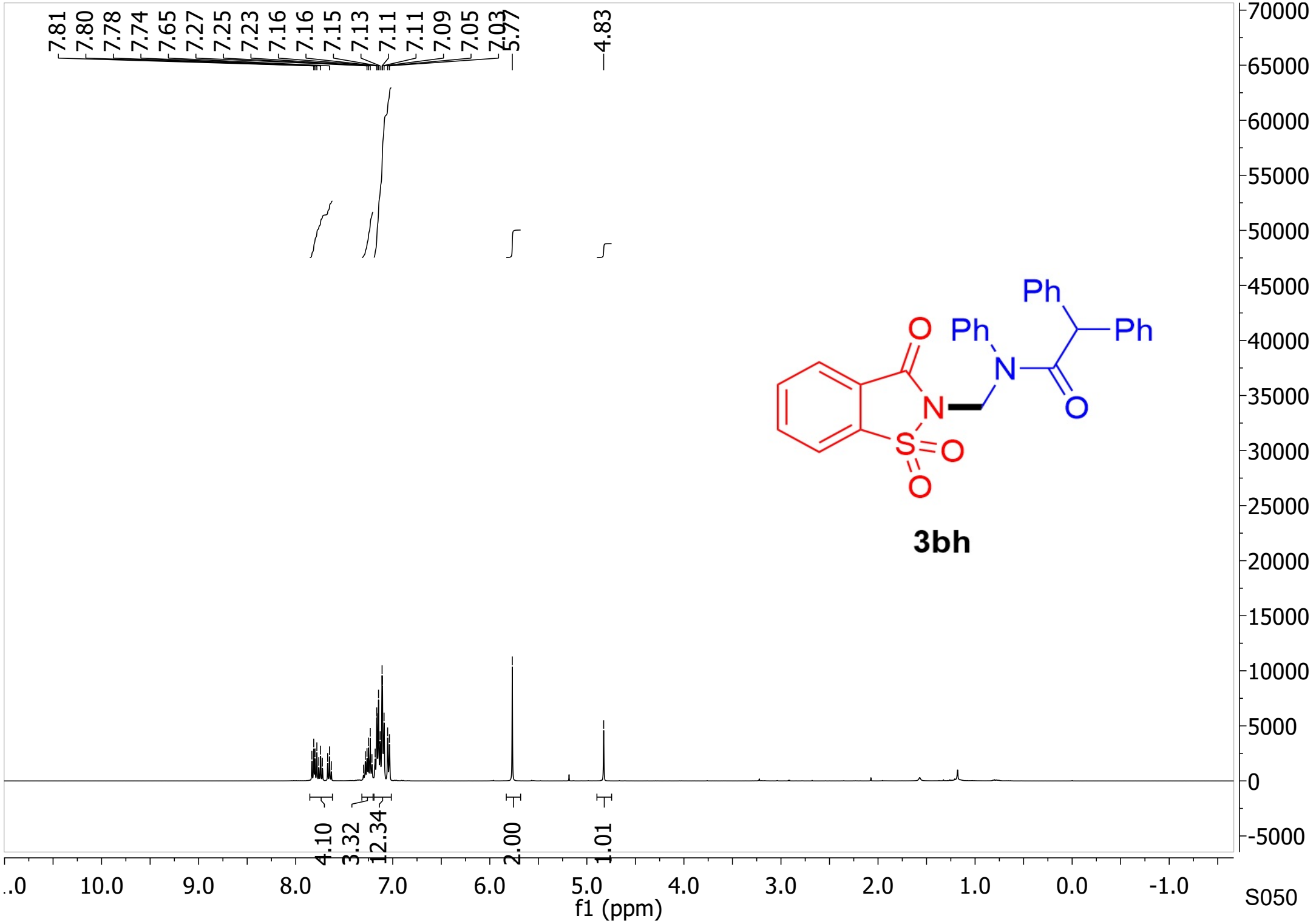

171.11
158.44
140.47
137.98
135.19
134.27
129.92
128.80
128.47
126.44
125.47
121.05
77.37
77.06
76.74
50.32
22.49
O
Ph
O
N
N
S
O
O
3be
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
S045

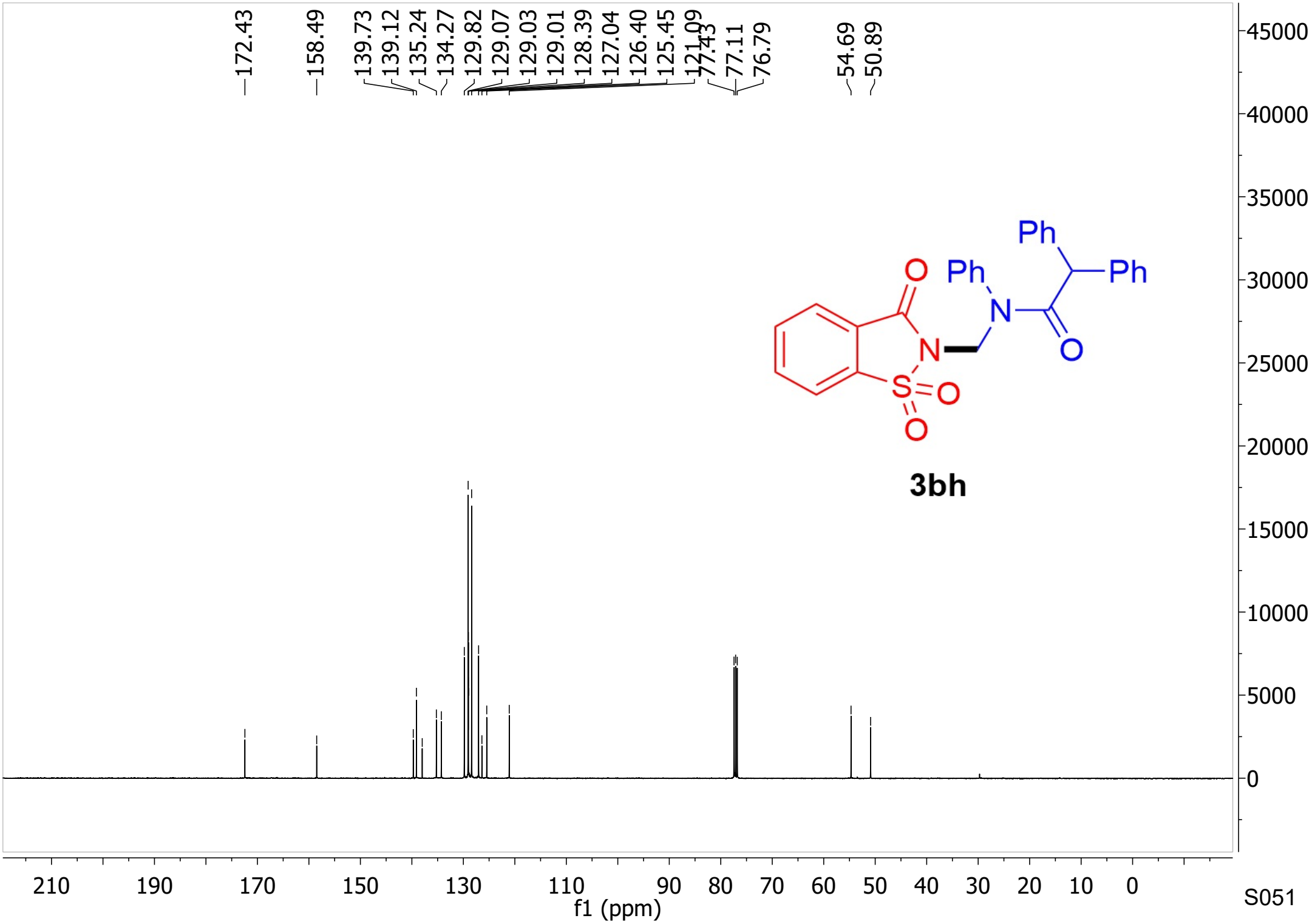

8.09
8.07
8.05
7.92
7.90
7.87
7.86
7.85
7.83
7.81
7.26
5.53
5.42
3.33
3.31
3.30
3.28
3.16
3.03
2.83
2.81
2.80
2.78
2.76
1.21
1.20
1.16
1.14
O
N
O
N
S
O
O
3bf
1.03
3.06
2.00
0.31
3.01
0.72
6.22
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

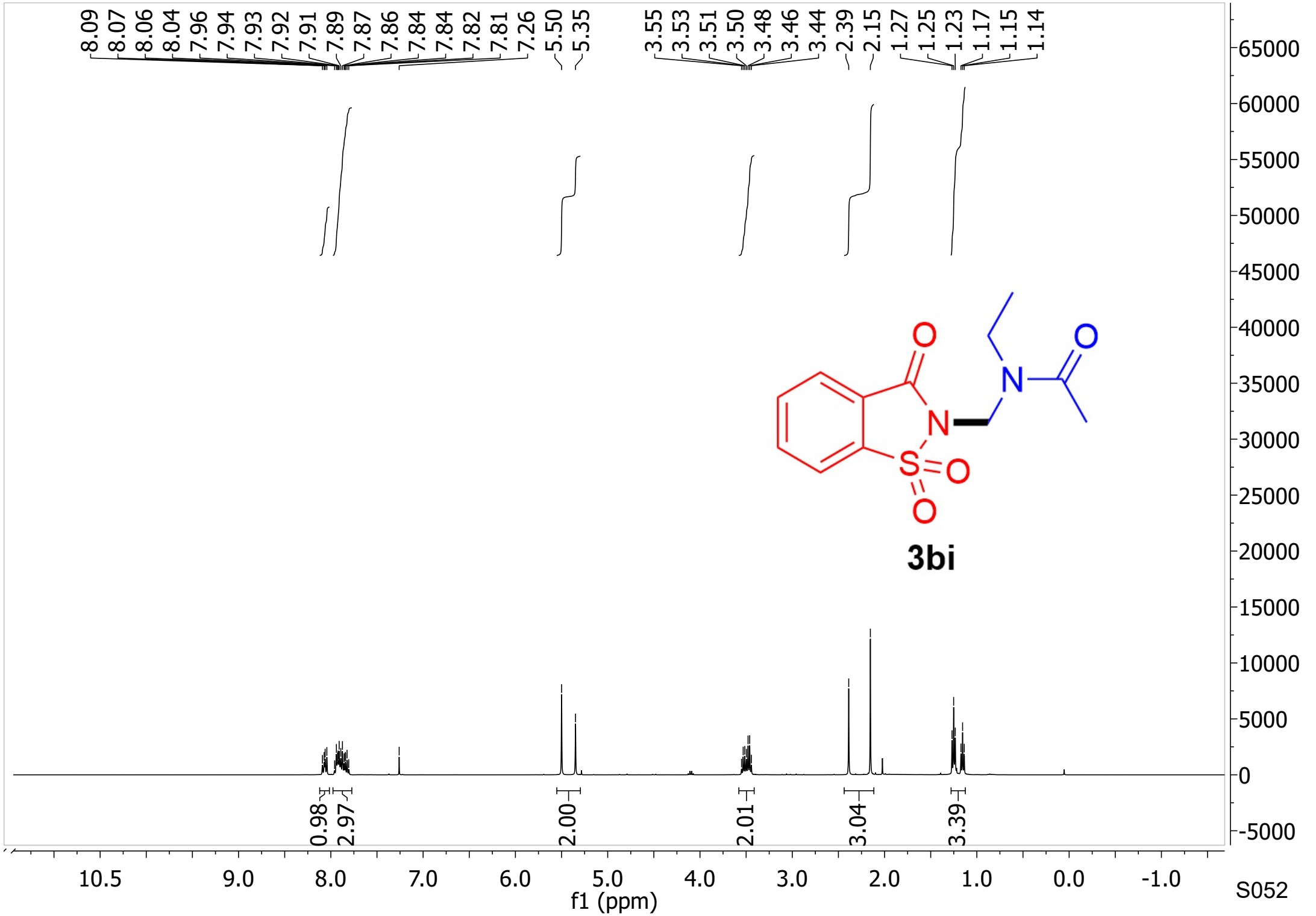

177.97
159.24
138.00
135.50
135.18
134.72
134.31
126.74
125.66
125.44
121.20
121.02
77.37
77.05
76.73
53.70
50.94
34.37
33.18
30.51
29.69
19.76
18.84
O
O
N
N
S
O
O
3bf
4000
3500
3000
2500
2000
1500
1000
500
0
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
S047

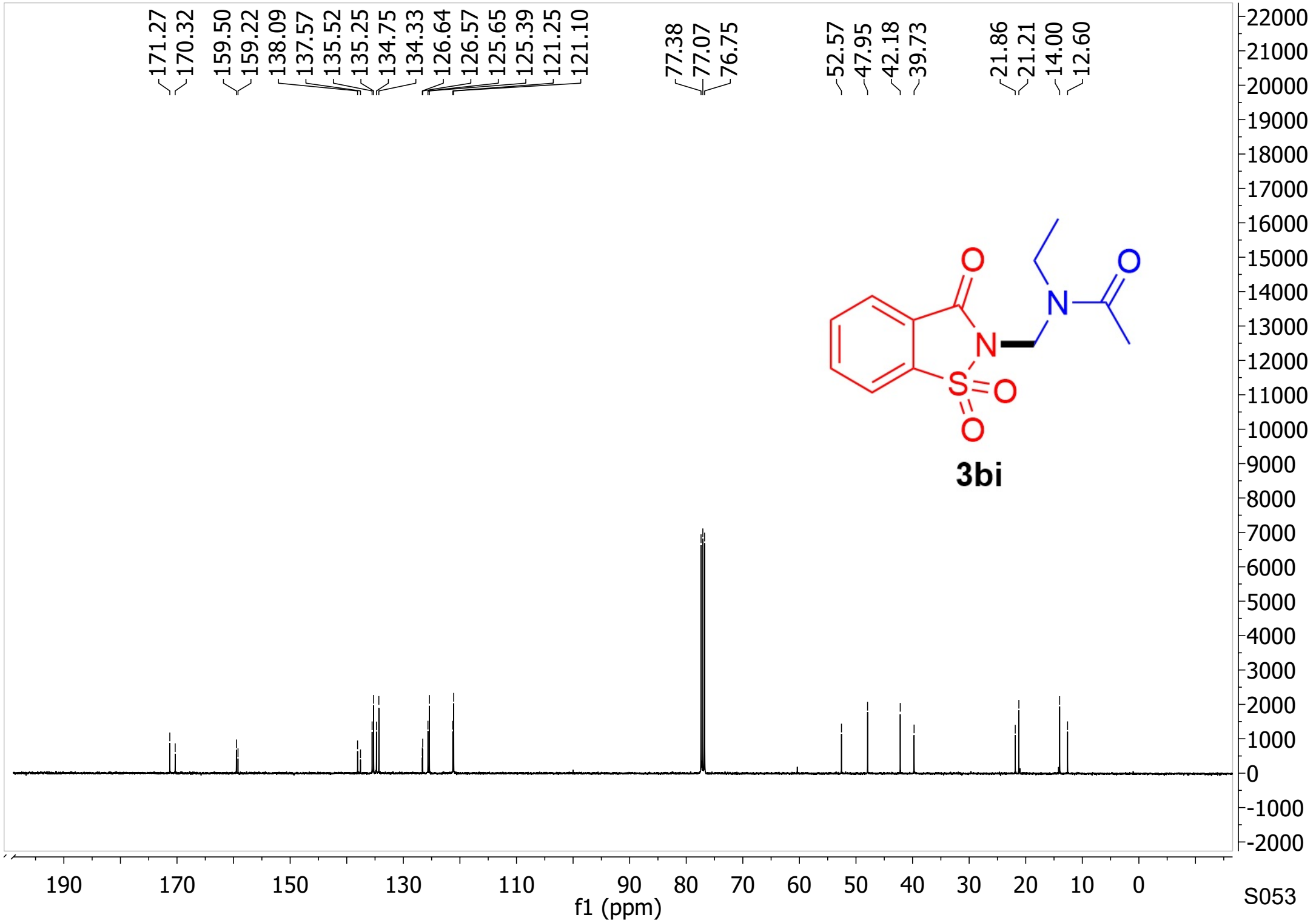

8.09
8.06
8.04
7.95
7.93
7.92
7.90
7.89
7.87
7.85
7.84
7.84
7.82
7.81
7.26
5.51
5.38
3.11
3.03
3.02
2.65
2.33
2.31
2.29
1.74
1.72
1.70
1.68
1.66
1.01
0.99
0.97
0.95
0.94
O
O
N
N
O
S
O
O
3bg
0.96
2.94
2.00
3.05
2.01
2.08
3.03
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

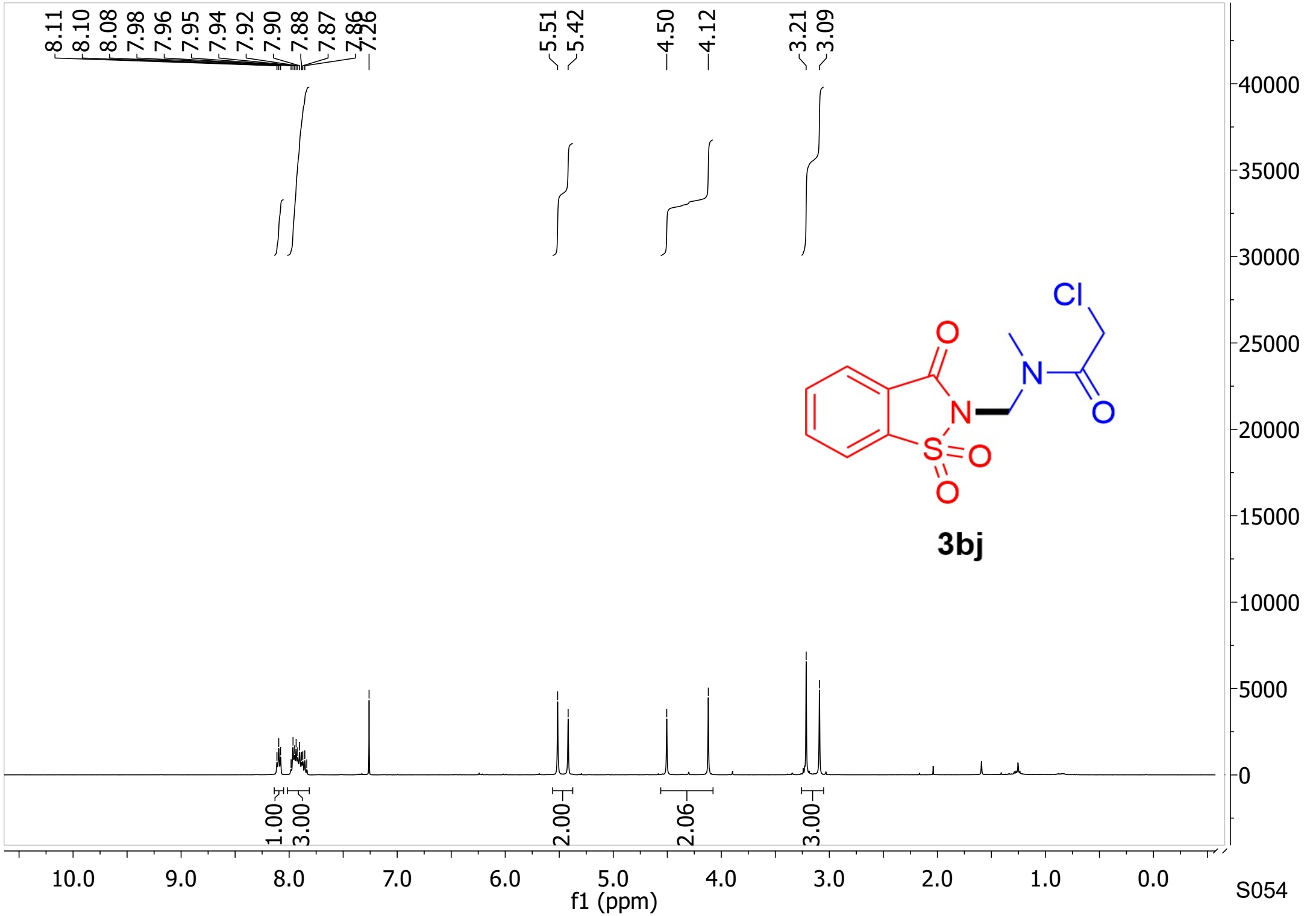

173.01
172.29
158.26
158.11
136.97
134.49
134.19
133.72
133.33
130.52
128.20
125.69
124.62
124.41
120.20
120.02
76.38
76.06
75.74
34.23
33.74
33.47
31.88
17.61
16.98
12.87
12.83
O
O
N
N
S
O
O
3bg
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
S049

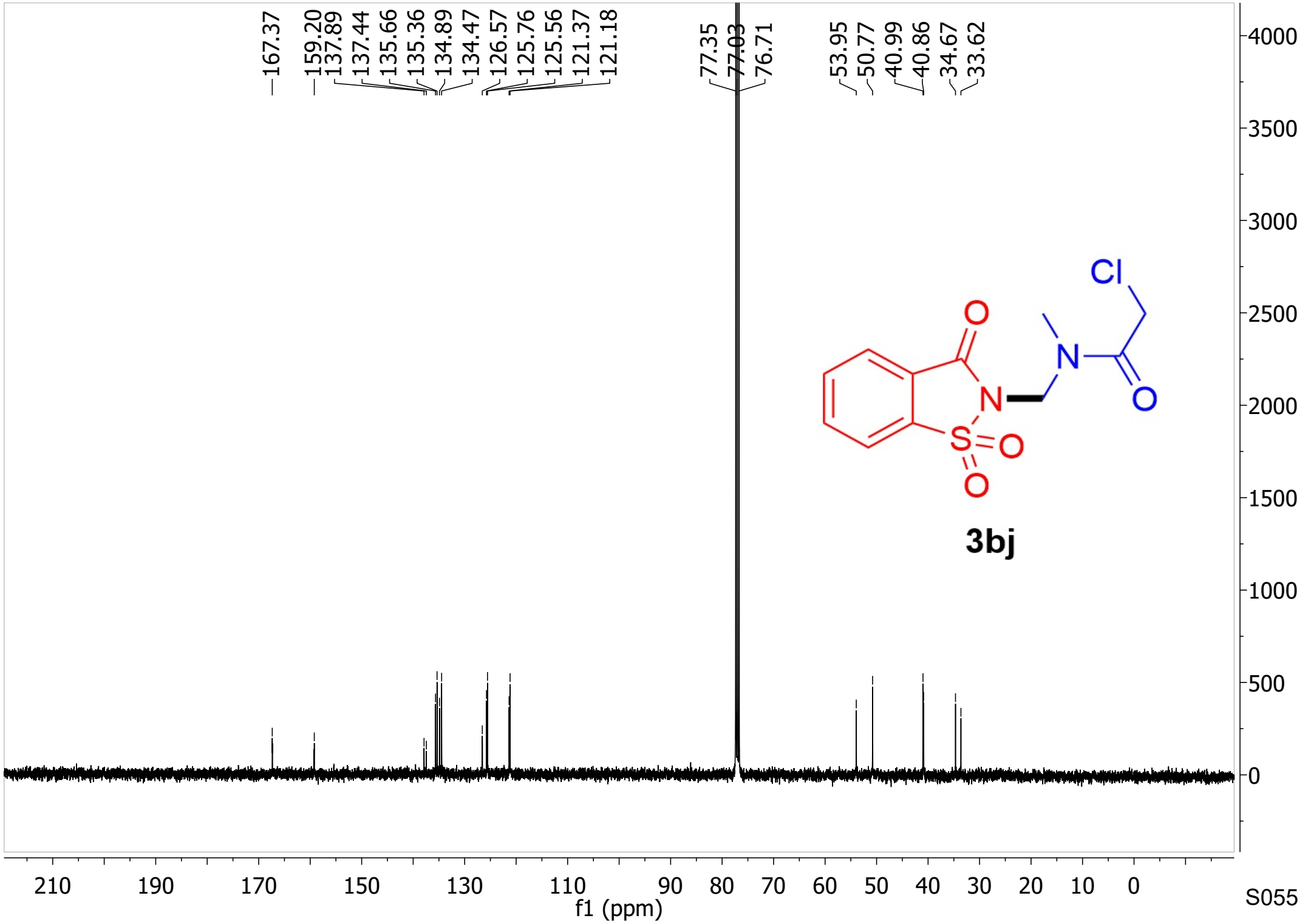

7.81
7.80
7.78
7.74
7.65
7.27
7.25
7.23
7.16
7.16
7.15
7.13
7.11
7.11
7.09
7.05
7.03
5.77
4.83
Ph
Ph
Ph
O
N
N
O
S
O
O
O
3bh
4.10
3.32
12.34
2.00
1.01
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
..0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)
S050

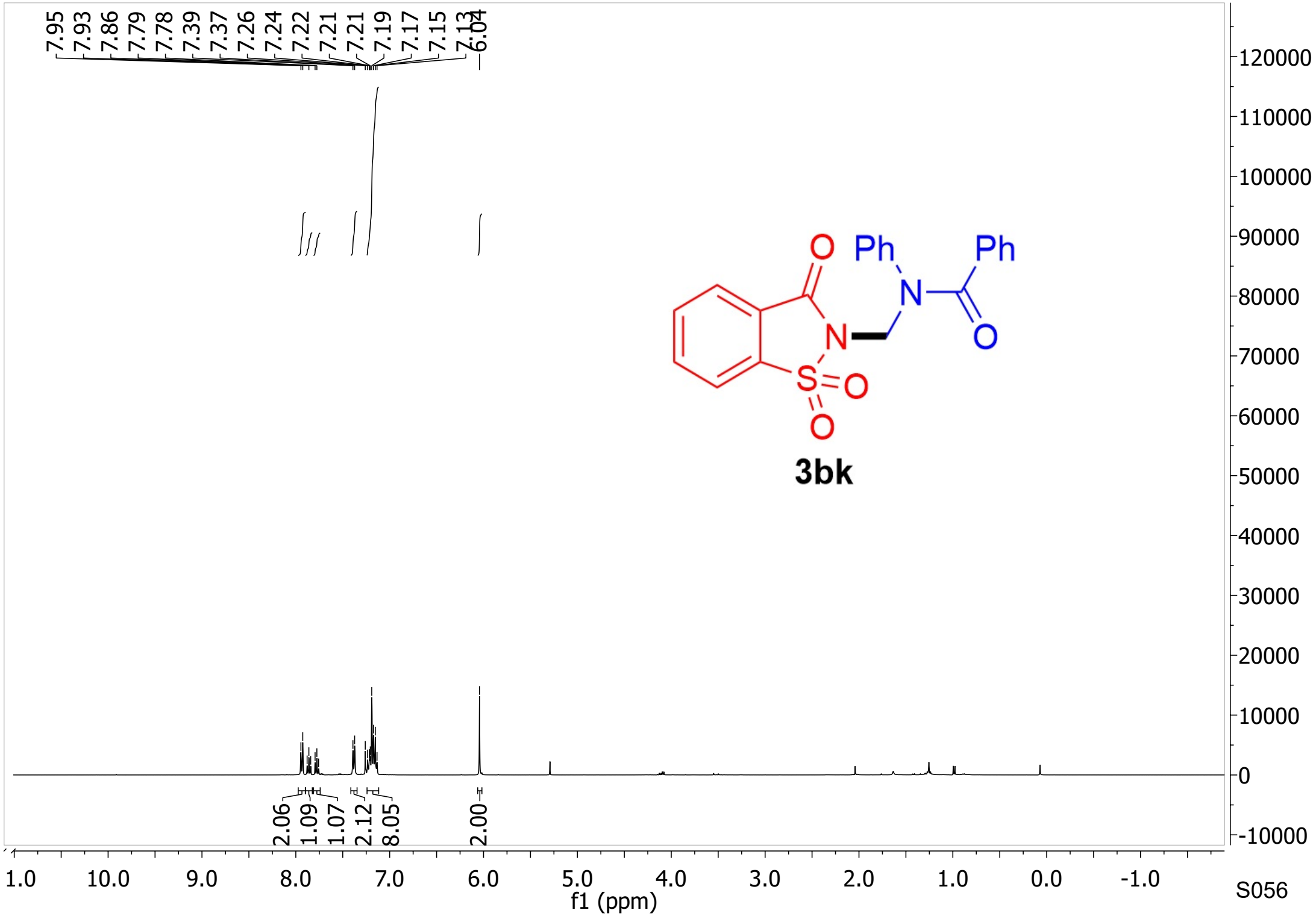

172.43
158.49
139.73
139.12
135.24
134.27
129.82
129.07
129.03
129.01
128.39
127.04
126.40
125.45
121.09
77.43
77.11
76.79
54.69
50.89
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
O
Ph
Ph
N
Ph
N
O
S
O
O
3bh
S051

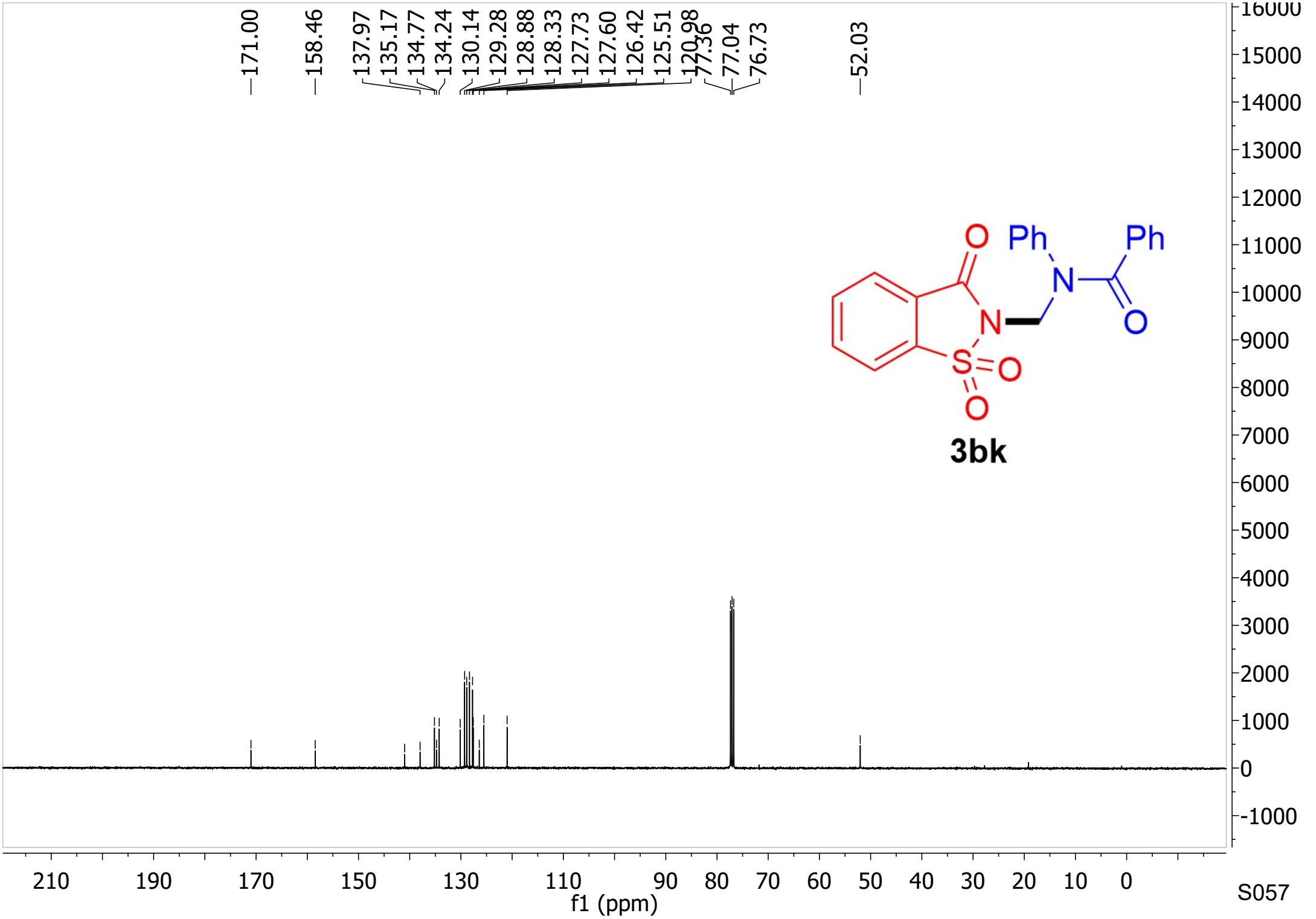

8.09
8.07
8.06
8.04
7.96
7.94
7.93
7.92
7.91
7.89
7.87
7.86
7.84
7.84
7.82
7.81
7.26
5.50
5.35
3.55
3.53
3.51
3.50
3.48
3.46
3.44
2.39
2.15
1.27
1.25
1.23
1.17
1.15
1.14
O
O
N
N
S
O
O
3bi
0.98
2.97
2.00
2.01
3.04
3.39
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)
S052


171.27
170.32
159.50
159.22
138.09
137.57
135.52
135.25
134.75
134.33
126.64
126.57
125.65
125.39
121.25
121.10
77.38
77.07
76.75
52.57
47.95
42.18
39.73
21.86
21.21
14.00
12.60
O
N
O
N
S
O
O
3bi
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
S053

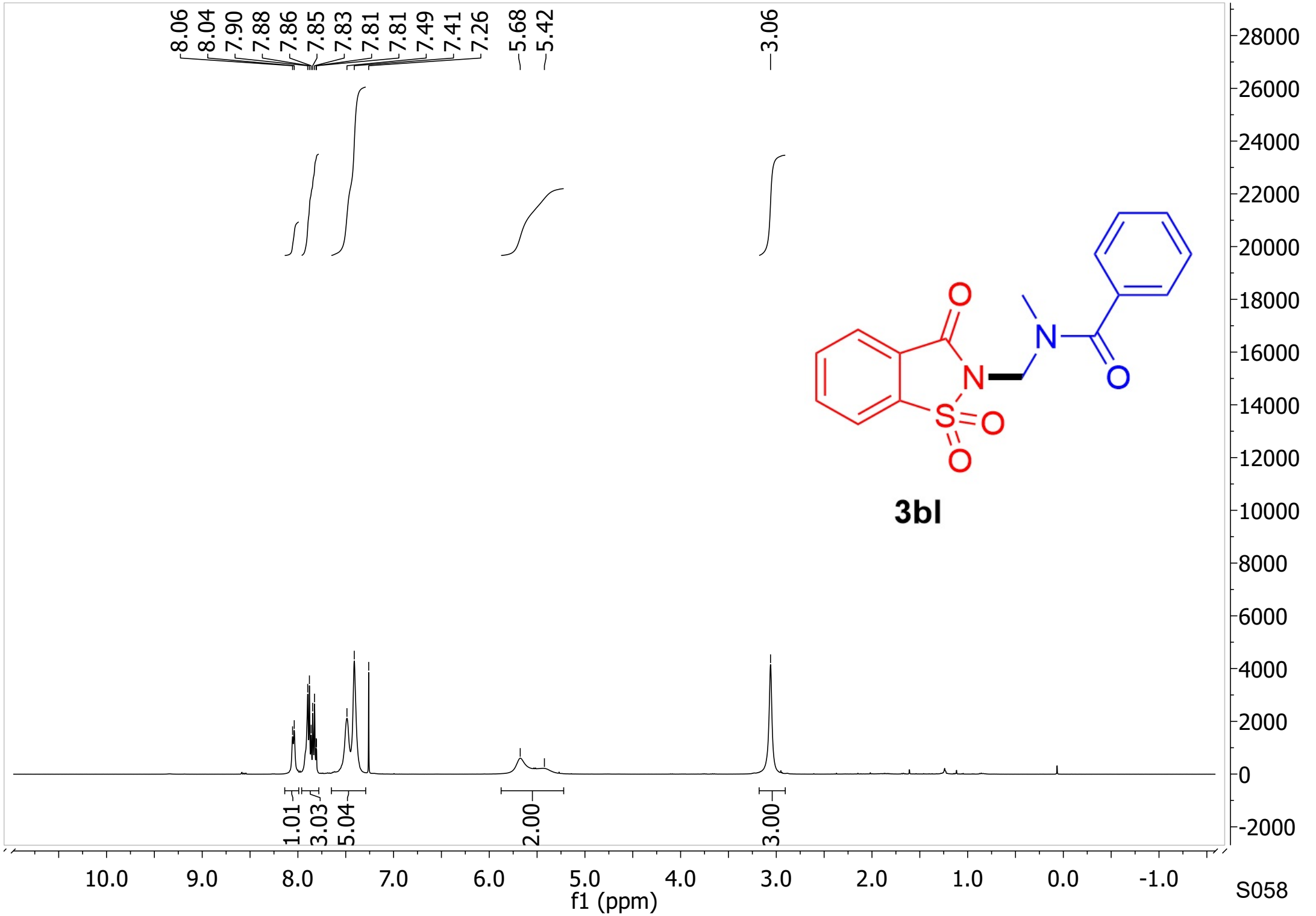

8.11
8.10
8.08
7.98
7.96
7.95
7.94
7.92
7.90
7.88
7.87
7.86
7.26
5.51
5.42
4.50
4.12
3.21
3.09
Cl
O
N
N
O
S
O
O
O
3bj
40000
35000
30000
25000
20000
15000
10000
5000
0
1.00
3.00
2.00
2.06
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
S054

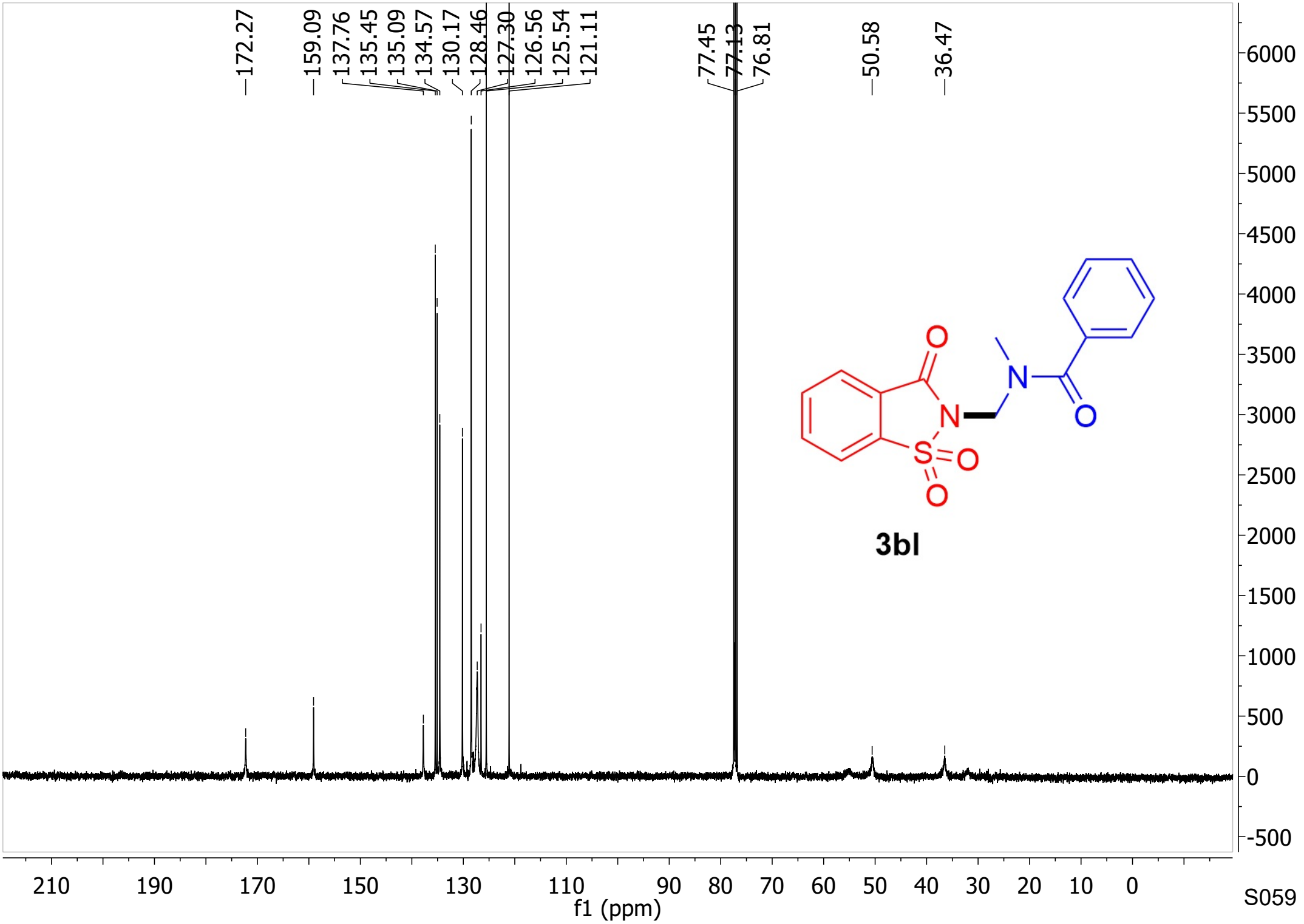

167.37
159.20
137.89
137.44
135.66
135.36
134.89
134.47
126.57
125.76
125.56
121.37
121.18
77.35
77.03
76.71
53.95
50.77
40.99
40.86
34.67
33.62
Cl
O
N
N
O
S
O
O
O
3bj
4000
3500
3000
2500
2000
1500
1000
500
0
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
S055

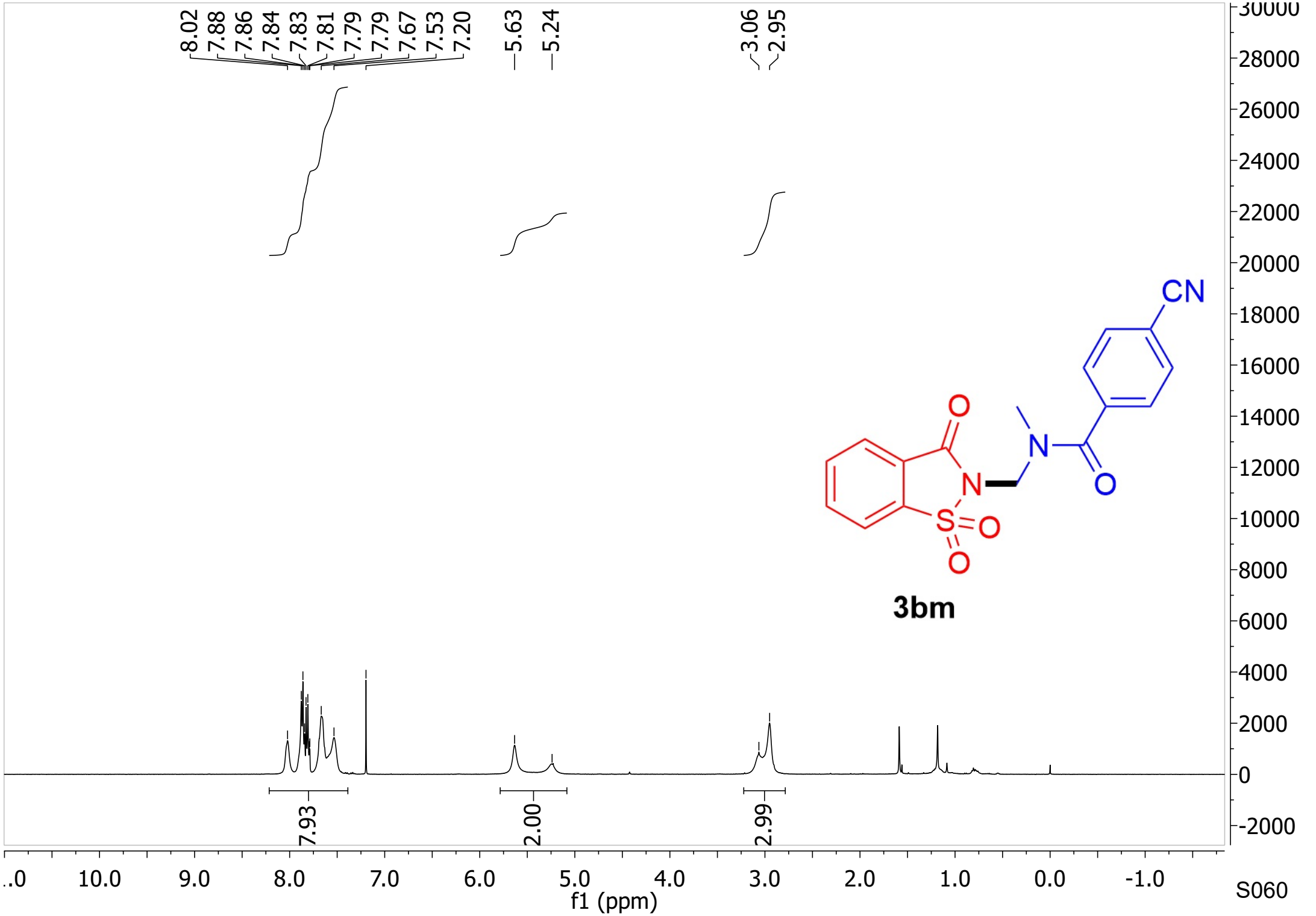

7.95
7.93
7.86
7.79
7.78
7.39
7.37
7.26
7.24
7.22
7.21
7.21
7.19
7.17
7.15
7.13
6.04
O
Ph
Ph
N
N
O
S
O
O
3bk
2.06
1.09
1.07
2.12
8.05
2.00
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
1.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)
S056

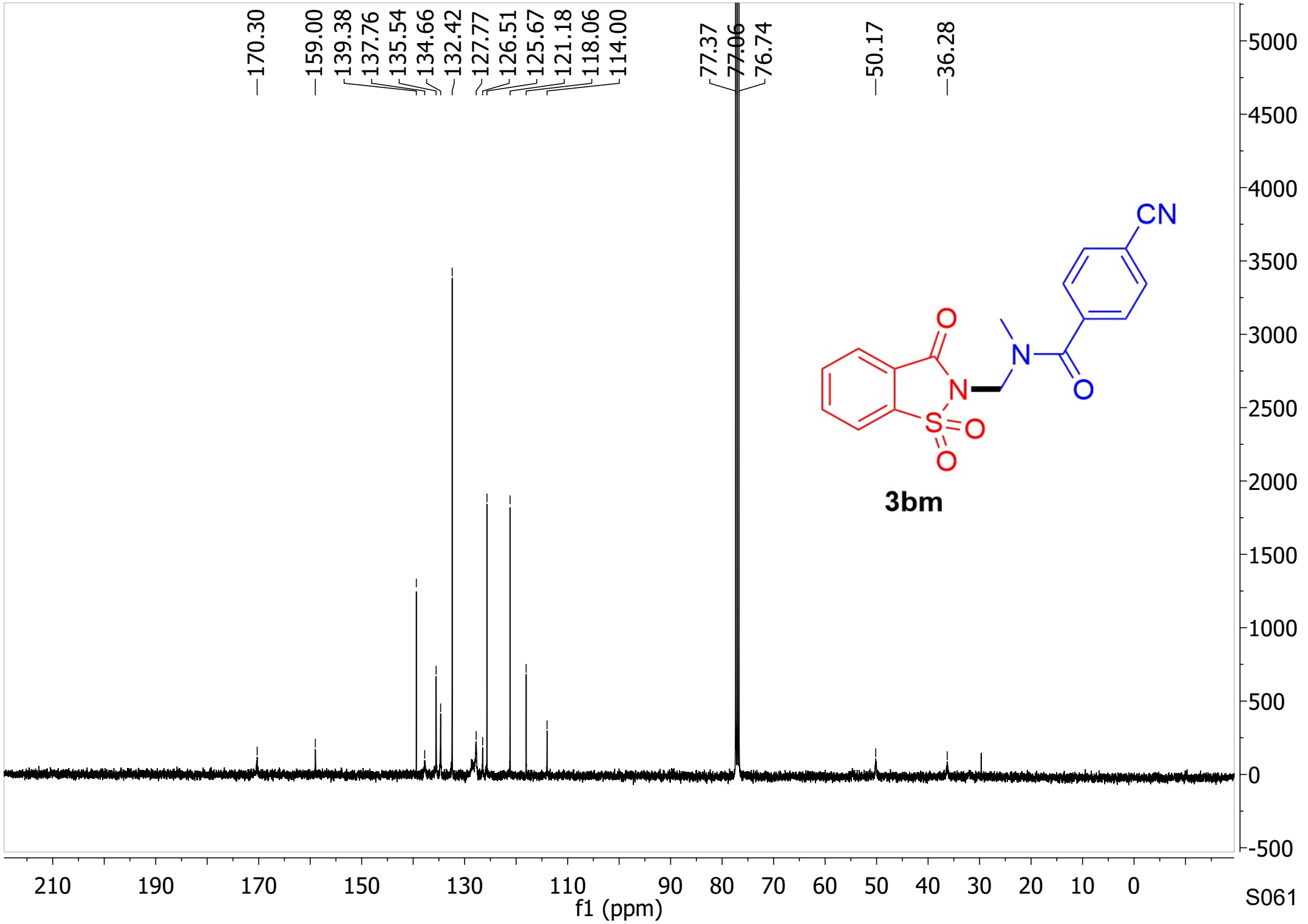

171.00
158.46
137.97
135.17
134.77
134.24
130.14
129.28
128.88
128.33
127.73
127.60
126.42
125.51
120.98
77.36
77.04
76.73
52.03
O
Ph
Ph
N
N
O
S
O
O
3bk
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

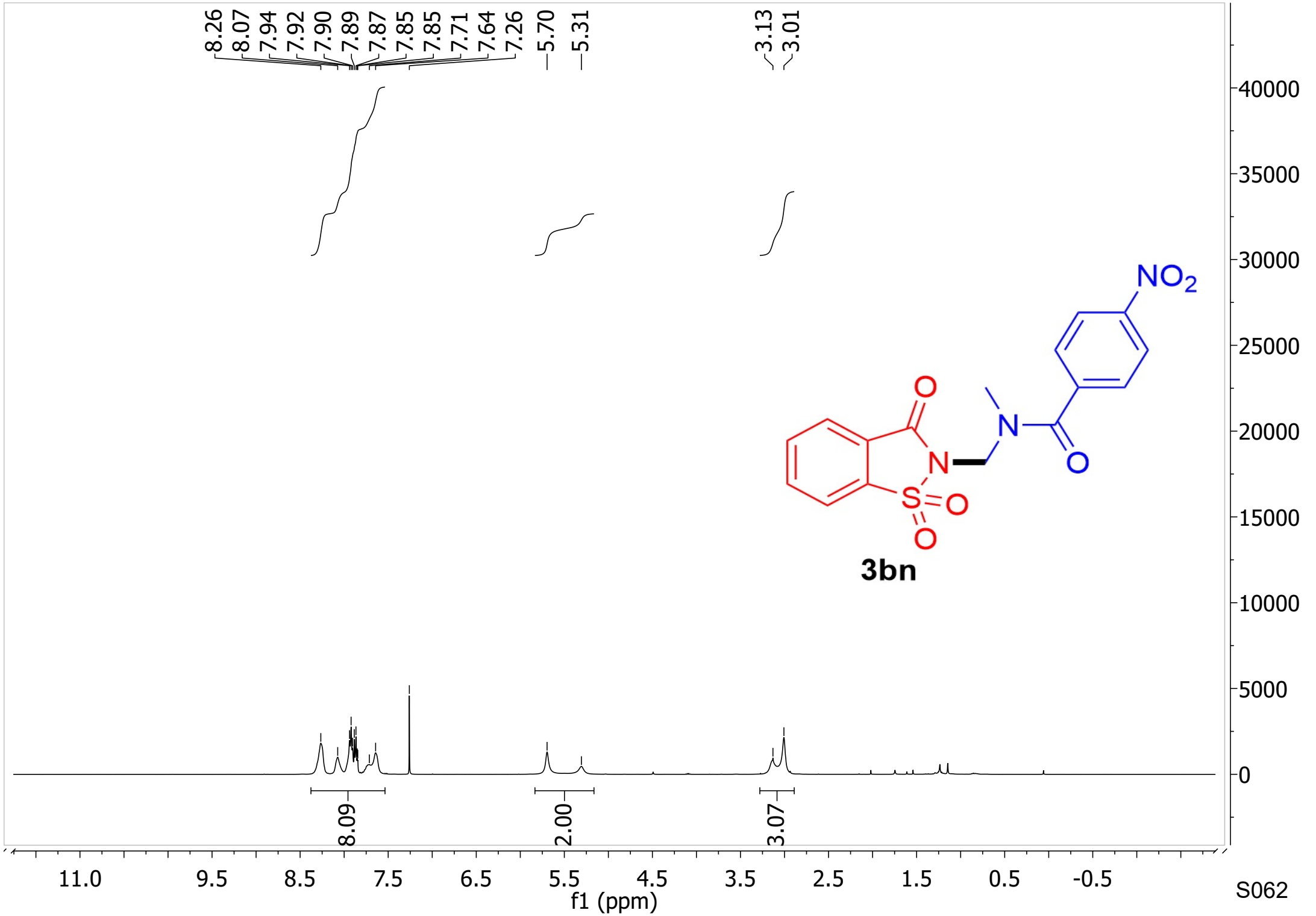
S057

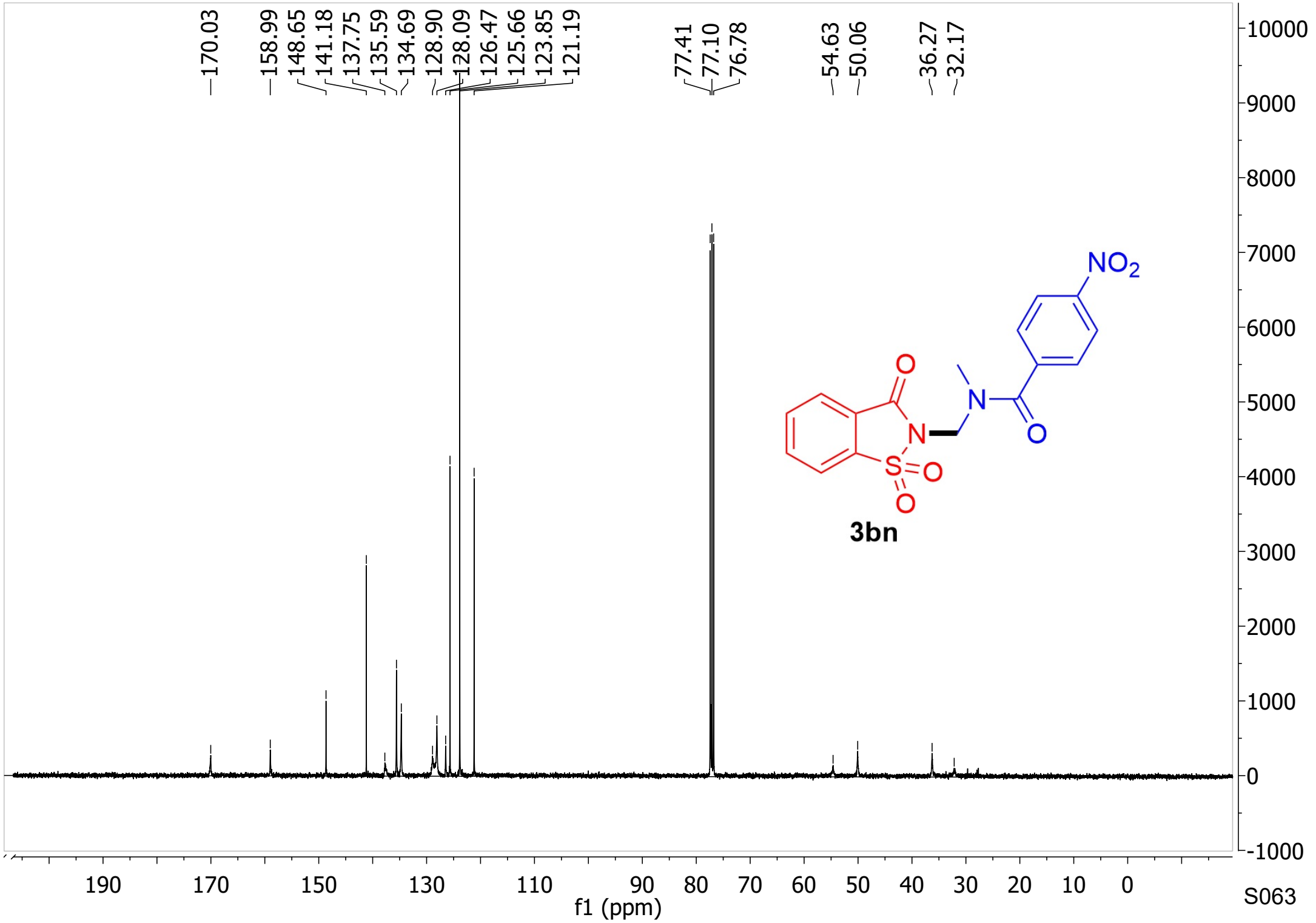

8.06
8.04
7.90
7.88
7.86
7.85
7.83
7.81
7.81
7.49
7.41
7.26
5.68
5.42
3.06
O
N
N
O
S
O
O
O
3bl
1.01
3.03
5.04
2.00
3.00
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)
S058

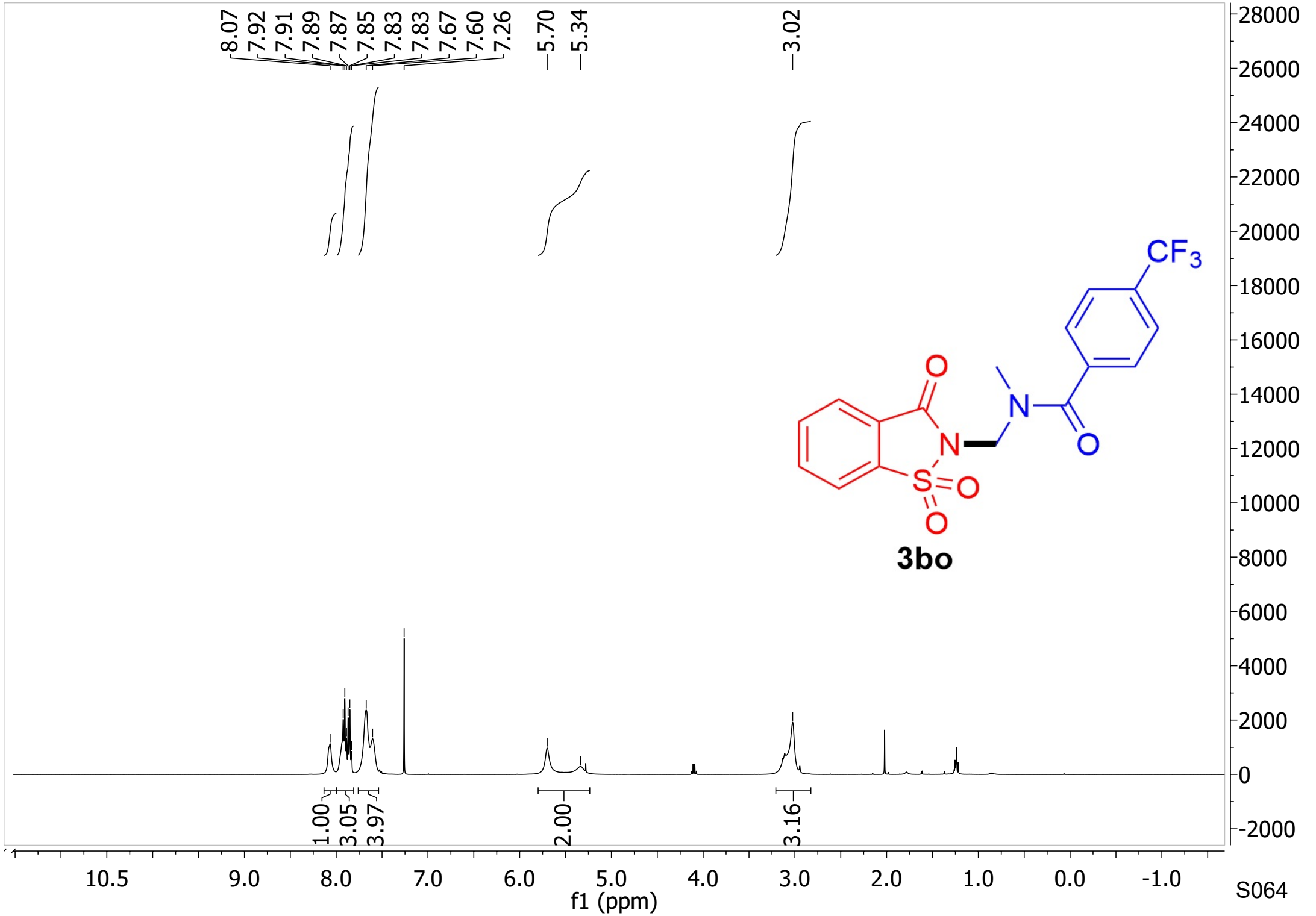

172.27
159.09
137.76
135.45
135.09
134.57
130.17
128.46
127.30
126.56
125.54
121.11
77.45
77.13
76.81
50.58
36.47
O
N
O
S
O
O
N
O
3bl
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
S059

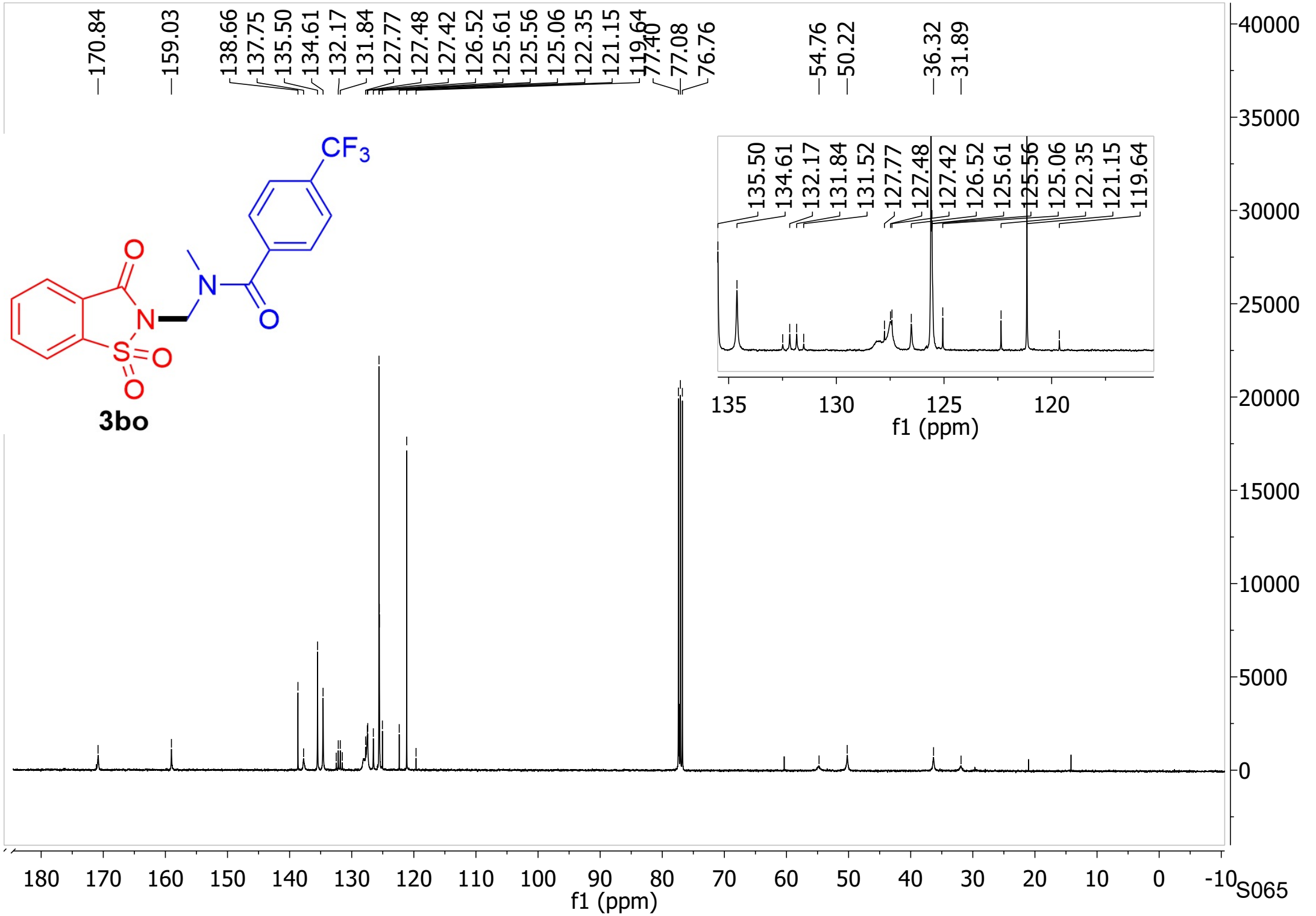

8.02
7.88
7.86
7.84
7.83
7.81
7.79
7.79
7.67
7.53
7.20
5.63
5.24
3.06
2.95
CN
O
N
N
O
S
O
O
3bm
7.93
2.00
2.99
f1 (ppm)
S060

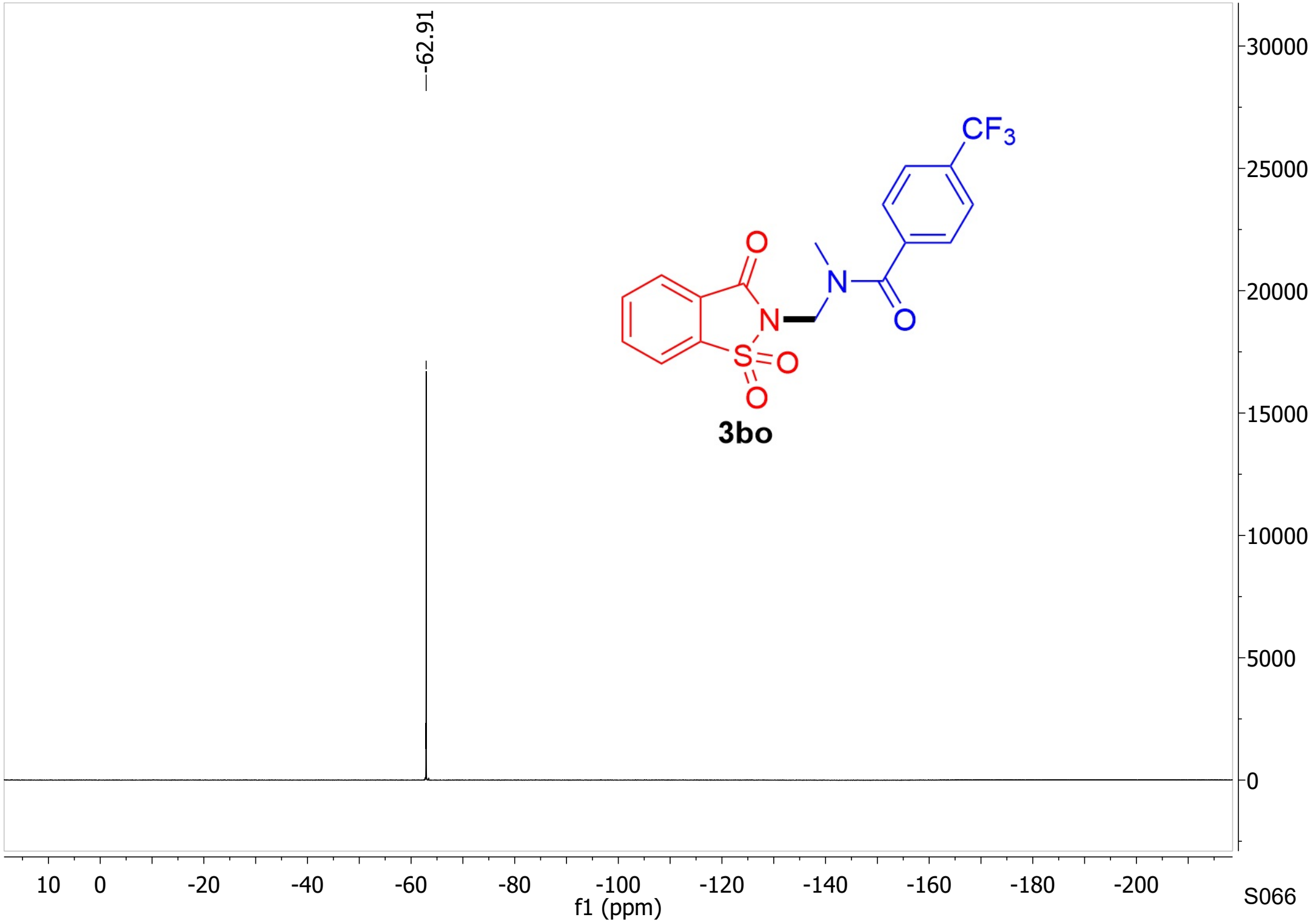

170.30
159.00
139.38
137.76
135.54
134.66
132.42
127.77
126.51
125.67
121.18
118.06
114.00
77.37
77.06
76.74
50.17
36.28
CN
O
N
O
N
O
S
O
O
3bm
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
S061

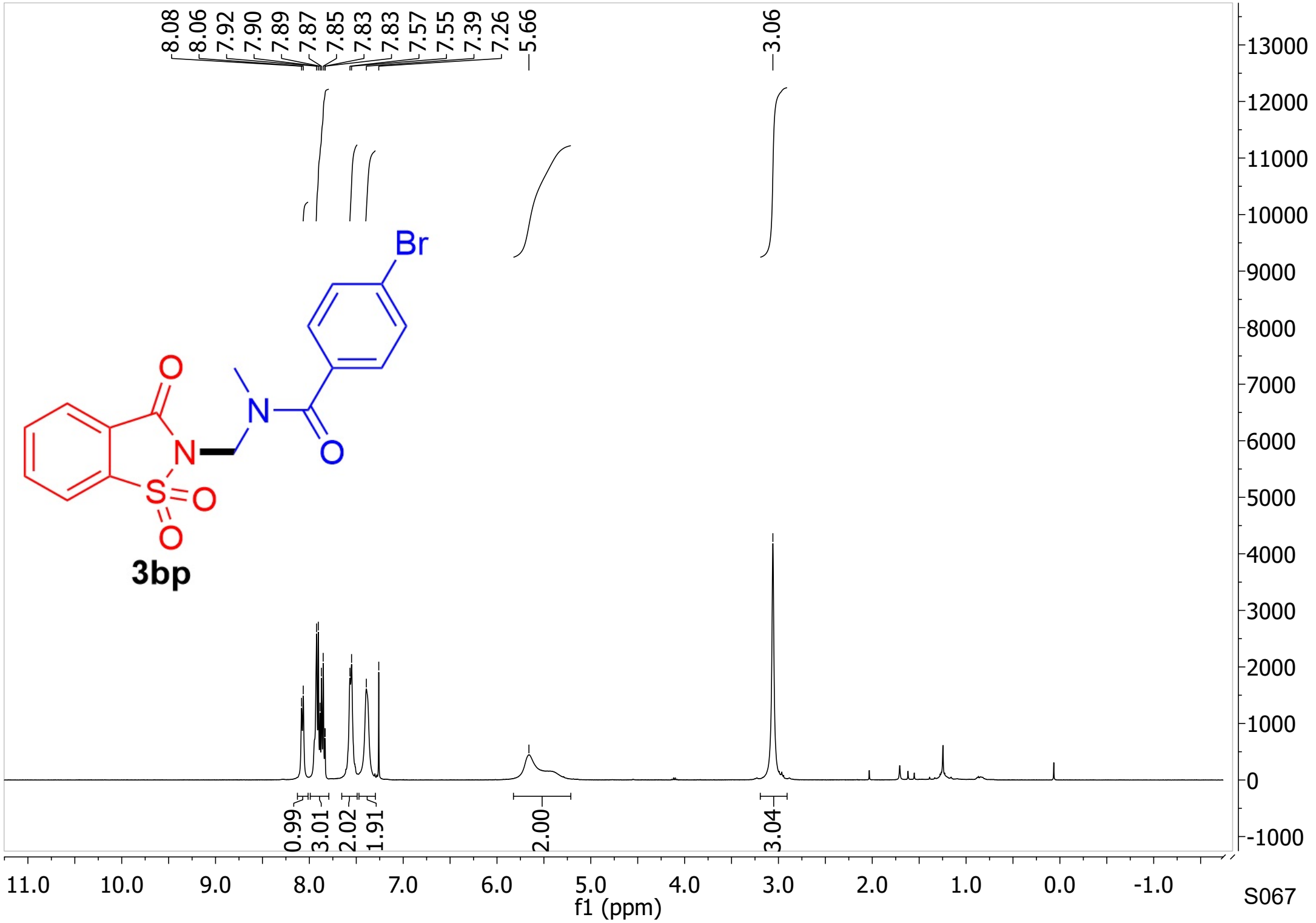

8.26
8.07
7.94
7.92
7.90
7.89
7.87
7.85
7.85
7.71
7.64
7.26
5.70
5.31
3.13
3.01
NO2
O
N
N
O
S
O
O
3bn
40000
35000
30000
25000
20000
15000
10000
5000
0
8.09
2.00
3.07
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)
S062

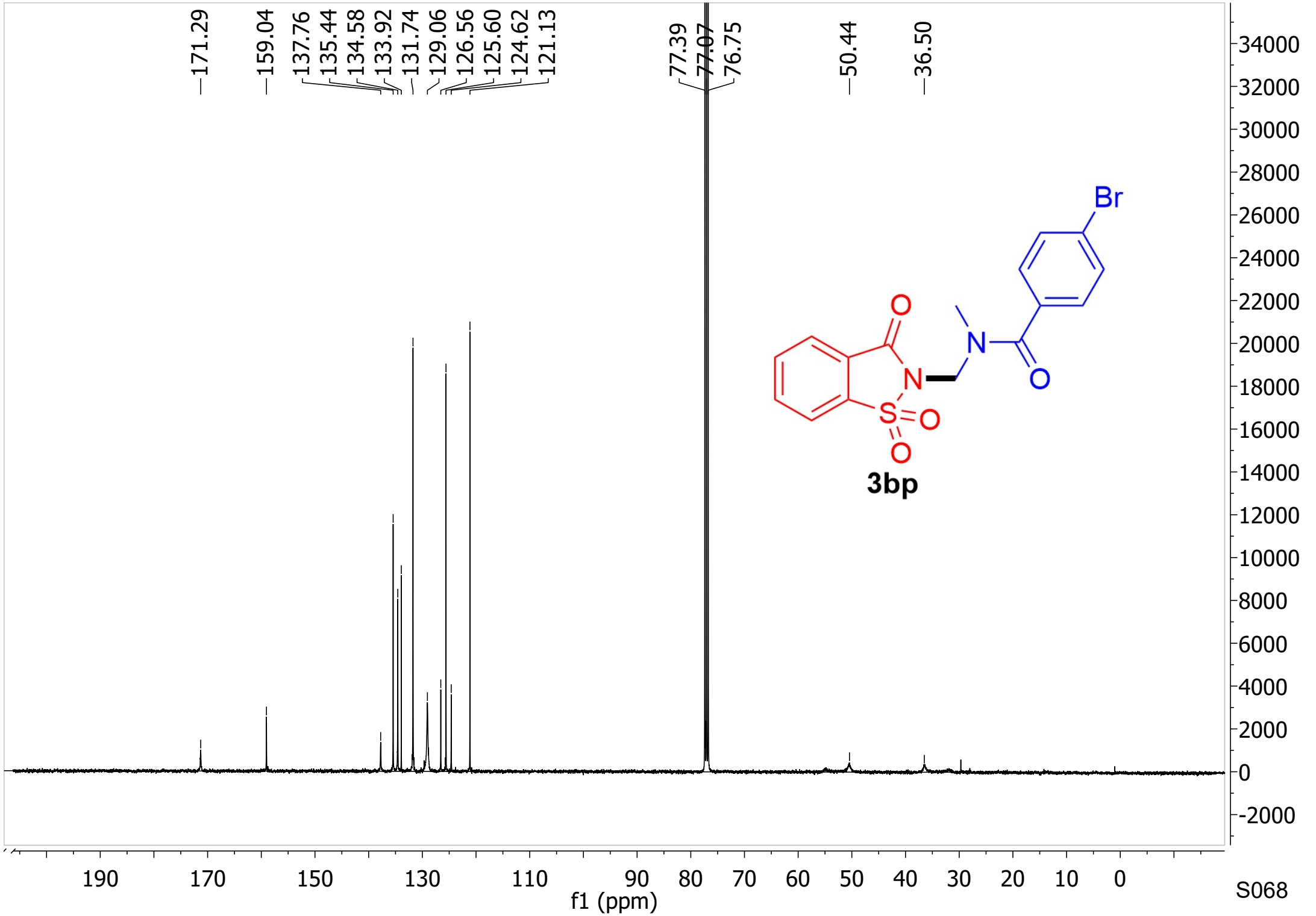

170.03
158.99
148.65
141.18
137.75
135.59
134.69
128.90
128.09
126.47
125.66
123.85
121.19
77.41
77.10
76.78
54.63
50.06
36.27
32.17
NO2
O
N
N
O
S
O
O
O
3bn
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
S063

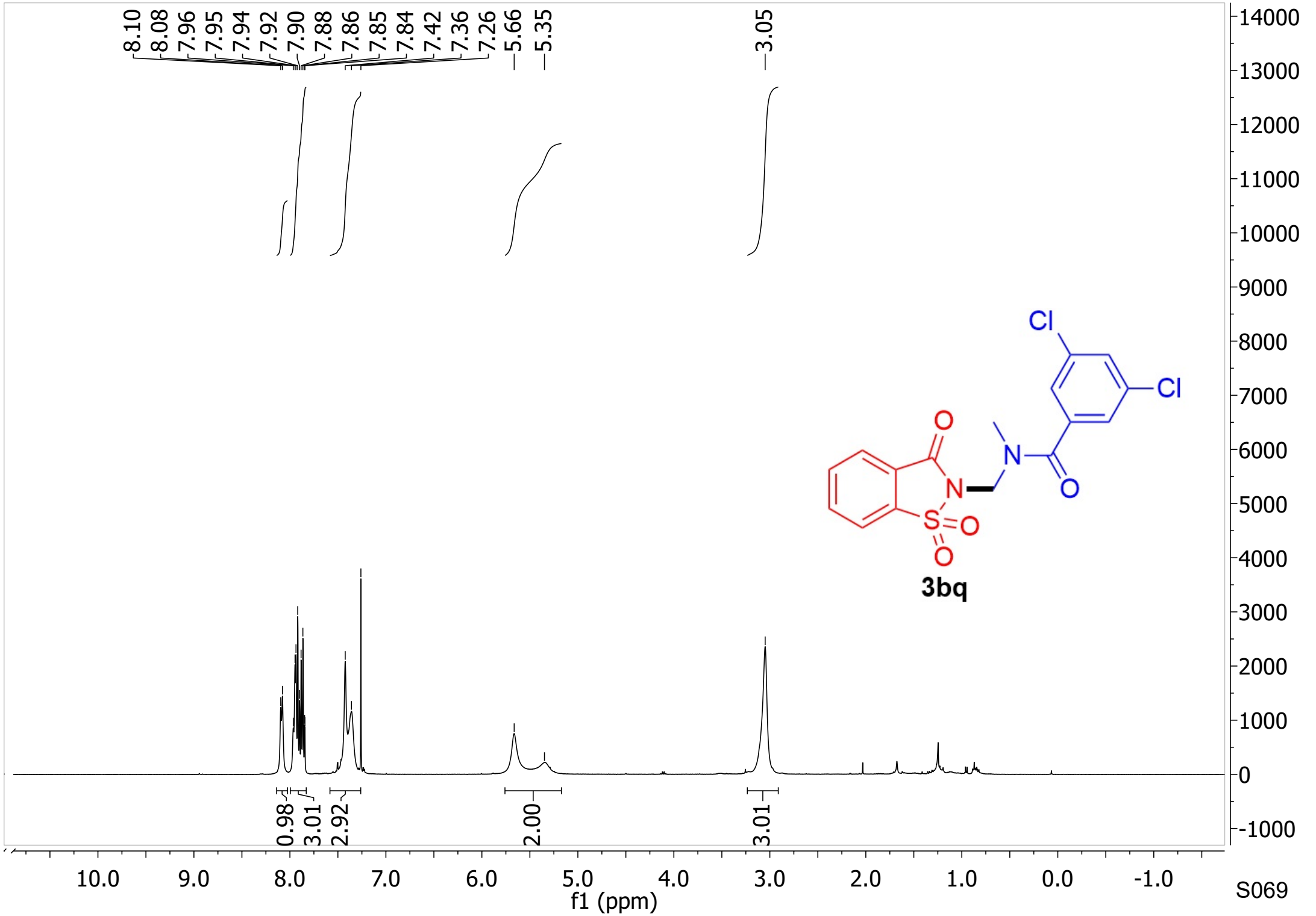

8.07
7.92
7.91
7.89
7.87
7.85
7.83
7.83
7.67
7.60
7.26
5.70
5.34
3.02
CF3
O
N
N
O
S
O
O
O
3bo
1.00
3.05
3.97
2.00
3.16
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)
S064

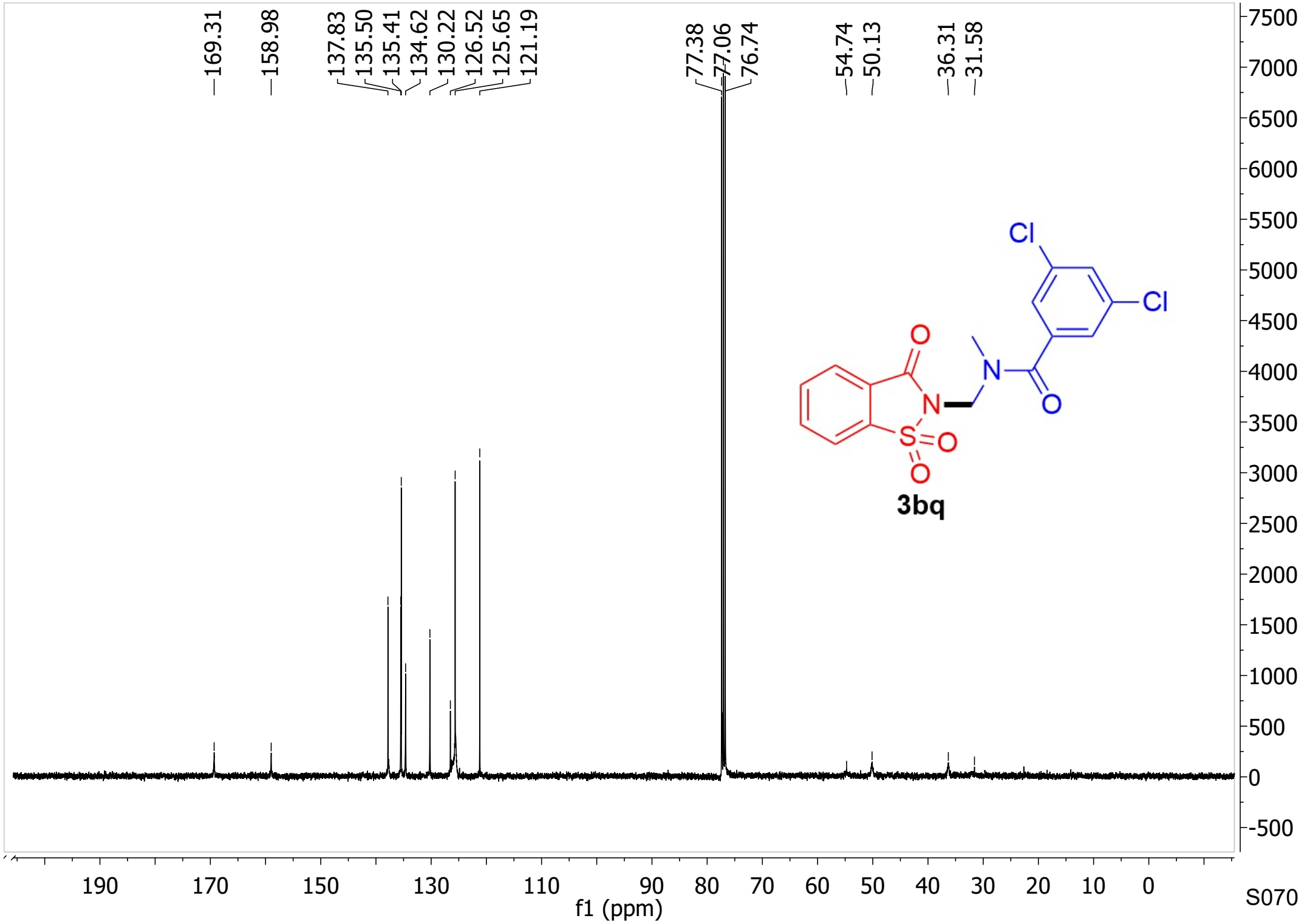

170.84
159.03
138.66
137.75
135.50
134.61
132.17
131.84
127.77
127.48
127.42
126.52
125.61
125.56
125.06
122.35
121.15
119.64
77.40
77.08
76.76
54.76
50.22
36.32
31.89
CF3
O
N
O
N
S
O
O
O
3bo
135.50
134.61
132.17
131.84
131.52
127.77
127.48
127.42
126.52
125.61
125.56
125.06
122.35
121.15
119.64
135
130
125
120
f1 (ppm)
40000
35000
30000
25000
20000
15000
10000
5000
0
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
S065

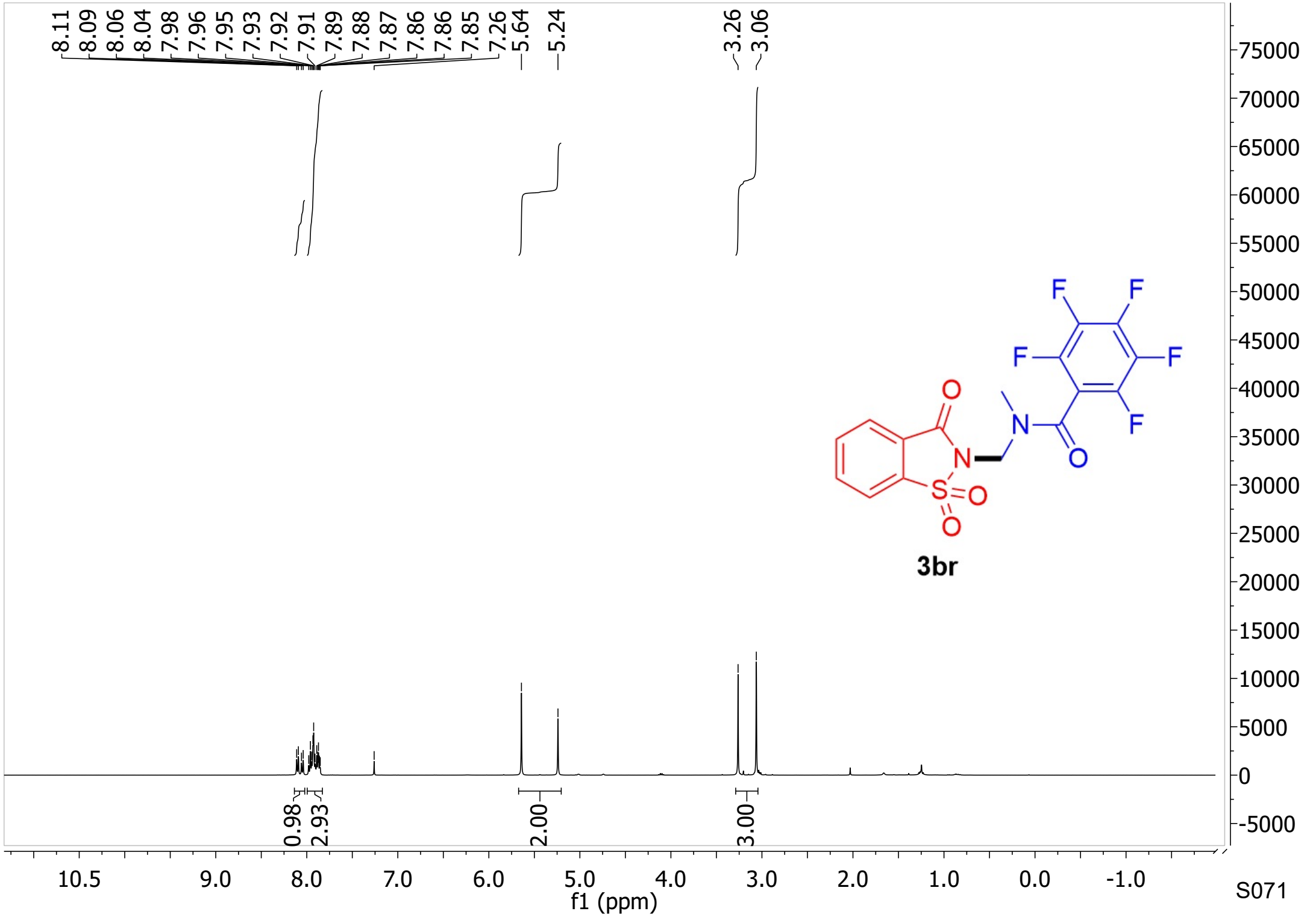

-62.91
CF3
O
N
N
O
S
O
O
O
3bo
30000
25000
20000
15000
10000
5000
0
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)
S066

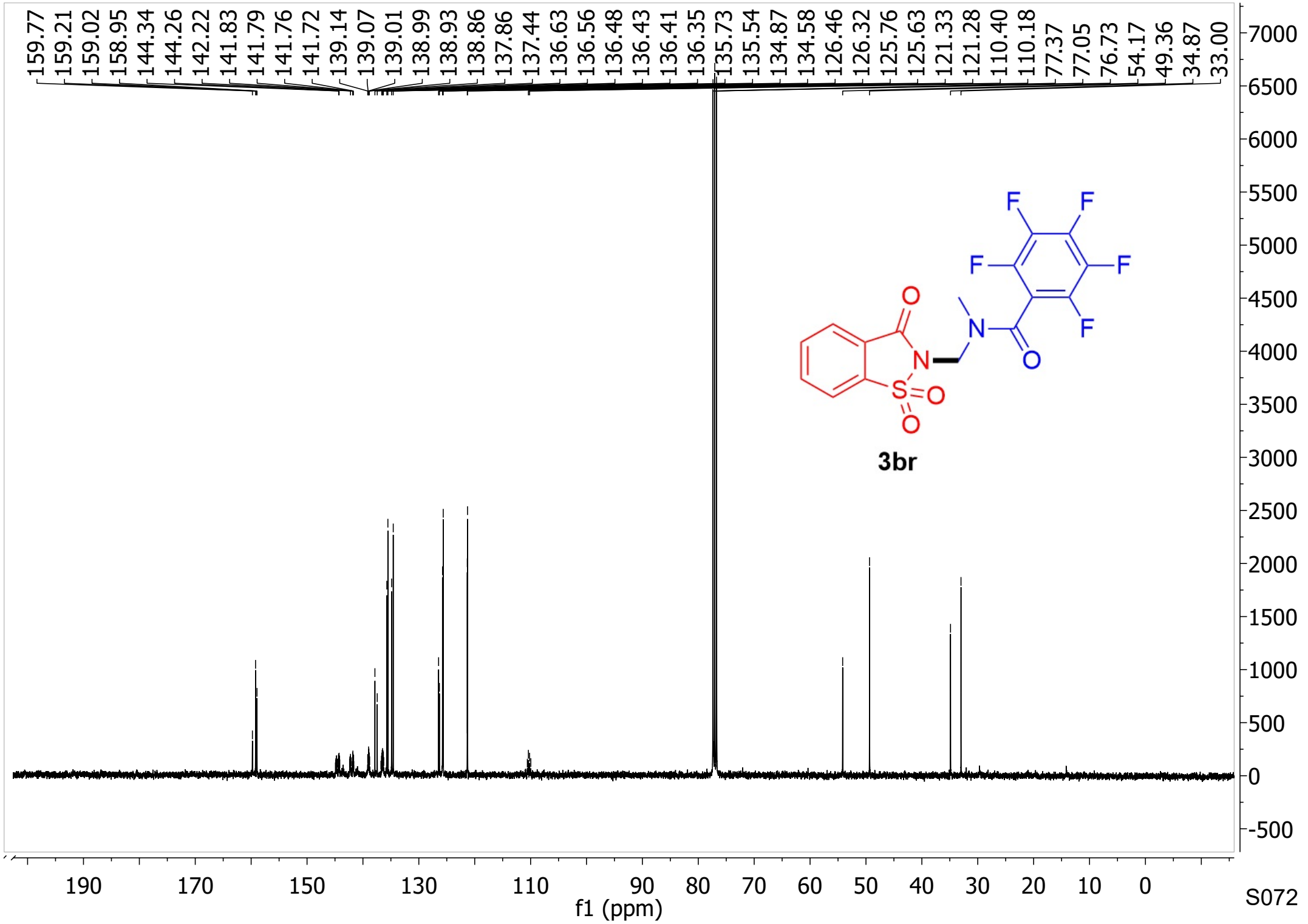

8.08
8.06
7.92
7.90
7.89
7.87
7.85
7.83
7.83
7.57
7.55
7.39
7.26
5.66
3.06
Br
O
N
O
N
O
S
O
O
3bp
0.99
3.01
2.02
1.91
2.00
3.04
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)
S067

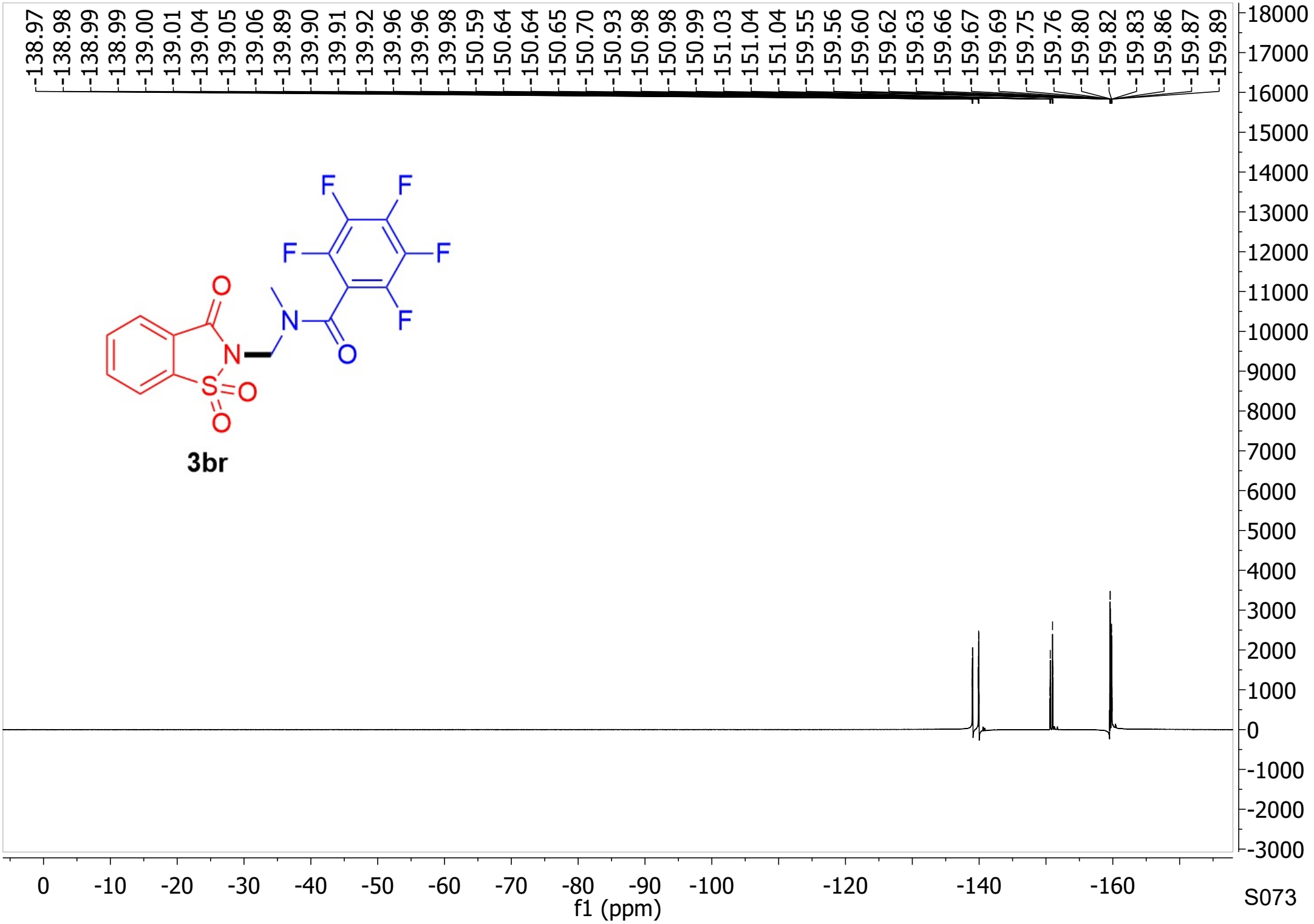

171.29
159.04
137.76
135.44
134.58
133.92
131.74
129.06
126.56
125.60
124.62
121.13
77.39
77.07
76.75
50.44
36.50
Br
O
N
N
O
S
O
O
O
3bp
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
S068

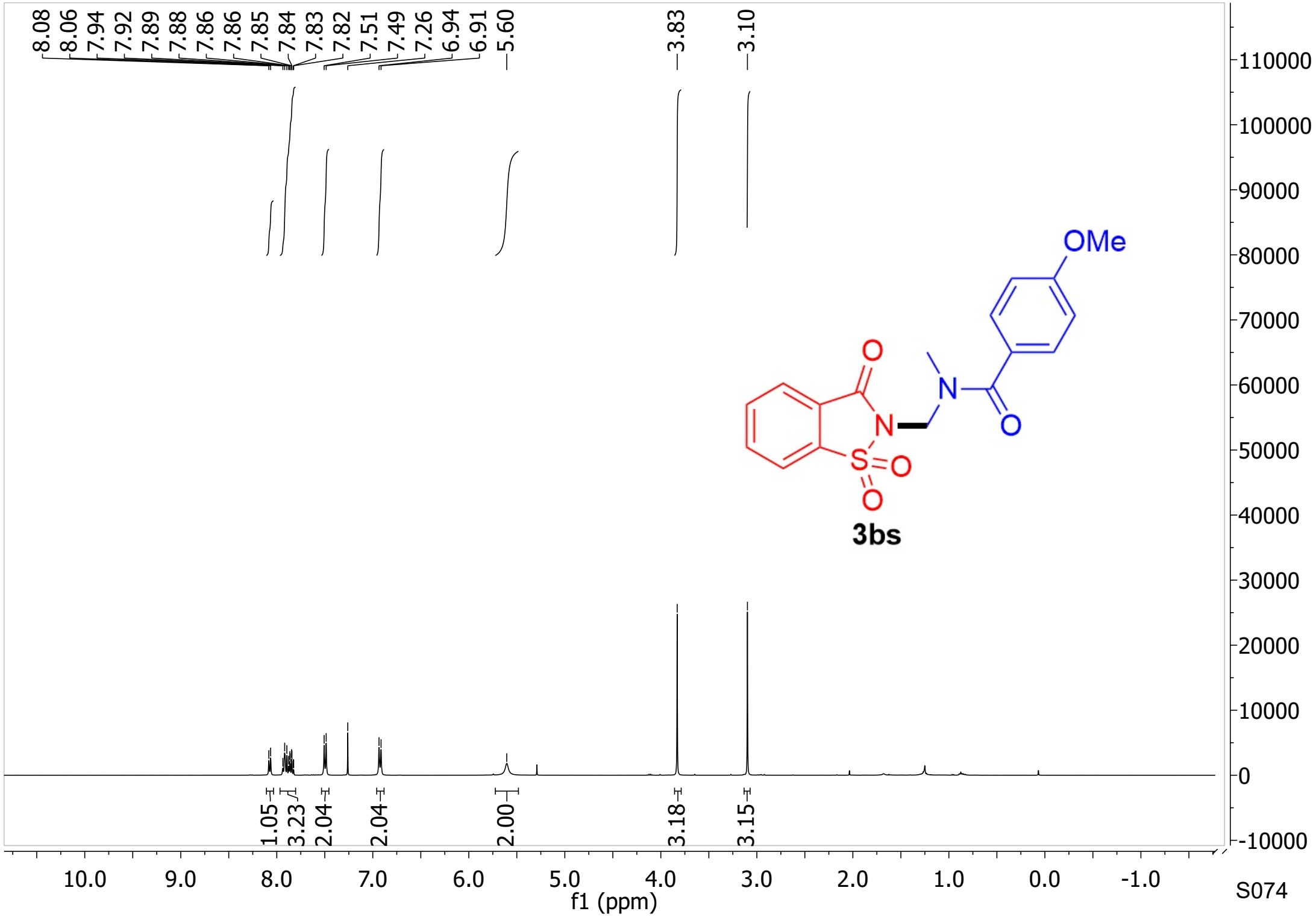

8.10
8.08
7.96
7.95
7.94
7.92
7.90
7.88
7.86
7.85
7.84
7.42
7.36
7.26
5.66
5.35
3.05
0.98
3.01
2.92
2.00
3.01
Cl
Cl
O
N
N
O
S
O
O
3bq
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)
S069

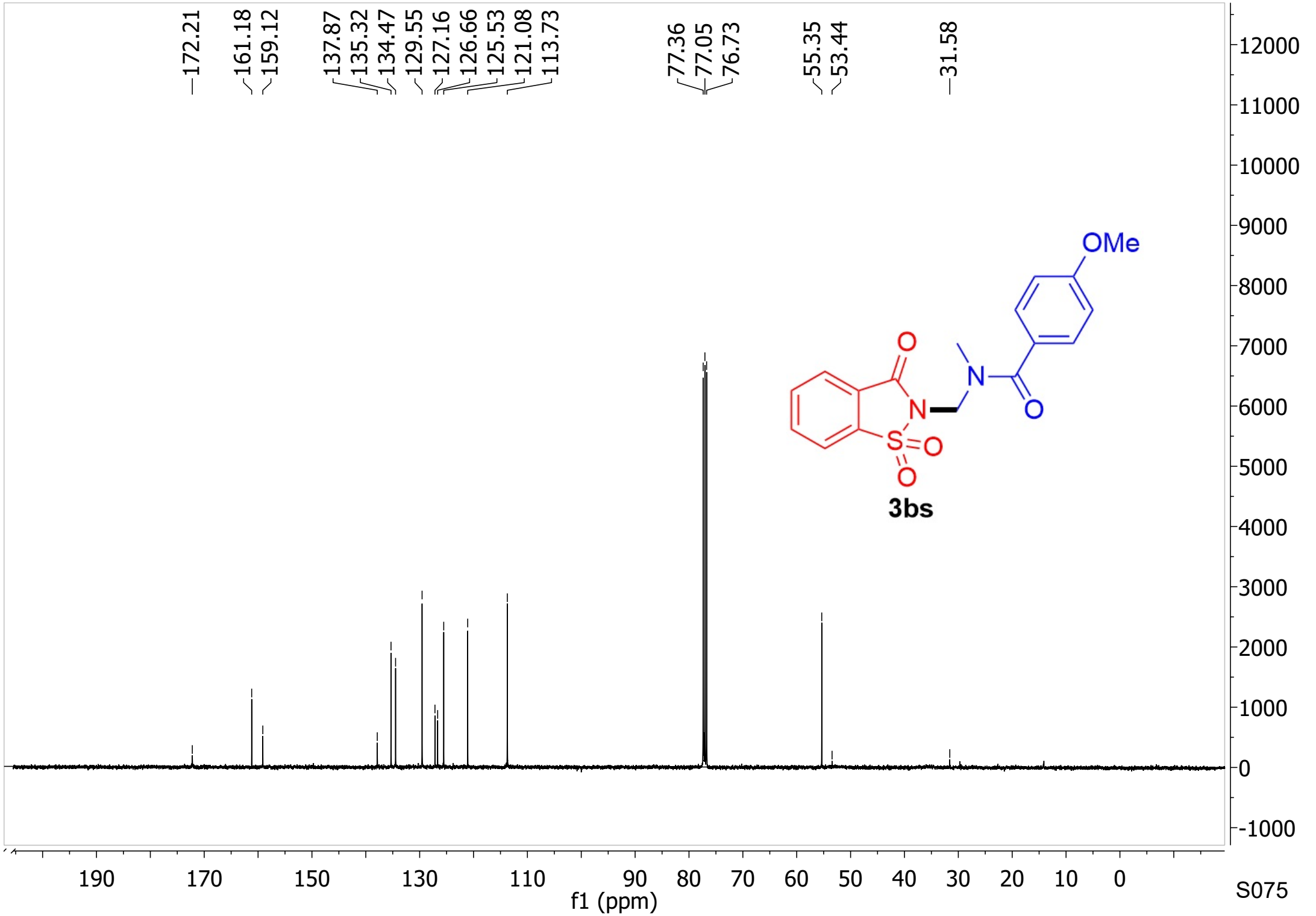

169.31
158.98
137.83
135.50
135.41
134.62
130.22
126.52
125.65
121.19
77.38
77.06
76.74
54.74
50.13
36.31
31.58
Cl
Cl
O
N
N
O
S
O
O
3bq
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
S070

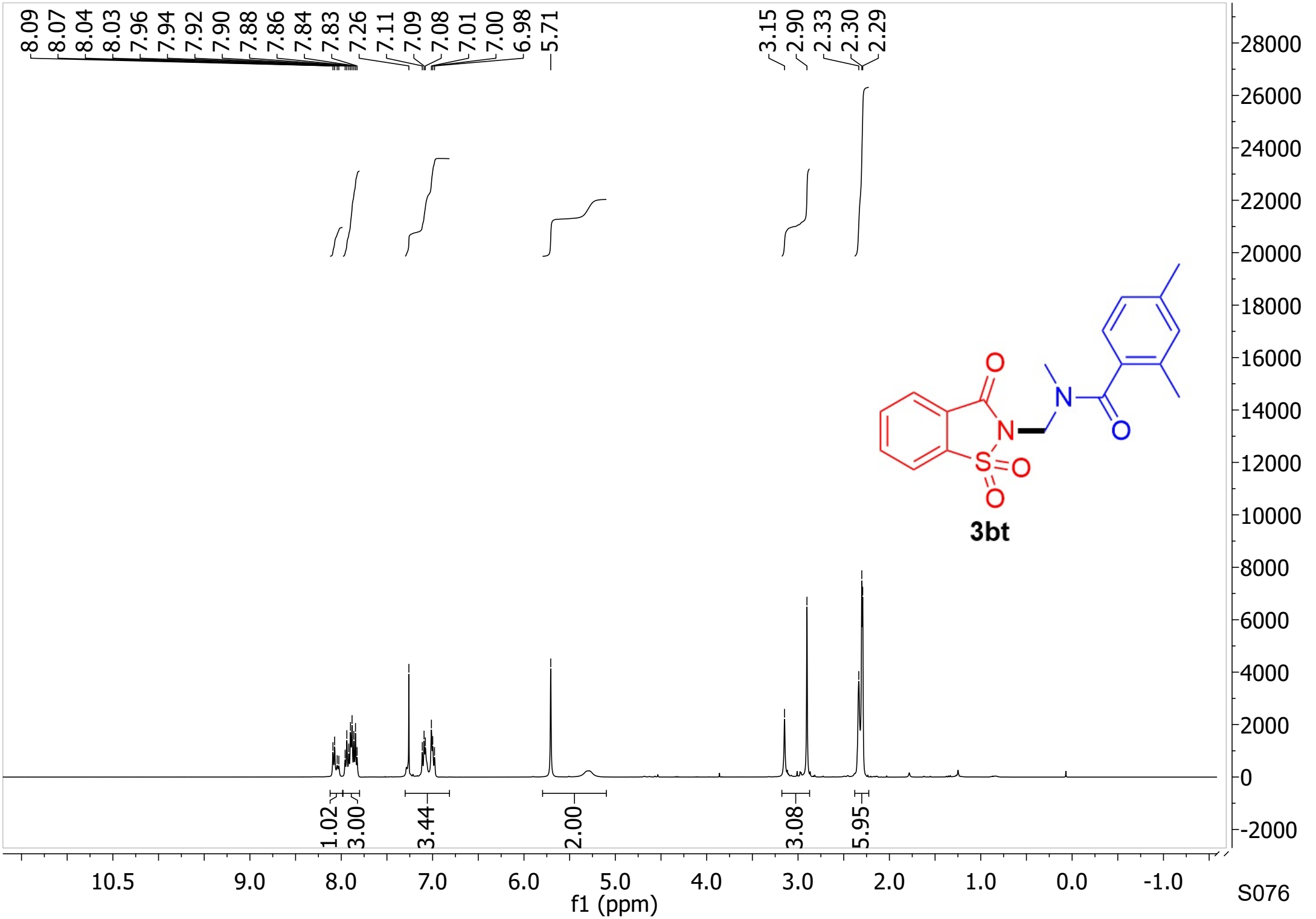

8.11
8.09
8.06
8.04
7.98
7.96
7.95
7.93
7.92
7.91
7.89
7.88
7.87
7.86
7.86
7.85
7.26
5.64
5.24
3.26
3.06
F
F
F
F
F
O
N
N
O
S
O
O
O
3br
0.98
2.93
2.00
3.00
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)
S071

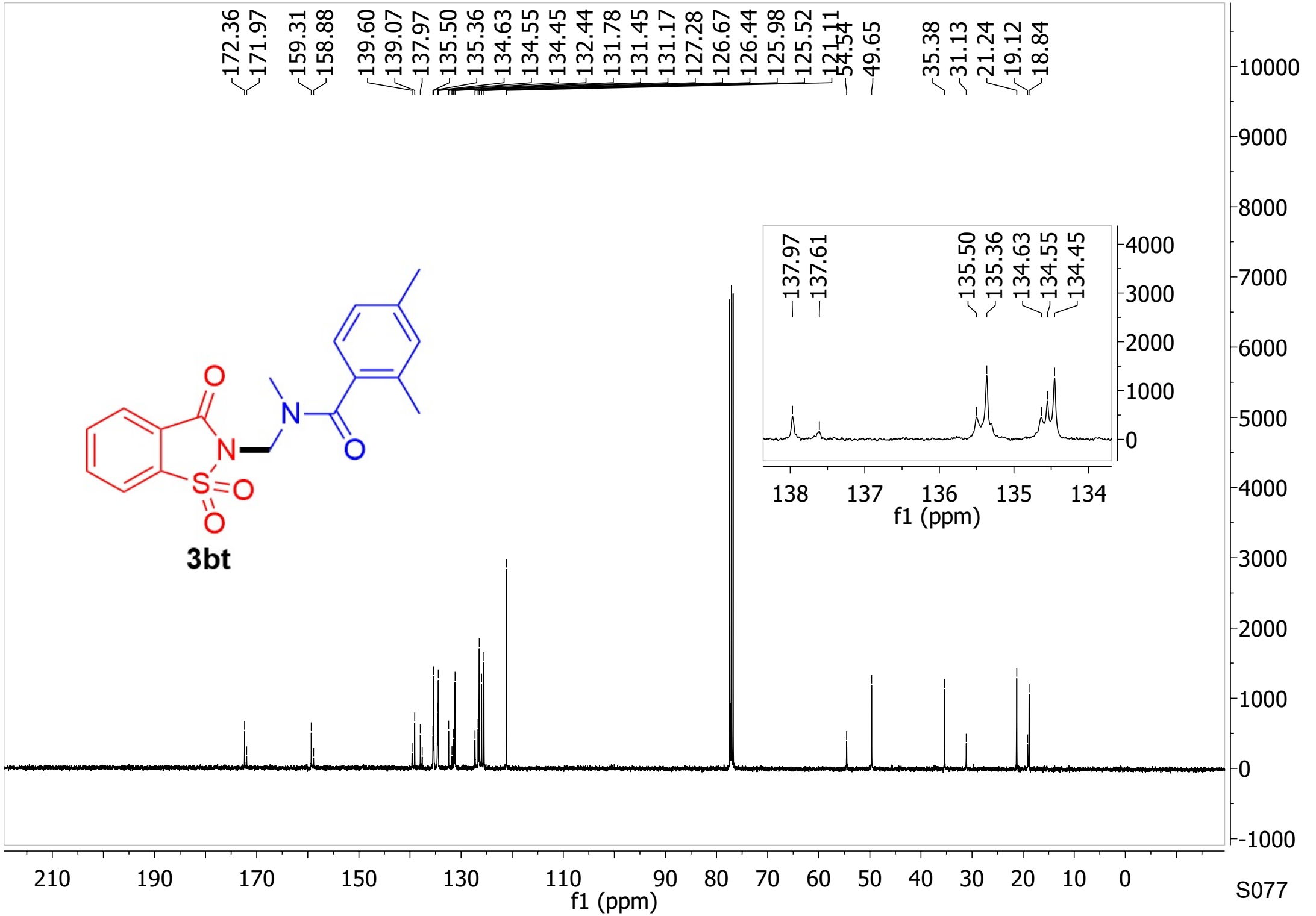

159.77
159.21
159.02
158.95
144.34
144.26
142.22
141.83
141.79
141.76
141.72
139.14
139.07
139.01
138.99
138.93
138.86
137.86
137.44
136.63
136.56
136.48
136.43
136.41
136.35
135.73
135.54
134.87
134.58
126.46
126.32
125.76
125.63
121.33
121.28
110.40
110.18
77.37
77.05
76.73
54.17
49.36
34.87
33.00
F
F
F
F
F
O
N
N
O
S
O
O
3br
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
S072

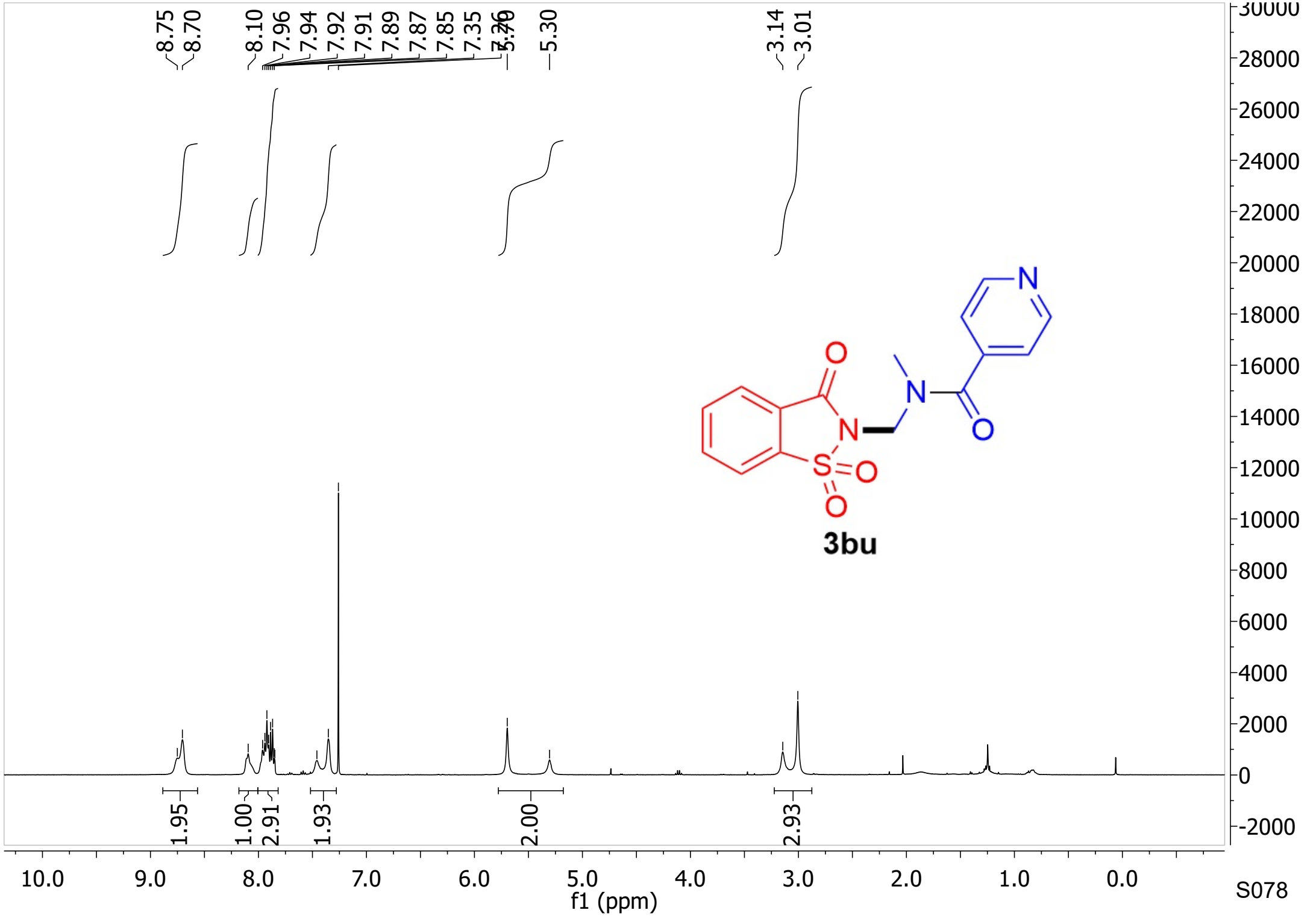

-138.97
-138.98
-138.99
-138.99
-139.00
-139.01
-139.04
-139.05
-139.06
-139.89
-139.90
-139.91
-139.92
-139.96
-139.96
-139.98
-150.59
-150.64
-150.64
-150.65
-150.70
-150.93
-150.98
-150.98
-150.99
-151.03
-151.04
-151.04
-159.55
-159.56
-159.60
-159.62
-159.63
-159.66
-159.67
-159.69
-159.75
-159.76
-159.80
-159.82
-159.83
-159.86
-159.87
-159.89
F
F
F
F
F
O
N
N
O
S
O
O
3br
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
-3000
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
f1 (ppm)
S073

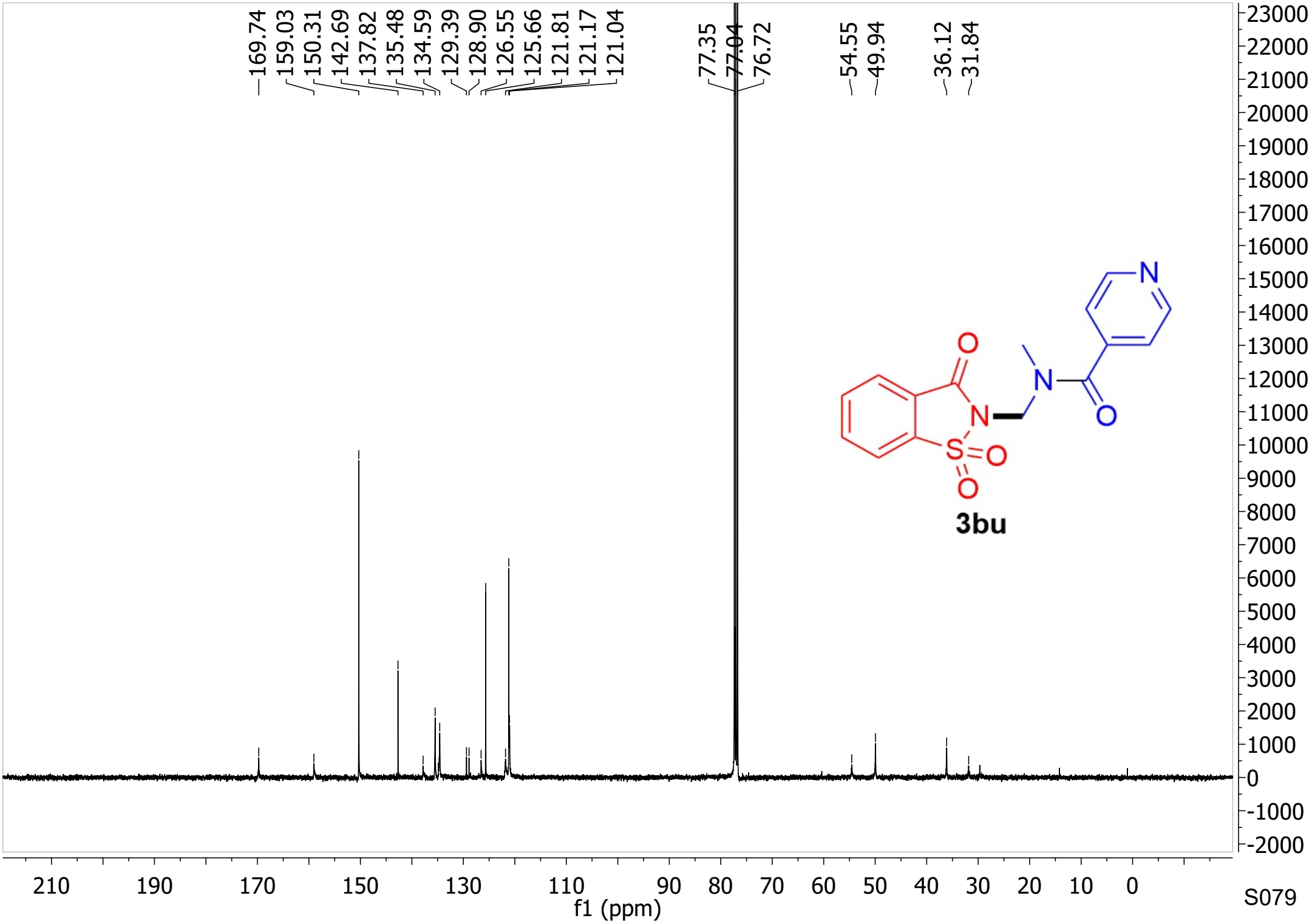

8.08
8.06
7.94
7.92
7.89
7.88
7.86
7.86
7.85
7.84
7.83
7.82
7.51
7.49
7.26
6.94
6.91
5.60
3.83
3.10
OMe
O
N
O
N
S
O
O
O
3bs
1.05
3.23
2.04
2.04
2.00
3.18
3.15
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)


172.21
161.18
159.12
137.87
135.32
134.47
129.55
127.16
126.66
125.53
121.08
113.73
77.36
77.05
76.73
55.35
53.44
31.58
OMe
O
N
N
O
S
O
O
O
3bs
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
S075


8.09
8.07
8.04
8.03
7.96
7.94
7.92
7.90
7.88
7.86
7.84
7.83
7.26
7.11
7.09
7.08
7.01
7.00
6.98
5.71
3.15
2.90
2.33
2.30
2.29
O
N
S
O
O
N
O
3bt
1.02
3.00
3.44
2.00
3.08
5.95
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)


172.36
171.97
159.31
158.88
139.60
139.07
137.97
135.50
135.36
134.63
134.55
134.45
132.44
131.78
131.45
131.17
127.28
126.67
126.44
125.98
125.52
121.11
54.54
49.65
35.38
31.13
21.24
19.12
18.84
O
N
N
O
S
O
O
3bt
137.97
137.61
135.50
135.36
134.63
134.55
134.45
138
137
136
135
134
f1 (ppm)
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
4000
3000
2000
1000
0
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
S077


8.75
8.70
8.10
7.96
7.94
7.92
7.91
7.89
7.87
7.85
7.35
5.30
3.14
3.01
1.95
1.00
2.91
1.93
2.00
2.93
3bu
f1 (ppm)
S078


169.74
159.03
150.31
142.69
137.82
135.48
134.59
129.39
128.90
126.55
125.66
121.81
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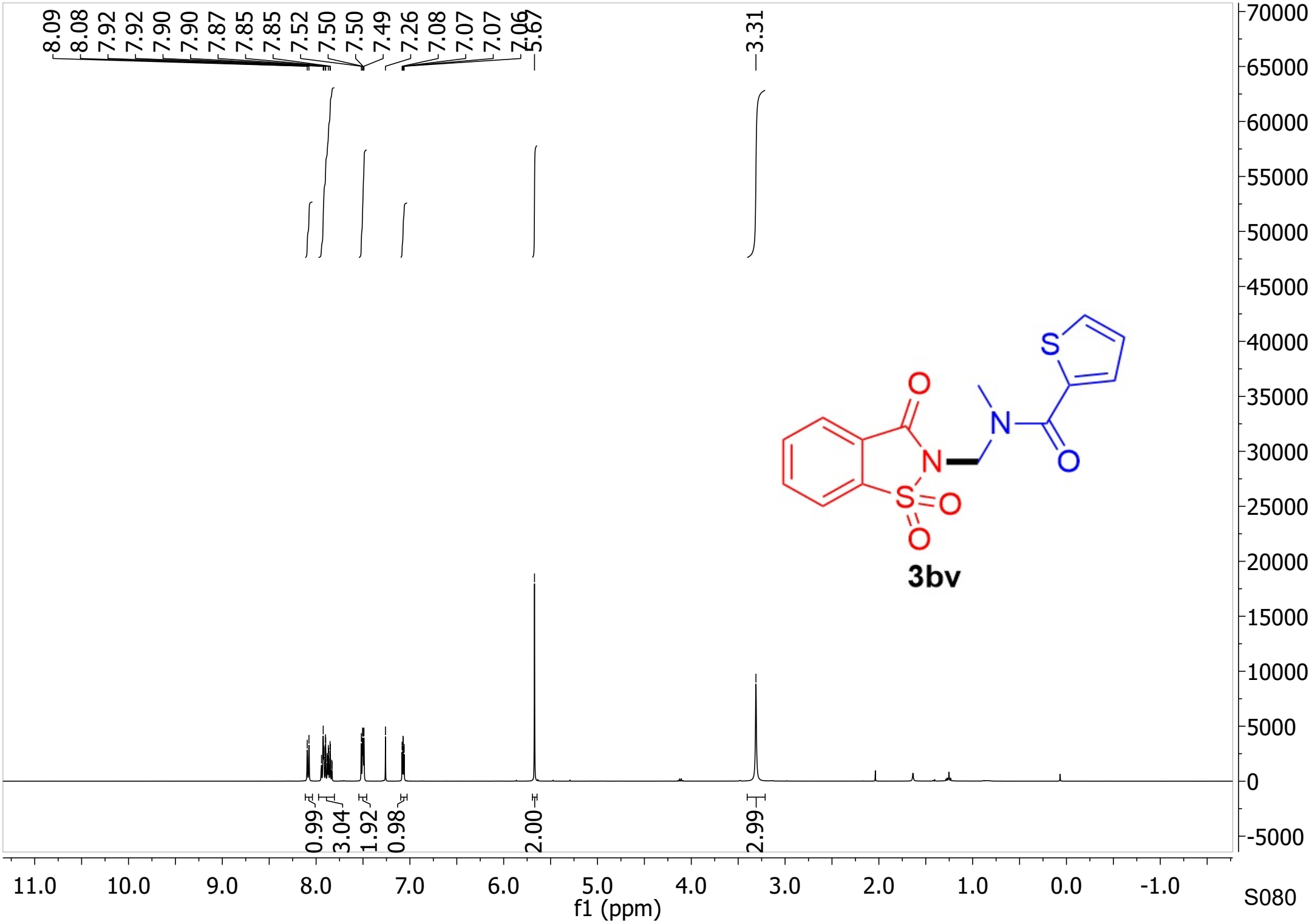
3bu
f1 (ppm)
S079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7.49
7.26
7.08
7.07
7.07
7.06
5.67
3.31
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3.04
1.92
0.98
2.00
2.99
O
N
S
O
N
S
O
O
3bv
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
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10.0
9.0
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f1 (ppm)
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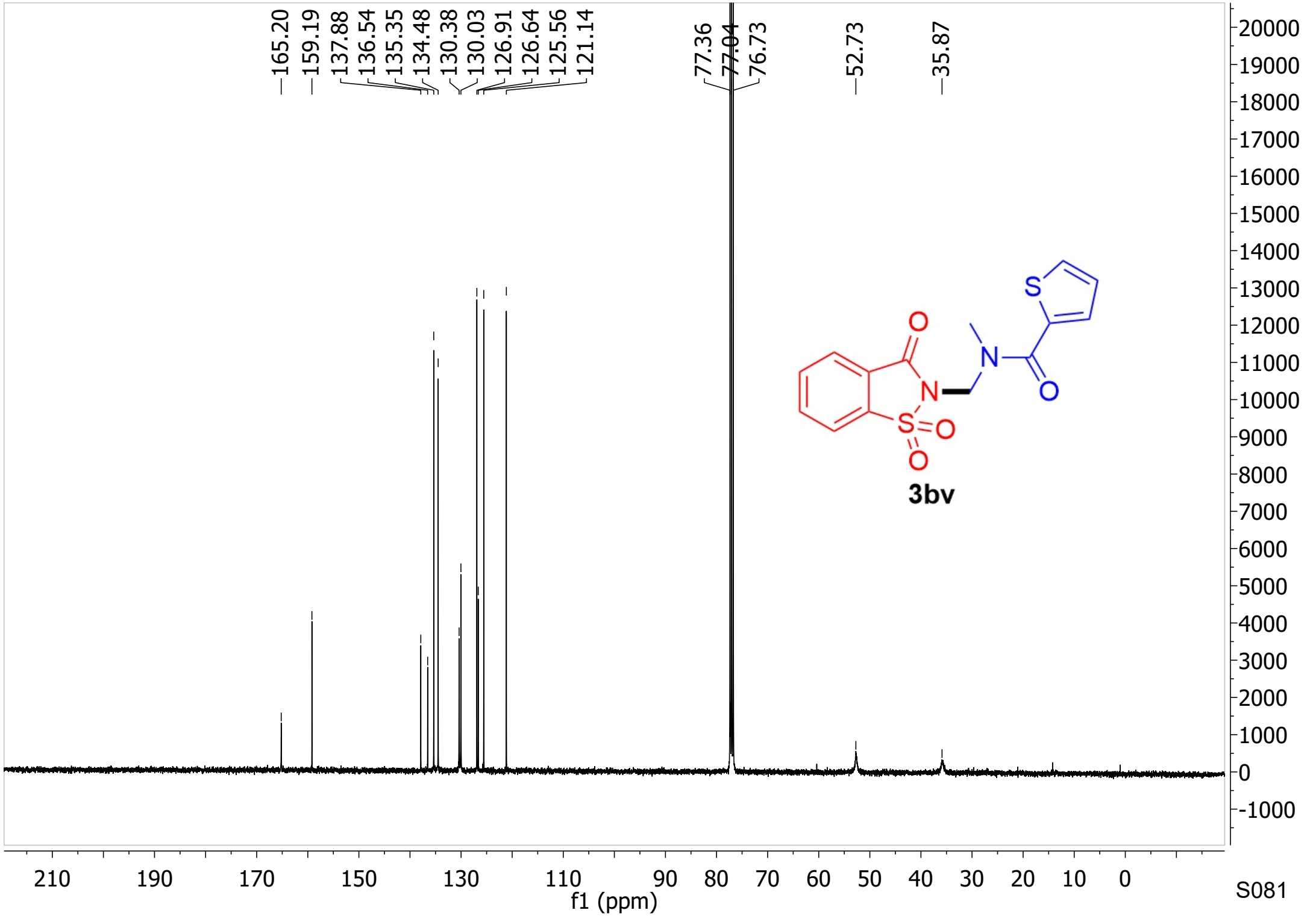
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77.36
77.04
76.73
52.73
35.87
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
O
N
S
O
N
O
S
O
O
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150
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110
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50
40
30
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10
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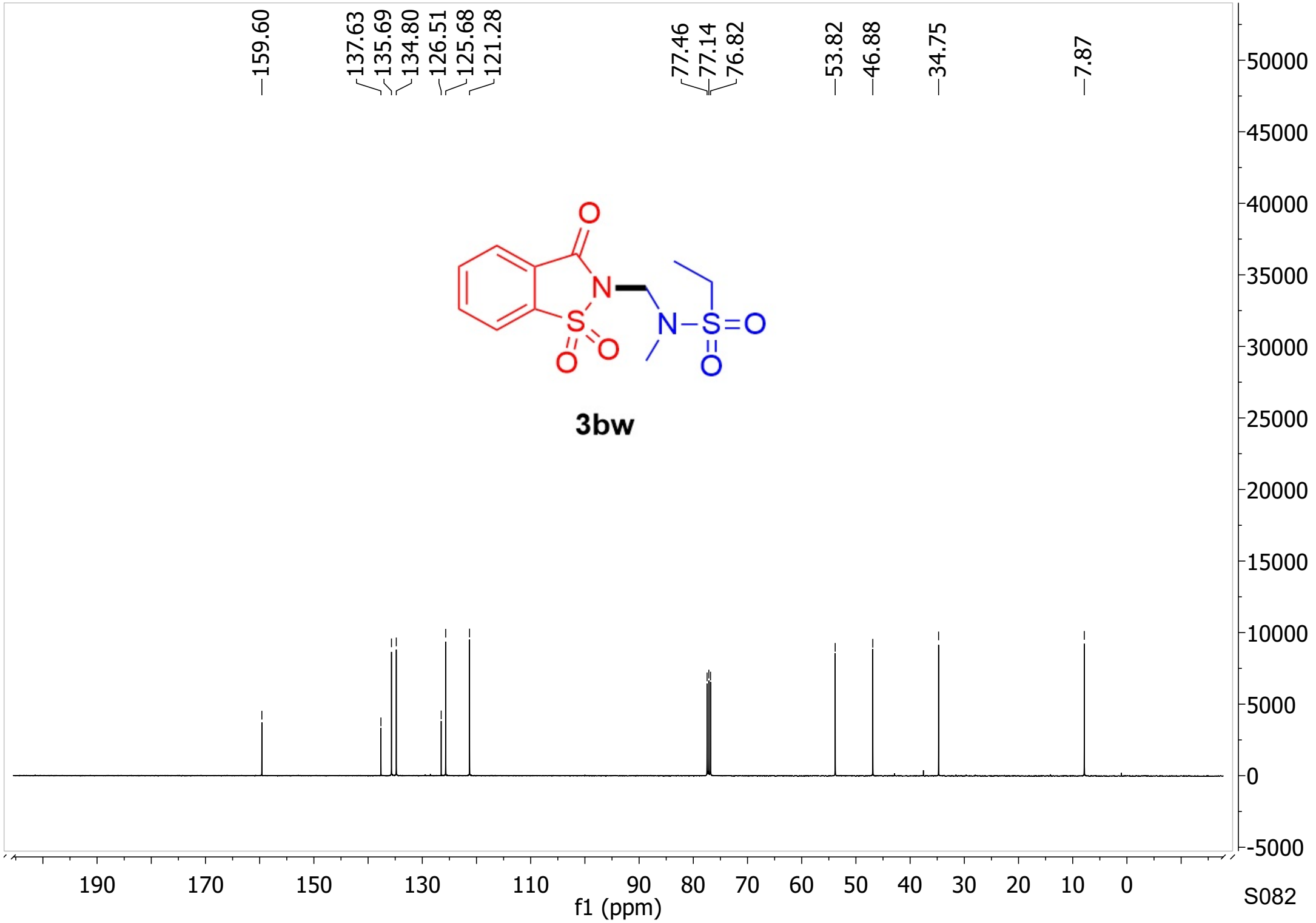
f1 (ppm)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O
O
N
S
O
O
3bw
50000
45000
40000
35000
30000
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20000
15000
10000
5000
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150
130
110
90
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30
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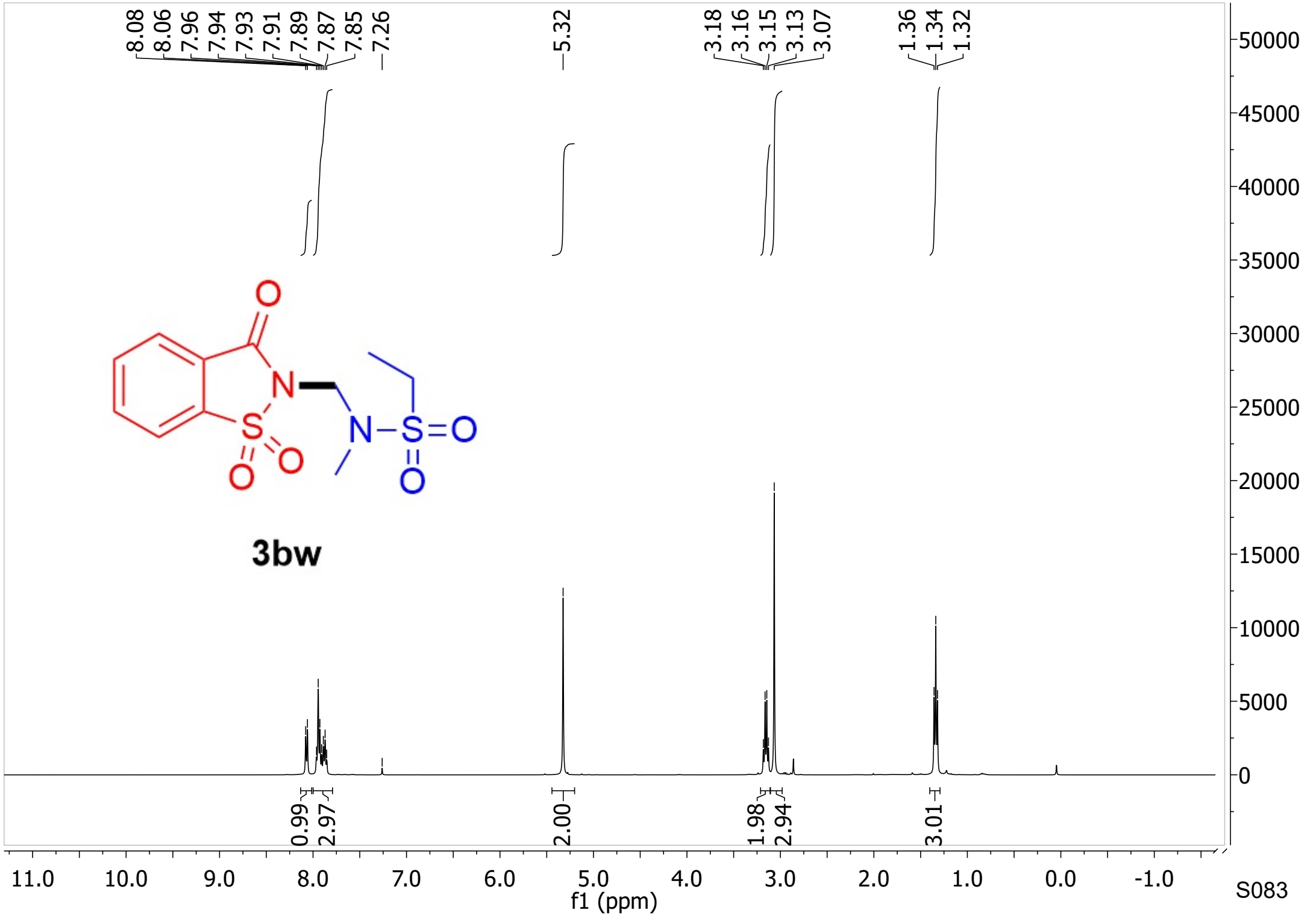
S082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7.87
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3.18
3.16
3.15
3.13
3.07
1.36
1.34
1.32
3bw
0.99
2.97
2.00
1.98
2.94
3.01
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
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f1 (ppm)
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40000
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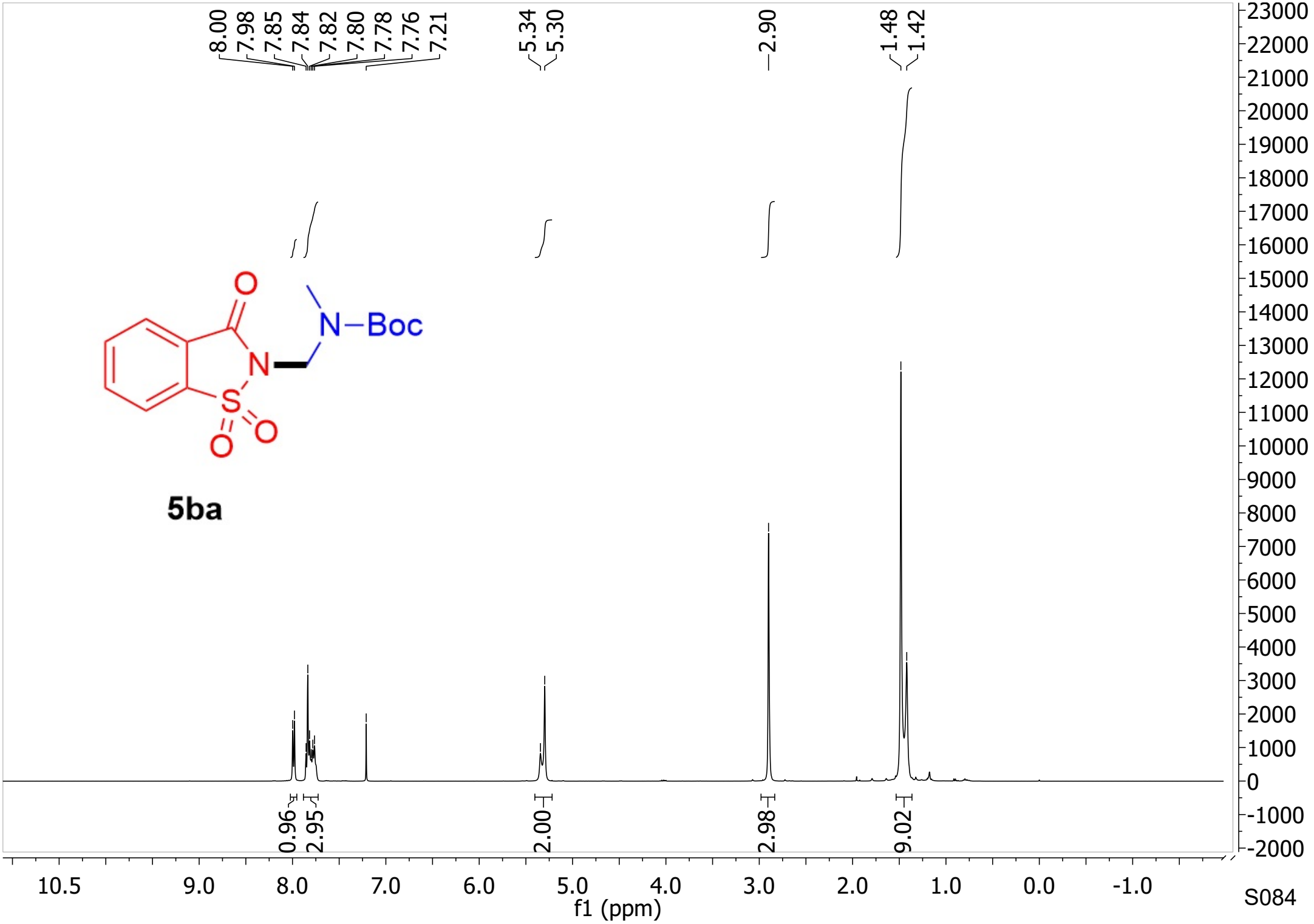
25000
20000
15000
10000
5000
0
S083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7.82
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N–Boc
5ba
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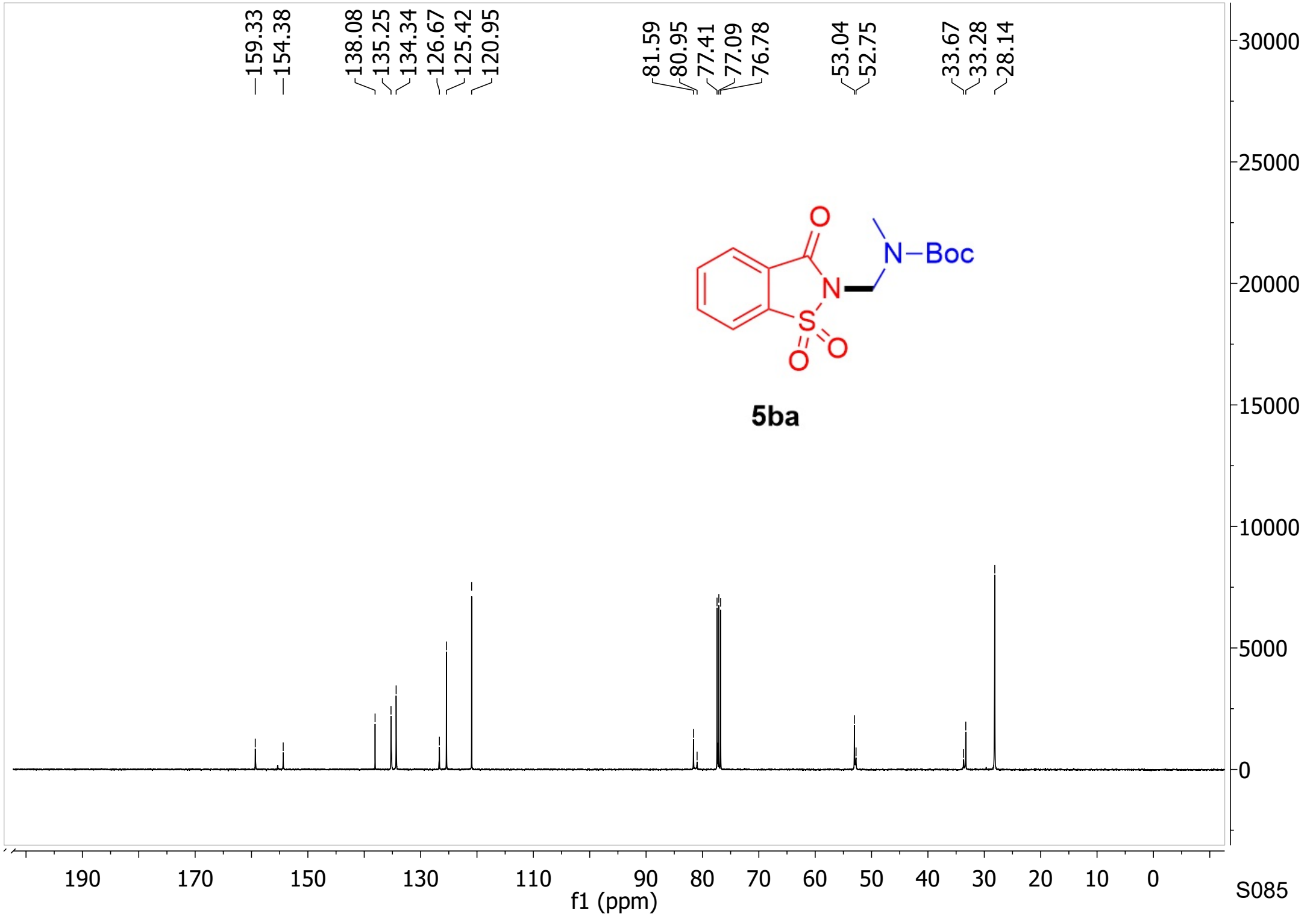
2.98
9.02
f1 (ppm)
S084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76.78
53.04
52.75
33.67
33.28
28.14
O
N
N–Boc
S
O
O
5ba
30000
25000
20000
15000
10000
5000
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150
130
110
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50
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30
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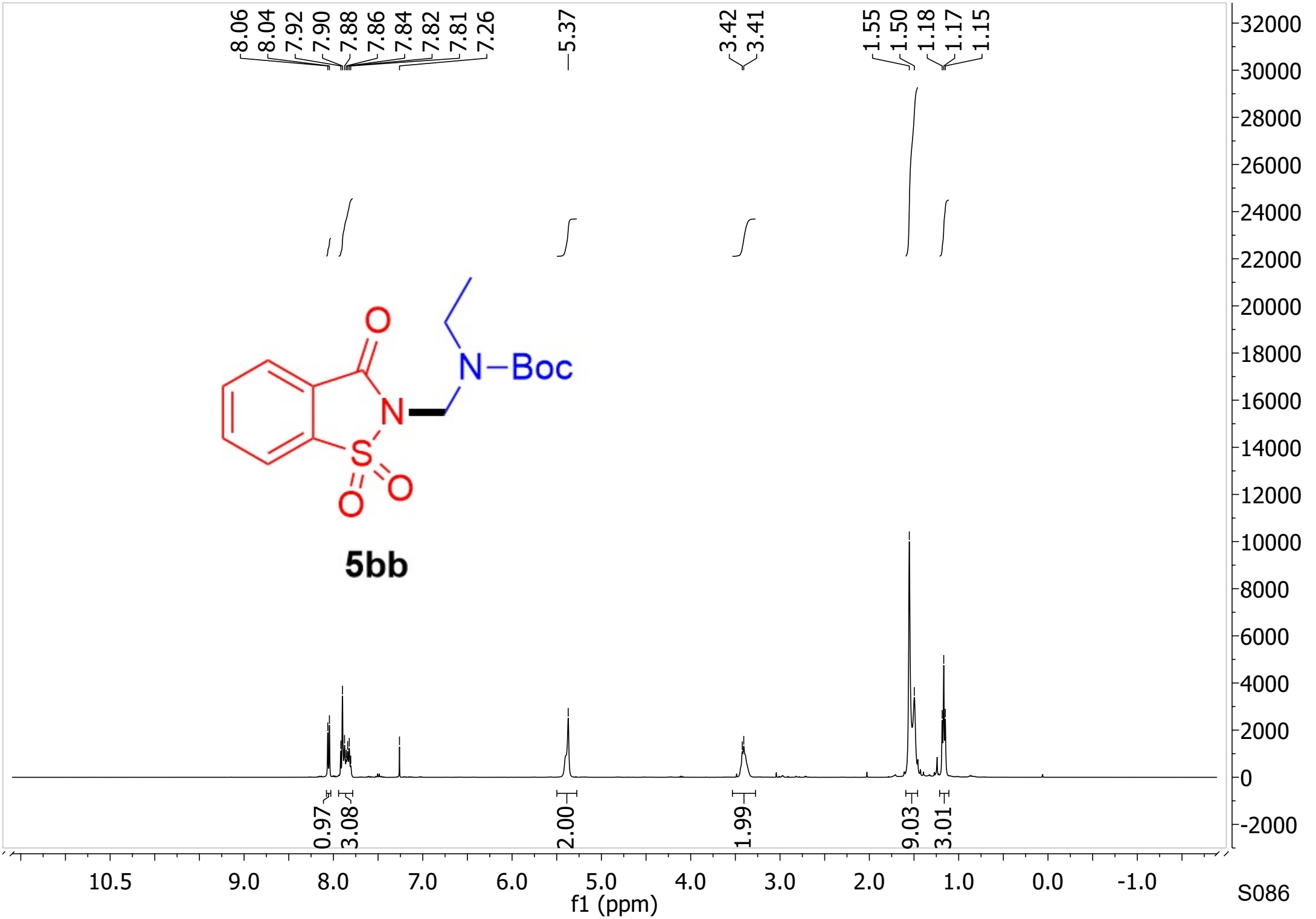
10
0
f1 (ppm)
S085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7.81
7.26
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3.42
3.41
1.55
1.50
1.18
1.17
1.15
O
N–Boc
N
S
O
O
5bb
0.97
3.08
2.00
1.99
9.03
3.01
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
10.5
9.0
8.0
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5.0
4.0
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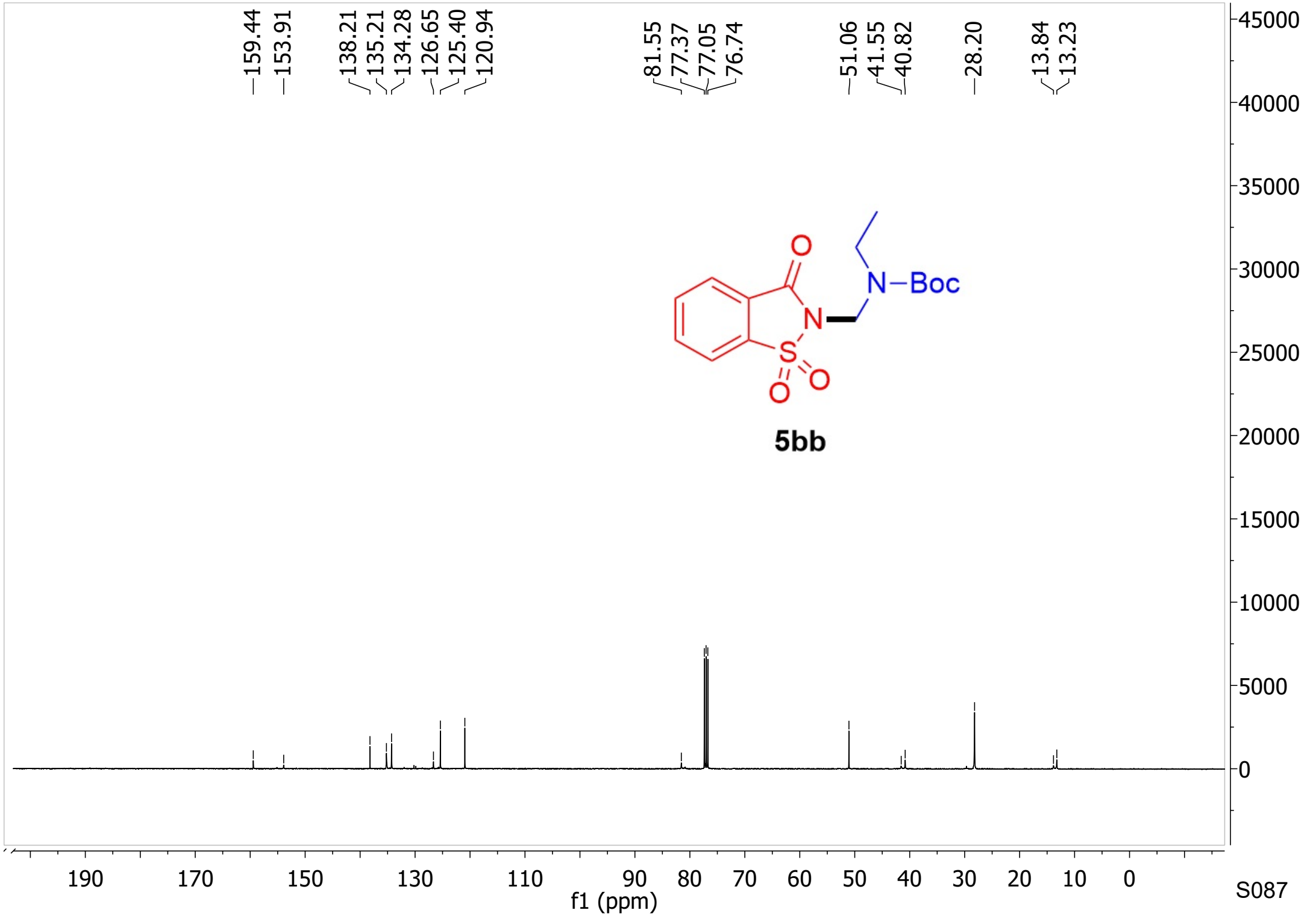
1.0
0.0
-1.0
f1 (ppm)
S086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51.06
41.55
40.82
28.20
13.84
13.23
N–Boc
5bb
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
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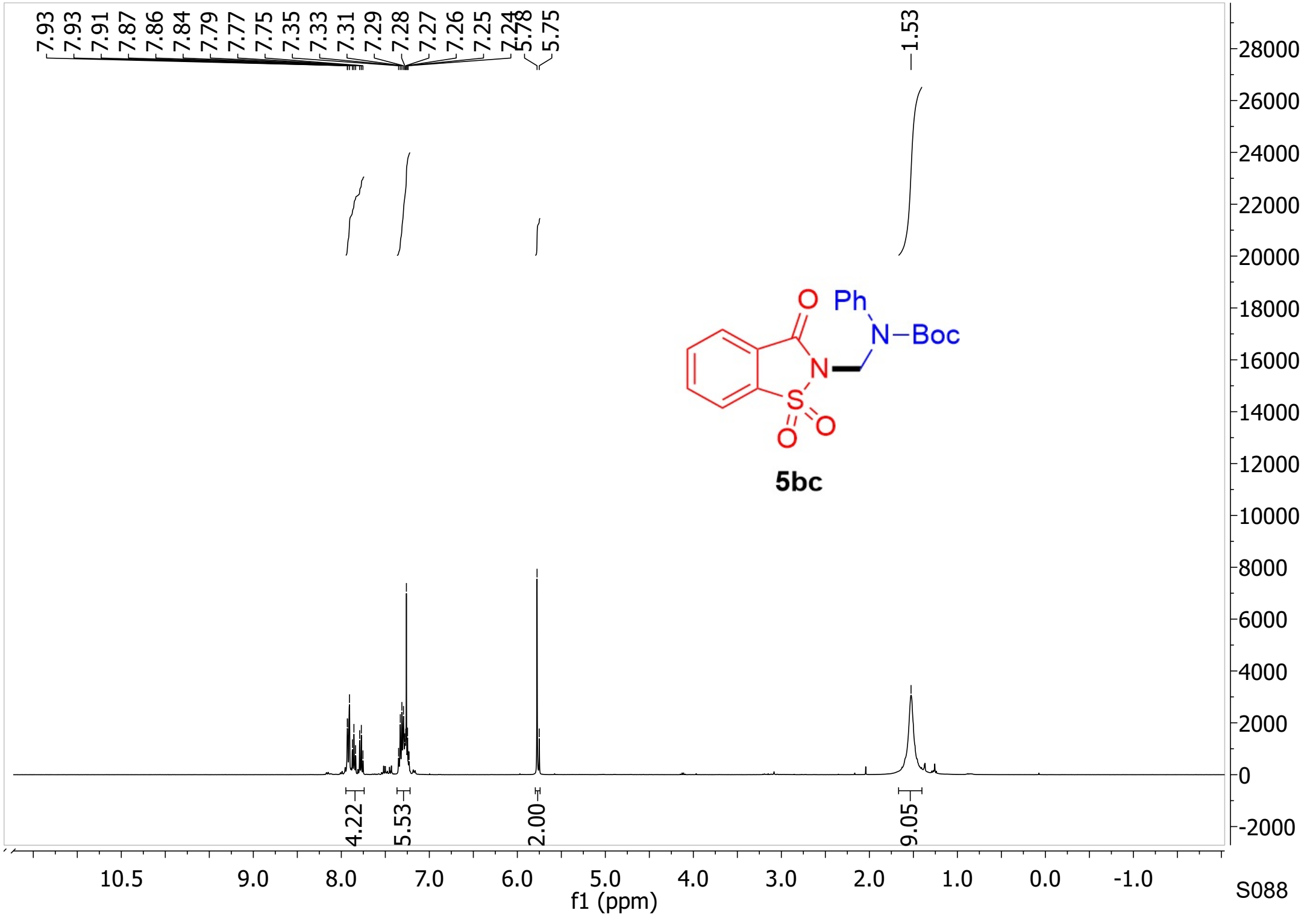
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
S087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7.77
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7.31
7.29
7.28
7.27
7.26
7.25
7.24
5.78
5.75
1.53
O
Ph
N–Boc
N
S
O
O
5bc
4.22
5.53
2.00
9.05
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
10.5
9.0
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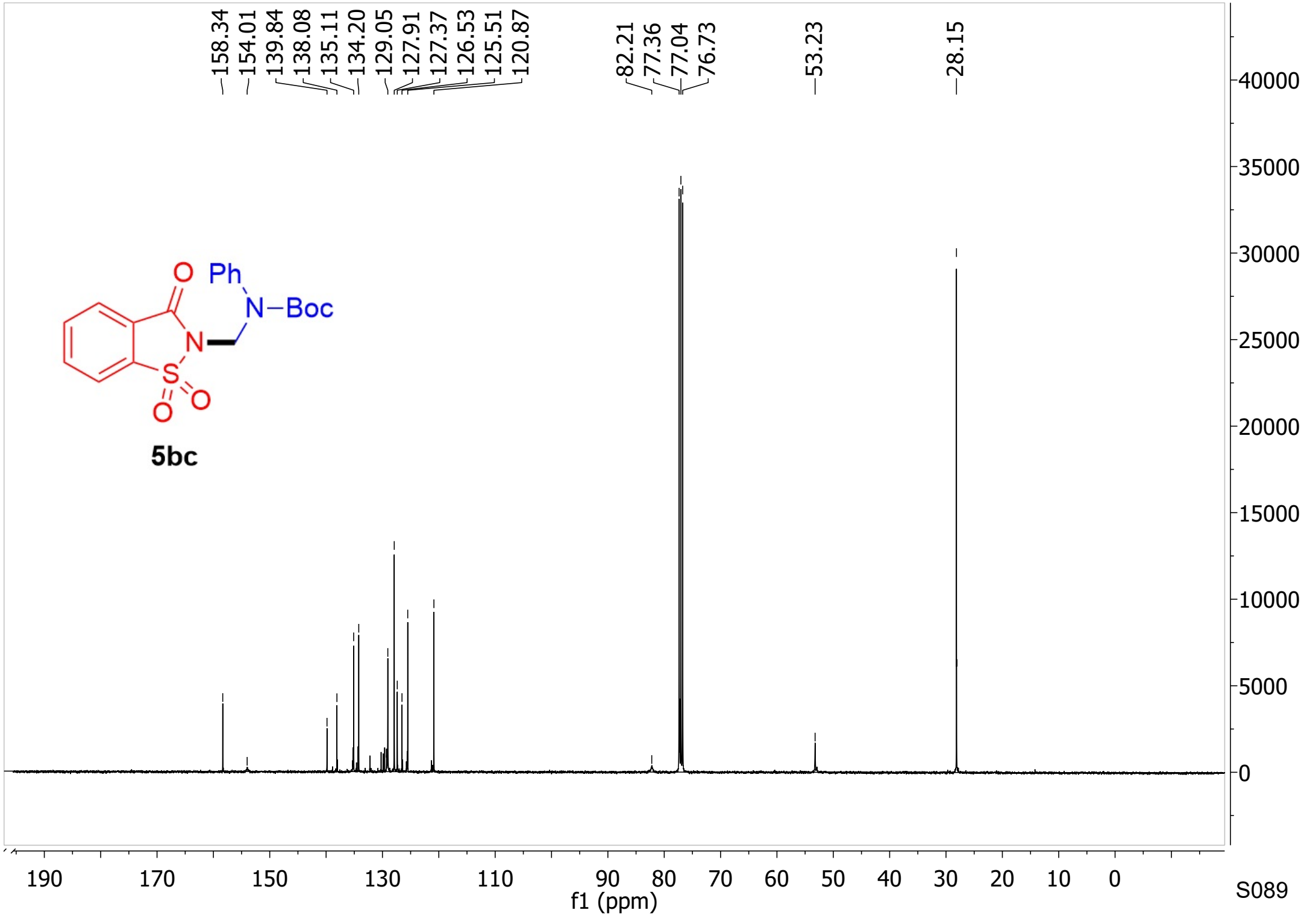
f1 (ppm)
S088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127.91
127.37
126.53
125.51
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82.21
77.36
77.04
76.73
53.23
28.15
O
Ph
N–Boc
N
S
O
O
5bc
40000
35000
30000
25000
20000
15000
10000
5000
0
190
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150
130
110
90
80
70
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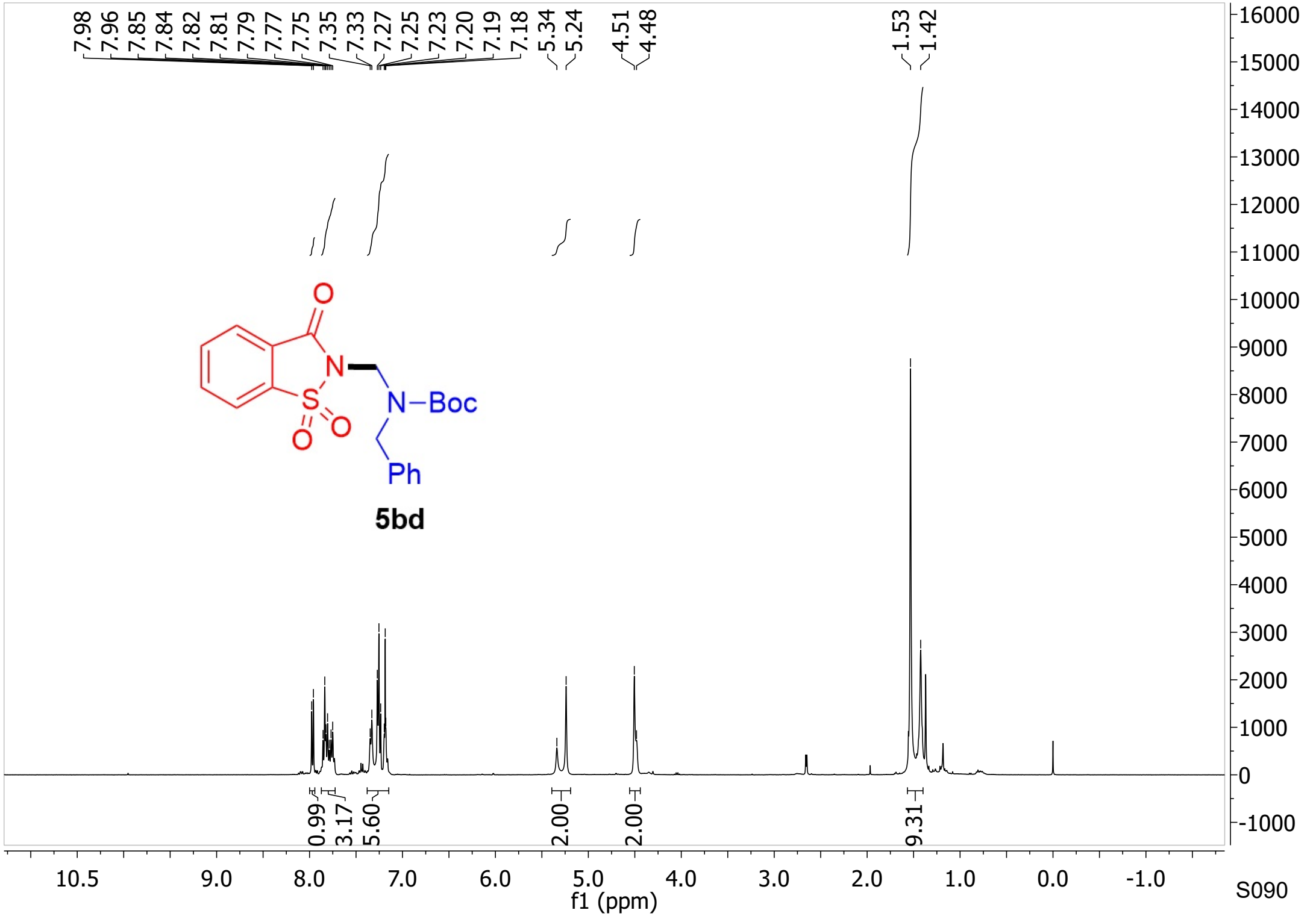
50
40
30
20
10
0
f1 (ppm)
S089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7.33
7.27
7.25
7.23
7.20
7.19
7.18
5.34
5.24
4.51
4.48
1.53
1.42
O
N
S
O
O
N–Boc
Ph
5bd
0.99
3.17
5.60
2.00
2.00
9.31
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10.5
9.0
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5.0
4.0
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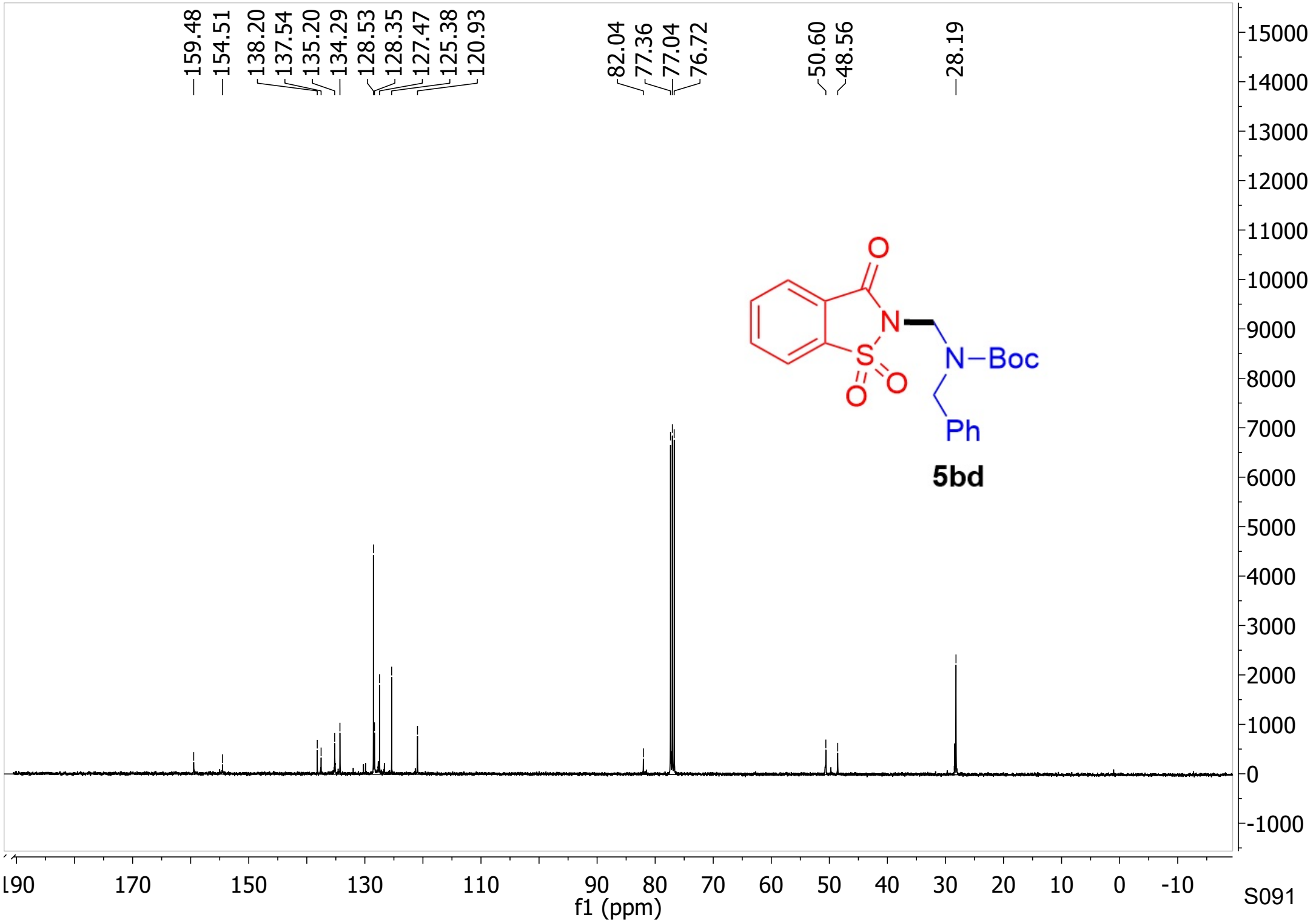
2.0
1.0
0.0
-1.0
f1 (ppm)
S090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76.72
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48.56
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O
N
S
O
O
N–Boc
Ph
5bd
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
190
170
150
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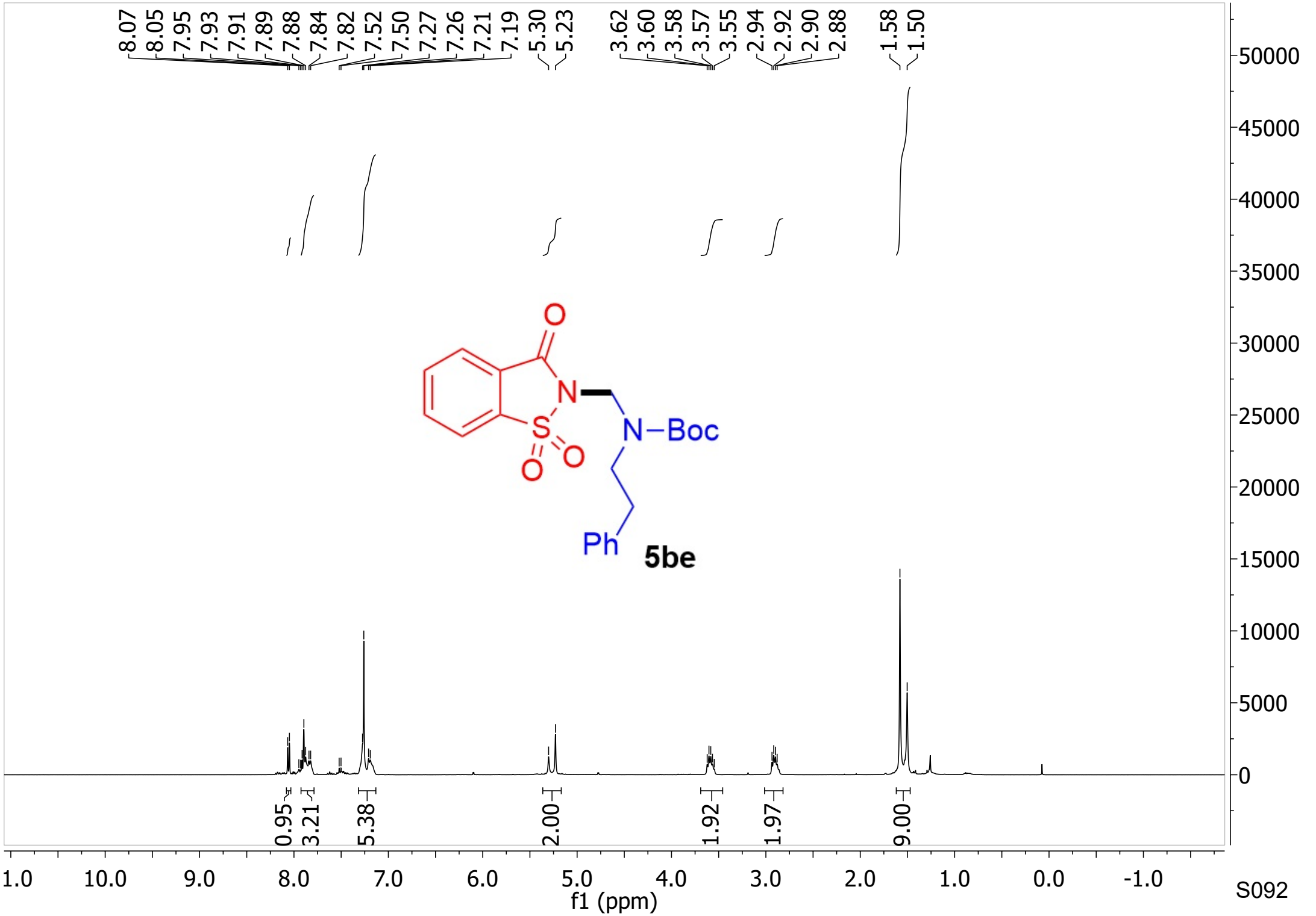
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
S091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7.21
7.19
5.30
5.23
3.62
3.60
3.58
3.57
3.55
2.94
2.92
2.90
2.88
1.58
1.50
O
N
S
O
O
N–Boc
Ph
5be
0.95
3.21
5.38
2.00
1.92
1.97
9.00
50000
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35000
30000
25000
20000
15000
10000
5000
0
1.0
10.0
9.0
8.0
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4.0
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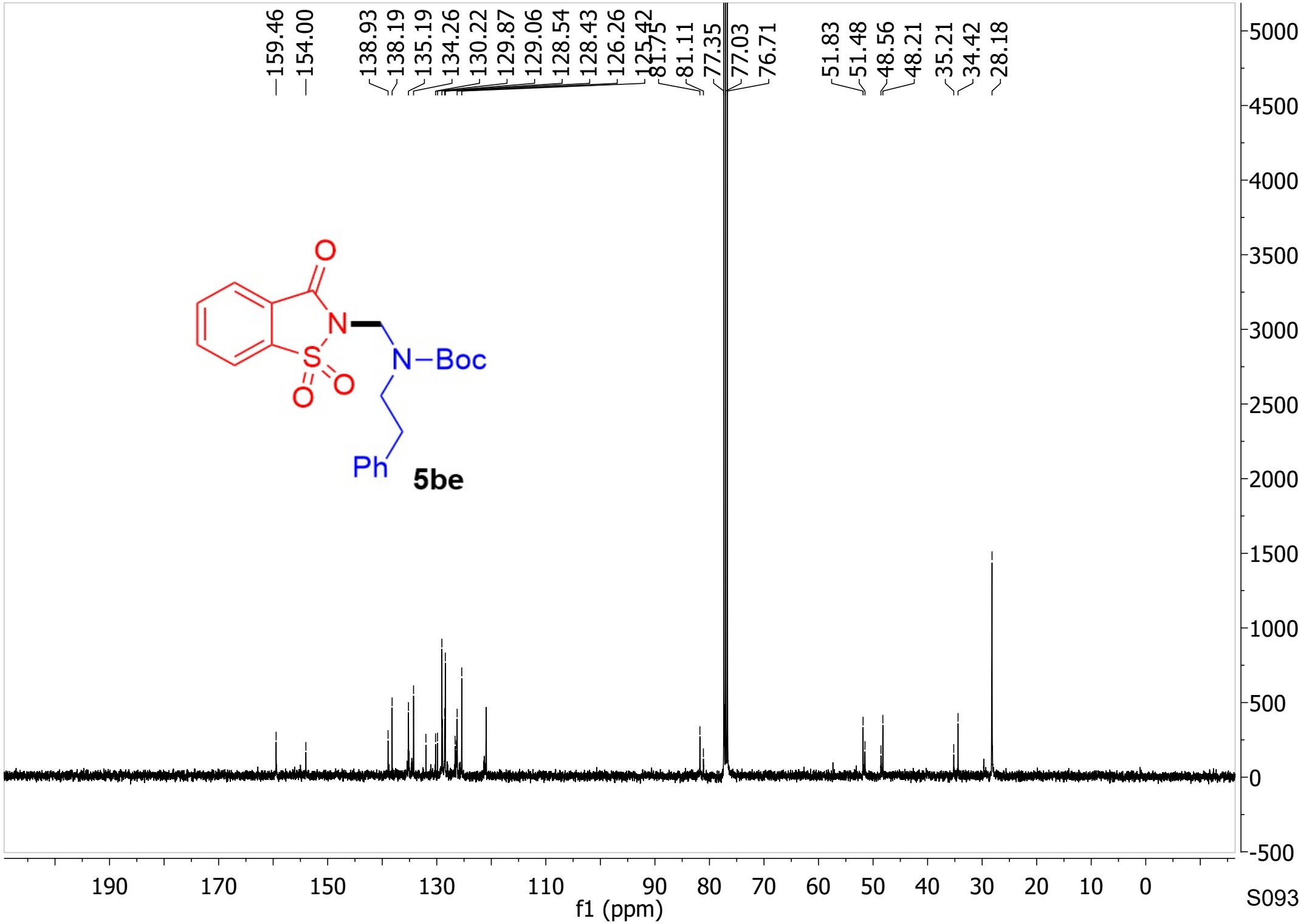
f1 (ppm)
S092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125.42
81.75
81.11
77.35
77.03
76.71
51.83
51.48
48.56
48.21
35.21
34.42
28.18
O
N
S
O
O
N–Boc
Ph
5be
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
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170
150
130
110
90
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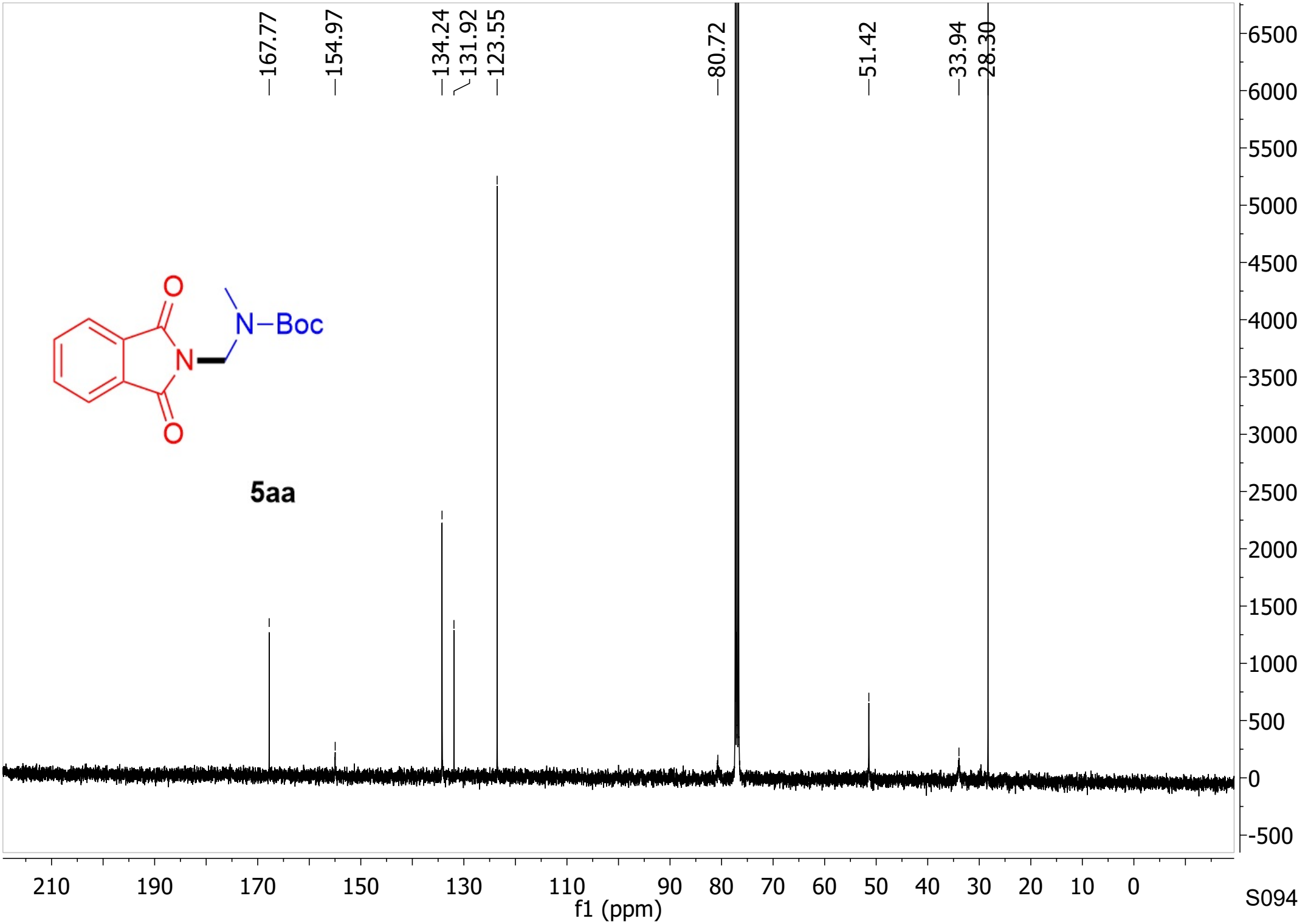
30
20
10
0
f1 (ppm)
S093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O
N
N–Boc
O
5aa
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
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190
170
150
130
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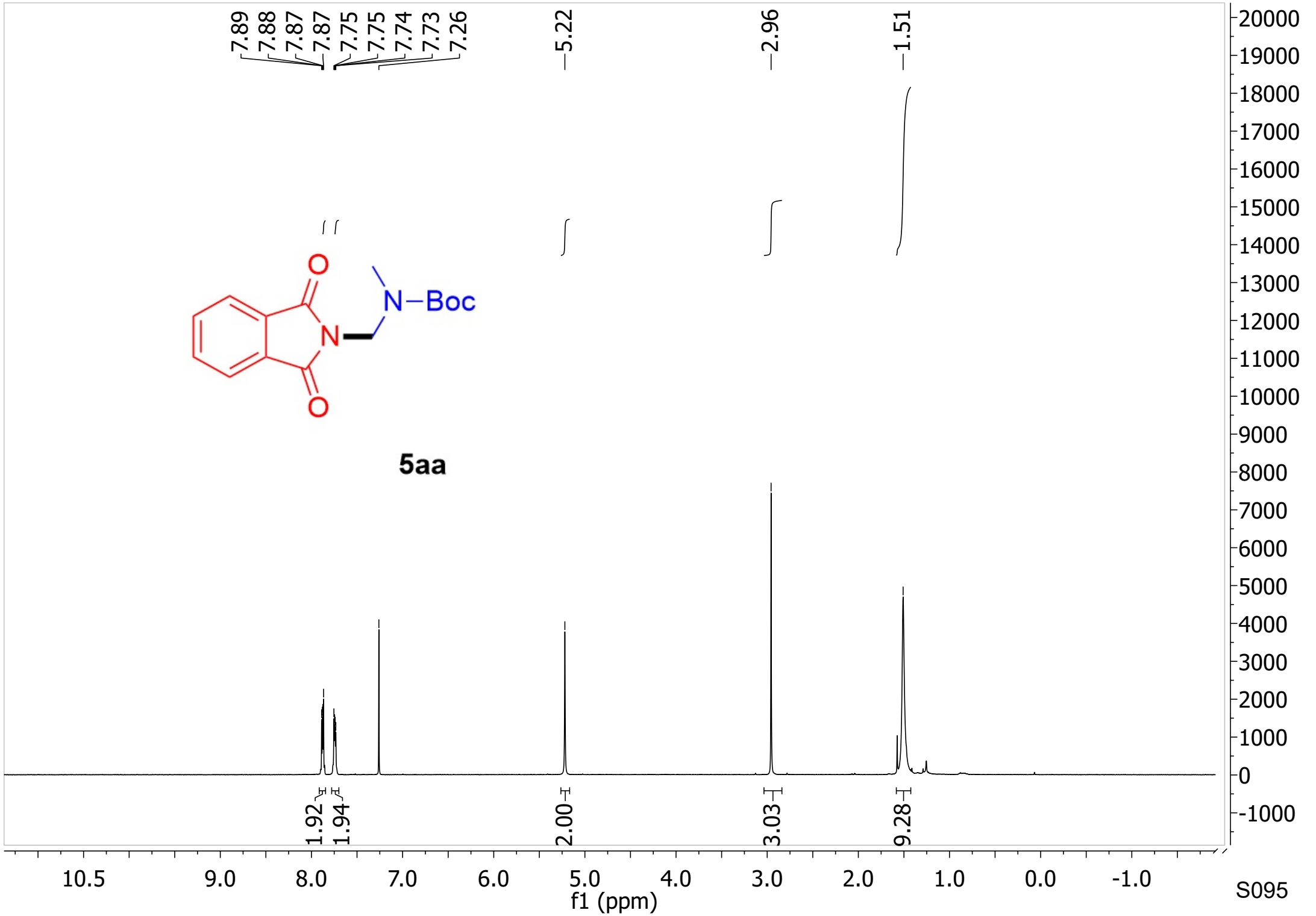
70
60
50
40
30
20
10
0
f1 (ppm)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7.87
7.87
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7.75
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7.73
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2.96
1.51
O
N
N–Boc
O
5aa
1.92
1.94
2.00
3.03
9.28
20000
19000
18000
17000
16000
15000
14000
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11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
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9.0
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5.0
4.0
3.0
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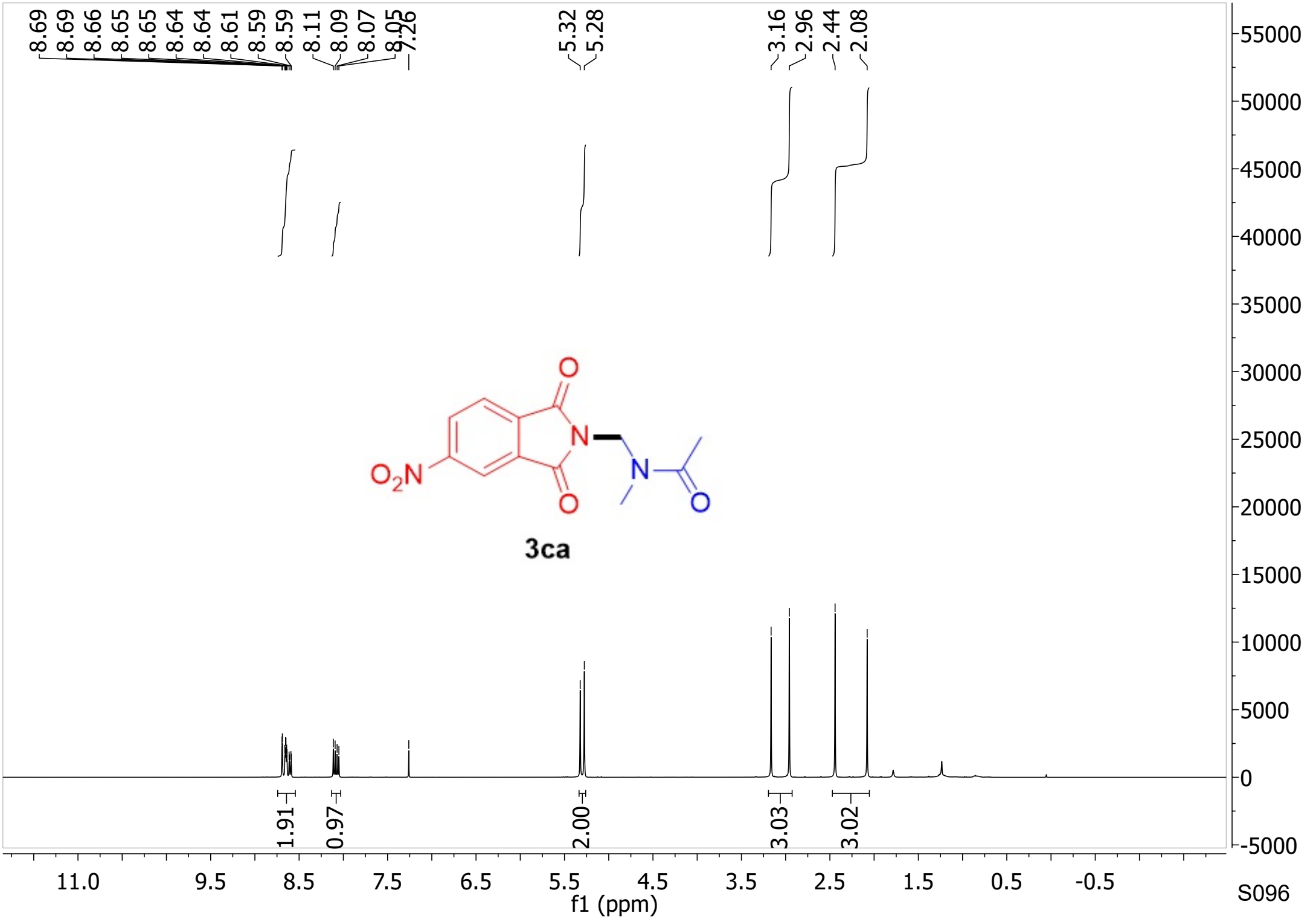
f1 (ppm)
S095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8.07
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5.32
5.28
3.16
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2.44
2.08
O
N
N
O
O
O2N
3ca
1.91
0.97
2.00
3.03
3.02
55000
50000
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40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
11.0
9.5
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5.5
4.5
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1.5
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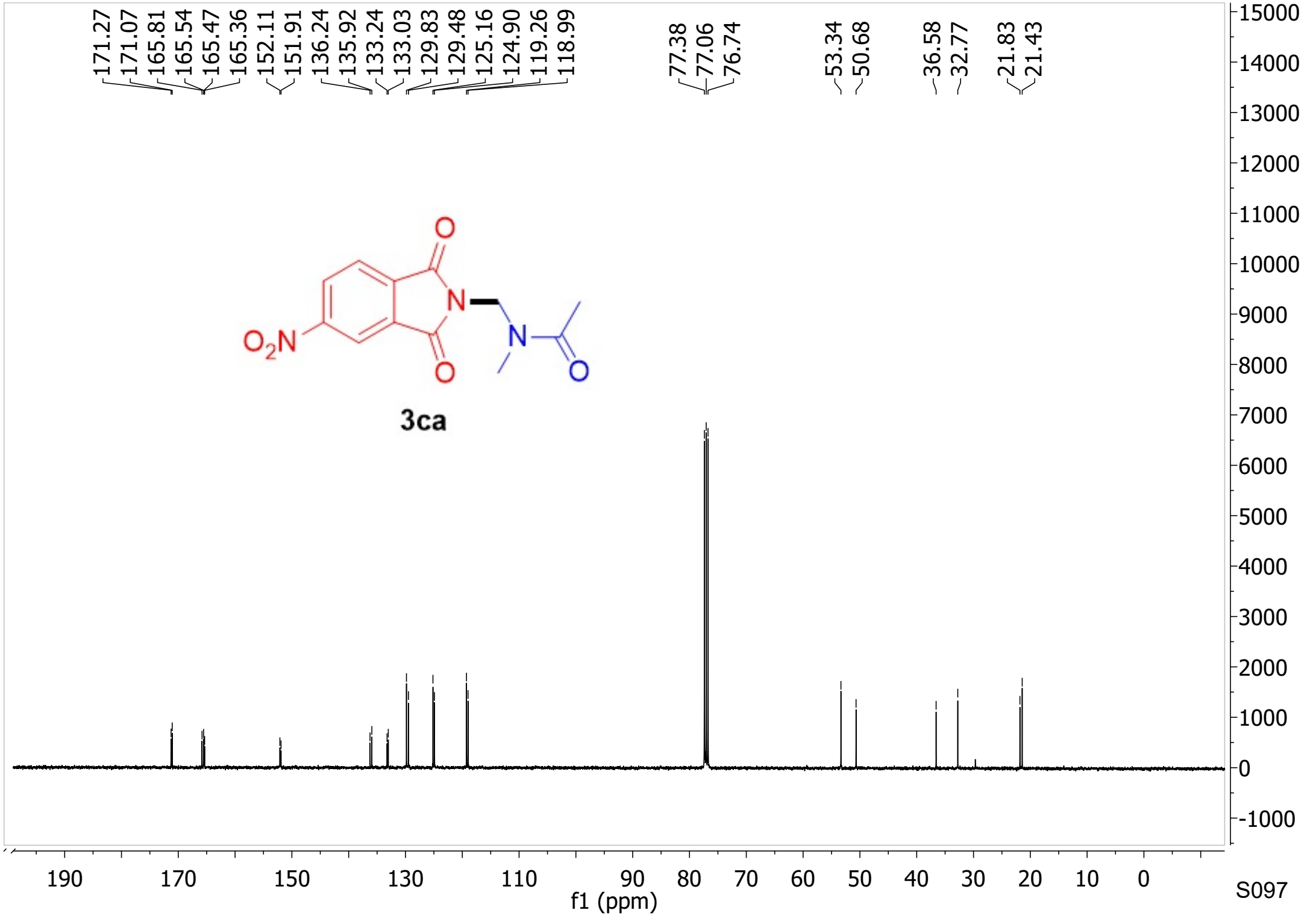
-0.5
f1 (ppm)
S096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133.03
129.83
129.48
125.16
124.90
119.26
118.99
77.38
77.06
76.74
53.34
50.68
36.58
32.77
21.83
21.43
O
N
O2N
N
O
O
3ca
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
S097

Computational Methods

The optimization of the reactants, products, intermediates and transition states was performed at the density functional theory level using the program suite Gaussian 09.[1] The B3LYP method[2] was employed for all calculations along with the 6-311+G(d,p) basis set for all atoms with the exception of Br, which was treated with the MWB28 relativistic Stuttgart-Dresden pseudopotential. The lithium counter ion was not taken into account in the calculations. The gradient threshold used for all geometry optimization was 4.5×10^{-4} Hartree/Bohr. The implicit solvatation method employed for all calculations was the polarizable conductor calculation model (CPCM).[3,4] Frequency calculations were conducted to determine if each optimization was aa a minimum (reactants, products and intermediates) or a maximum (transition states) in the potential energy surface. Furthermore, each transition state was confirmed via intrinsic reaction coordinate (IRC) calculations. The excited state properties of the Br-phthalimide-Li*O*t*Bu adduct were obtained with the time-dependent density functional (TD-DFT) formalism.[5,6] The activation free energy for the single electron transfer (SET) was calculated through Marcus-Hush theory with equation S1,[7]

$$\Delta G_{SET}^{\neq} = \frac{\lambda}{4}\left(1 + \frac{\Delta G_{rel}}{\lambda}\right)^2 \qquad \text{(eq. S1)}$$

where ΔG_{rel} is the relative difference in free energies of the SET step and λ refers to the reorganization energy.

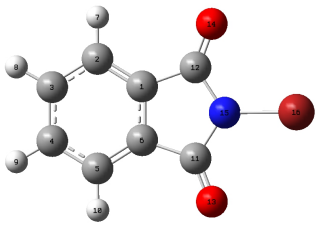
References

1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G .A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M, Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09 Revision E.01. Gaussian Inc. Wallingford CT 2009.
2. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652.; C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785-789.
3. V. Barone and M. Cossi, *J. Phys. Chem. A*, 1998, **102**, 1995-2001.
4. M. Cossi, N. Rega, G. Scalmani and V. Barone, *J. Comput. Chem.*, 2003, **24**, 669-681.
5. G. Scalamini, M. J. Frisch, B. Mennucci, J. Tomaso, R. Cammi, V. Barone, *J. Phys. Chem.*, 2006, **124**, 094107:1-15.
6. A. D. Laurent, C. Adamo, D. Jacquemin, *Phys. Chem. Chem. Phys.*, 2014, **16**, 14334-14356.
7. C. Adouama, M. E. Budén, W. D. Guerra, M. Puiatti, B. Joseph, S. M. Barolo, R. A. Rossi, M. Médebielle, *Org. Lett.*, 2019, **21**, 320-324.

Computational Data

Cartesian coordinates

N-bromophthalimide



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.000116	1.388291	0.698062
2	6	0	0.000079	2.568095	1.422786
3	6	0	0.000297	3.766652	0.698758
4	6	0	0.000297	3.766652	-0.698758
5	6	0	0.000079	2.568095	-1.422786
6	6	0	-0.000116	1.388291	-0.698062
7	1	0	0.000094	2.563320	2.505628
8	1	0	0.000495	4.710635	1.230453
9	1	0	0.000495	4.710635	-1.230453
10	1	0	0.000094	2.563320	-2.505628
11	6	0	-0.000367	-0.022389	-1.181666
12	6	0	-0.000367	-0.022389	1.181666
13	8	0	-0.000141	-0.452973	-2.307655
14	8	0	-0.000141	-0.452973	2.307655
15	7	0	-0.001039	-0.792835	0.000000
16	35	0	0.000276	-2.690236	0.000000

Zero-point correction= 0.104357 (Hartree/Particle)

Thermal correction to Energy= 0.113865

Thermal correction to Enthalpy= 0.114810

Thermal correction to Gibbs Free Energy= 0.067932

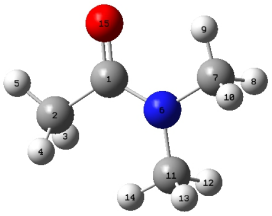
Sum of electronic and zero-point Energies= -525.867773

Sum of electronic and thermal Energies= -525.858265

Sum of electronic and thermal Enthalpies= -525.857321

Sum of electronic and thermal Free Energies= -525.904199

N,N-dimethylacetamide

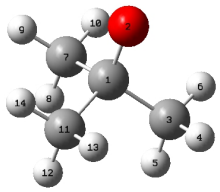


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.723894	-0.291345	-0.000089
2	6	0	-1.774516	0.806918	-0.000110
3	1	0	-1.692941	1.444551	0.883495
4	1	0	-1.693003	1.444543	-0.883722
5	1	0	-2.751956	0.329288	-0.000065
6	7	0	0.587769	0.078553	-0.000732
7	6	0	1.634749	-0.937685	-0.000046
8	1	0	2.264017	-0.830604	0.889298
9	1	0	1.177741	-1.922938	-0.002441
10	1	0	2.267500	-0.827776	-0.886520
11	6	0	1.069770	1.454748	0.000341
12	1	0	1.683170	1.638042	0.888690
13	1	0	1.687802	1.637417	-0.884874
14	1	0	0.248576	2.164249	-0.002137
15	8	0	-1.067743	-1.477807	0.000353

Zero-point correction= 0.129189 (Hartree/Particle)
Thermal correction to Energy= 0.137153
Thermal correction to Enthalpy= 0.138097
Thermal correction to Gibbs Free Energy= 0.095417
Sum of electronic and zero-point Energies= -287.797106
Sum of electronic and thermal Energies= -287.789142
Sum of electronic and thermal Enthalpies= -287.788197
Sum of electronic and thermal Free Energies= -287.830877

Recommended a0 for SCRF calculation = 4.18 angstrom

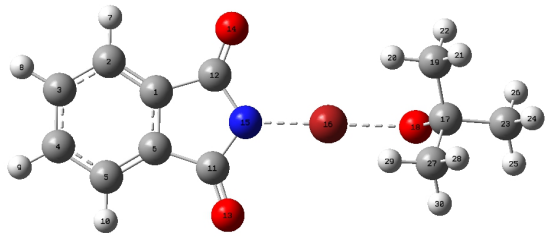
t-butoxide anion



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.000030	-0.000049	0.132247
2	8	0	-0.000882	0.000187	1.504169
3	6	0	0.891635	-1.145588	-0.432979
4	1	0	0.520717	-2.110769	-0.071025
5	1	0	0.915297	-1.175680	-1.530995
6	1	0	1.918322	-1.022983	-0.070956
7	6	0	0.546749	1.344531	-0.433406
8	1	0	0.561718	1.379618	-1.531410
9	1	0	-0.072576	2.172772	-0.071794
10	1	0	1.567996	1.505826	-0.070847
11	6	0	-1.437645	-0.199111	-0.434124
12	1	0	-1.475223	-0.204094	-1.532192
13	1	0	-1.845273	-1.149573	-0.072454
14	1	0	-2.088175	0.604687	-0.072107

Zero-point correction= 0.120428 (Hartree/Particle)
Thermal correction to Energy= 0.126753
Thermal correction to Enthalpy= 0.127697
Thermal correction to Gibbs Free Energy= 0.091777
Sum of electronic and zero-point Energies= -233.107250
Sum of electronic and thermal Energies= -233.100925
Sum of electronic and thermal Enthalpies= -233.099981
Sum of electronic and thermal Free Energies= -233.135901

t-butoxide *N*-bromophthalimide complex (S_0)

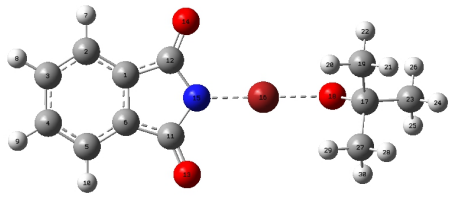


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.024903	0.706088	0.044589
2	6	0	-4.184708	1.450390	0.184205
3	6	0	-5.387410	0.748856	0.340738
4	6	0	-5.408818	-0.649085	0.354521
5	6	0	-4.228277	-1.390237	0.212085
6	6	0	-3.046137	-0.684866	0.058224
7	1	0	-4.163223	2.533758	0.173004
8	1	0	-6.316333	1.296267	0.453234
9	1	0	-6.354093	-1.165361	0.477548
10	1	0	-4.240160	-2.473772	0.222076
11	6	0	-1.628911	-1.154842	-0.116107
12	6	0	-1.594194	1.129305	-0.138161
13	8	0	-1.250389	-2.314247	-0.153225
14	8	0	-1.181004	2.275958	-0.196897
15	7	0	-0.833029	-0.025526	-0.226210
16	35	0	1.197691	-0.059382	-0.462528
17	6	0	4.200941	0.028154	0.275216
18	8	0	3.327996	-0.110369	-0.826044
19	6	0	4.017953	1.392367	0.973369
20	1	0	3.007949	1.483640	1.381130
21	1	0	4.730033	1.522615	1.795704
22	1	0	4.168979	2.203620	0.254877
23	6	0	5.629043	-0.055146	-0.302029
24	1	0	6.385503	0.035425	0.485474
25	1	0	5.772850	-1.012301	-0.811328
26	1	0	5.788703	0.746385	-1.028897
27	6	0	4.005260	-1.109449	1.299950
28	1	0	4.724069	-1.036476	2.123392
29	1	0	2.998375	-1.077142	1.723996
30	1	0	4.137519	-2.079552	0.811456

```
 Zero-point correction=                          0.227512 (Hartree/Particle)
 Thermal correction to Energy=                    0.244878
 Thermal correction to Enthalpy=                  0.245822
 Thermal correction to Gibbs Free Energy=         0.179765
 Sum of electronic and zero-point Energies=           -759.015660
 Sum of electronic and thermal Energies=              -758.998294
 Sum of electronic and thermal Enthalpies=            -758.997350
 Sum of electronic and thermal Free Energies=         -759.063408

Excited State   1:  3.000-A     2.9816 eV  415.82 nm  f=0.0000  <S**2>=2.000
    60A -> 63A      -0.24449
    61A -> 63A      -0.24700
    62A -> 63A      -0.59867
    60B -> 63B       0.24449
    61B -> 63B       0.24700
    62B -> 63B       0.59867
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-KS) =  -759.133598719
 Copying the excited state density for this state as the 1-particle RhoCI density.

 Excited State   2:  1.000-A     3.0008 eV  413.17 nm  f=0.0001  <S**2>=0.000
    62A -> 63A       0.70557
    62B -> 63B       0.70557

 Excited State   3:  3.000-A     3.0343 eV  408.61 nm  f=0.0000  <S**2>=2.000
    57A -> 63A      -0.13212
    60A -> 63A       0.30839
    61A -> 63A       0.47915
    62A -> 63A      -0.36652
    57B -> 63B       0.13212
    60B -> 63B      -0.30839
    61B -> 63B      -0.47915
    62B -> 63B       0.36652

 Excited State   4:  1.000-A     3.1696 eV  391.16 nm  f=0.0007  <S**2>=0.000
    61A -> 63A       0.70059
    61B -> 63B       0.70059

 Excited State   5:  3.000-A     3.1955 eV  387.99 nm  f=0.0000  <S**2>=2.000
    55A -> 63A       0.11989
    57A -> 63A      -0.17302
    58A -> 64A       0.13197
    60A -> 63A       0.48343
```

```
    61A -> 63A      -0.42634
    55B -> 63B      -0.11989
    57B -> 63B       0.17302
    58B -> 64B      -0.13197
    60B -> 63B      -0.48343
    61B -> 63B       0.42634

Excited State   6:  3.000-A     3.3458 eV  370.57 nm  f=0.0000  <S**2>=2.000
    61A -> 65A       0.67895
    61A -> 67A       0.14228
    61B -> 65B      -0.67895
    61B -> 67B      -0.14228

Excited State   7:  3.000-A     3.4077 eV  363.83 nm  f=0.0000  <S**2>=2.000
    59A -> 63A       0.68700
    59B -> 63B      -0.68700

Excited State   8:  3.000-A     3.4462 eV  359.77 nm  f=0.0000  <S**2>=2.000
    62A -> 65A      -0.68809
    62A -> 67A      -0.12023
    62B -> 65B       0.68809
    62B -> 67B       0.12023

Excited State   9:  3.000-A     3.5362 eV  350.62 nm  f=0.0000  <S**2>=2.000
    54A -> 63A      -0.21742
    55A -> 63A      -0.11422
    57A -> 63A       0.53064
    58A -> 64A      -0.25262
    60A -> 63A       0.24861
    60A -> 68A      -0.11694
    54B -> 63B       0.21742
    55B -> 63B       0.11422
    57B -> 63B      -0.53064
    58B -> 64B       0.25262
    60B -> 63B      -0.24861
    60B -> 68B       0.11694

Excited State  10:  1.000-A     3.7289 eV  332.49 nm  f=0.0090  <S**2>=0.000
    60A -> 63A       0.69762
    60B -> 63B       0.69762
SavETr:  write IOETrn=   770 NScale= 10 NData=  16 NLR=1 LETran=    190.
```

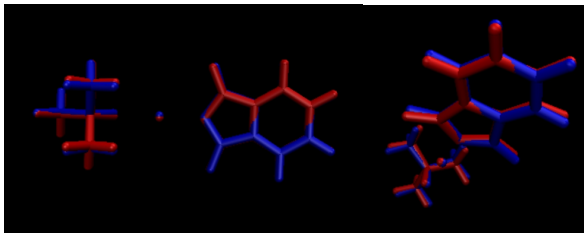
t-butoxide *N*-bromophthalimide complex (S_1)



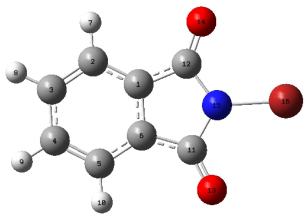
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.023950	-0.697125	0.059072
2	6	0	4.232867	-1.390701	0.216948
3	6	0	5.397644	-0.651177	0.358378
4	6	0	5.372469	0.766489	0.342535
5	6	0	4.182069	1.460554	0.185060
6	6	0	2.999124	0.721037	0.040244
7	1	0	4.253289	-2.474649	0.229352
8	1	0	6.345150	-1.162813	0.484098
9	1	0	6.301278	1.314177	0.455093
10	1	0	4.163800	2.544546	0.172146
11	6	0	1.623216	1.119702	-0.139343
12	6	0	1.662844	-1.148031	-0.109323
13	8	0	1.112078	2.268434	-0.209648
14	8	0	1.193985	-2.315851	-0.161280
15	7	0	0.841187	-0.029700	-0.227383
16	35	0	-1.189546	-0.067141	-0.463045
17	6	0	-4.184729	0.032211	0.278703
18	8	0	-3.312375	-0.120917	-0.821900
19	6	0	-3.989168	-1.095512	1.314263
20	1	0	-2.982600	-1.060002	1.738425
21	1	0	-4.708389	-1.011725	2.135974
22	1	0	-4.123428	-2.070072	0.835662
23	6	0	-5.611829	-0.053407	-0.299048
24	1	0	-6.367515	0.048023	0.487519
25	1	0	-5.768937	0.740699	-1.034386
26	1	0	-5.758355	-1.015652	-0.797607
27	6	0	-3.995309	1.403575	0.961036
28	1	0	-4.708354	1.544072	1.780460
29	1	0	-2.985774	1.495035	1.369489
30	1	0	-4.142766	2.207192	0.233524

Zero-point correction= 0.224176 (Hartree/Particle)
Thermal correction to Energy= 0.241691
Thermal correction to Enthalpy= 0.242636
Thermal correction to Gibbs Free Energy= 0.176292
Sum of electronic and zero-point Energies= -758.902665
Sum of electronic and thermal Energies= -758.885150
Sum of electronic and thermal Enthalpies= -758.884206
Sum of electronic and thermal Free Energies= -758.950549

Structure comparison of S0(blue) and S1(red). RMSD: 0.169



N-bromophthalimide radical anion

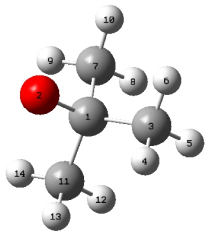


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.000015	1.354431	0.717155
2	6	0	0.000011	2.568883	1.423669
3	6	0	0.000043	3.757271	0.711630
4	6	0	0.000043	3.757271	-0.711630
5	6	0	0.000011	2.568883	-1.423669
6	6	0	-0.000015	1.354431	-0.717155
7	1	0	0.000010	2.570834	2.508530
8	1	0	0.000069	4.703351	1.242054
9	1	0	0.000069	4.703351	-1.242054
10	1	0	0.000010	2.570834	-2.508530
11	6	0	-0.000049	-0.004763	-1.200298
12	6	0	-0.000049	-0.004763	1.200298
13	8	0	-0.000032	-0.482400	-2.347079
14	8	0	-0.000032	-0.482400	2.347079
15	7	0	-0.000130	-0.768045	0.000000

16	35	0	0.000039	-2.673243	0.000000

Zero-point correction= 0.101514 (Hartree/Particle)
Thermal correction to Energy= 0.111219
Thermal correction to Enthalpy= 0.112163
Thermal correction to Gibbs Free Energy= 0.064346
Sum of electronic and zero-point Energies= -525.977509
Sum of electronic and thermal Energies= -525.967803
Sum of electronic and thermal Enthalpies= -525.966859
Sum of electronic and thermal Free Energies= -526.014677

t-butoxide radical



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.022851	0.000179	0.078789
2	8	0	-0.158896	-0.002651	1.449323
3	6	0	1.510957	-0.002327	-0.301056
4	1	0	2.002187	-0.890228	0.104903
5	1	0	1.644441	-0.000827	-1.386032
6	1	0	2.005865	0.882234	0.107740
7	6	0	-0.696373	1.268567	-0.457782
8	1	0	-0.590993	1.300435	-1.544962
9	1	0	-1.755717	1.247142	-0.198646
10	1	0	-0.243070	2.167942	-0.036409
11	6	0	-0.701359	-1.264188	-0.461263
12	1	0	-0.596050	-1.292875	-1.548547
13	1	0	-0.251355	-2.166508	-0.042715
14	1	0	-1.760597	-1.239502	-0.202044

Zero-point correction= 0.120153 (Hartree/Particle)

Thermal correction to Energy= 0.126406

Thermal correction to Enthalpy= 0.127350

Thermal correction to Gibbs Free Energy= 0.090751

Sum of electronic and zero-point Energies= -232.961837

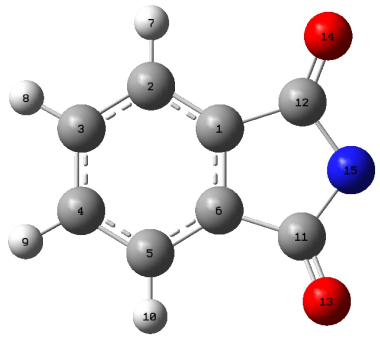
Sum of electronic and thermal Energies= -232.955584

Sum of electronic and thermal Enthalpies= -232.954640

Sum of electronic and thermal Free Energies= -232.991239

Recommended a0 for SCRF calculation = 4.06 angstrom

Phthalimide radical



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.005697	0.143289	0.701016
2	6	0	0.008087	1.327886	1.427831
3	6	0	0.001286	2.518789	0.703829
4	6	0	0.001286	2.518789	-0.703829
5	6	0	0.008087	1.327886	-1.427831
6	6	0	0.005697	0.143289	-0.701016
7	1	0	0.010775	1.324255	2.510532
8	1	0	-0.005814	3.465910	1.229816
9	1	0	-0.005814	3.465910	-1.229816
10	1	0	0.010775	1.324255	-2.510532
11	6	0	0.010888	-1.272686	-1.149464
12	6	0	0.010888	-1.272686	1.149464
13	8	0	-0.112315	-1.720310	-2.268322
14	8	0	-0.112315	-1.720310	2.268322
15	7	0	0.210804	-2.094673	0.000000

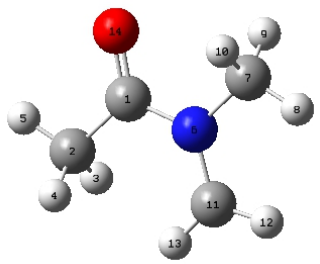
Zero-point correction= 0.100994 (Hartree/Particle)
Thermal correction to Energy= 0.109031
Thermal correction to Enthalpy= 0.109975
Thermal correction to Gibbs Free Energy= 0.066815
Sum of electronic and zero-point Energies= -512.446220
Sum of electronic and thermal Energies= -512.438184
Sum of electronic and thermal Enthalpies= -512.437240
Sum of electronic and thermal Free Energies= -512.480400

Bromo anion

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	35	0	0.000000	0.000000	0.000000

Zero-point correction= 0.000000 (Hartree/Particle)
Thermal correction to Energy= 0.001416
Thermal correction to Enthalpy= 0.002360
Thermal correction to Gibbs Free Energy= -0.016176
Sum of electronic and zero-point Energies= -13.557361
Sum of electronic and thermal Energies= -13.555945
Sum of electronic and thermal Enthalpies= -13.555001
Sum of electronic and thermal Free Energies= -13.573537

N,N-dimethylacetamide radical

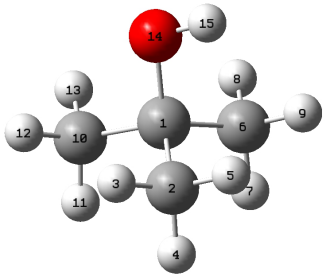


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.664759	-0.323024	-0.000047

2	6	0	-1.834516	0.631561	0.000071
3	1	0	-1.821776	1.277216	0.882864
4	1	0	-1.822464	1.276877	-0.882966
5	1	0	-2.751318	0.045880	0.000457
6	7	0	0.606554	0.222876	-0.000097
7	6	0	1.730274	-0.725516	-0.000010
8	1	0	2.660449	-0.162624	-0.001826
9	1	0	1.687266	-1.359783	0.885823
10	1	0	1.685189	-1.362071	-0.884057
11	6	0	0.875187	1.572965	0.000236
12	1	0	1.905603	1.885903	0.000234
13	1	0	0.066408	2.281773	-0.001338
14	8	0	-0.811544	-1.547401	-0.000002

Zero-point correction= 0.115499 (Hartree/Particle)
Thermal correction to Energy= 0.123259
Thermal correction to Enthalpy= 0.124203
Thermal correction to Gibbs Free Energy= 0.082985
Sum of electronic and zero-point Energies= -287.154576
Sum of electronic and thermal Energies= -287.146816
Sum of electronic and thermal Enthalpies= -287.145872
Sum of electronic and thermal Free Energies= -287.187091

t-butanol

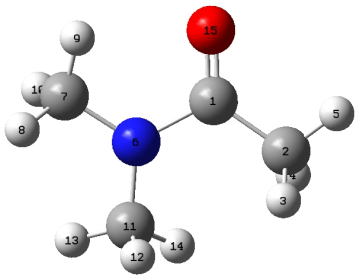


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.006713	0.000003	0.009767
2	6	0	0.676866	-1.263408	-0.527333
3	1	0	0.200974	-2.157482	-0.116916
4	1	0	0.614388	-1.307901	-1.618186
5	1	0	1.736241	-1.279254	-0.251590
6	6	0	0.676093	1.263934	-0.527103

7	1	0	0.613540	1.308614	-1.617945
8	1	0	0.199685	2.157637	-0.116480
9	1	0	1.735469	1.280358	-0.251403
10	6	0	-1.498422	-0.000424	-0.322665
11	1	0	-1.650590	-0.000380	-1.404549
12	1	0	-1.982235	-0.887193	0.094473
13	1	0	-1.982778	0.885980	0.094619
14	8	0	0.055619	-0.000114	1.458739
15	1	0	0.983417	-0.000092	1.722070

Zero-point correction= 0.134595 (Hartree/Particle)
Thermal correction to Energy= 0.141383
Thermal correction to Enthalpy= 0.142327
Thermal correction to Gibbs Free Energy= 0.105547
Sum of electronic and zero-point Energies= -233.622356
Sum of electronic and thermal Energies= -233.615568
Sum of electronic and thermal Enthalpies= -233.614624
Sum of electronic and thermal Free Energies= -233.651403

N,N-dimethylacetamide radical cation

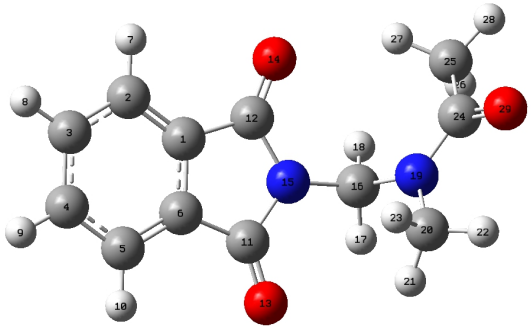


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.785090	-0.320787	0.000689
2	6	0	1.814695	0.759079	-0.029004
3	1	0	1.633117	1.466370	-0.840293
4	1	0	1.814390	1.312423	0.914221
5	1	0	2.786263	0.288885	-0.161363
6	7	0	-0.635144	0.101689	-0.003952
7	6	0	-1.663016	-0.908388	-0.034644
8	1	0	-2.452310	-0.585208	-0.718047
9	1	0	-1.241594	-1.869921	-0.307822

10	1	0	-2.105656	-0.971272	0.971026
11	6	0	-1.022074	1.492470	0.034507
12	1	0	-0.969954	1.890162	-0.991128
13	1	0	-2.046232	1.579206	0.390182
14	1	0	-0.335841	2.067283	0.654608
15	8	0	0.984456	-1.502999	0.035875

Zero-point correction= 0.127326 (Hartree/Particle)
Thermal correction to Energy= 0.135234
Thermal correction to Enthalpy= 0.136178
Thermal correction to Gibbs Free Energy= 0.094665
Sum of electronic and zero-point Energies= -287.543283
Sum of electronic and thermal Energies= -287.535374
Sum of electronic and thermal Enthalpies= -287.534430
Sum of electronic and thermal Free Energies= -287.575943

Radical-radical coupling product

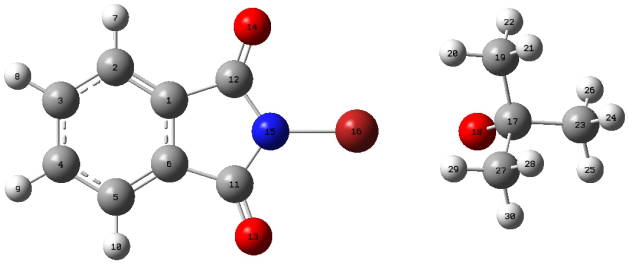


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.811709	-0.776915	-0.024080
2	6	0	2.794791	-1.688401	0.325519
3	6	0	4.073067	-1.185072	0.592893
4	6	0	4.342516	0.184492	0.507142
5	6	0	3.342836	1.097148	0.151293
6	6	0	2.080629	0.589146	-0.110283
7	1	0	2.582296	-2.748466	0.390071
8	1	0	4.868121	-1.866594	0.871022
9	1	0	5.342356	0.543604	0.720161
10	1	0	3.547833	2.158501	0.083596
11	6	0	0.826118	1.287602	-0.505263

12	6	0	0.378778	-0.992284	-0.367087
13	8	0	0.637006	2.467653	-0.703421
14	8	0	-0.244050	-2.029518	-0.437766
15	7	0	-0.152401	0.282821	-0.622767
16	6	0	-1.538562	0.534160	-1.021456
17	1	0	-1.535341	1.496328	-1.534878
18	1	0	-1.833451	-0.239537	-1.722498
19	7	0	-2.463205	0.578761	0.095121
20	6	0	-2.295841	1.679393	1.048210
21	1	0	-1.918959	2.553599	0.517357
22	1	0	-3.257091	1.911195	1.500683
23	1	0	-1.591904	1.419226	1.844781
24	6	0	-3.409992	-0.381384	0.357774
25	6	0	-3.615947	-1.493322	-0.652784
26	1	0	-3.922699	-1.097291	-1.624453
27	1	0	-2.704947	-2.078445	-0.791366
28	1	0	-4.404720	-2.139920	-0.274013
29	8	0	-4.093315	-0.321966	1.378910

Zero-point correction= 0.226319 (Hartree/Particle)
Thermal correction to Energy= 0.241767
Thermal correction to Enthalpy= 0.242711
Thermal correction to Gibbs Free Energy= 0.182213
Sum of electronic and zero-point Energies= -799.735744
Sum of electronic and thermal Energies= -799.720296
Sum of electronic and thermal Enthalpies= -799.719352
Sum of electronic and thermal Free Energies= -799.779850

EDA complex TS



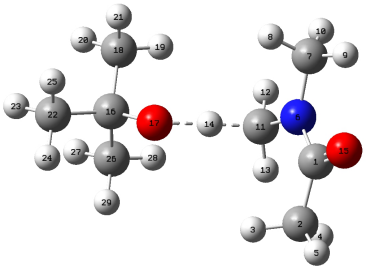
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.086344	0.707528	0.050614

2	6	0	-4.246117	1.452931	0.183539
3	6	0	-5.450255	0.752071	0.329820
4	6	0	-5.473355	-0.645761	0.340412
5	6	0	-4.293076	-1.388240	0.205237
6	6	0	-3.109290	-0.683735	0.061434
7	1	0	-4.223102	2.536112	0.174766
8	1	0	-6.379213	1.300277	0.436709
9	1	0	-6.419944	-1.161239	0.455248
10	1	0	-4.305853	-2.471610	0.212783
11	6	0	-1.698718	-1.161959	-0.102777
12	6	0	-1.660918	1.136380	-0.121144
13	8	0	-1.314492	-2.315977	-0.138322
14	8	0	-1.238862	2.276423	-0.174992
15	7	0	-0.896278	-0.026457	-0.207646
16	35	0	0.989285	-0.057569	-0.416948
17	6	0	4.492316	0.022766	0.214233
18	8	0	3.602876	-0.117627	-0.859356
19	6	0	4.317511	1.389204	0.919008
20	1	0	3.307850	1.480338	1.328912
21	1	0	5.032082	1.522519	1.739769
22	1	0	4.464992	2.200593	0.199298
23	6	0	5.926469	-0.059126	-0.355488
24	1	0	6.686269	0.034454	0.429665
25	1	0	6.071782	-1.017231	-0.863720
26	1	0	6.085121	0.740119	-1.085945
27	6	0	4.308602	-1.108455	1.254012
28	1	0	5.029804	-1.030956	2.076008
29	1	0	3.302011	-1.075463	1.679985
30	1	0	4.440061	-2.081979	0.771193

Zero-point correction= 0.226278 (Hartree/Particle)
Thermal correction to Energy= 0.243296
Thermal correction to Enthalpy= 0.244240
Thermal correction to Gibbs Free Energy= 0.178517
Sum of electronic and zero-point Energies= -758.997338
Sum of electronic and thermal Energies= -758.980321
Sum of electronic and thermal Enthalpies= -758.979376
Sum of electronic and thermal Free Energies= -759.045100

Imaginary frequency (1): -44.37

HAT TS

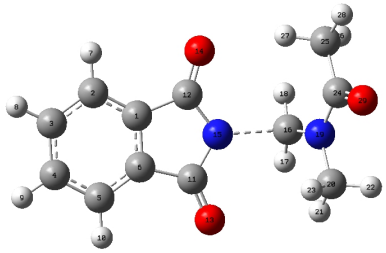


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.739827	-0.412638	0.182421
2	6	0	2.489249	-1.860245	-0.183157
3	1	0	1.488364	-2.181134	0.114249
4	1	0	2.587953	-2.020916	-1.259801
5	1	0	3.228576	-2.468222	0.333518
6	7	0	1.888461	0.539546	-0.349561
7	6	0	2.053479	1.938577	0.052257
8	1	0	1.348769	2.195879	0.848706
9	1	0	3.066680	2.088886	0.413038
10	1	0	1.867113	2.582201	-0.808343
11	6	0	0.719831	0.213567	-1.087751
12	1	0	0.419366	1.038290	-1.732669
13	1	0	0.804396	-0.716793	-1.642078
14	1	0	-0.216735	0.043586	-0.311237
15	8	0	3.671326	-0.088573	0.912537
16	6	0	-2.484793	-0.067999	0.127930
17	8	0	-1.168924	-0.178812	0.639804
18	6	0	-2.769979	1.365387	-0.351221
19	1	0	-2.123696	1.627594	-1.193368
20	1	0	-3.808201	1.470386	-0.678911
21	1	0	-2.587945	2.077827	0.457163
22	6	0	-3.385251	-0.407650	1.337772
23	1	0	-4.436525	-0.348918	1.041980
24	1	0	-3.177807	-1.417992	1.696576
25	1	0	-3.211585	0.297557	2.153350
26	6	0	-2.720881	-1.084141	-1.002281
27	1	0	-3.758072	-1.051369	-1.347565
28	1	0	-2.075091	-0.866839	-1.857861
29	1	0	-2.502894	-2.096906	-0.654368

Zero-point correction= 0.247960 (Hartree/Particle)
Thermal correction to Energy= 0.262991
Thermal correction to Enthalpy= 0.263935
Thermal correction to Gibbs Free Energy= 0.203140
Sum of electronic and zero-point Energies= -520.753031
Sum of electronic and thermal Energies= -520.738001
Sum of electronic and thermal Enthalpies= -520.737057
Sum of electronic and thermal Free Energies= -520.797851

Imaginary frequency (1): -1050.53

Radical-radical coupling TS



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.993792	-0.736850	-0.043111
2	6	0	3.054067	-1.581815	0.237122
3	6	0	4.288958	-0.990026	0.533262
4	6	0	4.438611	0.399717	0.544368
5	6	0	3.358543	1.245278	0.259310
6	6	0	2.143245	0.649837	-0.032456
7	1	0	2.935085	-2.658706	0.227769
8	1	0	5.143194	-1.618277	0.757416
9	1	0	5.406579	0.828156	0.777034
10	1	0	3.471477	2.322854	0.266839
11	6	0	0.808465	1.244781	-0.378595
12	6	0	0.563430	-1.031404	-0.395608
13	8	0	0.527169	2.427352	-0.495165
14	8	0	0.042953	-2.129437	-0.526026
15	7	0	-0.063505	0.187505	-0.548223
16	6	0	-1.947894	0.454222	-1.185087
17	1	0	-1.703304	1.358876	-1.721956

18	1	0	-1.994461	-0.457093	-1.759655
19	7	0	-2.798091	0.586364	-0.143019
20	6	0	-2.891184	1.879943	0.553990
21	1	0	-2.441846	2.644025	-0.075210
22	1	0	-3.935632	2.116709	0.745285
23	1	0	-2.356818	1.834268	1.504339
24	6	0	-3.469384	-0.512766	0.444434
25	6	0	-3.355644	-1.854575	-0.229929
26	1	0	-3.761615	-1.818591	-1.244379
27	1	0	-2.313097	-2.179810	-0.291126
28	1	0	-3.929972	-2.569466	0.354996
29	8	0	-4.119927	-0.325174	1.452584

Zero-point correction= 0.223655 (Hartree/Particle)
Thermal correction to Energy= 0.238938
Thermal correction to Enthalpy= 0.239883
Thermal correction to Gibbs Free Energy= 0.179647
Sum of electronic and zero-point Energies= -799.698534
Sum of electronic and thermal Energies= -799.683251
Sum of electronic and thermal Enthalpies= -799.682307
Sum of electronic and thermal Free Energies= -799.742542