Supporting Information

A diversity-Oriented Synthesis of Polyheterocycles *via* Cyclocondensation of Azomethine Imine

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S1. General Considerations

All the reactions were carried out using dried reaction vessel with Teflon screw caps. Ortho-substituted benzaldehyde was synthesized by reported literature.[1] Aryl sulfonyl hydrazides were also synthesized by previously described protocol.[2] Other substrates such as isocyanides, allenoates, α-halohydroxamates and aliphatic cyclicketones were purchased from Sigma, TCI, and spectrochem used as such without any further purification. THF and toluene were freshly dried and distilled kept under an inert atmosphere. Other reagents were purchased from Aldrich or Spectrochem used as such without purification. Analytical TLC was performed using 2 x 4 cm plate coated with a 0.25mm thickness of silica gel (60F-254 Merck), and visualization was accomplished with UV light or I_2/ $KMnO_4$ staining. Melting points were uncorrected. ^{1}H, ^{13}C NMR, Recorded on Bruker's Ascend 500MHz spectrophotometer operating at 500.3 MHz for ^{1}H and 125.8 MHz for ^{13}C experiments; spectra were recorded at 295 K in $CDCl_3$; chemical shifts were calibrated to the residual proton and carbon resonance of the solvent: $CDCl_3$ (^{1}H δ 7.269; ^{13}C δ 77.0). Mass spectra were recorded on electrospray ionization

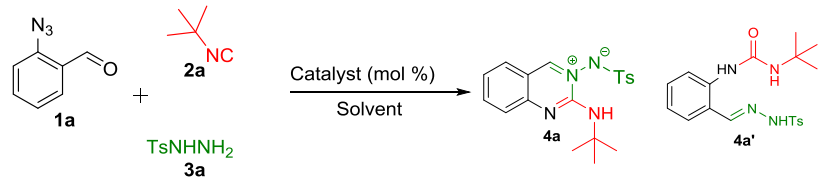
quadrupole time of flight (ESI-QTOF-MS). The abbreviations used: s=singlet, d=doublet, t=triplet, q=quartet, dd=double doublet, m=multiplet, br s = broad singlet & br = broad signal.

S2. Synthesis of azomethine imine 4

S2.1. Detailed Screening of 3-CR for the synthesis of azomethine imine

Initially, we started with the screening of various parameters for the synthesis of azomethine amine from a mixture of 2-azidobenzaldehyde **1a**, *tert*-butyl isocyanide **2a** and tosyl hydrazide **3a** in toluene at ambient temperature. At the outset, different palladium sources were examined as a catalyst in this reaction. Of these, $Pd(OAc)_2$ produced the azomethine imine **4a** in 51% yield in (table 1, entry 1). In contrast, other Pd-salts such as $Pd(PPh_3)_4$, $Pd(PPh_3)_2Cl_2$, $PdCl_2$, and $Pd_2(dba_3)$ filed to promote this reaction (entry 2-5). The presence of a nagging side product, urea **4a'**, was observed, which was successfully ruled out by employing 4 Å molecular sieves (entry 6). On the basis of a survey of different solvents, toluene gave the best result with 85 % yield of **4a** (entry 6-11). The reaction stumbled in DMF (entry 12). The efficiency was not affected when the catalytic amount of $Pd(OAc)_2$ was reduced to 7.5 mol% (entry13). However, the further reduction in catalytic loading had a detrimental effect on the overall yield of the title compound (entry 14). Reaction failed to initiate in the absence of a catalyst (entry 15). After screening the solvent, it was found that toluene and THF are acting as the best solvent for the reaction.

Table S1: Optimization of 3-CR for the synthesis of azomethine imine[a]



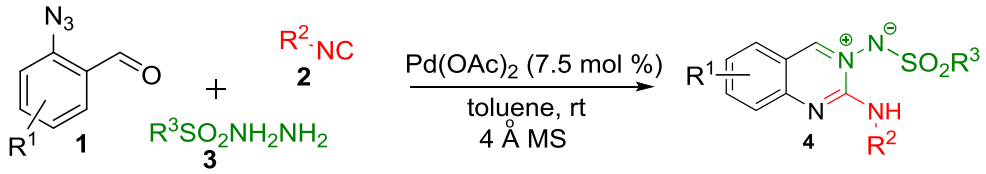
Entry	Catalyst	Additive	Solvent	Isolated yield[b]	
				4a	4a'
1.	$Pd(OAc)_2$(10 mol%)	-	toluene	51	41
2.	$Pd(PPh_3)_4$ (10 mol%)	-	toluene	35[c]	55
3.	$Pd(PPh_3)_2Cl_2$(10 mol%)	-	toluene	23[c]	36
4.	$PdCl_2$ (10 mol%)	-	toluene	0[c]	0
5.	$Pd_2(dba)_3$ (10 mol%)	-	toluene	15[c]	10
6.	$Pd(OAc)_2$ (10 mol%)	4 Å MS	toluene	85	-
7.	$Pd(OAc)_2$ (10 mol%)	4 Å MS	THF	82	-
8.	$Pd(OAc)_2$(10 mol%)	4 Å MS	MeCN	5[c]	-
9.	$Pd(OAc)_2$(10 mol%)	4 Å MS	DMSO	43[c]	-
10.	$Pd(OAc)_2$(10 mol%)	4 Å MS	Dioxane	56	-
11.	$Pd(OAc)_2$(10 mol%)	4 Å MS	DCE	45[c]	-
12.	$Pd(OAc)_2$(10 mol%)	4 Å MS	DMF	0	-
13.	$Pd(OAc)_2$ (7.5 mol%)	4 Å MS	THF	86	-
14.	$Pd(OAc)_2$ (5 mol%)	4 Å MS	THF	75	-
15.	-	4 Å MS	THF	0[c]	-

[a]Reaction Condition: 2-azidobenzaldehyde (0.10 mmol), isocyanide (0.12 mmol), tosylhydrazide, catalyst, solvent (1 ml) at room temperature. [b]Isolated yield after column chromatography. [C]**1a** recovered.

S2.2. Experimental procedure for the synthesis of azomethine imine 4

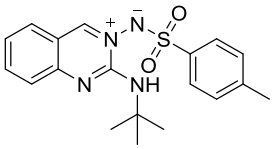
To a 10 mL reaction vial was charged with 2-azidobenzaldehyde **1** (1.0 equiv), *tert*-butylisocyanide **2** (1.2 equiv), $Pd(OAc)_2$ (7.5 mol %,), 4 Å MS and aryl sulfonyl hydrazide **3** (1.1 equiv.) in toluene at

room temperature. After stirring for 30 min at room temperature, starting material was completely disappeared and a yellow suspension was obtained. The suspension was then quenched by water and extracted with EtOAc (3x15ml). After removal of solvents in vacuo, the residue was subjected to column chromatography on silica gel (100-200 mesh) using 20:80 EtOAc and hexane as eluent to give desired product **4**.



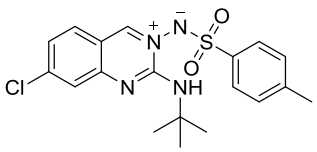
S2.3. Analytical data of compound 4

4a. (2-(*tert*-butylamino)quinazolin-3-ium-3-yl)(tosyl)amide



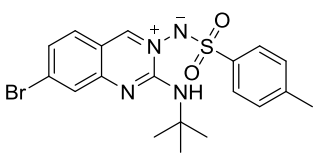
Prepared by following experimental procedure **S2.2**. Yellow solid, Yield: 0.214 g (85%); R_f = 0.4 (EtOAc/hexanes: 20/80 **^{1}H NMR (δ ppm):** (500 MHz, $CDCl_3$), 9.39 (s, 1H), 7.85 (t, 1H, *J* = 7.5 Hz), 7.77 (d, 1H, *J* = 5 Hz), 7.60 (d, 1H, *J* = 5 Hz) 7.53 (d, 2H, *J* = 5 Hz), 7.39 (t, 1H, *J* = 10 Hz), 7.20 (s, 1H), 7.17 (d, 2H, *J* = 5 Hz), 2.35 (s, 3H), 1.18 (s, 9H). **^{13}C{^{1}H} NMR (δ ppm):** (125 MHz, $CDCl_3$), 154.8, 150.3, 148.2, 141.7, 141.1, 137.9, 129.6, 128.7, 126.1, 126.0, 124.9, 117.2, 52.2, 27.6, 21.3. **HRMS** (EI) calcd for $C_{19}H_{23}N_4O_2S$ ($M+H^+$) 371.1536, found 371.1529

4b. (2-(*tert*-butylamino)-7-chloroquinazolin-3-ium-3-yl)(tosyl)amide



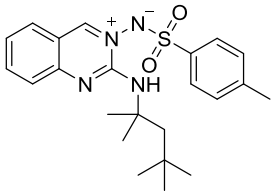
Prepared by following experimental procedure **S2.2**.Yellow solid, Yield: 0.178 g (73%); R_f = 0.4 (EtOAc/hexanes: 20/80); **^{1}H NMR (δ ppm):** (500 MHz, $CDCl_3$), 9.40 (s, 1H), 7.73 (d, 1H, *J* = 7.5 Hz), 7.64 (s, 1H), 7.55 (d, 2H, *J* = 8.7 Hz) 7.36-7.34 (m, 2H), 7.20 (d, 2H, *J* = 8.0 Hz), 2.38 (s, 3H), 1.20 (s, 9H). **^{13}C{^{1}H} NMR (δ ppm):** (125 MHz, $CDCl_3$), 154.3, 150.4, 148.5, 144.8, 141.8, 129.8, 129.6, 128.6, 126.3, 126.1, 125.3, 115.5, 52.4, 27.5, 21.3; **HRMS** (EI) calcd for $C_{19}H_{22}ClN_4O_2S$ ($M+H^+$) 405.1147, found 405.1149.

4c. (7-bromo-2-(*tert*-butylamino)quinazolin-3-ium-3-yl)(tosyl)amide



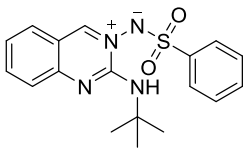
Prepared by following experimental procedure **S2.2**. Yield: 0.156 g (79%); R_f = 0.4 (EtOAc/hexanes: 20/80); **^{1}H NMR (δ ppm):** (500 MHz, $CDCl_3$), 9.40 (s, 1H), 7.84 (s, 1H), 7.65 (d, 1H, *J* = 8.7 Hz), 7.55 (d, 2H, *J* = 8.2 Hz) 7.49 (dd, 1H, *J* = 1.5, 8.7 Hz), 7.35 (br s, 1H), 7.20 (d, 2H, *J* = 8.0 Hz), 2.38 (s, 3H), 1.20 (s, 9H). **^{13}C{^{1}H} NMR (δ ppm):** (125 MHz, $CDCl_3$), 154.4, 150.2, 148.7, 141.8, 140.9, 133.8, 129.6, 129.5, 128.9, 128.6, 126.1, 115.7, 52.5, 27.5, 21.3. **HRMS** (EI) calcd for $C_{19}H_{22}BrN_4O_2S$ ($M+H^+$) 449.0642 found 449.0631.

4d. tosyl(2-((2,4,4-trimethylpentan-2-yl)amino)quinazolin-3-ium-3-yl)amide



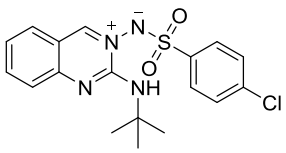
Prepared by following experimental procedure **S2.2**.Yellow solid, Yield: 0.252 g (86%); R_f = 0.4 (EtOAc/hexanes: 20/80); **^{1}H NMR (δ ppm):** (500 MHz, $CDCl_3$), 10.15 (s, 1H), 7.79 (d, 1H, *J* = 10 Hz), 7.22 (d, 2H, *J* = 10 Hz), 6.69 (d, 2H, *J* = 10 Hz), 6.64 (t, 1H, *J* =10 Hz), 6.43 (d, 1H, *J* =7 Hz) 6.27 (t, 1H, *J* = 10 Hz), 4.47 (s, 1H), 1.79 (s, 3H), 1.28 (s, 2H,), 0.90 (s, 6H), 0.47 (s, 9H). **^{13}C{^{1}H} NMR (δ ppm):** (125 MHz, $CDCl_3$), 154.4, 149.1, 144.6, 140.3, 135.5, 131.8, 131.2, 130.0, 127.3, 120.5, 118.6, 117.7, 54.7, 51.4, 31.6, 31.4, 30.0, 21.6. **HRMS** (EI) calcd for $C_{23}H_{31}N_4O_2S$ ($M+H^+$) 427.2162 found 427.2155.

4e. (2-(*tert*-butylamino)quinazolin-3-ium-3-yl)(phenylsulfonyl)amide



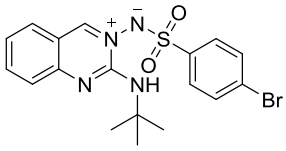
Prepared by following experimental procedure **S2.2**. Yield: 0.176 g (73%); R_f = 0.3 (EtOAc/hexanes: 20/80); **^{1}H NMR (δ ppm):** (500 MHz, $CDCl_3$), 9.41 (s, 1H), 7.87 (t, 1H, *J* = 7.6 Hz), 7.80 (d, 1H, *J* = 8.1 Hz), 7.67 (d, 2H, *J* = 7.4 Hz), 7.62 (d, 1H, *J* = 8.5 Hz) 7.47 (t, 1H, *J* = 7.4 Hz), 7.40 (t, 3H, *J* = 7.5 Hz), 7.19 (br s, 1H), 1.18 (s, 9H). **^{13}C{^{1}H} NMR (δ ppm):** (125 MHz, $CDCl_3$), 154.9, 150.4, 148.2, 144.1, 138.1, 131.2, 129.1, 128.8, 128.6, 126.1, 125.1, 117.2, 52.2, 27.6. **HRMS** (EI) calcd for $C_{18}H_{21}N_4O_2S$ ($M+H^+$) 357.138 found 357.1357.

4f. (2-(*tert*-butylamino)quinazolin-3-ium-3-yl)((4-chlorophenyl)sulfonyl)amide (4h)



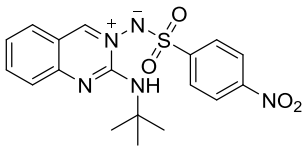
Prepared by following experimental procedure **S2.2**. Yield: 0.199 g (75%); R_f = 0.4 (EtOAc/hexanes: 20/80); **^{1}H NMR (δ ppm):** (500 MHz, $CDCl_3$), 9.39 (s, 1H), 7.89 (t, 1H, *J* = 8.3 Hz), 7.82 (d, 1H, *J* = 8.7 Hz), 7.63-7.59 (m, 2H, *J* = 8.6 Hz), 7.46 (d, 1H, *J* = 8.2 Hz), 7.41 (t, 1H, *J* = 8.2 Hz) 7.37 (d, 2H, *J* = 8.2 Hz), 7.13 (br, s, 1H), 1.23 (s, 9H). **^{13}C{^{1}H} NMR (δ ppm):** (125 MHz, $CDCl_3$), 155.1, 150.6, 148.1, 142.5, 138.3, 137.5, 129.2, 128.9, 127.6, 126.1, 125.2, 117.2, 52.4, 27.7. **HRMS** (EI) calcd for $C_{18}H_{20}ClN_4O_2S$ ($M+H^+$) 391.099 found 391.0975.

4g. (2-(*tert*-butylamino)quinazolin-3-ium-3-yl)((4-iodophenyl)sulfonyl)amide



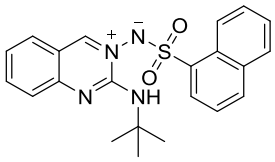
Prepared by following experimental procedure **S2.2**. Yield: 0.206 g (70%); R_f = 0.4 (EtOAc/hexanes: 20/80); **^{1}H NMR (δ ppm):** (500 MHz, $CDCl_3$), 9.39 (s, 1H), 7.88 (t, 1H, *J* = 8.3 Hz), 7.82 (d, 2H, *J* = 8.7 Hz), 7.63 (d, 2H, *J* = 8.6 Hz), 7.52 (s, 2H), 7.42 (t, 1H, *J* = 8.2 Hz), 7.11 (br, s, 1H), 1.22 (s, 9H). **^{13}C{^{1}H} NMR (δ ppm):** (125 MHz, $CDCl_3$), 155.1, 150.6, 148.0, 143.0, 138.3, 132.2, 128.9, 127.8, 126.1, 125.9, 125.2, 117.2, 52.4, 27.7. **HRMS** (EI) calcd for $C_{18}H_{20}BrN_4O_2S$ ($M+H^+$) 435.0485 found 435.0464.

4h. (2-(*tert*-butylamino)quinazolin-3-ium-3-yl)((4-nitrophenyl)sulfonyl)amide



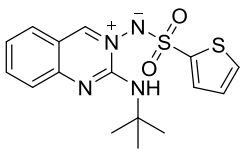
Prepared by following experimental procedure **S2.2**. Yield: 0.177 g (65%); R_f = 0.4 (EtOAc/hexanes: 20/80); **^{1}H NMR (δ ppm):** (500 MHz, CDCl3), 9.39 (s, 1H), 8.27 (d, 2H, *J* = 8.7 Hz), 7.94 (t, 1H, *J* = 8.3 Hz), 7.87 (d, 2H, *J* = 8.6 Hz), 7.83 (d, 1H, *J* = 8.2 Hz), 7.68 (d, 1H, *J* = 8.5 Hz), 7.47 (t, 1H, *J* = 8.2 Hz), 7.09 (br s, 1H), 1.20 (s, 9H). **13C{1H} NMR (δ ppm):** (125 MHz, $CDCl_3$), 154.7, 150.7, 150.1, 149.2, 147.9, 138.6, 128.8, 127.3, 126.3, 125.5, 125.2, 117.2, 54.5, 27.8. **HRMS** (EI) calcd for $C_{18}H_{20}N_5O_4S$ ($M+H^+$) 402.1231 found 402.1237

4i. (2-(*tert*-butylamino)quinazolin-3-ium-3-yl)(naphthalen-1-ylsulfonyl)amide



Prepared by following experimental procedure **S2.2**.Yield: 0.207 g (75%); R_f = 0.4 (EtOAc/hexanes: 20/80); **^{1}H NMR (δ ppm):** (500 MHz, $CDCl_3$), 9.44 (s, 1H), 9.10 (d, 1H, *J* = 8.6 Hz), 7.95 (d, 2H, *J* = 8.2 Hz), 7.85 (d, 2H, *J* = 7.3 Hz), 7.80 (d, 1H, *J* = 8.2 Hz), 7.70 (t, 1H, *J* = 7.15 Hz), 7.61 (t, 1H, *J* = 7.2 Hz), 7.56 (d, 1H, *J* = 8.7 Hz), 7.40 (t, 1H, *J* = 7.3 Hz), 7.34 (t, 1H, *J* = 7.9 Hz), 6.87 (s, 1H), 0.72 (s, 9H). **^{13}C{^{1}H} NMR (δ ppm):** (125 MHz, $CDCl_3$), 155.3, 150.4, 148.2, 138.9, 137.9, 134.5, 132.5, 128.9, 128.7, 128.5, 128.3, 127.5, 126.7, 126.0, 125.7, 124.9, 124.2, 117.1, 51.9, 27.1. **HRMS** (EI) calcd for $C_{22}H_{23}N_4O_2S$ ($M+H^+$) 407.1536 found 407.1523.

4j. (2-(*tert*-butylamino)quinazolin-3-ium-3-yl)(thiophen-2-ylsulfonyl)amide



Prepared by following experimental procedure **S2.2**. Yellow solid, Yield: 0.192 g (78%); R_f = 0.5 (EtOAc/hexanes: 20/80); **^{1}H NMR (δ ppm):** (500 MHz, $CDCl_3$), 9.37 (s, 1H), 7.87 (t, *J* = 1.5 Hz), 7.77 (d, 1H *J* = 10 Hz), 7.62 (d, 1H, *J* = 5 Hz), 7.41-7.38 (m, 2H), 7.27-7.26 (m, 2H), 6.97-6.95 (m, 1H), 1.29 (s, 9H,). **^{13}C{^{1}H} NMR (δ ppm):** (125 MHz, $CDCl_3$), 154.7, 150.6, 148.2, 145.4, 138.2, 130.5, 129.3, 128.8, 127.3, 126.1, 125.1, 117.1, 52.4, 27.8. **HRMS (EI)** calcd for $C_{16}H_{19}N_4O_2S_2$ ($M+H^+$) 363.0944 found 363.0954.

S2.4. Crytallographic data of compound 4f

Colourless crystals of compounds **4f** were grown by slow evaporation of mixed solvents of petroleum ether and dichloromethane at room temperature. The determination of unit cell and intensity data collection was performed using a Xcalibur, Atlas diffractometer at 293(2) K. Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm was performed with CrysAlisPro 1.171.38.46 (Rigaku Oxford Diffraction, 2015). Structure was solved with the SHELXT (Sheldrick, 2015) and refined with the SHELXL (Sheldrick, 2015). Crystallographic data (excluding structure factors) for the structures in this manuscript have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1894385 (for **4f**).

This data can be obtained free of charge from the Cambrige Crystallographic Data Centers via www.ccdc.cam.ac.uk/data_request/cif.

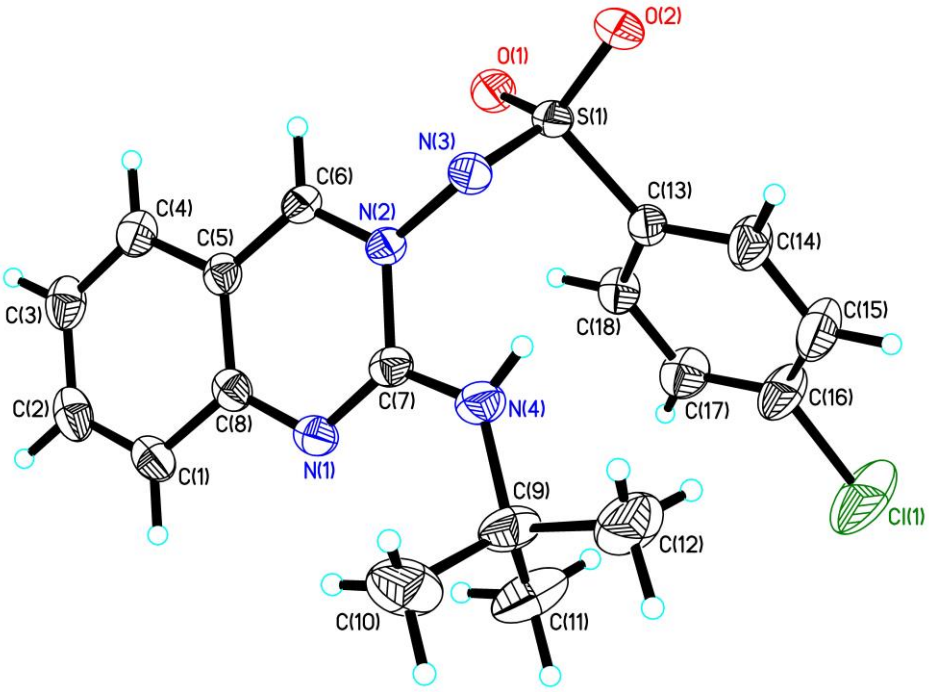


Figure 1. The X-ray crystal structure of compound **4f** showing with ORTEP diagram using 50% ellipsoidal plot.

Structure refinement for 4f

Identification Code	CCDC No. 1895385
Emperical formula	$C_{18}H_{19}ClN_4O_2S$
Formula Weight	390.88
Crystal System	triclinic
Space group	P -1
a/Å	7.6748(4)
b/Å	9.3670(4)
c/Å	13.8037(6)
α/°	84.937(4)
β/°	89.503(4)
γ/°	80.948(4)
V	976.15(8) $Å^3$
Temperature	293(2) K

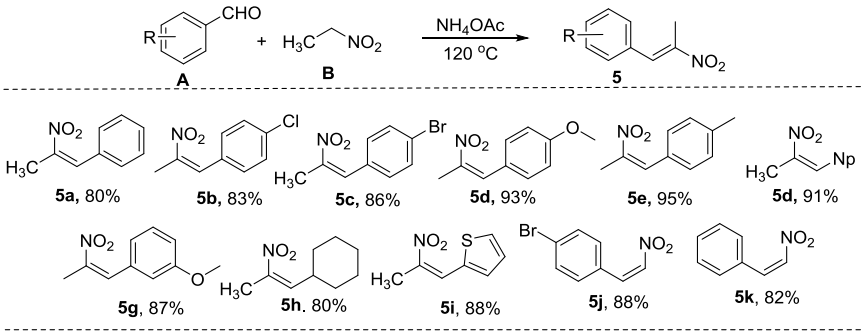
Z	2
μ	0.29 mm^{-1}
F(000)	408.0
D_c	1.330 Mg m^{-1}
Crystal size	0.30 x 0.25 x 0.15 mm
Reflections measured	8061
Unique	3621
R1	0.0454 for 3479 $F_o > 4\sigma(F_o)$ and 0.0631 for all 4530 data and 242 parameters

Unit cell determination and intensity data collection was performed with 83 % completeness at 293 (2) K. Structure solutions by direct methods and refinements by full-matrix least-squares methods on F_2

S3. Synthesis of Compound 6

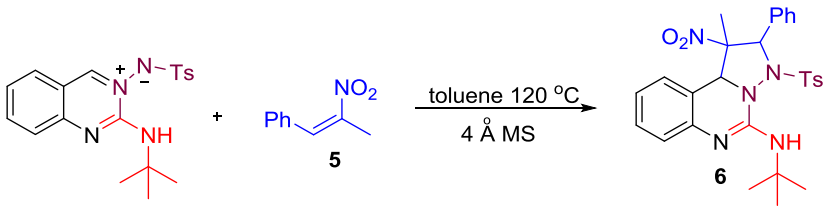
3.1. Experimental procedure for the synthesis of *β*-aryl nitroalkenes 5:

To a 50 mL round-bottomed flask equipped with a condenser was charged aryl aldehyde (10 mmol), ammonium acetate (13 mmol) and 1-nitroethane (30 mL). The mixture was stirred and refluxed at 120 ^{o}C for 2 hours and then concentrated. The residue was re-dissolved in CH_2Cl_2 (50 mL), washed sequentially with brine and water (50 ml), dried over Na_2SO_4. The crude product was purified *via* SiO_2 flash chromatography, using 0 – 5% ethyl acetate in pet ether as eluent, to afford *β*-aryl nitroalkenes. (Yields: 80–95%).



S3.2. Screening of 4-CR for the synthesis of 6[a]

Initially, we started a reaction with azomethine amine and nitro olefins in toluene catalytic amount of palladium acetate at 120 ^{o}C pleasingly we found the desired product in 90 % yield. In the absence of catalyst reaction well proceed without decreasing the yield. Further, we screened different solvents such as THF, DCE, DMSO, dioxane, and toluene. The highest yield of **6** was obtained in toluene which concluded that toluene was the best optimal solvent for this reaction.

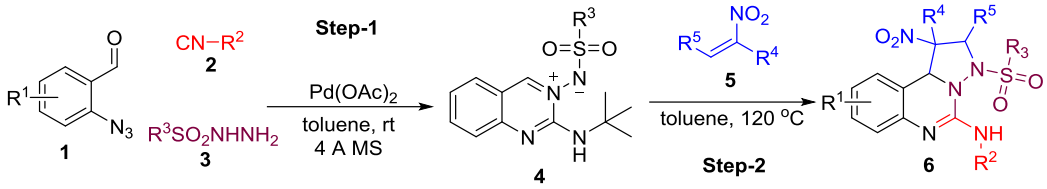


S. No.	Catalyst	solvent	temp (^{o}C)	Time (h)	Yield[b] (%)
1.	$Pd(OAc)_2$	toluene	110	2	90
2.	-	toluene	110	2	88
3.	-	DMSO	110	2	75
4.	-	THF	110	2	68
5.	-	1,4-dioxane	110	2	65
6.	-	DCE	110	2	80
7.	-	-	110	2	0
8.	-	toluene	60	28	50
9.	-	toluene	Rt	48	0

[a]All reaction was carried out using 1.0 mmol 2-azidoaldehyde, 1.2 mmol *tert*-butyl isocyanide, 1.0 mmol tosylhydrazide and 0.65 mmol nitro olefins using standard schlenk techniques. the [b]Isolated yield of **6**.

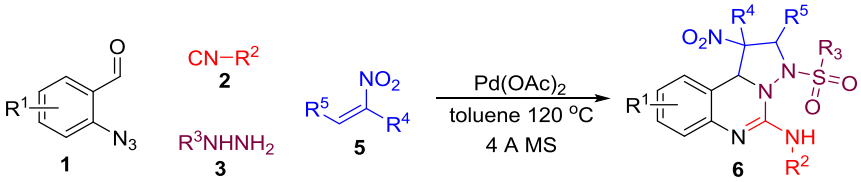
S3.3. Experimental procedure for *sequential* synthesis of 6 (Method A):

In a 20 mL Schlenk tube Azomethine imine (1.0 equiv.) **4** and nitro olefin (0.65 equiv) was dissolved in toluene and reaction was stirred at 120 °C for 2 h. The reaction mixture was diluted with ethyl acetate (15 mL) and extracted with water, organic layer evaporated under vaccum. The crude product was purified by column chromatography to afford the desired product **6**.



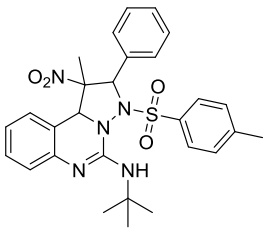
3.4. Experimental procedure for *one-pot* synthesis of 6 (Method B):

2-Azidobenzaldehyde (1.0 equiv), isocyanide (1.2 equiv), $Pd(OAc)_2$ (7.5 mol %), 4Å MS, Aryl sulfonyl hydrazide (1.1 equiv.), and nitro olefin (0.65 equiv.) toluene were added to a 20 mL Schlenk tube. The formed mixture was stirred at 120 °C for 2 h. The reaction mixture was diluted with ethyl acetate (15 mL) and extracted with water, organic layer evaporated under vaccum. The crude product was purified by column chromatography to afford the desired product **6**.



S3.5. Analytical data of compound 6

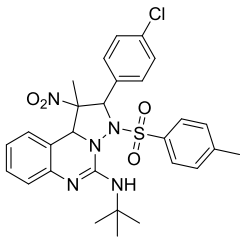
6a. N-(*tert*-butyl)-1-methyl-1-nitro-2-phenyl-3-tosyl-1,2,3,10b-tetrahydropyrazolo[1,5-*c*]quinazolin-5-amine



Yellow solid, Yield: (Method A: 0.14g, 82%, Method B: 012 g, 71%) m.p.: 168−170 °C, **^{1}H NMR (δ ppm)**: (500 MHz, $CDCl_3$),7.98 (d, 1H, *J* = 8.2 Hz), 7.45(d, 2H, *J* = 8.05 Hz), 7.42-7.38 (m, 3H), 7.37-7.32 (m, 2H), 7.19 (t, 1H, *J* = 7.2 Hz), 7.04 (d, 1H, *J* = 7.4 Hz), 6.77(t,1H, *J* = 7.3 Hz), 6.34 (d, 1H, *J* = 6.8 Hz), 5.89 (br s, 1H), 5.73 (s, 1H), 4.19 (s, 1H), 2.50 (s, 3H), 1.56 (s, 9H), 0.79 (s, 3H); **^{13}C{1H}-NMR** (125 MHz, $CDCl_3$): 149.5, 146.4, 142.4, 134.8, 130.3, 129.9, 129.7, 128.9, 128.8, 127.3, 125.2, 124.1, 121.9, 115.8, 114.1, 98.4, 71.9, 68.0, 52.1, 29.1, 21.8, 14.2. **HRMS** (EI) calcd for $C_{28}H_{32}N_5O_4S$ ($M+H^+$) 534.217, found 534.2157**.**

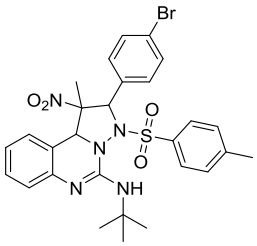
6b. N-(*tert*-butyl)-2-(4-chlorophenyl)-1-methyl-1-nitro-3-tosyl-1,2,3,10-b-tetrahydropyrazolo[1,5-c]quinazolin-5-amine

Reddish Yellow solid, Yield: (Method A: 0.14 g, 77 %, Method B: 0.12 g 63%) m. p. 165−168 °C; **^{1}H NMR (δ ppm):** (500 MHz, $CDCl_3$), 7.97 (d, 2H, *J* = 8.2 Hz), 7.46 (d, 2H, *J* = 8.0 Hz), 7.41 (d, 2H, *J*



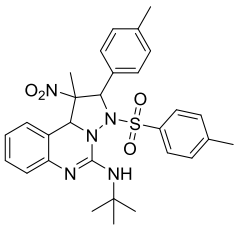
= 8.7 Hz), 7.30 (d, 2H, *J* = 7.7 Hz*)*, 7.23 (dt, 1H, *J* = 1.3, 8.7 Hz), 7.05 (d, 1H, *J* = 7.8 Hz), 6.79 (dt, 1H, *J* = 6.5, 7.4 Hz), 6.35 (d,1H, J = 6.6 Hz), 5.81 (s, 1H), 5.69 (s, 1H), 4.18 (s, 1H), 2.51 (s, 3H), 1.55 (s, 9H), 0.807 (s, 3H); **^{13}C{1H}-NMR** (125 MHz, $CDCl_3$):149.3, 146.6, 142.3, 134.9, 133.4, 130.4, 130.3, 129.7, 129.7, 129.2, 128.8, 125.2, 124.2, 122.1, 115.7, 98.2, 71.2, 68.0, 52.1, 29.1, 21.9, 14.3. **HRMS** (EI) calcd for $C_{28}H_{31}ClN_5O_4S$ ($M+H^+$) 568.178 found 568.1768

6c. 2-(4-bromophenyl)-N-(*tert*-butyl)-1-methyl-1-nitro-3-tosyl-1,2,3,10b-tetrahydropyrazolo[1,5-c]quinazolin-5-amine



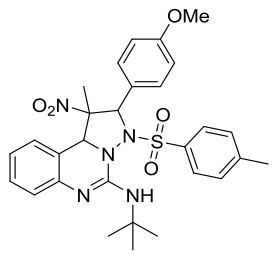
Yellow Solid**,** Yield: (Method A: 0.18 g, 90%, Method B, 0.17, 83%); m.p. = 164-166 ^oC**; ^{1}H NMR (δ ppm):** (500 MHz, $CDCl_3$), 7.6 (d, 2H, *J* = 7.8 Hz), 7.56 (d, 2H, *J* = 8.1 Hz), 7.46 (d, 2H, *J* = 7.9 Hz), 7.26-7.19 (m, 3H*)*, 7.05 (d,1H, *J* = 7.9 Hz), 6.79 (t, 1H, *J* = 7.4 Hz), 6.35 (d,1H, *J* =7.6 Hz), 5.80 (s, 1H), 5.67 (s, 1H), 4.17 (s, 1H), 2.51 (s, 3H), 1.54 (s, 9H), 0.805 (s, 3H); **^{13}C{1H}-NMR** (125 MHz, $CDCl_3$): 149.3, 146.6, 142.3, 133.9, 132.2, 130.4, 130.3, 129.7, 129.7, 129.1, 125.2, 124.2, 123.1, 122.1, 115.7, 98.2, 71.3, 68.0, 52.1, 29.2, 14.3. **HRMS** (EI) calcd for $C_{28}H_{31}BrN_5O_4S$ ($M+H^+$) 612.1275 found 612.1265.

6d. N-(*tert*-butyl)-1-methyl-1-nitro-2-(p-tolyl)-3-tosyl-1,2,3,10b-tetrahydropyrazolo[1,5-c]quinazolin-5-amine



Yellow Solid, Yield (Method A: 0.113 g 61%, Method B: 0.093 g 50%); m.p.= 170-172 ^oC; **^{1}H NMR (δ ppm):** (500 MHz, $CDCl_3$), 7.98 (d, 2H, *J* = 8.3 Hz), 7.45 (d, 2H, *J* = 8.1 Hz), 7.21-7.18 (m, 5H), 7.04 (d, 1H, *J* = 7.7 Hz*)*, 6.77 (dt, 1H, *J* = 1, 7.5 Hz), 6.34 (d, 1H, *J* = 7.5 Hz), 5.86 (s, 1H), 5.69 (s, 1H), 4.19 (s, 1H), 2.51 (s, 3H), 2.36 (s, 3H), 1.55 (s, 9H), 0.85 (s, 3H); **^{13}C{1H}-NMR** (125 MHz, $CDCl_3$): 149.5, 146.3, 138.7, 131.8, 130.2, 129.7, 129.6, 129.0, 128.8, 127.3, 125.9, 125.2, 124.1, 122.5, 122.4, 98.4, 71.8, 67.9, 51.8, 29.1, 21.8, 21.1, 14.2. **HRMS** (EI) calcd for $C_{29}H_{34}N_5O_4S$ ($M+H^+$) 548.2326 found 548.2315.

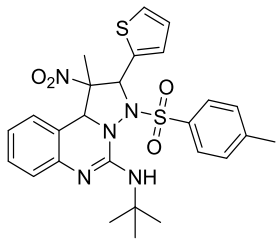
6e. N-(*tert*-butyl)-3-((4-methoxyphenyl)sulfonyl)-1-methyl-1-nitro-2-phenyl-1,2,3,10b-tetrahydropyrazolo[1,5-c]quinazolin-5-amine



Yellow Solid, Yield (Method A: 0.137 g 72%, method B: 0.128 g 67%); m.p.=171-173^oC; **^{1}H NMR (δ ppm):** (500 MHz, $CDCl_3$), 7.97 (d, 2H, *J* = 8.1 Hz), 7.45 (d, 2H, *J* = 8.05 Hz), 7.24 (s, 2H), 7.19 (t, 1H, *J* = 7.5 Hz*)*, 7.04 (d, 1H, *J* = 7.9 Hz), 6.93 (d, 2H, *J* = 8.7 Hz), 6.77 (t, 1H, J = 7.45 Hz), 6.34 (d, 1H, *J* = 7.4 Hz), 5.85 (s, 1H), 5.66 (s, 1H), 4.19 (s, 1H), 3.82 (s, 3H), 2.50 (s, 3H), 1.55 (s, 9H), 0.81 (s, 3H); **^{13}C{1H}-NMR** (125 MHz, $CDCl_3$): 159.9,

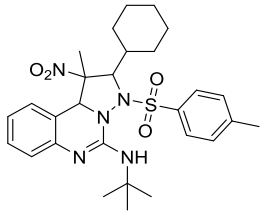
149.5, 146.4, 142.4, 130.2, 129.9, 129.7, 128.7, 126.7, 125.2, 124.1, 121.9, 115.9, 114.3, 98.4, 71.7, 67.9, 55.3, 52.0, 29.2, 21.9, 14.2. **HRMS** (EI) calcd for $C_{29}H_{34}N_5O_5S$ ($M+H^+$): 564.2275 found 564.2263

6f. N-(*tert*-butyl)-1-methyl-1-nitro-2-(thiophen-2-yl)-3-tosyl-1,2,3,10 b-tetrahydropyrazolo[1,5-c]quinazolin-5-amine



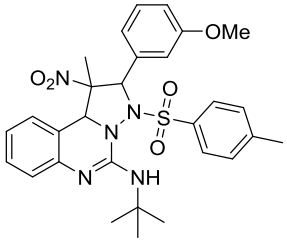
Yellow Solid, Yield (Method A: 0124 g 68%, Method B: 0.102 g 56%); m.p.=170-177°C; **^{1}H NMR (δ ppm):** (500 MHz, $CDCl_3$), 7.97 (d, 2H, *J* = 7.7 Hz), 7.44 (d, 2H, *J* = 7.2 Hz), 7.36 (d, 1H, *J* = 4.4 Hz), 7.21 (s, 1H*)*, 7.04 (d, 2H, *J* = 3.8 Hz), 6.97(s, 1H), 6.77 (s, 1H), 6.40 (d, 1H, *J* = 6.6 Hz), 6.01 (s, 1H), 5.67 (s, 1H), 4.29 (s, 1H), 2.50 (s, 3H), 1.51 (s, 9H), 0.98 (s, 3H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$):149.1, 146.5, 142.6, 138.4, 130.3, 129.8, 127.7, 126.6, 126.3, 125.4, 124.0, 122.6, 121.9, 120.2, 115.8, 98.2, 67.9, 67.8, 52.0, 28.9, 21.9, 13.9. **HRMS** (EI) calcd for $C_{26}H_{30}N_5O_4S_2$ ($M+H^+$): 540.1734 found 540.1741

6g. N-(*tert*-butyl)-2-cyclohexyl-1-methyl-1-nitro-3-tosyl-1,2,3,10 b-tetrahydropyrazolo[1,5-c]quinazolin-5-amine



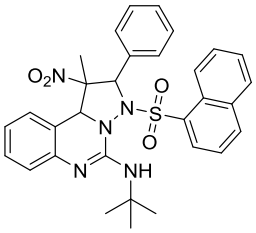
Off white solid, Yield (Method A: 0.125 g, 69%, Method B: 0.115, 63%); m.p.=136-139 °C; **^{1}H NMR** (δ ppm): (500 MHz, $CDCl_3$), 7.91 (d, 2H, *J* = 8.05 Hz), 7.37 (d, 2H, *J* = 8 Hz), 7.22 (q, 2H, *J* = 7.4 Hz), 7.01 (d, 1H, *J* = 7.8 Hz*)*, 6.80 (t, 1H, *J* = 7.3 Hz), 6.36 (d, 1H, *J* = 7.4 Hz), 5.28 (s, 1H), 4.53 (d, 1H, *J* = 9.4 Hz), 4.25 (s, 1H), 3.16 (s, 2H), 2.45 (s, 3H), 1.96 (d, 2H), 1.73 (s, 2H), 1.35 (s, 9H), 1.25 (s, 4H), 0.88-0.84 (m, 3H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): 149.2, 145.8, 142.8, 130.2, 129.9, 129.8, 125.9, 125.6, 123.9, 121.9, 116.6, 98.2, 72.4, 69.2, 51.5, 46.1, 40.1, 31.3, 28.9, 26.0, 21.8, 13.9 **HRMS** (EI) calcd for $C_{28}H_{38}N_5O_4S$ ($M+H^+$): 540.2639 found 540.2634

6h. N-(*tert*-butyl)-2-(3-methoxyphenyl)-1-methyl-1-nitro-3-tosyl-1,2,3,10b-tetrahydropyrazolo [1,5-c]quinazolin-5-amine



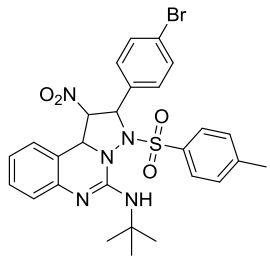
Yield (Method A: 0.127 g, 67%, Method B: 0.116, 61%); m.p. = 178-183°C; **^{1}H NMR** (δ ppm): (500 MHz, $CDCl_3$), 7.99 (d, 2H, *J* = 7.5 Hz), 7.49 (d, 2H, *J* = 7.1 Hz), 7.39-7.31 (m, 3H), 6.91-6.85 (m, 4H*)*, 6.36 (d, 1H, *J* = 7.15 Hz), 5.70 (s, 1H), 4.98 (s, 1H), 4.25 (s, 1H), 3.83 (s, 3H), 2.52 (s, 3H), 1.62 (s, 9H), 0.81(s, 3H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): 160.0, 149.5, 146.4, 136.3, 130.2, 130.0, 129.9, 129.7, 128.8, 126.0, 125.2, 124.1, 121.9, 11.5, 115.8, 113.9, 113.5, 98.4, 71.8, 68.1, 55.3, 52.1, 29.9, 14.0. **HRMS (EI)** calcd for $C_{29}H_{34}N_5O_5S$ (M+H+): 564.2275 found 564.2276

6i. N-(*tert*-butyl)-1-methyl-3-(naphthalen-1-ylsulfonyl)-1-nitro-2-phenyl-1,2,3,10b-tetrahydropyrazolo[1,5-c]quinazolin-5-amine



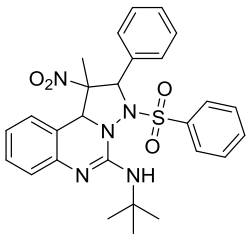
Yellow Solid, Yield (Method A: 0.124 g, 64%, Method B: 0.113 g, 57%, m.p.=137-142°C; **^{1}H NMR (δ ppm):** (500 MHz, $CDCl_3$), 8.66 (d, 2H, *J* = 8.55 Hz), 8.48 (d, 1H, *J* = 7.3 Hz), 8.24 (d, 1H, *J* = 8.2 Hz), 8.00 (d, 1H, *J* = 8.0 Hz*)*, 7.67-7.61 (m, 2H), 7.58 (t, 1H, *J* = 7.7 Hz), 7.42 (d, 3H, *J* =5.8 Hz), 7.35 (d, 1H, *J* = 7.7 Hz), 7.20 (t, 1H, *J* = 7.8 Hz), 6.97 (d, 1H, *J* = 7.9 Hz), 6.82 (d, 1H, *J* = 7.3Hz), 6.58 (d, 1H, *J* = 7.5 Hz), 6.19 (s, 1H), 5.18 (s, 1H), 4.77 (s, 1H), 1.07 (s, 9H), 0.86 (s, 3H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): 148.5, 142.3, 136.5, 134.5, 134.4, 133.8, 130.1, 129.4, 129.3, 129.2, 129.1, 128.9, 128.8, 128.0, 127.6, 125.7, 124.7, 124.6, 123.9,122.0, 116.3, 98.0, 70.2, 68.7, 51.4, 28.5, 14.5. **HRMS** (EI) calcd for $C_{31}H_{32}N_5O_4S$ ($M+H^+$): 570.2170, found 570.2160

6j. 2-(4-bromophenyl)-N-(*tert*-butyl)-1-nitro-3-tosyl-1,2,3,10b-tetrahydropyrazolo[1,5-c]quinazolin-5-amine



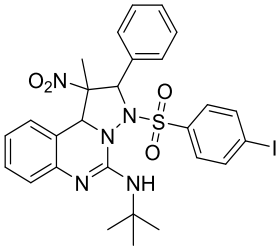
Yield (Method A: 0.140 g, 69%, Method B: 0.103, 51%); m.p. = 132-135°C; **^{1}H NMR (δ ppm):** (500 MHz, $CDCl_3$), 7.95 (d, 2H, *J* = 8.1 Hz), 7.55 (d, 2H, *J* = 8.3 Hz), 7.45 (d, 2H, *J* = 8.0 Hz), 7.30 (d, 2H, *J* = 8.3 Hz*)*, 7.25(t, 1H, *J* = 7.3 Hz), 7.07 (d, 1H, *J* = 7.8 Hz), 6.83 (t, 1H, *J* = 7.4 Hz), 6.54 (d, 1H, *J* = 7.3 Hz), 5.50 (d, 1H, *J* = 7.5), 5.42 (s, 1H), 4.96 (s, 1H,), 4.09 (d, 1H, *J* = 9.4 Hz), 2.51 (s, 3H), 1.41 (s, 9H); **^{13}C{^{1}H} NMR** (125 MHz, CDCl3): 148.3, 146.5, 140.9, 135.9, 132.4, 130.8, 130.6, 130.4, 129.4, 128.9, 125.5, 124.3, 123.4, 122.2, 116.7, 96.7, 67.1, 64.9, 52.0, 28.9,21.8. **HRMS** (EI) calcd for $C_{27}H_{29}BrN_5O_4S$ ($M+H^+$): 598.1118 Found 598.1130.

6k. N-(*tert*-butyl)-1-methyl-1-nitro-2-phenyl-3-(phenylsulfonyl)-1,2,3,10b-tetrahydropyrazolo [1,5-c]quinazolin-5-amine



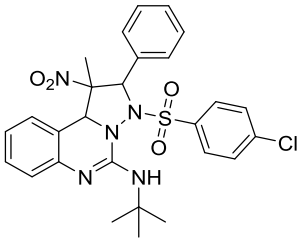
Yield (Method A: 0.139 g, 79%, Method B: 0.118 g, 67%) m.p.=170-175 °C; **^{1}H NMR (δ ppm):** (500 MHz, $CDCl_3$), 8.12 (d, 2H, *J* = 7.5 Hz), 7.82 (t, 1H, *J* = 7.4 Hz), 7.69 (t, 2H, *J* = 7.7 Hz), 7.43-7.35 (m, 5H*)*, 7.22 (t, 1H, *J* = 7.4 Hz), 7.04 (d, 1H, *J* = 7.9 Hz), 6.77 (t, 1H, *J* = 7.4 Hz), 6.31 (d, 1H, *J* = 7.35), 5.87 (s, 1H), 5.74 (s, 1H), 4.11 (s, 1H), 1.57 (s,9H), 0.79 (s, 3H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): 149.3, 142.3, 138.2, 135.1, 134.7, 132.8, 130.4, 129.7, 128.9, 127.3, 125.2, 124.1, 122.1, 116.4, 115.8, 98.4, 72.0, 68.1, 52.1, 29.1, 14.2. **HRMS** (EI) calcd for $C_{27}H_{30}N_5O_4S$ ($M+H^+$): 520.2013 Found 520.2004.

6l N-(*tert*-butyl)-3-((4-iodophenyl)sulfonyl)-1-methyl-1-nitro-2-phenyl-1,2,3,10b tetrahydropyrazolo [1,5-c]quinazolin-5-amine



Yield (Method A: 0.142 g, 65%, Method B: 0.120 g, 55%); m.p.=173°C; **^{1}H NMR (δ ppm)**: (500 MHz, $CDCl_3$), 8.04 (d, 2H, *J* = 8.4 Hz), 7.81 (d, 2H, *J* = 8.5 Hz), 7.45-7.36 (m, 4H), 7.32 (d, 2H, *J* = 6.6 Hz), 7.25 (t, 1H, *J* = 8.2 Hz), 7.12 (d, 1H, *J* = 7.6 Hz), 6.84 (t, 1H, *J* = 7.3 Hz), 6.40 (d, 1H, *J* = 7.5 Hz), 5.91 (s, 1H), 5.73 (s, 1H), 4.24 (s, 1H), 1.58 (s, 9H), 0.80 (s, 3H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$):149.2, 139.1, 134.4, 132.5, 130.8, 130.6, 129.2, 129.1, 129.0, 127.3, 125.2, 123.9, 122.5, 115.4, 103.6, 98.3, 72.2, 68.3, 52.5, 29.1, 14.2. **HRMS** (EI) calcd for $C_{27}H_{29}IN_5O_4S$ ($M+H^+$):646.098, found 646.0902.

6m. N-(*tert*-butyl)-3-((4-chlorophenyl)sulfonyl)-1-methyl-1-nitro-2phenyl-1,2,3,10b-tetrahydropyrazolo [1,5-c] quinazolin-5-amine



Yellow Solid, Yield (Method A: 0.131 g, 70 %, Method B: 0.107 g, 57%); m.p.=177-181°C; **^{1}H NMR (δ ppm):** (500 MHz, $CDCl_3$), 8.05 (d, 2H, *J* = 8.5 Hz), 7.65 (d, 2H, *J* = 8.5 Hz), 7.44-7.36 (m, 3H), 7.33 (d, 2H, *J* = 5.7 Hz), 7.24 (t, 1H, *J* = 7.3 Hz), 7.05 (d, 1H, *J* = 7.8 Hz), 6.81 (t, 1H, *J* = 7.3 Hz), 6.37 (d, 1H, *J* = 7.3 Hz), 5.84 (s, 1H), 5.72 (s, 1H), 4.2 (s, 1H), 1.57 (s, 9H), .80 (s, 3H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): 149.1, 142.2, 142.1, 134.5, 131.4, 131.1, 130.5, 130.0, 129.0, 127.3, 125.2, 124.2, 122.3, 115.6, 112.9, 98.5, 72.2, 68.4, 52.2, 29.1, 22.7, 14.1. **HRMS** (EI) calcd for $C_{27}H_{29}ClN_5O_4S$ ($M+H^+$): 554.1624 Found 554.1618.

3.6. Crystallographic Data

X-ray quality crystals of **6c** were grown by slow evaporation method by mixing of hexane and DCM at room temperature. Suitable crystals for single crystal X-ray diffractions were loaded on a Bruker AXS Smart Apex CCD diffractometer. All the structures were solved by direct methods using SHELXS-97 and refined by full-matrix least squares on F2 using SHELXL-97 and OLEX[2]. The details pertaining to the data collection and refinement for 6c are given in Table S3.6. Non-hydrogen atoms were refined with anisotropic displacement parameters. All the hydrogen atoms were included in idealized positions and their positions were refined isotropically by a riding model.

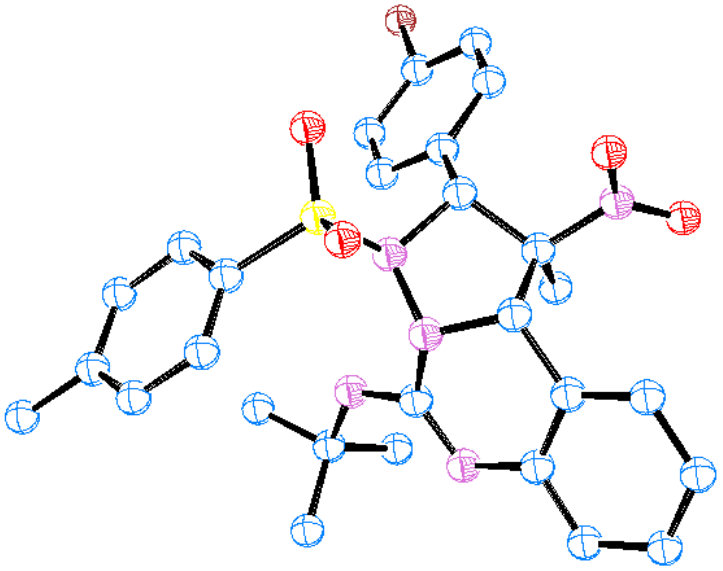


Figure S2: Ortep diagram of **6c** drawn at 50% probability. The hydrogen atoms have been omitted for clarity.

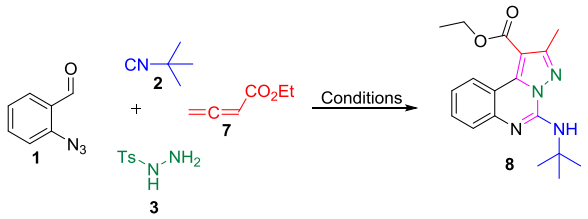
Table S3.6.1 Crystal data and structure refinement for 6c.

Identification code	MCR_A122_030_07_07_2017_0m
Empirical formula	$C_{28}H_{30}BrN_5O_4S$
Formula weight	612.53
Temperature/K	296.15
Crystal system	triclinic
Space group	P-1
a/Å	11.1312(14)
b/Å	12.9663(17)
c/Å	19.980(3)
α/°	82.601(2)
β/°	89.156(2)
γ/°	78.132(2)
Volume/Å^3	2798.4(6)
Z	4
ρ_{calc}g/cm^3	1.454
μ/mm^{-1}	1.587
F(000)	1264.0
Crystal size/mm^3	0.18 × 0.18 × 0.16
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.06 to 57.42
Index ranges	$-14 \leq h \leq 14$, $-16 \leq k \leq 17$, $-26 \leq l \leq 23$
Reflections collected	21705

Independent reflections	12453 [R_{int} = 0.0356, R_{sigma} = 0.0568]
Data/restraints/parameters	12453/0/714
Goodness-of-fit on F^2	1.073
Final R indexes [I>=2σ (I)]	R_1 = 0.0684, wR_2 = 0.1785
Final R indexes [all data]	R_1 = 0.0908, wR_2 = 0.2357
Largest diff. peak/hole / e Å^{-3}	2.59/-1.40

4. Synthesis of compound 8

***Table* S4.1** Optimization of 4-CR for the synthesis of compound **8**[a]

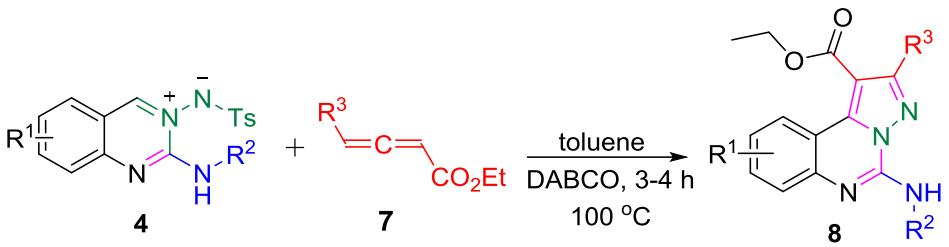


Entry	Solvent	Base	temp (°C)	Time (h)	8
1.	toluene	-	rt	24	10[a]
2.	toluene	-	100	4	55
3.	THF	-	70	4	-
4.	^{i}PrOH	-	70	4	40
5.	1,2-DCE	-	100	4	25
6.	DMF	-	100	4	-
7.	Dioxane	-	100	4	30
8.	DMF	-	rt	24	-
9.	DMF	Et_3N	70	4	20
10.	DMF	NMP	70	4	15
11.	DMF	DBU	70	4	-
12.	DMF	pyrolidine	100	4	10
13.	DMF	DABCO	rt	24	50
14.	DMF	DABCO	100	4	57
15.	toluene	DABCO	rt	24	65
16.	**toluene**	**DABCO**	**100**	**4**	**80**
17.	**toluene**	**DABCO**	**rt**	**4**	**15**

[b]Reaction carried for overnight

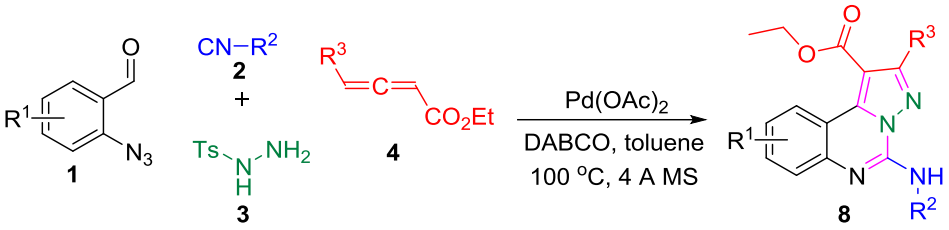
S4.2. Experimental procedure for the *sequential* synthesis of 8 (Method C)

To a reaction vial (10ml) was charged with azomethine imine **4** (1.0 equiv) allenoates **7** (2 equiv) in toluene as solvent (1ml) and DABCO (1 equiv) stirred at 100 °C and monitored the reaction on TLC. After consuming starting material was completely reaction mixture was quenched by water and extracted with EtOAc (3x15ml). After removal of solvents in vacuo, the residue was subjected to column chromatography on silica gel (100-200 mesh) using hexane as eluent to give desired product **8**.



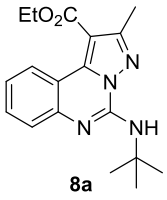
S4.3. Experimental procedure for the *one-pot* synthesis of 8 (Method D)

2-Azidobenzaldehyde (1.0 equiv), isocyanide (1.2 equiv), $Pd(OAc)_2$ (7.5 mol%), 4 Å MS, *p*-tosyl hydrazide (1.1 equiv) in toluene at room temeparature in 20 mL Schlenk tube, monitor the reaction for 15 min. after formation of azomethine imine **4**, allenoates **7** (2 equiv) was added with (1 equiv) DABCO in reaction mixture stirred at 100 °C and monitor the reaction on TLC. After consuming azomethine imine, **4** was completely reaction mixture was quenched by water and extracted with EtOAc (3x15ml). After removal of solvents in vacuo, the residue was subjected to column chromatography on silica gel (100-200 mesh) using hexane as eluent to give desired product **8**.



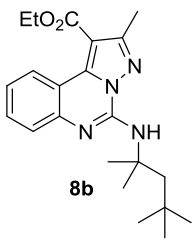
S4.4. Analytical data of 8

8a. ethyl 5-(*tert*-butylamino)-2-methylpyrazolo[1,5-c]quinazoline-1-carboxylate.



White solid, Yield: (Method C: 0.091 g, 82%, Method D: 0.083 g, 75 %); **^{1}H NMR (δ/ppm, $CDCl_3$):** 9.31 (d, 1H, *J* = 8.2 Hz), 7.69 (d, 1H, *J* = 8.2 Hz) 7.61 (t, 1H, *J* = 8.0 Hz), 7.34 (t, 1H, *J* = 8.0 Hz), 6.49 (br s, 1H), 4.49 (q, 2H, *J* = 7.1 Hz), 2.67 (s, 3H) 1.66 (s, 9H), 1.50 (t, 3H, *J* = 7.2 Hz). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): 164.5, 154.1, 143.6, 141.8, 141.5, 130.9, 126.8, 126.1, 122.7, 115.3, 107.2, 60.5, 52.1, 29.0, 15.7, 14.4. **HRMS (EI)** calcd for $C_{18}H_{23}N_4O_2$ ($M+H^+$) 327.1816 found 327.1802.

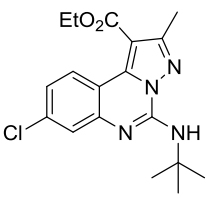
8b. ethyl 2-methyl-5-((2,4,4-trimethylpentan-2-yl)amino)pyrazolo[1,5-c]quinazoline-1-carboxylate.



Light yellow oil, Yield: (Method C: 0.092 g, 71%, Method D: 0.078 g, 61%); **^{1}H NMR (δ ppm)**: (500 MHz, $CDCl_3$)**:** 9.29 (d, 1H, *J* = 8.2 Hz), 7.68 (d, 1H, *J* = 8.2 Hz) 7.60 (t, 1H, *J* = 8.1 Hz), 7.33 (t, 1H, *J* = 8.1 Hz), 6.60 (br s, 1H), 4.49 (q, 2H, *J* = 7.1 Hz), 2.66 (s, 3H), 2.08 (s, 2H), 1.71 (s, 6H), 1.49 (t, 3H, *J* = 7.2 Hz), 1.05 (s,

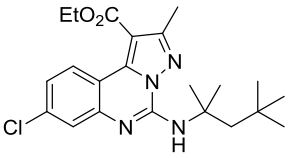
9H). **$^{13}C\{^{1}H\}$ NMR** (125 MHz, $CDCl_3$): 164.5, 153.9, 148.4, 143.7, 141.7, 130.8, 126.8, 126.1, 125.9, 122.6, 115.3, 60.4, 55.8, 51.7, 31.5, 29.7, 29.4, 15.6, 14.4. **HRMS (EI)** calcd for $C_{22}H_{31}N_4O_2$ ($M+H^+$) 383.2442 found 383.2454.

8c. ethyl 5-(*tert*-butylamino)-8-chloro-2-methylpyrazolo[1,5-c]quinazoline-1-carboxylate.



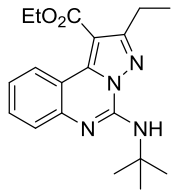
Colourless liquid, Yield: (Method C: 0.085 g, 70%, Method D: 0.076 g, 63%); **^{1}H NMR (δ ppm)**: (500 MHz, $CDCl_3$)**:** 9.30 (d, 1H, *J* = 8.8 Hz), 7.68 (s, 1H) 7.28 (dd, 1H, *J* = 2.2, 8.9 Hz), 6.56 (br s, 1H), 4.48 (q, 2H, *J* = 7.2 Hz), 2.66 (s, 3H), 1.65 (s, 9H), 1.49 (t, 3H, *J* = 7.2 Hz) **$^{13}C\{^{1}H\}$ NMR** (125 MHz, $CDCl_3$): 164.3, 154.3, 147.1, 144.7, 142.3, 136.6, 128.3, 125.3, 123.1, 113.8, 107.4, 60.6, 52.2, 28.9, 15.7, 14.4. HRMS (EI) calcd for $C_{18}H_{22}ClN_4O_2$ ($M+H^+$) 361.1426 found 361.1420.

8d. ethyl 8-chloro-2-methyl-5-((2,4,4-trimethylpentan-2-yl)amino)pyrazolo[1,5-c]quinazoline-1-carboxylate.



Colourless liquid, Yield: (Method C: 0.090g, 69%, Method D: 0.080 g, 62%); **^{1}H NMR (δ ppm)**: (500 MHz, $CDCl_3$) 9.30 (d, 1H, *J* = 8.8 Hz), 7.67 (s, 1H) 7.27 (dd, 1H, *J* = 2.2, 8.9 Hz), 6.66 (br s, 1H), 4.48 (q, 2H, *J* = 7.2 Hz), 2.66 (s, 3H), 2.06 (s, 2H), 1.70 (s, 6H,) 1.49 (t, 3H, *J* = 7.2 Hz) 1.04 (s, 9H), **$^{13}C\{^{1}H\}$ NMR** (125 MHz, $CDCl_3$): 164.4, 154.3, 147.1, 144.7, 142.1, 136.5, 128.3, 125.3, 122.9, 113.7, 107.4, 60.6, 55.9, 51.6, 31.8, 31.5, 29.4, 15.8, 14.4. HRMS (EI) calcd for $C_{22}H_{30}ClN_4O_2$ ($M+H^+$) 417.2052 found 417.2033.

8e. ethyl 5-(*tert*-butylamino)-2-ethylpyrazolo[1,5-c]quinazoline-1-carboxylate.

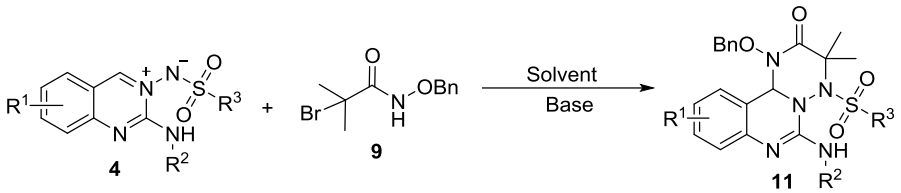


Colorless oil, Yield: (Method C: 0.087 g, 63%, Method D: 0.070 g, 52%); **^{1}H NMR (δ ppm)**: (500 MHz, $CDCl_3$)**:** 9.24 (d, 1H, *J* = 7.9 Hz), 7.69 (d, 2H, *J* = 8.2 Hz) 7.60 (t, 1H, *J* = 8.1 Hz), 7.33 (t, 1H, *J* = 7.8 Hz), 6.52 (br s, 1H), 4.50 (q, 2H, *J* = 7.2 Hz), 3,1 (q, 2H, *J* = 7.2 Hz) 1.67 (s, 9H), 1.50 (t, 3H), 0.92(t, 3H); **$^{13}C\{^{1}H\}$ NMR** (125 MHz, $CDCl_3$): 164.5, 158.9, 143.6, 139.2, 130.7, 126.7, 126.1, 122.6, 115.5, 114.0, 106.5, 60.5, 52.0, 29.0, 14.3, 14.1, 13.4. HRMS (EI) calcd for $C_{19}H_{25}N_4O_2$ ($M+H^+$) 341.1972 found 341.1985..

S5. Synthesis of compound 11

S5.1 Screening of 4-CR for the synthesis of 11

***Table 5.1*: Optimization of the reaction condition for method E[a]:**



Entry	Solvent	Base	Yield[b]
1	THF	K_2CO_3	NR
2	DMSO	K_2CO_3	5
3	Acetonitrile	K_2CO_3	70
4	MeOH	K_2CO_3	10
5	1,2-DCE	K_2CO_3	15
6	1,4-dioxane	K_2CO_3	10
7	DMF	K_2CO_3	NR
8	toluene	K_2CO_3	80
9	toluene	DBU	15
10	toluene	K_3PO_4	10
11	toluene	DABCO	10
12	toluene	Na_2CO_3	55
13	toluene	Cs_2CO_3	30
14	toluene	Et_3N	20
15	toluene	K_2CO_3	80[c]
16	toluene	K_2CO_3	55[d]

[a]Reaction conditions: **4a** (0.11 mmol), **9a**, (0.22 mmol), base (0.22 mmol), solvent (0.2 mL), 70 °C, 3 h. [b]Yields are of isolated product after column chromatography. [c]Reaction at 90 °C. [d]Reaction at room temperature after 12 h; nr: no reaction.

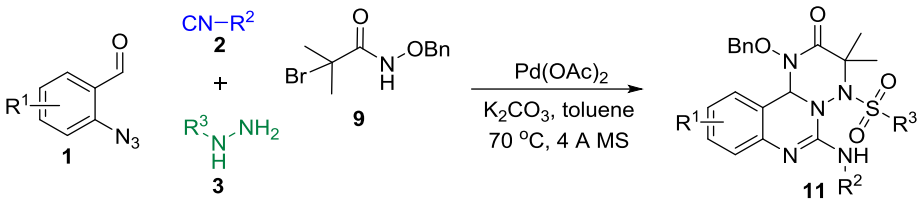
S5.2. Experimental procedure for the *sequential* synthesis of 11 (Method E)

To a reaction vial (10 mL) was charged with azomethine imine **4** (1.0 equiv), *N*-(benzyloxy)-2-bromo-2-methylpropanamide **9** (2.0 equiv) and K_2CO_3 (2.0 equiv) in toluene as solvent (1.0 mL) stirred at 70 °C and monitor the reaction progress on TLC. After completion of the reaction on TLC, the mixture was quenched by water and extracted with EtOAc (3 x 15 mL). After removal of solvents in vacuo, the residue was subjected to column chromatography on silica gel (100-200 mesh) using hexane as eluent to give the desired product **11**.

S5.3. Experimental procedure for the *one-pot* synthesis of 11 (Method F)

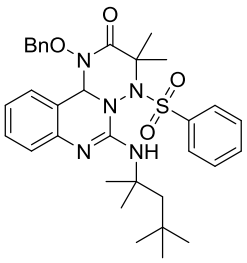
2-Azidobenzaldehyde (1.0 equiv), isocyanide (1.2 equiv), $Pd(OAc)_2$ (7.5 mol%), 4 Å MS, *p*-toluene sulfonylhydrazide (1.1 equiv) in toluene at room temeprature in 20 mL Schlenk tube, monitor the reaction for 15 min. after formation of azomethine imine **4**, *N*-(benzyloxy)-2-bromo-2-methylpropanamide **9** (2 equiv) and K_2CO_3 (2.0 equiv) was added in reaction mixture and stirred at 70 °C for 1-2 h. The progress of the reaction was monitored on TLC. After completion of the reaction, the

mixture was quenched by water and extracted with EtOAc (3 x 15 mL). After removal of solvents in vacuo, the residue was subjected to column chromatography on silica gel (100-200 mesh) using hexane as eluent to give desired product **11**.



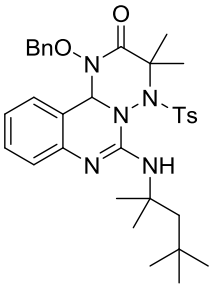
S5.4. Analytical data

11a. 1-(benzyloxy)-3,3-dimethyl-4-(phenylsulfonyl)-6-((2,4,4-trimethylpentan-2-yl)amino)-1,3,4,11b-tetrahydro-2H-[1,2,4]triazino[2,3-c]quinazolin-2-one



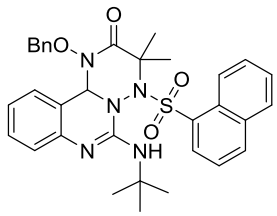
Colourless liquid, Yield: 0.052 g (72%); R_f 0.4 (7:3 EtOAc/hexane); **^{1}H NMR (δ ppm)**: (500 MHz, $CDCl_3$)**:** 7.89 (d, 2H, *J* = 7.5 Hz), 7.69 (d, 1H, *J* = 7.0 Hz), 7.52 (t, 2H, *J* = 7.3 Hz), 7.47 (t, 1H, *J* = 7.3 Hz), 7.26-7.16 (m, 4H), 7.04 (t, 1H, *J* = 7.0 Hz), 6.95 (d, 1H, *J* = 6.9 Hz), 6.88 (d, 2H, *J* = 6.9 Hz), 5.53 (s, 1H), 5.30 (s, 1H), 4.79 (d, 1H, *J* = 8.4 Hz), 3.87 (d, 1H, *J* = 8.3 Hz), 2.22 (d, 1H, *J* = 14.6 Hz), 2.04 (s, 3H), 2.0 (s, 3H), 1.61 (d, 1H, *J* = 14.5 Hz), 1.28 (s, 6H), 1.01 (s, 9H). **^{13}C{^{1}H} NMR (δ ppm):** (125 MHz, $CDCl_3$): 167.4, 146.9, 143.3, 137.6, 134.2, 133.7, 131.2, 129.9, 129.3, 129.0, 128.8, 128.7, 128.2, 123.3, 121.4, 115.7, 78.7, 71.8, 70.8, 55.9, 50.8, 31.6, 29.3, 29.2, 27.9, 25.9. **HRMS** (EI) calcd for $C_{33}H_{42}N_5O_4S$ ($M+H^+$):604.2952, found 604.2932.

11b. 1-(benzyloxy)-3,3-dimethyl-4-tosyl-6-((2,4,4-trimethylpentan-2-yl)amino)-1,3,4,11b-tetrahydro-2H-[1,2,4]triazino[2,3-c]quinazolin-2-one



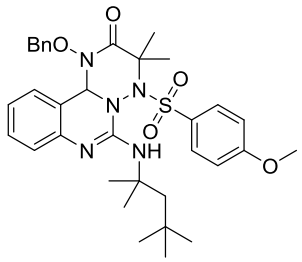
Colourless liquid, Yield: 0.061 g (85%); R_f 0.5 (7:3 EtOAc/hexane); **^{1}H NMR (δ ppm)**: (500 MHz, $CDCl_3$)**:** 7.66 (d, 2H, *J* = 8.2 Hz), 7.35 (t, 1H, 7.7 Hz), 7.19 (t, 2H, *J* = 4.0 Hz), 7.15-7.09 (m, 3H), 7.06 (d, 1H, *J* = 7.9 Hz), 6.92 (t, 1H, J = 7.4 Hz), 6.87 (d, 1H, *J* = 7.4 Hz), 6.79 (d, 2H, *J* = 7.1 Hz), 5.51 (s, 1H), 5.17 (s, 1H), 4.68 (d, 1H, *J* = 8.6 Hz), 3.78 (d, 1H, *J* = 8.6 Hz), 2.35 (s, 3H), 2.10 (d, 1H, *J* = 14.7 Hz), 1.92 (s, 3H), 1.90 (s, 3H), 1.47 (s, 1H), 1.18 (s, 6H), 0.91 (s, 9H). **^{13}C{^{1}H} NMR (δ ppm):** (125 MHz, $CDCl_3$): 167.5, 147.0, 145.3, 143.4, 134.8, 133.9, 131.1, 129.9, 129.8, 129.1, 128.7, 128.6, 128.2, 123.2, 121.3, 115.8, 78.6, 71.8, 70.7, 55.9, 50.9, 31.6, 29.2, 29.0, 27.9, 25.8, 21.6. **HRMS** (EI) calcd for $C_{34}H_{44}N_5O_4S$ ($M+H^+$):618.3109, found 618.3129.

11c. 1-(benzyloxy)-6-(*tert*-butylamino)-3,3-dimethyl-4-(naphthalen-1-ylsulfonyl)-1,3,4,11b-tetrahydro-2H-[1,2,4]triazino[2,3-c]quinazolin-2-one



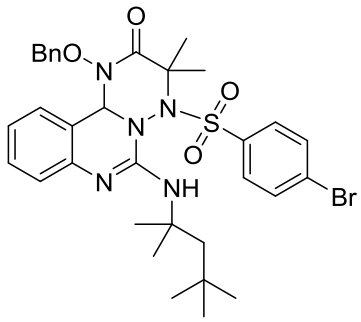
White solid, Yield: 0.055 g (75%); M. P. 153-155 ^{o}C; R_f 0.5 (7:3 EtOAc/hexane); **^{1}H NMR (δ ppm)**: (500 MHz, $CDCl_3$)**:** 8.90 (d, 1H, *J* = 8.2 Hz), 8.22 (d, 1H, *J* = 7.3 Hz), 8.15 (d, 1H, *J* = 8.1 Hz), 7.99 (d, 1H, *J* = 7.5 Hz), 7.63-7.55 (m, 2H), 7.53 (t, 1H, *J* = 7.8 Hz), 7.41 (t, 1H, *J* = 7.1 Hz), 7.26-7.19 (m, 3H), 7.11 (d, 1H, J = 7.1 Hz), 7.04-6.98 (m, 2H), 6.87 (d, 2H, J = 7.1 Hz), 6.24 (s, 1H), 4.77 (d, 1H, *J* = 8.7 Hz), 4.68 (s, 1H), 3.94 (d, 1H, *J* = 8.7 Hz), 2.23 (s, 3H), 2.11 (s, 3H), 0.77 (s, 9H). **^{13}C{^{1}H} NMR (δ ppm):** (125 MHz, CDCl3): 167.2, 146.5, 143.1, 139.3, 136.0, 134.2, 133.8, 133.3, 131.8, 130.9, 129.9, 129.4, 129.3, 129.1, 128.9, 128.8, 128.2, 127.2, 124.4, 124.0, 123.0, 121.4, 115.9, 78.3, 72.1, 70.9, 51.2, 29.7, 27.9, 27.6, 26.4. **HRMS** (EI) calcd for $C_{33}H_{36}N_5O_4S$ ($M+H^+$):598.2483, found 598.2466.

11d. 1-(benzyloxy)-4-((4-methoxyphenyl)sulfonyl)-3,3-dimethyl-6-((2,4,4-trimethylpentan-2-yl)amino)-1,3,4,11b-tetrahydro-2H-[1,2,4]triazino[2,3-c]quinazolin-2-one



Colourless liquid, Yield: 0.050 g (70%); R_f 0.35 (8:2 EtOAc/hexane); **^{1}H NMR (δ ppm)**: (500 MHz, $CDCl_3$)**:** 7.80 (d, 2H, *J* = 8.4 Hz), 7.44-7.36 (m, 3H), 7.26-7.20 (m, 2H), 7.16 (d, 1H, *J* = 7.8 Hz), 7.04-6.97 (m, 1H), 6.95 (d, 2H, *J* = 8.4 Hz), 6.88 (d, 2H, *J* = 7.0 Hz), 5.63 (s, 1H), 5.30 (s, 1H), 4.99 (s, 1H), 4.78 (d, 1H, *J* = 8.4 Hz), 3.88 (s, 3H), 2.23 (d, 1H, *J* = 14.6 Hz), 2.02 (s, 3H), 2.0 (s, 3H), 1.56 (d, 1H, *J* = 13.5 Hz), 1.31 (s, 6H), 1.00 (s, 9H). **^{13}C{^{1}H} NMR (δ ppm):** (125 MHz, CDCl3): 167.5, 164.1, 147.1, 143.4, 133.8, 131.3, 131.1, 129.9, 128.9, 128.8, 128.7, 128.2, 123.2, 121.3, 115.8, 114.4, 78.6, 71.7, 70.5, 55.9, 55.8, 50.8, 31.6, 31.9, 29.7, 27.9, 25.8. **HRMS** (EI) calcd for $C_{34}H_{44}N_5O_5S$ ($M+H^+$):634.3058, found 634.3035.

11e: 1-(benzyloxy)-4-((4-bromophenyl)sulfonyl)-3,3-dimethyl-6-((2,4,4-trimethylpentan-2-yl)amino)-1,3,4,11b-tetrahydro-2H-[1,2,4]triazino[2,3-c]quinazolin-2-one

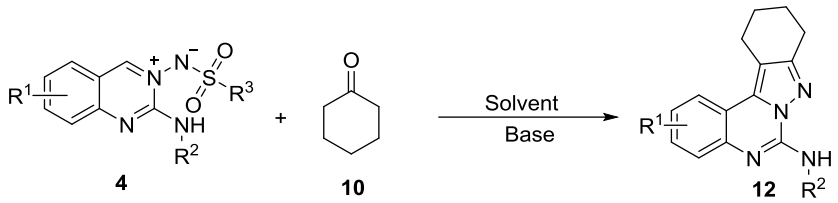


Colourless liquid, Yield: 0.052 g (70%); R_f 0.35 (7:3 EtOAc/hexane); **^{1}H NMR (δ ppm)**: (500 MHz, $CDCl_3$)**:** 7.74 (d, 2H, *J* = 8.6 Hz), 7.64 (d, 2H, *J* = 8.6 Hz), 7.47 (dt, 1H, *J* = 7.8, 1.35 Hz), 7.26-7.25 (m, 1H), 7.06 (t, 1H, *J* = 7.4 Hz),7.00-6.98 (m, 1H), 6.98 (d, 2H, *J* = 7.0 Hz), 5.61 (s, 1H), 5.21 (br s, 1H), 4.78 (d, 1H, *J* = 8.6 Hz), 3.89 (d, 1H, *J* = 8.6 Hz), 2.20 (d, 1H, *J* = 14.6 Hz), 2.03 (s, 3H), 2.0 (s, 3H), 1.45 (s, 1H), 1.41 (s, 3H), 1.32 (s, 3H), 1.01 (s, 9H). **^{13}C{^{1}H} NMR (δ ppm): (125 MHz, $CDCl_3$):** 167.2, 146.7, 143.2, 136.6, 133.8, 132.5, 131.3, 130.5, 129.9, 128.8, 128.6, 128.2, 123.4, 121.6, 115.7, 114.1, 78.7, 71.8, 70.8, 56.0, 50.9, 31.6, 27.9, 25.9. 14.1. **HRMS** (EI) calcd for $C33H_{41}BrN_5O_4S$ ($M+H^+$):682.2057, found 682.2043.

S6. Synthesis of compound 12

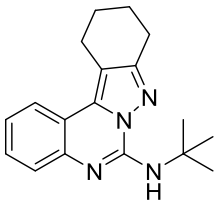
S6.1 Experimental procedure for the *sequential* synthesis of 12 (Method G)

To a reaction vial (10 mL) was charged with azomethine imine **4** (1.0 equiv), cyclohexanone **10** (2.0 equiv) and K_3PO_4 (2.0 equiv) in ethanol as solvent (1.0 mL) stirred at 80 °C and monitor the reaction progress on TLC. After completion of the reaction on TLC, the mixture was quenched by water and extracted with EtOAc (3 x 15 mL). After removal of solvents in vacuo, the residue was subjected to column chromatography on silica gel (100-200 mesh) using hexane as eluent to give desired product **12**.



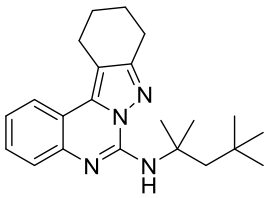
S6.2. Analytical data of 12

12a. N-(*tert*-butyl)-9,10,11,12-tetrahydroindazolo[2,3-c]quinazolin-6-amine



Colorless oil, Yield: 0.061 g (85%); R_f 0.6 (8:2 EtOAc/hexane); **^{1}H NMR (δ ppm)**: (500 MHz, $CDCl_3$):7.89 (d, 1H, *J* = 7.8 Hz), 7.64 (d, 1H, *J* = 8.1 Hz), 7.47 (td, 1H, *J* = 8.3, 1.3 Hz), 7.26-7.23 (m, 1H), 6.30 (bs, 1H), 3.02 (d, 2H, *J* = 5.6 Hz), 2.89 (d, 2H, *J* = 5.6 Hz), 1.94 (t, 4H, *J* = 3.0 Hz), 1.64 (s, 9H). **^{13}C{^{1}H} NMR** (δ ppm): (125 MHz, CDCl3): 152.1, 142.3, 141.9, 135.0, 128.6, 125.8, 122.9, 122.3, 117.4, 110.5, 51.8, 29.2, 24.0, 23.3, 22.9, 22.1. **HRMS** (EI) calcd for $C_{18}H_{23}N_4$ ($M+H^+$):295.1917, found 295.1921.

12b: N-(2,4,4-trimethylpentan-2-yl)-9,10,11,12-tetrahydroindazolo[2,3-c]quinazolin-6-amine

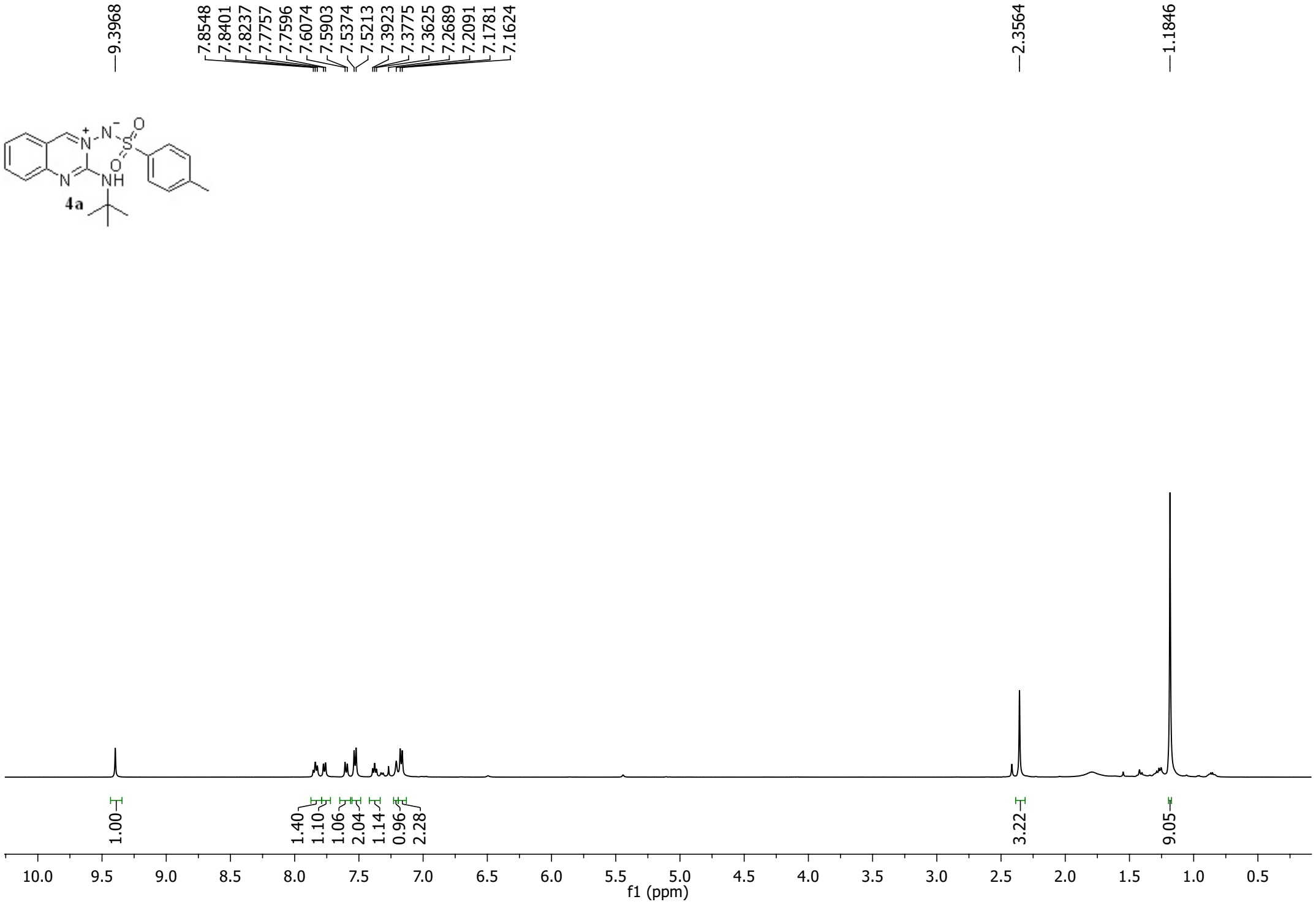


White solid, Yield: 0.061 g (85%); m. p. 104-105 °C; R_f 0.5 (8:2 EtOAc/hexane); **^{1}H NMR (δ ppm)**: (500 MHz, $CDCl_3$): (500 MHz, $CDCl_3$)**:**7.89 (d, 1H, *J* = 7.7 Hz), 7.65 (d, 1H, *J* = 8.1 Hz), 7.48 (td, 1H, *J* = 8.2, 1.1 Hz), 7.25 (t, 1H, *J* = 7.8 Hz), 6.38 (bs, 1H), 3.02 (d, 2H, *J* = 5.4 Hz), 2.89 (d, 2H, *J* = 5.2 Hz), 2.09 (s, 2H), 1.94 (d, 4H, *J* = 2.9 Hz), 1.68 (s, 6H), 1.03 (s, 9H). **^{13}C{^{1}H}** NMR (δ ppm): (125 MHz, $CDCl_3$): 152.0, 142.2, 141.9, 134.9, 128.5, 125.8, 122.8, 122.2, 117.4, 110.4, 55.5, 51.5, 31.5, 29.7, 29.6, 24.0, 23.3, 22.9, 22.2. **HRMS** (EI) calcd for $C_{22}H_{31}N_4$ ($M+H^+$):351.2543, found 351.2529.

S7. References

1. B. J. Stokes, S.Liu, T. G. Driver, *J. Am. Chem. Soc.* 2011, **133**, 4702.
2. F.-L. Yang, X.-T. Ma; S.-K. Tian, *Chem. Eur. J*., 2012, **18**, 1582.

S8. Copy of ^{1}H and ^{13}C NMR spectrum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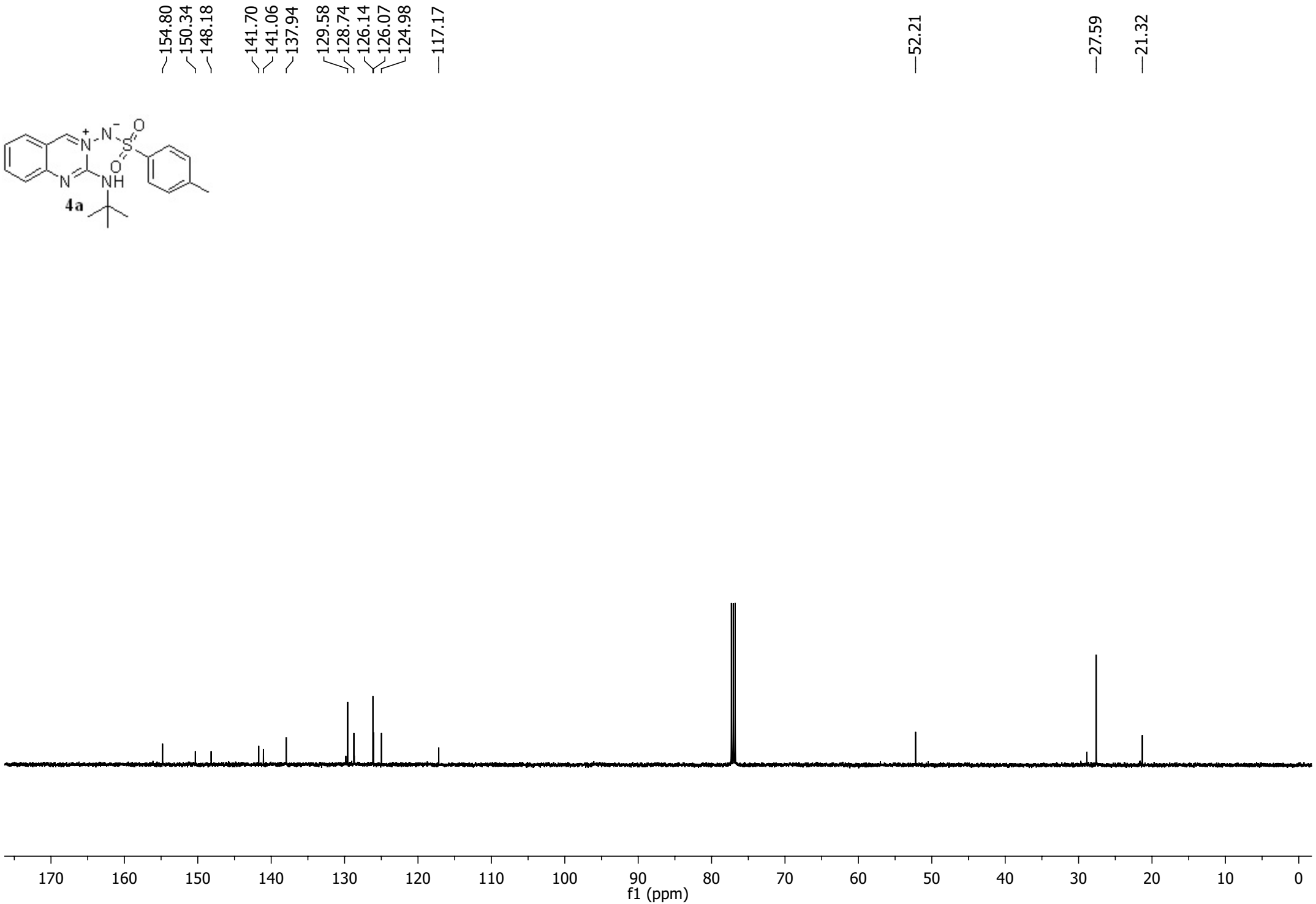
7.7757
7.7596
7.6074
7.5903
7.5374
7.5213
7.3923
7.3775
7.3625
7.2689
7.2091
7.1781
7.1624
2.3564
1.1846
4a
1.00
1.40
1.10
1.06
2.04
1.14
0.96
2.28
3.22
9.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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141.06
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128.74
126.14
126.07
124.98
117.17
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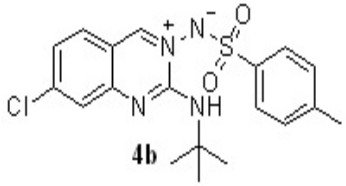
27.59
21.32
4a
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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N
NH
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O
S
O
4b

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7.3687
7.3565
7.3431
7.2895
7.2088
7.1930
2.3868
1.2059
1.00
1.37
1.03
2.11
2.38
2.42
3.39
9.26
11.5
10.5
9.5
9.0
8.5
8.0
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7.0
6.5
6.0
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5.0
4.5
4.0
3.5
3.0
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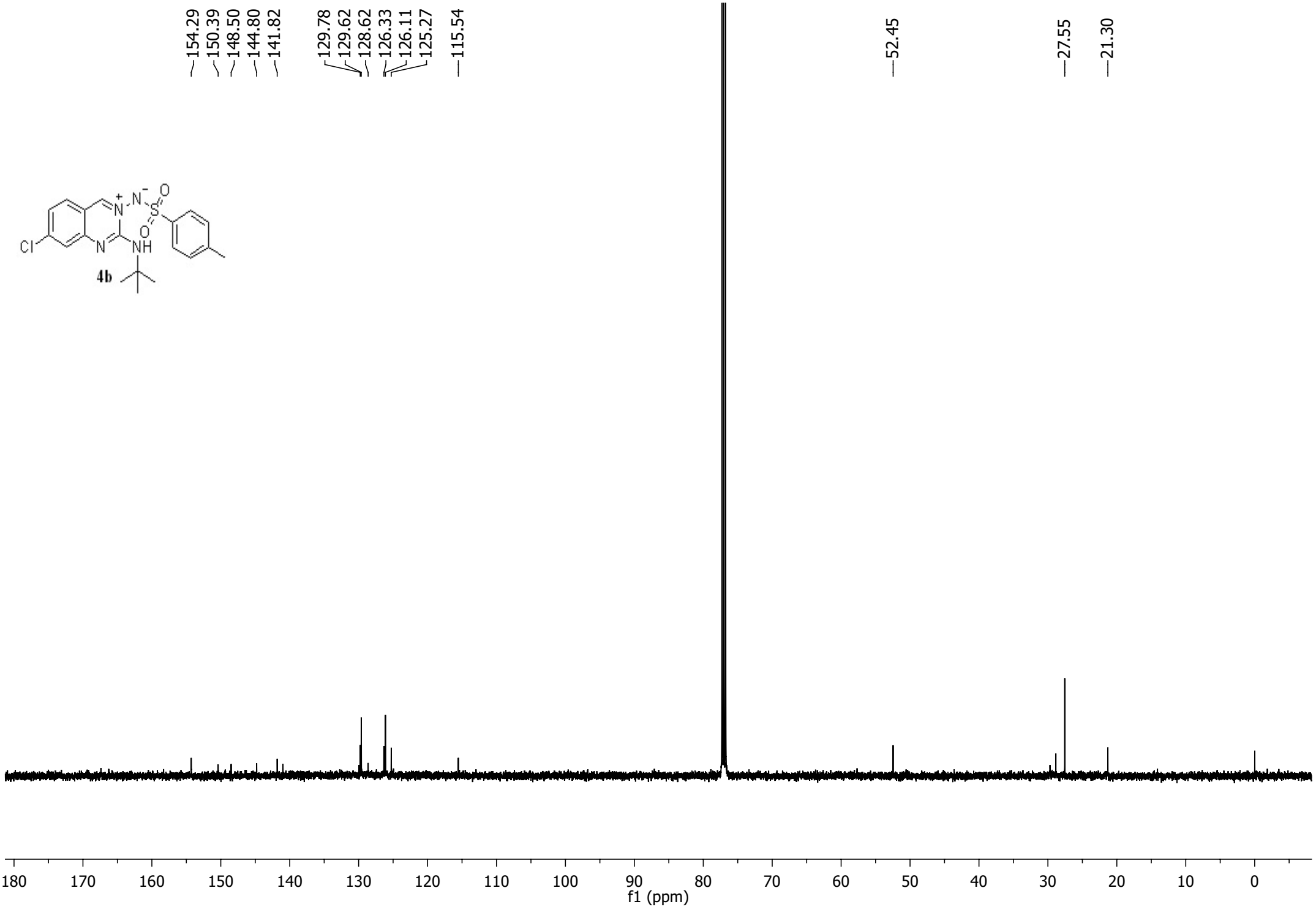
-1.0
-1.5
-2.0
f1 (ppm)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126.11
125.27
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52.45
27.55
21.30
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O
S
4b
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130
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110
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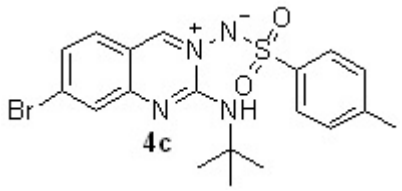
50
40
30
20
10
0
f1 (ppm)


Br
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NH
O
O
S
N
N
4c

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7.5372
7.4951
7.4920
7.4777
7.4745
7.3502
7.2871
7.2023
7.1862
2.3798
1.2015
1.00
1.21
1.23
2.09
1.06
1.25
2.43
3.37
9.42
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4.0
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0.0
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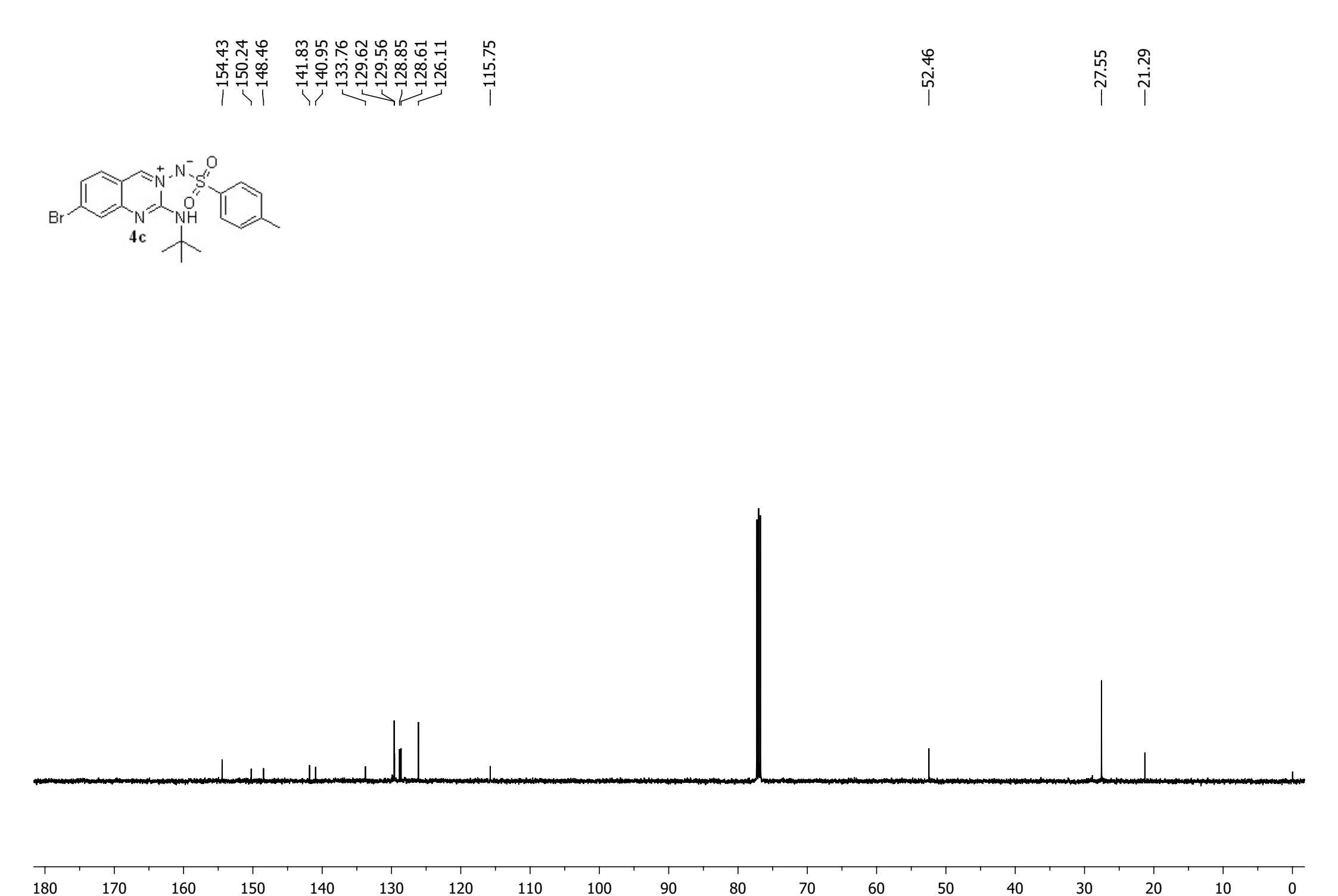
-1.0
f1 (ppm)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52.46
27.55
21.29
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O
O
S
4c
180
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130
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90
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50
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30
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10
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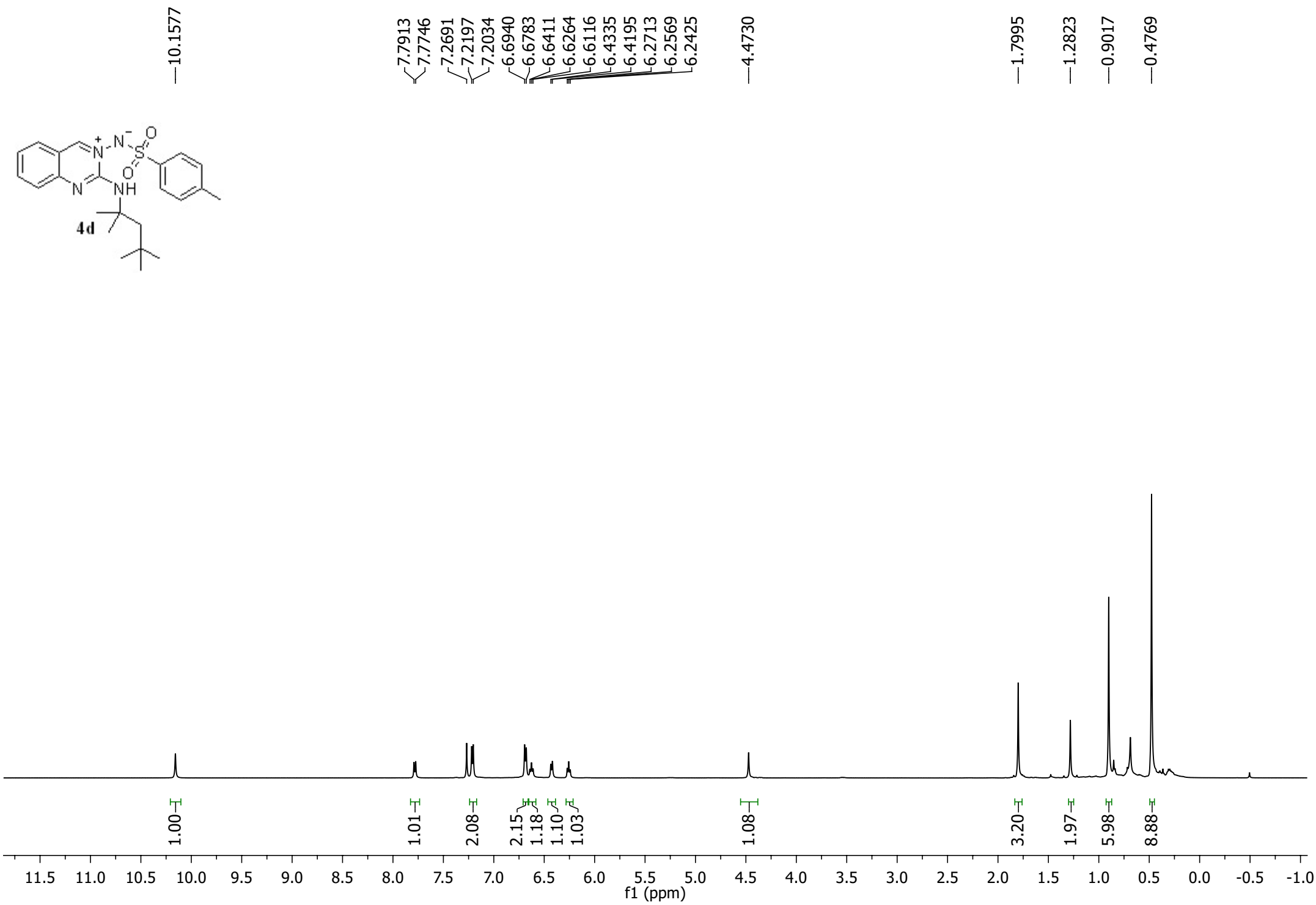
f1 (ppm)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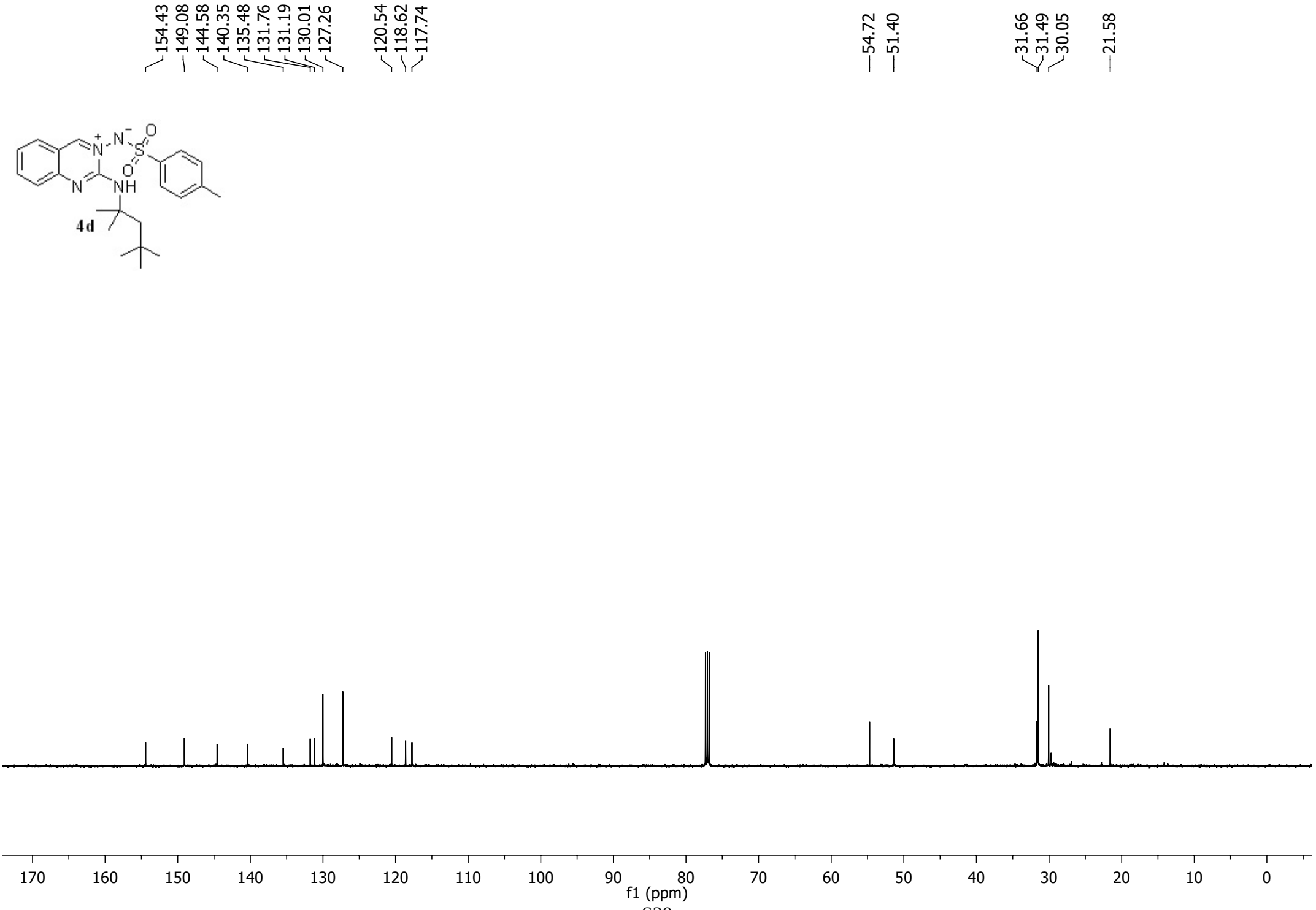
6.4335
6.4195
6.2713
6.2569
6.2425
4.4730
1.7995
1.2823
0.9017
0.4769
4d
1.00
1.01
2.08
2.15
1.18
1.10
1.03
1.08
3.20
1.97
5.98
8.88
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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21.58
4d
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120
110
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90
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50
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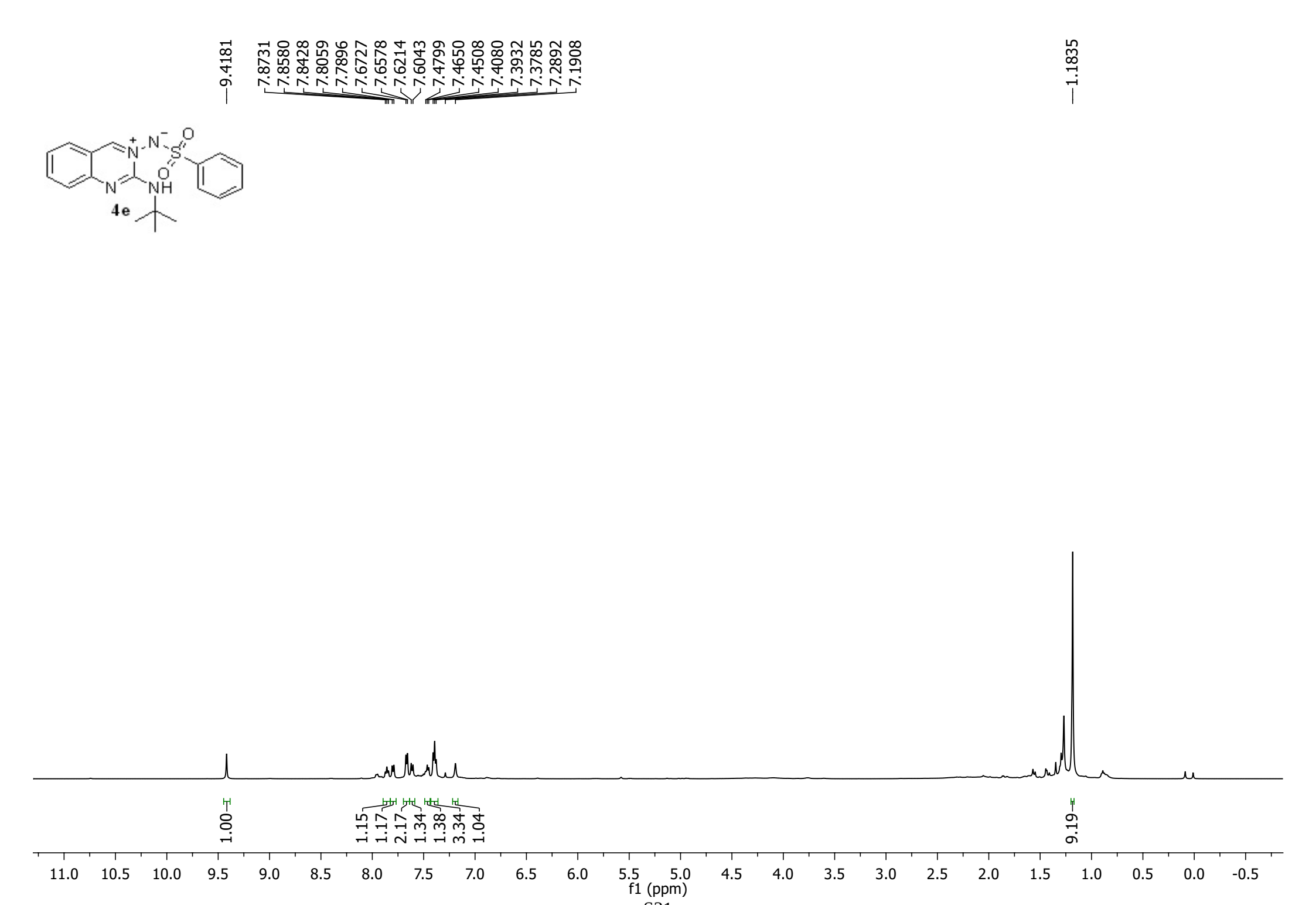
30
20
10
0
f1 (ppm)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4e
1.00
1.15
1.17
2.17
1.34
1.38
3.34
1.04
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11.0
10.5
10.0
9.5
9.0
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8.0
7.5
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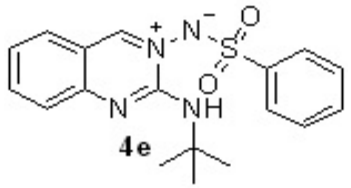
f1 (ppm)


4e

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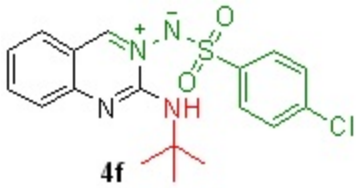
f1 (ppm)


N
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O
O
NH
Cl

4f

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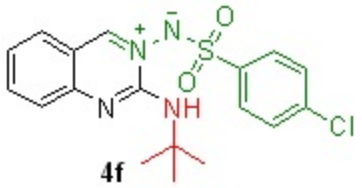
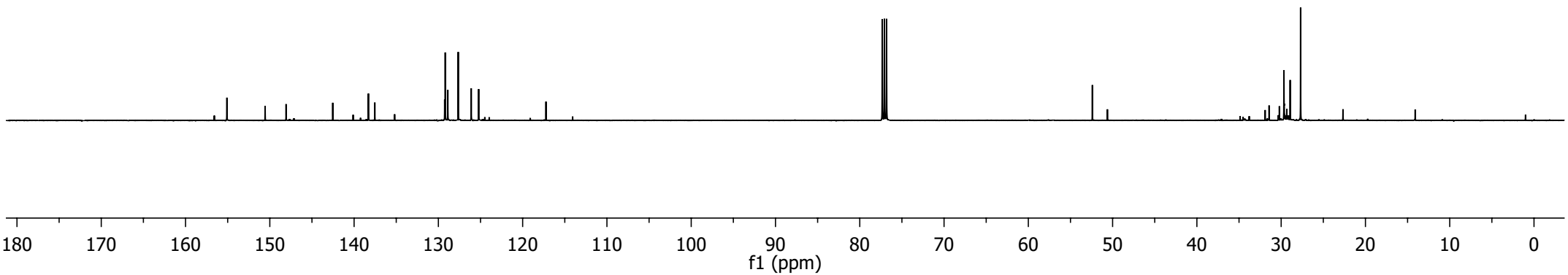
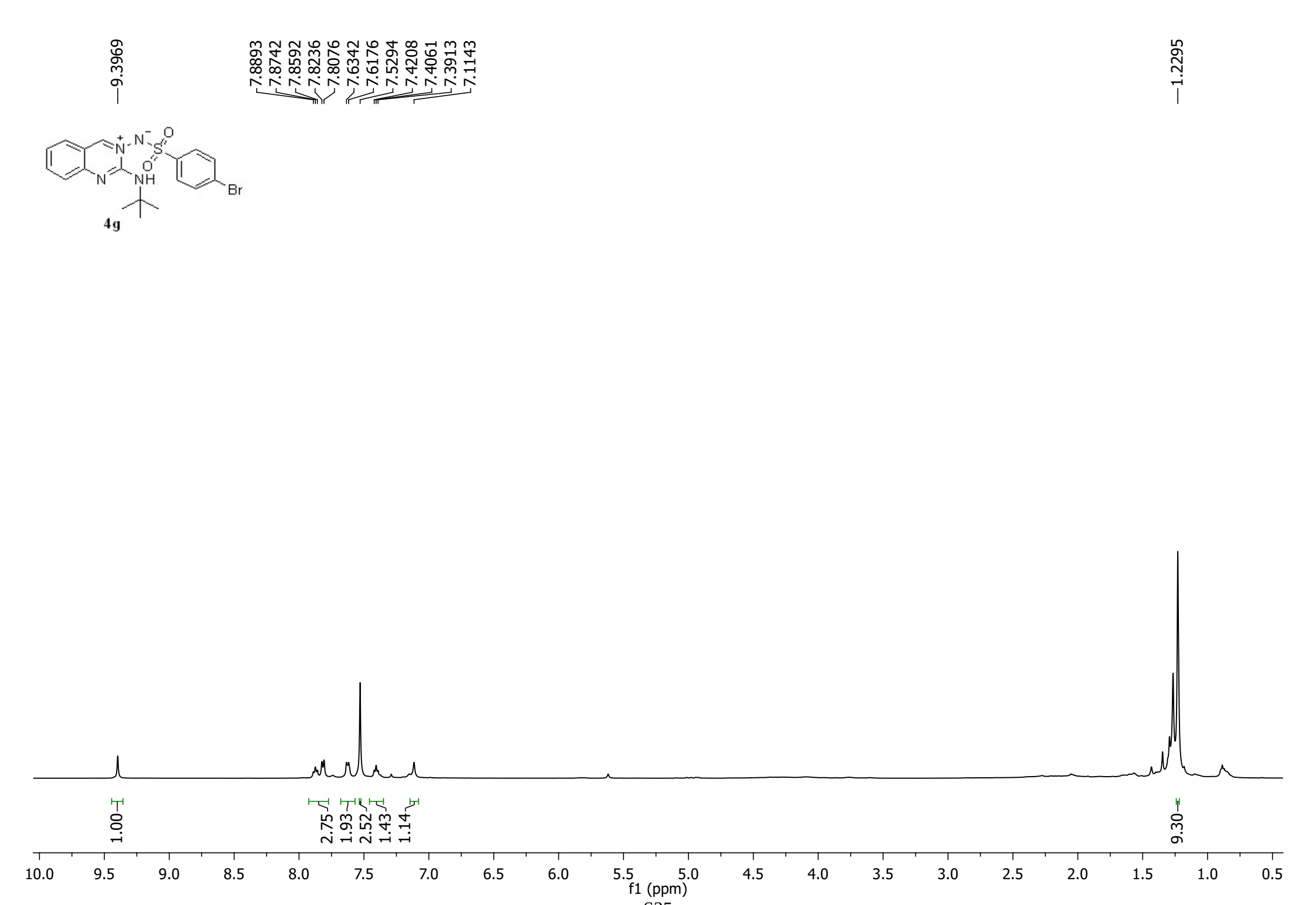
1.33
1.14
2.23
0.86
0.90
2.42
1.09
9.60
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



4f

155.09
150.56
148.07
142.53
138.30
137.54
130.16
129.18
128.88
127.64
126.10
125.22
117.23
52.40
27.69

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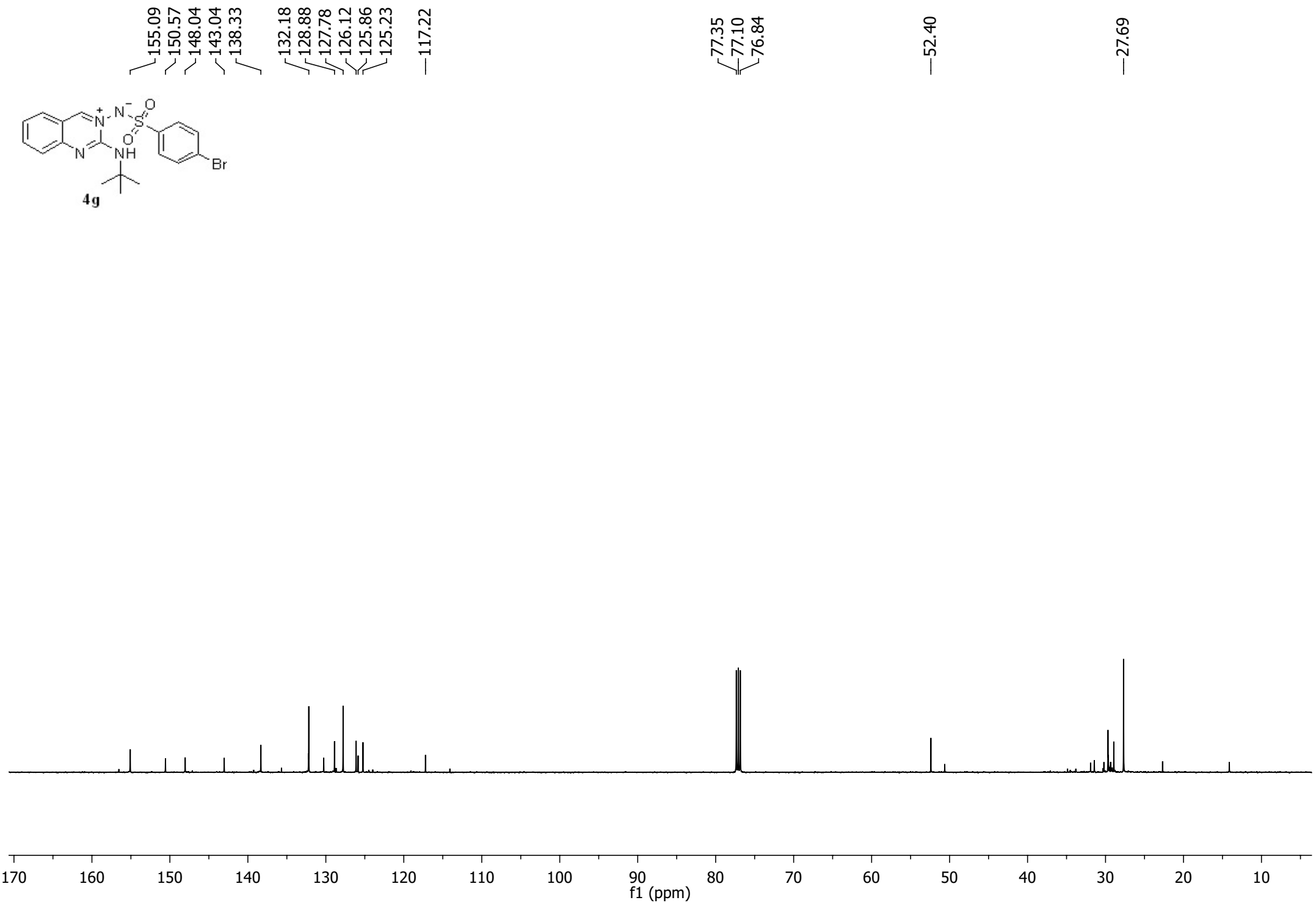
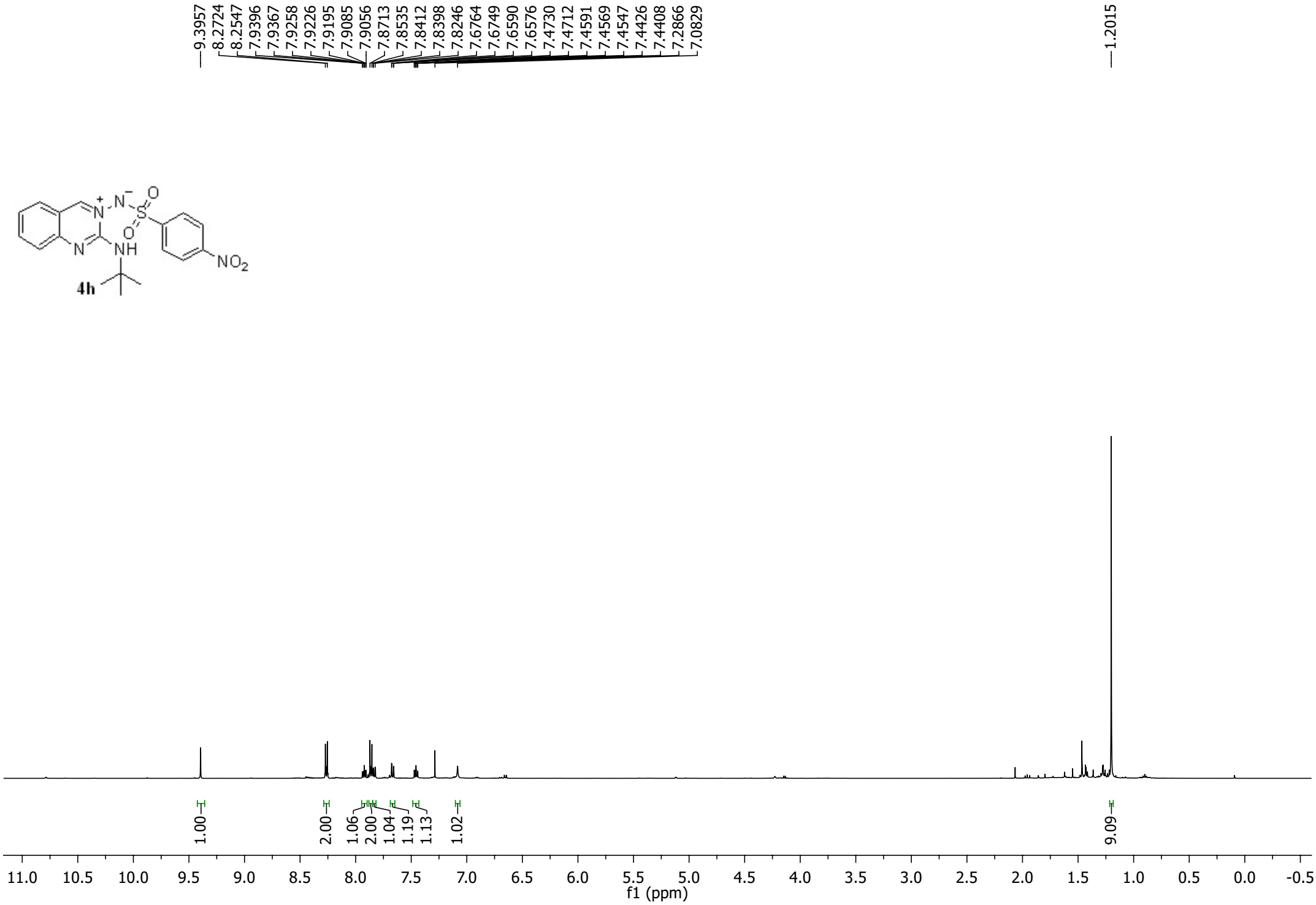
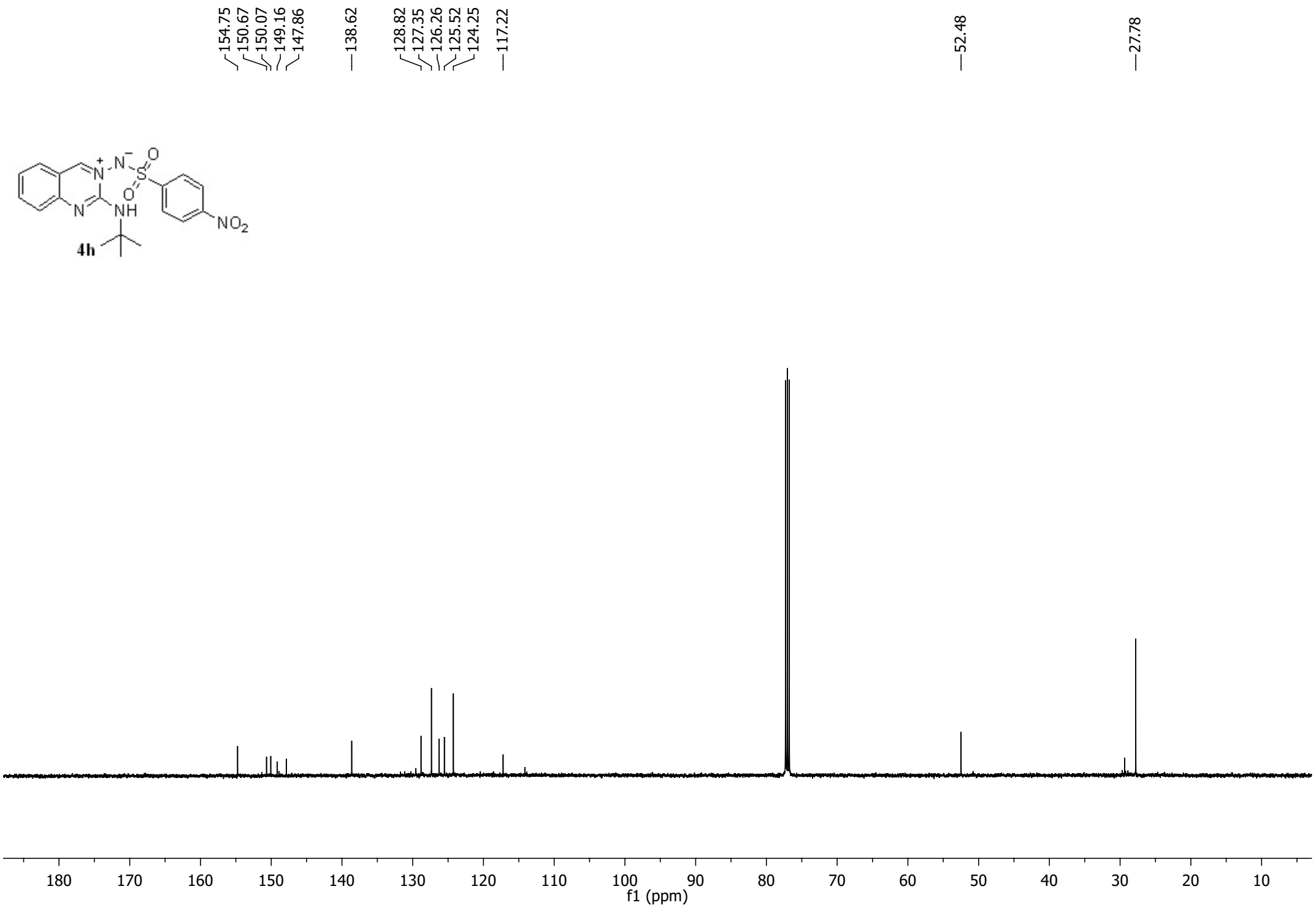
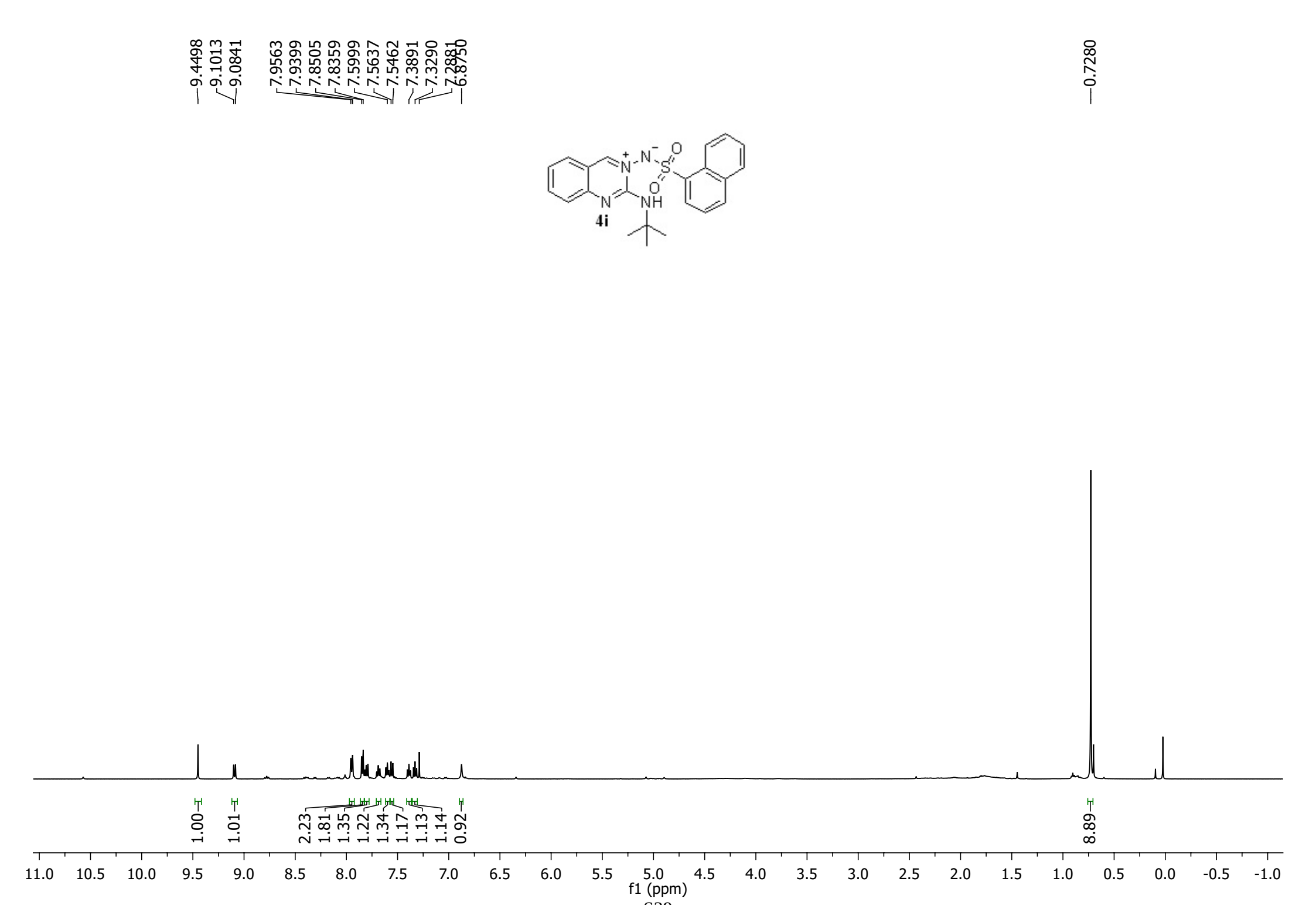
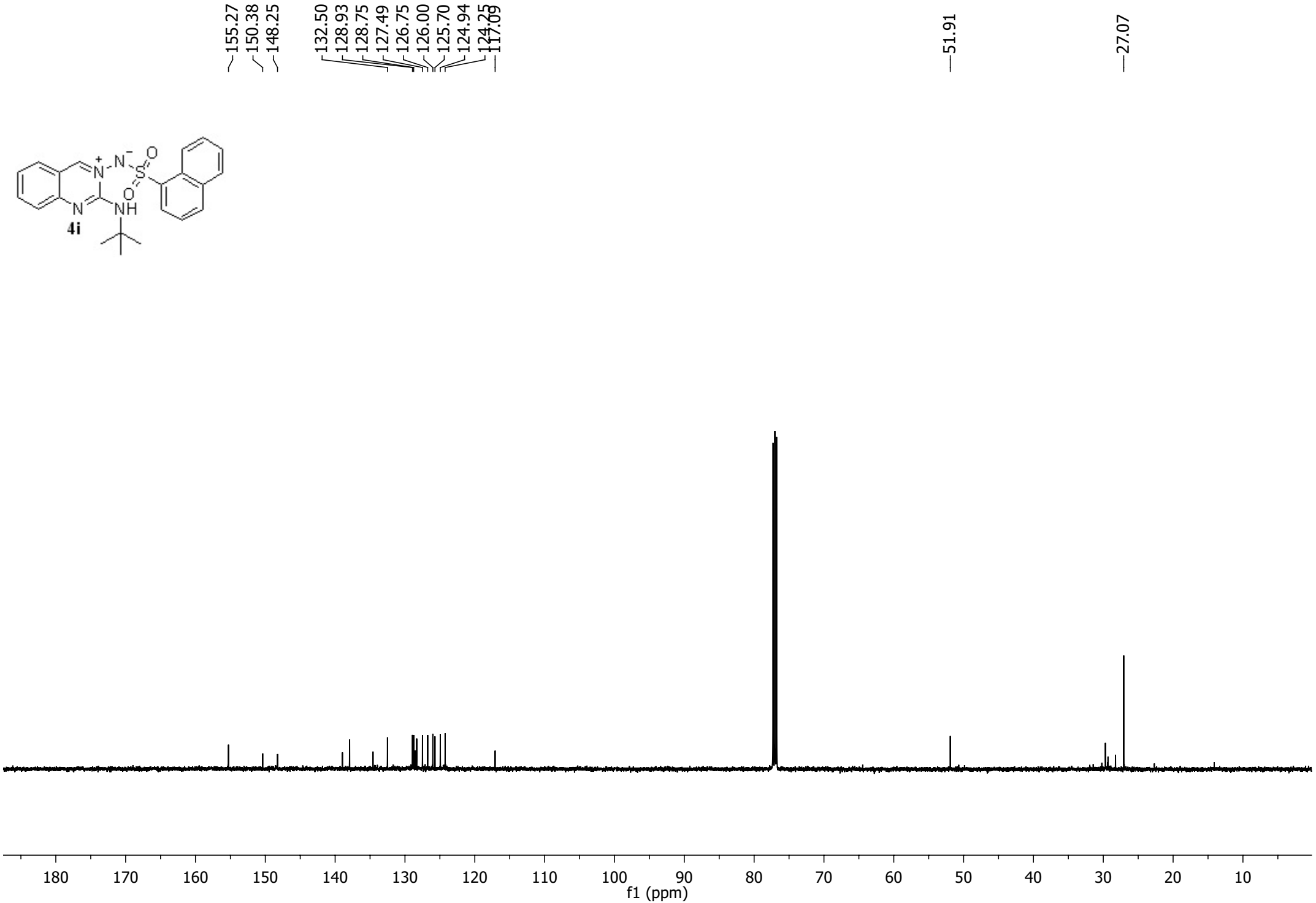
7.8742
7.8592
7.8236
7.8076
7.6342
7.6176
7.5294
7.4208
7.4061
7.3913
7.1143
1.2295
Br
4g
1.00
2.75
1.93
2.52
1.43
1.14
9.30
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

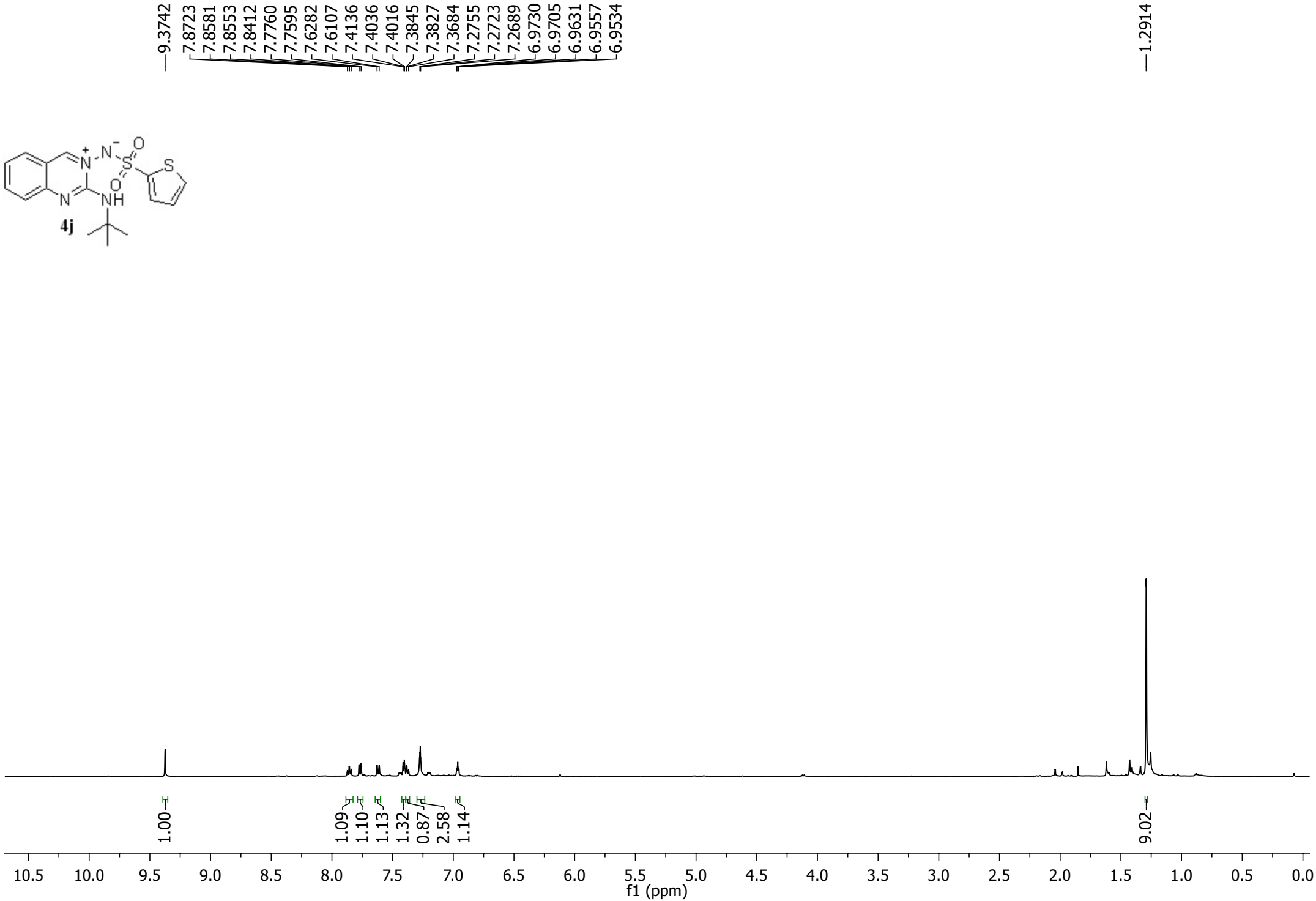

155.09
150.57
148.04
143.04
138.33
132.18
128.88
127.78
126.12
125.86
125.23
117.22
77.35
77.10
76.84
52.40
27.69
Br
4g
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

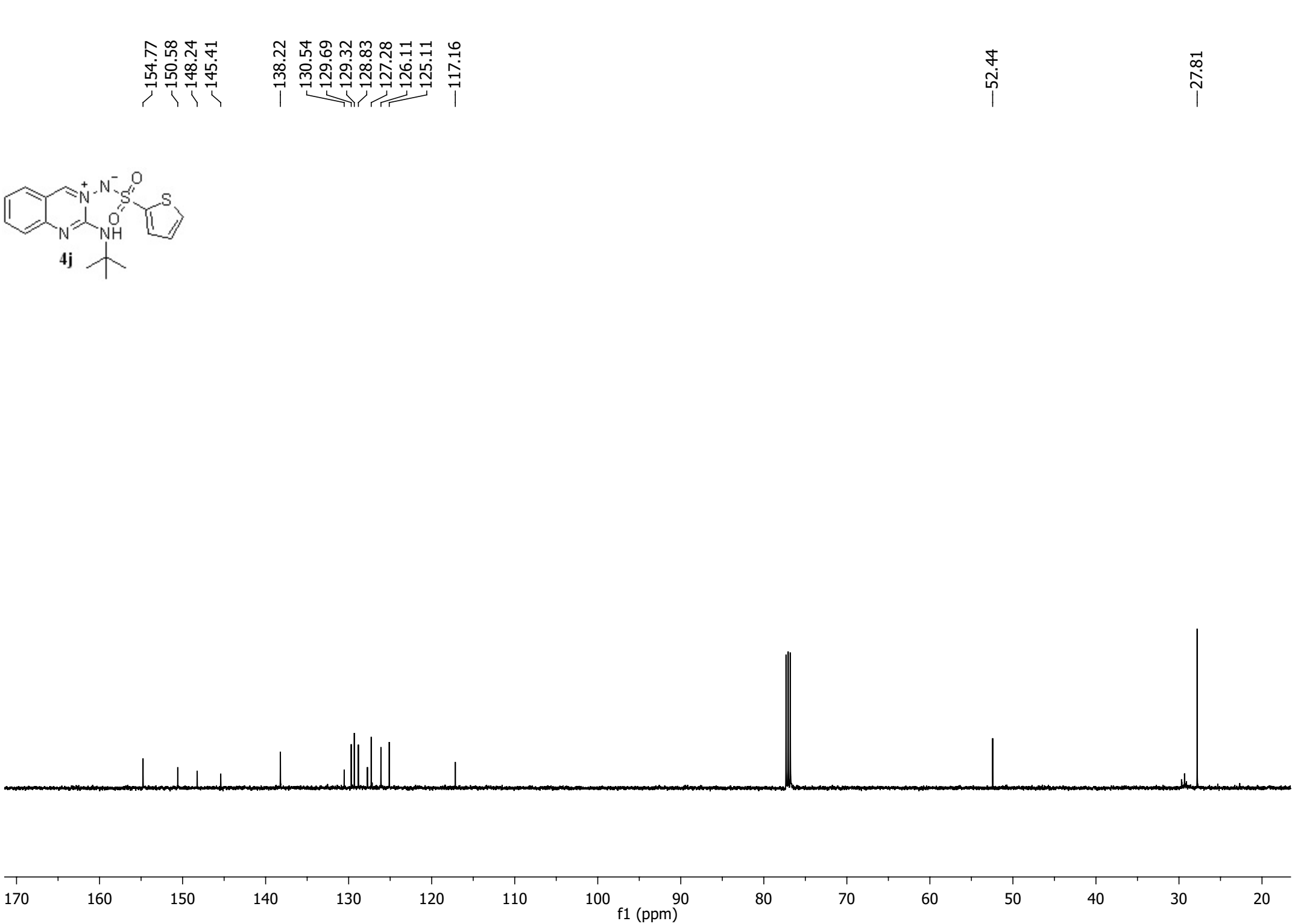

9.3957
8.2724
8.2547
7.9396
7.9367
7.9258
7.9226
7.9195
7.9085
7.9056
7.8713
7.8535
7.8412
7.8398
7.8246
7.6764
7.6749
7.6590
7.6576
7.4730
7.4712
7.4591
7.4569
7.4547
7.4426
7.4408
7.2866
7.0829
1.2015
4h
1.00
2.00
1.06
2.00
1.04
1.19
1.13
1.02
9.09
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

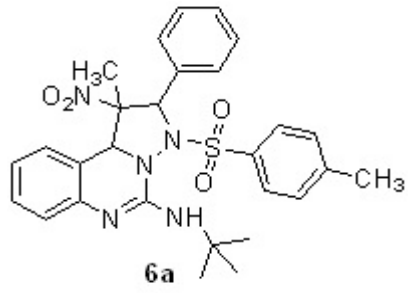

154.75
150.67
150.07
149.16
147.86
138.62
128.82
127.35
126.26
125.52
124.25
117.22
52.48
27.78
NO2
4h
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


9.4498
9.1013
9.0841
7.9563
7.9399
7.8505
7.8359
7.5999
7.5637
7.5462
7.3891
7.3290
7.2881
6.8750
0.7280
4i
1.00
1.01
2.23
1.81
1.35
1.22
1.34
1.17
1.13
1.14
0.92
8.89
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


155.27
150.38
148.25
132.50
128.93
128.75
127.49
126.75
126.00
125.70
124.94
124.25
117.09
51.91
27.07
4i
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

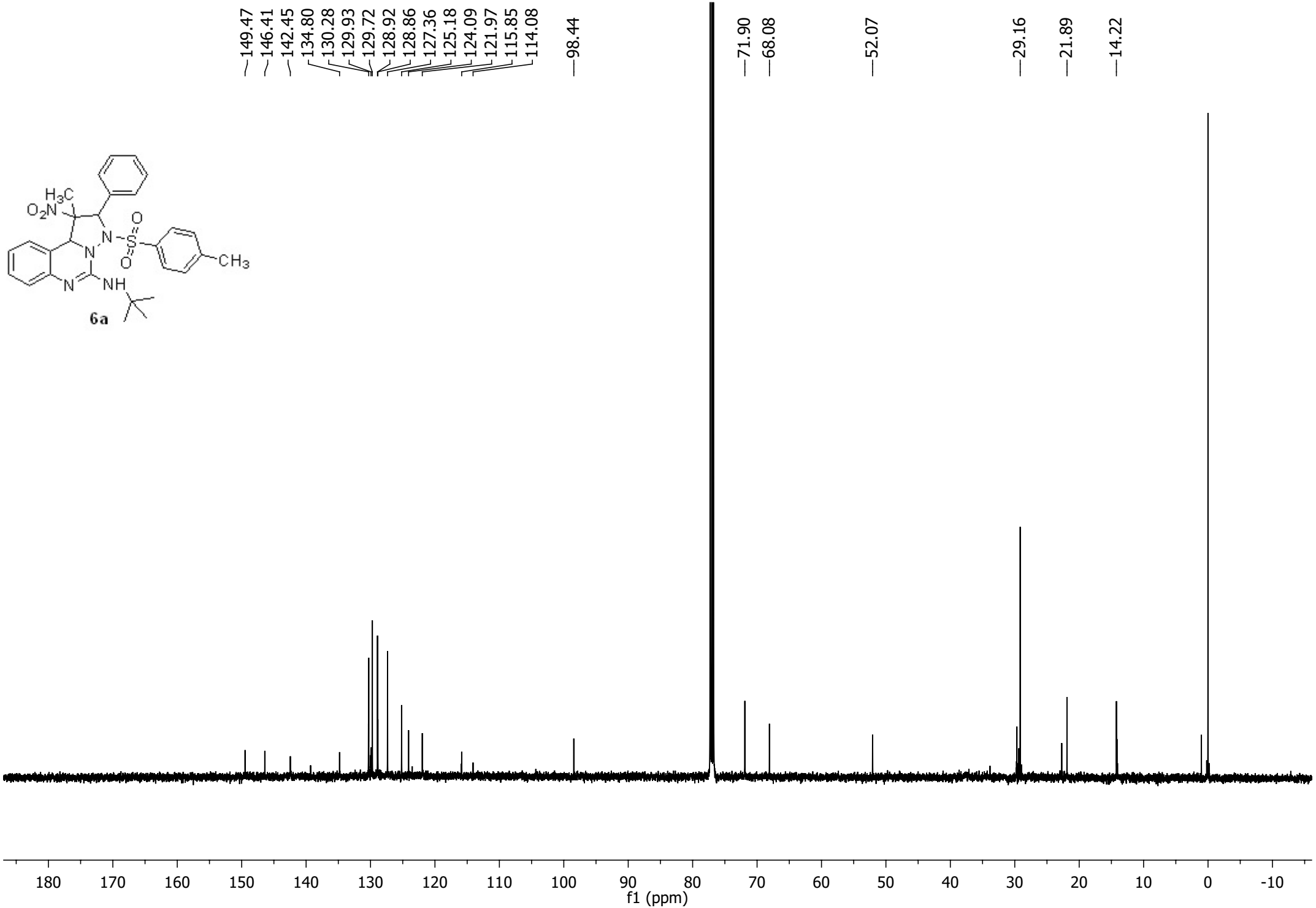

9.3742
7.8723
7.8581
7.8553
7.8412
7.7760
7.7595
7.6282
7.6107
7.4136
7.4036
7.4016
7.3845
7.3827
7.3684
7.2755
7.2723
7.2689
6.9730
6.9705
6.9631
6.9557
6.9534
1.2914
4j
1.00
1.09
1.10
1.13
1.32
0.87
2.58
1.14
9.02
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

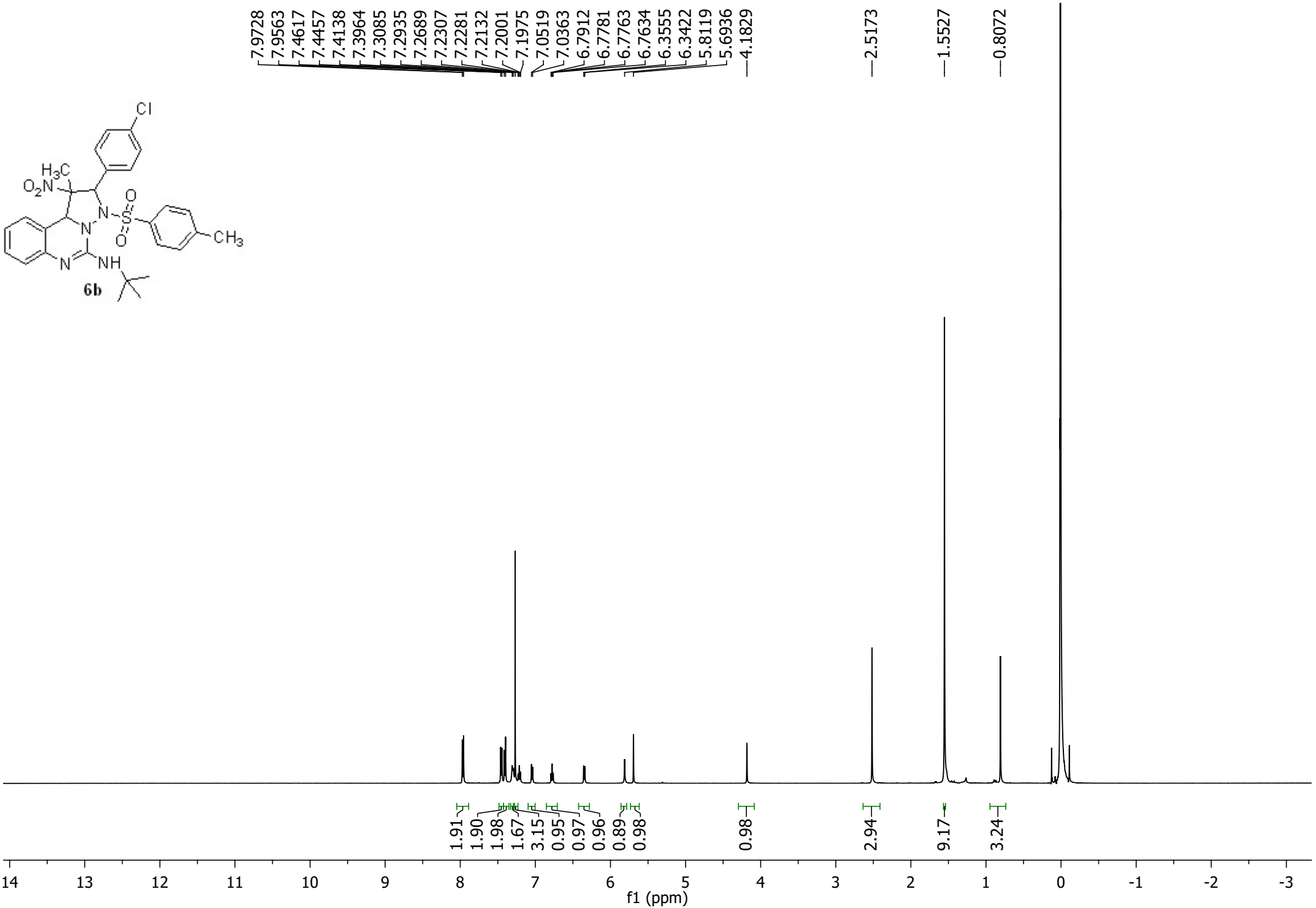

154.77
150.58
148.24
145.41
138.22
130.54
129.69
129.32
128.83
127.28
126.11
125.11
117.16
52.44
27.81
4j
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

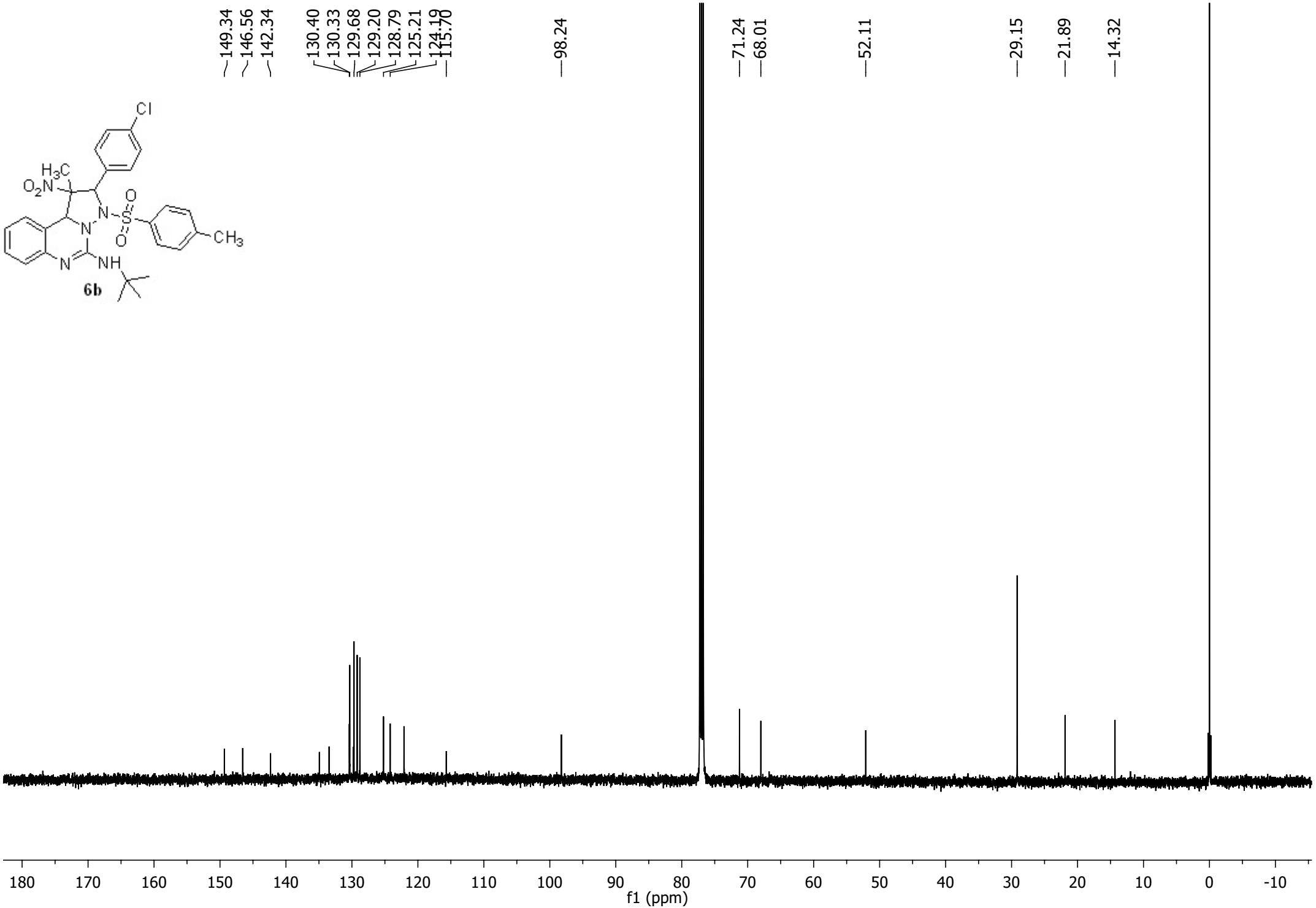

H3C
O2N
O
N
S
O
N
N
CH3
NH

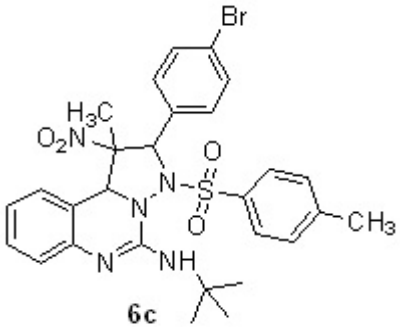
6a

7.9817
7.9652
7.4513
7.4352
7.4195
7.4064
7.3906
7.3738
7.3598
7.3367
7.3229
7.2589
7.1987
7.1843
7.1819
7.0434
7.0285
6.7752
6.7606
6.7458
6.3408
6.3272
5.8803
5.7328
4.1926
2.5058
1.5590
0.7913
0.0008
1.84
2.19
3.17
2.42
1.24
0.95
0.91
0.91
0.80
1.00
0.91
3.09
9.38
3.20
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)


149.47
146.41
142.45
134.80
130.28
129.93
129.72
128.92
128.86
127.36
125.18
124.09
121.97
115.85
114.08
98.44
71.90
68.08
52.07
29.16
21.89
14.22
H3C
O2N
N
S
O
O
CH3
N
NH
6a
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

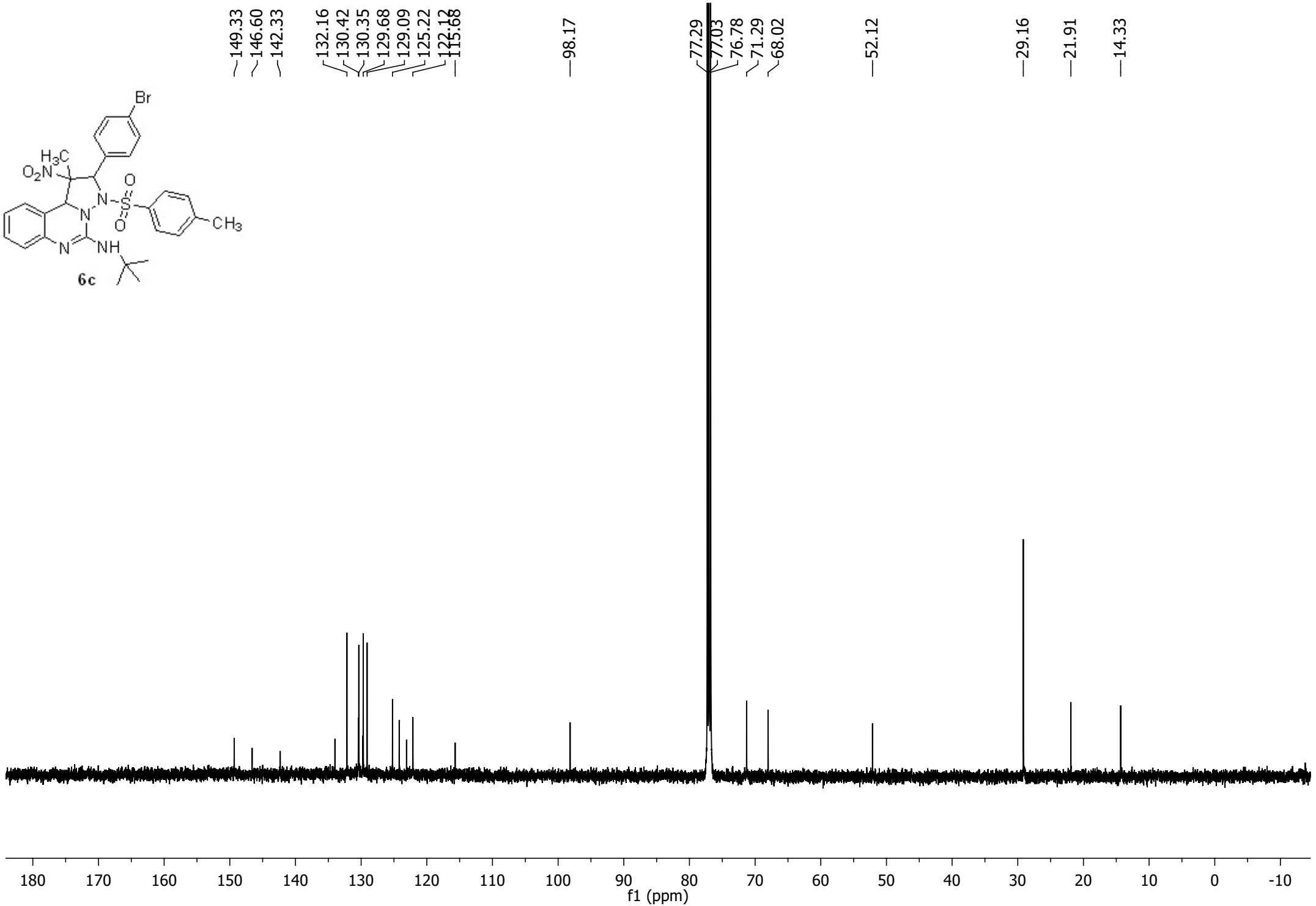

7.9728
7.9563
7.4617
7.4457
7.4138
7.3964
7.3085
7.2935
7.2689
7.2307
7.2281
7.2132
7.2001
7.1975
7.0519
7.0363
6.7912
6.7781
6.7763
6.7634
6.3555
6.3422
5.8119
5.6936
4.1829
2.5173
1.5527
0.8072
Cl
H3C
O2N
O
O
S
N
N
CH3
N
NH
6b
1.91
1.90
1.98
1.67
3.15
0.95
0.97
0.96
0.89
0.98
0.98
2.94
9.17
3.24
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

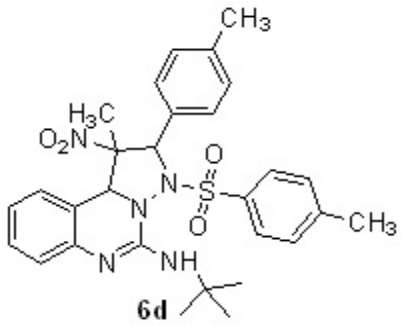

149.34
146.56
142.34
130.40
130.33
129.68
129.20
128.79
125.21
124.19
115.70
98.24
71.24
68.01
52.11
29.15
21.89
14.32
Cl
H3C
O2N
N
S
O
O
CH3
N
NH
6b
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Br
H3C
O2N
O
N
S
O
N
CH3
N
NH

6c

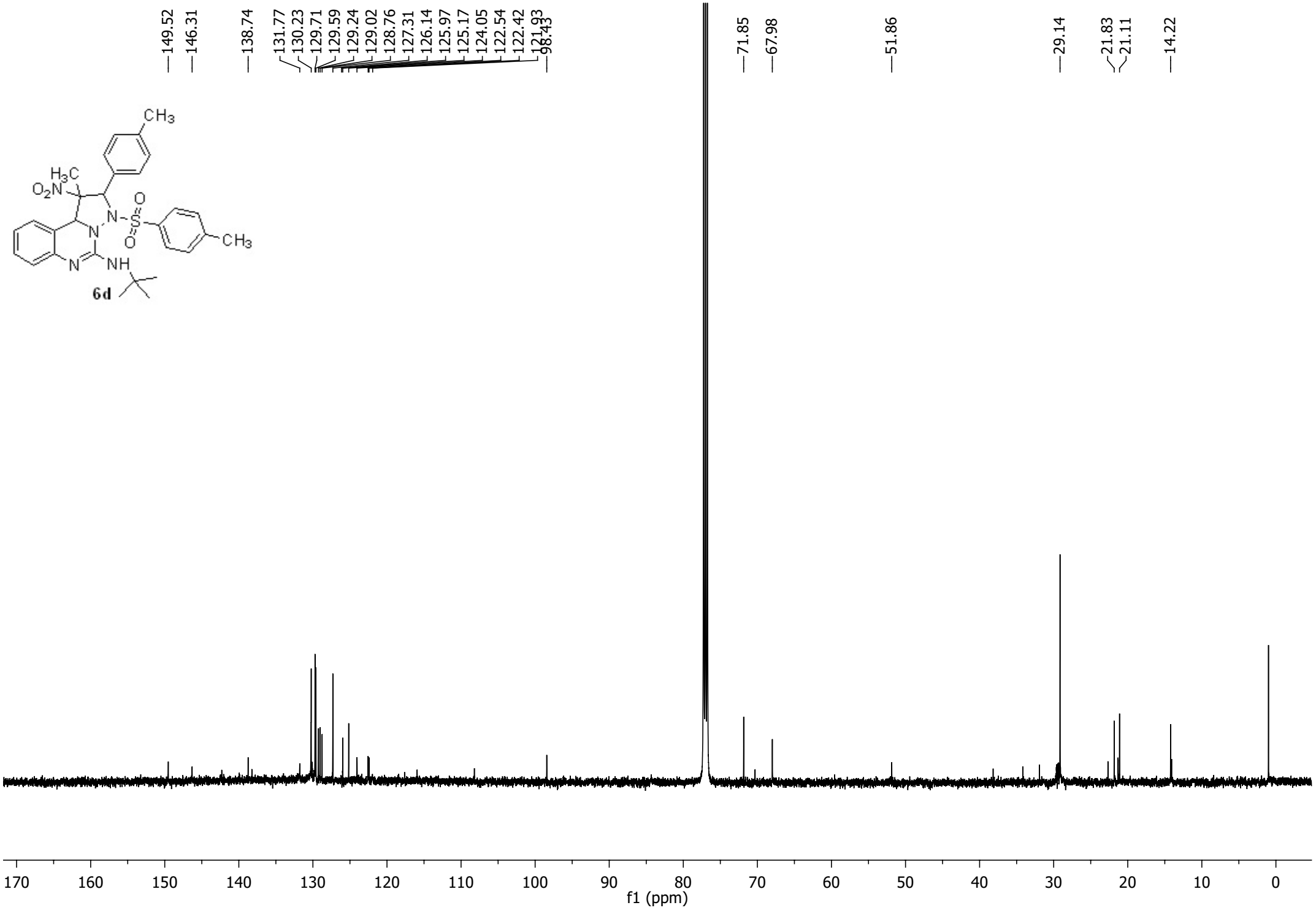
7.9683
7.9527
7.5675
7.5513
7.4601
7.4443
7.2687
7.2453
7.2295
7.2139
7.1986
7.0504
7.0346
6.7913
6.7764
6.7616
6.3537
6.3385
5.8029
5.6731
4.1768
2.5156
1.5482
0.8050
2.00
1.99
1.90
1.26
2.10
0.98
1.05
0.98
0.91
1.06
1.03
2.99
9.20
2.98
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

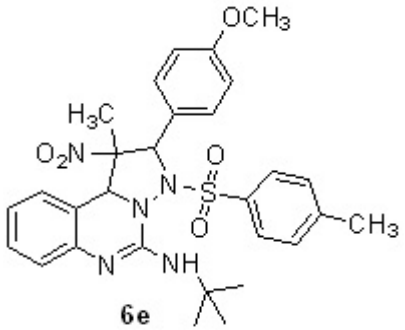

149.33
146.60
142.33
132.16
130.42
130.35
129.68
129.09
125.22
122.12
115.68
98.17
77.29
77.03
76.78
71.29
68.02
52.12
29.16
21.91
14.33
Br
H3C
O2N
O
N
S
O
CH3
N
NH
6c
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CH3
H3C
O2N
O
N
S
O
CH3
N
N
NH

6d

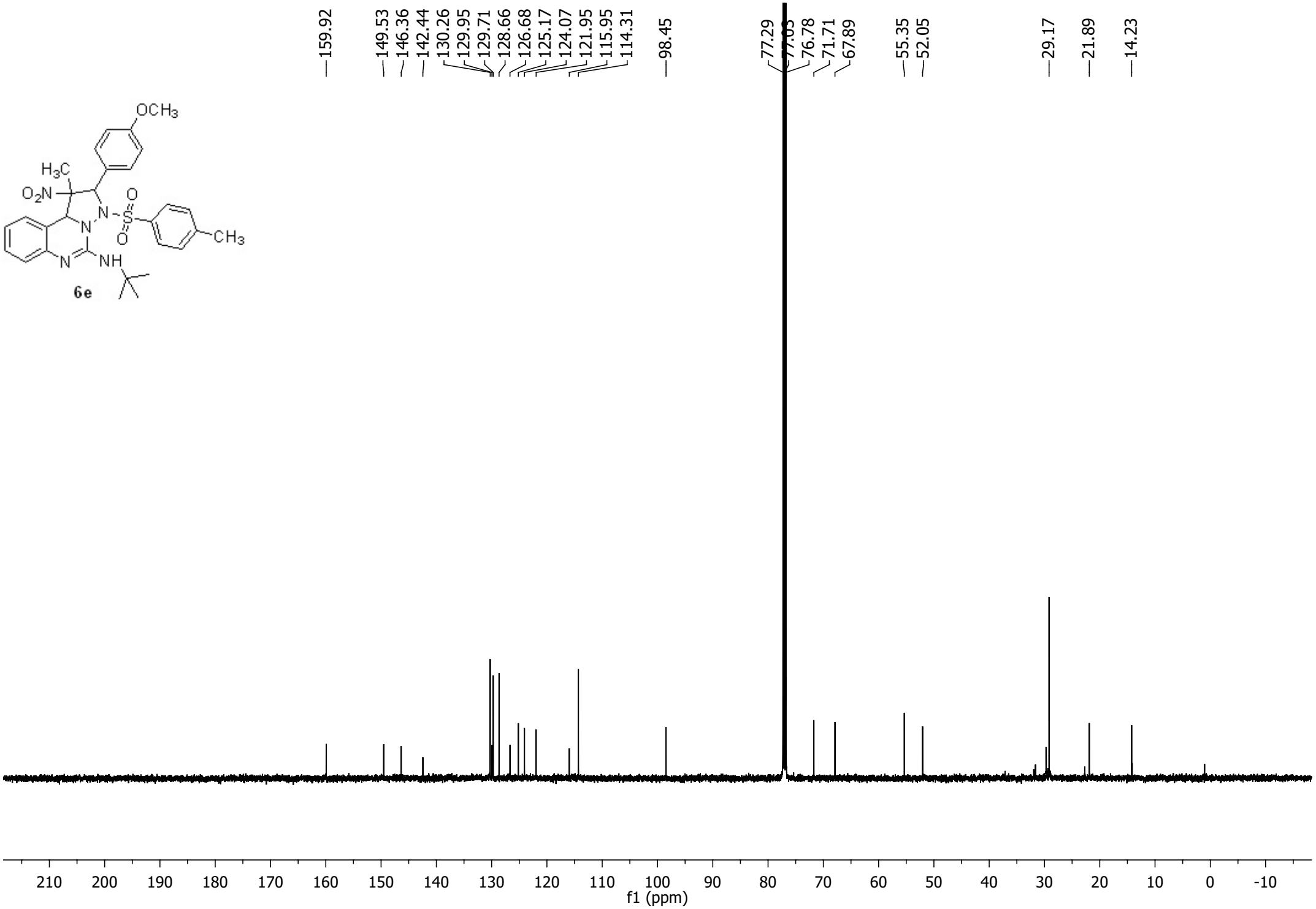
7.9820
7.9654
7.4523
7.4361
7.2193
7.2019
7.0409
6.7621
6.7602
6.3476
6.3320
5.8688
5.6902
4.1993
2.5107
2.3663
1.5587
0.8526
2.07
2.23
4.99
1.04
1.11
1.00
0.95
1.01
0.98
2.96
3.12
9.02
2.99
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

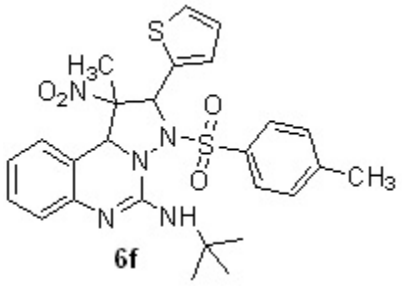

149.52
146.31
138.74
131.77
130.23
129.71
129.59
129.24
129.02
128.76
127.31
126.14
125.97
125.17
124.05
122.54
122.42
121.93
98.43
71.85
67.98
51.86
29.14
21.83
21.11
14.22
CH3
H3C
O2N
O
N
S
O
CH3
N
NH
6d
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OCH3
H3C
O2N
O
N
S
O
N
CH3
N
NH

6e

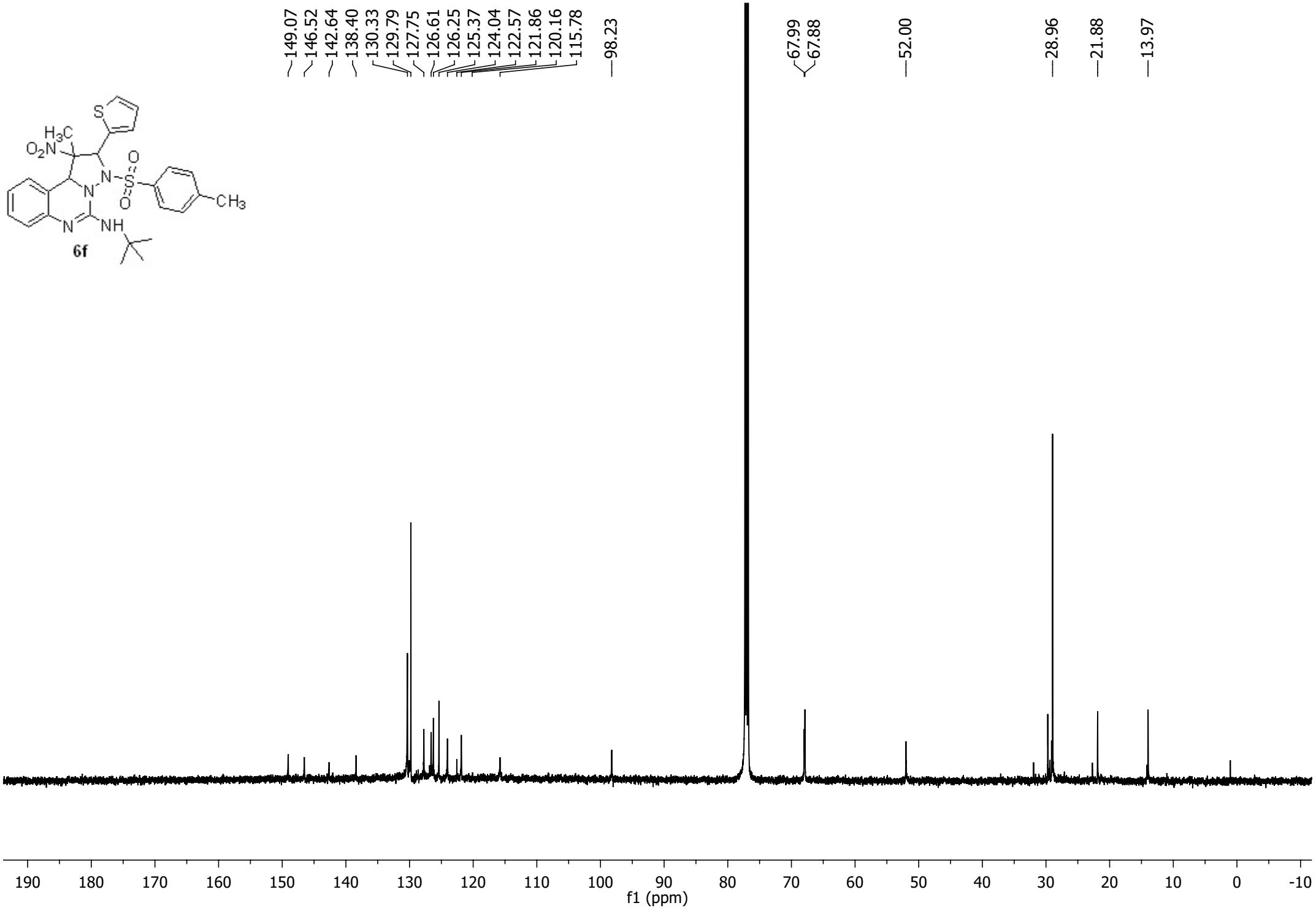
7.9772
7.9609
7.4516
7.4355
7.2681
7.2473
7.2147
7.1997
7.1842
7.0406
7.0247
6.9356
6.9181
6.7755
6.7606
6.7457
6.3480
6.3331
5.8517
5.6601
4.1969
3.8281
2.5094
1.5583
0.8158
2.07
2.11
1.88
1.28
1.07
2.06
1.05
1.04
1.00
1.04
1.05
3.14
3.11
9.18
3.32
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

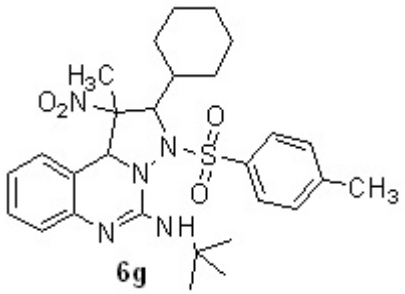

159.92
149.53
146.36
142.44
130.26
129.95
129.71
128.66
126.68
125.17
124.07
121.95
115.95
114.31
98.45
77.29
77.03
76.78
71.71
67.89
55.35
52.05
29.17
21.89
14.23
OCH3
H3C
O2N
N
S
O
O
CH3
N
NH
6e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


S
H3C
O2N
O
N
S
O
N
N
CH3
NH

6f

7.9768
7.9614
7.4488
7.4344
7.3629
7.3541
7.2687
7.2122
7.0457
7.0381
6.9759
6.7765
6.4048
6.3916
6.0176
5.6793
4.2935
2.5091
1.5119
0.9836
2.01
2.21
1.29
1.28
1.09
0.99
1.00
1.11
1.09
1.01
1.16
3.15
9.09
3.37
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.5
f1 (ppm)


149.07
146.52
142.64
138.40
130.33
129.79
127.75
126.61
126.25
125.37
124.04
122.57
121.86
120.16
115.78
98.23
67.99
67.88
52.00
28.96
21.88
13.97
6f
f1 (ppm)


H3C
O2N
N
N
S
O
O
CH3
N
NH

6g

7.9195
7.9034
7.3737
7.3577
7.2689
7.2108
7.1949
7.0149
6.7877
6.3852
6.3504
5.2804
4.5374
4.5185
4.2556
3.1695
2.4573
1.9702
1.9533
1.7323
1.3582
1.2596
0.8852
0.8732
0.8604
0.8461
2.29
2.25
1.93
1.08
1.18
1.24
1.00
1.24
1.28
2.45
3.19
2.54
1.87
9.85
4.09
3.13
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
1.5
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0.5
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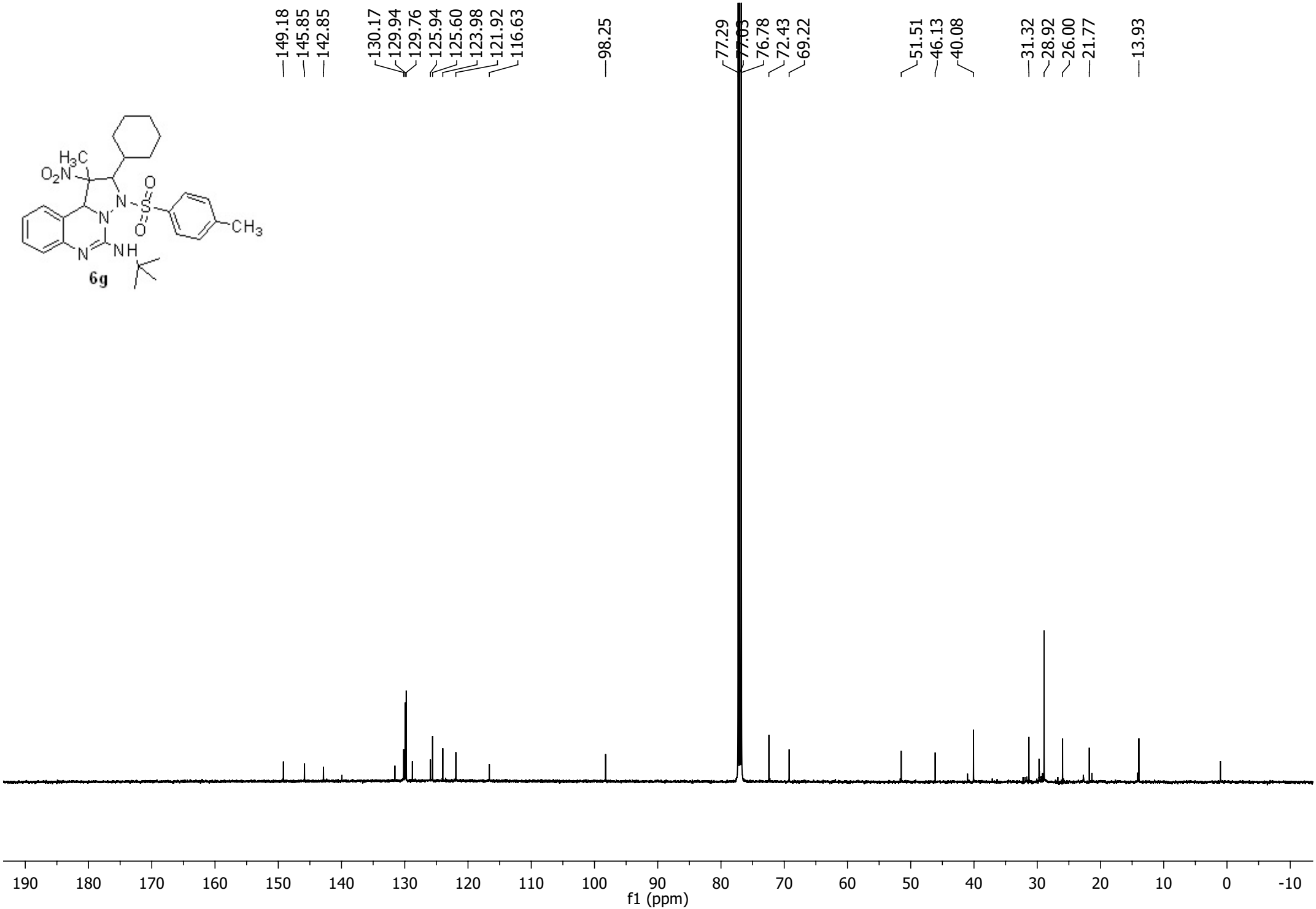
-0.5
f1 (ppm)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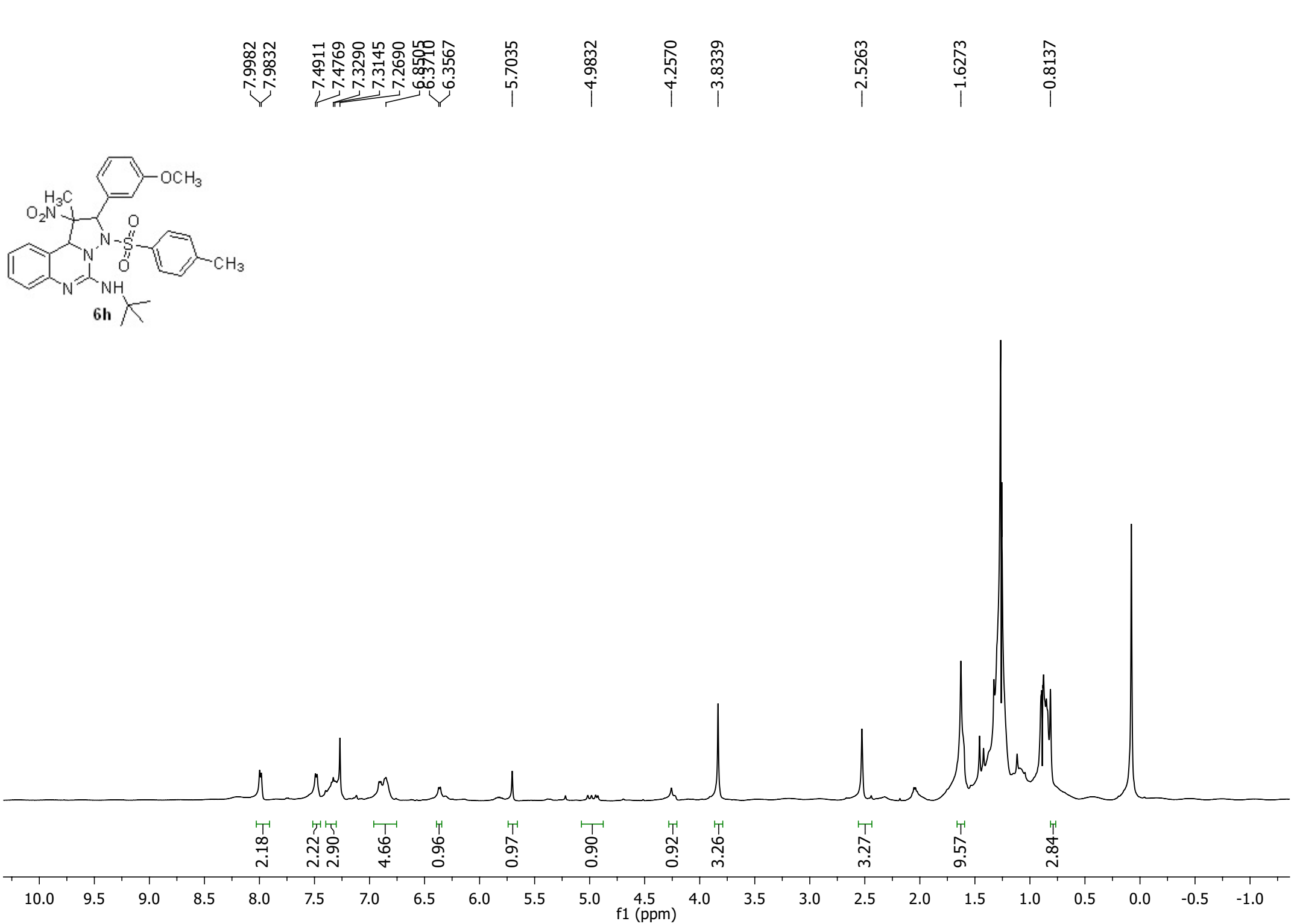
145.85
142.85
130.17
129.94
129.76
125.94
125.60
123.98
121.92
116.63
98.25
77.29
76.78
72.43
69.22
51.51
46.13
40.08
31.32
28.92
26.00
21.77
13.93
6g
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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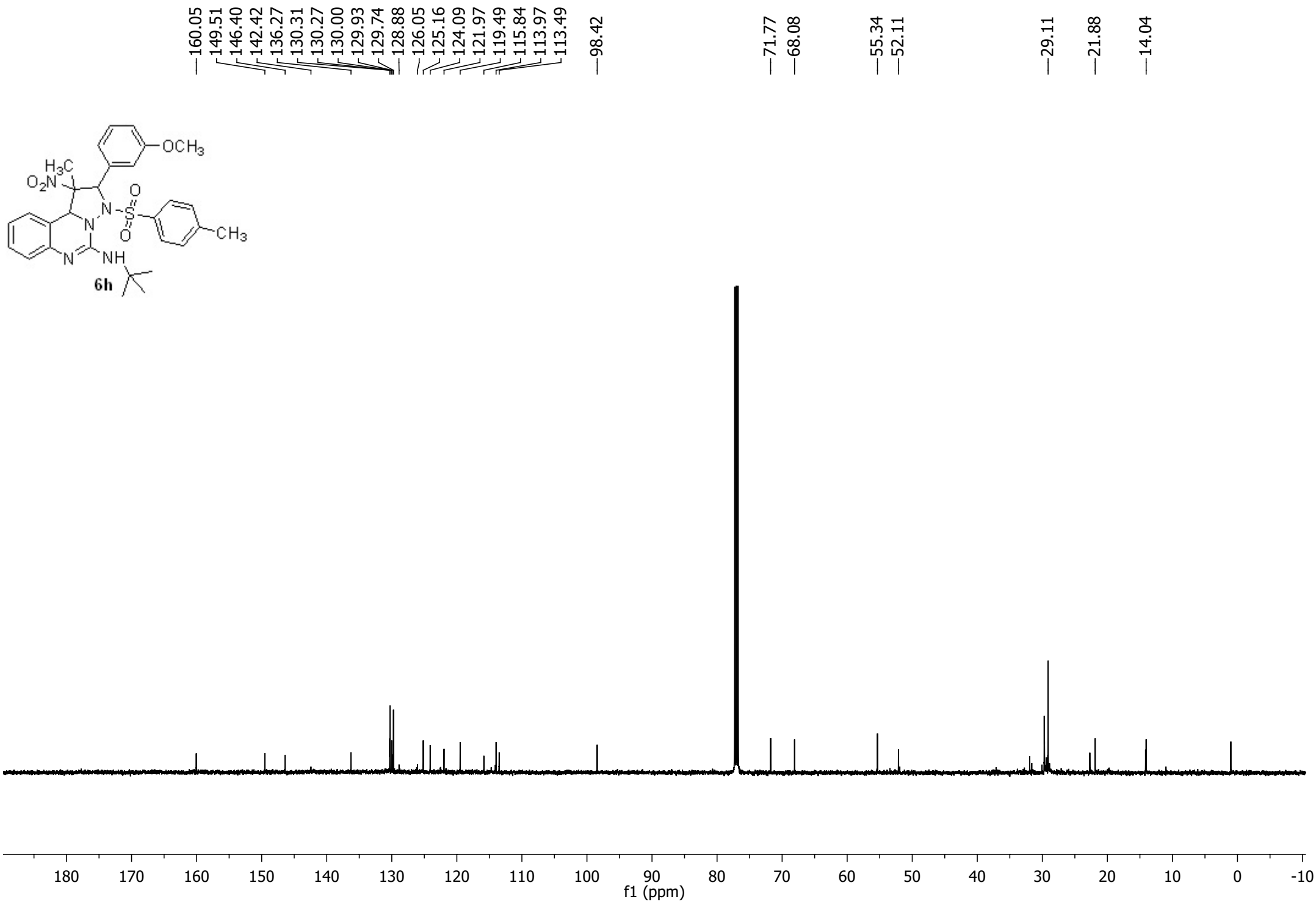
7.9832
7.4911
7.4769
7.3290
7.3145
7.2690
6.8505
6.3710
6.3567
5.7035
4.9832
4.2570
3.8339
2.5263
1.6273
0.8137
OCH3
H3C
O2N
O
S
O
N
N
CH3
N
NH
6h
2.18
2.22
2.90
4.66
0.96
0.97
0.90
0.92
3.26
3.27
9.57
2.84
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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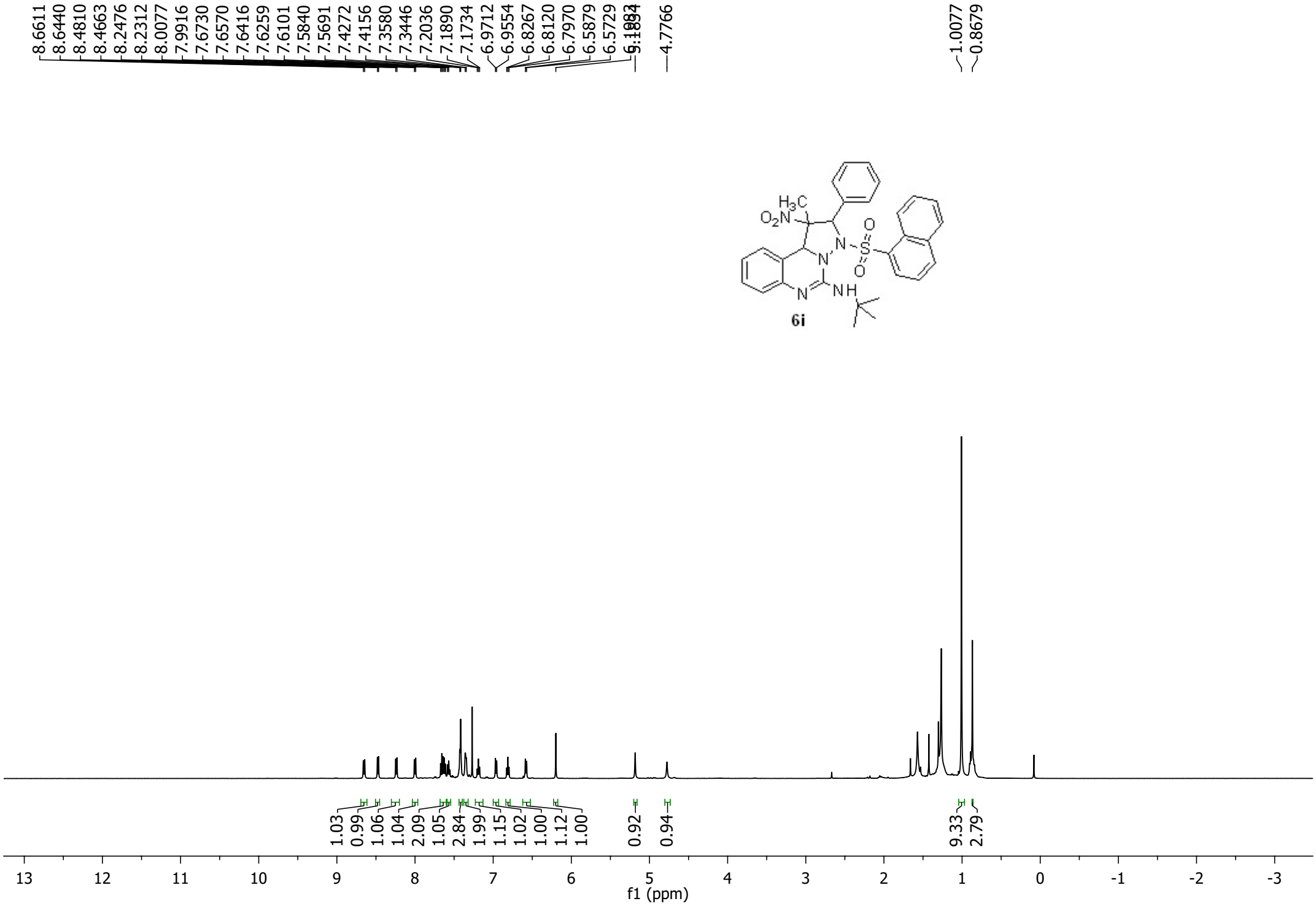
130.31
130.27
130.00
129.93
129.74
128.88
126.05
125.16
124.09
121.97
119.49
115.84
113.97
113.49
98.42
71.77
68.08
55.34
52.11
29.11
21.88
14.04
OCH3
H3C
O2N
N
S
O
O
CH3
N
NH
6h
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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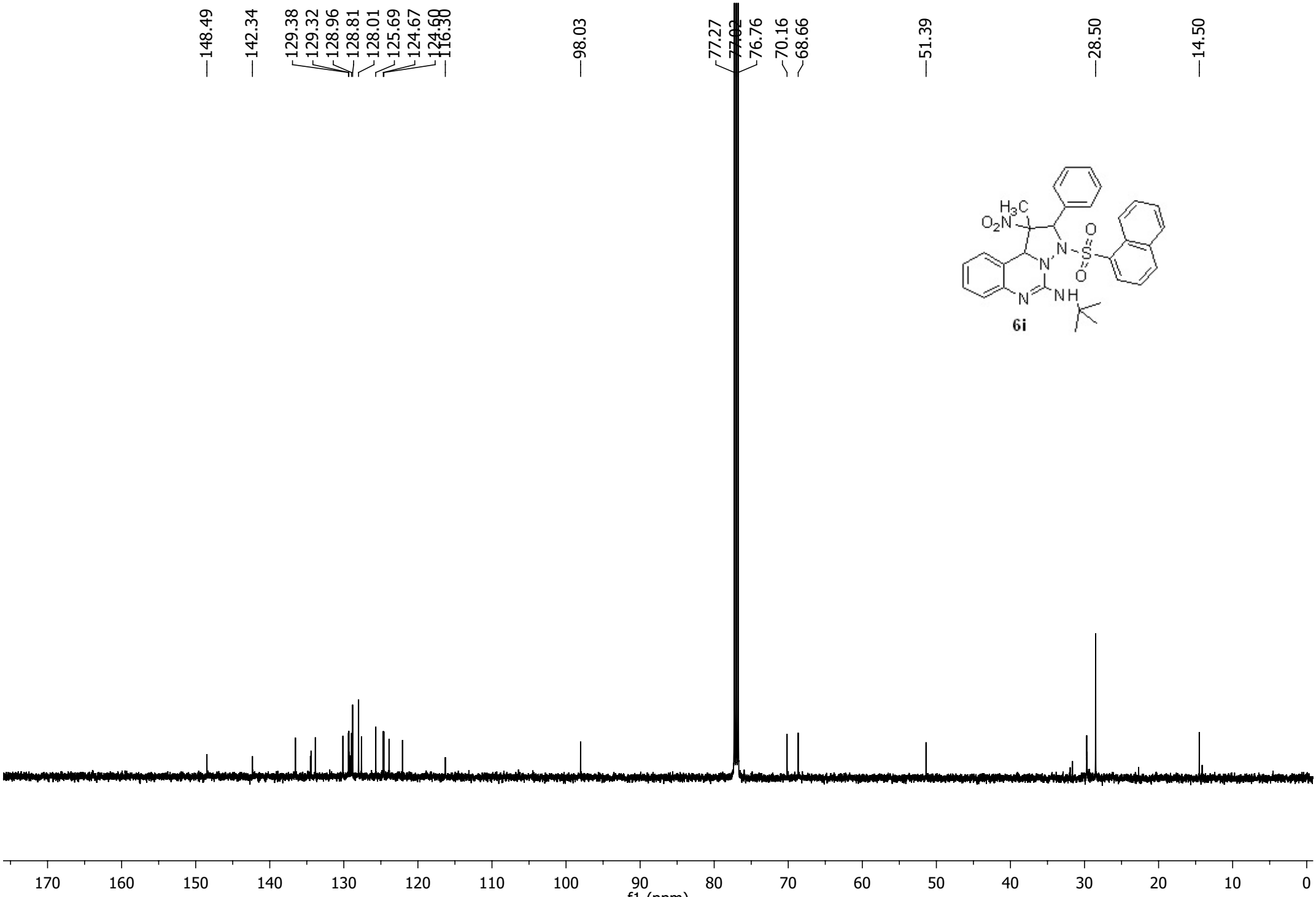
8.4810
8.4663
8.2476
8.2312
8.0077
7.9916
7.6730
7.6570
7.6416
7.6259
7.6101
7.5840
7.5691
7.4272
7.4156
7.3580
7.3446
7.2036
7.1890
7.1734
6.9712
6.9554
6.8267
6.8120
6.7970
6.5879
6.5729
4.7766
1.0077
0.8679
6i
1.03
0.99
1.06
1.04
2.09
1.05
2.84
1.99
1.15
1.02
1.00
1.12
1.00
0.92
0.94
9.33
2.79
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)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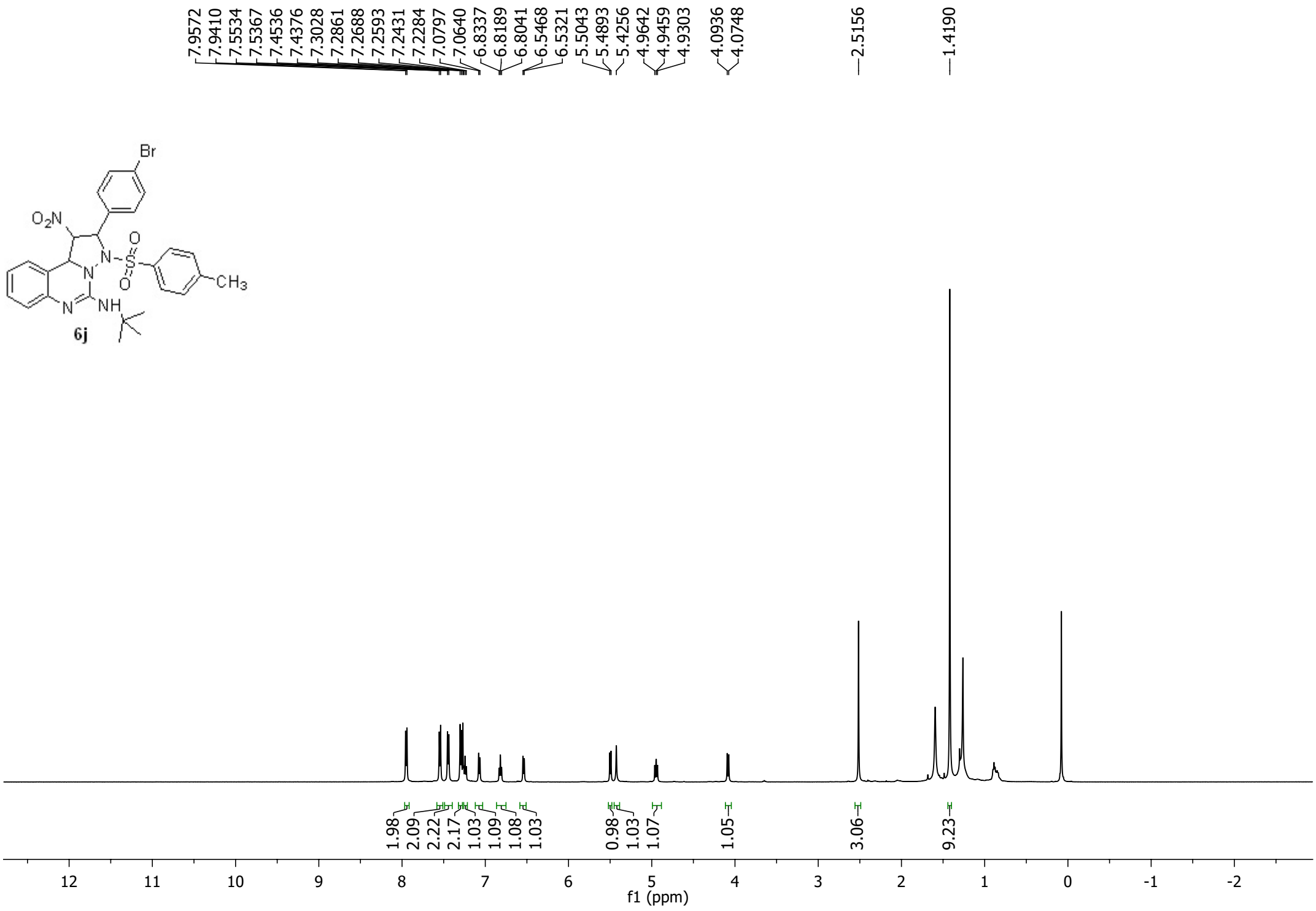
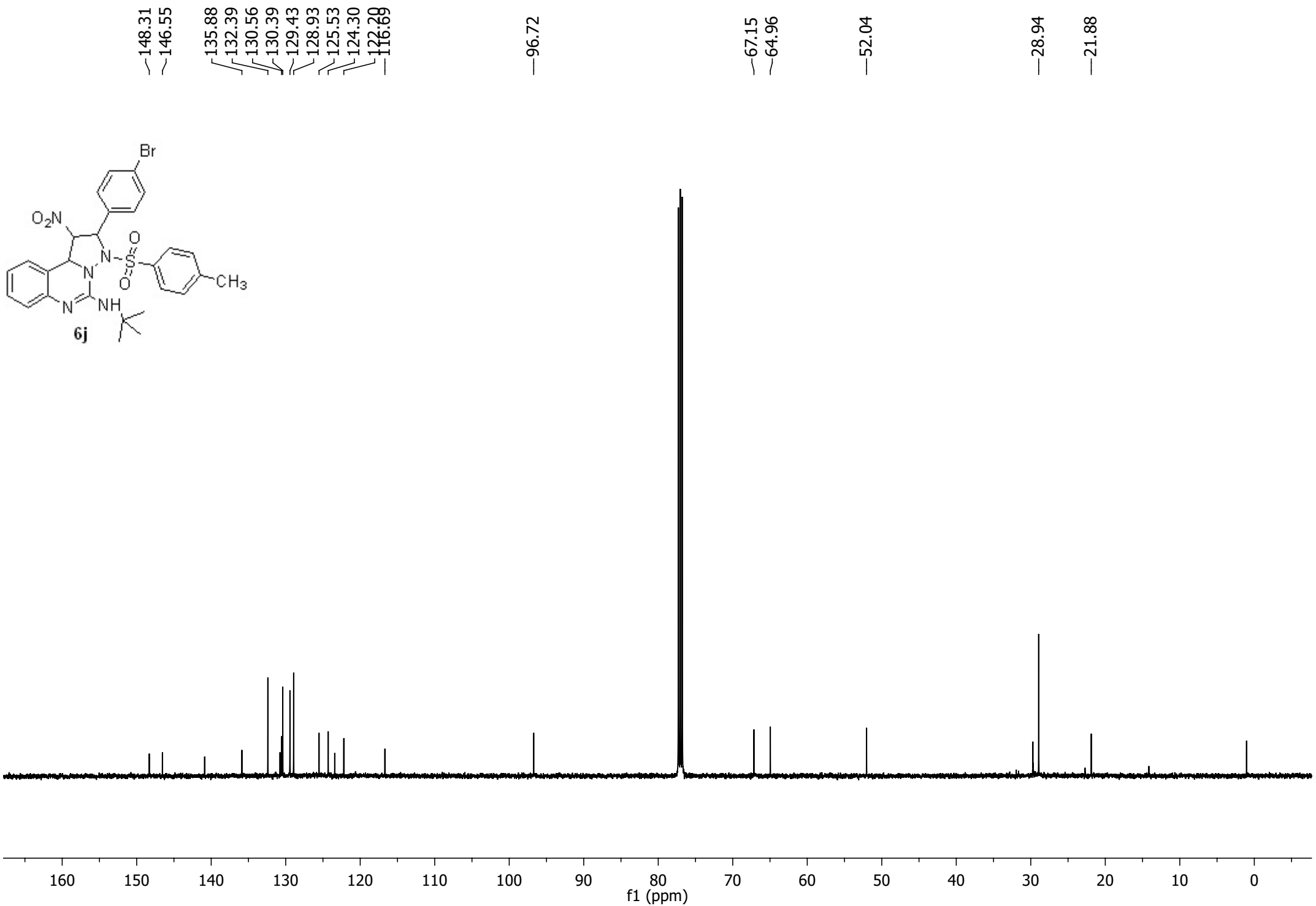
142.34
129.38
129.32
128.96
128.81
128.01
125.69
124.67
124.60
116.30
98.03
77.27
77.02
76.76
70.16
68.66
51.39
28.50
14.50
6i
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.9572
7.9410
7.5534
7.5367
7.4536
7.4376
7.3028
7.2861
7.2688
7.2593
7.2431
7.2284
7.0797
7.0640
6.8337
6.8189
6.8041
6.5468
6.5321
5.5043
5.4893
5.4256
4.9642
4.9459
4.9303
4.0936
4.0748
2.5156
1.4190
Br
O2N
O
S
O
CH3
N
N
NH
6j
1.98
2.09
2.22
2.17
1.03
1.09
1.08
1.03
0.98
1.03
1.07
1.05
3.06
9.23
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)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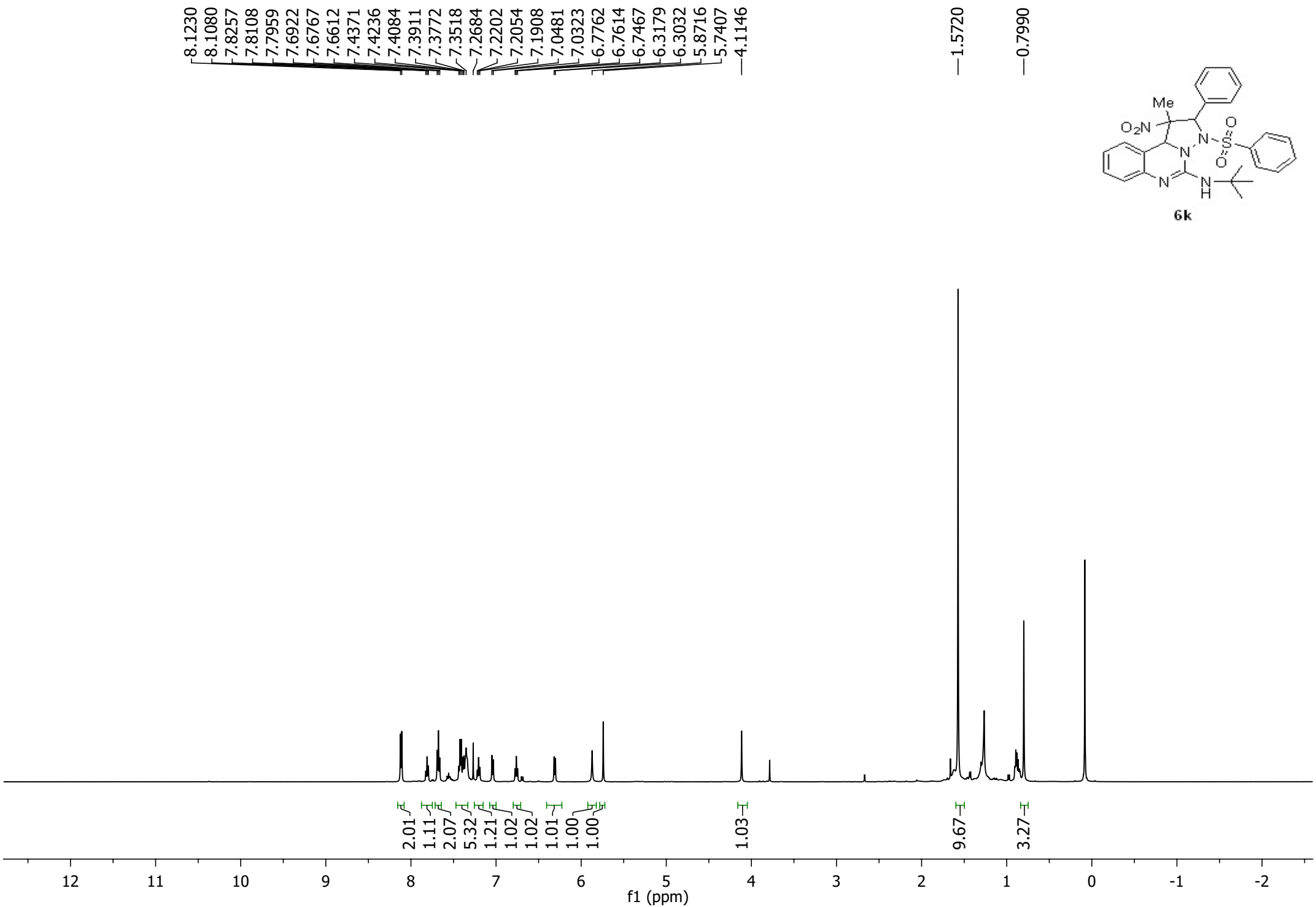
146.55
135.88
132.39
130.56
130.39
129.43
128.93
125.53
124.30
96.72
67.15
64.96
52.04
28.94
21.88
Br
O2N
O
S
O
CH3
N
N
NH
6j
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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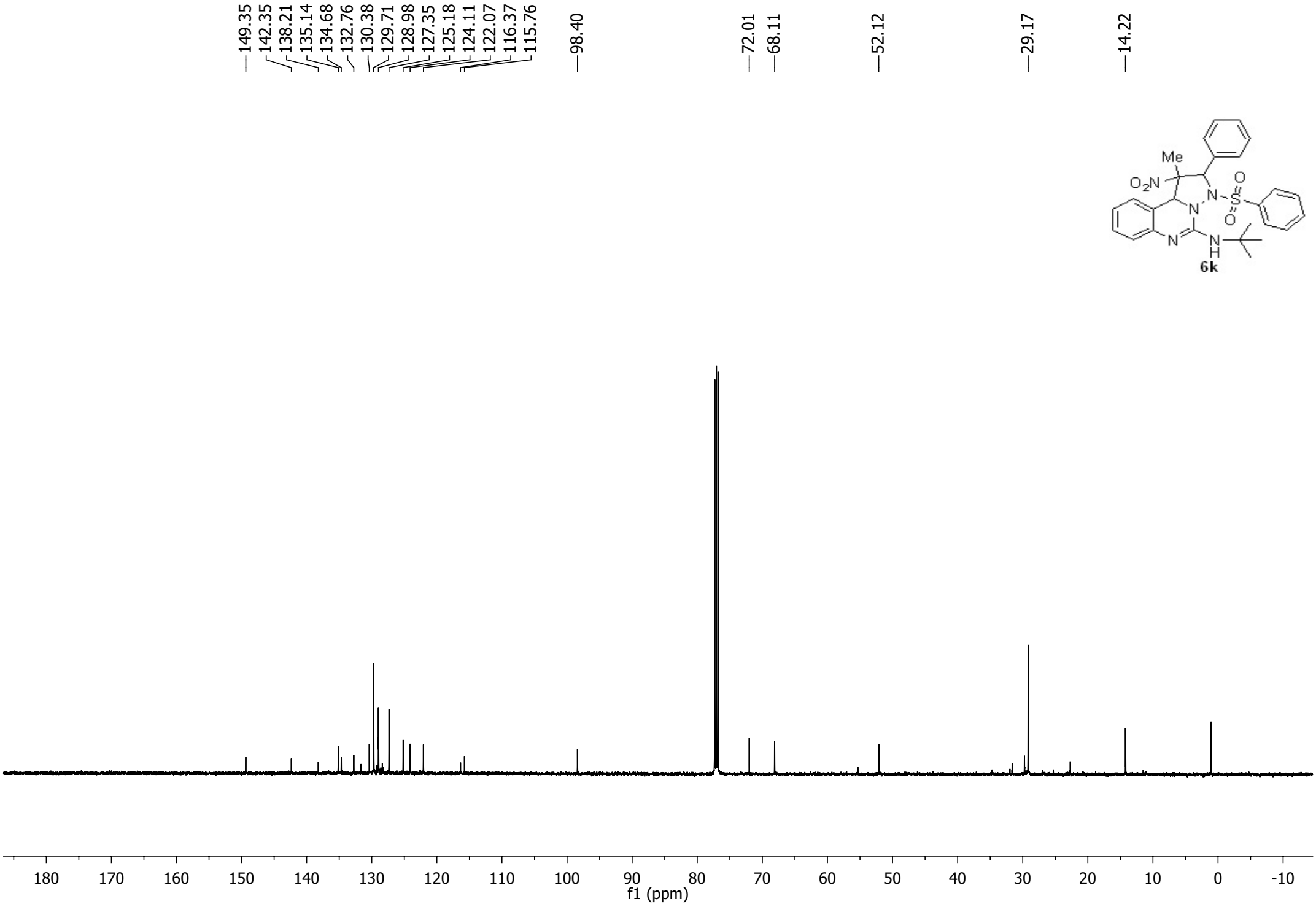
7.8257
7.8108
7.7959
7.6922
7.6767
7.6612
7.4371
7.4236
7.4084
7.3911
7.3772
7.3518
7.2684
7.2202
7.2054
7.1908
7.0481
7.0323
6.7762
6.7614
6.7467
6.3179
6.3032
5.8716
5.7407
4.1146
1.5720
0.7990
Me
O2N
N
N
S
O
O
N
H
6k
2.01
1.11
2.07
5.32
1.21
1.02
1.02
1.01
1.00
1.00
1.03
9.67
3.27
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)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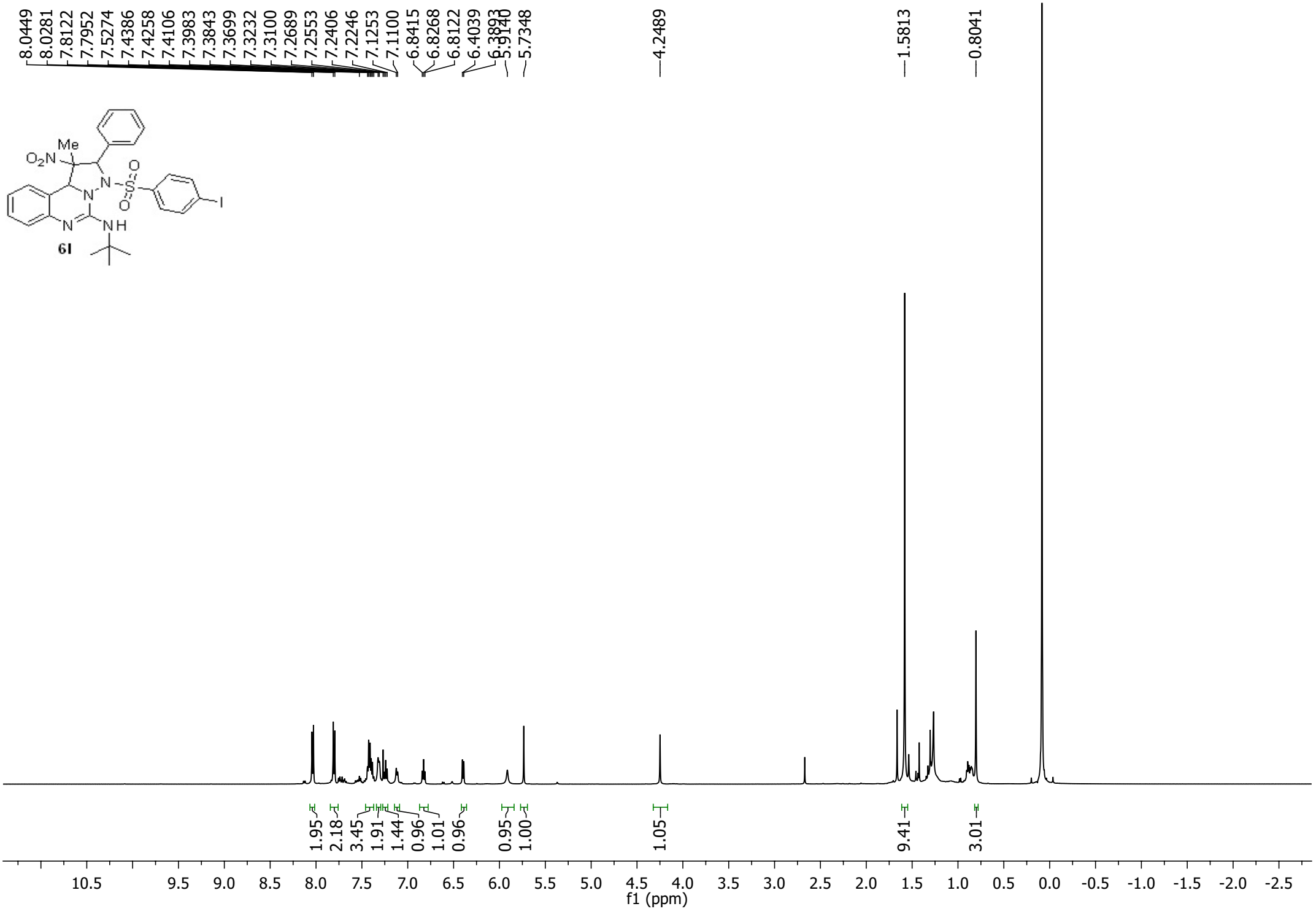
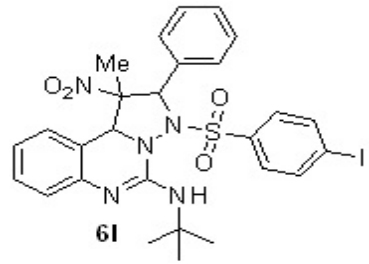
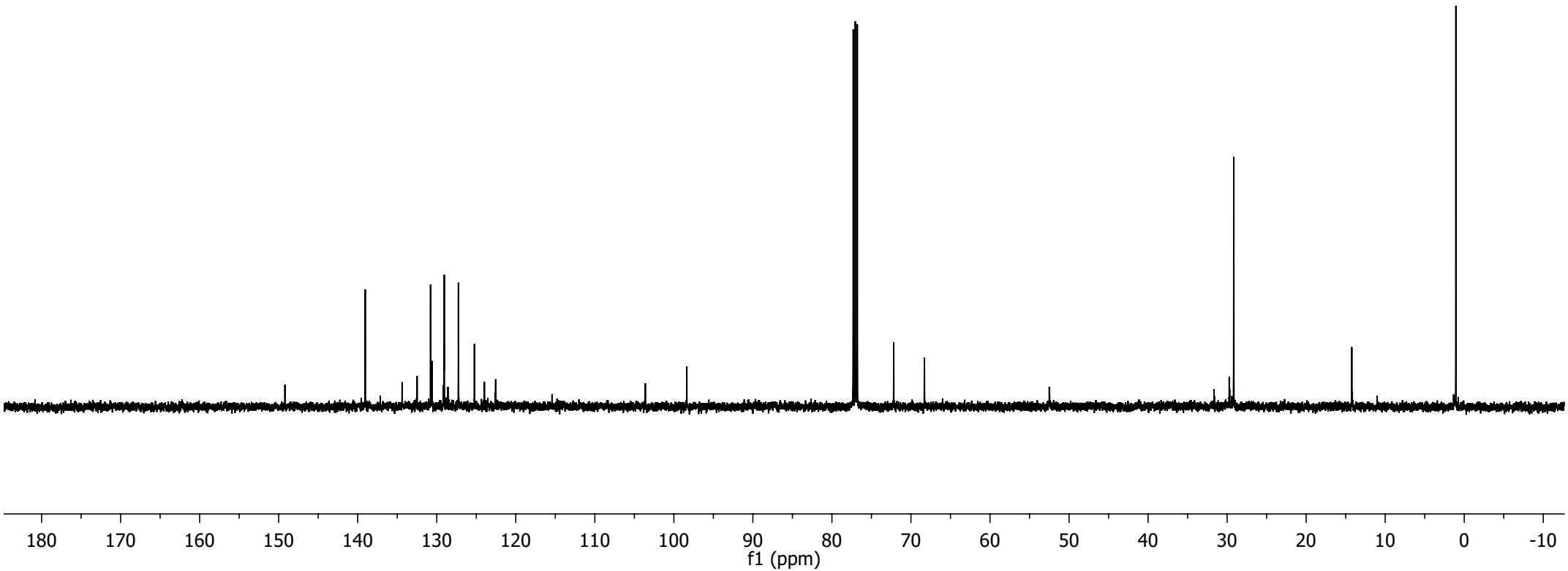
142.35
138.21
135.14
134.68
132.76
130.38
129.71
128.98
127.35
125.18
124.11
122.07
116.37
115.76
98.40
72.01
68.11
52.12
29.17
14.22
Me
O2N
N
N
S
O
O
N
H
6k
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

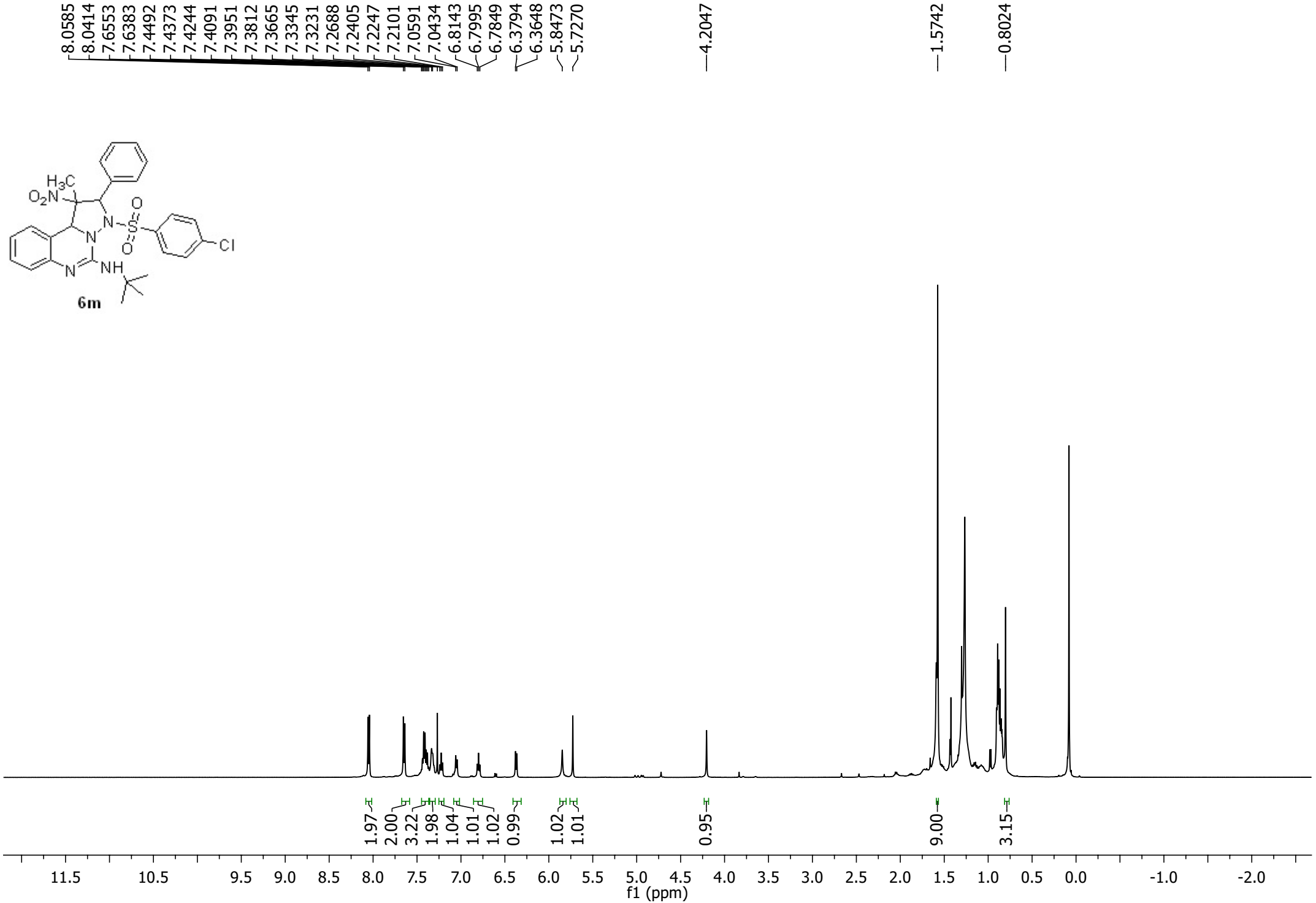

8.0449
8.0281
7.8122
7.7952
7.5274
7.4386
7.4258
7.4106
7.3983
7.3843
7.3699
7.3232
7.3100
7.2689
7.2553
7.2406
7.2246
7.1253
7.1100
6.8415
6.8268
6.8122
6.4039
6.3893
5.9140
5.7348
4.2489
1.5813
0.8041
Me
O2N
N
S
O
O
I
N
NH
6l
1.95
2.18
3.45
1.91
1.44
0.96
1.01
0.96
0.95
1.00
1.05
9.41
3.01
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
f1 (ppm)



6l

149.20
139.05
132.49
130.78
130.60
129.08
129.05
127.26
125.23
123.97
122.54
115.40
103.61
98.36
77.30
77.04
76.79
72.18
68.30
52.50
29.16
14.23

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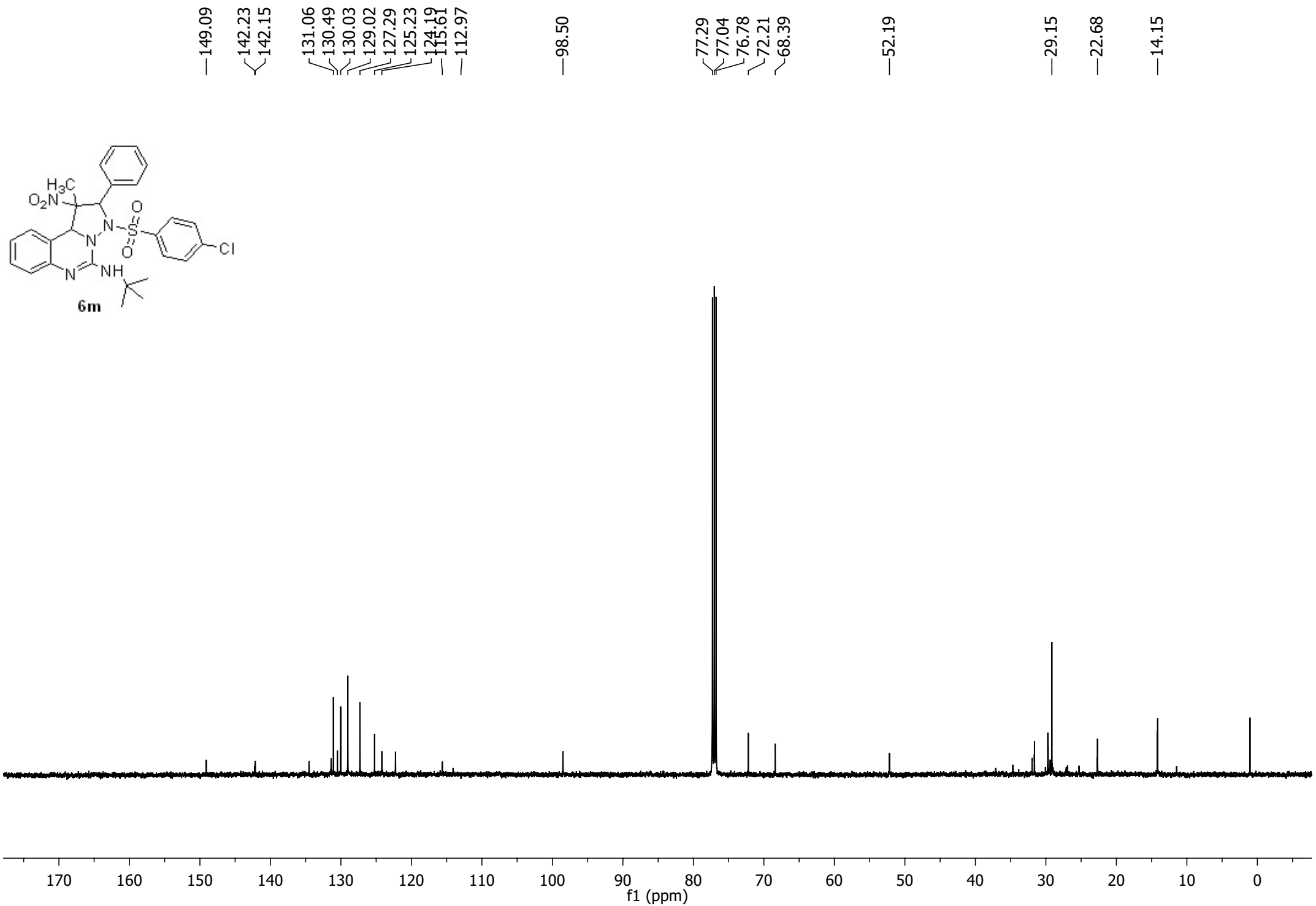
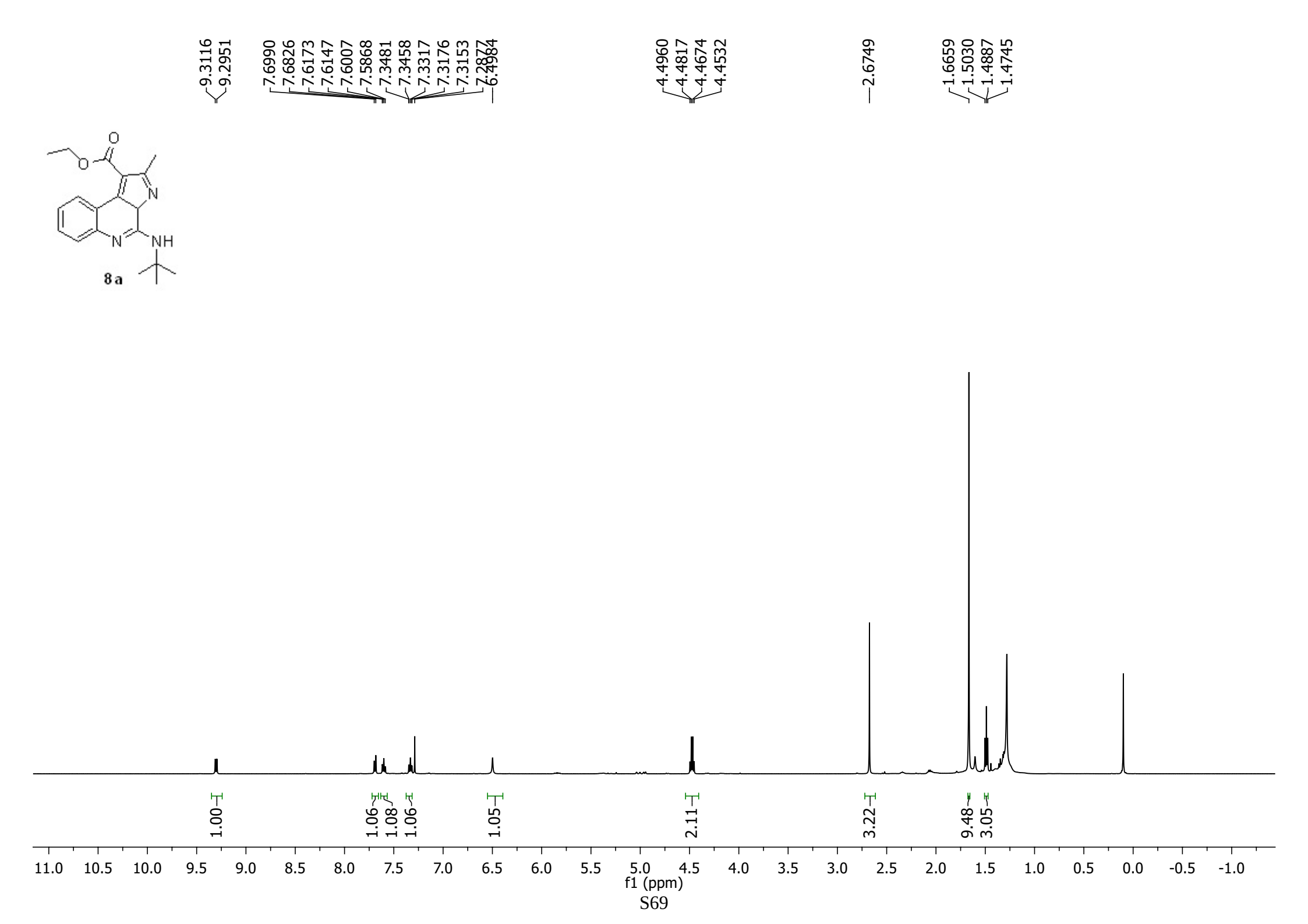
7.6383
7.4492
7.4373
7.4244
7.4091
7.3951
7.3812
7.3665
7.3345
7.3231
7.2688
7.2405
7.2247
7.2101
7.0591
7.0434
6.8143
6.7995
6.7849
6.3794
6.3648
5.8473
5.7270
4.2047
1.5742
0.8024
H3C
O2N
N
S
O
O
Cl
NH
6m
1.97
2.00
3.22
1.98
1.04
1.01
1.02
0.99
1.02
1.01
0.95
9.00
3.15
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
-2.0
f1 (ppm)


149.09
142.23
142.15
131.06
130.49
130.03
129.02
127.29
125.23
124.19
115.61
112.97
98.50
77.29
77.04
76.78
72.21
68.39
52.19
29.15
22.68
14.15
6m
f1 (ppm)


9.3116
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7.6826
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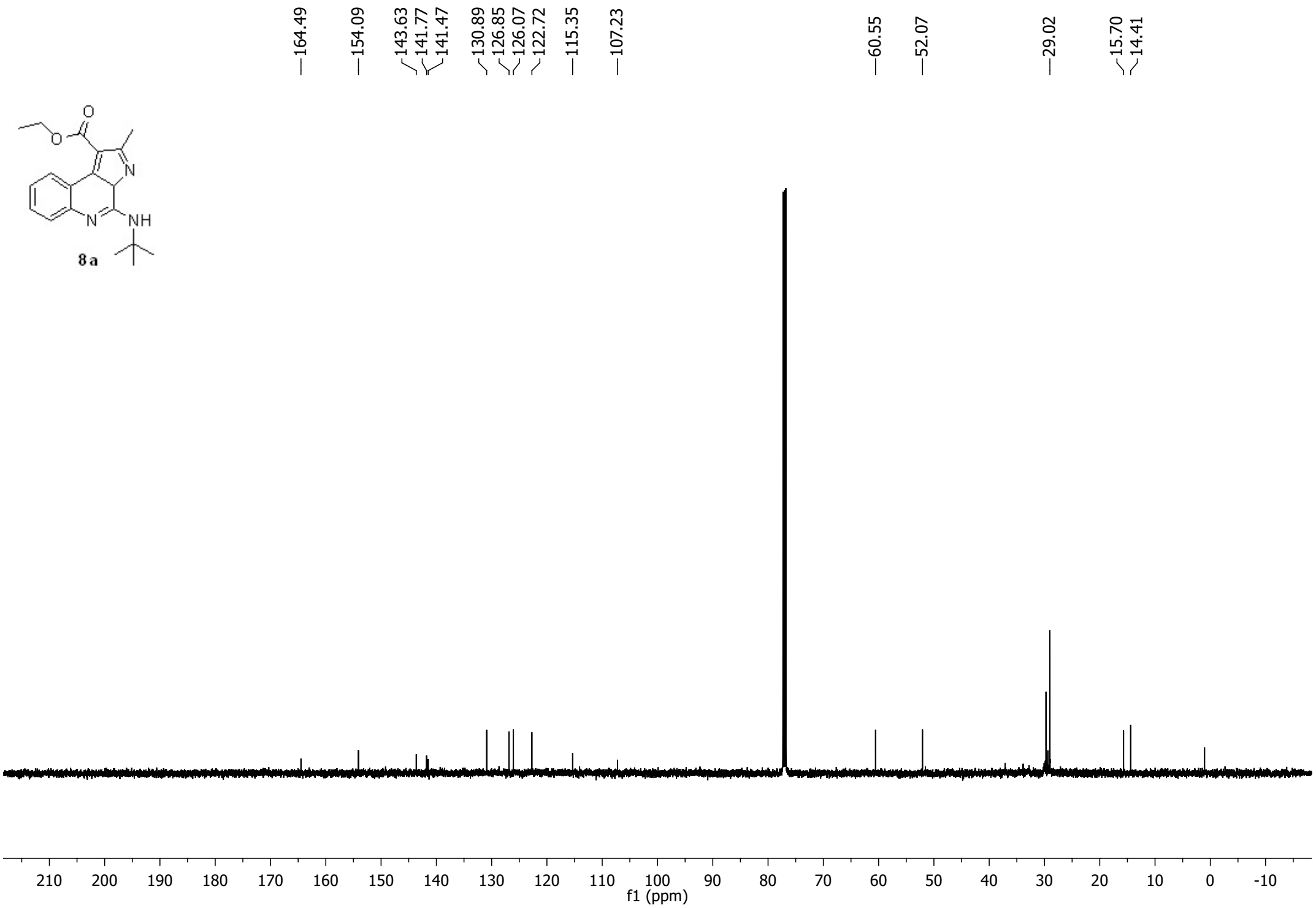
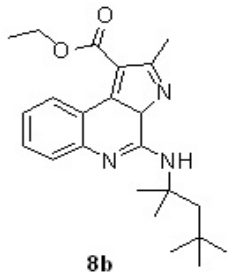
7.6147
7.6007
7.5868
7.3481
7.3458
7.3317
7.3176
7.3153
7.2877
6.4984
4.4960
4.4817
4.4674
4.4532
2.6749
1.6659
1.5030
1.4887
1.4745
O
O
N
N
NH
8a
1.00
1.06
1.08
1.06
1.05
2.11
3.22
9.48
3.05
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


164.49
154.09
143.63
141.77
141.47
130.89
126.85
126.07
122.72
115.35
107.23
60.55
52.07
29.02
15.70
14.41
O
O
N
N
NH
8a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



8b

9.2903
9.2737
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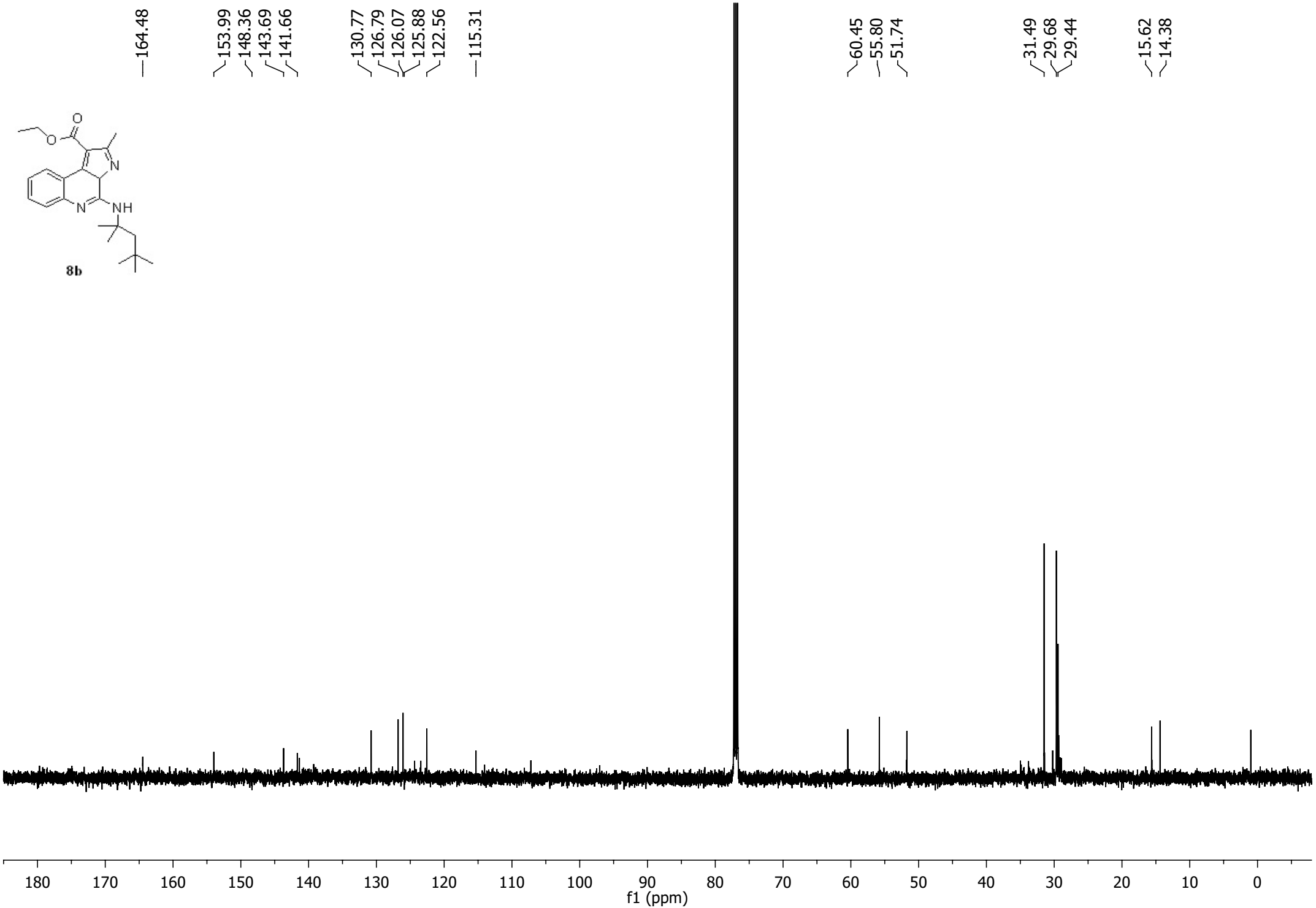
7.6735
7.6065
7.5901
7.5763
7.3368
7.3203
7.3063
7.2857
6.6009
4.4990
4.4847
4.4704
4.4562
2.6694
2.0877
1.7165
1.4999
1.4856
1.4713
1.3652
1.3168
1.2891
1.0567
1.00
1.00
1.07
1.31
1.03
2.05
3.01
2.23
6.22
3.28
9.84
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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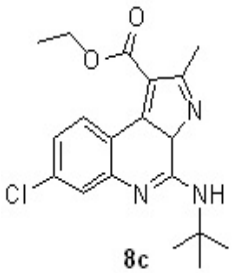
141.66
130.77
126.79
126.07
125.88
122.56
115.31
60.45
55.80
51.74
31.49
29.68
29.44
15.62
14.38
O
O
N
N
NH
8b
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
N
Cl
N
NH

8c

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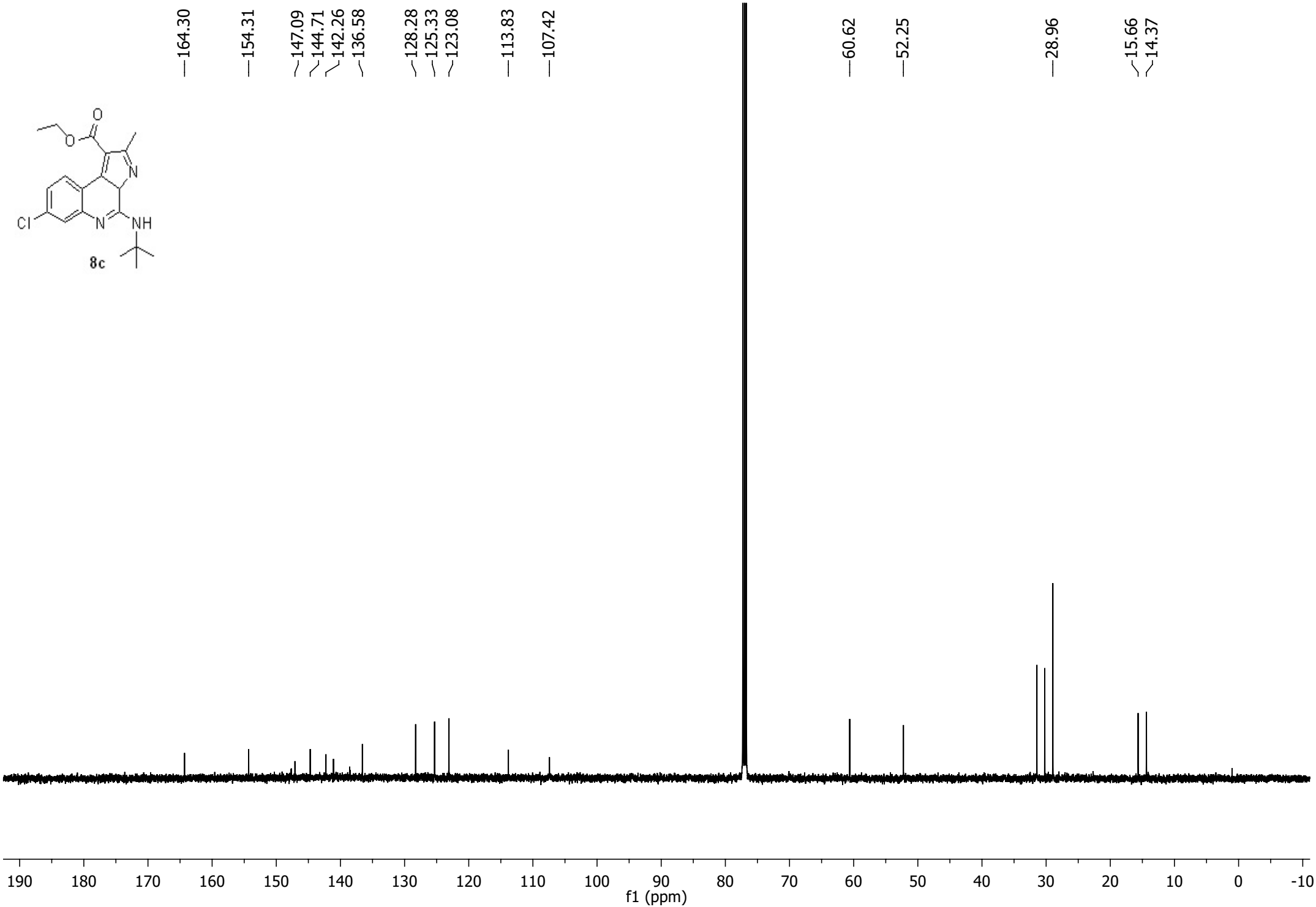
9.2870
7.6857
7.6814
7.2866
7.2805
7.2761
7.2627
6.5613
4.4882
4.4739
4.4596
4.4454
2.6680
1.6529
1.4963
1.4820
1.4677
1.00
0.96
1.25
0.95
2.10
3.13
9.67
3.32
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


164.30
154.31
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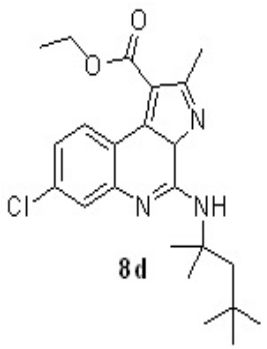
144.71
142.26
136.58
128.28
125.33
123.08
113.83
107.42
60.62
52.25
28.96
15.66
14.37
O
O
N
Cl
N
NH
8c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
O
N
Cl
N
NH

8d

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7.6783
7.6740
7.2899
7.2759
7.2714
7.2581
7.2537
6.6641
4.4863
4.4720
4.4578
4.4435
2.6642
2.0663
1.7003
1.4957
1.4814
1.4672
1.2829
1.0497
1.00
0.98
0.98
0.89
2.01
2.99
2.53
6.74
3.75
9.13
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
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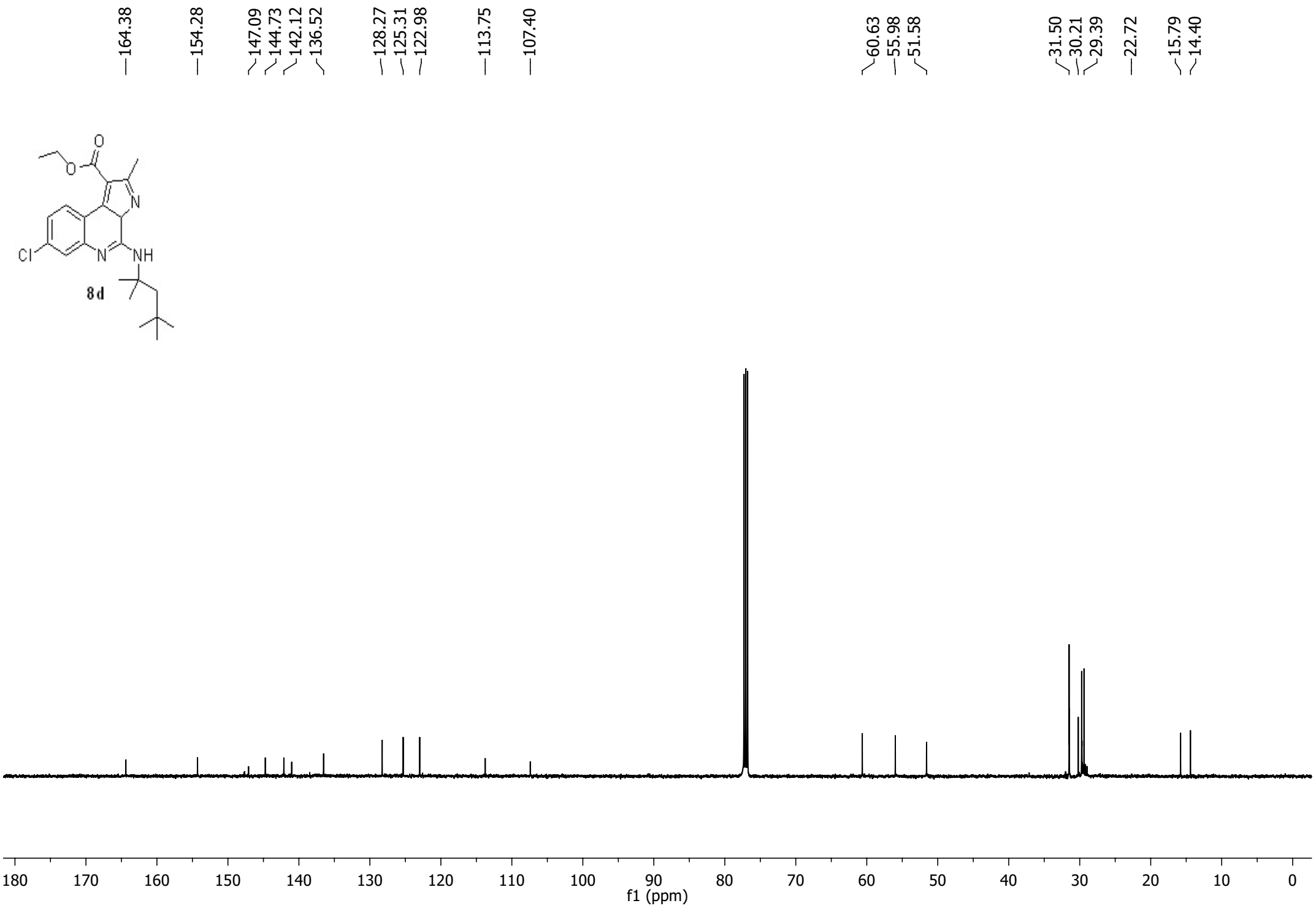
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125.31
122.98
113.75
107.40
60.63
55.98
51.58
31.50
30.21
29.39
22.72
15.79
14.40
O
O
N
Cl
N
NH
8d
180
170
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130
120
110
100
90
80
70
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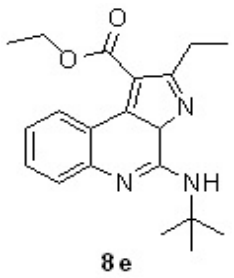
50
40
30
20
10
0
f1 (ppm)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N
NH

8e

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7.5875
7.5732
7.3353
7.3192
7.3047
6.5209
4.5067
4.4924
4.4782
4.4639
3.1312
3.1162
3.1012
3.0863
1.6720
1.5038
1.4896
1.4753
0.9252
0.9119
0.8981
1.00
1.04
1.23
1.33
0.87
2.51
2.10
9.59
2.76
2.89
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
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-0.5
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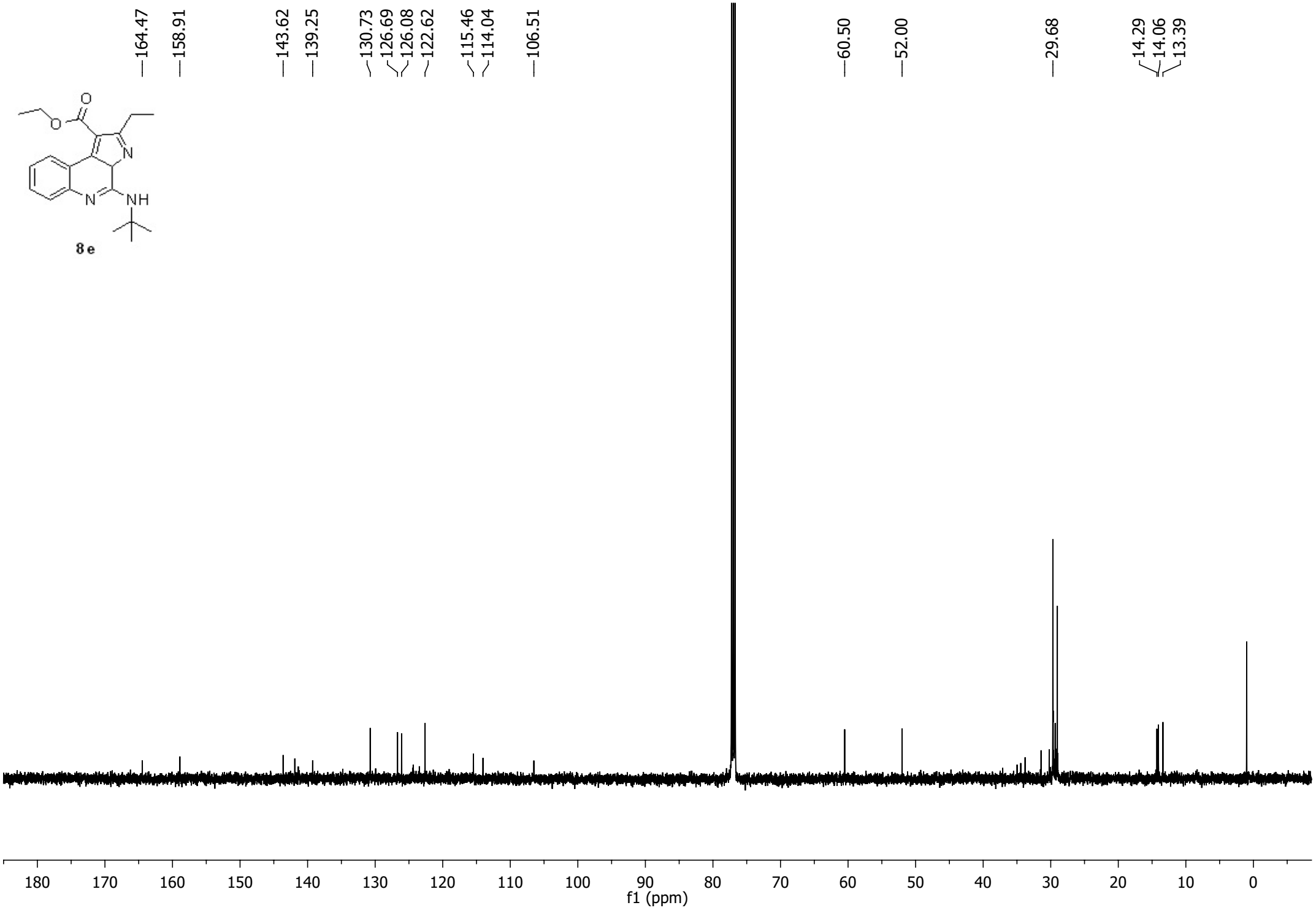
-1.5
f1 (ppm)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114.04
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29.68
14.29
14.06
13.39
O
O
N
N
NH
8e
180
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130
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110
100
90
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70
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50
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10
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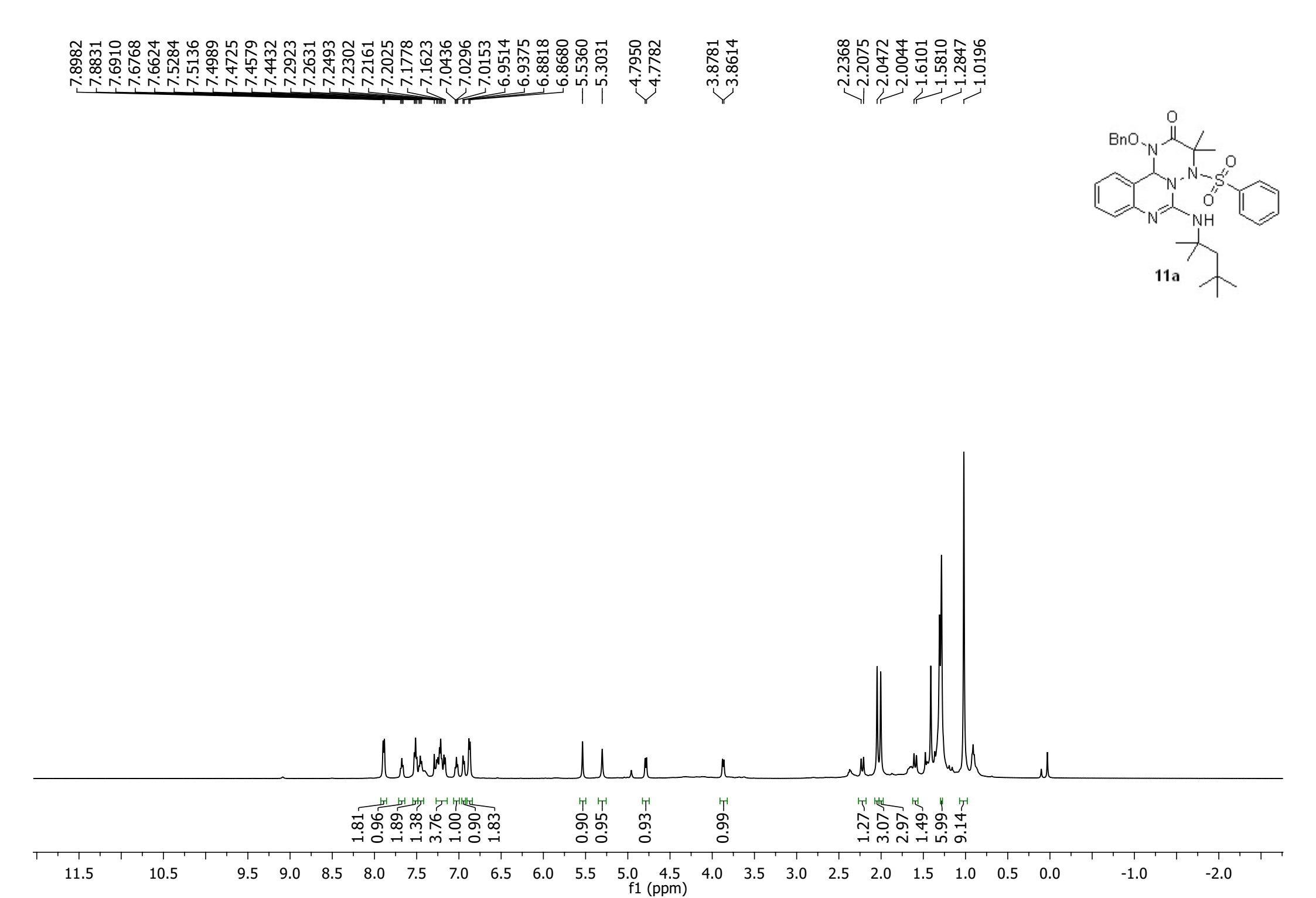
f1 (ppm)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7.4725
7.4579
7.4432
7.2923
7.2631
7.2493
7.2302
7.2161
7.2025
7.1778
7.1623
7.0436
7.0296
7.0153
6.9514
6.9375
6.8818
6.8680
5.5360
5.3031
4.7950
4.7782
3.8781
3.8614
2.2368
2.2075
2.0472
2.0044
1.6101
1.5810
1.2847
1.0196
BnO
N
O
N
N
S
O
O
N
NH
11a
1.81
0.96
1.89
1.38
3.76
1.00
0.90
1.83
0.90
0.95
0.93
0.99
1.27
3.07
2.97
1.49
5.99
9.14
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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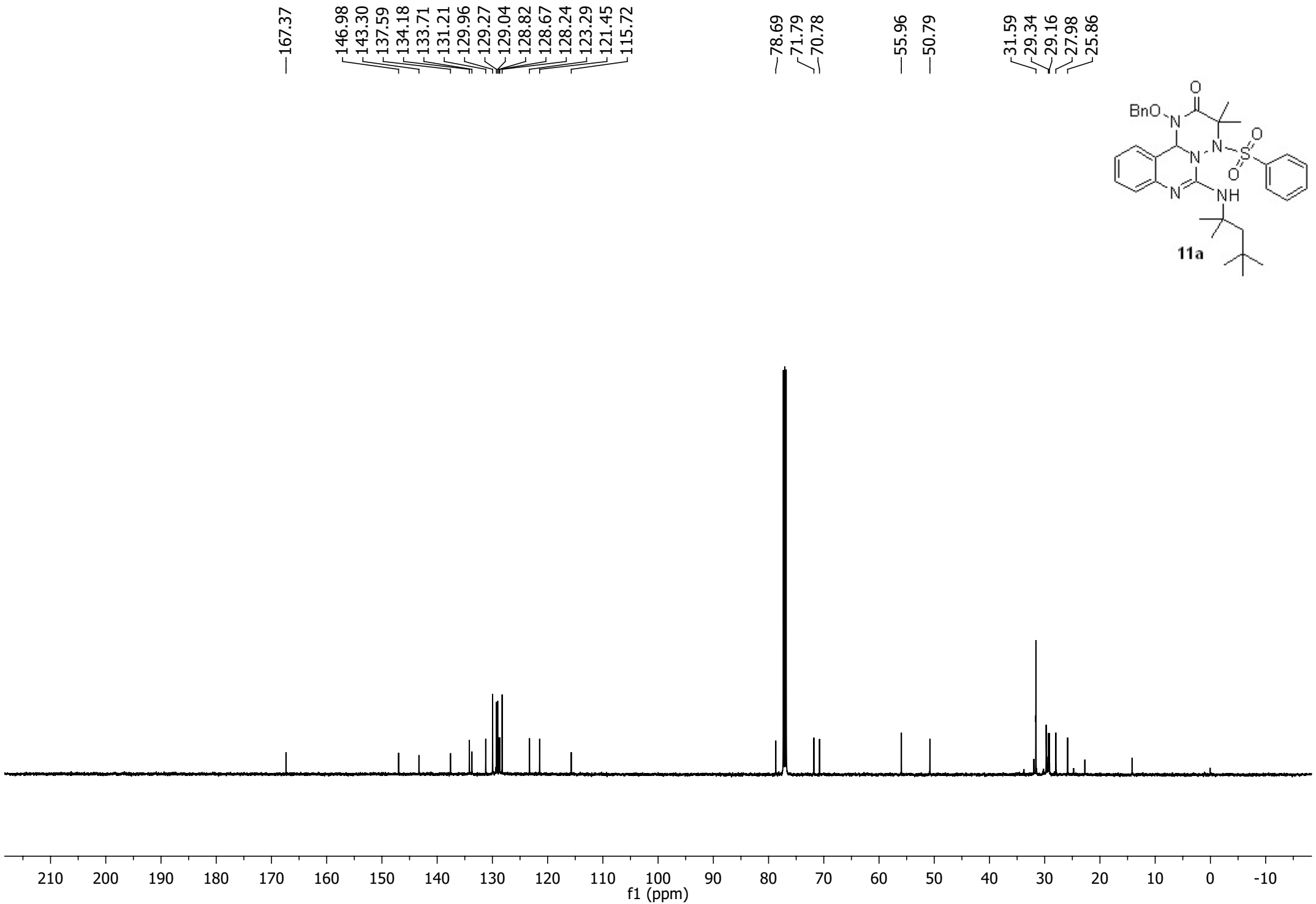
-2.0
f1 (ppm)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128.67
128.24
123.29
121.45
115.72
78.69
71.79
70.78
55.96
50.79
31.59
29.34
29.16
27.98
25.86
BnO
N
O
N
N
S
O
O
N
NH
11a
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200
190
180
170
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100
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80
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30
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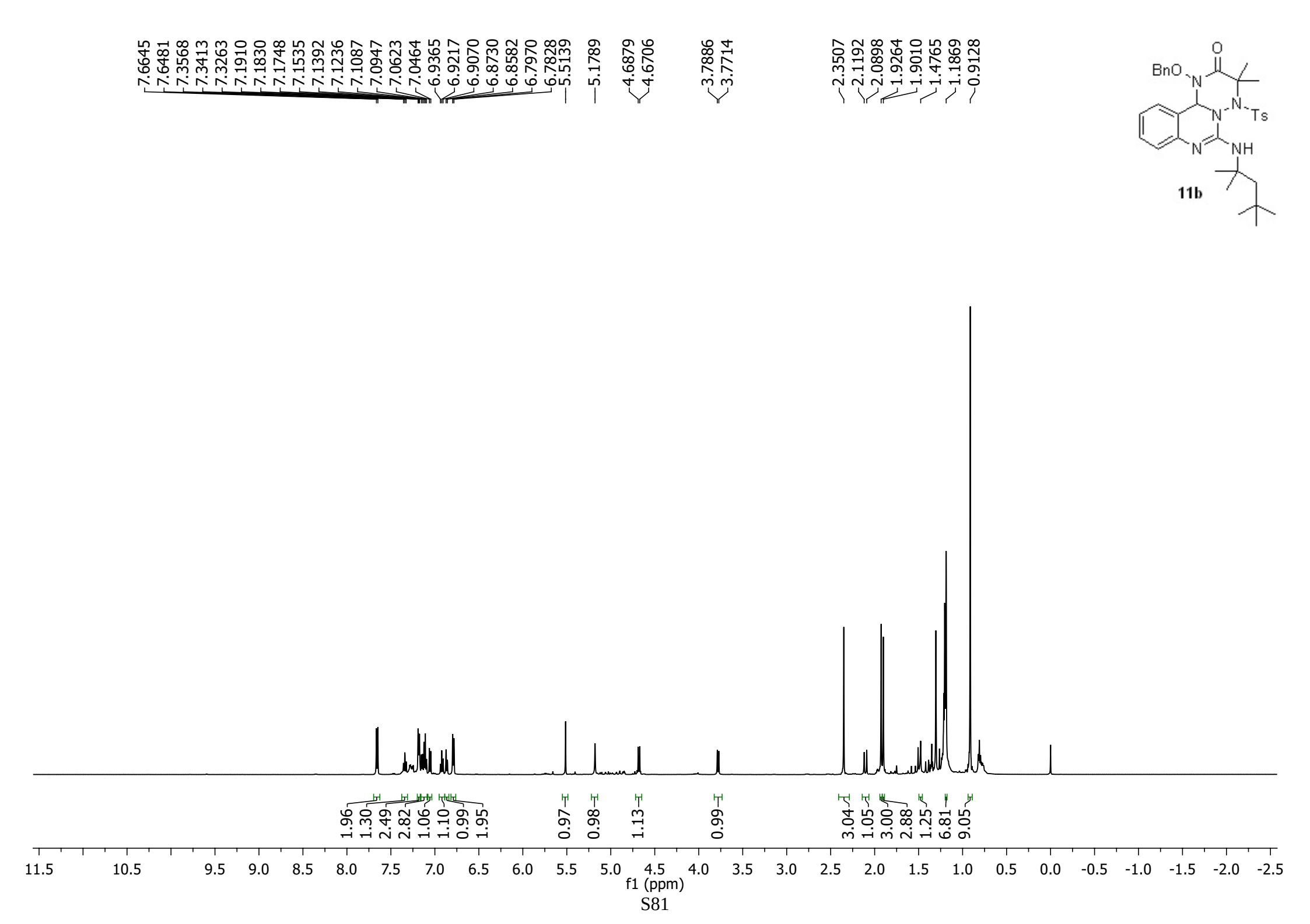
-10
f1 (ppm)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7.1830
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7.1535
7.1392
7.1236
7.1087
7.0947
7.0623
7.0464
6.9365
6.9217
6.9070
6.8730
6.8582
6.7970
6.7828
5.5139
5.1789
4.6879
4.6706
3.7886
3.7714
2.3507
2.1192
2.0898
1.9264
1.9010
1.4765
1.1869
0.9128
BnO
O
N
N
N
Ts
NH
11b
1.96
1.30
2.49
2.82
1.06
1.10
0.99
1.95
0.97
0.98
1.13
0.99
3.04
1.05
3.00
2.88
1.25
6.81
9.05
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
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0.5
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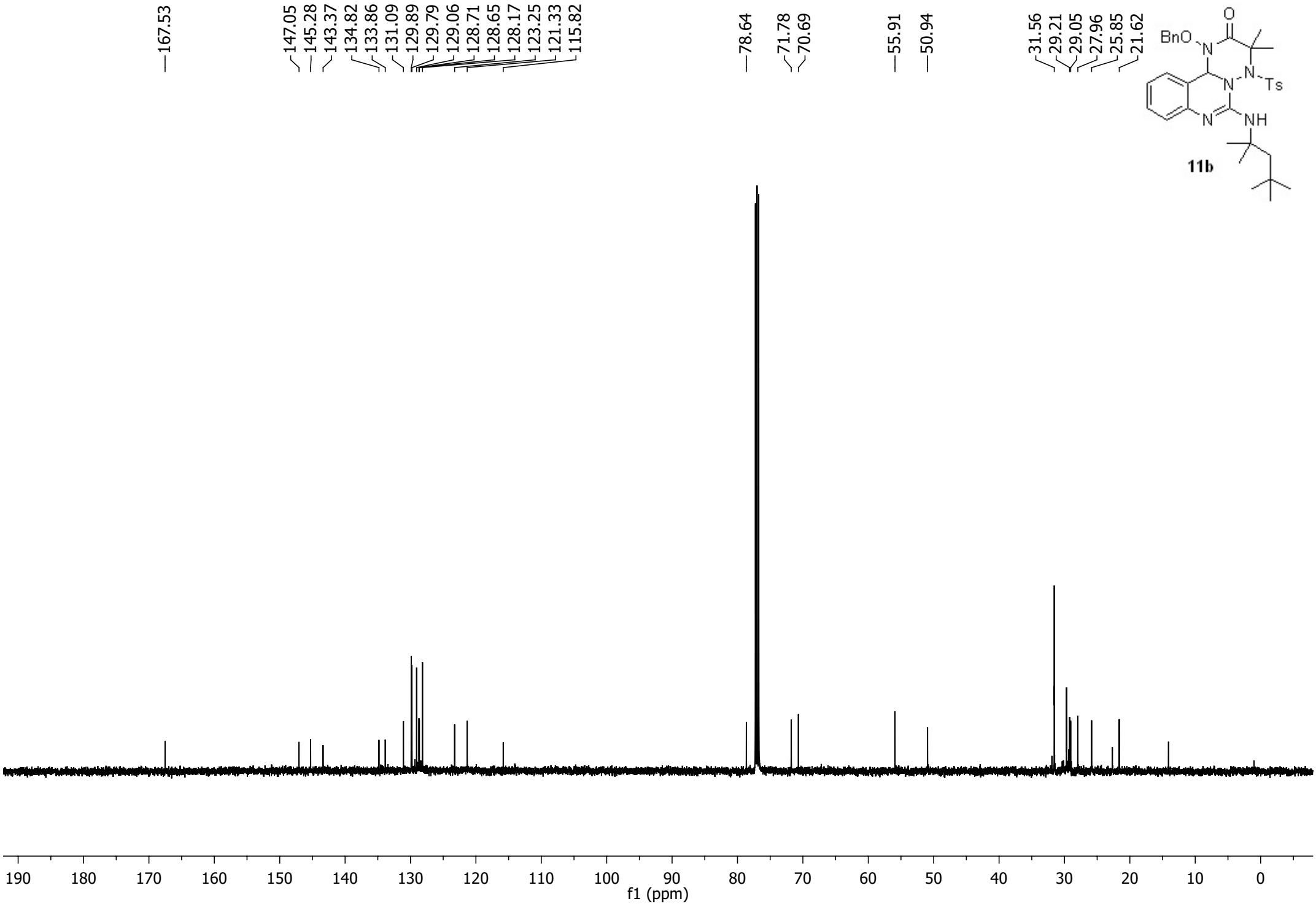
-0.5
-1.0
-1.5
-2.0
-2.5
f1 (ppm)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129.06
128.71
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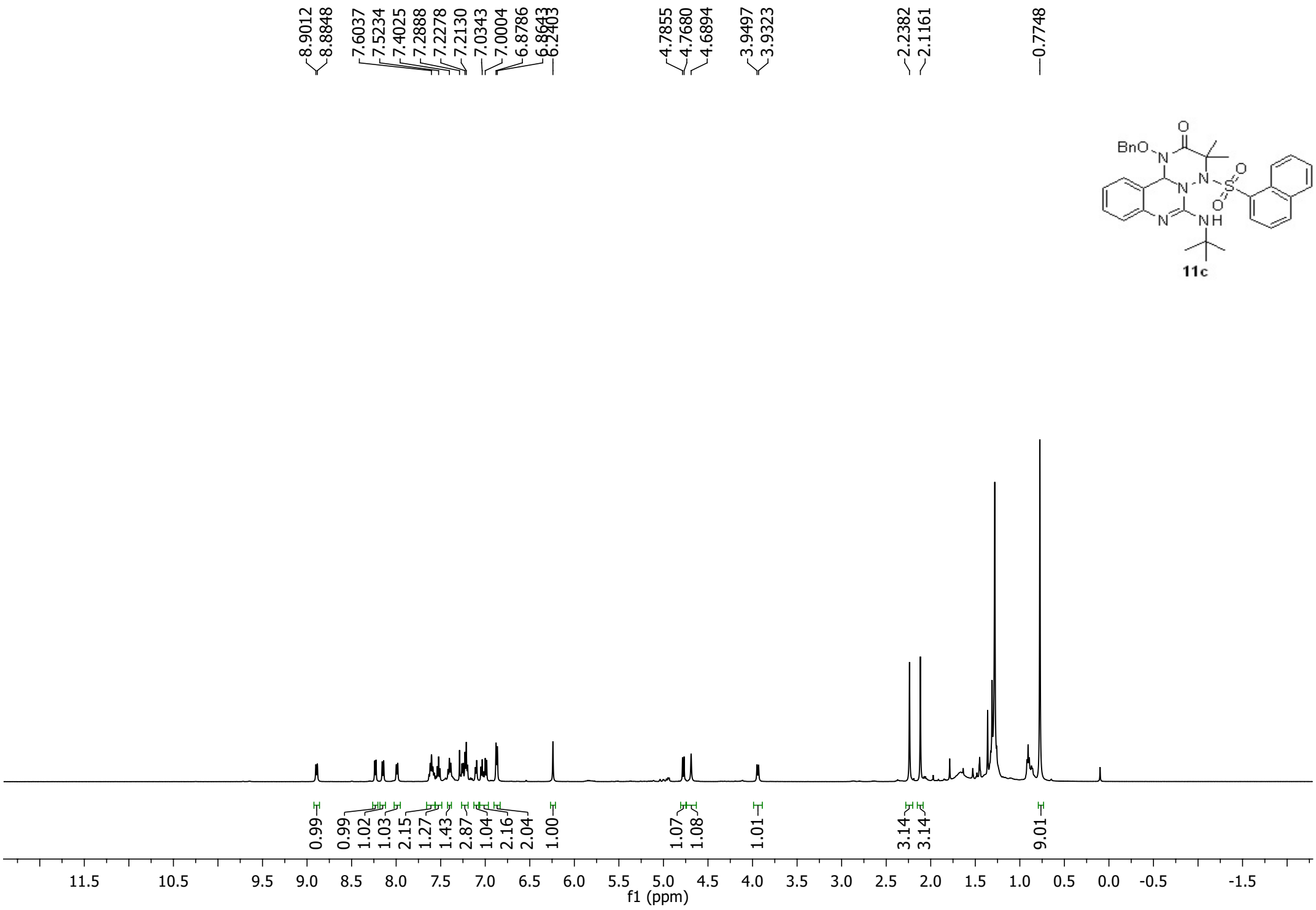
128.17
123.25
121.33
115.82
78.64
71.78
70.69
55.91
50.94
31.56
29.21
29.05
27.96
25.85
21.62
BnO
O
N
N
N
Ts
NH
11b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.0004
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6.8643
6.2403
4.7855
4.7680
4.6894
3.9497
3.9323
2.2382
2.1161
0.7748
BnO
O
N
N
N
S
O
O
NH
11c
0.99
0.99
1.02
1.03
2.15
1.27
1.43
2.87
1.04
2.16
2.04
1.00
1.07
1.08
1.01
3.14
3.14
9.01
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
1.5
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0.0
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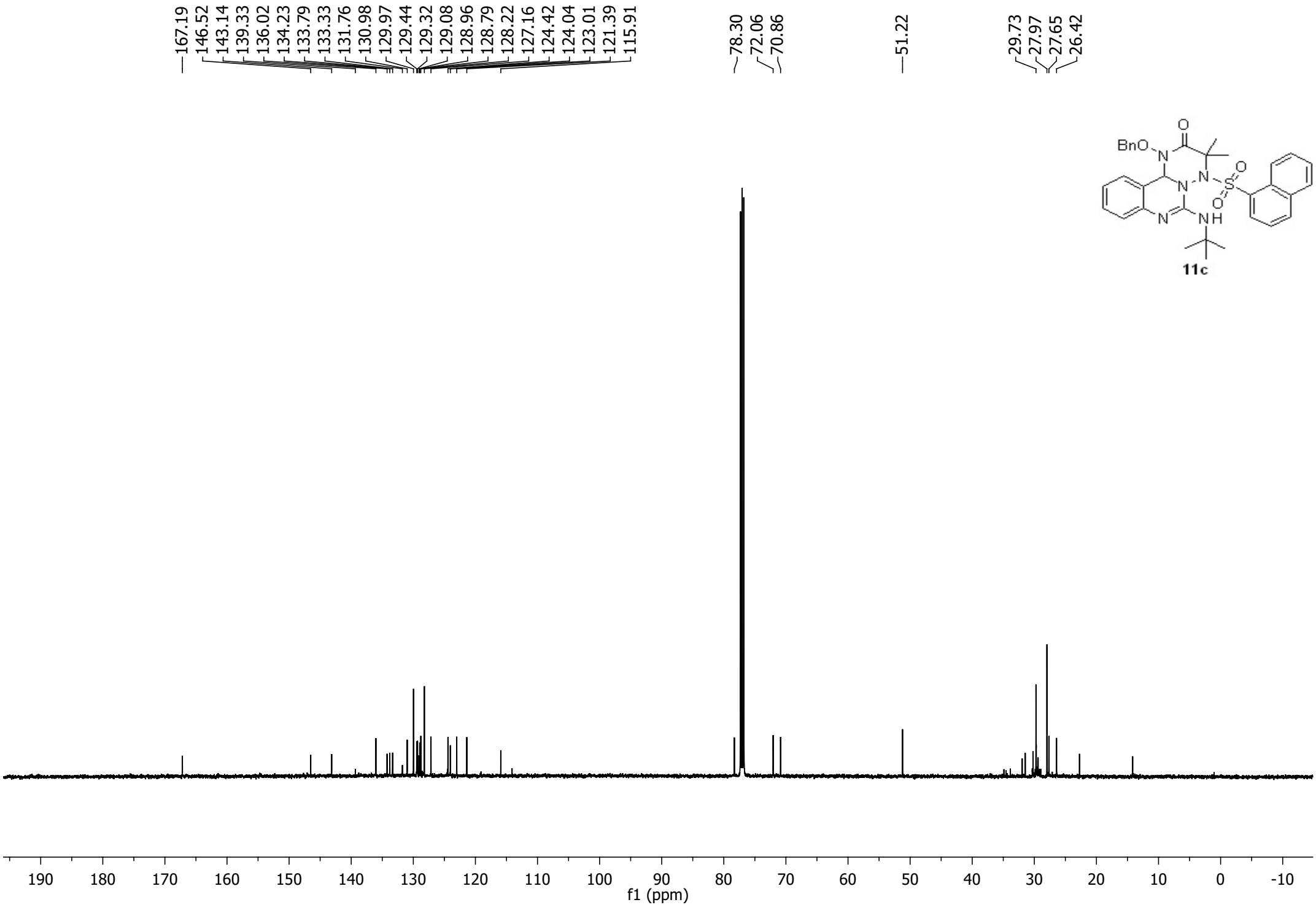
-1.5
f1 (ppm)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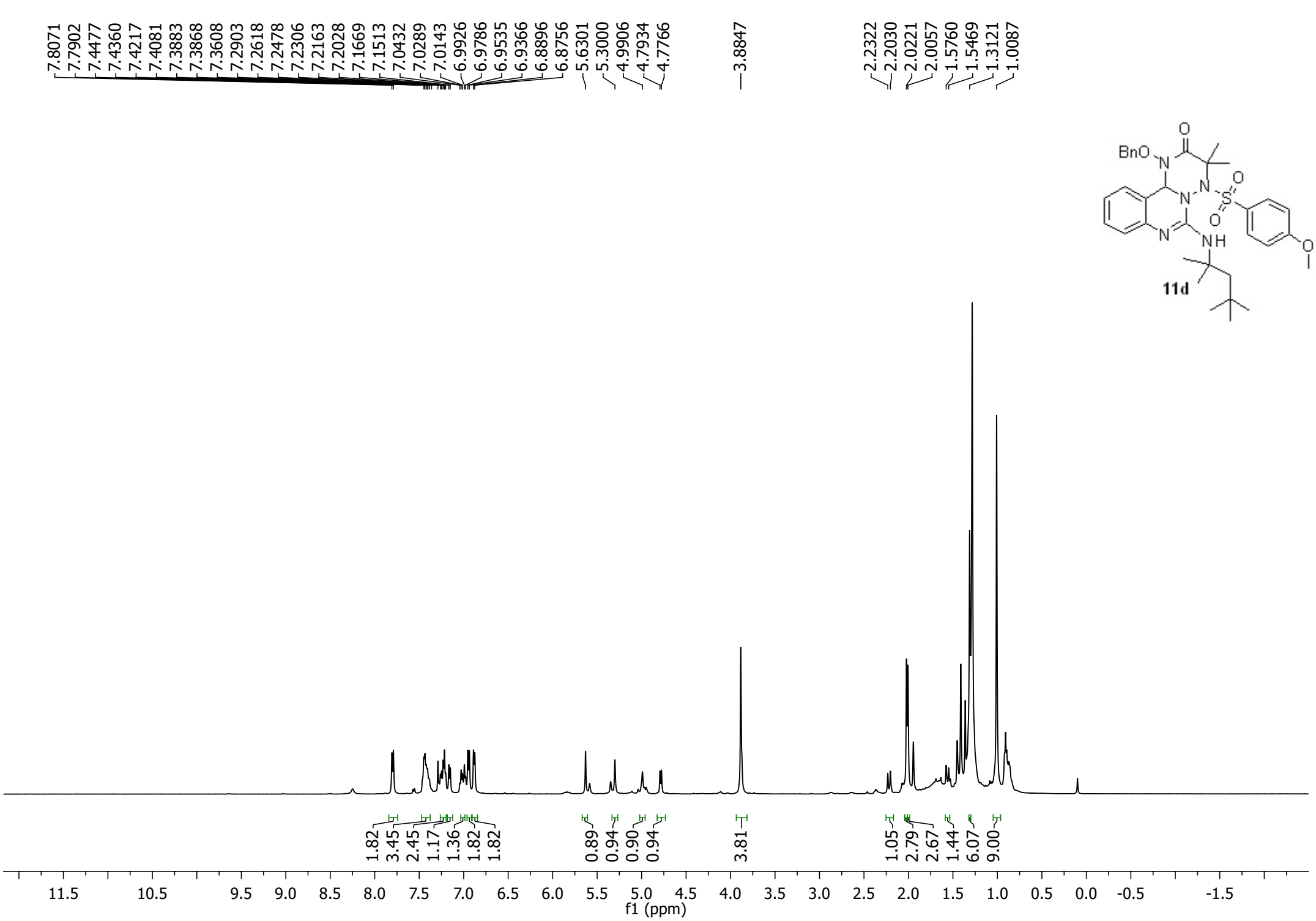
133.33
131.76
130.98
129.97
129.44
129.32
129.08
128.96
128.79
128.22
127.16
124.42
124.04
123.01
121.39
115.91
78.30
72.06
70.86
51.22
29.73
27.97
27.65
26.42
BnO
O
N
N
N
S
O
O
N
NH
11c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.2478
7.2306
7.2163
7.2028
7.1669
7.1513
7.0432
7.0289
7.0143
6.9926
6.9786
6.9535
6.9366
6.8896
6.8756
5.6301
5.3000
4.9906
4.7934
4.7766
3.8847
2.2322
2.2030
2.0221
2.0057
1.5760
1.5469
1.3121
1.0087
BnO
N
O
N
N
S
O
O
N
NH
O
11d
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3.45
2.45
1.17
1.36
1.82
1.82
0.89
0.94
0.90
0.94
3.81
1.05
2.79
2.67
1.44
6.07
9.00
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.5
2.0
1.5
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0.0
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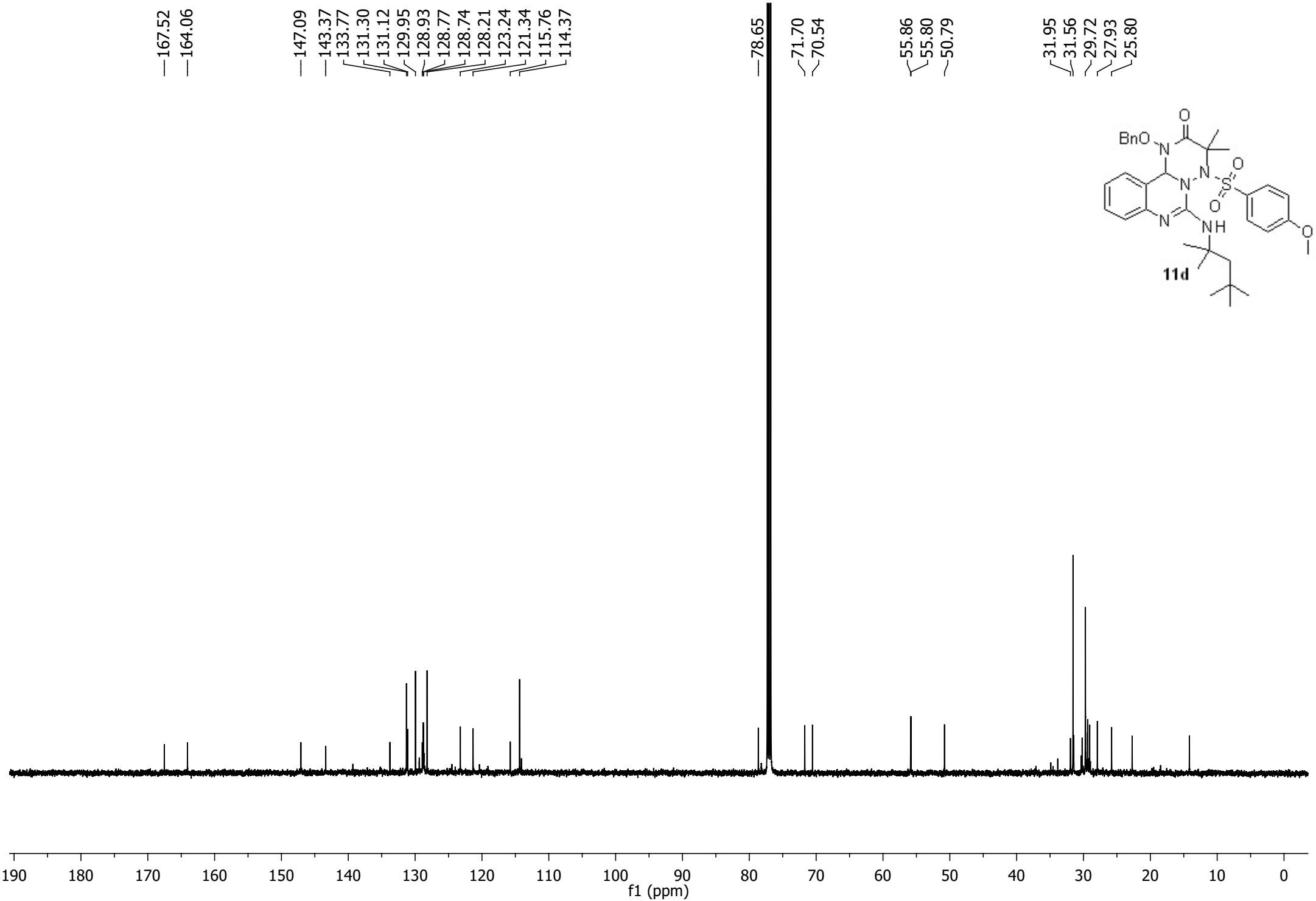
-1.5
f1 (ppm)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128.21
123.24
121.34
115.76
114.37
78.65
71.70
70.54
55.86
55.80
50.79
31.95
31.56
29.72
27.93
25.80
BnO
O
N
N
N
S
O
O
NH
O
11d
190
180
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110
100
90
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50
40
30
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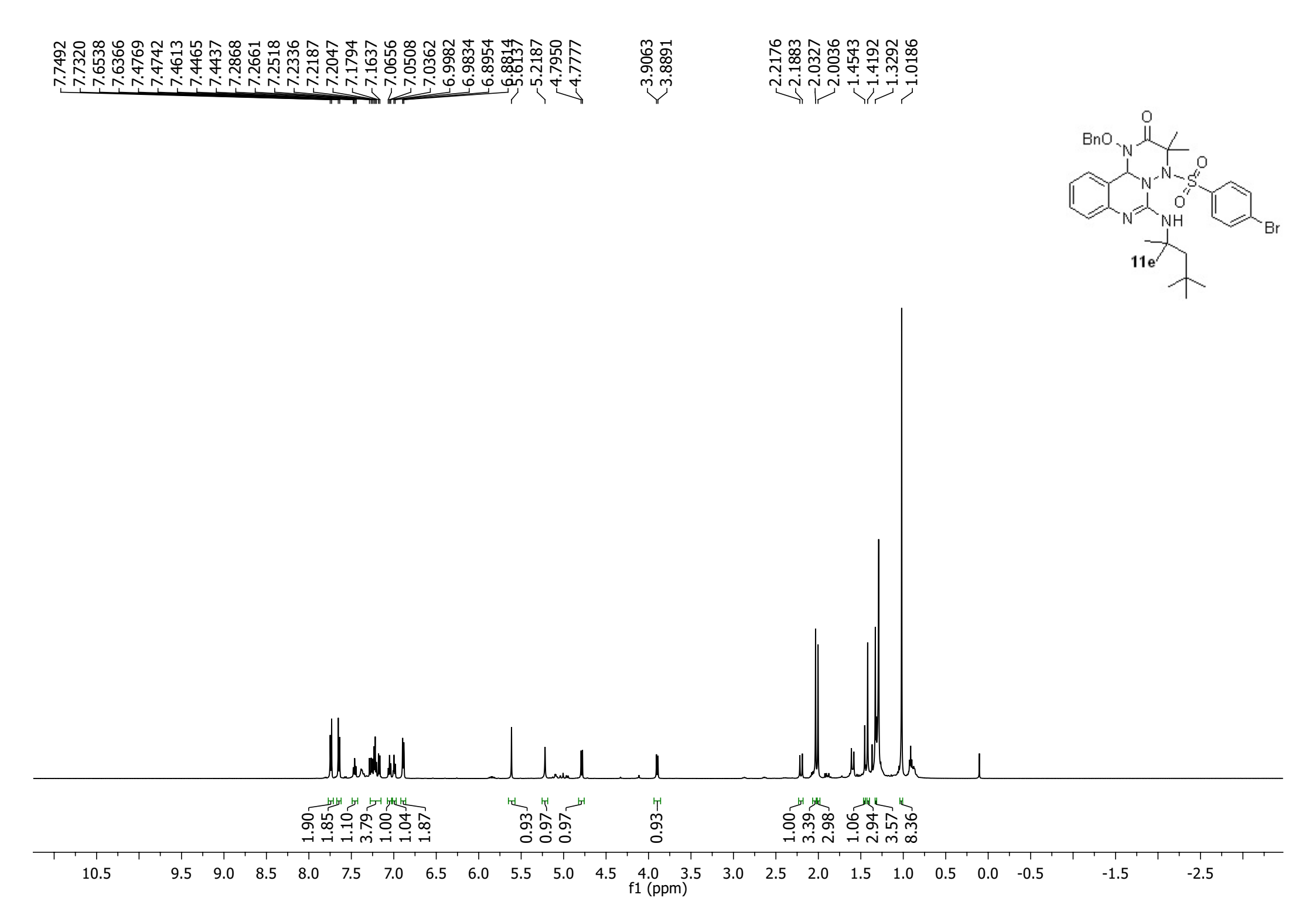
f1 (ppm)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7.2047
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7.1637
7.0656
7.0508
7.0362
6.9982
6.9834
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6.8814
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5.2187
4.7950
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2.0327
2.0036
1.4543
1.4192
1.3292
1.0186
BnO
N
O
S
Br
NH
11e
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1.85
1.10
3.79
1.00
1.04
1.87
0.93
0.97
0.97
0.93
1.00
3.39
2.98
1.06
2.94
3.57
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8.5
8.0
7.5
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
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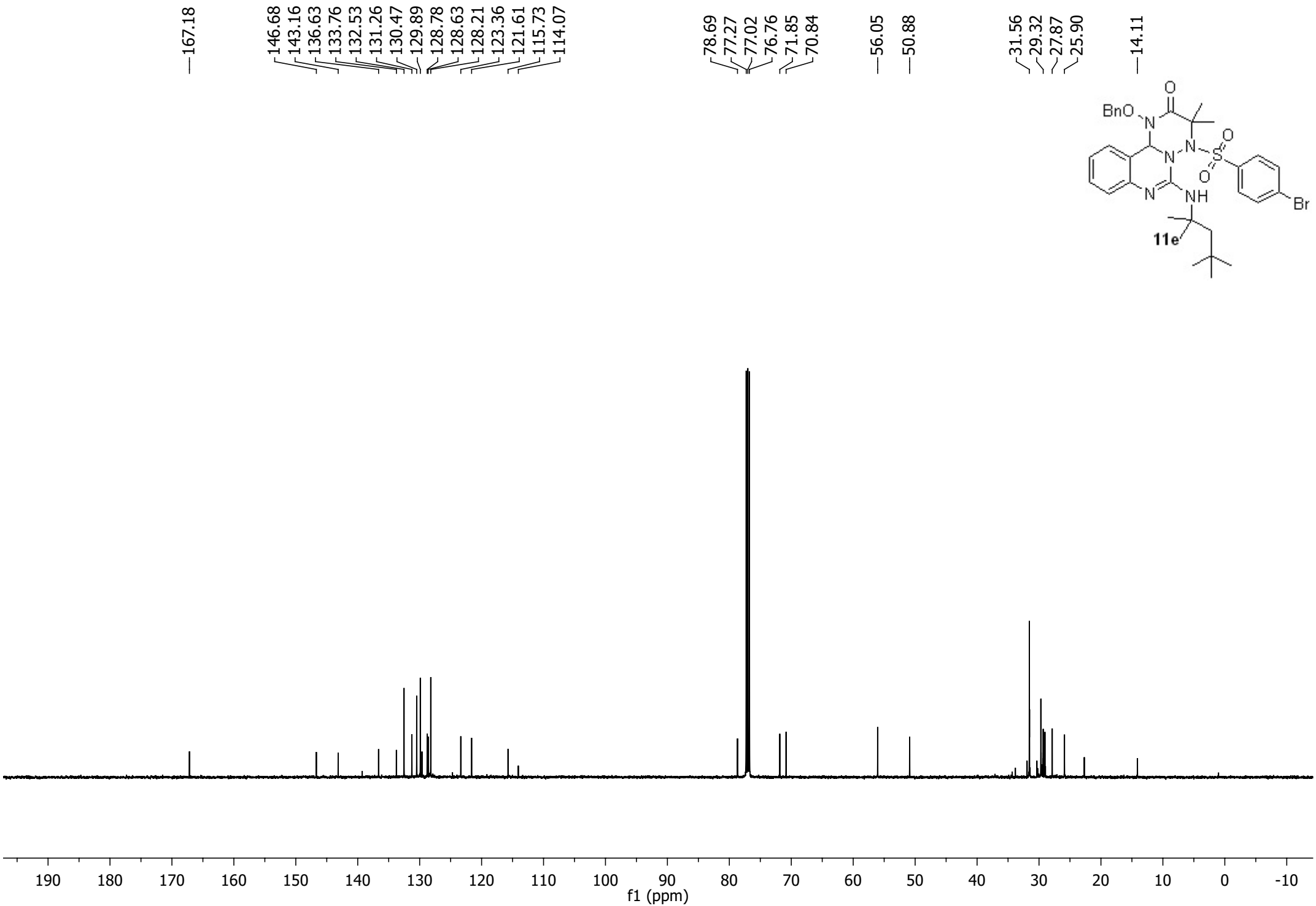
-2.5
f1 (ppm)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128.21
123.36
121.61
115.73
114.07
78.69
77.27
77.02
76.76
71.85
70.84
56.05
50.88
31.56
29.32
27.87
25.90
14.11
BnO
N
O
S
NH
Br
11e
190
180
170
160
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140
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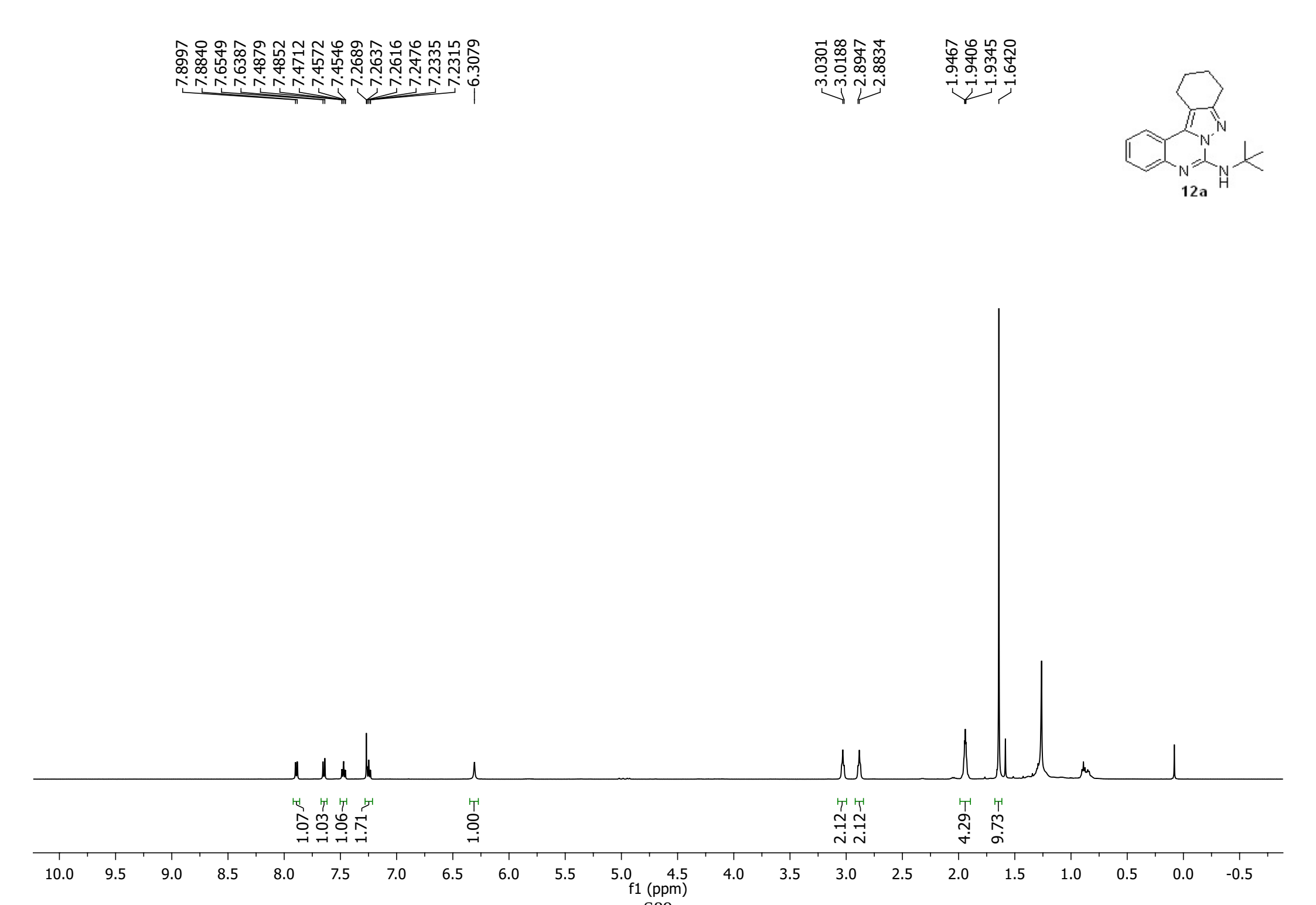
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.2616
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7.2335
7.2315
6.3079
3.0301
3.0188
2.8947
2.8834
1.9467
1.9406
1.9345
1.6420
12a
1.07
1.03
1.06
1.71
1.00
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2.12
4.29
9.73
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
2.5
2.0
1.5
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0.5
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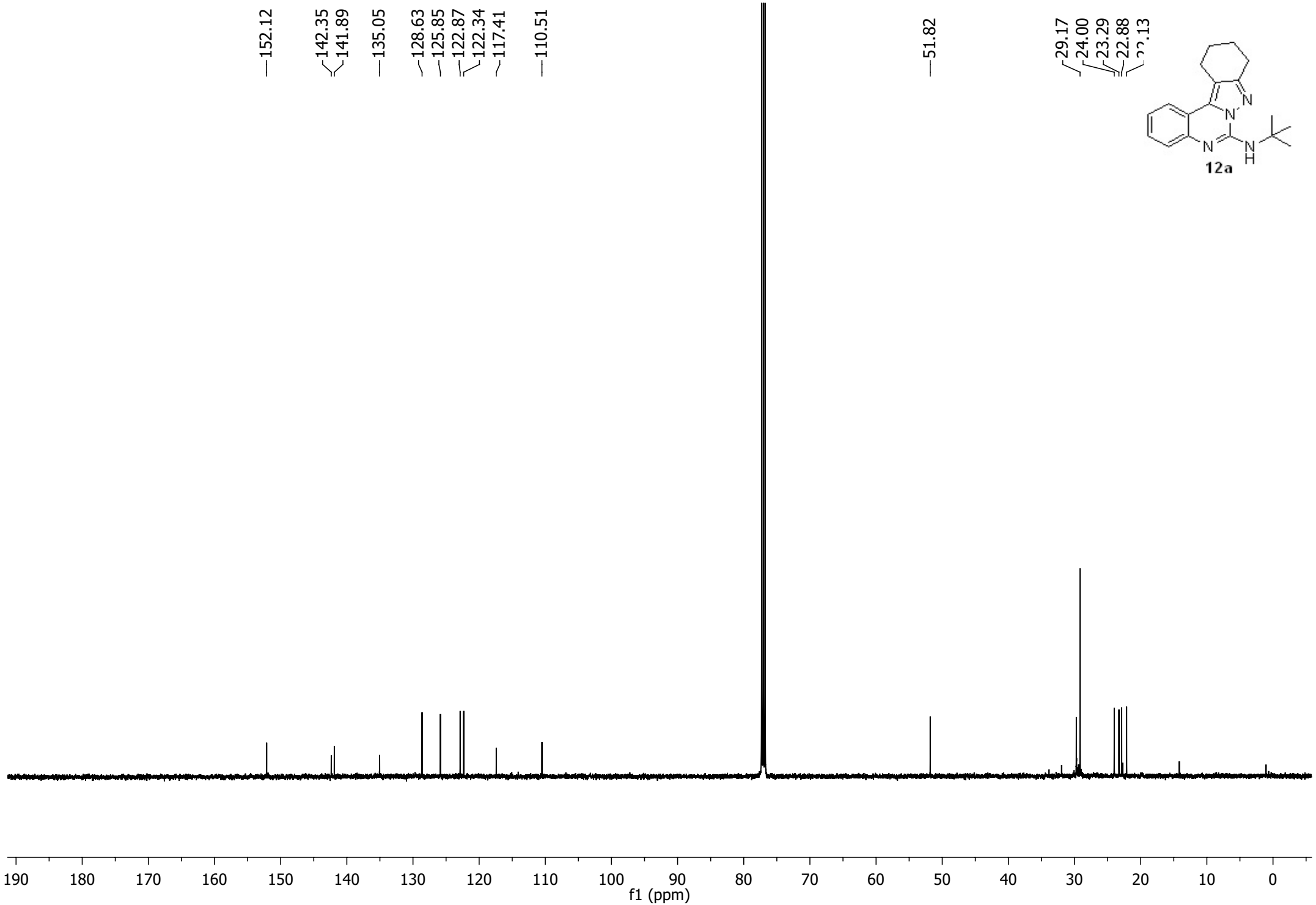
-0.5
f1 (ppm)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51.82
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24.00
23.29
22.88
12a
190
180
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120
110
100
90
80
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50
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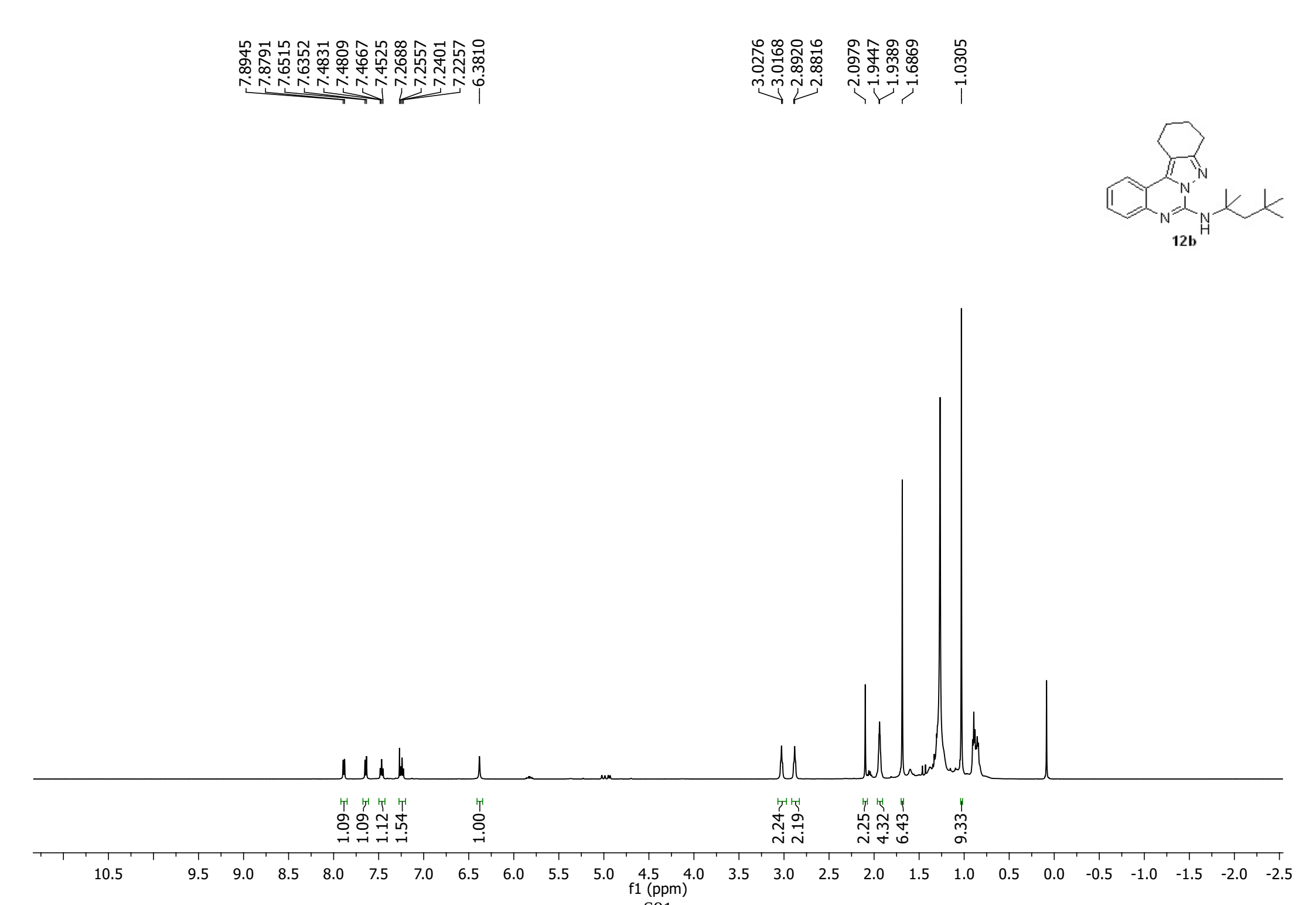
f1 (ppm)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7.2257
6.3810
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3.0168
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2.0979
1.9447
1.9389
1.6869
1.0305
12b
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1.54
1.00
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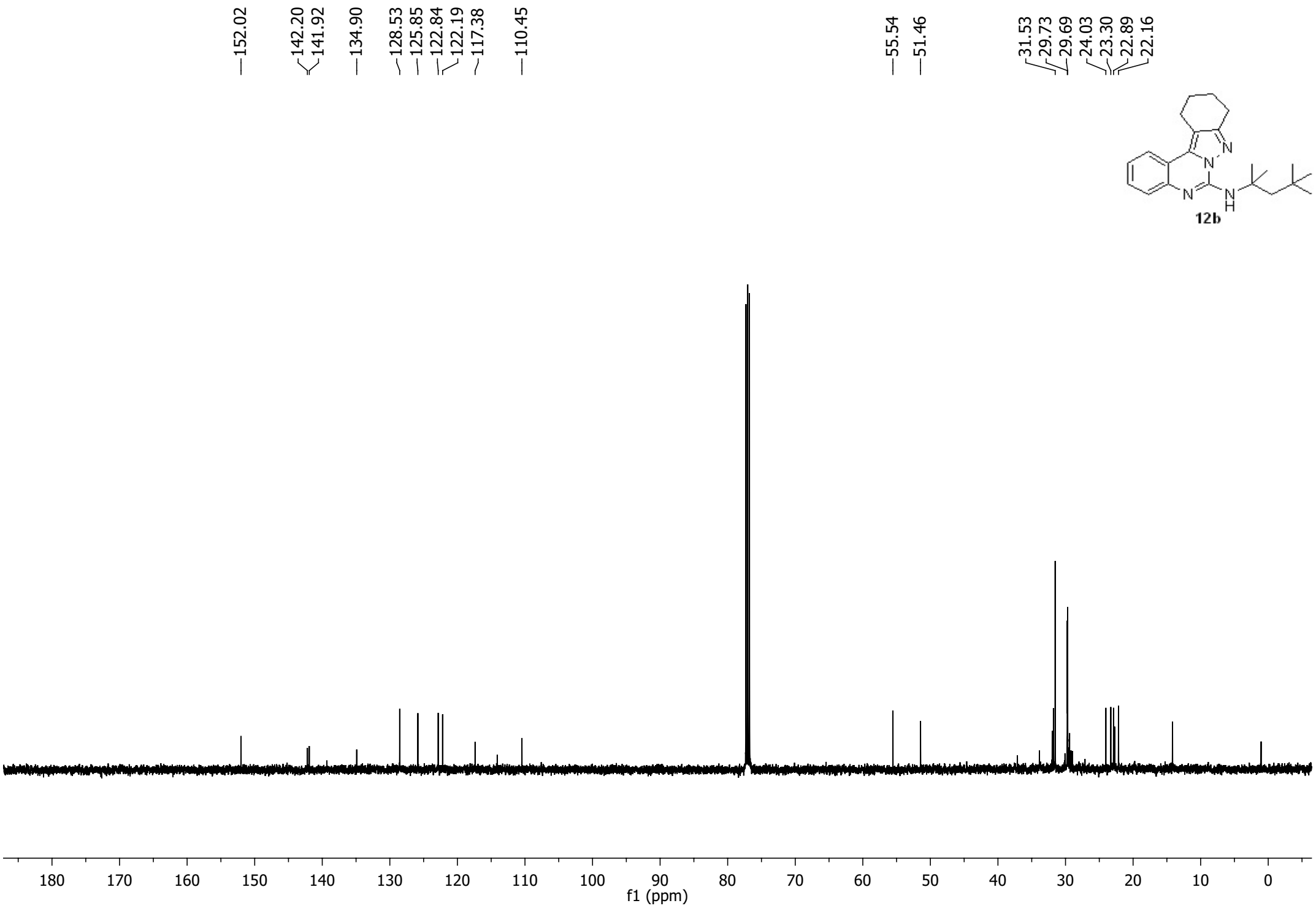
2.25
4.32
6.43
9.33
f1 (ppm)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122.19
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110.45
55.54
51.46
31.53
29.73
29.69
24.03
23.30
22.89
22.16
12b
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)