Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

An Unprecedented N- to C-sulfonyl migration in the reaction of azomethine amine and allenoates: Access to arylsulfonylmethyl substituted pyrazolo[1,5-c]quinazoline and mechanistic studies

Table of Content

S1. General Considerations

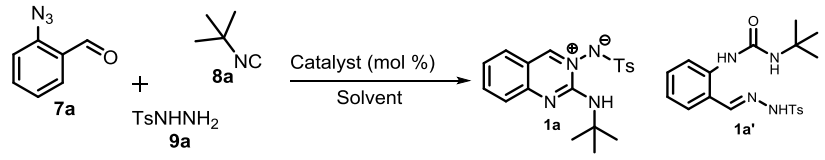
All the reactions were carried in a dried reaction vessel with Teflon screw caps. All solvents were used in synthesis purchased from Spectrochem, and CDH used as such. Aliphatic isocyanides were purchased from Sigma-Aldrich and Alfa aesar. Other reagents were purchased from Aldrich or Spectrochem and used as such without purification. Analytical TLC was performed using a 2 x 4 cm plate coated with 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 and ^{13}C NMR spectra were recorded on Bruker's Ascend 500MHz spectrophotometer operating at 500.3 MHz for ^{1}H and 125.8 MHz for ^{13}C experiments. All 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).

S2 Synthesis of azomethine imine.

S2.1 Optimization for the synthesis of azomethine imine 1.

To optimize the reaction conditions, we started with the reaction of 2-azidobenzaldehyde **7a**, *tert*-butyl isocyanide **8a,** and tosyl hydrazide **9a** in THF 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 **1a** in 57% yield in (table 1, entry 1). In contrast, other Pd-salts failed to promote this reaction (entry 2-3). The presence of a nagging side product, urea **1a'**, was successfully ruled out by employing 4 Å molecular sieves (entry 4). Different solvents were screened, THF gave the best result with 85 % yield of **1a** (entry 5-9). After testing the solvent, it was found that toluene and THF are acting as the best solvent for the reaction.

Table S1: Optimization of one-pot strategy for generation of azomethine imine[a]



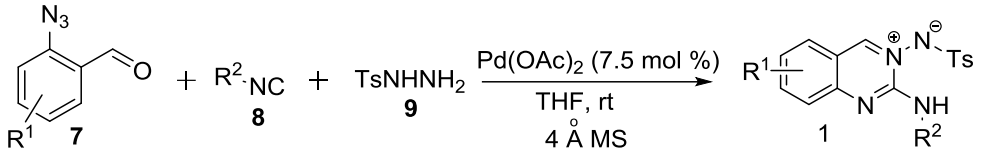
Entry	Catalyst	Additive	Solvent	Isolated yield[b]	
				1a	1a'
1.	$Pd(OAc)_2$	-	THF	57	36
2.	$Pd(PPh_3)_4$	-	THF	35[c]	55
3.	$Pd_2(dba)_3$	-	THF	15[c]	10
4.	$Pd(OAc)_2$	4 Å MS	THF	85	-
5.	$Pd(OAc)_2$	4 Å MS	toluene	81	-
6.	$Pd(OAc)_2$	4 Å MS	MeCN	5[c]	-
7.	$Pd(OAc)_2$	4 Å MS	DMSO	43[c]	-
8.	$Pd(OAc)_2$	4 Å MS	Dioxane	56	-
9.	$Pd(OAc)_2$	4 Å MS	DCE	45[c]	-

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

S2.2. Experimental procedure of azomethine 1

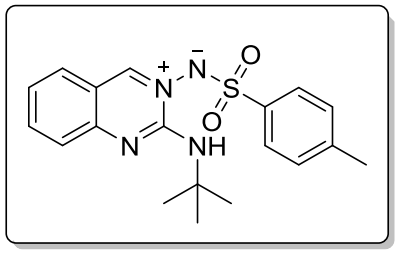
A mixture of 2-azidobenzaldehyde **7** (0.68 mmol, 1.0 equiv), *tert*-butylisocyanide **8** (0.816 mmol, 1.2 equiv), $Pd(OAc)_2$ (7.5 mol %,), 4 Å MS, and $TsNHNH_2$ **9** (0.748 mmol, 1.1 equiv) in THF was stirred at rt. The reaction was monitor by TLC. On completion of reaction, the reaction mixture was diluted with water and extracted with EtOAc (3 x 15ml). The organic layer was separated, dried over sodium sulfate, and concentrated in *vacuo* to obtain crude

reaction mixture, the crude was purified by column chromatography on silica gel using 20:80 EtOAc and hexane as eluent to give desired product **1**.



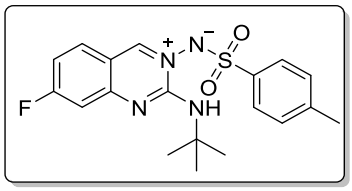
S2.3 Analytical data of azomethine imine 1

1a. (2-(*tert*-butylamino)quinazolin-3-ium-3-yl)(tosyl)amide



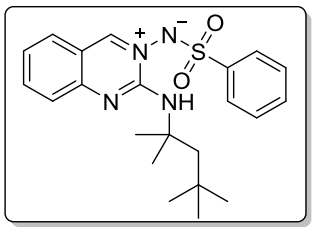
Yellow solid, Yield: 0.214 g (85%); **^{1}H NMR (δ ppm):** (500 MHz, $CDCl_3$), 9.39 (s, 1H), 7.85 (t, 1H, *J* = 7.5 Hz), 7.77 (d, 1H, *J* = 5 Hz), 7.60 (d, 1H, *J* = 5 Hz) 7.53 (d, 2H, *J* = 5 Hz), 7.39 (t, 1H, *J* = 10 Hz), 7.20 (s, 1H), 7.17 (d, 2H, *J* = 5 Hz), 2.35 (s, 3H), 1.18 (s, 9H). **^{13}C{^{1}H} 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

1b. (2-(tert-butylamino)-7-fluoroquinazolin-3-ium-3-yl)(tosyl)amide



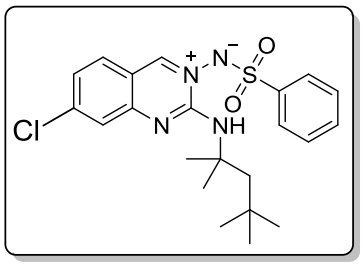
Yellow solid, Yield: 0.200 g (81%); **^{1}H NMR (δ ppm):** (500 MHz, $CDCl_3$), 9.38 (s, 1H), 7.83-7.82 (m, 2H), 7.53 (d, 2H, *J* = 6.7 Hz), 7.35 (d, 1H, *J* = 8.2 Hz) 7.28 (br, s, 1H), 7.21 (d, 2H, *J* = 7.8 Hz), 2.36 (s, 3H), 1.17 (s, 9H). **^{13}C{^{1}H} NMR (δ ppm):** (125 MHz, $CDCl_3$), 154.6, 148.4, 141.8, 140.9, 131.9, 129.9, 129.6, 128.6, 126.1, 116.3, 114.5, 110.9, 54.4, 27.5, 21.3.

1c. (phenylsulfonyl)(2-((2,4,4-trimethylpentan-2-yl)amino)quinazolin-3-ium-3-yl)amide



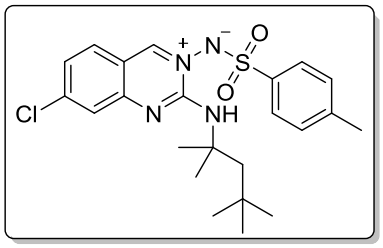
Yellow solid, Yield: 0.210 g (75%); (500 MHz, $CDCl_3$), 9.42 (s, 1H), 7.87 (t, 1H, *J* = 7.0 Hz), 7.79 (d, 1H, *J* = 8.2 Hz), 7.77-7.68 (m, 2H) 7.63 (d, 1H, *J* = 8.6 Hz), 7.47 (d, 1H, *J* = 7.35 Hz),7.42-7.38 (m, 3H), 7.35 (s, 1H), 1.64 (s, 2H), 1.23 (s, 6H), 0.91 (s, 9H); **^{13}C{^{1}H} NMR (δ ppm):** (125 MHz, $CDCl_3$), 154.5, 150.2, 147.9, 144.1, 137.9, 131.3, 129.1, 128.7, 126.1, 126.1 124.9, 117.1, 56.1, 50.7, 31.5, 31.4, 27.7.

1d. (7-chloro-2-((2,4,4-trimethylpentan-2-yl)amino)quinazolin-3-ium-3-yl)(phenyl sulfonyl)amide



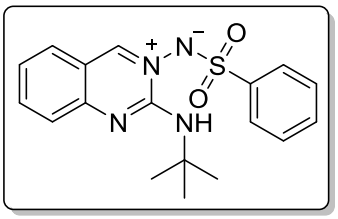
Yellow solid, Yield: 0.252 g (86%); **^{1}H NMR (δ ppm):** (500 MHz, $CDCl_3$), 9.41 (s, 1H), 7.75 (d, 1H, *J* = 8.7 Hz), 7.69 (dd, 2H, *J* = 8.1 Hz), 7.64 (s, 1H), 7.49-7.46 (m, 1H), 7.42-7.39 (m, 3H), 7.35 (dd, 1H, *J* =10 Hz), 1.61 (s, 2H), 1.21 (s, 6H), 0.91 (s, 9H). **^{13}C{^{1}H} NMR (δ ppm):** (125 MHz, $CDCl_3$): 154.2, 150.3, 148.2, 144.9, 143.9, 131.4, 129.9, 129.2, 126.4, 126.1, 125.2, 115.4, 56.4, 50.7, 31.5, 31.3, 27.7.

1e. (7-chloro-2-((2,4,4-trimethylpentan-2-yl)amino)quinazolin-3-ium-3-yl)(tosyl)amide



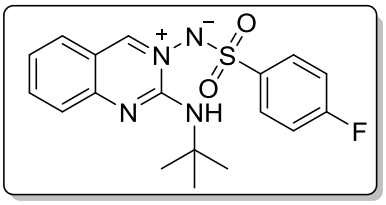
Yellow solid, Yield: 0.221 g (87%); (500 MHz, $CDCl_3$), 9.37 (s, 1H), 7.75-7.73 (m, 2H), 7.59-7.56 (m, 3H), 7.47 (s, 1H), 7.21 (d, 2H, *J* = 8 Hz), 2.38 (s, 3H) , 1.65 (s, 2H), 1.27 (s, 6H), 0.90 (s, 9H). **^{13}C{^{1}H} NMR (δ ppm):** (125 MHz, $CDCl_3$), 152.7, 148.2, 147.8, 141.9, 140.8, 138.4, 130.7, 129.7, 127.6, 126.6, 126.2, 117.4, 52.3, 50.8, 31.5, 31.3, 27.8, 21.3.

1g. (2-(tert-butylamino)quinazolin-3-ium-3-yl)(phenylsulfonyl)amide



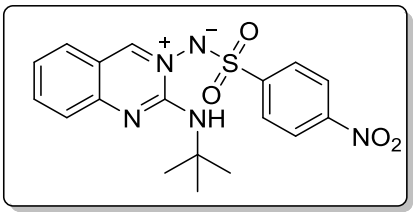
Yellow solid, Yield: 0.225 g (77%); (500 MHz, $CDCl_3$), 9.39 (s, 1H), 7.85 (t, 1H, *J* = 7.5 Hz), 7.78 (d, 1H, *J* = 5 Hz), 7.65 (d, 2H, *J* = 7.4 Hz) 7.60 (d, 1H, *J* = 5 Hz) 7.45 (d, 1H, *J* = 5 Hz), 7.38 (t, 1H, *J* = 10 Hz), 7.17 (s, 1H), 1.16 (s, 9H); **^{13}C{^{1}H} NMR (δ ppm):** (125 MHz, $CDCl_3$), 154.9, 150.4, 148.2, 144.1, 138.1, 131.2, 129.1, 128.8, 126.1, 126.0, 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.

1h. (2-(tert-butylamino)quinazolin-3-ium-3-yl)((4-fluorophenyl)sulfonyl)amide



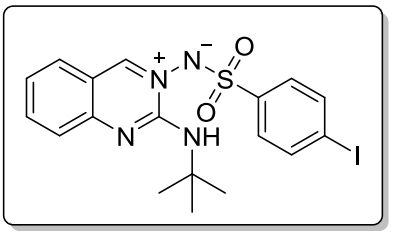
Yellow solid, Yield: 0.208 g (82%); **^{1}H NMR (δ ppm):** (500 MHz, $CDCl_3$), 9.40 (s, 1H), 7.90-7.86 (m, 1H), 7.81 (d, 1H, *J* = 8.3 Hz), 7.70-7.67 (m, 2H) 7.65 (dd, 2H, *J* = 0.6, 8.6 Hz), 7.43 (dt, 1H, *J* = 8.05 Hz), 7.21 (s, 1H), 7.10 (t, 2H, *J* = 8.6 Hz), 1.24 (s, 9H); **^{13}C{^{1}H} NMR (δ ppm):** (125 MHz, $CDCl_3$), 154.9, 150.5, 148.1, 138.3, 128.8, 128.7, 128.6, 126.1, 125.2, 117.2, 116.1, 115.9, 52.3, 27.7.

1j. (2-(tert-butylamino)quinazolin-3-ium-3-yl)((4-nitrophenyl)sulfonyl)amide



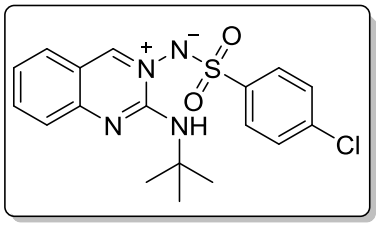
Yellow Solid, Yield: 0.186 g (67%); R_f = 0.4 (EtOAc/hexanes: 20/80); **^{1}H NMR (δ ppm):** (500 MHz, CDCl3), 9.39 (s, 1H), 8.25 (d, 2H, *J* = 8.7 Hz), 7.92 (t, 1H, *J* = 8.3 Hz), 7.85 (d, 2H, *J* = 8.6 Hz), 7.82 (d, 1H, *J* = 8.2 Hz), 7.65 (d, 1H, *J* = 8.5 Hz), 7.45 (t, 1H, *J* = 8.2 Hz), 7.09 (br s, 1H), 1.18 (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

1k. (2-(tert-butylamino)quinazolin-3-ium-3-yl)((4-iodophenyl)sulfonyl)amide



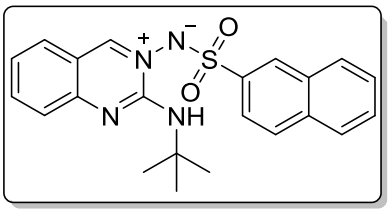
Yellow solid, Yield: 0.236 g (72%); **^{1}H NMR (δ ppm):** (500 MHz, CDCl3), 9.38 (s, 1H), 7.90 (t, 1H, *J* = 7.4 Hz), 7.80 (d, 1H, *J* = 8.1 Hz), 7.76 (d, 2H, *J* = 8.4 Hz), 7.67 (d, 1H, *J* = 8.6 Hz), 7.43 (t, 1H, *J* = 7.4 Hz), 7.40 (d, 2H, *J* = 8.4 Hz), 7.14 (br s, 1H), 1.24 (s, 9H); **^{13}C{^{1}H} NMR (δ ppm):** (125 MHz, $CDCl_3$), 155.0, 150.6, 148.0, 138.3, 138.2, 137.4, 128.8, 127.8, 127.7, 126.2, 125.2, 117.2, 52.4, 27.7.

1l. (2-(*tert*-butylamino)quinazolin-3-ium-3-yl)((4-chlorophenyl)sulfonyl)amide



Yellow solid, Yield: 0.206 g (78%); **^{1}H NMR (δ ppm):** (500 MHz, $CDCl_3$), 9.38 (s, 1H), 7.87 (t, 1H, *J* = 8.3 Hz), 7.80 (d, 1H, *J* = 8.7 Hz), 7.61-7.57 (m, 2H, *J* = 8.6 Hz), 7.44 (d, 1H, *J* = 8.2 Hz), 7.40 (t, 1H, *J* = 8.2 Hz) 7.35 (d, 2H, *J* = 8.2 Hz), 7.12 (br, s, 1H), 1.21 (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.

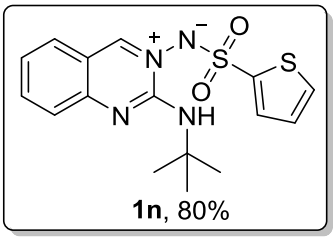
1m. (2-(*tert*-butylamino)quinazolin-3-ium-3-yl)(naphthalen-1-ylsulfonyl)amide



Yellow solid, Yield: 0.215 g (78%); **^{1}H NMR (δ ppm):** (500 MHz, $CDCl_3$), 9.42 (s, 1H), 9.08 (d, 1H, *J* = 8.6 Hz), 7.93 (d, 2H, *J* = 8.2 Hz), 7.83 (d, 2H, *J* = 7.3 Hz), 7.78 (d, 1H, *J* = 8.2 Hz), 7.68 (t, 1H, *J* = 7.15 Hz), 7.59 (t, 1H, *J* = 7.2 Hz), 7.54 (d, 1H, *J* = 8.7 Hz), 7.38 (t, 1H, *J* = 7.3 Hz), 7.32 (t, 1H, *J* = 7.9 Hz), 6.85 (s, 1H), 0.70 (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,

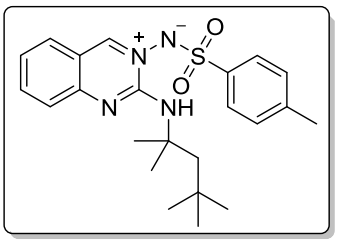
128.5, 128.3, 127.5, 126.7, 126.0, 125.7, 124.9, 124.2, 117.1, 51.9, 27.1. **HRMS** (EI) calcd for $C_{22}H_{23}N_4O_2S$ ($M+H^+$) 407.1536 found 407.1523.

1n. 4j. (2-(*tert*-butylamino)quinazolin-3-ium-3-yl)(thiophen-2-ylsulfonyl)amide



Yellow solid, Yield: 0.196 g (80%); 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 (d, 1H, *J* = 5 Hz), 1.29 (s, 9H,); **^{13}C{1H} NMR (δ ppm):** (125 MHz, CDCl3), 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.

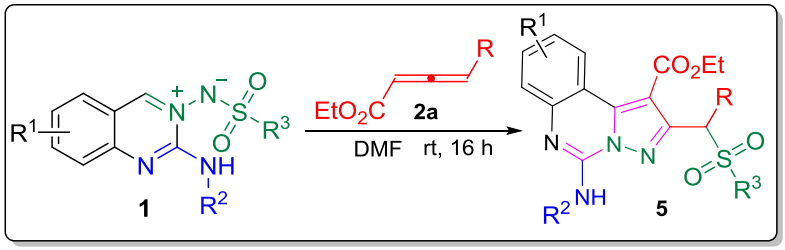
1o. tosyl(2-((2,4,4-trimethylpentan-2-yl)amino)quinazolin-3-ium-3-yl)amide



Yellow solid, Yield: 0.254 g (87%); **^{1}H NMR (δ ppm):** (500 MHz, $CDCl_3$), 10.15 (s, 1H), 7.79 (d, 1H, *J* = 10 Hz), 7.21 (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{1H} 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.

S3 Synthesis of [1,3]-sulfonyl migration compound 5

S3.1 Experimental procedure for the synthesis of 5

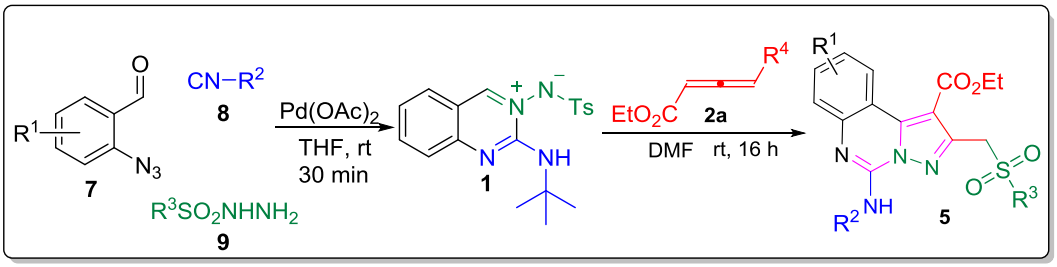


Azomethine imine **1** (1 equiv.) allenoate **2** (1.2 equiv.) were dissolved in DMF, and the reaction mixture was stirred at ambient temperature. Reaction progress was periodically monitored by using TLC. After complete consumption of the starting material, the reaction mixture was quenched with cold water and extracted with EtOAc (3x15ml). The combined organic layer

was dried over Na_2SO_4 and filtered. The filtrate was concentrated *in vacuo*. The resulting mixture was purified by column chromatography on silica gel (100-200 mesh) using 10:90 EtOAc and hexane as eluent to give the desired product **5**.

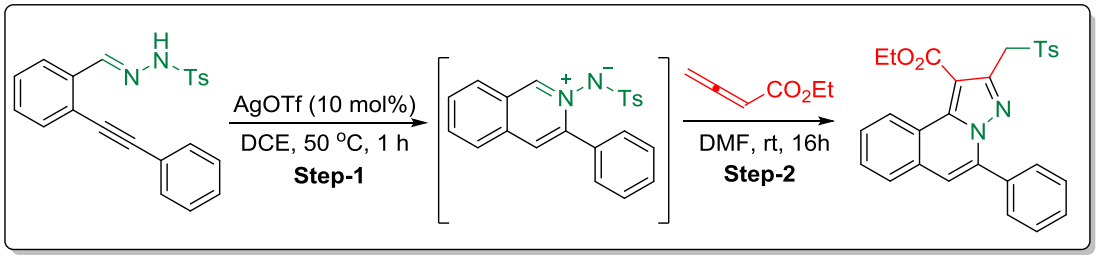
S3.2 One-pot *sequential* experimental procedure for the synthesis of 5.

In a 10 mL reaction vial, 2-azidobenzaldehyde **7** (1.0 equiv), isocyanide **8** (1.2 equiv), $Pd(OAc)_2$ (7.5 mol %,), 4 Å MS, and aryl sulphonyl hydrazide **9** (1 equiv) were dissolved in THF. The reaction mixture was stirred at rt. The reaction was monitor on TLC, and after the formation of azomethine imine **1**, the organic solvent was evaporated and replaced by DMF (1.0 mL). Subsequently, allenoate **2** (1.2 equiv.) was introduced, and the reaction mixture was stirred for 16 h at rt. Reaction progress was periodically monitored on TLC. After the complete consumption of the starting material, the reaction mixture was diluted with cold water and extracted with EtOAc (3x15ml). The combined organic layer was dried over Na_2SO_4 and filtered. The filtrate was concentrated *in vacuo*. The resulting mixture was purified by column chromatography on silica gel using 10:90 EtOAc and hexane as eluent to give the desired product **5**.



S3.3 Experimental procedure for the 5q.

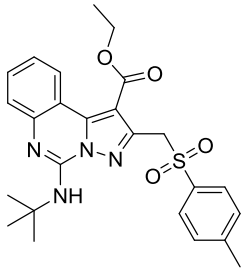
Step-1: In a 10 mL reaction vial, *N*`-(2-alkynyl benzylidene)hydrazide (0.2 mmol, 1 equiv.) was dissolved in DCE. The reaction mixture was stirred at 50 ℃ in the presence of catalyst AgOTf (10 mol %) in the air for 1 h. After completion of the starting material, the solvent was evaporated to obtain a crude residue.



Step-2: Crude of step-1 was dissolved in DMF and allenoate (1.2 equiv) were added, the reaction was stirred at rt for 16 h. The progress of the reaction was monitored on TLC.

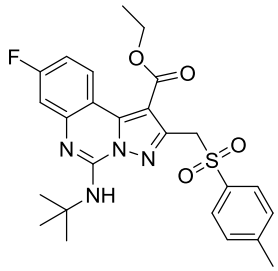
S3.4. Analytical data [1,3]-sulfonyl migration compound 5

5a. ethyl 5-(tert-butylamino)-2-(tosylmethyl)pyrazolo[1,5-c]quinazoline-1-carboxylate



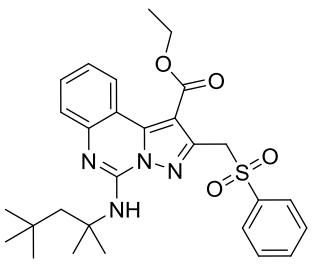
Off-white solid, Yield: 0.106 g (82 %); **^{1}H NMR (δ/ppm):** 9.17 (d, 1H, *J* = 8.2 Hz), 7.70 (d, 1H, *J* = 8.2 Hz) 7.63-7.60 (m, 3H), 7.36 (t, 1H, *J* = 7.5 Hz), 7.30 (m, 3H), 6.13 (s, 1H), 5.02 (s, 2H), 4.42 (q, 2H, *J* = 8.1 Hz), 2.46 (s, 3H), 1.60 (s, 6H), 1.51 (t, 3H, *J* = 7.15 Hz). **^{13}C{^{1}H} NMR (δ ppm):** (125 MHz, $CDCl_3$)**:** 163.2, 144.6, 143.4, 141.3, 141.2, 135.8, 131.3, 129.4, 128.7. 126.7, 123.1, 115.1, 114.1, 108.6, 61.2, 55.7, 52.1, 28.9, 21.7, 14.1. **HRMS** (EI) calcd for $C_{25}H_{29}N_4O_4S$ ($M+H^+$) 481.1904 found 481.1937.

5b. ethyl 5-(tert-butylamino)-8-fluoro-2-(tosylmethyl)pyrazolo[1,5-c]quinazoline-1-carboxylate



(IPA used as solvent in reaction): White solid, Yield: 0.075 g (78%); m.p. 152-153 °C; **^{1}H NMR (δ/ppm):** 9.27 (dd, 1H, *J* = 6.45, 2.65 Hz), 7.64 (d, 2H, *J* = 8.1 Hz), 7.34-7.28 (m, 4H), 7.09 (t, 1H, *J* = 8.2 Hz), 6.20 (br s, 1H), 5.01 (s, 2H), 4.41 (q, 2H, *J* = 7.1 Hz), 2.47 (s, 3H) 1.59 (s, 9H), 1.50 (t, 3H, *J* = 7.15 Hz). **^{13}C{^{1}H} NMR (δ ppm):** (125 MHz, $CDCl_3$)**:** 163.1, 145.7, 144.8 (*J* = 15 Hz), 141.8, 141.1, 135.8, 129.5, 129.2. 129.1, 128.7, 111.8 (*J* = 22 Hz), 111.3 (21.2 Hz), 108.3, 61.3, 55.7, 52.3, 28.8, 21.7, 14.3 **HRMS** (EI) calcd for $C_{25}H_{28}FN_4O_4S$ ($M+H^+$) 499.181 found to be 499.1801.

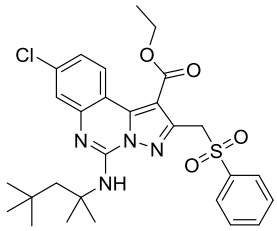
5c. ethyl 2-((phenylsulfonyl)methyl)-5-((2,4,4-trimethylpentan-2-yl)amino)pyrazolo[1,5-c]quinazoline-1-carboxylate



Light yellow solid, Yield: 0.061 g (71%); m.p. 161-162 °C; **^{1}H NMR (δ/ppm)**: 9.17 (d, 1H, *J* = 8.2 Hz), 7.73-7.68 (m, 3H), 7.65-7.61 (m, 2H), 7.50 (t, 2H, *J* = 7.5), 7.36 (t, 1H, *J* = 7.5 Hz), 6.19 (s, 1H), 5.05 (s, 1H), 4.45 (q, 2H, *J* = 7.1 Hz), 2.00 (s, 2H), 1.63 (s, 6H) 1.53 (t, 3H, *J* = 7.15 Hz), 0.98 (s, 9H), **^{13}C{^{1}H} NMR (δ ppm):** (125 MHz, $CDCl_3$): 163.2, 144.5, 143.4, 141.2, 141.1, 139.3, 138.6, 133.7, 131.3, 128.9, 128.6, 126.2, 123.0,

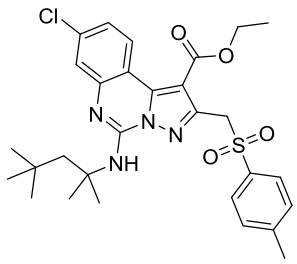
115.0, 114.1, 108.7, 61.3, 55.9, 55.8, 51.5, 31.9, 31.5, 29.7, 22.7, 14.2. **HRMS** (EI) calcd for $C_{28}H_{35}N_4O_4S$ ($M+H^+$) 523.2374 found to be 523 .2400.

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



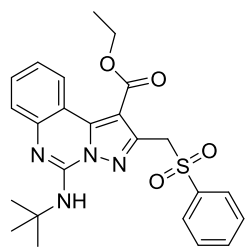
(IPA used as solvent in reaction): Light yellow solid, Yield: 0.097 g (78%); **^{1}H NMR (δ/ppm):** 9.17 (d, 1H, *J* = 8.8 Hz), 7.73(d, 2H, *J* = 7.3 Hz), 7.68 (d, 1H, *J* = 2.5 Hz), 7.66 (t, 1H, *J* = 7.5 Hz), 7.50 (t, 2H, *J* = 7.7 Hz), 7.29-7.27 (m, 1H), 6.26 (s, 1H), 5.03 (s, 2H), 4.45 (q, 2H, *J* = 8.1 Hz), 1.98 (s, 2H), 1.62 (s, 6H), 1.52 (t, 3H, *J* = 7.15 Hz), 0.98 (s, 6H). **^{13}C{^{1}H} NMR (δ ppm):** (125 MHz, $CDCl_3$)**:** 163.0, 144.9, 144.5, 141.6, 140.9, 138.8, 137.1, 133.7, 128.9, 128.6, 128.1, 125.5, 123.5, 113.5, 108.9, 61.3, 56.1, 55.8, 51.6, 31.7, 31.4, 29.2, 14.3. **HRMS** (EI) calcd for $C_{28}H_{34}ClN_4O_4S$ ($M+H^+$) 557.1984

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



(IPA used as solvent in reaction): White solid, Yield: 0.090 g (73%), **^{1}H NMR (δ/ppm):** 9.17 (d, 1H, *J* = 8.8 Hz), 7.68 (s, 1H), 7.60 (d, 2H, *J* = 8.2 Hz), 7.29-7.27 (m, 3H), 6.29 (s, 1H), 5.01 (s, 2H), 4.48 (q, 2H, *J* = 8.1 Hz), 2.45 (s, 3H), 1.98 (s, 9H), 1.62 (s, 6H), 1.52 (t, 3H, *J* = 7.15 Hz), 0.98 (s, 6H). **^{13}C{^{1}H} NMR (δ ppm):** (125 MHz, $CDCl_3$)**:** 163.1, 145.0, 144.6, 144.5, 141.6, 140.8, 137.1, 135.9, 129.5, 129.2. 128.6, 128.1, 125.5, 123.4, 113.5, 108.9, 61.3, 56.1, 55.8, 51.6, 31.7, 31.4, 29.2, 21.6, 14.3. **HRMS** (EI) calcd for $C_{29}H_{36}ClN_4O_4S$ ($M+H^+$) 571.2141 found 571.2127.

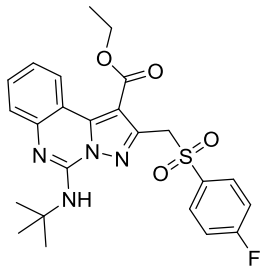
5g. ethyl 5-(tert-butylamino)-2-((phenylsulfonyl)methyl)pyrazolo[1,5-c]quinazoline-1-carboxylate.



Light yellow solid, Yield: 0.074 g (74%); m.p. 141.6-142.2 °C; **^{1}H NMR (δ/ppm):** 9.17 (d, 1H, *J* = 7.45 Hz), 7.75 (d, 2H, *J* = 8.5 Hz), 7.70-7.62 (m, 3H), 7.52 (t, 2H, *J* = 8.2 Hz, *J* = 1.25 Hz), 7.36 (t, 1H, *J* = 8.5 Hz), 6.09 (br s, 1H), 5.04 (s, 2H), 4.42 (q, 2H, *J* = 7.1 Hz), 1.59 (s, 9H), 1.51 (t, 3H, *J* = 7.15 Hz). **^{13}C{^{1}H} NMR (δ ppm):** (125 MHz, $CDCl_3$)**:** 163.2, 144.5, 143.4,

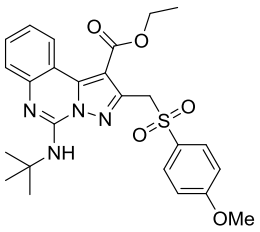
141.2, 138.6, 134.3, 133.7, 131.4, 128.9, 128.8, 126.7, 126.2, 123.1, 115.1, 108.6, 101.7, 61.2, 55.7, 52.2, 28.9, 14.3. **HRMS** (EI) calcd for $C_{24}H_{27}N_4O_4S$ (M+H$^+$) 467.1748 found 467.1751.

5h. ethyl 5-(tert-butylamino)-2-(((4-fluorophenyl)sulfonyl)methyl)pyrazolo[1,5-c]quinazoline-1-carboxylate



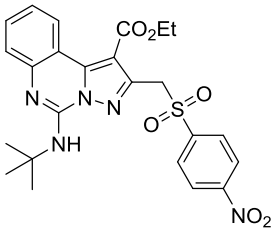
Light yellow solid, Yield: 0.067 g (70%); m.p. 162-164 ^{o}C, **^{1}H NMR (δ/ppm):** 9.16 (d, 1H, *J* = 7.45 Hz), 7.75-7.69 (m, 3H), 7.65 (dt, 1H, *J* = 7.1, 1.05 Hz), 7.37 (dt, 1H, *J* = 8.3, 1.1 Hz), 7.19 (t, 2H, *J* = 15.15 Hz, *J* = 8.5 Hz), 6.05 (s, 1H), 5.05 (s, 2H), 4.46 (q, 2H, *J* = 14.3 Hz, *J* = 7.15 Hz), 1.59 (s, 9H), 1.53 (t, 3H, *J* = 7.15 Hz). **^{13}C{^{1}H} NMR (δ ppm):** (125 MHz, $CDCl_3$)**:** 163.1, 144.5, 143.4, 141.3, 141.2, 131.7, 131.5, 126.7, 126.3, 123.2, 116.2, 116.0, 115.0, 114.1, 108.6, 61.3, 55.8, 52.2, 29.7, 14.3. **HRMS** (EI) calcd for $C_{24}H_{26}FN_4O_4S$ (M+H$^+$) 485.1654 found 485.1671.

5i. ethyl 5-(tert-butylamino)-2-(((4-methoxyphenyl)sulfonyl)methyl)pyrazolo[1,5-c]quinazoline-1-carboxylate



Creamy white solid, Yield: 0.068 g (71%); m.p. 149-151 ^{o}C **^{1}H NMR (δ/ppm):** 9.17 (d, 1H, *J* = 8 Hz), 7.70-7.62 (m, 4H), 7.36 (t, 1H, *J* = 7.65 Hz), 6.95 (d, 2H, *J* = 8.8 Hz), 6.13 (s, 1H), 5.01 (s, 2H), 4.44 (q, 2H, *J* = 7.1 Hz), 3.88 (s, 3H), 1.59 (s, 9H), 1.52 (t, 3H, *J* = 7.1 Hz**). ^{13}C{^{1}H} NMR (δ ppm):** (125 MHz, $CDCl_3$)**:** 163.8, 144.8, 143.4, 141.3, 141.1, 131.3, 130.9, 130.1, 126.7, 126.2, 123.1, 115.1, 114.1, 113.9, 108.6, 61.3, 55.9, 55.7, 55.1, 52.1, 29.7.14.2. **HRMS** (EI) calcd for $C_{25}H_{29}N_4O_5S$ (M+H) 497.1853 found

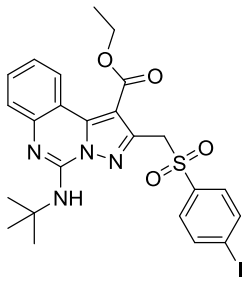
5j. ethyl 5-(tert-butylamino)-2-(((4-nitrophenyl)sulfonyl)methyl)pyrazolo[1,5-c]quinazoline-1-carboxylate



yellow oil, Yield: 0.060 g (63%); **^{1}H NMR (δ/ppm):** 9.15 (d, 1H, *J* = 7.8.2 Hz), 8.35 (d, 2H, *J* = 8.7 Hz) 7.95 (d, 2H, *J* = 8.7 Hz), 7.72 (d, 1H, *J* = 8.2 Hz), 7.66 (t, 1H, *J* = 8.1 Hz), 7.38-7.28 (m, 1H), 5.98 (br s, 1H), 5.11 (s, 2H), 4.47 (q, 2H, *J* = 7.5 Hz), 1.55 (s, 9H), 1.53 (t, 3H, *J* = 7.25 Hz). **^{13}C{^{1}H} NMR (δ ppm):** (125 MHz, $CDCl_3$)**:** 162.9, 150.9 144.2, 143.9,

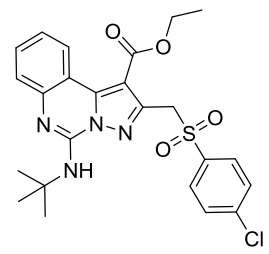
143.5, 141.4, 141.0, 131.6, 130.3, 126.7, 126.4, 123.9, 123.3, 114.9, 108.6, 108.6, 61.4, 55.6, 52.2, 28.8, 14.2. HRMS (EI) calcd for $C_{24}H_{26}N_4O_6S$ (M+H) 512.1599 found 512.1598.

5k. ethyl 5-(tert-butylamino)-2-(((4-iodophenyl)sulfonyl)methyl)pyrazolo[1,5-c]quinazoline-1-carboxylate



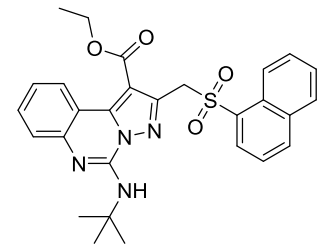
Light yellow solid, Yield: 0.061 g (67%); m.p. 165-167 ^oC; **^{1}H NMR (δ/ppm)**: 9.17 (d, 1H, *J* = 7.45 Hz), 7.87 (d, 2H, *J* = 8.5 Hz), 7.71 (d, 1H, *J* = 7.5 Hz), 7.65 (dt, 1H, *J* = 8.2 Hz, *J* = 1.25 Hz), 7.43 (d, 2H, *J* = 8.5 Hz), 7.37-7.34 (m, 1H), 6.05 (br s, 1H), 5.03 (s, 2H), 4.46 (q, 2H, *J* = 7.1 Hz), 1.61 (s, 9H), 1.53 (t, 3H, *J* = 7.15 Hz). **^{13}C{^{1}H} NMR (δ ppm):** (125 MHz, $CDCl_3$): 163.1, 144.4, 143.5, 141.2, 138.1, 131.5, 130.2, 126.7, 126.3, 123.1, 119.0 115.0, 114.1, 108.6, 101.7, 61.4, 55.6, 52.2, 28.9, 14.3. **HRMS** (EI) calcd for $C_{24}H_{26}IN_4O_4S$ (M+H) 593.0714 found 593.0731.

5l. ethyl 5-(tert-butylamino)-2-(((4-chlorophenyl)sulfonyl)methyl)pyrazolo[1,5-c]quinazoline-1-carboxylate



White crystalline solid, Yield: 0.065 g (68%); **^{1}H NMR (δ/ppm):** 9.17 (d, 1H, *J* = 7.4 Hz), 7.71-7.62 (m, 4H), 7.48 (d, 2H, *J* = 8.3 Hz), 7.37 (t, 1H, *J* = 8.5 Hz), 6.03 (br s, 1H), 5.04 (s, 2H), 4.46 (q, 2H, *J* = 7.1 Hz), 1.60 (s, 9H), 1.53 (t, 3H, *J* = 7.15 Hz). **^{13}C{^{1}H} NMR (δ ppm):** (125 MHz, $CDCl_3$)**:** 163.1, 144.4, 143.4, 141.2, 141.1, 140.5, 136.9, 131.5, 130.3, 129.1, 126.7, 126.3, 123.2, 115.0, 108.6, 61.3, 55.6, 52.2, 28.9, 14.3. **HRMS** (EI) calcd for $C_{24}H_{26}ClN_4O_4S$ ($M+H^+$) 501.1358 found 501.1367

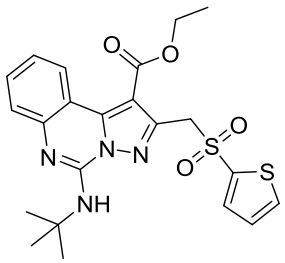
5m. ethyl 5-(tert-butylamino)-2-((naphthalen-1-ylsulfonyl)methyl)pyrazolo[1,5-c]quinazoline-1-carboxylate



Light yellow solid, Yield: 0.070 g (74%); **^{1}H NMR (δ/ppm):** 9.14 (d, 1H, *J* = 8.2 Hz), 8.70 (d, 1H, *J* = 7.3 Hz), 8.14 (d, 1H, *J* = 8.2 Hz), 8.06 (d, 1H, *J* = 8.2 Hz), 7.98-7.97 (m, 1H), 7.66-7.57 (m, 4H), 7.50 (t, 1H, *J* = 7.6 Hz), 7.34 (t, 1H, J = 8.2 Hz), 5.65 (br s, 1H), 5.20 (s, 2H), 4.36 (q, 2H, *J* = 7.5 Hz), 1.49 (s, 9H), 1.47 (t, 3H, *J* = 7.2 Hz**^{13}C{^{1}H} NMR (δ ppm):** (125 MHz, $CDCl_3$)**:** 163.1, 144.4, 141.1, 141.0, 143.5, 135.2, 133.8, 133.7, 131.4,

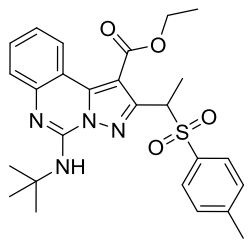
131.3, 129.6, 128.9, 128.7, 127.0, 126.7, 126.2, 124.3, 123.1, 114.9, 108.8, 61.2, 55.6, 51.9, 28.7, 14.2. **HRMS** (EI) calcd for $C_{28}H_{29}N_4O_4S$ (M+H) 517.1904 found 517.1927.

5n. ethyl 5-(tert-butylamino)-2-((thiophen-2-ylsulfonyl)methyl)pyrazolo[1,5-c]quinazoline-1-carboxylate



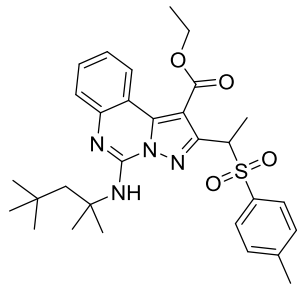
Colorless oil, Yield: 0.072 g (73%); **^{1}H NMR (δ/ppm):** 9.20 (d, 1H, *J* = 8.25 Hz), 7.72 (m, 2H), 7.65 (m, 1H), 7.53 (dd, 1H, *J* = 3.7, 1.15 Hz), 7.36 (t, 1H, *J* = 8.2 Hz), 7.13 (dt, 1H, *J* = 3.95 Hz), 6.21 (br s, 1H), 5.14 (s, 2H), 4.45 (q, 2H, *J* = 7.15 Hz), 1.62 (s, 9H), 1.52 (t, 3H, *J* = 7.15 Hz). **^{13}C{^{1}H} NMR (δ ppm):** (125 MHz, $CDCl_3$)**:** 163.1, 144.4, 143.4, 141.3, 141.3, 139.5, 134.9, 134.4, 131.4, 127.7, 126.8, 126.2, 123.1, 115.0, 108.7, 61.3, 56.9, 52.2, 28.9, 14.3. **HRMS** (EI) calcd for $C_{22}H_{25}N_4O_4S_2$ (M+H) 473.1312 found 473.1311.

5o. ethyl 5-(tert-butylamino)-2-(1-tosylethyl)pyrazolo[1,5-c]quinazoline-1-carboxylate



White solid, Yield: 0.070 g (70%);**^{1}H NMR (δ/ppm):** 9.04 (d, 1H, *J* = 8.2 Hz), 7.70 (d, 1H, *J* = 7.9 Hz), 7.63 (t, 1H, *J* = 7.1 Hz), 7.56 (d, 2H, *J* = 8.1 Hz), 7.34 (t, 1H, *J* = 7.3 Hz), 7.29-7.26 (m, 2H) 6.21 (br s, 1H), 5.63 (q, 1H, *J* = 7.1 Hz), 4.49 (q, 2H, *J* = 7.15 Hz), 2.24 (s, 3H), 1.85 (d, 3H, *J* = 7.1 Hz), 1.64 (s, 9H), 1.52 (t, 3H, *J* = 7.15 Hz). **^{13}C{^{1}H} NMR (δ ppm):** (125 MHz, $CDCl_3$)**:** 163.6, 148.9, 144.6, 143.4, 141.4, 140.7, 133.7, 131.2, 129.6, 129.2, 126.5, 126.2, 122.9, 115.1, 108.9, 61.2, 58.6, 52.1, 28.9, 21.7, 14.3, 14.2. **HRMS** (EI) calcd for $C_{26}H_{31}N_4O_4S$ ($M+H^+$) 495.2061 found to be 495.2075.

5p. ethyl 2-(1-tosylethyl)-5-((2,4,4-trimethylpentan-2-yl)amino)pyrazolo[1,5-c]quinazoline-1-carboxylate



(IPA used as solvent in reaction); White solid, Yield: 0.054 g (70%);**^{1}H NMR (δ/ppm):** 9.06 (d, 1H, *J* = 8.2 Hz), 7.69 (d, 1H, *J* = 7.5 Hz), 7.64-7.69 (m, 1H), 7.50 (d, 2H, *J* = 8.2 Hz), 7.34-7.29 (m, 2H), 7.24 (d, 2H, *J* = 8.0 Hz), 6.42 (br s, 1H), 5.63 (q, 1H, *J* = 7.4 Hz), 4.51 (q, 2H, *J* = 7.0 Hz), 2.43 (s, 3H), 1.93 (d, 2H, *J* = 5.7 Hz), 1.83 (d, 3H, *J* = 7.1 Hz), 1.68 (d, 6H, *J* = 9.8 Hz), 1.54 (t, 3H, *J* = 7.15 Hz), 1.02 (s, 9H); **^{13}C{^{1}H} NMR (δ ppm):** (125 MHz, $CDCl_3$)**:** 163.2, 149.1, 144.5, 143.4, 141.3, 140.7, 133.7, 131.1, 129.6,

129.2, 126.5, 126.3, 122.9, 115.1, 109.0, 61.2, 58.7, 55.8, 52.9, 31.7, 31.5, 29.1, 28.7, 21.6, 14.3, 14.2. **HRMS** (EI) calcd for $C_{30}H_{39}N_4O_4S$ ($M+H^+$) 551.2687 found 551.2660

S4. Crystallographic data

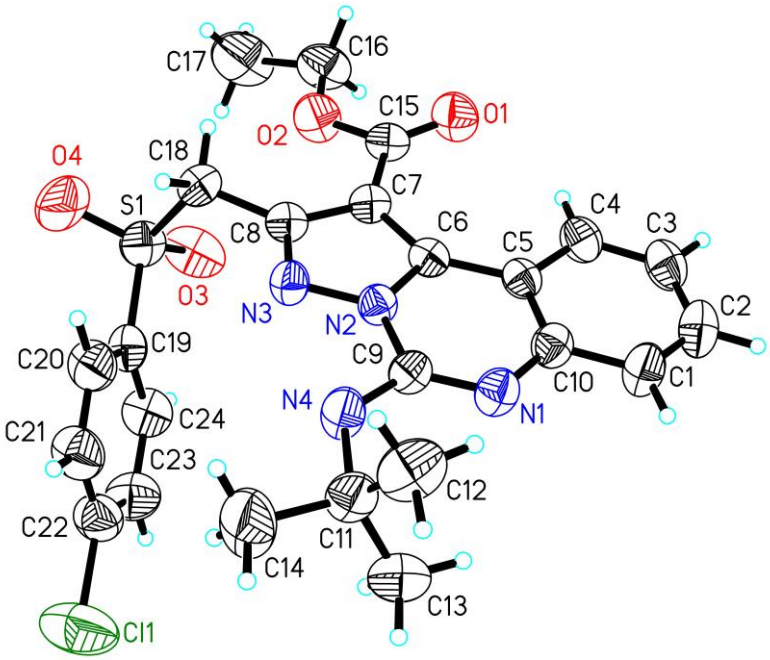


Figure S1. The X-ray crystal structure of compound **5l** showing with ORTEP diagram using 30% ellipsoidal plot

Colorless crystals of **5l** 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 an 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). The 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 1899156 (for **5l**). This data can be obtained free of charge from the Cambridge Crystallographic Data Centers via www.ccdc.cam.ac.uk/data_request/cif.

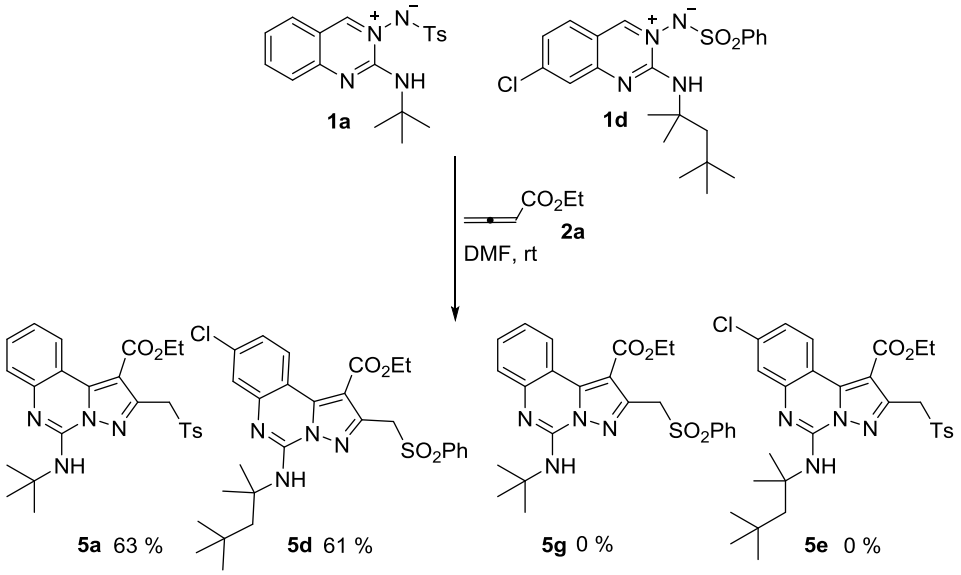
S4.1. Crystal refinement detail

$C_{24}H_{25}ClN_4O_4S$, M = 500.99, monoclinic, space group: P2(1)/c, a= 22.4467 (13), b = 18.9064 (9), c = 1.4637 (5) Å, α = 90.000(0), β = 97.463 (5) , γ = 90.000(0), V = 4823.8 (4) $Å^3$, T = 293(2) K, Z = 8, μ = 0.284 mm−1, F(000) = 2096, D_c = 1.380 Mg m^{-1}, crystal size 0.25 x 0.20 x 0.15 mm, 6708 reflections measured, 3621 unique, R1 = 0.0769 for 7311 Fo > 4sig(Fo) and 0.1147 for all 11318 data and 629 parameters. Unit cell determination and intensity data collection was performed with 85 % completeness at 293 (2) K. Structure solutions by direct methods and refinements by full-matrix least-squares methods on F_2. [CCDC NO: 1899156]

S5 Control Experiment

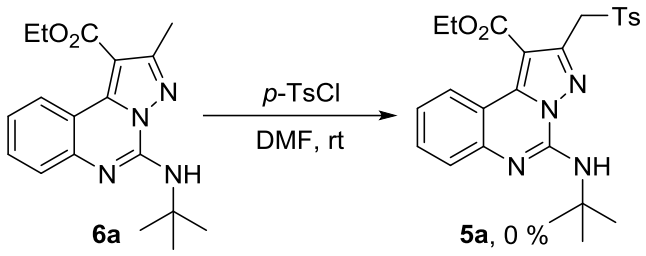
S5.1. Cross-over experiment between 1a and 1d

A solution of **1a** and **1d** (1:1 ratio) in DMF (1.0 mL) was placed in a sealed tube. The allenoate **2a** (2.4 equiv) in DMF (1.0 mL) was then introduced. The reaction mixture was stirred for 16 h at room temperature. The progress of the reaction was periodically monitored by TLC. After the complete conversion of the starting material, the reaction mixture was diluted with water and extracted with EtOAc (3 x 15ml), and the organic layer was dried over anhydrous sodium sulfate. The organic layer was combined and evaporated under the reduced pressure, and the residue was subjected to column chromatography on silica gel (100-200 mesh) using 10:90 EtOAc and hexane as eluent to afford the corresponding products **5a** and **5d** in 63% and 61% yield, respectively. No crossover products **5e** and **5g** have been detected.



S5.2. Intermolecular experiment

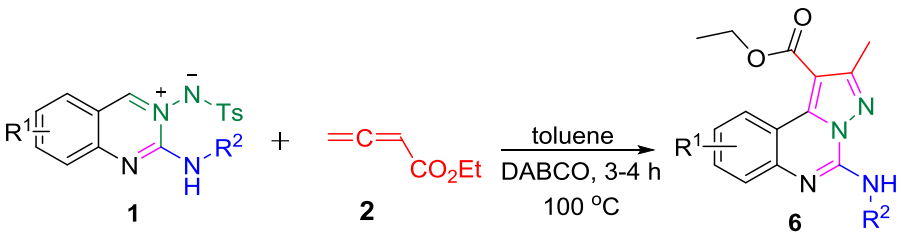
In a reaction vial, **6a** was dissolved in DMF. Tosyl chloride (1 equiv.) was added (as a source of sulfonyl group), and the reaction mixture was stirred for 16 h. Reaction progress was monitored on TLC. After prolonging the reaction, no desired product was obtained, **6a** was recovered as such. The result indicated that an intermolecular sulphonyl step was unlikely.



S5.2.1 Synthesis of compound 6a

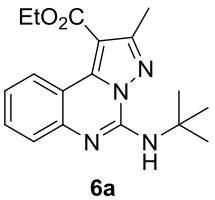
S5.2.2 Experimental procedure for compound 6a

A reaction of azomethine imine **1** (1.0 equiv) and allenoate **2** (1.2 equiv) was carried out in toluene. The reaction mixture was stirred at ambient temperature and monitored by TLC. After complete consumption of starting material on TLC, the reaction mixture was quenched by water, extracted with EtOAc (3 x 15ml), dried over anhydrous sodium sulfate, and concentrated *in vacuo*. The crude residue so obtained was subjected to column chromatography on silica gel (100-200 mesh) using hexane as eluent to give the desired product **6**.



S5.2.3 Analytical data of 6:

Ethyl 5-(*tert*-butylamino)-2-methylpyrazolo[1,5-c]quinazoline-1-carboxylate



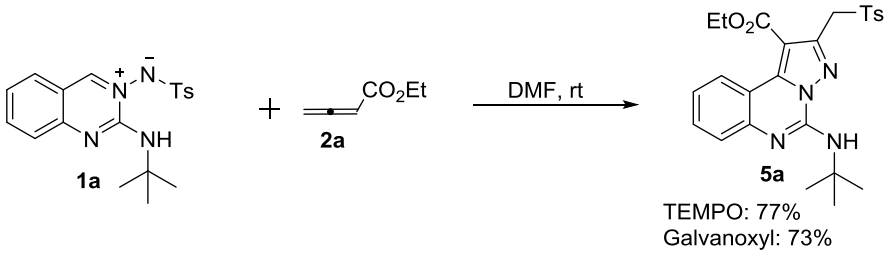
6a

White solid, Yield: (82%); **^{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 NMR (δ/ppm, $CDCl_3$)**: 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 $C_{18}H_{22}N_4O_2$ ($M+H^+$) 327.1816 found 327.1802.

S.5.3. Free Radical experiment

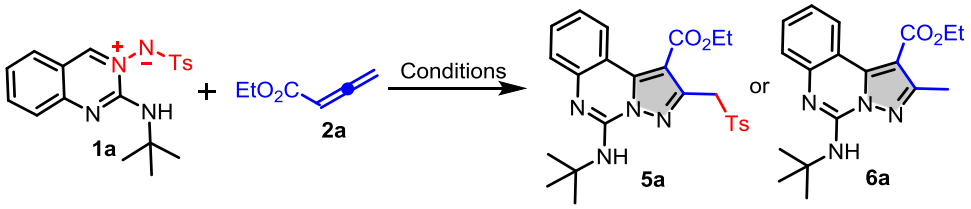
In a reaction vial (10 mL), **1a** and **2a** were dissolved in DMF, and a radical quencher was added. The reaction mixture was stirred at rt for the overnight. The desired product was isolated in good yield after workup and purification by column chromatography, as described section S3.1. The experimental result revealed that [1,3]-sulphonyl migration does not affect by free radical which suggested that no formation of free radicals in reaction.



S5.4. Chemical Kinetic Studies

S5.4.1 General Methods: Chemical kinetic study was performed by monitoring the reaction mixture using ^{1}H NMR (500 MHz) spectroscopy with dibenzyl ether as an internal standard. The spectra were processed and integrated with MestReNova (8.0.2), and the data were processed in Excel (2010). The reported initial rates are the average of three independent experiments.

S5.4.2 General Procedure: The Chemical kinetic study was performed in a 10 ml reaction vial. Azomethine imine **1a** (10 mg, 0.027 mmol) and allenoate **2a (**3.63 mg, 0.032 mmol) were taken and dissolved in solvent (DMF, IPA, and toluene). The reaction was stirred at 70 ^{o}C and quenched at different intervals of time. All reaction solution was evaporated under vacuum. The mixture was then transferred into a standard 5 mm bore NMR tube and subjected to ^{1}H NMR (500 MHz) spectroscopy using dibenzyl ether as the internal standard.



Entry	solvent	Dielectric constant (ε)	Temp (in °C)	Time (h)	Initial Rate of Reaction for the formation of 5a (in $mmolL^{-1}$)	Initial Rate of Reaction for the formation of 6a (in $mmolL^{-1}$)
1.	Toluene	2.38	70	16	0.01	5.06
2.	^{i}PrOH	17.9	70	16	0.813	3.52
3.	DMF	36.7	70	4	8.68	ND

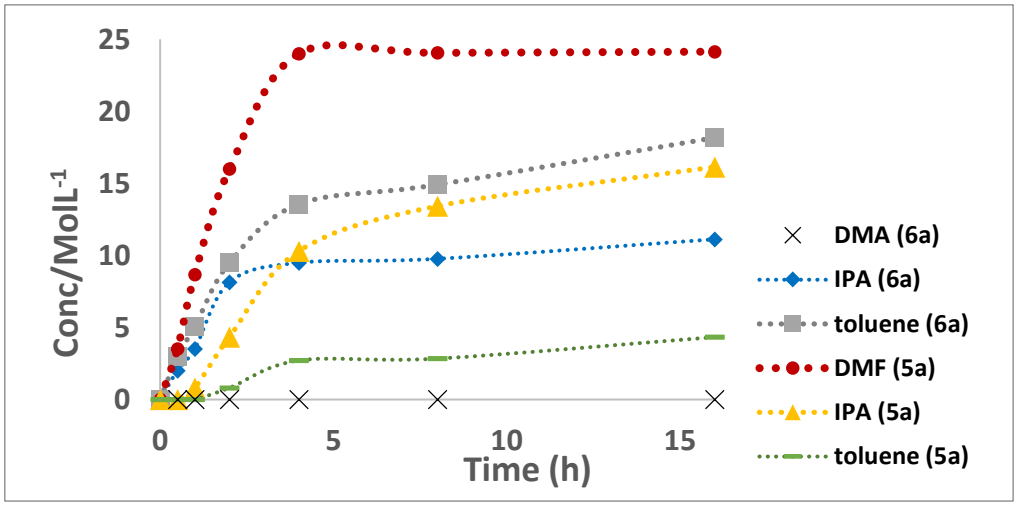
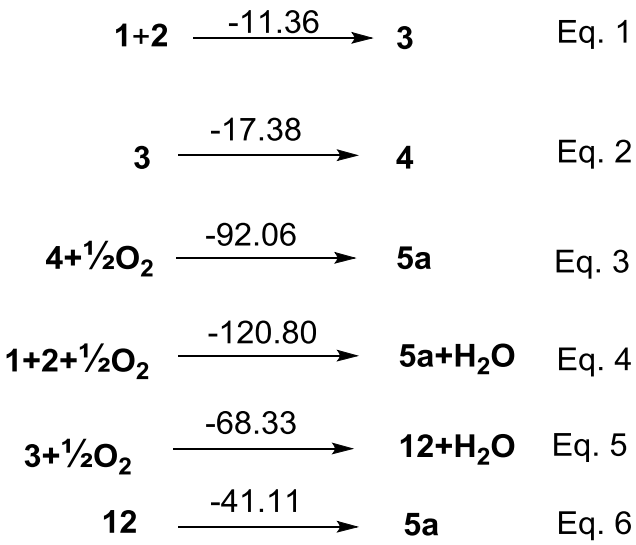


Figure S2 A Plot of concentration *vs*. time

S6. Computational Studies

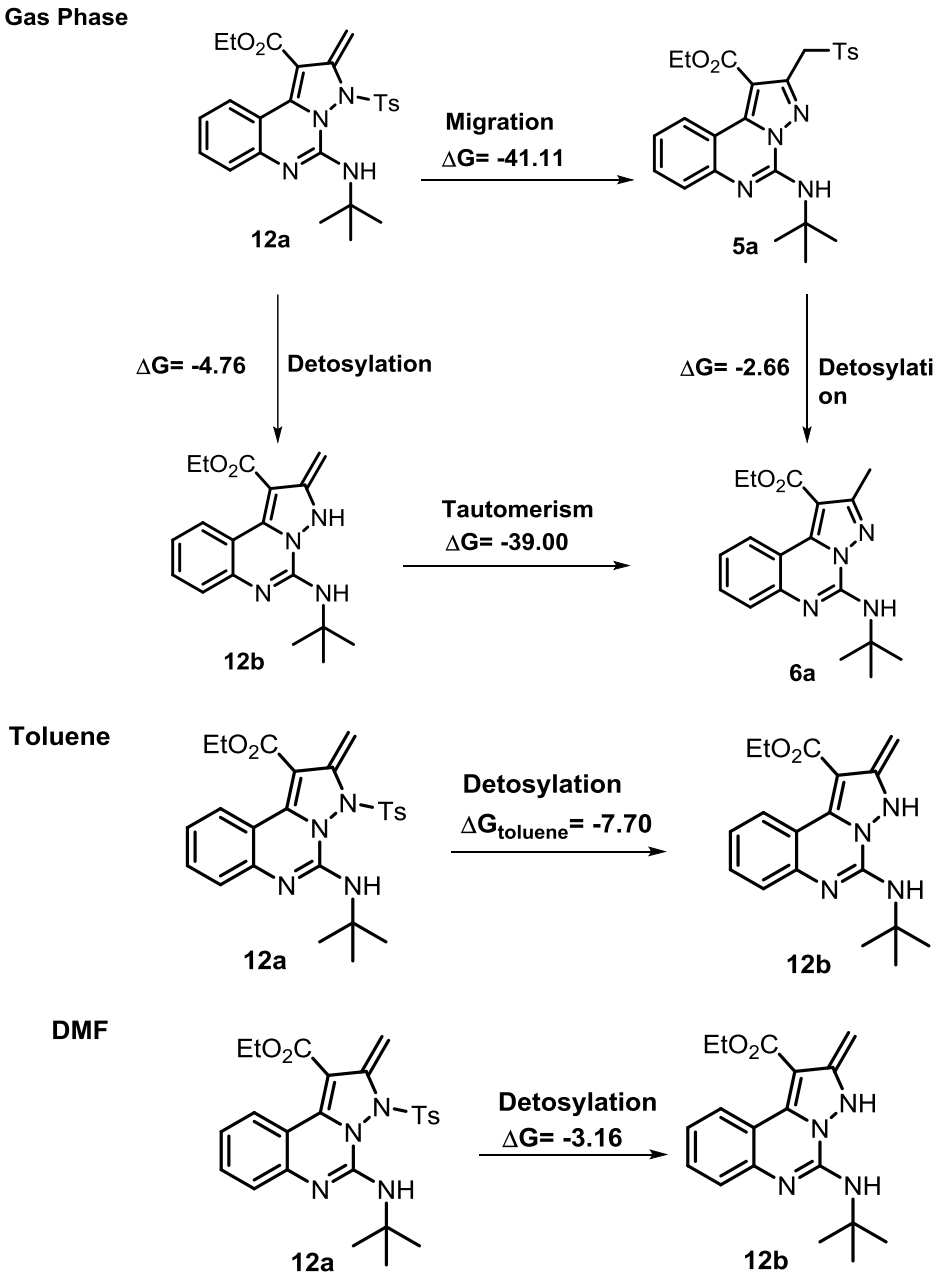


S6.1 DFT studies for the formation of side product 6a.'

Quantum chemical studies reveal that detosylation is a thermodynamically favorable process from all intermediates (**3a**, **5a**, **12a**). This process is exergonic by 20.64, 2.66, and 43.76

kcal/mol for **3a**, **5a**, and **12a** respectively. The detosylation energy values suggest that detosylation is most favorable for **12a** then for **3a** followed by **5a**.

Energetics of detosylation from different intermediates:



All ΔG values are given in kcal/mol.

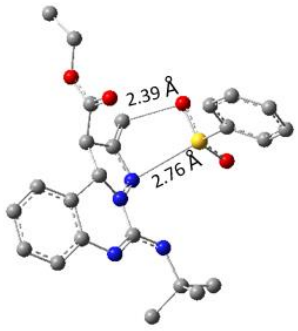
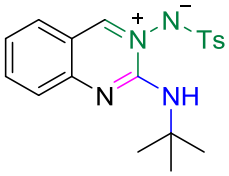
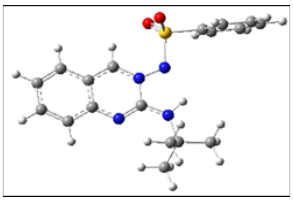


Figure S3: Structure of TS 1.

1a: Absolute Energy= -1465.278286



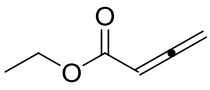


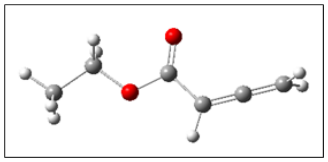
0 1

C	5.46031300	-1.49749000	0.06914200
C	4.75280800	-0.31029200	0.06502700
C	3.34022300	-0.33003600	-0.02454800
C	2.67336100	-1.58700600	-0.10389300
C	3.42009600	-2.79410900	-0.10051900
C	4.79579000	-2.74693100	-0.01492700
H	6.54405300	-1.47546700	0.13759400
H	5.25297200	0.65049500	0.12835300
C	1.26922100	-1.56610600	-0.19960100
H	2.89548500	-3.74335700	-0.16311100
H	5.37334800	-3.66576500	-0.01014500
C	1.33086400	0.81718900	-0.10733300
H	0.68269600	-2.47036300	-0.30584500
N	2.63881100	0.83752200	-0.03547400
N	0.59014900	-0.41168800	-0.18533300
N	0.56028500	1.91621200	-0.12242700
H	-0.43291600	1.70119700	-0.15318800

C	0.99837300	3.33066200	-0.04206600
C	1.73731700	3.59151000	1.28451000
H	1.09354800	3.35187300	2.13716100
H	2.64536600	2.98926800	1.35085800
H	2.01562700	4.64862800	1.35085500
C	-0.29389000	4.16307800	-0.09091800
H	-0.05222300	5.22826900	-0.03905900
H	-0.84364700	3.98483900	-1.02174300
H	-0.94958900	3.92364400	0.75370900
C	1.89106200	3.68358400	-1.24703100
H	1.35778300	3.50354500	-2.18624400
H	2.16542900	4.74297900	-1.20558000
H	2.80613800	3.08830900	-1.24417100
N	-0.76794700	-0.24238500	-0.27810400
S	-1.68025100	-1.55377100	0.21690900
O	-1.43311600	-1.87009100	1.64033600
O	-1.58995200	-2.67986600	-0.74248000
C	-3.29871900	-0.79346000	0.05449600
C	-3.86153600	-0.15372700	1.16016800
C	-3.97357500	-0.88488300	-1.16379100
C	-5.12838400	0.42033000	1.03390700
H	-3.31852400	-0.12399200	2.09875000
C	-5.23938300	-0.30589100	-1.27797700
H	-3.51651600	-1.41054300	-1.99501100
C	-5.81386500	0.34694800	-0.18291900
H	-5.58172600	0.91723200	1.88643100
H	-5.77793200	-0.37071600	-2.21865900
H	-6.80035600	0.79205500	-0.27533100

2a: Absolute Energy= -383.790316

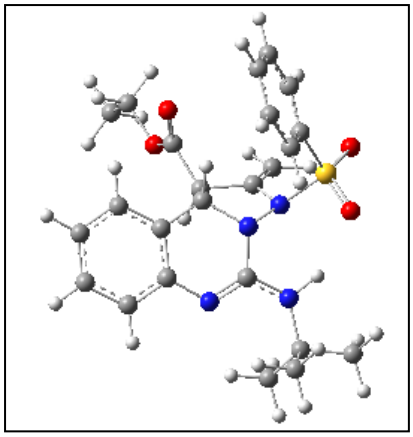




0 1

C	2.52078000	-0.40544300	0.00006900
H	4.31448200	0.11009700	0.93086100
H	4.31481400	0.11071800	-0.92974600
C	3.77485500	-0.04992600	0.00041300
C	1.25685600	-0.77017600	-0.00039100
H	0.98215100	-1.82199500	-0.00075900
C	0.14917500	0.22096200	-0.00026600
O	0.26486500	1.43081500	-0.00012600
O	-1.04398800	-0.42162800	-0.00029500
C	-2.22361100	0.42000100	0.00006000
H	-2.19127000	1.06424700	0.88411800
H	-2.19176100	1.06421700	-0.88404700
C	-3.43643200	-0.49094500	0.00037700
H	-4.34944900	0.11364900	0.00056500
H	-3.44807200	-1.13066900	-0.88730500
H	-3.44765500	-1.13060600	0.88810800

3a Absolute Energy= -1849.086700



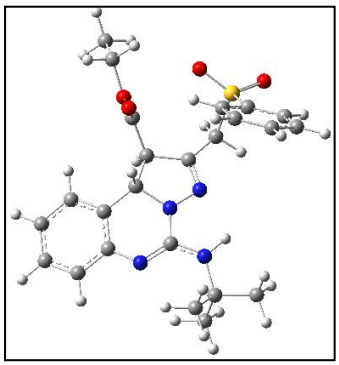
0 1

C	0.47557200	-4.05947800	2.90924500
C	1.45575500	-3.45749200	2.12342800
C	1.15792200	-2.32226900	1.34675500
C	-0.15455600	-1.81092600	1.37865300
C	-1.13027100	-2.41063100	2.17987600
C	-0.82328200	-3.53787600	2.94581500
H	0.72592700	-4.93473500	3.50243800
H	2.46925700	-3.84547800	2.09484400
C	-0.47719200	-0.62549800	0.51236800
H	-2.13174900	-1.98788400	2.20623300
H	-1.58515900	-3.99826000	3.56735100
C	1.96047800	-0.63086300	-0.03620800
N	2.17642400	-1.74881300	0.58763500
N	0.74363000	0.11323200	0.10528300
N	2.89377100	-0.03306000	-0.81535200
H	2.69010500	0.92578200	-1.06604100
C	4.30261900	-0.46228200	-1.00272200
C	5.06075300	-0.45676900	0.33956200
H	5.04127200	0.54294900	0.78682800
H	4.61048700	-1.16372400	1.03891800
H	6.10708300	-0.73934900	0.17873200
C	4.92280100	0.57613700	-1.95389400
H	5.97072900	0.32765400	-2.14465200

H	4.39591000	0.59357100	-2.91425700
H	4.88843200	1.58229700	-1.52034000
C	4.35626600	-1.85497100	-1.65685900
H	3.81797200	-1.84996700	-2.61069600
H	5.39853900	-2.12987600	-1.85208200
H	3.90931400	-2.60803100	-1.00617800
N	0.37732100	0.89420700	-1.02152600
C	-0.71605300	0.25647000	-1.70509500
C	-1.16208700	-0.92864800	-0.84761800
S	0.37923200	2.61550900	-0.67456700
O	1.77519900	2.87493600	-0.30482600
O	-0.23566100	3.25323000	-1.83963700
C	-0.64950200	2.89031000	0.76520400
C	-2.01022400	3.15479500	0.58060800
C	-0.07196000	2.82834400	2.03727700
C	-2.81079800	3.35370000	1.70600600
H	-2.42337500	3.21392600	-0.41989400
C	-0.88837400	3.02782000	3.15159500
H	0.98979300	2.63842800	2.14206100
C	-2.25268300	3.28710900	2.98624600
H	-3.86903700	3.55993000	1.58098200
H	-0.45710200	2.98353400	4.14684400
H	-2.88206100	3.44134600	3.85765200
C	-2.67479100	-1.03148600	-0.74567200
O	-3.35465900	-0.47756300	0.09572500
C	-4.62012600	-1.97548400	-1.74832900
O	-3.17461500	-1.81276500	-1.72076300
H	-4.93498000	-2.40211100	-0.79161300
H	-5.07674600	-0.98581600	-1.84338500
C	-4.95633200	-2.87967700	-2.91789800
H	-6.04010000	-3.02816100	-2.96486100
H	-4.62926500	-2.43897300	-3.86442200

H	-4.47964800	-3.85817500	-2.80799000
C	-1.18168400	0.61741000	-2.90332300
H	-2.00743800	0.07033000	-3.34344000
H	-0.76744800	1.45723400	-3.44493400
H	-0.77285800	-1.85946500	-1.27421300
H	-1.11918700	0.07673200	1.05280100

4a: **Absolute Energy**= -1849.114399



0 1

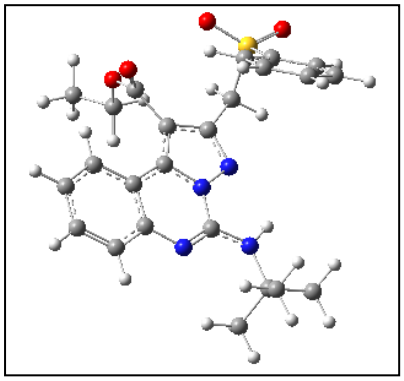
C	-4.22485400	3.93788700	0.33520500
C	-4.40758700	2.55675600	0.33598100
C	-3.30591600	1.68181100	0.30451600
C	-2.00505600	2.24347700	0.28402700
C	-1.83166400	3.62867800	0.28065500
C	-2.93658600	4.48360000	0.30261400
H	-5.09100700	4.59336100	0.35857700
H	-5.40286700	2.12387600	0.35445400
C	-0.86086700	1.26756500	0.36661800
H	-0.82825200	4.04789700	0.27366700
H	-2.79287400	5.55961500	0.30364000
C	-2.58417200	-0.49941900	-0.04222500
N	-3.55629200	0.30578300	0.28387600
N	-1.28884800	-0.02381300	-0.19490900
N	-2.74217100	-1.83388500	-0.25732500

H	-1.90162600	-2.31103100	-0.55313700
C	-4.02315700	-2.56015300	-0.43661700
C	-4.83476000	-2.53498500	0.87213000
H	-4.25691900	-2.98061800	1.68879100
H	-5.09050400	-1.51001600	1.14571100
H	-5.75832900	-3.11112300	0.74846900
C	-3.63362100	-4.00881300	-0.77608700
H	-4.53324700	-4.61563100	-0.91201200
H	-3.05375700	-4.05717800	-1.70565200
H	-3.04164200	-4.45674700	0.03002500
C	-4.83821900	-1.95405400	-1.59568500
H	-4.26760600	-1.99201400	-2.53015400
H	-5.76529800	-2.52003800	-1.73745700
H	-5.09497200	-0.91429600	-1.38375300
N	-0.30210600	-0.66629400	-0.86515700
C	0.71330900	0.12895600	-0.99320500
C	0.44075100	1.53103600	-0.42756900
C	1.88375500	-0.30459500	-1.80036500
H	1.61963800	-1.15902400	-2.42620400
H	2.27796800	0.50227000	-2.42764800
S	3.40737400	-0.85174600	-0.88733500
O	4.25372200	-1.50134200	-1.90550200
O	3.90925600	0.30300500	-0.11861200
C	2.85582100	-2.10341700	0.28181600
C	2.43101600	-1.70713600	1.55304800
C	2.87079400	-3.44446600	-0.10920500
C	2.00419800	-2.68889200	2.45009700
H	2.44353900	-0.65877200	1.83391100
C	2.44322400	-4.41408700	0.80017300
H	3.23194500	-3.71701100	-1.09522200
C	2.00856700	-4.03576900	2.07443100
H	1.67329200	-2.39964800	3.44282400

H	2.45791000	-5.46205500	0.51654100
H	1.67902200	-4.79364100	2.77921700
C	1.54579000	2.09452100	0.46523800
O	1.67906500	1.81504300	1.64017700
C	3.48403600	3.47299300	0.49530800
O	2.32461500	2.94288900	-0.21419400
H	3.12378300	4.02419700	1.36880100
H	4.07967600	2.62291400	0.83359400
C	4.24215300	4.35900400	-0.47256200
H	5.11829100	4.77977600	0.03164200
H	4.58891900	3.78527900	-1.33683600
H	3.61955800	5.18668800	-0.82642600
H	-0.57396300	1.10466100	1.41869000
H	0.29225700	2.22395700	-1.26704600

5a:

Absolute Energy= -1847.971333



0 1

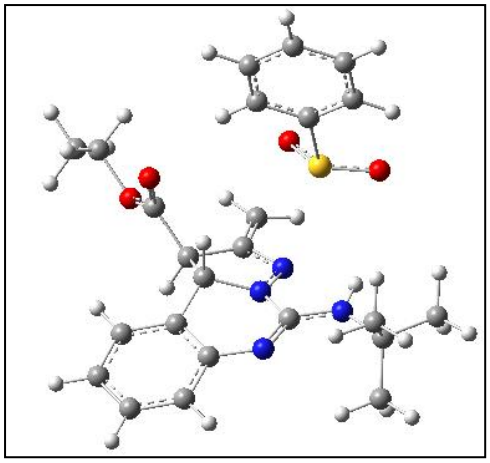
C	-3.51621600	3.42528200	2.15116000
C	-3.86770200	2.25630500	1.49650100
C	-2.89732000	1.49673100	0.80698500
C	-1.54756900	1.95898400	0.79398200

C	-1.20740300	3.14654700	1.47658800
C	-2.18130300	3.87254400	2.14433400
H	-4.27504100	3.99686800	2.67777900
H	-4.89023900	1.89321500	1.49611200
C	-0.60984200	1.14565200	0.05969900
H	-0.17631000	3.47703900	1.50154300
H	-1.90822400	4.78194300	2.67021700
C	-2.44679300	-0.38985800	-0.46426800
N	-3.31341500	0.33754500	0.17892600
N	-1.09954700	0.00105000	-0.52968900
N	-2.72502900	-1.54176300	-1.11374500
H	-1.92448300	-1.97934300	-1.55187100
C	-4.04035400	-2.21933400	-1.21833600
C	-4.55254200	-2.61495600	0.17979400
H	-3.83339500	-3.27099200	0.68153200
H	-4.71133800	-1.73071400	0.80006100
H	-5.50244200	-3.15229600	0.08880400
C	-3.78807600	-3.48235800	-2.05823400
H	-4.71987200	-4.04147100	-2.17956500
H	-3.41624200	-3.22592700	-3.05682600
H	-3.06056500	-4.14223500	-1.57176300
C	-5.05582200	-1.30953800	-1.93562900
H	-4.69433800	-1.04185900	-2.93409400
H	-6.01079700	-1.83427600	-2.04543200
H	-5.22605100	-0.39313300	-1.36735900
N	-0.15747800	-0.70408500	-1.19868200
C	0.96389600	0.01219400	-1.06479100
C	0.74798800	1.18769200	-0.29192000
C	2.20175000	-0.55848700	-1.67335000
H	1.94768400	-1.45367000	-2.24293500
H	2.73664600	0.14101200	-2.32234800
S	3.53406300	-1.06505800	-0.49610200

O	4.38918100	-1.99799800	-1.25343700
O	4.08366600	0.17534100	0.07694900
C	2.71617800	-1.97929300	0.82081500
C	2.27628600	-1.28840400	1.95364800
C	2.55295200	-3.36042900	0.68615000
C	1.64613300	-2.00887800	2.97114300
H	2.43309400	-0.21769300	2.04005500
C	1.92262000	-4.06593000	1.71287600
H	2.93372600	-3.86788100	-0.19391000
C	1.46833100	-3.39044100	2.85032700
H	1.30095800	-1.48860100	3.85932600
H	1.79567500	-5.14102000	1.62862300
H	0.98122100	-3.94386300	3.64799000
C	1.72825900	2.19979000	0.20894600
O	1.95830900	2.33195400	1.39309100
C	1.95090500	3.09410900	-2.06611100
O	2.33795800	3.01896700	-0.67398800
H	2.40350300	2.25767300	-2.60845200
H	0.86260000	3.01910400	-2.15115500
C	2.46193200	4.41815000	-2.60551800
H	2.21098600	4.50491800	-3.66799000
H	2.00785800	5.25696400	-2.07032400
H	3.54802400	4.48539400	-2.49774200

TS 1:

Absolute Energy= -1849.068069



0 1

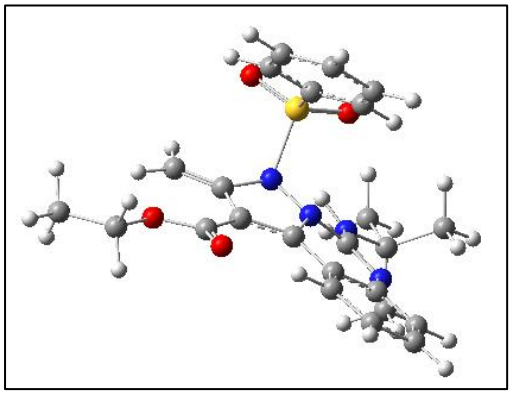
C	-2.92272700	4.45579000	1.81193700
C	-3.36724500	3.19135400	1.42998800
C	-2.48213400	2.26171400	0.85673600
C	-1.12598800	2.63815500	0.68760100
C	-0.68824100	3.90290700	1.07862500
C	-1.58360400	4.82030800	1.63636600
H	-3.62352100	5.16078500	2.24976000
H	-4.40392400	2.89813800	1.56076000
C	-0.21482600	1.56164400	0.16548100
H	0.35726000	4.17622100	0.95958200
H	-1.23676900	5.80409000	1.93647300
C	-2.28711700	0.24962800	-0.30547100
N	-2.98484600	1.00915800	0.48888300
N	-0.99996800	0.66015200	-0.70179600
N	-2.69365400	-0.92536600	-0.83245000
H	-2.00177400	-1.42058300	-1.38276400
C	-4.02781100	-1.56176100	-0.68421200
C	-4.29080900	-1.90640700	0.79425500
H	-3.51346900	-2.57617900	1.17633200
H	-4.30784000	-1.00307900	1.40740800
H	-5.25724600	-2.41294200	0.88971500

C	-3.96589500	-2.85082100	-1.52029700
H	-4.91734400	-3.38462700	-1.44594300
H	-3.78326100	-2.62831100	-2.57743400
H	-3.17217600	-3.51731300	-1.16598100
C	-5.12512800	-0.63166700	-1.23428500
H	-4.93801000	-0.39685800	-2.28740100
H	-6.09872600	-1.12772700	-1.16162900
H	-5.16741800	0.30080800	-0.66809600
N	-0.31395800	0.10129900	-1.67410000
C	0.86331700	0.77166200	-1.80394300
C	0.97421500	1.89370600	-0.75464100
S	1.09555100	-2.16242700	-0.95173900
O	0.44413400	-3.27754600	-1.72650000
O	2.43442300	-1.64064200	-1.48986800
C	1.58411000	-2.89147300	0.65948800
C	2.30798900	-2.12524700	1.57507400
C	1.16184100	-4.18637500	0.95789100
C	2.62854200	-2.68371100	2.81461100
H	2.62030000	-1.11563100	1.32879500
C	1.49756400	-4.73640400	2.19934400
H	0.59895800	-4.74639700	0.21849400
C	2.22637300	-3.98707000	3.12678300
H	3.19432800	-2.09960000	3.53477800
H	1.18727800	-5.74957500	2.43905500
H	2.47983100	-4.41578600	4.09213300
C	2.31100600	1.87957700	-0.02293000
O	2.50119500	1.37821400	1.06640300
C	4.60865000	2.48603400	-0.20063500
O	3.25877600	2.48655200	-0.75426700
H	4.57476900	2.97251700	0.77814900
H	4.91574400	1.44663900	-0.05571800
C	5.50406700	3.22075000	-1.17794700

H	6.52614700	3.24348600	-0.78639400
H	5.52276600	2.72033700	-2.15059200
H	5.16881500	4.25208700	-1.32266100
C	1.79272700	0.32149100	-2.69574900
H	2.76592800	0.78796600	-2.77282000
H	1.52883900	-0.43805400	-3.41752300
H	0.85373300	2.86577900	-1.24695400
H	0.16346900	0.95061000	1.00396500

12:

Absolute Energy:-1847.905818



0 1

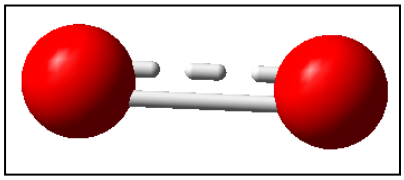
C	-1.15621400	4.63214300	1.34078900
C	-2.03356500	3.65870100	0.89082100
C	-1.55575300	2.44634300	0.34921900
C	-0.14155300	2.24004000	0.26032200
C	0.73227800	3.25226200	0.71811000
C	0.23191200	4.42902100	1.25545900
H	-1.54591300	5.55633200	1.75885000
H	-3.10839000	3.79884400	0.93949800
C	0.28226000	0.97321000	-0.30600500
H	1.79780400	3.08668200	0.64843600
H	0.91937000	5.19041900	1.61054900
C	-2.09709500	0.37080200	-0.50667500

N	-2.49491800	1.54749600	-0.11076000
N	-0.74211100	0.01238000	-0.38356000
N	-2.91728200	-0.55567500	-1.04424800
H	-2.49726000	-1.46255700	-1.18879800
C	-4.40372100	-0.51316100	-1.07970000
C	-4.97869400	-0.39886600	0.34507000
H	-4.63479600	-1.23294500	0.96498300
H	-4.67067900	0.53833700	0.81287900
H	-6.07299900	-0.42479700	0.30560300
C	-4.83210400	-1.85020900	-1.70850200
H	-5.92226700	-1.89306300	-1.78282000
H	-4.41903200	-1.96144000	-2.71729800
H	-4.50196200	-2.69828800	-1.09791500
C	-4.88169400	0.65264800	-1.96413700
H	-4.47090700	0.55989200	-2.97497600
H	-5.97468200	0.63719300	-2.03401700
H	-4.56993700	1.61167400	-1.54736100
N	-0.25437700	-1.20918600	-0.89274800
C	1.06431700	-0.89665500	-1.41951200
C	1.42617500	0.42745700	-0.88336200
S	-0.23579500	-2.47347400	0.43375100
O	-1.62780700	-2.48034100	0.89718500
O	0.37509200	-3.64674000	-0.18970800
C	0.81795700	-1.88295600	1.75356100
C	2.17247800	-2.23275500	1.74059100
C	0.26755100	-1.07960600	2.75730000
C	2.99400700	-1.75357300	2.76136600
H	2.55941700	-2.87308800	0.95633000
C	1.10569900	-0.60712800	3.76809700
H	-0.79089900	-0.84575900	2.75021700
C	2.46360900	-0.93998200	3.76776700
H	4.04676200	-2.01829200	2.77158400

H	0.69633100	0.01822100	4.55521600
H	3.10988800	-0.56824400	4.55723600
C	2.74554900	1.04697700	-1.00482400
O	3.15464700	2.02531000	-0.39238600
C	4.86282800	0.94163500	-2.08987800
O	3.53289500	0.39966200	-1.90314200
H	4.77411400	1.98332700	-2.41244100
H	5.38346000	0.93460700	-1.12737100
C	5.56623400	0.08440200	-3.12577900
H	6.57456400	0.47448900	-3.29977600
H	5.65537600	-0.95283100	-2.78794500
H	5.02642500	0.09451200	-4.07758400
C	1.67310900	-1.77507200	-2.23504100
H	2.67468400	-1.59328700	-2.59203600
H	1.16303300	-2.68664000	-2.51777400

Oxygen

Absolute Energy= -150.281280

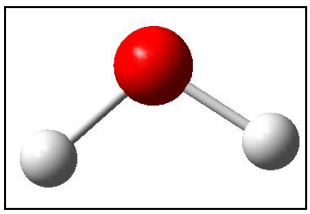


0 1

O	0.00000000	0.00000000	0.60755900
O	0.00000000	0.00000000	-0.60755900

Water

Absolute Energy= -76.430409

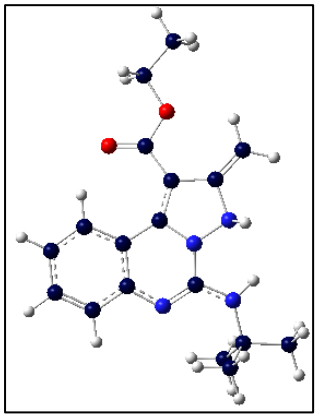


0 1

O	0.00000000	0.00000000	0.11650800
H	0.00000000	0.76943900	-0.46603000
H	0.00000000	-0.76943900	-0.46603000

12a_toluene

Absolute Energy: -1068.355013



0 1

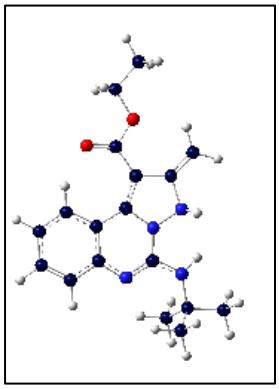
C	0.90419600	4.33707400	-0.03561400
C	1.78185800	3.26697600	-0.02584400
C	1.30726600	1.93633700	-0.05656700
C	-0.10725700	1.70350900	-0.08788400
C	-0.97968100	2.81675400	-0.09112000
C	-0.48365600	4.11083000	-0.06953000
H	1.29026000	5.35242100	-0.01449000
H	2.85614800	3.41674100	0.00424400
C	-0.53821600	0.31640200	-0.15036300
H	-2.04451800	2.63663500	-0.10216900
H	-1.17391700	4.94863900	-0.07591900
C	1.84401100	-0.29879500	-0.12044200
N	2.25535500	0.93650500	-0.02486700

N	0.50325800	-0.58373100	-0.31258500
N	2.66714500	-1.38382700	-0.10874800
H	2.19023000	-2.24863400	0.12079100
C	4.13090500	-1.37166700	0.16303400
C	4.86298800	-0.58956500	-0.94137900
H	4.65027200	-1.02385300	-1.92383600
H	4.55888900	0.45820700	-0.94747900
H	5.94329800	-0.63984200	-0.77024300
C	4.56330500	-2.84720400	0.12080300
H	5.63841200	-2.92484100	0.30429900
H	4.05051400	-3.43448300	0.89197800
H	4.35049800	-3.29183300	-0.85733500
C	4.43334000	-0.77935900	1.55342400
H	3.91729100	-1.34716900	2.33539700
H	5.50930700	-0.82702500	1.75219400
H	4.11547000	0.26351200	1.61042700
N	0.04111500	-1.91752800	-0.36135200
C	-1.39712700	-1.84544000	-0.23024700
C	-1.73517800	-0.41700900	-0.10263200
C	-3.08694600	0.09640900	0.09151500
O	-3.41483300	1.26473200	0.28728500
C	-5.39475900	-0.48378200	0.25392900
O	-4.01929100	-0.88847900	0.04716700
H	-5.47270400	0.01346600	1.22520100
H	-5.66680100	0.24208700	-0.51816100
C	-6.25468000	-1.73219600	0.18553100
H	-7.30435700	-1.46005100	0.33731300
H	-6.16526400	-2.22032000	-0.78988800
H	-5.97113900	-2.44944600	0.96186600
C	-2.11418800	-2.98650000	-0.25213100
H	-1.60080100	-3.94049300	-0.31730600
H	-3.19047300	-2.97627200	-0.21393400

H	0.30718700	-2.31405800	-1.26259400

12a_dmf

Absolute Energy: -1068.348876



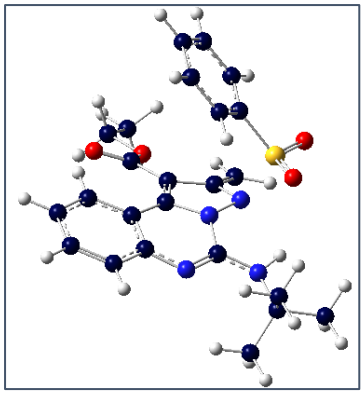
0 1

C	0.90752900	4.33530100	0.00500100
C	1.78397700	3.26399900	0.00219800
C	1.30754200	1.93601500	-0.04903500
C	-0.10698900	1.70479700	-0.09261700
C	-0.97825100	2.81858500	-0.08103900
C	-0.47949000	4.11116200	-0.03657900
H	1.29488500	5.34981100	0.04218400
H	2.85847300	3.40968500	0.03964500
C	-0.53995900	0.31813600	-0.17041900
H	-2.04339200	2.63973300	-0.10386400
H	-1.16916900	4.94949800	-0.03275700
C	1.84330000	-0.29733900	-0.12905600
N	2.25594000	0.93420500	-0.02023700
N	0.50502100	-0.58172800	-0.33321300
N	2.66618400	-1.38639900	-0.12273900
H	2.18309000	-2.24680400	0.11113700
C	4.12550500	-1.37211200	0.16448100
C	4.86536100	-0.58214700	-0.92928300
H	4.66508000	-1.01400600	-1.91544500

H	4.55336900	0.46330200	-0.93458500
H	5.94438600	-0.62567600	-0.74753100
C	4.56265700	-2.84627300	0.11946000
H	5.63665500	-2.92298500	0.31052900
H	4.04631600	-3.43866200	0.88478500
H	4.35813900	-3.28779700	-0.86192400
C	4.41475900	-0.78481100	1.56013600
H	3.89252500	-1.35597400	2.33581300
H	5.48889900	-0.83101400	1.76970500
H	4.09377100	0.25700300	1.61726600
N	0.04539000	-1.91776600	-0.38754300
C	-1.39355700	-1.84661400	-0.23005700
C	-1.73412100	-0.41702600	-0.12259200
C	-3.09055500	0.09813400	0.04252300
O	-3.43028400	1.27240800	0.14477400
C	-5.38923500	-0.48211200	0.25315600
O	-4.01466500	-0.89738500	0.07951800
H	-5.47264900	0.07694600	1.19015900
H	-5.65866400	0.19532200	-0.56288300
C	-6.24765300	-1.73391400	0.26025500
H	-7.29889300	-1.45677800	0.39237200
H	-6.15391500	-2.28154500	-0.68265600
H	-5.96381100	-2.40177100	1.07942500
C	-2.10447200	-2.98987400	-0.22201200
H	-1.58749600	-3.94266200	-0.27340700
H	-3.17999500	-2.98378200	-0.16857600
H	0.28616200	-2.29363900	-1.30474400

12b_toluene

Absolute Energy: -1847.913482



0 1

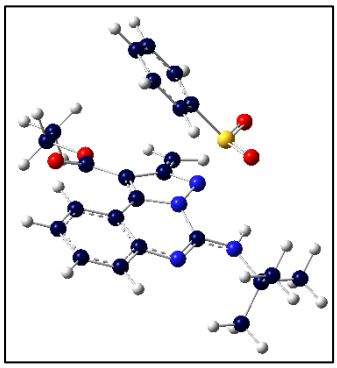
C	-1.19530900	4.61869600	1.36866900
C	-2.06840700	3.63762600	0.92602500
C	-1.58579700	2.42948800	0.37803500
C	-0.17050100	2.23645800	0.27470400
C	0.69846300	3.25596200	0.72543500
C	0.19406300	4.42812800	1.26959900
H	-1.58917000	5.53851900	1.79210400
H	-3.14362700	3.77020100	0.98706900
C	0.25895800	0.97336800	-0.29532800
H	1.76446600	3.09910900	0.64584800
H	0.87799400	5.19482000	1.61993900
C	-2.11565200	0.34826300	-0.47272700
N	-2.52108800	1.52319400	-0.07558200
N	-0.75637300	0.00206200	-0.35431200
N	-2.92808000	-0.58567300	-1.00432500
H	-2.49376200	-1.47900700	-1.18674200
C	-4.41370400	-0.54607300	-1.07827600
C	-5.02403200	-0.42506900	0.33075900
H	-4.70155300	-1.25918900	0.96191900
H	-4.72441100	0.51167100	0.80479200
H	-6.11677900	-0.44639000	0.26188000
C	-4.82512000	-1.88639300	-1.71108200
H	-5.91305600	-1.92994400	-1.81115400

H	-4.38815200	-2.00180000	-2.70925100
H	-4.50913600	-2.73136100	-1.08910500
C	-4.87198500	0.61477300	-1.97987600
H	-4.43686700	0.51811800	-2.98009900
H	-5.96274900	0.59627900	-2.07588000
H	-4.57339200	1.57667100	-1.55985900
N	-0.26327200	-1.21640900	-0.86475300
C	1.04283500	-0.89117500	-1.41576700
C	1.39952700	0.43853600	-0.88947800
S	-0.20307800	-2.46785400	0.47341000
O	-1.58276700	-2.48153800	0.97387200
O	0.38817500	-3.64692800	-0.16280900
C	0.88607000	-1.87025400	1.75876200
C	2.24045900	-2.21928500	1.71083800
C	0.36055600	-1.06308900	2.77341800
C	3.08757000	-1.73644700	2.70885800
H	2.61042300	-2.86139700	0.92010300
C	1.22445600	-0.58781200	3.76098100
H	-0.69717000	-0.82734000	2.79462600
C	2.58229300	-0.92053600	3.72661200
H	4.14007300	-2.00108900	2.69271800
H	0.83483400	0.03869300	4.55691500
H	3.24813600	-0.54736400	4.49871500
C	2.70997200	1.07104300	-1.03926800
O	3.11894900	2.05726700	-0.43589200
C	4.80980900	0.97516700	-2.16847900
O	3.48302900	0.43020000	-1.94958700
H	4.70993400	2.01288800	-2.49933400
H	5.34921700	0.97488300	-1.21676500
C	5.49402400	0.11155600	-3.21115300
H	6.49722100	0.50431700	-3.40617600
H	5.59328200	-0.92246200	-2.86666700

H	4.93660700	0.11411400	-4.15274500
C	1.64521700	-1.76518800	-2.24102000
H	2.63890900	-1.57665600	-2.61632500
H	1.13797200	-2.68130500	-2.51439500

12b_dfm

Absolute Energy: -1847.921752



0 1

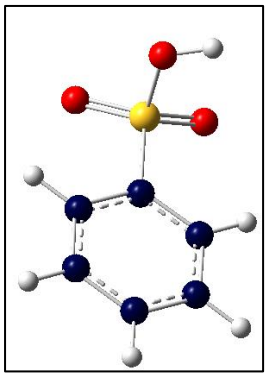
C	-1.31682100	4.57460300	1.50118900
C	-2.17433500	3.57536500	1.06739700
C	-1.67478900	2.38812500	0.48844800
C	-0.25741100	2.23598400	0.34604200
C	0.59479900	3.27340300	0.78792500
C	0.07452300	4.42454000	1.36201000
H	-1.72426200	5.47639100	1.94927400
H	-3.25042800	3.68049800	1.16094600
C	0.19139000	0.99195200	-0.24983600
H	1.66221400	3.14540800	0.68020400
H	0.74587300	5.20465900	1.70674600
C	-2.16840700	0.30692400	-0.38557600
N	-2.59706700	1.46587400	0.03865900
N	-0.79879300	-0.00451600	-0.29143200
N	-2.95994400	-0.64245600	-0.91487600
H	-2.48604400	-1.48383900	-1.21250600

C	-4.44215000	-0.62208600	-1.04863700
C	-5.10644500	-0.49359300	0.33438800
H	-4.79833500	-1.31702700	0.98665600
H	-4.83974000	0.45161800	0.81093000
H	-6.19481600	-0.53235400	0.22268000
C	-4.81400600	-1.97462600	-1.67946000
H	-5.89661600	-2.03049500	-1.82031700
H	-4.33840600	-2.09741600	-2.65889800
H	-4.51216000	-2.80762500	-1.03516900
C	-4.88056000	0.52256100	-1.98108000
H	-4.41278500	0.41564300	-2.96535400
H	-5.96722300	0.49408300	-2.11202200
H	-4.60471100	1.49335400	-1.56523000
N	-0.28904100	-1.20492500	-0.82366500
C	0.99156500	-0.84008300	-1.41178900
C	1.32793300	0.49397800	-0.88241600
S	-0.14453500	-2.45663400	0.50828500
O	-1.47449400	-2.44883600	1.13091900
O	0.35390100	-3.64850100	-0.18658800
C	1.06990800	-1.90039300	1.69383000
C	2.40650600	-2.27959300	1.52120600
C	0.65474400	-1.09518100	2.76095800
C	3.34951200	-1.83029700	2.44660400
H	2.69399000	-2.91840100	0.69470300
C	1.61337600	-0.65621600	3.67522300
H	-0.38988300	-0.83210300	2.87997400
C	2.95505700	-1.01949600	3.51648900
H	4.38954000	-2.11869900	2.33371600
H	1.30997700	-0.03533500	4.51185200
H	3.69458600	-0.67542800	4.23276700
C	2.61673400	1.16115000	-1.06519500
O	3.02632600	2.13682200	-0.44065400

C	4.67415900	1.14264700	-2.28301600
O	3.36078100	0.57297700	-2.02752000
H	4.54631600	2.18646800	-2.58286200
H	5.24917100	1.12035900	-1.35321200
C	5.32751900	0.31702600	-3.37416300
H	6.31710800	0.73013100	-3.59361400
H	5.45320200	-0.72407600	-3.06169100
H	4.73560700	0.33919900	-4.29416100
C	1.59353200	-1.69078500	-2.26134700
H	2.57135800	-1.47447200	-2.66295700
H	1.10282700	-2.61739900	-2.53022200

TsOH_toluene:

Absolute Energy: -856.001157



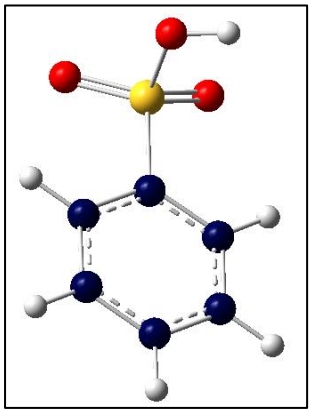
0 1

C	2.38713100	-1.20967100	0.04313200
C	3.08052300	0.00513200	0.05611900
C	2.38501500	1.21670600	-0.00065000
C	0.99001200	1.22275700	-0.06472800
C	0.31494500	-0.00035900	-0.07284800
C	0.99313900	-1.22137200	-0.02344100
H	2.92982100	-2.14888800	0.07931600

H	2.92565100	2.15783800	-0.00075500
H	0.43731600	2.15376800	-0.12440300
H	0.44220200	-2.15492700	-0.04631500
S	-1.47276800	-0.00726300	-0.13715900
O	-1.94473500	1.29858100	-0.60654100
O	-1.92547200	-1.25196500	-0.74702900
O	-1.90208100	-0.13803400	1.44755700
H	-2.06212500	0.75352300	1.80502200
H	4.16515200	0.00707700	0.10428000

TsOH_dmf

Absolute Energy: -856.008332



0 1

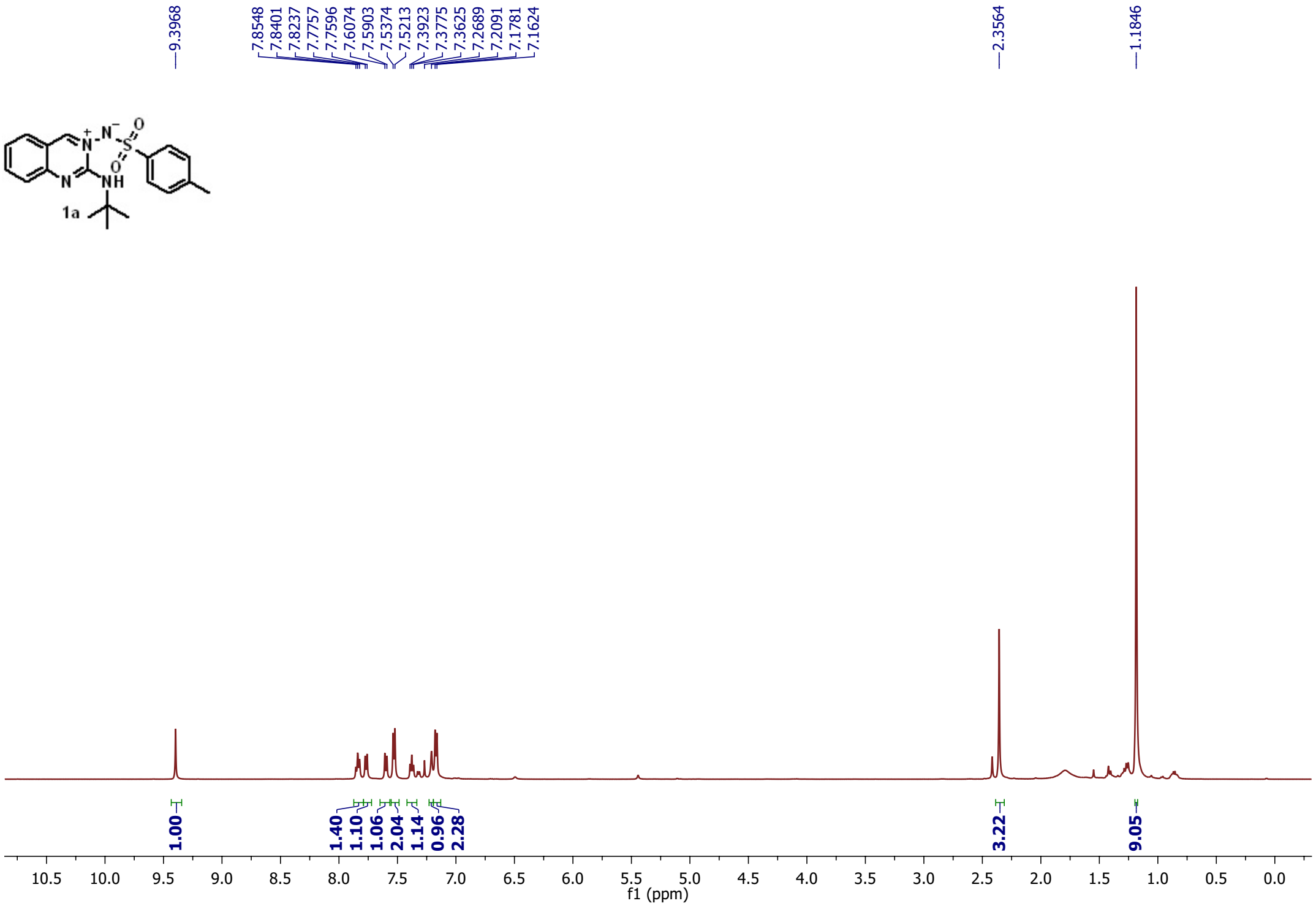
C	2.38365900	-1.21516600	0.03166800
C	3.07999100	-0.00164800	0.05273300
C	2.38803000	1.21260700	0.00513200
C	0.99304200	1.22356300	-0.05921600
C	0.31554400	0.00125400	-0.07681500
C	0.98958100	-1.22324800	-0.03348600
H	2.92366100	-2.15587500	0.06284600
H	2.93054300	2.15232600	0.01566000
H	0.44496200	2.15785800	-0.10333400
H	0.43921000	-2.15702500	-0.05708000

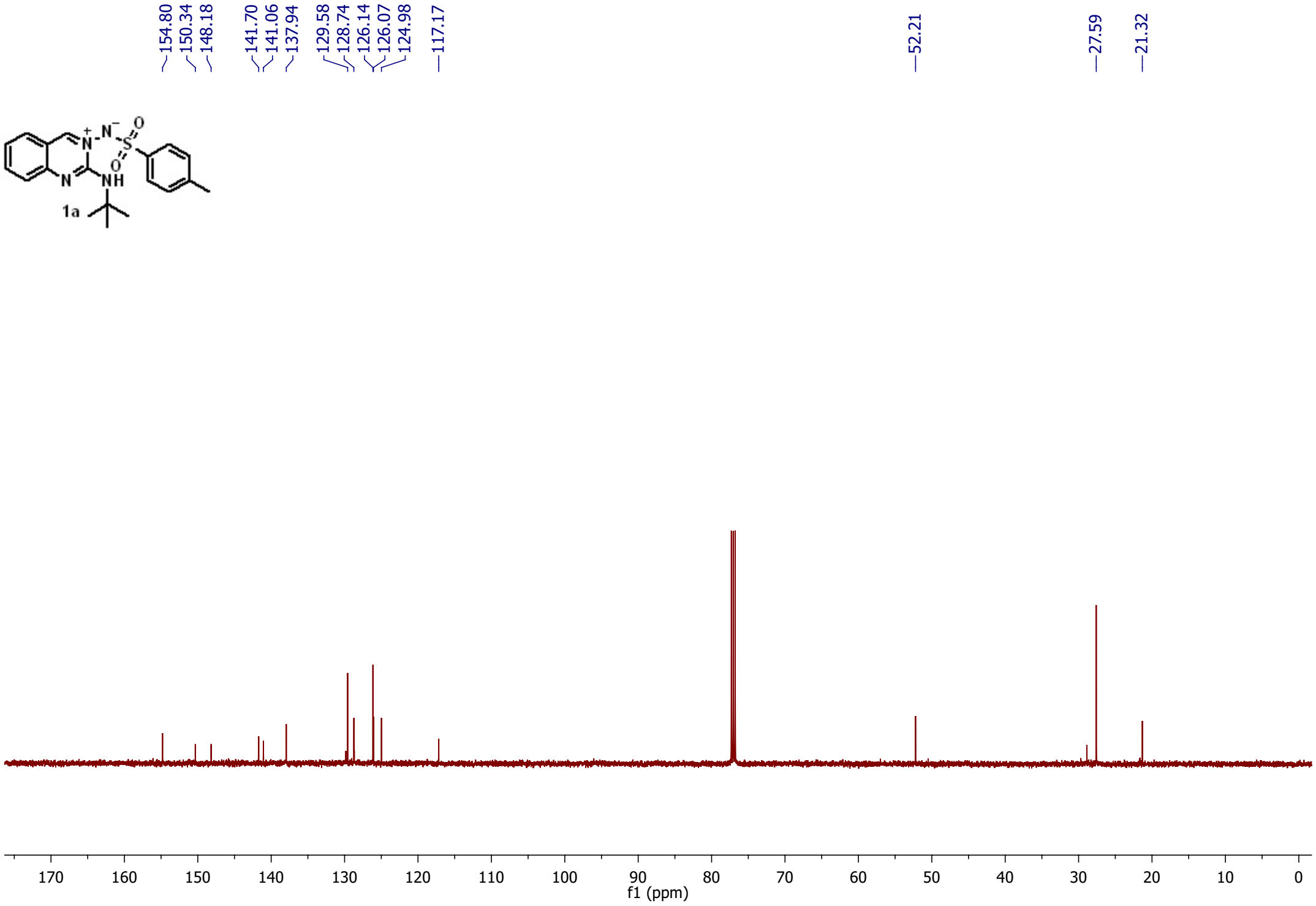
S	-1.46994000	0.00095300	-0.13105600
O	-1.94349600	1.30275000	-0.61225100
O	-1.94465900	-1.23836700	-0.74513300
O	-1.91463200	-0.15255200	1.44070600
H	-1.86045700	0.71161900	1.88965200
H	4.16434800	-0.00297900	0.10247500

S7 References

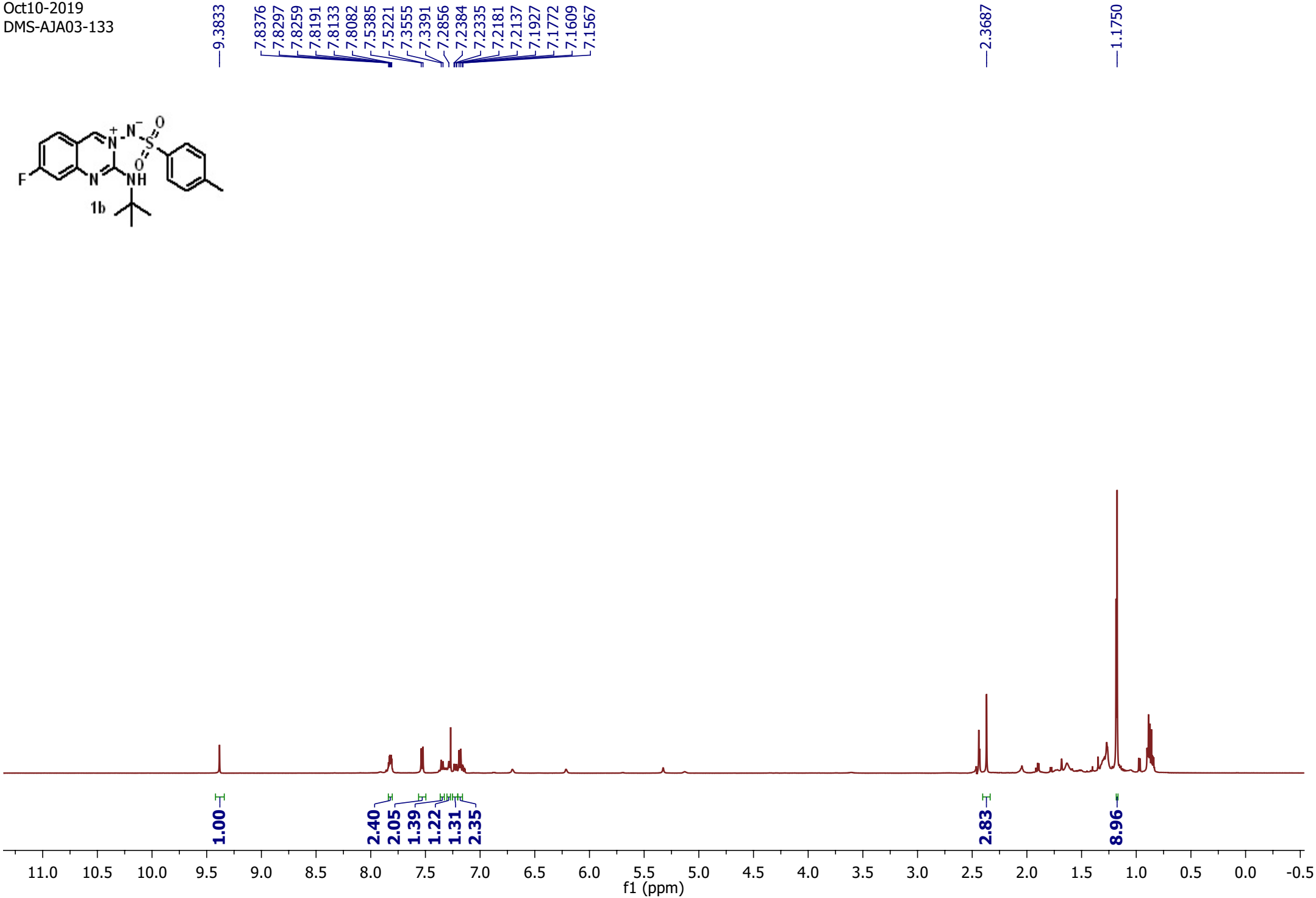
1. Z. Chen, L. Gao, S. Ye, Q. Ding, J. Wu, *Chem. Commun*., **2012**, *48*, 3975–3977

S8 Copy of ^{1}H and ^{13}C spectra

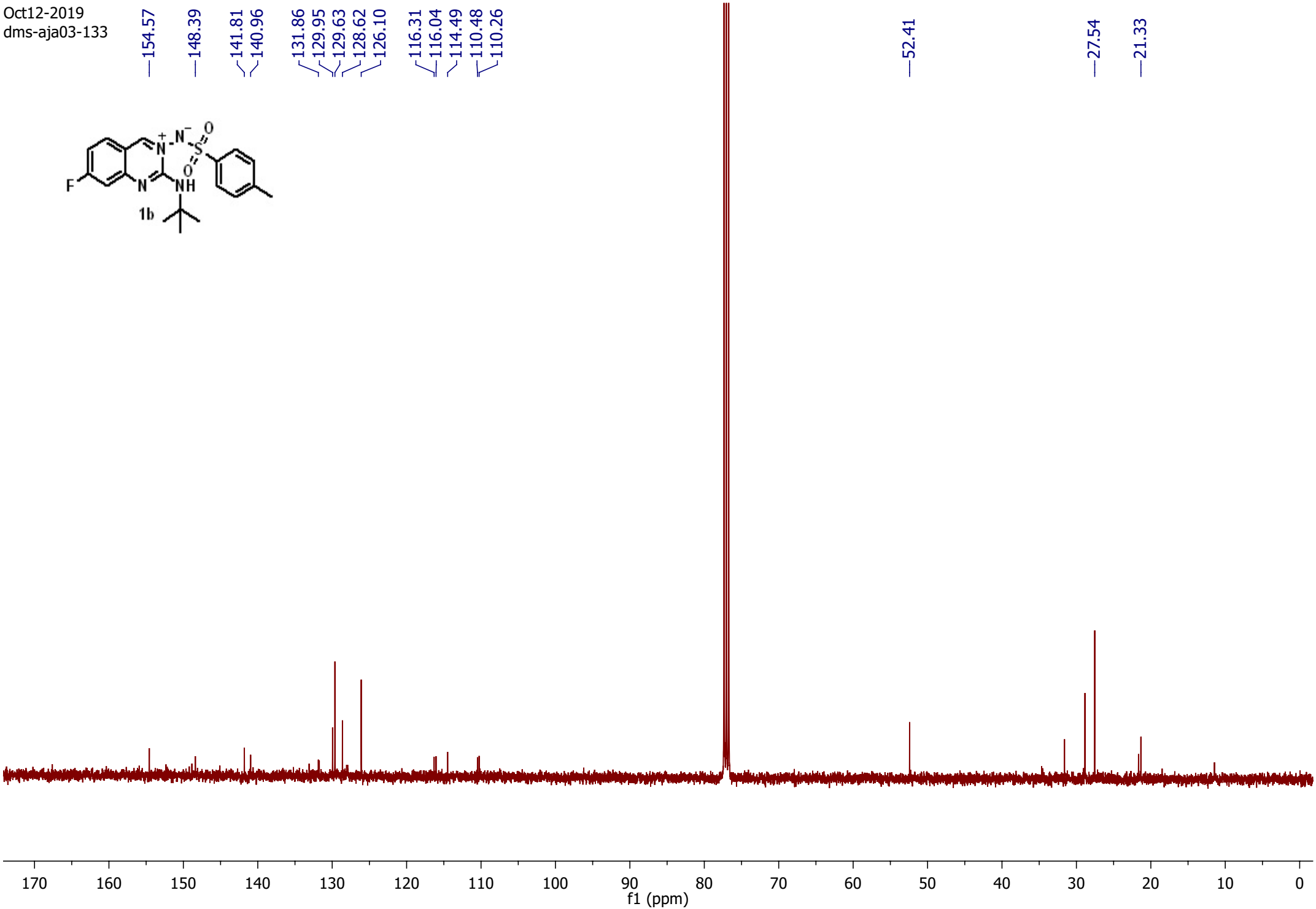

9.3968
7.8548
7.8401
7.8237
7.7757
7.7596
7.6074
7.5903
7.5374
7.5213
7.3923
7.3775
7.3625
7.2689
7.2091
7.1781
7.1624
2.3564
1.1846
1a
1.00
1.40
1.10
1.06
2.04
1.14
0.96
2.28
3.22
9.05
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


154.80
150.34
148.18
141.70
141.06
137.94
129.58
128.74
126.14
126.07
124.98
117.17
52.21
27.59
21.32
1a
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

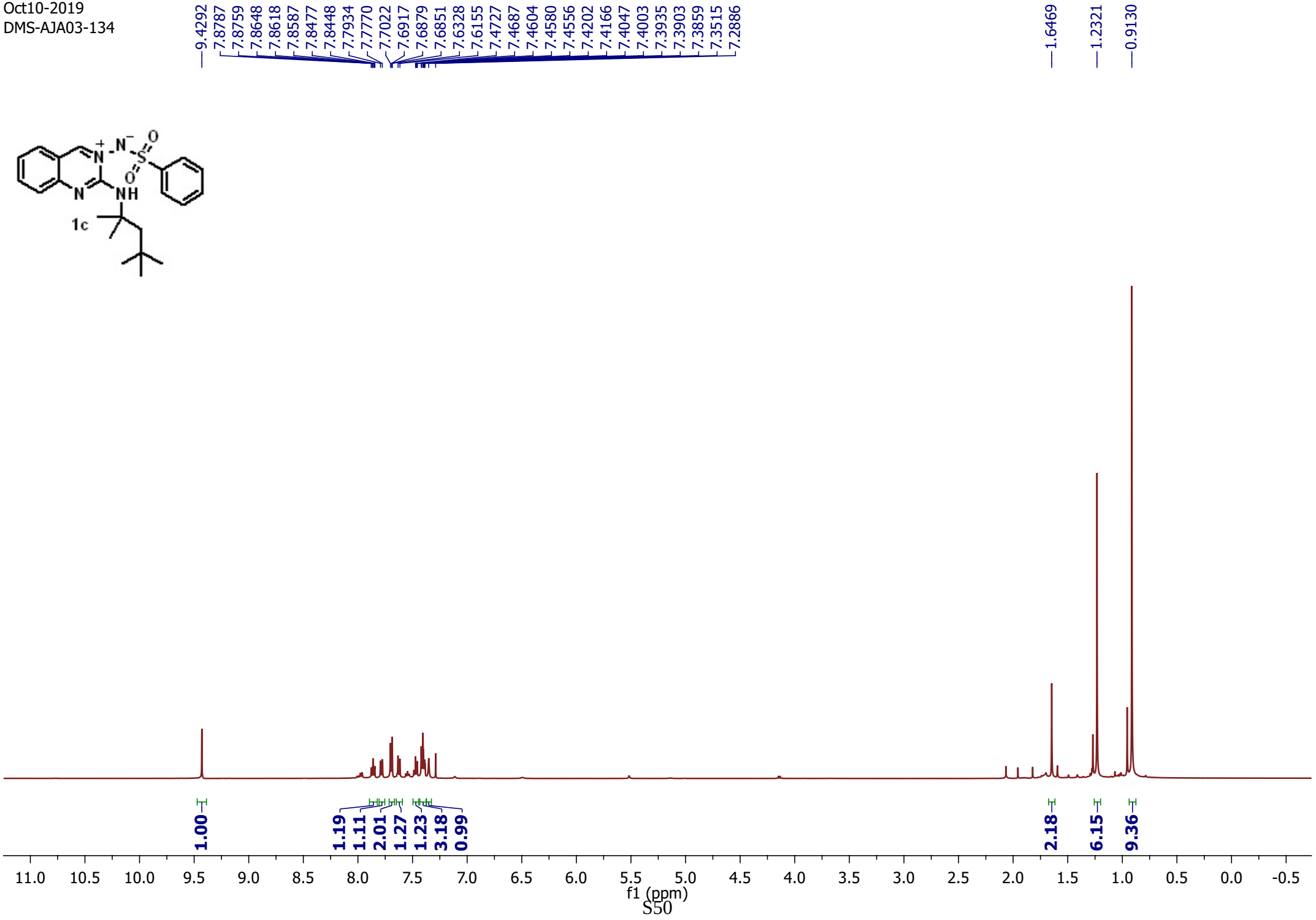
Oct10-2019
DMS-AJA03-133



Oct12-2019
dms-aja03-133

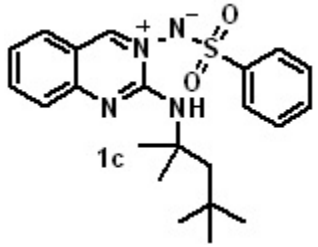


Oct10-2019
DMS-AJA03-134

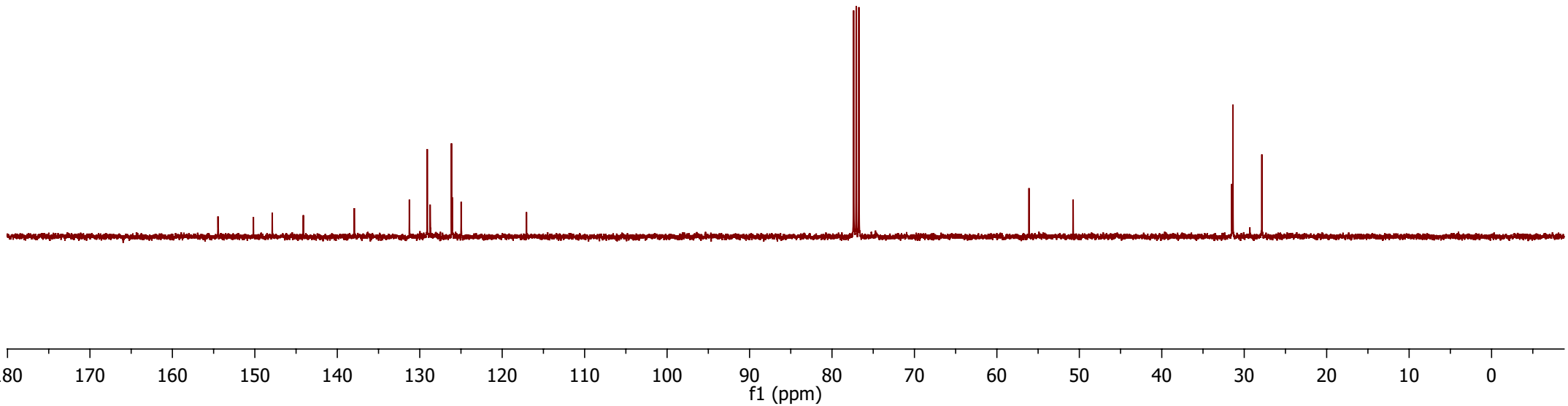


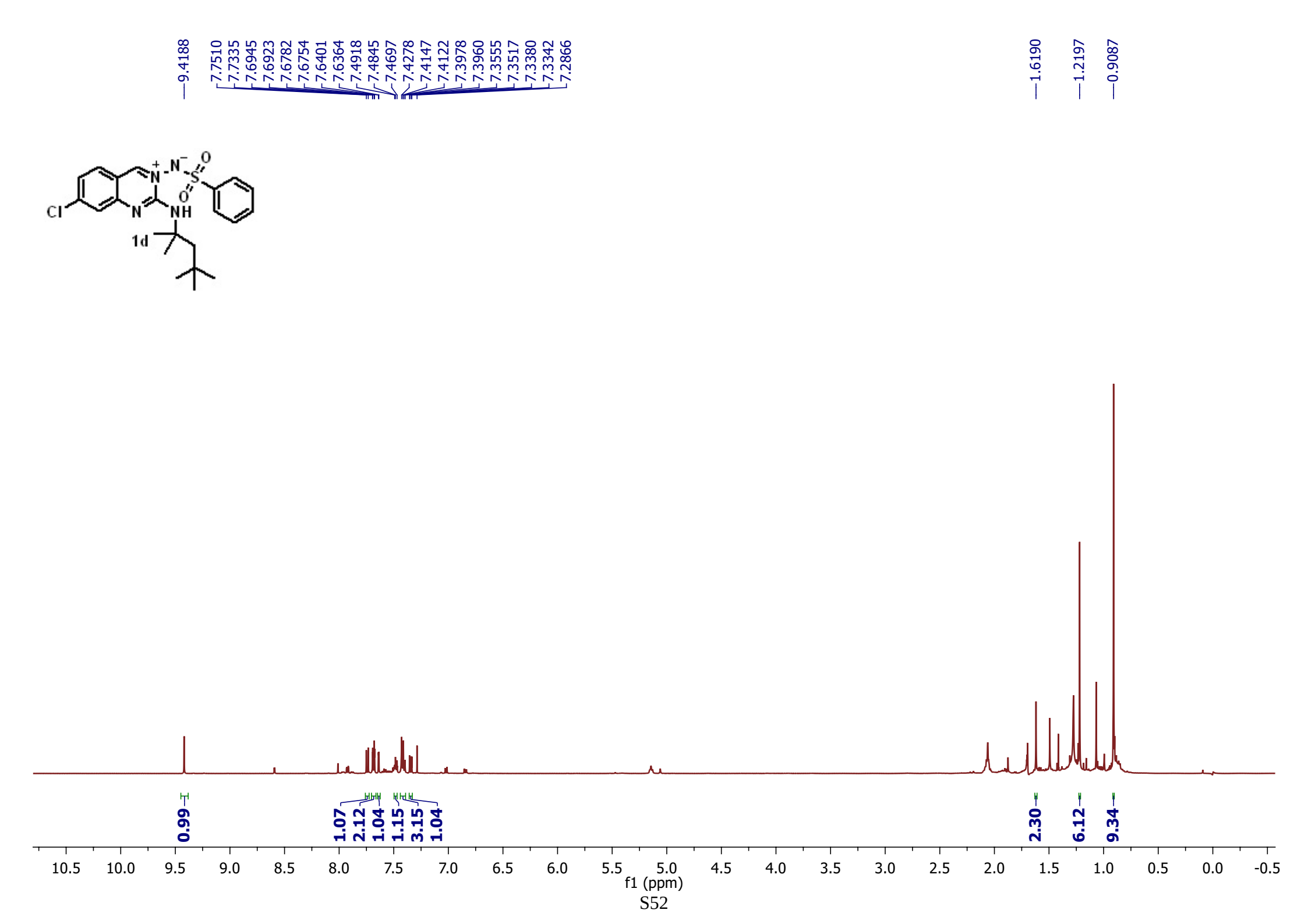
Oct12-2019
dms-aja03-134

154.47
150.17
147.89
144.12
137.94
131.26
129.09
128.74
126.15
126.06
124.97
117.05
56.10
50.75
31.50
31.37
27.86



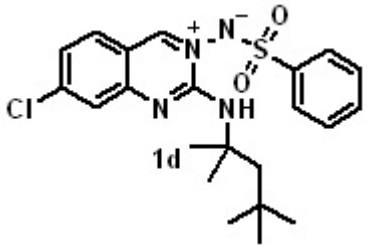
1c

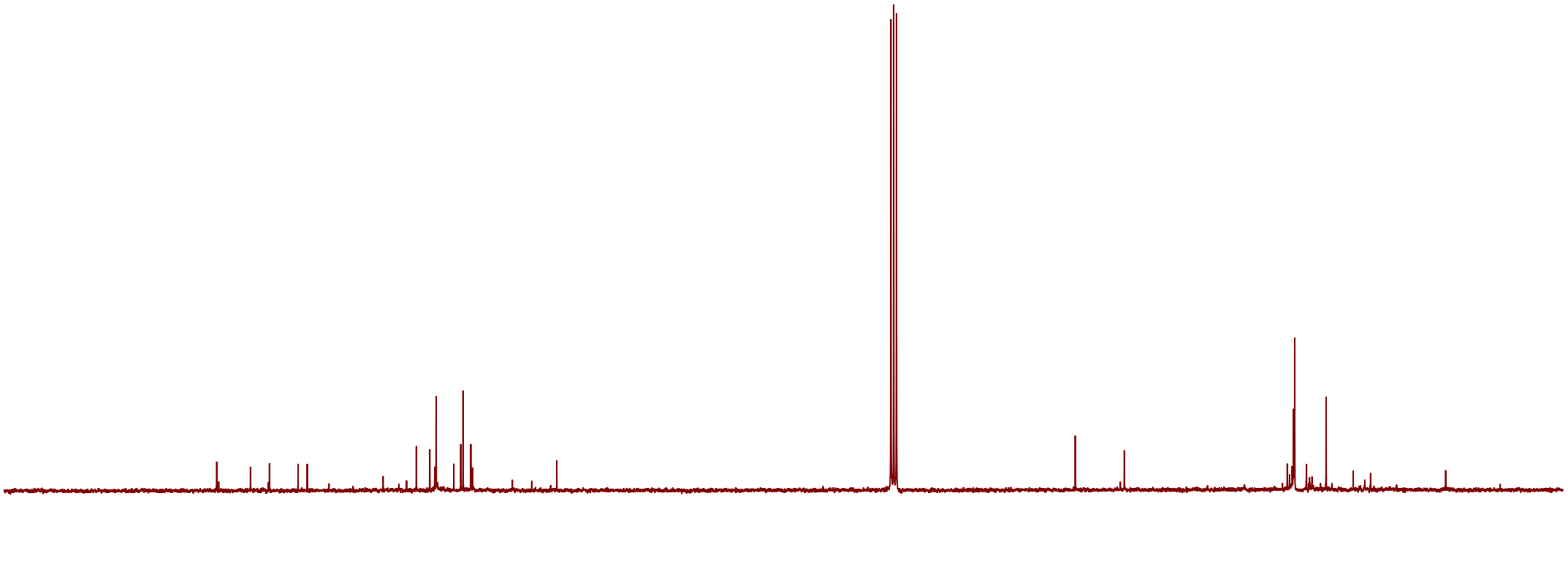



9.4188
7.7510
7.7335
7.6945
7.6923
7.6782
7.6754
7.6401
7.6364
7.4918
7.4845
7.4697
7.4278
7.4147
7.4122
7.3978
7.3960
7.3555
7.3517
7.3380
7.3342
7.2866
1.6190
1.2197
0.9087
Cl
N
NH
1d
0.99
1.07
2.12
1.04
1.15
3.15
1.04
2.30
6.12
9.34
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

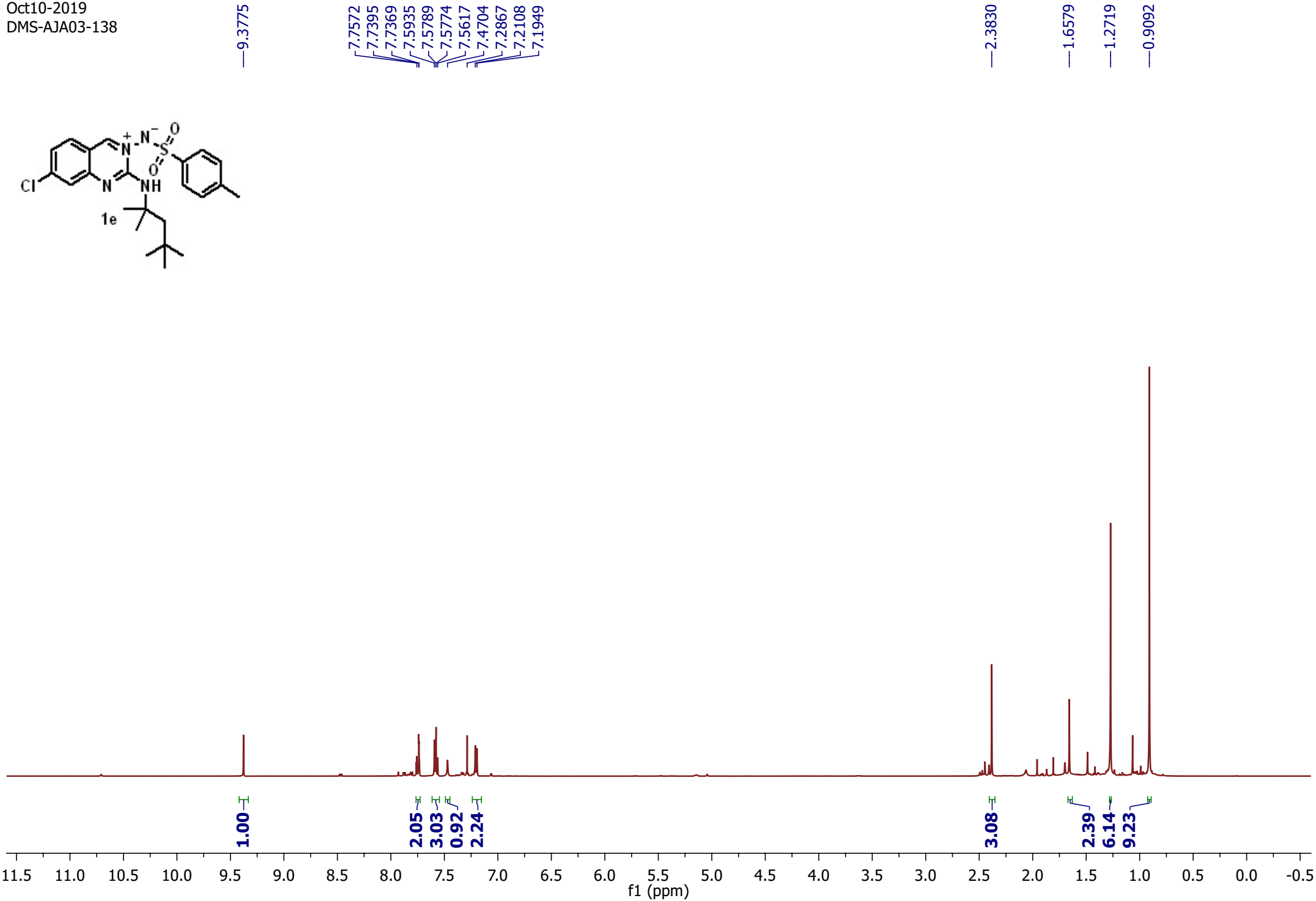
Oct12-2019
dms-aja-4cl-ph,1,1,3,3

154.17
150.33
148.17
144.91
143.87
131.44
129.91
129.18
126.37
126.11
125.23
115.44
56.37
50.77
31.50
31.36
27.78



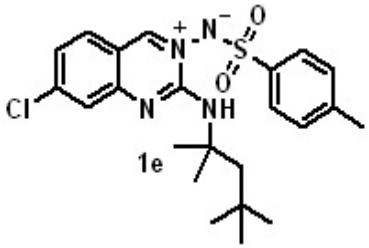


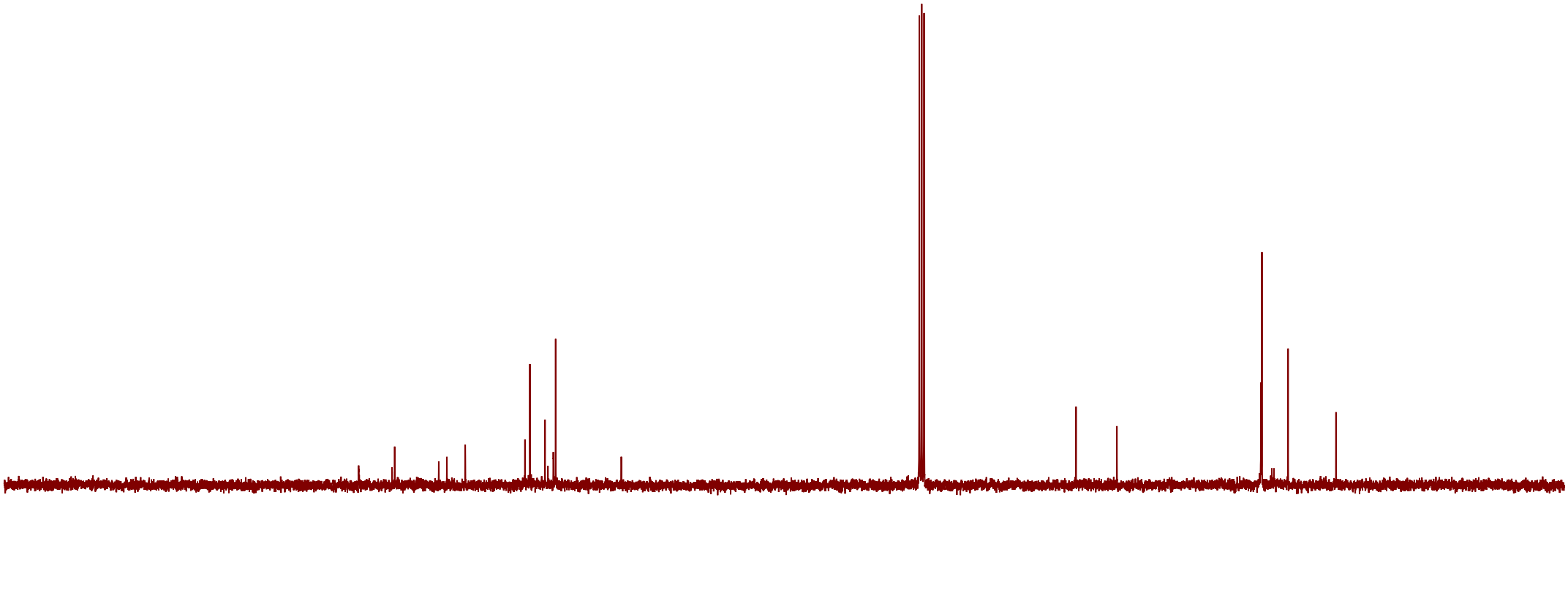
Oct10-2019
DMS-AJA03-138

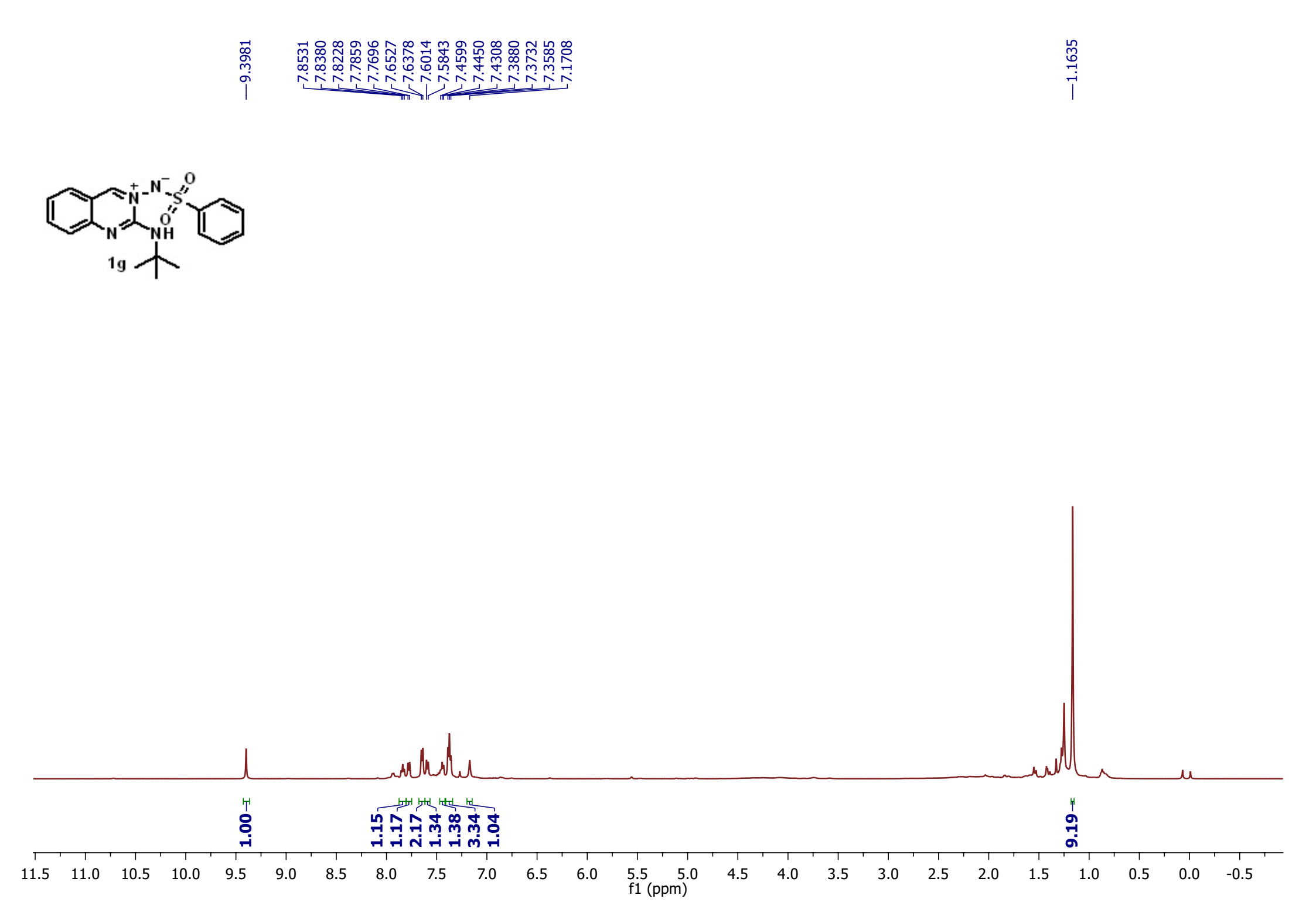


Oct12-2019
dms-aja03-135

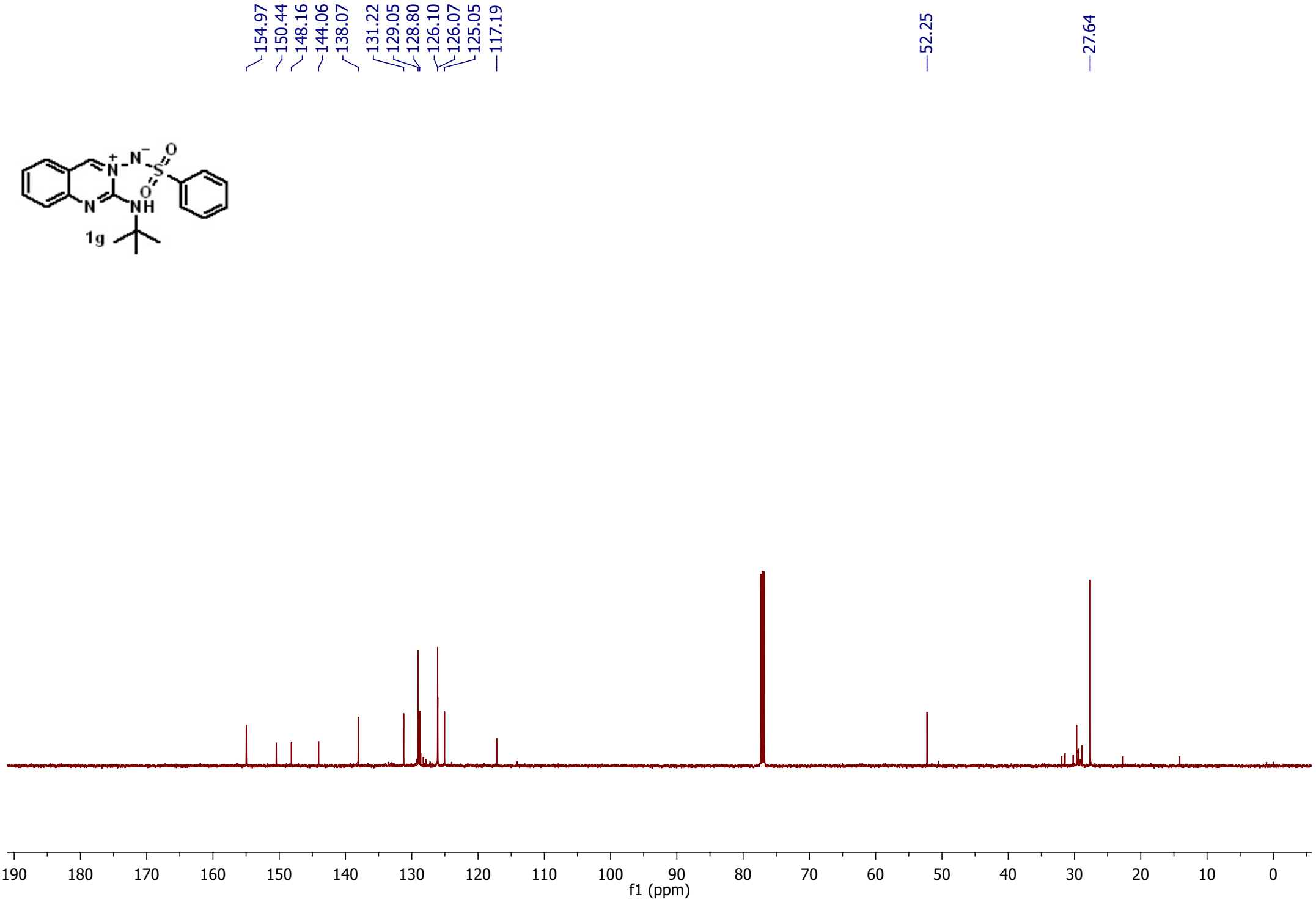
152.70
148.23
147.86
141.94
140.84
138.38
130.36
129.70
127.66
126.55
126.23
117.41
56.32
50.83
31.48
31.34
27.83
21.38



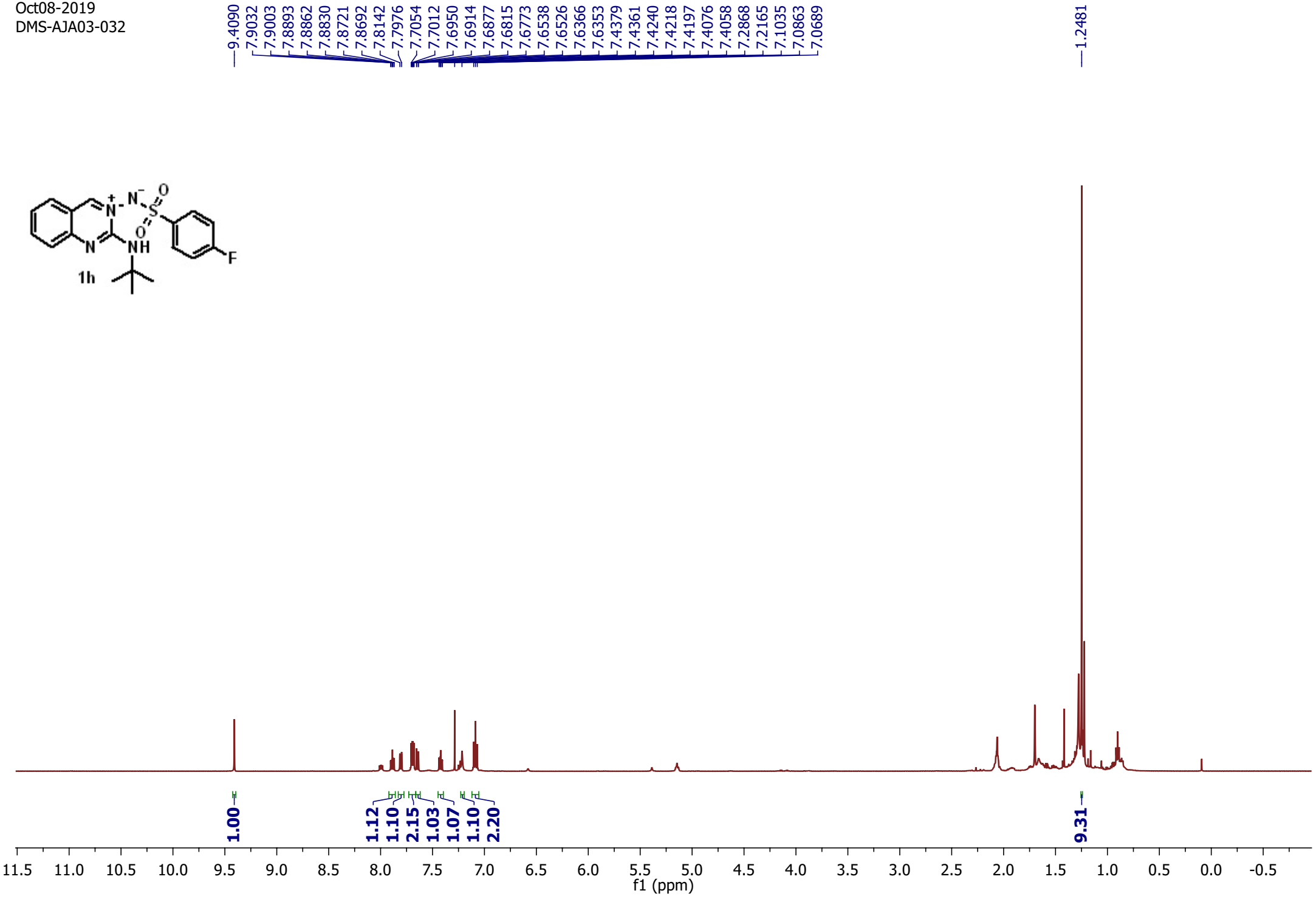



9.3981
7.8531
7.8380
7.8228
7.7859
7.7696
7.6527
7.6378
7.6014
7.5843
7.4599
7.4450
7.4308
7.3880
7.3732
7.3585
7.1708
1.1635
1g
1.00
1.15
1.17
2.17
1.34
1.38
3.34
1.04
9.19
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

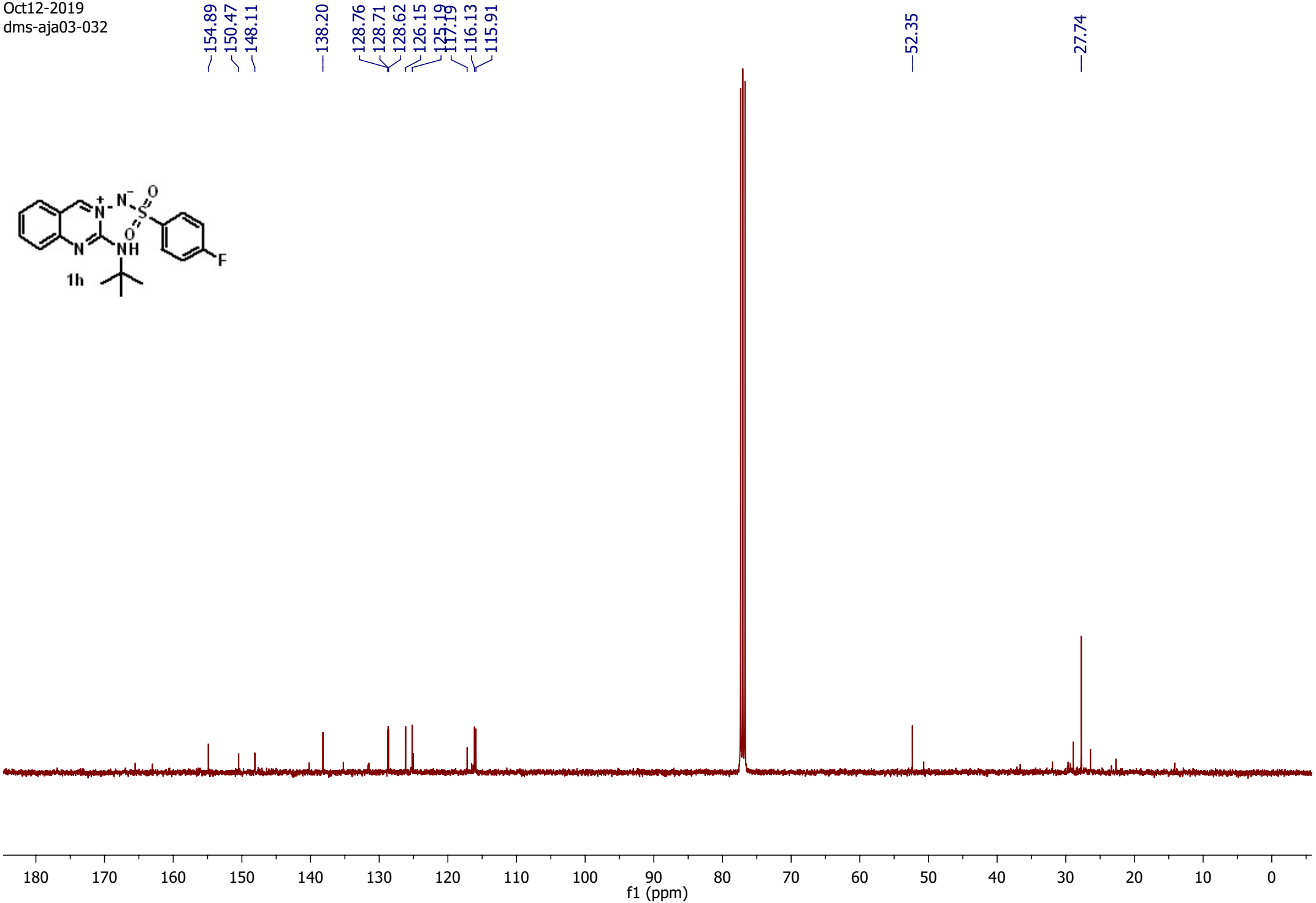
1g

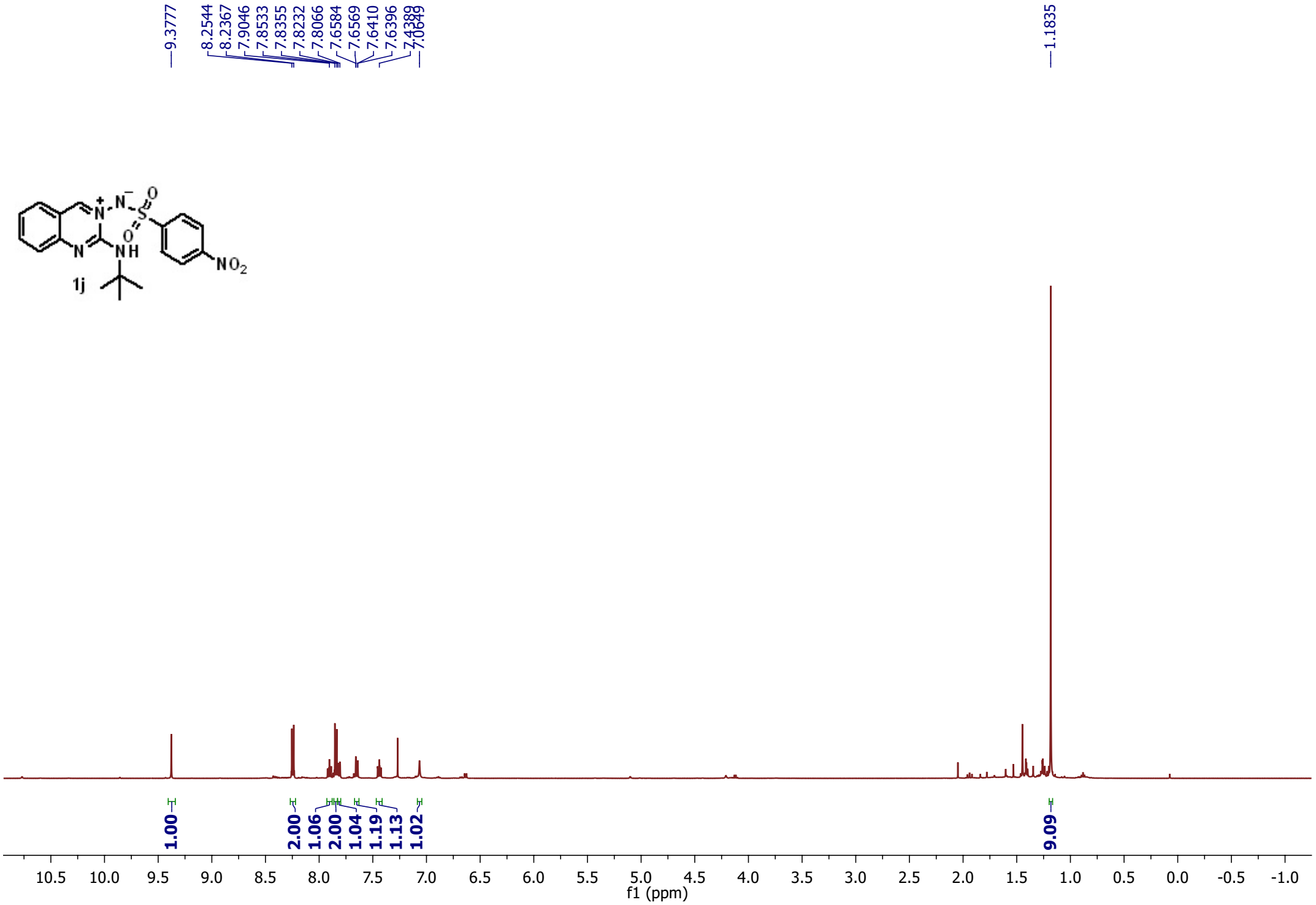

154.97
150.44
148.16
144.06
138.07
131.22
129.05
128.80
126.10
126.07
125.05
117.19
52.25
27.64
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

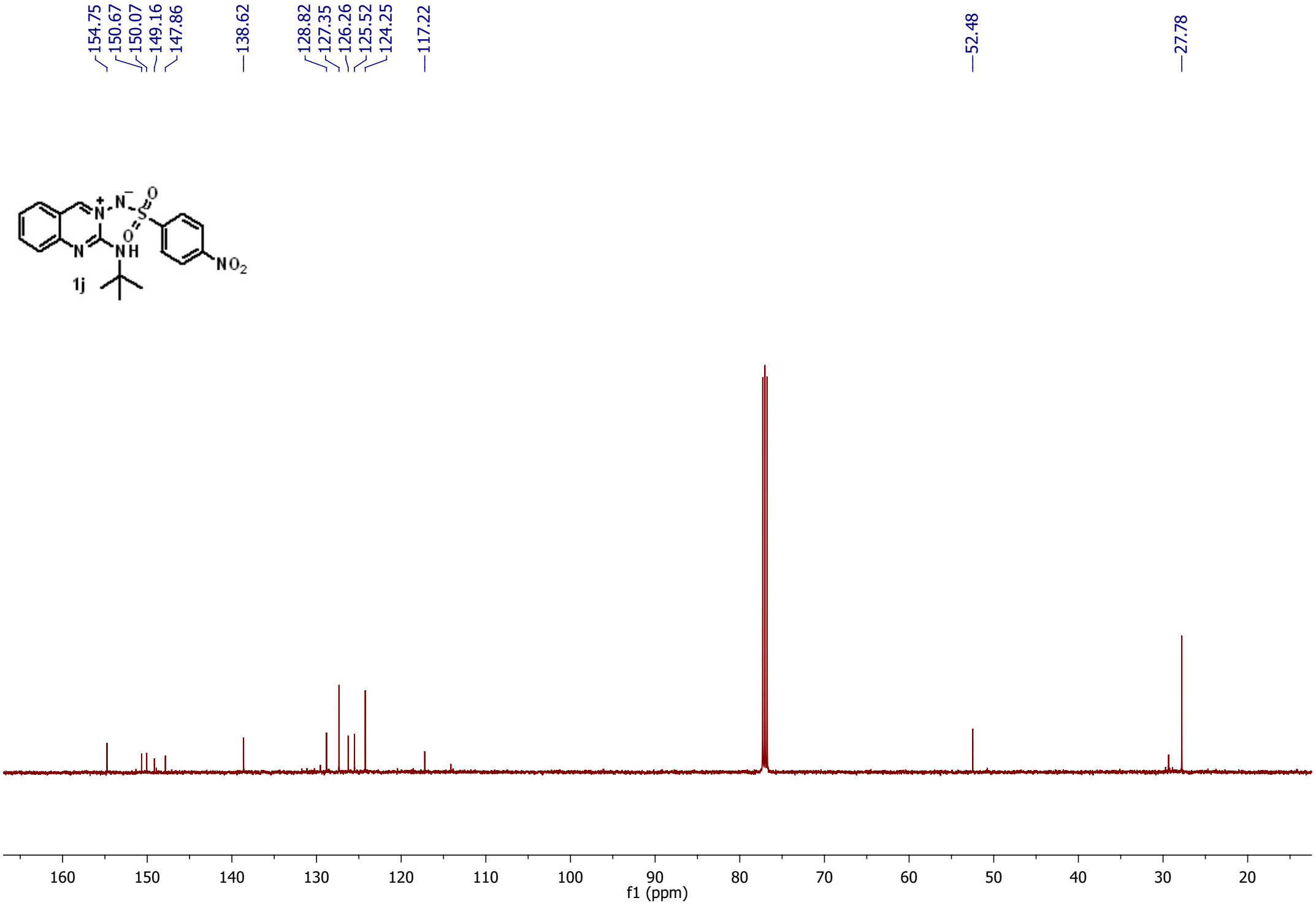
Oct08-2019
DMS-AJA03-032



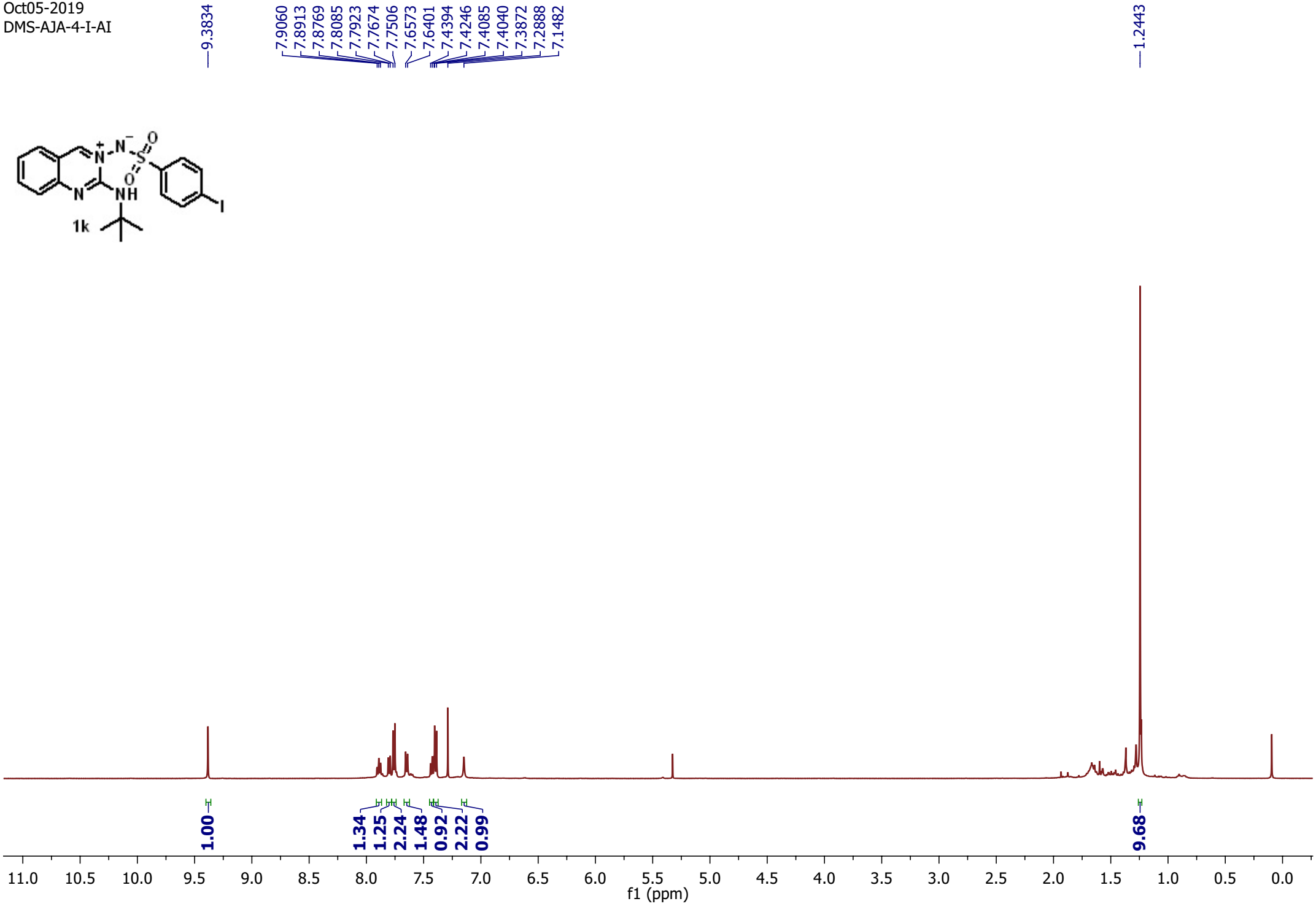
Oct12-2019
dms-aja03-032




9.3777
8.2544
8.2367
7.9046
7.8533
7.8355
7.8232
7.8066
7.6584
7.6569
7.6410
7.6396
7.4389
7.0649
1.1835
1j
1.00
2.00
1.06
2.00
1.04
1.19
1.13
1.02
9.09
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)


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
1j
NO2
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

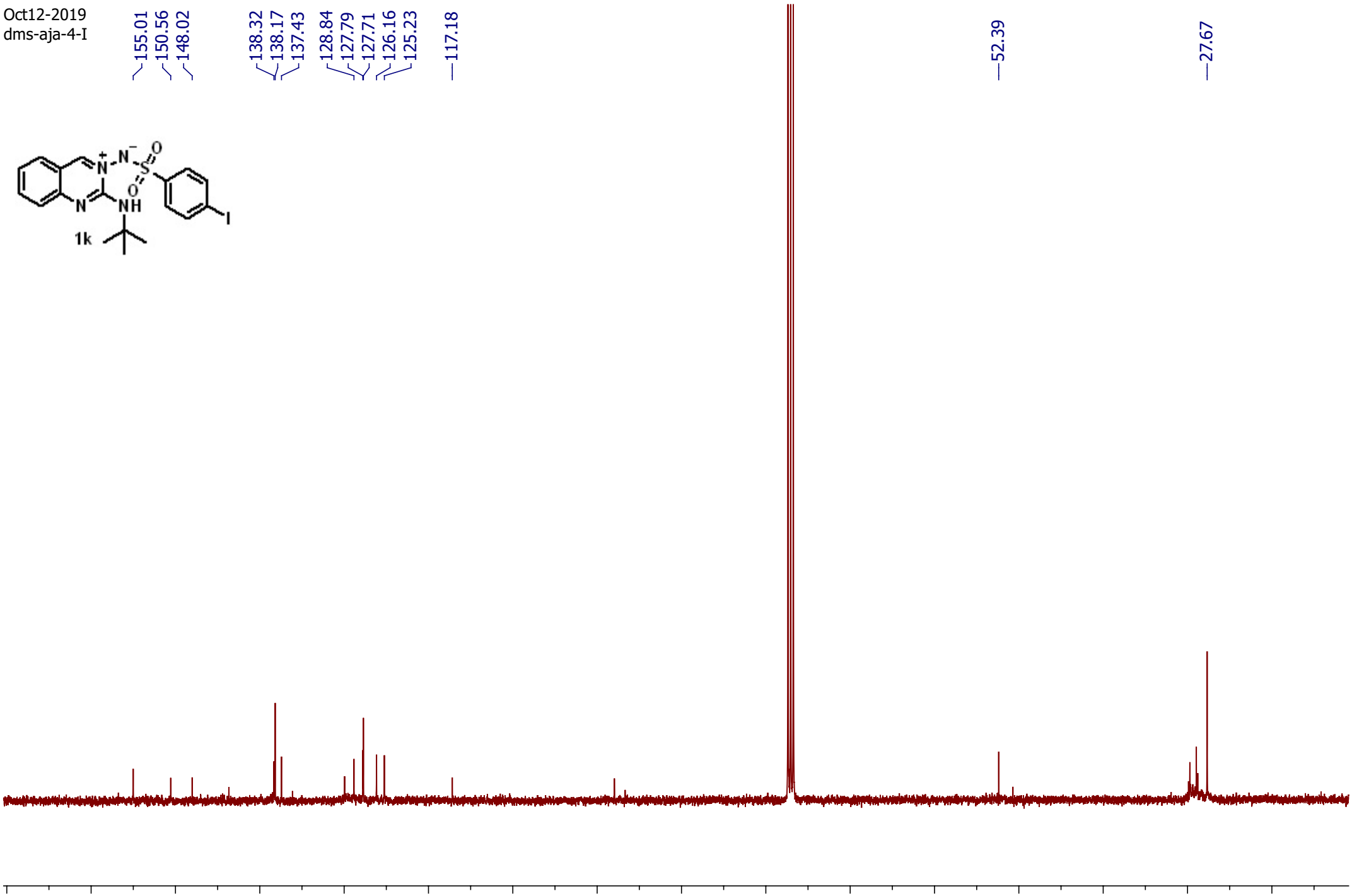
Oct05-2019
DMS-AJA-4-I-AI

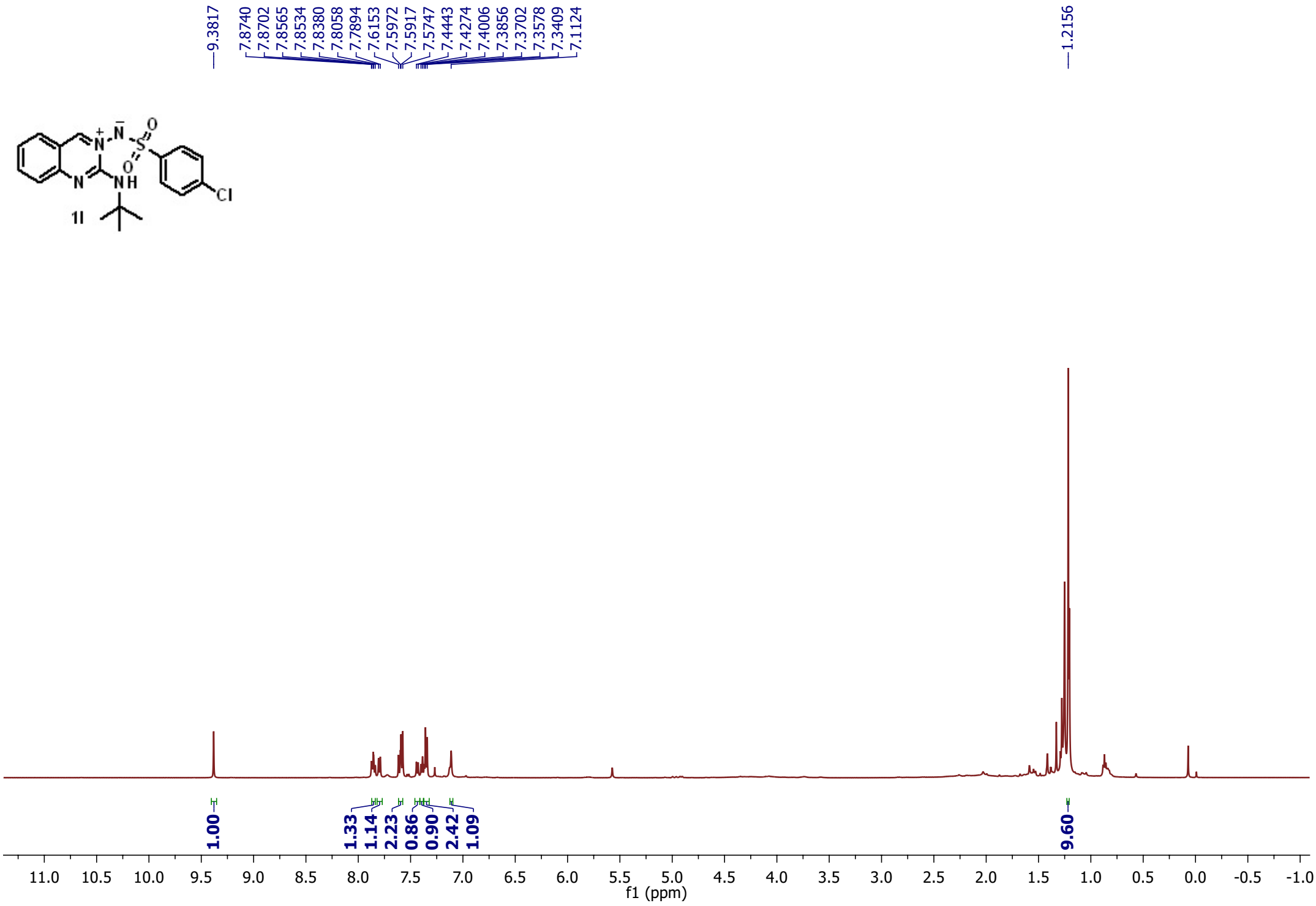


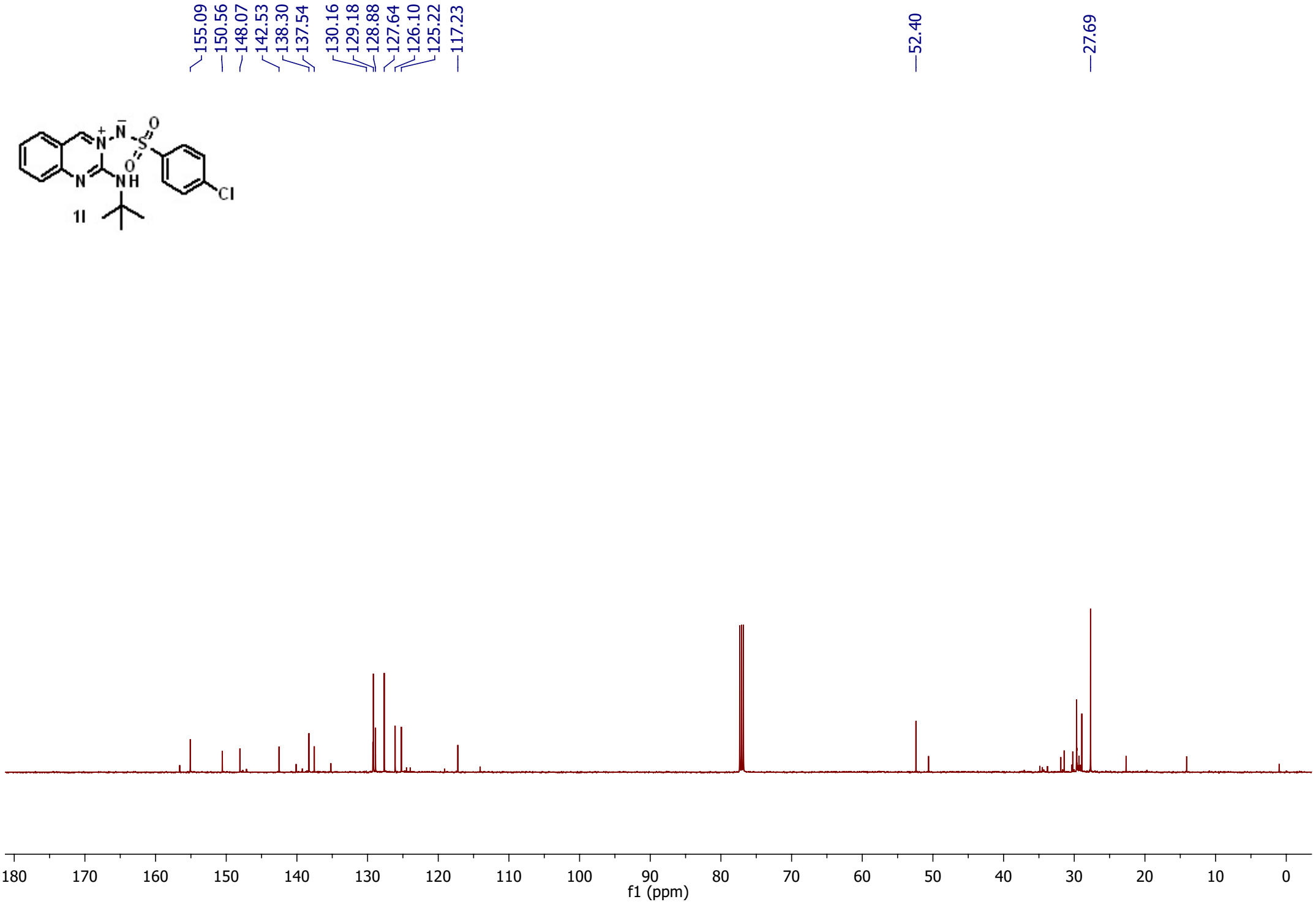
Oct12-2019
dms-aja-4-I

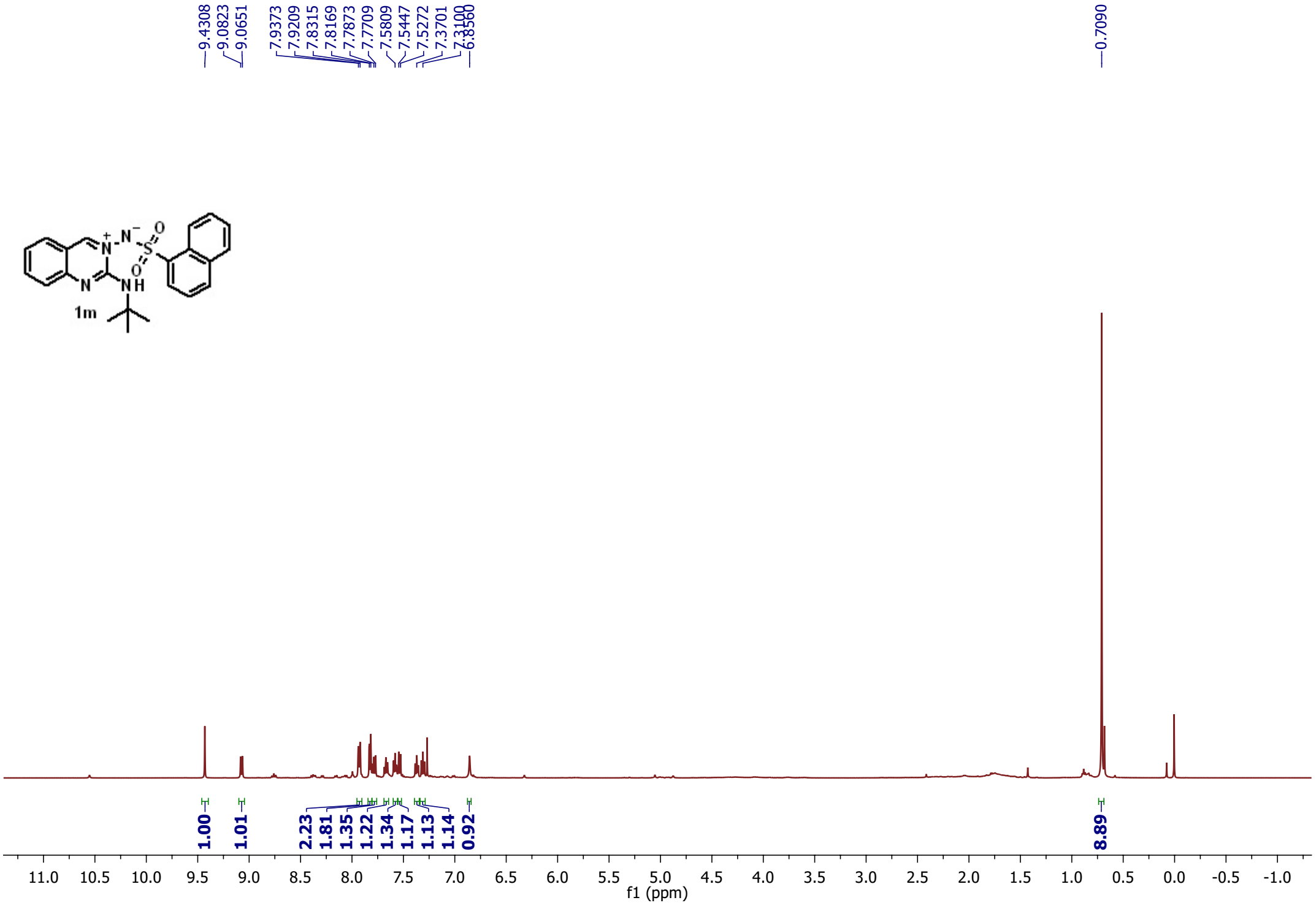
155.01
150.56
148.02
138.32
138.17
137.43
128.84
127.79
127.71
126.16
125.23
117.18
52.39
27.67

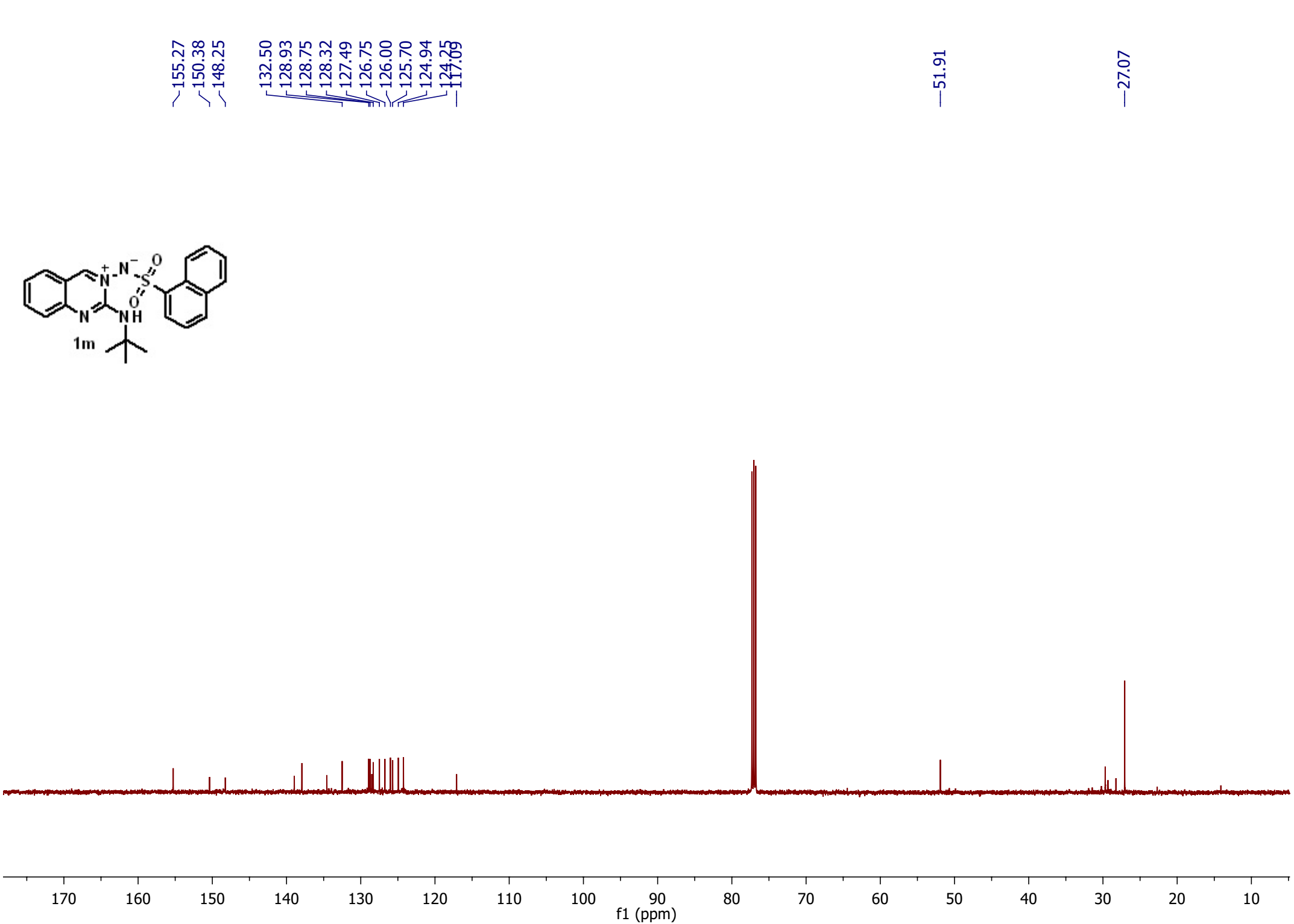
1k

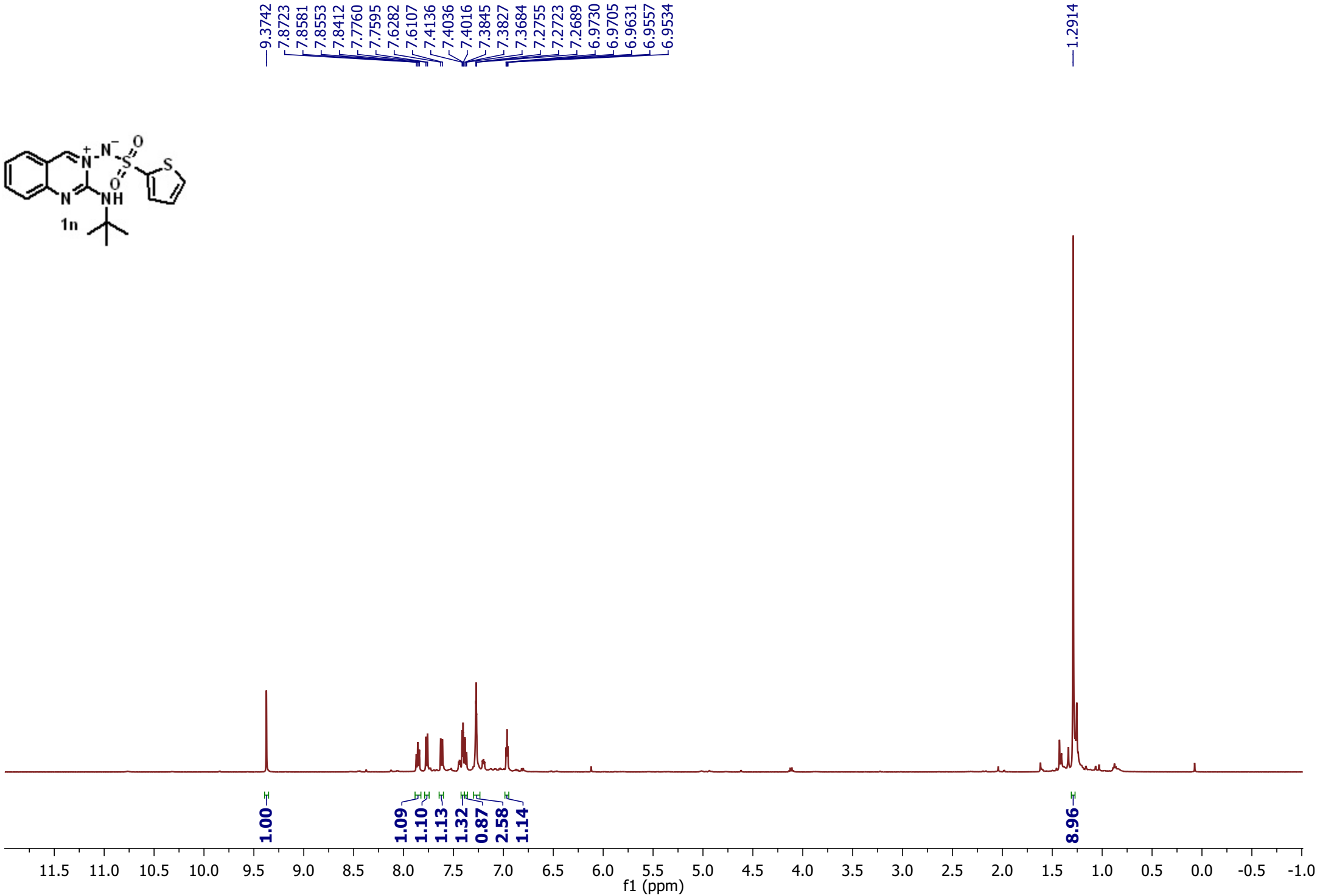


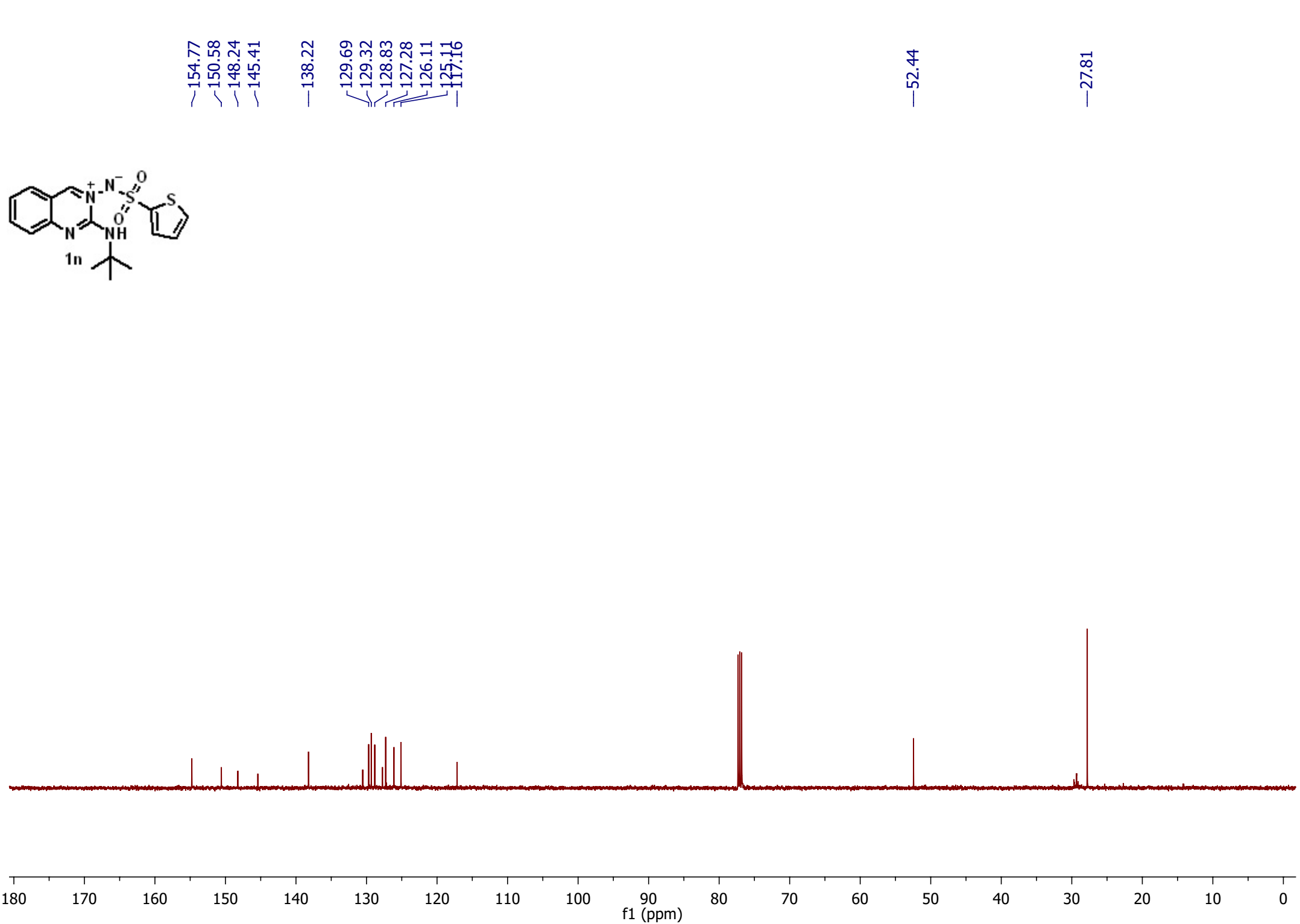

9.3817
7.8740
7.8702
7.8565
7.8534
7.8380
7.8058
7.7894
7.6153
7.5972
7.5917
7.5747
7.4443
7.4274
7.4006
7.3856
7.3702
7.3578
7.3409
7.1124
1.2156
1l
Cl
1.00
1.33
1.14
2.23
0.86
0.90
2.42
1.09
9.60
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

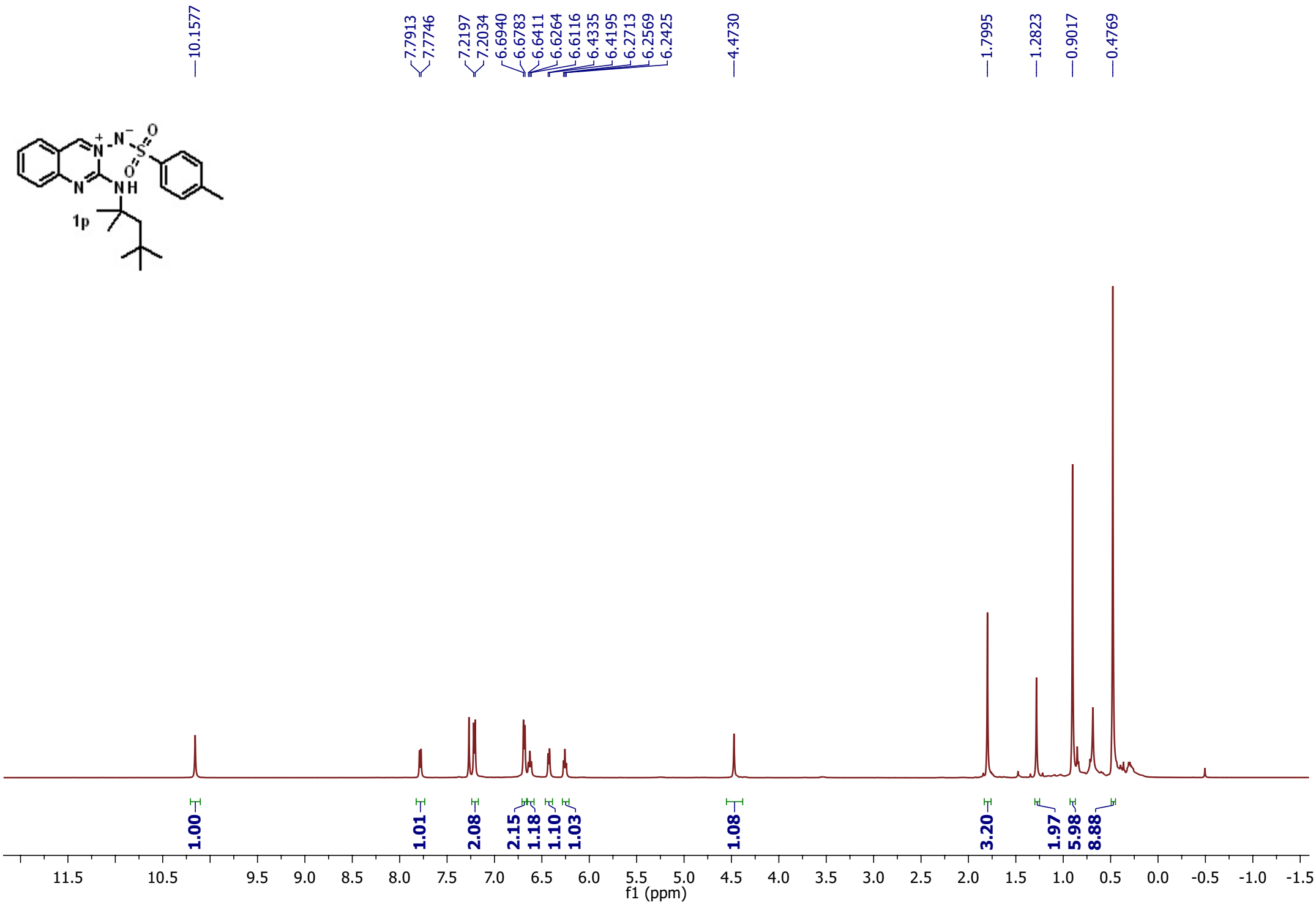

155.09
150.56
148.07
142.53
138.30
137.54
130.16
129.18
128.88
127.64
126.10
125.22
117.23
52.40
27.69
Cl
1l
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

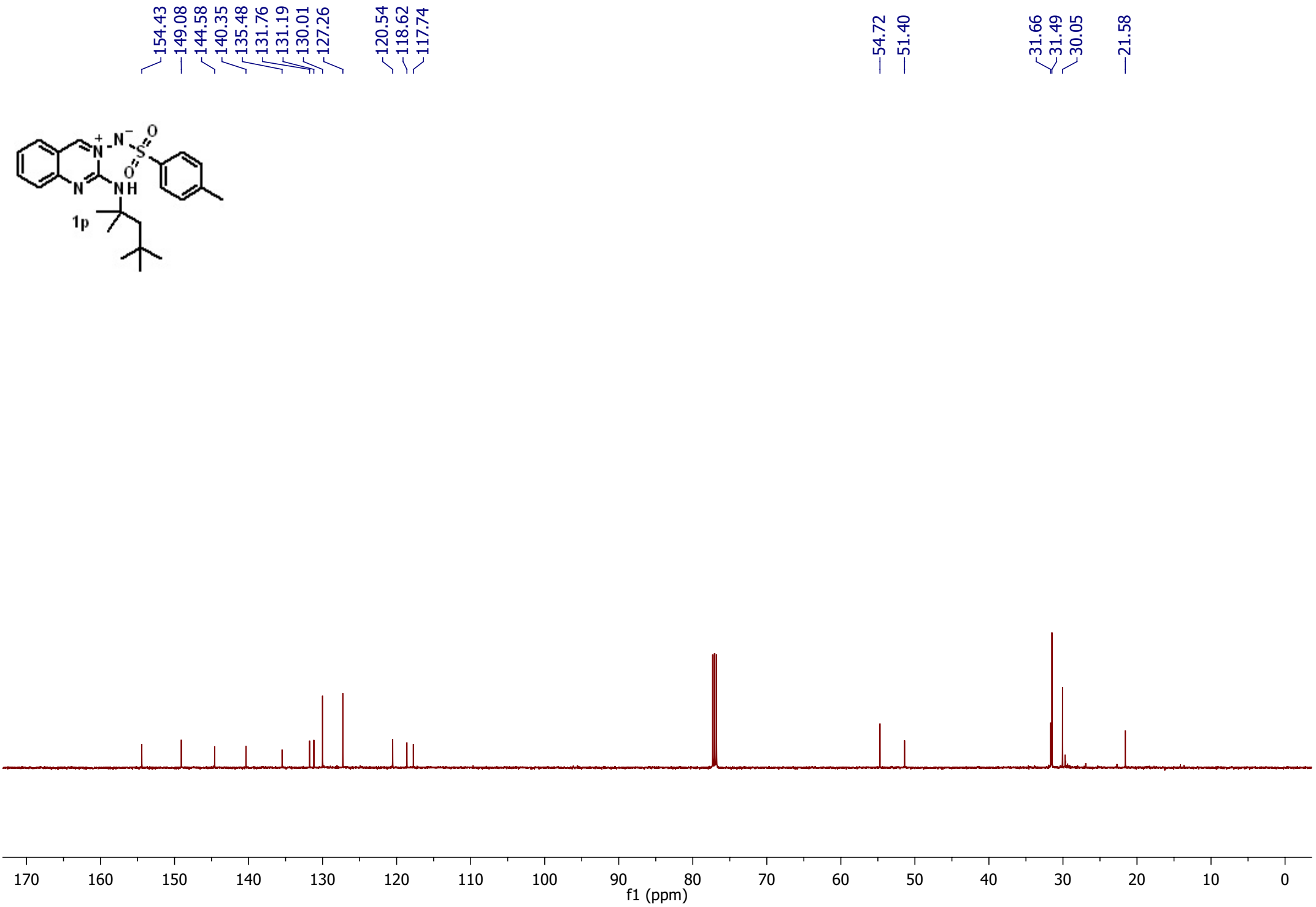

9.4308
9.0823
9.0651
7.9373
7.9209
7.8315
7.8169
7.7873
7.7709
7.5809
7.5447
7.5272
7.3701
7.3100
6.8560
0.7090
1m
1.00
1.01
2.23
1.81
1.35
1.22
1.34
1.17
1.13
1.14
0.92
8.89
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

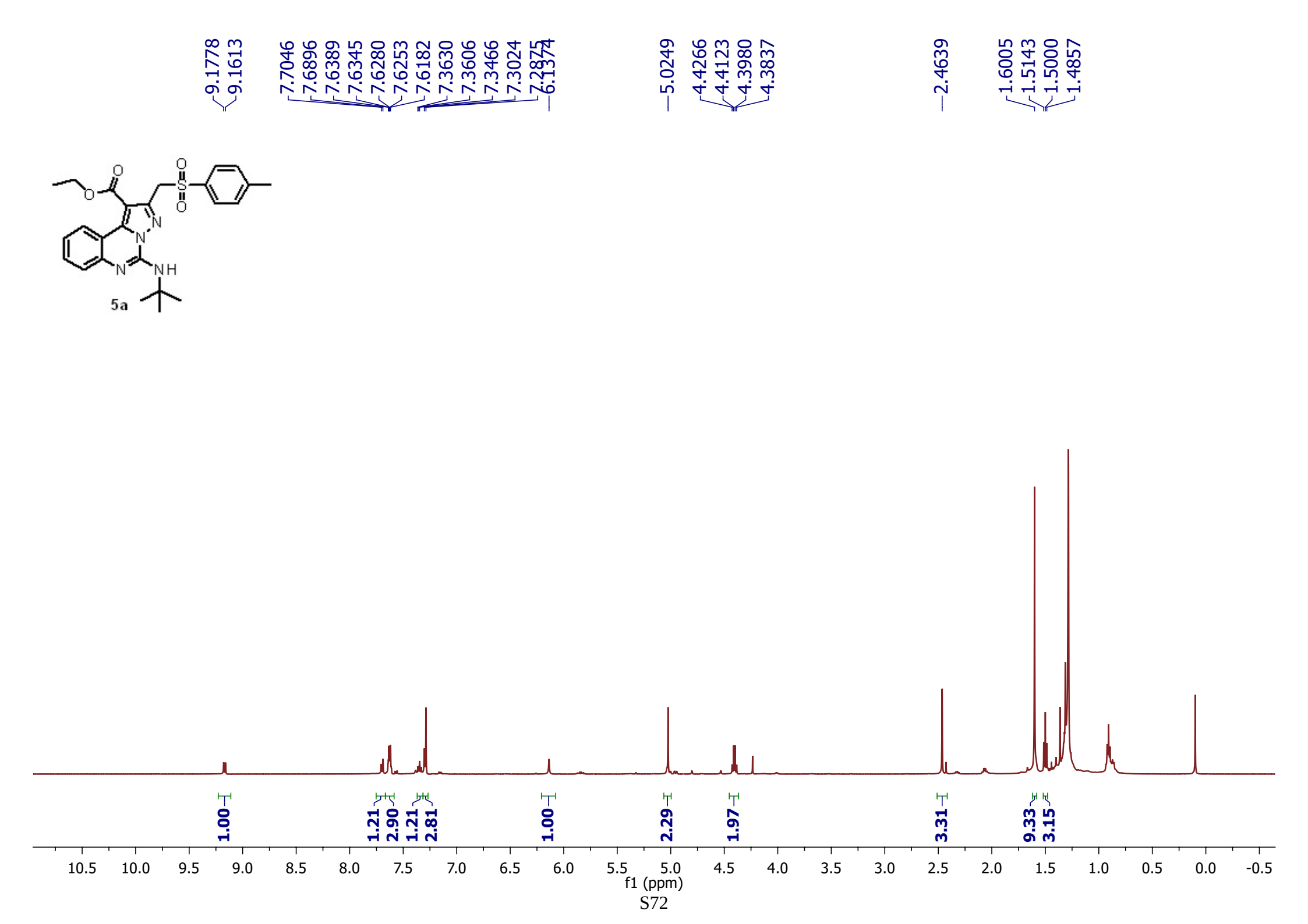

155.27
150.38
148.25
132.50
128.93
128.75
128.32
127.49
126.75
126.00
125.70
124.94
124.25
117.09
51.91
27.07
1m
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

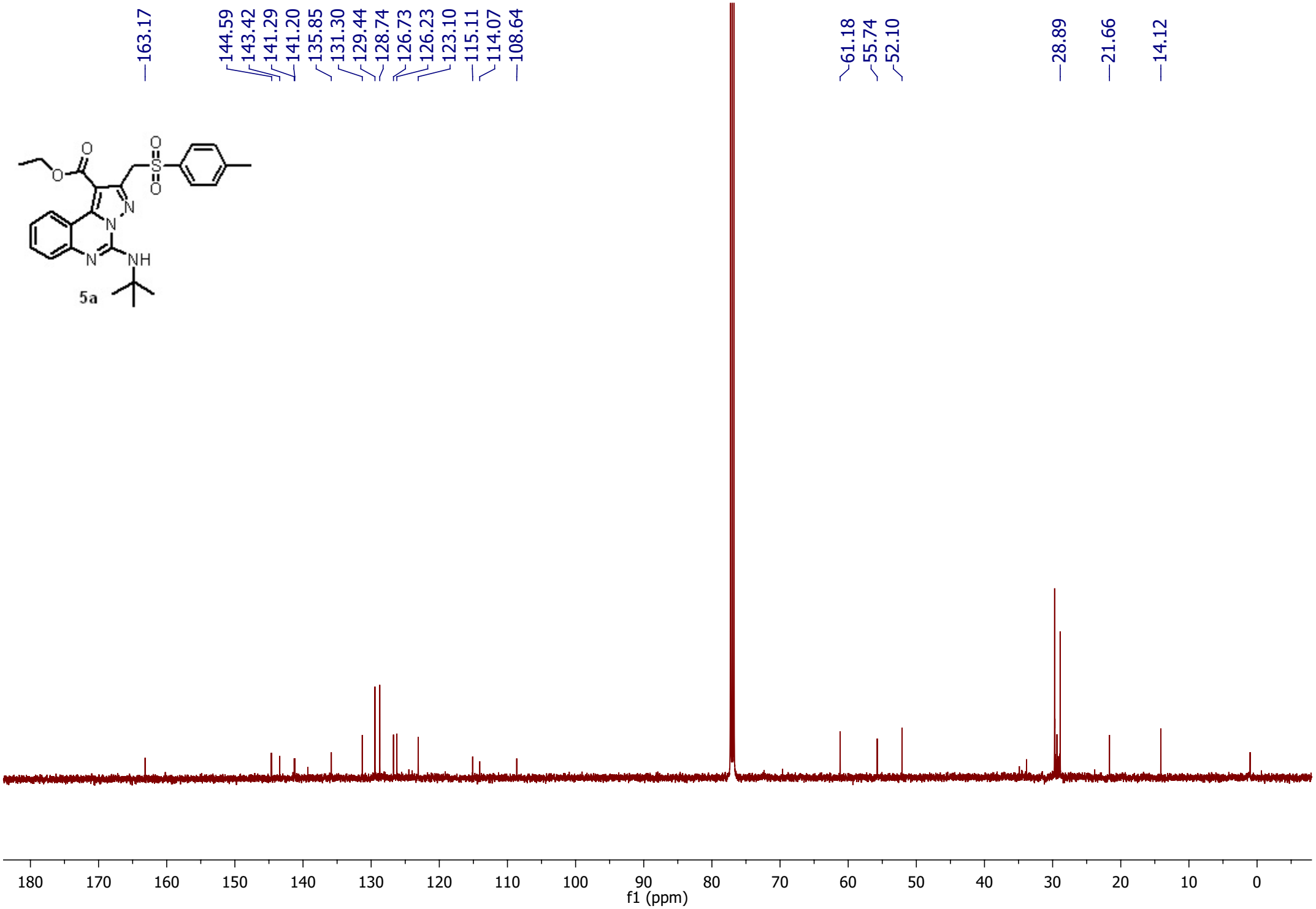

9.3742
7.8723
7.8581
7.8553
7.8412
7.7760
7.7595
7.6282
7.6107
7.4136
7.4036
7.4016
7.3845
7.3827
7.3684
7.2755
7.2723
7.2689
6.9730
6.9705
6.9631
6.9557
6.9534
1.2914
1n
1.00
1.09
1.10
1.13
1.32
0.87
2.58
1.14
8.96
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

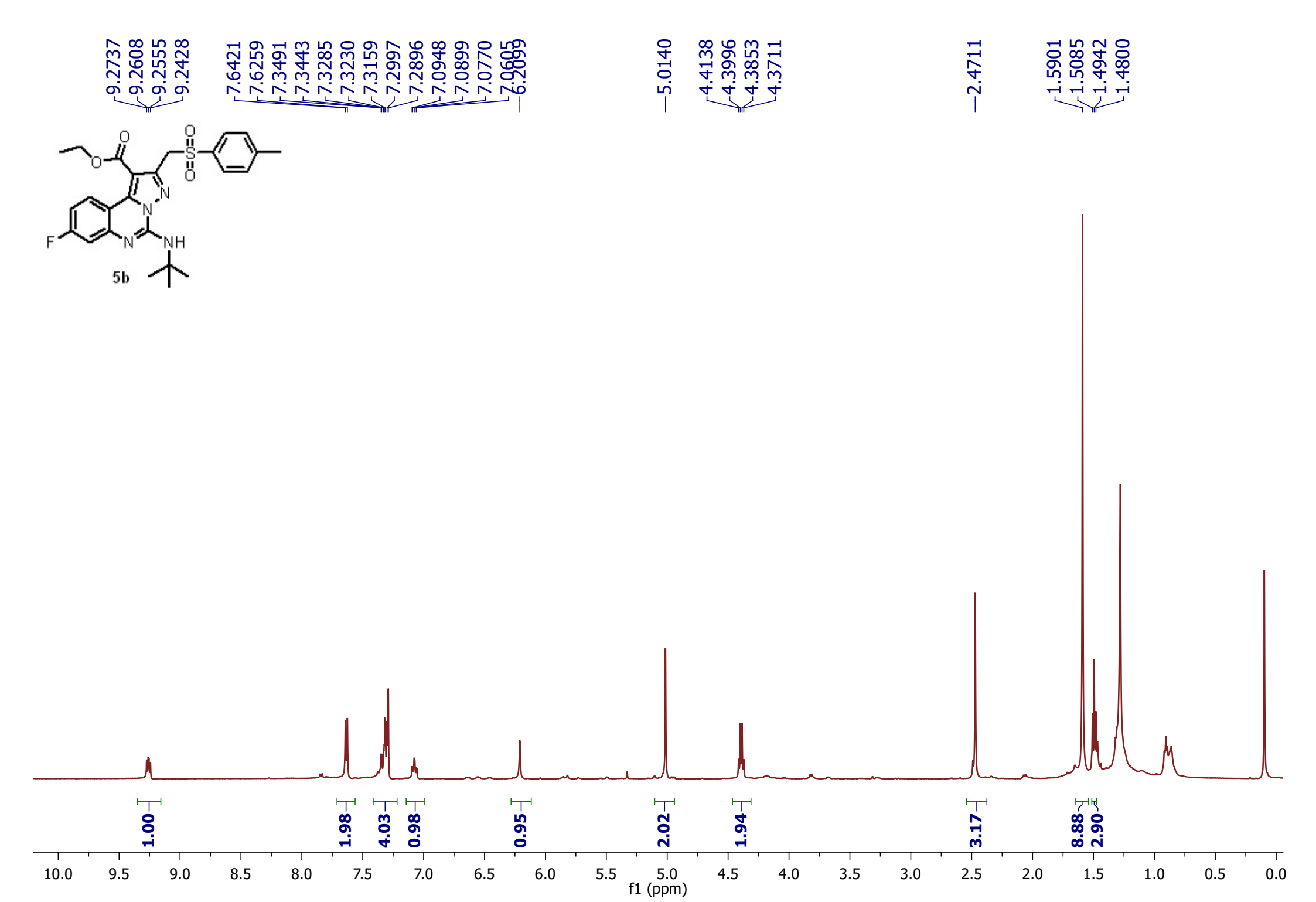

154.77
150.58
148.24
145.41
138.22
129.69
129.32
128.83
127.28
126.11
125.11
117.16
52.44
27.81
1n
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

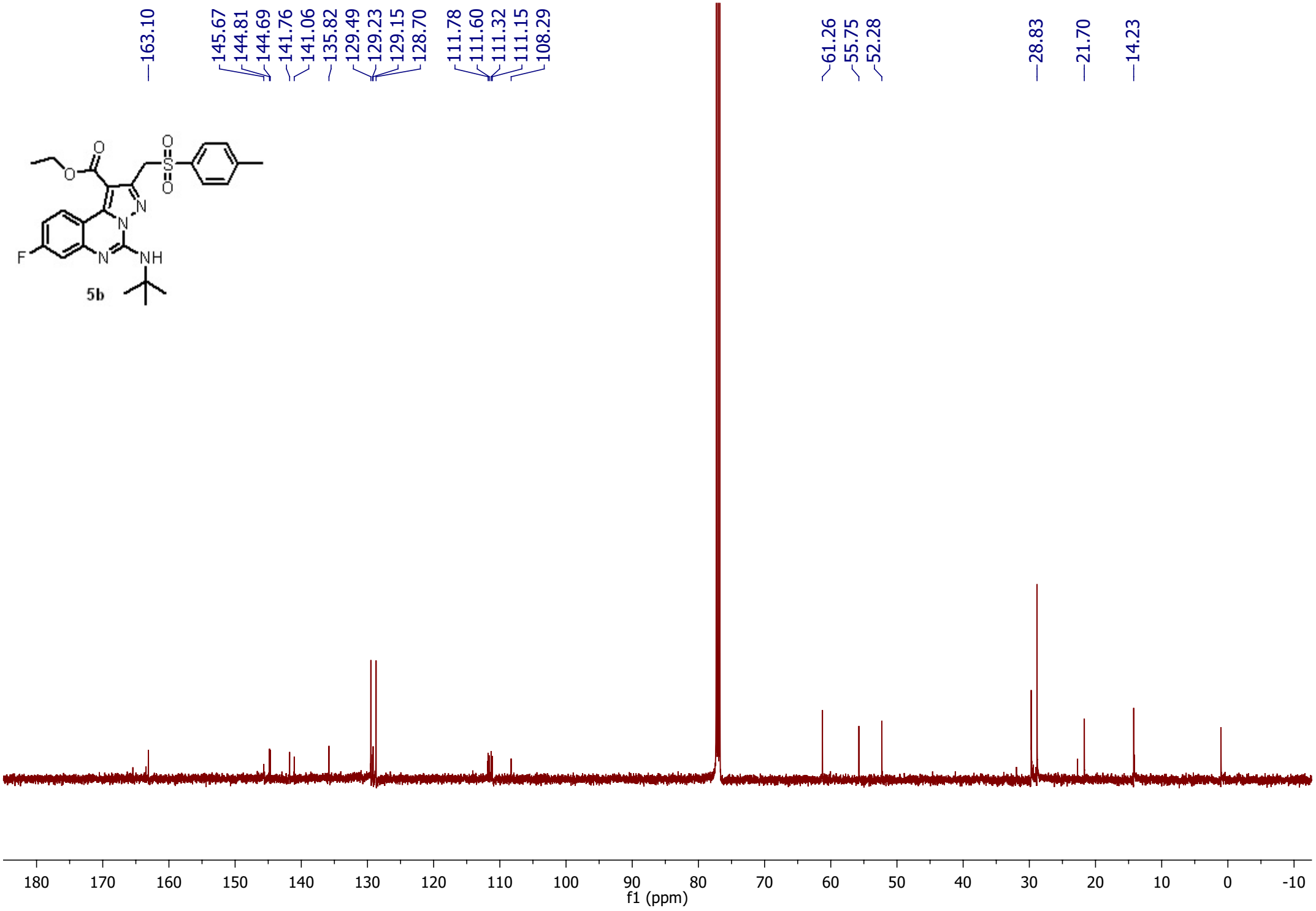

10.1577
7.7913
7.7746
7.2197
7.2034
6.6940
6.6783
6.6411
6.6264
6.6116
6.4335
6.4195
6.2713
6.2569
6.2425
4.4730
1.7995
1.2823
0.9017
0.4769
1p
1.00
1.01
2.08
2.15
1.18
1.10
1.03
1.08
3.20
1.97
5.98
8.88
f1 (ppm)

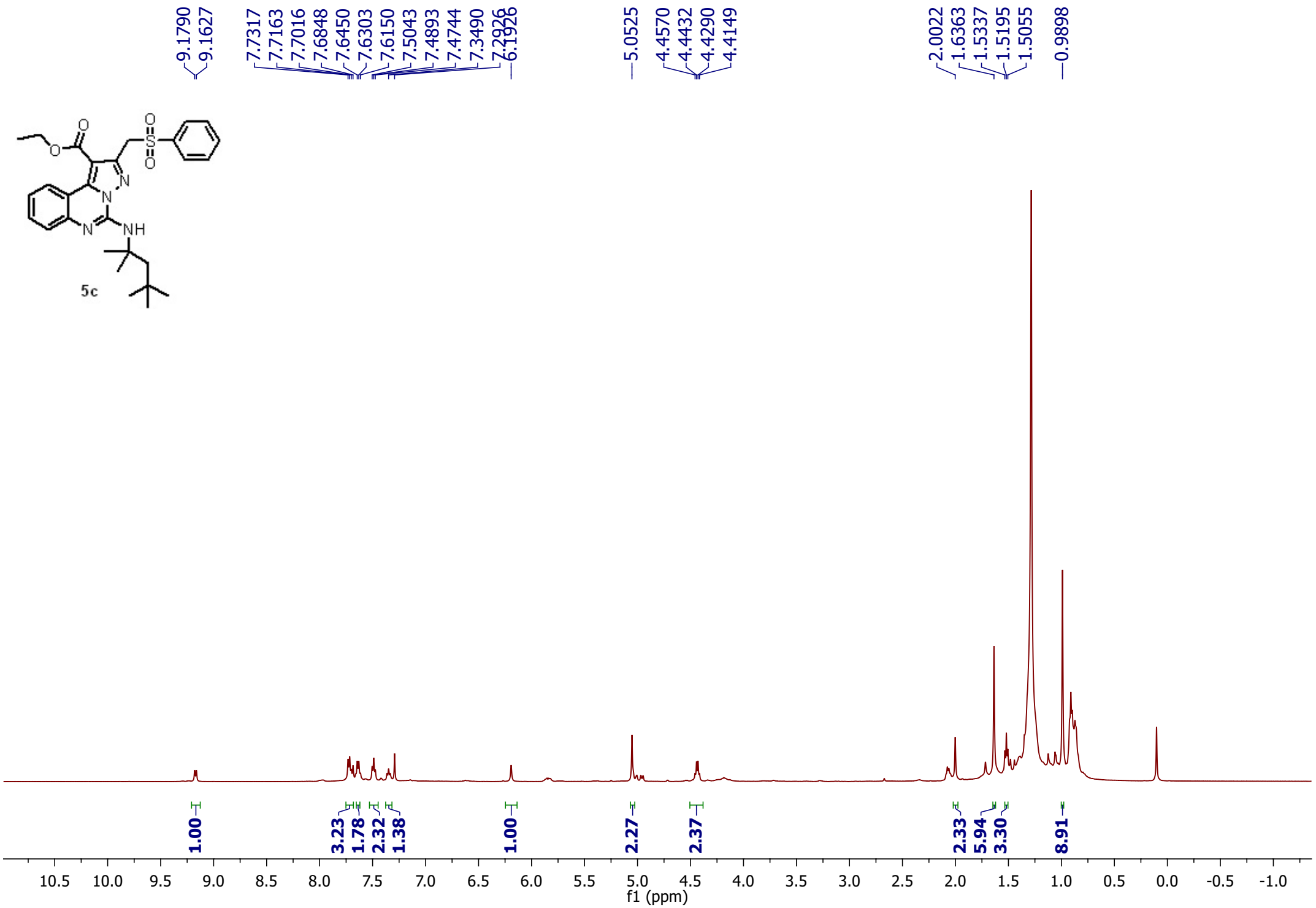

154.43
149.08
144.58
140.35
135.48
131.76
131.19
130.01
127.26
120.54
118.62
117.74
54.72
51.40
31.66
31.49
30.05
21.58
1p
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

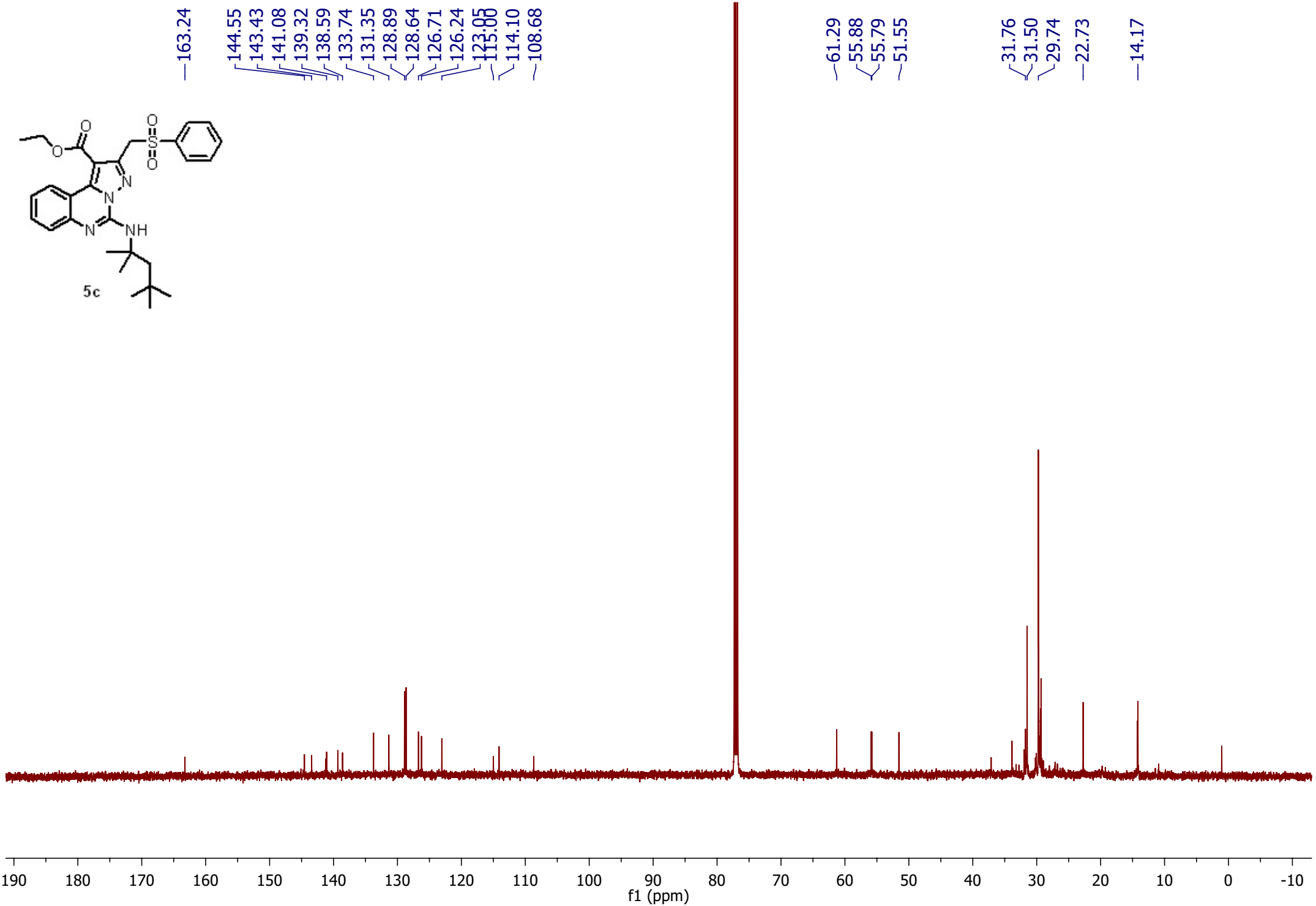

9.1778
9.1613
7.7046
7.6896
7.6389
7.6345
7.6280
7.6253
7.6182
7.3630
7.3606
7.3466
7.3024
7.2875
6.1374
5.0249
4.4266
4.4123
4.3980
4.3837
2.4639
1.6005
1.5143
1.5000
1.4857
5a
1.00
1.21
2.90
1.21
2.81
1.00
2.29
1.97
3.31
9.33
3.15
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


163.17
144.59
143.42
141.29
141.20
135.85
131.30
129.44
128.74
126.73
126.23
123.10
115.11
114.07
108.64
61.18
55.74
52.10
28.89
21.66
14.12
O
O
O
S
O
N
N
N
NH
5a
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.2737
9.2608
9.2555
9.2428
7.6421
7.6259
7.3491
7.3443
7.3285
7.3230
7.3159
7.2997
7.2896
7.0948
7.0899
7.0770
7.0605
6.2099
5.0140
4.4138
4.3996
4.3853
4.3711
2.4711
1.5901
1.5085
1.4942
1.4800
5b
1.00
1.98
4.03
0.98
0.95
2.02
1.94
3.17
8.88
2.90
f1 (ppm)

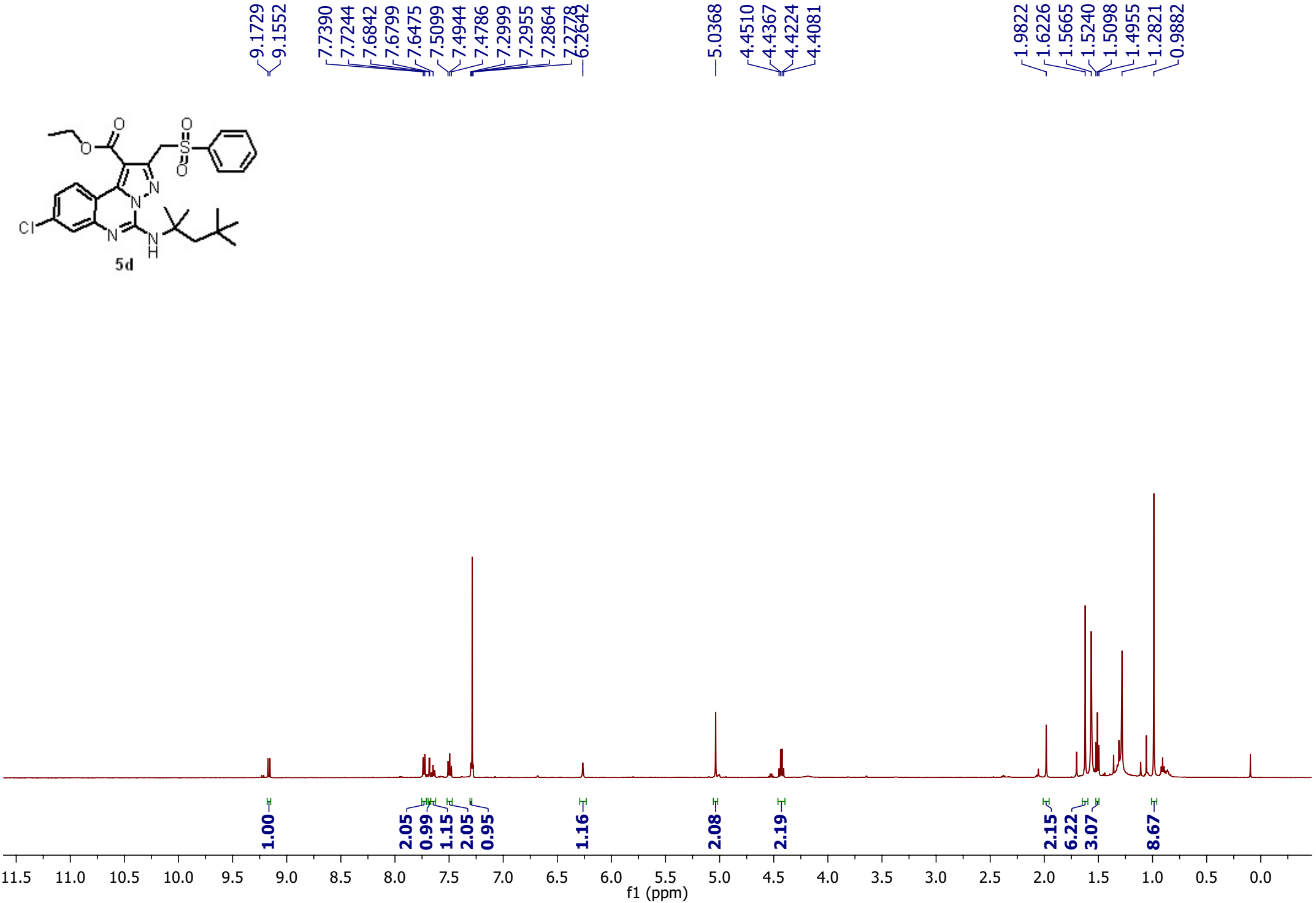

163.10
145.67
144.81
144.69
141.76
141.06
135.82
129.49
129.23
129.15
128.70
111.78
111.60
111.32
111.15
108.29
61.26
55.75
52.28
28.83
21.70
14.23
O
O
O
S
O
O
N
N
F
N
NH
5b
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

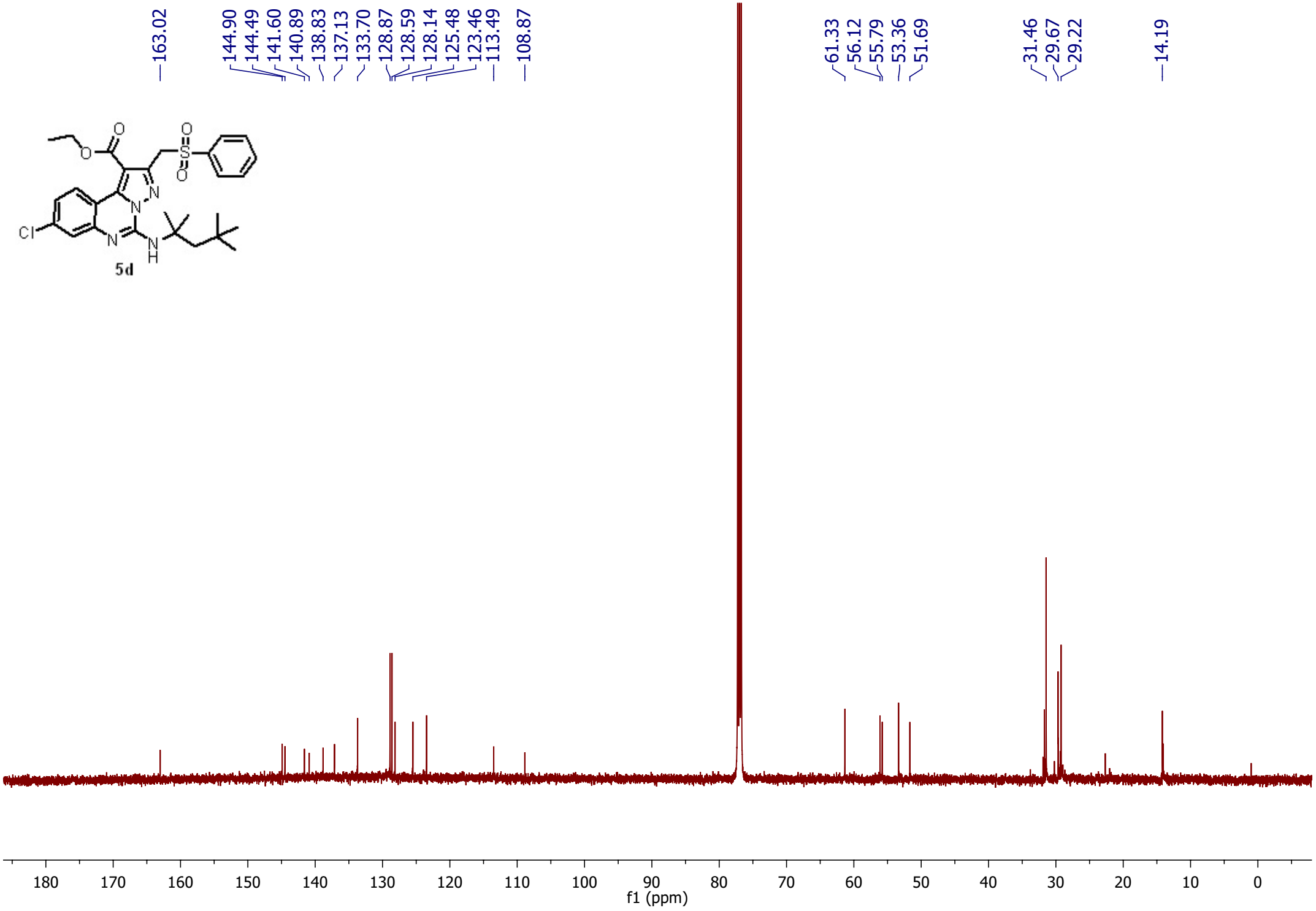

9.1790
9.1627
7.7317
7.7163
7.7016
7.6848
7.6450
7.6303
7.6150
7.5043
7.4893
7.4744
7.3490
7.2926
6.1928
5.0525
4.4570
4.4432
4.4290
4.4149
2.0022
1.6363
1.5337
1.5195
1.5055
0.9898
5c
1.00
3.23
1.78
2.32
1.38
1.00
2.27
2.37
2.33
5.94
3.30
8.91
f1 (ppm)


163.24
144.55
143.43
141.08
139.32
138.59
133.74
131.35
128.89
128.64
126.71
126.24
123.05
115.00
114.10
108.68
61.29
55.88
55.79
51.55
31.76
31.50
29.74
22.73
14.17
5c
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
O
S
O
N
N
Cl
N
N
H

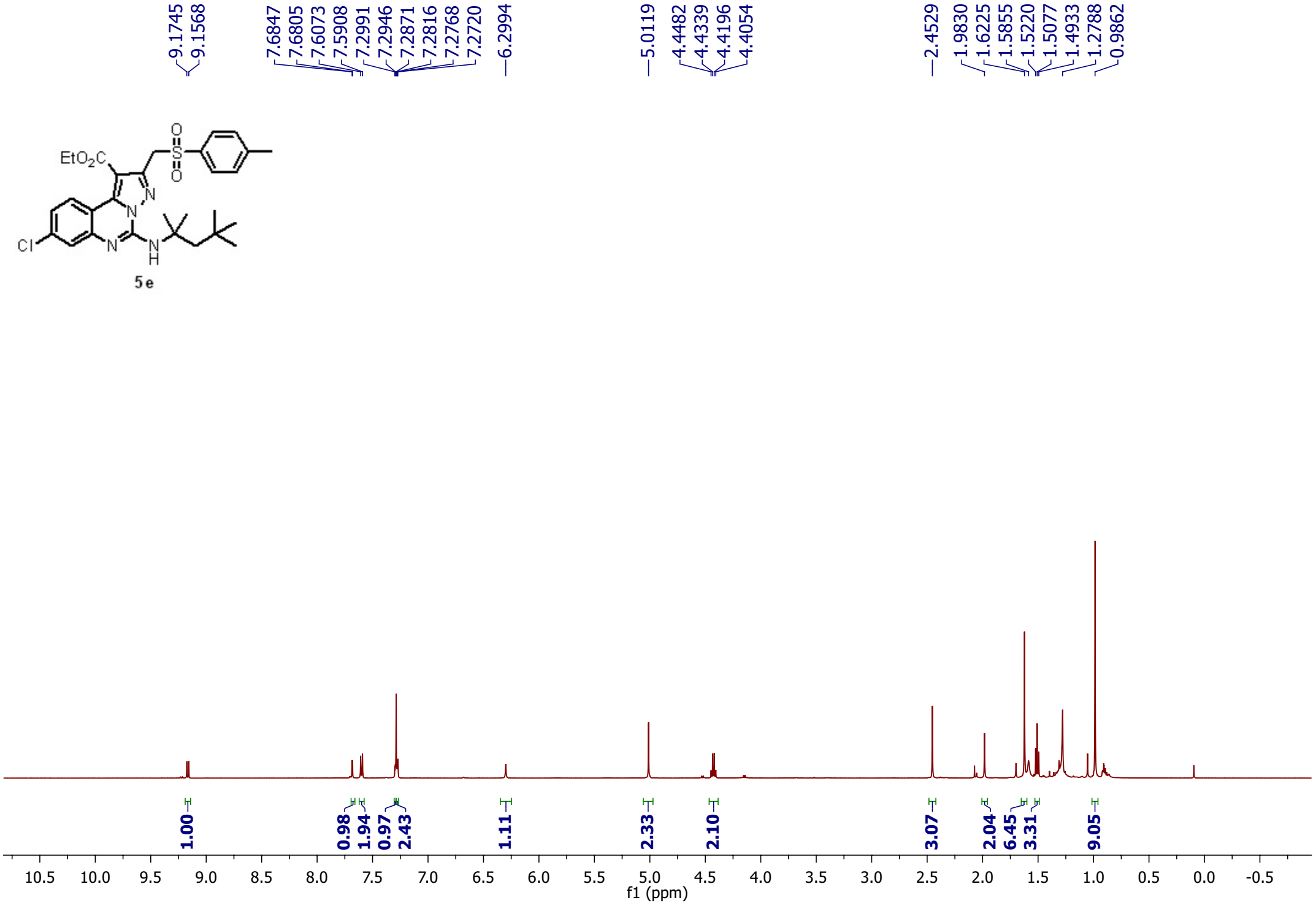
5d

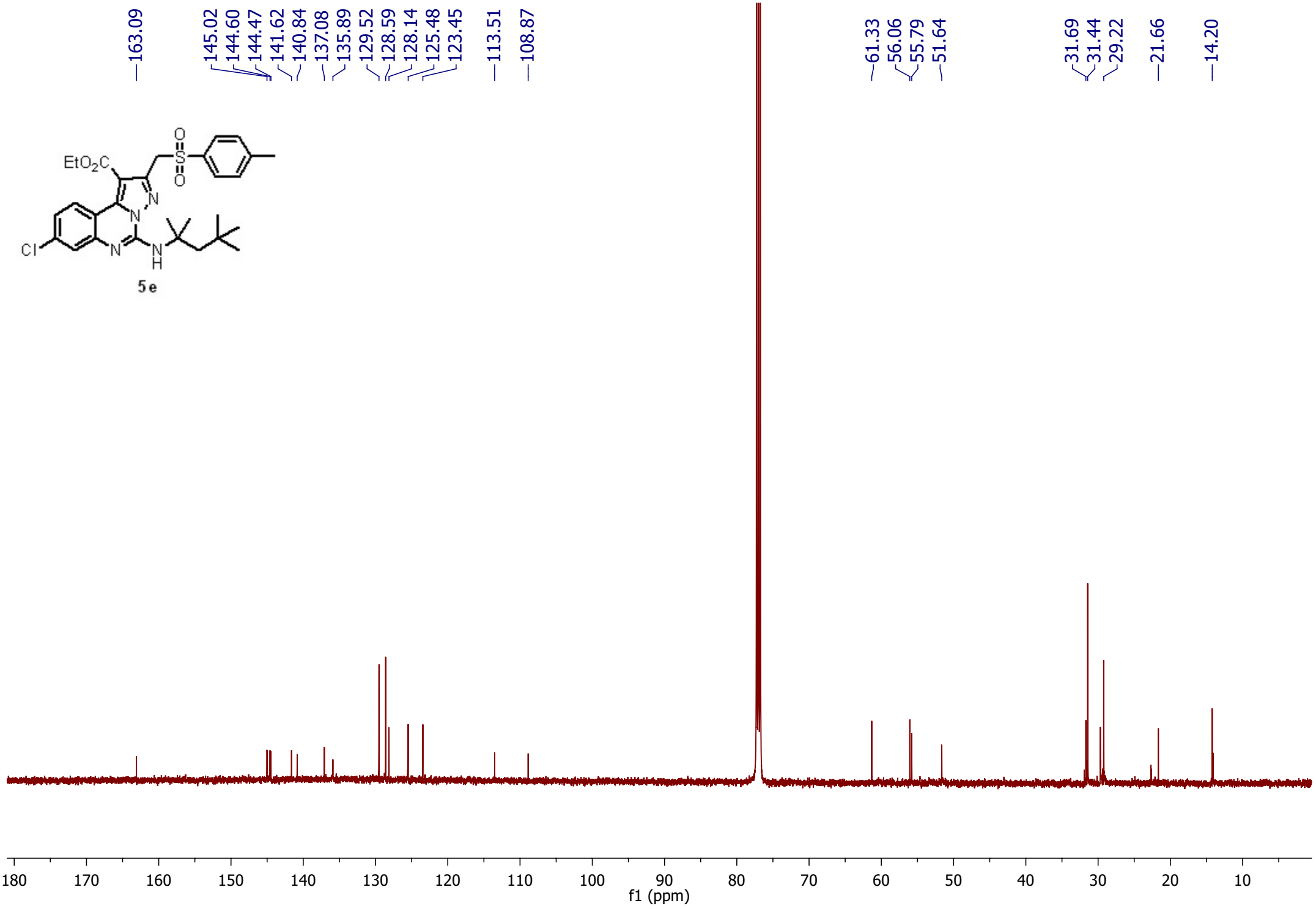

9.1729
9.1552
7.7390
7.7244
7.6842
7.6799
7.6475
7.5099
7.4944
7.4786
7.2999
7.2955
7.2864
7.2778
6.2642
5.0368
4.4510
4.4367
4.4224
4.4081
1.9822
1.6226
1.5665
1.5240
1.5098
1.4955
1.2821
0.9882
1.00
2.05
0.99
1.15
2.05
0.95
1.16
2.08
2.19
2.15
6.22
3.07
8.67
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
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
f1 (ppm)

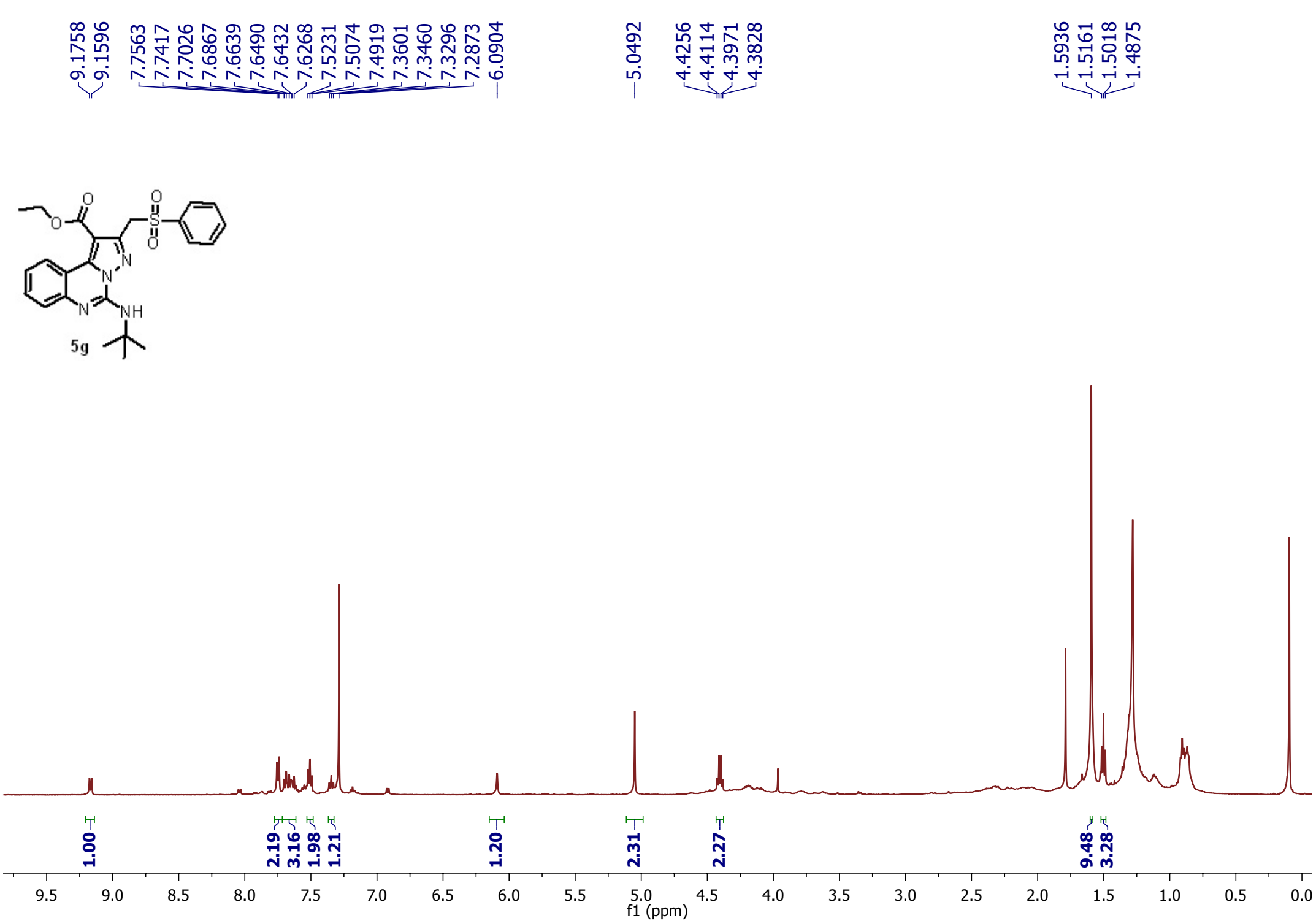

163.02
144.90
144.49
141.60
140.89
138.83
137.13
133.70
128.87
128.59
128.14
125.48
123.46
113.49
108.87
61.33
56.12
55.79
53.36
51.69
31.46
29.67
29.22
14.19
5d
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

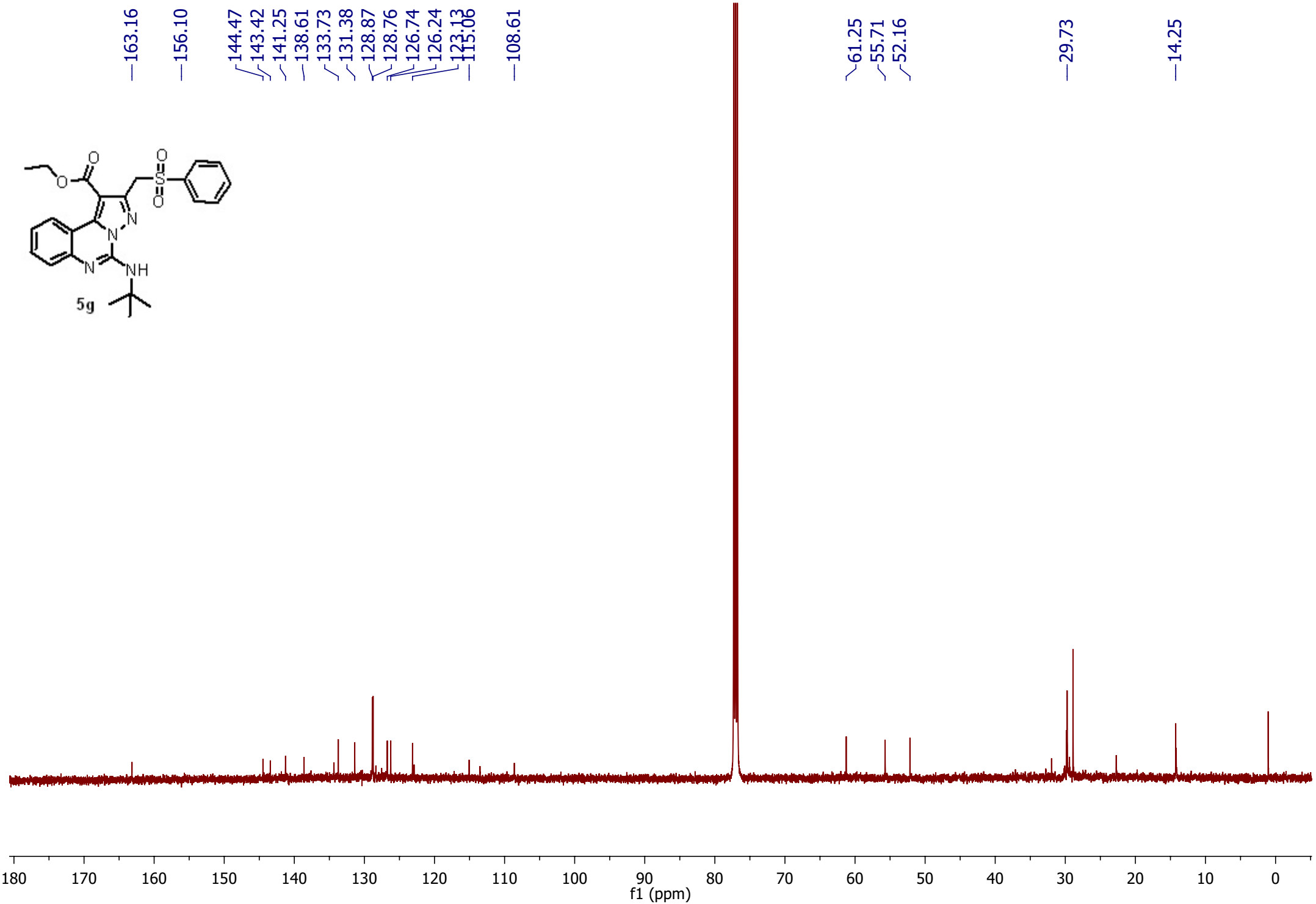
EtO2C
O
O
S
N
N
Cl
N
N
H

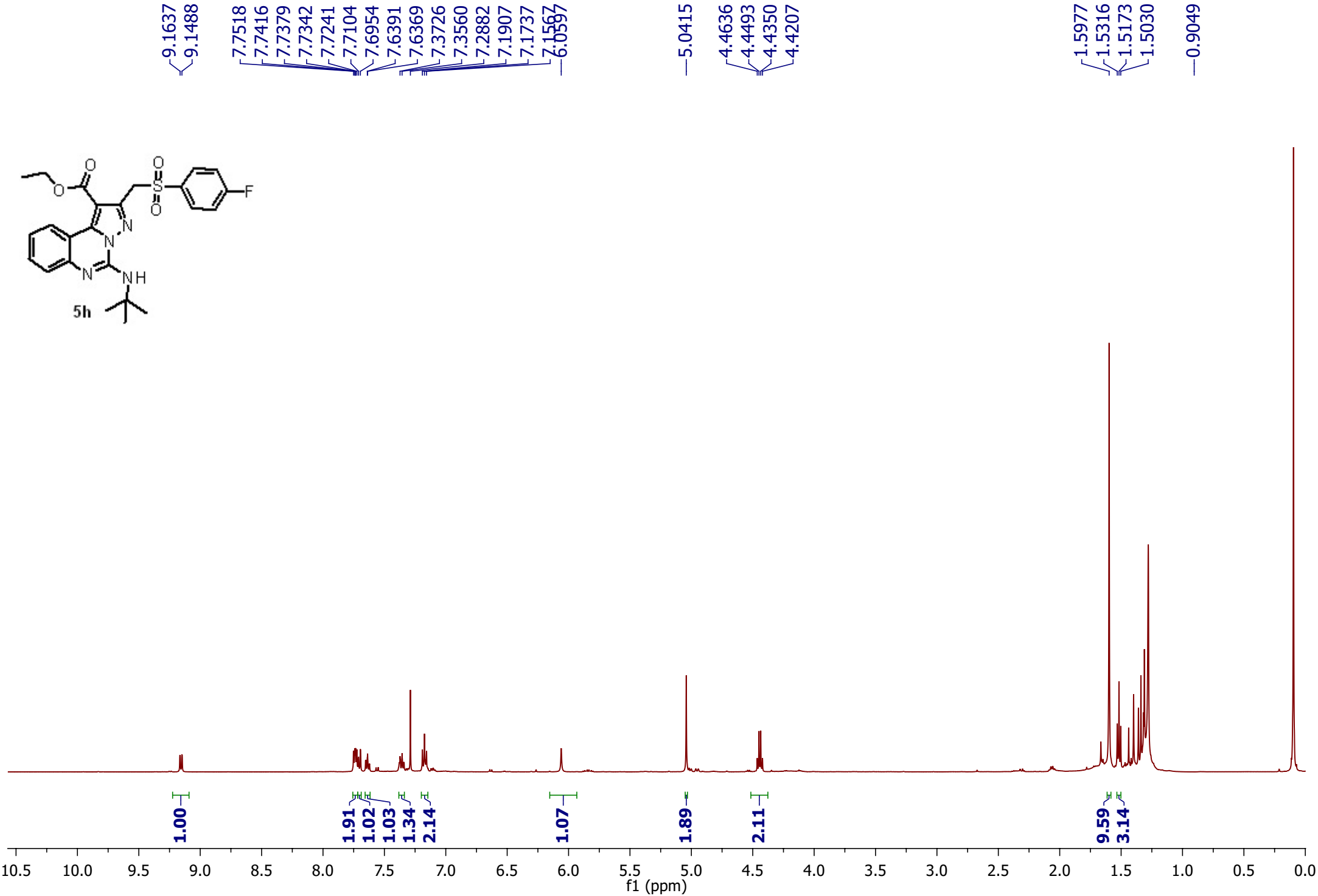
5e

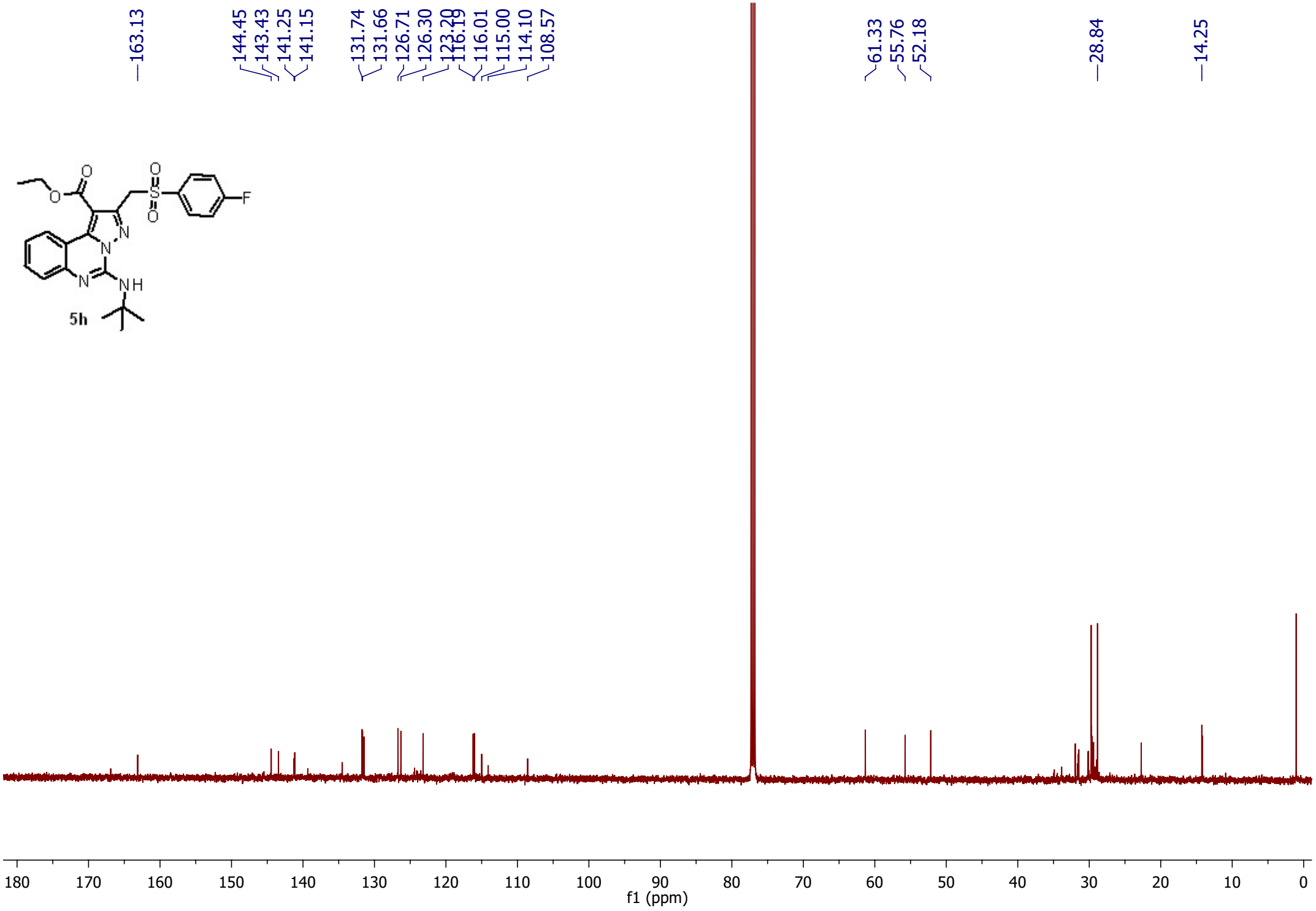

9.1745
9.1568
7.6847
7.6805
7.6073
7.5908
7.2991
7.2946
7.2871
7.2816
7.2768
7.2720
6.2994
5.0119
4.4482
4.4339
4.4196
4.4054
2.4529
1.9830
1.6225
1.5855
1.5220
1.5077
1.4933
1.2788
0.9862
1.00
0.98
1.94
0.97
2.43
1.11
2.33
2.10
3.07
2.04
6.45
3.31
9.05
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

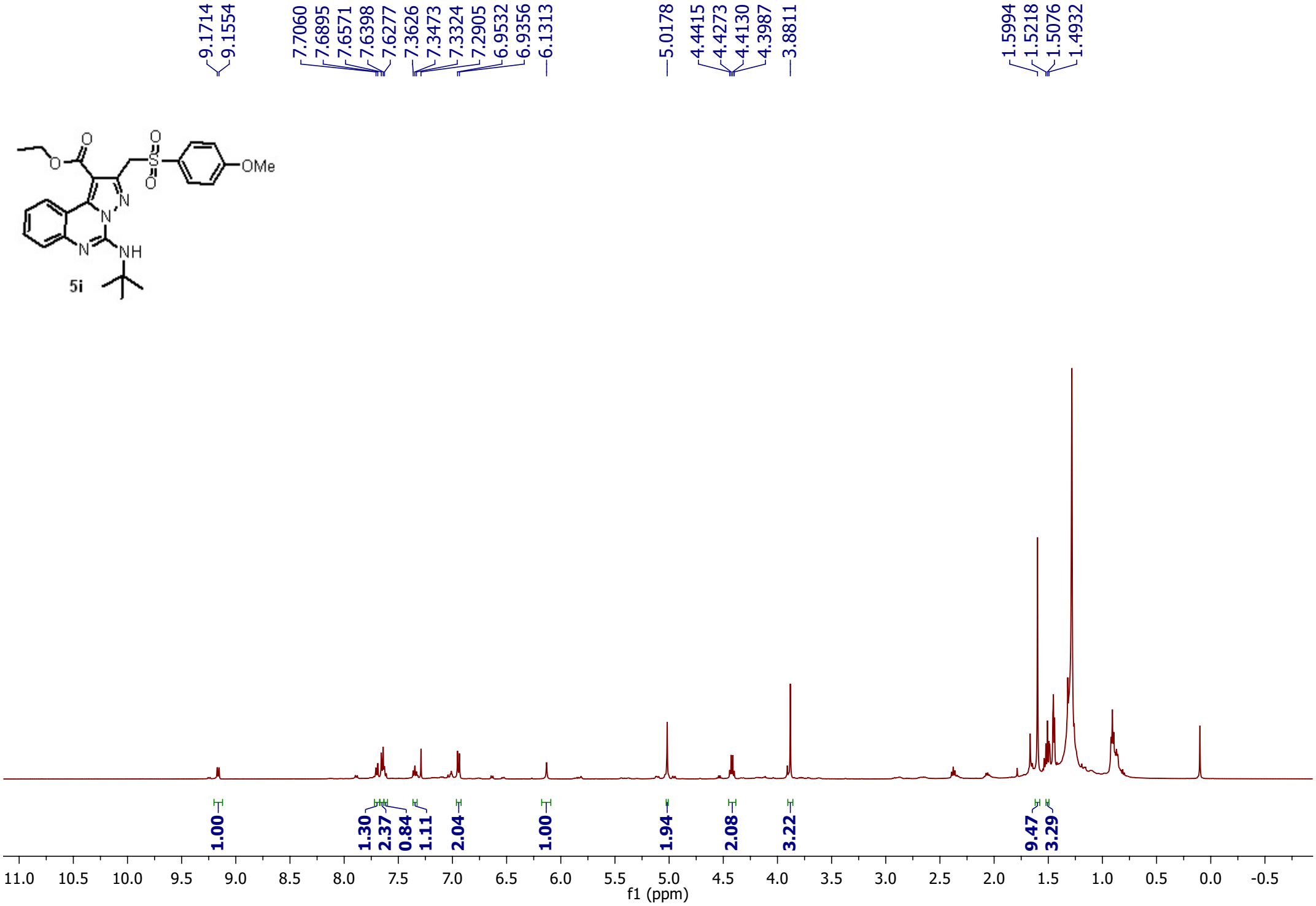

163.09
145.02
144.60
144.47
141.62
140.84
137.08
135.89
129.52
128.59
128.14
125.48
123.45
113.51
108.87
61.33
56.06
55.79
51.64
31.69
31.44
29.22
21.66
14.20
EtO2C
Cl
N
N
N
N
H
O
S
O
5e
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

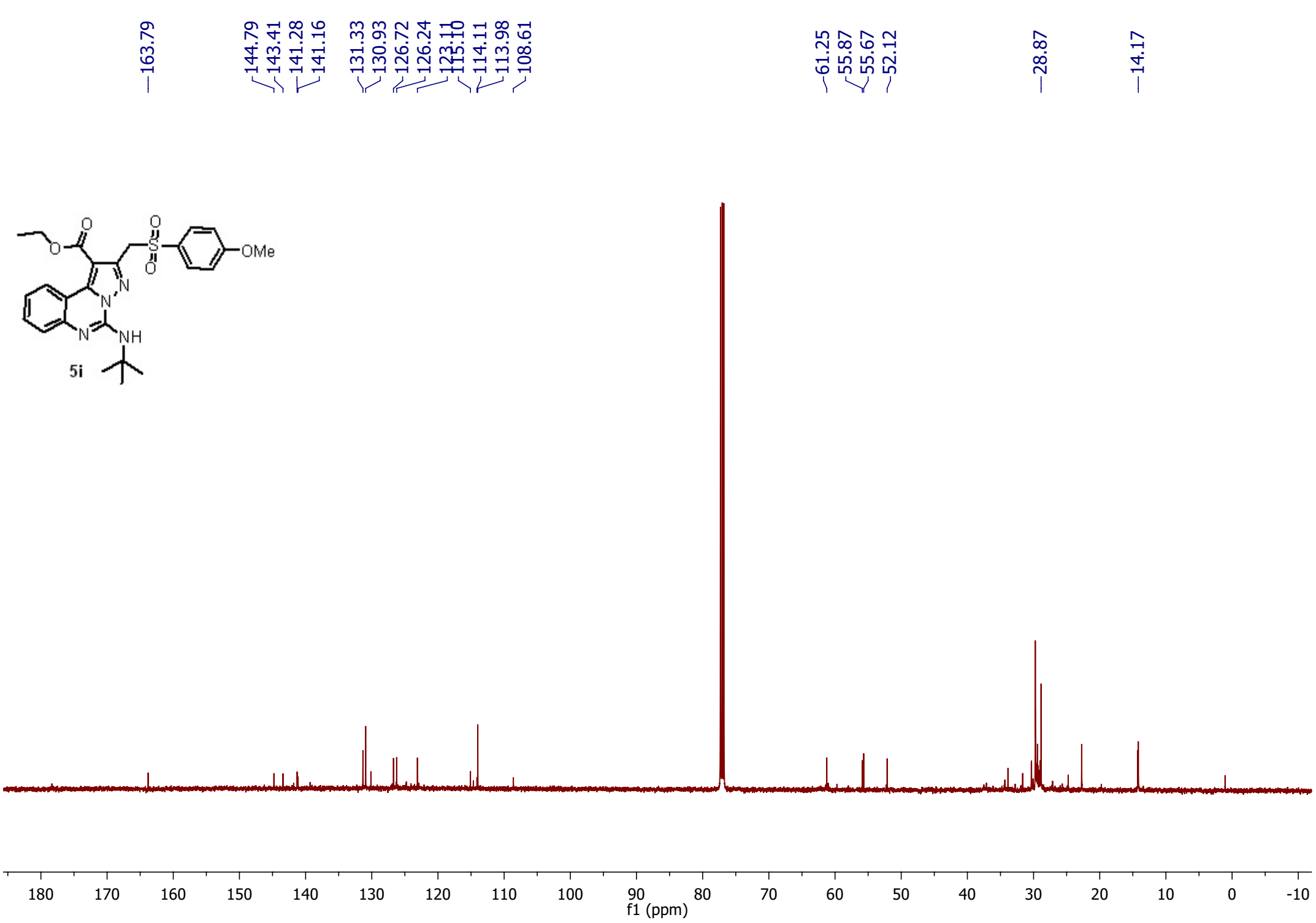

9.1758
9.1596
7.7563
7.7417
7.7026
7.6867
7.6639
7.6490
7.6432
7.6268
7.5231
7.5074
7.4919
7.3601
7.3460
7.3296
7.2873
6.0904
5.0492
4.4256
4.4114
4.3971
4.3828
1.5936
1.5161
1.5018
1.4875
5g
1.00
2.19
3.16
1.98
1.21
1.20
2.31
2.27
9.48
3.28
f1 (ppm)


163.16
156.10
144.47
143.42
141.25
138.61
133.73
131.38
128.87
128.76
126.74
126.24
123.13
115.06
108.61
61.25
55.71
52.16
29.73
14.25
O
O
O
O
S
N
N
N
NH
5g
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.1637
9.1488
7.7518
7.7416
7.7379
7.7342
7.7241
7.7104
7.6954
7.6391
7.6369
7.3726
7.3560
7.2882
7.1907
7.1737
7.1567
6.0597
5.0415
4.4636
4.4493
4.4350
4.4207
1.5977
1.5316
1.5173
1.5030
0.9049
5h
1.00
1.91
1.02
1.03
1.34
2.14
1.07
1.89
2.11
9.59
3.14
f1 (ppm)

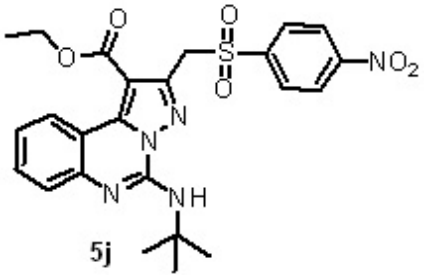

163.13
144.45
143.43
141.25
141.15
131.74
131.66
126.71
126.30
123.20
116.19
116.01
115.00
114.10
108.57
61.33
55.76
52.18
28.84
14.25
5h
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.1714
9.1554
7.7060
7.6895
7.6571
7.6398
7.6277
7.3626
7.3473
7.3324
7.2905
6.9532
6.9356
6.1313
5.0178
4.4415
4.4273
4.4130
4.3987
3.8811
1.5994
1.5218
1.5076
1.4932
OMe
NH
5i
1.00
1.30
2.37
0.84
1.11
2.04
1.00
1.94
2.08
3.22
9.47
3.29
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)

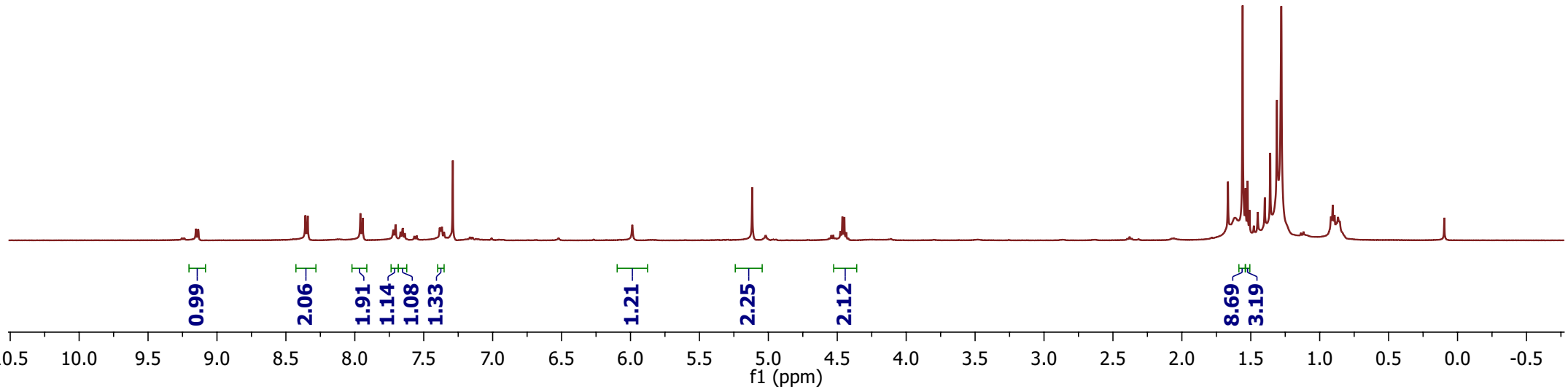

163.79
144.79
143.41
141.28
141.16
131.33
130.93
126.72
126.24
123.11
115.10
114.11
113.98
108.61
61.25
55.87
55.67
52.12
28.87
14.17
OMe
NH
5i
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

DS-AJA02-088
DMS-AJA02-088

9.1526
9.1361
8.3586
8.3411
7.9596
7.9422
7.7211
7.7047
7.6683
7.6520
7.3843
7.3817
7.3679
7.3537
7.2890
5.9869
5.1167
4.4769
4.4626
4.4483
4.4341
1.5590
1.5374
1.5229
1.5086

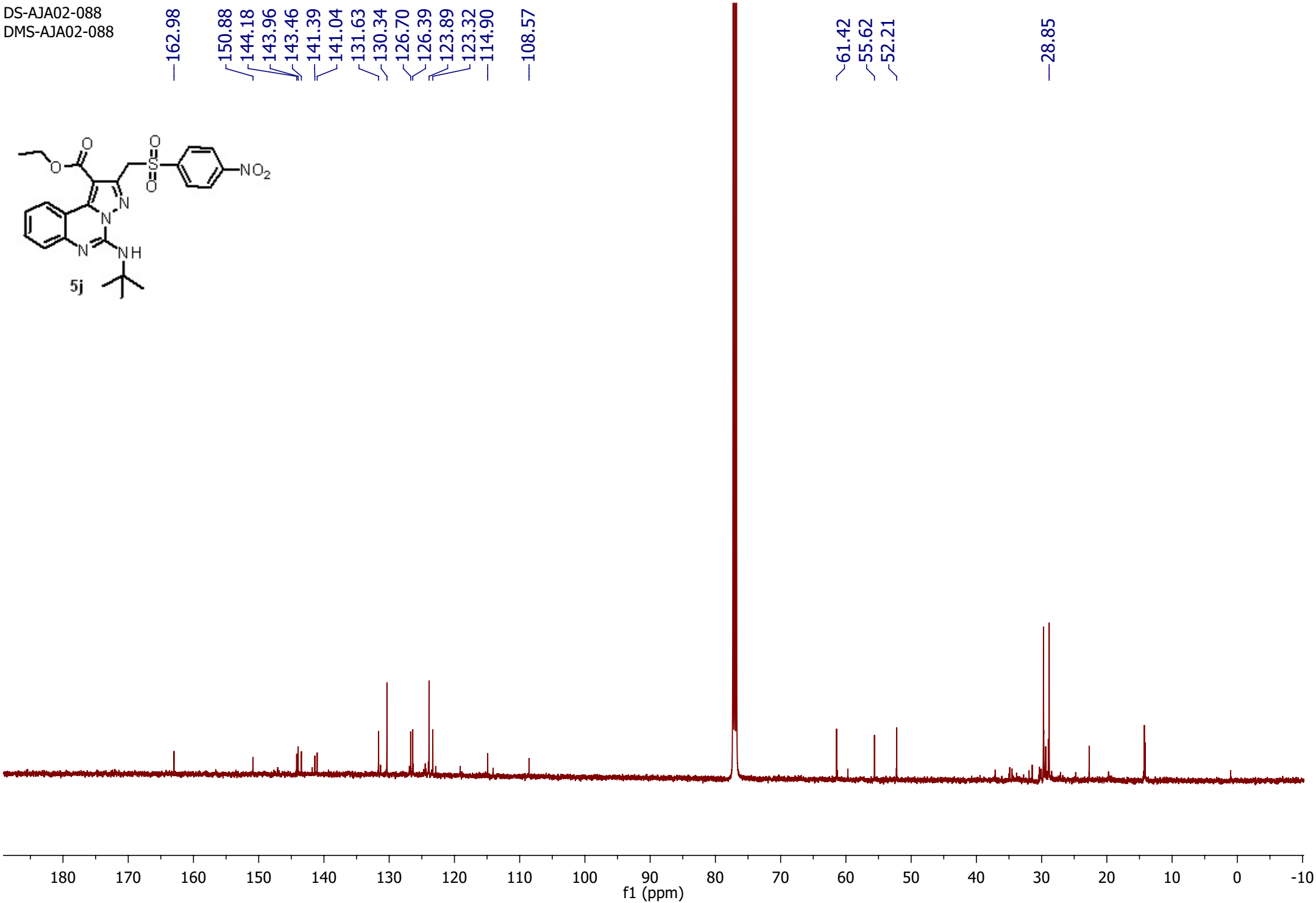


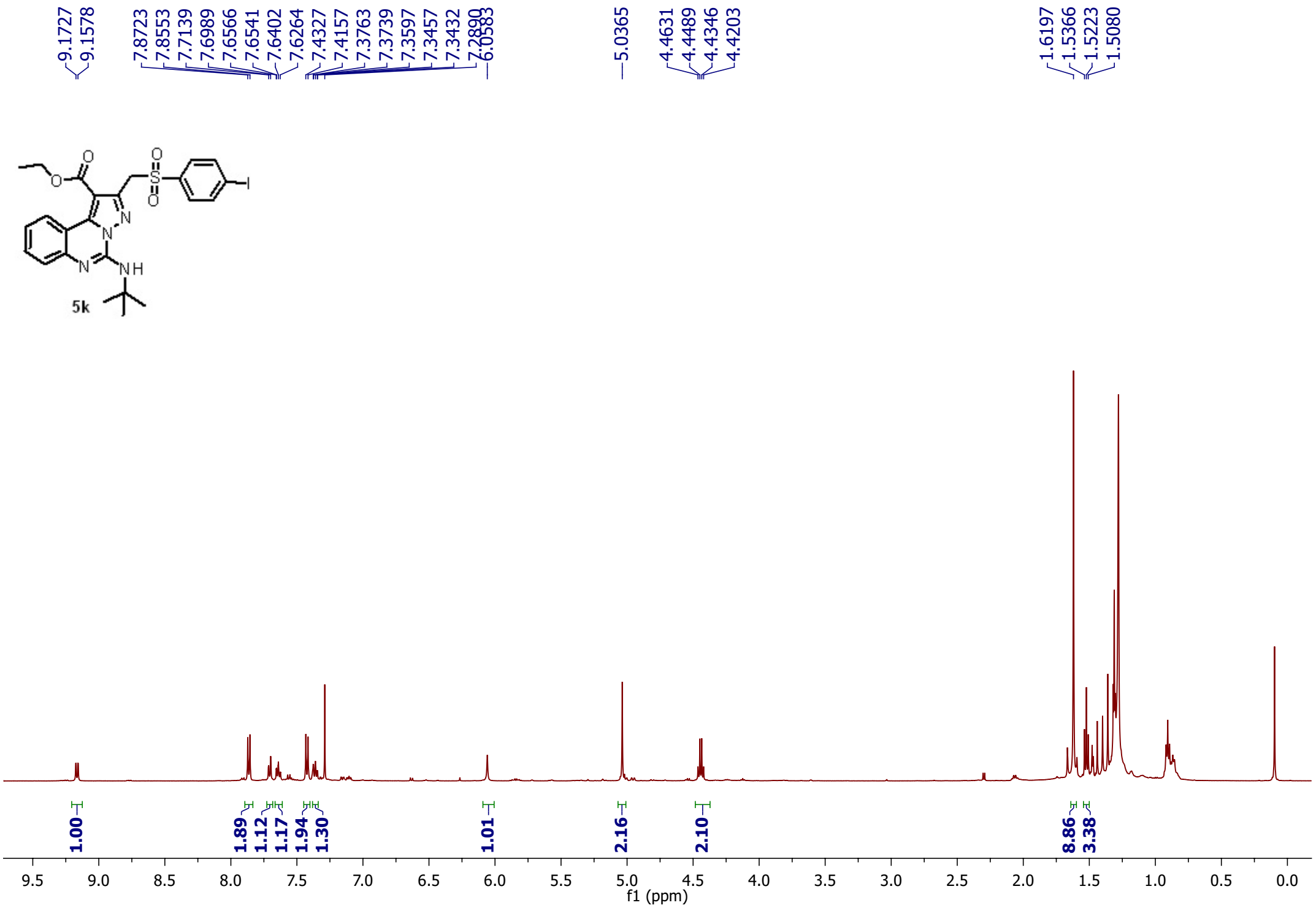
5j

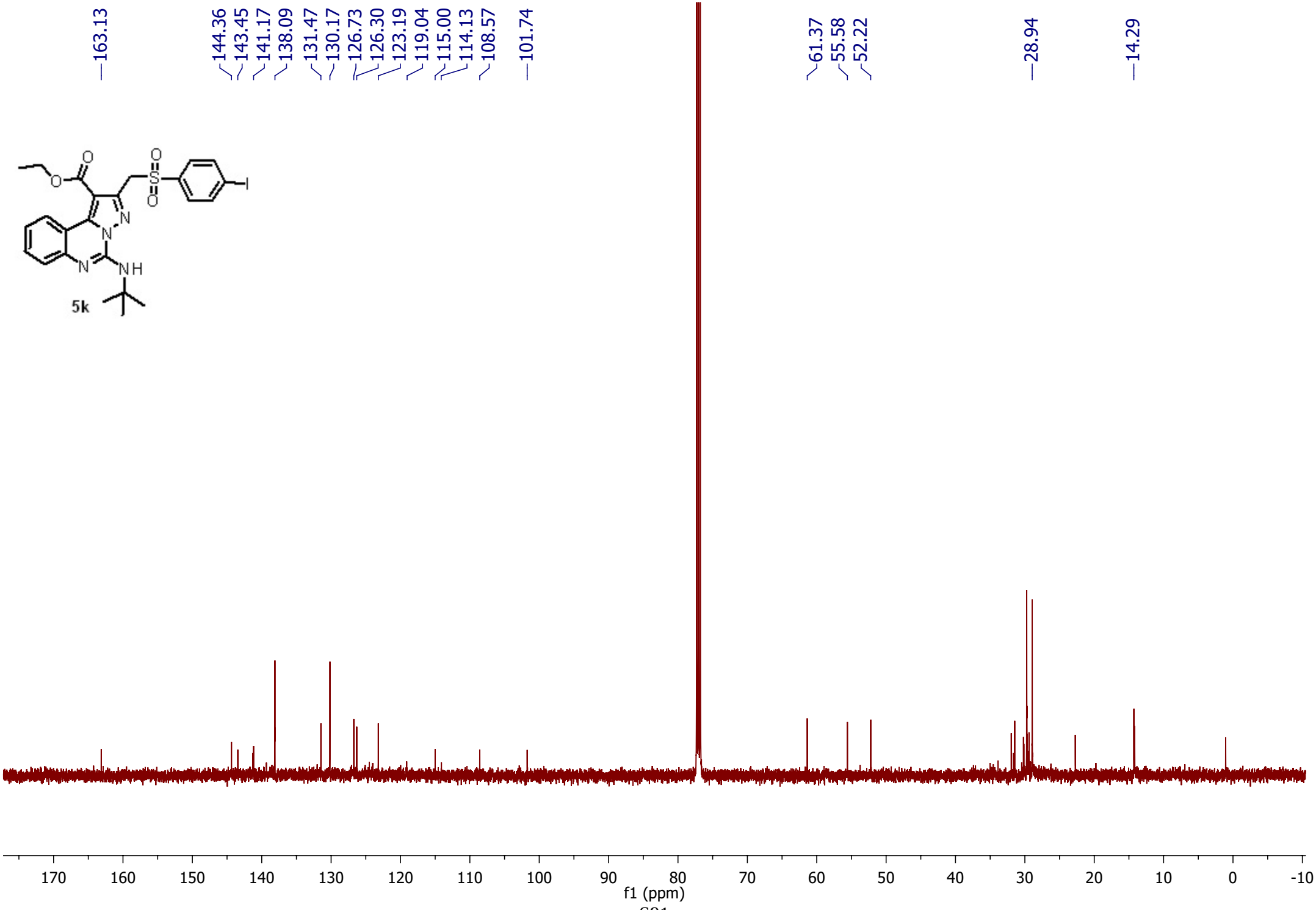


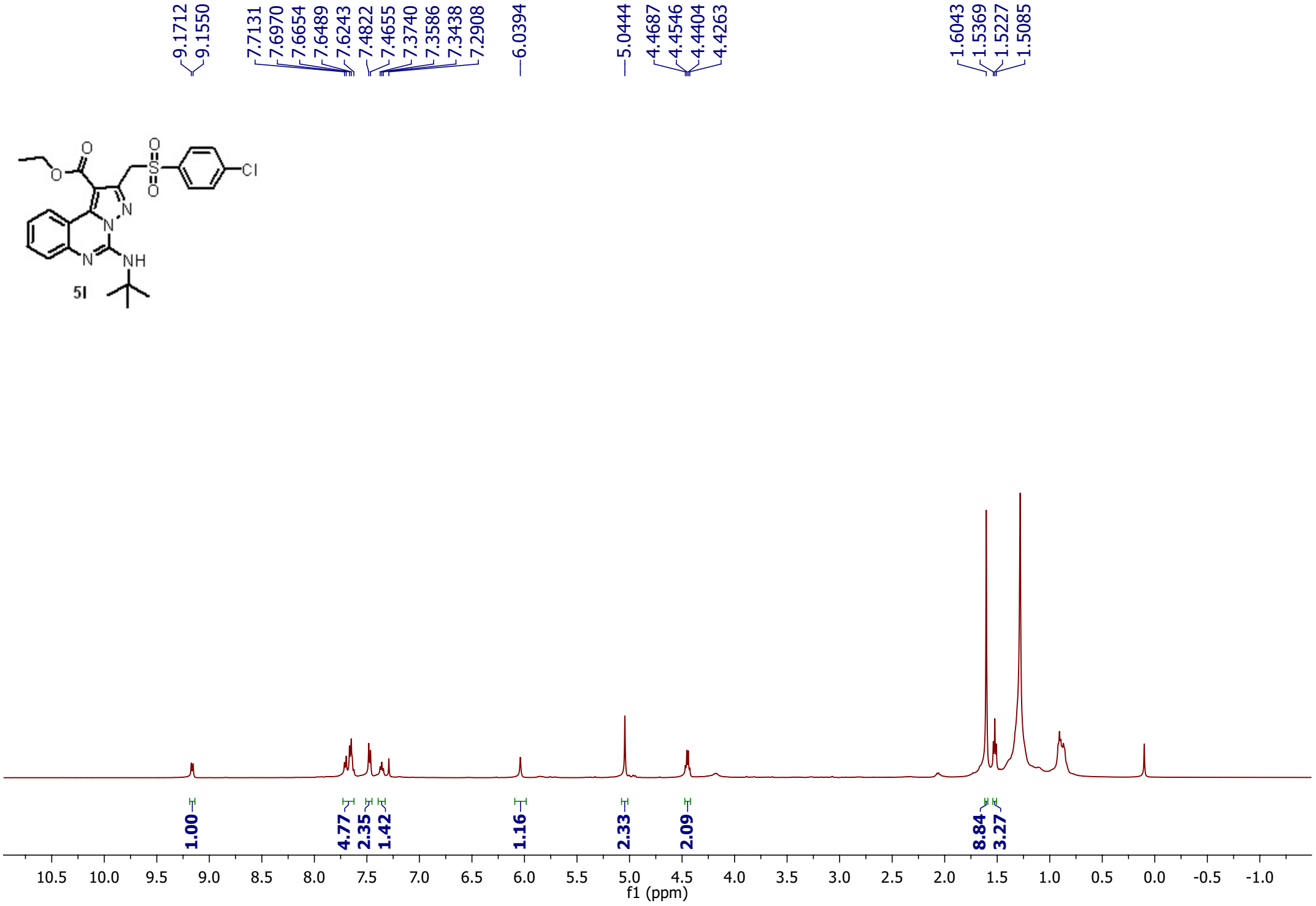
DS-AJA02-088
DMS-AJA02-088

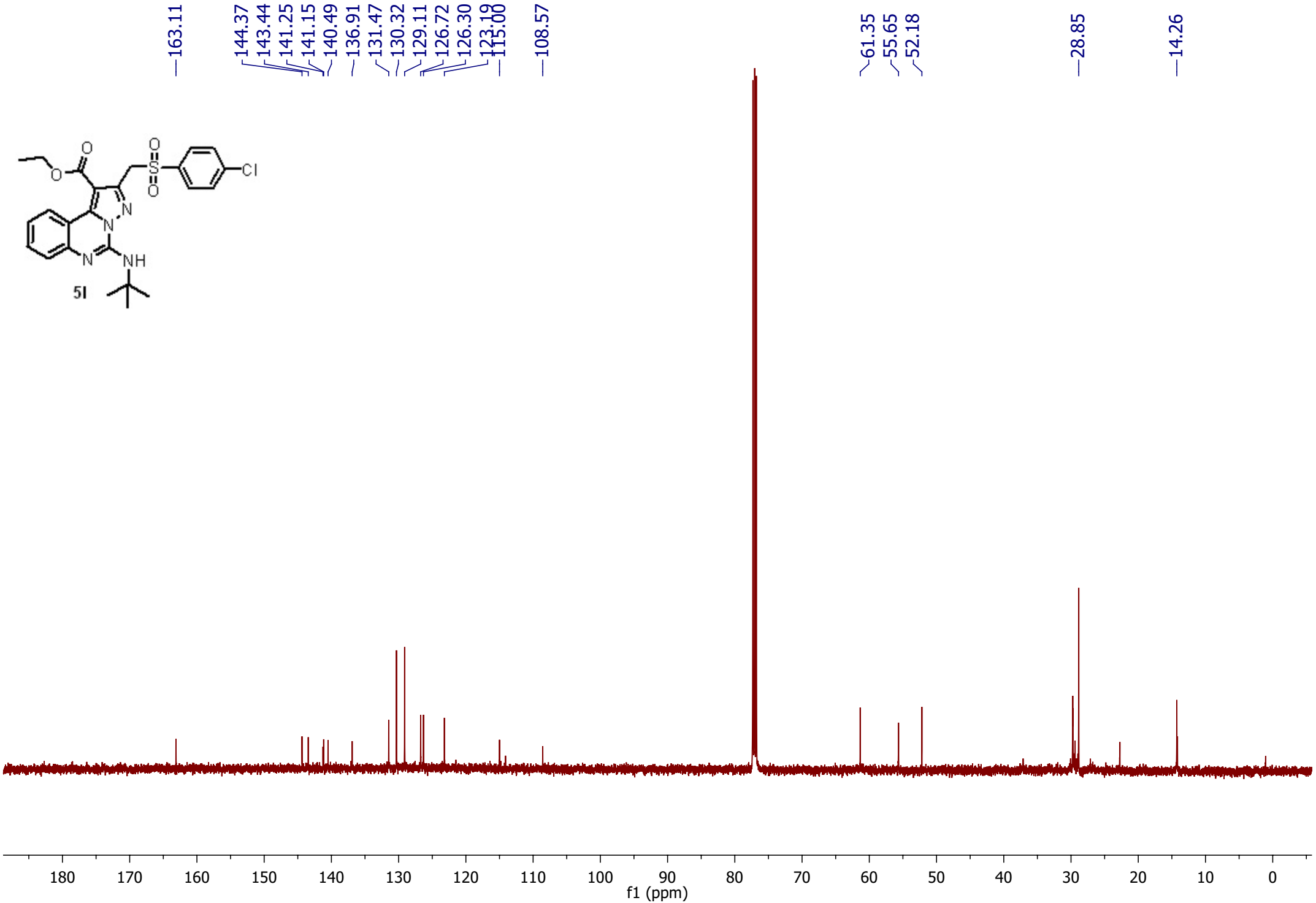
5j

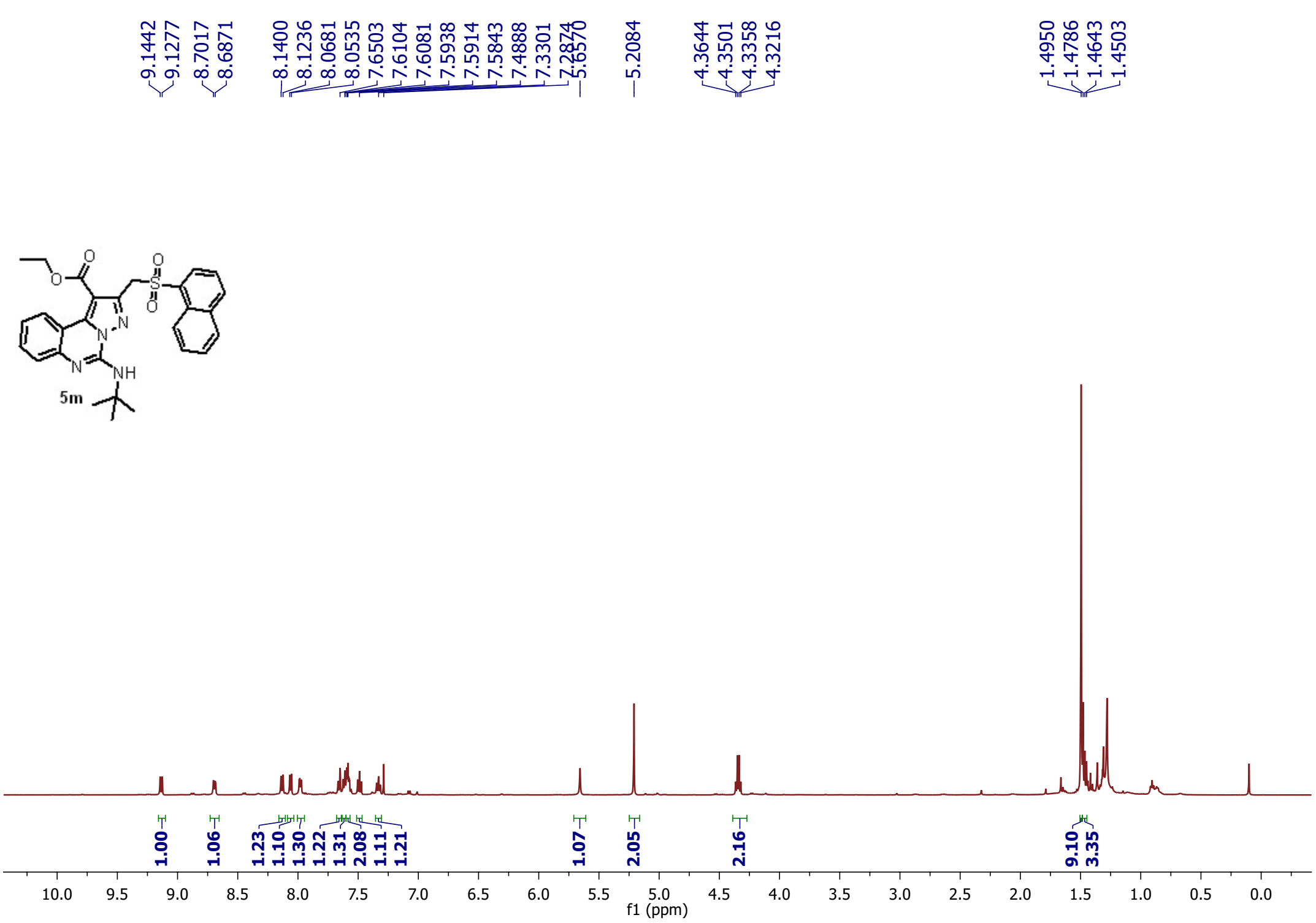


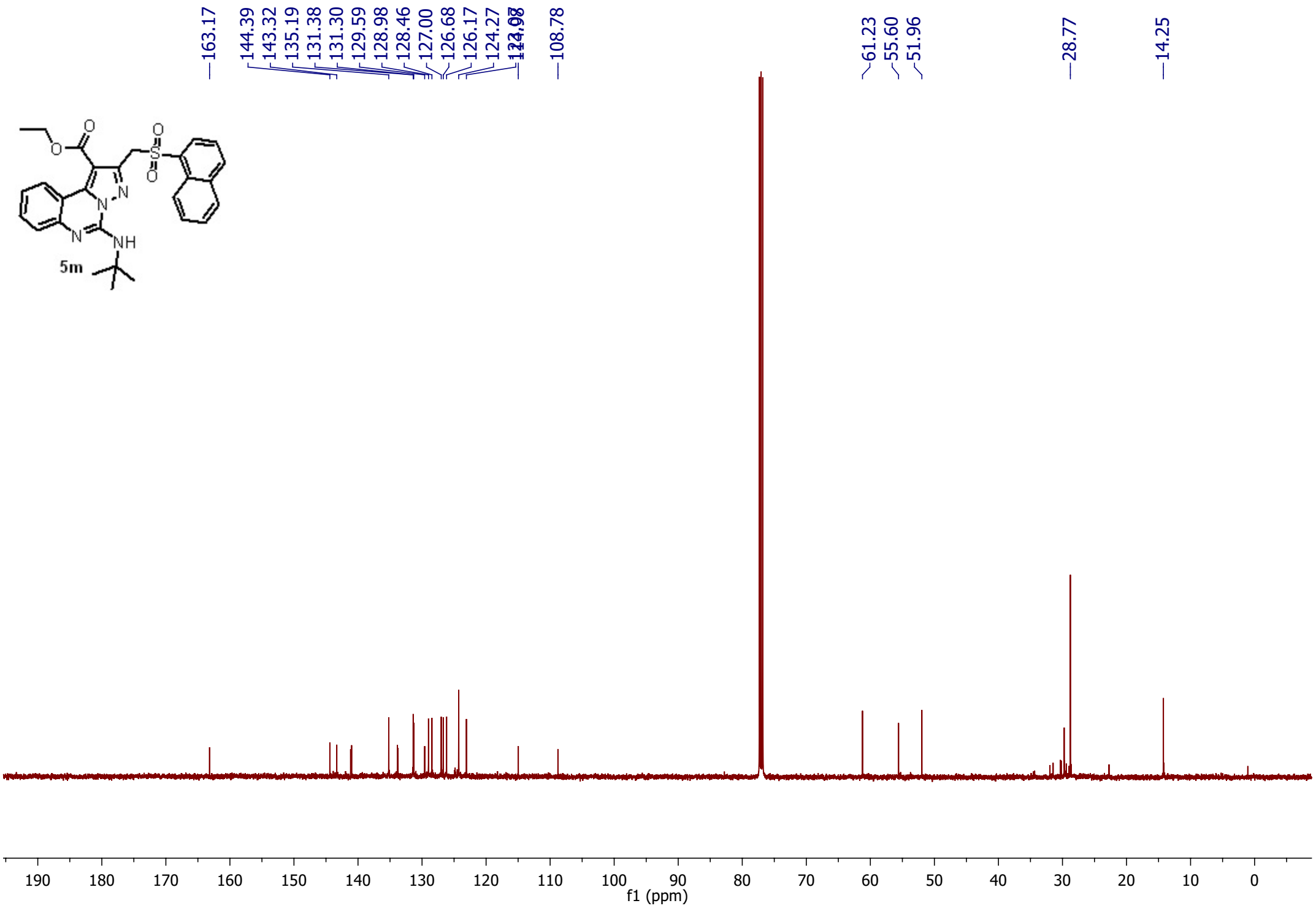

9.1727
9.1578
7.8723
7.8553
7.7139
7.6989
7.6566
7.6541
7.6402
7.6264
7.4327
7.4157
7.3763
7.3739
7.3597
7.3457
7.3432
7.2890
6.0583
5.0365
4.4631
4.4489
4.4346
4.4203
1.6197
1.5366
1.5223
1.5080
5k
1.00
1.89
1.12
1.17
1.94
1.30
1.01
2.16
2.10
8.86
3.38
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

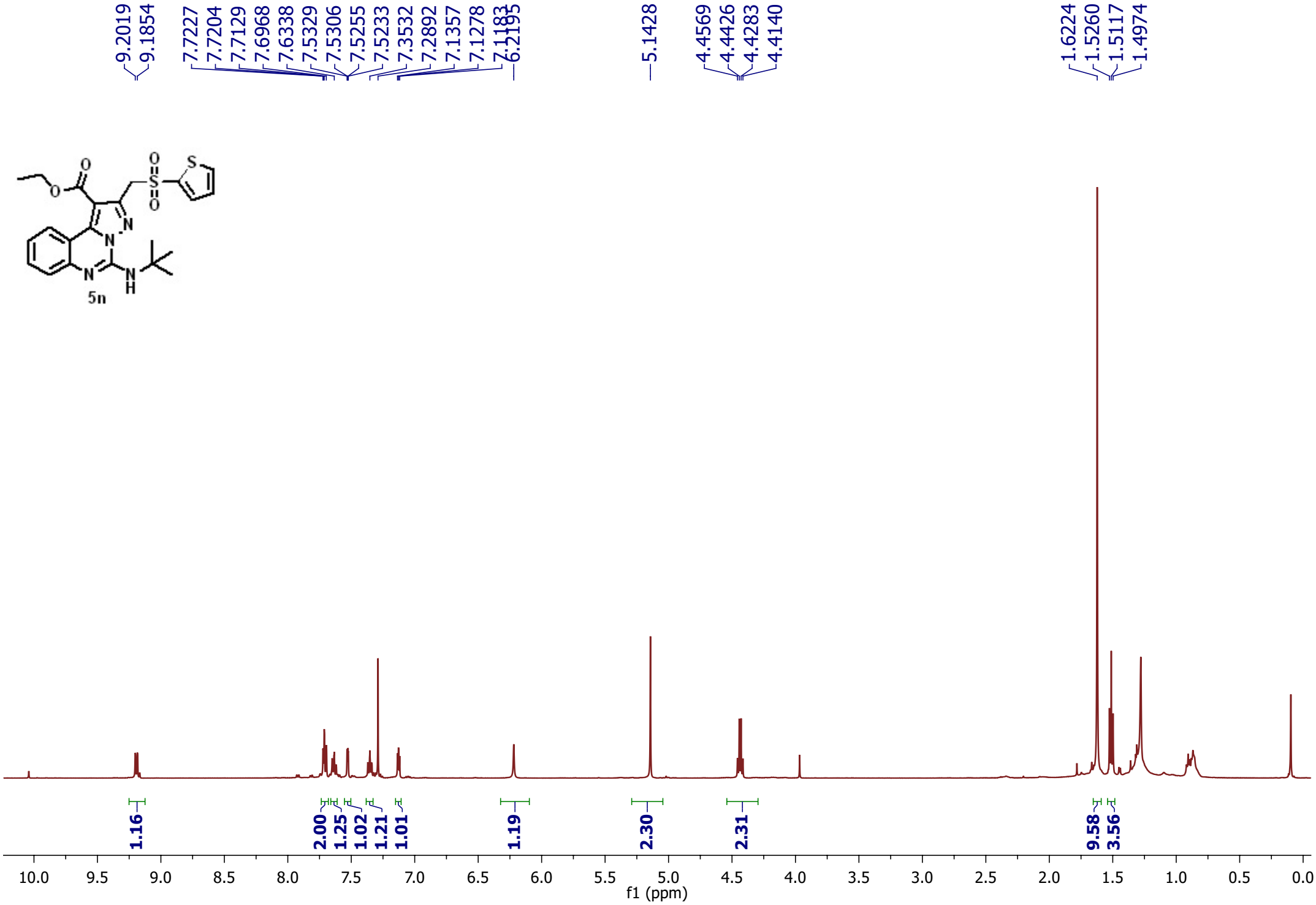

163.13
144.36
143.45
141.17
138.09
131.47
130.17
126.73
126.30
123.19
119.04
115.00
114.13
108.57
101.74
61.37
55.58
52.22
28.94
14.29
5k
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

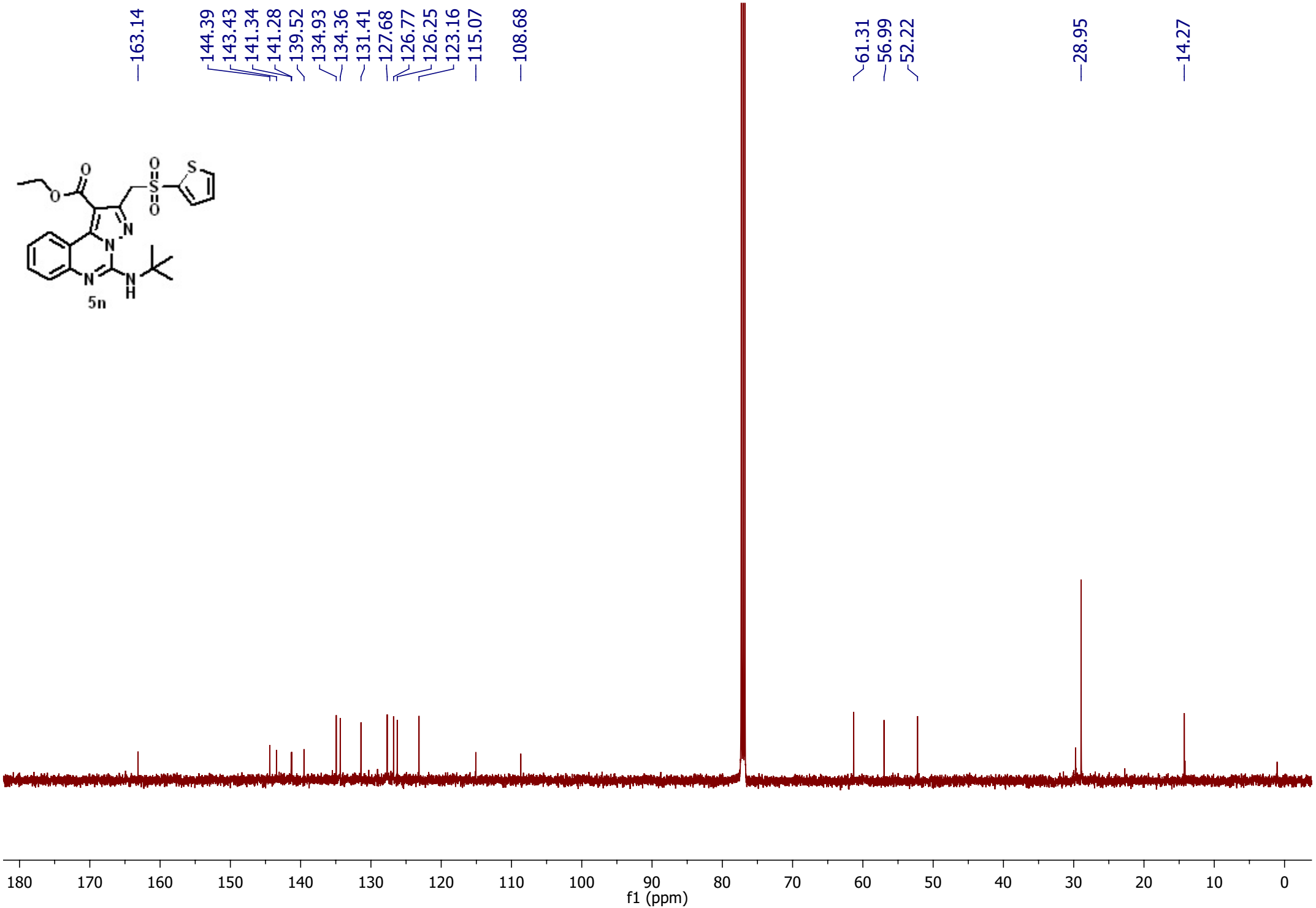

9.1712
9.1550
7.7131
7.6970
7.6654
7.6489
7.6243
7.4822
7.4655
7.3740
7.3586
7.3438
7.2908
6.0394
5.0444
4.4687
4.4546
4.4404
4.4263
1.6043
1.5369
1.5227
1.5085
O
O
O
S
O
Cl
N
N
N
NH
5l
1.00
4.77
2.35
1.42
1.16
2.33
2.09
8.84
3.27
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

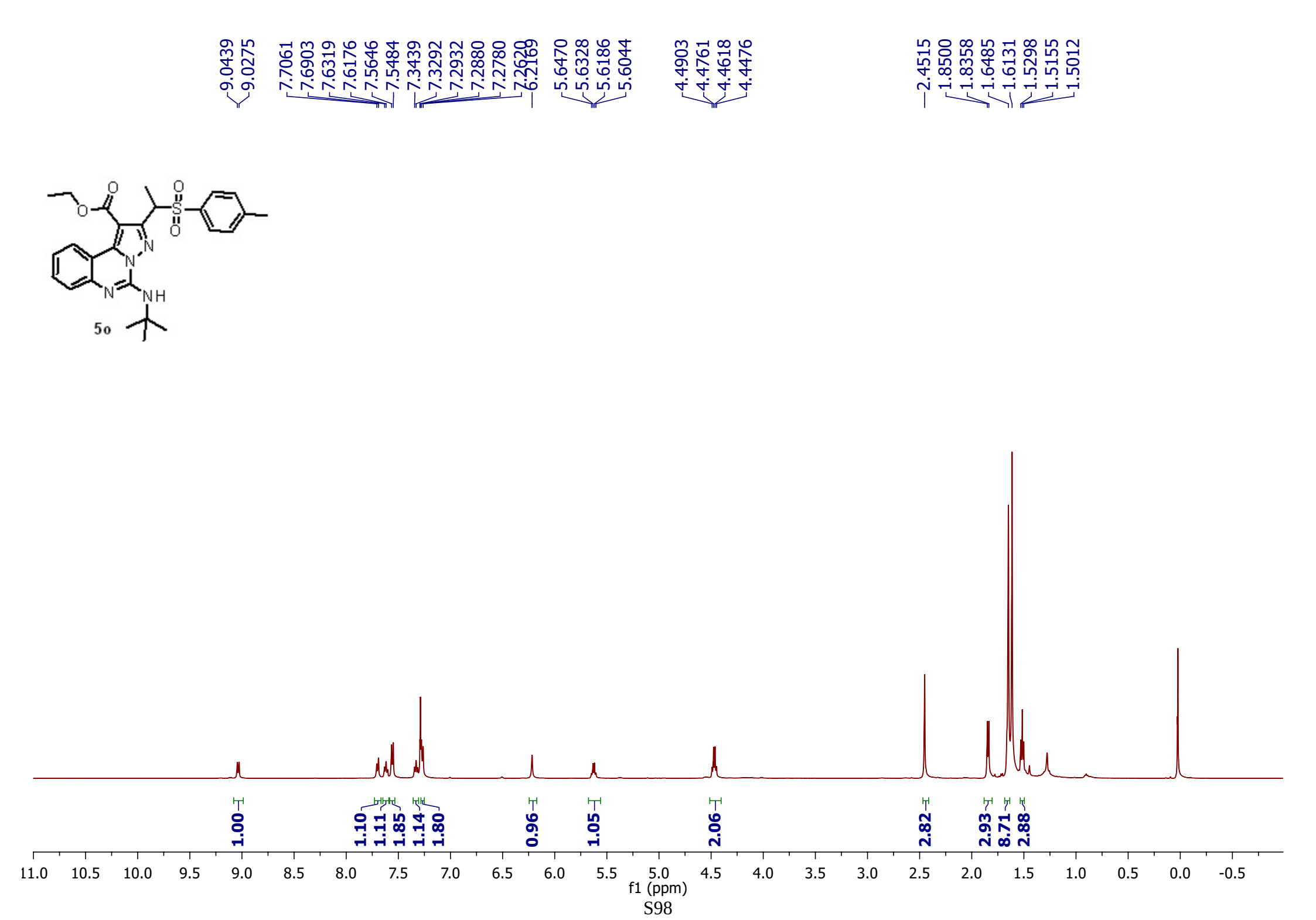

163.11
144.37
143.44
141.25
141.15
140.49
136.91
131.47
130.32
129.11
126.72
126.30
123.19
115.00
108.57
61.35
55.65
52.18
28.85
14.26
O
O
O
S
O
Cl
N
N
N
NH
5l
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

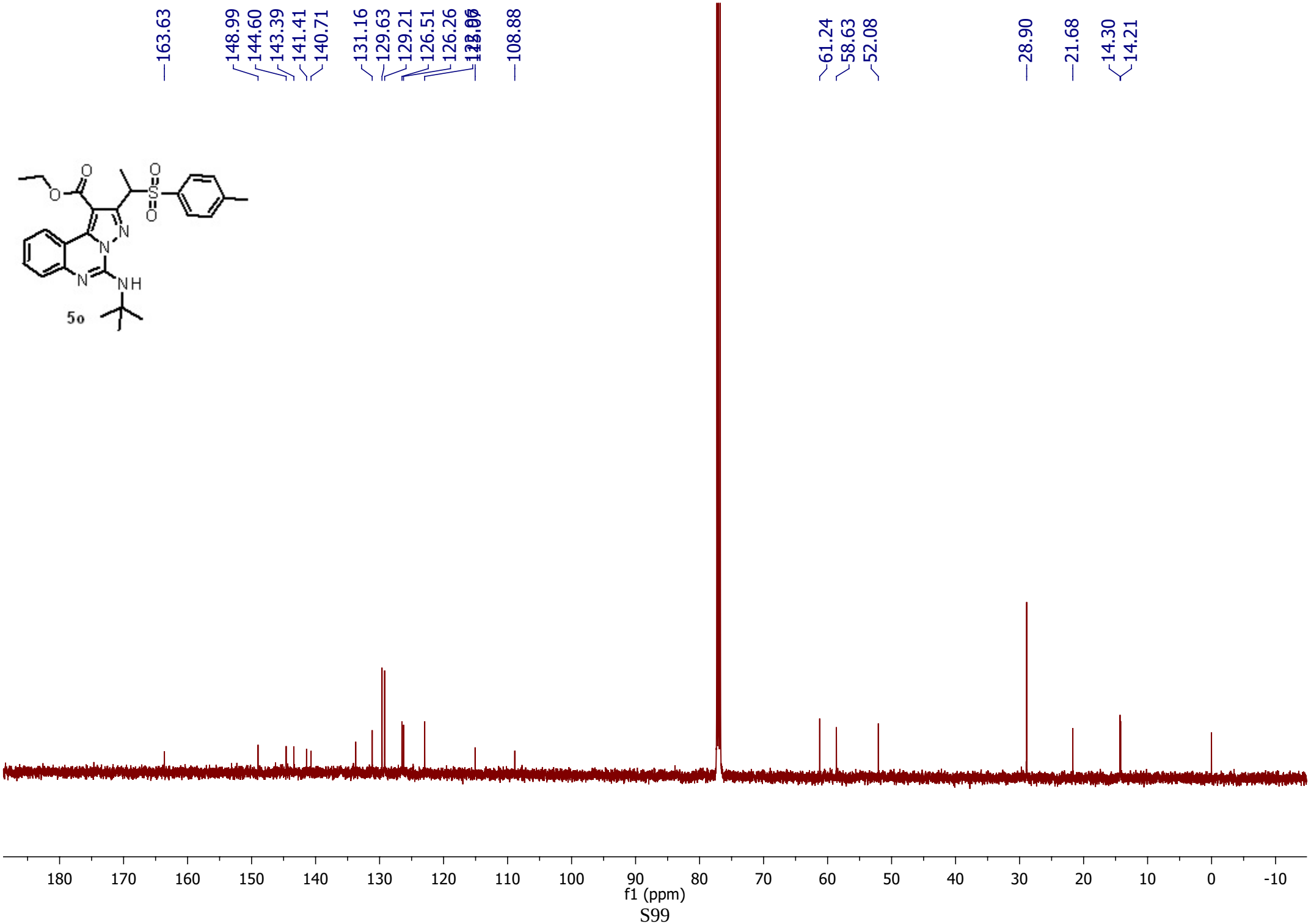

9.1442
9.1277
8.7017
8.6871
8.1400
8.1236
8.0681
8.0535
7.6503
7.6104
7.6081
7.5938
7.5914
7.5843
7.4888
7.3301
7.2874
5.6570
5.2084
4.3644
4.3501
4.3358
4.3216
1.4950
1.4786
1.4643
1.4503
5m
1.00
1.06
1.23
1.10
1.30
1.22
1.31
2.08
1.11
1.21
1.07
2.05
2.16
9.10
3.35
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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)

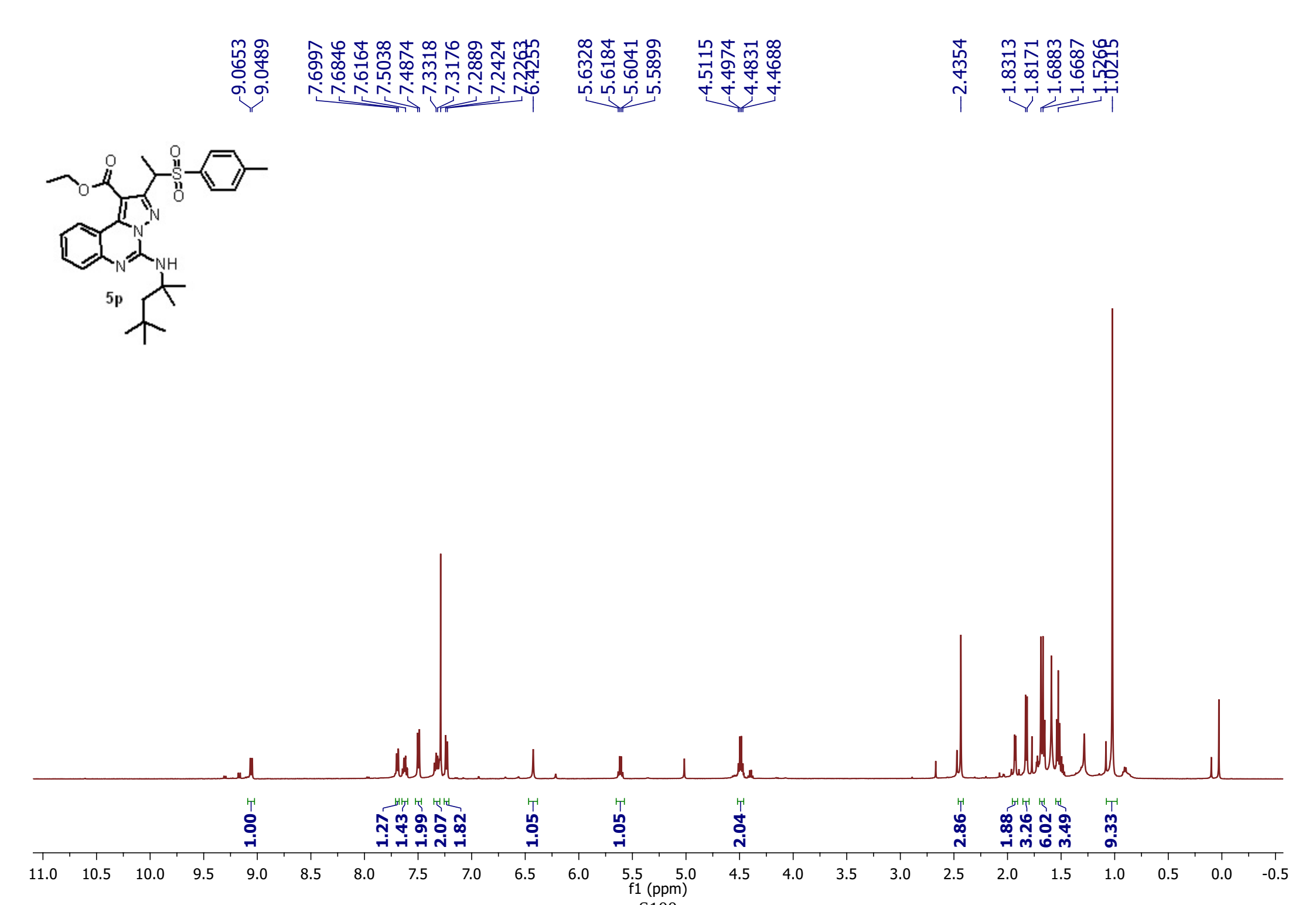

163.17
144.39
143.32
135.19
131.38
131.30
129.59
128.98
128.46
127.00
126.68
126.17
124.27
108.78
61.23
55.60
51.96
28.77
14.25
5m
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

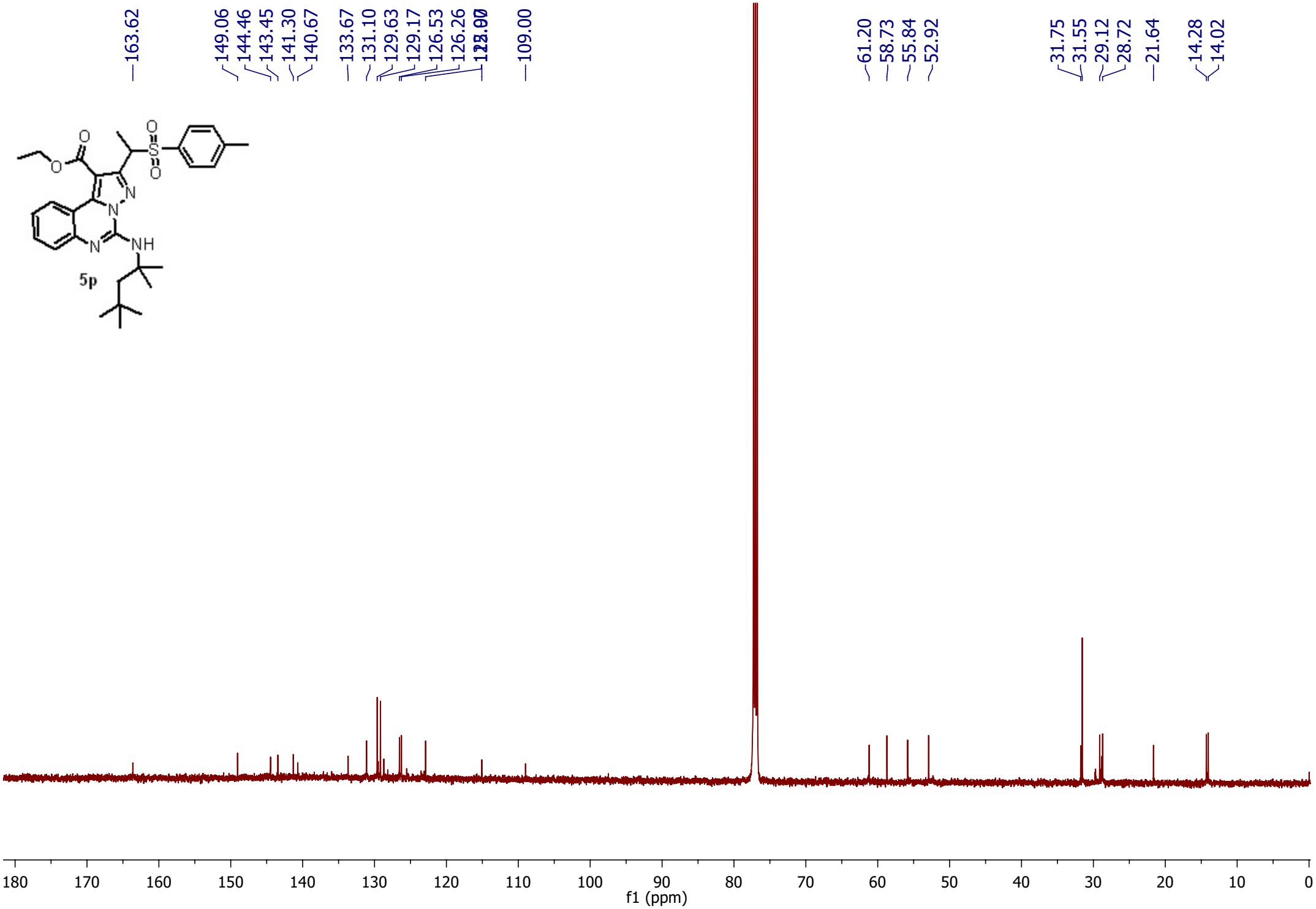

9.2019
9.1854
7.7227
7.7204
7.7129
7.6968
7.6338
7.5329
7.5306
7.5255
7.5233
7.3532
7.2892
7.1357
7.1278
7.1183
6.2195
5.1428
4.4569
4.4426
4.4283
4.4140
1.6224
1.5260
1.5117
1.4974
5n
1.16
2.00
1.25
1.02
1.21
1.01
1.19
2.30
2.31
9.58
3.56
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


163.14
144.39
143.43
141.34
141.28
139.52
134.93
134.36
131.41
127.68
126.77
126.25
123.16
115.07
108.68
61.31
56.99
52.22
28.95
14.27
5n
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.0439
9.0275
7.7061
7.6903
7.6319
7.6176
7.5646
7.5484
7.3439
7.3292
7.2932
7.2880
7.2780
7.2620
6.2169
5.6470
5.6328
5.6186
5.6044
4.4903
4.4761
4.4618
4.4476
2.4515
1.8500
1.8358
1.6485
1.6131
1.5298
1.5155
1.5012
5o
1.00
1.10
1.11
1.85
1.14
1.80
0.96
1.05
2.06
2.82
2.93
8.71
2.88
f1 (ppm)


163.63
148.99
144.60
143.39
141.41
140.71
131.16
129.63
129.21
126.51
126.26
108.88
61.24
58.63
52.08
28.90
21.68
14.30
14.21
5o
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


9.0653
9.0489
7.6997
7.6846
7.6164
7.5038
7.4874
7.3318
7.3176
7.2889
7.2424
7.2263
6.4255
5.6328
5.6184
5.6041
5.5899
4.5115
4.4974
4.4831
4.4688
2.4354
1.8313
1.8171
1.6883
1.6687
1.5266
1.0215
5p
1.00
1.27
1.43
1.99
2.07
1.82
1.05
1.05
2.04
2.86
1.88
3.26
6.02
3.49
9.33
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)


163.62
149.06
144.46
143.45
141.30
140.67
133.67
131.10
129.63
129.17
126.53
126.26
109.00
61.20
58.73
55.84
52.92
31.75
31.55
29.12
28.72
21.64
14.28
14.02
5p
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)