Electronic Supporting Information

Ionic Liquid-Catalysed Regioselective Oxygenation of Quinoxalin-2(1*H*)-ones Under Visible-Light Conditions

Gaurav Badhani,[†] Mangesh Biramya Valvi,[†] Subbarayappa Adimurthy[†]*

[†]*Academy of Scientific & Innovative Research (AcSIR), Ghaziabad 201002, INDIA; CSIR–Central Salt & Marine Chemicals Research Institute, G. B. Marg, Bhavnagar-364 002. Gujarat, INDIA.*

E-mail: adimurthy@csmcri.res.in

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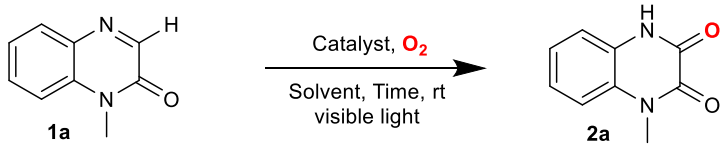
Table S1: Optimisation of reaction conditions for the oxygenation of quinoxalinone



1a **2a**

Entry	Catalyst (mol%)	Solvent	Time (hr)	Yield (%)
1	TBAH (25)	CH_3CN	24	72
2	TMAH (25)	CH_3CN	24	76
3	TMAH (25)	EtOH	24	ND
4	TMAH (25)	H_2O	24	ND
5	TMAH (25)	DCM	24	58
6	TMAH (25)	Acetone	24	80
7	TMAH (25)	Acetone	12	89
8	**TMAH (20)**	**Acetone**	**12**	**89**
9	TMAH (15)	Acetone	12	75
10	TMAH (20)	Acetone	6	60
11	TBAB (20)	Acetone	12	ND
12	TBAI (20)	Acetone	12	ND
13	Choline chloride (20)	Acetone	12	ND
14	BMIM-Br (20)	Acetone	12	ND
15	BMIM-PF6 (20)	Acetone	12	ND
16[b]	TMAH (20)	Acetone	12	88
17[c]	TMAH (20)	Acetone	12	ND
18[d]	TMAH (20)	Acetone	12	ND
19[e]	TMAH (20)	Acetone	12	35
20[f]	TMAH (20)	Acetone	12	72
21[g]	TMAH (20)	Acetone	12	ND
22[h]	TMAH (20)	Acetone	12	ND

[a] Reaction Conditions: **1a** (0.2 mmol), solvent 1.0 mL, white LED (10 W), open air, isolated yield. [b] Under O_2 (balloon) atmosphere; [c] Under N_2 atmosphere, [d] Without light at rt, [e] TMAH (25% solution in methanol), [f] blue LED, [g] green LED, [h] red LED. BMIM-Br is 1-Butyl-3-methylimidazolium bromide and BMIM-PF_6 is 1-Butyl-3-methylimidazolium hexafluorophosphate

Competitive experiment:

A clean washed reaction tube equipped with a magnetic stir bar was charged with 1-methylquinoxalin-2(1*H*)-one **1a** (16.0 mg, 0.10 mmol), 1-benzylquinoxalin-2(1*H*)-one **1l** (23.6 mg, 0.10 mmol), TMAH (20 mol%), and solvent Acetone (2mL), the above mixture was stirred for 3h at RT under visible-light. The mixture was stirred for 3 hours at room temperature under visible light. Following this, the crude reaction mixture was analyzed by NMR in CD_3CN to calculate the yield of the respective products using ^1H NMR. The results indicate that *N*-aryl-substituted quinoxalinones exhibit a slightly higher reactivity compared to *N*-alkyl-substituted quinoxalinones.

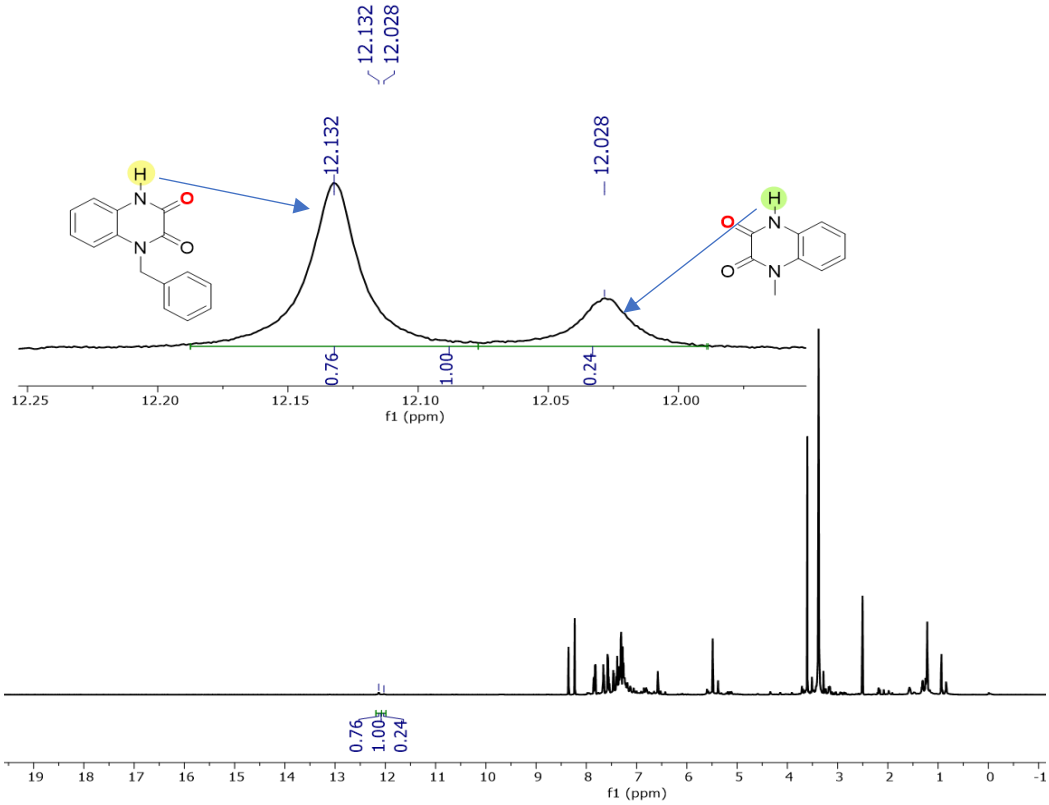


Fig. S1. NMR analysis for competitive experiment

Light On-Off experiment:

To investigate the role of continuous visible light irradiation in driving the reaction, we performed a set of four parallel light on/off experiments (Figure S2). Initially, visible light irradiation was continued up to 2 hours, light was switched off, and one of the reaction yield was isolated (28%). The rest of three reactions continued stirring for another 2 hours in absence of visible light and one of the reaction yield was isolated after total four hours, the yield was remains at 28%. Further, visible light irradiation was continued for another 2 hours and yield was isolated (44%) for another reaction after 6 h total time. The last reaction was continued further 2 hours in absence of light and the same yield was observed after total 8 h. The light on/off reactions indicates that, the absence of visible light there is no reaction takes place, suggests the essential role of visible light in the transformation. All these set of reactions performed at 0.2 mmol scale of **1a** and TMAH (20 mol%) under the optimised conditions.

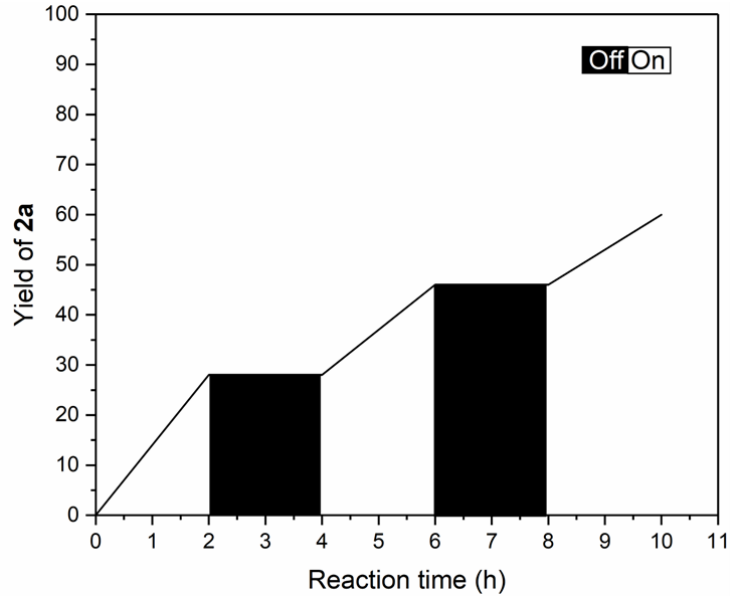


Fig. S2. Light On-Off experiment

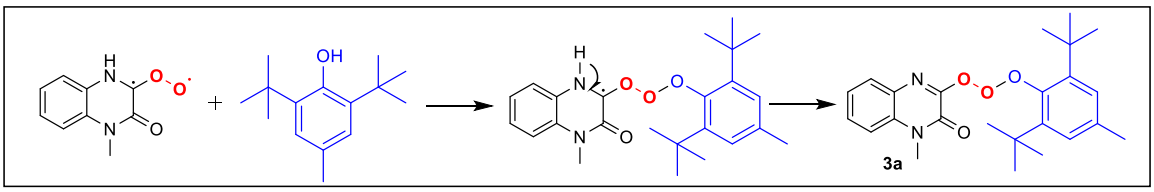
Mechanistic study

Radical scavenging experiment in the presence of TEMPO (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl

A clean washed reaction tube equipped with a magnetic stir bar was charged with 1-methylquinoxalin-2(1*H*)-one **1a** (32.0 mg, 0.20 mmol), TMAH (20 mol%), TEMPO (93.75 mg, 0.60 mmol) and solvent Acetone (1ml), the above mixture was stirred for 12h at RT under visible-light. Upon analysis by GC-MS, it was observed that the yield of compound **2a** was 15%, indicating a reduction in yield, which suggests the potential involvement of radical formation in the reaction pathway. Unfortunately, no adduct resulting from the interaction between TEMPO and 1a was detected during the analysis.

Radical scavenging experiment in the presence of BHT 3,5-Di-tert-4-butylhydroxytoluene

A clean washed reaction tube equipped with a magnetic stir bar was charged with 1-methylquinoxalin-2(1*H*)-one **1a** (32.0 mg, 0.20 mmol), TMAH (20 mol%), BHT (132.0 mg, 0.60 mmol) and solvent Acetone (1mL), the above mixture was stirred for 12h at RT under visible-light. However, the expected product **2a** was not obtained, providing further evidence for the involvement of a radical mechanism in the reaction pathway. To investigate possible intermediates, a sample was withdrawn for GC-MS analysis before the reaction completion. Intriguingly, after just 3 hours, a BHT-linked adduct, **3a** (9.1% GC yield) (Scheme S1), and an oxidized intermediate of 1-methylquinoxalin-2(1*H*)-one, **3b**, were identified (0.74% GC yield). The presence of **3a** was further confirmed through HRMS analysis.



Scheme S1: Formation of BHT linked adduct **3a**

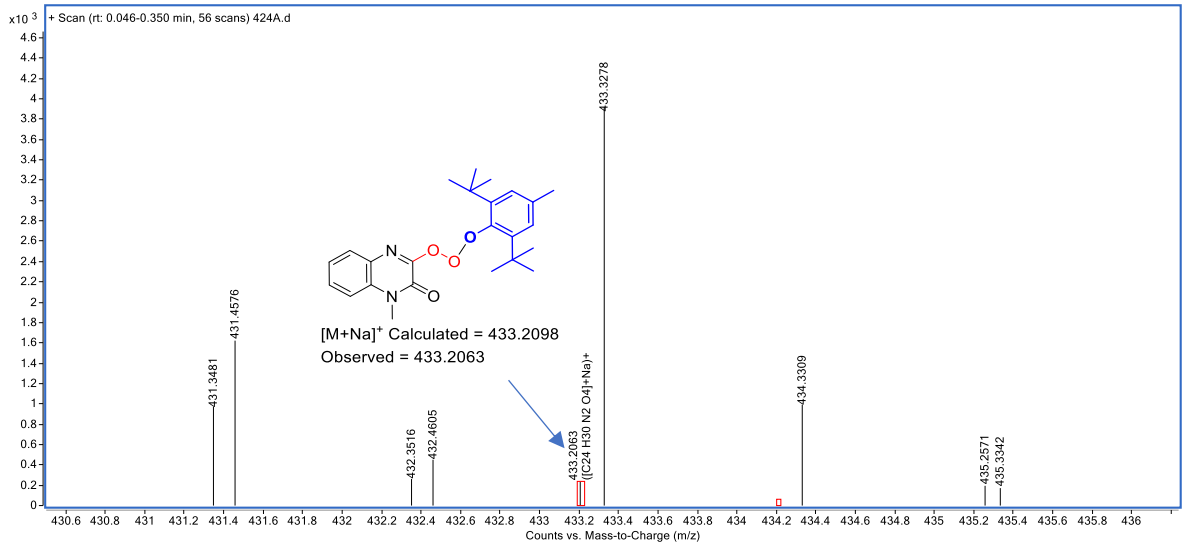


Fig. S3. HRMS spectra of **3a**

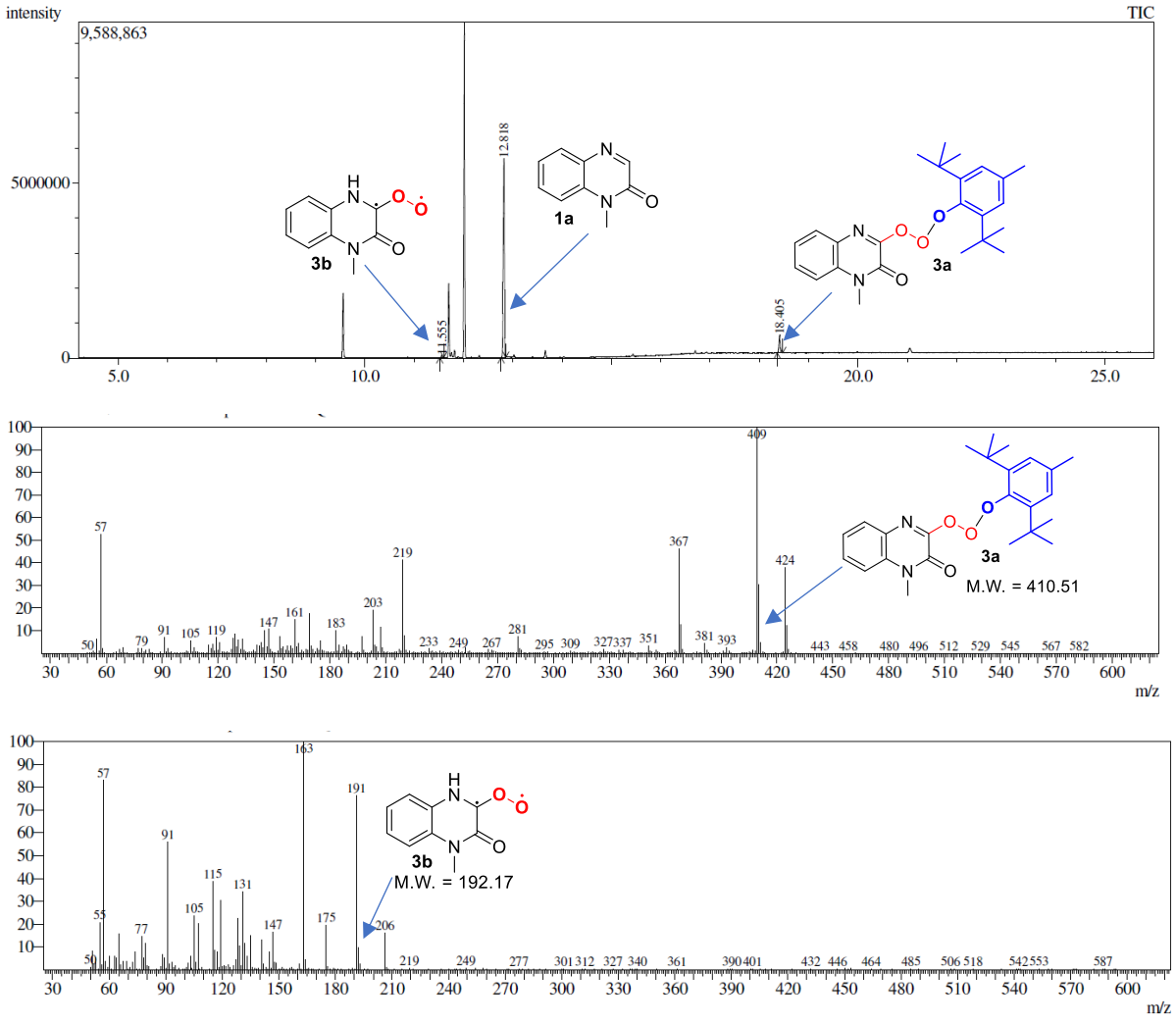


Fig. S4. GCMS spectra of **3a** and **3b**

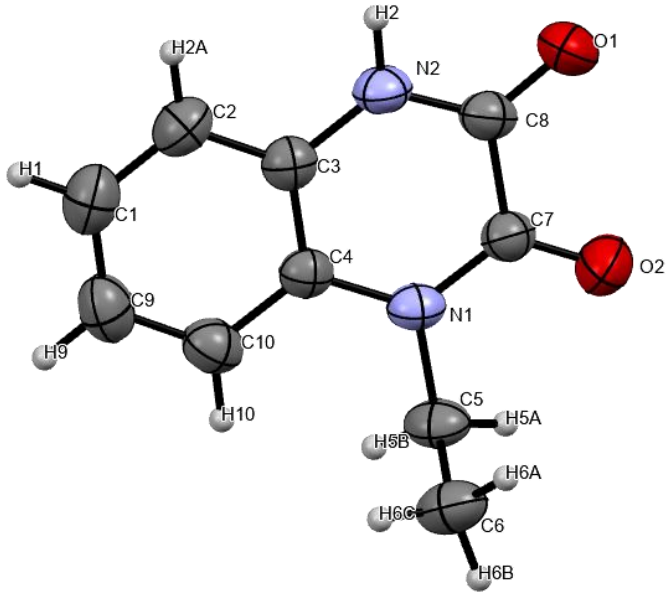


Fig. S5. Thermal ellipsoid plot for the crystal structure **2b (CCDC 2293003)**

Table S2: Crystal Data and Refinement Parameters (Experimental: X-ray part)

Identification code	**2b**
Empirical formula	$C_{10}H_{10}N_2O_2$
Formula weight	190.20
Temperature/K	298
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	4.8051(3)
b/Å	11.2889(8)
c/Å	16.6472(11)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	903.02(10)
Z	4
ρ_{calc}g/cm^3	1.399
μ/mm^{-1}	0.100
F(000)	400.0
Crystal size/mm^3	0.27 × 0.08 × 0.06
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.36 to 49.974
Index ranges	$-5 \leq h \leq 5$, $-13 \leq k \leq 13$, $-19 \leq l \leq 19$
Reflections collected	43533
Independent reflections	1599 [R_{int} = 0.0846, R_{sigma} = 0.0223]
Data/restraints/parameters	1599/0/132
Goodness-of-fit on F^2	1.148
Final R indexes [I>=2σ (I)]	R_1 = 0.0374, wR_2 = 0.0881
Final R indexes [all data]	R_1 = 0.0533, wR_2 = 0.1006
Largest diff. peak/hole / e Å^{-3}	0.13/-0.17
Flack parameter	0.3(8)
CCDC	2293003

Crystal of suitable size was selected for the organic compound, immersed in partone oil and then mounted on the tip of a glass fiber using epoxy resin. Intensity data for all three crystals were collected at 100 and 150 K using graphite monochromatised MoKα (α = 0.71073Å) radiation on diffractometer equipped with CCD area detector. The data integration and reduction were processed.1 An empirical absorption correction was applied to the collected reflections.2 The structures were solved by direct methods3 and refined on F2 by the full-matrix least-squares technique 4 package. Graphics are generated.5,6 Non-hydrogen atoms were refined anisotropically till convergence is reached and the hydrogen atoms of the organic compound is stereochemically fixed. Crystallographic parameters for the compound is given in Table S2.

1. Sheldrick, G. M.; SAINT 5.1 ed.; Siemens Industrial Automation Inc.: Madison, WI, 1995.
2. SADABS, Empirical Absorption Correction Program; University of Göttingen: Göttingen, Germany 1997.
3. Sheldrick, G. M.; SHELXTL Reference Manual: Version 5.1; Bruker AXS: Madison, WI 1997.
4. Sheldrick, G.M. SHELXL-97: Program for Crystal Structure Refinement; University of Göttingen: Göttingen, Germany (1997).
5. A.L.Spek, Acta Cryst. 2009, D65, 148-155
6. Mercury 1.3, Supplied with Cambridge Structural Database; CCDC: Cambridge, U.K., (2003).

Experimental section

General information: All commercially available chemicals and reagents were used without any further purification unless otherwise indicated. ^{1}H and ^{13}C {H} NMR spectra were recorded at 600/500 and 150/125 MHz respectively. The spectra were recorded in $CDCl_3$, DMDO-d_6 and CD_3CN as solvent. Multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); m (multiplet); dd (doublet of doublets), etc. and coupling constants (J) were given in Hz. Chemical shifts are reported in ppm relative to TMS as an internal standard for ^{1}H NMR. Chemical shifts were reported in ppm on the δ scale relative to Me_4Si (δ = 0.00 for ^{1}H-NMR), $CDCl_3$ (δ = 7.26 for ^{1}H NMR and δ = 77.160 for $^{13}C\{^{1}H\}$-NMR) and DMSO-d_6 (δ = 2.50 for ^{1}H NMR and δ = 39.52 for $^{13}C\{^{1}H\}$-NMR). Additional peaks at δ = 1.56 – 1.61 ppm in ^{1}H-NMR spectra of compounds recorded in $CDCl_3$ and δ = 3.39 ppm in ^{1}H-NMR spectra of compounds recorded in DMSO-d_6 correspond to water, present if any. Melting Points of solid compounds were measured by Thermo Scientific MEL TEMP instrument. GC spectral data were recorded on a Shimadzu GC-2014. HRMS (SI) spectra were recorded on a Micromass Q-Tof microTM instrument. GCMS spectral data were acquired on a Shimadzu GC-2010 Plus coupled with GCMS-TQ8040 instrument. Single crystal structures were determined using a Bruker D8 QUEST (CCD) diffractometer. Progress of the reactions were monitored by thin layer chromatography (TLC). All products were purified through column chromatography using silica gel 100-200 mesh size using hexane/ethyl acetate as eluent, unless otherwise indicated.

General procedure (A) for the synthesis of quinoxalin-2(1*H*)-one derivatives: To a stirred solution of 1,2-phenylenediamines (5 mmol, 1.0 equiv.) in EtOH (40 mL) was added ethyl glyoxalate (6 mmol, 1.2 equiv.). After addition, the resultant reaction mixture was stirred at 80 °C until the raw material disappears and gave quinoxalin-2(1H)-one. For alkylation, the corresponding alkyl halide (1.6 equiv.) was added to a suspension of quinoxalinone (1.0 equiv.) and K_2CO_3 (1.2 equiv.) in DMF (16 mL). The mixture was stirred at room temperature (monitored by TLC). After completion of reaction, saturated solution of NH_4Cl (5 mL) was added to the reaction system, and

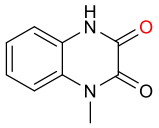
then added ethyl acetate (10 mL) and water (10 mL) to extract the reaction mixture. The residue was purified by column chromatography on silica gel to afford the alkylated quinoxalinone.

General procedure (B) for the synthesis of 1,4-dihydroquinoxaline-2,3-dione derivatives: To an oven-dried completely evacuated 15 mL borosilicate glass tube (15 x 150 mm) equipped with a magnetic stir bar, added 1-methylquinoxalin-2(1*H*)-one **(1a)** (32.0 mg, 0.20 mmol), tetramethylammonium hydroxide TMAH ionic liquid (25% TMAH + 75% water) (20 mol%), and Acetone (1 mL). Then the reaction mixture stirred in an open reaction tube at room temperature under visible light conditions by using 10 W white LED (Philips) for 12 h. The progress of the reaction was monitored by (TLC), After completion of the reaction, the resulting mixture was extracted by ethyl acetate and the organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under high vacuum, then 5 mL ethyl acetate and 5 mL of petroleum ether was added. After 30 min, reaction mixture was filtered and washed with petroleum ether to get the desired product quinoxaline-2,3(1*H*,4*H*)-diones.

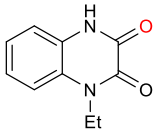
General procedure (C) for the synthesis of 1,4-dihydroquinoxaline-2,3-dione derivatives: To an oven-dried completely evacuated reaction tube equipped with a magnetic stir bar, added ethyl 2-(2-oxoquinoxalin-1(2*H*)-yl)acetate **(1g)** (46.5 mg, 0.20 mmol), tetramethylammonium hydroxide TMAH ionic liquid (20 mol%), and Acetone (1 mL). Then the reaction mixture was stirred in an open reaction tube at room temperature under visible light conditions by using 10 W white LED for 12 h. The progress of the reaction was monitored by (TLC), After completion of the reaction, the mixture was purified through column chromatography using silica gel (60% EtOAc/hexane) to obtain ethyl 2-(2,3-dioxo-3,4-dihydroquinoxalin-1(2*H*)-yl)acetate **(2g)** in 72 % yield (35.7 mg).

General procedure (D) for the synthesis of biologically active compound 2ab: To an oven-dried completely evacuated reaction tube equipped with a magnetic stir bar, added 1-methyl-1,4-dihydroquinoxaline-2,3-dione **(2a)** (88.10 mg, 0.50 mmol), $POCl_3$ (1.5 equiv.), acetonitrile (5 mL) and reaction mixture reflux for 6 h. The progress of the reaction was monitored by (TLC), After completion of the reaction, the mixture was purified through column chromatography using silica gel (20% EtOAc/hexane) to obtain 3-chloro-1-methylquinoxalin-2(1*H*)-one **(2aa)** in 78 % yield (76.0 mg). Then **2aa** (39 mg, 0.20 mmol) and 4-iodoaniline (1.2 equiv.) were added in 2 mL acetonitrile and the reaction mixture was stirred at 80 °C overnight. After completion of the reaction, the mixture was purified through column chromatography using silica gel (20% EtOAc/hexane) to obtain 3-((4-iodophenyl)amino)-1-methylquinoxalin-2(1*H*)-one **(2ab)** in 85 % yield (64.0 mg).

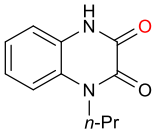
Characterization data



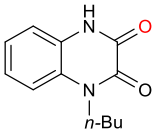
1-methyl-1,4-dihydroquinoxaline-2,3-dione (2a):[1] Compound **2a** was purified by following the GP-B. Yield (31.3 mg, 89% yield, white solid); **^{1}H NMR** (600 MHz, DMSO-d_6) δ 12.02 (s, 1H), 7.37 – 7.35 (m, 1H), 7.22 – 7.17 (m, 3H), 3.52 (s, 3H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 155.27, 153.60, 127.23, 125.57, 123.55, 123.22, 115.39, 115.04, 29.66.



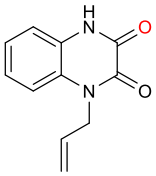
1-ethyl-1,4-dihydroquinoxaline-2,3-dione (2b):[1] Compound **2b** was purified by following the GP-B. Yield (34.2 mg, 90% yield, white solid); **^{1}H NMR** (600 MHz, DMSO-d_6) δ 12.07 (s, 1H), 7.46 – 7.44 (m, 1H), 7.27 – 7.20 (m, 3H), 4.19 (q, *J* = 7.1 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 154.78, 153.62, 125.89, 125.83, 123.47, 123.37, 115.81, 114.78, 37.31, 12.06.



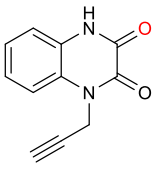
1-propyl-1,4-dihydroquinoxaline-2,3-dione (2c): Compound **2c** was purified by following the GP-B. Yield (34.7 mg, 85% yield, white solid); mp 178 – 180 ºC; **IR (KBr):** ν = 1688, 1386, 1211, 740, 658, 589 cm^{-1}; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 12.08 (s, 1H), 7.37 (d, *J* = 7.9 Hz, 1H), 7.22 – 7.12 (m, 3H), 4.13 – 4.03 (m, 2H), 1.67 (h, *J* = 7.7 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 160.35, 158.89, 131.39, 130.99, 128.70, 128.56, 121.11, 120.13, 84.42, 84.20, 83.98, 48.92, 25.17, 16.36; **HRMS (ESI-QTOF):** m/z calcd for $C_{11}H_{12}NaN_2O_2$ $[M + Na]^+$: 227.0791; found: 227.0796.



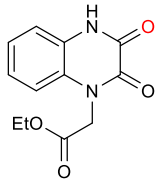
1-butyl-1,4-dihydroquinoxaline-2,3-dione (2d):[2] Compound **2d** was purified by following the GP-B. Yield (40.6 mg, 93% yield, light yellow solid); **^{1}H NMR** (600 MHz, DMSO-d_6) δ 12.10 (s, 1H), 7.45 – 7.40 (m, 1H), 7.28 – 7.19 (m, 3H), 4.14 (t, *J* = 1.95 Hz, 2H), 1.64 (p, *J* = 7.5 Hz, 2H), 1.43 (h, *J* = 7.4 Hz, 2H), 1.00 – 0.96 (m, 3H); **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 155.05, 153.60, 126.15, 125.79, 123.49, 123.35, 115.80, 114.95, 41.90, 28.66, 19.58, 13.75.



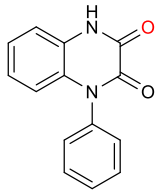
1-allyl-1,4-dihydroquinoxaline-2,3-dione (2e):[1] Compound **2e** was purified by following the GP-B. Yield (31.5 mg, 78% yield, light yellow solid); **^{1}H NMR** (600 MHz, DMSO-d_6) δ 12.07 (s, 1H), 7.28 – 7.25 (m, 1H), 7.21 – 7.14 (m, 3H), 5.94 – 5.88 (m, 1H), 5.19 – 5.13 (m, 2H), 4.78 – 4.74 (m, 2H); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 155.57, 154.16, 132.06, 126.74, 126.27, 124.08, 123.65, 117.44, 116.16, 115.96, 44.98.



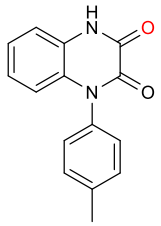
1-(prop-2-yn-1-yl)-1,4-dihydroquinoxaline-2,3-dione (2f):[1] Compound **2f** was purified by following the GP-B. Yield (32.4 mg, 81% yield, yellow solid); **^{1}H NMR** (600 MHz, DMSO-d_6) δ 12.16 (s, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.30 – 7.25 (m, 3H), 5.04 – 4.97 (m, 2H), 3.36 (t, *J* = 2.4 Hz, 1H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 154.66, 153.36, 125.75, 125.57, 124.01, 123.28, 115.80, 115.34, 78.08, 75.13, 31.98.



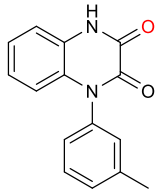
ethyl 2-(2,3-dioxo-3,4-dihydroquinoxalin-1(2*H*)-yl)acetate (2g):[1] Compound **2g** was purified by following the GP-C. Yield (35.7 mg, 72% yield, light yellow solid); eluent: 60% ethyl acetate/hexane; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 12.21 (s, 1H), 7.30 (d, *J* = 7.9 Hz, 1H), 7.24 – 7.16 (m, 3H), 4.98 (s, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 1.22 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 167.59, 155.28, 126.41, 125.47, 115.90, 114.90, 61.37, 44.22, 14.03.



1-phenyl-1,4-dihydroquinoxaline-2,3-dione (2h):[1] Compound **2h** was purified by following the GP-B. Yield (39.0 mg, 82% yield, light yellow solid); **^{1}H NMR** (600 MHz, DMSO-d_6) δ 12.13 (s, 1H), 7.63 (t, *J* = 7.7 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.14 (t, *J* = 7.7 Hz, 1H), 6.98 (t, *J* = 7.8 Hz, 1H), 6.31 (d, *J* = 8.2 Hz, 1H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 155.63, 154.78, 137.01, 130.65, 129.61, 129.22, 129.09, 128.99, 126.22, 124.01, 123.38, 116.03.

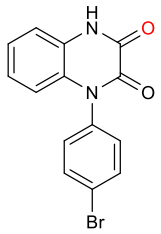


1-(p-tolyl)-1,4-dihydroquinoxaline-2,3-dione (2i):[1] Compound **2i** was purified by following the GP-C. Yield (40.6 mg, 93% yield, light yellow solid); eluent: 60% ethyl acetate/hexane; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.11 (s, 1H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.34 (d, *J* = 8.2 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 155.13, 154.23, 138.55, 133.89, 130.56, 128.75, 128.22, 125.63, 123.40, 122.81, 115.55, 115.51, 20.79.

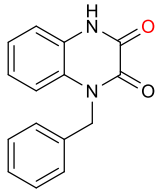


1-(m-tolyl)-1,4-dihydroquinoxaline-2,3-dione (2j): Compound **2j** was purified by following the GP-B. Yield (40.8 mg, 81% yield, light yellow solid); mp 328 – 330 °C; **IR (KBr):** ν = 1692, 1388, 867, 739, 662, 589 cm^{-1}; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.20 (s, 1H), 7.51 (t, *J* = 7.7 Hz, 1H), 7.37 (d, *J* = 7.7 Hz, 1H), 7.23 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.20 (s, 1H), 7.17 (d, *J* = 8.1 Hz, 1H), 7.15 – 7.11 (m, 1H), 7.01 – 6.96 (m, 1H), 6.33 (dd, *J* = 7.9, 0.9 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 155.04, 154.25, 139.75, 136.43, 129.90,

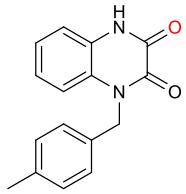
129.69, 128.79, 128.63, 125.68, 125.44, 123.44, 122.82, 115.56, 20.81; **HRMS (ESI-QTOF):** m/z calcd for $C_{15}H_{12}N_2NaO_2$ $[M + Na]^+$: 275.0791; found: 275.0798.



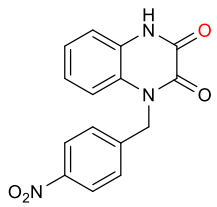
1-(4-bromophenyl)-1,4-dihydroquinoxaline-2,3-dione (2k): Compound **2k** was purified by following the GP-C. Yield (48.2 mg, 76% yield, light yellow solid); eluent: 60% ethyl acetate/hexane; mp 350 – 352 ºC; **IR (KBr):** ν = 1684, 1486, 1372, 824, 772, 612, 517 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 12.12 (s, 1H), 7.83 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.23 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.15 (t, *J* = 8.1 Hz, 1H), 6.99 (t, *J* = 8.5 Hz, 1H), 6.36 (d, *J* = 8.6 Hz, 1H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 155.07, 154.14, 135.86, 133.19, 130.94, 128.45, 125.73, 123.57, 122.92, 122.27, 115.45; **HRMS (ESI-QTOF):** m/z calcd for $C_{14}H_9BrN_2NaO_2$ $[M + Na]^+$: 338.9740; found: 338.9751.



1-benzyl-1,4-dihydroquinoxaline-2,3-dione (2l):[1] Compound **2l** was purified by following the GP-C. Yield (44.4 mg, 88% yield, yellow solid); eluent: 60% ethyl acetate/hexane; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 12.13 (s, 1H), 7.34 – 7.30 (m, 4H), 7.27 – 7.24 (m, 1H), 7.22 – 7.17 (m, 2H), 7.14 (t, *J* = 7.3 Hz, 1H), 7.07 (t, *J* = 7.3 Hz, 1H), 5.38 (s, 2H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 155.74, 153.71, 135.77, 128.67, 127.26, 126.69, 126.31, 125.92, 123.68, 123.13, 115.73, 115.48, 45.61.

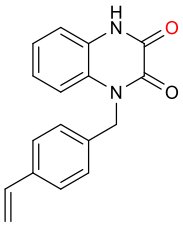


1-(4-methylbenzyl)-1,4-dihydroquinoxaline-2,3-dione (2m):[2] Compound **2m** was purified by following the GP-C. Yield (41.5 mg, 78% yield, light yellow solid); eluent: 60% ethyl acetate/hexane; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 12.10 (s, 1H), 7.18 (t, *J* = 9.2 Hz, 4H), 7.14 – 7.11 (m, 3H), 7.08 – 7.04 (m, 1H), 5.33 (s, 2H), 2.25 (s, 3H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 155.67, 153.66, 136.38, 132.69, 129.18, 126.66, 126.24, 125.86, 123.60, 123.06, 115.66, 115.48, 45.33, 20.61.

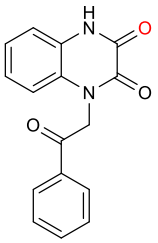


1-(4-nitrobenzyl)-1,4-dihydroquinoxaline-2,3-dione (2n):[2] Compound **2n** was purified by following the GP-C. Yield (40.4 mg, 68% yield, yellow solid); eluent: 60% ethyl acetate/hexane; **^{1}H NMR** (600 MHz, DMSO-d_6)

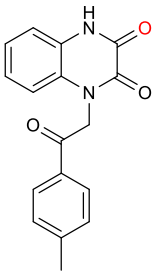
δ 12.14 (s, 1H), 8.18 (d, *J* = 7.7 Hz, 2H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 7.09 – 7.04 (m, 1H), 5.51 (s, 2H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 155.85, 153.71, 146.82, 143.85, 127.99, 126.23, 126.07, 123.85, 123.75, 123.19, 115.84, 115.23, 45.41.



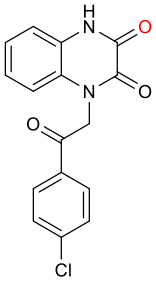
1-(4-vinylbenzyl)-1,4-dihydroquinoxaline-2,3-dione (2o): Compound **2o** was purified by following the GP-C. Yield (46.2 mg, 83% yield, yellow solid); eluent: 60% ethyl acetate/hexane; mp 248 – 250 °C; **IR (KBr):** ν = 1693, 1386, 1216, 1009, 824, 745 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 12.12 (s, 1H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.22 – 7.12 (m, 3H), 7.07 (t, *J* = 8.4 Hz, 1H), 6.69 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.79 (d, *J* = 17.7 Hz, 1H), 5.37 (s, 2H), 5.23 (d, *J* = 11.0 Hz, 1H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 155.73, 153.69, 136.20, 135.46, 127.02, 126.41, 126.27, 125.91, 123.67, 123.11, 115.72, 115.46, 114.32, 45.43; **HRMS (ESI-QTOF):** m/z calcd for $C_{17}H_{14}N_2NaO_2$ [M + Na]$^+$: 301.0948; found: 301.0955.



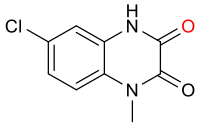
1-(2-oxo-2-phenylethyl)-1,4-dihydroquinoxaline-2,3-dione (2p):[2] Compound **2p** was purified by following the GP-C. Yield (47.1 mg, 84% yield, yellow solid); eluent: 60% ethyl acetate/hexane; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 12.29 (s, 1H), 8.20 (d, *J* = 7.2 Hz, 2H), 7.81 (t, *J* = 7.5 Hz, 1H), 7.68 (t, *J* = 7.7 Hz, 2H), 7.33 – 7.29 (m, 2H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.19 – 7.15 (m, 1H), 5.86 (s, 2H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 192.31, 155.25, 153.35, 134.22, 130.32, 128.96, 126.72, 125.45, 123.80, 123.37, 115.78, 115.15, 49.55.



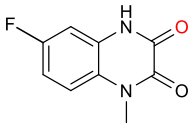
1-(2-oxo-2-(*p*-tolyl)ethyl)-1,4-dihydroquinoxaline-2,3-dione (2q): Compound **2q** was purified by following the GP-C. Yield (46.0 mg, 78% yield, yellow solid); eluent: 60% ethyl acetate/hexane; mp 305 – 307 °C; **IR (KBr):** ν = 1707, 1604, 1405, 1221, 976, 810 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 12.29 (s, 1H), 8.10 (d, *J* = 8.1 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.34 – 7.22 (m, 3H), 7.21 – 7.14 (m, 1H), 5.83 (s, 2H), 2.50 (s, 3H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 191.71, 155.24, 153.36, 144.80, 129.48, 129.33, 129.12, 128.39, 126.72, 125.44, 123.77, 123.36, 115.78, 115.12, 49.38, 21.29; **HRMS (ESI-QTOF):** m/z calcd for $C_{17}H_{14}N_2NaO_3$ [M + Na]$^+$: 317.0897; found: 317.0904.



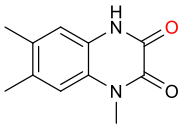
1-(2-(4-chlorophenyl)-2-oxoethyl)-1,4-dihydroquinoxaline-2,3-dione (2r): Compound **2r** was purified by following the GP-C. Yield (45.3 mg, 72% yield, yellow solid); eluent: 60% ethyl acetate/hexane; mp 315 – 318 ^{o}C; **IR (KBr):** ν = 1702, 1462, 1381, 1211, 881, 479 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 12.23 (s, 1H), 8.15 (d, J = 8.6 Hz, 2H), 7.70 (d, J = 8.5 Hz, 2H), 7.28 – 7.23 (m, 2H), 7.19 (t, J = 7.9 Hz, 1H), 7.13 – 7.10 (m, 1H), 5.79 (s, 2H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 192.06, 155.78, 153.86, 139.68, 133.63, 130.80, 129.62, 127.22, 126.00, 124.37, 123.90, 116.33, 115.70, 50.10; **HRMS (ESI-QTOF):** m/z calcd for $C_{16}H_{11}ClN_2NaO_3$ $[M + Na]^+$: 337.0351; found: 337.0357.



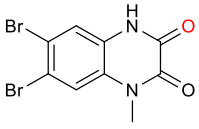
6-chloro-1-methyl-1,4-dihydroquinoxaline-2,3-dione (2s):[1] Compound **2s** was purified by following the GP-B. Yield (30.3 mg, 72% yield, light yellow solid); **^{1}H NMR** (600 MHz, DMSO-d_6) δ 12.09 (s, 1H), 7.43 – 7.38 (m, 1H), 7.21 (d, J = 9.7 Hz, 1H), 7.13 (d, J = 8.5 Hz, 1H), 3.48 (s, 3H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 155.61, 153.75, 128.99, 127.60, 125.12, 123.64, 117.13, 115.29, 30.30.



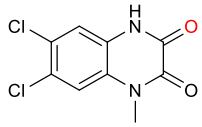
6-fluoro-1-methyl-1,4-dihydroquinoxaline-2,3-dione (2t):[1] Compound **2t** was purified by following the GP-C. Yield (41.0 mg, 80% yield, yellow solid); eluent: 60% ethyl acetate/hexane; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 12.07 (s, 1H), 7.37 (dd, J = 9.1, 4.9 Hz, 1H), 7.04 (td, J = 8.8, 2.7 Hz, 1H), 6.95 (dd, J = 9.2, 2.7 Hz, 1H), 3.50 (s, 3H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 156.52 ($J_{C\text{-}F}$ = 238.55 Hz), 154.71, 153.61, 126.73 ($J_{C\text{-}F}$ = 11.55 Hz), 124.08, 116.58 ($J_{C\text{-}F}$ = 9.15 Hz), 109.61 ($J_{C\text{-}F}$ = 22.65 Hz), 101.98 ($J_{C\text{-}F}$ = 27.00 Hz), 29.93; ^{19}F NMR (565 MHz, DMSO-d_6) δ -119.23.



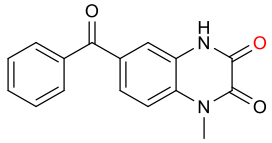
1,6,7-trimethyl-1,4-dihydroquinoxaline-2,3-dione (2u):[1] Compound **2u** was purified by following the GP-B. Yield (29.0 mg, 71% yield, yellow solid); **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.87 (s, 1H), 7.13 (s, 1H), 6.91 (s, 1H), 3.48 (s, 3H), 2.25 (s, 3H), 2.19 (s, 3H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 155.17, 153.55, 131.62, 131.36, 124.97, 123.16, 115.97, 115.74, 29.57, 19.15, 18.77.



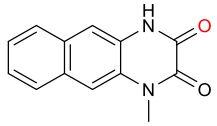
6,7-dibromo-1-methyl-1,4-dihydroquinoxaline-2,3-dione (2v): Compound **2v** was purified by following the GP-B. Yield (58 mg, 87% yield, light yellow solid); mp 320 – 322 °C; **IR (KBr):** ν = 1688, 1476, 1377, 1136, 909, 777, 488 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 12.11 (s, 1H), 7.68 (s, 1H), 7.42 (s, 1H), 3.48 (s, 3H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 155.44, 153.80, 128.77, 126.98, 119.97, 119.52, 117.58, 117.35, 30.48; **HRMS (ESI-QTOF):** m/z calcd for $C_9H_6Br_2N_2NaO_2$ $[M + Na]^+$: 356.8668; found: 356.8671.



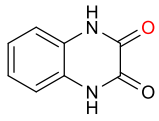
6,7-dichloro-1-methyl-1,4-dihydroquinoxaline-2,3-dione (2w):[1] Compound **2w** was purified by following the GP-C. Yield (37.0 mg, 76% yield, yellow solid); eluent: 60% ethyl acetate/hexane; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 12.09 (s, 1H), 7.58 (s, 1H), 7.26 (s, 1H), 3.47 (s, 3H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 154.84, 153.19, 127.63, 125.84, 124.97, 124.78, 116.57, 115.97, 30.02.



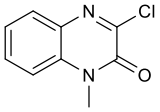
6-benzoyl-1-methyl-1,4-dihydroquinoxaline-2,3-dione (2x): Compound **2x** was purified by following the GP-C. Yield (42.6 mg, 76% yield, yellow solid); eluent: 60% ethyl acetate/hexane; mp 288 – 290 °C; **IR (KBr):** ν = 1701, 1453, 1391, 1320, 1240, 702 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 12.10 (s, 1H), 7.74 – 7.72 (m, 2H), 7.70 (t, J = 7.4 Hz, 1H), 7.64 (d, J = 1.7 Hz, 1H), 7.60 – 7.55 (m, 3H), 7.51 (d, J = 8.6 Hz, 1H), 3.56 (s, 3H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 194.30, 155.41, 153.36, 137.20, 132.54, 131.59, 130.88, 129.43, 128.58, 125.06, 116.81, 115.02, 29.97; **HRMS (ESI-QTOF):** m/z calcd for $C_{16}H_{12}N_2NaO_3$ $[M + Na]^+$: 303.0741; found: 303.0757.



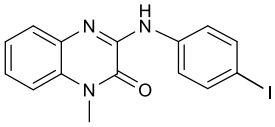
1-methyl-1,4-dihydrobenzo[g]quinoxaline-2,3-dione (2y): Compound **2y** was purified by following the GP-C. Yield (36.6 mg, 81% yield, orange solid); eluent: 60% ethyl acetate/hexane; mp 318 – 320 °C; **IR (KBr):** ν = 6184, 1514, 1386, 1268, 858, 758 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 12.21 (s, 1H), 7.95 (dd, J = 5.7, 3.4 Hz, 1H), 7.88 – 7.84 (m, 1H), 7.81 (s, 1H), 7.58 (s, 1H), 7.47 (dd, J = 6.2, 3.2 Hz, 2H), 3.63 (s, 3H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 154.95, 153.37, 129.38, 129.25, 127.70, 127.36, 126.38, 125.84, 125.49, 125.05, 111.66, 111.07, 29.84; **HRMS (ESI-QTOF):** m/z calcd for $C_{13}H_{10}N_2NaO_2$ $[M + Na]^+$: 249.0635; found: 249.0640.



1,4-dihydroquinoxaline-2,3-dione (2z):[2] Compound **2z** was purified by following the GP-C. Yield (12.3 mg, 38% yield, yellow solid); eluent: 60% ethyl acetate/hexane; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.91 (s, 2H), 7.14 – 7.12 (m, 2H), 7.1 – 7.07 (m, 2H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 155.20, 125.62, 123.05, 115.16.



3-chloro-1-methylquinoxalin-2(1*H*)-one (2aa):[3] Compound **2aa** was purified by following the GP-D. Yield (76.0 mg, 78% yield, white solid); eluent : 20% ethyl acetate/hexane; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.82 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.62 (ddd, *J* = 8.6, 7.3, 1.4 Hz, 1H), 7.41 – 7.38 (m, 1H), 7.35 (d, *J* = 8.6 Hz, 1H), 3.78 (s, 3H); **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 151.83, 148.90, 133.38, 131.80, 131.20, 129.77, 124.57, 114.11, 30.67.



3-((4-iodophenyl)amino)-1-methylquinoxalin-2(1*H*)-one (2ab): Compound **2ab** was purified by following the GP-D. Yield (64.0 mg, 88% yield, light yellow solid); eluent : 20% ethyl acetate/hexane; mp 225 – 227 ºC; **IR (KBr):** ν = 1622, 1298, 1162, 1078, 742, 514 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 9.60 (s, 1H), 8.02 (d, *J* = 8.7 Hz, 2H), 7.68 (d, *J* = 8.7 Hz, 2H), 7.57 – 7.54 (m, 1H), 7.46 (d, *J* = 8.3 Hz, 1H), 7.36 (t, *J* = 8.1 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 3.70 (s, 3H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 151.10, 146.12, 139.47, 137.10, 132.26, 130.04, 126.13, 125.35, 123.87, 122.20, 114.51, 86.00, 29.53. **HRMS (ESI-QTOF):** m/z calcd for $C_{15}H_{13}N_3IO$ $[M + H]^+$: 378.0098; found: 378.0093.

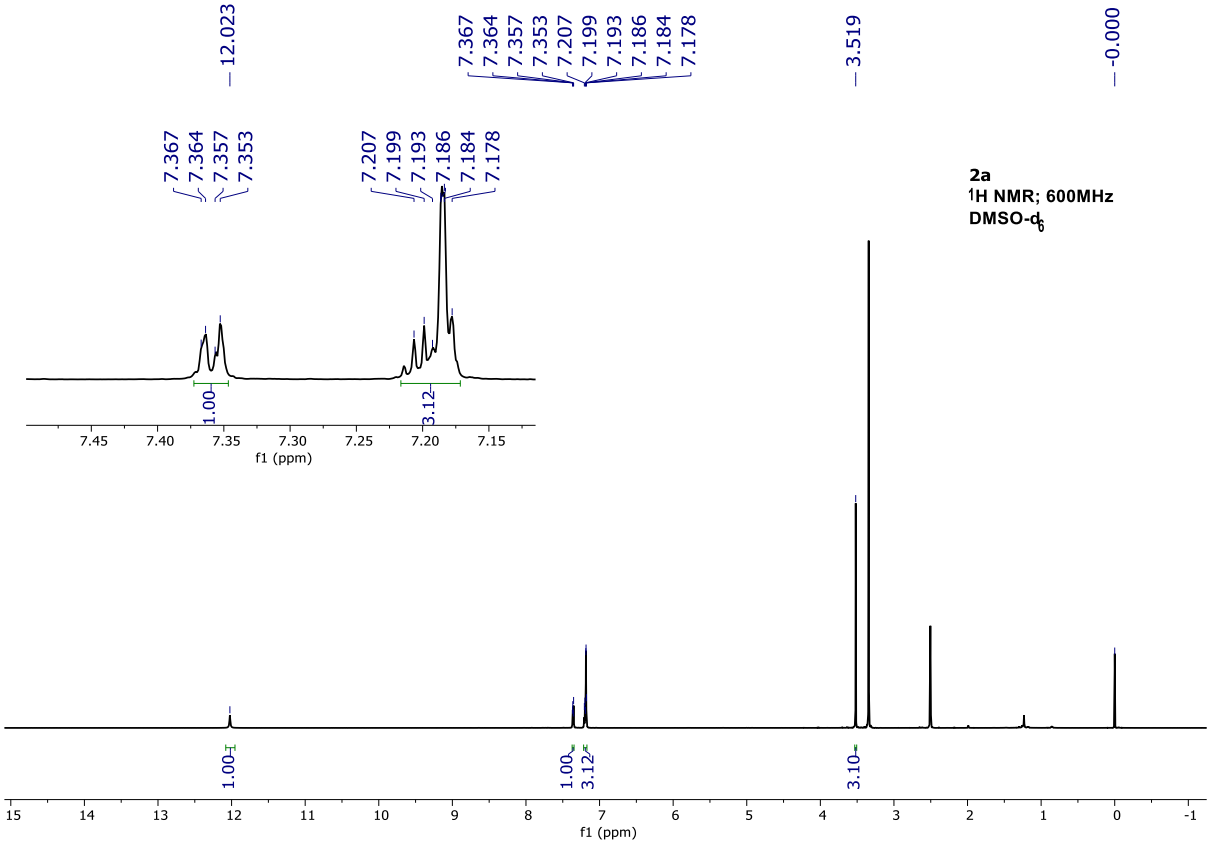
References:

1 S. Peng, D. Hu, J.-L. Hu, Y.-W. Lin, S.-S. Tang, H.-S. Tang, J.-Y. He, Z. Cao and W.-M. He, *Adv. Synth. Catal.*, 2019, **361**, 5721–5726.

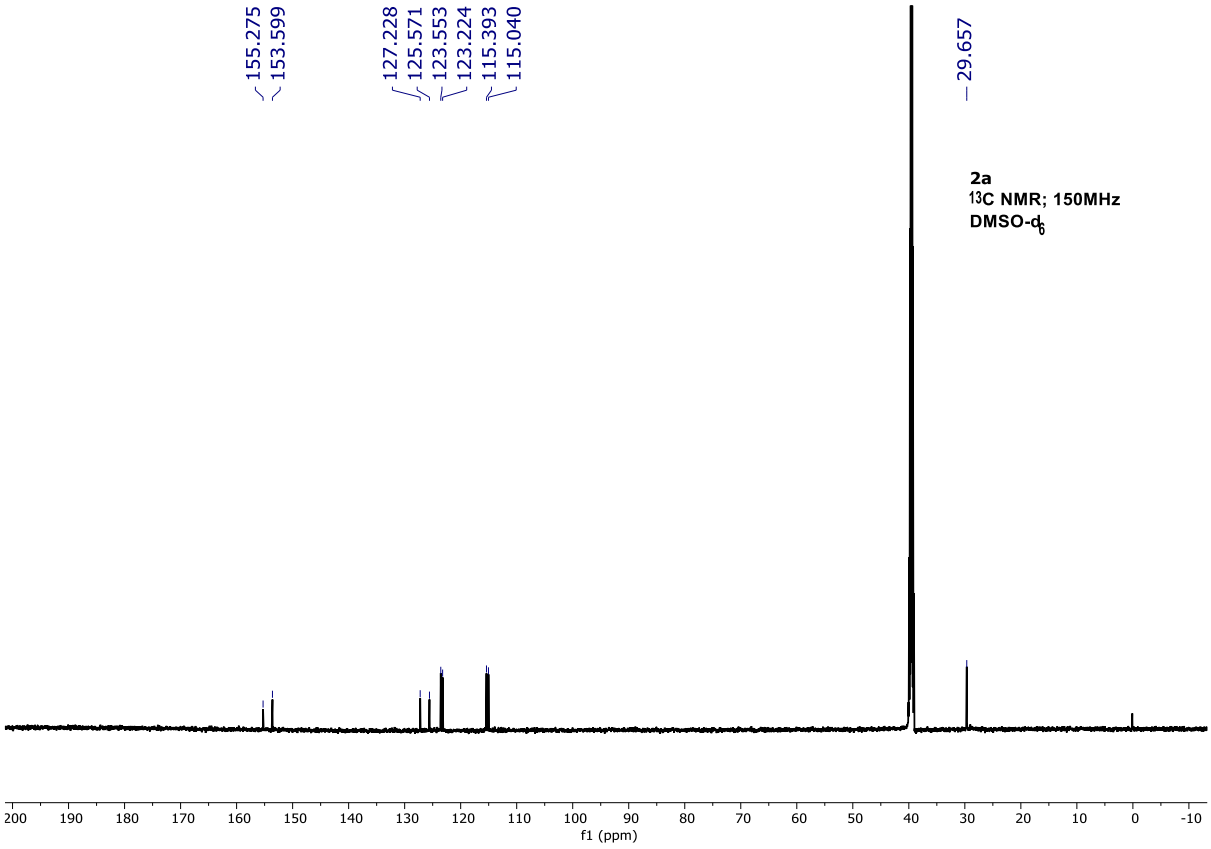
2 S. Sau and P. Mal, *European J. Org. Chem.*, 2022, **2022**, e202200425.

3 M. C. Wu, M. Z. Li, J. Y. Chen, J. A. Xiao, H. Y. Xiang, K. Chen and H. Yang, *Chem. Commun.*, 2022, **58**, 11591–11594.

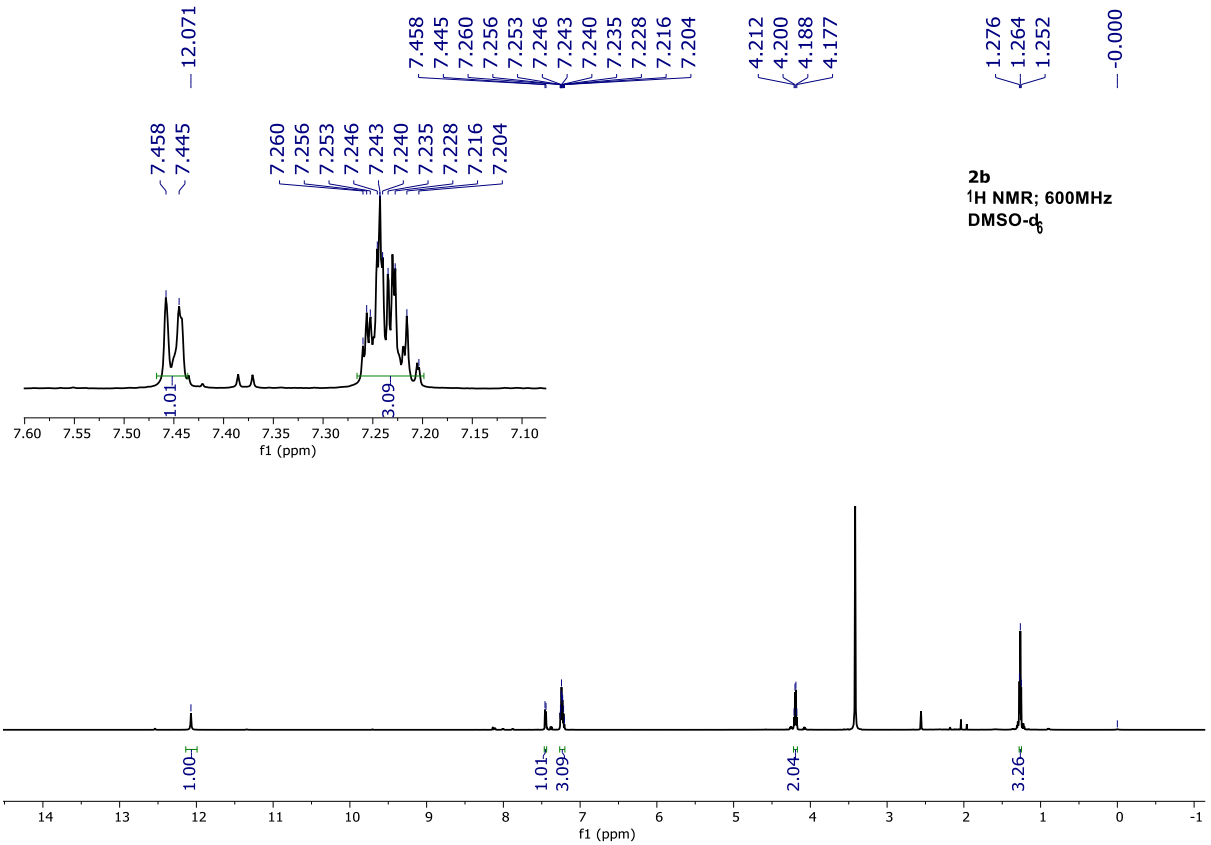
Copies of ^{1}H, ^{13}C & ^{19}F NMR



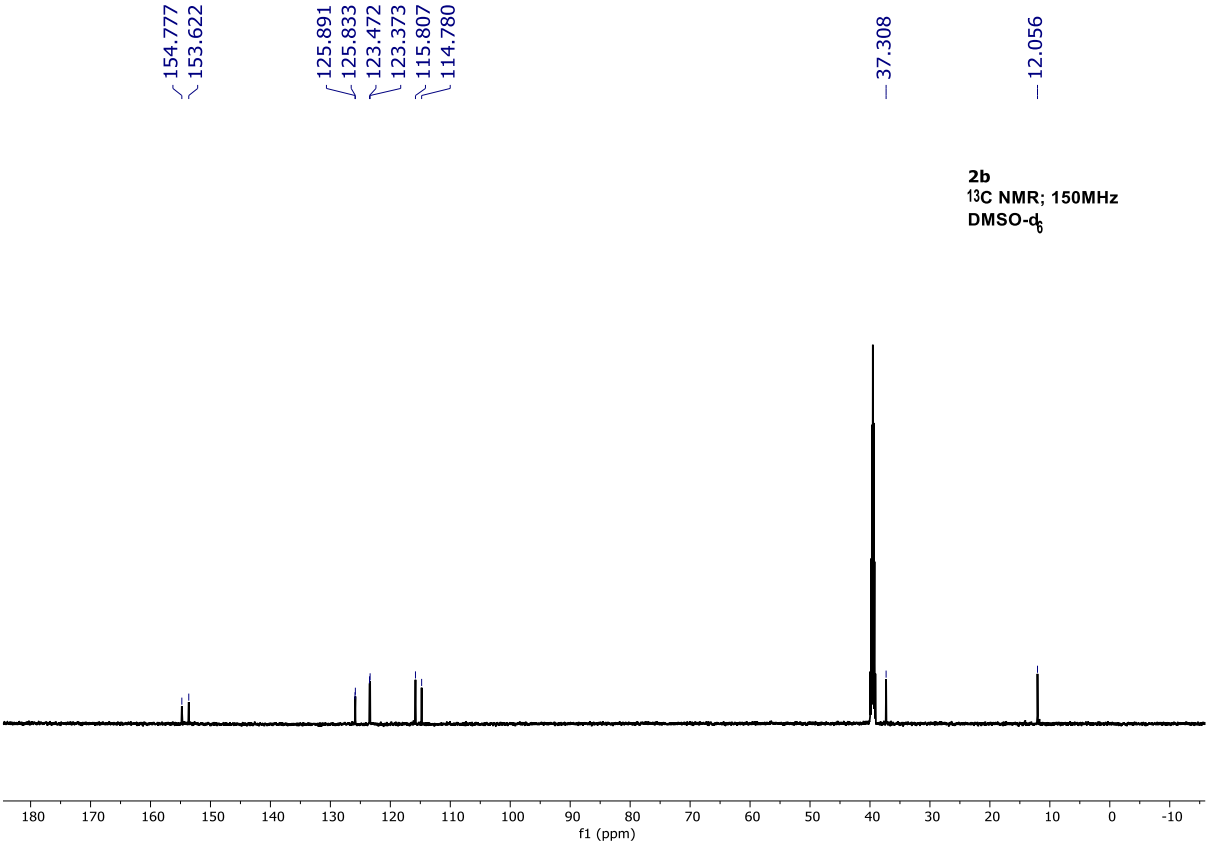
^{1}H NMR of **2a**



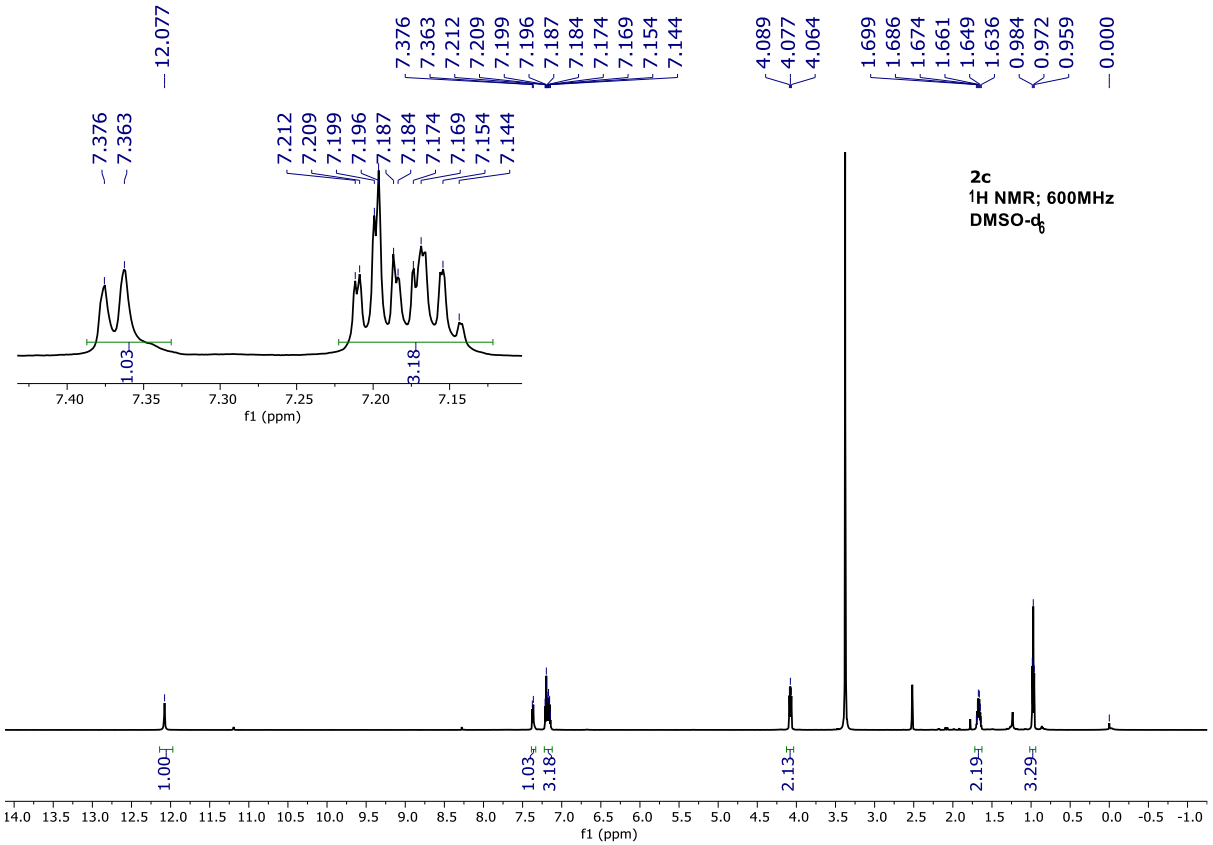
^{13}C NMR of **2a**



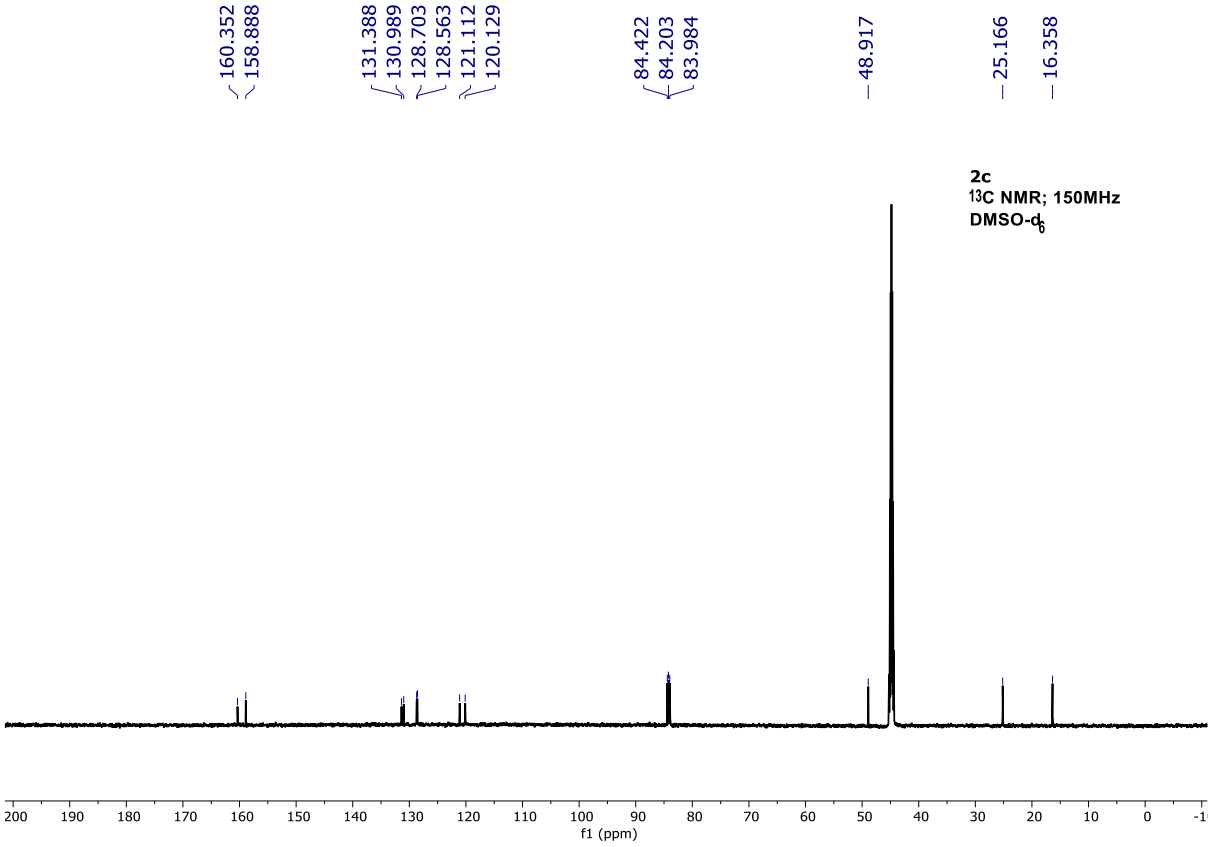
^{1}H NMR of **2b**



^{13}C NMR of **2b**



^{1}H NMR of **2c**



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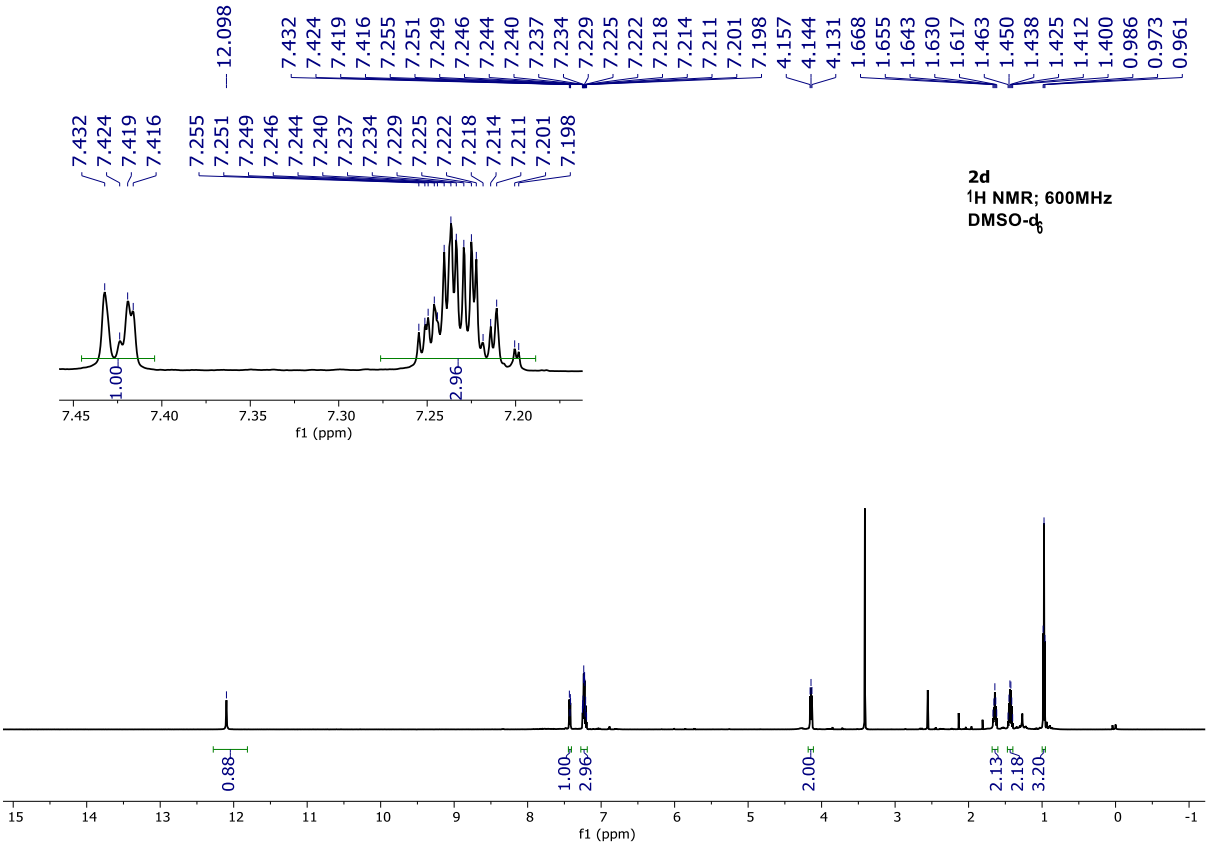

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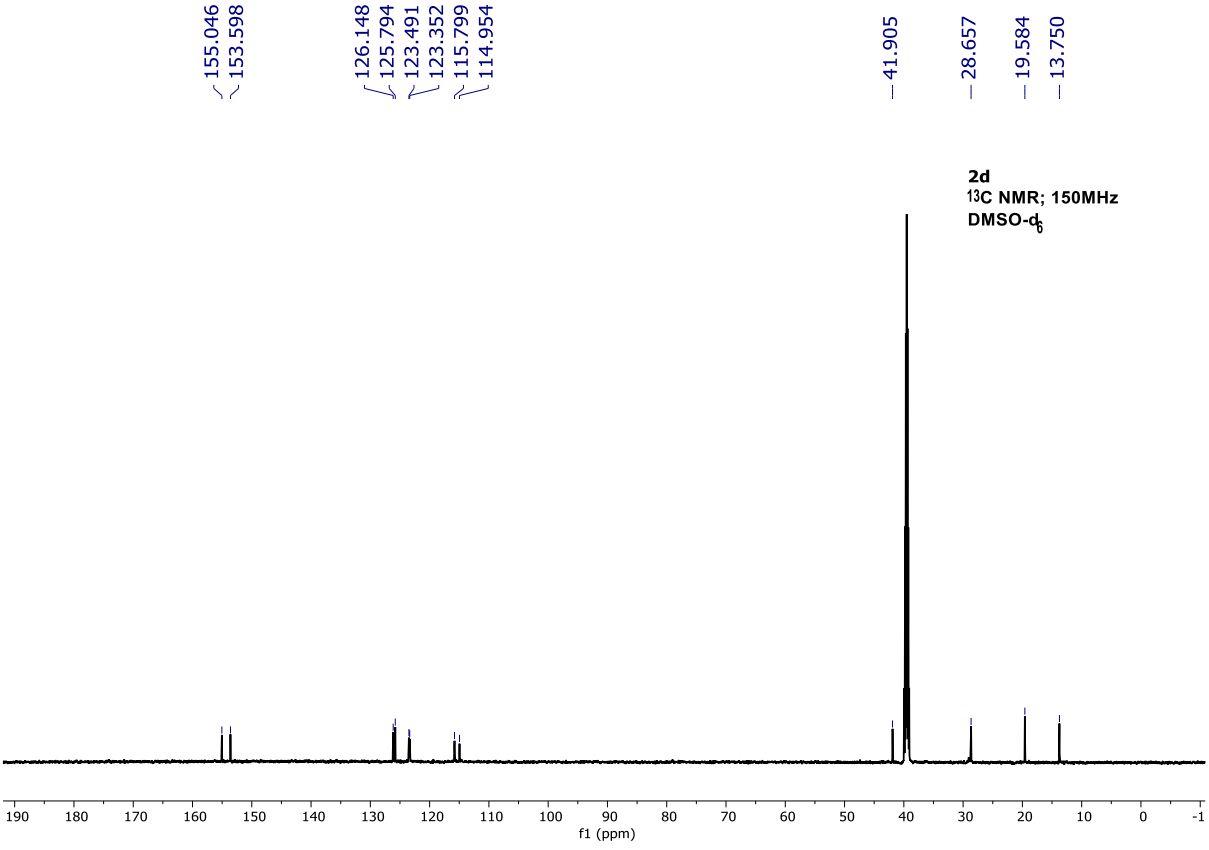

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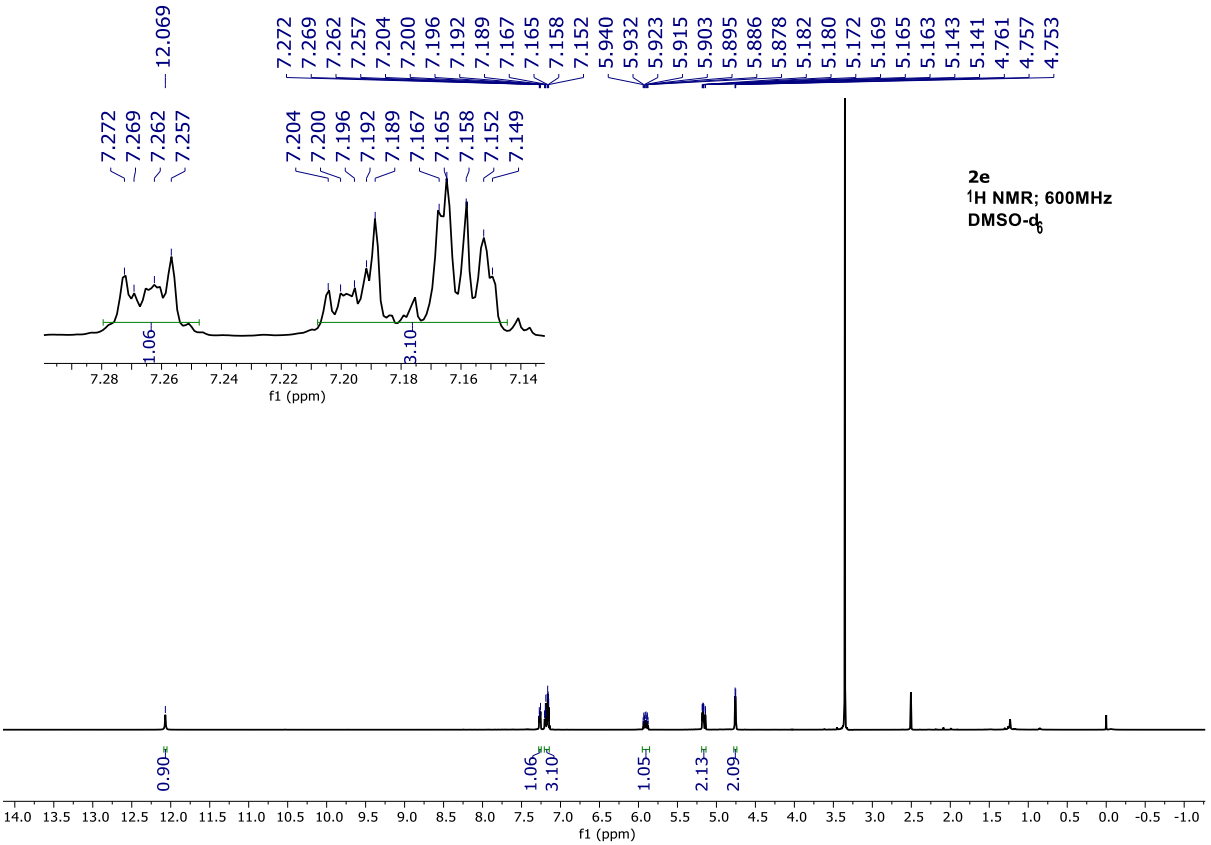
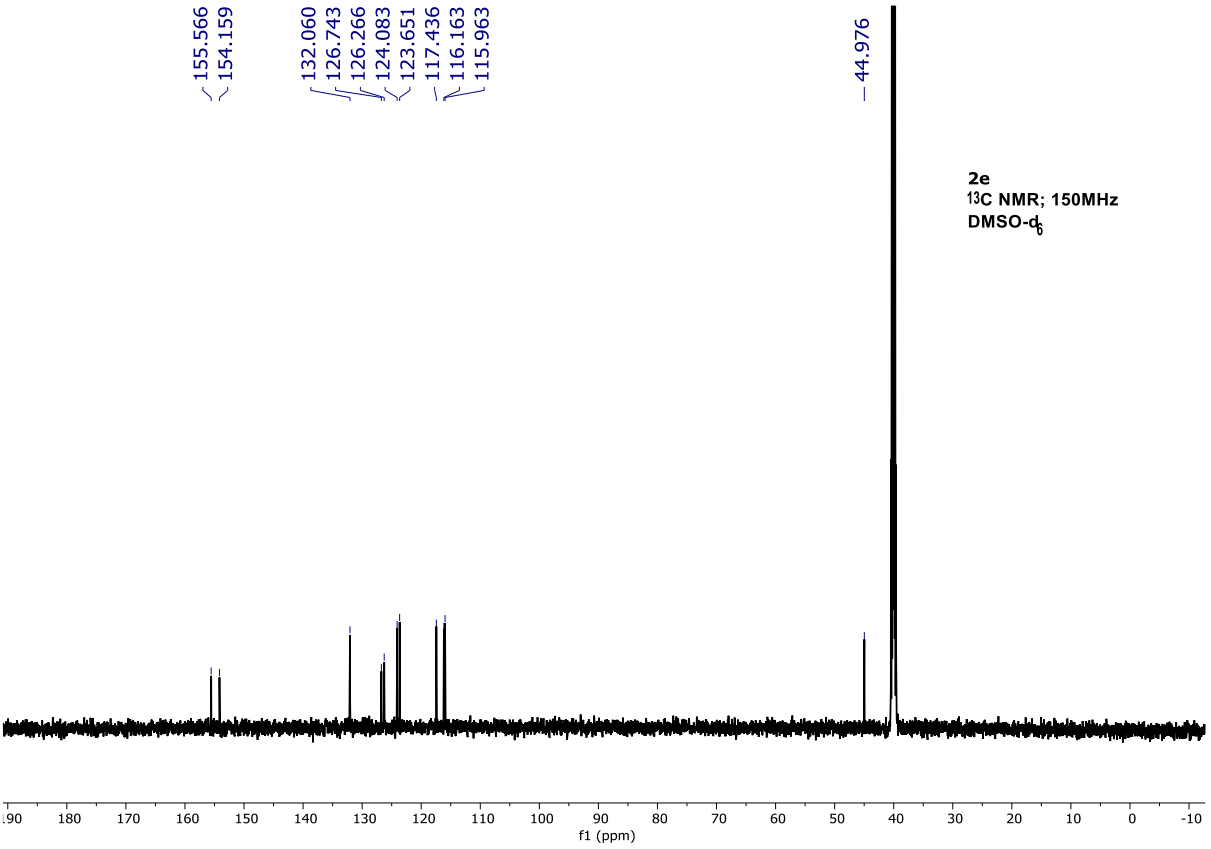


^{1}H NMR of **2e**



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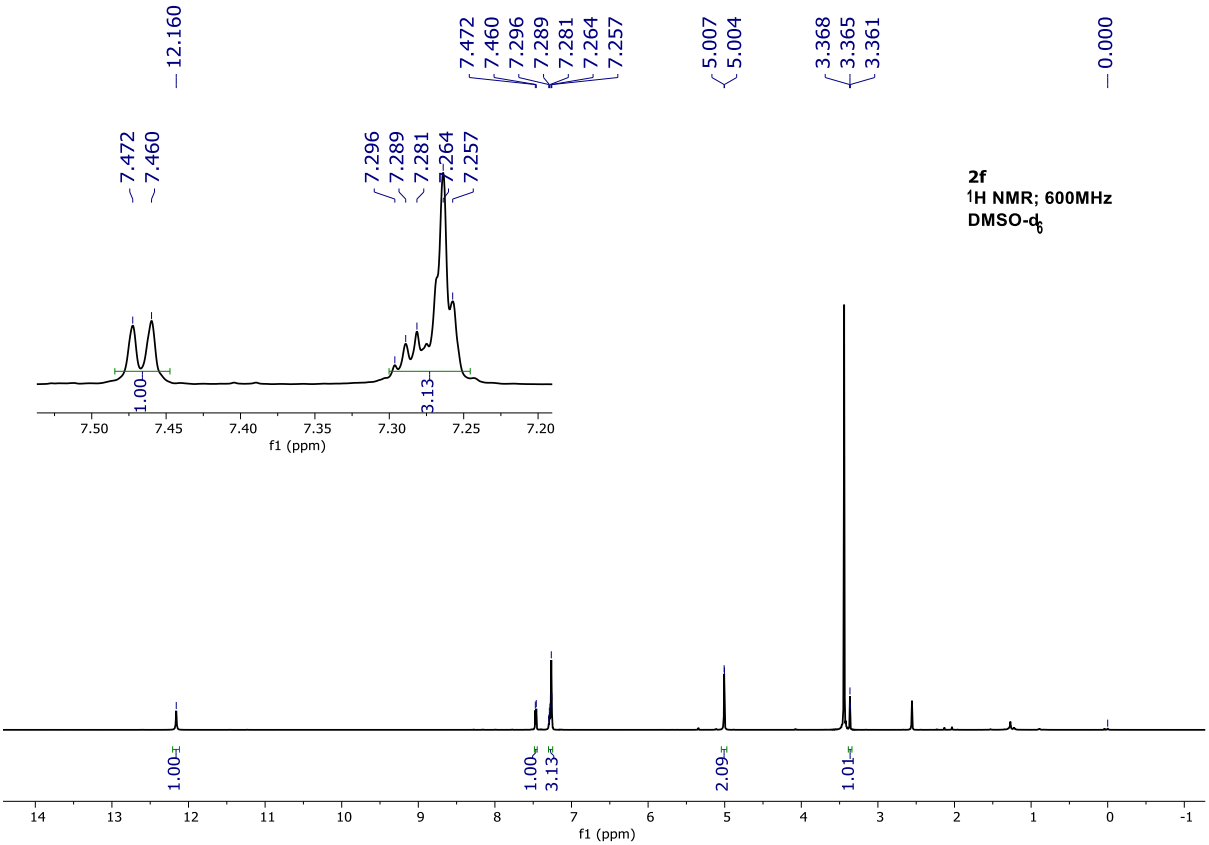
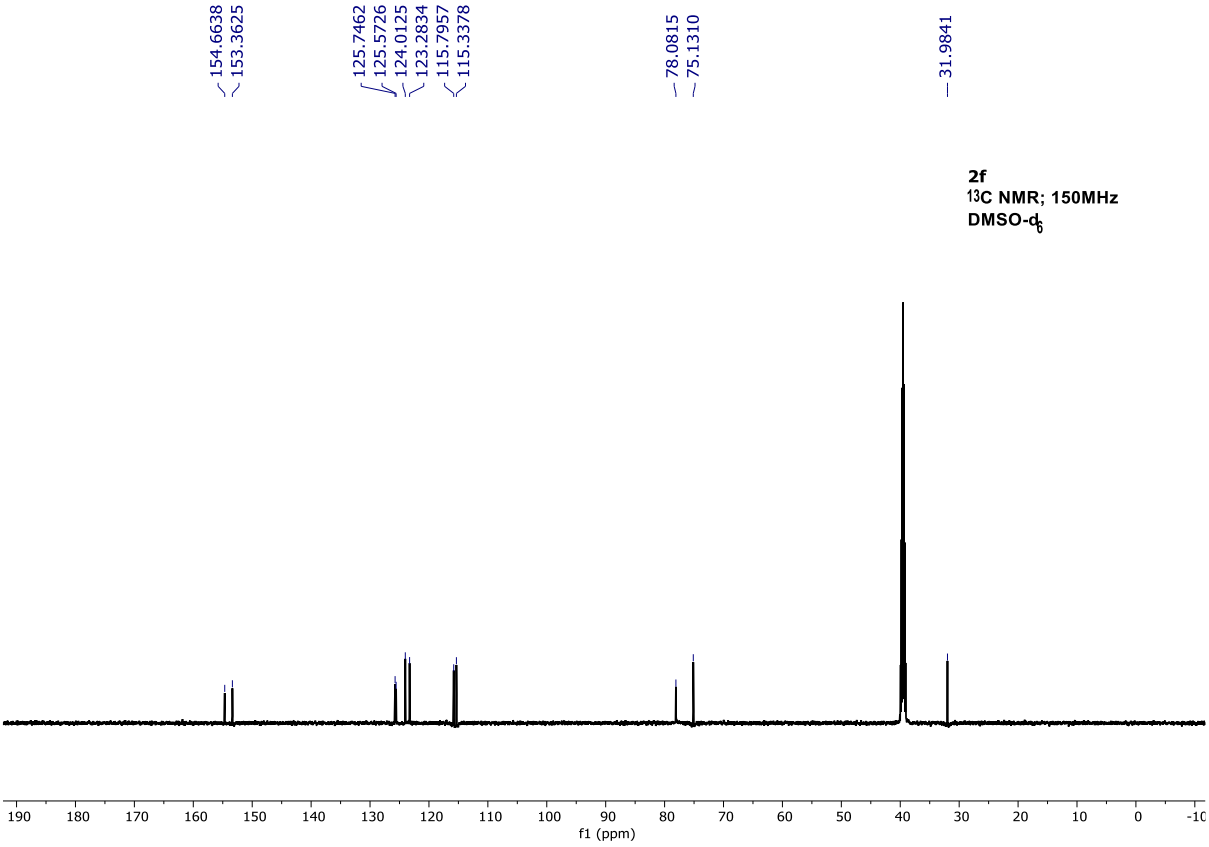


^{1}H NMR of **2f**



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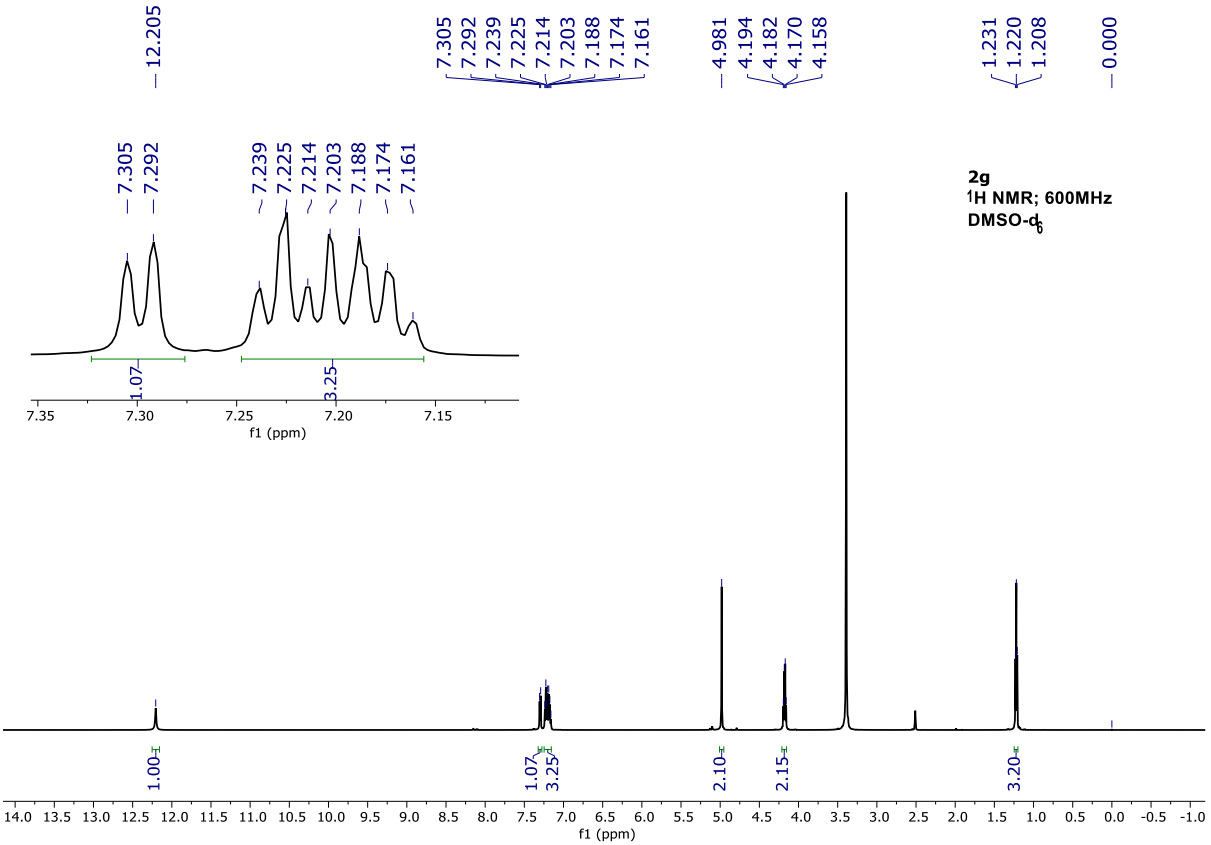

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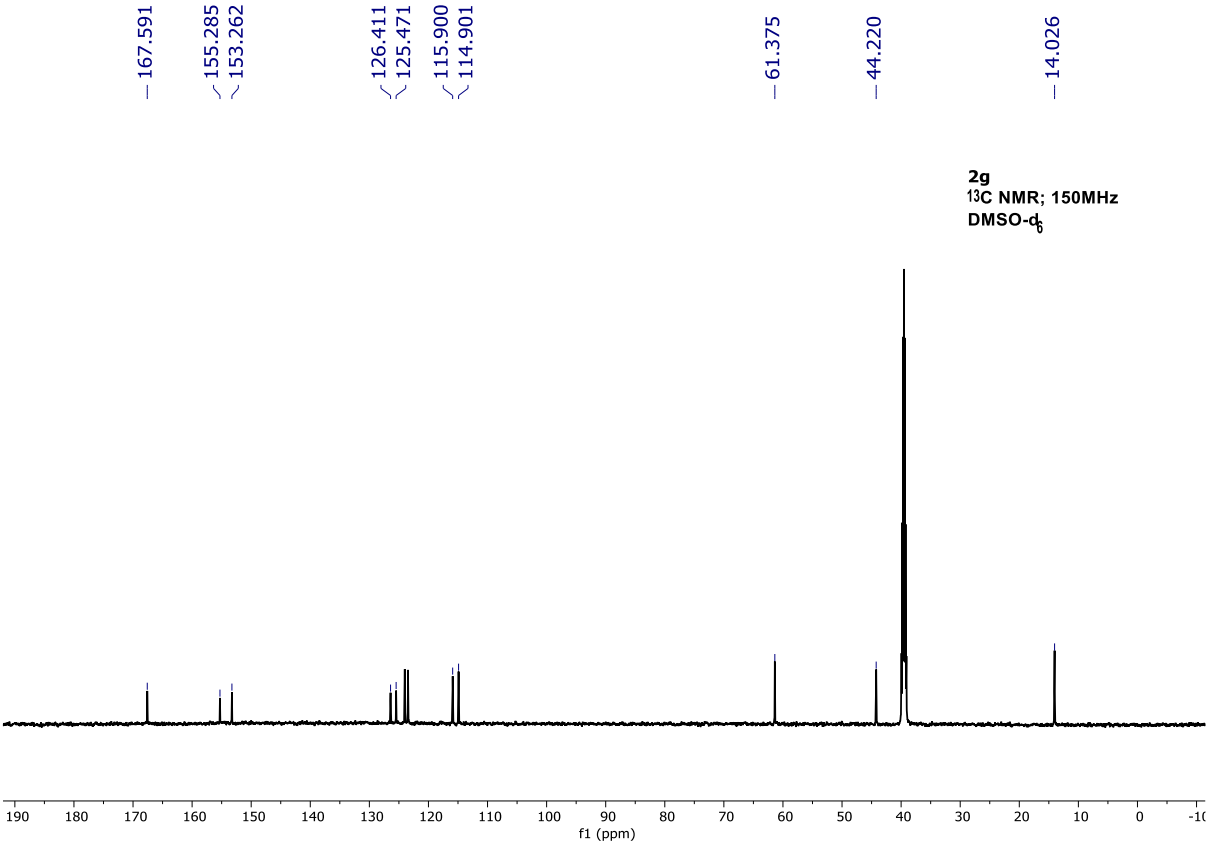

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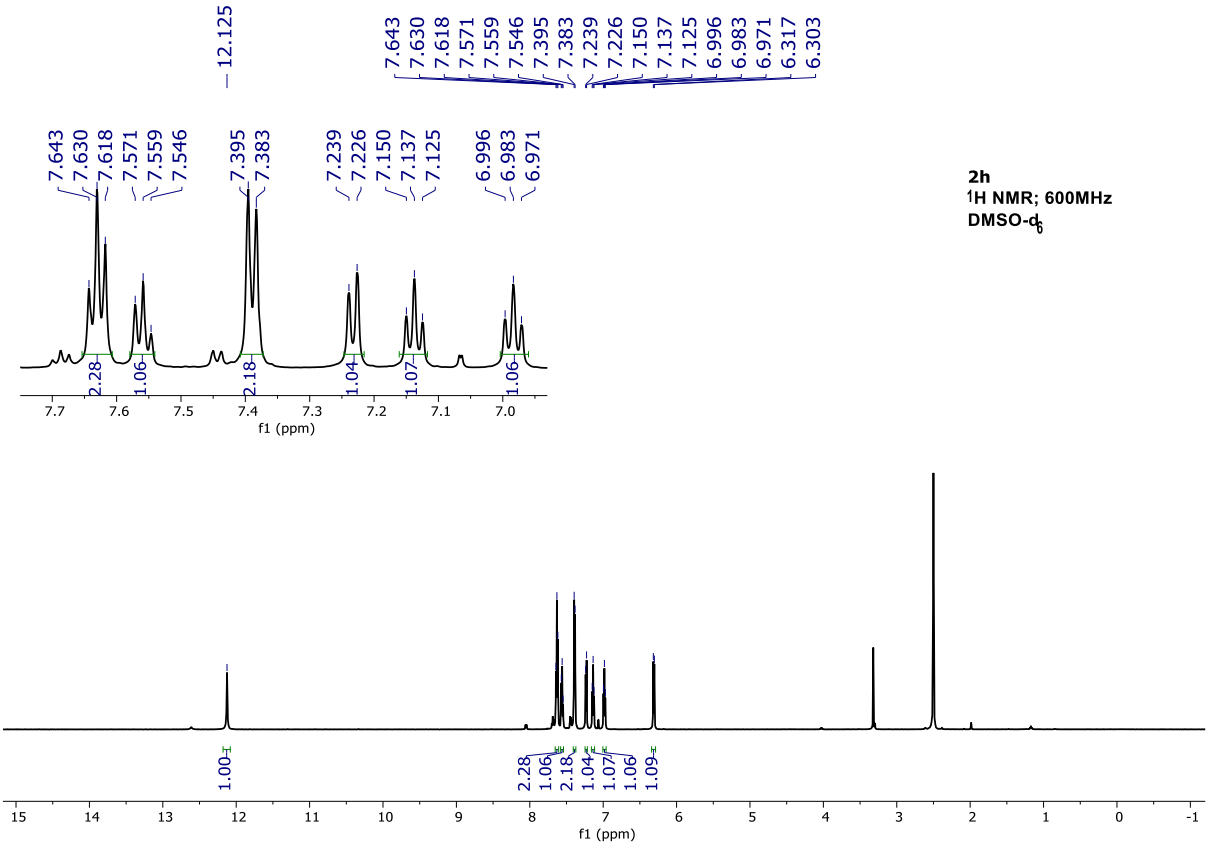

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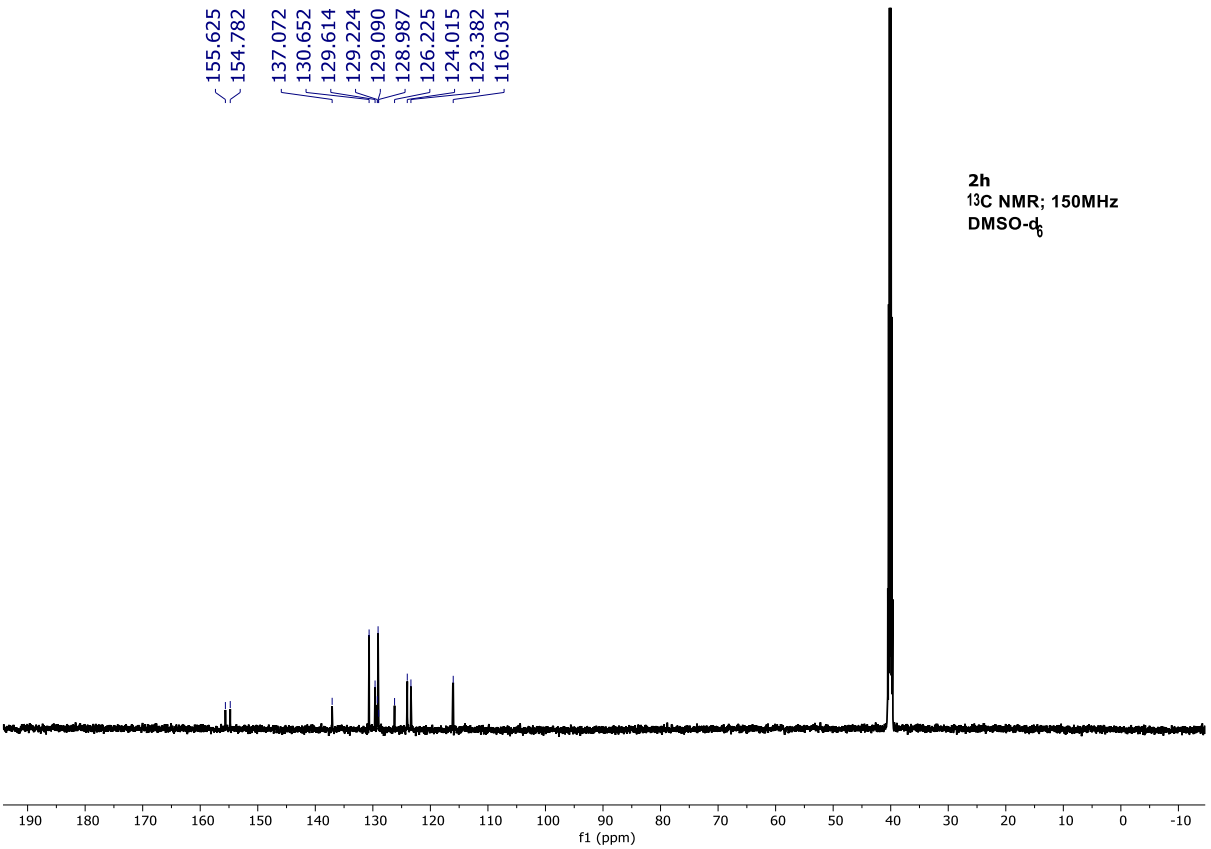

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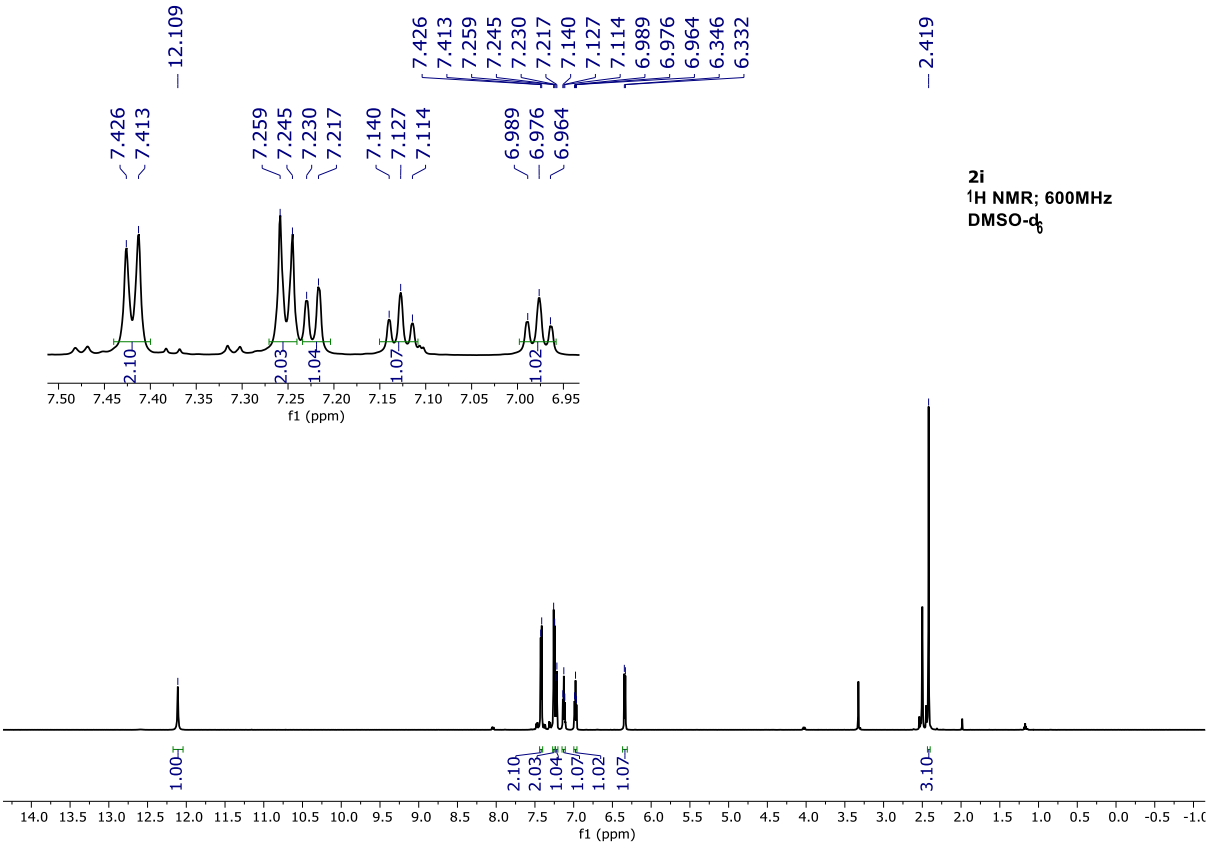

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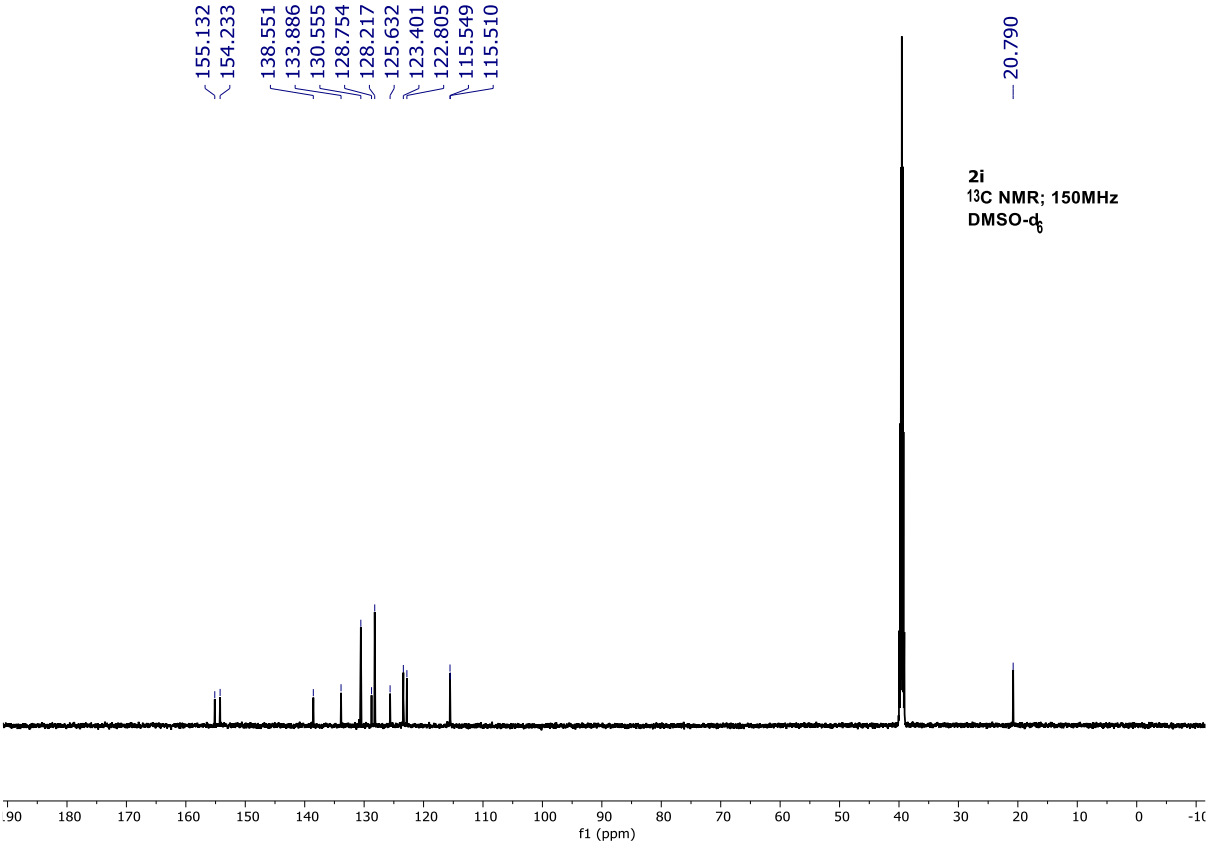

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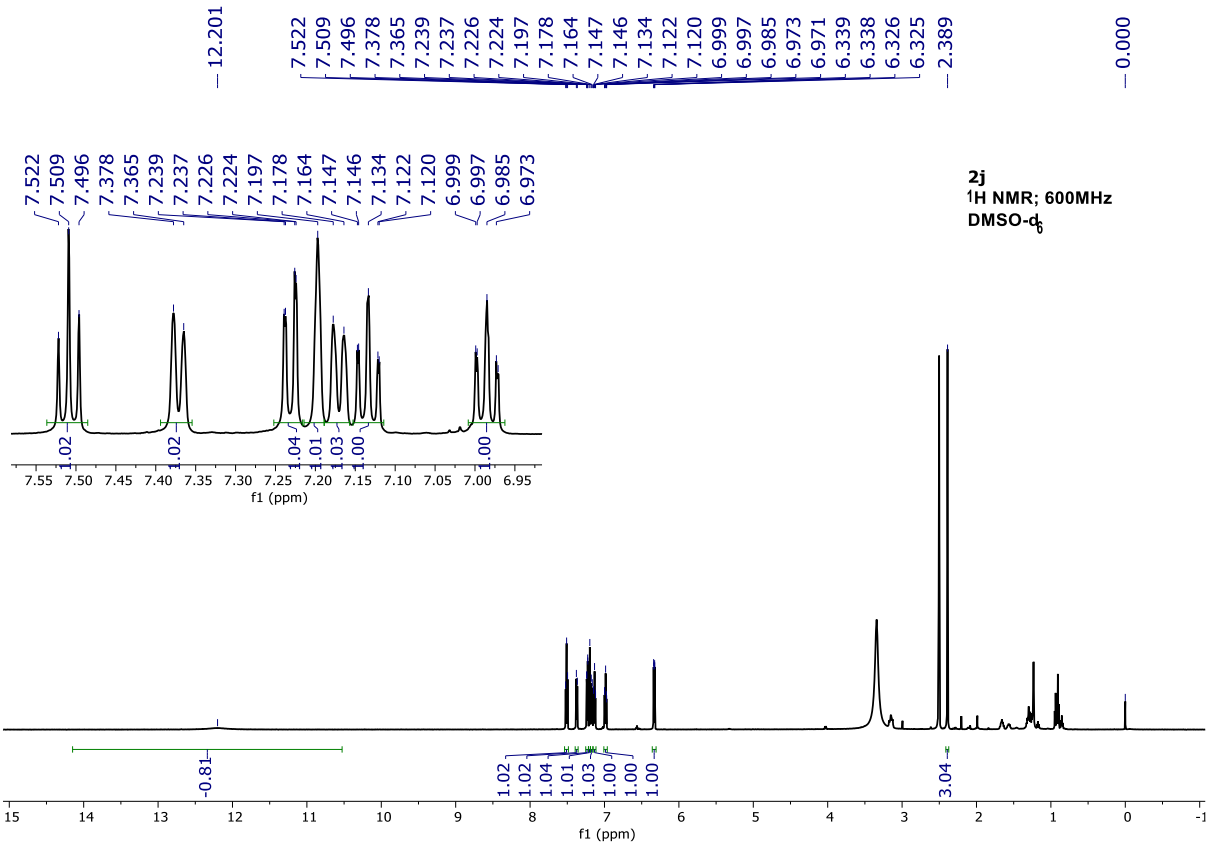

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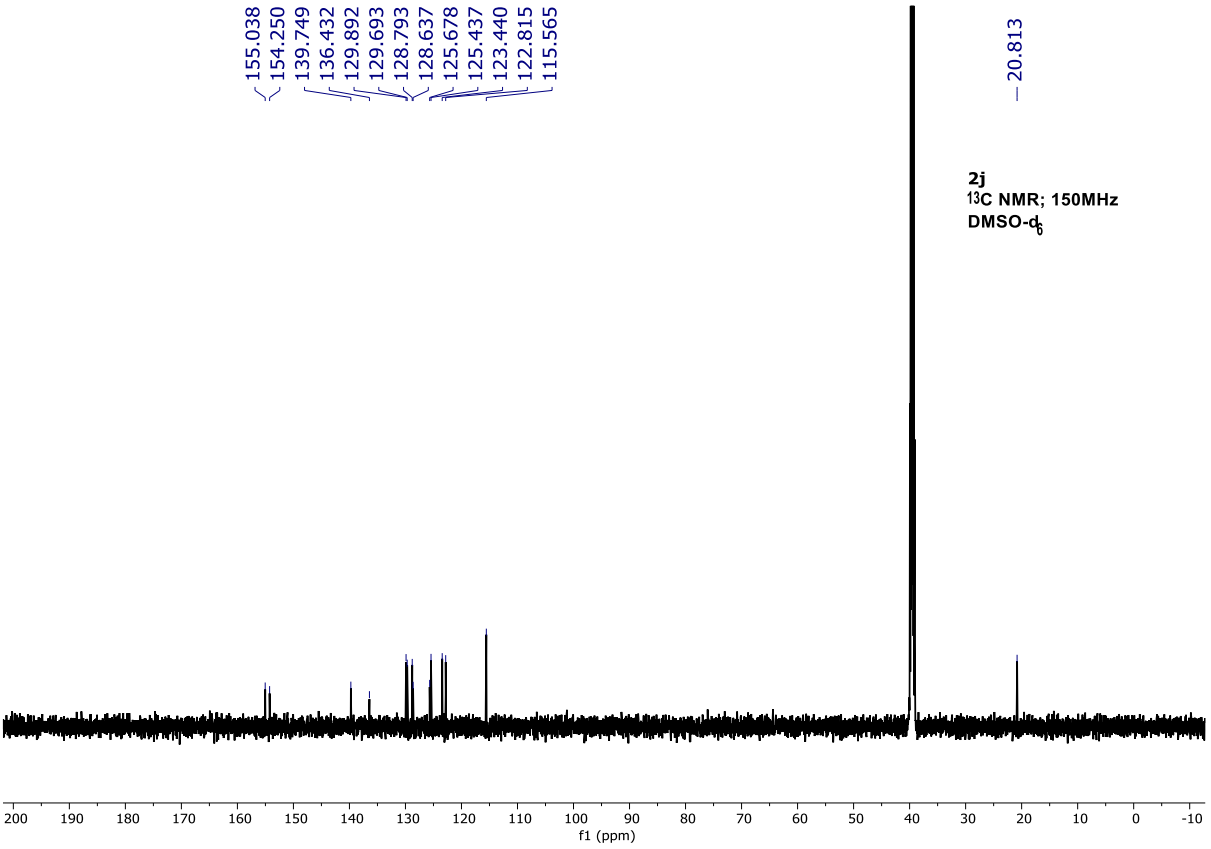

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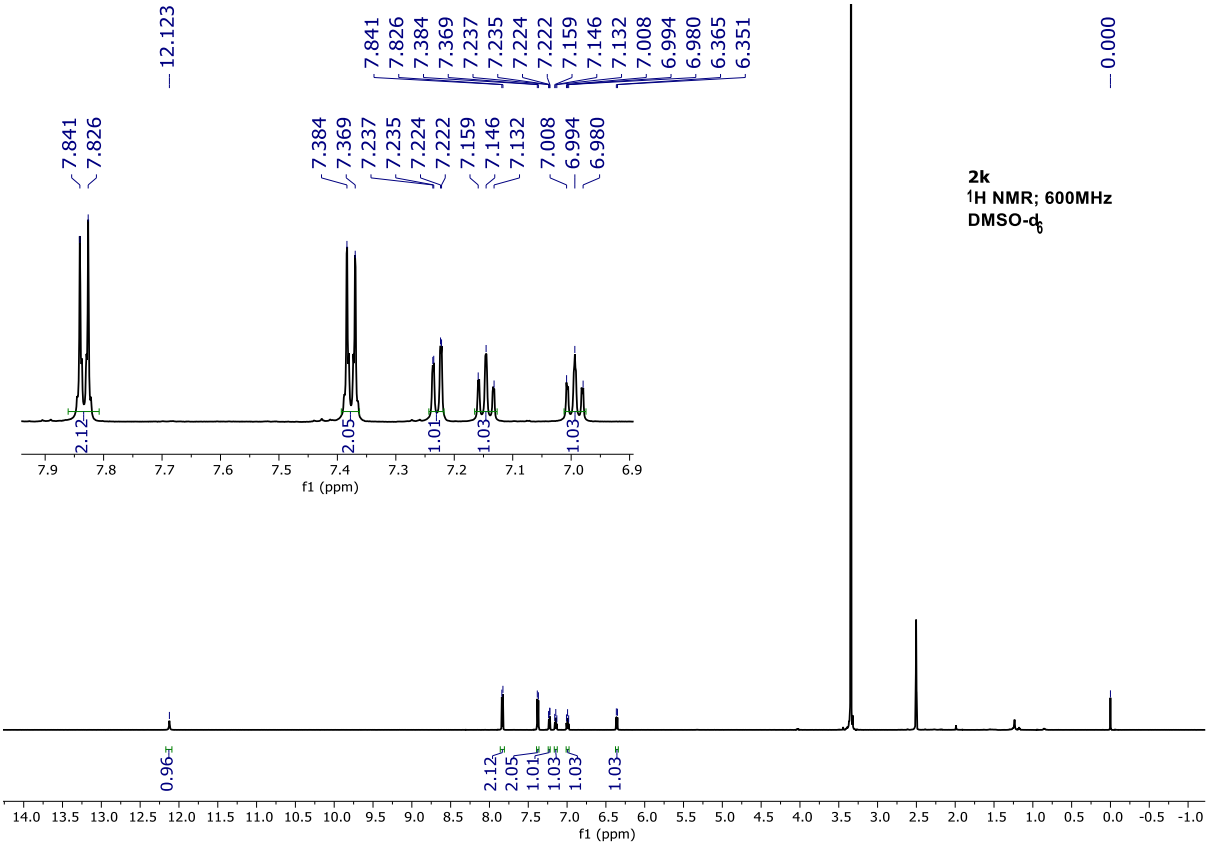

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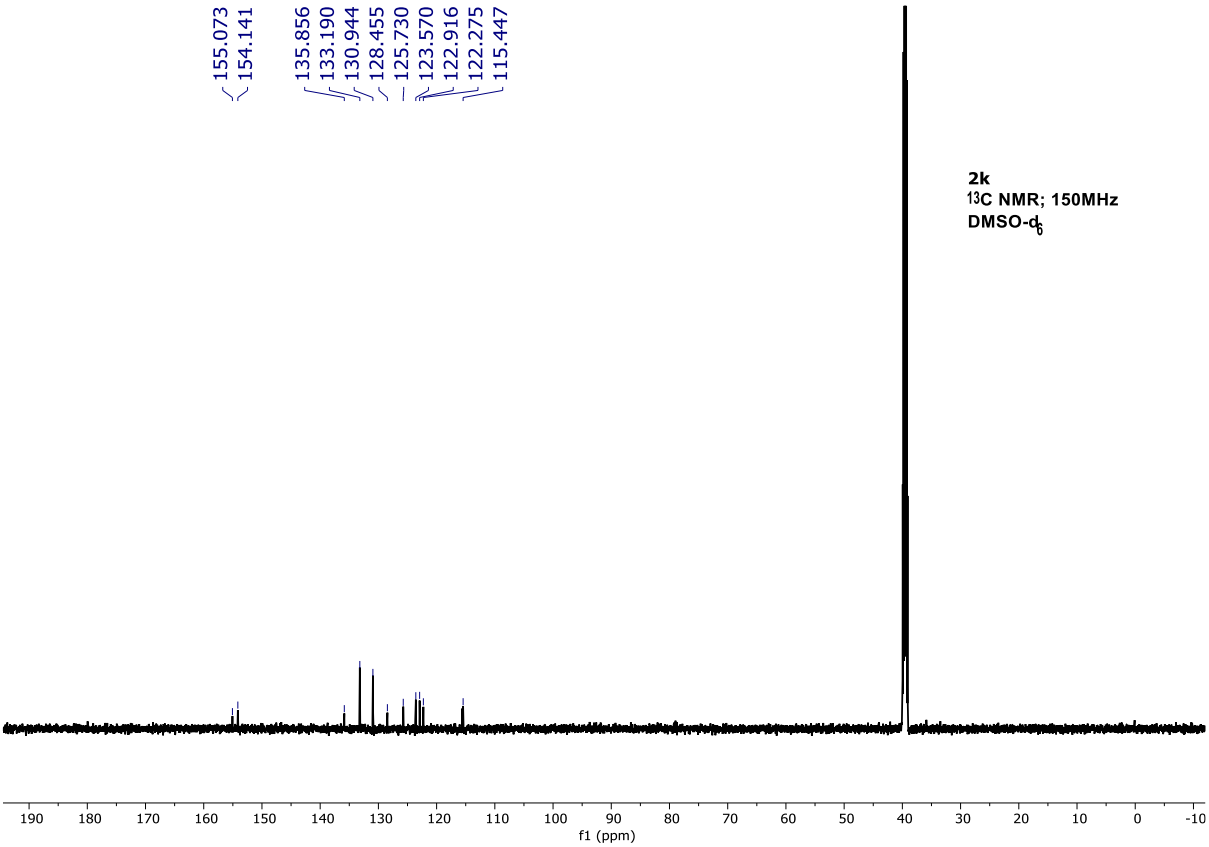

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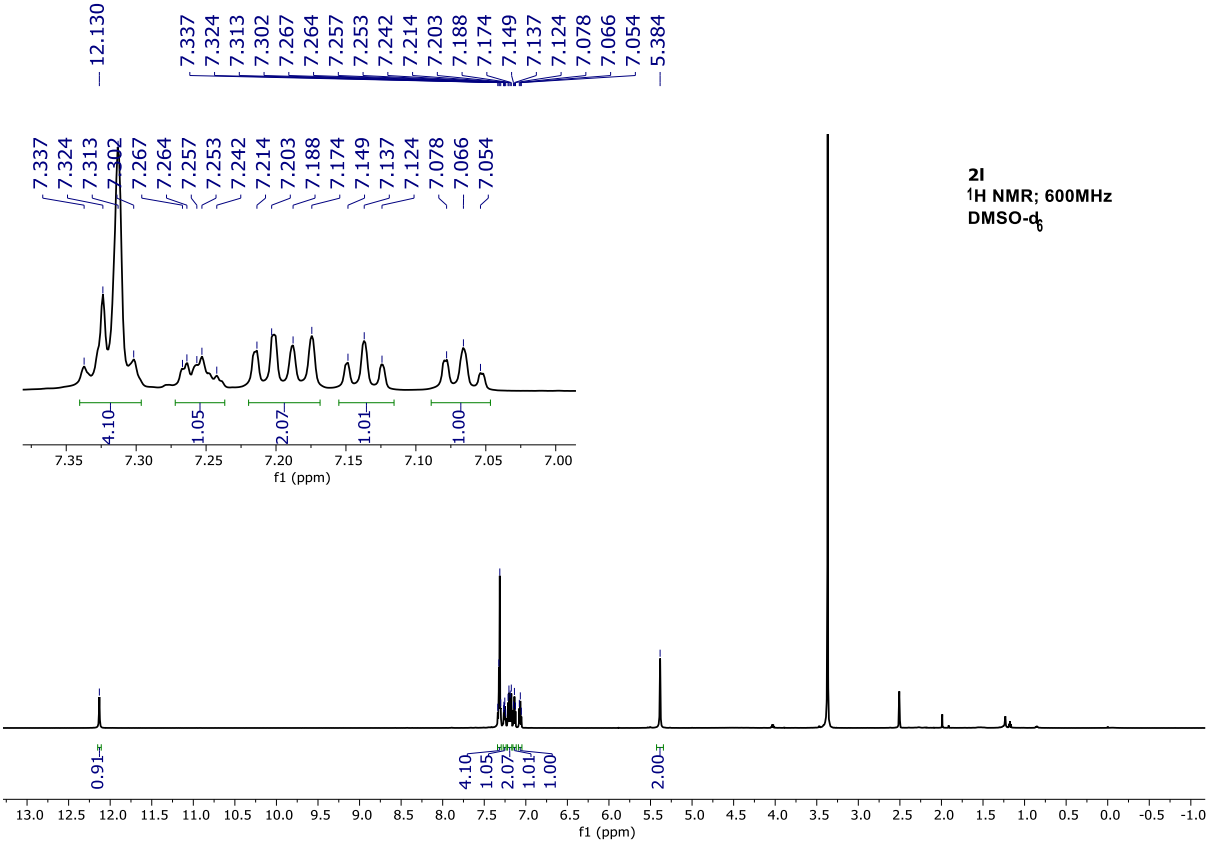

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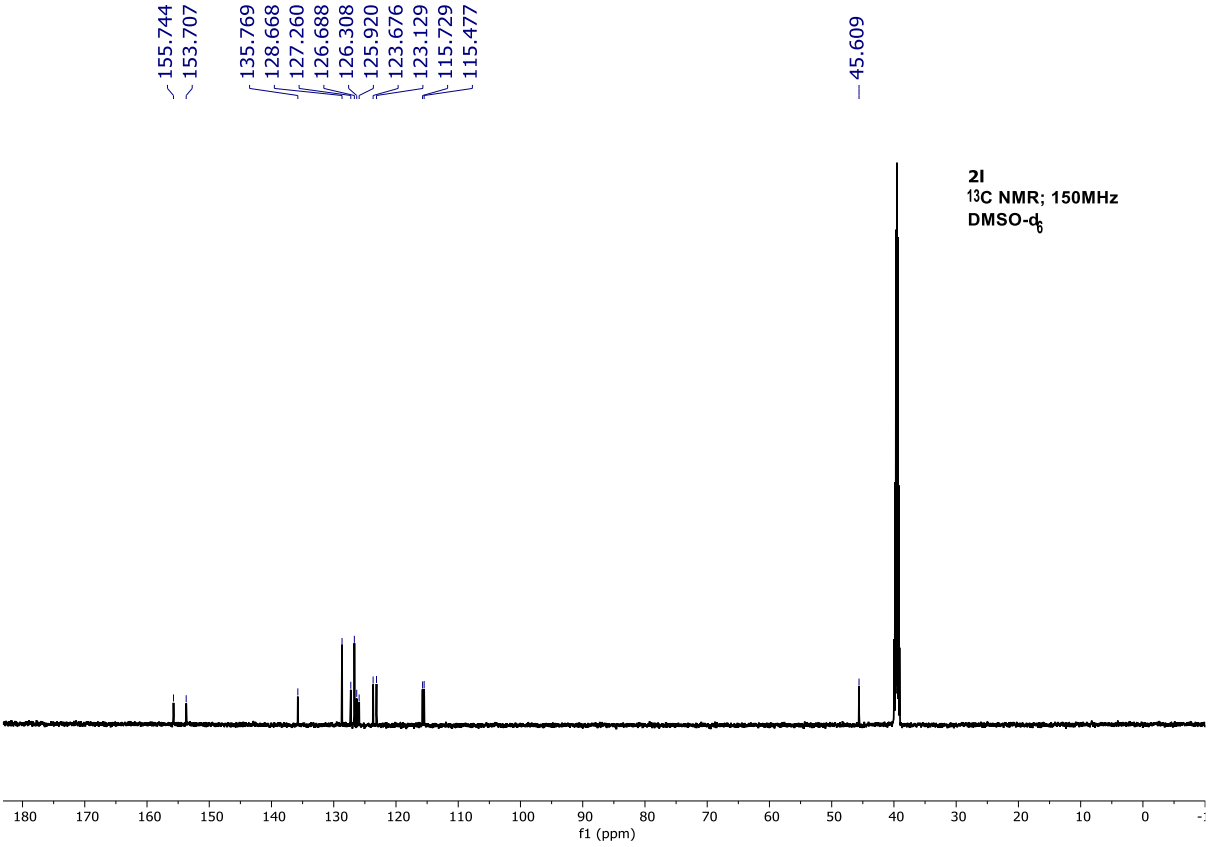

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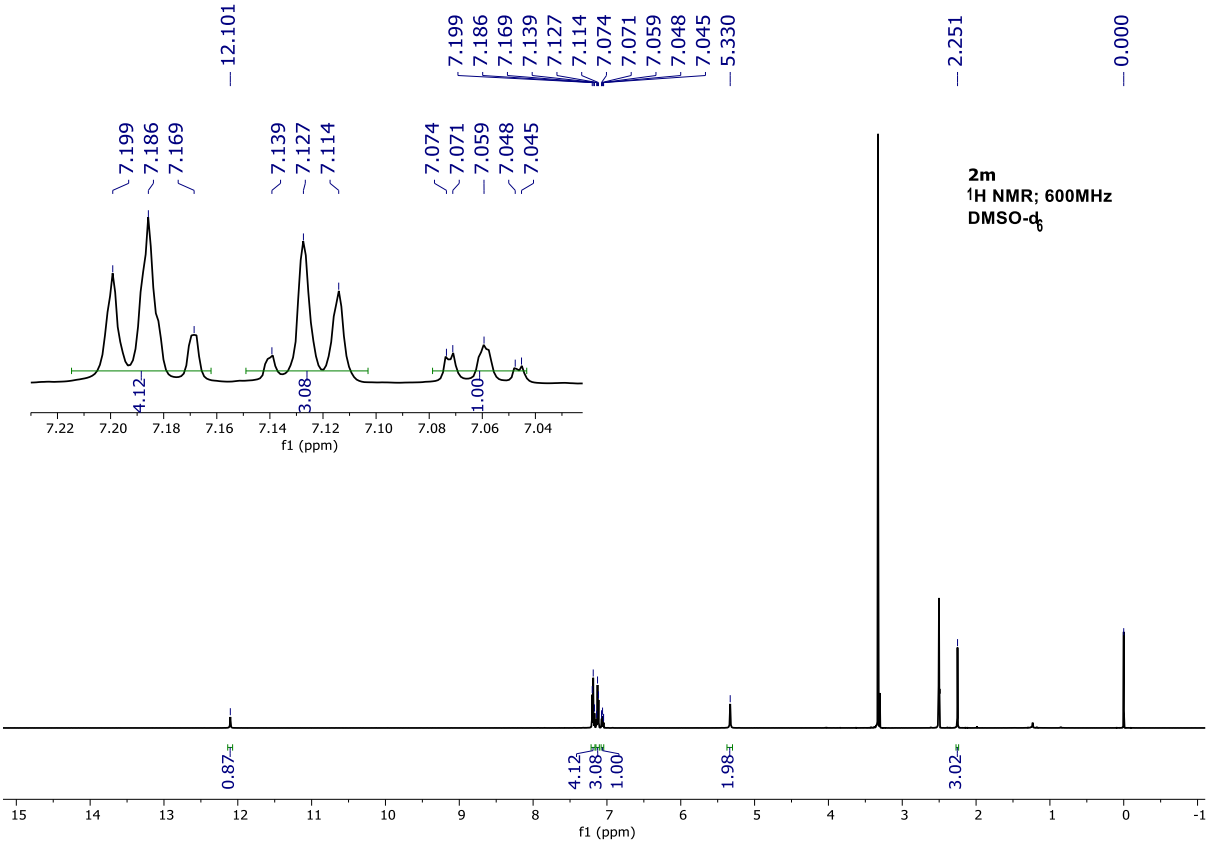

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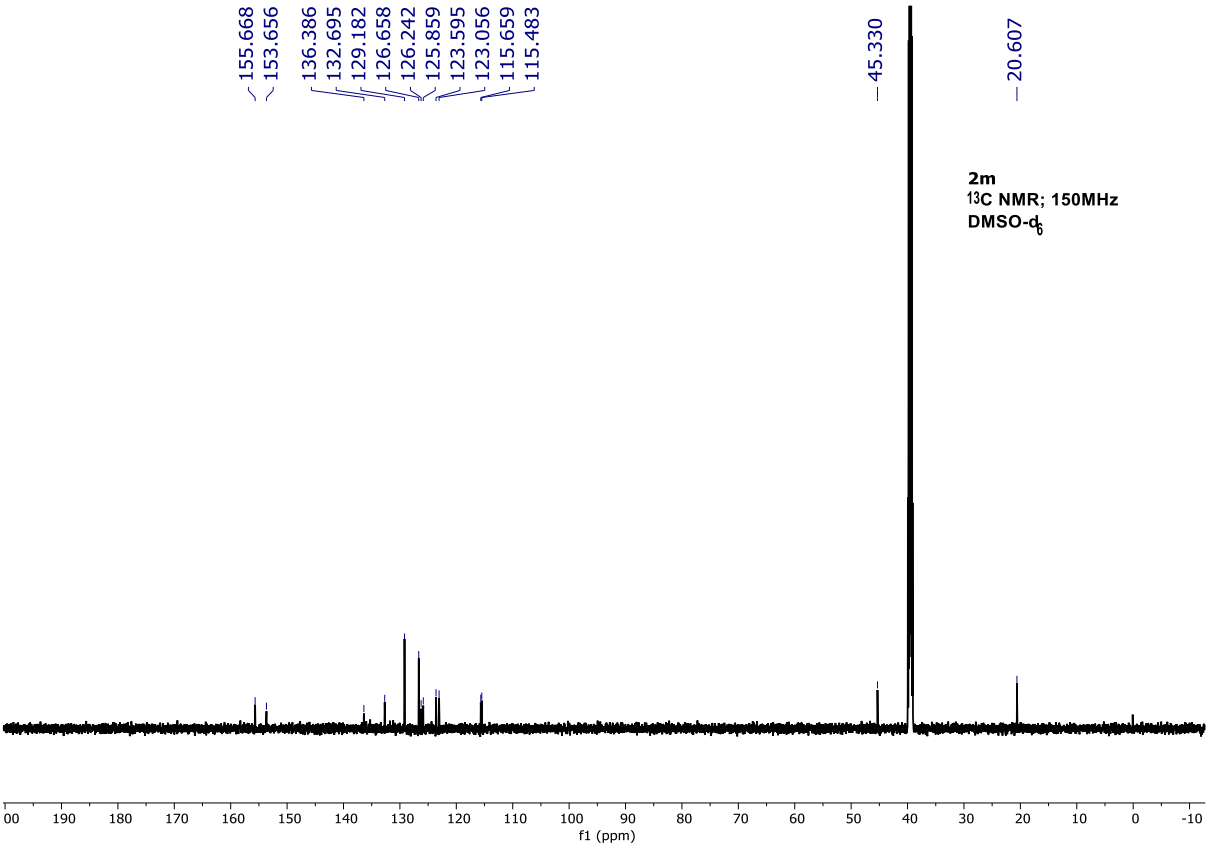

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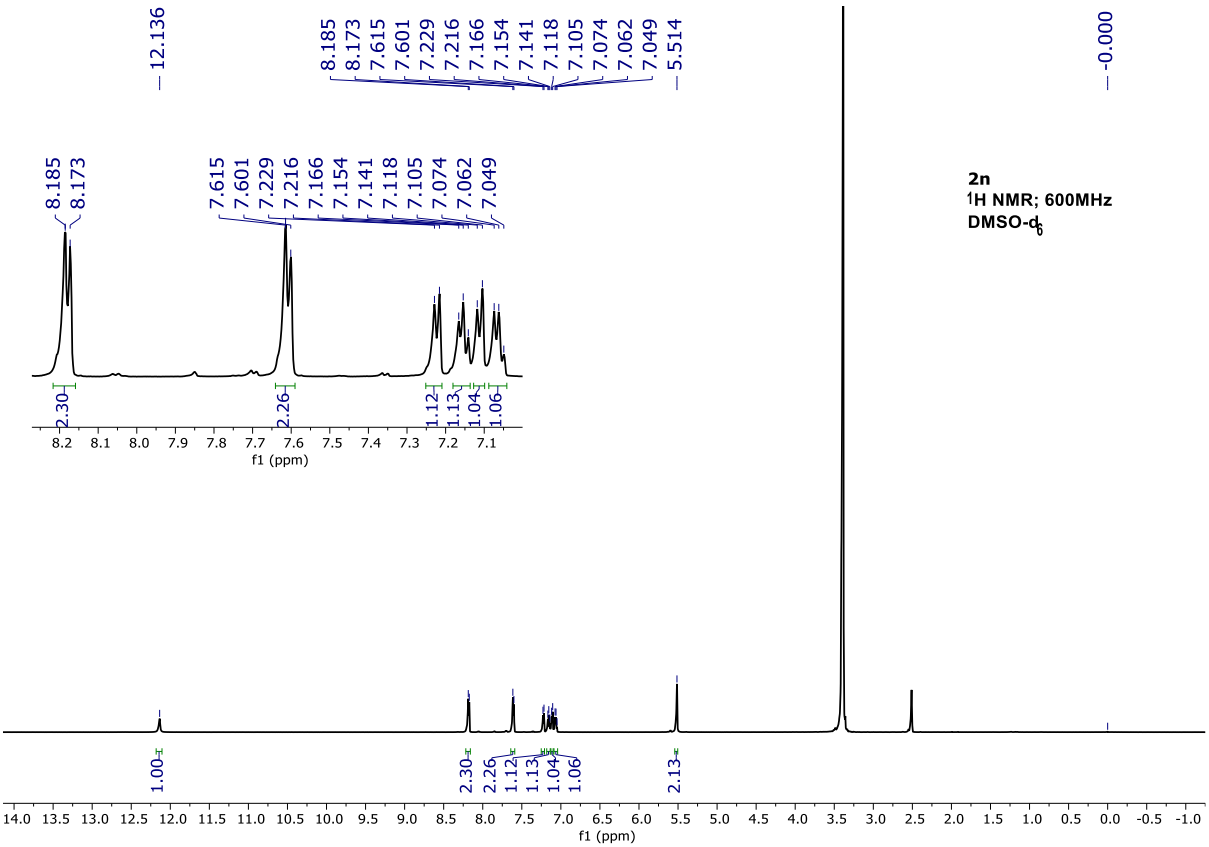

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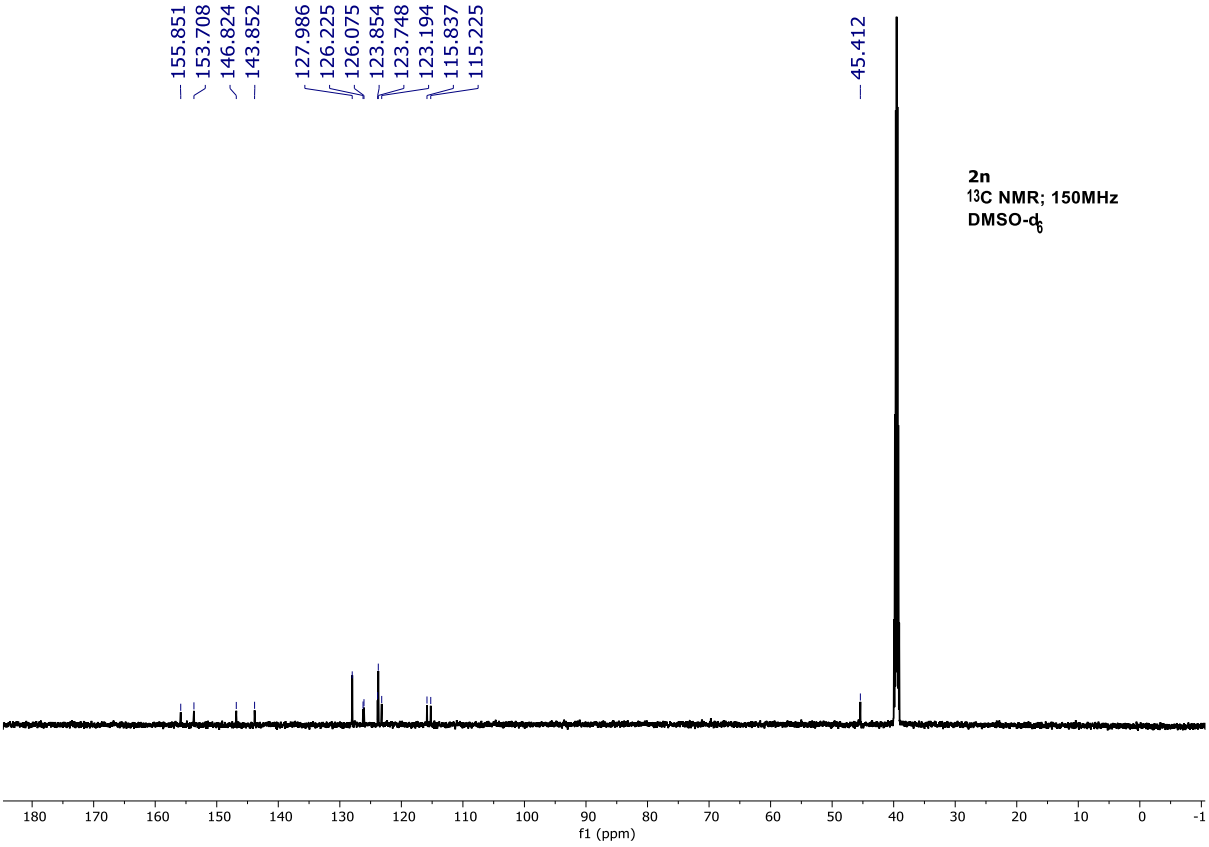

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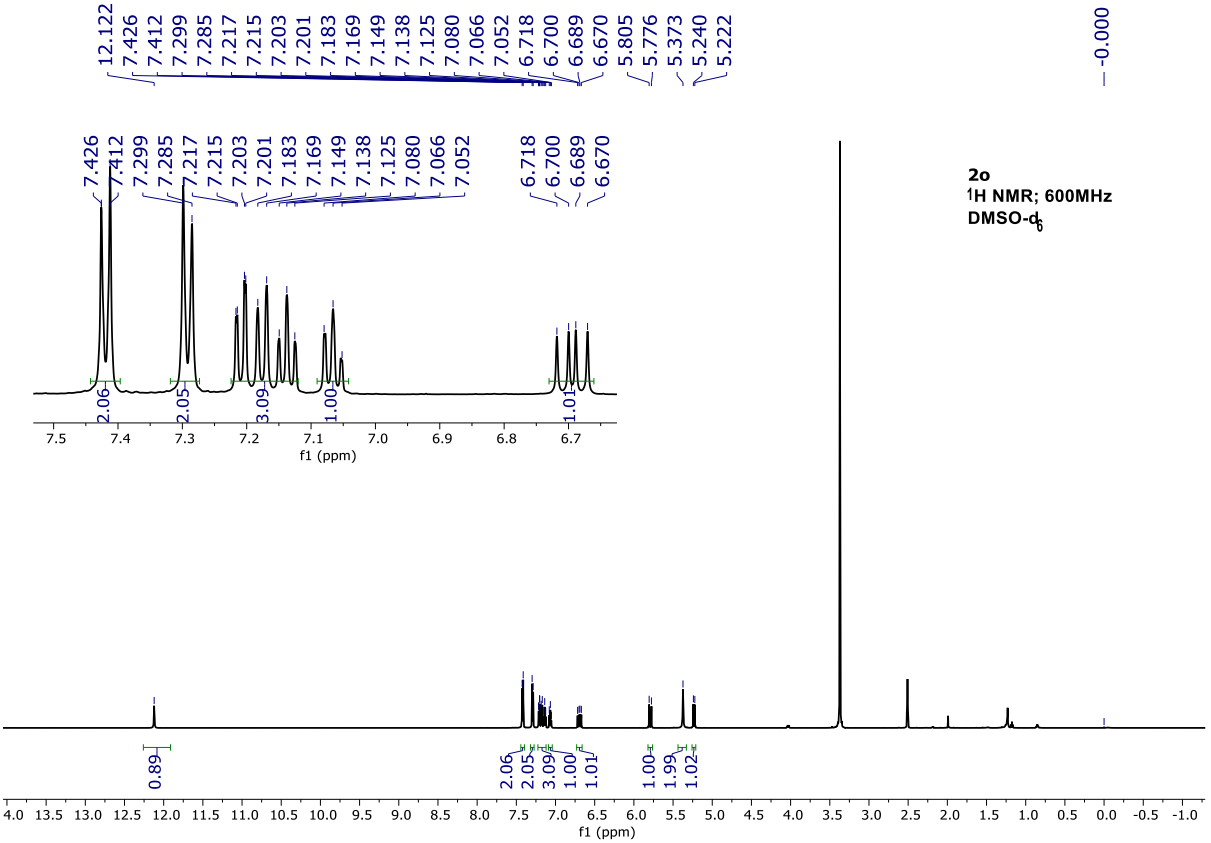

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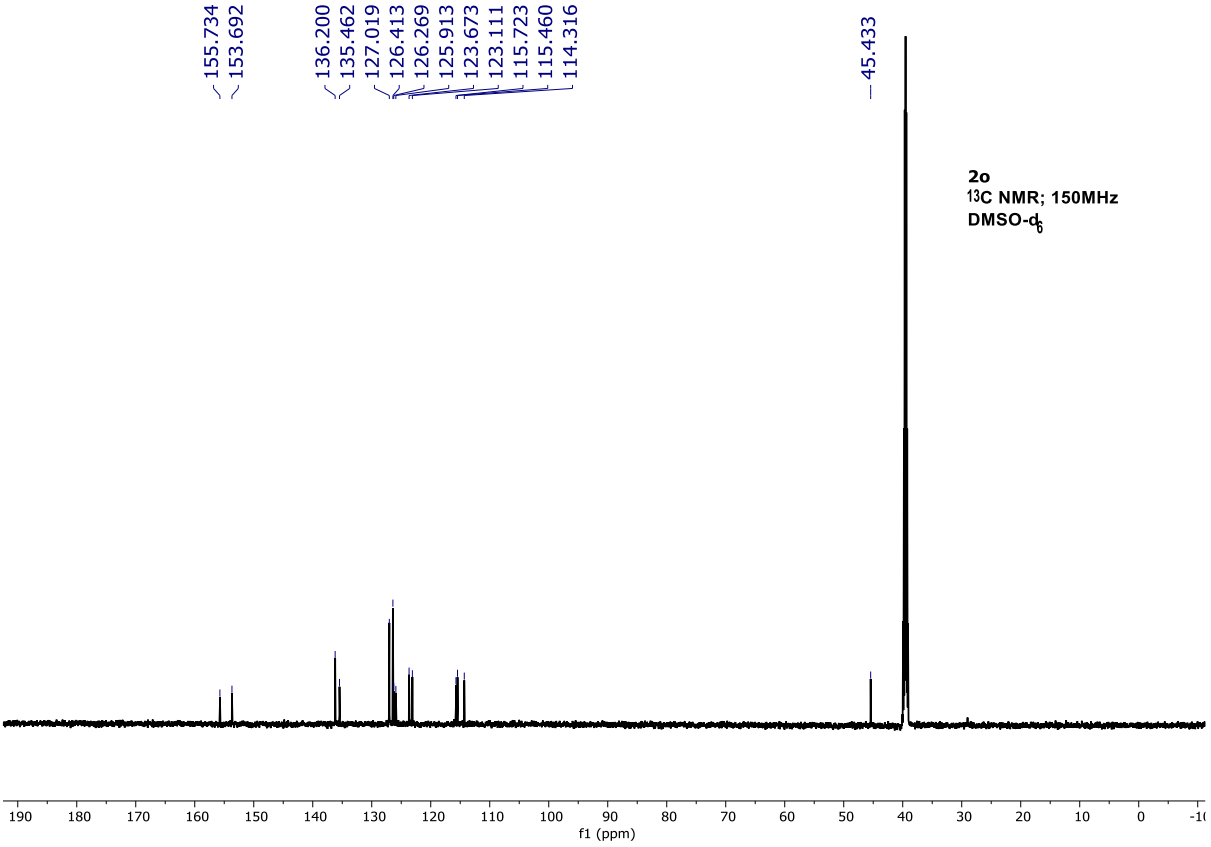

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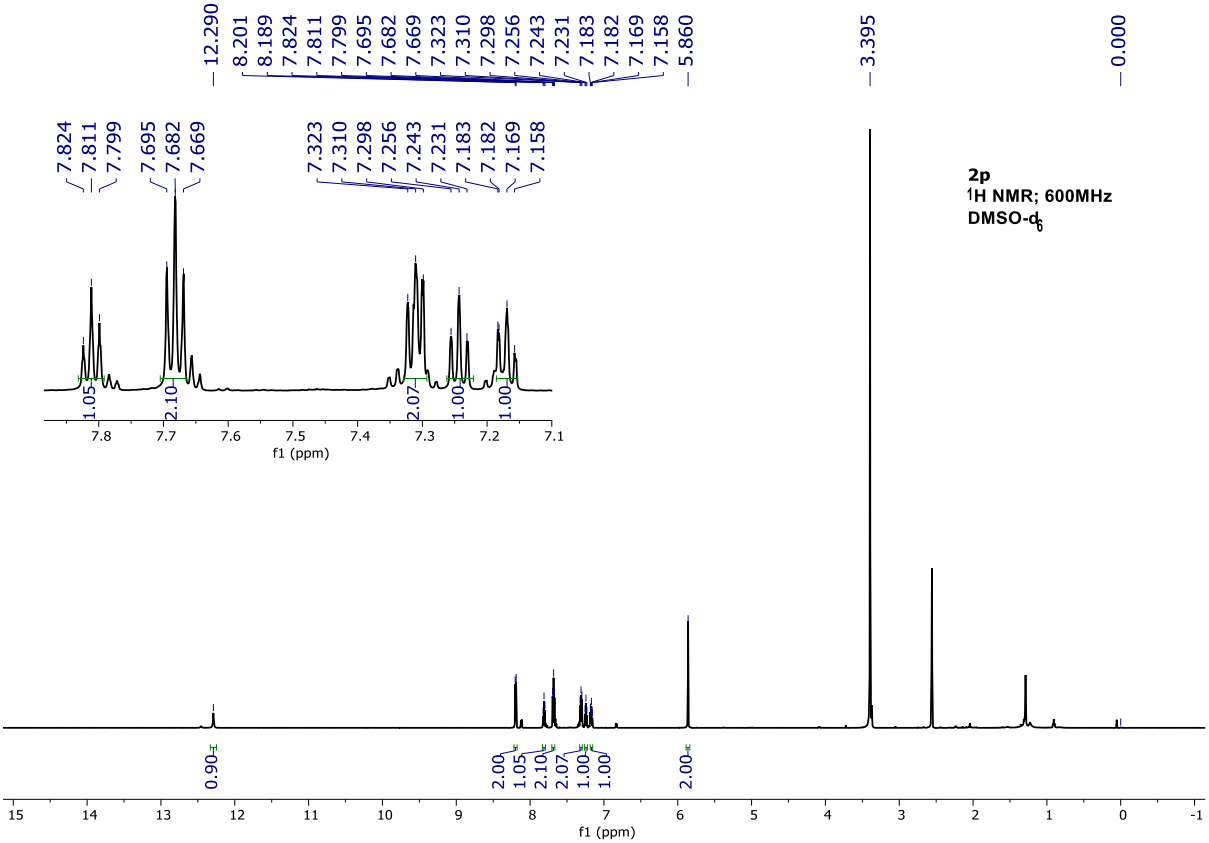

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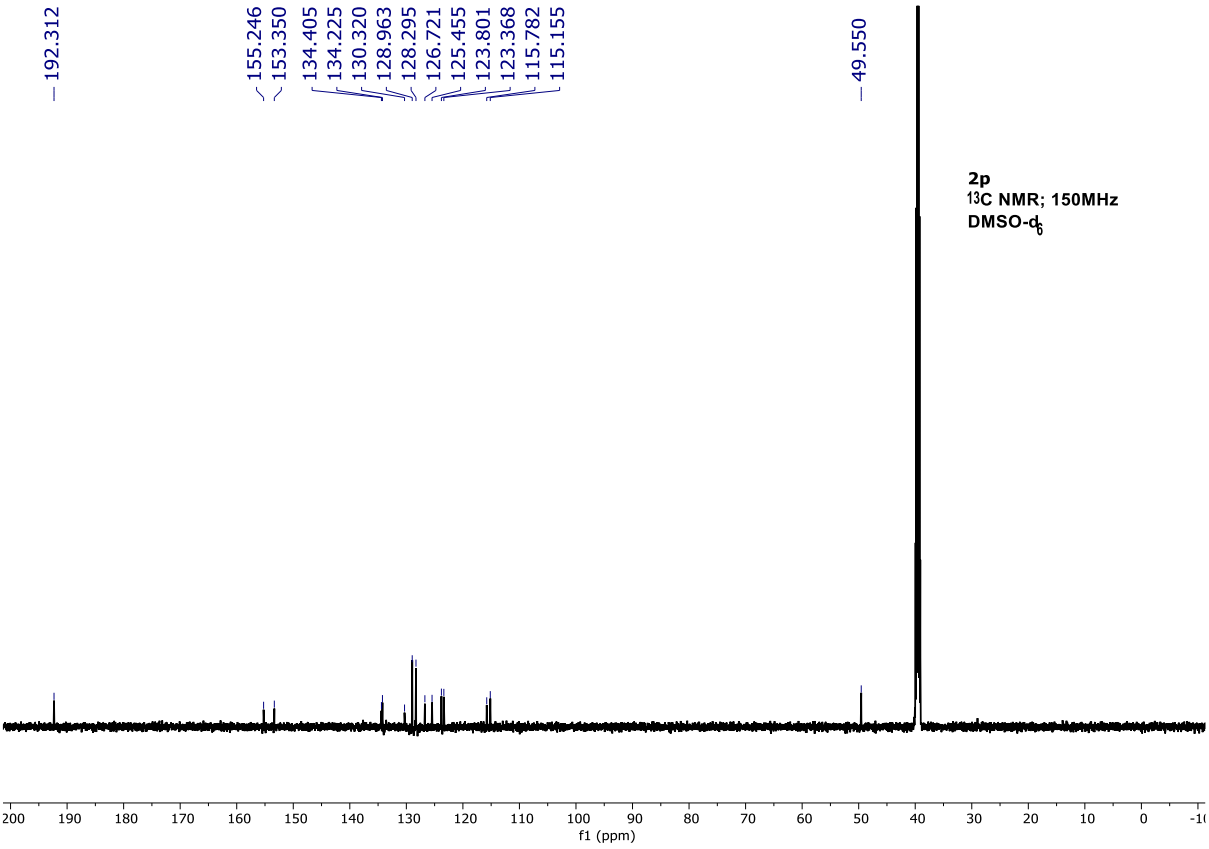

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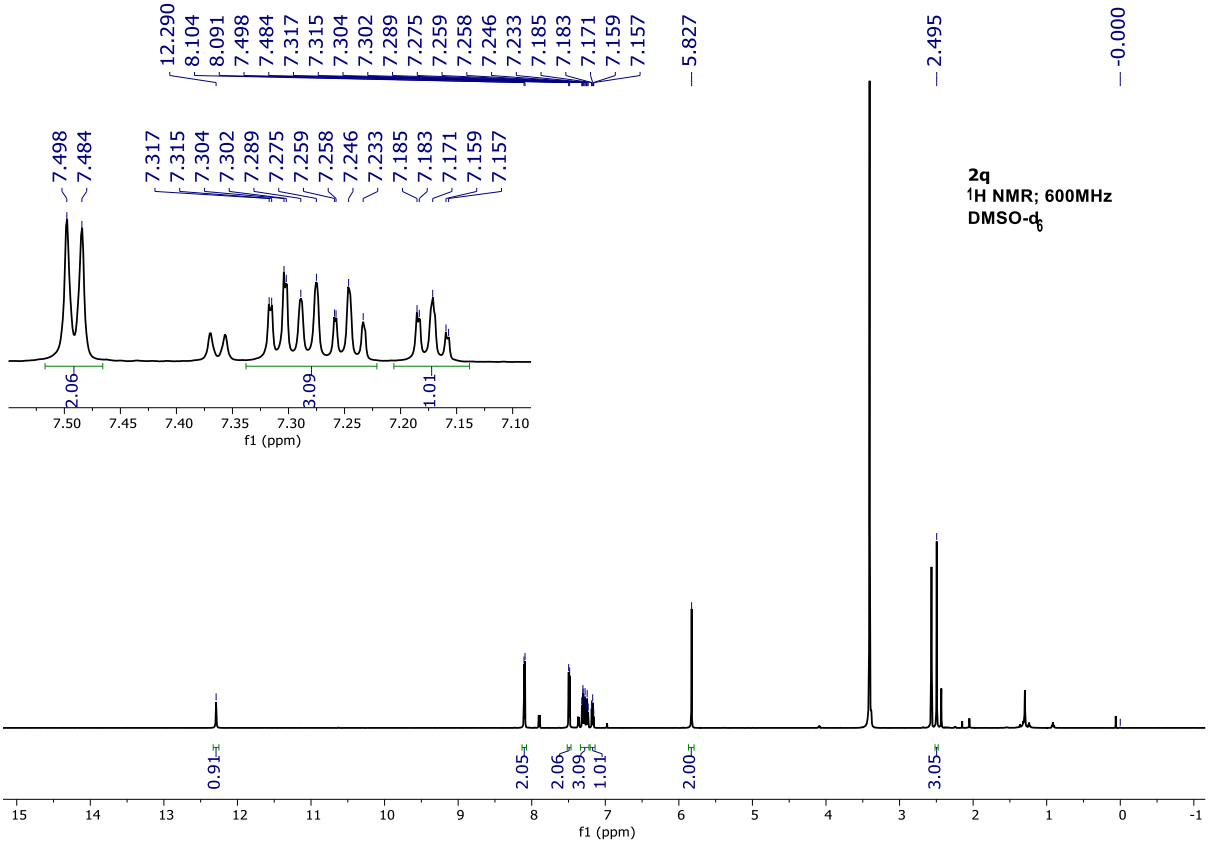

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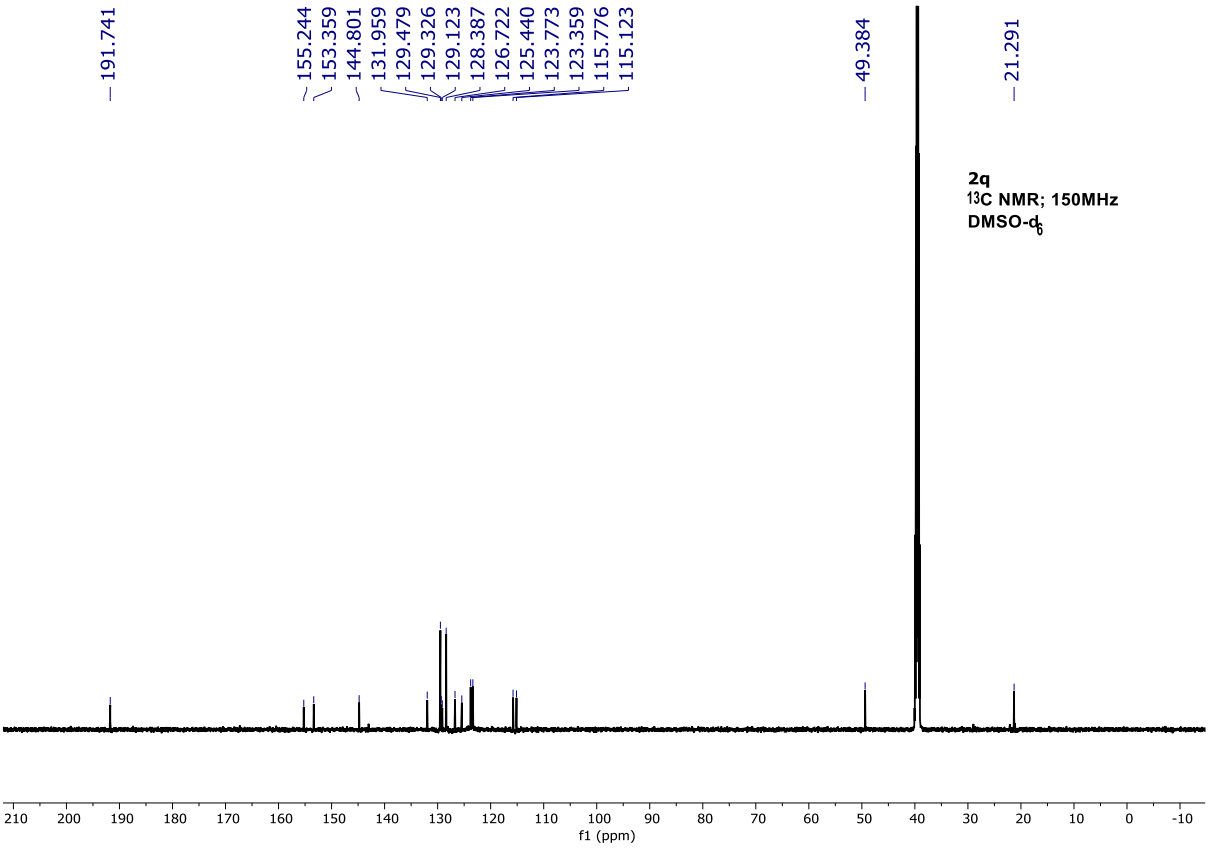

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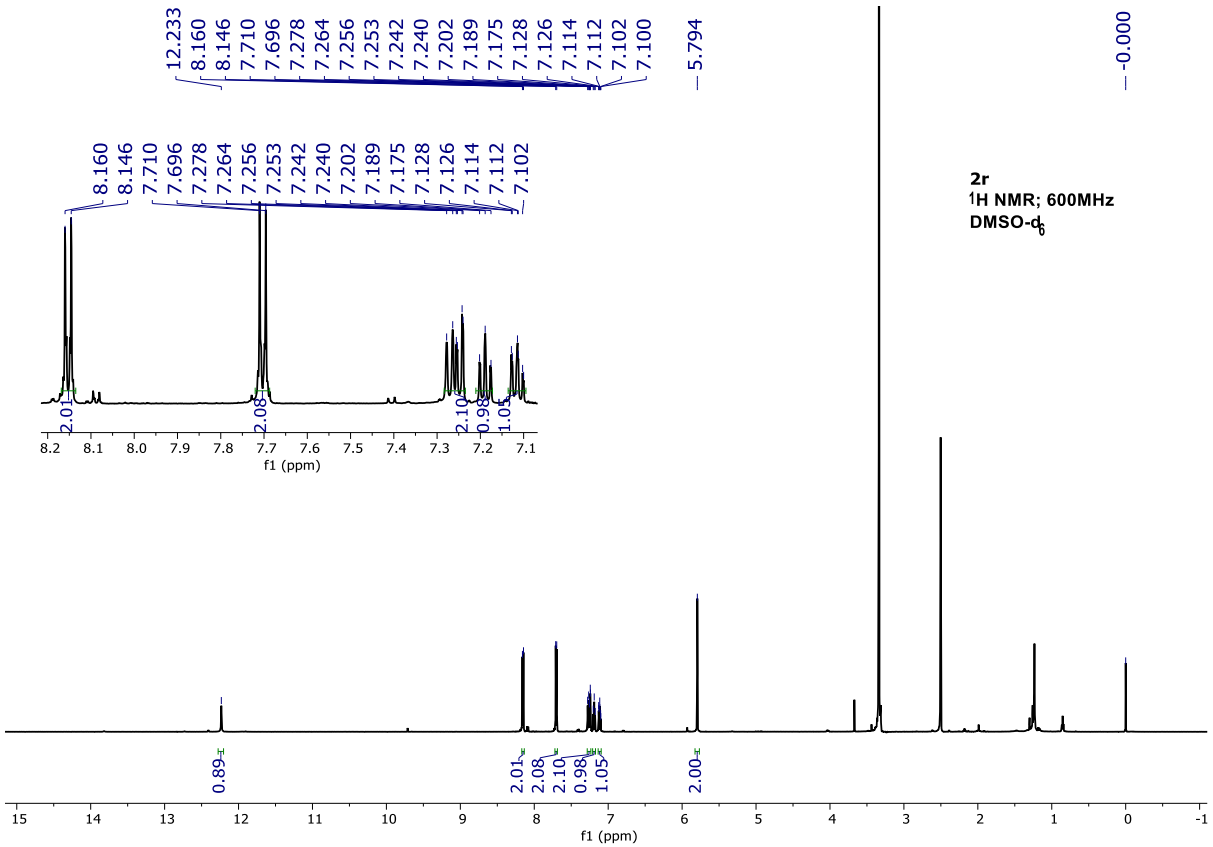

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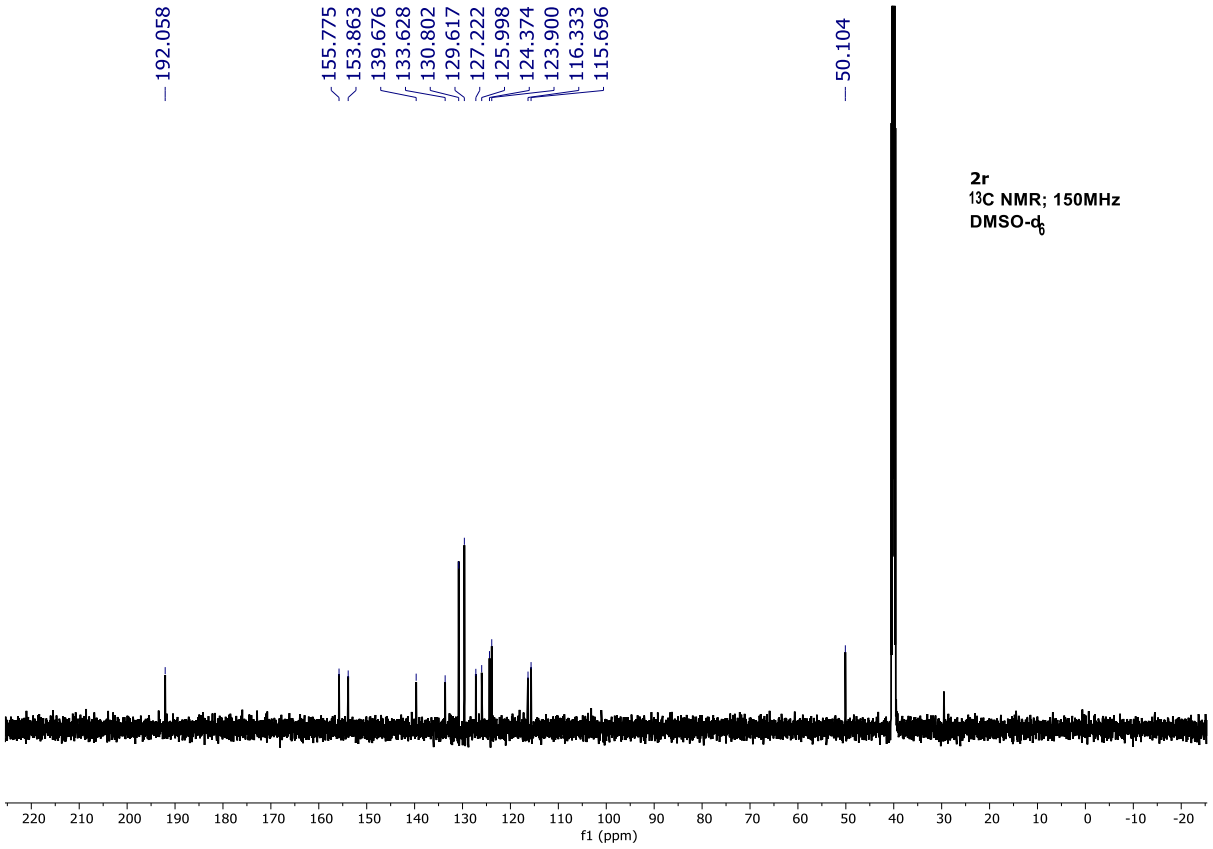

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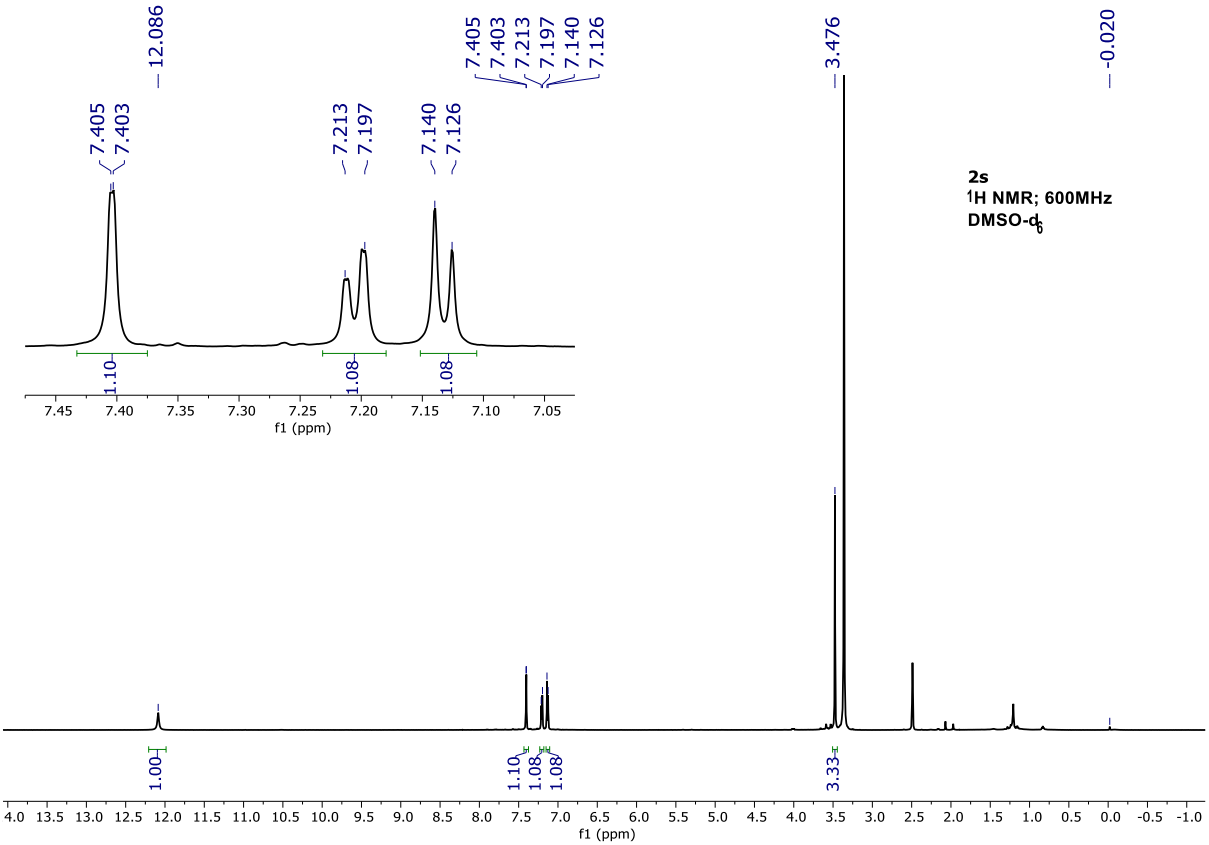

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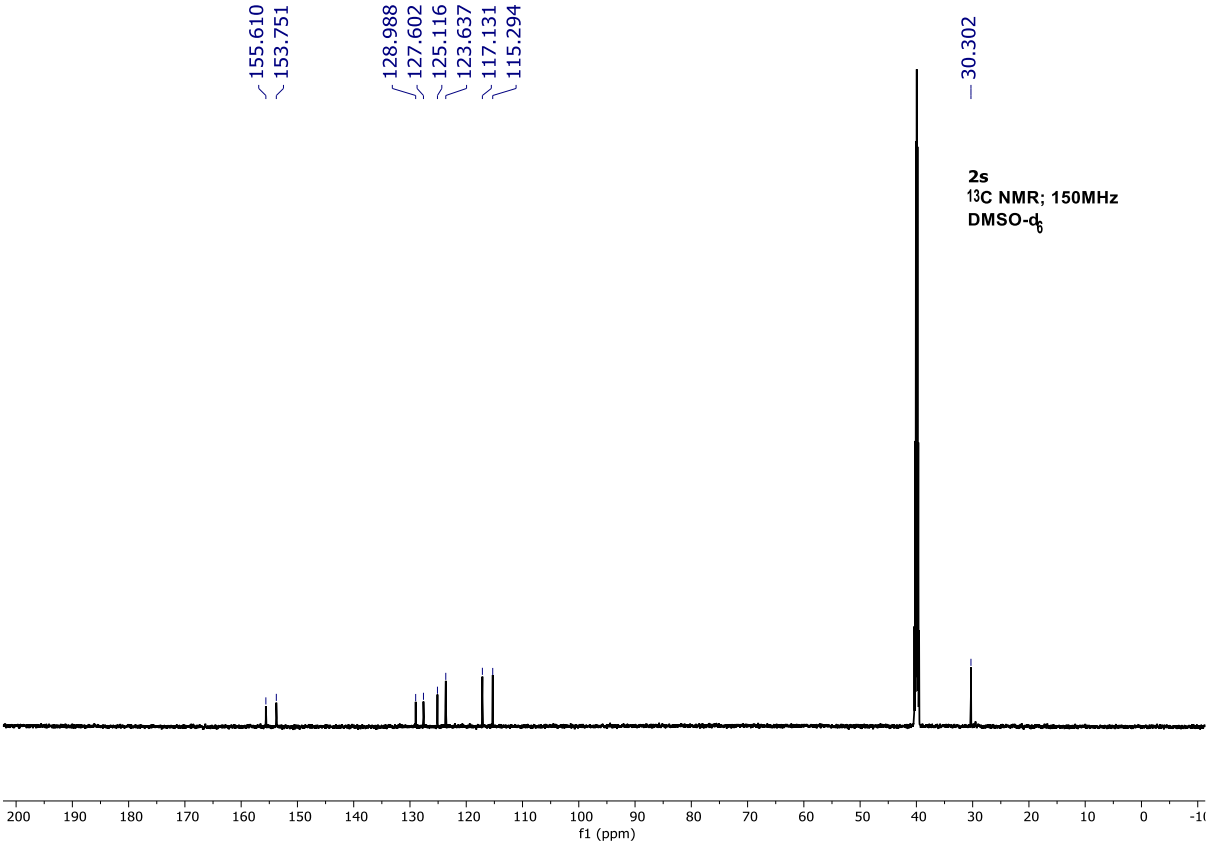

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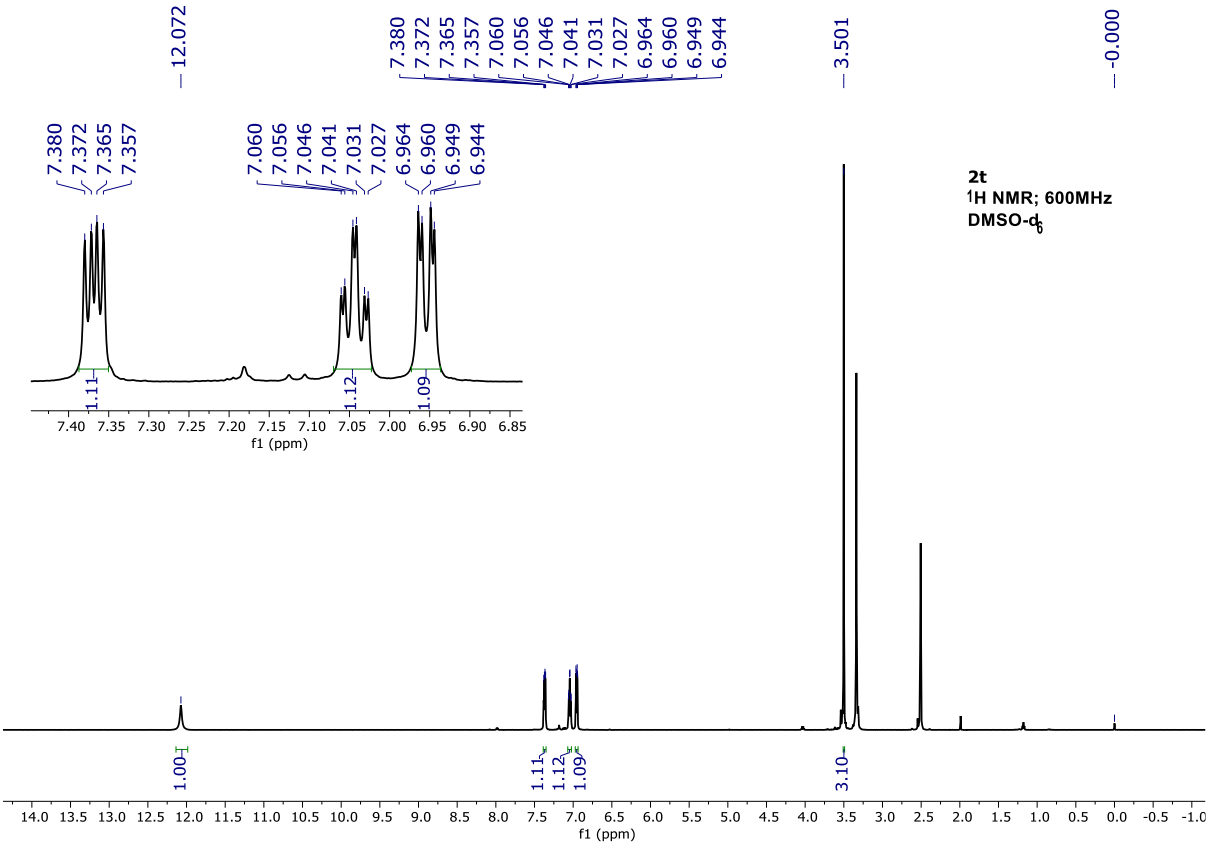

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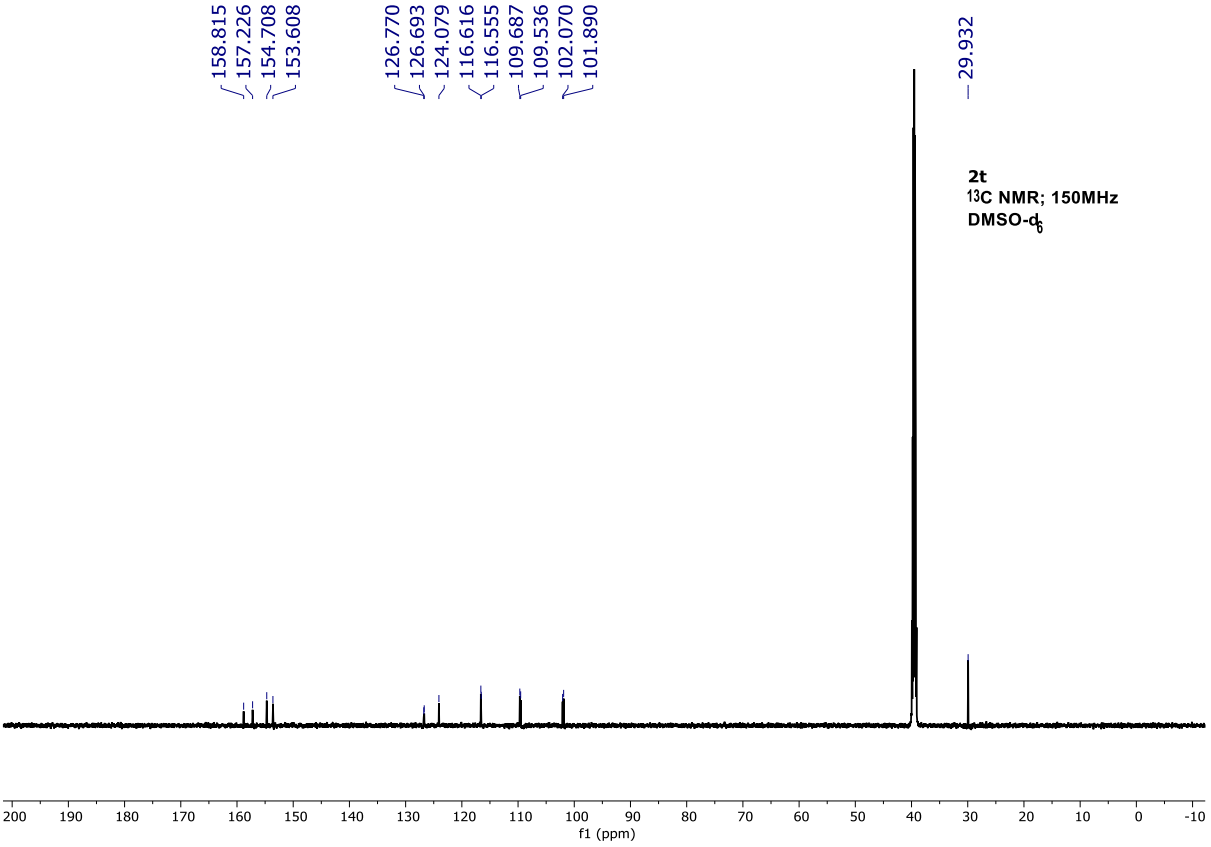

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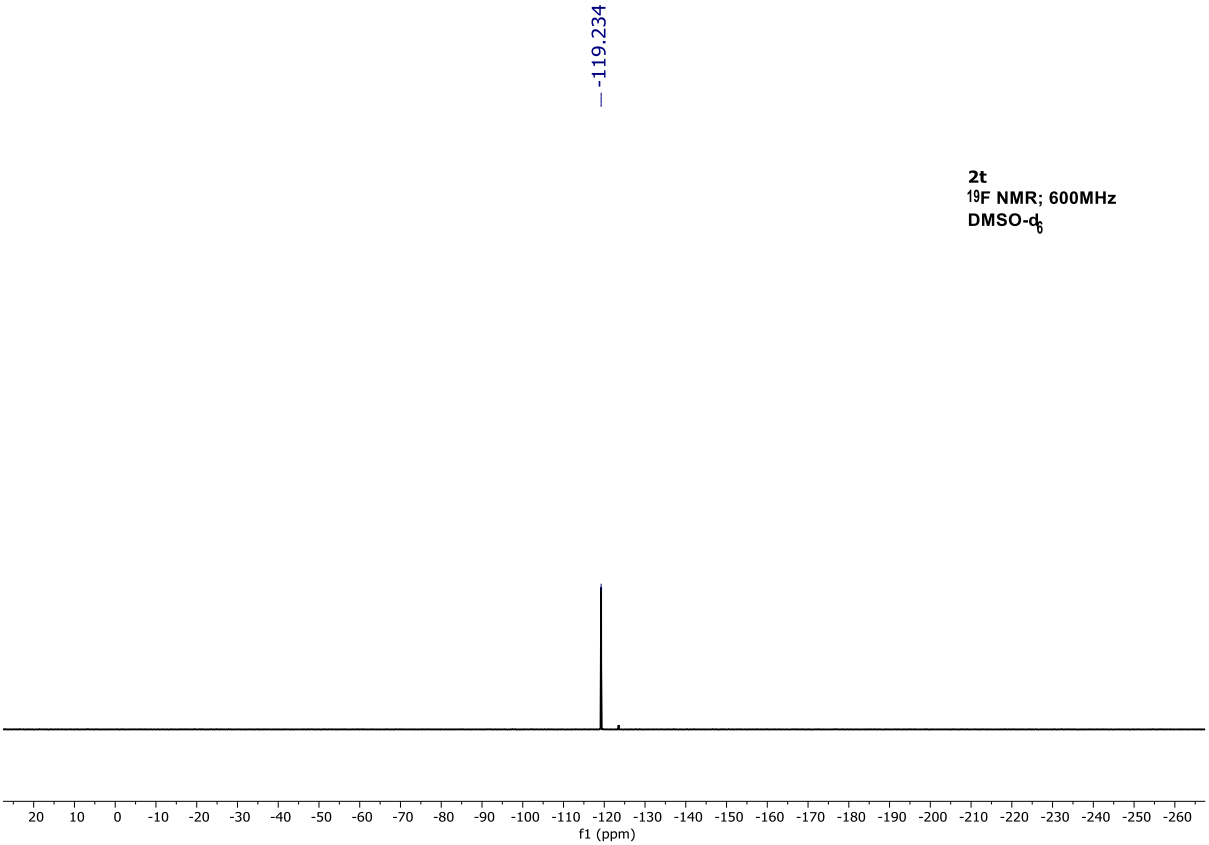

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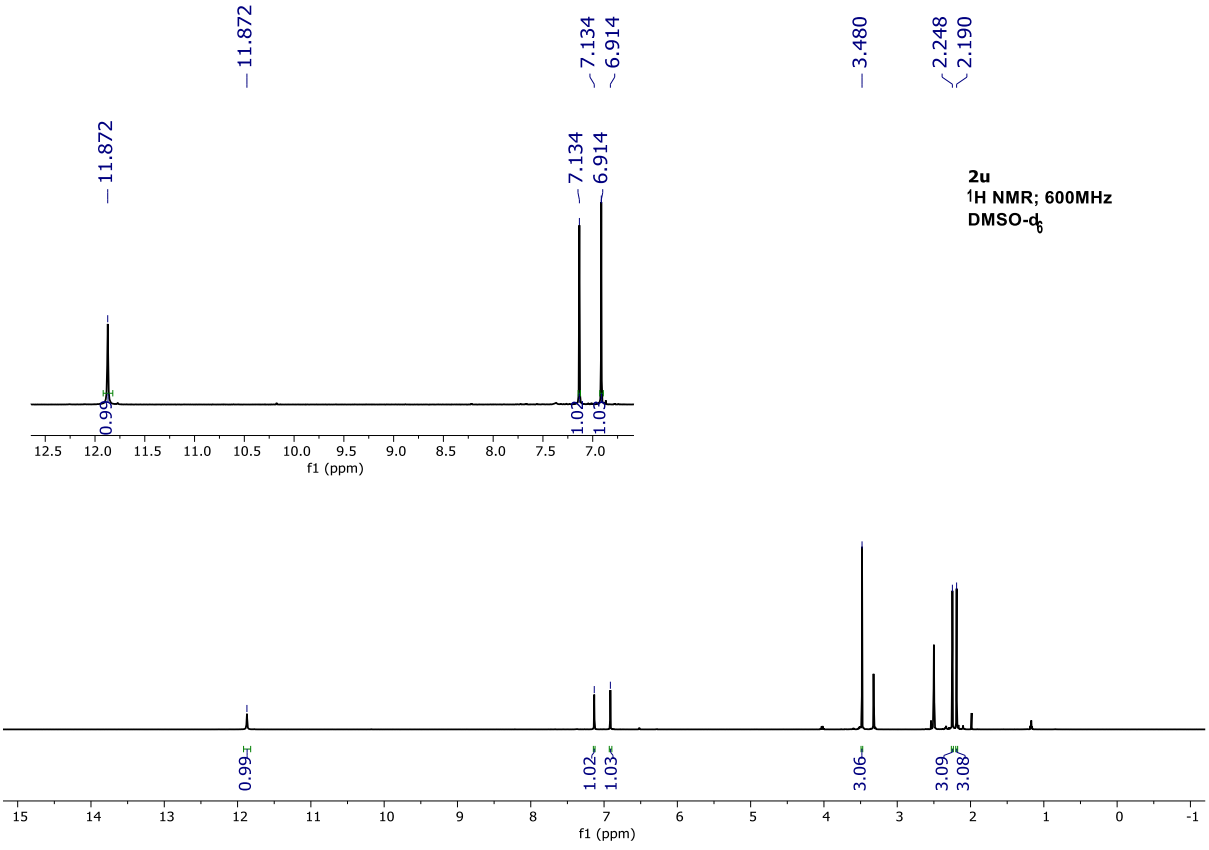

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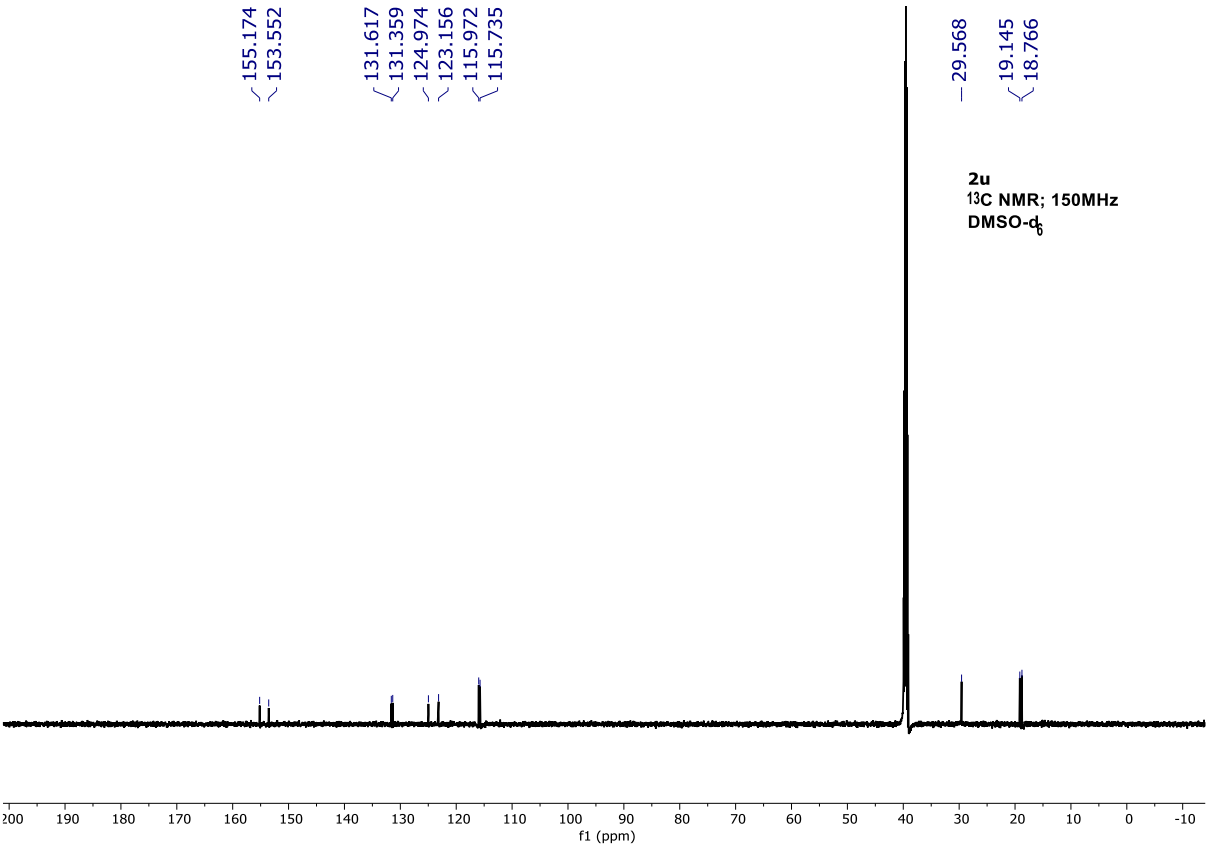

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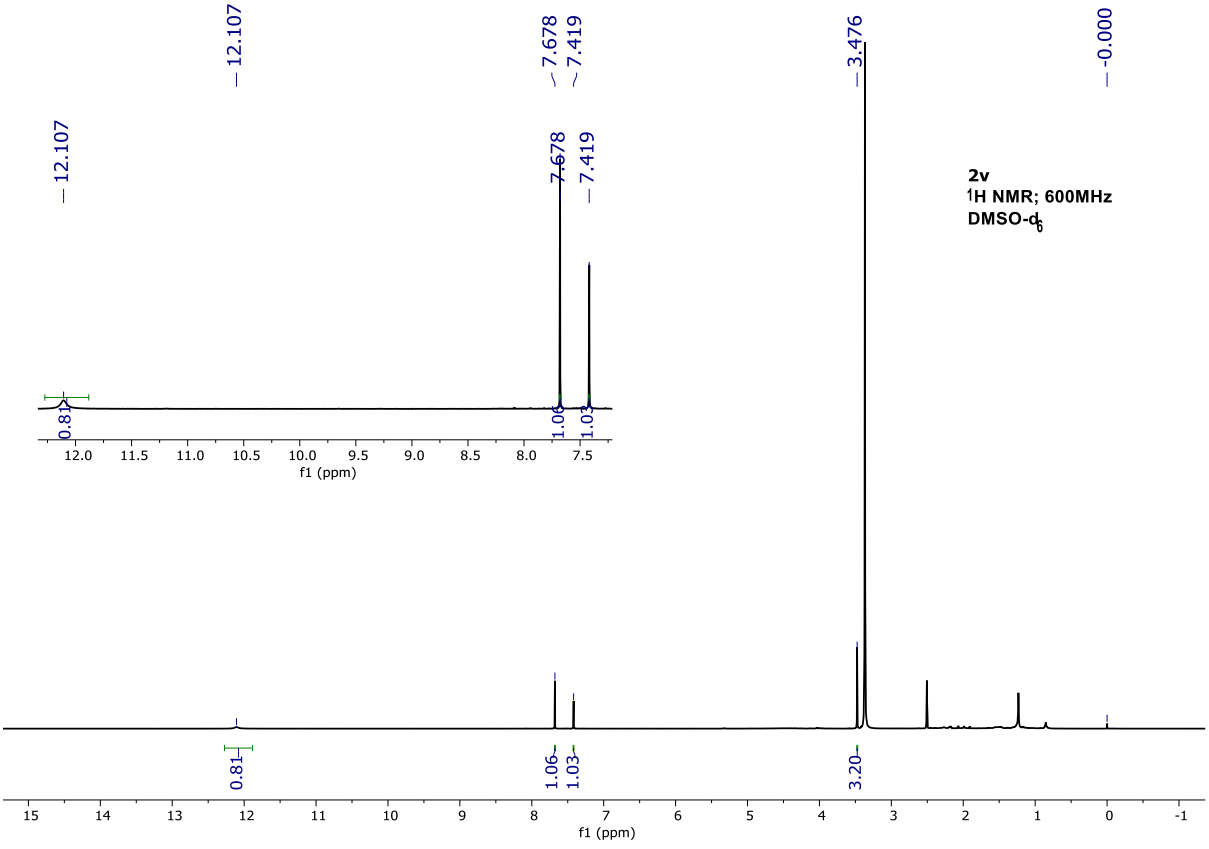

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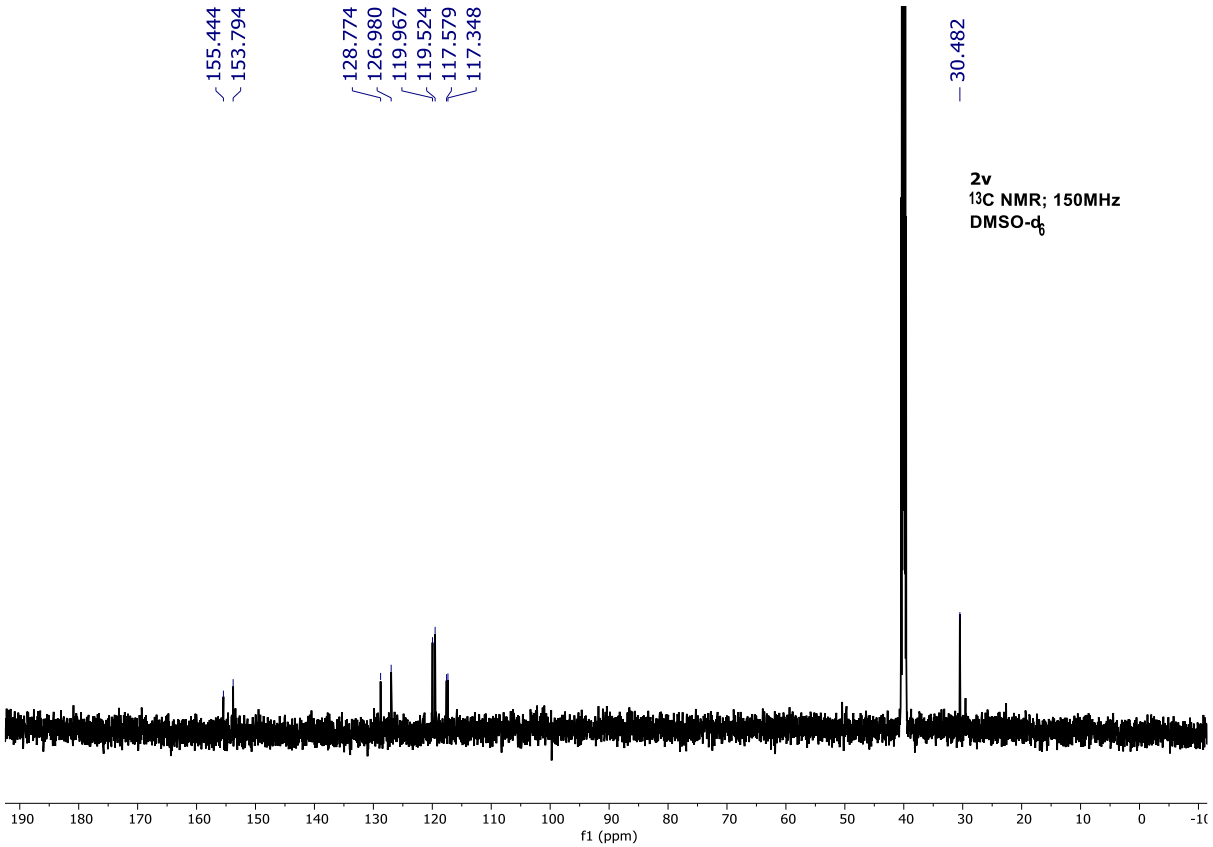

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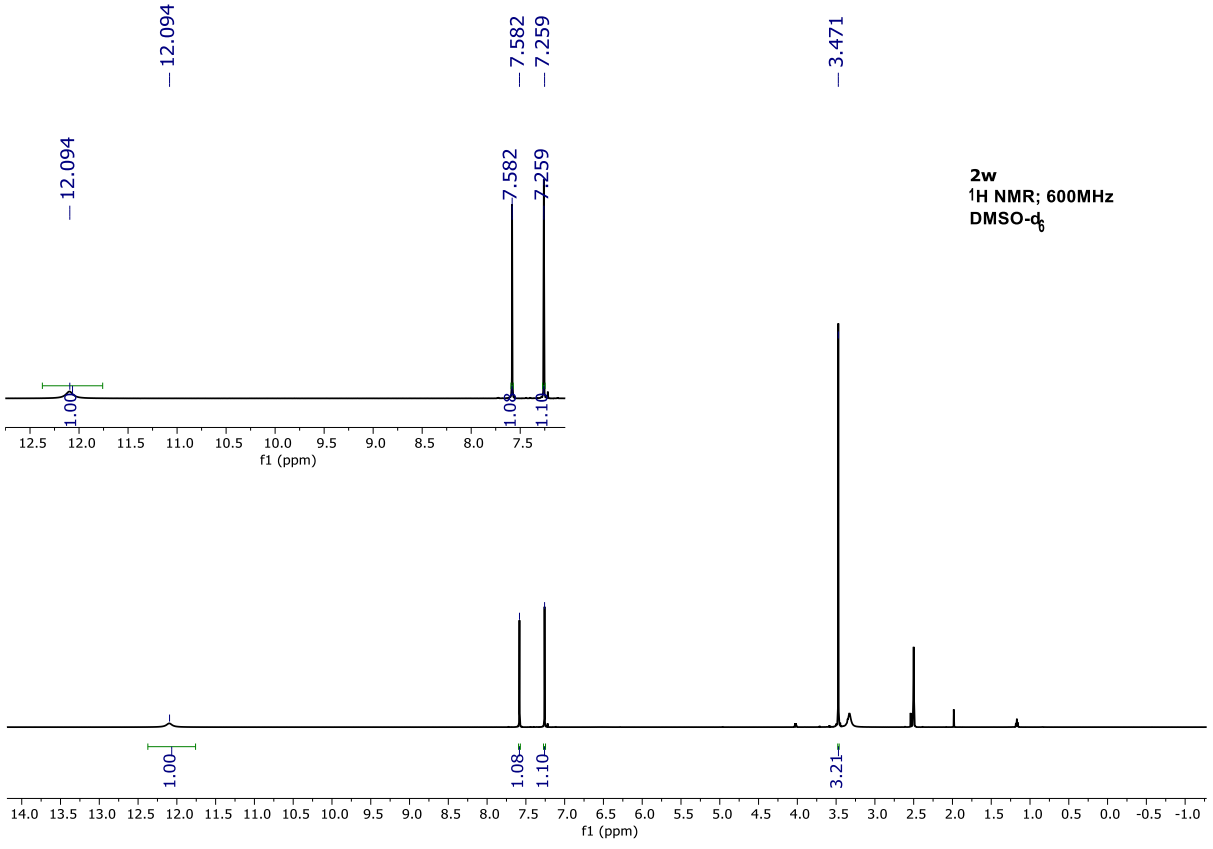

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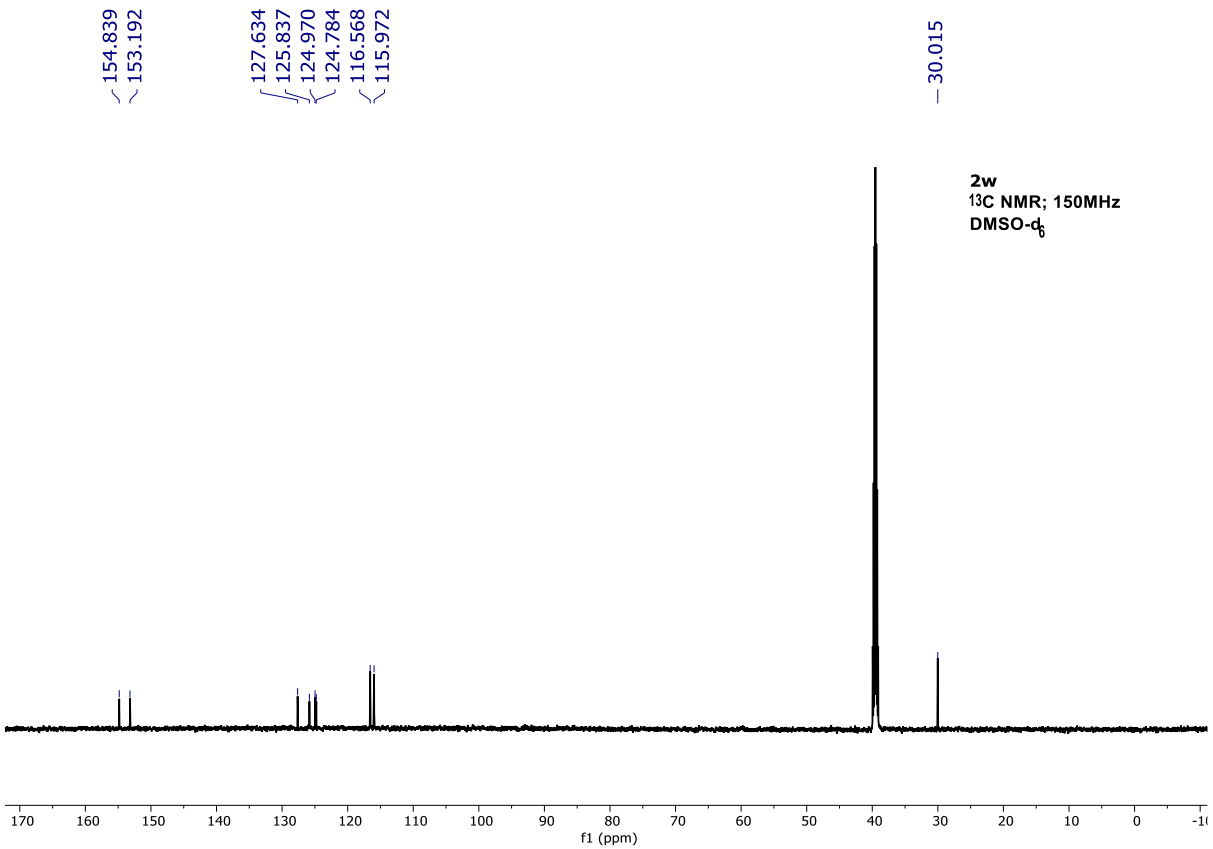

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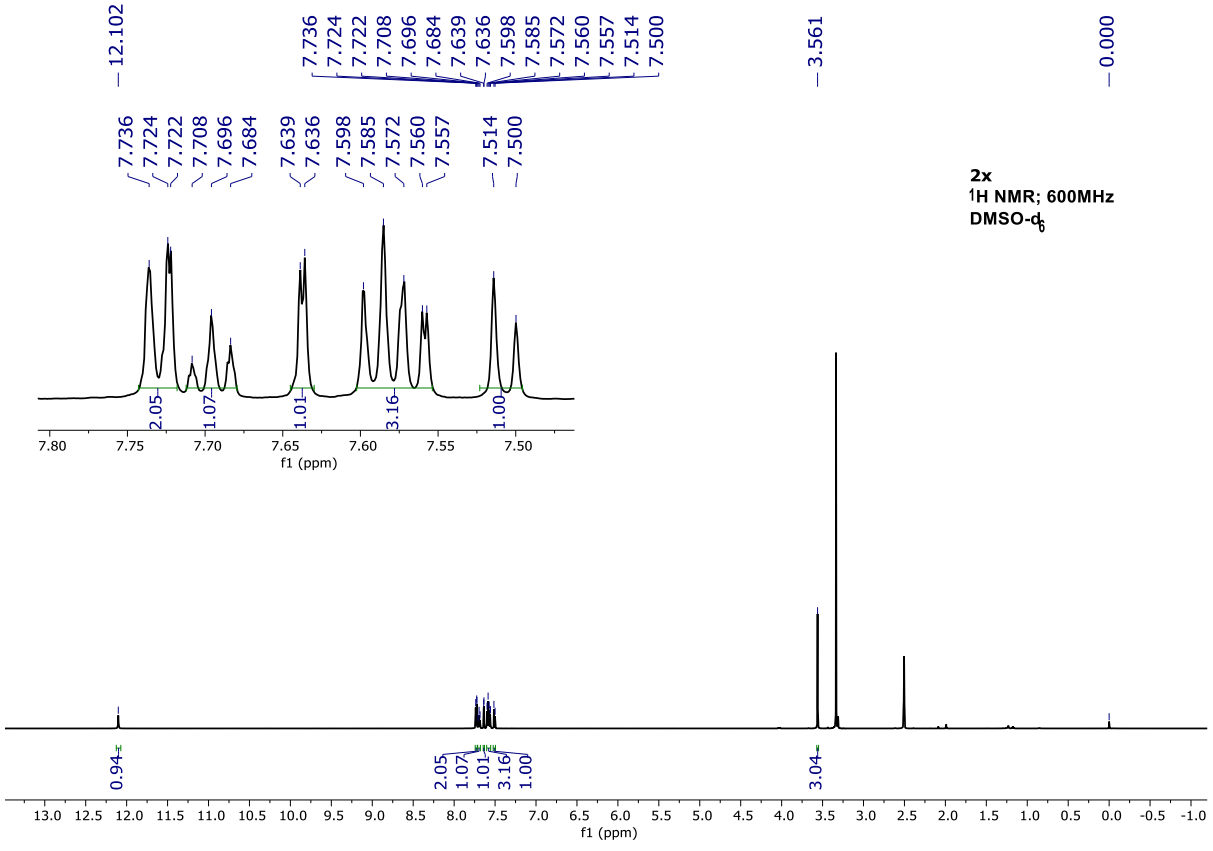
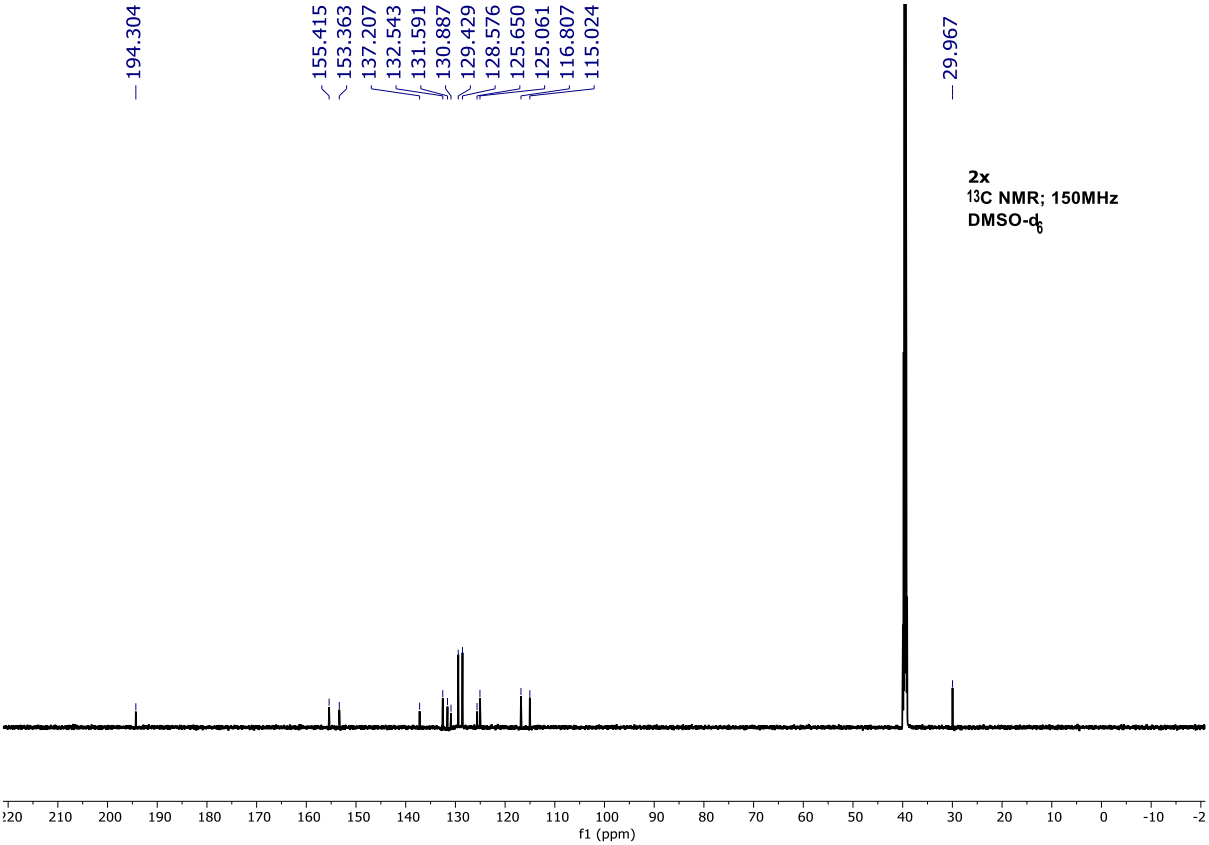
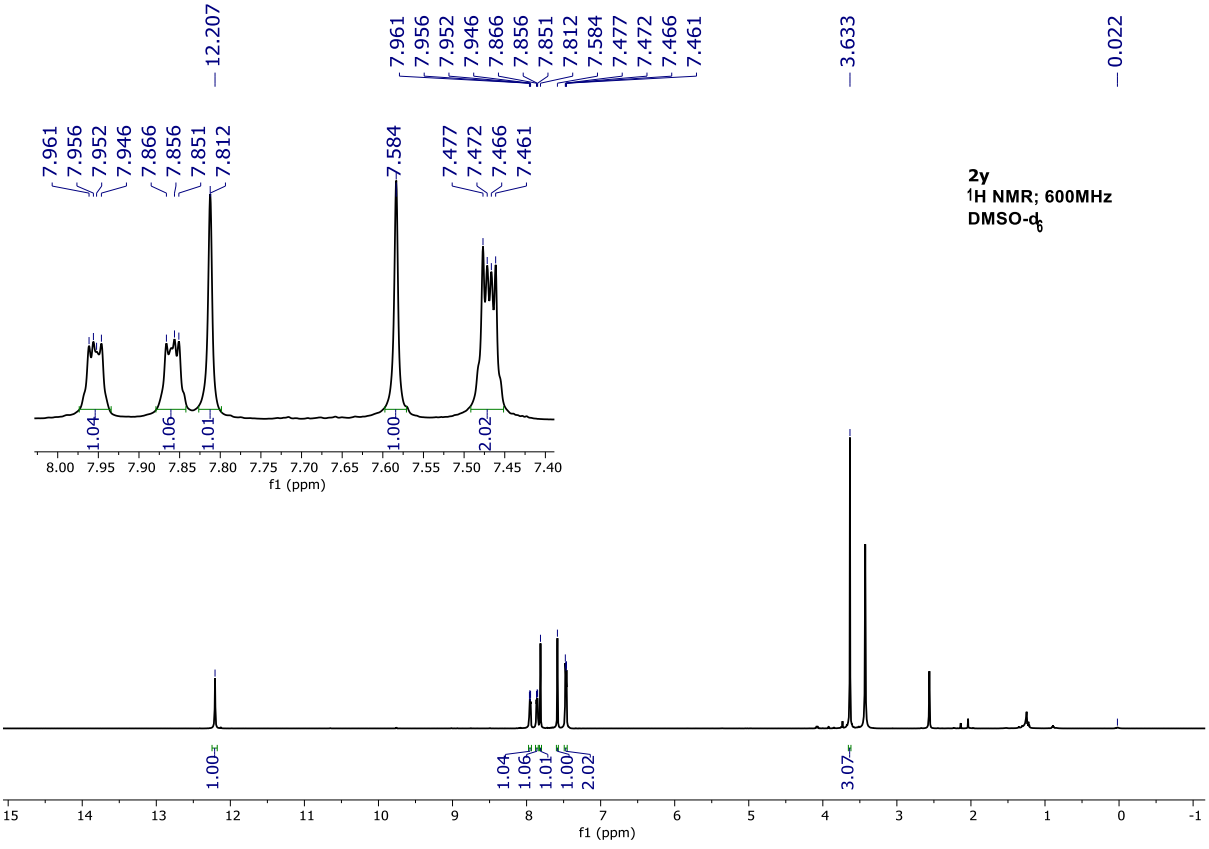


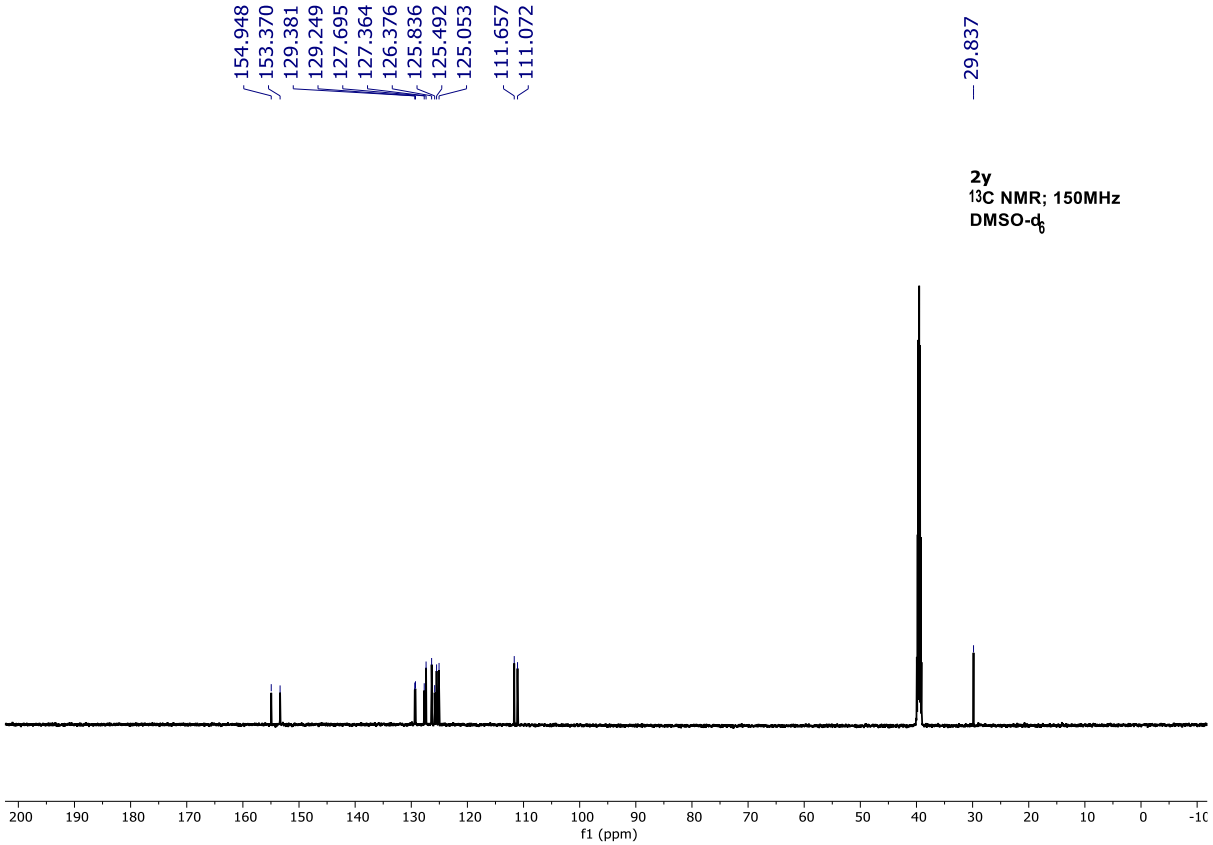
^{1}H NMR of **2x**



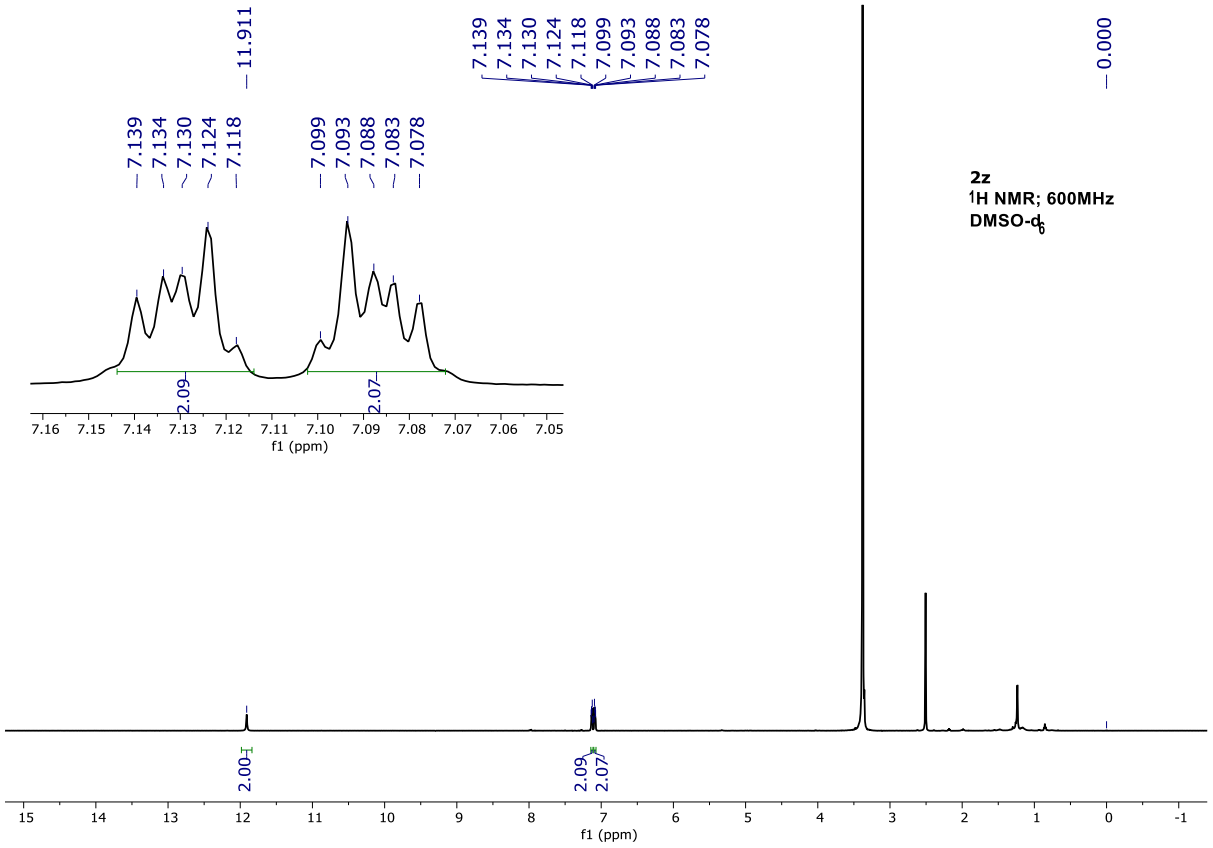
^{13}C NMR of **2x**



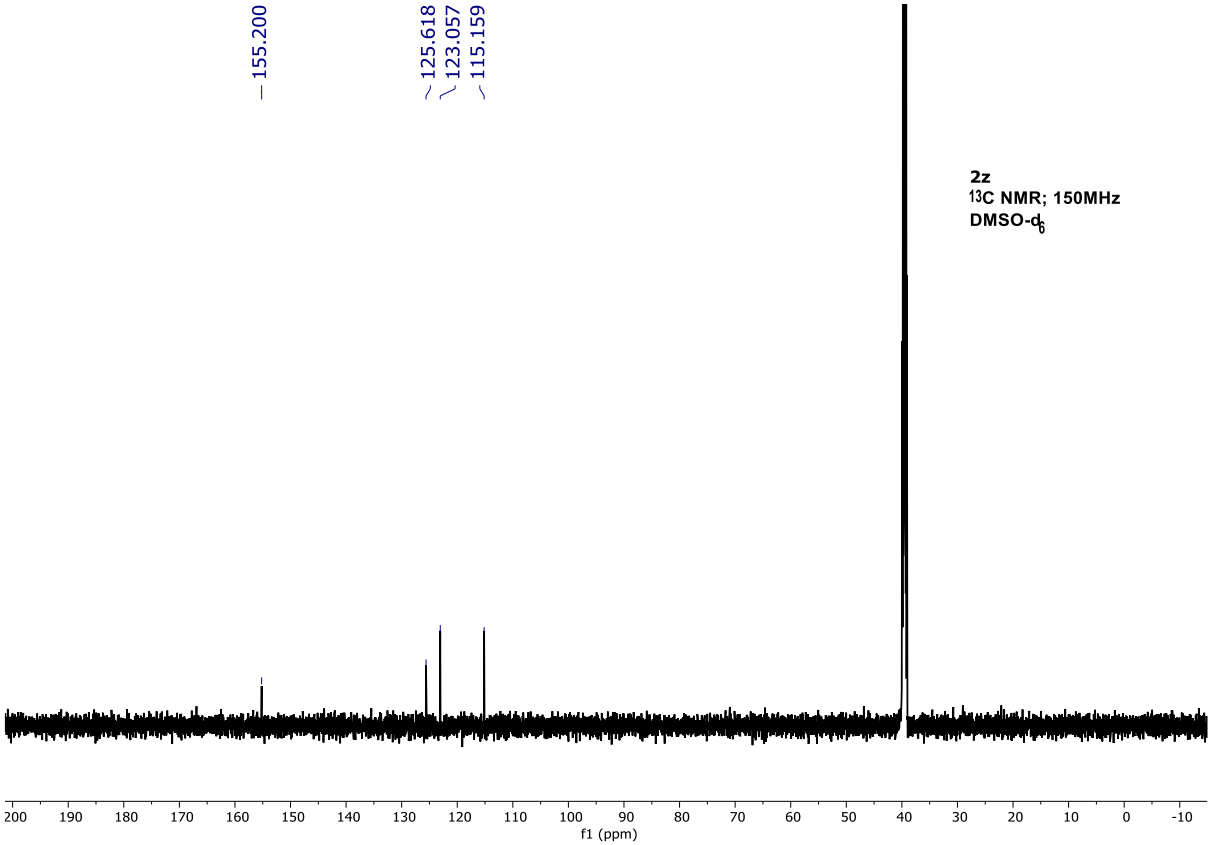
^{1}H NMR of **2y**



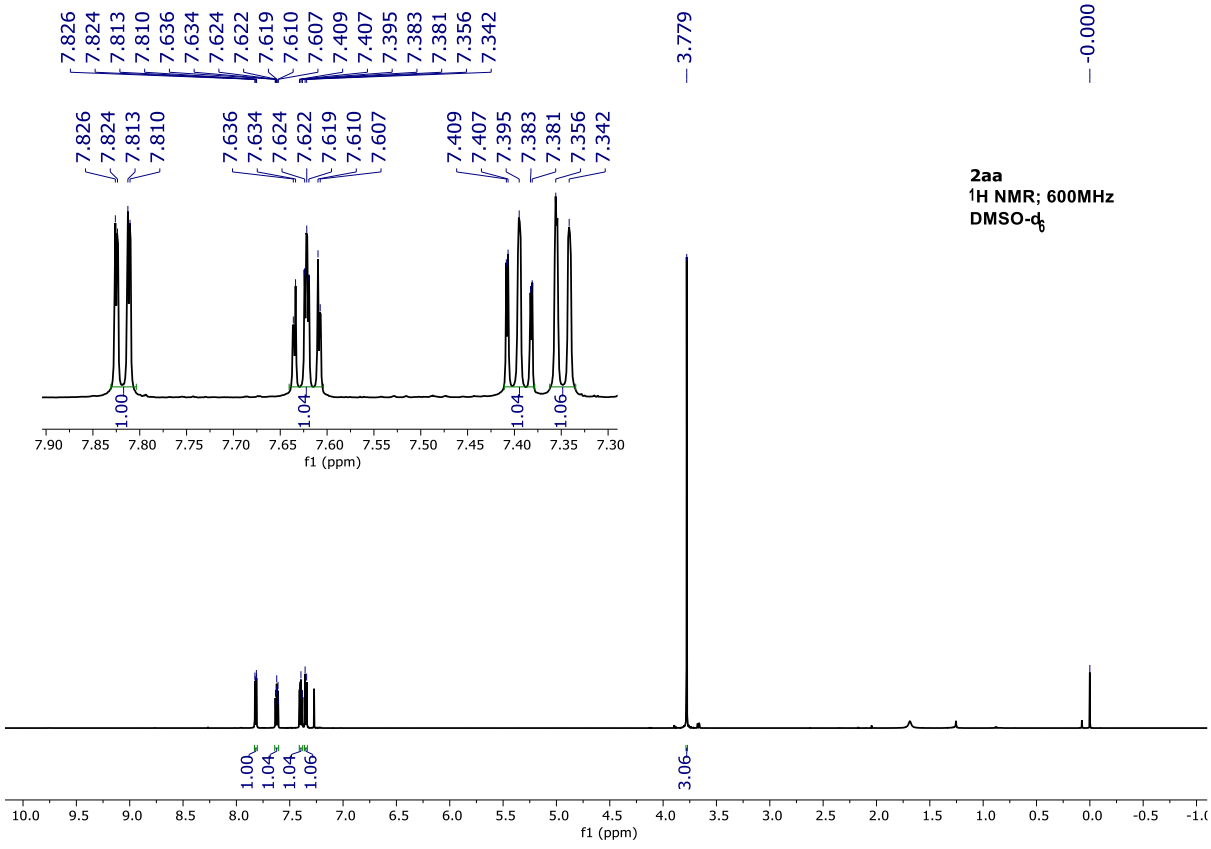
^{13}C NMR of **2y**



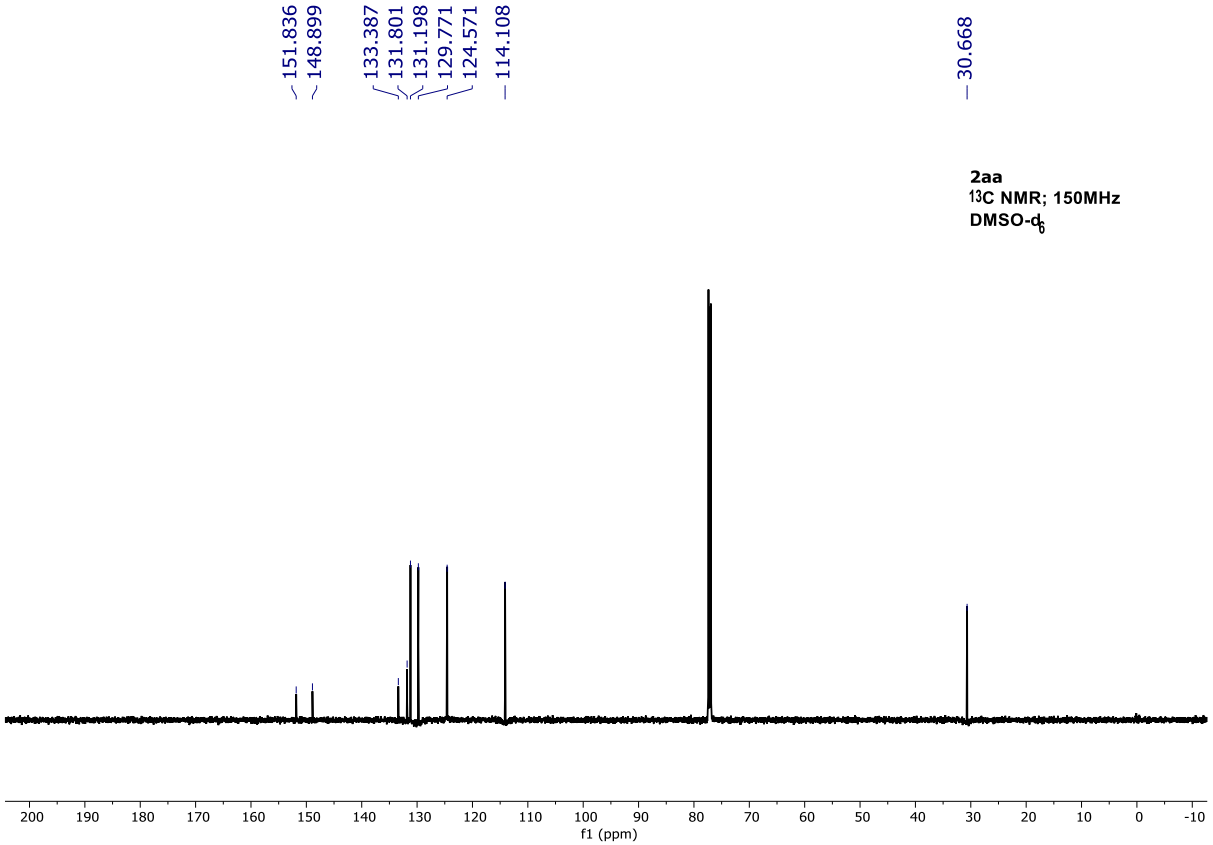
^{1}H NMR of **2z**



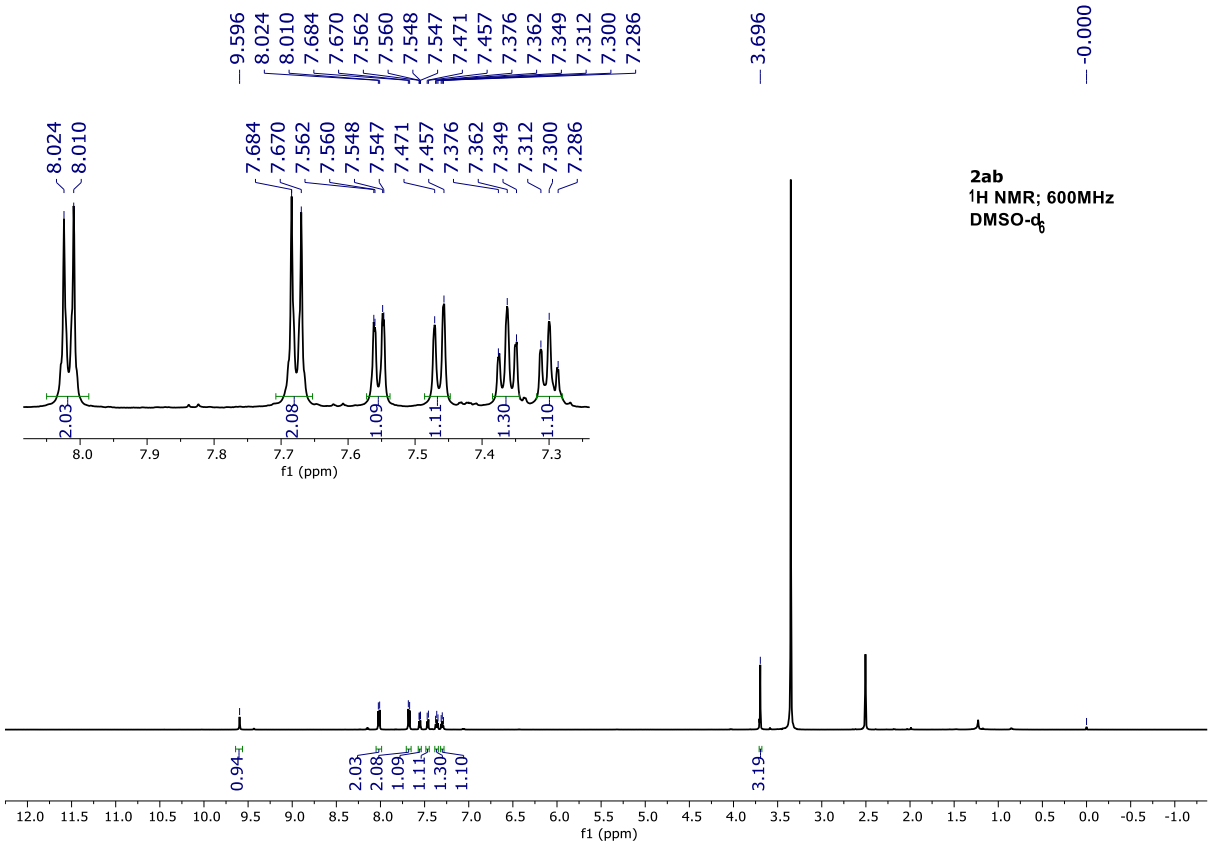
^{13}C NMR of **2z**



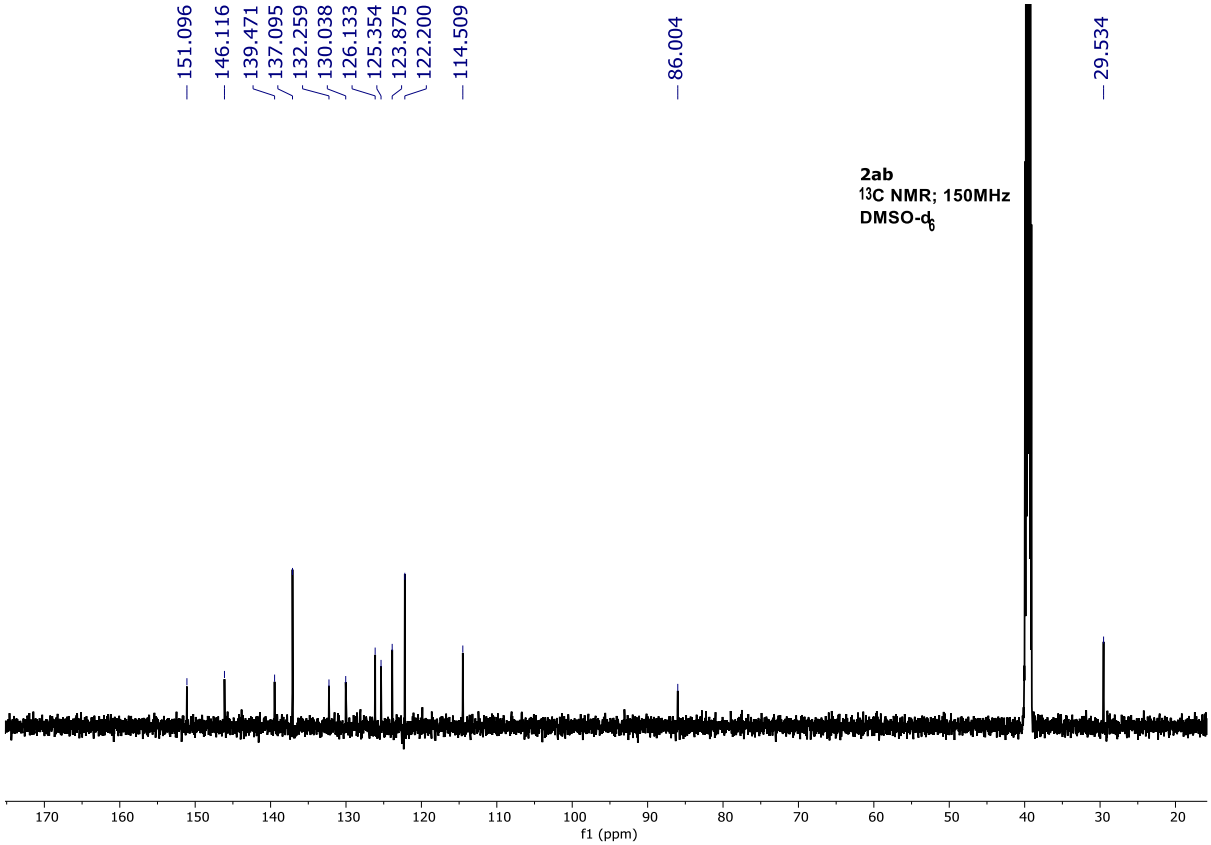
^{1}H NMR of **2aa**



^{13}C NMR of **2aa**

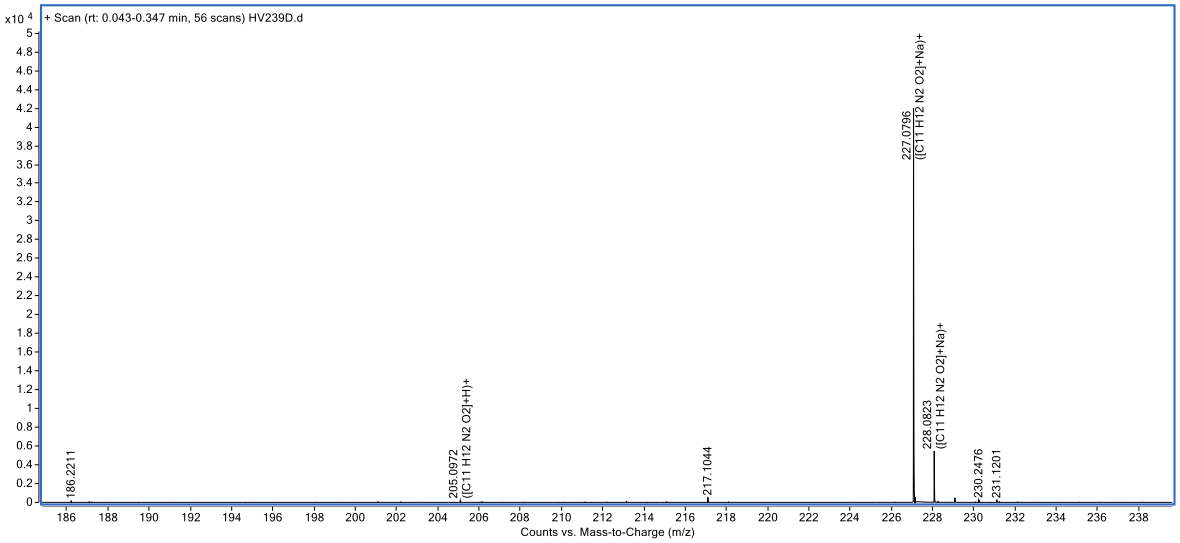


^{1}H NMR of **2ab**

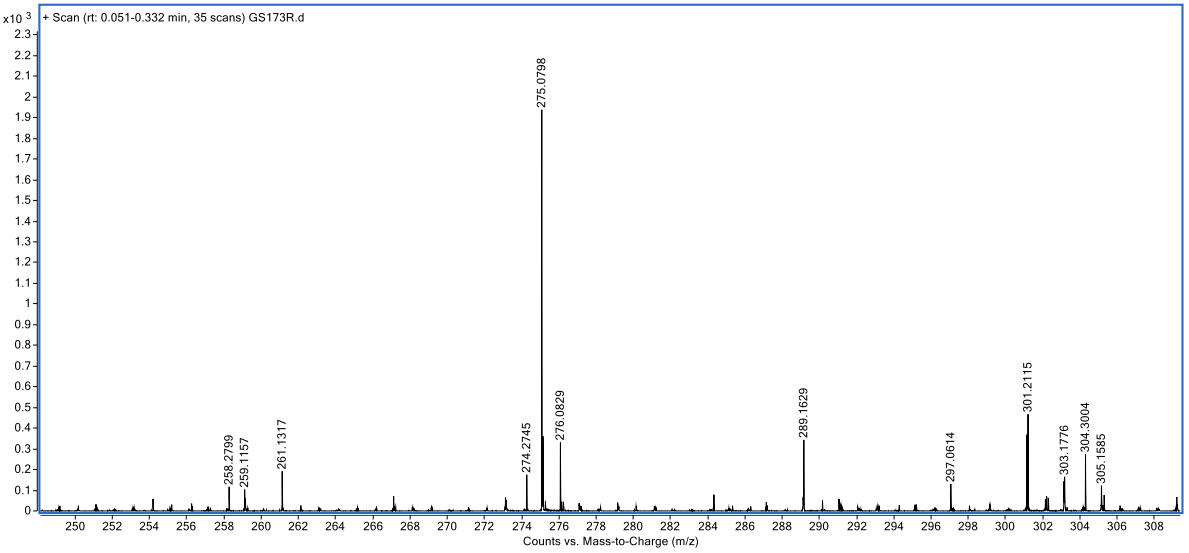


^{13}C NMR of **2ab**

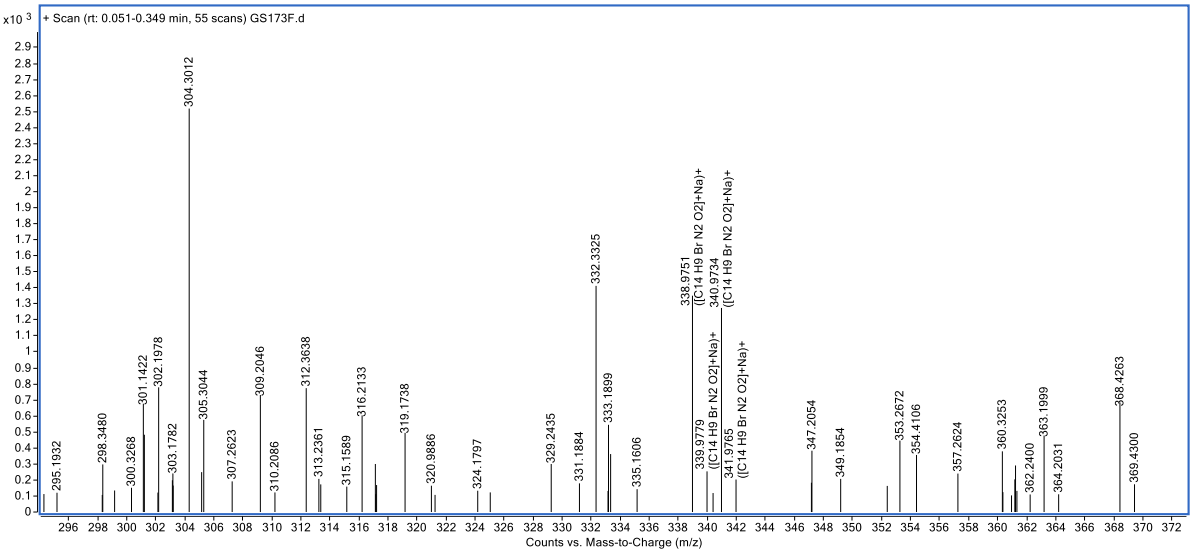
Copies of HRMS Spectra for New Compounds



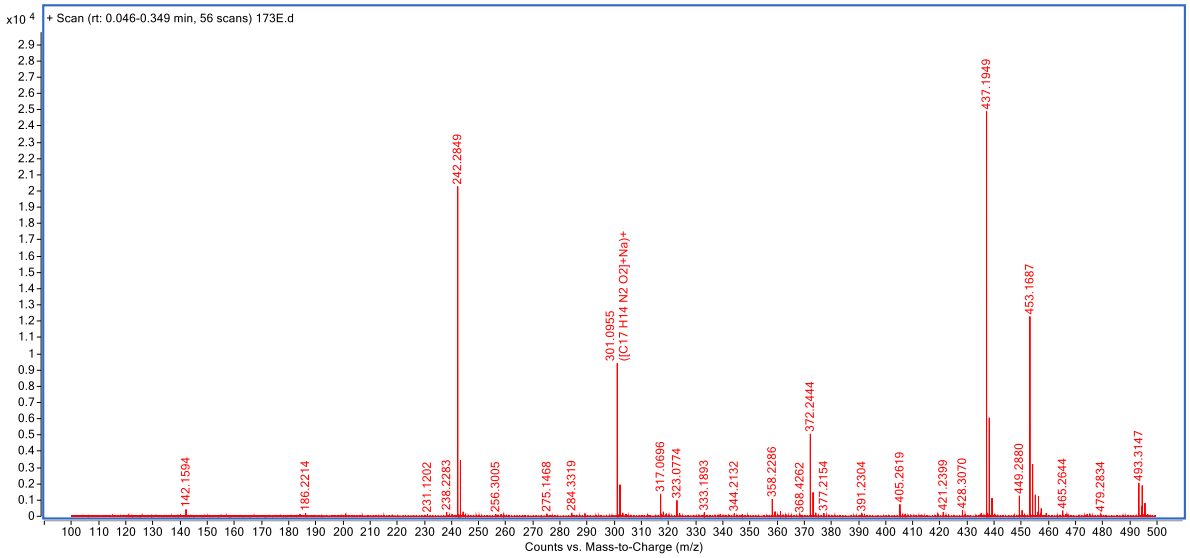
HRMS of **2c**



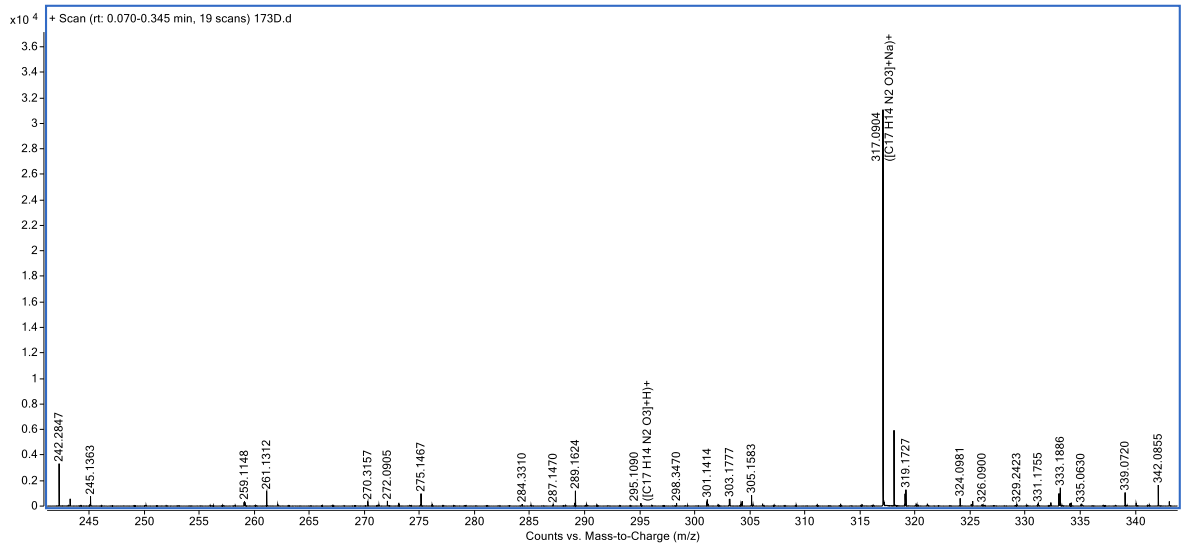
HRMS of **2j**



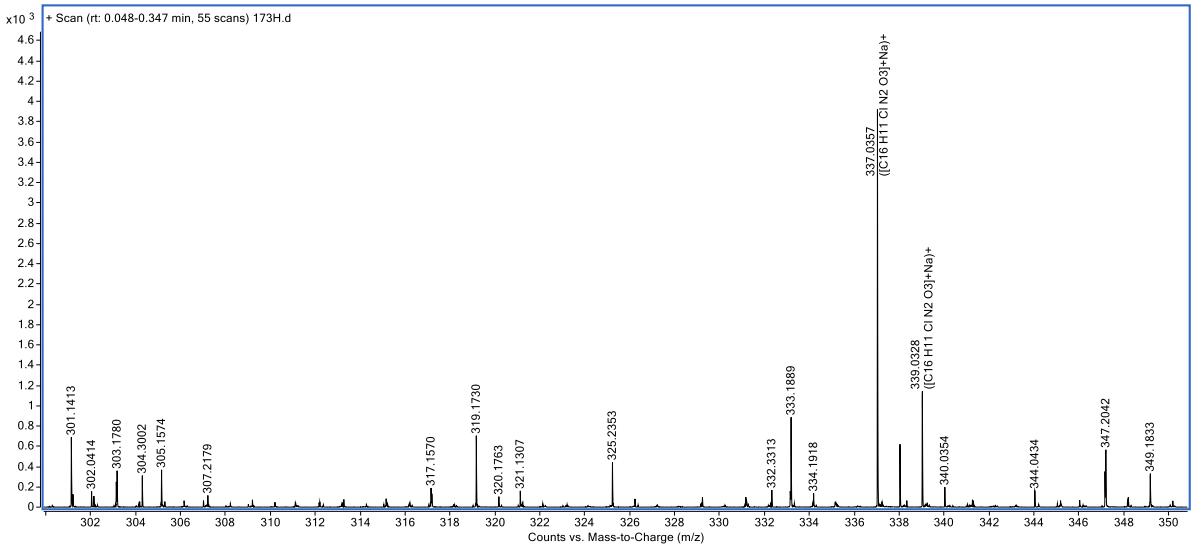
HRMS of **2k**



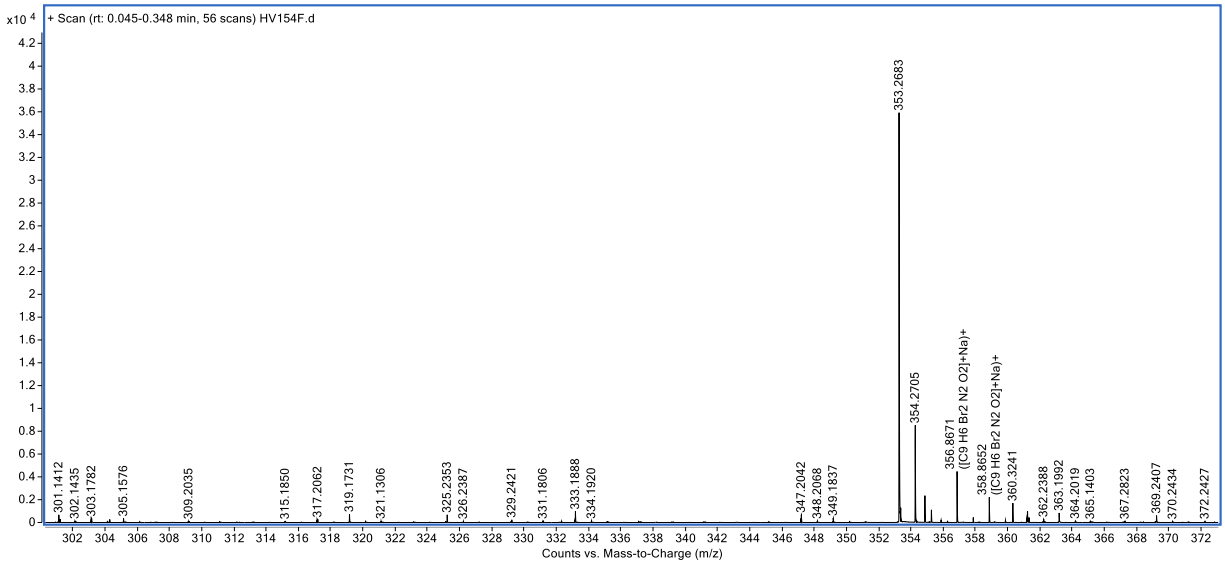
HRMS of **2o**



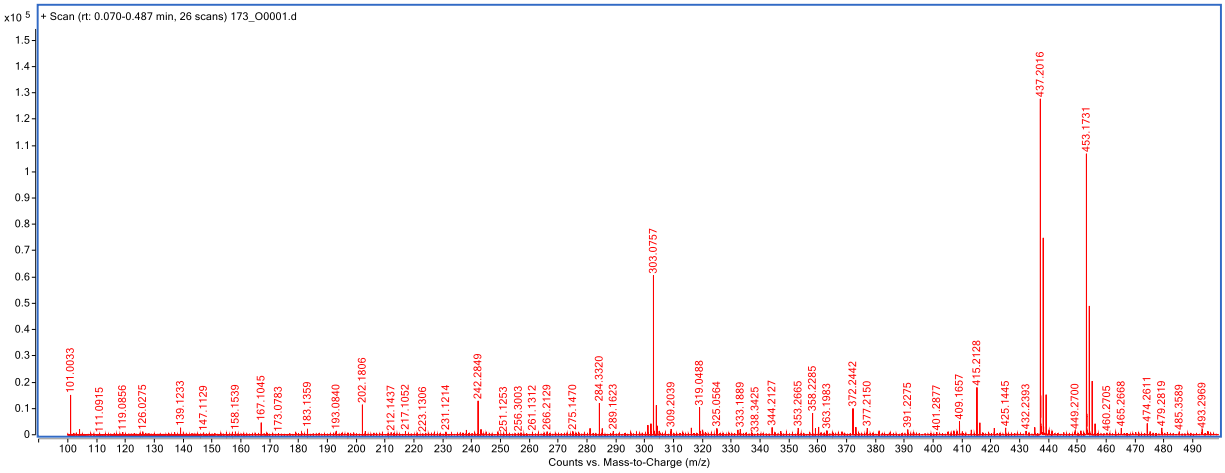
HRMS of **2q**



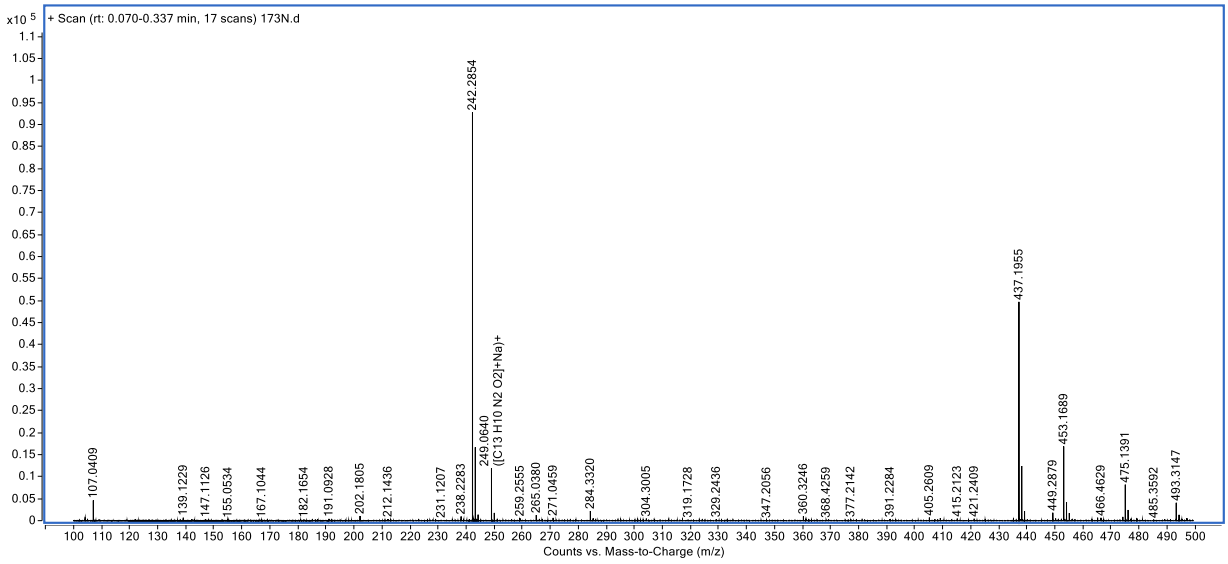
HRMS of **2r**



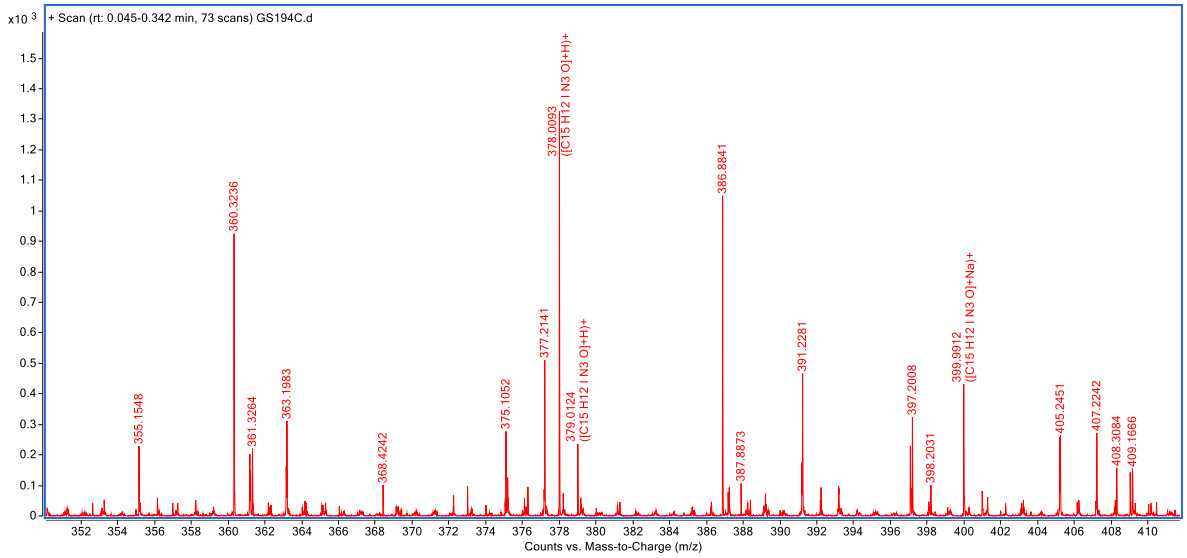
HRMS of **2v**



HRMS of **2x**



HRMS of **2y**



HRMS of **2ab**

Fig S6. Photograph of reaction setup