Practical scale up synthesis of carboxylic acids and their bioisosteres 5-substituted-1*H*-tetrazoles catalyzed by graphene oxide-based solid acid carbocatalyst

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MATERIALS AND METHODS

The nitrile substrates were either purchased from Alfa Aesar or Spectrochem. The graphite powder (150 mesh size) was bought from Central Drug House (P) Ltd., India. Double distilled water was used for the preparation of all aqueous solutions. All solvents and reagents were obtained commercially and used as received.

CHNS analysis was performed using Elemental Analyser system (Model Vario Micro cube, Germany) CHNS analyser. Nitrogen adsorption/desorption isotherm data was collected on Micromeritics Gemini Model 2380 surface area analyser. UV-visible spectra were obtained using Perkin Elmer Lambda35 UV-Visible spectrophotometer. FTIR spectra were collected on Perkin Elmer FTIR Spectrometer using KBr disc method between 4000-400 cm^{-1}. TGA was performed under nitrogen atmosphere from RT-800 ℃ at a constant heating rate of 10 ℃/min and a gas flow of 200 cm^3/min on a Perkin Elmer, Pyris diamond TGA/DTA. PXRD results were recorded on Bruker High resolution X-ray diffractometer in 2θ range of 5-50° with a scan rate of 5° min^{-1}. The Raman spectra were obtained on Renishaw Laser Raman Spectrometer over the wavenumber range of 1000-2000 cm^{-1} using a laser of wavelength 514 nm. The SEM images and EDX spectra were acquired using Jeol Scanning Electron Microscope coupled with EDX. TEM images were obtained on Technai 200 Kv Transmission Electron Microscope by dispersing the sample in aqueous ethanolic solution and drop casting them onto copper grid coated with an amorphous carbon film. ^1H and ^{13}C NMR spectra were acquired on Jeol 400 MHz spectrometer using DMSO-d_6 as solvent. The chemical shift values are reported in ppm with respect to tetramethylsilane (internal standard). The mass spectra were recorded on Agilent LCMS with Quadruple time of flight. Single crystal X-ray analysis was performed on Crysalis PRO (Oxford Diffraction) with graphite mono75 chromate Mo Kα radiation (λ = 0.71073 Å) and the structure was elucidated by direct method using SHELXL.

Computational Methods: In this work, the reported computational calculations were carried out using Gaussian 09 package.[S1] The 6-311+G(d,p)[S2] basis set was used in accordance with M06-2X18 density functional method for all geometry optimization and frequency analyses with the inclusion of solvation effect in the calculation. The frequency calculations were carried out at 298.15 K for all stationary points at the same level of theory as the geometry optimizations to ascertain the nature of the stationary points, while the characterization of ground and transition states were done by none and one imaginary frequency, respectively. The calculated relative energies are free energies at 298.15 K with respect to the reactants.

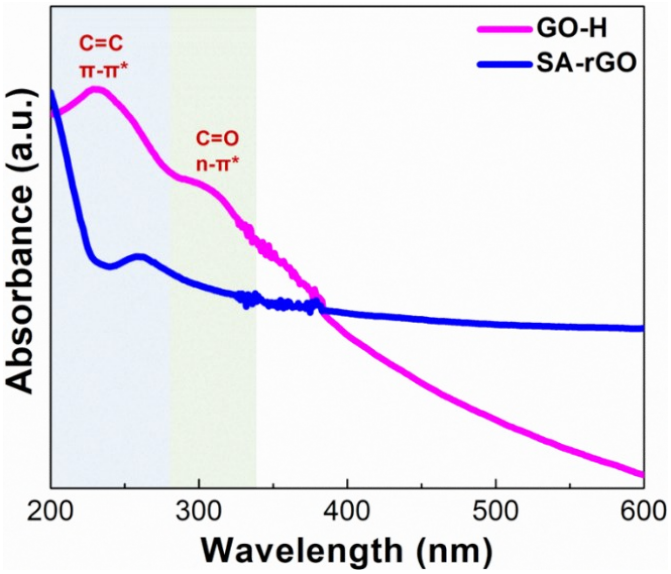
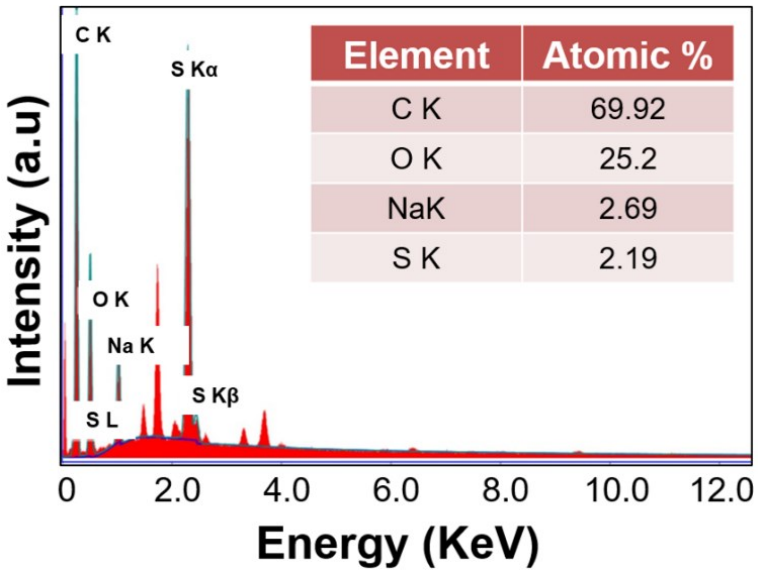


Figure S1. UV-Visible spectra of GO-H and SA-rGO.



Element	Atomic %
C K	69.92
O K	25.2
NaK	2.69
S K	2.19

Figure S2. SEM-EDS analysis of SA-rGO.

Table S1. CHNS elemental analysis result of GO-H and SA-rGO.

Sample	C [%]	H [%]	N [%]	S [%]
GO-H	46.42	2.56	0.33	0.84
SA-rGO	49.96	3.14	0.33	5.13

Table S2. Acid group analysis results of SA-rGO.

Sample	Sulfur content (%)[a]	Oxygen content (%)[b]	Concentration of -SO_3H groups (mmol g^{-1})[c]	Total acid sites (mmol g^{-1})[d]
SA-rGO	5.13	41.44	1.60	2.40

[a]Obtained from CHNS elemental analysis.

[b]Calculated from difference of CHNS elemental analysis data.

[c]Calculated from sulfur content obtained from CHNS elemental analysis.

[d]Calculated from back acid-base titration.

Determination of acidity of SA-rGO

The density of total acidic sites on SA-rGO was calculated by back acid–base titration.[S3] First, 100 mg of SA-rGO was ultrasonicated in a water bath for 15 min under nitrogen atmosphere to degas CO_2. Next, 10 mL of freshly prepared 0.042 N NaOH solution was added and the mixture was stirred for 2 h at RT. Subsequently, the mixture was centrifuged at 8000 rpm for 2 min and washed three times with double distilled water. The filtrate containing excess NaOH solution was then back titrated with freshly prepared 0.1 N HCl solution till neutralization point, monitored by using phenolphthalein indicator to evaluate the total concentration of acidic sites in SA-rGO (Section S1).

Section S1. Calculation of acidic strength of SA-rGO[S4]

It was found that 1.8 mL of HCl was required to reach the neutralization point.

$$V_{NaOH} \text{ X } S_{NaOH} = V_{HCl} \text{ X } S_{HCl}$$

$$V_{NaOH} \text{ X } 0.042 = 1.8 \text{ X } 0.1$$

$$V_{NaOH} = 4.2857 \text{ mL}$$

Therefore, the volume of NaOH required to neutralize the acidic sites in SA-rGO = (10-4.2857) mL = 5.7143 mL.

$$V_{NaOH} \text{ X } S_{NaOH} = V_{SA\text{-}rGO} \text{ X } S_{SA\text{-}rGO}$$

$$5.7143 \text{ X } 0.042 = 10 \text{ X } S_{SA\text{-}rGO}$$

$$S_{SA\text{-}rGO} = 0.024 \text{ N}$$

The equivalent weight of sulfonic acid group (-SO_3H) is 81.

That is, 1000 mL of 1 N SA-rGO would contain 81 g free sulfonic acid sites.

So, 10 mL of 0.024 N SA-rGO solution contains 0.01944 g free sulfonic acid sites.

0.01944 g free sulfonic acid sites= 0.24 mmol free sulfonic acid sites.

100 mg sample of SA-rGO contains 0.24 mmol free sulfonic acid.

Thus, 1000 mg sample of SA-rGO would contain 2.4 mmol free sulfonic acid sites.

That is, total acid sites in SA-rGO= 2.40 mmol g^{-1}.

Section S2. Calculation of TOF values of SA-rGO

Concentration of -SO_3H groups (active centres) = 1.60 mmol g^{-1} = 0.00160 mmol mg^{-1}

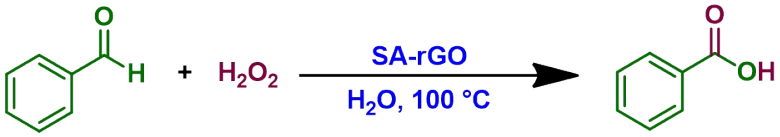
Amount of SA-rGO used in catalysis = 10 mg

Number of active centres used in catalysis = 10 mg × 0.00160 mmol mg^{-1} = 0.0160 mmol

$$\text{TON} = \frac{Moles\ of\ product\ formed}{Number\ of\ active\ centres}$$

$$\text{TOF} = \frac{TON}{Reaction\ time}$$

Calculation of Green Chemistry metrics for the synthesis of benzoic acid 2a

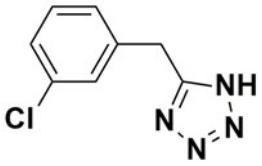


Molecular Weight (g/mol)	106.12	34.01		122.12
Amount used/produced (mmol)	1	1.1		0.94
Amount used/produced (g)	0.106	0.037		0.115

Table S3. Green chemistry metrics for the synthesis of benzoic acid **2a**.

Metric	Significance	Formula	Ideal value	Calculated value for 2a
Environmental factor (E-factor)	The actual amount of waste generated in a process	$\frac{(Total\ mass\ of\ raw\ materials - Total\ mass\ of\ products)}{Mass\ of\ product}$	0	$\frac{[(0.106 + 0.037) - 0.115]}{0.115}$ = **0.24**
Process Mass Intensity (PMI)	The ratio of total mass of materials to the mass of the isolated product	$\frac{\sum Mass\ of\ materials}{Total\ mass\ of\ isolated\ product}$	1	$\frac{(0.106 + 0.037)}{0.115}$ = **1.24**
Reaction Mass Efficiency (RME %)	The efficiency with which reactant mass ends up in the desired product	$\frac{Total\ mass\ of\ isolated\ product}{\sum Mass\ of\ materials} \times 100$	100%	$\frac{0.115}{(0.106 + 0.037)} \times 100$ = **80.4%**
Atom Economy (AE %)	The conversion efficiency of chemical process in terms of all atoms involved and the desired products generated	$\frac{MW\ of\ desired\ product}{\sum MW\ of\ materials} \times 100$	100%	$\frac{122.12}{(106.12 + 34.01)} \times 100$ = **87.1%**

Carbon Efficiency (CE %)	The ratio of amount of carbon in desired product to the amount of carbon in reactants	$\frac{Total\ carbon\ in\ product}{\sum Carbon\ in\ materials} \times 100$	100%	$\frac{7}{7} \times 100$ = **100%**



5-(3-chlorobenzyl)-1*H*-tetrazole (3k)

Table S4. Single crystal X-ray crystallographic data of compound **5k**.

CCDC No.	**1953617**
Empirical formula	$C_8H_7ClN_4$
Formula weight	194.63
Temperature	296 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P21/n
Hall group	-P 2yn
Unit cell dimensions	a = 4.8058 (5) Å α = 90°
	b = 26.6823 (19) Å β = 106.575° (14)
	c = 7.1899 (7) Å γ = 90°
Volume	883.65 (15) $Å^3$
Z	4
Density (calculated)	1.463 g cm^{-3}
Absorption coefficient	0.386 mm^{-1}
F (000)	400.0
Theta range for data collection	3.327-25.349°
Index Ranges	$-5 \leq h \leq 5$
	$-32 \leq k \leq 32$
	$-8 \leq l \leq 8$
Reflections collected	1617
Completeness to theta	99.9 %
Absorption correction	Multi-scan
Refinement method	Full-matrix least-squares on F2
Goodness-of-fit on F2	1.206
Final R indices [I>2sigma(I)]	R1(reflections) = 0.0718 (1379) wR2(reflections) = 0.1463 (1617)

Table S5. Scale up synthesis of Benzoic acid **2a**.[a]

Entry	Benzaldehyde scale (mmol)	H_2O_2 (mmol)	H_2O (mL)	Time (h)	Yield (%)[b]
1	100	110	200	10	91

[a]Reaction conditions: Benzaldehyde (mmol), 30% H_2O_2 (1.1 equiv., mmol), H_2O (mL) and SA-rGO (0.5 g). [b]Isolated yield

Table S6. Scale up synthesis of 5-phenyl-1*H*-tetrazole **5a**.[a]

Entry	Benzonitrile scale (mmol)	NaN_3 (mmol)	DMSO (mL)	Time (h)	Yield (%)[b]
1	100	150	300	9	89

[a]Reaction conditions: Benzonitrile (mmol), NaN_3 (mmol), DMSO (mL) and SA-rGO (0.5 g).
[b]Isolated yield

Table S7. Reusability results of SA-rGO for the synthesis of Benzoic acid **2a**.[a]

Number of cycles	Isolated yield (%)
1	94
2	94
3	93
4	93
5	92
6	91
7	91
8	91

[a]Reaction conditions: Benzaldehyde (1 mmol), 30% H_2O_2 (1.1 equiv.), H_2O (2 mL), SA-rGO (10 mg) and Time (6 h).

Table S8. Reusability results of SA-rGO for the synthesis of 5-phenyl-1*H*-tetrazole **5a**.[a]

Number of cycles	Isolated yield (%)
1	94
2	94
3	94
4	92
5	92
6	90
7	90
8	90

[a]Reaction conditions: Benzonitrile (1mmol), NaN_3 (1.5 mmol), DMSO (3 mL), SA-rGO (10 mg) and Time (4 h).

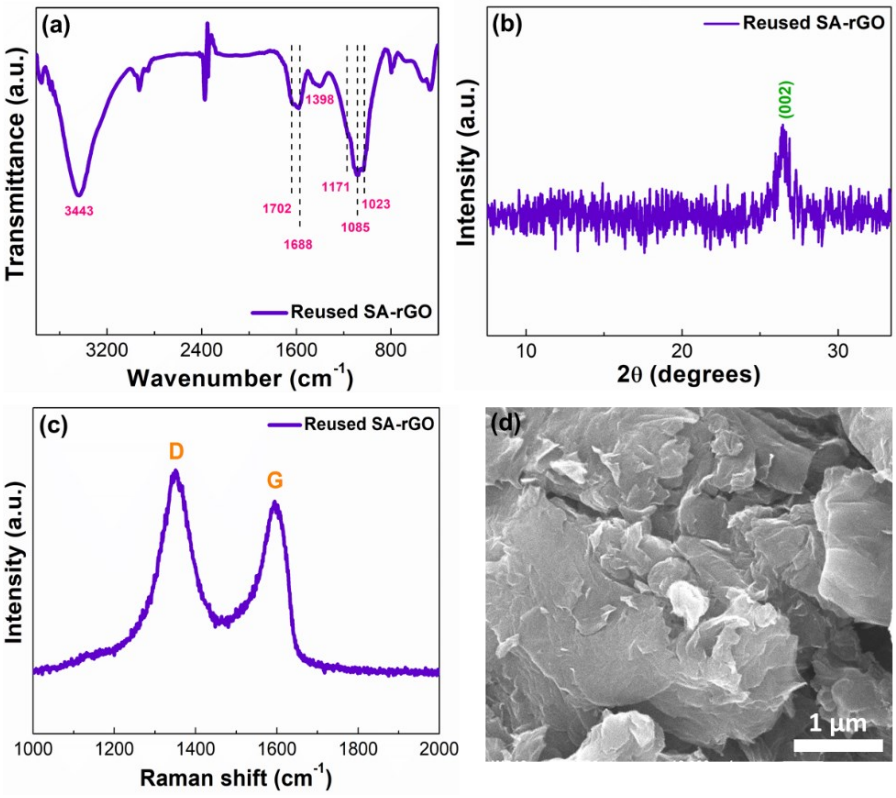


Figure S3. (a) FTIR spectrum (b) XRD pattern (c) Raman spectrum (d) SEM image of SA-rGO reused for eight consecutive cycles.

Table S9. Comparison of the present work with the previous literature for the oxidation of benzaldehyde to benzoic acid.

S. No.	Catalyst system	Catalyst amount	Reaction conditions	Yield (%)[a]	Ref.
1	**SA-rGO**	**10 mg**	**30% H_2O_2 (1.1 equiv.) H_2O (2 mL), 100 ℃, 6 h**	**94**	**PW**
2	$[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$ (5 mmol scale)	0.05 mmol	H_2O_2 (2.5 equiv.) Neat, 90 ℃, 3 h	85	S5
3	CS-423 (10 mmol scale)	5 wt%	H_2O_2 (1.5 equiv.) Acetic acid (5 mL), 90 ℃, 7 h	92	S6
4	β-cyclodextrin	0.1 mmol	H_2O_2 (5 equiv.) PTSA (1 mmol), 50 ℃, 15 h	98	S7
5	$(PhSe)_2$	0.006 g	H_2O_2 10% (1 equiv.) H_2O (0.2 mL), RT, 6 h	>99	S8
6	NGO	8 mg	H_2O_2 (1.1 equiv.) H_2O (2 mL), 80 ℃, 12 h	>99[b]	S9
7	$[(NH_4)_4[CuMo_6O_{18}(OH)_6]$	0.1 mol%	O_2 balloon Na_2CO_3 (0.1 equiv.), H_2O (2 mL), 50 ℃, 12 h	99	S10
8	I_2/NaOH (5 mmol scale)	0.5 mmol/ 1 mmol	70% aq. TBHP (20 mmol) H_2O (2 mL), 70 ℃, 10-16 h	96	S11

[a]Isolated yields. [b]Conversion (%).

Table S10. Comparison of the present work with the previous literature for the synthesis of 5-phenyl-1*H*-tetrazole.

S. No.	Catalyst system	Catalyst amount	Reaction conditions	Yield (%)[a]	Ref.
1	**SA-rGO**	**10 mg**	**DMSO (3 mL), 120 ℃, 4 h**	**94**	**PW**
2	GO/ZnO nanocomposites	0.03 g	DMF (5 mL), 120 ℃, 30 h	78	S12
3	Graphene	0.03 g	DMF (5 mL), 120 ℃, 36 h	63	S13
4	SiO_2-H_2SO_4	500 mg	DMF (10 mL), Reflux, 5 h	88	S14
5	Functionalized MCM-41-SO_3H (MCMBSA)	5 mg	DMF (10 mL), 100 ℃, 8 h	85	S15
6	MCM-41-SO_3H	50 mg	DMF (2 mL), 80 ℃, 120 min	90	S16
7	Sulfamic acid (H_3NSO_3)	9.7 mg	DMF (5 mL), 120 ℃, 6 h	93	S17
8	Amberlyst-15	50 mg	DMSO (3 mL), 85 ℃, 12 h	91	S18
9	Fe_3O_4@SiO2-APTES-TFA	0.1 g	EtOH (3 mL), 80 ℃, 4 h	95	S19
10	SO_3H-carbon	10 mg	DMF (5 mL), 100 ℃, 6 h	92	S20

[a]Isolated yields.

Physical and Spectroscopic data of synthesized carboxylic acids

Benzoic acid (2a). White solid. Yield: 115 mg (94 %). ^{1}HNMR (400 MHz, DMSO-d_6) δ (ppm): 12.95 (s, 1H), 7.92-7.90 (m, 2H), 7.59-7.54 (m, 1H), 7.44 (dd, J = 10.6, 4.7 Hz, 2H). ^{13}CNMR (101 MHz, DMSO-d_6) δ (ppm): 168.01, 133.46, 131.08, 129.77, 129.11.

4-cyanobenzoic acid (2b). White solid. Yield: 140 mg (95 %). ^{1}HNMR (400 MHz, DMSO-d_6) δ (ppm): 8.10 (d, J = 8.1 Hz, 2H), 7.99 (d, J = 8.1 Hz, 2H). ^{13}CNMR (101 MHz, DMSO-d_6) δ (ppm): 166.52, 135.29, 133.12, 130.38, 118.64, 115.53.

4-nitrobenzoic acid (2c). Light yellow solid. Yield: 159 mg (95 %). ^{1}HNMR (400 MHz, DMSO-d_6) δ (ppm): 8.24 (d, J = 8.8 Hz, 2H), 8.09 (d, J = 8.3 Hz, 2H). ^{13}CNMR (101 MHz, DMSO-d_6) δ (ppm): 166.30, 150.47, 136.83, 131.17, 124.18.

4-formylbenzoic acid (2d). White solid. Yield: 140 mg (93 %). ^{1}HNMR (400 MHz, DMSO-d_6) δ (ppm): 13.42 (s, 1H), 10.12 (s, 1H), 8.14 (d, J = 2.0 Hz, 2H), 8.04 (d, J = 8.0 Hz, 2H). ^{13}CNMR (101 MHz, DMSO-d_6) δ (ppm): 193.60, 167.19, 139.30, 136.05, 130.43, 130.08.

4-methoxybenzoic acid (2e). White solid. Yield: 140 mg (92 %). ^{1}HNMR (400 MHz, DMSO-d_6) δ (ppm): 12.67 (s, 1H), 7.91 (d, J = 8.6 Hz, 2H), 7.03 (d, J = 8.7 Hz, 2H), 3.83 (s, 3H). ^{13}CNMR (101 MHz, DMSO-d_6) δ (ppm): 167.49, 163.29, 131.81, 123.40, 114.25, 55.86.

2-hydroxybenzoic acid (2f). White solid. Yield: 124 mg (90 %). ^{1}HNMR (400 MHz, DMSO-d_6) δ (ppm): 7.75 (dd, J = 7.8, 1.4 Hz, 1H), 7.49-7.45 (m, 1H), 6.92-6.86 (m, 2H). ^{13}CNMR (101 MHz, DMSO-d_6) δ (ppm): 172.47, 161.65, 136.21, 130.79, 119.72, 117.62, 113.40.

Terephthalic acid (2g). White solid. Yield: 149 mg (89 %). ^{1}HNMR (400 MHz, DMSO-d_6) δ (ppm): 7.97 (s, 4H). ^{13}CNMR (101 MHz, DMSO-d_6) δ (ppm): 167.32, 134.86, 129.99.

Stearic acid (2h). White solid. Yield: 247 mg (87 %). ^{1}HNMR (400 MHz, $CDCl_3$) δ (ppm): 2.27 (t, J = 7.5 Hz, 2H), 1.59-1.52 (m, 2H), 1.19 (s, 28H), 0.81 (t, J = 6.8 Hz, 3H). ^{13}CNMR (101 MHz, $CDCl_3$) δ (ppm): 180.54, 34.13, 31.94, 29.71, 29.68, 29.66, 29.61, 29.45, 29.38, 29.26, 29.07, 24.68, 22.70, 14.11.

Physical and Spectroscopic data of synthesized 5-substituted-1*H*-tetrazoles

5-phenyl-1*H*-tetrazole (5a). White solid. Yield: 137 mg (94 %). Mp: 216-218 ℃. ^{1}HNMR (400 MHz, DMSO-d_6) δ (ppm): 16.85 (s, 1H), 8.01 (t, J = 3.7 Hz, 2H), 7.57 (td, J = 9.5, 6.1 Hz, 3H). ^{13}CNMR (101 MHz, DMSO-d_6) δ (ppm): 155.82, 131.80, 129.95, 127.48, 124.59. FTIR (cm^{-1}): 2984, 1606, 1463, 1253, 724. HRMS (ESI): m/z calcd. for $C_7H_6N_4$: 146.0596, $[M+H]^+$ found: 147.0666.

5-(4-chlorophenyl)-1*H*-tetrazole (5b). White solid. Yield: 171 mg (95 %). Mp: 264-266 ℃. ^{1}HNMR (400 MHz, DMSO-d_6) δ (ppm): 8.00 (d, J = 7.3 Hz, 2H), 7.63 (d, J = 8.6 Hz, 2H). ^{13}CNMR (101 MHz, DMSO-d_6) δ (ppm): 155.41, 136.42, 130.08, 129.23, 123.72. FTIR (cm^{-1}): 2626, 1607, 1430, 1081, 828. HRMS (ESI): m/z calcd. for $C_7H_5ClN_4$: 180.0207, $[M+H]^+$ found: 181.0280.

5-(4-bromophenyl)-1*H*-tetrazole (5c). Brown solid. Yield: 214 mg (95 %). Mp: 232-234 ℃. ^{1}HNMR (400 MHz, DMSO-d_6) δ (ppm): δ 7.94 (d, J = 8.4 Hz, 2H), 7.79 (d, J = 8.4 Hz, 2H). ^{13}CNMR (101 MHz, DMSO-d_6) δ (ppm): 155.54, 133.00, 129.39, 125.23, 124.06. FTIR (cm^{-1}): 2902, 2846, 1716, 1600, 1054, 981, 827, 737. HRMS (ESI): m/z calcd. for $C_7H_5BrN_4$: 223.9703, $[M+H]^+$ found: 224.9777.

4-(1*H*-tetrazol-5-yl)benzaldehyde (5d). Grey solid. Yield: 158 mg (91 %). Mp: 182-184 ℃. ^{1}HNMR (400 MHz, DMSO-d_6) δ (ppm): 10.03 (s, 1H), 8.19 (d, J = 8.3 Hz, 2H), 8.05 (d, J = 8.3 Hz, 2H). ^{13}CNMR (101 MHz, DMSO-d_6) δ (ppm): 193.12, 155.96, 138.08, 130.84, 130.03, 128.08. FTIR (cm^{-1}): 3403, 3083, 2357, 1936, 1671, 1579, 440, 1085, 984, 834. HRMS (ESI): m/z calcd. for $C_8H_6N_4O$: 174.0538, $[M+H]^+$ found: 175.0610.

4-(1*H*-tetrazol-5-yl)benzonitrile (5e). Straw colored solid. Yield: 157 mg (92 %). Mp: 190-192 ℃. ^{1}HNMR (400 MHz, DMSO-d_6) δ (ppm): 8.22-7.99 (m, 4H). ^{13}CNMR (101 MHz, DMSO-d_6) δ (ppm): 155.88, 133.84, 129.34, 128.12, 118.71, 113.89. FTIR (cm^{-1}): 3091, 3008, 2918, 2850, 2763, 2609, 2229, 1644, 1565, 1494, 1431, 1277, 1150, 1063, 984, 849, 747. HRMS (ESI): m/z calcd. for $C_8H_5N_5$: 171.0540, $[M+H]^+$ found: 172.0612.

2-chloro-4-(1*H*-tetrazol-5-yl)pyridine (5f). White solid. Yield: 157 mg (87 %). Mp: 196-200 ℃. ^{1}HNMR (400 MHz, DMSO-d_6) δ (ppm): 8.60 (d, J = 5.1 Hz, 1H), 8.05 (s, 1H), 7.99 (d, J = 5.1 Hz, 1H). ^{13}CNMR (101 MHz, DMSO-d_6) δ (ppm): 155.18, 151.89, 151.80, 136.30, 121.76, 120.81. FTIR (cm^{-1}): 3091, 1854, 1612, 1393, 1008, 864. HRMS (ESI): m/z calcd. for $C_7H_7N_5$: 181.0154, $[M+H]^+$ found: 182.0226.

4-(1*H*-tetrazol-5-yl)aniline (5g). Light orange solid. Yield: 140 mg (87 %). Mp: 266-268 ℃. ^{1}HNMR (400 MHz, DMSO-d_6) δ (ppm): 7.34 (d, J = 8.6 Hz, 2H), 6.56 (d, J = 8.6 Hz, 2H), 6.10 (s, 2H). ^{13}CNMR (101 MHz, DMSO-d_6) δ (ppm): 162.70, 152.96, 133.62, 121.08, 112.10, 96.21. FTIR (cm^{-1}): 3383, 3196, 2636, 1661, 1346, 1087, 897. HRMS (ESI): m/z calcd. for $C_7H_7N_5$: 161.0701, $[M+H]^+$ found: 162.0773.

N,N-dimethyl-4-(1*H*-tetrazol-5-yl)aniline (5h). Brown solid. Yield: 166 mg (88 %). Mp: 79-81 ℃. ^{1}HNMR (400 MHz, DMSO-d_6) δ (ppm): 7.46 (d, J = 8.9 Hz, 2H), 6.67 (d, J = 8.9 Hz, 2H), 2.92 (s, 6H). ^{13}CNMR (101 MHz, DMSO-d_6) δ (ppm): 153.57, 133.94, 121.25, 113.98, 95.93. FTIR (cm^{-1}): 3431, 3382, 2212, 1704, 1605, 1519, 1367, 1174, 815. HRMS (ESI): m/z calcd. for $C_9H_{11}N_5$: 189.1014, $[M+H]^+$ found: 190.1087.

5-(p-tolyl)-1*H*-tetrazole (5i). White solid. Yield: 144 mg (90 %). Mp: 244-246 ℃. ^{1}HNMR (400 MHz, DMSO-d_6) δ (ppm): 7.89 (d, J = 6.9 Hz, 2H), 7.37 (d, J = 6.9 Hz, 2H), 2.34 (s, 3H). ^{13}CNMR (101 MHz, DMSO-d_6) δ (ppm): 155.58, 141.74, 130.45, 127.40, 121.78, 21.55. FTIR (cm^{-1}): 2917, 2845, 1889, 1615, 1163, 984, 818, 734. HRMS (ESI): m/z calcd. for $C_8H_8N_4$: 160.0744, $[M+H]^+$ found: 161.0824.

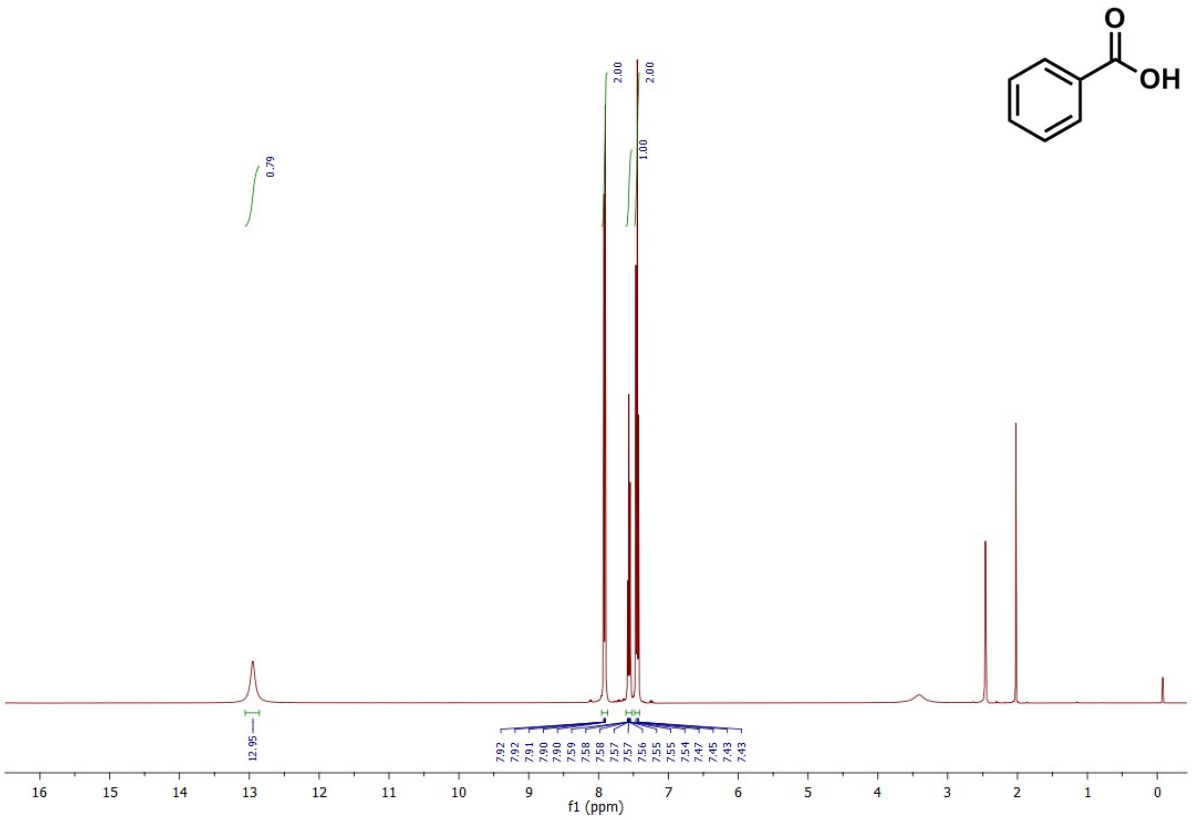
5-(3-bromo-4-methoxyphenyl)-1*H*-tetrazole (5j). White solid. Yield: 235 mg (92 %). Mp: 196-198 ℃. ^{1}HNMR (400 MHz, DMSO-d_6) δ (ppm): 8.18 (d, J = 2.4 Hz, 1H), 7.99 (dd, J = 3.7 Hz, 1H), 7.30 (d, J = 8.6 Hz, 1H), 3.90 (s, 3H). ^{13}CNMR (101 MHz, DMSO-d_6) δ (ppm): 157.98, 154.58, 131.74, 128.55, 118.38, 113.85, 111.81, 57.13. FTIR (cm^{-1}): 2916, 2566, 1642, 1268, 1156, 896. HRMS (ESI): m/z calcd. for $C_8H_7BrN_4O$: 253.9800, $[M+H]^+$ found: 254.9873.

5-(3-chlorobenzyl)-1*H*-tetrazole (5k). White solid. Yield: 177 mg (91 %). Mp: 130-134 ℃. ^{1}HNMR (400 MHz, DMSO-d_6) δ (ppm): 7.29-7.35 (m, 3H), 7.20 (d, J = 6.9 Hz, 1H), 4.28 (s, 2H). ^{13}CNMR (101 MHz, DMSO-d_6) δ (ppm): 155.45, 138.81, 133.72, 131.07, 129.22, 128.05, 127.58, 28.95. FTIR (cm^{-1}): 3115, 2850, 2722, 2624, 1595, 1554, 1414, 1047, 994, 881, 794, 748. HRMS (ESI): m/z calcd. for $C_8H_7ClN_4$: 194.0364, $[M+H]^+$ found: 195.0436.

5-((phenylsulfonyl)methyl)-1*H*-tetrazole (5l). Yellow solid. Yield: 195 mg (87 %). Mp: 172-174 ℃. ^{1}HNMR (400 MHz, DMSO-d_6) δ (ppm): 7.70-7.75 (m, 3H), 7.58-7.61 (m, 2H), 5.20 (s, 2H). ^{13}CNMR (101 MHz, DMSO-d_6) δ (ppm): 148.56, 138.21, 135.01, 129.99, 128.56, 50.79. FTIR (cm^{-1}): 3028, 2852, 1592, 1550, 1448, 1398, 1148, 1031, 736, 672. HRMS (ESI): m/z calcd. for $C_8H_8N_4O_2S$: 224.0368, $[M+H]^+$ found: 225.0440.

benzyl (4-(1*H*-tetrazol-5-yl)phenyl)carbamate (5m). Light brown solid. Yield: 242 mg (82 %). Mp: 129-130 ℃. ^{1}HNMR (400 MHz, DMSO-d_6) δ (ppm): 10.30 (s, 1H), 7.71 (d, J = 8.7 Hz, 2H), 7.62 (d, J = 8.7 Hz, 2H), 7.31-7.41 (m, 5H), 5.15 (s, 2H). ^{13}CNMR (101 MHz, DMSO-d_6) δ (ppm): 171.85, 153.62, 144.06, 136.66, 133.84, 129.01, 128.80, 128.73, 119.67, 118.59, 66.80. FTIR (cm^{-1}): 3098, 1725, 1592, 1448, 1031, 834, 739. HRMS (ESI): m/z calcd. for $C_{15}H_{13}N_6O_2$: 295.1069, $[M+H]^+$ found: 296.1141.

1,4-di(1H-tetrazol-5-yl)benzene (5n). White solid. Yield: 191 mg (90 %). Mp: 268-270 ℃. ^{1}HNMR (400 MHz, DMSO-d_6) δ (ppm): 8.04 (s, 4H). ^{13}CNMR (101 MHz, DMSO-d_6) δ (ppm): 170.23, 133.75, 128.15. FTIR (cm^{-1}): 3382, 2238, 1579, 1442, 1072, 989, 839. HRMS (ESI): m/z calcd. for $C_8H_6N_8$: 214.0715, $[M+H]^+$ found: 215.0787.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1.00
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12.95
7.92
7.92
7.91
7.91
7.90
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7.59
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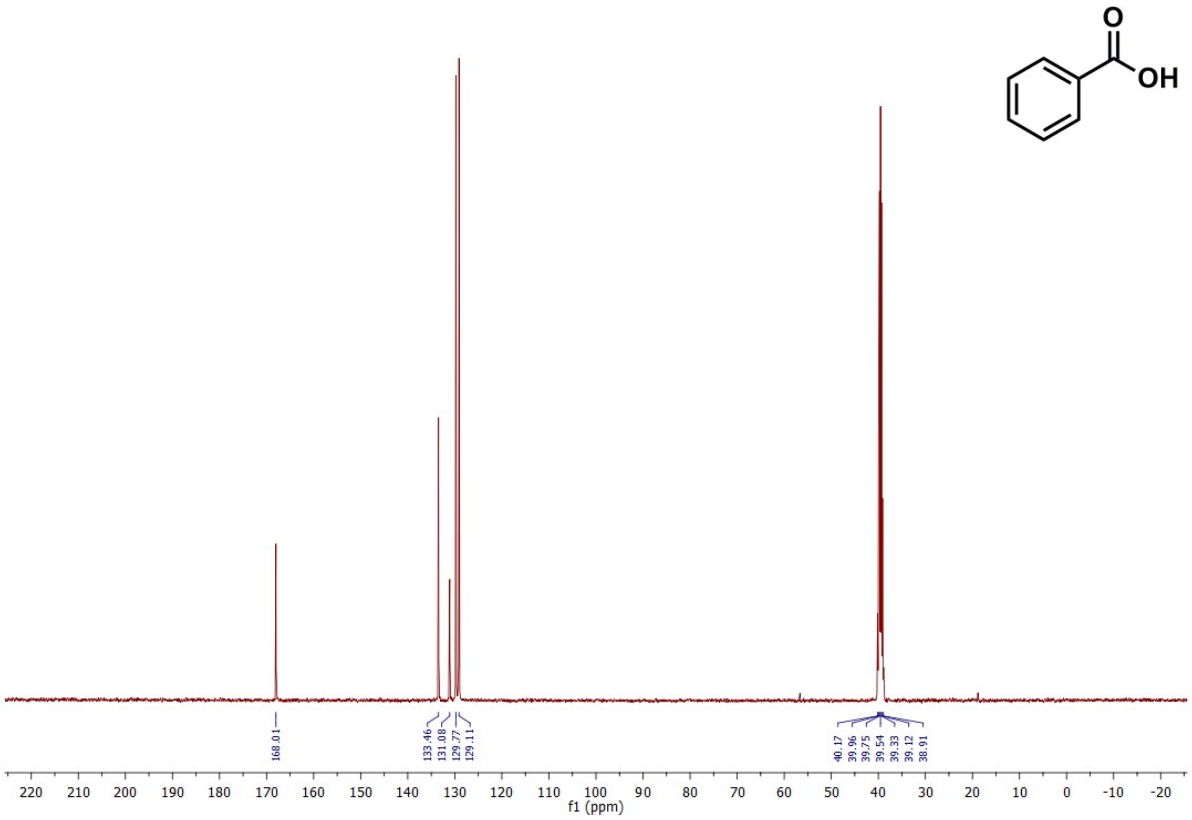
7.47
7.45
7.43
7.43
f1 (ppm)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OH
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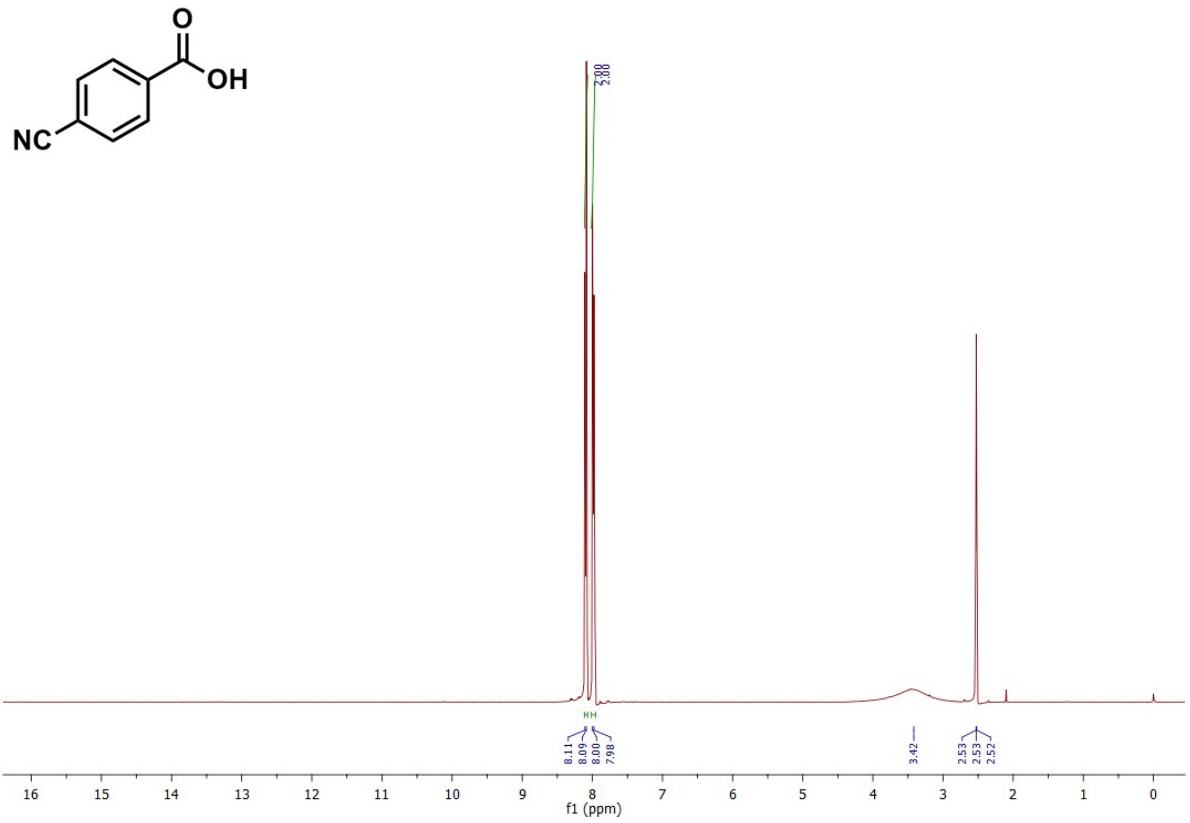
38.91
f1 (ppm)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8.00
7.98
3.42
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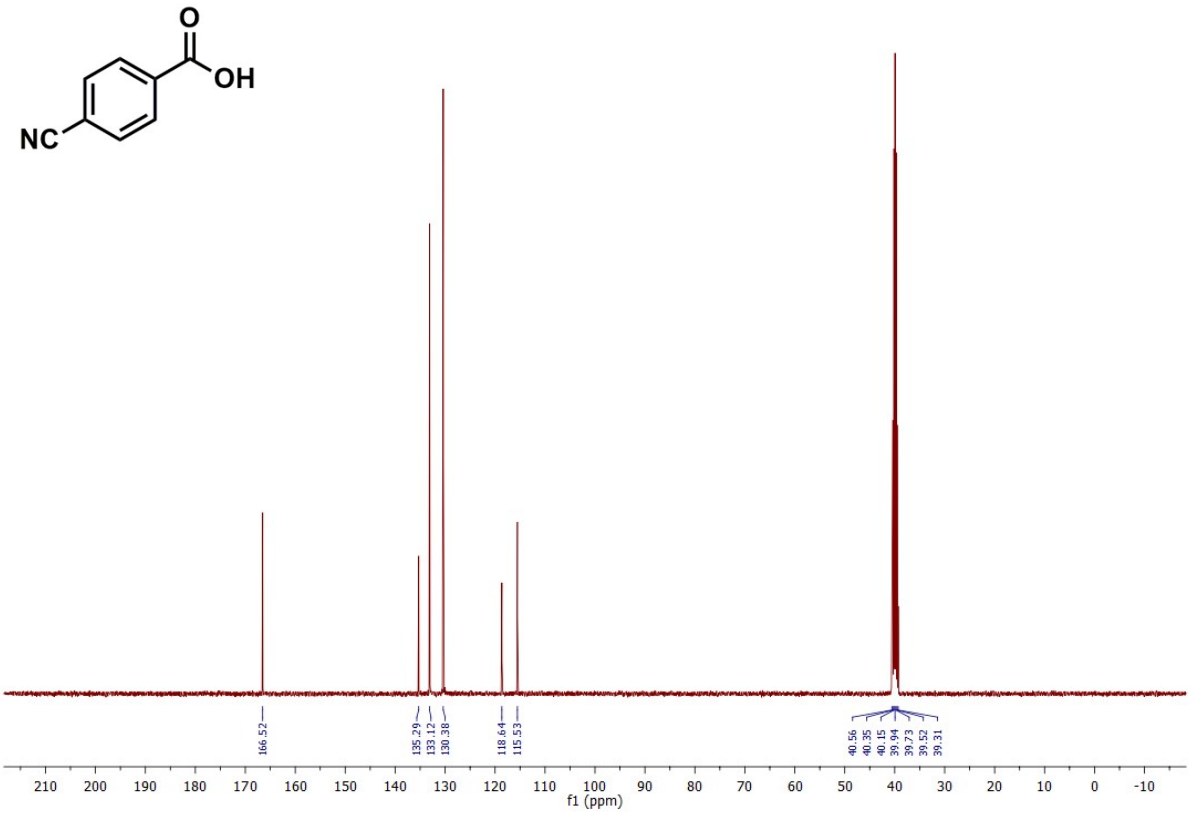
2.53
2.52
f1 (ppm)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40.35
40.15
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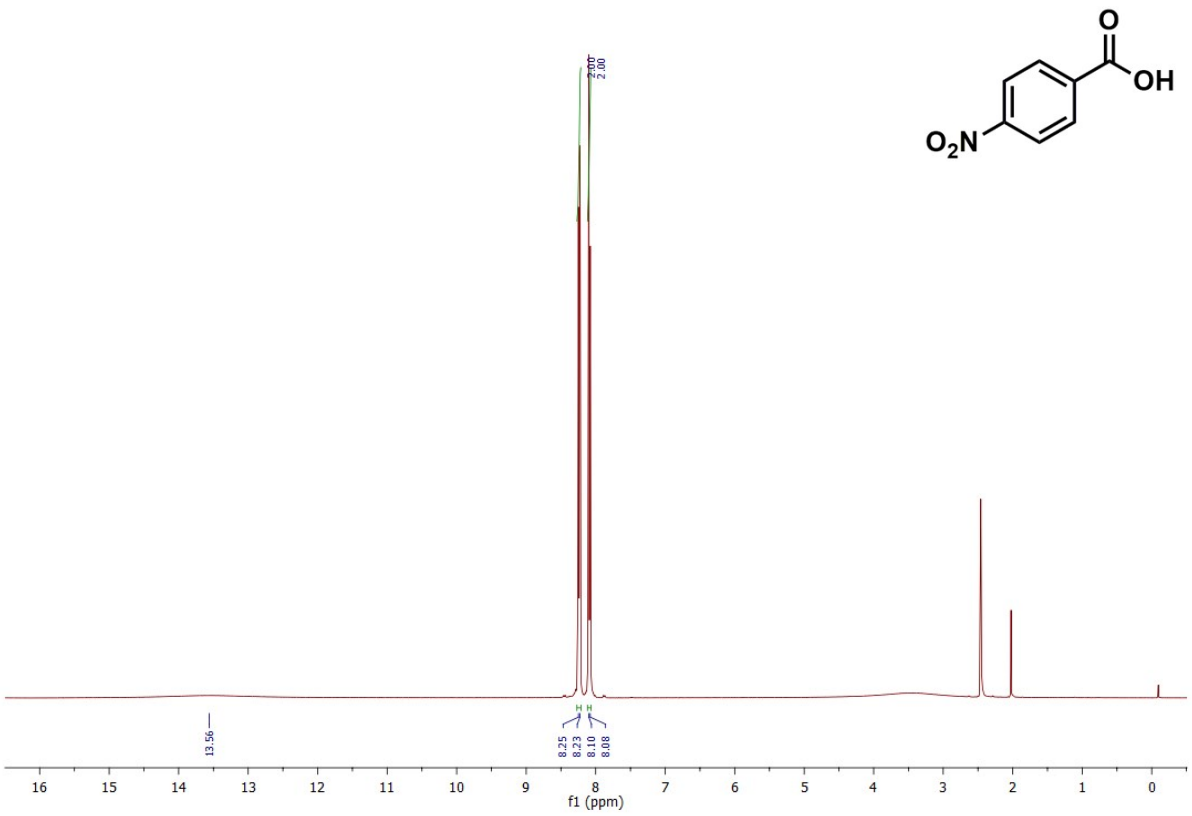
39.52
39.31
f1 (ppm)


O
OH
O2N
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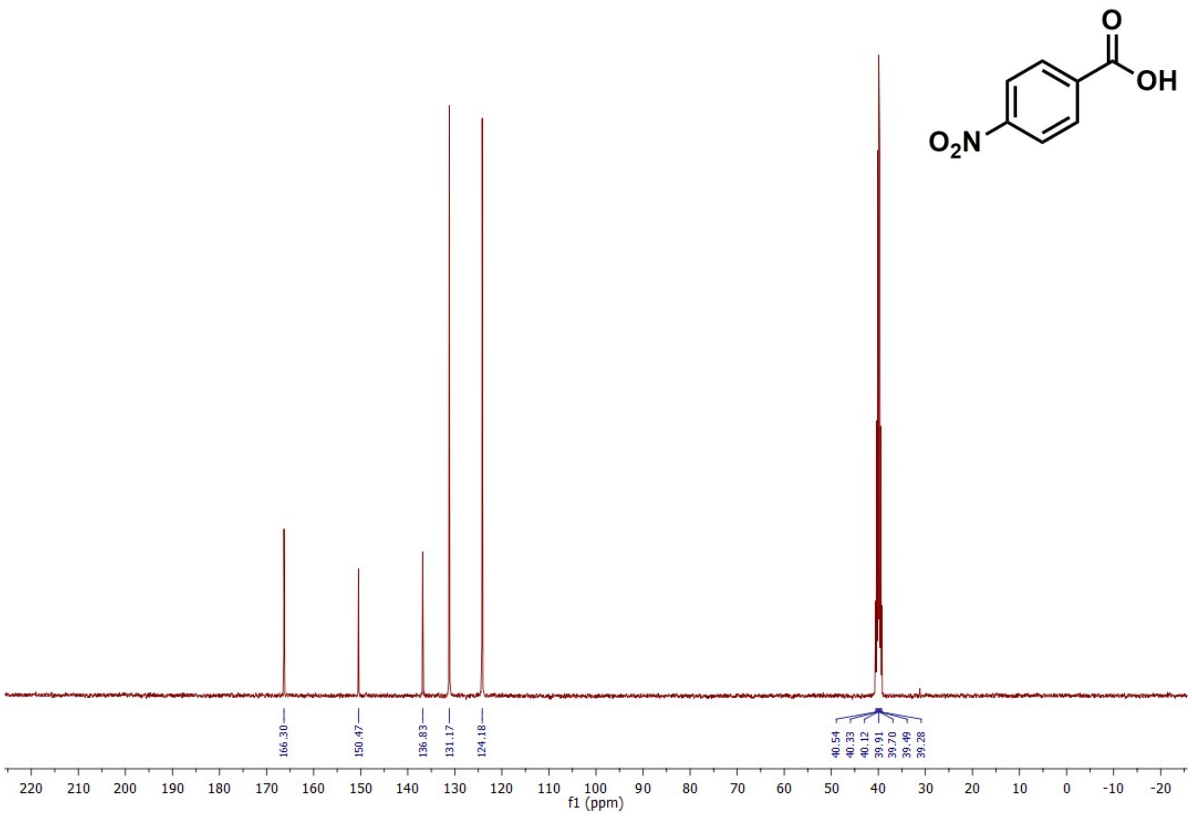
2.00
13.56
8.25
8.23
8.10
8.08
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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OH
O2N
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136.83
131.17
124.18
40.54
40.33
40.12
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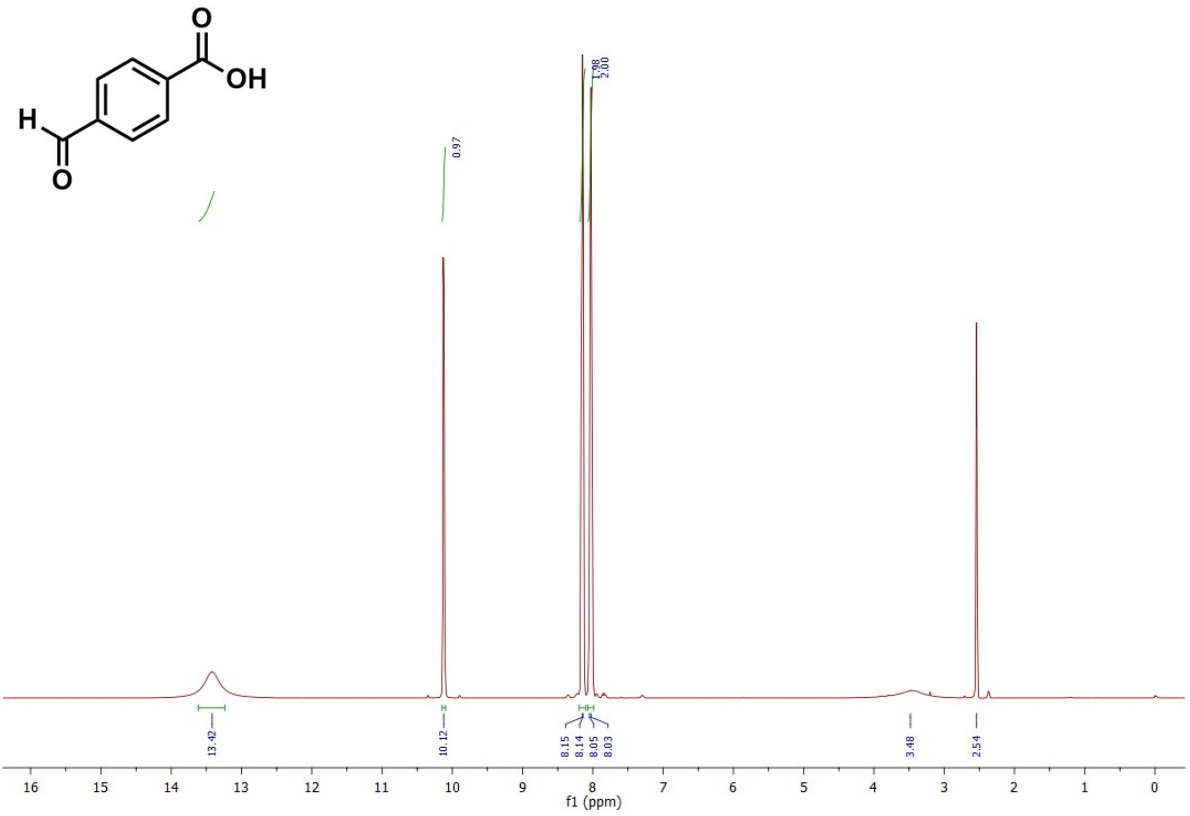
39.70
39.49
39.28
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


O
OH
H
O
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8.15
8.14
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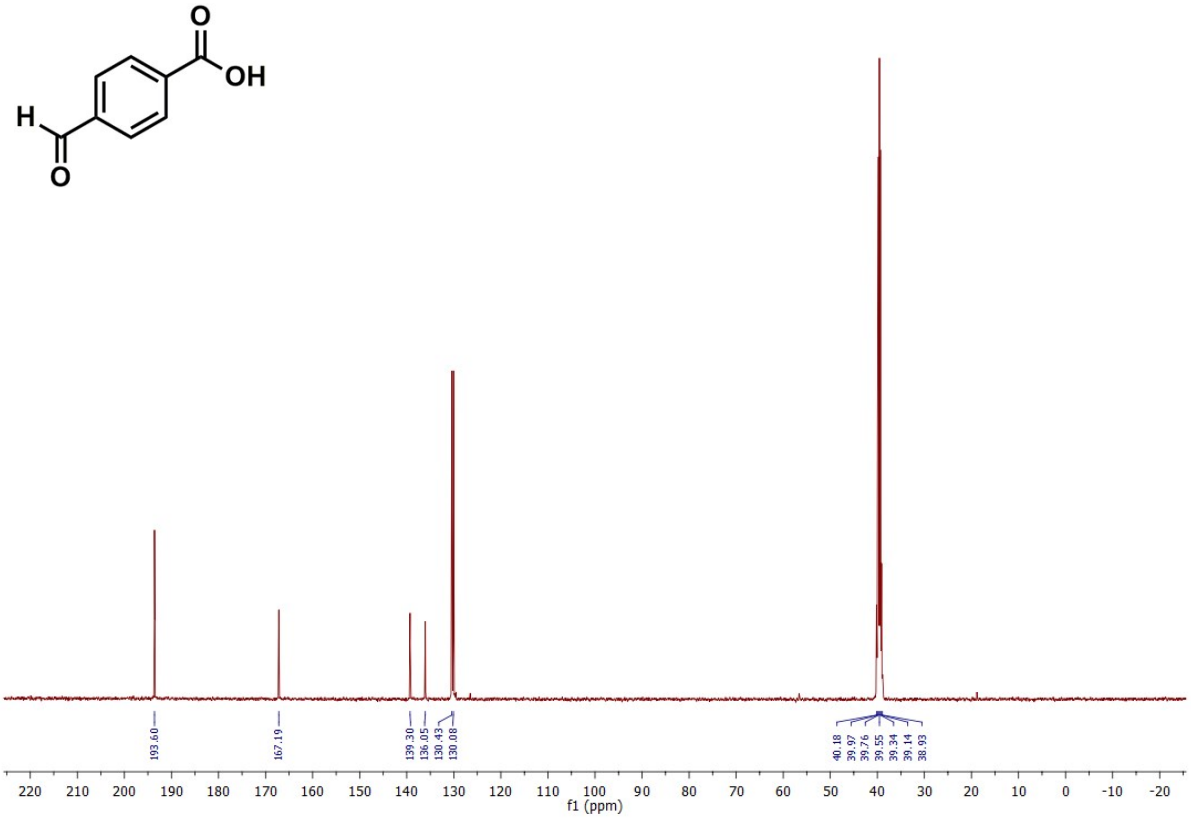
8.03
3.48
2.54
f1 (ppm)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OH
H
O
193.60
167.19
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136.05
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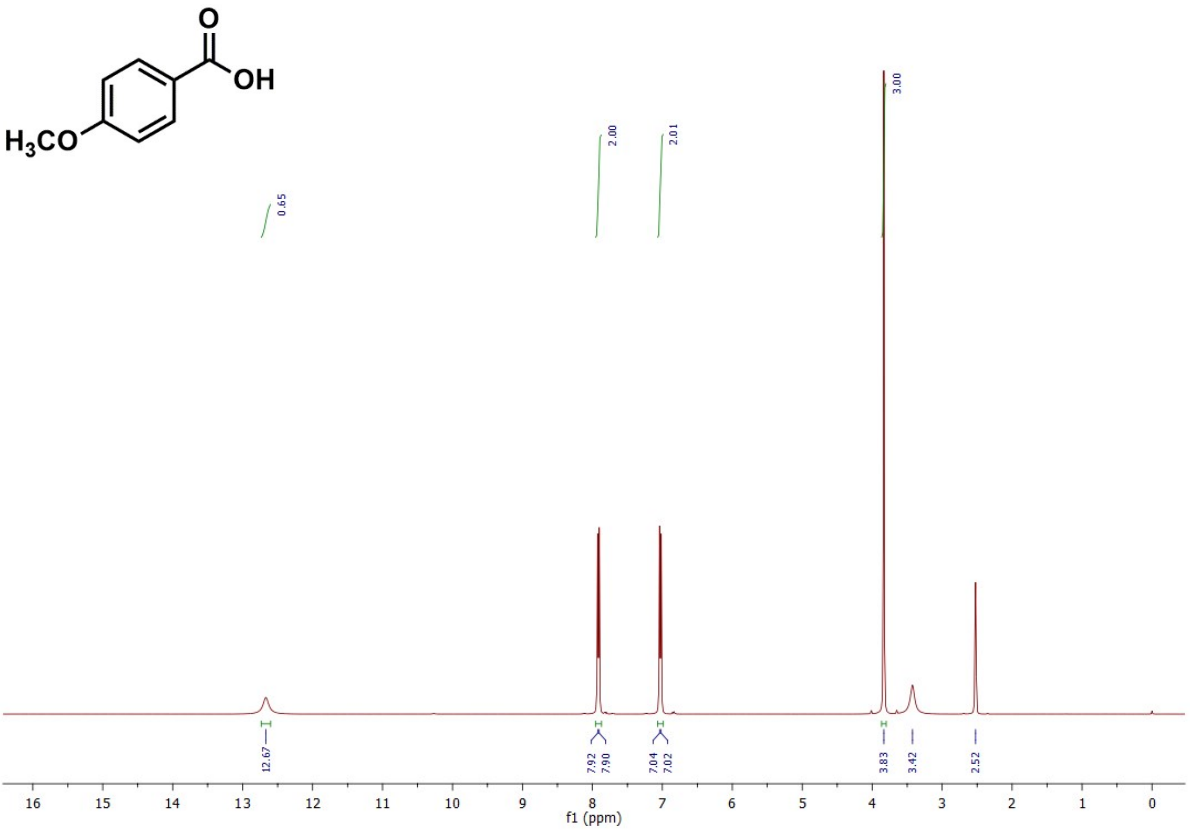
39.55
39.34
39.14
38.93
f1 (ppm)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OH
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3.00
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7.92
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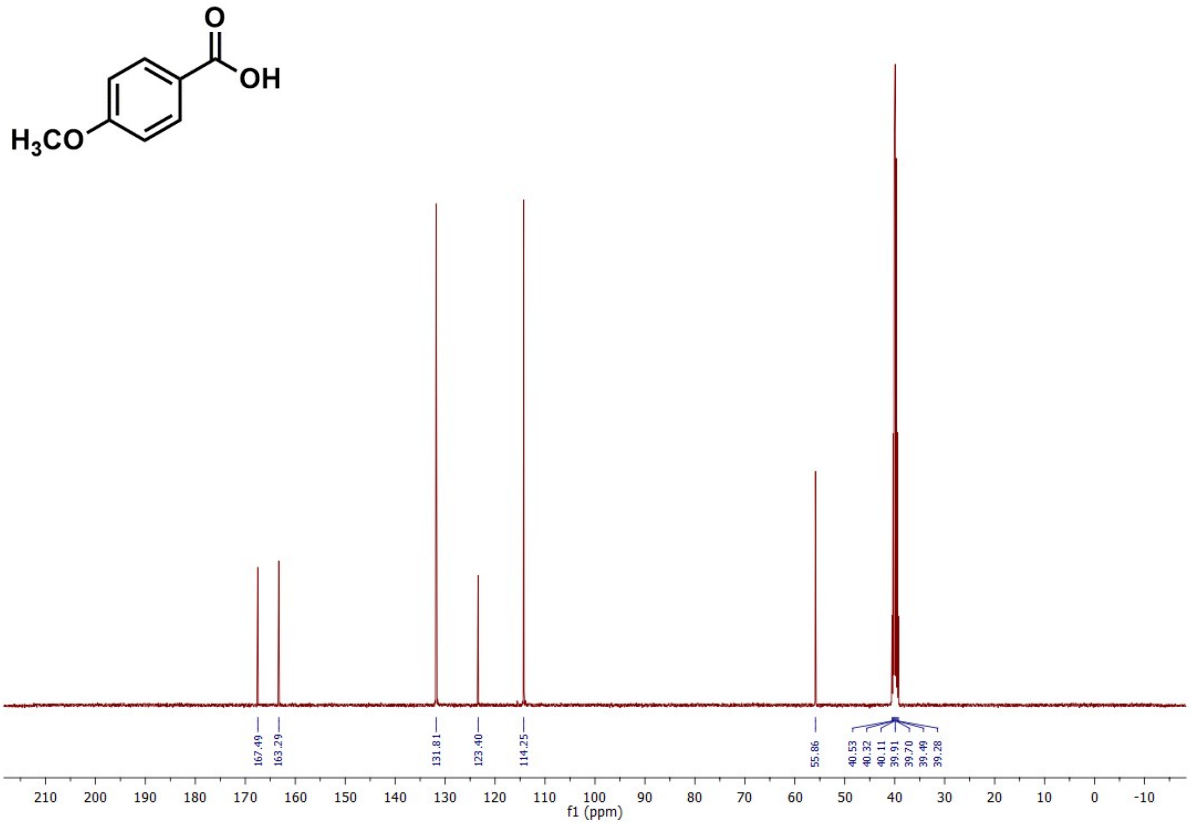
7.04
7.02
3.83
3.42
2.52
f1 (ppm)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OH
H3CO
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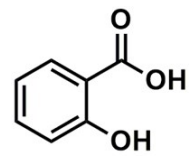
40.32
40.11
39.91
39.70
39.49
39.28
f1 (ppm)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OH
OH

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1.00
1.00
13.82
11.28
7.76
7.76
7.76
7.74
7.74
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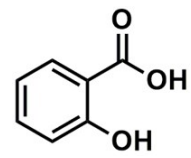
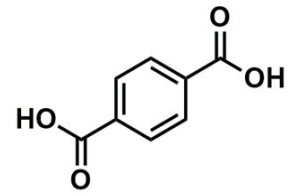
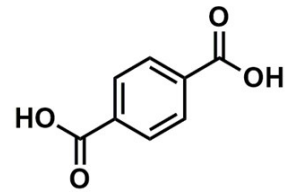
7.49
7.49
7.47
7.47
7.47
7.45
7.45
6.92
6.90
6.88
6.88
6.86
6.86
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


O
OH
OH

172.47
161.65
136.21
130.79
119.72
117.62
113.40
40.64
40.43
40.22
40.01
39.80
39.60
39.39
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


HO
O
O
OH

4.00
7.97
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


HO
O
O
OH

167.32
134.86
129.99
40.13
39.92
39.71
39.50
39.29
39.08
38.87
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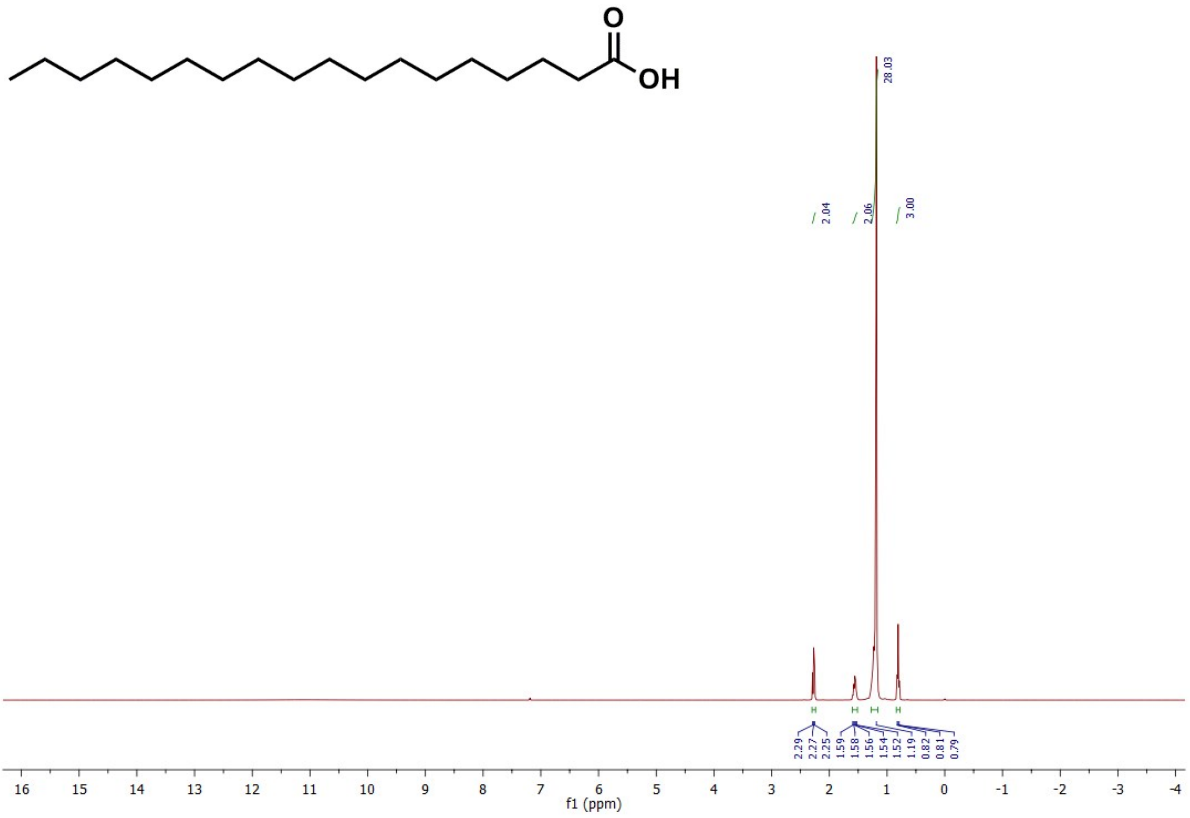
f1 (ppm)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OH
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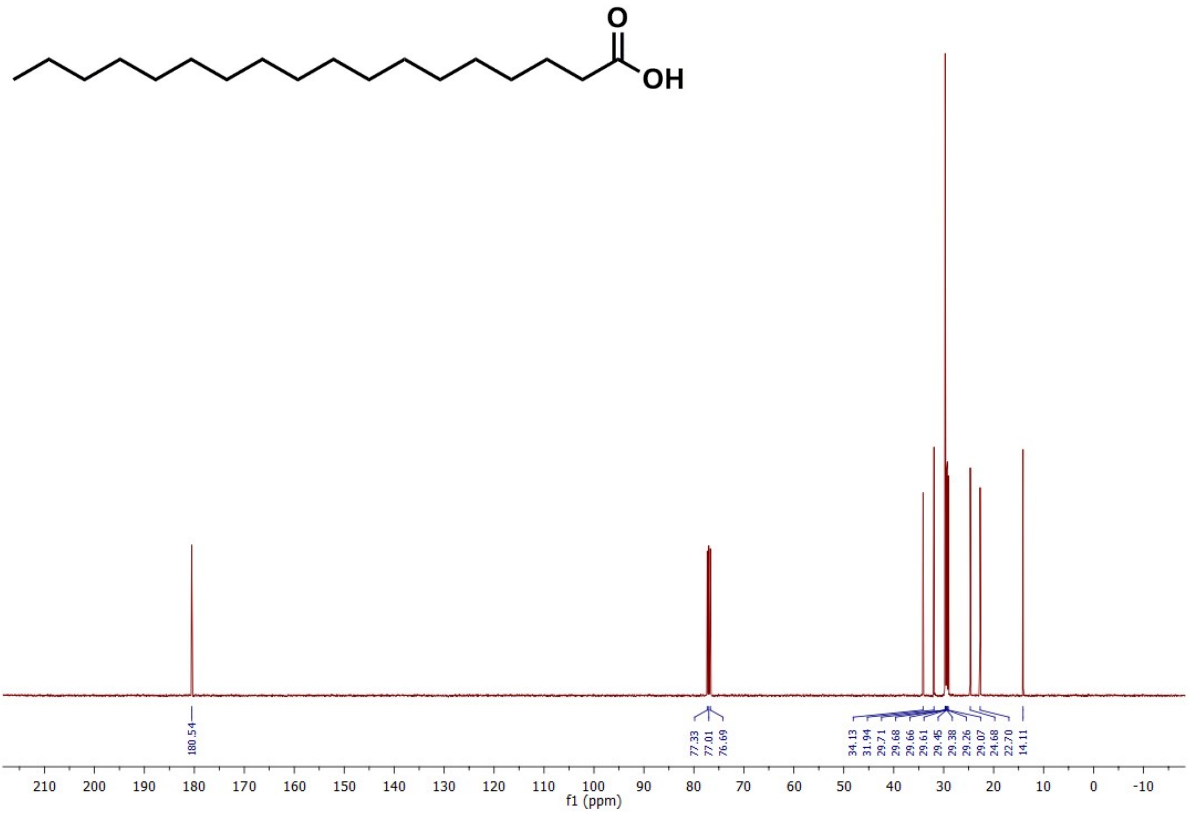
2.04
2.06
3.00
2.29
2.27
2.25
1.59
1.58
1.56
1.54
1.52
1.19
0.82
0.81
0.79
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)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OH
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29.61
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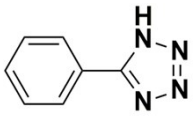
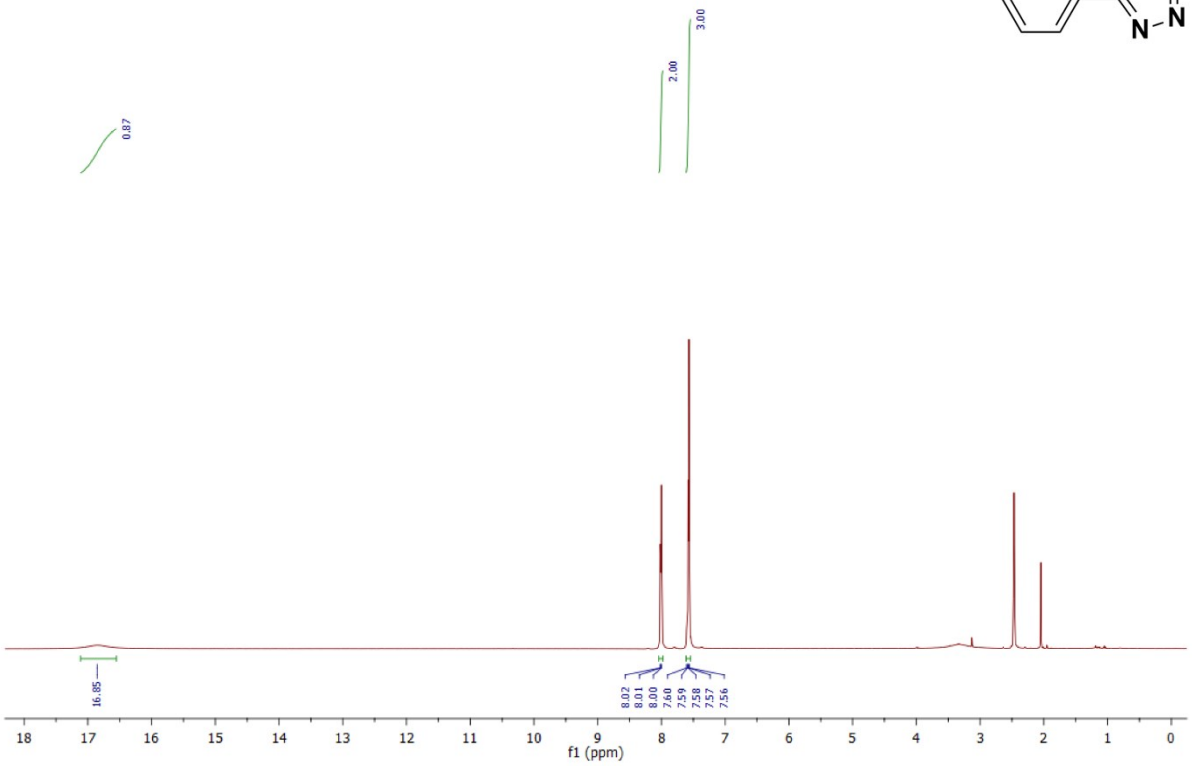
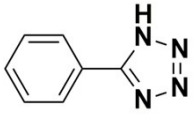
29.38
29.26
29.07
24.68
22.70
14.11
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

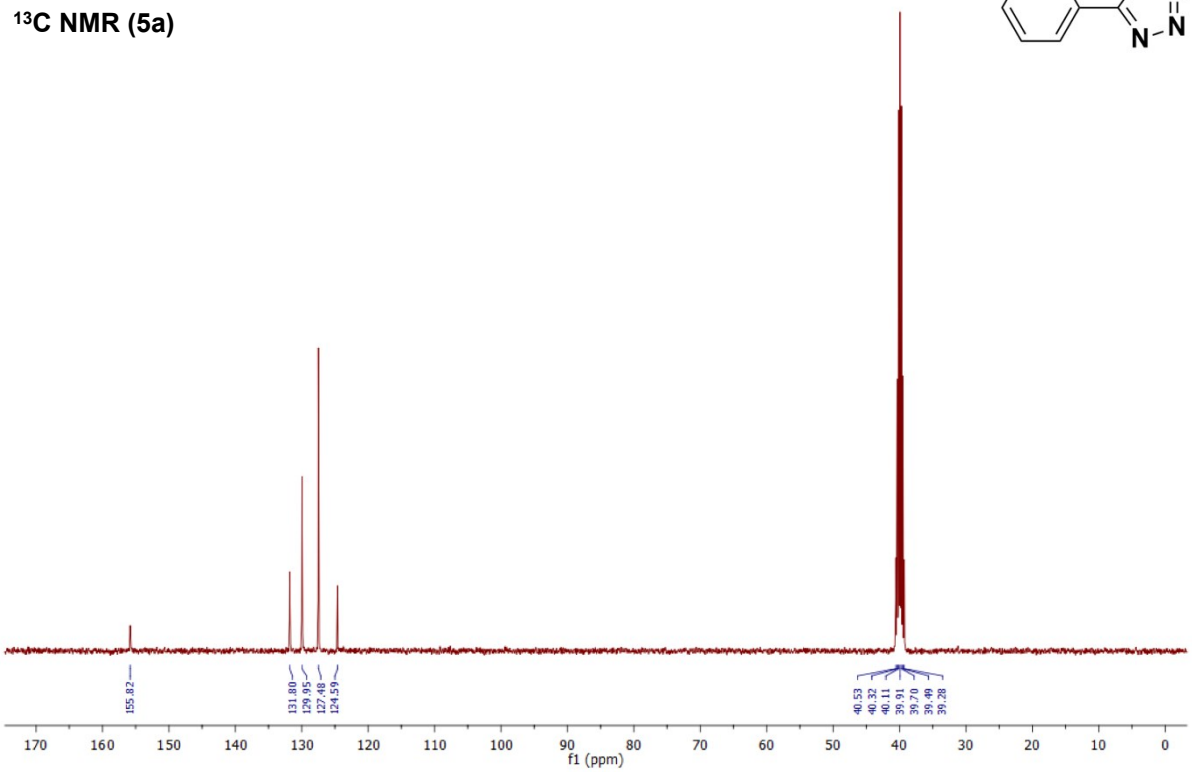
^{1}H NMR (5a)



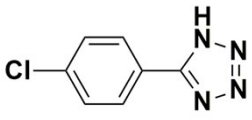


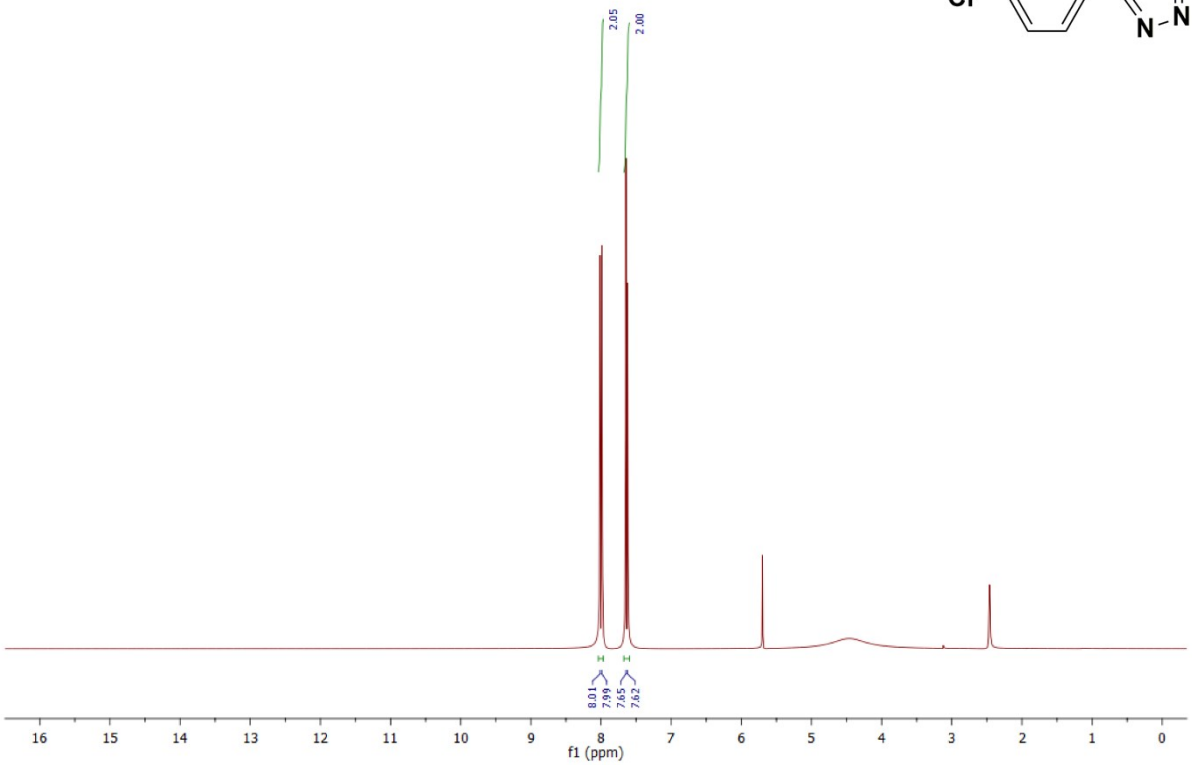
^{13}C NMR (5a)



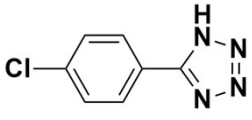


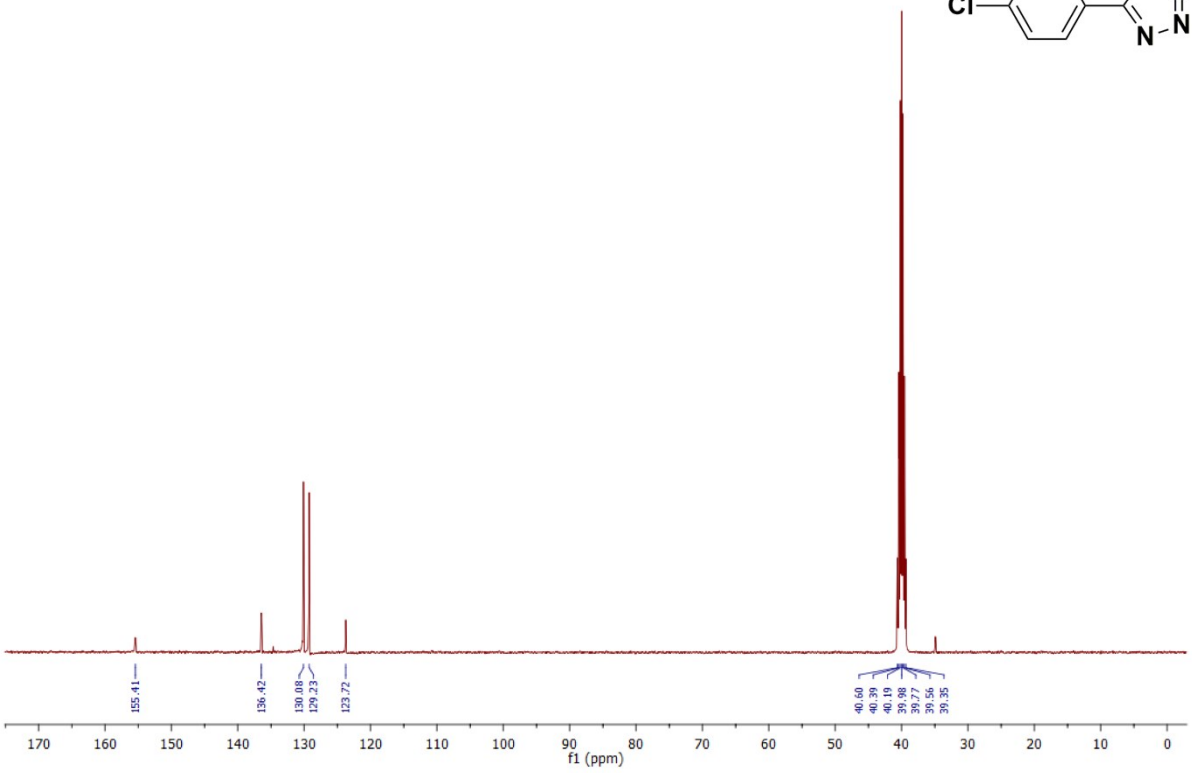
^{1}H NMR (5b)



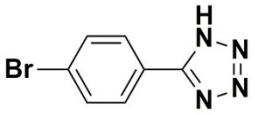


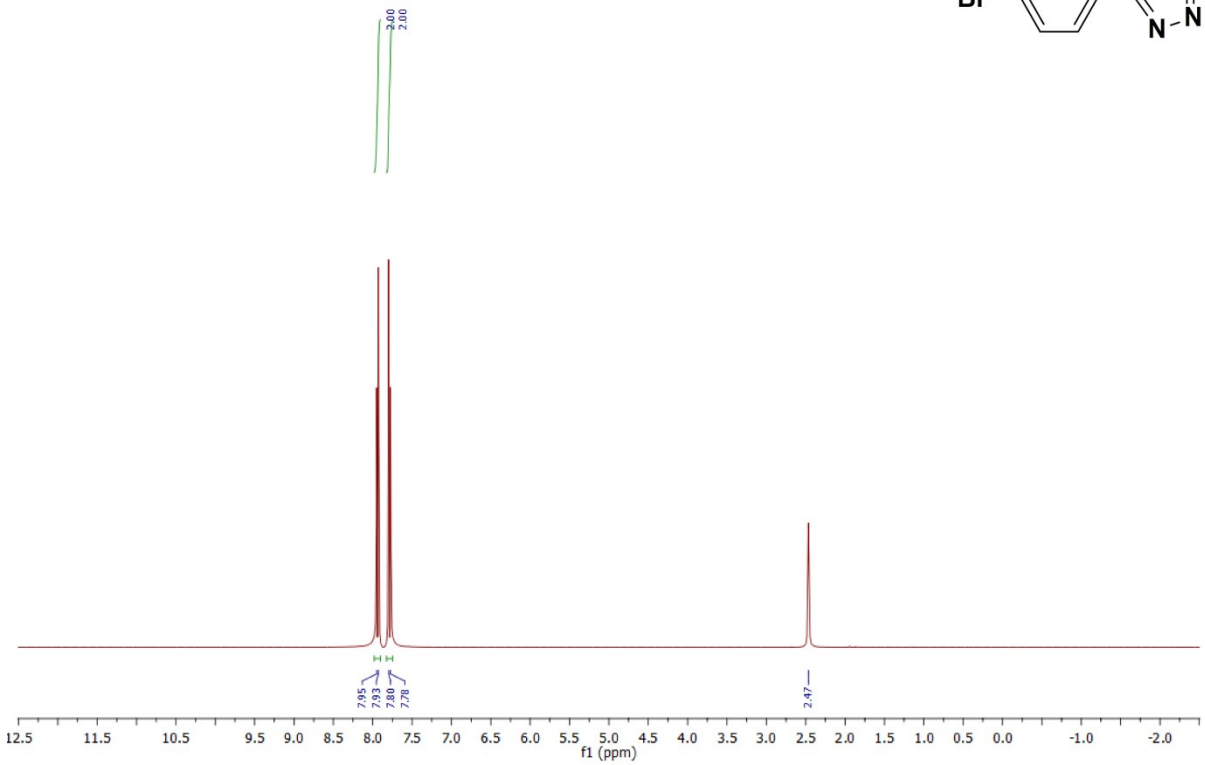
^{13}C NMR (5b)



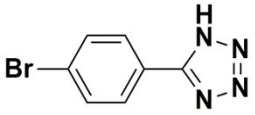


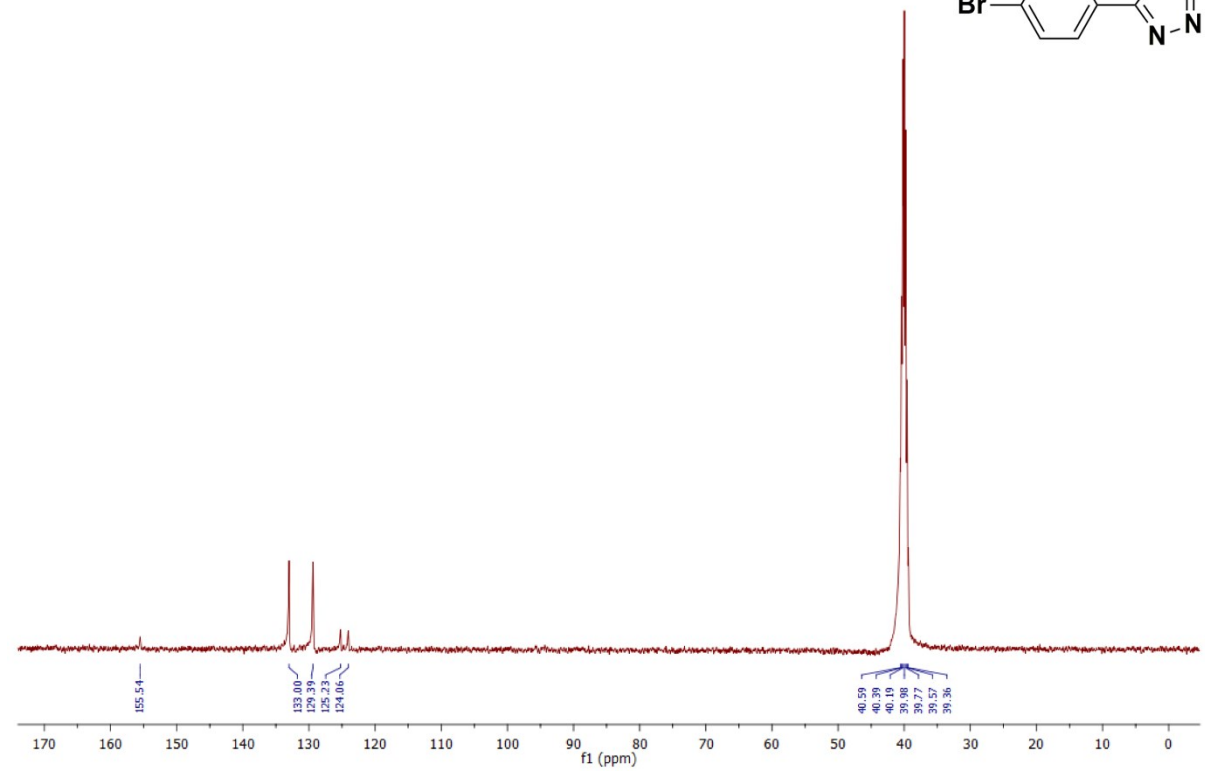
^{1}H NMR (5c)



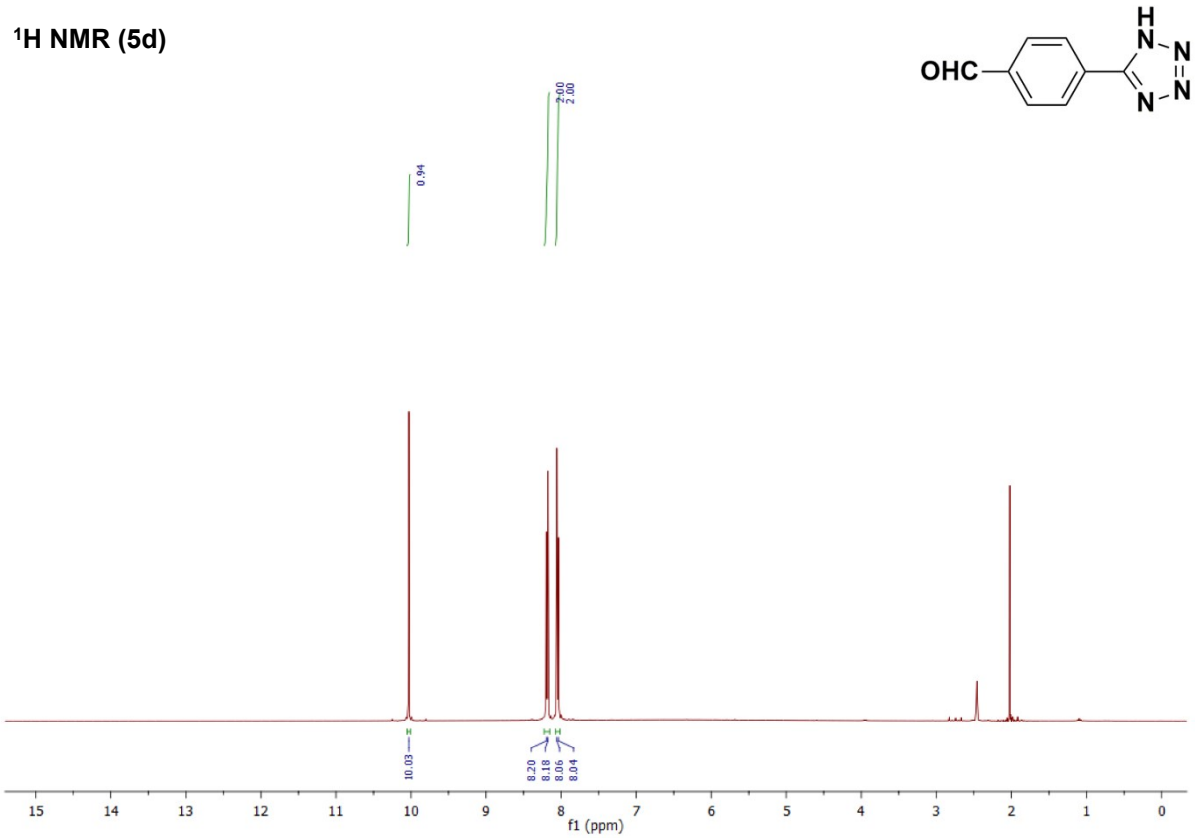


^{13}C NMR (5c)

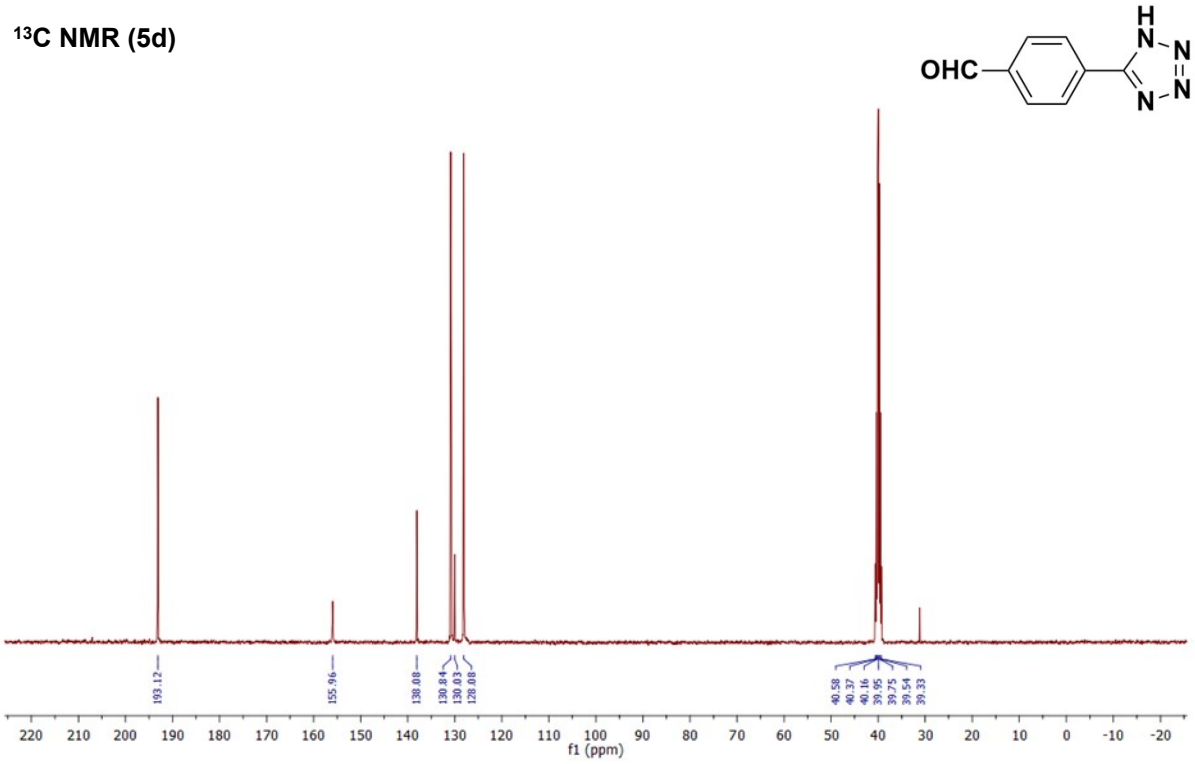




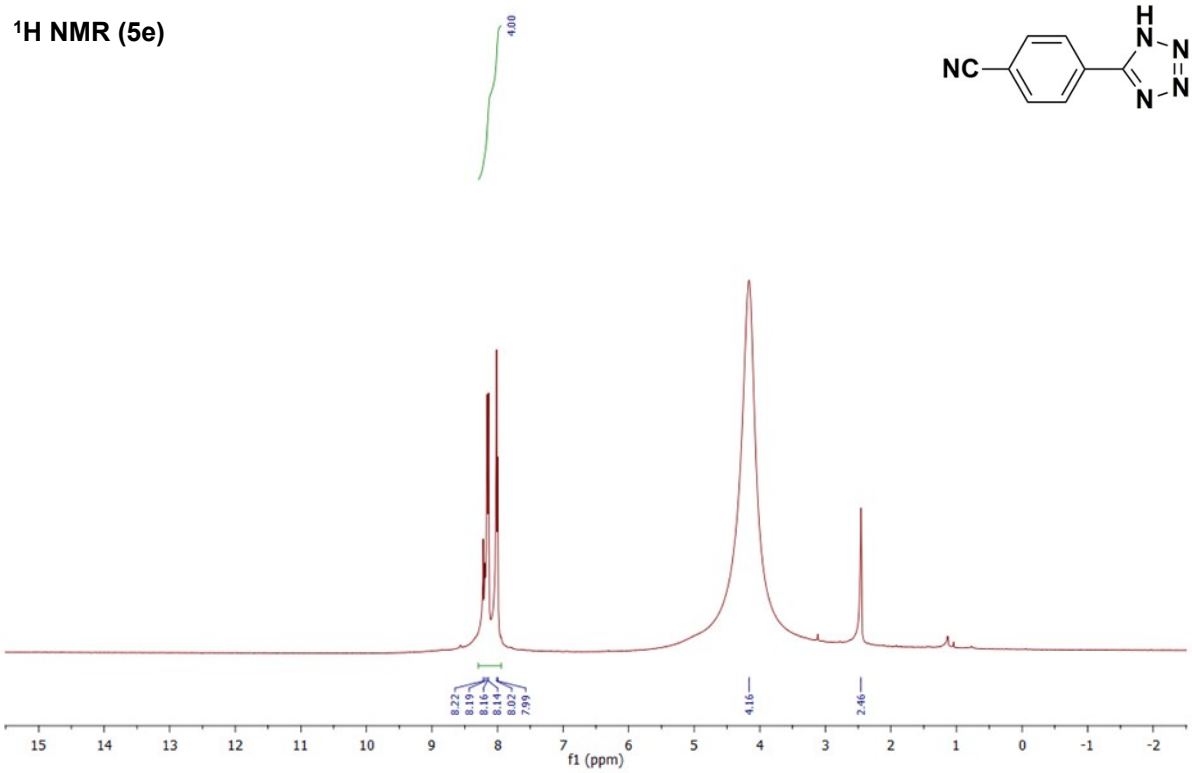
^{1}H NMR (5d)



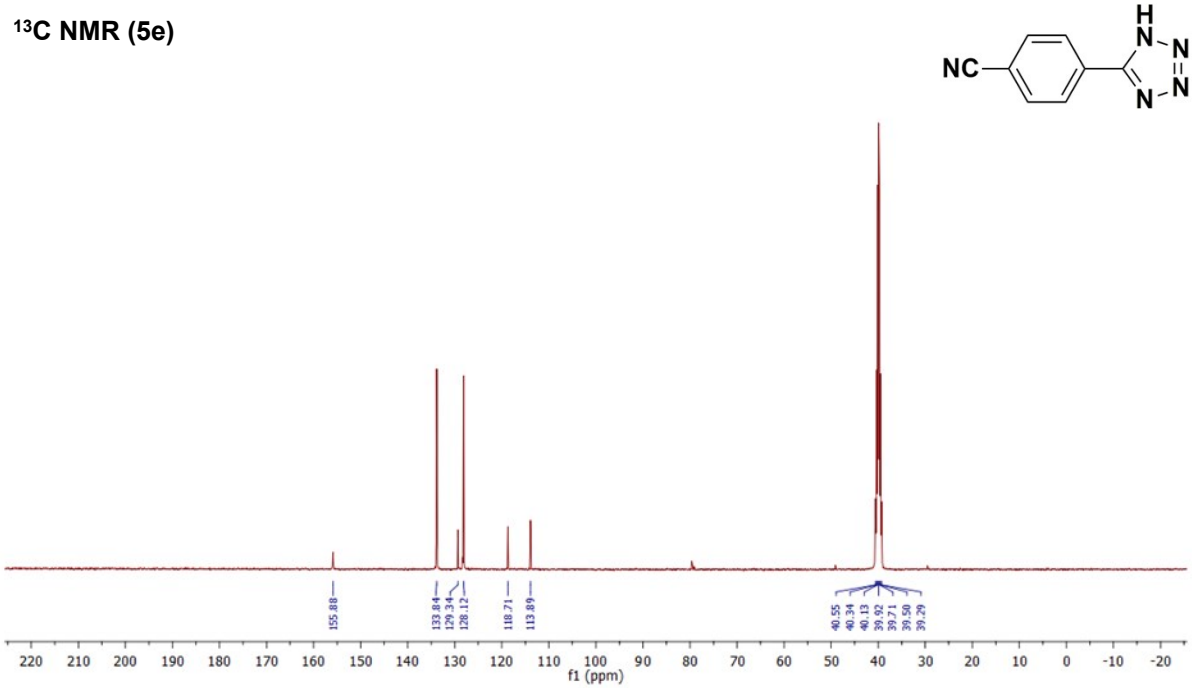
^{13}C NMR (5d)



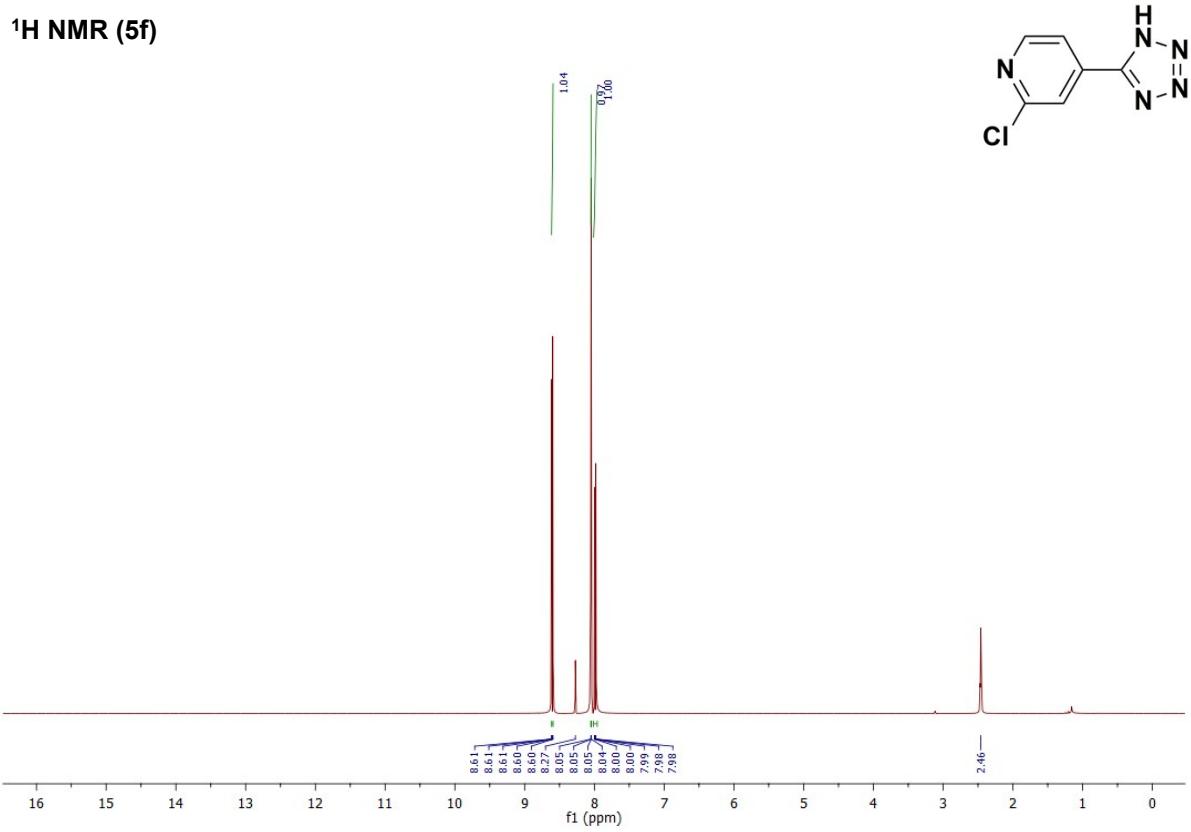
^{1}H NMR (5e)



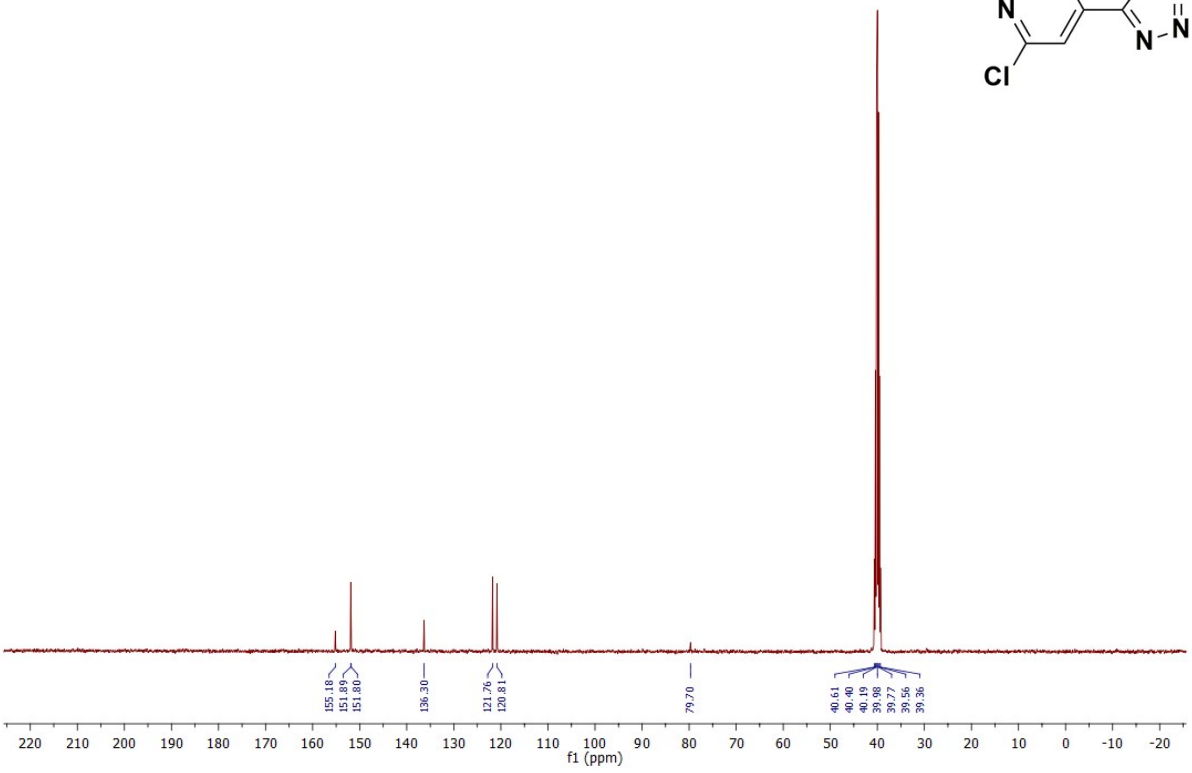
^{13}C NMR (5e)



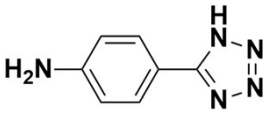
^{1}H NMR (5f)

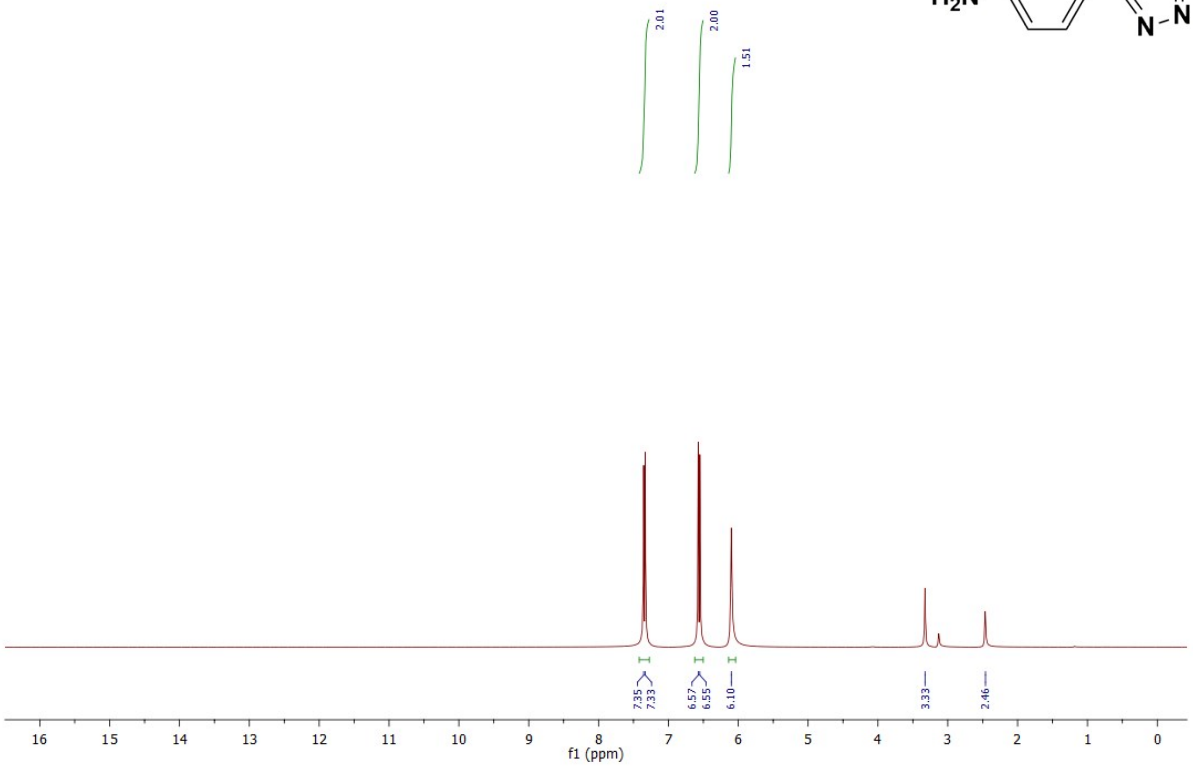


^{13}C NMR (5f)



^{1}H NMR (5g)





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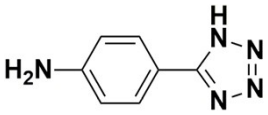
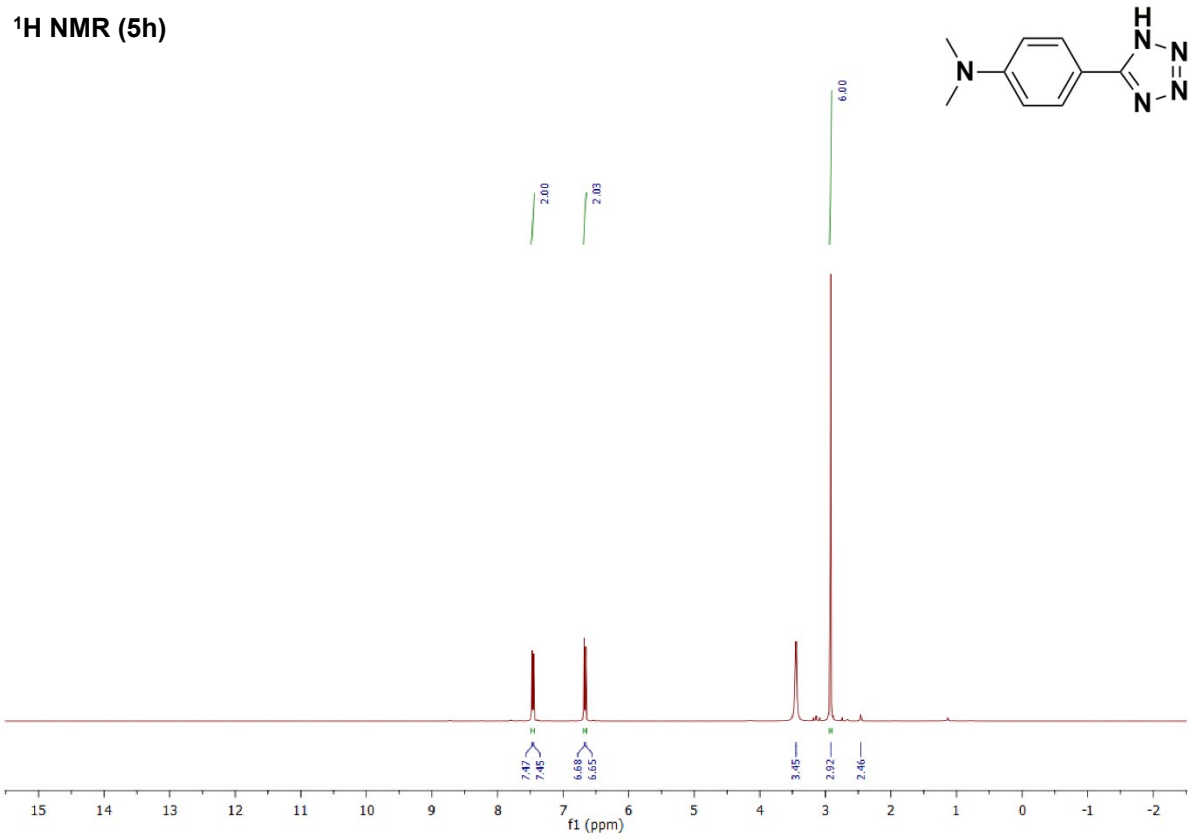
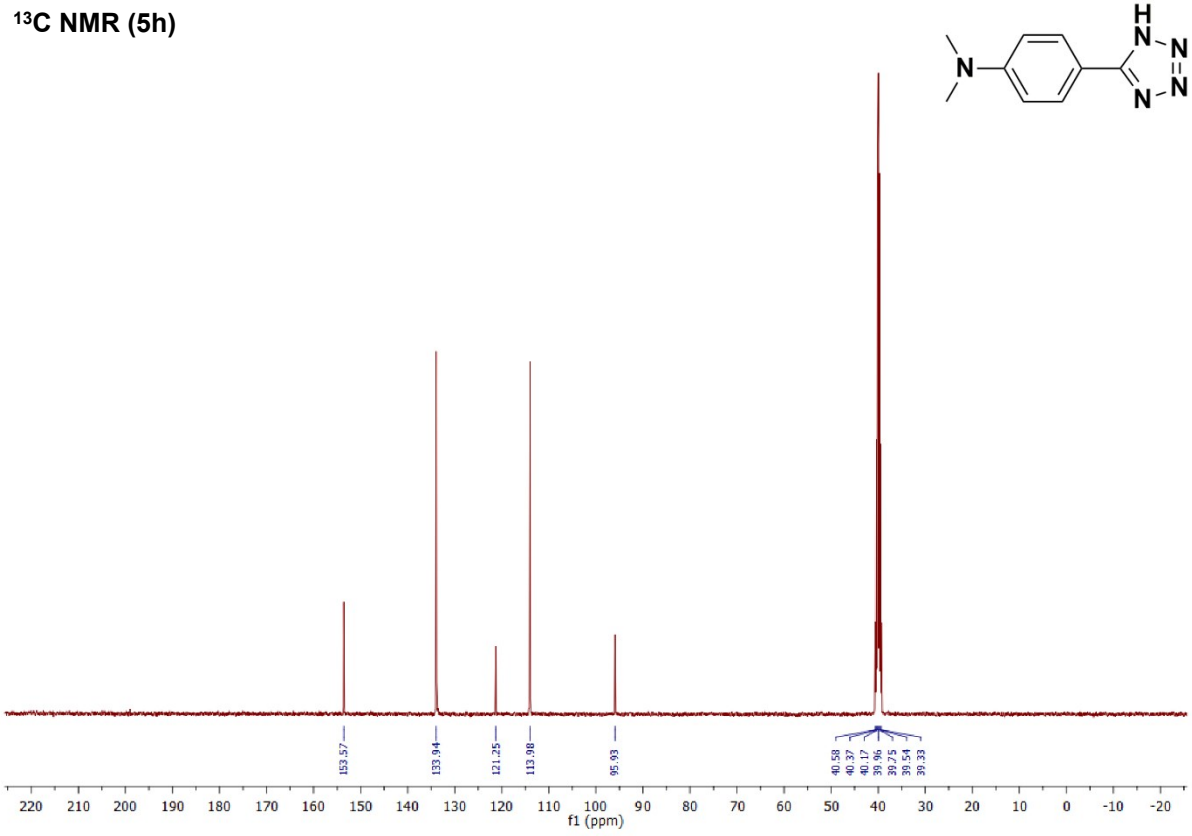


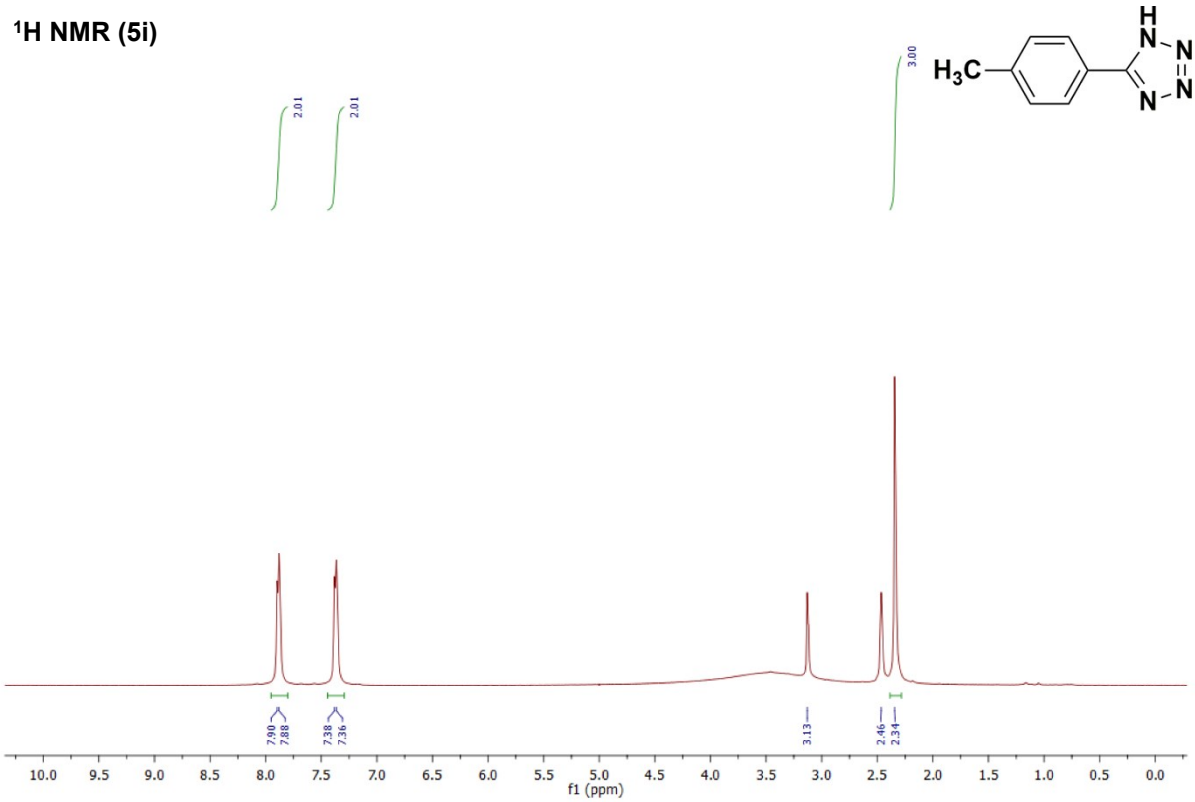
^{1}H NMR (5h)



^{13}C NMR (5h)



^{1}H NMR (5i)



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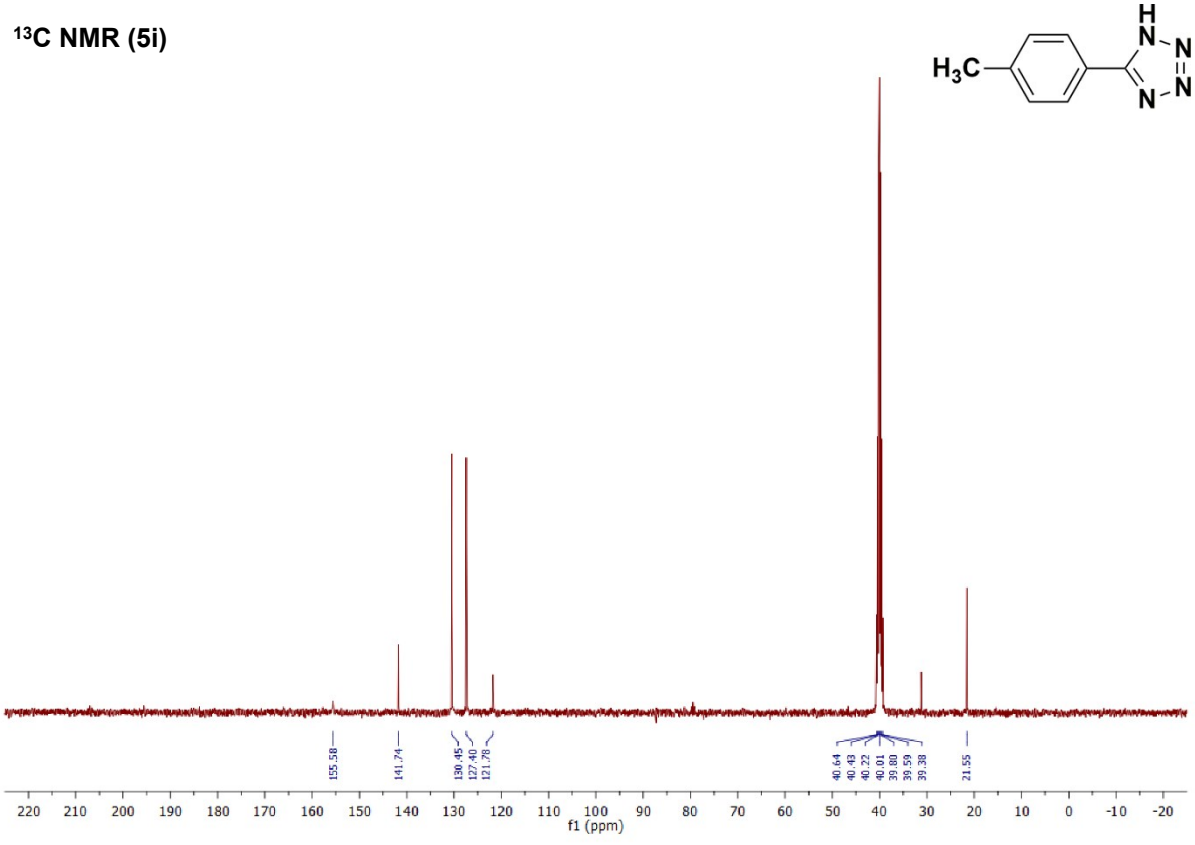

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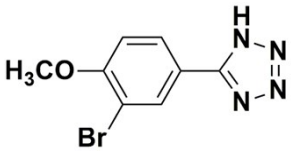

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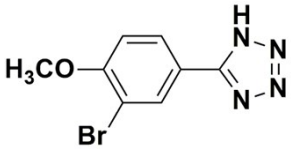

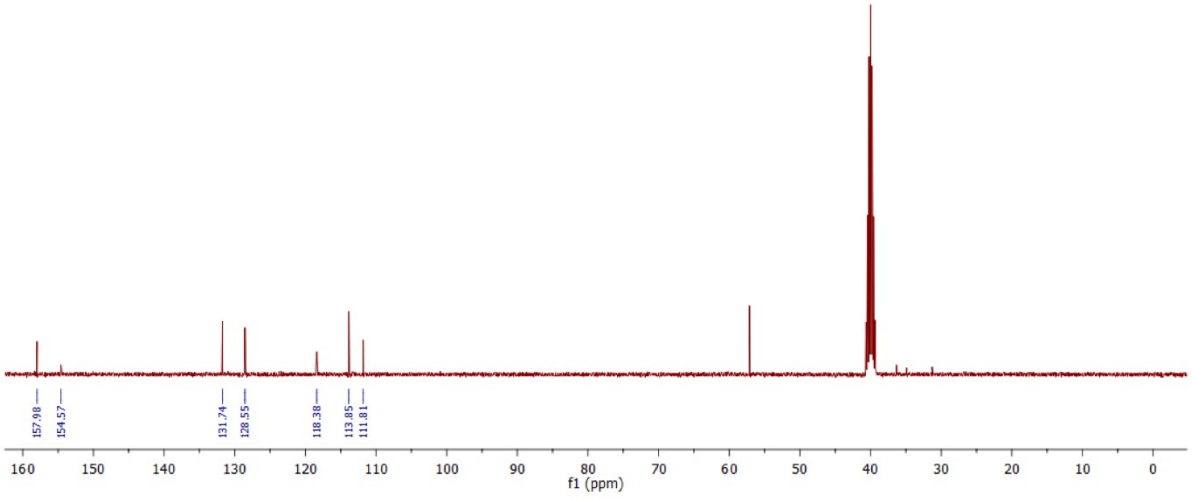

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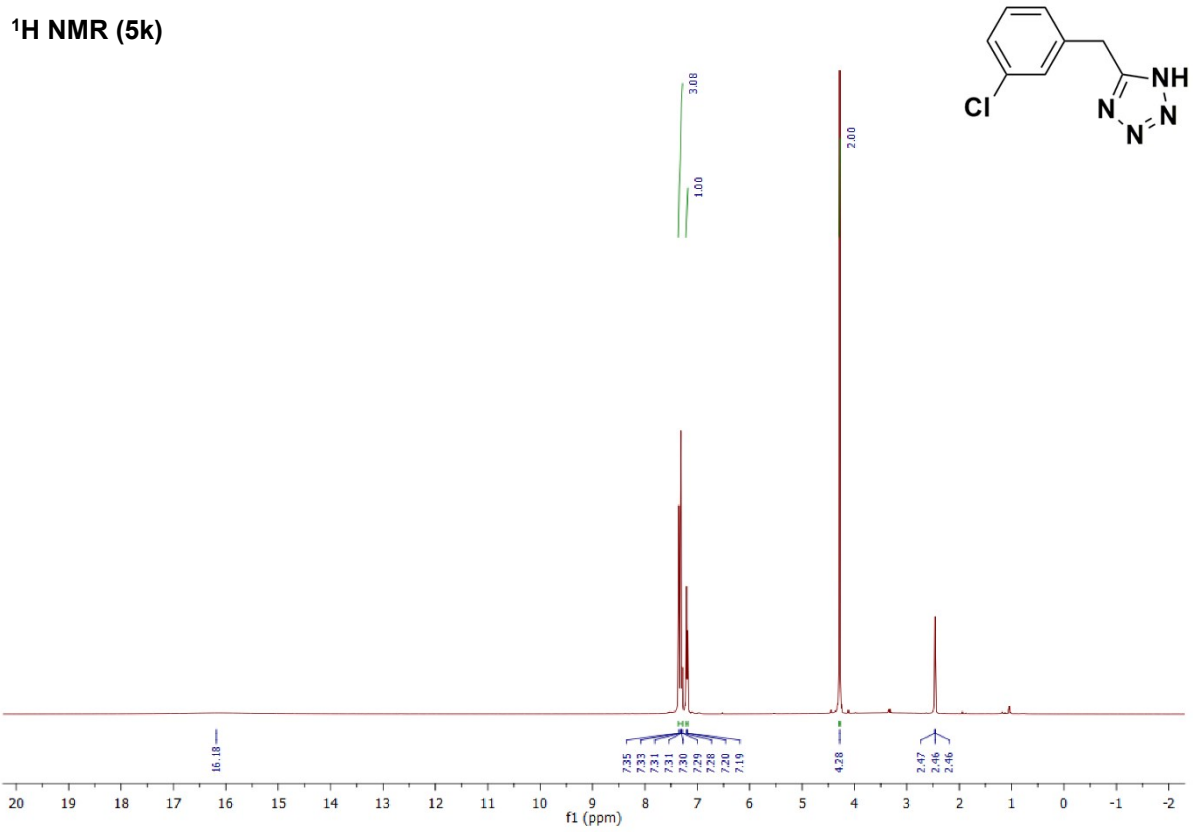

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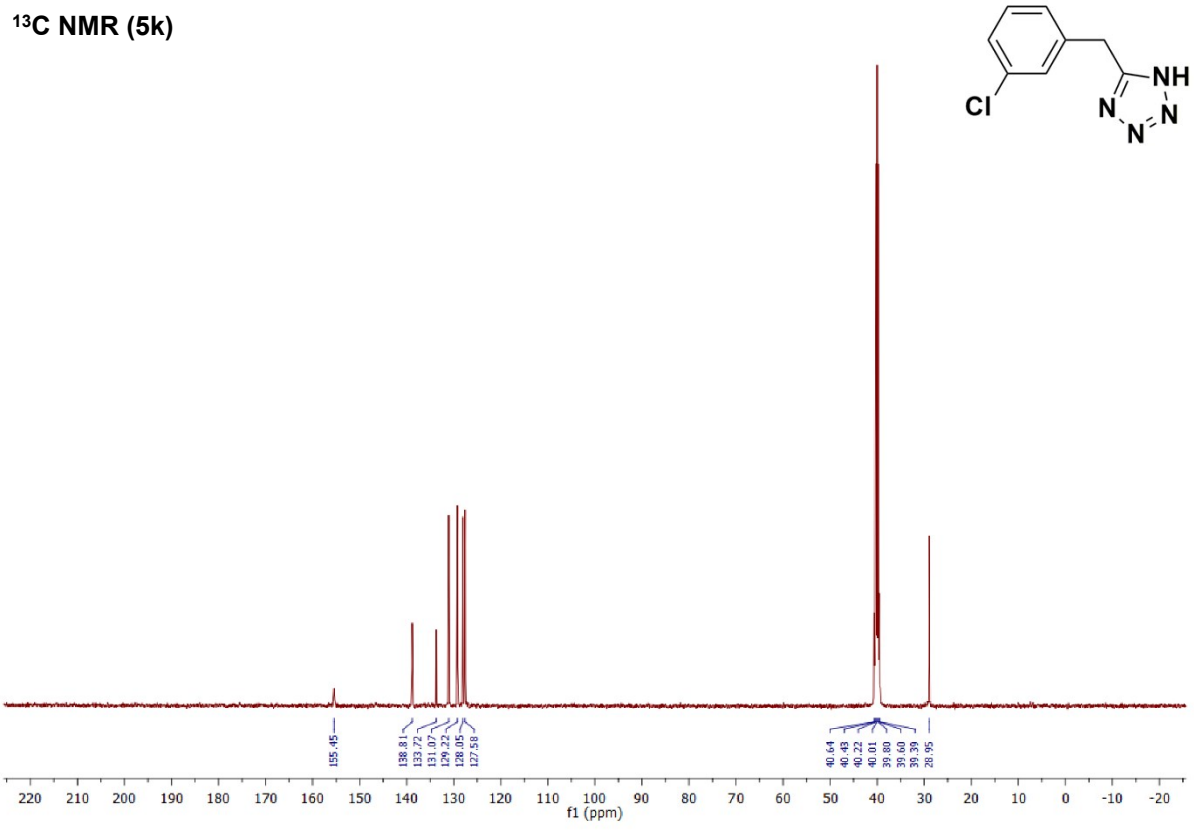

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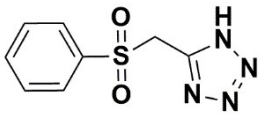

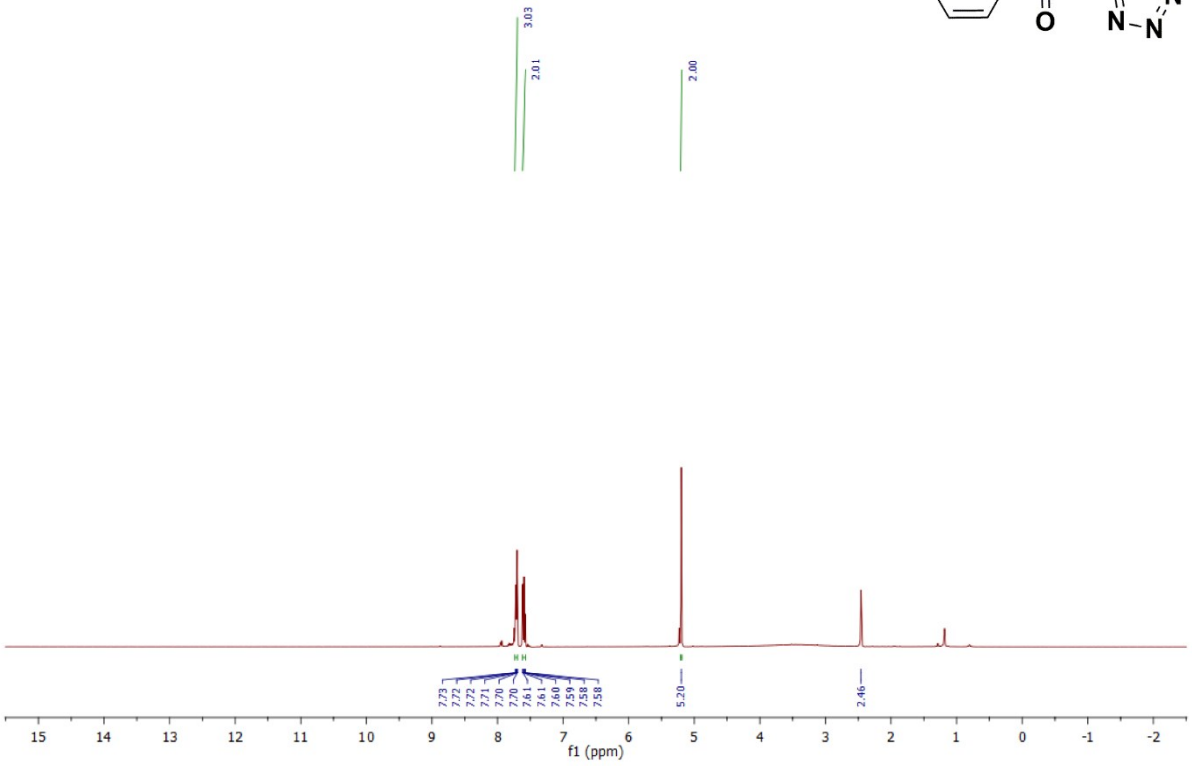

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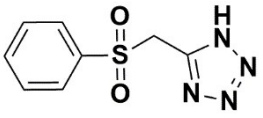

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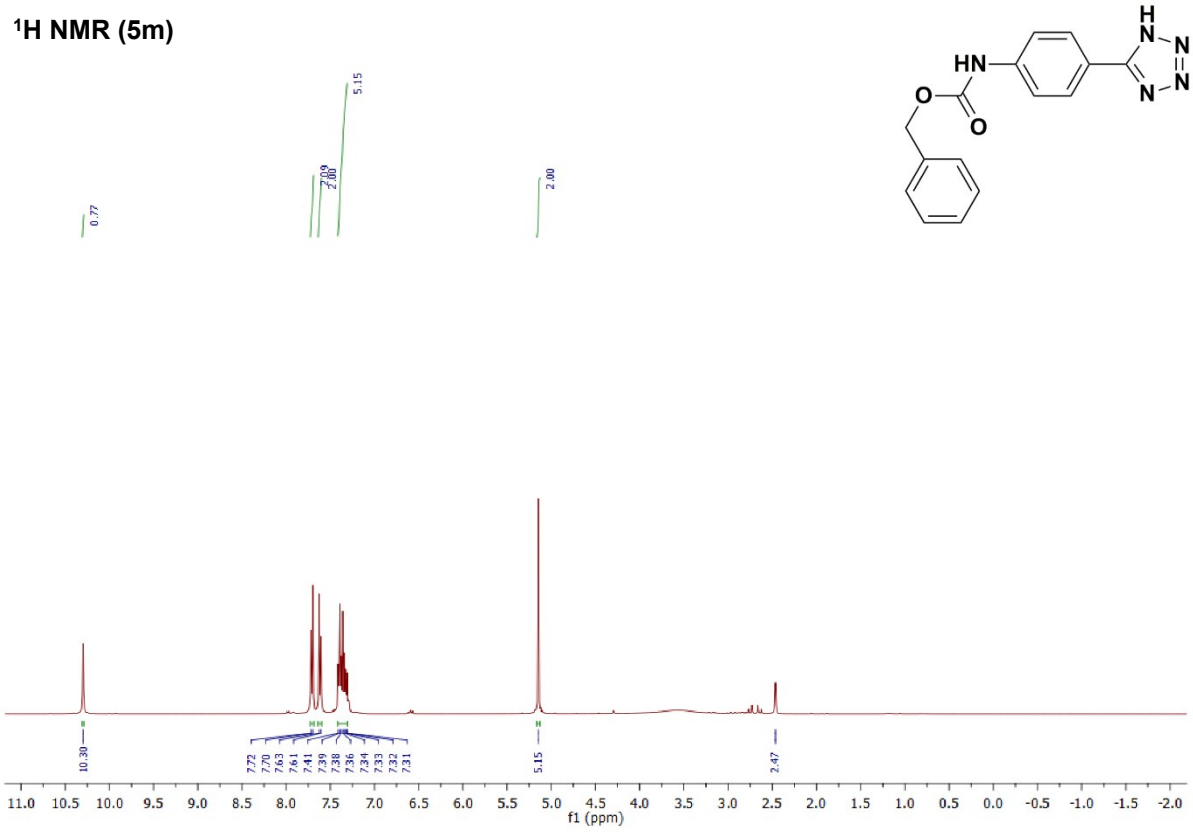

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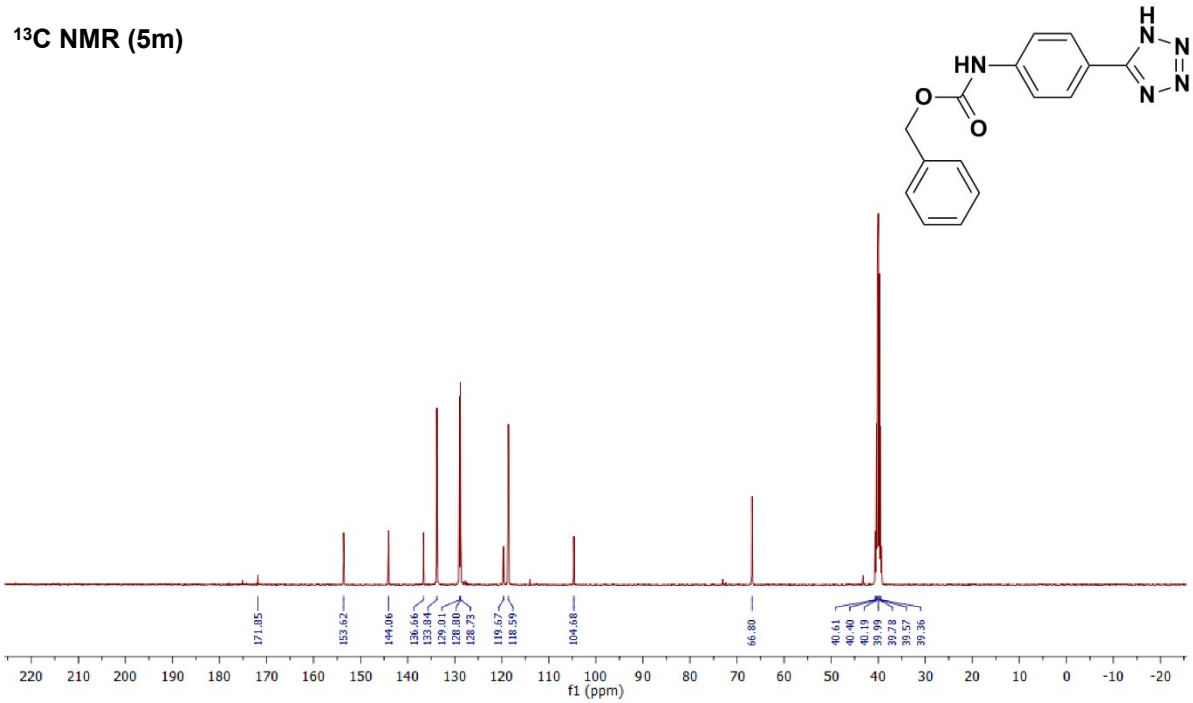

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