Supplemental Information

Highly-Stable Silverton-Type U^{IV}-Containing Polyoxomolybdates Frameworks for the Heterogeneous Catalytic Synthesis of Quinazolinones†

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1. General Information

Materials and methods

Reagents were all obtained from commercial sources and used without further purification. *CAUTION! Appropriate precautions are essential for handling all uranium compounds.*

The FT-IR spectrum was obtained by using a Fourier transform infrared (FT-IR) (4000-500 cm^{-1}) spectrometer (Thermo Nicolet iS5) at 0.5 cm^{-1} resolution and 16 scans. Raman spectra were performed on an RM5 spectrometer (Edinburgh Instrument) from 1200-100 cm^{-1}. Thermogravimetric analyses (TGA) were performed under air atmosphere on Mettler-Toledo TGA/SDTA 851^e thermalanalyzer from 25 to 1000 °C. Powder X-ray diffraction (PXRD) was performed on a Bruker D8 Advance diffractometer with Cu Kα radiation (λ = 1.5406 Å) at room temperature. Scanning electron microscope (SEM) figures and energy disperse spectroscopy (EDS) results were collected on a Zeiss Gemini Sigma 300 VP SEM with EDS. X-ray photoelectron spectra (XPS) were collected on an X-ray photoelectron spectroscopy (Shimadzu AXIS Supra+). The ^1H, and ^{13}C spectra were recorded on a Brucker ADVANCE III spectrometer at 500 MHz and 126 MHz, and chemical shifts were reported in parts per million (ppm). Flash column chromatography was performed using silica gel of 200-300 mesh. The GC analysis was performed on Agilent 7890B equipped with a capillary column (HP-5, 30 m × 0.25 μm) using a flame ionization detector.

X-ray crystallography

The single crystal X-ray diffraction data were collected on Bruker D8 Smart Apex II diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Intensities were collected by *ω*-scan and reduced on *APEX 3* and a multi-scan absorption correction was applied.[1] The structures were solved and refined on *Olex2* using the *SHELX* package.[2] Parameters of the crystal data collection and refinement are given in Table S1. The CSD numbers are 2222603, 2222722, and 2222723.

2. Experimental

Synthesis of $Na_3H_3(H_2O)_9[FeUMo_{12}O_{42}]\cdot 4.5H_2O$ (FeUMo)

$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.5 mmol, 0.1179 g), $Fe_2(SO_4)_3$ (0.25 mmol, 0.1 g) were dissolved in a 10 mL H_2O. A solution of $Na_2S_2O_4$ (0.5 mmol, 0.0871 g) in 5 mL H_2O was then dropwise added into the above solution. $UO_2(NO_3)_2\cdot 6H_2O$ (0.1 mmol, 0.0502g) was then added into the dark green solution

when the drip was done. The mixture was stirred until the solid dissolved completely and then was adjusted to pH = 4.2 using 1 M H_2SO_4. The solution was stirred for another 30 min before being sealed into a 25 mL Teflon-lined autoclave and heated at 120 °C. Black crystals of **FeUMo** were collected after five days. FT-IR (cm^{-1}): 3400 (m), 3184 (m), 1609 (m), 1409 (m), 940 (s), 905 (s), 842(vs), 601 (vs).

Synthesis of $Na_{3.6}H_{2.4}(H_2O)_9[CoUMo_{12}O_{42}]\cdot 4.5H_2O$ (CoUMo)

The synthesis of **CoUMo** was similar to that of **FeUMo** except for the usage of $CoSO_4\cdot 7H_2O$ (0.5 mmol, 0.1406 g) instead of $Fe_2(SO_4)_3$. Brown crystals of **CoUMo** were collected after five days. FT-IR (cm^{-1}): 3192 (m), 1606 (m), 1406 (m), 937 (s), 905 (s), 853(vs), 591 (vs).

Synthesis of $Na_{3.3}H_{2.7}(H_2O)_9[Ni_{0.58}UMo_{12}O_{42}]\cdot 4.5H_2O$ (NiUMo)

The synthesis of **NiUMo** was similar to that of **FeUMo** except for the usage of LiAc/HAc (10 mL, 1 M, pH = 4.8) and $NiSO_4\cdot 7H_2O$ (0.5 mmol, 0.1404 g) instead of 10 mL H_2O and $FeSO_4$. Brown crystals of **NiUMo** were collected after five days. FT-IR (cm^{-1}): 3200 (m), 1610 (m), 1409 (m), 933 (s), 904 (s), 863(vs), 589 (vs).

Synthesis of $Na_{5.8}H_{2.2}[UMo_{12}O_{42}]\cdot 13.5H_2O$ (NaUMo)

The synthesis of **NaUMo** was similar to that of **FeUMo** except for the usage of Na_2SO_4 (5 mmol, 0.7102 g) instead of $Fe_2(SO_4)_3$. Orange crystals of **NaUMo** were collected after five days. FT-IR (cm^{-1}): 3524 (m), 3201 (m), 3030 (m), 2843 (m), 1606 (m), 1422 (m), 905 (s), 903 (vs), 627 (vs), 595 (vs).

Synthesis discussion

To the best of our knowledge, there is no known U^{VI}-heteroatom in Silverton-type structure. Two reasons can explain the existence of U^{IV} instead of U^{VI} in this work. In terms of synthesis, $Na_2S_2O_4$ acts as a strong reductant, and partial Mo^{VI} and UO_2^{2+} (and Fe^{3+}) are reduced into low valence. The color changes of the solution in synthesis procedures from yellow (**FeUMo**) or pink (**CoUMo**) or green (**NiUMo**) to dark blue and then brown indicated the valence changes. The final solution is a reducing atmosphere. UO_2^{2+} with relatively strong oxidability cannot continue to exist. From the standpoint of coordination chemistry, UO_2^{2+} is the only stable existing form of U^{VI} in solution. The biggest

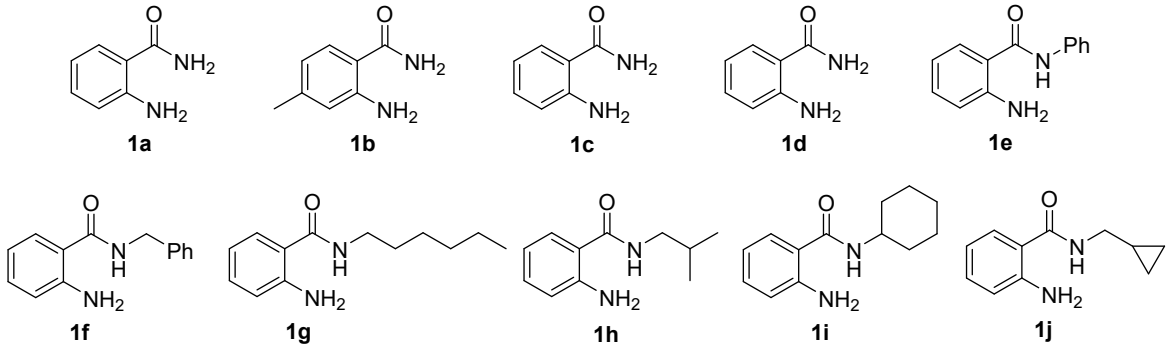
coordination number of UO_2^{2+} is only 6 at the equator position and the corresponding bonds have to be close to the equatorial plane. The two oxygen atoms of the U-O triple bond (1.8 Å) in UO_2^{2+} are always inset and could only join in very weak coordination bonds with alkali metals at most. While, Silverton-type POMs could only tolerate a few cases of lanthanides and actinides as heteroatoms including Ce^{4+}, Gd^{3+}, Th^{4+}, U^{4+}, Np^{4+}, and $Pu^{4+,}$ and so on. Those heteroatoms all show high coordination numbers up to 12. Other ions are difficult to meet this requirement including UO_2^{2+}. The weak coordination chemical basis of uranyl is insufficient to support the assembly of uranyl into Silverton-type structures. Thus, the existence of U^{VI}-heteroatom in Silverton-$\{UMo_{12}O_{42}\}$ has not been found yet.

For the synthesis of **NiUMo**, the same procedure was first used instead of LiAc/HAc buffer. But we can only obtain a kind of densely packed crystals in a big sheet shape (named **Ni-1**) that covered all the surfaces of the Teflon liner exposed to the solution. The crystals scraped from the Teflon liner all have bad quality and it is difficult to find a good single crystal. This kind of crystal in a big sheet shape may have some kind of similar Silverton-type but we could not find a suitable single crystal for X-ray diffraction after many attempts. This phenomenon may be attributed to the stronger hydrolysis effect of Ni^{2+}. Thus, we tried to use LiAc/HAc buffer to improve this problem. Fortunately, we finally obtained isostructural **NiUMo** with better crystal qualities. OAc^- may effectively relieve the hydrolysis of Ni^{2+}, while Li^+ may play a key role in the self-assembly of **NiUMo**. The unsaturated occupancy of Ni^{2+} ions in **NiUMo** may be the result of a combination of factors.

Typical procedure of the condensation reaction

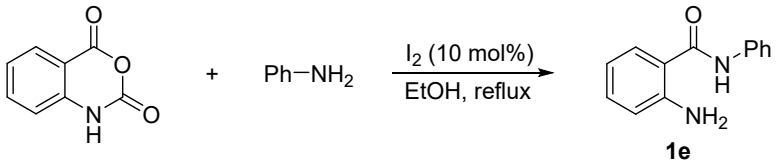
In a reaction vial of 4 mL, 2-aminobenzamide (**1**, 0.2 mmol), aldehyde (**2**, 0.2 mmol), **NiUMo** (3 mol%) and CH_3CN (1 mL) were added. Then the reactions were carried out in screw cap vials with a Teflon seal at 90 °C for 2 h. After cooling to room temperature, the mixture was further purified by column chromatography (petroleum ether/EtOAc) to afford the desired products.

General procedure for the synthesis of substrates 1



Substrates **1a**-**1d** are commercially available.

Synthesis of substrate **1e**[3]



Isatoic anhydride (5 mmol), aniline (5 mmol), and iodine (127 mg, 0.5 mmol) were added to EtOH (10 mL), and the mixture was heated at reflux in the air. The progress of the reaction was monitored by TLC. Upon completion, the solvent was distilled off and the residue was diluted with EtOAc. The mixture was quenched with saturated $Na_2S_2O_3$ solution and then washed with brine. The organic layer was dried over anhydrous Na_2SO_4, concentrated, and then purified by flash column chromatography on silica gel to afford the desired substrate **1e**.

Synthesis of substrate **1f**-**1j**[3]

Isatoic anhydride (5 mmol) and aniline (5 mmol) were added to DMF (25 mL) and the mixture was stirred at 50 °C in air for 3 h. Upon completion, the solution was diluted with EtOAc and then washed with brine. The organic layer was dried over anhydrous Na_2SO_4, concentrated, and then purified by flash column chromatography on silica gel to afford the desired substrate.

3. Characterization of crystals

Table S1. Crystallographic data and structure refinement**.**

Code	**FeUMo**	**CoUMo**	**NiUMo**	**NaUMo**
CSD No.	2222603	2222722	2222723	2292524
Empirical formula	$H_{30}FeMo_{12}Na_3O_{55.5}U$	$H_{29.4}CoMo_{12}Na_{3.6}O_{55.5}U$	$H_{29.7}Ni_{0.58}Mo_{12}Na_{3.3}O_{55.5}U$	$H_{29.2}Mo_{12}Na_{5.8}O_{55.5}U$
Fw	2432.37	2459.19	2438.43	2440.08
T (K)	150	150	100	150
Crystal system	cubic	cubic	cubic	trigonal
Space group	*Ia*-3	*Ia*-3	*Ia*-3	*R*-3
a (Å)	26.0130(2)	25.9609(3)	25.9532(8)	19.0319(3)
b (Å)	26.0130(2)	25.9609(3)	25.9532(8)	19.0319(3)
c (Å)	26.0130(2)	25.9609(3)	25.9532(8)	11.4460(5)
α (°)	90	90	90	90
β (°)	90	90	90	90
γ (°)	90	90	90	120
V (Å^3)	17602.4(4)	17496.8(6)	17481.3(16)	3590.45(19)
F (000)	18064.0	18176.0	17954.0	3399.0
Z	16	16	16	3
ρ_{calcd} (g·cm^{-3})	3.671	3.718	3.673	3.386
μ (mm^{-1})	7.450	7.549	7.426	6.584
Reflections collected	18752	25767	23550	11019
Unique reflections	2600 (R_{int} = 0.0223)	2589 (R_{int} = 0.0383)	3353 (R_{int} = 0.0447)	1985 (R_{int} = 0.0261)
Parameter	256	247	247	167
GOOF on F^2	1.128	1.131	1.126	1.093
R_1[a] [$I \geq 2\sigma(I)$]	0.0218	0.0235	0.0231	0.0201
wR_2[b] (all data)	0.0513	0.0549	0.0608	0.0494

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, [b] $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

Table S2. Selected bond lengths (Å).

FeUMo			
U1-O5	2.495(4)	U1-O8	2.493(4)
U2-O13	2.502(4)	U2-O14	2.494(4)
Mo1-O1	1.743(4)	Mo1-O3	1.703(4)
Mo1-O4	1.924(4)	Mo1-O5	2.293(4)
Mo1-O5#2	1.921(4)	Mo1-O8#5	2.246(4)
Mo2-O4	1.949(4)	Mo2-O5	2.268(4)
Mo2-O6	1.709(4)	Mo2-O7	1.711(4)
Mo2-O8#5	2.266(4)	Mo2-O8	1.947(4)
Mo3-O2	1.751(4)	Mo3-O9	1.692(4)
Mo3-O10	1.938(4)	Mo3-O13#6	2.221(4)
Mo3-O14	1.917(4)	Mo3-O14#4	2.304(4)
Mo4-O10	1.964(4)	Mo4-O11	1.702(4)
Mo4-O12	1.703(4)	Mo4-O13	1.955(4)
Mo4-O13#6	2.263(4)	Mo4-O14#4	2.284(4)
Fe1-O1	2.092(4)	Fe1-O2	2.072(4)
Symmetry transformations used to generate equivalent atoms: #1 1-X, 1-Y, -Z; #2 1-Y, 1/2+Z, 1/2-X; #3 Y, 1/2-Z, -1/2+X; #4 1/2-Z, 1-X, -1/2+Y; #5 1/2+Z, X, 1/2-Y; #6 Z, 1/2+X, 1-Y.			
CoUMo			
U1-O4	2.491(4)	U1-O5	2.490(4)
U2-O11	2.489(4)	U2-O12	2.493(4)
Mo1-O1	1.740(4)	Mo1-O2	1.705(4)
Mo1-O3	1.927(4)	Mo1-O4	2.290(4)
Mo1-O4#3	1.922(4)	Mo1-O5#2	2.249(4)
Mo2-O3	1.944(4)	Mo2-O4	2.263(4)
Mo2-O5#2	2.262(4)	Mo2-O5	1.945(4)
Mo2-O6	1.707(4)	Mo2-O7	1.708(4)
Mo3-O8	1.738(4)	Mo3-O9	1.696(4)
Mo3-O10	1.935(4)	Mo3-O11#3	1.919(4)
Mo3-O11	2.298(4)	Mo3-O12#8	2.225(4)
Mo4-O10	1.963(4)	Mo4-O11	2.279(4)
Mo4-O12	1.951(4)	Mo4-O12#8	2.263(4)
Mo4-O13	1.705(4)	Mo4-O14	1.709(4)
Co1-O1	2.090(4)	Co1-O8	2.076(4)
Symmetry transformations used to generate equivalent atoms: #1 1-Y, 1-Z, 1-X; #2 1-Z, 1-X, 1-Y; #3 Y, Z, X; #4 Z, X, Y; #5 1-X, 1-Y, 1-Z; #6 3/2-Y, 3/2-Z, 3/2-X; #7 3/2-X, 3/2-Y, 3/2-Z; #8 3/2-Z, 3/2-X, 3/2-Y.			
NiUMo			
U1-O6	2.489(4)	U1-O7	2.498(4)
U2-O9	2.490(4)	U2-O14	2.486(4)
Mo1-O1	1.740(4)	Mo1-O2	1.702(4)
Mo1-O3	1.948(4)	Mo1-O6#1	2.232(4)

Mo1-O7	1.920(3)	Mo1-O7#3	2.290(3)
Mo2-O3	1.965(4)	Mo2-O4	1.707(4)
Mo2-O5	1.706(3)	Mo2-O6#1	2.264(3)
Mo2-O6	1.949(3)	Mo2-O7#3	2.277(3)
Mo3-O8	1.733(4)	Mo3-O9#3	2.285(3)
Mo3-O9	1.925(3)	Mo3-O10	1.704(4)
Mo3-O11	1.935(3)	Mo3-O14#6	2.253(4)
Mo4-O9#3	2.266(3)	Mo4-O11	1.948(4)
Mo4-O12	1.708(4)	Mo4-O13	1.716(4)
Mo4-O14#6	2.267(3)	Mo4-O14	1.944(3)
Ni1-O1	2.075(4)	Ni1-O8	2.099(4)

Symmetry transformations used to generate equivalent atoms: #1 Y, 1/2-Z, -1/2+X; #2 1/2+Z, X, 1/2-Y; #3 1-Y, 1/2+Z, 1/2-X; #4 1-X, 1-Y, -Z; #5 1/2-Z, 1-X, -1/2+Y; #6 -1/2+Y, 1-Z, X.

Table S3. Bond valence calculations for **FeUMo, CoUMo**, and **NiUMo**.

Code	Atom	BVS	Valence
FeUMo	U1	4.27	+4
	U2	4.23	+4
	Mo1	5.96	+6
	Mo2	5.95	+6
	Mo3	5.98	+6
	Mo4	5.95	+6
	Fe1	2.34	+2
CoUMo	U1	4.31	+4
	U2	4.31	+4
	Mo1	5.96	+6
	Mo2	6.00	+6
	Mo3	6.01	+6
	Mo4	5.93	+6
	Co1	2.09	+2
NiUMo	U1	4.28	+4
	U2	4.34	+4
	Mo1	5.94	+6
	Mo2	5.94	+6
	Mo3	5.96	+6
	Mo4	5.94	+6
	Ni1	1.86	+2

Bond valence sum (BVS) analysis: The BVS values (V*i*) of metal atoms were calculated using the following equation:[4]

$$V_i = \Sigma \exp[(r_0 - r_{ij})/B] \qquad (1)$$

where r_0 is the bond valence parameter for a given atom pair, r_{ij} is the bond length between atoms *i* and *j* obtained from the crystal structure, and B is a constant with the value 0.37 Å.

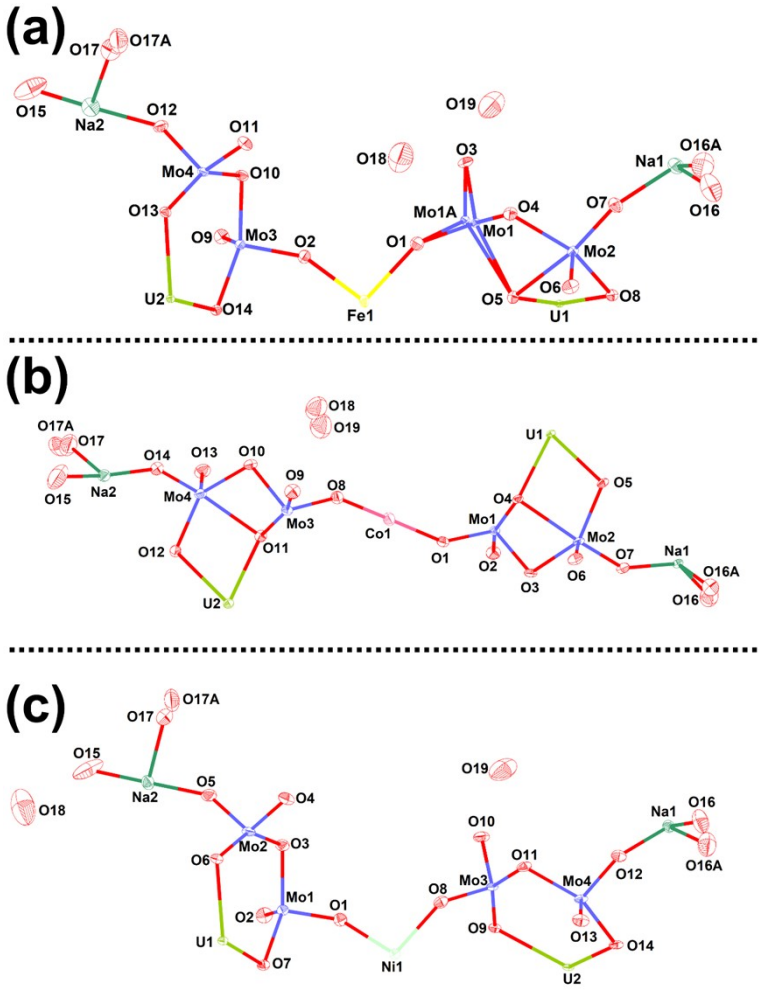


Figure S1. View of the asymmetric units of (a) **FeUMo**, (b) **CoUMo**, and (c) **NiUMo** in ellipsoid mode with 50% probability.

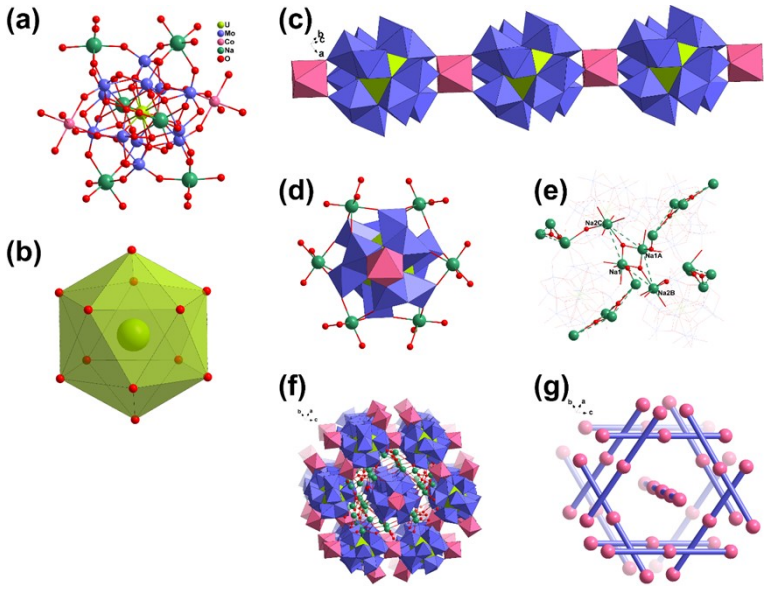


Figure S2. (a) Ball-and-stick view of the $\{CoUMo_{12}\}$ unit; (b) the 1D chain of $\{CoUMo_{12}\}_n$; (c) the coordination environment of U1; (d) the six disordered Na ions coordinated with the $\{CoUMo_{12}\}$ unit; (e) View of the tetranuclear Na-H_2O cluster; (f) the 3D packing structure of **CoUMo**; (g) the simplified diagram of the 3D packing structure, pink balls and blue sticks represent Co ions and $\{UMo_{12}\}$ units, respectively.

CoUMo is isomorphic with **FeUMo** (Figure S2a). Single crystal X-ray diffraction analysis revealed that **CoUMo** also crystallized in the *Ia*-3 space group. The asymmetric unit of **CoUMo** is also the 1/6 of the whole structure and consists of two 1/6 U^{IV} (U1 and U2), one 1/3 Co^{II} (Co1), four Mo^{VI} (Mo1-Mo4), two disordered Na ions (1.36 occupancy in total), other fourteen oxygen atoms (O1-O14) from the $\{UMo_{12}\}$ units, three coordination and one and a half lattice water molecules. The 12-coordinated U1 and U2 ions in the center of the Silverton-type $\{UMo_{12}O_{42}\}$ polyanion are also tetravalent. The bond lengths of U1-O4, U1-O5, U2-O11, and U2-O12 are 2.491(4), 2.490(4), 2.489(4), and 2.493(4) Å, respectively. The coordination environments of U1 and U2 also show a near-perfect regular icosahedron (Figure S2b). The bond lengths of Mo-O bonds are in the range of 1.705(4)-2.298(4) Å. Both Mo1 and Mo2, Mo3 and Mo4 exhibit weak interaction with the distance of 3.1199(7) and 3.1299(7) Å, respectively. Co1 is coordinated with six terminus oxygen atoms (O1/O1#3/O1#4/O8/O8#3/O8#4) from two adjacent $\{UMo_{12}O_{42}\}$ units with the bond length of 2.090(4) and 2.076(4) Å, respectively. The valences of U1, U2, Mo1-Mo4, and Co1 are also confirmed by bond valence sum (BVS) calculation (Table S3). Both Na1 and Na2 ions are also coordinated by

three terminus oxygen atoms from one $\{UMo_{12}O_{42}\}$ unit and three water molecules. Thus, one $\{UMo_{12}O_{42}\}$ unit is coordinated with two Co^{II} ions and six Na ions (Figure S2d). Adjacent $\{UMo_{12}O_{42}\}$ units are alternately connected by Co^{II} ions to form a $\{CoUMo_{12}\}_n$ 1D chain (Figure S2c). The adjacent Na ions are connected by bridging water molecules (O15/O15A) to form a rhombic tetranuclear Na-H_2O cluster (Figure S2e). One tetranuclear Na-H_2O cluster then connects with four adjacent equivalent tetranuclear Na-H_2O clusters by the connection of bridging water molecules (O17/O17A). The 1D chain of $\{CoUMo_{12}\}_n$ is then extended by the connection of Na ions and bridging water molecules to form the 3D packing structures of **CoUMo** (Figure S2f). The directions of the 1D chains in **CoUMo** also have four directions in space which could also be simplified as a ball-and-stick schematic diagram (Figure S2g). The space torsion angle of adjacent 1D chains is about 70.529°.

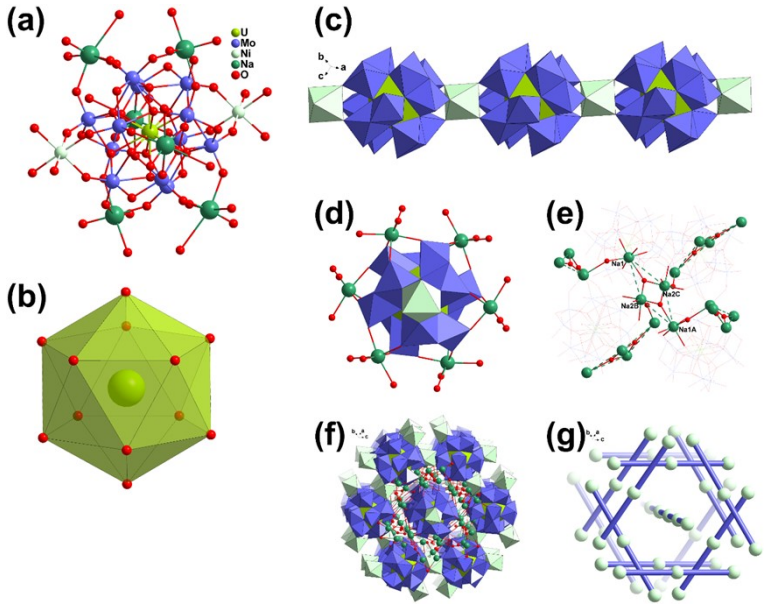


Figure S3. (a) Ball-and-stick view of the $\{NiUMo_{12}\}$ unit; (b) the 1D chain of $\{NiUMo_{12}\}_n$; (c) the coordination environment of U1; (d) the six disordered Na ions coordinated with the $\{NiUMo_{12}\}$ unit; (e) View of the tetranuclear Na-H_2O cluster; (f) the 3D packing structure of **NiUMo**; (g) the simplified diagram of the 3D packing structure, light green balls and blue sticks represent Ni ions and $\{UMo_{12}\}$ units, respectively.

NiUMo is isomorphic with **FeUMo** (Figure S3a). Single crystal X-ray diffraction analysis revealed that **NiUMo** also crystallized in the *Ia*-3 space group. The asymmetric unit of **NiUMo** is also the 1/6 of the whole structure and consists of two 1/6 U^{IV} (U1 and U2), one 0.192 Ni^{II} (Ni1), four Mo^{VI} (Mo1-Mo4), two disordered Na ions (1.1 occupancy in total), other fourteen oxygen atoms (O1-O14) from the $\{UMo_{12}\}$ units, three coordination and one and a half lattice water molecules. The 12-coordinated U1 and U2 ions in the center of the Silverton-type $\{UMo_{12}O_{42}\}$ polyanion are also tetravalent. The bond lengths of U1-O6, U1-O7, U2-O9, and U2-O14 are 2.489(4), 2.498(4), 2.490(4), and 2.486(4) Å, respectively. The coordination environments of U1 and U2 also show a near-perfect regular icosahedron (Figure S3b). The bond lengths of Mo-O bonds are in the range of 1.702(4)-2.290(3) Å. Both Mo1 and Mo2, Mo3 and Mo4 exhibit weak interaction with the distance of 3.1330(6) and 3.1268(6) Å, respectively. Ni1 is coordinated with six terminus oxygen atoms (O1/O1#3/O1#5/O8/O8#3/O8#5) from two adjacent $\{UMo_{12}O_{42}\}$ units with the bond length of 2.075(4) and 2.099(4) Å, respectively. The occupancy of Ni1 is only about 0.576 calculated by the program. For comparison, both Fe1 in **FeUMo** and Co1 in **CoUMo** have a 100% occupancy. The

valences of U1, U2, Mo1-Mo4, and Ni1 are also confirmed by bond valence sum (BVS) calculation (Table S3). Both Na1 and Na2 ions are also coordinated by three terminus oxygen atoms from one $\{UMo_{12}O_{42}\}$ unit and three water molecules. One $\{UMo_{12}O_{42}\}$ unit is coordinated with two Ni^{II} ions and six Na ions (Figure S3d). Adjacent $\{UMo_{12}O_{42}\}$ units are alternately connected by Ni^{II} ions to form a $\{NiUMo_{12}\}_n$ 1D chain (Figure S3c). The adjacent Na ions are connected by bridging water molecules (O16/O16A) to form a rhombic tetranuclear Na-H_2O cluster (Figure S3e). One tetranuclear Na-H_2O cluster then connects with four adjacent equivalent tetranuclear Na-H_2O clusters by the connection of bridging water molecules (O17/O17A). The 1D chain of $\{NiUMo_{12}\}_n$ is then extended by the connection of Na ions and bridging water molecules to form the 3D packing structures of **NiUMo** (Figure S3f). The directions of the 1D chains in **NiUMo** also have four directions in space (Figure S3g). The space torsion angle of adjacent 1D chains is also about 70.529°.

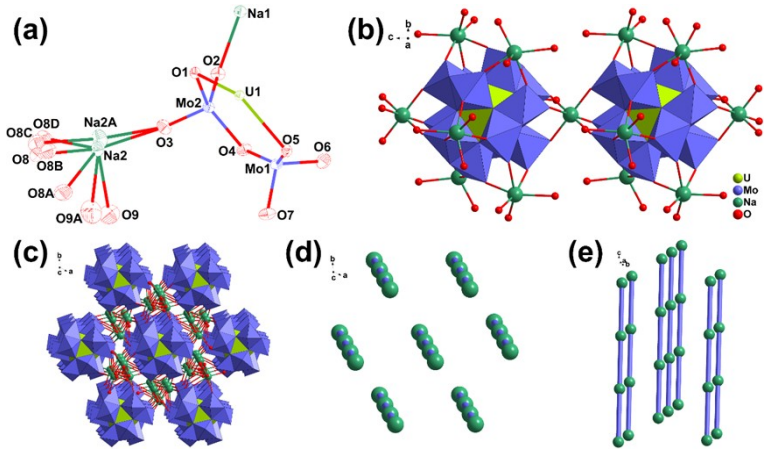


Figure S4. (a) View of the asymmetric units of **NaUMo** in ellipsoid mode with 50% probability; (b) structural representation of the constitutional unit; (c) the 3D packing structure; (d-e) the simplified diagram of the 3D packing structure from two directions. Green balls and blue sticks represent Na1 ion and $\{UMo_{12}\}$ units, respectively.

The basic constitutional unit of **NaUMo** is similar to **FeUMo**, **CoUMo**, and **NiUMo**, but **NaUMo** shows different space symmetry and crystallizes in the *R*-3 space group in the trigonal crystal system. The asymmetric unit of **NaUMo** is 1/6 of the complete structure and consists of one 1/6 U^{IV} (U1), two Mo^{VI} (Mo1, Mo2), seven bridging or terminal oxygen atoms from $\{UMo_{12}O_{42}\}$ unit (O1-O7), one ordered (Na1) and two disordered Na ions (Na2, Na2A), and seven disordered water molecules (O8, O8A-O8D, O9, O9A, 2.25 occupancy in total) (Figure S4a). Two adjacent Silverton-type $\{UMo_{12}O_{42}\}$ units are connected by a Na1 to form the 1D chain structure with a formula of $\{NaUMo_{12}O_{42}\}_n$ (Figure S4b). Adjacent $\{NaUMo_{12}O_{42}\}_n$ 1D chains are then connected by Na2, Na2A, and bridging water molecules to form the 3D packing structures of **NaUMo** with a parallel-arranged configuration (Figure S4c-e). The different 3D packing configurations are the main difference between **NaUMo** and the above three compounds.

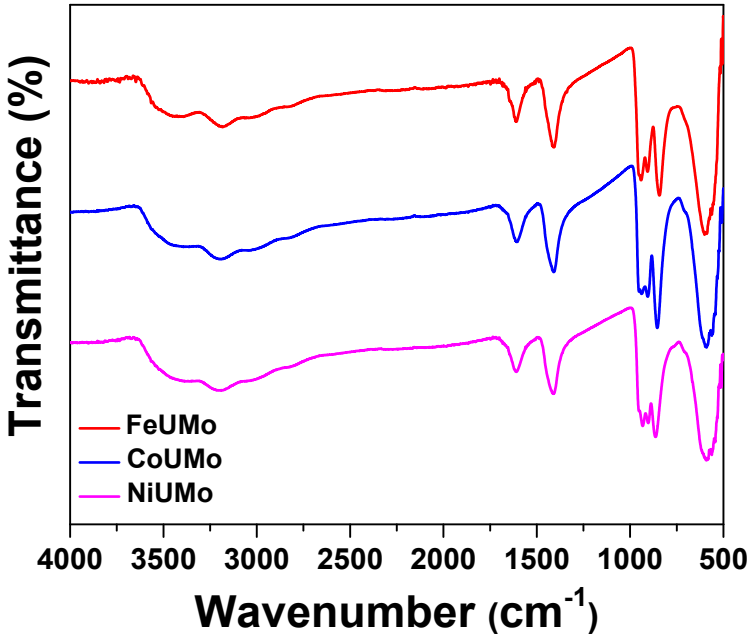


Figure S5. FT-IR spectra of **FeUMo**, **CoUMo**, **and NiUMo**.

The FT-IR spectra of **FeUMo**, **CoUMo**, **and NiUMo** showed typical bands of Silverton-type polyoxomolybdates. The bands in the range of 1000~500 cm^{-1} should be attributed to the vibrations of $\nu(Mo{=}O_t)$, $\nu(Mo\text{-}O_b\text{-}Mo)$, and $\nu(Mo\text{-}O\text{-}X)$ (X = Fe, Co, and Ni), respectively. The bands around 1400 cm^{-1} may be attributed to the vibrations of $\nu(O\text{-}X)$ or $\nu(Mo\text{-}O\text{-}Na)$ bonds. The bands around 1610 and 3200 cm^{-1} are attributed to the vibration of water molecules.

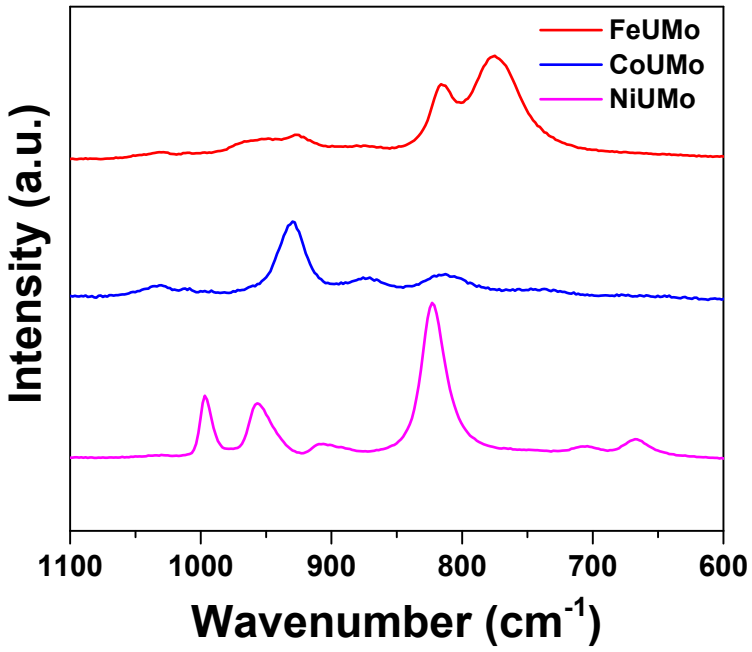


Figure S6. Raman spectra of **FeUMo**, **CoUMo**, and **NiUMo**.

According to the reference, the U-O band in $\{UMo_{12}\}$ should be around 660 cm^{-1}, which can be found in **NiUMo** as a weak peak.[5] The bands around 800 cm^{-1} and 1000~900 cm^{-1} should be the attributed to the vibration of X-O-Mo (X = Fe, Co, and Ni), Mo-O-Mo and $Mo{=}O_t$, respectively.

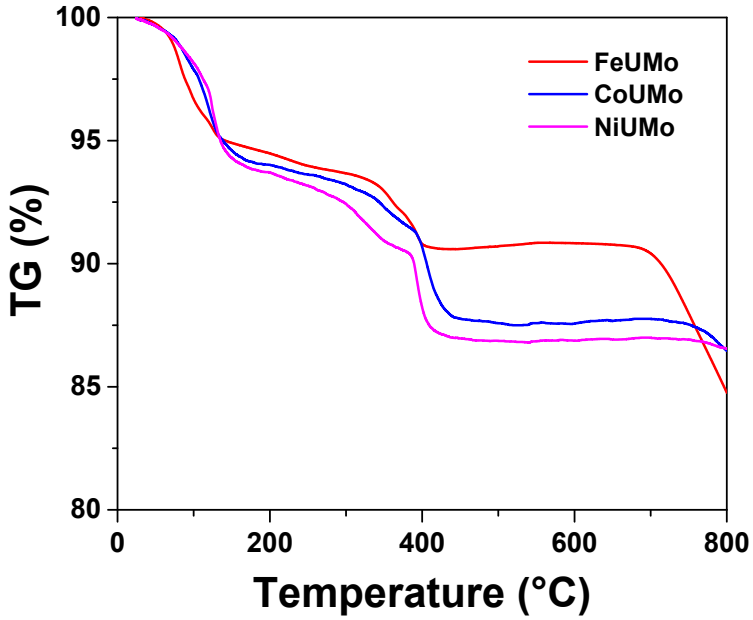


Figure S7. TGA curves of **FeUMo**, **CoUMo**, and **NiUMo**.

The thermostabilities of **FeUMo**, **CoUMo**, and **NiUMo** were evaluated by TGA, which indicates that the frameworks of these compounds could keep stable before ~400 °C. The theoretical weight losses of water molecules are about 10% at ~400 °C, but only **FeUMo** matches this result. The collapse of inorganic frameworks or the highly disordered water molecules in the structures of **CoUMo** and **NiUMo** may be responsible for this difference.

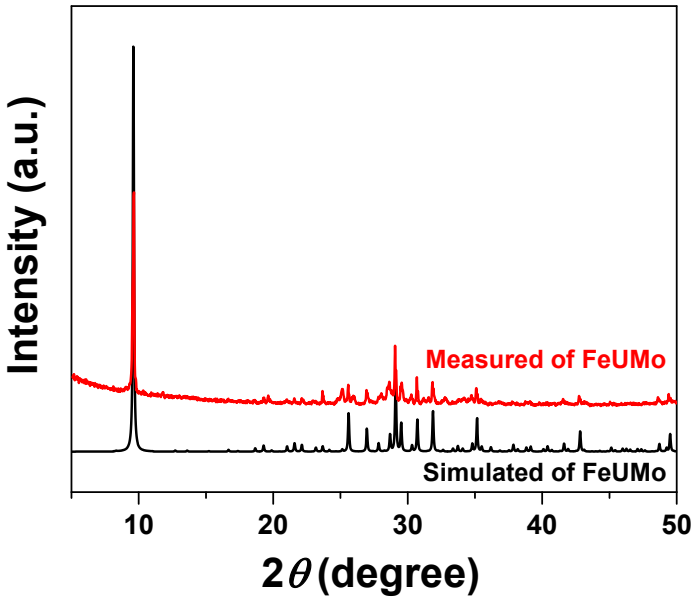


Figure S8. PXRD patterns of **FeUMo**.

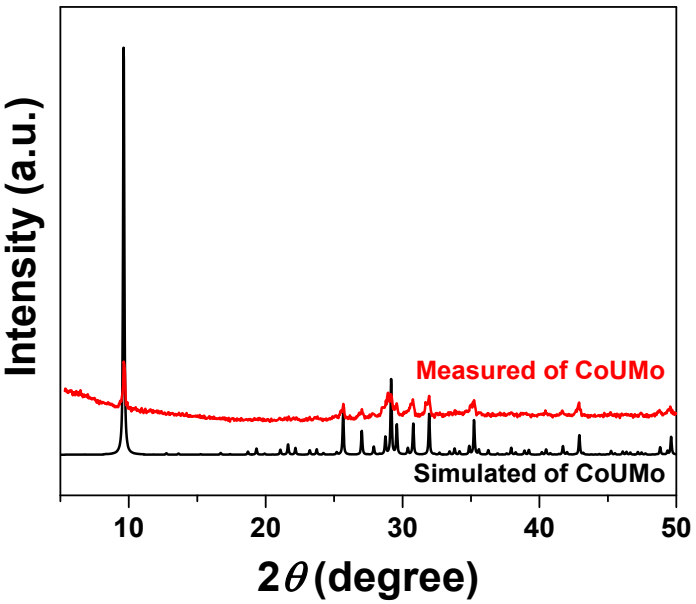


Figure S9. PXRD patterns of **CoUMo**.

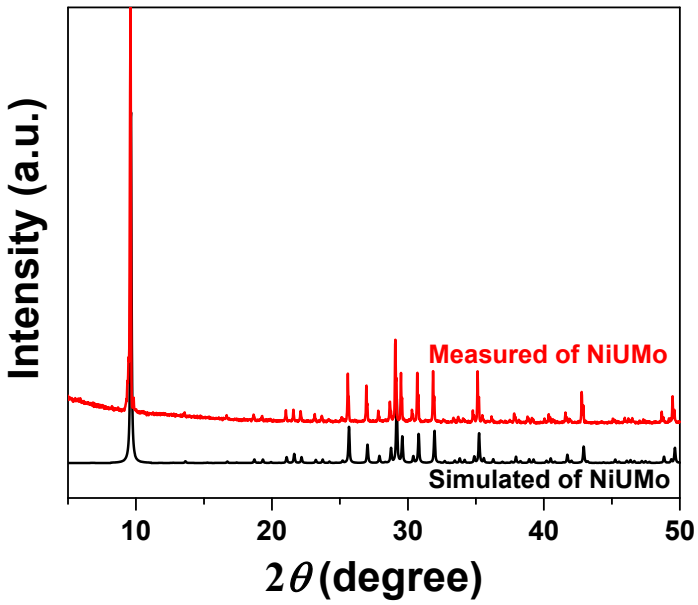


Figure S10. PXRD patterns of **NiUMo**.

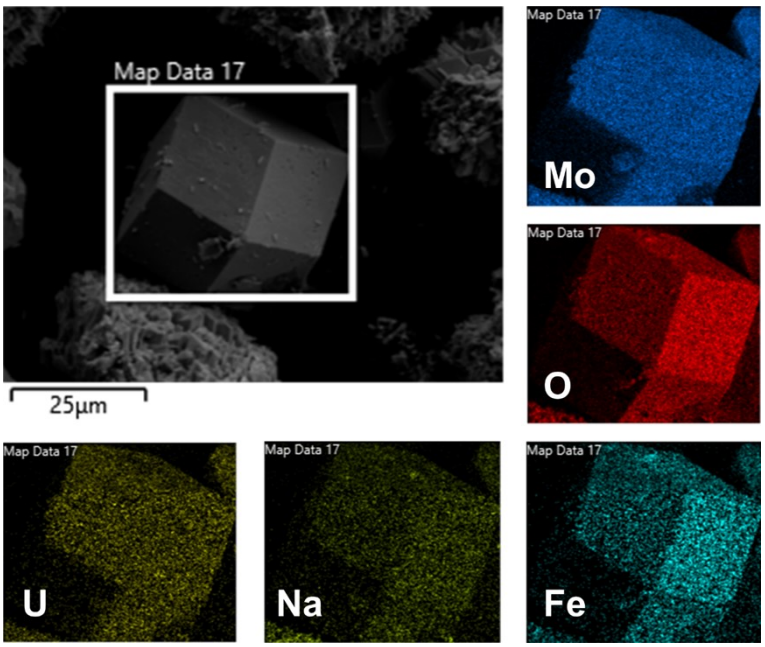


Figure S11. EDS mapping of **FeUMo**.

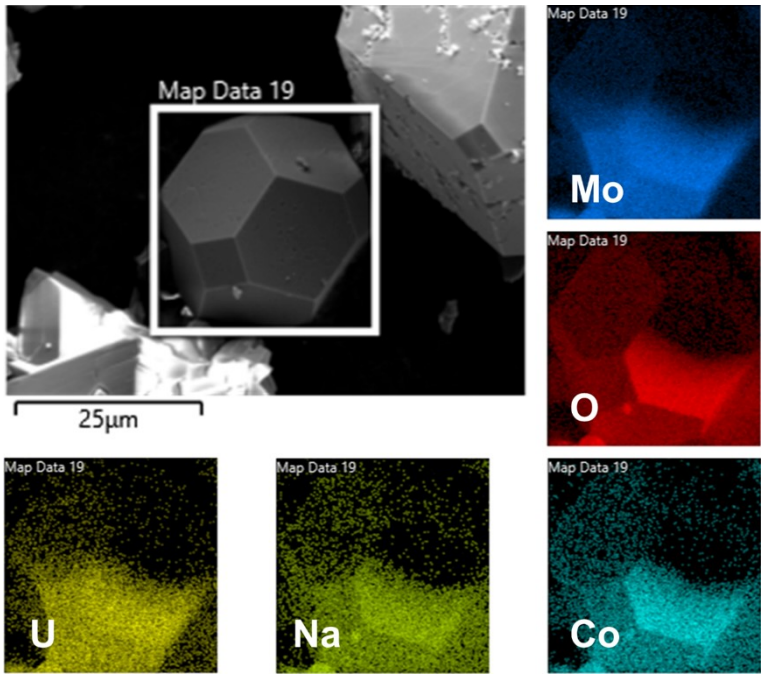


Figure S12. EDS mapping of **CoUMo**.

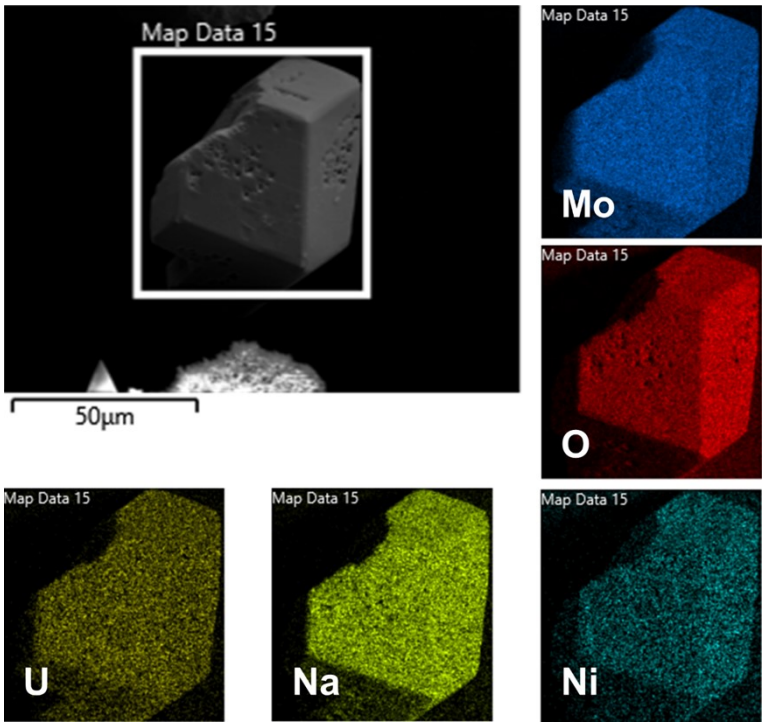


Figure S13. EDS mapping of **NiUMo**.

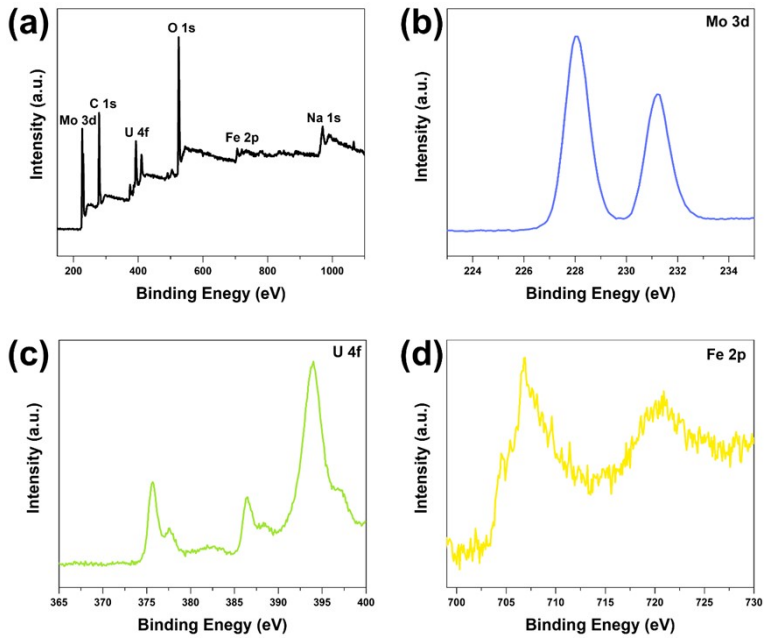


Figure S14. The XPS of **FeUMo**.

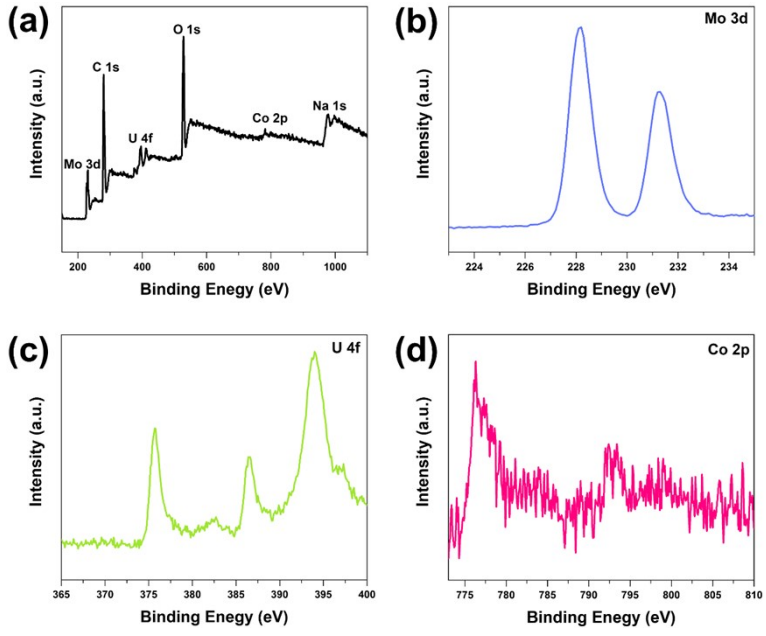


Figure S15. The XPS of **CoUMo**.

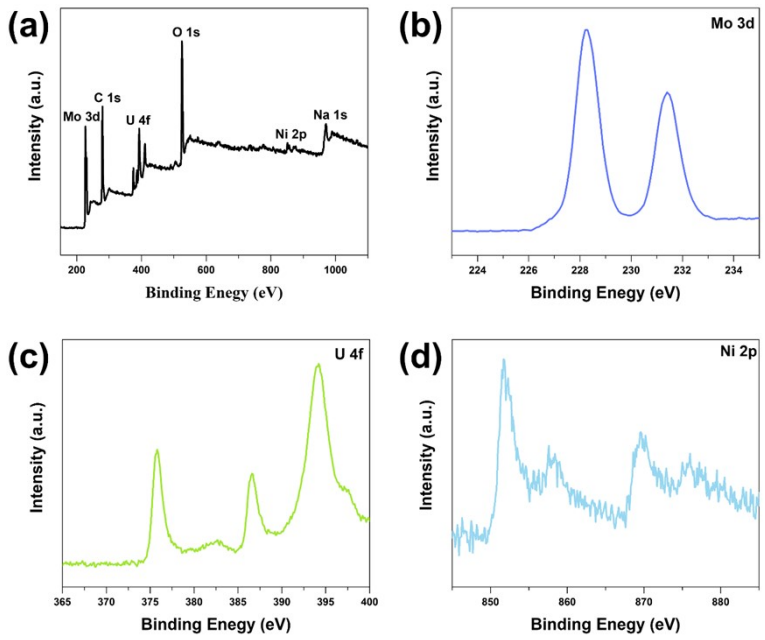


Figure S16. The XPS of **NiUMo**.

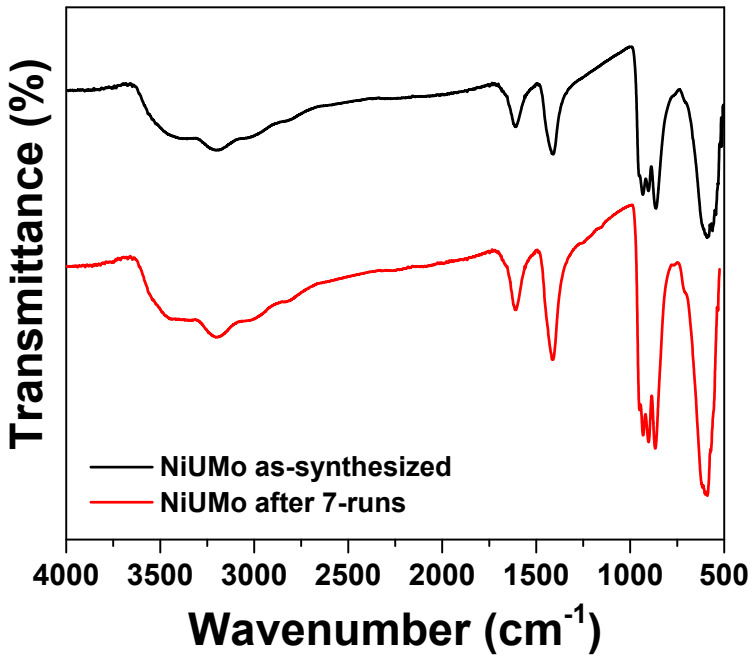


Figure S17. FT-IR spectra comparison of **NiUMo** before and after 7 runs of catalytic reactions.

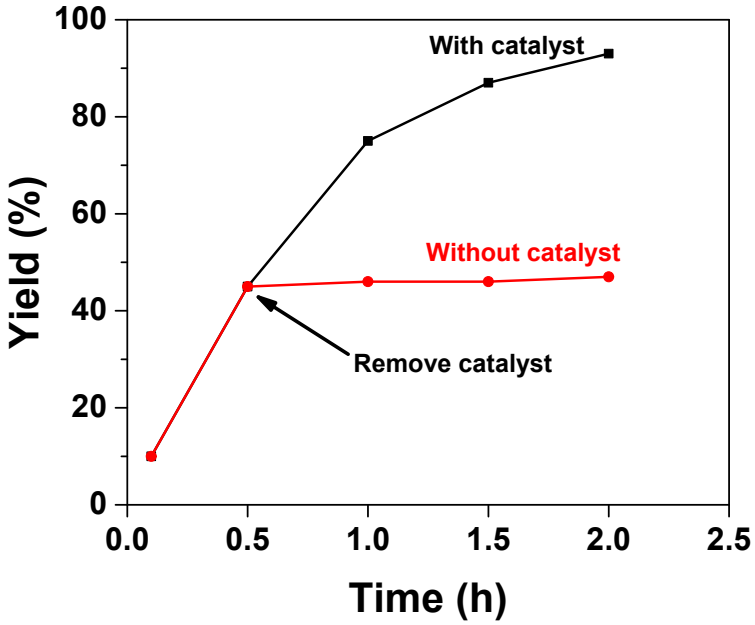
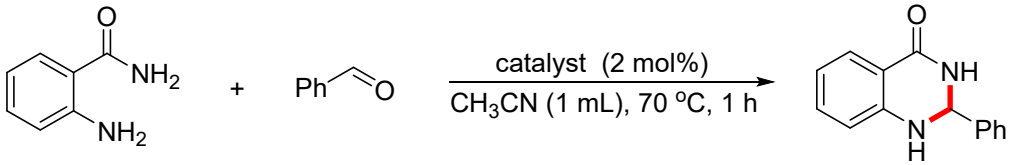


Figure S18. The thermal filtration experiments.

4. Optimization of reaction conditions

Table S4. Examination of the catalysts

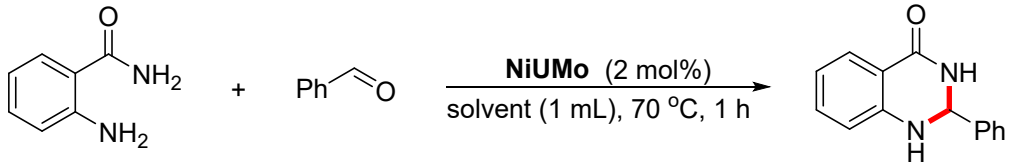


1a 0.2 mmol | **2a** 0.2 mmol | **3a**

Entry	Catalyst	Yield (%)[a]
1		24
2	**FeUMo**	45
3	**CoUMo**	43
4	**NiUMo**	**68**

[a] The conversions and yields were determined by GC with biphenyl as the internal standard.

Table S5. Examination of solvents

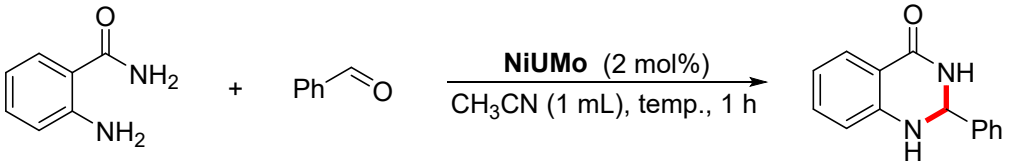


1a 0.2 mmol | **2a** 0.2 mmol | **3a**

Entry	Solvent	Yield (%)[a]
1	Ph-Cl	49
2	EtOH	58
3	*i*-PrOH	65
4	**CH_3CN**	**68**
5	DCE	60
6	DMSO	62
7	DMF	57

[a] The conversions and yields were determined by GC with biphenyl as the internal standard.

Table S6. Investigation of the reaction temperature

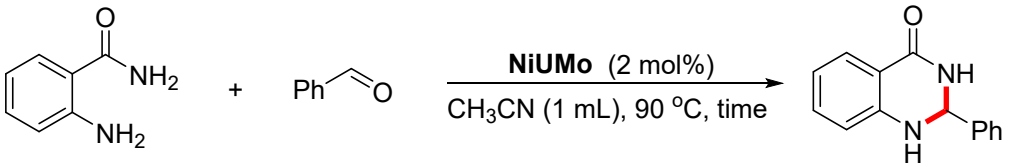


1a 0.2 mmol | **2a** 0.2 mmol | **3a**

Entry	Temperature	Yield (%)[a]
1	70	68
2	80	73
3	**90**	**82**
4	100	81

[a] The conversions and yields were determined by GC with biphenyl as the internal standard.

Table S7. Investigation of the reaction time

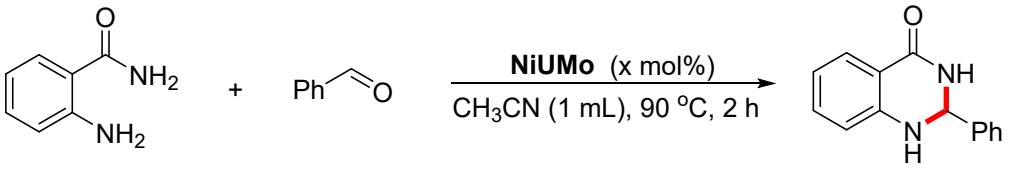


1a 0.2 mmol | **2a** 0.2 mmol | **3a**

Entry	Time (h)	Yield (%)[a]
1	1	82
2	1.5	84
3	**2**	**87**
4	2.5	87

[a] The conversions and yields were determined by GC with biphenyl as the internal standard.

Table S8. Optimization of catalyst loading

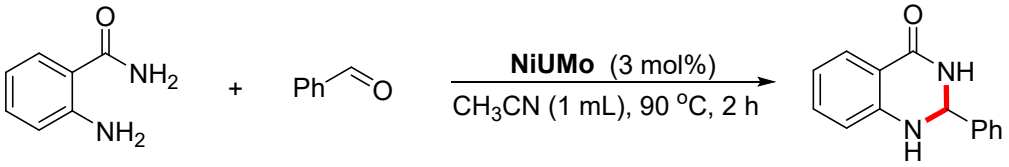


1a 0.2 mmol **2a** 0.2 mmol **3a**

Entry	Loading	Yield (%)[a]
1	2	87
2	2.5	89
3	**3**	**93**
4	3.5	92

[a] The conversions and yields were determined by GC with biphenyl as the internal standard.

Table S9. Control experiments



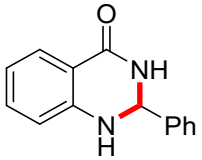
1a **2a** **3a**

Entry	Catalyst	Yield (%)[a]
1		30
2	$NiSO_4 \cdot 7H_2O$	69
3	NaUMo	46
4	Mixture of $NiSO_4 \cdot 7H_2O$ and **NaUMo**	81
5	**NiUMo**	**93**

[a] Isolated yield.

5. NMR data[6]

2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (3a)

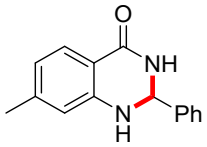


By following the typical procedure, the product was obtained as a white solid with a 91% yield.

^{1}H NMR (500 MHz, DMSO-d6) δ = 8.48 (s, 1H), 7.76 (d, *J*=7.6, 1H), 7.61 (d, *J*=7.4, 2H), 7.41 (dt, *J*=23.3, 7.0, 3H), 7.32 (t, *J*=7.5, 1H), 7.25 (s, 1H), 6.89 (d, *J*=8.1, 1H), 6.76 (t, *J*=7.4, 1H), 5.88 (s, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ = 164.38, 148.47, 142.07, 133.95, 129.05, 128.89, 127.99, 127.44, 117.77, 115.48, 115.02, 67.24.

7-methyl-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (3b)

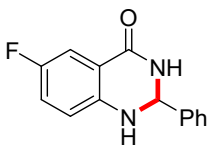


By following the typical procedure, the product was obtained as a white solid with a 90% yield.

^{1}H NMR (500 MHz, DMSO-d6) δ = 8.29 (s, 1H), 7.54 (dd, *J*=14.3, 7.6, 3H), 7.42 – 7.34 (m, 3H), 7.10 (s, 1H), 6.60 (s, 1H), 6.53 (d, *J*=7.9, 1H), 5.77 (s, 1H), 2.22 (s, 3H).

^{13}C NMR (126 MHz, DMSO-d6) δ = 164.22, 148.33, 143.90, 142.30, 128.88, 128.81, 127.93, 127.30, 118.96, 114.91, 113.16, 67.04, 21.88.

6-fluoro-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (3c)



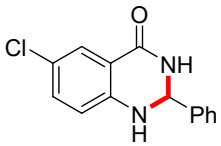
By following the typical procedure, the product was obtained as a yellow solid with an 87% yield.

^{1}H NMR (500 MHz, DMSO-d6) δ = 8.53 (s, 1H), 7.53 (d, *J*=7.3, 2H), 7.38 (dt, *J*=18.0, 5.0, 4H), 7.21

– 7.11 (m, 2H), 6.82 (dd, *J*=8.8, 4.4, 1H), 5.79 (s, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ = 163.36 (d, *J* = 2.2 Hz), 155.23 (d, *J* = 233.5 Hz), 145.13, 141.59, 129.07, 128.84, 127.47, 121.28 (d, *J* = 23.4 Hz), 116.66 (d, *J* = 7.0 Hz), 116.18 (d, *J* = 6.7 Hz), 113.01 (d, *J* = 23.0 Hz), 67.24.

6-chloro-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (3d)

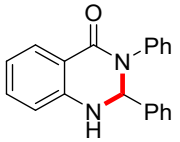


By following the typical procedure, the product was obtained as a yellow solid with an 85% yield.

^{1}H NMR (500 MHz, DMSO-d6) δ = 8.53 (s, 1H), 7.55 (d, *J*=2.5, 1H), 7.49 (d, *J*=7.1, 2H), 7.42 – 7.36 (m, 4H), 7.29 (dd, *J*=8.7, 2.6, 1H), 6.79 (d, *J*=8.7, 1H), 5.80 (s, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ = 162.92, 147.08, 141.69, 133.58, 129.09, 128.89, 127.32, 126.89, 121.22, 116.89, 116.49, 66.90.

2,3-diphenyl-2,3-dihydroquinazolin-4(1*H*)-one (3e)

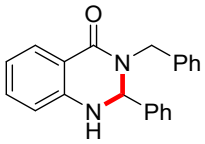


By following the typical procedure, the product was obtained as a white solid with a 74% yield.

^{1}H NMR (500 MHz, DMSO-d6) δ = 7.80 (d, *J*=7.7, 1H), 7.72 (s, 1H), 7.43 (d, *J*=7.5, 2H), 7.35 – 7.23 (m, 8H), 7.19 (t, *J*=6.8, 1H), 6.81 (d, *J*=8.1, 1H), 6.74 (t, *J*=7.5, 1H), 6.33 (s, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ = 162.83, 147.09, 141.32, 141.21, 134.29, 129.12, 128.89, 128.80, 128.52, 127.09, 126.72, 126.50, 118.05, 115.86, 115.32, 73.14.

3-benzyl-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (3f)

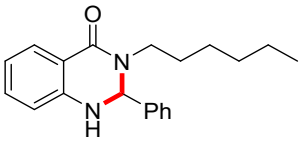


By following the typical procedure, the product was obtained as a white solid with 82% yield.

^{1}H NMR (500 MHz, DMSO-d6) δ = 7.75 (d, *J*=6.8, 1H), 7.43 (d, *J*=2.3, 1H), 7.36 – 7.21 (m, 11H), 6.69 (dd, *J*=15.6, 7.8, 2H), 5.77 (d, *J*=2.5, 1H), 5.36 (d, *J*=15.4, 1H), 3.83 (d, *J*=15.4, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ = 162.93, 146.83, 141.09, 137.97, 133.95, 129.07, 128.96, 128.94, 128.16, 127.93, 127.64, 126.64, 117.75, 115.10, 114.87, 70.31, 47.61.

3-hexyl-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (3g)

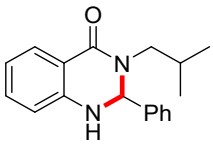


By following the typical procedure, the product was obtained as a white solid with a 93% yield.

^{1}H NMR (500 MHz, DMSO-d6) δ = 7.71 (d, *J*=6.8, 1H), 7.33 (ddd, *J*=22.7, 18.1, 7.2, 6H), 7.21 – 7.16 (m, 1H), 6.71 – 6.63 (m, 2H), 5.87 (d, *J*=2.2, 1H), 3.97 – 3.83 (m, 1H), 2.82 – 2.69 (m, 1H), 1.62 – 1.41 (m, 2H), 1.21 (s, 6H), 0.82 (t, *J*=6.7, 3H).

^{13}C NMR (126 MHz, DMSO-d6) δ = 162.73, 146.77, 141.69, 133.52, 128.93, 128.79, 127.92, 126.66, 117.52, 115.52, 114.70, 70.71, 44.88, 31.48, 27.86, 26.51, 22.53, 14.35.

3-isobutyl-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (3h)

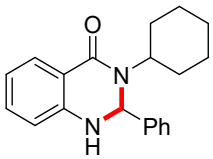


By following the typical procedure, the product was obtained as a white solid with a 90% yield.

^{1}H NMR (500 MHz, DMSO-d6) δ = 7.64 (d, *J*=7.4, 1H), 7.44 (d, *J*=2.3, 1H), 7.35 – 7.25 (m, 5H), 7.18 (t, *J*=7.1, 1H), 6.64 (dd, *J*=7.6, 5.2, 2H), 5.79 (d, *J*=2.5, 1H), 3.89 (dd, *J*=13.3, 7.7, 1H), 2.45 (dd, *J*=13.3, 7.1, 1H), 1.99 (dp, *J*=13.6, 6.8, 1H), 0.88 (dd, *J*=33.2, 6.6, 6H).

^{13}C NMR (126 MHz, DMSO-d6) δ = 163.06, 146.66, 141.60, 133.58, 128.94, 128.65, 127.94, 126.48, 117.57, 115.67, 114.83, 70.65, 52.22, 27.25, 20.40, 20.35.

3-cyclohexyl-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (3i)

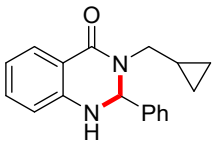


By following the typical procedure, the product was obtained as a white solid with an 80% yield.

^{1}H NMR (500 MHz, DMSO-d6) δ = 7.70 (d, *J*=7.1, 1H), 7.37 – 7.11 (m, 7H), 6.64 (t, *J*=7.5, 1H), 6.59 (d, *J*=8.1, 1H), 5.92 (d, *J*=2.7, 1H), 4.45 – 4.34 (m, 1H), 1.75 – 0.97 (m, 10H).

^{13}C NMR (126 MHz, DMSO-d6) δ = 162.32, 146.02, 143.46, 133.37, 128.62, 128.26, 128.03, 126.30, 117.69, 116.84, 114.95, 66.33, 53.34, 30.88, 30.77, 26.02, 25.99, 25.34.

3-(cyclopropylmethyl)-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (3j)

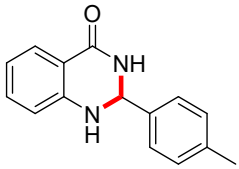


By following the typical procedure, the product was obtained as a white solid with a 92% yield.

^{1}H NMR (500 MHz, DMSO-d6) δ = 7.69 (d, *J*=7.7, 1H), 7.40 – 7.26 (m, 6H), 7.21 – 7.17 (m, 1H), 6.65 (dd, *J*=11.7, 5.4, 2H), 5.97 (d, *J*=2.4, 1H), 3.79 (dd, *J*=14.0, 6.6, 1H), 2.74 (dd, *J*=14.0, 7.1, 1H), 1.05 – 0.96 (m, 1H), 0.46 – 0.40 (m, 1H), 0.35 – 0.23 (m, 2H), 0.14 (td, *J*=9.2, 5.0, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ = 162.82, 146.62, 141.70, 133.65, 128.93, 128.75, 127.96, 126.60, 117.55, 115.45, 114.73, 70.65, 48.85, 10.24, 4.34, 3.47.

2-(p-tolyl)-2,3-dihydroquinazolin-4(1*H*)-one (3k)

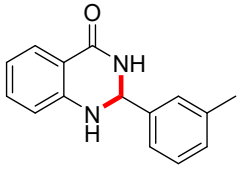


By following the typical procedure, the product was obtained as a white solid with an 87% yield.

^{1}H NMR (500 MHz, DMSO-d6) δ = 8.31 (s, 1H), 7.65 (d, *J*=7.6, 1H), 7.41 (d, *J*=8.0, 2H), 7.25 (t, *J*=7.7, 1H), 7.20 (d, *J*=7.9, 2H), 7.10 (s, 1H), 6.78 (d, *J*=8.1, 1H), 6.69 (t, *J*=7.4, 1H), 5.74 (s, 1H), 2.30 (s, 3H).

^{13}C NMR (126 MHz, DMSO-d6) δ = 164.22, 148.44, 139.10, 138.24, 133.78, 129.32, 127.86, 127.31, 117.59, 115.47, 114.92, 66.91, 21.22.

2-(m-tolyl)-2,3-dihydroquinazolin-4(1*H*)-one (3l)

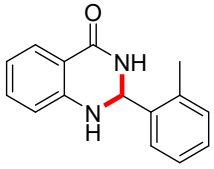


By following the typical procedure, the product was obtained as a white solid with an 85% yield.

^{1}H NMR (500 MHz, DMSO-d6) δ = 8.31 (s, 1H), 7.65 (d, *J*=7.6, 1H), 7.37 – 7.23 (m, 4H), 7.18 (d, *J*=7.2, 1H), 7.12 (s, 1H), 6.78 (d, *J*=8.1, 1H), 6.69 (t, *J*=7.4, 1H), 5.75 (s, 1H), 2.32 (s, 3H).

^{13}C NMR (126 MHz, DMSO-d6) δ = 164.19, 148.42, 141.96, 137.94, 133.82, 129.60, 128.74, 128.01, 127.87, 124.52, 117.60, 115.39, 114.89, 67.15, 21.56.

2-(o-tolyl)-2,3-dihydroquinazolin-4(1*H*)-one (3m)



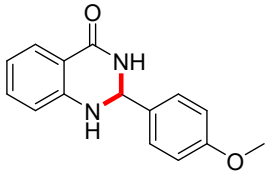
By following the typical procedure, the product was obtained as a white solid with 81% yield.

^{1}H NMR (500 MHz, DMSO-d6) δ = 8.19 (s, 1H), 7.73 (d, *J*=7.7, 1H), 7.64 (d, *J*=7.0, 1H), 7.32 –

7.23 (m, 4H), 6.97 (s, 1H), 6.84 (d, *J*=8.1, 1H), 6.76 (t, *J*=7.4, 1H), 6.07 (s, 1H), 2.48 (s, 3H).

^{13}C NMR (126 MHz, DMSO-d6) δ = 164.67, 149.10, 138.52, 136.65, 133.76, 131.19, 129.02, 127.97, 126.46, 117.76, 115.40, 115.01, 65.20, 19.32.

2-(4-methoxyphenyl)-2,3-dihydroquinazolin-4(1*H*)-one (3n)

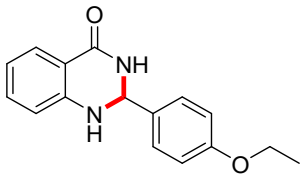


By following the typical procedure, the product was obtained as a white solid with 82% yield.

^{1}H NMR (500 MHz, DMSO-d6) δ = 8.25 (s, 1H), 7.62 (d, *J*=7.7, 1H), 7.43 (d, *J*=8.4, 2H), 7.25 (t, *J*=7.6, 1H), 7.05 (s, 1H), 6.95 (d, *J*=8.4, 2H), 6.75 (d, *J*=8.1, 1H), 6.68 (t, *J*=7.4, 1H), 5.72 (s, 1H), 3.74 (s, 3H).

^{13}C NMR (126 MHz, DMSO-d6) δ = 164.24, 159.89, 148.53, 133.86, 133.75, 128.73, 127.84, 117.59, 115.46, 114.89, 114.09, 66.79, 55.62.

2-(4-ethoxyphenyl)-2,3-dihydroquinazolin-4(1*H*)-one (3o)

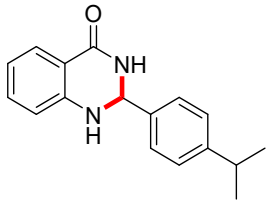


By following the typical procedure, the product was obtained as a white solid with an 80% yield.

^{1}H NMR (500 MHz, DMSO-d6) δ = 8.27 (s, 1H), 7.66 (d, *J*=7.7, 1H), 7.44 (d, *J*=8.6, 2H), 7.26 (t, *J*=7.6, 1H), 7.07 (s, 1H), 6.94 (d, *J*=8.7, 2H), 6.79 (d, *J*=8.1, 1H), 6.70 (t, *J*=7.4, 1H), 5.74 (s, 1H), 4.00 (q, *J*=6.9, 2H), 1.31 (t, *J*=7.0, 3H).

^{13}C NMR (126 MHz, DMSO-d6) δ = 164.29, 159.19, 148.57, 133.76, 133.72, 128.75, 127.87, 117.60, 115.47, 114.92, 114.54, 66.89, 63.53, 15.10.

2-(4-isopropylphenyl)-2,3-dihydroquinazolin-4(1*H*)-one (3p)

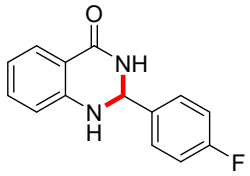


By following the typical procedure, the product was obtained as a white solid with 84% yield.

^{1}H NMR (500 MHz, DMSO-d6) δ = 8.29 (s, 1H), 7.65 (d, *J*=7.7, 1H), 7.45 (d, *J*=8.1, 2H), 7.26 (dd, *J*=14.5, 7.6, 3H), 7.11 (s, 1H), 6.77 (d, *J*=8.1, 1H), 6.69 (t, *J*=7.5, 1H), 5.75 (s, 1H), 2.94 – 2.85 (m, 1H), 1.20 (d, *J*=7.0, 6H).

^{13}C NMR (126 MHz, DMSO-d6) δ = 164.23, 149.34, 148.50, 139.45, 133.76, 127.87, 127.50, 126.73, 117.56, 115.43, 114.87, 67.10, 33.75, 24.38.

2-(4-fluorophenyl)-2,3-dihydroquinazolin-4(1*H*)-one (3q)

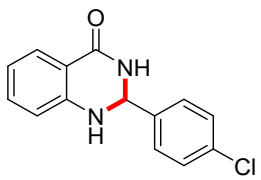


By following the typical procedure, the product was obtained as a white solid with a 90% yield.

^{1}H NMR (500 MHz, DMSO-d6) δ = 8.33 (s, 1H), 7.62 (d, *J*=6.8, 1H), 7.55 (dd, *J*=8.6, 5.6, 2H), 7.29 – 7.20 (m, 3H), 7.13 (s, 1H), 6.76 (d, *J*=8.1, 1H), 6.69 (t, *J*=7.4, 1H), 5.79 (s, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ = 164.07, 162.59 (d, *J* = 244.2 Hz), 148.29, 138.23 (d, *J* = 2.8 Hz), 133.85, 129.53 (d, *J* = 8.4 Hz), 127.84, 117.74, 115.58 (d, *J* = 21.5 Hz), 115.41, 114.92, 66.40.

2-(4-chlorophenyl)-2,3-dihydroquinazolin-4(1*H*)-one (3r)

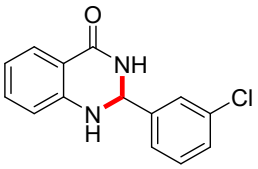


By following the typical procedure, the product was obtained as a white solid with an 89% yield.

^{1}H NMR (500 MHz, DMSO-d6) δ = 8.41 (s, 1H), 7.63 (d, *J*=7.6, 1H), 7.53 (d, *J*=8.3, 2H), 7.46 (d, *J*=8.4, 2H), 7.26 (t, *J*=7.5, 1H), 7.19 (s, 1H), 6.77 (d, *J*=8.1, 1H), 6.69 (t, *J*=7.4, 1H), 5.80 (s, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ = 164.05, 148.16, 141.06, 133.92, 133.51, 129.26, 128.81, 127.87, 117.80, 115.40, 114.96, 66.27.

2-(3-chlorophenyl)-2,3-dihydroquinazolin-4(1*H*)-one (3s)

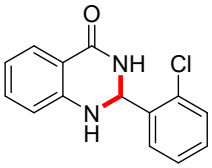


By following the typical procedure, the product was obtained as a white solid with an 86% yield.

^{1}H NMR (500 MHz, DMSO-d6) δ = 8.48 (s, 1H), 7.65 (d, *J*=7.7, 1H), 7.57 (s, 1H), 7.47 (d, *J*=4.7, 1H), 7.41 (dd, *J*=7.7, 5.7, 2H), 7.31 – 7.22 (m, 2H), 6.80 (d, *J*=8.1, 1H), 6.70 (t, *J*=7.5, 1H), 5.83 (s, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ = 164.04, 148.00, 144.83, 134.01, 133.54, 130.77, 128.78, 127.90, 127.25, 125.89, 117.87, 115.36, 115.00, 66.09.

2-(2-chlorophenyl)-2,3-dihydroquinazolin-4(1*H*)-one (3t)

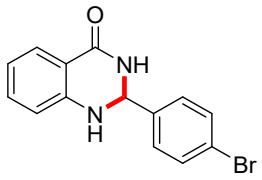


By following the typical procedure, the product was obtained as a white solid with 82% yield.

^{1}H NMR (500 MHz, DMSO-d6) δ = 8.27 (s, 1H), 7.68 (d, *J*=6.3, 2H), 7.54 – 7.47 (m, 1H), 7.43 – 7.36 (m, 2H), 7.27 (t, *J*=7.1, 1H), 7.05 (s, 1H), 6.79 (d, *J*=8.1, 1H), 6.73 (t, *J*=7.4, 1H), 6.16 (s, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ = δ 164.18, 148.15, 138.32, 133.95, 132.35, 130.78, 130.07, 129.22, 127.94, 127.88, 117.96, 115.15, 115.06, 64.17.

2-(4-bromophenyl)-2,3-dihydroquinazolin-4(1*H*)-one (3u)

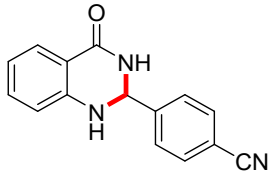


By following the typical procedure, the product was obtained as a yellow solid with a 90% yield.

^{1}H NMR (500 MHz, DMSO-d6) δ = 8.40 (s, 1H), 7.70 – 7.54 (m, 3H), 7.45 (d, *J*=8.4, 2H), 7.25 (t, *J*=7.0, 1H), 7.19 (s, 1H), 6.76 (d, *J*=8.1, 1H), 6.69 (t, *J*=7.4, 1H), 5.77 (s, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ = 164.01, 148.13, 141.52, 133.91, 131.72, 129.58, 127.86, 122.09, 117.79, 115.40, 114.95, 66.28.

4-(4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)benzonitrile (3v)

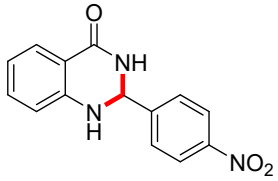


By following the typical procedure, the product was obtained as a yellow solid with an 88% yield.

^{1}H NMR (500 MHz, DMSO-d6) δ = 8.53 (s, 1H), 7.88 (d, *J*=8.3, 2H), 7.67 (d, *J*=8.2, 2H), 7.61 (d, *J*=7.7, 1H), 7.32 (s, 1H), 7.26 (t, *J*=7.6, 1H), 6.77 (d, *J*=8.1, 1H), 6.68 (t, *J*=7.5, 1H), 5.86 (s, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ = 163.83, 147.81, 134.04, 132.90, 129.11, 128.17, 127.87, 119.15, 117.91, 115.35, 114.98, 111.53, 65.97.

2-(4-nitrophenyl)-2,3-dihydroquinazolin-4(1*H*)-one (3w)



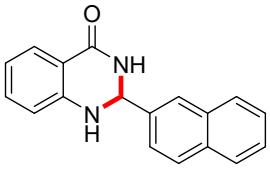
By following the typical procedure, the product was obtained as a yellow solid with an 80% yield.

^{1}H NMR (500 MHz, DMSO-d6) δ = 8.61 (s, 1H), 8.26 (d, *J*=8.7, 2H), 7.77 (d, *J*=8.7, 2H), 7.64 (d,

J=7.5, 1H), 7.38 (s, 1H), 7.27 (t, *J*=7.1, 1H), 6.80 (d, *J*=8.1, 1H), 6.69 (t, *J*=7.5, 1H), 5.96 (s, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ = 163.88, 149.74, 147.86, 147.74, 134.07, 128.52, 127.92, 124.05, 117.97, 115.36, 115.04, 65.81.

2-(naphthalen-2-yl)-2,3-dihydroquinazolin-4(1*H*)-one (3x)

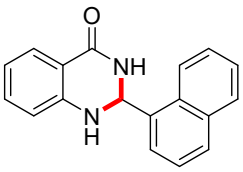


By following the typical procedure, the product was obtained as a white solid with an 86% yield.

^{1}H NMR (500 MHz, DMSO-d6) δ = 8.43 (s, 1H), 8.01 – 7.91 (m, 4H), 7.72 (d, *J*=8.5, 1H), 7.67 (d, *J*=6.8, 1H), 7.54 (dd, *J*=6.2, 3.2, 2H), 7.30 – 7.22 (m, 2H), 6.79 (d, *J*=8.0, 1H), 6.70 (t, *J*=7.4, 1H), 5.96 (s, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ = 164.12, 148.39, 139.32, 133.86, 133.48, 132.94, 128.62, 128.46, 128.07, 127.88, 126.92, 126.88, 126.37, 125.34, 117.68, 115.42, 114.91, 67.32.

2-(naphthalen-1-yl)-2,3-dihydroquinazolin-4(1*H*)-one (3y)

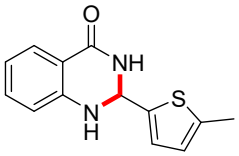


By following the typical procedure, the product was obtained as a white solid with 82% yield.

^{1}H NMR (500 MHz, DMSO-d6) δ = 8.64 (d, *J*=7.7, 1H), 8.43 (s, 1H), 8.03 (dd, *J*=11.4, 8.2, 2H), 7.80 (t, *J*=7.0, 2H), 7.64 – 7.56 (m, 3H), 7.33 (t, *J*=7.6, 1H), 7.21 (s, 1H), 6.87 (d, *J*=8.1, 1H), 6.80 (t, *J*=7.5, 1H), 6.57 (s, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ = 164.71, 149.03, 135.64, 134.31, 133.86, 131.08, 129.95, 129.16, 128.13, 126.66, 126.62, 126.37, 125.74, 125.14, 117.87, 115.54, 115.11, 66.56.

2-(5-methylthiophen-2-yl)-2,3-dihydroquinazolin-4(1*H*)-one (3z)

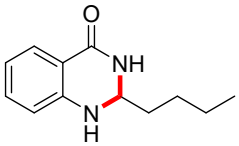


By following the typical procedure, the product was obtained as a white solid with a 77% yield.

^{1}H NMR (500 MHz, DMSO-d6) δ = 8.42 (s, 1H), 7.64 (d, *J*=7.6, 1H), 7.25 (dd, *J*=12.0, 5.0, 2H), 6.79 (d, *J*=8.1, 1H), 6.69 (t, *J*=7.4, 1H), 6.15 (d, *J*=3.0, 1H), 5.99 (d, *J*=2.2, 1H), 5.73 (s, 1H), 2.21 (s, 3H).

^{13}C NMR (126 MHz, DMSO-d6) δ = 163.88, 153.00, 151.95, 147.67, 133.76, 127.78, 117.68, 115.39, 115.00, 108.65, 106.81, 60.79, 13.79.

2-butyl-2,3-dihydroquinazolin-4(1*H*)-one (3aa)



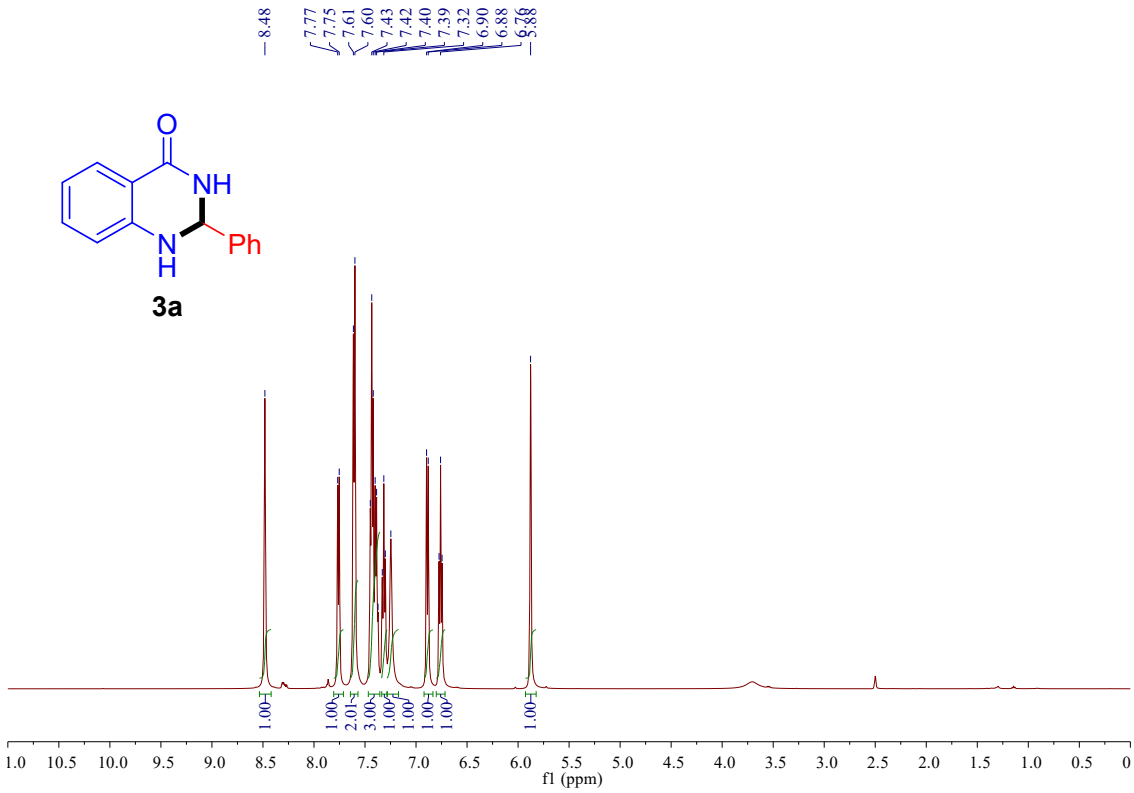
By following the typical procedure, the product was obtained as a white solid with a 71% yield.

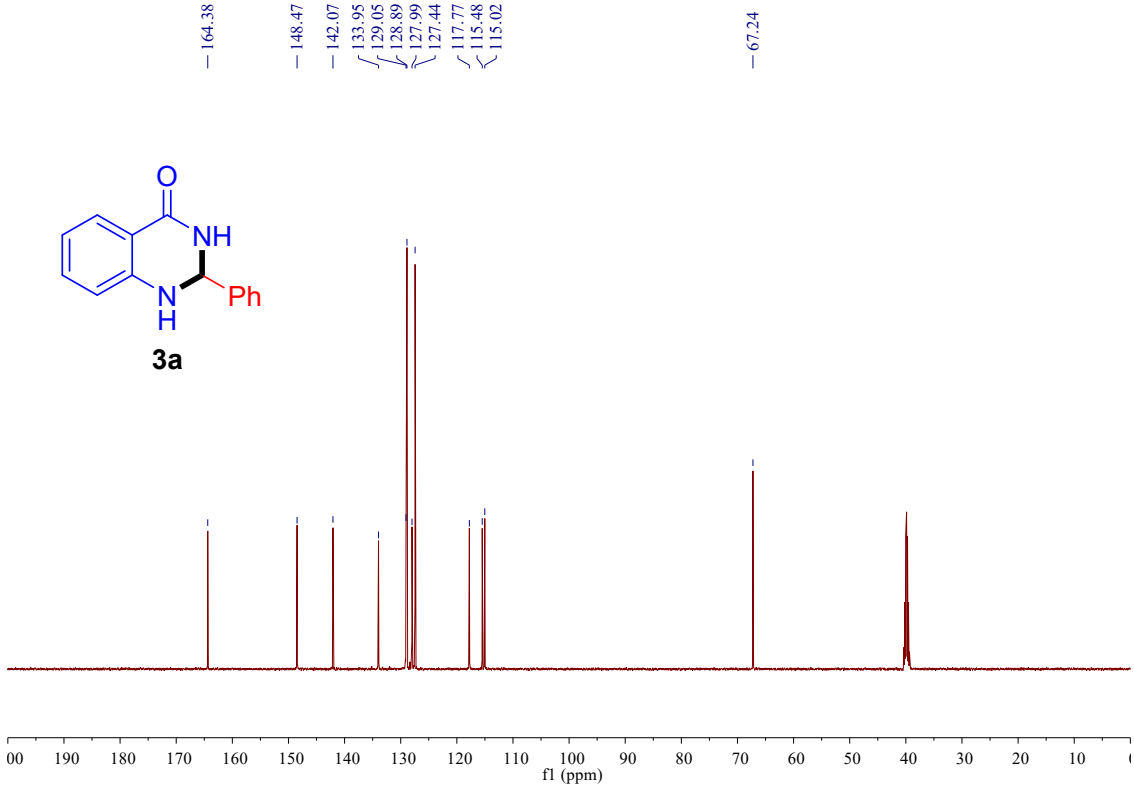
^{1}H NMR (500 MHz, DMSO-d6) 7.92 (s, 1H), 7.58 (d, *J*=7.7, 1H), 7.22 (t, *J*=7.6, 1H), 6.73 (d, *J*=8.1, 1H), 6.65 (t, *J*=7.4, 1H), 6.57 (s, 1H), 4.68 (s, 1H), 1.68 – 1.59 (m, 2H), 1.39 (dt, *J*=14.9, 7.6, 2H), 1.33 – 1.24 (m, 2H), 0.88 (t, *J*=7.2, 3H).

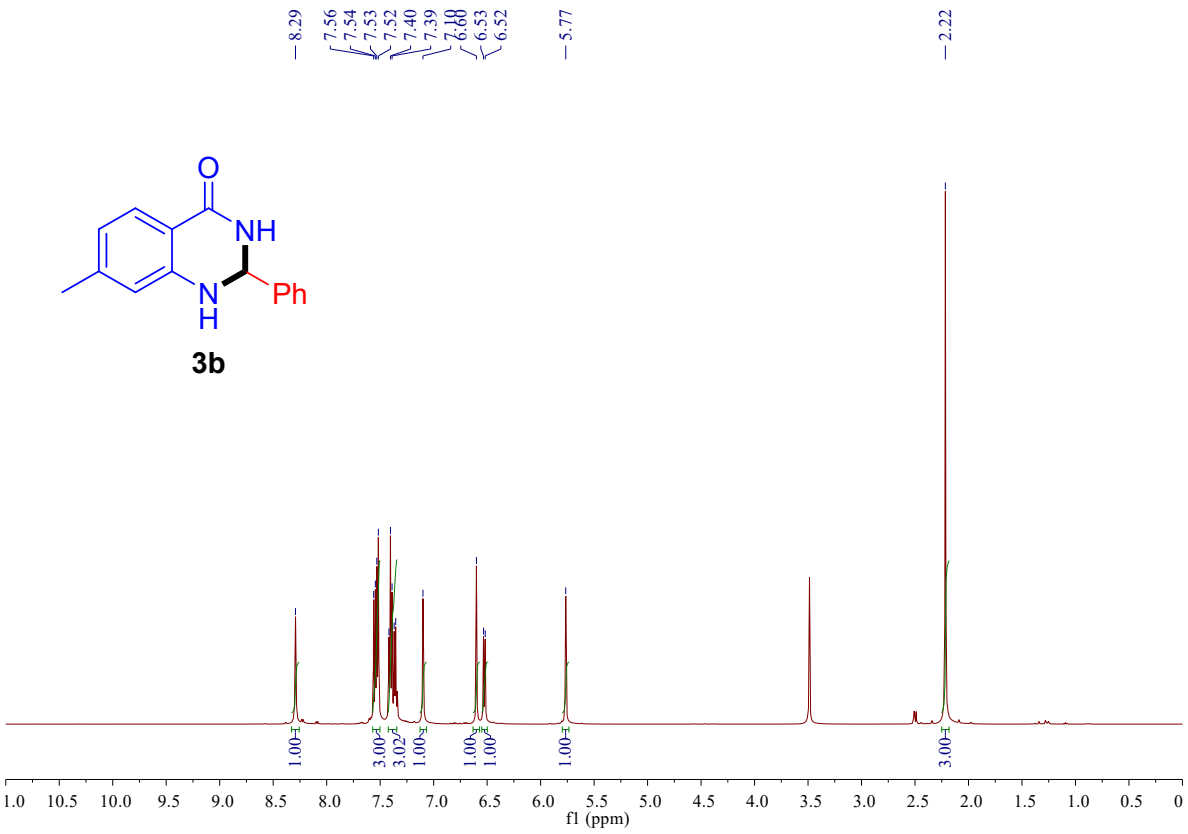
^{13}C NMR (126 MHz, DMSO-d6) δ = 164.43, 148.99, 133.50, 127.82, 117.33, 115.47, 114.83, 64.88, 35.21, 25.90, 22.56, 14.42.

---

6. NMR Spectra



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7.40
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7.10
6.80
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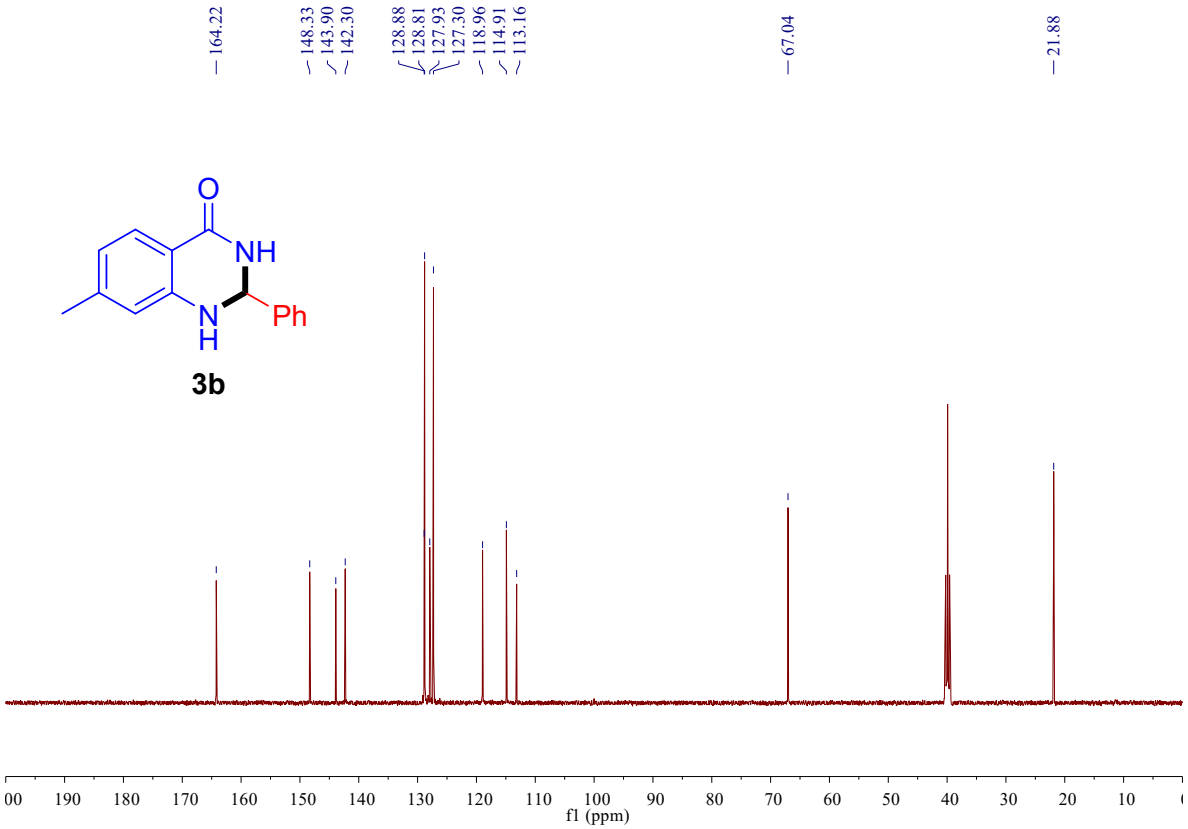
6.52
5.77
2.22
O
NH
N
H
Ph
3b
1.00
3.00
3.02
1.00
1.00
1.00
1.00
3.00
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)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127.30
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114.91
113.16
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O
NH
N
H
Ph
3b
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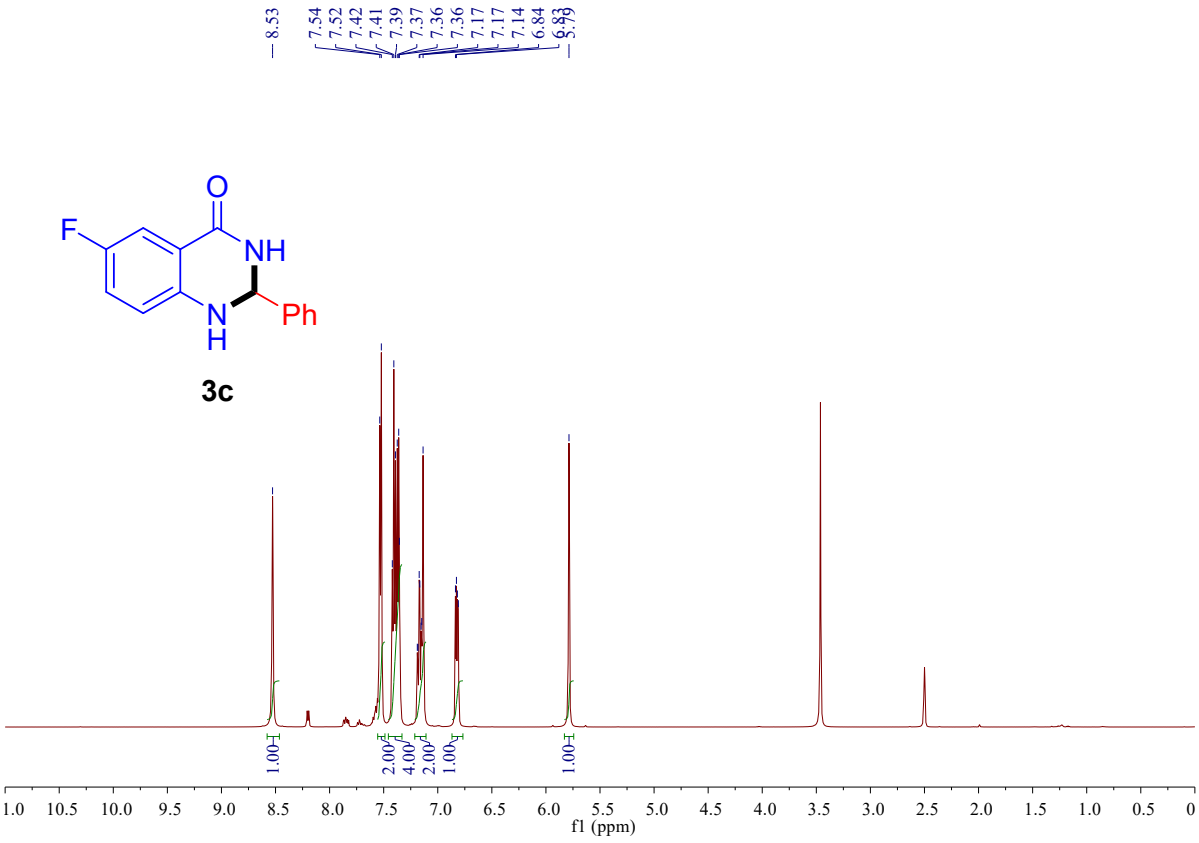
f1 (ppm)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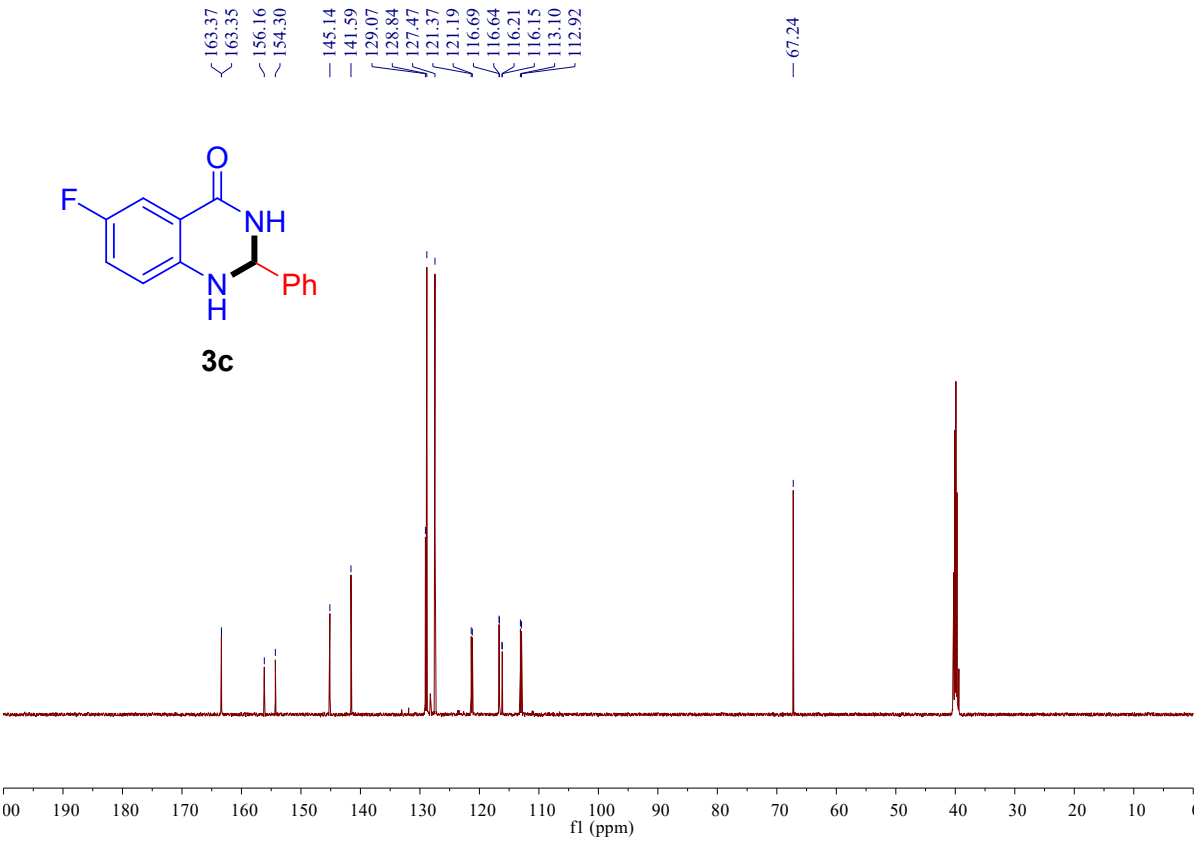
7.36
7.36
7.17
7.17
7.14
6.84
6.83
6.78
O
F
NH
N
H
Ph
3c
1.00
2.00
4.00
2.00
1.00
1.00
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)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116.21
116.15
113.10
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H
Ph
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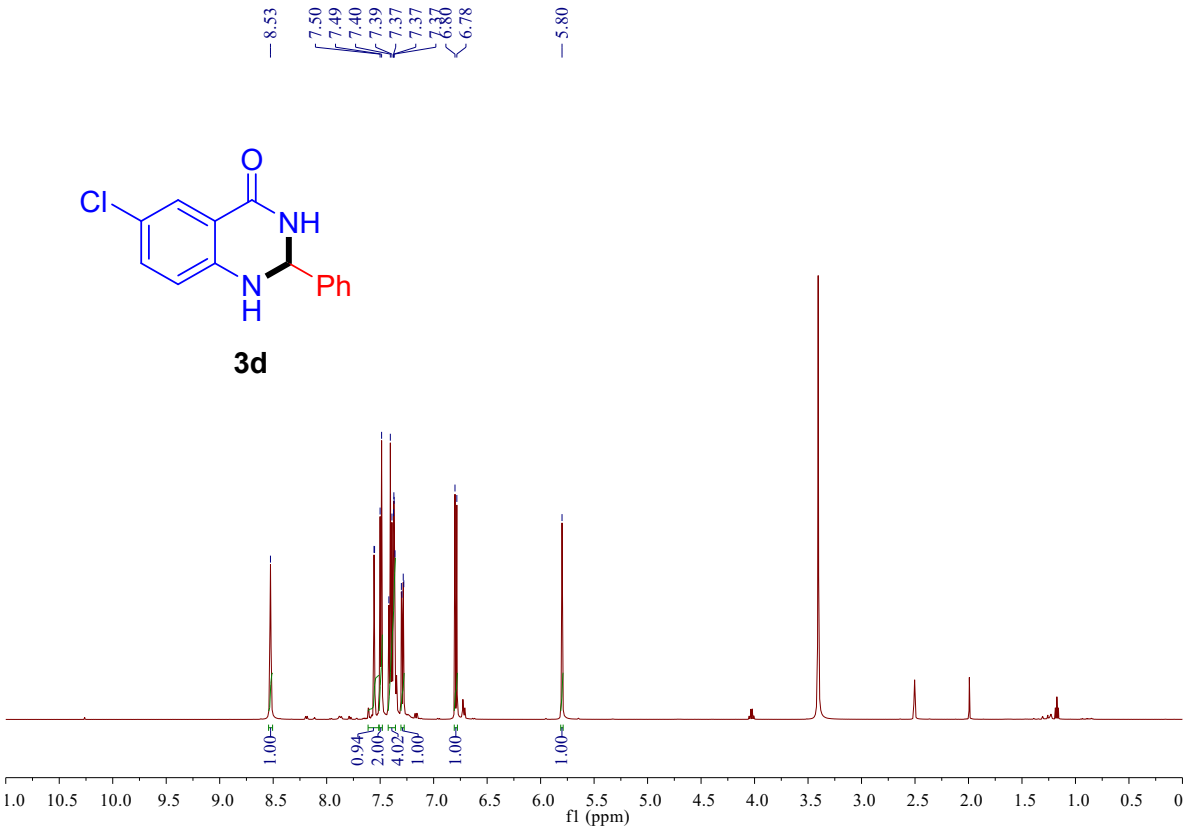
f1 (ppm)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7.37
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6.78
5.80
Cl
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H
Ph
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2.00
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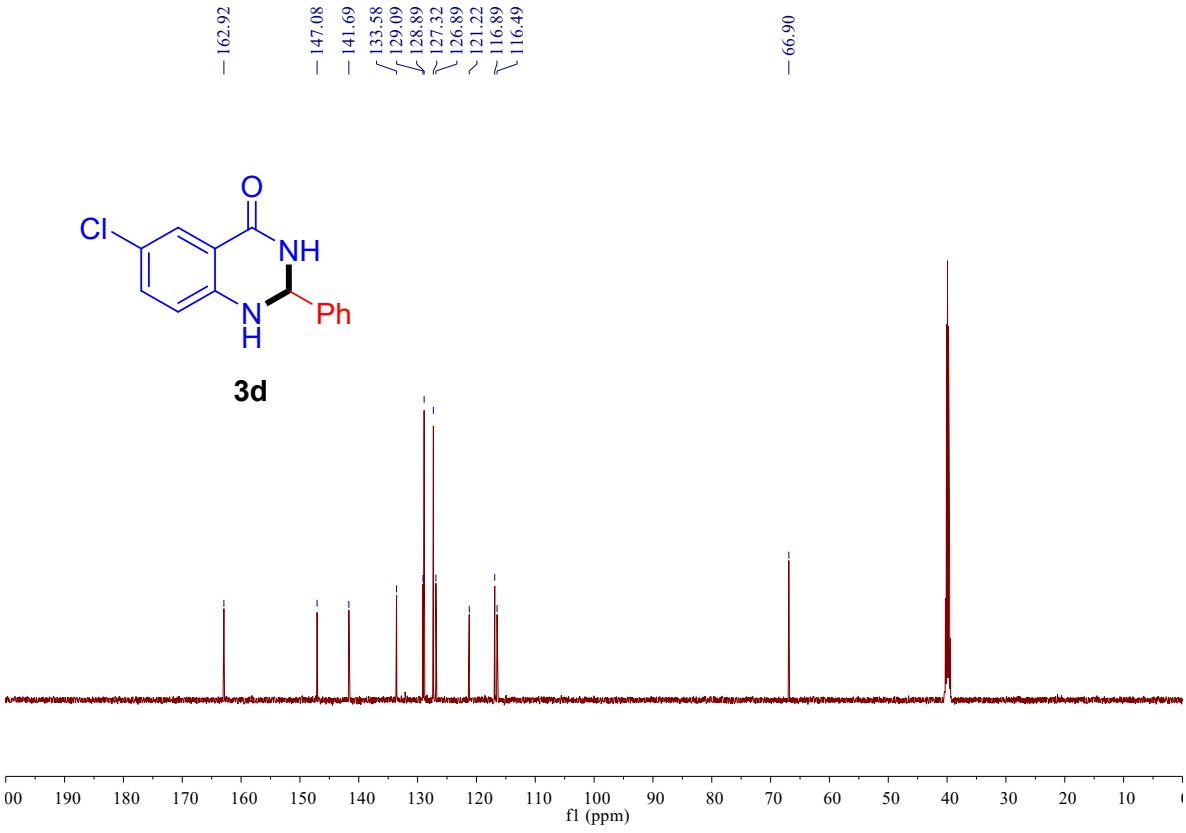
1.00
1.00
f1 (ppm)

3d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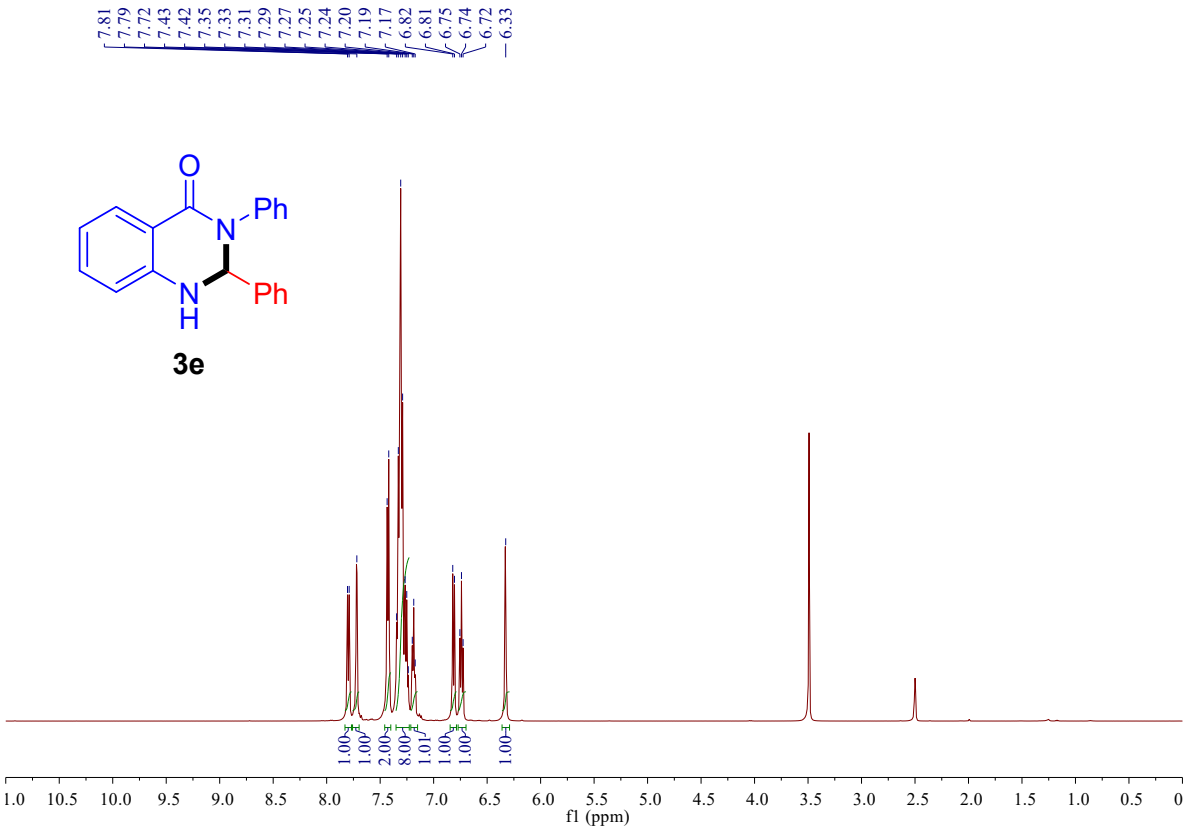
N
H
Ph
f1 (ppm)

3d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7.24
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7.19
7.17
6.82
6.81
6.75
6.74
6.72
6.33
O
Ph
N
N
H
Ph
3e
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1.00
2.00
8.00
1.01
1.00
1.00
1.00
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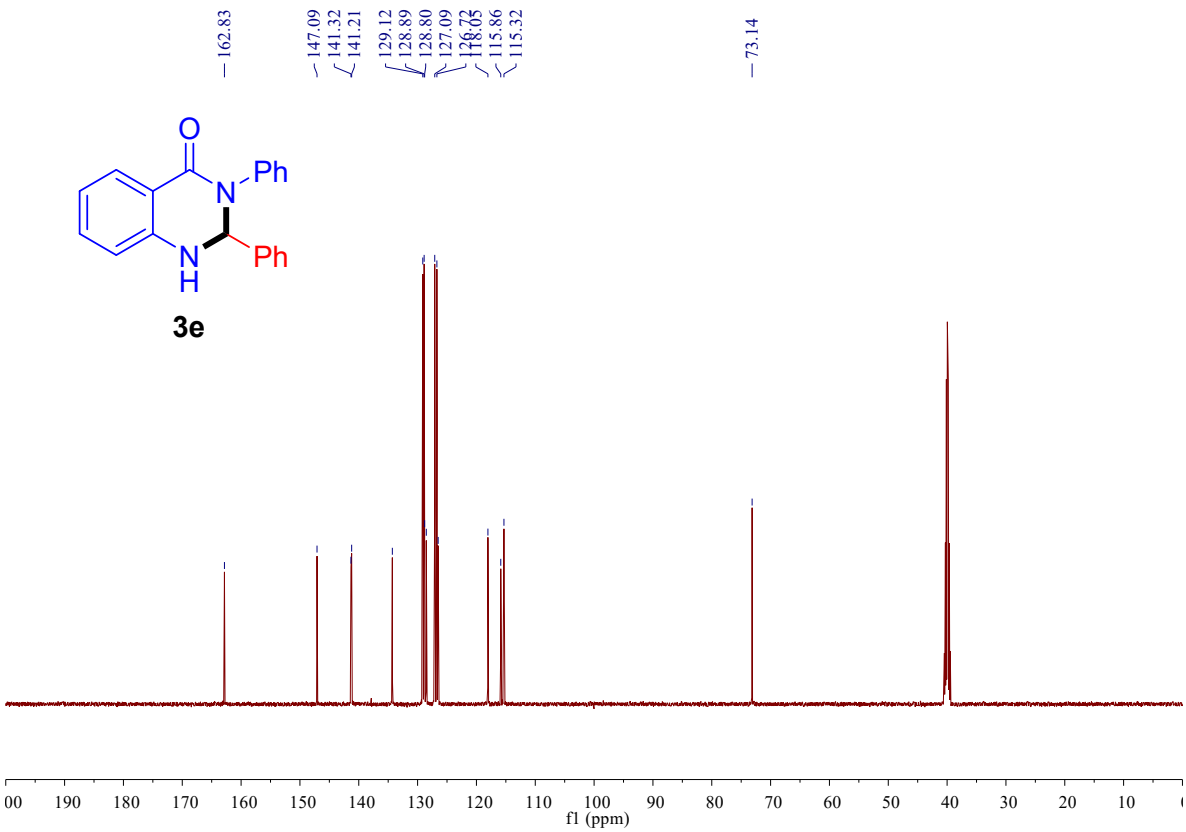
f1 (ppm)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127.09
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Ph
N
N
H
Ph
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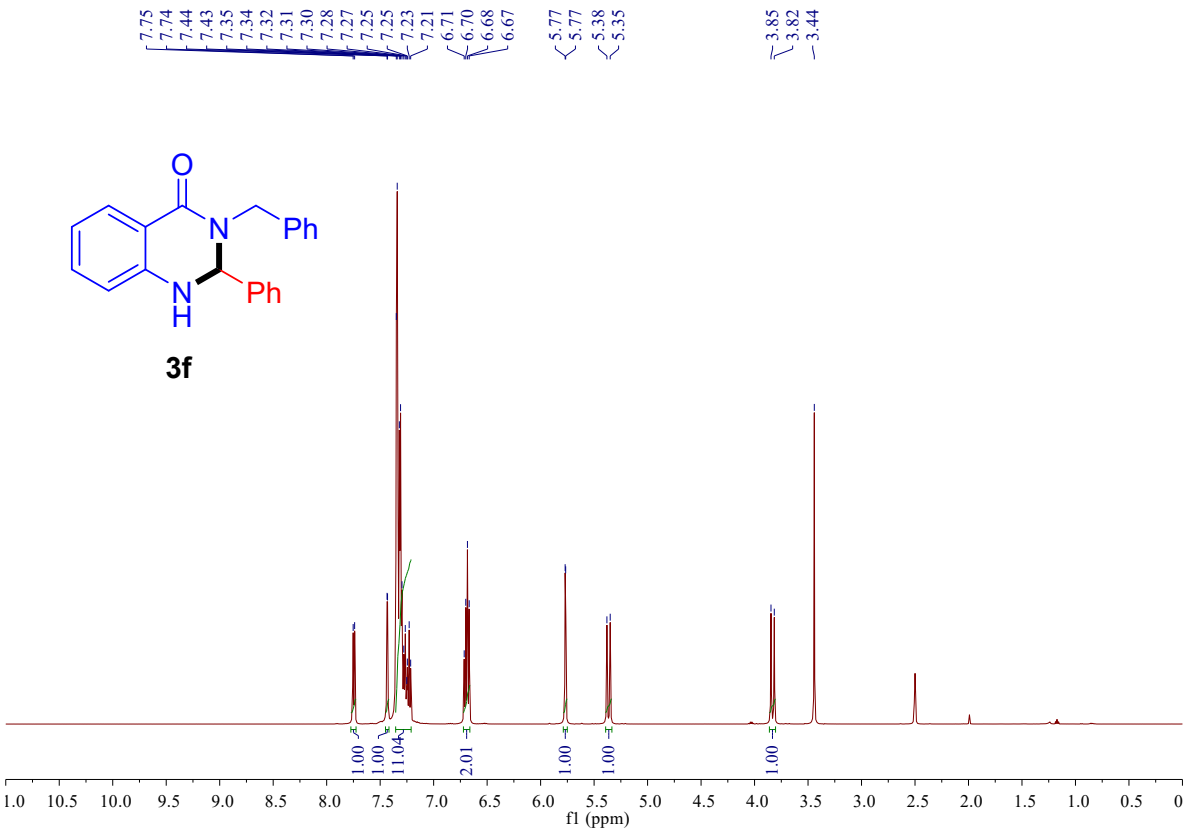
f1 (ppm)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7.23
7.21
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6.70
6.68
6.67
5.77
5.77
5.38
5.35
3.85
3.82
3.44
O
N
Ph
N
H
Ph
3f
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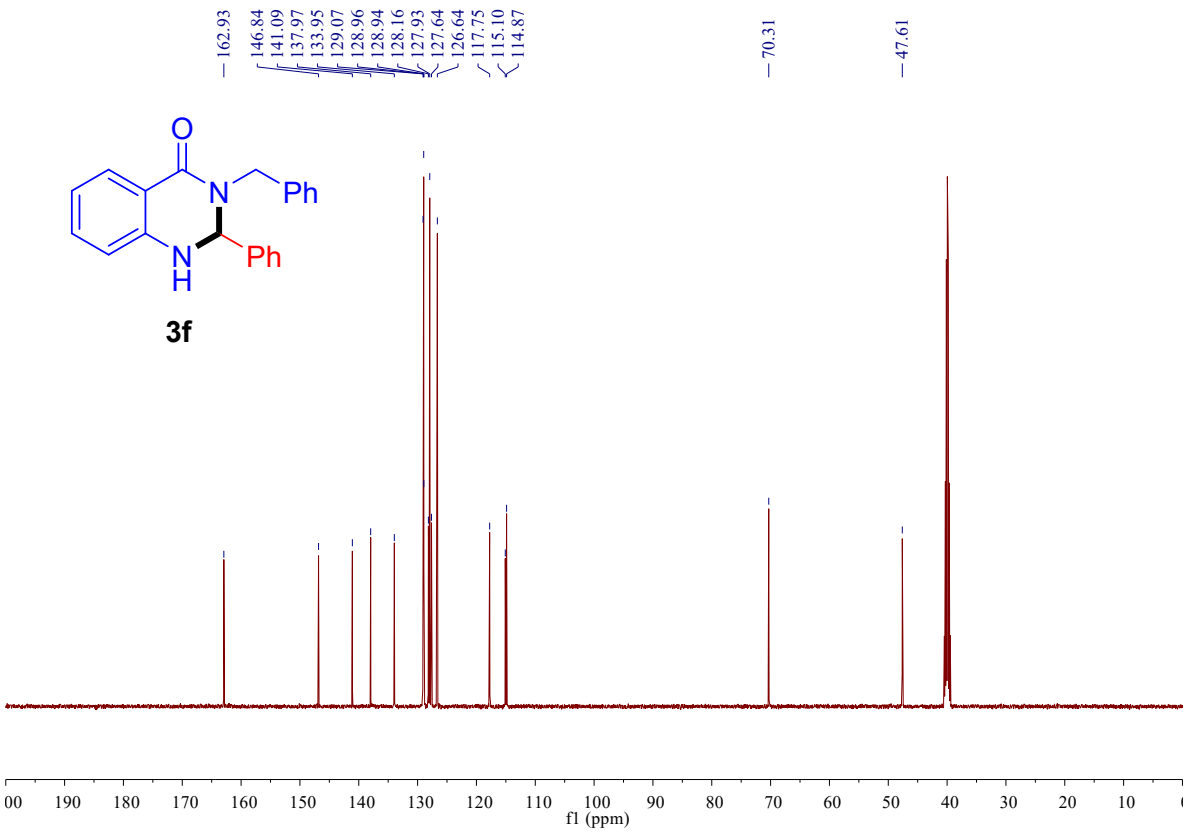
1.00
11.04
2.01
1.00
1.00
1.00
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)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115.10
114.87
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Ph
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H
Ph
3f
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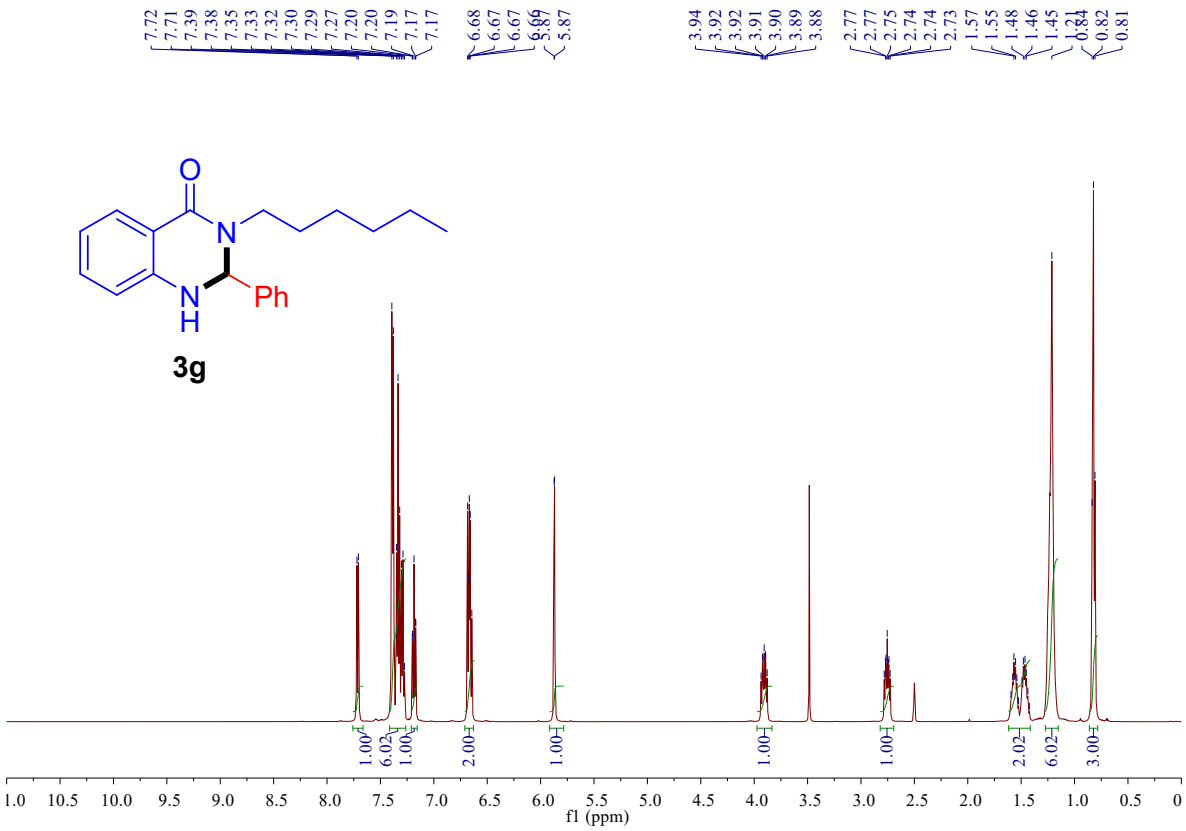
f1 (ppm)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6.67
6.67
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5.87
3.94
3.92
3.92
3.91
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2.77
2.75
2.74
2.74
2.73
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1.55
1.48
1.46
1.45
1.21
0.84
0.82
0.81
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1.00
2.00
1.00
1.00
1.00
2.02
6.02
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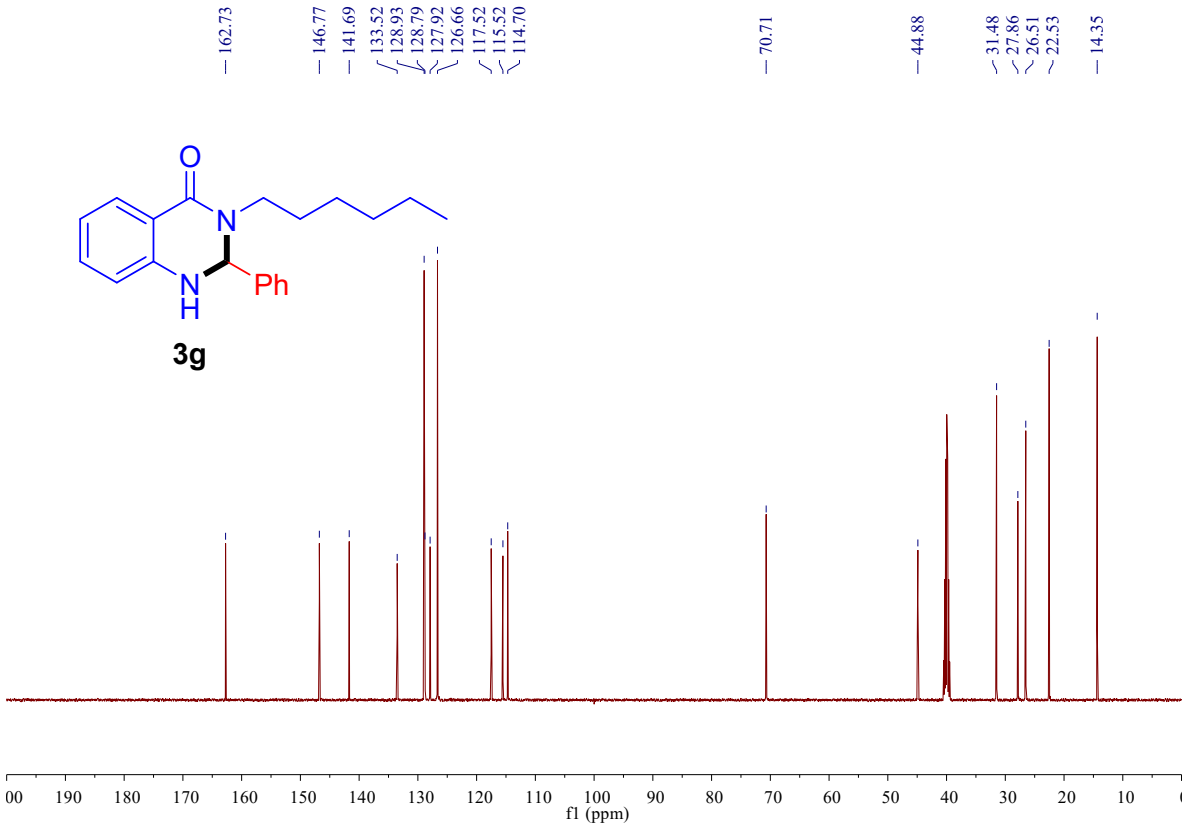
f1 (ppm)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27.86
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H
Ph
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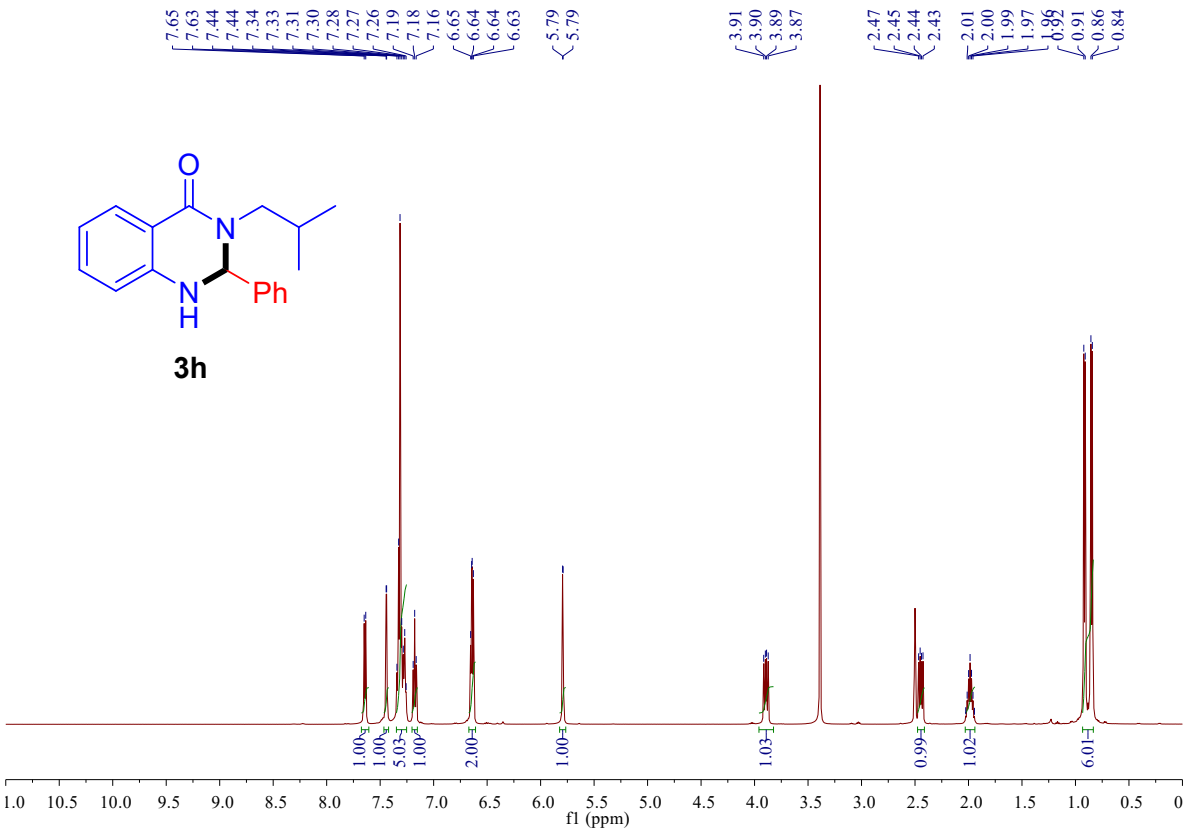
f1 (ppm)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0.91
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Ph
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1.03
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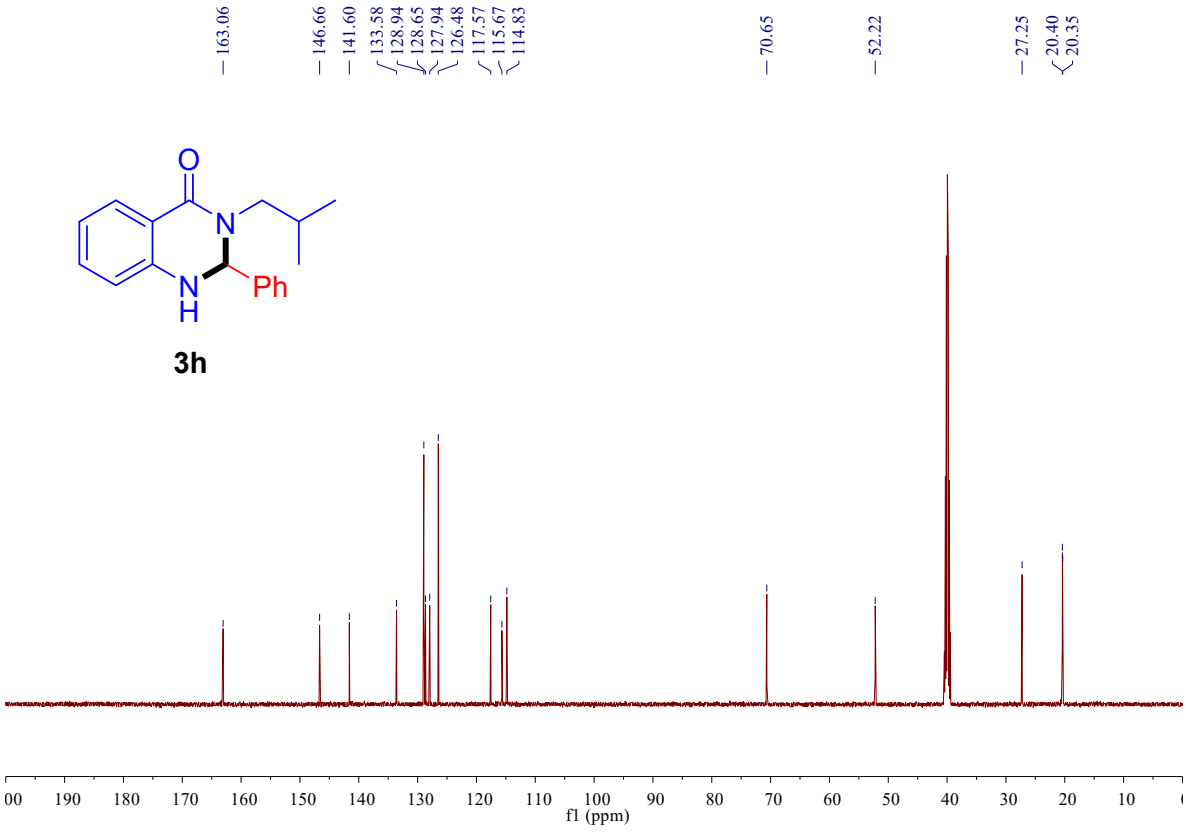
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O
N
N
H
Ph
3h
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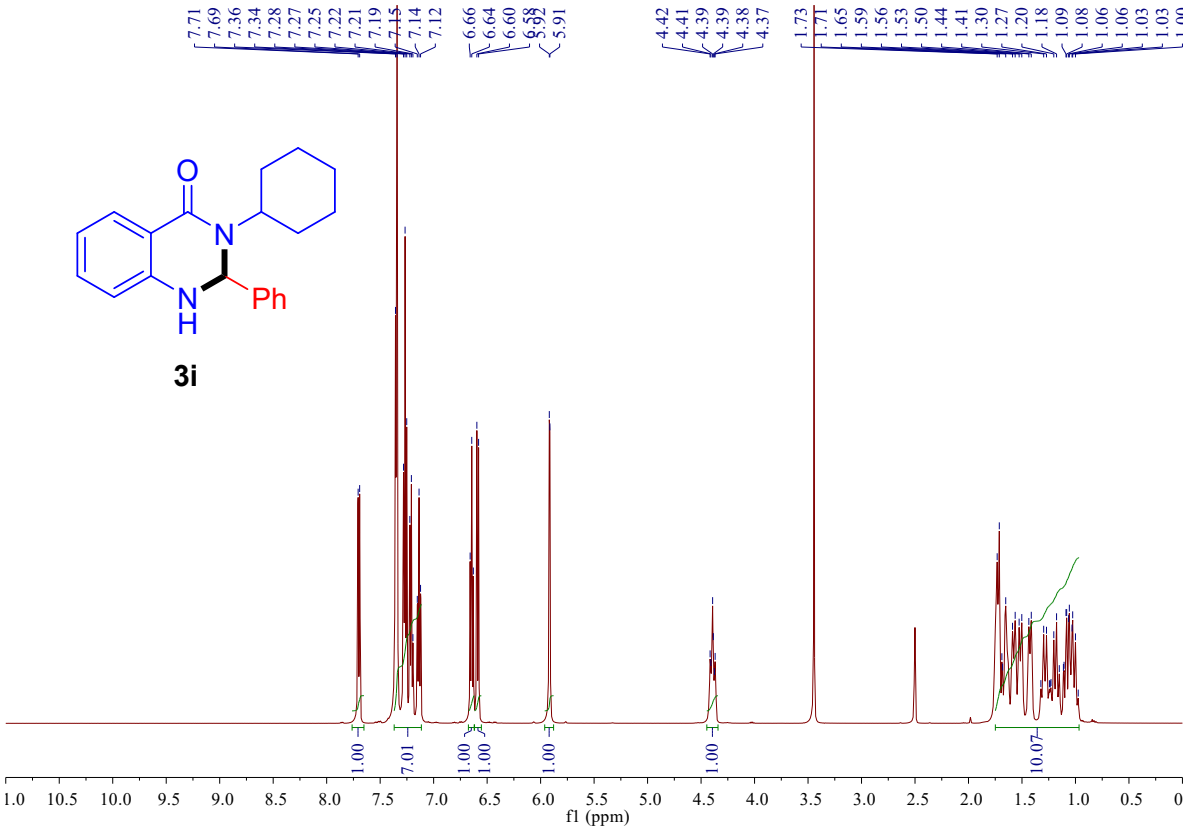
f1 (ppm)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1.09
1.08
1.06
1.06
1.03
1.03
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N
N
H
Ph
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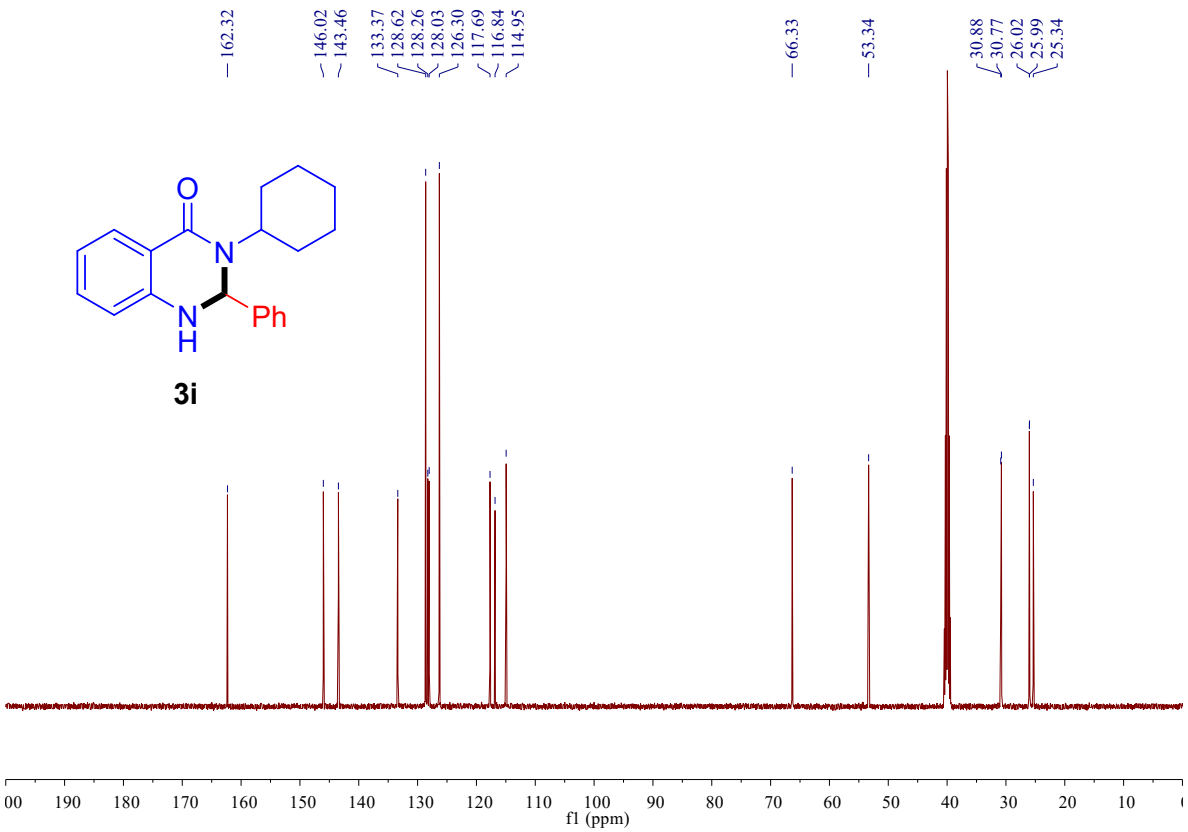
f1 (ppm)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53.34
30.88
30.77
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N
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Ph
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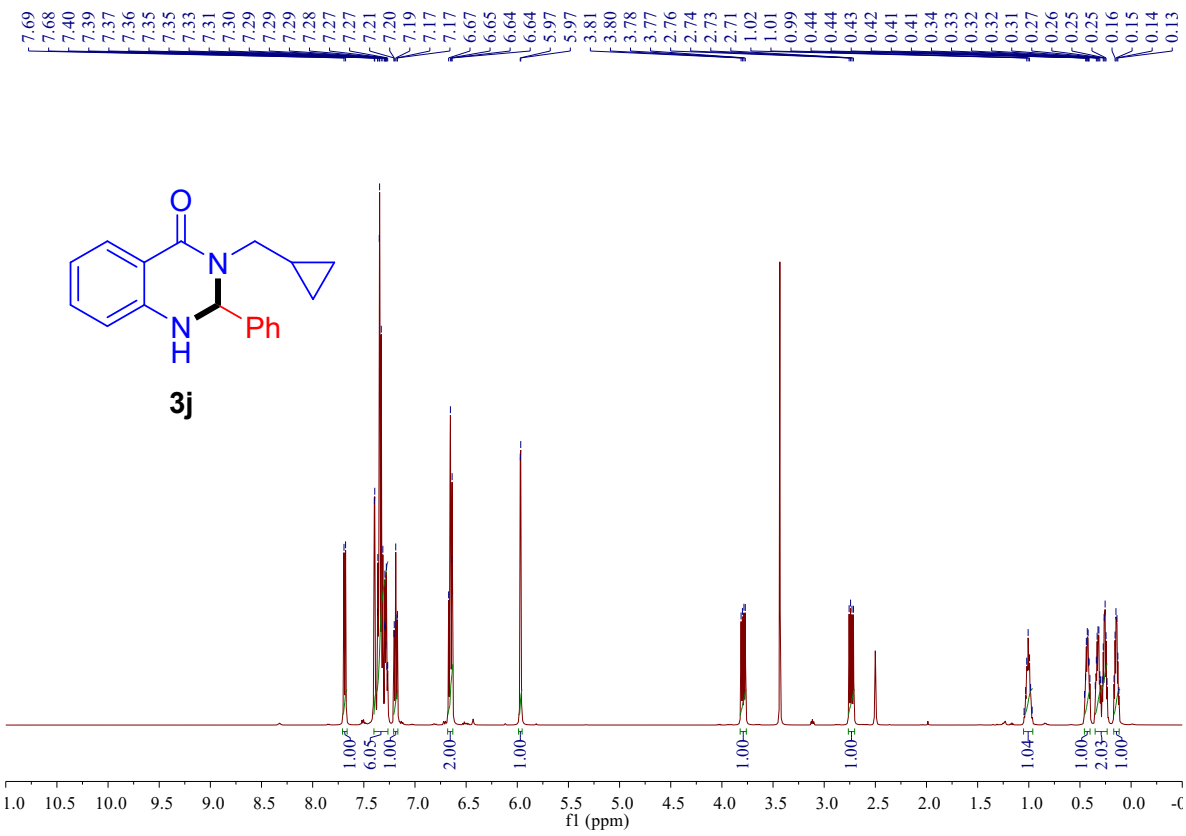
f1 (ppm)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3.81 3.80 3.78 3.77 2.76 2.74 2.73 2.71 1.02 1.01 0.99 0.44 0.44 0.43 0.42 0.41 0.41 0.34 0.33 0.32 0.32 0.31 0.27 0.26 0.25 0.25 0.16 0.15 0.14 0.13
O
N
N
H
Ph
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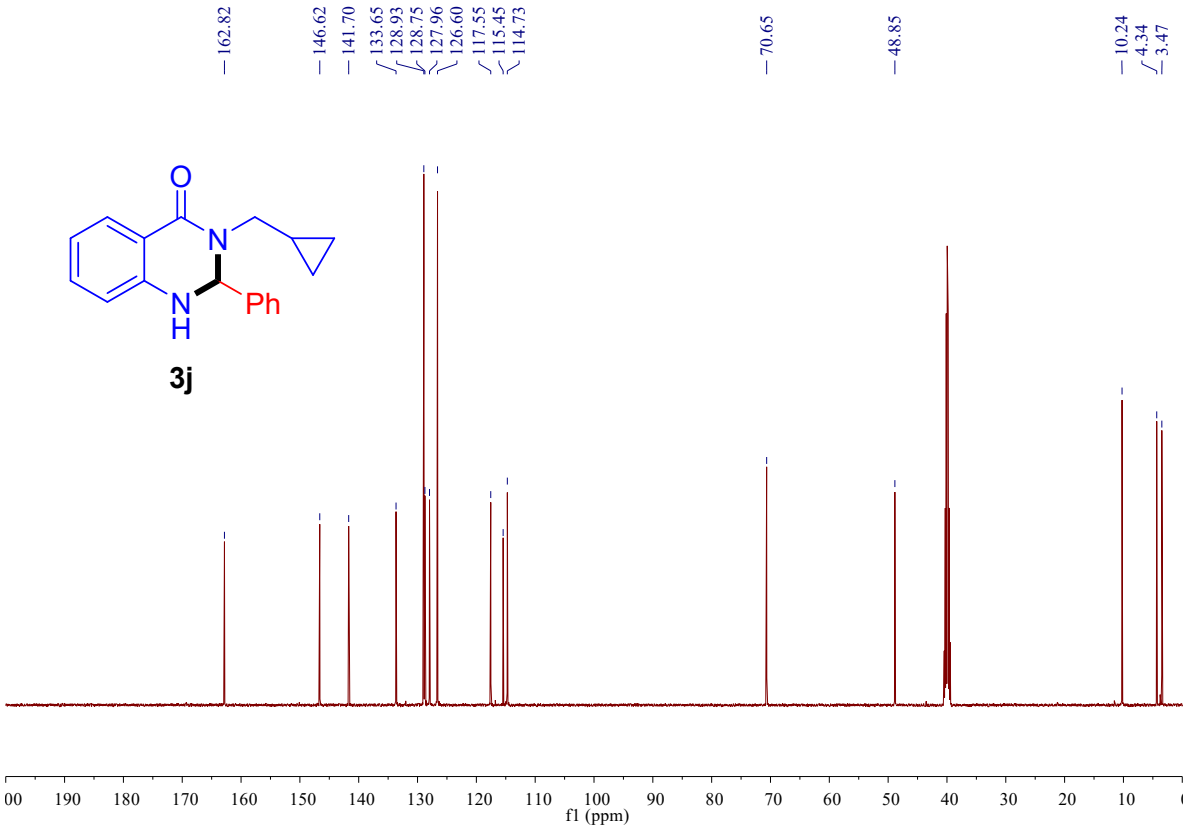
f1 (ppm)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70.65
48.85
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Ph
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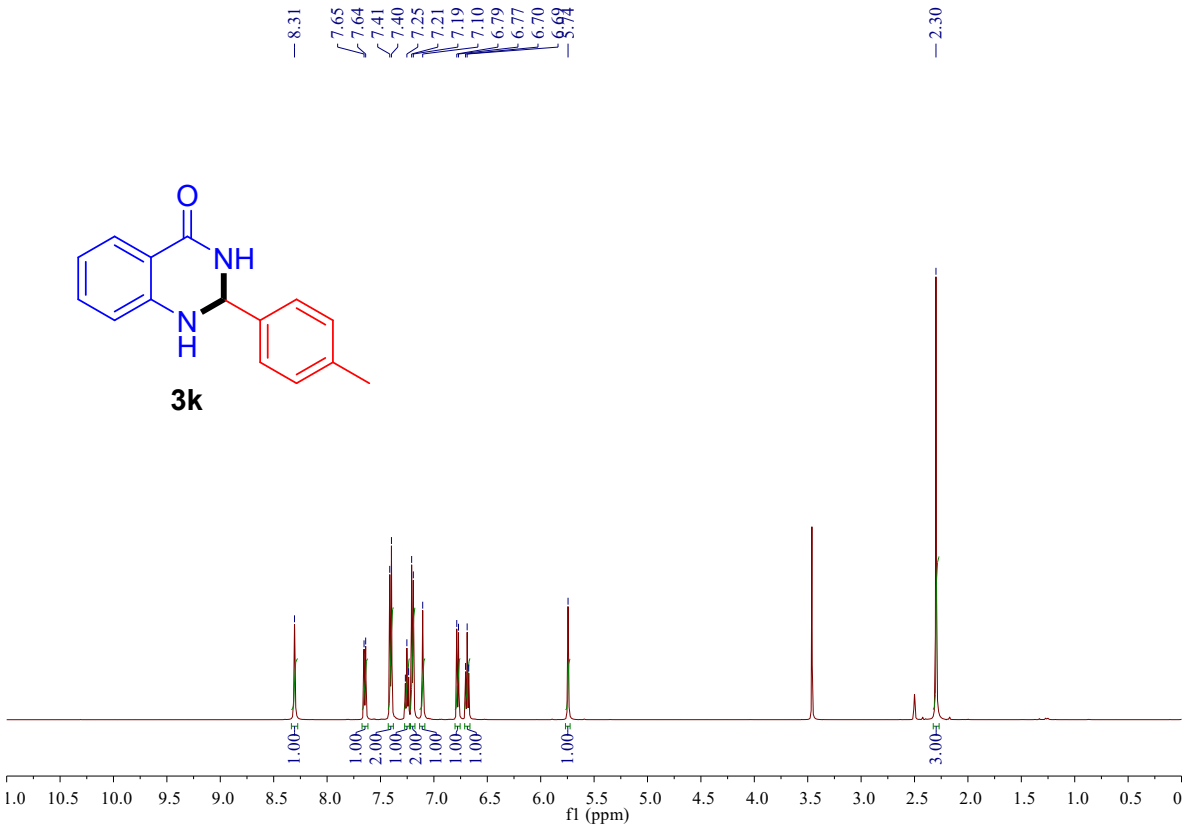
f1 (ppm)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H
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2.00
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1.00
1.00
1.00
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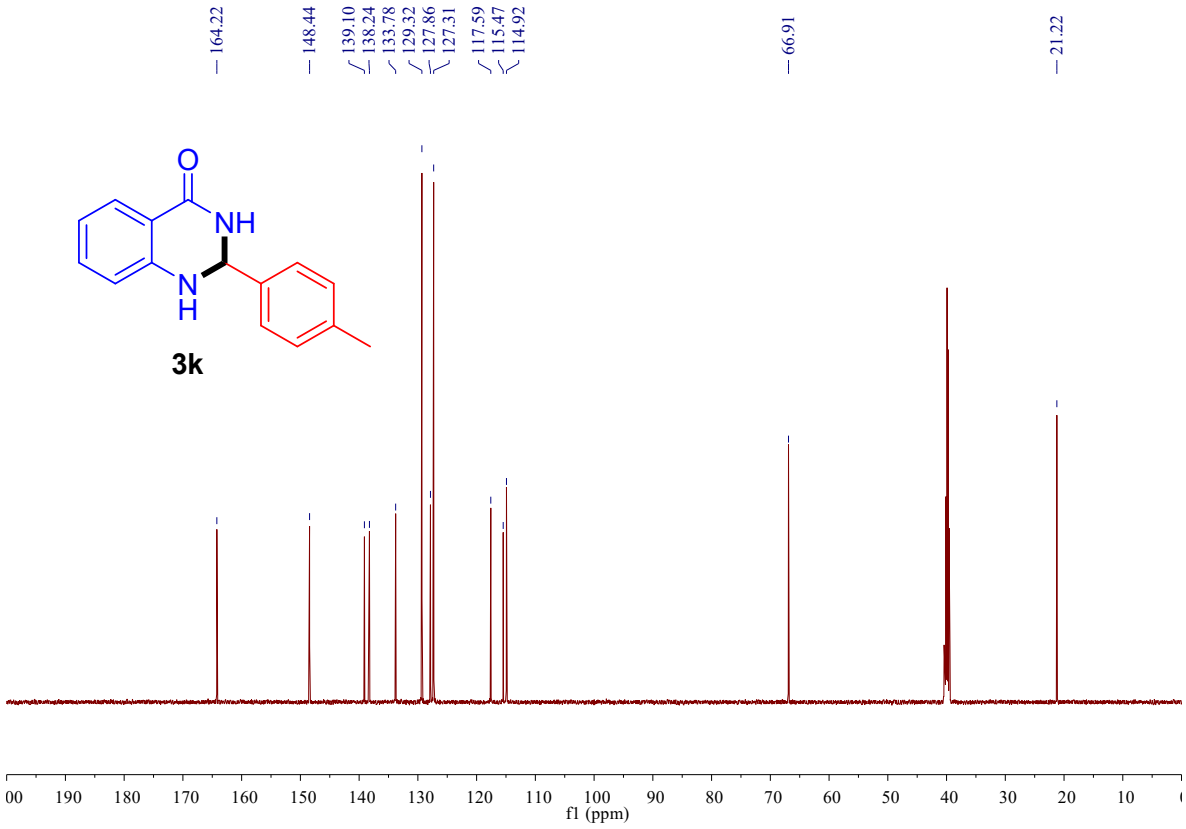
f1 (ppm)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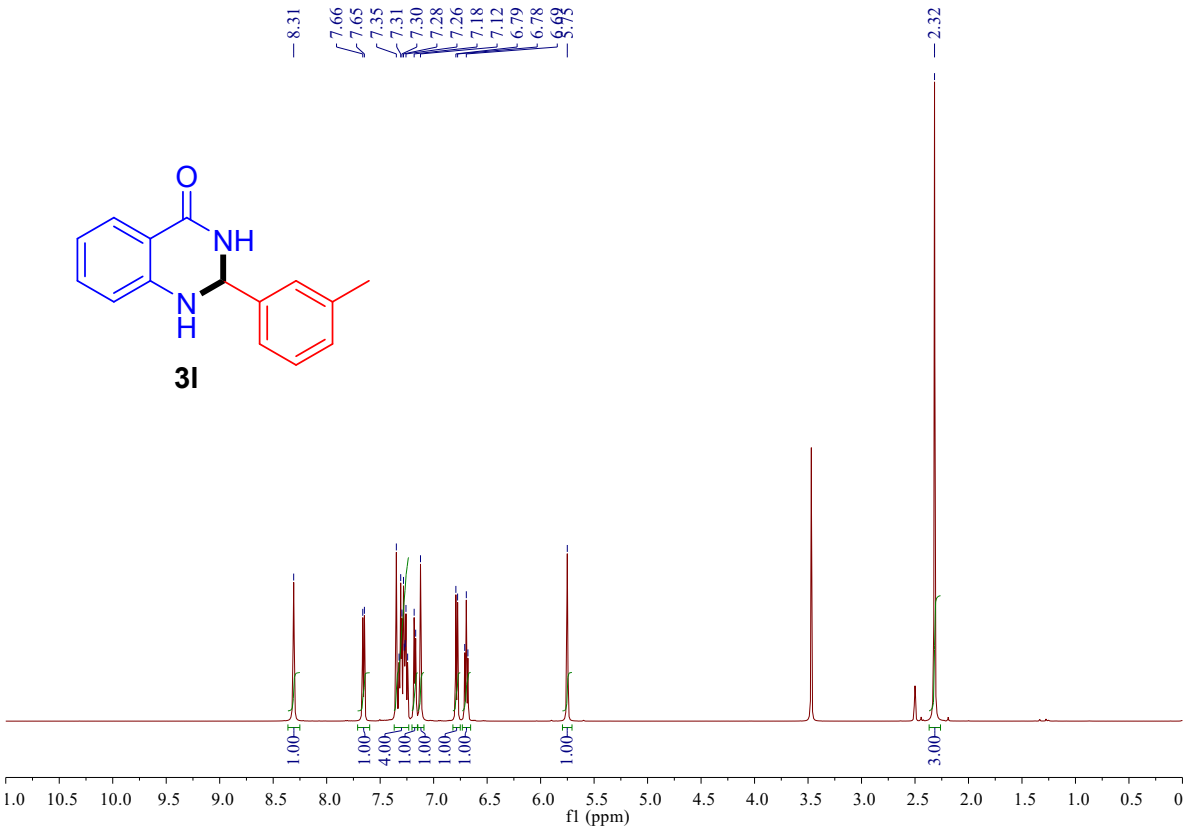
f1 (ppm)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4.00
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1.00
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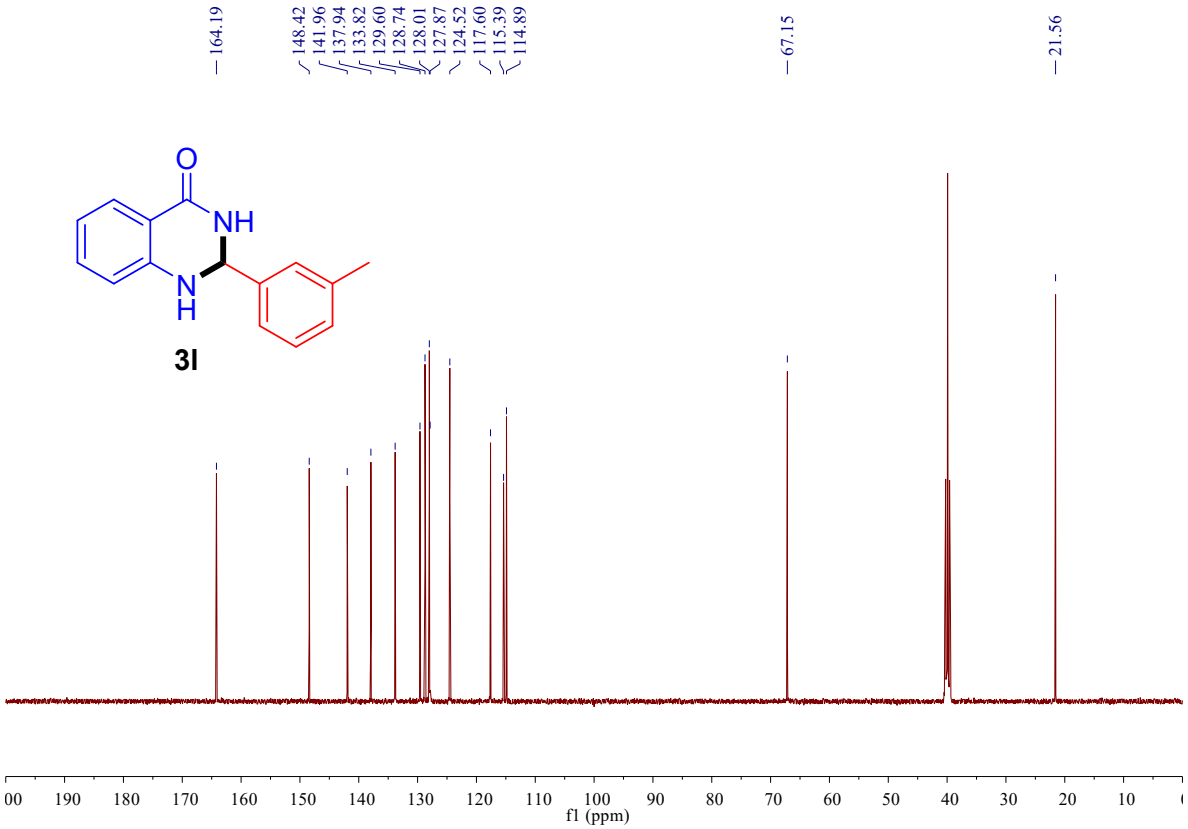
3.00
f1 (ppm)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O
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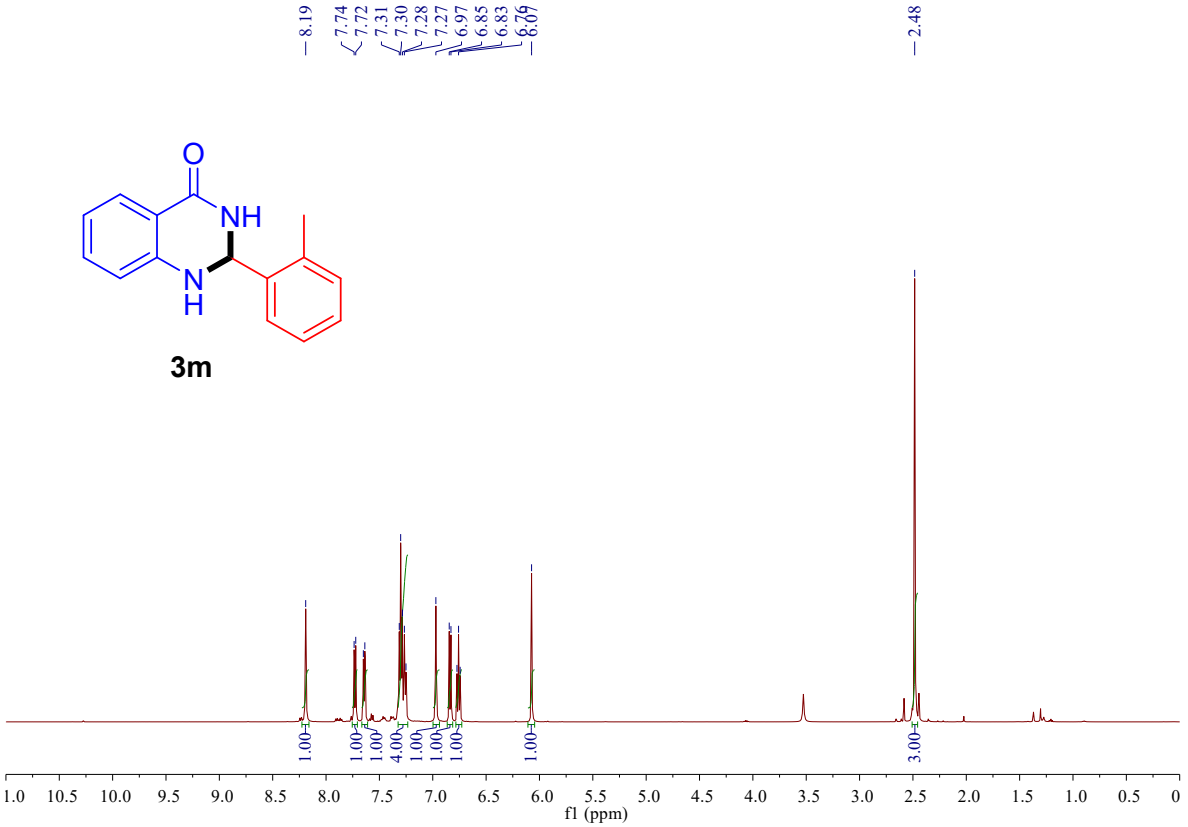
N
H
3l
f1 (ppm)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6.07
2.48
O
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N
H
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1.00
1.00
4.00
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1.00
1.00
3.00
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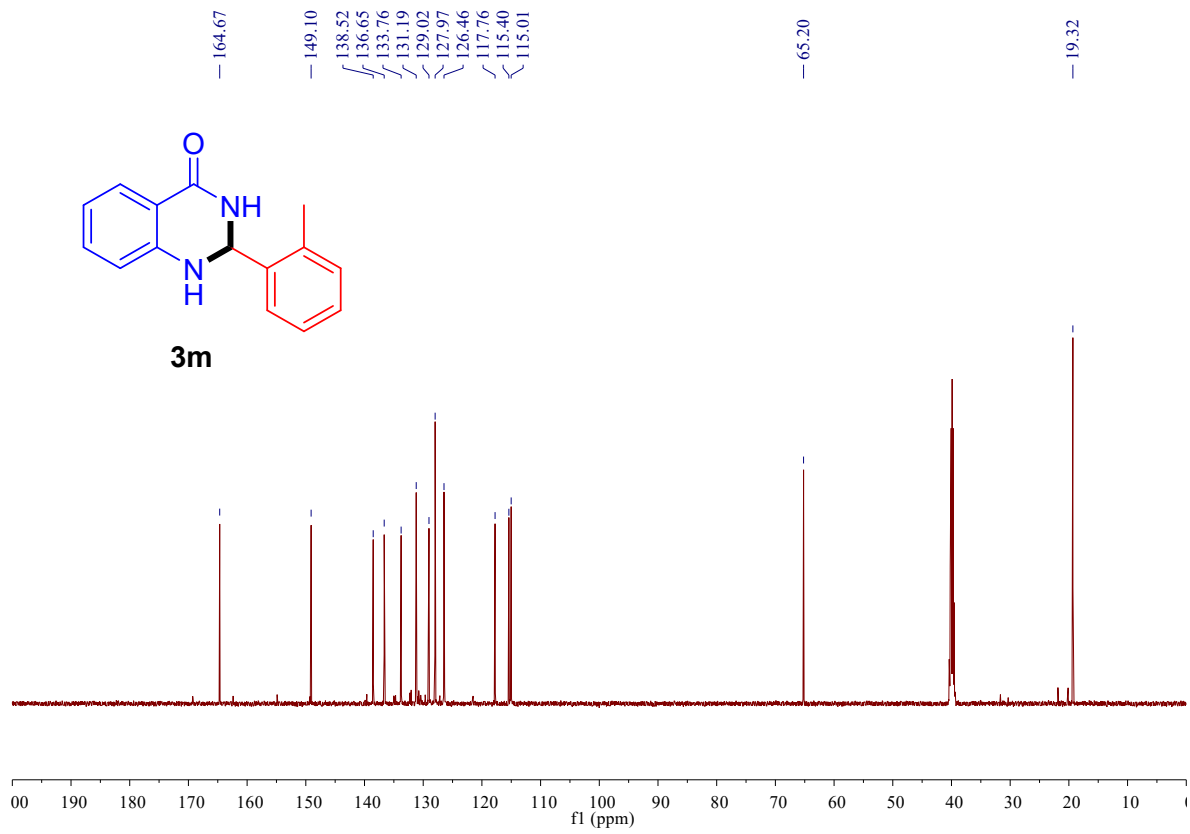
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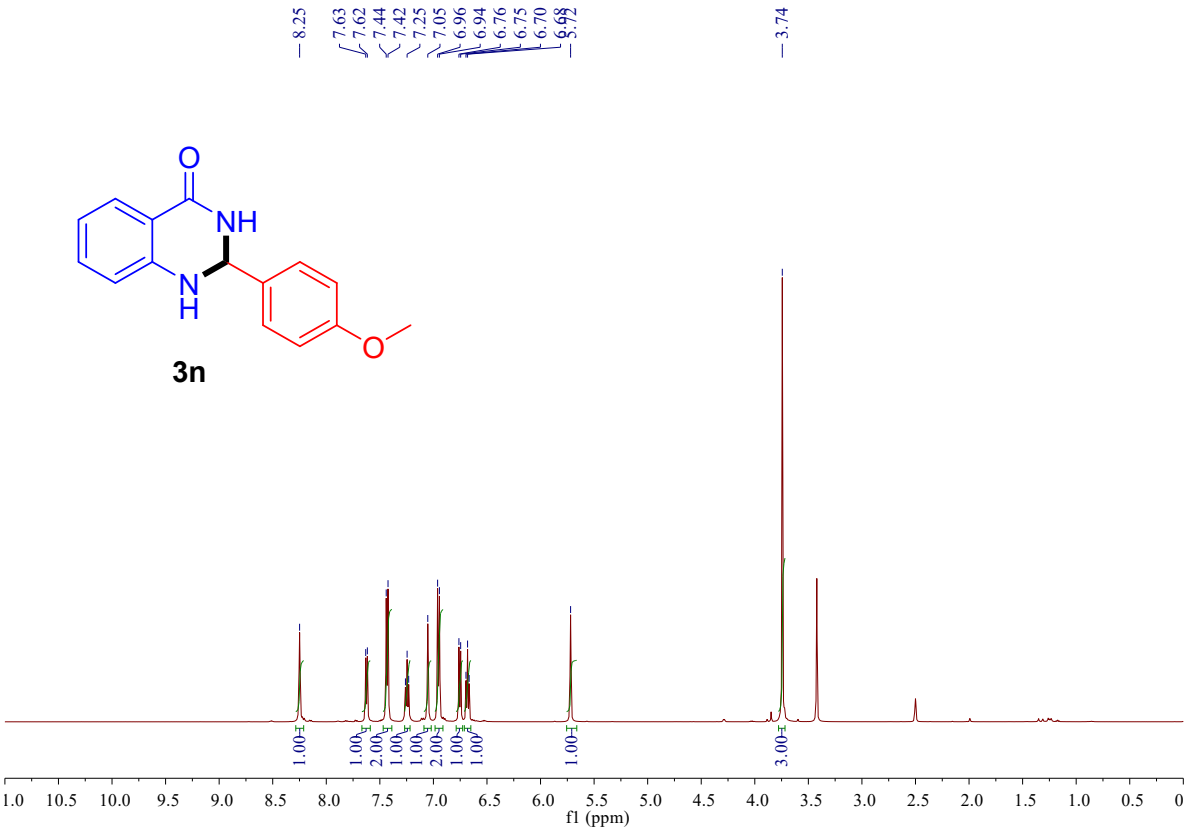
19.32
O
NH
N
H
3m
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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7.62
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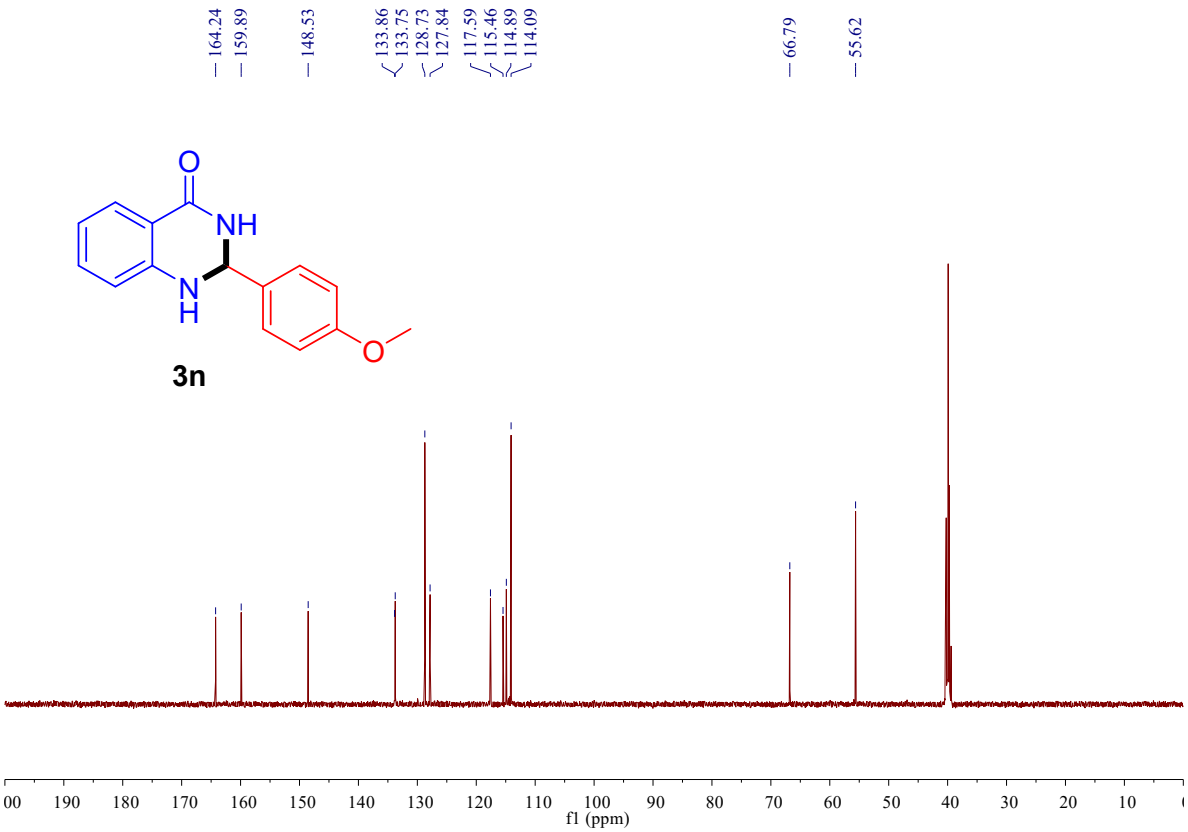
7.42
7.25
7.05
6.96
6.94
6.76
6.75
6.70
6.68
5.72
3.74
O
NH
N
H
O
3n
1.00
1.00
2.00
1.00
1.00
2.00
1.00
1.00
1.00
3.00
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)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133.75
128.73
127.84
117.59
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114.89
114.09
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NH
N
H
O
3n
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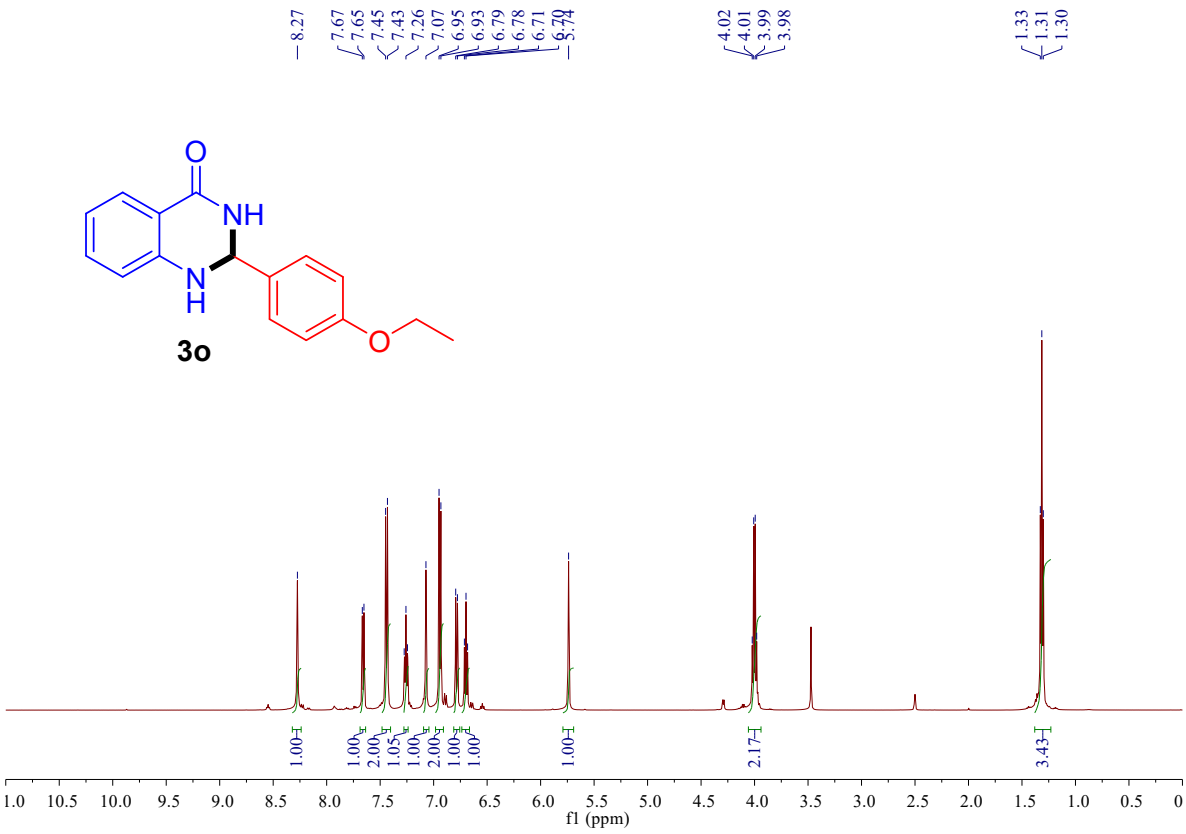
f1 (ppm)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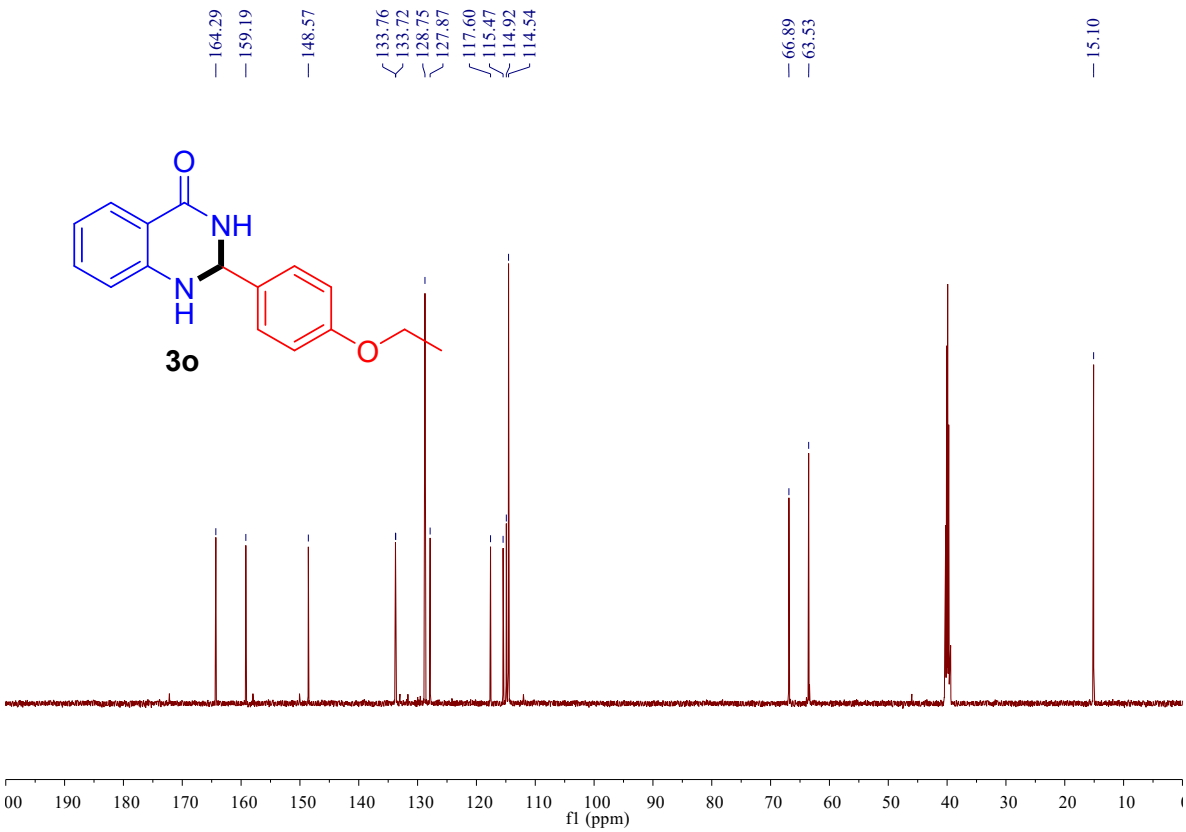
6.95
6.93
6.79
6.78
6.71
6.70
5.74
4.02
4.01
3.99
3.98
1.33
1.31
1.30
O
NH
N
H
O
3o
1.00
1.00
2.00
1.05
1.00
2.00
1.00
1.00
1.00
2.17
3.43
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)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148.57
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128.75
127.87
117.60
115.47
114.92
114.54
66.89
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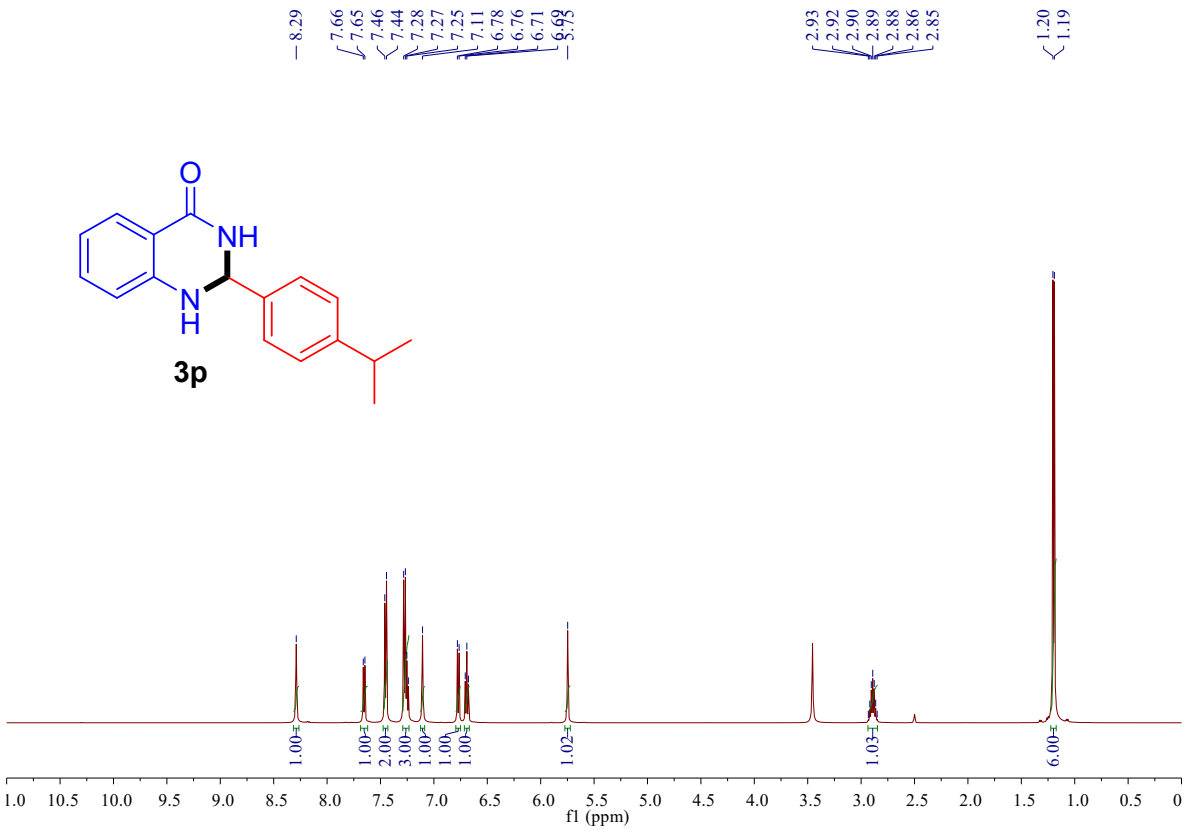
f1 (ppm)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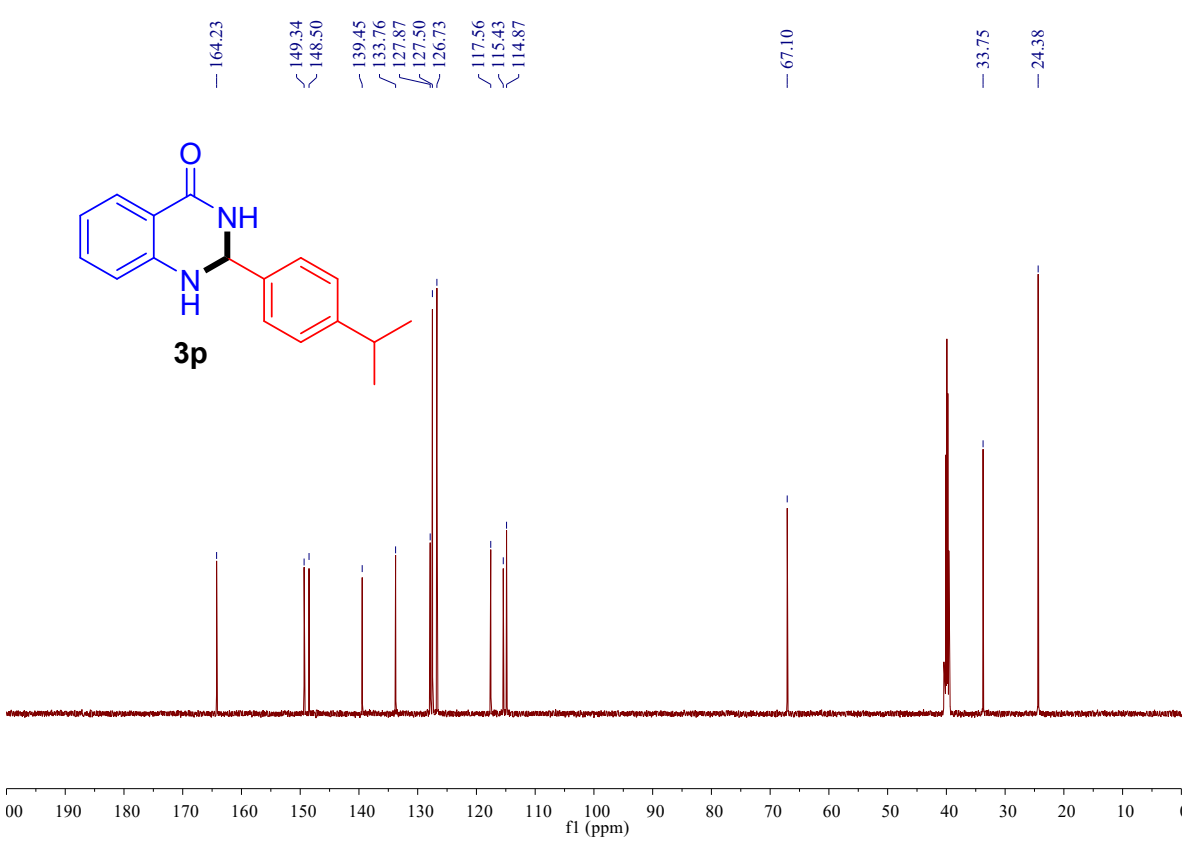
7.25
7.11
6.78
6.76
6.71
6.69
3.93
2.93
2.92
2.90
2.89
2.88
2.86
2.85
1.20
1.19
O
NH
N
H
3p
1.00
1.00
2.00
3.00
1.00
1.00
1.00
1.02
1.03
6.00
f1 (ppm)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67.10
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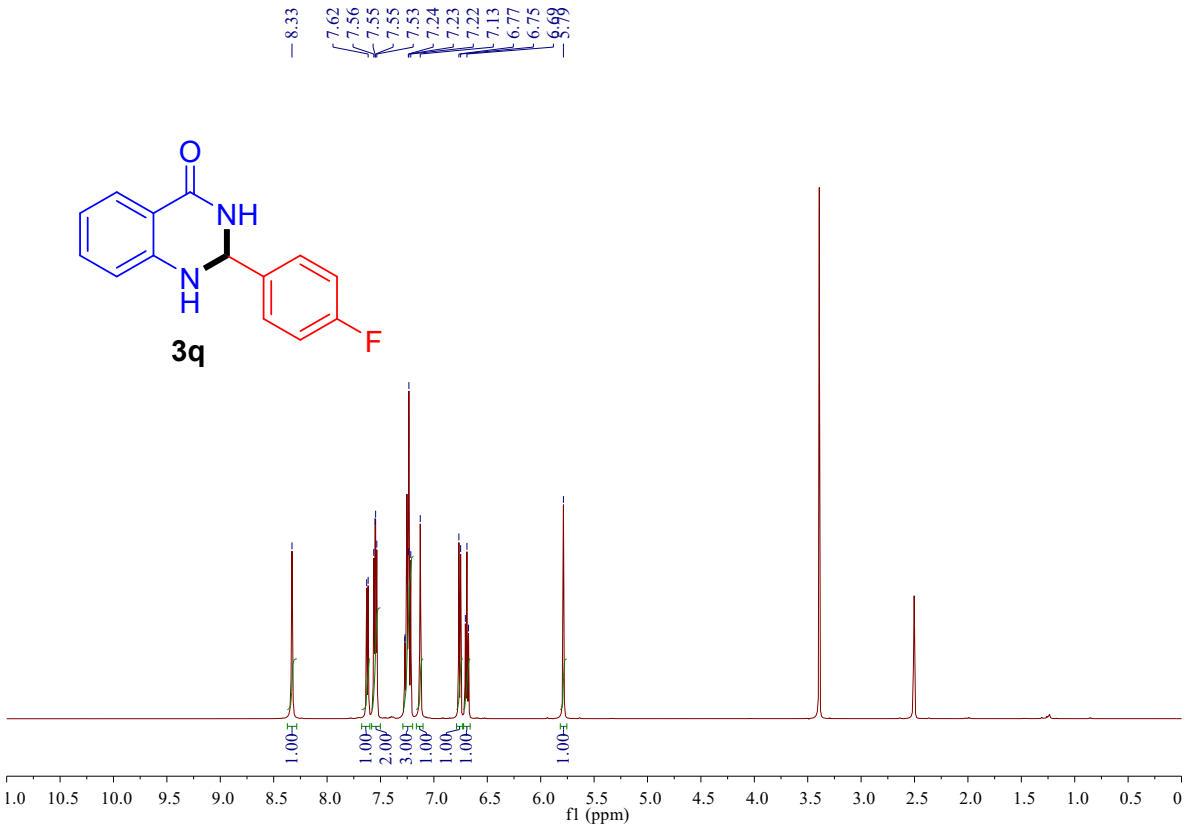
NH
N
H
3p
f1 (ppm)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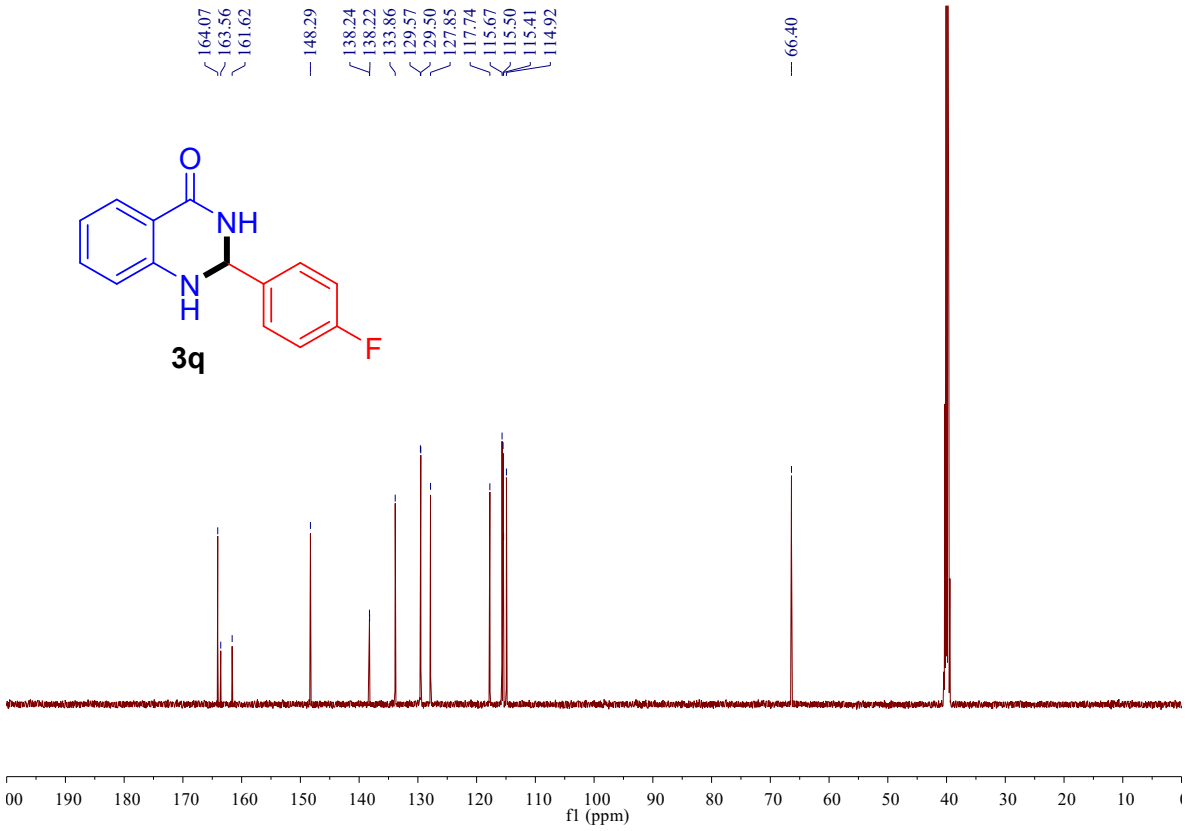
7.53
7.24
7.23
7.22
7.13
6.77
6.75
6.69
5.78
O
NH
N
H
F
3q
1.00
1.00
2.00
3.00
1.00
1.00
1.00
1.00
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)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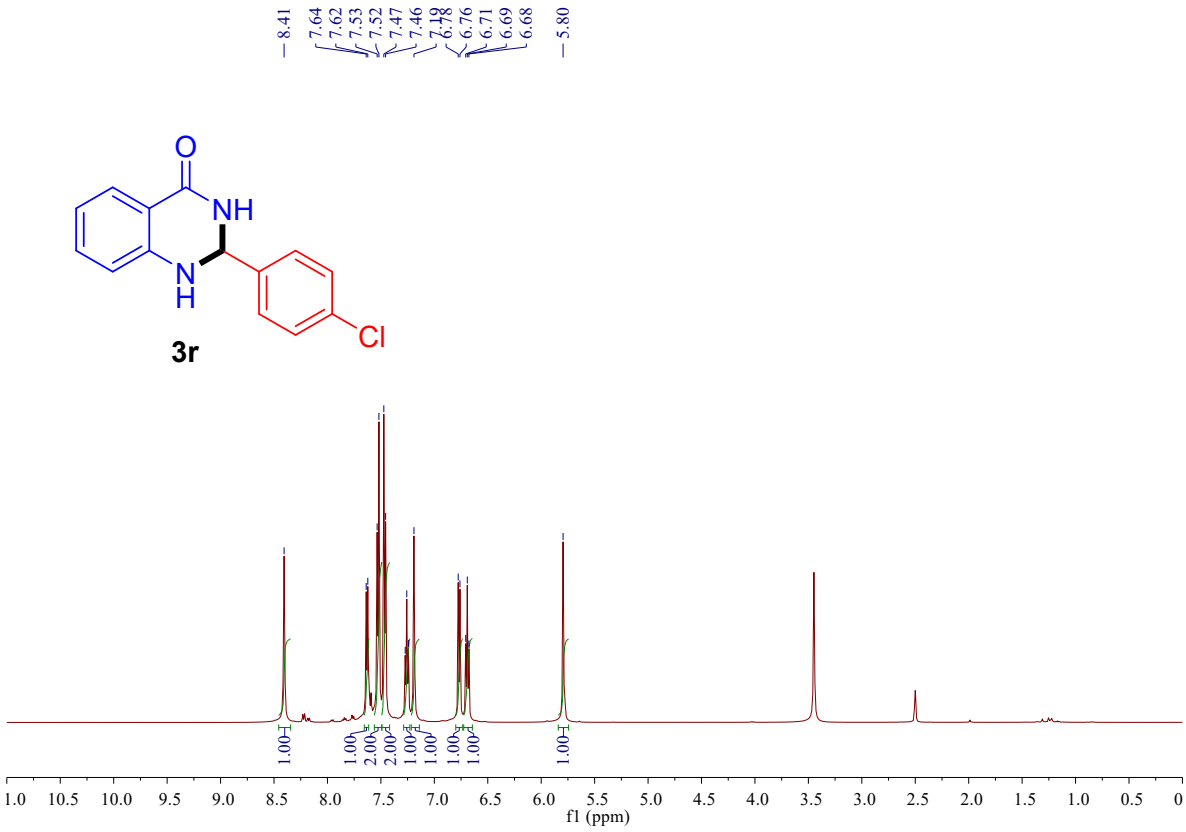
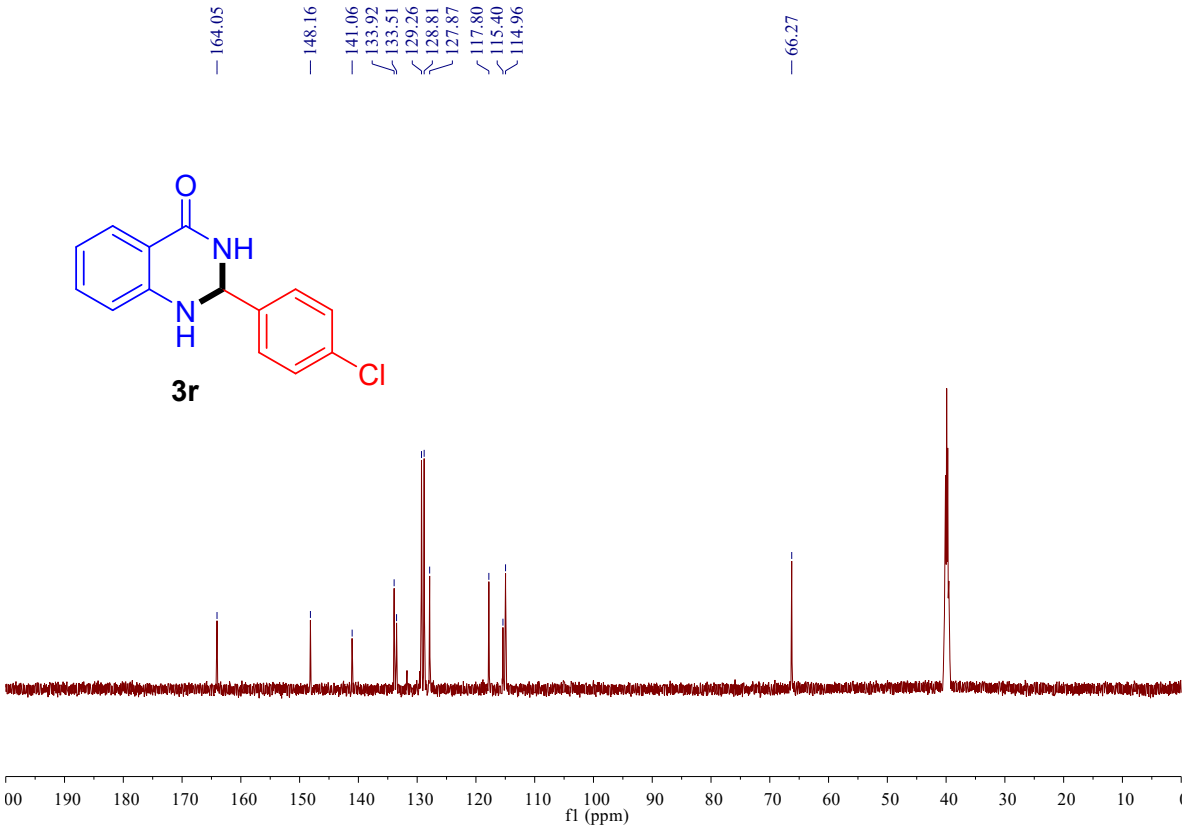
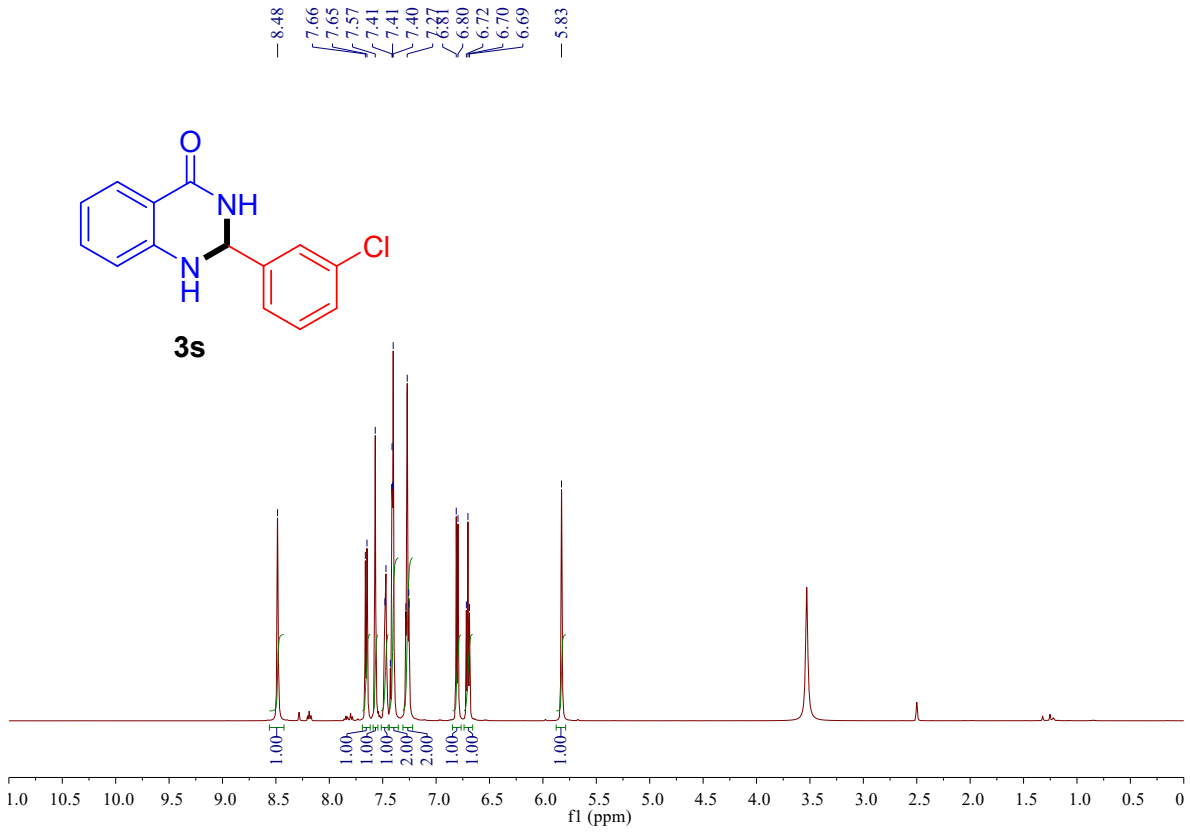
163.56
161.62
148.29
138.24
138.22
133.86
129.57
129.50
127.85
117.74
115.67
115.50
115.41
114.92
66.40
O
NH
N
H
F
3q
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


8.41
7.64
7.62
7.53
7.52
7.47
7.46
6.76
6.71
6.69
6.68
5.80
O
NH
N
H
Cl
3r
1.00
1.00
2.00
2.00
1.00
1.00
1.00
1.00
1.00
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)


164.05
148.16
141.06
133.92
133.51
129.26
128.81
127.87
117.80
115.40
114.96
66.27
O
NH
N
H
Cl
3r
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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7.66
7.65
7.57
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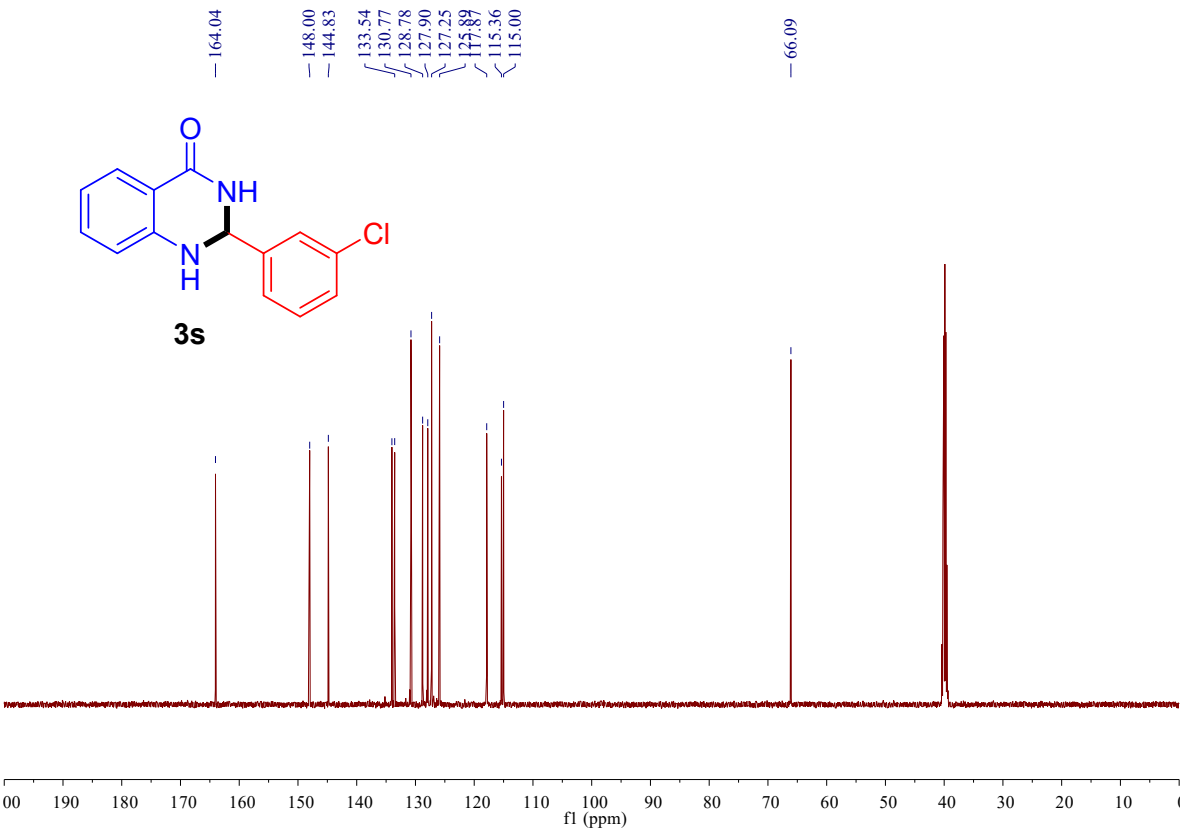
7.41
7.40
6.80
6.72
6.70
6.69
5.83
O
NH
N
H
Cl
3s
1.00
1.00
1.00
1.00
2.00
2.00
1.00
1.00
1.00
f1 (ppm)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144.83
133.54
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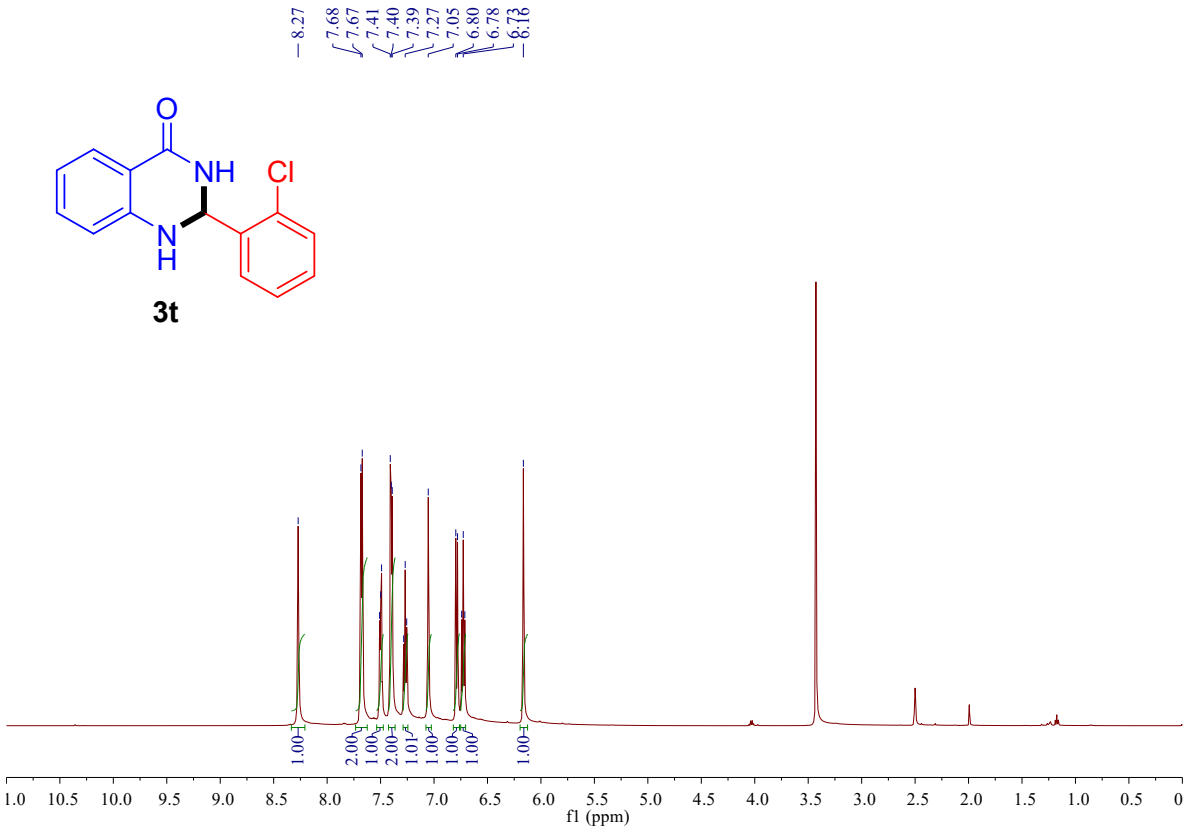
127.90
127.25
115.36
115.00
66.09
O
NH
N
H
Cl
3s
f1 (ppm)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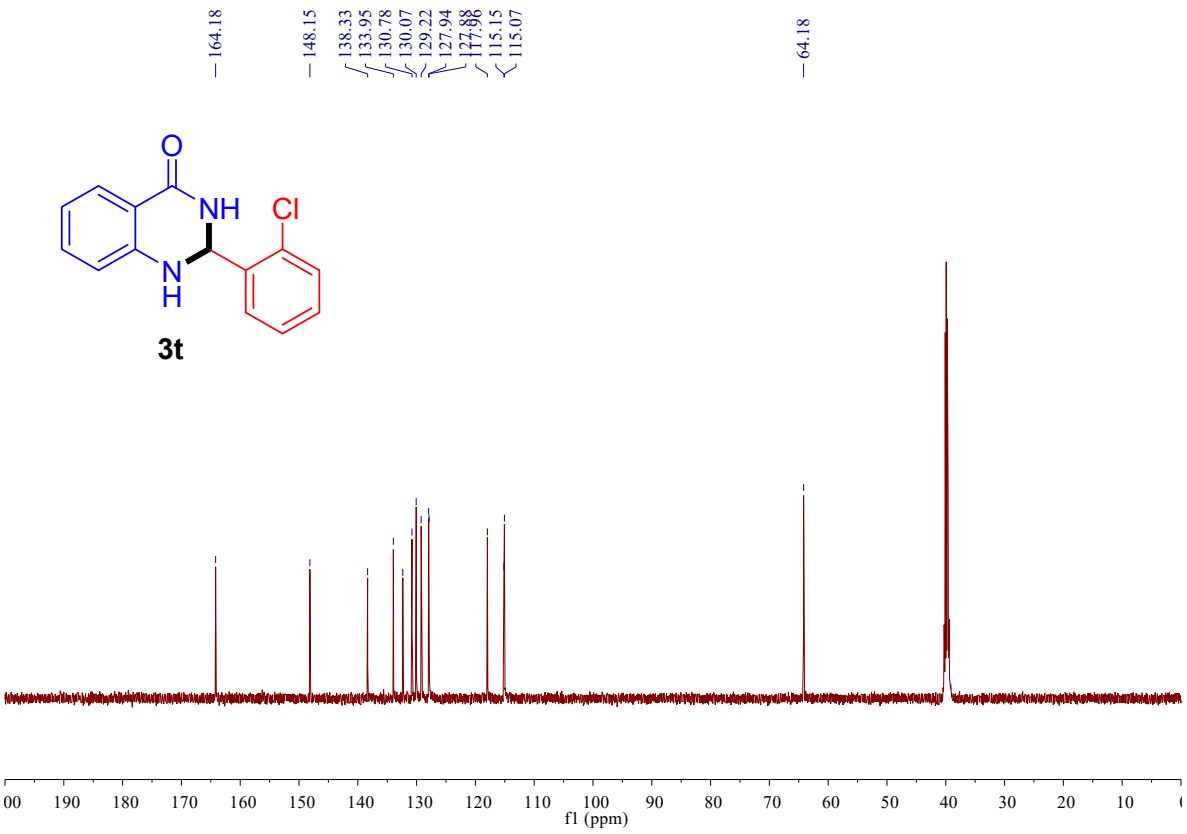
7.68
7.67
7.41
7.40
7.39
7.27
7.05
6.80
6.78
6.73
6.16
O
NH
Cl
N
H
3t
1.00
2.00
1.00
2.00
1.01
1.00
1.00
1.00
1.00
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)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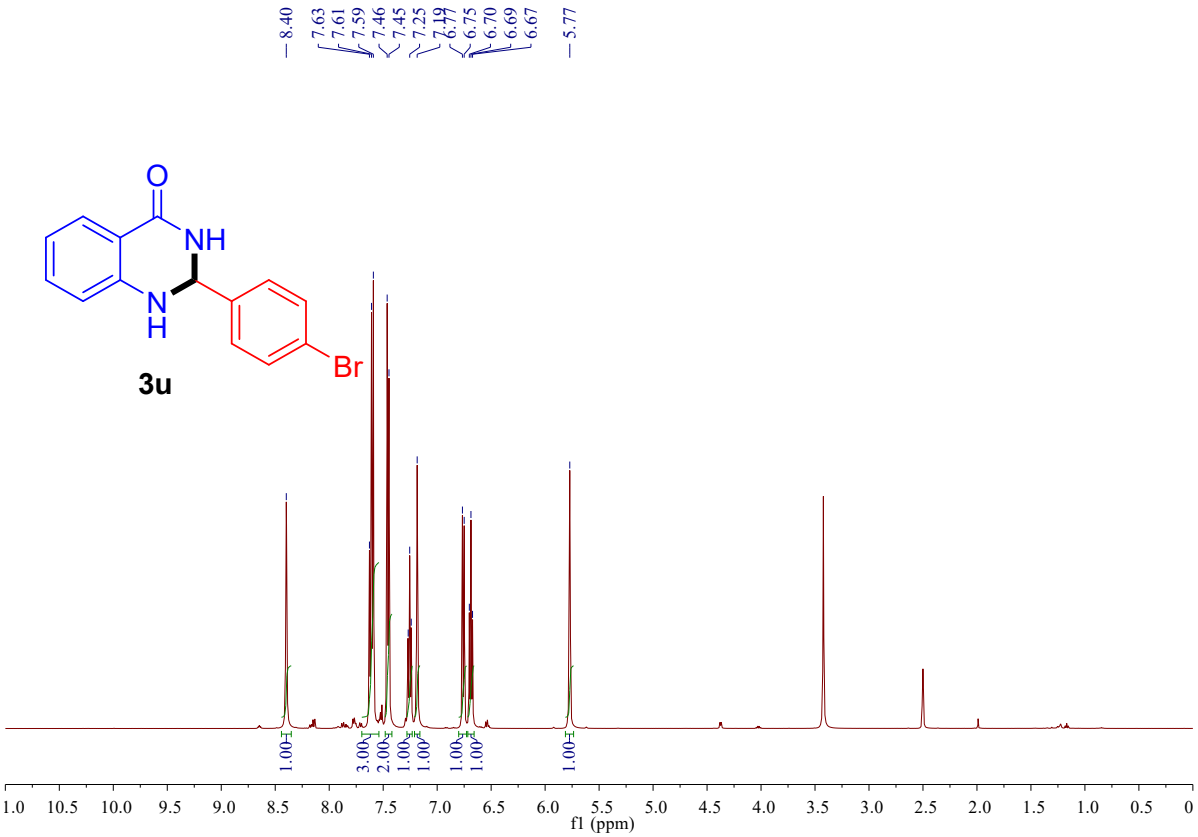
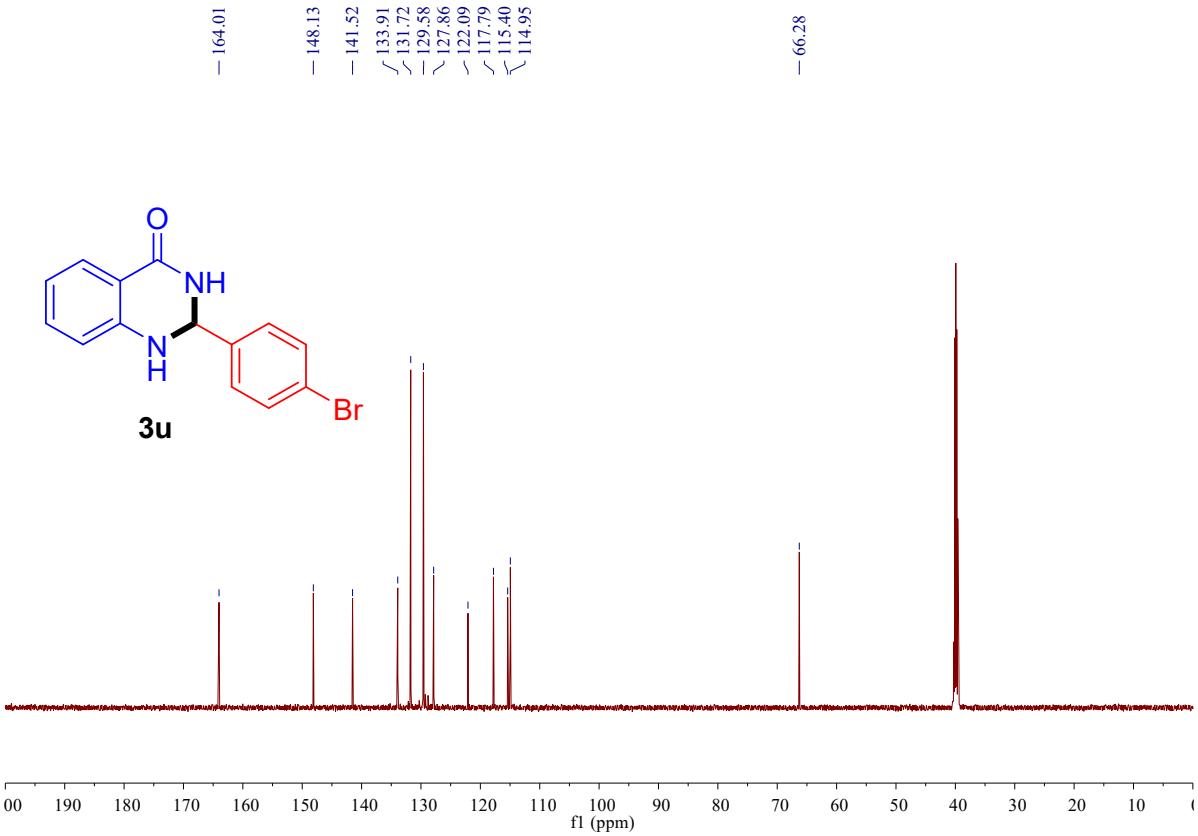
148.15
138.33
133.95
130.78
130.07
129.22
127.94
115.15
115.07
64.18
O
NH
Cl
N
H
3t
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


8.40
7.63
7.61
7.59
7.46
7.45
7.25
6.77
6.75
6.70
6.69
6.67
5.77
O
NH
N
H
Br
3u
1.00
3.00
2.00
1.00
1.00
1.00
1.00
1.00
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)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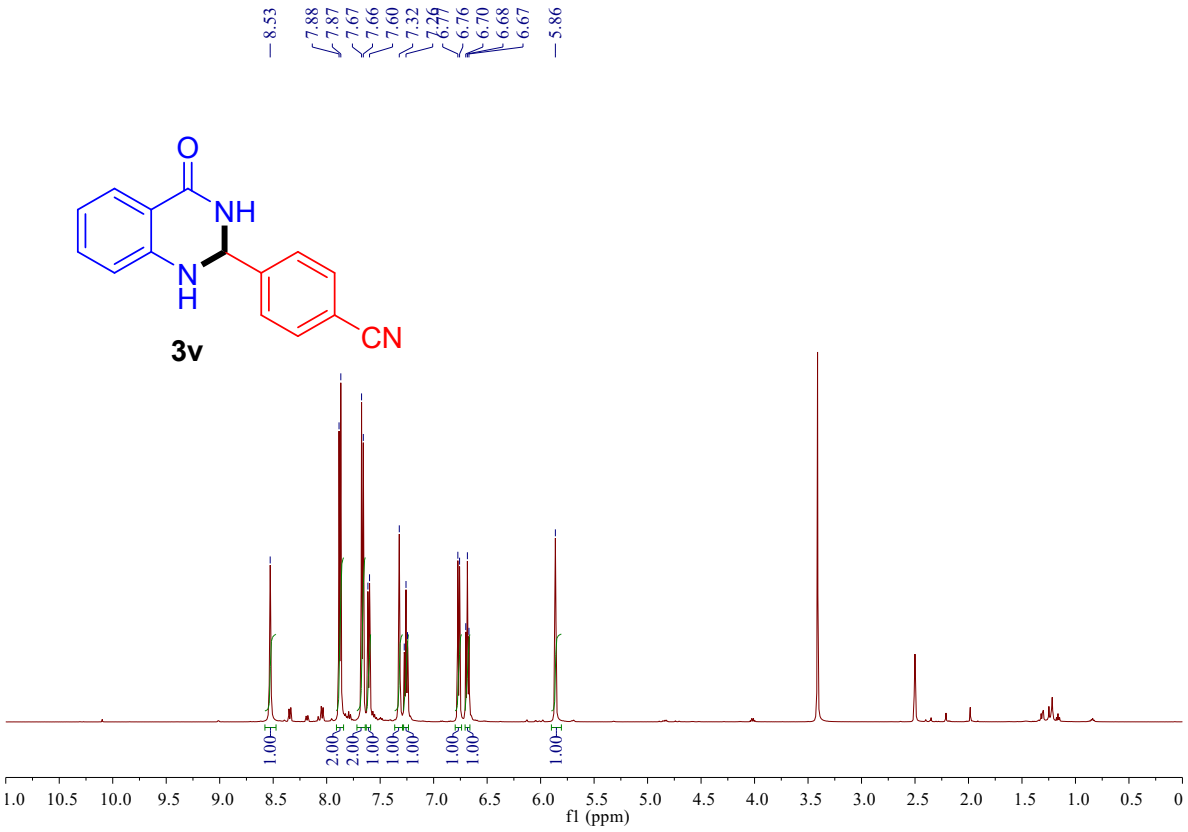
148.13
141.52
133.91
131.72
129.58
127.86
122.09
117.79
115.40
114.95
66.28
O
NH
N
H
Br
3u
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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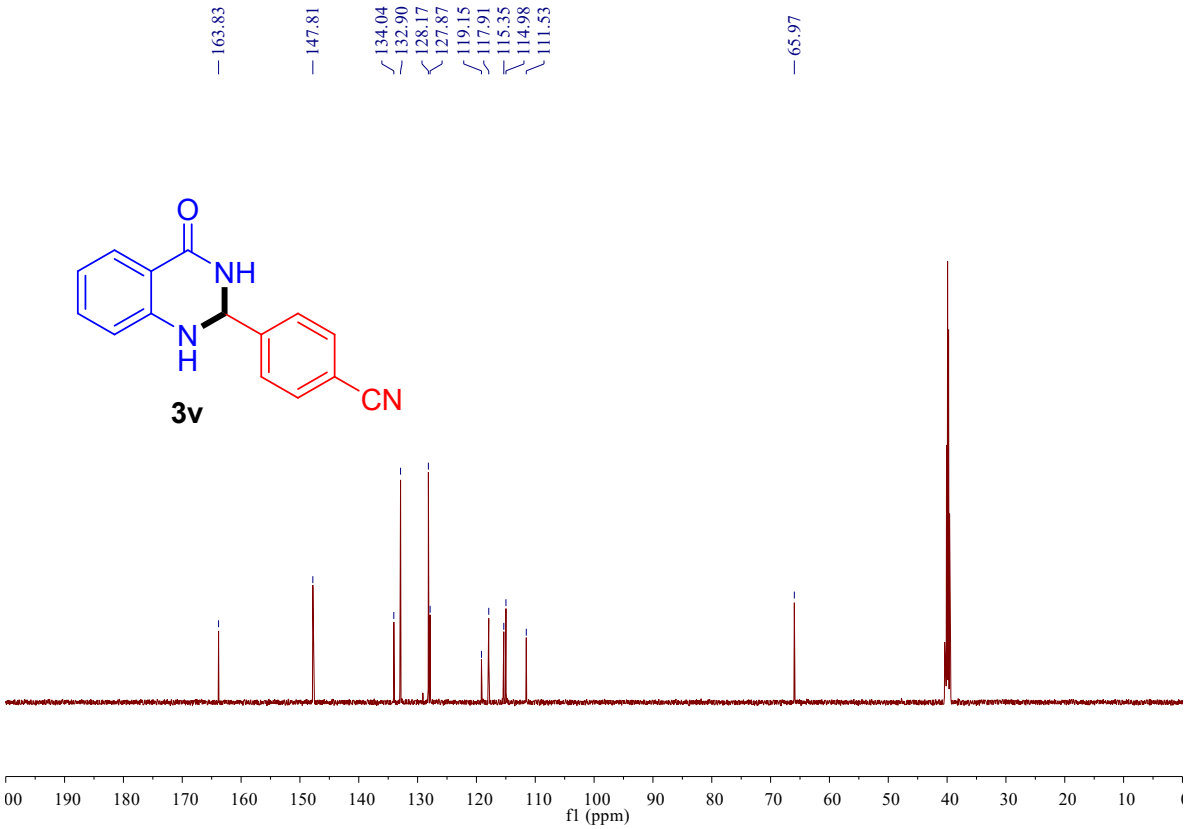
7.88
7.87
7.67
7.66
7.60
7.32
6.76
6.70
6.68
6.67
5.86
O
NH
N
H
CN
3v
1.00
2.00
2.00
1.00
1.00
1.00
1.00
1.00
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)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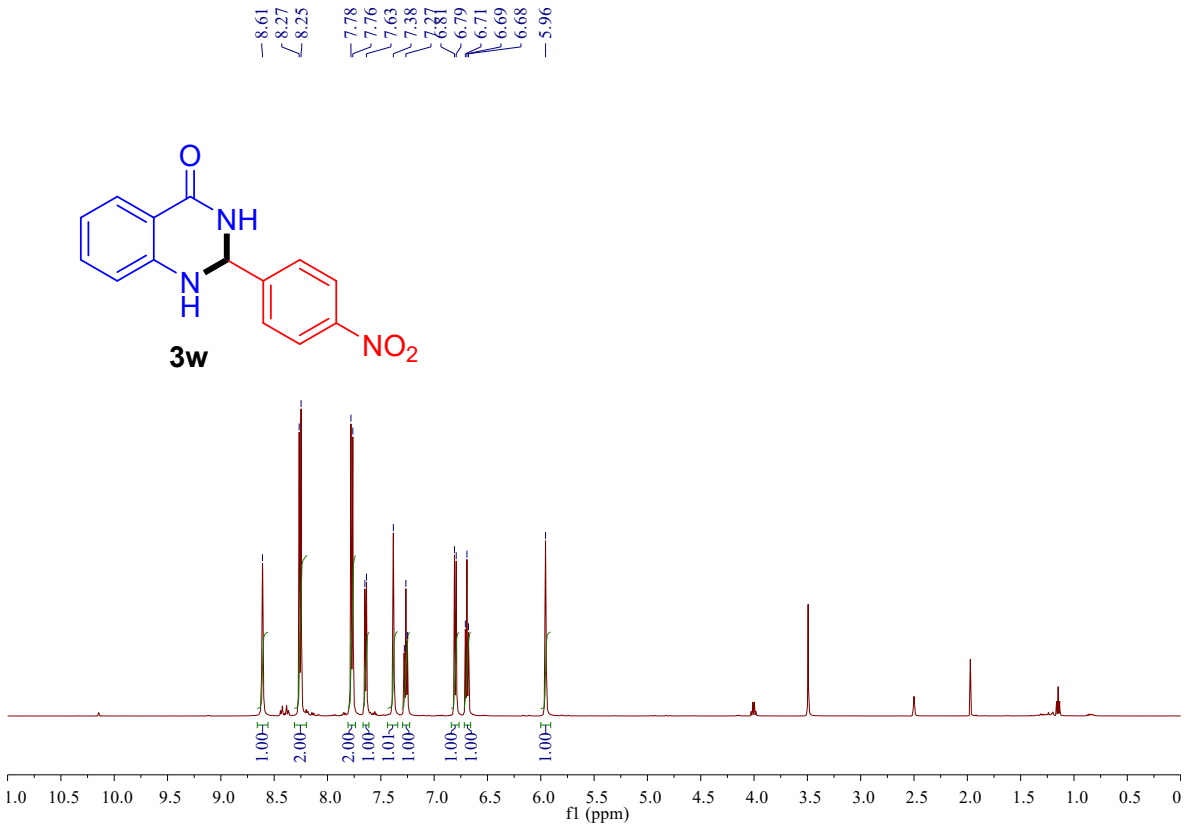
134.04
132.90
128.17
127.87
119.15
117.91
115.35
114.98
111.53
65.97
O
NH
N
H
CN
3v
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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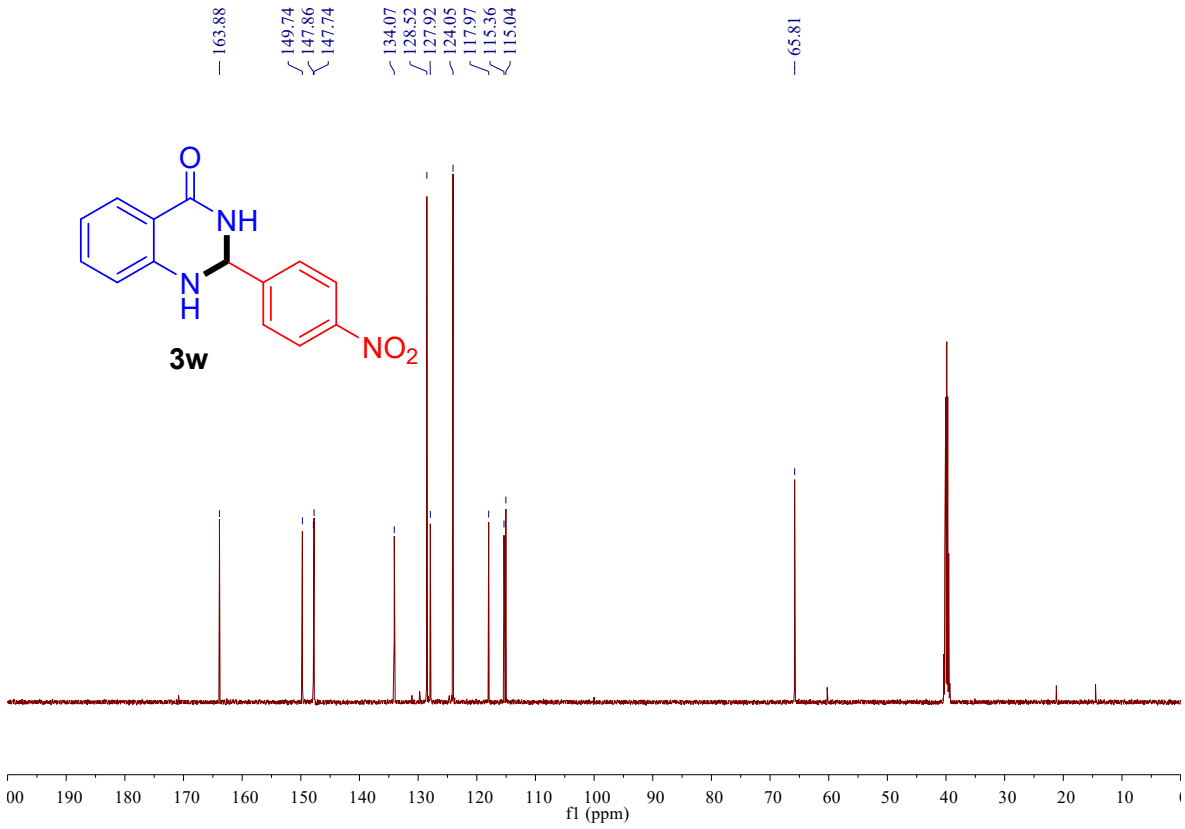
8.25
7.78
7.76
7.63
7.38
7.27
6.81
6.79
6.71
6.69
6.68
5.96
O
NH
N
H
NO2
3w
1.00
2.00
2.00
1.00
1.01
1.00
1.00
1.00
1.00
f1 (ppm)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147.74
134.07
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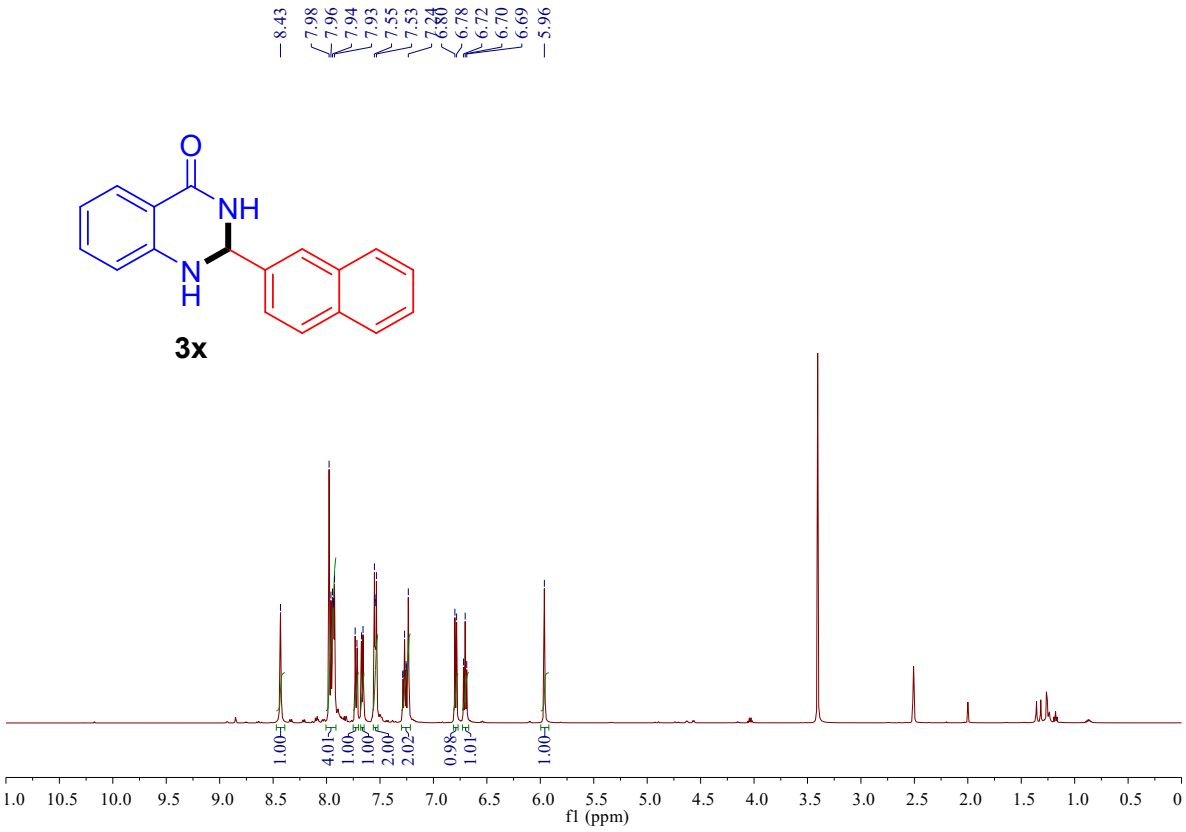
117.97
115.36
115.04
65.81
O
NH
N
H
NO2
3w
f1 (ppm)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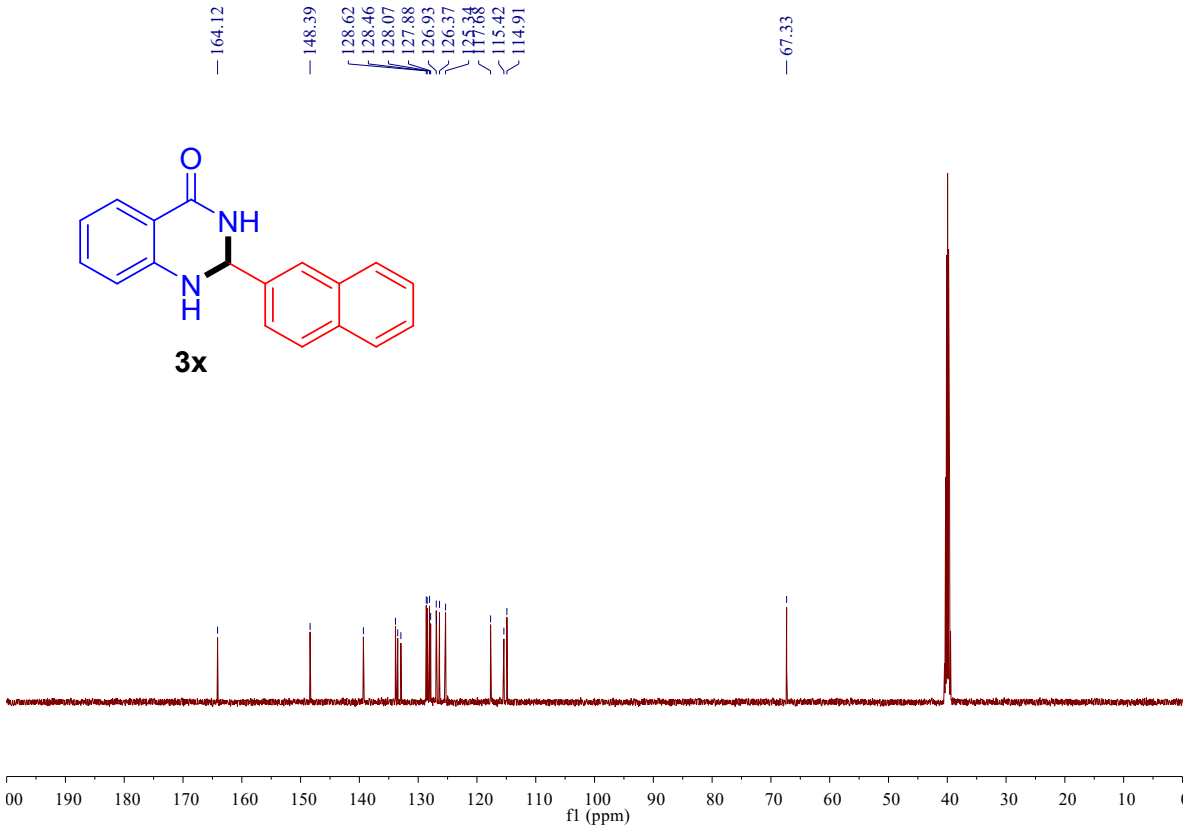
7.96
7.94
7.93
7.55
7.53
7.24
6.80
6.78
6.72
6.70
6.69
5.96
O
NH
N
H
3x
1.00
4.01
1.00
1.00
2.00
2.02
0.98
1.01
1.00
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)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128.46
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126.37
125.34
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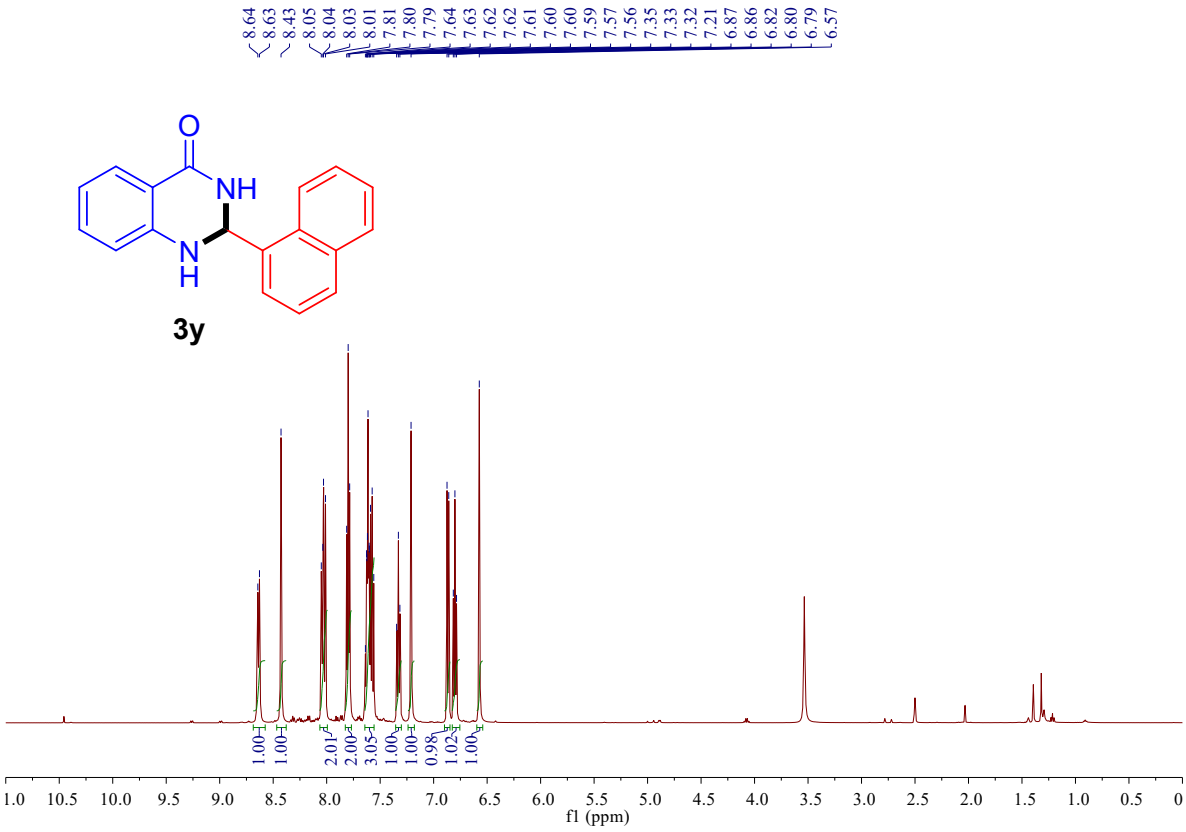
67.33
O
NH
N
H
3x
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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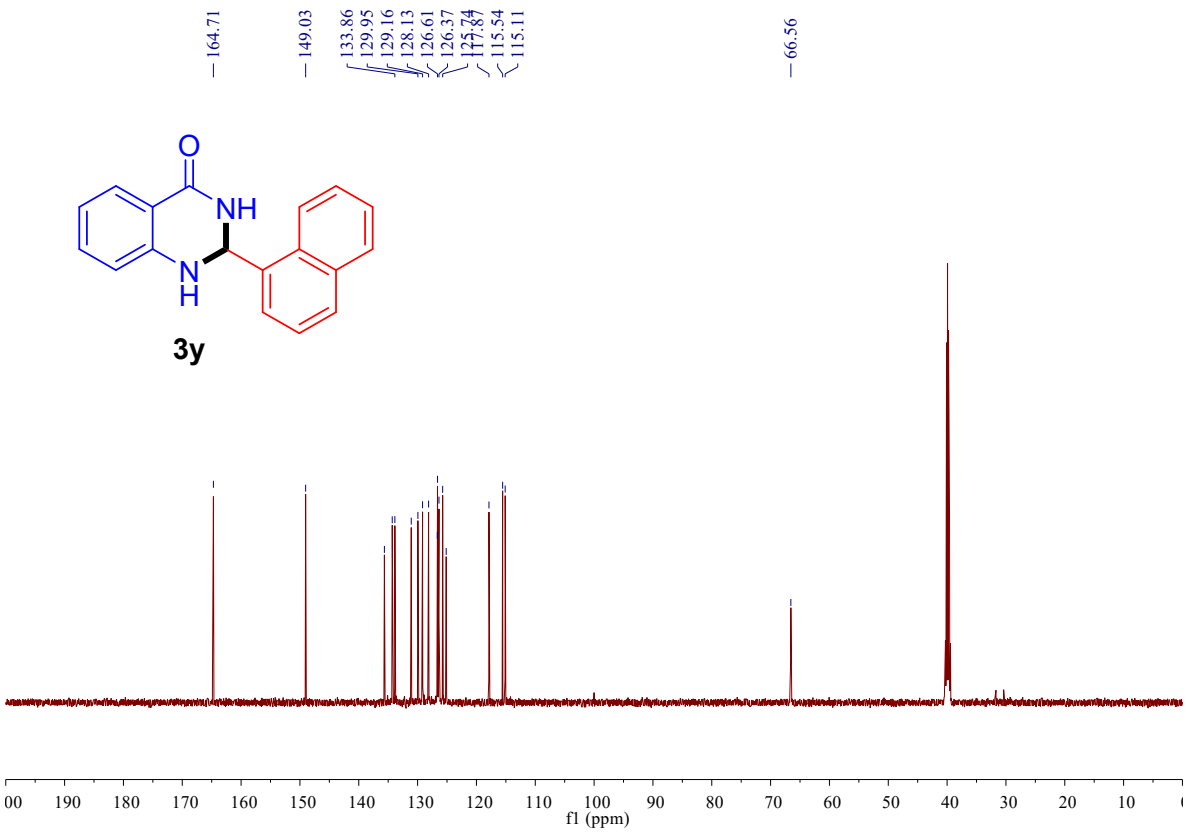
8.04
8.03
8.01
7.81
7.80
7.79
7.64
7.63
7.62
7.62
7.61
7.60
7.60
7.59
7.57
7.56
7.35
7.33
7.32
7.21
6.87
6.86
6.82
6.80
6.79
6.57
O
NH
N
H
3y
1.00
1.00
2.01
2.00
3.05
1.00
1.00
0.98
1.02
1.00
f1 (ppm)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129.95
129.16
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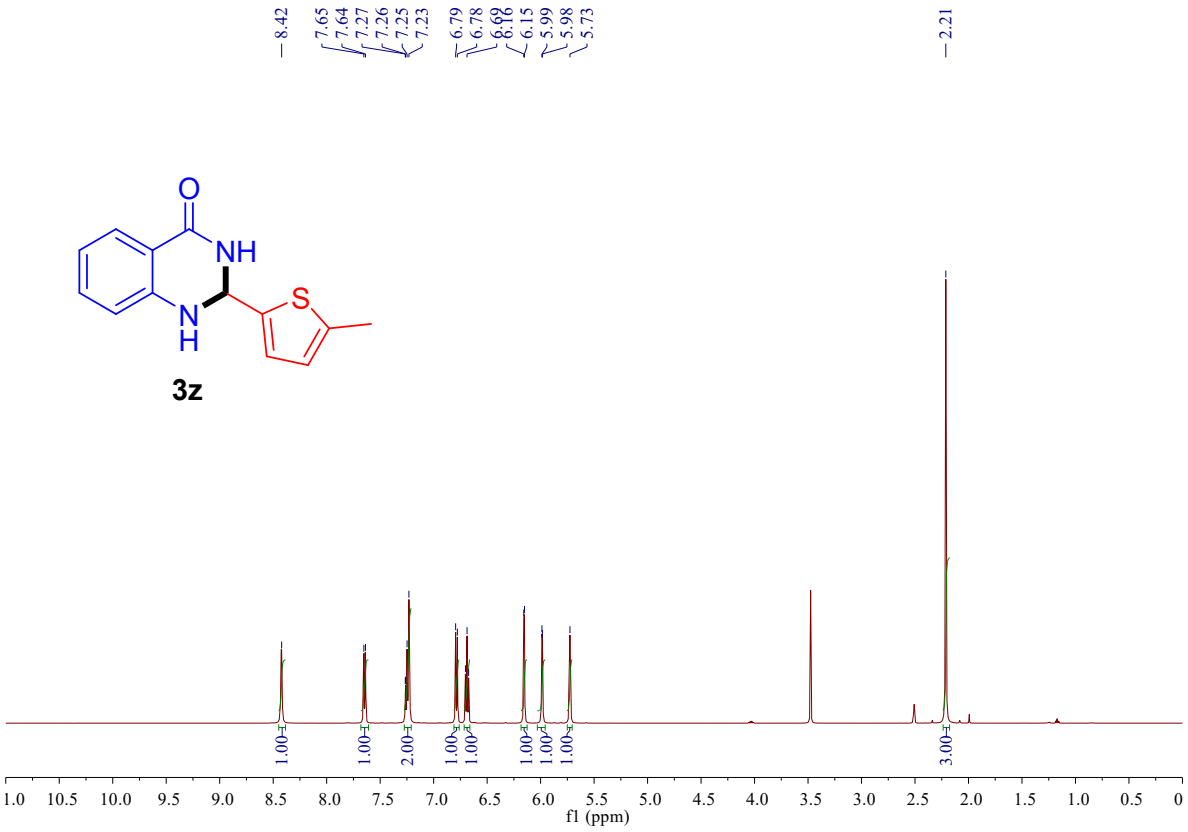
125.74
117.87
115.54
115.11
66.56
O
NH
N
H
3y
f1 (ppm)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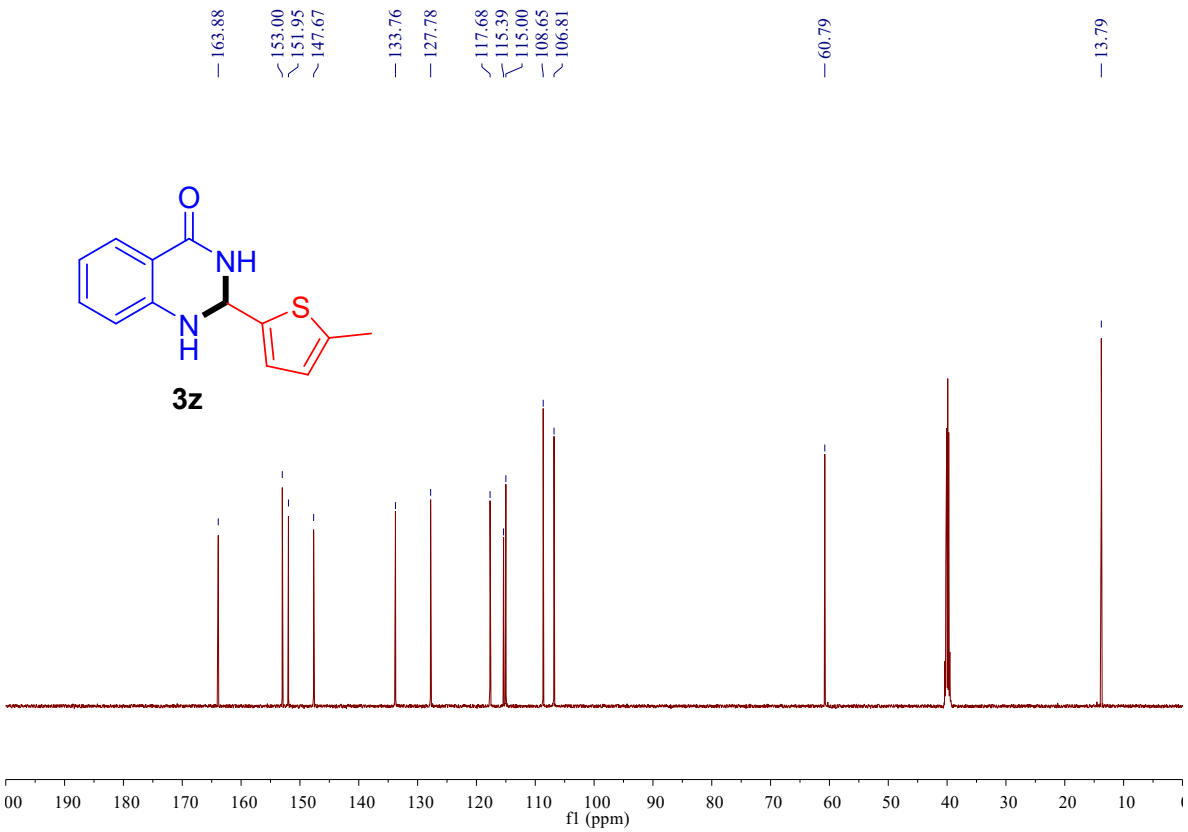
7.26
7.25
7.23
6.79
6.78
6.69
6.68
6.15
5.99
5.98
5.73
2.21
O
NH
N
H
S
3z
1.00
1.00
2.00
1.00
1.00
1.00
1.00
1.00
3.00
f1 (ppm)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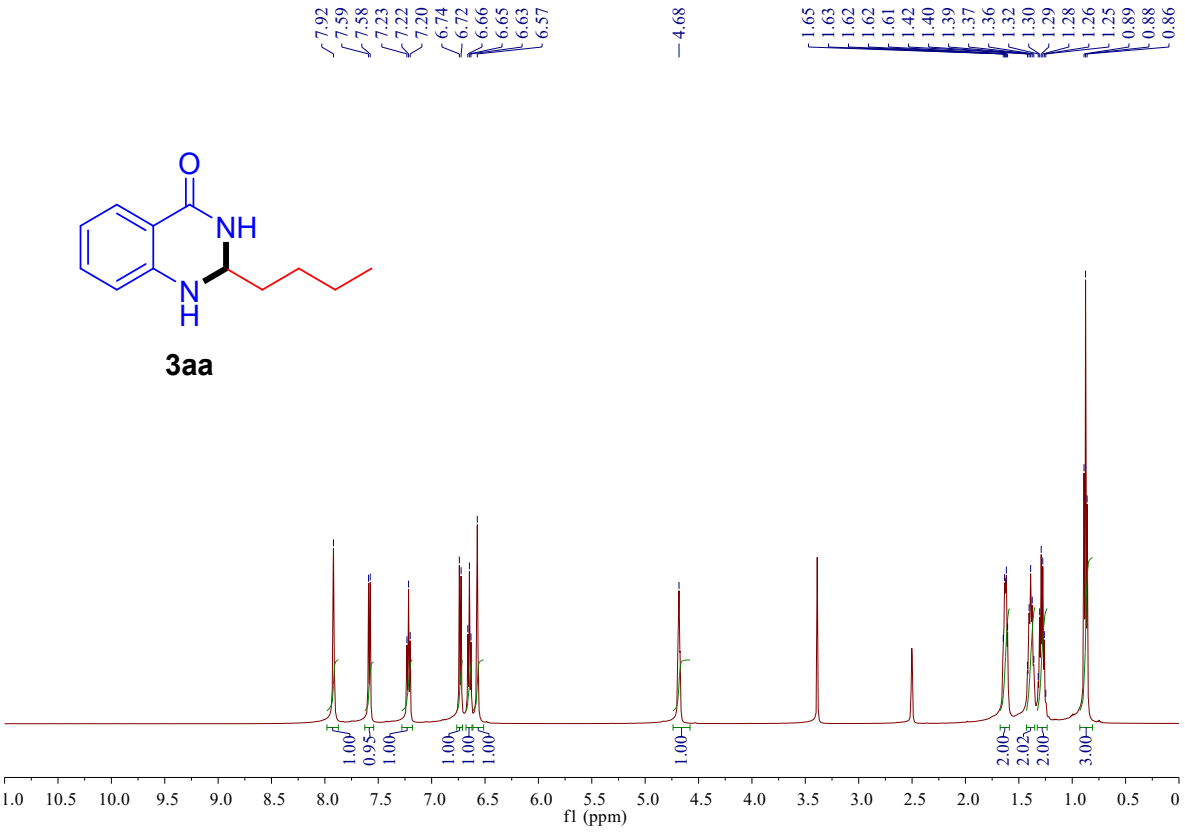
133.76
127.78
117.68
115.39
115.00
108.65
106.81
60.79
13.79
O
NH
N
H
S
3z
f1 (ppm)


7.92
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7.23
7.22
7.20
6.74
6.72
6.66
6.65
6.63
6.57
4.68
1.65
1.63
1.62
1.62
1.61
1.42
1.40
1.39
1.37
1.36
1.32
1.30
1.29
1.28
1.26
1.25
0.89
0.88
0.86
O
NH
N
H
3aa
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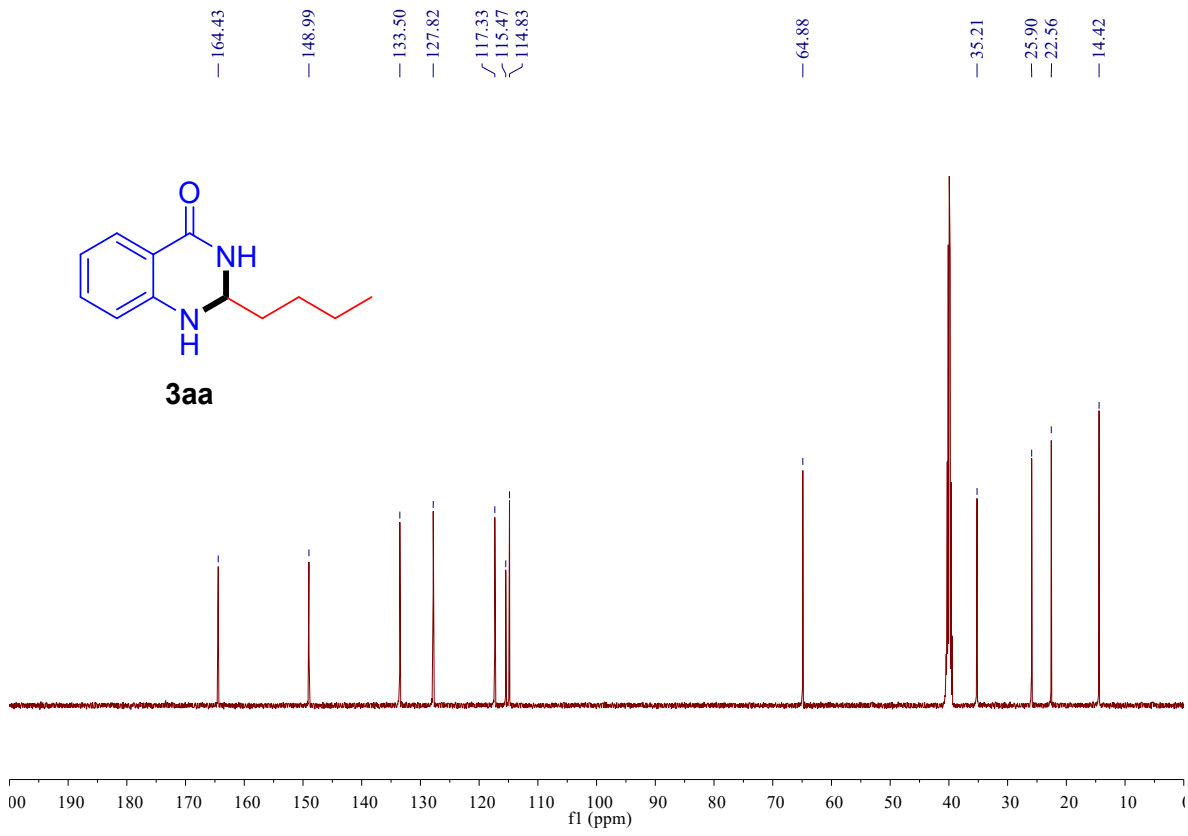
0.95
1.00
1.00
1.00
1.00
1.00
2.00
2.02
2.00
3.00
f1 (ppm)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117.33
115.47
114.83
64.88
35.21
25.90
22.56
14.42
O
NH
N
H
3aa
f1 (ppm)

7. Reference

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