Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting information

A Bifunctional Molecular Catalyst Builtup of L-Proline Grafted Polyoxometalate for One-pot Three-component Green Synthesis of Heterocycles

Guoyong Dai, [a,b] Qi Li, [a] Dejin Zang, *[a, c] and Yongge Wei, *[a, b]

[a] G. Dai, Q. Li, Dr D. Zang,* Prof. Dr. Y. Wei* Key Lab of Organic Optoelectronics & Molecular Engineering of Ministry of Education, Department of Chemistry, Tsinghua University, Beijing 100084, P. R. China E-mail: yonggewei@tsinghua.edu.cn

[b] Prof. Dr. Y. Wei* State Key Laboratory of Natural and Biomimetic Drugs, Peking University, Beijing 100191, P.R. China. E-mail: ygwei@pku.edu.cn

[c] Prof. Dr. D. Zang,* School of Pharmacy and Pharmaceutical Sciences & Institute of Materia Medica, Shandong First Medical University & Shandong Academy of Medical Sciences, NHC Key Laboratory of biotechnology drugs (Shandong Academy of Medical Sciences), Key Lab for Rare & Uncommon Diseases of Shandong Province, Jinan 250117, China. E-mail: zangdejin_lm@163.com

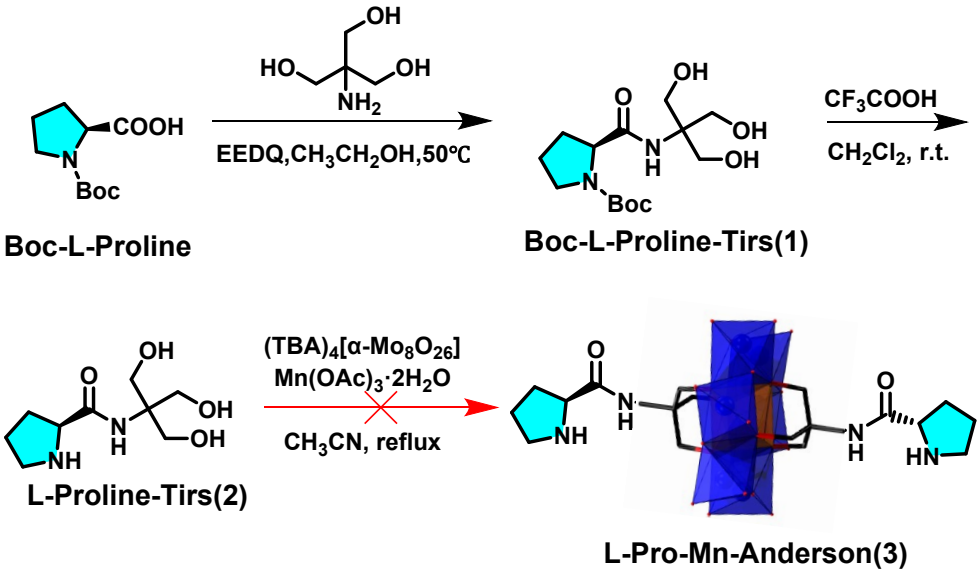
Contents

1. General experimental conditions.

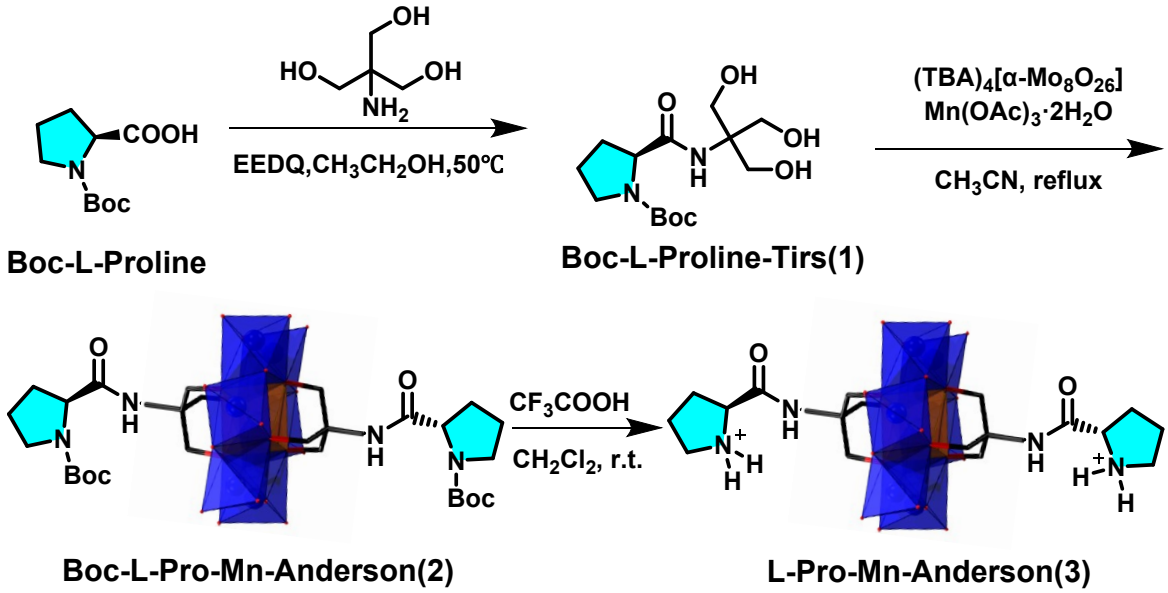
Mn-Anderson POMs were prepared according to literature methods[1]. All reagents were purchased without further treatment except dimethylacetamide (DMAC). DMAC was dried with calcium hydride before use. 1H-NMR spectra were recorded using a JEOL JNM-EXC 400 spectrometer. ESI-MS spectra were recorded on a Thermo Q Exactive spectrometer. Elemental analysis was measured with Elementar Vario EL III element analyzer. Infrared spectroscopy was recorded on a Bruker Vertex FT-IR spectrometer with a diamond ATR mode in the range of 400−4000 cm^{-1}. X-ray photoelectron spectroscopy (XPS) experiments were carried out on a scanning X-ray microprobe (ESCALAB Xi+, Thermo Fisher Scientific) operated at 15 kV and 100 eV with monochromated Al K_α radiation. The XPS spectra were calibrated with C1s = 284.8 eV and fitted using XPSPEAK41 software with Shirley background type and free parameters. The CD spectra were recorded on a circular dichroism chiroptical spectrometer (Chirascan plus) at 20 °C. A suitable single crystal of compound **2** and **3** was selected. Data collection was performed using graphite-monochromated Cu K_α radiation (λ = 1.5418 Å). Data reduction, cell refinement, and experimental absorption correction were performed with a software package. Data collection and reduction were performed in CrysAlisPro 1.171.39.46. The structure solution and refinement were performed with SHLEX-97[2] and Olex1.2.[3] The multi-scan method was used for the absorption correction. The structure was solved by direct methods and refined against F^2 by full matrix least-squares techniques. All non-hydrogen atoms were refined anisotropically. Crystal data and CCDC codes were listed in Table S1.

2. Synthesis and characterization of L-Pro-Mn-Anderson POM

Synthetic route 1:



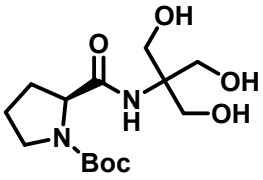
Synthetic route 2:



Scheme S1. Synthetic routes of L-proline grafted Mn-Anderson POM.

2.1 Compound 1: Boc-L-Pro-Tris

$C_{14}H_{26}N_2O_6$

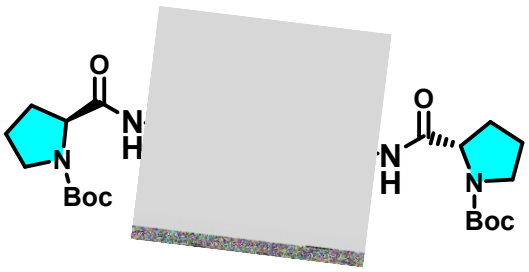


Mixture of Boc-L-Proline (2.15 g, 10 mmol), Tris (1.21 g, 10 mmol), EEDQ (1.2 eq, 2.97 g), CH_3CH_2OH (30 mL) in a 50 mL round bottle was stirred for 12 h at 50°C. After the reaction temperature was cooled down to the room temperature, the solvents were removed under vacuum and the pure purple product of Por-tris was obtained by crystallization in ethyl acetate (m=2.83 g, yield=89 %). **Yield:** 2.83 g, 89 %;

^{1}H NMR (400 MHz, D_2O):δ 4.14 (d, J = 19.9 Hz, 1H), 3.66 (s, 6H), 3.32 (d, J = 6.9 Hz, 2H), 2.15 (d, J = 8.2 Hz, 1H), 1.91 – 1.68 (m, 3H), 1.32 (d, J = 10.6 Hz, 9H).**^{13}C NMR (100 MHz, CD_3Cl,)**: δ 174.56 (s), 155.72 (s), 81.22 (s), 64.86 (s), 62.11 (s), 61.43 (s), 61.10 (s), 47.42 (s), 30.02 (s), 28.40 (s), 24.67 (s). **ESI-MS**(C14H26N2O6): [M-1], 317.4.

2.2 Compound 2: Boc-L-Pro-Mn-Anderson POM

$[(C_4H_9)_4N]_3\{MnMo_6O_{18}[(OCH_2)_3CNHC_{10}H_{16}NO_3]_2\}$

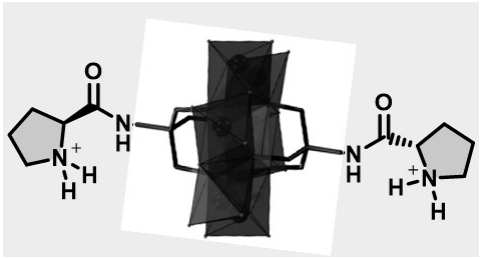


A mixture of $(TBA)_4[\alpha\text{-}Mo_8O_{26}]$[4] (4.31 g, 2 mmol), $Mn(OAc)_3{\cdot}2H_2O$ (0.80 g, 3 mmol) and Boc-L-Pro-Tris (0.64 g; 7 mmol) was refluxed in MeCN (100 mL) for 16 h. The resulting bright orange solution was allowed to cool down to room

temperature. This crude mixture was purified *via* crystallization by Et_2O diffusion. After a day, orange crystals were formed, isolated and analyzed. Single crystals suitable for X-ray diffraction were grown from MeCN by slow Et_2O diffusion.

Yield: 4.98 g, 0.476 mmol, 82 % based on Mo; **^{1}H NMR** (600 MHz, ACETONITRILE-D3) 1H NMR (600 MHz, ACETONITRILE-D3) δ 4.33 – 4.01 (m, 2H), 3.43 (s, 2H), 3.30 (s, 2H), 3.11 (s, 24H), 1.82 (d, J = 36.1 Hz, 6H), 1.62 (s, 24H), 1.40 (d, J = 41.0 Hz, 42H), 0.97 (s, 36H), 60.0-66.0 ppm (s, br, $6CH_2$); **IR(ATR)**:ν (cm^{-1}) 3436 (w), 3065 (m), 2966 (ν C-H, S), 2877 (ν C-H, S), 1687 (ν C=O, S), 1553 (m), 1477 (m), 1396 (m), 1311 (W), 1252 (W), 1166 (m), 1117 (m), 1030 (m), 943 (ν Mo=O, vs), 924 (ν Mo=O, vs), 905 (ν Mo=O, vs), 665 (ν Mo-O-Mo, vs, br.), 564 (m). **Elemental analysis:** Calc. for $[(C_4H_9)_4N]_3\{MnMo_6O_{18}[(OCH_2)_3CNHC_{10}H_{16}NO_3]_2\}$ (2276.67 $g.mol^{-1}$): C 38.70, H 6.03, N 7.09 Found: C 38.62, H 6.03, N 7.09. ESI-MS: Peak envelopes were observed with central peaks at m/z 896. 442(z = -2), 516. 867(z = -3) were assigned as $[(C_4H_9)_4N]\{MnMo_6O_{18}[(OCH_2)_3CNHC_{10}H_{16}NO_3]_2\}^{2-}$ (predicted: 895.865) and $\{MnMo_6O_{18}[(OCH_2)_3CNHC_{10}H_{16}NO_3]_2\}^{3-}$ (predicted: 516.42), respectively.

2.3 Compound 3: L-Pro-Mn-Anderson POM $[(C_4H_9)_4N]H_2\{MnMo_6O_{18}[(OCH_2)_3CNHC_5H_8NO]_2\}$



At 0 °C the $[(C_4H_9)_4N]_3\{MnMo_6O_{18}[(OCH_2)_3CNHC_{10}H_{16}NO_3]_2\}$(2.28 g, 1 mmol) was added to the solution of CF_3COOH (2.5 mL) in CH2Cl2 (10 mL), and then the reaction mixture was warmed to room temperature and stirred for 4 h before removal of all solvents in vacuo to yield the product as the corresponding TFA salt. This was then dissolved in DMF (10 mL). To the suspension, 5 mL of 1.0 M tetrabutylammonium hydroxide in methanol was added. After stirring for 30

minutes, add CH_2Cl_2(30 mL), the resulting solids were obtained by the centrifugal separation and washed dichloromethane. Single crystals suitable for X-ray diffraction were grown from DMSO by slow Et_2O diffusion.

Yield: 1.035 g, 0.476 mmol, 81.1 % based on Mo; **^{1}H NMR** (400 MHz, DMSO-D6) δ 65.00 (s, 5H), 1H NMR (400 MHz, DMSO-D6) δ 4.34 (s, 2H), 3.30 (s, 2H), 3.13 (s, 8H), 2.22 (s, 2H), 1.83 (d, J = 38.9 Hz, 6H), 1.53 (s, 8H), 1.27 (s, 8H), 0.90 (s, 12H); **IR(ATR)**:ν (cm^{-1}) 3446 (w),3088 (ν C-H, m), 2967 (ν C-H, m), 2878 (ν C-H, m), 1684 (ν C=O, s), 1568 (m), 1463 (m), 1386 (m), 1324 (W),1204(s), 1164 (s), 1052 (m), 949 (ν Mo=O, vs), 921 (ν Mo=O, vs), 901 (ν Mo=O, vs), 793 (m), 670 (ν Mo-O-Mo, vs, br.), 570(m). **Elemental analysis:** Calc. for $[(C_4H_9)_4N]H_2\{MnMo_6O_{18}[(OCH_2)_3CNHC_5H_8NO]$ (1593.51 $g.mol^{-1}$): C 38.70, H 6.03, N 7.09 Found: C 38.62, H 6.03, N 7.09. ESI-MS: Peak envelopes were observed with central peaks at m/z 1350.268 (z = -1), 676. 264(z = -2) were assigned as $H_2\{MnMo_6O_{18}[(OCH_2)_3CNHC_5H_8NO]_2\}^-$ (predicted: 1351.04) and $H\{MnMo_6O_{18}[(OCH_2)_3CNHC_5H_8NO]_2\}^{2-}$ (predicted: 675.015).

2.4 Single crystal XRD

Table S1. Crystal data and structure refinement for compound **2** and **3.**

Compound	2	3
CCDC number	2049197	2049194
Empirical formula	$C_{81}H_{161.5}MnMo_6N_{9.5}O_{30}$	$C_{46}H_{106}MnMo_{7.5}N_4O_{44}S_{14}$
Formula weight	2379.27	2642.67
Temperature/K	109.3(8)	293(2)
Crystal system	monoclinic	orthorhombic
Space group	$P2_1$	$P2_12_12$
a/Å	24.1600(5)	33.5555(4)
b/Å	14.7868(3)	30.4959(4)
c/Å	33.2539(11)	9.33799(9)
α/°	90	90
β/°	103.708(3)	90
γ/°	90	90
Volume/Å^3	11541.6(5)	9555.6(2)
Z	4	4
ρ_{calc}g/cm^3	1.369	1.837
μ/mm^{-1}	6.597	12.431
F(000)	4924.0	5304.0
Crystal size/mm^3	0.4 × 0.05 × 0.05	0.2 × 0.03 × 0.03
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.066 to 142.972	7.834 to 152.786
Index ranges	-28 ≤ h ≤ 29, -17 ≤ k ≤ 17, -33 ≤ l ≤ 40	-39 ≤ h ≤ 42, -38 ≤ k ≤ 37, -7 ≤ l ≤ 11
Reflections collected	81684	69366
Independent reflections	40519 [R_{int} = 0.0804, R_{sigma} = 0.1145]	19625 [R_{int} = 0.0598, R_{sigma} = 0.0594]
Data/restraints/parameters	40519/1245/2338	19625/42/1040
Goodness-of-fit on F^2	1.042	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0872, wR_2 = 0.2165	R_1 = 0.0482, wR_2 = 0.1165
Final R indexes [all data]	R_1 = 0.1161, wR_2 = 0.2342	R_1 = 0.0533, wR_2 = 0.1195
Largest diff. peak/hole / e Å^{-3}	1.44/-1.40	1.58/-1.40
Flack parameter	0.070(9)	0.020(6)

2.5 NMR spectra of compound 1-3

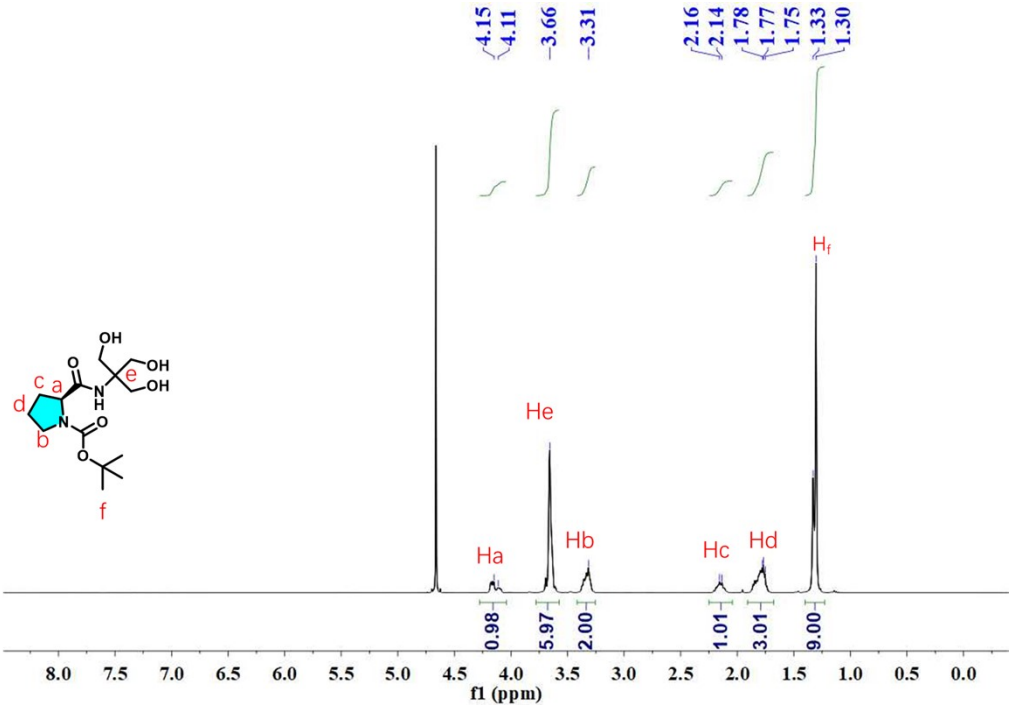


Figure S1. ^{1}H-NMR spectrum of **1**.

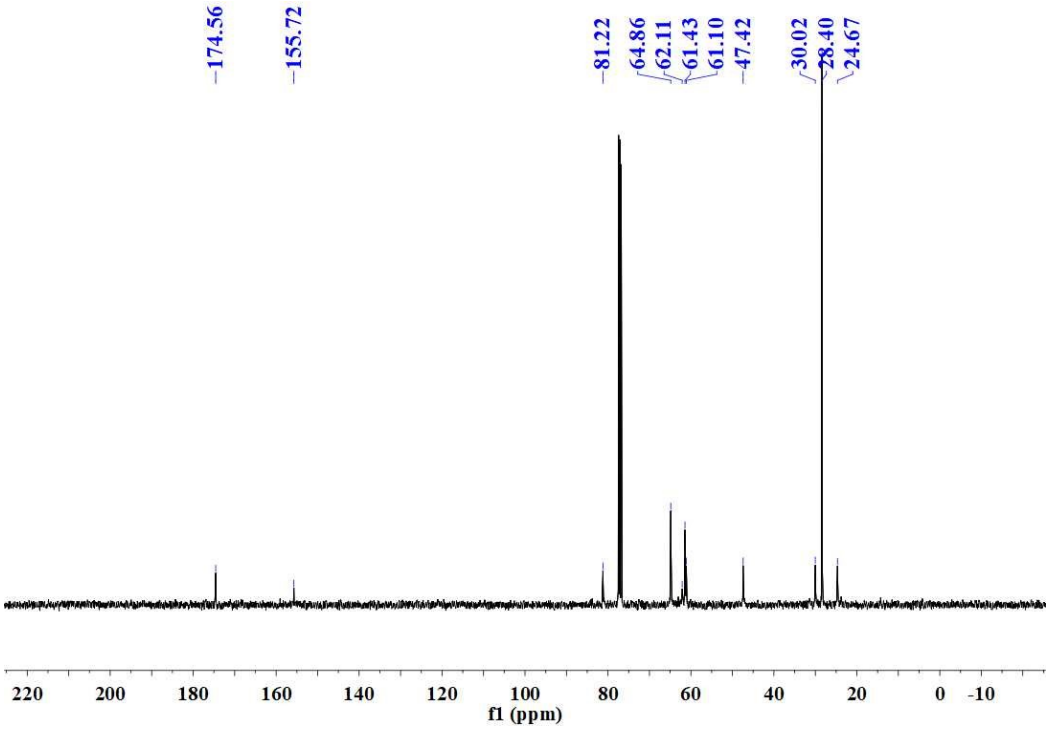


Figure S2. ^{13}C-NMR spectrum of **1**.

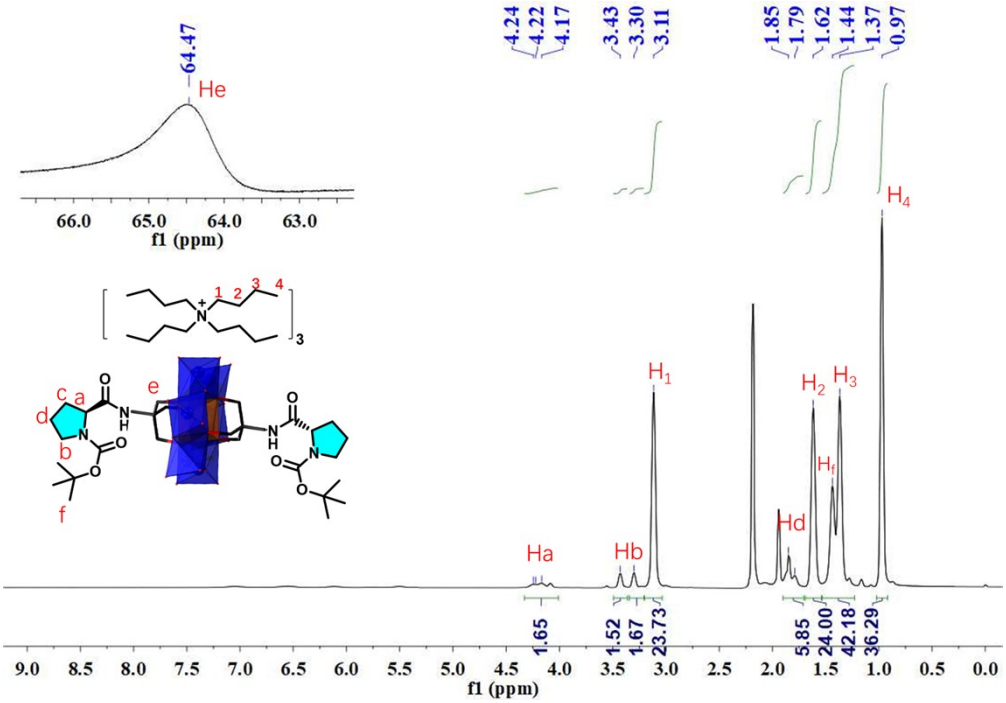


Figure S3. ^{1}H-NMR spectrum of **2**.

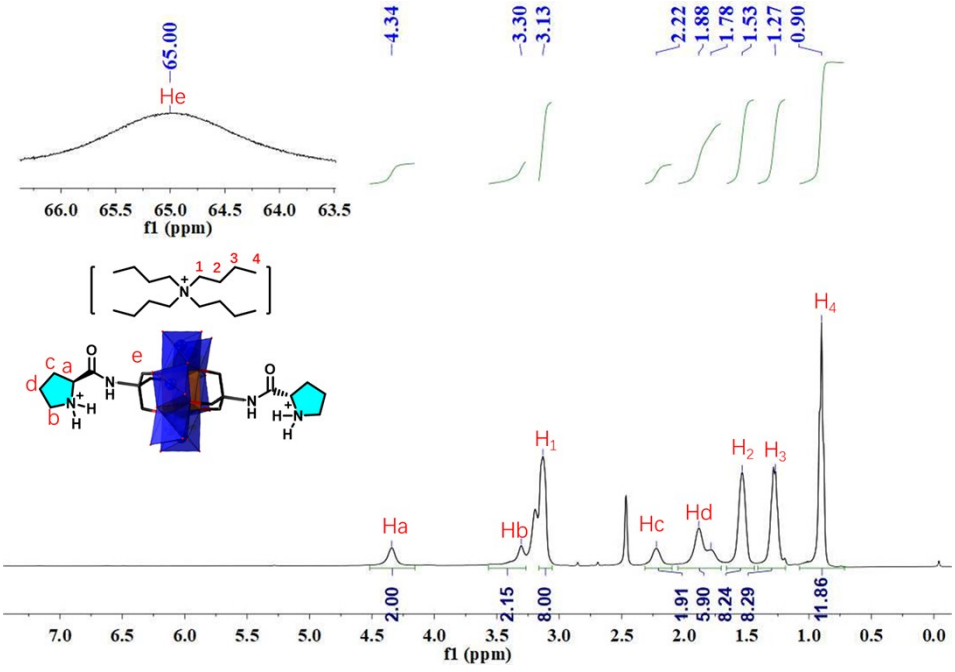


Figure S4. ^{1}H-NMR spectrum of **3**.

^{1}H NMR spectra indicates the equivalent ratio of L-proline derivatives: TBA as 2: 3 for compound **2**. Near 65 ppm, a broad signal is found for both compounds **2** and **3** which originates the $(OCH_2)_3$- protons of Tris close to the Mn^{III} center (Fig.

S3-S4).

2.6 FT-IR spectra

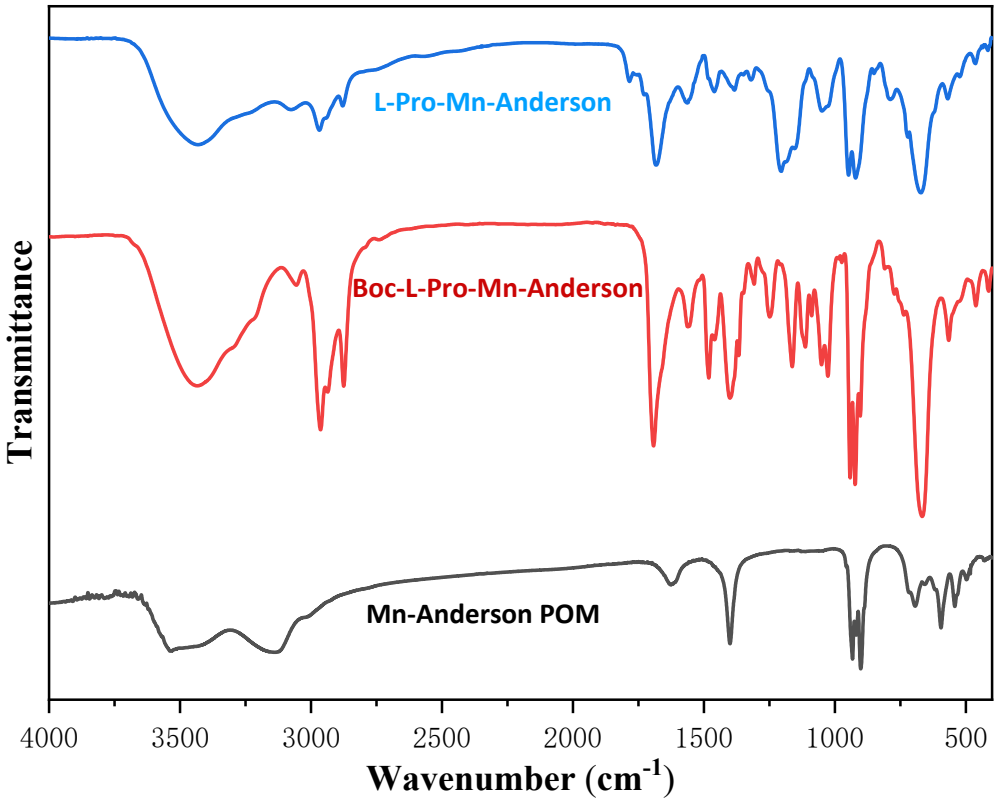


Figure S5. FT-IR spectrum of **Mn-Anderson POM** (black curve), **2** (red curve), **3** (blue curve).

IR spectra of these compounds are very similar within 400-1000cm^{-1}, and in accordance with the typical Anderson-type structures. The characteristic peaks at 932, 917 and 900 cm-1 in **Mn-Anderson POM** while 934, 924 and 905 cm-1 in compound **2** and 949, 921 cm-1 and 901 cm-1 in compound **3** correspond to the vibrations of Mo=O groups and this at 675 cm−1 in **Mn-Anderson POM**, while 665 cm-1 in compound **2**, 670 cm−1 in compound **3** belong to the vibrations of the Mo–O–Mo groups. The characteristic peaks at 1117, 1030 cm-1 in compound **2** while 1164, 1052 cm^{-1} in compound **3** are assigned to the vibration peak of the C–O bonds bridging the **Mn-Anderson-type POM** and the **L-Proline-Tris**, demonstrating the grafting of triol onto the surface of the POMs successfully.

2.7 Thermal analysis

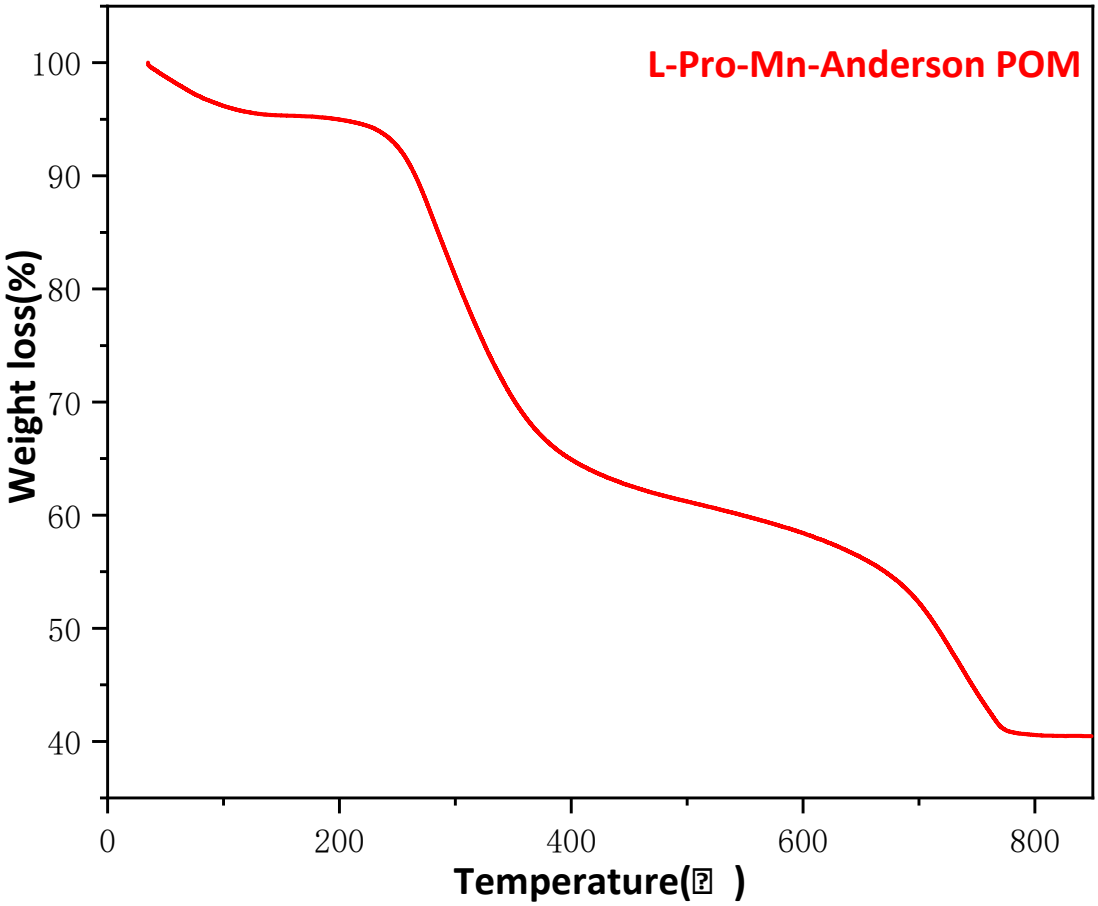


Figure S6. TGA spectrum of compound **Mn-Anderson POM** and **3** The preliminary thermal studies on compound **3** were conducted by using thermal gravimetric analyses (TGA). It clearly shows two weight-loss regions. The first step at 200−360°C was the reduction in TBA counterions. The second step at 360−700°C was the decomposition of the organic triol moiety and the decomposition of the cluster.

2.8 XPS spectra

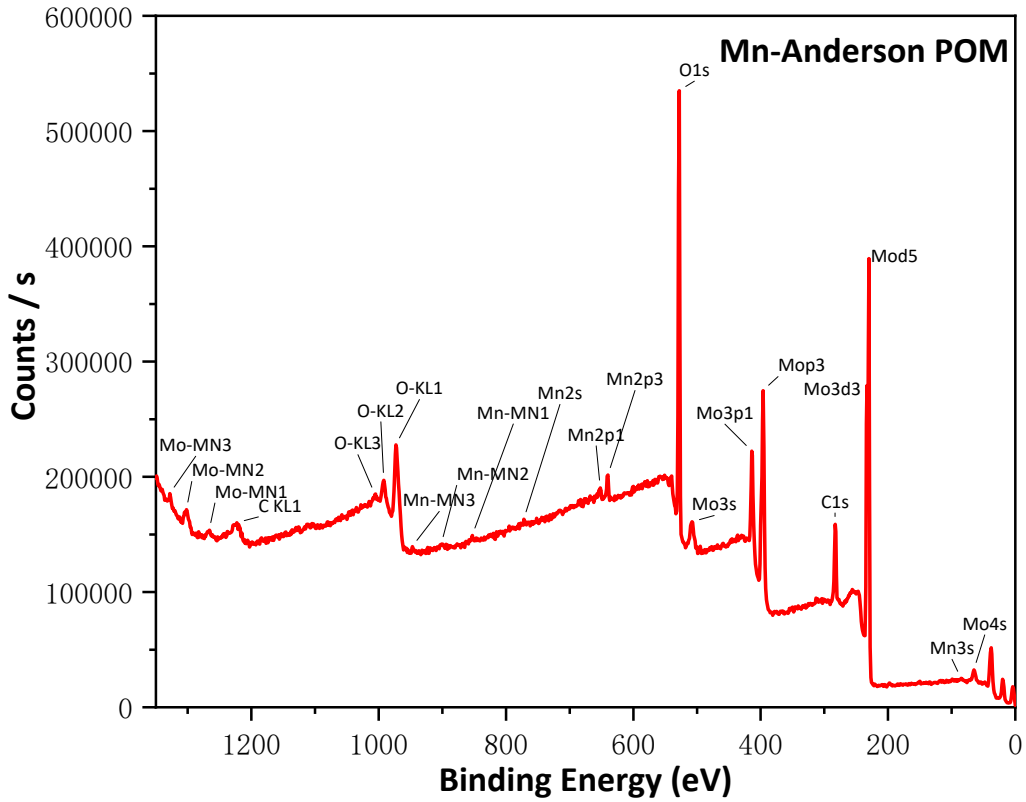


Figure S7. XPS spectrum of the **Mn-Anderson POM**

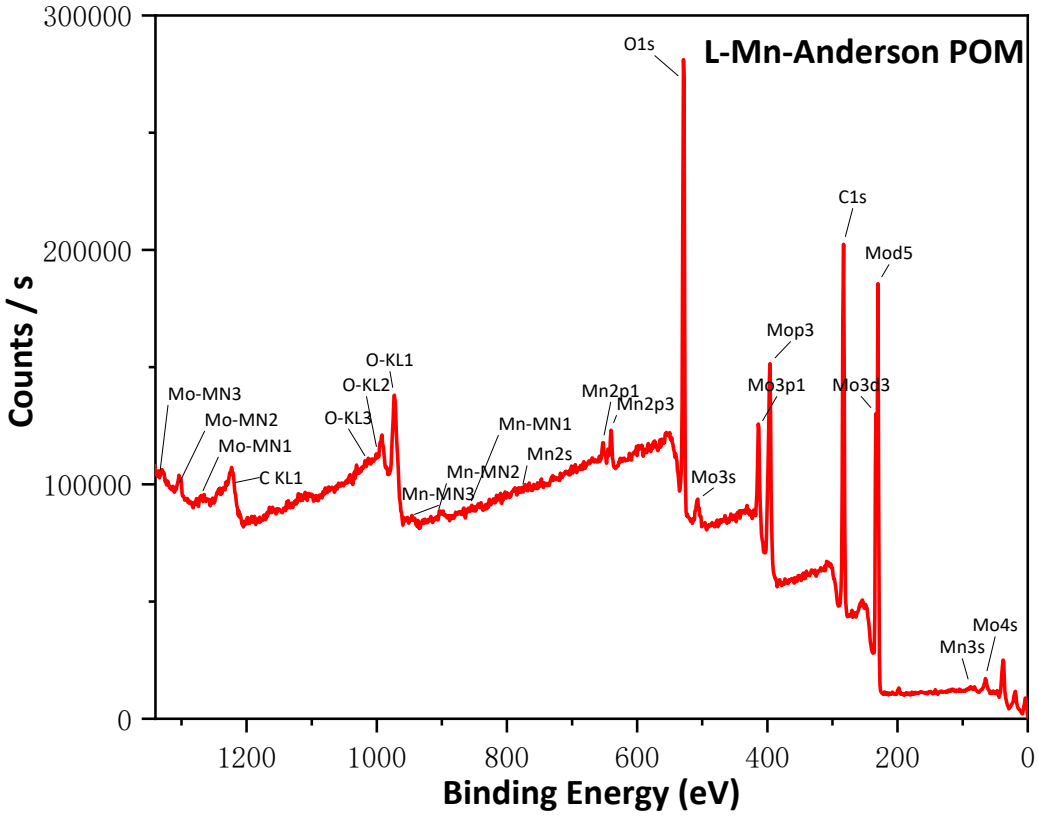


Figure S8. XPS spectrum of compound **3**

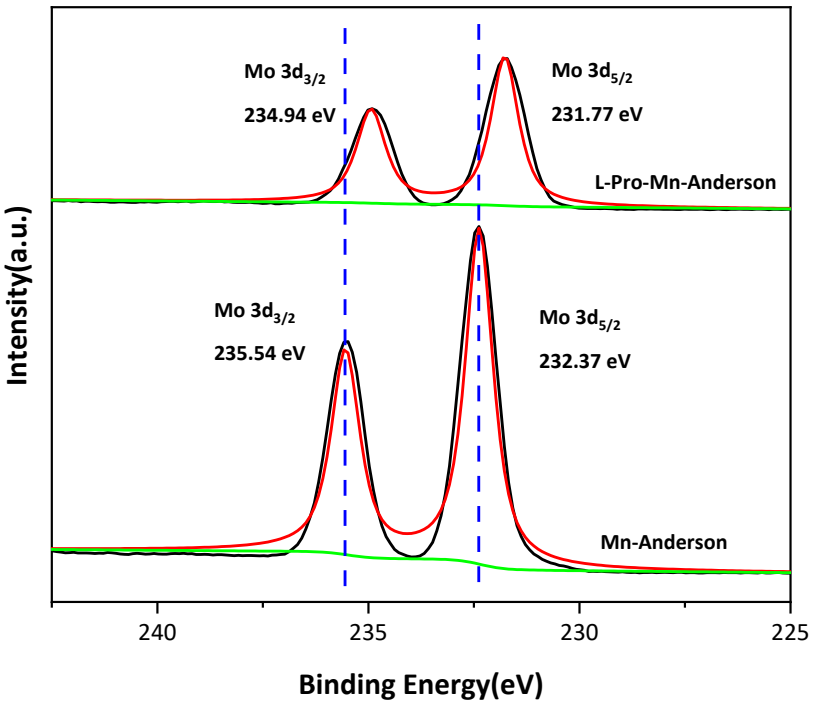


Figure S9. Mo 3d XPS spectrum of the **Mn-Anderson POM** and **3**.

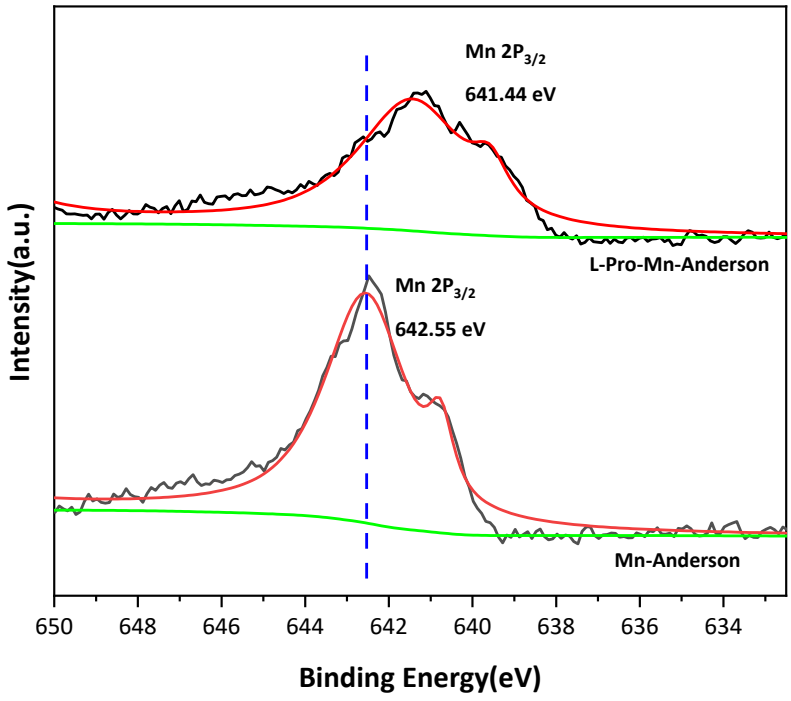


Figure S10. Mn 3p XPS spectrum of the **Mn-Anderson POM** and **3**.

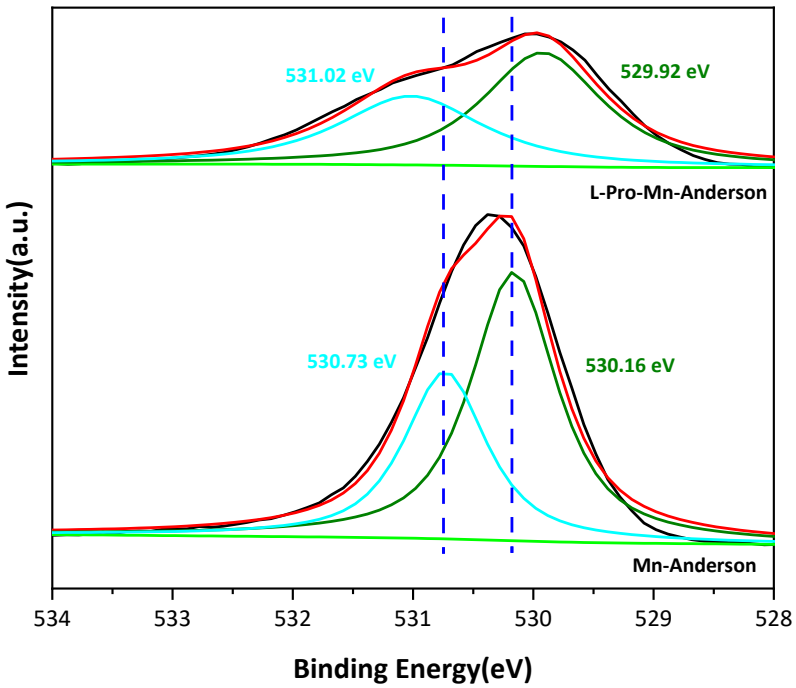


Figure S11. O 1s XPS spectrum of the **Mn-Anderson POM** and **3**.

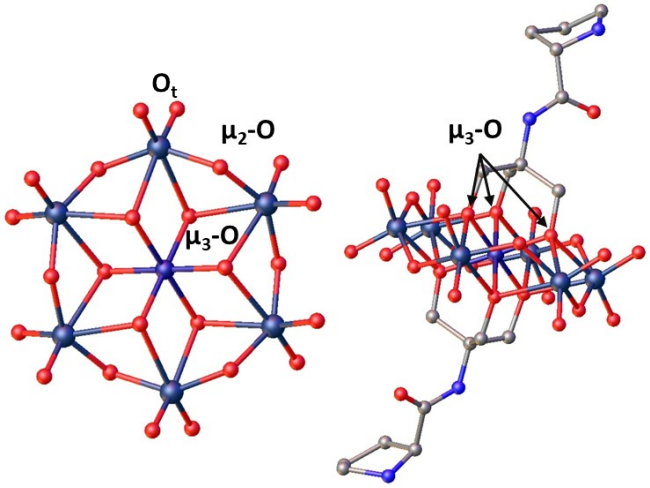


Figure S12. There are three types of oxygen atoms (red spheres) in Anderson-type POMs: terminal oxygen atoms (**O_t**), double-bridged (**μ_2-O**), triple-bridged (**μ_3-O**). L-Proline-Tris and Mn-Anderson are covalently linked *via* **μ_3-O**. Ball and stick representation with Mn navy blue, Mo dark teal, C gray, O red. H atoms have been omitted for clarity.

2.9 Cyclic voltammogram analysis

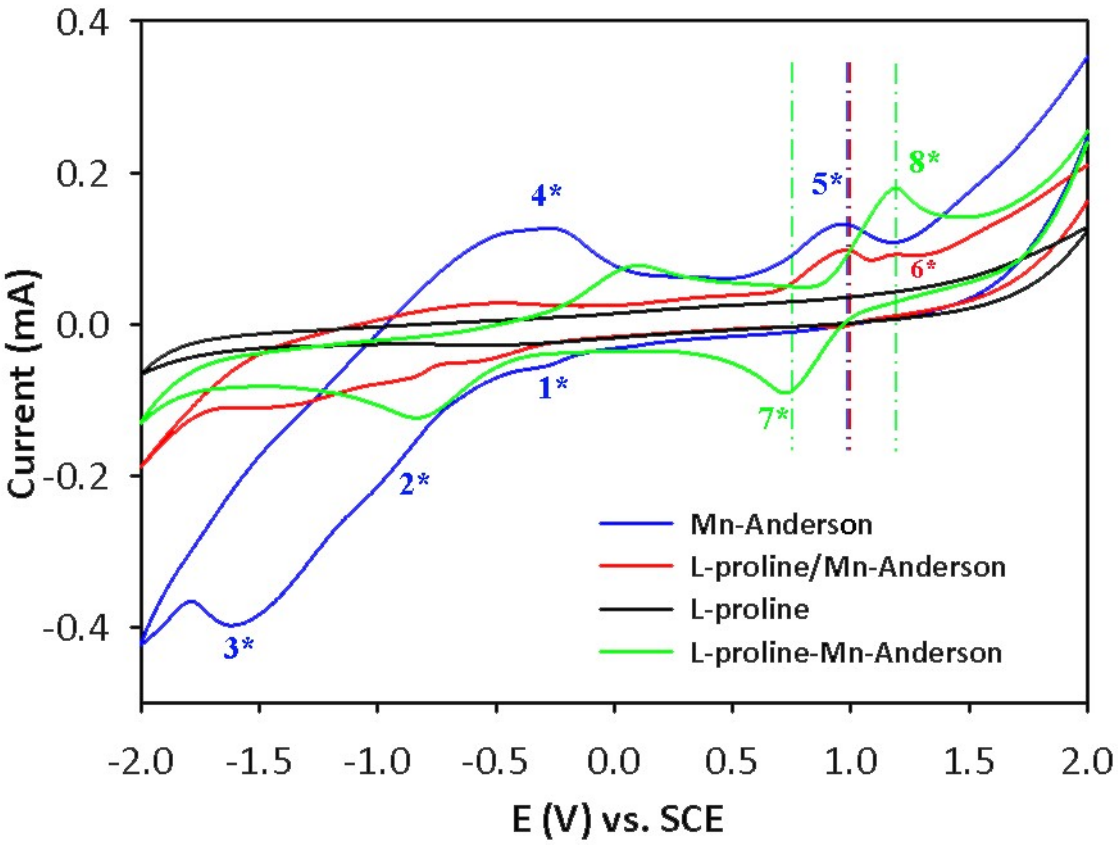


Figure S13. CVs comparison of the applied Mn-Anderson POM (red curve), L-Proline (blue curve), L-Proline/Mn-Anderson POM (green curve), L-Pro-Mn-Anderson POM (purple curve), the numbers plus asterisk represent the occurrence order and number of relevant redox peaks. Cyclic voltammetry was carried out under DMSO/H_2O (1:1) solution with 0.1 M $TBAPF_6$, 4×10^{-3} M related analyst, respectively. Scan rate: 100 mV s^{-1}.

2.10 Circular dichroism spectra

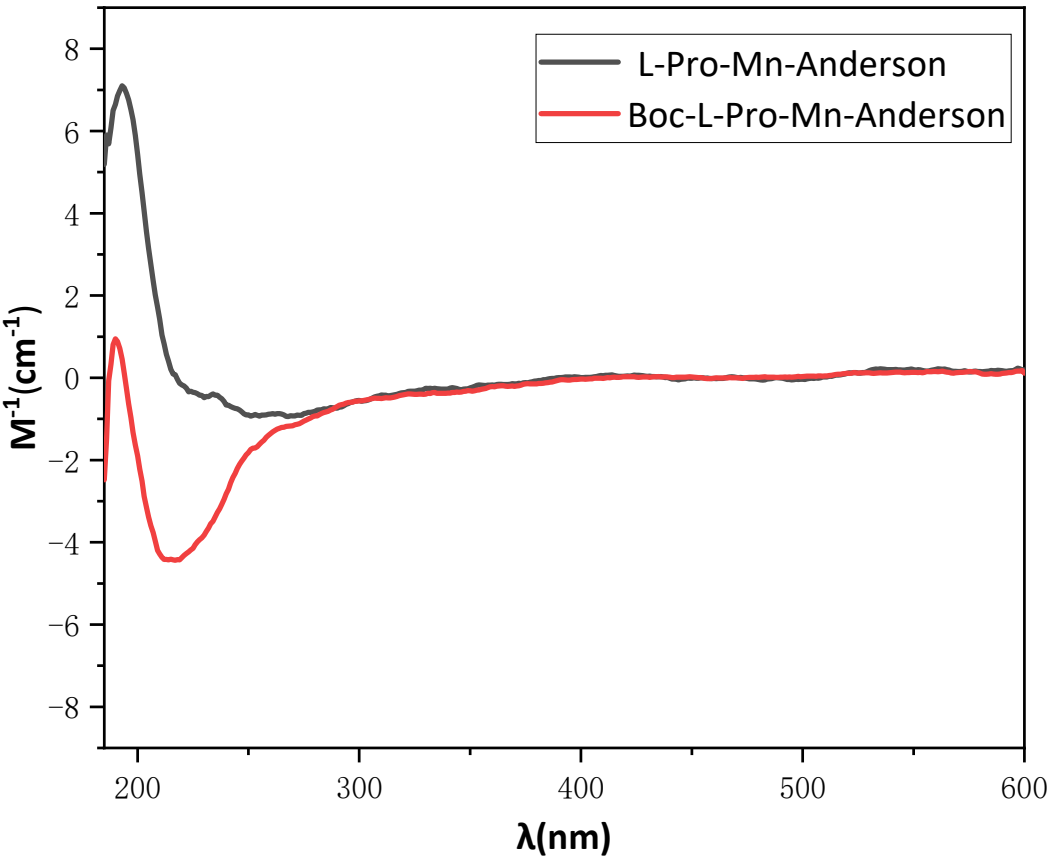


Figure S14. CD spectra of Boc-L-Pro-Mn-Anderson in CH_3CN (red curve), CD spectra of L-Pro-Mn-Anderson in H_2O (black curve).

3. Catalytic studies

Table S2. Catalytic performance of various catalysts in the selective oxidation of benzyl alcohol to benzaldehyde.[a]

Entry	Catalyst	Time (h)	Yields (%)[b]
1	No catalyst	24	<1
2	L-Proline	24	<1
3	Mn-Anderson POM	8	72
4	L-Proline/Mn-Anderson POM[C]	8	56
5	L-Pro-Mn-Anderson POM[d]	8	83
6	L-Pro-Mn-Anderson POM[d]	12	97
7	L-Pro-Mn-Anderson POM[d]	16	97

[a] Reaction conditions: benzyl alcohol (1 mmol), catalyst (0.005 mmol), H_2O (1 mL) and H_2O_2 30% (3 mmol) at 90℃.

[b] The yield of isolated products.

[c] Mixture.

[d] Covalent bonding.

we used the 4-chlorobenzyl alcohol as the model substrate to evaluate the oxidation catalytic activity of L-Pro-Mn-Anderson. Using H_2O_2 as a co-oxidant, almost no product was detected after 24 hours of reaction with either L-proline or in the absence of a catalyst. (<1%) (entry **1**-**2**). Mn-Anderson showed superior oxidation performance compared to L-Proline/Mn-Anderson (entry **3**-**4**), which was also consistent with the results of electrochemical tests (Fig. **S13**), possibly due to the mixing of L-Proline/Mn-Anderson to produce hydrogen bonds or other interactions to occupy the catalytic sites, thereby affecting its catalytic performance. L-Pro-Mn-Anderson performed optimally in the oxidation reaction.[5]

Table S3. Optimization of the selective oxidation of benzyl alcohol to benzaldehyde.[a]

Entry	Cat. (mmol)	Solvent	Temp (°C)	Sel.[b](%)	Yields (%)[c]
1	0.005	H_2O	70	>99	73
2	0.005	H_2O	80	>99	86
3	0.005	H_2O	90	>99	97
4	0.005	H_2O	100	96	91
5	0.005	CH_3OH	90	40	35
6	0.005	EtOH	90	46	39
7	0.005	CH_3CN	90	65	58
8	0.02	H_2O	90	98	93
9	0.01	H_2O	90	>99	96
10	0.001	H_2O	90	>99	90

[a] Reaction conditions: reaction time(12 h), benzyl alcohol (1 mmol), catalyst (0.01 mmol), H_2O (3 mL) and H_2O_2 30% (3 mmol).

[b] Selectivity was determined by GC and confirmed by GC-MS.

[c] The yield of isolated products.

The influence of the amount of catalyst, solvent and tem-perature on the catalytic oxidation performance was investigated. It was found that the solvent had a great influence on the selectivity of the product (entry **3**,**5**-**7**). Gratifyingly, aldehydes could be exclusively selec-tively produced in H_2O (97% yield with 99% selectivity) (entry **3**). Only when the temperature reaches 100 °C, the selectivity decreased a little (96% selectivity) (entry **4**). The different amount of catalyst only affects the yield of aldehyde (entry **8**-**10**).

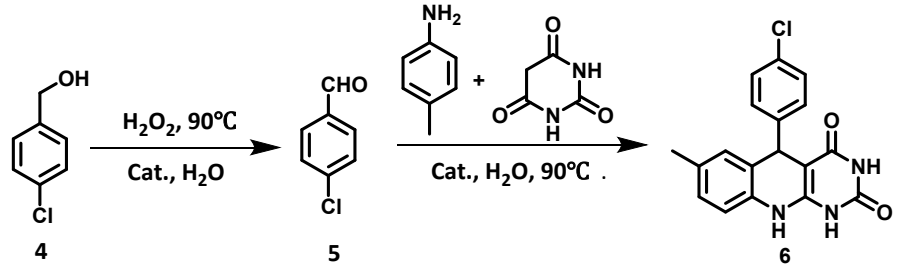


Table S4. Optimization of the three-component coupling reaction between benzyl alcohol, anilines, and barbituric acids[a]

Entry	Cat. (%)	Time		Yields(%)[b]	
		A(h)	B(h)	5	6
1	No catalyst	12	12	<1	-
2	$H_3PW_{12}O_{40}$ (0.5)	12	12	85	-
3	L-Proline(1)	12	12	<1	-
4	Mn-Anderson(0.5)	12	12	90	-
5	L-Proline/Mn-Anderson (1/0.5)	12	12	<1	65
6	L-Pro-Mn-Anderson(0.5)	12	12	<1	90
7	L-Pro-Mn-Anderson(0.5)	0	12	43	-
8	L-Pro-Mn-Anderson(2)	12	12	<1	89
9	L-Pro-Mn-Anderson(1)	12	12	<1	89
10	L-Pro-Mn-Anderson(0.1)	12	12	<1	78

[a] Reaction conditions: 4-CH_3-aniline (1 mmol), 4-Cl-benzaldehyde (1 mmol), barbituric acid (1 mmol) , H_2O (2 mL), H_2O_2 30% (3 mmol) at reflux.
[b] The yield of isolated products.

3.1 General procedure for the synthesis of 5-aryl-pyrimido[4,5-b]-quinoline-dione derivatives 6

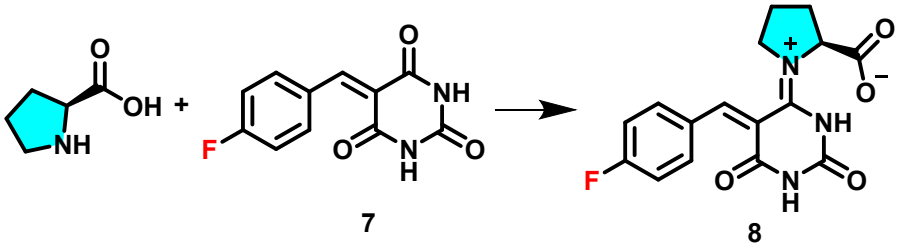
0.50 mol-% of the catalyst **3** (**L-Mn-Anderson POM**) was dissolved in 1 mL of water in 25 mL round bottomed flask by stirring. Thereafter, 1 mmol of alcohol was added followed by the slow addition of 3 mmol of aqueous 30 % H_2O_2 drop wise by stirring. The reaction temperature was set at 90 °C for A hours. followed by the addition of aromatic amine compound(1 mmol), barbituric acid (0.13 g, 1 mmol) in refluxing H_2O for B hours. After completion of the reaction, as confirmed by TLC, the reaction mixture was cooled down to r.t. The precipitate was collected by filtration and washed with H_2O (10 mL) and EtOH (5 mL) to afford the pure product **6**.

3.2 General Procedure for the Synthesis of pyrido [3,4-b] pyrazole derivatives 9.

0.50 mol-% of the catalyst **3** (**L-Mn-Anderson POM**) was dissolved in 1 mL of

water in 25 mL round bottomed flask by stirring. Thereafter, 1 mmol of alcohol was added followed by the slow addition of 3 mmol of aqueous 30 % H_2O_2 drop wise by stirring. The reaction temperature was set at 90 °C for A hours. followed by the addition of 3-methyl-1-phenyl-1H-pyrazol-5-amine (1 mmol), Meldrum's acid (1 mmol),in refluxing H_2O for C hours. After completion of the reaction, as confirmed by TLC, the reaction mixture was cooled to r.t. The precipitate was collected by filtration and washed with H_2O (10 mL) and EtOH (5 mL) to afford the pure product **9**.

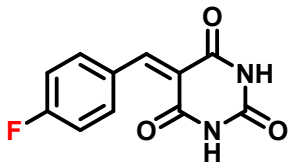
4. Mechanistic Experiment



Scheme S2. L-Proline activates 5-Arylidene Barbiturate (**7**)

4.1 Synthesis and Characterization of the 5-arylidene Barbiturate (7)

0.50 mol-% of the catalyst **3** (**L-Mn-Anderson POM**) was dissolved in 1 mL of water in 25 mL round bottomed flask by stirring. Thereafter, 1 mmol of 4-F-benzyl alcohol was added followed by the slow addition of 2 mmol of aqueous 30 % H_2O_2 drop wise by stirring. The reaction temperature was set at 90 °C for 12 hours. followed by the addition of barbituric acid (0.13 g, 1 mmol) in refluxing H_2O for 12 hours. After completion of the reaction, as confirmed by TLC, the reaction mixture was filtered and the precipitated product was washed with water (3 × 10 mL) to afford the pure compound.



^{1}H NMR (400 MHz, DMSO-D6) δ 11.36 (s), 11.22 (s), 8.27 – 8.09 (m), 7.27 (dd, J = 8.7, 8.0 Hz).^{13}C NMR (101 MHz, DMSO-D6) δ 165.95 (s), 163.92 (s), 163.44 (s), 162.26 (s), 153.97 (s), 150.72 (s), 136.89 (d, J = 9.3 Hz), 129.74 (s), 119.21 (s), 115.85 (s), 115.63 (s).^{19}F NMR: (376 MHz, DMSO-D6) δ -105.85 (s).

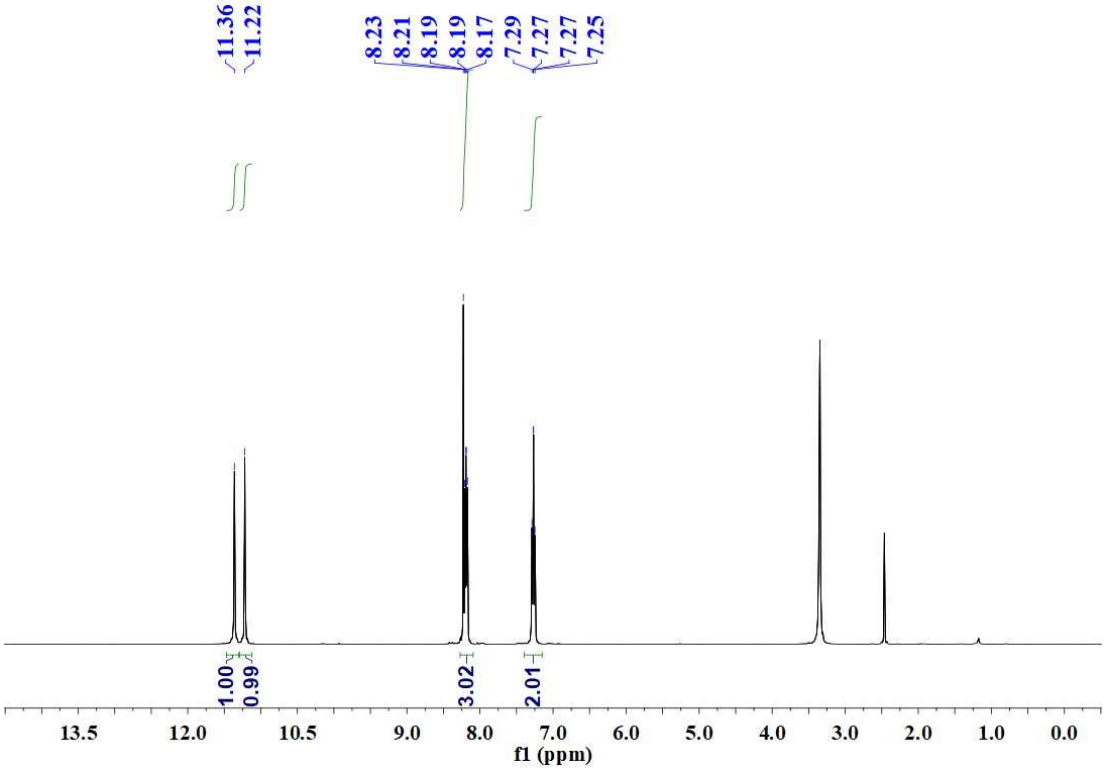


Figure S15. ^{1}H NMR spectra of 5-arylidene Barbiturate (7)

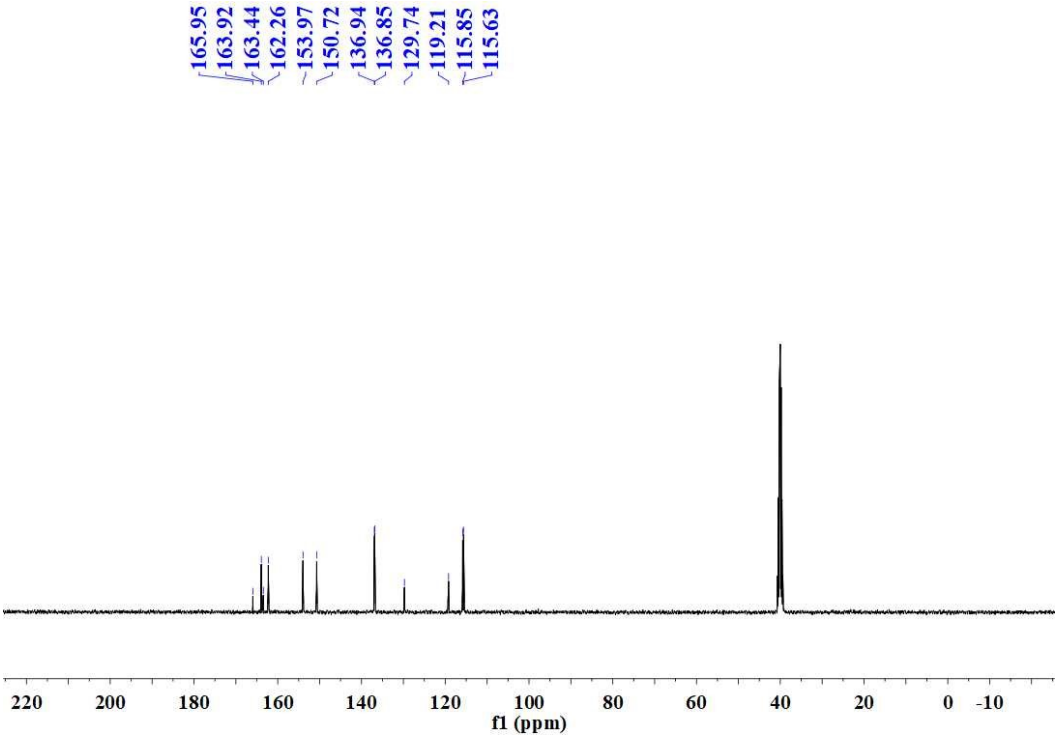


Figure S16. ^{13}C NMR spectra of 5-arylidene Barbiturate (7)

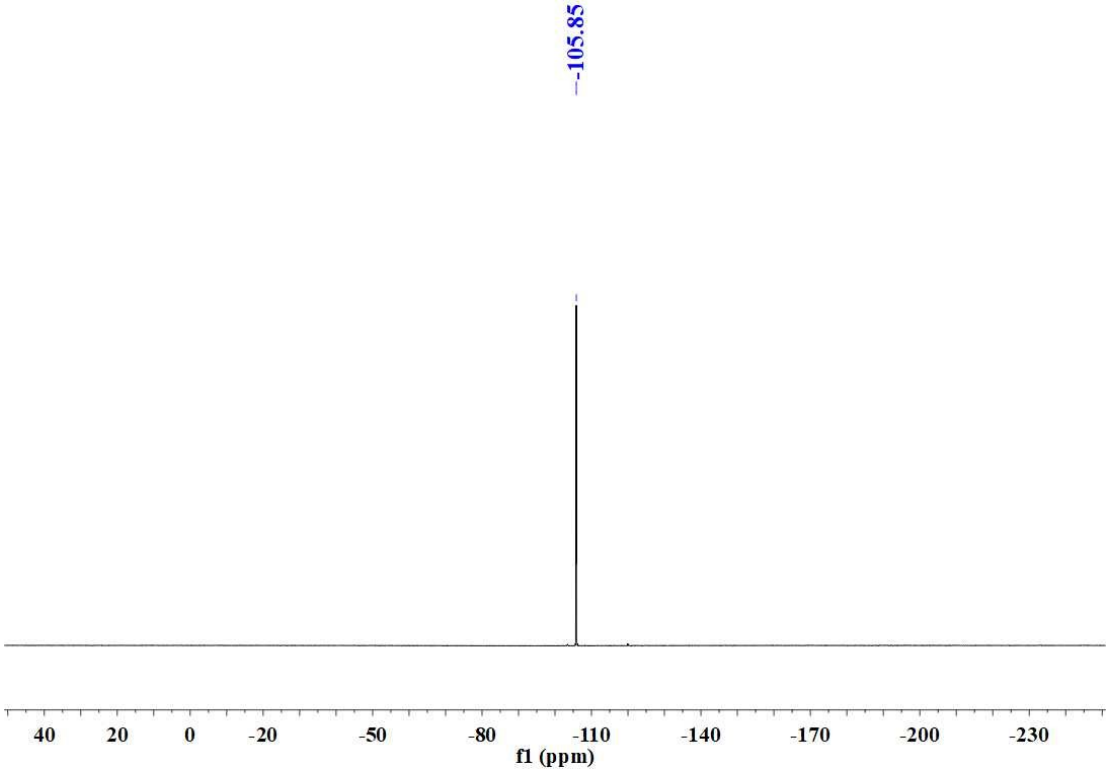


Figure S17. ^{19}F NMR spectra of 5-arylidene Barbiturate (7)

4.2 Study of Reaction Mechanisms

An oven-dried 5 mL vial was charged with catalyst (0.01 mmol, 1 equiv.), DMSO (1 mL) and 5-arylidene barbiturate (0.01 mmol, 1 equiv.). The mixture was allowed to stand at ambient temperature for 1 hours. An aliquot was used for 19F NMR characterization.

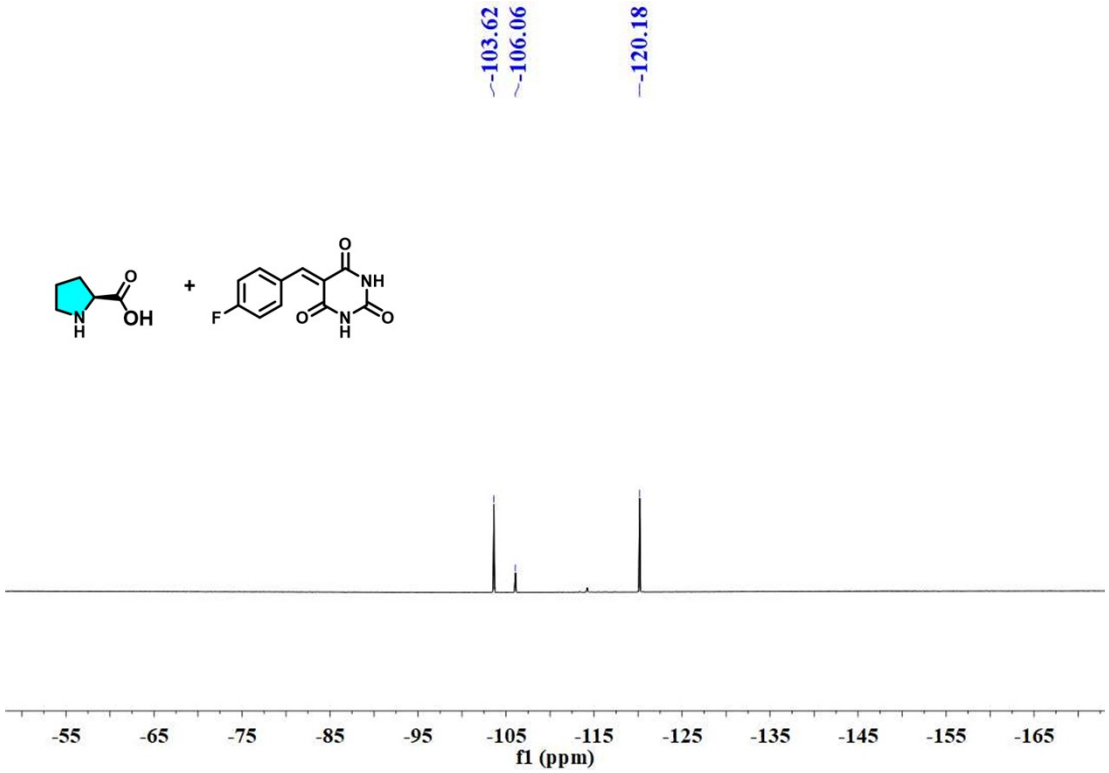


Figure S18.[19]F NMR spectra of **7/L-Proline** (1/1 mole ratio)

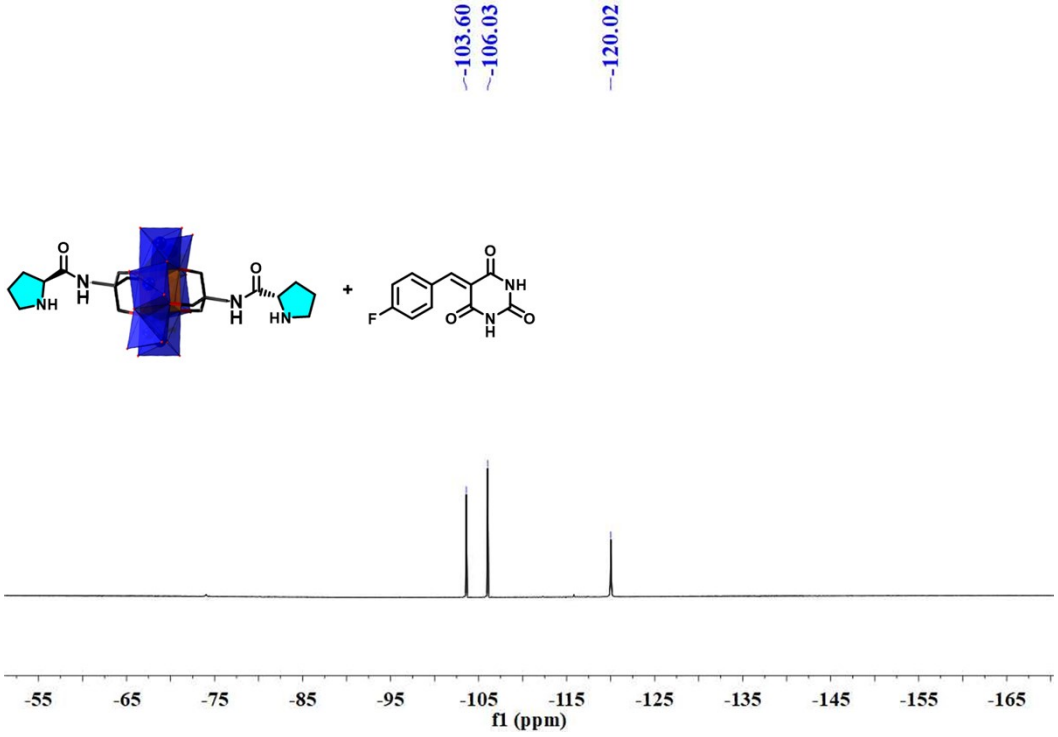


Figure S19. [19]F NMR spectra of **7/L-Pro-Mn-Anderson** (1/1 mole ratio)

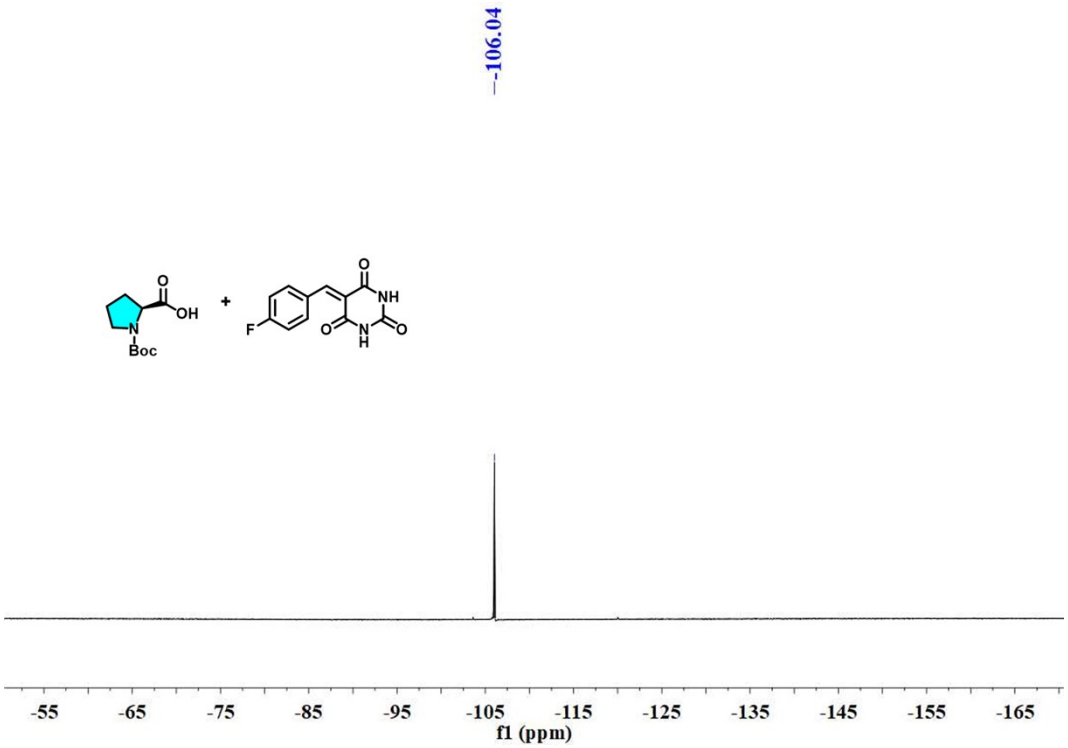


Figure S20.[19]F NMR spectra of **7**/**Boc-L-Proline** (1/1 mole ratio)

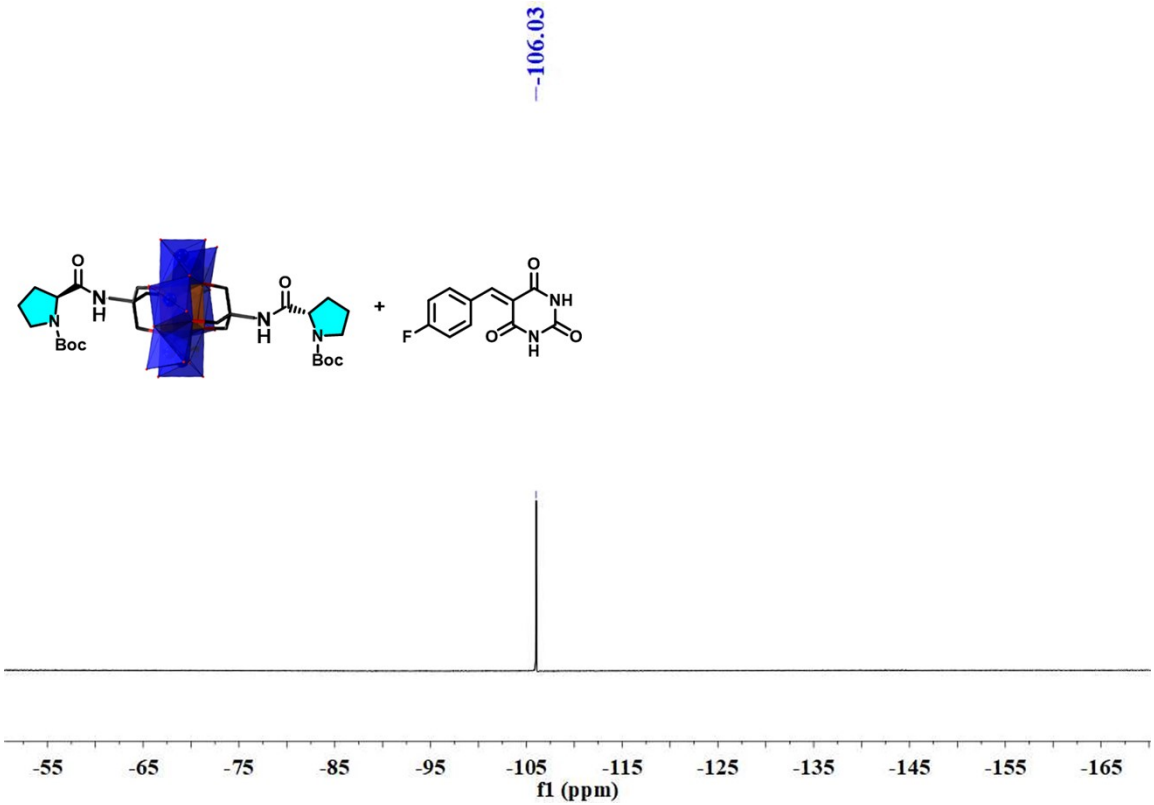


Figure S21.[19]F NMR spectra of **7**/**Boc-L-Pro-Mn-Anderson** (1/1 mole ratio)

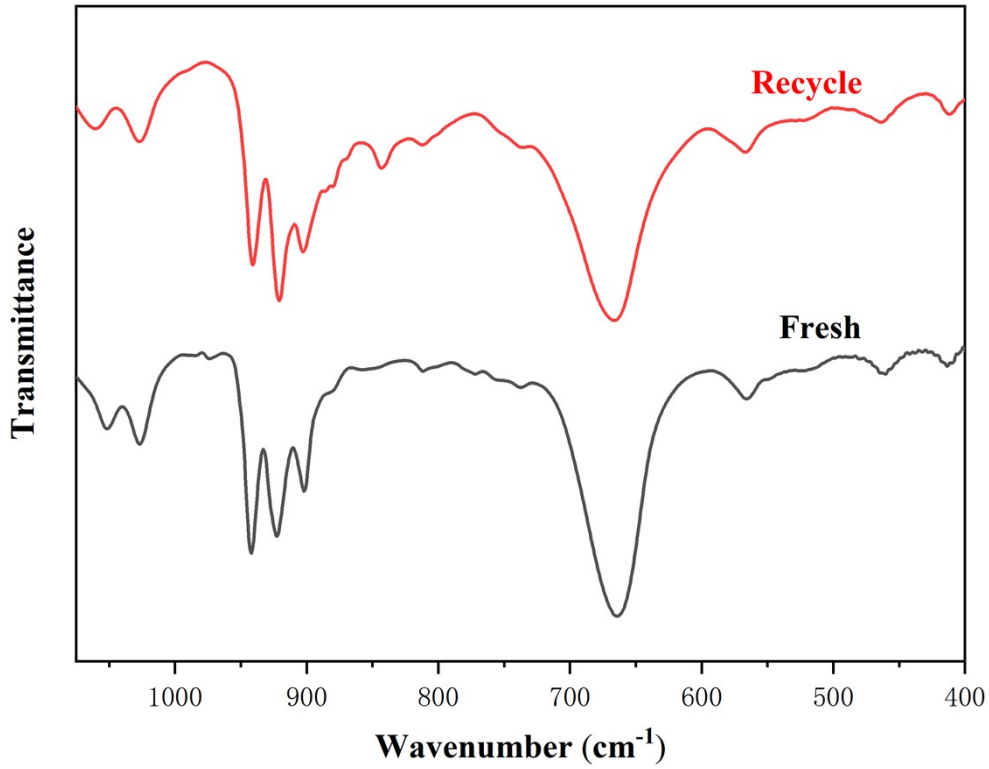


Figure S22. FT-IR spectrum of **Mn-Anderson POM** :**Fresh** (black curve), **Recycle** (red curve).

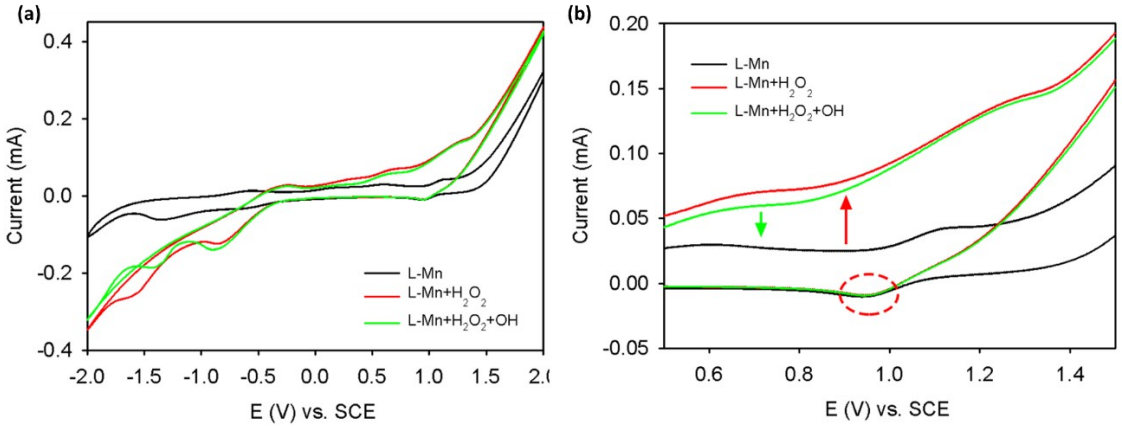
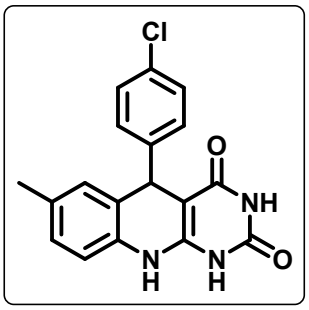
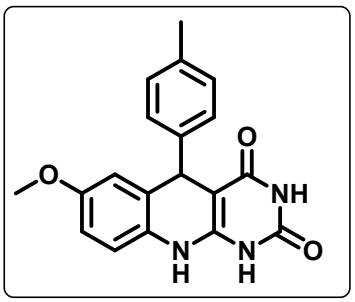


Figure S23. CVs comparison of the applied (a) Only the catalyst (L-Pro-Mn-Anderson POM) in the reaction system; (b) Add H2O2 to the reaction system in (a) (red curve), (c) Add alcohol to the reaction system in (b) (green curve), the numbers plus asterisk represent the occurrence order and number of relevant redox peaks. Cyclic voltammetry was carried out under DMSO/H2O (1:1) solution with 0.1 M TBAPF6, 1×10-3 M related analyst, respectively. Scan rate: 100 mV s-1.

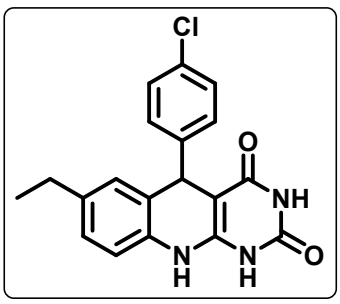
5. NMR data of isolated compounds.



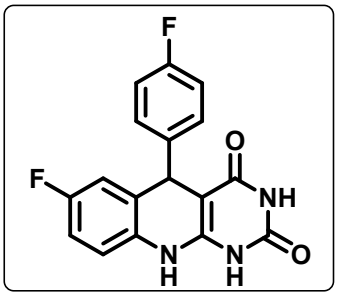
6a: Yield: 90%, ^{1}H NMR (400 MHz, DMSO-D6) δ 10.51 (s), 10.25 (s), 8.71 (s), 7.32 – 7.12 (m), 6.89 (d, J = 5.0 Hz), 4.99 (s), 2.10 (s); ^{13}C NMR (101 MHz, DMSO-D6) δ 163.22 (s), 150.70 (s), 147.49 (s), 146.37 (s), 133.40 (s), 132.58 (s), 131.04 (s), 130.25 (s), 129.43 (s), 128.56 (d, J = 19.8 Hz), 124.43 (s), 116.44 (s), 85.37 (s), 20.84 (s).
This compound was known.[6]



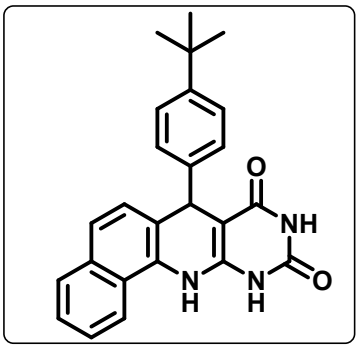
6b: Yield: 91%, ^{1}H NMR (400 MHz, DMSO-D6) δ 10.45 (s, 1H), 10.21 (s, 1H), 8.62 (s, 1H), 7.04 (d, J = 8.0 Hz, 2H), 6.93 (dd, J = 14.8, 8.7 Hz, 3H), 6.66 (d, J = 6.9 Hz, 2H), 4.94 (s, 1H), 3.58 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (101 MHz, DMSO-D6) δ 163.23 (s), 155.73 (s), 150.77 (s), 146.36 (s), 145.44 (s), 135.45 (s), 129.32 (d, J = 15.3 Hz), 127.33 (s), 126.53 (s), 117.28 (s), 114.85 (s), 113.26 (s), 85.07 (s), 55.72 (s), 21.04 (s).
This compound was known.[6]



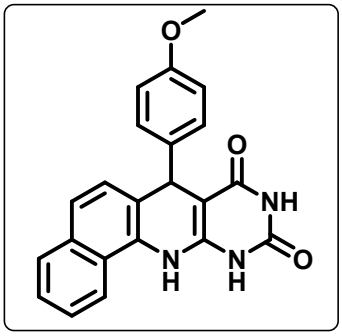
6c: Yield: 93%, ^{1}H NMR (400 MHz, DMSO-D6) δ 10.53 (s), 10.26 (s), 8.72 (s), 7.20 (q, J = 8.6 Hz), 6.92 (dd, J = 6.2, 4.3 Hz), 5.01 (s), 2.40 (q, J = 7.5 Hz), 1.03 (t, J = 7.6 Hz); ^{13}C NMR (101 MHz, DMSO-D6) δ 163.22 (s), 150.70 (s), 147.39 (s), 146.43 (s), 139.12 (s), 133.67 (s), 131.04 (s), 129.40 (s), 129.09 (s), 128.65 (s), 127.20 (s), 124.41 (s), 116.48 (s), 85.38 (s), 27.97 (s), 16.11 (s).



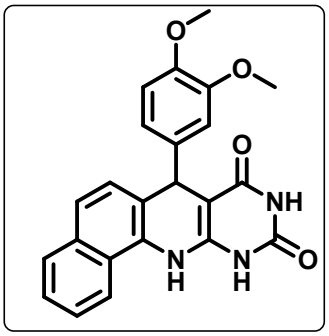
6d: Yield: 85%, ^{1}H NMR (400 MHz, DMSO-D6) δ 10.54 (s, 1H), 10.36 (s, 1H), 8.85 (s, 1H), 7.19 (dd, J = 8.5, 5.7 Hz, 2H), 7.06 – 6.87 (m, 5H), 5.05 (s, 1H); ^{13}C NMR (101 MHz, DMSO-D6) δ 163.21 (s), 162.43 (s), 160.02 (s), 159.75 (s), 157.37 (s), 150.77 (s), 146.44 (s), 144.10 (s), 132.43 (s), 129.25 (d, J = 8.0 Hz), 126.83 (d, J = 7.1 Hz), 117.99 (d, J = 8.1 Hz), 116.20 (s), 116.06 (d, J = 22.7 Hz), 115.58 (s), 115.37 (s), 114.81 (s), 114.58 (s), 84.85 (s).



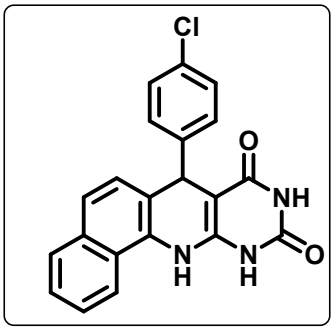
6e: Yield: 87%, ^{1}H NMR (400 MHz, DMSO-D6) δ 10.63 (s), 9.97 (s), 9.03 (s), 7.86 (dd, J = 29.3, 8.3 Hz), 7.61 (t, J = 7.6 Hz), 7.56 – 7.42 (m), 7.26 (d, J = 8.5 Hz), 7.15 (dd, J = 16.8, 8.2 Hz), 5.11 (s), 1.15 (s); 13C NMR (101 MHz, DMSO-D6) δ 163.35 (s), 150.40 (s), 148.82 (s), 146.25 (s), 145.21 (s), 132.80 (s), 130.14 (s), 129.00 (s), 128.21 (s), 127.36 (s), 126.82 (s), 126.54 (s), 125.53 (s), 123.29 (s), 122.33 (s), 120.41 (d, J = 9.4 Hz), 86.66 (s), 34.54 (s), 31.64 (s).



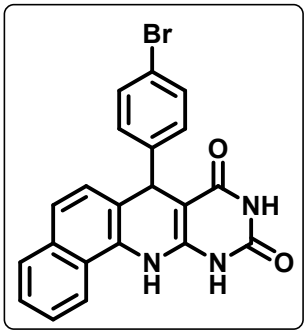
6f: Yield: 83%, ^{1}H NMR (400 MHz, DMSO-D6) δ 10.87 (s), 10.42 (s), 8.36 (d, J = 8.3 Hz), 7.87 – 7.76 (m), 7.49 (dt, J = 16.6, 7.7 Hz), 7.27 – 7.14 (m), 6.92 (d, J = 8.7 Hz), 6.77 (d, J = 8.5 Hz), 4.69 (d, J = 10.7 Hz), 3.72 (s); 13C NMR (101 MHz, DMSO-D6) δ 170.63 (s), 167.84 (s), 158.93 (s), 153.95 (s), 133.32 (s), 132.56 (s), 131.90 (s), 130.13 (s), 128.66 (s), 126.65 (s), 126.14 (s), 123.10 (s), 122.76 (s), 122.18 (d, J = 9.4 Hz), 114.70 (s), 55.81 – 55.61 (m), 55.42 (d, J = 28.1 Hz), 44.40 (s).
This compound was known.[7]



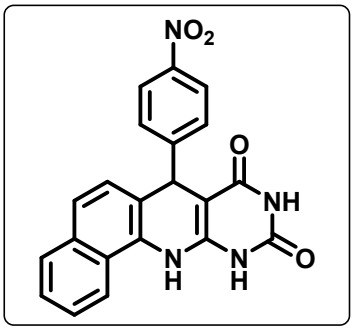
6g: Yield: 81%, ^{1}H NMR (400 MHz, DMSO-D6) δ 10.65 (s), 9.96 (s), 9.01 (s), 7.90 (d, J = 8.5 Hz), 7.82 (d, J = 8.1 Hz), 7.61 (dd, J = 11.3, 4.0 Hz), 7.48 (dd, J = 15.8, 8.1 Hz), 7.31 (d, J = 8.5 Hz), 6.95 (d, J = 1.9 Hz), 6.72 (d, J = 8.3 Hz), 6.62 (dd, J = 8.3, 1.9 Hz), 5.11 (s), 3.66 (s), 3.60 (s); ^{13}C NMR (101 MHz, DMSO-D6) δ 163.44 (s), 150.41 (s), 148.92 (s), 147.78 (s), 146.16 (s), 141.08 (s), 132.79 (s), 130.02 (s), 129.00 (s), 128.21 (s), 126.77 (s), 126.51 (s), 123.20 (s), 122.34 (s), 120.45 (s), 119.73 (s), 112.50 (s), 112.10 (s), 86.72 (s), 56.04 (s).



6h: Yield: 91%, ^{1}H NMR (400 MHz, DMSO-D6) δ 10.68 (s), 9.98 (s), 9.05 (s), 7.89 (d, J = 8.5 Hz), 7.82 (d, J = 7.9 Hz), 7.60 (dd, J = 8.3, 1.1 Hz), 7.52 – 7.44 (m), 7.27 – 7.20 (m), 5.18 (s); ^{13}C NMR (101 MHz, DMSO-D6) δ 163.34 (s), 150.36 (s), 147.09 (s), 146.26 (s), 132.90 (s), 131.25 (s), 130.18 (s), 129.75 (s), 129.02 (s), 128.68 (s), 128.04 (s), 126.79 (d, J = 20.0 Hz), 123.40 (s), 122.33 (s), 120.50 (s), 119.58 (s), 86.23 (s).
This compound was known.[7]

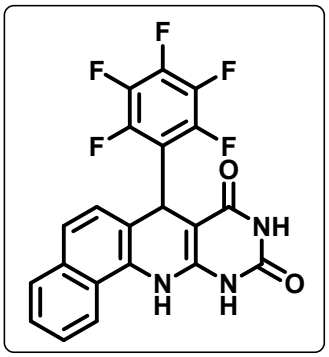


6i: Yield: 90%, ^{1}H NMR (400 MHz, DMSO-D6) δ 10.68 (s), 9.98 (s), 9.04 (s), 7.89 (d, J = 8.5 Hz), 7.82 (d, J = 8.2 Hz), 7.62 (t, J = 7.6 Hz), 7.52 – 7.43 (m), 7.35 (d, J = 8.4 Hz), 7.25 – 7.17 (m), 5.17 (s); ^{13}C NMR (101 MHz, DMSO-D6) δ 163.34 (s), 150.36 (s), 147.51 (s), 146.26 (s), 132.90 (s), 131.61 (s), 130.16 (s), 129.03 (s), 128.04 (s), 126.80 (d, J = 19.8 Hz), 123.41 (s), 122.33 (s), 120.50 (s), 119.76 (s), 119.50 (s), 86.17 (s).



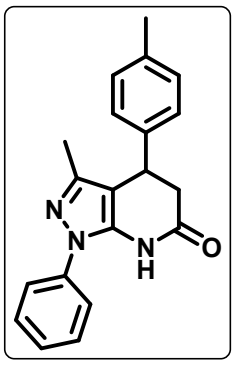
6j: Yield: 92%, ^{1}H NMR (400 MHz, DMSO-D6) δ 10.72 (s), 10.03 (s), 9.14 (s), 8.05 (d, J = 8.7 Hz), 7.91 (d, J = 8.6 Hz), 7.82 (d, J = 8.0 Hz), 7.55 – 7.43 (m), 7.23 (d, J = 8.5 Hz), 5.36 (s); ^{13}C NMR (101 MHz, DMSO-D6) δ 163.33 (s), 155.32 (s), 150.35 (s), 146.44 (s), 133.03 (s), 130.36 (s), 129.14 (d, J = 18.4 Hz), 127.93 (s), 126.94 (d, J = 12.0 Hz), 124.11 (s), 123.56 (s), 122.36 (s), 120.57 (s), 118.62 (s), 85.67 (s).

This compound was known.[7]



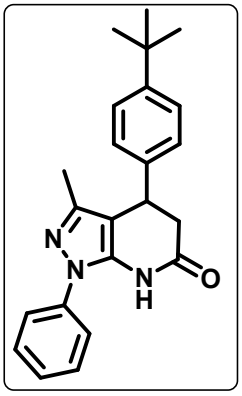
6k: Yield: 87%, ^{1}H NMR (400 MHz, DMSO-D6) δ 10.73 (s), 9.95 (s), 9.19 (s), 7.86 (dd, J = 17.0, 8.1 Hz), 7.55 (ddd, J = 28.7, 18.1, 7.4 Hz), 7.02 (d, J = 7.8 Hz), 5.67 (s); ^{13}C NMR (101 MHz, DMSO-D6) δ 163.17 (s), 150.19 (s), 146.69 (s),

133.25 (s), 130.90 (s), 129.05 (s), 127.19 (d, J = 11.6 Hz), 123.68 (s), 122.04 (s), 120.50 (s), 115.35 (s), 82.57 (s), 31.18 (s).

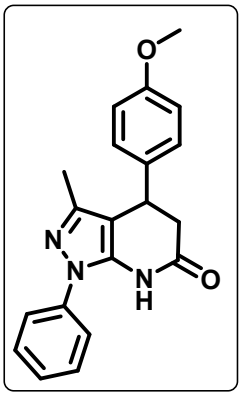


9a: Yield: 95%, ^{1}H NMR (400 MHz, DMSO) δ 10.51 (s, 1H), 7.76 – 6.96 (m, 9H), 4.18 (dd, J = 6.7, 4.7 Hz, 1H), 3.01 (dd, J = 15.6, 7.3 Hz, 1H), 2.62 (dd, J = 15.6, 4.5 Hz, 1H), 2.27 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 170.50 (s), 145.80 (s), 140.51 (s), 139.27 (s), 138.51 (s), 136.27 (s), 129.69 (d, J = 4.1 Hz), 127.21 (d, J = 6.5 Hz), 123.11 (s), 104.02 (s), 34.05 (s), 21.05 (s), 12.48 (s).

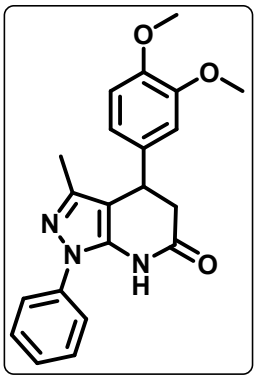
This compound was known.[8]



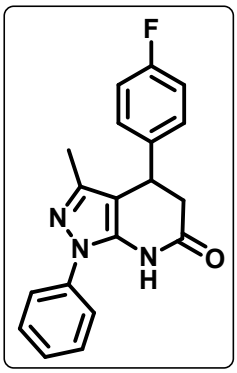
9b: Yield: 97%, ^{1}H NMR (400 MHz, DMSO) δ 10.52 (s, 1H), 7.52 (dd, J = 13.4, 7.4 Hz, 4H), 7.35 (d, J = 7.5 Hz, 3H), 7.13 (d, J = 7.8 Hz, 2H), 4.19 (s, 1H), 3.04 (dd, J = 15.5, 7.1 Hz, 1H), 2.64 (dd, J = 15.5, 2.9 Hz, 1H), 1.93 (s, 3H), 1.27 (s, 9H). ^{13}C NMR (101 MHz, DMSO) δ 170.53 (s), 149.47 (s), 145.79 (s), 140.50 (s), 139.21 (s), 138.54 (s), 129.66 (s), 127.06 (d, J = 21.8 Hz), 126.91 – 126.67 (m), 125.90 (s), 123.13 (s), 104.10 (s), 40.55 (d, J = 21.1 Hz), 40.26 (s), 40.13 (d, J = 21.0 Hz), 40.02 (s), 40.02 (s), 39.71 (d, J = 21.0 Hz), 39.40 (s), 34.60 (s), 33.82 (s), 31.61 (s), 12.49 (s).



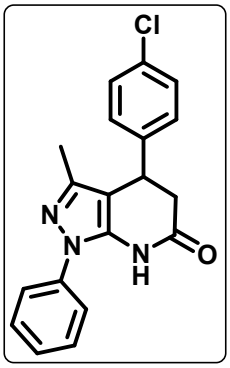
9c: Yield: 95%, ^{1}H NMR (400 MHz, DMSO) δ 10.51 (s, 1H), 7.51 (dt, J = 15.6, 7.9 Hz, 4H), 7.35 (t, J = 7.1 Hz, 1H), 7.13 (d, J = 8.6 Hz, 2H), 6.90 (d, J = 8.6 Hz, 2H), 4.18 (dd, J = 6.9, 4.9 Hz, 1H), 3.73 (s, 3H), 2.99 (dd, J = 15.6, 7.2 Hz, 1H), 2.63 (dd, J = 15.6, 4.8 Hz, 1H), 1.90 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 170.51 (s), 158.52 (s), 145.78 (s), 139.20 (s), 138.54 (s), 135.37 (s), 129.66 (s), 128.41 (s), 127.15 (s), 123.10 (s), 114.54 (s), 104.24 (s), 55.51 (s), 33.67 (s), 12.50 (s).
This compound was known.[9]



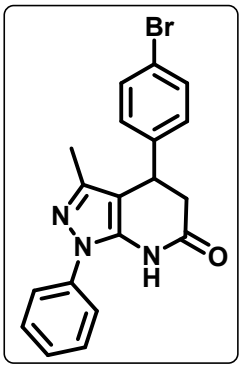
9d: Yield: 86%, white solid, ^{1}H NMR (400 MHz, DMSO) δ 10.50 (s, 1H), 7.51 (dt, J = 15.6, 7.9 Hz, 4H), 7.35 (t, J = 7.1 Hz, 1H), 6.89 (d, J = 8.2 Hz, 2H), 6.66 (dd, J = 8.2, 1.8 Hz, 1H), 4.23 – 4.12 (m, 1H), 3.73 (d, J = 3.9 Hz, 6H), 2.97 (dd, J = 15.6, 7.1 Hz, 1H), 2.69 (dd, J = 15.6, 5.1 Hz, 1H), 1.91 (s, 3H).^{13}C NMR (101 MHz, DMSO) δ 170.63 (s), 149.37 (s), 148.14 (s), 145.80 (s), 139.20 (s), 138.55 (s), 135.85 (s), 129.67 (s), 127.13 (s), 123.05 (s), 119.11 (s), 112.42 (s), 111.49 (s), 104.22 (s), 55.97 (s), 34.17 (s), 12.56 (s).
This compound was known.[9]



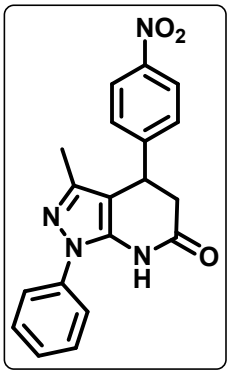
9e: Yield: 91%, white solid, ^{1}H NMR (400 MHz, DMSO) δ 10.56 (s, 1H), 7.69 – 6.99 (m, 9H), 4.27 (s, 1H), 3.02 (dd, J = 15.7, 7.2 Hz, 1H), 2.65 (dd, J = 15.7, 4.7 Hz, 1H), 1.90 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 170.31 (s), 162.72 (s), 160.31 (s), 145.74 (s), 139.62 (s), 139.31 (s), 138.48 (s), 129.67 (s), 129.31 (d, J = 8.1 Hz), 127.23 (s), 123.17 (s), 115.99 (s), 115.78 (s), 103.78 (s), 33.71 (s), 12.49 (s).
This compound was known.[8]



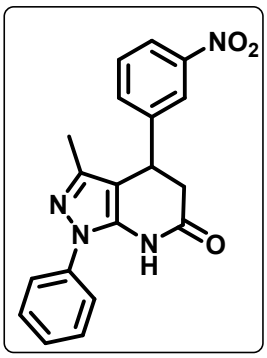
9f: Yield: 97%, white solid, ^{1}H NMR (400 MHz, DMSO) δ 10.57 (s, 1H), 7.59 – 7.21 (m, 9H), 4.27 (dd, J = 7.2, 4.7 Hz, 1H), 3.04 (dd, J = 15.7, 7.3 Hz, 1H), 2.64 (dd, J = 15.7, 4.7 Hz, 1H), 1.90 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 170.21 (s), 145.75 (s), 142.52 (s), 139.39 (s), 138.46 (s), 131.81 (s), 129.67 (s), 129.34 (s), 129.14 (s), 127.25 (s), 123.18 (s), 103.41 (s), 33.81 (s), 12.51 (s).
This compound was known.[9]



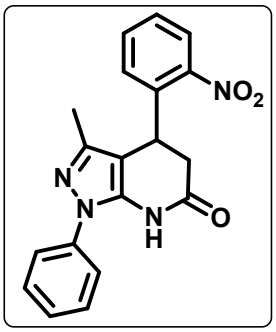
9g: Yield: 96%, white solid, ^{1}H NMR (400 MHz, DMSO) δ 10.57 (s, 1H), 7.61 – 7.46 (m, 6H), 7.37 (d, J = 7.1 Hz, 1H), 7.18 (d, J = 8.4 Hz, 2H), 4.25 (dd, J = 7.1, 4.7 Hz, 1H), 3.04 (dd, J = 15.7, 7.3 Hz, 1H), 2.64 (dd, J = 15.7, 4.6 Hz, 1H), 1.91 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 170.19 (s), 145.76 (s), 142.96 (s), 139.40 (s), 138.46 (s), 132.06 (s), 129.70 (d, J = 4.9 Hz), 127.26 (s), 123.18 (s), 120.29 (s), 103.33 (s), 33.86 (s), 12.51 (s).
This compound was known.[9]



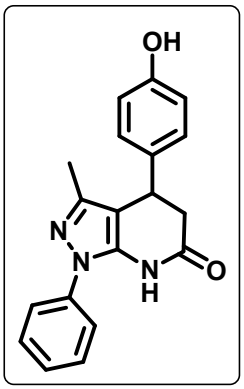
9h: Yield: 95%, white solid, ^{1}H NMR (400 MHz, DMSO) δ 10.66 (s, 1H), 8.22 (d, J = 8.6 Hz, 2H), 7.66 – 7.17 (m, 7H), 4.46 (dd, J = 7.1, 4.7 Hz, 1H), 3.12 (dd, J = 15.8, 7.4 Hz, 1H), 2.69 (dd, J = 15.8, 4.6 Hz, 1H), 1.91 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 169.90 (s), 151.44 (s), 146.94 (s), 145.78 (s), 139.56 (s), 138.39 (s), 129.69 (s), 128.86 (s), 127.36 (s), 124.46 (s), 123.29 (s), 102.65 (s), 34.29 (s), 12.53 (s).
This compound was known.[9]



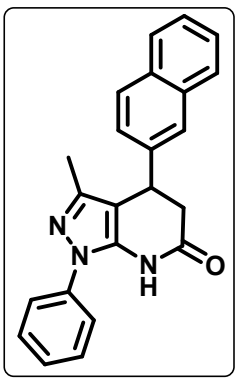
9i: Yield: 87%, white solid, ^{1}H NMR (400 MHz, DMSO) δ 10.66 (s, 1H), 8.19 – 8.06 (m, 2H), 7.68 (dt, J = 15.6, 7.7 Hz, 2H), 7.53 (dt, J = 15.6, 7.9 Hz, 4H), 7.37 (t, J = 7.2 Hz, 1H), 4.49 (dd, J = 7.1, 4.9 Hz, 1H), 3.10 (dd, J = 15.8, 7.3 Hz, 1H), 2.73 (dd, J = 15.8, 4.8 Hz, 1H), 1.91 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 170.00 (s), 148.56 (s), 145.81 (d, J = 12.9 Hz), 139.59 (s), 138.40 (s), 134.39 (s), 130.84 (s), 129.70 (s), 127.35 (s), 123.25 (s), 122.41 (s), 122.10 (s), 102.85 (s), 34.03 (s), 12.56 (s).
This compound was known.[9]



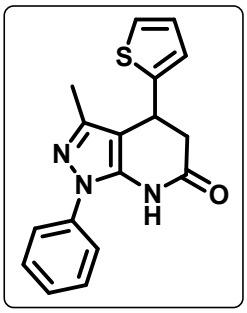
9j: Yield: 63%, white solid, ^{1}H NMR (400 MHz, DMSO) δ 10.69 (s, 1H), 8.07 – 7.93 (m, 1H), 7.69 (t, J = 7.2 Hz, 1H), 7.63 – 7.46 (m, 5H), 7.41 – 7.29 (m, 2H), 4.66 (dd, J = 7.4, 5.4 Hz, 1H), 3.15 (dd, J = 15.9, 7.6 Hz, 1H), 2.68 (dd, J = 15.9, 5.3 Hz, 1H), 1.79 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 169.70 (s), 149.40 (s), 145.65 (s), 140.18 (s), 138.36 (s), 136.78 (s), 134.04 (s), 129.72 (d, J = 5.2 Hz), 128.94 (s), 127.40 (s), 124.99 (s), 123.35 (s), 102.29 (s), 30.04 (s), 12.26 (s).
This compound was known.[8]



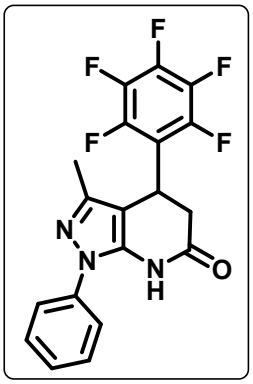
9k: Yield: 91%, white solid, ^{1}H NMR (400 MHz, DMSO) δ 10.48 (s, 1H), 9.30 (s, 1H), 7.51 (dt, J = 15.4, 7.9 Hz, 4H), 7.35 (t, J = 7.0 Hz, 1H), 7.00 (d, J = 8.3 Hz, 2H), 6.72 (d, J = 8.3 Hz, 2H), 4.20 – 4.05 (m, 1H), 2.96 (dd, J = 15.6, 7.1 Hz, 1H), 2.61 (dd, J = 15.6, 4.7 Hz, 1H), 1.90 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 170.62 (s), 156.56 (s), 145.80 (s), 139.13 (s), 138.55 (s), 133.58 (s), 129.66 (s), 128.33 (s), 127.12 (s), 123.08 (s), 115.84 (s), 104.44 (s), 33.70 (s), 12.50 (s).



9l: Yield: 88%, white solid, ^{1}H NMR (400 MHz, DMSO) δ 10.56 (s), 7.91 – 7.78 (m), 7.64 (s), 7.54 (d, J = 7.6 Hz), 7.46 (ddd, J = 5.8, 5.3, 2.5 Hz), 7.41 – 7.29 (m), 4.38 (dd, J = 7.0, 5.1 Hz), 3.06 (dd, J = 15.8, 7.3 Hz), 2.73 (dd, J = 15.7, 5.0 Hz), 1.85 (s). ^{13}C NMR (101 MHz, DMSO) δ 170.50 (s), 145.98 (s), 141.11 (s), 139.54 (s), 138.61 (s), 133.56 (s), 132.59 (s), 129.76 (s), 129.03 (s), 128.09 (d, J = 5.9 Hz), 127.29 (s), 126.82 (s), 126.23 (d, J = 12.6 Hz), 125.61 (s), 123.23 (s), 103.75 (s), 34.77 (s), 12.63 (s).

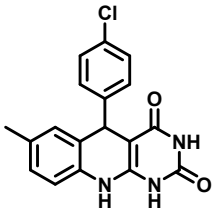


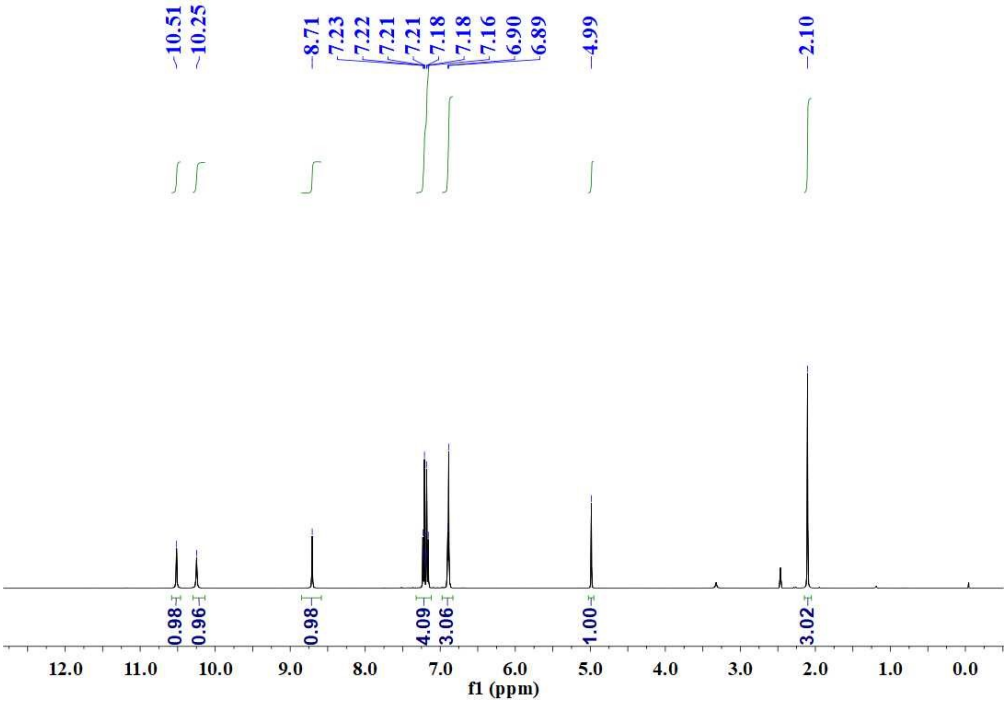
9m: Yield: 93%, white solid, ^{1}H NMR (400 MHz, DMSO) δ 10.55 (s), 7.46 (dt, J = 15.4, 7.8 Hz), 7.31 (t, J = 7.1 Hz), 6.97 – 6.84 (m), 4.48 (dd, J = 6.7, 3.1 Hz), 3.07 (dd, J = 15.7, 7.0 Hz), 2.70 (dd, J = 15.7, 3.2 Hz), 2.04 (s). ^{13}C NMR (101 MHz, DMSO) δ 170.11 (s), 147.83 (s), 145.65 (s), 139.07 (s), 138.50 (s), 129.75 (s), 127.69 (s), 127.34 (s), 124.99 (s), 124.40 (s), 123.23 (s), 104.49 (s), 44.04 (s), 29.81 (s), 12.42 (s).
This compound was known.[9]



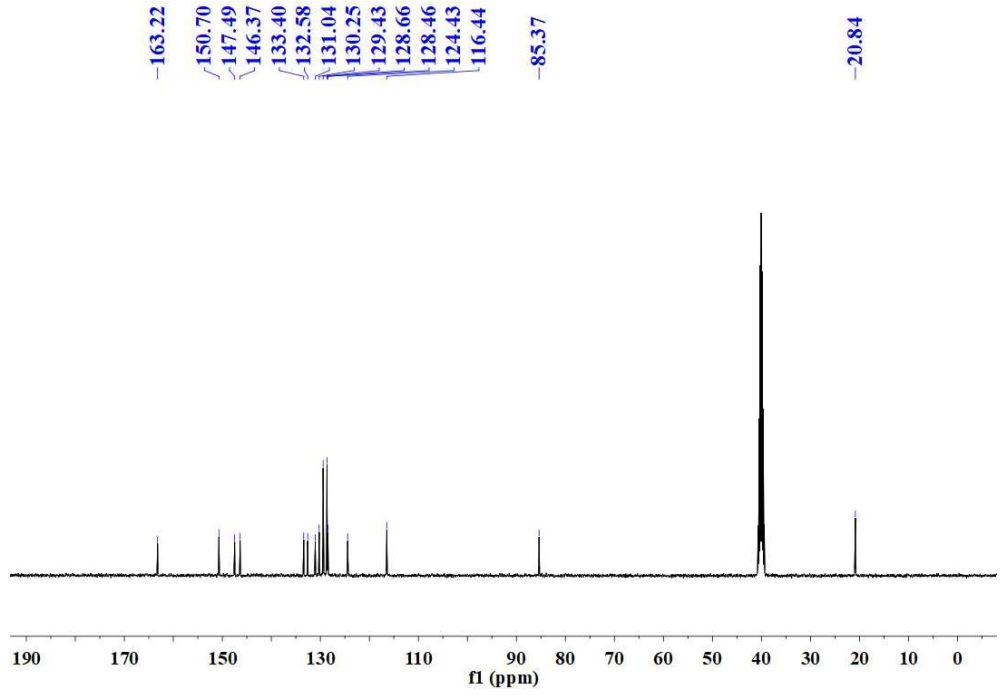
9n: Yield: 87%, white solid, ^{1}H NMR (400 MHz, DMSO) δ 10.72 (s, 1H), 7.66 – 7.26 (m, 5H), 4.87 – 4.51 (m, 1H), 3.23 (dd, J = 16.9, 9.4 Hz, 1H), 2.66 (dd, J = 16.9, 2.7 Hz, 1H), 1.95 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 169.44 (s), 145.80 (s), 139.60 (s), 138.21 (s), 129.69 (s), 127.48 (s), 123.57 (s), 98.85 (s), 36.38 (s), 24.11 (s), 12.03 (s).

6. NMR spectra of isolated compounds.

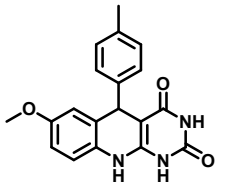


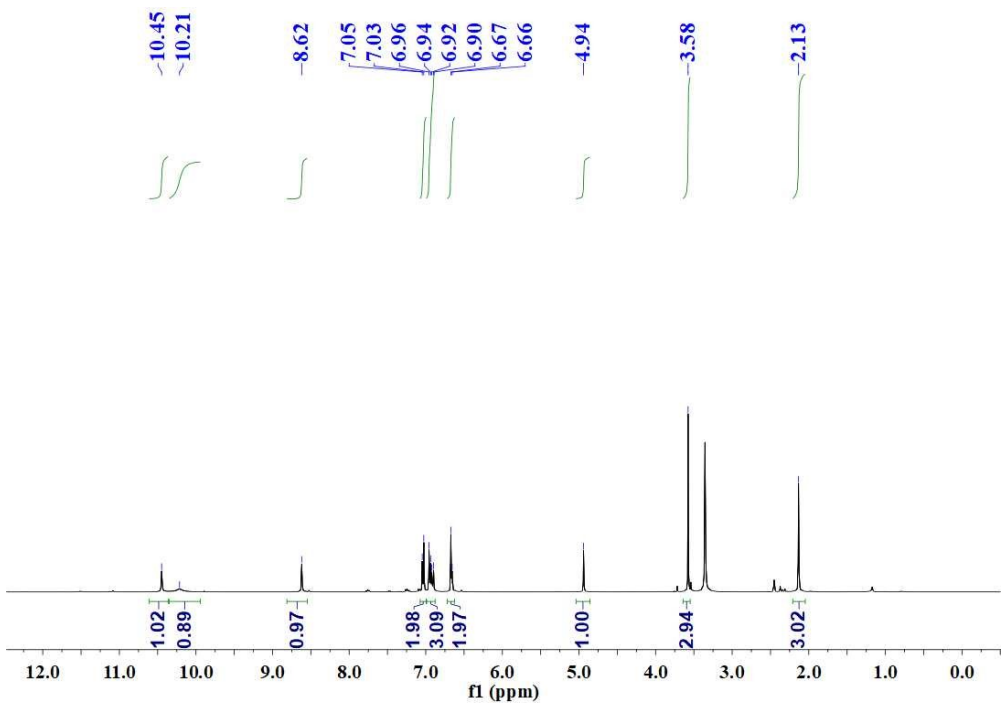


^{1}H NMR spectra of 6a

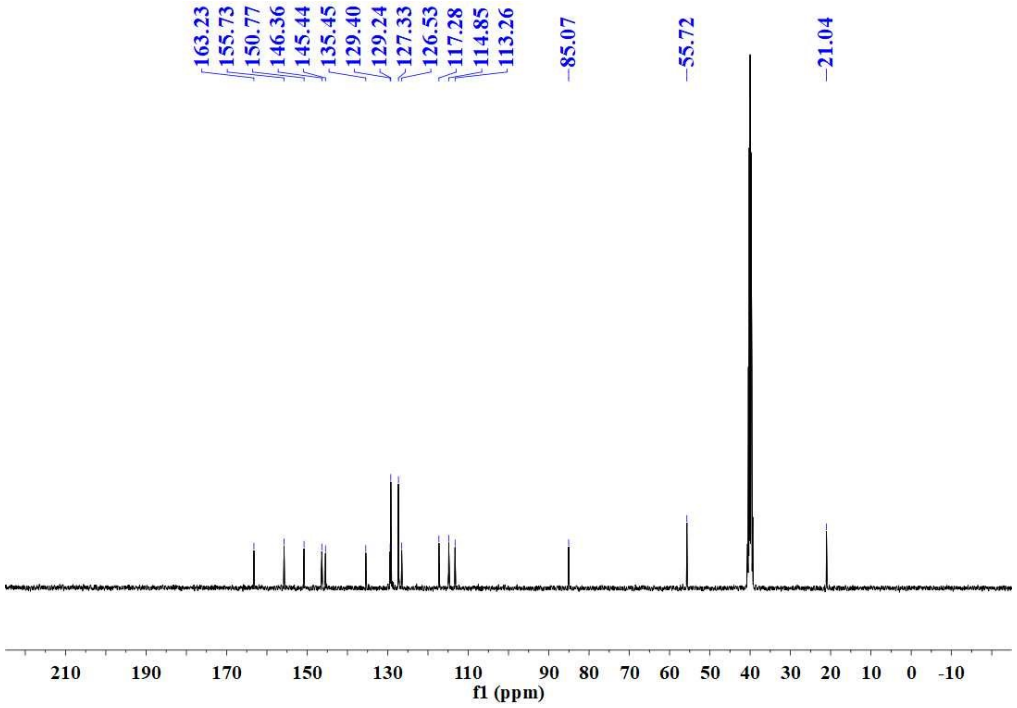


^{13}C NMR spectra of 6a

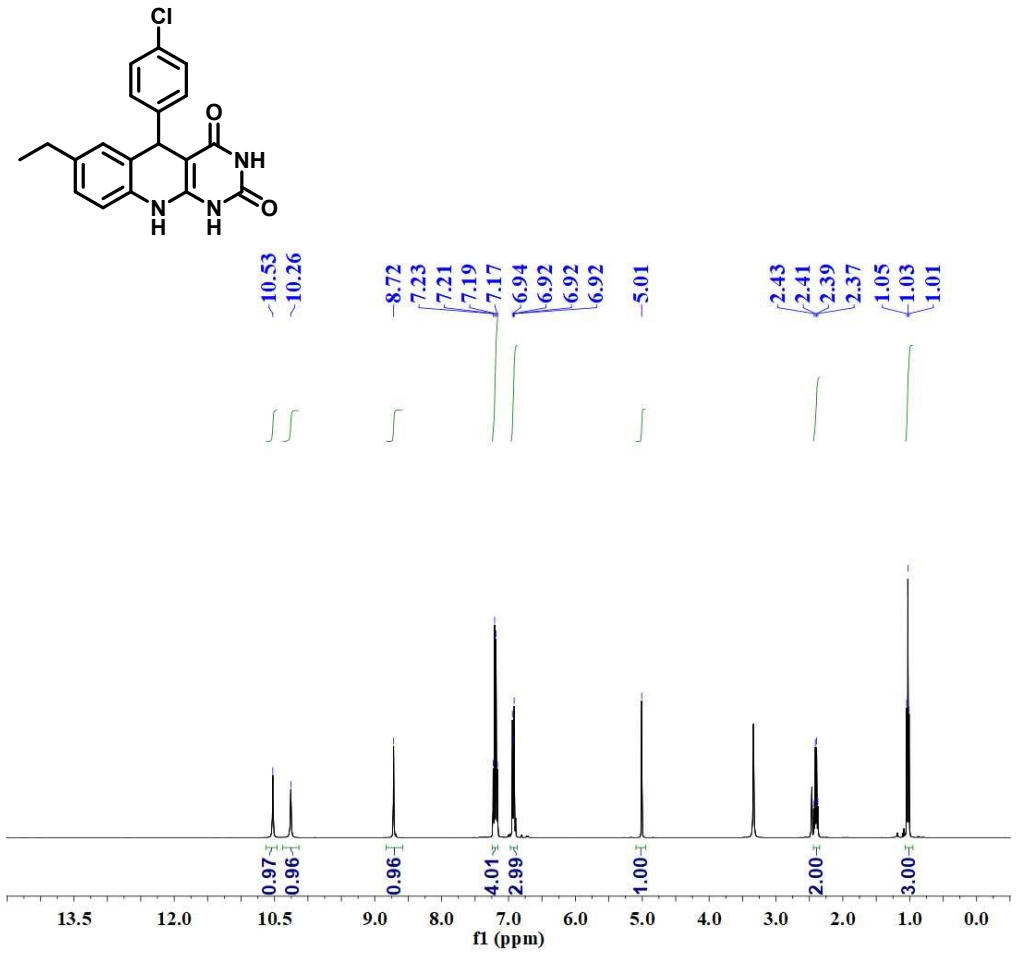




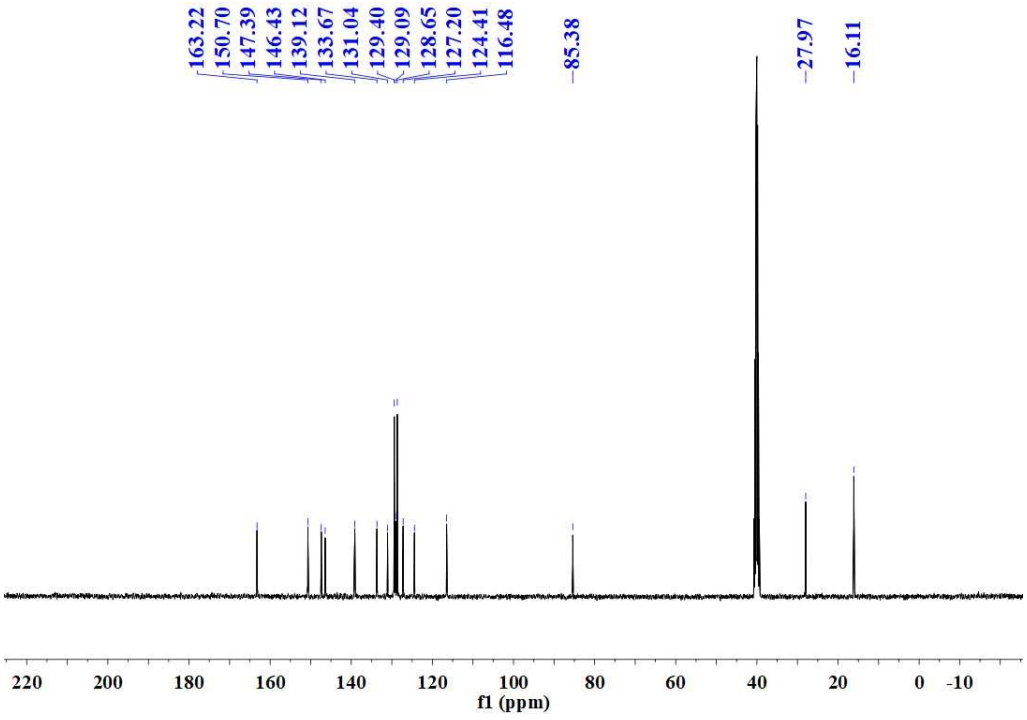
^{1}H NMR spectra of 6b



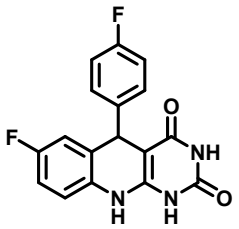
^{13}C NMR spectra of 6b

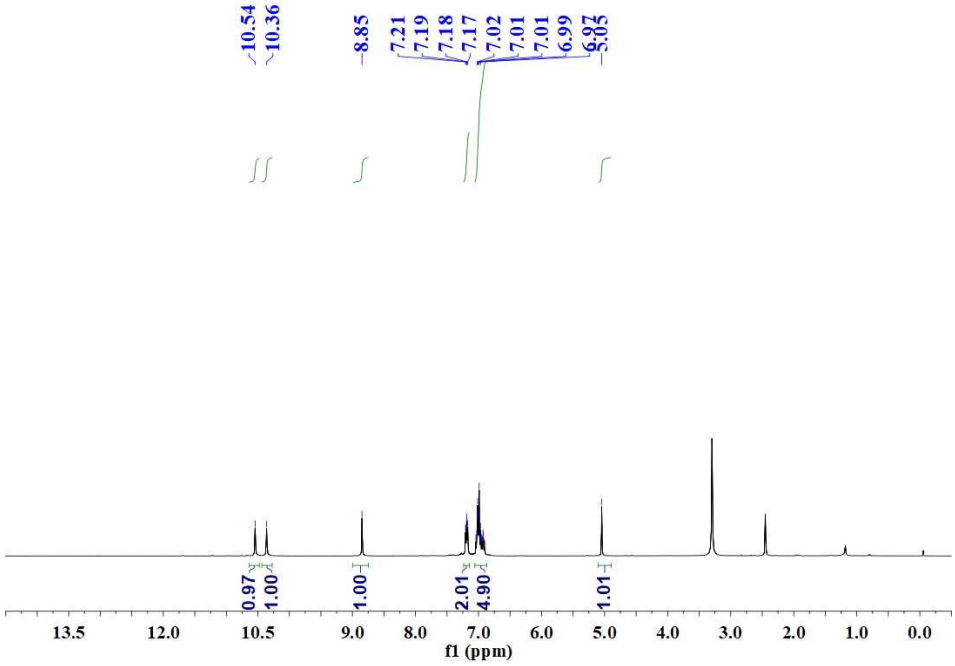


^{1}H NMR spectra of 6c

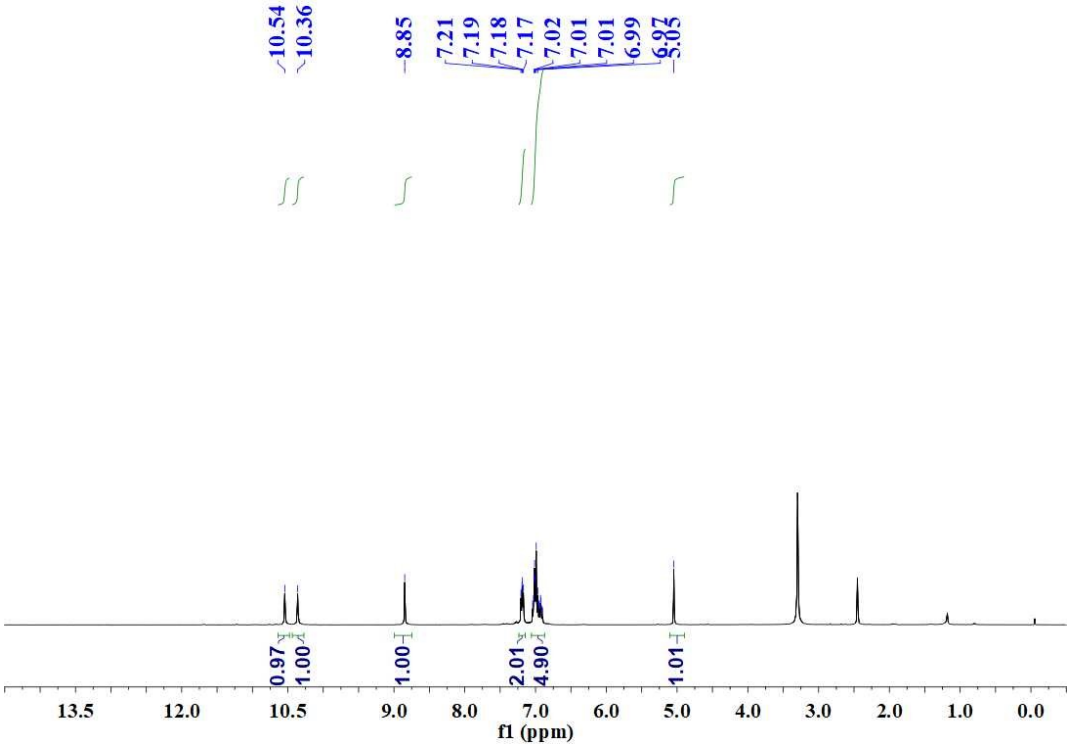


^{13}C NMR spectra of 6c

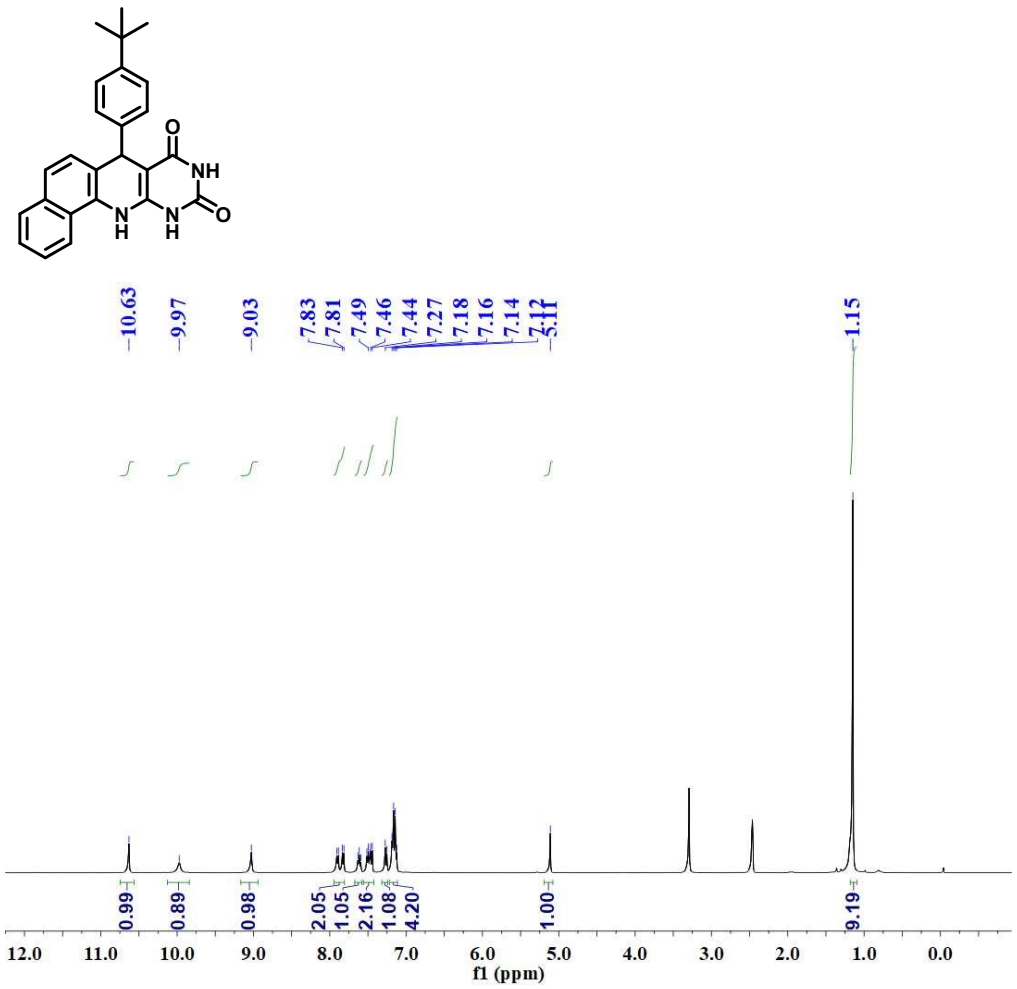




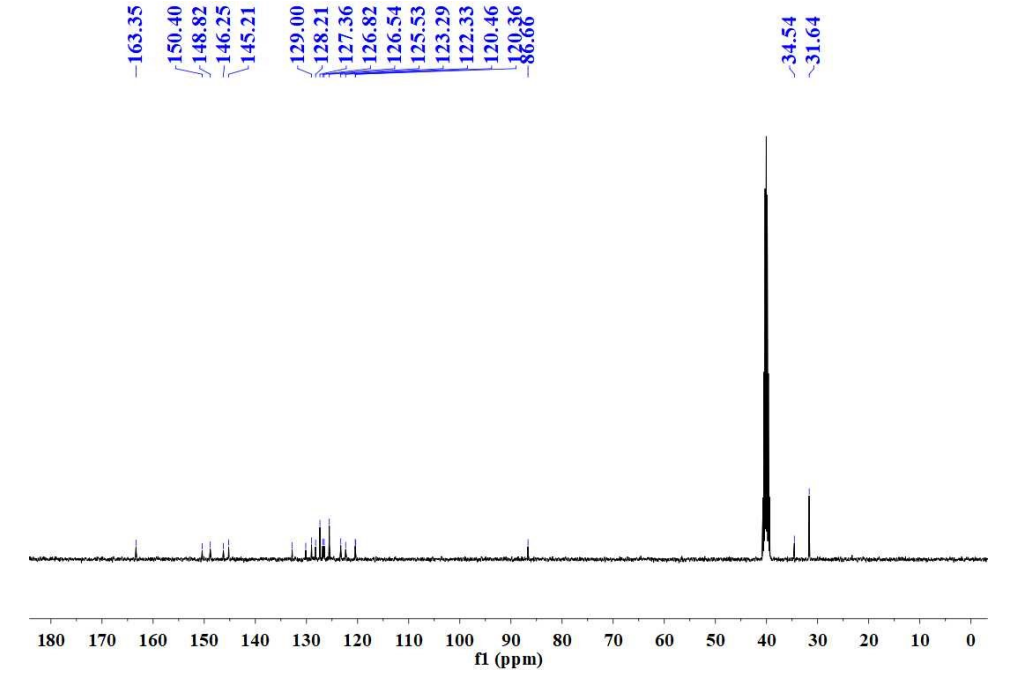
^{1}H NMR spectra of 6d



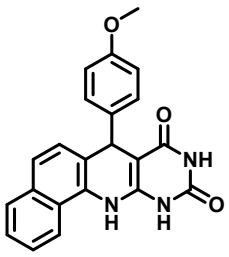
^{13}C NMR spectra of 6d

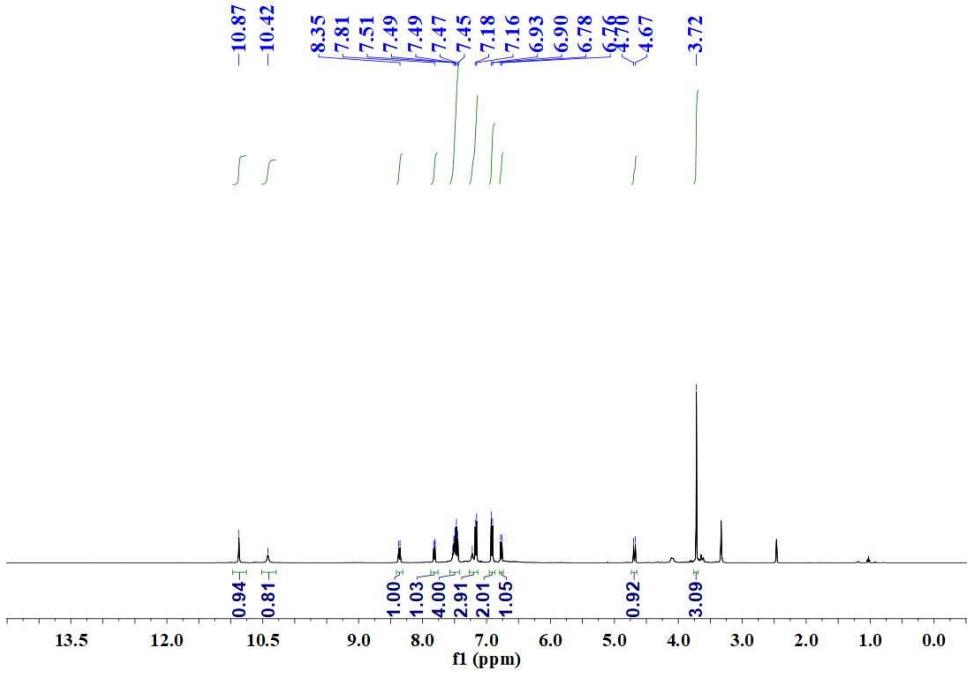


^{1}H NMR spectra of 6e

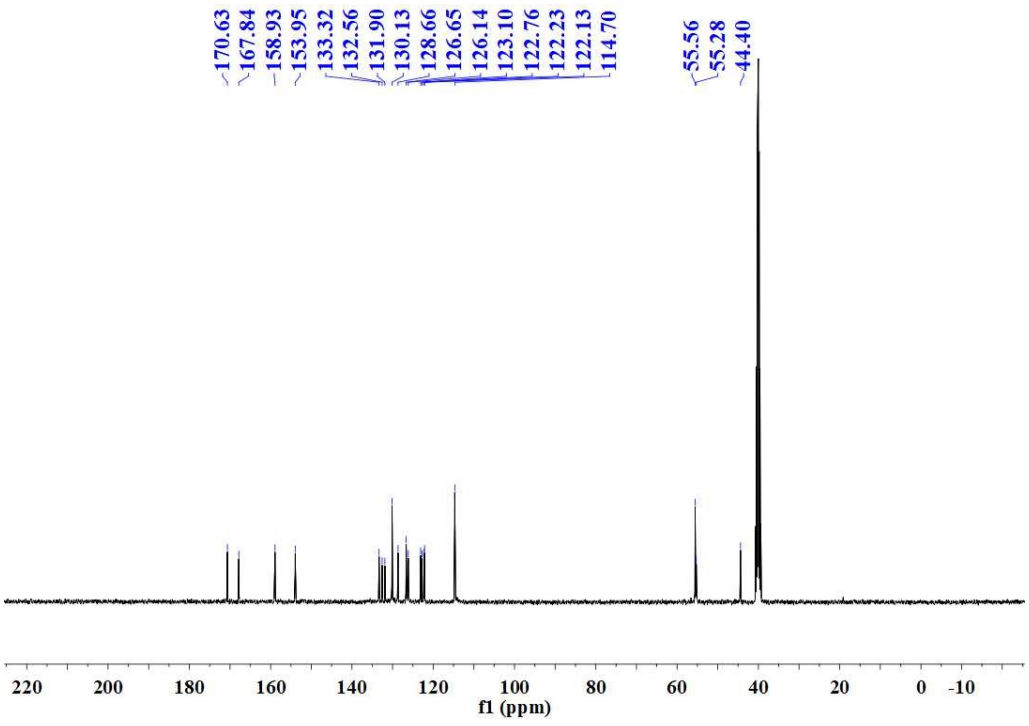


^{13}C NMR spectra of 6e

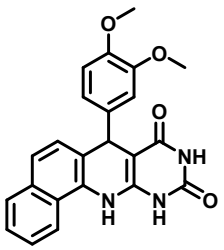


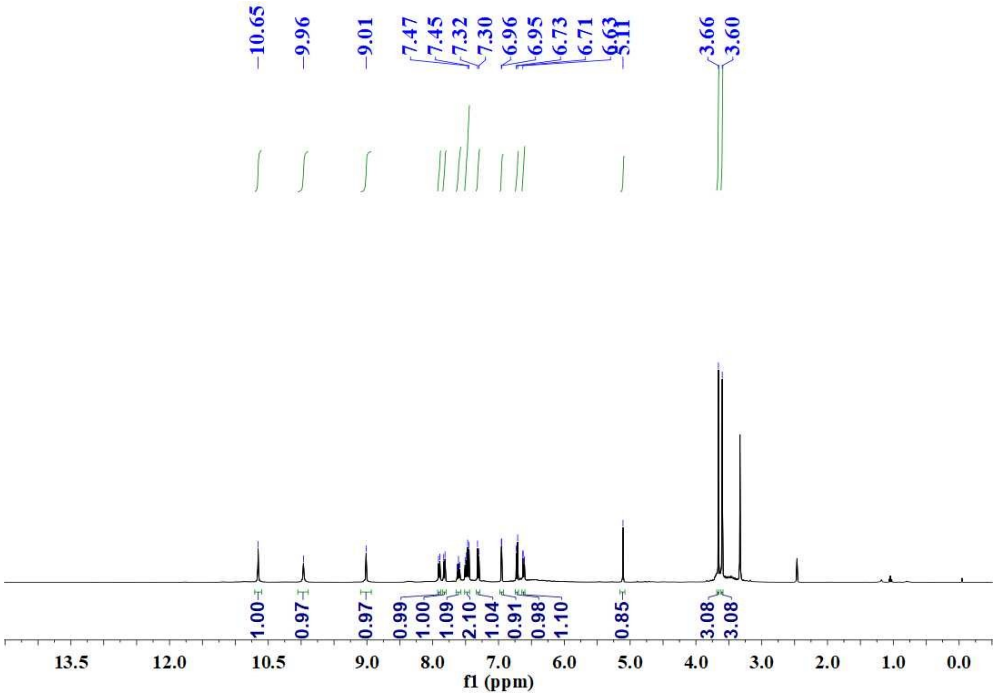


^{1}H NMR spectra of 6f

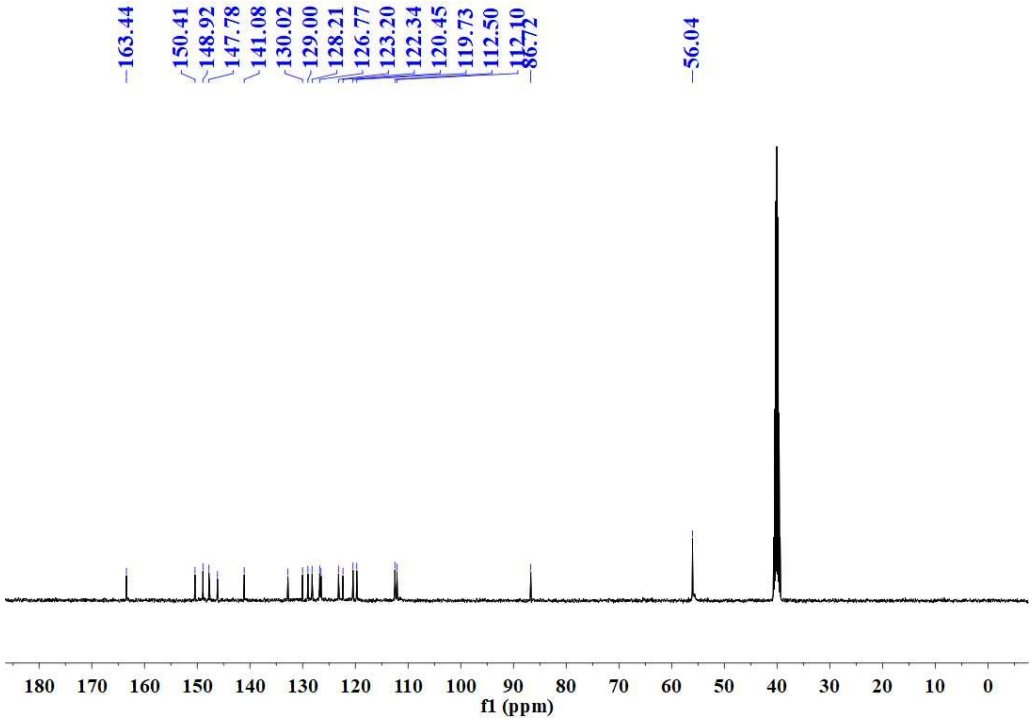


^{13}C NMR spectra of 6f

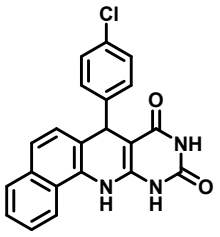


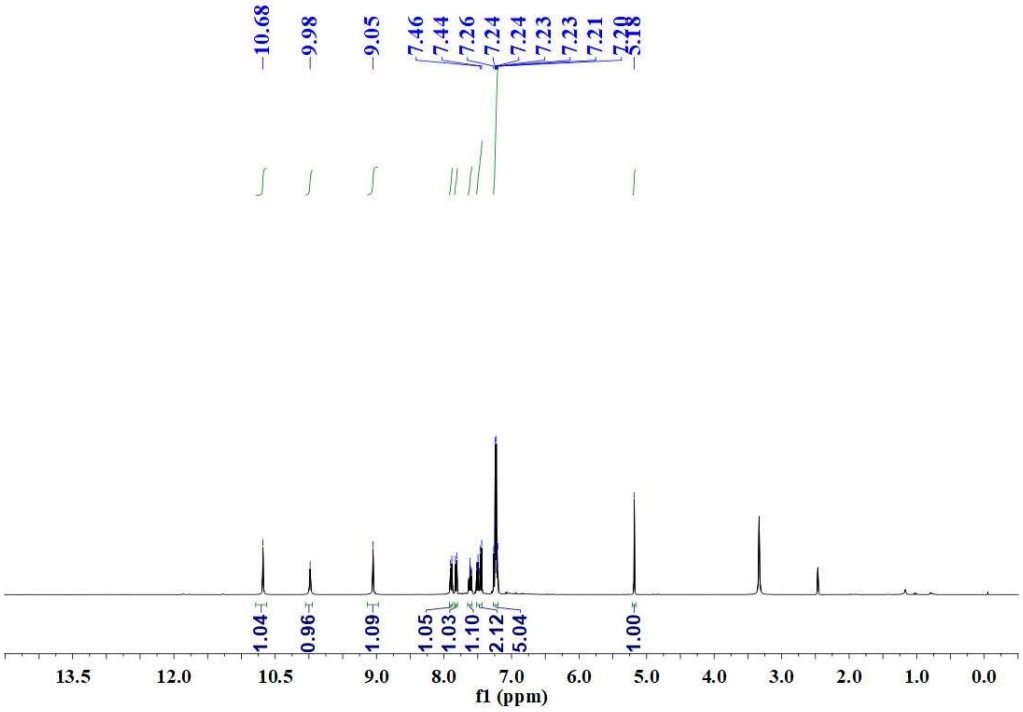


^{1}H NMR spectra of 6g

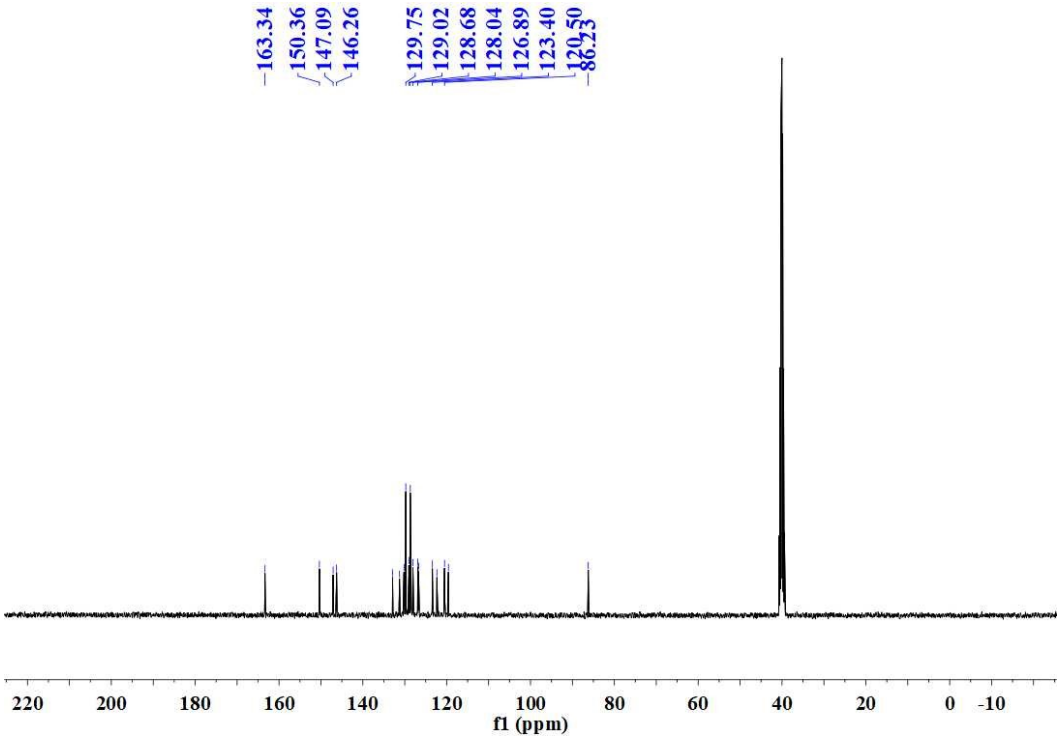


^{13}C NMR spectra of 6g

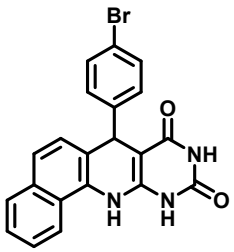


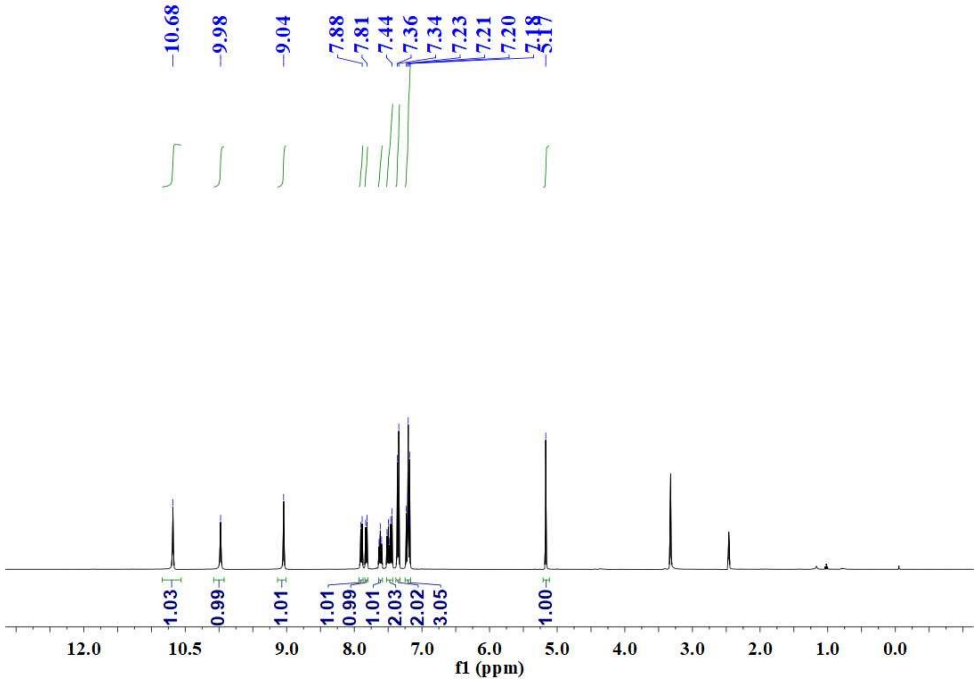


^{1}H NMR spectra of 6h

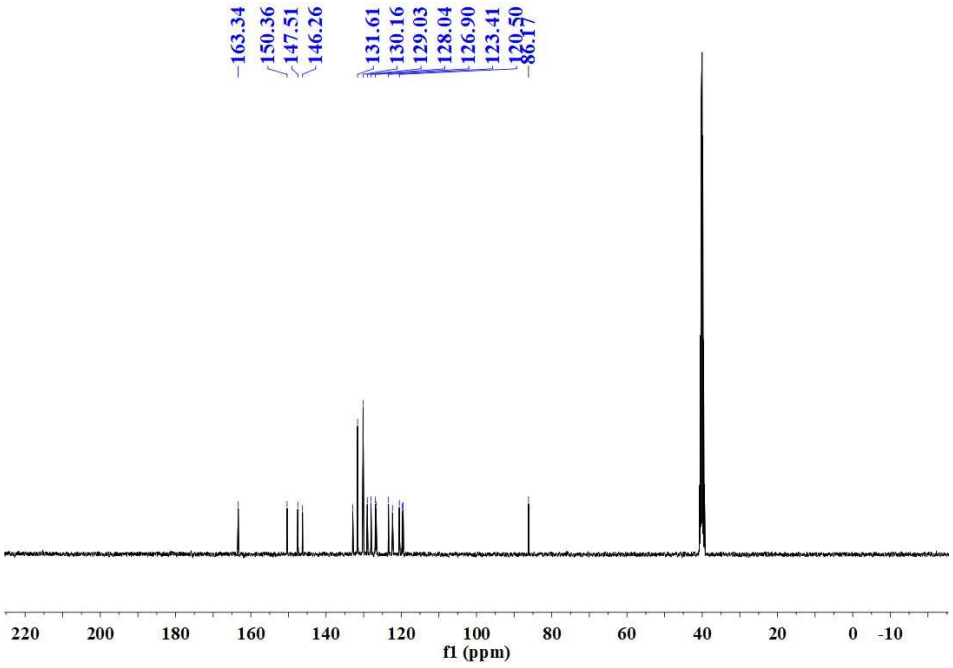


^{13}C NMR spectra of 6h

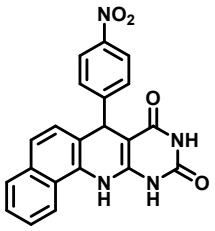


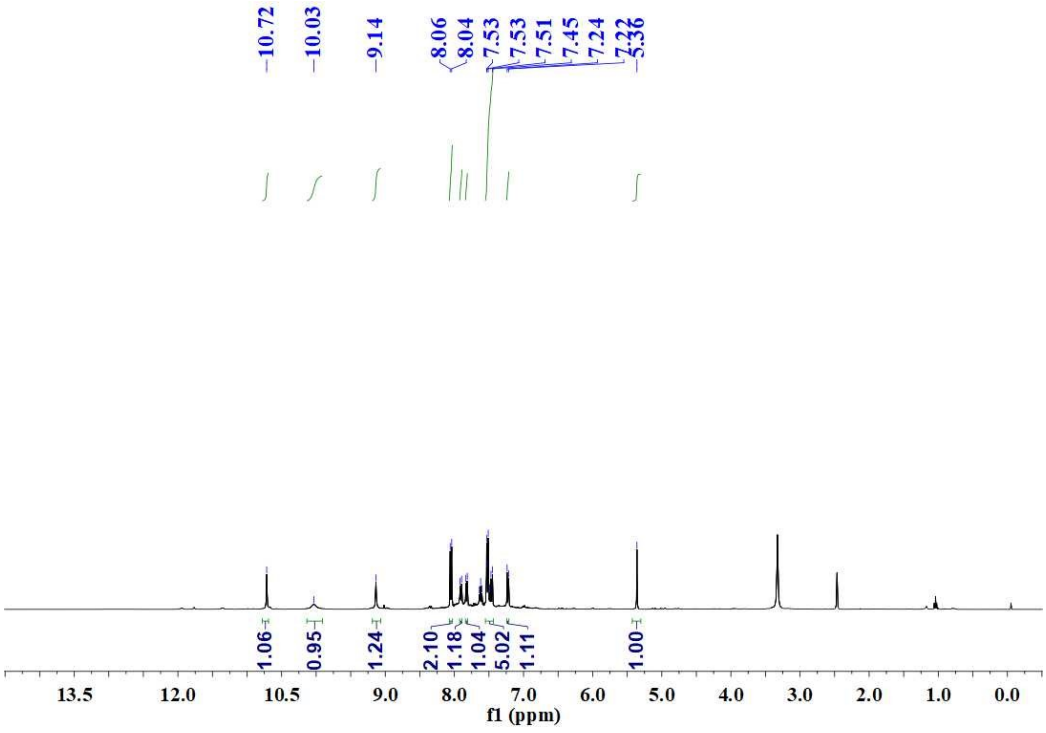


^{1}H NMR spectra of 6i

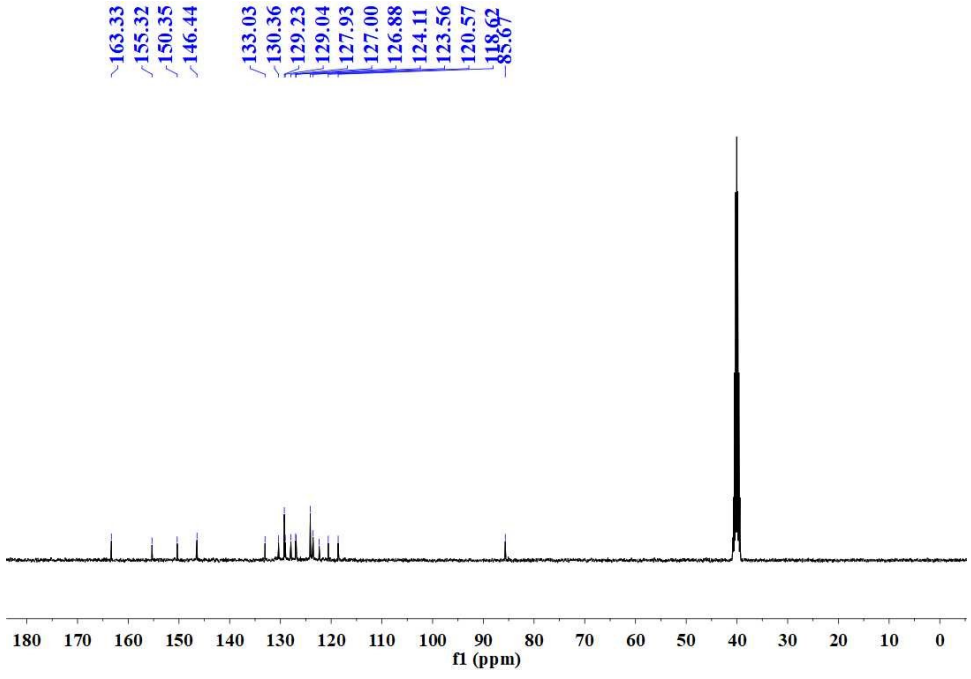


^{13}C NMR spectra of 6i

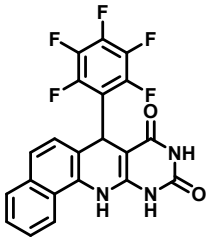


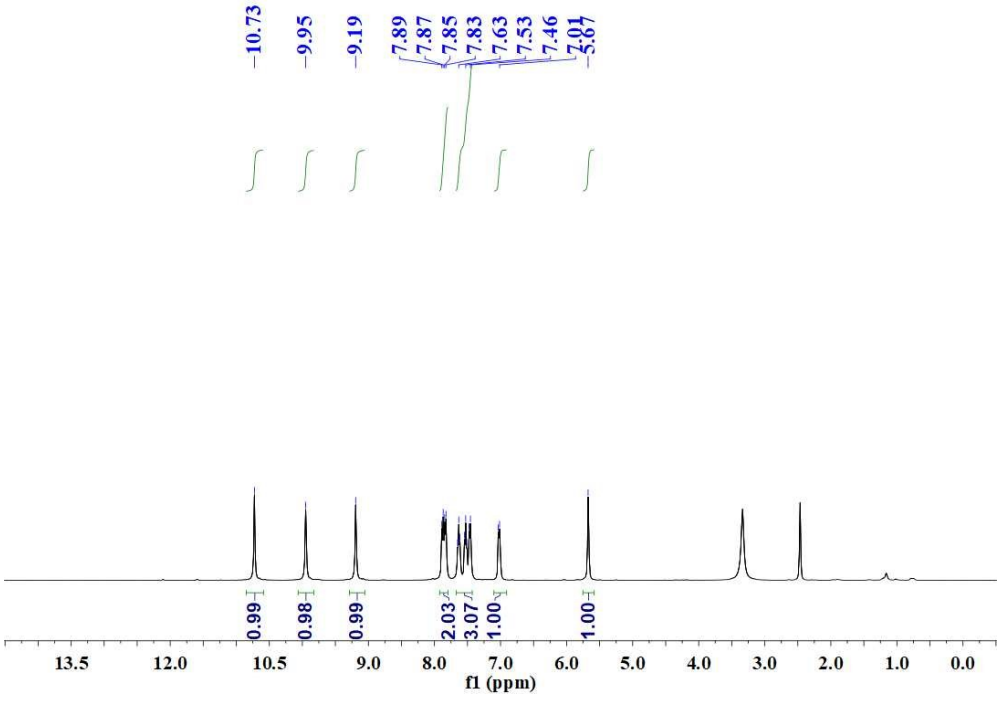


^{1}H NMR spectra of 6j

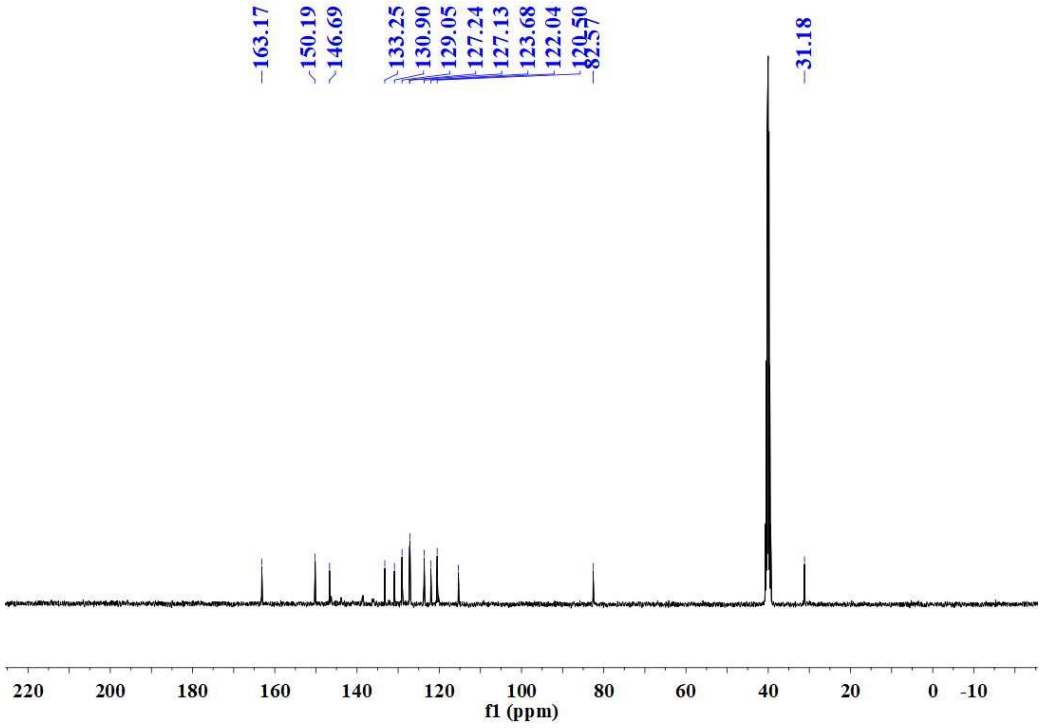


^{13}C NMR spectra of 6j

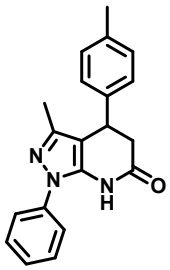


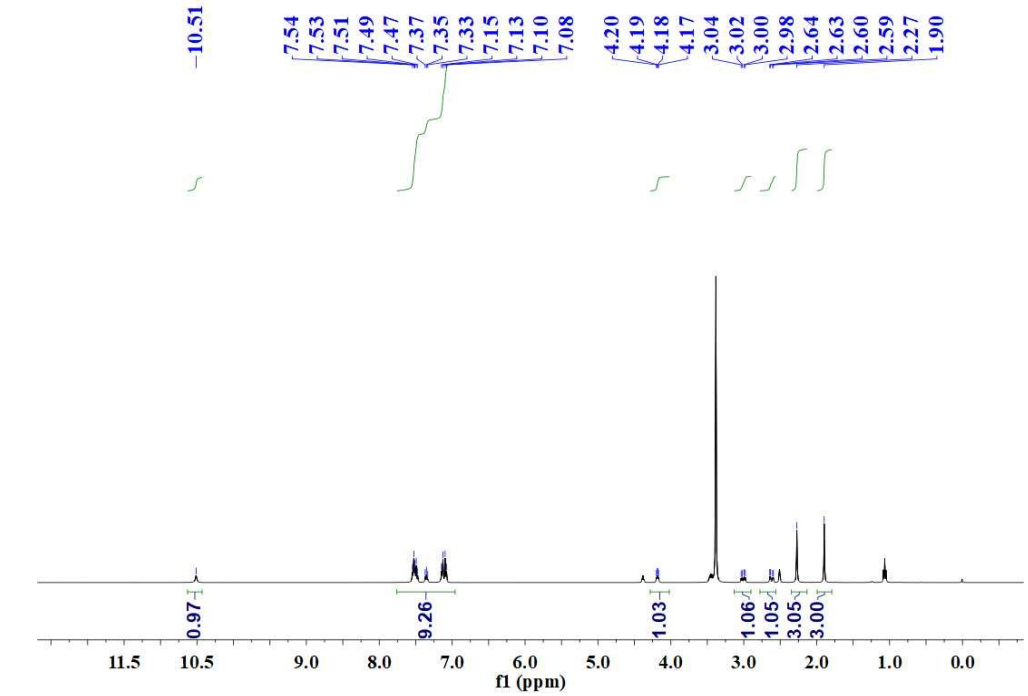


^{1}H NMR spectra of 6k

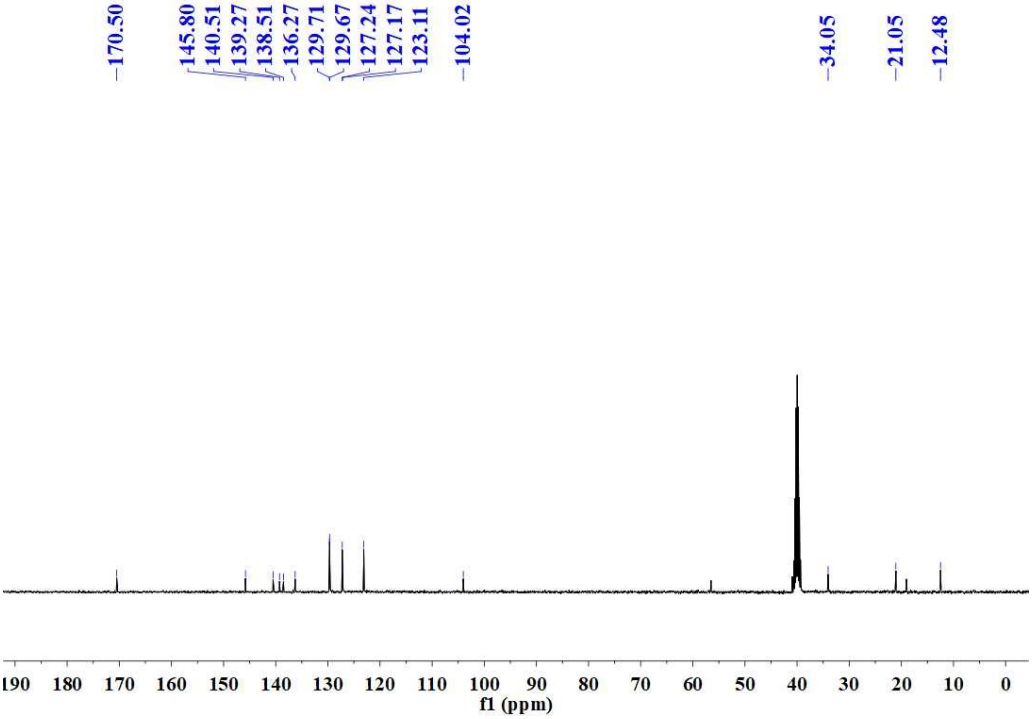


^{13}C NMR spectra of 6k

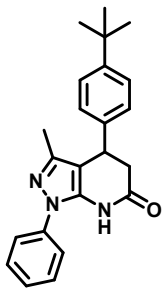


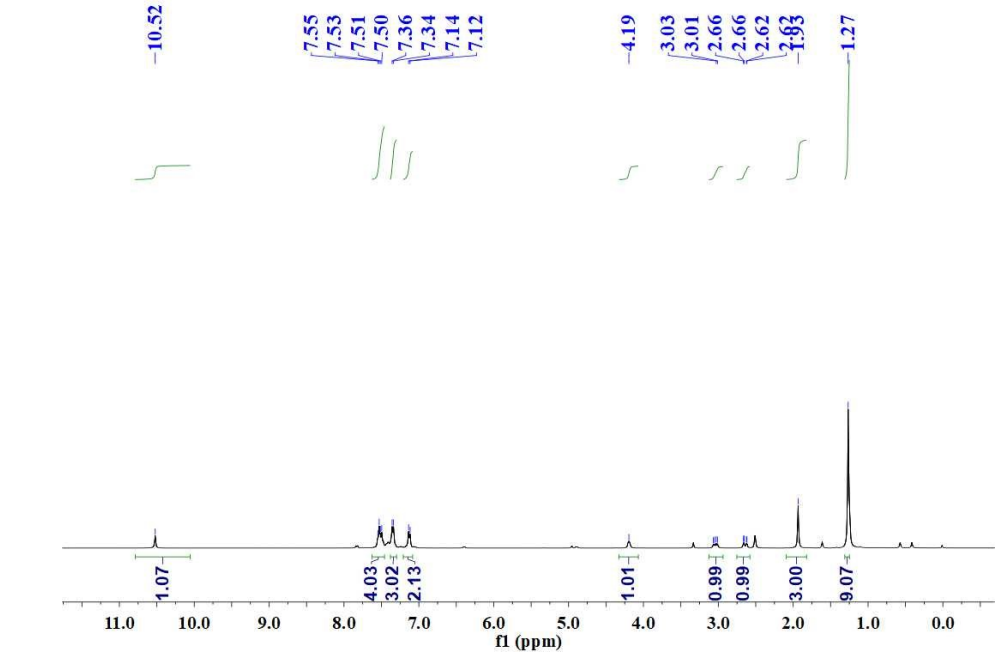


^{1}H NMR spectra of 9a

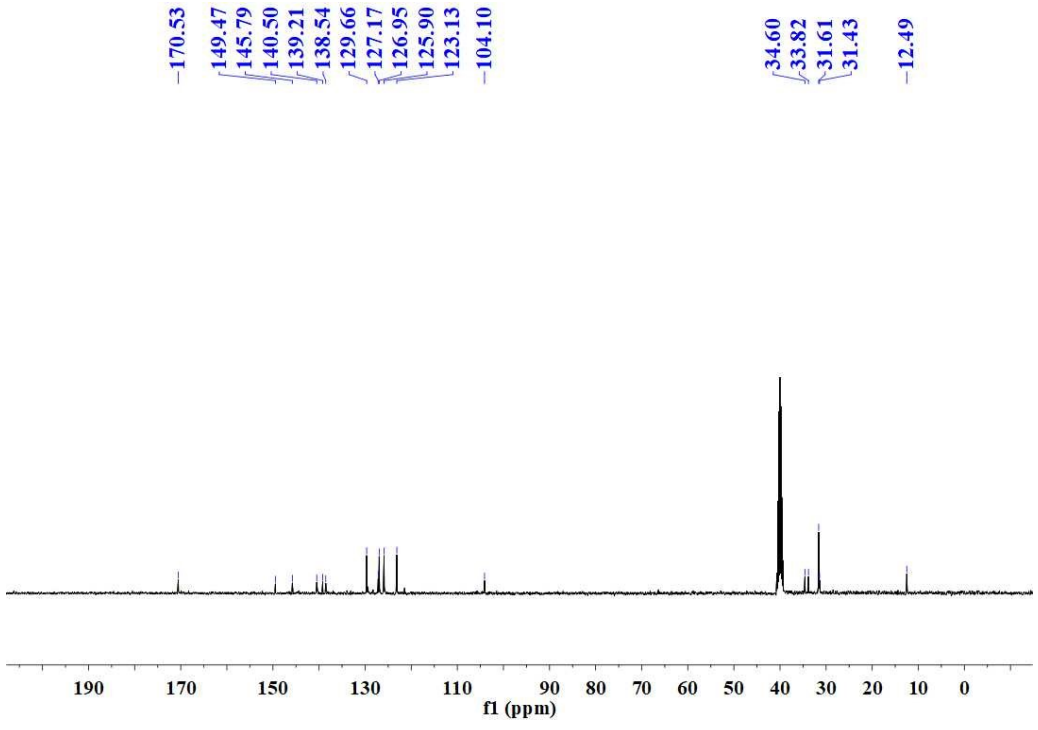


^{13}C NMR spectra of 9a

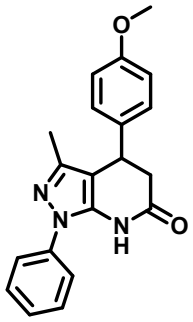


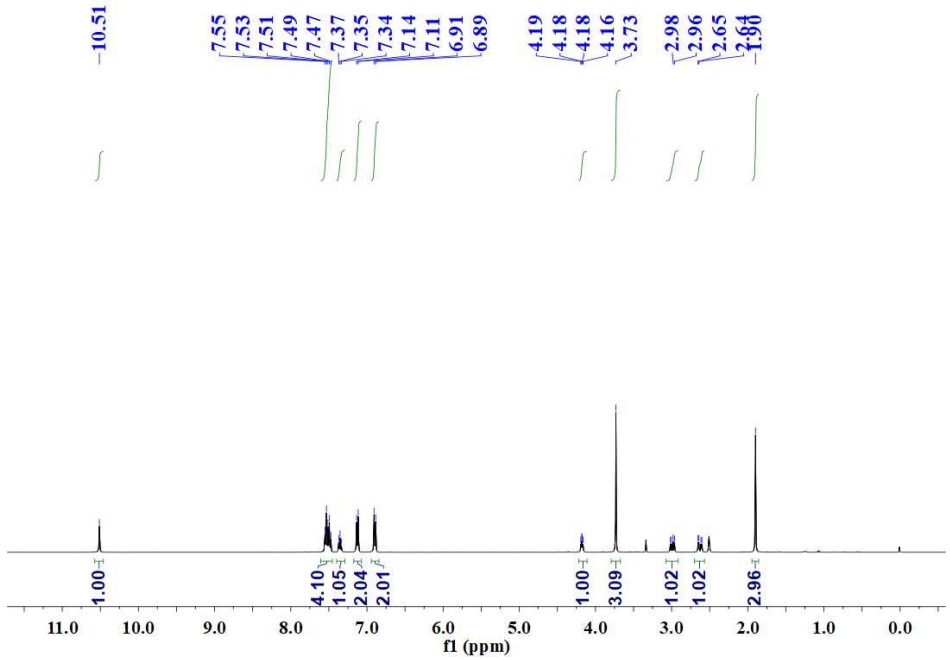


^{1}H NMR spectra of 9b

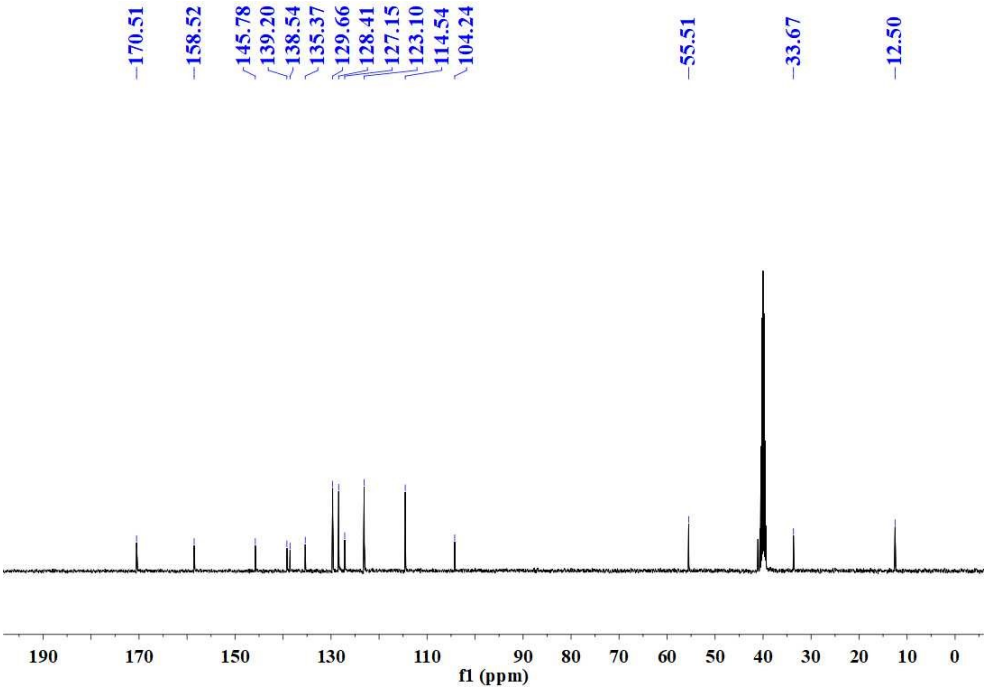


^{13}C NMR spectra of 9b

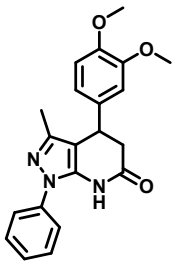


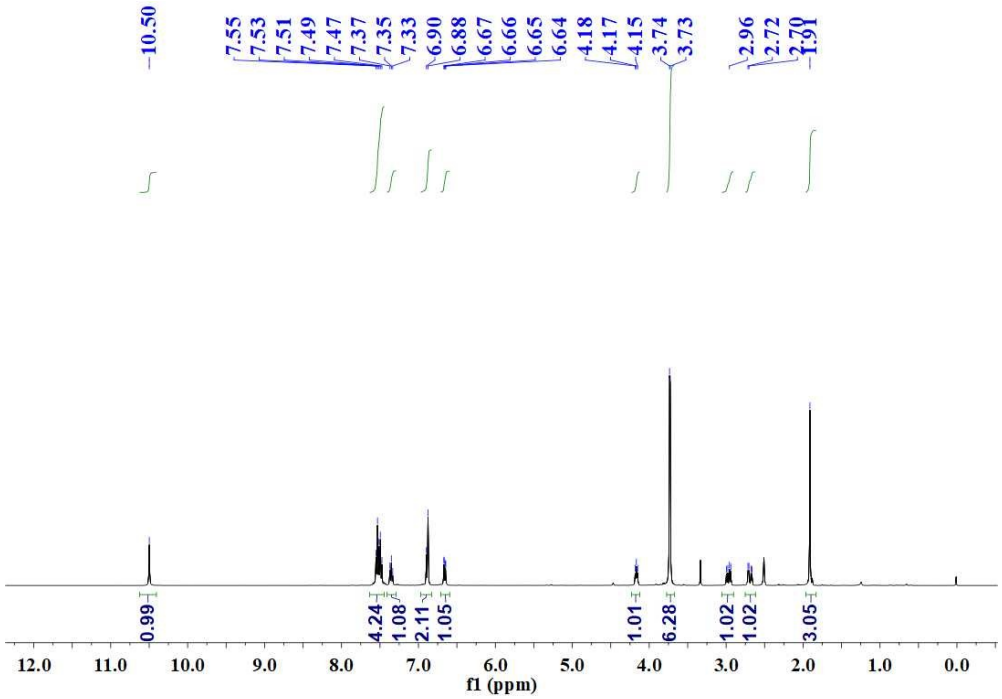


^{1}H NMR spectra of 9c

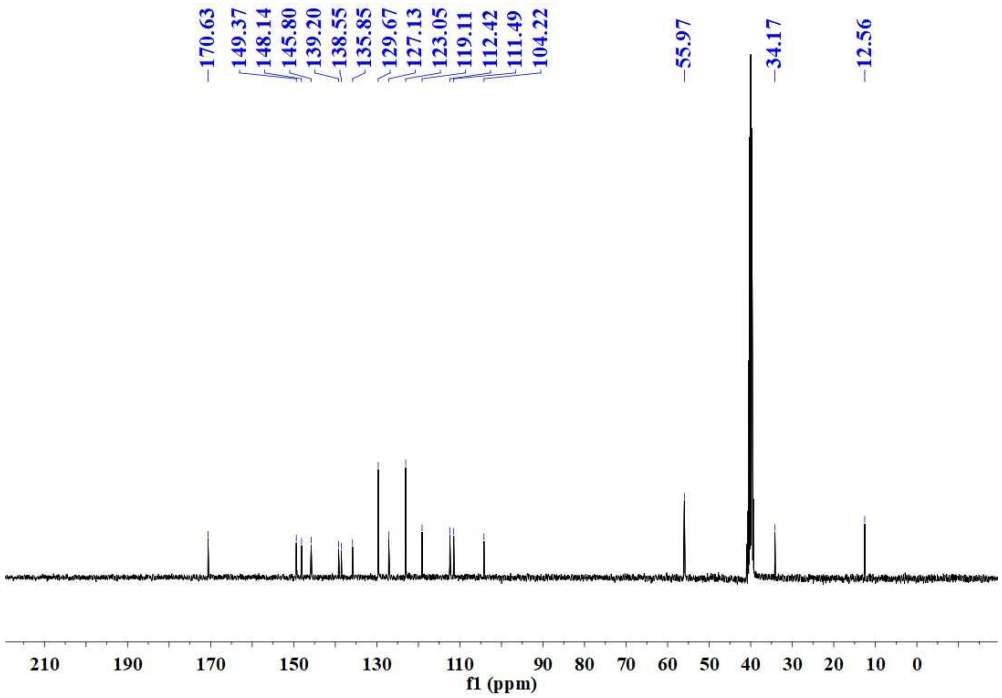


^{13}C NMR spectra of 9c

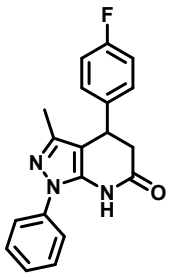


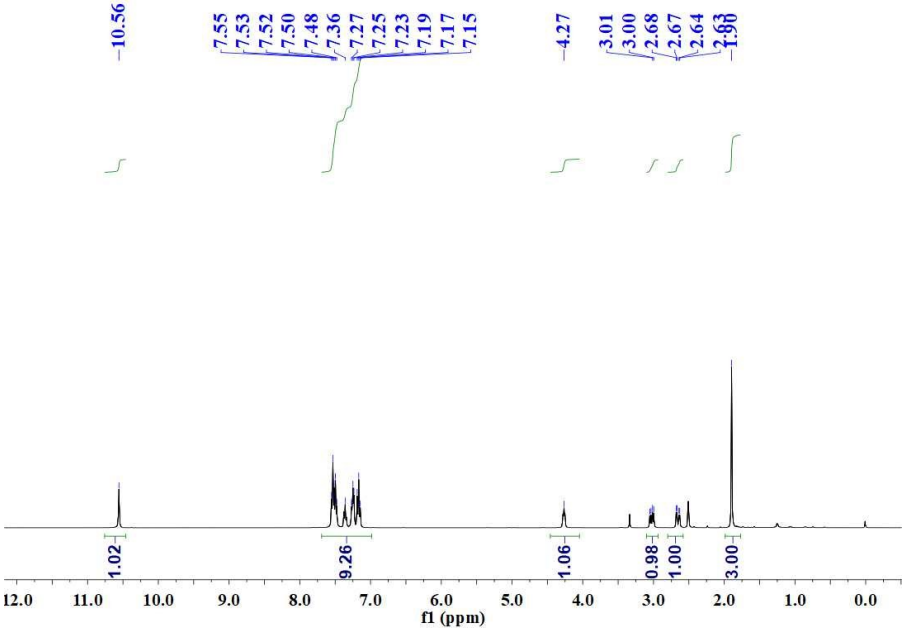


^{1}H NMR spectra of 9d

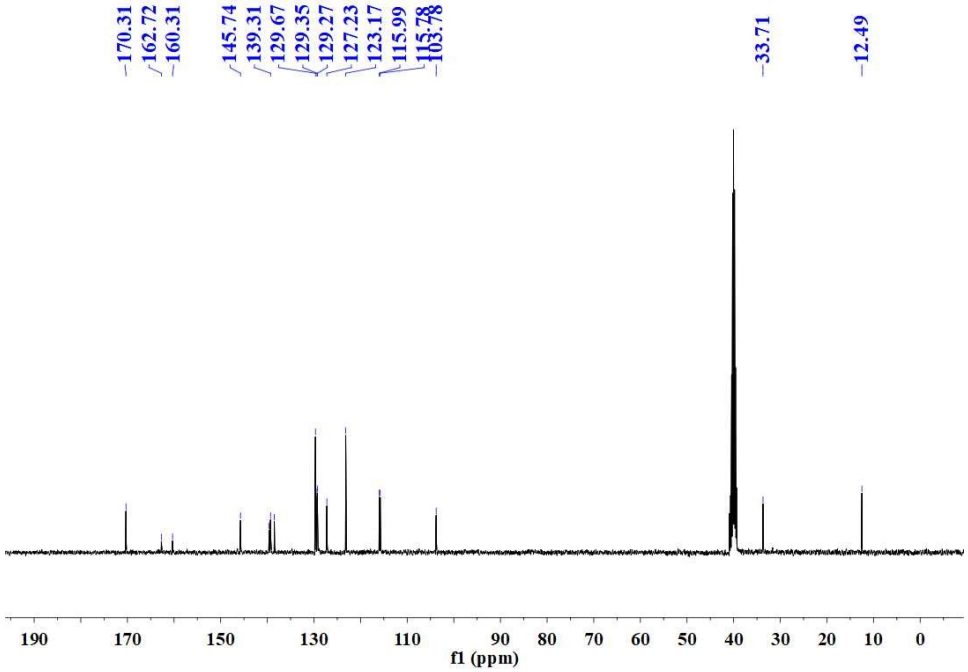


^{13}C NMR spectra of 9d

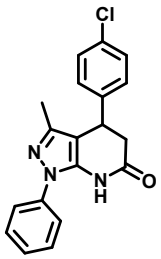


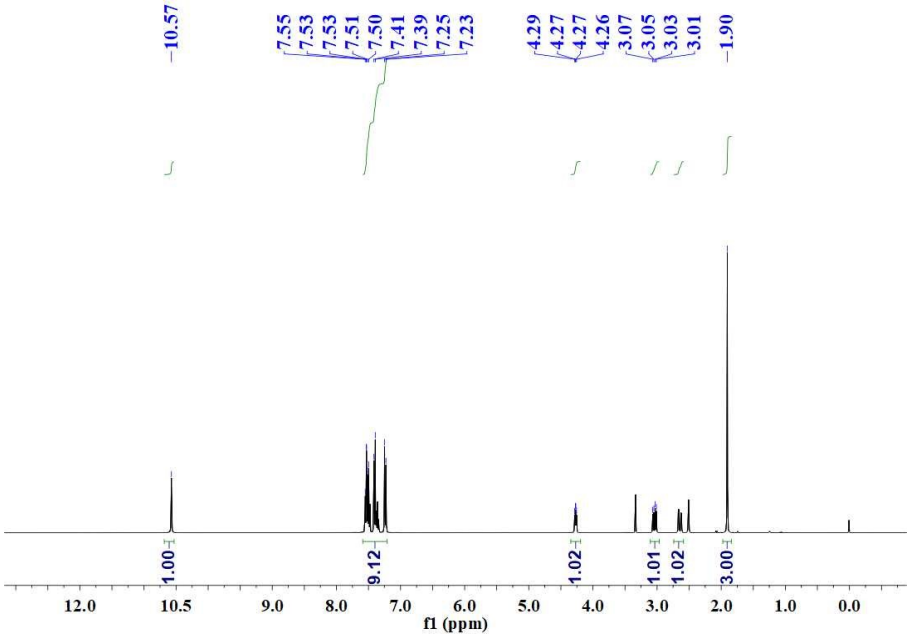


^{1}H NMR spectra of 9e

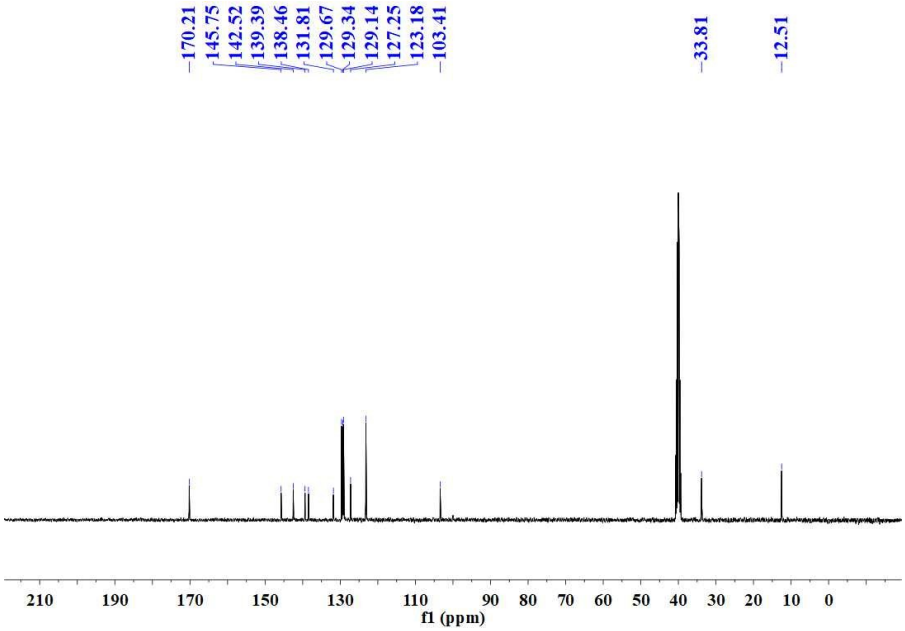


^{13}C NMR spectra of 9e

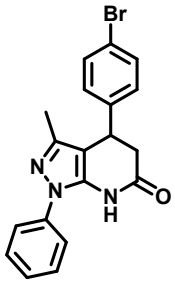


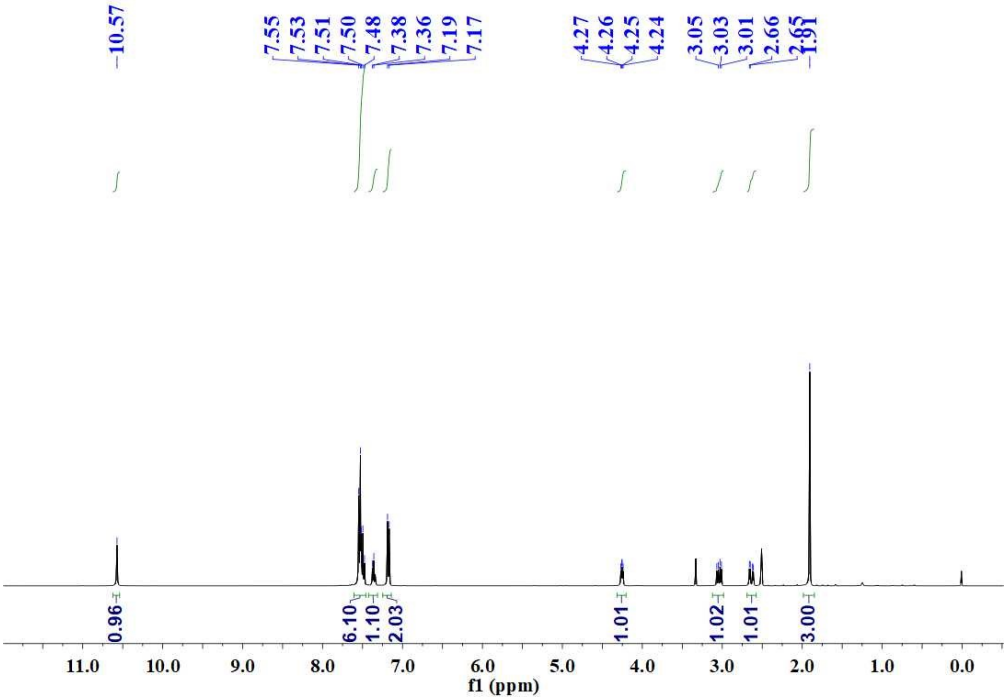


^{1}H NMR spectra of 9f

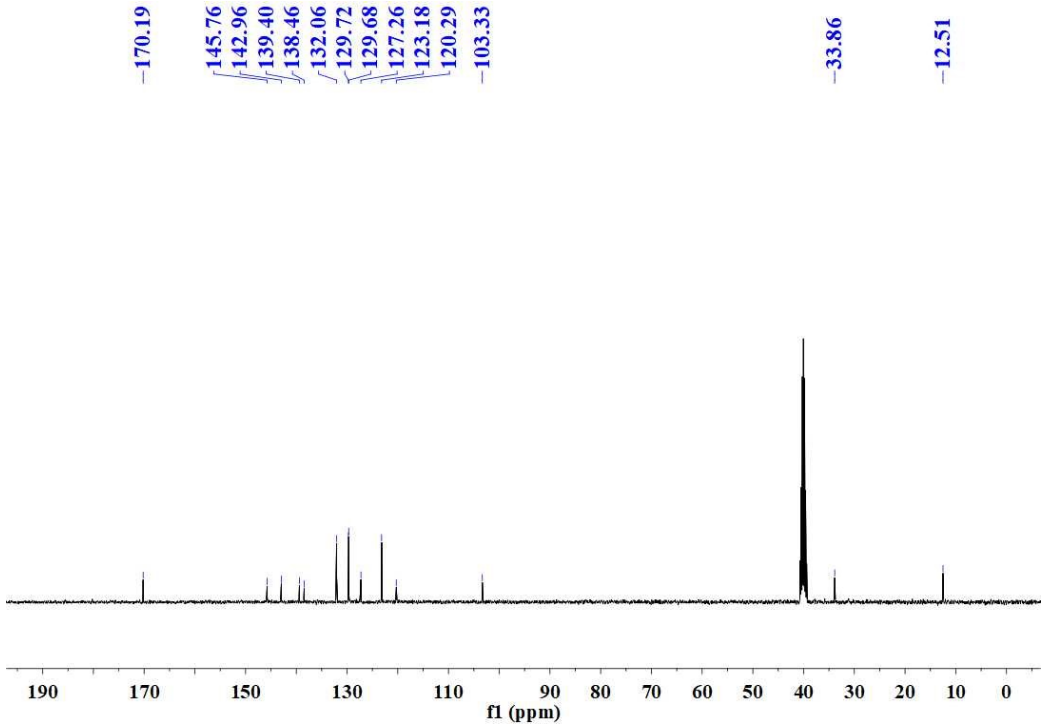


^{13}C NMR spectra of 9f

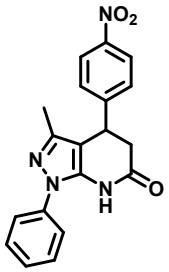


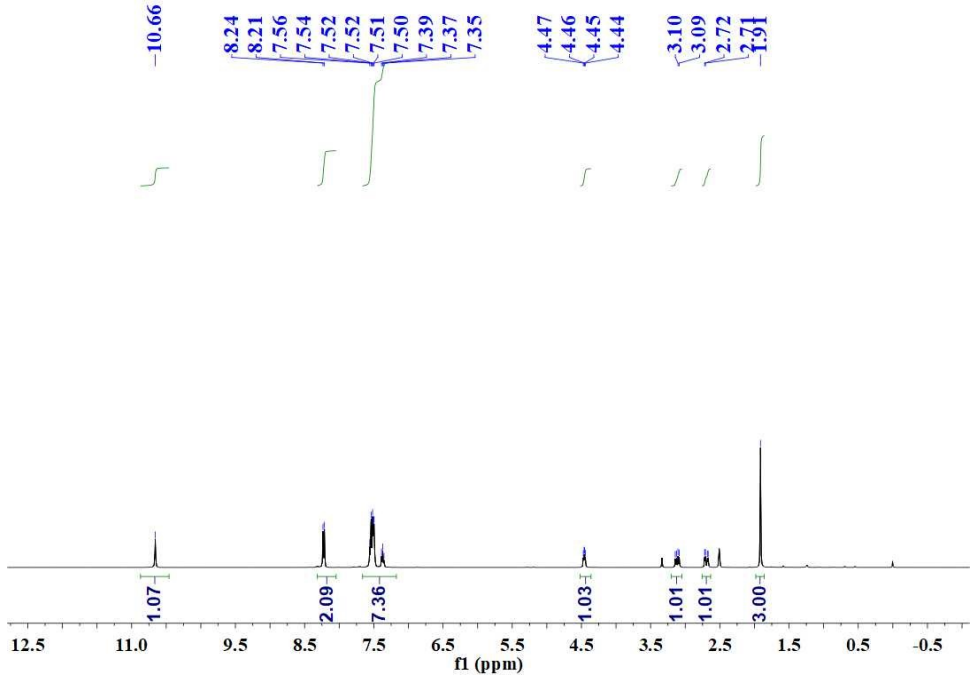


^{1}H NMR spectra of 9g

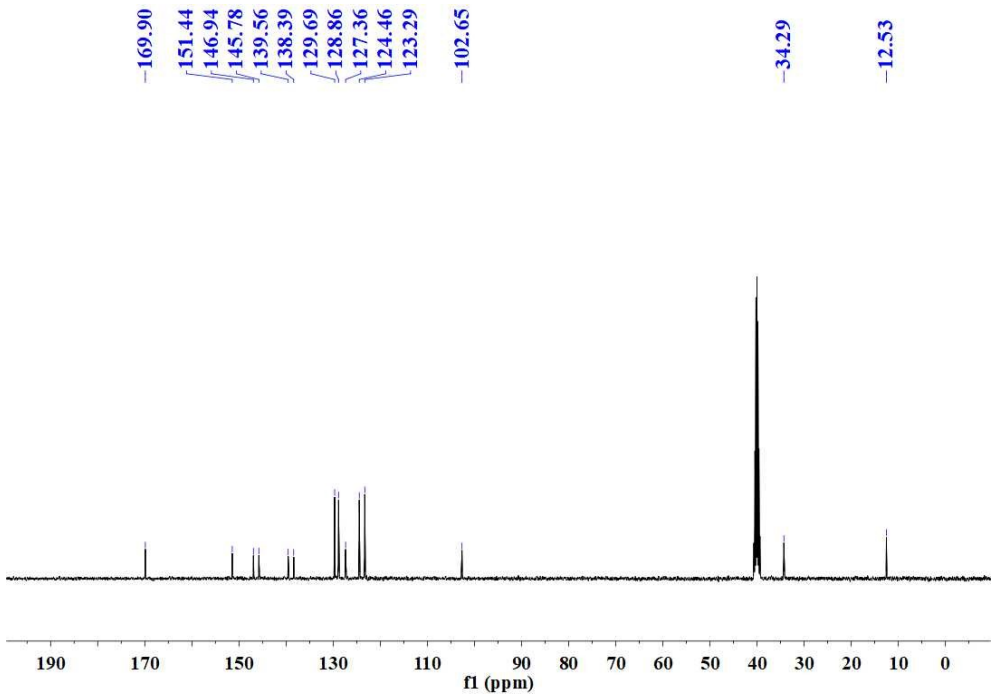


^{13}C NMR spectra of 9g

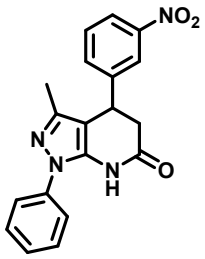


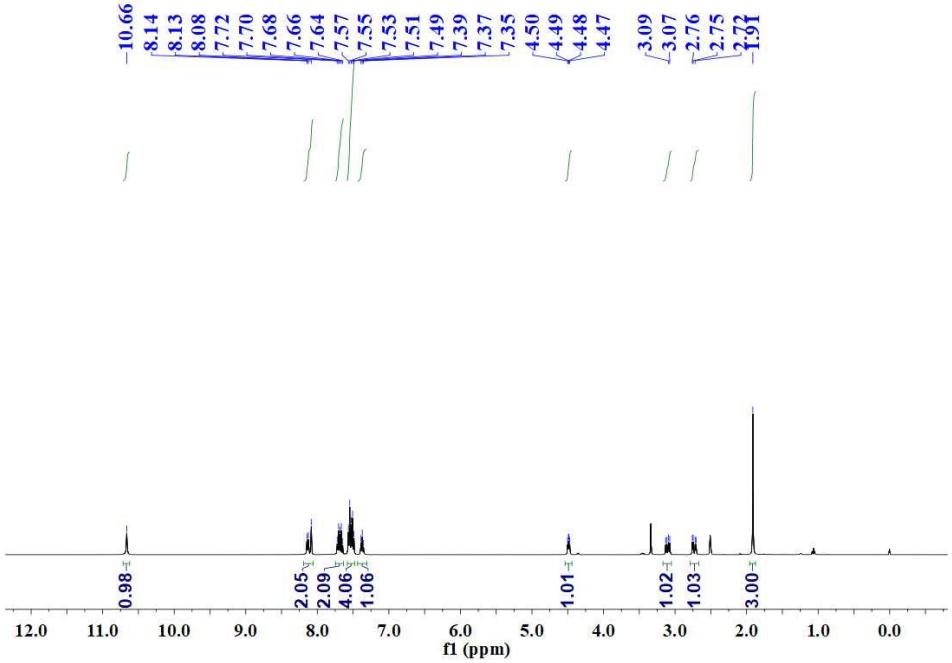


^{1}H NMR spectra of 9h

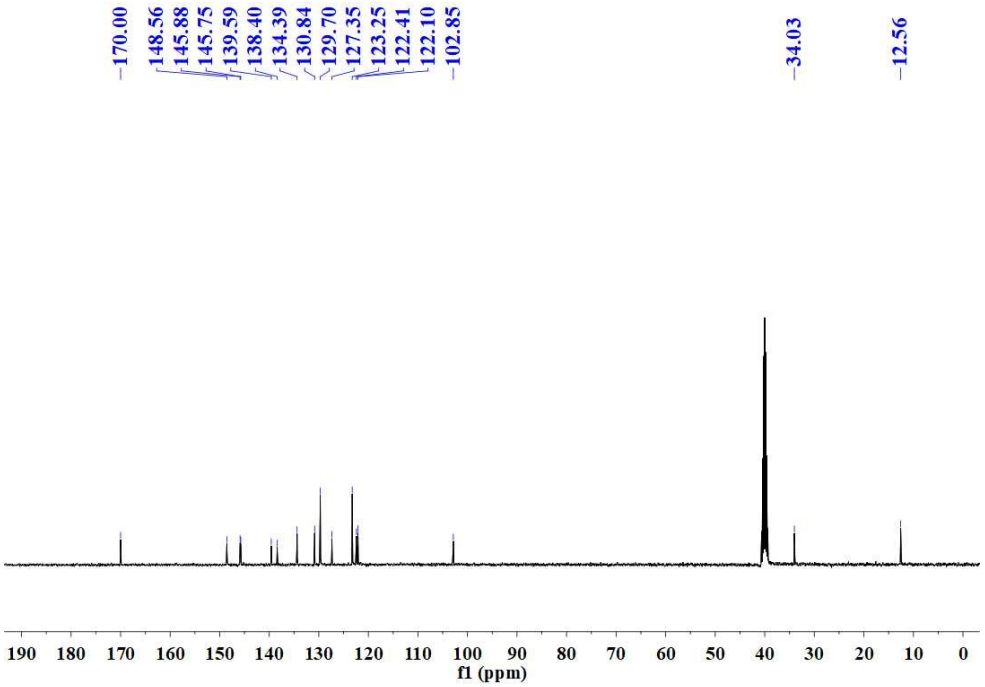


^{13}C NMR spectra of 9h

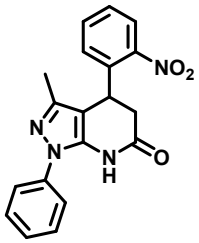


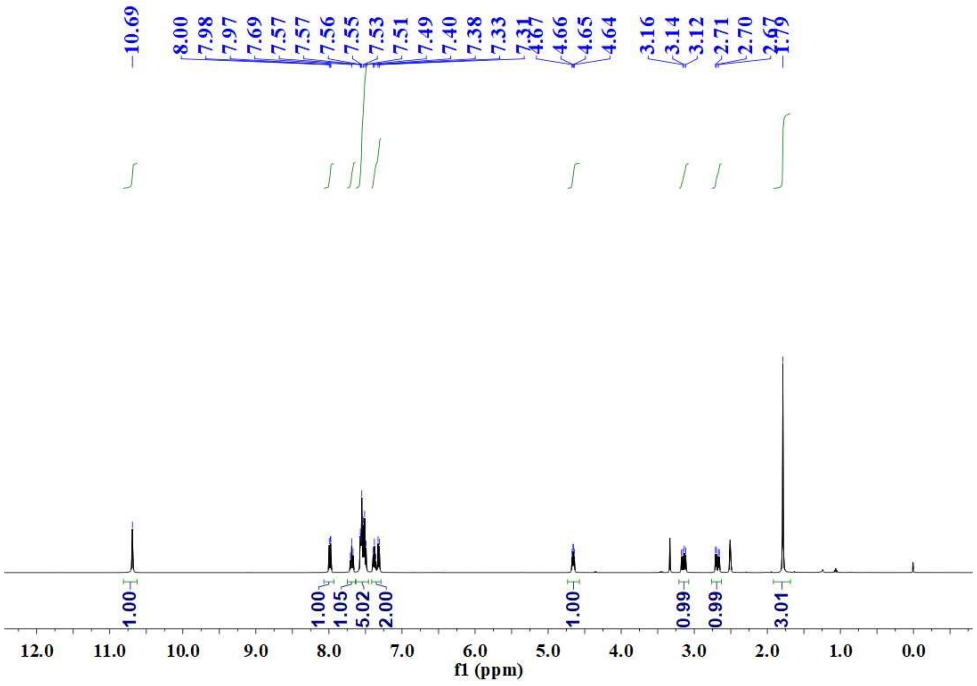


^{1}H NMR spectra of 9i

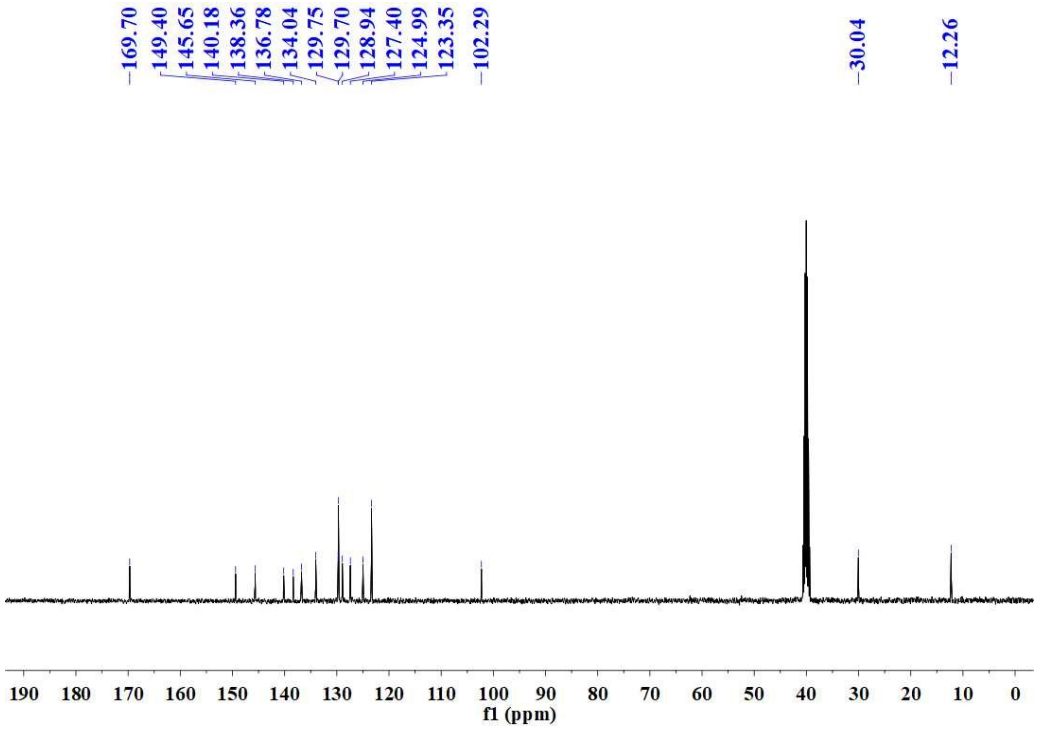


^{13}C NMR spectra of 9i

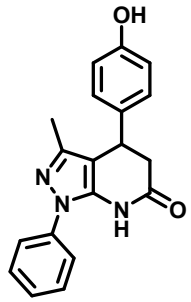


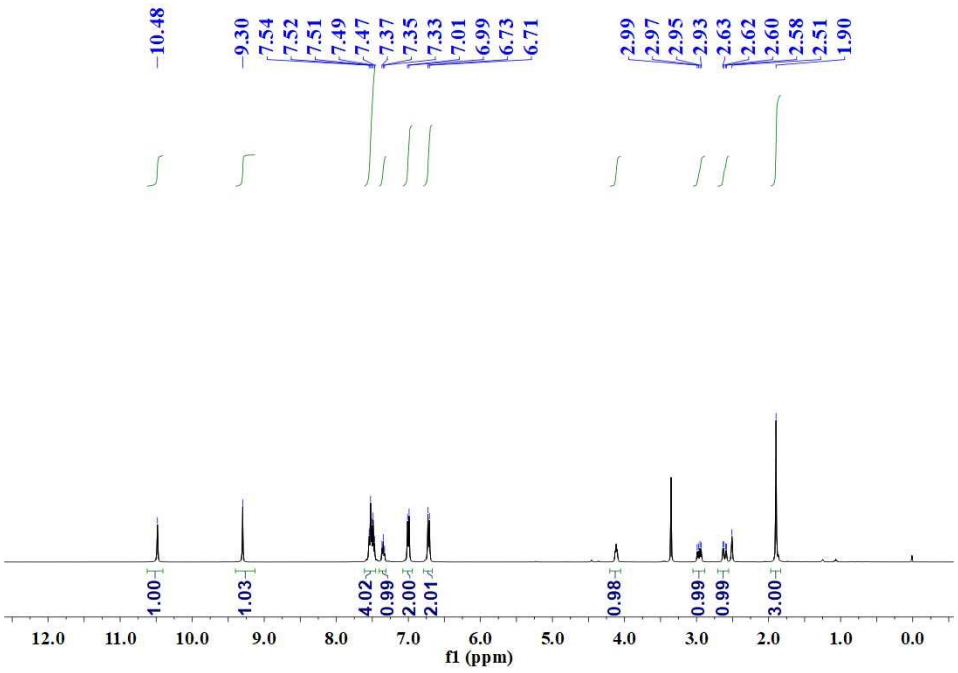


^{1}H NMR spectra of 9j

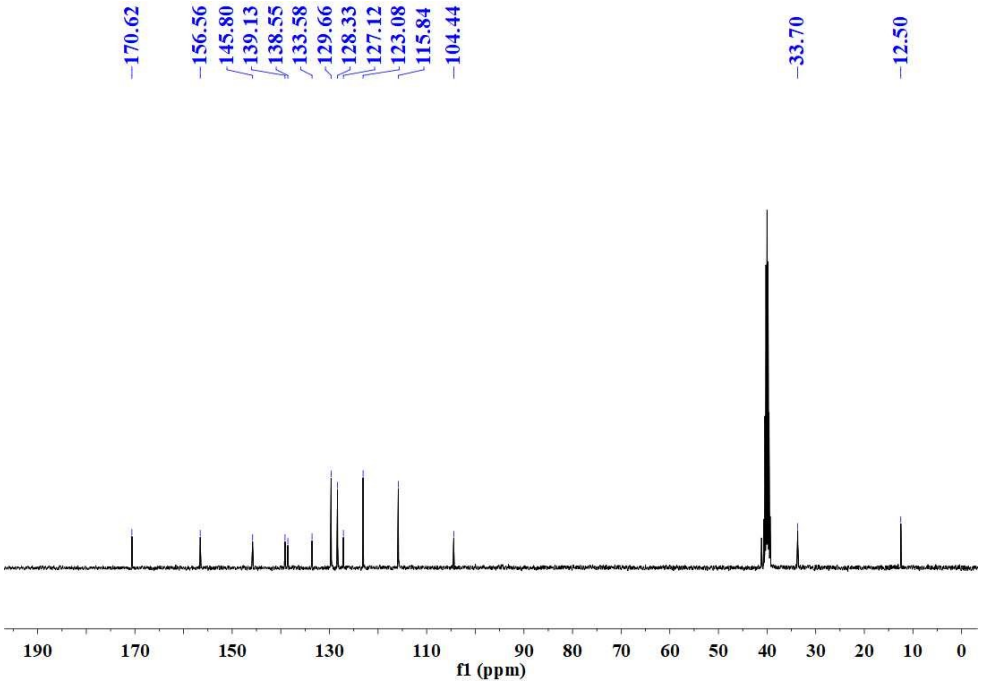


^{13}C NMR spectra of 9j

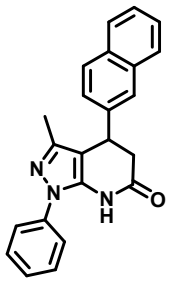


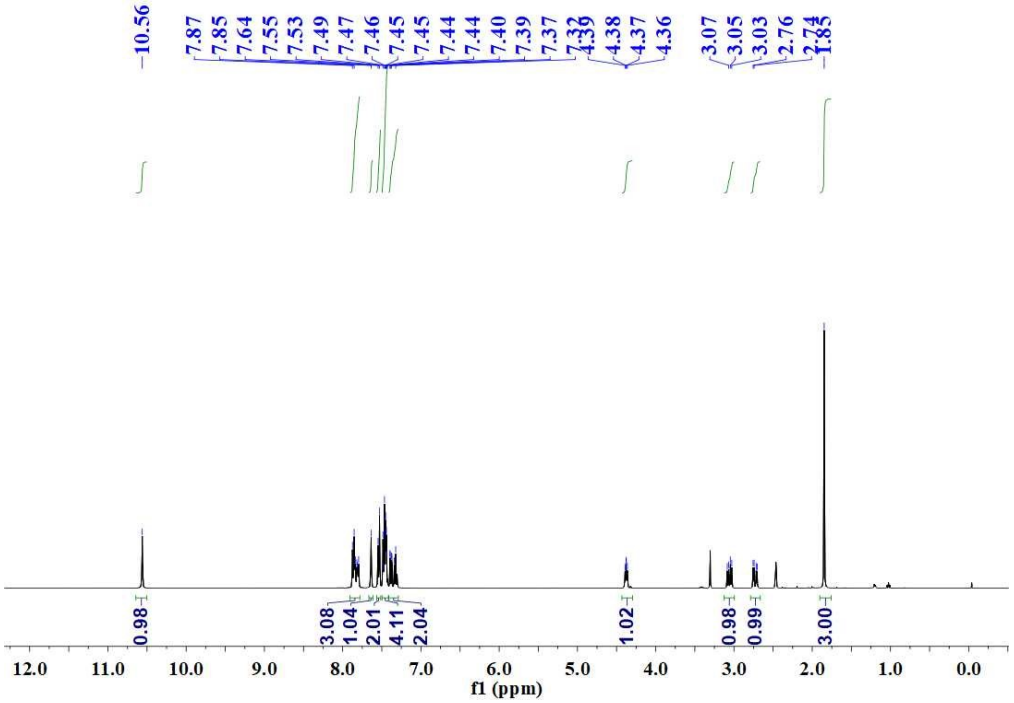


^{1}H NMR spectra of 9k

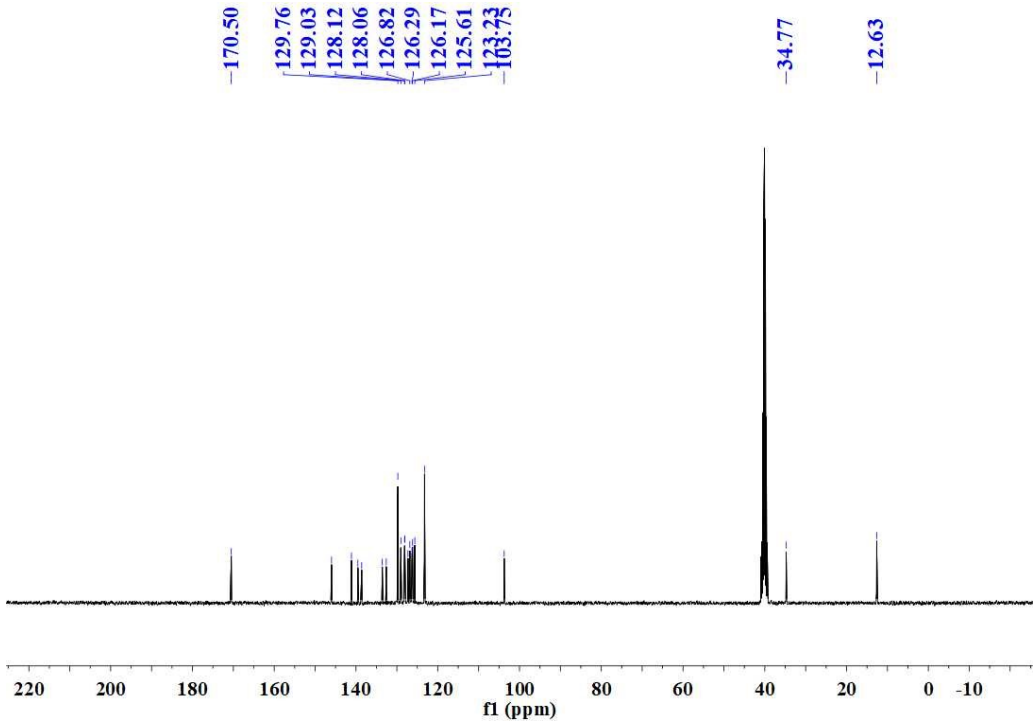


^{13}C NMR spectra of 9k

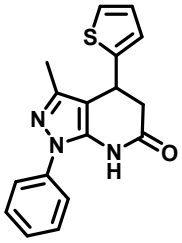


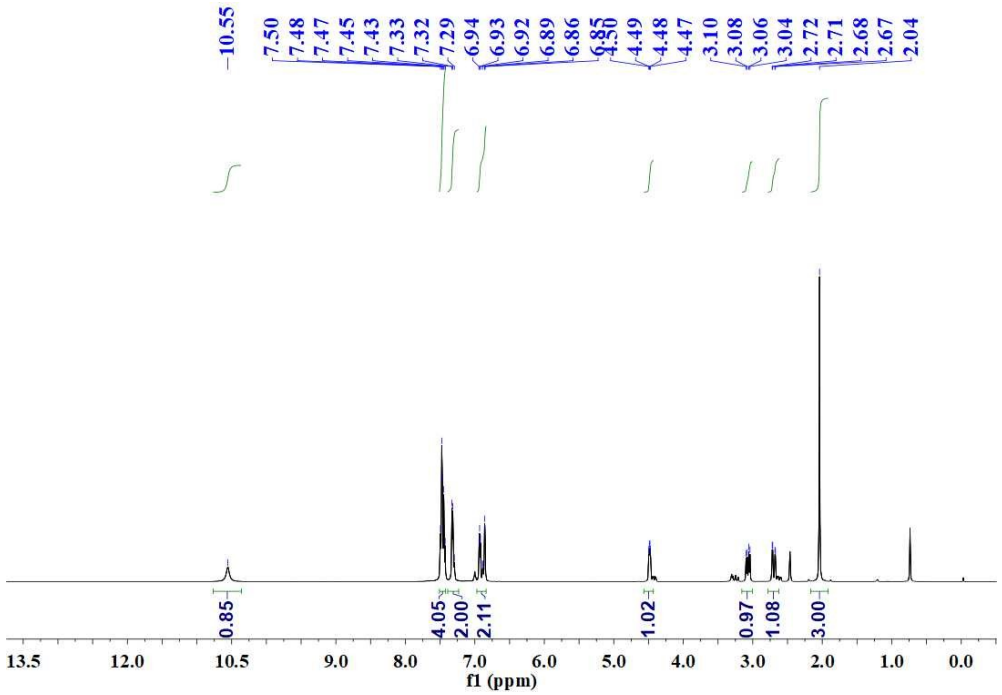


^{1}H NMR spectra of 9l

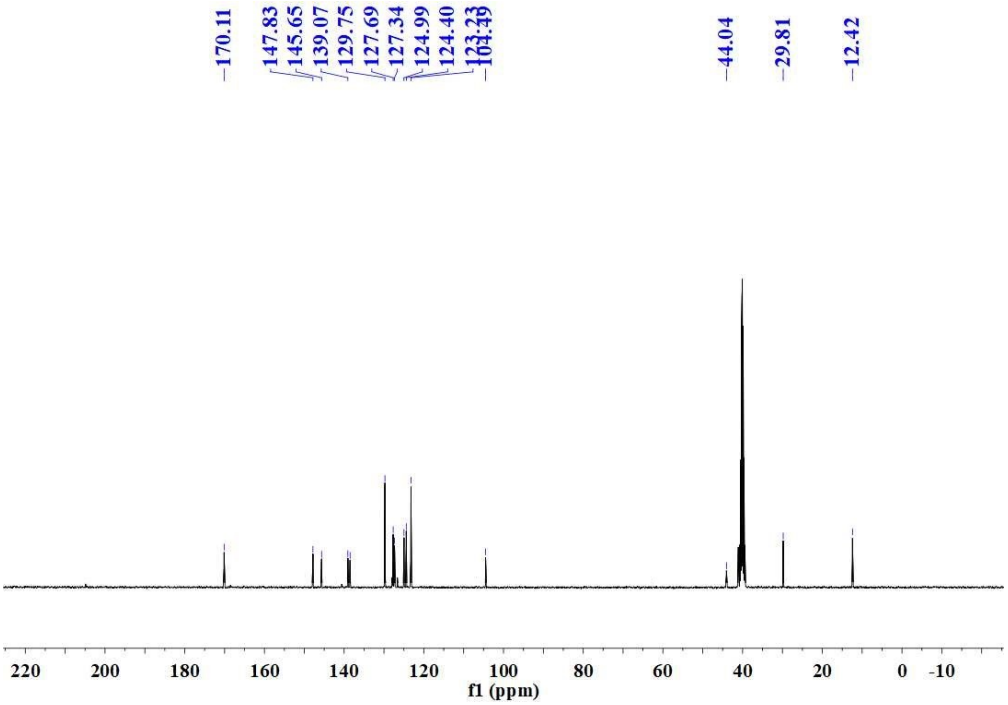


^{13}C NMR spectra of 9l

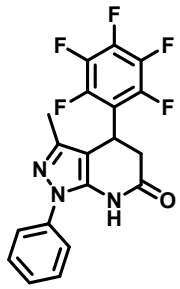


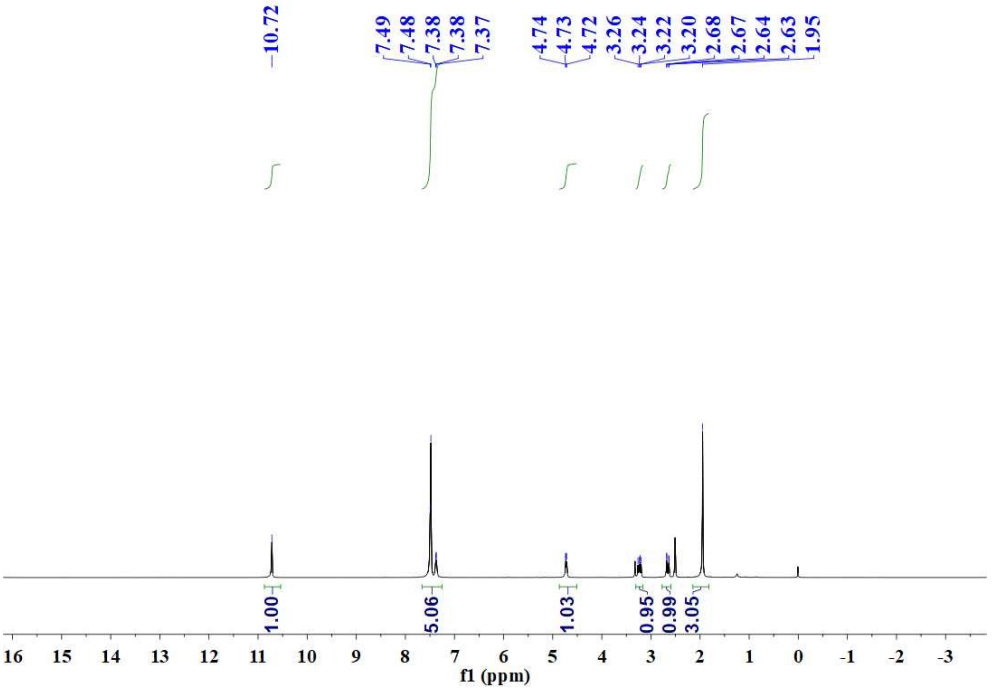


^{1}H NMR spectra of 9m

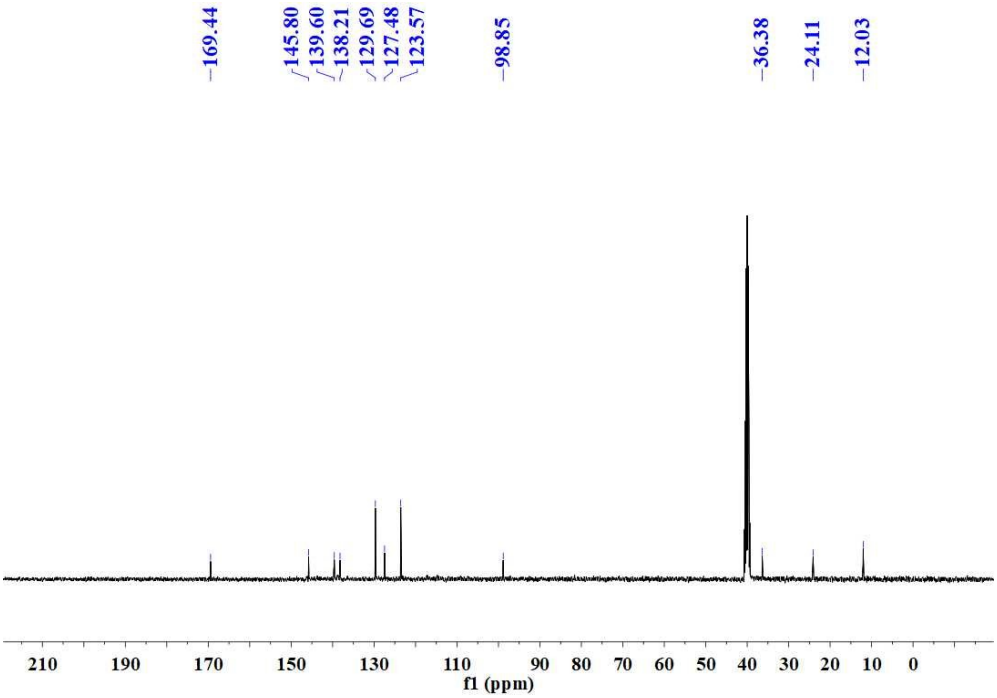


^{13}C NMR spectra of 9m





^{1}H NMR spectra of 9n



^{13}C NMR spectra of 9n

7. Reference

[1] Q. Xu, S. Yuan, L. Zhu, J. Hao, Y. Wei, Synthesis of novel bis(Triol)-functionalized Anderson clusters serving as potential synthons for forming organic-inorganic hybrid chains, Chem Commun (Camb), 53 (2017) 5283-5286.

[2] G.M. Sheldrick, A short history of SHELX, Acta Crystallographica a-Foundation and Advances, 64 (2008) 112-122.

[3] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program, Journal of Applied Crystallography, 42 (2009) 339-341.

[4] A. Macdonell, N.A. Johnson, A.J. Surman, L. Cronin, Configurable Nanosized Metal Oxide Oligomers *via* Precise "Click" Coupling Control of Hybrid Polyoxometalates, J Am Chem Soc, 137 (2015) 5662-5665.

[5] M. Arefian, M. Mirzaei, H. Eshtiagh-Hosseini, Structural insights into two inorganic-organic hybrids based on chiral amino acids and polyoxomolybdates, Journal of Molecular Structure, 1156 (2018) 550-558.

[6] G.S. Nongthombam, G.K. Kharmawlong, J.E. Kumar, R. Nongkhlaw, UV365 light promoted catalyst-free synthesis of pyrimido[4,5-b]quinoline-2,4-diones in aqueous-glycerol medium, New Journal of Chemistry, 42 (2018) 9436-9442.

[7] H.Y. Guo, Y. Yu, One-pot synthesis of 7-aryl-11,12-dihydrobenzo[h]pyrimido-[4,5-b]quinoline-8,10 (7H,9H)-diones via three-component reaction in ionic liquid, Chinese Chemical Letters, 21 (2010) 1435-1438.

[8] X. Zhang, D. Li, X. Fan, X. Wang, X. Li, G. Qu, J. Wang, Ionic liquid-promoted multi-component reaction: novel and efficient preparation of pyrazolo[3,4-b]pyridinone, pyrazolo[3,4-b]-quinolinone and their hybrids with pyrimidine nucleoside, Mol Divers, 14 (2010) 159-167.

[9] C.-L. Shi, H. Chen, D.-Q. Shi, An Efficient One-Pot Synthesis of Pyrazolo 3,4-b pyridinone Derivatives Catalyzed by L-Proline, Journal of Heterocyclic Chemistry, 48 (2011) 351-354.