

Supporting Information

The largest Se-4f cluster incorporated polyoxometalate with high Lewis acid-base catalytic activity

Meng-Ying Yao^{a,+}, Yu-Feng Liu^{b,+}, Xin-Xiong Li^{*a}, Guo-ping Yang^{*b} Shou-Tian Zheng^{*a}

^aState Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry, Fuzhou University, Fuzhou, Fujian 350108, China.

^bJiangxi Key Laboratory for Mass Spectrometry and Instrumentation, Jiangxi Province Key Laboratory of Synthetic Chemistry, East China University of Technology, Nanchang 330013, China.

+ These authors contributed equally to this work

E-mail: lxz@fzu.edu.cn; erick@ecut.edu.cn; stzheng@fzu.edu.cn

1. General Information	S2
2. Experimental	S2
3. Characterization of compound 1-Eu	S3
4. Optimize reaction conditions	S9
5. Characterization of Substrates and Products	S10
6. NMR Spectra	S13
7. Notes and References	S25

1. General Information

Materials and Methods

$\text{Na}_2\text{K}_8[\text{A-}\alpha\text{-GeW}_9\text{O}_{34}]\cdot 25\text{H}_2\text{O}$ was synthesized on the basis of literature method and proved by IR spectroscopy.¹ Aqueous solution of $\text{Ln}(\text{ClO}_4)_3$ was synthesized on the basis of literature method, too.² All the other reactants and solvents were obtained from commercial sources and used for reactions without further purification. Powder XRD patterns were obtained using a RIGAKU-Miniflex II diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). IR spectra were recorded on PerkinElmer Spectrum One FT-IR infrared spectrophotometer with pressed KBr pellets in the range of $4000\text{-}500 \text{ cm}^{-1}$. Fluorescence spectra were measured with an Edinburgh FLS980 fluorescence spectrophotometer in the solid-state at room temperature. The electrospray ionization mass spectroscopy was measured on a Thermo Scientific Exactive Plus mass spectrometer (German) and processed on a Bruker Data Analysis (Version 4.0) software. The theoretical peak was simulated on a Bruker Isotope Pattern software. Thermogravimetric analyses were performed on a Mettler Toledo TGA/SDTA 851^e analyzer under an N_2 -flow atmosphere with a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$ in the temperature of $25\text{-}800 \text{ }^\circ\text{C}$.

X-ray Crystallography

Single-crystal X-ray diffraction data of **1-Eu** was collected on a Hybrid Pixel Array detector equipped with Ga $K\alpha$ radiation ($\lambda = 1.3405 \text{ \AA}$) at about 100 K. The structure of **1-Eu** was solved through direct methods and refined by full-matrix least-squares refinements based on F^2 adopting the SHELX-2018 program package. The Se(4) ions in **1-Eu** were disordered and scattered over four positions. All non-H atoms were located with successive difference Fourier syntheses and refined anisotropically except for part of lattice water molecules. The H atoms of the free water molecules and coordinated water molecules have not been included in the final refinement. The SQUEEZE function in PLATON was used to remove the residual electronic density of those highly disordered guest water molecules. The quantity of free water molecules was determined by thermogravimetric analysis (Fig. S7). Crystallographic data and structure refinements for **1-Eu** is summarized in Table S1. CCDC 2164174 contains supplementary crystallographic data for this paper, which is available free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

2. Experimental Information

Synthesis of compound 1-Eu

A mixture of $\text{Na}_2\text{K}_8[\text{A-}\alpha\text{-GeW}_9\text{O}_{34}]\cdot 25\text{H}_2\text{O}$ (0.065 mmol, 200 mg), SeO_2 (0.72 mmol, 80 mg), 4-Picolinic acid (0.24 mmol, 30 mg) and dimethylamine hydrochloride (DMAHCl) (0.61 mmol 50 mg) were dissolved in 4.0 mL distilled water, and then 0.20 mL 1M $\text{Eu}(\text{ClO}_4)_3$ was added with ultrasonic vibration for 5 mins. After the resulting mixture stood for 12 hours, colorless crystals were obtained. Yield: 36.25% based on $\text{Na}_2\text{K}_8[\text{A-}\alpha\text{-GeW}_9\text{O}_{34}]\cdot 25\text{H}_2\text{O}$. IR (Fig. S8): 3400(s), 1596(s), 1403(s), 1250(w), 950(w), 890(w), 842(w), 798(s), 725(w), 666(w), 530(w). Elemental analyses calcd (found %) for $\text{H}_{16}\text{C}_{24}\text{Eu}_{10}\text{Ge}_4\text{Se}_{13}\text{W}_{36}\text{N}_4\text{O}_{232}$: C, 2.13 (2.46); H, 0.12 (0.21); N, 0.41 (0.48).

Typical procedure of the 1-Eu catalyzed condensation reaction

Benzoyl hydrazine **1a** (0.2 mmol), acetylacetone **2a** (0.2 mmol), **1-Eu** (0.3 mol%), and DMC (0.5 mL) were added to a 4-mL reaction vial. Then the reaction was carried out in screw cap vials with a Teflon seal at $120 \text{ }^\circ\text{C}$ for 90 min. After reaction, the mixture was purified by column chromatography (petroleum ether/EtOAc) to obtain the desired products (The gram-scale reaction was carried out in a 8-mL reaction vial. The solid desired products could be obtained by recrystallization.).

3. Characterization of compound 1-Eu

Table S1 Crystal Data and Structure Refinement for **1-Eu**

<i>Empirical formula</i>	H ₁₆ C ₂₄ N ₄ Ge ₄ Se ₁₃ Eu ₁₀ W ₃₆ O ₂₂₄	<i>F(000)</i>	23376
<i>Formula weight</i>	13399.45	<i>Temperature (K)</i>	100(2)
<i>Crystal system</i>	Tetragonal	<i>σ (g/cm³)</i>	2.739
<i>Space group</i>	I4 ₁ /a	<i>μ(mm⁻¹)</i>	16.485
<i>a (Å)</i>	36.32910(10)	<i>Completeness</i>	99.6%
<i>b (Å)</i>	36.32910(10)	<i>GOF on F²</i>	0.996
<i>c (Å)</i>	24.62060(10)	<i>Reflns Collected</i>	74258
<i>V (Å³)</i>	32494.4(2)	<i>unique restraints</i>	13
<i>A</i>	90	<i>Parameters</i>	757
<i>B</i>	90	<i>R_{int}</i>	0.0468
<i>Γ</i>	90	<i>Final R indices</i> (<i>I</i> = 2σ(<i>I</i>))	<i>R</i> ₁ = 0.0442, <i>wR</i> ₂ = 0.1130
<i>Z</i>	4	<i>R indices (all data)</i>	<i>R</i> ₁ = 0.0593, <i>wR</i> ₂ = 0.1167

^a*R*₁ = Σ ||*F*_o| - |*F*_c|| / Σ |*F*_o|, ^b*wR*₂ = [Σ*w*(*F*_o² - *F*_c²)² / Σ*w*(*F*_o²)]^{1/2}, *w* = 1/[σ²(*F*_o²) + (*xP*)² + *yP*], *P* = (*F*_o² + 2*F*_c²)/3, where *x* = 0.0401, *y* = 0 for **1-Eu**.

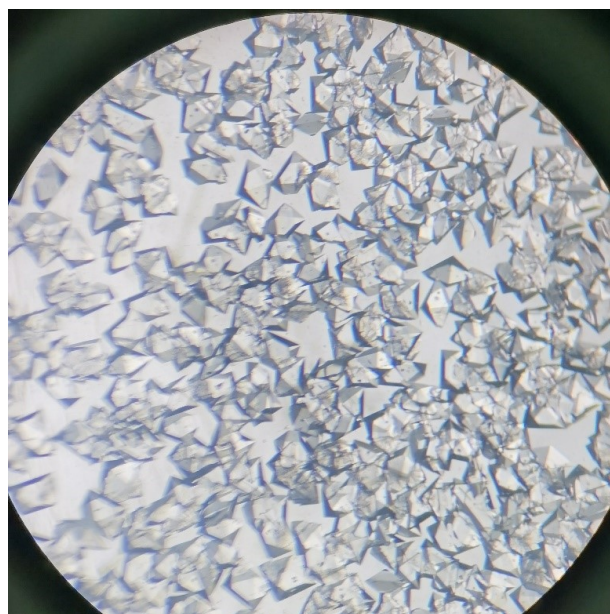


Fig. S1. Optical photograph of **1-Eu**.

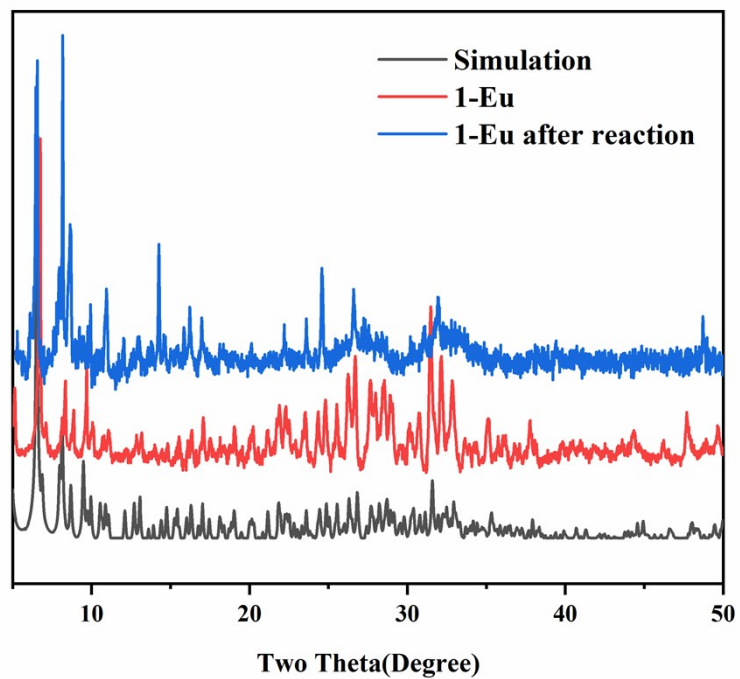


Fig. S2. Simulated and experimental PXRD patterns of **1-Eu**.

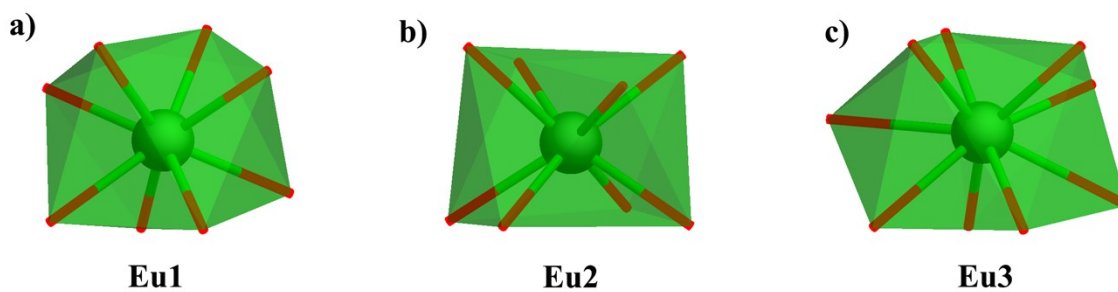


Fig. S3. (a) Coordination mode of Eu^{3+} ; (b) Coordination mode of Eu^{3+} ions; (c) Coordination mode of Eu^{3+} .

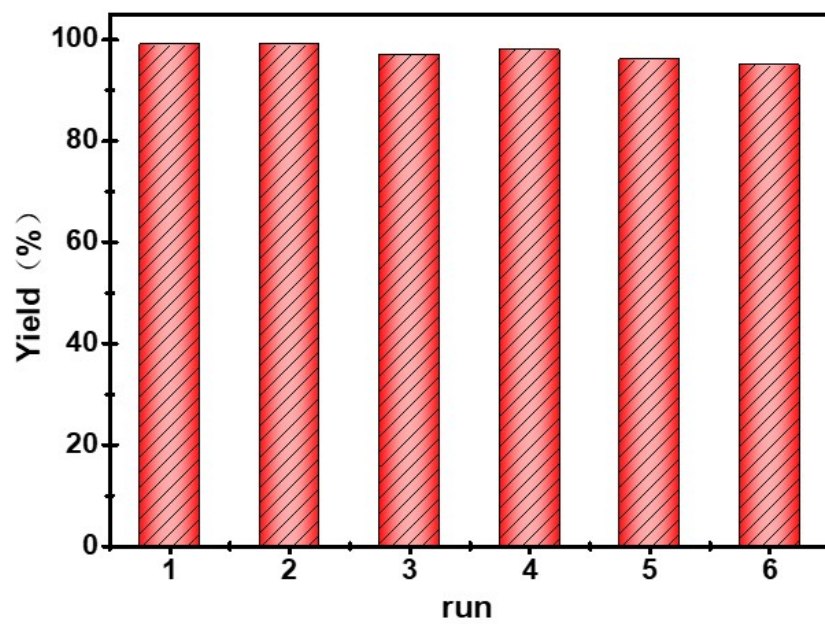


Fig. S4. Recyclability of catalyst 1-Eu.

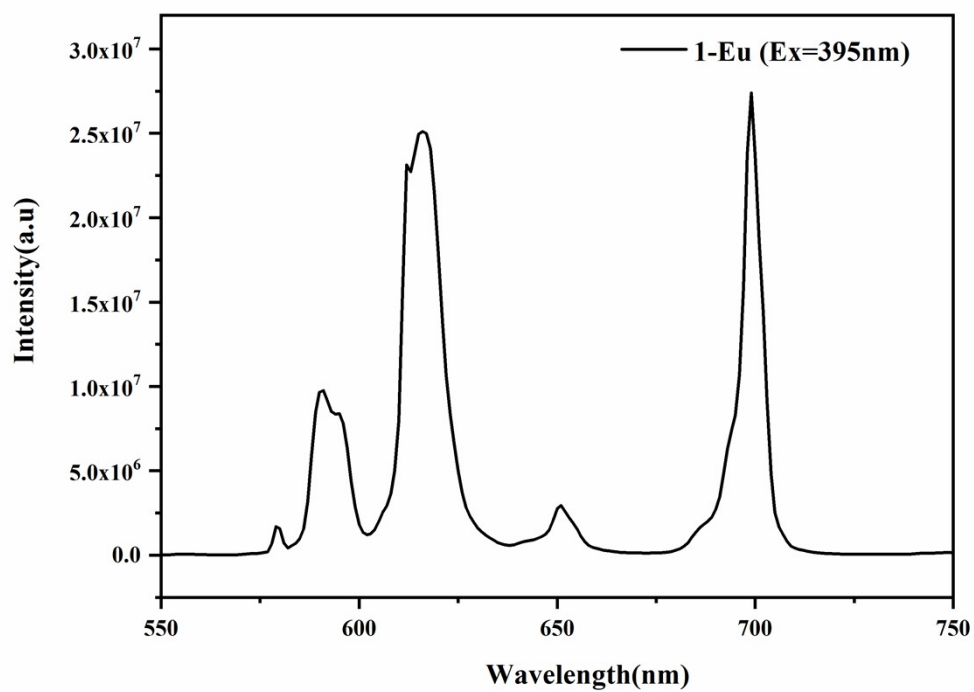


Fig. S5. Emission spectra of 1-Eu.

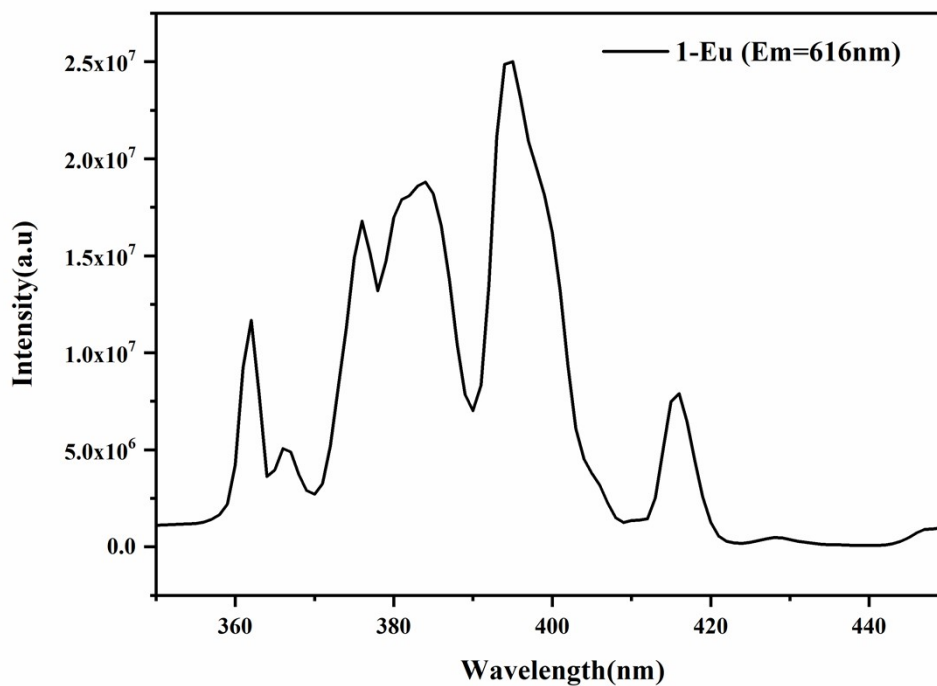


Fig. S6. Excitation spectra of 1-Eu.

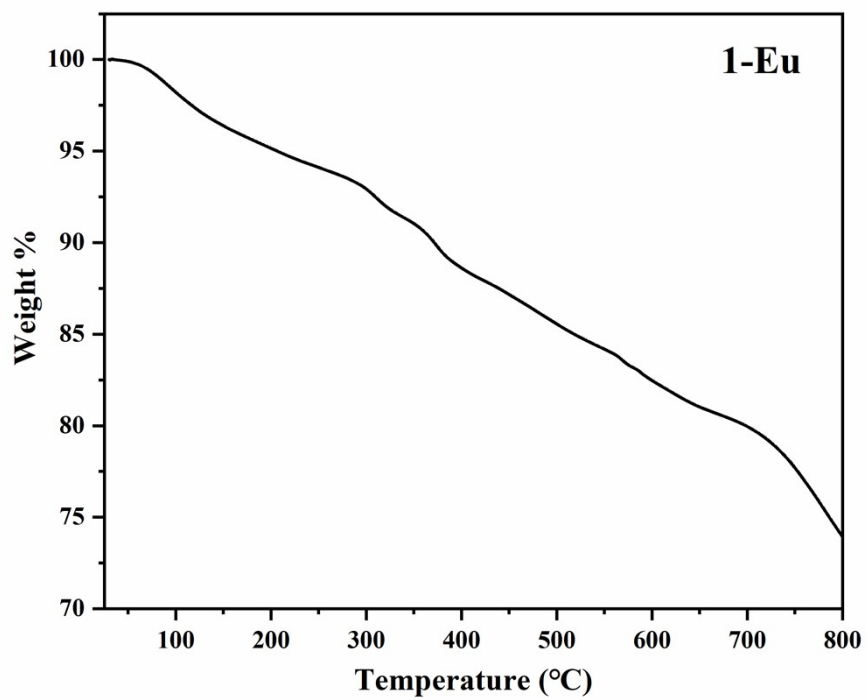


Fig. S7. TG curve of 1-Eu.

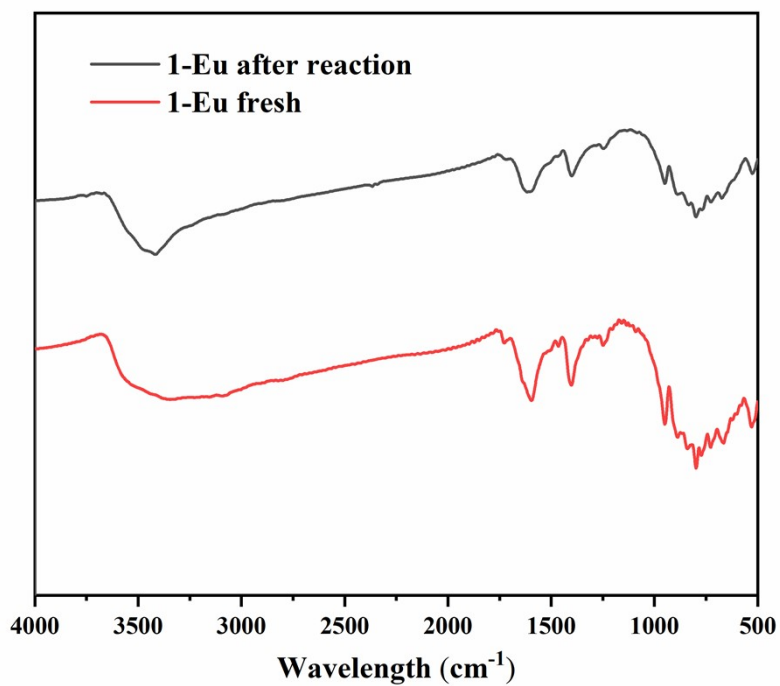


Fig. S8. IR spectra of 1-Eu.

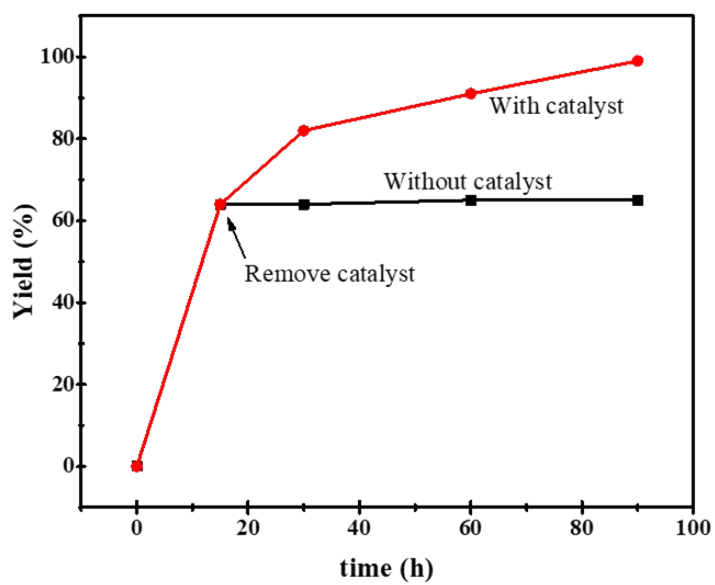


Fig S9. Hot filtration test for 1-Eu.

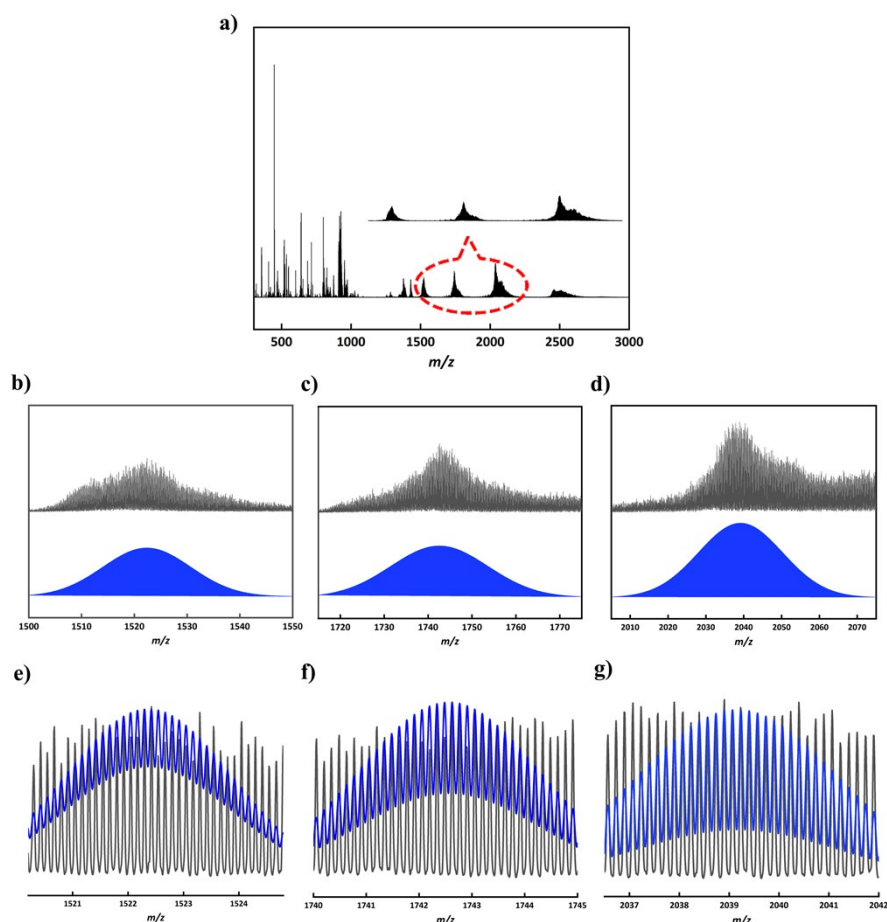


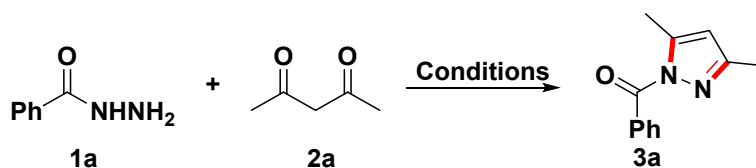
Fig S10. a) electrospray ionization mass spectrometry spectrum of compound **1-Eu** at m/z of 400 – 3000; b) Experimental (upper, black) and simulated (under, blue) peak of $\{H_{10}[Eu_{10}Se_{13}O_{28}(H_2O)_5](GeW_9O_{34})_4\}^{8-}$; c) Experimental (upper, black) and simulated (under, blue) peak of $\{H_{11}[Eu_{10}Se_{13}O_{28}(H_2O)_6](GeW_9O_{34})_4\}^{7-}$; d) Experimental (upper, black) and simulated (under, blue) peak of $\{H_{12}[Eu_{10}Se_{13}O_{28}(H_2O)_8](GeW_9O_{34})_4\}^{6-}$; e) Details of experimental (upper, black) and simulated (under, blue) peaks of $\{H_{10}[Eu_{10}Se_{13}O_{28}(H_2O)_5](GeW_9O_{34})_4\}^{8-}$; f) Details of experimental (upper, black) and simulated (under, blue) peaks of $\{H_{11}[Eu_{10}Se_{13}O_{28}(H_2O)_6](GeW_9O_{34})_4\}^{7-}$; g) Details of experimental (upper, black) and simulated (under, blue) peaks of $\{H_{12}[Eu_{10}Se_{13}O_{28}(H_2O)_8](GeW_9O_{34})_4\}^{6-}$.

The electrospray ionization mass spectrometry spectrum of the compound shows three identifiable peaks including one -6, one -7 and one -8 signals (the charge can be further proved by checking the intervals of each isotopic peak). The peak at -2038.90, -1742.63 and -1522.42 can be identified as $\{H_{12}[Eu_{10}Se_{13}O_{28}(H_2O)_8](GeW_9O_{34})_4\}^{6-}$ (calcd. m/z = -2039.17), $\{H_{11}[Eu_{10}Se_{13}O_{28}(H_2O)_6](GeW_9O_{34})_4\}^{7-}$ (calcd. m/z = -1742.57) and $\{H_{10}[Eu_{10}Se_{13}O_{28}(H_2O)_5](GeW_9O_{34})_4\}^{8-}$ (calcd. m/z = -1522.37). The result indicates that the skeleton of our cluster remain intact when the crystals dissolve in water.

cluster	Charge	weight	m/e (Simulated)	m/e (experimental)
$H_{10}\{[Eu_{10}Se_{13}O_{28}(H_2O)_5](GeW_9O_{34})_4\}$	-8	12178.98	-1522.37	-1522.42
$H_{11}\{[Eu_{10}Se_{13}O_{28}(H_2O)_6](GeW_9O_{34})_4\}$	-7	12198.00	-1742.57	-1742.63
$H_{12}\{[Eu_{10}Se_{13}O_{28}(H_2O)_8](GeW_9O_{34})_4\}$	-6	12235.04	-2039.17	-2038.90

4. Optimize reaction conditions

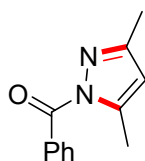
Table S2. Condition optimization for the condensation reaction.^a



Entry	Catalyst (mol%)	Temp. (°C)	Time (min)	Solvent (mL)	Yield (%) ^b
1	—	r.t.	15	DMC	3
2	α -GeW ₉ O ₃₄ (1.2)	r.t.	15	DMC	8
3	Eu(ClO ₄) ₃ (3.0)	r.t.	15	DMC	17
4	α -GeW ₉ O ₃₄ (1.2) + Eu(ClO ₄) ₃ (3.0)	r.t.	15	DMC	29
5	1-Eu (0.3)	r.t.	15	DMC	40
6	1-Eu (0.3)	60	15	DMC	48
7	1-Eu (0.3)	80	15	DMC	51
8	1-Eu (0.3)	100	15	DMC	57
9	1-Eu (0.3)	120	15	DMC	64
10	1-Eu (0.3)	120	30	DMC	82
11	1-Eu (0.3)	120	60	DMC	91
12	1-Eu (0.3)	120	90	DMC	99
14	1-Eu (0.2)	120	90	DMC	86
16	1-Eu (0.3)	120	90	EtOH	55
17	1-Eu (0.3)	120	90	CH ₃ CN	87
18	1-Eu (0.3)	120	90	toluene	78
19	1-Eu (0.3)	120	90	Ph-Cl	93

^a Reaction conditions: benzoyl hydrazine **1a** (0.2 mmol), acetylacetone **2a** (0.2 mmol), solvent (0.5 mL). ^b The yields were determined by GC with biphenyl as the internal standard.

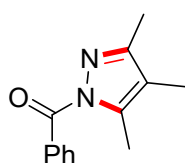
5. Characterization of Substrates and Products³



(3,5-dimethyl-1H-pyrazol-1-yl)(phenyl)methanone (3a)

¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.00 (d, *J* = 7.1 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 6.05 (s, 1H), 2.63 (s, 3H), 2.25 (s, 3H);

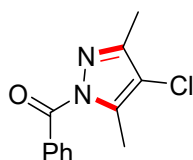
¹³C NMR (101 MHz, CDCl₃): δ (ppm) 168.23, 151.95, 144.92, 133.21, 132.25, 131.21, 127.68, 110.94, 14.17, 13.70.



phenyl(3,4,5-trimethyl-1H-pyrazol-1-yl)methanone (3b)

¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.97 (d, *J* = 7.1 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 2.56 (s, 3H), 2.20 (s, 3H), 1.96 (s, 3H);

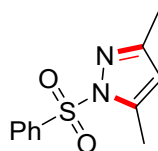
¹³C NMR (101 MHz, CDCl₃): δ (ppm) 168.34, 152.46, 140.45, 133.74, 132.18, 131.26, 127.79, 117.48, 12.54, 12.38, 7.71.



(4-chloro-3,5-dimethyl-1H-pyrazol-1-yl)(phenyl)methanone (3c)

¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.96 (d, *J* = 7.1 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 2.64 (s, 3H), 2.27 (s, 3H);

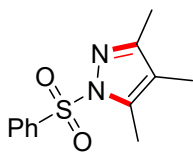
¹³C NMR (101 MHz, CDCl₃): δ (ppm) 167.87, 149.53, 140.34, 132.72, 132.52, 131.39, 127.95, 114.85, 12.34, 11.80.



3,5-dimethyl-1-(phenylsulfonyl)-1H-pyrazole (3d)

¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.92 (d, *J* = 7.2 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 5.88 (s, 1H), 2.47 (s, 3H), 2.17 (s, 3H);

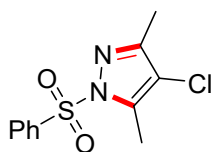
¹³C NMR (101 MHz, CDCl₃): δ (ppm) 153.61, 144.24, 138.33, 133.99, 129.27, 127.48, 110.90, 13.82, 13.09.



3,4,5-trimethyl-1-(phenylsulfonyl)-1H-pyrazole (3e)

¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.88 (d, *J* = 7.3 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 2.37 (s, 3H), 2.12 (s, 3H), 1.80 (s, 3H);

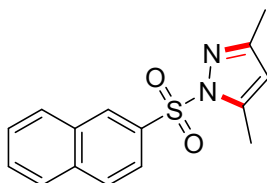
¹³C NMR (101 MHz, CDCl₃): δ (ppm) 153.92, 139.73, 138.47, 133.79, 129.20, 127.36, 117.41, 12.40, 11.30, 7.99.



4-chloro-3,5-dimethyl-1-(phenylsulfonyl)-1H-pyrazole (3f)

¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.95 (d, *J* = 7.3 Hz, 2H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 2H), 2.49 (s, 3H), 2.21 (s, 3H);

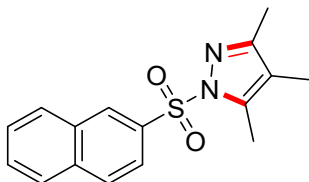
¹³C NMR (101 MHz, CDCl₃): δ (ppm) 151.13, 139.44, 137.75, 134.37, 129.43, 127.71, 113.93, 11.86, 11.25.



3,5-dimethyl-1-(naphthalen-2-ylsulfonyl)-1H-pyrazole (3g)

¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.55 (s, 1H), 7.96-7.83 (m, 4H), 7.60 (dt, *J* = 15.1, 6.2 Hz, 2H), 5.88 (s, 1H), 2.53 (s, 3H), 2.17 (s, 3H);

¹³C NMR (101 MHz, CDCl₃): δ (ppm) 153.60, 144.23, 135.32, 135.16, 131.92, 129.65, 129.54, 129.52, 129.35, 127.95, 127.80, 122.13, 110.88, 13.84, 13.19.

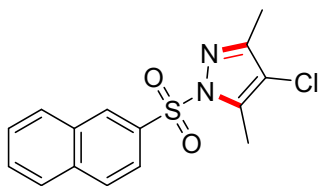


3,4,5-trimethyl-1-(naphthalen-2-ylsulfonyl)-1H-pyrazole (3h)

¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.53 (s, 1H), 7.96-7.82 (m, 4H), 7.64-7.56 (m, 2H), 2.44 (s, 3H), 2.13 (s, 3H), 1.80 (s, 3H);

¹³C NMR (101 MHz, CDCl₃): δ (ppm) 153.93, 139.73, 135.37, 135.24, 131.94, 129.56, 129.49, 129.42, 129.16,

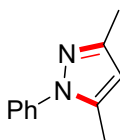
127.92, 127.72, 122.18, 117.40, 12.42, 11.41, 7.99.



4-chloro-3,5-dimethyl-1-(naphthalen-2-ylsulfonyl)-1H-pyrazole (3i)

¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.57 (s, 1H), 8.00-7.84 (m, 4H), 7.69-7.60 (m, 2H), 2.54 (s, 3H), 2.20 (s, 3H);

¹³C NMR (101 MHz, CDCl₃): δ (ppm) 151.10, 139.42, 135.48, 134.52, 131.93, 129.84, 129.79, 129.72, 129.59, 128.00, 127.95, 122.10, 113.92, 11.87, 11.34.



3,5-dimethyl-1-phenyl-1H-pyrazole (3j)

¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.46-7.40 (m, 4H), 7.36-7.30 (m, 1H), 5.99 (s, 1H), 2.30 (d, *J* = 2.7 Hz, 6H);

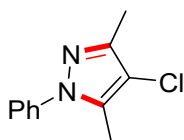
¹³C NMR (101 MHz, CDCl₃): δ (ppm) 148.93, 139.93, 139.37, 128.97, 127.23, 124.76, 106.91, 13.51, 12.37.



3,4,5-trimethyl-1-phenyl-1H-pyrazole (3k)

¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.45-7.39 (m, 4H), 7.34-7.28 (m, 1H), 2.25 (s, 3H), 2.22 (s, 3H), 1.98 (s, 3H);

¹³C NMR (101 MHz, CDCl₃): δ (ppm) 148.05, 140.19, 136.02, 128.95, 126.93, 124.66, 113.23, 11.89, 10.97, 8.20.

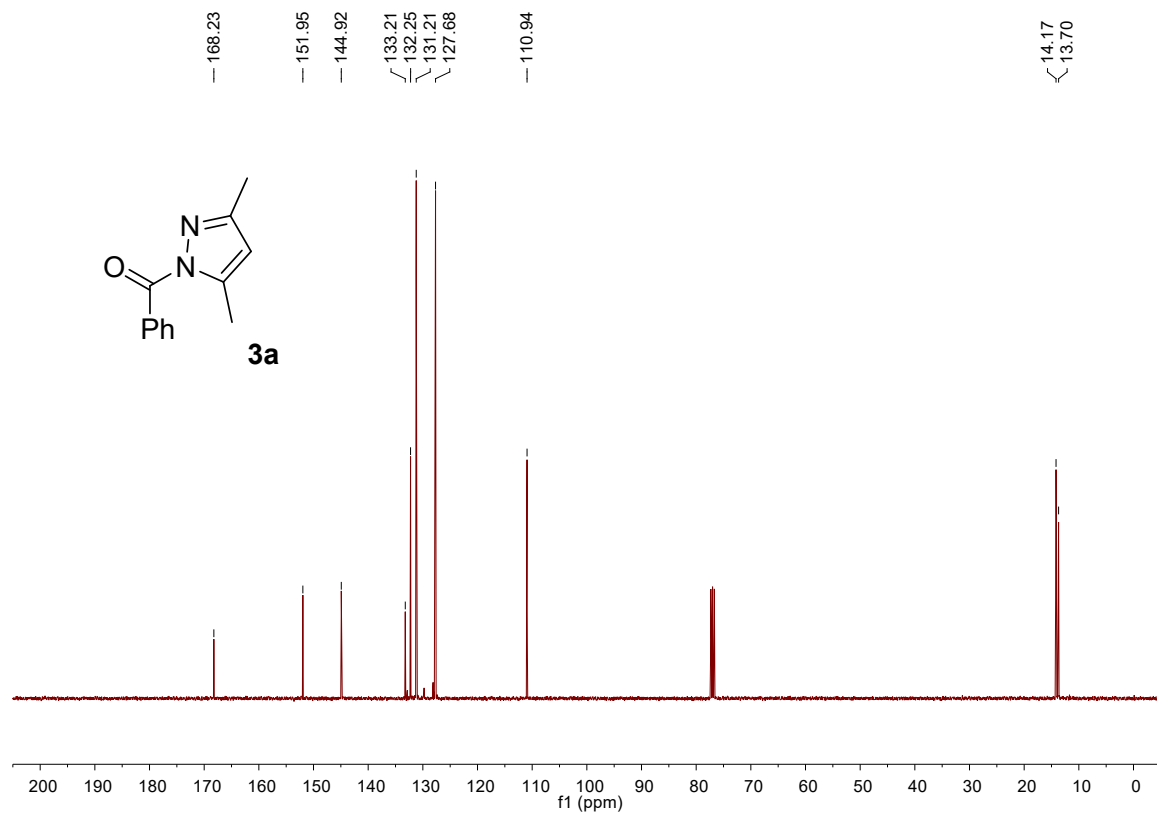
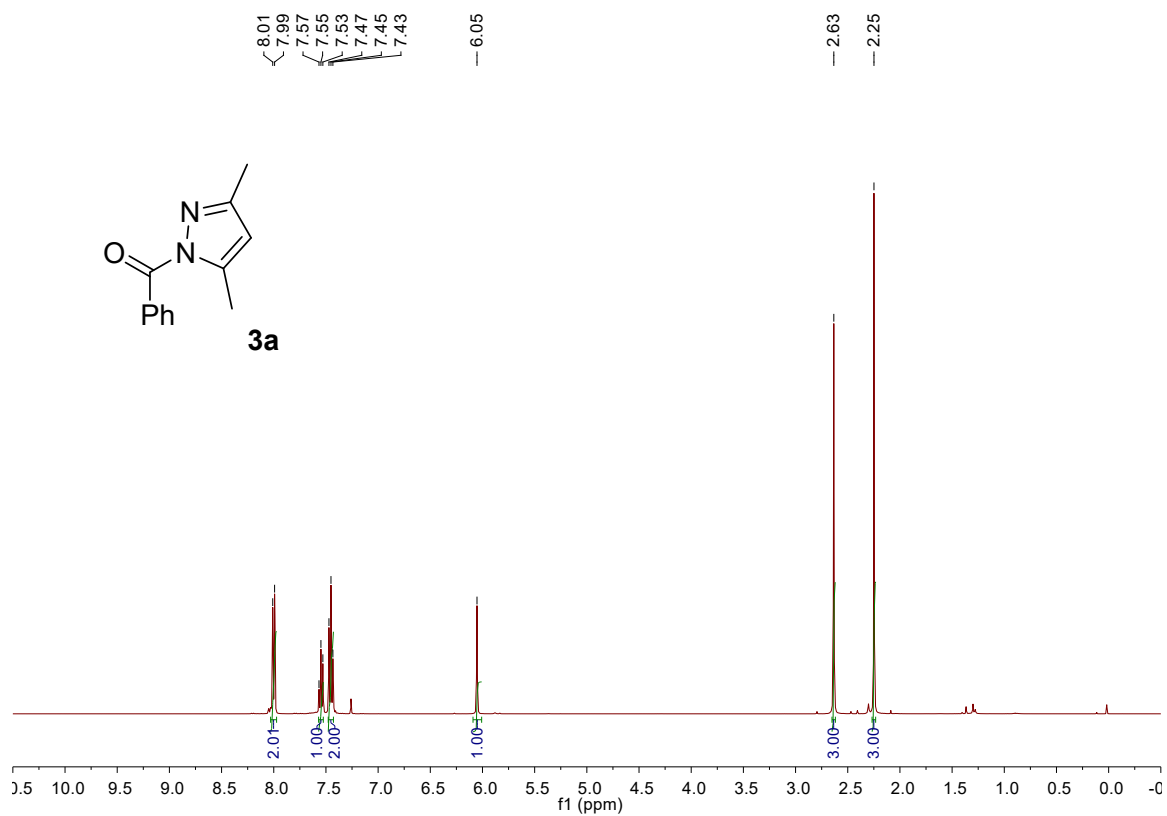


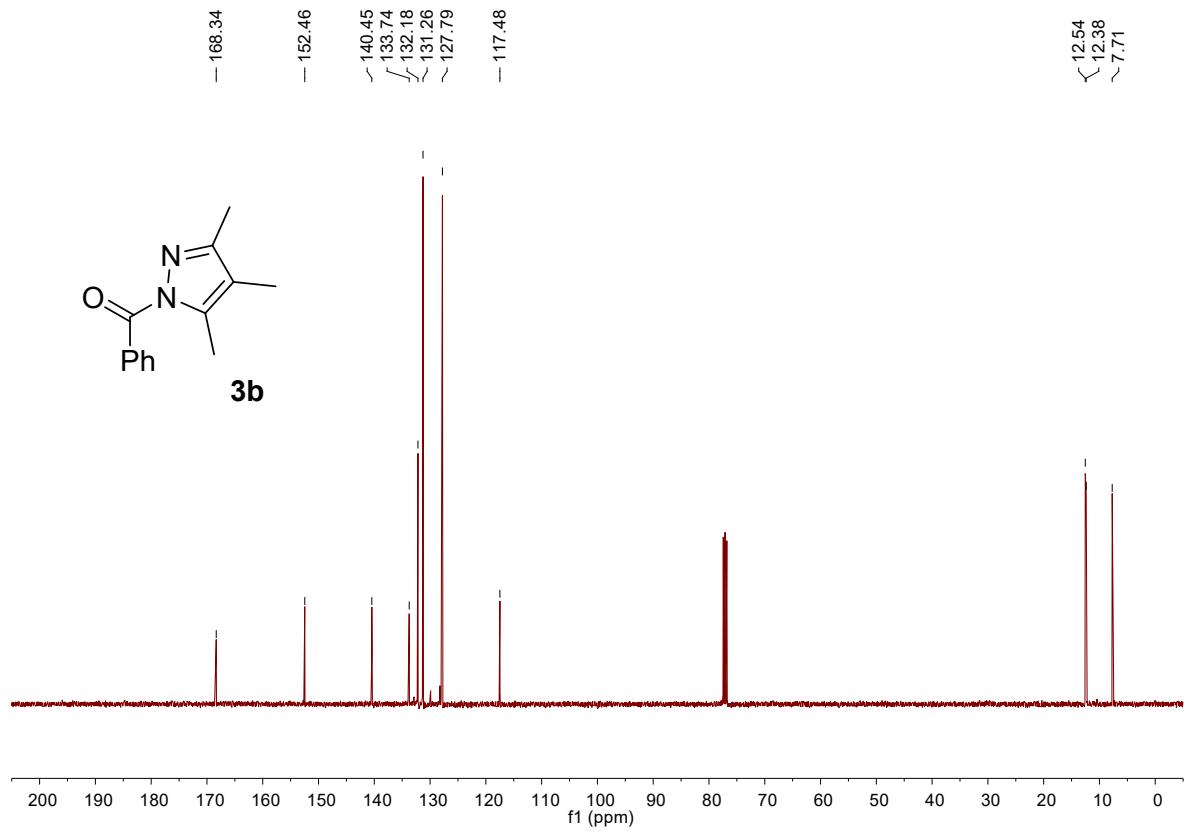
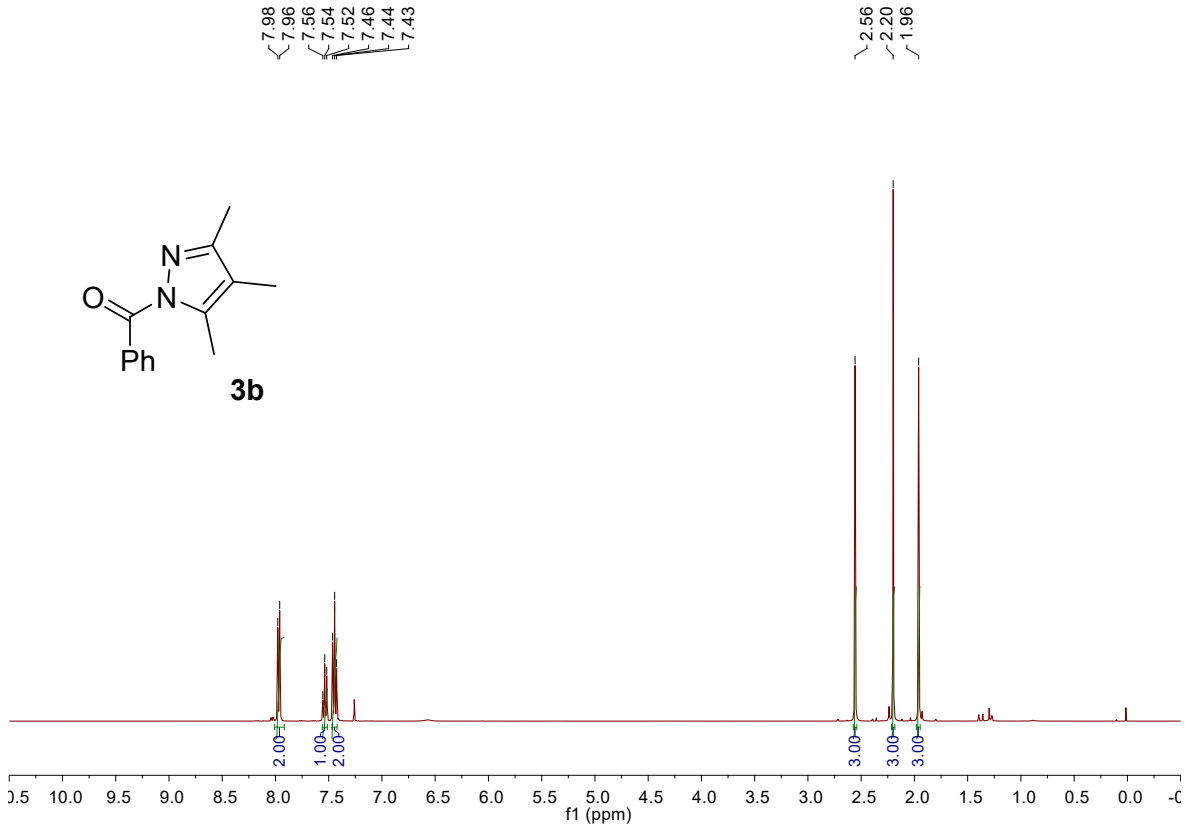
4-chloro-3,5-dimethyl-1-phenyl-1H-pyrazole (3l)

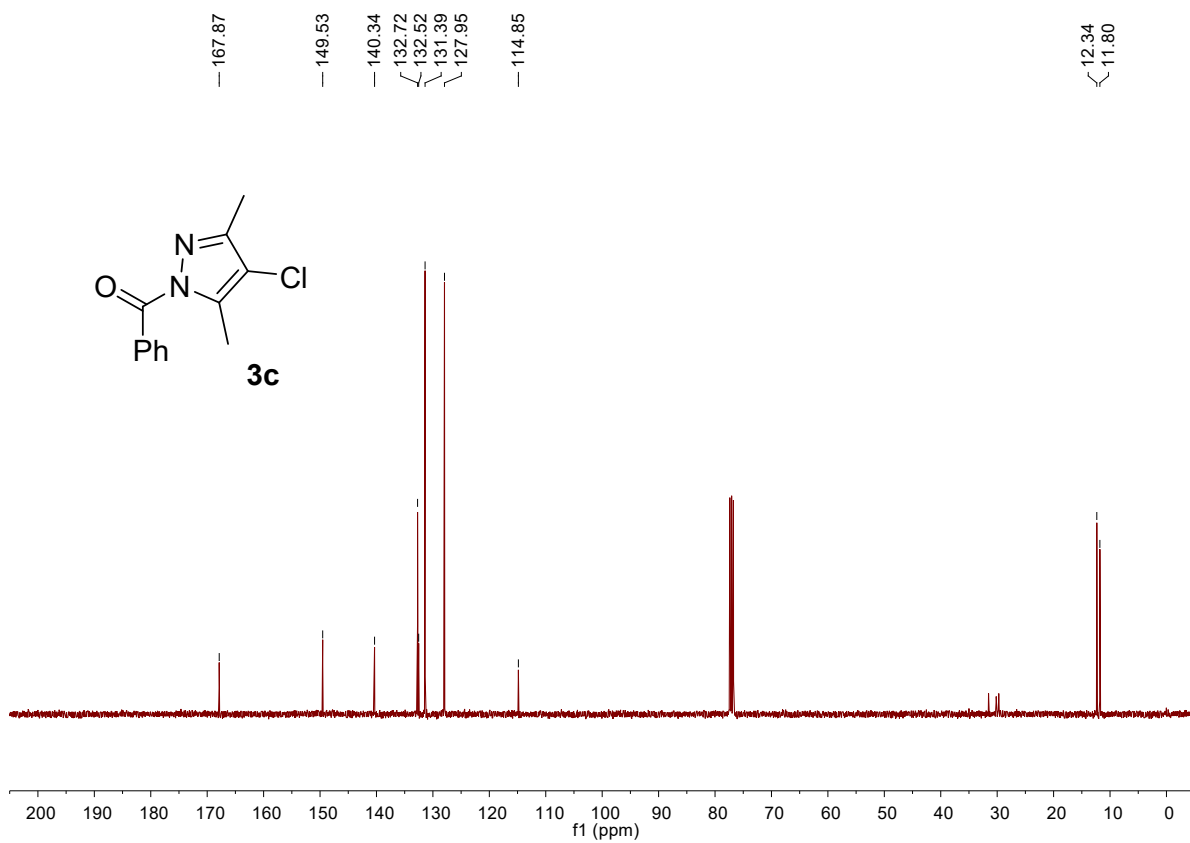
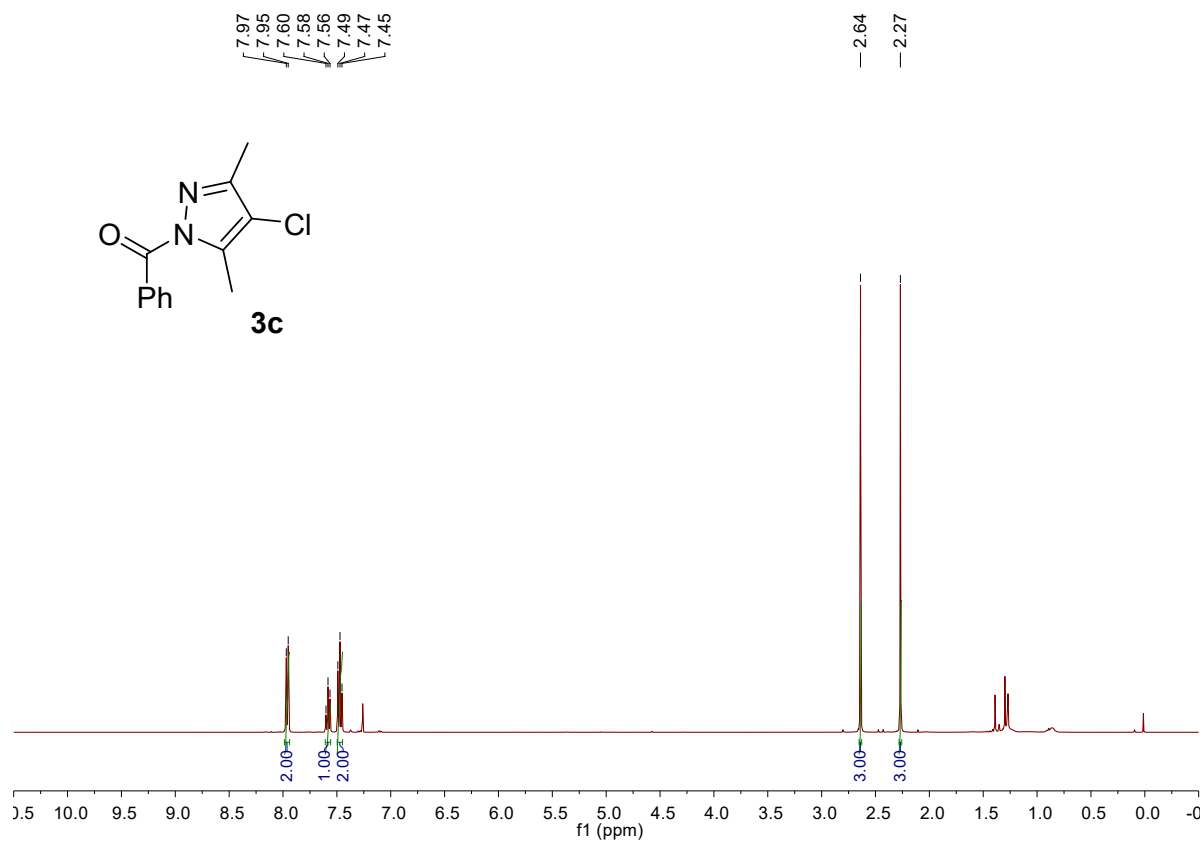
¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.50-7.36 (m, 5H), 2.31 (d, *J* = 2.9 Hz, 6H);

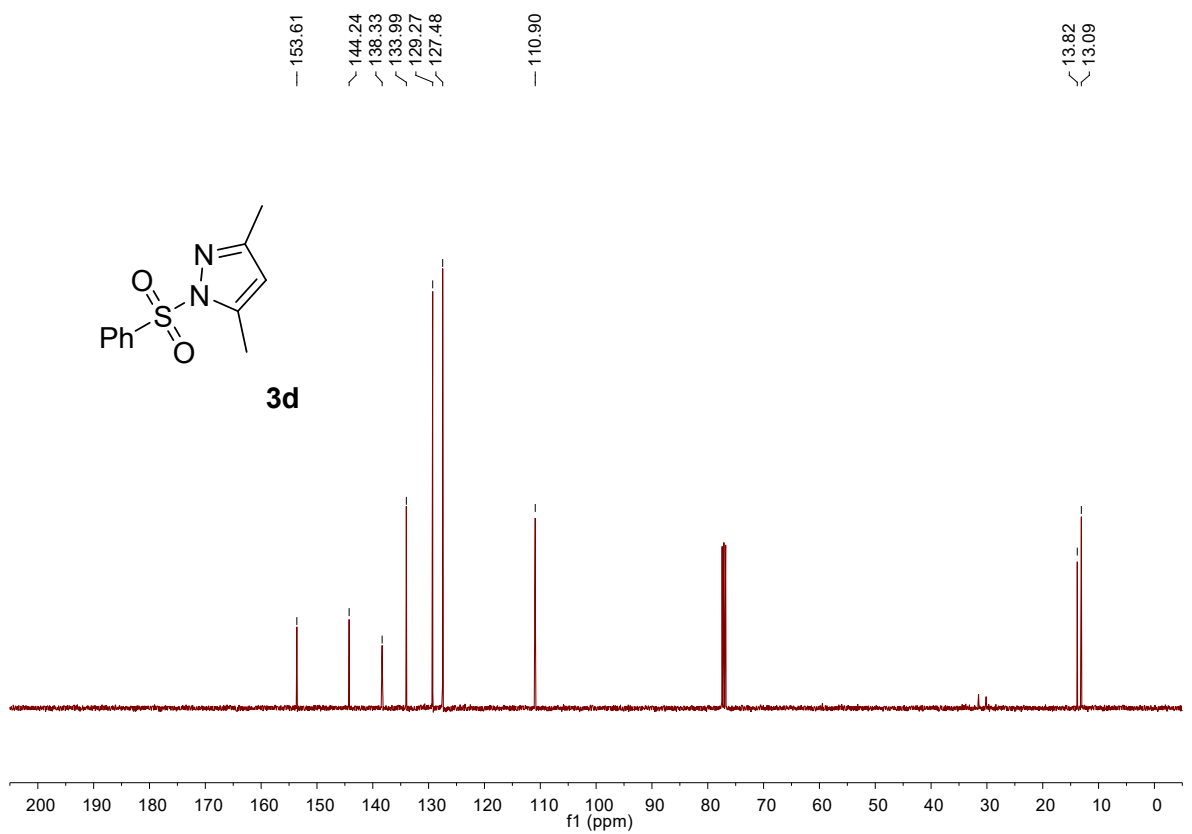
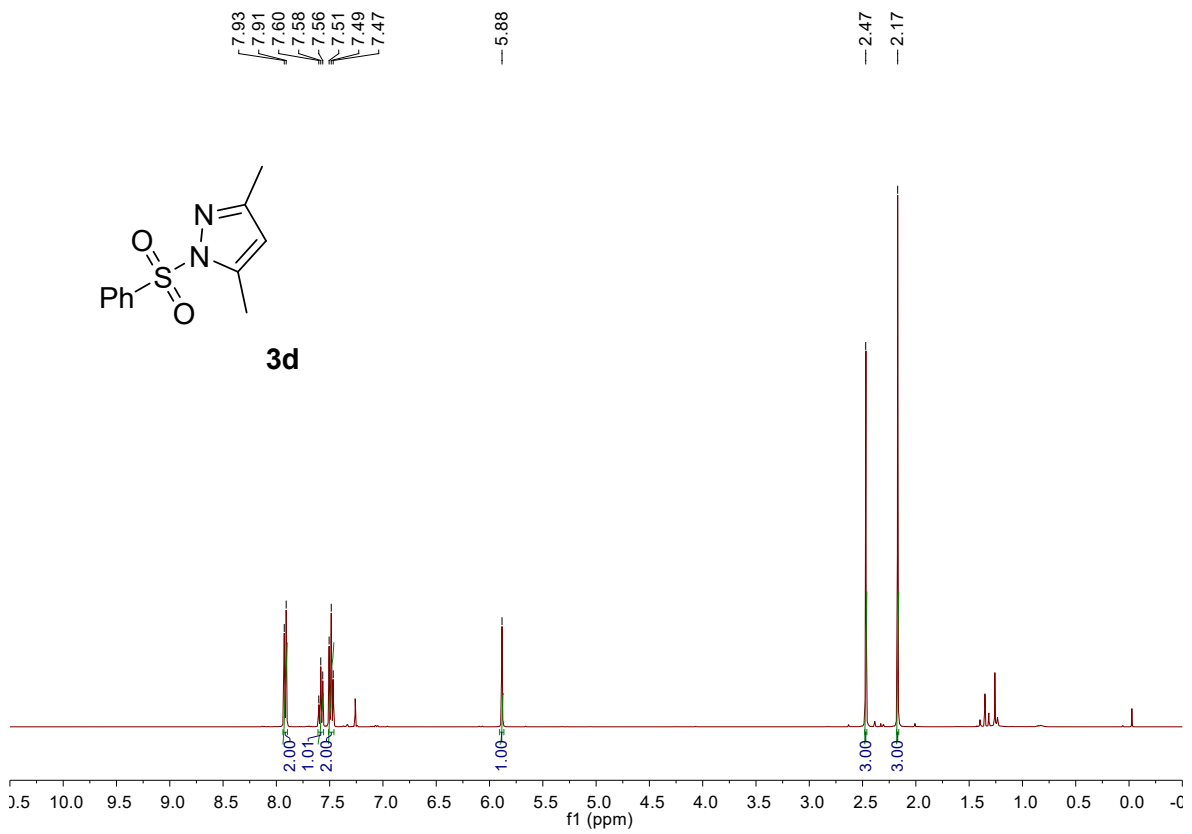
¹³C NMR (101 MHz, CDCl₃): δ (ppm) 146.03, 139.74, 135.71, 129.16, 127.72, 124.55, 109.83, 11.39, 10.82.

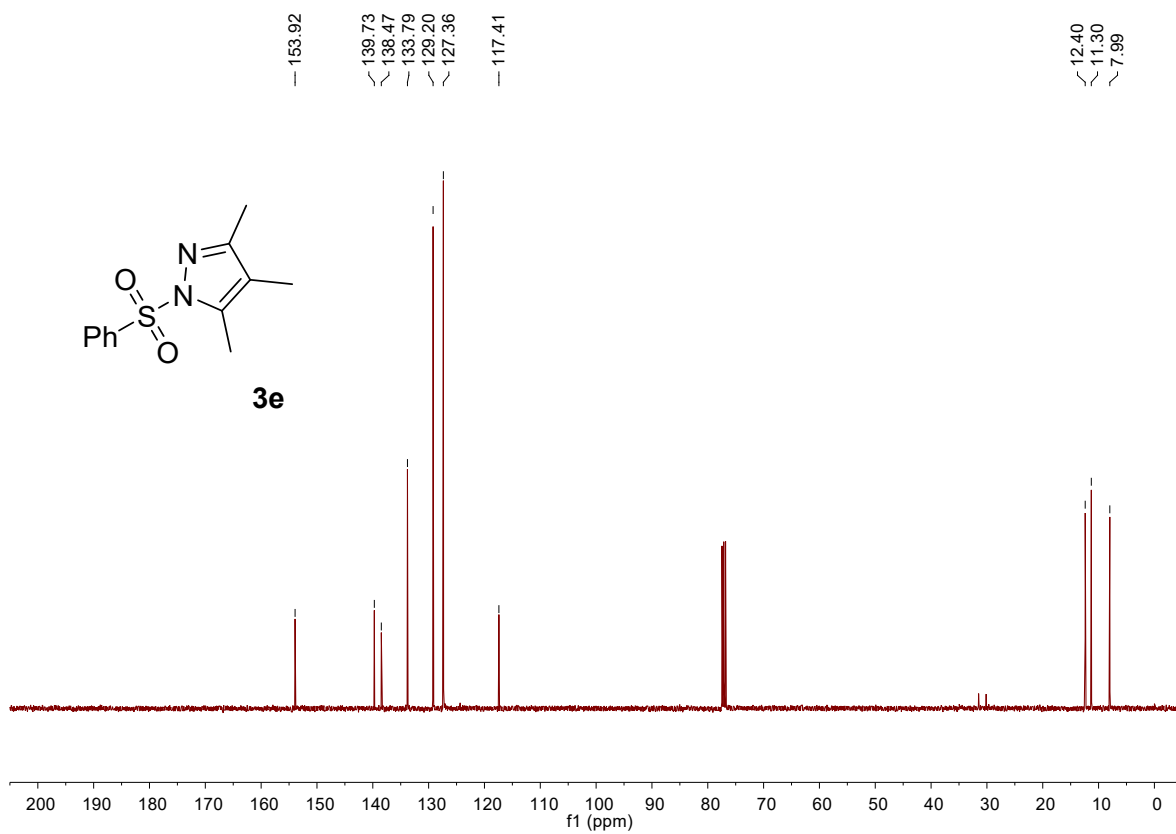
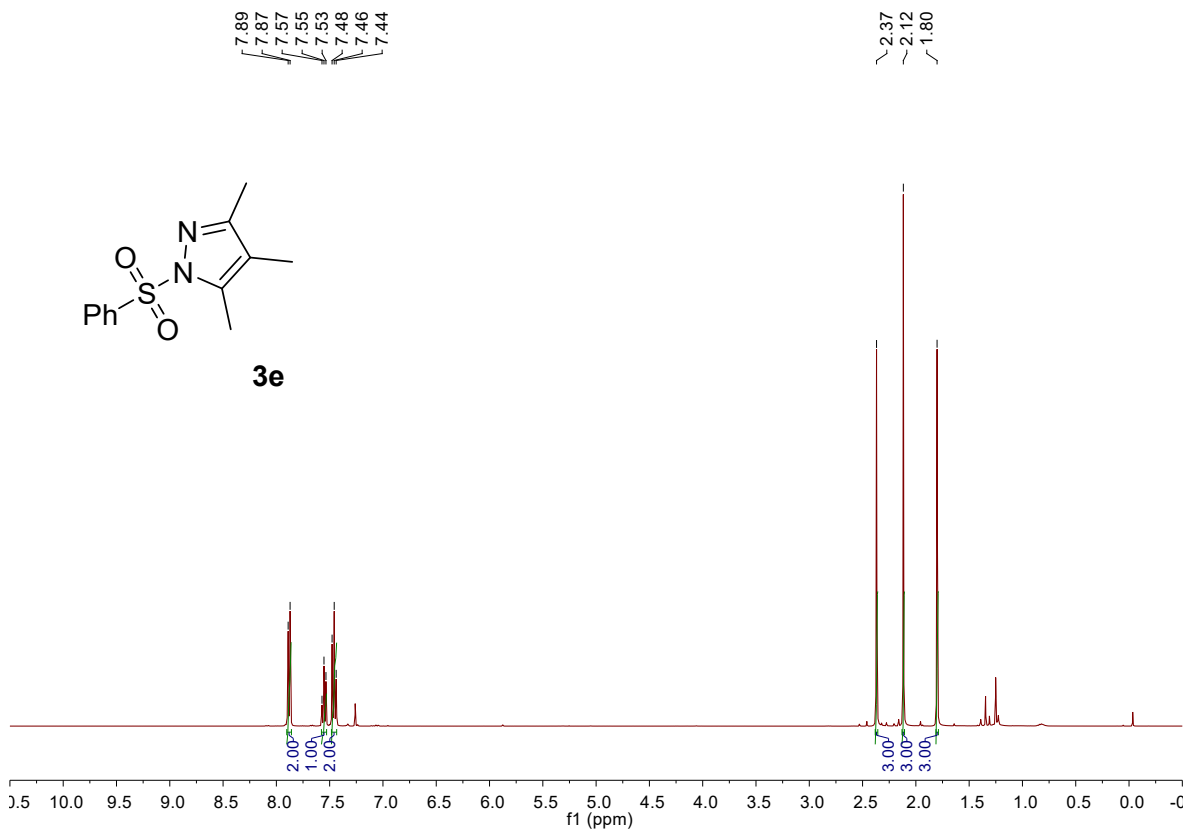
6. NMR Spectra

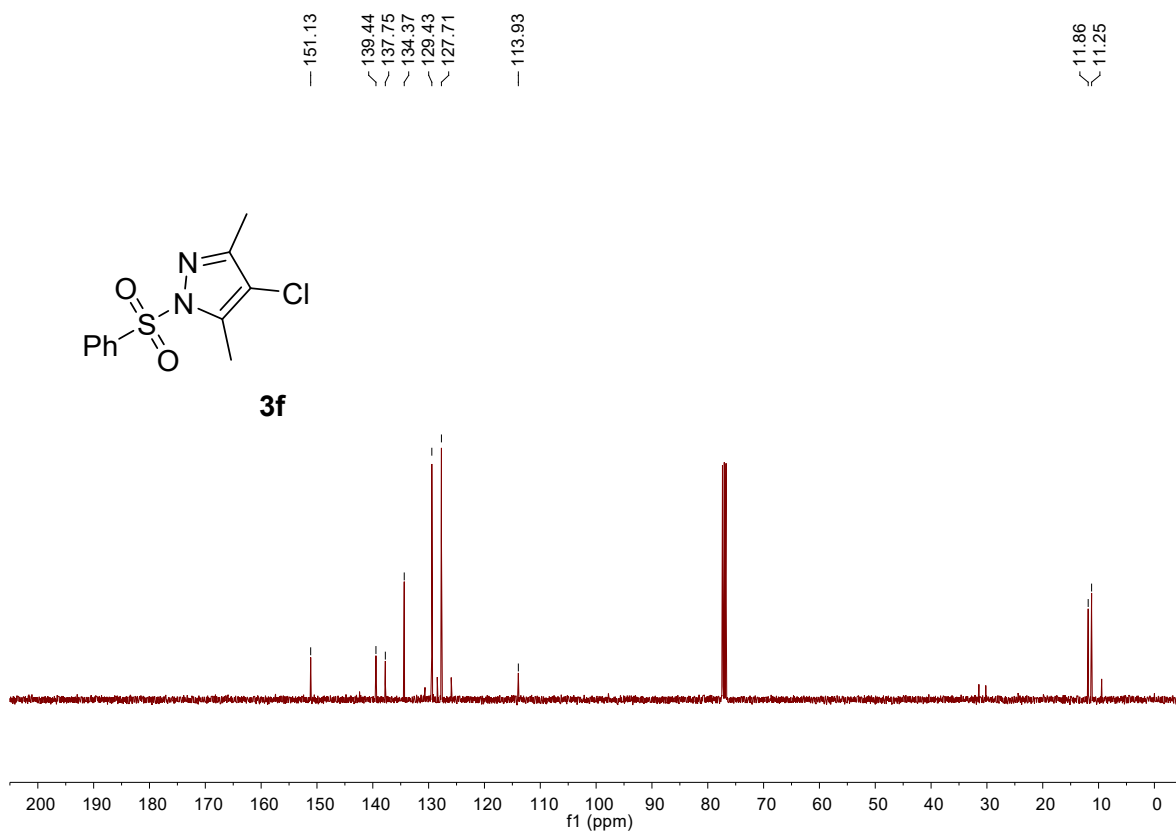
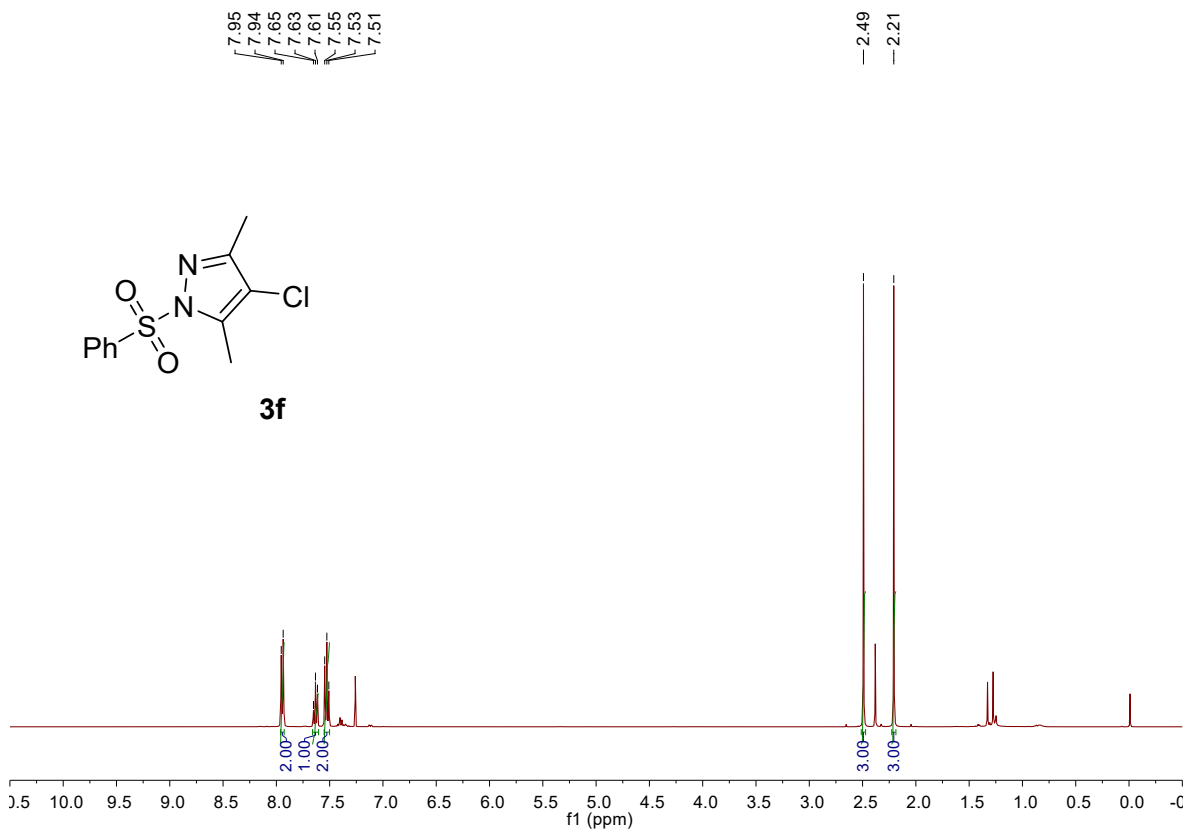


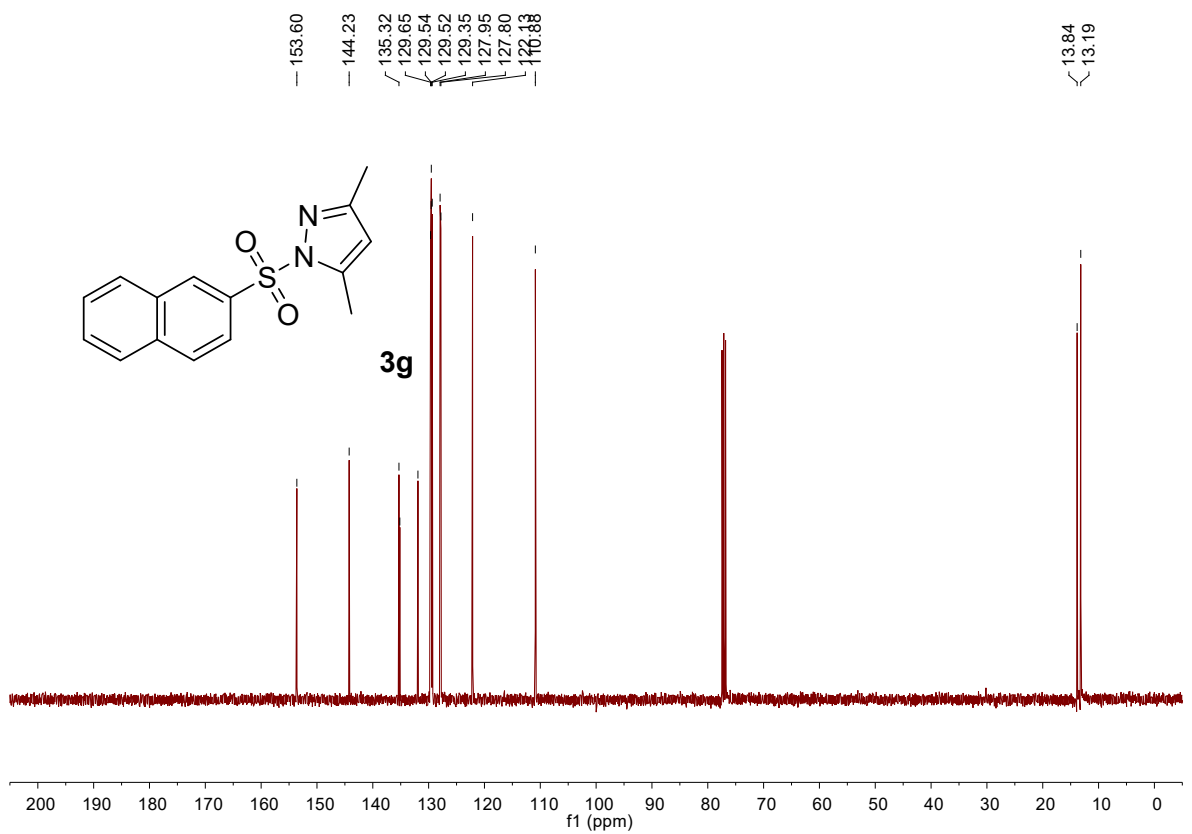
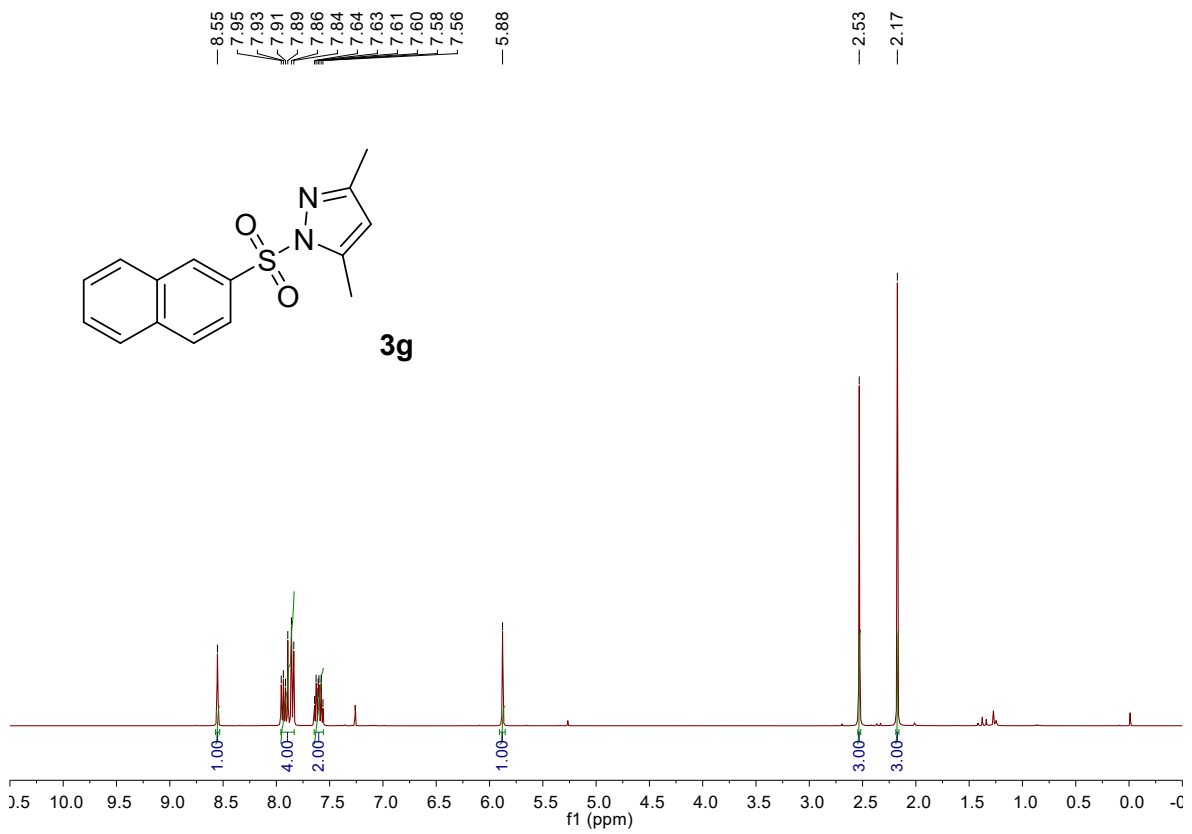


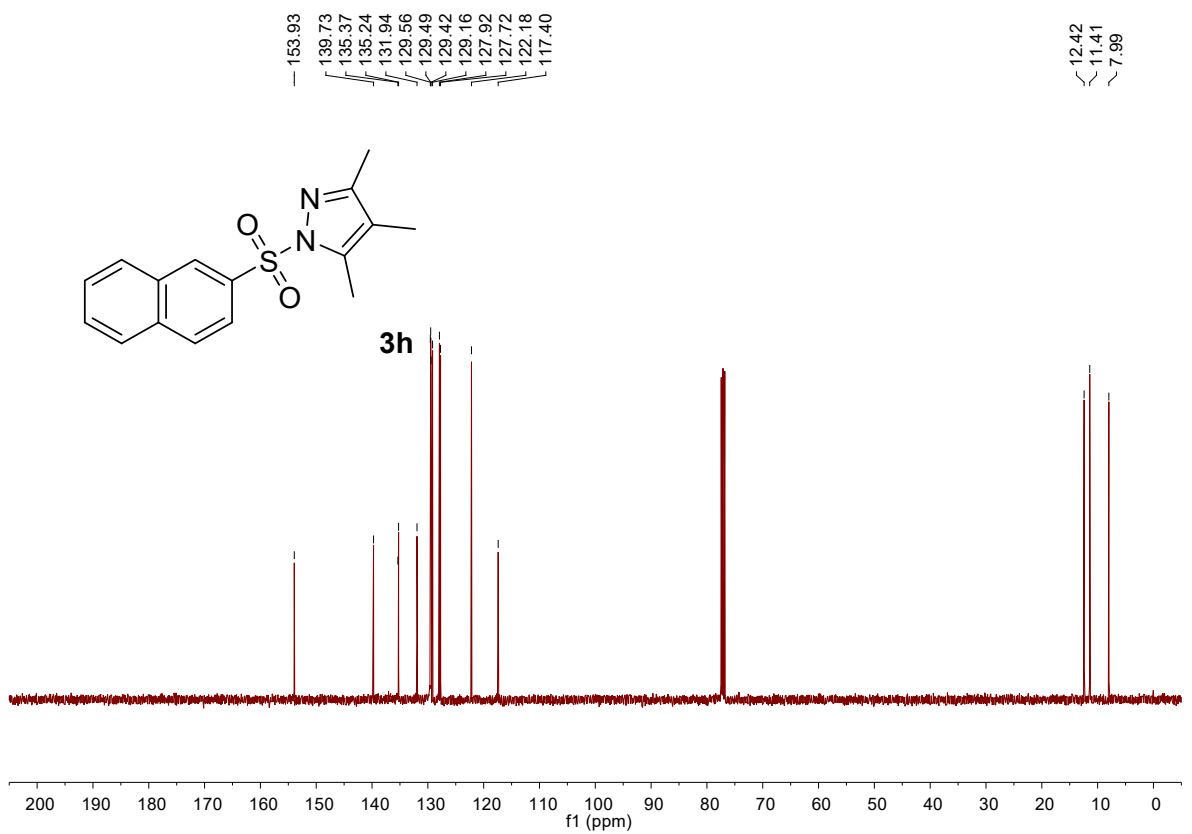
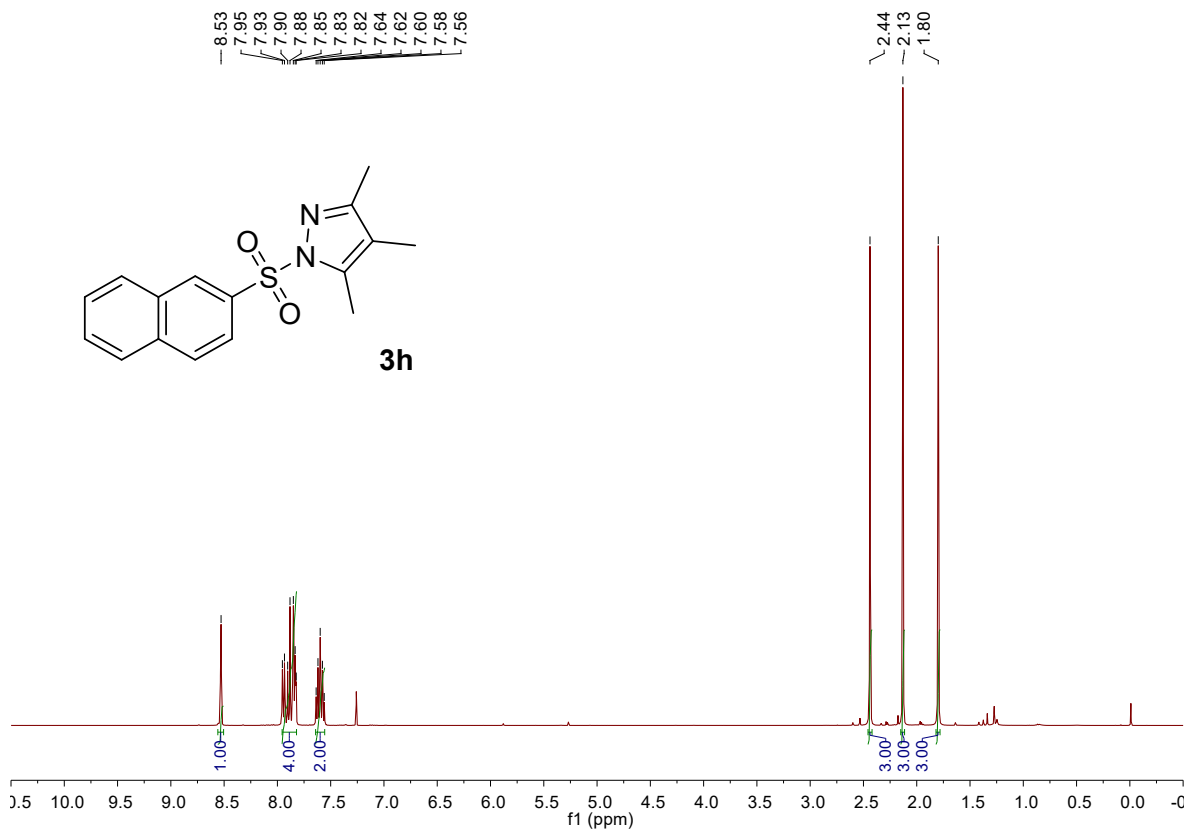


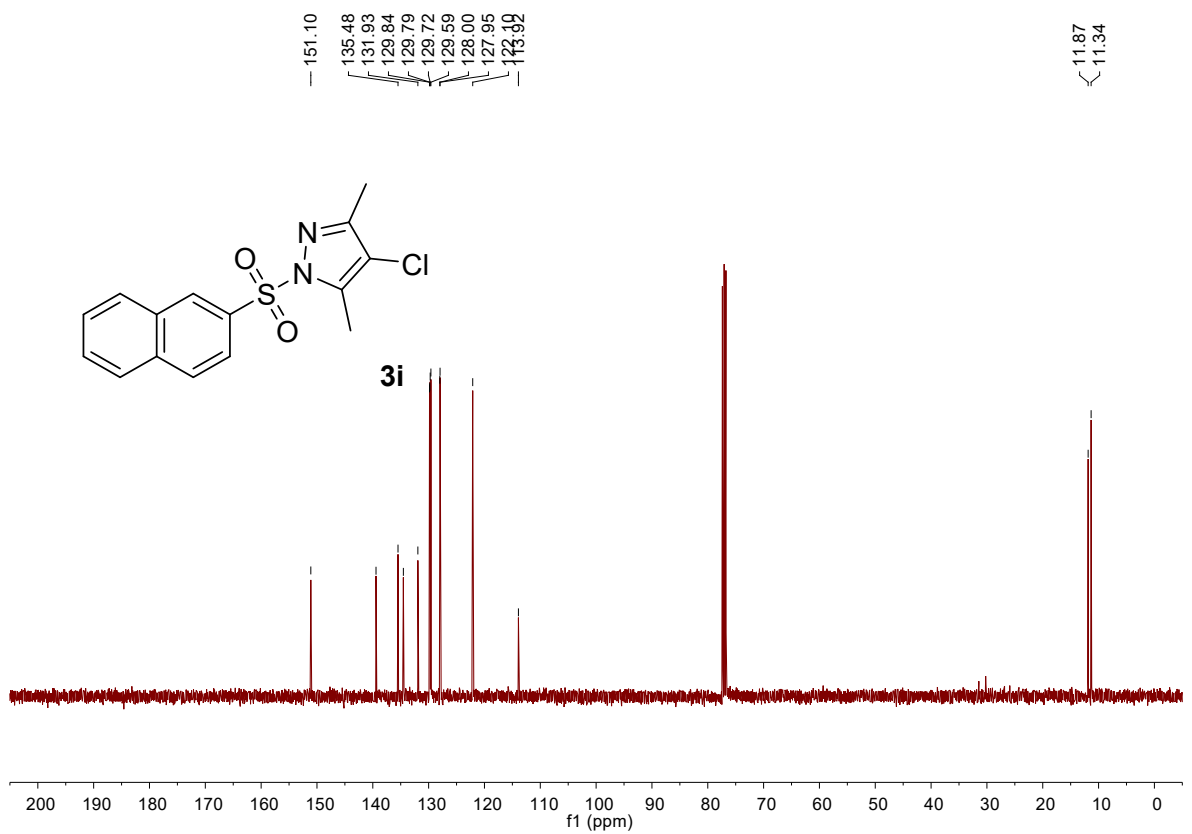
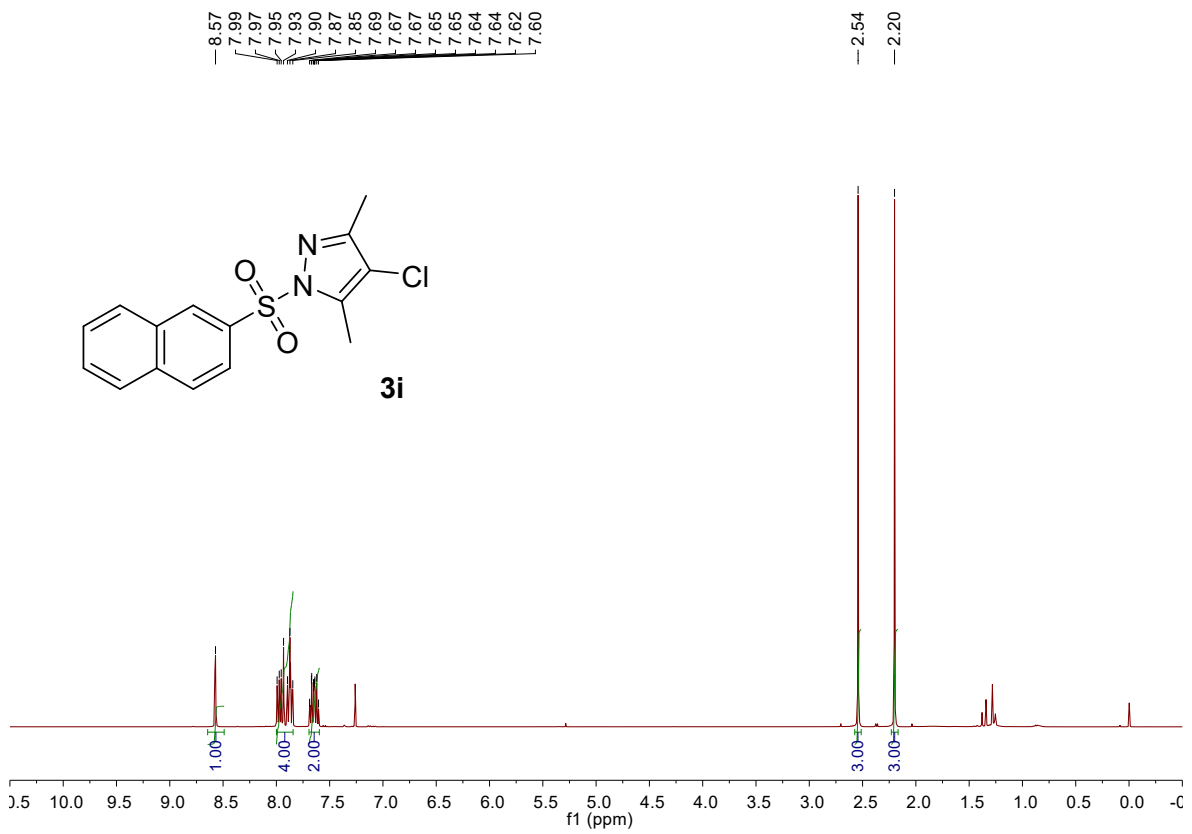


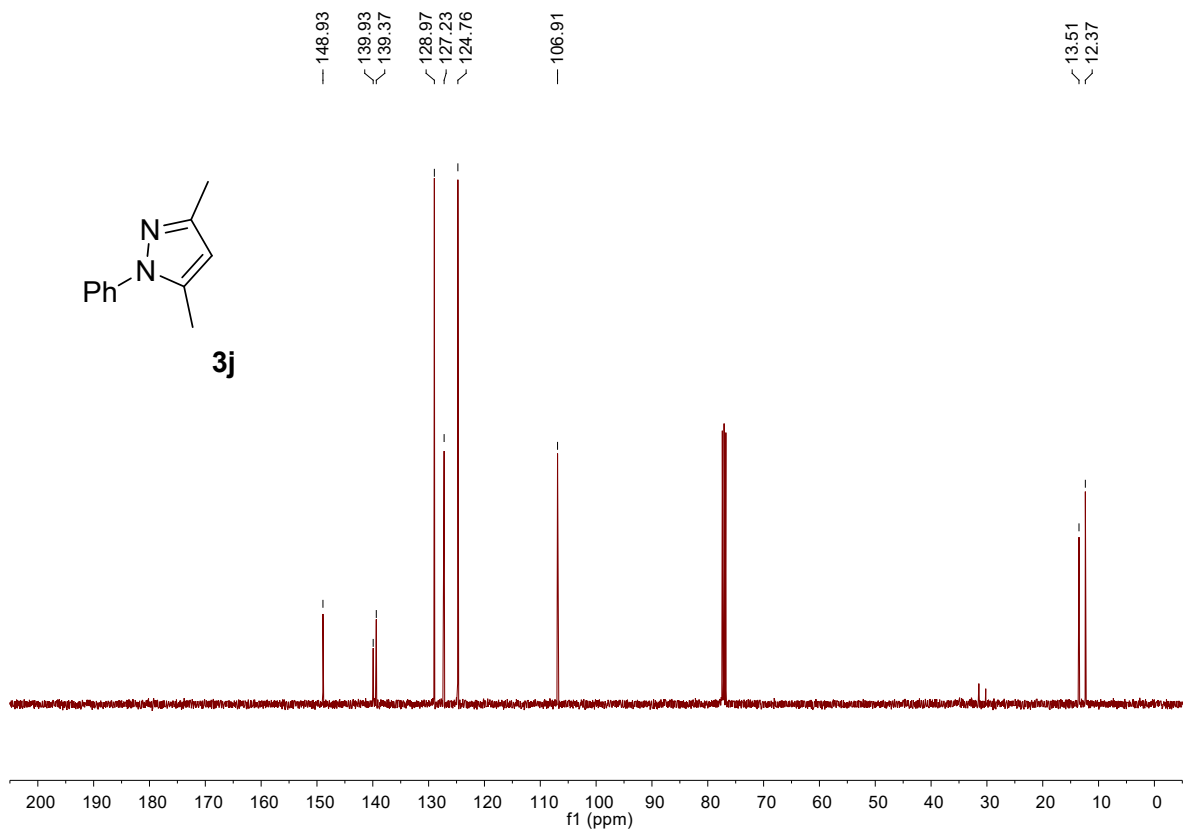
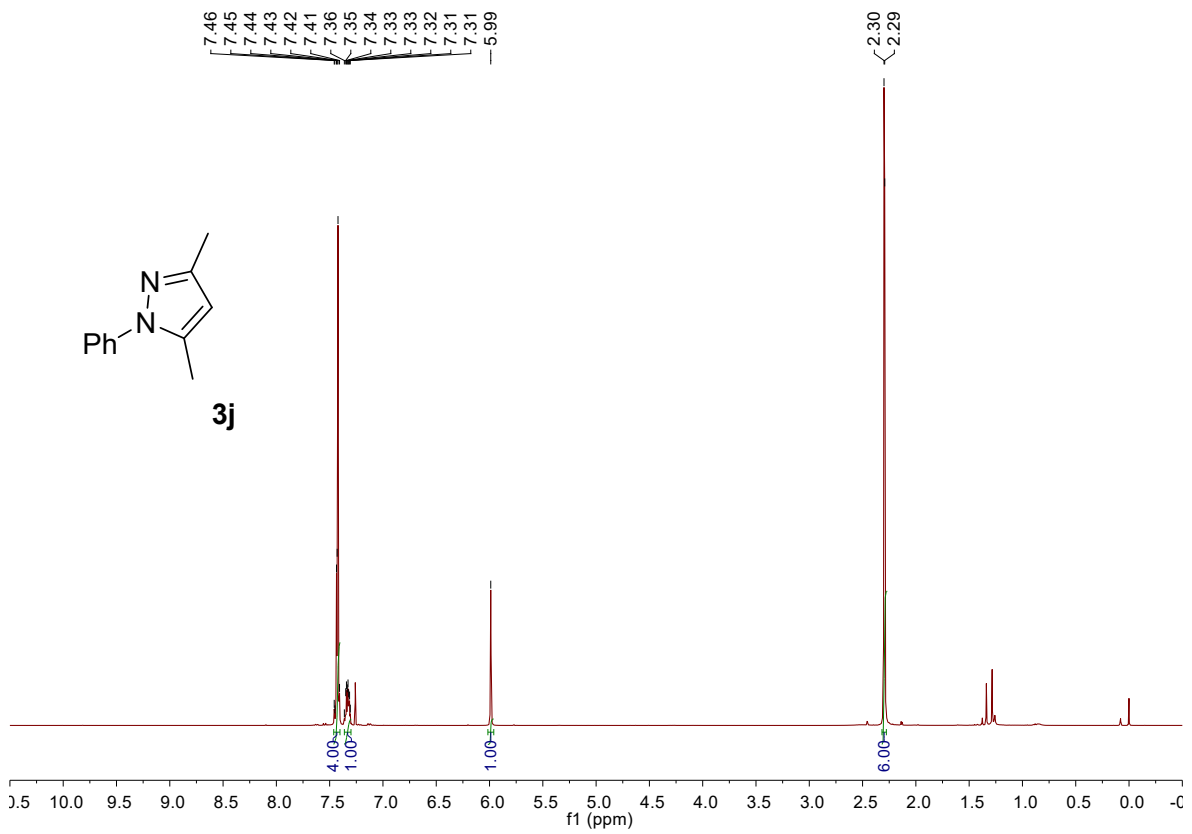


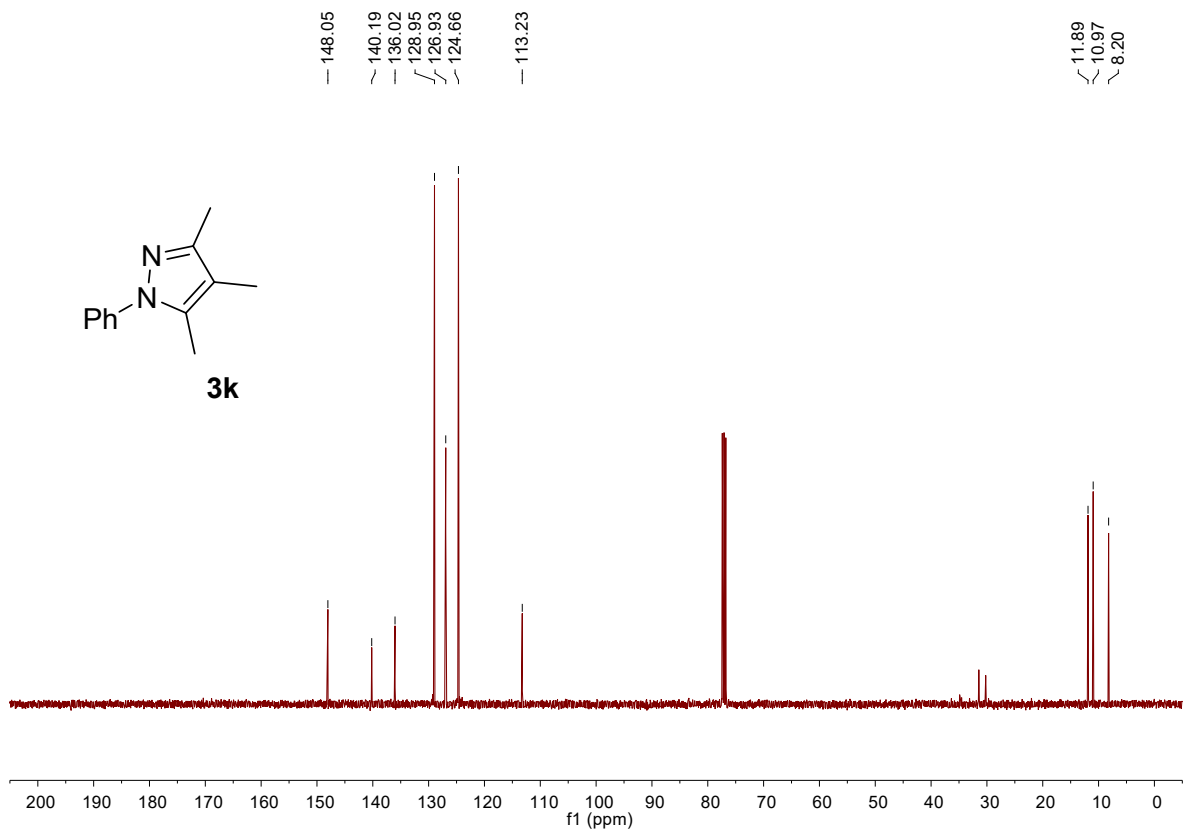
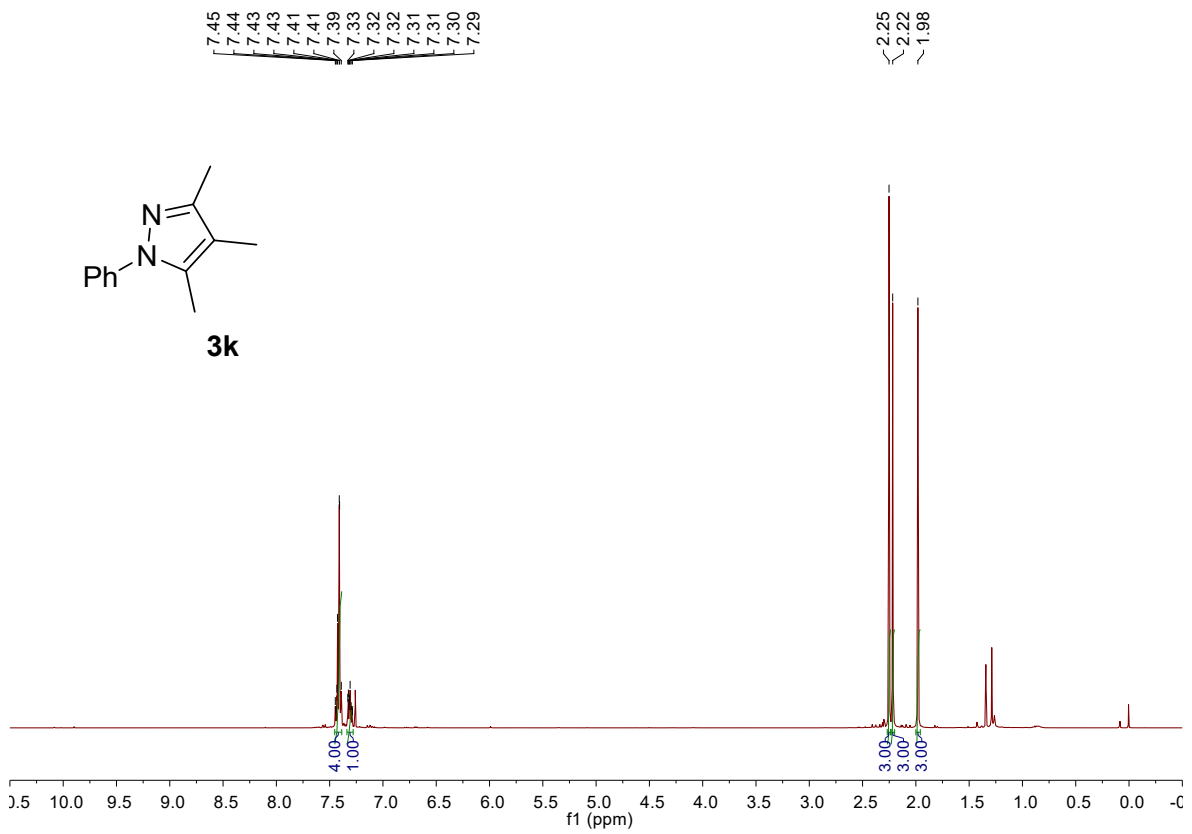


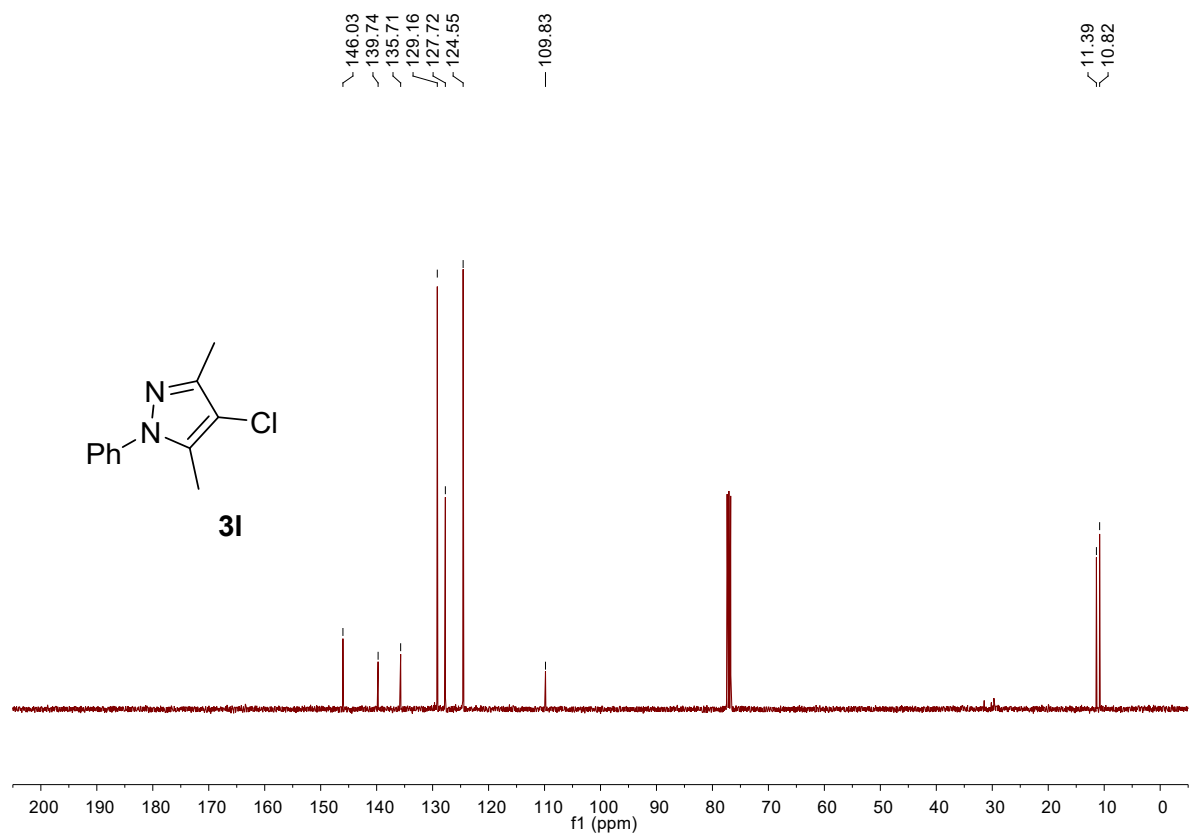
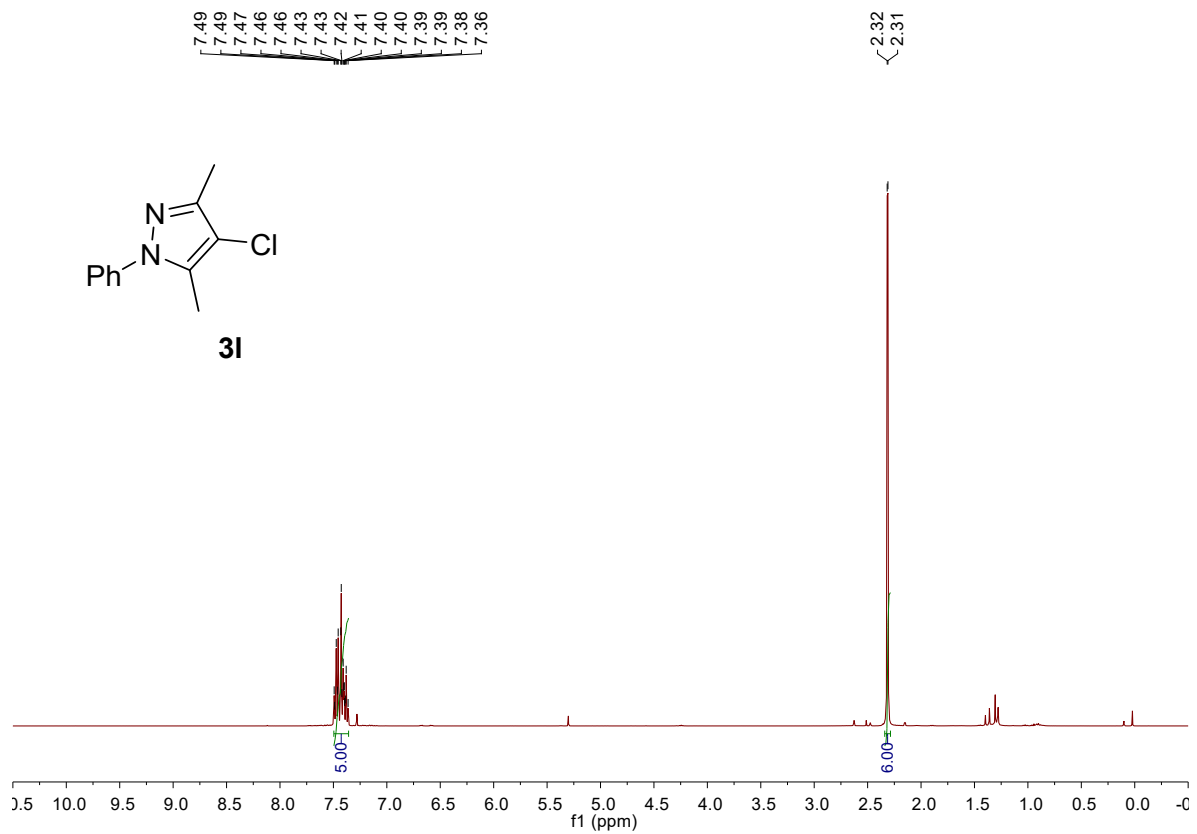












7. Notes and References

1. D. Menozzi, E. Biavardi, C. Massera, F.-P. Schmidtchen, A. Cornia and E. Dalcanale, *Supramolecular Chemistry*, 2010, **22**, 768-775.
2. Y. J. Wang, S. Y. Wu, Y. Q. Sun, X. X. Li and S. T. Zheng, *Chem. Commun.*, 2019, **55**, 2857-2860.
3. (a) G.-P. Yang, S.-X. Shang, B. Yu and C.-W. Hu, *Inorg. Chem. Front.*, 2018, **5**, 2472-2477; (b) B. R. Vaddula, R. S. Varma and J. Leazer, *Tetrahedron Lett.*, 2013, **54**, 1538-1541.