Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Self-assembly of Keggin-type U(VI)-containing tungstophosphates with a sandwich structure: an efficient catalyst for the synthesis of sulfonyl pyrazoles

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1. General Information

Materials and Methods

$Na_9[A\text{-}PW_9O_{34}]\cdot 7H_2O$ was prepared according to the reported method.[1] Other reagents were of reagent grade quality, obtained from commercial sources, and used without further purification. *CAUTION! Uranium compounds are radioactive and can cause cancers and skin and eye irritation.*

The FT-IR spectra were obtained by using a Fourier transform infrared (FT-IR) (4000-500 cm^{-1}) spectrometer (Thermo Nicolet iS5) at 0.5 cm^{-1} resolution and 16 scans. Powder X-ray diffraction (PXRD) was performed on a Bruker D8 Advance diffractometer with Cu Kα radiation (λ = 1.5406 Å) at room temperature.

The single crystal X-ray diffraction data was collected on Bruker D8 Smart Apex II diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Intensities were collected by *ω*-scan and reduced on *APEX 3* (Bruker AXS Inc., 2016) and a multi-scan absorption correction was applied.[2] Hydrogen atoms of partial water molecular were added in calculated positions. The structures were solved and refined on *Olex2* using *SHELXTL* package.[3] Parameters of the crystal data collection and refinement are given in Table S1. The CSD numbers are 2067677 and 2067678.

Methods for the Characterization of Products

The starting materials were commercially available and were used without further purification. The products were isolated by column chromatography on silica gel (200-300 mesh) using petroleum ether (60-90 ℃) and ethyl acetate. All compounds were characterized by ^1H NMR and ^{13}C NMR spectrometry, which were consistent with those reported in related literatures. NMR spectra were determined on Bruker Ascend 500 in $CDCl_3$. ^1H NMR chemical shifts were referenced to residual solvent as determined relative to $CDCl_3$ (7.26 ppm). The ^{13}C NMR chemical shifts were reported in ppm relative to the carbon resonance of $CDCl_3$ (central peak is 77.0 ppm). ^1H NMR peaks were labeled as singlet (s), doublet (d), triplet (t), and multiplet (m). The coupling constants, *J*, are reported in Hertz (Hz). GC analyses were performed on Agilent 7890B equipped with a capillary column (HP-5, 30 m × 0.25 μm) using a flame ionization detector.

2. Experiment

Synthesis of $Na_{11}H(H_2O)_{31}[Na(UO_2)(PW_9O_{34})]_2 \cdot 7H_2O$ (1)

$UO_2(OAc)_2 \cdot 2H_2O$ (0.2 mmol, 0.0848 g) was dissolved in 20 mL 0.25 M NaCl solution. $Na_9[A\text{-}PW_9O_{34}] \cdot 7H_2O$ (0.2 mmol, 0.5125 g) was then added into the solution. The mixture was stirred until $Na_9[A\text{-}PW_9O_{34}] \cdot 7H_2O$ dissolved completely and then was adjusted to pH = 5.1 using 1 M HCl. The cloudy solution was stirred at 85 °C for 30 min. After cooling to room temperature, 5 g NaCl was added into the mixture and stirred for 5 min. The mixture was filtered and the filtrate was kept stand still at room temperature. Crystals will come out after one night. Yellow irregular block crystals of **1** were collected after 7 days. IR (cm^{-1}; s, strong; m, medium; w, weak): 3394 (s), 1635 (m), 1061 (s), 1009 (m), 947 (s), 912 (s), 858 (s), 839 (s), 781 (vs), 720 (vs), 665 (vs), 512 (w), 501 (w).

Synthesis of $Na_{12}(H_2O)_{29}[Na(UO_2)(PW_9O_{34})]_2 \cdot 7H_2O$ (2)

The synthesis procedure of **2** is similar to **1** except the pH was adjusted to 6.9. Yellow parallelogram plate crystals of **2** were collected after 7 days. IR (cm^{-1}; s, strong; m, medium; w, weak): 3389 (s), 1635 (m), 1061 (s), 1009 (m), 947 (m), 913 (s), 860 (s), 840 (s), 780 (vs), 719 (vs), 665 (vs), 570 (s), 506 (w).

Typical procedure of the compound 1 catalyzed condensation reaction

To a 4 mL reaction vial, benzenesulfonyl hydrazide (1 mmol), 3-methyl-2,4-pentanedione (1 mmol), compound **1** (1 mol%) and EtOH (0.1 mL) were added. Then the reaction was carried out in screw cap vials with a Teflon seal at 80 °C for the desired time. After reaction, the mixture was purified by column chromatography (petroleum ether/EtOAc) to afford the desired products. However, some products could also be obtained by recrystallization.

3. Characterization of 1 and 2.

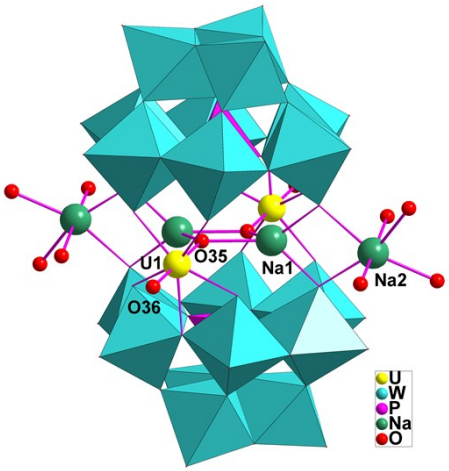


Fig. S1 Polyhedral representation view of the polyanion in **1**.

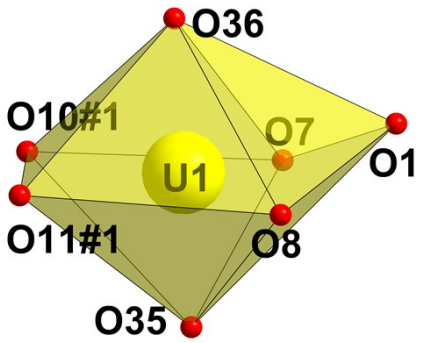


Fig. S2 Coordination mode of U1 in **1**.

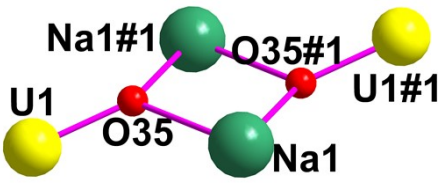


Fig. S3 View of the $\{NaUO_2\}_2$ in **1**.

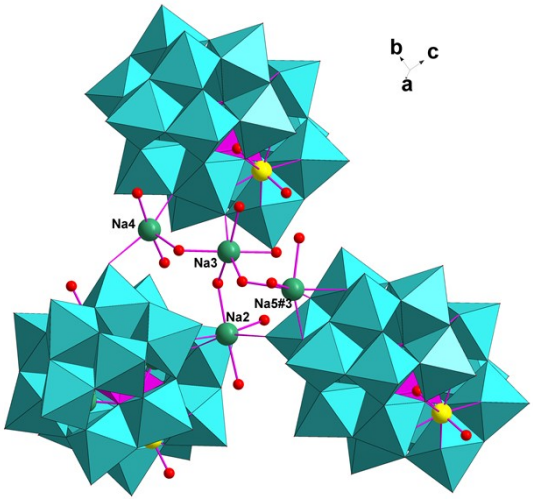


Fig. S4 Coordination modes of Na2, Na3, Na4 and Na5 in **1**.

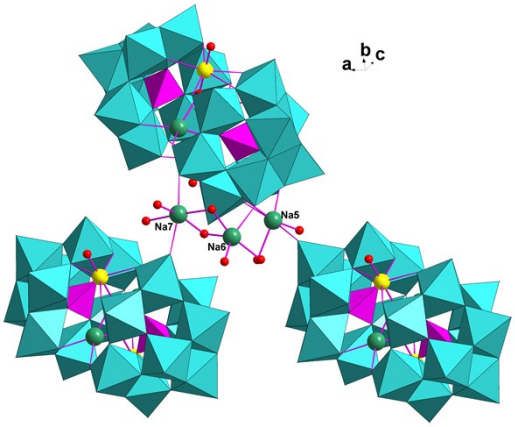


Fig. S5 Coordination modes of Na5, Na6 and Na7 in **1**.

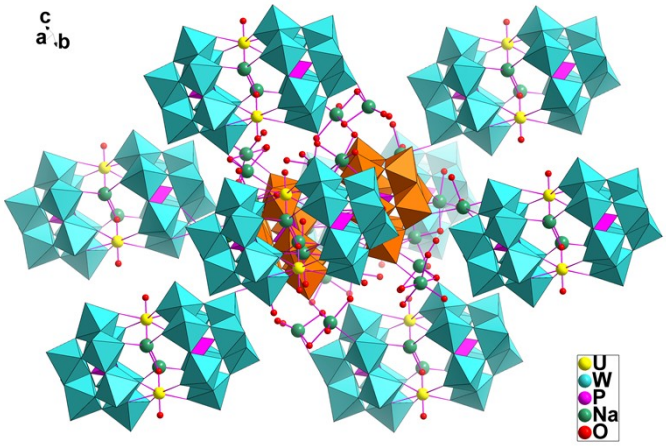


Fig. S6 One $[Na(UO_2)(PW_9O_{34})]_2^{12-}$ polyanion (orange) is surrounded by eight adjacent polyanions (aqua) in **1**.

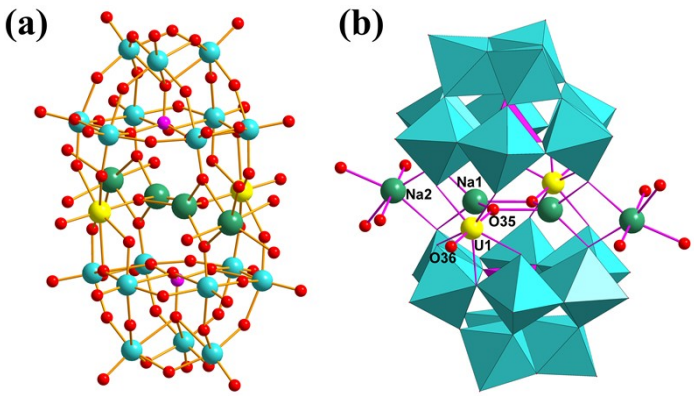


Fig. S7 Keggin-sandwich structure of **2**; (a) ball and stick representation view; (b) polyhedral representation view of the polyanion.

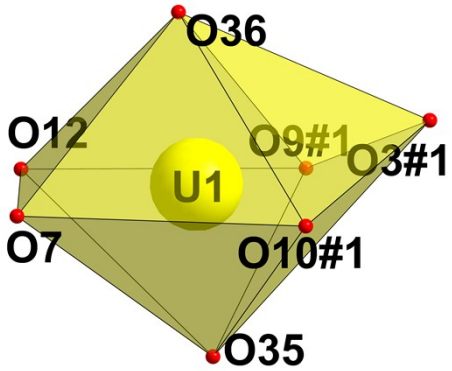


Fig. S8 Coordination mode of U1 in **2**.

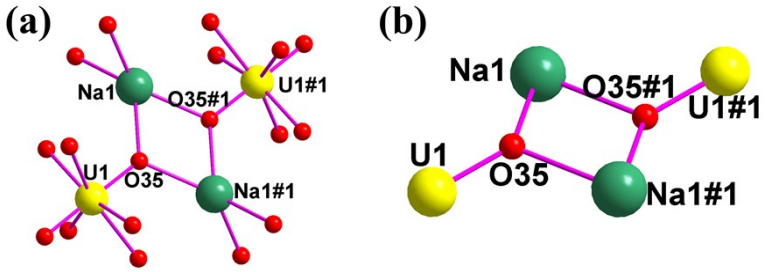


Fig. S9 Top view (a) and side view (b) of the $\{NaUO_2\}_2$ cluster in **2**.

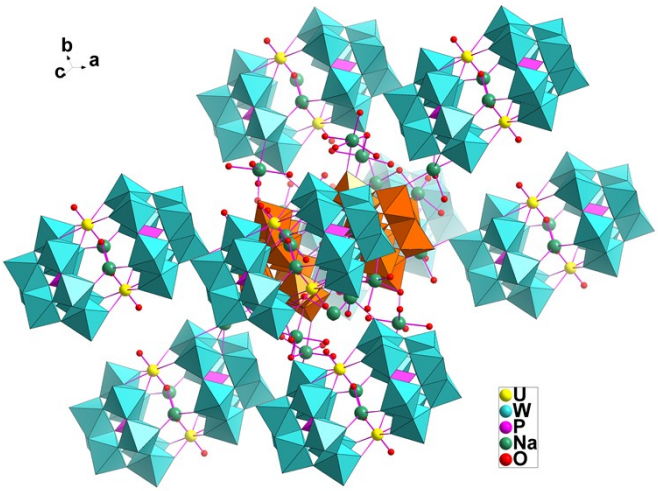


Fig. S10 One $[Na(UO_2)(PW_9O_{34})]_2^{12-}$ polyanion (orange) is surrounded by eight adjacent polyanions (aqua) in **2**.

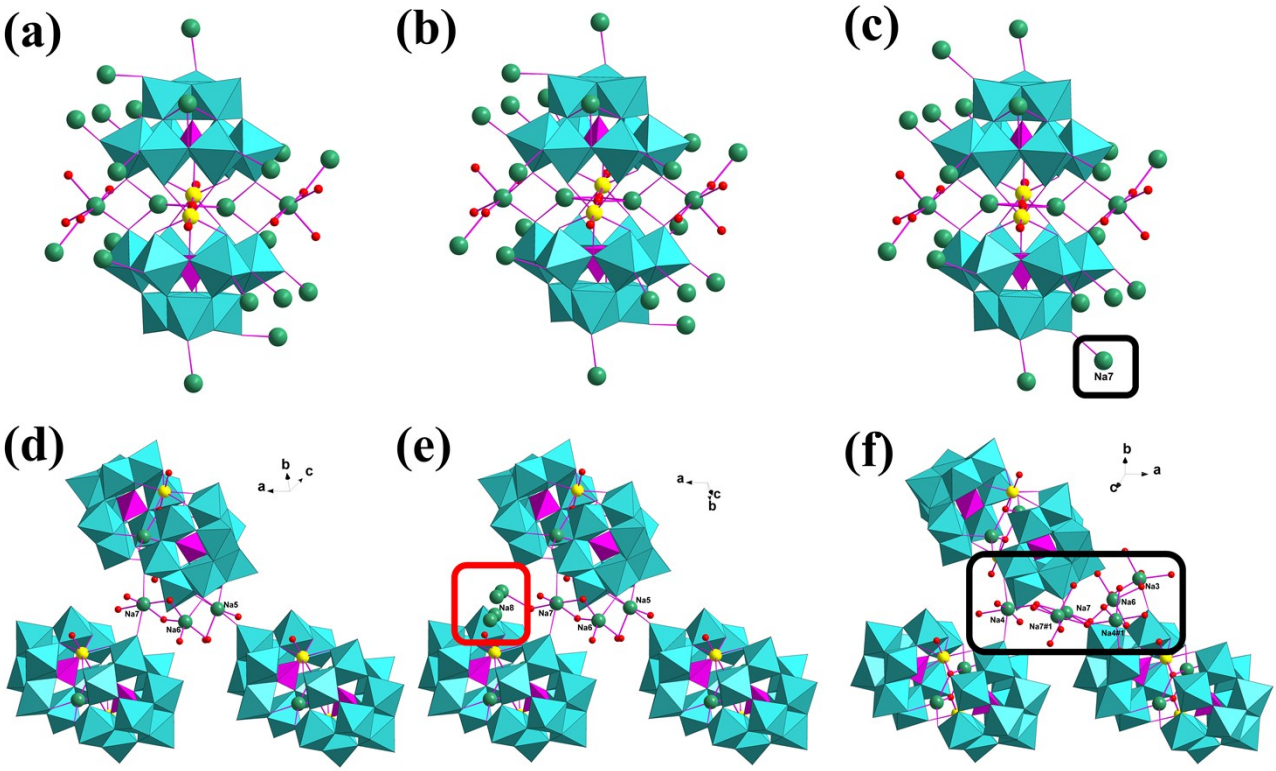


Fig. S11 All the Na(I) ions coordinated with one $[Na(UO_2)(PW_9O_{34})]_2^{12-}$ polyanion in (a) **1**, (b) **2** and (c) the reported structure; the structural comparison between (d) **1**, (e) **2** and (f) the reported structure.

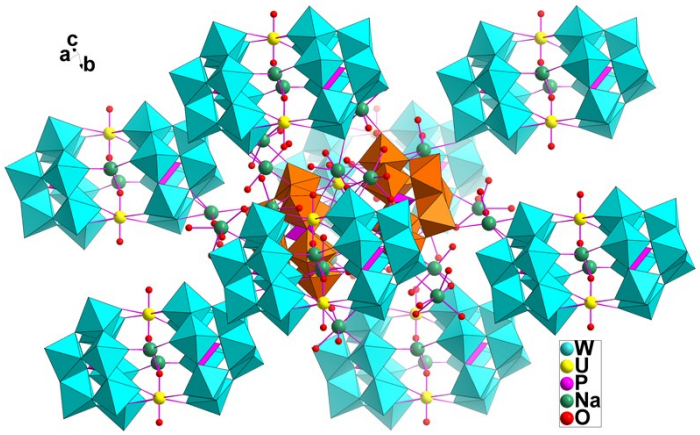


Fig. S12 One $[Na(UO_2)(PW_9O_{34})]_2^{12-}$ polyanion (orange) is surrounded by eight adjacent polyanions (aqua) in the reported structure.

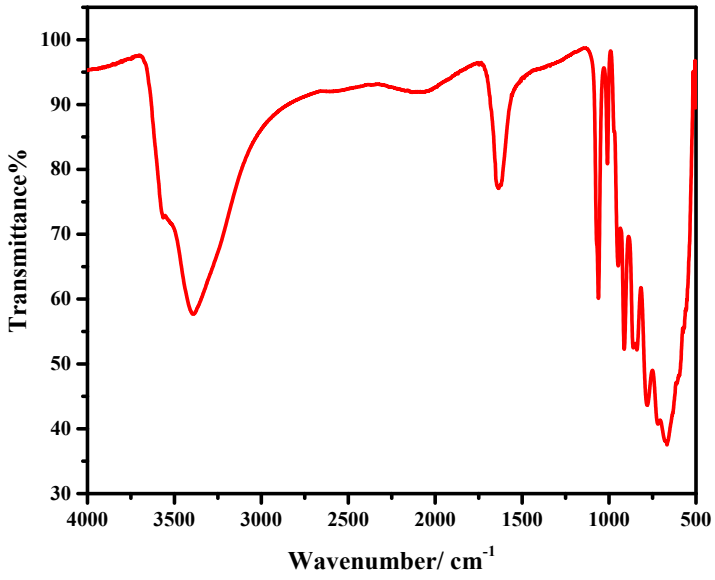


Fig. S13 FT-IR spectrum of **1**.

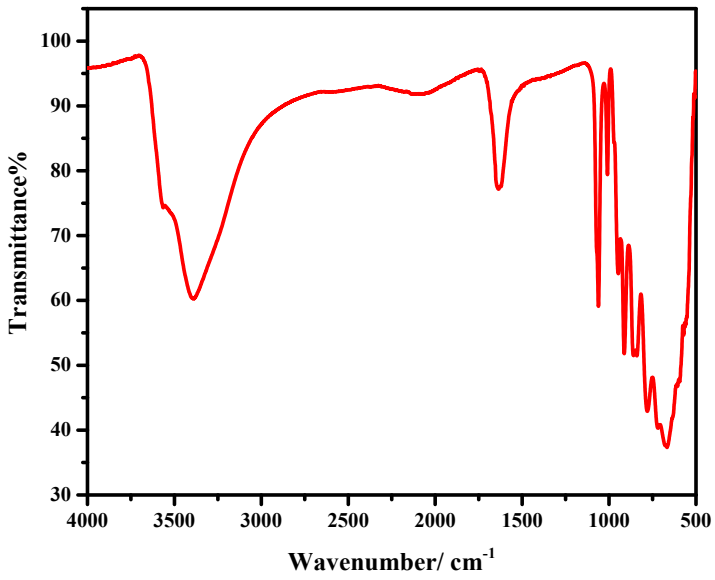


Fig. S14 FT-IR spectrum of **2**.

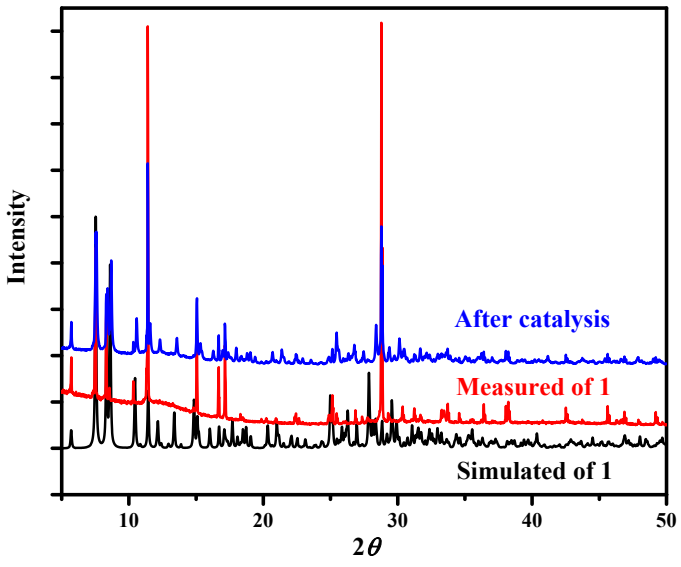


Fig. S15 PXRD pattern of **1**.

The PXRD patterns of **1** before and after the catalytic reaction match well with the simulated PXRD, indicating the stability of **1** in the reaction.

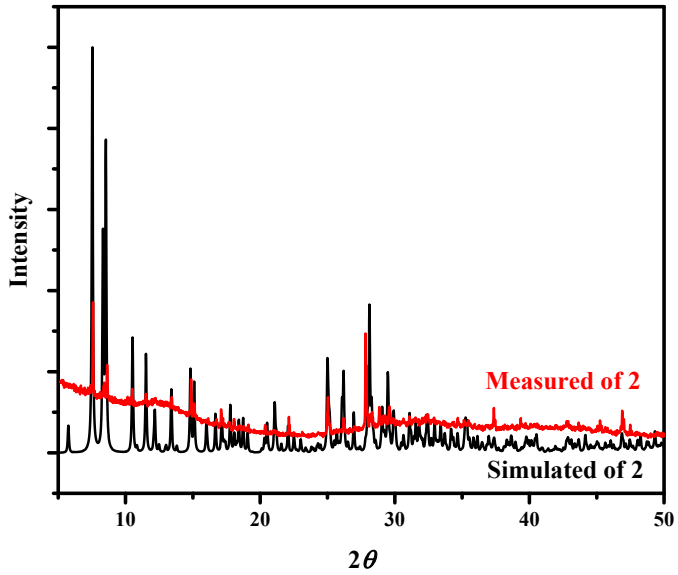
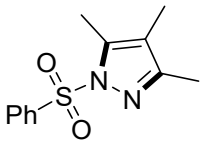


Fig. S16 PXRD pattern of **2**.

Table S1 Crystallographic data and structure refinement for **1**, **2** and the reported structure.

	1	**2**	the reported structure
CSD No.	2067677	2067678	-
Empirical formula	$Na_{13}O_{110}P_2U_2W_{18}H_{77}$	$Na_{14}O_{108}P_2U_2W_{18}H_{72}$	$Na_{14}O_{110}U_2P_2W_{18}H_{76}$
Fw	5983.78	5959.73	6005.77
T/K	150	149.97	173(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$
a/Å	16.7726(3)	16.7416(4)	16.6797(8)
b/Å	14.6382(3)	14.6282(3)	14.6412(7)
c/Å	21.2673(4)	21.2633(7)	21.2925(10)
α(°)	90	90	90
β(°)	112.7500(10)	112.6870(10)	112.2600(10)
γ(°)	90	90	90
V/Å^3	4815.33(16)	4804.5(2)	4812.3(4)
F (000)	5292.0	5272.0	5312.0
Z	2	2	2
ρ_{calcd} (g·cm^{-3})	4.127	4.127	4.145
μ (mm^{-1})	24.977	25.035	24.997
Reflections collected	46446	39677	52355
Unique reflections	11971 (R_{int} = 0.0430)	11886 (R_{int} = 0.0415)	11682 (R_{int} = 0.1068)
Parameter	676	676	572
GOOF on F^2	1.062	1.071	1.156
R_1 [I ≥ 2σ(I)]	0.0273	0.0278	0.0549
wR_2 (all data)	0.0540	0.0568	0.1548
Largest diff. peak/hole/e Å^{-3}	1.77/-1.44	1.33/-1.84	3.72/-4.22

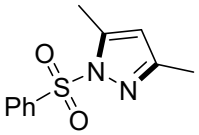
4. Characterization of Products [4]



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

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.90 (d, J = 7.4 Hz, 2H), 7.58 (t, J = 7.5 Hz, 1H), 7.48 (t, J = 7.8 Hz, 2H), 2.39 (s, 3H), 2.14 (s, 3H), 1.82 (s, 3H);

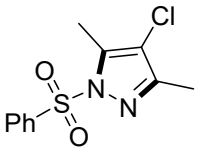
^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 154.01, 139.75, 138.45, 133.84, 129.25, 127.42, 117.45, 12.48, 11.38, 8.06.



3,5-dimethyl-1-(phenylsulfonyl)-1*H*-pyrazole (3b)

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.97-7.90 (m, 2H), 7.49-7.61 (m, 3H), 5.92 (s, 1H), 2.48 (s, 3H), 2.18 (s, 3H);

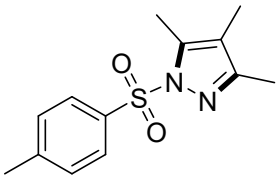
^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 153.60, 144.20, 138.08, 134.10, 129.31, 127.32, 110.98, 13.77, 13.03.



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

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.96 (d, J = 7.4 Hz, 2H), 7.65 (t, J = 7.5 Hz, 1H), 7.54 (t, J = 7.8 Hz, 2H), 2.50 (s, 3H), 2.22 (s, 3H);

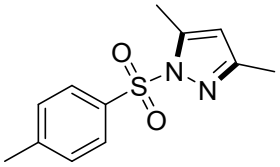
^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 151.15, 139.43, 137.61, 134.48, 129.49, 127.67, 113.94, 11.90, 11.28.



3,4,5-trimethyl-1-tosyl-1*H*-pyrazole (3d)

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.81 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 2.40 (s, 6H), 2.15 (s, 3H), 1.83 (s, 3H);

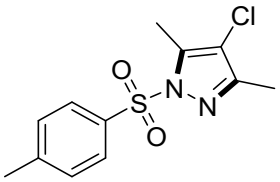
^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 153.76, 144.95, 139.61, 135.50, 129.87, 127.46, 117.29, 21.68, 12.47, 11.36, 8.05.



3,5-dimethyl-1-tosyl-1*H*-pyrazole (3e)

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.82 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 5.91 (s, 1H), 2.48 (s, 3H), 2.38 (s, 3H), 2.18 (s, 3H);

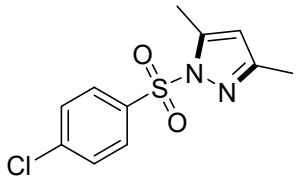
^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 153.40, 145.25, 144.04, 135.20, 129.91, 127.43, 110.83, 21.59, 13.80, 13.06.



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

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.84 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 2.49 (s, 3H), 2.42 (s, 3H), 2.21 (s, 3H);

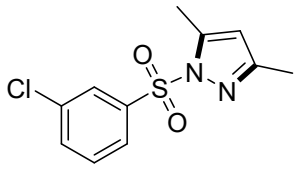
^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 150.93, 145.74, 139.30, 134.68, 130.10, 127.75, 113.78, 21.74, 11.91, 11.27.



1-((4-chlorophenyl)sulfonyl)-3,5-dimethyl-1*H*-pyrazole (3g)

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.90 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 7.2 Hz, 2H), 5.94 (s, 1H), 2.50 (s, 3H), 2.20 (s, 3H);

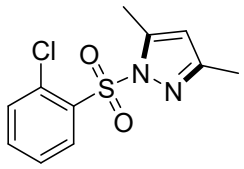
^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 154.04, 144.36, 140.70, 136.59, 129.64, 129.00, 111.15, 13.84, 13.13.



1-((3-chlorophenyl)sulfonyl)-3,5-dimethyl-1*H*-pyrazole (3h)

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.94 (s, 1H), 7.84 (s, 1H), 7.47-7.59 (m, 2H), 5.97 (s, 1H), 2.51 (s, 3H), 2.21 (s, 3H);

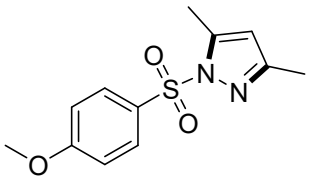
^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 154.16, 144.44, 139.67, 135.33, 134.20, 130.72, 127.40, 125.61, 111.27, 13.82, 13.11.



1-((2-chlorophenyl)sulfonyl)-3,5-dimethyl-1*H*-pyrazole (3i)

^{1}H NMR (500 MHz, $CDCl_3$): *δ* (ppm) 8.12 (d, *J* = 8.3 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.45 (d, *J* = 7.7 Hz, 2H), 5.95 (s, 1H), 2.57 (s, 3H), 2.14 (s, 3H);

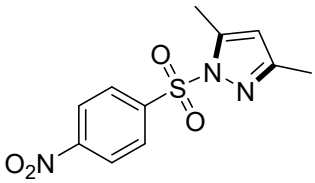
^{13}C NMR (126 MHz, $CDCl_3$): *δ* (ppm) 153.60, 146.08, 135.99, 135.19, 132.57, 132.04, 131.67, 127.36, 109.85, 13.83, 13.51.



1-((4-methoxyphenyl)sulfonyl)-3,5-dimethyl-1*H*-pyrazole (3j)

^{1}H NMR (500 MHz, $CDCl_3$): *δ* (ppm) 7.88 (d, *J* = 9.0 Hz, 2H), 6.96 (d, *J* = 9.0 Hz, 2H), 5.90 (s, 1H), 3.84 (s, 3H), 2.48 (s, 3H), 2.19 (s, 3H);

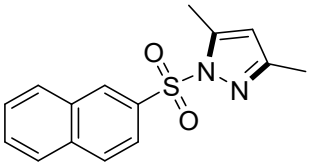
^{13}C NMR (126 MHz, $CDCl_3$): *δ* (ppm) 163.95, 153.24, 143.89, 129.78, 129.51, 114.48, 110.70, 55.72, 13.81, 13.12.



3,5-dimethyl-1-((4-nitrophenyl)sulfonyl)-1*H*-pyrazole (3k)

^{1}H NMR (500 MHz, $CDCl_3$): *δ* (ppm) 8.37 (t, *J* = 8.0 Hz, 2H), 8.16 (t, *J* = 7.9 Hz, 2H), 5.97 (d, *J* = 7.2 Hz, 1H), 2.52 (d, *J* = 7.3 Hz, 3H), 2.20 (d, *J* = 7.5 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): *δ* (ppm) 154.93, 150.73, 144.85, 143.52, 129.06, 124.56, 111.64, 13.89, 13.20.



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

^{1}H NMR (500 MHz, $CDCl_3$): *δ* (ppm) 8.56 (s, 1H), 7.93-7.82 (m, 4H), 7.59 (dt, J = 15.0, 6.9 Hz, 2H), 5.89 (s, 1H), 2.54 (s, 3H), 2.18 (s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 153.65, 144.25, 135.26, 135.03, 131.84, 129.72, 129.59, 129.47, 129.32, 127.95, 127.84, 122.04, 110.96, 13.88, 13.23.

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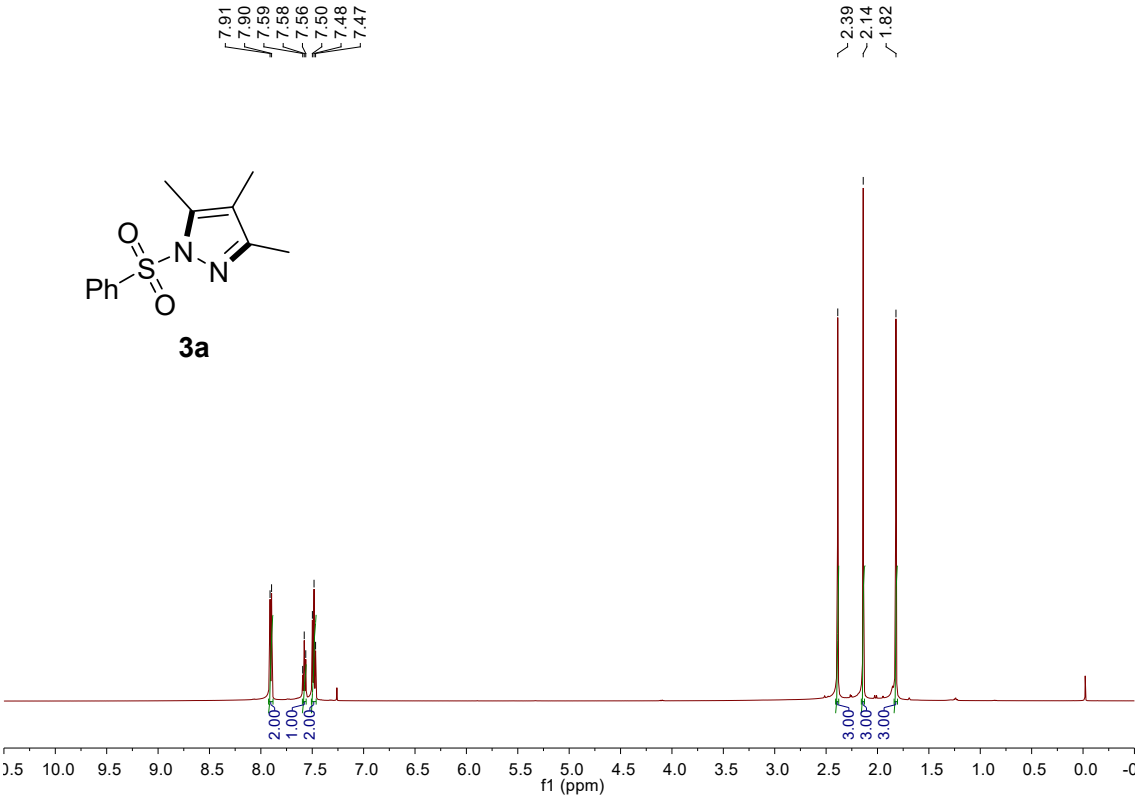
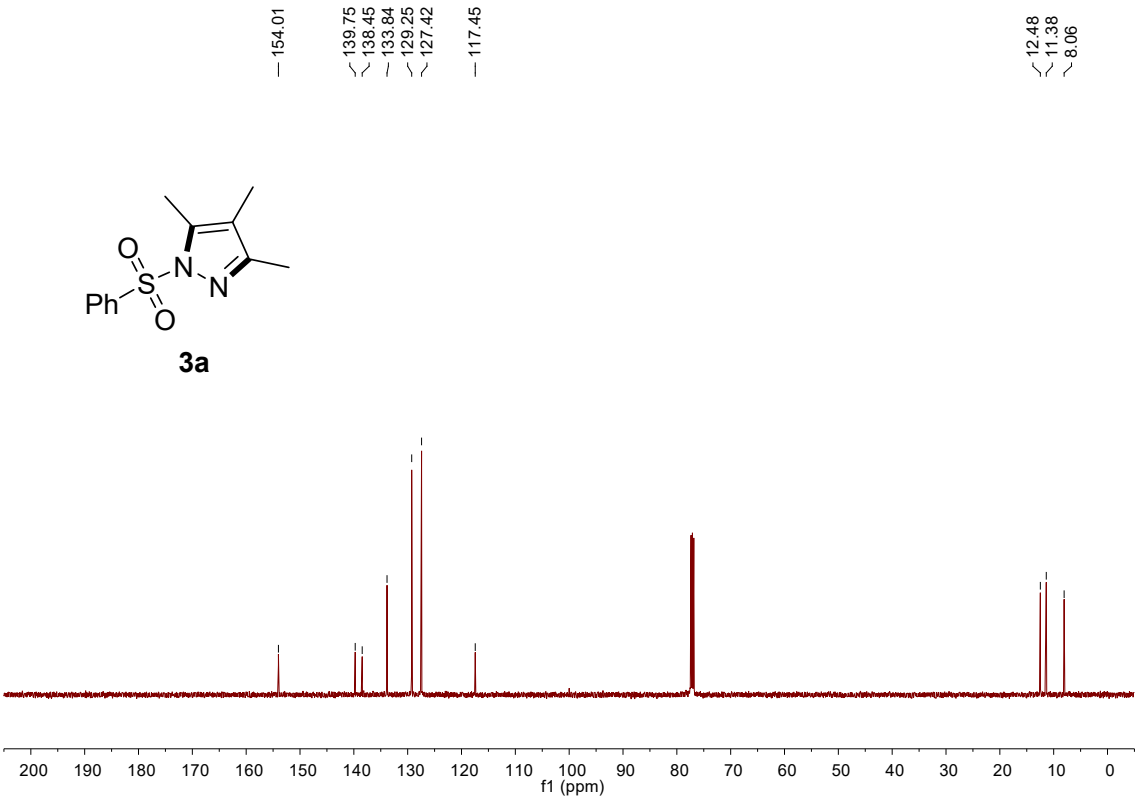
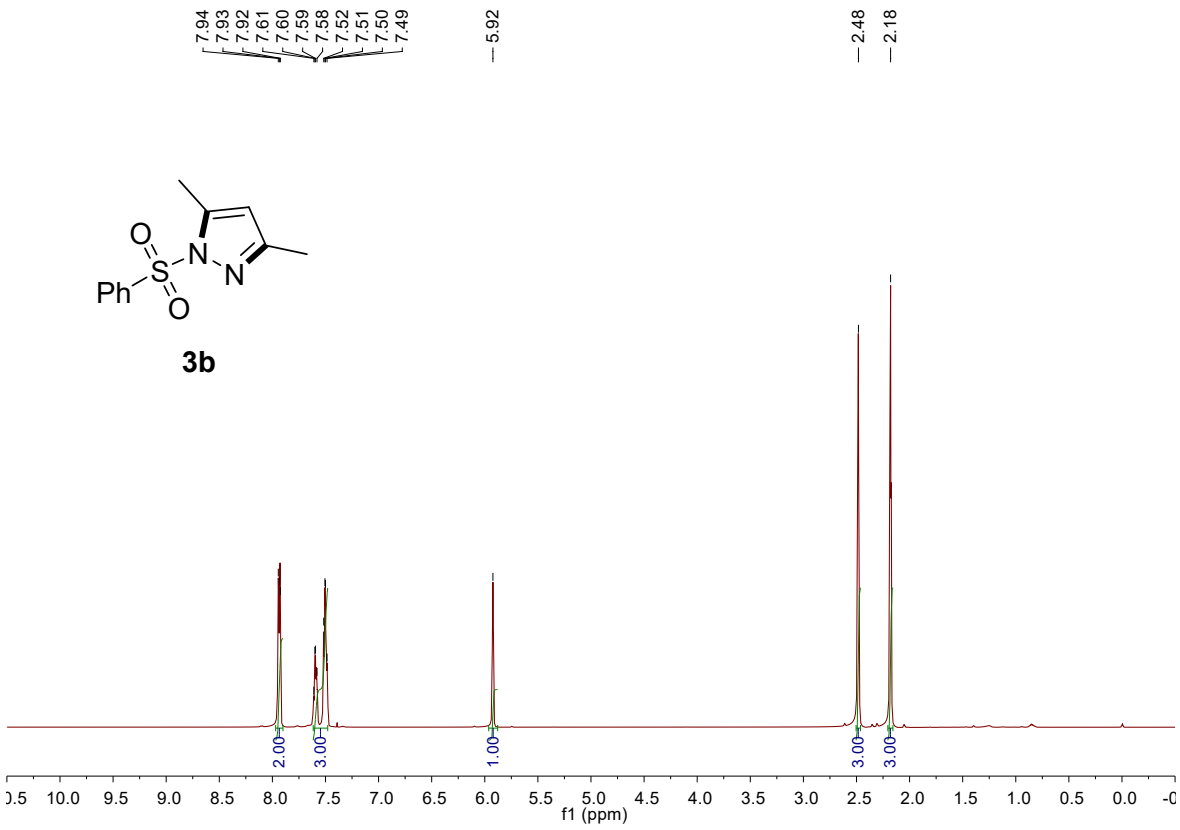
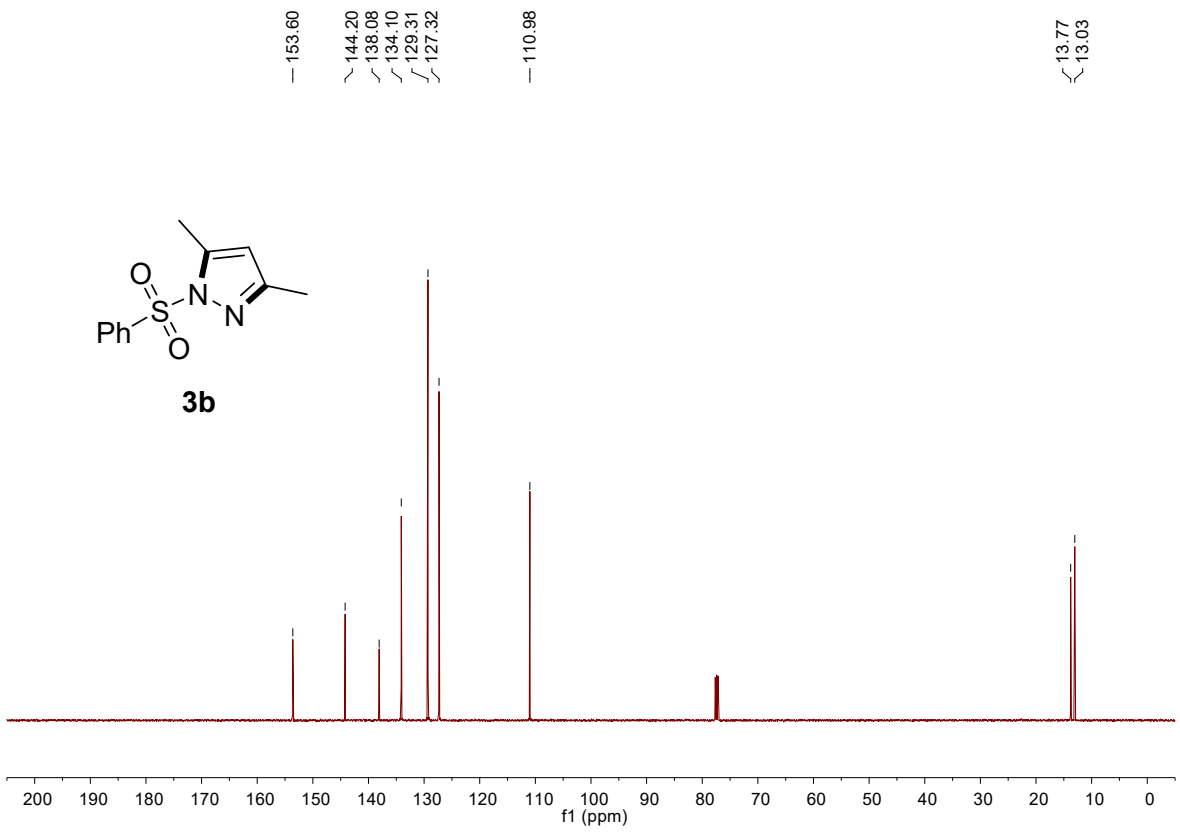
5. NMR Spectra



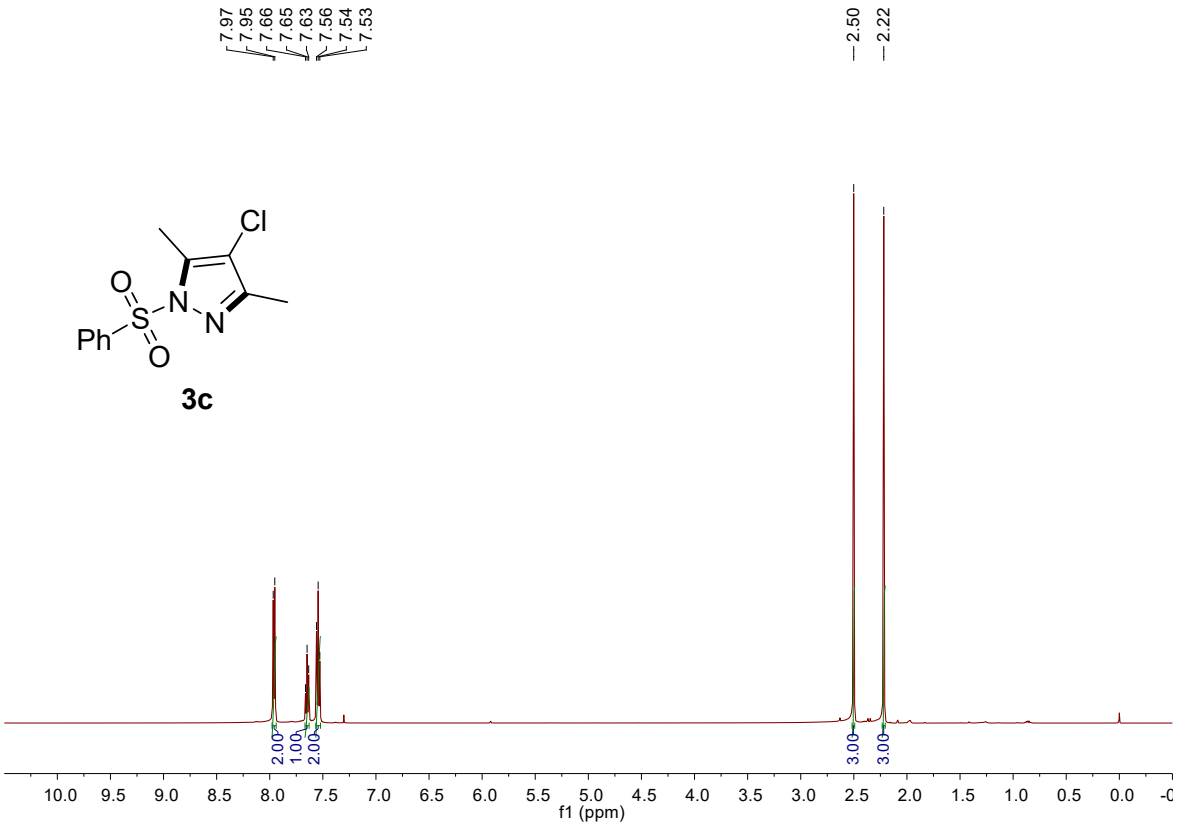


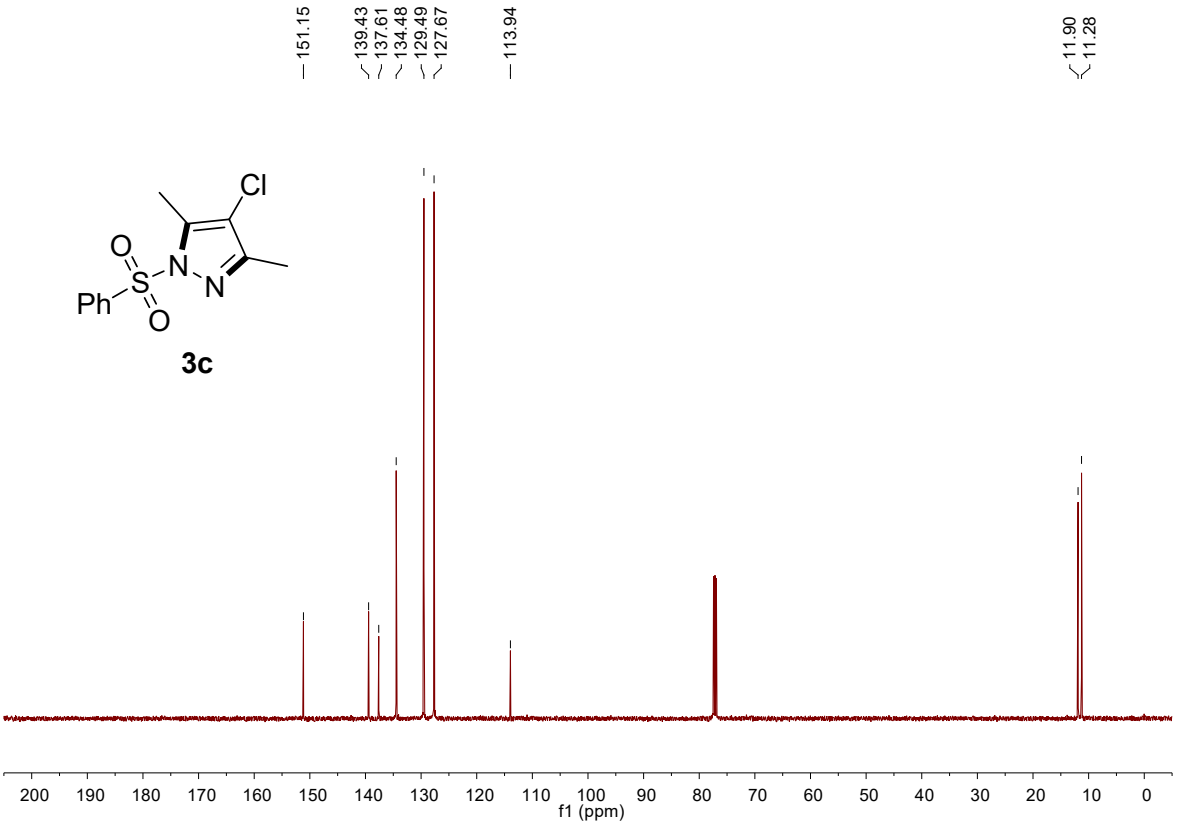

7.94
7.93
7.92
7.61
7.60
7.59
7.58
7.52
7.51
7.50
7.49
5.92
2.48
2.18
O
S
N
N
Ph
O
2.00
3.00
1.00
3.00
3.00
f1 (ppm)

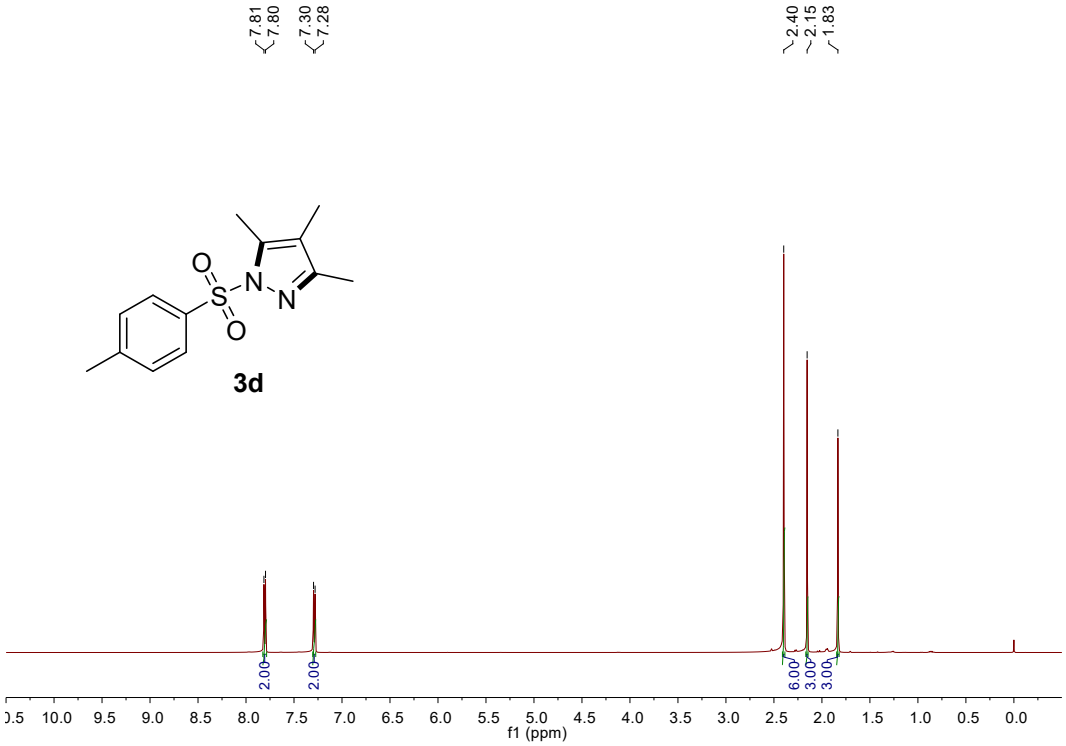
3b

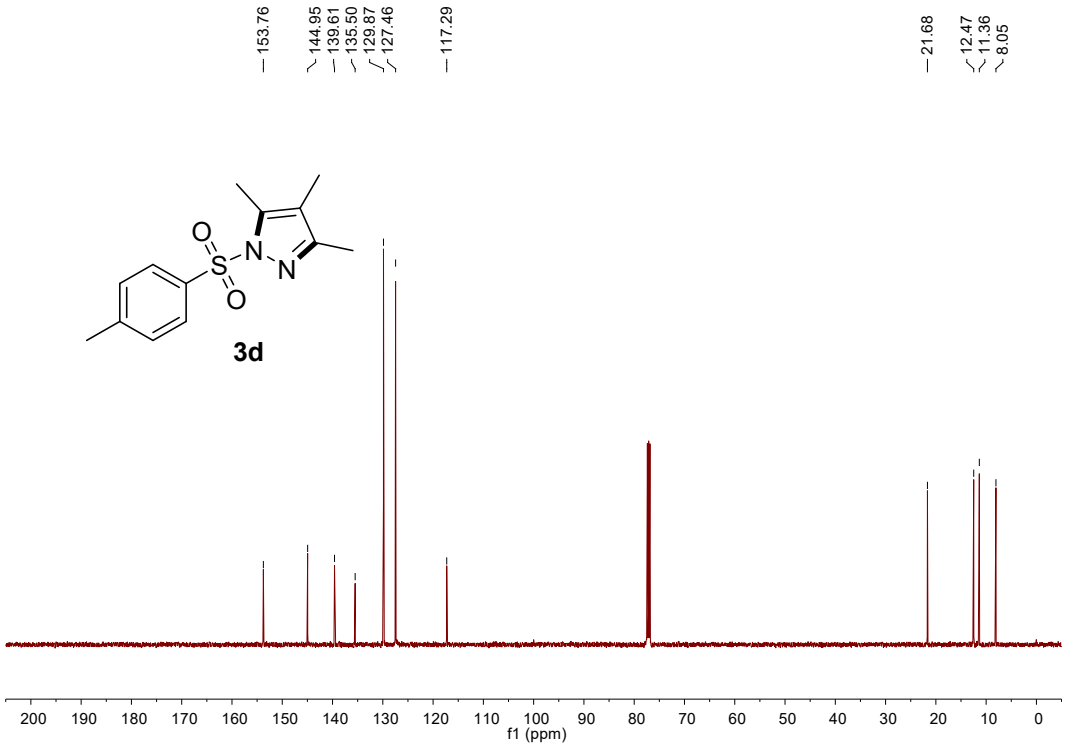

153.60
144.20
138.08
134.10
129.31
127.32
110.98
13.77
13.03
O
S
N
N
Ph
O
f1 (ppm)

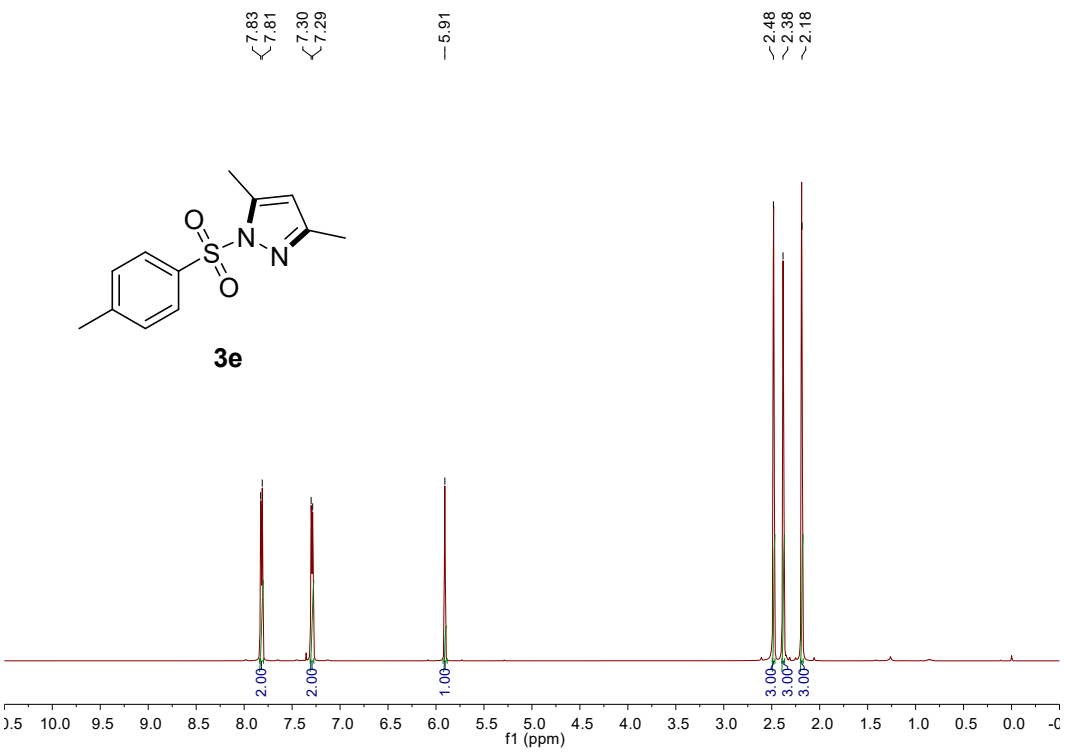
3b

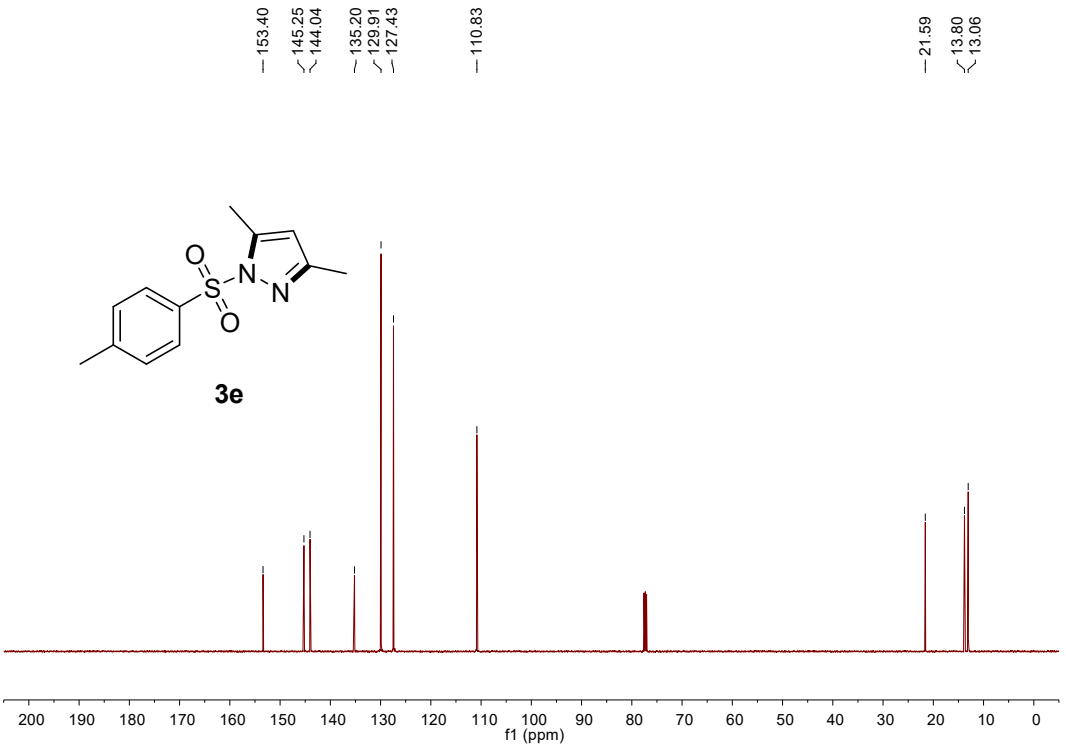

7.97
7.95
7.66
7.65
7.63
7.56
7.54
7.53
2.50
2.22
Cl
O
S
N
N
Ph
O
3c
2.00
1.00
2.00
3.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


151.15
139.43
137.61
134.48
129.49
127.67
113.94
11.90
11.28
Cl
O
S
N
N
Ph
O
3c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.81
7.80
7.30
7.28
2.40
2.15
1.83
3d
2.00
2.00
6.00
3.00
3.00
f1 (ppm)


153.76
144.95
139.61
135.50
129.87
127.46
117.29
21.68
12.47
11.36
8.05
3d
f1 (ppm)


7.83
7.81
7.30
7.29
5.91
2.48
2.38
2.18
3e
2.00
2.00
1.00
3.00
3.00
3.00
f1 (ppm)


153.40
145.25
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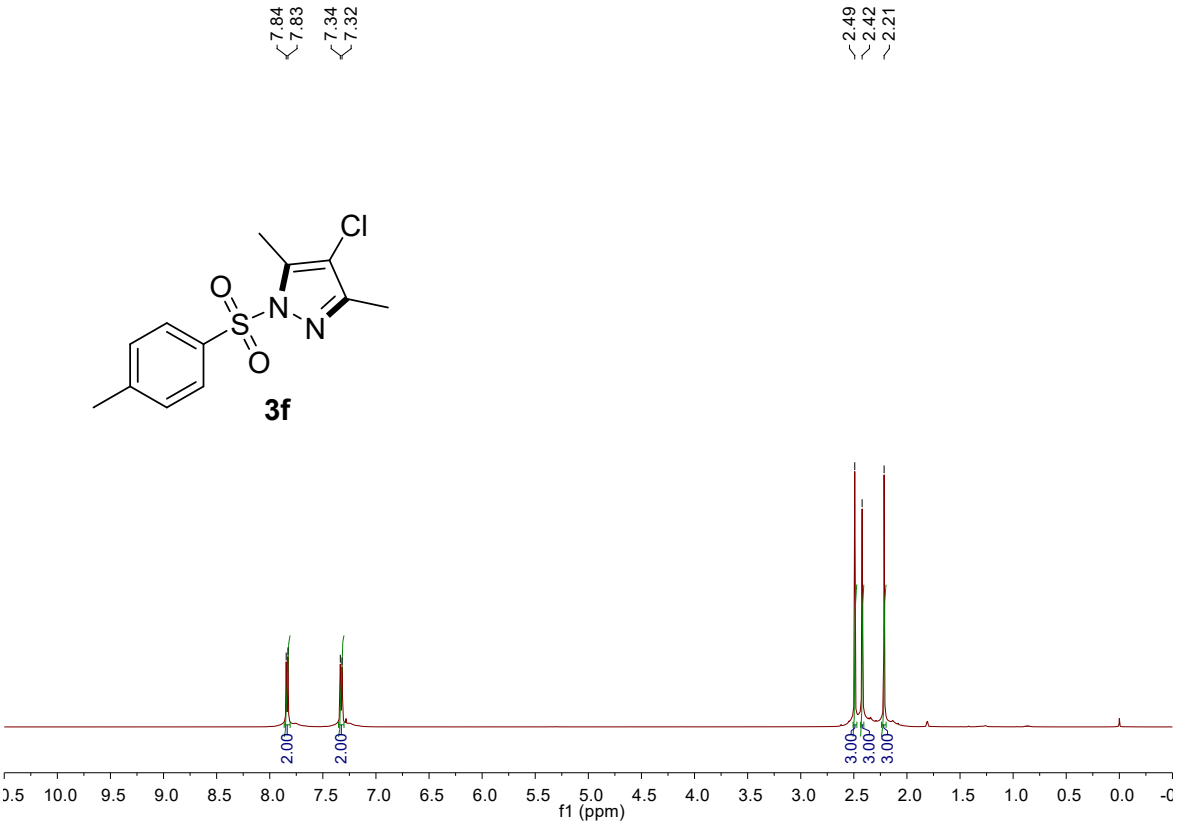
127.43
110.83
21.59
13.80
13.06
3e
f1 (ppm)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7.83
7.34
7.32
2.49
2.42
2.21
Cl
O
S
O
N
N
3f
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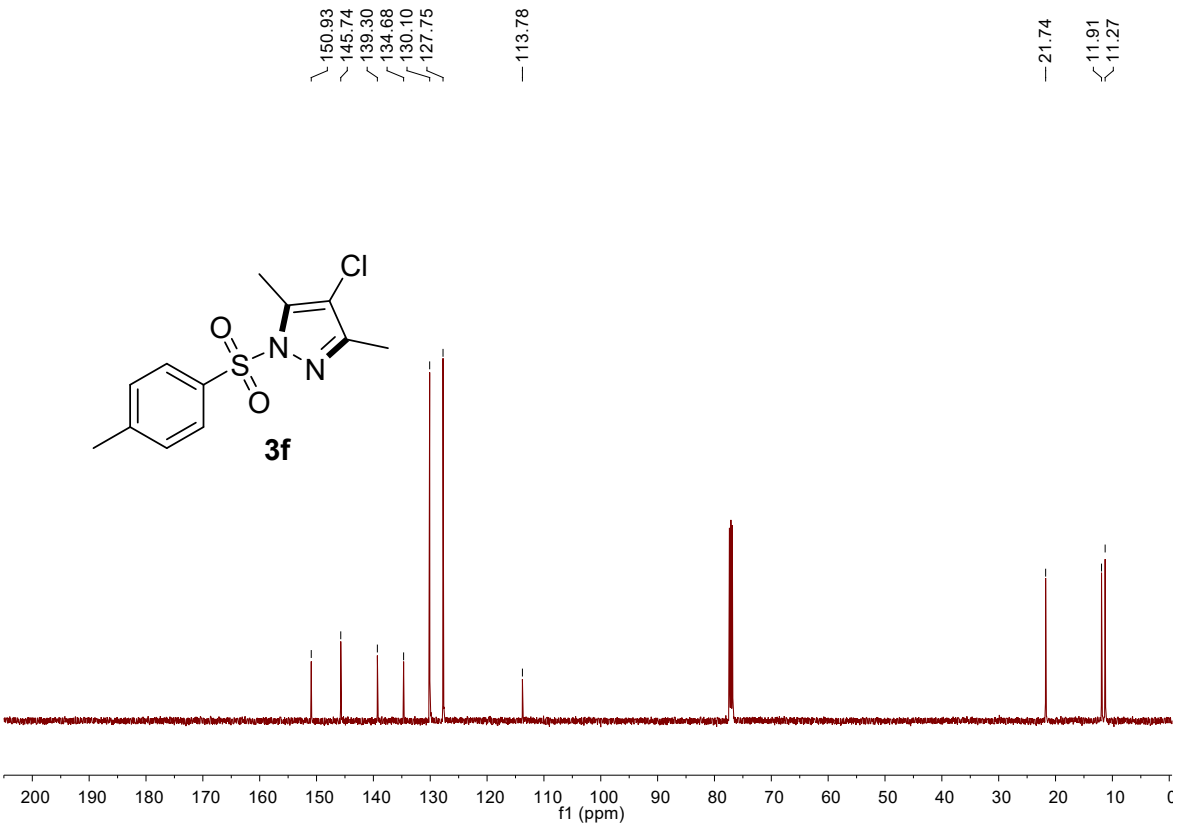
2.00
3.00
3.00
3.00
f1 (ppm)


150.93
145.74
139.30
134.68
130.10
127.75
113.78
21.74
11.91
11.27
Cl
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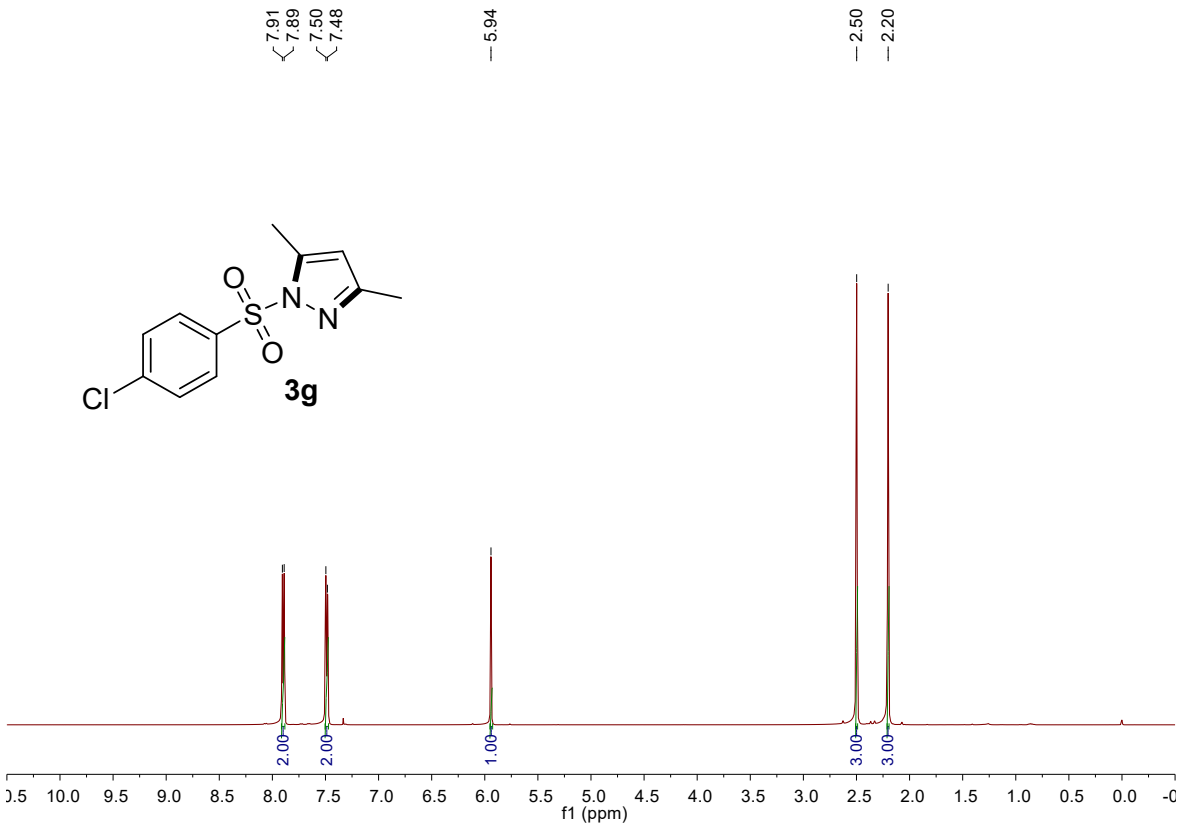
S
O
N
N
3f
f1 (ppm)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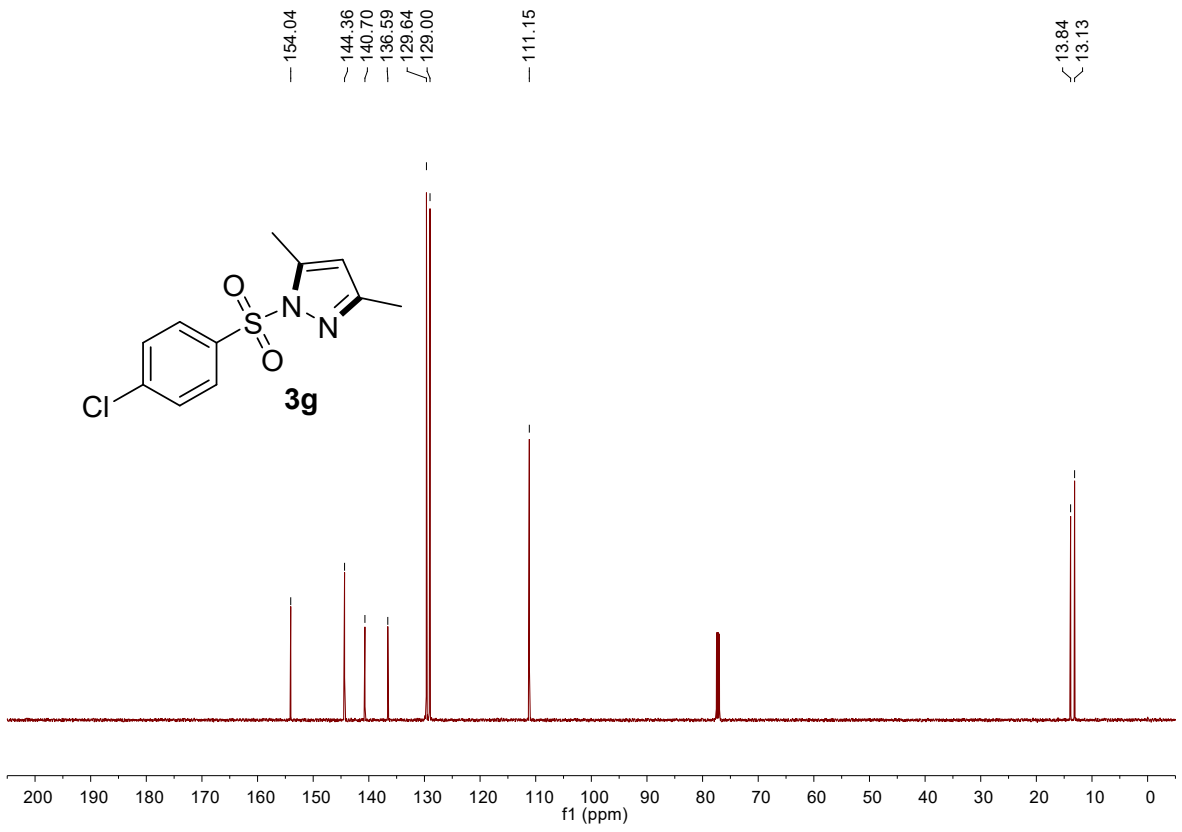
7.89
7.50
7.48
5.94
2.50
2.20
3g
2.00
2.00
1.00
3.00
3.00
f1 (ppm)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144.36
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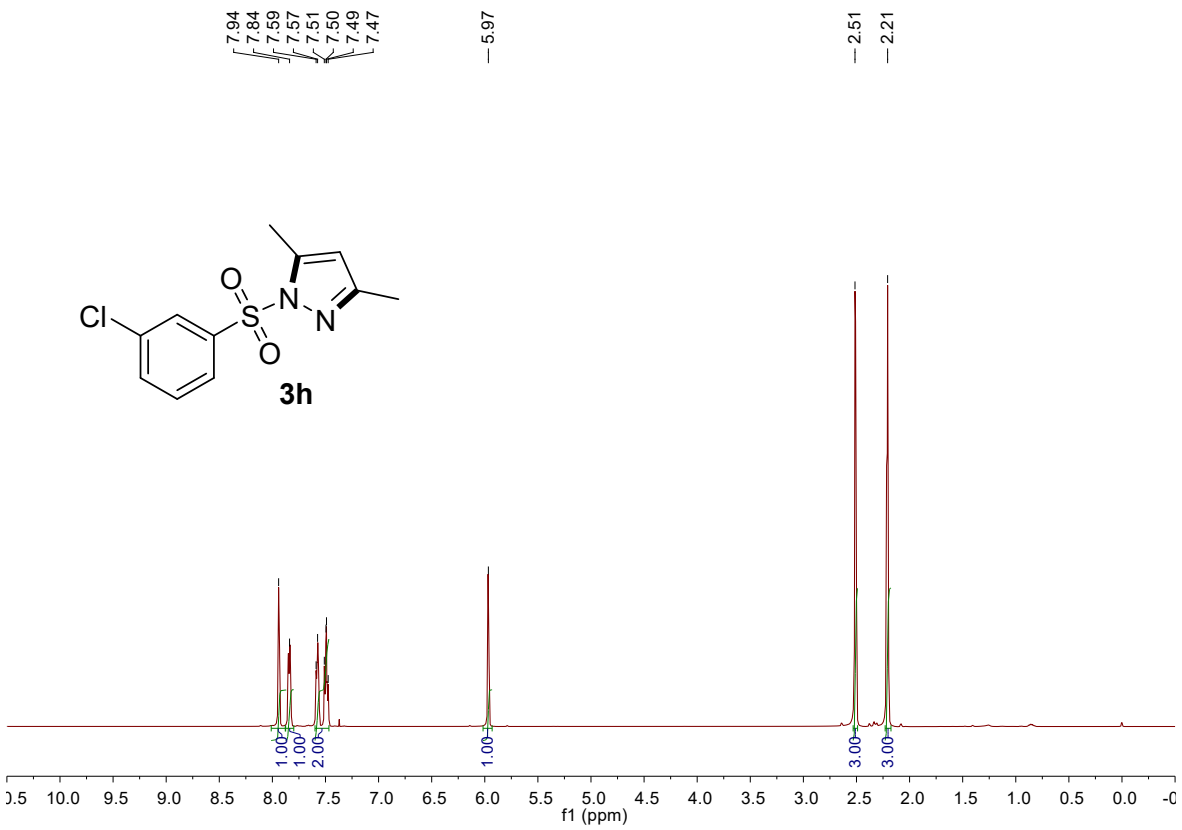
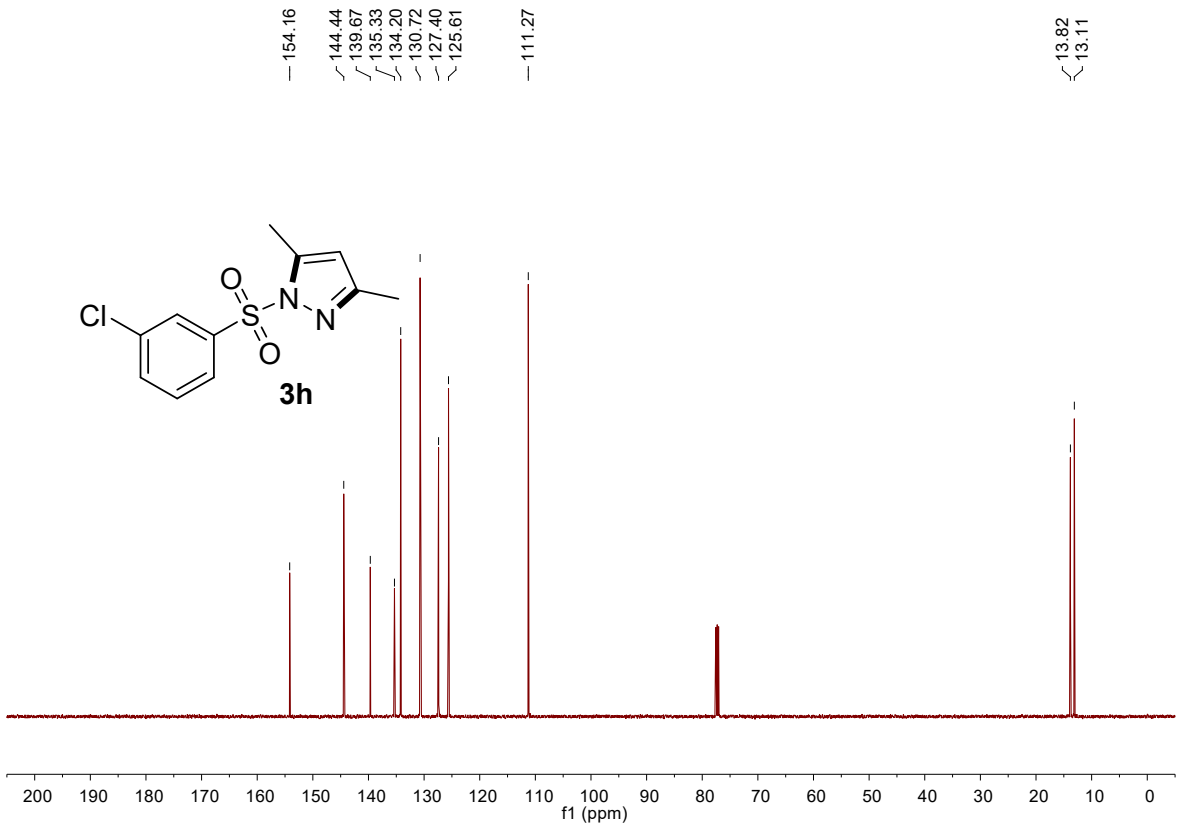
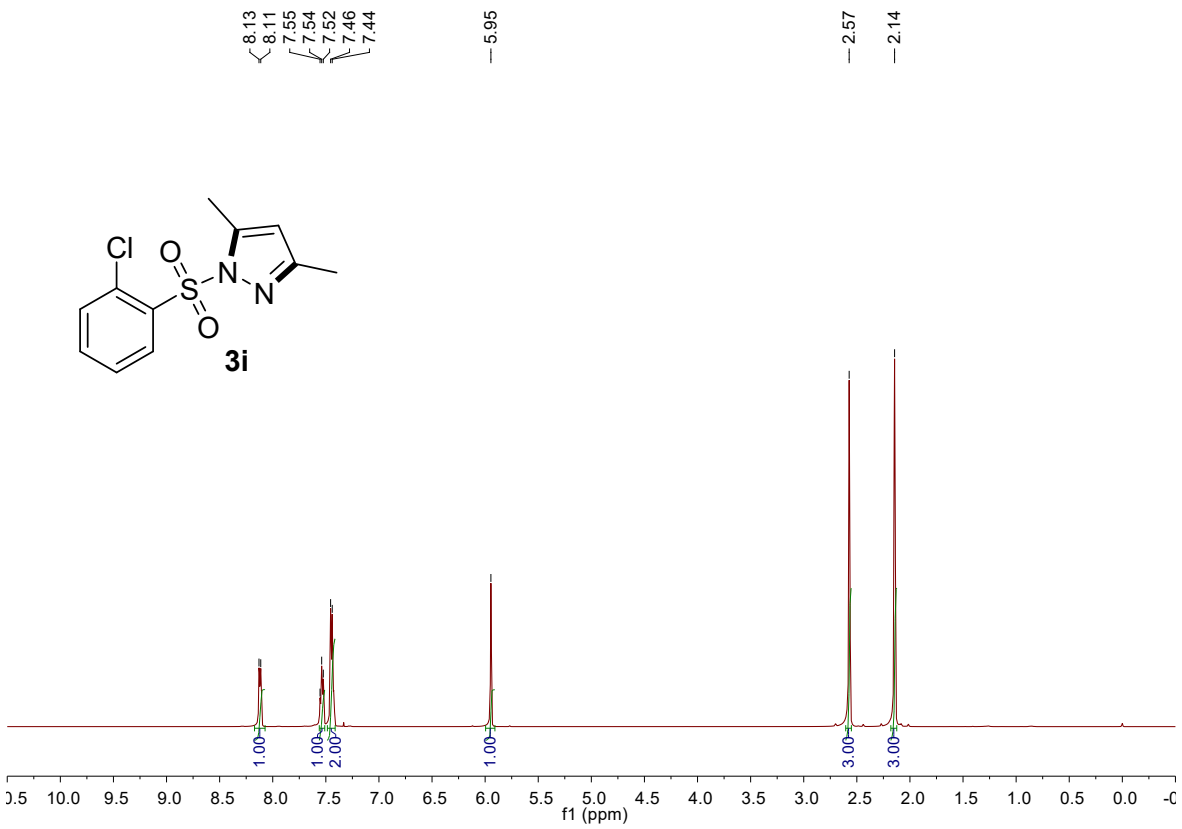
129.64
129.00
111.15
13.84
13.13
3g
f1 (ppm)


7.94
7.84
7.59
7.57
7.51
7.50
7.49
7.47
5.97
2.51
2.21
Cl
O
S
O
N
N
3h
1.00
1.00
2.00
1.00
3.00
3.00
f1 (ppm)


154.16
144.44
139.67
135.33
134.20
130.72
127.40
125.61
111.27
13.82
13.11
Cl
O
S
O
N
N
3h
f1 (ppm)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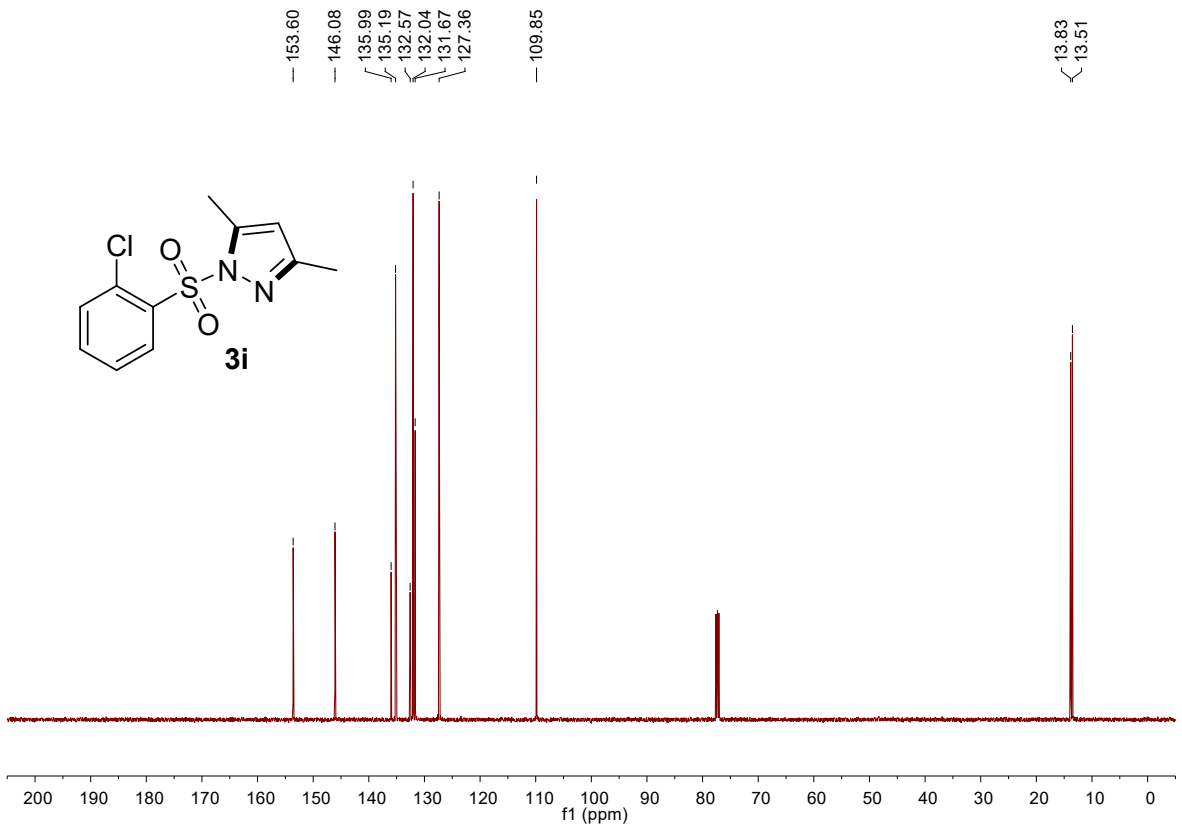
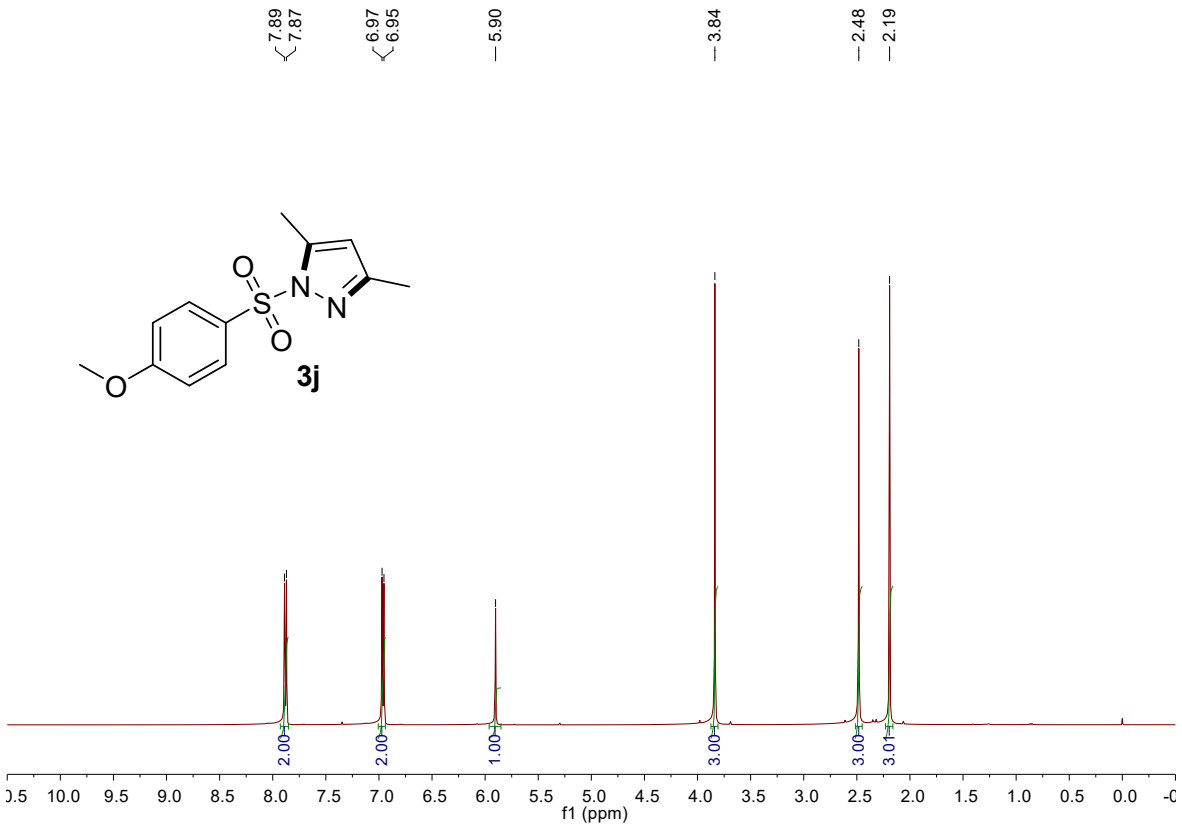
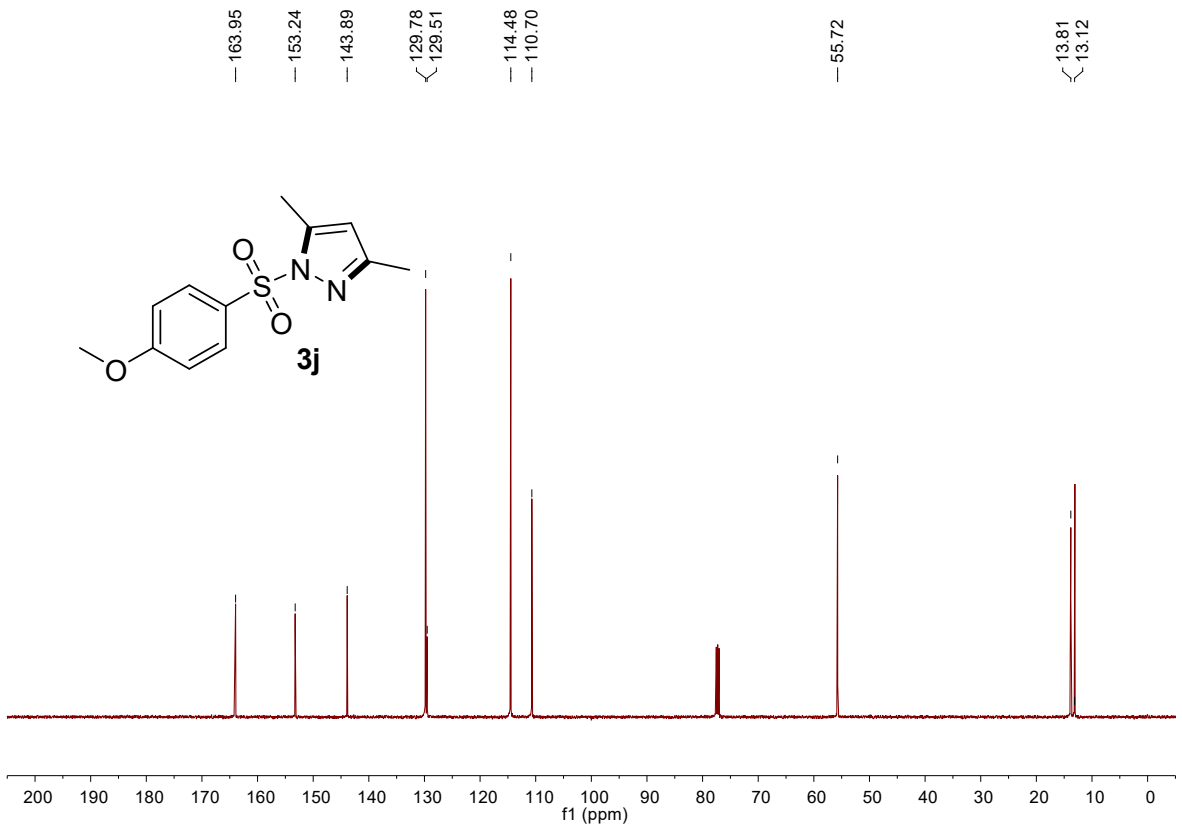
8.11
7.55
7.54
7.52
7.46
7.44
5.95
2.57
2.14
Cl
O
S
O
N
N
3i
1.00
1.00
2.00
1.00
3.00
3.00
f1 (ppm)


153.60
146.08
135.99
135.19
132.57
132.04
131.67
127.36
109.85
13.83
13.51
Cl
O
S
O
N
N
3i
f1 (ppm)


7.89
7.87
6.97
6.95
5.90
3.84
2.48
2.19
3j
2.00
2.00
1.00
3.00
3.00
3.01
f1 (ppm)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153.24
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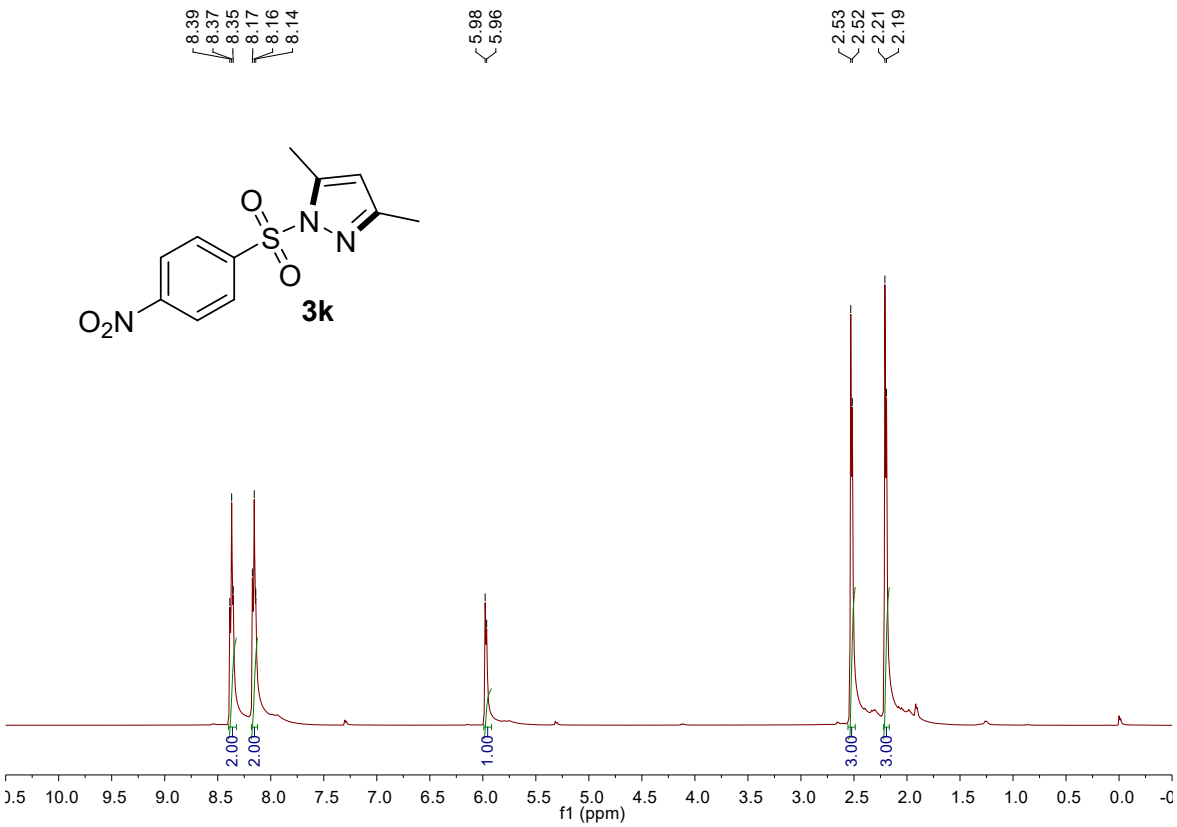
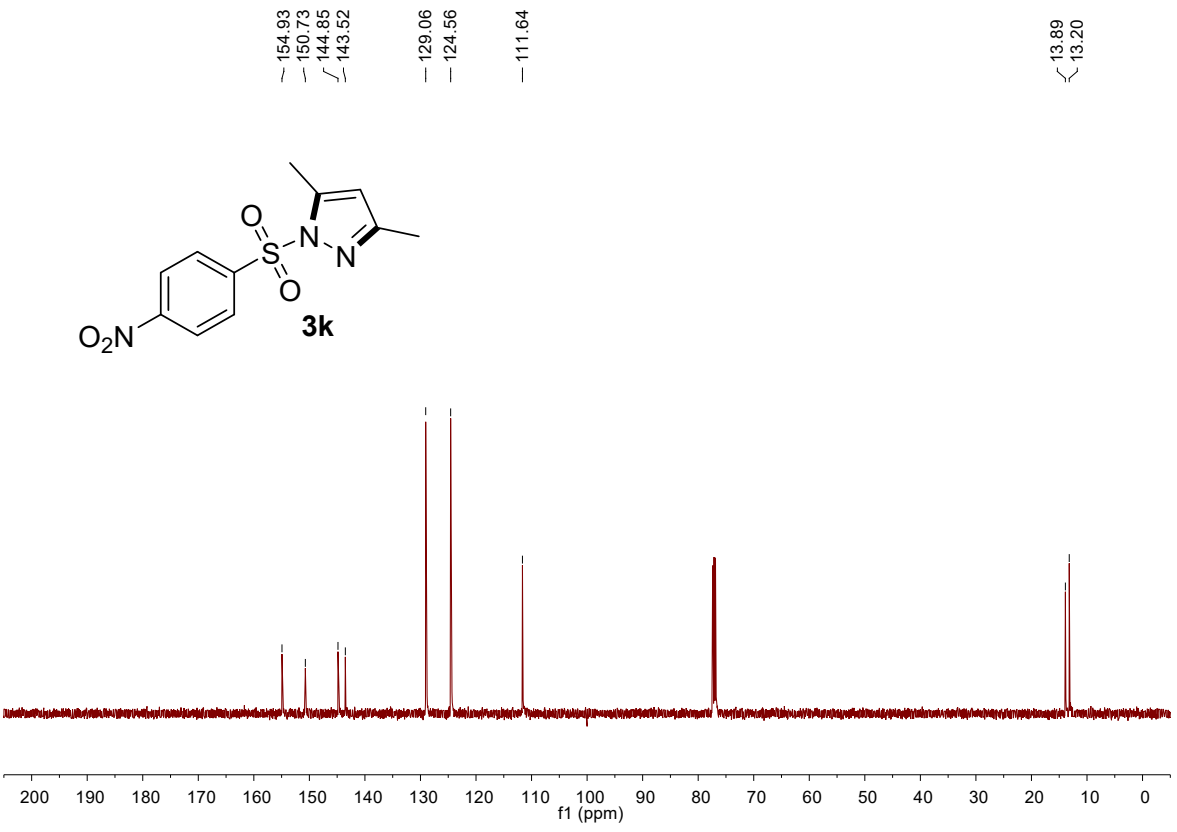
114.48
110.70
55.72
13.81
13.12
3j
f1 (ppm)


8.39
8.37
8.35
8.17
8.16
8.14
5.98
5.96
2.53
2.52
2.21
2.19
O
S
N
N
O
O2N
3k
2.00
2.00
1.00
3.00
3.00
f1 (ppm)


154.93
150.73
144.85
143.52
129.06
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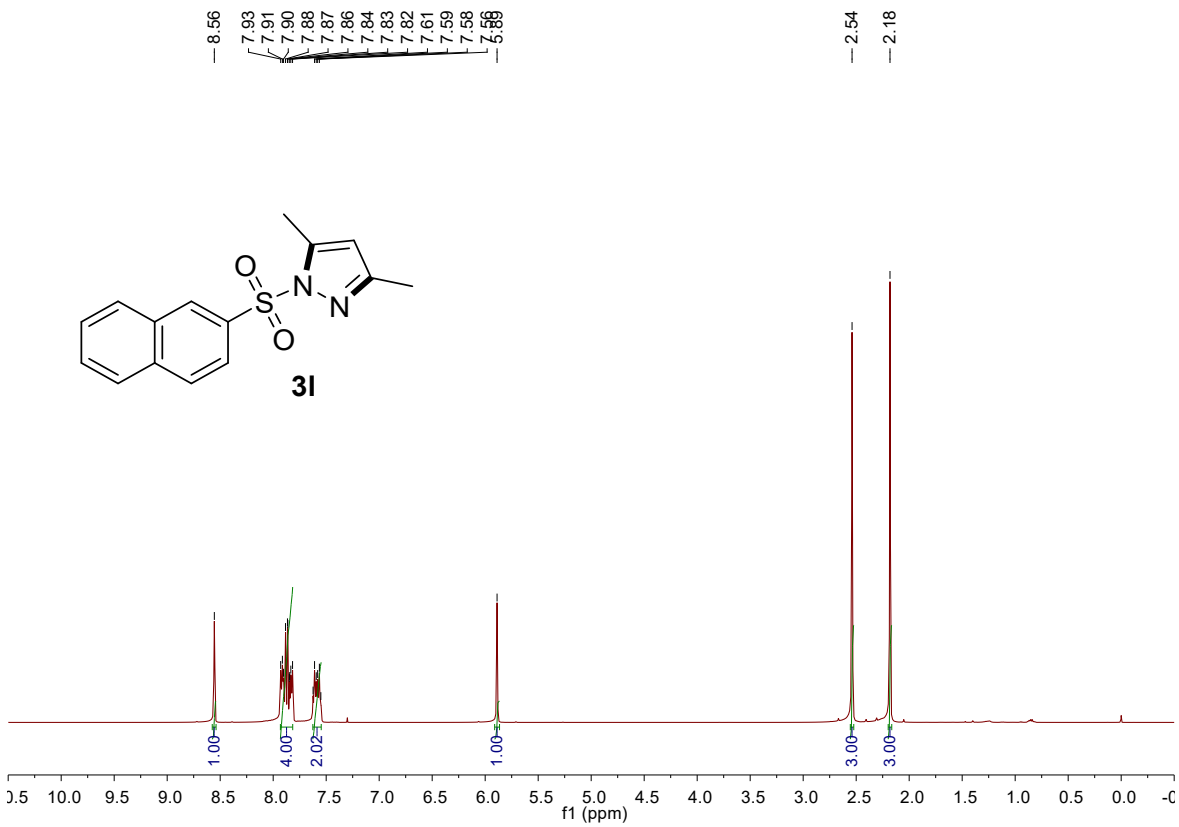
111.64
13.89
13.20
O
S
N
N
O
O2N
3k
f1 (ppm)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7.93
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7.84
7.83
7.82
7.61
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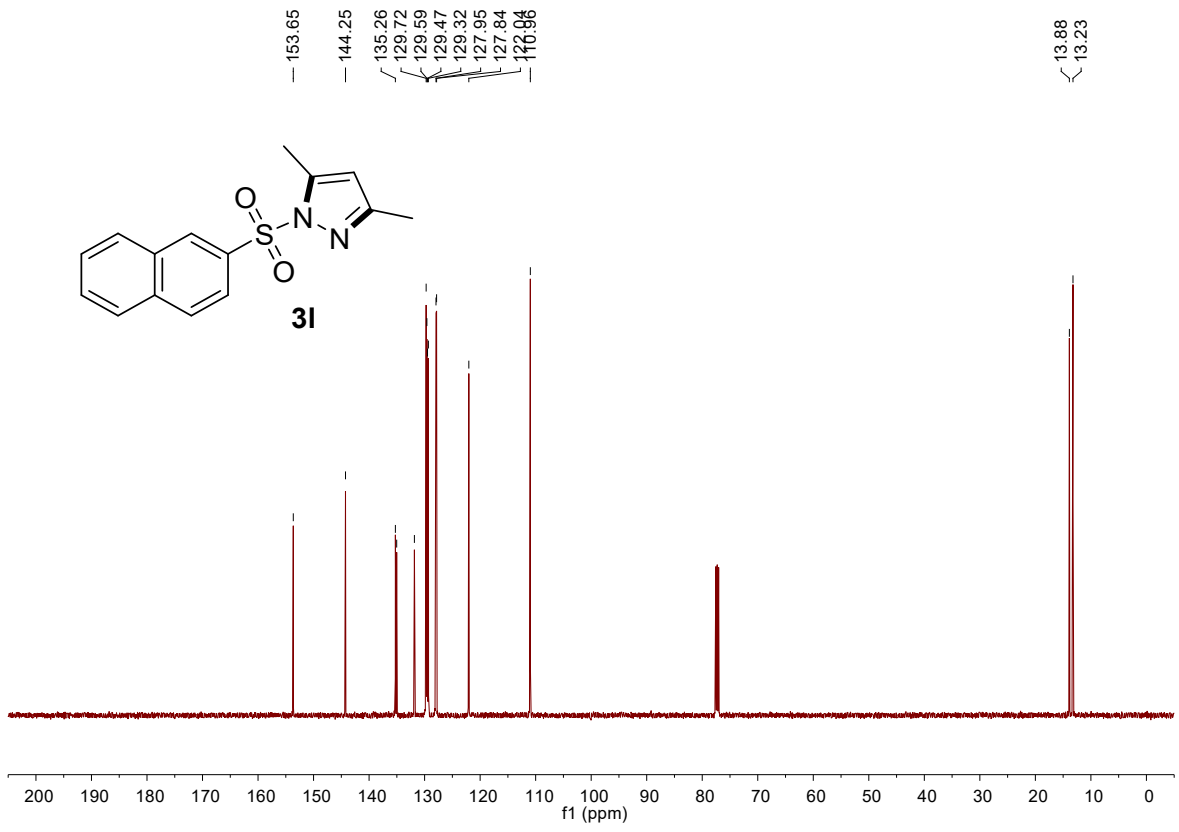
3.00
f1 (ppm)


153.65
144.25
135.26
129.72
129.59
129.47
129.32
127.95
127.84
13.88
13.23
3I
f1 (ppm)

6. Notes and References

[1] A. P. Ginsberg, *Inorg. Synth*. **1990**, 27, 100.

[2] Bruker, *APEX3*, *SAINT* and *SADABS*, Bruker AXS Inc., Madison, Wisconsin, USA, **2016**.

[3] (a) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, 42, 339; (b) G. M. Sheldrick, *Acta Cryst*. **2015**, A71, 3; (c) G. M. Sheldrick, *Acta Cryst*. **2015**, C71, 3.

[4] (a) W. Xiong, J. X. Chen, M. C. Liu, J. C. Ding, H. Y. Wu, W. K. Su, *J. Brazil. Chem. Soc.* **2009**, 20, 367; (b) G. P. Yang, S. X. Shang, B. Yu, C. W. Hu, *Inorg. Chem. Front.* **2018**, 5, 2472; (c) G. S. Kumar, W. Kaminsky, K. J. R. Prasad, *Synthetic Commun.* **2015,** 45, 1751; (d) B. R. Vaddula, R. S. Varma, J. Leazer, *Tetrahedron Lett.* **2013,** 54, 1538.