

# Supporting Information

## Visible-light-promoted organic dyes-catalysed sulfidation and phosphorylation of arylhydrazines toward aromatic sulfides and diphenylphosphoryl hydrazides

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## 1. General information

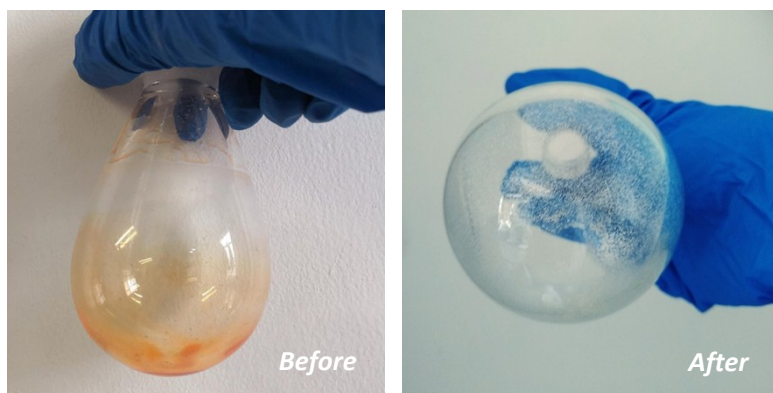
All the arylhydrazines, thioethers, diphenylphosphine oxide and solvents were purchased from commercial suppliers and used without further purification. Silica gel was purchased from Qing Dao Hai Yang Chemical Industry. The  $^1\text{H}$  NMR (400 MHz),  $^{13}\text{C}$  NMR (101 MHz) and  $^{31}\text{P}$  NMR (162 MHz) spectra data were recorded on Bruker advance 400 MHz spectrometer using  $\text{CDCl}_3$  or  $\text{DMSO-}d_6$  as solvent.  $^{13}\text{C}$  NMR (101 MHz) and  $^{31}\text{P}$  NMR (162 MHz) spectra being recorded with broad band proton decoupled.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra was recorded with tetramethylsilane ( $\delta = 0.00$  ppm) as internal reference. EI-MS data were recorded on Shimadzu GCMS QP2010 Ultra. High resolution mass spectra (HRMS) were obtained with a Waters Micromass Q-ToF Micro instrument using the ESI technique.

## 2. Experimental procedure for synthesis of 3a-3k

To a 25 mL reaction tube, arylhydrazine (0.5 mmol), thioether (3.5 mmol),  $\text{Na}_2\text{-eosin Y}$  (5 mol%),  $\text{H}_2\text{O}_2$  (1 equiv.) were dissolved in DMSO (1.5 mL), and then the tube was stirred under the irradiation of 20 W blue LEDs at room temperature for 8 h. After reaction, the mixture was diluted with water and extracted with EA (ethyl acetate) (25 mL $\times$ 3). The combined organic layers were collected and dried by anhydrous  $\text{Na}_2\text{SO}_4$ . The residue was purified by column chromatography on silica gel to afford the desired products.

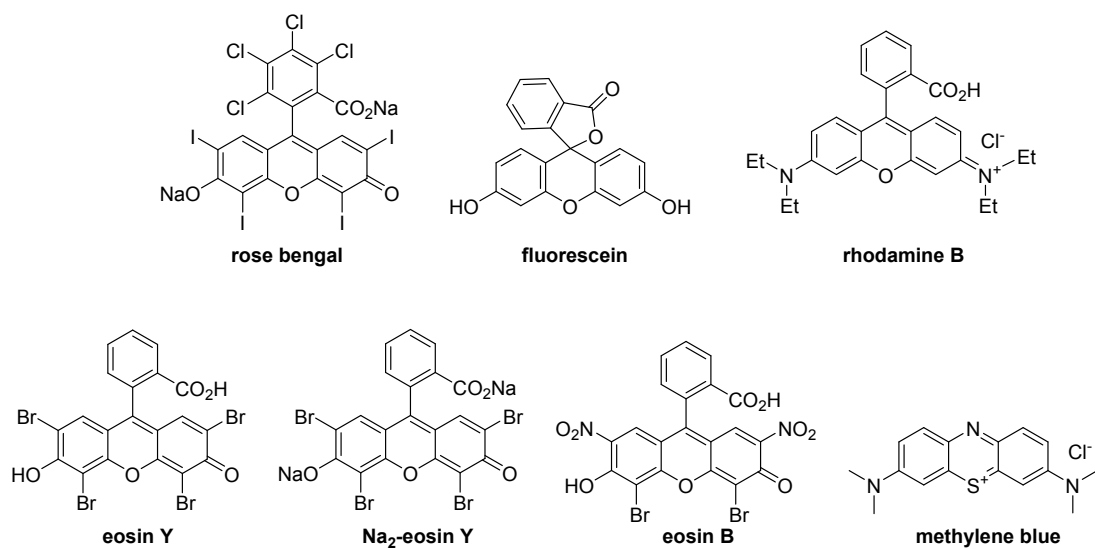
## 3. Experimental procedure for synthesis of 7a-7j

To a 25 mL reaction tube, arylhydrazine (0.55 mmol), diphenylphosphine oxide (0.5 mmol), rose bengal (10 mol%),  $\text{Cs}_2\text{CO}_3$  (1 equiv.) were dissolved in  $\text{CH}_3\text{CN}$  (1.5 mL), and then the tube was stirred under the irradiation of 20 W white LEDs at room temperature for 9 h. After reaction, the mixture was diluted with water and extracted with EA (25 mL $\times$ 3). The combined organic layers were collected and dried by anhydrous  $\text{Na}_2\text{SO}_4$ . The solution was distilled under reduced pressure to move solvent  $\text{CH}_3\text{CN}$ . Because the product cannot dissolve in EA, the reaction system was then washed by EA (5 mL $\times$ 3). Then the white solid product was obtained after removing organic layers dissolved in EA from reaction system.



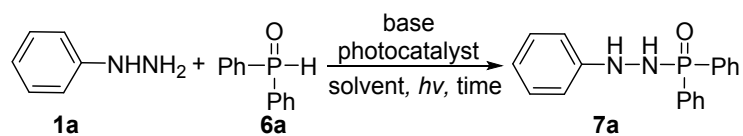
**Figure S1** Before and after washing reaction system using EA

#### 4. Optimization of the reaction conditions <sup>a</sup>



**Scheme S1** Structures of organic dyes

**Table S1** Optimization of the phosphorylation reaction conditions <sup>a</sup>



Entry	PC (Photocatalyst)	Base	Solvent	Yield <sup>b</sup> (%)
1	Na <sub>2</sub> -eosin Y	Cs <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	42
2	rose bengal	Cs <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	55
3	fluorescein	Cs <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	24
4	rhodamine B	Cs <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	35
5	eosin Y	Cs <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	15
6	eosin B	Cs <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	10
7	MB <sup>+</sup>	Cs <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	32
8	rose bengal	NaHCO <sub>3</sub>	CH <sub>3</sub> CN	13
9	rose bengal	2,6-Lutidine	CH <sub>3</sub> CN	7
10	rose bengal	TBD	CH <sub>3</sub> CN	7
11	rose bengal	DBU	CH <sub>3</sub> CN	3
12	rose bengal	Et <sub>3</sub> N	CH <sub>3</sub> CN	6
13	rose bengal	TMG	CH <sub>3</sub> CN	12
14	rose bengal	Na <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	9
15	rose bengal	K <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	11
16	rose bengal	K <sub>3</sub> PO <sub>4</sub>	CH <sub>3</sub> CN	19
17	rose bengal	Na <sub>2</sub> HPO <sub>4</sub>	CH <sub>3</sub> CN	33
18	rose bengal	Cs <sub>2</sub> CO <sub>3</sub>	PEG-400	26
19	rose bengal	Cs <sub>2</sub> CO <sub>3</sub>	PEG-600	21
20	rose bengal	Cs <sub>2</sub> CO <sub>3</sub>	EC	12
21	rose bengal	Cs <sub>2</sub> CO <sub>3</sub>	PC	18
22	rose bengal	Cs <sub>2</sub> CO <sub>3</sub>	DCE	28
23	rose bengal	Cs <sub>2</sub> CO <sub>3</sub>	THF	40
24	rose bengal	Cs <sub>2</sub> CO <sub>3</sub>	DMF	0
25	rose bengal	Cs <sub>2</sub> CO <sub>3</sub>	1,4-dioxane	30
25	rose bengal	Cs <sub>2</sub> CO <sub>3</sub>	toluene	30
26 <sup>c</sup>	rose bengal	Cs <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	33
27 <sup>d</sup>	rose bengal	Cs <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	trace
28 <sup>e</sup>	rose bengal	Cs <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	40
29 <sup>f</sup>	rose bengal	Cs <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	32
30 <sup>g</sup>	rose bengal	Cs <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	15
31 <sup>h</sup>	rose bengal	Cs <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	20
31 <sup>i</sup>	rose bengal	Cs <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	30
<b>32<sup>j</sup></b>	rose bengal	<b>Cs<sub>2</sub>CO<sub>3</sub></b>	<b>CH<sub>3</sub>CN</b>	<b>62</b>
33 <sup>k</sup>	rose bengal	Cs <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	30

<sup>a</sup> Reaction conditions unless otherwise specified: To a reaction tube, **1a** (0.55 mmol), **6a** (0.5 mmol), PC (photocatalyst) (10 mol%), base (1 equiv), solvent (1.5 mL) were added, then the tube was capped and stirred under the irradiation of 20 W white LEDs for 12 h at room temperature. TBD = 1,5,7-Triazabicyclo[4.4.0]dec-5-ene, DBU = 1,8-Diazabicyclo[5.4.0]undec-7-ene, TMG = 1,1,3,3-tetramethylguanidine, EC = Ethylene carbonate, PC = Propylene carbonate. <sup>b</sup> Yields were given by <sup>31</sup>P NMR. <sup>c</sup> Cs<sub>2</sub>CO<sub>3</sub> (1.5 equiv). <sup>d</sup> **6a** (1 mmol). <sup>e</sup> **1a** (1 mmol). <sup>f</sup> Cs<sub>2</sub>CO<sub>3</sub> (0.75 equiv). <sup>g</sup> Cs<sub>2</sub>CO<sub>3</sub> (0.5 equiv). <sup>h</sup> 3 h. <sup>i</sup> 5 h. <sup>j</sup> 9 h. <sup>k</sup> 24h.

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## 5. Control experiments

HR-MS calc. for C<sub>15</sub>H<sub>24</sub>NOS<sup>+</sup> (**4a**) m/z = 266.1573 found 266.1581

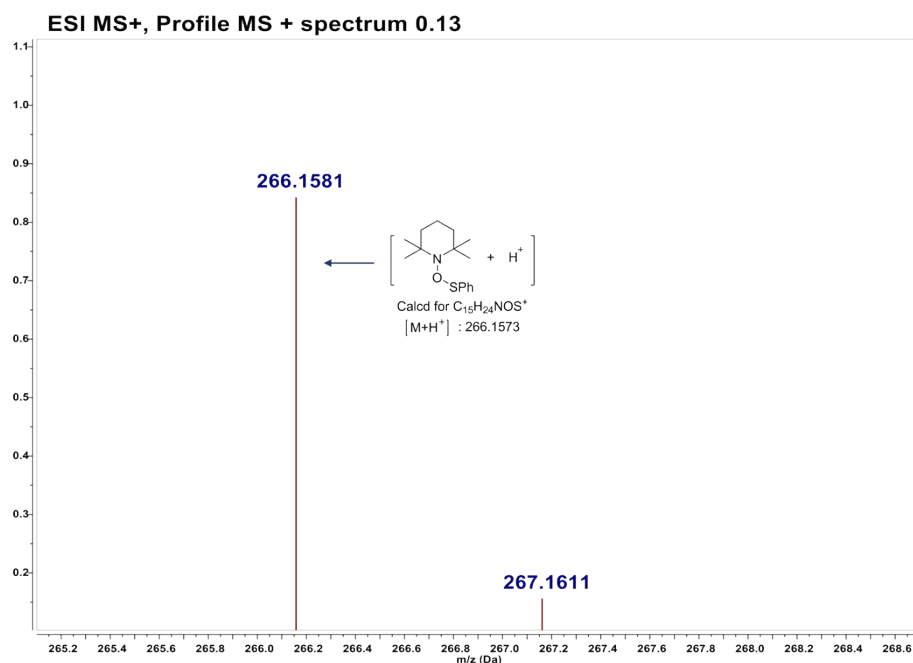


Figure S2. HR-MS spectrum of compound **4a**

HR-MS calc. for C<sub>21</sub>H<sub>28</sub>NaO<sup>+</sup> (**5a**) m/z = 319.2038 found 319.2052

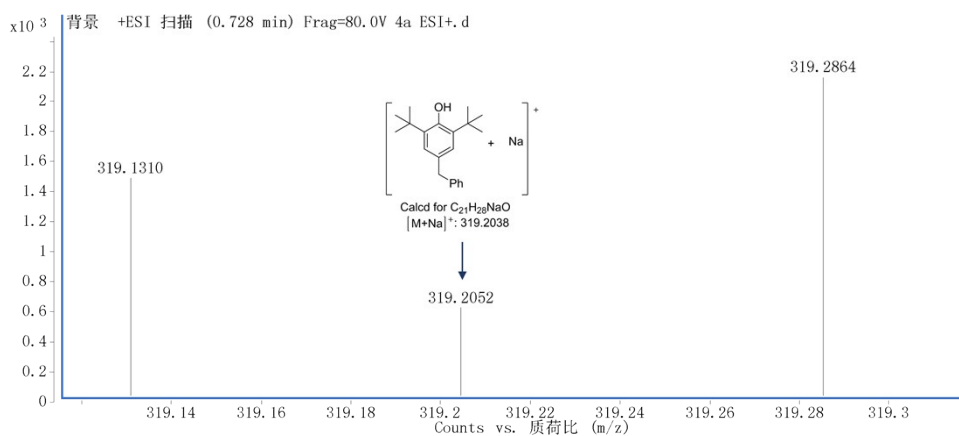


Figure S3. HR-MS spectrum of compound **5a**

HR-MS calc. for  $C_{21}H_{28}NO_2P^+$  (**8a**)  $m/z = 358.1930$  found 358.1941

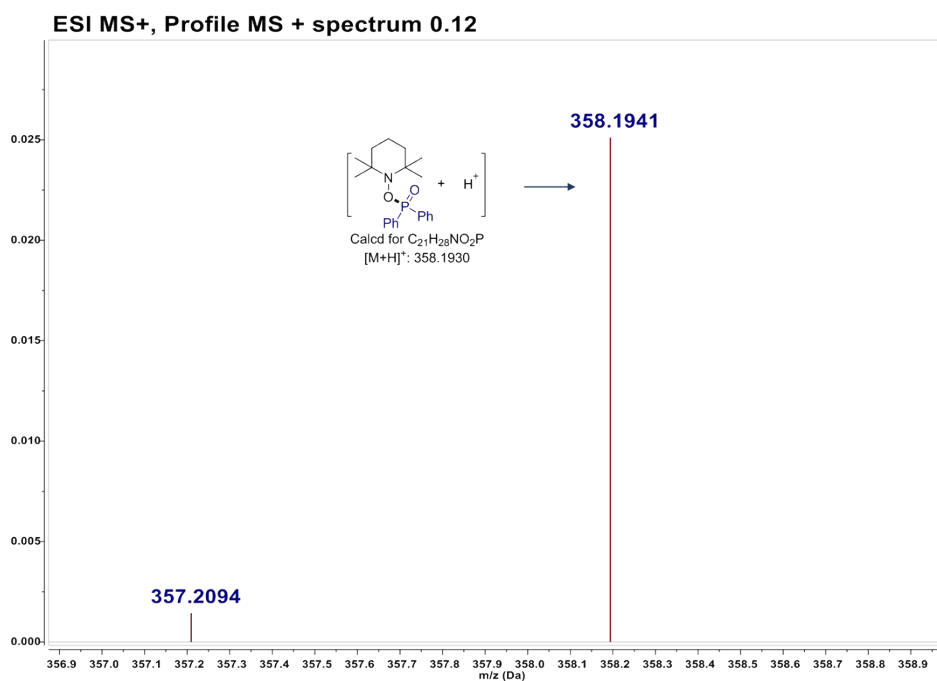
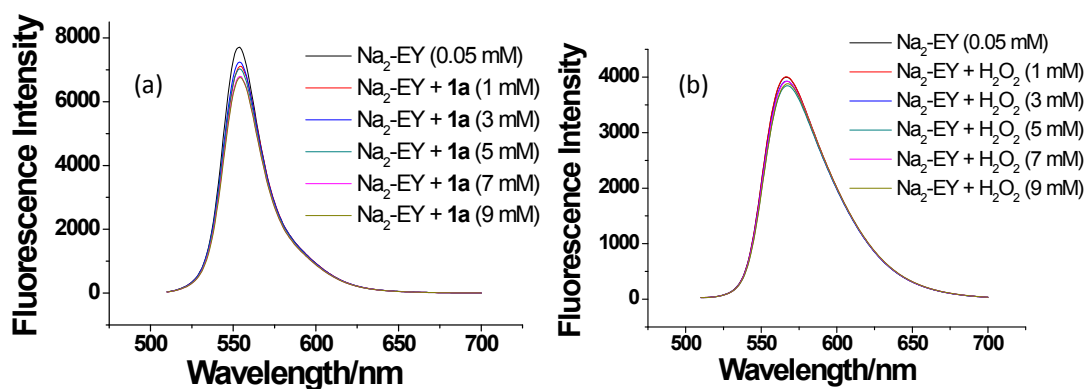


Figure S4. HR-MS spectrum of compound **8a**

## 6. Luminescence quenching experiments

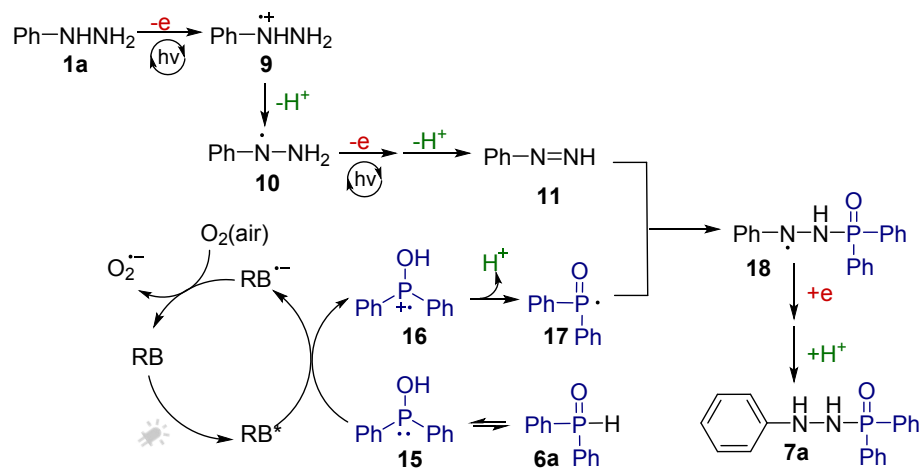
Emission intensities were recorded using a F-4600 FL Spectrophotometer. First, the emission intensity of Na<sub>2</sub>-eosin Y (Na<sub>2</sub>-EY) solutions was observed at 554 nm. In a typical experiment, the emission spectrum of a 5 × 10<sup>-5</sup> M solution of Na<sub>2</sub>-eosin Y (Na<sub>2</sub>-EY) and different concentration of phenyl hydrazine **1a**, diphenyl disulfide **2a** and H<sub>2</sub>O<sub>2</sub> in degassed anhydrous DMSO in 10 mm path length quartz cuvette was collected.



**Figure S5.** Luminescence quenching study: (a) the emission spectra of a 5 × 10<sup>-5</sup> M solution of Na<sub>2</sub>-EY with various concentrations of **1a** in degassed anhydrous DMSO excited at 490 nm; (b) the emission spectra of a 5 × 10<sup>-5</sup> M solution of Na<sub>2</sub>-EY with various concentrations of H<sub>2</sub>O<sub>2</sub> in degassed anhydrous DMSO excited at 490 nm

## 7. The mechanism of phosphorylation reaction

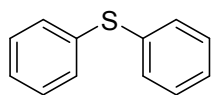
Based on the results of control experiments and literature reports, we proposed the reaction mechanism as shown in Scheme S2. Firstly, photocatalyst rose bengal (RB) transformed to the excited state RB\* under the irradiation of visible light. Diphenylphosphine oxide **6a** could exist in equilibrium with its trivalent tautomer phosphinous acid **15**. Then via a single electron transfer (SET) process, RB\* was reductively quenched by phosphinous acid **15** with the generation of RB<sup>•-</sup> and radical anion **16**. Deprotonation of radical anion **16** afforded the phosphorus-centered radical **17**. Single electron oxidation of RB\* by O<sub>2</sub> (air) generated ground state RB and O<sub>2</sub><sup>•-</sup>. Meanwhile, phenyl hydrazine **1a** transferred to radical **10** through oxidation followed by deprotonation. Then via the same SET process and deprotonation rendered radical **10** transfer to azobenzene **11**. An addition of phosphorus-centered radical **17** to azobenzene **11** delivered phosphorylated hydrazine radical **18**. The product **7a** was obtained from radical **18** in the presence of an electron and a proton which were generated in the reaction system.



**Scheme S2** The proposed mechanism of phosphorylation reaction

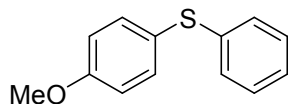


## 8. Characterization data



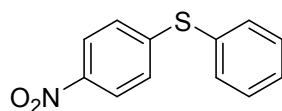
Diphenylsulfane (**3a**)<sup>1</sup>

Colorless oil, 68% yield (64 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.48 – 7.43 (m, 4H), 7.42 – 7.36 (m, 4H), 7.36 – 7.30 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 135.90, 131.15, 129.32, 127.16.



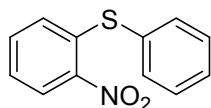
4-methoxyphenylphenylsulfane (**3b**)<sup>2</sup>

Colorless oil, 64% yield (69 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.50 (d, J = 2.1 Hz, 1H), 7.48 (d, J = 2.2 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.26 – 7.18 (m, 3H), 6.97 (d, J = 2.2 Hz, 1H), 6.96 (d, J = 2.1 Hz, 1H), 3.87 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 159.91, 138.73, 135.49, 129.02, 128.23, 125.83, 124.31, 115.07, 55.42.



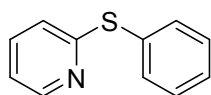
4-nitrophenylphenylsulfane (**3c**)<sup>2</sup>

Yellow oil, 20% yield (23 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.26 (dd, J = 8.3, 1.5 Hz, 1H), 7.66 – 7.59 (m, 2H), 7.52 (dd, J = 5.0, 1.9 Hz, 3H), 7.36 (m, 1H), 7.24 (m, 1H), 6.89 (dd, J = 8.2, 1.3 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 135.95, 133.43, 131.00, 130.13, 130.03, 128.31, 125.78, 124.94.



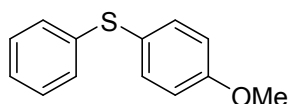
2-nitrophenylphenylsulfane (**3d**)<sup>3</sup>

Yellow oil, 17% yield (20 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.26 (dd, J = 8.3, 1.4 Hz, 1H), 7.62 (dd, J = 7.1, 2.5 Hz, 2H), 7.52 (dd, J = 5.1, 1.9 Hz, 3H), 7.40 – 7.34 (m, 1H), 7.27 – 7.22 (m, 1H), 6.89 (dd, J = 8.3, 1.3 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 145.00, 139.50, 135.92, 133.41, 131.02, 130.12, 130.02, 128.32, 125.76, 124.94.



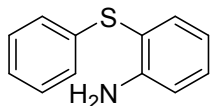
2-phenylthiopyridine (**3e**)<sup>1</sup>

Colorless oil, 71% yield (65 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.45 (dd, J = 5.0, 1.8 Hz, 1H), 7.62 (dd, J = 6.6, 3.0 Hz, 2H), 7.50 – 7.40 (m, 4H), 7.05 – 6.99 (m, 1H), 6.90 (d, J = 8.1 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 161.60, 149.60, 136.76, 135.00, 131.03, 129.68, 129.14, 121.34, 119.91.



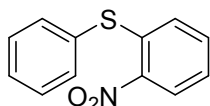
Methoxyphenylphenylsulfane (**3f**)<sup>2</sup>

Colorless oil, 74% yield (80 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.50 (d, J = 2.1 Hz, 1H), 7.48 (d, J = 2.2 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.26 – 7.18 (m, 3H), 6.97 (d, J = 2.2 Hz, 1H), 6.96 (d, J = 2.1 Hz, 1H), 3.87 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 159.91, 138.73, 135.49, 129.02, 128.23, 125.83, 124.31, 115.07, 55.42.



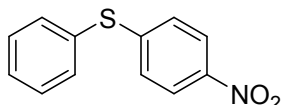
4-phenylthioaniline (**3g**)<sup>4</sup>

Yellow oil, 70% yield (71 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.49 (dd, J = 7.7, 1.6 Hz, 1H), 7.25 (dd, J = 8.3, 7.0 Hz, 3H), 7.17 – 7.09 (m, 3H), 6.84 – 6.77 (m, 2H), 4.32 (s, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 148.88, 137.52, 136.86, 131.18, 129.04, 126.43, 125.45, 118.77, 115.39, 114.36.



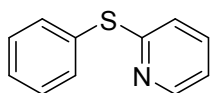
2-nitrophenyl phenyl sulfane (**3h**)<sup>3</sup>

Yellow oil, 15% yield (17 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.26 (dd, J = 8.3, 1.4 Hz, 1H), 7.62 (dd, J = 7.1, 2.5 Hz, 2H), 7.52 (dd, J = 5.1, 1.9 Hz, 3H), 7.40 – 7.34 (m, 1H), 7.27 – 7.22 (m, 1H), 6.89 (dd, J = 8.3, 1.3 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 145.00, 139.50, 135.92, 133.41, 131.02, 130.12, 130.02, 128.32, 125.76, 124.94.



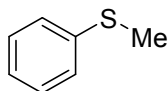
4-nitrophenyl phenyl sulfane (**3i**)<sup>2</sup>

Yellow oil, 18% yield (21 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.26 (dd, J = 8.3, 1.5 Hz, 1H), 7.66 – 7.59 (m, 2H), 7.52 (dd, J = 5.0, 1.9 Hz, 3H), 7.36 (m, 1H), 7.24 (m, 1H), 6.89 (dd, J = 8.2, 1.3 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 135.95, 133.43, 131.00, 130.13, 130.03, 128.31, 125.78, 124.94.



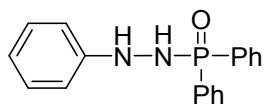
2-phenylthiopyridine (**3j**)<sup>1</sup>

Colorless oil, 75% yield (70 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.45 (dd, J = 5.0, 1.8 Hz, 1H), 7.62 (dd, J = 6.6, 3.0 Hz, 2H), 7.50 – 7.40 (m, 4H), 7.05 – 6.99 (m, 1H), 6.90 (d, J = 8.1 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 161.60, 149.60, 136.76, 135.00, 131.03, 129.68, 129.14, 121.34, 119.91.



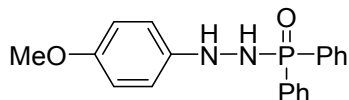
Methyl phenyl sulfane (**3k**)<sup>5</sup>

Colorless oil, 71% yield (44 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.39 – 7.32 (m, 4H), 7.21 (m, 1H), 2.54 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 138.52, 128.91, 126.63, 125.07, 15.86.



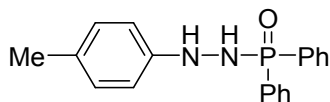
*N',P,P*-triphenylphosphinic hydrazide (**7a**)<sup>6</sup>

White solid, 55% yield (85 mg). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.95 – 7.87 (m, 4H), 7.57 – 7.46 (m, 7H), 7.44 (d, *J* = 10.6 Hz, 1H), 7.14 (dd, *J* = 8.5, 7.1 Hz, 2H), 7.04 – 6.99 (m, 2H), 6.72 – 6.66 (m, 1H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 150.84 (d, *J* = 5.2 Hz), 133.72, 132.43 (d, *J* = 9.1 Hz), 132.05 (d, *J* = 2.5 Hz), 128.87 (d, *J* = 5.3 Hz), 128.78, 118.83, 113.41. <sup>31</sup>P NMR (162 MHz, DMSO-*d*<sub>6</sub>) δ 25.49.



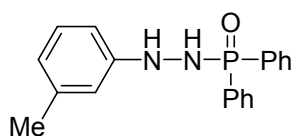
*N'*-(4-methoxyphenyl)-*P,P*-diphenylphosphinic hydrazide (**7b**)

White solid, 76% yield (128 mg). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.11 – 7.87 (m, 4H), 7.50 (m, 2H), 7.47 – 7.38 (m, 4H), 6.94 (d, *J* = 8.9 Hz, 2H), 6.79 (d, *J* = 8.9 Hz, 2H), 5.58 (d, *J* = 3.2 Hz, 1H), 4.93 (d, *J* = 17.0 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 132.65, 131.60 (d, *J* = 5.9 Hz), 131.22 (d, *J* = 10.5 Hz), 129.02 (d, *J* = 66.3 Hz), 128.58 (d, *J* = 3.7 Hz), 128.49 (d, *J* = 6.8 Hz), 114.20, 113.88, 55.31 (d, *J* = 31.4 Hz). <sup>31</sup>P NMR (162 MHz, DMSO-*d*<sub>6</sub>) δ 12.87. HRMS (ESI) calcd. for C<sub>19</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>P [M+H]<sup>+</sup>: 339.1257, found: 339.1256.



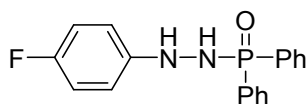
*P,P*-diphenyl-*N'*-(*p*-tolyl)phosphinic hydrazide (**7c**)

White solid, 67% yield (108 mg). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.95 – 7.85 (m, 4H), 7.57 – 7.44 (m, 6H), 7.38 (d, *J* = 24.2 Hz, 1H), 7.27 (d, *J* = 3.9 Hz, 1H), 6.98 – 6.89 (m, 4H), 2.18 (s, 3H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 146.16, 132.22 (d, *J* = 3.6 Hz), 132.11, 131.20, 129.92, 129.60, 128.59 (d, *J* = 12.5 Hz), 113.54, 20.55. <sup>31</sup>P NMR (162 MHz, DMSO-*d*<sub>6</sub>) δ 20.85. HRMS (ESI) calcd. for C<sub>19</sub>H<sub>19</sub>N<sub>2</sub>OP [M+H]<sup>+</sup>: 323.1308, found: 323.1307.



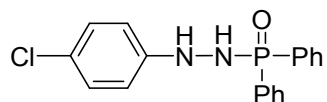
*P,P*-diphenyl-*N'*-(*m*-tolyl)phosphinic hydrazide (**7d**)

White solid, 68% yield (109 mg). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.98 – 7.83 (m, 4H), 7.63 – 7.47 (m, 6H), 7.43 (d, *J* = 24.5 Hz, 1H), 7.37 (d, *J* = 3.7 Hz, 1H), 7.01 (d, *J* = 7.7 Hz, 1H), 6.86 – 6.77 (m, 2H), 6.51 (d, *J* = 7.4 Hz, 1H), 2.22 (s, 3H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 150.84 (d, *J* = 5.2 Hz), 137.84, 133.75, 132.45 (d, *J* = 8.5 Hz), 132.04, 128.84 (d, *J* = 12.3 Hz), 119.73, 114.00, 110.71, 21.84. <sup>31</sup>P NMR (162 MHz, DMSO-*d*<sub>6</sub>) δ 19.01. HRMS (ESI) calcd. for C<sub>19</sub>H<sub>19</sub>N<sub>2</sub>OPNa [M+Na]<sup>+</sup>: 345.1133, found: 345.1130.



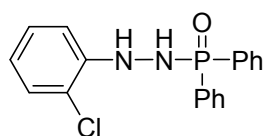
*N'*-(4-fluorophenyl)-*P,P*-diphenylphosphinic hydrazide (**7e**)

White solid, 74% yield (121 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  7.99 – 7.82 (m, 4H), 7.59 – 7.46 (m, 7H), 7.45 (d,  $J = 4.2$  Hz, 1H), 7.08 – 6.93 (m, 4H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{DMSO-}d_6$ )  $\delta$  156.27 (d,  $J = 233.0$  Hz), 147.43, 133.66, 132.43 (d,  $J = 9.3$  Hz), 132.09 (d,  $J = 2.9$  Hz), 128.87 (d,  $J = 12.2$  Hz), 115.27 (d,  $J = 22.0$  Hz), 114.56 (d,  $J = 7.4$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{DMSO-}d_6$ )  $\delta$  20.95. HRMS (ESI) calcd. for  $\text{C}_{18}\text{H}_{16}\text{FN}_2\text{OP}$   $[\text{M}+\text{H}]^+$ : 327.1063, found: 327.1063.



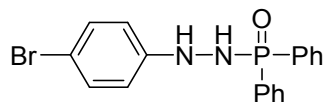
*N'*-(4-chlorophenyl)-*P,P*-diphenylphosphinic hydrazide (**7f**)

White solid, 69% yield (118 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  7.98 – 7.84 (m, 4H), 7.68 (d,  $J = 3.5$  Hz, 1H), 7.61 – 7.44 (m, 7H), 7.17 (d,  $J = 8.8$  Hz, 2H), 7.02 (d,  $J = 8.9$  Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{DMSO-}d_6$ )  $\delta$  149.82, 133.48, 132.42 (d,  $J = 9.0$  Hz), 132.19 (d,  $J = 4.4$  Hz), 128.89 (d,  $J = 12.3$  Hz), 128.62, 122.02, 114.84.  $^{31}\text{P}$  NMR (162 MHz,  $\text{DMSO-}d_6$ )  $\delta$  21.59. HRMS (ESI) calcd. for  $\text{C}_{18}\text{H}_{16}\text{ClN}_2\text{OP}$   $[\text{M}+\text{H}]^+$ : 343.0762, found: 343.0768. HRMS (ESI) calcd. for  $\text{C}_{18}\text{H}_{16}\text{ClN}_2\text{OP}$   $[\text{M}+\text{H}]^+$ : 343.0762, found: 343.0768.



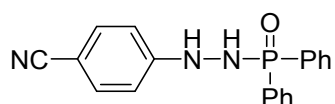
*N'*-(2-chlorophenyl)-*P,P*-diphenylphosphinic hydrazide (**7g**)

White solid, 63% yield (108 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.04 – 7.88 (m, 4H), 7.63 – 7.43 (m, 8H), 7.32 – 7.17 (m, 2H), 6.97 (d,  $J = 4.4$  Hz, 1H), 6.82 – 6.73 (m, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{DMSO-}d_6$ )  $\delta$  161.87 (d,  $J = 3.7$  Hz), 147.62, 137.76, 133.36, 132.57 (d,  $J = 9.2$  Hz), 132.17 (d,  $J = 2.6$  Hz), 132.09, 128.85 (d,  $J = 12.0$  Hz), 114.92, 107.54.  $^{31}\text{P}$  NMR (162 MHz,  $\text{DMSO-}d_6$ )  $\delta$  21.36. HRMS (ESI) calcd. for  $\text{C}_{18}\text{H}_{16}\text{ClN}_2\text{OP}$   $[\text{M}+\text{H}]^+$ : 343.0762, found: 343.0761.



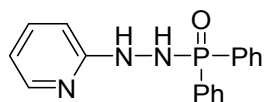
*N'*-(4-bromophenyl)-*P,P*-diphenylphosphinic hydrazide (**7h**)

White solid, 78% yield (150 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.03 – 7.82 (m, 4H), 7.71 (d,  $J = 3.4$  Hz, 1H), 7.58 (d,  $J = 12.5$  Hz, 1H), 7.56 – 7.46 (m, 7H), 7.28 (d,  $J = 8.8$  Hz, 2H), 6.98 (d,  $J = 8.9$  Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{DMSO-}d_6$ )  $\delta$  150.25 (d,  $J = 5.1$  Hz), 133.47, 132.43 (d,  $J = 8.9$  Hz), 132.18 (d,  $J = 3.3$  Hz), 131.46, 128.90 (d,  $J = 12.0$  Hz), 115.36, 109.57.  $^{31}\text{P}$  NMR (162 MHz,  $\text{DMSO-}d_6$ )  $\delta$  21.13. HRMS (ESI) calcd. for  $\text{C}_{18}\text{H}_{16}\text{BrN}_2\text{OP}$   $[\text{M}+\text{H}]^+$ : 387.0256, found: 387.0252.



*N'*-(4-cyanophenyl)-*P,P*-diphenylphosphinic hydrazide (**7i**)

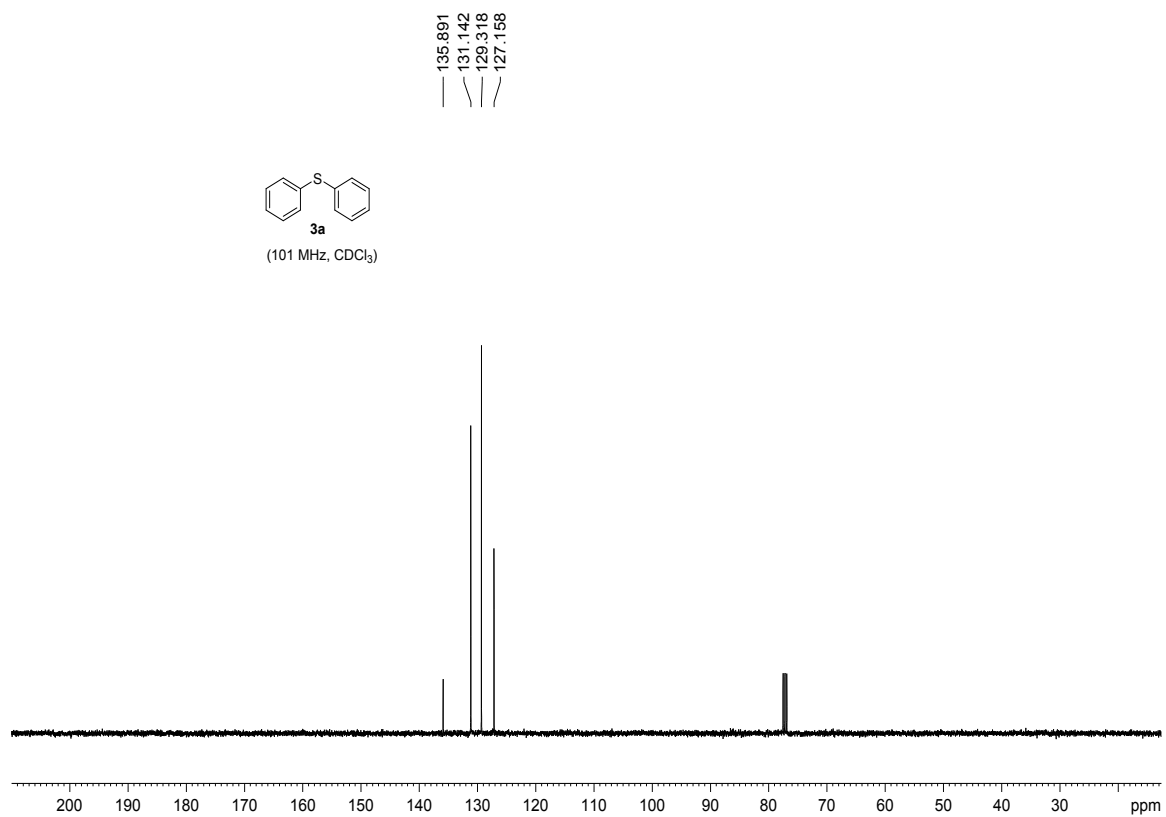
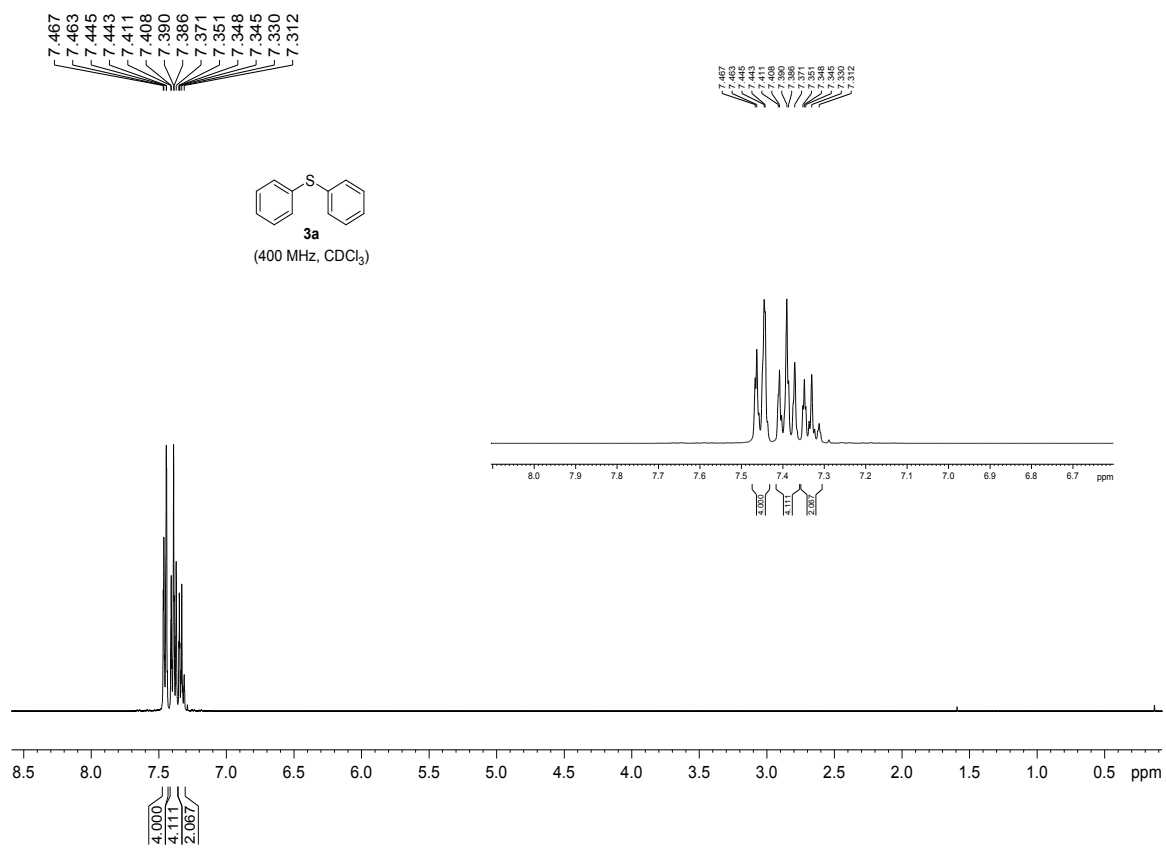
White solid, 87% yield (145 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.43 (d,  $J = 2.3$  Hz, 1H), 8.06 – 7.86 (m, 4H), 7.80 (d,  $J = 23.0$  Hz, 1H), 7.59 – 7.45 (m, 8H), 7.08 (d,  $J = 8.6$  Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{DMSO-}d_6$ )  $\delta$  154.57, 133.49, 132.95, 132.43 (d,  $J = 9.1$  Hz), 131.68, 128.98 (d,  $J = 12.3$  Hz), 120.72, 112.88, 98.95.  $^{31}\text{P}$  NMR (162 MHz,  $\text{DMSO-}d_6$ )  $\delta$  21.49. HRMS (ESI) calcd. for  $\text{C}_{19}\text{H}_{16}\text{N}_3\text{OP}$   $[\text{M}+\text{H}]^+$ : 334.1104, found: 334.1107.

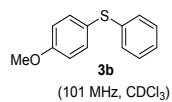
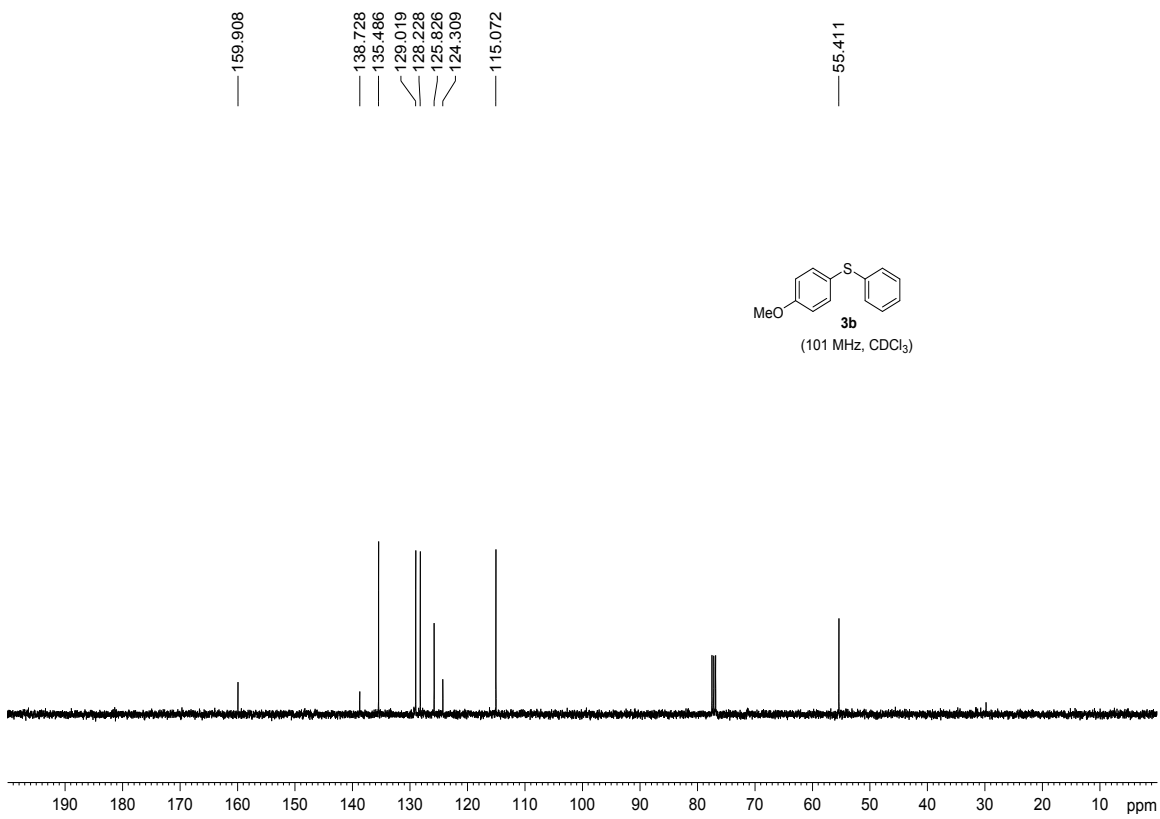
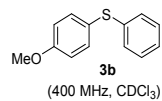
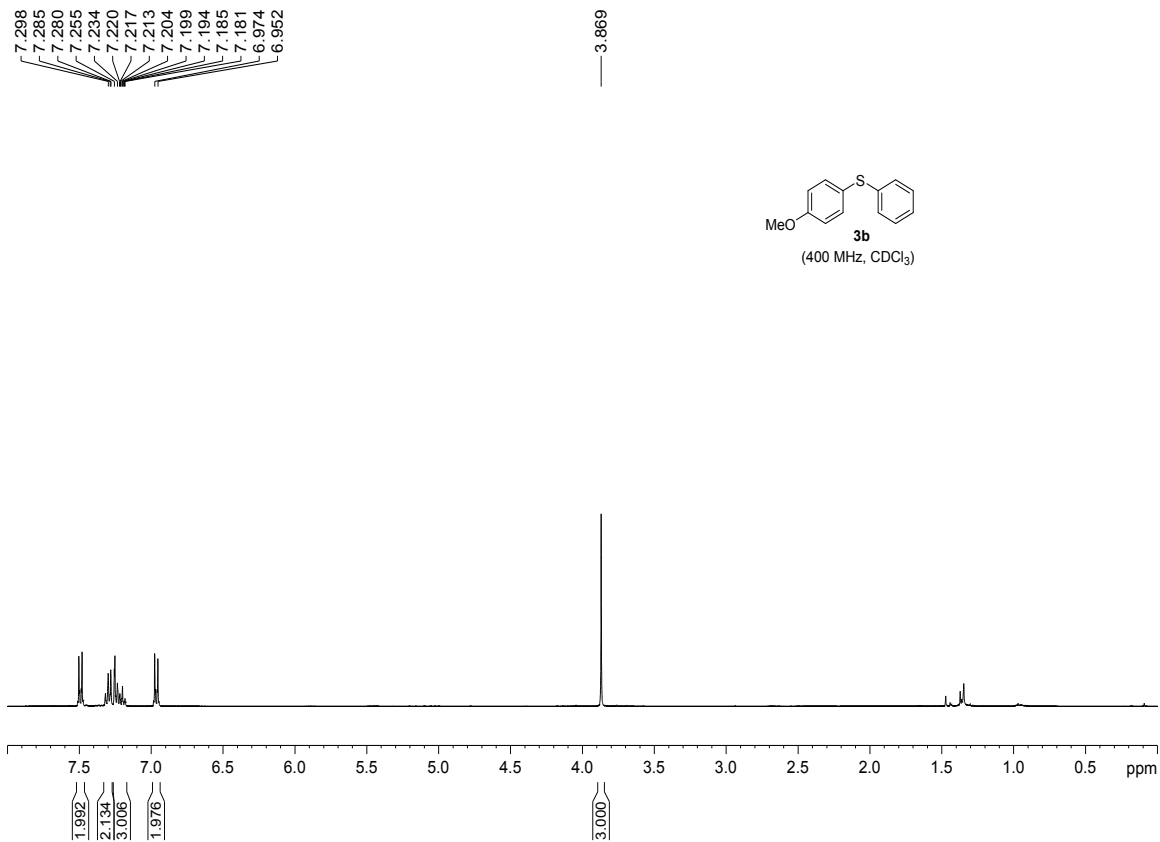


*P,P*-diphenyl-*N'*-(pyridin-2-yl)phosphinic hydrazide (**7j**)

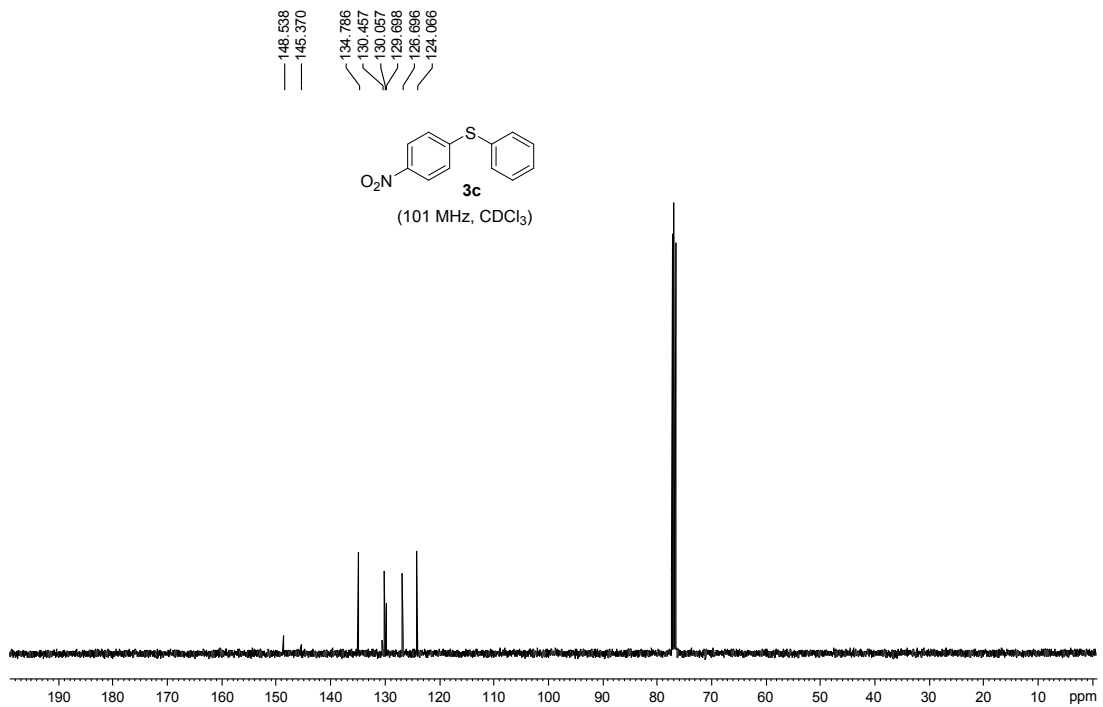
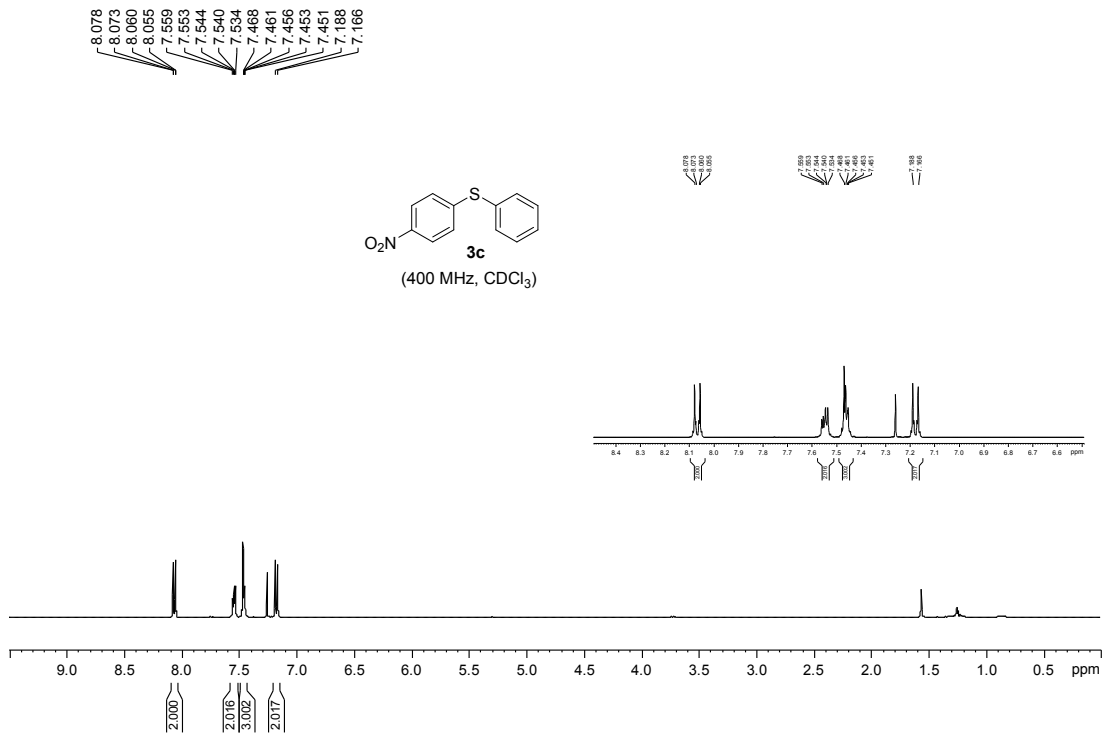
White solid, 50% yield (77 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.01 (dd,  $J = 5.0, 1.7$  Hz, 1H), 7.97 – 7.86 (m, 5H), 7.67 (d,  $J = 26.3$  Hz, 1H), 7.60 – 7.53 (m, 3H), 7.52 – 7.45 (m, 4H), 7.13 (d,  $J = 8.5$  Hz, 1H), 6.68 (dd,  $J = 7.0, 4.9$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{DMSO-}d_6$ )  $\delta$  161.87 (d,  $J = 3.7$  Hz), 147.62, 137.76, 132.72 (d,  $J = 127.9$  Hz), 132.57 (d,  $J = 9.2$  Hz), 132.17 (d,  $J = 2.6$  Hz), 128.85 (d,  $J = 12.1$  Hz), 114.92, 107.54.  $^{31}\text{P}$  NMR (162 MHz,  $\text{DMSO-}d_6$ )  $\delta$  21.61. HRMS (ESI) calcd. for  $\text{C}_{17}\text{H}_{16}\text{N}_3\text{OP}$   $[\text{M}+\text{H}]^+$ : 310.1104, found: 310.1112.

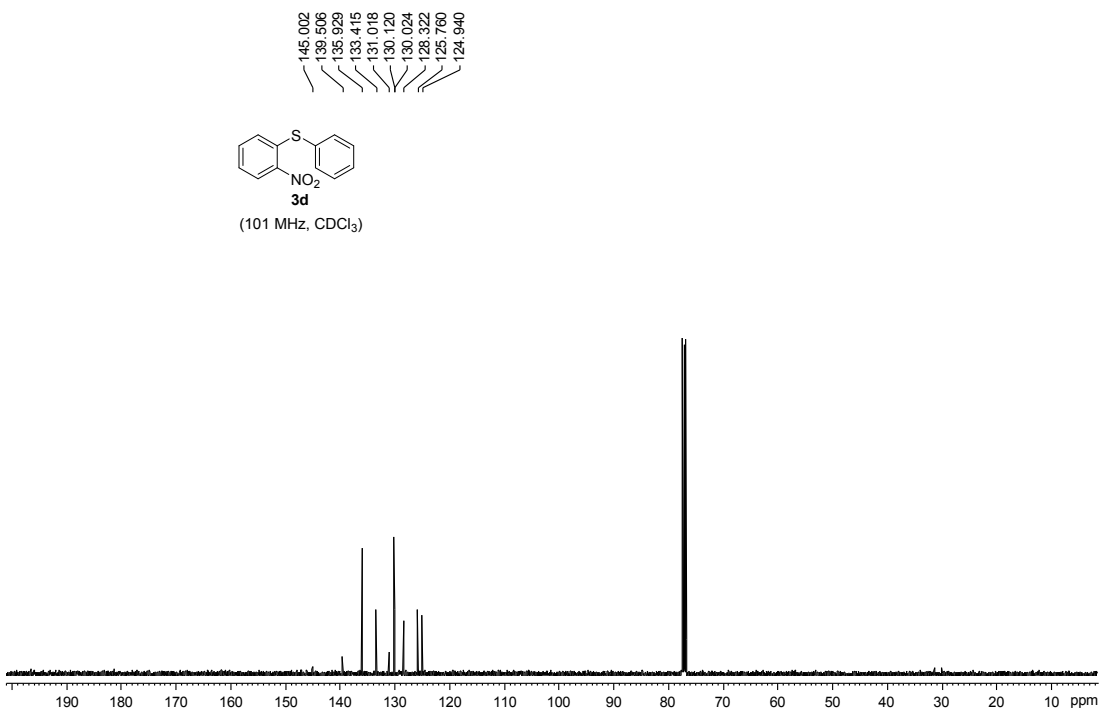
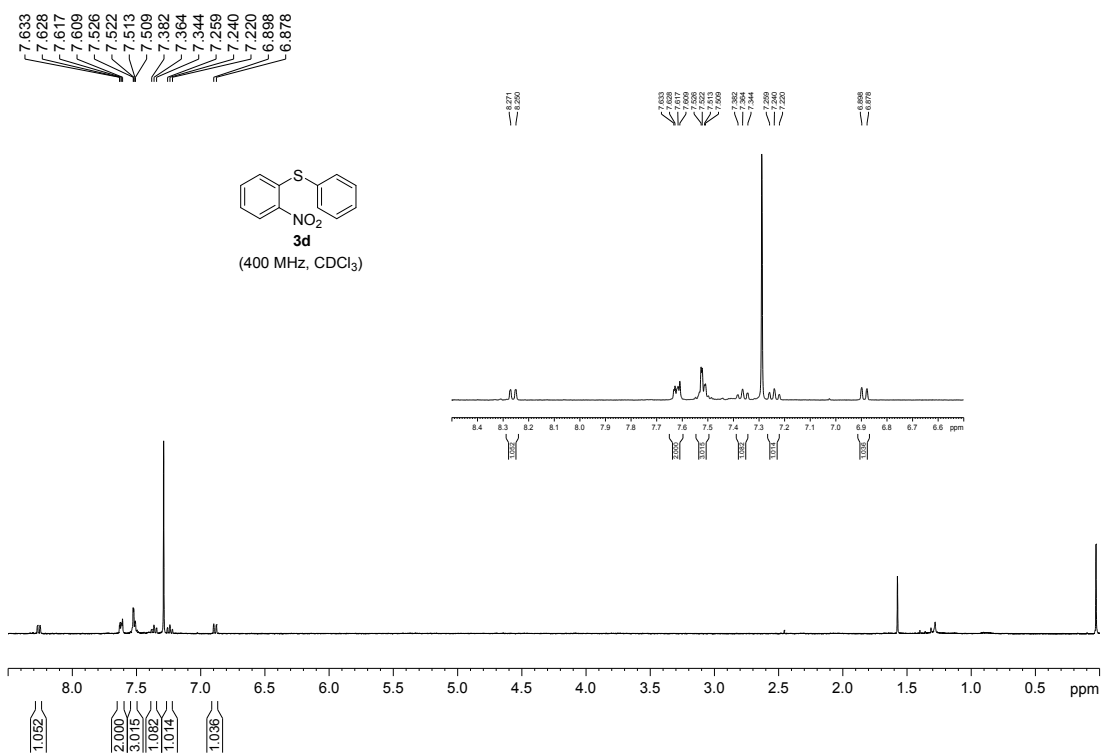
## 9. $^1\text{H}$ , $^{13}\text{C}$ and $^{31}\text{P}$ NMR spectra



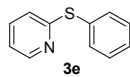








8.444  
7.636  
7.633  
7.627  
7.618  
7.614  
7.494  
7.490  
7.475  
7.470  
7.455  
7.453  
7.445  
7.440  
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7.033  
7.020  
7.014  
7.002  
6.915  
6.913  
6.894  
6.893

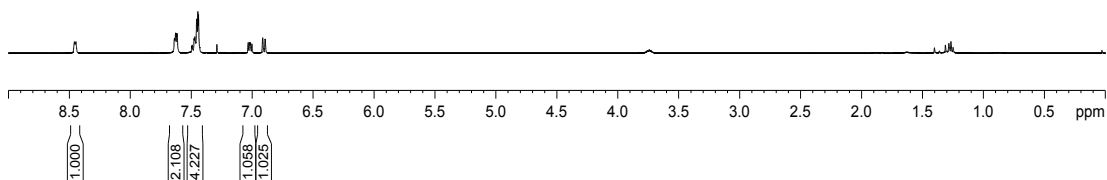
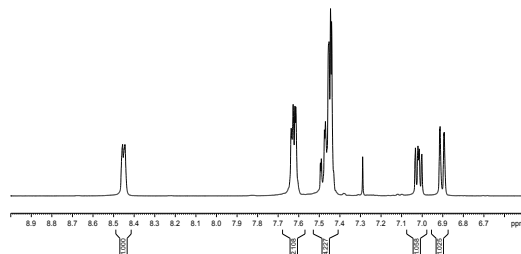


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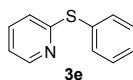
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8.442

7.636  
7.633  
7.627  
7.618  
7.614  
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7.475  
7.470  
7.455  
7.453  
7.445  
7.440  
7.431

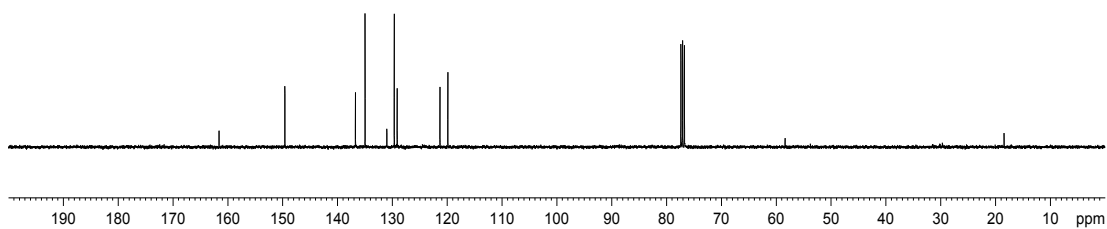
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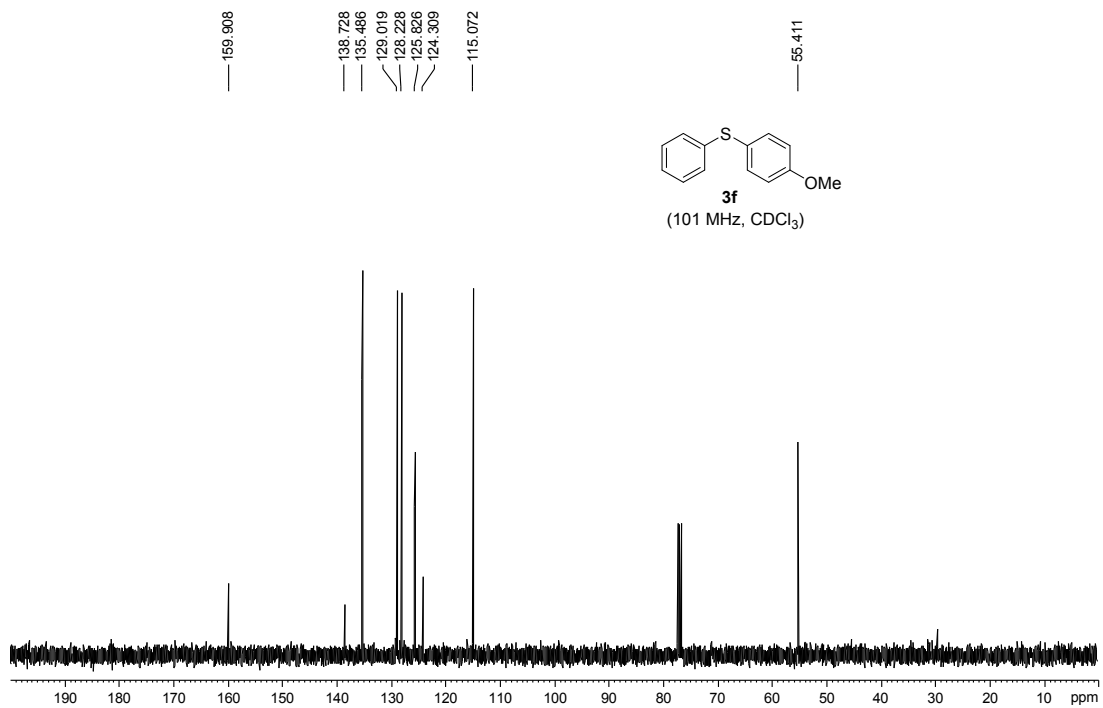
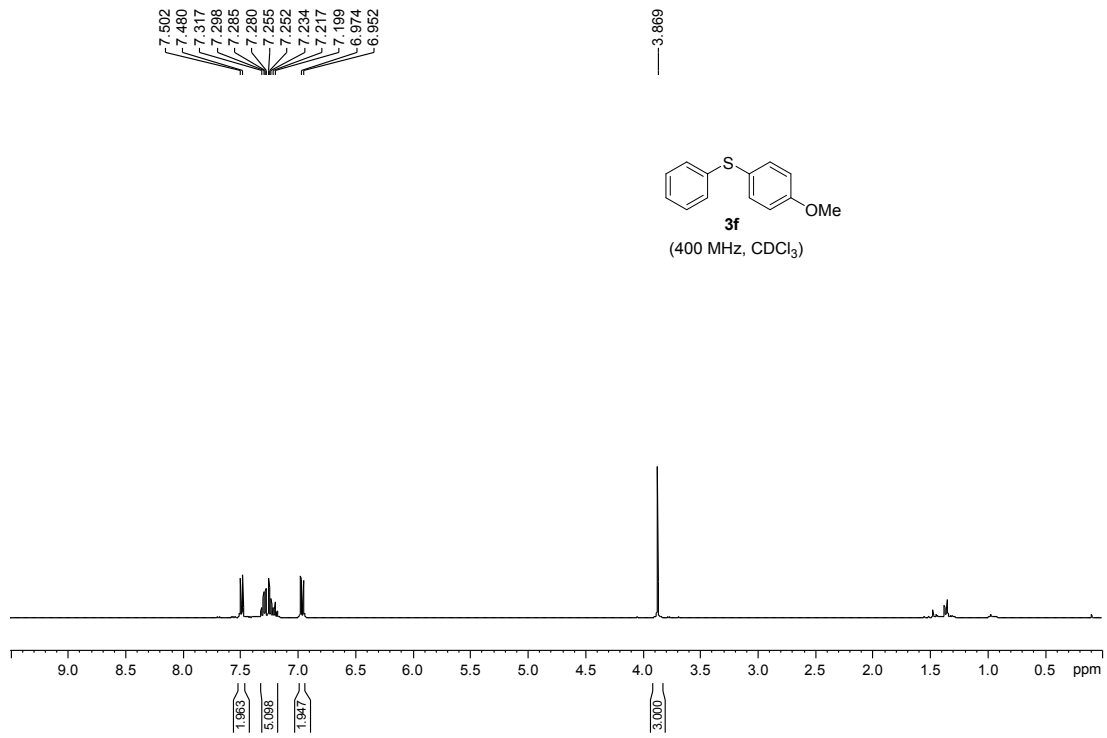


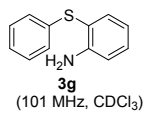
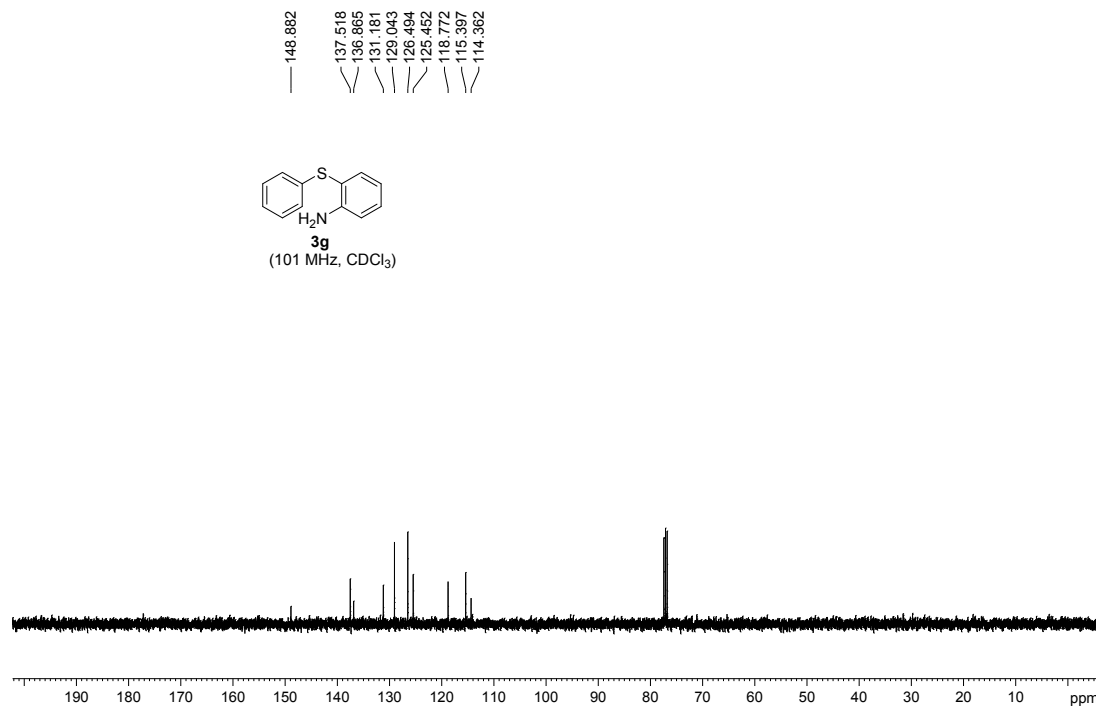
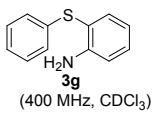
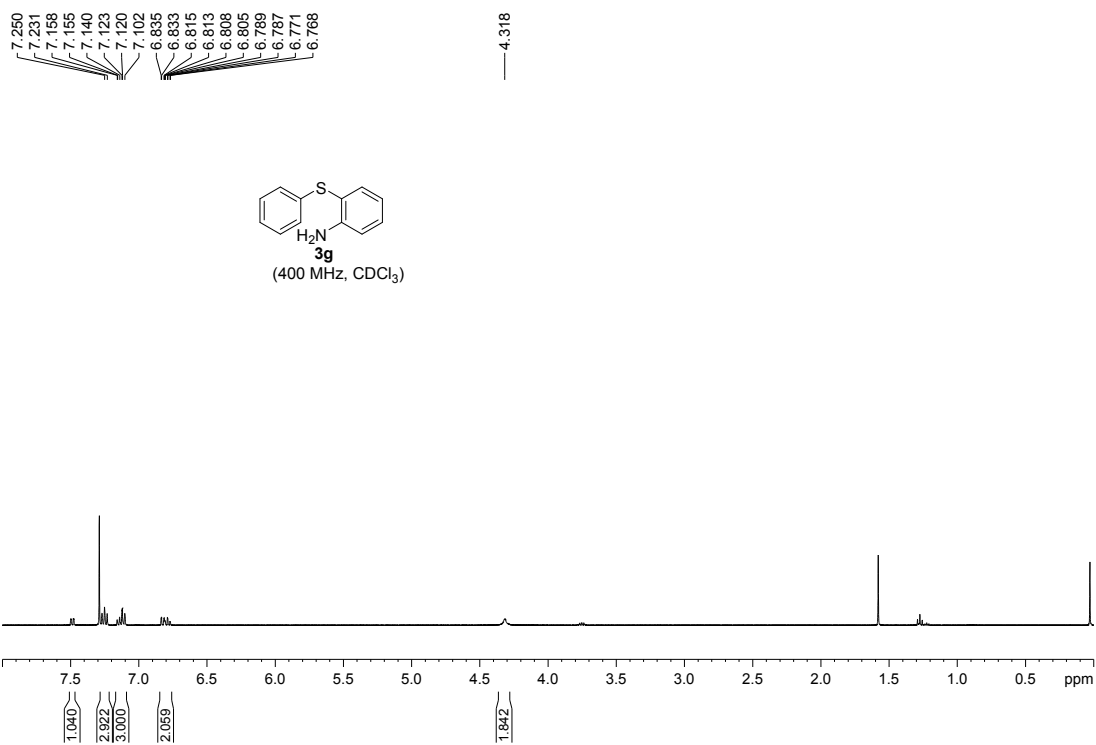
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134.998  
131.029  
129.674  
129.140  
121.338  
119.904



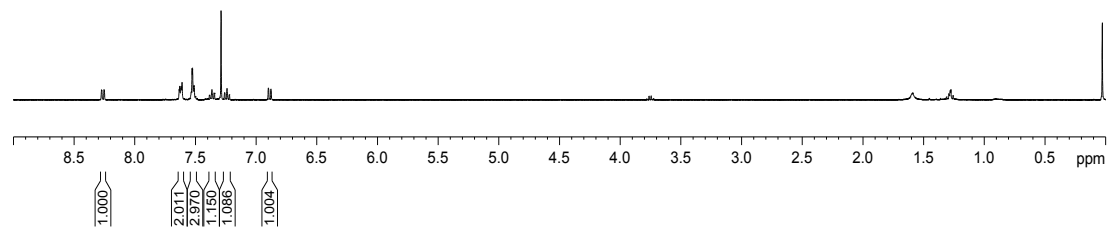
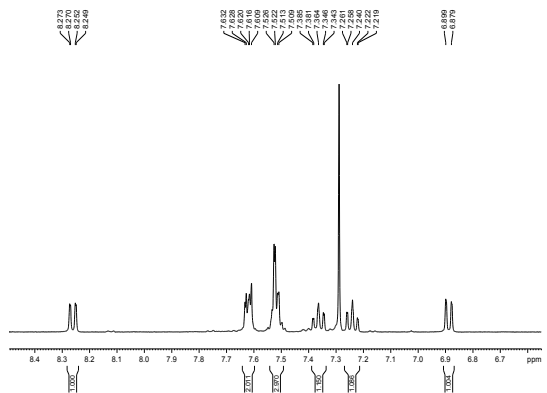
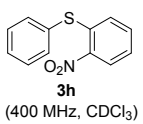
(101 MHz, CDCl<sub>3</sub>)



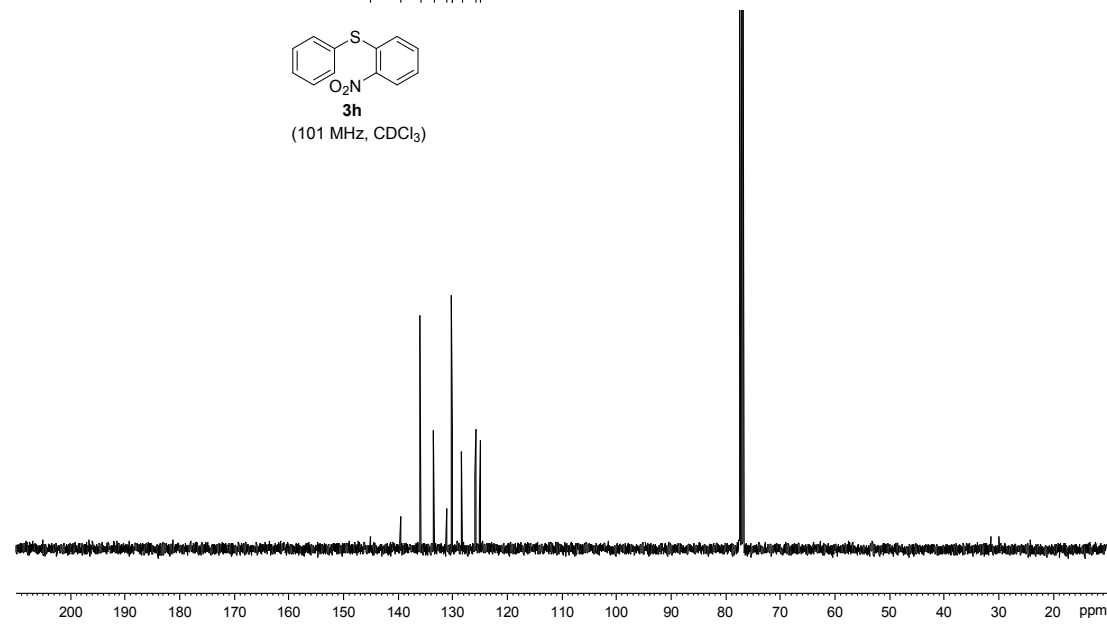
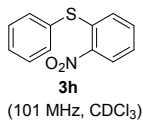




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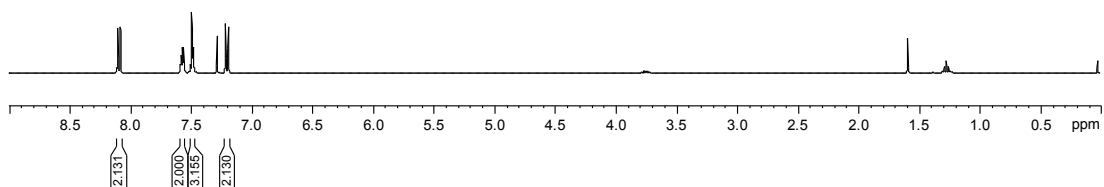
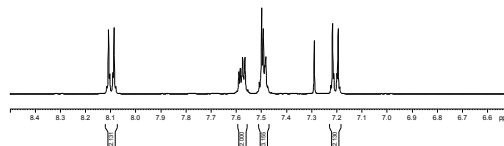
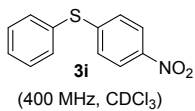


145.002  
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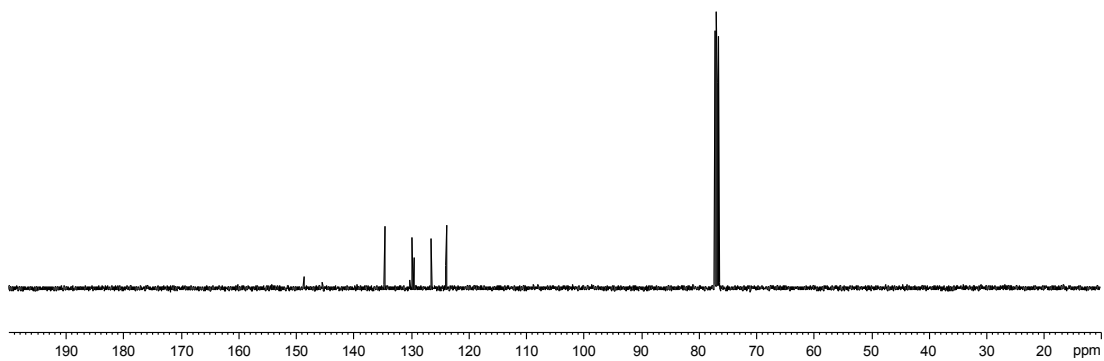
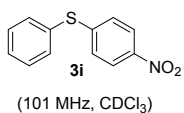


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8.08  
7.58  
7.57  
7.56  
7.49  
7.48  
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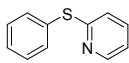


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7.419

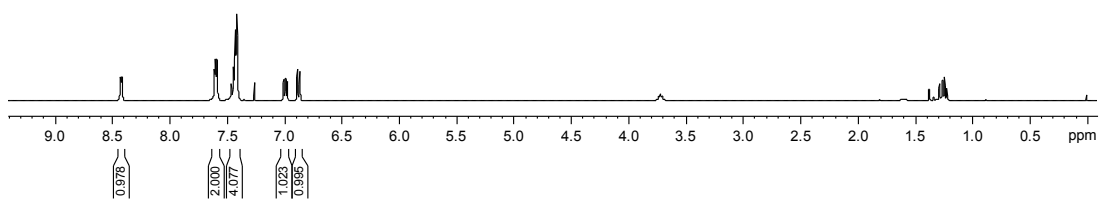
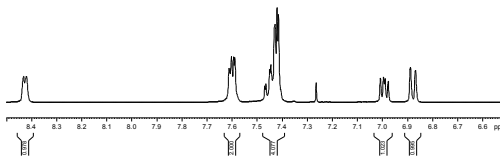
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6.875  
6.866

7.428  
7.419  
7.414



**3j**

(400 MHz, CDCl<sub>3</sub>)



161.592

149.592

136.758

134.998

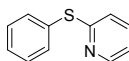
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129.674

129.140

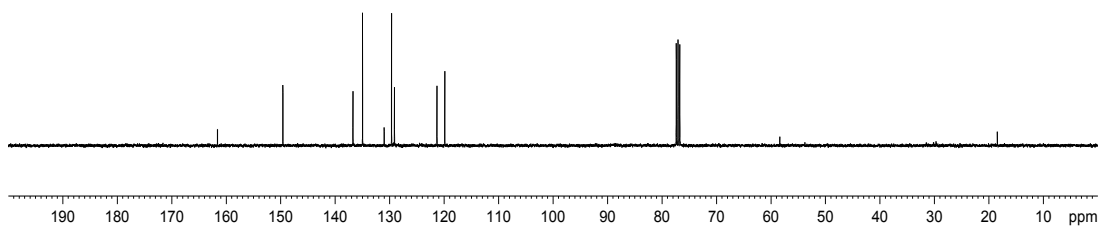
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119.904

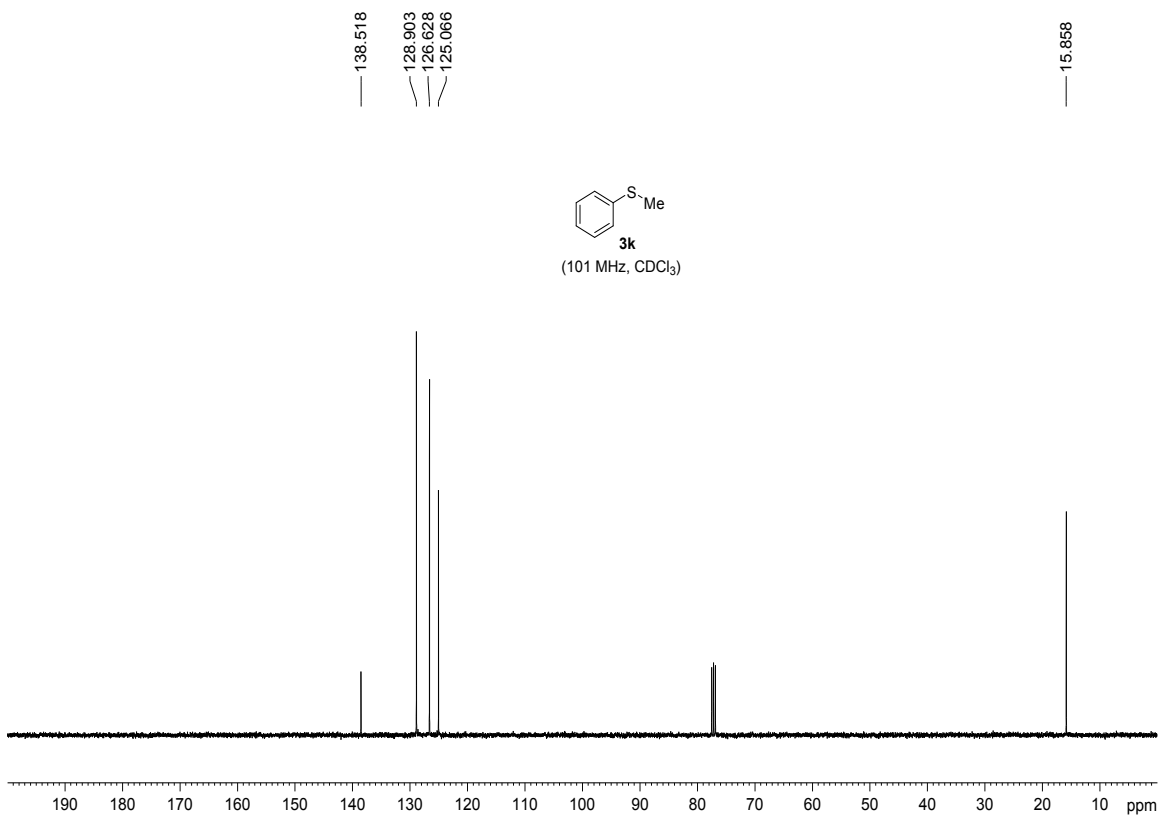
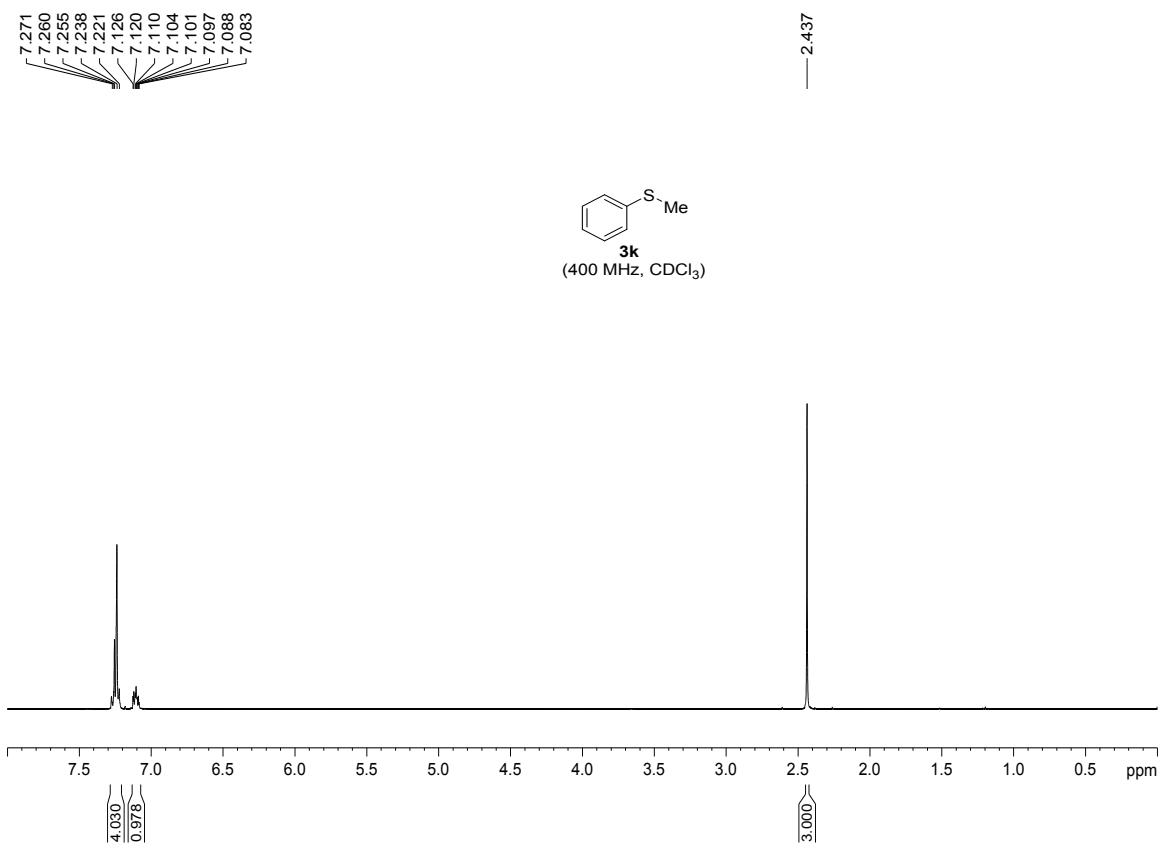


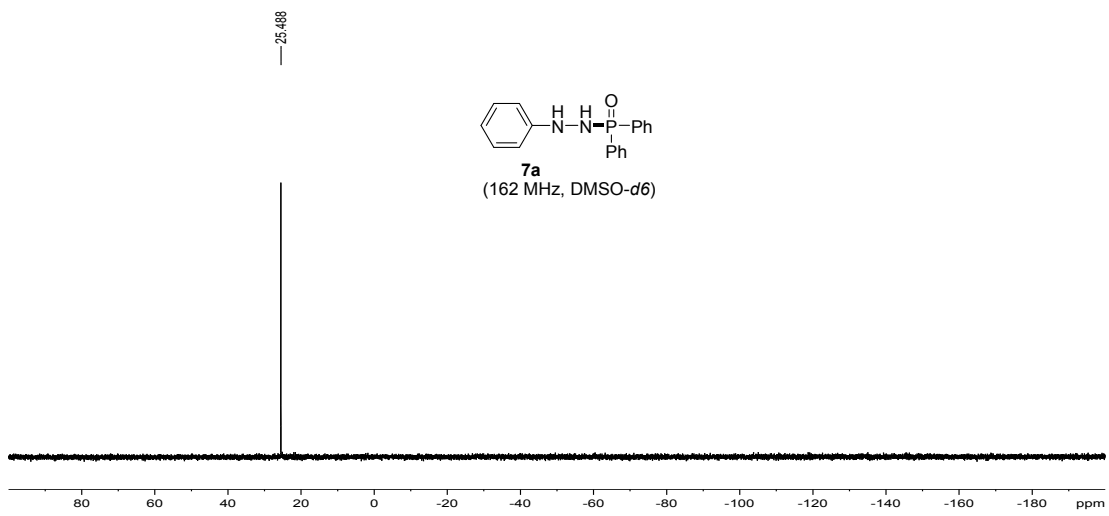
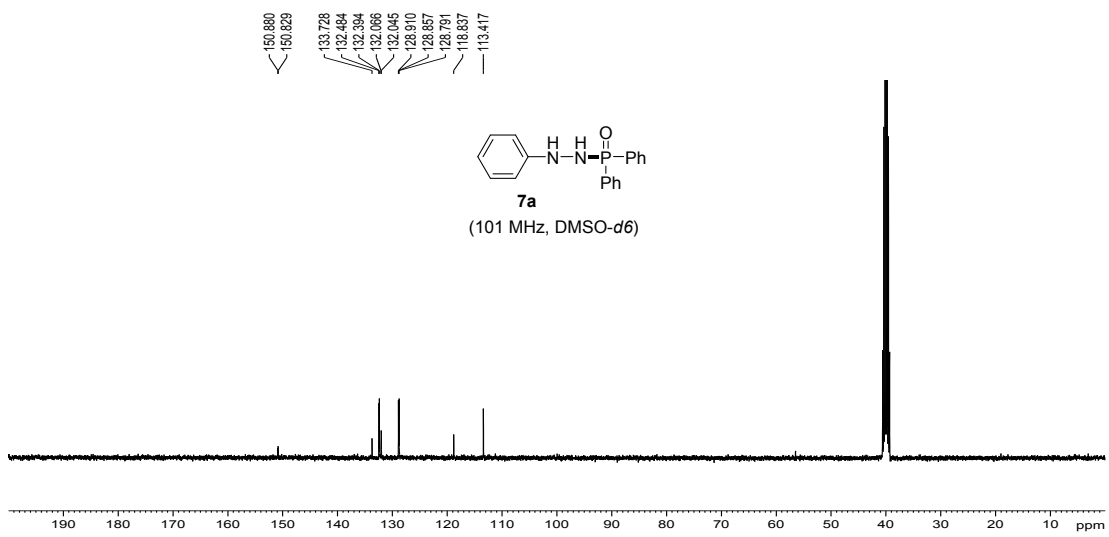
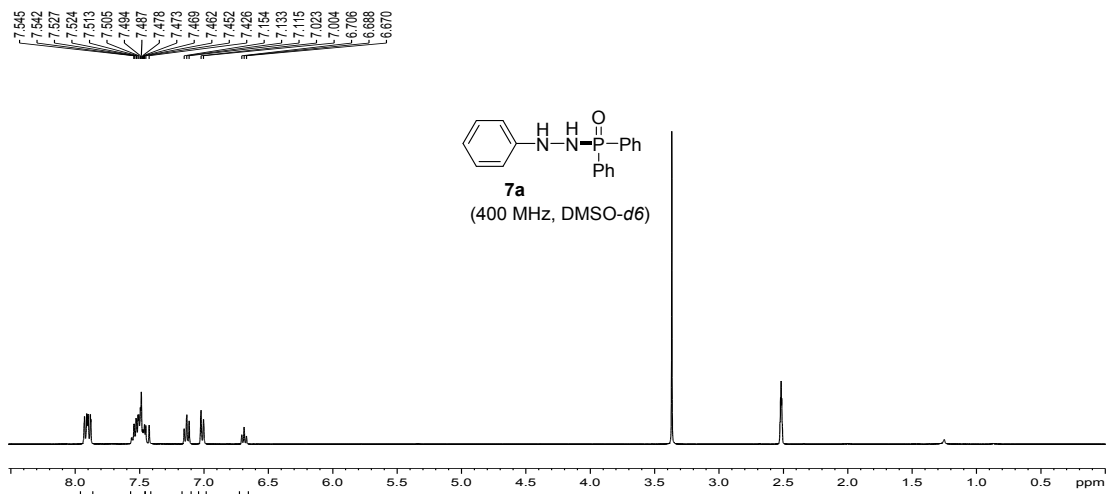
**3j**

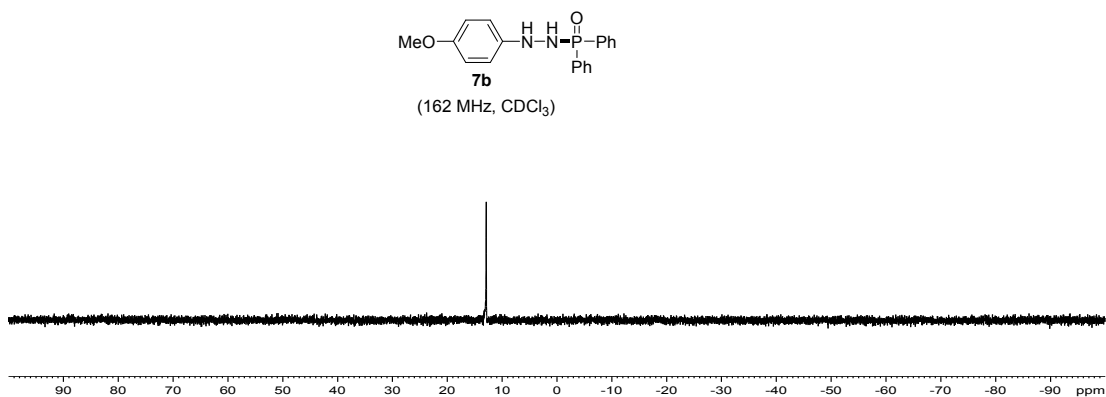
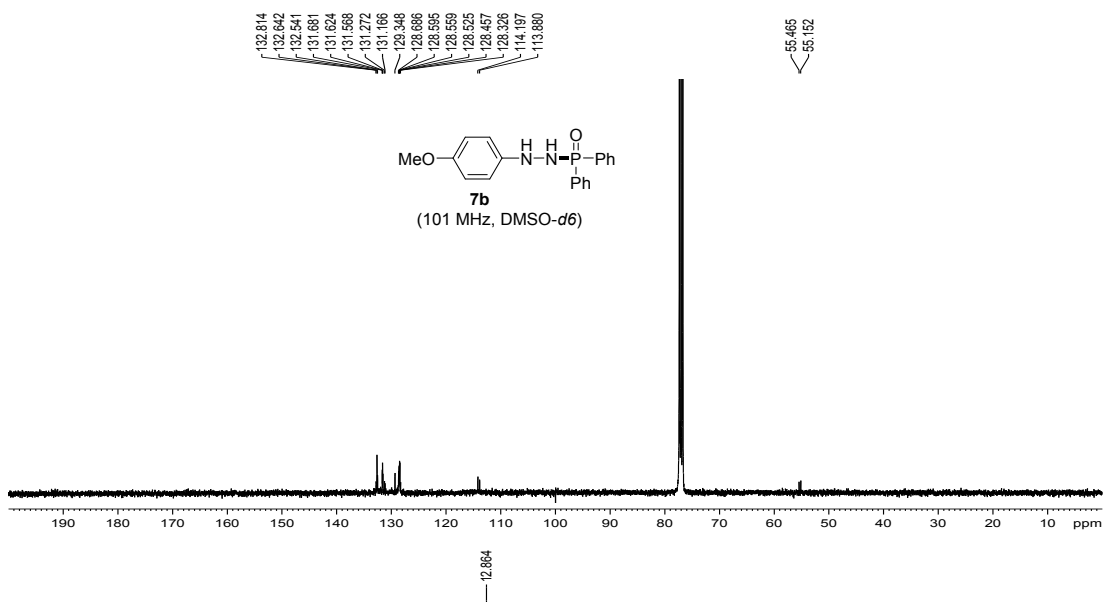
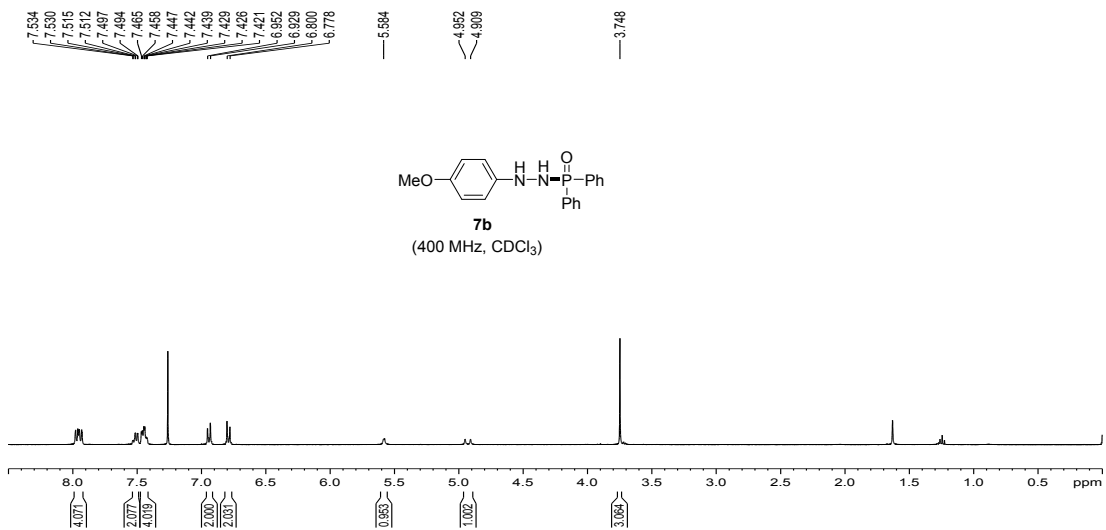
(101 MHz, CDCl<sub>3</sub>)

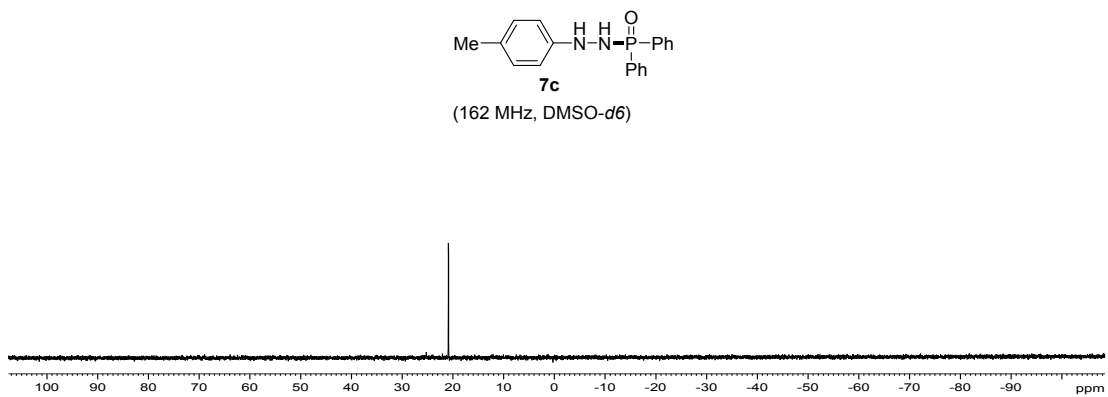
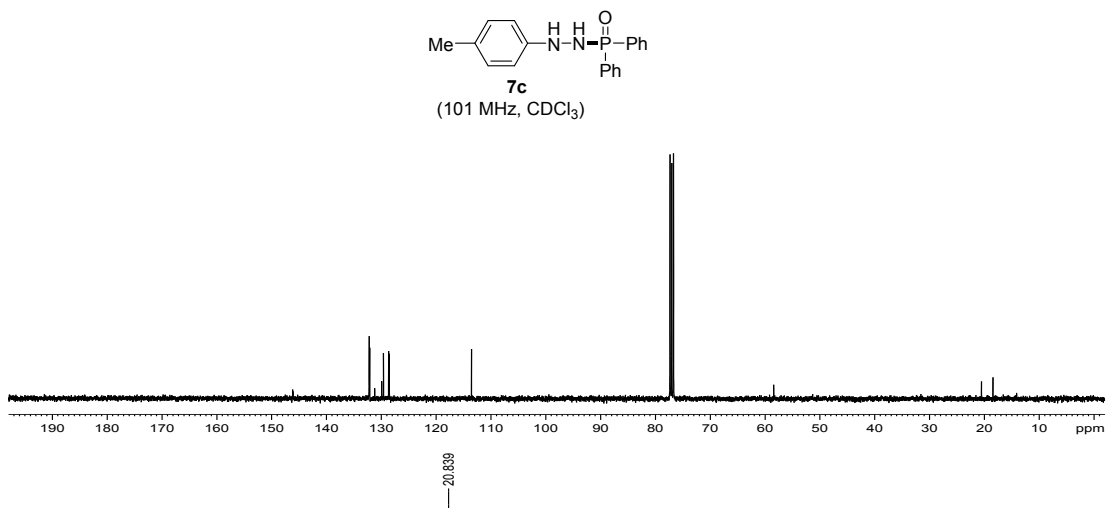
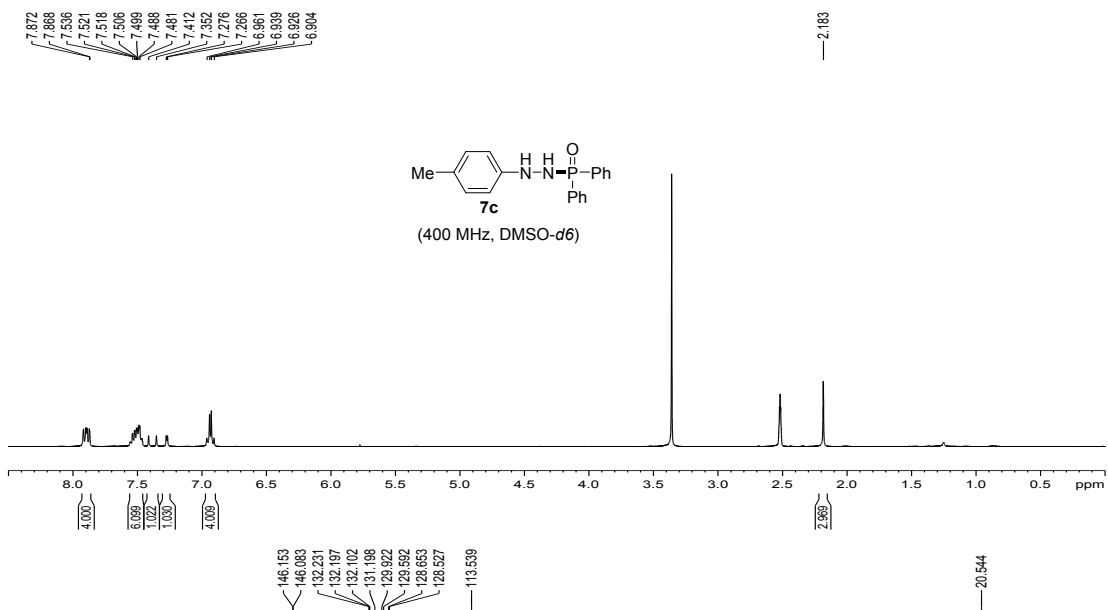


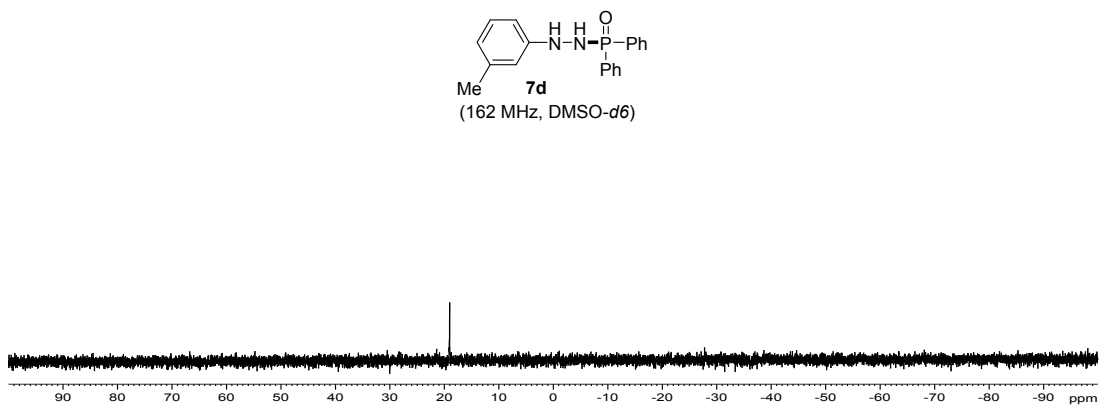
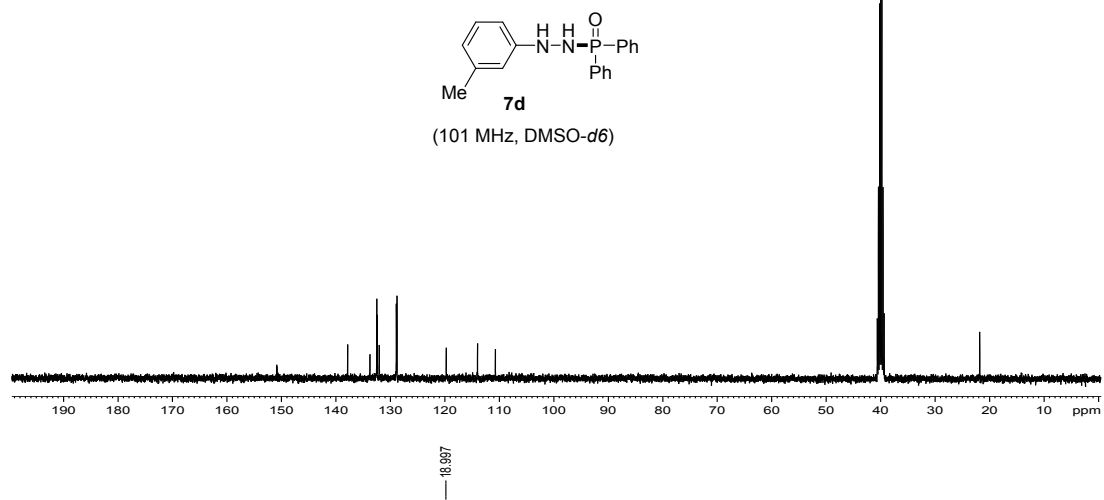
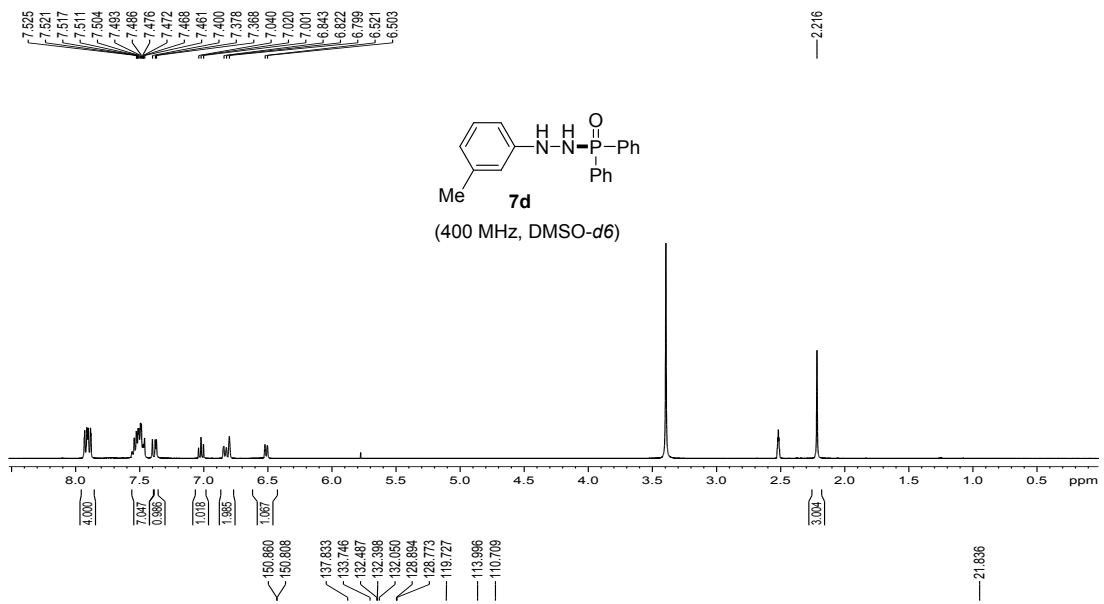




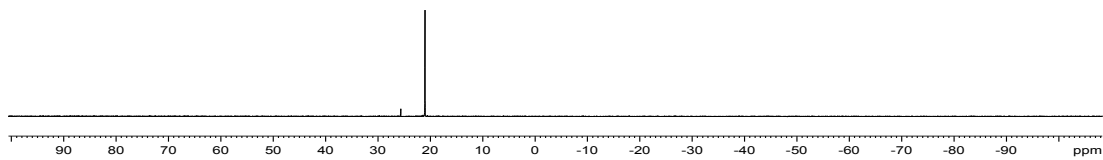
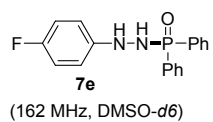
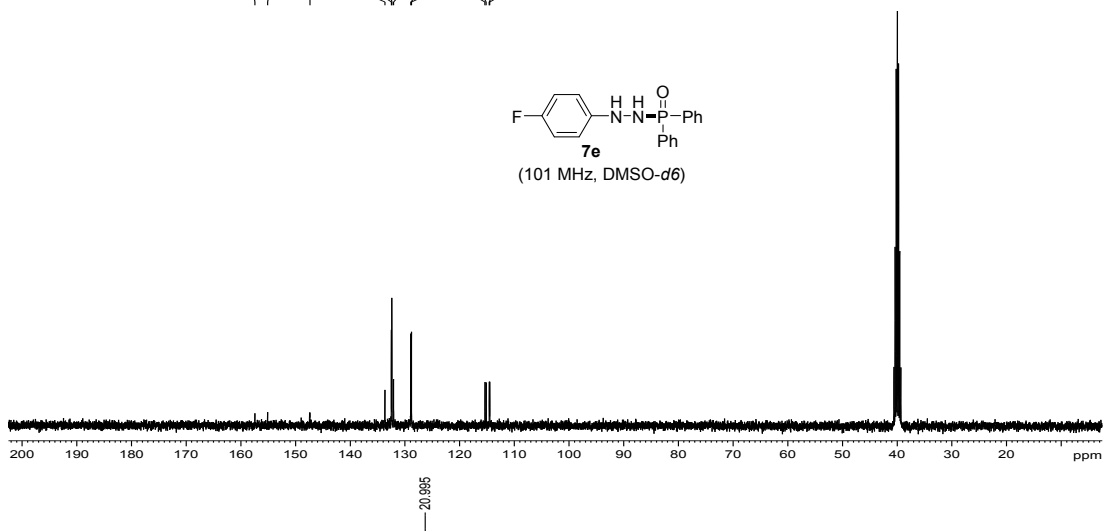
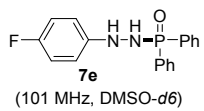
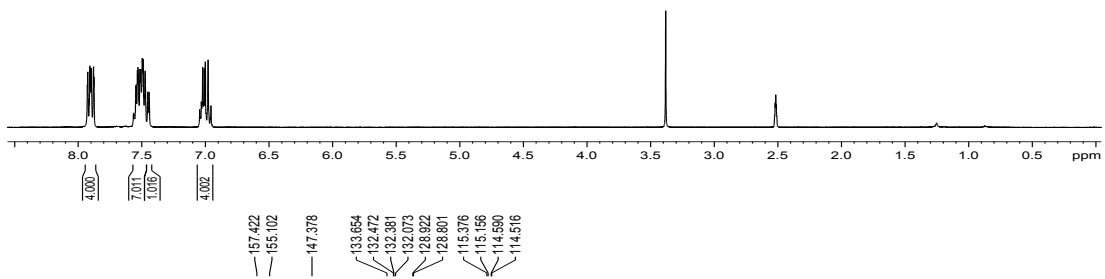


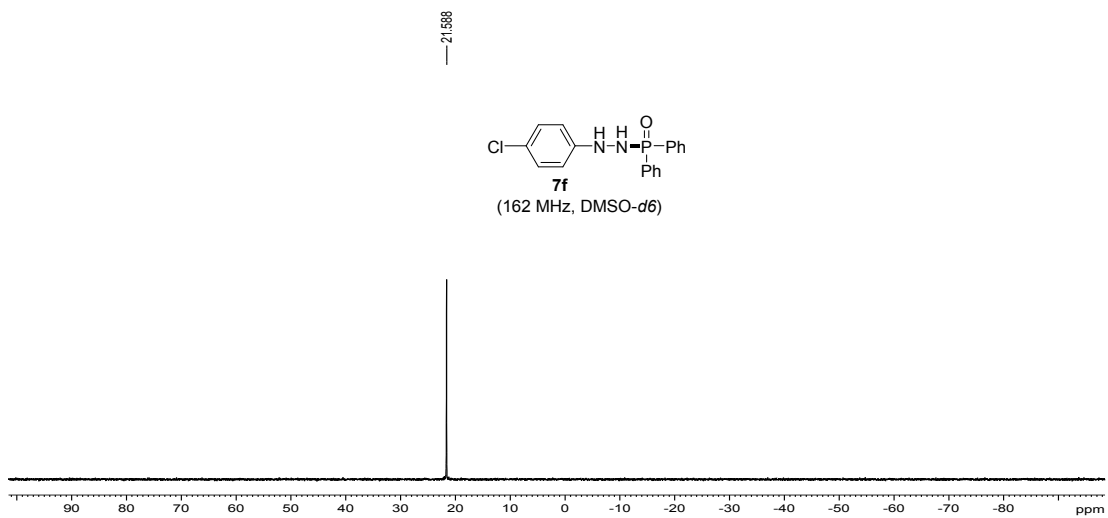
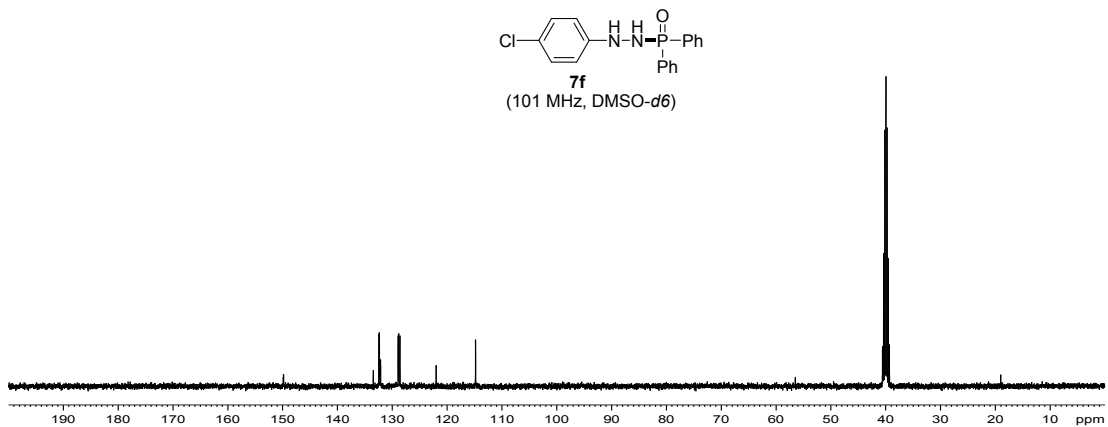
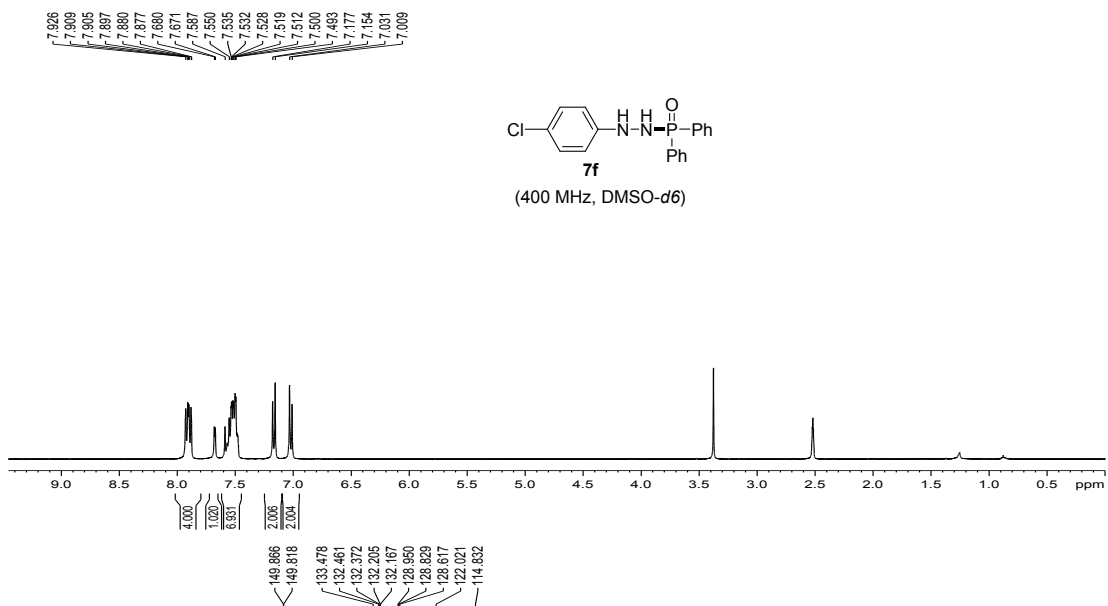


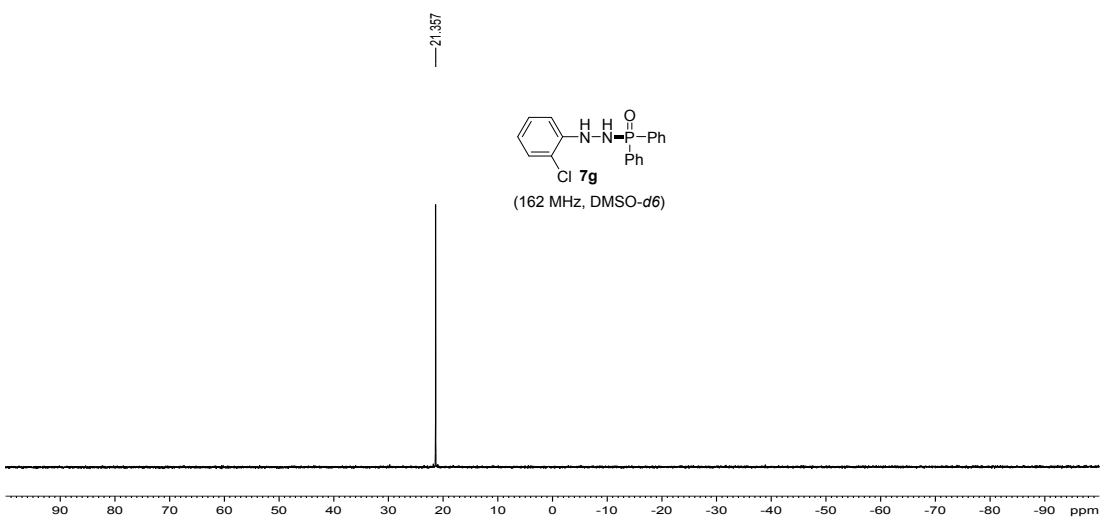
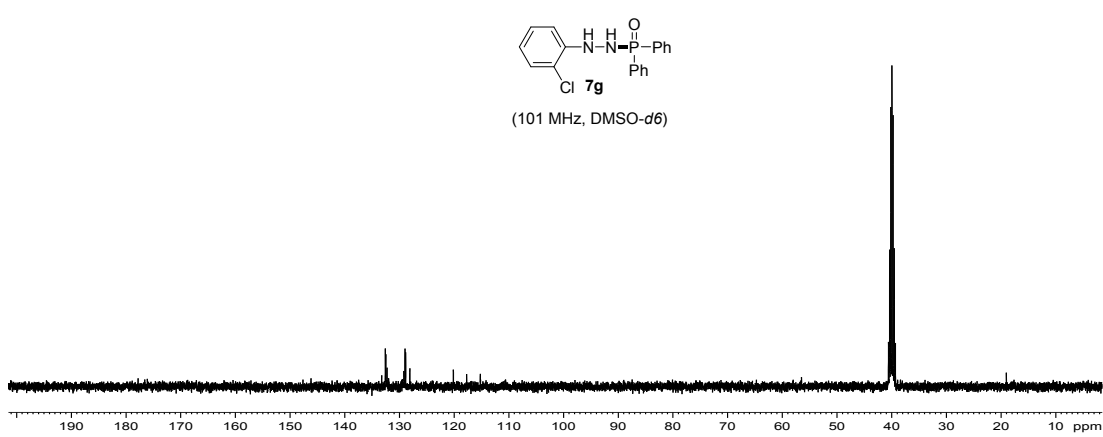
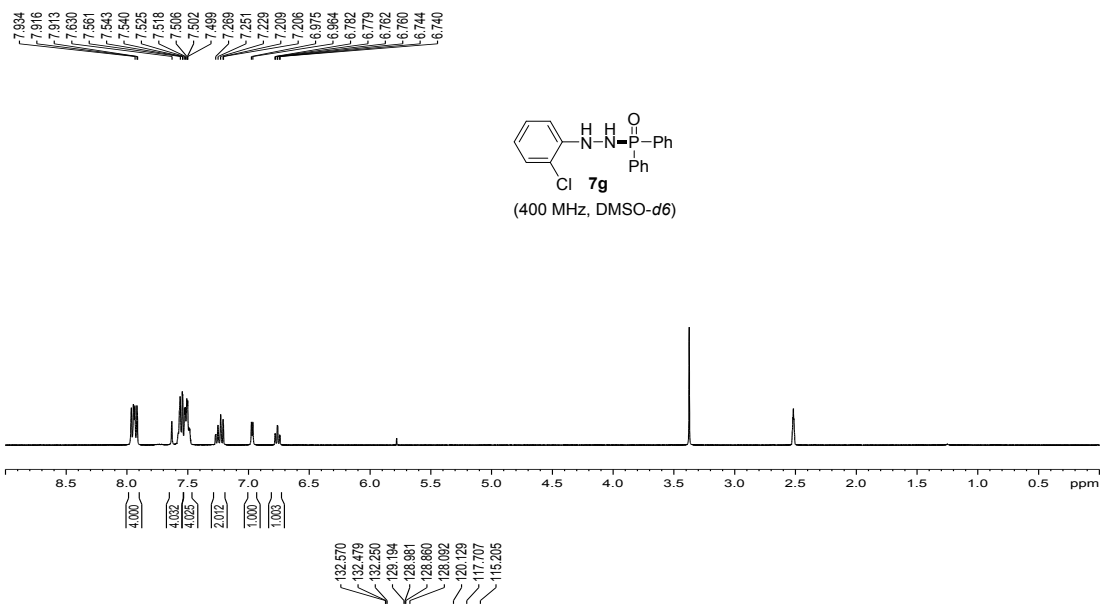




7.539  
7.535  
7.522  
7.514  
7.511  
7.506  
7.495  
7.492  
7.488  
7.479  
7.473  
7.467  
7.462  
7.441  
7.045  
7.032  
7.015  
7.009  
7.001  
6.995  
6.979  
6.957

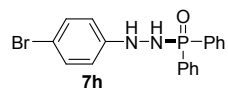




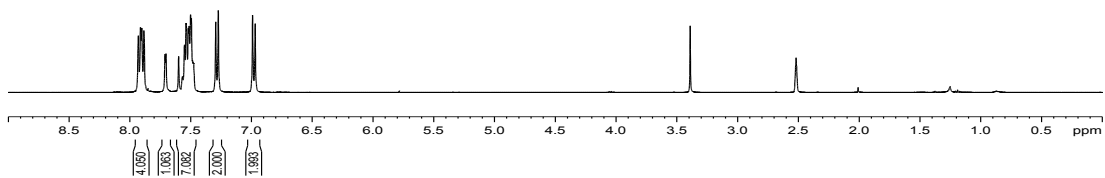




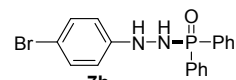
7.909  
7.901  
7.883  
7.770  
7.702  
7.598  
7.566  
7.549  
7.537  
7.534  
7.518  
7.511  
7.499  
7.492  
7.483  
7.479  
7.476  
7.294  
7.272  
6.991  
6.969



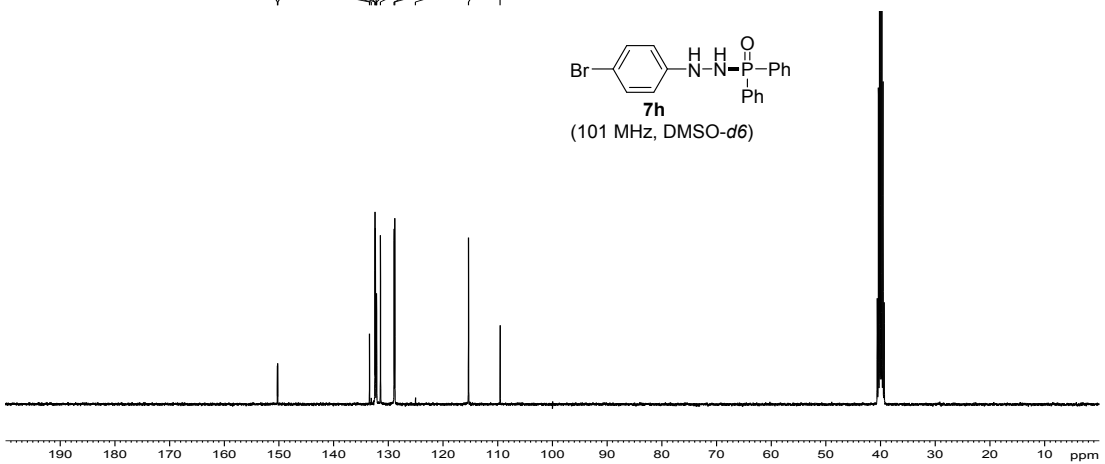
(400 MHz, DMSO-*d*<sub>6</sub>)



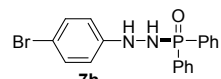
150.271  
150.220  
133.485  
133.138  
132.467  
132.377  
132.187  
132.157  
131.453  
128.855  
128.836  
123.051  
115.361  
108.566



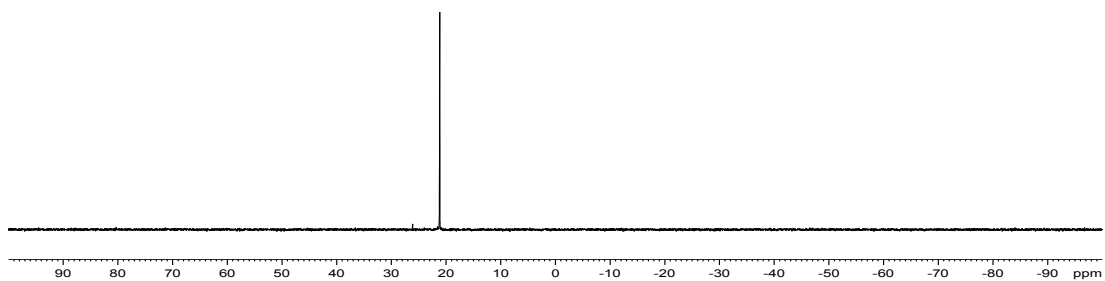
(101 MHz, DMSO-*d*<sub>6</sub>)

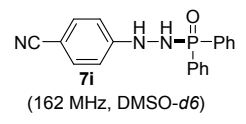
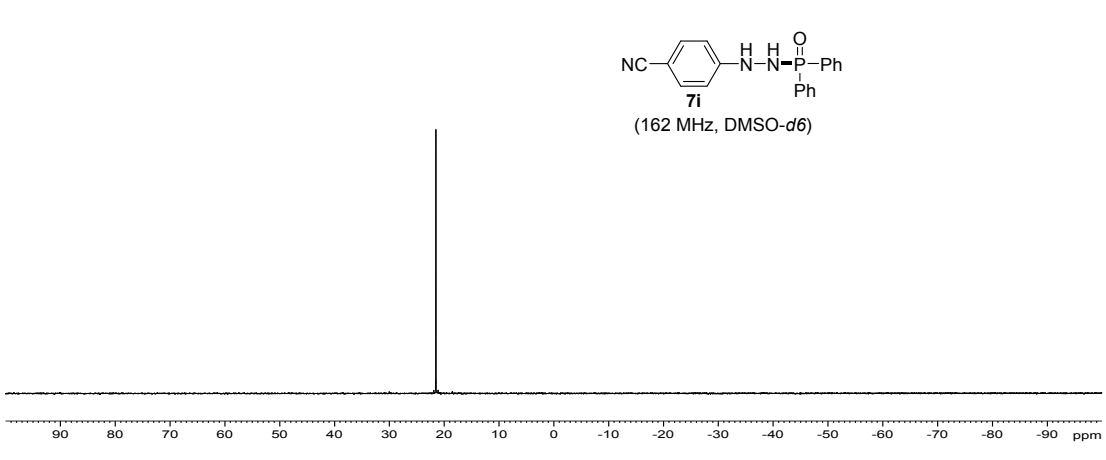
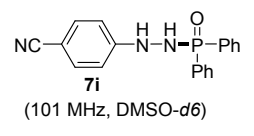
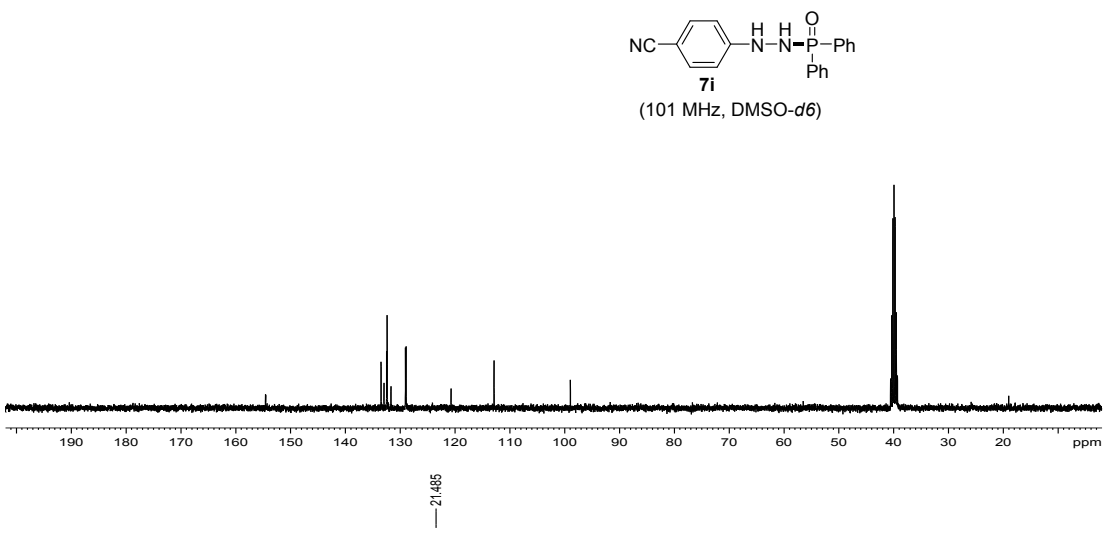
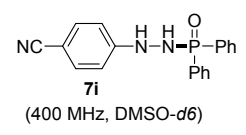
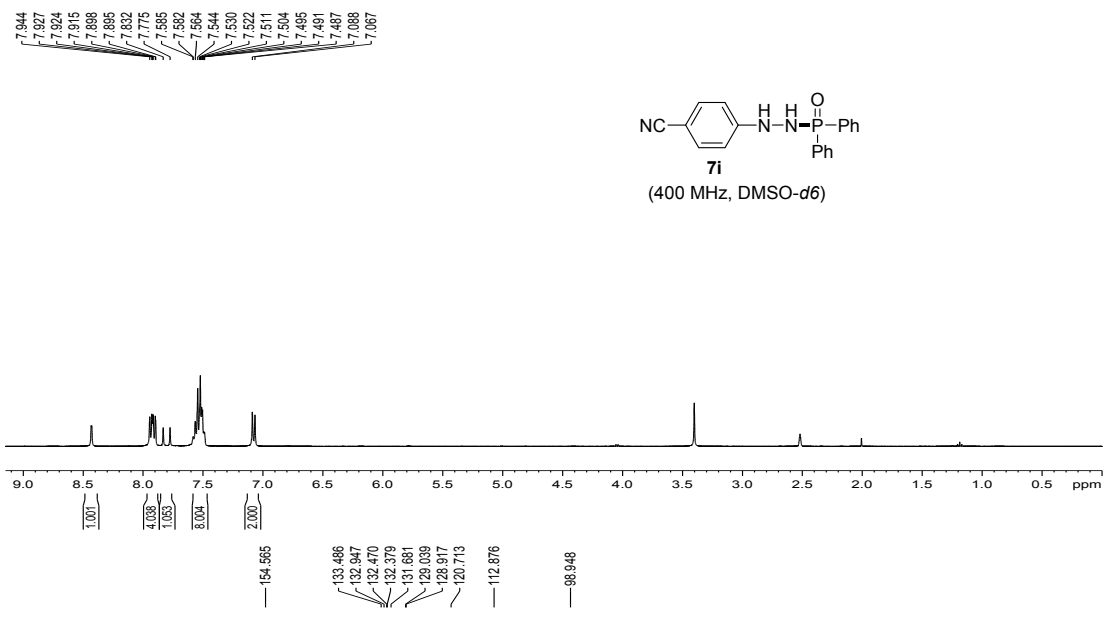


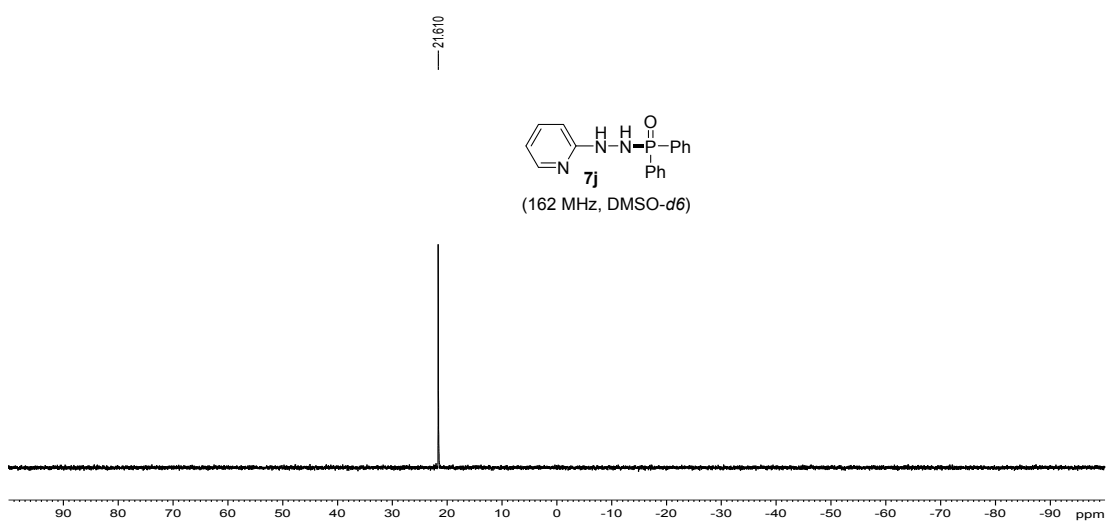
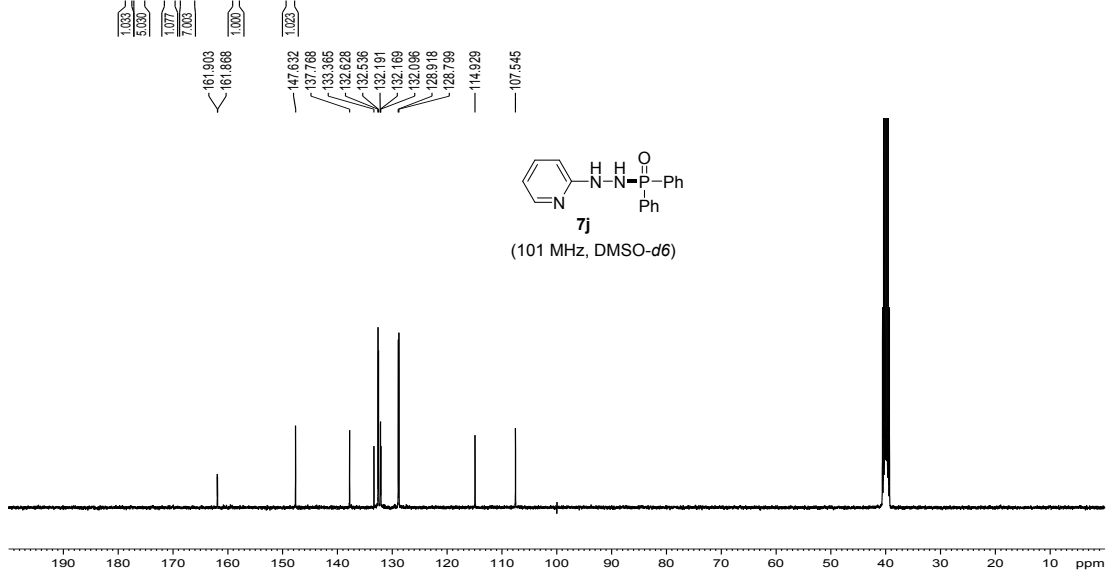
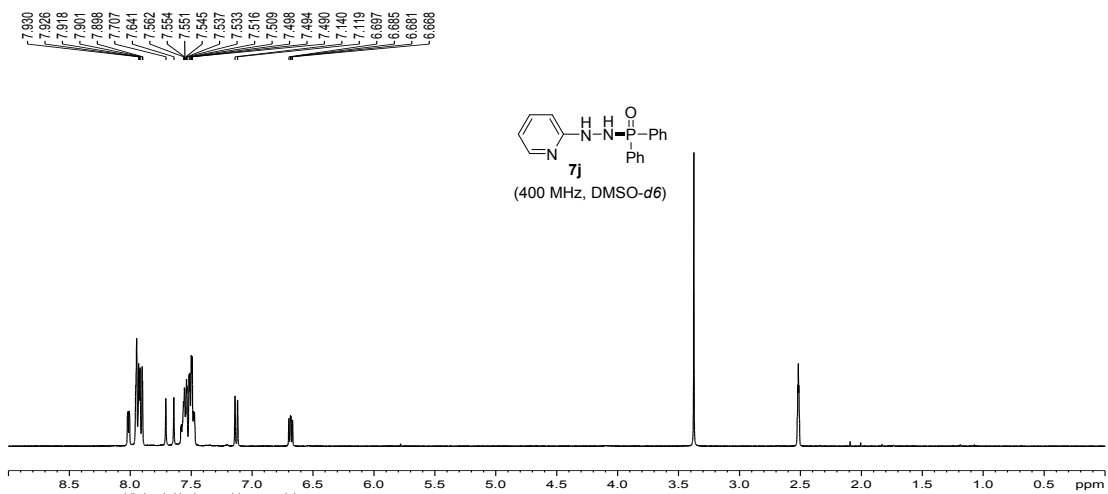
21.134



(162 MHz, DMSO-*d*<sub>6</sub>)







## 10. References

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