

# Supporting Information for

## BF<sub>3</sub>-Promoted Reactions of $\alpha$ -Amino Acetals with Alkynes to 2,5-Disubstituted Pyrroles

Zhi-Yuan Gao,<sup>a</sup> Yu He,<sup>a</sup> Lan-Yang Li,<sup>a</sup> Jie-Sheng Tian,<sup>b\*</sup> and Teck-Peng Loh<sup>a,c\*</sup>

<sup>a</sup> School of Chemistry and Molecular Engineering, Nanjing Tech University (NanjingTech), Nanjing 211816, P. R. China.

<sup>b</sup> School of Chemistry and Chemical Engineering, Northwestern Polytechnical University (NPU), Xi'an 710072, China.

<sup>c</sup> School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371.

Email: tjs@nwpu.edu.cn; teckpeng@ntu.edu.sg

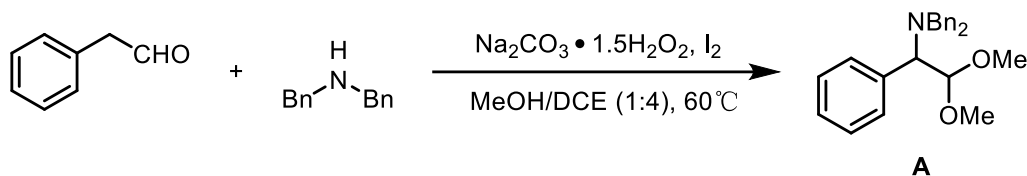
### Table of contents

1. General Information.....	2
2. General Procedure for the Synthesis of $\alpha$ -Amino Acetals.....	3
3. Optimization Study .....	12
4. Procedure for BF <sub>3</sub> -Promoted Cyclization for Pyrrole Synthesis .....	13
5. Synthesis of 2,5-Diphenylpyrrole <b>3a</b> on 1 mmol Scale.....	32
6. References.....	33
7. <sup>1</sup> H, <sup>13</sup> C and <sup>19</sup> F NMR data.....	34

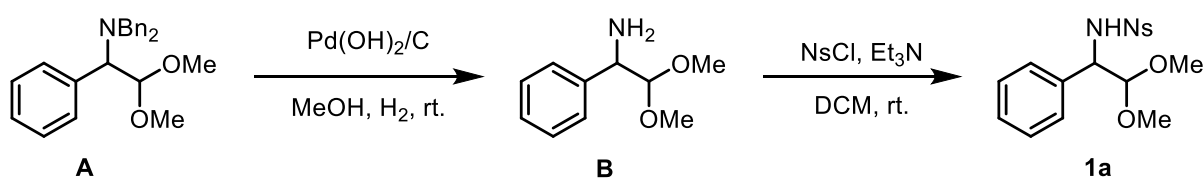
## 1. General Information

All reactions were carried out without exclusion of air or moisture. Boron trifluoride etherate were purchased from commercial suppliers, and used directly as received. Commercial solvents and reagents were used without further purification.  $\alpha$ -Amino acetal were prepared according to the reported procedures. Reactions were monitored through thin layer chromatography [Merck 60 F254 precoated silica gel plate (0.2 mm thickness)]. Subsequent to elution, spots were visualized using UV radiation (254 nm) on Spectroline Model ENf-24061/F 254 nm. Flash chromatography was performed using Merck silica gel 60 with distilled solvents. HRMS spectra were recorded on a Waters Q-Tof Premier Spectrometer.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on Bruker Avance or Joel 400 MHz spectrophotometer ( $\text{CDCl}_3$  as solvent). Chemical shifts for  $^1\text{H}$  NMR spectra are reported as  $\delta$  in units of parts per million (ppm) downfield from  $\text{SiMe}_4$  ( $\delta$  0.0) and relative to the signal of chloroform ( $\delta$  7.260, singlet). Multiplicities were given as: s (singlet); brs (broad singlet); d (doublet); t (triplet); q (quartet); dd (doublets of doublet); m (multiplets); and etc. Coupling constants are reported as a  $J$  value in Hz. Carbon nuclear magnetic resonance spectra ( $^{13}\text{C}$  NMR) are reported as  $\delta$  in units of parts per million (ppm) downfield from  $\text{SiMe}_4$  ( $\delta$  0.0) and relative to the signal of chloroform-d ( $\delta$  77.00, triplet).

## 2. General Procedure for the Synthesis of $\alpha$ -Amino Acetals<sup>[1]</sup>



Iodine (0.51 g, 2 mmol, 0.2 equiv) was added to a mixture of sodium percarbonate (1.57 g, 10 mmol, 1.0 equiv), dibenzylamine (1.92 mL, 10 mmol), and phenylacetaldehyde (1.34 mL, 12 mmol, 1.2 equiv) in methanol (10 mL)/dichloroethane (40 mL) at room temperature. The mixture was stirred at  $40^\circ\text{C}$  until dibenzylamine was completely converted by TLC detection. The resulting reaction mixture was mixed with a small amount of silica gel and concentrated. The crude product was purified by flash column chromatography (silica gel; ethyl acetate or diethyl ether/hexane = 1:100, v/v) to afford the desired product **A** as the yellow solid (2.89 g, 80%).

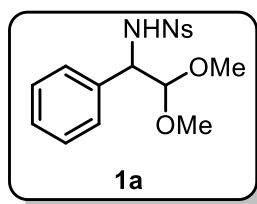


A mixture of product **A** (2.89 g, 8 mmol) and 20%wt  $\text{Pd}(\text{OH})_2/\text{C}$  (578 mg) in methanol (40 mL) was stirred 24 h under  $\text{H}_2$ . The reaction mixture was filtered over Celite with EtOAc. The solvent was removed under a reduced pressure and the residue was used for further reaction without purification<sup>[2]</sup>.

$\text{Et}_3\text{N}$  (2.43g, 24 mmol, 3.0 equiv) and 4-nitrobenzenesulfonyl chloride

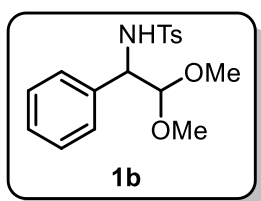
(1.77g, 8 mmol, 1.0 equiv) was sequentially added to a stirred solution of above residue in anhydrous dichloromethane (30 mL) at 0 °C. Then the resulting mixture was stirred overnight at room temperature until the completion of reaction. The resulting mixture was poured into an aqueous saturated solution of Na<sub>2</sub>CO<sub>3</sub> (25 mL), extracted with dichloromethane (2 × 30 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel using petroleum ether/ethyl acetate to obtain the pure product **1a**.

#### ***N*-(2,2-dimethoxy-1-phenylethyl)-4-nitrobenzenesulfonamide (1a)**



White solid; mp 123.8–125.4 °C; Prepared following the general procedure outlined above using phenylacetaldehyde. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.08 (m, 2H), 7.73 (m, 2H), 7.21–6.97 (m, 5H), 5.69 (d, *J* = 6.4 Hz, 1H), 4.55 (dd, *J* = 6.3, 4.4 Hz, 1H), 4.37 (d, *J* = 3.8 Hz, 1H), 3.33 (s, 3H), 3.27 (s, 3H) ppm; **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 149.5, 146.4, 135.8, 128.3, 128.3, 128.1, 127.9, 123.6, 105.8, 59.5, 55.8, 55.6 ppm; **HRMS (ESI) m/z:** [M+H]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>18</sub>N<sub>2</sub>O<sub>6</sub>S 367.0964; Found 367.0965.

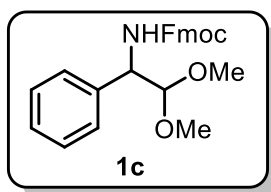
#### ***N*-(2,2-dimethoxy-1-phenylethyl)-4-methylbenzenesulfonamide (1b)**



White solid; mp 76.9–77.6 °C; Prepared following the general procedure outlined above using

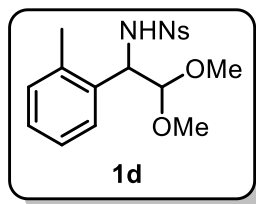
phenylacetaldehyde and tosyl chloride. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.57–7.44 (m, 2H), 7.18–7.12 (m, 5H), 7.11–7.07 (m, 2H), 5.40 (d, *J* = 5.8 Hz, 1H), 4.42–4.36 (m, 1H), 4.33 (d, *J* = 4.7 Hz, 1H), 3.29 (s, 3H), 3.23 (s, 3H), 2.34 (s, 3H) ppm; **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 142.9, 137.1, 136.4, 129.1, 128.0, 127.9, 127.6, 127.1, 106.1, 59.0, 55.9, 55.0, 21.4 ppm; **HRMS (ESI) m/z:** [M+H]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>21</sub>NO<sub>4</sub>S 336.1270; Found 336.1267. The spectroscopic data for this product match the literature data.<sup>[3]</sup>

**(9H-fluoren-9-yl)methyl 3,3-dimethoxy-2-phenylpropanoate (1c)**



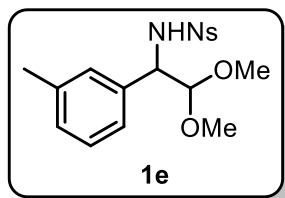
White solid; mp 75.4–76.6 °C; Prepared following the general procedure outlined above using phenylacetaldehyde and 9-fluorenylmethyl chloroformate. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.76 (d, *J* = 7.3 Hz, 2H), 7.60 (d, *J* = 5.6 Hz, 2H), 7.45–7.27 (m, 9H), 5.66 (d, *J* = 7.8 Hz, 1H), 4.91 (d, *J* = 8.1 Hz, 1H), 4.55–4.31 (m, 3H), 4.22 (s, 1H), 3.43 (s, 3H), 3.38 (s, 3H) ppm; **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 155.9, 143.9, 141.2, 128.4, 127.6, 127.6, 127.3, 127.0, 127.0, 125.0, 119.9, 106.1, 66.7, 56.5, 55.7, 55.7, 47.2 ppm; **HRMS (ESI) m/z:** [M+H]<sup>+</sup> Calcd for C<sub>25</sub>H<sub>25</sub>NO<sub>4</sub> 404.1862; Found 404.1865.

***N*-(2,2-dimethoxy-1-(*o*-tolyl)ethyl)-4-nitrobenzenesulfonamide (1d)**



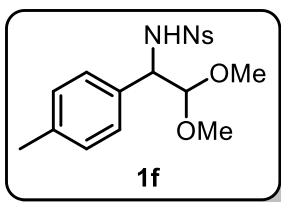
White solid; mp 138.6–139.6 °C; Prepared following the general procedure outlined above using (2-methylphenyl)acetaldehyde. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.12 – 7.99 (m, 2H), 7.76–7.60 (m, 2H), 7.11–6.96 (m, 2H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.86–6.74 (m, 1H), 5.65 (d, *J* = 5.8 Hz, 1H), 4.90 (dd, *J* = 5.8, 4.8 Hz, 1H), 4.35 (d, *J* = 4.7 Hz, 1H), 3.35 (s, 3H), 3.26 (s, 3H), 2.36 (s, 3H) ppm; **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 149.4, 146.4, 136.4, 134.1, 130.2, 128.1, 127.8, 127.5, 125.8, 123.5, 105.8, 56.1, 55.2, 55.1, 19.4 ppm; **HRMS (ESI) m/z:** [M+H]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>20</sub>N<sub>2</sub>O<sub>6</sub>S 381.1120; Found 381.1126.

***N*-(2,2-dimethoxy-1-(*m*-tolyl)ethyl)-4-nitrobenzenesulfonamide (1e)**



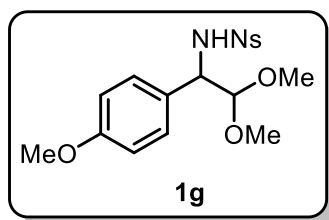
White solid; mp 134.3–135.1 °C; Prepared following the general procedure outlined above using (3-methylphenyl)acetaldehyde. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.17–7.90 (m, 2H), 7.81–7.59 (m, 2H), 7.11–6.85 (m, 3H), 6.81 (s, 1H), 5.58 (d, *J* = 5.9 Hz, 1H), 4.51 (m, 1H), 4.36 (d, *J* = 4.3 Hz, 1H), 3.34 (s, 3H), 3.28 (s, 3H), 2.15 (s, 3H) ppm; **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 149.4, 146.4, 137.9, 135.5, 128.8, 128.5, 128.3, 128.2, 125.2, 123.4, 105.7, 59.4, 55.7, 55.5, 21.2 ppm; **HRMS (ESI) m/z:** [M+H]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>20</sub>N<sub>2</sub>O<sub>6</sub>S 381.1120; Found 381.1125.

### ***N*-(2,2-dimethoxy-1-(*p*-tolyl)ethyl)-4-nitrobenzenesulfonamide (1f)**



White solid; mp 105.2–106.4 °C; Prepared following the general procedure outlined above using (4-methylphenyl)acetaldehyde. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.20–7.97 (m, 2H), 7.72 (m, 2H), 7.11–6.80 (m, 4H), 5.66 (d, *J* = 6.4 Hz, 1H), 4.50 (dd, *J* = 6.4, 4.4 Hz, 1H), 4.36 (d, *J* = 4.4 Hz, 1H), 3.33 (s, 3H), 3.27 (s, 3H), 2.24 (s, 3H) ppm; **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 149.3, 146.4, 138.0, 132.6, 128.9, 128.3, 127.9, 123.5, 105.7, 59.2, 55.7, 55.5, 20.9 ppm; **HRMS (ESI) m/z:** [M+H]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>20</sub>N<sub>2</sub>O<sub>6</sub>S 381.1120; Found 381.1114.

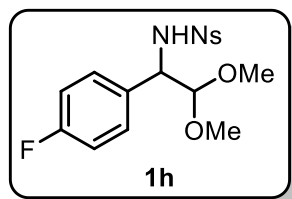
### ***N*-(2,2-dimethoxy-1-(4-methoxyphenyl)ethyl)-4-nitrobenzenesulfonamide (1g)**



White solid; mp 136.9–137.5 °C; Prepared following the general procedure outlined above using (4-methoxyphenyl)acetaldehyde. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.27–7.96 (m, 2H), 7.83–7.53 (m, 2H), 7.08–6.90 (m, 2H), 6.75–6.53 (m, 2H), 5.57 (d, *J* = 5.9 Hz, 1H), 4.49 (m, 1H), 4.34 (d, *J* = 4.4 Hz, 1H), 3.71 (s, 3H), 3.34 (s, 3H), 3.28 (s, 3H) ppm; **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 159.4, 149.5, 146.5, 129.2, 128.3, 127.7, 123.5, 113.6, 105.8, 58.9, 55.8, 55.6, 55.2 ppm; **HRMS (ESI) m/z:** [M+H]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>20</sub>N<sub>2</sub>O<sub>7</sub>S 397.1069; Found 397.1061.

***N*-(1-(4-fluorophenyl)-2,2-dimethoxyethyl)-4-nitrobenzenesulfonamid**

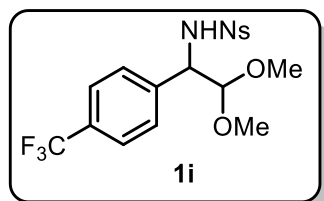
**e (1h)**



White solid; mp 116.4–117.1 °C; Prepared following the general procedure outlined above using (4-fluoro-phenyl)acetaldehyde. <sup>1</sup>H NMR

(400 MHz, CDCl<sub>3</sub>): δ 8.26–7.95 (m, 2H), 7.82–7.52 (m, 2H), 7.18–7.02 (m, 2H), 6.86–6.70 (m, 2H), 5.63 (d, *J* = 6.1 Hz, 1H), 4.51 (dd, *J* = 6.1, 4.2 Hz, 1H), 4.32 (d, *J* = 4.2 Hz, 1H), 3.33 (s, 3H), 3.26 (s, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 162.4 (d, *J* = 247.8 Hz), 149.6, 146.3, 131.8 (d, *J* = 3.4 Hz), 129.6 (d, *J* = 8.2 Hz), 128.3, 123.7, 115.2 (d, *J* = 21.6 Hz), 105.8, 58.8, 56.0, 55.8 ppm; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -113.2; HRMS (ESI) *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>17</sub>N<sub>2</sub>O<sub>6</sub>SF 385.0869; Found 385.0872.

***N*-(2,2-dimethoxy-1-(4-(trifluoromethyl)phenyl)ethyl)-4-nitrobenzene sulfonamide (1i)**



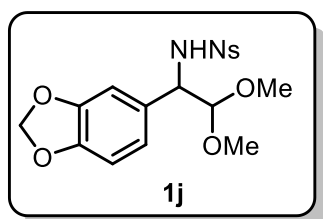
White solid; mp 126.3–126.9 °C; Prepared following the general procedure outlined above using (4-trifluoromethyl-phenyl)acetaldehyde. <sup>1</sup>H

NMR (400 MHz, CDCl<sub>3</sub>): δ 8.27–8.02 (m, 2H), 7.91–7.61 (m, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.8 Hz, 2H), 5.63 (d, *J* = 6.2 Hz, 1H), 4.57 (dd, *J* = 6.2, 4.2 Hz, 1H), 4.37 (d, *J* = 4.1 Hz, 1H), 3.34 (s, 3H), 3.28



(s, 3H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  149.7, 146.0, 140.0, 130.5, 130.2, 128.4, 128.3, 125.2 (q,  $J = 4.0$  Hz), 123.8, 105.5, 59.0, 56.1, 55.9 ppm;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -62.6; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{17}\text{N}_2\text{O}_6\text{SF}_3$  435.0837; Found 435.0837.

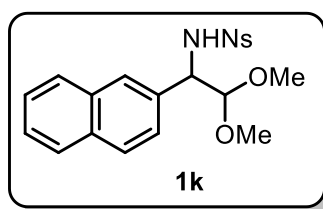
***N*-(1-(benzo[*d*][1,3]dioxol-5-yl)-2,2-dimethoxyethyl)-4-nitrobenzenesulfonamide (1j)**



Light yellow solid; mp 166.8–167.7 °C; Prepared following the general procedure outlined above using 2-(benzo[*d*][1,3]dioxol-5-yl)acetaldehyde.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.26–7.98 (m, 2H), 7.85–7.61 (m, 2H), 6.62 (s, 2H), 6.43 (s, 1H), 5.83 (d,  $J = 20.0$  Hz, 2H), 5.50 (d,  $J = 5.9$  Hz, 1H), 4.51–4.36 (m, 1H), 4.32 (d,  $J = 4.4$  Hz, 1H), 3.36 (s, 3H), 3.30 (s, 3H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  149.5, 147.5, 147.4, 146.4, 129.5, 128.4, 123.5, 122.2, 107.9, 107.8, 105.7, 101.2, 59.2, 55.8, 55.6 ppm; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_8\text{S}$  411.0862; Found 411.0866.

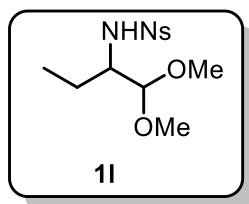
***N*-(2,2-dimethoxy-1-(naphthalen-2-yl)ethyl)-4-nitrobenzenesulfonamide (1k)**



Light yellow solid; mp 142.6–143.7 °C; Prepared following the general procedure outlined above

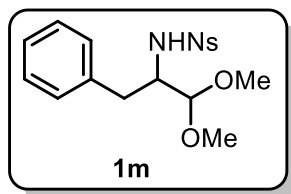
using 2-naphthaleneacetaldehyde. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.86–7.80 (m, 2H), 7.74–7.69 (m, 1H), 7.67–7.62 (m, 2H), 7.65–7.54 (m, 1H), 7.51–7.48 (m, 1H), 7.47–7.40 (m, 2H), 7.21 (dd, *J* = 8.5, 1.8 Hz, 1H), 5.79 (d, *J* = 6.3 Hz, 1H), 4.71 (dd, *J* = 6.2, 4.5 Hz, 1H), 4.49 (d, *J* = 4.5 Hz, 1H), 3.36 (s, 3H), 3.30 (s, 3H) ppm; **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 149.1, 146.2, 132.8, 132.7, 132.5, 128.1, 128.1, 127.7, 127.5, 127.4, 126.5, 126.4, 125.3, 123.3, 105.6, 59.6, 55.8, 55.4 ppm; **HRMS (ESI) m/z:** [M+H]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>20</sub>N<sub>2</sub>O<sub>6</sub>S 417.1120; Found 417.1113.

#### ***N*-(1,1-dimethoxybutan-2-yl)-4-nitrobenzenesulfonamide (1l)**



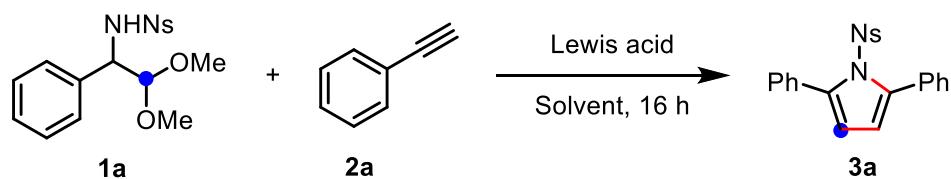
White solid; mp 105.4–106.1 °C; Prepared following the general procedure outlined above using butyraldehyde. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.49–8.21 (m, 2H), 8.08–8.03 (m, 2H), 4.94 (d, *J* = 8.8 Hz, 1H), 4.09 (d, *J* = 2.9 Hz, 1H), 3.33 (s, 3H), 3.32–3.28 (m, 1H), 3.17 (s, 3H), 1.70–1.52 (m, 1H), 1.49–1.38 (m, 1H), 0.85 (t, *J* = 7.5 Hz, 3H) ppm; **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 149.7, 147.3, 128.3, 123.9, 105.8, 57.8, 56.7, 55.9, 23.4, 10.2 ppm; **HRMS (ESI) m/z:** [M+H]<sup>+</sup> Calcd for C<sub>12</sub>H<sub>18</sub>N<sub>2</sub>O<sub>6</sub>S 319.0964; Found 319.0971.

#### ***N*-(1,1-dimethoxy-3-phenylpropan-2-yl)-4-nitrobenzenesulfonamide (1m)**



White solid; mp 113.2–114.7 °C; Prepared following the general procedure outlined above using phenylpropyl aldehyde. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.11–8.06 (m, 2H), 7.68–7.64 (m, 2H), 7.16–7.02 (m, 3H), 6.98 (dd, *J* = 7.7, 1.7 Hz, 2H), 4.93 (d, *J* = 8.8 Hz, 1H), 4.30 (d, *J* = 2.7 Hz, 1H), 3.65–3.53 (m, 1H), 3.46 (s, 3H), 3.38 (s, 3H), 2.96 (dd, *J* = 14.1, 5.1 Hz, 1H), 2.63 (dd, *J* = 14.1, 9.4 Hz, 1H) ppm; **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 149.4, 146.2, 137.2, 129.2, 128.5, 127.8, 126.5, 123.8, 105.8, 58.0, 57.0, 56.7, 35.3 ppm; **HRMS (ESI) m/z:** [M+H]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>20</sub>N<sub>2</sub>O<sub>6</sub>S 381.1120; Found 381.1126.

### 3. Optimization Study<sup>a</sup>

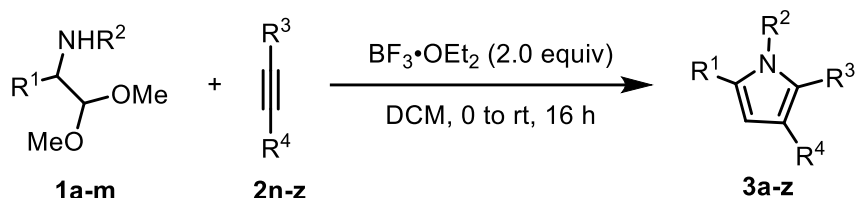


Entry	Mediator	Solvent	Temperature	Yield <sup>b</sup>
1	FeCl <sub>3</sub> (2.0 equiv)	DCM	RT	44%
2	TiCl <sub>4</sub> (2.0 equiv)	DCM	RT	52%
3	In(OTf) <sub>3</sub> (2.0 equiv)	DCM	RT	N.R.
4	TMSOTf (2.0 equiv)	DCM	RT	29%
5	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> (0.2 equiv)	DCM	RT	30%
6	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> (2.0 equiv)	DCM	RT	45%
7	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> (2.0 equiv)	DCM	50 °C	61%
8	BF <sub>3</sub> •OEt <sub>2</sub> (2.0 equiv)	DCM	RT	65%
9	BF <sub>3</sub> •OEt <sub>2</sub> (1.0 equiv)	DCM	RT	45%
10	BF <sub>3</sub> •OEt <sub>2</sub> (4.0 equiv)	DCM	RT	59%
11	BF <sub>3</sub> •OEt <sub>2</sub> (2.0 equiv)	DCM	0 °C	65%
12	BF <sub>3</sub> •OEt <sub>2</sub> (2.0 equiv)	DCM	50 °C	34%
13	BF <sub>3</sub> •OEt <sub>2</sub> (2.0 equiv)	DCM	0 °C to RT	78%
14	BF <sub>3</sub> •OEt <sub>2</sub> (2.0 equiv)	CH <sub>3</sub> CN	0 °C to RT	N.R.
15	BF <sub>3</sub> •OEt <sub>2</sub> (2.0 equiv)	THF	0 °C to RT	Trace
16	BF <sub>3</sub> •OEt <sub>2</sub> (2.0 equiv)	DCE	0 °C to RT	47%

<sup>a</sup>Conditions: *N*-Ns- $\alpha$ -amino acetal **1a** (0.2 mmol, 73 mg), phenyl acetylene **2a** (0.4 mmol, 41 mg), boron trifluoride etherate (0.4 mmol, 57 mg) in solvent (2.0 mL) under air atmosphere at 0 °C to rt for 16 h.

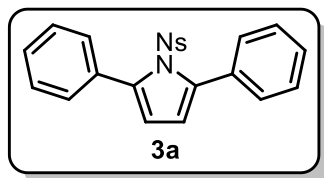
<sup>b</sup>Isolated yields. DCM = Dichloromethane. THF = Tetrahydrofuran. DCE = Dichloroethane.

## 4. Procedure for BF<sub>3</sub>-Promoted Cyclization for Pyrrole Synthesis



$\alpha$ -Amino acetal **1a-m** (0.2 mmol, 1.0 equiv), alkynes **2n-z** (0.4 mmol, 2.0 equiv) and boron trifluoride etherate (0.4 mmol, 2.0 equiv) was sequentially added to anhydrous dichloromethane (2 mL) at 0 °C. Then the resulting mixture was stirred overnight at room temperature until the completion of reaction. The resulting mixture was poured into an aqueous saturated solution of Na<sub>2</sub>CO<sub>3</sub> (10 mL), extracted with dichloromethane (2 × 10 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel using petroleum ether/ethyl acetate to obtain the pure product **3a-z**.

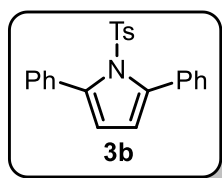
### 1-((4-Nitrophenyl)sulfonyl)-2,5-diphenyl-1H-pyrrole (**3a**)



This compound was prepared by the general procedure described above, affording the desired product **3a** as yellow solid (63 mg, 78% yield) through the purification by flash column chromatography (silica gel; ethyl acetate /hexane = 1/50, v/v). mp 183.1–185.4 °C.  $R_f$  = 0.5 (PE:EA =

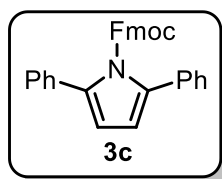
10:1); **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.16–8.12 (m, 2H), 7.54–7.50 (m, 4H), 7.48–7.42 (m, 6H), 7.38–7.33 (m, 2H), 6.32 (s, 2H) ppm; **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 150.3, 141.9, 141.3, 132.6, 129.4, 128.4, 128.2, 127.8, 123.4, 118.2 ppm; **HRMS (ESI) m/z:** [M+H]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>S 405.0909; Found 405.0907.

### 2,5-Diphenyl-1-tosyl-1H-pyrrole (3b)



This compound was prepared by the general procedure described above, affording the desired product **3b** as yellow solid (49 mg, 65% yield) through the purification by flash column chromatography (silica gel; ethyl acetate/hexane = 1/50, v/v). mp 138.2–139.1 °C. *R<sub>f</sub>* = 0.5 (PE:EA = 10:1); **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.54 (m, 4H), 7.50–7.33 (m, 6H), 7.08 (s, 4H), 6.27 (s, 2H), 2.36 (s, 3H) ppm; **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 144.3, 141.2, 134.5, 133.3, 129.6, 128.7, 127.9, 127.5, 126.9, 117.4, 21.5 ppm; **HRMS (ESI) m/z:** [M+H]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>19</sub>NO<sub>2</sub>S 374.1215; Found 374.1218.

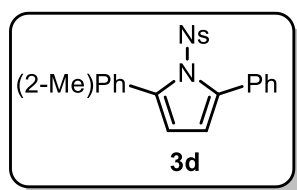
### (9H-fluoren-9-yl)methyl 2,5-diphenyl-1H-pyrrole-1-carboxylate (3c)



This compound was prepared by the general procedure described above, affording the desired product **3c** as yellow solid (60 mg, 68% yield) through the

purification by flash column chromatography (silica gel; ethyl acetate /hexane = 1/50, v/v). mp 136.2–137.7 °C.  $R_f$  = 0.5 (PE:EA = 10:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.74 (d,  $J$  = 7.6 Hz, 2H), 7.48 (m, 4H), 7.44–7.37 (m, 6H), 7.36–7.32 (m, 2H), 7.28–7.23 (m, 4H), 6.41 (s, 2H), 4.35 (d,  $J$  = 7.1 Hz, 2H), 3.70 (t,  $J$  = 7.1 Hz, 1H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  151.8, 143.0, 141.0, 136.6, 133.5, 128.4, 128.0, 127.7, 127.5, 127.0, 125.0, 119.8, 112.9, 69.3, 46.1 ppm; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{31}\text{H}_{23}\text{NO}_2$  442.1807; Found 442.1802.

### 1-((4-Nitrophenyl)sulfonyl)-2-phenyl-5-(*o*-tolyl)-1H-pyrrole (3d)

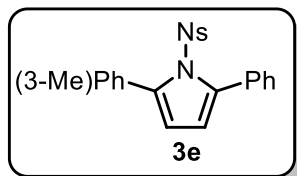


This compound was prepared by the general procedure described above, affording the desired product **3d** as yellow solid (57 mg, 68% yield)

through the purification by flash column chromatography (silica gel; ethyl acetate /hexane = 1/50, v/v). mp 168.1–168.9 °C.  $R_f$  = 0.5 (PE:EA = 10:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.24–8.07 (m, 2H), 7.52–7.47 (m, 2H), 7.46–7.42 (m, 3H), 7.41–7.37 (m, 2H), 7.35 (dd,  $J$  = 7.3, 1.3 Hz, 1H), 7.30 (d,  $J$  = 6.9 Hz, 1H), 7.28–7.22 (m, 1H), 7.16 (dd,  $J$  = 7.5, 1.2 Hz, 1H), 6.34 (d,  $J$  = 3.3 Hz, 1H), 6.23 (d,  $J$  = 3.3 Hz, 1H), 2.41 (s, 3H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.3, 142.9, 139.8, 139.1, 138.5, 132.5, 132.4, 130.3, 130.0, 129.9, 128.8, 128.3, 128.3, 127.7, 125.1, 123.6, 117.7, 117.5, 20.6 ppm; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for

C<sub>23</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>S 419.1066; Found 419.1069.

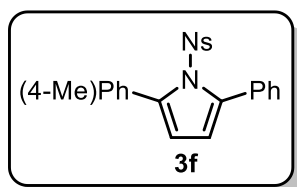
### 1-((4-Nitrophenyl)sulfonyl)-2-phenyl-5-(m-tolyl)-1H-pyrrole (3e)



This compound was prepared by the general procedure described above, affording the desired product **3e** as yellow solid (51 mg, 61% yield)

through the purification by flash column chromatography (silica gel; ethyl acetate /hexane = 1/50, v/v). mp 160.1–161.2 °C.  $R_f$  = 0.5 (PE:EA = 10:1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.16–8.12 (m, 2H), 7.50 (dd,  $J$  = 7.8, 2.0 Hz, 2H), 7.44 (ddd,  $J$  = 7.2, 4.2, 1.6 Hz, 3H), 7.38–7.34 (m, 2H), 7.34–7.29 (m, 3H), 7.26–7.22 (m, 1H), 6.30 (s, 1H), 2.45 (s, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 150.3, 142.1, 141.6, 141.2, 137.4, 132.6, 132.5, 130.1, 129.4, 129.2, 128.3, 128.3, 127.8, 127.7, 126.5, 123.3, 118.1, 118.0, 21.4 ppm; HRMS (ESI)  $m/z$ : [M+H]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>S 419.1066; Found 419.1064.

### 1-((4-Nitrophenyl)sulfonyl)-2-phenyl-5-(p-tolyl)-1H-pyrrole (3f)



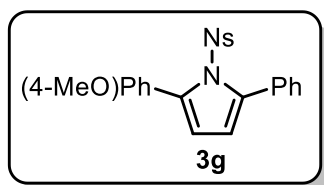
This compound was prepared by the general procedure described above, affording the desired product **3f** as yellow solid (58 mg, 69% yield)

through the purification by flash column chromatography (silica gel; ethyl acetate /hexane = 1/50, v/v). mp 170.2–171.3 °C.  $R_f$  = 0.5 (PE:EA =



10:1); **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.20–8.14 (m, 2H), 7.50 (dd, *J* = 6.6, 3.2 Hz, 2H), 7.44 (dt, *J* = 5.6, 2.8 Hz, 3H), 7.40 (dt, *J* = 9.1, 2.3 Hz, 2H), 7.35 (dd, *J* = 7.3, 1.4 Hz, 1H), 7.31 (d, *J* = 6.8 Hz, 1H), 7.28–7.23 (m, 1H), 7.17 (dd, *J* = 7.5, 1.2 Hz, 1H), 6.34 (d, *J* = 3.3 Hz, 1H), 6.23 (d, *J* = 3.2 Hz, 1H), 2.42 (s, 3H) ppm; **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 150.3, 142.9, 139.8, 139.1, 138.5, 132.5, 132.4, 130.3, 130.0, 129.9, 128.8, 128.3, 128.3, 127.7, 125.1, 123.6, 117.7, 117.5, 20.7 ppm; **HRMS (ESI) m/z:** [M+H]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>S 419.1066; Found 419.1059.

**2-(4-Methoxyphenyl)-1-((4-nitrophenyl)sulfonyl)-5-phenyl-1H-pyrrole (3g)**



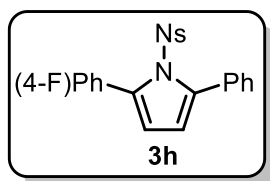
This compound was prepared by the general procedure described above, affording the desired product **3g** as yellow solid (30 mg, 34% yield)

through the purification by flash column chromatography (silica gel; ethyl acetate /hexane = 1/50, v/v). mp 152.3–153.4 °C. **R<sub>f</sub>** = 0.3 (PE:EA = 10:1); **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.16–8.10 (m, 2H), 7.51 (dd, *J* = 7.4, 2.3 Hz, 2H), 7.44 (dq, *J* = 7.2, 2.7, 2.1 Hz, 3H), 7.39–7.35 (m, 2H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.07 (dd, *J* = 8.6, 1.8 Hz, 2H), 6.96 (ddd, *J* = 8.3, 2.5, 0.8 Hz, 1H), 6.32 (d, *J* = 3.3 Hz, 1H), 6.30 (d, *J* = 3.3 Hz, 1H), 3.89 (s, 3H) ppm; **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 158.9, 150.3, 141.9, 141.4, 141.1, 133.8, 132.5, 129.4, 128.8, 128.4, 128.3, 127.8, 123.4, 121.8,

118.3, 118.1, 115.1, 113.9, 55.3 ppm; **HRMS (ESI) m/z:**  $[M+H]^+$  Calcd for  $C_{23}H_{18}N_2O_5S$  435.1015; Found 435.1021.

### 2-(4-Fluorophenyl)-1-((4-nitrophenyl)sulfonyl)-5-phenyl-1H-pyrrole

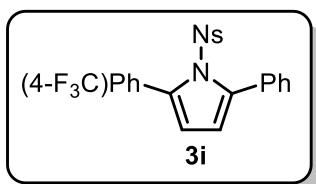
**(3h)**



This compound was prepared by the general procedure described above, affording the desired product **3h** as yellow solid (57 mg, 59% yield)

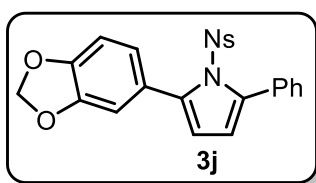
through the purification by flash column chromatography (silica gel; ethyl acetate /hexane = 1/50, v/v). mp 170.3–171.6 °C.  $R_f$  = 0.4 (PE:EA = 10:1);  **$^1H$  NMR (400 MHz,  $CDCl_3$ ):**  $\delta$  8.18–8.13 (m, 2H), 7.50–7.39 (m, 6H), 7.38–7.33 (m, 2H), 7.31 (dt,  $J$  = 7.7, 1.2 Hz, 1H), 7.27–7.22 (m, 1H), 7.12 (tdd,  $J$  = 8.4, 2.6, 1.0 Hz, 1H), 6.35 (d,  $J$  = 3.3 Hz, 1H), 6.30 (d,  $J$  = 3.3 Hz, 1H) ppm;  **$^{13}C$  NMR (100 MHz,  $CDCl_3$ ):**  $\delta$  163.4, 160.9, 150.4, 141.8 (d,  $J$  = 2.9 Hz), 140.0 (d,  $J$  = 2.8 Hz), 134.7 (d,  $J$  = 8.4 Hz), 132.2, 129.5, 129.4 (d,  $J$  = 8.5 Hz), 128.6, 128.2, 127.9, 125.0 (d,  $J$  = 3.1 Hz), 123.5, 119.0, 118.1, 116.2 (d,  $J$  = 22.7 Hz), 115.2 (d,  $J$  = 21.2 Hz) ppm;  **$^{19}F$  NMR (376 MHz,  $CDCl_3$ ):**  $\delta$  -112.5; **HRMS (ESI) m/z:**  $[M+H]^+$  Calcd for  $C_{22}H_{15}FN_2O_4S$  423.0815; Found 423.0821.

### 1-((4-Nitrophenyl)sulfonyl)-2-phenyl-5-(4-(trifluoromethyl)phenyl)-1H-pyrrole (3i)



This compound was prepared by the general procedure described above, affording the desired product **3i** as yellow solid (67 mg, 71% yield) through the purification by flash column chromatography (silica gel; ethyl acetate /hexane = 1/50, v/v). mp 178.3–179.1 °C.  $R_f$  = 0.4 (PE:EA = 10:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.2–8.1 (m, 2H), 7.7 (q,  $J$  = 8.4 Hz, 4H), 7.5 (m, 5H), 7.4–7.3 (m, 2H), 6.4 (d,  $J$  = 3.3 Hz, 1H), 6.3 (d,  $J$  = 3.3 Hz, 1H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.4, 142.3, 141.6, 139.8, 136.2, 132.0, 129.6, 129.3, 128.7, 128.2, 127.9, 125.4, 124.8 (q,  $J$  = 4.1 Hz), 123.5, 122.7, 119.7, 118.3 ppm;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -62.3; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{23}\text{H}_{15}\text{N}_2\text{O}_4\text{SF}_3$  473.0783; Found 473.0787.

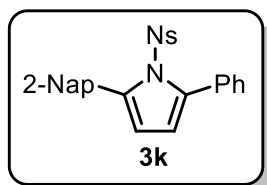
### 2-(Benzo[d][1,3]dioxol-5-yl)-1-((4-nitrophenyl)sulfonyl)-5-phenyl-1H-pyrrole (**3j**)



This compound was prepared by the general procedure described above, affording the desired product **3j** as yellow solid (33 mg, 37% yield) through the purification by flash column chromatography (silica gel; ethyl acetate /hexane = 1/50, v/v). mp 125.6–127.1 °C.  $R_f$  = 0.5 (PE:EA = 10:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.18–8.13 (m, 2H), 7.50–7.41 (m, 5H), 7.40–7.36 (m, 2H), 7.00 (d,  $J$  = 1.7 Hz, 1H), 6.93 (dd,  $J$  = 8.0, 1.7

Hz, 1H), 6.87 (d,  $J = 8.0$  Hz, 1H), 6.27 (d,  $J = 3.3$  Hz, 1H), 6.23 (d,  $J = 3.3$  Hz, 1H), 6.05(s, 2H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.3, 148.0, 147.2, 142.0, 141.1, 141.0, 132.7, 129.3, 128.3, 128.3, 127.8, 126.6, 123.4, 123.1, 118.2, 117.7, 110.1, 107.8, 101.4 ppm; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{23}\text{H}_{18}\text{N}_2\text{O}_6\text{S}$  451.0964; Found 451.0962.

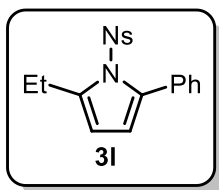
**2-(Naphthalen-2-yl)-1-((4-nitrophenyl)sulfonyl)-5-phenyl-1H-pyrrole (3k)**



This compound was prepared by the general procedure described above, affording the desired product **3k** as yellow solid (63 mg, 69% yield)

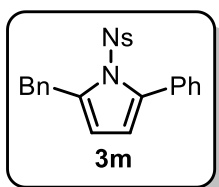
through the purification by flash column chromatography (silica gel; ethyl acetate /hexane = 1/50, v/v). mp 142.7–144.2 °C.  $R_f = 0.4$  (PE:EA = 10:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.12–8.08 (m, 2H), 7.94–7.88 (m, 4H), 7.71 (dd,  $J = 8.5, 1.7$  Hz, 1H), 7.59–7.53 (m, 4H), 7.52–7.41 (m, 3H), 7.37–7.33 (m, 2H), 6.42 (d,  $J = 3.3$  Hz, 1H), 6.35 (d,  $J = 3.3$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.2, 141.7, 141.5, 141.4, 132.9, 132.7, 132.5, 130.2, 129.4, 128.4, 128.2, 128.1, 127.8, 127.7, 127.7, 127.6, 127.2, 126.5, 126.5, 123.4, 118.9, 118.4 ppm; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{26}\text{H}_{18}\text{N}_2\text{O}_4\text{S}$  455.1066; Found 455.1060.

**2-Ethyl-1-((4-nitrophenyl)sulfonyl)-5-phenyl-1H-pyrrole (3l)**



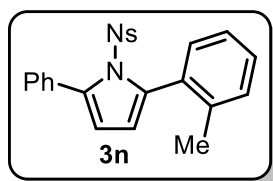
This compound was prepared by the general procedure described above, affording the desired product **3l** as yellow solid (39 mg, 55% yield) through the purification by flash column chromatography (silica gel; ethyl acetate /hexane = 1/50, v/v). mp 148.7–149.3 °C.  $R_f$  = 0.5 (PE:EA = 10:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.22–8.17 (m, 2H), 7.55–7.51 (m, 2H), 7.38–7.27 (m, 5H), 6.15–6.10 (m, 2H), 2.97 (qd,  $J$  = 7.4, 1.0 Hz, 2H), 1.33 (t,  $J$  = 7.4 Hz, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.2, 144.1, 141.5, 138.2, 132.4, 130.4, 128.2, 127.7, 127.4, 124.0, 116.5, 113.0, 23.0, 13.5 ppm; **HRMS (ESI) m/z**:  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_4\text{S}$  357.0909; Found 357.0904.

### 2-Benzyl-1-((4-nitrophenyl)sulfonyl)-5-phenyl-1H-pyrrole (3m)



This compound was prepared by the general procedure described above, affording the desired product **3m** as yellow solid (38 mg, 46% yield) through the purification by flash column chromatography (silica gel; ethyl acetate /hexane = 1/50, v/v). mp 161.1–162.9 °C.  $R_f$  = 0.5 (PE:EA = 10:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.18–7.98 (m, 2H), 7.51–7.18 (m, 12H), 6.13 (d,  $J$  = 3.3 Hz, 1H), 6.00 (d,  $J$  = 3.3 Hz, 1H), 4.33 (s, 2H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.1, 144.0, 138.5, 138.2, 138.0, 132.1, 130.8, 129.1, 128.5, 128.4, 127.9, 127.4, 126.6, 123.8, 116.1, 115.9, 35.6 ppm; **HRMS (ESI) m/z**:  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{23}\text{H}_{18}\text{N}_2\text{O}_4\text{S}$  419.1066; Found 419.1069.

### 1-((4-Nitrophenyl)sulfonyl)-2-phenyl-5-(*o*-tolyl)-1H-pyrrole (**3n**)

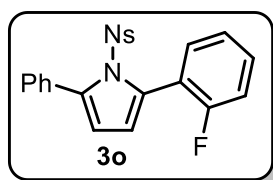


This compound was prepared by the general procedure described above, affording the desired product **3n** as yellow solid (52 mg, 62% yield)

through the purification by flash column chromatography (silica gel; ethyl acetate /hexane = 1/50, v/v). mp 168.9–169.8 °C.  $R_f$  = 0.5 (PE:EA = 10:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.19–8.15 (m, 2H), 7.52–7.49 (m, 2H), 7.44 (dd,  $J$  = 5.2, 2.1 Hz, 3H), 7.42–7.38 (m, 2H), 7.36 (dd,  $J$  = 7.3, 1.4 Hz, 1H), 7.33–7.23 (m, 2H), 7.17 (dd,  $J$  = 7.5, 1.2 Hz, 1H), 6.35 (d,  $J$  = 3.2 Hz, 1H), 6.24 (d,  $J$  = 3.3 Hz, 1H), 2.42 (s, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.3, 142.9, 139.8, 139.1, 138.5, 132.5, 132.4, 130.3, 130.0, 129.9, 128.8, 128.3, 128.3, 127.7, 125.1, 123.6, 117.7, 117.5, 20.6 ppm; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{23}\text{H}_{18}\text{N}_2\text{O}_4\text{S}$  419.1066; Found 419.1061.

### 2-(2-Fluorophenyl)-1-((4-nitrophenyl)sulfonyl)-5-phenyl-1H-pyrrole

(**3o**)

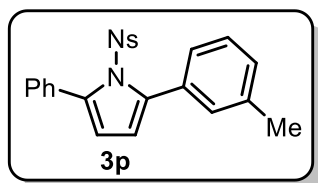


This compound was prepared by the general procedure described above, affording the desired product **3o** as yellow solid (59 mg, 70% yield)

through the purification by flash column chromatography (silica gel;

ethyl acetate /hexane = 1/50, v/v). mp 180.4–181.5 °C.  $R_f$  = 0.4 (PE:EA = 10:1);  **$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.18–8.10 (m, 2H), 7.50–7.40 (m, 7H), 7.36 (d,  $J$  = 8.4 Hz, 2H), 7.25 (d,  $J$  = 7.2 Hz, 1H), 7.20 (d,  $J$  = 9.2 Hz, 1H), 6.42 (d,  $J$  = 3.3 Hz, 1H), 6.31 (dd,  $J$  = 3.3, 0.5 Hz, 1H) ppm;  **$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  161.2, 158.8, 150.3, 142.5, 133.8, 132.0, 131.6 (d,  $J$  = 2.6 Hz), 130.3, 130.2, 129.9, 128.6, 128.2, 127.7, 123.6, 121.1 (d,  $J$  = 14.1 Hz), 119.1 (d,  $J$  = 2.0 Hz), 117.6, 115.5 (d,  $J$  = 21.9 Hz) ppm;  **$^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ ):**  $\delta$  -113.0; **HRMS (ESI)  $m/z$ :**  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{22}\text{H}_{15}\text{FN}_2\text{O}_4\text{S}$  423.0815; Found 423.0818.

### 1-((4-Nitrophenyl)sulfonyl)-2-phenyl-5-(*m*-tolyl)-1H-pyrrole (**3p**)

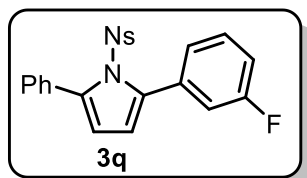


This compound was prepared by the general procedure described above, affording the desired product **3p** as yellow solid (45 mg, 54% yield)

through the purification by flash column chromatography (silica gel; ethyl acetate /hexane = 1/50, v/v). mp 160.4–161.5 °C.  $R_f$  = 0.5 (PE:EA = 10:1);  **$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.16–8.12 (m, 2H), 7.50 (dd,  $J$  = 7.7, 2.0 Hz, 2H), 7.47–7.41 (m, 3H), 7.38–7.31 (m, 5H), 7.26–7.22 (m, 1H), 6.30 (s, 2H), 2.45 (s, 3H) ppm;  **$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  150.3, 142.0, 141.6, 141.2, 137.4, 132.6, 132.5, 130.1, 129.4, 129.2, 128.3, 128.3, 127.8, 127.7, 126.5, 123.3, 118.2, 118.0, 21.4 ppm; **HRMS (ESI)  $m/z$ :**  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{23}\text{H}_{18}\text{N}_2\text{O}_4\text{S}$  419.1066; Found 419.1070.

## 2-(3-Fluorophenyl)-1-((4-nitrophenyl)sulfonyl)-5-phenyl-1H-pyrrole

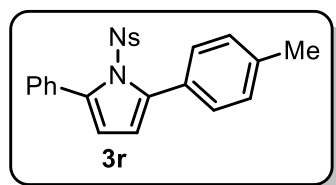
(3q)



This compound was prepared by the general procedure described above, affording the desired product **3q** as yellow solid (61 mg, 72% yield)

through the purification by flash column chromatography (silica gel; ethyl acetate /hexane = 1/50, v/v). mp 179.5–181.1 °C.  $R_f$  = 0.4 (PE:EA = 10:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.17–8.13 (m, 2H), 7.50–7.39 (m, 6H), 7.38–7.34 (m, 2H), 7.31 (dt,  $J$  = 7.7, 1.3 Hz, 1H), 7.27–7.23 (m, 1H), 7.12 (tdd,  $J$  = 8.4, 2.6, 1.0 Hz, 1H), 6.35 (d,  $J$  = 3.3 Hz, 1H), 6.30 (d,  $J$  = 3.3 Hz, 1H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  163.4, 160.9, 150.4, 141.9, 140.0, 134.7 (d,  $J$  = 8.5 Hz), 132.2, 129.5, 129.4 (d,  $J$  = 8.5 Hz), 128.6, 128.3, 127.9, 125.0 (d,  $J$  = 3.1 Hz), 123.5, 119.0, 118.1, 116.2 (d,  $J$  = 22.8 Hz), 115.2 (d,  $J$  = 21.1 Hz) ppm;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -113.2; **HRMS (ESI) m/z**:  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{22}\text{H}_{15}\text{FN}_2\text{O}_4\text{S}$  423.0815; Found 423.0809.

## 1-((4-Nitrophenyl)sulfonyl)-2-phenyl-5-(p-tolyl)-1H-pyrrole (3r)

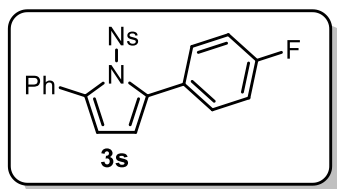


This compound was prepared by the general procedure described above, affording the desired product **3r** as yellow solid (55 mg, 66%



yield) through the purification by flash column chromatography (silica gel; ethyl acetate /hexane = 1/50, v/v). mp 170.5–171.9 °C.  $R_f$  = 0.5 (PE:EA = 10:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.17–8.12 (m, 2H), 7.53 (dd,  $J$  = 7.7, 1.7 Hz, 2H), 7.47–7.40 (m, 5H), 7.39–7.35 (m, 2H), 7.27 (d,  $J$  = 7.8 Hz, 2H), 6.31 (d,  $J$  = 3.3 Hz, 1H), 6.28 (d,  $J$  = 3.3 Hz, 1H), 2.46 (s, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.2, 141.9, 141.5, 141.0, 138.4, 132.7, 129.7, 129.3, 129.3, 128.5, 128.2, 128.2, 127.8, 123.3, 118.3, 117.8, 21.3 ppm; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{23}\text{H}_{18}\text{N}_2\text{O}_4\text{S}$  419.1066; Found 419.1065.

**2-(4-Fluorophenyl)-1-((4-nitrophenyl)sulfonyl)-5-phenyl-1H-pyrrole (3s)**

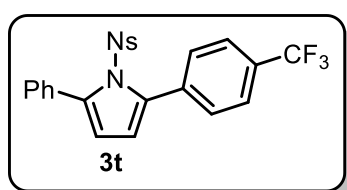


This compound was prepared by the general procedure described above, affording the desired product **3s** as yellow solid (71 mg, 84% yield)

through the purification by flash column chromatography (silica gel; ethyl acetate /hexane = 1/50, v/v). mp 169.7–170.4 °C.  $R_f$  = 0.4 (PE:EA = 10:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.18–8.12 (m, 2H), 7.54–7.46 (m, 4H), 7.46–7.41 (m, 3H), 7.37–7.32 (m, 2H), 7.17–7.10 (m, 2H), 6.31 (d,  $J$  = 3.3 Hz, 1H), 6.29 (d,  $J$  = 3.3 Hz, 1H). ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.1, 161.6, 150.4, 142.0, 141.3, 140.1, 132.5, 131.1 (d,  $J$  = 8.3 Hz), 129.4, 128.8 (d,  $J$  = 3.5 Hz), 128.5, 128.2, 127.9, 123.5, 118.1 (d,

$J = 1.9$  Hz), 114.9 (d,  $J = 21.8$  Hz) ppm;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -112.5; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{22}\text{H}_{15}\text{FN}_2\text{O}_4\text{S}$  423.0815; Found 423.0819.

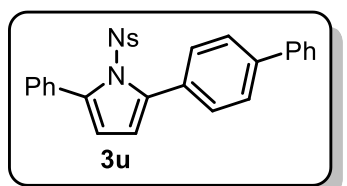
### 1-((4-Nitrophenyl)sulfonyl)-2-phenyl-5-(4-(trifluoromethyl)phenyl)-1H-pyrrole (3t)



This compound was prepared by the general procedure described above, affording the desired product **3t** as yellow solid (40 mg, 42%

yield) through the purification by flash column chromatography (silica gel; ethyl acetate /hexane = 1/50, v/v). mp 179.7–180.6 °C.  $R_f = 0.4$  (PE:EA = 10:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.17–8.13 (m, 2H), 7.73–7.64 (m, 4H), 7.49–7.42 (m, 5H), 7.36–7.31 (m, 2H), 6.41 (d,  $J = 3.3$  Hz, 1H), 6.32 (d,  $J = 3.3$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.5, 142.3, 141.8, 139.8, 136.2, 132.0, 130.2, 129.9, 129.6, 129.3, 128.8, 128.2, 127.9, 124.9 (q,  $J = 4.1$  Hz), 123.6, 119.7, 118.2 ppm;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -62.4 ; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{23}\text{H}_{15}\text{F}_3\text{N}_2\text{O}_4\text{S}$  473.0783; Found 473.0786.

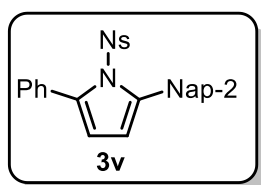
### 2-([1,1'-Biphenyl]-4-yl)-1-((4-nitrophenyl)sulfonyl)-5-phenyl-1H-pyrrole (3u)



This compound was prepared by the general

procedure described above, affording the desired product **3u** as yellow solid (67 mg, 70% yield) through the purification by flash column chromatography (silica gel; ethyl acetate /hexane = 1/50, v/v). mp 168.5–169.4 °C.  $R_f$  = 0.4 (PE:EA = 10:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.2–8.1 (m, 2H), 7.7 (m, 4H), 7.6–7.6 (m, 2H), 7.6–7.4 (m, 7H), 7.4–7.4 (m, 3H), 6.4 (d,  $J$  = 3.3 Hz, 1H), 6.3 (d,  $J$  = 3.3 Hz, 1H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.5, 142.1, 141.7, 141.3, 141.2, 140.4, 132.8, 131.7, 129.9, 129.6, 129.0, 128.6, 128.5, 128.0, 127.8, 127.2, 126.6, 123.6, 118.6, 118.5 ppm; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{28}\text{H}_{20}\text{N}_2\text{O}_4\text{S}$  480.1222; Found 480.1215.

**2-(Naphthalen-2-yl)-1-((4-nitrophenyl)sulfonyl)-5-phenyl-1H-pyrrole**  
**(3v)**



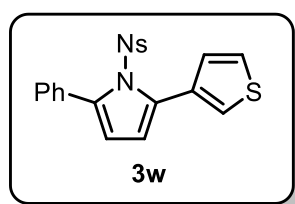
This compound was prepared by the general procedure described above, affording the desired product **3v** as yellow solid (51 mg, 56% yield)

through the purification by flash column chromatography (silica gel; ethyl acetate /hexane = 1/50, v/v). mp 142.7–143.9 °C.  $R_f$  = 0.4 (PE:EA = 10:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.14–8.07 (m, 2H), 7.95–7.88 (m, 4H), 7.71 (dd,  $J$  = 8.5, 1.7 Hz, 1H), 7.59–7.53 (m, 4H), 7.51–7.43 (m, 3H), 7.38–7.32 (m, 2H), 6.42 (d,  $J$  = 3.2 Hz, 1H), 6.35 (d,  $J$  = 3.2 Hz, 1H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.2, 141.7, 141.5, 141.4, 132.9,

132.7, 132.5, 130.2, 129.4, 128.4, 128.2, 128.1, 127.8, 127.7, 127.7, 127.6, 127.2, 126.5, 126.5, 123.4, 118.9, 118.4 ppm; **HRMS (ESI) m/z:**  $[M+H]^+$  Calcd for  $C_{26}H_{18}N_2O_4S$  455.1066; Found 455.1058.

### 1-((4-nitrophenyl)sulfonyl)-2-phenyl-5-(thiophen-3-yl)-1H-pyrrole

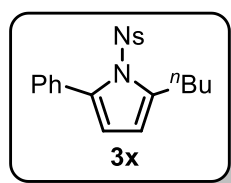
(3w)



This compound was prepared by the general procedure described above, affording the desired product **3w** as yellow solid (30 mg, 37% yield)

through the purification by flash column chromatography (silica gel; ethyl acetate /hexane = 1/50, v/v). mp 195.8–196.7 °C.  $R_f$  = 0.5 (PE:EA = 10:1);  **$^1H$  NMR (400 MHz,  $CDCl_3$ ):**  $\delta$  8.17–8.11 (m, 2H), 7.54–7.46 (m, 2H), 7.47–7.39 (m, 3H), 7.38–7.34 (m, 3H), 7.31 (dd,  $J$  = 3.0, 1.3 Hz, 1H), 7.24 (dd,  $J$  = 5.0, 1.3 Hz, 1H), 6.33–6.26 (m, 2H) ppm;  **$^{13}C$  NMR (100 MHz,  $CDCl_3$ ):**  $\delta$  150.3, 142.4, 140.7, 135.6, 132.9, 132.8, 129.5, 129.4, 128.4, 128.2, 127.8, 124.8, 124.5, 123.5, 117.8, 117.4 ppm; **HRMS (ESI) m/z:**  $[M+H]^+$  Calcd for  $C_{20}H_{14}N_2O_4S_2$  411.0474; Found 411.0470.

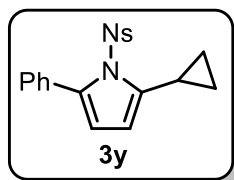
### 2-Butyl-1-((4-nitrophenyl)sulfonyl)-5-phenyl-1H-pyrrole (3x)



This compound was prepared by the general procedure described above, affording the desired product **3x** as

yellow solid (26 mg, 34% yield) through the purification by flash column chromatography (silica gel; ethyl acetate /hexane = 1/50, v/v). mp 122.9–123.9 °C.  $R_f$  = 0.5 (PE:EA = 10:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.22–8.16 (m, 2H), 7.55–7.49 (m, 2H), 7.37–7.31 (m, 3H), 7.28 (dd,  $J$  = 7.9, 1.7 Hz, 2H), 6.11 (q,  $J$  = 3.3 Hz, 2H), 2.97–2.89 (m, 2H), 1.73 (p,  $J$  = 7.5 Hz, 2H), 1.44 (dq,  $J$  = 14.6, 7.4 Hz, 2H), 0.98 (t,  $J$  = 7.4 Hz, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.2, 144.0, 140.4, 138.3, 132.4, 130.4, 128.2, 127.7, 127.5, 123.9, 116.6, 114.0, 31.6, 29.5, 22.4, 13.9 ppm; **HRMS (ESI)  $m/z$** :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_4\text{S}$  385.1222; Found 385.1226.

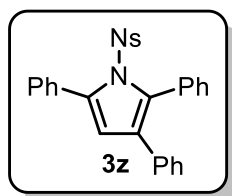
### 2-Cyclopropyl-1-((4-nitrophenyl)sulfonyl)-5-phenyl-1H-pyrrole (**3y**)



This compound was prepared by the general procedure described above, affording the desired product **3y** as yellow solid (22 mg, 30% yield) through the purification by flash column chromatography (silica gel; ethyl acetate /hexane = 1/50, v/v). mp 134.8–135.9 °C.  $R_f$  = 0.4 (PE:EA = 10:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.25–8.19 (m, 2H), 7.67–7.61 (m, 2H), 7.39–7.30 (m, 5H), 6.09 (d,  $J$  = 3.4 Hz, 1H), 5.91 (d,  $J$  = 3.4 Hz, 1H), 2.35 (ddd,  $J$  = 14.1, 8.5, 5.8 Hz, 1H), 1.03–0.89 (m, 2H), 0.66–0.49 (m, 2H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.2, 144.3, 141.6, 138.0, 132.5, 130.3, 128.2, 128.0, 127.5, 123.9, 116.0, 111.1, 9.9, 8.5 ppm;

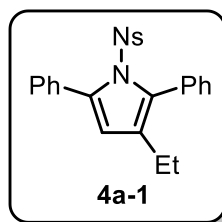
**HRMS (ESI) m/z:**  $[M+H]^+$  Calcd for  $C_{19}H_{16}N_2O_4S$  369.0909; Found 369.0905.

### 1-((4-Nitrophenyl)sulfonyl)-2,3,5-triphenyl-1H-pyrrole (**3z**)



This compound was prepared by the general procedure described above, affording the desired product **3z** as yellow solid (30 mg, 31% yield) through the purification by flash column chromatography (silica gel; ethyl acetate/hexane = 1/50, v/v). mp 236.2–237.9 °C.  $R_f$  = 0.5 (PE:EA = 10:1);  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  8.19–8.11 (m, 2H), 7.62–7.55 (m, 2H), 7.49–7.43 (m, 3H), 7.42–7.33 (m, 5H), 7.30–7.26 (m, 2H), 7.20–7.11 (m, 3H), 7.03–6.89 (m, 2H), 6.46 (s, 1H) ppm;  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  150.4, 143.0, 140.0, 134.7, 133.6, 132.8, 131.8, 131.3, 130.0, 129.7, 128.8, 128.6, 128.5, 128.4, 128.3, 128.0, 128.0, 127.2, 123.7, 119.6 ppm; **HRMS (ESI) m/z:**  $[M+H]^+$  Calcd for  $C_{24}H_{20}N_2O_4S$  481.1222 ; Found 481.1226.

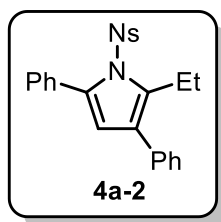
### 3-Ethyl-1-((4-nitrophenyl)sulfonyl)-2,5-diphenyl-1H-pyrrole (**4a-1**)



This compound was prepared by the general procedure described above, affording the desired product **4a-1** as yellow solid (43 mg, 50% yield) through the purification by flash column chromatography (silica

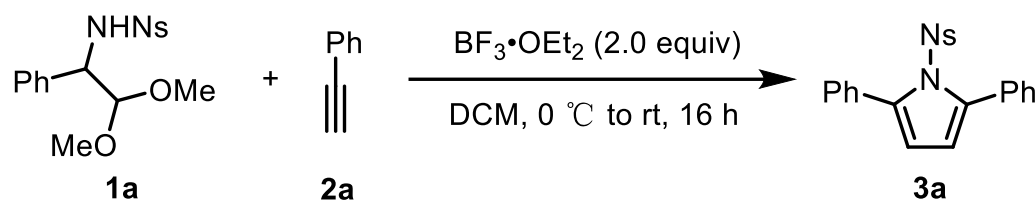
gel; ethyl acetate /hexane = 1/50, v/v). mp 230.6–231.9 °C.  $R_f$  = 0.4 (PE:EA = 10:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.19–8.14 (m, 2H), 7.55–7.51 (m, 2H), 7.50–7.38 (m, 6H), 7.39–7.36 (m, 4H), 6.28 (s, 1H), 2.30 (q,  $J$  = 7.6 Hz, 2H), 0.99 (t,  $J$  = 7.6 Hz, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.2, 142.3, 140.1, 134.8, 132.9, 132.7, 131.8, 130.6, 129.4, 128.2, 128.2, 128.1, 127.7, 127.6, 123.3, 119.6, 19.1, 14.5 ppm; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_4\text{S}$  433.1222; Found 433.1229.

### 2-Ethyl-1-((4-nitrophenyl)sulfonyl)-3,5-diphenyl-1H-pyrrole (4a-2)



This compound was prepared by the general procedure described above, affording the desired product **4a-2** as yellow solid (17 mg, 20% yield) through the purification by flash column chromatography (silica gel; ethyl acetate /hexane = 1/50, v/v). mp 225.3–226.7 °C.  $R_f$  = 0.1 (PE:EA = 10:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.28–8.23 (m, 2H), 8.01–7.97 (m, 2H), 7.78–7.72 (m, 1H), 7.52–7.44 (m, 3H), 7.37–7.29 (m, 4H), 7.24–7.21 (m, 2H), 7.03 (s, 1H), 2.46 (q,  $J$  = 7.6 Hz, 2H), 1.03 (t,  $J$  = 7.6 Hz, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.1, 145.2, 139.4, 138.4, 138.1, 134.0, 130.1, 129.5, 128.7, 128.4, 127.4, 126.4, 125.9, 125.3, 124.2, 120.8, 26.8, 15.8 ppm; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_4\text{S}$  433.1222; Found 433.1224.

## 5. Synthesis of 2,5-Diphenylpyrrole 3a on 1 mmol Scale



*N*-Ns- $\alpha$ -Amino acetal **1a** (366 mg, 1.0 mmol, 1.0 equiv), alkynes **2a** (204 mg, 2.0 mmol, 2.0 equiv) and boron trifluoride etherate (142 mg, 2.0 mmol, 2.0 equiv) was sequentially added to anhydrous dichloromethane (5 mL) at 0 °C. Then the resulting mixture was stirred overnight at room temperature until the completion of reaction. The resulting mixture was poured into an aqueous saturated solution of  $\text{Na}_2\text{CO}_3$  (20 mL), extracted with dichloromethane ( $2 \times 20$  mL), dried over  $\text{Na}_2\text{SO}_4$ , and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel; ethyl acetate /hexane = 1/50, v/v) to afford the desired product **3a** (246.4 mg, 61% yield).



## 6. References

- [1] J.-S. Tian, T.-P. Loh, Copper-catalyzed  $\alpha$ -amination of Aliphatic Aldehydes. *Chem. Commun.*, 2011, **47**, 5458-5460.
- [2] J.-S. Tian, K. W. J. Ng, J.-R. Wong, T.-P. Loh,  $\alpha$ -Amination of Aldehydes Catalyzed by In Situ Generated Hypoiodite. *Angew. Chem. Int. Ed.*, 2012, **51**, 9105-9109.
- [3] P. W. Davies, N. Martin, Counterion Effects in a Gold-Catalyzed Synthesis of Pyrroles from Alkynyl Aziridines. *Org. Lett.* 2009, **11**, 2293–2296.

## 7. $^1\text{H}$ , $^{13}\text{C}$ and $^{19}\text{F}$ NMR data

### *N*-(2,2-dimethoxy-1-phenylethyl)-4-nitrobenzenesulfonamide (**1a**)

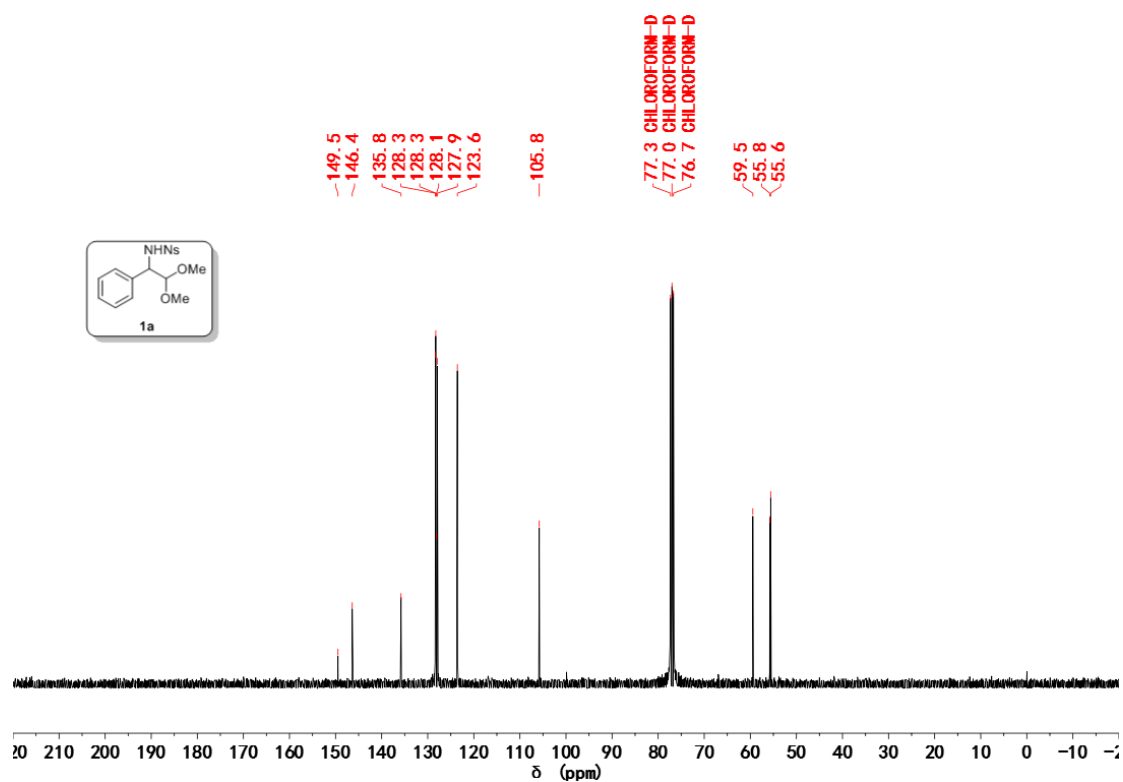
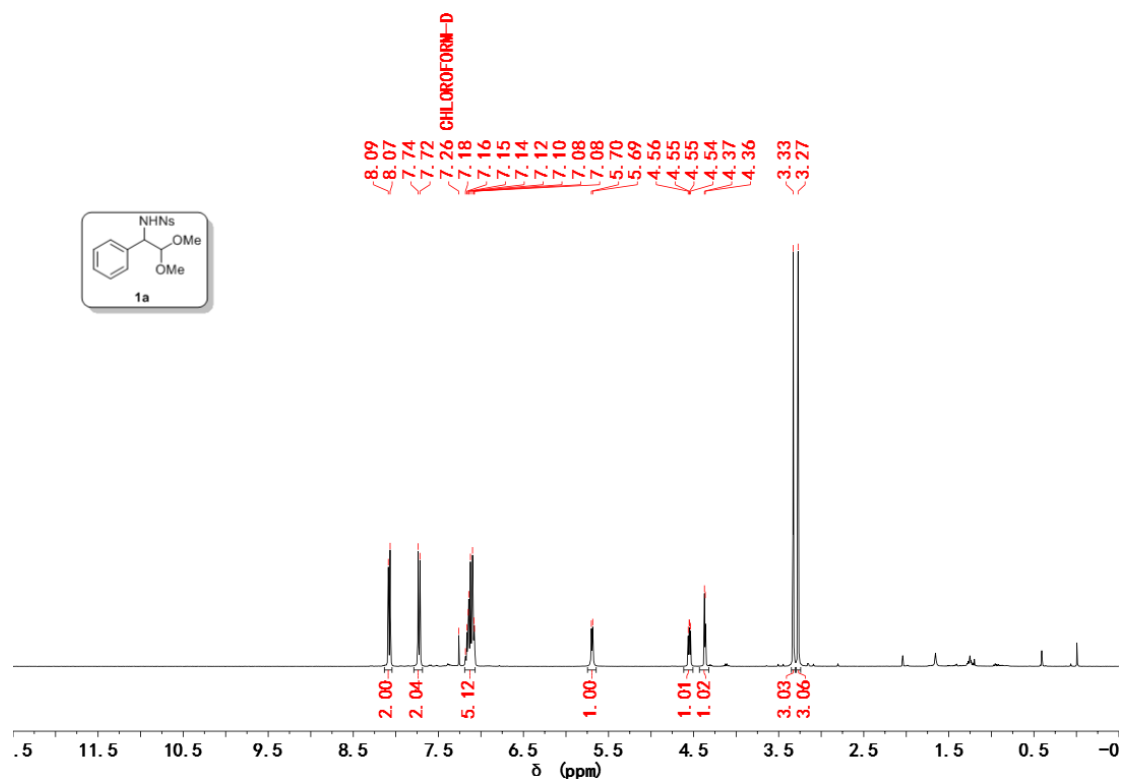


Figure S1.  $^1\text{H}$  NMR of **1a** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **1a** (100 MHz,  $\text{CDCl}_3$ )

# *N*-(2,2-dimethoxy-1-phenylethyl)-4-methylbenzenesulfonamide (**1b**)

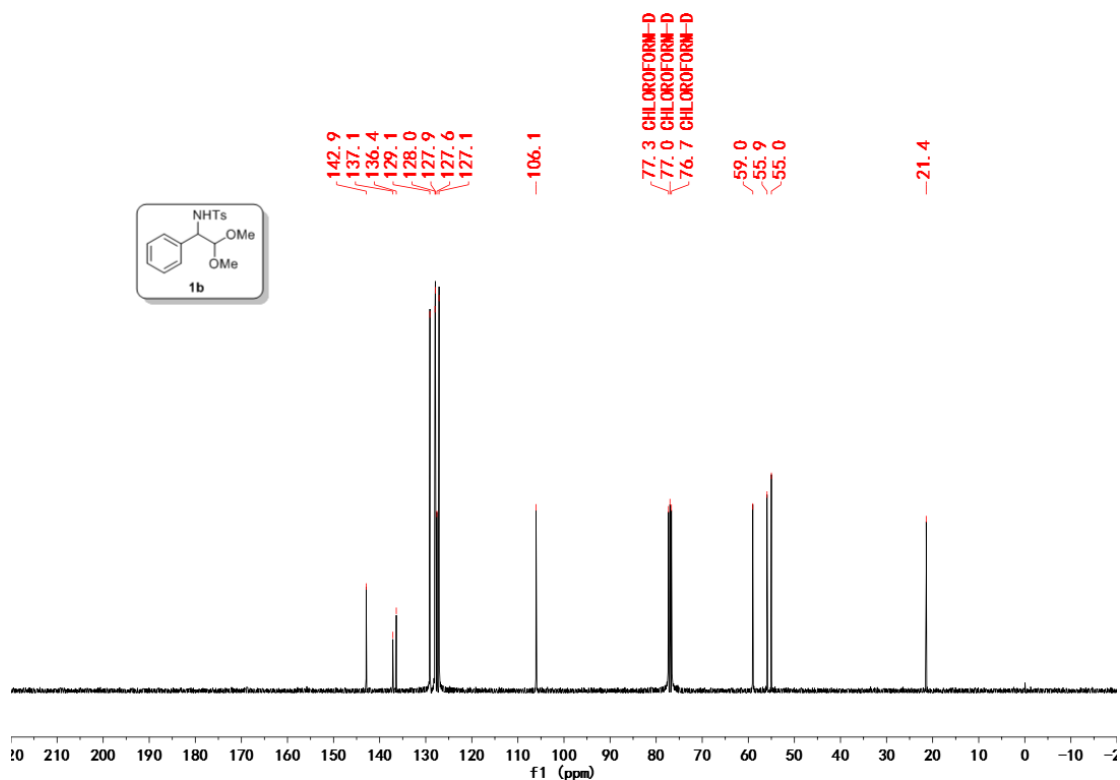
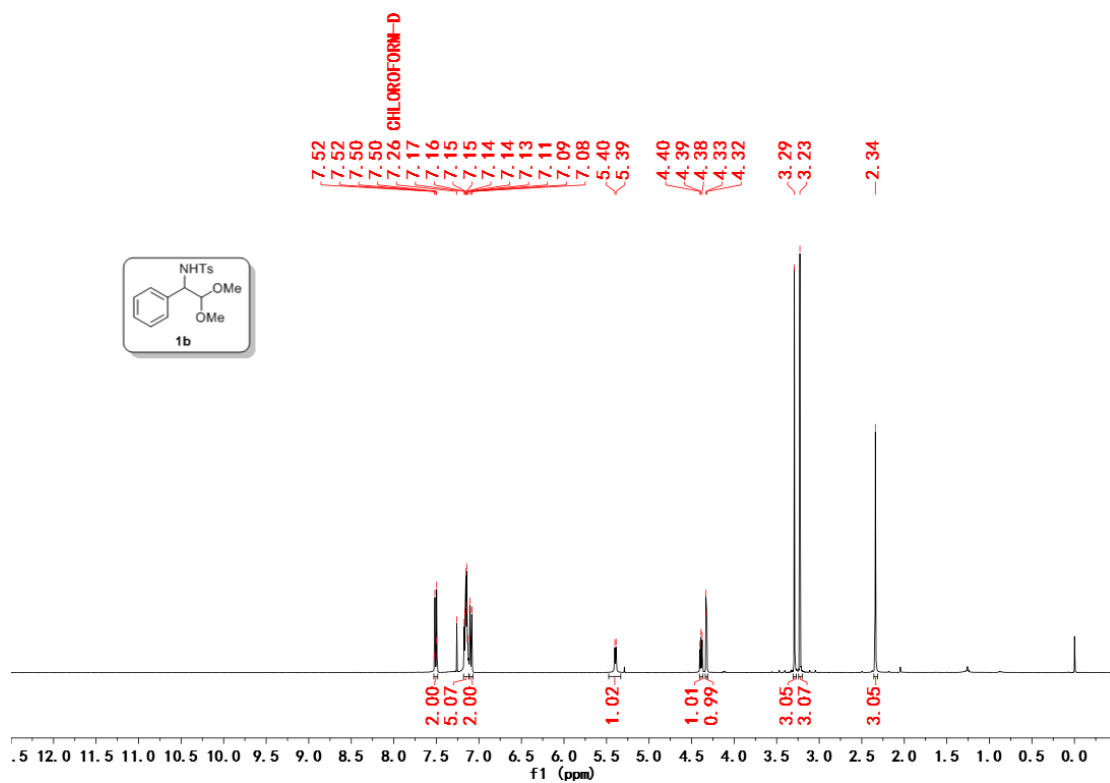


Figure S2. <sup>1</sup>H NMR of **1b** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **1b** (100 MHz, CDCl<sub>3</sub>)

# (9H-fluoren-9-yl)methyl 3,3-dimethoxy-2-phenylpropanoate (1c)

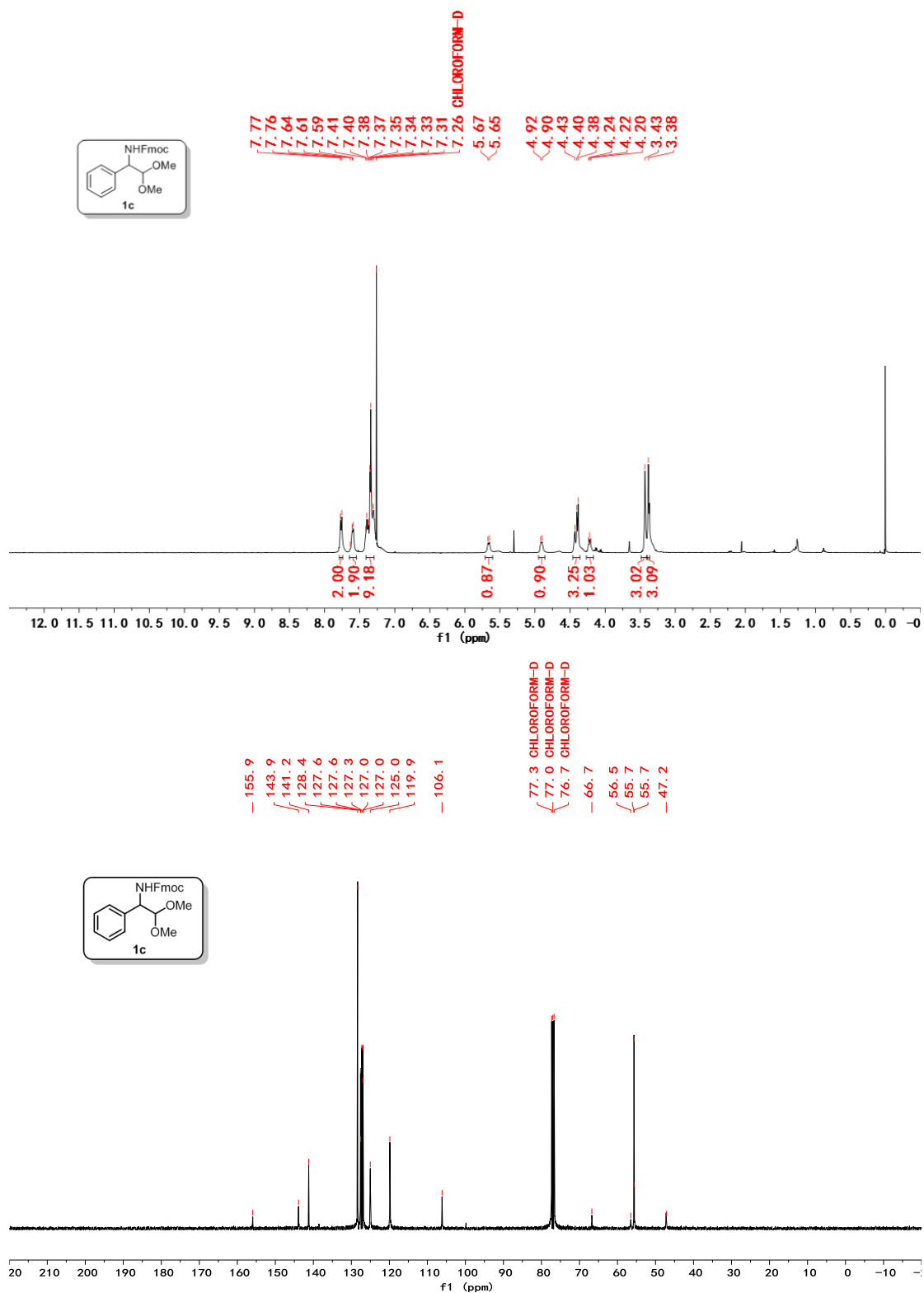


Figure S3. <sup>1</sup>H NMR of 1c (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of 1c (100 MHz, CDCl<sub>3</sub>)

# *N*-(2,2-dimethoxy-1-(*o*-tolyl)ethyl)-4-nitrobenzenesulfonamide (**1d**)

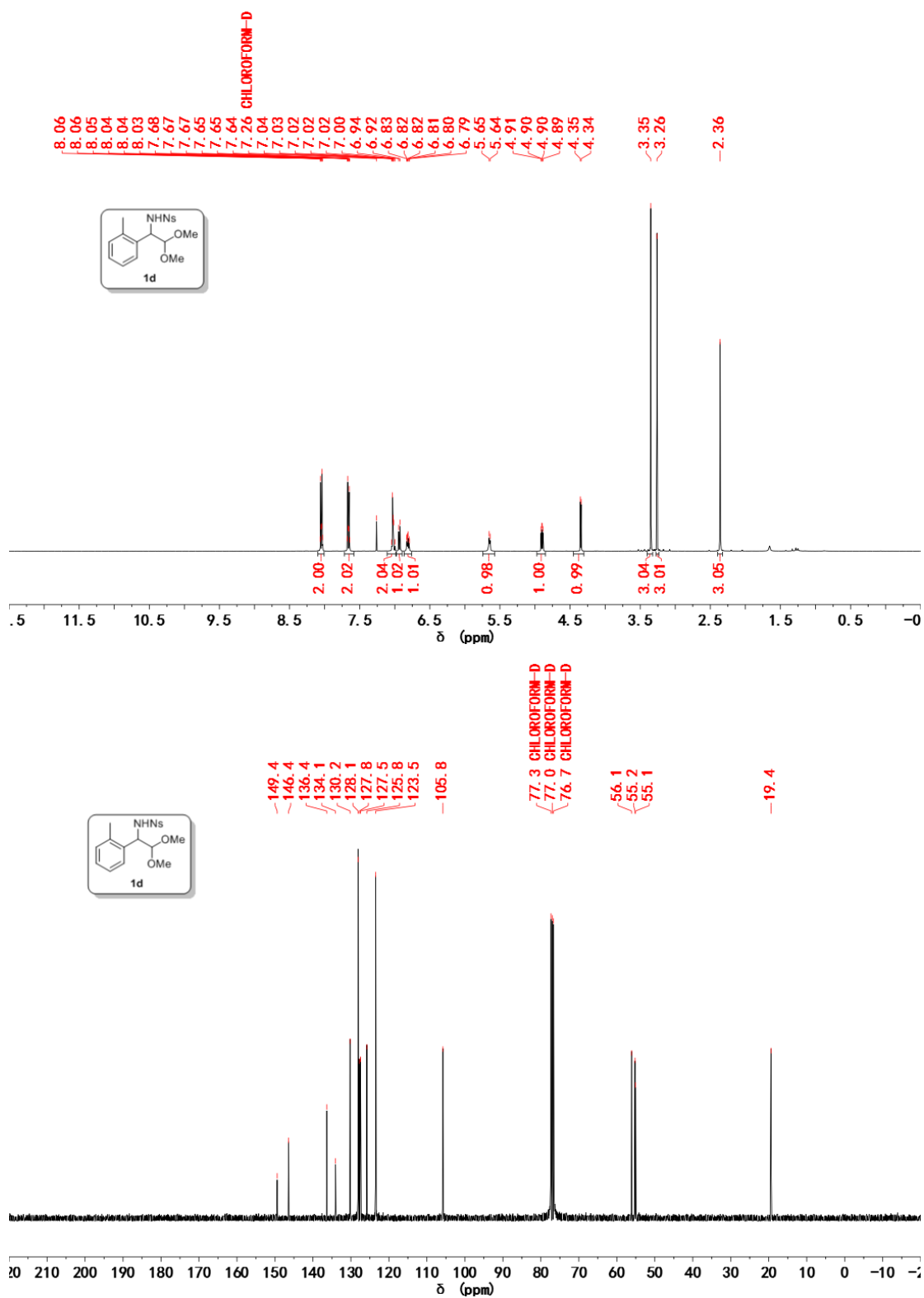


Figure S4. <sup>1</sup>H NMR of **1d** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **1d** (100 MHz, CDCl<sub>3</sub>)

# *N*-(2,2-dimethoxy-1-(*m*-tolyl)ethyl)-4-nitrobenzenesulfonamide (**1e**)

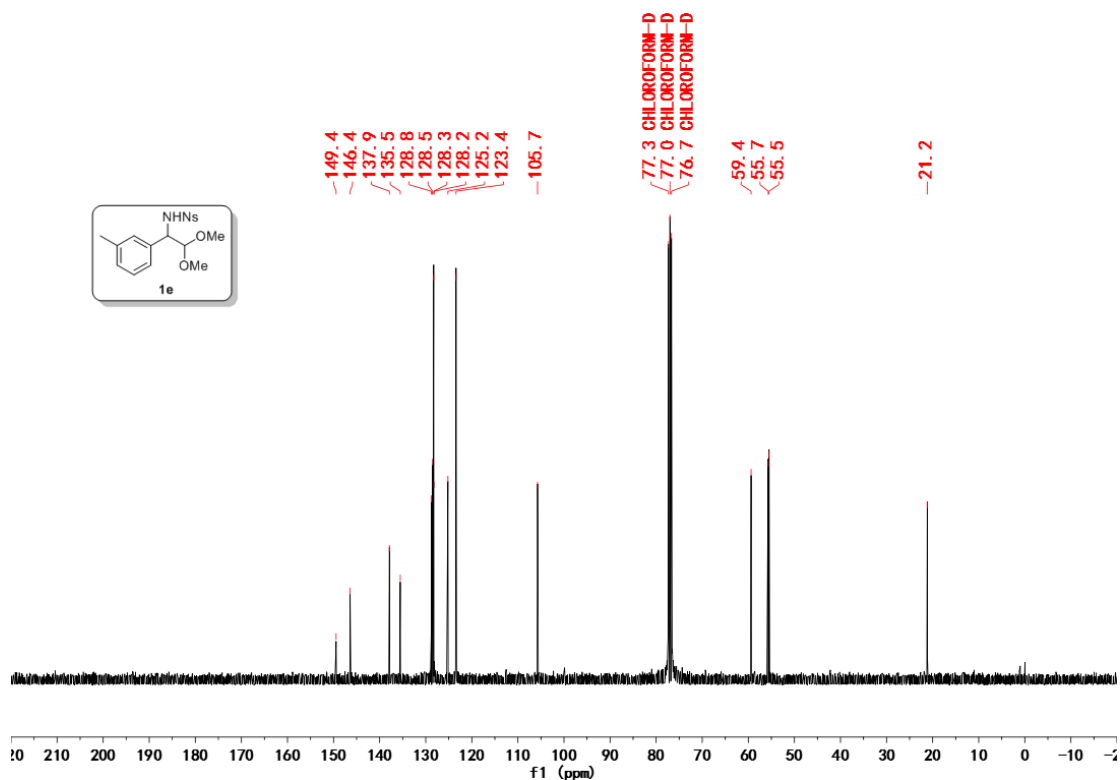
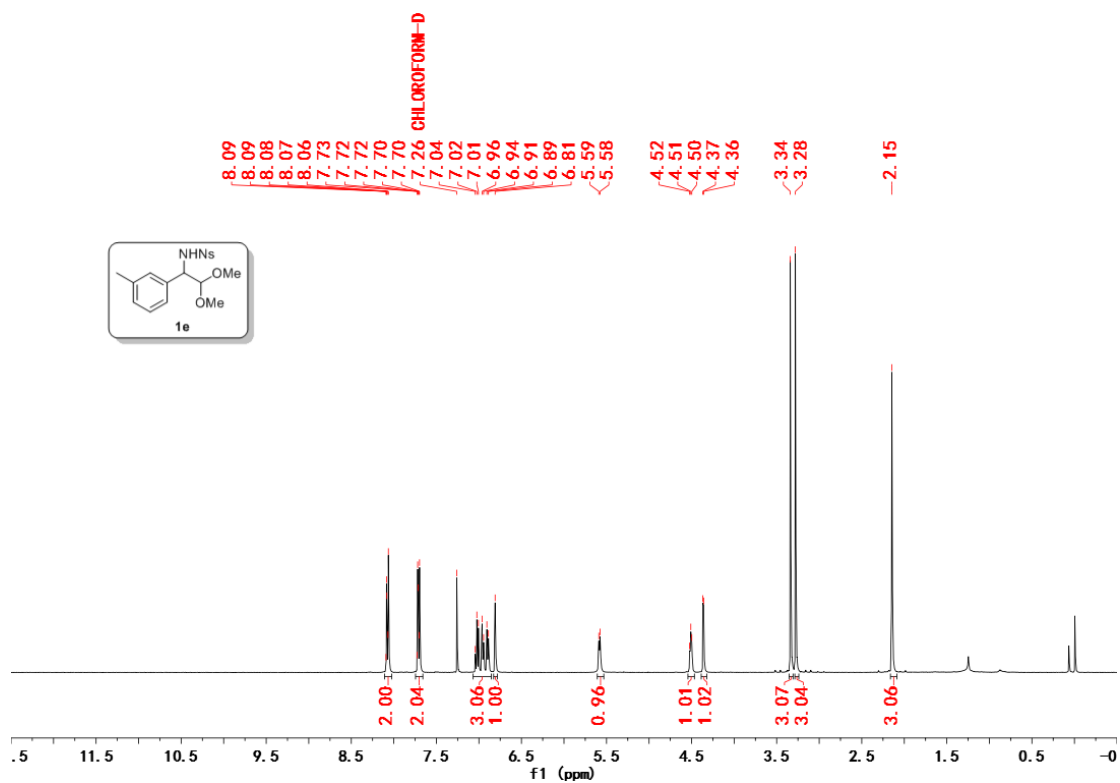
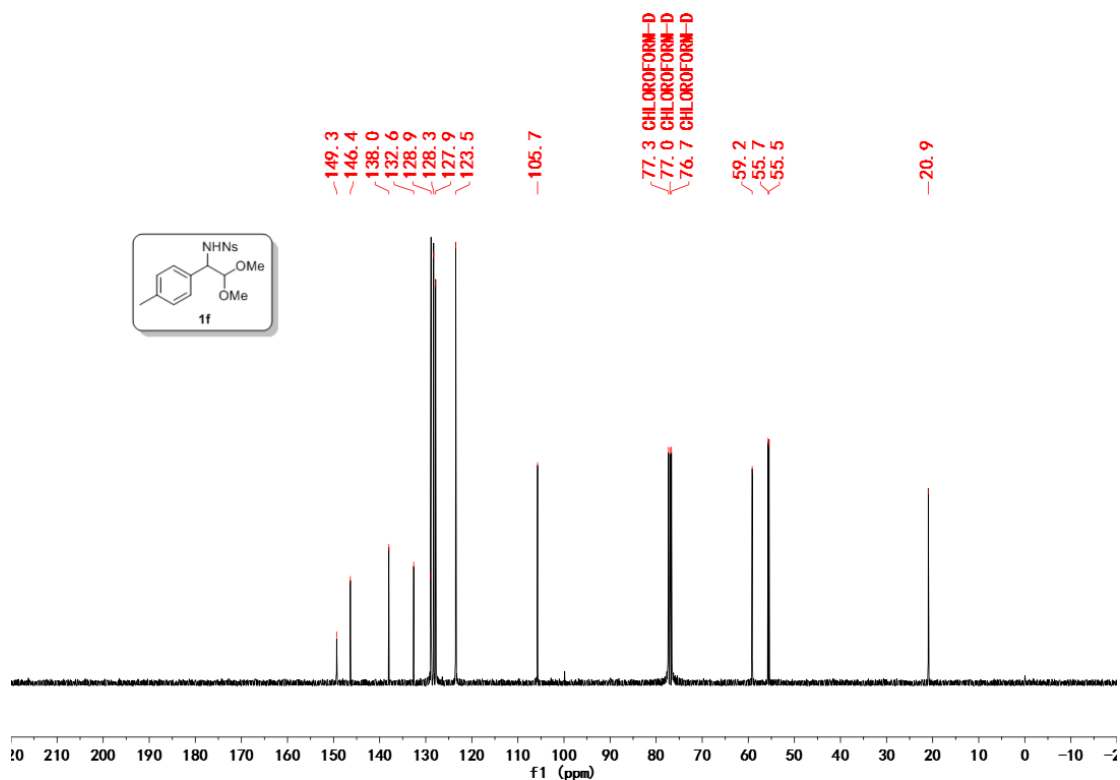
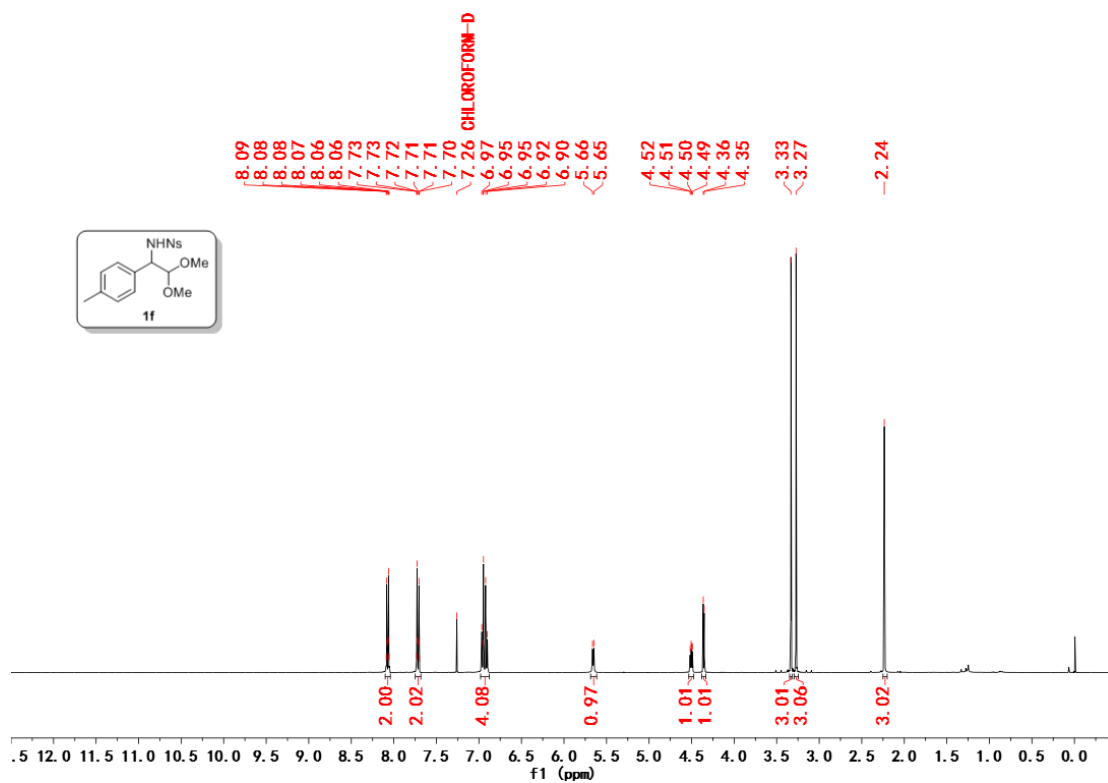


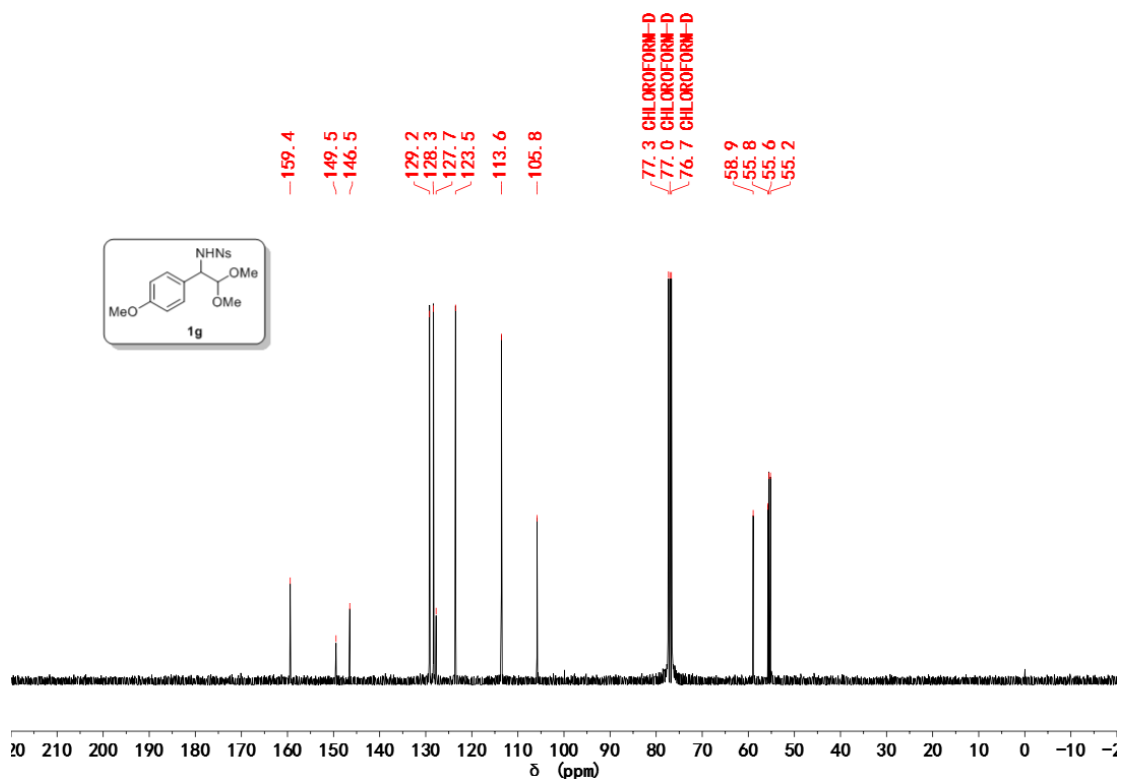
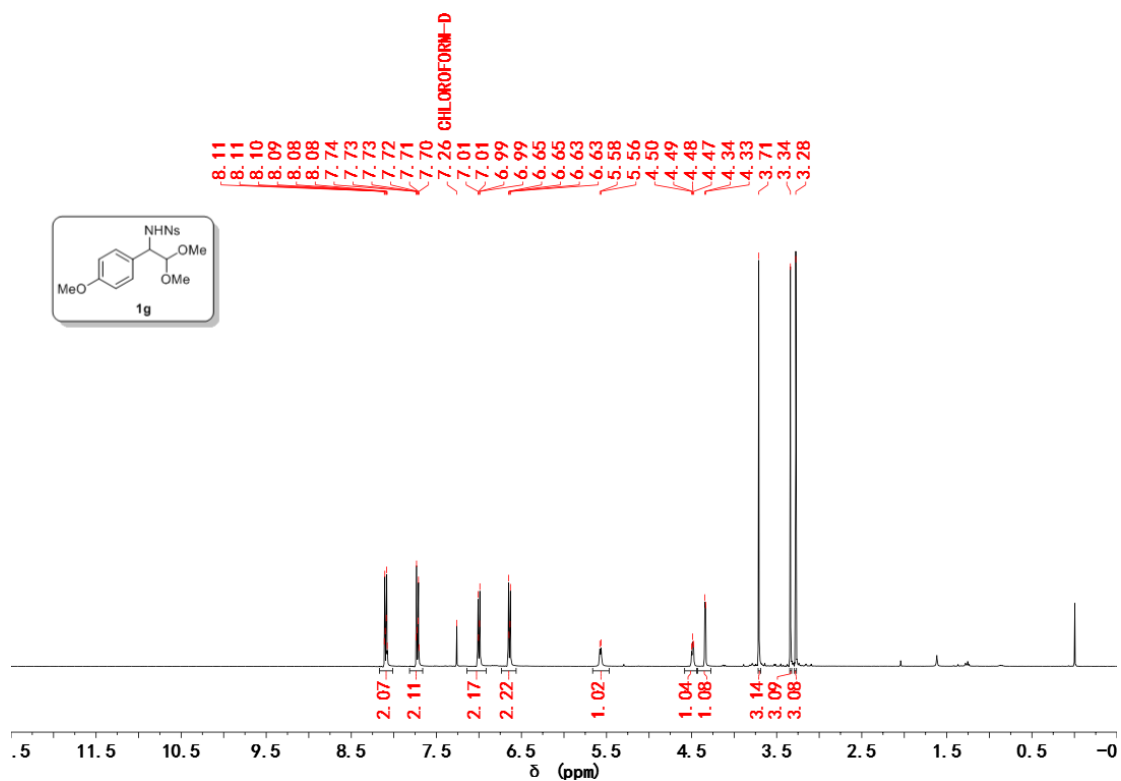
Figure S5. <sup>1</sup>H NMR of **1e** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **1e** (100 MHz, CDCl<sub>3</sub>)

***N*-(2,2-dimethoxy-1-(*p*-tolyl)ethyl)-4-nitrobenzenesulfonamide (**1f**)**



**Figure S6.** <sup>1</sup>H NMR of **1f** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **1f** (100 MHz, CDCl<sub>3</sub>)

***N*-(2,2-dimethoxy-1-(4-methoxyphenyl)ethyl)-4-nitrobenzenesulfonamide (1g)**

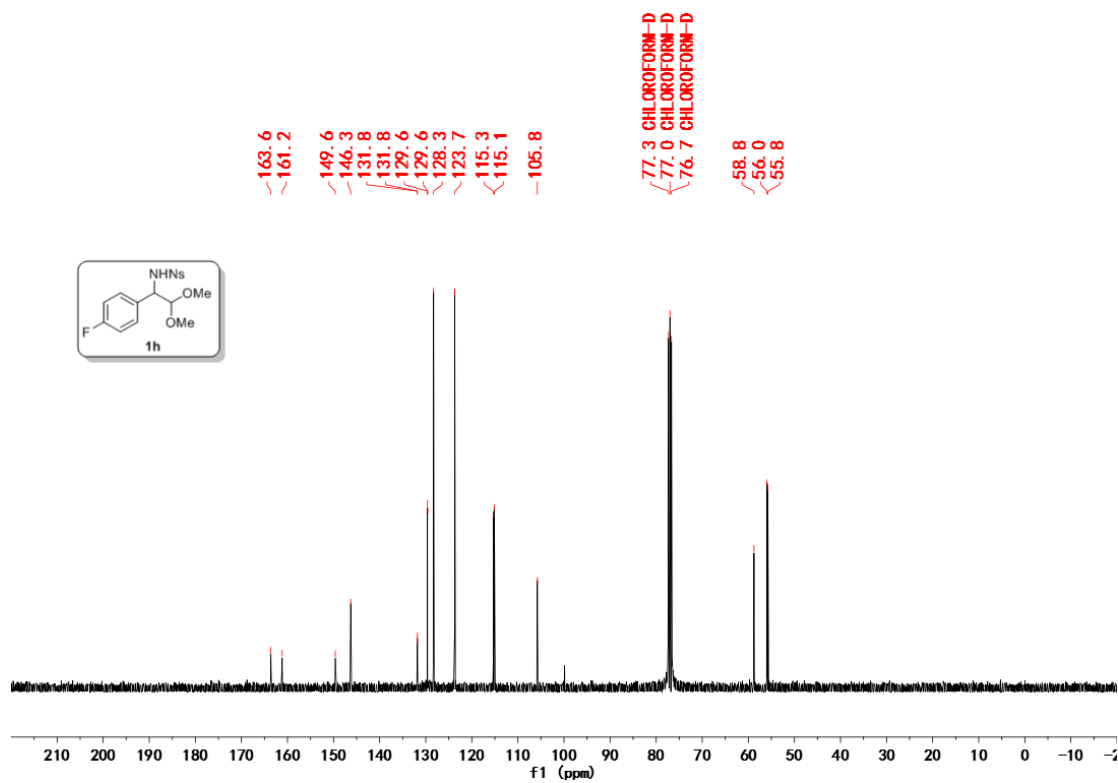
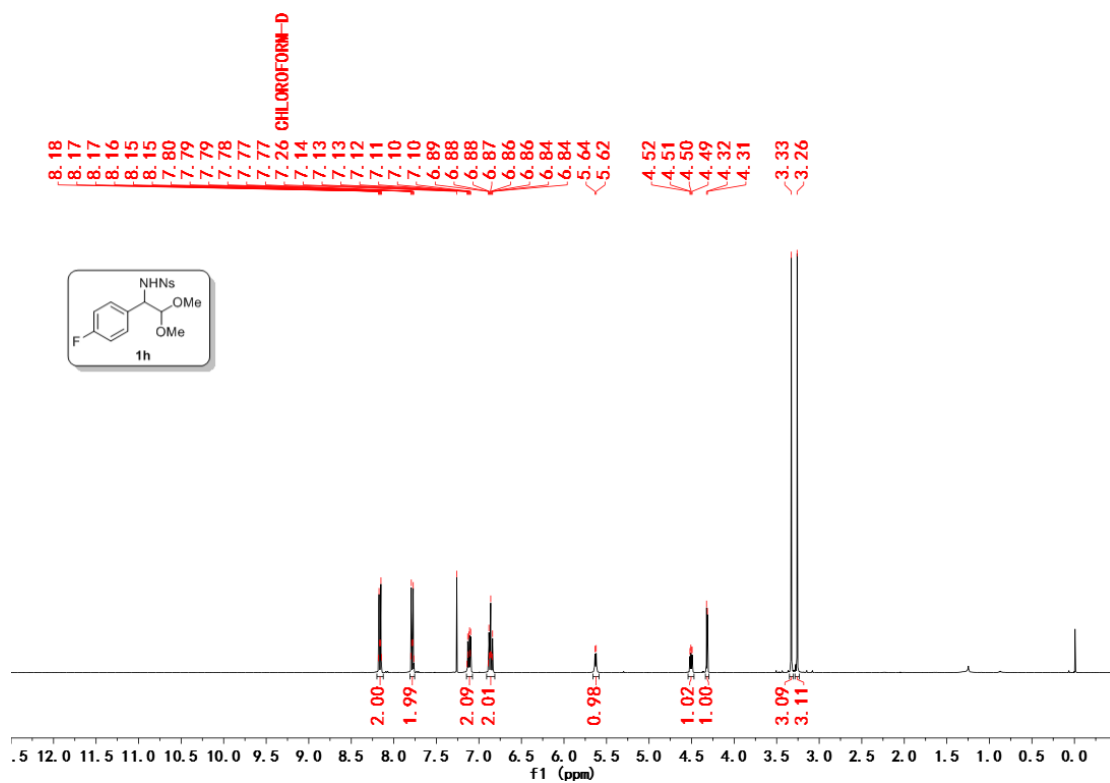


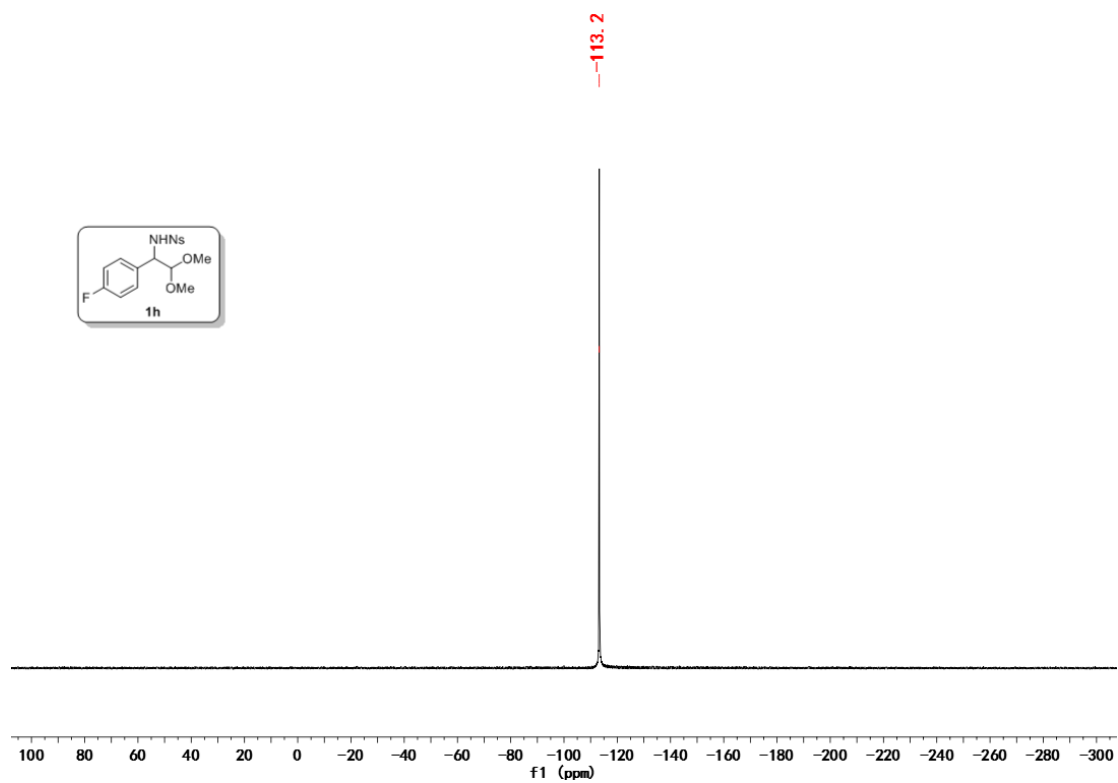
**Figure S7.** <sup>1</sup>H NMR of **1g** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **1g** (100 MHz, CDCl<sub>3</sub>)



# *N*-(1-(4-fluorophenyl)-2,2-dimethoxyethyl)-4-nitrobenzenesulfonamid

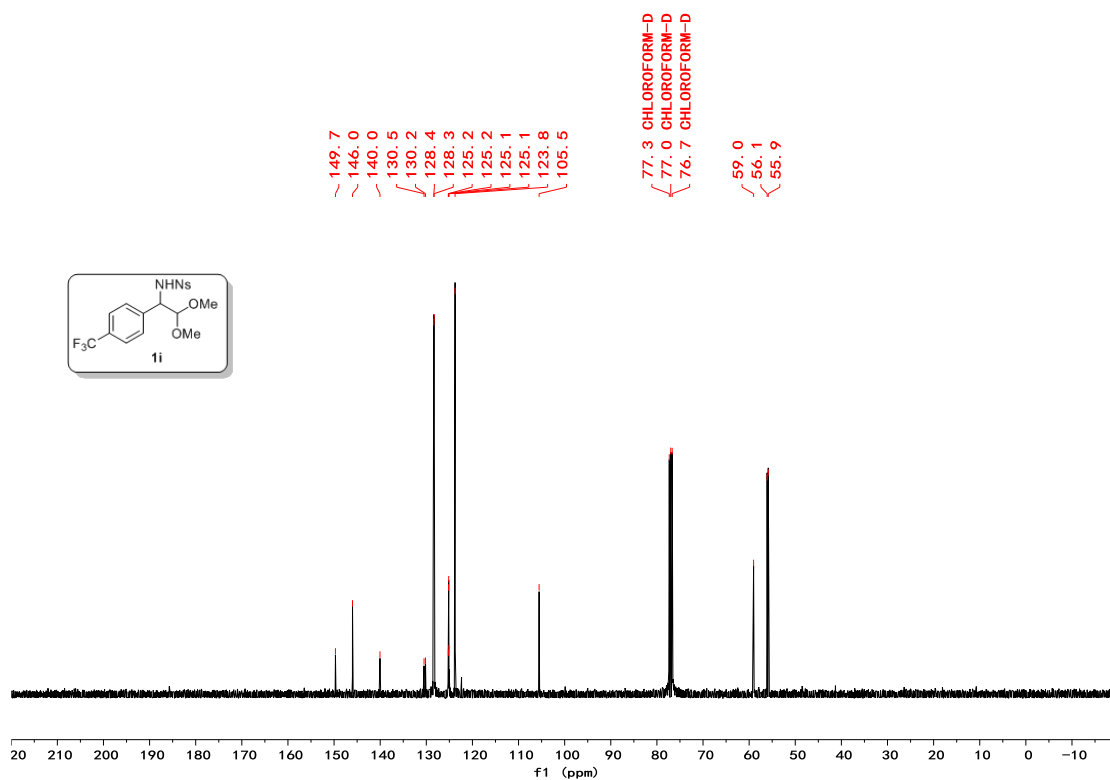
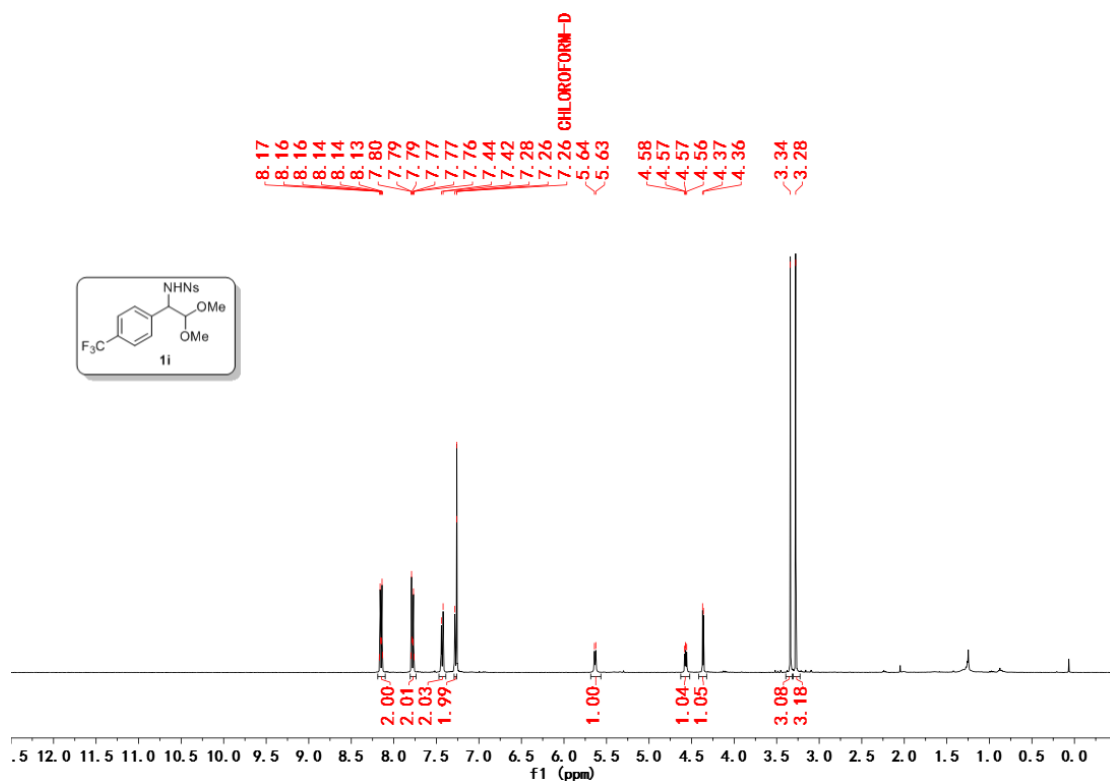
e (1h)

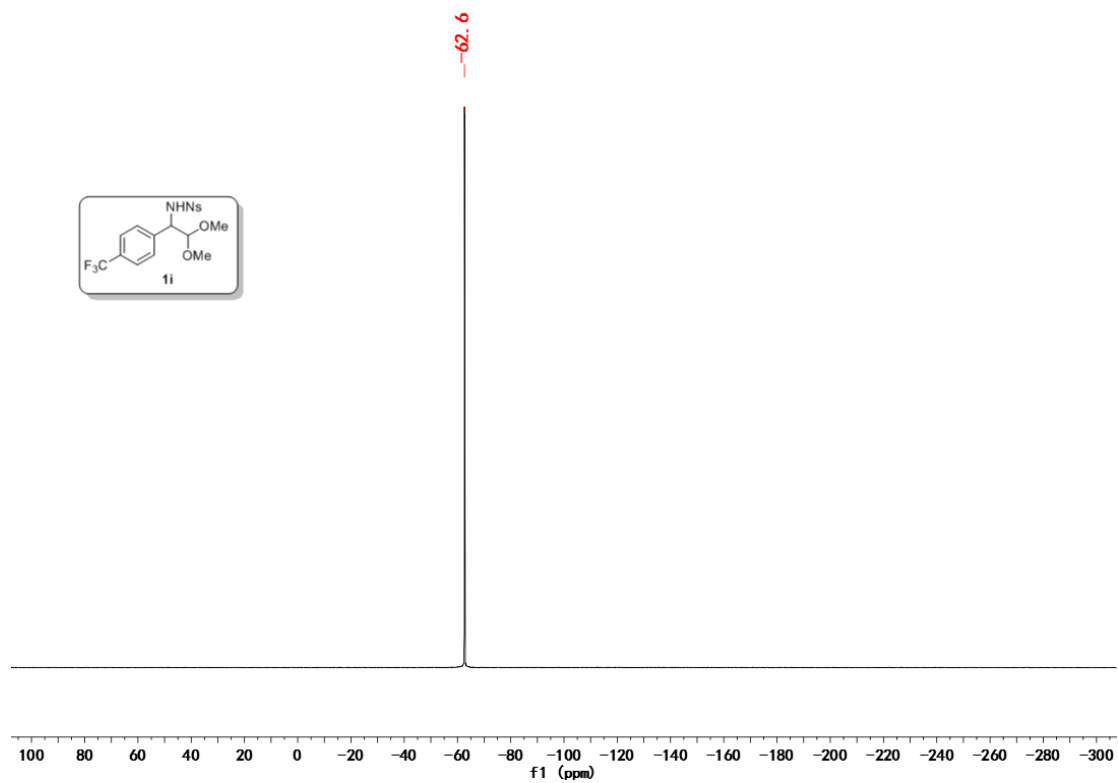




**Figure S8.** <sup>1</sup>H NMR of **1h** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **1h** (100 MHz, CDCl<sub>3</sub>)

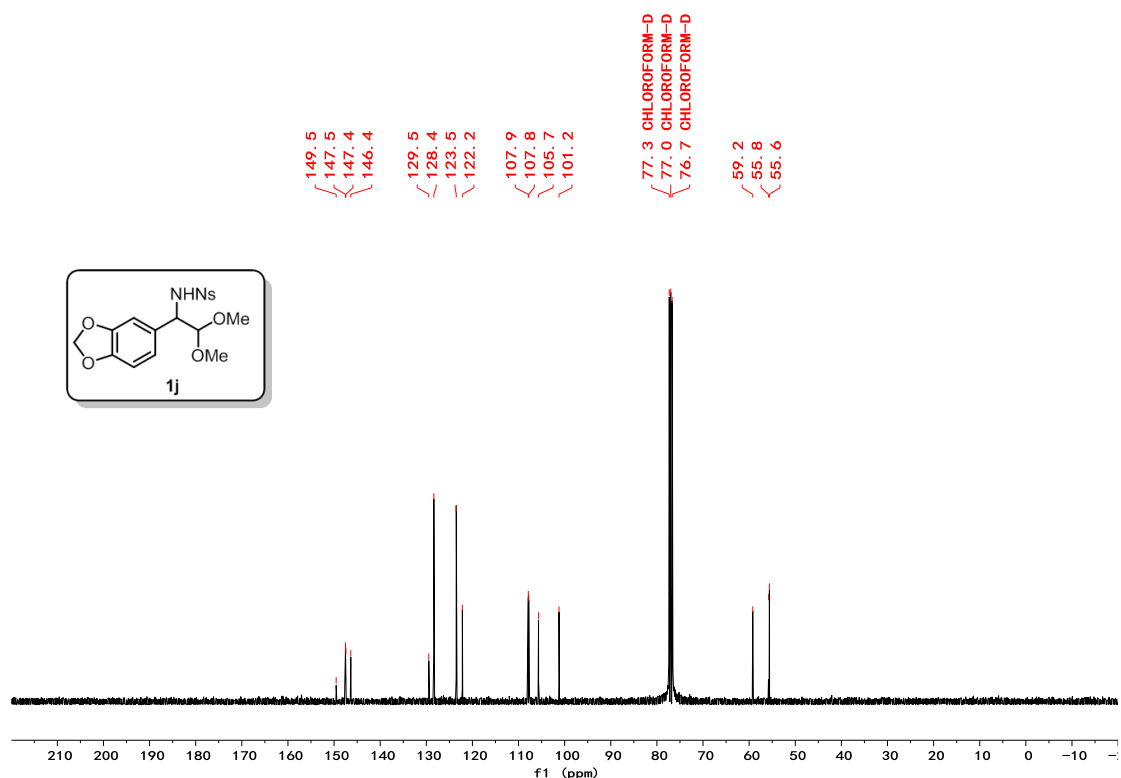
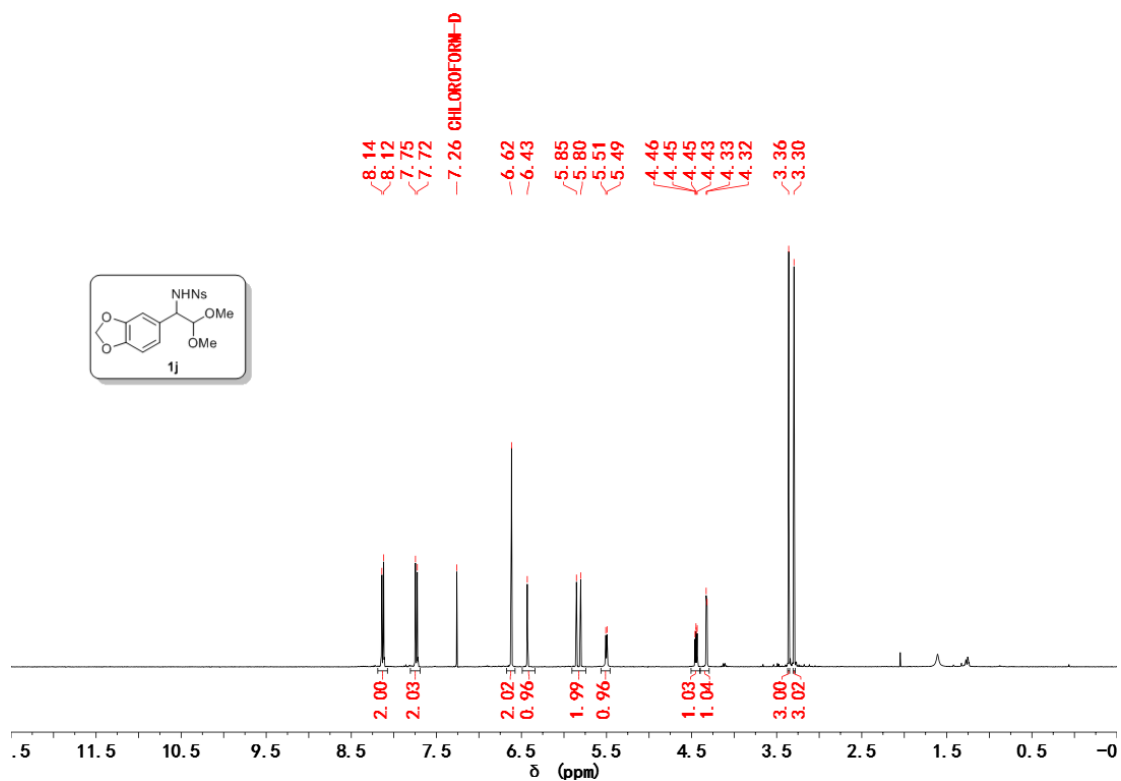
***N*-(2,2-dimethoxy-1-(4-(trifluoromethyl)phenyl)ethyl)-4-nitrobenzene sulfonamide (1i)**





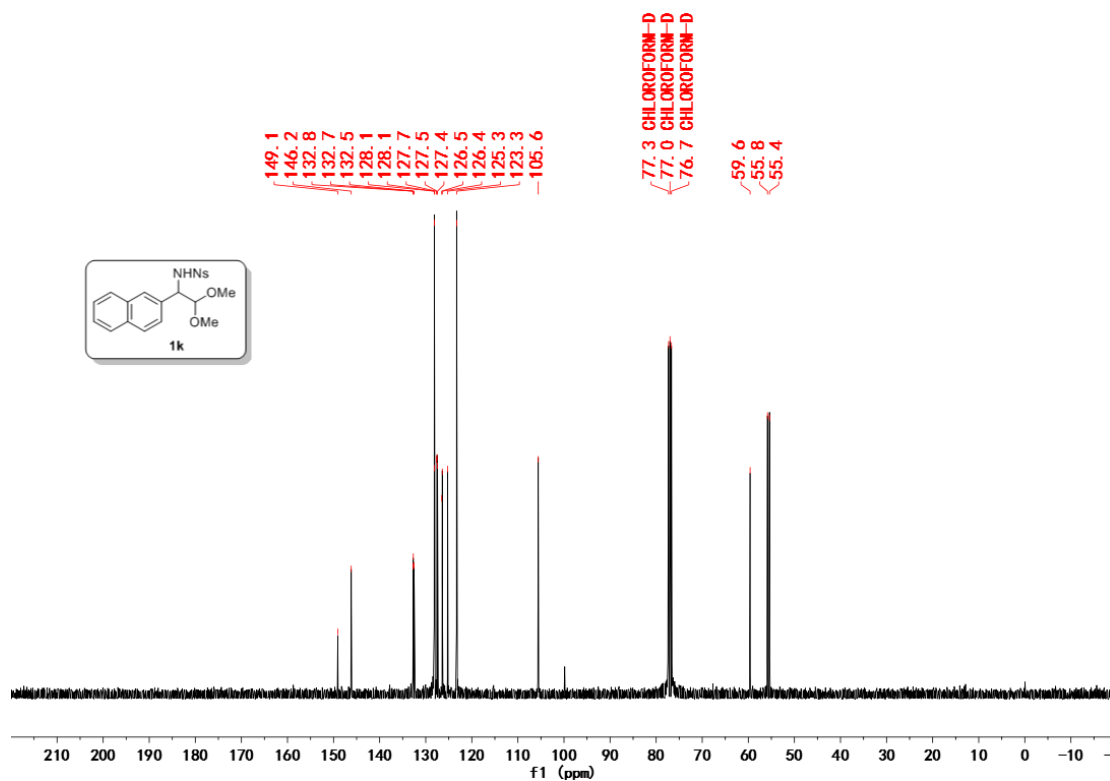
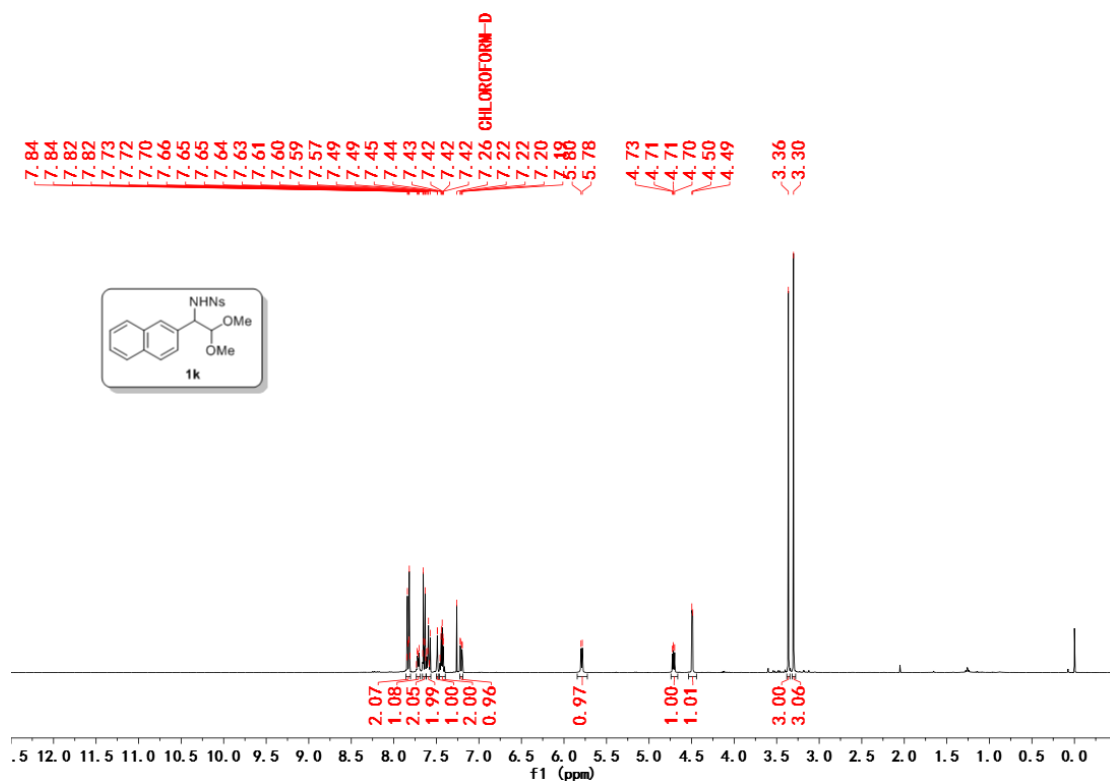
**Figure S9.**  $^1\text{H}$  NMR of **1i** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **1i** (100 MHz,  $\text{CDCl}_3$ )

***N*-(1-(benzo[d][1,3]dioxol-5-yl)-2,2-dimethoxyethyl)-4-nitrobenzenesulfonamide (1j)**



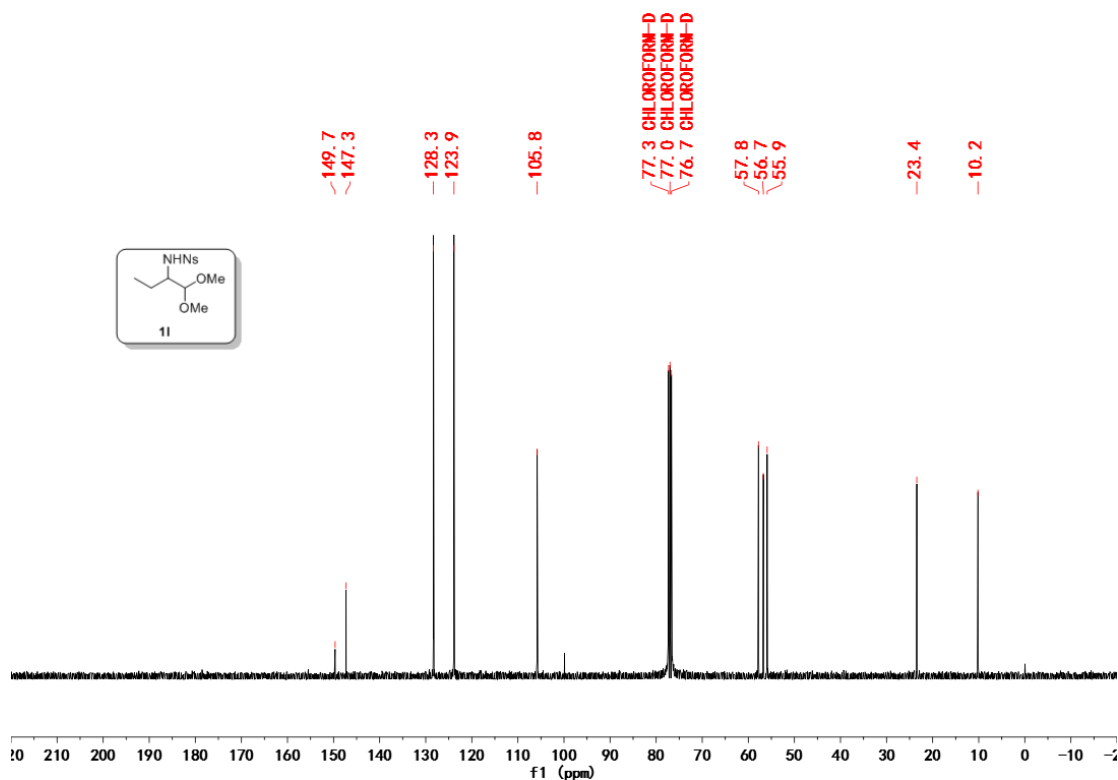
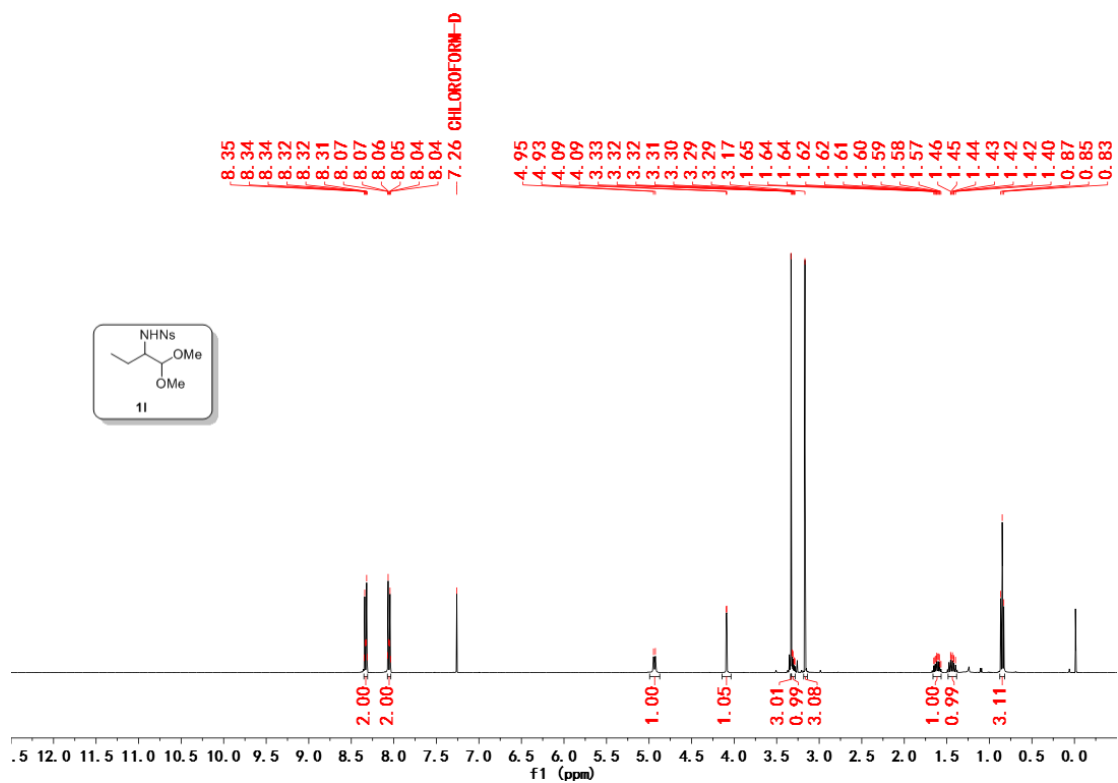
**Figure S10.** <sup>1</sup>H NMR of 1j (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of 1j (100 MHz, CDCl<sub>3</sub>)

***N*-(2,2-dimethoxy-1-(naphthalen-2-yl)ethyl)-4-nitrobenzenesulfonamide (1k)**



**Figure S11.** <sup>1</sup>H NMR of **1k** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **1k** (100 MHz, CDCl<sub>3</sub>)

***N*-(1,1-dimethoxybutan-2-yl)-4-nitrobenzenesulfonamide (**11**)**



**Figure S12.** <sup>1</sup>H NMR of **11** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **11** (100 MHz, CDCl<sub>3</sub>)

# *N*-(1,1-dimethoxy-3-phenylpropan-2-yl)-4-nitrobenzenesulfonamide

(1m)

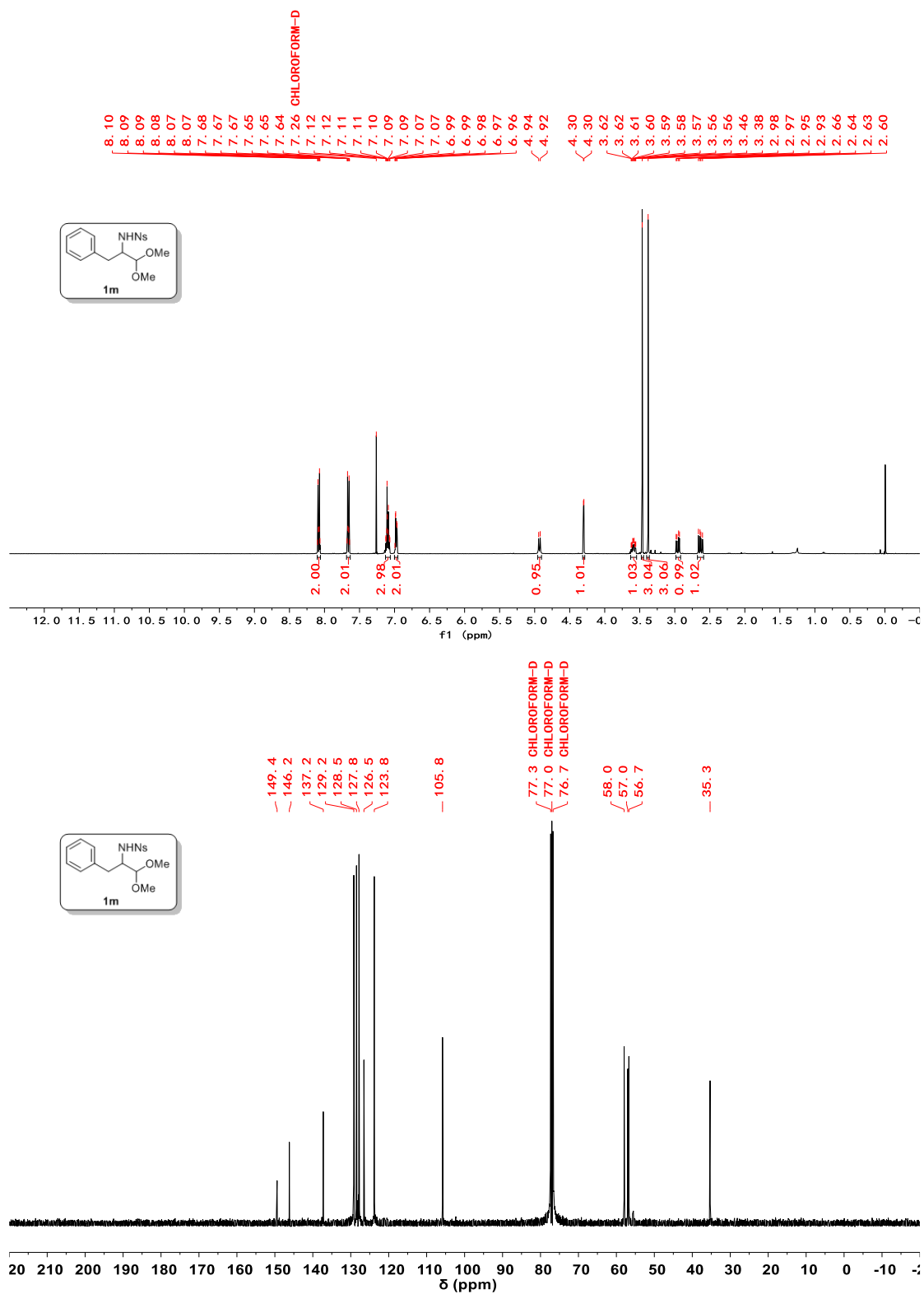


Figure S13. <sup>1</sup>H NMR of **1m** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **1m** (100 MHz, CDCl<sub>3</sub>)



# 1-((4-Nitrophenyl)sulfonyl)-2,5-diphenyl-1H-pyrrole (3a)

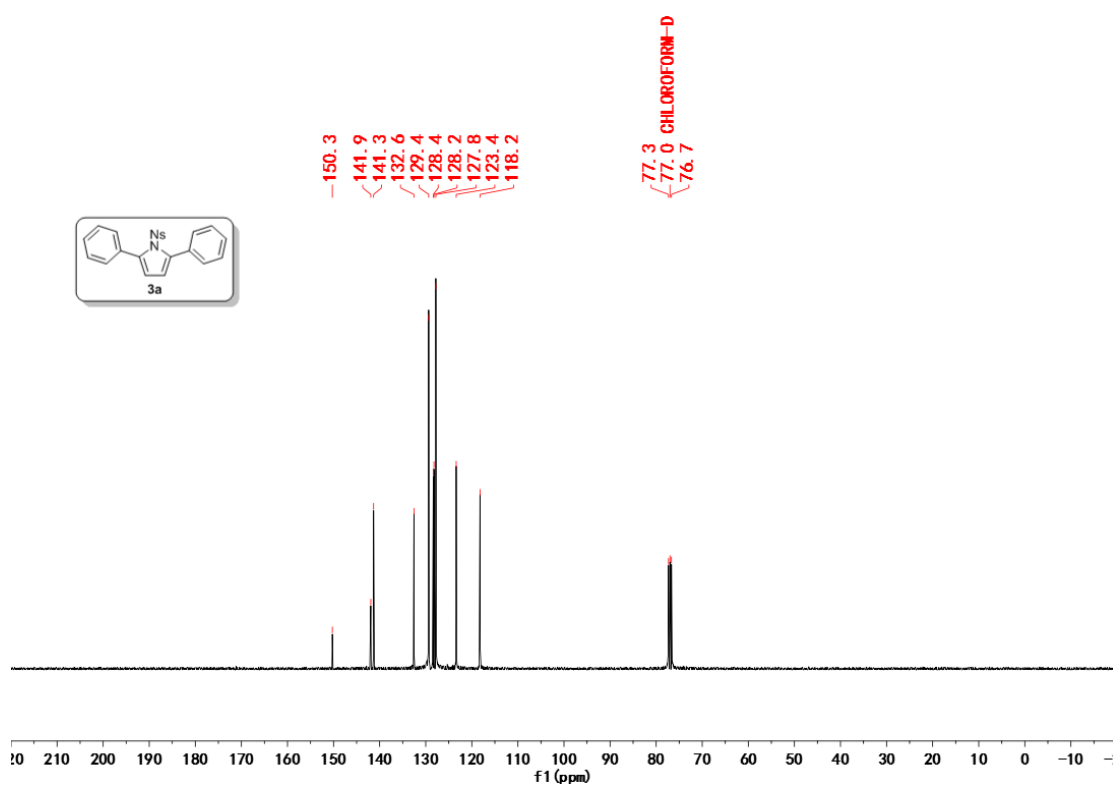
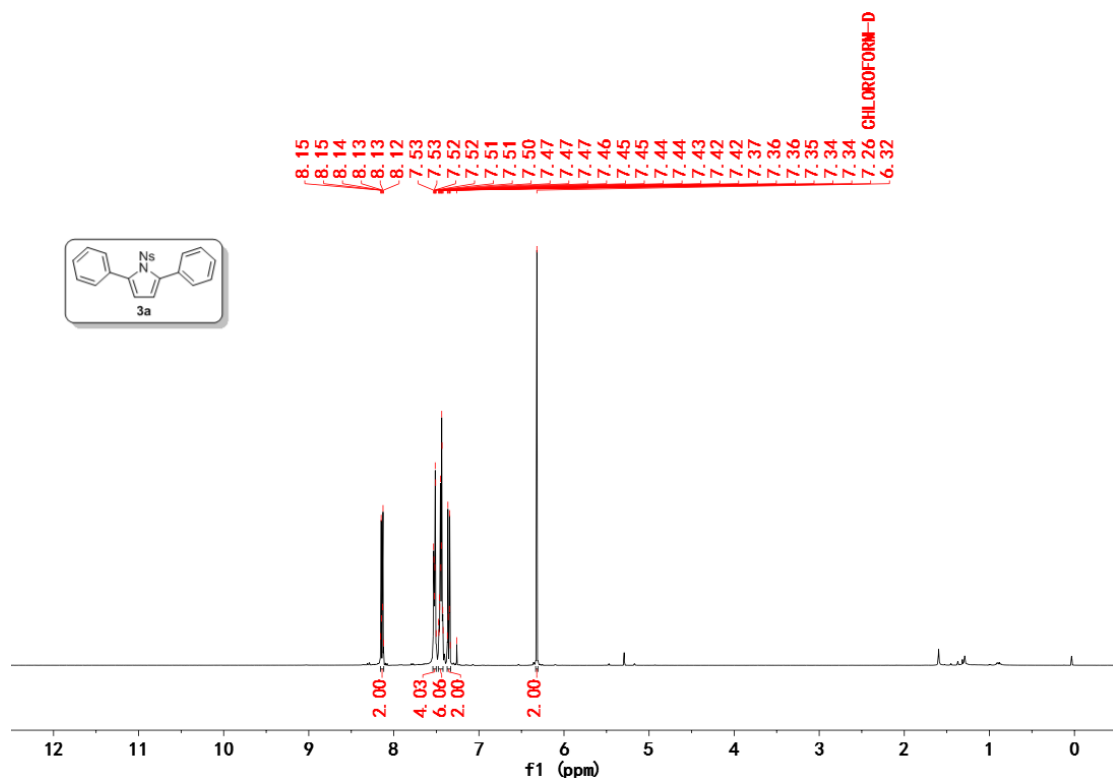


Figure S14. <sup>1</sup>H NMR of 3a (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of 3a (100 MHz, CDCl<sub>3</sub>)

## 2,5-Diphenyl-1-tosyl-1H-pyrrole (3b)

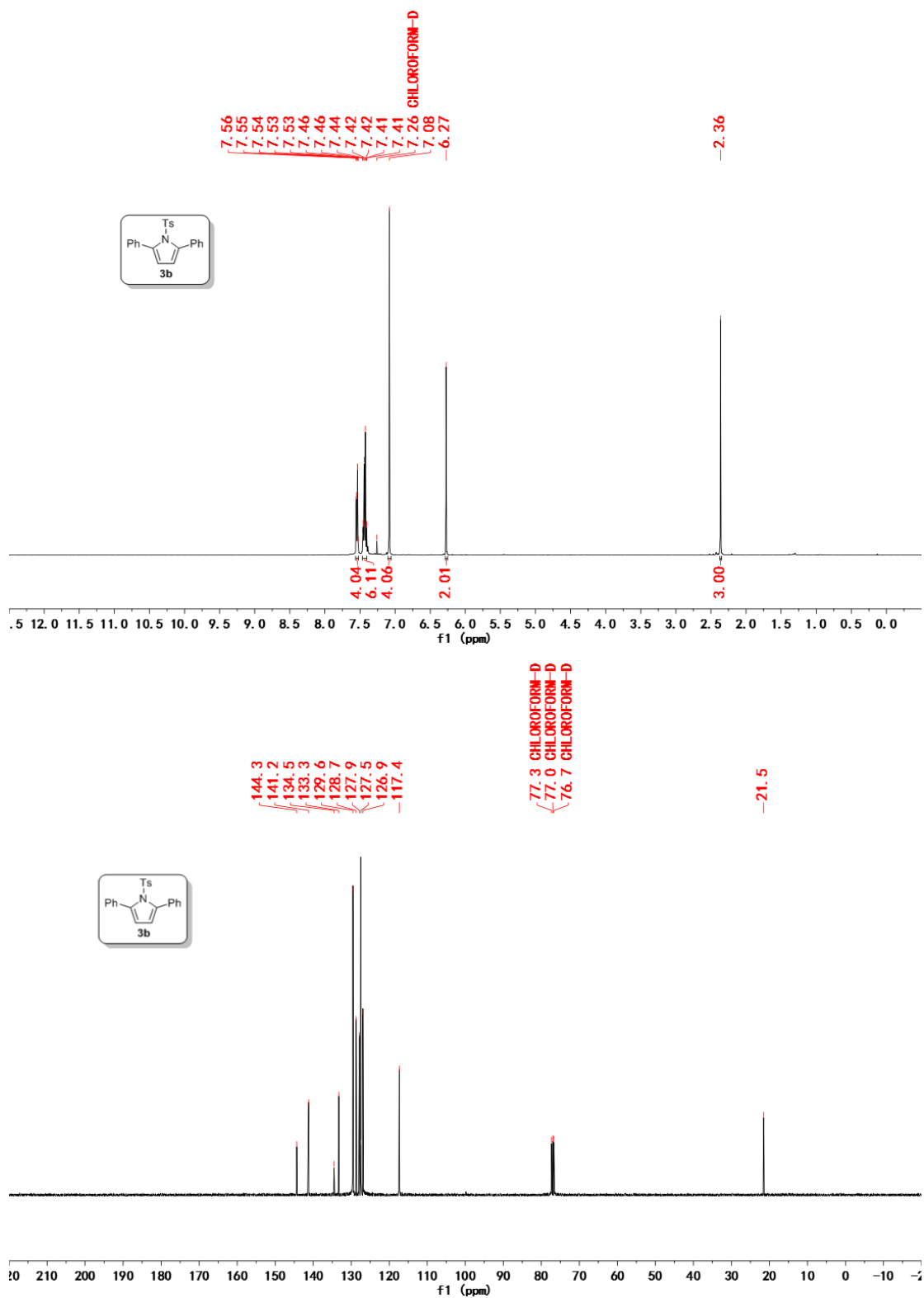


Figure S15. <sup>1</sup>H NMR of 3b (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of 3b (100 MHz, CDCl<sub>3</sub>)

(9H-fluoren-9-yl)methyl 2,5-diphenyl-1H-pyrrole-1-carboxylate (**3c**)

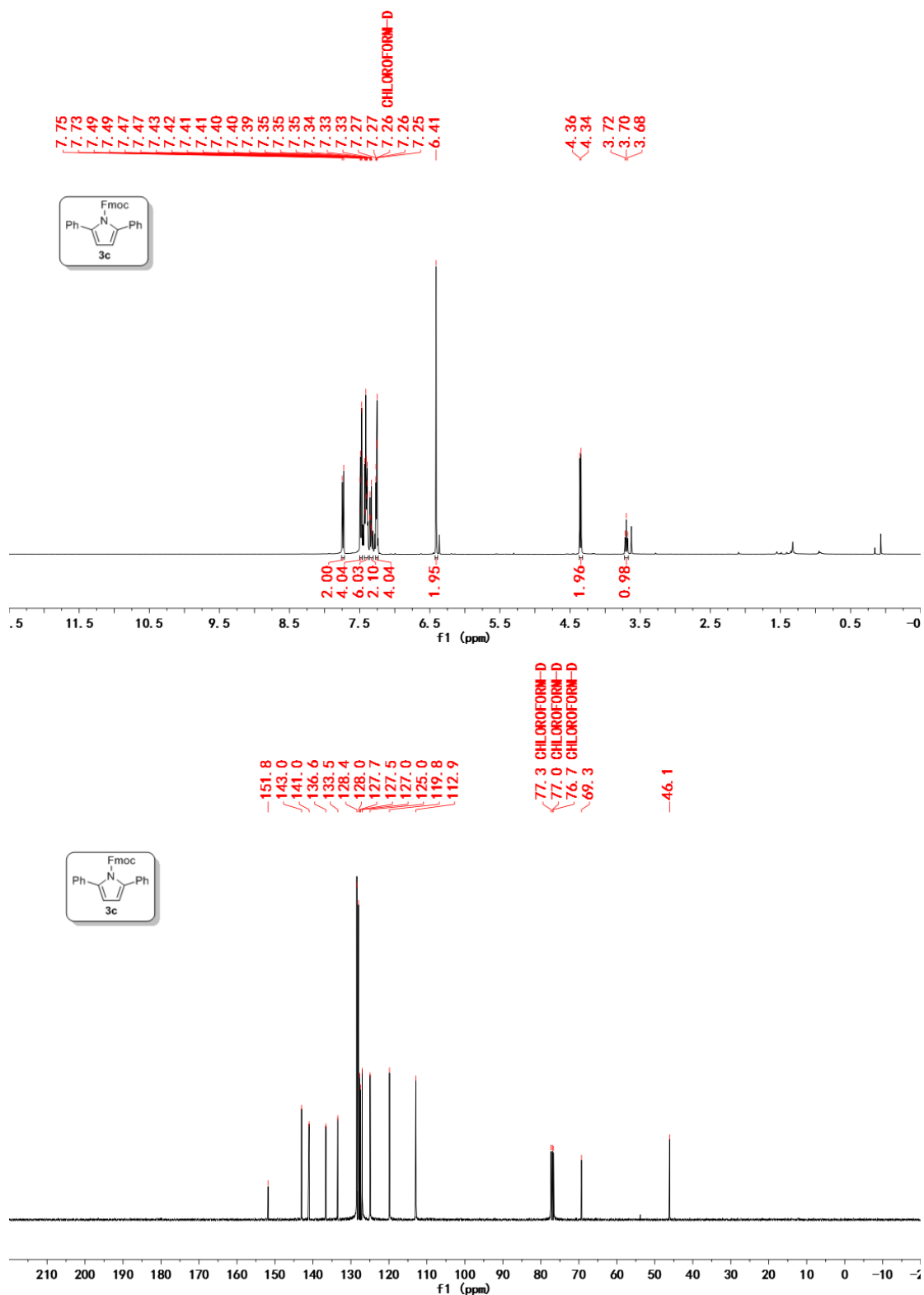


Figure S16. <sup>1</sup>H NMR of **3c** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **3c** (100 MHz, CDCl<sub>3</sub>)

# 1-((4-Nitrophenyl)sulfonyl)-2-phenyl-5-(o-tolyl)-1H-pyrrole (3d)

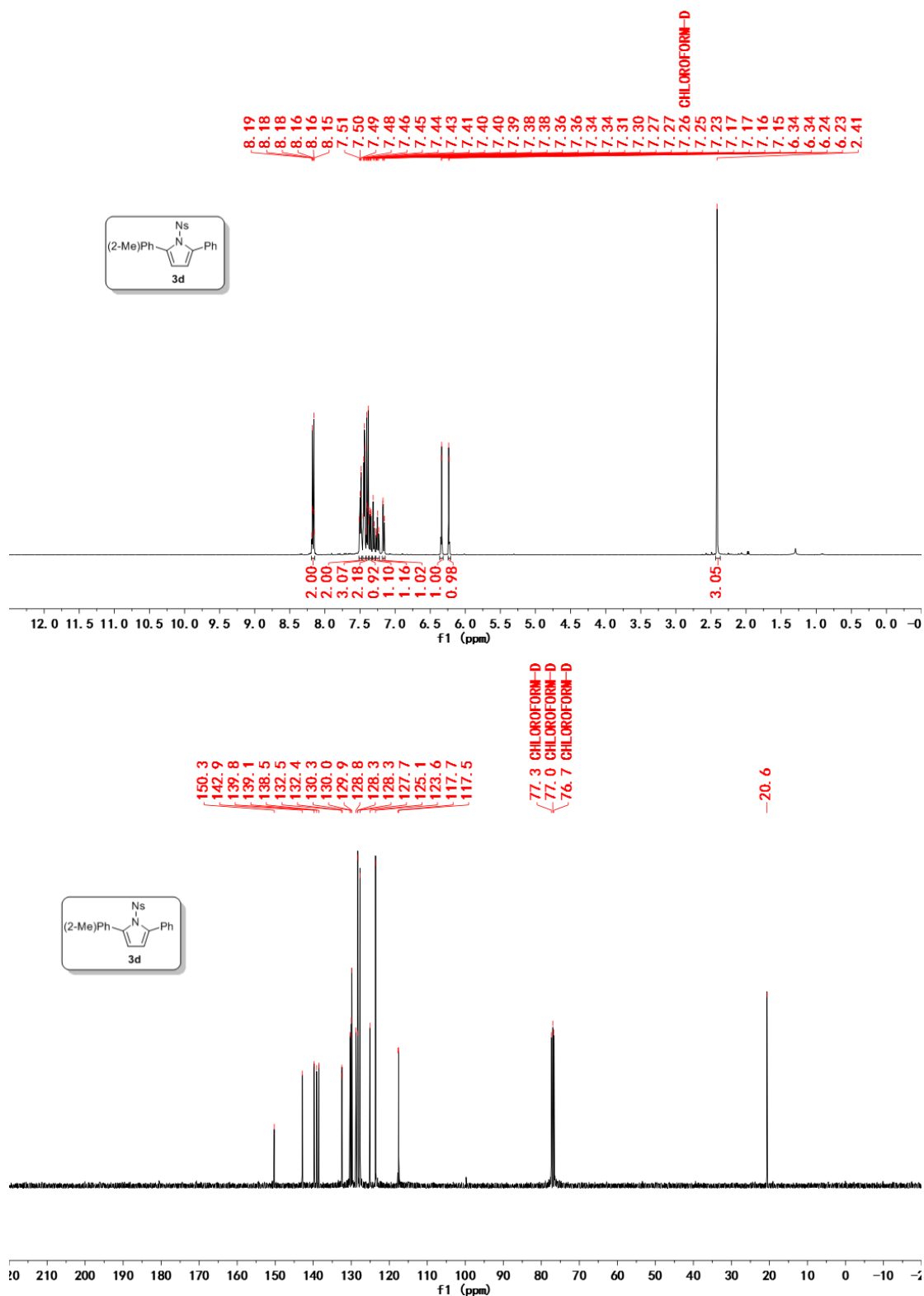


Figure S17. <sup>1</sup>H NMR of 3d (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of 3d (100 MHz, CDCl<sub>3</sub>)

# 1-((4-Nitrophenyl)sulfonyl)-2-phenyl-5-(m-tolyl)-1H-pyrrole (3e)

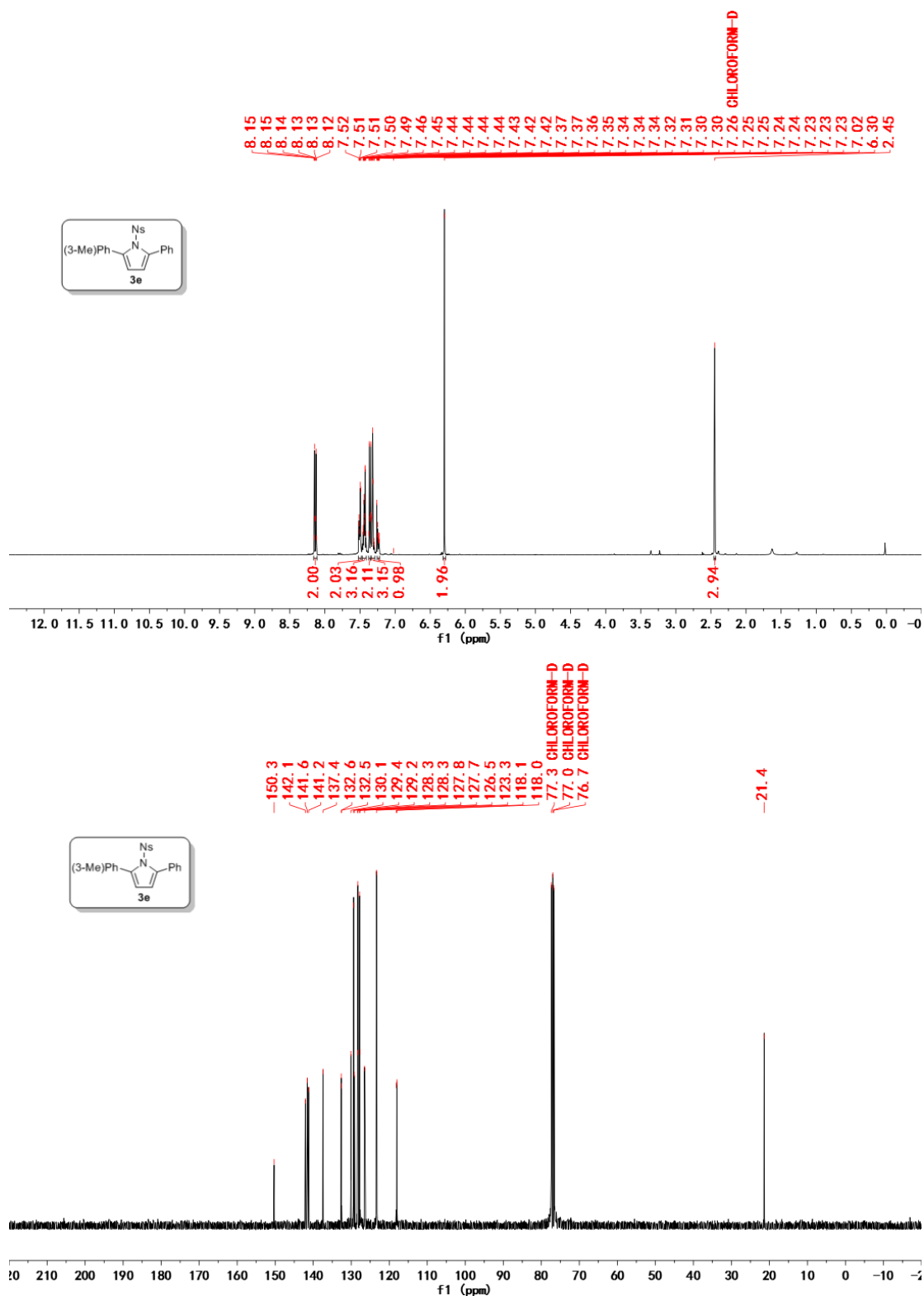


Figure S18. <sup>1</sup>H NMR of 3e (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of 3e (100 MHz, CDCl<sub>3</sub>)

# 1-((4-Nitrophenyl)sulfonyl)-2-phenyl-5-(p-tolyl)-1H-pyrrole (3f)

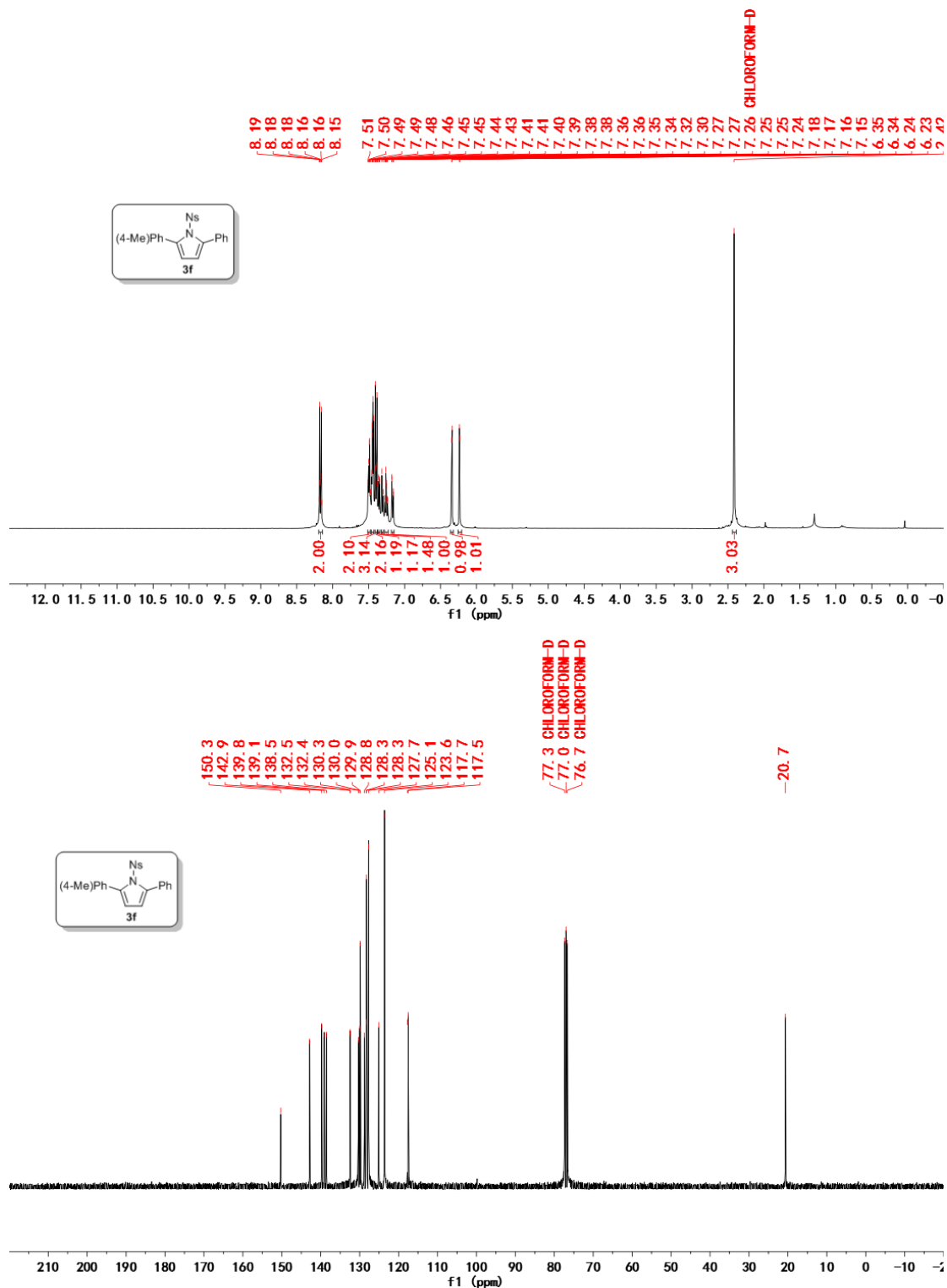
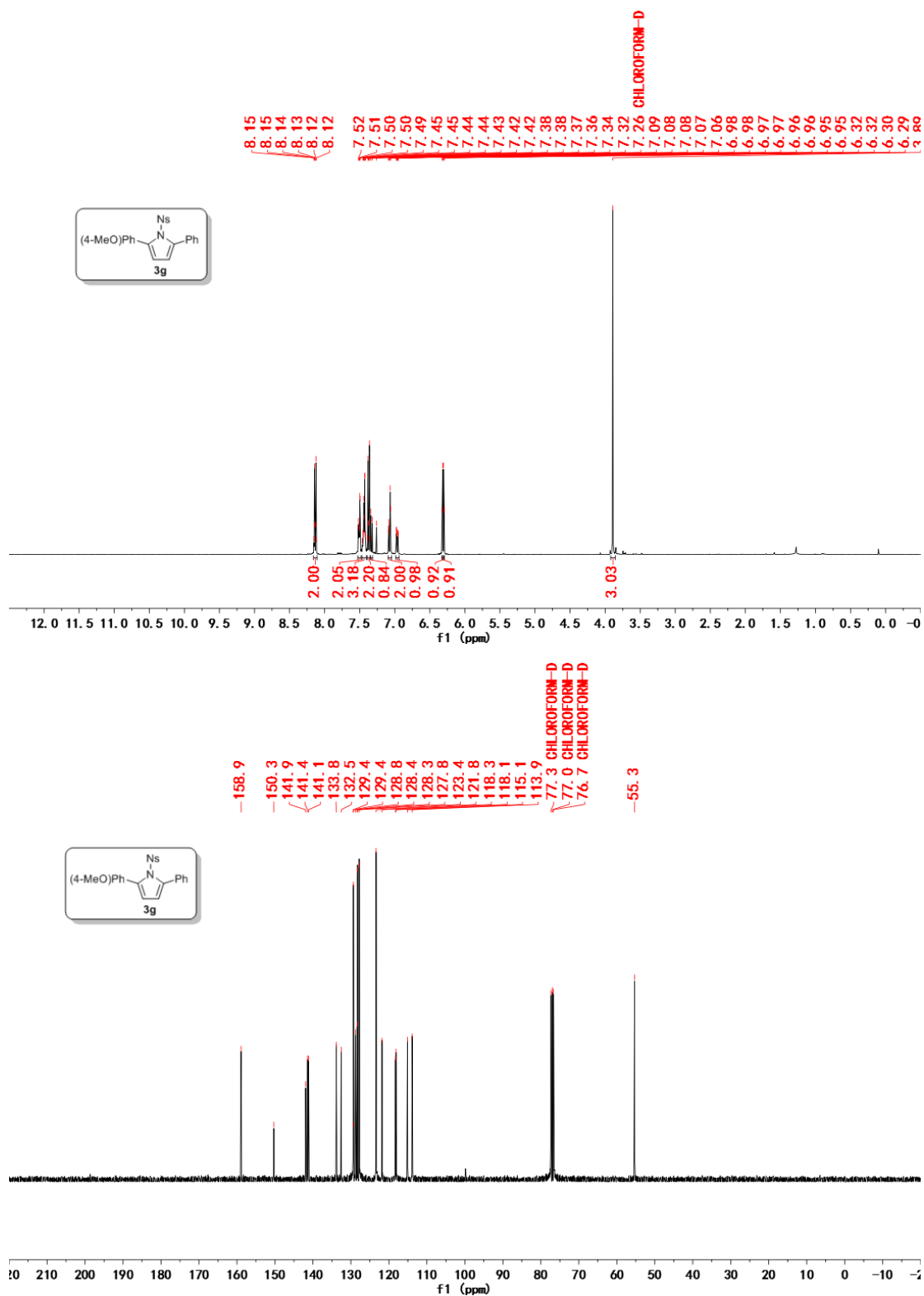


Figure S19. <sup>1</sup>H NMR of 3f (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of 3f (100 MHz, CDCl<sub>3</sub>)

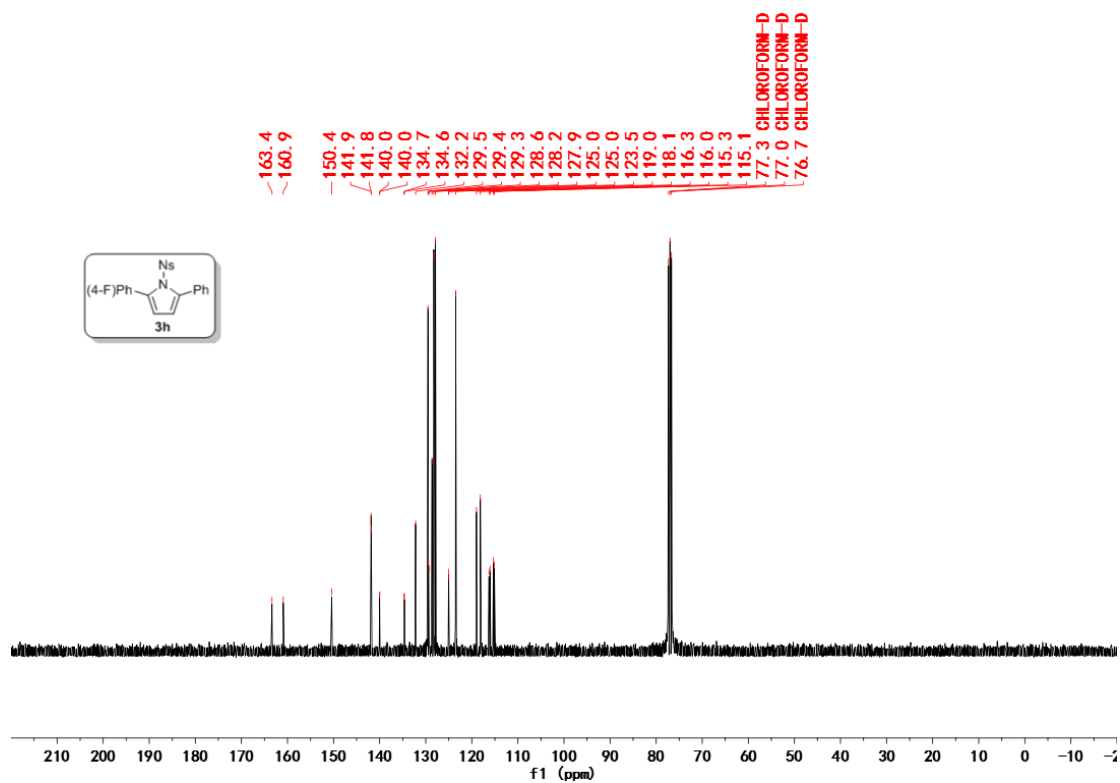
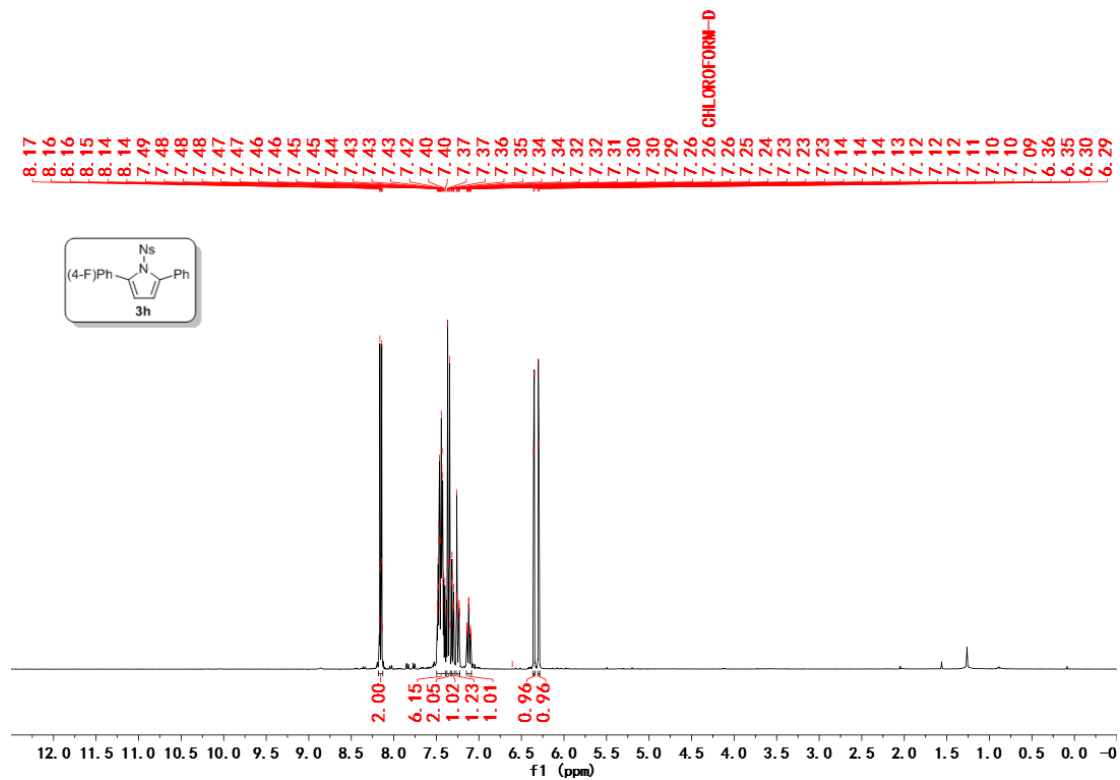
**2-(4-Methoxyphenyl)-1-((4-nitrophenyl)sulfonyl)-5-phenyl-1H-pyrrole  
e (3g)**



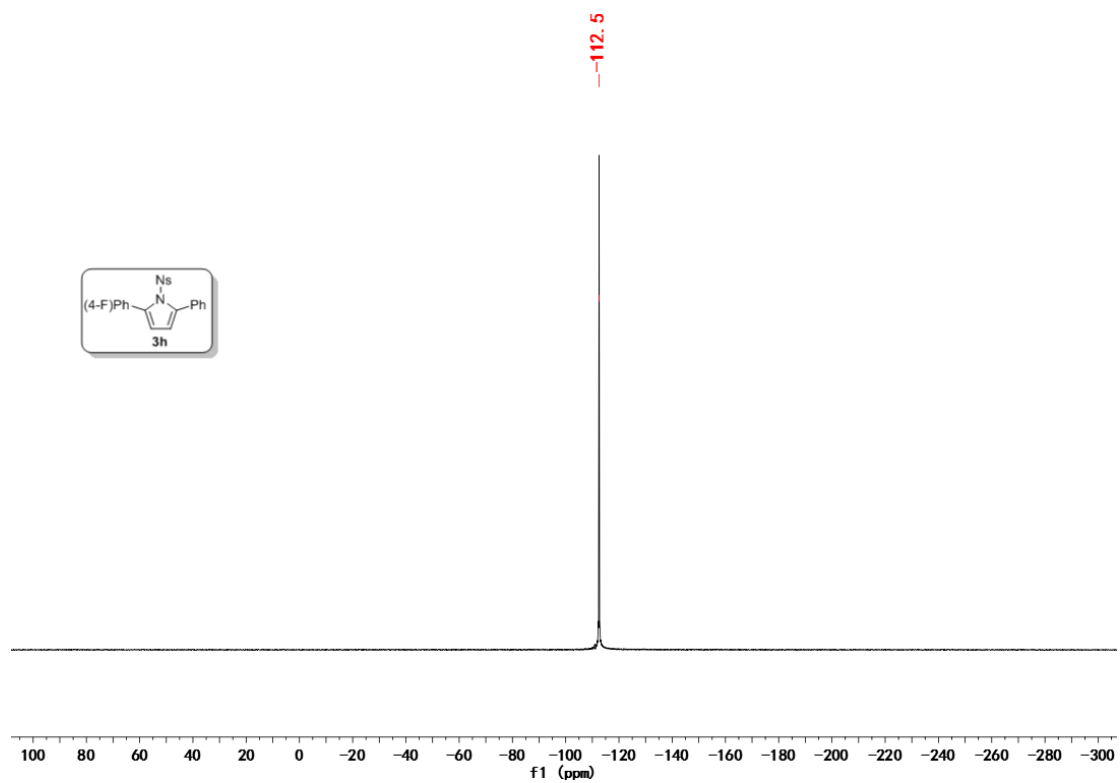
**Figure S20.** <sup>1</sup>H NMR of **3g** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **3g** (100 MHz, CDCl<sub>3</sub>)

# 2-(4-Fluorophenyl)-1-((4-nitrophenyl)sulfonyl)-5-phenyl-1H-pyrrole

(3h)



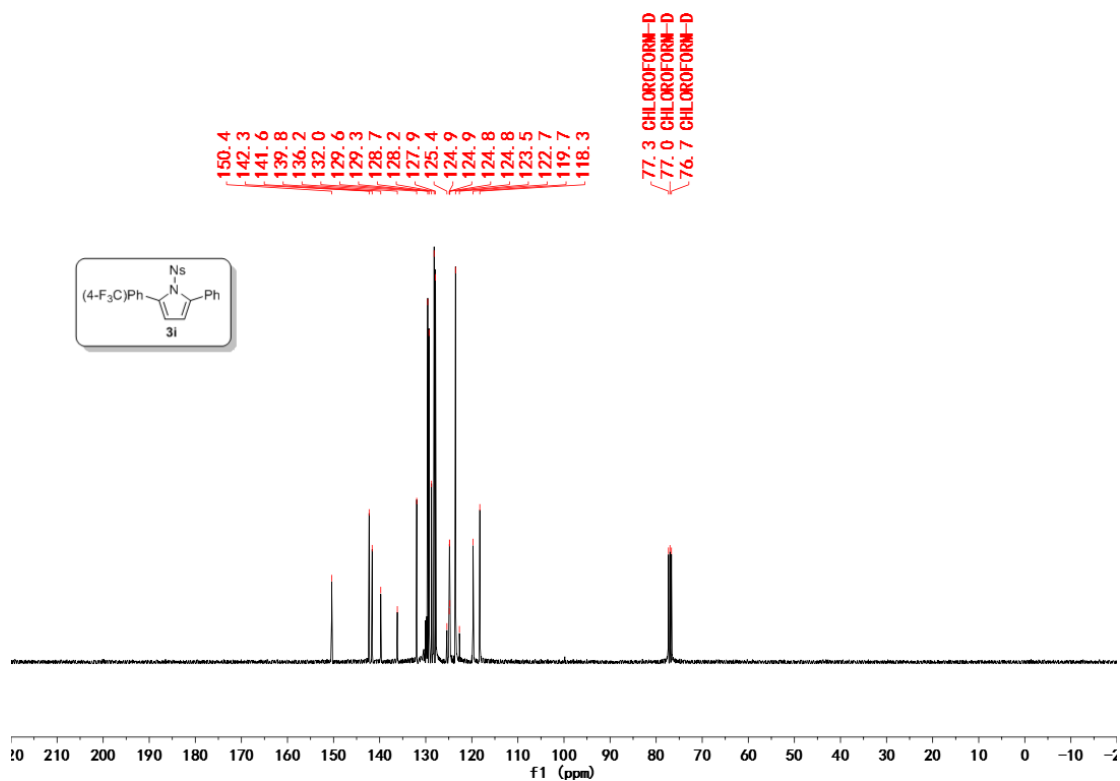
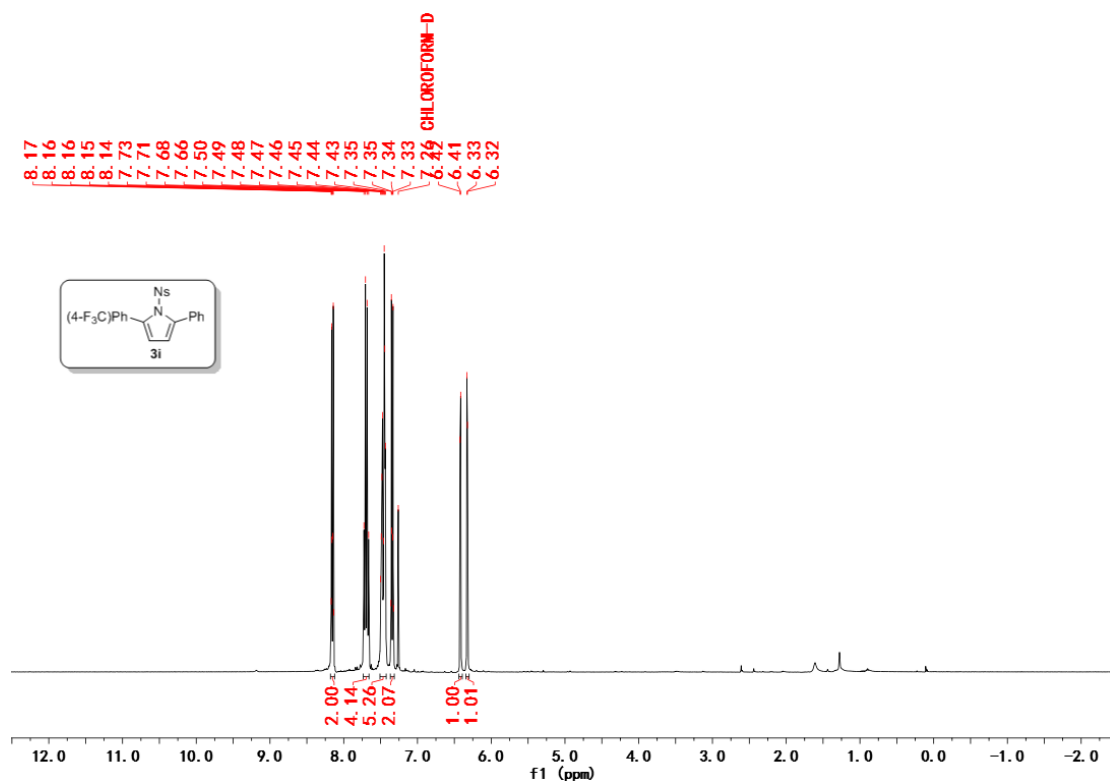


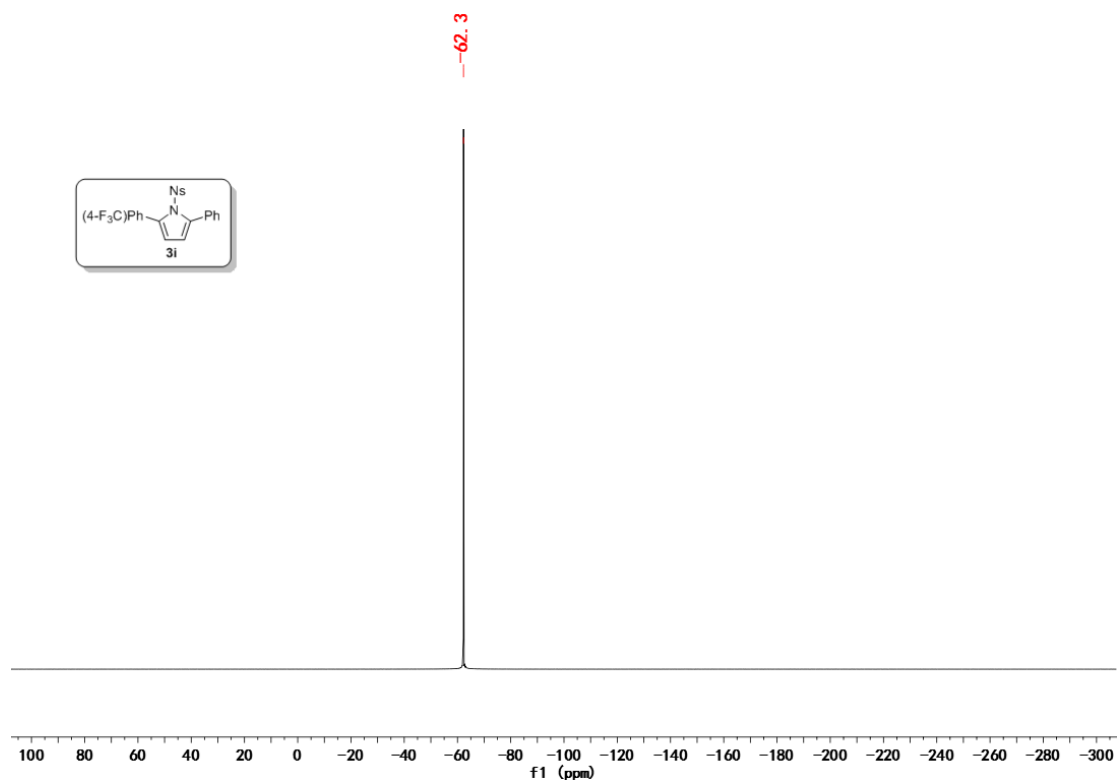


**Figure S21.** <sup>1</sup>H NMR of **3h** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **3h** (100 MHz, CDCl<sub>3</sub>)

# 1-((4-Nitrophenyl)sulfonyl)-2-phenyl-5-(4-(trifluoromethyl)phenyl)-1

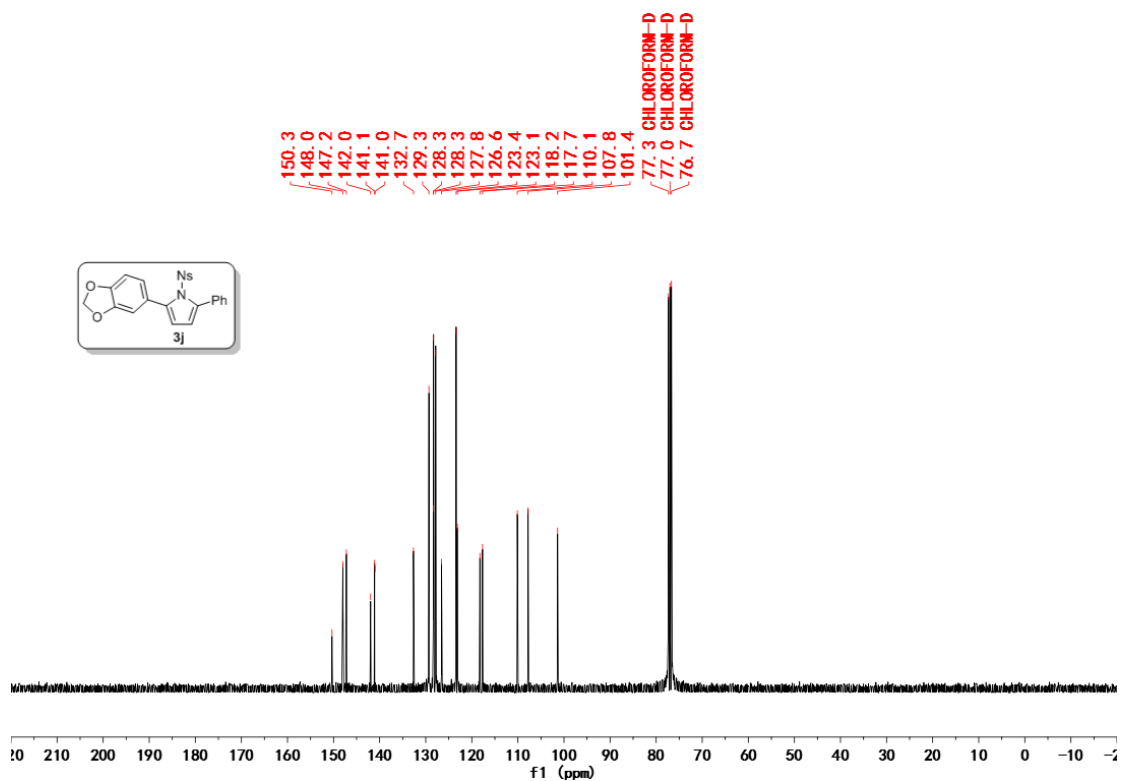
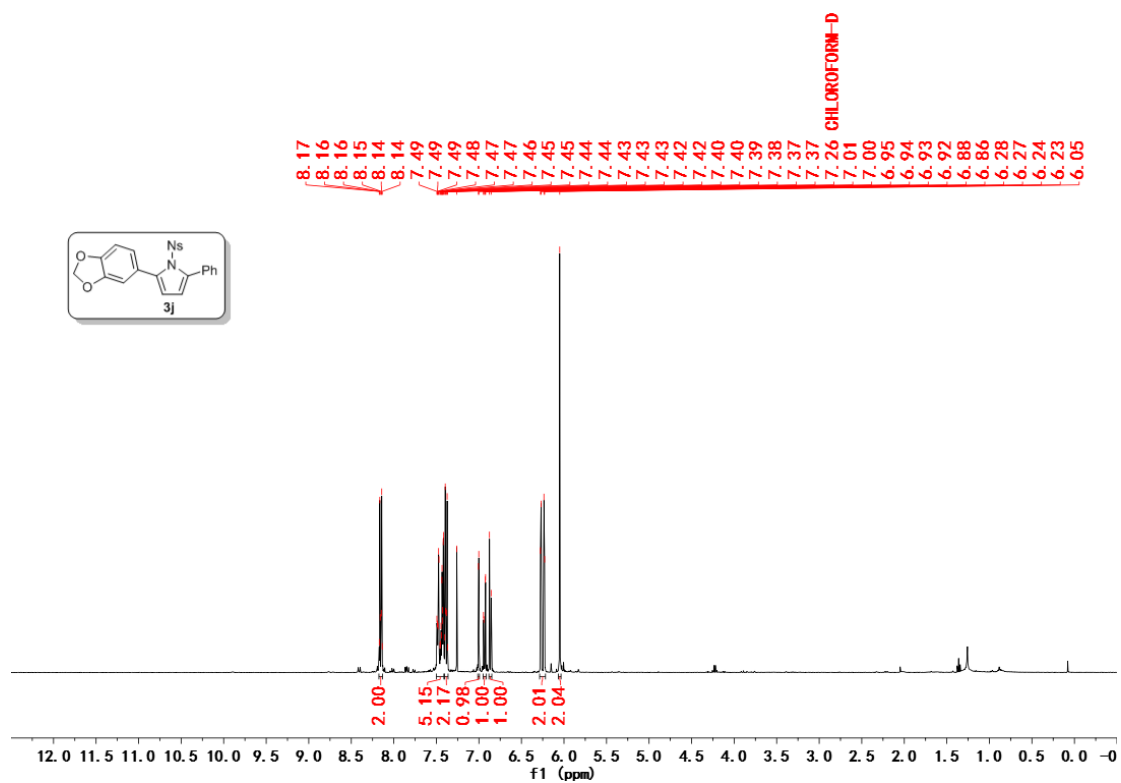
## H-pyrrole (3i)





**Figure S22.**  $^1\text{H}$  NMR of **3i** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **3i** (100 MHz,  $\text{CDCl}_3$ )

**2-(Benzo[d][1,3]dioxol-5-yl)-1-((4-nitrophenyl)sulfonyl)-5-phenyl-1H-pyrrole (3j)**



**Figure S23.** <sup>1</sup>H NMR of 3j (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of 3j (100 MHz, CDCl<sub>3</sub>)

# 2-(Naphthalen-2-yl)-1-((4-nitrophenyl)sulfonyl)-5-phenyl-1H-pyrrole

(3k)

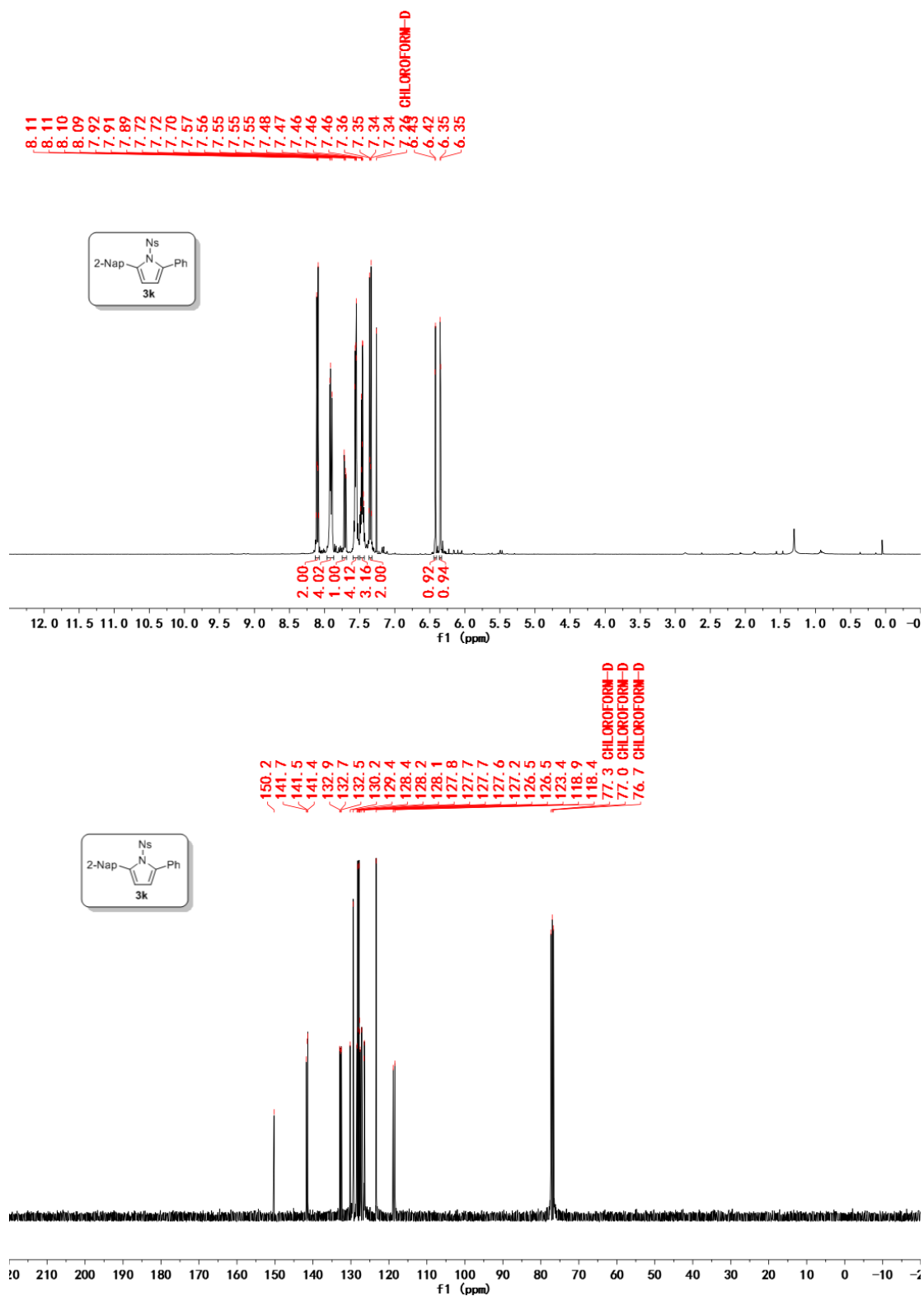


Figure S24. <sup>1</sup>H NMR of 3k (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of 3k (100 MHz, CDCl<sub>3</sub>)

## 2-Ethyl-1-((4-nitrophenyl)sulfonyl)-5-phenyl-1H-pyrrole (31)

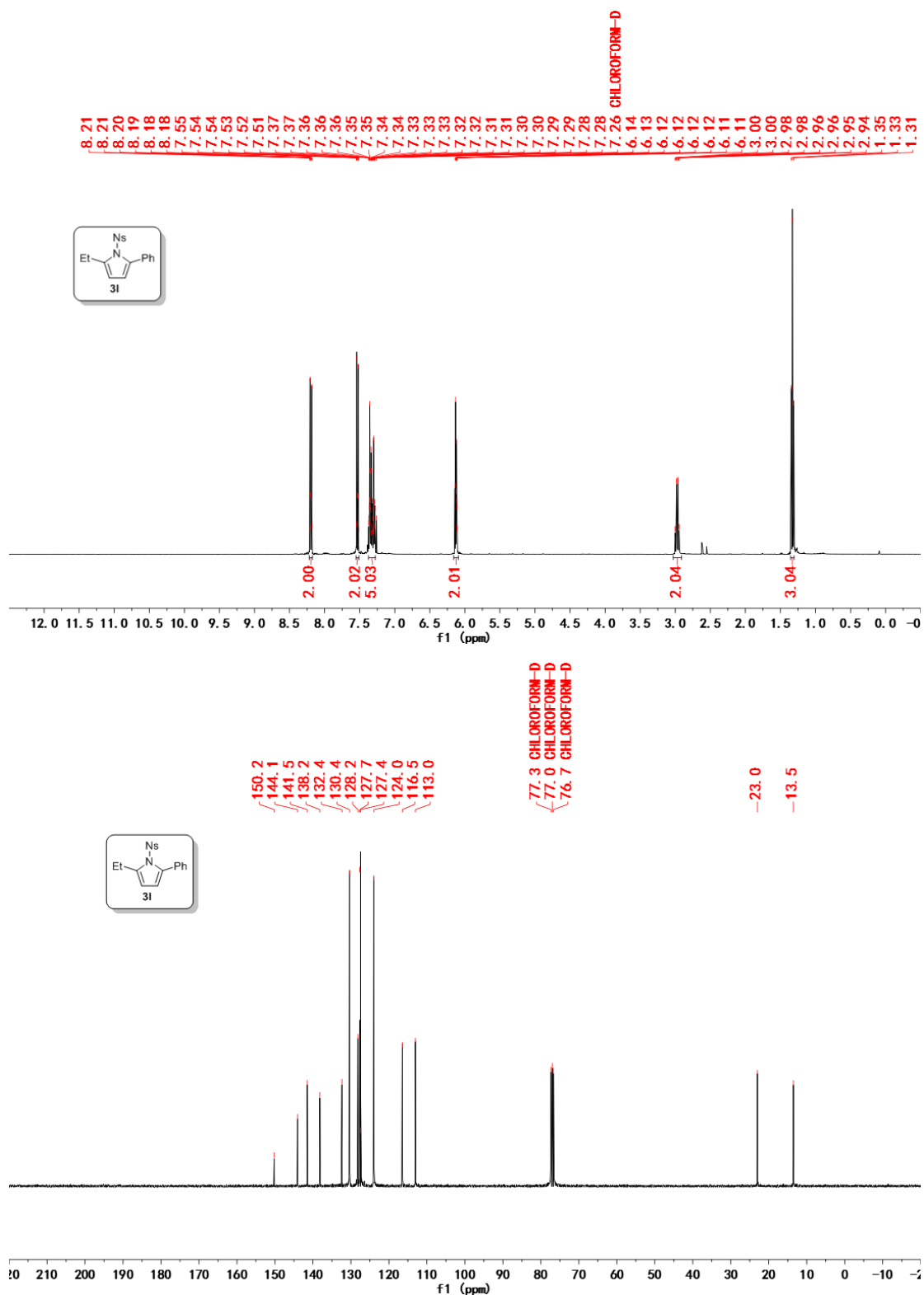


Figure S25. <sup>1</sup>H NMR of 31 (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of 31 (100 MHz, CDCl<sub>3</sub>)

## 2-Benzyl-1-((4-nitrophenyl)sulfonyl)-5-phenyl-1H-pyrrole (3m)

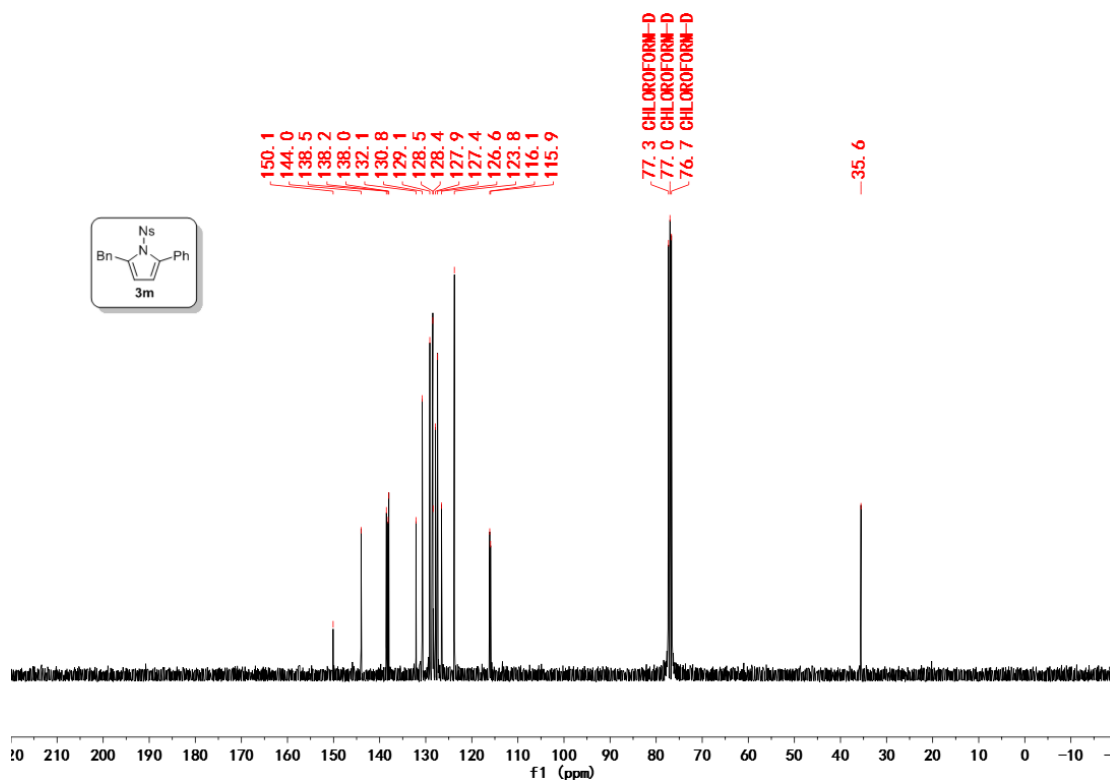
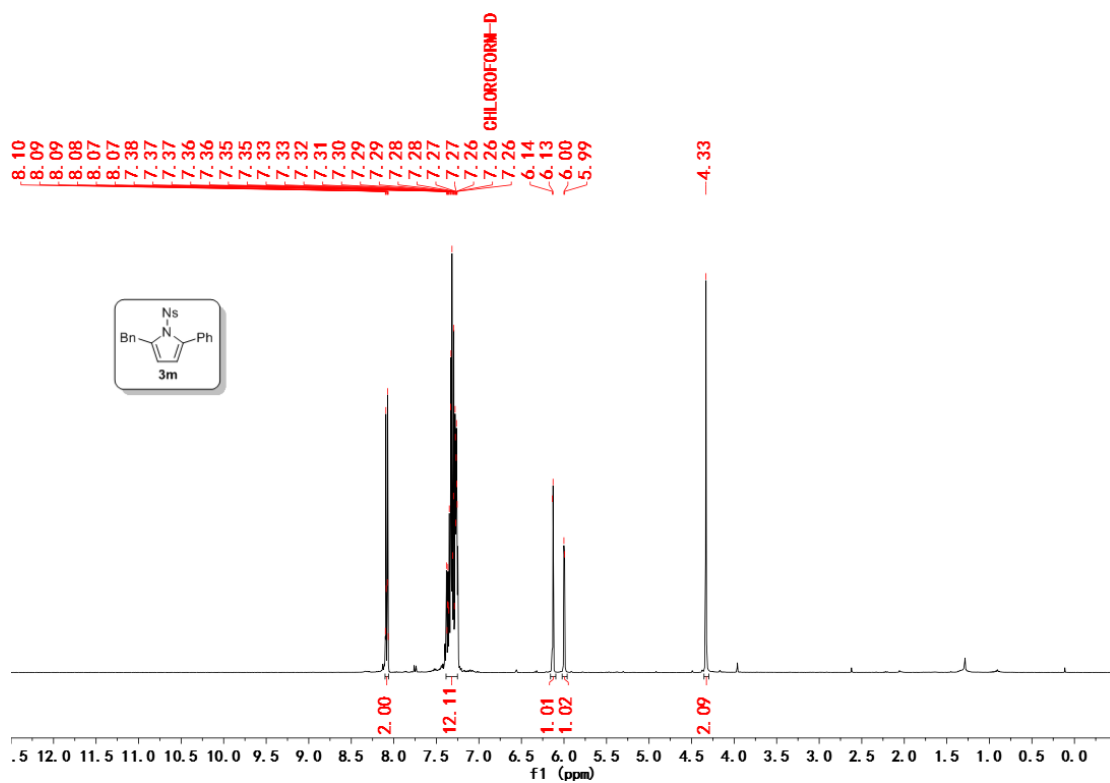


Figure S26. <sup>1</sup>H NMR of **3m** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **3m** (100 MHz, CDCl<sub>3</sub>)

# 1-((4-Nitrophenyl)sulfonyl)-2-phenyl-5-(*o*-tolyl)-1H-pyrrole (3n)

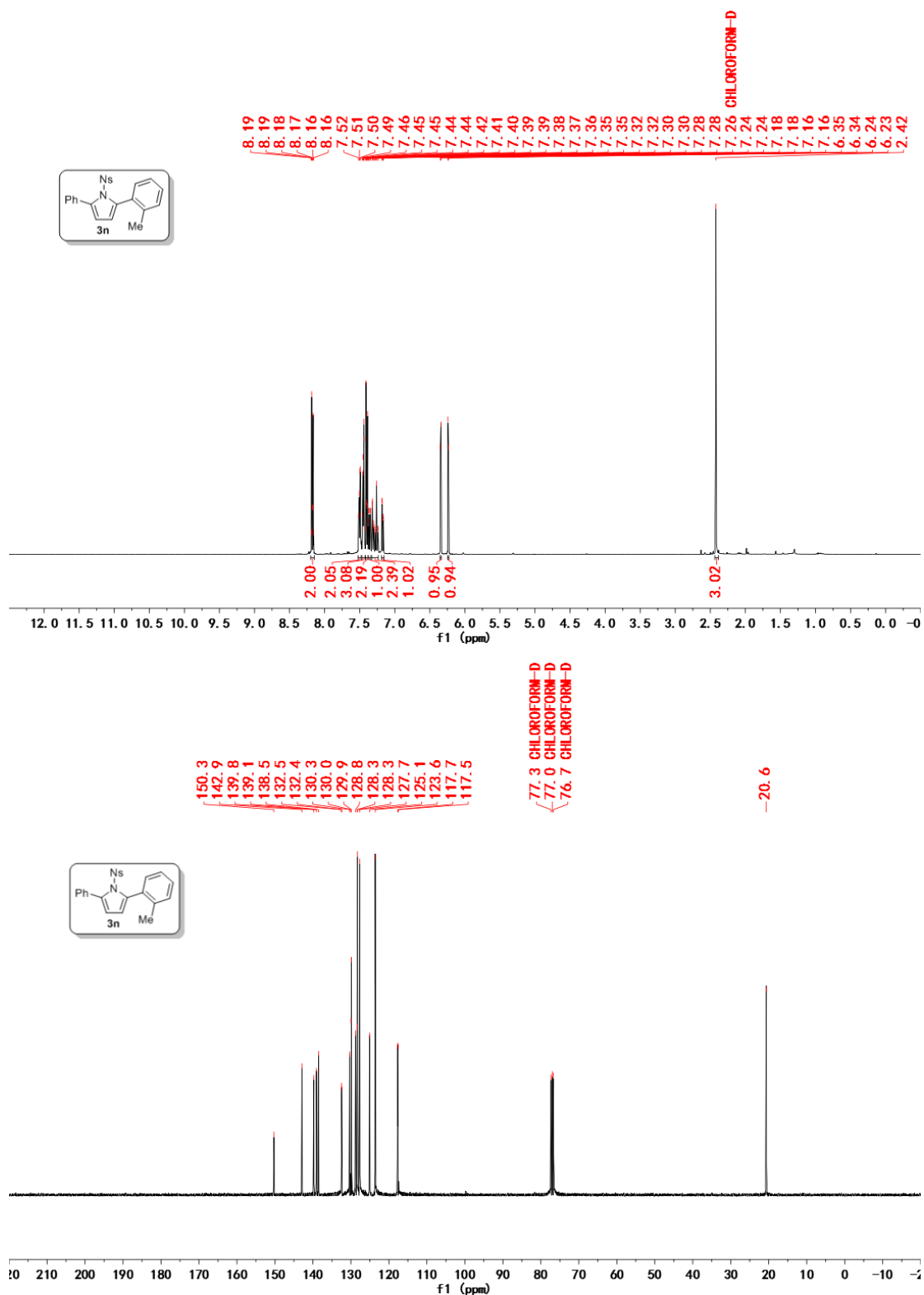
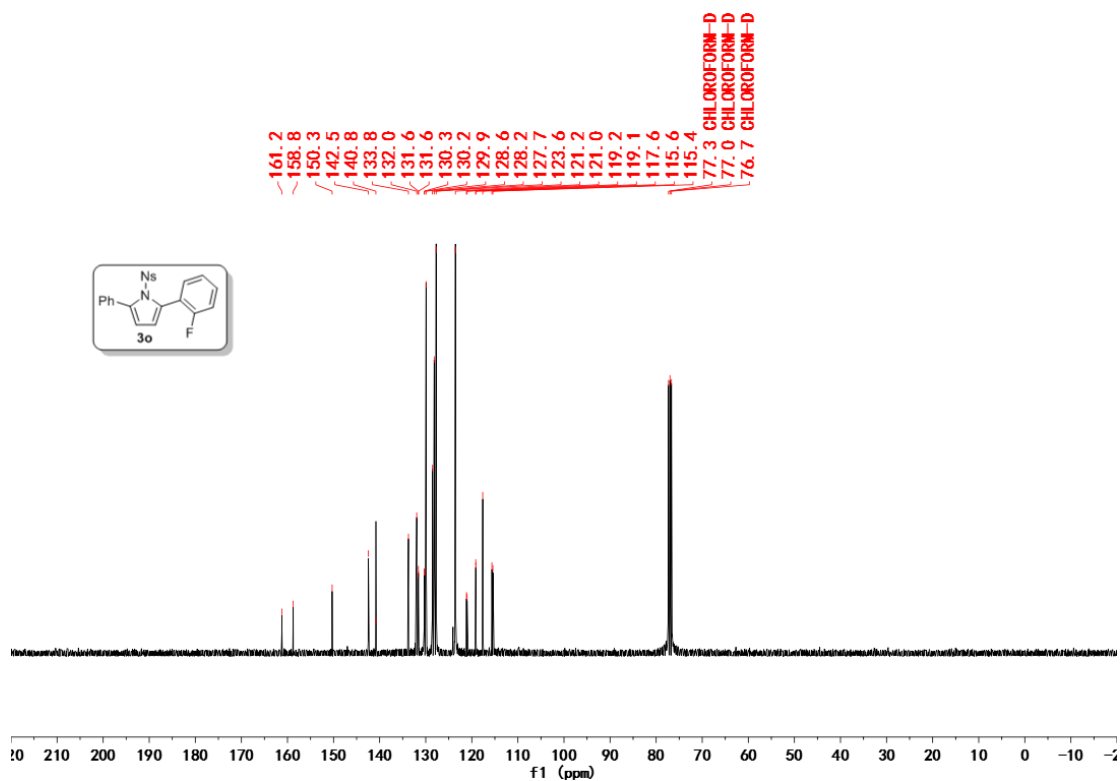
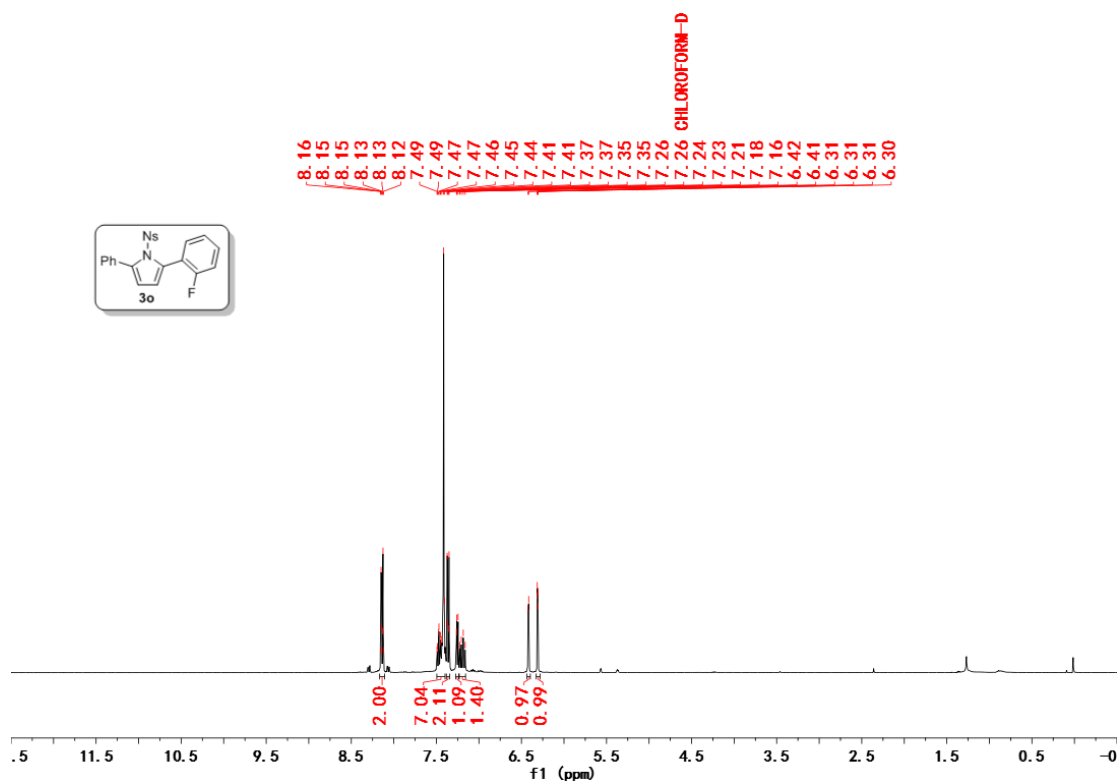


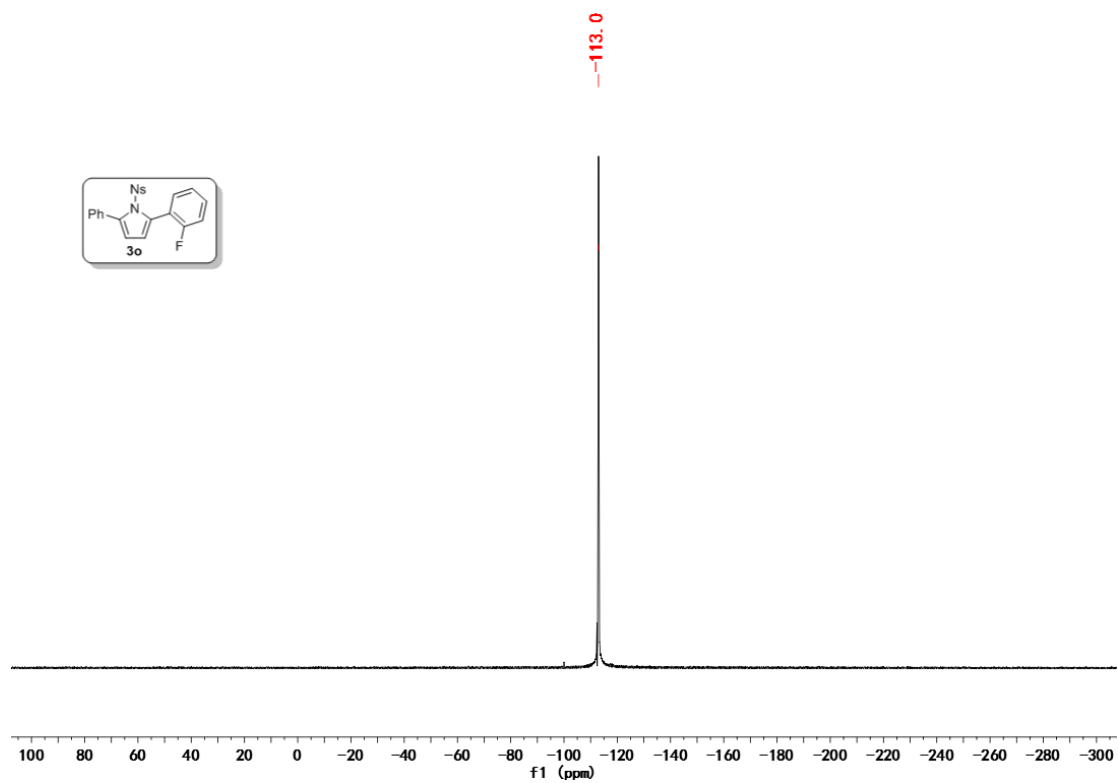
Figure S27. <sup>1</sup>H NMR of 3n (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of 3n (100 MHz, CDCl<sub>3</sub>)



# 2-(2-Fluorophenyl)-1-((4-nitrophenyl)sulfonyl)-5-phenyl-1H-pyrrole

(3o)





**Figure S28.** <sup>1</sup>H NMR of **3o** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **3o** (100 MHz, CDCl<sub>3</sub>)

# 1-((4-Nitrophenyl)sulfonyl)-2-phenyl-5-(m-tolyl)-1H-pyrrole (3p)

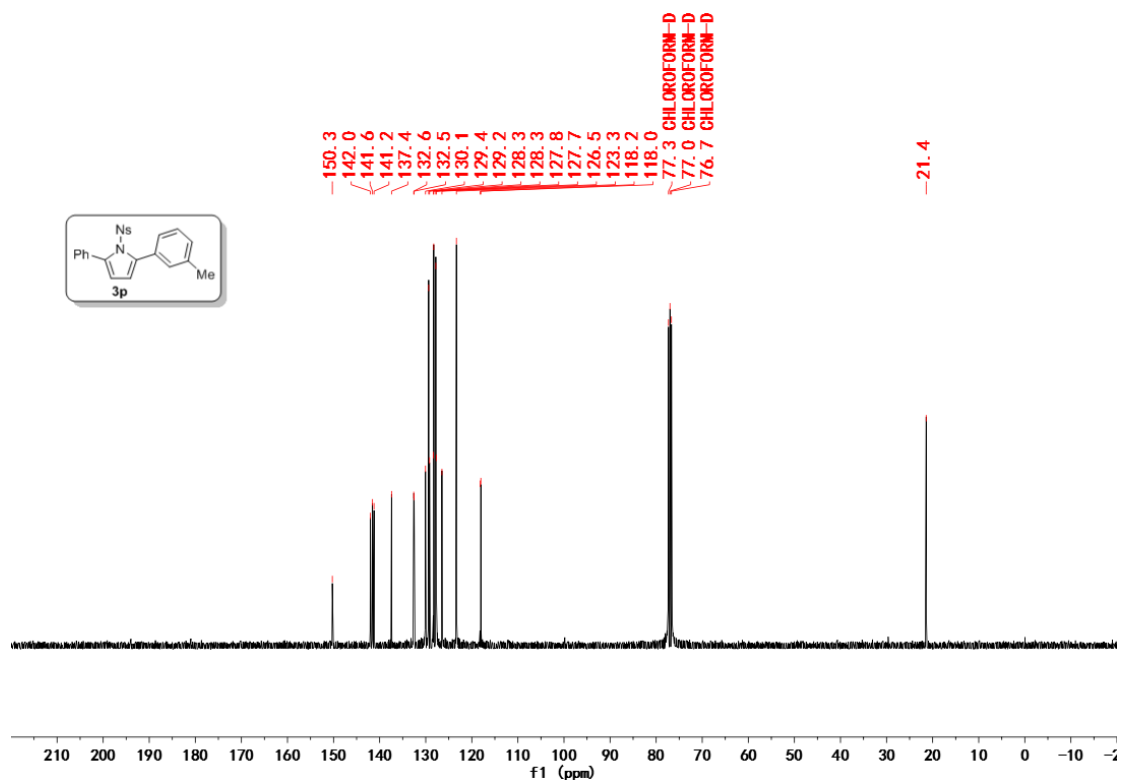
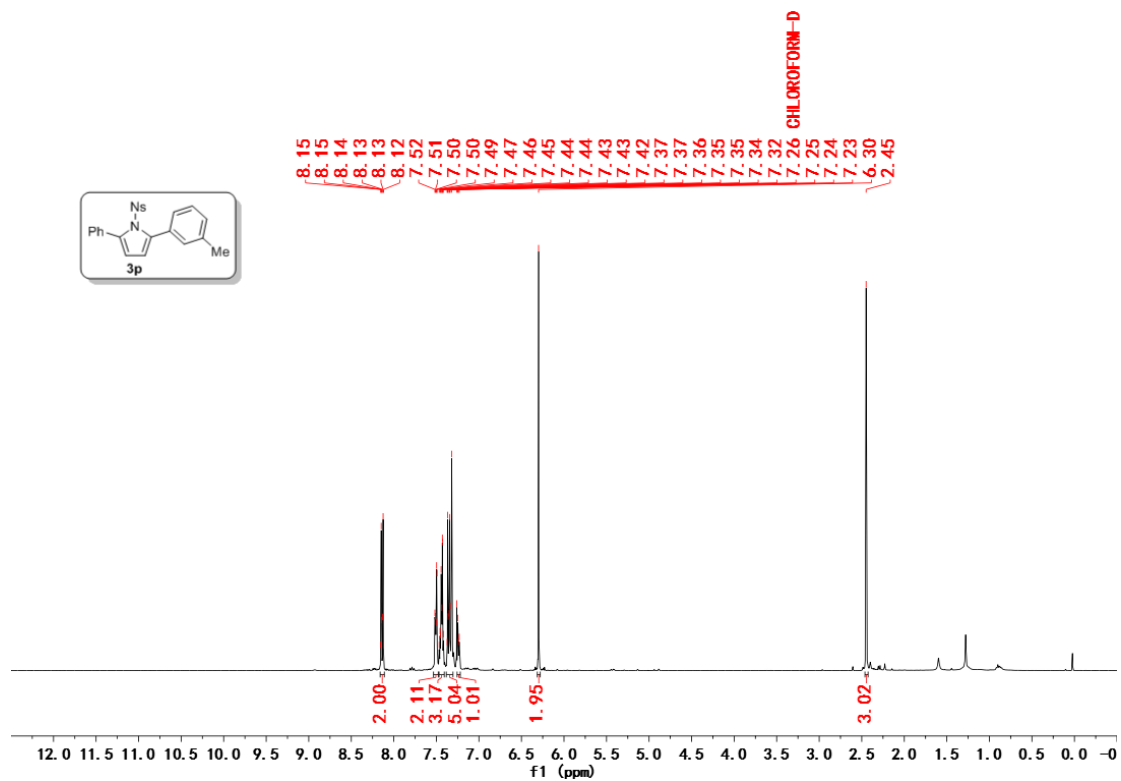
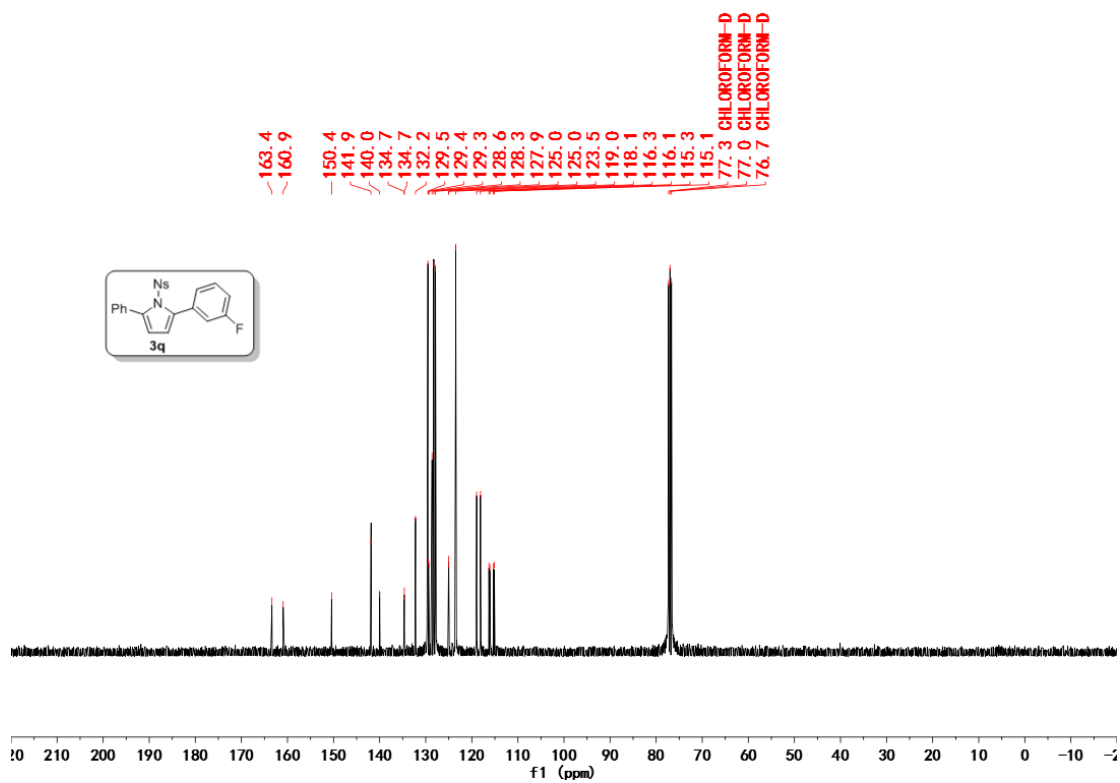
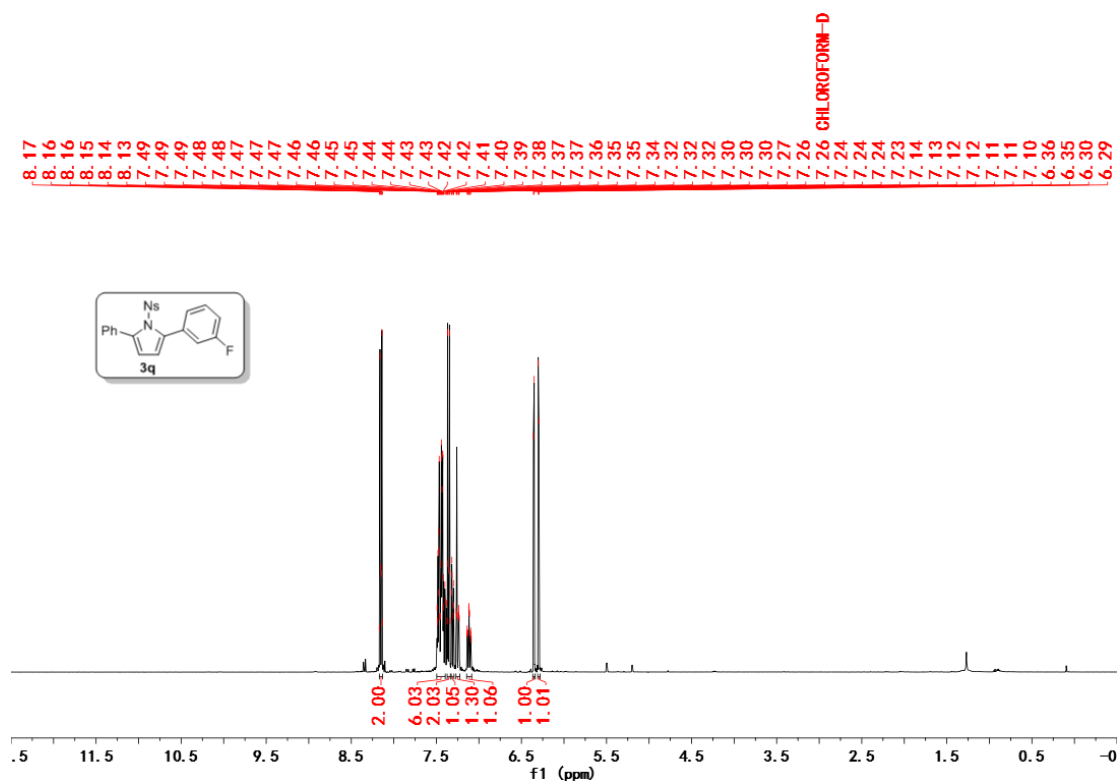
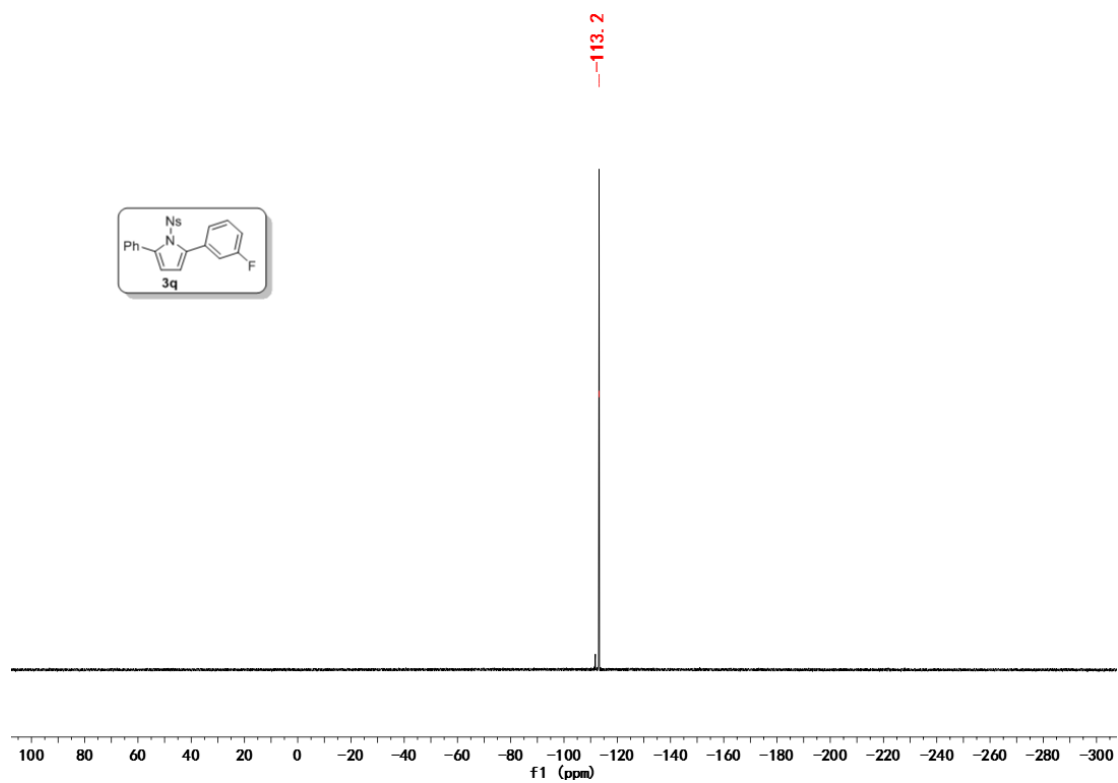


Figure S29. <sup>1</sup>H NMR of 3p (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of 3p (100 MHz, CDCl<sub>3</sub>)

# 1-(3-Fluorophenyl)-1-((4-nitrophenyl)sulfonyl)-5-phenyl-1H-pyrrole

(3q)





**Figure S30.**  $^1\text{H}$  NMR of **3q** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **3q** (100 MHz,  $\text{CDCl}_3$ )

# 1-((4-Nitrophenyl)sulfonyl)-2-phenyl-5-(p-tolyl)-1H-pyrrole (3r)

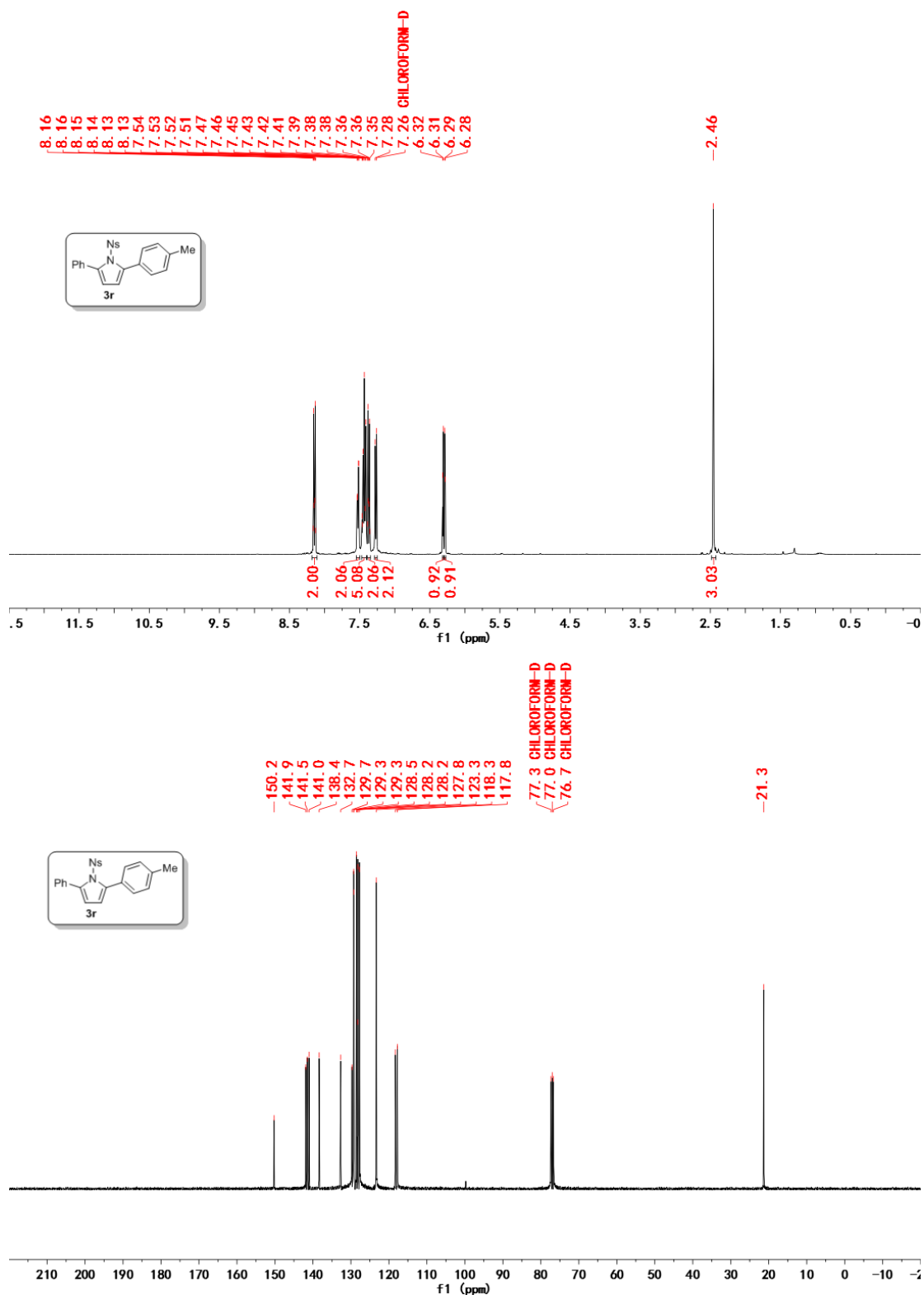
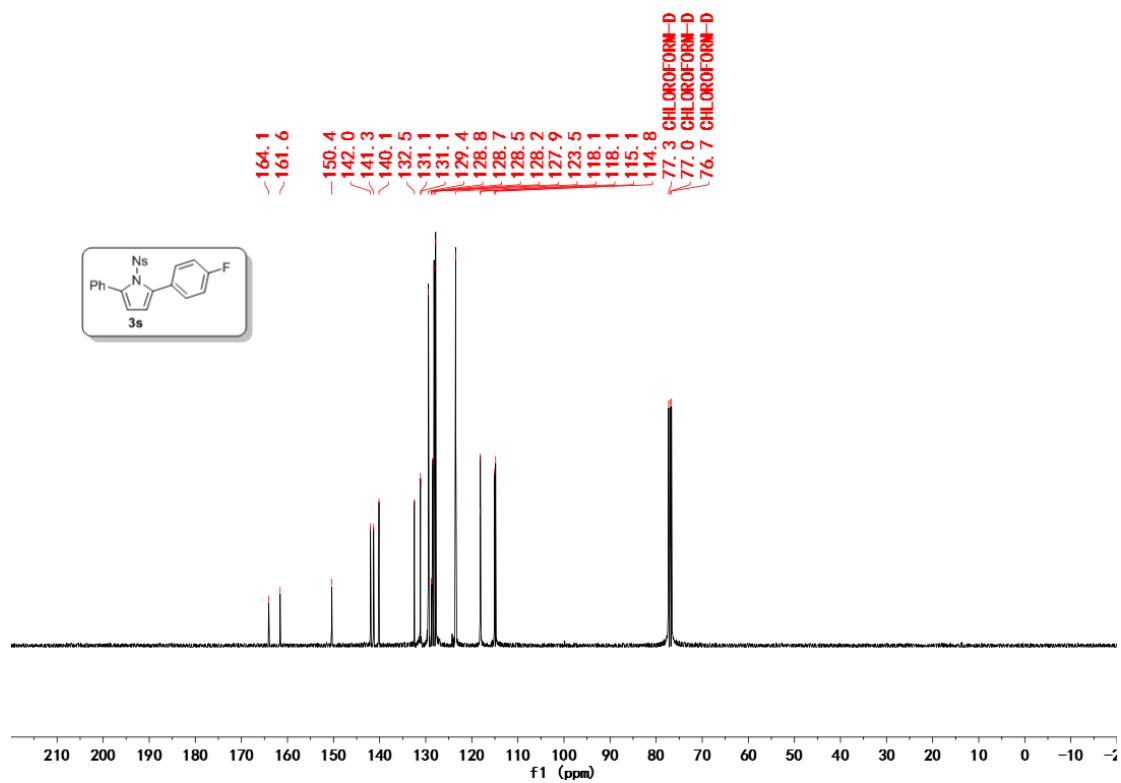
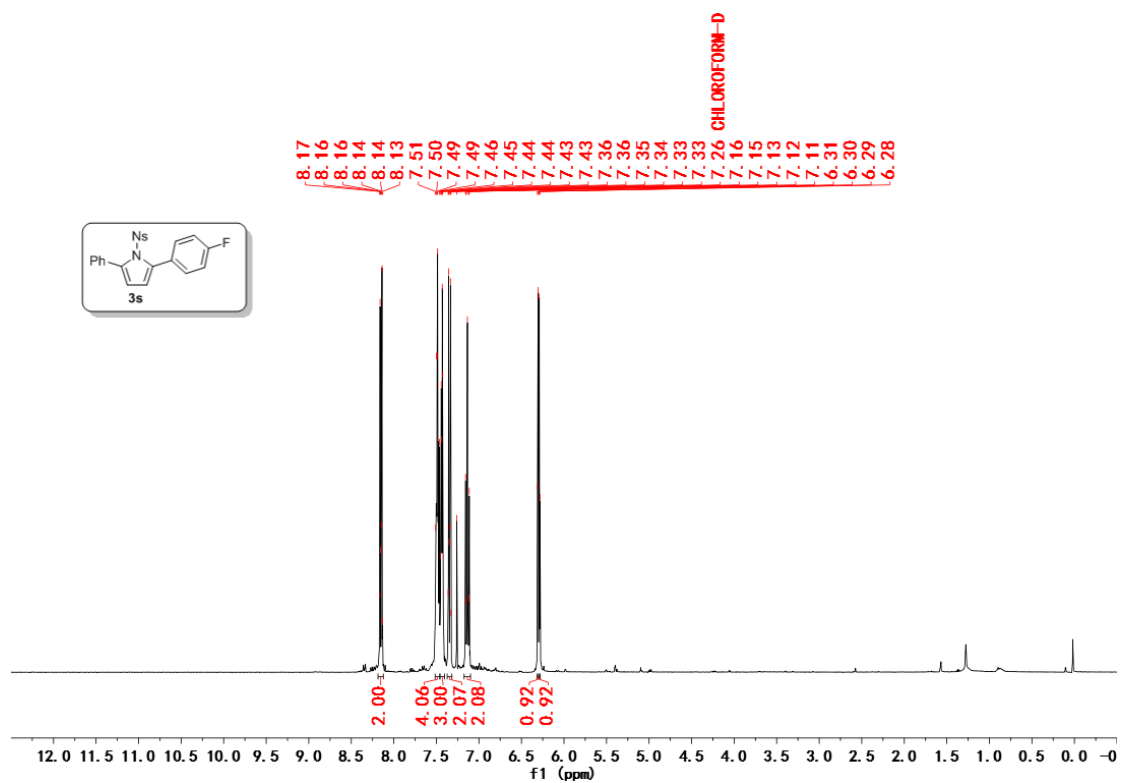
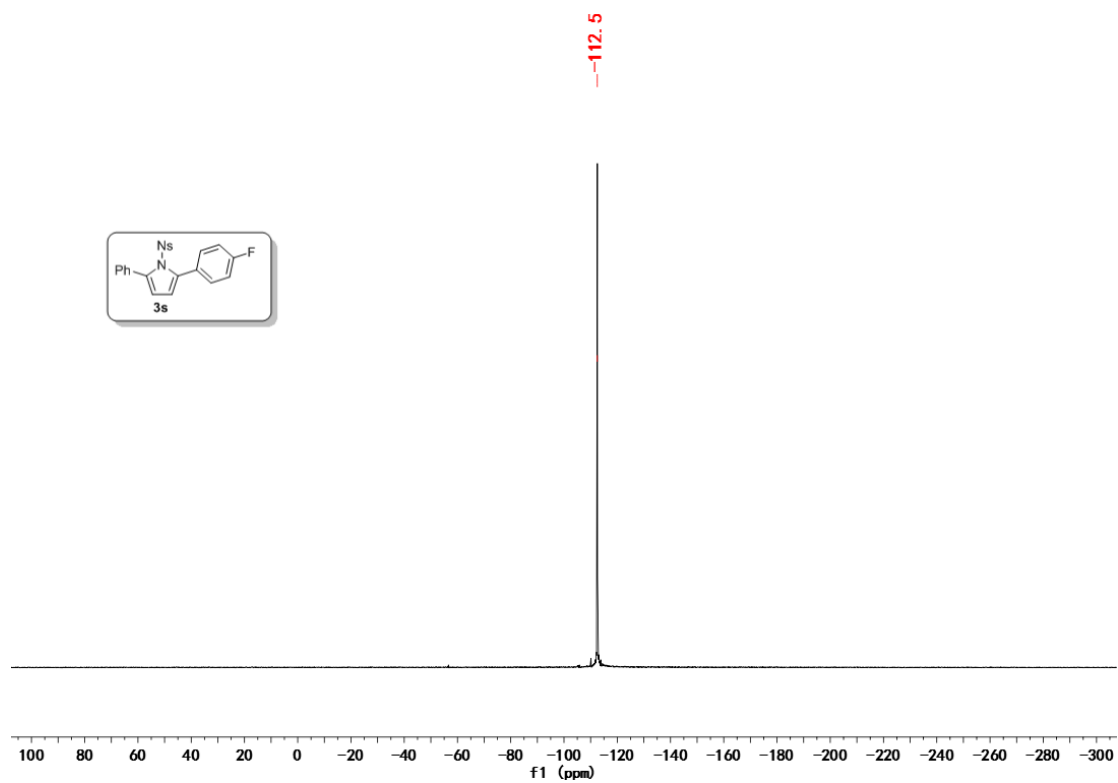


Figure S31. <sup>1</sup>H NMR of **3r** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **3r** (100 MHz, CDCl<sub>3</sub>)

# 2-(4-Fluorophenyl)-1-((4-nitrophenyl)sulfonyl)-5-phenyl-1H-pyrrole

(3s)

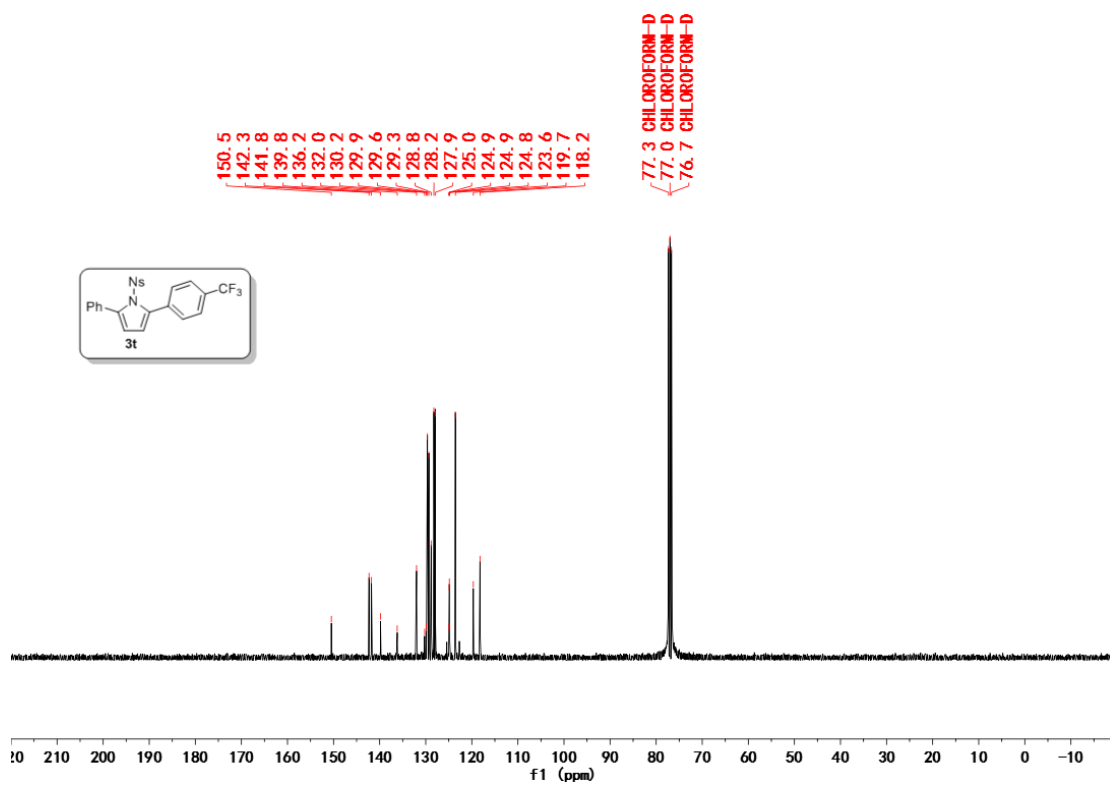
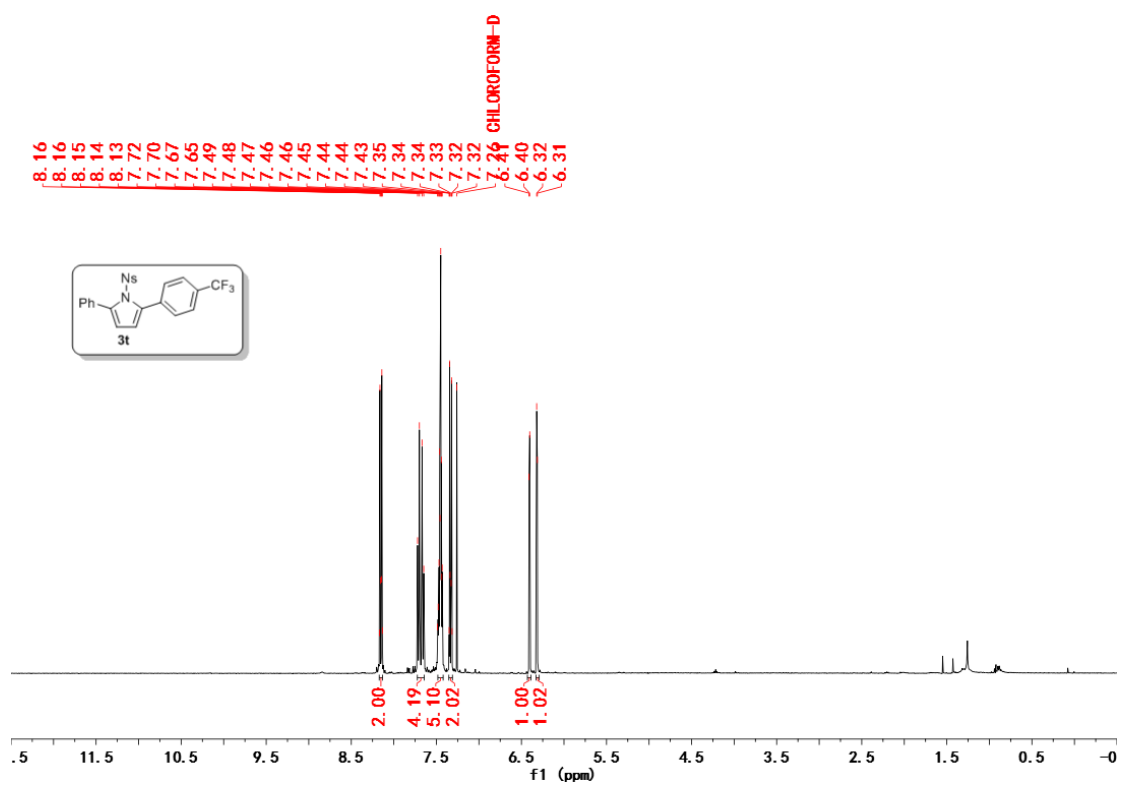


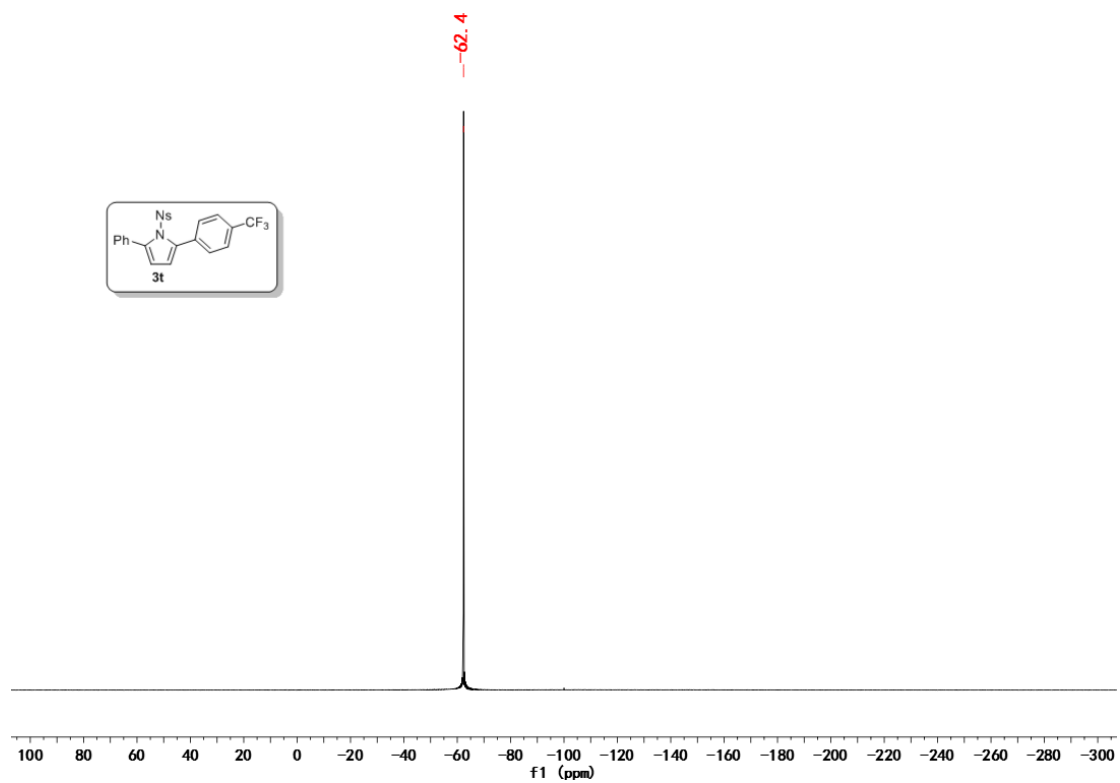


**Figure S32.** <sup>1</sup>H NMR of **3s** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **3s** (100 MHz, CDCl<sub>3</sub>)



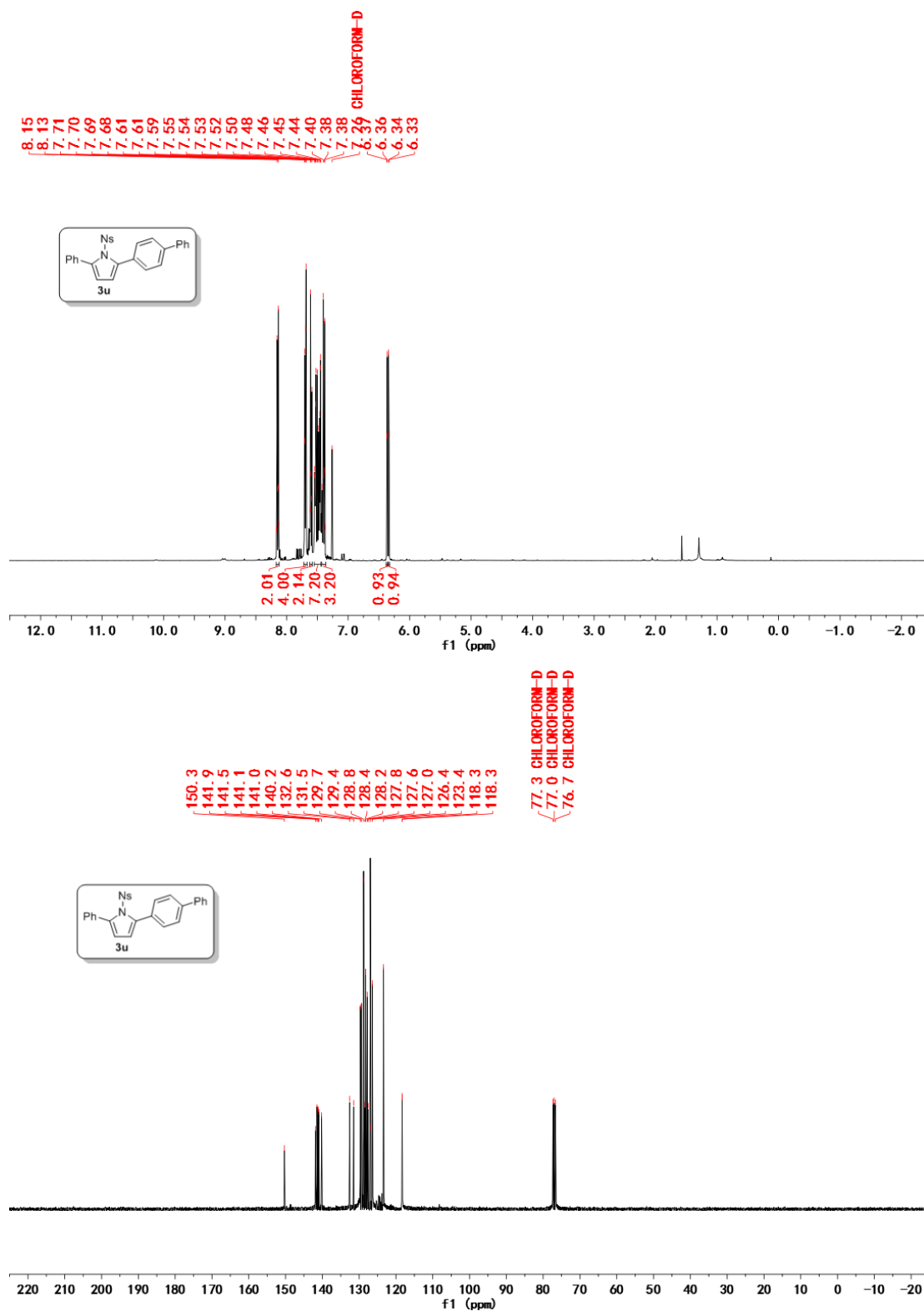
# 1-((4-Nitrophenyl)sulfonyl)-2-phenyl-5-(4-(trifluoromethyl)phenyl)-1H-pyrrole (3t)





**Figure S33.**  $^1\text{H}$  NMR of **3t** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **3t** (100 MHz,  $\text{CDCl}_3$ )

**2-([1,1'-Biphenyl]-4-yl)-1-((4-nitrophenyl)sulfonyl)-5-phenyl-1H-pyrrole (3u)**



**Figure S34.** <sup>1</sup>H NMR of **3u** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **3u** (100 MHz, CDCl<sub>3</sub>)

# 2-(Naphthalen-2-yl)-1-((4-nitrophenyl)sulfonyl)-5-phenyl-1H-pyrrole

(3v)

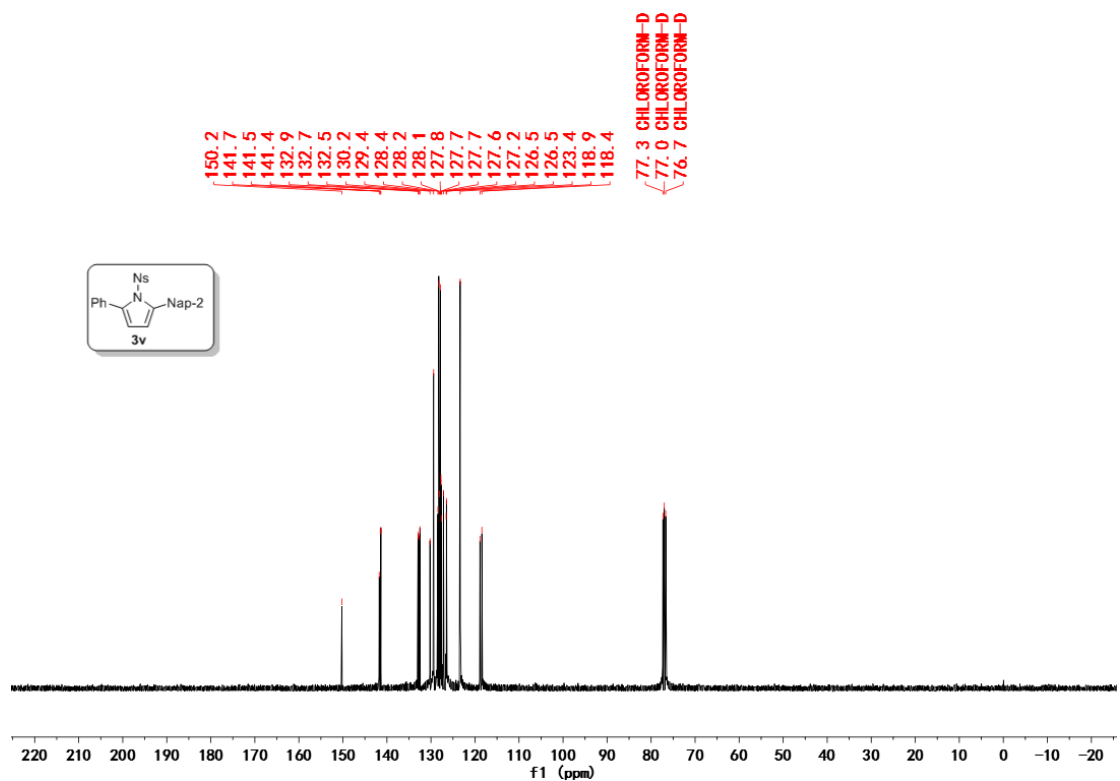
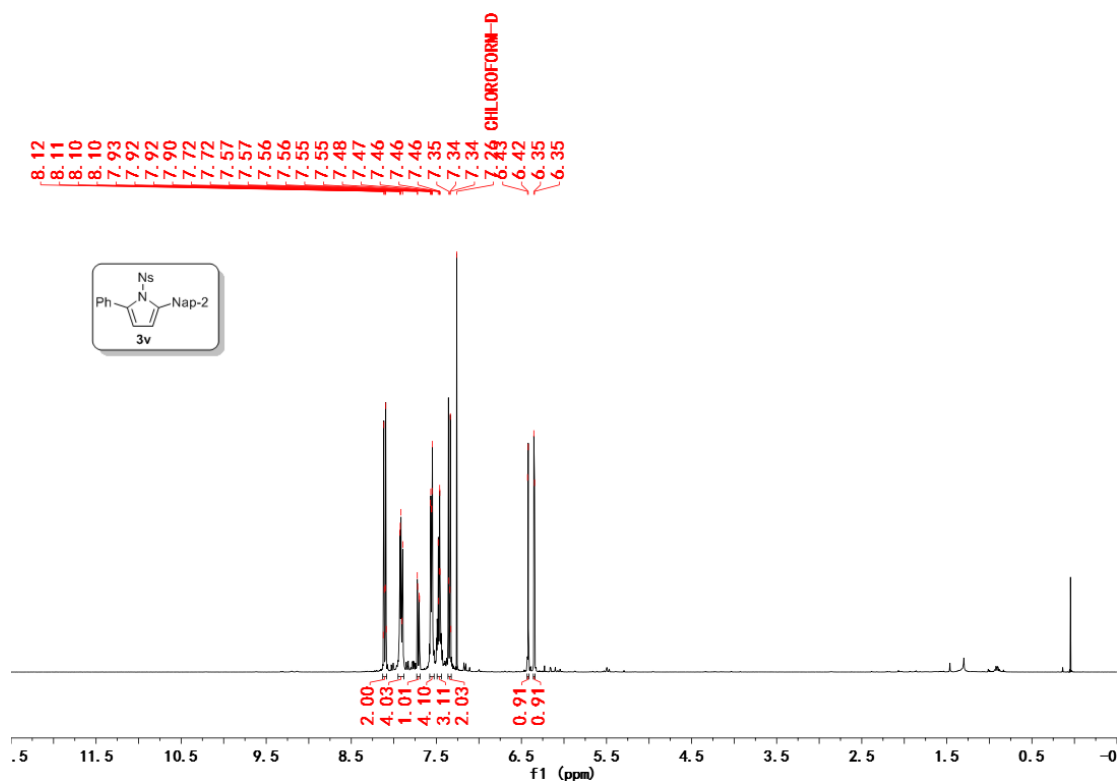


Figure S35. <sup>1</sup>H NMR of 3v (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of 3v (100 MHz, CDCl<sub>3</sub>)

# 1-((4-nitrophenyl)sulfonyl)-2-phenyl-5-(thiophen-3-yl)-1H-pyrrole

(3w)

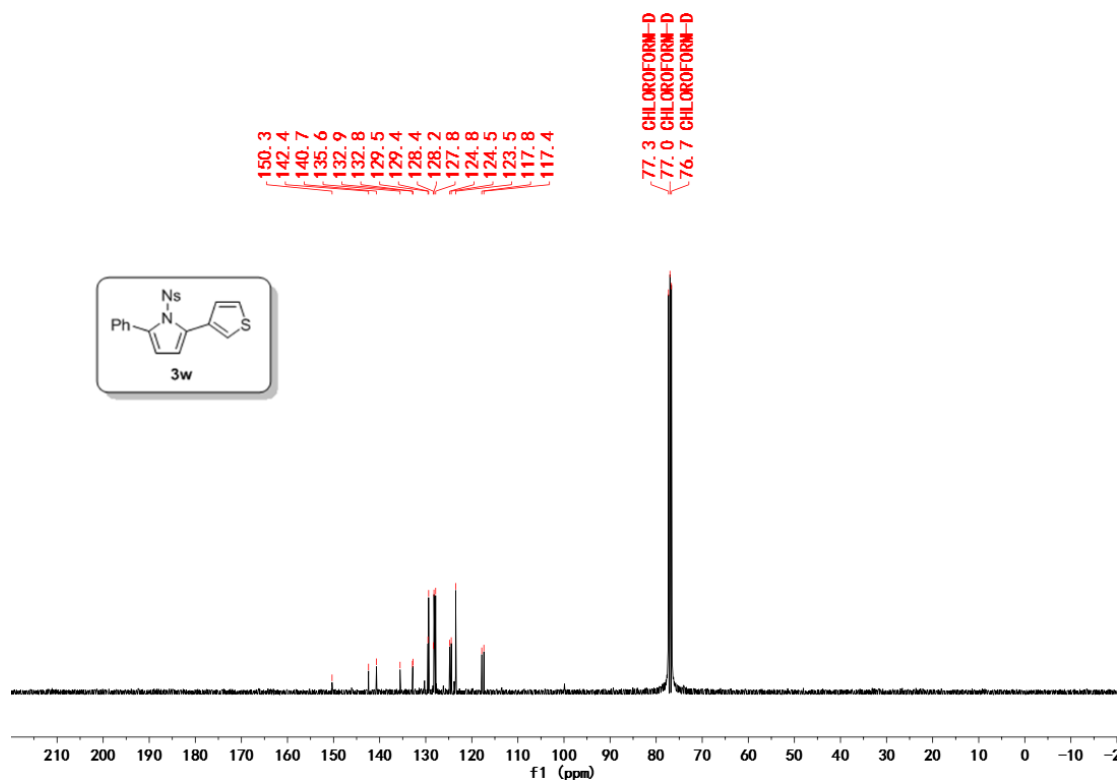
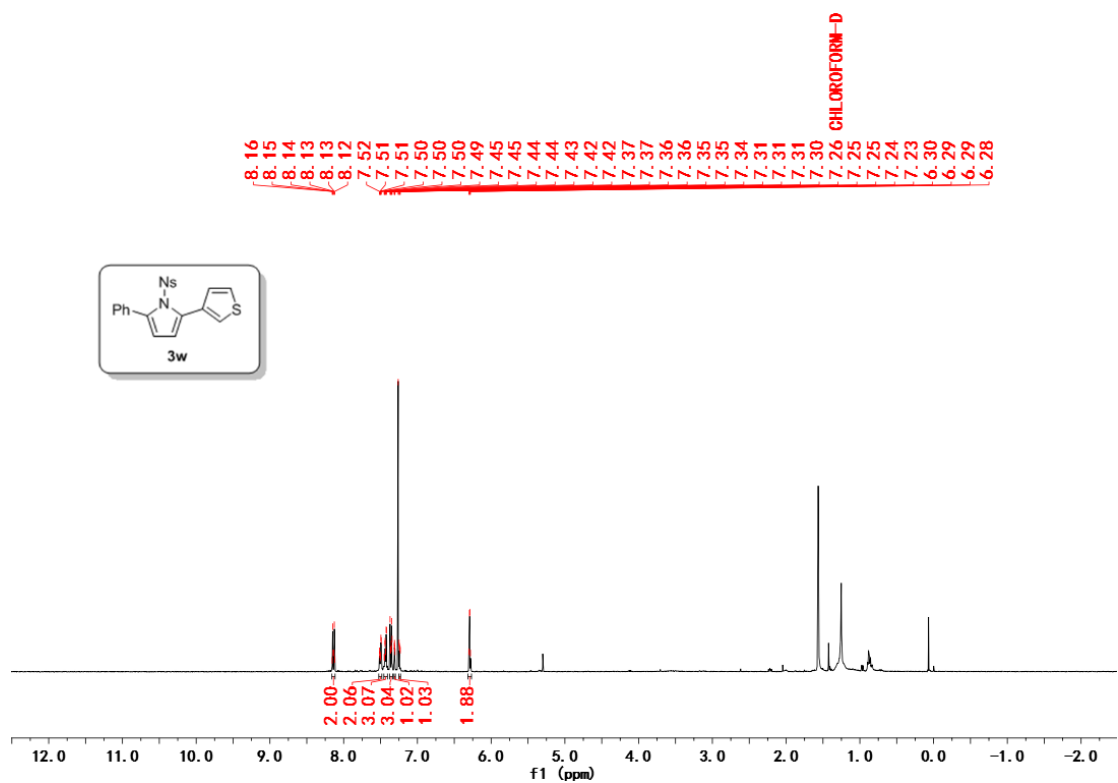


Figure S36. <sup>1</sup>H NMR of 3w (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of 3w (100 MHz, CDCl<sub>3</sub>)

## 2-Butyl-1-((4-nitrophenyl)sulfonyl)-5-phenyl-1H-pyrrole (3x)

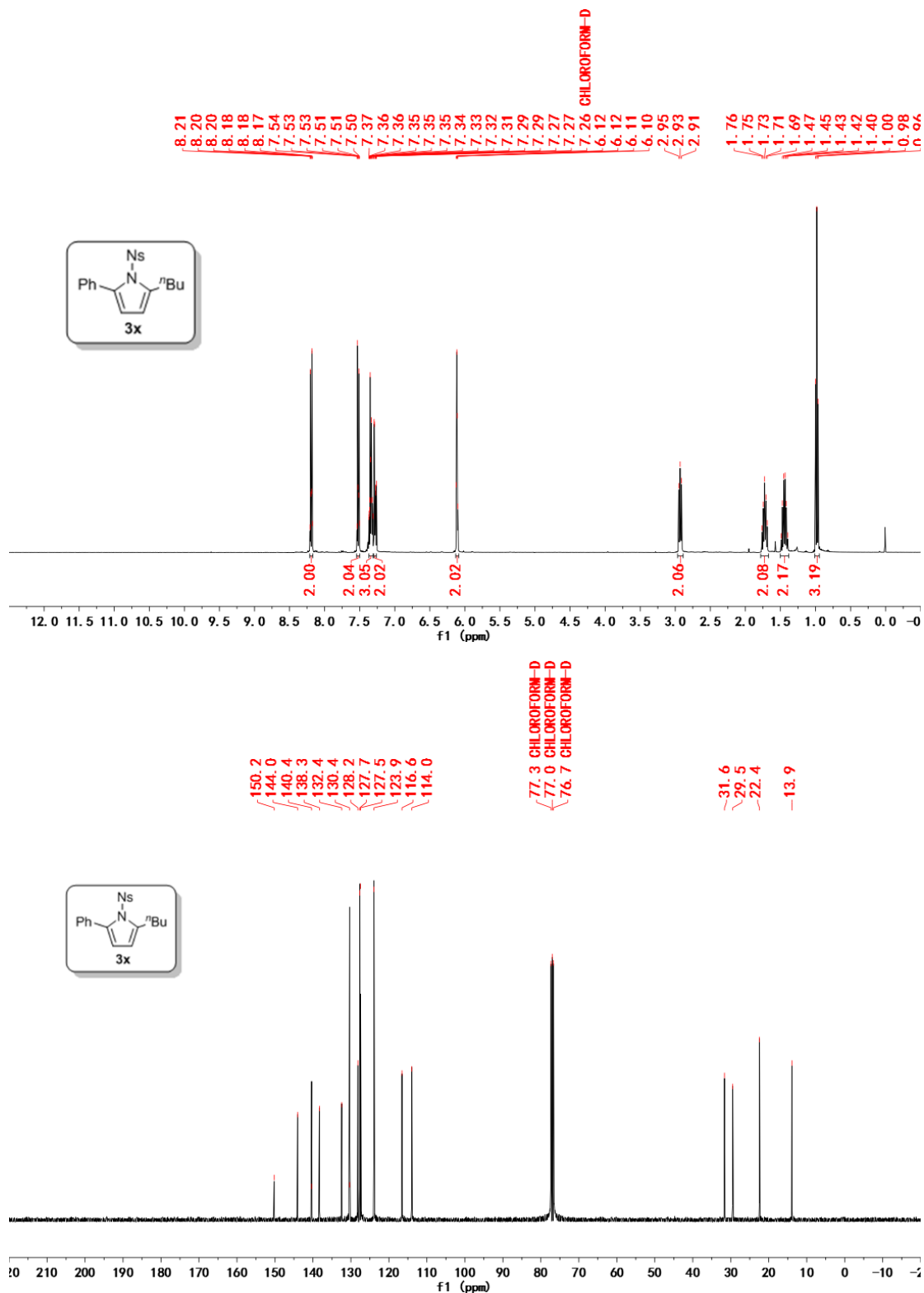


Figure S37. <sup>1</sup>H NMR of 3x (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of 3x (100 MHz, CDCl<sub>3</sub>)

## 2-Cyclopropyl-1-((4-nitrophenyl)sulfonyl)-5-phenyl-1H-pyrrole (3y)

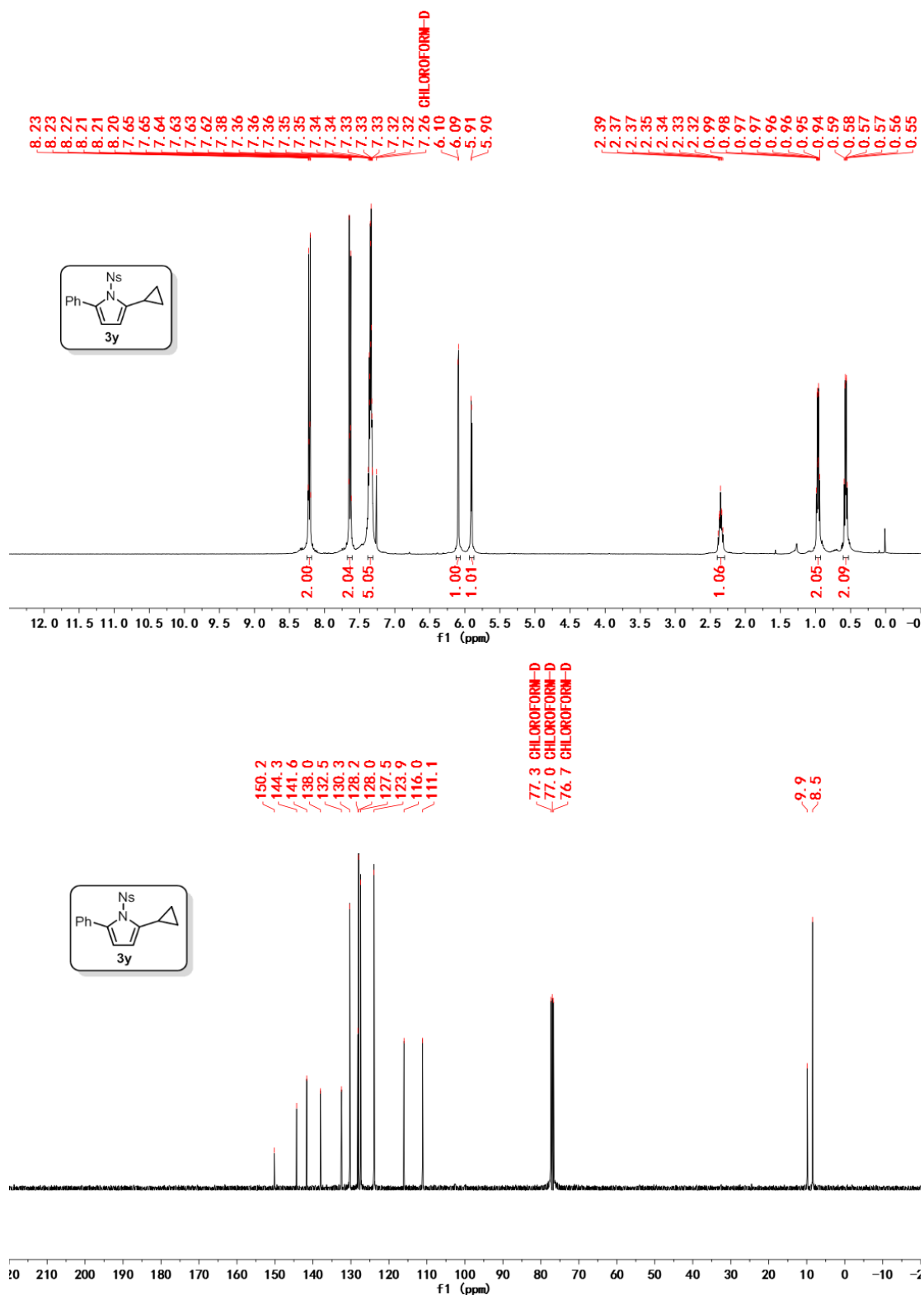


Figure S38. <sup>1</sup>H NMR of **3y** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **3y** (100 MHz, CDCl<sub>3</sub>)

# 1-((4-Nitrophenyl)sulfonyl)-2,3,5-triphenyl-1H-pyrrole (3z)

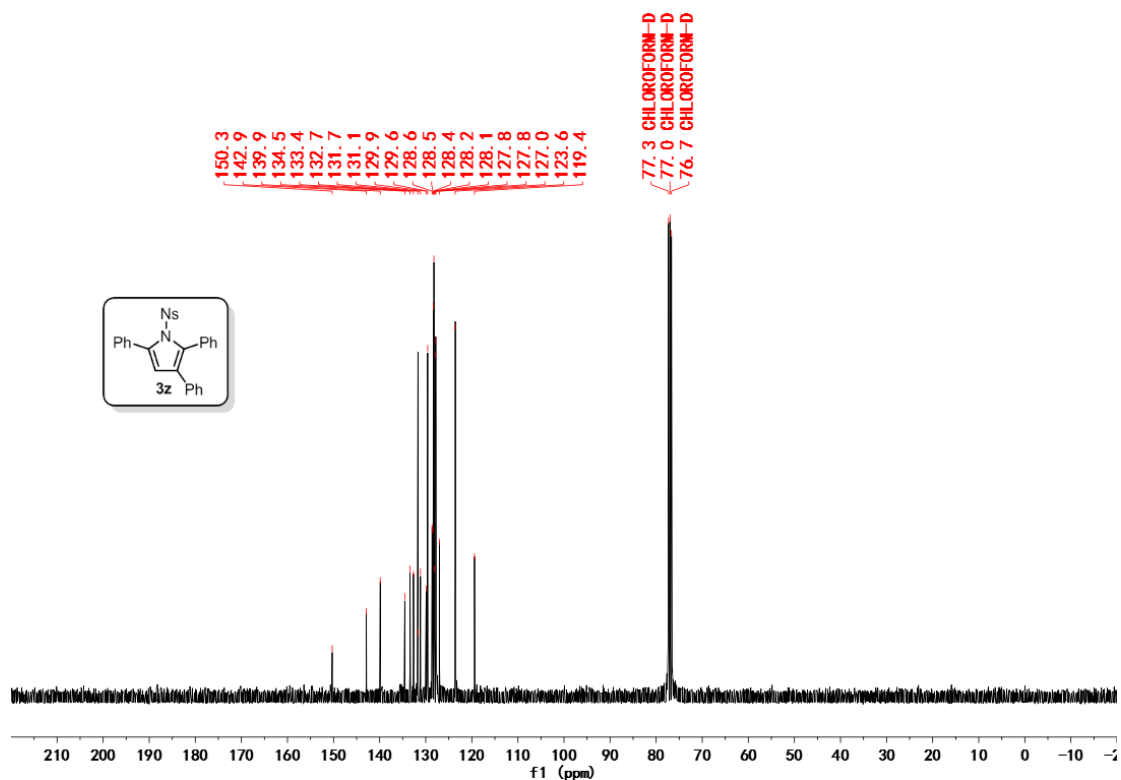
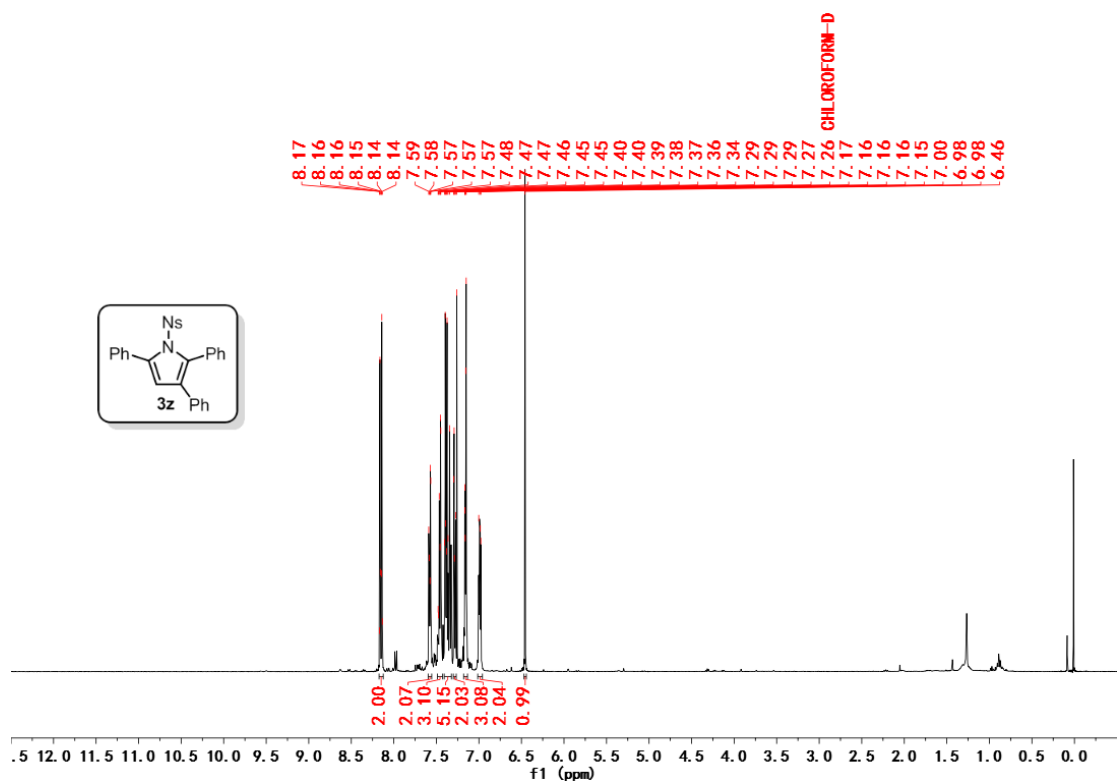


Figure S39. <sup>1</sup>H NMR of 3z (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of 3z (100 MHz, CDCl<sub>3</sub>)



### 3-Ethyl-1-((4-nitrophenyl)sulfonyl)-2,5-diphenyl-1H-pyrrole (4a-1)

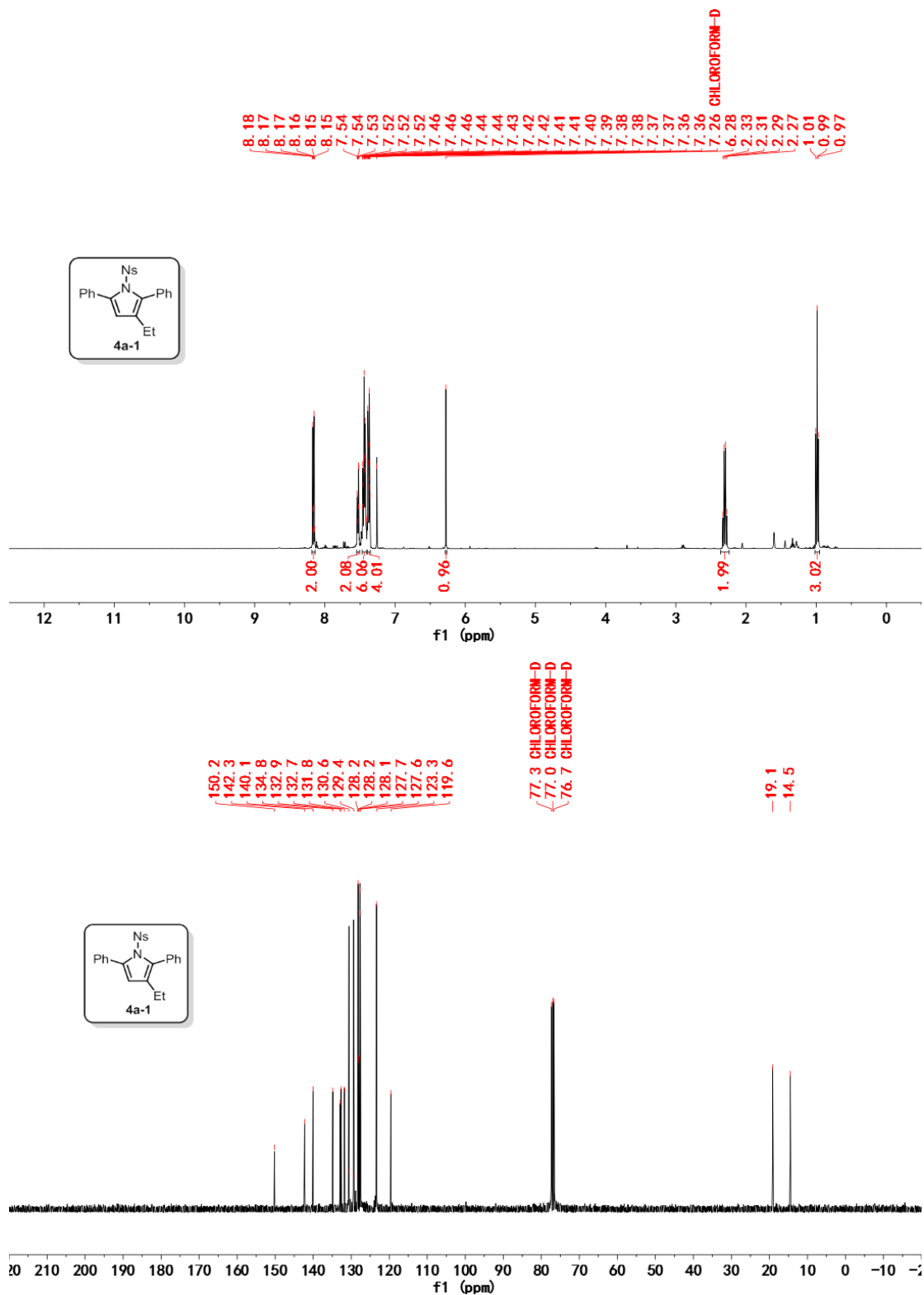


Figure S40. <sup>1</sup>H NMR of **4a-1** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **4a-1** (100 MHz, CDCl<sub>3</sub>)

## 2-Ethyl-1-((4-nitrophenyl)sulfonyl)-3,5-diphenyl-1H-pyrrole (3z-2)

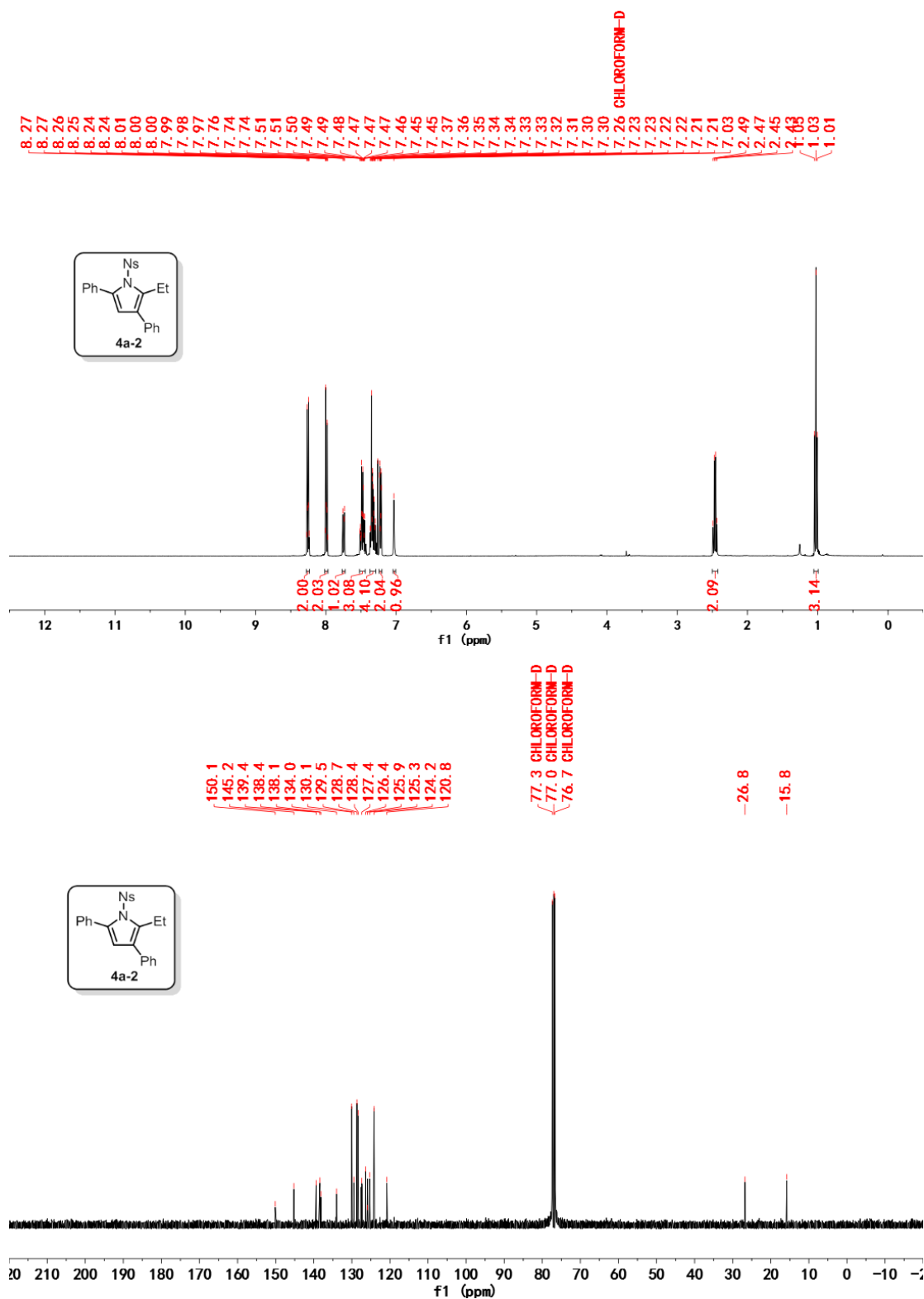


Figure S41. <sup>1</sup>H NMR of 4a-2 (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of 4a-2 (100 MHz, CDCl<sub>3</sub>)