

*Supporting Information:*

Dative Directing Group Effects in Ti-Catalyzed [2+2+1] Pyrrole Synthesis: Chemo- and Regioselective Alkyne Heterocoupling

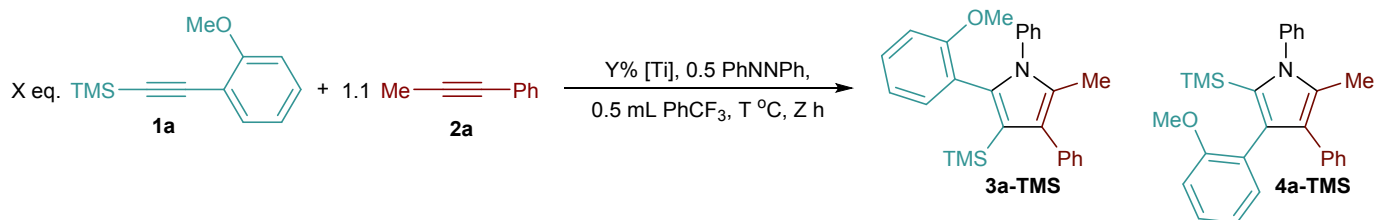
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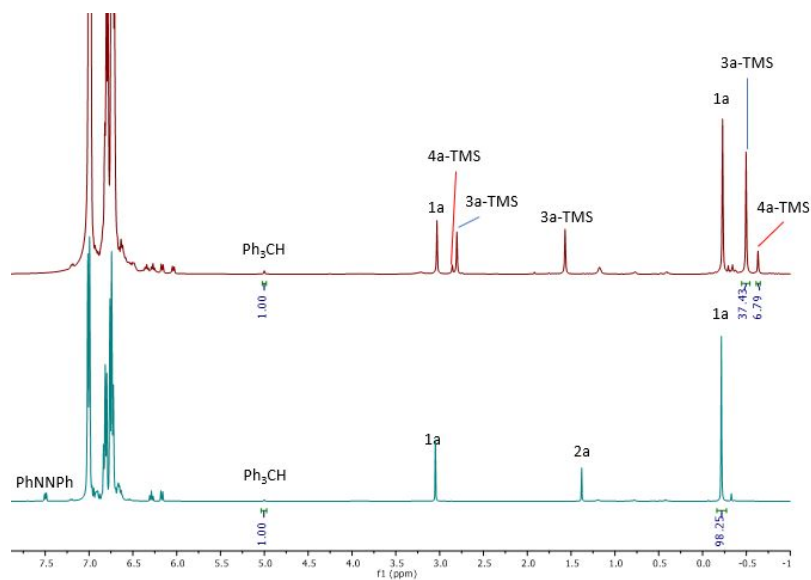
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## Reaction Condition Optimization (Table 1)

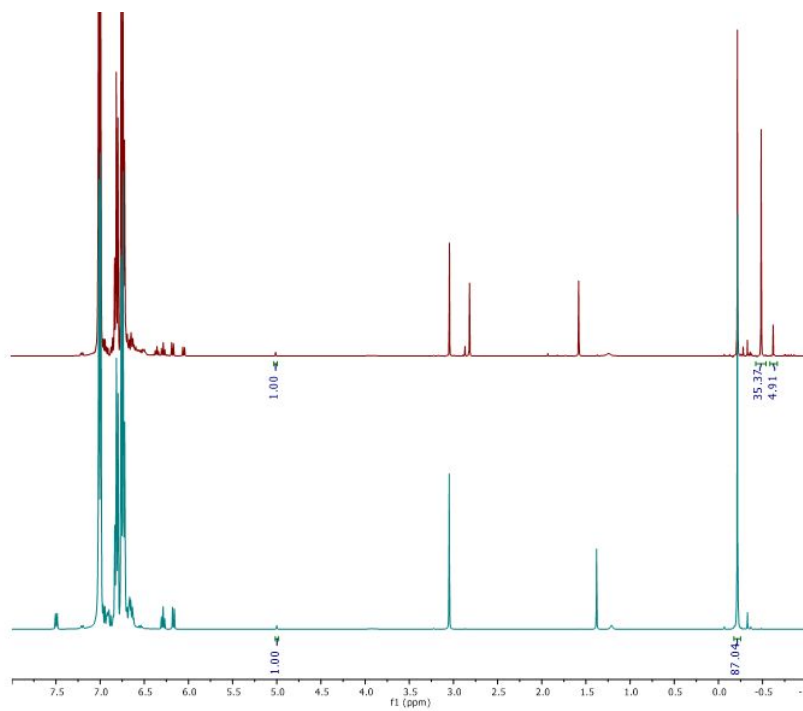
### Reaction Spectra



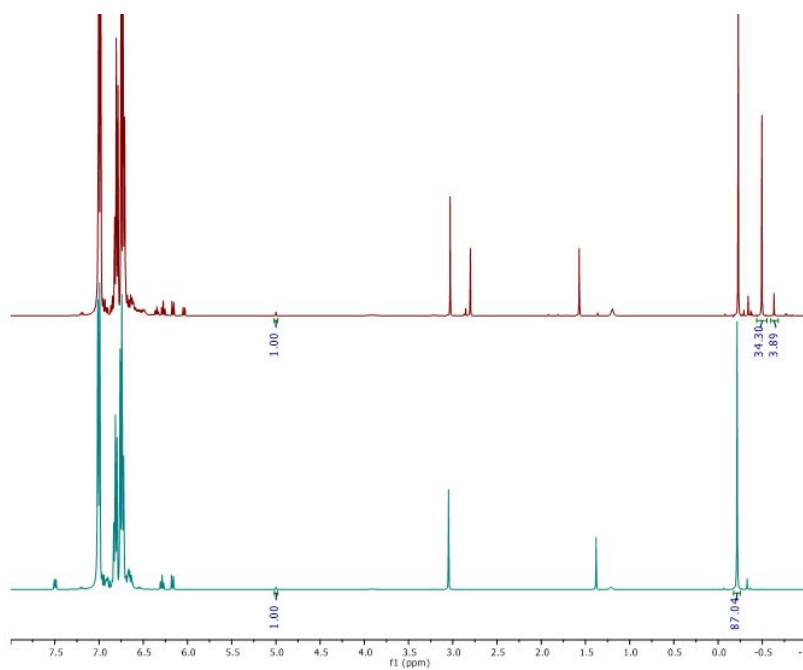
### No-D <sup>1</sup>H NMR Spectra



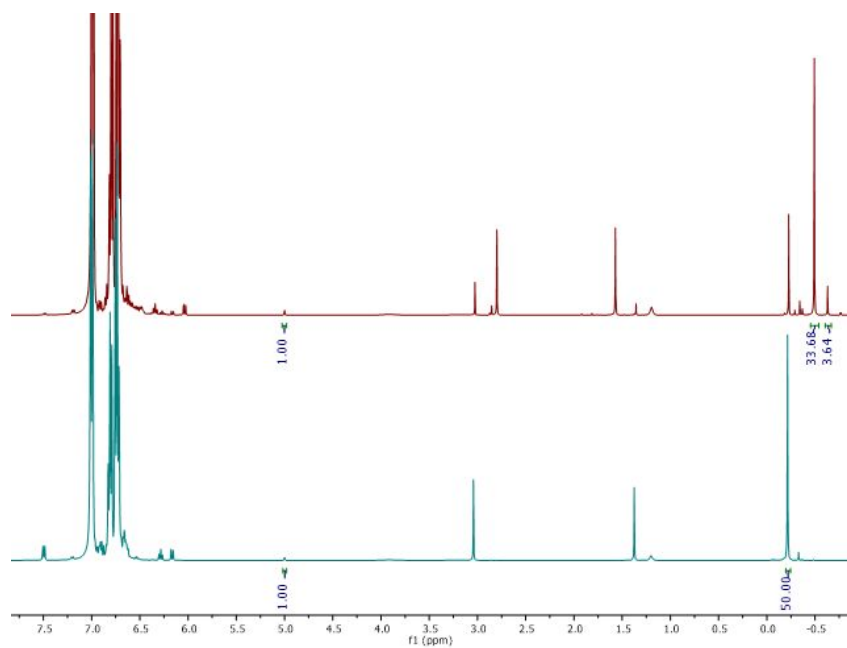
**Figure S1.** No-D <sup>1</sup>H NMR spectrum of the optimization in PhCF<sub>3</sub> at Time = 1 h (top), Time = 0 h (bottom) (Table 1, entry 2).



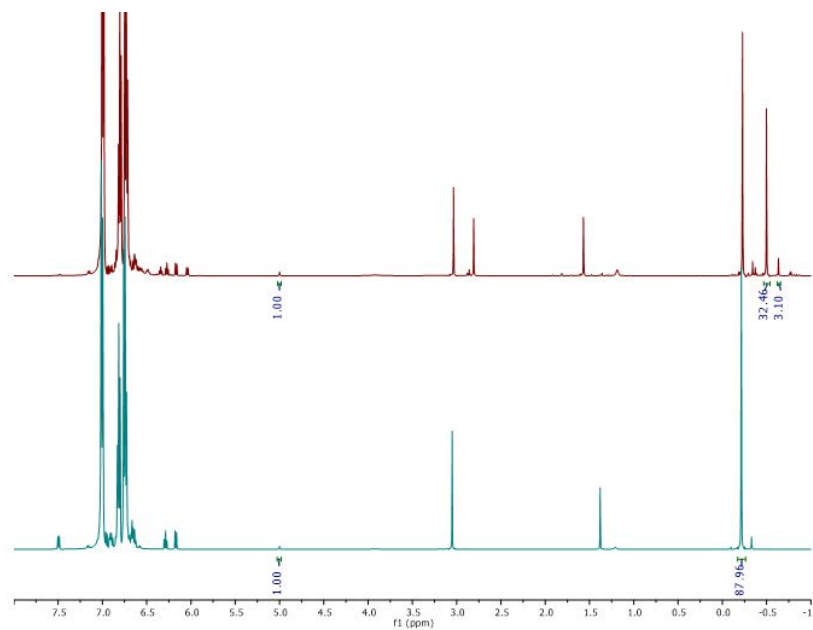
**Figure S2.** No-D <sup>1</sup>H NMR spectrum of the optimization in PhCF<sub>3</sub> at Time = 1 h (top), Time = 0 h (bottom) (Table 1, entry 3).



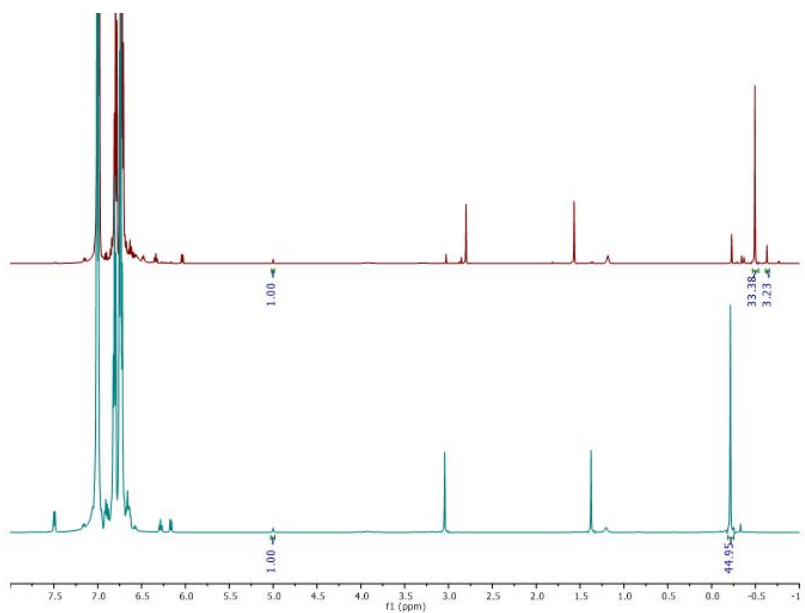
**Figure S3.** No-D <sup>1</sup>H NMR spectrum of the optimization in PhCF<sub>3</sub> at Time = 2 h (top), Time = 0 h (bottom) (Table 1, entry 4).



**Figure S4.** No-D  $^1\text{H}$  NMR spectrum of the optimization in  $\text{PhCF}_3$  at Time = 2 h (top), Time = 0 h (bottom) (Table 1, entry 5).



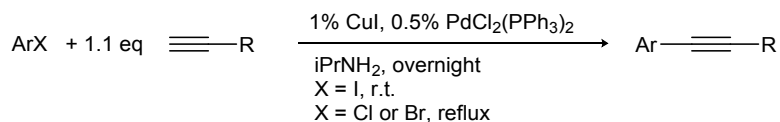
**Figure S5.** No-D  $^1\text{H}$  NMR spectrum of the optimization in  $\text{PhCF}_3$  at Time = 24 h (top), Time = 0 h (bottom) (Table 1, entry 6).



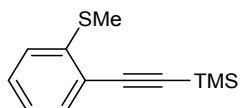
**Figure S6.** No-D  $^1\text{H}$  NMR spectrum of the optimization in  $\text{PhCF}_3$  at Time = 24 h (top), Time = 0 h (bottom) (Table 1, entry 7).

## Substrate Synthesis

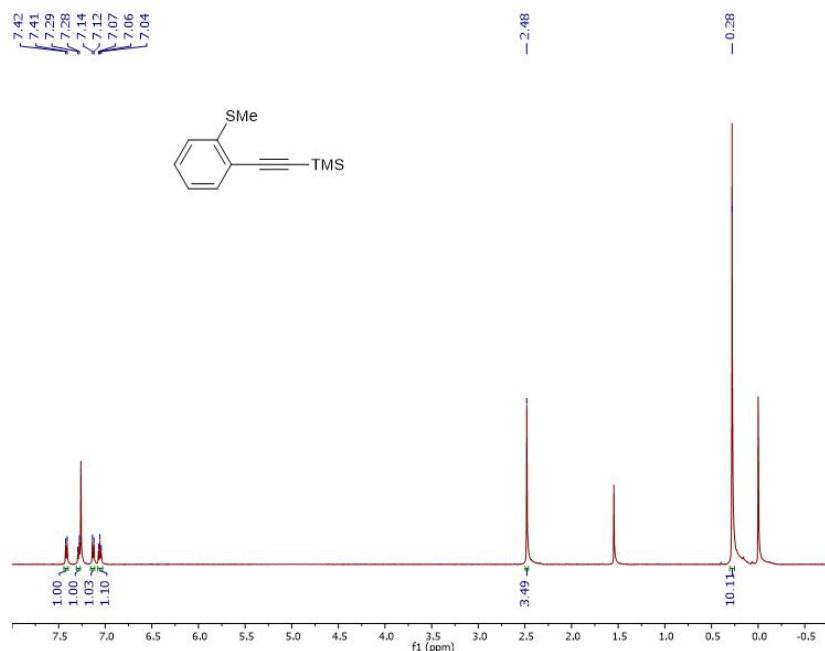
### General Procedure for (Trimethylsilyl)ethynyl Arenes



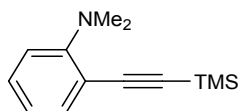
Aryl chloride, bromide or iodide (10 mmol, 1 eq.) was added to a 100 mL Schlenk flask with CuI (19 mg, 0.1 mmol, 0.01 eq.) and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (35 mg, 0.05 mmol, 0.005 eq.). Diisopropylamine (50 mL) was charged under nitrogen and the mixture was degassed 3 times. The terminal alkyne (22 mmol, 1.1 eq.) was added via syringe. The reaction was stirred overnight under reflux (aryl chloride and bromide) or at ambient temperature (aryl iodide), and monitored by <sup>1</sup>H NMR to ensure all the aryl halides were consumed. If there were any unreacted aryl halides, an extra equivalent of ethynyltrimethylsilane would be added. After the reaction completed, the mixture was filtered through a sintered glass frit and the filtrate was collected and concentrated. The residue was purified by passing through an alumina plug eluted by hexanes and concentrated in vacuo. The crude product was purified by either distillation under reduced pressure, silica gel flash chromatography, or recrystallization from cold methanol to yield the desired product.



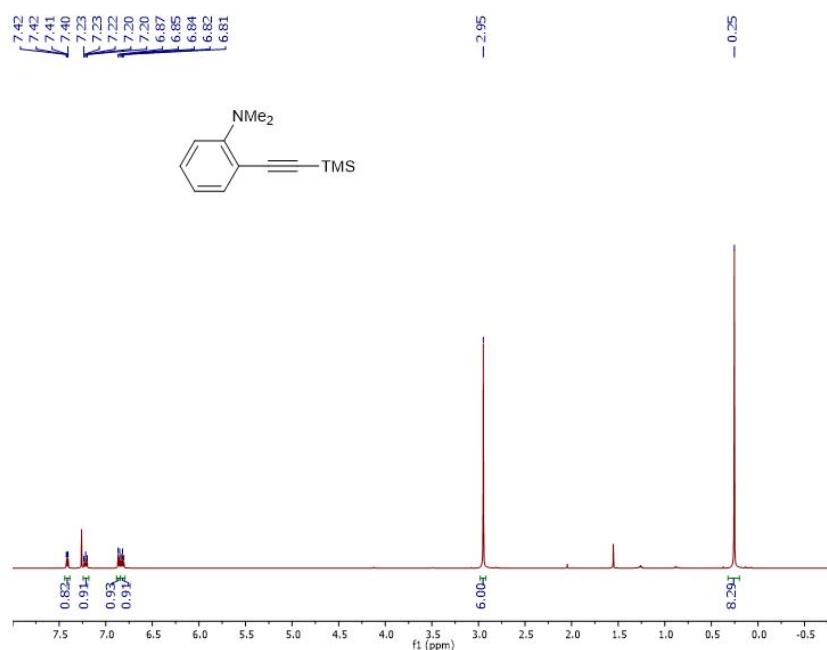
**methyl(2-(prop-1-yn-1-yl)phenyl)sulfane (1i)** 2-Iodothioanisole was purchased from Oakwood Chemical. Purification was carried out by distillation under reduced pressure. Colorless oily solid, 68% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 7.41 (d, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 1H), 7.28 (d, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 1H), 7.13 (d, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 1H), 7.06 (t, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 1H), 2.48 (s, 3H), 0.28 (s, 9H) ppm. Spectral data was consistent with literature values.<sup>1</sup>



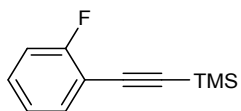
**Figure S7.**  $^1\text{H}$  NMR spectrum of **1i** in  $\text{CDCl}_3$ .



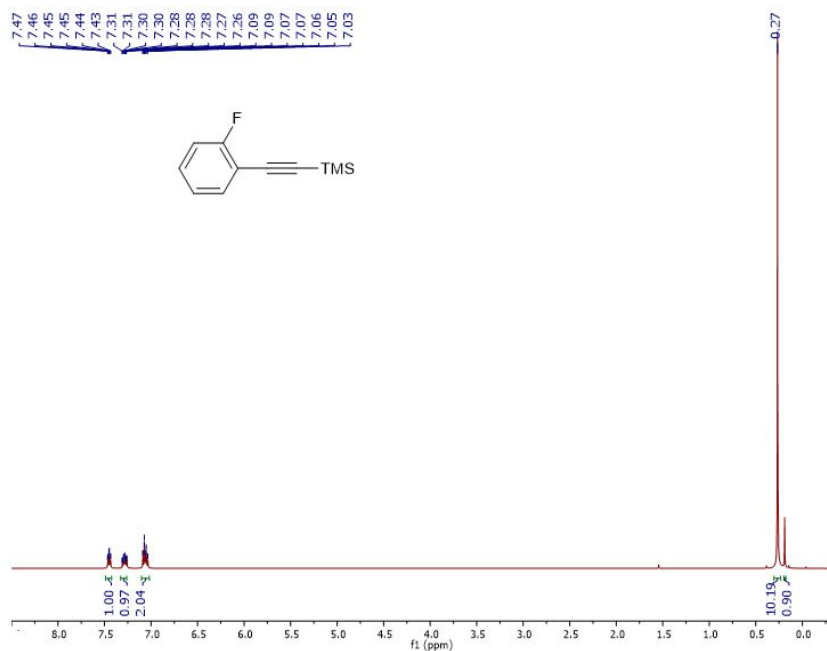
**N,N-dimethyl-2-((trimethylsilyl)ethynyl)aniline (1j)** 2-Iodothioanisole was synthesized according to literature procedure<sup>2</sup> starting from 2-iodoaniline purchased from Oakwood Chemical. Purification was carried out by distillation under reduced pressure. Colorless liquid, 47% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.41 (dd,  $^3J_{\text{HH}} = 6.7$ ,  $2.3$  Hz, 1H), 7.22 (ddd,  $^3J_{\text{HH}} = 8.4$ ,  $7.3$ ,  $^4J_{\text{HH}} = 1.6$  Hz, 1H), 6.86 (d,  $^3J_{\text{HH}} = 8.3$ Hz, 1H), 6.82 (dt,  $^3J_{\text{HH}} = 7.6$ ,  $^4J_{\text{HH}} = 0.7$  Hz, 1H), 2.95 (s, 6H), 0.25 (s, 9H) ppm. Spectral data was consistent with literature values.<sup>3</sup>



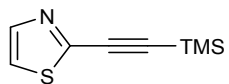
**Figure S8.**  $^1\text{H}$  NMR spectrum of **1j** in  $\text{CDCl}_3$ .



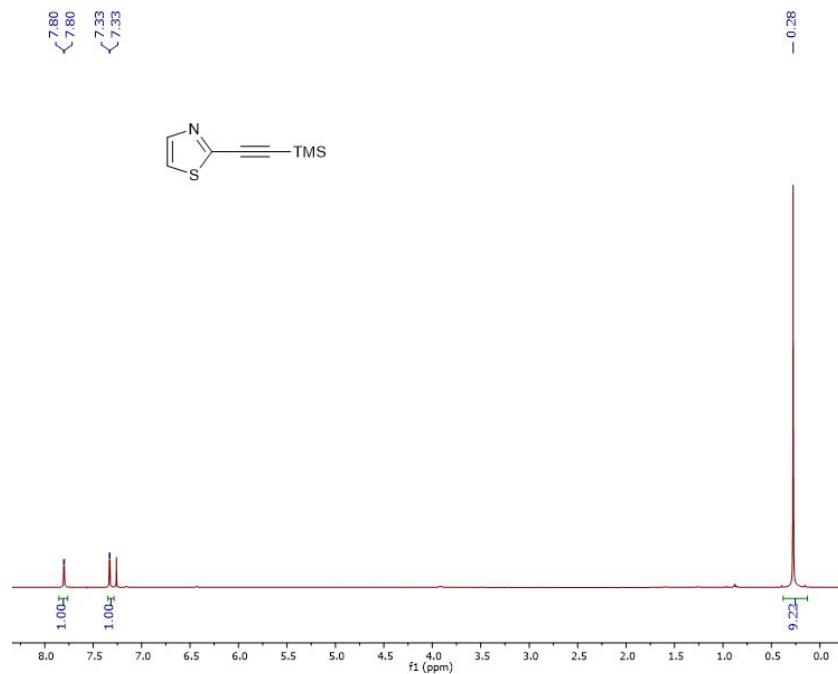
**((2-fluorophenyl)ethynyl)trimethylsilane (1k)** 1-Fluoro-2-iodobenzene was purchased from Oakwood Chemical. Purification was carried out by distillation under reduced pressure. Pale yellow solid, 94% yield (96% purity).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.45 (dt,  $^3J_{\text{HH}} = 7.4$ ,  $^4J_{\text{HH}} = 1.8$  Hz, 1H), 7.31-7.26 (m, 1H), 7.09-7.03 (m, 2H), 0.27 (s, 9H) ppm. Spectral data was consistent with literature values.<sup>4</sup>



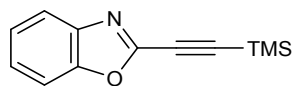
**Figure S9.**  $^1\text{H}$  NMR spectrum of **1k** in  $\text{CDCl}_3$ .



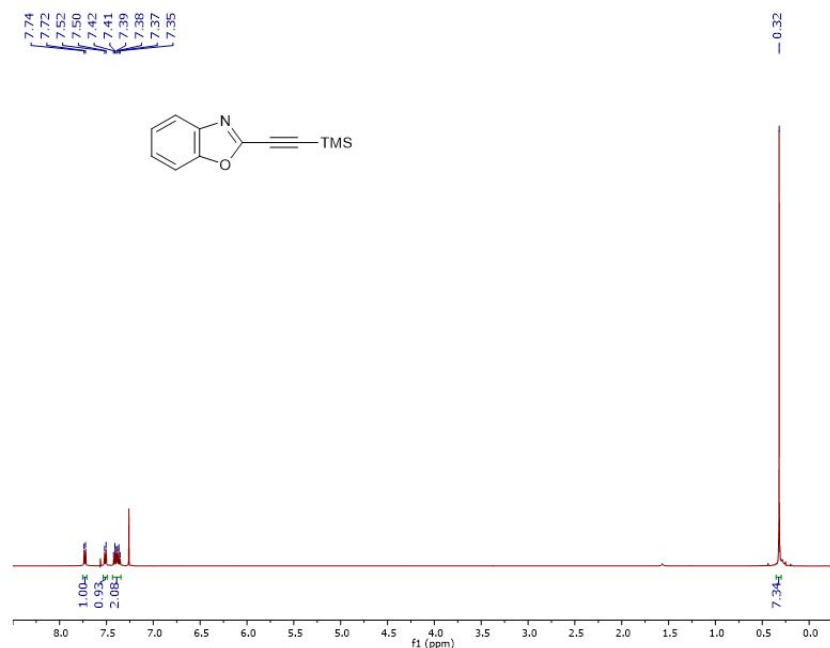
**2-((trimethylsilyl)ethynyl)thiazole (1q)** 2-Bromothiazole was purchased from Oakwood Chemical. Purification was carried out by silica gel column chromatography using 2.5 % EA/Hex eluent. Pale yellow oil, 38% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.80 (d,  $^3J_{\text{HH}} = 3.3$  Hz, 1H), 7.33 (d,  $^3J_{\text{HH}} = 3.3$  Hz, 1H), 0.28 (s, 9H) ppm. Spectral data was consistent with literature values.<sup>5</sup>



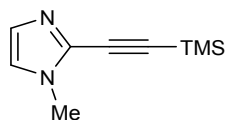
**Figure S10.** <sup>1</sup>H NMR spectrum of **1q** in CDCl<sub>3</sub>.



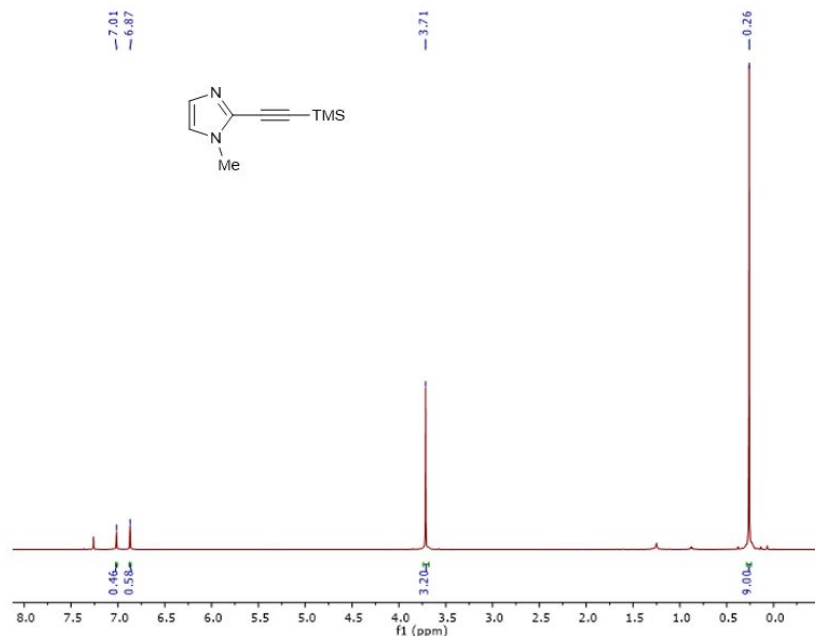
**2-((trimethylsilyl)ethynyl)benzo[d]oxazole (1r)** 2-Chlorobenzo[d]oxazole was purchased from Oakwood Chemical. Purification was carried out by silica gel column chromatography using 2.5 % EA/Hex eluent. Brown solid, 37% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 7.73 (d, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, 1H), 7.51 (d, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, 1H), 7.42-7.35 (m, 2H), 0.32 (s, 9H) ppm. Spectral data was consistent with literature values.<sup>6</sup>



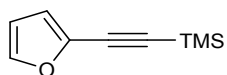
**Figure S11.** <sup>1</sup>H NMR spectrum of **1r** in CDCl<sub>3</sub>.



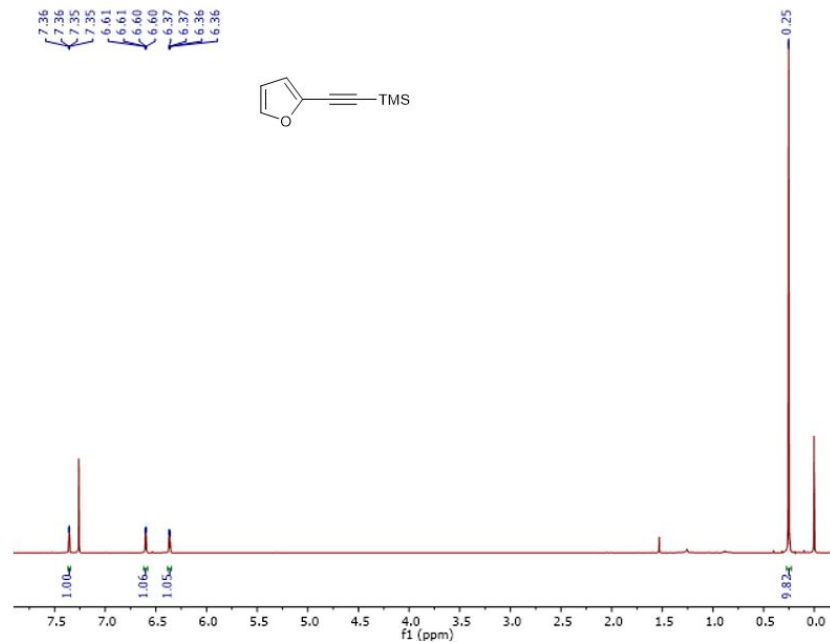
**1-methyl-2-((trimethylsilyl)ethynyl)-1H-imidazole (1s)** 1-Methyl-2-iodoimidazole was synthesized according to literature procedure<sup>7</sup> from 1-methylimidazole purchased from Oakwood Chemical. Purification was carried out by silica gel column chromatography using 75 % EA/Hex eluent. Dark solid, 7% yield. **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz): δ 7.01 (s, 1H), 6.87 (s, 1H), 3.71 (s, 3H), 0.26 (s, 9H) ppm. Spectral data was consistent with literature values.<sup>8</sup>



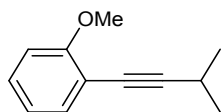
**Figure S12.** <sup>1</sup>H NMR spectrum of **1s** in CDCl<sub>3</sub>.



**(furan-2-ylethynyl)trimethylsilane (1t)** 2-Iodofuran was synthesized according to literature procedure<sup>9</sup> from furan purchased from Oakwood Chemical. Purification was carried out by silica gel column chromatography using 3 % EA/Hex eluent. Light brown oil (color due to minor decomposition), 30% yield. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.36 (dd, 1H, <sup>3</sup>J<sub>HH</sub> = 1.8 Hz and <sup>4</sup>J<sub>HH</sub> = 0.6 Hz, *o*-C5-*H*), 6.60 (dd, 1H, <sup>3</sup>J<sub>HH</sub> = 3.4 Hz and <sup>4</sup>J<sub>HH</sub> = 0.6 Hz, *m*-C3-*H*), 6.36 (dd, 1H, <sup>3</sup>J<sub>HH</sub> = 3.4 Hz and <sup>3</sup>J<sub>HH</sub> = 1.9 Hz, *m*-C4-*H*), 0.25 (s, 9H, TMS) ppm. Spectral data was consistent literature values.<sup>10</sup>



**Figure S13.** <sup>1</sup>H NMR spectrum of **1t** in CDCl<sub>3</sub>.



**Methoxy-2-(3-methylbut-1-yn-1-yl)benzene (1w)** 2-Iodoanisole was purchased from Oakwood Chemical. Purification was carried out by distillation under reduced pressure. Colorless oil, 75% yield (98% purity). **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz): δ 7.37 (d, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 1H), 7.22 (dt, <sup>3</sup>J<sub>HH</sub> = 7.4, <sup>4</sup>J<sub>HH</sub> = 0.9 Hz, 1H), 6.89-6.84 (m, 2H), 3.87 (s, 3H), 2.85 (sept, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 1H), 1.28 (d, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 6H) ppm. **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz): δ 159.9, 133.9, 129.0, 120.5, 113.2, 110.7, 100.2, 75.9, 56.0, 23.3, 21.6 ppm. **GC-HRMS**: calculated for C<sub>12</sub>H<sub>14</sub>O [M<sup>+</sup>] 174.1045; found 174.1033.

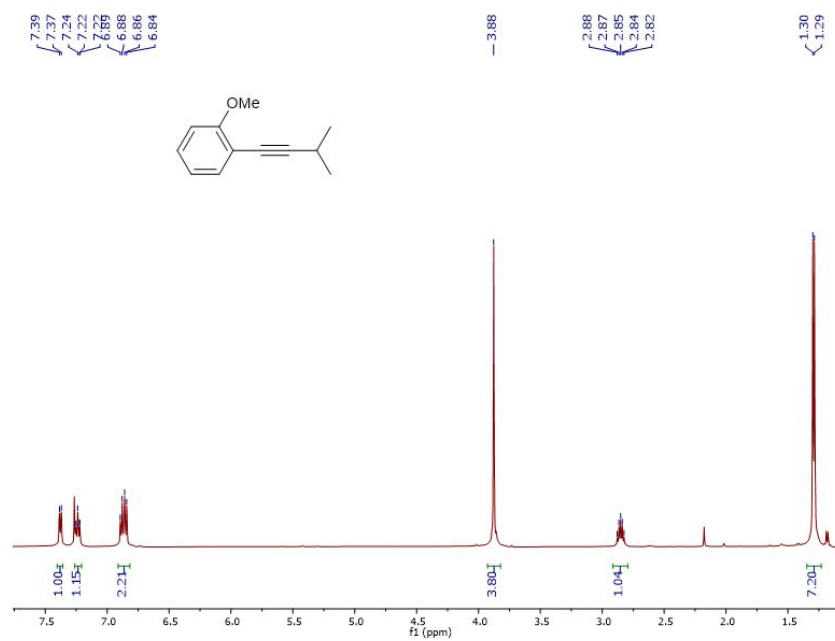


Figure S14. <sup>1</sup>H NMR spectrum of **1w** in CDCl<sub>3</sub>.

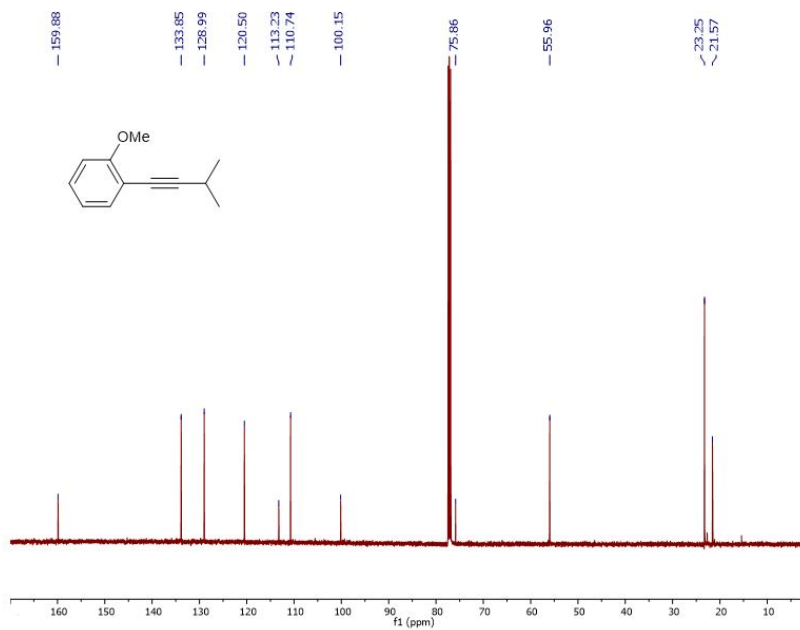
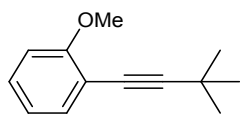
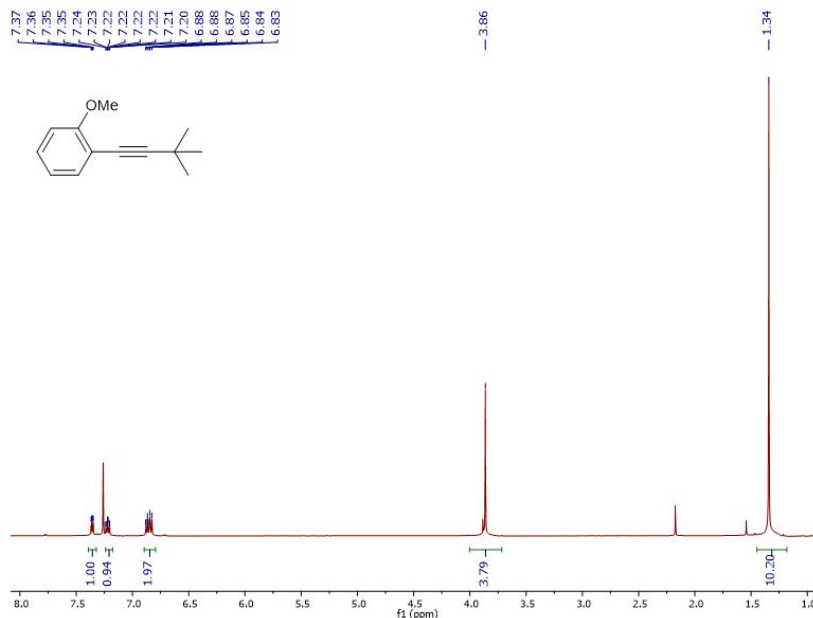


Figure S15. <sup>13</sup>C NMR spectrum of **1w** in CDCl<sub>3</sub>.

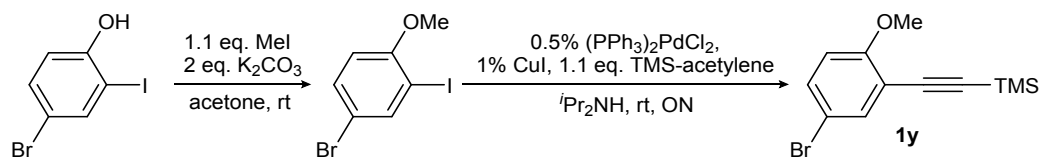


**1-(3,3-dimethylbut-1-yn-1-yl)-2-methoxybenzene (1x)** 2-Iodoanisole was purchased from Oakwood Chemical. Purification was carried out by distillation under reduced pressure. Pale yellow oil, 16% yield. <sup>1</sup>H

**NMR** (CDCl<sub>3</sub>, 500 MHz): δ 7.35 (dd, <sup>3</sup>J<sub>HH</sub> = 7.6, <sup>4</sup>J<sub>HH</sub> = 1.6 Hz, 1H), 7.22 (ddd, <sup>3</sup>J<sub>HH</sub> = 8.4, 7.6, <sup>4</sup>J<sub>HH</sub> = 1.7 Hz, 1H), 6.88-6.83 (m, 2H), 3.86, (s, 3H), 1.34 (s, 9H) ppm. Spectral data was consistent with literature values.<sup>11</sup>



**Figure S16.** <sup>1</sup>H NMR spectrum of **1x** in CDCl<sub>3</sub>.



**((5-bromo-2-methoxyphenyl)ethynyl)trimethylsilane (1y)** 4-bromo-2-iodophenol was synthesized according to literature procedure<sup>12</sup> from 2-iodophenol purchased from Oakwood Chemical. The obtained phenol was used without further purification. The 4-bromo-2-iodophenol was reacted with iodomethane (0.68 mL, 11 mmol, 1.1 eq.) in the presence of K<sub>2</sub>CO<sub>3</sub> (2.76 g, 20 mmol, 2 eq.) in acetone at ambient temperature. When full consumption of the starting phenol was apparent by <sup>1</sup>H NMR, the reaction was diluted with water and extracted by diethyl ether. The resulting 4-bromo-2-iodoanisole was purified through a short plug of silica gel with hexanes eluent. After the Sonogashira coupling reaction, the crude oil was purified by silica gel column chromatography with 2% EA/hexanes eluent to give a white solid (50% overall yield with respect to 2-iodophenol). **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz): δ 7.54 (d, <sup>4</sup>J<sub>HH</sub> = 2.5 Hz, 1H), 7.36 (dd, <sup>3</sup>J<sub>HH</sub> = 8.8, <sup>4</sup>J<sub>HH</sub> = 2.5 Hz, 1H), 6.72 (d, <sup>3</sup>J<sub>HH</sub> = 8.9 Hz, 1H), 3.86, (s, 3H), 0.26 (s, 9H) ppm. **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 101 MHz): δ 159.6, 136.5, 132.8, 114.5, 112.4, 112.2, 100.3, 99.7, 56.3, 0.1 ppm. **GC-HRMS**: calculated for C<sub>12</sub>H<sub>5</sub>OBrSi [M<sup>+</sup>] 282.0076; found 282.0049.

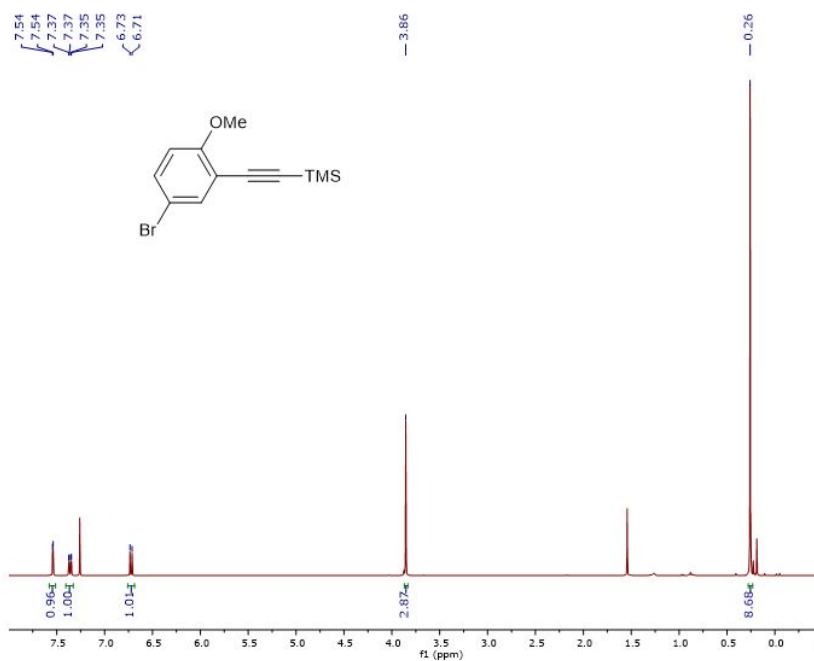


Figure S17. <sup>1</sup>H NMR spectrum of **1y** in CDCl<sub>3</sub>.

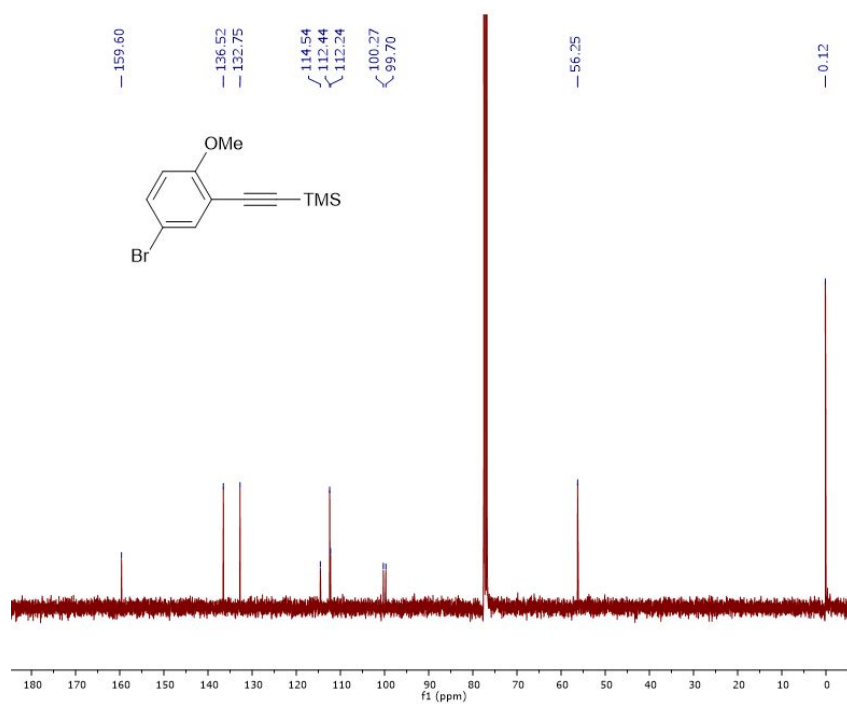
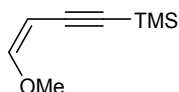


Figure S18. <sup>13</sup>C NMR spectrum of **1y** in CDCl<sub>3</sub>.

## General Procedure for Alkynyl Trimethylsilanes Synthesized from Terminal Alkynes



Terminal alkyne (30 mmol) was deprotonated in dry THF (20 mL) by n-BuLi solution (2.5 M, 12.6 mL, 31.5 mmol, 1.05 eq.) slowly at -78 °C under nitrogen. After the slow addition, the mixture was allowed to warm up to ambient temperature for 30 minutes. To the mixture, chlorotrimethylsilane (4.2 mL, 33 mmol, 1.1 eq.) was added at -78 °C under nitrogen. The reaction was stirred overnight at ambient temperature and quenched with saturated NH<sub>4</sub>Cl solution then extracted with hexanes (30 mL x 3). The mixture was concentrated and the residue was distilled under reduced pressure to yield the pure product.



**(Z)-(4-methoxybut-3-en-1-yn-1-yl)trimethylsilane (1b)** The starting material (Z)-1-methoxybut-1-en-3-yne was synthesized from 1,4-dichloro-2-butyne according to literature procedure.<sup>13</sup> Purification was carried out by distillation under reduced pressure. Colorless oil, 46% yield (containing 8% of the trans isomer). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 6.26 (d, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, 1H), 4.56 (d, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, 1H), 3.78 (s, 3H), 0.19 (s, 9H) ppm. Spectral data was consistent with literature values.<sup>14</sup>

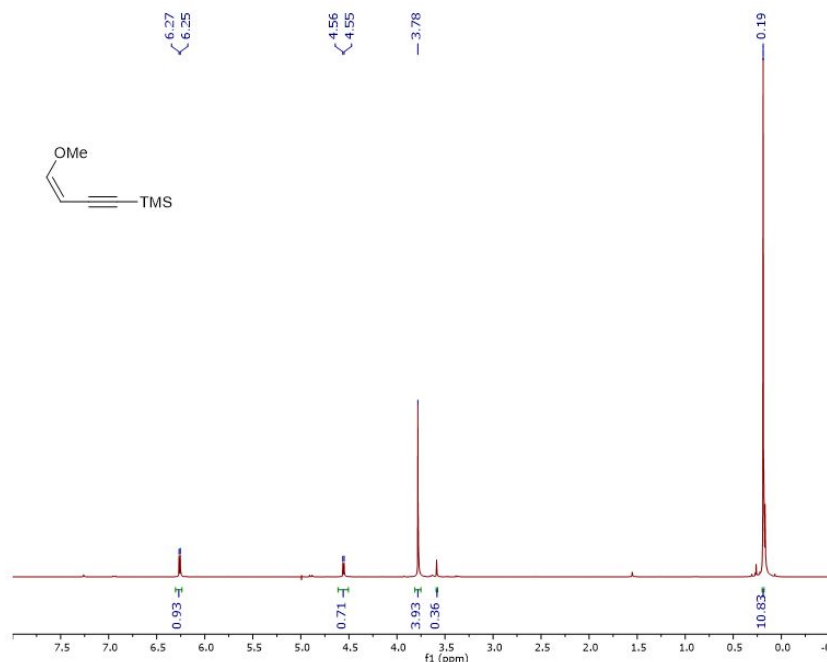
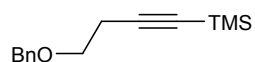
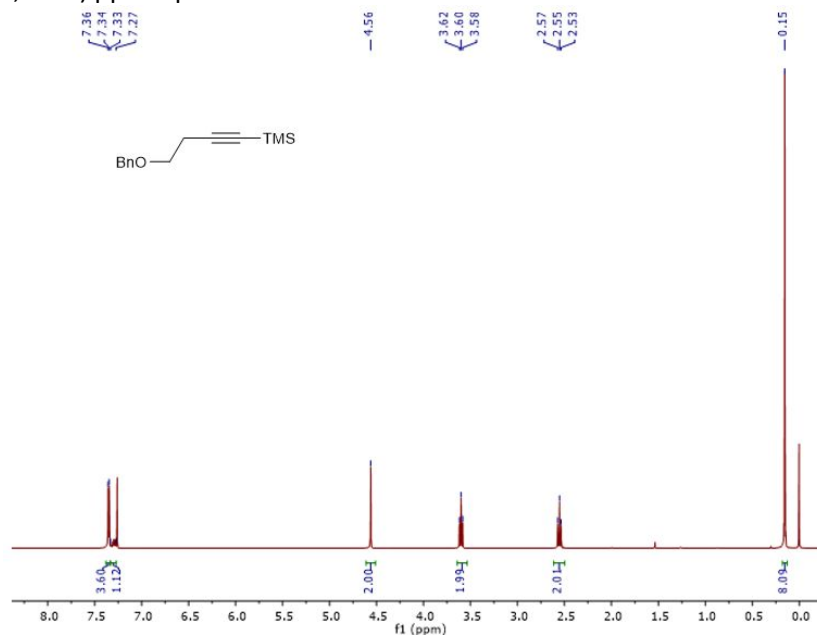


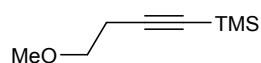
Figure S19. <sup>1</sup>H NMR spectrum of **1b** in CDCl<sub>3</sub>.



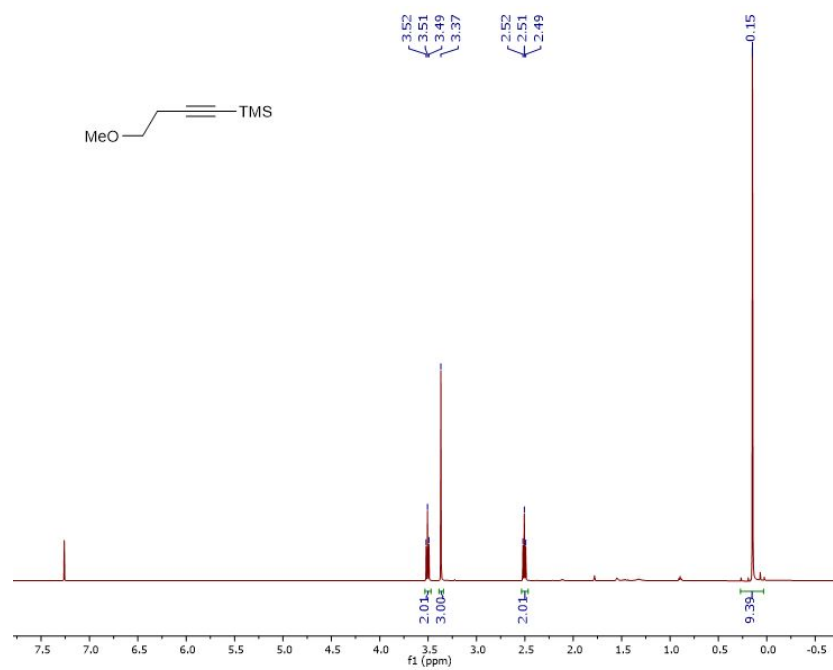
**(4-(benzyloxy)but-1-yn-1-yl)trimethylsilane (1c)** The starting material ((but-3-yn-1-yloxy)methyl)benzene was synthesized according to literature procedure.<sup>15</sup> from 3-butyn-1-ol purchased from Oakwood Chemical. Purification was carried out by distillation under reduced pressure. Colorless oil, 34% yield. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.35 (m, 4H), 7.33 – 7.27 (m, 1H), 4.56 (s, 2H), 3.60 (t, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, 2H), 2.55 (t, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, 2H), 0.15 (s, 9H, TMS) ppm. Spectral data was consistent with literature values.<sup>16</sup>



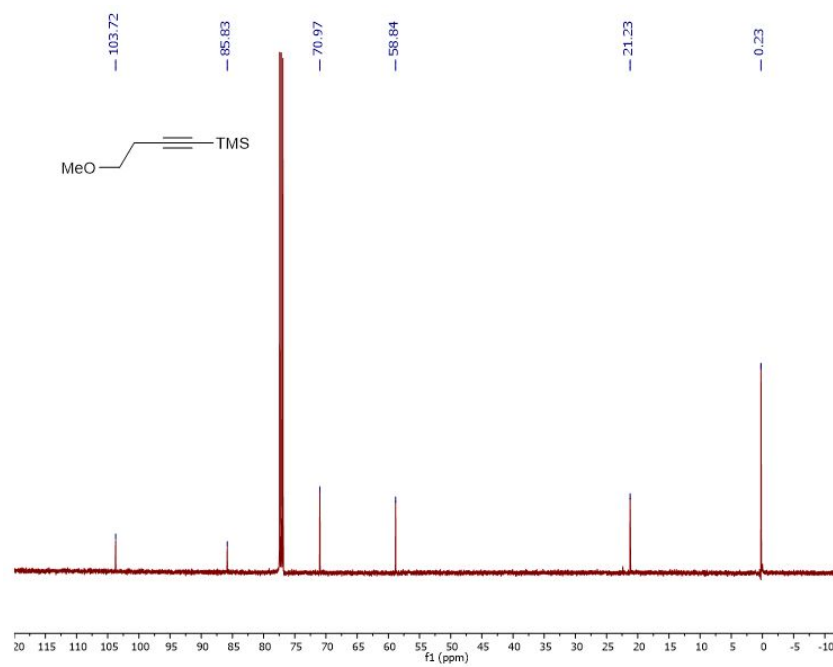
**Figure S20.** <sup>1</sup>H NMR spectrum of **1c** in CDCl<sub>3</sub>.



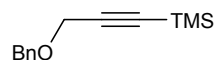
**(4-methoxybut-1-yn-1-yl)trimethylsilane (1d)** The starting material 4-Methoxybut-1-yne was synthesized according to literature procedure<sup>17</sup> from 3-butyn-1-ol purchased from Oakwood Chemical. Purification was carried out by distillation under reduced pressure. Colorless oil, 20% yield. **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz): δ 3.51 (t, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 2H), 3.37 (s, 3H), 2.51 (t, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 2H), 0.15 (s, 9H) ppm. **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz): δ 103.7, 85.8, 71.0, 58.8, 21.2, 0.2 ppm. **GC-HRMS**: calculated for C<sub>8</sub>H<sub>16</sub>OSi [M-H<sup>+</sup>] 155.0892; found 155.0890.



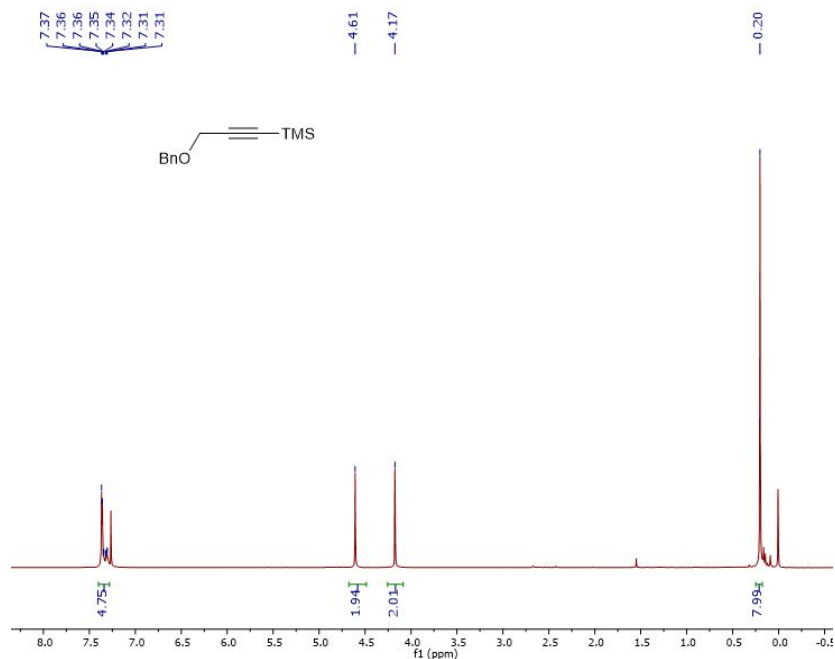
**Figure S21.** <sup>1</sup>H NMR spectrum of **1d** in CDCl<sub>3</sub>.



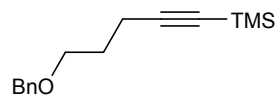
**Figure S22.** <sup>13</sup>C NMR spectrum of **1d** in CDCl<sub>3</sub>.



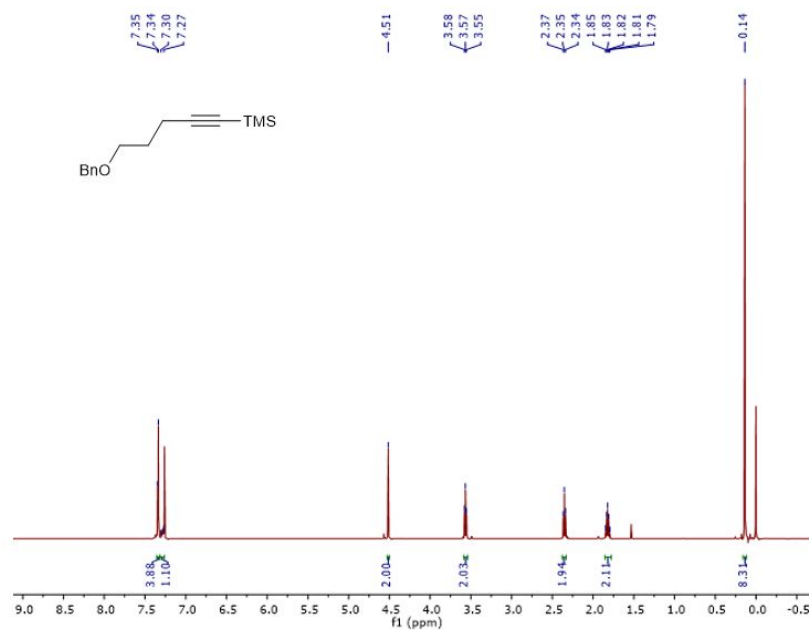
**(3-(benzyloxy)prop-1-yn-1-yl)trimethylsilane (1e)** The starting material ((Prop-2-yn-1-yloxy)methyl)benzene was synthesized according to literature procedure<sup>18</sup> from propargyl bromide purchased from Sigma-Aldrich. Purification was carried out by distillation under reduced pressure. Colorless oil, 60% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.37-7.31 (m, 5H), 4.61 (s, 2H), 4.17 (s, 2H), 0.20 (s, 9H) ppm. Spectral data was consistent with literature values.<sup>19</sup>



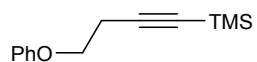
**Figure S23.** <sup>1</sup>H NMR spectrum of **1e** in CDCl<sub>3</sub>.



**(5-(benzyloxy)pent-1-yn-1-yl)trimethylsilane (1g)** The starting material ((pent-4-yn-1-yloxy)methyl)benzene was synthesized according to literature procedure<sup>15</sup> from 4-pentyn-1-ol purchased from Oakwood Chemical. Purification was carried out by distillation under reduced pressure. Colorless oil, 34% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.35 – 7.34 (m, 4H, Ph-H), 7.30 – 7.27 (m, 1H, Ph-H), 4.51 (s, 2H, OCH<sub>2</sub>-Ph), 3.57 (t, <sup>3</sup>J<sub>HH</sub> = 6.3 Hz, 2H, OCH<sub>2</sub>-CH<sub>2</sub>CH<sub>2</sub>), 2.35 (t, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, 2H, OCH<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>), 1.82 (pent, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 2H, OCH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 0.14 (s, 9H, TMS) ppm. Spectral data was consistent with literature values.<sup>20</sup>



**Figure S24.**  $^1\text{H}$  NMR spectrum of **1g** in  $\text{CDCl}_3$ .



**trimethyl(4-phenoxybut-1-yn-1-yl)silane (1h)** The starting material (but-3-yn-1-yloxy)benzene was synthesized according to literature procedure<sup>21</sup> from 3-butyn-1-ol purchased from Oakwood Chemical. Purification was carried out by distillation under reduced pressure. Colorless oil, 53% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.28 ( $^3J_{\text{HH}}$ ,  $J = 8.0$  Hz, 2H), 6.96 (t,  $^3J_{\text{HH}} = 7.3$  Hz, 1H), 6.91 ( $^3J_{\text{HH}}$ ,  $J = 8.5$  Hz, 2H), 4.09 (t,  $^3J_{\text{HH}} = 7.3$  Hz, 2H), 2.72 (t,  $^3J_{\text{HH}} = 7.3$  Hz, 2H), 0.17 (s, 9H) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  158.6, 129.6, 121.2, 114.9, 102.8, 86.6, 66.2, 21.1, 0.2 ppm. **GC-HRMS:** calculated for  $\text{C}_{13}\text{H}_{18}\text{OSi}$  [ $\text{M}-\text{H}^+$ ] 217.1049; found 217.1023.

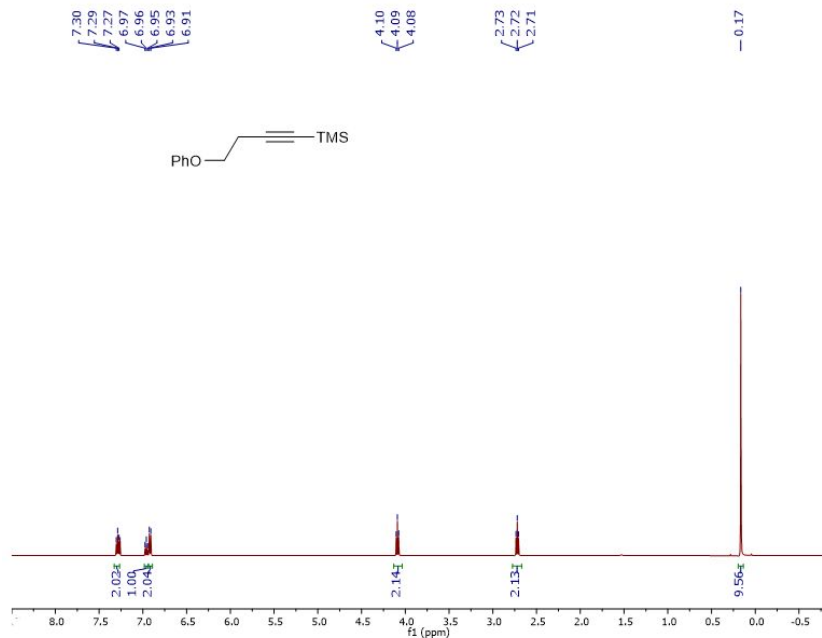


Figure S25.  $^1\text{H}$  NMR spectrum of **1h** in  $\text{CDCl}_3$ .

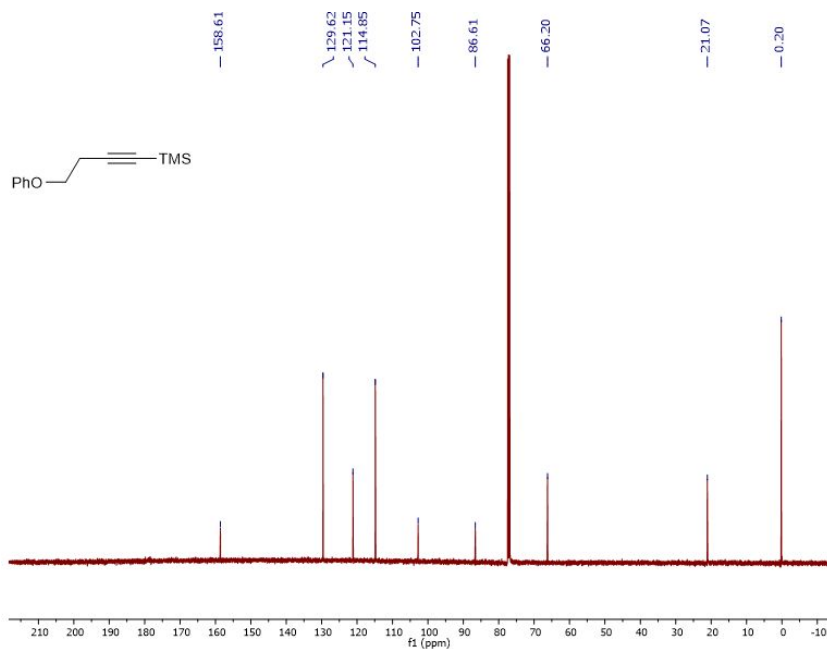
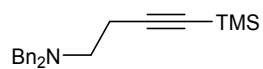


Figure S26.  $^{13}\text{C}$  NMR spectrum of **1h** in  $\text{CDCl}_3$ .



**N,N-dibenzyl-4-(trimethylsilyl)but-3-yn-1-amine (1i)** The starting material *N,N*-dibenzylbut-3-yn-1-amine was synthesized according to literature procedure<sup>22</sup> from 3-butyn-1-ol purchased from Oakwood Chemical. Purification was carried out by distillation under reduced pressure. White solid, 37% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,

500 MHz):  $\delta$  7.40 (d,  $^3J_{HH} = 7.4$  Hz, 4H), 7.31 (t,  $^3J_{HH} = 7.4$  Hz, 4H), 7.23 (t,  $^3J_{HH} = 7.3$  Hz, 2H), 3.62 (s, 4H), 2.69 (t,  $^3J_{HH} = 7.2$  Hz, 2H), 2.43 (t,  $^3J_{HH} = 7.2$  Hz, 2H), 0.15 (s, 9H) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 126 MHz):  $\delta$  139.8, 128.8, 128.3, 127.0, 106.0, 85.5, 58.2, 52.2, 18.7, 0.3 ppm. ESI-HRMS: calculated for  $\text{C}_{21}\text{H}_{28}\text{NSi}$   $[\text{M}+\text{H}^+]$  322.1991; found 322.1986.

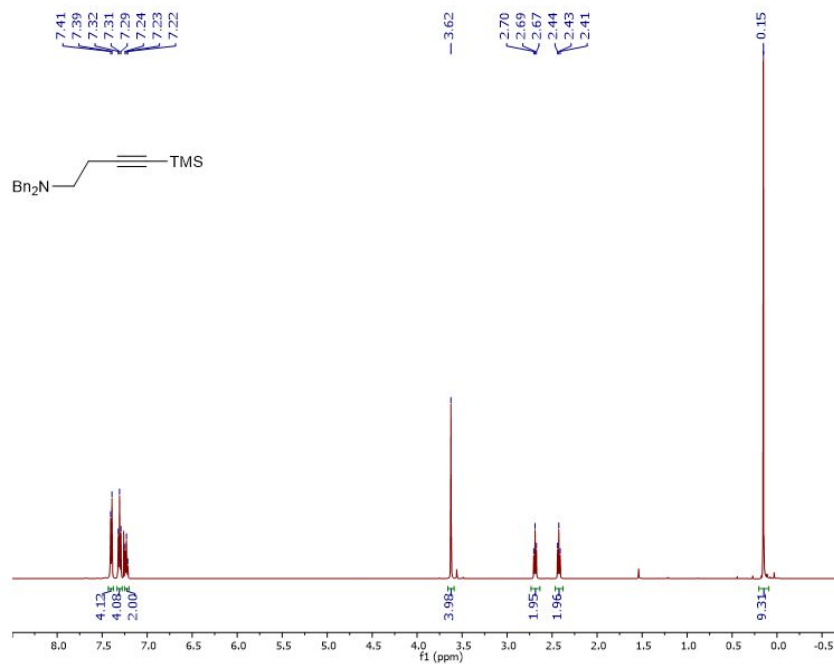


Figure S27.  $^1\text{H}$  NMR spectrum of **1I** in  $\text{CDCl}_3$ .

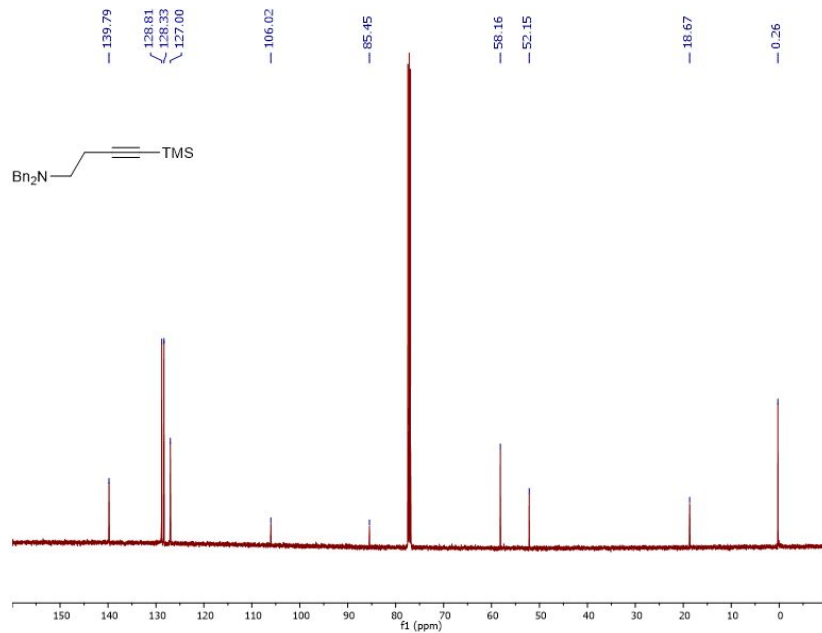
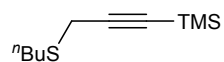
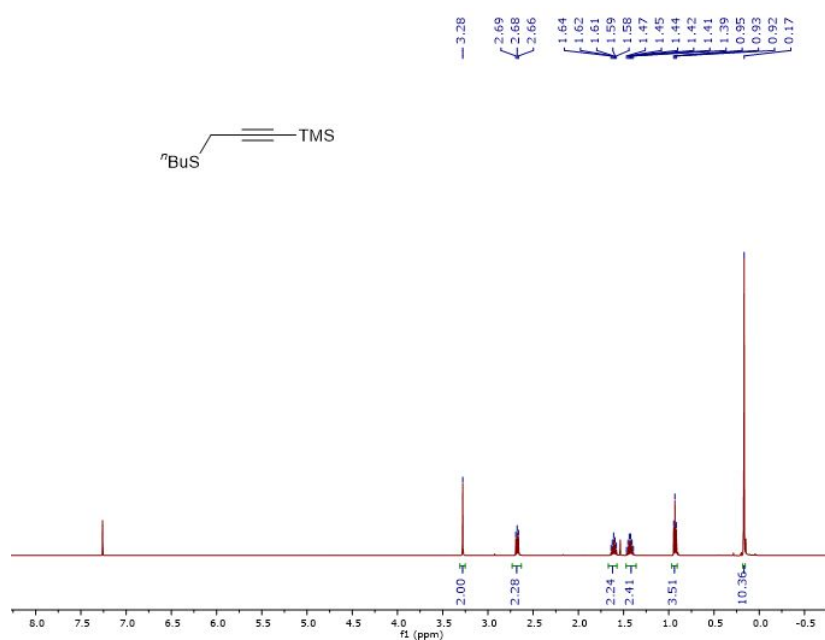


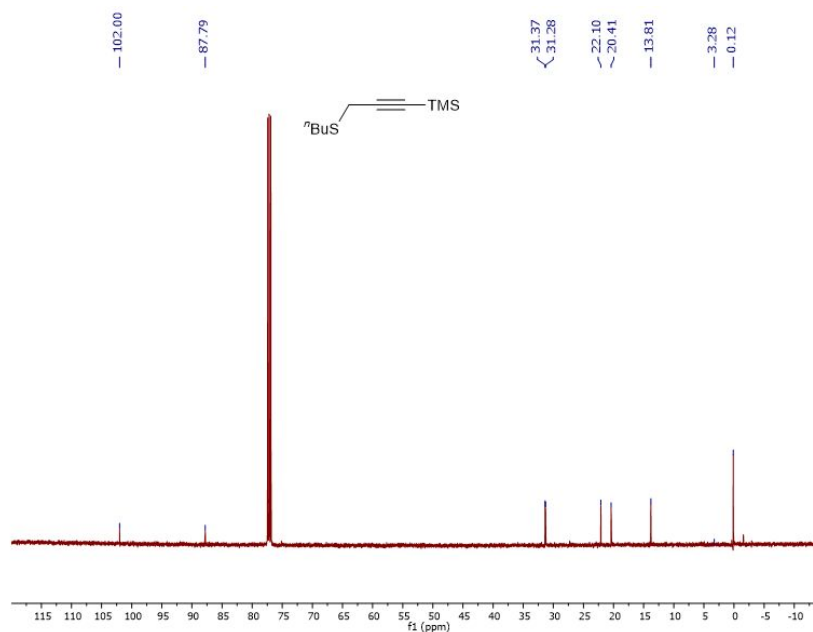
Figure S28.  $^{13}\text{C}$  NMR spectrum of **1I** in  $\text{CDCl}_3$ .



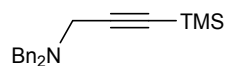
**(3-(butylthio)prop-1-yn-1-yl)trimethylsilane (1m)** The starting material butyl(prop-2-yn-1-yl)sulfane was synthesized according to literature procedure<sup>23</sup> from propargyl bromide purchased from Sigma-Aldrich. Purification was carried out by distillation under reduced pressure. Colorless liquid, 10% yield. **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz): δ 3.28 (s, 2H), 2.68 (t, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, 2H), 1.61 (pent, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, 2H), 1.43 (hex, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 2H), 0.93 (t, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, 3H), 0.17 (s, 9H) ppm. **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 126 MHz): δ 102.0, 87.8, 31.4, 31.3, 22.1, 20.4, 13.8, 3.3, 0.1 ppm. **GC-HRMS**: calculated for C<sub>10</sub>H<sub>20</sub>SSi [M<sup>+</sup>] 200.1055; found 200.1044.



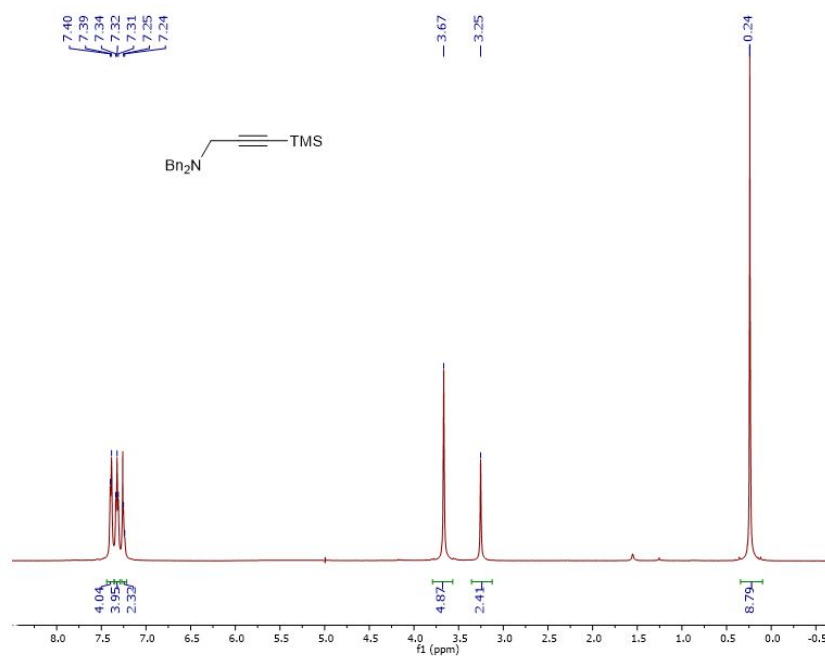
**Figure S29.** <sup>1</sup>H NMR spectrum of **1m** in CDCl<sub>3</sub>.



**Figure S30.**  $^{13}\text{C}$  NMR spectrum of **1m** in  $\text{CDCl}_3$ .

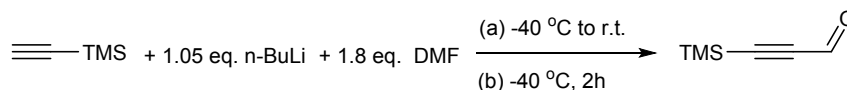


**N,N-dibenzyl-3-(trimethylsilyl)prop-2-yn-1-amine (1n)** The starting material N,N-dibenzylprop-2-yn-1-amine was synthesized according to literature procedure<sup>24</sup> from propargyl bromide purchased from Sigma-Aldrich. Purification was carried out by distillation under reduced pressure. Colorless liquid, 71% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.39 (d,  $^3J_{\text{HH}} = 7.1$  Hz, 4H), 7.32 (t,  $^3J_{\text{HH}} = 7.3$  Hz, 4H), 7.25 (t,  $^3J_{\text{HH}} = 7.3$  Hz, 2H), 3.67 (s, 4H), 3.25 (s, 2H), 0.24 (s, 9H) ppm. Spectral data was consistent with literature values.<sup>25</sup>

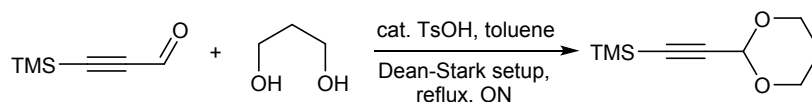


**Figure S31.**  $^1\text{H}$  NMR spectrum of **1n** in  $\text{CDCl}_3$ .

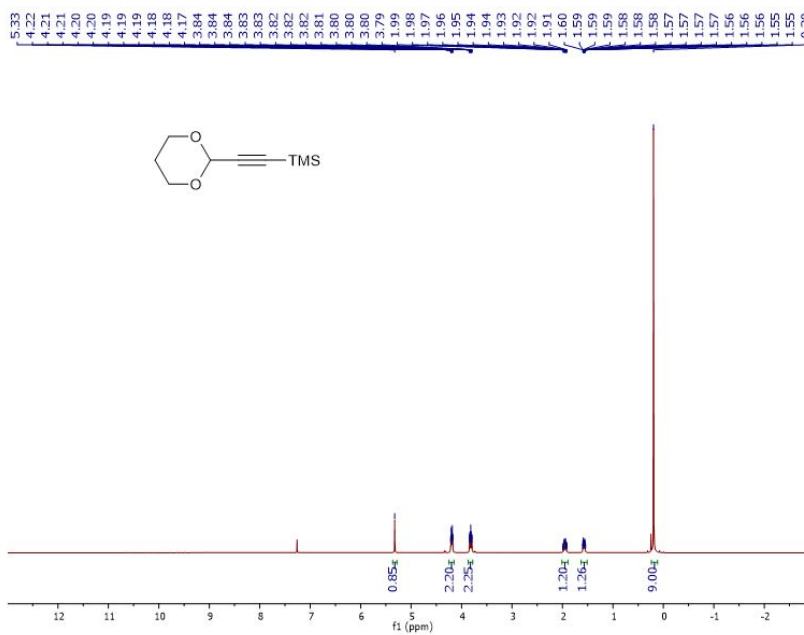
## Synthesis of (trimethylsilyl)ethynyl dioxane/dithiane



**Synthesis of (trimethylsilyl)propionaldehyde for **1f** and **1o**.** Trimethylsilyl acetylene (4.25 mL, 30 mmol) dry diethyl ether (20 mL) deprotonated by slow addition of an <sup>n</sup>BuLi solution (2.5 M, 12.6 mL, 31.5 mmol, 1.05 eq.) at -40 °C under nitrogen. After the slow addition, the mixture was allowed to warm up to ambient temperature for 30 minutes. The mixture was then cooled back down to -40 °C, and anhydrous N,N-dimethyl formaldehyde (4.27mL, 54 mmol, 1.8 eq.) was added quickly nitrogen. The reaction was slowly warmed back to ambient temperature and stirred for 30 minutes. The reaction was then cooled to 0 °C, and the mixture was poured into a buffer solution composed of KOH (6.73 g), H<sub>3</sub>PO<sub>4</sub> (8.21 mL, 85%), and DI water (154 mL). The mixture was extracted with diethyl ether (50 mL x 3) and the organic layer was washed by DI water (50 mL) and brine (50 mL). The combined organic solution was dried over MgSO<sub>4</sub> and concentrated on the rotatory evaporator. The crude product of 3-(trimethylsilyl)propionaldehyde was used without further purification.



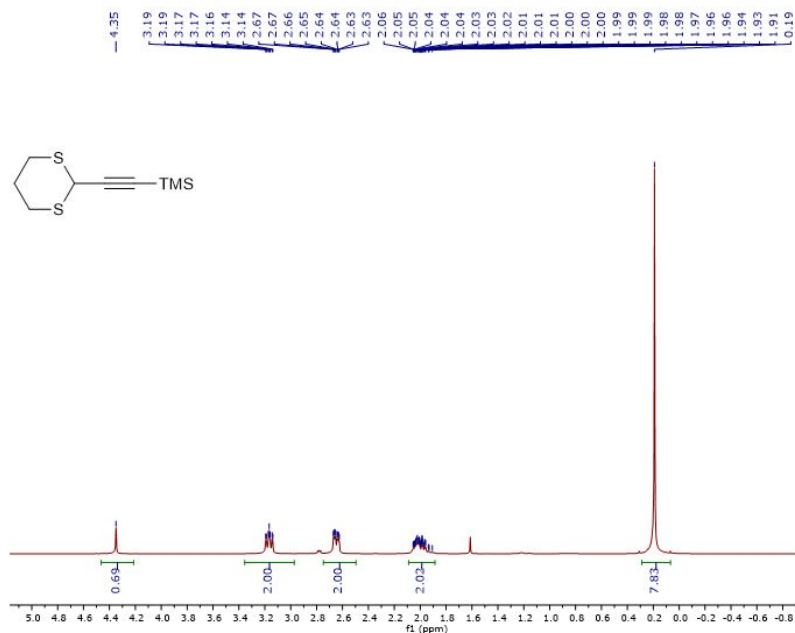
**((1,3-dioxan-2-yl)ethynyl)trimethylsilane (**1f**)** 3-(trimethylsilyl)propionaldehyde was mixed with 1,3-propanediol (15 mL) and tosylic acid (0.7g) in toluene (15 mL) and the mixture was heated overnight in a Dean-Stark apparatus. The reaction mixture was washed with water (50 mL x 3) and the aqueous layer was extracted with diethyl ether (50 mL). The combined organics were then dried over MgSO<sub>4</sub> and concentrated on the rotatory evaporator. The crude product was purified by alumina column chromatography using 10 % EA/Hex eluent to yield a colorless oil (10% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 5.33 (s, 1H), 4.22-4.17 (m, 2H), 3.84-3.79 (m, 2H), 1.99-1.91 (m, 1H), 1.60-1.54 (m, 1H), 0.19 (s, 9H) ppm. Spectral data was consistent with literature values.<sup>26</sup>



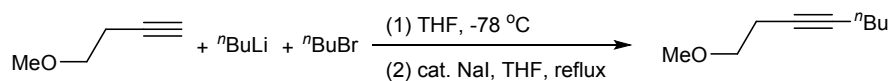
**Figure S32.** <sup>1</sup>H NMR spectrum of **1f** in CDCl<sub>3</sub>.



**((1,3-dioxan-2-yl)ethynyl)trimethylsilane (1o)** 1o was synthesized according to literature procedure.<sup>27</sup> The product was recrystallized from methanol to yield a colorless solid (12% yield). <sup>1</sup>H NMR (500 MHz, CCl<sub>4</sub>): δ 4.35 (s, 1H), 3.17 (ddd, <sup>3</sup>J<sub>HH</sub> = 13.8, 10.5, <sup>4</sup>J<sub>HH</sub> = 2.6 Hz, 2H), 2.65 (ddd, <sup>3</sup>J<sub>HH</sub> = 14.3, 6.1, <sup>4</sup>J<sub>HH</sub> = 2.9 Hz, 2H), 3.84-3.79 (m, 2H), 2.06-1.91 (m, 2H), 0.19 (s, 9H) ppm. Spectral data was consistent with literature values.<sup>27</sup>



**Figure S33.** <sup>1</sup>H NMR spectrum of **1o** in CCl<sub>4</sub>.



**1-Methoxyoct-3-yne (1z)** The starting material 4-Methoxybut-1-yne was synthesized according to literature procedure<sup>17</sup> from 3-butyne-1-ol purchased from Oakwood Chemical. The crude 4-Methoxybut-1-yne was purified by distillation under ambient pressure and used without further purification. 4-Methoxybut-1-yne (2.5 g, 30 mmol) in dry THF (20 mL) was then deprotonated by slow addition of an <sup>n</sup>BuLi solution (2.5 M, 12.6 mL, 31.5 mmol, 1.05 eq.) at -78 °C under nitrogen. After the slow addition, the mixture was allowed to warm up ambient temperature for 30 minutes. To this mixture, 1-bromobutane (3.54 mL, 33 mmol, 1.1 eq.) and NaI (0.90 g, 6 mmol, 0.2 eq.) were added under nitrogen. The reaction was stirred at reflux for 2 days. The mixture was quenched with D.I. water (30 mL) then extracted with diethyl ether (30 mL x 3). The organic layer was dried over MgSO<sub>4</sub> and then concentrated. The residue was distilled under reduced pressure to yield a clear liquid (0.4 g, 9% yield).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 3.47 (t, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, 2H), 3.37 (s, 3H), 2.43 (tt, <sup>3</sup>J<sub>HH</sub> = 7.0, <sup>4</sup>J<sub>HH</sub> = 2.4 Hz, 2H), 2.15 (tt, <sup>3</sup>J<sub>HH</sub> = 7.0, <sup>4</sup>J<sub>HH</sub> = 2.4 Hz, 2H) 1.49-1.35 (m, 4H), 0.90 (t, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 3H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 126 MHz): δ 81.5, 76.7, 71.6, 58.8, 31.2, 22.1, 20.1, 18.6, 13.8 ppm. **GC-HRMS:** calculated for C<sub>9</sub>H<sub>16</sub>O [M-H<sup>+</sup>] 139.1123; found 139.1124.

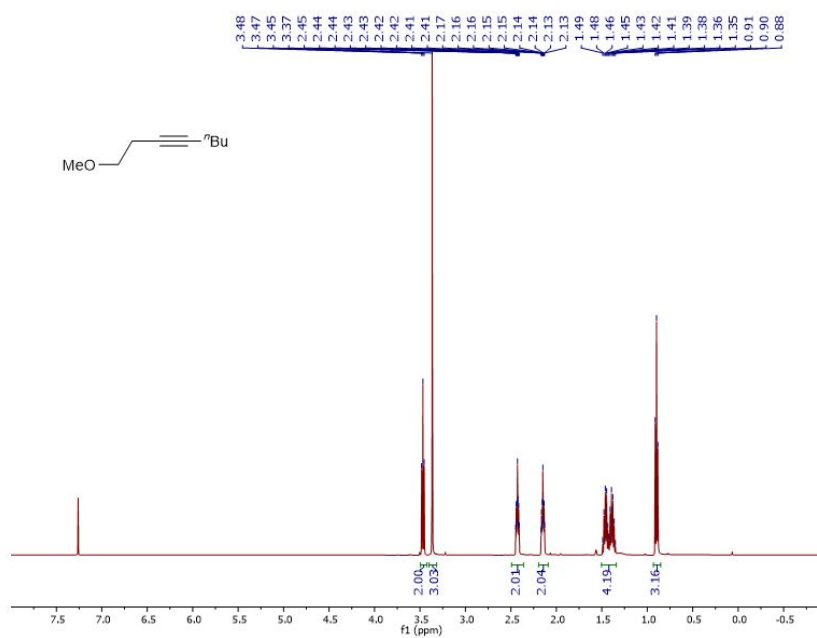


Figure S34. <sup>1</sup>H NMR spectrum of **1z** in CDCl<sub>3</sub>.

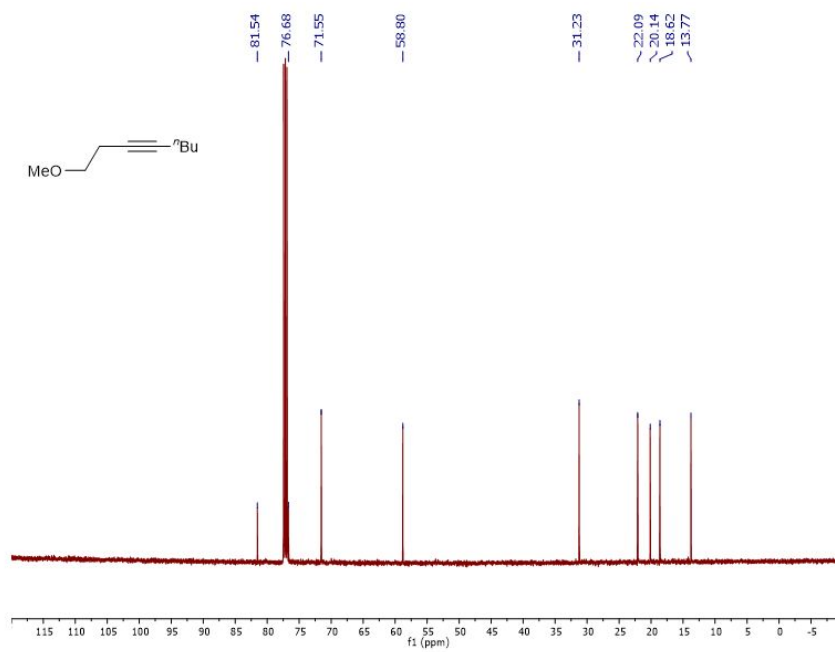
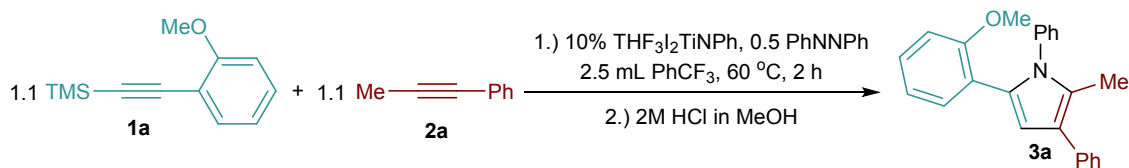


Figure S35. <sup>13</sup>C NMR spectrum of **1z** in CDCl<sub>3</sub>.

## Product Isolation, Characterization, and No-D $^1\text{H}$ NMR Spectra

### Synthesis of 5-(2-methoxyphenyl)-2-methyl-1,3-diphenyl-1*H*-pyrrole (**3a**)



The product was isolated by silica gel chromatography using 5% EA/Hex eluent to give a pale-yellow oil. (120 mg, 64% corrected yield).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.53 (app d, 2H,  $^3J_{\text{HH}} = 7.1$  Hz, Ar-H), 7.39 (t, 2H,  $^3J_{\text{HH}} = 7.7$  Hz, Ar-H), 7.30 – 7.27 (m, 2H, Ar-H), 7.24 – 7.14 (m, 6H, Ar-H), 6.87 (t, 1H,  $^3J_{\text{HH}} = 7.4$  Hz, Ar-H), 6.66 (d, 1H,  $^3J_{\text{HH}} = 8.2$  Hz, Ar-H), 6.50 (s, 1H, *m*-pyr-H), 3.41 (s, 3H, O- $\text{CH}_3$ ), 2.29 (s, 3H, *o*-pyr- $\text{CH}_3$ )

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  156.7, 139.7, 137.4, 132.1, 130.6, 128.7, 128.4, 128.3, 128.2, 128.0, 126.8, 125.3, 122.9, 122.6, 120.4, 110.5, 110.1, 54.9, 12.9.

GC-HRMS: calculated for  $\text{C}_{24}\text{H}_{21}\text{NO}$  [ $\text{M}^+$ ] 339.1623; found 339.1615.

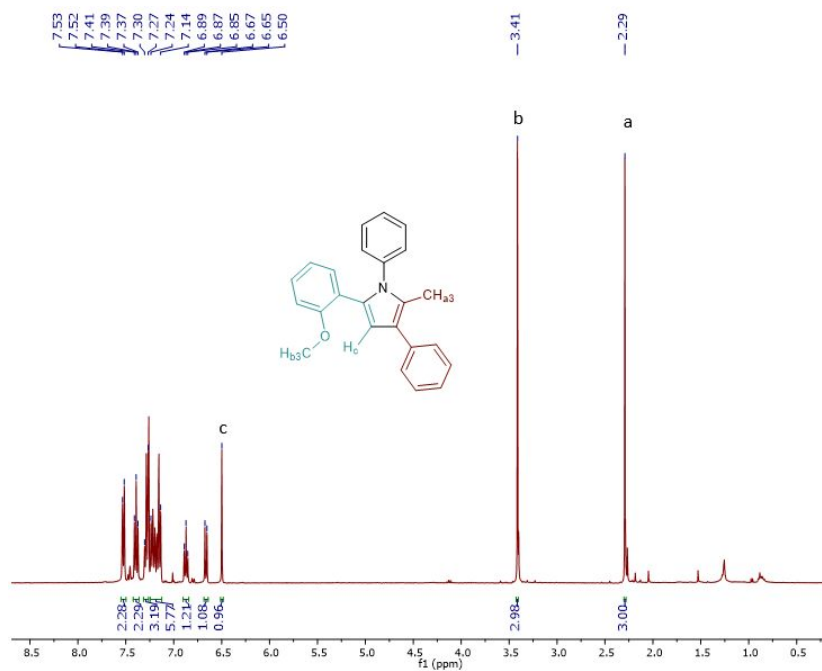
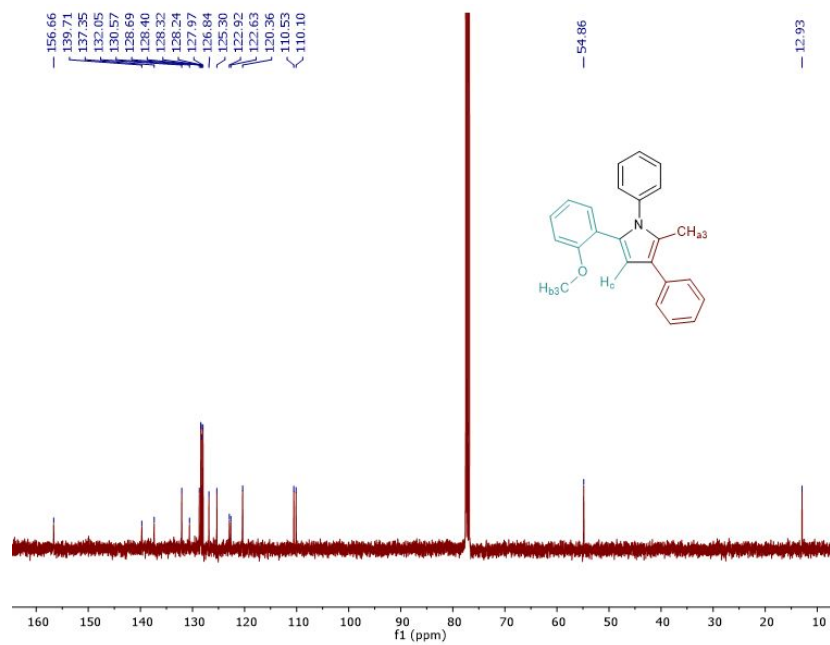
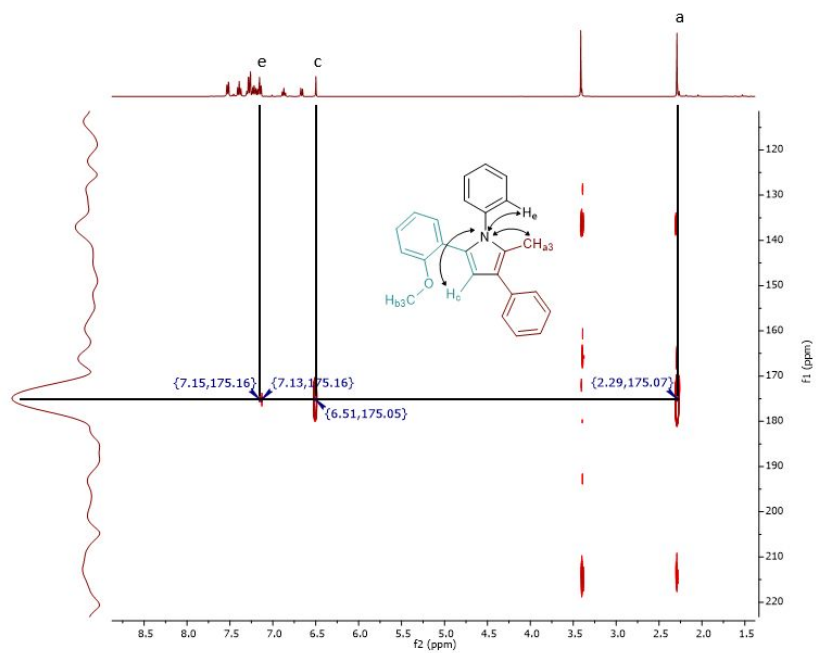


Figure S36.  $^1\text{H}$  NMR spectrum of **3a** in  $\text{CDCl}_3$ .



**Figure S37.**  $^{13}C$  NMR spectrum of **3a** in  $CDCl_3$ .



**Figure S38.**  $^1H$ - $^{15}N$  HMBC NMR spectrum of **3a** in  $CDCl_3$ .

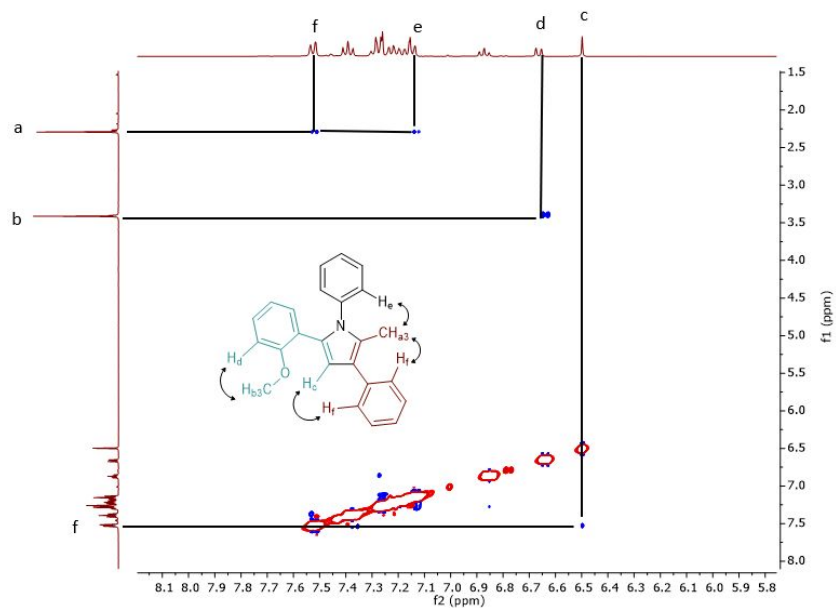
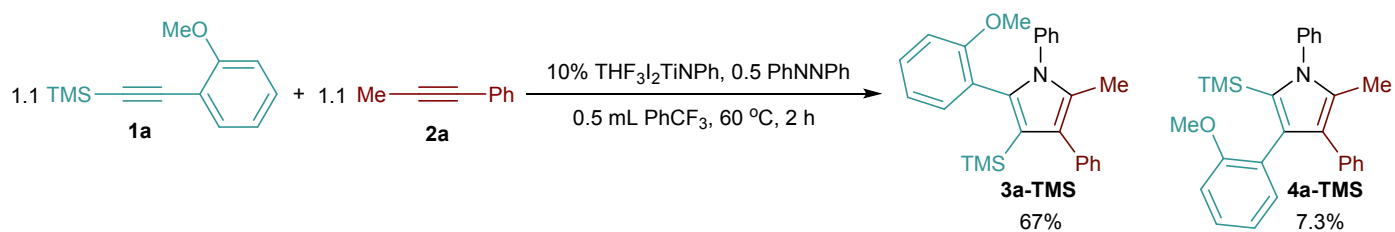
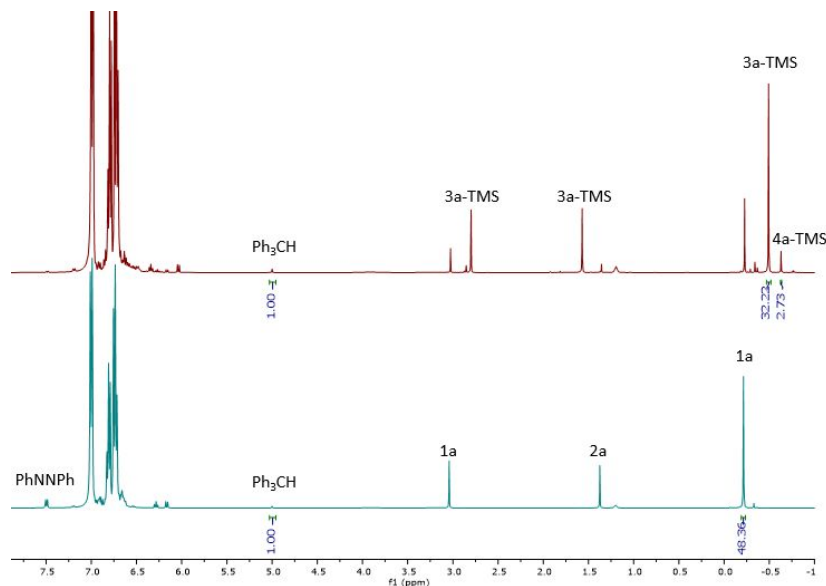


Figure S39. NOESY NMR spectrum of **3a** in  $\text{CDCl}_3$ .

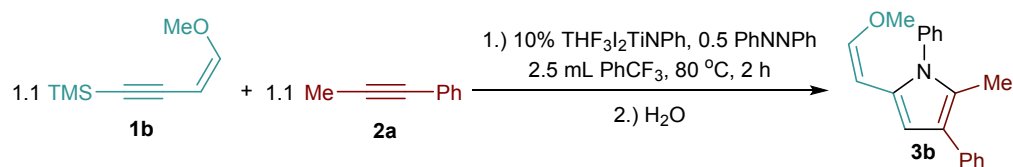
No-D  $^1\text{H}$  NMR spectra of the reactions of **1a** and **2a**





**Figure S40.** No-D  $^1\text{H}$  NMR reaction of **1a** and **2a** in  $\text{PhCF}_3$  at Time = 0 h (bottom), Time = 2 h (top) under Condition A.

### Synthesis of (Z)-5-(2-methoxyvinyl)-2-methyl-1,3-diphenyl-1H-pyrrole (**3b**)



Instead of acid workup, the reaction was quenched by 2 mL DI water, due to its instability in an acidic solution. The product was isolated by silica gel chromatography using 20% DCM/Hex eluent to give an oil which slightly decomposed during while concentrating and turned purple (58 mg, 40% yield).

$^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.65 (d,  $^3J_{\text{HH}} = 7.7$  Hz, 2H), 7.42 (s, 1H, 4- $\text{NC}_4\text{-H}$ ), 7.28 (t,  $^3J_{\text{HH}} = 7.6$  Hz, 2H), 7.11 (t,  $^3J_{\text{HH}} = 6.8$  Hz, 2H), 7.05–6.95 (m, 6H), 5.59 (d,  $^3J_{\text{HH}} = 6.8$  Hz, 1H,  $-\text{CH}=\text{CH}-\text{OMe}$ ), 5.01 (d,  $^3J_{\text{HH}} = 6.8$  Hz, 1H, 5- $\text{NC}_4\text{-CH}=\text{CH}-$ ), 3.18 (s, 3H,  $-\text{OCH}_3$ ), 2.08 (s, 3H, 2- $\text{NC}_4\text{-CH}_3$ ) ppm.

$^{13}\text{C}$  NMR (101 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  144.7, 139.2, 138.4, 129.3, 129.2, 128.8, 128.6, 125.5, 125.2, 123.7, 110.6, 96.9, 59.9, 12.3 ppm.

**GC-HRMS:** calculated for  $\text{C}_{20}\text{H}_{19}\text{NO}$  [ $\text{M}^+$ ] 289.1467; found 289.1443.

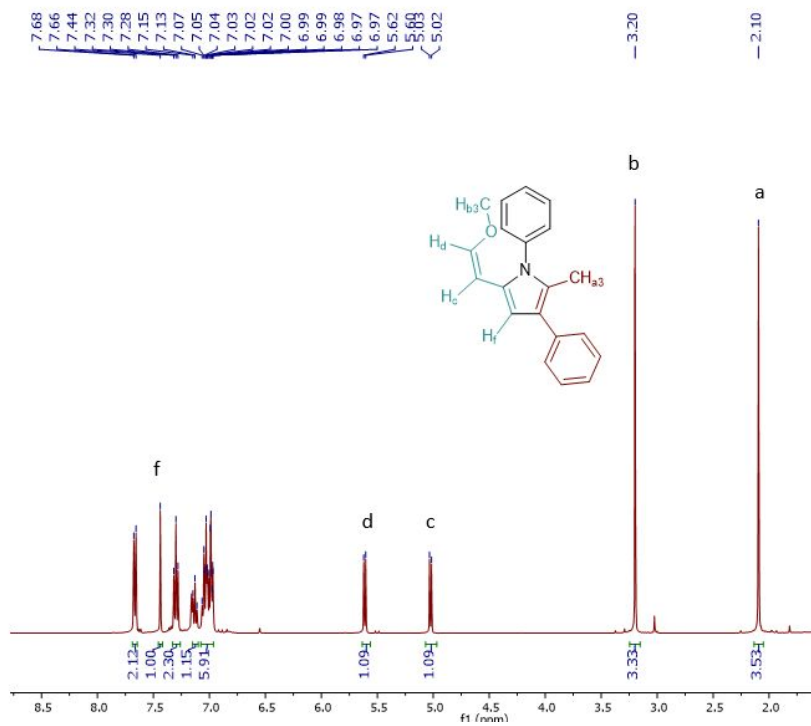


Figure S41.  $^1H$  NMR spectrum of **3b** in  $C_6D_6$ .

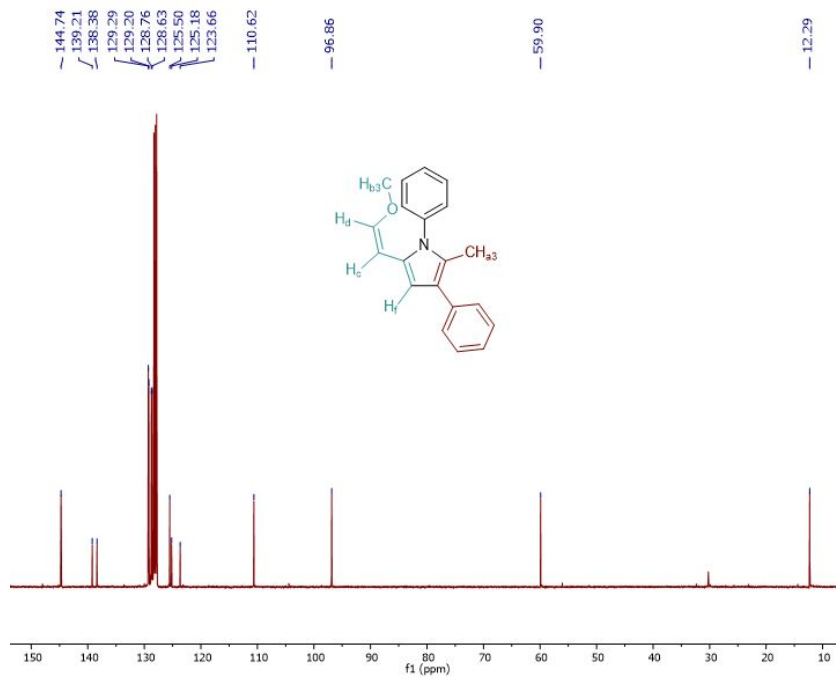
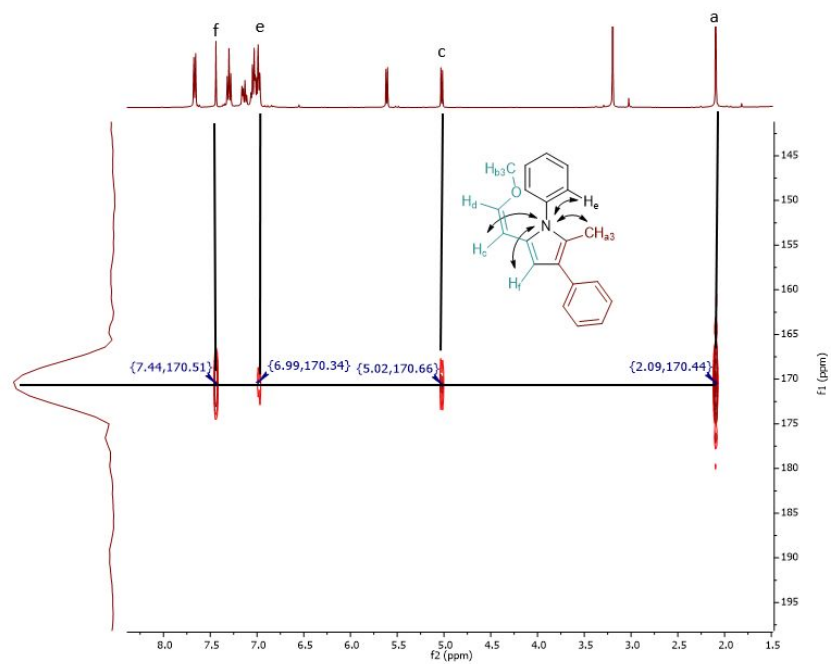
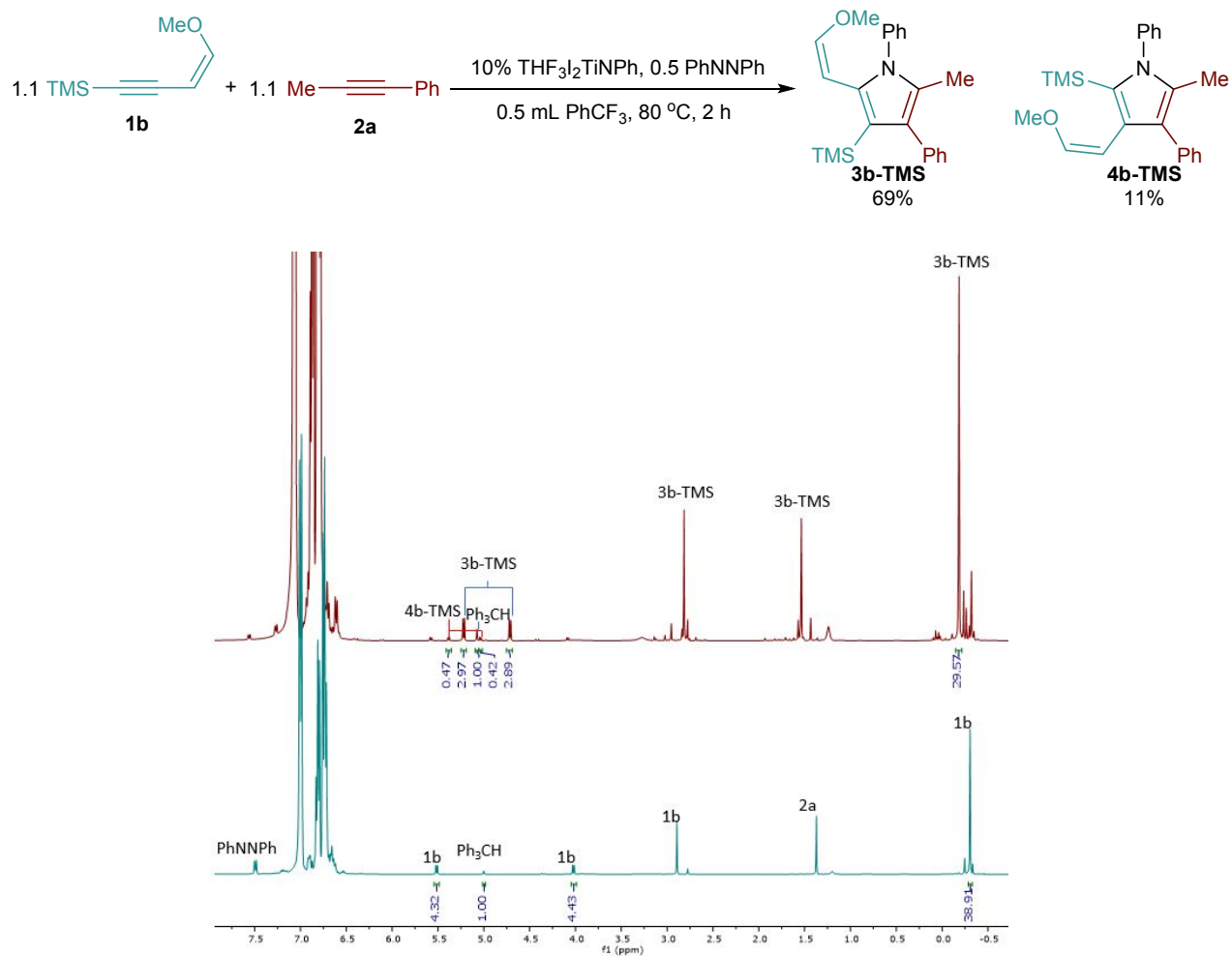


Figure S42.  $^{13}C$  NMR spectrum of **3b** in  $C_6D_6$ .

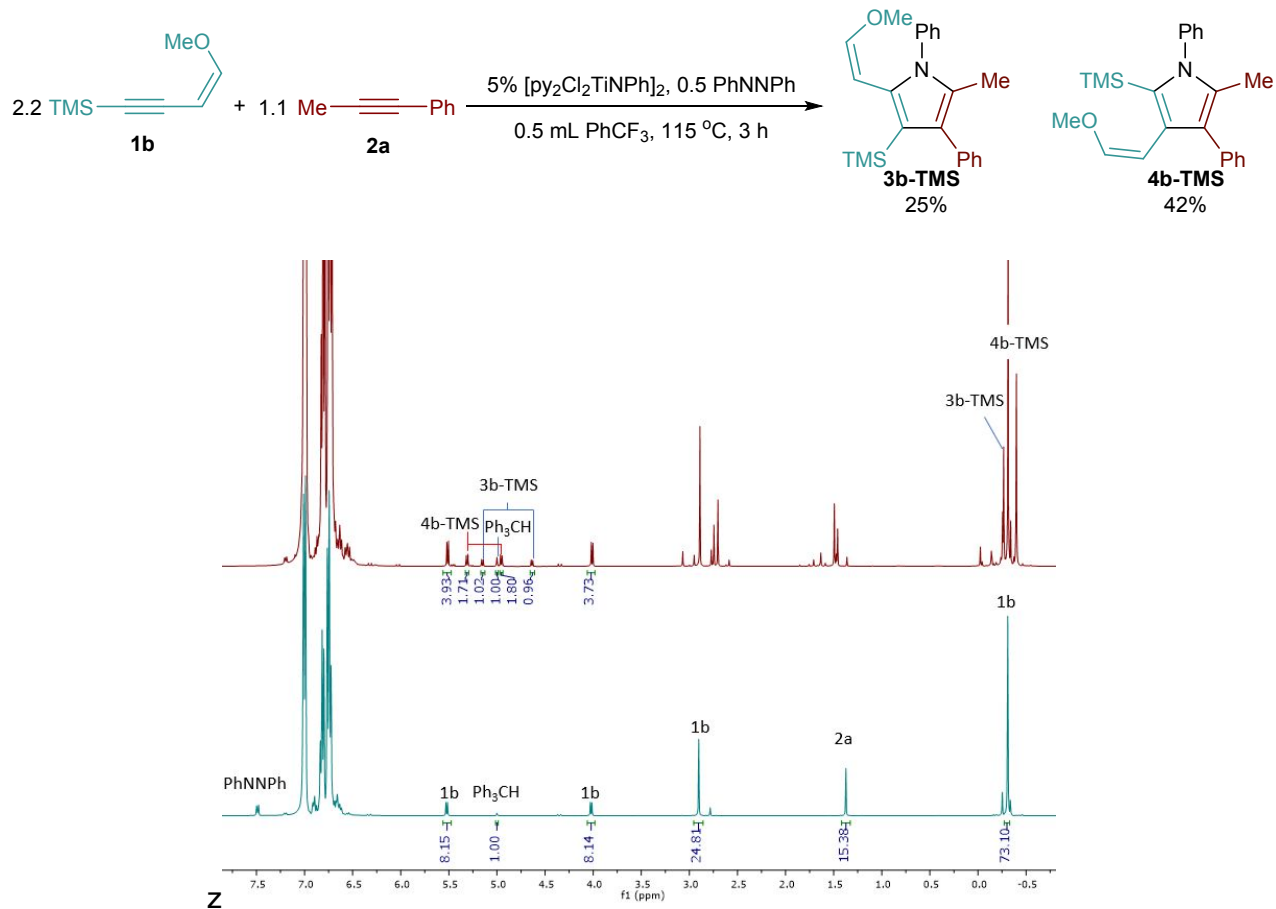


**Figure S43.**  $^1\text{H}$ - $^{15}\text{N}$  HMBC NMR spectrum of **3b** in  $\text{C}_6\text{D}_6$ .

No-D  $^1\text{H}$  NMR spectra of the reactions of **1b** and **2a**



**Figure S44.** No-D  $^1\text{H}$  NMR reaction of **1b** and **2a** in  $\text{PhCF}_3$  at Time = 0 h (bottom), Time = 2 h (top) under Condition A.



**Figure S45.** No-D  $^1\text{H}$  NMR reaction of **1b** and **2a** in  $\text{PhCF}_3$  at Time = 0 h (bottom), Time = 3 h (top) under Condition B.

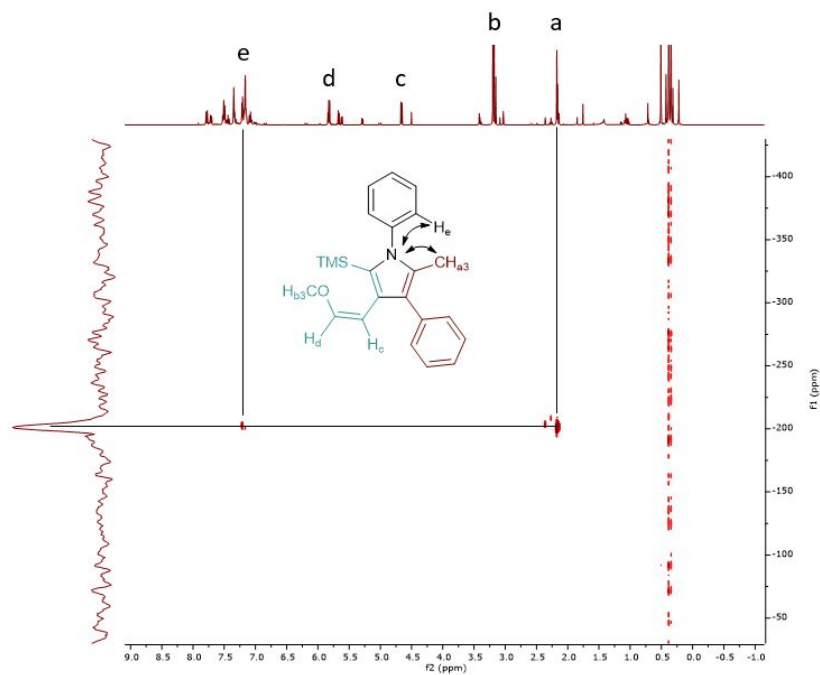
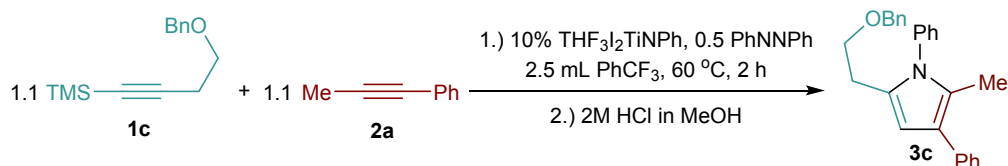


Figure S46.  $^1\text{H}$ - $^{15}\text{N}$  HMBC NMR of the crude reaction of **1b** and **2a** under Condition B after workup in  $\text{C}_6\text{D}_6$ .

### Synthesis of 5-(2-(benzyloxy)ethyl)-2-methyl-1,3-diphenyl-1H-pyrrole (**3c**)



The product was isolated by silica gel chromatography using 3% EA/Hex eluent to give a colorless oil (135 mg, 76% yield).

$^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.63-7.61 (m, 2H), 7.34 (t,  $^3J_{\text{HH}} = 7.6$  Hz, 2H), 7.21 (d,  $^3J_{\text{HH}} = 7.3$  Hz, 2H), 7.17-7.13 (m, 3H), 7.08 (tt,  $^3J_{\text{HH}} = 7.6$  Hz,  $^4J_{\text{HH}} = 2.4$  Hz, 1H), 7.02-6.95 (m, 3H), 6.87-6.85 (m, 2H), 6.41 (s, 1H, 4- $\text{NC}_4\text{-H}$ ), 4.27 (s, 2H,  $-\text{O}-\text{CH}_2-\text{C}_6\text{H}_5$ ), 3.53 (t, 2H  $^3J_{\text{HH}} = 7.3$  Hz, 2H,  $-\text{CH}_2-\text{OBn}$ ), 2.80 (t,  $^3J_{\text{HH}} = 7.2$  Hz, 2H, 5- $\text{NC}_4\text{-CH}_2$ -), 2.07 (s, 3H, 2- $\text{NC}_4\text{-CH}_3$ ) ppm.

$^{13}\text{C}$  NMR (101 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  139.3, 139.2, 138.4, 130.0, 129.2, 128.9, 128.8, 128.5, 128.5, 127.8, 127.6, 125.5, 125.3, 122.4, 107.6, 72.9, 70.1, 28.1, 12.2 ppm.

GC-HRMS: calculated for  $\text{C}_{26}\text{H}_{25}\text{NO}$  [ $\text{M}^+$ ] 367.1936; found 367.1917.

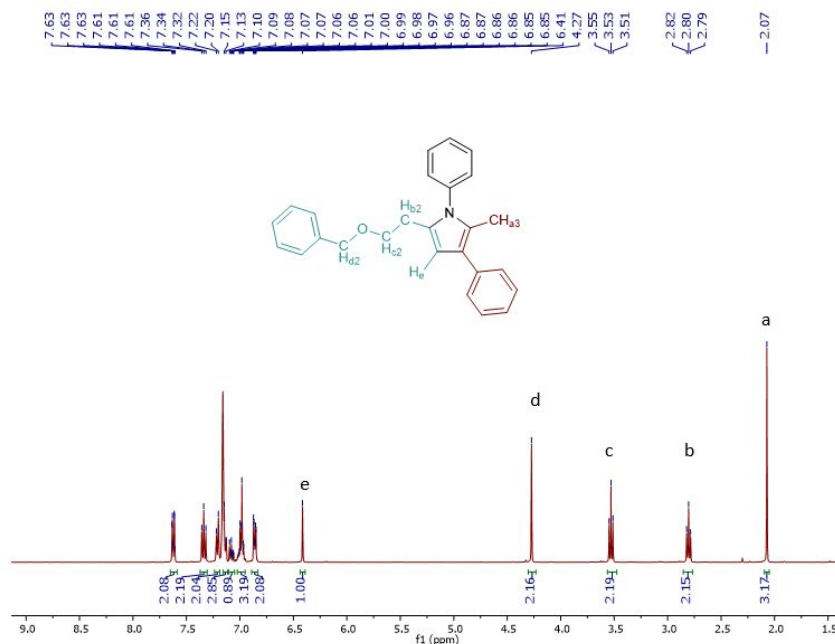
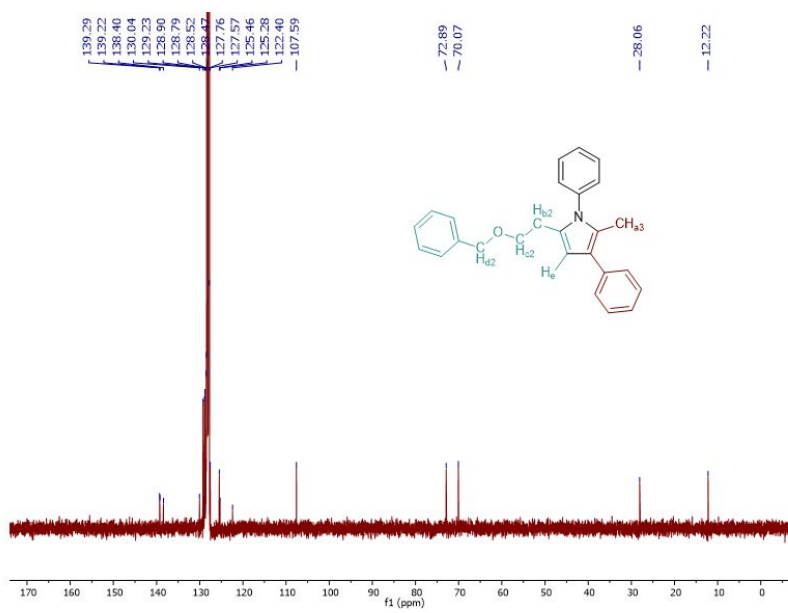
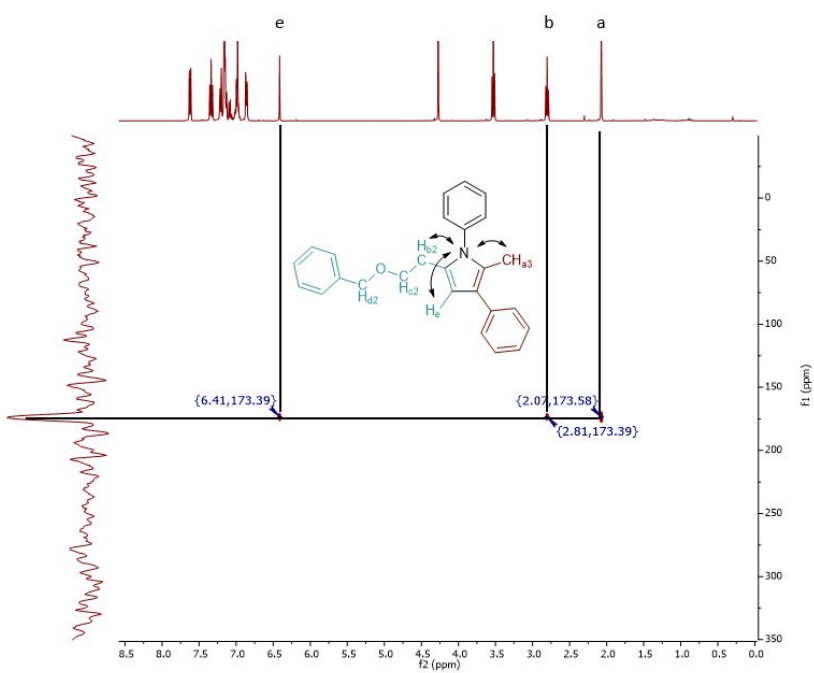


Figure S47.  $^1\text{H}$  NMR spectrum of **3c** in  $\text{C}_6\text{D}_6$ .

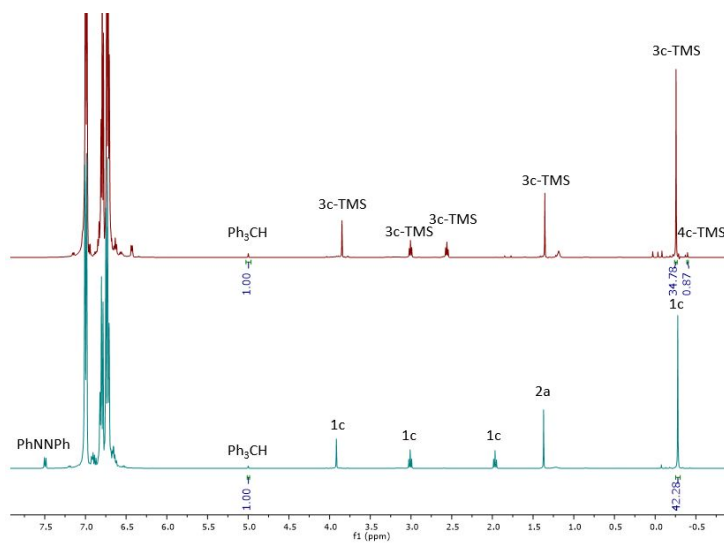
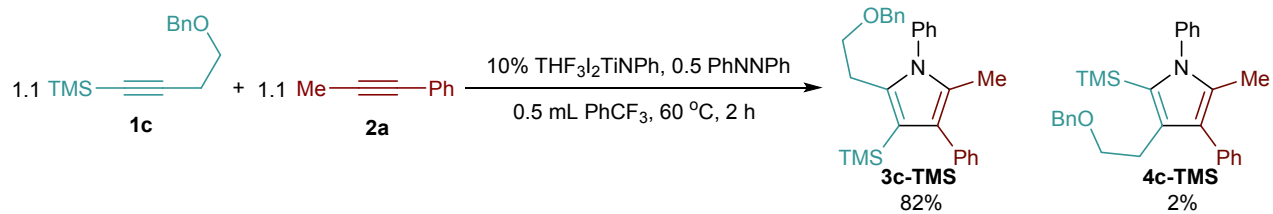


**Figure S48.**  $^{13}C$  NMR spectrum of **3c** in  $C_6D_6$ .

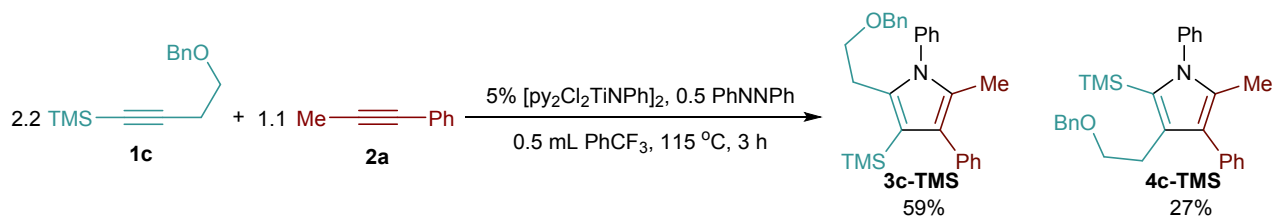


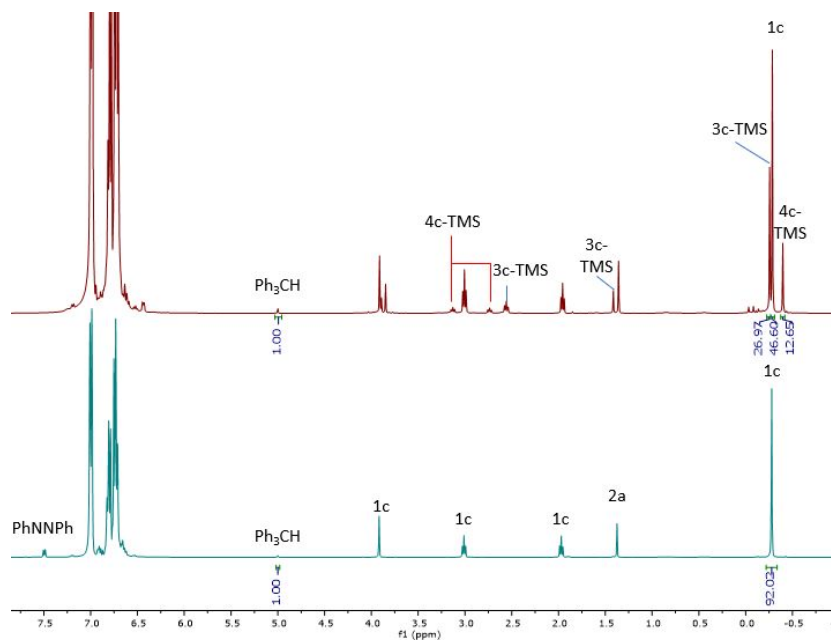
**Figure S49.**  $^1H$ - $^{15}N$  HMBC NMR spectrum of **3c** in  $C_6D_6$ .

**No-D  $^1H$  NMR spectra of the reactions of **1c** and **2a****



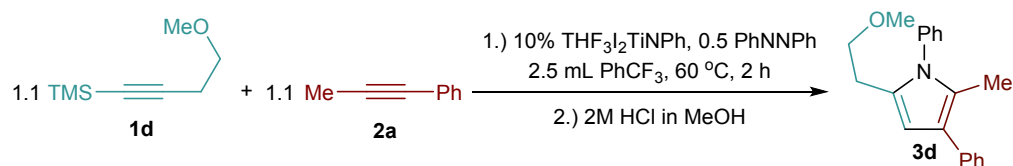
**Figure S50.** No-D  $^1\text{H NMR}$  reaction of **1c** and **2a** in  $\text{PhCF}_3$  at Time = 0 h (bottom), Time = 2 h (top) under Condition A.





**Figure S51.** No-D  $^1\text{H}$  NMR reaction of **1c** and **2a** in  $\text{PhCF}_3$  at Time = 0 h (bottom), Time = 3 h (top) under Condition B.

### Synthesis of 5-(2-methoxyethyl)-2-methyl-1,3-diphenyl-1*H*-pyrrole (**3d**)



The product was isolated by silica gel chromatography using 15% EA/Hex eluent to give a colorless oil (58 mg, 58% yield).

**$^1\text{H}$  NMR** (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.81 – 7.79 (m, 2H), 7.51 (tt, 2H,  $^3J_{\text{HH}} = 7.7, 1.8$  Hz), 7.34 – 7.31 (m, 2H), 7.20 – 7.12 (m, 2H), 7.08 – 7.06 (m, 2H), 6.60 (s, 1H, 4- $\text{NC}_4\text{-H}$ ), 3.59 (t, 2H,  $^3J_{\text{HH}} = 7.2$  Hz,  $-\text{CH}_2\text{-CH}_2\text{-OMe}$ ), 3.22 (s, 3H,  $-\text{OCH}_3$ ), 2.93 (t, 2H,  $^3J_{\text{HH}} = 7.2$  Hz, 5- $\text{NC}_4\text{-CH}_2\text{-}$ ), 2.25 (s, 3H, 2- $\text{NC}_4\text{-CH}_3$ ) ppm.

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  139.3, 138.4, 130.2, 129.2, 128.9, 128.79, 128.5, 125.5, 125.2, 122.4, 107.5, 72.4, 58.3, 27.9, 12.2 ppm. Spectral data was consistent with literature values.

**GC-HRMS:** calculated for  $\text{C}_{20}\text{H}_{21}\text{NO}$  [ $\text{M}^+$ ] 291.1623; found 291.1607.

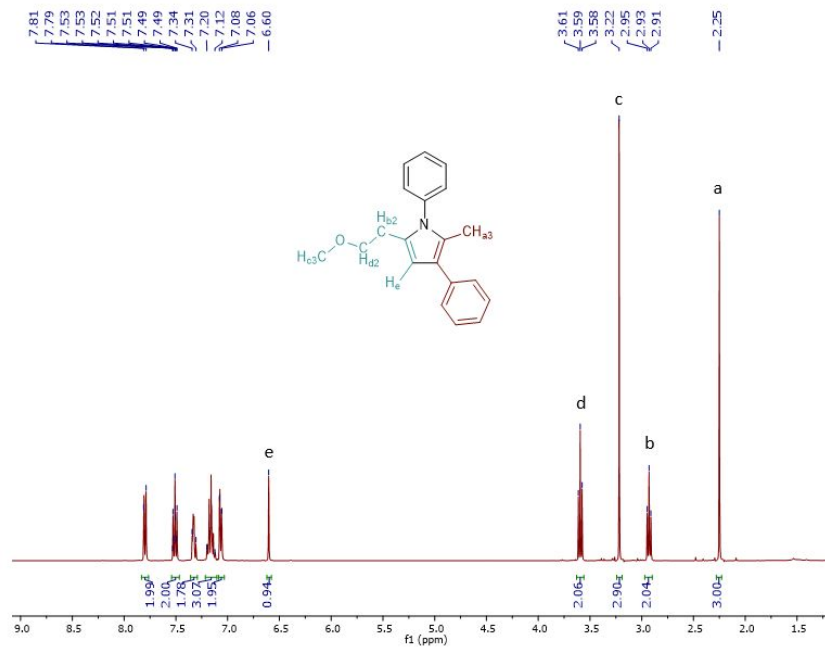


Figure S52.  $^1\text{H}$  NMR spectrum of **3d** in  $\text{C}_6\text{D}_6$ .

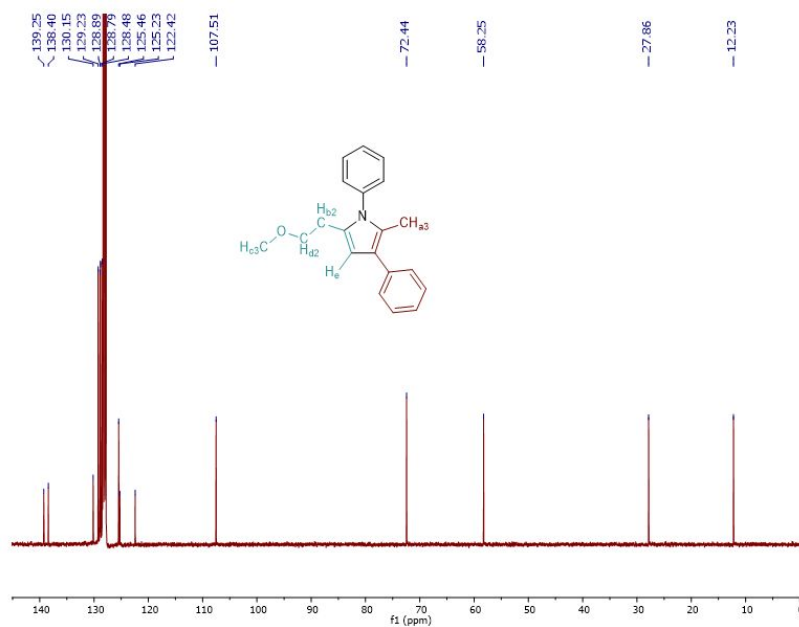
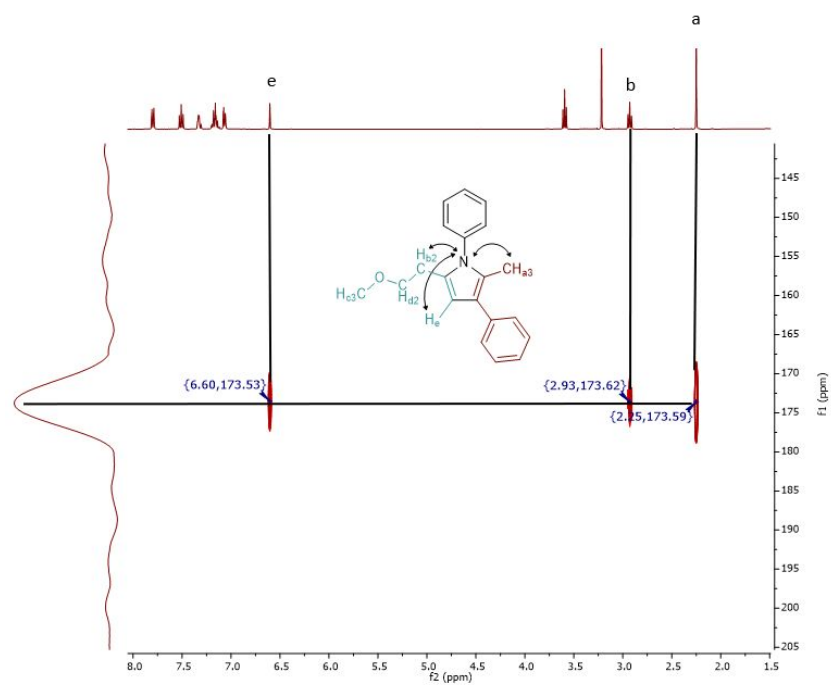
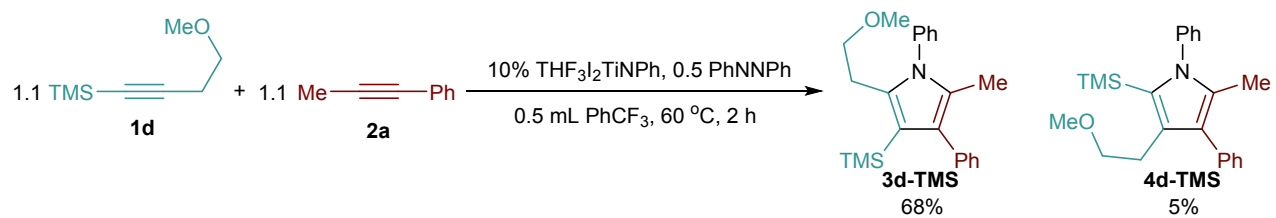


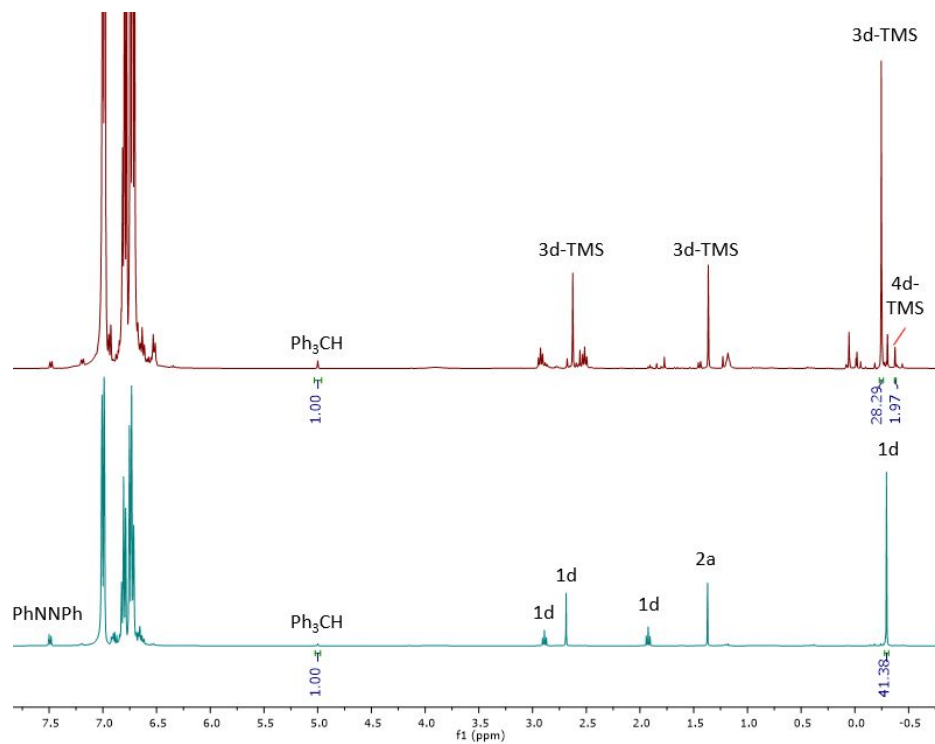
Figure S53.  $^{13}\text{C}$  NMR spectrum of **3d** in  $\text{C}_6\text{D}_6$ .



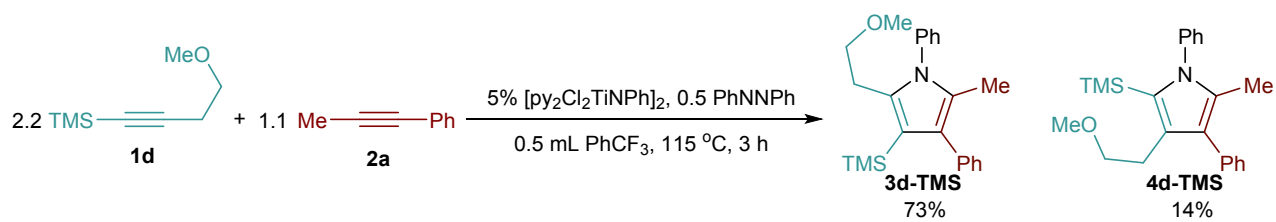
**Figure S54.**  $^1\text{H}$ - $^{15}\text{N}$  HMBC NMR spectrum of **3d** in  $\text{C}_6\text{D}_6$ .

**No-D  $^1\text{H}$  NMR spectra of the reactions of **1d** and **2a****





**Figure S55.** No-D  $^1\text{H}$  NMR reaction of **1d** and **2a** in  $\text{PhCF}_3$  at Time = 0 h (bottom), Time = 2 h (top) under Condition A.



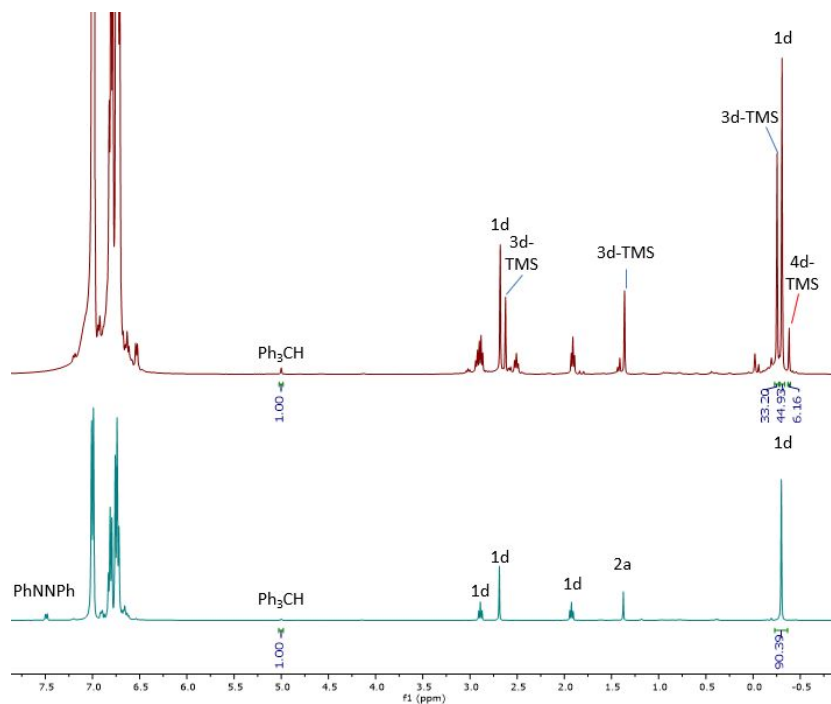


Figure S56. No-D  $^1\text{H}$  NMR reaction of **1d** and **2a** in  $\text{PhCF}_3$  at Time = 0 h (bottom), Time = 3 h (top) under Condition B.

### No-D $^1\text{H}$ NMR spectra of the reactions of **1e** and **2a**

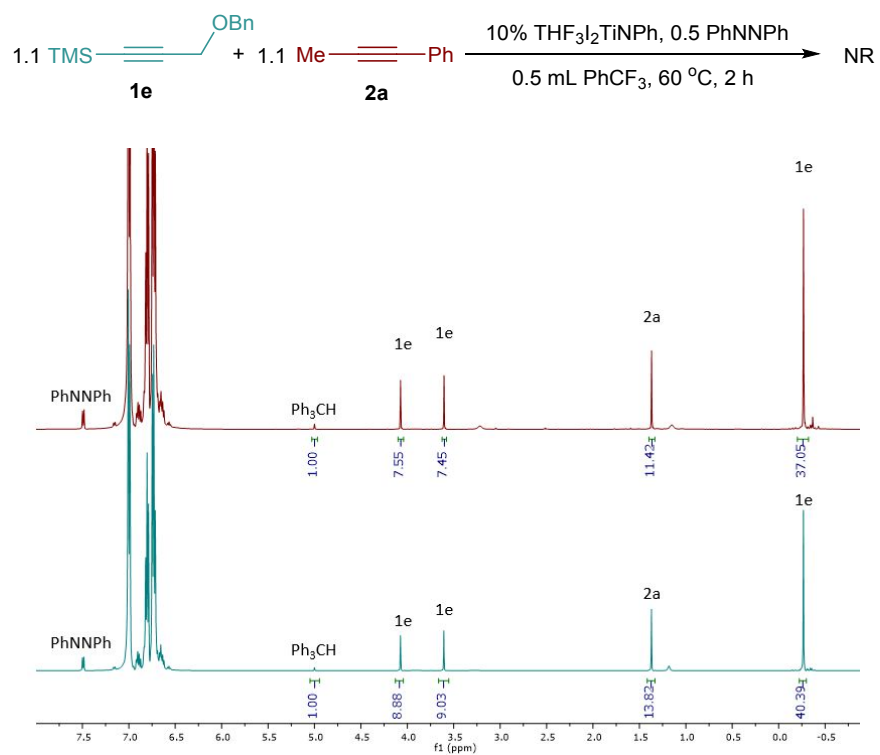
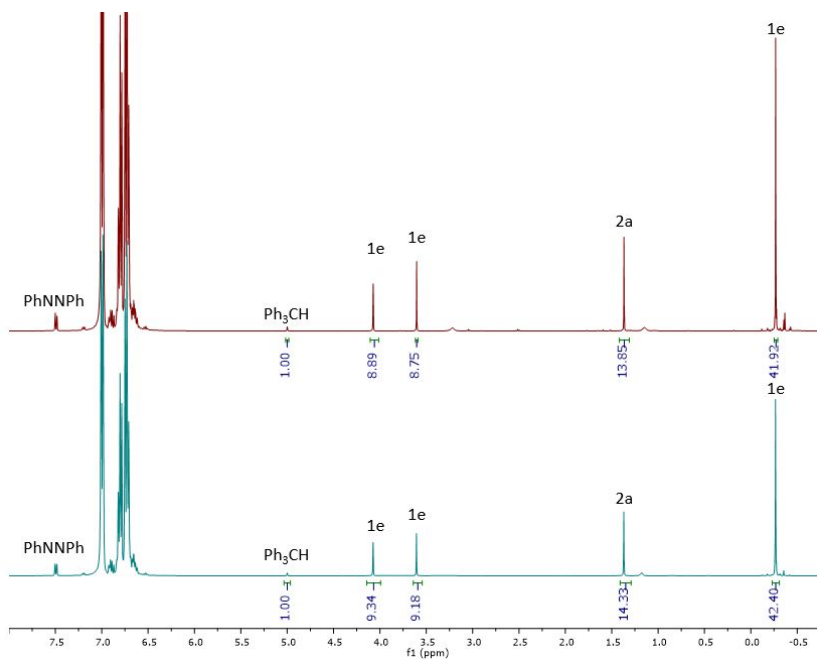
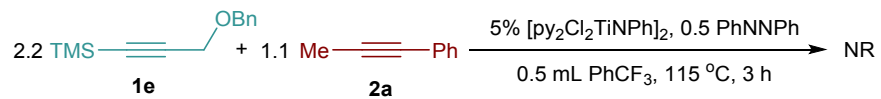
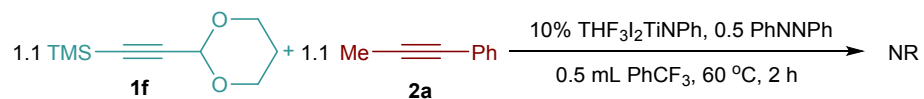


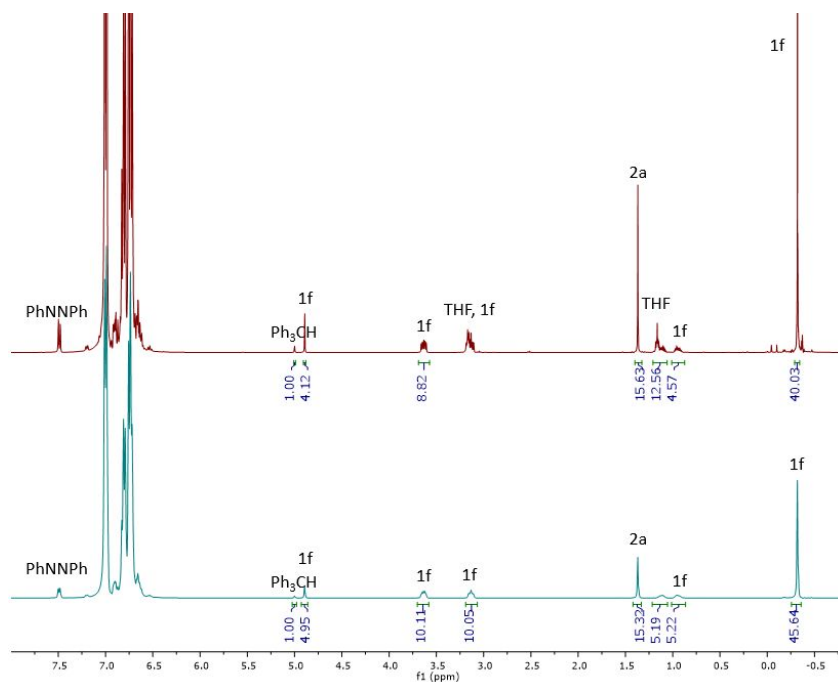
Figure S57. No-D  $^1\text{H}$  NMR reaction of **1e** and **2a** in  $\text{PhCF}_3$  at Time = 0 h (bottom), Time = 2 h (top) under Condition A.



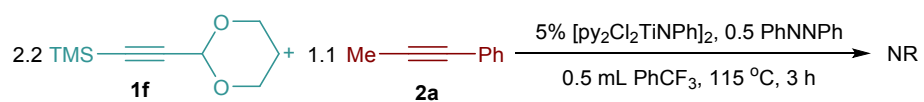
**Figure S58.** No-D <sup>1</sup>H NMR reaction of **1e** and **2a** in PhCF<sub>3</sub> at Time = 0 h (bottom), Time = 3 h (top) under Condition B.

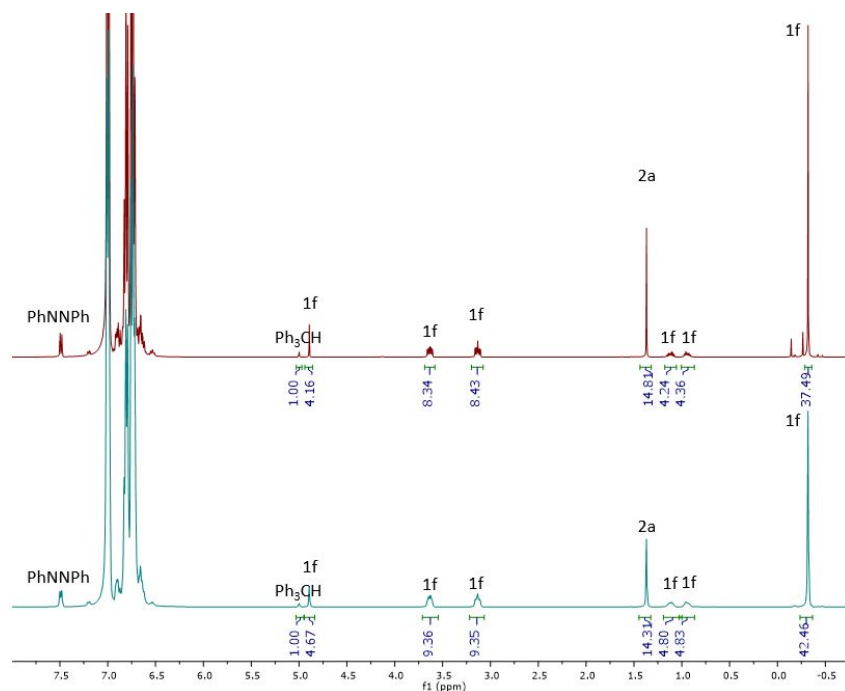
**No-D <sup>1</sup>H NMR spectra of the reactions of 1f and 2a**





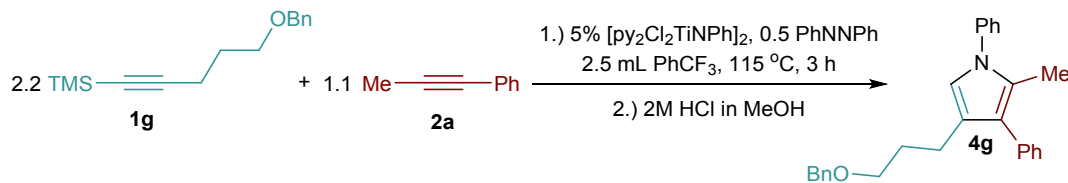
**Figure S59.** No-D  $^1\text{H}$  NMR reaction of **1f** and **2a** in  $\text{PhCF}_3$  at Time = 0 h (bottom), Time = 2 h (top) under Condition A.





**Figure S60.** No-D  $^1\text{H}$  NMR reaction of **1f** and **2a** in  $\text{PhCF}_3$  at Time = 0 h (bottom), Time = 3 h (top) under Condition B.

### Synthesis of 4-(3-(benzyloxy)propyl)-2-methyl-1,3-diphenyl-1H-pyrrole (**4g**)



The product was isolated by silica gel chromatography using 2% EA/Hex eluent to give a colorless oil (166 mg, 87% yield).

$^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.58-7.56 (m, 2H), 7.42-7.38 (m, 4H), 7.28-7.24 (m, 4H), 7.20-7.15 (m, 4H), 7.09-7.07 (m, 1H), 6.70 (s, 2H, 5- $\text{NC}_4\text{-H}$ ), 3.46 (t,  $^3J_{\text{HH}} = 6.4$  Hz, 2H,  $-\text{CH}_2\text{-OBn}$ ), 2.92 (t,  $^3J_{\text{HH}} = 7.3$  Hz, 2H, 4- $\text{NC}_4\text{-CH}_2\text{-CH}_2\text{CH}_2\text{OBn}$ ), 2.18 (s, 3H, 2- $\text{NC}_4\text{-CH}_3$ ), 2.06-1.99 (m, 2H,  $-\text{CH}_2\text{-CH}_2\text{OBn}$ ) ppm.

$^{13}\text{C}$  NMR (101 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  141.1, 139.7, 137.6, 130.6, 129.2, 128.6, 128.5, 127.8, 127.5, 126.6, 126.1, 125.9, 125.8, 124.2, 123.1, 118.9, 72.8, 70.2, 31.2, 22.9, 11.9 ppm.

**GC-HRMS:** calculated for  $\text{C}_{27}\text{H}_{27}\text{NO}$  [ $\text{M}^+$ ] 381.2093; found 381.2058.

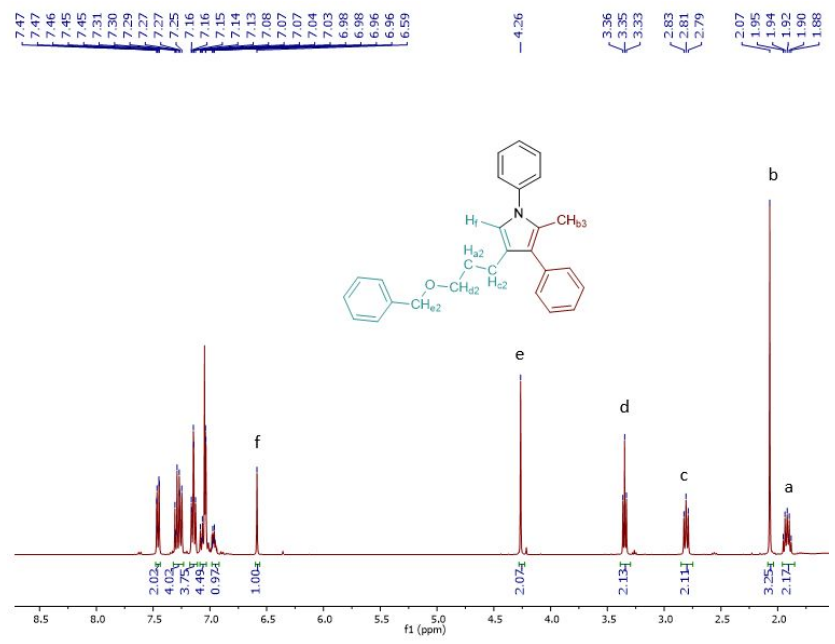


Figure S61. <sup>1</sup>H NMR spectrum of **4g** in C<sub>6</sub>D<sub>6</sub>.

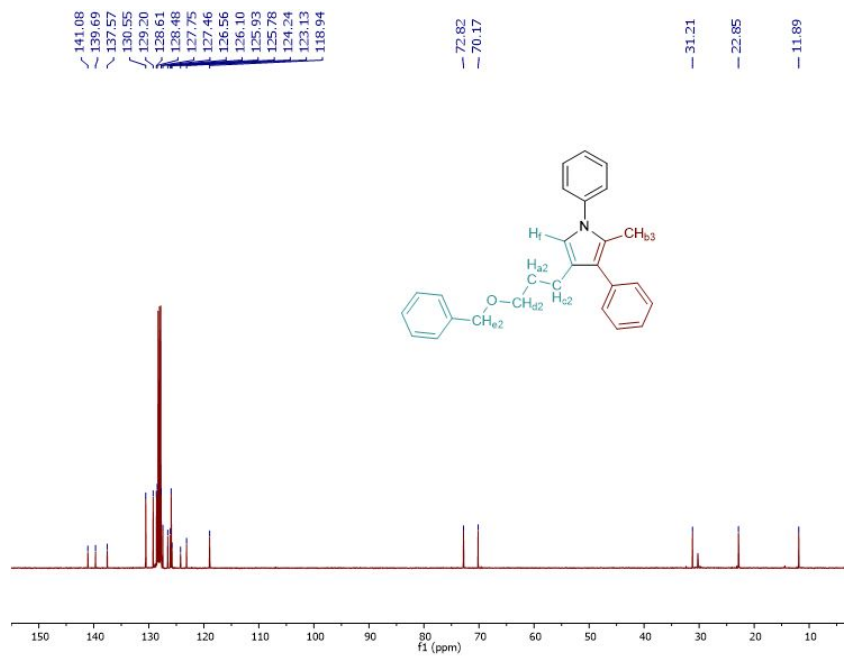


Figure S62. <sup>13</sup>C NMR spectrum of **4g** in C<sub>6</sub>D<sub>6</sub>.

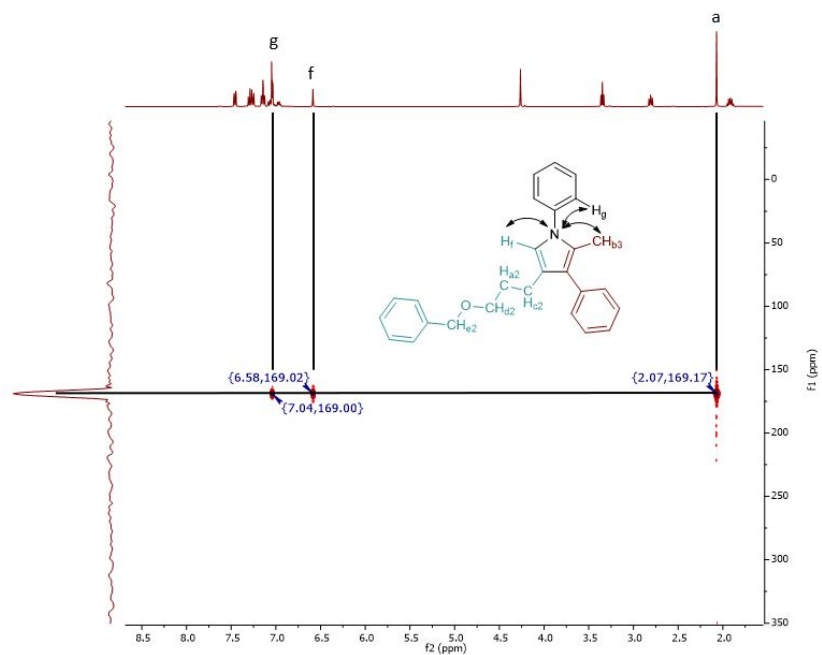
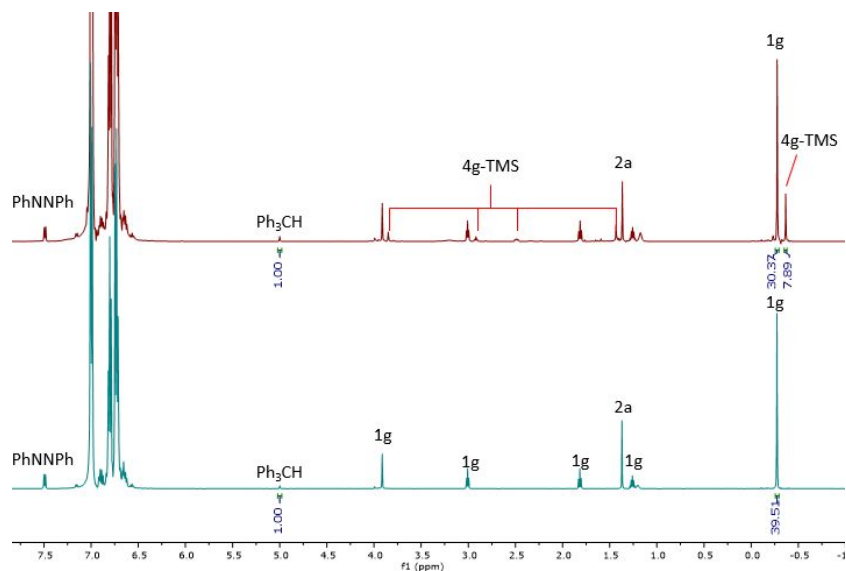
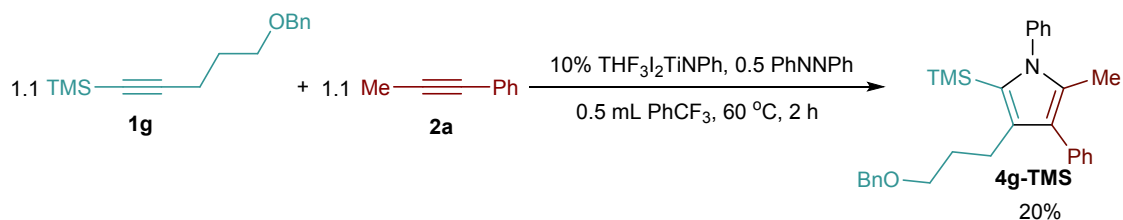
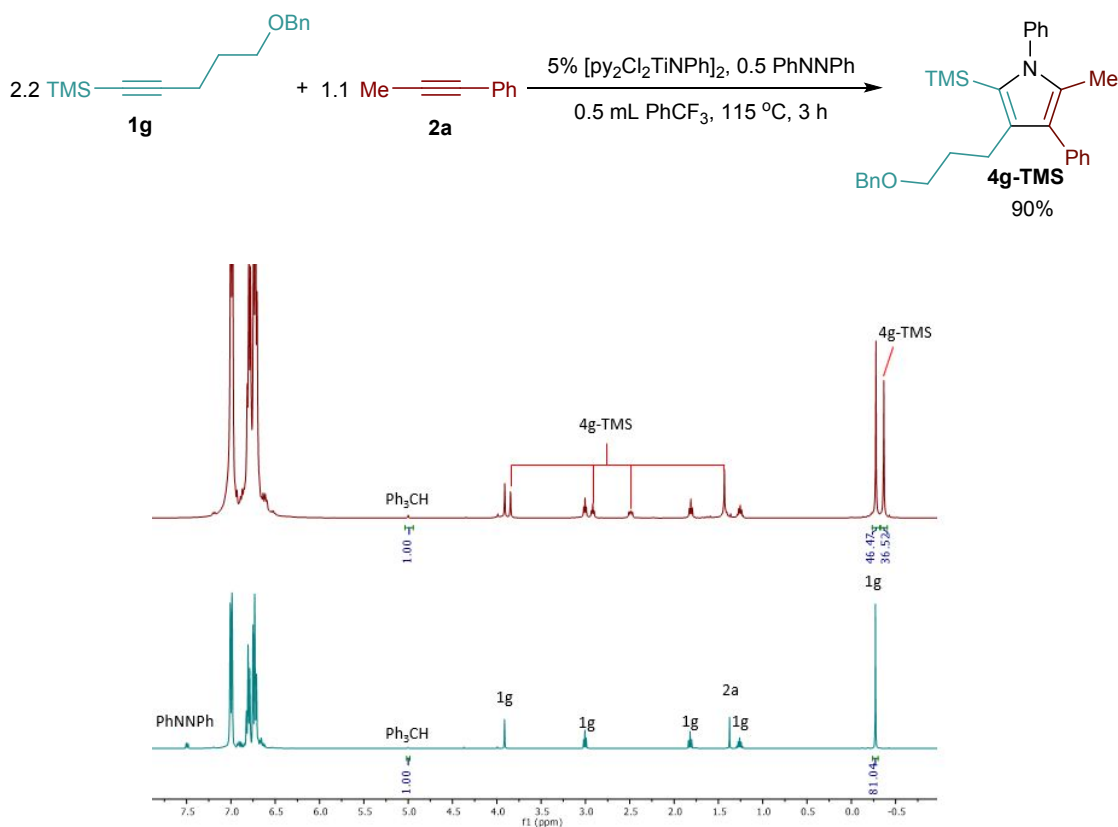


Figure S63.  $^1\text{H}$ - $^{15}\text{N}$  HMBC NMR spectrum of **4g** in  $\text{C}_6\text{D}_6$ .

### No-D $^1\text{H}$ NMR spectra of the reactions of **1g** and **2a**

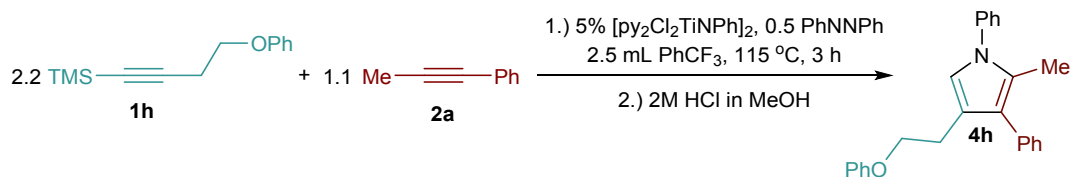


**Figure S64.** No-D  $^1\text{H}$  NMR reaction of **1g** and **2a** in  $\text{PhCF}_3$  at Time = 0 h (bottom), Time = 2 h (top) under Condition A.



**Figure S65.** No-D  $^1\text{H}$  NMR reaction of **1g** and **2a** in  $\text{PhCF}_3$  at Time = 0 h (bottom), Time = 3 h (top) under Condition B.

### Synthesis of 2-methyl-4-(2-phenoxyethyl)-1,3-diphenyl-1H-pyrrole (**4h**)



The product was isolated by silica gel chromatography using 3% EA/Hex eluent to give a white solid (17 mg, 10% yield).

$^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.56 (d,  $^3J_{\text{HH}} = 7.8$  Hz, 2H), 7.41 (t,  $^3J_{\text{HH}} = 7.5$  Hz, 2H), 7.30-7.26 (m, 2H), 7.21 (t,  $^3J_{\text{HH}} = 7.7$  Hz, 2H), 7.15-7.13 (m, 3H), 7.10-7.07 (m, 1H), 6.95-6.91 (m, 3H), 6.81 (s, 1H, 5-NC<sub>4</sub>-H), 4.09 (t,  $^3J_{\text{HH}} = 7.1$  Hz, 4-NC<sub>4</sub>-CH<sub>2</sub>-CH<sub>2</sub>-OPh, 2H), 3.23 (t,  $^3J_{\text{HH}} = 7.2$  Hz, 2H, 4-NC<sub>4</sub>-CH<sub>2</sub>-CH<sub>2</sub>OPh), 2.18 (s, 3H, 2-NC<sub>4</sub>-CH<sub>3</sub>) ppm.

$^{13}\text{C}$  NMR (101 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  159.6, 140.9, 137.2, 130.6, 129.7, 129.2, 128.7, 126.8, 126.3, 126.0, 125.8, 124.3, 120.7, 119.7, 119.2, 114.9, 68.6, 26.2, 11.8 ppm

GC-HRMS: calculated for C<sub>25</sub>H<sub>23</sub>NO [M<sup>+</sup>] 353.1780; found 353.1739.

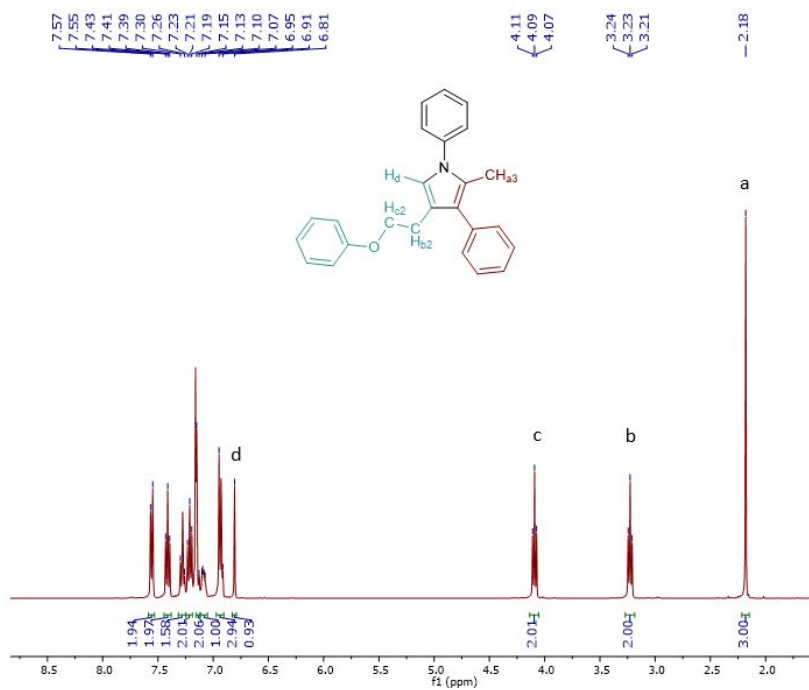


Figure S66. <sup>1</sup>H NMR spectrum of **4h** in C<sub>6</sub>D<sub>6</sub>.

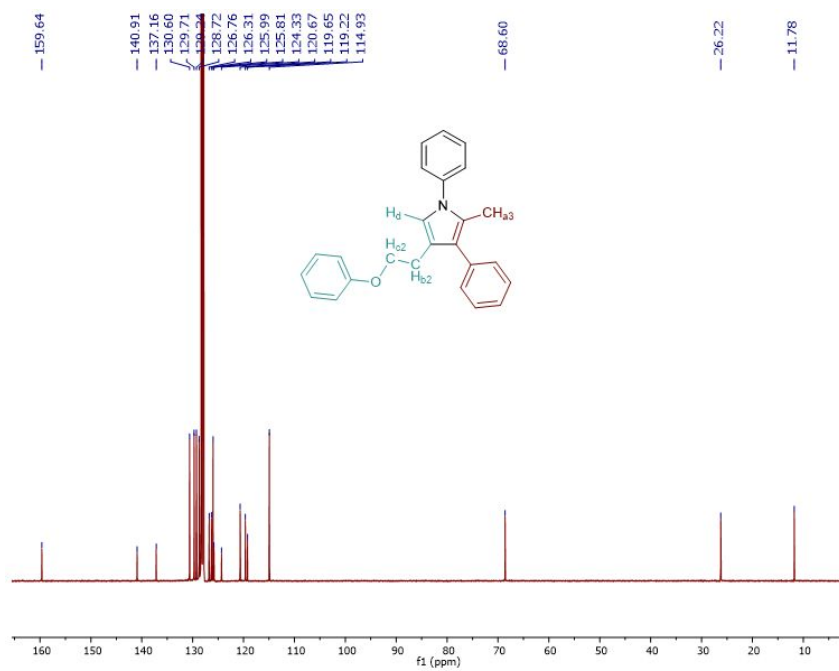
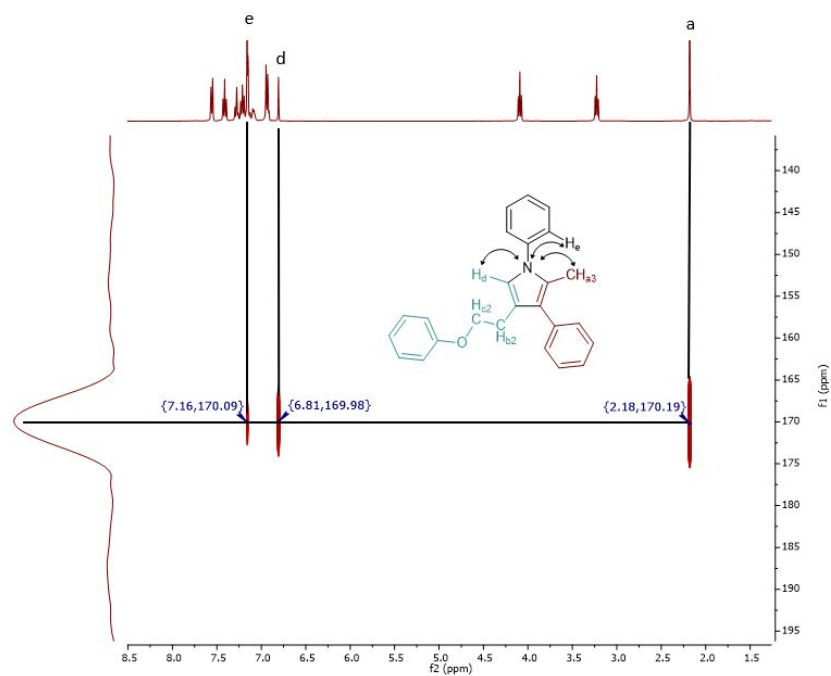
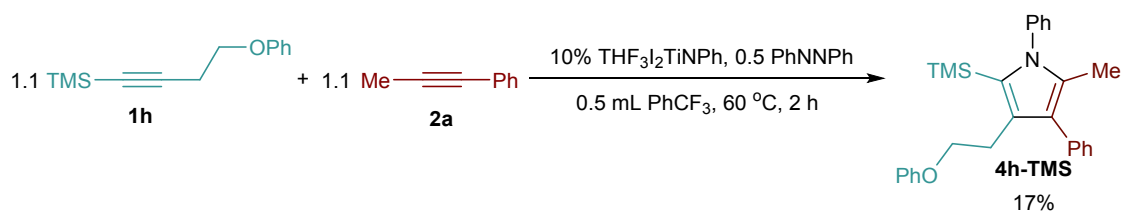


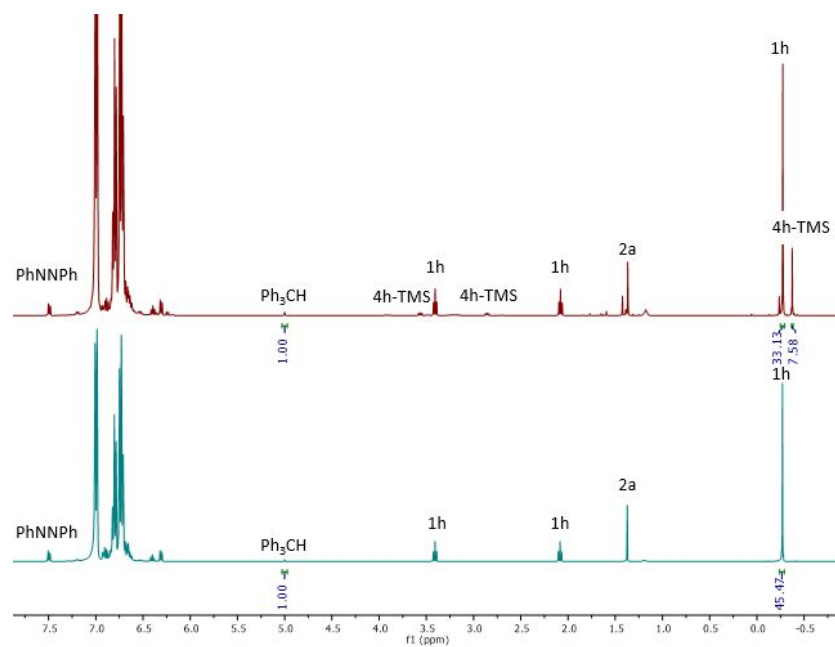
Figure S67. <sup>13</sup>C NMR spectrum of **4h** in C<sub>6</sub>D<sub>6</sub>.



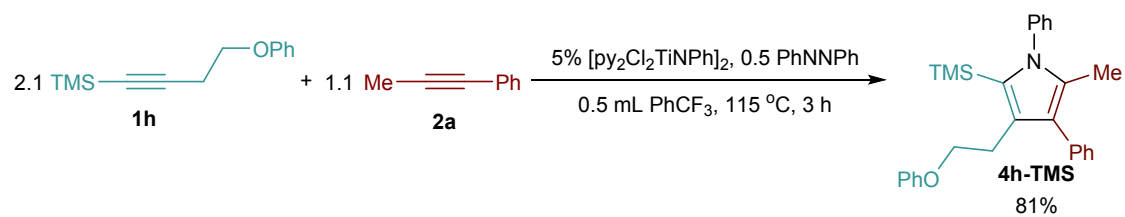
**Figure S68.**  $^1\text{H}$ - $^{15}\text{N}$  HMBC NMR spectrum of **4h** in  $\text{C}_6\text{D}_6$ .

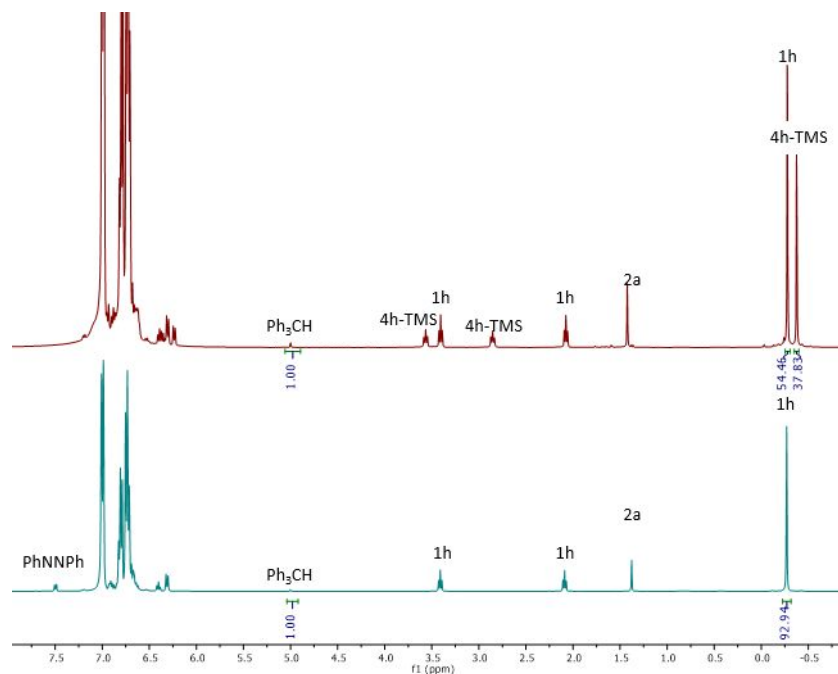
**No-D  $^1\text{H}$  NMR spectra of the reactions of **1h** and **2a****





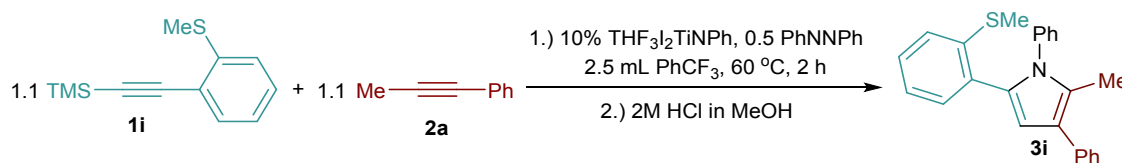
**Figure S69.** No-D  $^1\text{H}$  NMR reaction of **1h** and **2a** in  $\text{PhCF}_3$  at Time = 0 h (bottom), Time = 2 h (top) under Condition A.





**Figure S70.** No-D  $^1\text{H}$  NMR reaction of **1h** and **2a** in  $\text{PhCF}_3$  at Time = 0 h (bottom), Time = 3 h (top) under Condition B.

### Synthesis of 2-methyl-5-(2-(methylthio)phenyl)-1,3-diphenyl-1*H*-pyrrole (**3i**)



Upon acidic work-up, the crude product was purified by recrystallization in hexanes to give the desired compound as a white solid (60 mg, 34 %).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.58 (app d,  $^3J_{\text{HH}} = 7.9$  Hz, 2H), 7.44 (t,  $^3J_{\text{HH}} = 7.7$  Hz, 2H), 7.34 – 7.28 (m, 3H), 7.24 – 7.13 (m, 5H), 7.01 – 6.99 (m, 1H), 6.96 – 6.92 (m, 1H), 6.61 (s, 1H, 4- $\text{NC}_4\text{-H}$ ), 2.40 (s, 3H, S- $\text{CH}_3$ ), 2.33 (s, 3H, 2- $\text{NC}_4\text{-CH}_3$ ) ppm.

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  139.9, 138.8, 137.2, 132.1, 131.8, 130.8, 128.6, 128.5, 128.4, 128.2, 127.9, 127.2, 126.7, 125.4, 124.4, 123.8, 122.3, 111.1, 15.9, 12.8 ppm.

GC-HRMS: calculated for  $\text{C}_{24}\text{H}_{21}\text{NS}$  [ $\text{M}^+$ ] 355.1395; found 355.1359.

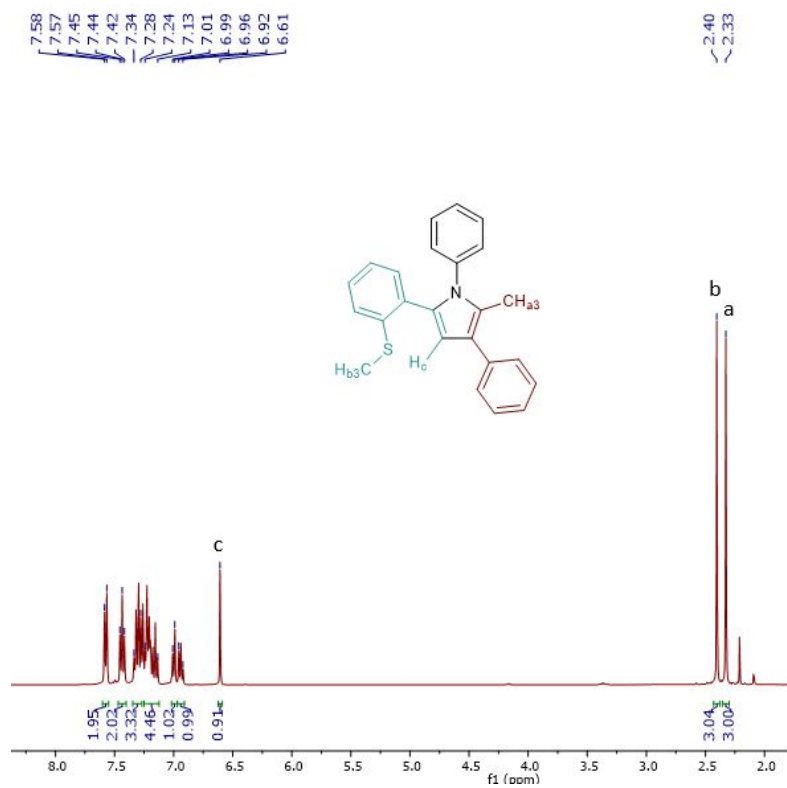


Figure S71.  $^1\text{H}$  NMR spectrum of **3i** in  $\text{CDCl}_3$ .

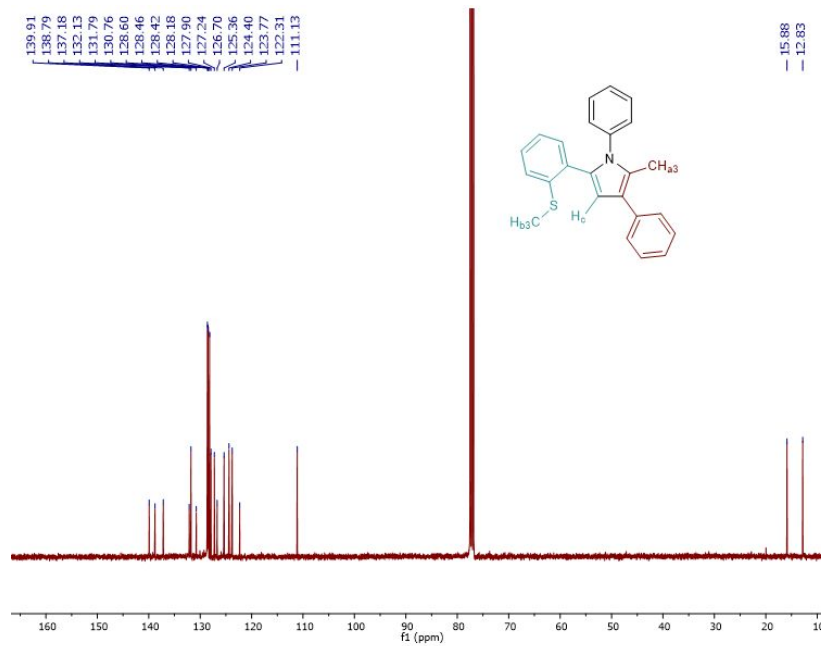
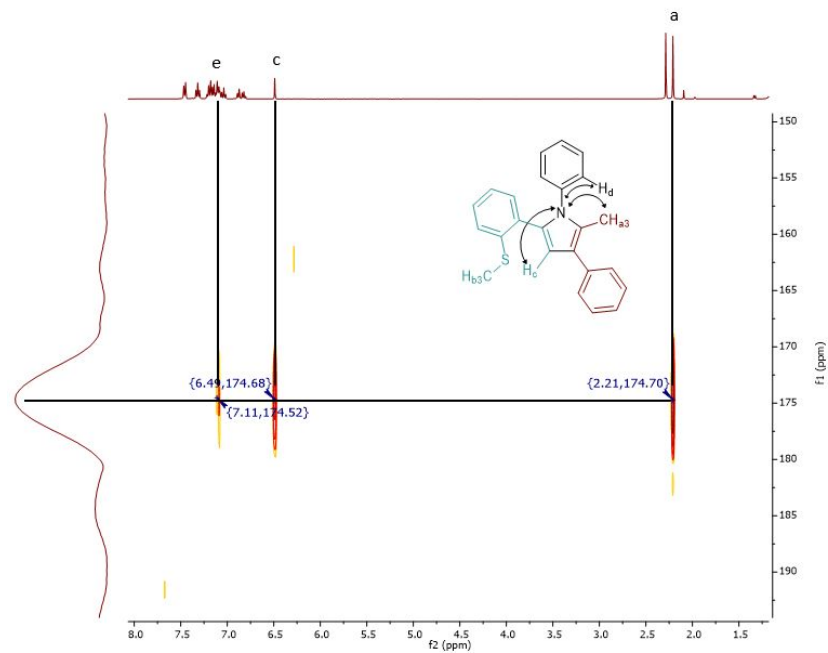
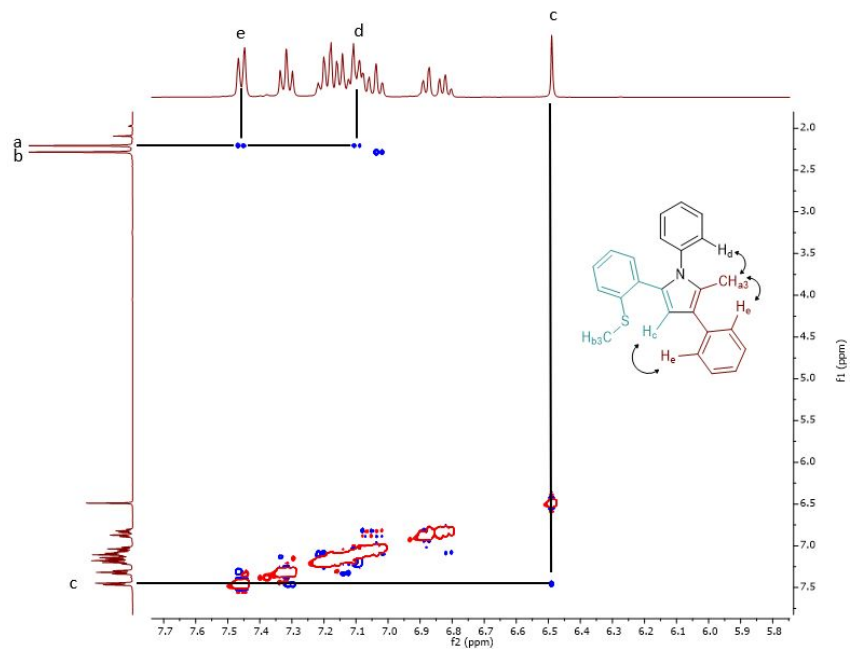


Figure S72.  $^{13}\text{C}$  NMR spectrum of **3i** in  $\text{CDCl}_3$ .

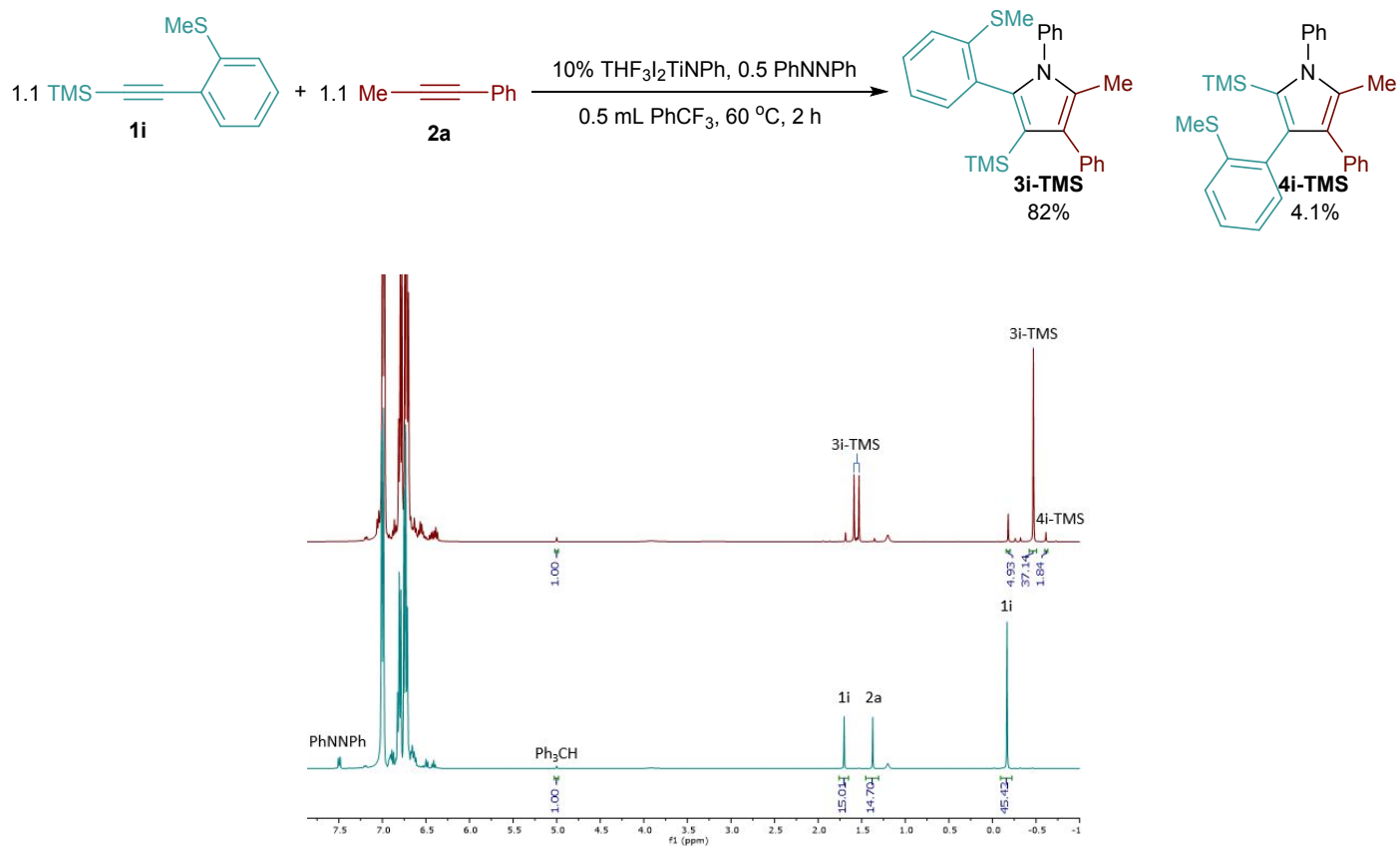


**Figure S73.**  $^1\text{H}$ - $^{15}\text{N}$  HMBC NMR spectrum of **3i** in  $\text{CDCl}_3$ .

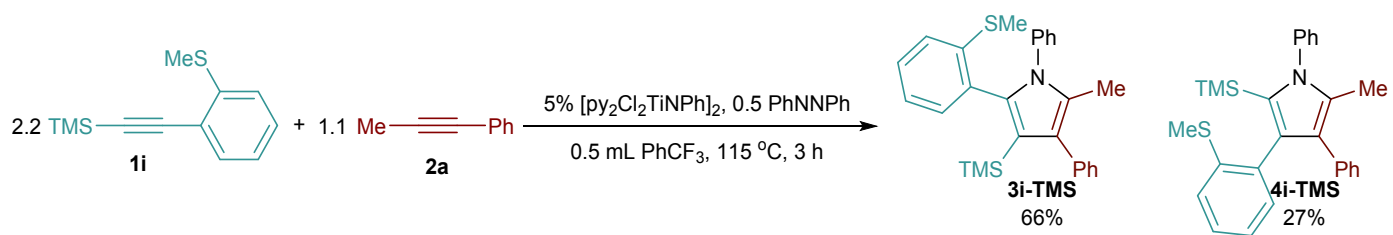


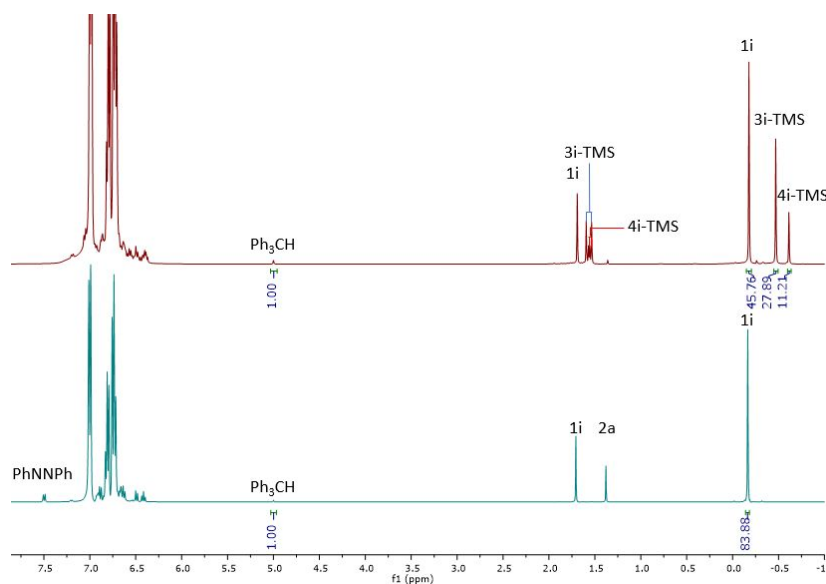
**Figure S74.** NOESY NMR spectrum of **3i** in  $\text{CDCl}_3$ .

### No-D <sup>1</sup>H NMR spectra of the reactions of **1i** and **2a**



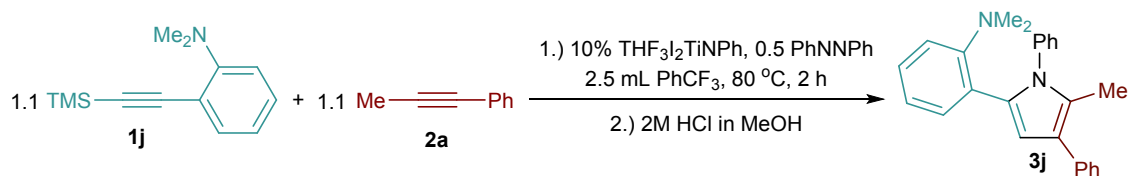
**Figure S75.** No-D <sup>1</sup>H NMR reaction of **1i** and **2a** in PhCF<sub>3</sub> at Time = 0 h (bottom), Time = 2 h (top) under Condition A.





**Figure S76.** No-D  $^1\text{H}$  NMR reaction of **1i** and **2a** in  $\text{PhCF}_3$  at Time = 0 h (bottom), Time = 3 h (top) under Condition B.

### Synthesis of *N,N*-dimethyl-2-(5-methyl-1,4-diphenyl-1*H*-pyrrol-2-yl)aniline (**3j**)

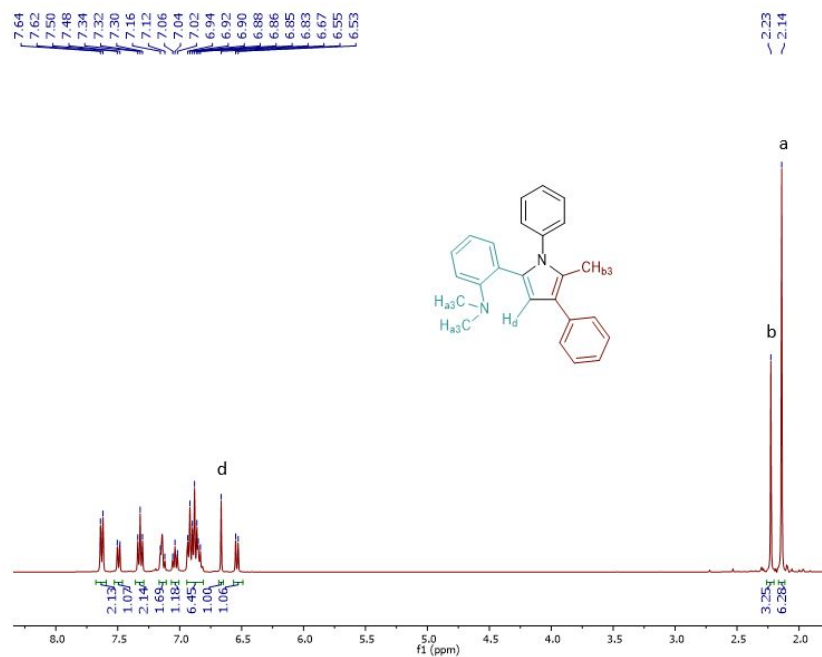


The product was isolated by silica gel chromatography using 8% EA/Hex eluent to give a colorless solid (51 mg, 29% yield).

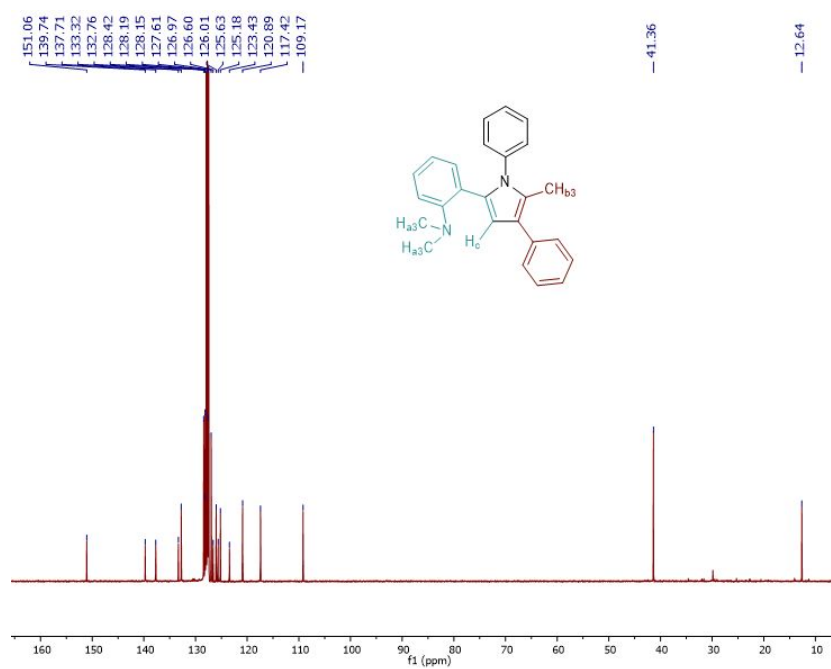
$^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.63 (d,  $^3J_{\text{HH}} = 8.1$  Hz, 2H), 7.49 (dd,  $^3J_{\text{HH}} = 7.5$  Hz,  $^4J_{\text{HH}} = 1.0$  Hz, 1H), 7.32 (t,  $^3J_{\text{HH}} = 7.6$  Hz, 2H), 7.16-7.12 (m, 1H), 7.04 (dt,  $^3J_{\text{HH}} = 7.5$  Hz,  $^4J_{\text{HH}} = 1.1$  Hz, 1H), 6.93-6.82 (m, 6H), 6.67 (s, 1H, 4- $\text{NC}_4\text{-H}$ ), 6.54 (d,  $^3J_{\text{HH}} = 8.1$  Hz, 1H), 2.23 (s, 3H, 2- $\text{NC}_4\text{-CH}_3$ ), 2.14 (s, 6H,  $-\text{N}(\text{CH}_3)_2$ ) ppm.

$^{13}\text{C}$  NMR (101 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  151.1, 139.7, 137.7, 133.3, 132.8, 128.4, 128.2, 128.2, 127.6, 127.0, 126.6, 126.0, 125.6, 125.2, 123.4, 120.9, 117.4, 109.2, 41.4, 12.6 ppm.

**GC-HRMS:** Calc for  $\text{C}_{25}\text{H}_{24}\text{N}_2$  [ $\text{M}^+$ ] 352.1939; found 352.1903.



**Figure S77.** <sup>1</sup>H NMR spectrum of **3j** in C<sub>6</sub>D<sub>6</sub>.



**Figure S78.** <sup>13</sup>C NMR spectrum of **3j** in C<sub>6</sub>D<sub>6</sub>.

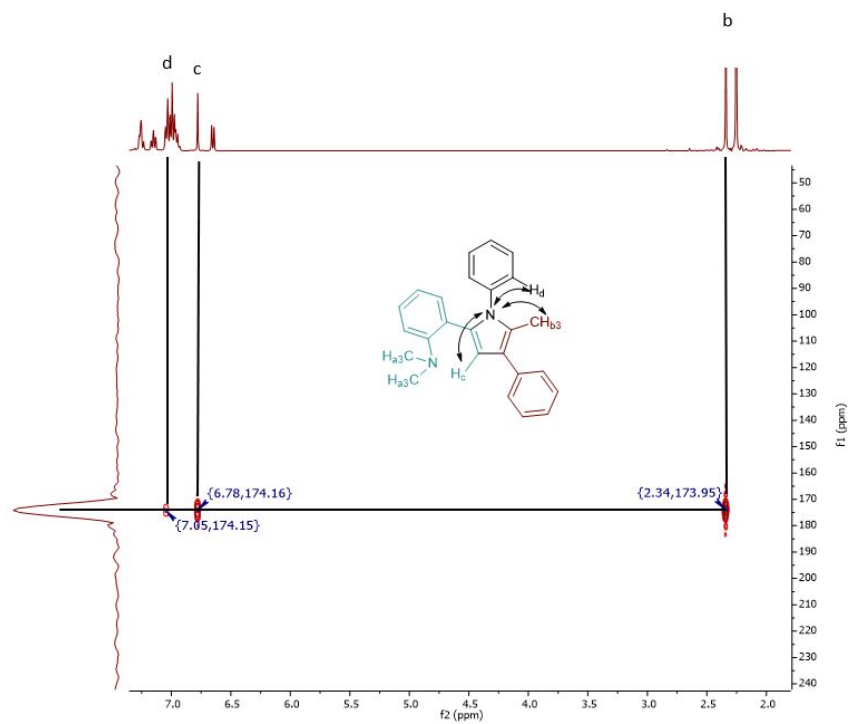


Figure S79.  $^1\text{H}$ - $^{15}\text{N}$  HMBC NMR spectrum of **3ja** in  $\text{C}_6\text{D}_6$ .

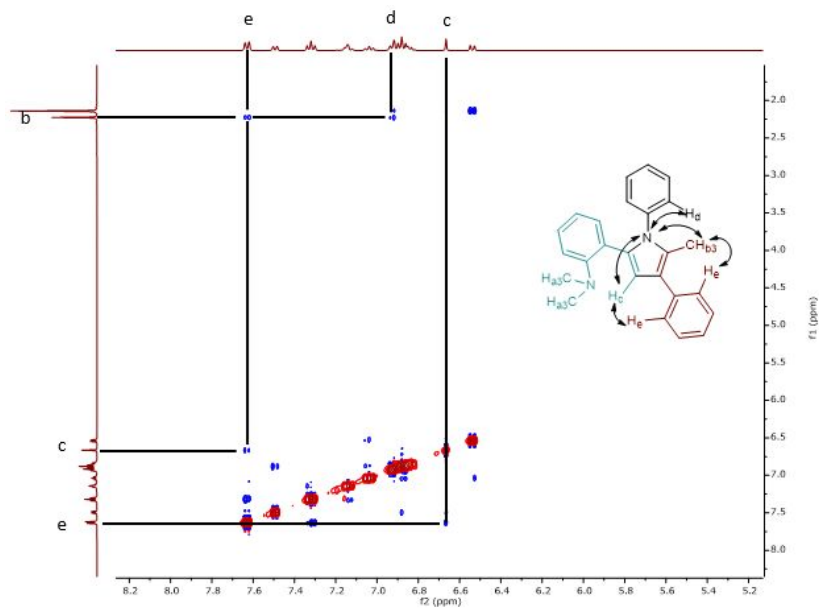
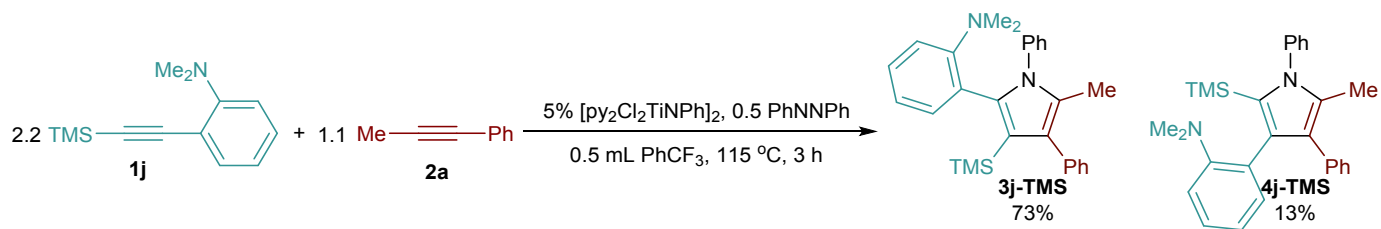
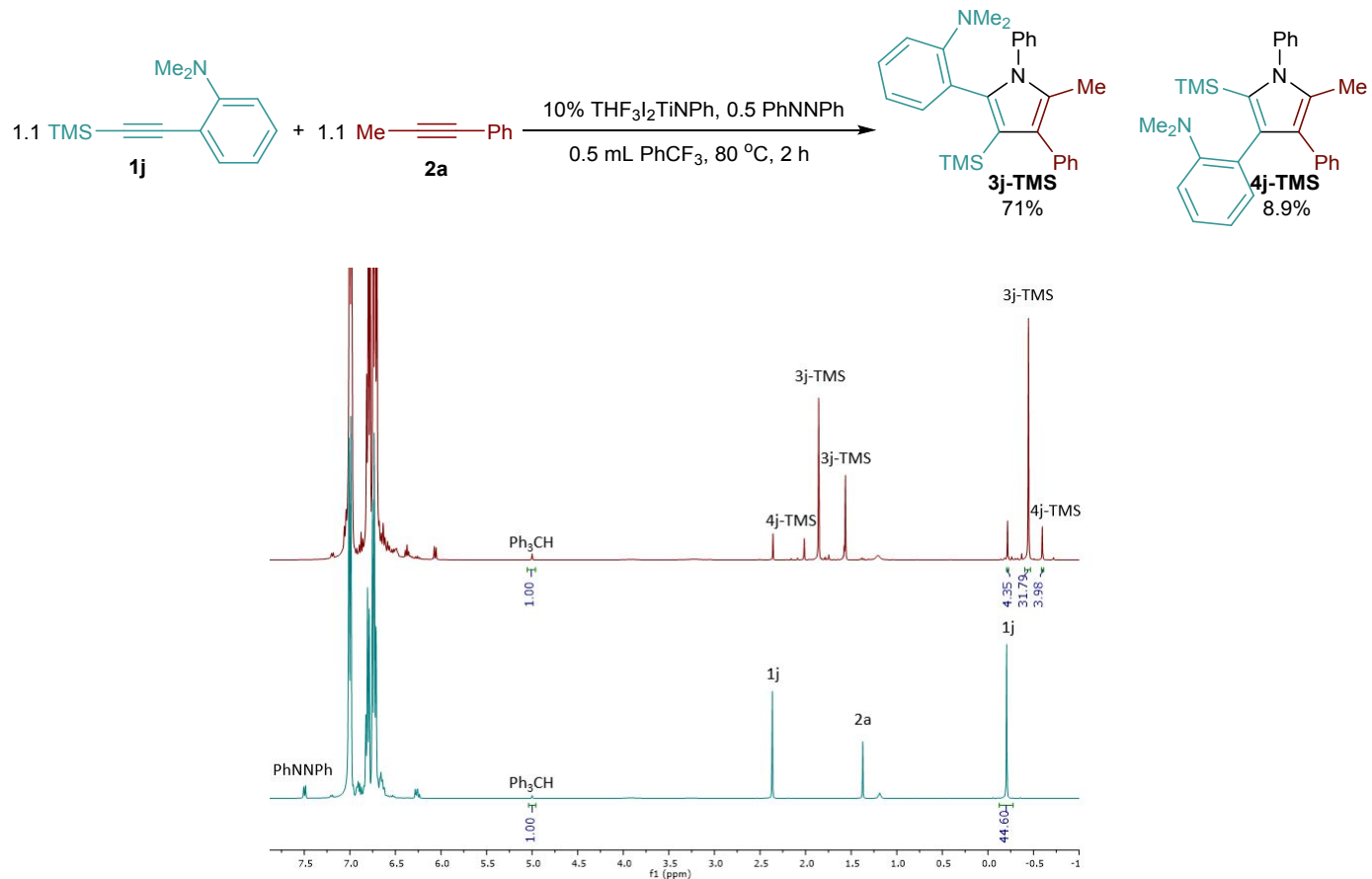
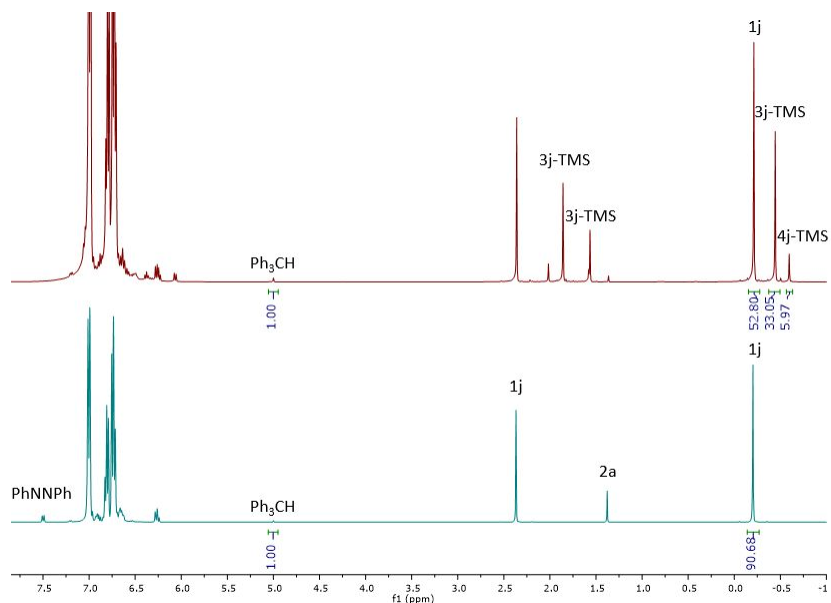


Figure S80. NOESY NMR spectrum of **3ja** in  $\text{C}_6\text{D}_6$ .

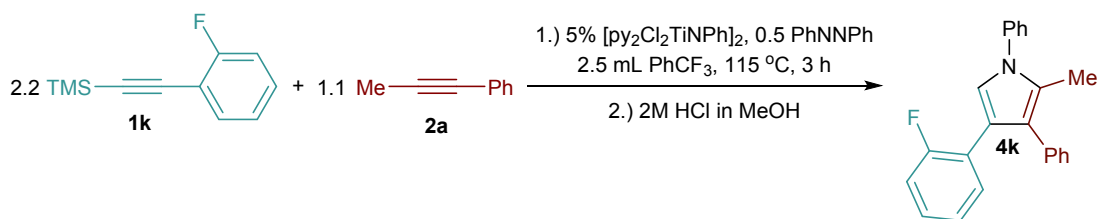
### No-D <sup>1</sup>H NMR spectra of the reactions of **1j** and **2a**





**Figure S82.** No-D  $^1\text{H}$  NMR reaction of **1j** and **2a** in  $\text{PhCF}_3$  at Time = 0 h (bottom), Time = 3 h (top) under Condition B.

### Synthesis of 4-(2-fluorophenyl)-2-methyl-1,3-diphenyl-1H-pyrrole (**4k**)



The product was purified by precipitating from hexanes and collected by filtration to give an off-white solid (89 mg, 57% yield).

$^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.38 (dd,  $^3J_{\text{HH}} = 8.3$  Hz,  $^4J_{\text{HH}} = 1.3$  Hz, 2H), 7.29 (dt,  $^3J_{\text{HH}} = 7.7$  Hz,  $^4J_{\text{HH}} = 1.8$  Hz, 1H), 7.19 (t,  $^3J_{\text{HH}} = 7.3$  Hz, 2H), 7.11-7.07 (m, 2H), 7.01-7.00 (m, 4H), 6.98-6.91 (m, 2H), 6.84-6.79 (m, 1H), 6.74 (dt,  $^3J_{\text{HH}} = 7.5$  Hz,  $^4J_{\text{HH}} = 1.2$  Hz, 1H), 2.07 (s, 3H, 2-NC<sub>4</sub>-CH<sub>3</sub>) ppm.

$^{13}\text{C}$  NMR (101 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  160.8 (d,  $^1J_{\text{CF}} = 246$  Hz, ArC-F), 140.5, 137.1, 132.1 (d,  $^3J_{\text{CF}} = 3.8$  Hz), 130.7, 129.3, 128.6, 127.4 (d,  $^3J_{\text{CF}} = 8.1$  Hz), 127.1, 126.8, 126.2, 126.1, 124.2 (d,  $^2J_{\text{CF}} = 14.6$  Hz), 123.9 (d,  $^4J_{\text{CF}} = 3.5$  Hz), 123.5, 121.8 (d,  $^3J_{\text{CF}} = 5.9$  Hz), 117.6, 116.0 (d,  $^2J_{\text{CF}} = 22.9$  Hz), 11.8 ppm.

**GC-HRMS:** calculated for  $\text{C}_{23}\text{H}_{18}\text{NF}$  [ $\text{M}^+$ ] 327.1423; found 327.1372.

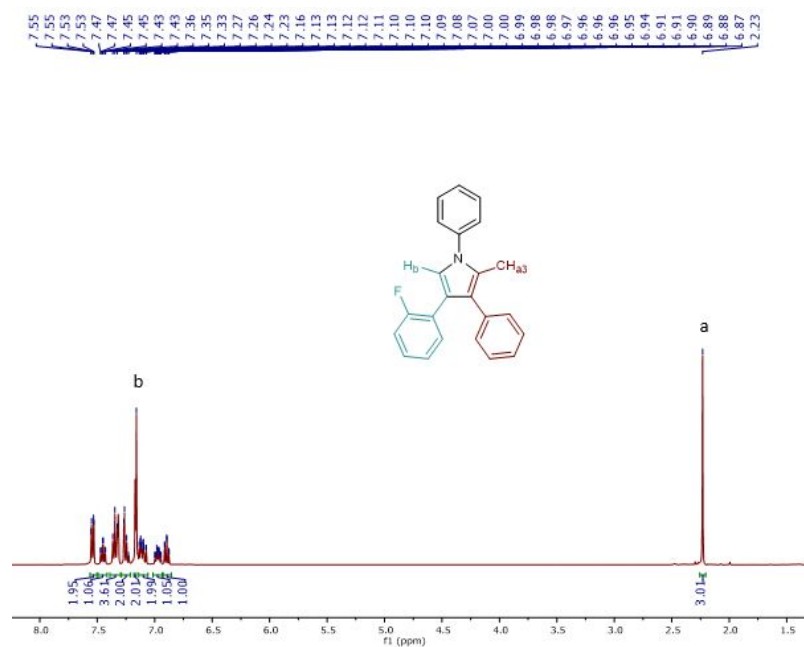


Figure S83. <sup>1</sup>H NMR spectrum of 4k in C<sub>6</sub>D<sub>6</sub>.

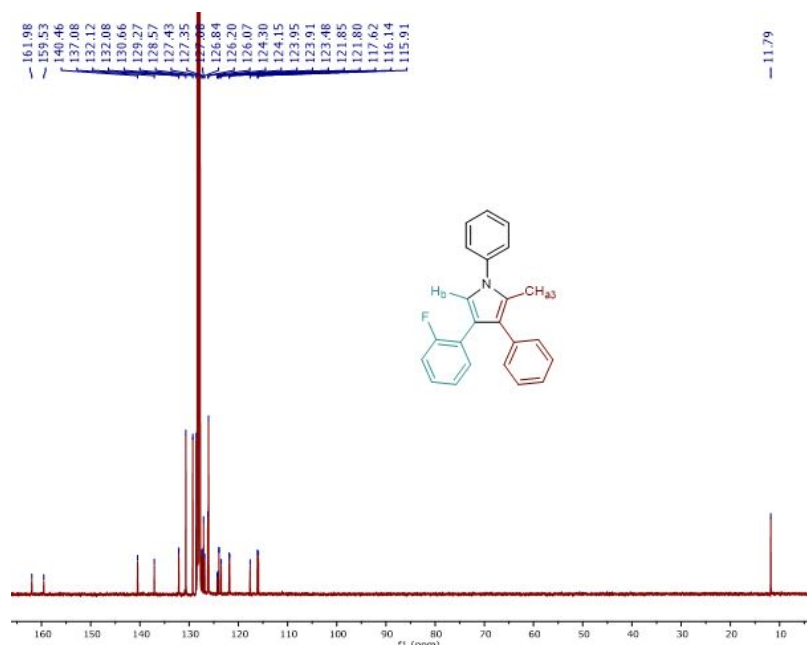
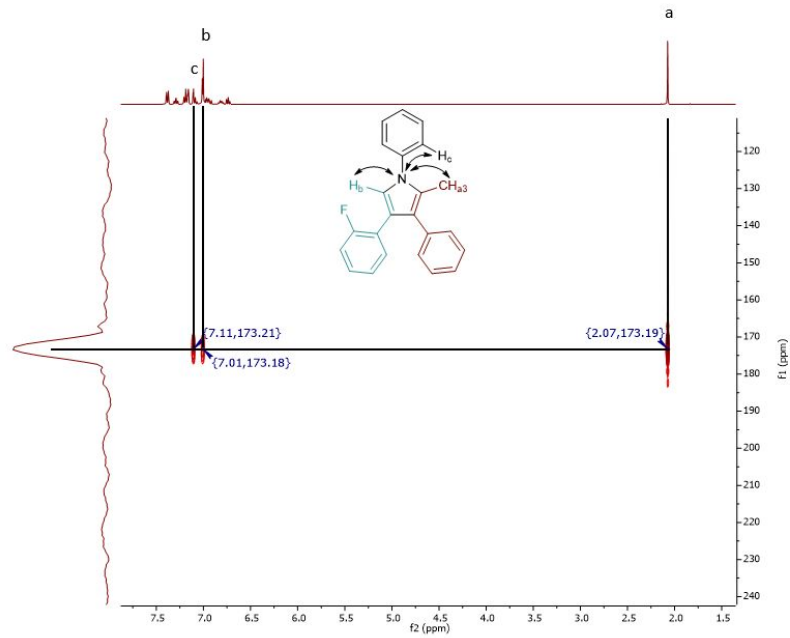
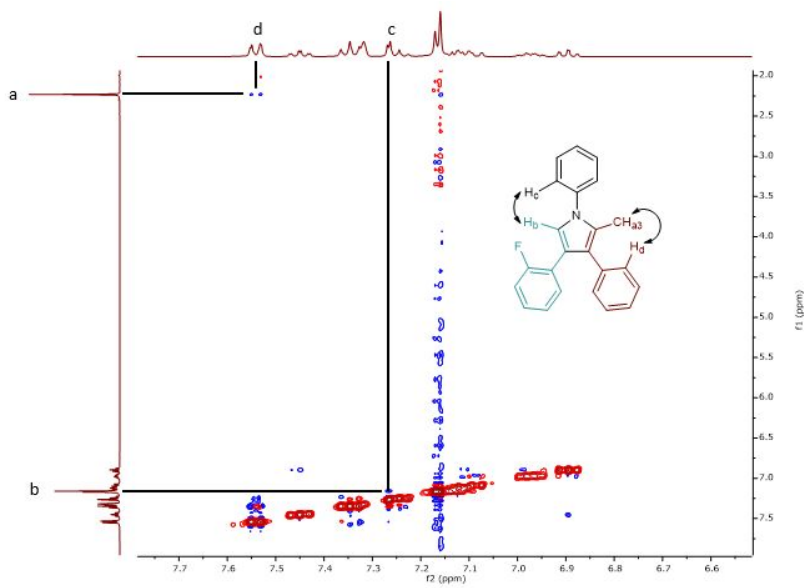


Figure S84. <sup>13</sup>C NMR spectrum of 4k in C<sub>6</sub>D<sub>6</sub>.



**Figure S85.**  $^1\text{H}$ - $^{15}\text{N}$  HMBC NMR spectrum of **4k** in  $\text{C}_6\text{D}_6$ .



**Figure S86.** NOESY NMR spectrum of **4k** in  $\text{C}_6\text{D}_6$ .

No-D  $^1\text{H}$  NMR spectra of the reactions of **1k** and **2a**

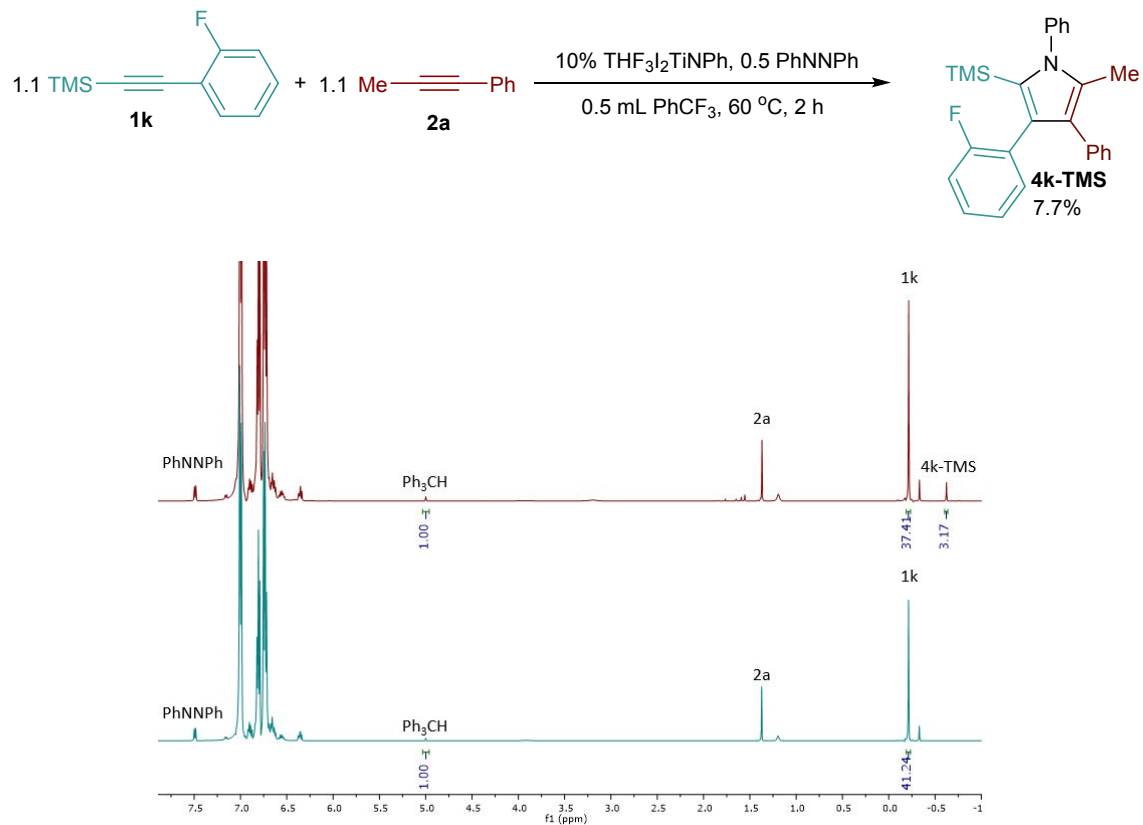
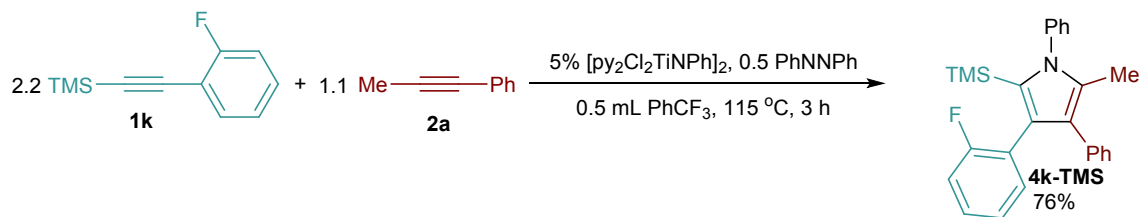
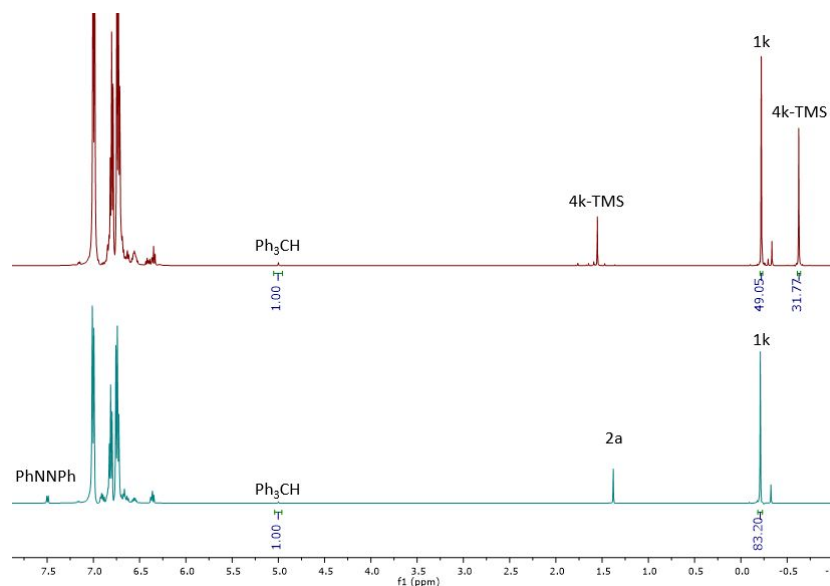


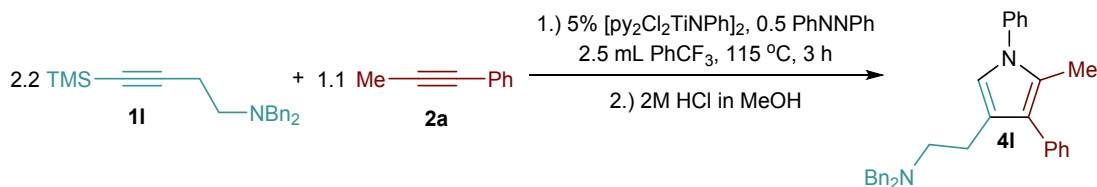
Figure S87. No-D  $^1\text{H}$  NMR reaction of **1k** and **2a** in  $\text{PhCF}_3$  at Time = 0 h (bottom), Time = 2 h (top) under Condition A.





**Figure S88.** No-D  $^1\text{H}$  NMR reaction of **1k** and **2a** in  $\text{PhCF}_3$  at Time = 0 h (bottom), Time = 3 h (top) under Condition B.

### Synthesis of N,N-dibenzyl-2-(5-methyl-1,4-diphenyl-1H-pyrrol-3-yl)ethan-1-amine (**4l**)

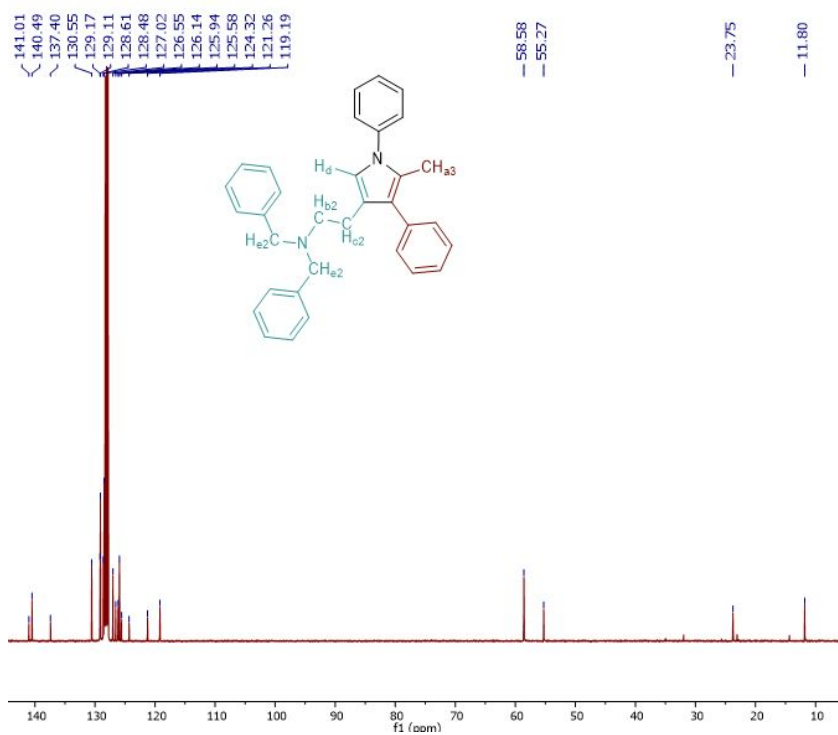
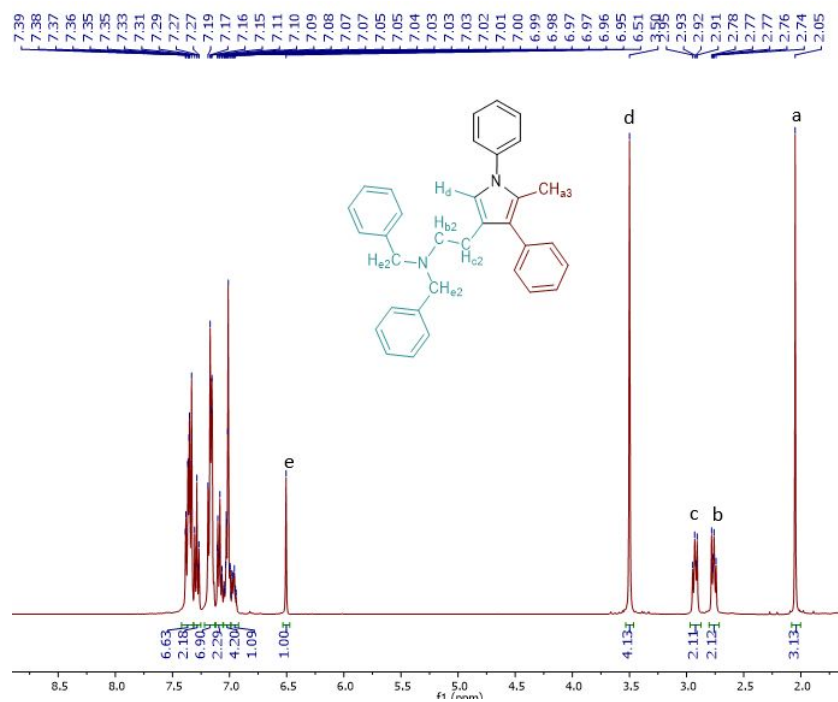


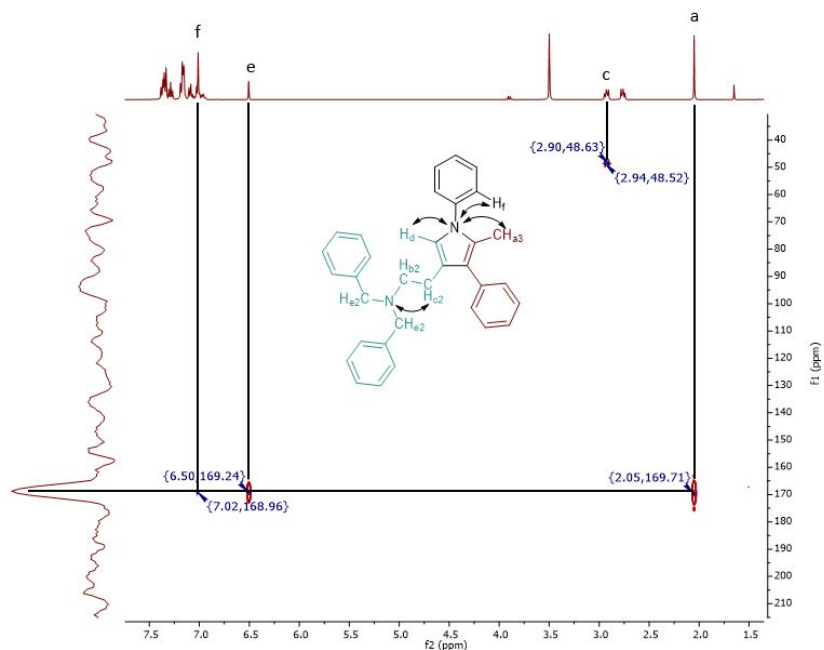
The product was isolated by silica gel chromatography using 4% EA/Hex eluent to give a white solid (130 mg, 57% yield).

$^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.38 – 7.27 (m, 8H), 7.19 – 7.16 (m, 5H), 7.10 – 7.06 (m, 2H), 7.05 – 6.94 (m, 5H), 6.94 (s, 1H, 5- $\text{NC}_4\text{-H}$ ), 3.50 (s, 4H, N- $\text{CH}_2\text{-Ph}$ ), 2.95 – 2.91 (m, 2H, 4- $\text{NC}_4\text{-CH}_2\text{-CH}_2\text{NBn}_2$ ), 2.78 – 2.74 (m, 2H, 4- $\text{NC}_4\text{-CH}_2\text{-CH}_2\text{NBn}_2$ ), 2.05 (s, 3H, 2- $\text{NC}_4\text{-CH}_3$ ) ppm

$^{13}\text{C}$  NMR (101 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  141.0, 140.5, 137.4, 130.6, 129.2, 129.1, 128.6, 128.5, 127.0, 126.6, 126.1, 125.9, 125.6, 124.3, 121.3, 119.2, 58.6, 55.3, 23.8, 11.8 ppm.

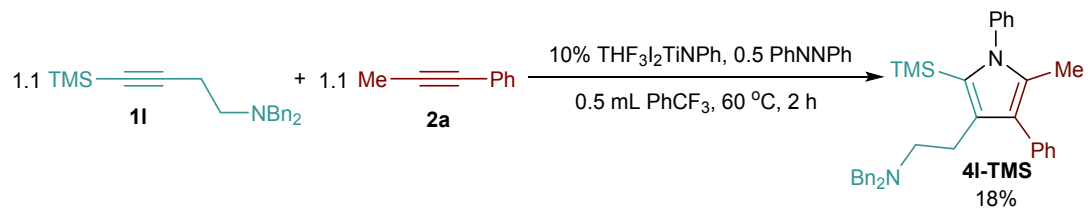
**GC-HRMS:** calculated for  $\text{C}_{33}\text{H}_{32}\text{N}_2$  [ $\text{M}-\text{H}_2^+$ ] 454.2409; found 454.2389.

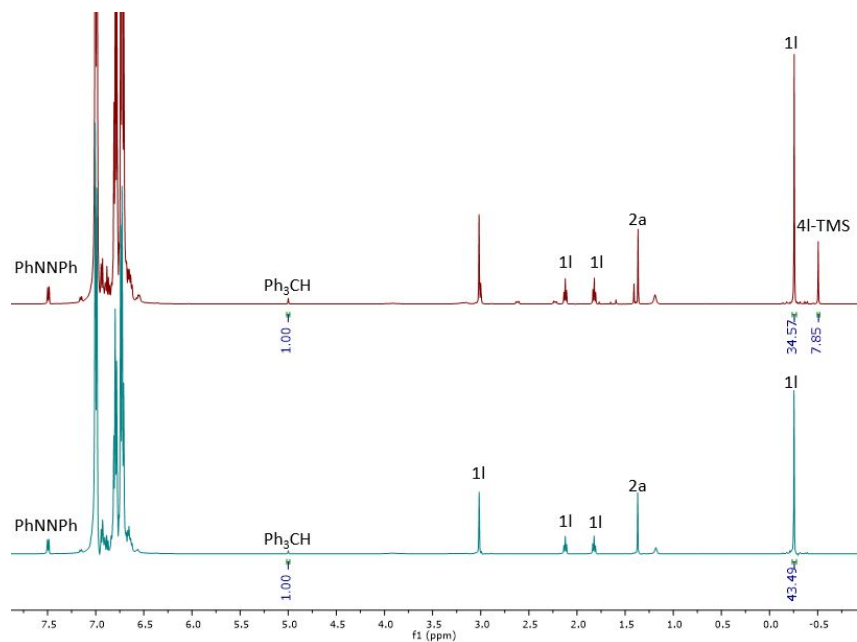




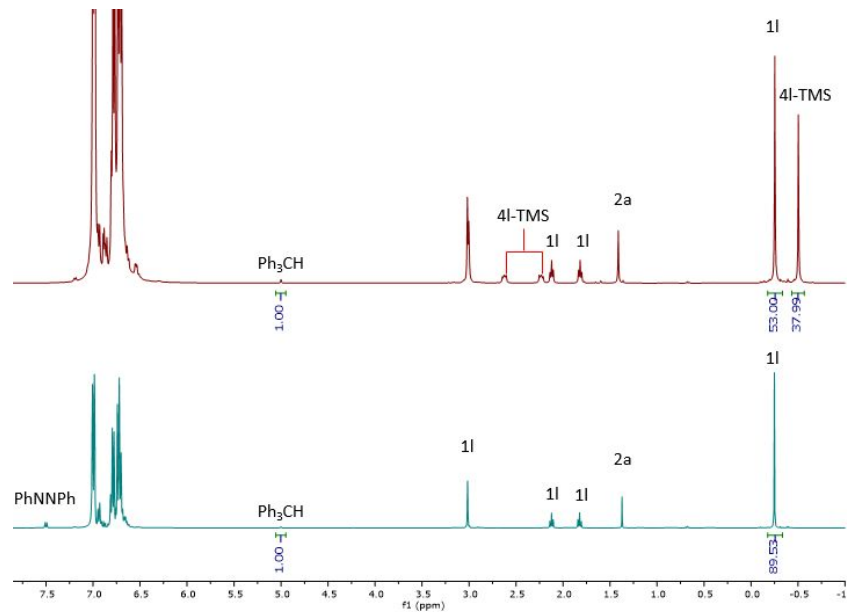
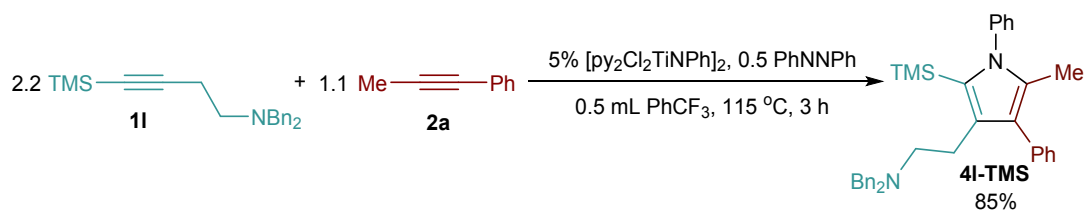
**Figure S91.**  $^1\text{H}$ - $^{15}\text{N}$  HMBC NMR spectrum of **4I** in  $\text{C}_6\text{D}_6$ .

**No-D  $^1\text{H}$  NMR spectra of the reactions of **1I** and **2a****



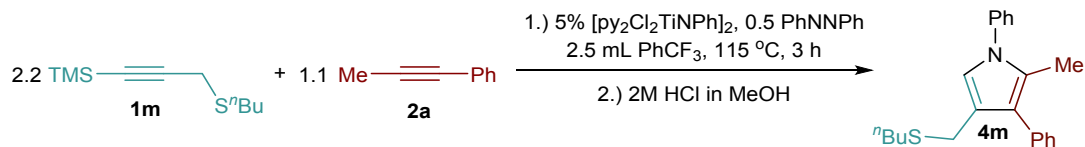


**Figure S92.** No-D  $^1\text{H}$  NMR reaction of **1l** and **2a** in  $\text{PhCF}_3$  at Time = 0 h (bottom), Time = 2 h (top) under Condition A.



**Figure S93.** No-D  $^1\text{H}$  NMR reaction of **1l** and **2a** in  $\text{PhCF}_3$  at Time = 0 h (bottom), Time = 3 h (top) under Condition B.

## Synthesis of 4-((butylthio)methyl)-2-methyl-1,3-diphenyl-1H-pyrrole (4m)

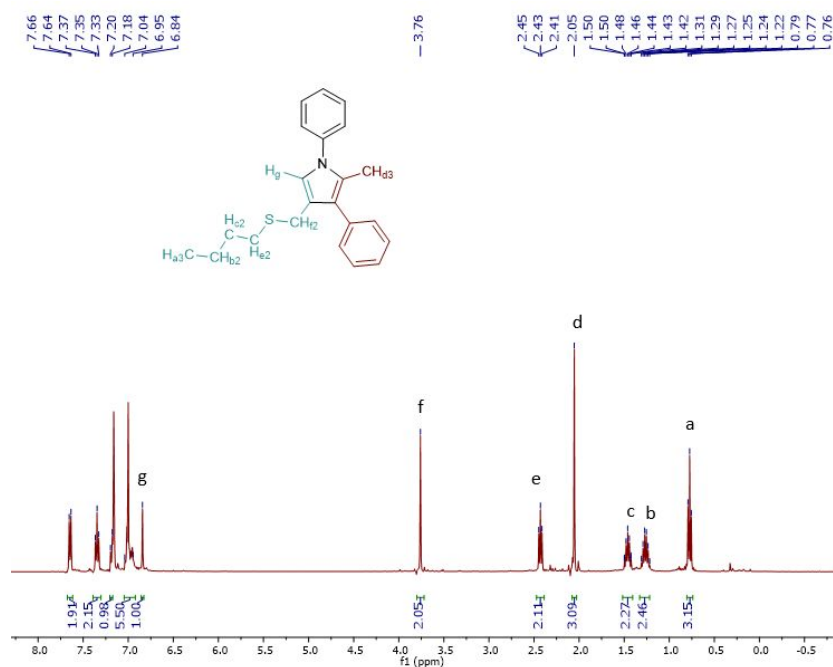


The product was isolated by silica gel chromatography using 3% EA/Hex eluent to give a pale-brown oil (58 mg, 35% yield).

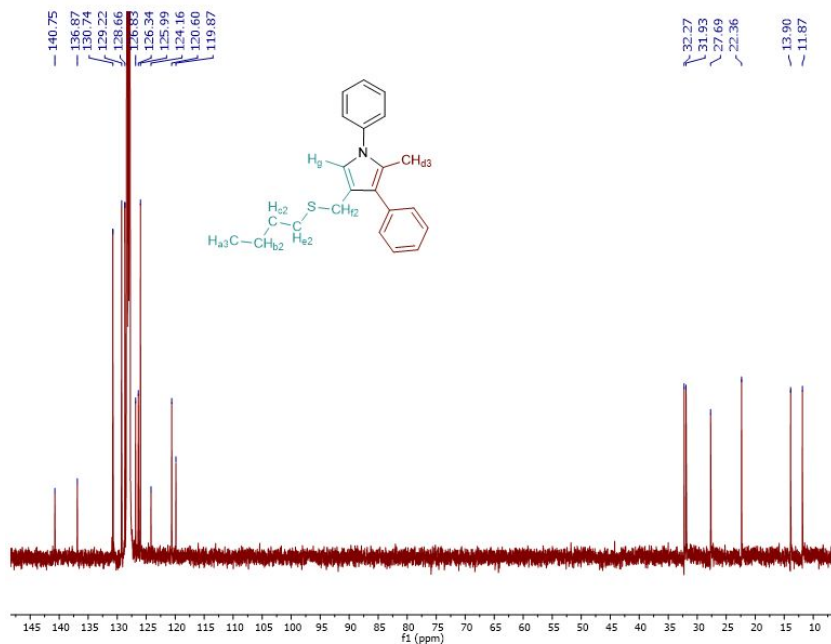
**<sup>1</sup>H NMR** (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.65 (d, <sup>3</sup>J<sub>HH</sub> = 8.1 Hz, 2H), 7.35 (t, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 2H), 7.20 – 7.18 (m, 2H), 7.04 – 6.95 (m, 5H), 6.84 (s, 1H, 5-NC<sub>4</sub>-H), 3.76 (s, 2H, 4-NC<sub>4</sub>-CH<sub>2</sub>-S<sup>n</sup>Bu), 2.43 (t, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, 2H, -S-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 2.05 (s, 3H, 2-NC<sub>4</sub>-CH<sub>3</sub>), 1.46 (p, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, 2H, -SCH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 1.26 (p, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, 2H, -SCH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 0.77 (t, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, 3H, -SCH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>) ppm.

**<sup>13</sup>C NMR** (101 MHz, C<sub>6</sub>D<sub>6</sub>) δ 140.8, 136.9, 130.7, 129.2, 128.7, 126.8, 126.3, 126.0, 124.2, 120.6, 119.9, 32.3, 31.9, 27.7, 22.4, 13.9, 11.9 ppm.

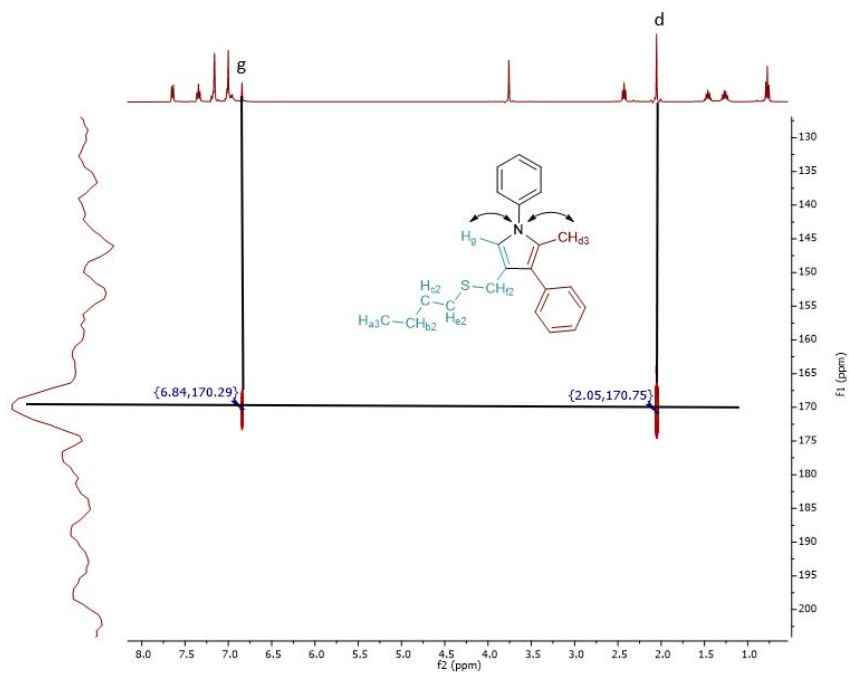
**GC-HRMS:** calculated for C<sub>22</sub>H<sub>25</sub>NS [M<sup>+</sup>] 335.1708; found 335.1687.



**Figure S94.** <sup>1</sup>H NMR spectrum of **4m** in C<sub>6</sub>D<sub>6</sub>.



**Figure S95.** <sup>13</sup>C NMR spectrum of **4m** in C<sub>6</sub>D<sub>6</sub>.



**Figure S96.** <sup>1</sup>H-<sup>15</sup>N HMBC NMR spectrum of **4m** in C<sub>6</sub>D<sub>6</sub>.

No-D <sup>1</sup>H NMR spectra of the reactions of **1m** and **2a**

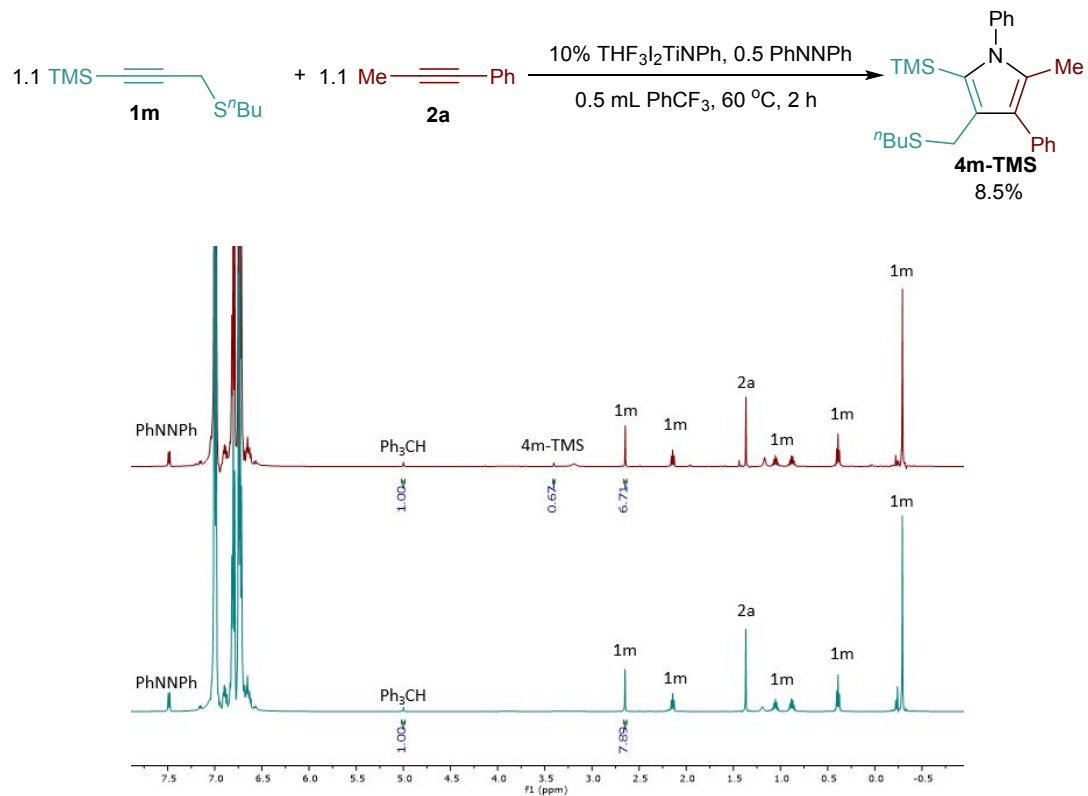
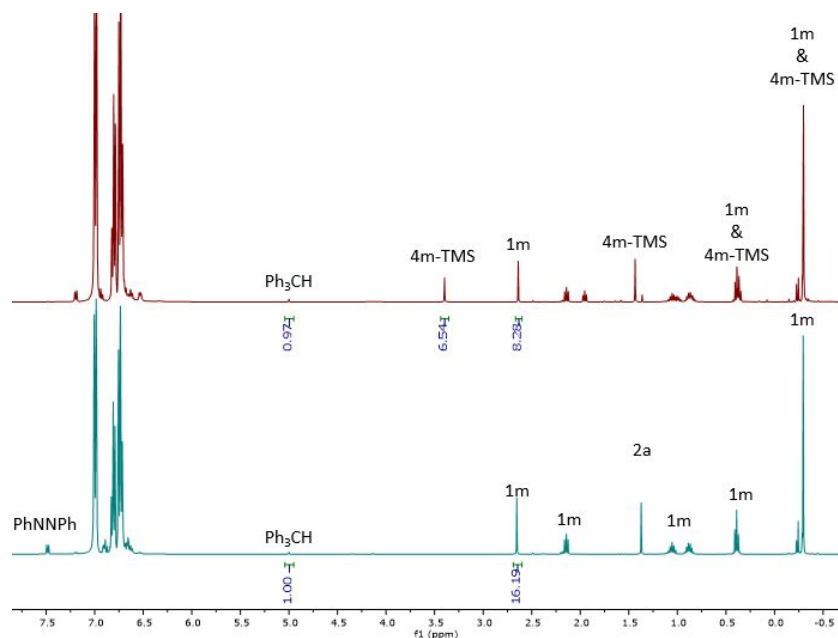
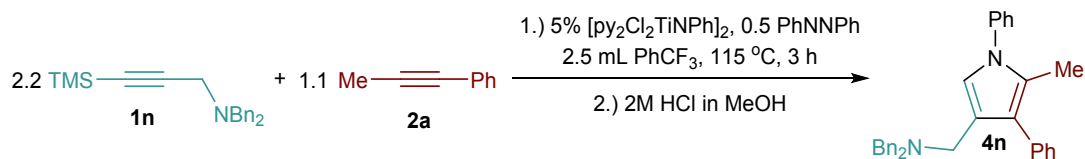


Figure S97. No-D <sup>1</sup>H NMR reaction of **1m** and **2a** in PhCF<sub>3</sub> at Time = 0 h (bottom), Time = 2 h (top) under Condition A.



**Figure S98.** No-D  $^1\text{H}$  NMR reaction of **1m** and **2a** in  $\text{PhCF}_3$  at Time = 0 h (bottom), Time = 3 h (top) under Condition B.

### Synthesis of N,N-dibenzyl-1-(5-methyl-1,4-diphenyl-1H-pyrrol-3-yl)methanamine (**4n**)



The product was isolated by silica gel chromatography using 5% EA/Hex eluent to give a white solid (25 mg, 11% yield).

$^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.46 – 7.44 (m, 2H), 7.34 – 7.28 (m, 6H), 7.21 – 7.18 (m, 2H), 7.16 – 7.14 (m, 2H), 7.09 – 7.06 (m, 3H), 7.02 – 7.01 (m, 4H), 6.08 (s, 1H, 5- $\text{NC}_4\text{-H}$ ), 6.97 – 6.95 (m, 1H), 3.73 (s, 2H, 2- $\text{NC}_4\text{-CH}_2\text{-NBn}_2$ ), 3.59 (s, 4H, -N- $\text{CH}_2\text{-Ph}$ ), 2.06 (s, 3H, 2- $\text{NC}_4\text{-CH}_3$ ) ppm.

$^{13}\text{C}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ ): 140.9, 140.5, 137.3, 130.8, 129.2, 129.1, 128.5, 128.5, 126.9, 126.8, 126.1, 126.1, 126.1, 124.5, 120.9, 120.8, 58.5, 50.5, 11.9 ppm.

**GC-HRMS:** calculated for  $\text{C}_{32}\text{H}_{30}\text{N}_2$  [ $\text{M}-\text{H}^+$ ] 441.2331; found 441.2306.

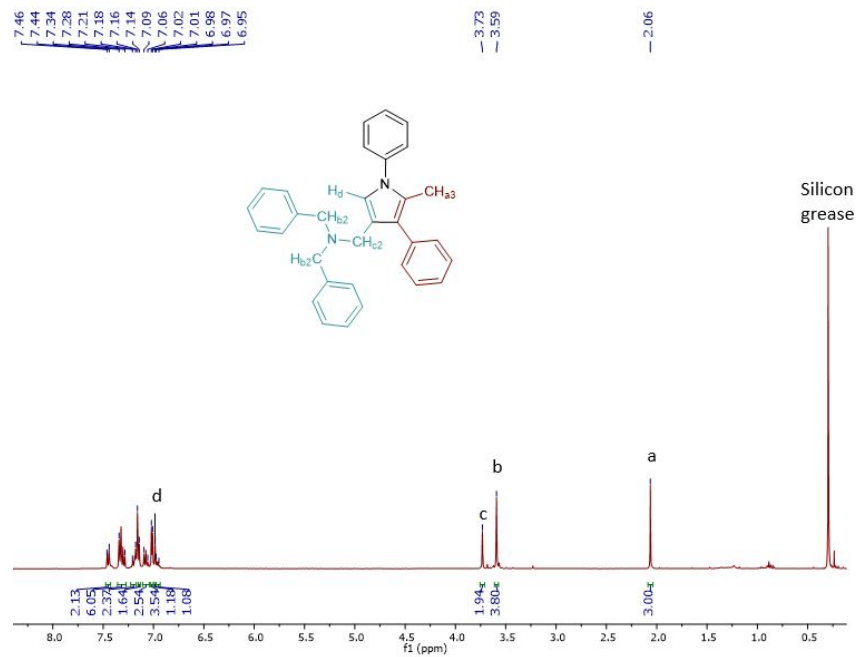


Figure S99. <sup>1</sup>H NMR spectrum of 4n in C<sub>6</sub>D<sub>6</sub>.

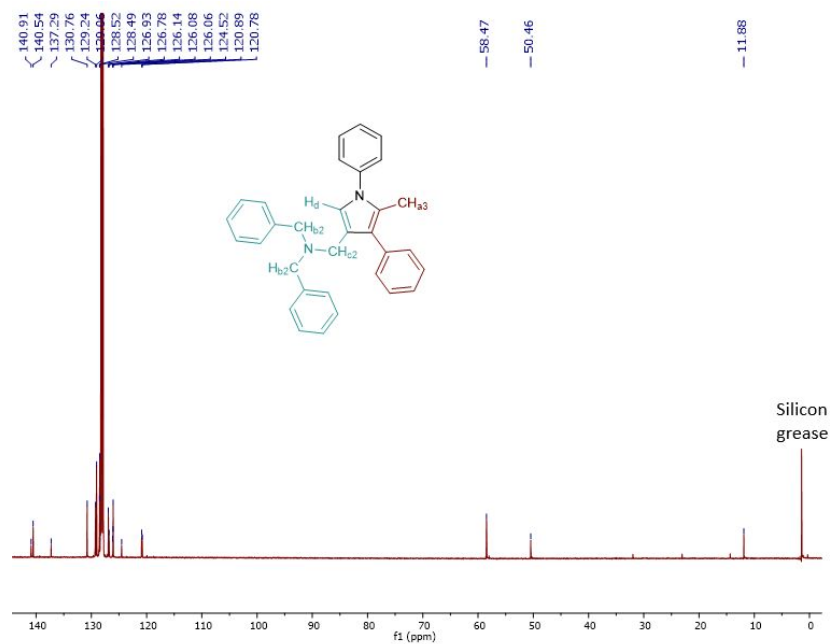


Figure S100. <sup>13</sup>C NMR spectrum of 4n in C<sub>6</sub>D<sub>6</sub>.

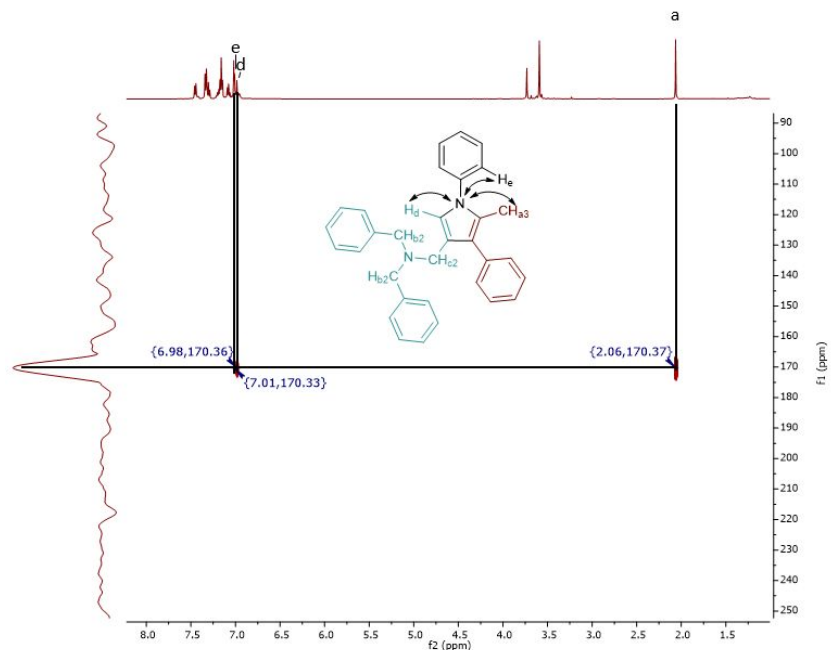
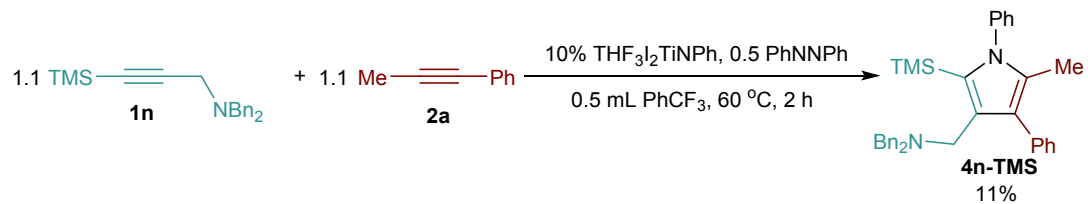
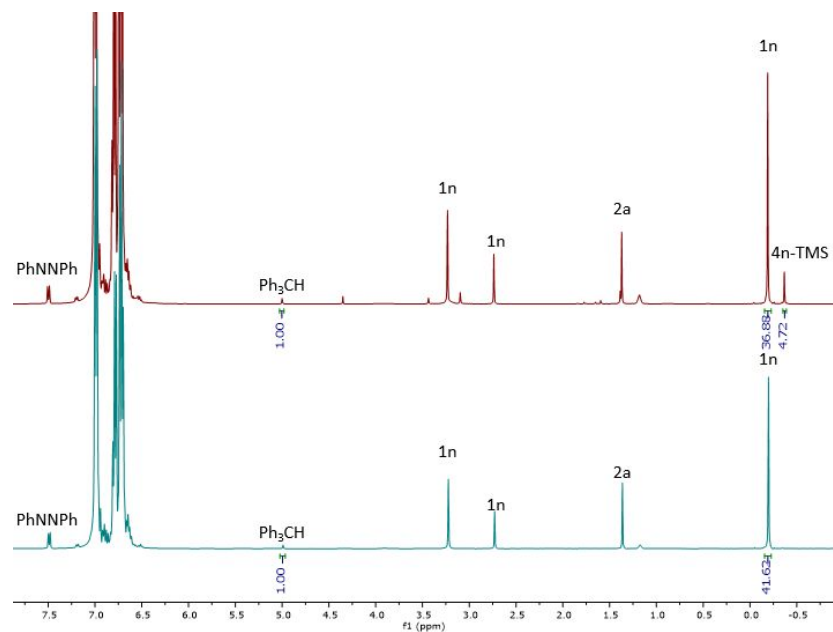


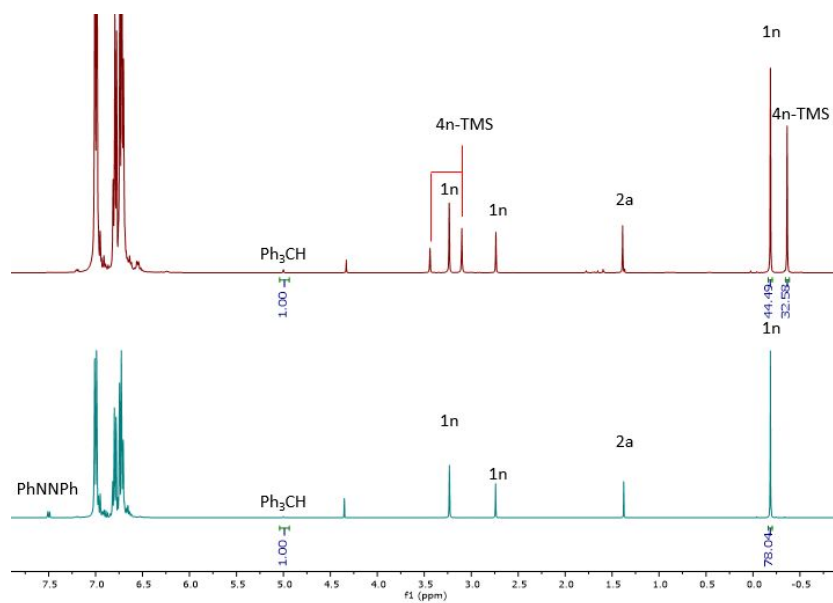
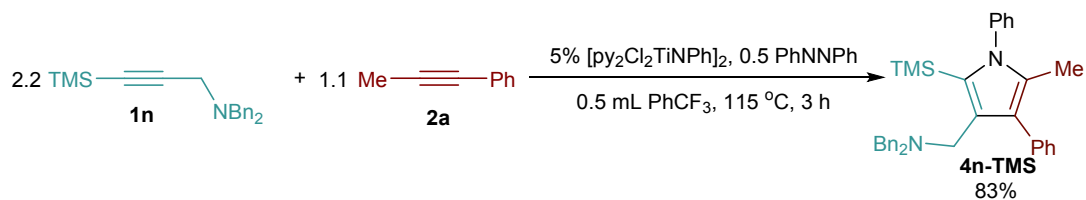
Figure S101.  $^1\text{H}$ - $^{15}\text{N}$  HMBC NMR spectrum of **4n** in  $\text{C}_6\text{D}_6$ .

#### No-D $^1\text{H}$ NMR spectra of the reactions of **1n** and **2a**



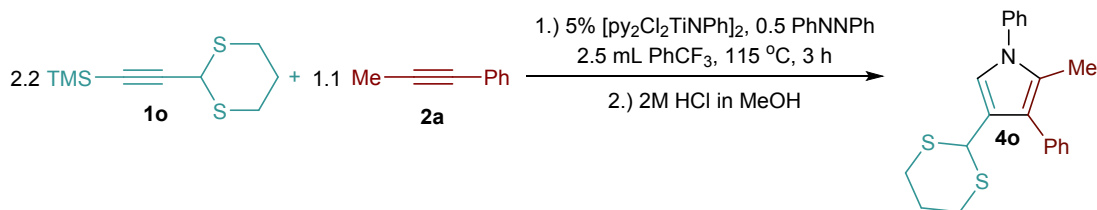


**Figure S102.** No-D  $^1\text{H}$  NMR reaction of **1n** and **2a** in  $\text{PhCF}_3$  at Time = 0 h (bottom), Time = 2 h (top) under Condition A.



**Figure S103.** No-D  $^1\text{H}$  NMR reaction of **1n** and **2a** in  $\text{PhCF}_3$  at Time = 0 h (bottom), Time = 3 h (top) under Condition B.

## Synthesis of 4-(1,3-dithian-2-yl)-2-methyl-1,3-diphenyl-1H-pyrrole (4o)



The product was purified by precipitating from methanol and collected by filtration washed with hexanes to give an off-white solid (126 mg, 72% yield).

<sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.75-7.73 (m, 2H), 7.38-7.35 (m, 3H, 5-NC<sub>4</sub>-H and Ar-H), 7.19 (tt, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, <sup>4</sup>J<sub>HH</sub> = 1.2 Hz) 6.96-6.91 (m, 3H), 6.83-6.80 (m, 2H), 5.36 (s, 1H, 4-NC<sub>4</sub>-CH-SS), 2.46 (td, <sup>3</sup>J<sub>HH</sub> = 13.4 Hz, <sup>4</sup>J<sub>HH</sub> = 2.3 Hz, 2H, -S-CH<sub>2</sub>-CH<sub>2</sub>-S-), 2.34 (dt, <sup>3</sup>J<sub>HH</sub> = 14.1 Hz, <sup>4</sup>J<sub>HH</sub> = 2.0 Hz, 2H, -S-CH<sub>2</sub>-CH<sub>2</sub>-S-), 1.98 (s, 3H, 2-NC<sub>4</sub>-H), 1.69 (m, 1H, -S-CH<sub>2</sub>-CH<sub>2</sub>-S-), 1.39 (m, 1H, -S-CH<sub>2</sub>-CH<sub>2</sub>-S-) ppm.

<sup>13</sup>C NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>): δ 140.3, 136.4, 130.7, 129.1, 128.8, 127.0, 126.6, 126.0, 125.5, 122.6, 122.1, 121.8, 43.3, 32.8, 25.6, 11.7 ppm.

GC-HRMS: calculated for C<sub>21</sub>H<sub>21</sub>NS<sub>2</sub> [M<sup>+</sup>] 351.1115; found 351.1089.

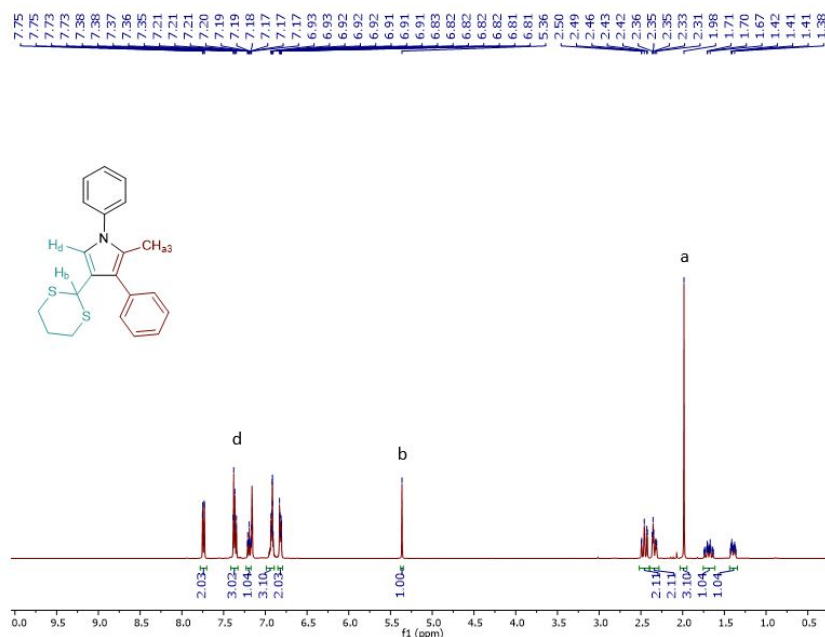


Figure S104. <sup>1</sup>H NMR spectrum of 4o in C<sub>6</sub>D<sub>6</sub>.

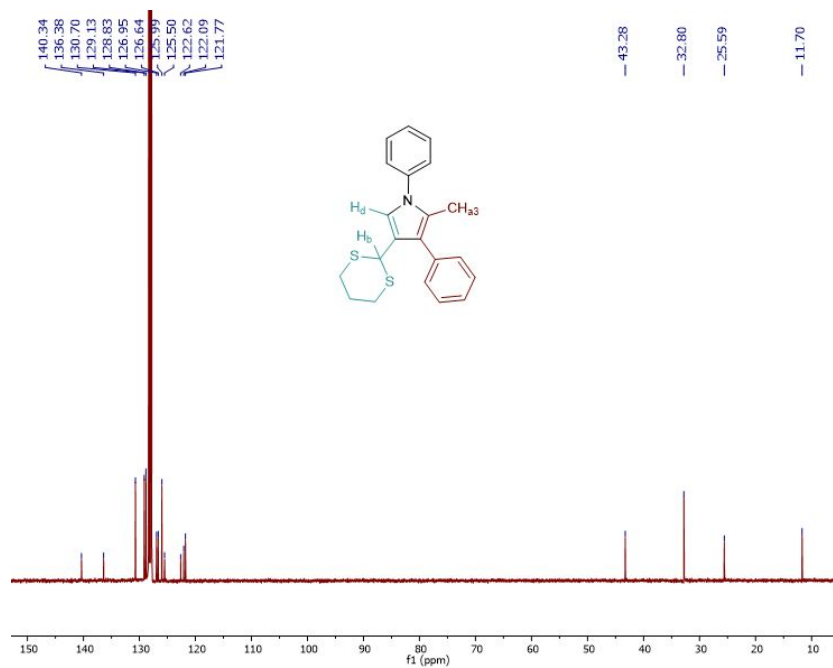


Figure S105.  $^{13}\text{C}$  NMR spectrum of **4o** in  $\text{C}_6\text{D}_6$ .

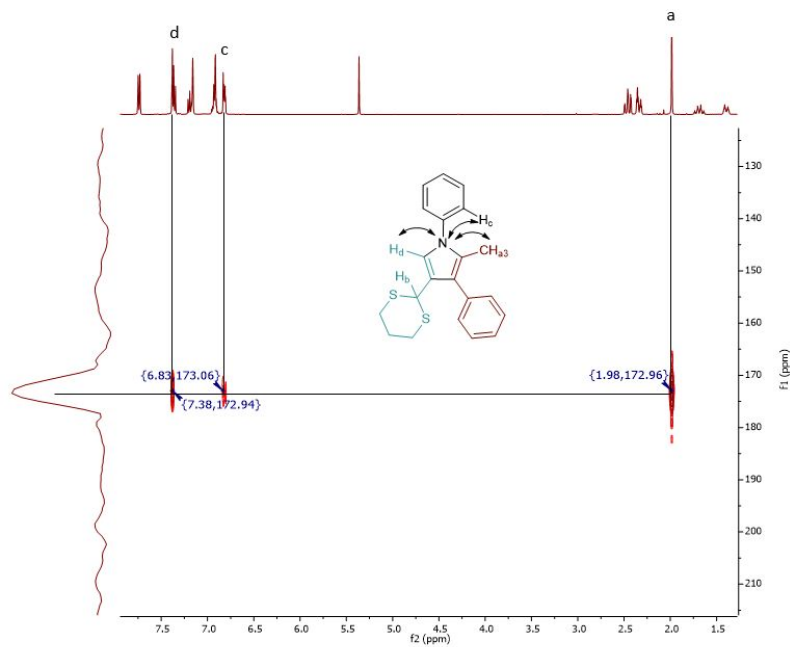


Figure S106.  $^1\text{H}$ - $^{15}\text{N}$  HMBC NMR spectrum of **4o** in  $\text{C}_6\text{D}_6$ .

No-D  $^1\text{H}$  NMR spectra of the reactions of **1o** and **2a**

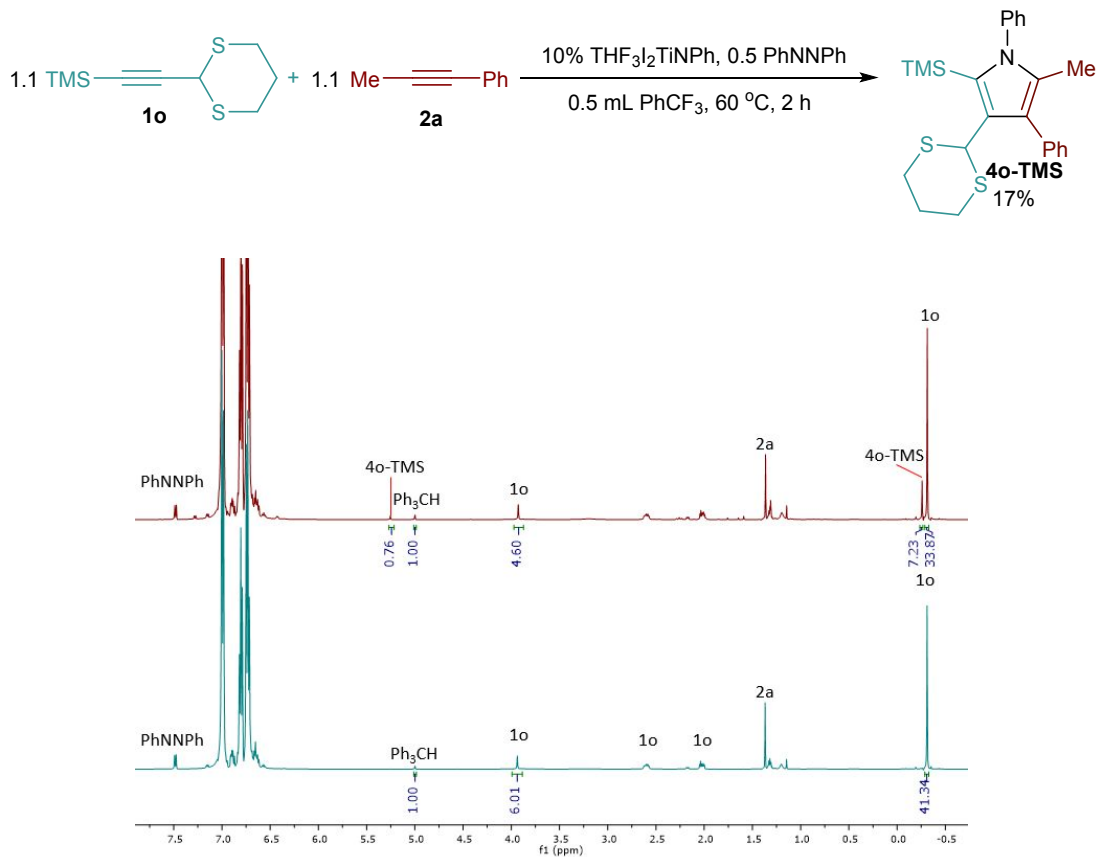
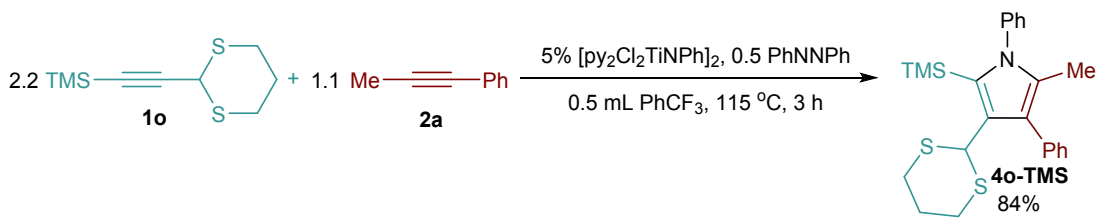


Figure S107. No-D  $^1\text{H}$  NMR reaction of **1o** and **2a** in  $\text{PhCF}_3$  at Time = 0 h (bottom), Time = 2 h (top) under Condition A.



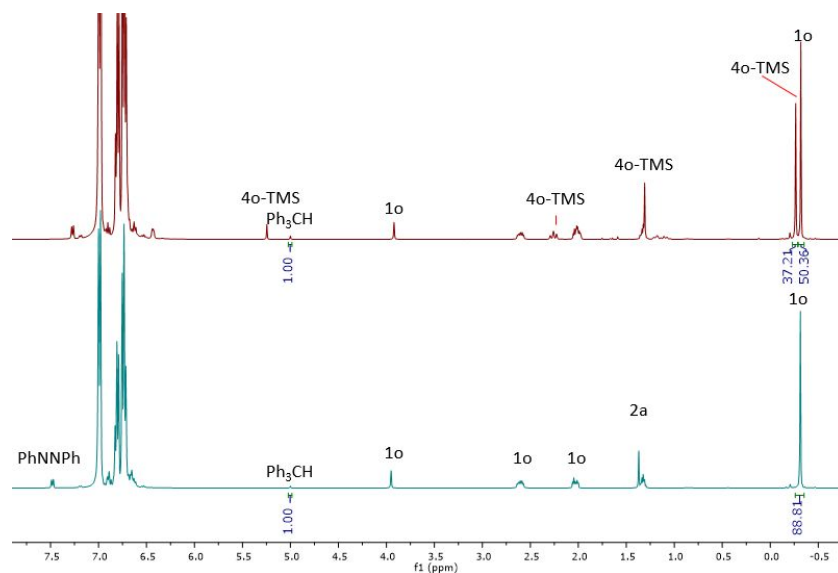
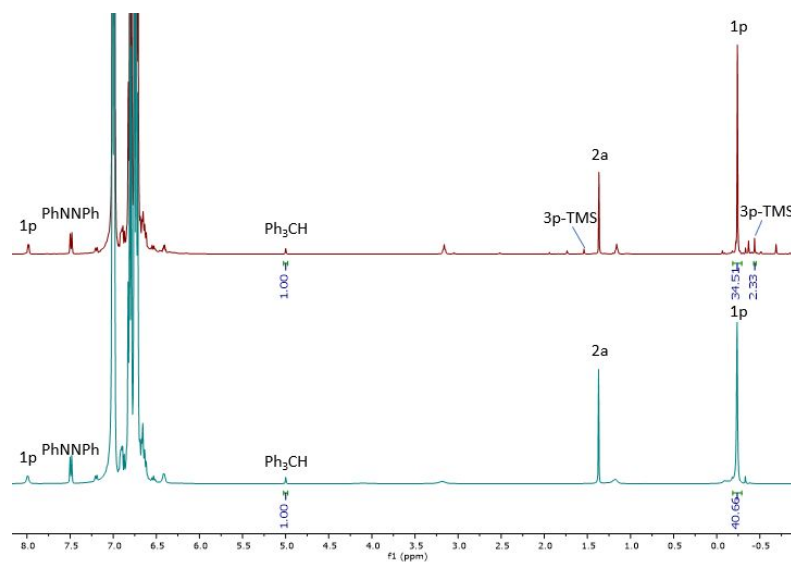
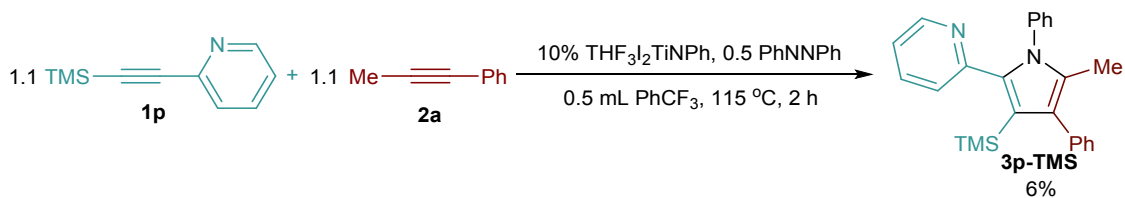


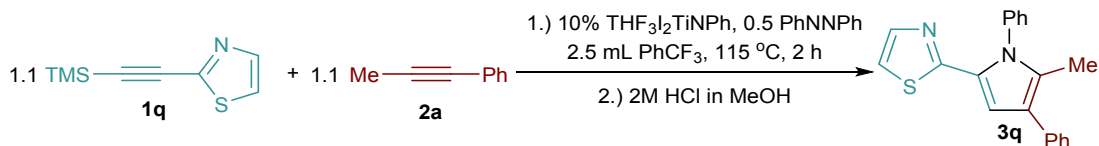
Figure S108. No-D <sup>1</sup>H NMR reaction of **1o** and **2a** in PhCF<sub>3</sub> at Time = 0 h (bottom), Time = 3 h (top) under Condition B.

### No-D <sup>1</sup>H NMR spectra of the reactions of **1p** and **2a**



**Figure S109.** No-D  $^1\text{H}$  NMR reaction of **1p** and **2a** in  $\text{PhCF}_3$  at Time = 0 h (bottom), Time = 2 h (top) under Condition A. NMR was assigned based on Ref S2.

### Synthesis of 2-(5-methyl-1,4-diphenyl-1H-pyrrol-2-yl)thiazole (**3q**)

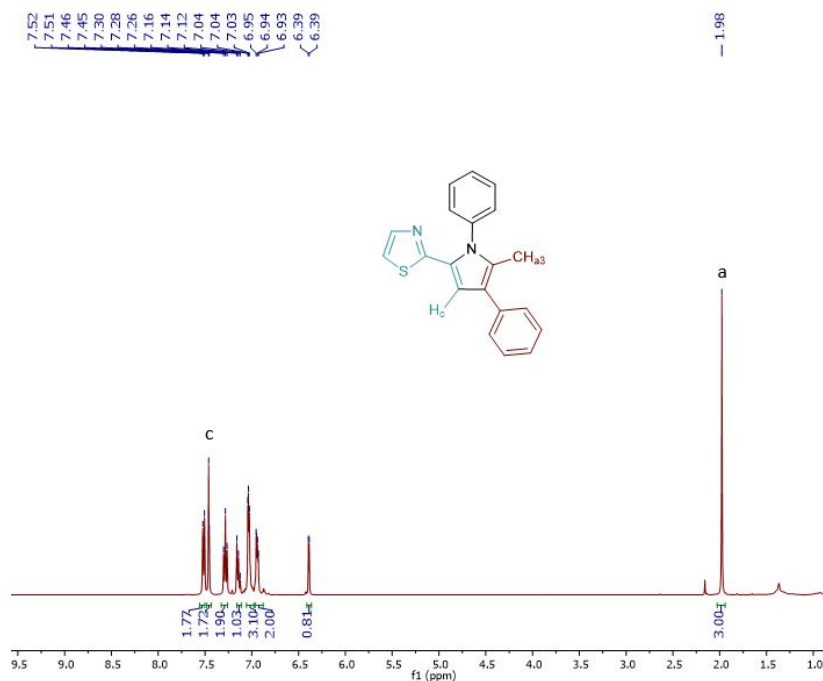


The product was isolated by silica gel chromatography using 5% EA/Hex eluent to give a white solid (61 mg, 38% yield).

$^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.51 (d,  $^3J_{\text{HH}} = 7.3$  Hz, 2H), 7.46 (m, 2H, 4-NC<sub>4</sub>-H and Ar-H), 7.28 (t,  $^3J_{\text{HH}} = 7.7$  Hz, 2H), 7.14 (t,  $J = 7.4$  Hz, 1H), 7.04-7.02 (m, 3H), 6.96-6.93 (m, 2H), 6.39 (d,  $^3J_{\text{HH}} = 3.2$  Hz, 1H), 1.98 (s, 3H, 2-NC<sub>4</sub>-CH<sub>3</sub>) ppm.

$^{13}\text{C}$  NMR (101 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  160.0, 143.1, 139.0, 137.0, 130.6, 129.6, 129.3, 128.9, 128.7, 128.7, 128.6, 126.1, 124.0, 116.3, 112.7, 12.1 ppm.

GC-HRMS: calculated for  $\text{C}_{20}\text{H}_{16}\text{N}_2\text{S}$  [ $\text{M}^+$ ] 316.1034; found 316.1000.



**Figure S110.**  $^1\text{H}$  NMR spectrum of **3q** in  $\text{C}_6\text{D}_6$ .

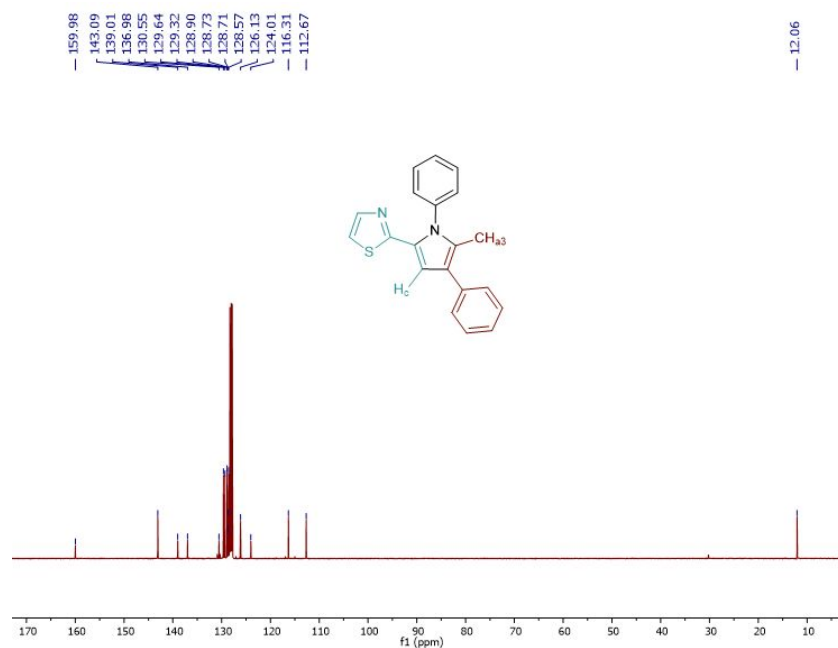


Figure S111.  $^{13}\text{C}$  NMR spectrum of **3q** in  $\text{C}_6\text{D}_6$ .

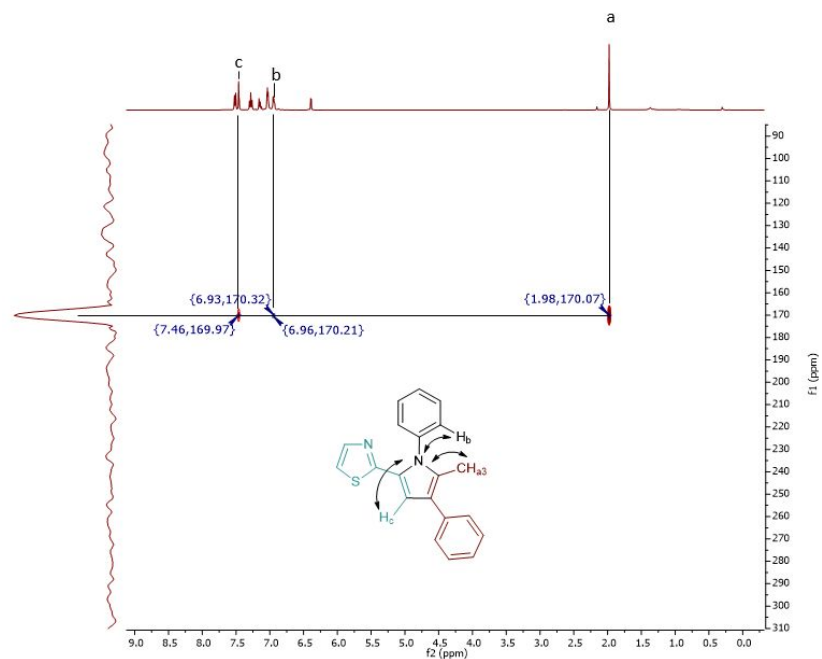


Figure S112.  $^1\text{H}$ - $^{15}\text{N}$  HMBC NMR spectrum of **3q** in  $\text{C}_6\text{D}_6$ .

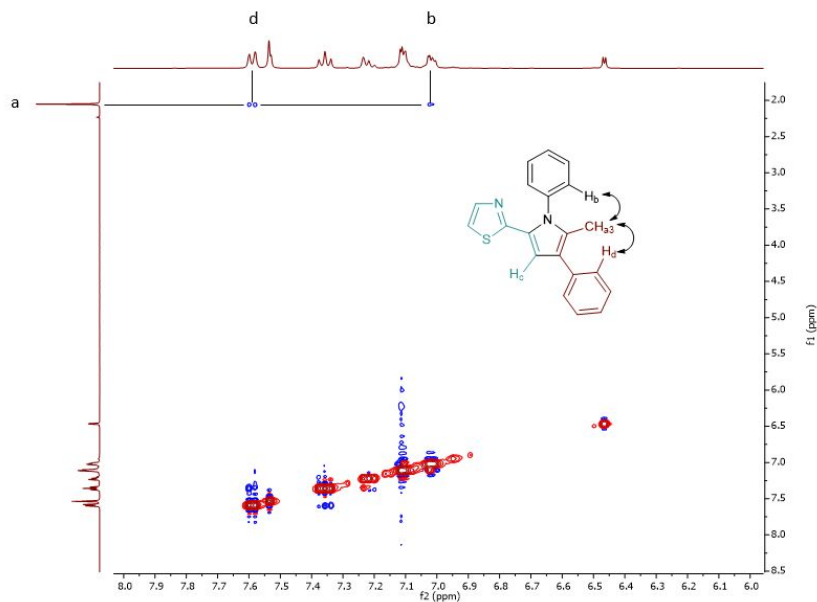


Figure S113. NOESY NMR spectrum of **3q** in  $C_6D_6$ .

No-D  $^1H$  NMR spectra of the reactions of **1q** and **2a**

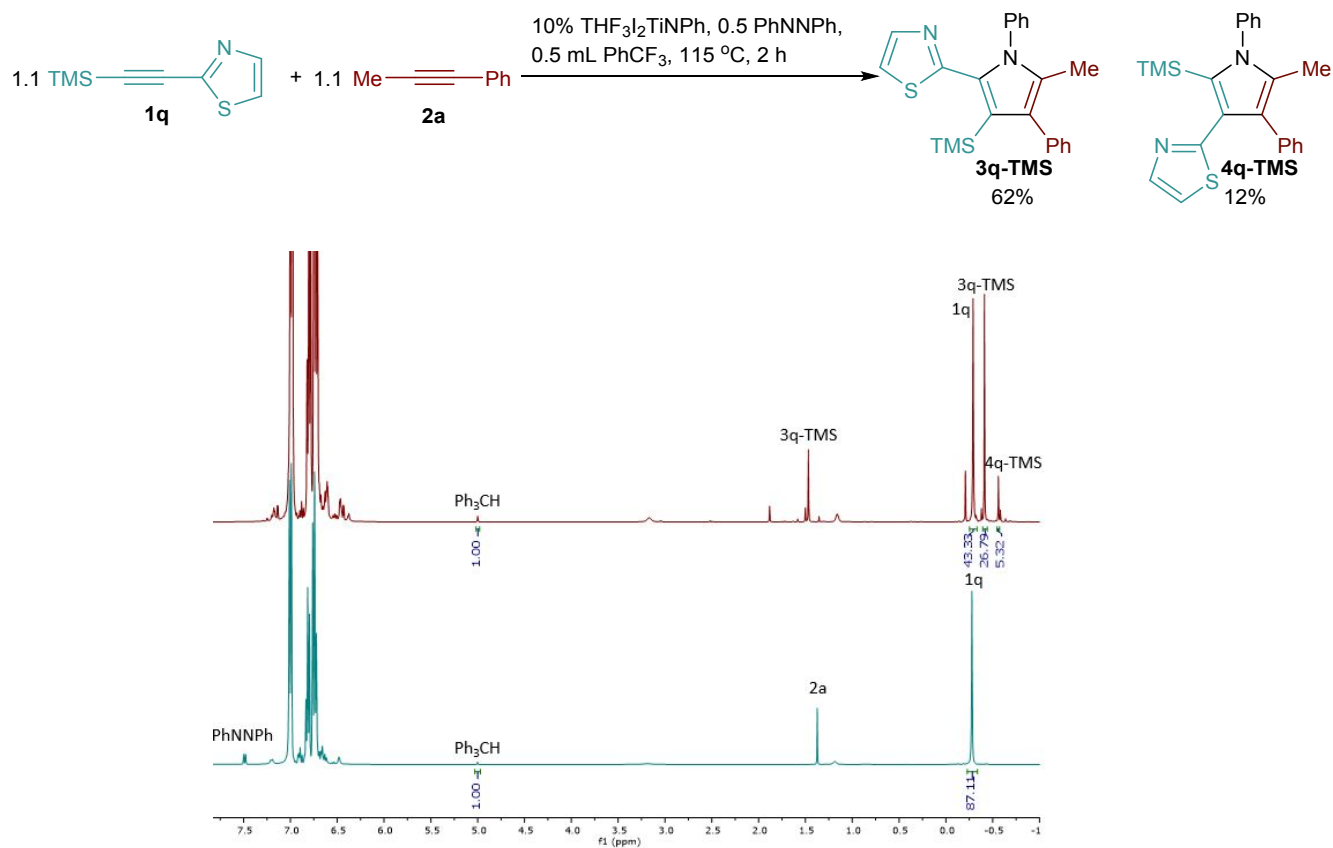


Figure S114. No-D  $^1H$  NMR reaction of **1q** and **2a** in  $PhCF_3$  at Time = 0 h (bottom), Time = 2 h (top) under Condition A.

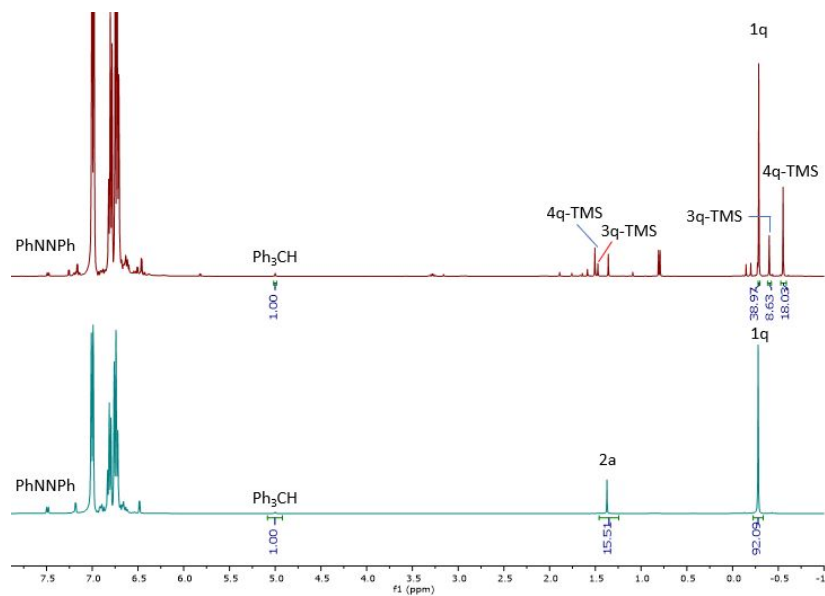
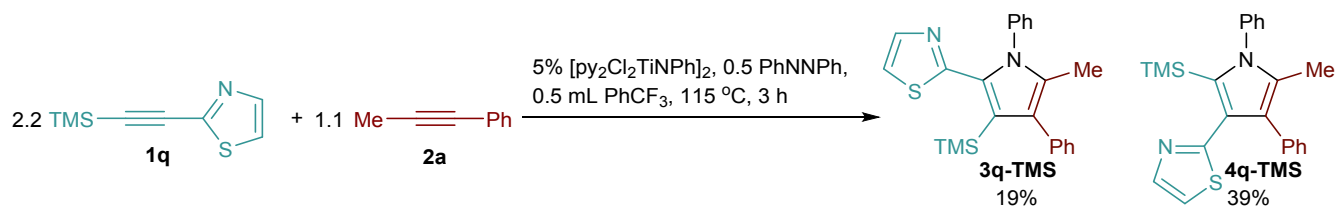
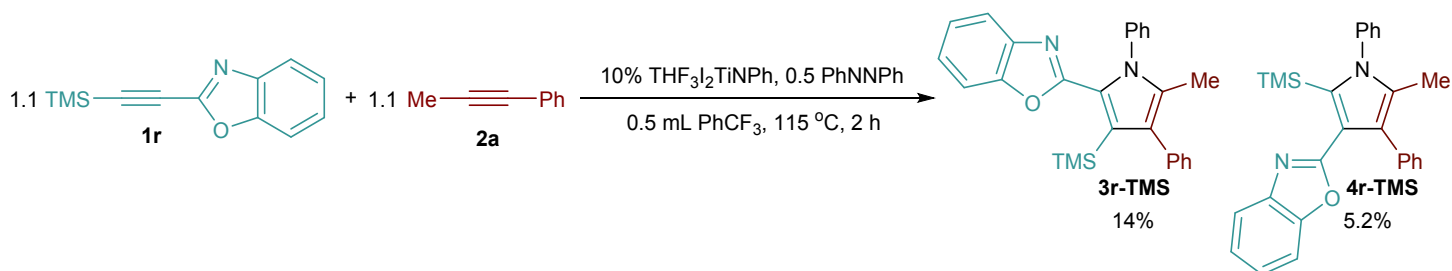


Figure S115. No-D <sup>1</sup>H NMR reaction of **1q** and **2a** in PhCF<sub>3</sub> at Time = 0 h (bottom), Time = 3 h (top) under Condition B.

### No-D <sup>1</sup>H NMR spectra of the reactions of **1r** and **2a**



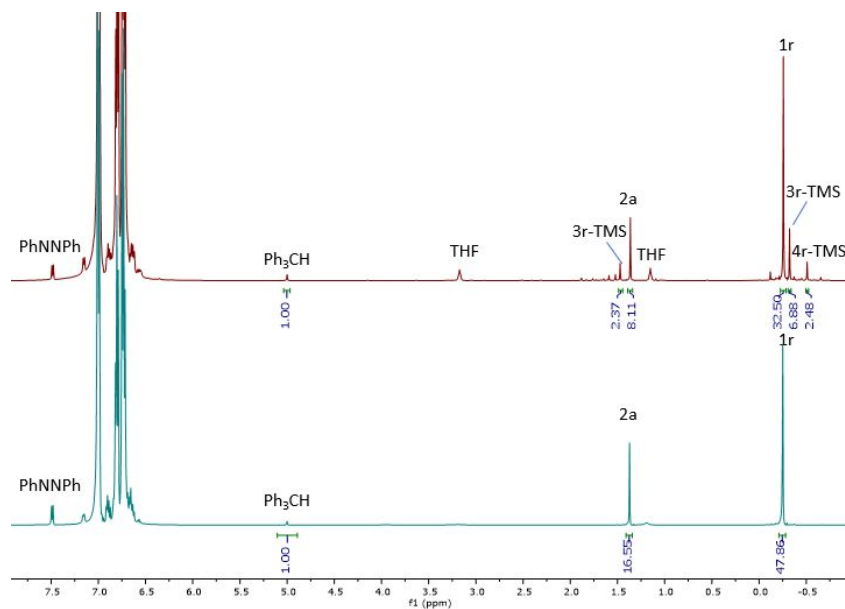
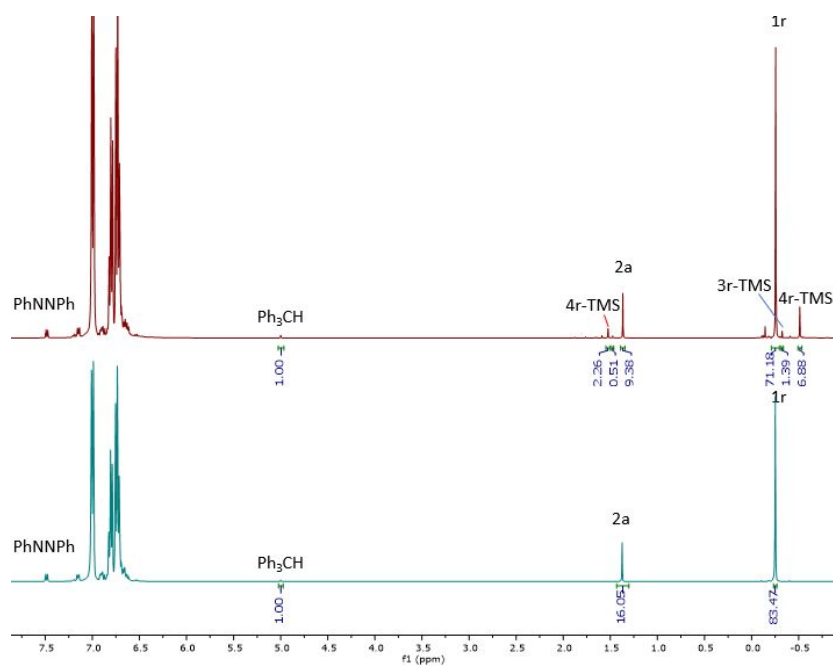
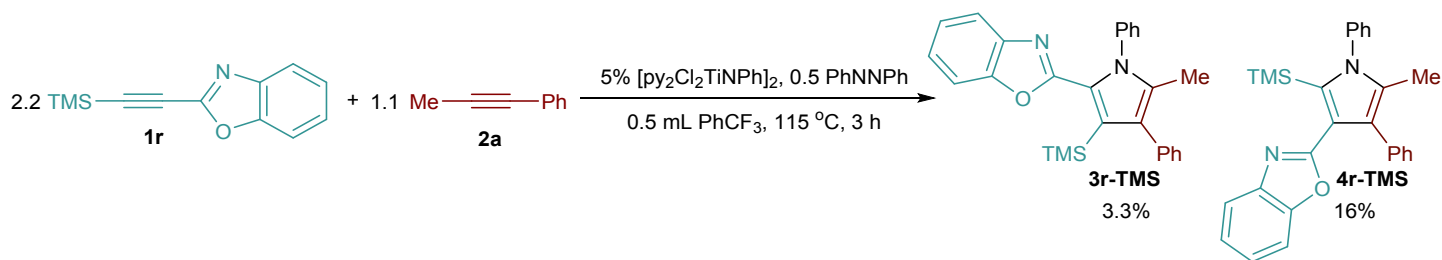
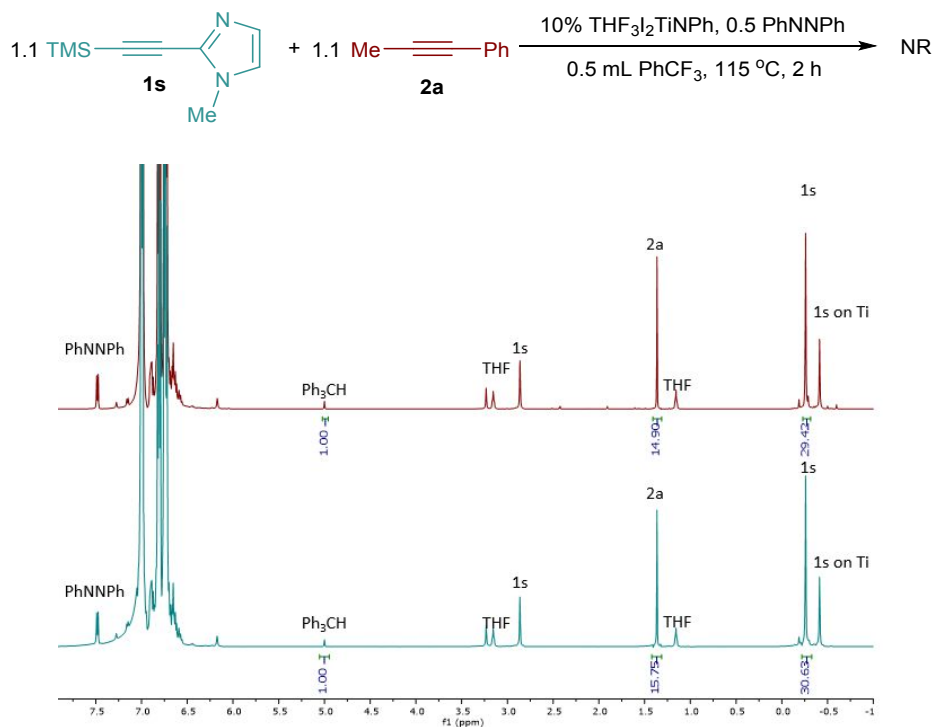


Figure S116. No-D <sup>1</sup>H NMR reaction of **1r** and **2a** in PhCF<sub>3</sub> at Time = 0 h (bottom), Time = 2 h (top) under Condition A.

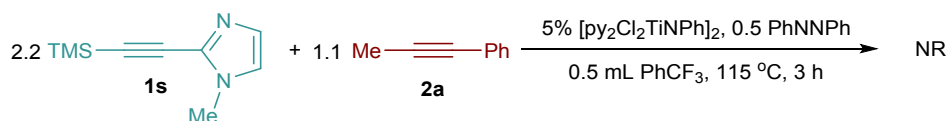


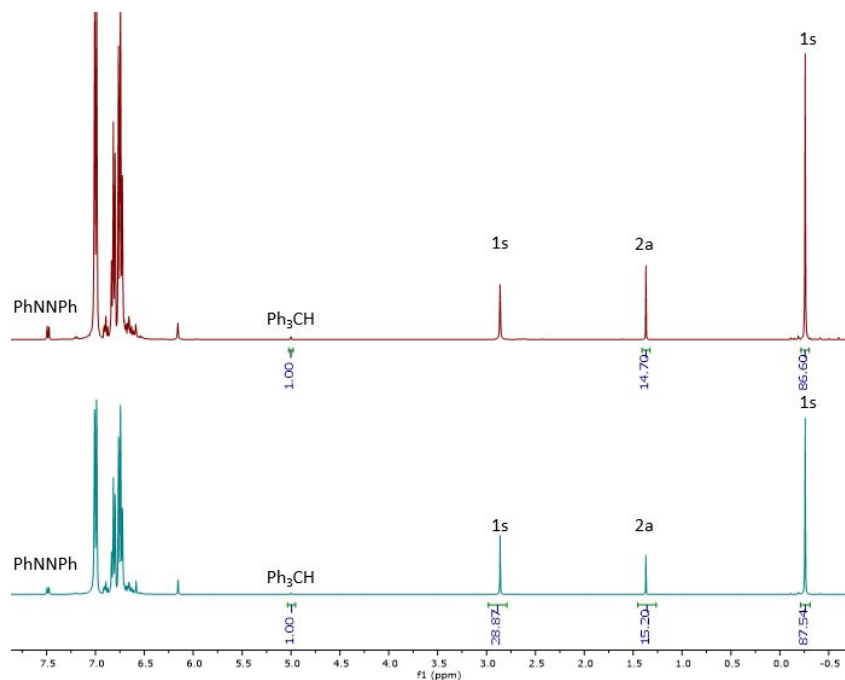
**Figure S117.** No-D  $^1\text{H}$  NMR reaction of **1r** and **2a** in  $\text{PhCF}_3$  at Time = 0 h (bottom), Time = 3 h (top) under Condition B.

**No-D  $^1\text{H}$  NMR spectra of the reactions of **1s** and **2a****



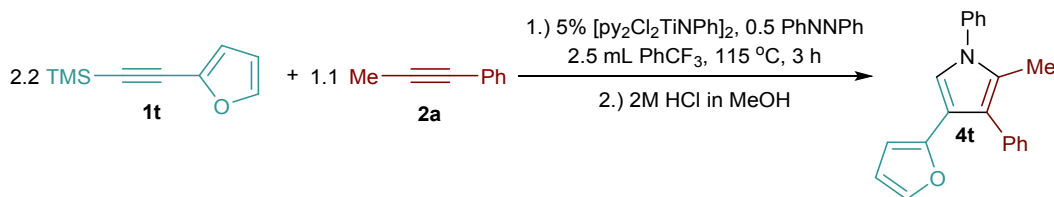
**Figure S118.** No-D  $^1\text{H}$  NMR reaction of **1s** and **2a** in  $\text{PhCF}_3$  at Time = 0 h (bottom), Time = 2 h (top) under Condition A.





**Figure S119.** No-D  $^1\text{H}$  NMR reaction of **1s** and **2a** in  $\text{PhCF}_3$  at Time = 0 h (bottom), Time = 3 h (top) under Condition B.

### Synthesis of 4-(furan-2-yl)-2-methyl-1,3-diphenyl-1H-pyrrole (**4t**)



The product was isolated by silica gel chromatography using 8% DCM/Hex eluent to give a colorless solid which slightly decomposed and turned brown while being concentrated (62 mg, 41% yield).

$^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.37-7.35 (m, 2H), 7.15-7.11 (m, 3H, 5- $\text{NC}_4\text{-H}$  and Ar-H), 7.06-7.00 (m, 3H), 6.90-6.82 (m, 5H), 5.98 (dd,  $^3J_{\text{HH}} = 3.2$  Hz,  $^3J_{\text{HH}} = 1.8$  Hz, 1H, 4- $\text{OC}_4\text{-H}$ ), 5.90 (d,  $^3J_{\text{HH}} = 3.2$  Hz, 1H, 5- $\text{OC}_4\text{-H}$ ), 1.83 (s, 3H, 2- $\text{NC}_4\text{-CH}_3$ ) ppm.

$^{13}\text{C}$  NMR (101 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  151.4, 140.4, 140.0, 136.9, 131.2, 129.3, 128.6, 127.3, 127.1, 126.8, 125.9, 121.9, 118.9, 115.9, 111.3, 104.6, 11.5 ppm.

GC-HRMS: calculated for C<sub>21</sub>H<sub>17</sub>NO [M<sup>+</sup>] 299.1310; found 299.1272.

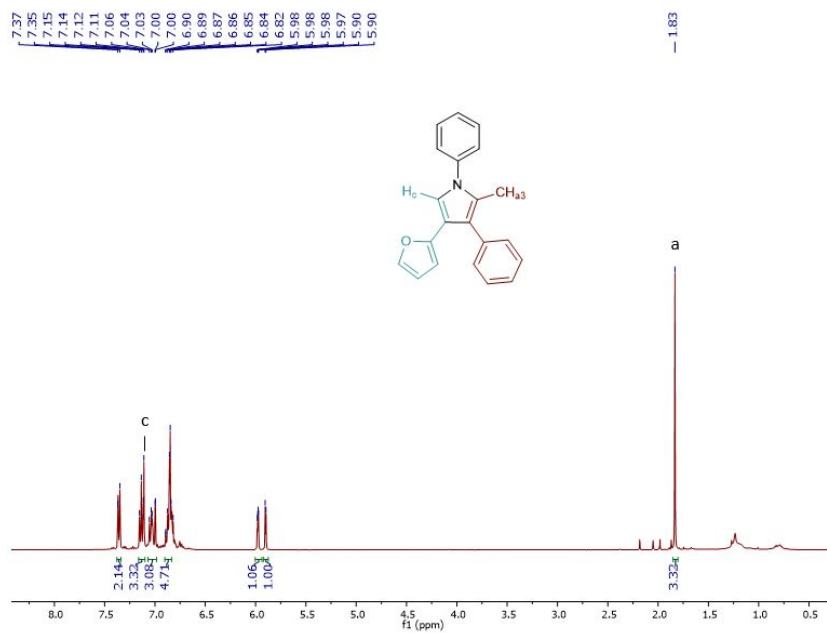


Figure S120. <sup>1</sup>H NMR spectrum of 4t in C<sub>6</sub>D<sub>6</sub>.

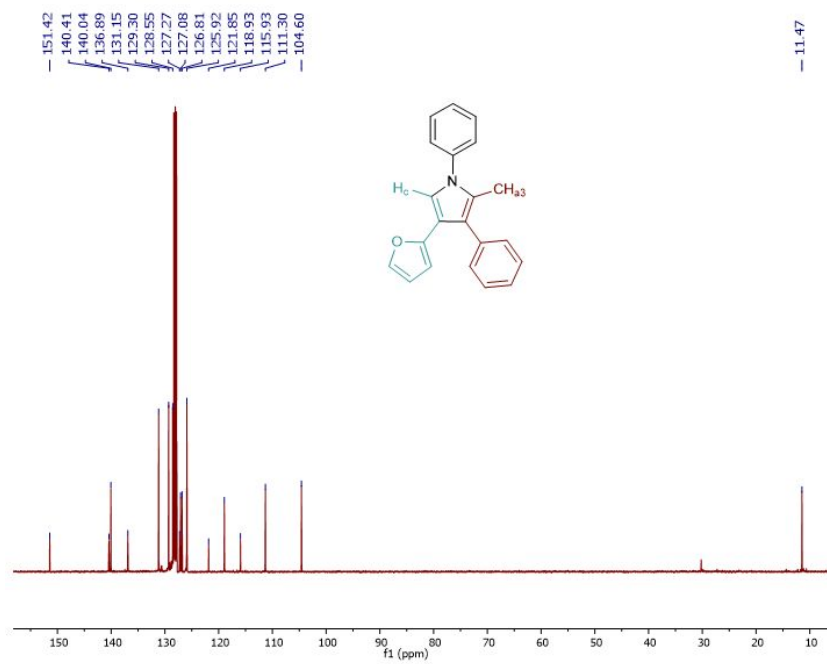


Figure S121. <sup>13</sup>C NMR spectrum of 4t in C<sub>6</sub>D<sub>6</sub>.

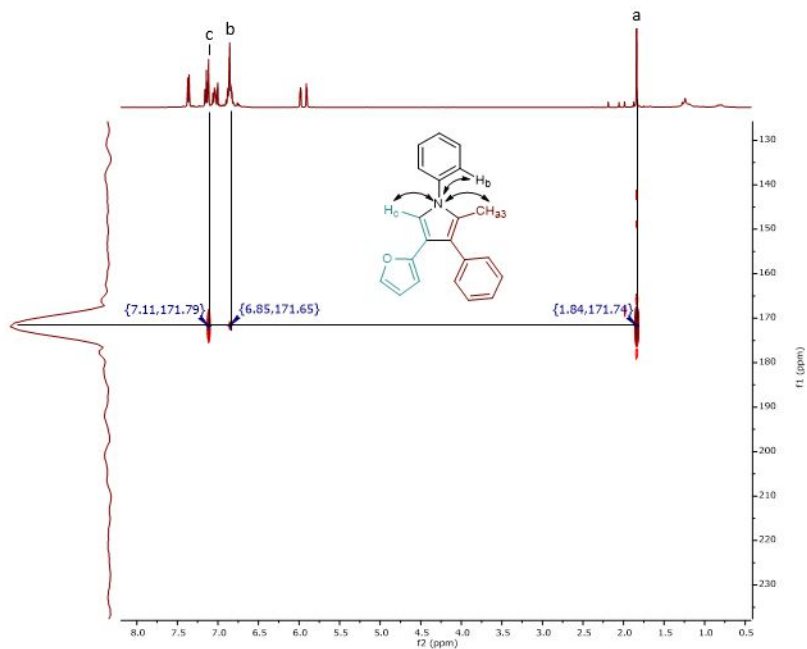


Figure S122.  $^1\text{H}$ - $^{15}\text{N}$  HMBC NMR spectrum of **4t** in  $\text{C}_6\text{D}_6$ .

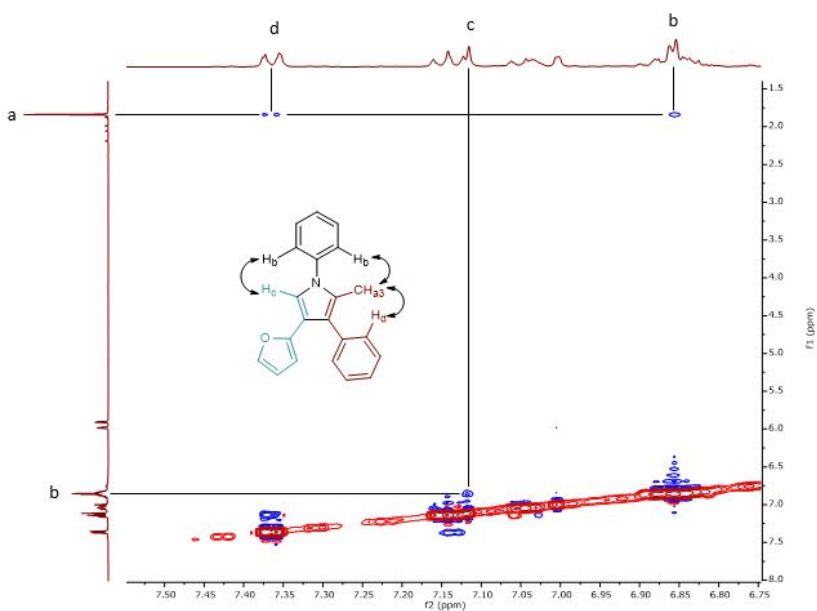


Figure S123. NOESY NMR spectrum of **4t** in  $\text{C}_6\text{D}_6$ .

No-D  $^1\text{H}$  NMR spectra of the reactions of **1t** and **2a**

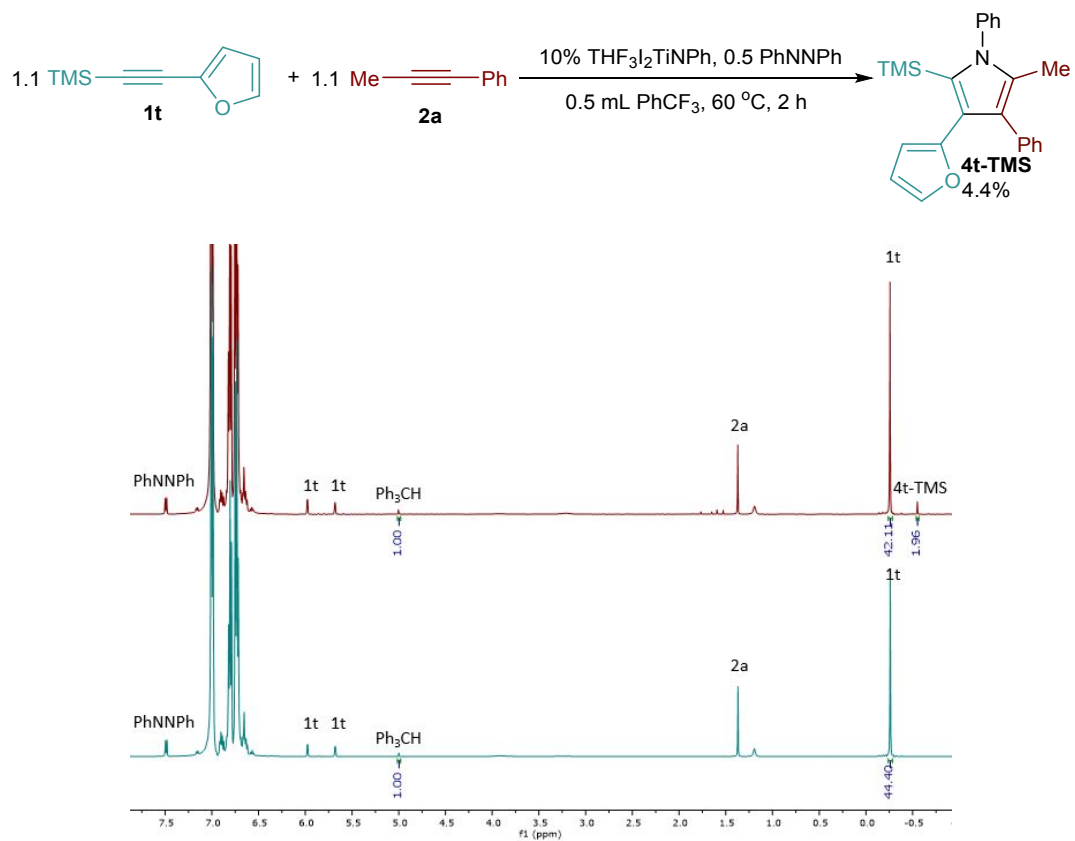
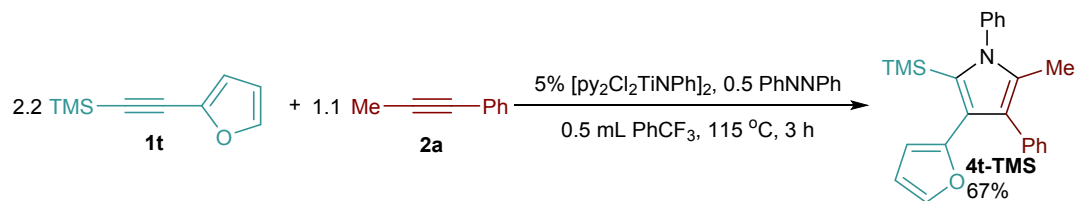


Figure S124. No-D  $^1\text{H}$  NMR reaction of **1t** and **2a** in  $\text{PhCF}_3$  at Time = 0 h (bottom), Time = 2 h (top) under Condition A.



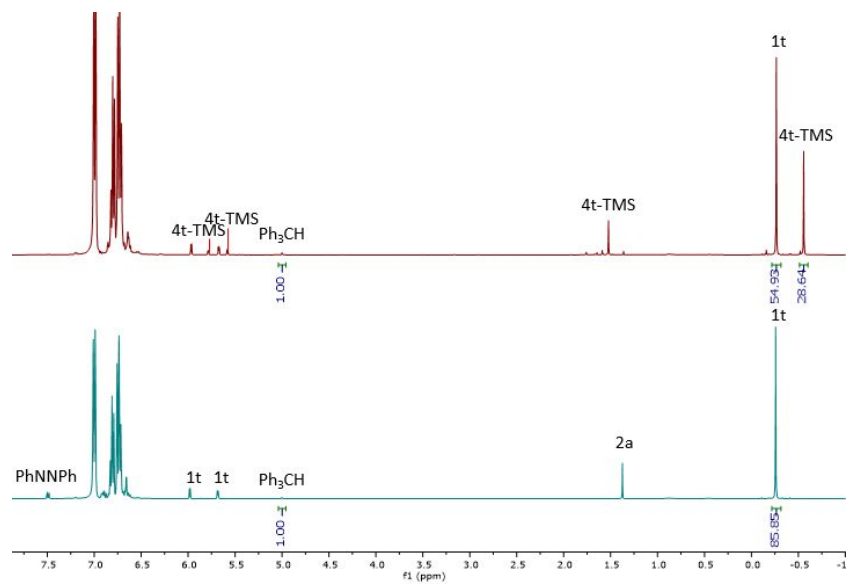
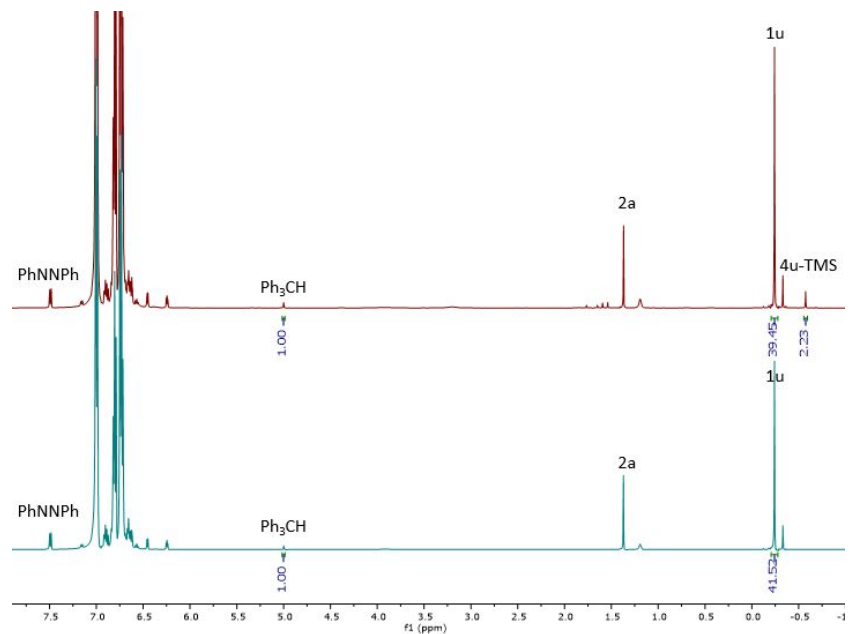
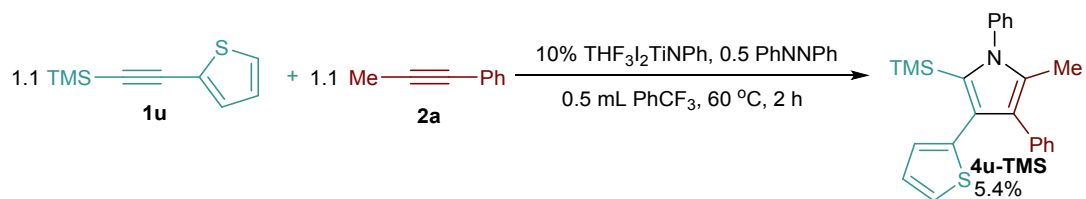


Figure S125. No-D  $^1\text{H}$  NMR reaction of **1t** and **2a** in  $\text{PhCF}_3$  at Time = 0 h (bottom), Time = 3 h (top) under Condition B.

### No-D $^1\text{H}$ NMR spectra of the reactions of **1u** and **2a**





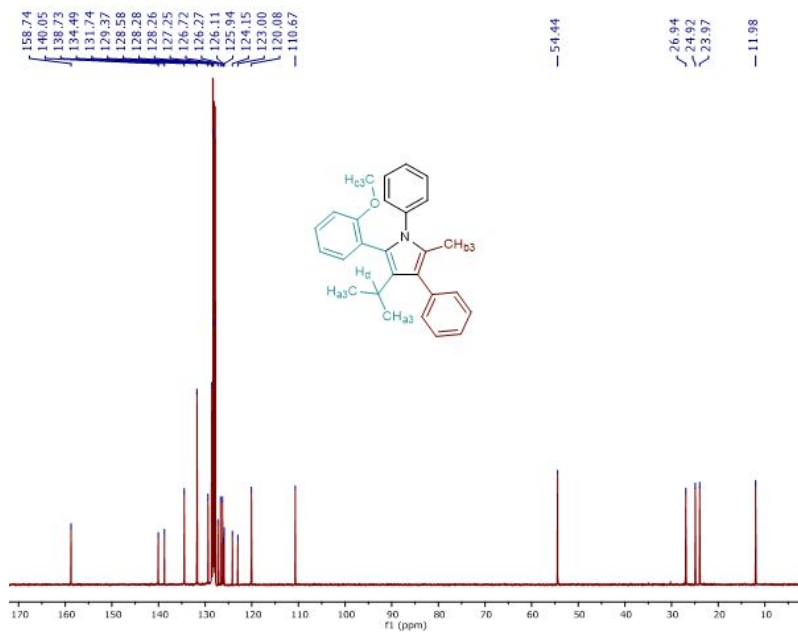


Figure S128.  $^{13}\text{C}$  NMR spectrum of **3w** in  $\text{C}_6\text{D}_6$ .

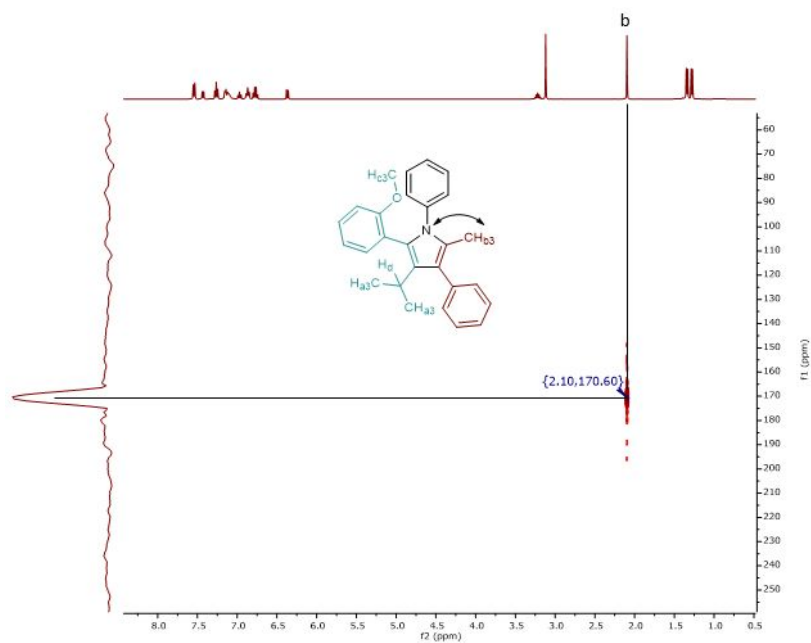


Figure S129.  $^1\text{H}$ - $^{15}\text{N}$  HMBC NMR spectrum of **3w** in  $\text{C}_6\text{D}_6$ .

No-D  $^1\text{H}$  NMR spectra of the reactions of **1w** and **2a**

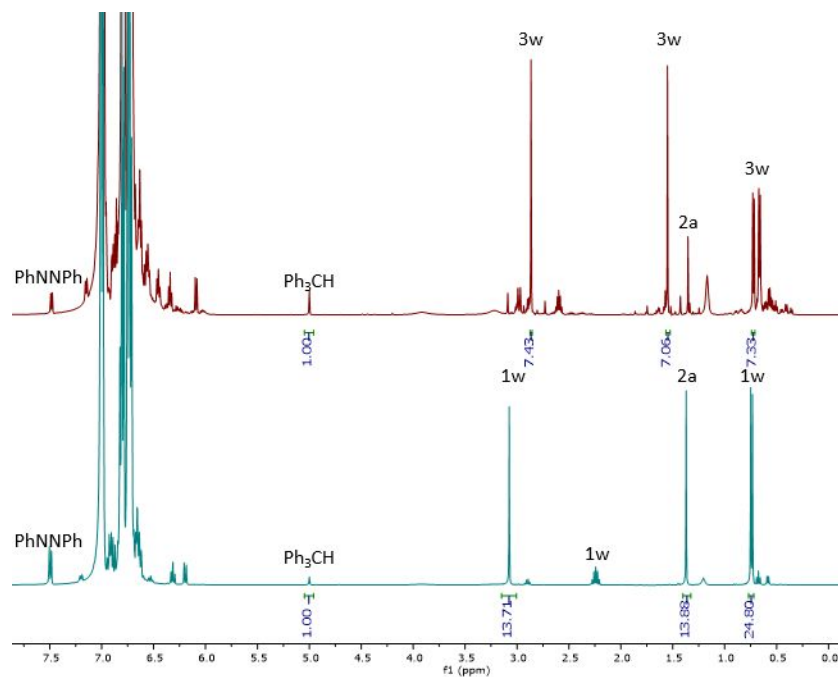
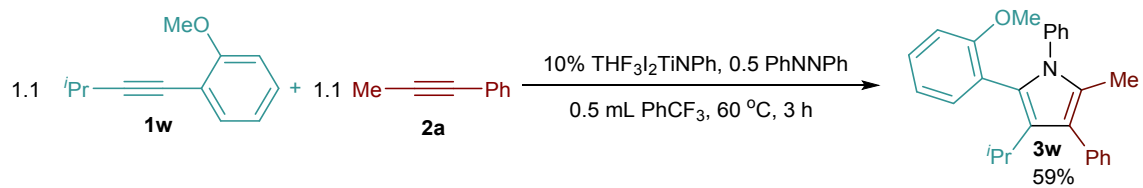
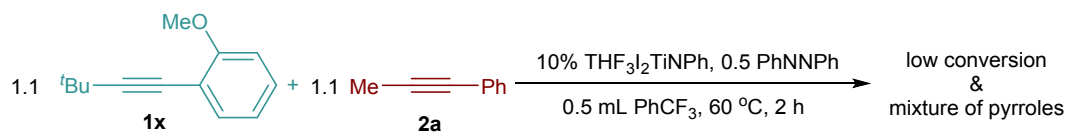
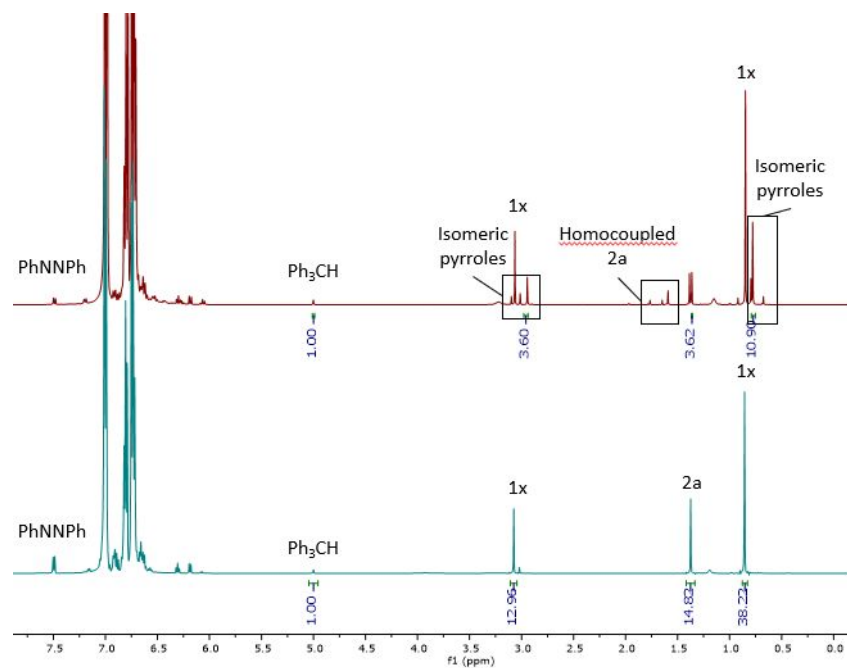


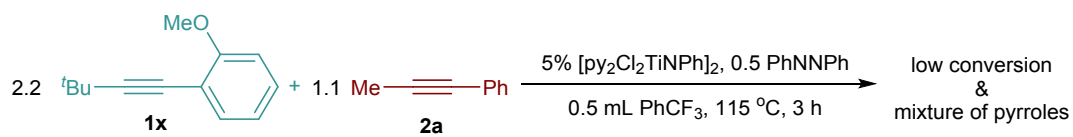
Figure S130. No-D  $^1\text{H}$  NMR reaction of **1w** and **2a** in  $\text{PhCF}_3$  at Time = 0 h (bottom), Time = 3 h (top) under Condition A.

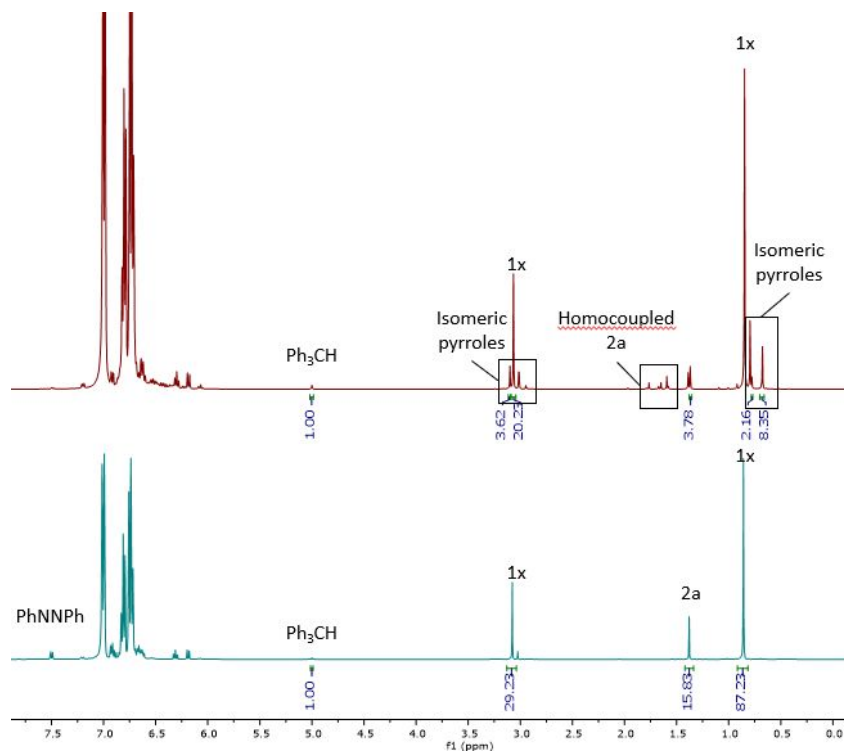
#### No-D $^1\text{H}$ NMR spectra of the reactions of **1x** and **2a**





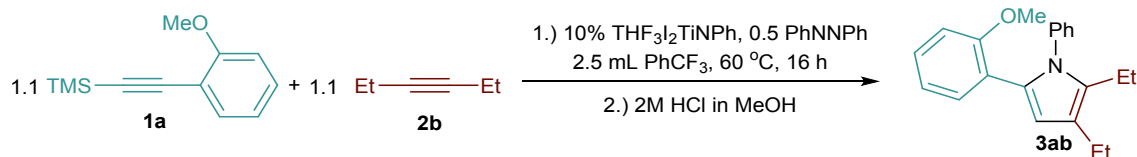
**Figure S131.** No-D  $^1\text{H}$  NMR reaction of **1x** and **2a** in  $\text{PhCF}_3$  at Time = 0 h (bottom), Time = 2 h (top) under Condition A.





**Figure S132.** No-D <sup>1</sup>H NMR reaction of **1x** and **2a** in PhCF<sub>3</sub> at Time = 0 h (bottom), Time = 3 h (top) under Condition B

### Synthesis of 2,3-diethyl-5-(2-methoxyphenyl)-1-phenyl-1H-pyrrole (**3ab**)



The product was isolated by silica gel chromatography using 20% DCM/Hex eluent to give a colorless oil (58 mg, 38% yield).

**<sup>1</sup>H NMR** (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.35 (dd, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, <sup>4</sup>J<sub>HH</sub> = 1.7 Hz, 1H), 7.11-7.09 (m, 2H), 6.97 (td, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, <sup>4</sup>J<sub>HH</sub> = 1.7 Hz, 1H), 6.92-6.82 (m, 3H), 6.77 (t, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, 1H), 6.5 (s, 1H, 4-NC<sub>4</sub>-H), 6.37 (d, <sup>3</sup>J<sub>HH</sub> = 8.2 Hz, 1H), 3.03 (s, 3H, -OCH<sub>3</sub>), 2.60 (app p, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 3-NC<sub>4</sub>-CH<sub>2</sub>-CH<sub>3</sub> and 2-NC<sub>4</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 1.34 (t, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 3H, 3-NC<sub>4</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 1.34 (t, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 3H, 2-NC<sub>4</sub>-CH<sub>2</sub>-CH<sub>3</sub>) ppm.

**<sup>13</sup>C NMR** (101 MHz, C<sub>6</sub>D<sub>6</sub>): δ 157.3, 140.9, 132.4, 131.9, 130.1, 128.5, 126.5, 124.3, 122.3, 120.5, 110.8, 110.7, 54.3, 20.0, 18.5, 16.3, 15.4 ppm.

**GC-HRMS:** calculated for C<sub>21</sub>H<sub>23</sub>NO [M<sup>+</sup>] 305.1780; found 305.1770.

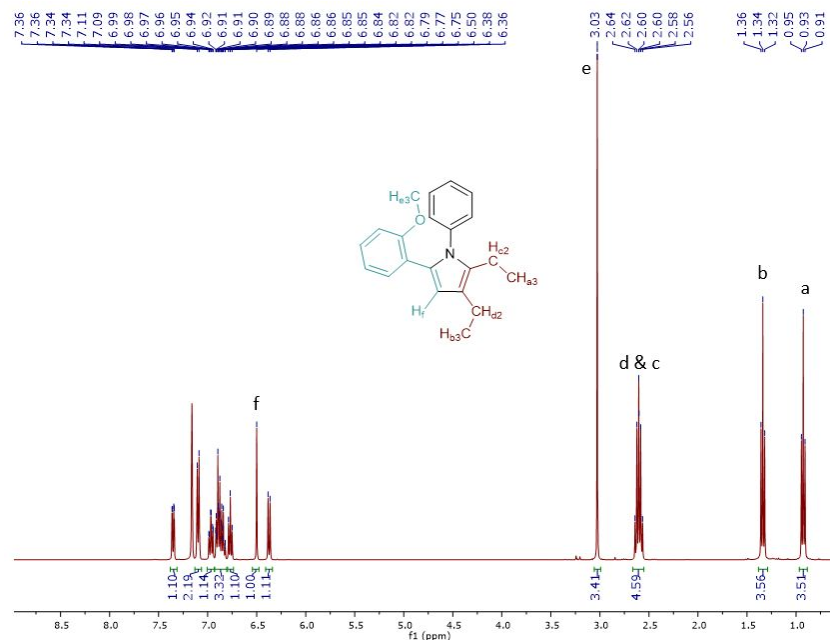


Figure S133. <sup>1</sup>H NMR spectrum of 3ab in C<sub>6</sub>D<sub>6</sub>.

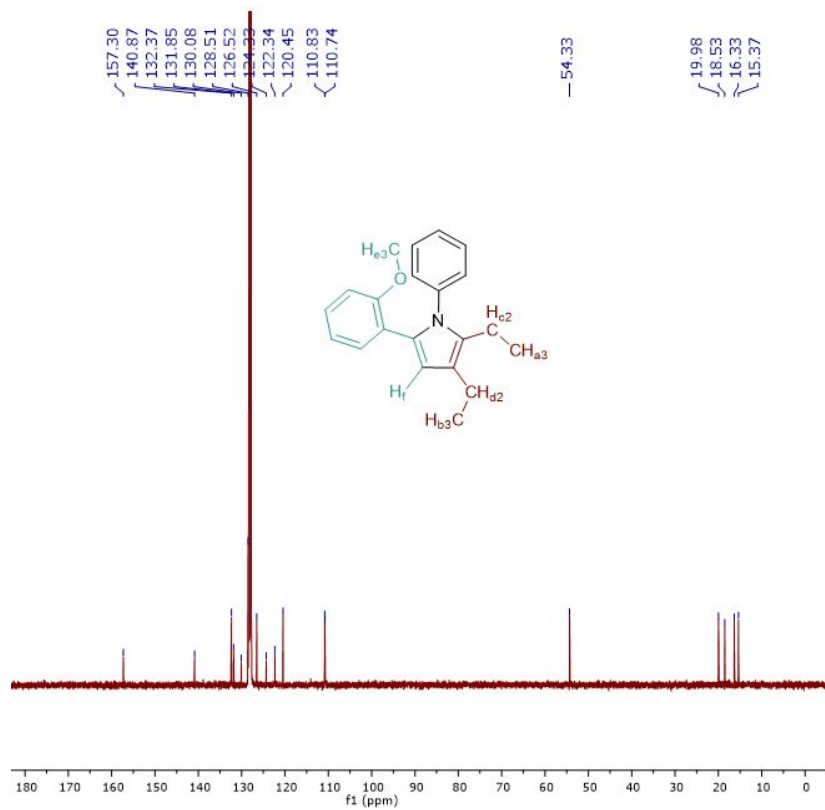


Figure S134. <sup>13</sup>C NMR spectrum of 3ab in C<sub>6</sub>D<sub>6</sub>.

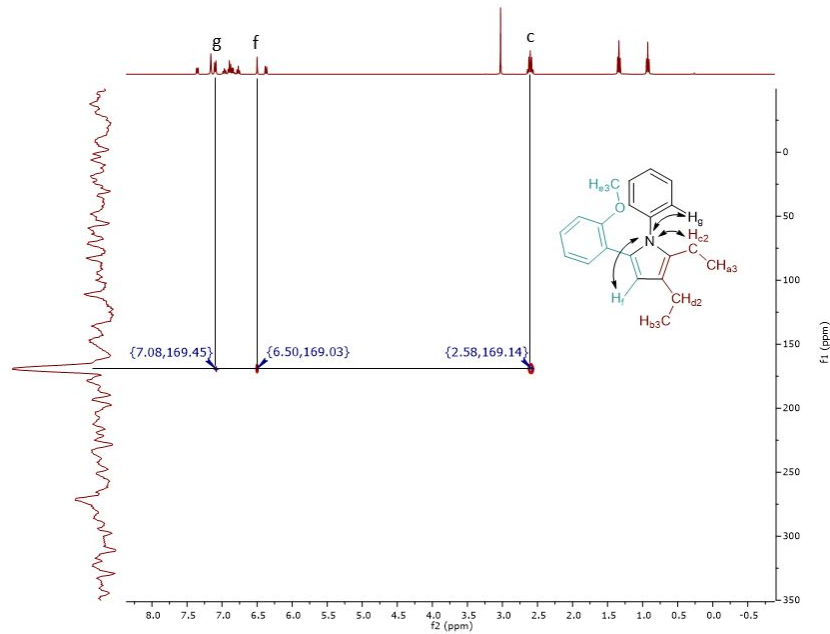


Figure S135.  $^1\text{H}$ - $^{15}\text{N}$  HMBC NMR spectrum of **3ab** in  $\text{C}_6\text{D}_6$ .

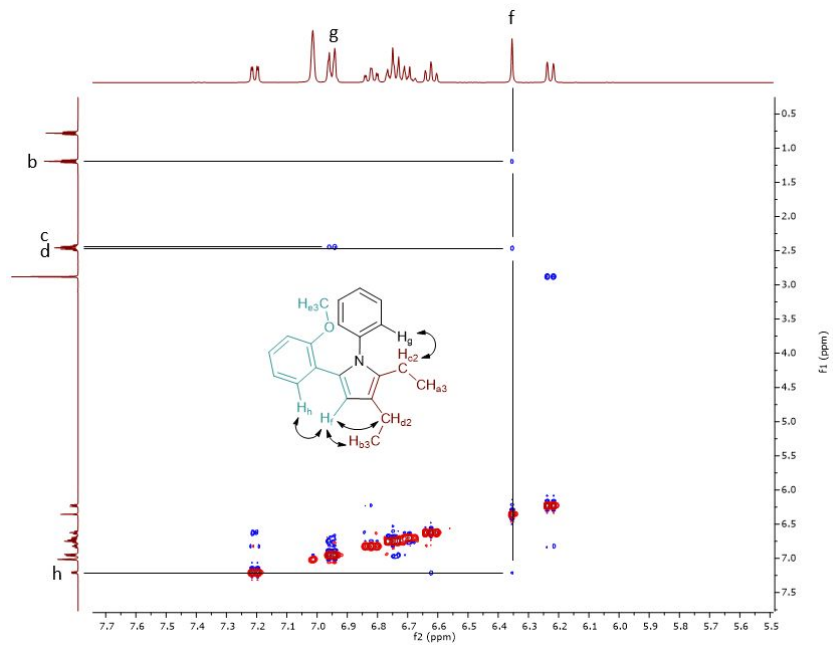
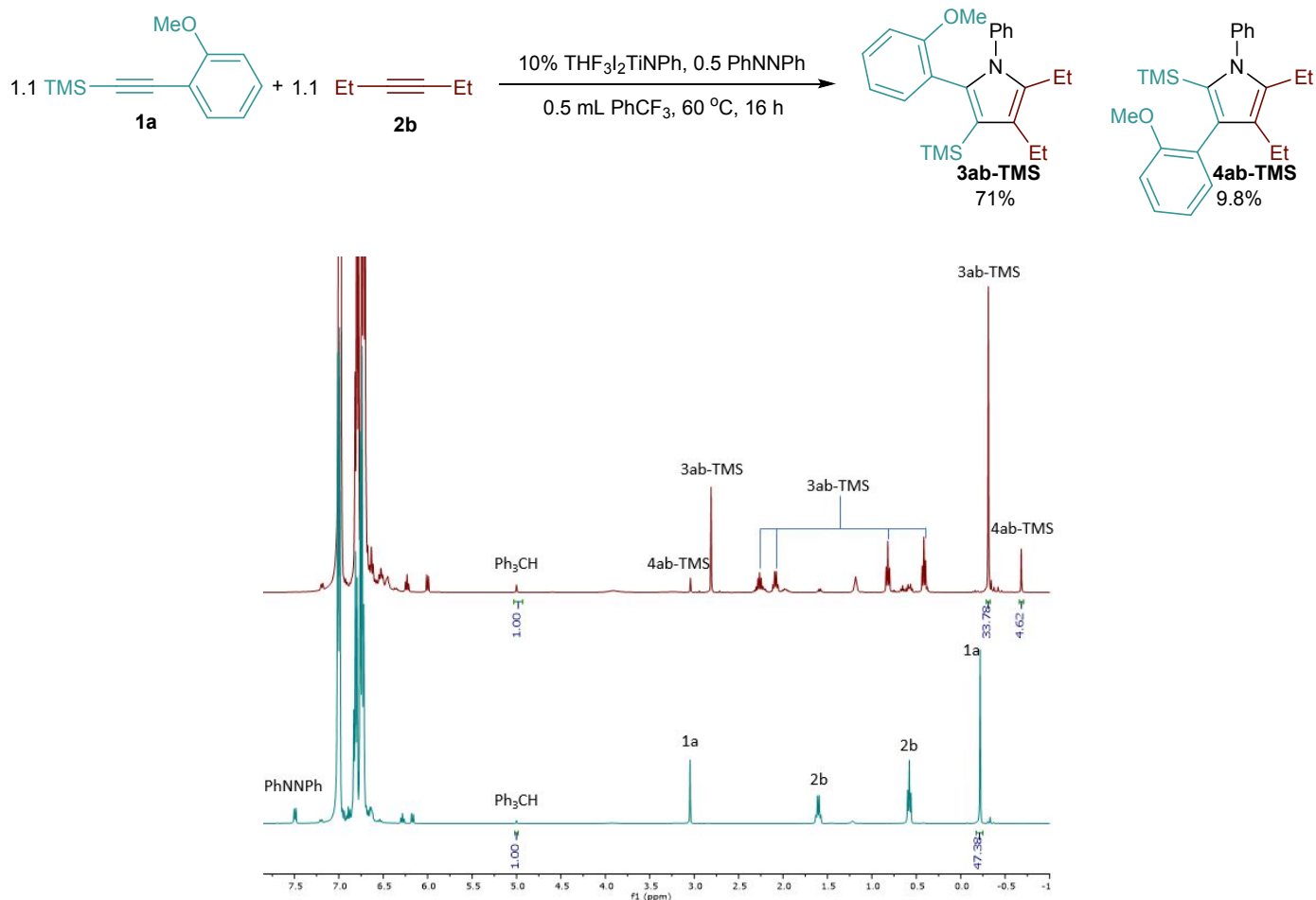


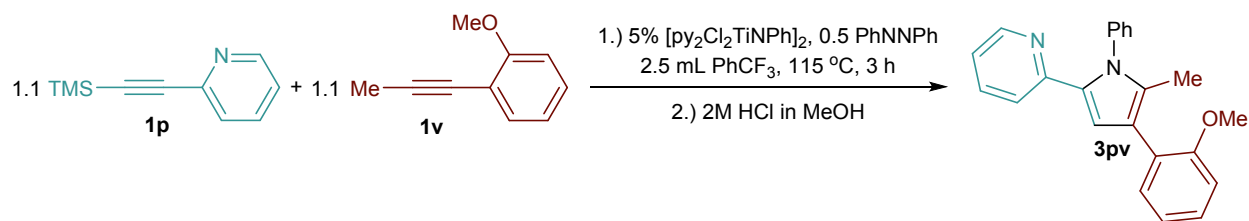
Figure S136. NOESY NMR spectrum of **3ab** in  $\text{C}_6\text{D}_6$ .

### No-D <sup>1</sup>H NMR spectra of the reactions of **1a** and **2b**



**Figure S137.** No-D <sup>1</sup>H NMR reaction of **1a** and **2b** in PhCF<sub>3</sub> at Time = 0 h (bottom), Time = 16 h (top) under Condition B.

### Synthesis of 2-(4-(2-methoxyphenyl)-5-methyl-1-phenyl-1H-pyrrol-2-yl)pyridine (**3pv**)



The product was isolated by silica gel chromatography using 16% EA/Hex eluent to give a white solid (87 mg, 65% yield).

$^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  8.31 (d,  $^3J_{\text{HH}} = 4.8$  Hz, 1H), 7.56 (dd,  $^3J_{\text{HH}} = 7.4$  Hz,  $^4J_{\text{HH}} = 1.7$  Hz, 1H), 7.38 (s, 1H, 3-NC<sub>4</sub>-H), 7.20-7.16 (m, 1H), 7.02-6.95 (m, 7H), 6.90 (td,  $^3J_{\text{HH}} = 7.9$  Hz,  $^4J_{\text{HH}} = 1.8$  Hz, 1H), 6.74 (d,  $^3J_{\text{HH}} = 8.2$  Hz), 6.41 (ddd,  $^3J_{\text{HH}} = 7.2, 4.8$  Hz,  $^4J_{\text{HH}} = 1.1$  Hz, 1H), 3.40 (s, 3H, -OCH<sub>3</sub>), 2.07 (s, 5-NC<sub>4</sub>-CH<sub>3</sub> ppm).

$^{13}\text{C}$  NMR (101 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  157.7, 152.7, 149.4, 141.0, 135.3, 133.3, 132.1, 131.5, 129.0, 128.9, 127.3, 126.7, 121.0, 120.8, 119.8, 114.6, 111.5, 55.1, 12.7 ppm.

GC-HRMS: calculated for  $\text{C}_{23}\text{H}_{20}\text{N}_2\text{O}$  [ $\text{M}^+$ ] 340.1576; found 340.1541.

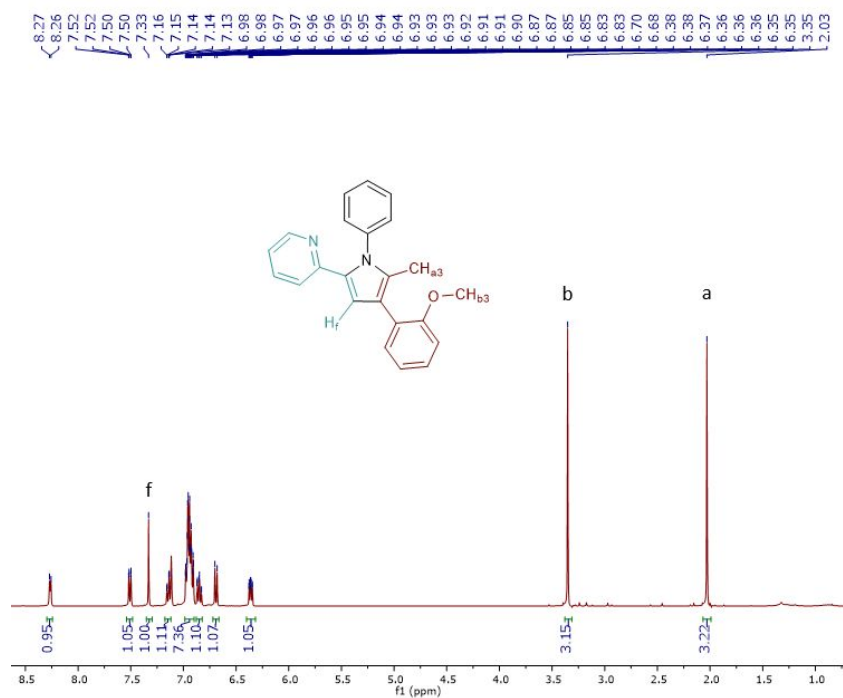


Figure S138.  $^1\text{H}$  NMR spectrum of **3pv** in  $\text{C}_6\text{D}_6$ .

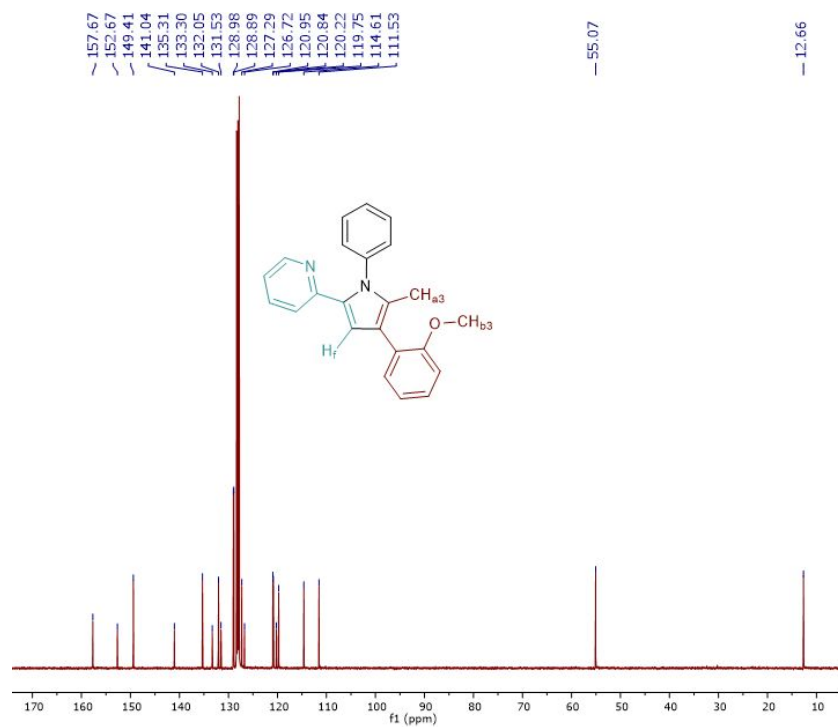


Figure S139.  $^{13}\text{C}$  NMR spectrum of **3pv** in  $\text{C}_6\text{D}_6$ .

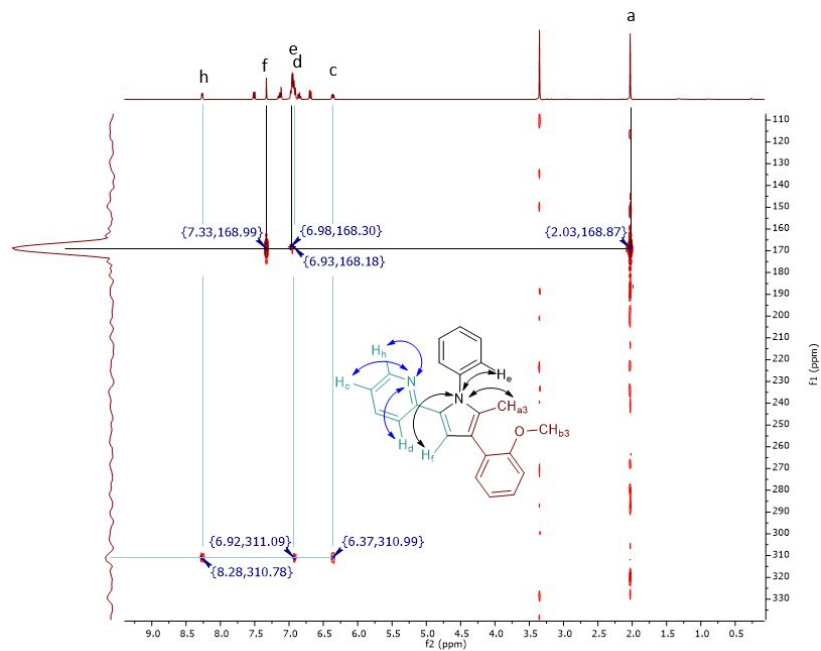


Figure S140.  $^1\text{H}$ - $^{15}\text{N}$  HMBC NMR spectrum of **3pv** in  $\text{C}_6\text{D}_6$ .

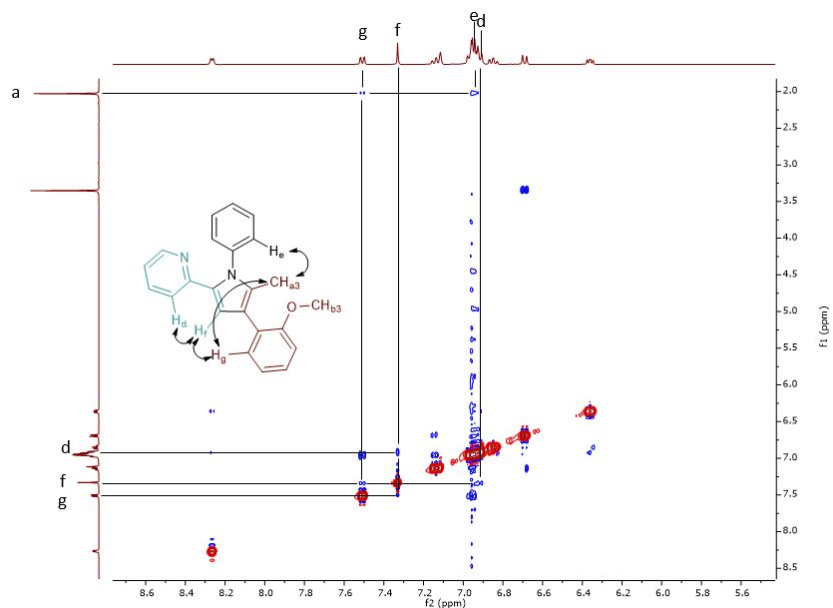
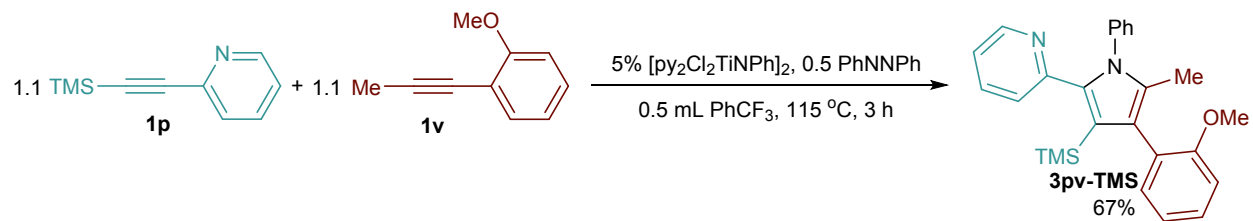


Figure S141. NOESY NMR spectrum of **3pv** in  $C_6D_6$ .

No-D  $^1H$  NMR spectra of the reactions of **1p** and **1v**



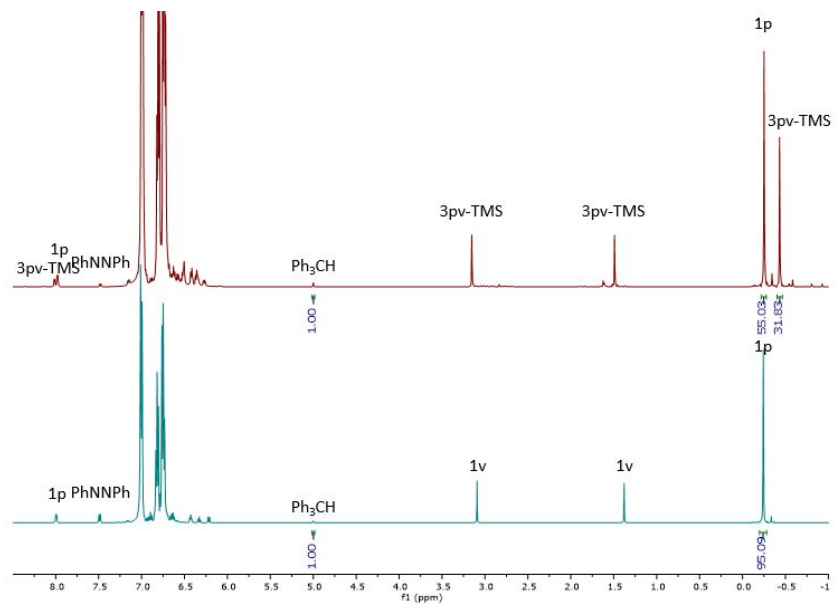


Figure S142. No-D  $^1\text{H}$  NMR reaction of **1p** and **1v** in  $\text{PhCF}_3$  at Time = 0 h (bottom), Time = 3 h (top) under Condition A.

**NMR Spectra of 5-(5-bromo-2-((2,3-difluorobenzyl)oxy)phenyl)-1-(4-bromophenyl)-2-methyl-3-phenyl-1H-pyrrole (**5y**)**

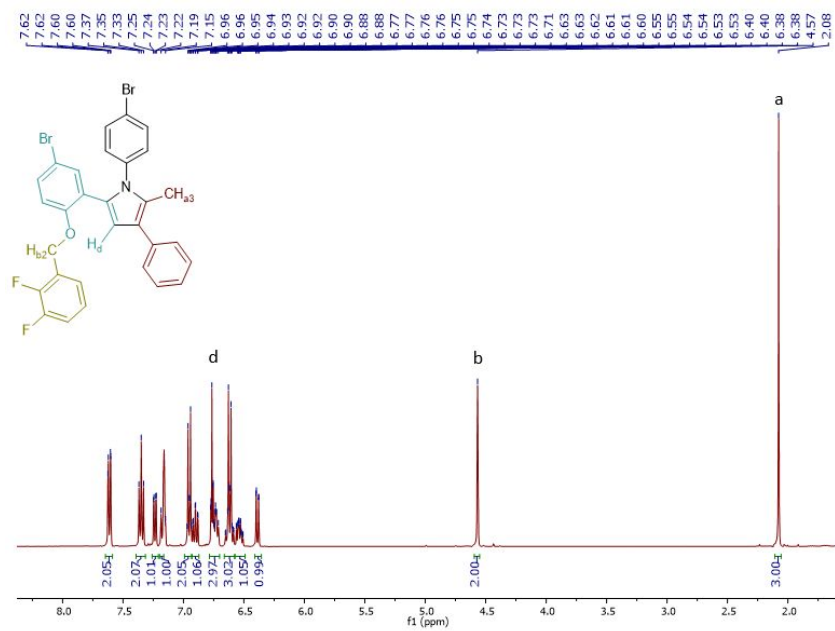
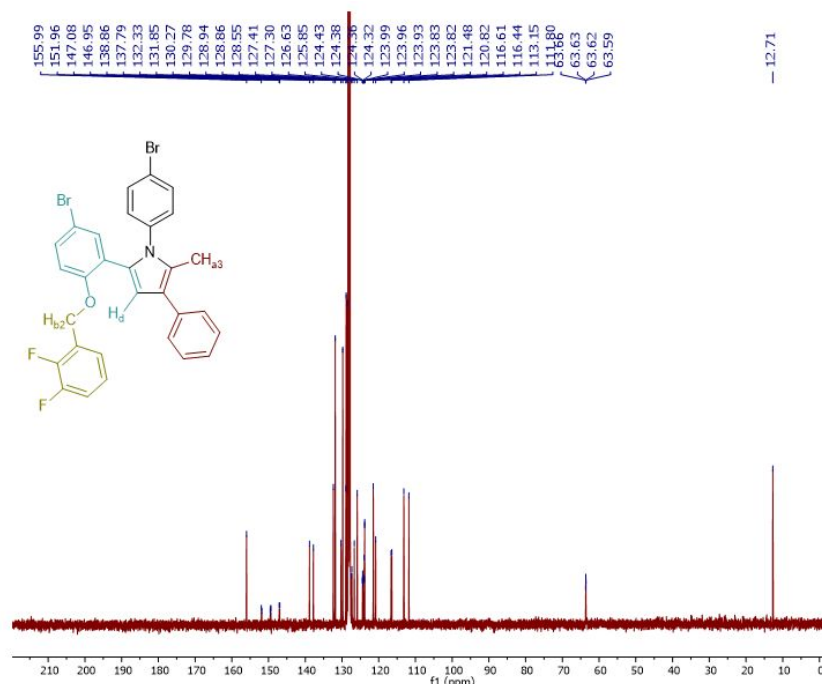


Figure S143.  $^1\text{H}$  NMR spectrum of **5y** in  $\text{C}_6\text{D}_6$ .



**Figure S144.**  $^1\text{H}$  NMR spectrum of **5y** in  $\text{C}_6\text{D}_6$ .

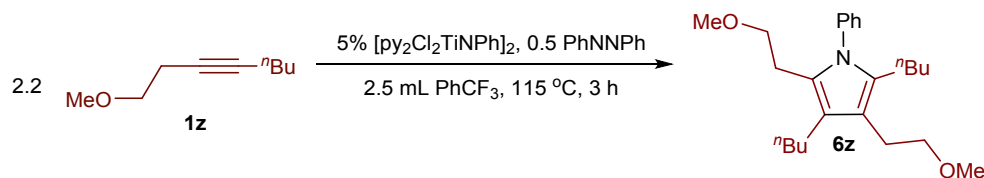
### General Synthesis of Multi-Substituted Pyrroles via Homocoupling Reactions

In a glovebox, to a 7 mL vial was added 41.0 mg PhNNPh (0.225 mmol, 0.5 eq.), 18.4 mg  $[(\text{py})_2\text{Cl}_2\text{TiNPh}]_2$  (0.05 mmol, 0.11 eq.), internal alkyne (compound **2**, 1.0 mmol, 2.2 eq.), and 2.5 mL  $\text{PhCF}_3$ . The reaction was then sealed with a Teflon screw cap and heated outside of the glovebox for 3 hours at 115 °C. The reaction was diluted by ethyl acetate, washed with DI water, dried over  $\text{Na}_2\text{SO}_4$  and concentrated prior to purification.

### General Procedure of No-D $^1\text{H}$ NMR Experiments for Homocoupling Reactions

In a glovebox, to an NMR tube was added 8.2 mg PhNNPh (0.045 mmol, 0.5 eq.), 6.1 mg  $[(\text{py})_2\text{Cl}_2\text{TiNPh}]_2$  (0.005 mmol, 0.055 eq.), internal alkyne (compound **1v** or **1z**, 0.2 mmol, 2.2 eq.), and 0.5 mL  $\text{PhCF}_3$ . The reaction was then sealed and heated outside of the glovebox for 1.5 or 3 hours at 115 °C. No-D  $^1\text{H}$  NMR spectra were collected on a Bruker Avance III HD NanoBay 400 MHz referenced to the proton signal of triphenylmethane ( $\text{Ph}_3\text{CH}$ , ppm = 5.0) at a delay time = 30 and acquisition time = 5.

### Synthesis of 2,4-dibutyl-3,5-bis(2-methoxyethyl)-1-phenyl-1H-pyrrole (**6z**)

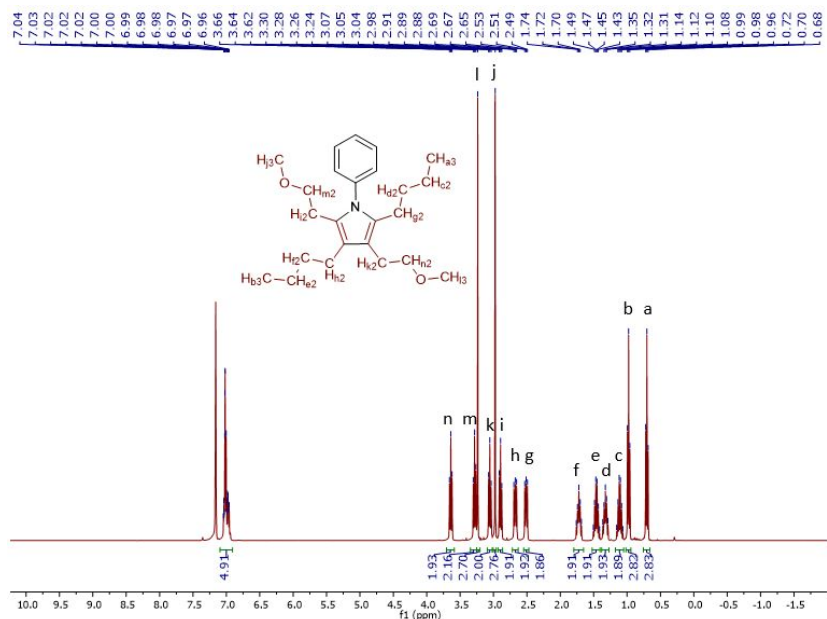


The product was isolated by silica gel chromatography using 3% EA/Hex eluent to give a colorless oil (116 mg, 62% yield).

**<sup>1</sup>H NMR** (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.04-6.96 (m, 5H), 3.64 (t, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, 2H, 3-NC<sub>4</sub>-CH<sub>2</sub>-CH<sub>2</sub>-OMe), 3.28 (t, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 2H, 5-NC<sub>4</sub>-CH<sub>2</sub>-CH<sub>2</sub>-OMe), 3.24 (s, 3H, 3-NC<sub>4</sub>-CH<sub>2</sub>-CH<sub>2</sub>-OCH<sub>3</sub>), 3.05 (t, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 2H, 3-NC<sub>4</sub>-CH<sub>2</sub>-CH<sub>2</sub>-OMe), 2.98 (s, 3H, 3-NC<sub>4</sub>-CH<sub>2</sub>-CH<sub>2</sub>-OCH<sub>3</sub>), 2.89 (t, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 2H, 5-NC<sub>4</sub>-CH<sub>2</sub>-CH<sub>2</sub>-OMe), 2.69-2.65 (m, 2H, 4-NC<sub>4</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 2.53-2.49 (m, 2H, 2-NC<sub>4</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 1.76-1.68 (m, 2H, 4-NC<sub>4</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 1.46 (app sex, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, 4-NC<sub>4</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 1.36-1.29 (m, 2H, 2-NC<sub>4</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 1.11 (app sex, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, 2-NC<sub>4</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 0.98 (t, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, 3H, 4-NC<sub>4</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 0.70 (t, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, 3H, 2-NC<sub>4</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>) ppm.

**<sup>13</sup>C NMR** (101 MHz, C<sub>6</sub>D<sub>6</sub>): δ 140.0, 130.7, 129.4, 129.0, 127.7, 125.2, 120.7, 115.2, 74.8, 73.0, 58.4, 58.1, 35.2, 33.5, 26.3, 26.0, 25.4, 25.1, 23.5, 22.8, 14.4, 14.0 ppm.

**GC-HRMS:** calculated for C<sub>24</sub>H<sub>37</sub>NO<sub>2</sub> [M<sup>+</sup>] 371.2824; found 371.2805.



**Figure S145.** <sup>1</sup>H NMR spectrum of **6z** in C<sub>6</sub>D<sub>6</sub>.

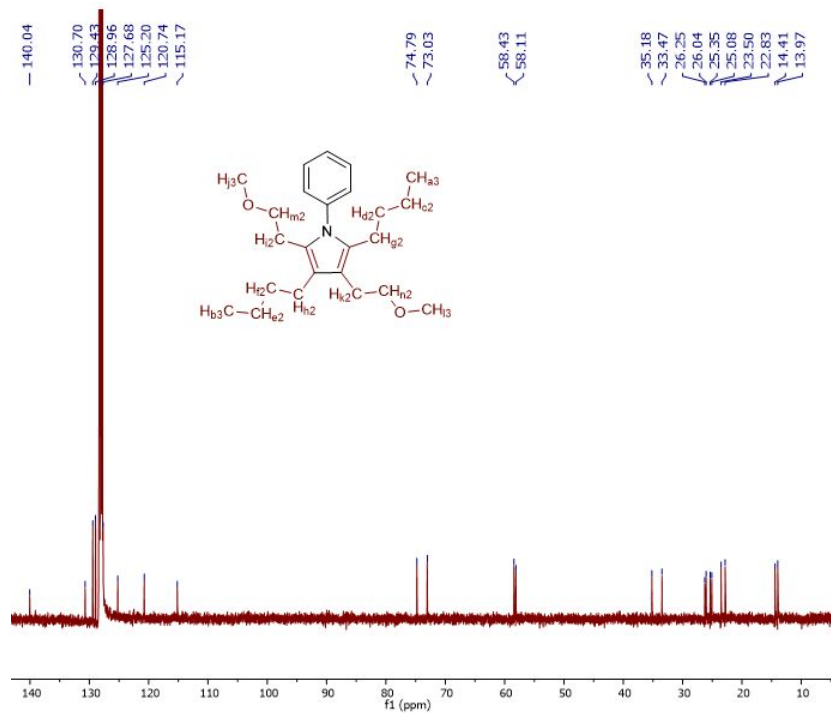


Figure S146.  $^{13}\text{C}$  NMR spectrum of **6z** in  $\text{C}_6\text{D}_6$ .

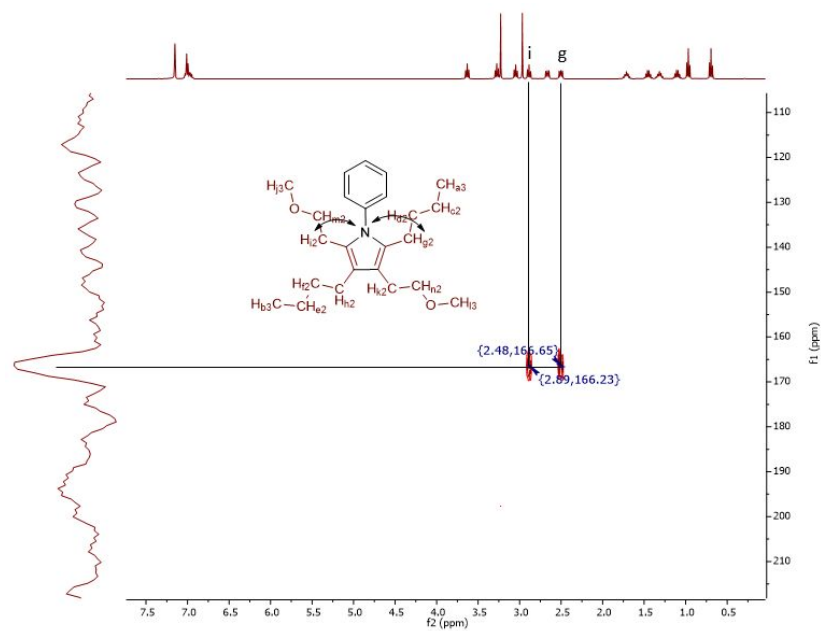
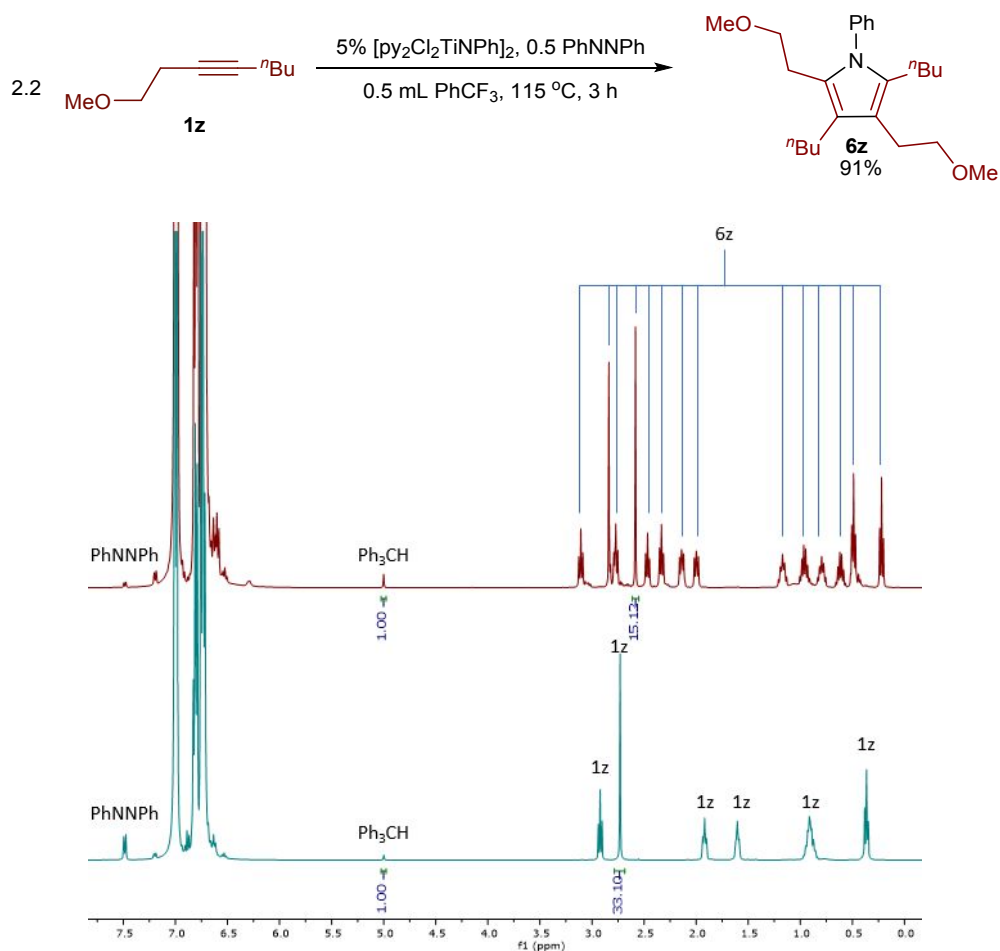


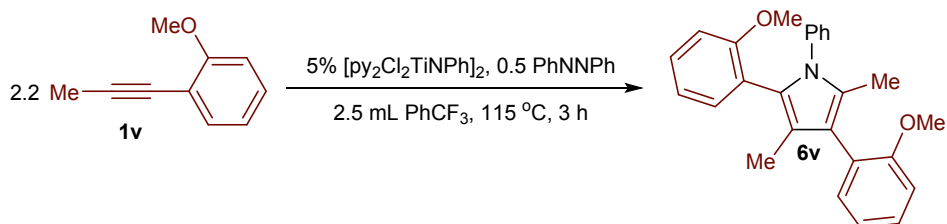
Figure S147.  $^1\text{H}-^{15}\text{N}$  HMBC NMR spectrum of **6z** in  $\text{C}_6\text{D}_6$ .

No-D  $^1\text{H}$  NMR spectra of the reactions of **1z**



**Figure S148.** No-D  $^1\text{H}$  NMR reaction of **1z** in  $\text{PhCF}_3$  at Time = 0 h (bottom), Time = 2 h (top) under Condition B.

### Synthesis of 2,4-bis(2-methoxyphenyl)-3,5-dimethyl-1-phenyl-1H-pyrrole (**6v**)



The product was isolated by silica gel chromatography using 8% EA/Hex eluent and then recrystallized from pentane to give a white solid (89 mg, 46% yield).

$^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$  at  $55 \text{ }^\circ\text{C}$ ):  $\delta$  7.43 (broad d,  $^3J_{\text{HH}} = 6.3 \text{ Hz}$ , 1H), 7.28 (broad d,  $^3J_{\text{HH}} = 7.1 \text{ Hz}$ , 1H), 7.19 (ddd,  $^3J_{\text{HH}} = 8.2$ , 7.2 Hz,  $^4J_{\text{HH}} = 1.8 \text{ Hz}$ , 1H), 7.09-7.07 (m, 2H), 7.01-6.96 (m, 2H), 6.91 (t,  $^3J_{\text{HH}} = 7.8 \text{ Hz}$ , 2H), 6.85-6.75 (m, 3H), 6.46 (d,  $^3J_{\text{HH}} = 8.2 \text{ Hz}$ , 1H), 3.41 (s, 3H, -OCH<sub>3</sub>), 3.13 (s, 3H, -OCH<sub>3</sub>), 2.20 (s, 3H, 3-NC<sub>4</sub>-CH<sub>3</sub>), 2.17 (s, 3H, 5-NC<sub>4</sub>-CH<sub>3</sub>) ppm.

$^{13}\text{C}$  NMR (101 MHz,  $\text{C}_6\text{D}_6$  at 55  $^\circ\text{C}$ ):  $\delta$  158.6, 158.3, 140.8, 133.6, 133.4, 128.6, 128.5, 128.2, 127.9, 127.2, 126.9, 126.7, 126.3, 123.9, 120.8, 120.4, 120.3, 118.1, 111.8, 111.2, 55.2, 54.6, 12.4, 11.3 ppm.

GC-HRMS: calculated for  $\text{C}_{26}\text{H}_{25}\text{NO}_2$  [ $\text{M}^+$ ] 383.1885; found 383.1851.

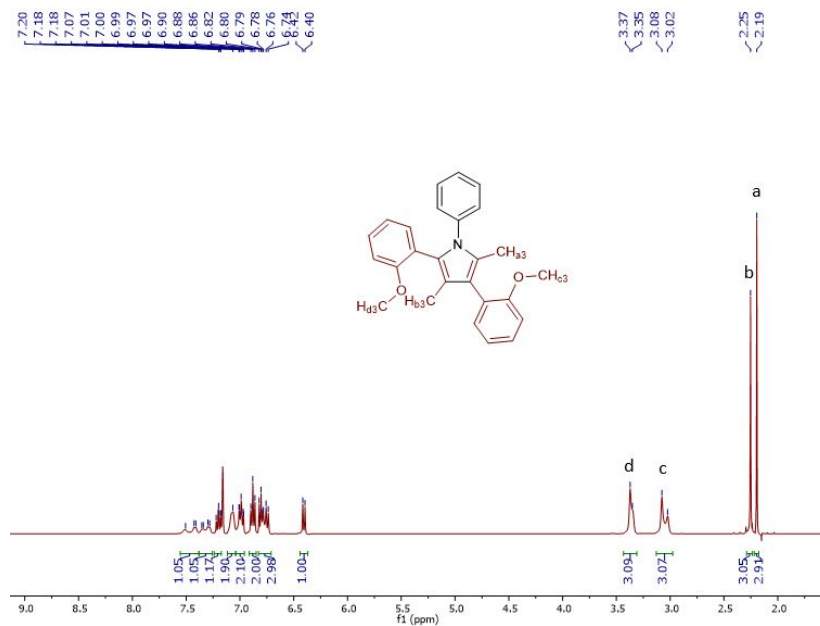


Figure S149.  $^1\text{H}$  NMR spectrum of **6v** in  $\text{C}_6\text{D}_6$  at ambient temperature.

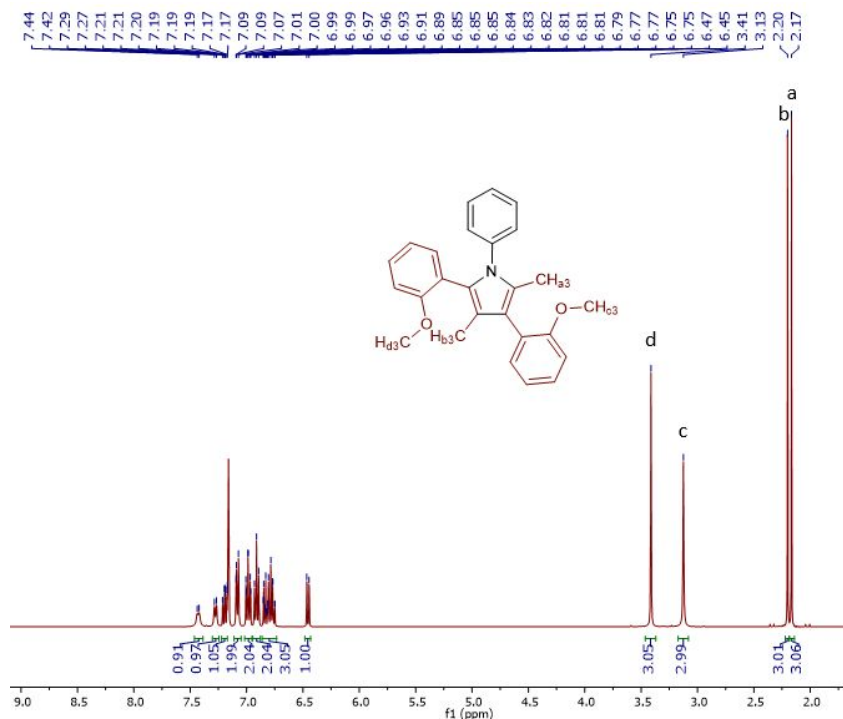
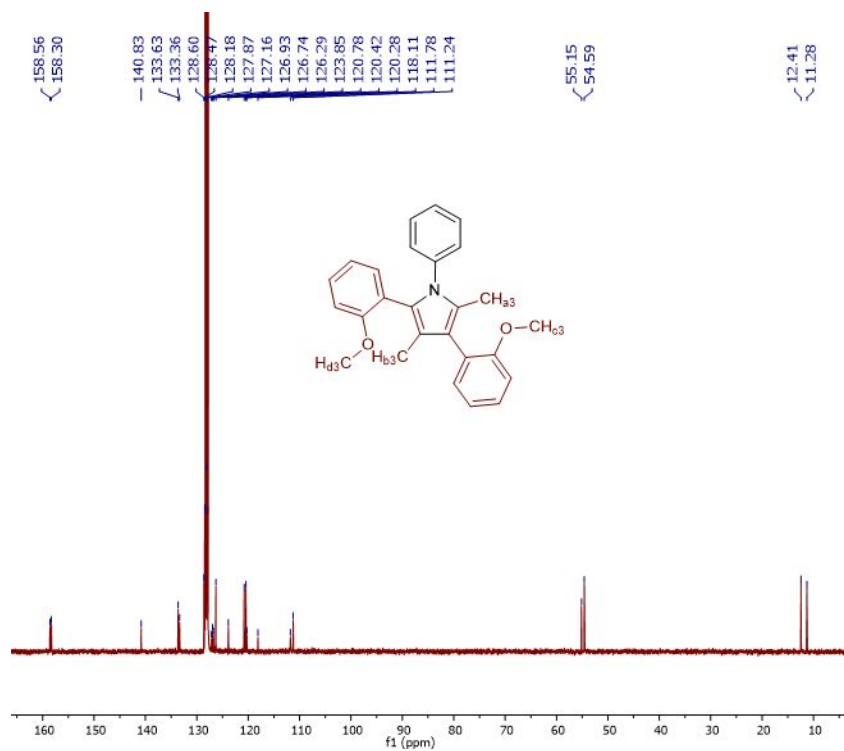
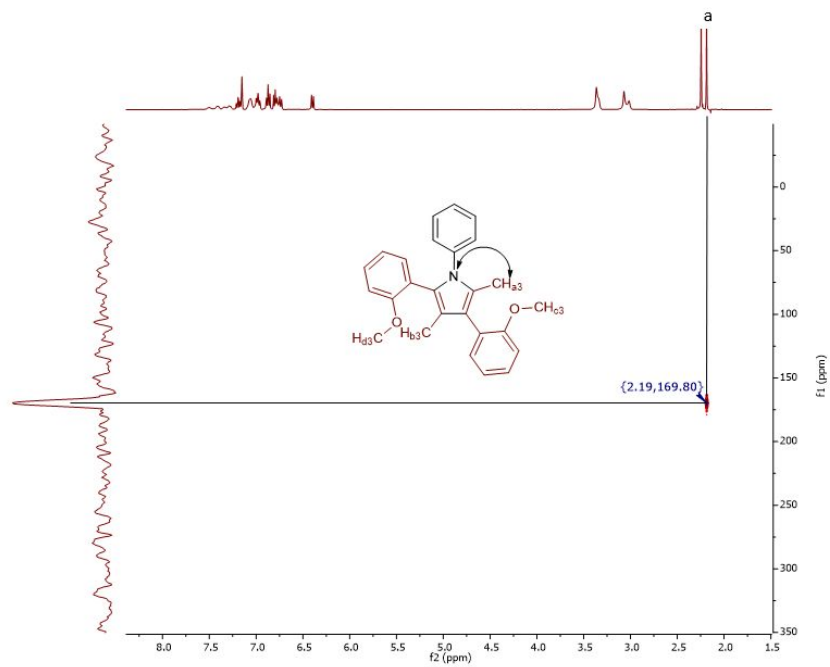


Figure S150.  $^1\text{H}$  NMR spectrum of **6v** in  $\text{C}_6\text{D}_6$  at 55  $^\circ\text{C}$ .

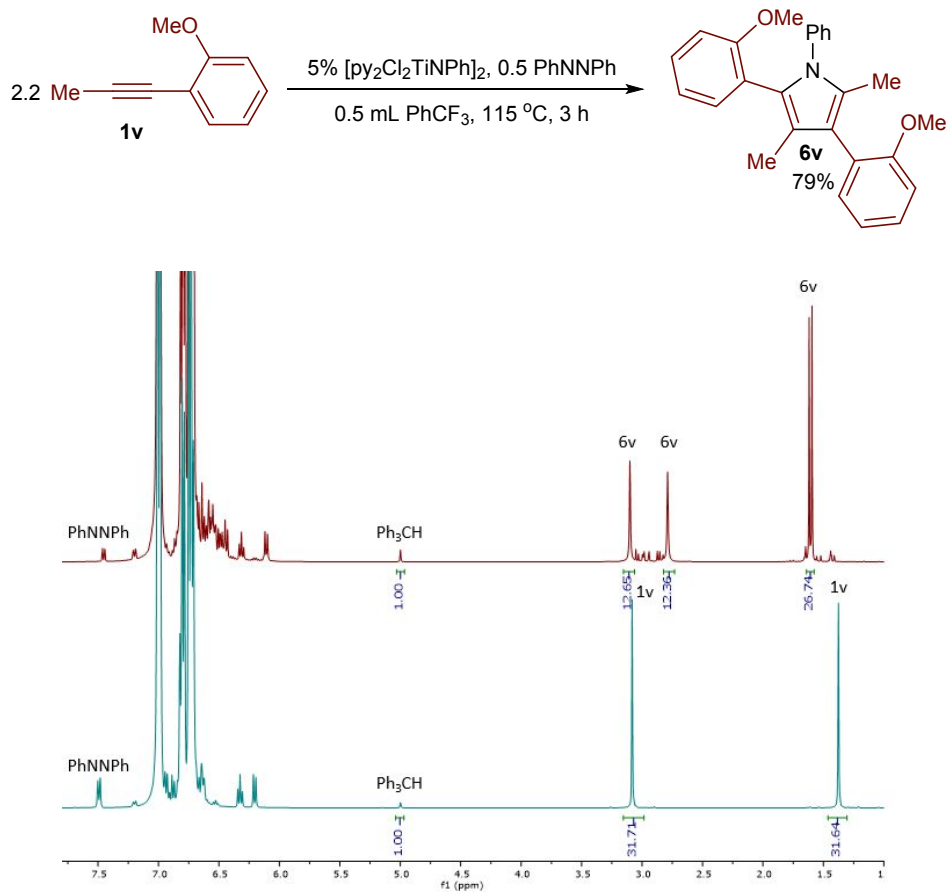


**Figure S151.** <sup>13</sup>C NMR spectrum of **6v** in C<sub>6</sub>D<sub>6</sub> at 55 °C.

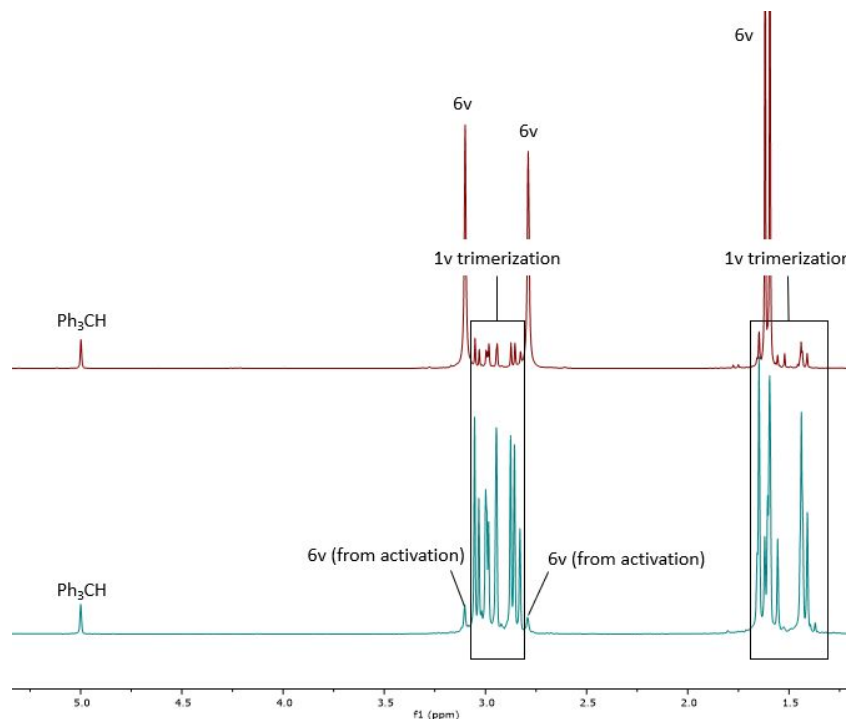


**Figure S152.** <sup>1</sup>H-<sup>15</sup>N HMBC NMR spectrum of **6v** in C<sub>6</sub>D<sub>6</sub> at ambient temperature.

### No-D $^1\text{H}$ NMR spectra of the reactions of **1v**

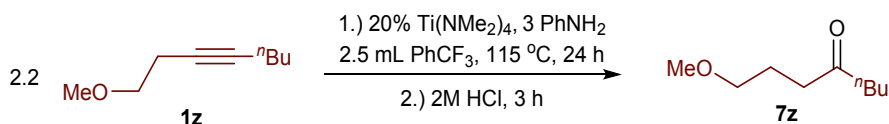


**Figure S153.** No-D  $^1\text{H}$  NMR reaction of **1v** in  $\text{PhCF}_3$  at Time = 0 h (bottom), Time = 2 h (top) under Condition B. The top spectrum was taken at 55  $^\circ\text{C}$  because of the rotameric character of **6v**.



**Figure S154.** No-D  $^1\text{H}$  NMR reaction of **1v** in  $\text{PhCF}_3$  at Time = 2 h under Condition B with (top) and without (bottom) azobenzene. Both spectra were taken at 55 °C because of the rotameric character of all the products, including **6v**.

### Synthesis of 1-Methoxyoctan-4-one (**7z**) from the Hydroamination Reaction



In a glovebox, to a 7 mL vial was added 140 mg **1z** (1 mmol, 1 eq.), 279 mg  $\text{PhNH}_2$  (3 mmol, 3 eq.), 44.8 mg  $\text{Ti}(\text{NMe}_2)_4$  (0.2 mmol, 0.2 eq.), and 2.5 mL  $\text{PhCF}_3$ . The reaction was then sealed with a Teflon screw cap and heated outside of the glovebox for 24 hours at 115 °C. The reaction cooled to room temperature and layered with 3 mL 2 M  $\text{HCl}_{(\text{aq})}$  and vigorously stirred for 3 hours. The aqueous layer was extracted by dichloromethane (2 mL X 3) and the volatiles of combined organic solution were removed in vacuo. The crude oil was mixed with 2 mL hexanes and filtered. Volatiles were removed in vacuo to yield a brown oil (108 mg, 67% yield).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.37 (t,  $^3J_{\text{HH}} = 6.1$  Hz, 2H,  $-\text{CH}_2-\text{OMe}$ ), 3.31 (s, 3H,  $-\text{OCH}_3$ ), 2.49 (t,  $^3J_{\text{HH}} = 7.3$  Hz, 2H,  $-\text{C}(\text{O})-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OMe}$ ), 2.40 (t,  $^3J_{\text{HH}} = 7.5$  Hz, 2H,  $-\text{C}(\text{O})-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$ ), 1.84 (app p,  $^3J_{\text{HH}} = 7.0$  Hz, 2H,  $-\text{C}(\text{O})\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OMe}$ ), 1.55 (app p,  $^3J_{\text{HH}} = 7.6$  Hz, 2H,  $-\text{C}(\text{O})\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$ ), 1.30 (app six,  $^3J_{\text{HH}} = 7.6$  Hz, 2H,  $-\text{C}(\text{O})\text{CH}_2\text{CH}_2-\text{CH}_2-\text{CH}_3$ ), 0.90 (t,  $^3J_{\text{HH}} = 7.4$  Hz, 3H,  $-\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2-\text{CH}_3$ ) ppm.

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  211.2, 71.9, 58.6, 42.8, 39.3, 26.1, 23.9, 22.5, 14.0 ppm.

ESI-HRMS: calculated for  $\text{C}_9\text{H}_{18}\text{O}_2$  [ $\text{M}+\text{Na}^+$ ] 181.1204; found 181.1215.

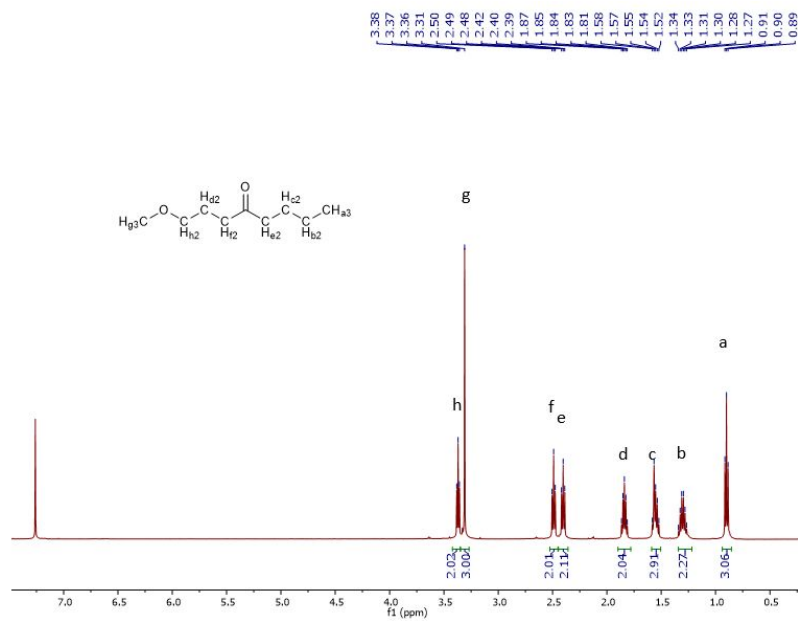


Figure S155. <sup>1</sup>H NMR spectrum of 7z in CDCl<sub>3</sub>.

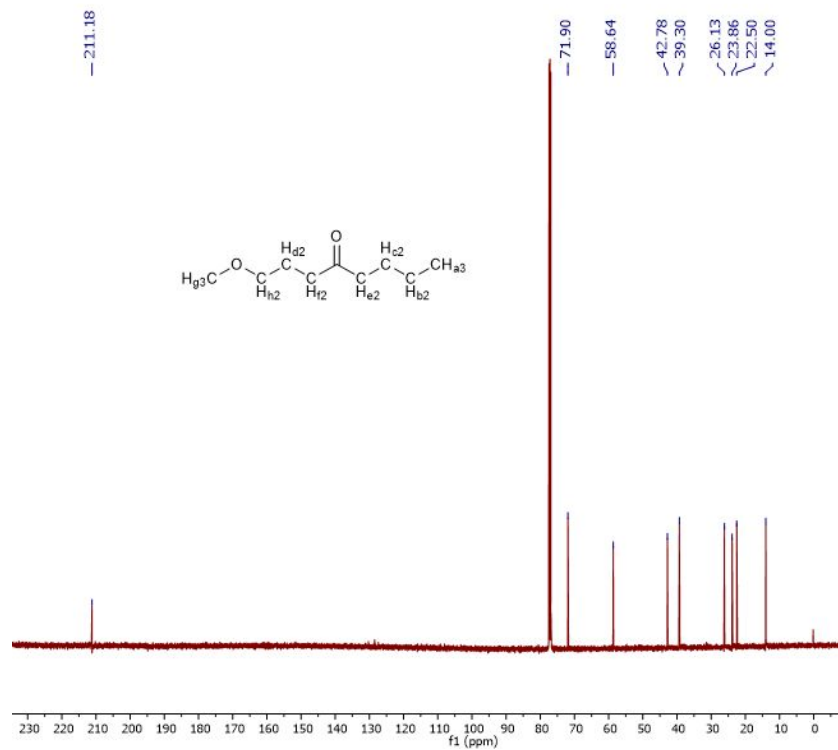
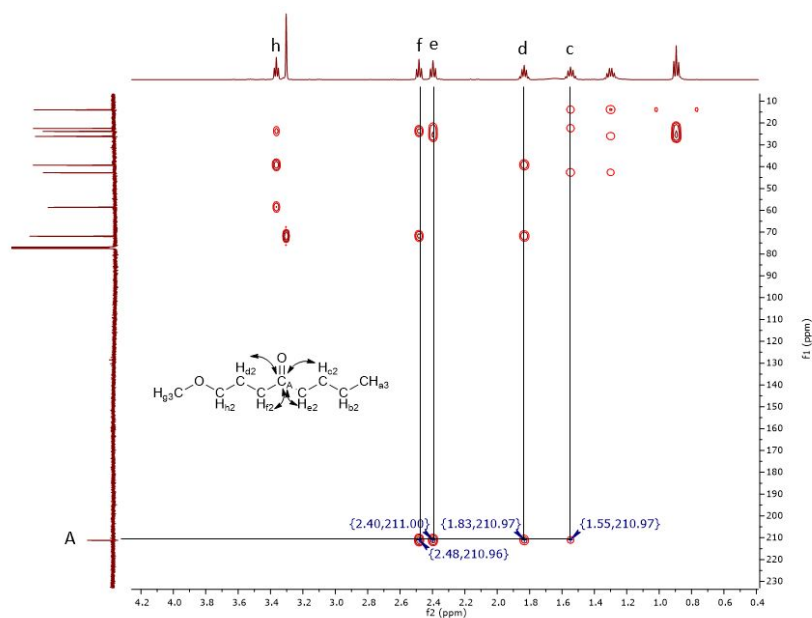


Figure S156. <sup>13</sup>C NMR spectrum of 7z in CDCl<sub>3</sub>.

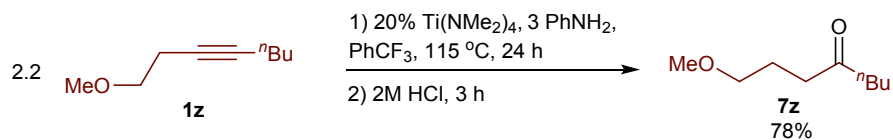


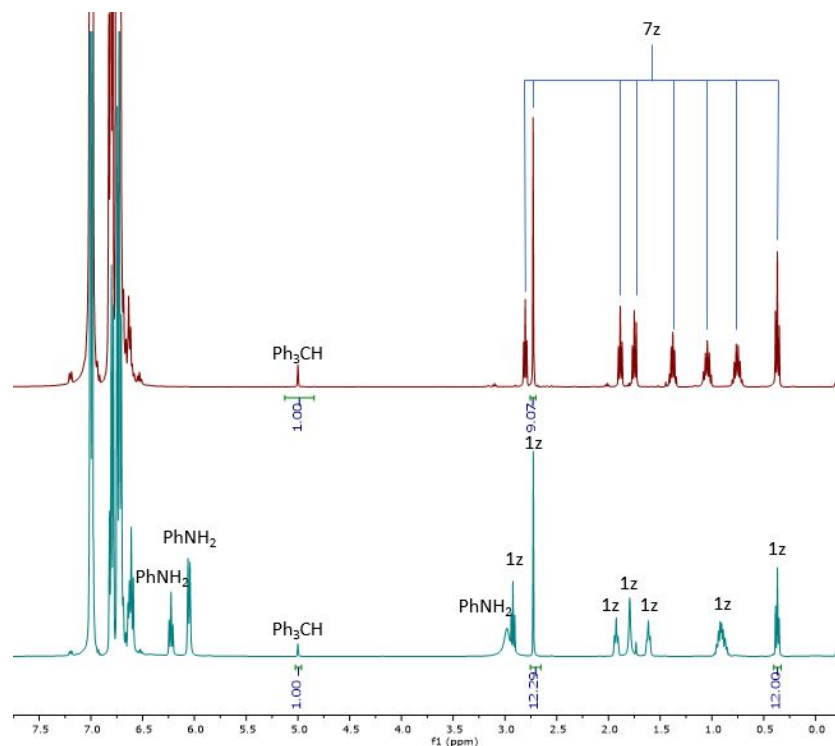
**Figure S157.** <sup>1</sup>H-<sup>13</sup>C HMBC NMR spectrum of **7z** in CDCl<sub>3</sub>.

### Procedure of No-D <sup>1</sup>H NMR Experiments for the Hydroamination Reaction

In a glovebox, to a NMR tube was added 28.0 mg **1z** (0.2 mmol, 1 eq.), 55.8 mg PhNH<sub>2</sub> (0.6 mmol, 3 eq.), 8.9 mg Ti(NMe<sub>2</sub>)<sub>4</sub> (0.04 mmol, 0.2 eq.), and 0.5 mL PhCF<sub>3</sub>. The reaction was then sealed and heated outside of the glovebox for 24 hours at 115 °C. The no-D <sup>1</sup>H NMR spectrum was collected on a Bruker Avance III HD NanoBay 400 MHz spectrometer referenced to the proton signal of triphenylmethane (Ph<sub>3</sub>CH, ppm = 5.0) at a delay time = 30 and acquisition time = 5.

### No-D <sup>1</sup>H NMR spectra of the reactions of **1z**





**Figure S158.** No-D  $^1\text{H}$  NMR reaction of **1z** in  $\text{PhCF}_3$  at Time = 0 h (bottom), Time = 24 h after acidic workup. (top).

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