

Supplementary Information for:

Generation of  $Ti^{II}$  Alkyne Trimerization Catalysts in the Absence of Strong Metal Reductants

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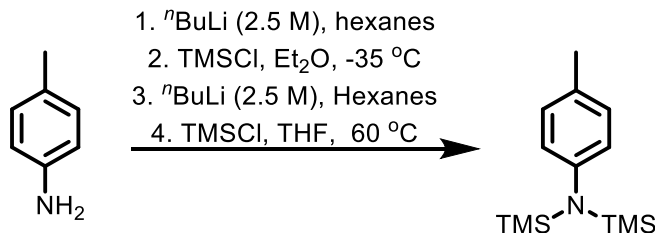
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### Additional General Considerations

1,2-di(*p*-tolyl)diazene<sup>1</sup> and 5,7-dodecadiyne<sup>2</sup> were prepared following literature procedures. Azobenzene<sup>3</sup> was purified *via* recrystallization and sublimation prior to use.

Synthesis of N-(*p*-tolyl)-N,N-bis(trimethylsilyl)amine



*p*-toluidine (4.26 g, 39.8 mmol, 1.0 equiv.) and 20 mL hexanes were added to a 250 mL round-bottom flask equipped with a stirbar and cooled to -35 °C in a N<sub>2</sub>-filled glovebox. <sup>n</sup>BuLi (2.5 M, 16 mL, 40.0 mmol, 1.0 equiv.) was then added dropwise to the reaction mixture with stirring. This was allowed to warm up to room temperature and stirred for 30 min. The resulting yellow/white precipitate (Li-NH-C<sub>6</sub>H<sub>4</sub>-CH<sub>3</sub>) was filtered and washed with 20 mL hexanes. The solids were dissolved in 30 mL Et<sub>2</sub>O and cooled to -35 °C before the dropwise addition of TMSCl (5.05 mL, 39.8 mmol, 1.0 equiv.). This was allowed to warm up to room temperature and stirred for 1 h, during which LiCl precipitate was formed. After which, the mixture was filtered through a celite plug and washed with 10 mL hexanes. The filtrate was concentrated *in vacuo* to remove ether before diluting with 20 mL hexanes. The hexane mixture was then transferred to a separate 250 mL round-bottom flask and *at room temperature* <sup>n</sup>BuLi (2.5 M, 16 mL, 40.0 mmol, 1.0 equiv.) was added in 3 portions (6 mL, 5 mL and 6 mL). During the addition, the solution refluxes, highlighting the necessity of using a sufficiently large flask (best results were obtained when this reaction was allowed to reflux from a fast <sup>n</sup>BuLi addition; slow or cold additions have complicated work-up). After stirring for 1 h, the mixture was filtered through a sintered glass frit, collecting approximately 7 g of the Li-(TMS)N-C<sub>6</sub>H<sub>4</sub>-CH<sub>3</sub> intermediate. The solid was diluted in 20 mL of THF in a 100 mL round bottom flask to give a yellow solution. TMSCl (6.0 mL, 47.2 mmol, 1.2 equiv.) was added dropwise *at room temperature* to the solution (caution: will exotherm). The mixture was heated overnight at 60 – 70 °C to give a clear, nearly colorless solution with white LiCl precipitate. This was cooled to room temperature, diluted with 20 mL hexanes, filtered through a plug of celite and concentrated *in vacuo* to give a cloudy suspension. The suspension was diluted with 5 mL hexanes, passed through a pipette plug of celite to remove residual LiCl and then concentrated *in vacuo* to give a nearly colorless oil of the title compound that should solidify at -35 °C (7.11 g, 71 % yield).

If the solution remains cloudy after concentrating, there may be residual LiCl, further dilution with hexanes and filtering will remove this. If the oil fails to solidify at -35 °C, then there may be residual solvents.

**<sup>1</sup>H-NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):** δ 6.91 (d, <sup>3</sup>J<sub>HH</sub> = 8.1 Hz, 2H, *m*-NTol-*H*), 6.81 (d, <sup>3</sup>J<sub>HH</sub> = 8.1 Hz, 2H, *o*-NTol-*H*), 2.12 (s, 3H, NC<sub>6</sub>H<sub>4</sub>-CH<sub>3</sub>), 0.12 (s, 18H, -Si(CH<sub>3</sub>)).

**<sup>13</sup>C-NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>):** δ 145.3, 133.3, 130.3, 129.6, 20.9, 2.3.

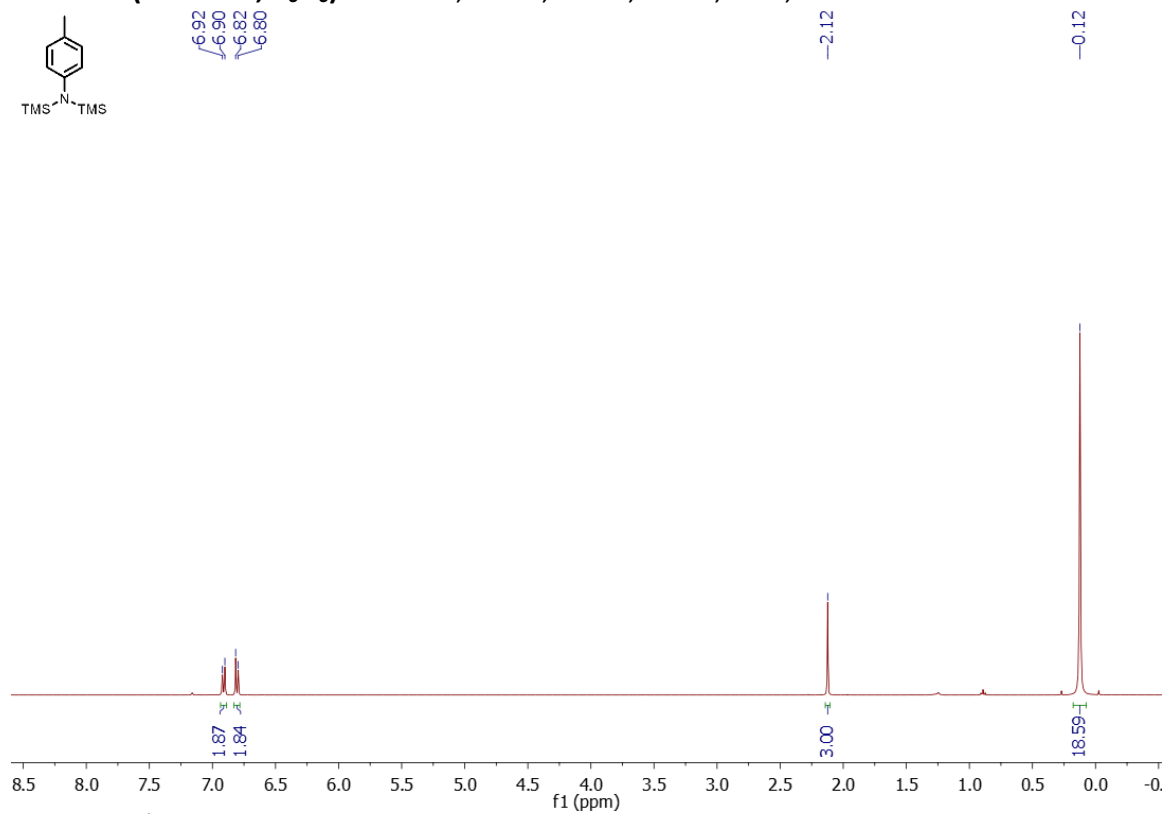


Figure S1: <sup>1</sup>H NMR spectrum of N-(*p*-tolyl)-N,N-bis(trimethylsilyl)amine in C<sub>6</sub>D<sub>6</sub>.

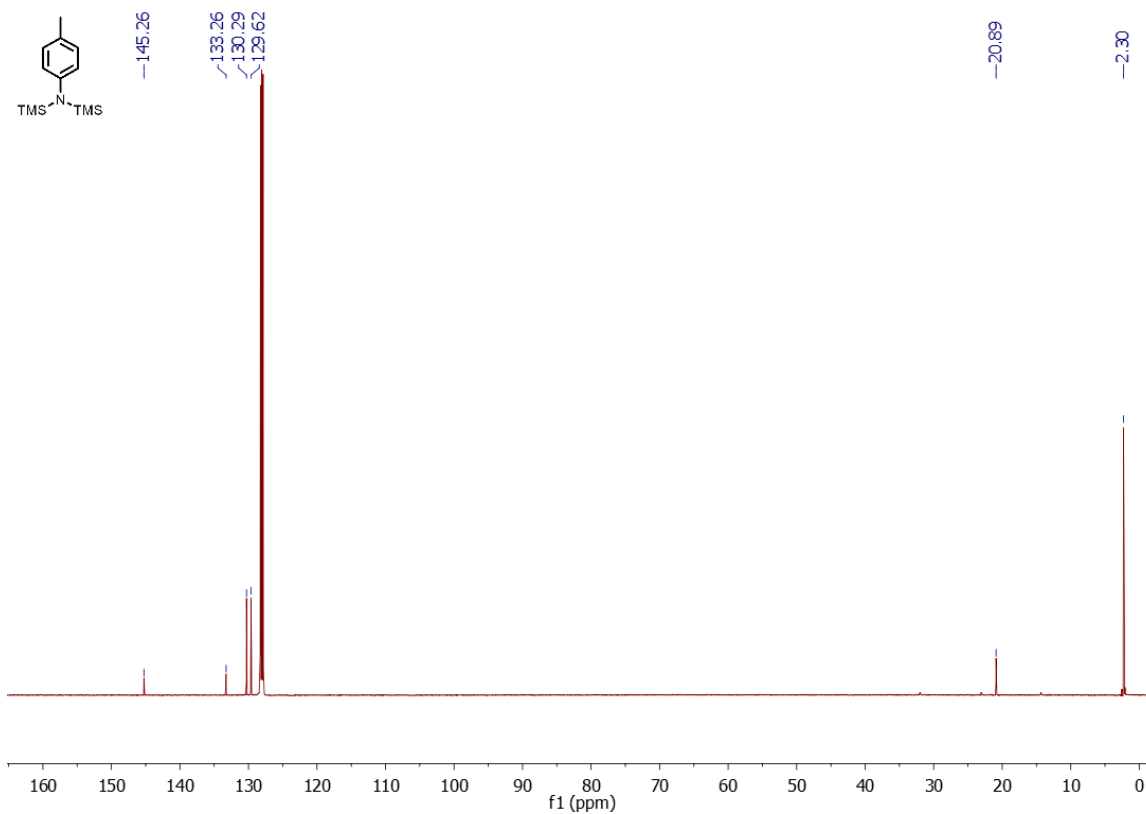
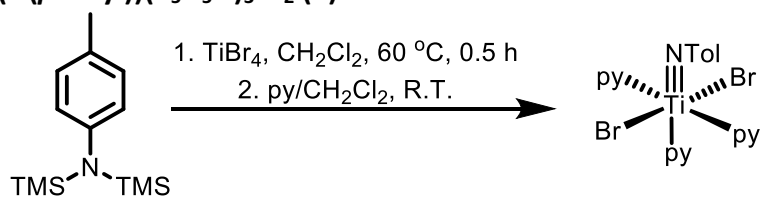


Figure S2: <sup>13</sup>C NMR spectrum of N-(*p*-tolyl)-N,N-bis(trimethylsilyl)amine in C<sub>6</sub>D<sub>6</sub>.

### Synthesis of Ti(*N*(*p*-tolyl))(C<sub>5</sub>H<sub>5</sub>N)<sub>3</sub>Br<sub>2</sub> (2)





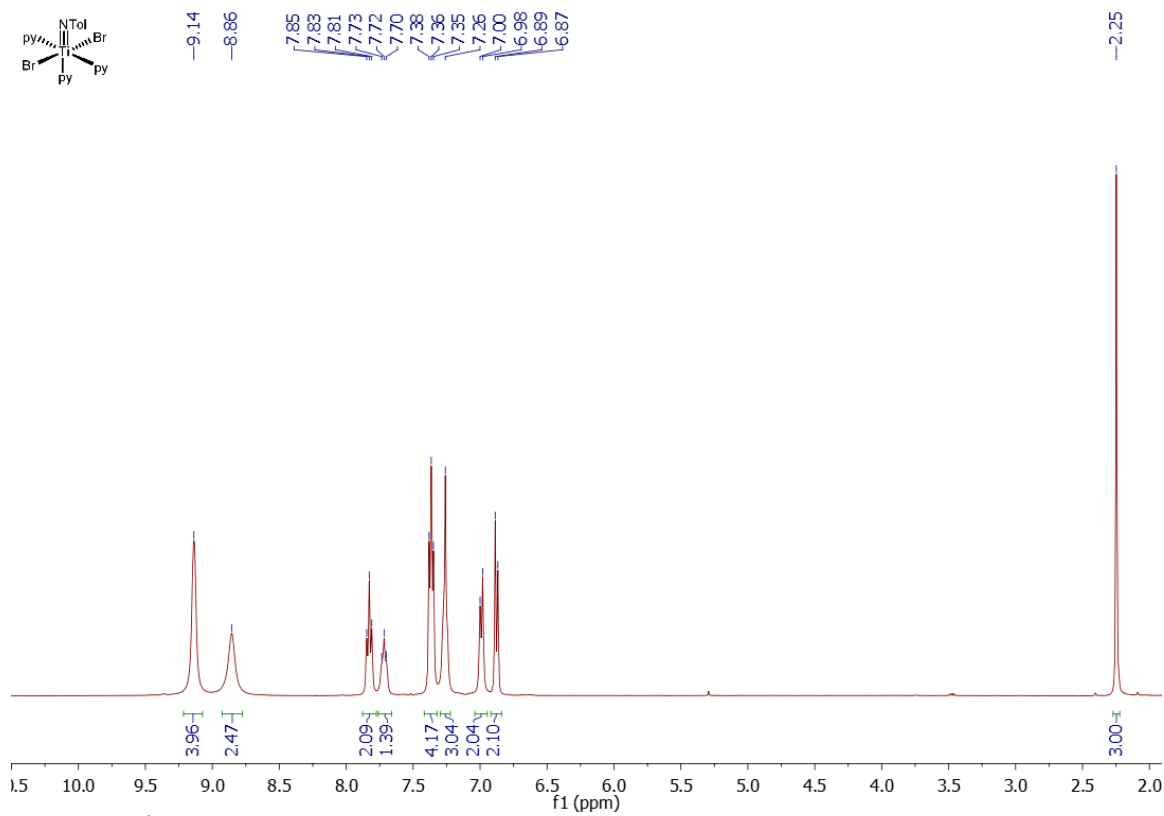


Figure S3: <sup>1</sup>H NMR spectrum of **2** in CDCl<sub>3</sub>.

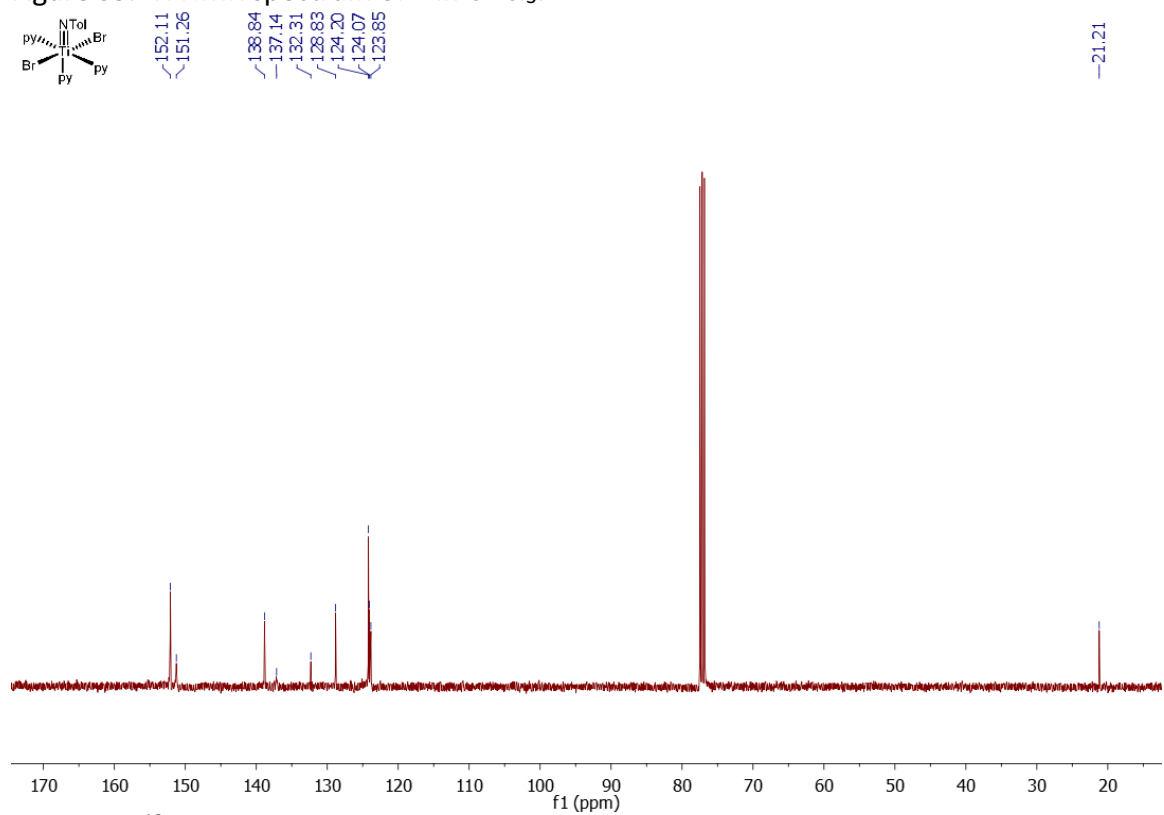


Figure S4: <sup>13</sup>C NMR spectrum of **2** in CDCl<sub>3</sub>.

Synthesis of  $\text{Ti}(\text{N}(p\text{-tolyl}))\text{THF}_3\text{I}_2$  (**3**)

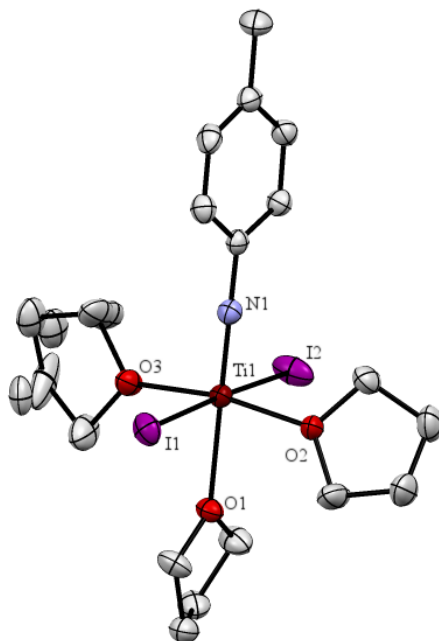
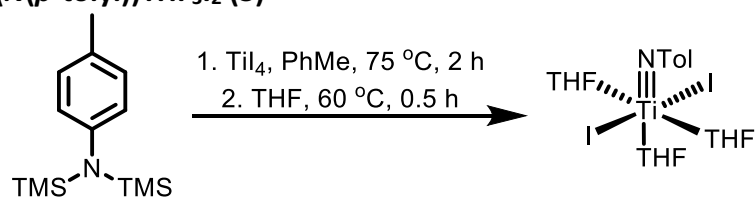


Figure S5: 50 % thermal ellipsoid drawing of **3**. Hydrogen atoms are omitted for clarity.

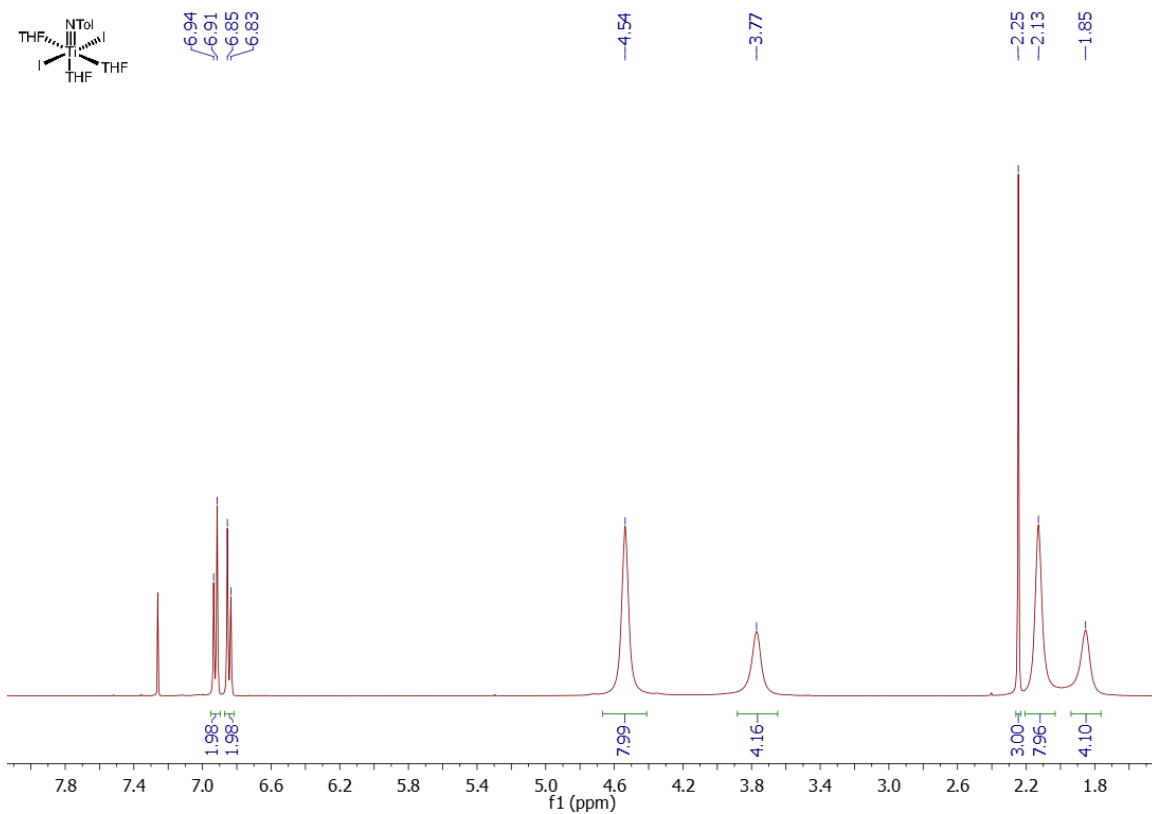


Figure S6: <sup>1</sup>H NMR spectrum of **3** in CDCl<sub>3</sub>.

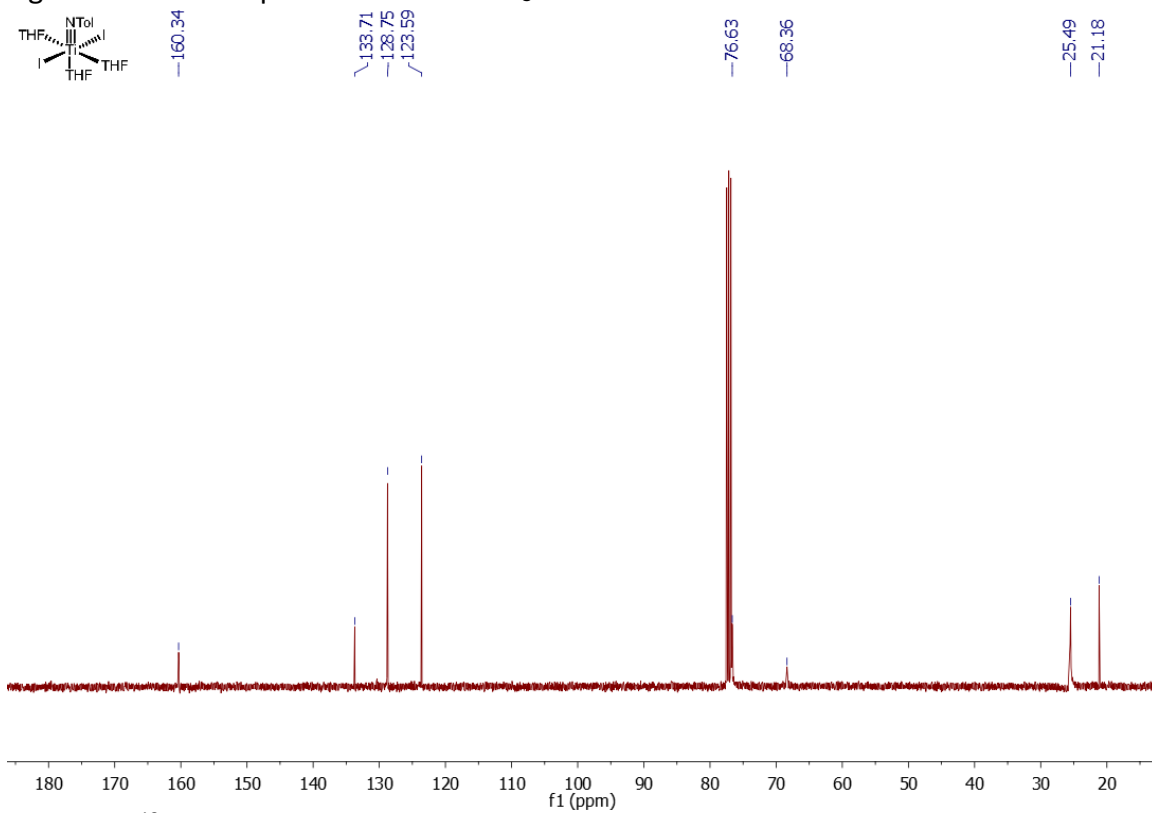


Figure S7: <sup>13</sup>C NMR spectrum of **3** in CDCl<sub>3</sub>.



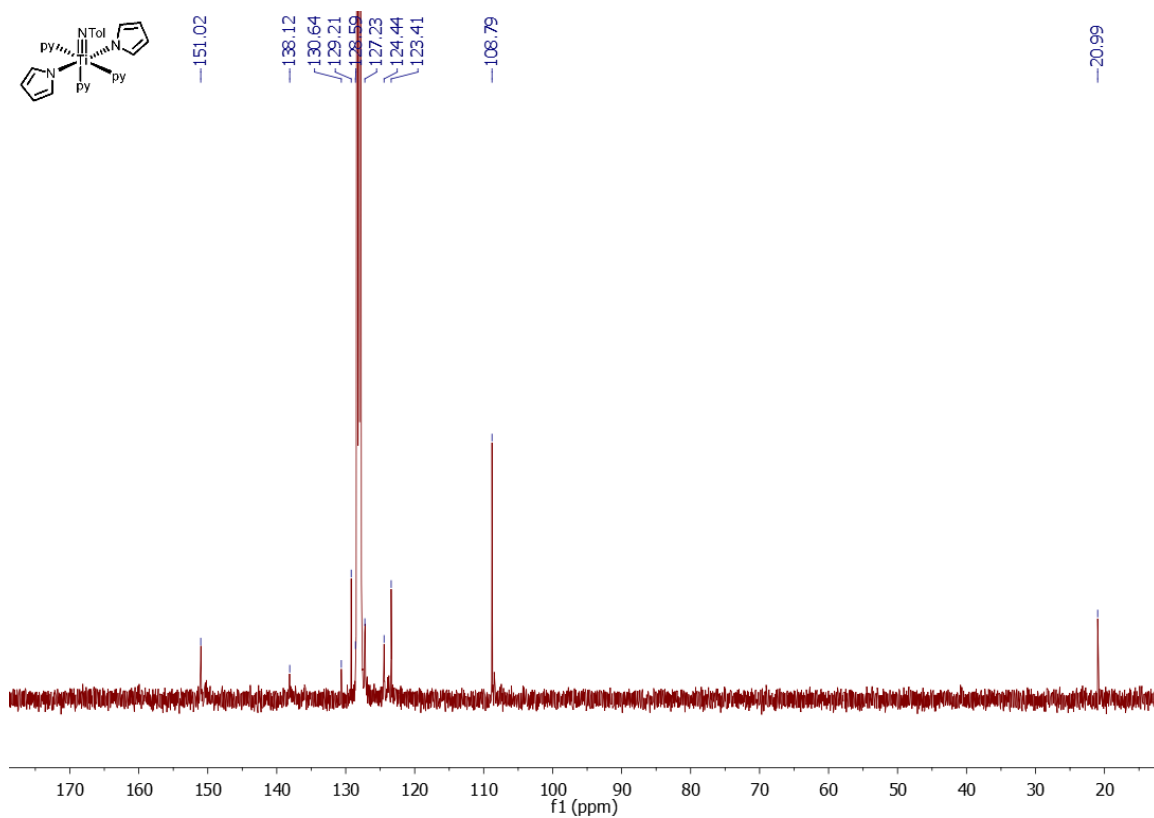
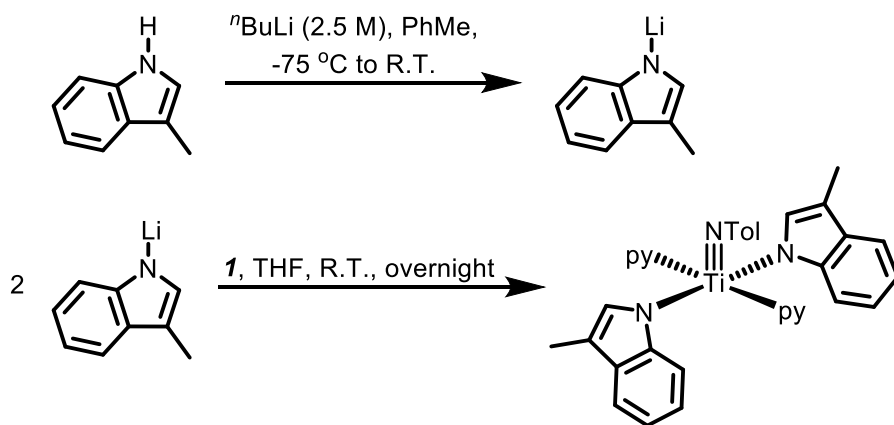


Figure S9:  $^{13}\text{C}$  NMR spectrum of **4** in  $\text{C}_6\text{D}_6$ .

### Synthesis of $\text{Ti}(\text{N}(p\text{-tolyl}))(\text{C}_5\text{H}_5\text{N})_2(\text{skatolide})_2$ (**5**)



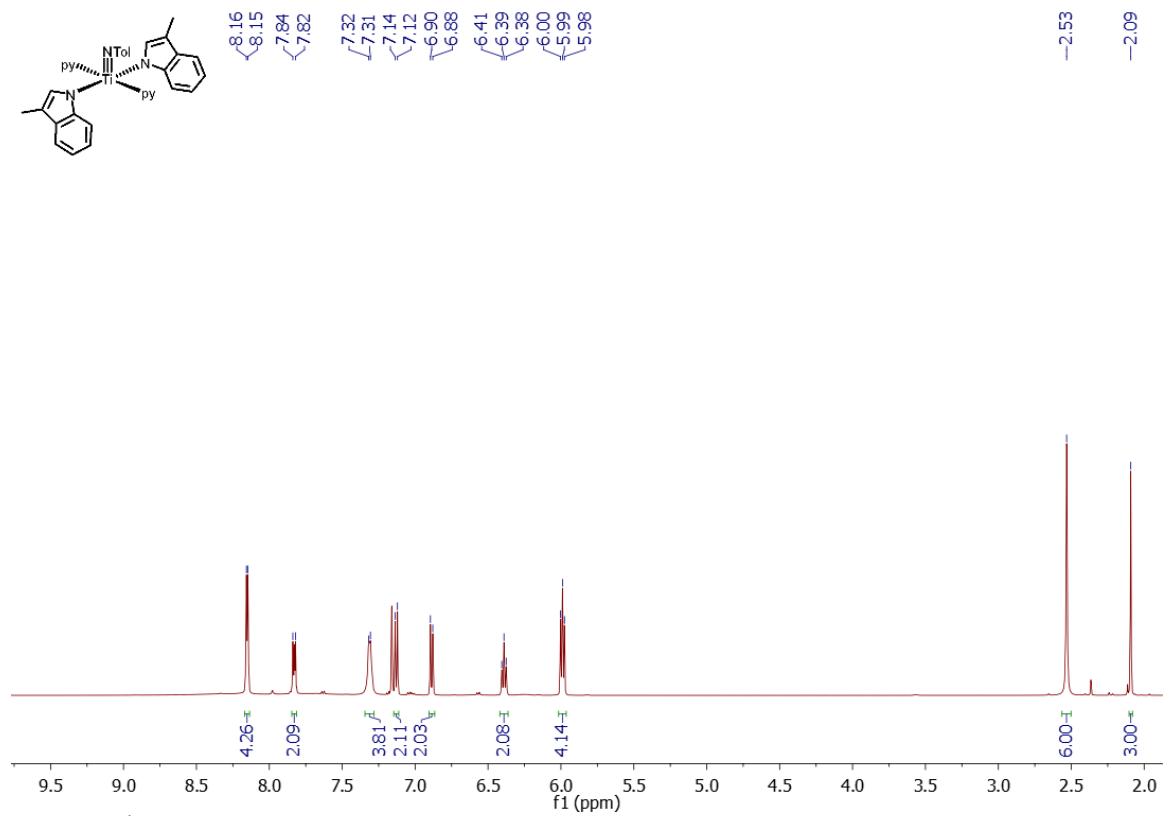


Figure S10: <sup>1</sup>H NMR spectrum of **5** in C<sub>6</sub>D<sub>6</sub>.

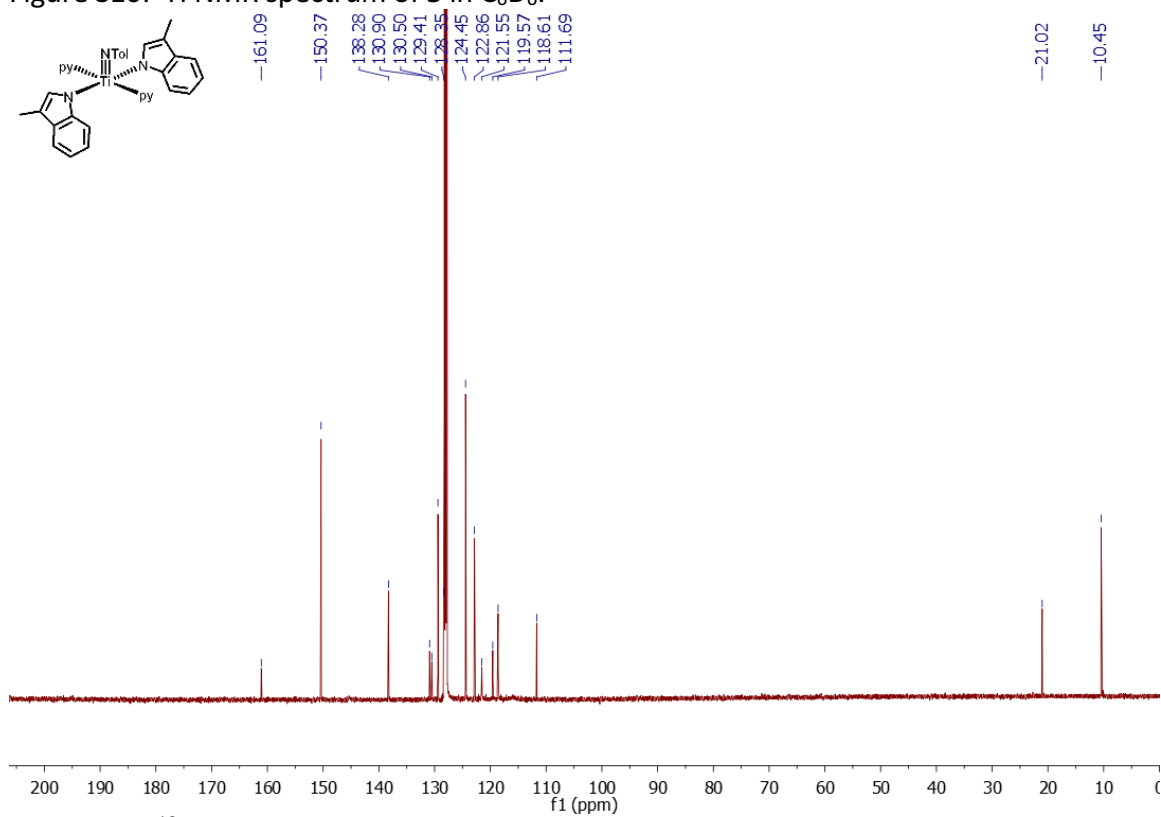


Figure S11: <sup>13</sup>C NMR spectrum of **5** in C<sub>6</sub>D<sub>6</sub>.

Synthesis of  $[\text{Ti}(\mu\text{-NPh})(\text{C}_5\text{H}_5\text{N})(2,6\text{-}i\text{Pr}_2\text{PhO})\text{Cl}]_2$  (**6**)

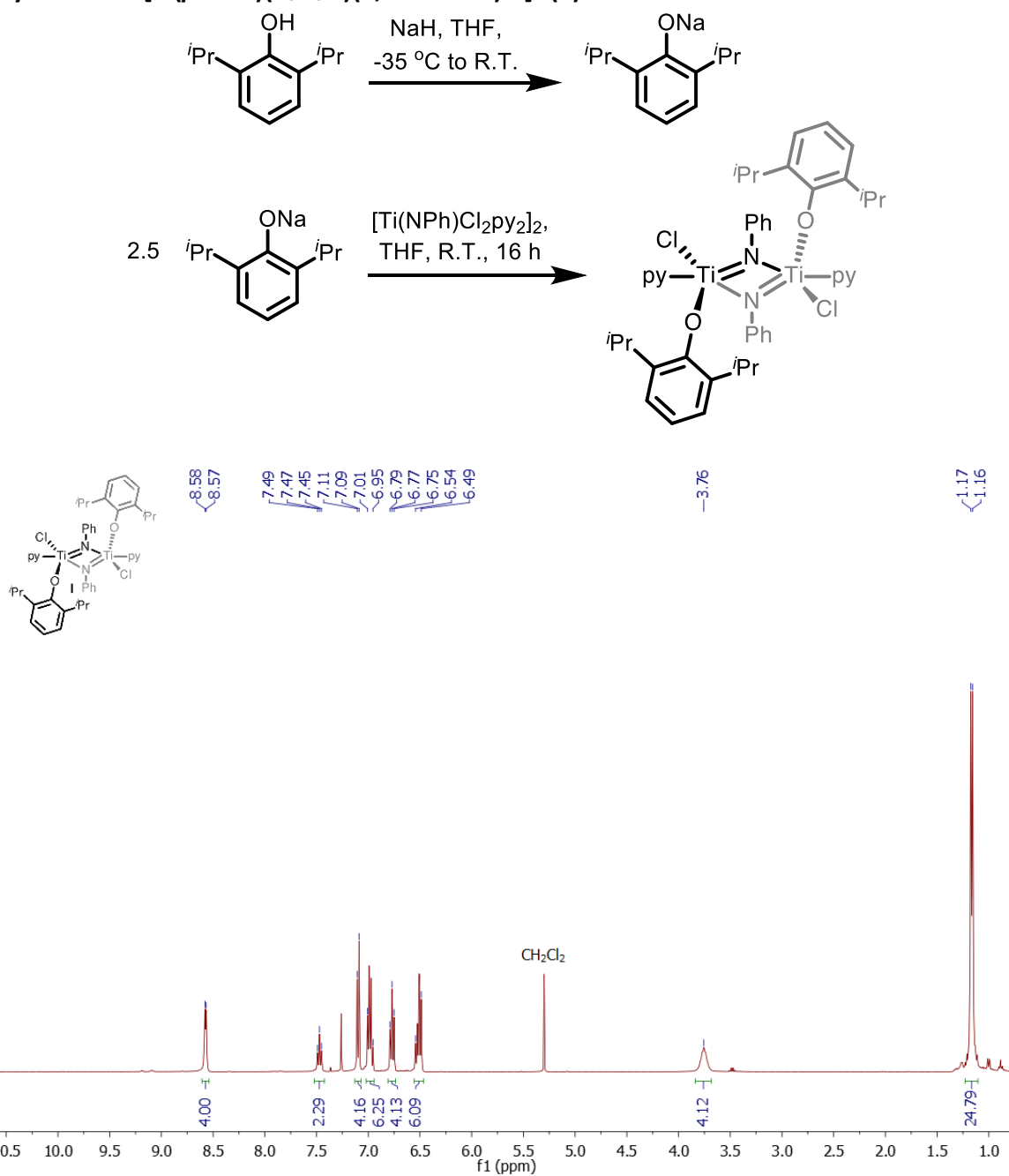


Figure S12:  $^1\text{H}$  NMR spectrum of **6** in CDCl<sub>3</sub>.

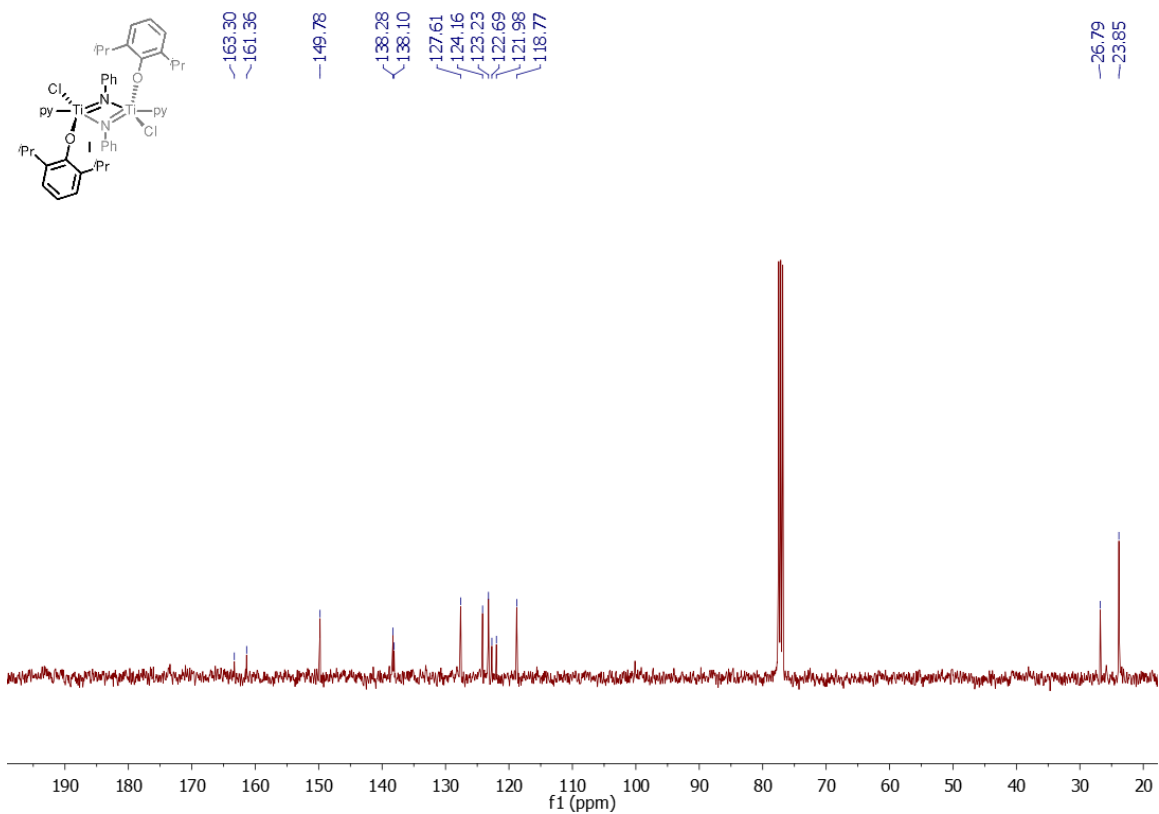
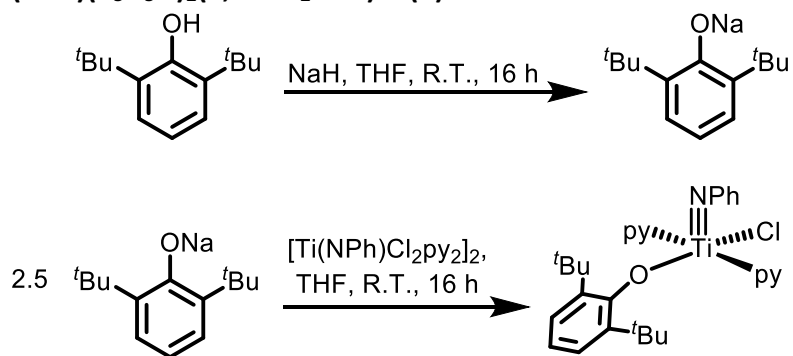


Figure S13:  $^{13}\text{C}$  NMR spectrum of **6** in  $\text{CDCl}_3$ .

### Synthesis of $\text{Ti}(\text{NPh})(\text{C}_5\text{H}_5\text{N})_2(2,6\text{-}^t\text{Bu}_2\text{PhO})\text{Cl}$ (**7**)





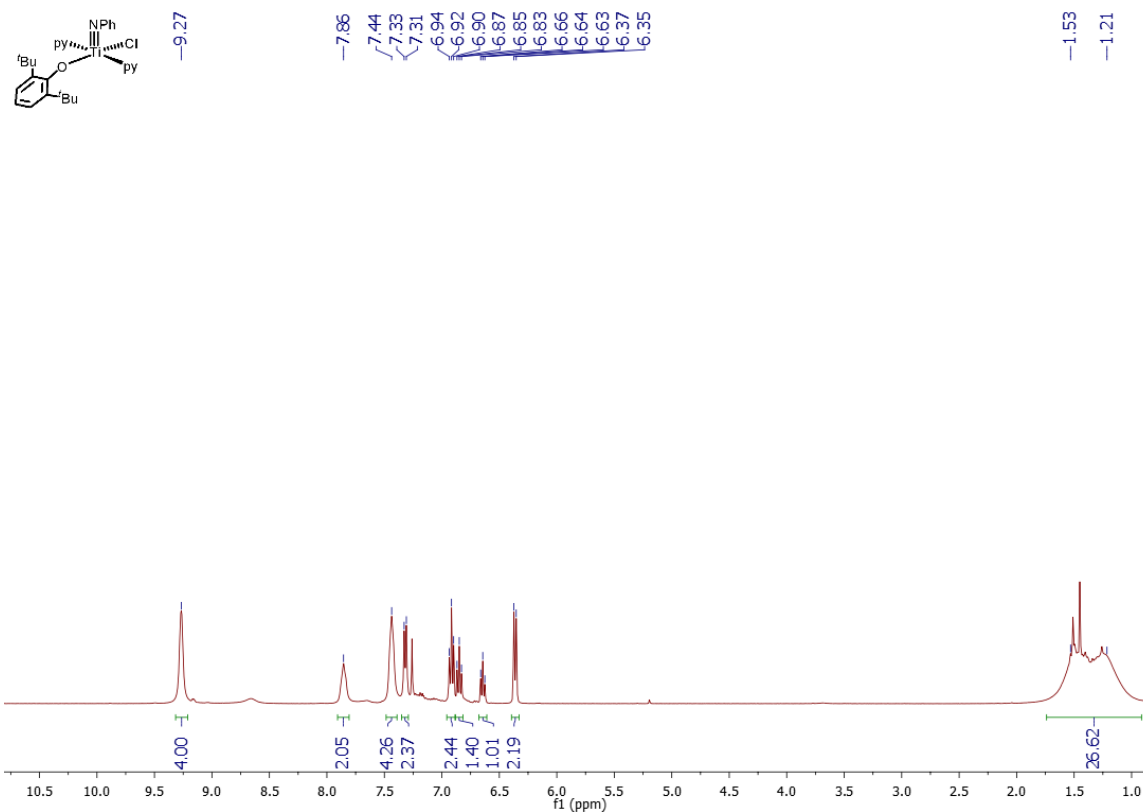
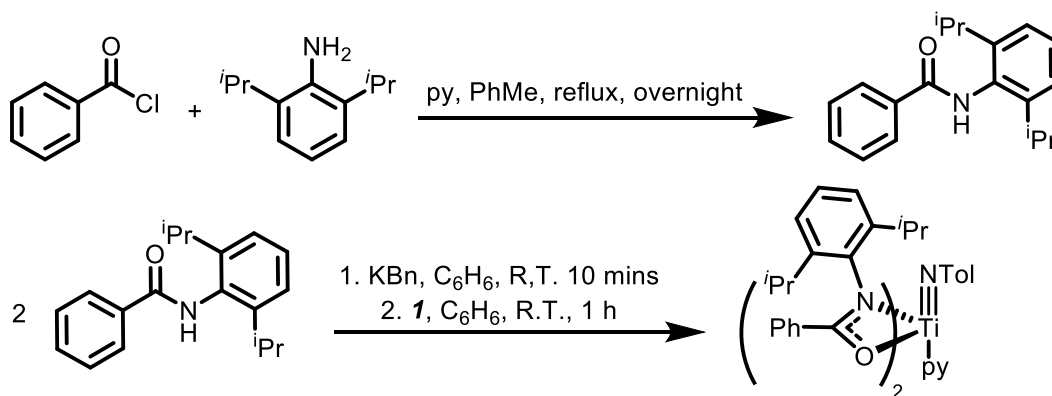


Figure S14:  $^1\text{H}$  NMR spectrum of **7** in  $\text{CDCl}_3$ .

**Synthesis of  $\text{Ti}(\text{N}(p\text{-tolyl}))(\text{C}_5\text{H}_5\text{N})((N\text{-}2',6'\text{-}i\text{Pr}_2\text{Ph})\text{phenylamidate})_2$  (**12**)**



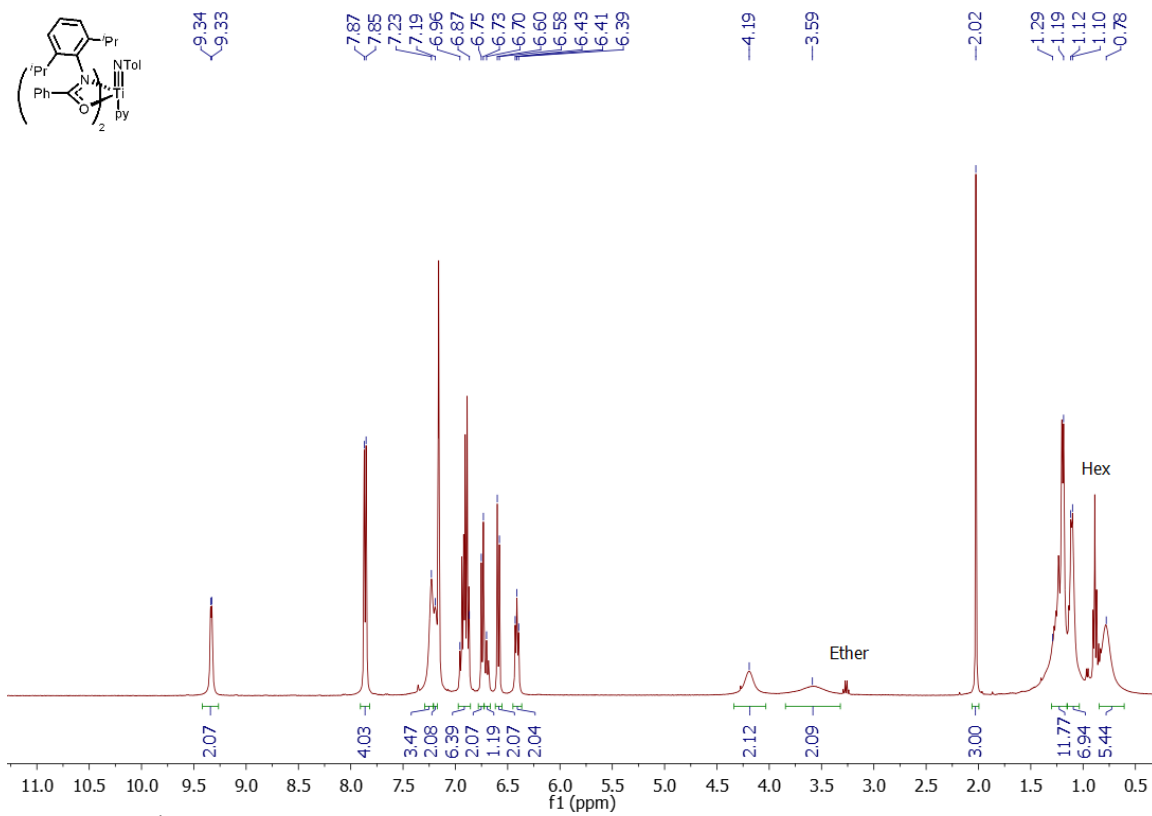


Figure S15:  $^1\text{H}$  NMR spectrum of **12** in  $\text{C}_6\text{D}_6$ .

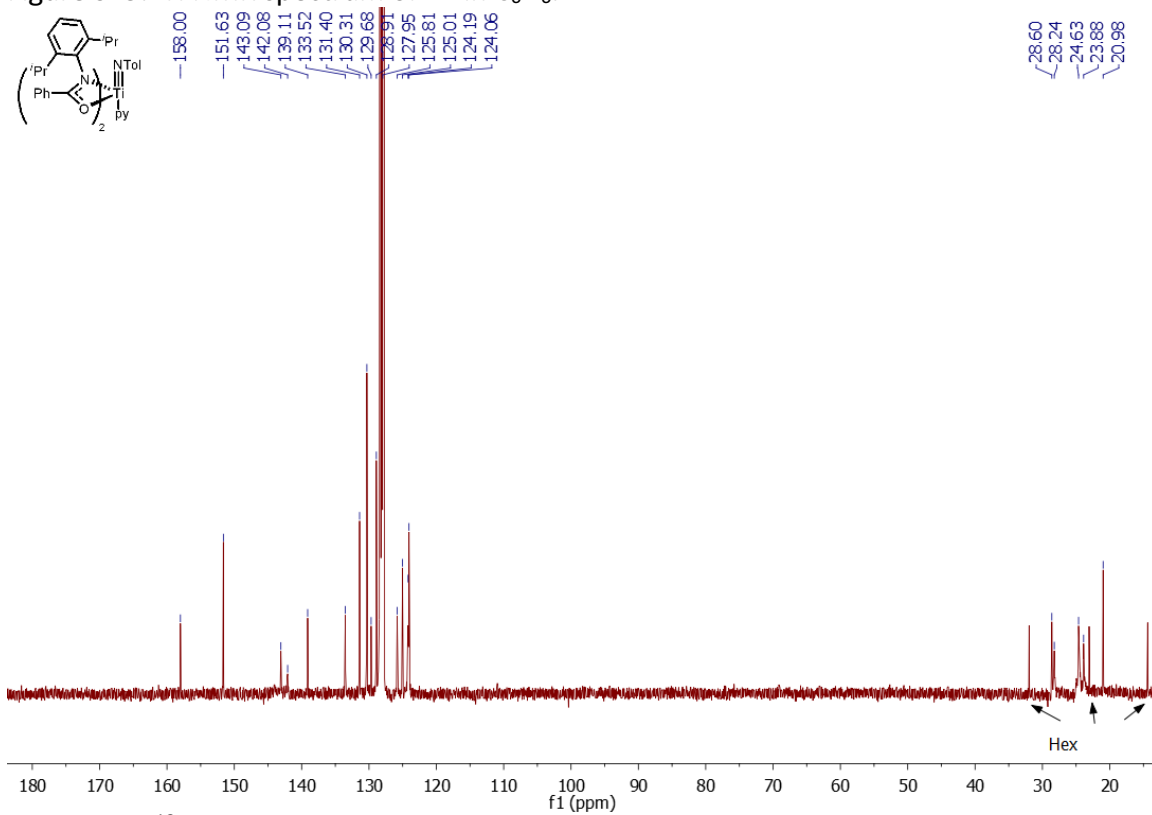


Figure S16:  $^{13}\text{C}$  NMR spectrum of **12** in  $\text{C}_6\text{D}_6$ .

Synthesis of Bis(2,6-*i*Pr<sub>2</sub>Ph-salicylaldimino)Ti(*N*(*p*-tolyl)) (**13**)

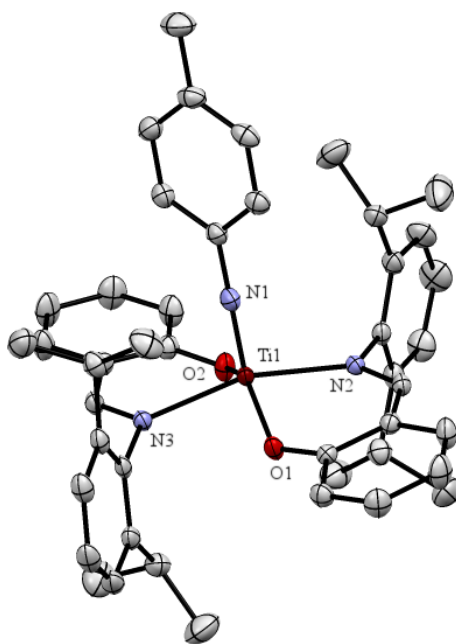
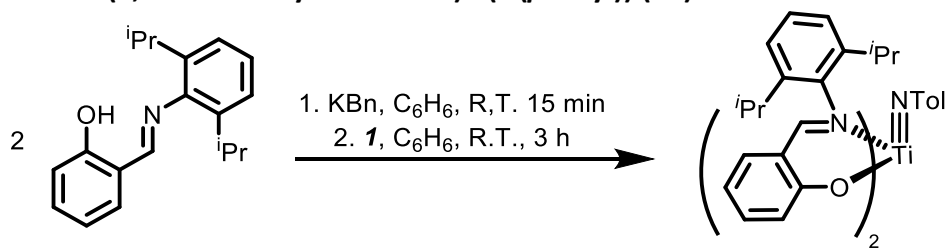


Figure S17: 50 % thermal ellipsoid drawing of **13**. Hydrogen atoms are omitted for clarity.

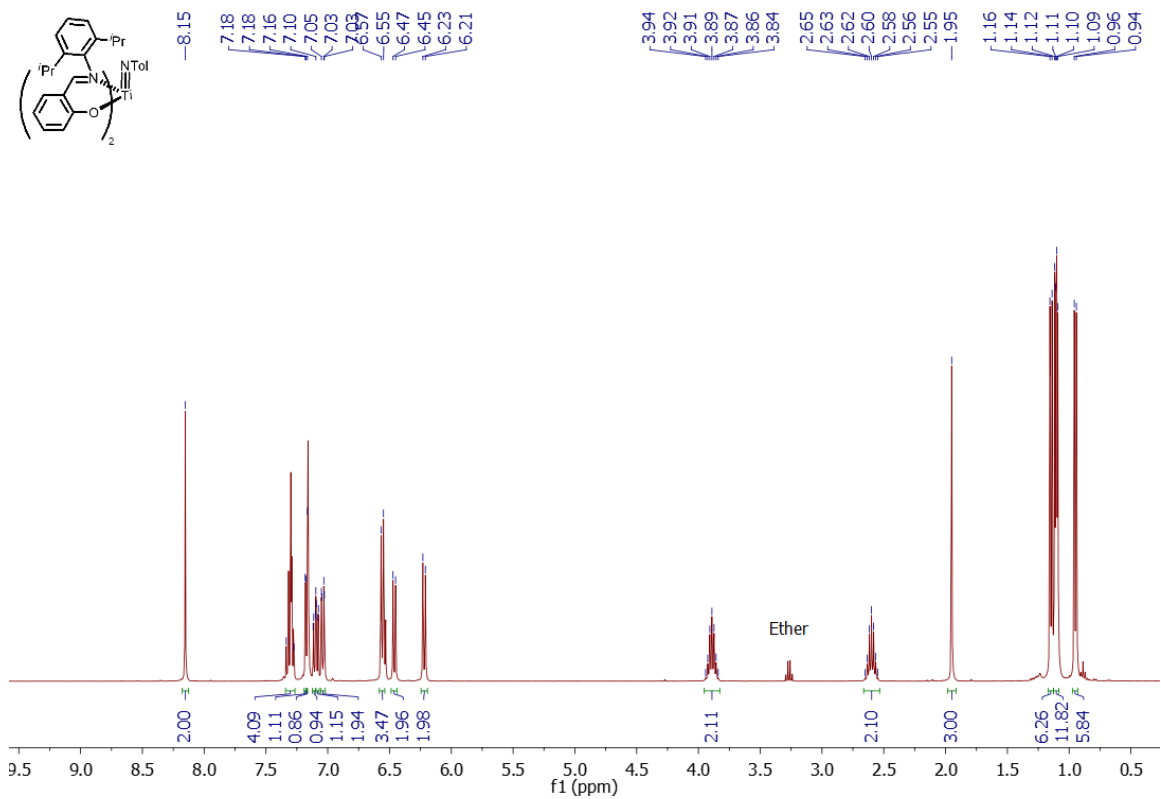


Figure S18: <sup>1</sup>H NMR spectrum of **13** in C<sub>6</sub>D<sub>6</sub>.

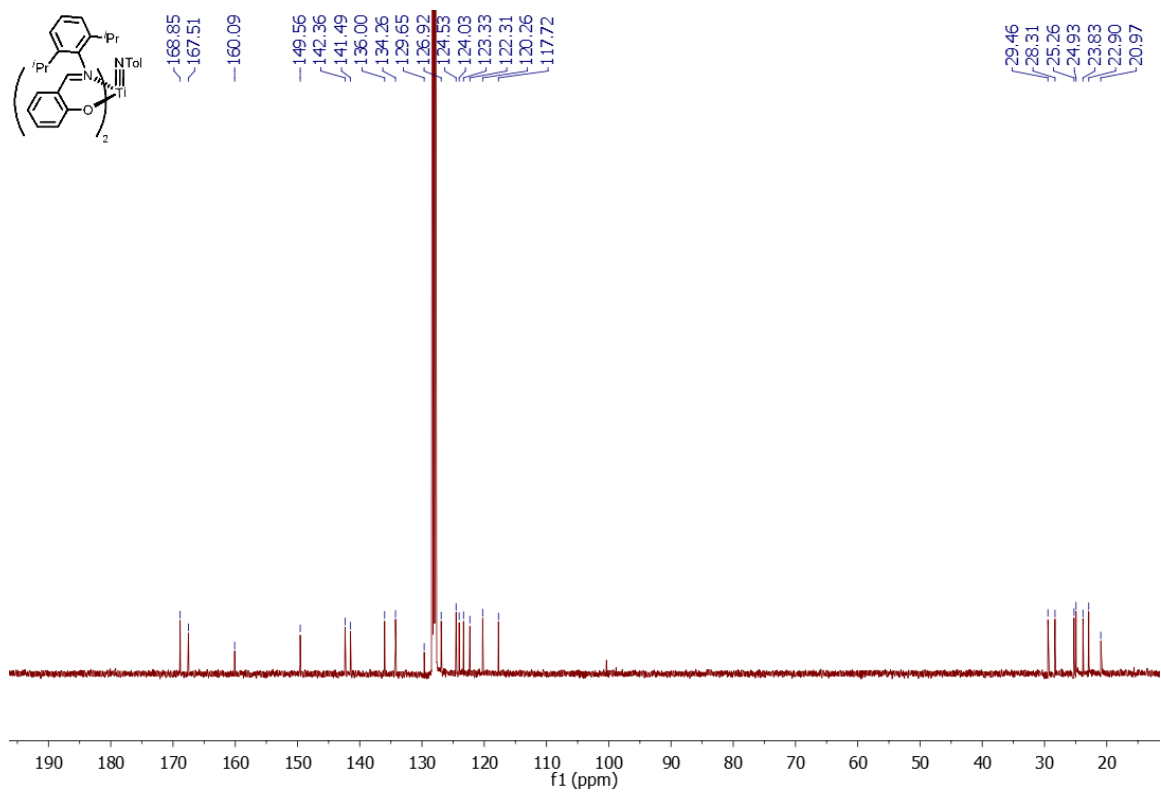


Figure S19: <sup>13</sup>C NMR spectrum of **13** in C<sub>6</sub>D<sub>6</sub>.

Synthesis of  $\text{Ti}(\text{N}(\textit{p}\text{-tolyl}))(\text{N,N}'\text{-}(2,6\text{-iPr}_2\text{Ph})_2\text{formamidinate})_2$  (**14**)

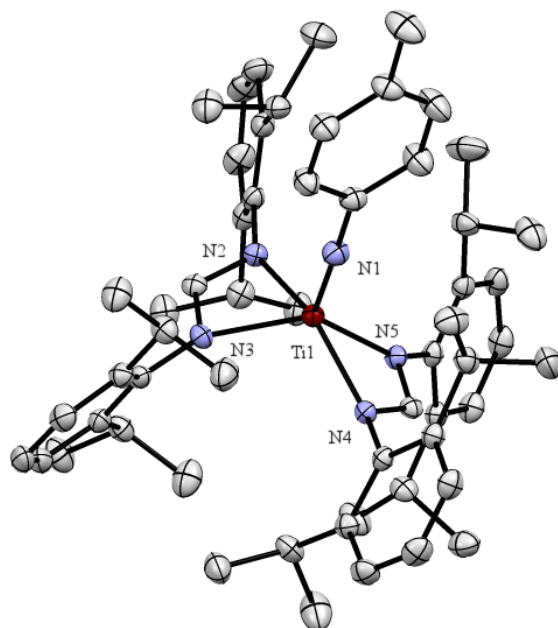
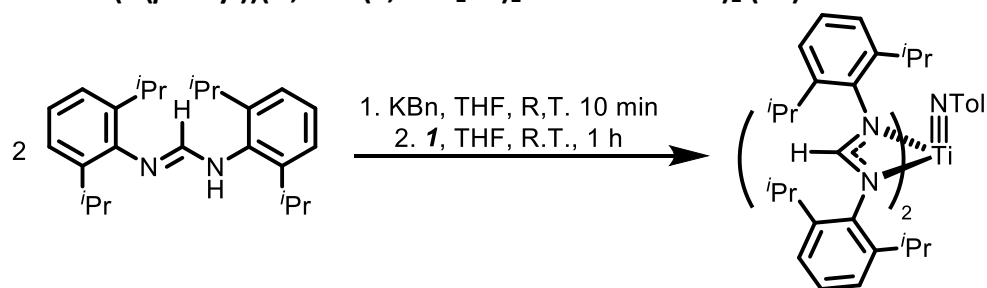


Figure S20: 50 % thermal ellipsoid drawing of **14**. Hydrogen atoms are omitted for clarity.

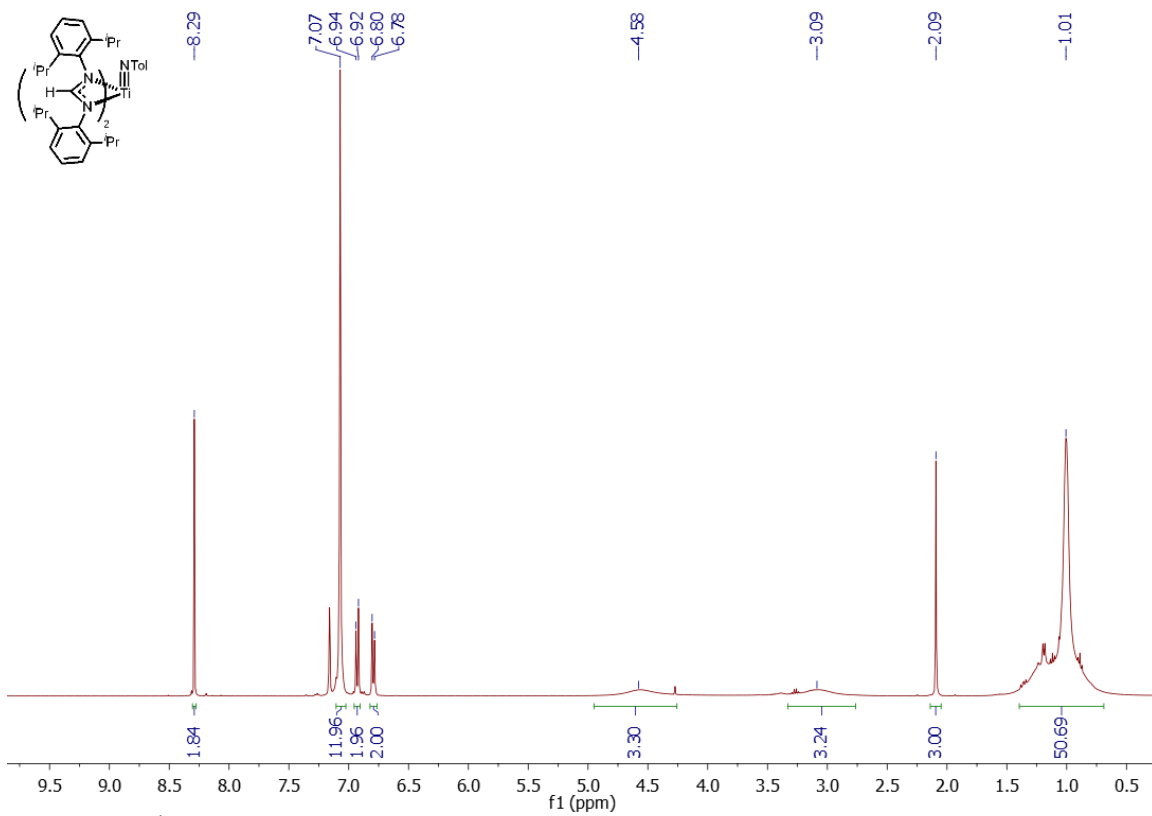


Figure S21: <sup>1</sup>H NMR spectrum of **14** in C<sub>6</sub>D<sub>6</sub>.

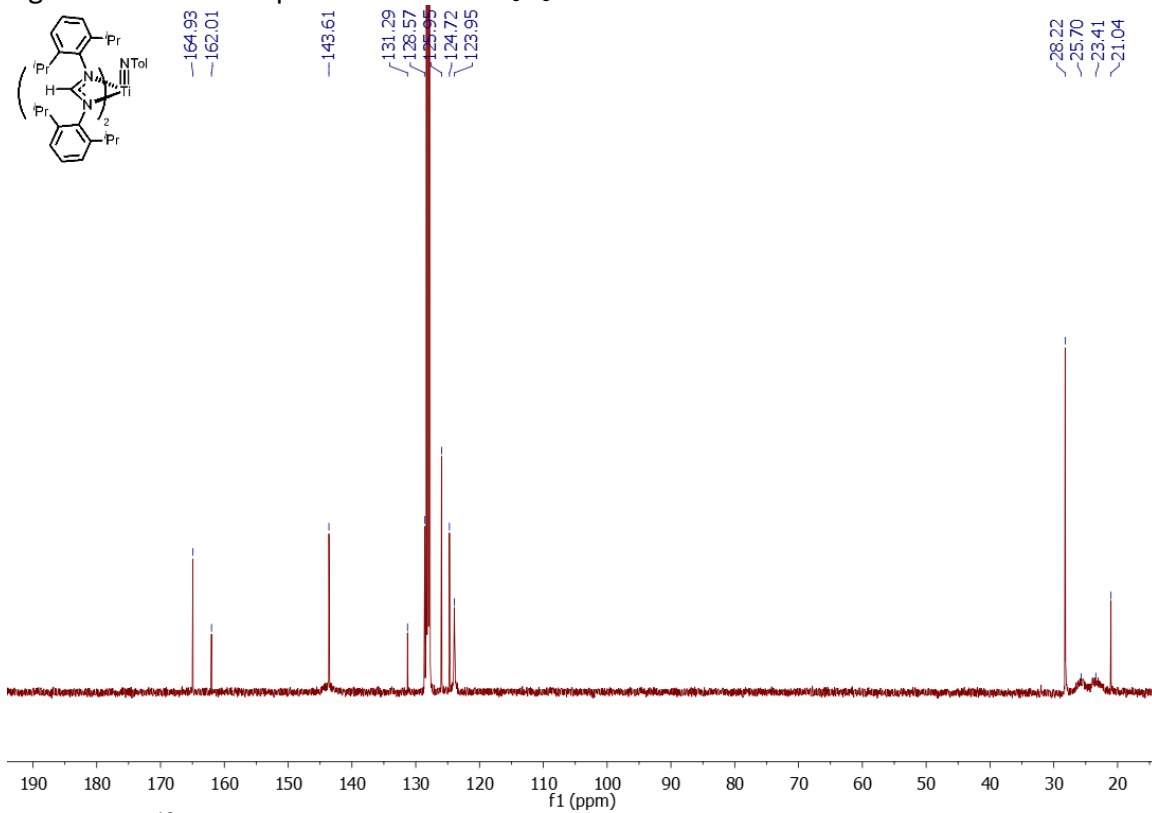


Figure S22: <sup>13</sup>C NMR spectrum of **14** in C<sub>6</sub>D<sub>6</sub>.

Synthesis of  $\text{Ti}(\text{N}(p\text{-tolyl}))(\text{C}_5\text{H}_5\text{N})(\text{N},\text{N}'\text{-(2,6-}i\text{Pr}_2\text{Ph)}_2\text{formamidinate})\text{Cl}$  (**15**)

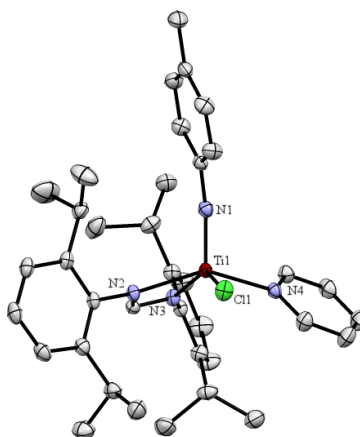
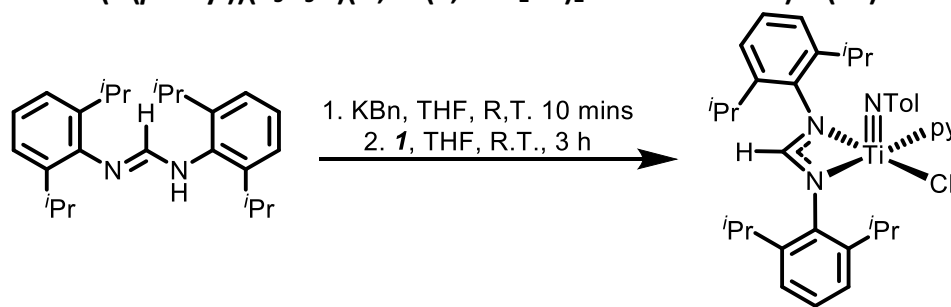


Figure S23: 50 % thermal ellipsoid drawing of **15**. Hydrogen atoms are omitted for clarity.

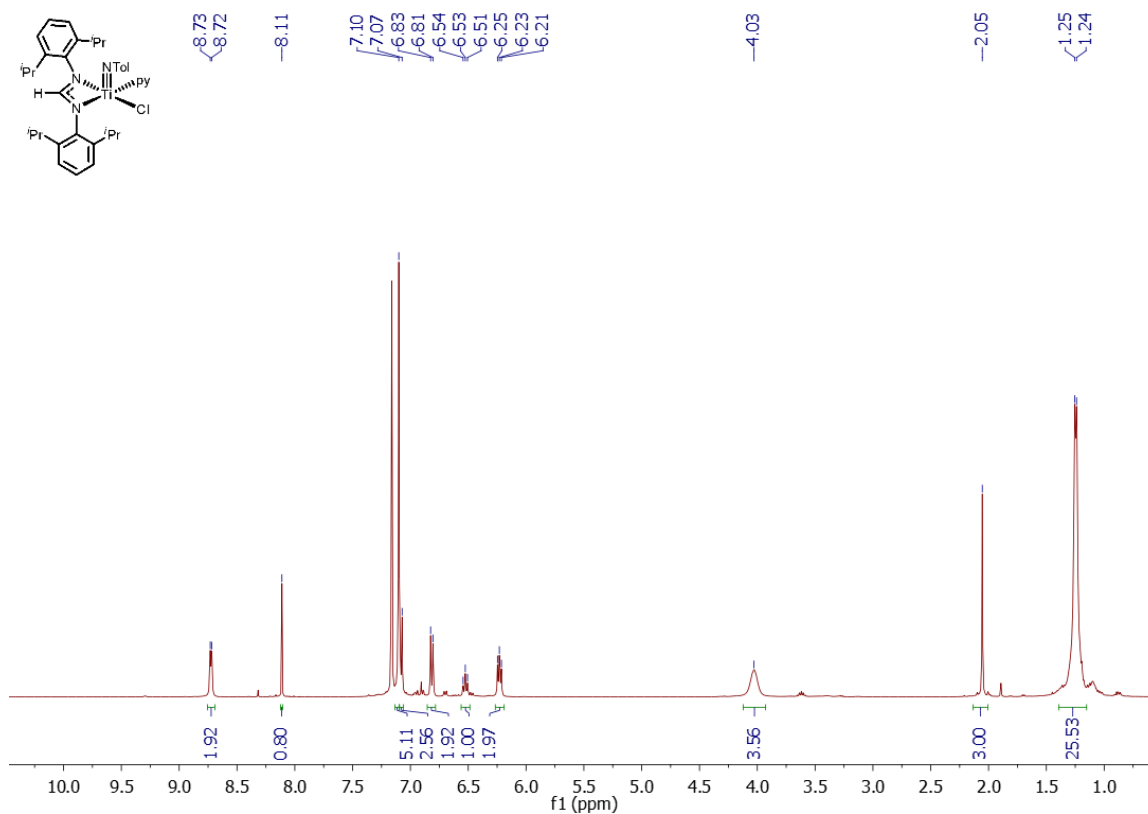


Figure S24:  $^1\text{H}$  NMR spectrum of **15** in  $\text{C}_6\text{D}_6$ .

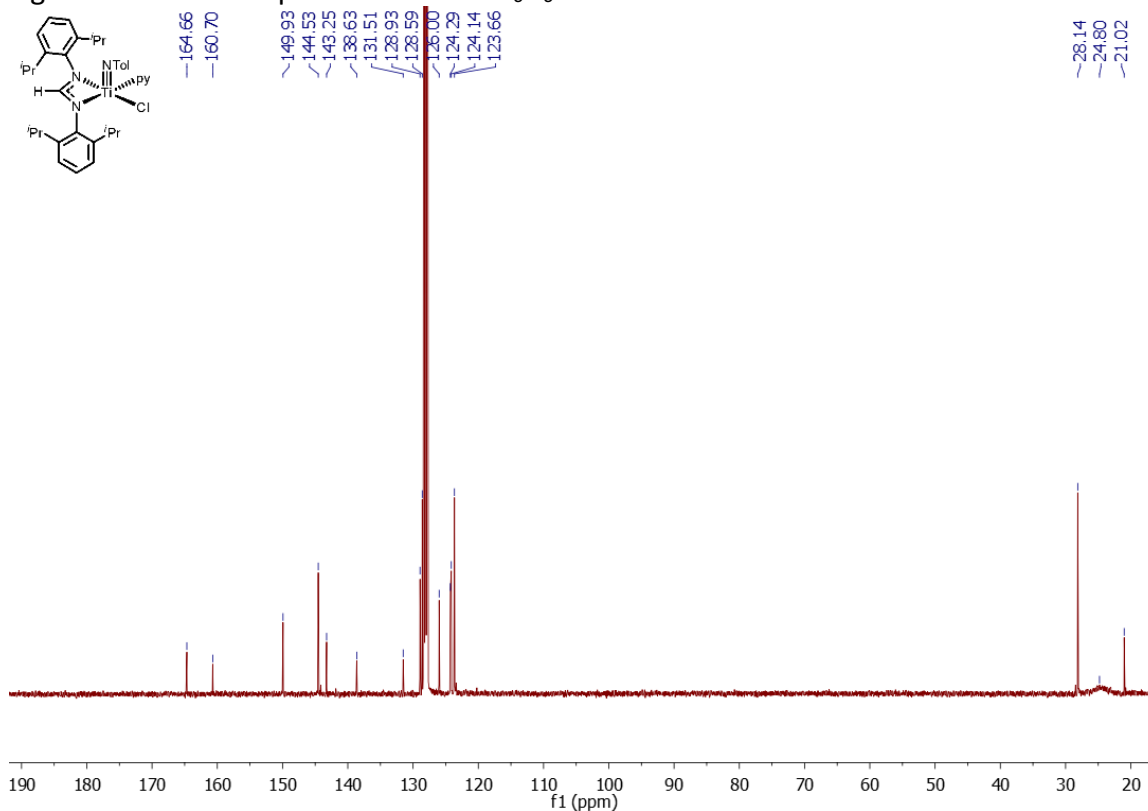
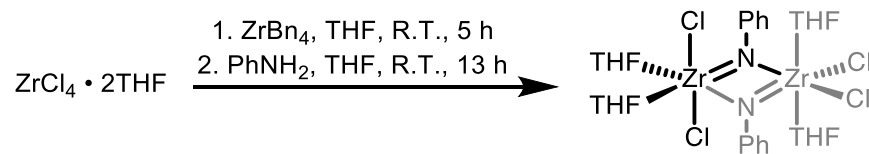


Figure S25:  $^{13}\text{C}$  NMR spectrum of **15** in  $\text{C}_6\text{D}_6$ .

**Synthesis of  $[\text{Zr}(\mu\text{-NPh})\text{THF}_2\text{Cl}_2]_2$  (**16**)<sup>4</sup>**





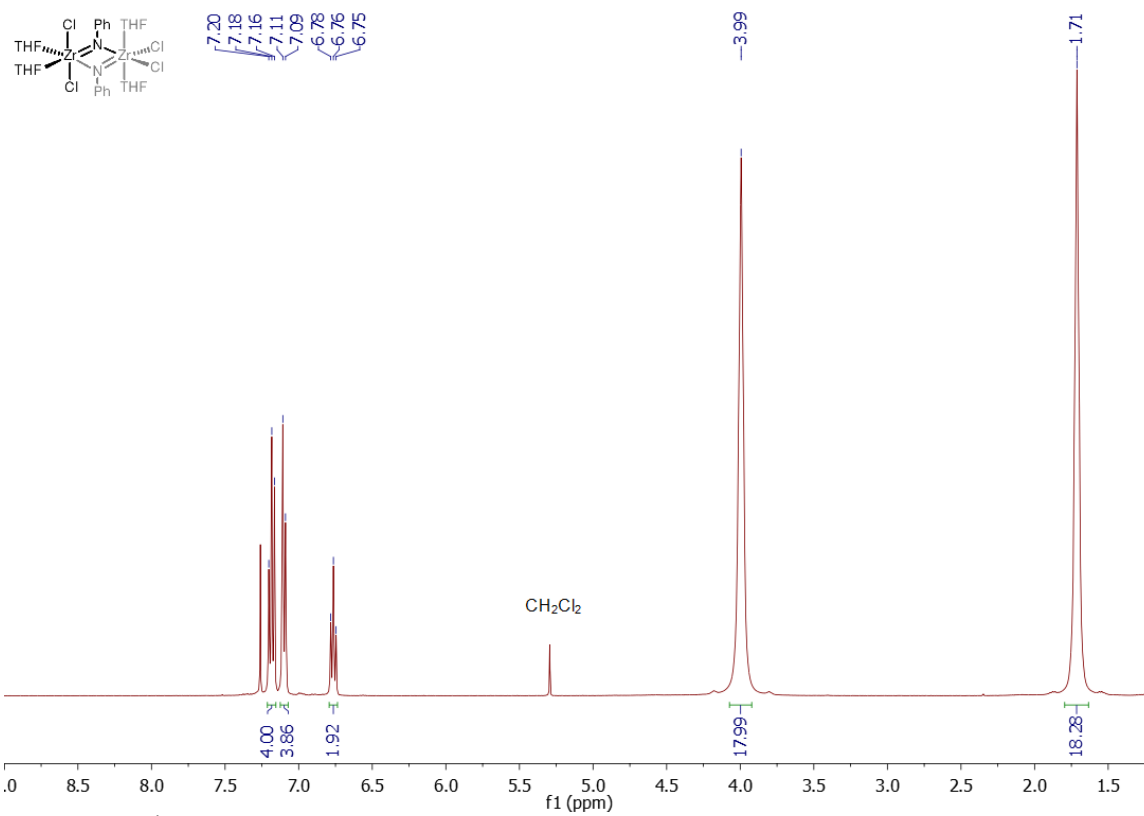


Figure S26:  $^1\text{H}$  NMR spectrum of **16** in  $\text{CDCl}_3$ .

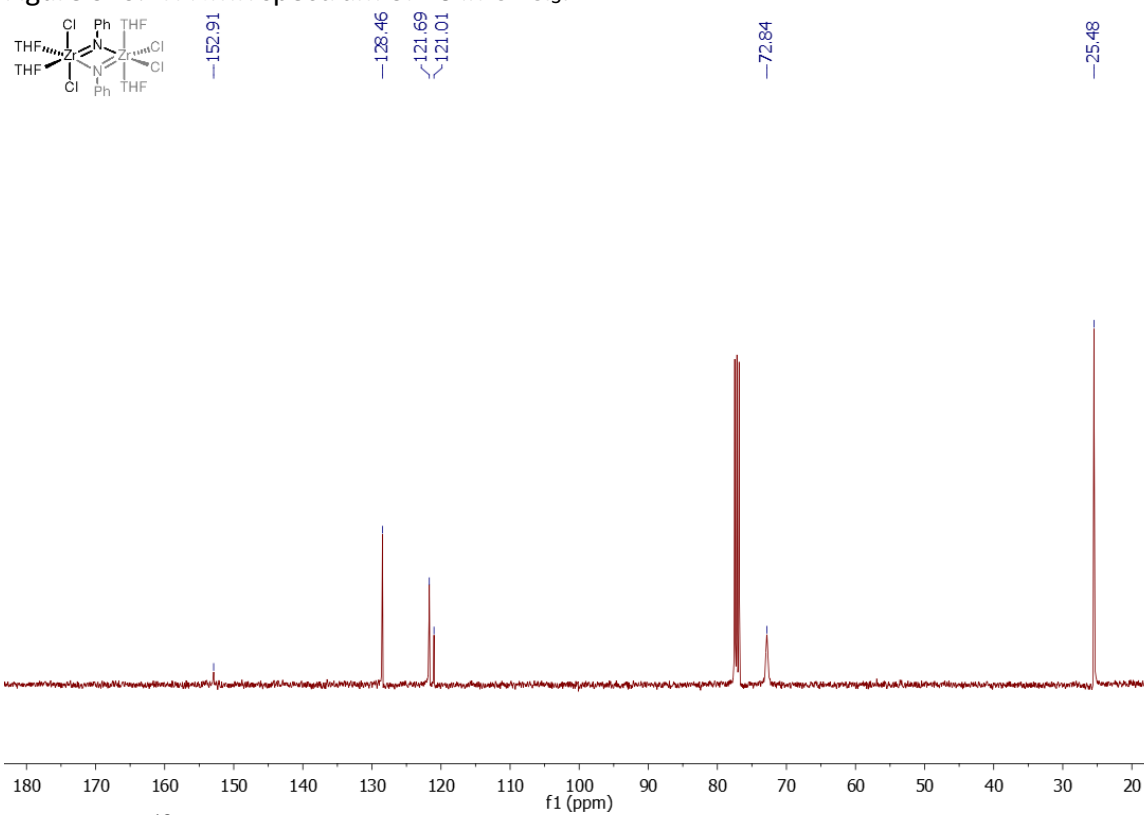
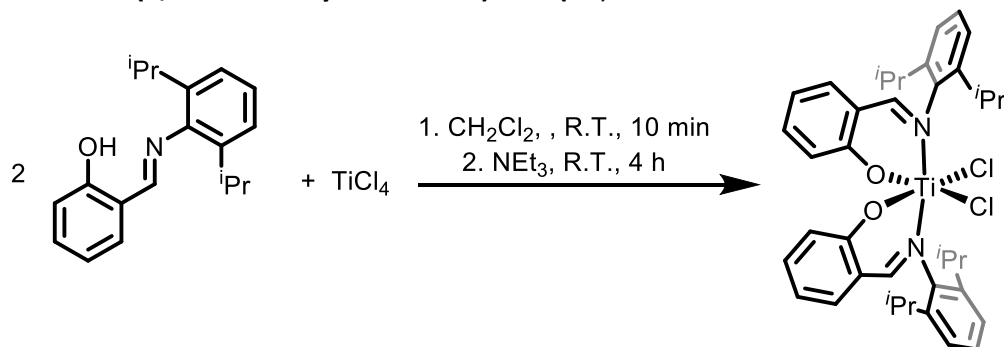


Figure S27:  $^{13}\text{C}$  NMR spectrum of **16** in  $\text{CDCl}_3$ .

### Synthesis of Bis(2,6-*i*-Pr<sub>2</sub>Ph-salicylaldimino)TiCl<sub>2</sub> (**17**)<sup>5</sup>

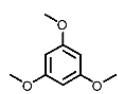


**17** was synthesized *via* slight modification of literature procedure.<sup>14</sup> N-(2',6'-diisopropylphenyl)(phenoxyimine) ligand (1.49 g, 5.28 mmol, 2.0 equiv.)<sup>6</sup> and 20 mL CH<sub>2</sub>Cl<sub>2</sub> were added to a 50 mL round-bottom flask equipped with a stirbar in a N<sub>2</sub>-filled glovebox. This solution was then added to a stirring solution of TiCl<sub>4</sub> (0.50 g, 2.64 mmol, 1.0 equiv.) and 30 mL CH<sub>2</sub>Cl<sub>2</sub> in a 100 mL round-bottom flask equipped with a stirbar. The orange-red solution was stirred at room temperature for 10 min before addition of NEt<sub>3</sub> (0.53 g, 0.74 mL, 5.28 mmol, 2.0 equiv.). The mixture was stirred at room temperature for 4 h before drying under vacuum to give a red solid. 50 mL of toluene was added to the red solid and the suspension filtered to remove NH<sub>4</sub>Cl. The filtrate was dried under vacuum and the remaining orange solid was washed with 2 x 10 mL hexanes and stirred in 10 mL hexanes for two days before filtering to yield title compound that matched NMR literature (1.23 g, 69 % yield).

### Characterization of substrates and standards in C<sub>6</sub>D<sub>5</sub>Br

#### 1,3,5-trimethoxybenzene

<sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>5</sub>Br): δ 6.12 (s, 3H, Ar-H), 3.51 (s, 9H, CH<sub>3</sub>).



-6.12

-3.51

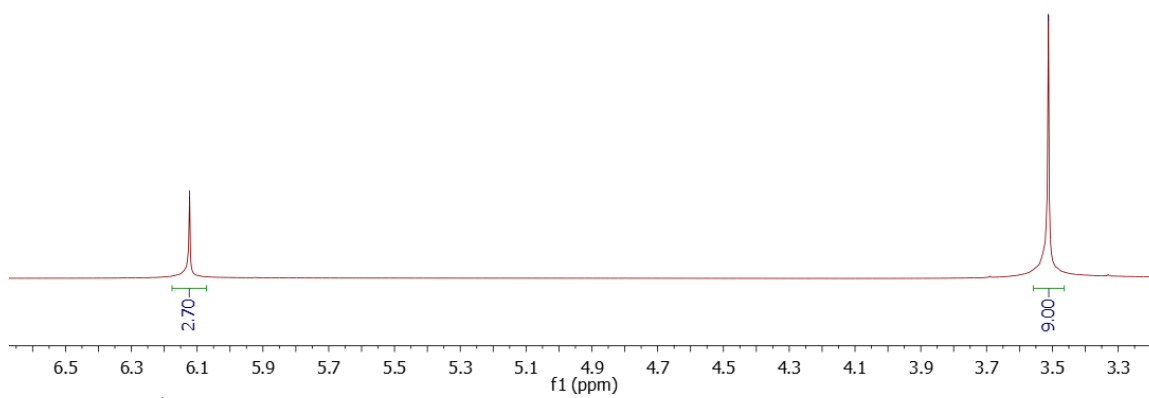


Figure S28:  $^1\text{H}$  spectrum of 1,3,5-trimethoxybenzene in  $\text{C}_6\text{D}_5\text{Br}$ .

**3-hexyne**

**$^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_5\text{Br}$ ):**  $\delta$  2.06 (q,  $^3J_{\text{HH}} = 7.4$  Hz, 4H,  $\text{CH}_2$ ), 1.02 (t,  $^3J_{\text{HH}} = 7.4$  Hz, 6H,  $\text{CH}_3$ ).

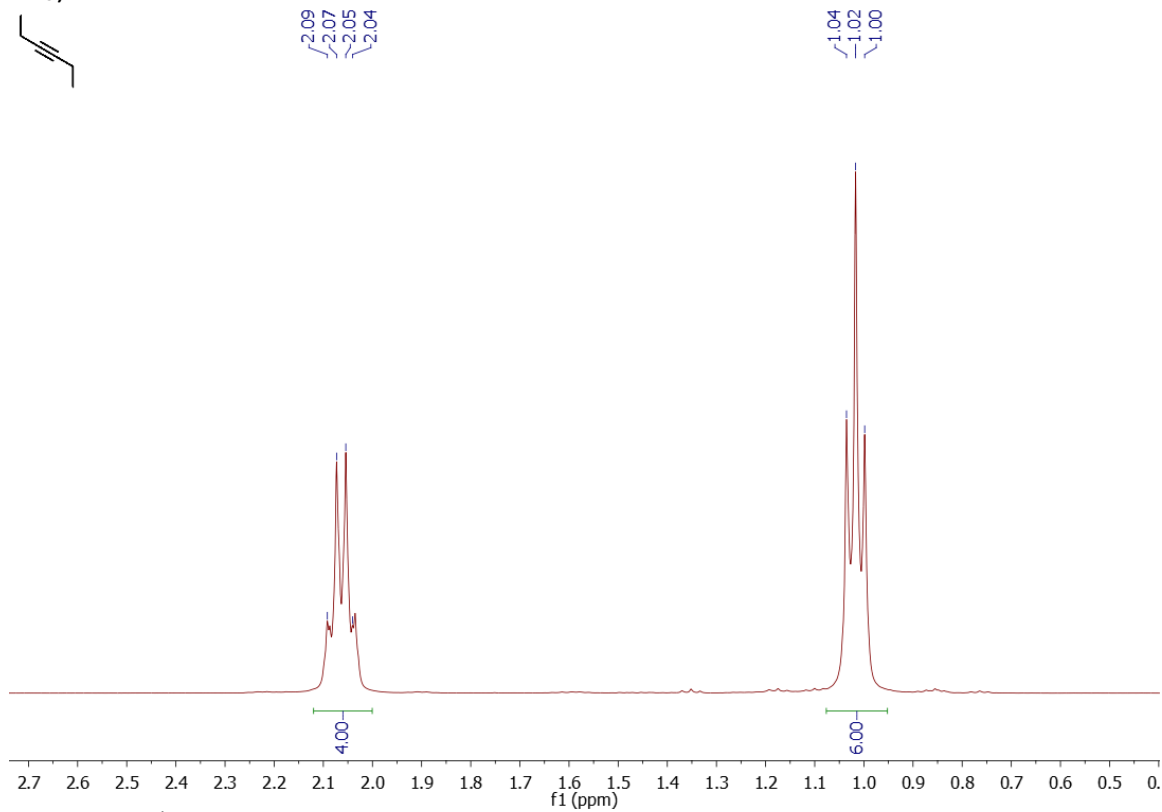


Figure S29:  $^1\text{H}$  spectrum of 3-hexyne in  $\text{C}_6\text{D}_5\text{Br}$ .

### 1-hexyne

$^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_5\text{Br}$ ):  $\delta$  2.02 (td,  $^3J_{\text{HH}} = 6.9$ ,  $^4J_{\text{HH}} = 2.6$  Hz, 2H,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.89 (t,  $^4J_{\text{HH}} = 2.6$  Hz, 1H,  $^n\text{Bu}\equiv\text{H}$ ), 1.38 – 1.23 (m, 4H,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 0.78 (t,  $^3J_{\text{HH}} = 7.2$  Hz, 3H,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ).

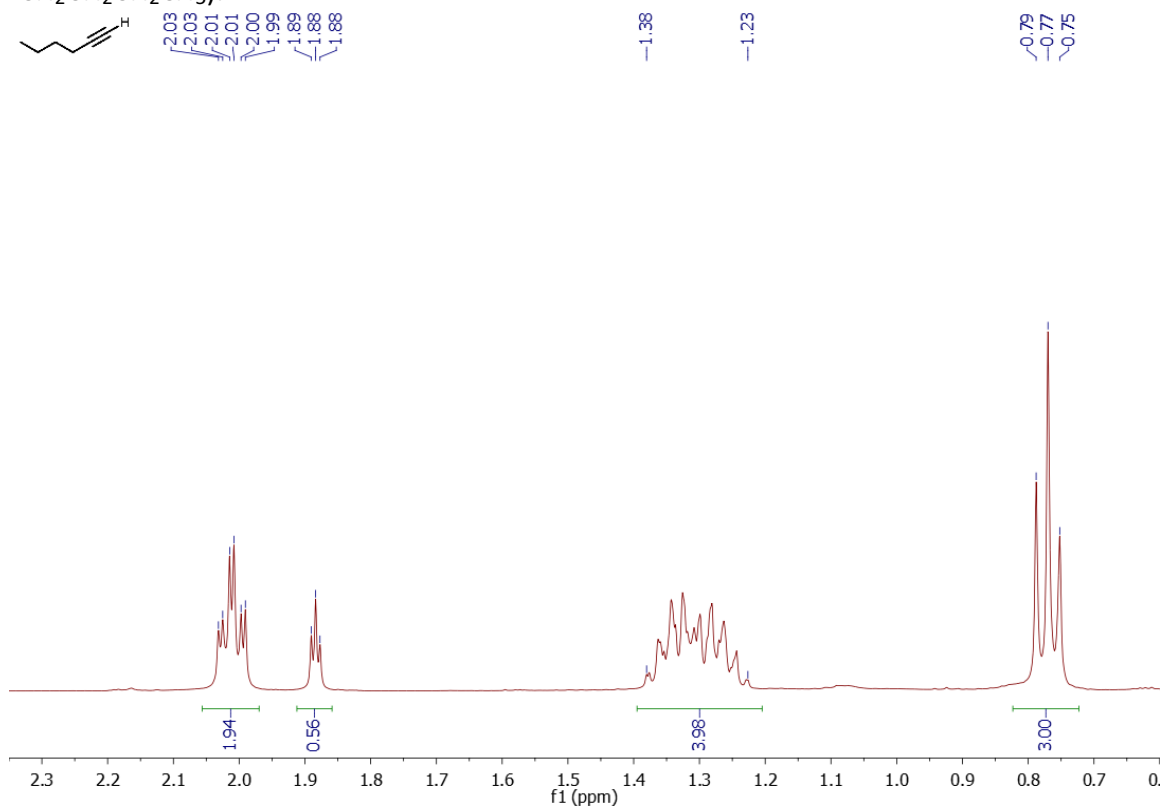


Figure S30:  $^1\text{H}$  spectrum of 1-hexyne in  $\text{C}_6\text{D}_5\text{Br}$ .

### 5,7-dodecadiyne

$^1\text{H NMR}$  (400 MHz,  $\text{C}_6\text{D}_5\text{Br}$ ):  $\delta$  2.08 (t,  $^3J_{\text{HH}} = 6.8$  Hz,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.35 – 1.19 (m, 8H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  and  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 0.75 (t,  $^3J_{\text{HH}} = 7.2$  Hz, 6H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ).

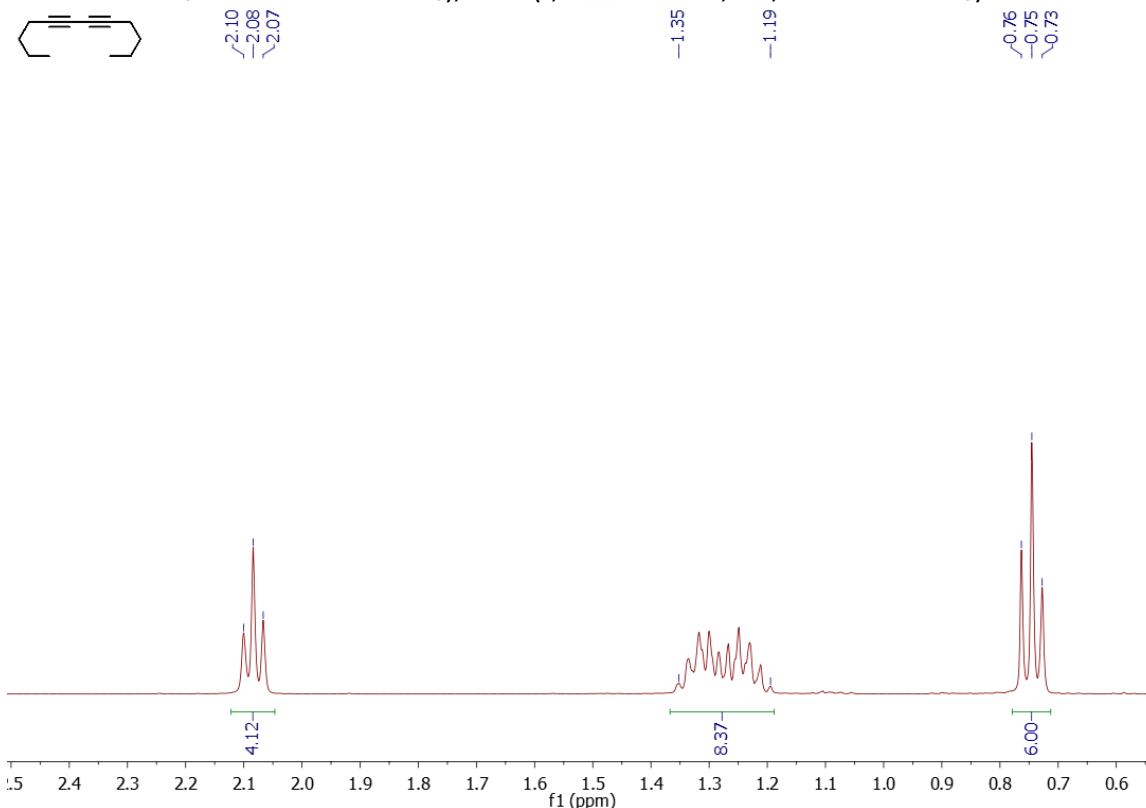
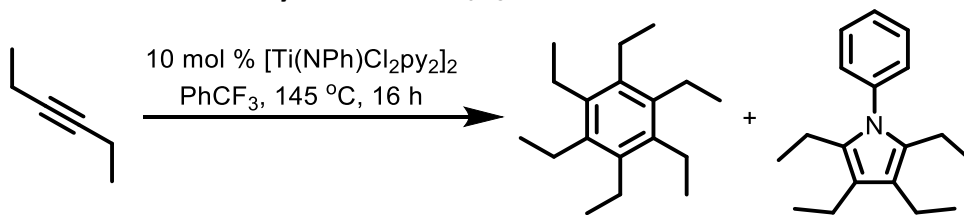


Figure S31:  $^1\text{H}$  spectrum of 5,7-dodecadiyne in  $\text{C}_6\text{D}_5\text{Br}$ .

### Characterization of hexaethylbenzene in $\text{C}_6\text{D}_5\text{Br}$



$[\text{Ti}(\text{NPh})\text{Cl}_2\text{py}_2]_2$  (10 mg, 0.0136 mmol, 10 mol % of Ti), 3-hexyne (22 mg, 0.268 mmol, 1 equiv.) and 1 mL of trifluorotoluene were added to a 20 mL scintillation vial equipped with a small stirbar in a  $\text{N}_2$ -filled glovebox. This was then sealed with a Teflon screw cap and heated overnight at 145 °C for 16 h. The reaction mixture was then quenched with a solution of 5 mL  $\text{CH}_2\text{Cl}_2$  : 5 mL  $\text{H}_2\text{O}$ . The organic layer was washed with 2 x 5 mL  $\text{H}_2\text{O}$ , 5 mL brine, dried over  $\text{MgSO}_4$ , filtered and concentrated to give a pale-yellow solid that contained a mixture of the title compound and 2,3,4,5-tetraethyl-1-(phenyl)pyrrole.

$^1\text{H NMR}$  (400 MHz,  $\text{C}_6\text{D}_5\text{Br}$ ):  $\delta$  2.61 (q,  $^3J_{\text{HH}} = 7.4$  Hz, 12H,  $\text{CH}_2$ ), 1.11 ppm (t,  $^3J_{\text{HH}} = 7.4$  Hz, 18H,  $\text{CH}_3$ ).

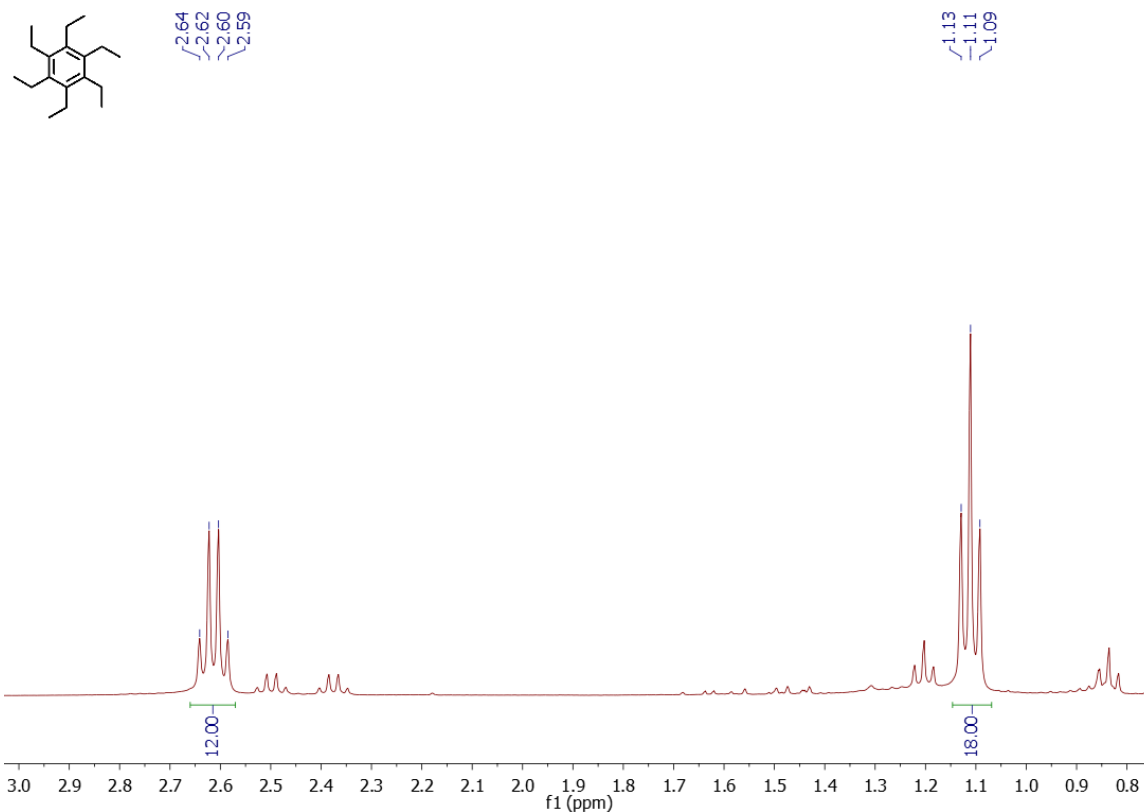
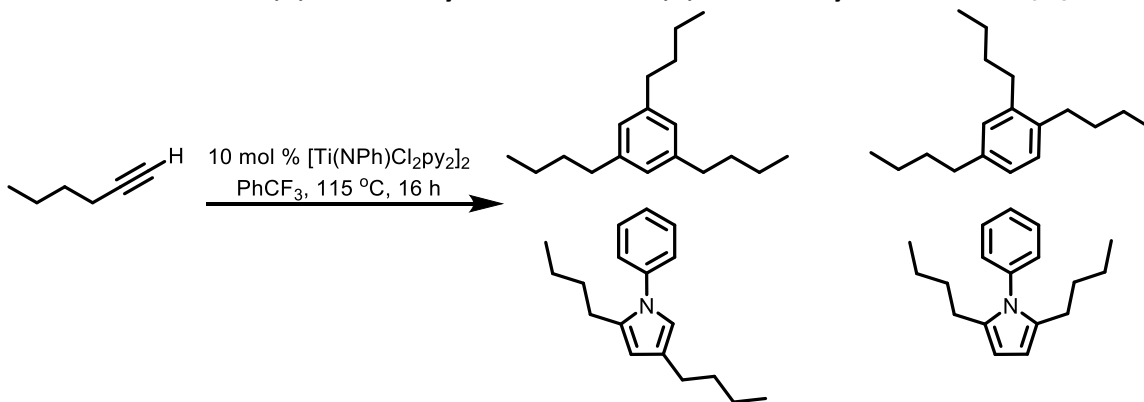


Figure S32:  $^1\text{H}$  spectrum of hexaethylbenzene in  $\text{C}_6\text{D}_5\text{Br}$ .

### Characterization of 1,3,5-tri-*n*-butyl-benzene and 1,2,4-tri-*n*-butyl-benzene in $\text{C}_6\text{D}_5\text{Br}$



$[\text{Ti}(\text{NPh})\text{Cl}_2\text{py}_2]_2$  (10 mg, 0.01 mmol, 10 mol % of Ti), 1-hexyne (22 mg, 0.268 mmol, 1 equiv.) and 1 mL of trifluorotoluene were added to a 20 mL scintillation vial equipped with a small stirbar in a  $\text{N}_2$ -filled glovebox. This was then sealed with a Teflon screw cap and heated overnight at 115 °C for 16 h. The reaction mixture was then quenched with a solution of 5 mL  $\text{CH}_2\text{Cl}_2$  : 5 mL  $\text{H}_2\text{O}$ . The organic layer was then washed with 2 x 5 mL  $\text{H}_2\text{O}$ , 5 mL brine, dried over  $\text{MgSO}_4$ , filtered and concentrated to give a yellow oil that contained a mixture of the title compounds, 2,4-di-*n*-butyl-1-phenyl-1*H*-pyrrole and 2,5-di-*n*-butyl-1-phenyl-1*H*-pyrrole.

### 1,3,5-tri-*n*-butyl-benzene

$^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_5\text{Br}$ ):  $\delta$  6.84 (s, 3H, Ar-H), 2.60 – 2.51 (m, 6H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.58 – 1.50 (m, 6H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.38 – 1.27 (m, 6H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 0.95 – 0.85 (m, 9H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ).

### 1,2,4-tri-*n*-butyl-benzene

$^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_5\text{Br}$ ):  $\delta$  7.06 (d,  $^3J_{\text{HH}} = 7.7$  Hz, 1H, C6-Ar-H), 6.97 (app d,  $^3J_{\text{HH}} = 7.1$  Hz, 2H, C3-Ar-H and C5-Ar-H), 2.60 – 2.51 (m, 6H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.58 – 1.50 (m, 6H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.38 – 1.27 (m, 6H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 0.95 – 0.85 (m, 9H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ).

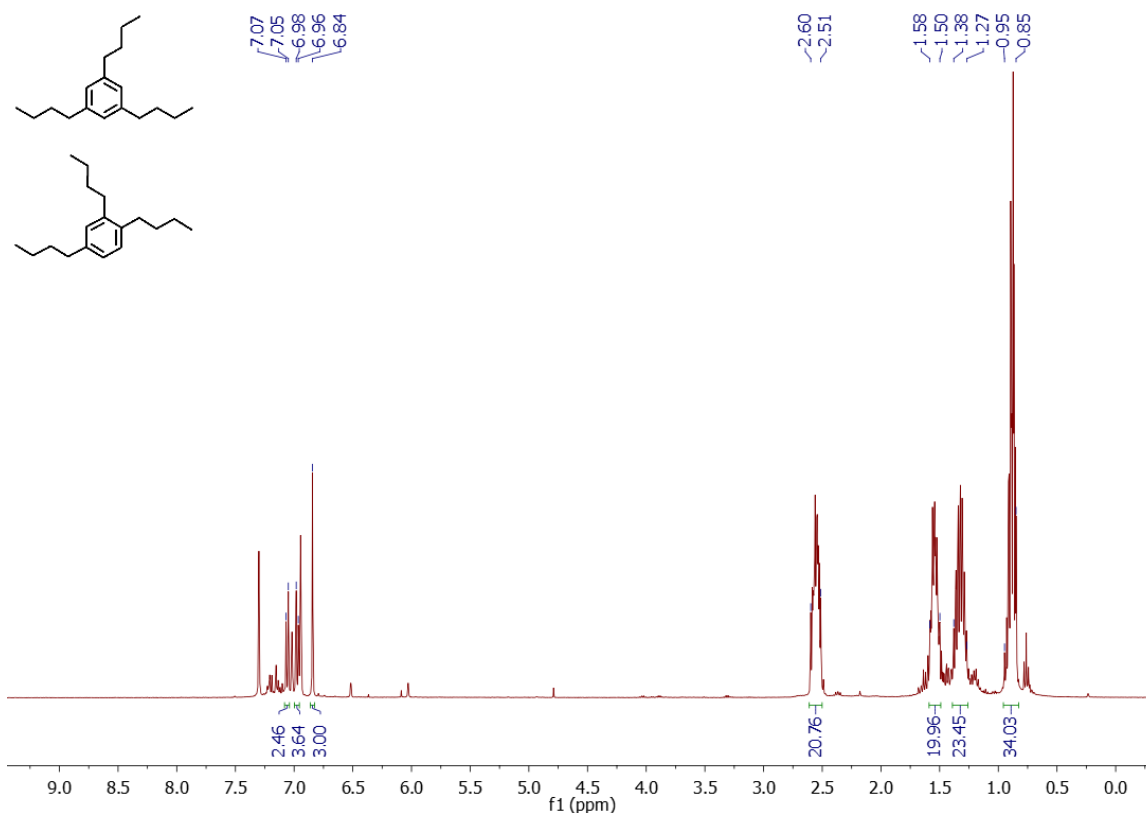


Figure S33:  $^1\text{H}$  spectrum of the mixture of 1,3,5-tri-*n*-butylbenzene and 1,2,4-tri-*n*-butylbenzene in  $\text{C}_6\text{D}_5\text{Br}$ .



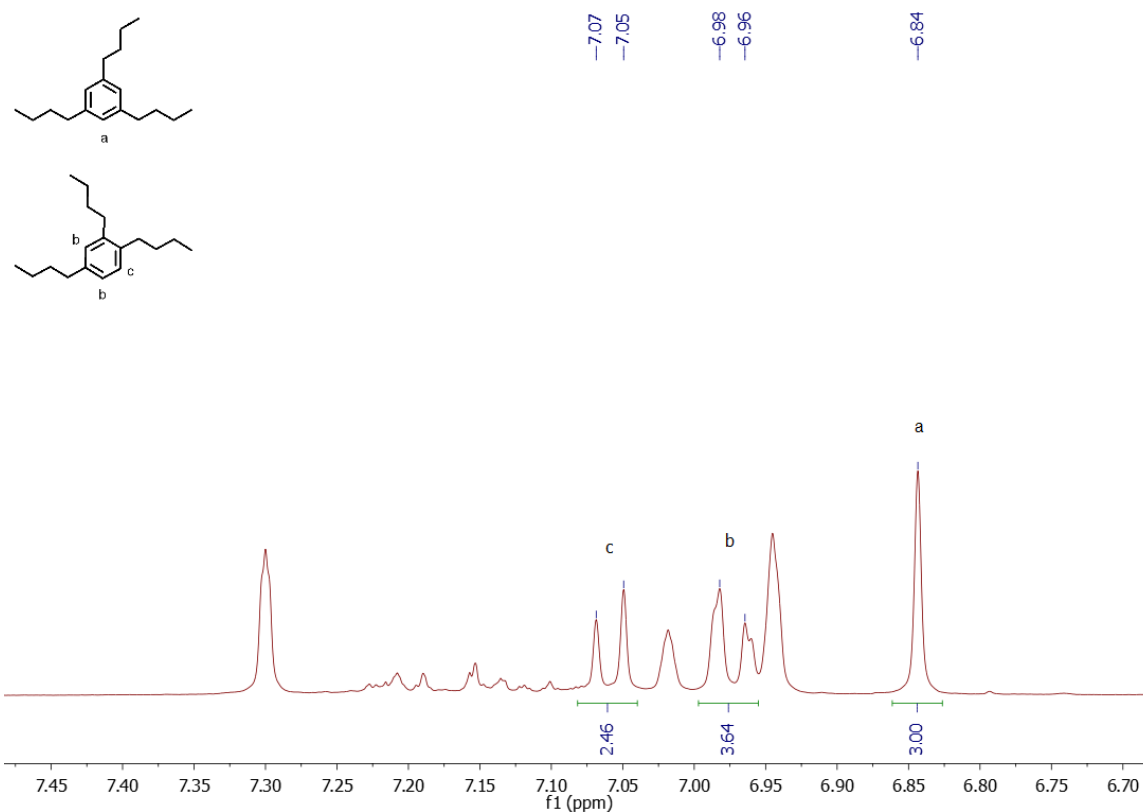


Figure S34: Zoom-in  $^1\text{H}$  spectrum of the mixture of 1,3,5-tri-*n*-butylbenzene and 1,2,4-tri-*n*-butylbenzene in  $\text{C}_6\text{D}_5\text{Br}$ .

#### Characterization of 2,3,4,5-tetraethyl-1-(*p*-tolyl)-1*H*-pyrrole in $\text{C}_6\text{D}_5\text{Br}$ <sup>7</sup>

The title compound was synthesized following literature procedure in a  $\text{N}_2$ -filled glovebox to give a dark brown solid that contained a mixture of the title compound and starting material 1,2-di(*p*-tolyl)diazene.

$^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_5\text{Br}$ ):  $\delta$  6.97 (app br s, 4H, Ar-*H*), 2.51 (q,  $^3J_{\text{HH}} = 7.5$  Hz, 4H, 2,5- $\text{CH}_2\text{CH}_3$ ), 2.40 (q,  $^3J_{\text{HH}} = 7.4$  Hz, 4H, 3,4- $\text{CH}_2\text{CH}_3$ ), 2.14 (s, 3H, Ar- $\text{CH}_3$ ), 1.21 (t,  $^3J_{\text{HH}} = 7.5$  Hz, 6H, 2,5- $\text{CH}_2\text{CH}_3$ ), 0.87 (t,  $^3J_{\text{HH}} = 7.4$  Hz, 6H, 3,4- $\text{CH}_2\text{CH}_3$ ).

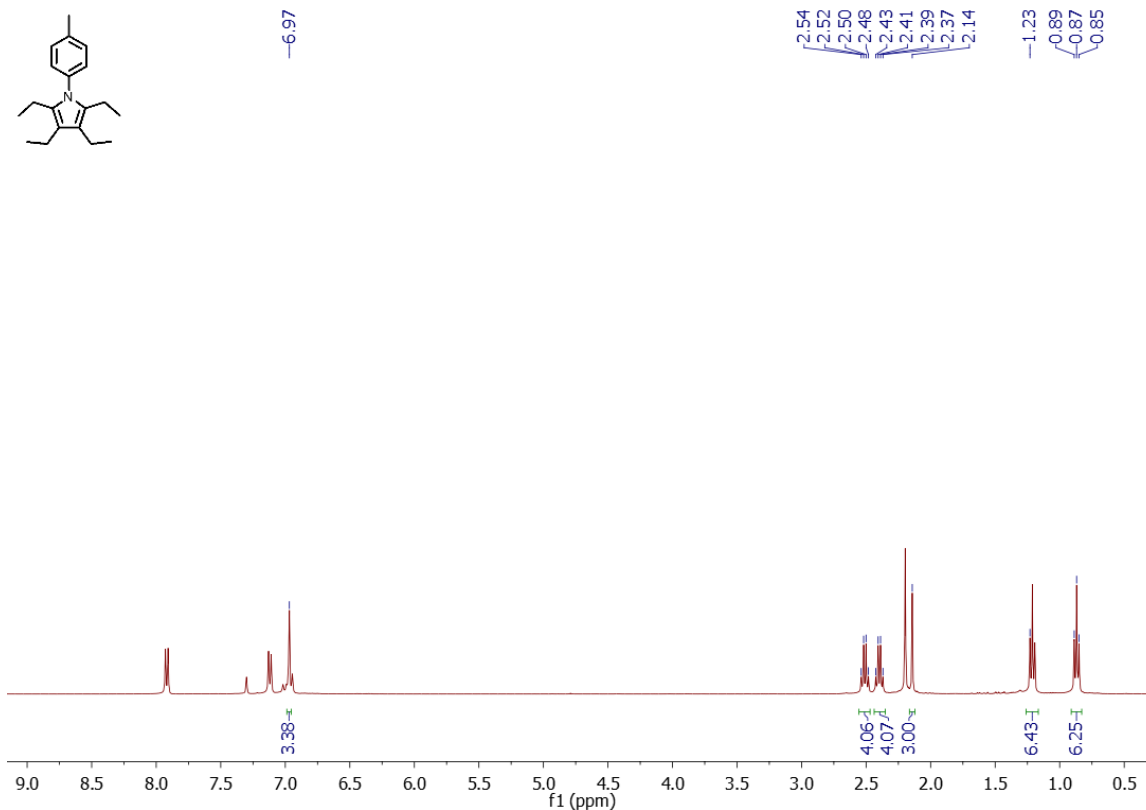


Figure S35: <sup>1</sup>H spectrum of 2,3,4,5-tetraethyl-1-(*p*-tolyl)-1*H*-pyrrole in C<sub>6</sub>D<sub>5</sub>Br.

### Characterization of 2,3,4,5-tetraethyl-1-phenyl-1*H*-pyrrole in C<sub>6</sub>D<sub>5</sub>Br<sup>7</sup>

The title compound was synthesized following literature procedure in a N<sub>2</sub>-filled glovebox to give the title compound as a colorless oil.

**<sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>5</sub>Br):** 7.22 – 7.18 (m, 2H, *m*-NPh-*H*), 7.15 – 7.12 (m, 1H, *p*-NPh-*H*), 7.06 (d, <sup>3</sup>*J*<sub>HH</sub> = 7.0 Hz, 2H, *o*-NPh-*H*), 2.50 (q, <sup>3</sup>*J*<sub>HH</sub> = 7.5 Hz, 4H, 3,4-CH<sub>2</sub>CH<sub>3</sub>), 2.37 (q, <sup>3</sup>*J*<sub>HH</sub> = 7.4 Hz, 4H, 2,5-CH<sub>2</sub>CH<sub>3</sub>), 1.20 (t, <sup>3</sup>*J*<sub>HH</sub> = 7.5 Hz, 6H, 2,5-CH<sub>2</sub>CH<sub>3</sub>), 0.83 (t, <sup>3</sup>*J*<sub>HH</sub> = 7.5 Hz, 6H, 3,4-CH<sub>2</sub>CH<sub>3</sub>).

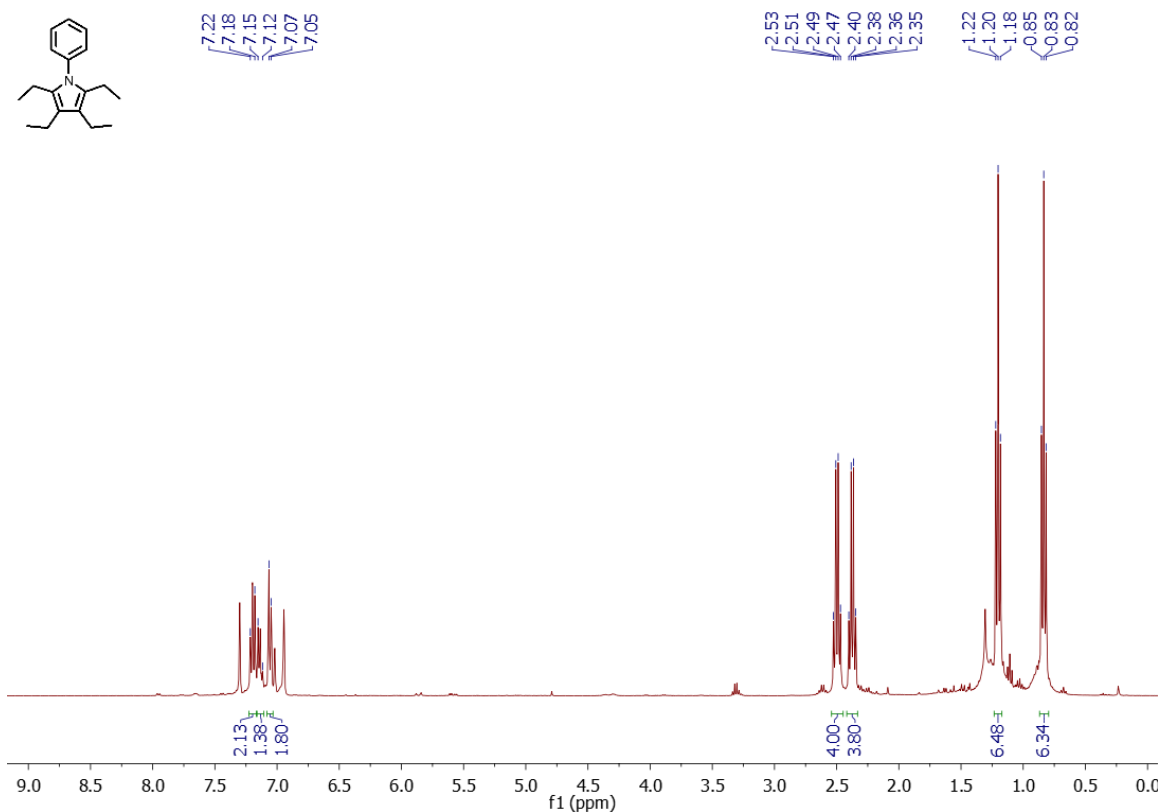
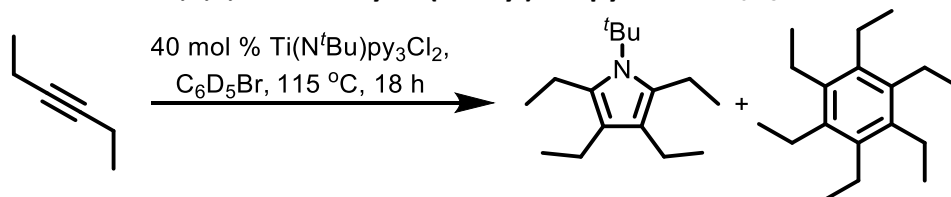


Figure S36:  $^1\text{H}$  spectrum of 2,3,4,5-tetraethyl-1-phenyl-1*H*-pyrrole in  $\text{C}_6\text{D}_5\text{Br}$ .

#### Characterization of 2,3,4,5-tetraethyl-1-(*t*-butyl)-1*H*-pyrrole in $\text{C}_6\text{D}_5\text{Br}$



$\text{Ti}(\text{N}^t\text{Bu})\text{py}_3\text{Cl}_2$  (51 mg, 0.119 mmol, 40 mol %), 3-hexyne (26 mg, 0.31 mmol, 1.0 equiv.) and 0.5 mL  $\text{C}_6\text{D}_5\text{Br}$  were added to a screw-cap NMR tube in a  $\text{N}_2$ -filled glovebox. This was then sealed with a Teflon screw cap and heated at 115 °C for 18 h. After which, the mixture was analysed by  $^1\text{H}$  NMR without any further work-up to give a mixture of the title compound, hexaethylbenzene and 3-hexyne.

$^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_5\text{Br}$ ):  $\delta$  2.69 (q,  $^3J_{\text{HH}} = 7.1$  Hz, 4H, 2,5- $\text{CH}_2\text{CH}_3$ ), 2.35 (q,  $^3J_{\text{HH}} = 7.1$  Hz, 4H, 3,4- $\text{CH}_2\text{CH}_3$ ), 1.46 (s, 9H,  $^t\text{Bu}$ ), 1.24 (d,  $^3J_{\text{HH}} = 6.8$  Hz, 6H, 2,5- $\text{CH}_2\text{CH}_3$ ).  
Peak for 3,4- $\text{CH}_2\text{CH}_3$  is hidden beneath the multiplet peak of  $\delta$  1.10 – 0.98.

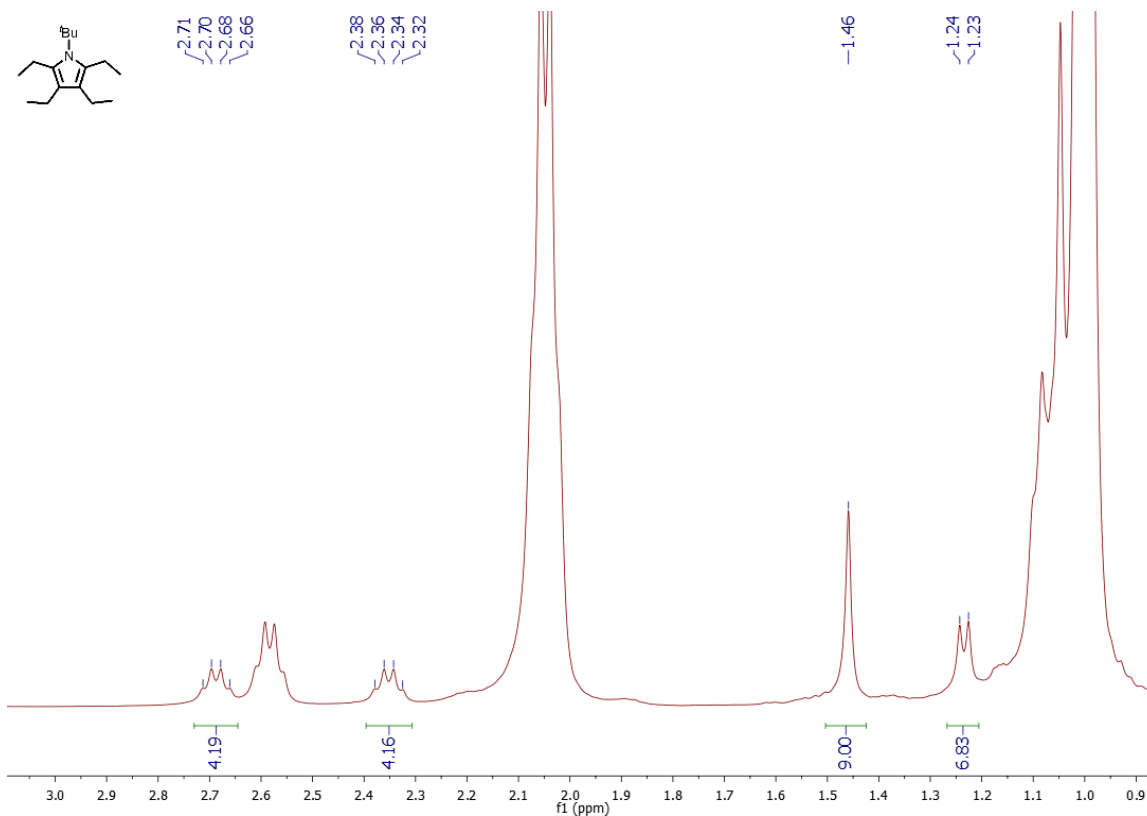
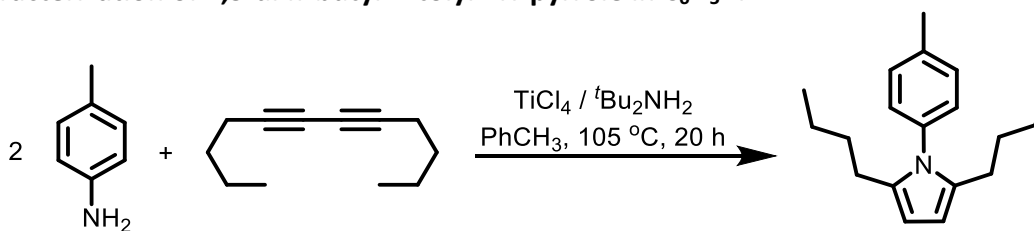


Figure S37:  $^1\text{H}$  spectrum of 2,3,4,5-tetraethyl-1-(*t*-butyl)-1*H*-pyrrole in  $\text{C}_6\text{D}_5\text{Br}$ .

### Characterization of 2,5-di-*n*-butyl-1-tolyl-1*H*-pyrrole in $\text{C}_6\text{D}_5\text{Br}$ <sup>8</sup>



The title compound was prepared *via* slight modification of the literature procedure.<sup>16</sup> *p*-toluidine (159 mg, 1.48 mmol, 2.0 equiv.), 5,7-dodecadiyne (121 mg, 0.746 mmol, 1.0 equiv.),  $\text{TiCl}_4$  (34 mg, 0.179 mmol, 24 mol %), *t*-butylamine (70 mg, 0.957 mmol, 1.3 equiv.) and 10 mL toluene were added to a 20 mL scintillation vial equipped with a small stirbar in a  $\text{N}_2$ -filled glovebox. This was then sealed with a Teflon screw cap and heated at 105 °C for 20 h. The reaction mixture was then concentrated *in vacuo* to dryness before dissolving in minimal hexanes. Product was purified with a neutral alumina column using 100 % hexanes as eluent. After the first spot on the TLC was obtained, more polar eluents were used: first 50 % hexanes : 50 % ether to 100 % ether eluent to collect the second spot. The fractions containing the second spot were dried *in vacuo* to give the title compound and starting reagent diyne.

**$^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_5\text{Br}$ ):**  $\delta$  7.02 (d,  $^3J_{\text{HH}} = 7.6$  Hz, 2H, *m*-NTol-*H*), 6.97 (d,  $^3J_{\text{HH}} = 8.7$  Hz, 2H, *o*-NTol-*H*), 6.08 (s, 2H, C3-*H* and C4-*H*), 2.38 (t,  $^3J_{\text{HH}} = 7.6$  Hz, 4H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 2.14 (s, 3H,  $\text{NC}_6\text{H}_4\text{-CH}_3$ ), 1.46 (pentet,  $^3J_{\text{HH}} = 7.4$  Hz, 4H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 0.75 (q,  $^3J_{\text{HH}} = 7.3$  Hz, 6H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ).

Peak for  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  is hidden beneath the multiplet at  $\delta$  1.35 – 1.15. There is also an overlap of the  $\delta$  0.75 signal with 5,7-dodecadiyne resulting in an apparent quartet. The NTol signals ( $\delta$  6.97 and  $\delta$  7.01) overlap with the residual protio impurities of  $\text{C}_6\text{D}_5\text{Br}$ .

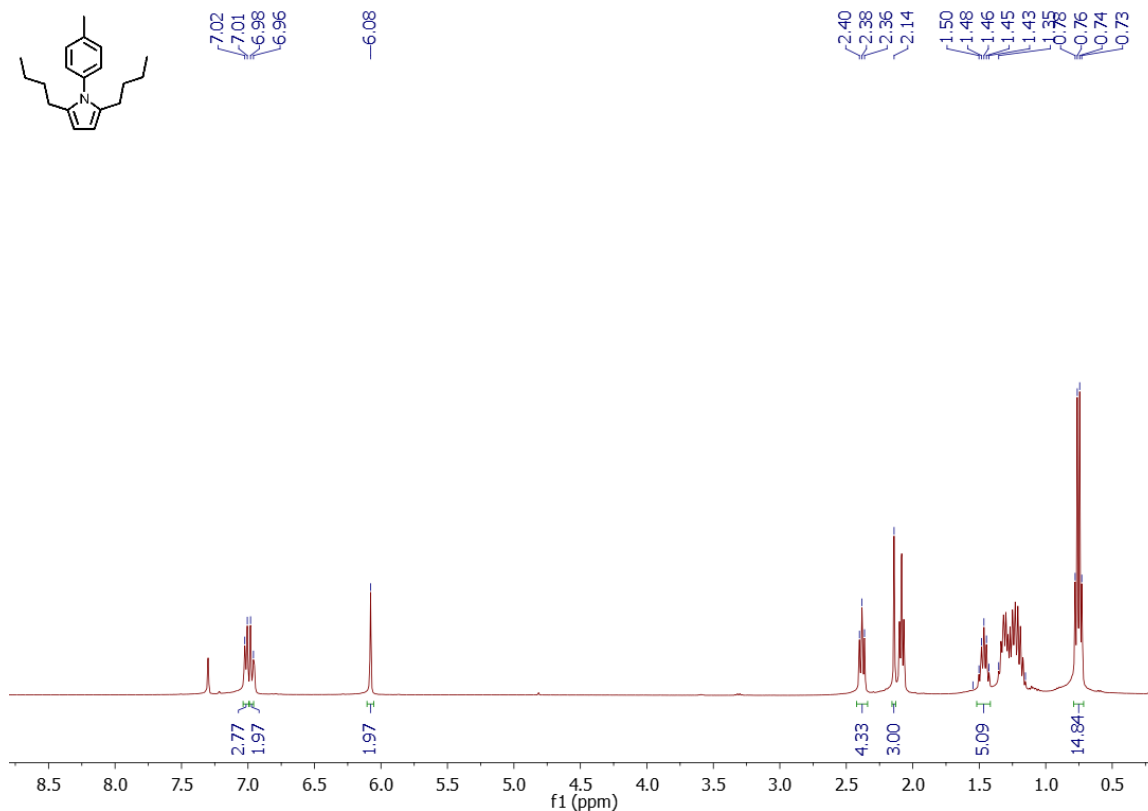


Figure S38:  $^1\text{H}$  spectrum of 2,5-di-*n*-butyl-1-tolyl-1H-pyrrole in  $\text{C}_6\text{D}_5\text{Br}$ .

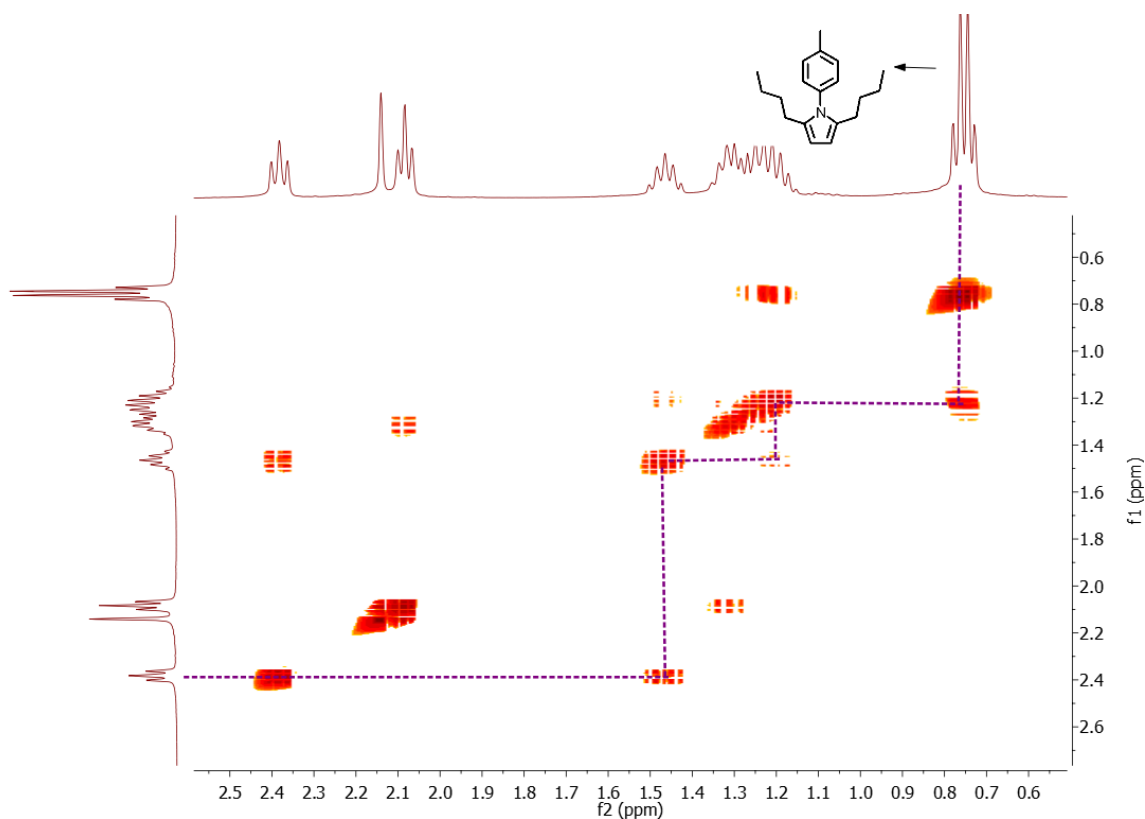
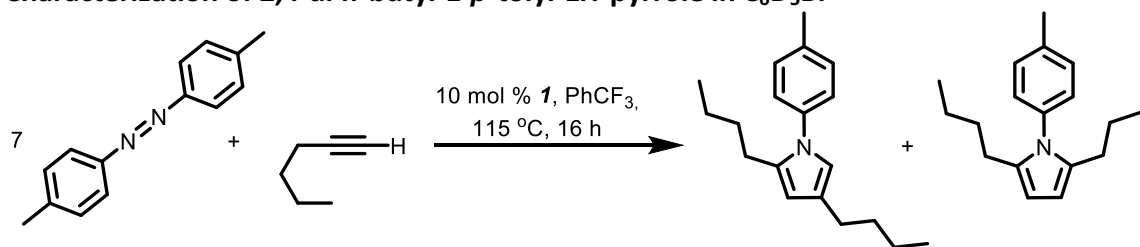


Figure S39: Zoom-in  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of 2,5-di-*n*-butyl-1-tolyl-1*H*-pyrrole in  $\text{C}_6\text{D}_5\text{Br}$ .

#### Characterization of 2,4-di-*n*-butyl-1-*p*-tolyl-1*H*-pyrrole in $\text{C}_6\text{D}_5\text{Br}$



**1** (10 mg, 0.0217 mmol, 10 mol %), 1,2-di(*p*-tolyl)diazene (306 mg, 1.46 mmol, 7.0 equiv.), 1-hexyne (17 mg, 0.207 mmol, 1.0 equiv.) and 1 mL of trifluorotoluene were added to a 20 mL scintillation vial equipped with a small stirbar in a  $\text{N}_2$ -filled glovebox. This was then sealed with a Teflon screw cap and heated overnight at 115 °C for 16 h. The reaction mixture was then concentrated *in vacuo* to dryness and 10 mL of cold hexanes was added to the reaction mixture. Insoluble material was filtered off and the filtrate was concentrated to give a black solid material that contained a mixture of the title compound, 2,5-di-*n*-butyl-1-tolyl-1*H*-pyrrole and 1,2-di(*p*-tolyl)diazene.

$^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_5\text{Br}$ ):  $\delta$  7.06 (d,  $^3J_{\text{HH}} = 8.2$  Hz, 2H, *m*-NTol-*H*), 6.99 (d,  $^3J_{\text{HH}} = 8.0$  Hz, 2H, *o*-NTol-*H*), 6.54 (s, 1H, C4-*H*), 6.03 (s, 1H, C2-*H*), 2.58 – 2.48 (m, 4H, *o*- $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  and *m*- $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 2.16 (s, 3H,  $\text{NC}_6\text{H}_4\text{-CH}_3$ ), 1.65 (app quintet,  $^3J_{\text{HH}} = 7.6$ , *o*- $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.52 – 1.37 (m, 4H, *o*- $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  and *m*- $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.22 (app

sextet,  $^3J_{HH} = 6.8$  Hz, 2H, *m*-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.93 (t,  $^3J_{HH} = 7.3$  Hz, 3H, *o*-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.77 (t,  $^3J_{HH} = 7.3$  Hz, 3H, *m*-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>).

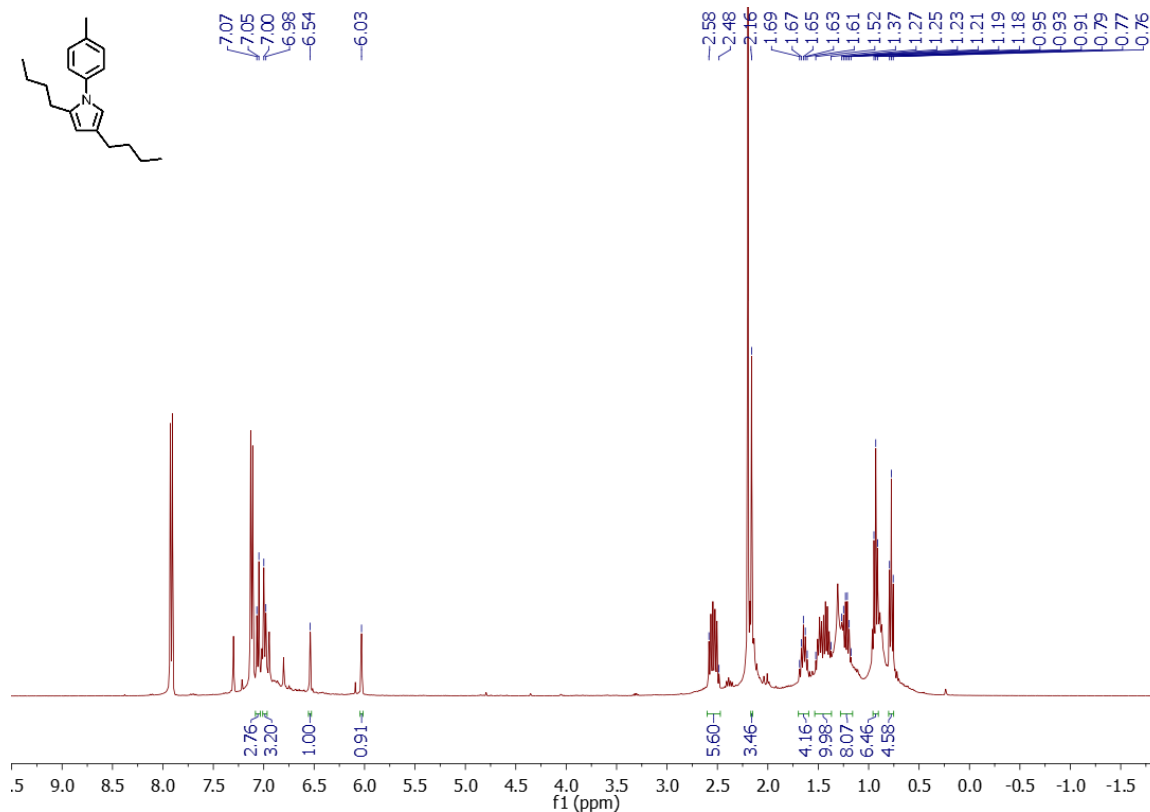


Figure S40: <sup>1</sup>H spectrum of 2,4-di-*n*-butyl-1-*p*-tolyl-1*H*-pyrrole in C<sub>6</sub>D<sub>5</sub>Br.

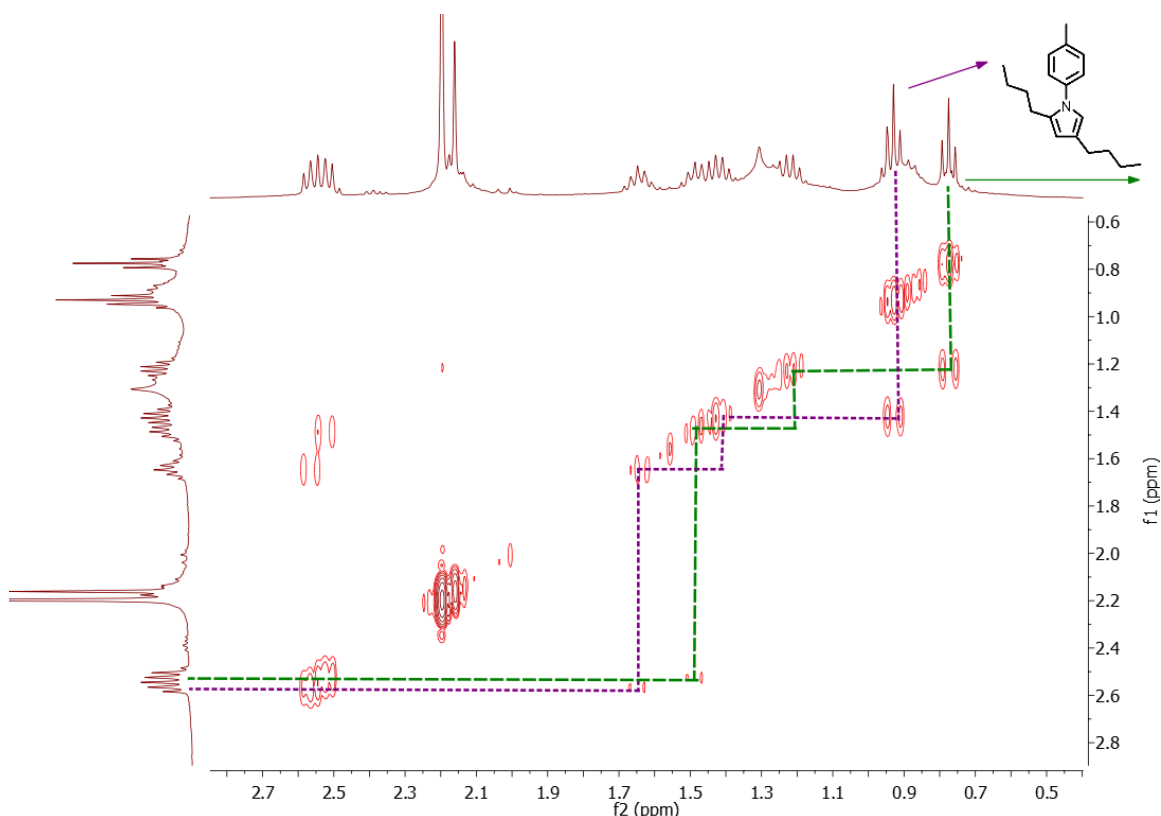
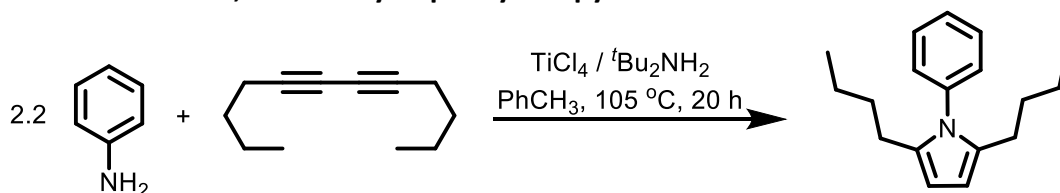


Figure S41: Zoom-in  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of 2,4-di-*n*-butyl-1-*p*-tolyl-1*H*-pyrrole in  $\text{C}_6\text{D}_5\text{Br}$ .

### Characterization of 2,5-di-*n*-butyl-1-phenyl-1*H*-pyrrole<sup>8</sup>



The title compound was prepared *via* slight modification of the literature procedure.<sup>16</sup> Aniline (46 mg, 0.493 mmol, 2.2 equiv.), 5,7-dodecadiyne (36 mg, 0.221 mmol, 1.0 equiv.),  $\text{TiCl}_4$  (14 mg, 0.0738 mmol, 33 mol %), *t*-butylamine (31 mg, 0.424 mmol, 1.9 equiv.) and 5 mL toluene were added to a 20 mL scintillation vial equipped with a small stirbar in a  $\text{N}_2$ -filled glovebox. This was then sealed with a Teflon screw cap and heated at 105 °C for 20 h. The reaction mixture was then concentrated *in vacuo* to dryness before dissolving in minimal  $\text{CH}_2\text{Cl}_2$ . The suspension was filtered and dried under vacuum at 65 °C overnight to remove majority of the diyne starting reagent. The product was then dissolved in  $\text{CHCl}_3$  to form an orange solution that was filtered through a basic alumina plug to give a pale yellow solution. The solution was once again dried under vacuum to give an oil that contained the title compound and starting reagent diyne.

$^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_5\text{Br}$ ):  $\delta$  7.23 (t,  $^3J_{\text{HH}} = 7.4$  Hz, 2H, *m*-NPh-*H*), 7.15 (t,  $^3J_{\text{HH}} = 7.4$  Hz, 1H, *p*-NPh-*H*), 7.07 (d,  $^3J_{\text{HH}} = 7.3$  Hz, 2H, *o*-NPh-*H*), 6.08 (s, 2H, C3-*H* and C4-*H*), 2.36 (t,  $^3J_{\text{HH}}$



= 7.6 Hz, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.44 (pentet, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.18 (sextet, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.75 (t, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, 6H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>).

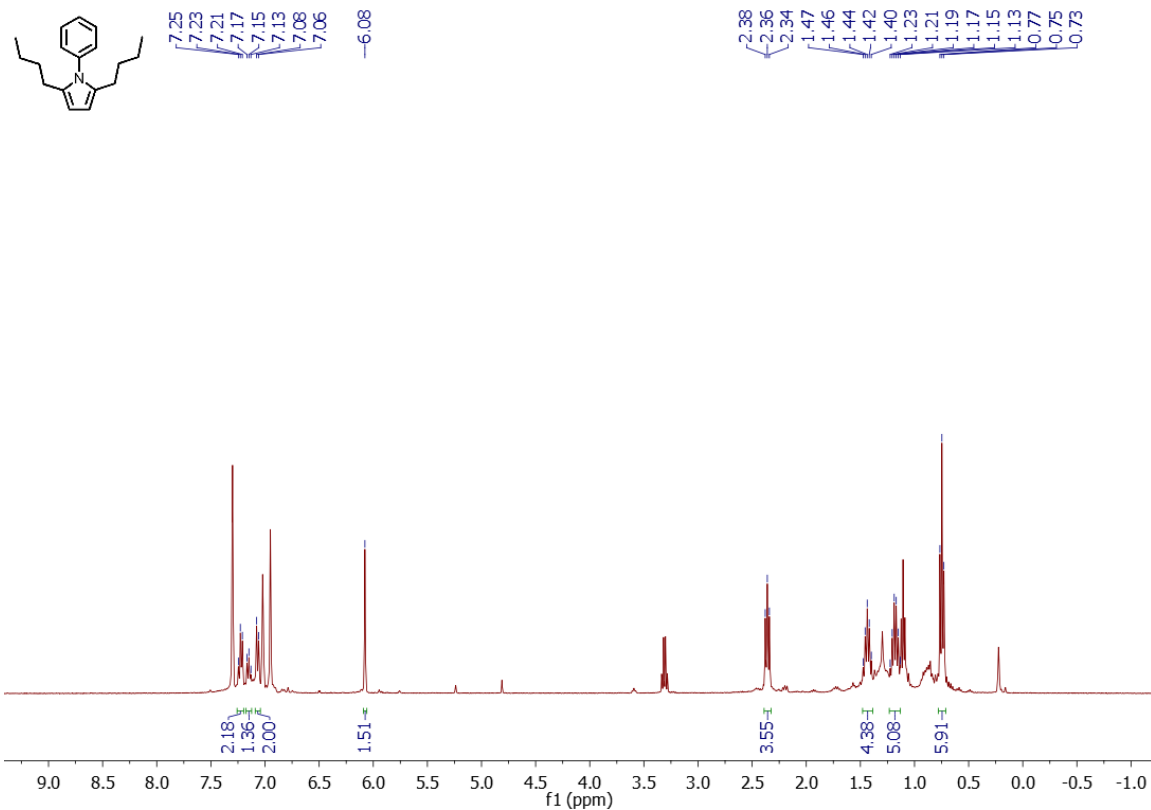


Figure S42: <sup>1</sup>H spectrum of 2,5-di-*n*-butyl-1-phenyl-1H-pyrrole in C<sub>6</sub>D<sub>5</sub>Br.

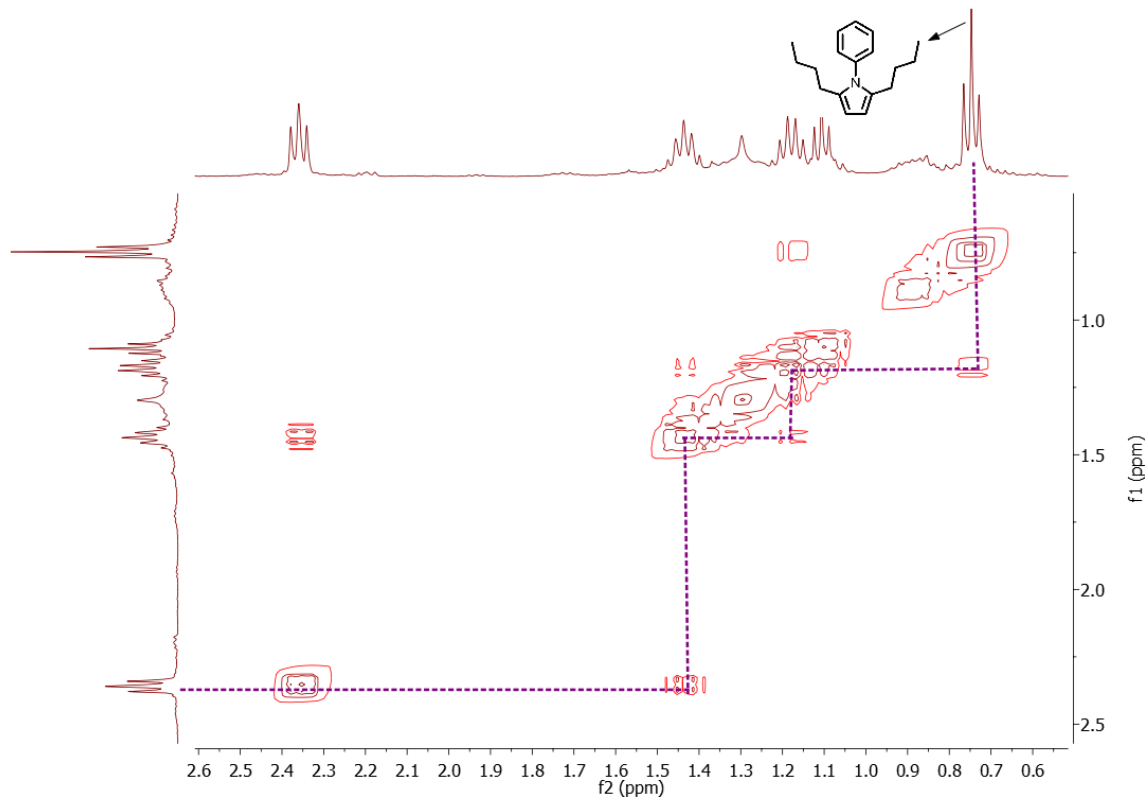
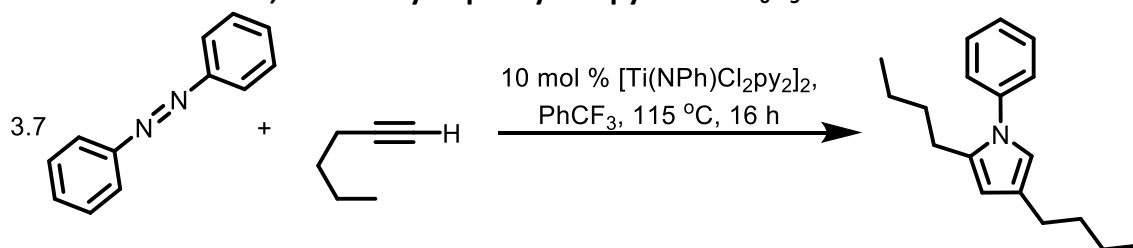


Figure S43: Zoom-in  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of 2,5-di-*n*-butyl-1-phenyl-1*H*-pyrrole in  $\text{C}_6\text{D}_5\text{Br}$ .

#### Characterization of 2,4-di-*n*-butyl-1-phenyl-1*H*-pyrrole in $\text{C}_6\text{D}_5\text{Br}$ <sup>7</sup>



The title compound was prepared *via* slight modification of the literature procedure.<sup>15</sup>  $[\text{Ti}(\text{NPh})\text{Cl}_2\text{py}_2]_2$  (47 mg, 0.0638 mmol, 10 mol % of Ti), azobenzene (106 mg, 0.582 mmol, 3.7 equiv.), 1-hexyne (13 mg, 0.158 mmol, 1.0 equiv.) and 1 mL trifluorotoluene were added to a 20 mL scintillation vial equipped with a small stirbar in a  $\text{N}_2$ -filled glovebox. This was then sealed with a Teflon screw cap and heated overnight at 115 °C for 16 h. The reaction mixture was then concentrated under vacuum to dryness before dissolving in minimal hexanes. The mixture was purified by neutral alumina column using 100 % hexanes as eluent to give a lightly yellow-colored oil that contained the title compound and some pyrrole decomposition products.

$^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_5\text{Br}$ ):  $\delta$  7.22 (t,  $^3J_{\text{HH}} = 7.6$  Hz, 2H, *m*-NPh-*H*), 7.15 (d,  $^3J_{\text{HH}} = 7.2$  Hz, 2H, *o*-NPh-*H*), 7.10 (app t,  $^3J_{\text{HH}} = 7.2$  Hz, 1H, *p*-NPh-*H*), 6.51 (s, 1H, C2-*H*), 6.02 (s, 1H, C4-*H*),

2.57 – 2.49 (m, 4H, *o*-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> and *m*-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.93 (t, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 3H, *o*-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.76 (t, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, 3H, *m*-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>).

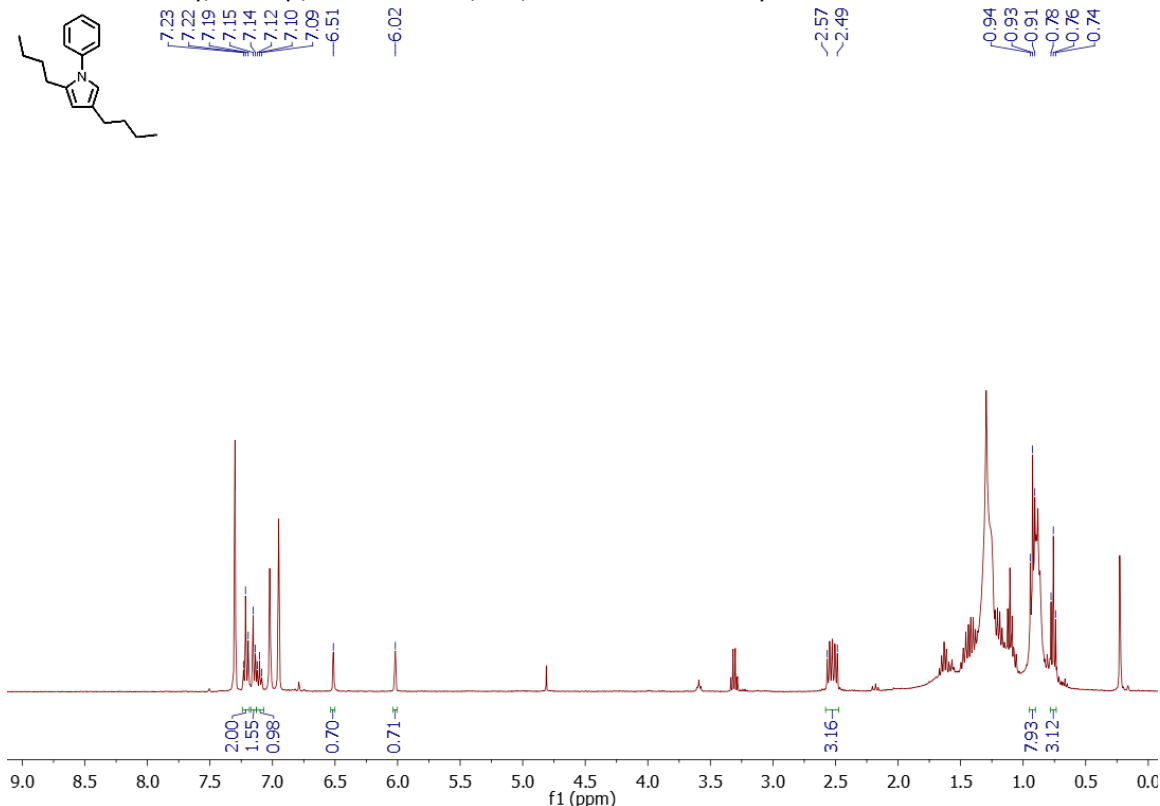
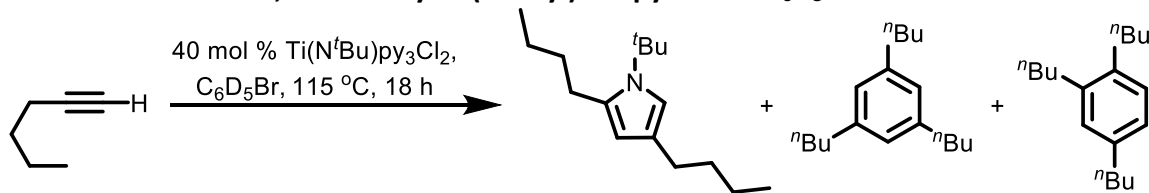


Figure S44: <sup>1</sup>H spectrum of 2,4-di-*n*-butyl-1-phenyl-1*H*-pyrrole in C<sub>6</sub>D<sub>5</sub>Br.

#### Characterization of 2,4-di-*n*-butyl-1-(*t*-butyl)-1*H*-pyrrole in C<sub>6</sub>D<sub>5</sub>Br



Ti(N<sup>*t*</sup>Bu)py<sub>3</sub>Cl<sub>2</sub> (52 mg, 0.122 mmol, 38 mol %), 1-hexyne (26 mg, 0.317 mmol, 1.0 equiv.) and 0.8 mL of C<sub>6</sub>D<sub>5</sub>Br were added to a screw-cap NMR tube in a N<sub>2</sub>-filled glovebox. This was then sealed with a Teflon screw cap and heated at 115 °C for 18 h. The mixture was analysed by <sup>1</sup>H NMR without any further work-up to give a mixture of the title compound, 1,3,5-tri-*n*-butylbenzene and 1,2,4-tri-*n*-butylbenzene.

**<sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>5</sub>Br):** δ 6.52 (s, 1H, C2-*H*), 5.94 (s, 1H, C4-*H*), 3.31 (q, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, 2H, *o*-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.69 – 2.65 (m, 2H, *p*-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.36 (s, 9H, <sup>*t*</sup>Bu), 1.10 (t, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, 3H, *o*-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>).

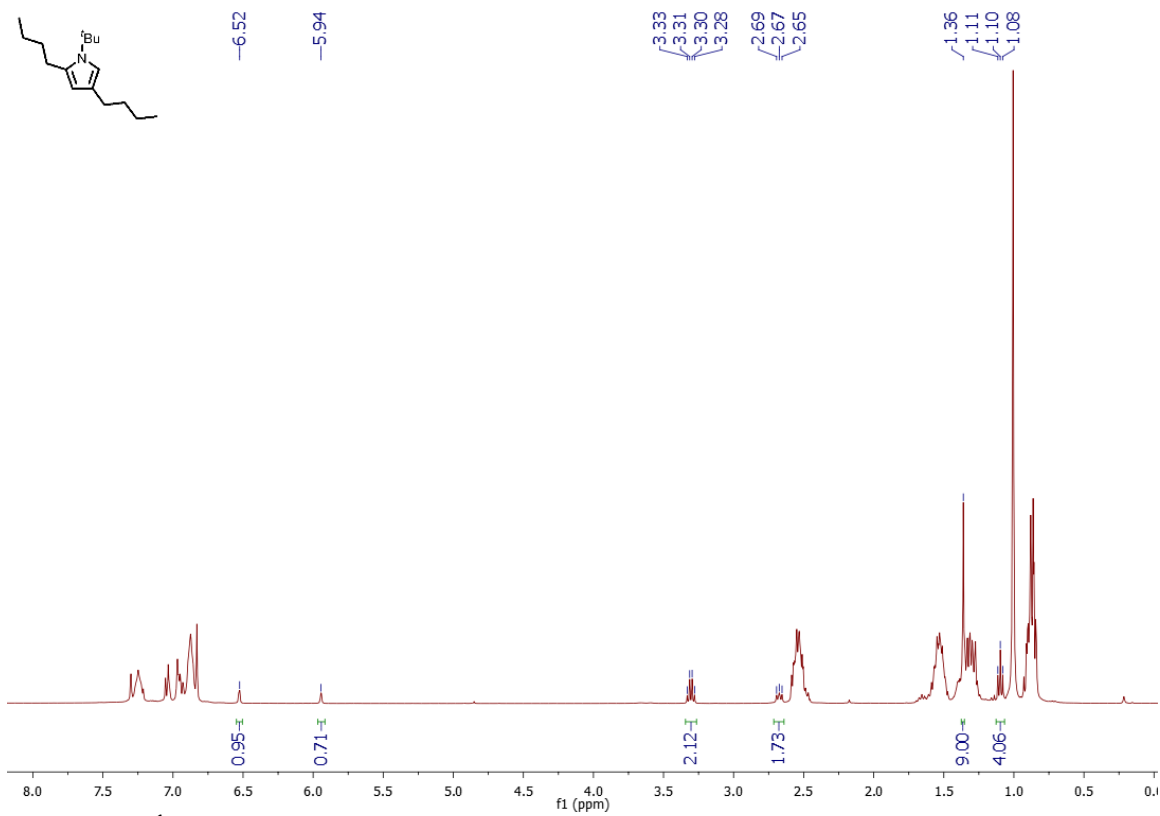


Figure S45: <sup>1</sup>H spectrum of 2,4-di-*n*-butyl-1-(*t*-butyl)-1*H*-pyrrole in C<sub>6</sub>D<sub>5</sub>Br.

## Representative Catalytic Spectra

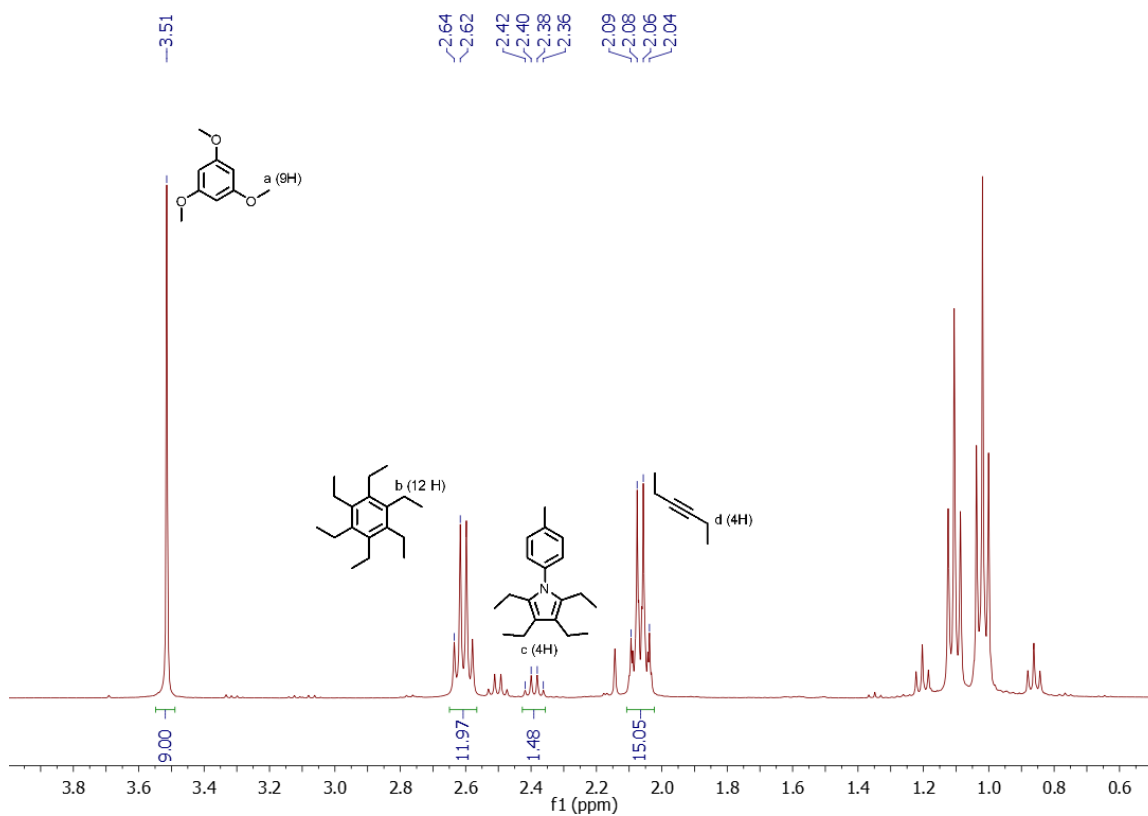


Figure S46: Representative zoom-in  $^1\text{H}$  spectrum of a 3-hexyne catalytic run in  $\text{C}_6\text{D}_5\text{Br}$  (115  $^\circ\text{C}$ /16 h/Precatalyst **2**).

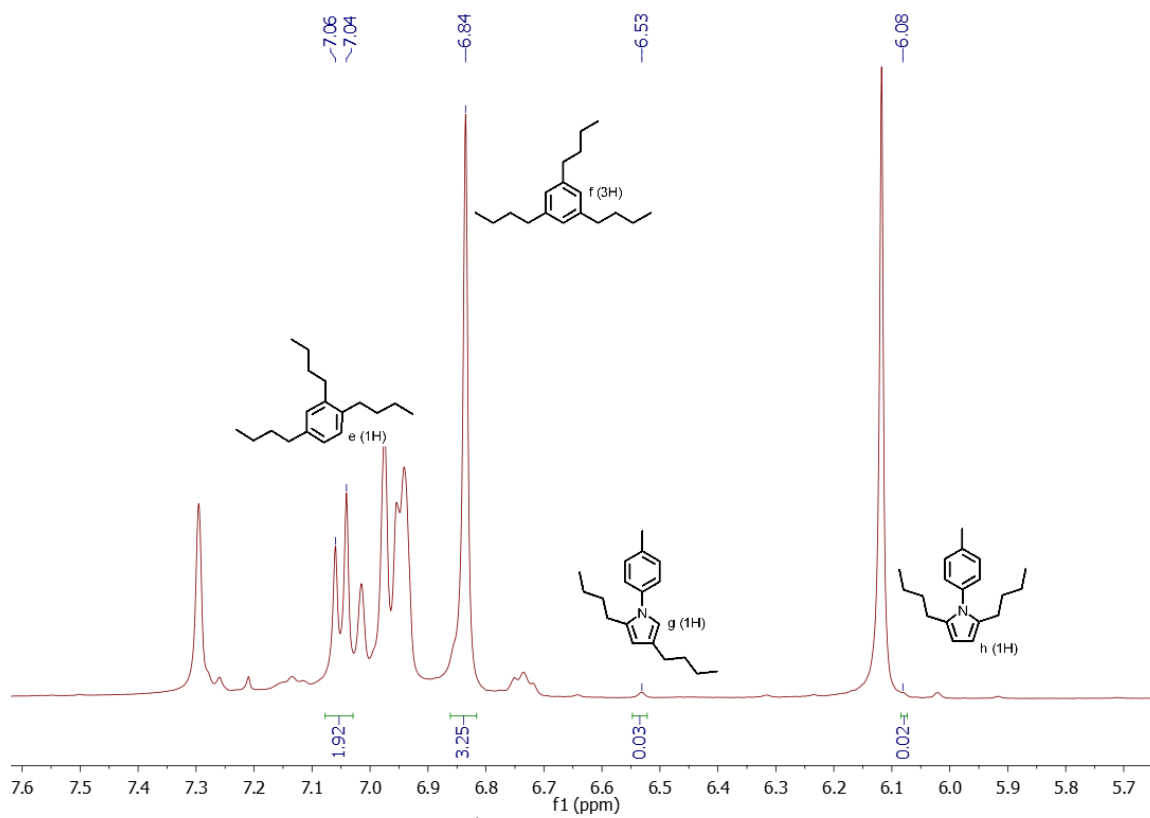


Figure S47: Representative zoom-in  $^1\text{H}$  spectrum of a 1-hexyne catalytic run in  $\text{C}_6\text{D}_5\text{Br}$  (115  $^\circ\text{C}$ /16 h/Precatalyst **2**).

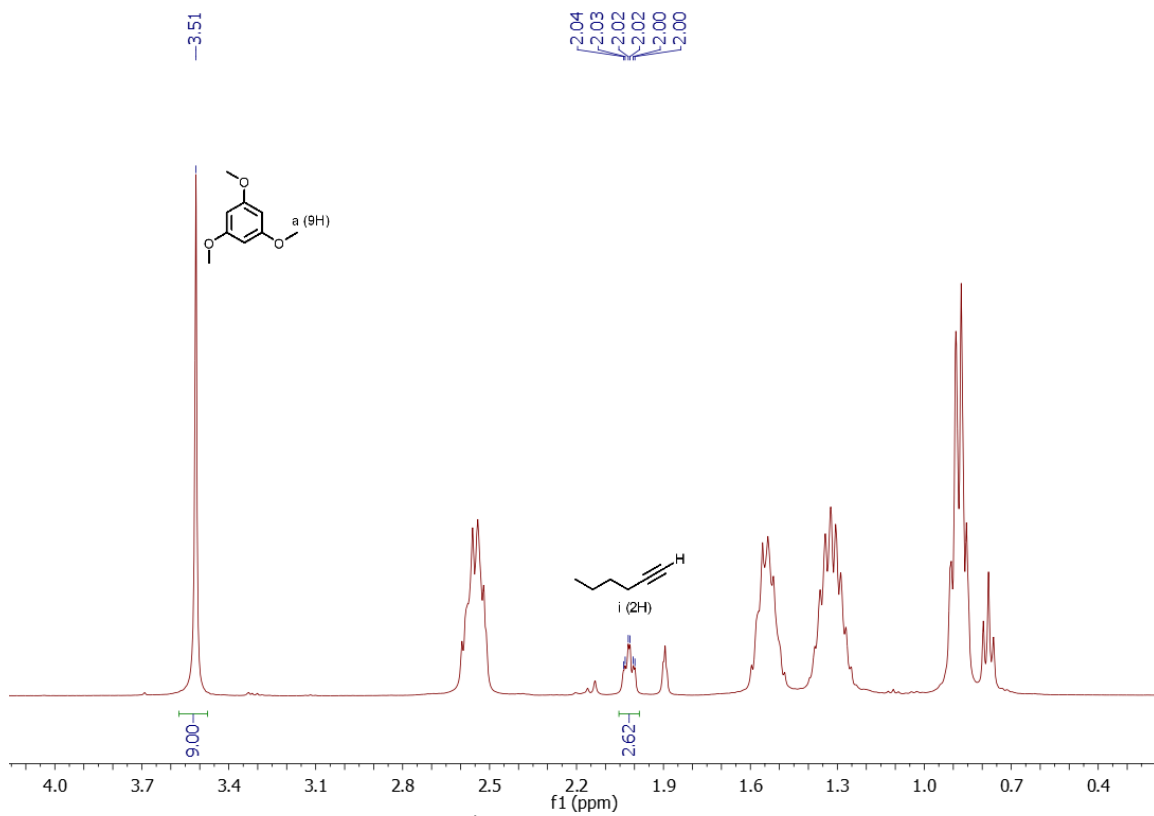


Figure S48: Representative zoom-in  $^1\text{H}$  spectrum of a 1-hexyne catalytic run in  $\text{C}_6\text{D}_5\text{Br}$  (115  $^\circ\text{C}$ /16 h/Precatalyst **2**).

## Alkyne trimerization mol balance data

Table S1: Alkyne trimerization mol balance

[Ti]	1-Hexyne <sup>a</sup>	3-Hexyne <sup>b</sup>
<b>1</b>	103 ± 8	92 ± 6
<b>2</b>	98 ± 1	81 ± 7
<b>3</b>	96 ± 2 <sup>c</sup>	102 ± 3 <sup>d</sup>
<b>4</b>	69 ± 1	72 ± 11
<b>5</b>	85 ± 2	95 ± 4
<b>6</b>	101 ± 10	68 ± 17
<b>7</b>	79 ± 8	60 ± 8
<b>8</b>	63 ± 3	84 ± 6
<b>9</b>	62 ± 0	89 ± 0
<b>10</b>	73 ± 2	93 ± 2
<b>11</b>	76 ± 0	59 ± 8
<b>12</b>	74 ± 5	59 ± 13
<b>13</b>	86 ± 9	58 ± 11
<b>14</b>	63 ± 11	83 ± 15
<b>15</b>	91 ± 8	81 ± 6
<b>16</b>	72 ± 3	66 ± 5

a. Conditions: 5 mol % [Ti], 0.4 M 1-hexyne, C<sub>6</sub>D<sub>5</sub>Br, 16 h, 115 °C, average of 2 - 4 runs.

b. Conditions: 5 mol % [Ti], 0.4 M 3-hexyne, C<sub>6</sub>D<sub>5</sub>Br, 16 h, 115 °C, average of 2 - 4 runs.

c. < 5 min, room temperature

d. 16 h, room temperature



### Preliminary kinetic studies

Precatalyst (5 mol %, 0.01 mmol, 0.02 M) and 0.5 mL of stock solution (3-Hexyne or 1-Hexyne) were added to a Teflon tape lined screw-cap NMR tube in a N<sub>2</sub>-filled glovebox. This was then sealed with a Teflon screw cap. Quantitative <sup>1</sup>H NMR spectra of the catalytic mixture were taken every 5 min (Acquisition time = 5 s, Delay time = 30 s, Dummy Scans = 0, Number of scans = 8) either at room temperature or 115 °C.

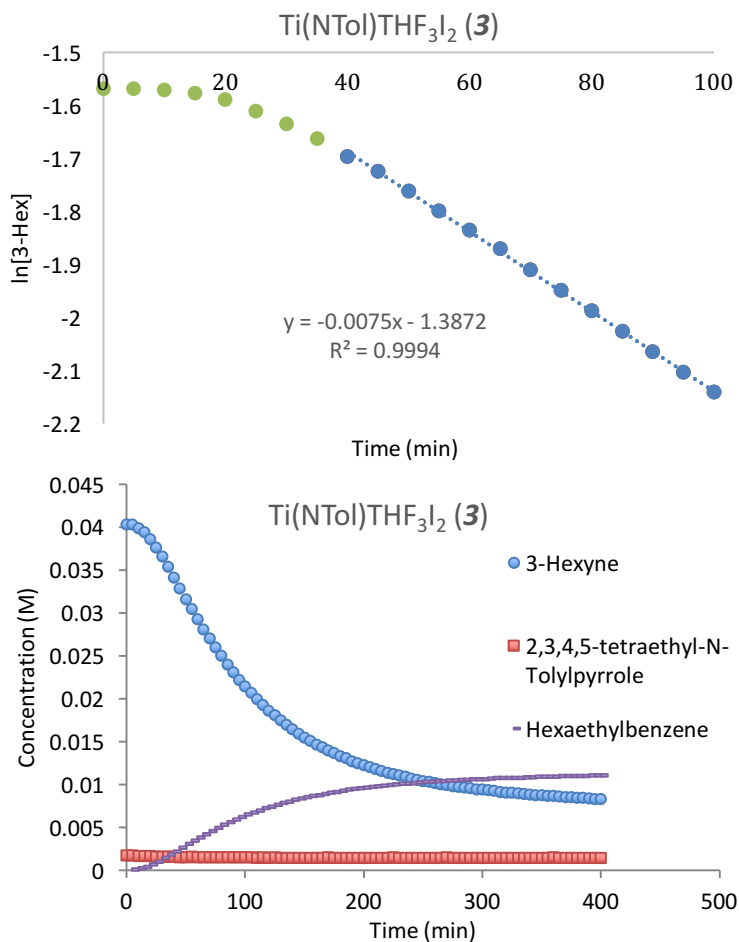


Figure S49: ln[Hex] vs. time for a 3-hexyne catalytic run in C<sub>6</sub>D<sub>5</sub>Br (R.T./Precatalyst **3**).

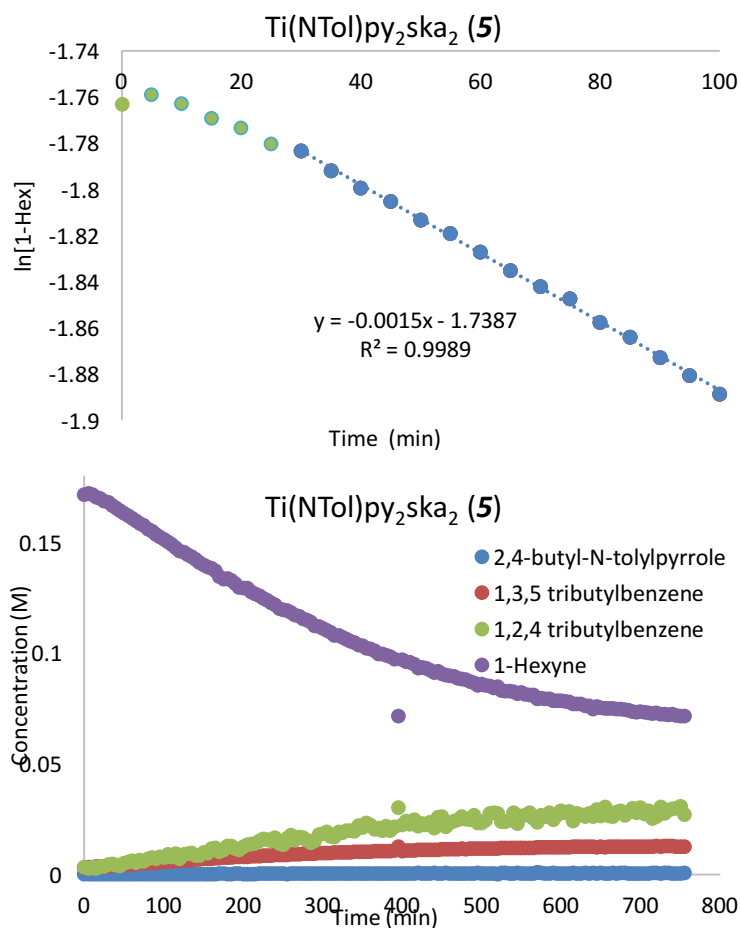


Figure S50:  $\ln[\text{Hex}]$  vs. time for a 1-hexyne catalytic run in  $\text{C}_6\text{D}_5\text{Br}$  (R.T./Precatalyst 5).

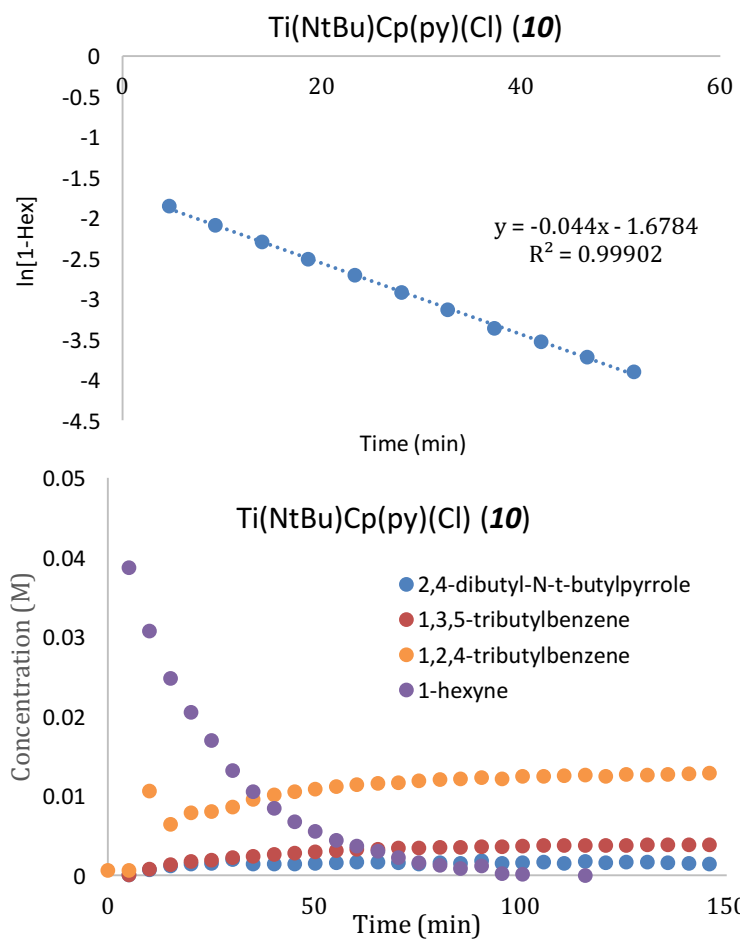


Figure S51:  $\ln[\text{Hex}]$  vs. time for a 1-hexyne catalytic run in  $\text{C}_6\text{D}_5\text{Br}$  (115 °C/Precatalyst **10**).

### Control reactions

Precatalyst (5 mol %, 0.01 mmol, 0.02 M) and 0.5 mL of stock solution (3-Hexyne or 1-Hexyne) were added to a Teflon tape lined screw-cap NMR tube in a N<sub>2</sub>-filled glovebox. This was then sealed with a Teflon screw cap and heated to 115 °C. Quantitative <sup>1</sup>H NMR spectra of the catalytic mixture were taken before and after heating on the Bruker Avance III HD 400 spectrometer (Acquisition time = 5 s, Delay time = 30 s, Dummy Scans = 0, Number of scans = 8).

Table S2: Control reactions

	Precatalyst	Time (h)	Substrate	% yield trimer (1,3,5- : 1,2,4-)
<b>1</b>	none	14	3-Hex	-
<b>2</b>	none	14	1-Hex	-
<b>3</b>	<b>17</b>	14	3-Hex	-
<b>4</b>	<b>17</b>	14	1-Hex	-
<b>5<sup>a</sup></b>	<b>17</b> + Mg*	16	3-Hex	6%
<b>6<sup>a</sup></b>	<b>17</b> + Mg*	16	1-Hex	37% (38 : 62)
<b>7</b>	ZrCl <sub>4</sub> •2THF	16	3-Hex	-
<b>8</b>	ZrCl <sub>4</sub> •2THF	16	1-Hex	-
<b>9</b>	ZrCl <sub>4</sub>	16	3-Hex	-
<b>10</b>	ZrCl <sub>4</sub>	16	1-Hex	-
<b>11<sup>b</sup></b>	ZrCl <sub>4</sub>	16	3-Hex	Trace
<b>12<sup>b</sup></b>	without I.S.	16	1-Hex	Trace
<b>13</b>	TiI <sub>4</sub>	16	3-Hex	-
<b>14</b>	TiI <sub>4</sub>	16	1-Hex	-

a. For entries 5 – 6, **17** (5 mol %, 6.8 mg, 0.01 mmol, 0.02 M), Mg\* (6 mol %, 5.0 mg, 0.012 mmol), 1,3,5-trimethoxybenzene (3.4 mg, 0.02 mmol, 0.04 M), 0.5 mL of Tol-d<sub>8</sub> and either 3-hexyne (22.7 μL, 0.2 mmol, 0.4 M) or 1-hexyne (23.0 μL, 0.2 mmol, 0.4 M) were added to the Teflon tape lined screw-cap NMR tube. Assignment of NMR peaks were made based on comparison with known C<sub>6</sub>D<sub>5</sub>Br spectra.

b. For entries 11 – 12, ZrCl<sub>4</sub> (10 mol %, 0.01 mmol, 0.02 M), 0.5 mL of C<sub>6</sub>D<sub>5</sub>Br and either 3-hexyne (11.4 μL, 0.1 mmol, 0.2 M) or 1-hexyne (11.5 μL, 0.1 mmol, 0.2 M) were added to the Teflon tape lined screw-cap NMR tube.

**Table S3.** Refined data and cell parameters for X-ray Structures

	<b>3</b>	<b>13</b>	<b>14</b>	<b>15</b>
CCDC Number	1524349	1524350	1524351	1524352
Empirical Formula	C <sub>20</sub> H <sub>29</sub> I <sub>2</sub> NO <sub>3</sub> Ti	C <sub>45</sub> H <sub>51</sub> N <sub>3</sub> O <sub>2</sub> Ti	C <sub>57</sub> H <sub>77</sub> N <sub>5</sub> Ti	C <sub>37</sub> H <sub>47</sub> ClN <sub>4</sub> Ti, 0.5(C <sub>6</sub> H <sub>14</sub> )
Formula weight	623.14	713.79	880.13	674.22
Temperature (K)	123(2)	123(2)	123(2)	123(2)
<i>a</i> , Å	14.324(5)	9.4769(7)	15.516(2)	11.142(3)
<i>b</i> , Å	10.083(4)	20.5440(13)	14.4749(17)	27.430(5)
<i>c</i> , Å	16.295(6)	20.9582(9)	23.531(5)	12.8602(12)
<i>α</i> , deg	90	90	90	90
<i>β</i> , deg	97.989(7)	95.330(4)	104.510(13)	103.355(12)
<i>γ</i> , deg	90	90	90	90
Volume, Å <sup>3</sup>	2330.6(15)	4062.8(4)	7135.7(5)	3824.0(13)
Z	4	4	4	4
Crystal System	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space Group	P 2 <sub>1</sub> /c	P 2 <sub>1</sub> /n	P 2 <sub>1</sub> /c	P 2 <sub>1</sub> /n
<i>d</i> <sub>calc</sub> , g/cm <sup>3</sup>	1.776	1.167	1.143	1.171
<i>θ</i> range, deg	2.39 to 28.91	3.01 to 74.64	2.94 to 74.75	3.22 to 75.12
<i>μ</i> , mm <sup>-1</sup>	3.034	2.078	1.715	2.768
Abs. Correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan
GOF	1.018	1.056	1.031	1.027
<i>R</i> <sub>1</sub> <sup>a</sup>	<i>R</i> 1 = 0.0273	<i>R</i> 1 = 0.0319	<i>R</i> 1 = 0.0386	<i>R</i> 1 = 0.0412
<i>wR</i> <sub>2</sub> <sup>b</sup> [ <i>I</i> > 2σ( <i>I</i> )]	<i>wR</i> 2 = 0.0688	<i>wR</i> 2 = 0.0919	<i>wR</i> 2 = 0.1091	<i>wR</i> 2 = 0.1131

<sup>a</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup>  $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$ .

## References

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