

## Supporting Information

for

### Synthesis and catalytic properties of palladium(II) complexes with P, $\pi$ -chelating ferrocene phosphinoallyl ligands and their non-tethered analogues

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## Synthesis of 5<sup>R</sup>

**Preparation of [PdCl(FcPPh<sub>2</sub>-κP)(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)] (5<sup>Ph</sup>).** In the air, a solution of (diphenylphosphino)ferrocene (FcPPh<sub>2</sub>; 111.1 mg, 0.30 mmol) in dichloromethane (3 mL) was added to a solution of [PdCl(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)<sub>2</sub>] (54.9 mg, 0.15 mmol) in the same solvent (3 mL). The flask was flushed with nitrogen and sealed. The orange reaction mixture was stirred at room temperature for 90 min and evaporated under reduced pressure. The solid residue was redissolved in dichloromethane (3 mL) and layered with hexane (12 mL). Crystals, which formed upon slow mixing of the solvents at -18 °C, were decanted, washed with cold pentane (3 × 4 mL), and dried under reduced pressure. Yield: 157.7 mg (95%), orange crystals.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.74 (d, <sup>3</sup>J<sub>HH</sub> = 12.1 Hz, 1 H, CH<sub>2</sub> of allyl), 3.22 (br d, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 1 H, CH<sub>2</sub> of allyl), 3.79 (dd, <sup>3</sup>J<sub>HH</sub> = 13.8 Hz, <sup>3</sup>J<sub>PH</sub> = 9.9 Hz, 1 H, CH<sub>2</sub> of allyl), 4.21 (s, 5 H, CH of C<sub>5</sub>H<sub>5</sub>), 4.37-4.41 (m, 2 H, CH of C<sub>5</sub>H<sub>4</sub>), 4.46 (vt, *J'* = 1.7 Hz, 2 H, CH of C<sub>5</sub>H<sub>4</sub>), 4.78 (td, <sup>3</sup>J<sub>HH</sub> ≈ <sup>3</sup>J<sub>PH</sub> ≈ 7.4 Hz, <sup>2</sup>J<sub>HH</sub> = 2.0 Hz, 1H, CH<sub>2</sub> of allyl) 5.59 (dddd, <sup>3</sup>J<sub>HH</sub> = 13.8, 12.0, 7.5, 6.7 Hz, 1H, CH of allyl), 7.32-7.46 (m, 6 H, Ph), 7.47-7.64 (m, 4 H Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 59.56 (d, *J*<sub>PC</sub> = 2 Hz, CH<sub>2</sub> of allyl), 70.04 (C<sub>5</sub>H<sub>5</sub>), 71.40 (d, *J*<sub>PC</sub> = 7 Hz, CH of C<sub>5</sub>H<sub>4</sub>), 71.42 (d, *J*<sub>PC</sub> = 7 Hz, CH of C<sub>5</sub>H<sub>4</sub>), 73.08 (d, <sup>1</sup>*J*<sub>PC</sub> = 49 Hz, C<sup>ipso</sup> of C<sub>5</sub>H<sub>4</sub>), 74.02 (d, *J*<sub>PC</sub> = 11 Hz, CH of C<sub>5</sub>H<sub>4</sub>), 74.22 (d, *J*<sub>PC</sub> = 12 Hz, CH of C<sub>5</sub>H<sub>4</sub>), 80.55 (d, *J*<sub>PC</sub> = 32 Hz, CH<sub>2</sub> of allyl), 117.43 (d, *J*<sub>PC</sub> = 5 Hz, CH of allyl), 128.20 (d, *J*<sub>PC</sub> = 10 Hz, 2 × CH of Ph), 130.09 (vt, *J'* = 3 Hz, CH of Ph), 133.18 (d, *J*<sub>PC</sub> = 12 Hz, CH of Ph), 133.28 (d, *J*<sub>PC</sub> = 12 Hz, CH of Ph), 134.82 (d, <sup>1</sup>*J*<sub>PC</sub> = 43 Hz, C<sup>ipso</sup> of Ph), 134.88 (d, <sup>1</sup>*J*<sub>PC</sub> = 43 Hz, C<sup>ipso</sup> of Ph). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 16.9 (s). ESI+ MS: *m/z* 517.0 ([M - Cl]<sup>+</sup>), 575.0 ([M + Na]<sup>+</sup>). Anal. Calc. for C<sub>25</sub>H<sub>24</sub>ClFePPd (553.2): C 54.28, H 4.37 %. Found: C 54.09, H 4.34%.

**Synthesis of [PdCl(FcPCy<sub>2</sub>-κP)(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)] (5<sup>Cy</sup>).** In the air, a solution of (dicyclohexylphosphino)ferrocene (FcPCy<sub>2</sub>; 115.0 mg, 0.30 mmol) in dichloromethane (3 mL) was added to a solution of [PdCl(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)<sub>2</sub>] (54.9 mg, 0.15 mmol) in the same solvent (3 mL). The reaction flask was flushed with nitrogen and sealed and the mixture was stirred at room temperature for 90 min. The orange-red solution was evaporated under reduced pressure and the oily residue was redissolved in dichloromethane (0.8 mL) and added to hexane (25 mL). The solution was slowly cooled to -18 °C. After one week, the separated crystals were decanted, washed with cold pentane (3 × 4 mL) and dried under reduced pressure. Yield: 146.6 mg (85%), orange-red crystals.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 399.95 MHz): δ 1.04-1.55 (m, 10 H, Cy), 1.62-2.33 (m, 12 H, Cy), 2.78 (d, <sup>3</sup>J<sub>HH</sub> = 11.9 Hz, 1 H, CH<sub>2</sub> of allyl), 3.72 (dd, <sup>3</sup>J<sub>HH</sub> = 13.9 Hz, <sup>4</sup>J<sub>HP</sub> = 9.1 Hz, 1 H, CH<sub>2</sub> of allyl), 4.08 (dt, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, <sup>2</sup>J<sub>HH</sub> = 2.0 Hz, 1 H, CH<sub>2</sub> of allyl), 4.22 (s, 5 H, CH of C<sub>5</sub>H<sub>5</sub>), 4.29-4.34 (m, 1H, CH of C<sub>5</sub>H<sub>4</sub>), 4.34-4.41 (m, 1H, CH of C<sub>5</sub>H<sub>4</sub>), 4.44 (vq, *J'* = 1.7 Hz, CH of C<sub>5</sub>H<sub>4</sub>), 4.72 (td, <sup>3</sup>J<sub>HH</sub> ≈ <sup>4</sup>J<sub>PH</sub> ≈ 7.4 Hz, <sup>2</sup>J<sub>HH</sub> = 2.0 Hz, 1 H, CH<sub>2</sub> of allyl), 5.49 (dddd, <sup>3</sup>J<sub>HH</sub> = 13.9, 11.8, 7.6, 6.6 Hz, 1 H, CH of allyl). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.58 MHz): δ 26.10 (2 × CH<sub>2</sub> of Cy), 26.81-27.21 (m, 4 × CH<sub>2</sub> of Cy), 28.81 (d, *J*<sub>PC</sub> = 5 Hz,

CH<sub>2</sub> of Cy), 28.84 (d,  $J_{PC} = 5$  Hz, CH<sub>2</sub> of Cy), 29.07 (CH<sub>2</sub> of Cy), 29.55 (CH<sub>2</sub> of Cy), 35.32 (d,  $^1J_{PC} = 23$  Hz, 2× CH of Cy), 52.18 (d,  $J_{PC} = 2$  Hz, CH<sub>2</sub> of allyl), 69.91 (C<sub>5</sub>H<sub>5</sub>), 70.05 (d,  $J_{PC} = 6$  Hz, CH of C<sub>5</sub>H<sub>4</sub>), 70.09 (d,  $J_{PC} = 6$  Hz, CH of C<sub>5</sub>H<sub>4</sub>), 72.80 (d,  $J_{PC} = 8$  Hz, CH of C<sub>5</sub>H<sub>4</sub>), 73.01 (d,  $^1J_{PC} = 36$  Hz, C<sup>ipso</sup> of C<sub>5</sub>H<sub>4</sub>), 73.34 (d,  $J_{PC} = 10$  Hz, CH of C<sub>5</sub>H<sub>4</sub>), 81.57 (d,  $J_{PC} = 29$  Hz, CH<sub>2</sub> of allyl), 115.92 (d,  $J_{PC} = 5$  Hz, CH of allyl). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 161.90 MHz): δ 30.6 (s). ESI+ MS:  $m/z$  529.1 ([M - Cl]<sup>+</sup>), 587.1 ([M + Na]<sup>+</sup>). Anal. Calc. for C<sub>25</sub>H<sub>36</sub>ClFePPd (565.3): C 53.12, H 6.42%. Found: C 53.07, H 6.40%.

## Catalytic Experiments

**Allylation of amines.** An oven-dried Schlenk flask was charged with the respective catalyst (typically 1 mol.% relative to cinnamyl acetate). After three vacuum-nitrogen cycles, cinnamyl acetate (83.4  $\mu\text{L}$ , 0.50 mmol) and secondary amine (morpholine or diethylamine, 1 or 2 eq.) were added under nitrogen backflow using an automatic pipette. The glass stopper was then replaced by a septum and the solvent (2 mL) was introduced *via* a syringe. The septum was replaced with the glass stopper again and the reaction flask was heated under stirring in a preheated oil bath (50  $^{\circ}\text{C}$ ) for 20 h. The reaction mixture was then evaporated under reduced pressure and the residue dissolved in dichloromethane (5 mL). The solution was transferred to a separatory funnel and washed with brine (5 mL). The aqueous phase was back-extracted with dichloromethane (5  $\times$  2 mL). The combined organic layers were dried over anhydrous magnesium sulfate, filtered through a PTFE syringe filter (0.45  $\mu\text{m}$  porosity), and evaporated under reduced pressure with a chromatography-grade silica gel. The preadsorbed product was loaded on a silica gel column (Interchim puriFlash, 30  $\mu\text{m}$ , 25 g) using a solid loader and purified on a Büchi Reveleris X2 automatic chromatograph with UV detection. Purification of 4-cinnamylmorpholine was performed using gradient elution from ethyl acetate/cyclohexane (30 % EtOAc) to pure ethyl acetate whereas *N,N*-diethylcinnamylamine was eluted with ethyl acetate/cyclohexane 1/1 + 1 % triethylamine isocratic mixture. The flow rate was 25 mL  $\text{min}^{-1}$  in both cases. The second band was collected and evaporated. The residue was evaporated several times from dichloromethane under reduced pressure to yield the product as pale yellow oil.

Analytical data for 4-cinnamylmorpholine (**7a**).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.41-2.58 (m, 4 H,  $\text{CH}_2$  morpholine), 3.14 (dd,  $^3J_{\text{HH}} = 6.8$  Hz,  $^4J_{\text{HH}} = 1.4$  Hz, 2 H,  $\text{CH}_2$  cinnamyl), 3.70-3.76 (m, 4 H,  $\text{CH}_2$  morpholine), 6.25 (dt,  $^3J_{\text{HH}} = 15.8$  Hz,  $^3J_{\text{HH}} = 6.8$  Hz, 1 H,  $\text{PhCH}=\text{CH}$ ), 6.53 (dt,  $^3J_{\text{HH}} = 15.8$  Hz,  $^4J_{\text{HH}} = 1.4$  Hz, 1 H,  $\text{PhCH}=\text{CH}$ ), 7.19-7.25 (m, 1 H, Ph), 7.27-7.34 (m, 2 H, Ph), 7.34-7.40 (m, 2 H, Ph).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  53.69 ( $\text{CH}_2$  morpholine), 61.46 ( $\text{CH}_2$  cinnamyl), 66.98 ( $\text{CH}_2$  morpholine), 126.07 ( $\text{PhCH}=\text{CH}$ ), 126.30 (CH of Ph), 127.55 (CH of Ph), 128.56 (CH of Ph), 133.34 ( $\text{PhCH}=\text{CH}$ ), 136.79 ( $\text{C}^{\text{ipso}}$  of Ph). The data agree with the literature.<sup>1</sup>

Analytical data for *N,N*-diethylcinnamylamine (**7b**).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.06 (t,  $^3J_{\text{HH}} = 7.2$  Hz, 6 H,  $\text{CH}_2\text{CH}_3$ ), 2.57 (q,  $^3J_{\text{HH}} = 7.2$  Hz, 4 H,  $\text{CH}_2\text{CH}_3$ ), 3.25 (dd,  $^3J_{\text{HH}} = 6.7$  Hz,  $^4J_{\text{HH}} = 1.4$  Hz, 2 H,  $\text{CH}_2$  cinnamyl), 6.29 (dt,  $^3J_{\text{HH}} = 15.9$  Hz,  $^3J_{\text{HH}} = 6.7$  Hz, 1 H,  $\text{PhCH}=\text{CH}$ ), 6.51 (dt,  $^3J_{\text{HH}} = 15.9$  Hz,  $^4J_{\text{HH}} = 1.4$  Hz, 1 H,  $\text{PhCH}=\text{CH}$ ), 7.16-7.41 (m, 5 H, Ph).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  11.72 ( $\text{CH}_2\text{CH}_3$ ), 46.73 ( $\text{CH}_2\text{CH}_3$ ), 55.61 ( $\text{CH}_2$  cinnamyl), 126.24 (CH of Ph), 127.28 (CH of Ph), 127.74 ( $\text{PhCH}=\text{CH}$ ), 128.53 (CH of Ph), 132.16 ( $\text{PhCH}=\text{CH}$ ), 137.19 ( $\text{C}^{\text{ipso}}$  of Ph). The data match those in the literature.<sup>1</sup>

Note: morpholine and diethyl amine were dried over sodium metal and distilled under nitrogen, acetonitrile was dried by standing over CaH<sub>2</sub> and distilled under nitrogen. Toluene was obtained from an MBRAUN SPS5 solvent purification system.

**Suzuki-Miyaura cross-coupling of benzoyl chloride with *p*-tolylboronic acid.** A Schlenk flask was charged with *p*-tolylboronic acid (167 mg, 1.25 mmol) and sodium carbonate (133 mg, 1.25 mmol). After three vacuum-nitrogen cycles, benzoyl chloride (174.0  $\mu$ L, 1.50 mmol) was added against nitrogen flow using an automatic pipette. The flask was then sealed with a septum and a solution of catalyst (0.1 mol.%, 0.5 mL of 2.5 mM solution in benzene-d<sub>6</sub>) was introduced *via* a syringe, followed by benzene-d<sub>6</sub> (2.5 mL) and degassed water (3 mL). The septum was replaced with a glass stopper and the reaction flask was heated under stirring in a preheated oil bath (50 °C) for 1 h. Then, the reaction vessel was cooled in cold water, and anisole (135.9  $\mu$ L, 1.25 mmol; internal standard) was added. In some cases, when the conversion was low, the organic layer solidified after cooling. To dissolve the crystallized material (presumably unreacted boronic acid), saturated aqueous sodium carbonate (5 mL) was added and the mixture was vigorously shaken. The organic layer was removed with a Pasteur pipette, dried over anhydrous magnesium sulfate, and filtered through a PTFE syringe filter (0.45  $\mu$ m porosity). The product yield was determined using <sup>1</sup>H NMR spectroscopy.

The reaction was also performed on a preparative scale. In this case, the procedure was nearly the same except that the catalyst **5<sup>Ph</sup>** (3.44 mg, 0.5 mol.%) was added as a solid, and toluene (3 mL) was employed as the solvent. The reaction mixture was transferred to a separatory funnel and diluted with diethyl ether (20 mL). The aqueous phase was separated, and the organic layer was washed successively with 3 M HCl (2 $\times$  20 mL), 5% KOH (4 $\times$  25 mL), and brine (2 $\times$  20 mL), dried over anhydrous magnesium sulfate and evaporated under vacuum with chromatographic silica. The crude preadsorbed product was loaded on a silica gel column (Interchim puriFlash, 30  $\mu$ m, 40 g) using a solid loader and purified using a Büchi Reveleris X2 automatic chromatograph with UV detection and ethyl acetate-hexane (3% EtOAc) as the eluent (flow rate 32 mL min<sup>-1</sup>). The major band was collected and evaporated under reduced pressure. Yield of 4-methylbenzophenone: 222 mg (91%), pale yellow oil.

Analytical data for 4-methylbenzophenone (**11**). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.43 (s, 3 H, CH<sub>3</sub>), 7.23-7.31 (m, 2 H, aromatics), 7.42-7.51 (m, 2 H, aromatics), 7.52-7.61 (m, 1 H, aromatics), 7.68-7.75 (m, 2 H, aromatics), 7.75-7.82 (m, 2 H, aromatics). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  21.64 (CH<sub>3</sub>), 128.20 (CH aromatic), 128.97 (CH aromatic), 129.91 (CH aromatic), 130.29 (CH aromatic), 132.15 (CH aromatic), 134.87 (C<sup>ipso</sup> aromatic), 137.95 (C<sup>ipso</sup> aromatic), 143.22 (C<sup>ipso</sup> aromatic), 196.47 (C=O). The data agree with the literature.<sup>2</sup>

## X-ray crystallography

The diffraction data ( $\pm h\pm k\pm l$ ,  $\theta_{\max} = 27.5^\circ$ ) for **1<sup>Ph</sup>** and **1<sup>Cy</sup>·0.2C<sub>6</sub>H<sub>14</sub>** were collected with a Bruker D8 VENTURE Kappa Duo diffractometer equipped with a Cryostream Cooler. Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) was used in both cases. The structures were solved by direct methods (SHELXT 2014 or 2018)<sup>3</sup> and refined using SHELXL-2017.<sup>4</sup> All nonhydrogen atoms were refined with anisotropic displacement parameters. The allyl hydrogen atoms in **1<sup>Ph</sup>** were identified on the difference electron density maps and refined as riding atoms with  $U_{\text{iso}}(\text{H})$  set to  $1.2U_{\text{eq}}(\text{C})$  of their bonding carbon atom. All other hydrogens were placed in their theoretical positions and refined similarly.

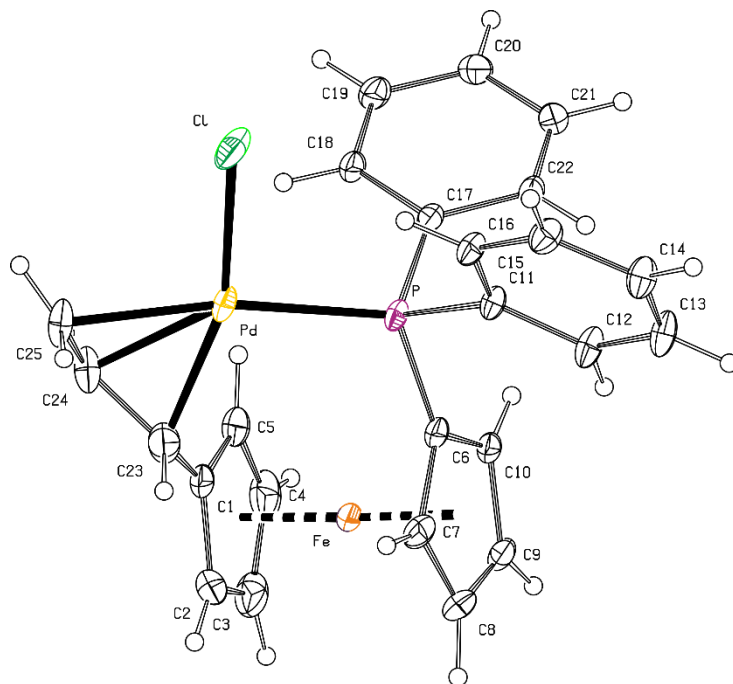
The structure of **4<sup>Cy</sup>** contained structural voids occupied by disordered hexane used for crystallization. The solvent contribution to the overall scattering was numerically removed using PLATON SQUEEZE.<sup>5</sup> In total, 175 electrons were removed *per* the unit cell, which matches the expected value (180 electrons calculated for 0.2 hexane *per* the complex molecule or 3.6 hexane molecule in the unit cell; space group  $R\bar{3}$ ,  $Z = 18$ ). In addition, the allyl moiety was disordered over two positions approximately related by rotation by  $180^\circ$  along the pivotal C1-C23 bond. The refined occupancies were 0.79:0.21.

Selected crystallographic data and structure refinement parameters are outlined in Table S1. All geometric data and structural diagrams were obtained using the PLATON program.<sup>6</sup> The numerical values were rounded to one decimal place relative to their standard deviations. Complete crystallographic data were deposited with the Cambridge Crystallographic Data Centre (CCDC) and can be accessed via [www.ccdc.cam.ac.uk/structures](http://www.ccdc.cam.ac.uk/structures). The CCDC deposition numbers are quoted in Table S1.

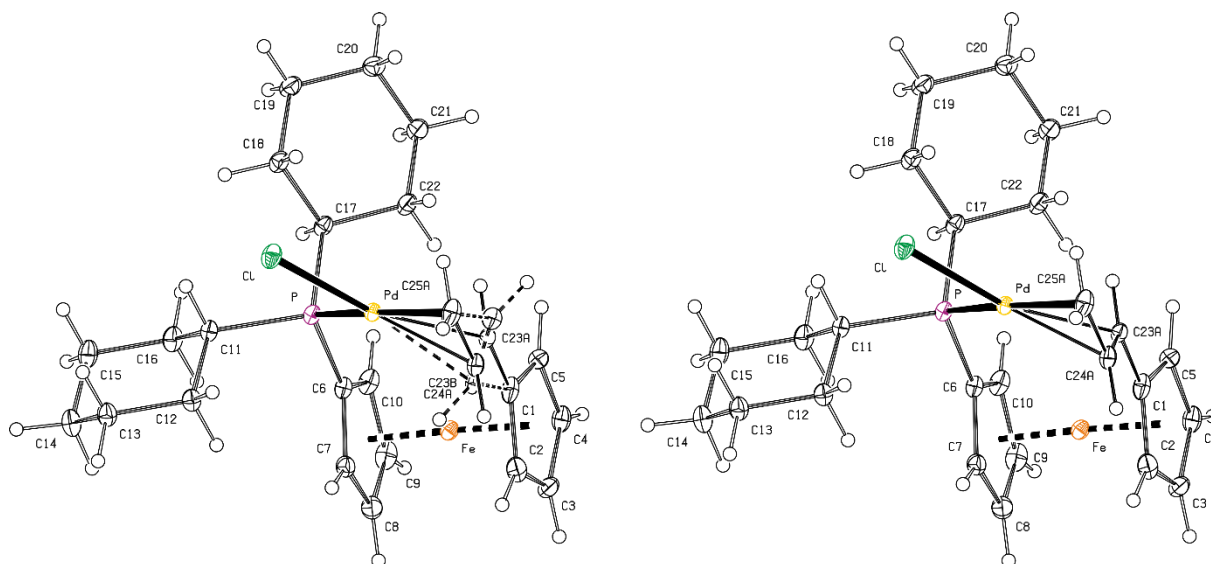
**Table S1** Selected crystallographic data and structure refinement parameters<sup>a</sup>

Compound	<b>1<sup>Ph</sup></b>	<b>1<sup>Cy</sup>·0.2C<sub>6</sub>H<sub>14</sub></b>
Formula	C <sub>25</sub> H <sub>22</sub> ClFePPd	C <sub>25</sub> H <sub>34</sub> ClFePPd·0.2C <sub>6</sub> H <sub>14</sub>
<i>M</i>	551.09	580.42
Crystal system	monoclinic	trigonal
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i> (no. 14)	<i>R</i> -3 (no. 148)
<i>T</i> [K]	150(2)	120(2)
<i>a</i> [Å]	11.4818(8)	30.9968(7)
<i>b</i> [Å]	9.5626(6)	30.9968(7)
<i>c</i> [Å]	19.859(1)	12.8371(4)
$\alpha$ [°]	90	90
$\beta$ [°]	100.978(2)	90
$\gamma$ [°]	90	120
<i>V</i> [Å <sup>3</sup> ]	2140.5(2)	10681.5(6)
<i>Z</i>	4	18
<i>F</i> (000)	1104	5364
$\mu$ (Mo K $\alpha$ ) [mm <sup>-1</sup> ]	1.727	1.561
Diffns collected	34775	87708
Independent diffns	4909	5452
Observed <sup>a</sup> diffns	4403	5146
<i>R</i> <sub>int</sub> <sup>b</sup> [%]	3.24	3.43
No. of parameters	262	281
<i>R</i> <sup>b</sup> obsd diffns [%]	2.81	1.97
<i>R</i> , <i>wR</i> <sup>b</sup> all data [%]	3.30, 6.69	2.12, 4.76
$\Delta\rho$ [e Å <sup>-3</sup> ]	1.26, -0.77	0.72, -0.60
CCDC ref. no.	2331020	2331021

<sup>a</sup> Diffractions with  $I > 2\sigma(I)$ . <sup>b</sup> Definitions:  $R_{\text{int}} = \Sigma |F_o^2 - F_o^2(\text{mean})| / \Sigma F_o^2$ , where  $F_o^2(\text{mean})$  is the average intensity of symmetry-equivalent diffractions.  $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ ,  $wR = [\Sigma \{w(F_o^2 - F_c^2)^2\} / \Sigma w(F_o^2)^2]^{1/2}$ ;  $w$  denotes the weighting factor,  $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$ , where  $a$  and  $b$  are structure-specific constants, and  $P = 1/3(F_o^2 + 2F_c^2)$ .



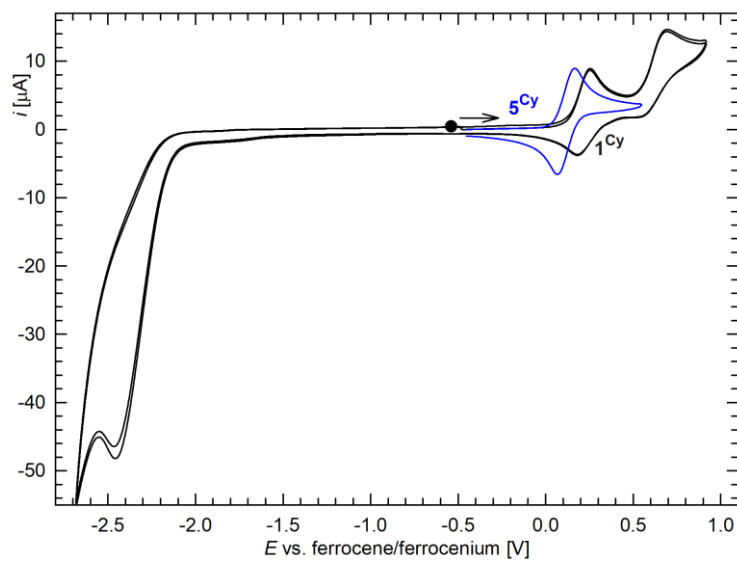
**Figure S1** PLATON plot of the molecular structure of **1<sup>Ph</sup>** showing atomic labels and displacement ellipsoids at the 30% probability level



**Figure S2** PLATON plots of the complex molecule in the structure of **1<sup>Cy</sup>·0.2C<sub>6</sub>H<sub>14</sub>** showing atomic labels and displacement ellipsoids at the 30% probability level (left: complete diagram, right: a drawing showing only the dominant orientation of the  $\pi$ -bound allyl moiety)

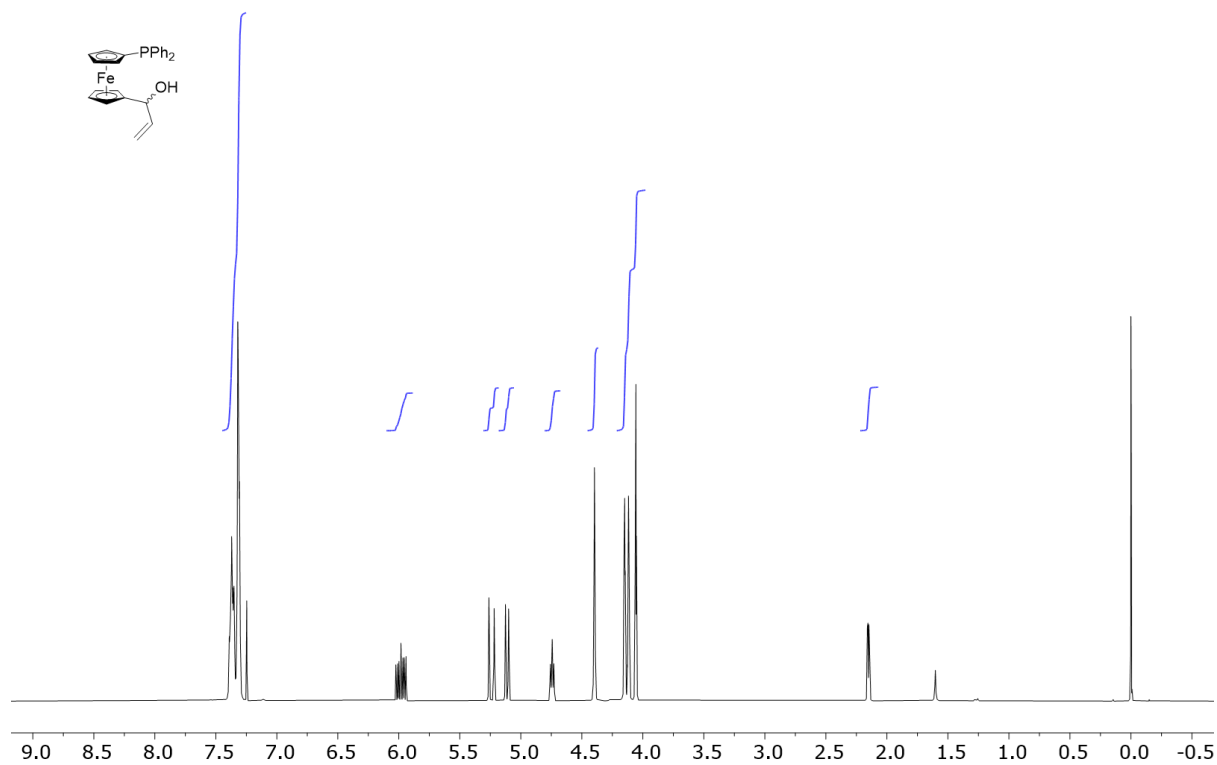


## Cyclic voltammograms of $1^{Cy}$ and $5^{Cy}$

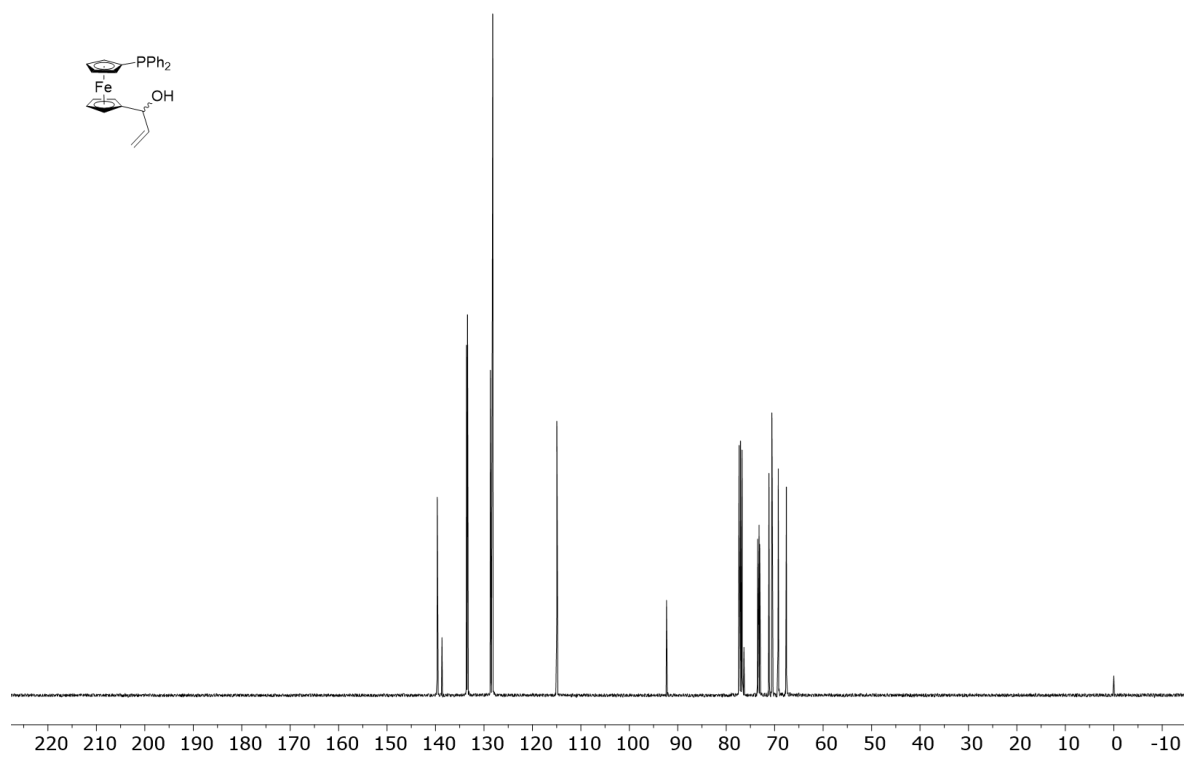


**Figure S3** Cyclic voltammograms of  $1^{Cy}$  (black lines) and  $5^{Cy}$  (blue line) recorded at a glassy carbon disk electrode in 0.1 M  $Bu_4N[PF_6]/CH_2Cl_2$  (scan rate:  $100\text{ mV s}^{-1}$ ). The scan direction is indicated by an arrow.

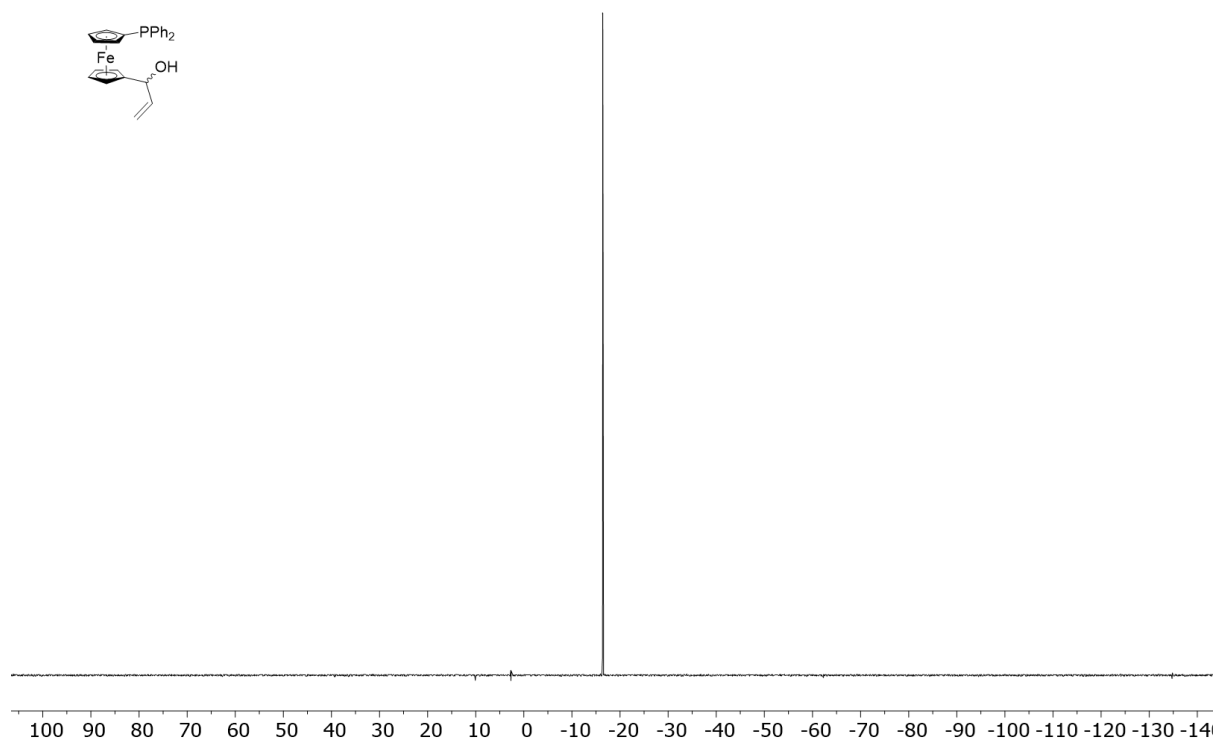
## Copies of the NMR spectra



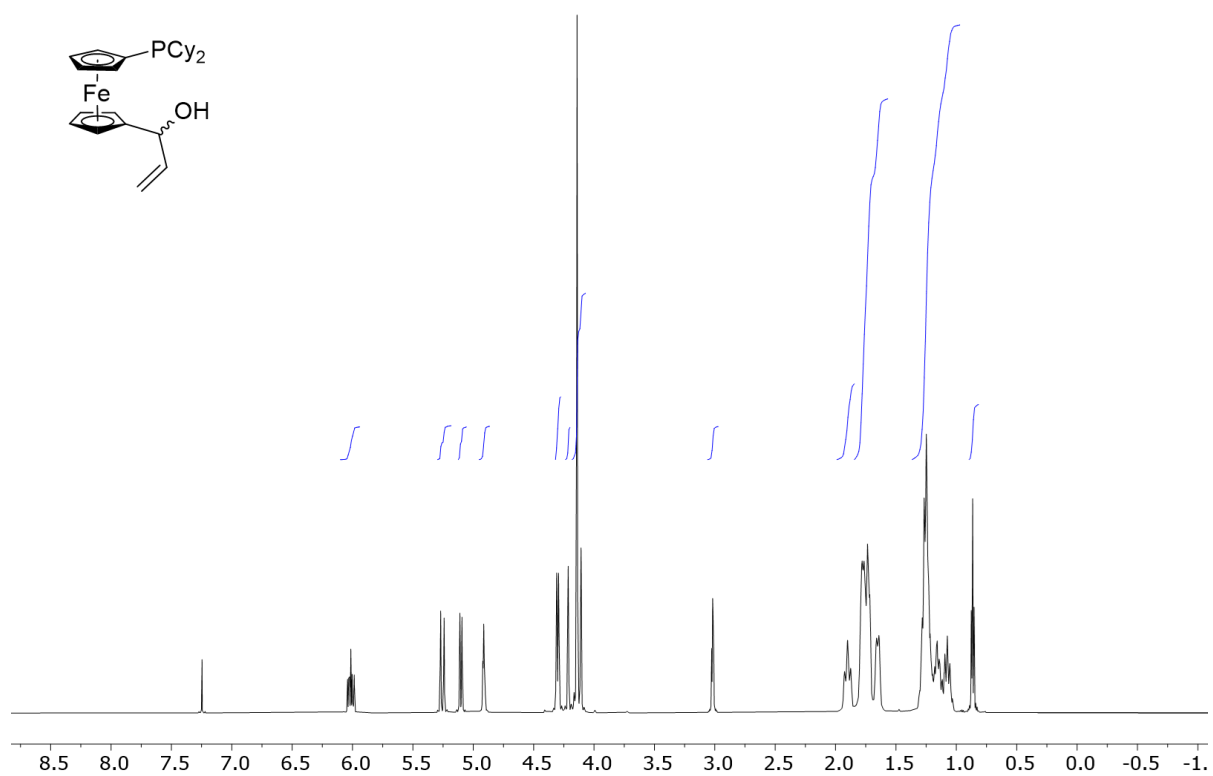
**Figure S4**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) spectrum of  $3^{\text{Ph}}$



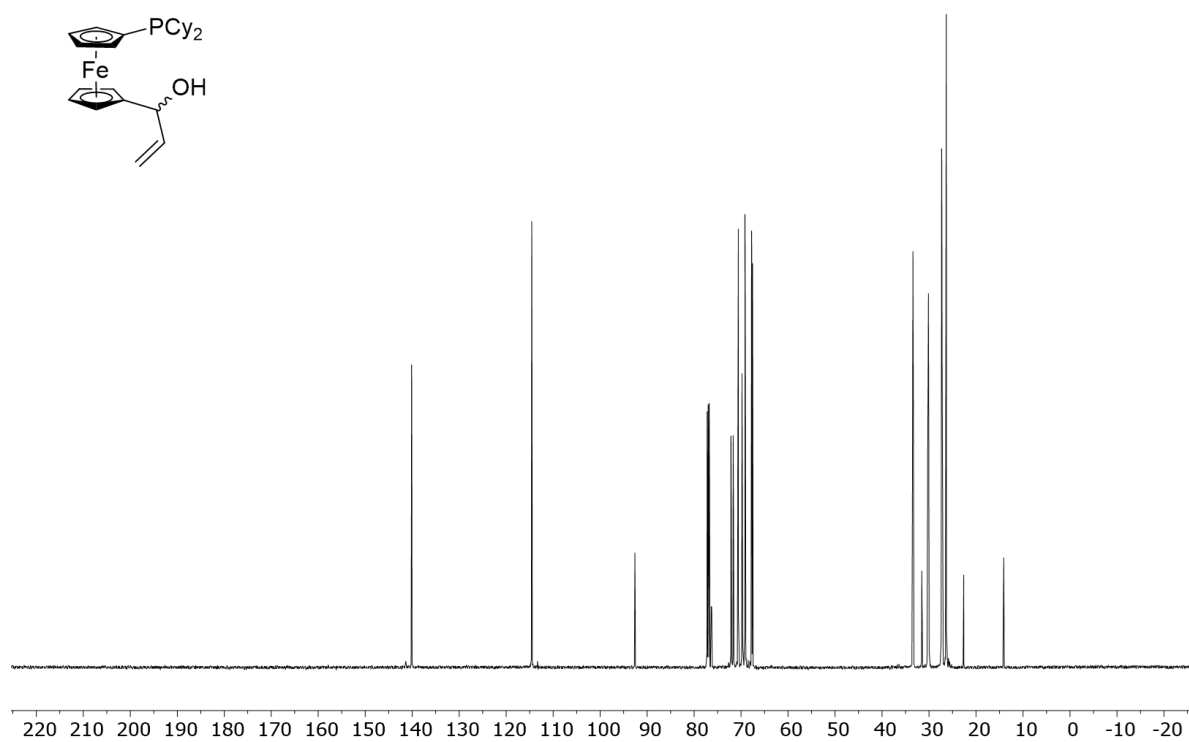
**Figure S5**  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 101 MHz) spectrum of  $3^{\text{Ph}}$



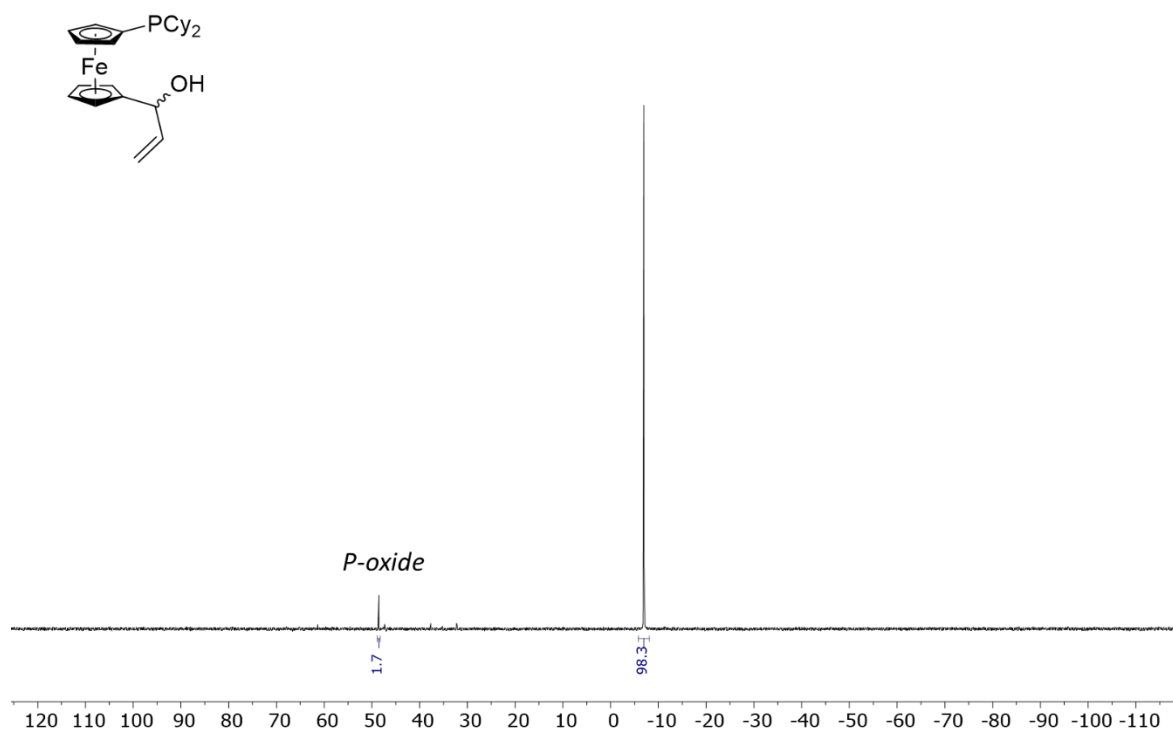
**Figure S6** <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 162 MHz) spectrum of **3<sup>Ph</sup>**



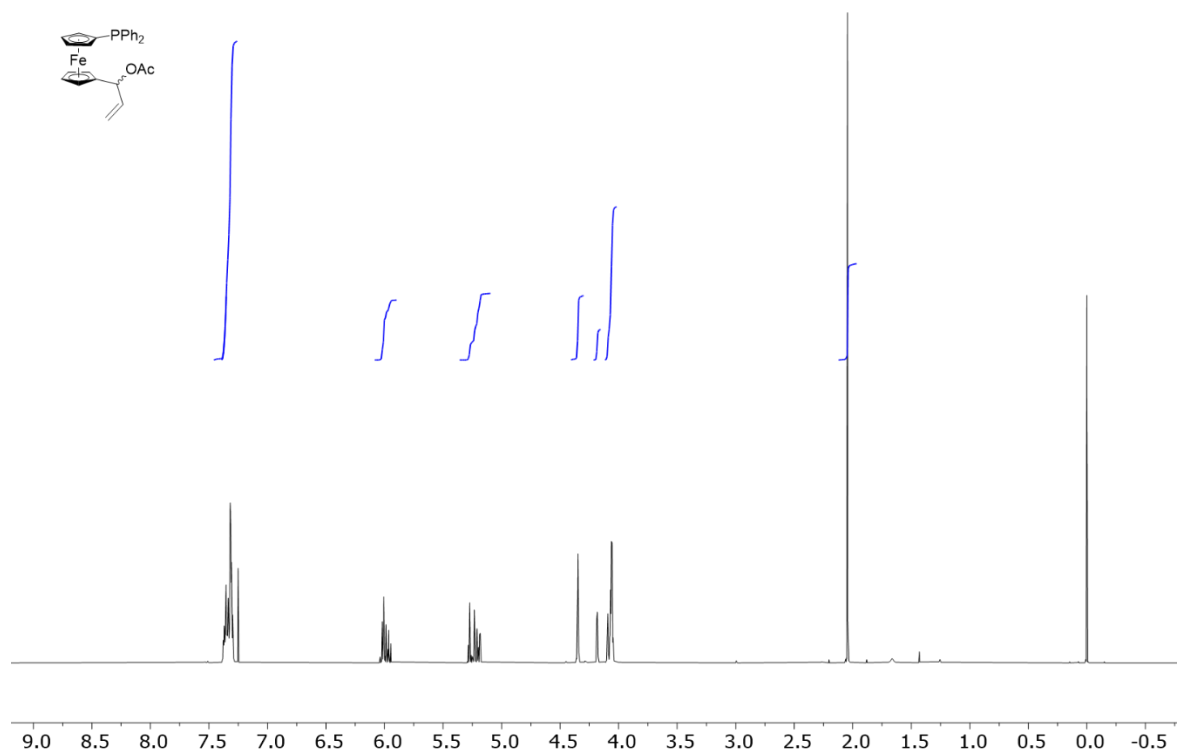
**Figure S7**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) spectrum of **3<sup>Cy</sup>**



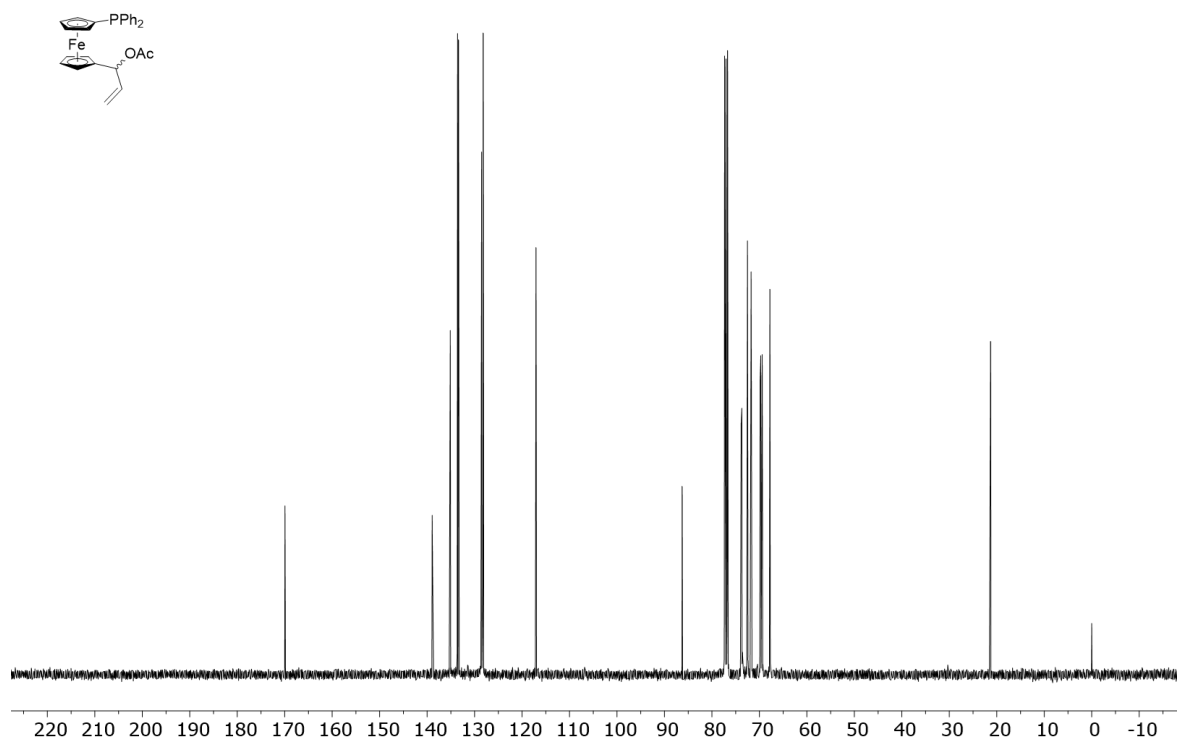
**Figure S8**  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 101 MHz) spectrum of **3<sup>Cy</sup>**



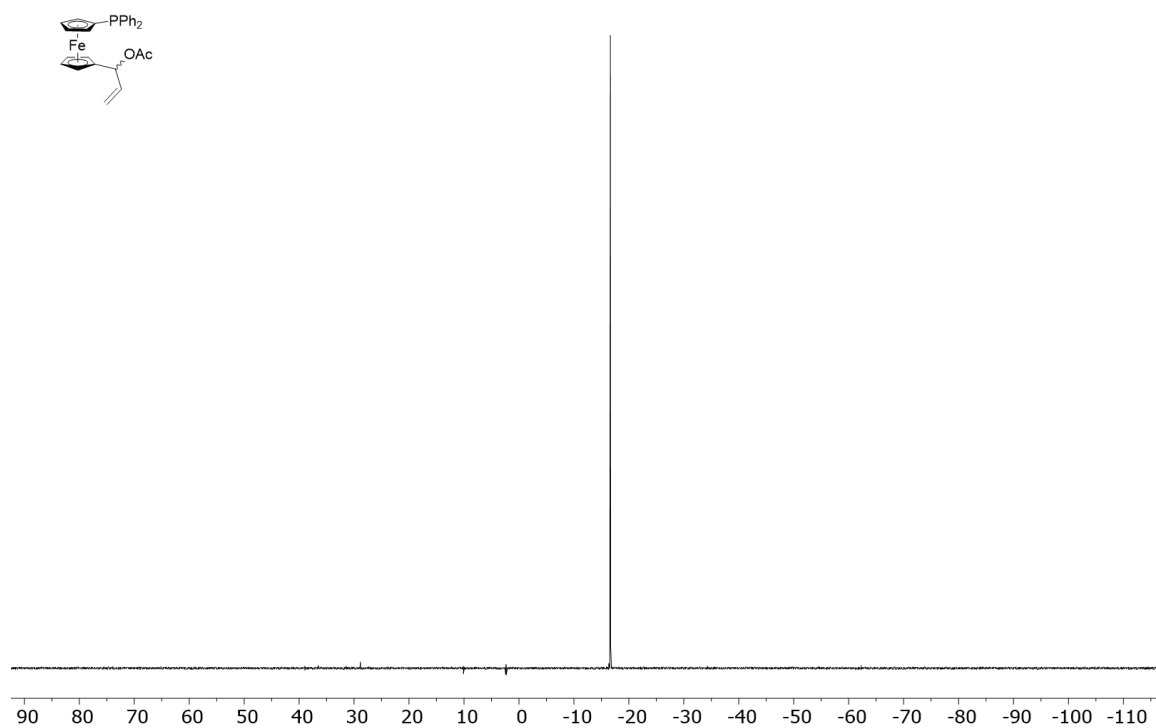
**Figure S9**  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 162 MHz) spectrum of **3<sub>Cy</sub>**



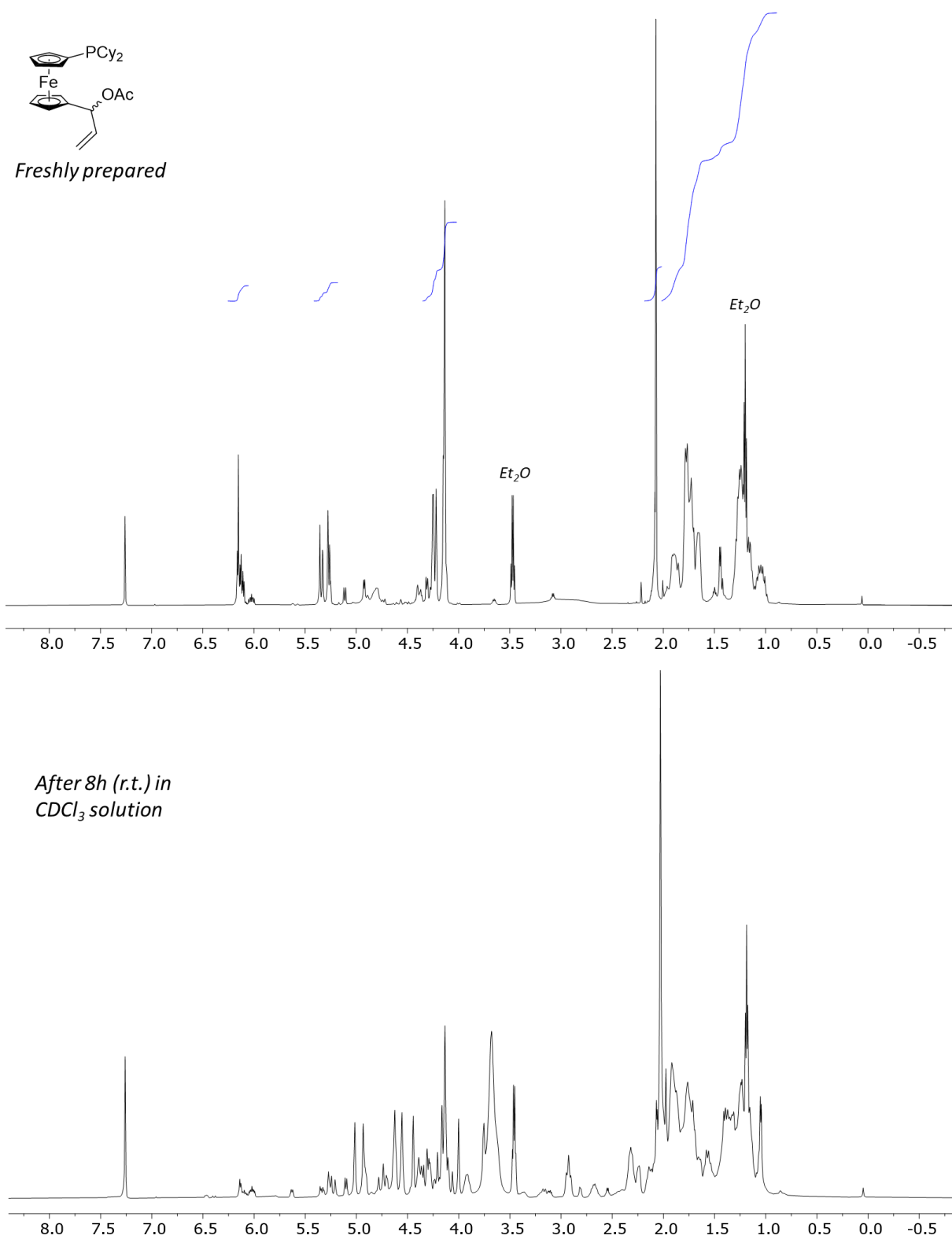
**Figure S10**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) spectrum of **4<sup>Ph</sup>**



**Figure S11**  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 101 MHz) spectrum of **4<sup>Ph</sup>**

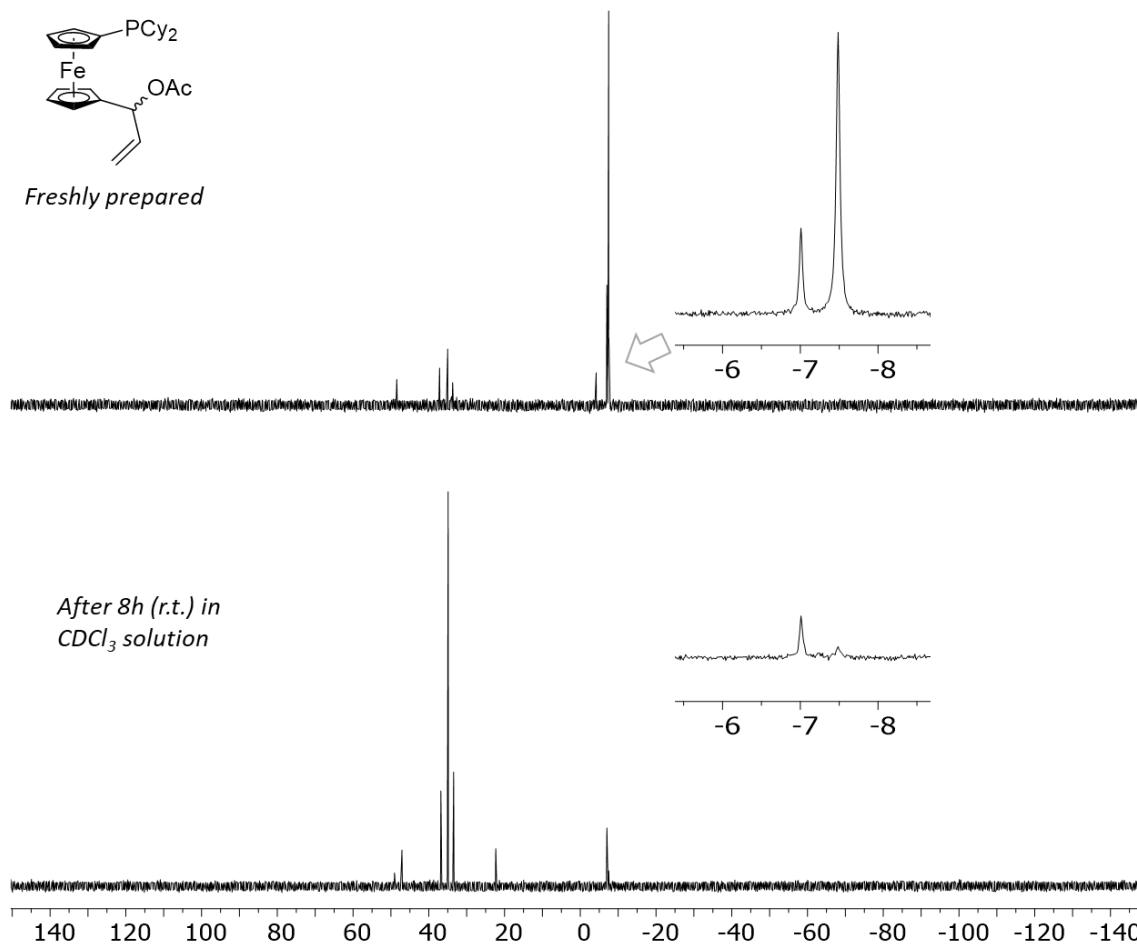


**Figure S12** <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 162 MHz) spectrum of **4<sup>Ph</sup>**

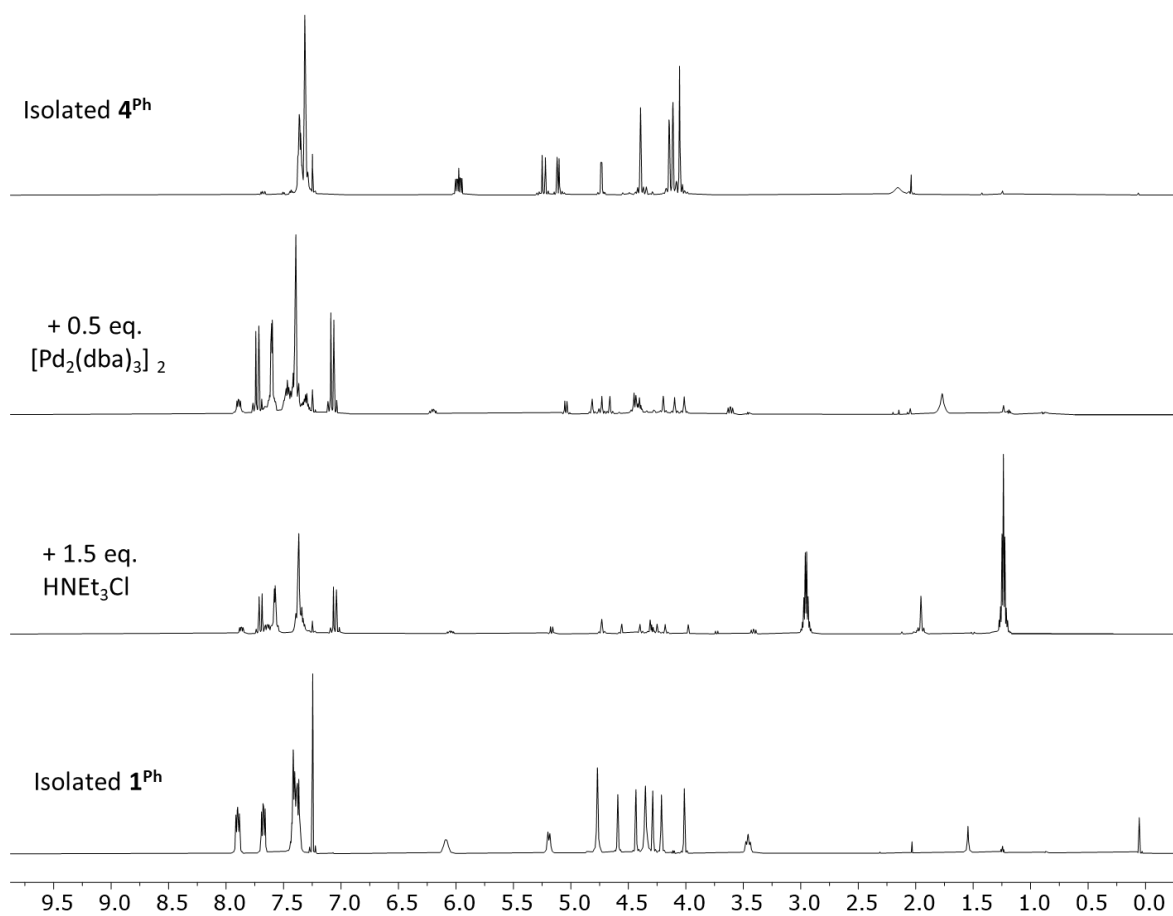


**Figure S13** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz) spectra of freshly prepared (crude) **4<sup>Cy</sup>** (top) and a sample aged in solution for 8 h (bottom)

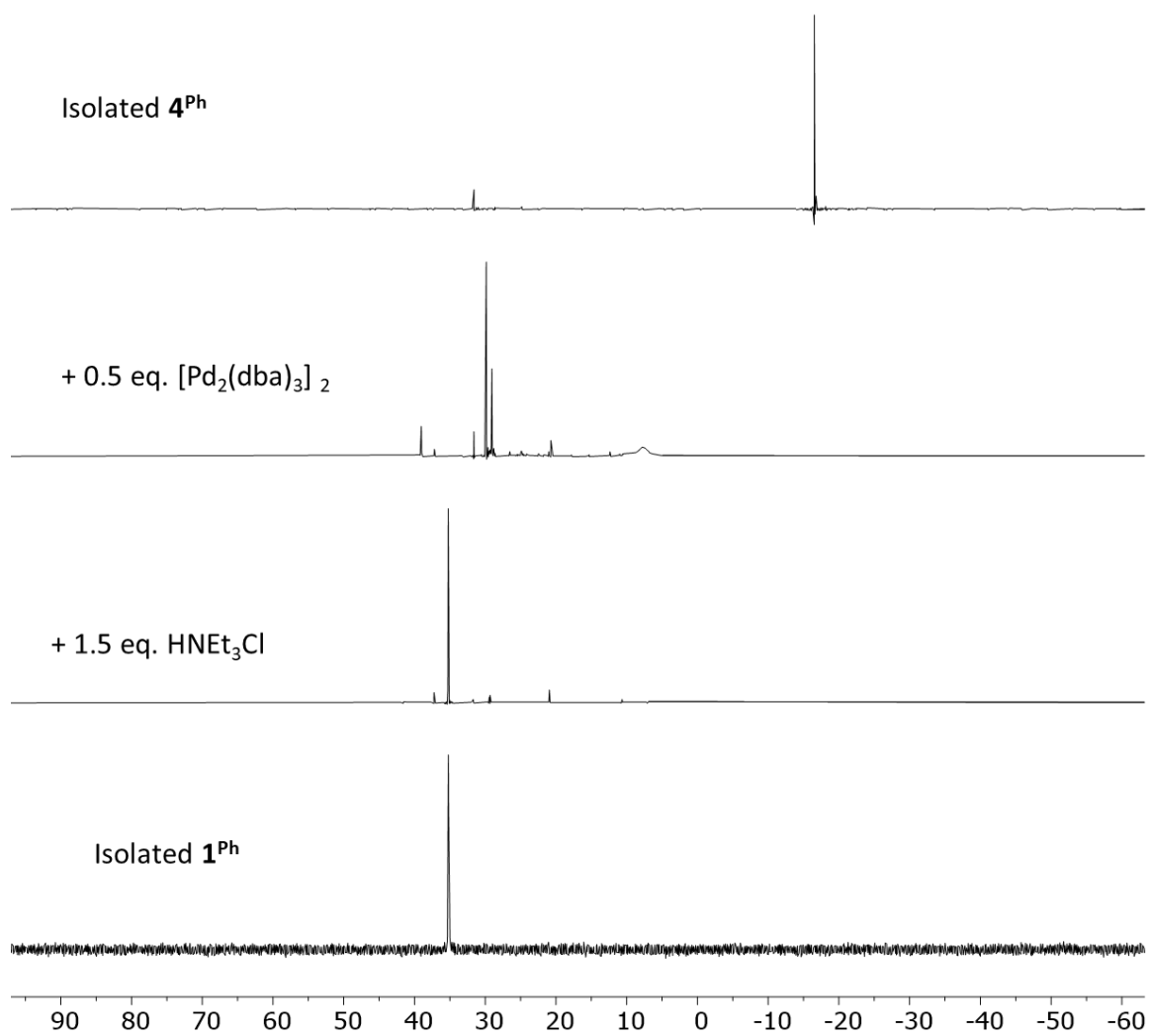




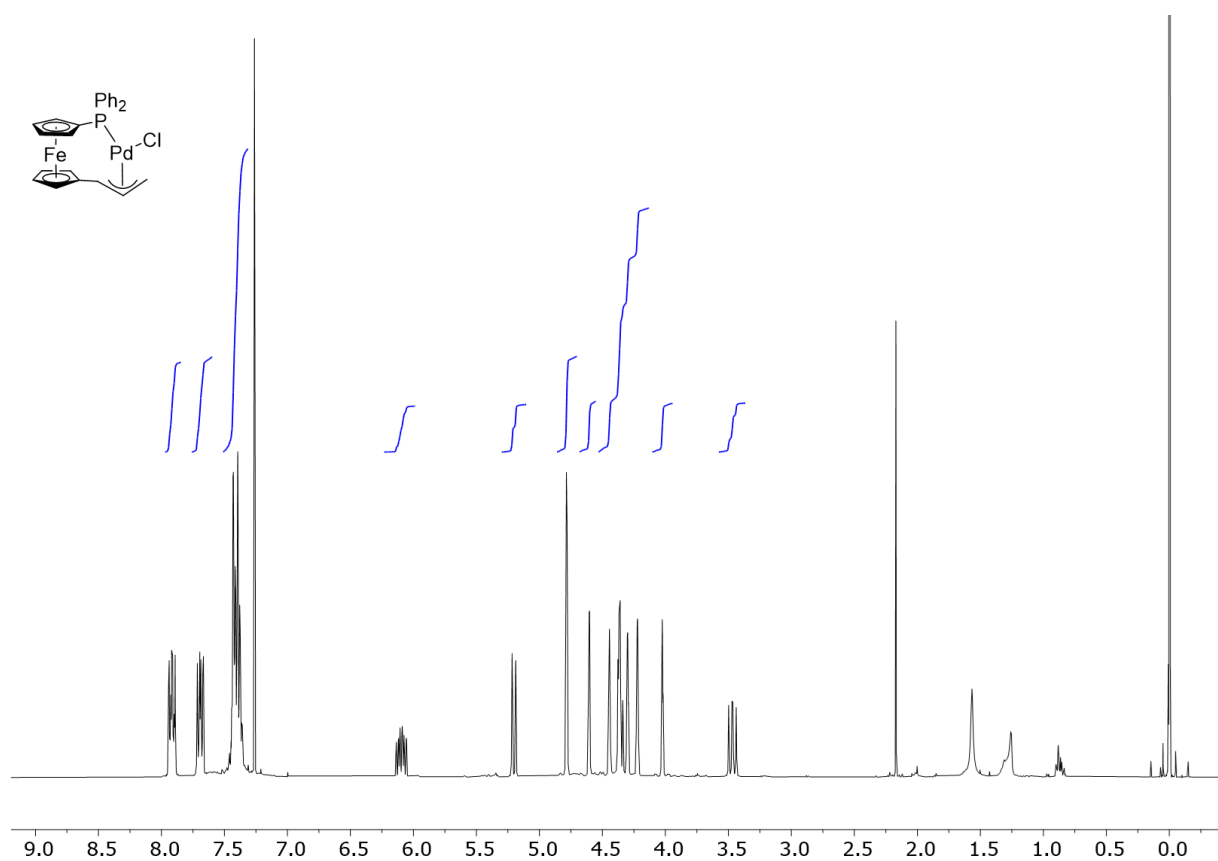
**Figure S14**  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 243 MHz) spectrum of freshly prepared  $4^{\text{Cy}}$  (top) and the same sample after standing for 8 h in solution (bottom)



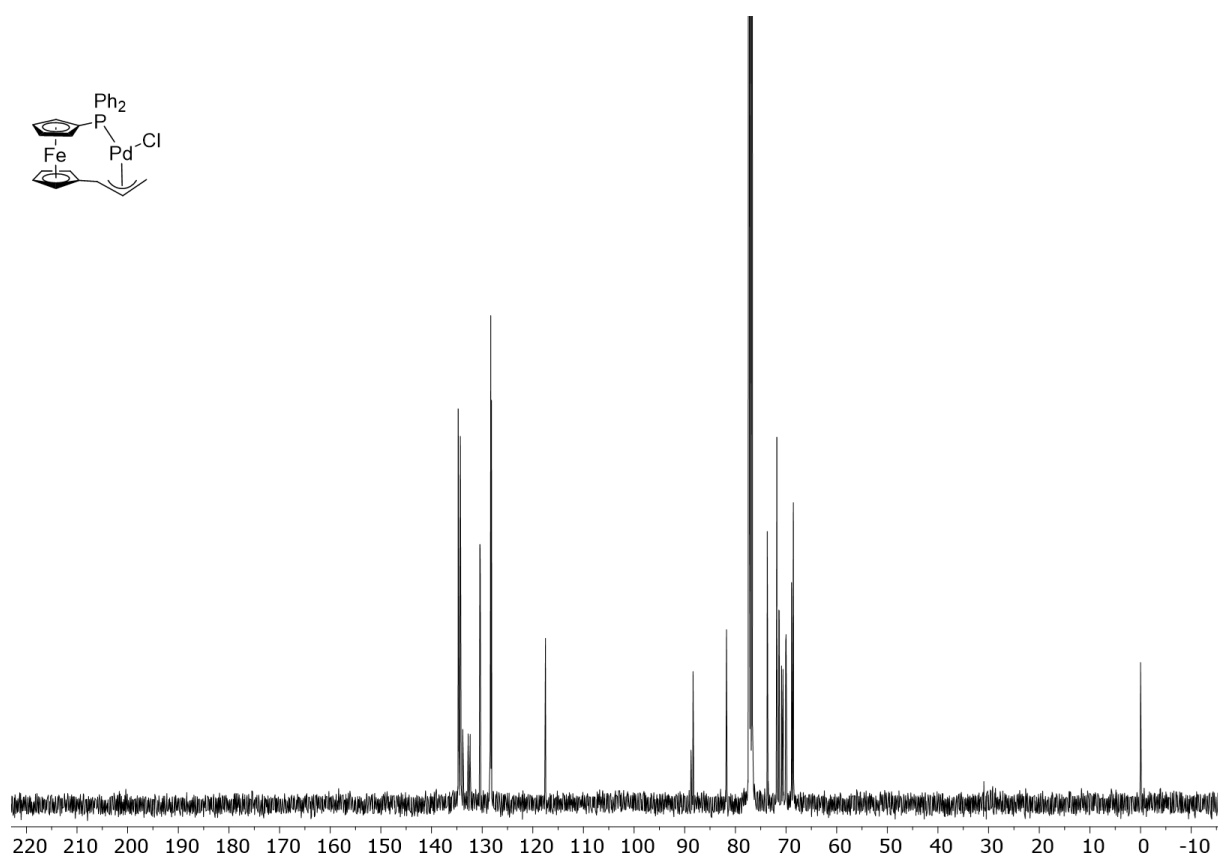
**Figure S15**  $^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ , 600 MHz) recorded during a complexation experiment



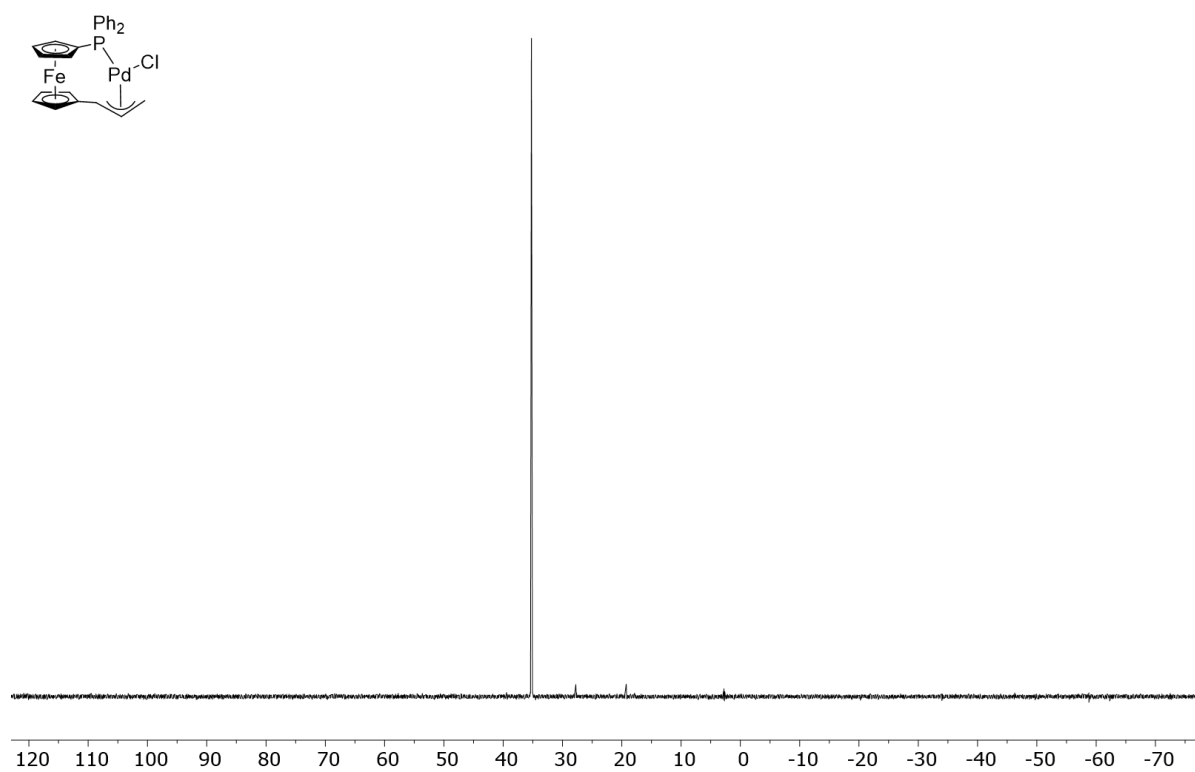
**Figure S16**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra ( $\text{CDCl}_3$ , 243 MHz) recorded during a complexation experiment



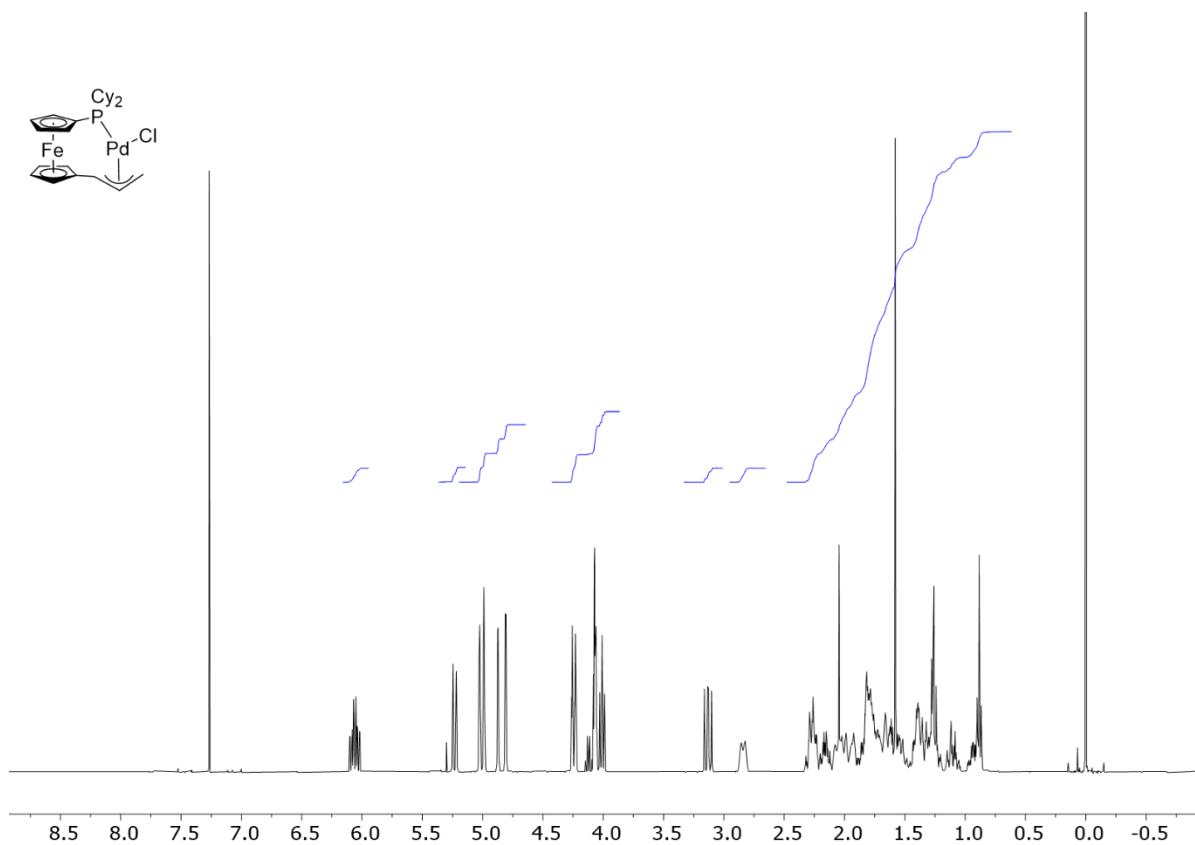
**Figure S17**  $^1H$  NMR (CDCl<sub>3</sub>, 400 MHz) spectrum of  $1^{Ph}$



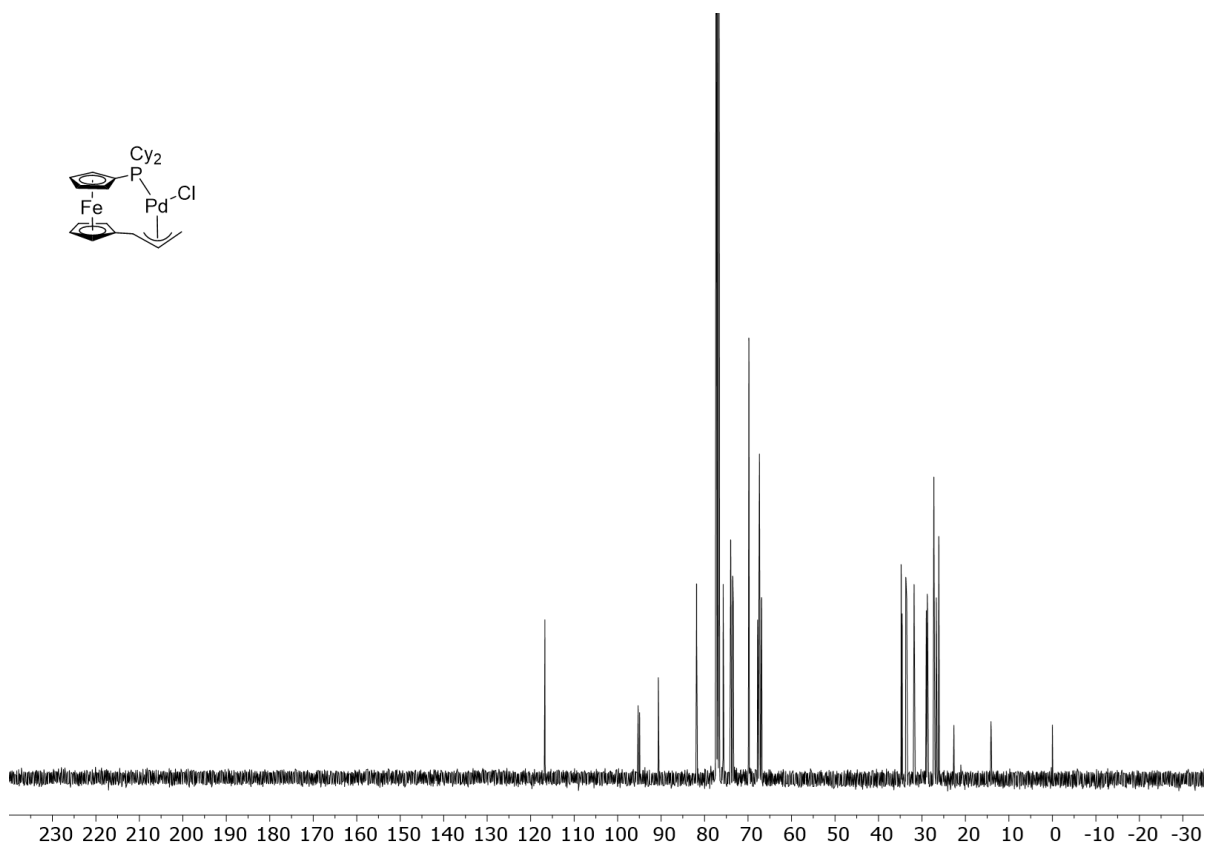
**Figure S18**  $^{13}C\{^1H\}$  NMR (CDCl<sub>3</sub>, 101 MHz) spectrum of  $1^{Ph}$



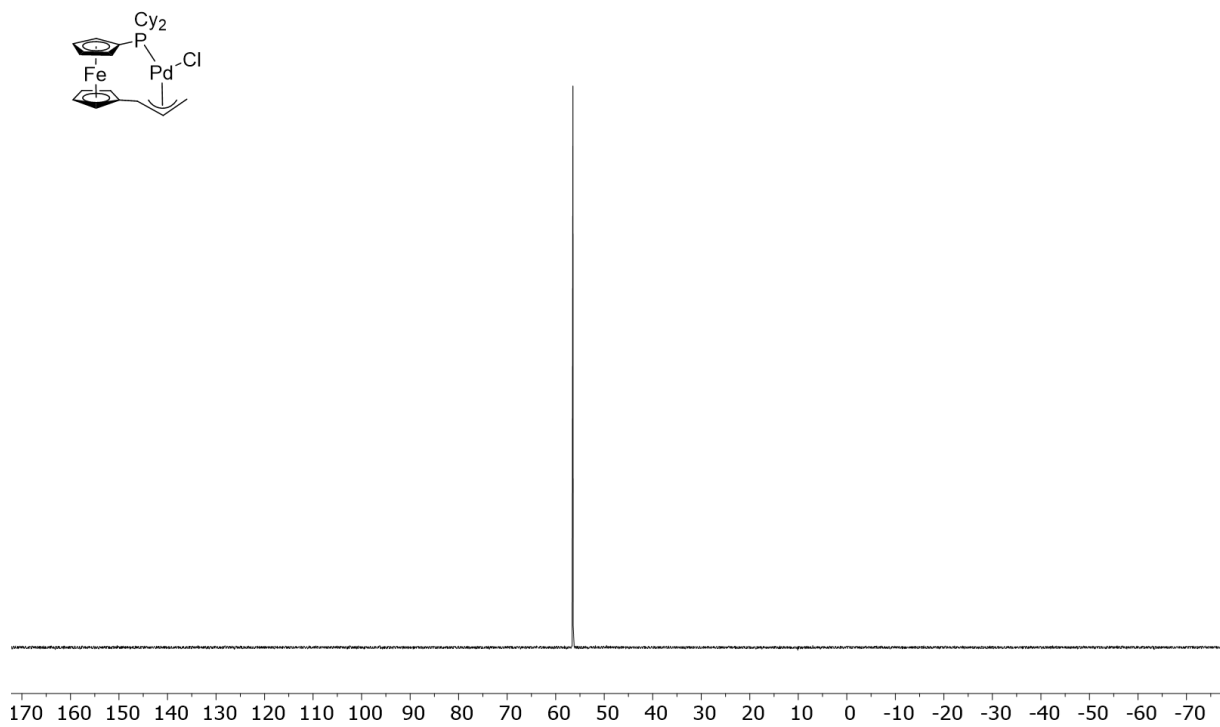
**Figure S19** <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 162 MHz) spectrum of **1<sup>Ph</sup>**



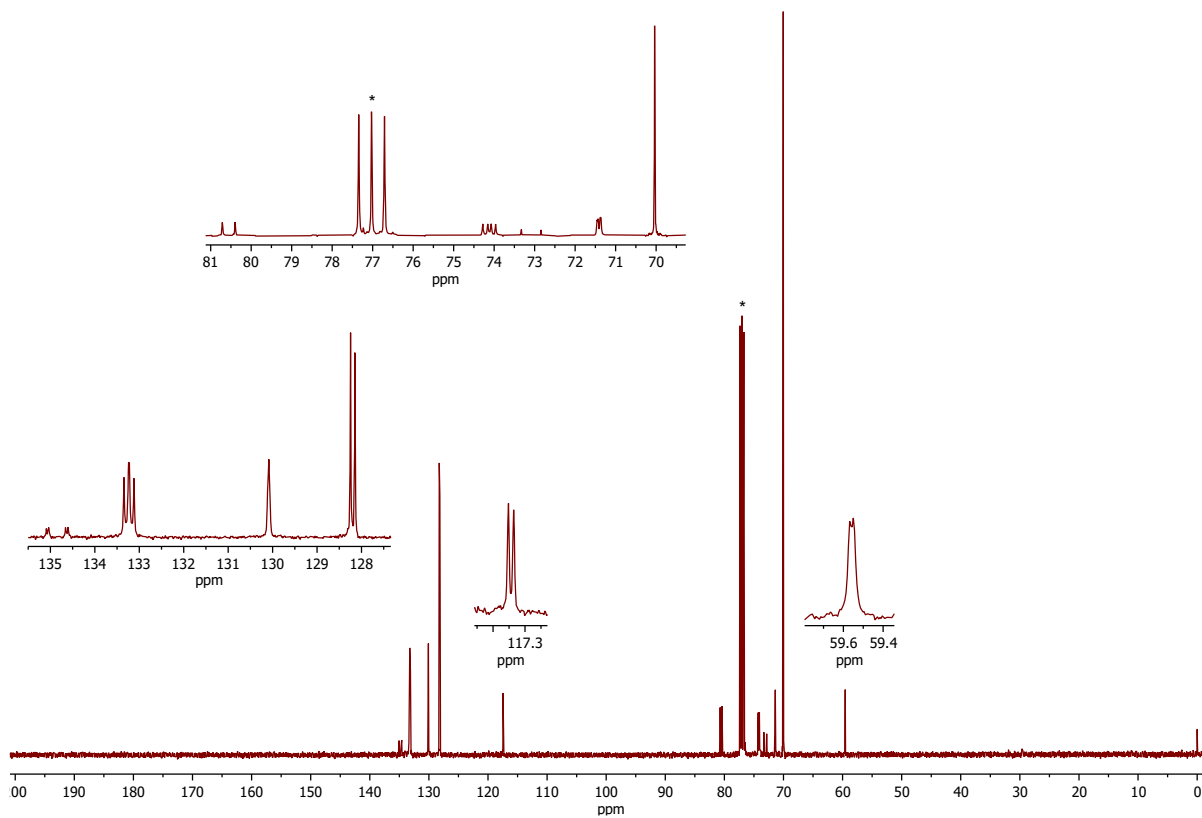
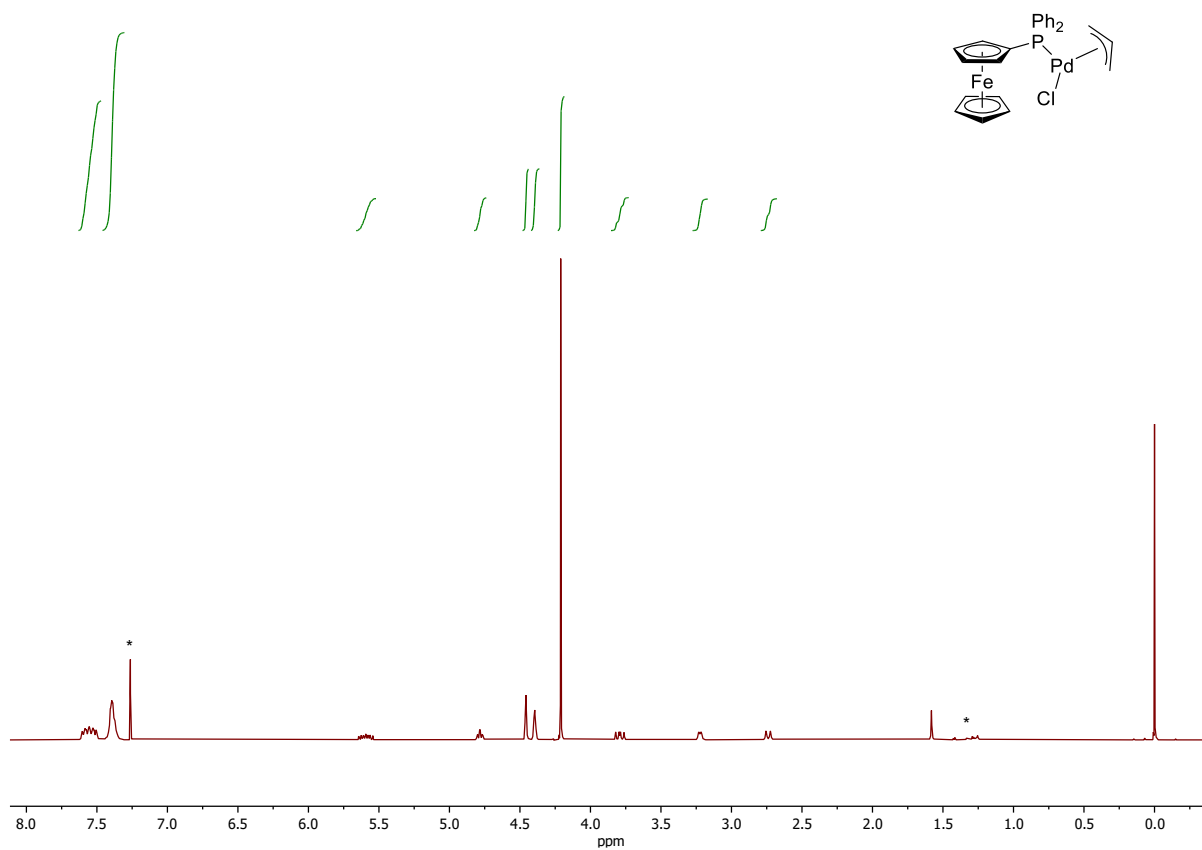
**Figure S20**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) spectrum of  $1^{\text{Cy}}$



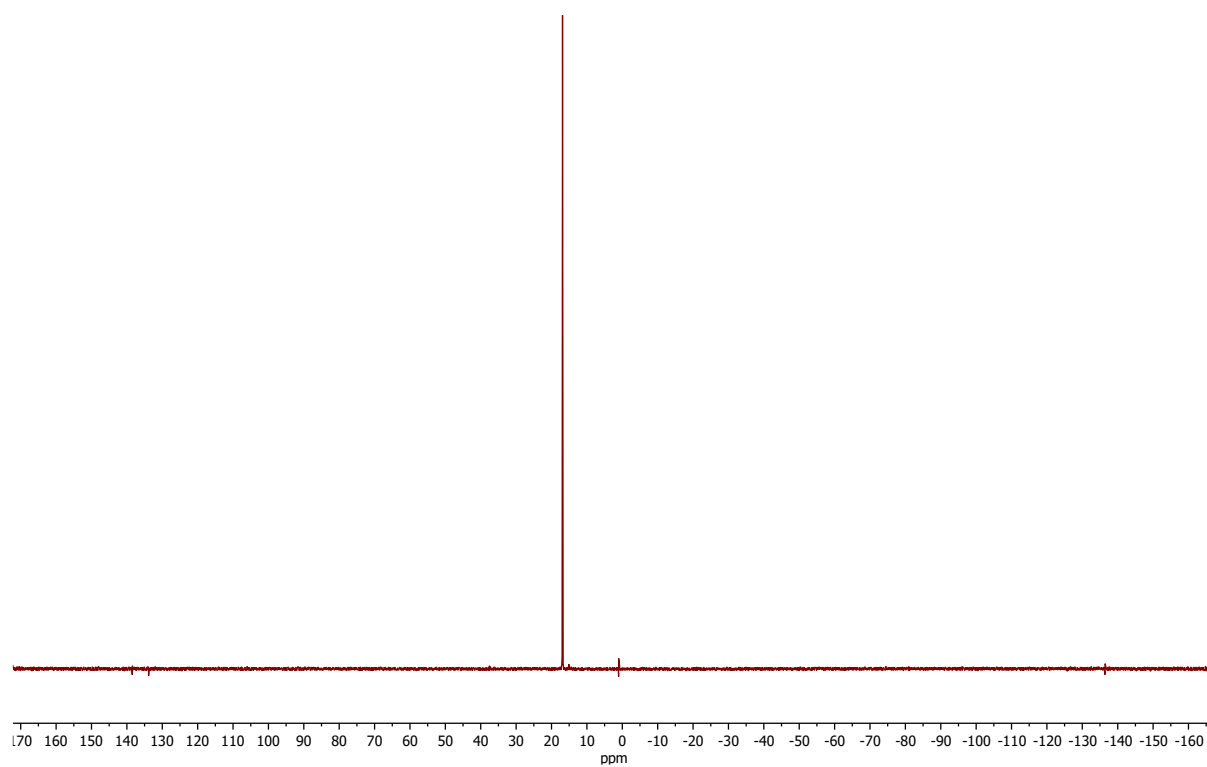
**Figure S21**  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 101 MHz) spectrum of  $1^{\text{Cy}}$



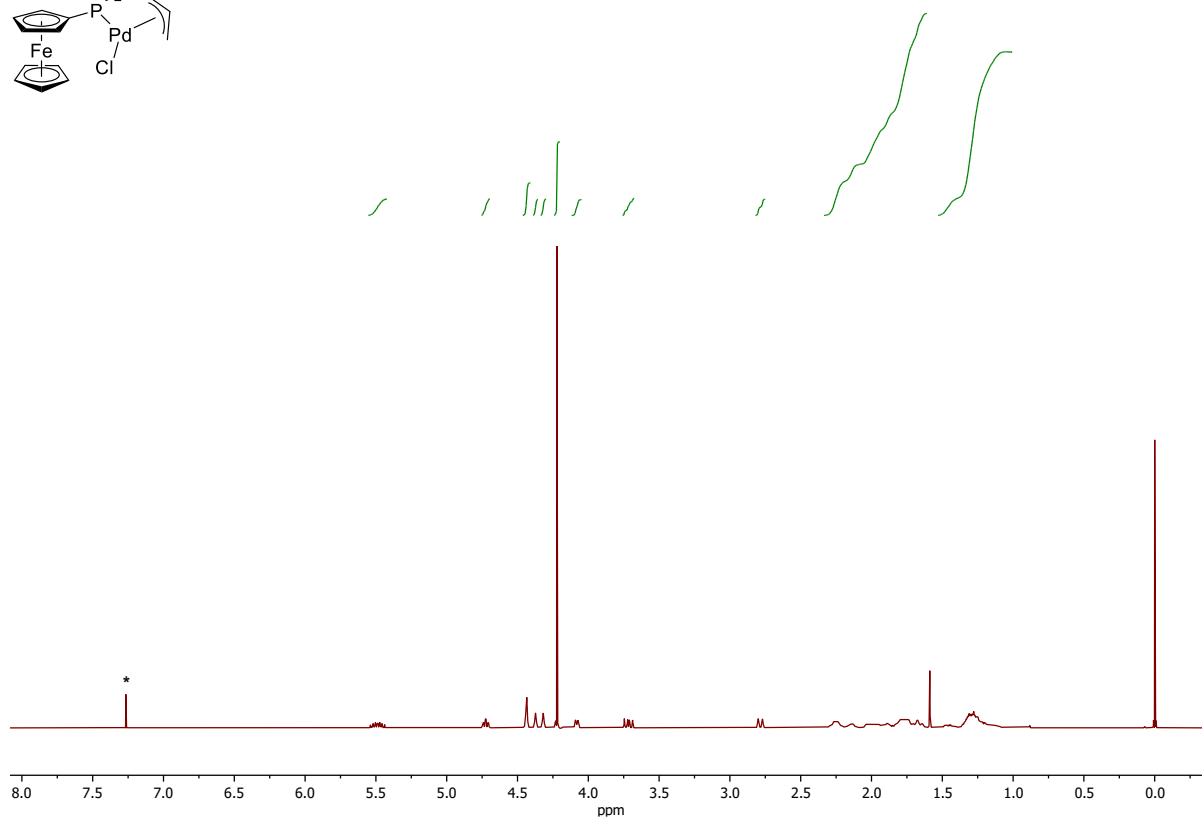
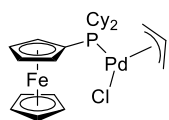
**Figure S22** <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 162 MHz) spectrum of **1<sup>Cy</sup>**



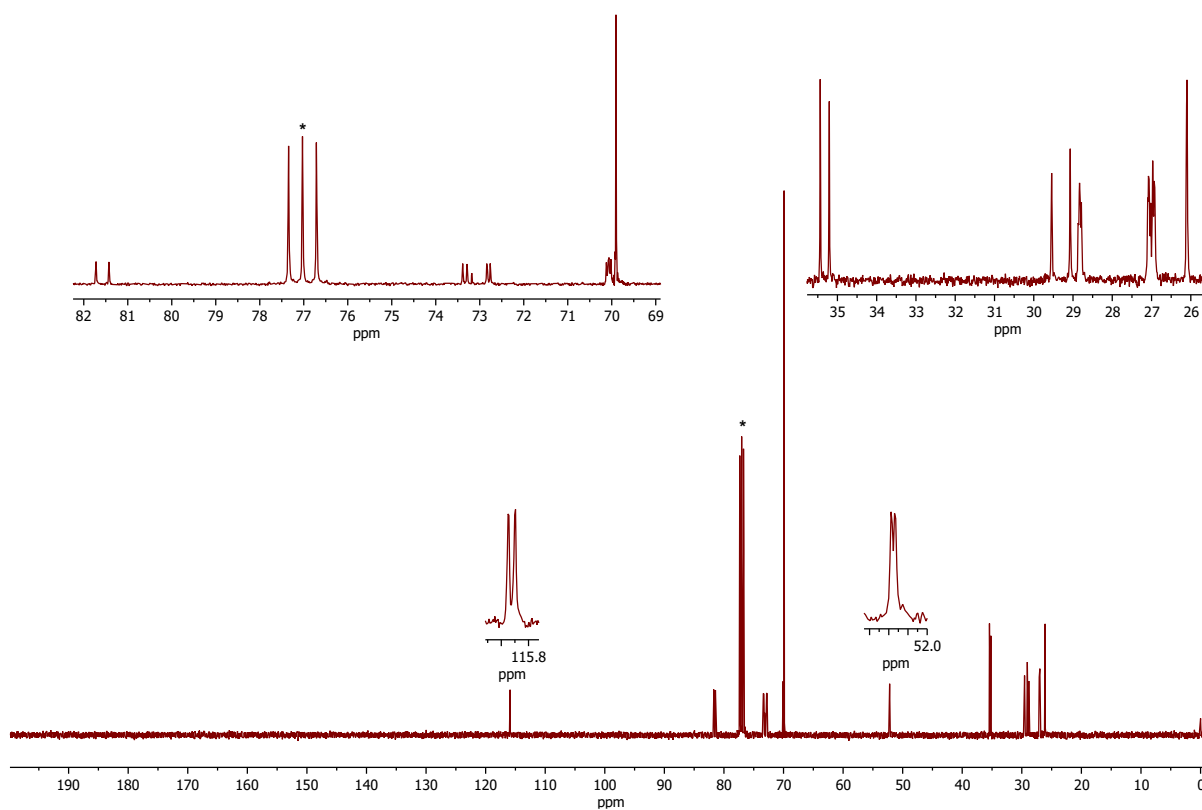




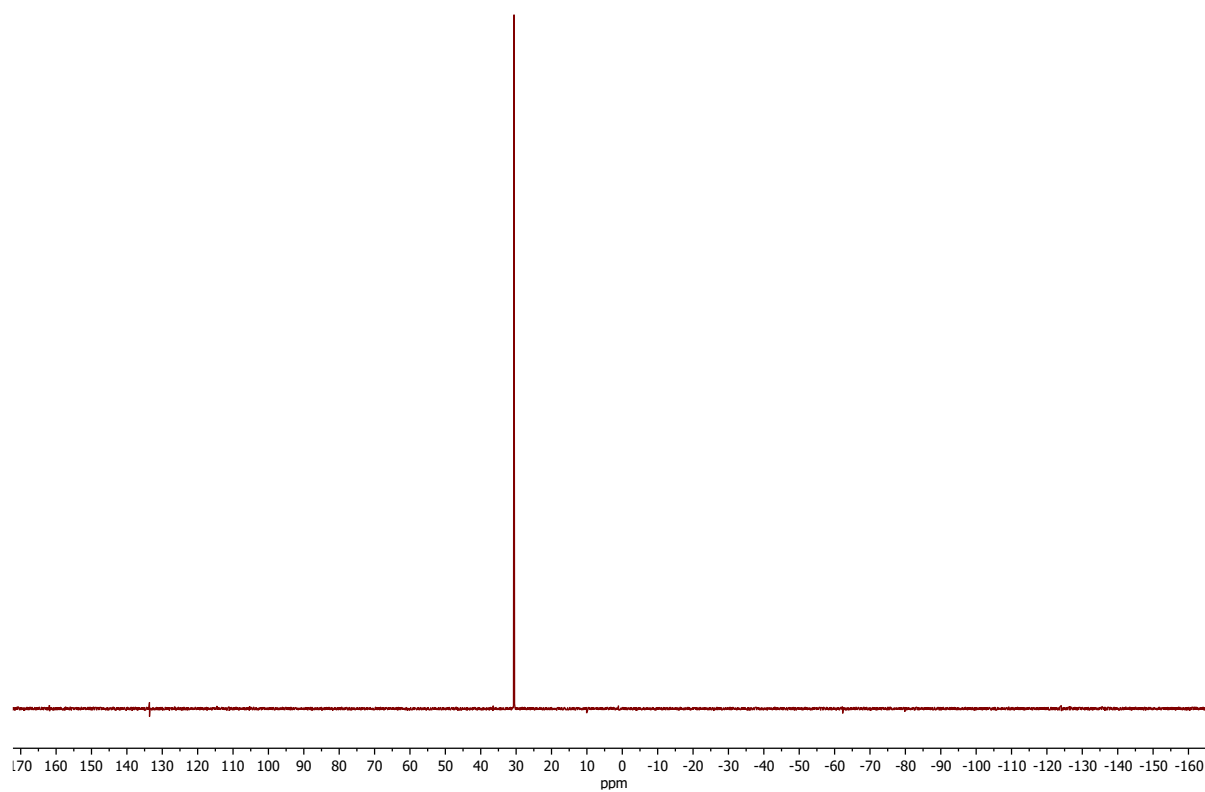
**Figure S25**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (162 MHz,  $\text{CDCl}_3$ ) of **5<sup>Ph</sup>**



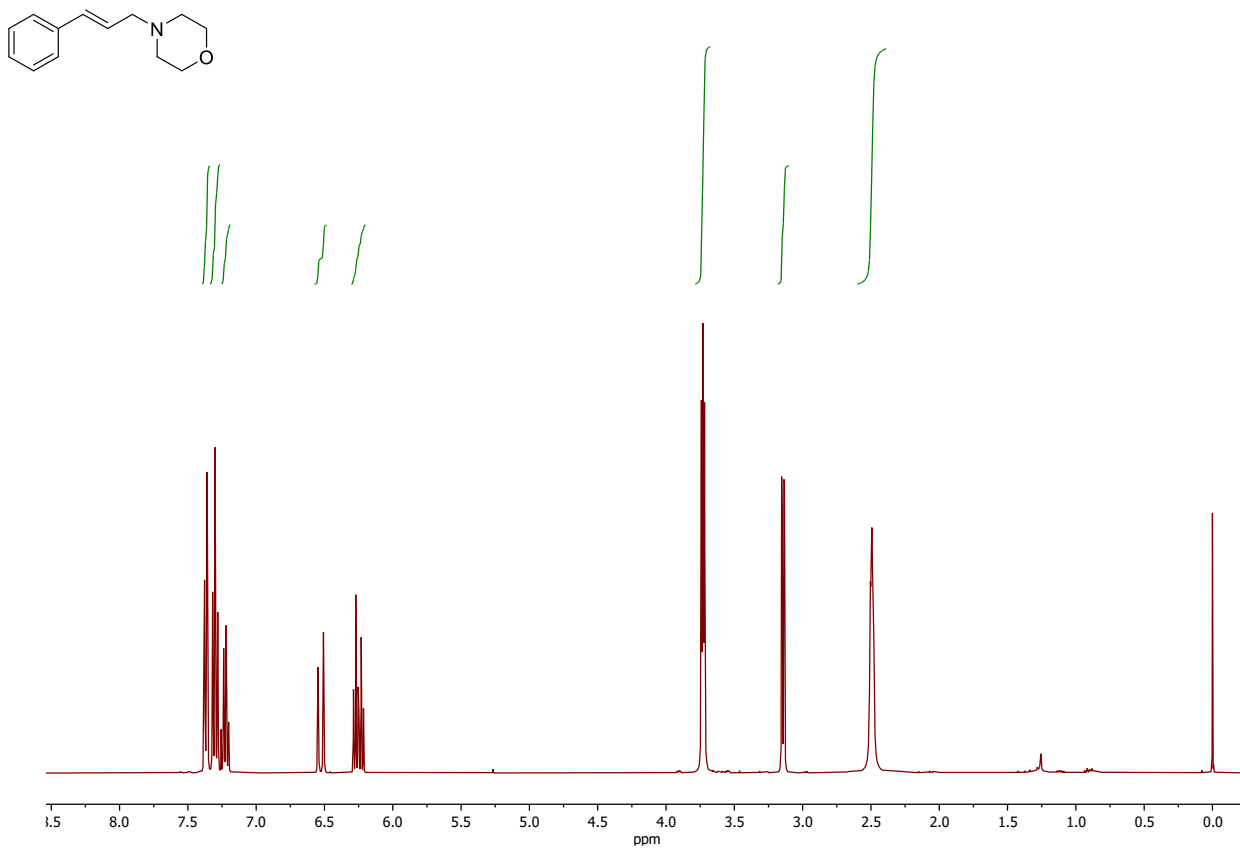
**Figure S26**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 400 MHz) of  $5^{\text{Cy}}$



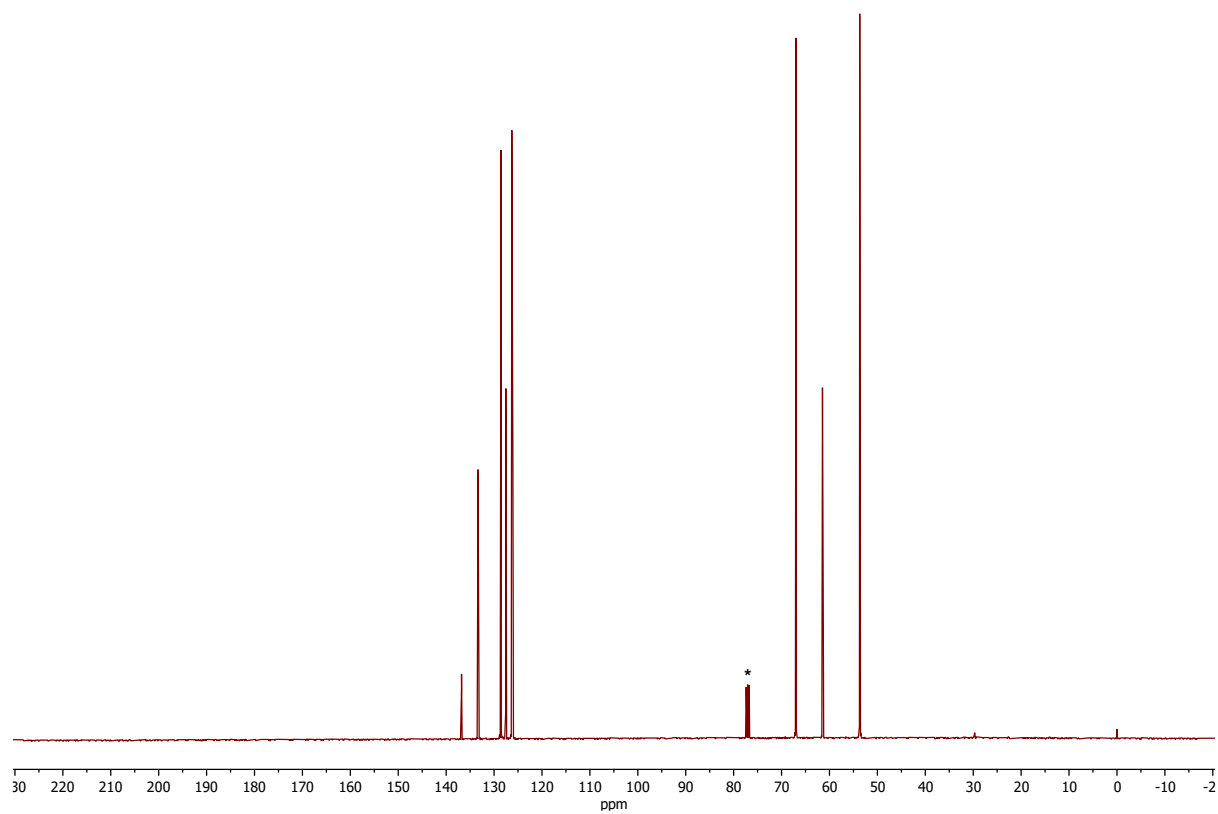
**Figure S27**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum ( $\text{CDCl}_3$ , 101 MHz) of  $5^{\text{Cy}}$



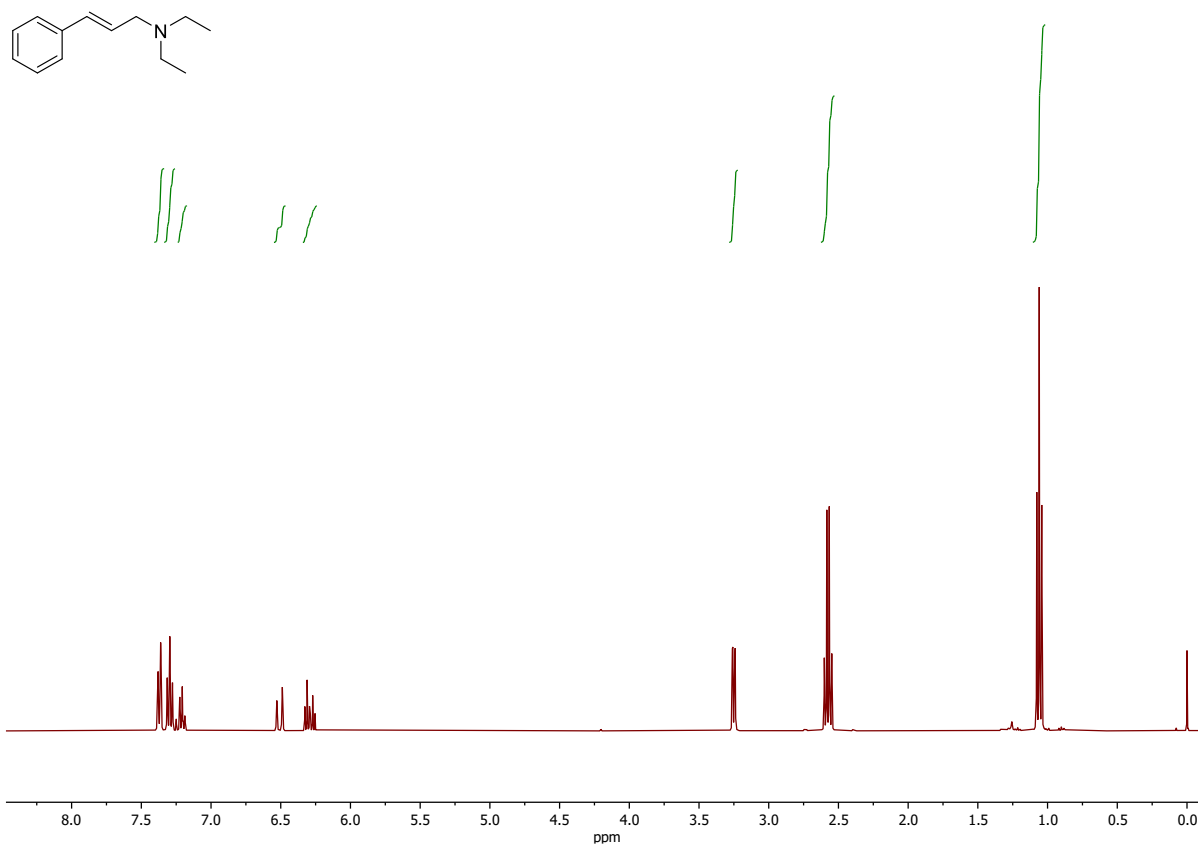
**Figure S28**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{CDCl}_3$ , 162 MHz) of **5cy**



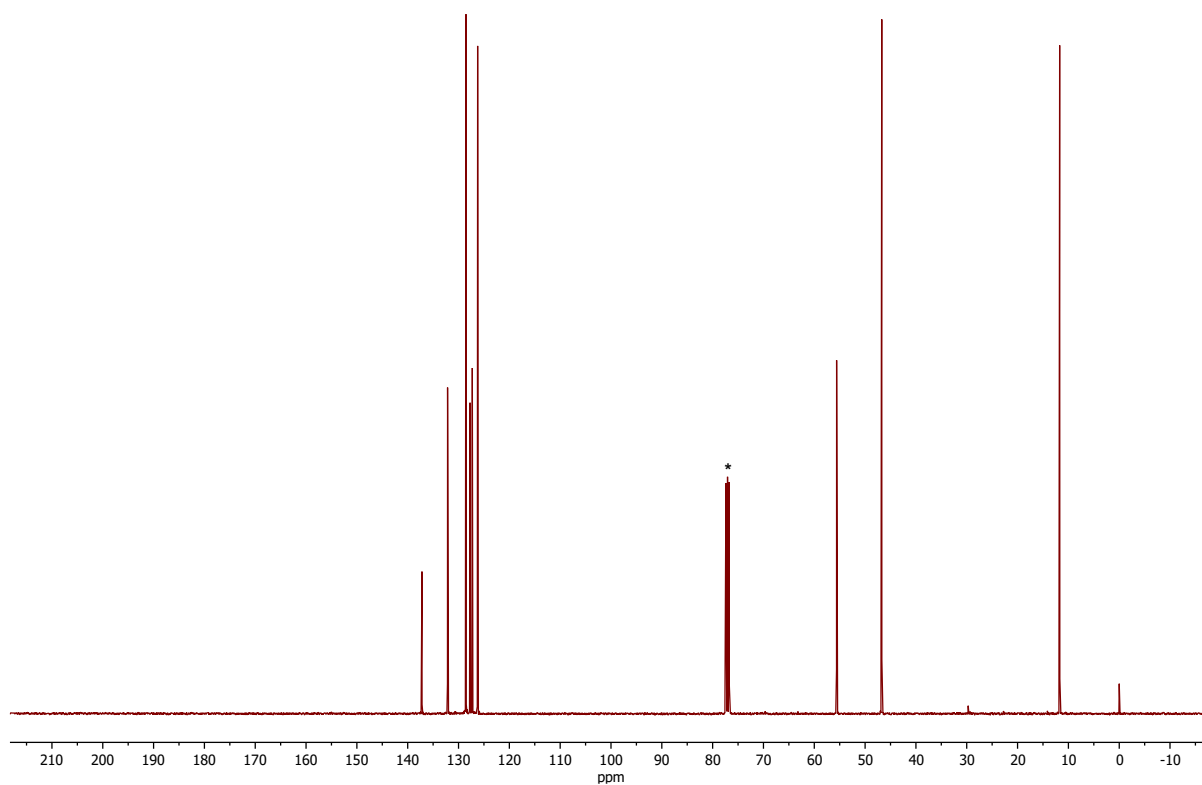
**Figure S29** <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of 4-cinnamylmorpholine (**7a**)



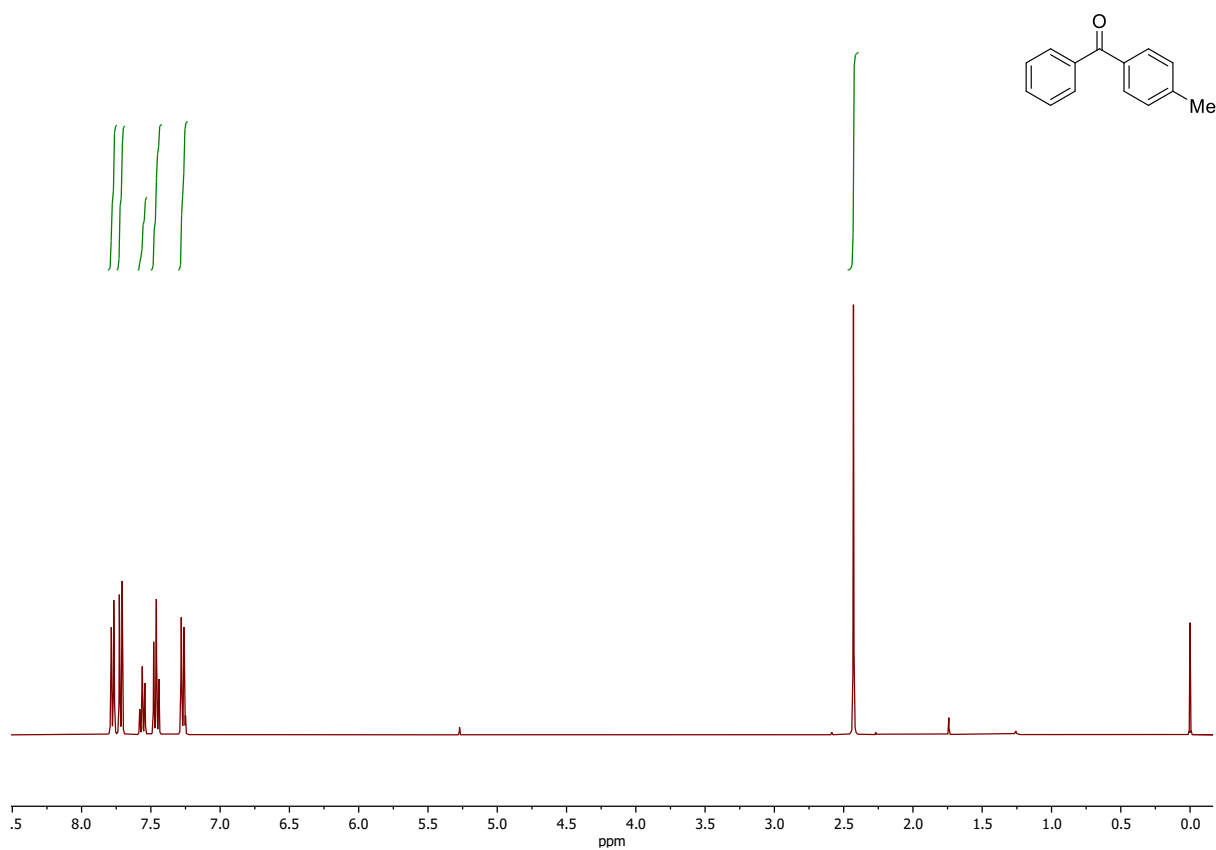
**Figure S30** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (CDCl<sub>3</sub>, 101 MHz) of 4-cinnamylmorpholine (**7a**)



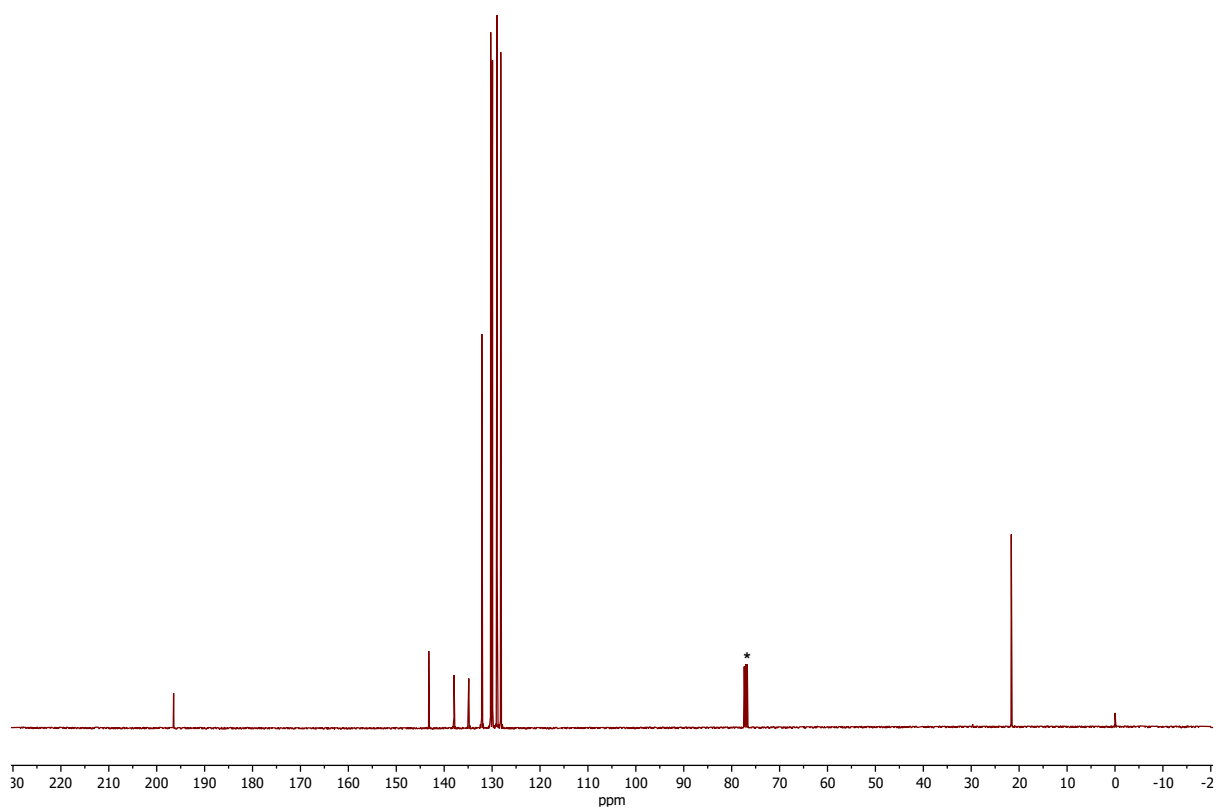
**Figure S31** <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of *N,N*-diethylcinnamylamine (**7b**)



**Figure S32** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (CDCl<sub>3</sub>, 101 MHz) of *N,N*-diethylcinnamylamine (**7b**)



**Figure S33**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 400 MHz) of 4-methylbenzophenone (**11**)



**Figure S34**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum ( $\text{CDCl}_3$ , 101 MHz) of 4-methylbenzophenone (**11**)

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