

## Synthesis of 2-ureido-4-ferrocenyl pyrimidine guests. Investigation of complementary molecular recognition of 2,6-diaminopyridine

Csaba Fehér,<sup>a</sup> Máté Papp,<sup>a</sup> Ágnes Gömöröy,<sup>b</sup> Lívia Nagy,<sup>c</sup> Johan Wouters,<sup>d</sup> György Lendvay,<sup>b,e</sup> Rita Skoda-Földes\*<sup>a</sup>

<sup>a</sup> Institute of Chemistry, Department of Organic Chemistry, University of Pannonia, Egyetem u. 10. (P.O.Box 158) H-8200 Veszprém, Hungary

<sup>b</sup> Instrumentation Center, Research Centre for Natural Sciences, Hungarian Academy of Sciences, H-1117 Budapest, Hungary

<sup>c</sup> János Szentágothai Research Center, University of Pécs, Ifjúság útja 20, H-7624 Pécs, Hungary

<sup>d</sup> Department of Chemistry, University of Namur, B-5000 Namur, Belgium

<sup>e</sup> Institute of Chemistry, Department of General and Inorganic Chemistry, University of Pannonia, H-8200 Veszprém, Hungary

<sup>f</sup> Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, H-1117 Budapest, Hungary

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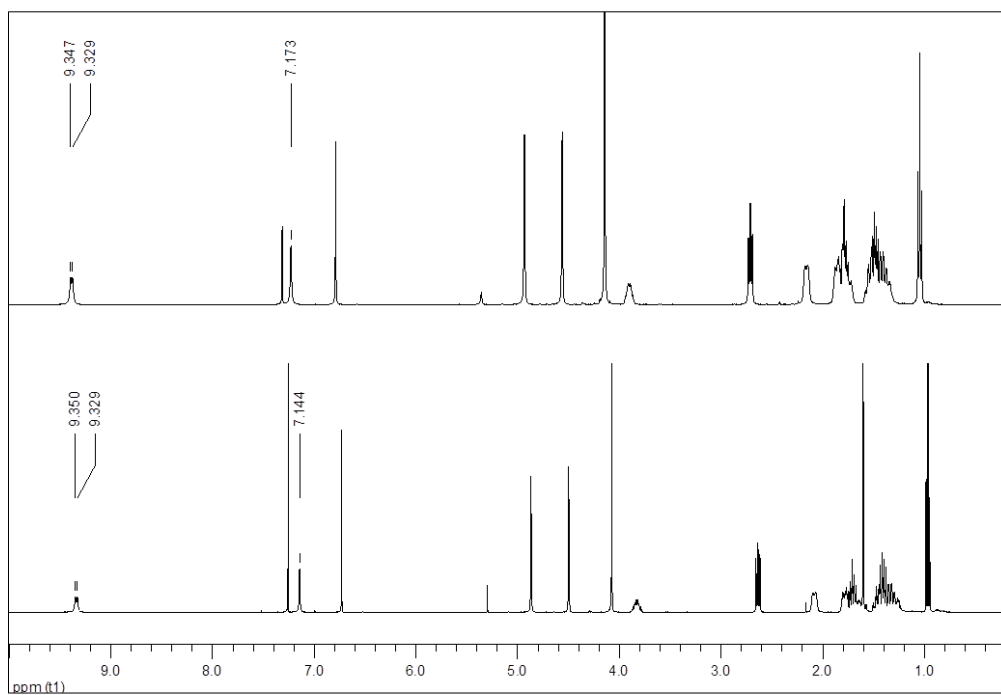


Figure S1. The change of the chemical shifts of NH protons of **5g** upon dilution (42mM (top), 7mM (bottom) in CDCl<sub>3</sub>)

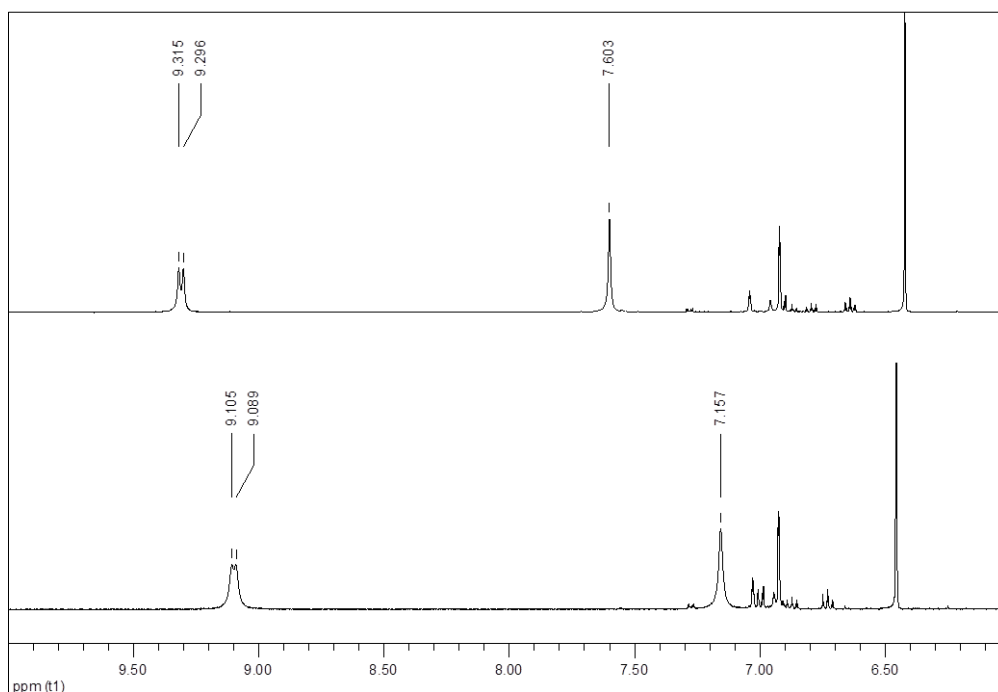


Figure S2. The change of the chemical shifts of NH protons of **5g** upon heating from 30 °C (top), to 80 °C (bottom) in toluene-d<sub>8</sub>.

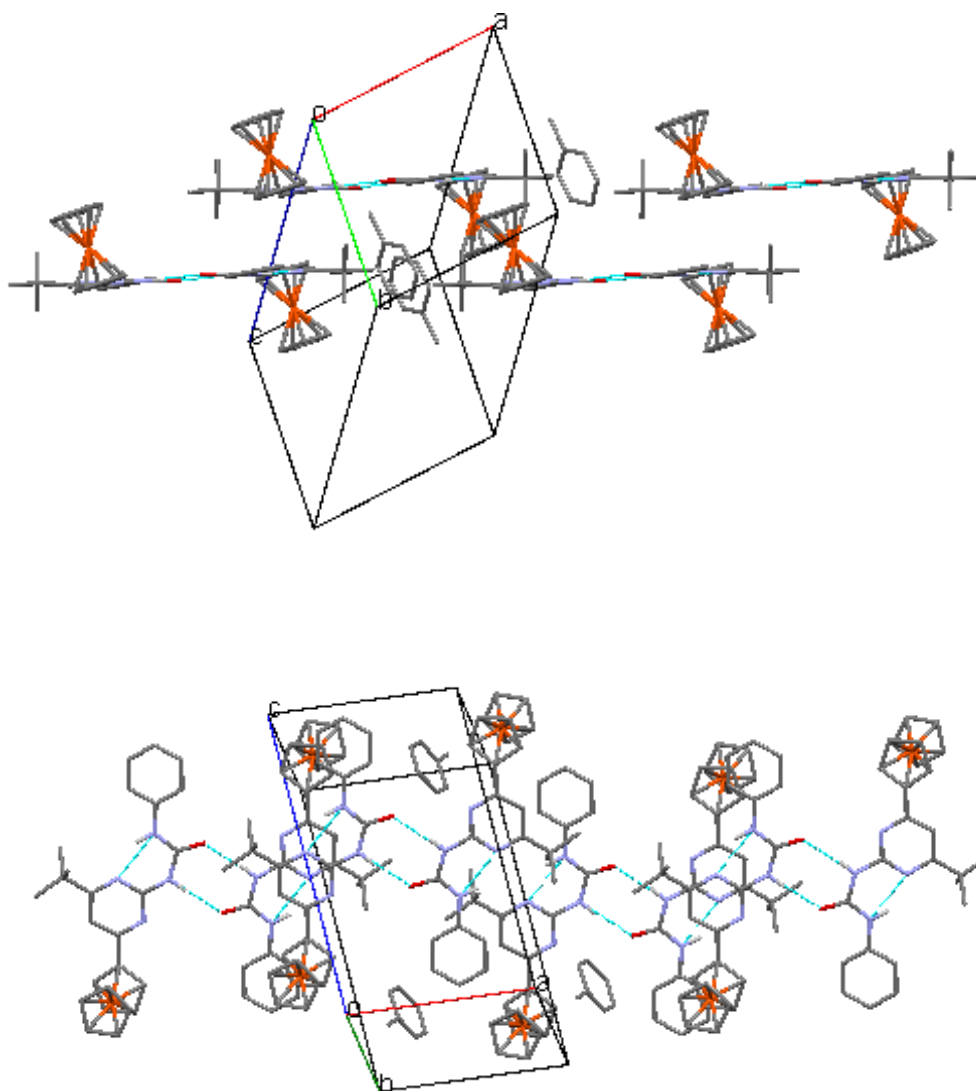


Figure S3. Two perpendicular views of the crystal packing of compound **5m**.

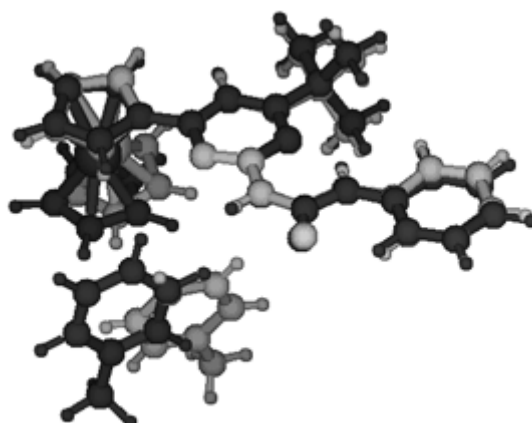


Figure S4. Comparison of the XRD structure (light grey) and the optimized structure (dark grey) of compound **5m**

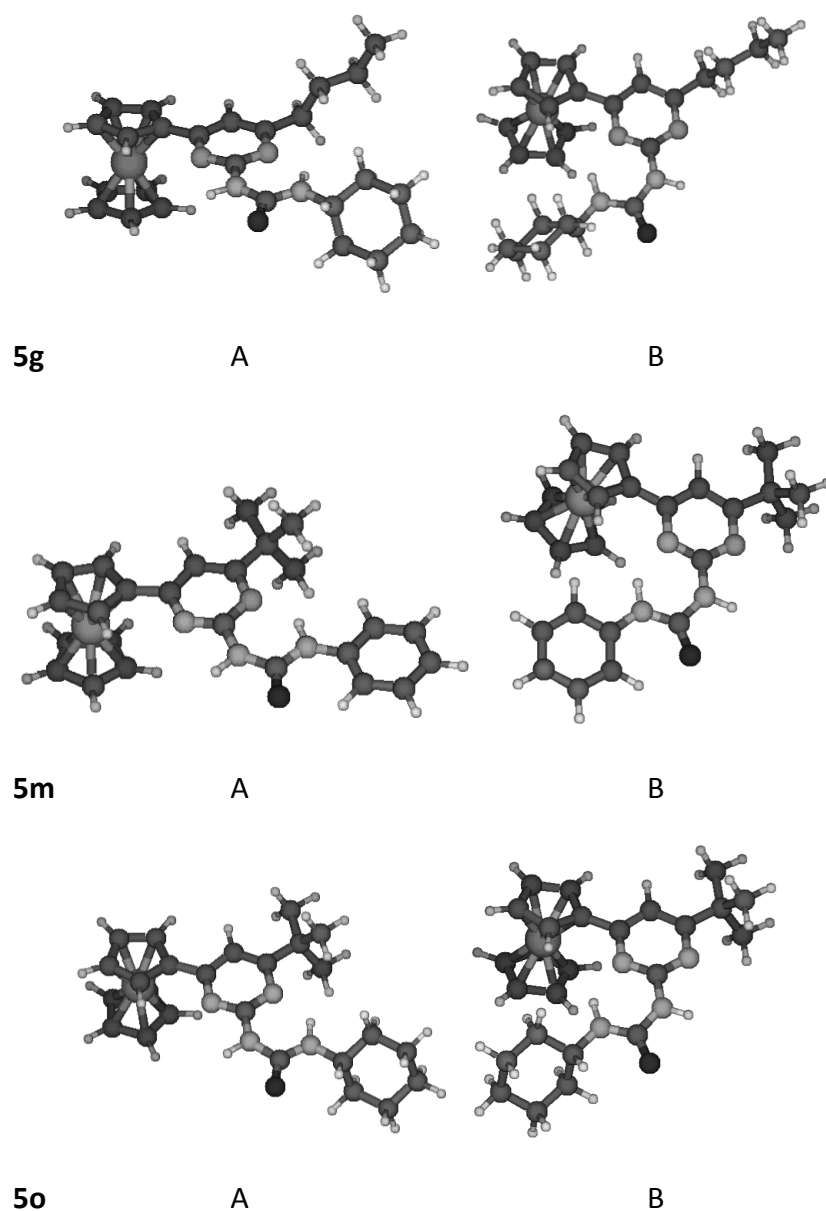


Figure S5. The optimized structures of the two possible conformers (A and B) of compounds **5g**, **5m** and **5o** using the CAM-B3LYP density functional with 6-31G\* basis set

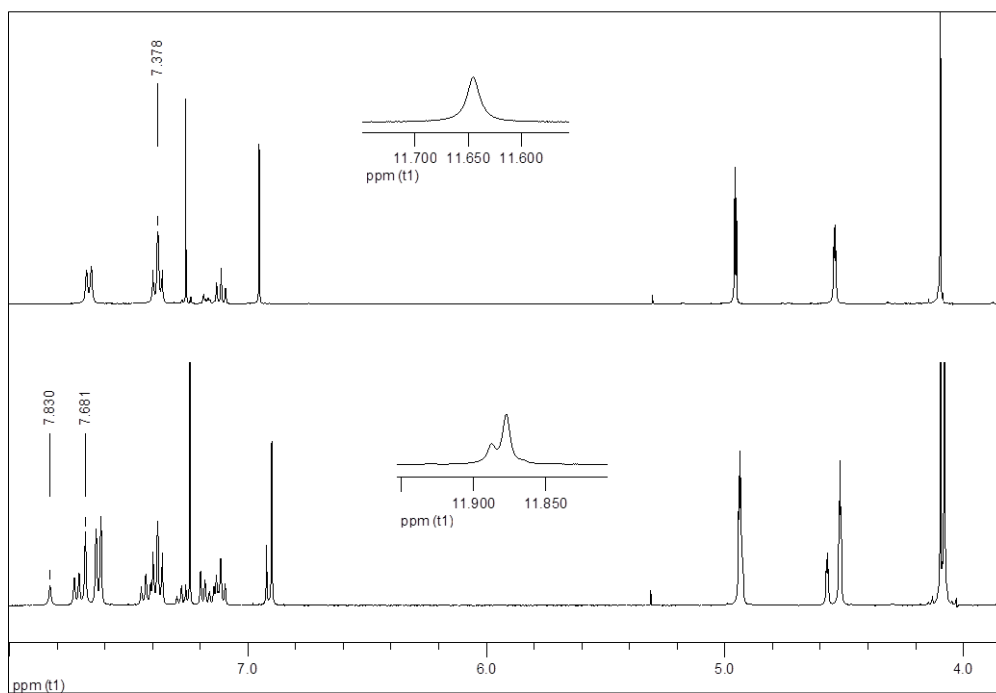


Figure S6.  $^1\text{H}$  NMR spectra of **5m** at 25 °C (top) and -60 °C (bottom).

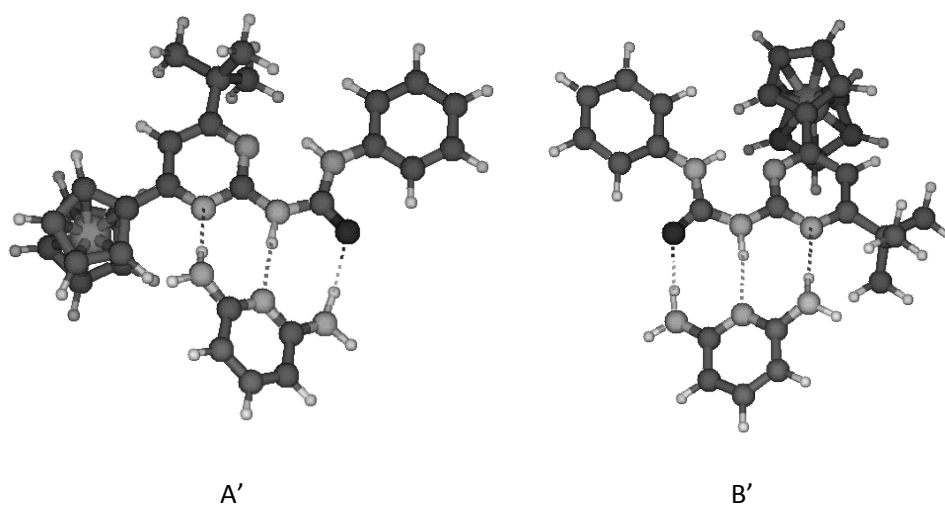


Figure S7. The optimized structures of the two possible conformers of compound **5m** with 2,6-diaminopyridine (**6**) using the CAM-B3LYP density functional and 6-31G\* basis set

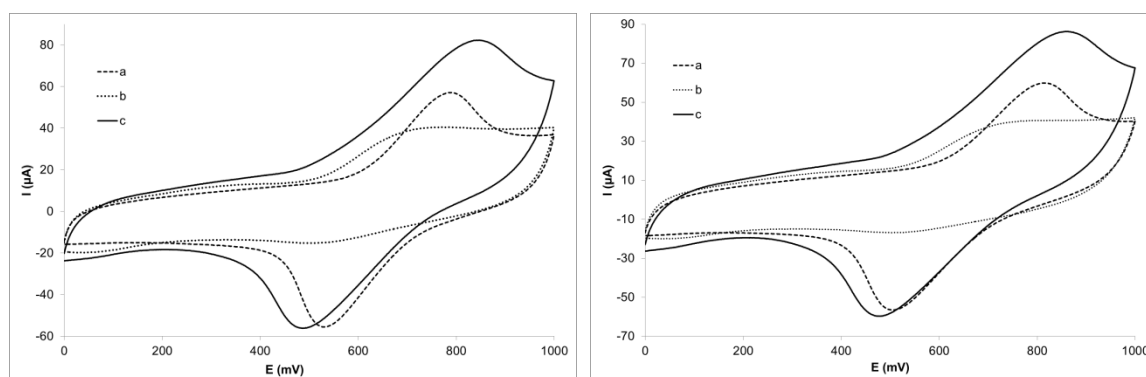


Figure S8. Cyclic voltammograms of **5g** (1 mM) ( $I_{5g}$ , a), **6** (1 mM) ( $I_6$ , b), **5g/6=1/1** mixture (1 mM for each component) ( $I_{5g+6}$ , c) on two different spectral graphite electrodes (OD= 3mm). Solvent: dichloromethane, supporting electrolyte: 0.1 M TBAClO<sub>4</sub>.

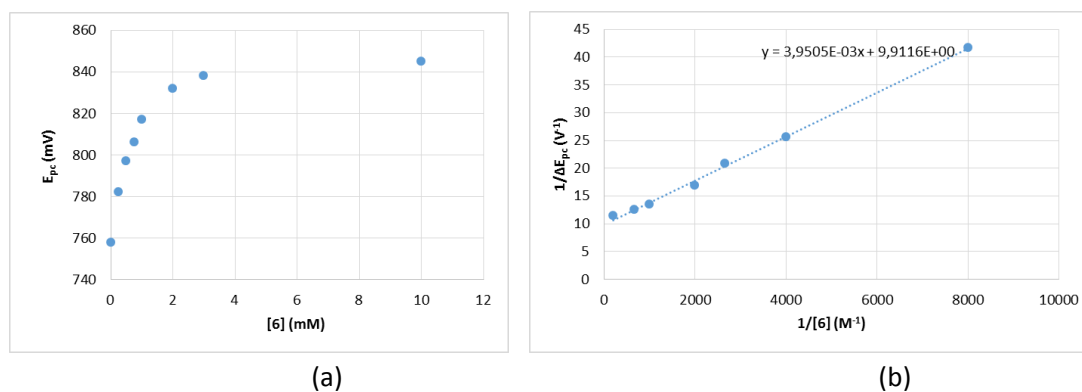
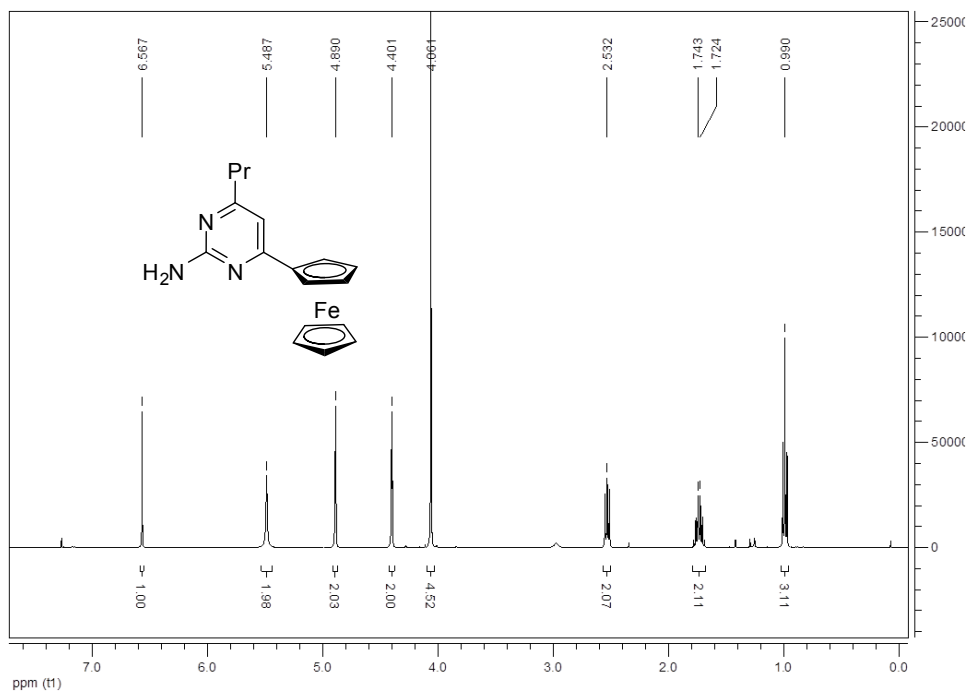
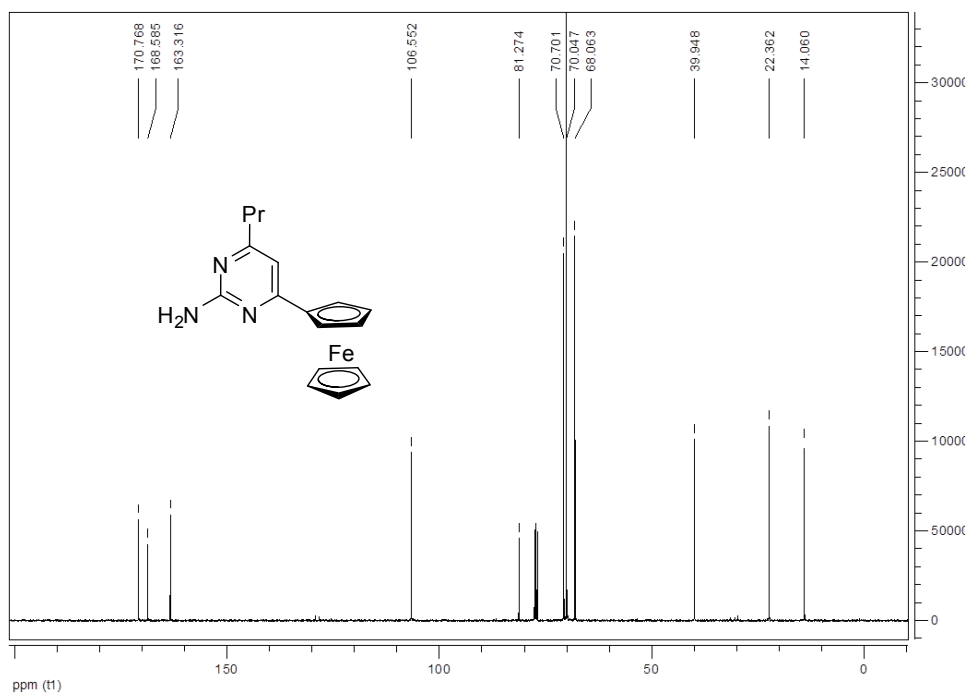


Figure S9. Titration of host **5g** (0.5 mM) with guest **6**. (a)  $E_{pc}$  values obtained by LSV. (b) Benesi-Hildebrand plot for host **5g** with guest **6** determined by LSV Solvent: dichloromethane, supporting electrolyte: 0.1 M TBAClO<sub>4</sub>, spectral graphite electrode (OD= 3mm).

Table S1. Change in the  $E_{pa}$  values of host **5g** and host-guest complex **5g+6** in CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN solvent mixtures. Concentrations: 1 mM (**5g**), 1mM (**5g**)+ 1mM (**6**). Supporting electrolyte: 0.1 M TBAClO<sub>4</sub>, spectral graphite electrode (OD= 3mm).

CH <sub>2</sub> Cl <sub>2</sub> /CH <sub>3</sub> CN ratio	$E_{pa}(\mathbf{5g+6})$ (mV)	$E_{pa}(\mathbf{5g})$ (mV)	$\Delta E_{pa}$ (mV)
1/0	796	767	29
5/1	744	731	13
2/1	707	697	10
1/1	682	674	8
1/2	673	667	6
1/5	675	667	8

Figure S10. <sup>1</sup>H NMR spectrum of 2-amino-4-ferrocenyl-6-propylpyrimidine (**4c**)Figure S11. <sup>13</sup>C NMR spectrum of 2-amino-4-ferrocenyl-6-propylpyrimidine (**4c**)



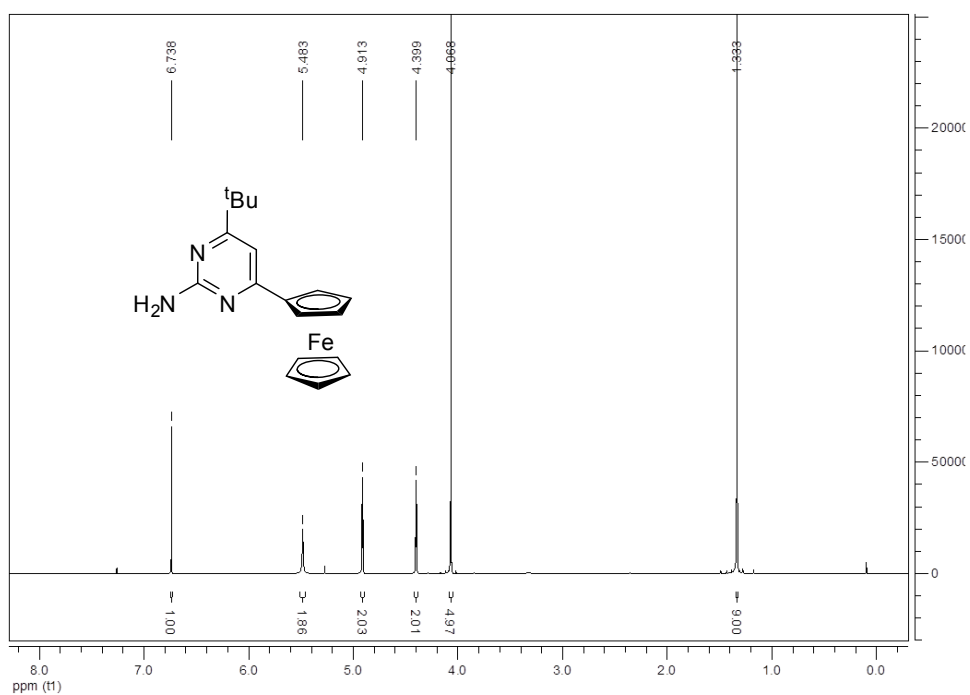


Figure S12. <sup>1</sup>H NMR spectrum of 2-amino-4-*tert*-butyl-6-ferrocenyl pyrimidine (**4d**)

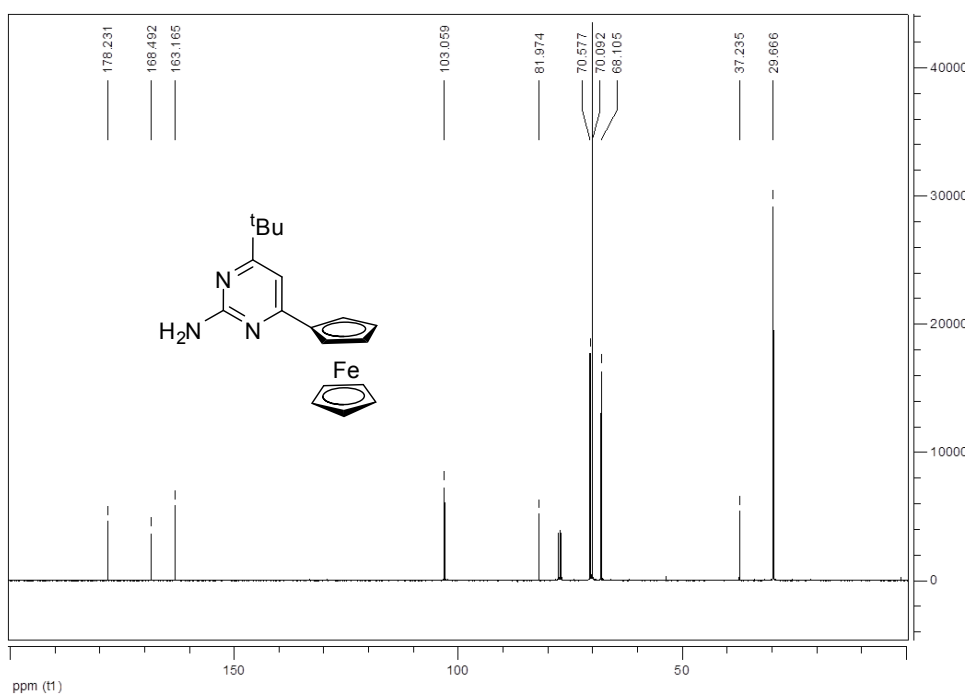


Figure S13. <sup>13</sup>C NMR spectrum of 2-amino-4-*tert*-butyl-6-ferrocenyl pyrimidine (**4d**)

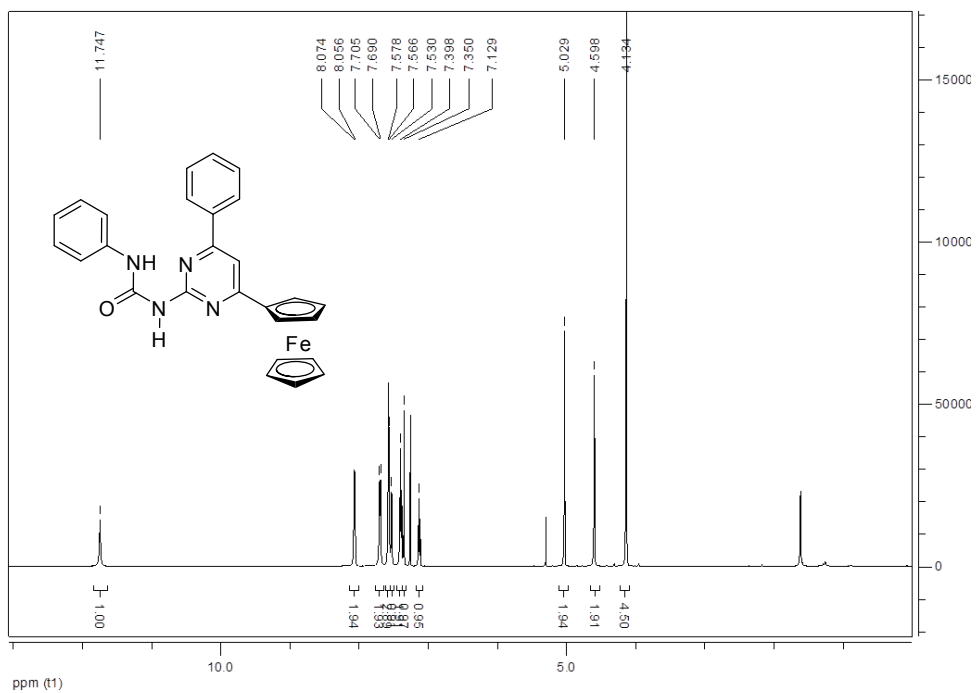


Figure S14.  $^1\text{H}$  NMR spectrum of 1-(4-ferrocenyl-6-phenylpyrimidin-2-yl)-3-phenylurea (**5a**)

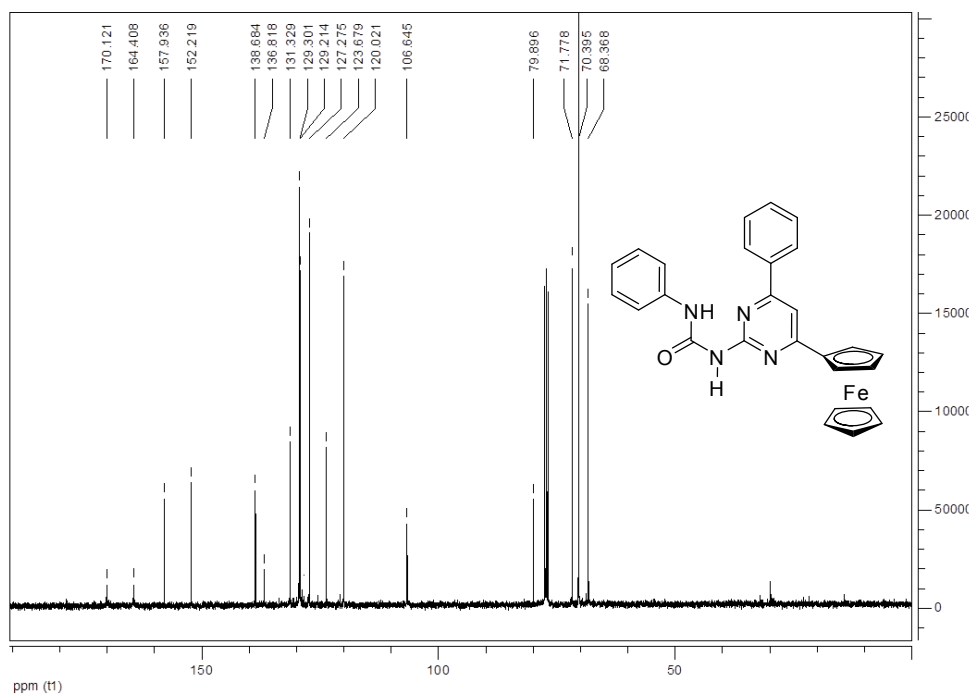


Figure S15.  $^{13}\text{C}$  NMR spectrum of 1-(4-ferrocenyl-6-phenylpyrimidin-2-yl)-3-phenylurea (**5a**)

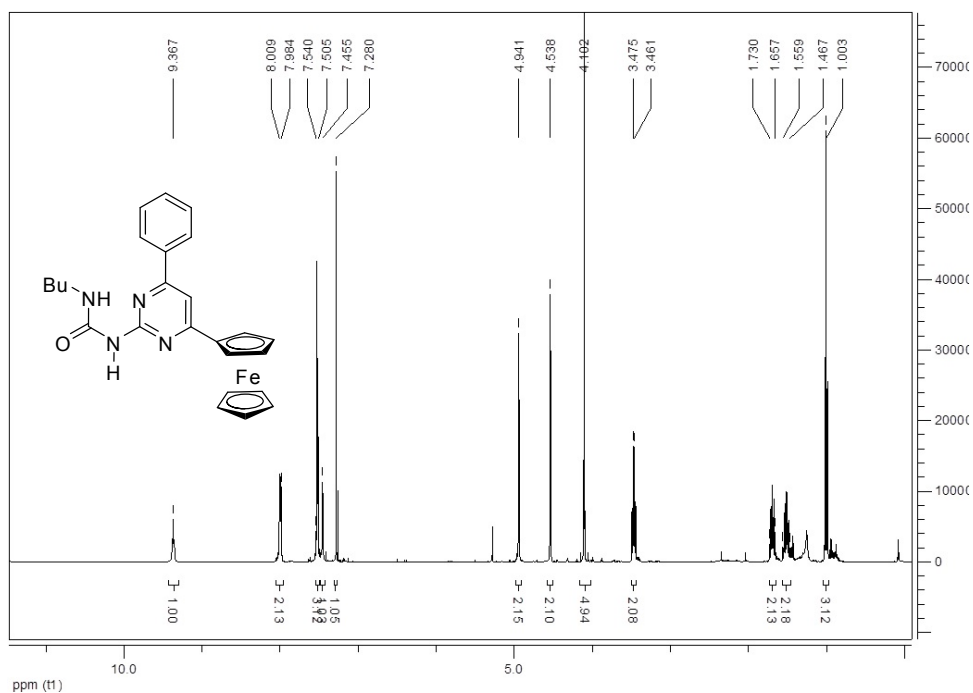


Figure S16.  $^1\text{H}$  NMR spectrum of 1-butyl-3-(4-ferrocenyl-6-phenylpyrimidin-2-yl)-urea (**5b**)

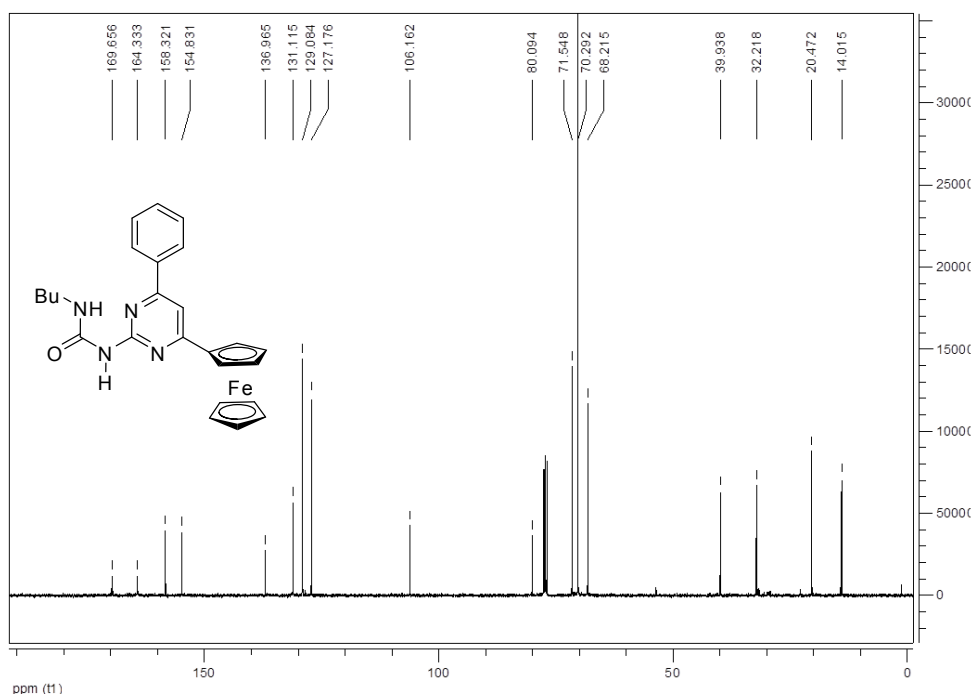
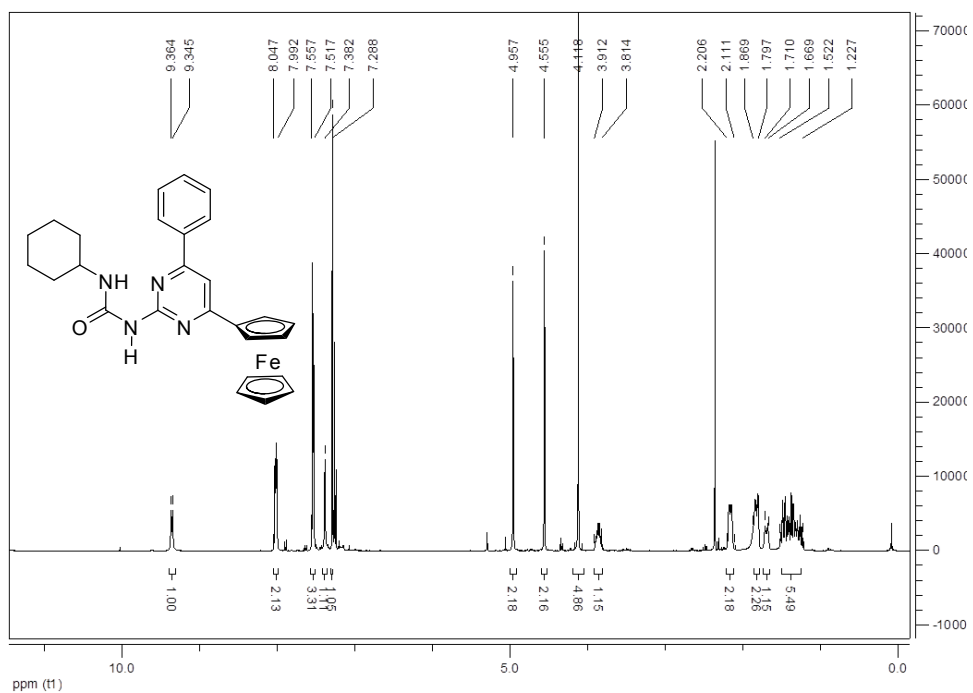
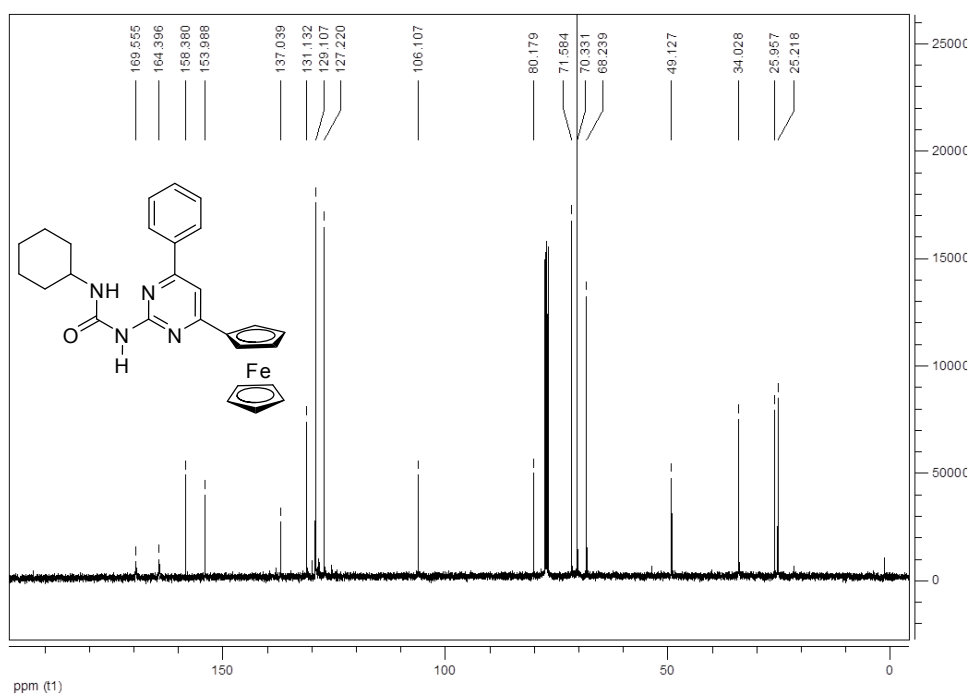


Figure S17.  $^{13}\text{C}$  NMR spectrum of 1-butyl-3-(4-ferrocenyl-6-phenylpyrimidin-2-yl)-urea (**5b**)

Figure S18. <sup>1</sup>H NMR spectrum of 1-cyclohexyl-3-(4-ferrocenyl-6-phenylpyrimidin-2-yl)-urea (5c)Figure S19. <sup>13</sup>C NMR spectrum of 1-cyclohexyl-3-(4-ferrocenyl-6-phenylpyrimidin-2-yl)-urea (5c)

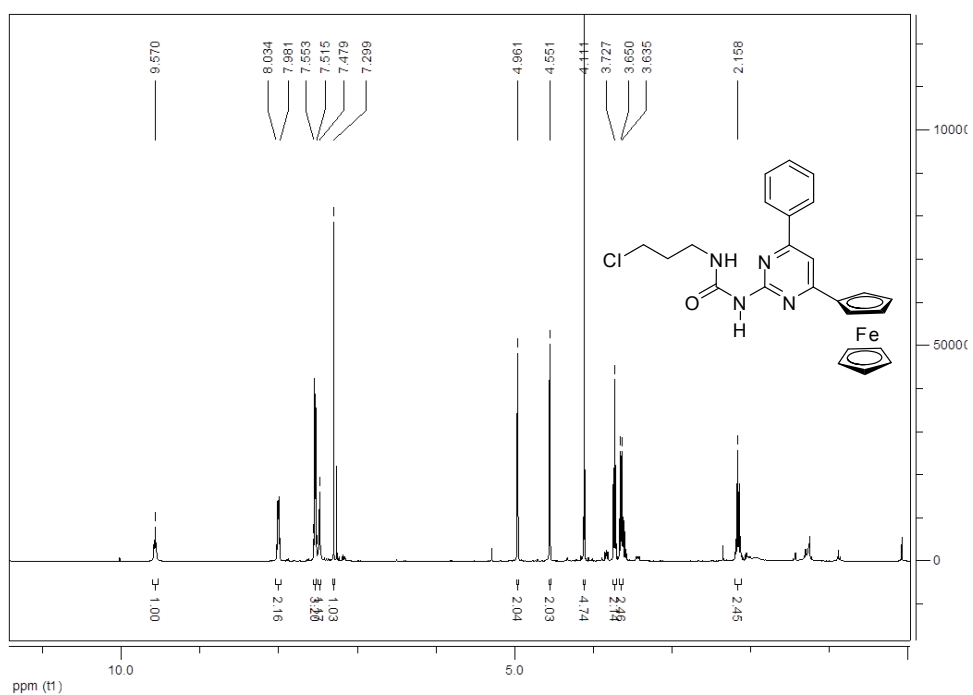


Figure S20. <sup>1</sup>H NMR spectrum of 1-(3-chloropropyl)-3-(4-ferrocenyl-6-phenylpyrimidin-2-yl)-urea (5d)

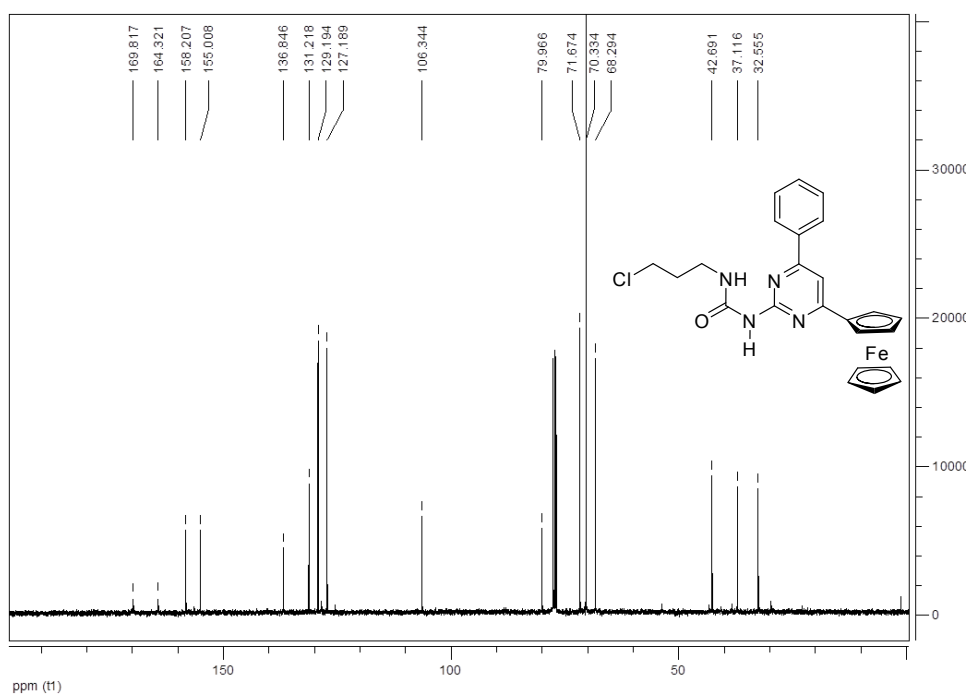
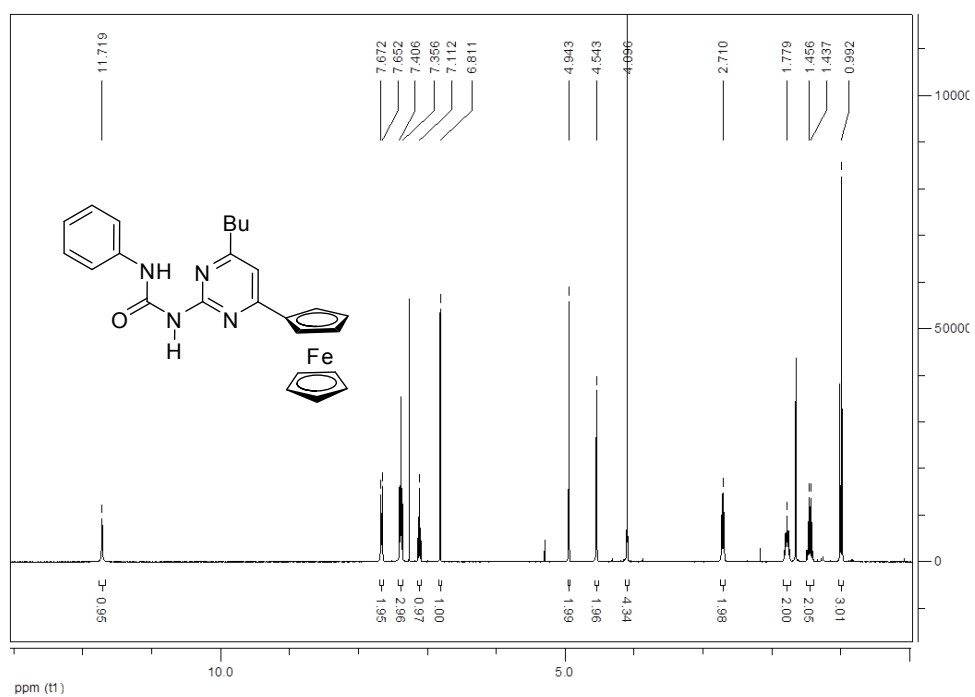
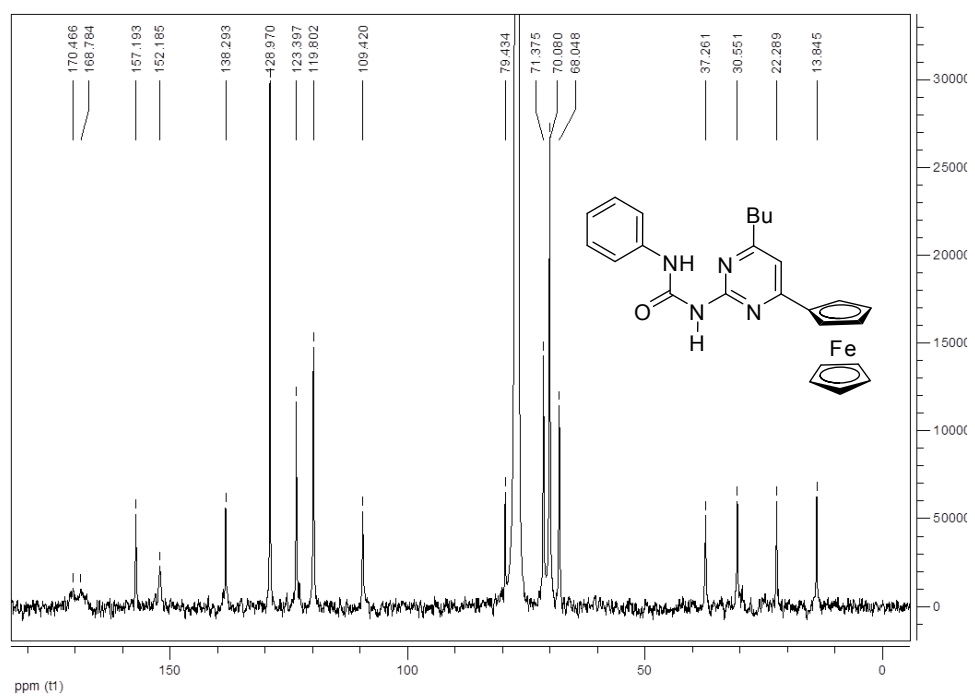
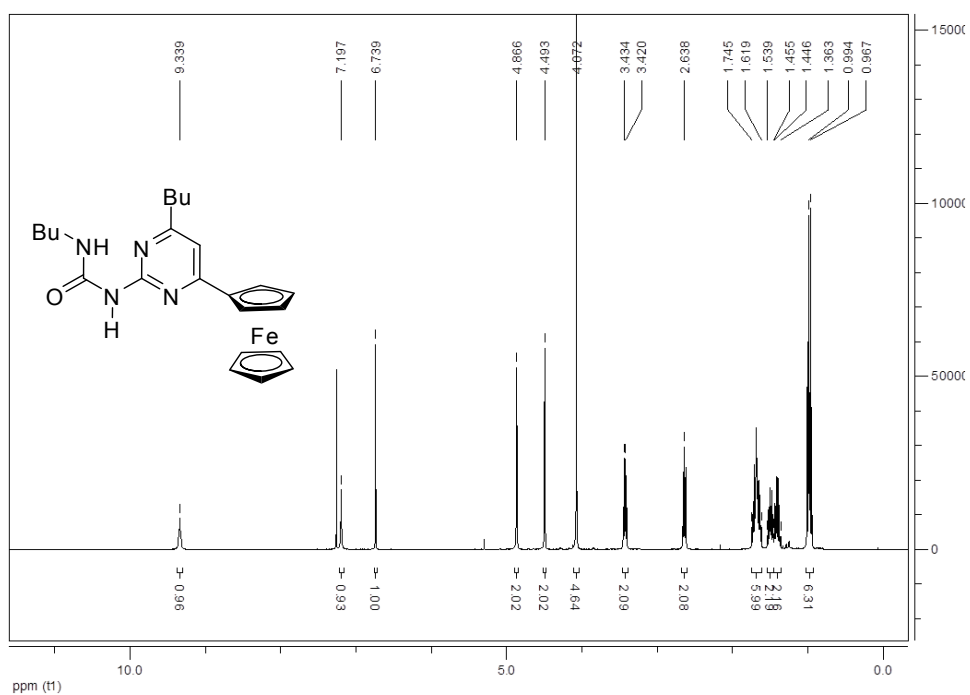
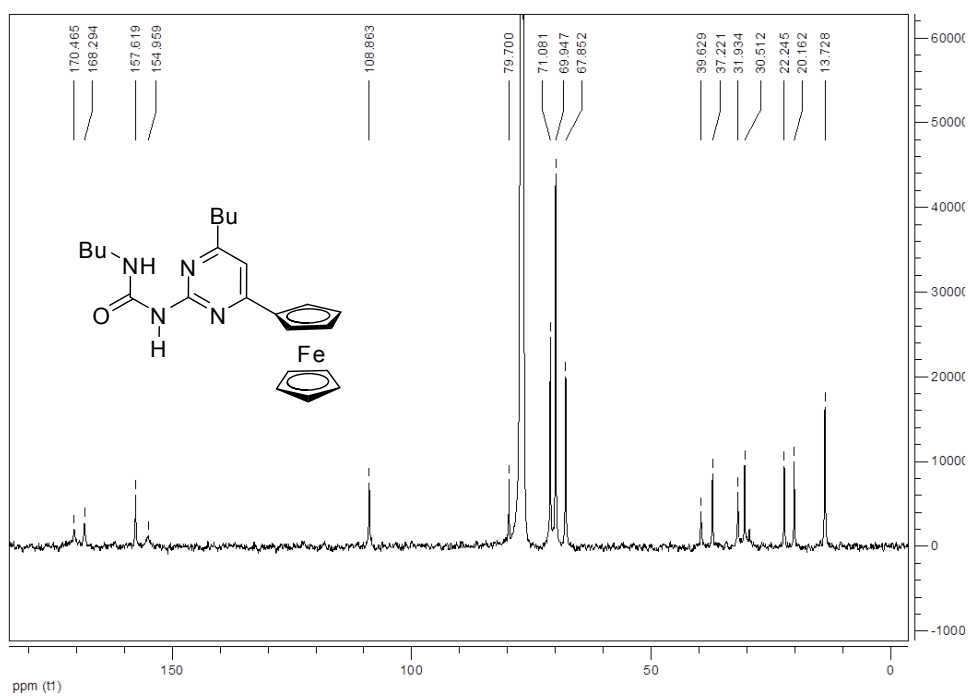


Figure S21. <sup>13</sup>C NMR spectrum of 1-(3-chloropropyl)-3-(4-ferrocenyl-6-phenylpyrimidin-2-yl)-urea (5d)

Figure S22.  $^1\text{H}$  NMR spectrum of 1-(4-butyl-6-ferrocenylpyrimidin-2-yl)-3-phenylurea (**5e**)Figure S23.  $^{13}\text{C}$  NMR spectrum of 1-(4-butyl-6-ferrocenylpyrimidin-2-yl)-3-phenylurea (**5e**)

Figure S24. <sup>1</sup>H NMR spectrum of 1-butyl-3-(4-butyl-6-ferrocenylpyrimidin-2-yl)-urea (5f)Figure S25. <sup>13</sup>C NMR spectrum of 1-butyl-3-(4-butyl-6-ferrocenylpyrimidin-2-yl)-urea (5f)

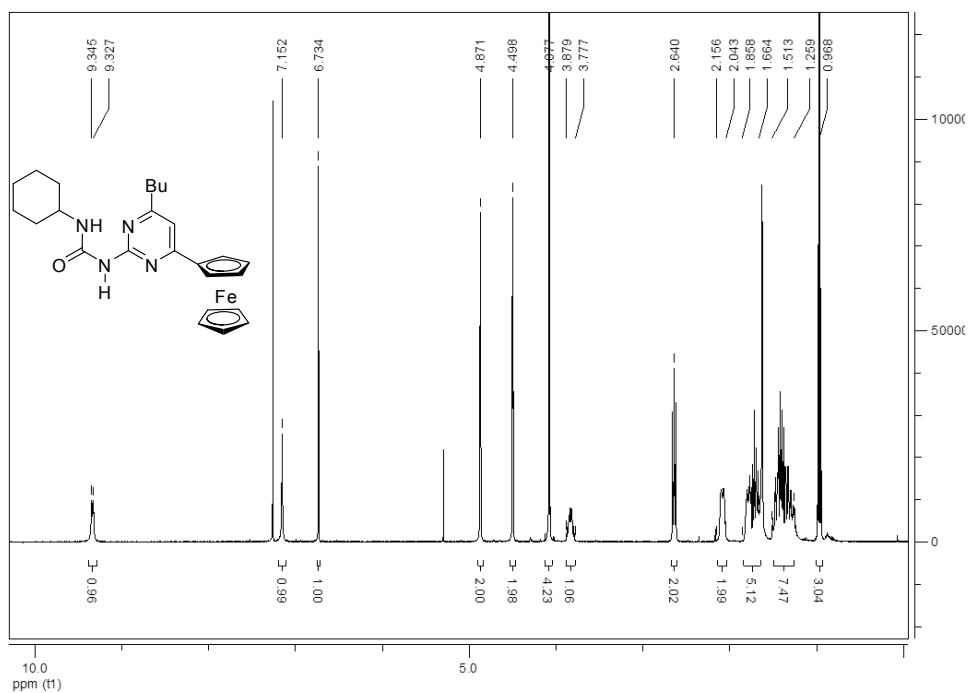


Figure S26. <sup>1</sup>H NMR spectrum of 1-(4-butyl-6-ferrocenylpyrimidin-2-yl)-3-cyclohexylurea (**5g**)

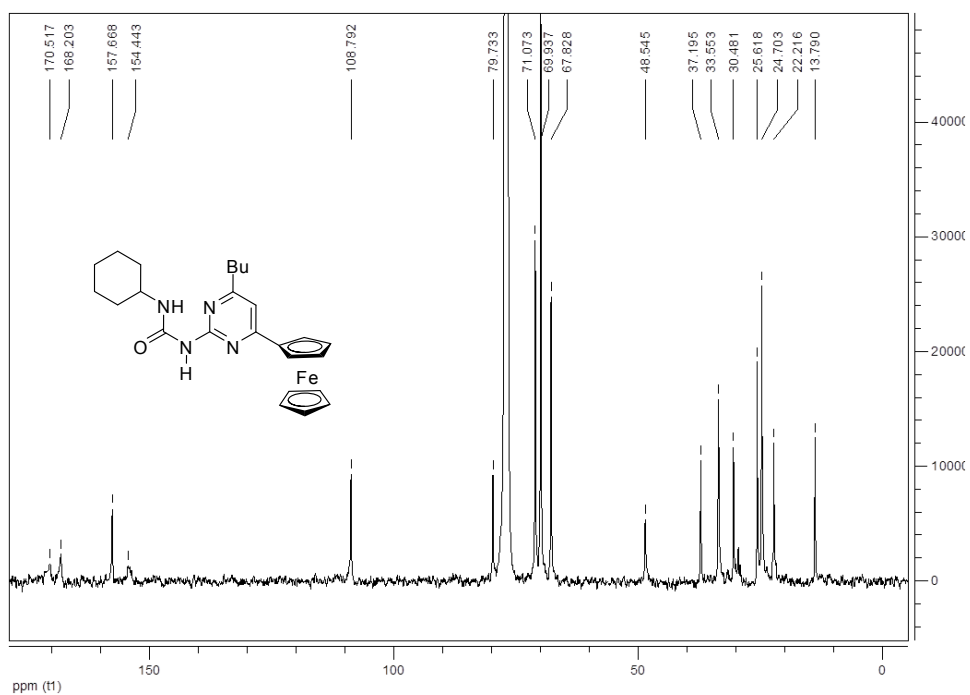


Figure S27. <sup>13</sup>C NMR spectrum of 1-(4-butyl-6-ferrocenylpyrimidin-2-yl)-3-cyclohexylurea (**5g**)



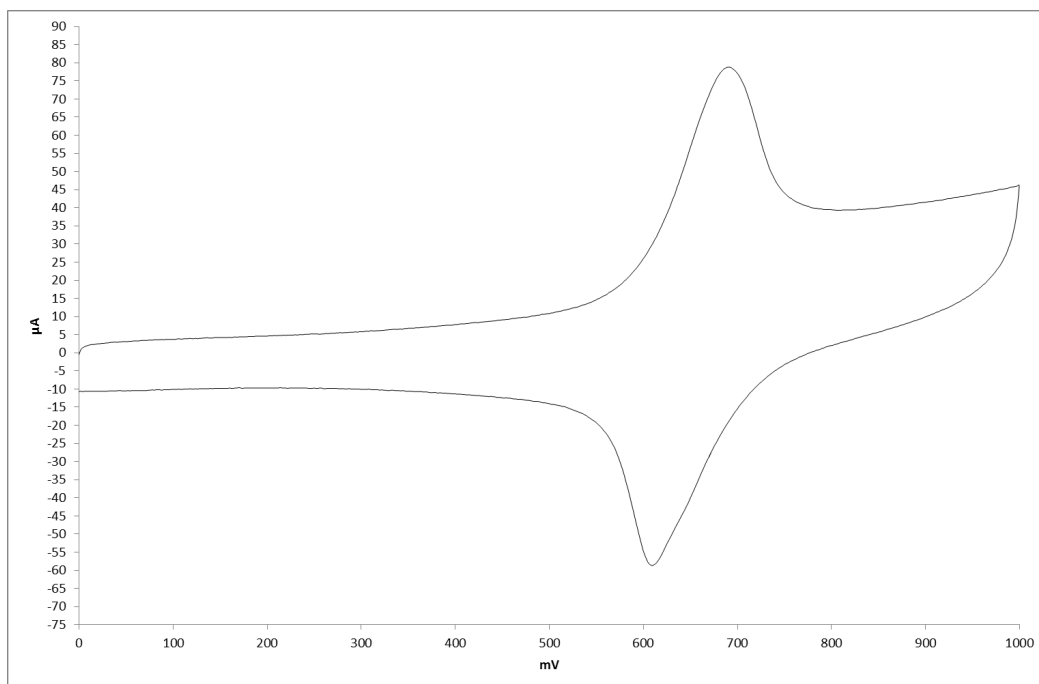


Figure S28. Cyclic voltammogram of **5g** (1 mM in acetonitrile, supporting electrolyte: 0.1 M TBAClO<sub>4</sub>, spectral graphite electrode (OD= 3mm))

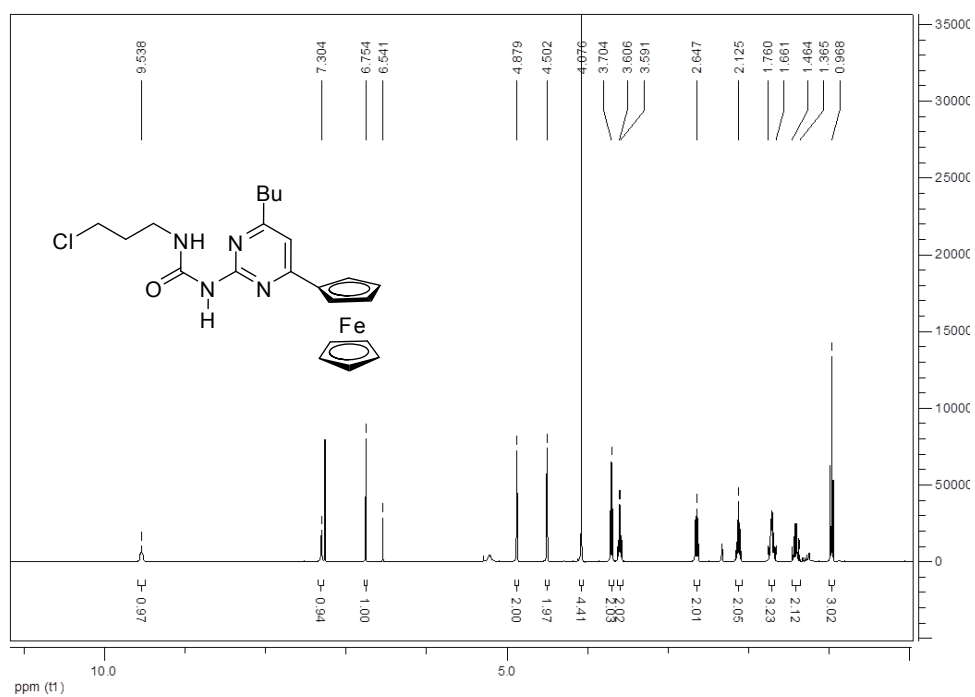


Figure S29. <sup>1</sup>H NMR spectrum of 1-(4-butyl-6-ferrocenylpyrimidin-2-yl)-3-(3-chloropropyl)urea (**5h**)

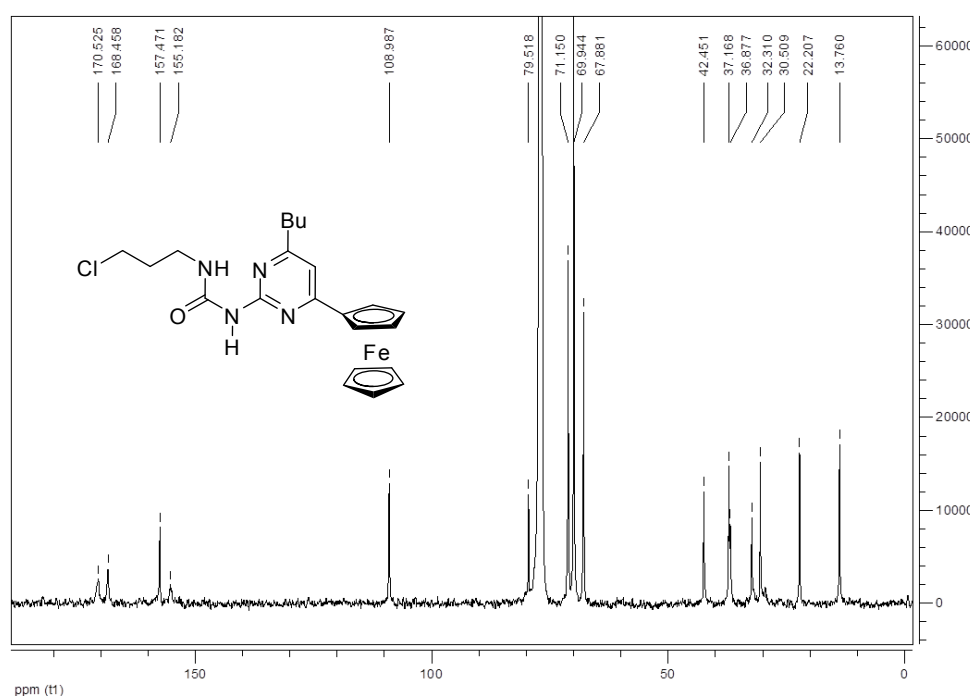
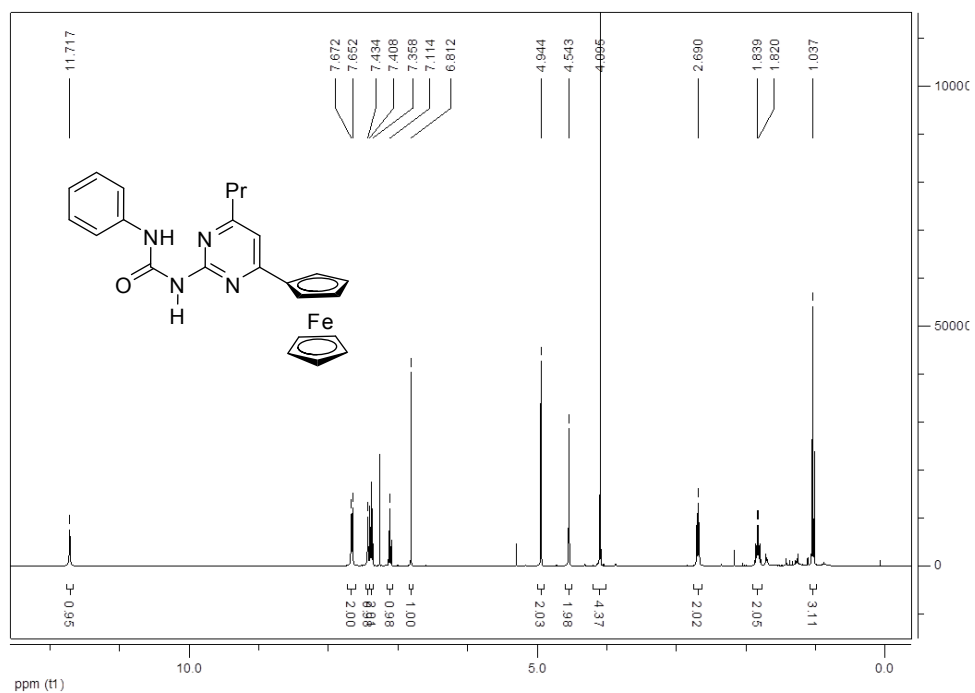
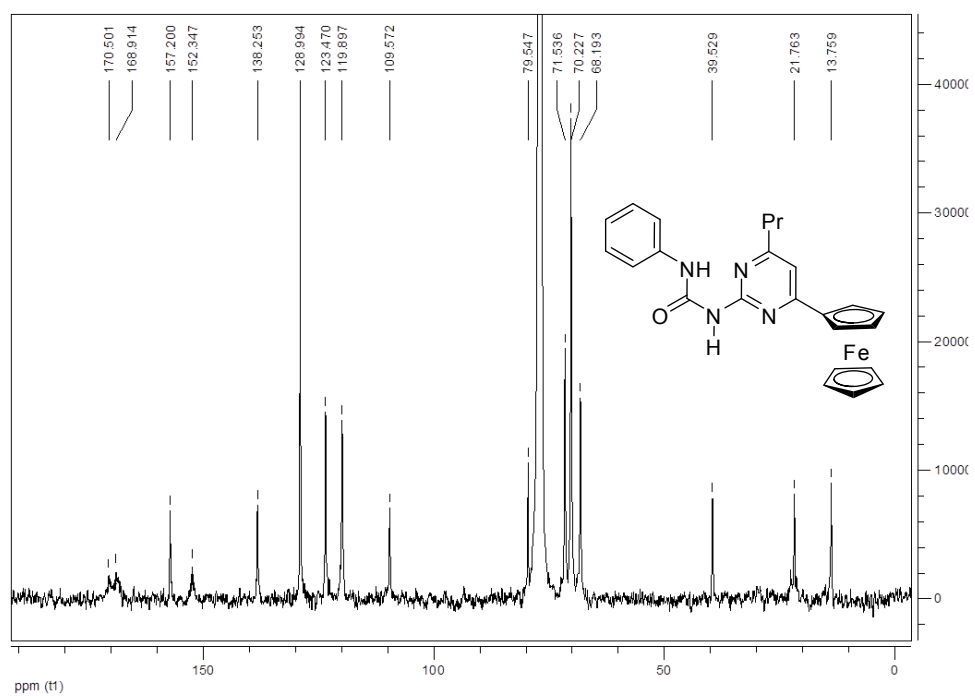


Figure S30. <sup>13</sup>C NMR spectrum of 1-(4-butyl-6-ferrocenylpyrimidin-2-yl)-3-(3-chloropropyl)urea (**5h**)

Figure S31.  $^1\text{H}$  NMR spectrum of 1-(4-ferrocenyl-6-propylpyrimidin-2-yl)-3-phenylurea (**5i**)Figure S32.  $^{13}\text{C}$  NMR spectrum of 1-(4-ferrocenyl-6-propylpyrimidin-2-yl)-3-phenylurea (**5i**)

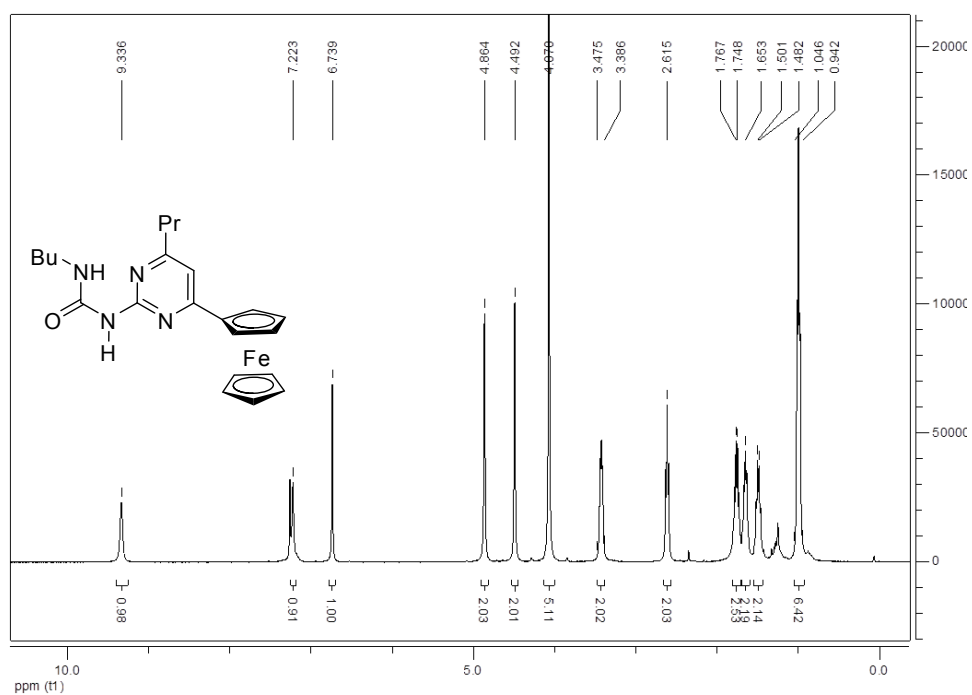


Figure S33. <sup>1</sup>H NMR spectrum of 1-butyl-3-(4-ferrocenyl-6-propylpyrimidin-2-yl)-urea (**5j**)

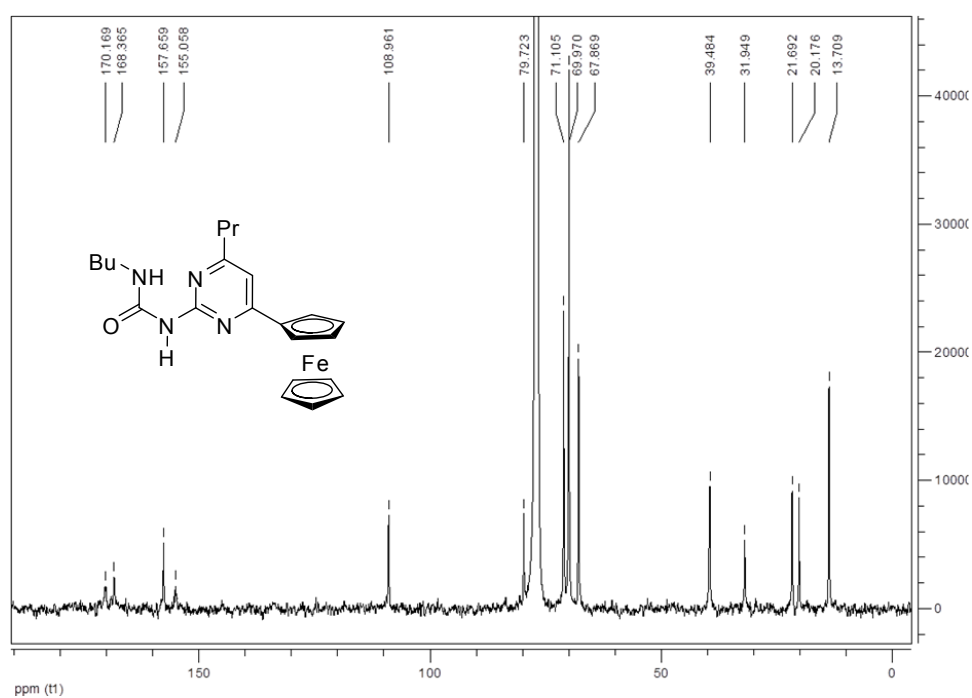


Figure S34. <sup>13</sup>C NMR spectrum of 1-butyl-3-(4-ferrocenyl-6-propylpyrimidin-2-yl)-urea (**5j**)

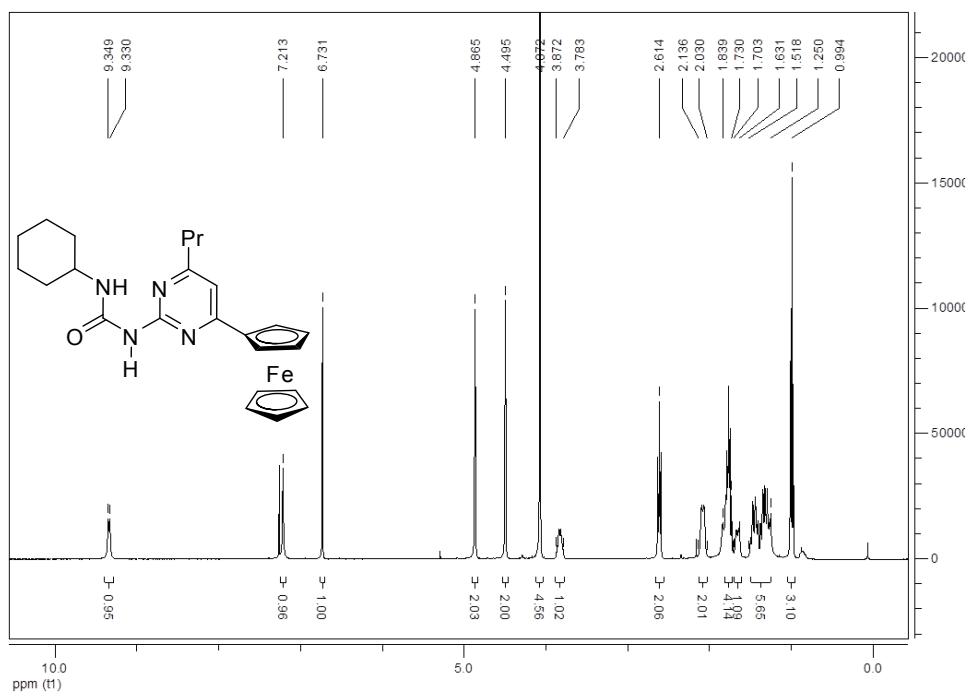


Figure S35.  $^1\text{H}$  NMR spectrum of 1-cyclohexyl-3-(4-ferrocenyl-6-propylpyrimidin-2-yl)-urea (**5k**)

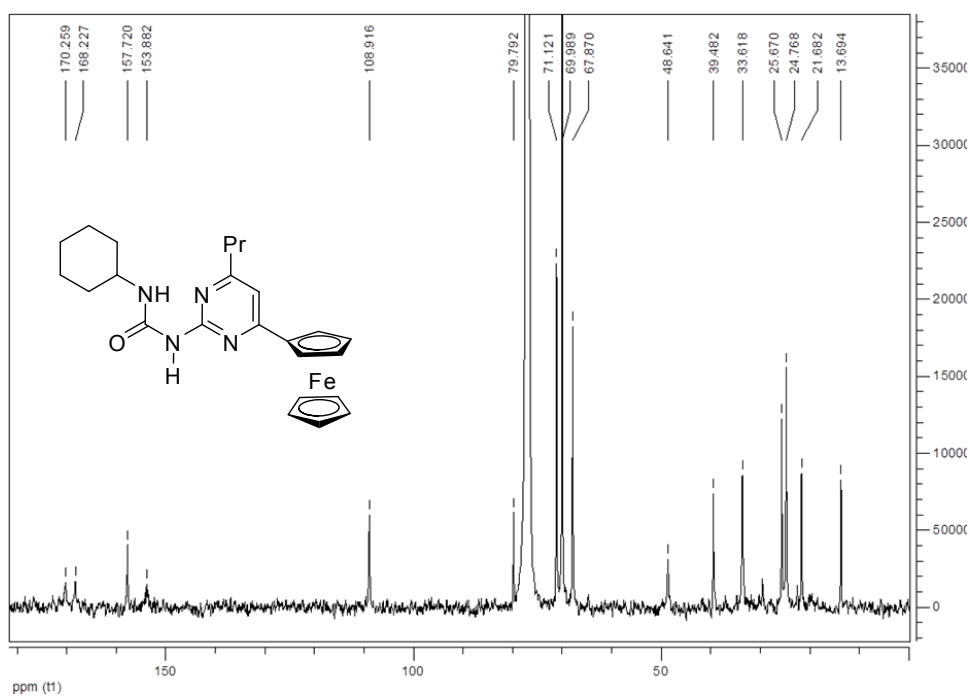


Figure S36.  $^{13}\text{C}$  NMR spectrum of 1-cyclohexyl-3-(4-ferrocenyl-6-propylpyrimidin-2-yl)-urea (**5k**)

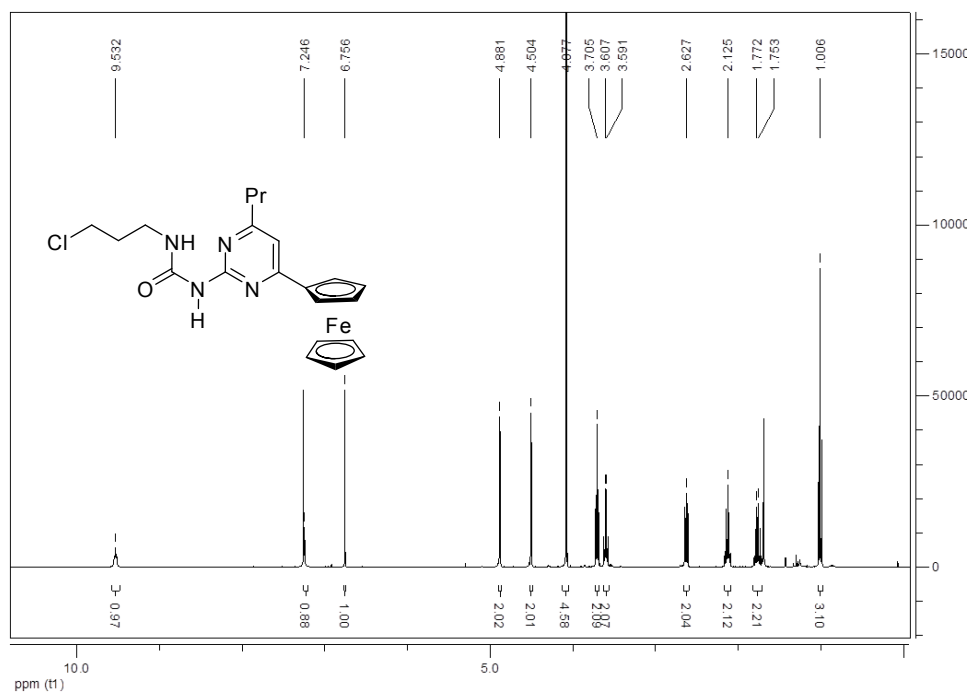


Figure S37. <sup>1</sup>H NMR spectrum of 1-(3-chloropropyl)-3-(4-ferrocenyl-6-propylpyrimidin-2-yl)-urea (**51**)

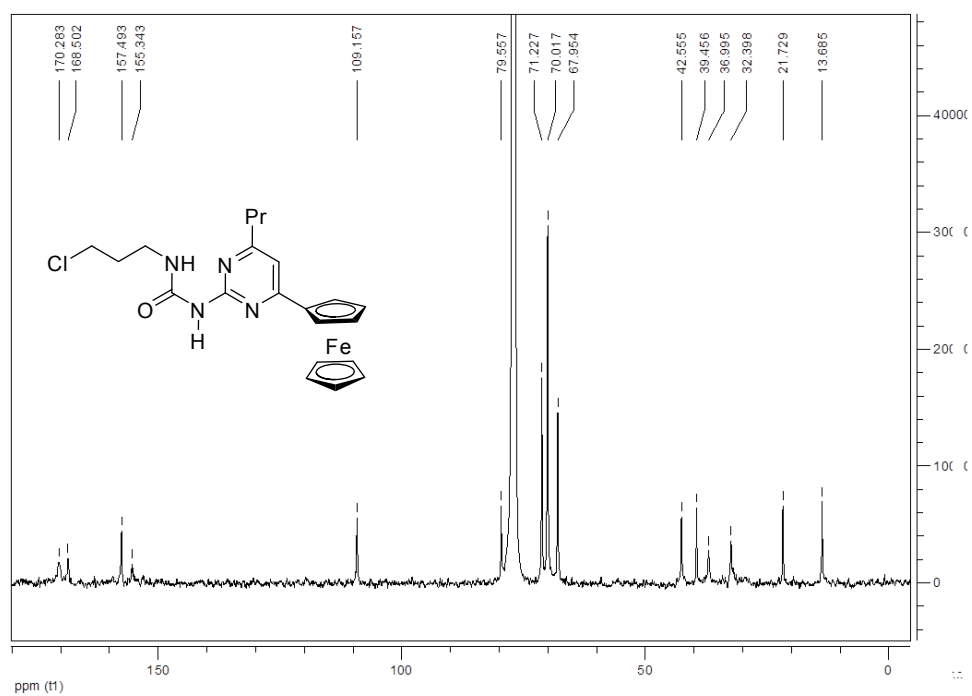
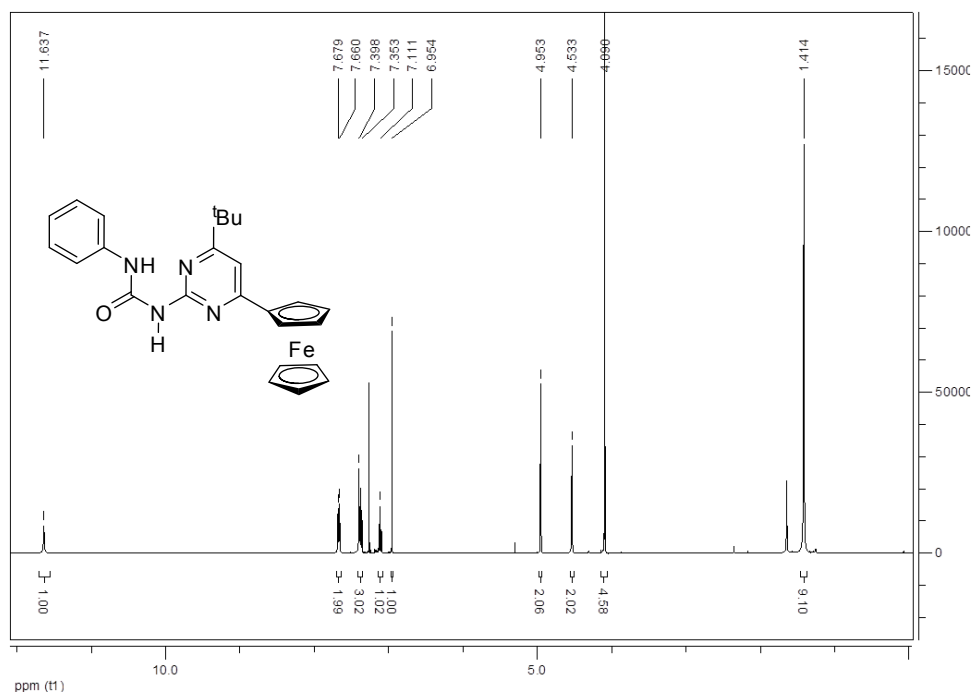
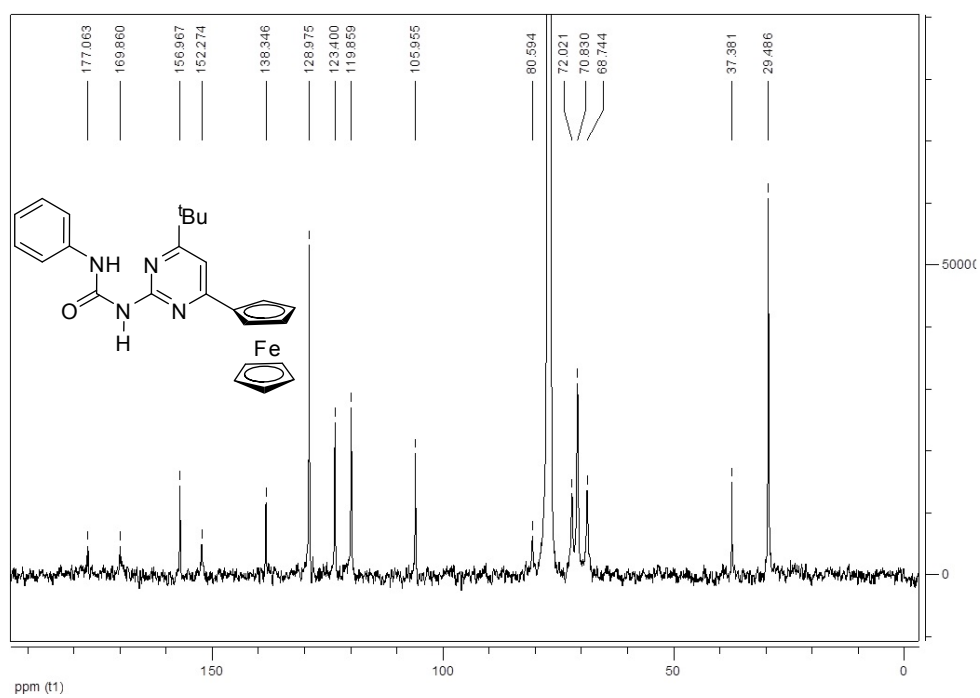


Figure S38. <sup>13</sup>C NMR spectrum of 1-(3-chloropropyl)-3-(4-ferrocenyl-6-propylpyrimidin-2-yl)-urea (**51**)

Figure S39. <sup>1</sup>H NMR spectrum of 1-(4-*tert*-butyl-6-ferrocenylpyrimidin-2-yl)-3-phenylurea (**5m**)Figure S40. <sup>13</sup>C NMR spectrum of 1-(4-*tert*-butyl-6-ferrocenylpyrimidin-2-yl)-3-phenylurea (**5m**)

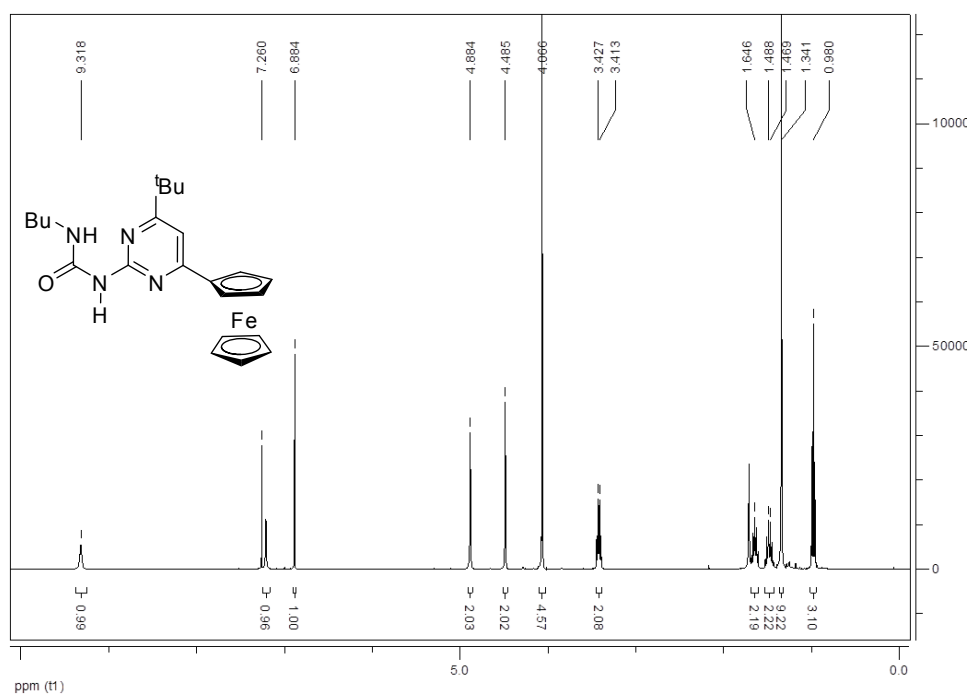


Figure S41. <sup>1</sup>H NMR spectrum of 1-butyl-3-(4-tert-butyl-6-ferrocenylpyrimidin-2-yl)-urea (5n)

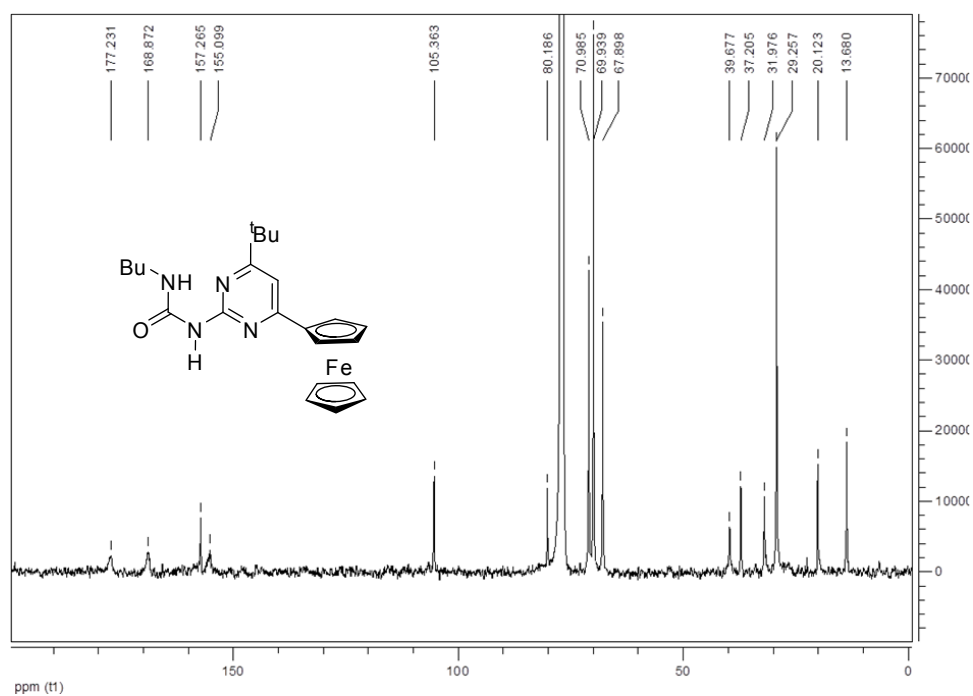


Figure S42. <sup>13</sup>C NMR spectrum of 1-butyl-3-(4-tert-butyl-6-ferrocenylpyrimidin-2-yl)-urea (5n)



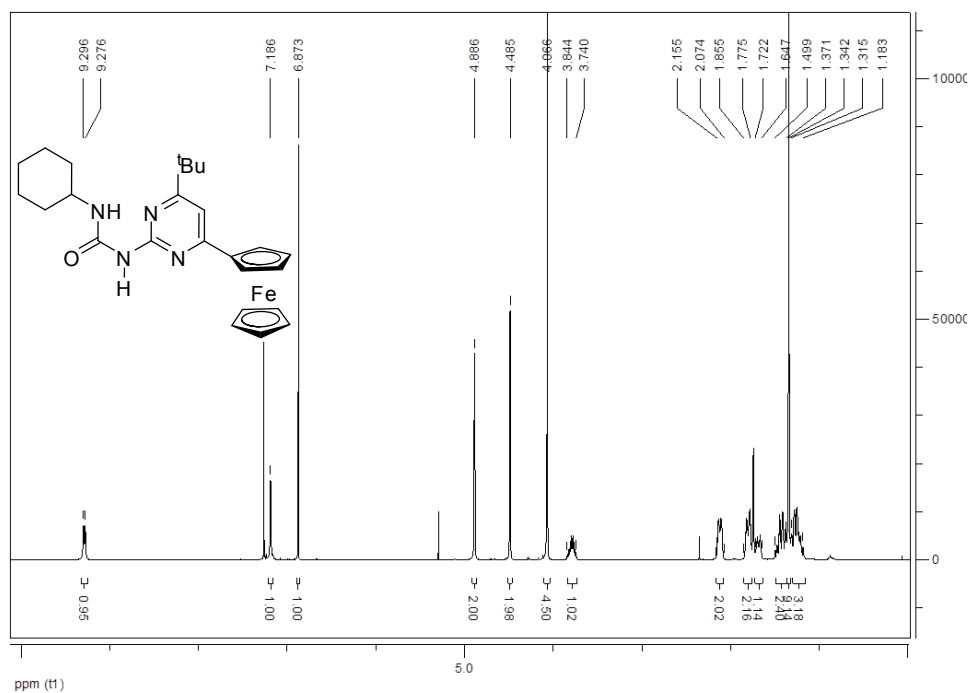


Figure S43. <sup>1</sup>H NMR spectrum of 1-(4-tert-butyl-6-ferrocenylpyrimidin-2-yl)-3-cyclohexylurea (**5o**)

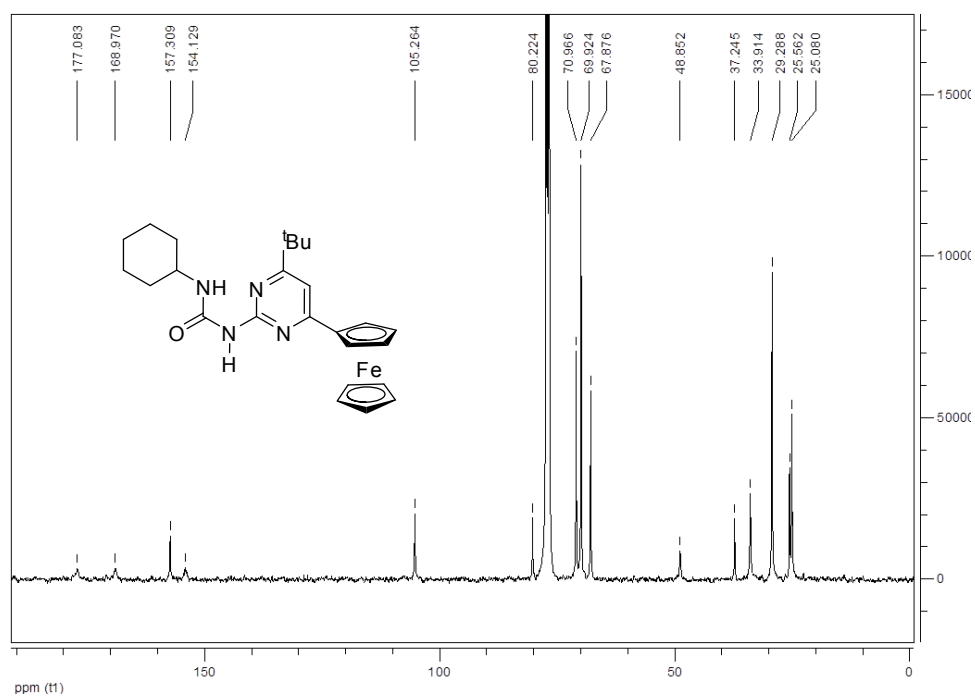


Figure S44. <sup>13</sup>C NMR spectrum of 1-(4-tert-butyl-6-ferrocenylpyrimidin-2-yl)-3-cyclohexylurea (**5o**)

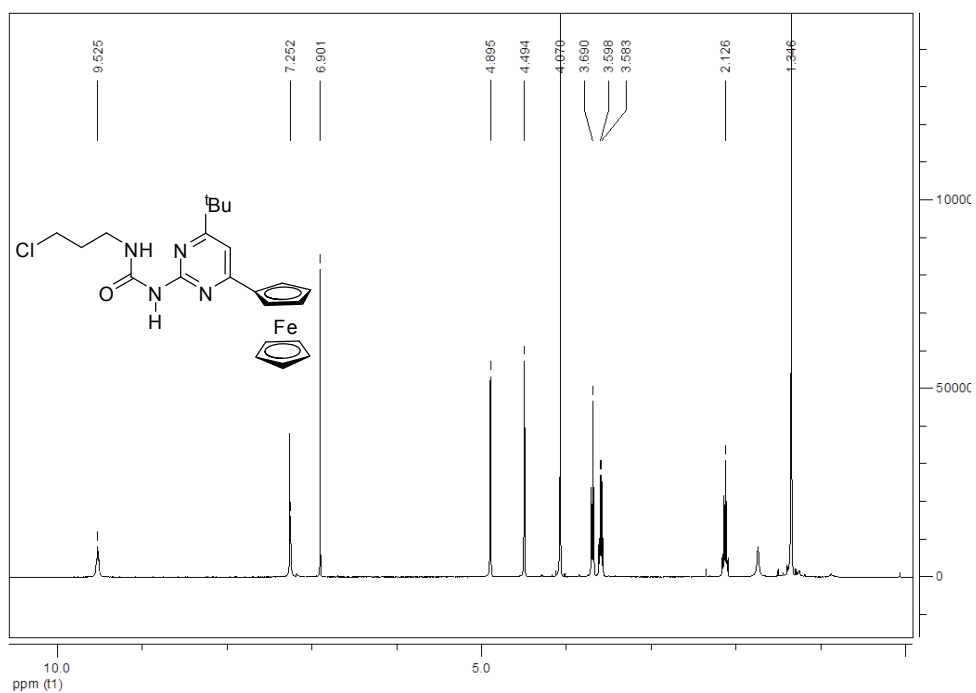


Figure S45. <sup>1</sup>H NMR spectrum of 1-(4-tert-butyl-6-ferrocenylpyrimidin-2-yl)-3-(3-chloropropyl)urea (5p)

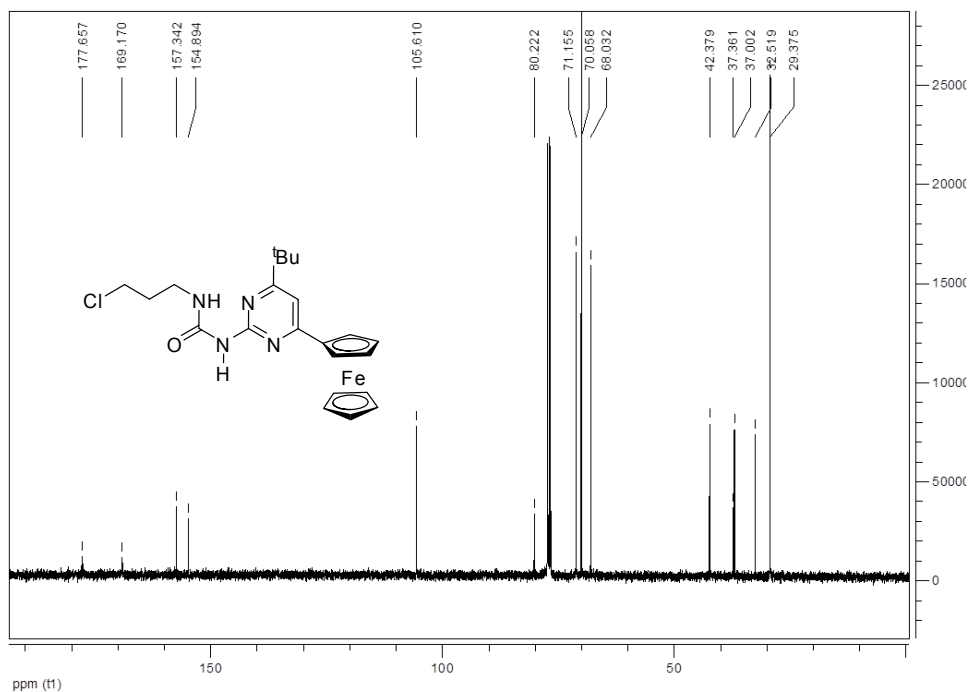


Figure S46. <sup>13</sup>C NMR spectrum of 1-(4-tert-butyl-6-ferrocenylpyrimidin-2-yl)-3-(3-chloropropyl)urea (5p)