

## Supporting Information

### **Towards Building Blocks for Metallosupramolecular Structures: Non-symmetrically-Functionalised Ferrocenyl Compounds**

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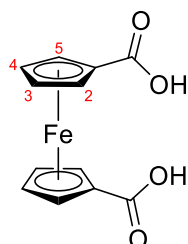
<sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra for compounds **5**, **6**, **8a**, **8b**, **9**, **10**, **11a** and **11b**

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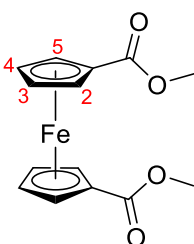
## Experimental

### *1,1'-Ferrocenedicarboxylic acid (Fc(COOH)<sub>2</sub>)*



*n*-BuLi (2.0 M, 50 mL, 0.1 mol) was added to a solution of TMEDA (15 mL, 0.1 mol) in *n*-hexane (40 mL) and stirred at rt for 10 min. A solution of ferrocene (7.75 g, 41.7 mmol) in *n*-hexane (300 mL) was added dropwise over a period of 30 min and the reaction mixture was stirred for a further 6 h. The mixture was cooled to  $-78\text{ }^{\circ}\text{C}$ , dry ice (10 g) added and left to warm to rt. The precipitate was collected by filtration, washed with cool Et<sub>2</sub>O (3 × 50 mL) and dissolved in water (50 mL). The solution was acidified to pH 1 using concentrated HCl, the resulting solid was filtered, washed with water and dried *in vacuo*. The crude product was recrystallized from hot AcOH to afford Fc(COOH)<sub>2</sub> (4.48 g, 39%) as dark red crystals. <sup>1</sup>H NMR (400 MHz, (CD<sub>3</sub>)<sub>2</sub>SO): δ 12.29 (s, 2H, 2 × COOH), 4.70 (s, 4H, 2 × H-2 and H-5), 4.46 (s, 4H, 2 × H-3 and H-4); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, (CD<sub>3</sub>)<sub>2</sub>SO): δ 171.6 (2 × C, 2 × C=O), 73.4 (2 × C, 2 × C-1), 72.8 (4 × CH, 2 × C-2 and C-5), 71.3 (4 × CH, 2 × C-3 and C-4); MS (ESI<sup>+</sup>): *m/z* 296.9821 [M + Na]<sup>+</sup> (*m*<sub>calc</sub> 296.9821). The spectroscopic data were in agreement with those reported in the literature.<sup>1</sup>

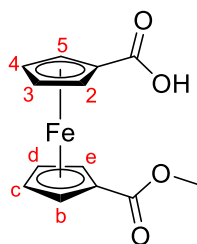
### *1,1'-Bis(methoxycarbonyl)ferrocene (Fc(COOMe)<sub>2</sub>)*



(COCl)<sub>2</sub> (5.31 mL, 61.9 mmol) was added to a suspension of Fc(COOH)<sub>2</sub> (3.39 g, 12.4 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (150 mL), followed by 1–2 drops of DMF. The reaction mixture was stirred at rt for 3 h, and then concentrated *in vacuo* to afford Fc(COCl)<sub>2</sub> (3.85 g, quant.) as a red solid which was used without further purification. Freshly prepared Fc(COCl)<sub>2</sub> (3.85 g, 12.4 mmol) was dissolved in MeOH (150 mL) and stirred at rt for 1 h. The solution was concentrated *in vacuo* and the crude residue purified by flash chromatography (CH<sub>2</sub>Cl<sub>2</sub>) to afford Fc(COOMe)<sub>2</sub> (3.63

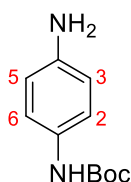
g, 97%) as an orange powder.  $R_f$  0.37 ( $\text{CH}_2\text{Cl}_2$  neat);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.83 (t, 4H,  $^3J = 1.9$  Hz,  $2 \times \text{H-2}$  and  $\text{H-5}$ ), 4.41 (t, 4H,  $^3J = 1.9$  Hz,  $2 \times \text{H-3}$  and  $\text{H-4}$ ), 3.82 (s, 6H,  $2 \times \text{CH}_3$ );  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  171.0 ( $2 \times \text{C}$ ,  $2 \times \text{COOCH}_3$ ), 73.0 ( $2 \times \text{C}$ ,  $2 \times \text{C-1}$ ), 72.8 ( $4 \times \text{C}$ ,  $2 \times \text{C-2}$  and  $\text{C-5}$ ), 71.7 ( $4 \times \text{C}$ ,  $2 \times \text{C-3}$  and  $\text{C-4}$ ), 51.8 ( $2 \times \text{CH}_3$ ,  $2 \times \text{COOCH}_3$ ); MS (ESI<sup>+</sup>):  $m/z = 325.0136$  [ $\text{M} + \text{Na}$ ]<sup>+</sup> ( $m_{\text{calc}} = 325.0134$ ). The spectroscopic data were in agreement with those reported in the literature.<sup>2</sup>

*1-Carboxy-1'-(methoxycarbonyl)ferrocene (Fc(COOH)(COOMe))*



A solution of NaOH in MeOH (4.72 mL, 2.8 M) was added to a solution of  $\text{Fc}(\text{COOMe})_2$  (3.63 g, 12.0 mmol) in acetone (150 mL) at rt over 5 min. The reaction was stirred for 18 h and then concentrated *in vacuo*. The crude residue was dissolved in water (200 mL) and the resultant solution acidified to pH 1 at 0 °C with concentrated HCl. The resulting precipitate was collected, washed with water ( $3 \times 50$  mL) and dried *in vacuo* to afford  $\text{Fc}(\text{COOH})(\text{COOMe})$  (3.15 g, 91%) as a yellow powder.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.88 (t, 4H,  $^3J = 1.7$  Hz,  $\text{H-2}$ ,  $\text{H-5}$ ,  $\text{H-b}$  and  $\text{H-e}$ ), 4.48 (t, 4H,  $^3J = 1.4$  Hz,  $\text{H-3}$ ,  $\text{H-4}$ ,  $\text{H-c}$  and  $\text{H-d}$ ), 3.84 (s, 3H,  $\text{CH}_3$ );  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  175.9 (C,  $\text{COOH}$ ), 170.9 (C,  $\text{COOCH}_3$ ), 73.5 ( $2 \times \text{CH}$ ,  $\text{C-2}$  and  $\text{C-5}$ ), 73.3 (C,  $\text{C-1}$ ), 73.1 ( $2 \times \text{CH}$ ,  $\text{C-b}$  and  $\text{C-e}$ ), 72.3 ( $2 \times \text{CH}$ ,  $\text{C-3}$  and  $\text{C-4}$ ), 72.1 ( $2 \times \text{CH}$ ,  $\text{C-c}$  and  $\text{C-d}$ ), 71.7 (C,  $\text{C-a}$ ), 51.9 ( $\text{CH}_3$ ,  $\text{COOCH}_3$ ); MS (ESI<sup>+</sup>):  $m/z = 310.9975$  [ $\text{M} + \text{Na}$ ]<sup>+</sup> ( $m_{\text{calc}} = 310.9977$ ). The spectroscopic data were in agreement with those reported in the literature.<sup>3</sup>

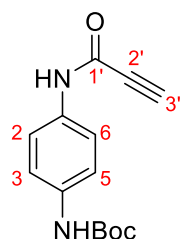
*tert-Butyl-(4-aminophenyl)carbamate (3)*



A solution of  $\text{Boc}_2\text{O}$  (10.1 g, 46 mmol) in  $\text{CH}_2\text{Cl}_2$  (100 mL) was added dropwise to a solution of *p*-phenylenediamine (10.0 g, 93 mmol) in  $\text{CH}_2\text{Cl}_2$  (200 mL) at 0 °C. The resultant solution was warmed to rt, stirred for 18 h and concentrated *in vacuo*. The crude residue was purified

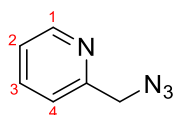
by flash chromatography (hexanes/EtOAc 2:1 → 1:1) to afford **3** (9.6 g, 99%) as an off-white solid.  $R_f$  0.36 (hexanes/EtOAc 2:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.12 (d, 2H,  $^3J = 8.2$  Hz, H-2 and H-6), 6.65-6.61 (m, 2H, H-3 and H-5), 6.27 (br s, 1H, NHCO), 3.53 (br s, 2H,  $\text{NH}_2$ ), 1.50 (s, 9H,  $\text{CO}_2\text{C}(\text{CH}_3)_3$ );  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  153.5 (C,  $\text{CO}_2\text{C}(\text{CH}_3)_3$ ), 142.5 (C, C-1), 129.9 (C, C-4), 121.1 ( $2 \times \text{CH}$ , C-2 and C-6), 115.7 ( $2 \times \text{CH}$ , C-3 and C-5), 80.1 (C,  $\text{CO}_2\text{C}(\text{CH}_3)_3$ ), 28.5 ( $3 \times \text{CH}_3$ ,  $\text{CO}_2\text{C}(\text{CH}_3)_3$ ); MS (ESI $^+$ ):  $m/z = 231.1105$  [ $\text{M} + \text{Na}$ ] $^+$  ( $m_{\text{calc}} = 231.1104$ ). The spectroscopic data were in agreement with those reported in the literature.<sup>4</sup>

*tert*-Butyl-(4-propiolamido)phenylcarbamate (**4**)



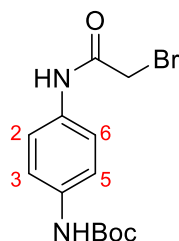
A solution of DIC (3.62 mL, 23.1 mmol) in  $\text{CH}_2\text{Cl}_2$  (150 mL) was added dropwise to a stirred suspension of propiolic acid (1.43 mL, 23.1 mmol) and **3** (4.01 g, 19.3 mmol) in  $\text{CH}_2\text{Cl}_2$  (80 mL) and DMF (20 mL) at 0 °C over 30 min. The reaction mixture was allowed to warm to rt and stirred for 24 h. The resultant solution was washed with saturated aqueous  $\text{NaHCO}_3$  (150 mL), water (150 mL) and brine (150 mL), dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated *in vacuo*. The crude residue was purified by flash chromatography (hexanes/EtOAc 3:2) to afford **4** (4.50 g, 90%) as a pale yellow solid.  $R_f$  0.47 (hexanes/EtOAc 3:2);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.54 (br s, 1H,  $\text{NHCOCCH}$ ), 7.45-7.42 (m, 2H, H-2 and H-6), 7.33 (d, 2H,  $^3J = 8.9$  Hz, H-3 and H-5), 6.49 (br s, 1H,  $\text{NHCO}_2\text{C}(\text{CH}_3)_3$ ), 2.91 (s, 1H, H-3'), 1.51 (s, 9H,  $\text{CO}_2\text{C}(\text{CH}_3)_3$ );  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  152.9 (C,  $\text{CO}_2\text{C}(\text{CH}_3)_3$ ), 149.6 (C, C-1'), 135.7 (C, C-1), 132.2 (C, C-4), 121.0 ( $2 \times \text{CH}$ , C-2 and C-6), 119.3 ( $2 \times \text{CH}$ , C-3 and C-5), 115.9 (CH, C-3'), 80.9 (C,  $\text{CO}_2\text{C}(\text{CH}_3)_3$ ), 74.1 (C, C-2'), 28.5 ( $3 \times \text{CH}_3$ ,  $\text{CO}_2\text{C}(\text{CH}_3)_3$ ); MS (ESI $^+$ ):  $m/z = 283.1050$  [ $\text{M} + \text{Na}$ ] $^+$  ( $m_{\text{calc}} = 283.1053$ ). The spectroscopic data were in agreement with those reported in the literature.<sup>5</sup>

## 2-(Azidomethyl)pyridine



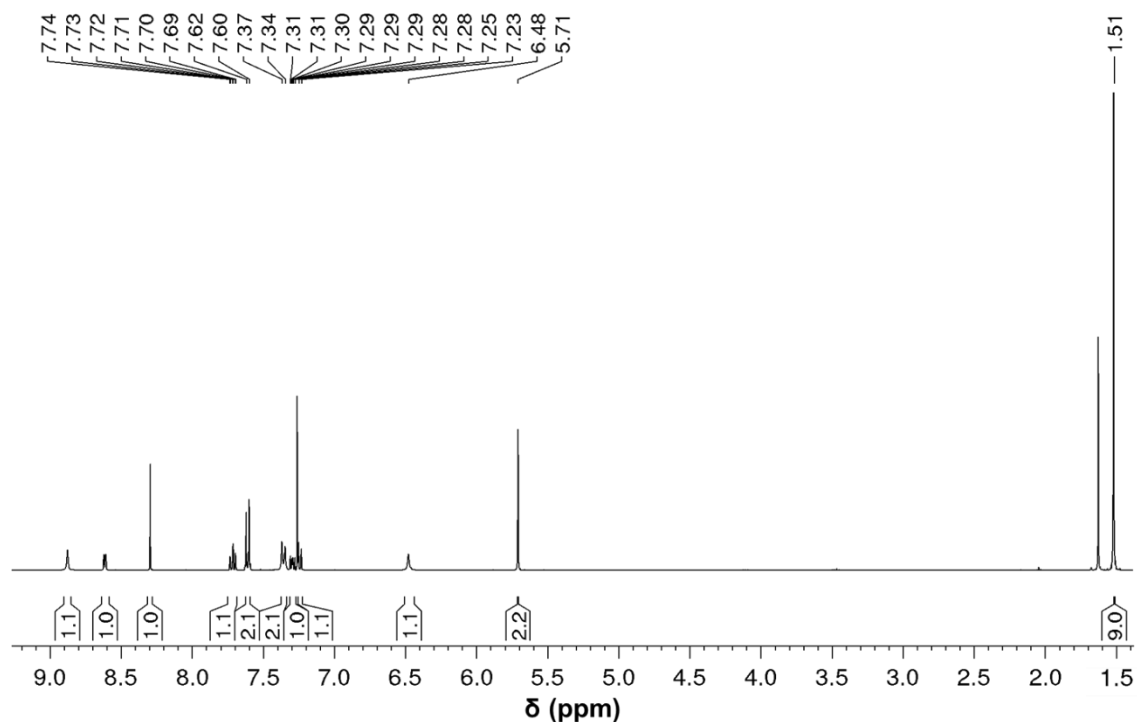
Sodium azide (3.11 g, 47.8 mmol) was added to a stirred solution of 2-(bromomethyl)pyridine hydrobromide (4.03 g, 15.9 mmol) in DMF (150 mL) and the reaction was stirred at 70 °C for 18 h. The reaction mixture was allowed to cool to rt, after which it was diluted with CH<sub>2</sub>Cl<sub>2</sub> (150 mL) and washed with water (5 × 100 mL). The organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated *in vacuo* to afford 2-(azidomethyl)pyridine (1.82 g, 85%) as a yellow oil which was used without further purification. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.60 (d, 1H, <sup>3</sup>J = 4.1 Hz, H-1), 7.71 (td, 1H, <sup>3</sup>J = 11.5 Hz, <sup>4</sup>J = 1.8 Hz, H-3), 7.34 (d, 1H, <sup>3</sup>J = 7.8 Hz, H-4), 7.24 (ddd, 1H, <sup>3</sup>J = 7.8 Hz, <sup>3</sup>J = 5.0 Hz, <sup>4</sup>J = 1.0 Hz, H-2), 4.49 (s, 2H, CH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 155.7 (C, C-5), 149.6 (CH, C-1), 137.0 (CH, C-3), 122.9 (CH, C-2), 122.0 (CH, C-4), 55.6 (CH<sub>2</sub>, CH<sub>2</sub>N<sub>3</sub>); MS (ESI<sup>+</sup>): *m/z* = 157.0480 [M + Na]<sup>+</sup> (*m*<sub>calc</sub> = 157.0485). The spectroscopic data were in agreement with those reported in the literature.<sup>6</sup>

## *tert*-Butyl-4-(2-bromoacetamido)phenylcarbamate (**7**)

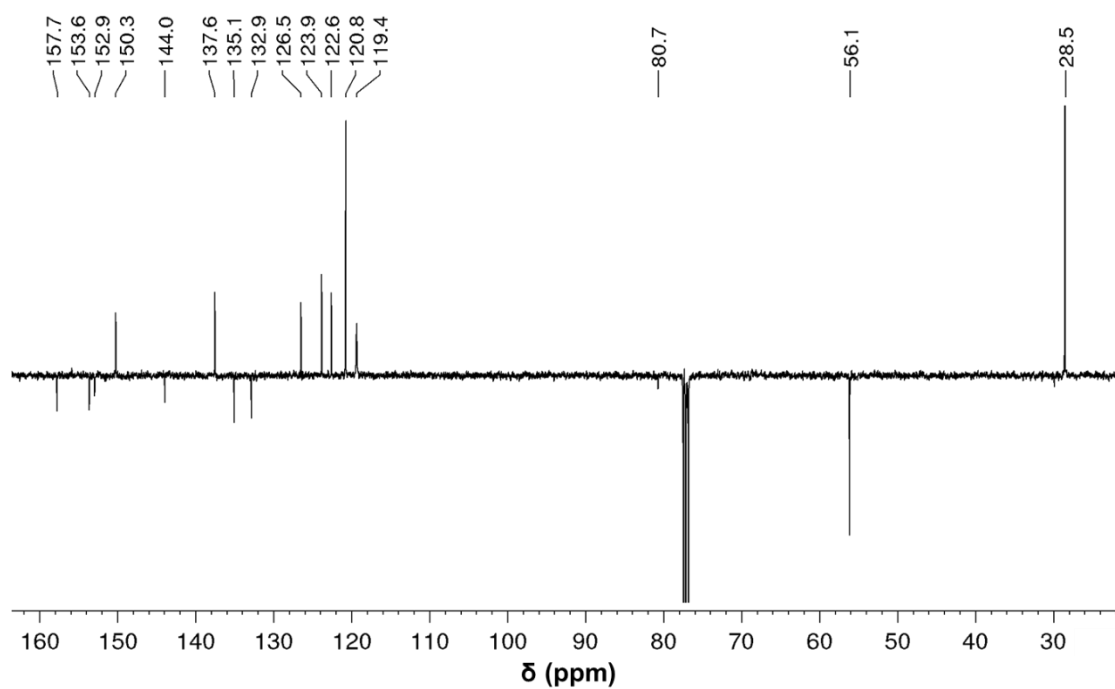


A solution of DIC (0.7 mL, 4.49 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (60 mL) was added dropwise to a stirred suspension of bromoacetic acid (0.62 g, 4.49 mmol) and **3** (0.85 g, 4.08 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 mL) at 0 °C over 30 min. The reaction mixture was allowed to warm to rt, stirred for 18 h and concentrated *in vacuo*. The crude residue was purified by flash chromatography (EtOAc) to afford **7** (1.22 g, 91%) as a white powder. *R*<sub>f</sub> 0.68 (hexanes/EtOAc 1:1); <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD): δ 7.48-7.44 (m, 2H, H-2 and H-6), 7.36 (d, 2H, <sup>3</sup>J = 9.0 Hz, H-3 and H-5), 3.95 (s, 2H, CH<sub>2</sub>), 1.51 (s, 9H, CO<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>OD): δ 167.4 (C, COCH<sub>2</sub>Br), 155.3 (C, CO<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>), 137.4 (C, C-1), 134.3 (C, C-4), 121.8 (2 × CH, C-2 and C-6), 120.2 (2 × CH, C-3 and C-5), 80.8 (C, CO<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>), 29.7 (CH<sub>2</sub>, COCH<sub>2</sub>Br), 28.7 (3 × CH<sub>3</sub>, CO<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>); MS (ESI<sup>+</sup>): *m/z* = 351.0312 [M + Na]<sup>+</sup> (*m*<sub>calc</sub> = 351.0315). The spectroscopic data were in agreement with those reported in the literature.<sup>7</sup>

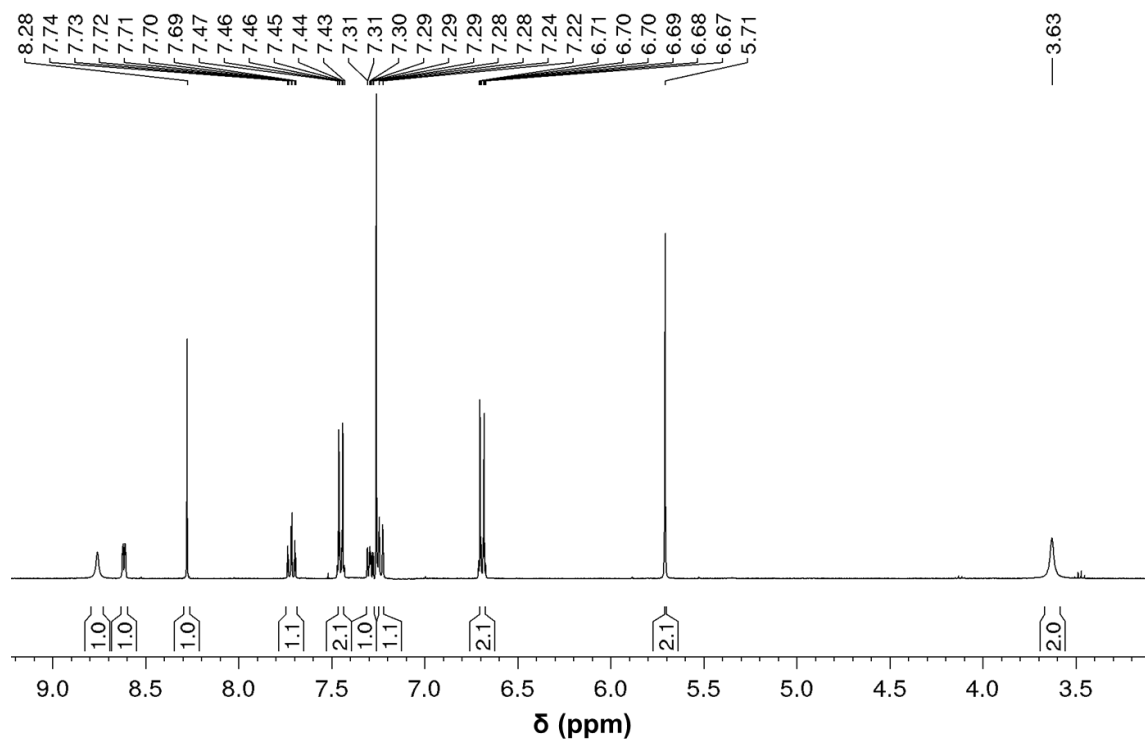
## $^1\text{H}$ and $^{13}\text{C}\{^1\text{H}\}$ DEPTQ NMR spectra



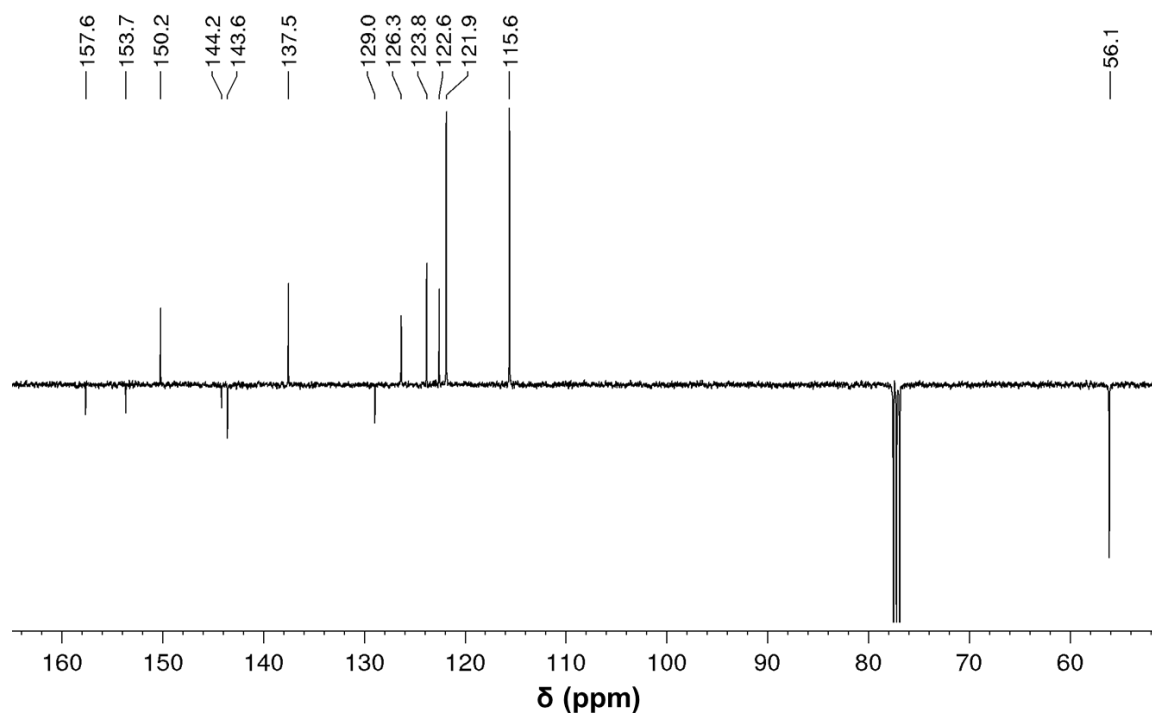
**Figure S1.**  $^1\text{H}$  NMR spectrum of *tert*-butyl-4-(*N*-1-(2-pyridinylmethyl)-1*H*-1,2,3-triazole-4-carboxamide)phenylcarbamate (**5**) measured in  $\text{CDCl}_3$ .



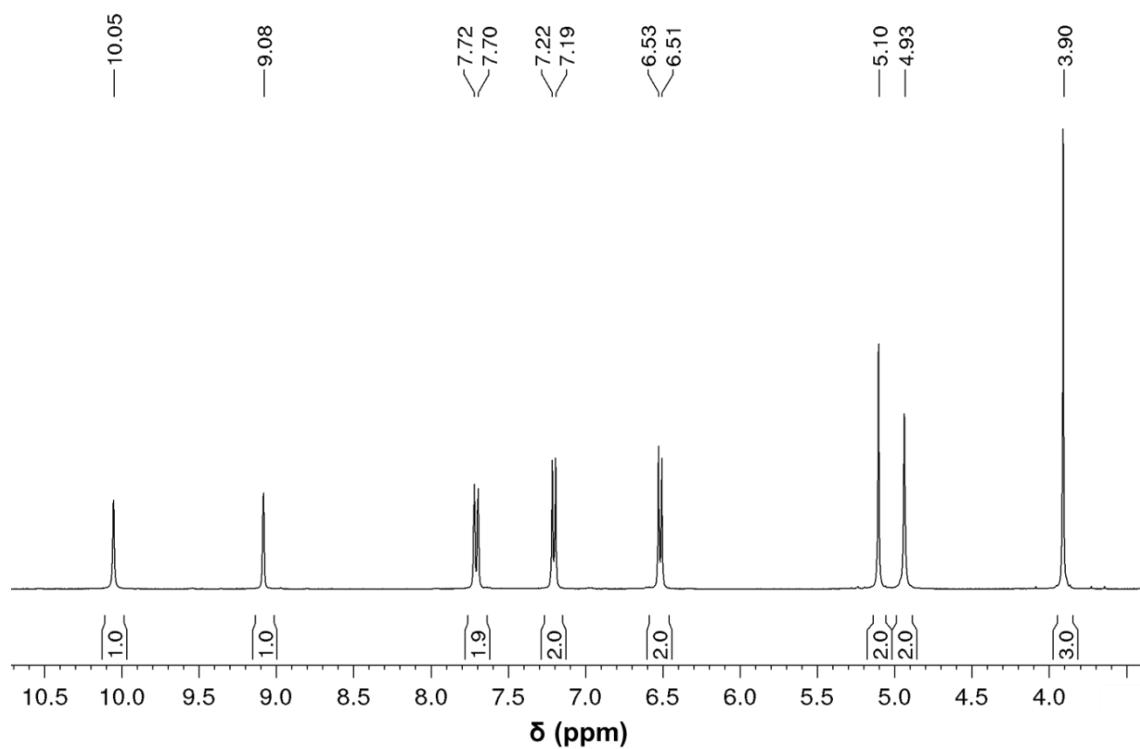
**Figure S2.**  $^{13}\text{C}\{^1\text{H}\}$  DEPTQ NMR spectrum of *tert*-butyl-4-(*N*-1-(2-pyridinylmethyl)-1*H*-1,2,3-triazole-4-carboxamide)phenylcarbamate (**5**) measured in  $\text{CDCl}_3$ .



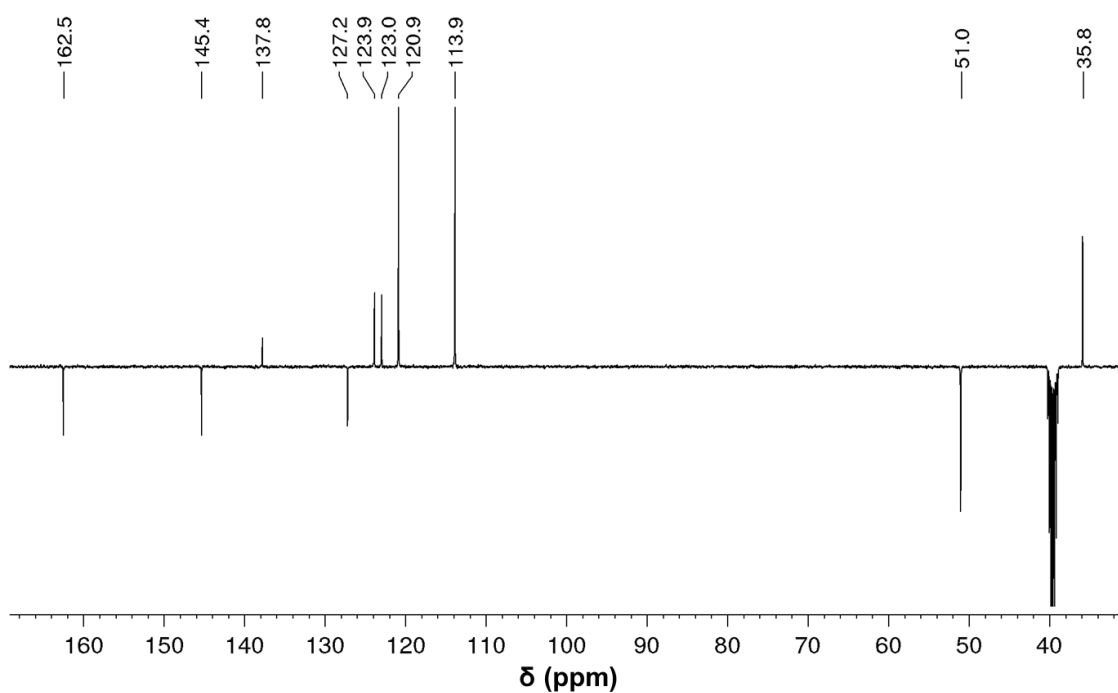
**Figure S3.**  $^1\text{H}$  NMR spectrum of *N*-(4-aminophenyl)-1-(2-pyridinylmethyl)-1*H*-1,2,3-triazole-4-carboxamide (**6**) measured in  $\text{CDCl}_3$ .



**Figure S4.**  $^{13}\text{C}\{^1\text{H}\}$  DEPTQ NMR spectrum of *N*-(4-aminophenyl)-1-(2-pyridinylmethyl)-1*H*-1,2,3-triazole-4-carboxamide (**6**) measured in  $\text{CDCl}_3$ .

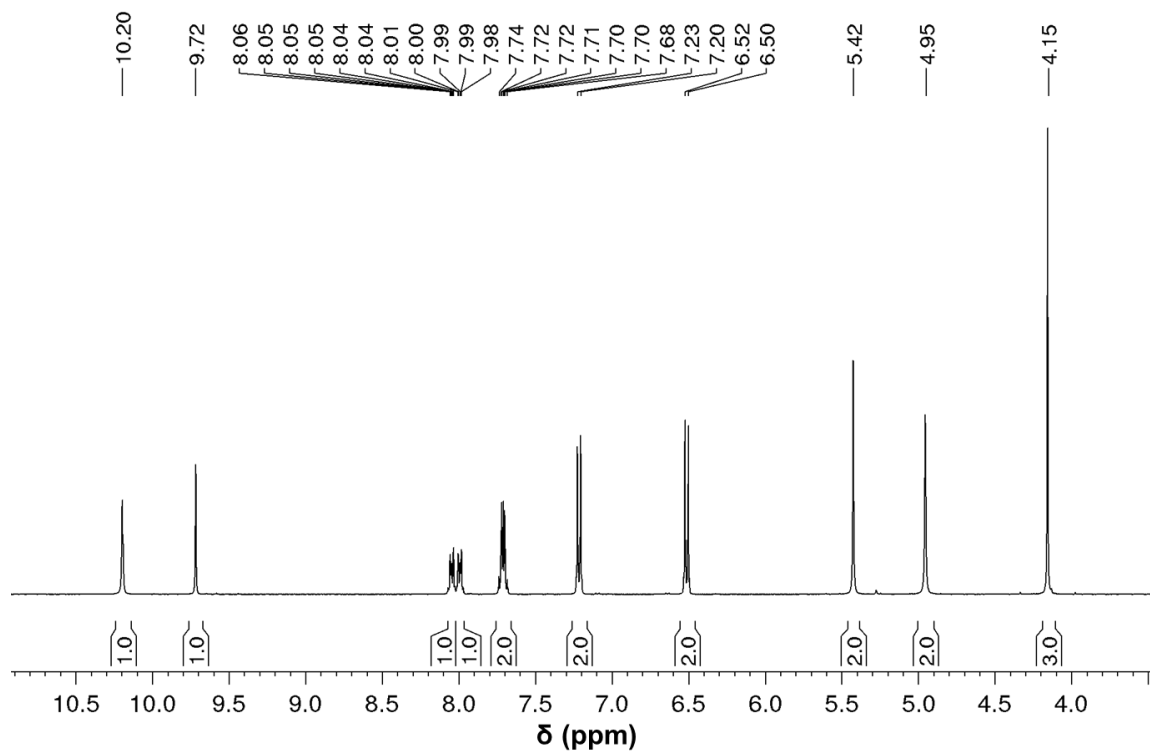


**Figure S5.**  $^1\text{H}$  NMR spectrum of *N*-(4-aminophenyl)-3-methyl-1*H*-imidazole-1-acetamide (**8a**) measured in  $(\text{CD}_3)_2\text{SO}$ .

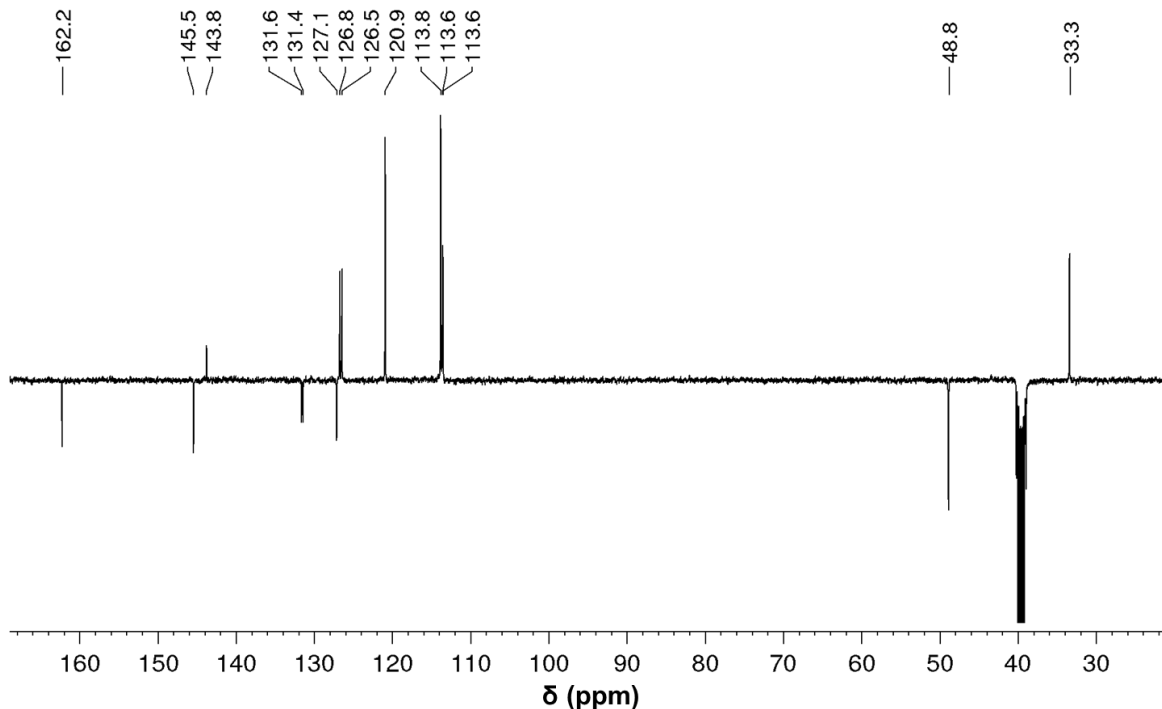


**Figure S6.**  $^{13}\text{C}\{^1\text{H}\}$  DEPTQ NMR spectrum of *N*-(4-aminophenyl)-3-methyl-1*H*-imidazole-1-acetamide (**8a**) measured in  $(\text{CD}_3)_2\text{SO}$ .

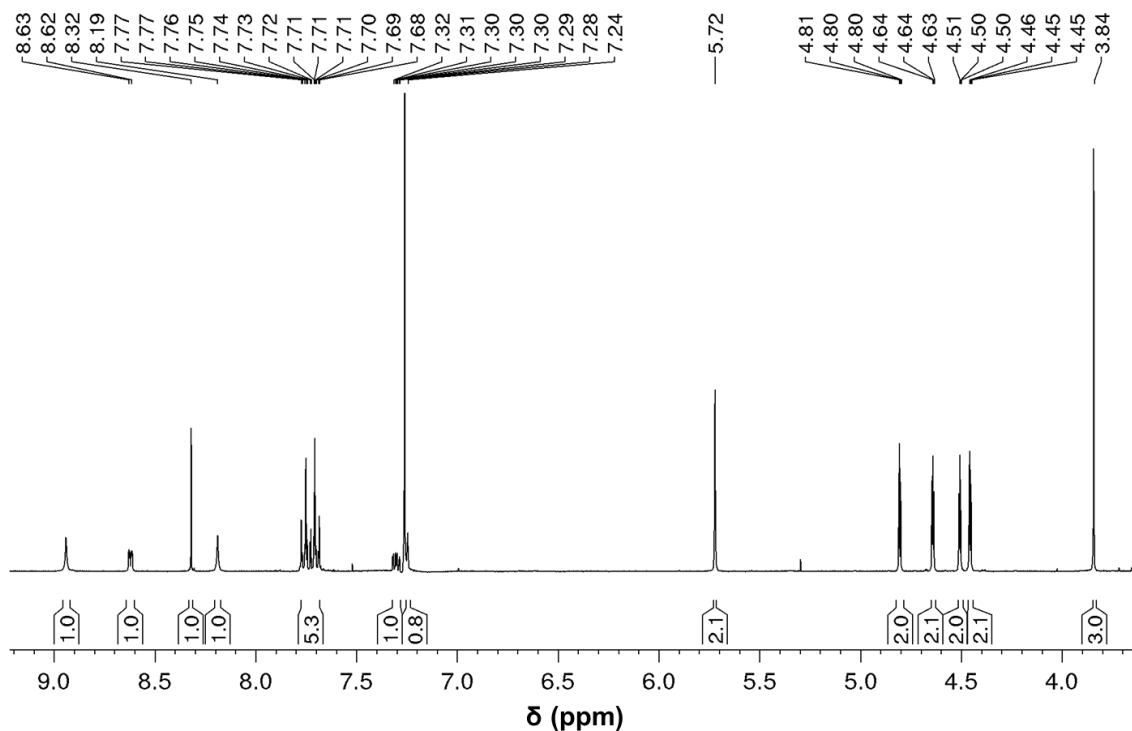




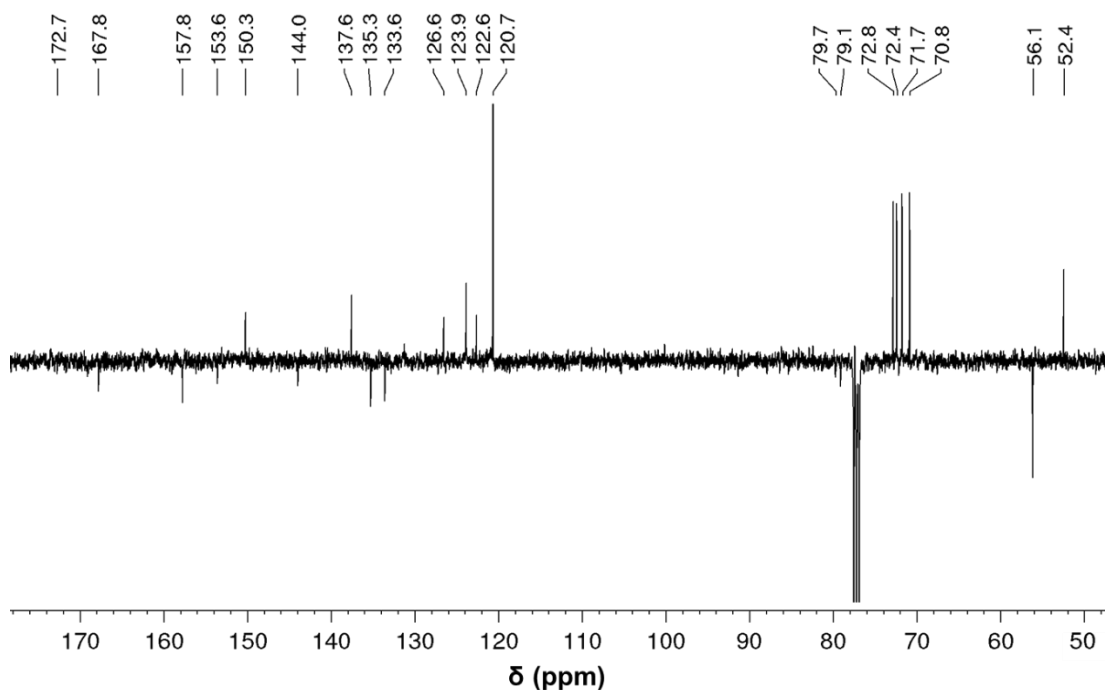
**Figure S7.**  $^1\text{H}$  NMR spectrum of *N*-(4-aminophenyl)-3-methyl-1*H*-benzimidazole-1-acetamide (**8b**) measured in  $(\text{CD}_3)_2\text{SO}$ .



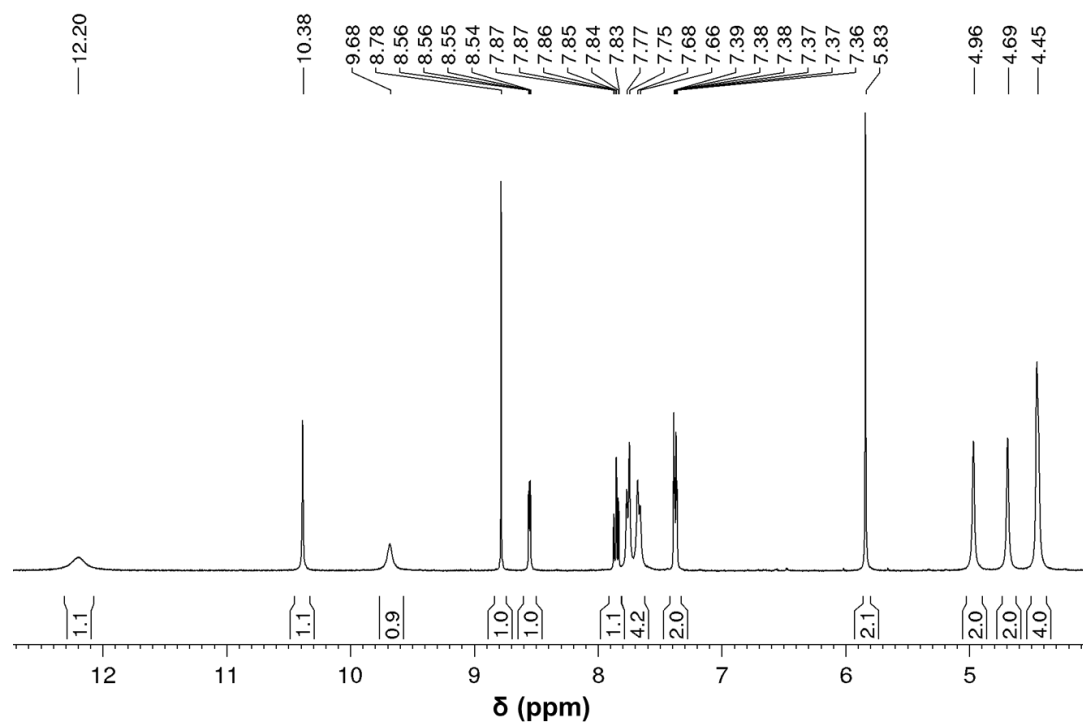
**Figure S8.**  $^{13}\text{C}\{^1\text{H}\}$  DEPTQ NMR spectrum of *N*-(4-aminophenyl)-3-methyl-1*H*-benzimidazole-1-acetamide (**8b**) measured in  $(\text{CD}_3)_2\text{SO}$ .



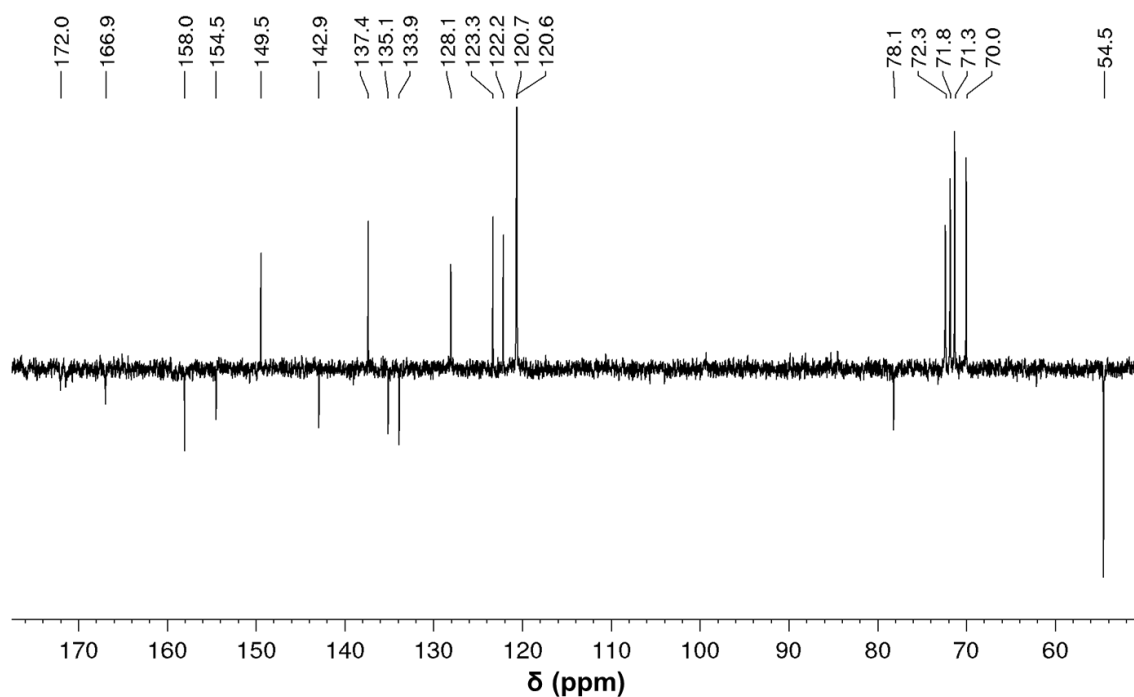
**Figure S9.**  $^1\text{H}$  NMR spectrum of 1-[[*N*-1-(2-pyridinylmethyl)-1*H*-1,2,3-triazole-4-carboxamide)-4-aminophenyl]carbonyl]-1'-(methoxycarbonyl)ferrocene (**9**) measured in  $\text{CDCl}_3$ .



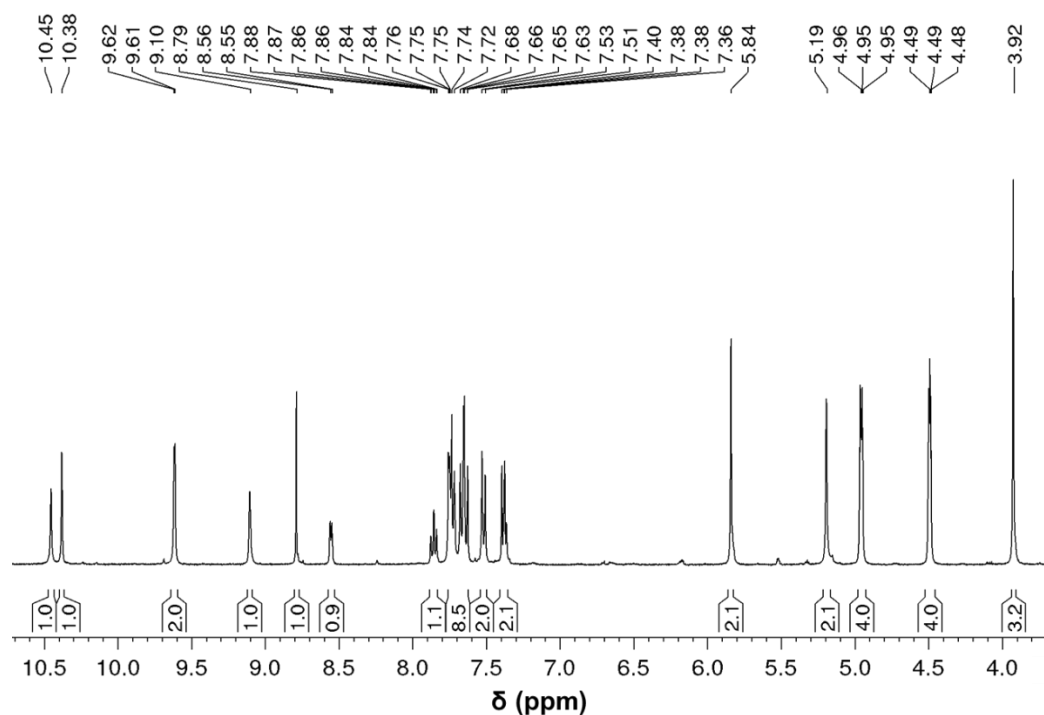
**Figure S10.**  $^{13}\text{C}\{^1\text{H}\}$  DEPTQ NMR spectrum of 1-[[*N*-1-(2-pyridinylmethyl)-1*H*-1,2,3-triazole-4-carboxamide)-4-aminophenyl]carbonyl]-1'-(methoxycarbonyl)ferrocene (**9**) measured in  $\text{CDCl}_3$ .



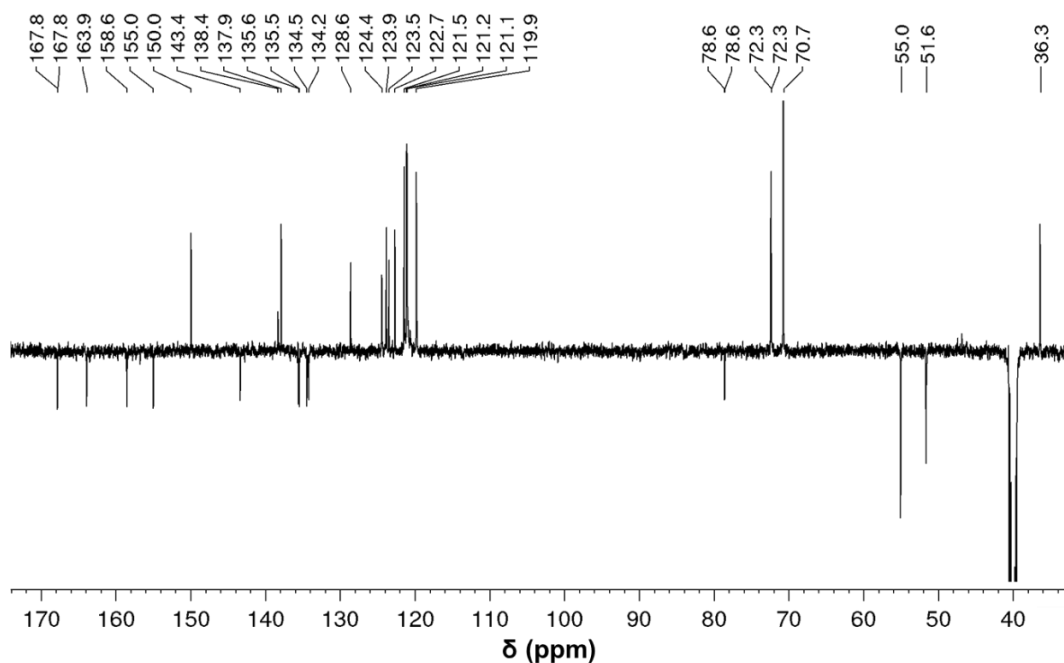
**Figure S11.**  $^1\text{H}$  NMR spectrum of 1-[[*N*-1-(2-pyridinylmethyl)-1*H*-1,2,3-triazole-4-carboxamide)-4-aminophenyl]carbonyl]-1'-(carboxy)ferrocene (**10**) measured in  $(\text{CD}_3)_2\text{SO}$ .



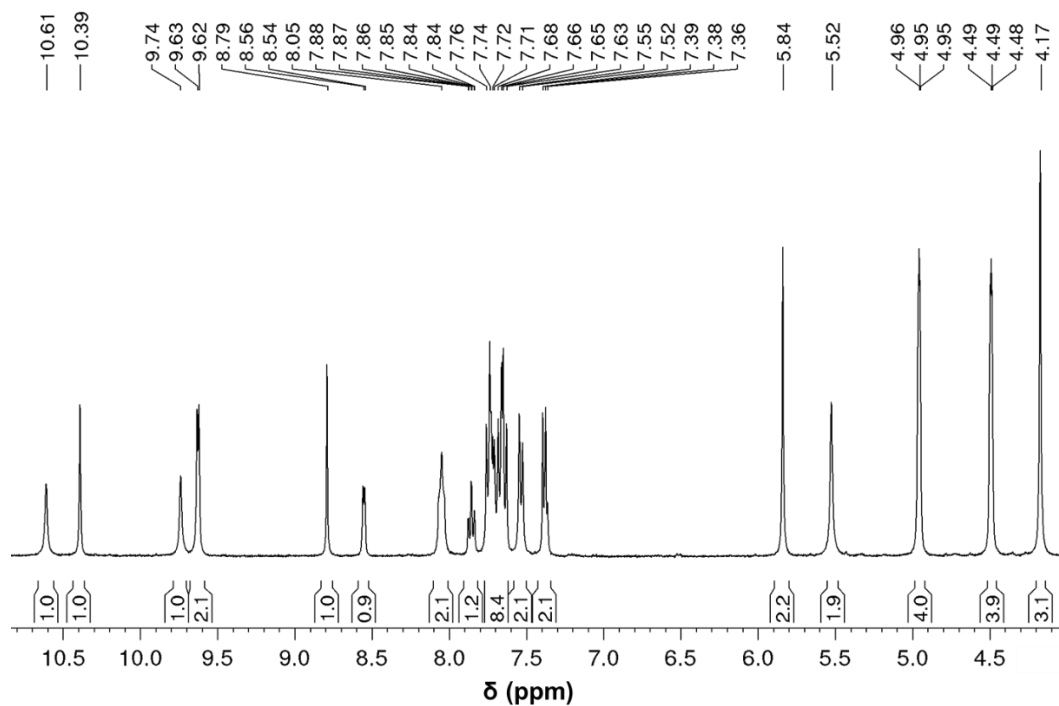
**Figure S12.**  $^{13}\text{C}\{^1\text{H}\}$  DEPTQ NMR spectrum of 1-[[*N*-1-(2-pyridinylmethyl)-1*H*-1,2,3-triazole-4-carboxamide)-4-aminophenyl]carbonyl]-1'-(carboxy)ferrocene (**10**) measured in  $(\text{CD}_3)_2\text{SO}$ .



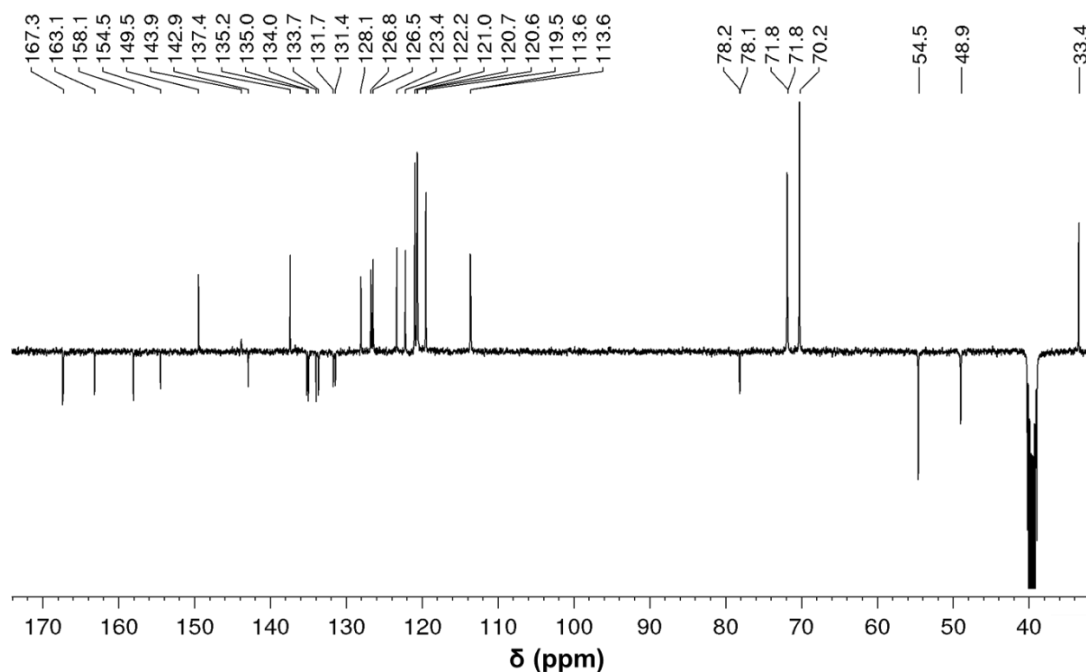
**Figure S13.**  $^1\text{H}$  NMR spectrum of 1-[[*N*-1-(2-pyridinylmethyl)-1*H*-1,2,3-triazole-4-carboxamide)-4-aminophenyl]carbonyl]-1'-[[*N*-3-methyl-1*H*-imidazolium-1-acetamide)-4-aminophenyl]carbonyl]ferrocene hexafluorophosphate (**11a**) measured in  $(\text{CD}_3)_2\text{SO}$ .



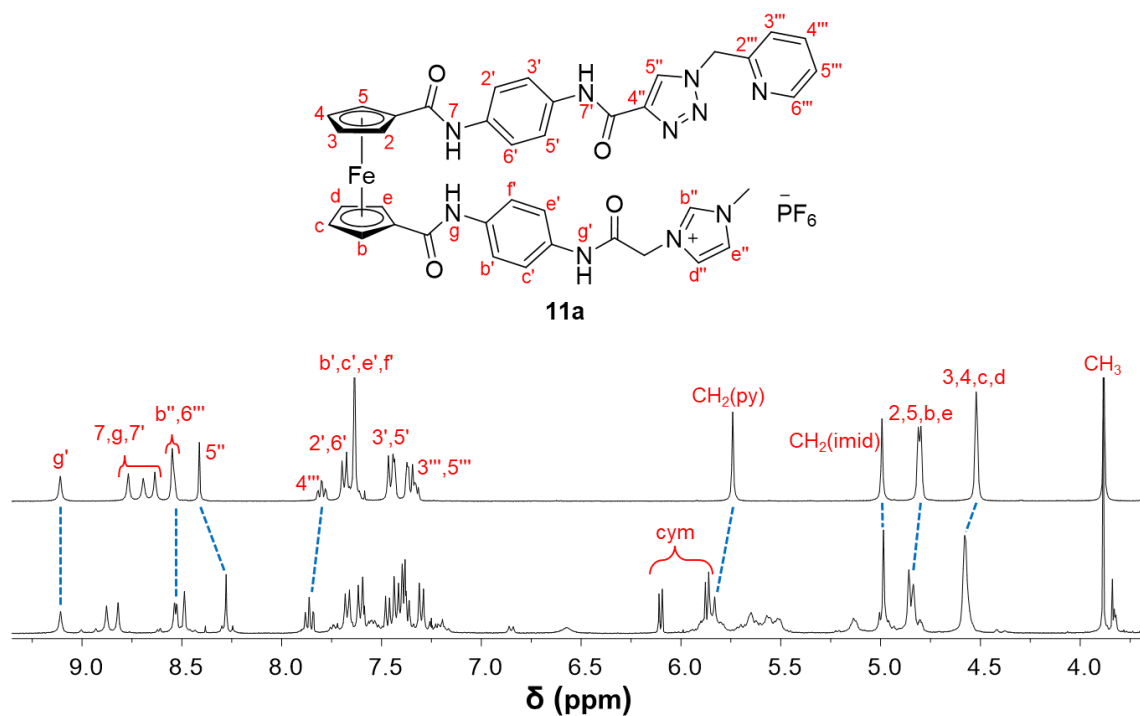
**Figure S14.**  $^{13}\text{C}\{^1\text{H}\}$  DEPTQ NMR spectrum of 1-[[*N*-1-(2-pyridinylmethyl)-1*H*-1,2,3-triazole-4-carboxamide)-4-aminophenyl]carbonyl]-1'-[[*N*-3-methyl-1*H*-imidazolium-1-acetamide)-4-aminophenyl]carbonyl]ferrocene hexafluorophosphate (**11a**) measured in  $(\text{CD}_3)_2\text{SO}$ .



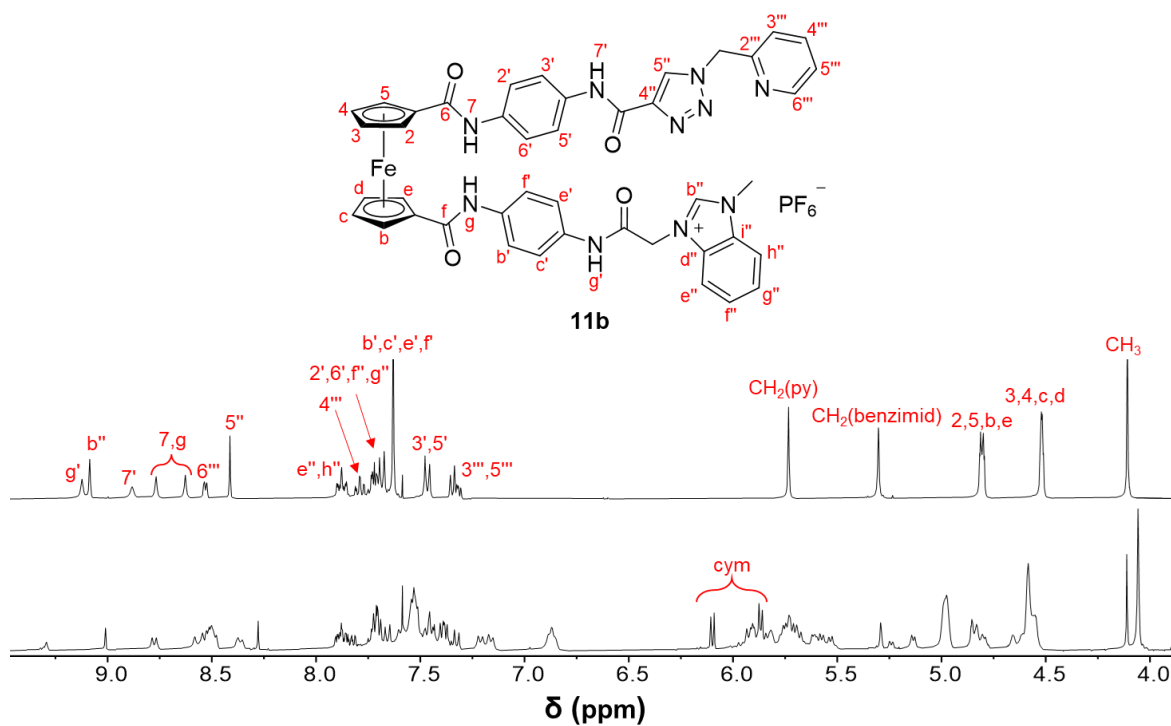
**Figure S15.**  $^1\text{H}$  NMR spectrum of 1-[[*N*-1-(2-pyridinylmethyl)-1*H*-1,2,3-triazole-4-carboxamide)-4-aminophenyl]carbonyl]-1'-[[*N*-3-methyl-1*H*-benzimidazolium-1-acetamide)-4-aminophenyl]carbonyl]ferrocene hexafluorophosphate (**11b**) measured in  $(\text{CD}_3)_2\text{SO}$ .



**Figure S16.**  $^{13}\text{C}\{^1\text{H}\}$  DEPTQ NMR spectrum of 1-[[*N*-1-(2-pyridinylmethyl)-1*H*-1,2,3-triazole-4-carboxamide)-4-aminophenyl]carbonyl]-1'-[[*N*-3-methyl-1*H*-benzimidazolium-1-acetamide)-4-aminophenyl]carbonyl]ferrocene hexafluorophosphate (**11b**) measured in  $(\text{CD}_3)_2\text{SO}$ .

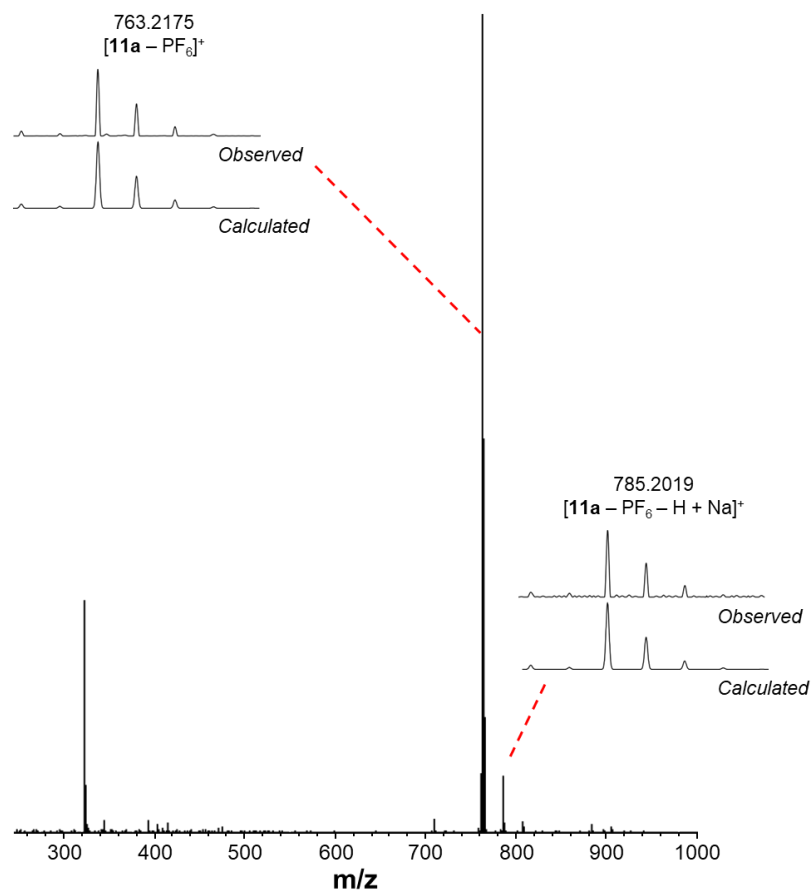


**Figure S17.** Stacked  $^1\text{H}$  NMR spectra of **11a** (top) and crude **12a** (bottom) measured in  $\text{CD}_3\text{CN}$ .

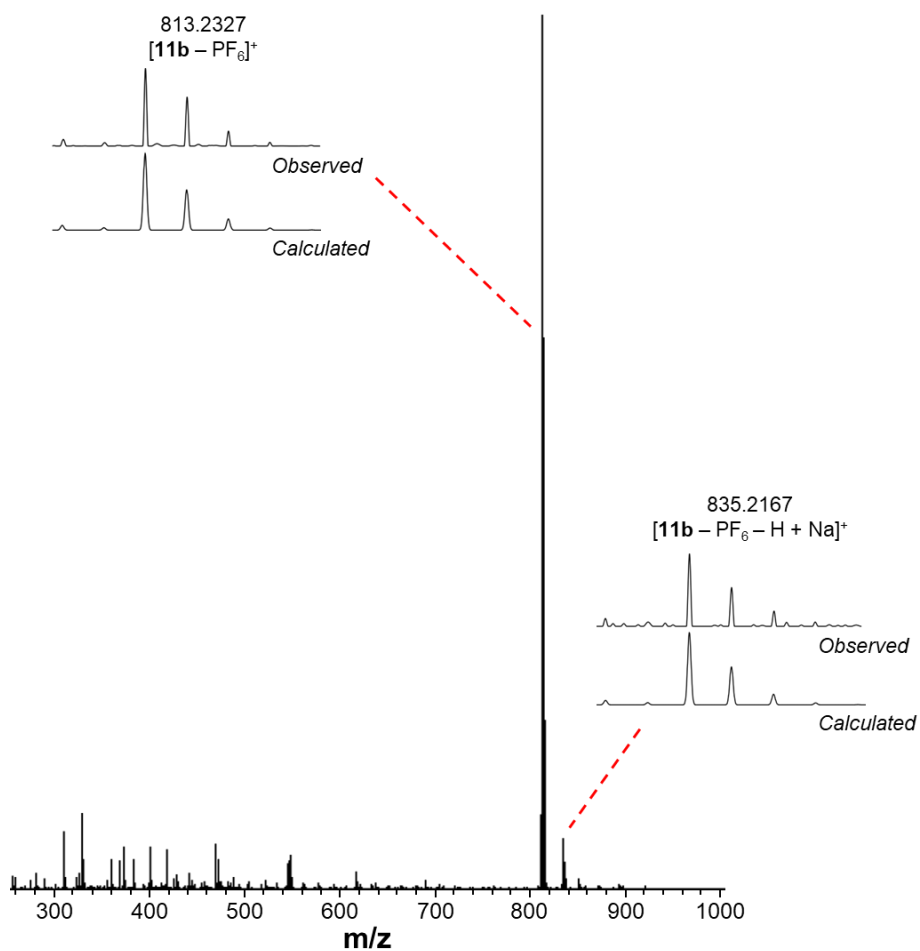


**Figure S18.** Stacked  $^1\text{H}$  NMR spectra of **11b** (top) and crude **12b** (bottom) measured in  $\text{CD}_3\text{CN}$ .

## ESI-mass spectra

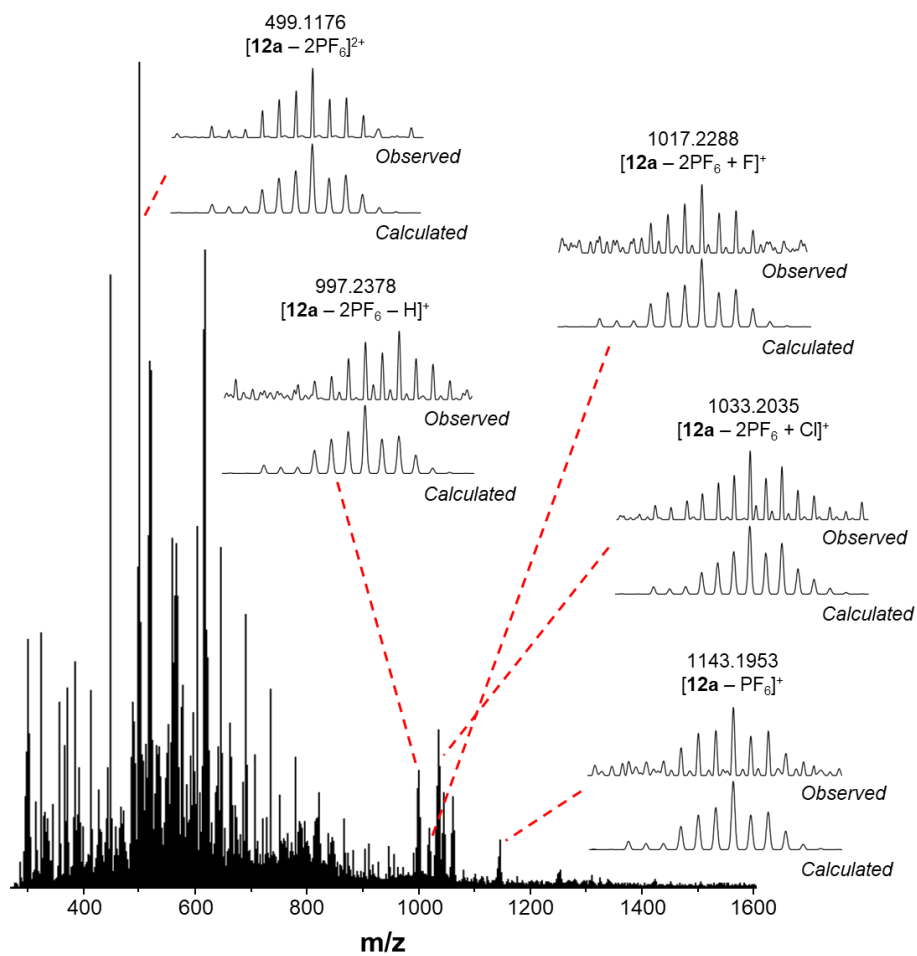


**Figure S19.** ESI-MS of **11a** highlighting the observed isotope pattern compared to calculated for the main peaks.

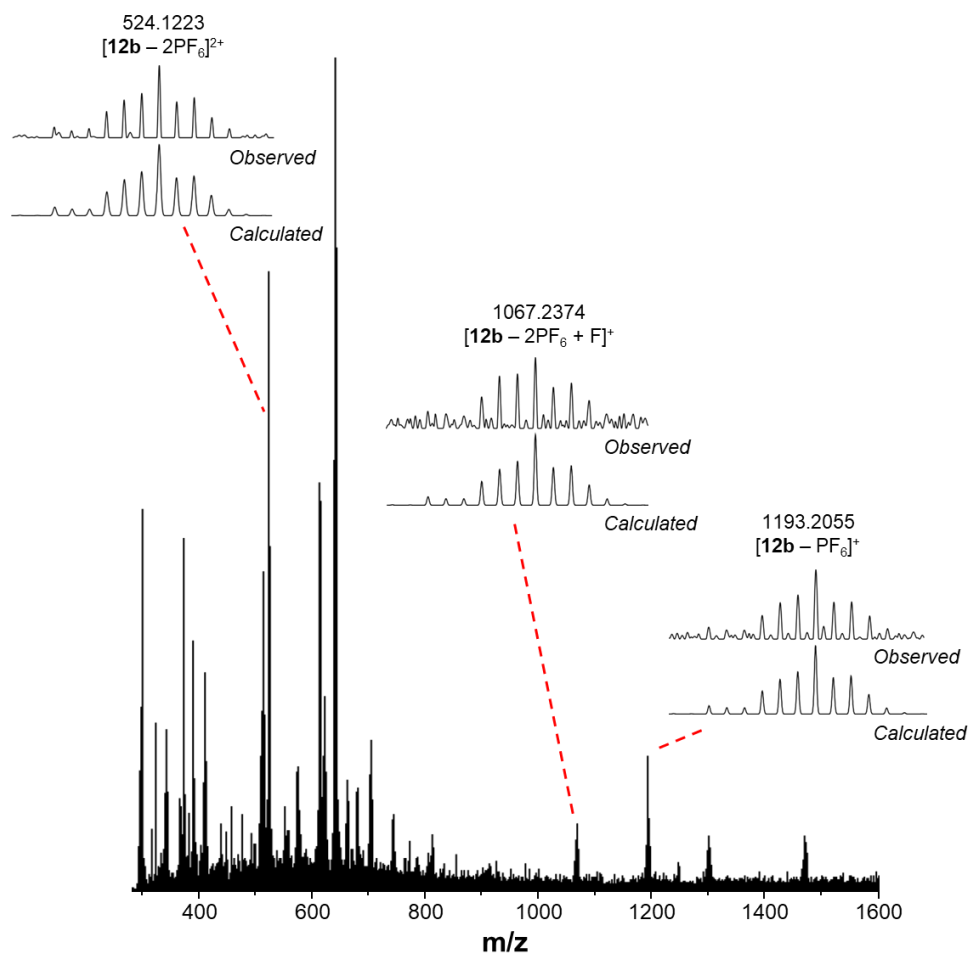


**Figure S20.** ESI-MS of **11b** highlighting the observed isotope pattern compared to calculated for the main peaks.





**Figure S21.** ESI-MS of a crude sample of **12a** highlighting the observed isotope pattern compared to calculated for the main peaks.



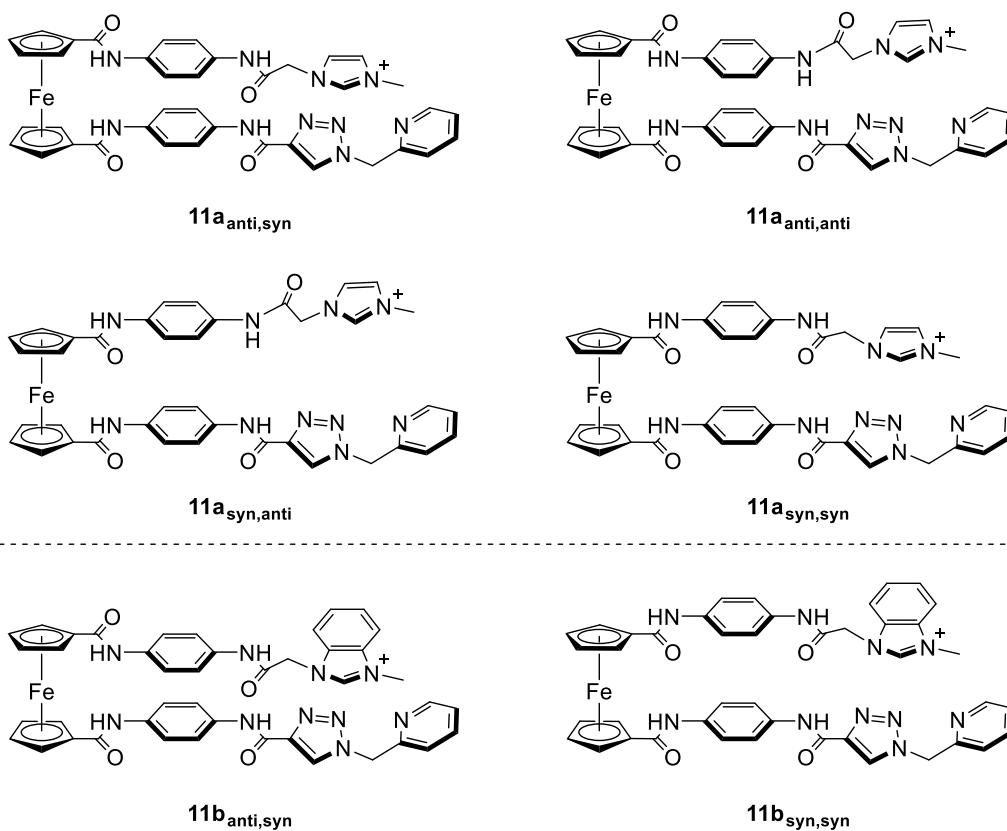
**Figure S22.** ESI-MS of a crude sample of **12b** highlighting the observed isotope pattern compared to calculated for the main peaks.

## DFT calculations

**Table S1.** Energy differences ( $\Delta E$ ) between various configurations of amide bonds in **11a** and **11b** relative to the lowest energy structures (**11a<sub>anti,syn</sub>** and **11b<sub>anti,syn</sub>**).

Configuration <sup>a</sup>	$\Delta E$ (kJ mol <sup>-1</sup> )
<b>11a<sub>anti,syn</sub></b>	-
<b>11a<sub>anti,anti</sub></b>	+10.73
<b>11a<sub>syn,anti</sub></b>	+26.41
<b>11a<sub>syn,syn</sub></b>	+35.45
<hr/>	
<b>11b<sub>anti,syn</sub></b>	-
<b>11b<sub>syn,syn</sub></b>	+27.33

Configurations not listed failed when running DFT calculations and were assumed to be unstable. Configurations of amide groups read from the ferrocene moiety to pyrti/NHC rings as shown in Figure S22.



**Figure S23.** Possible amide conformations of **11a** and **11b** calculated by DFT.

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