

## L-Proline Catalyzed Reaction of N-confused Porphyrin and Active Methylene Compounds

Bin Liu,<sup>1</sup> Xiaofang Li\*,<sup>1</sup> Jie Zhang,<sup>1</sup> Piotr J. Chmielewski\*,<sup>2</sup>

<sup>1</sup> Key Laboratory of Theoretical Chemistry and Molecular Simulation of Ministry of Education, Hunan Province College Key Laboratory of QSAR/QSPR, School of Chemistry and Chemical Engineering, Hunan University of Science and Technology, Xiangtan, Hunan 411201, China, E-mail: lixiaofang@iccas.ac.cn

<sup>2</sup> Department of Chemistry, University of Wrocław, 14 F. Joliot-Curie Street, 50 383 Wrocław, Poland, E-mail: piotr.chmielewski@chem.uni.wroc.pl

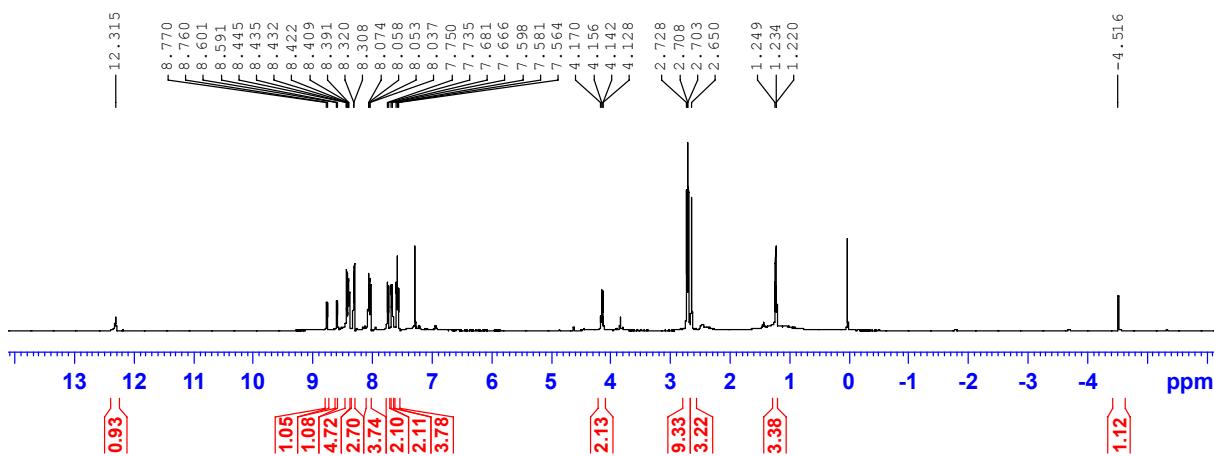
\*E-mail: lixiaofang@iccas.ac.cn; piotr.chmielewski@chem.uni.wroc.pl.

## Supporting Information

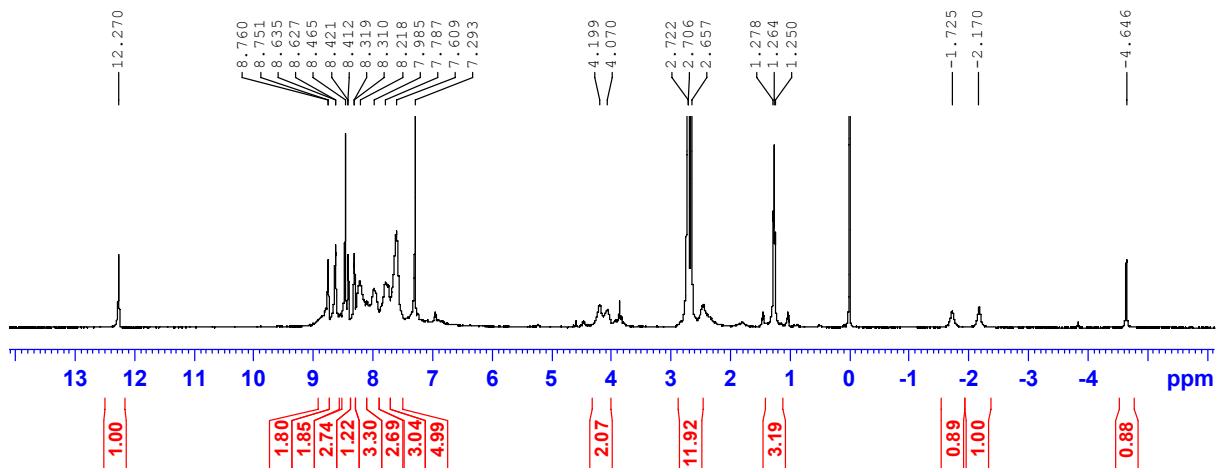
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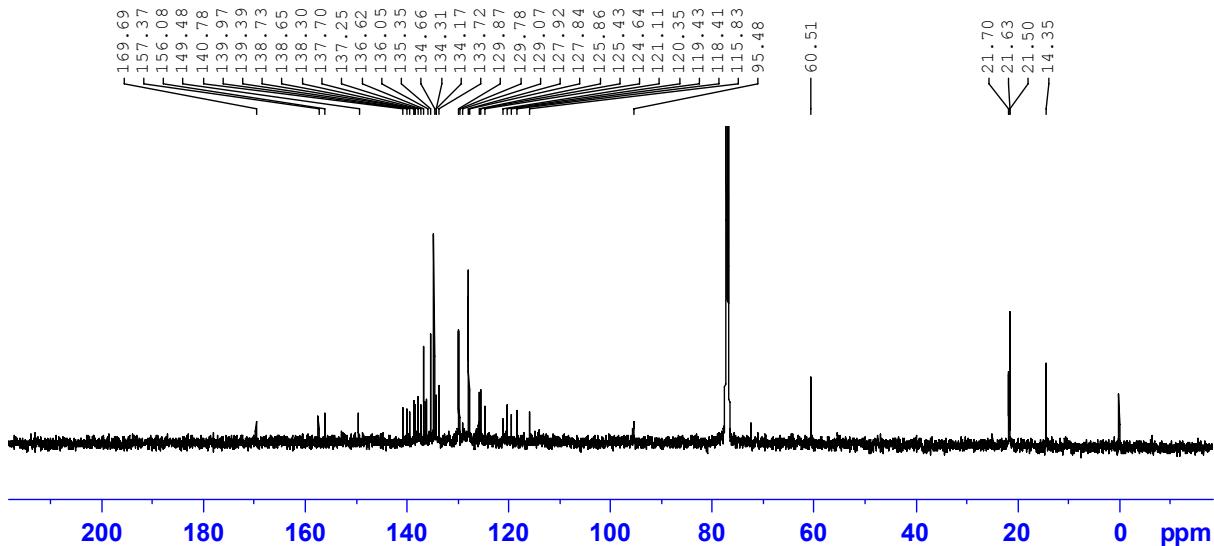
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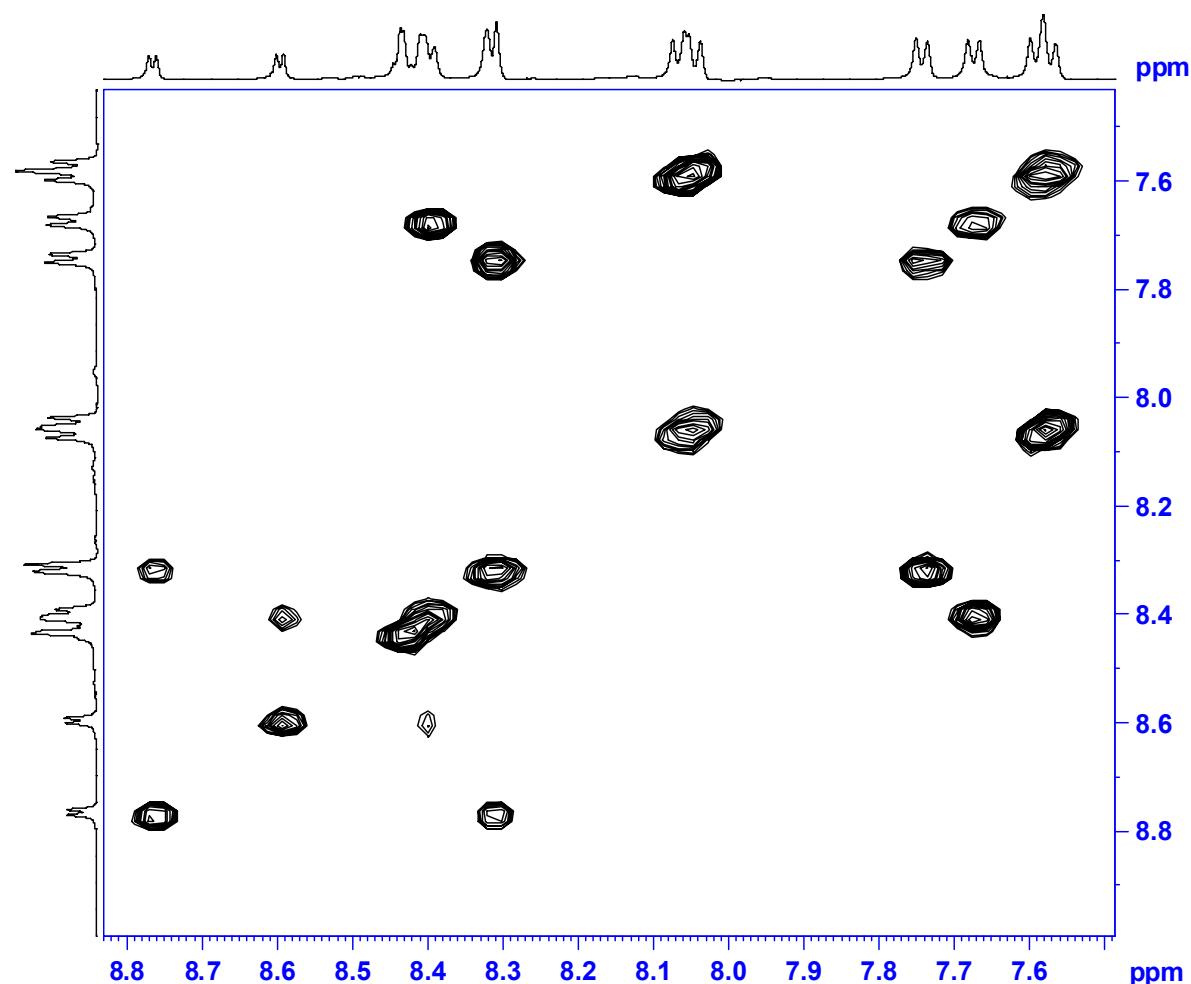
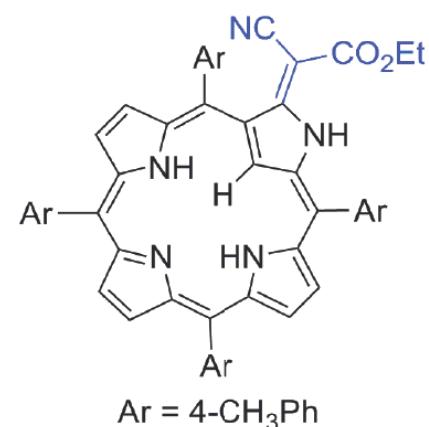
**Figure S1.**  $^1\text{H}$  NMR spectrum of **3a**, 298 K,  $\text{CDCl}_3$ .



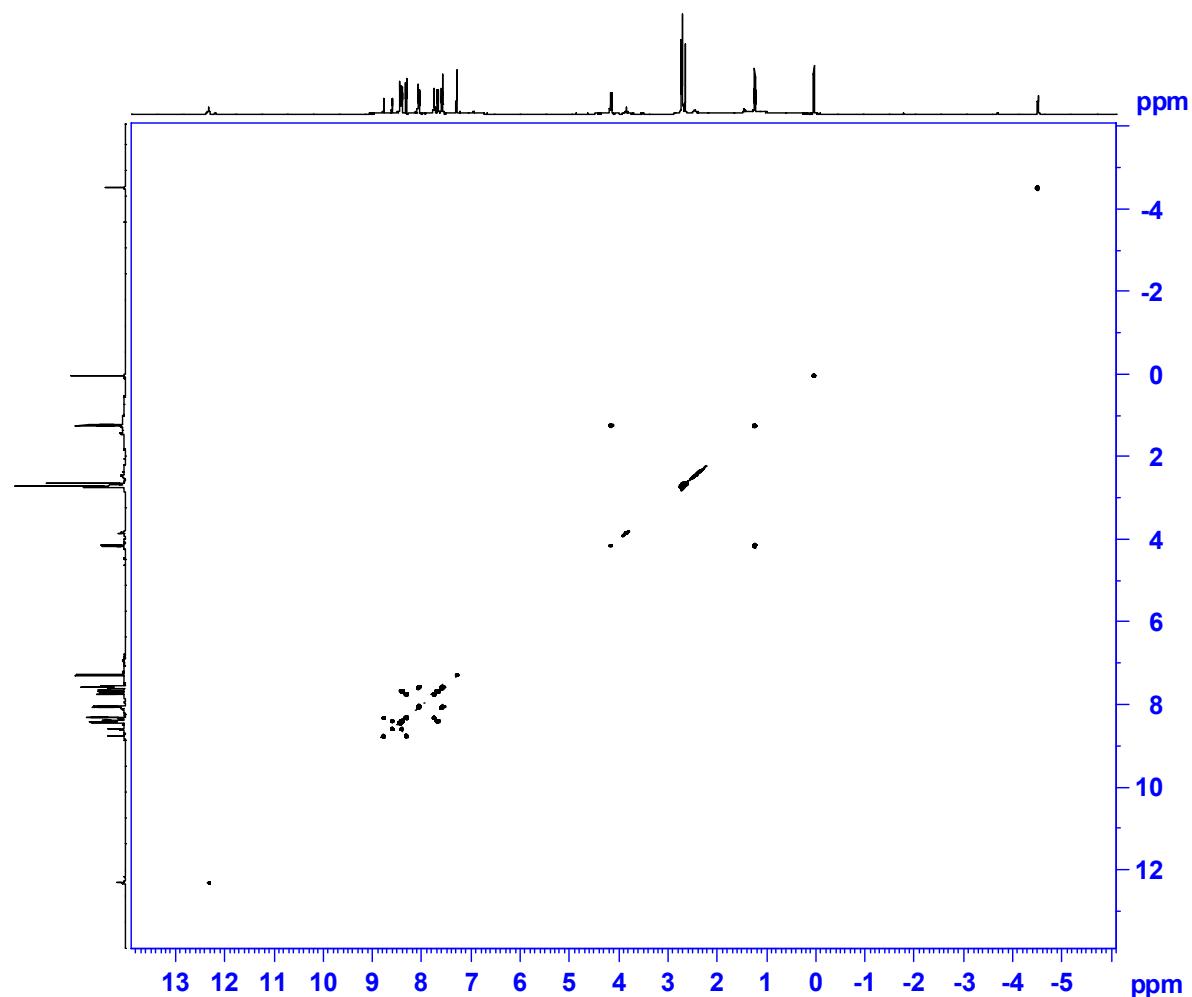
**Figure S2.**  $^1\text{H}$  NMR spectrum of **3a**, 235 K,  $\text{CDCl}_3$ .



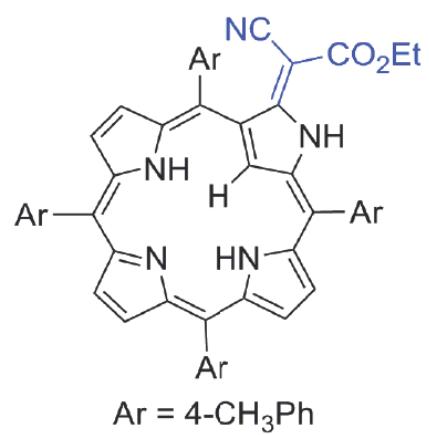
**Figure S3.**  $^{13}\text{C}$  NMR spectrum of **3a**, 298 K,  $\text{CDCl}_3$ .

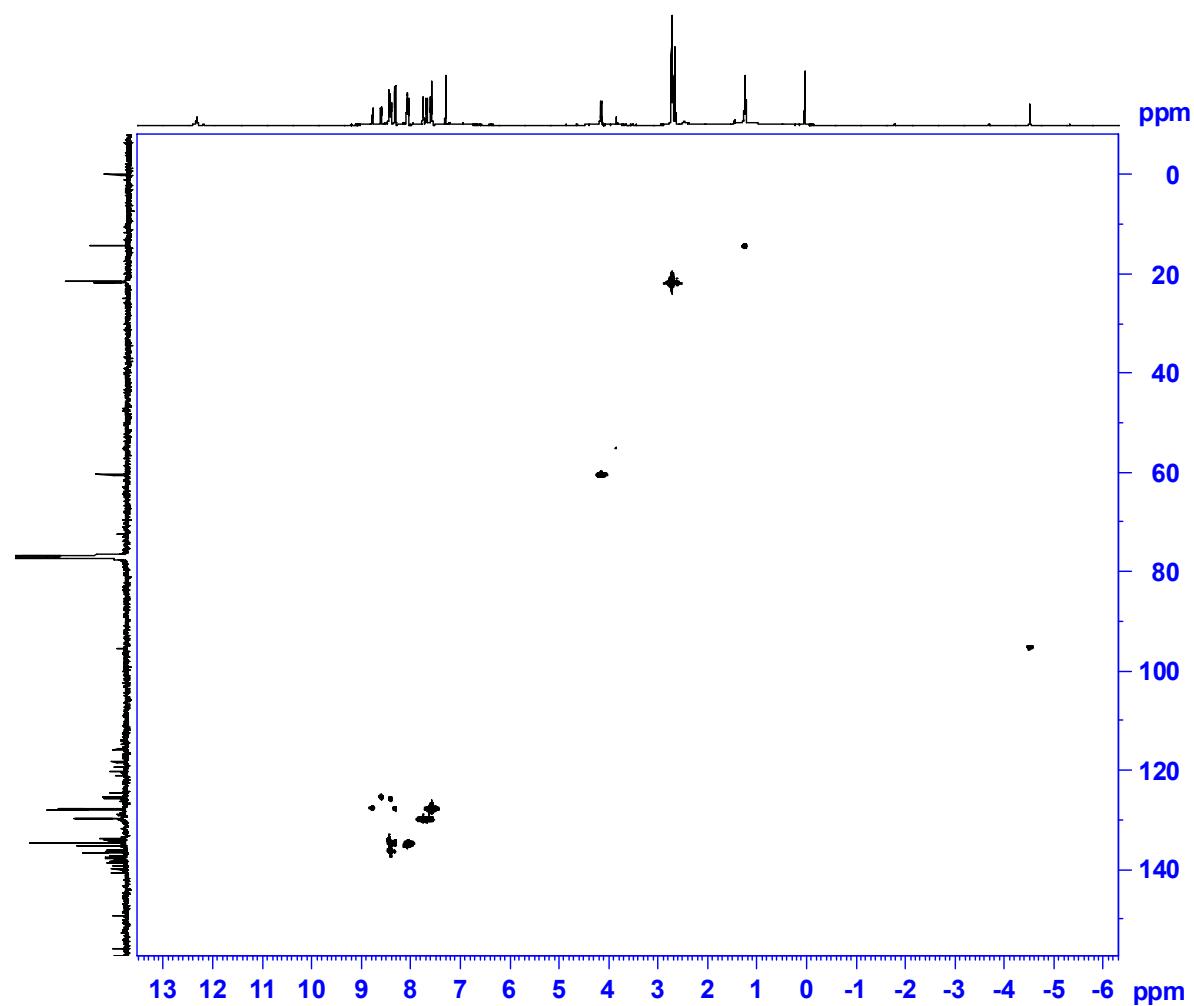


**Figure S4.** COSY spectrum of **3a** (low-field part).

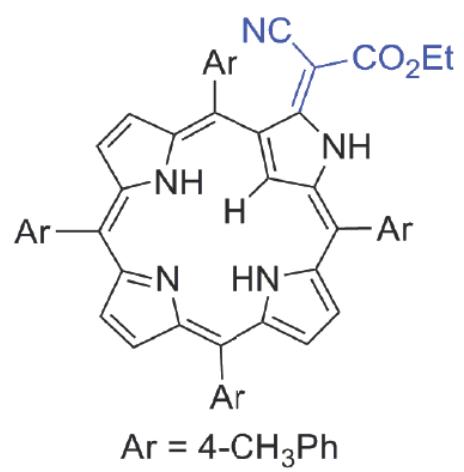


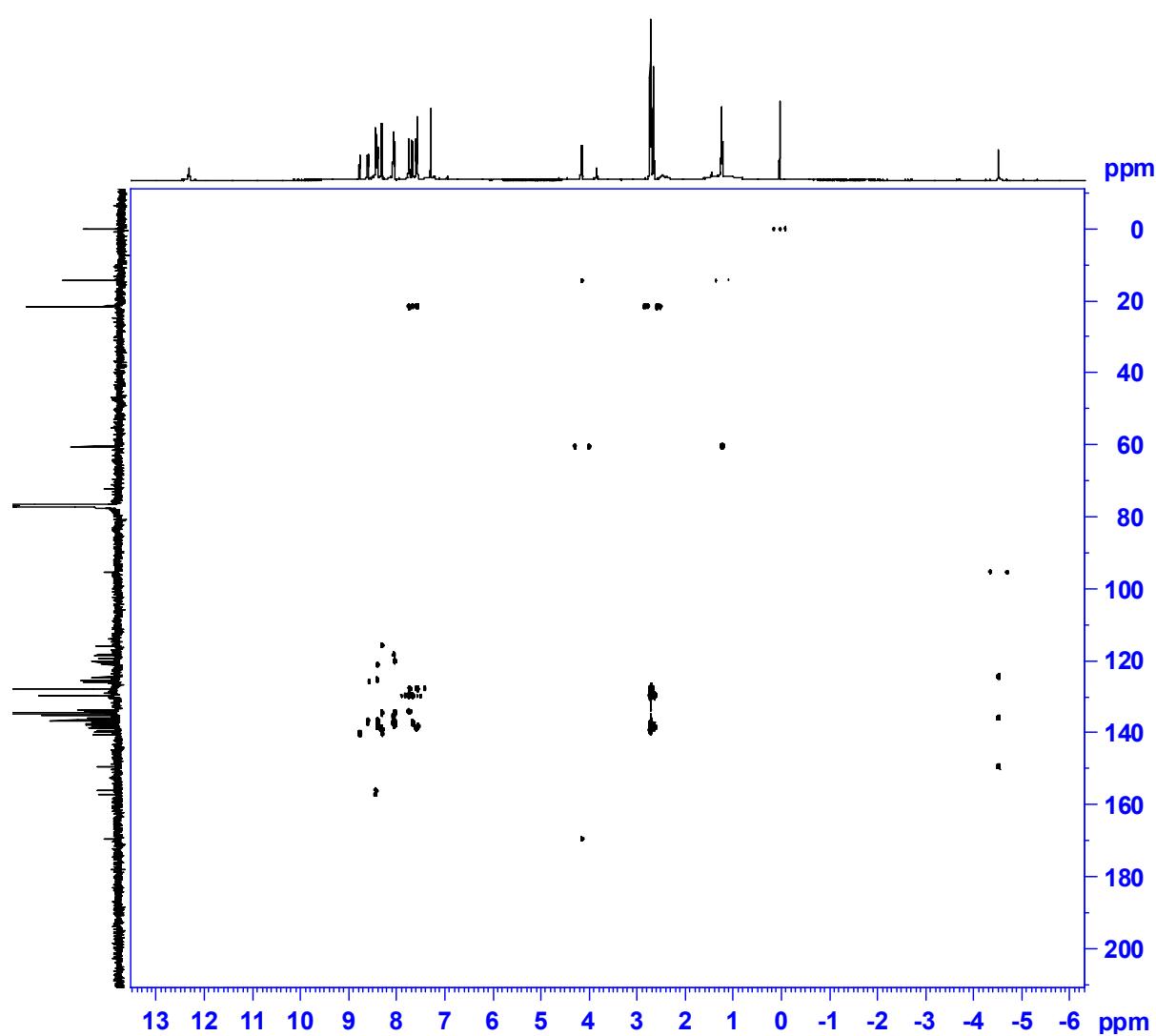
**Figure S5.** COSY spectrum of **3a** ( $\text{CDCl}_3$ , 298 K).



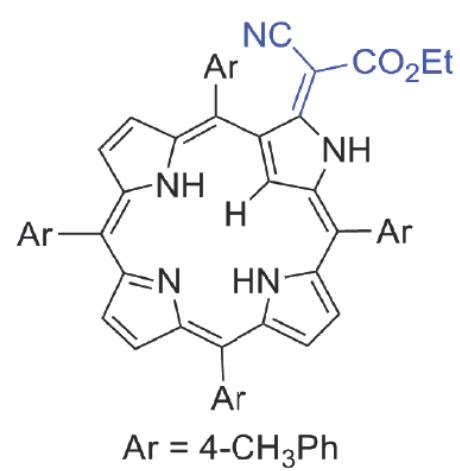


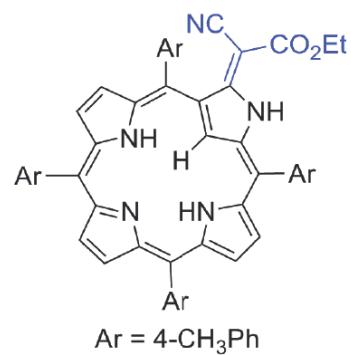
**Figure S6.** HMQC spectrum of **3a** ( $\text{CDCl}_3$ , 298 K).



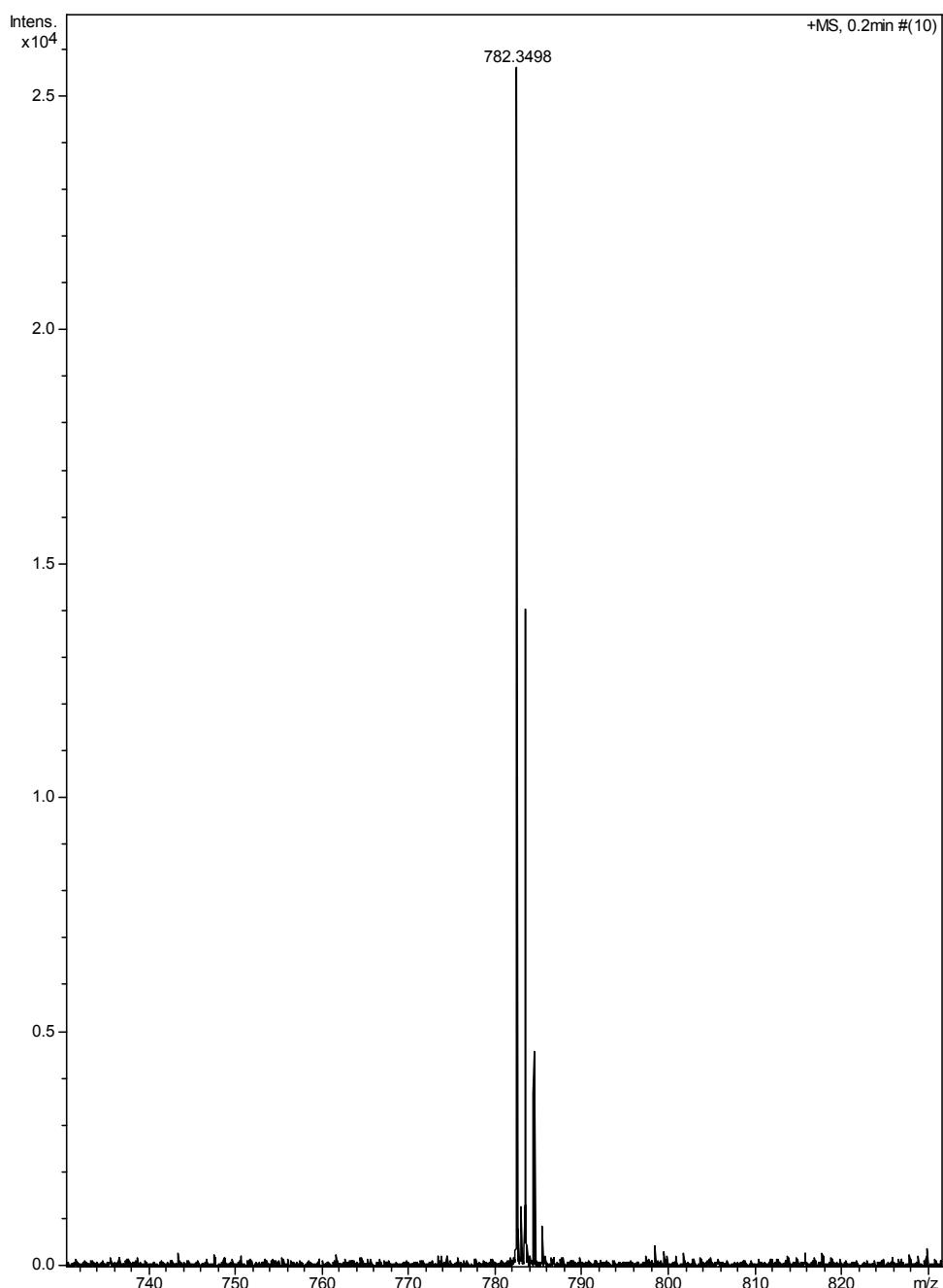


**Figure S7.** HMBC spectrum of **3a** ( $\text{CDCl}_3$ , 298 K).

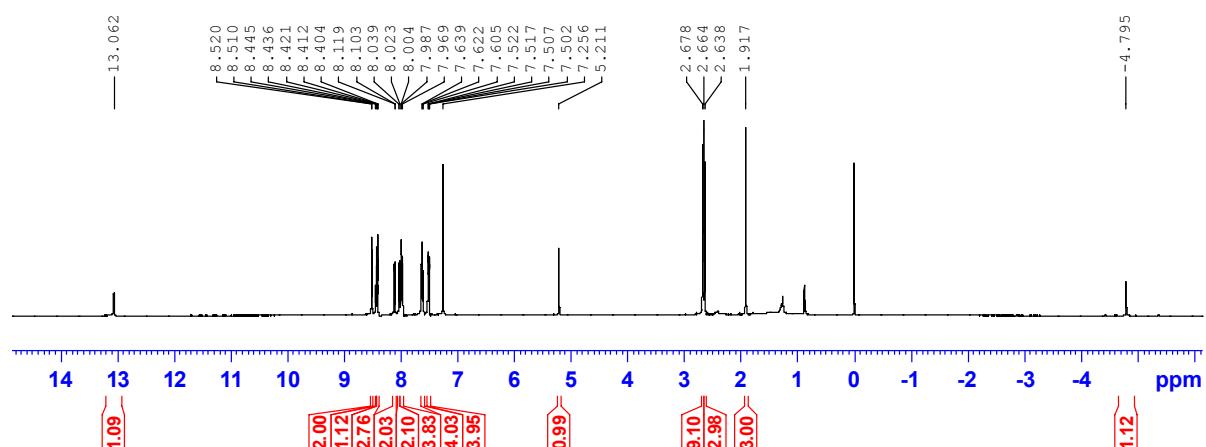




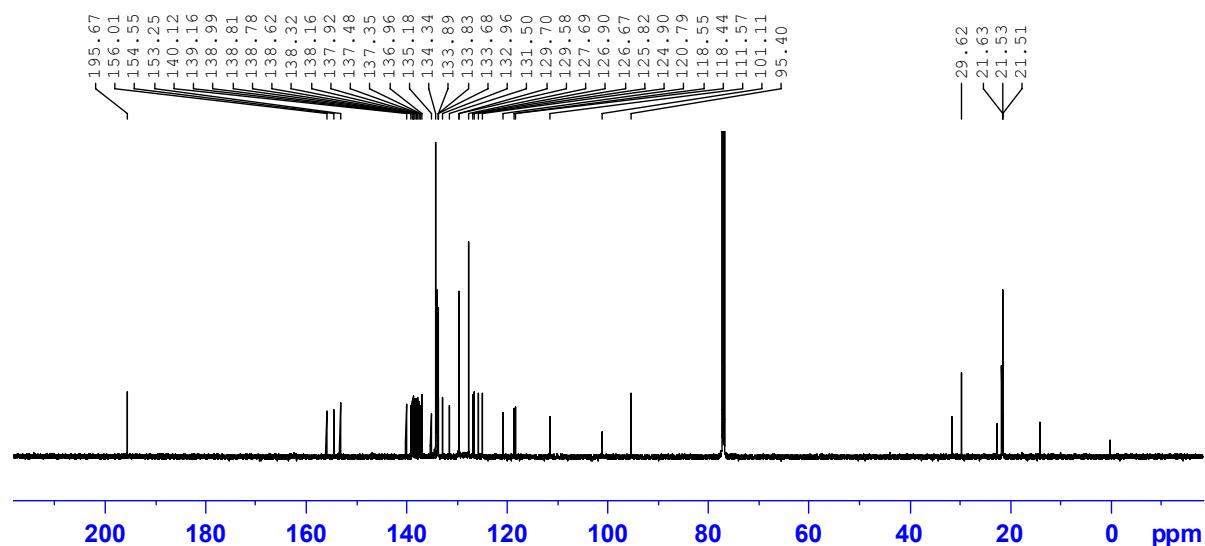
Ar = 4-CH<sub>3</sub>Ph



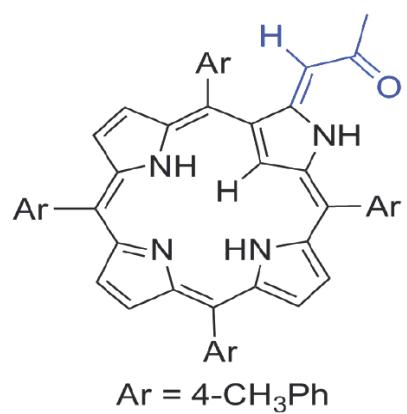
**Figure S8.** HRMS spectrum of 3a.

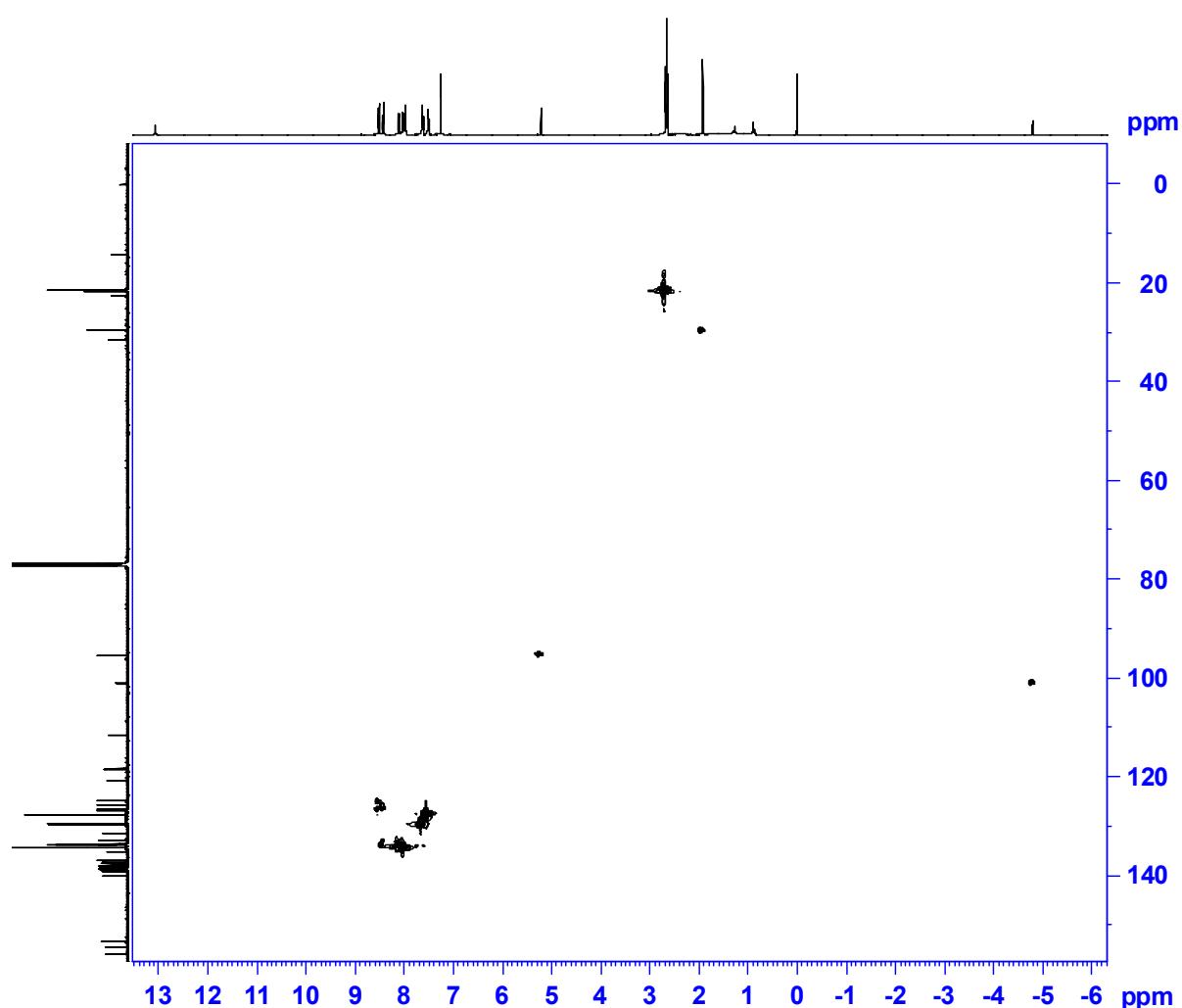


**Figure S9.** <sup>1</sup>H NMR spectrum of **3b** (298 K, CDCl<sub>3</sub>).

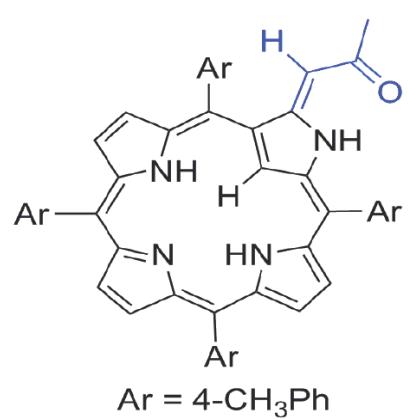


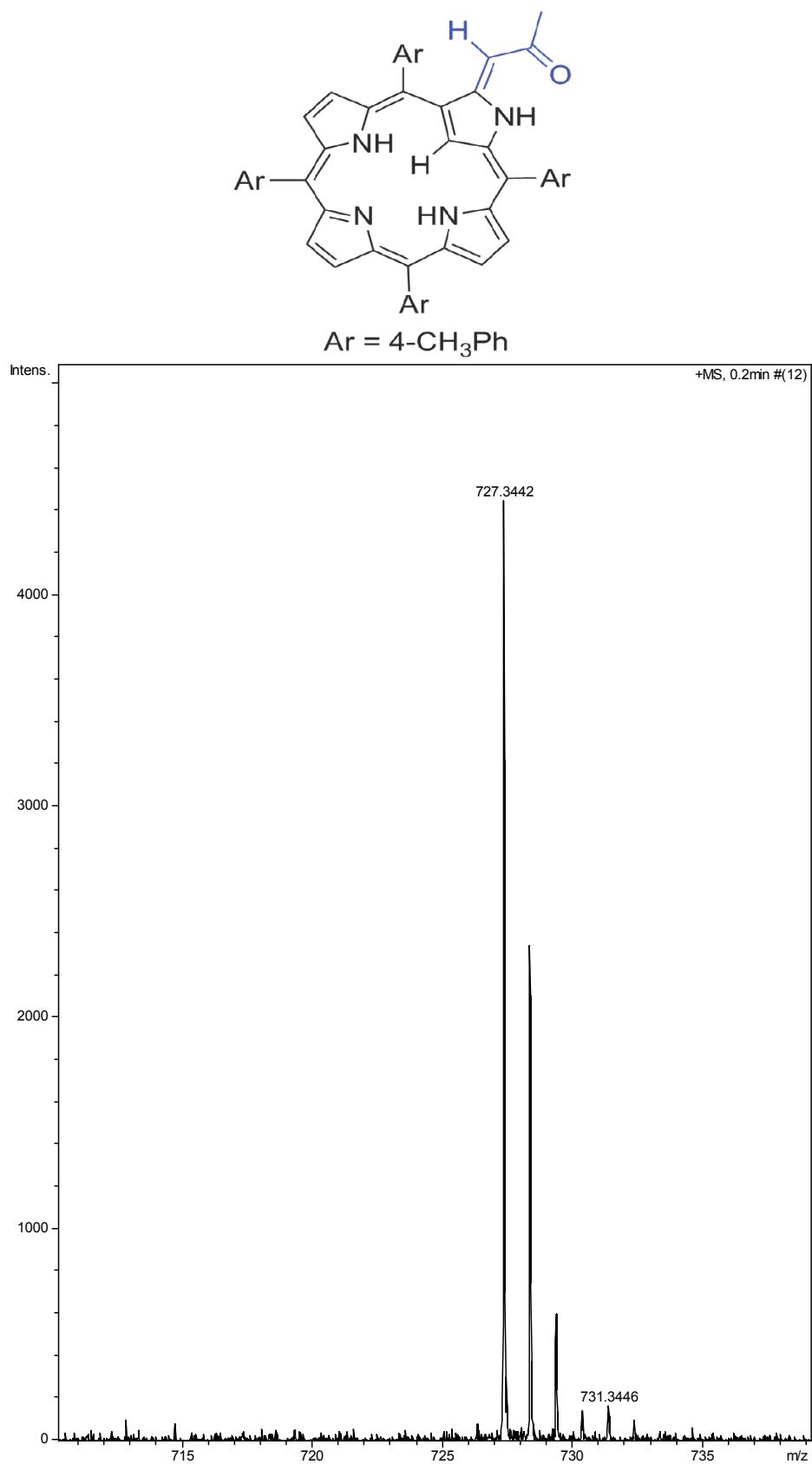
**Figure S10.** <sup>13</sup>C NMR spectrum of **3b** (298 K, CDCl<sub>3</sub>).



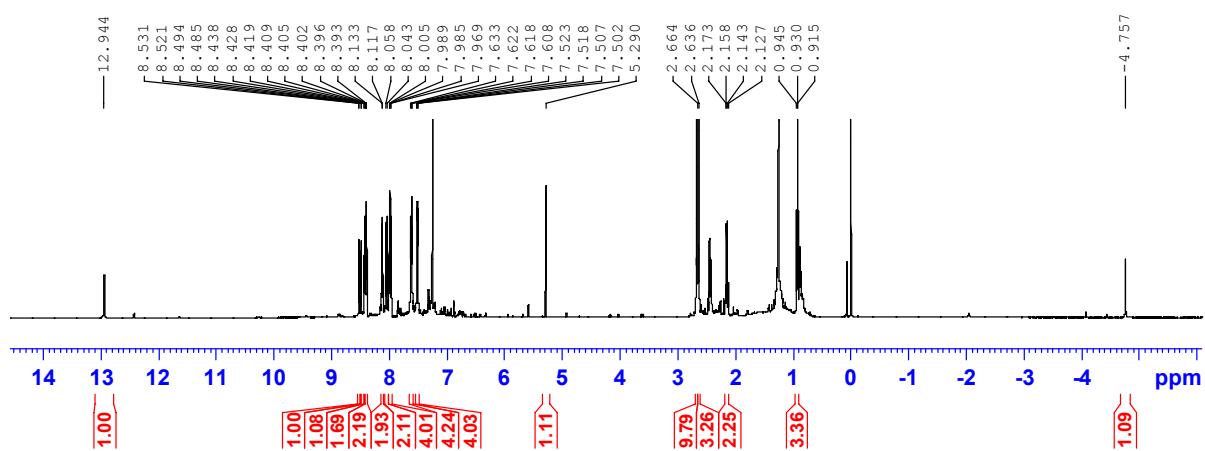


**Figure S11.** HSQC spectrum of **3b** (298 K,  $\text{CDCl}_3$ ).

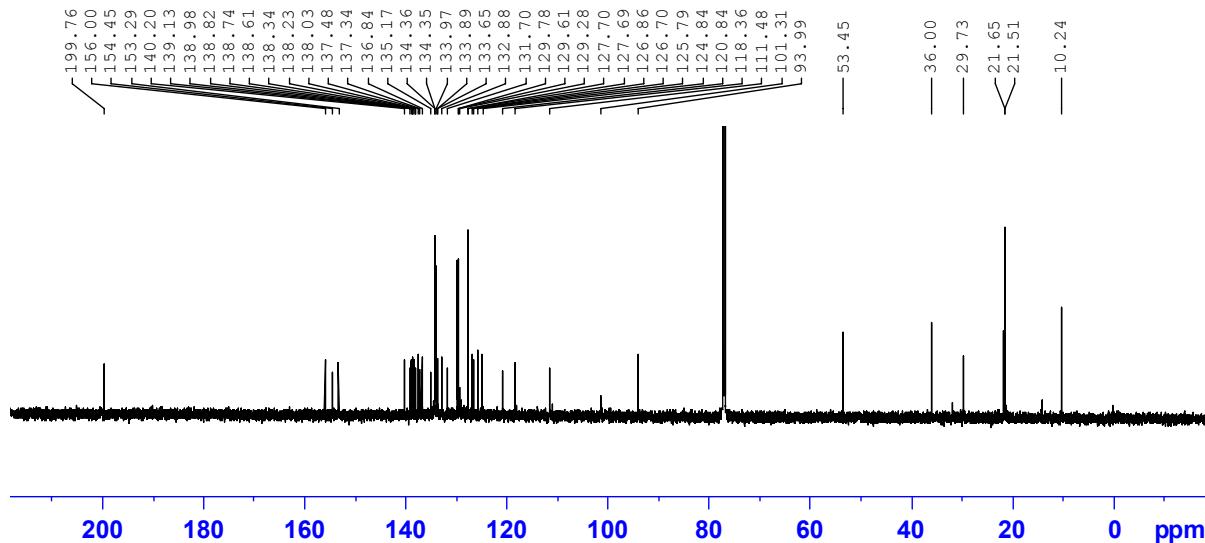




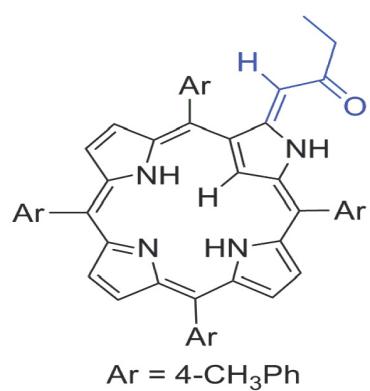
**Figure S12.** HRMS spectrum of **3b**.

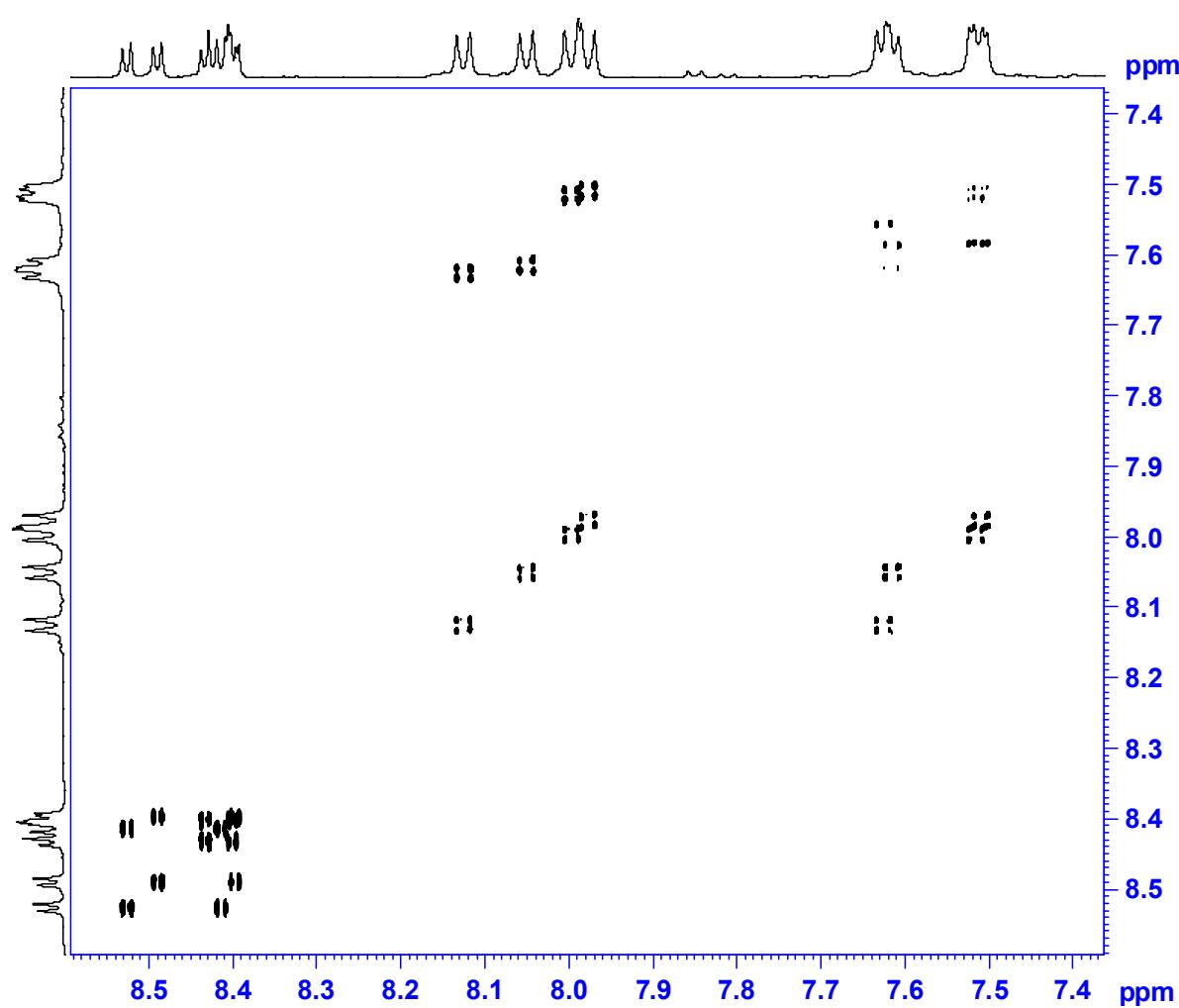


**Figure S13.** <sup>1</sup>H NMR spectrum of **3c** (298 K, CDCl<sub>3</sub>).

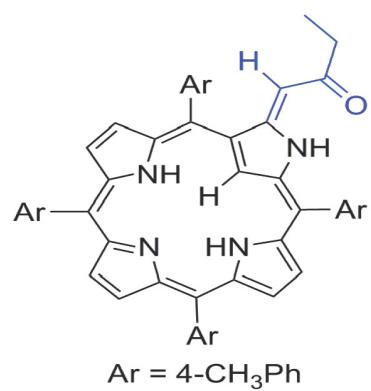


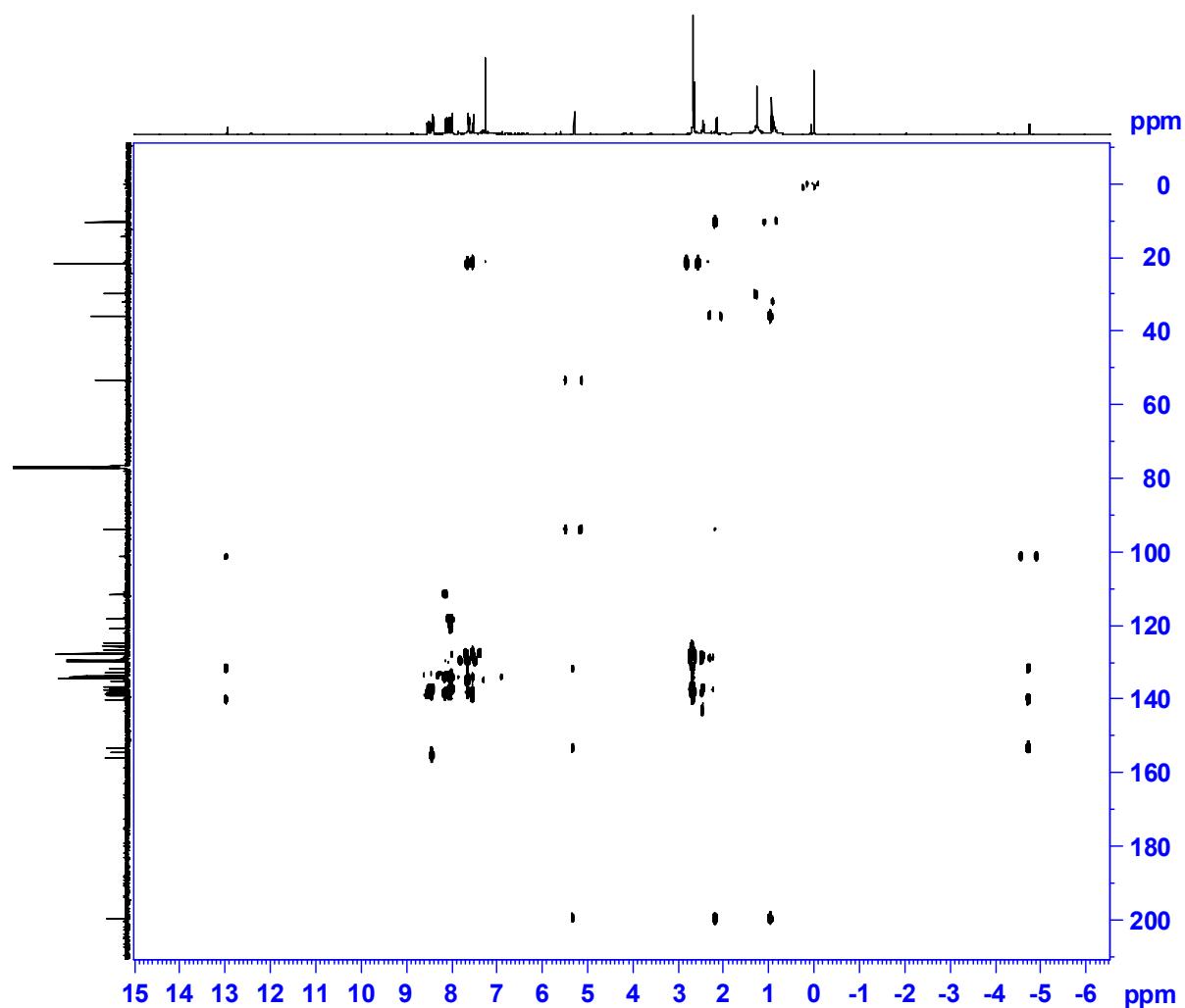
**Figure S14.** <sup>13</sup>C NMR spectrum of **3c** (298 K, CDCl<sub>3</sub>).



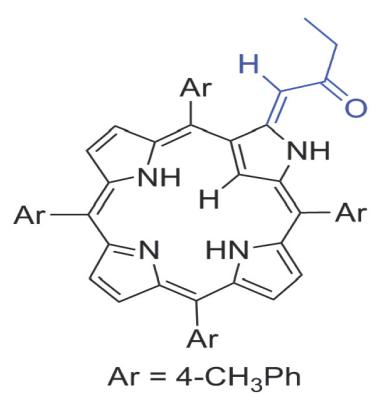


**Figure S15.** COSY spectrum of **3c** (low-field part).





**Figure S16.** HMBC spectrum of **3c** ( $\text{CDCl}_3$ , 298 K).



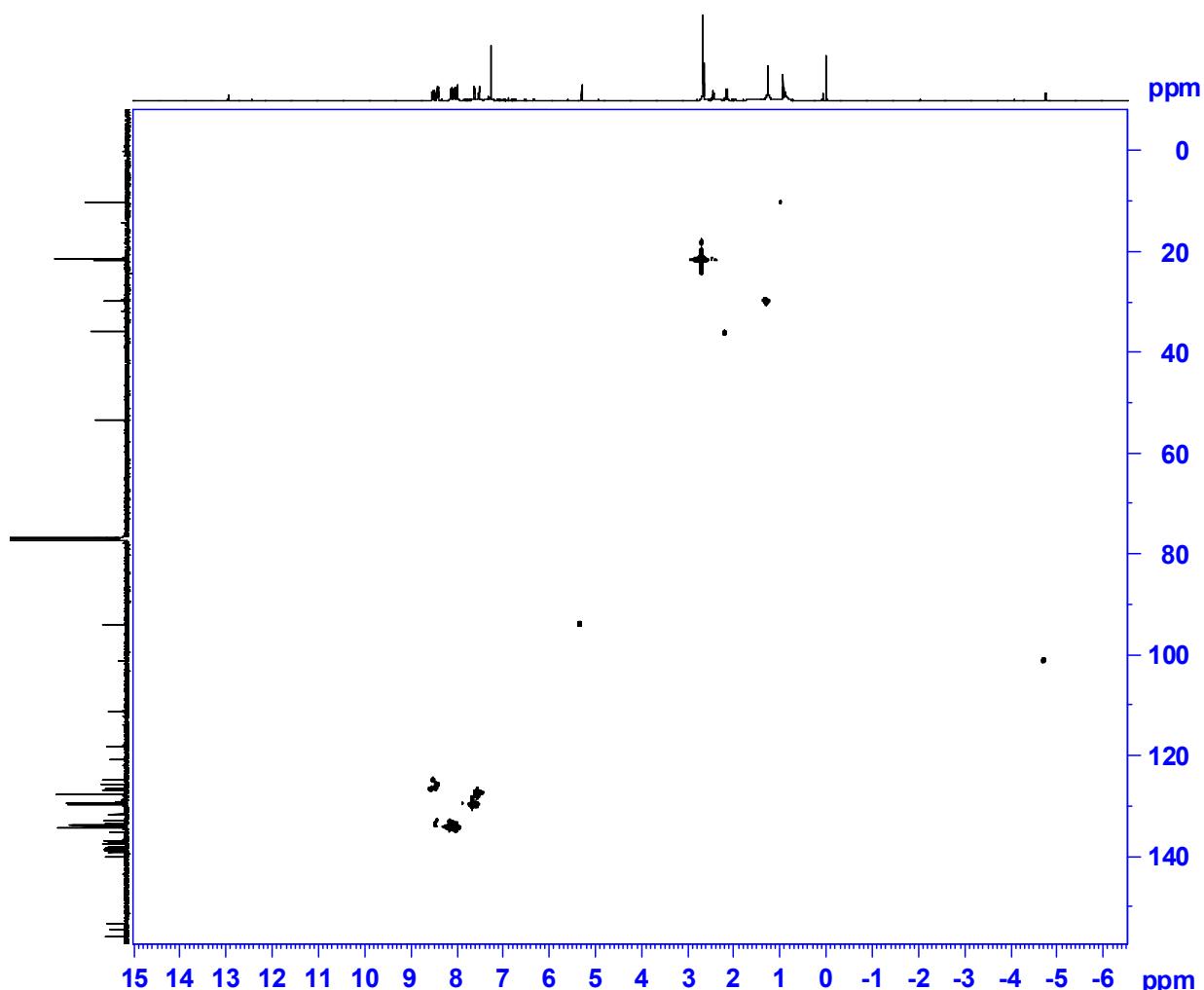
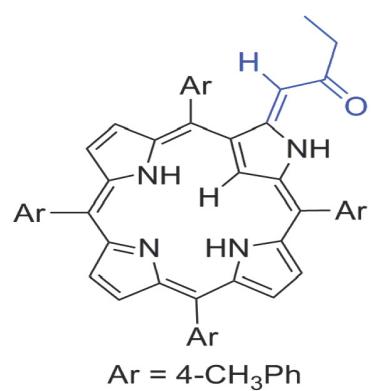
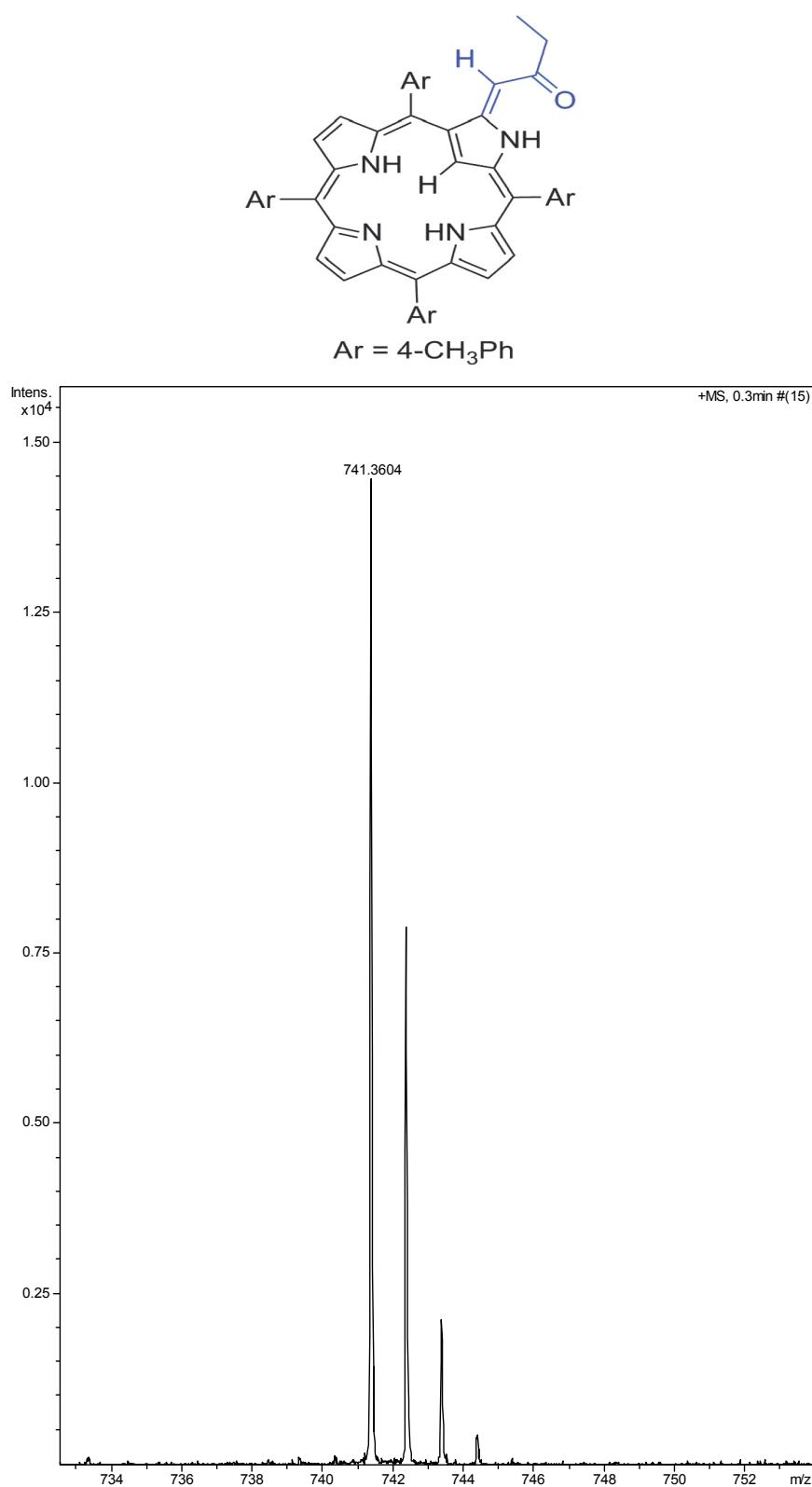
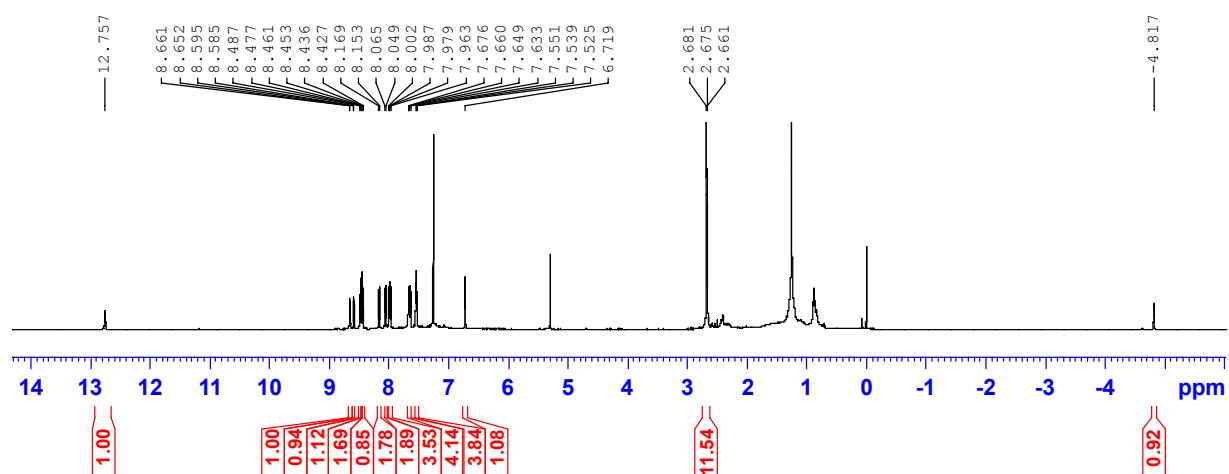


Figure S17. HSQC spectrum of **3c** ( $\text{CDCl}_3$ , 298 K).

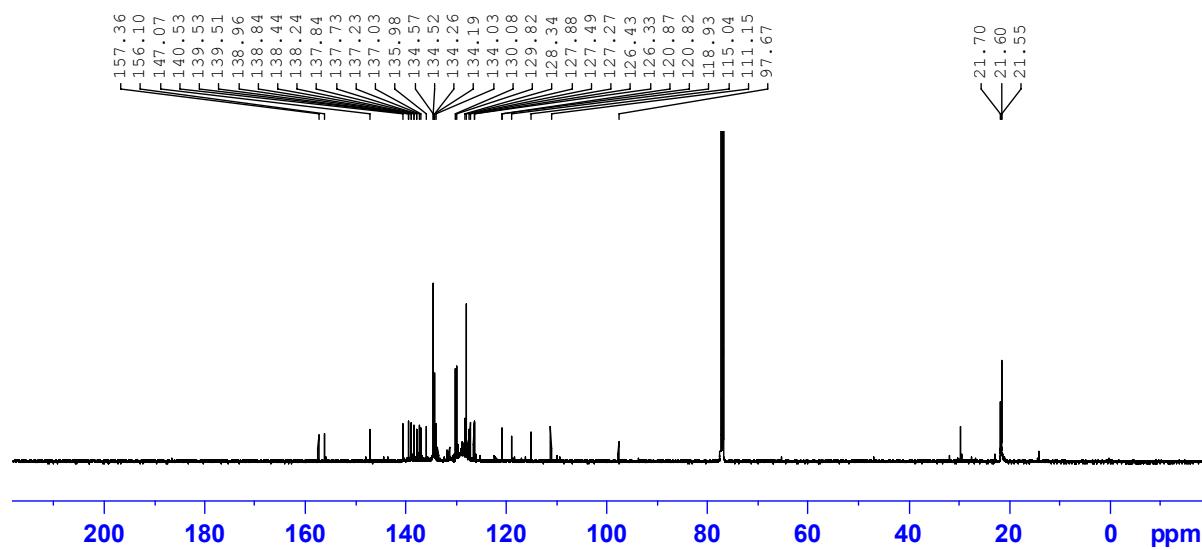




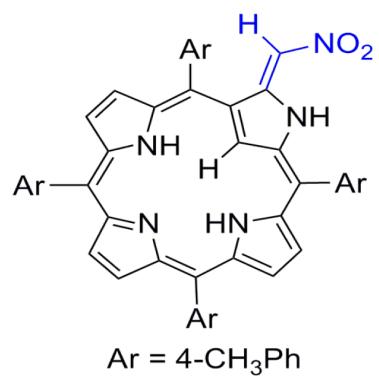
**Figure S18.** HRMS spectrum of **3c**.

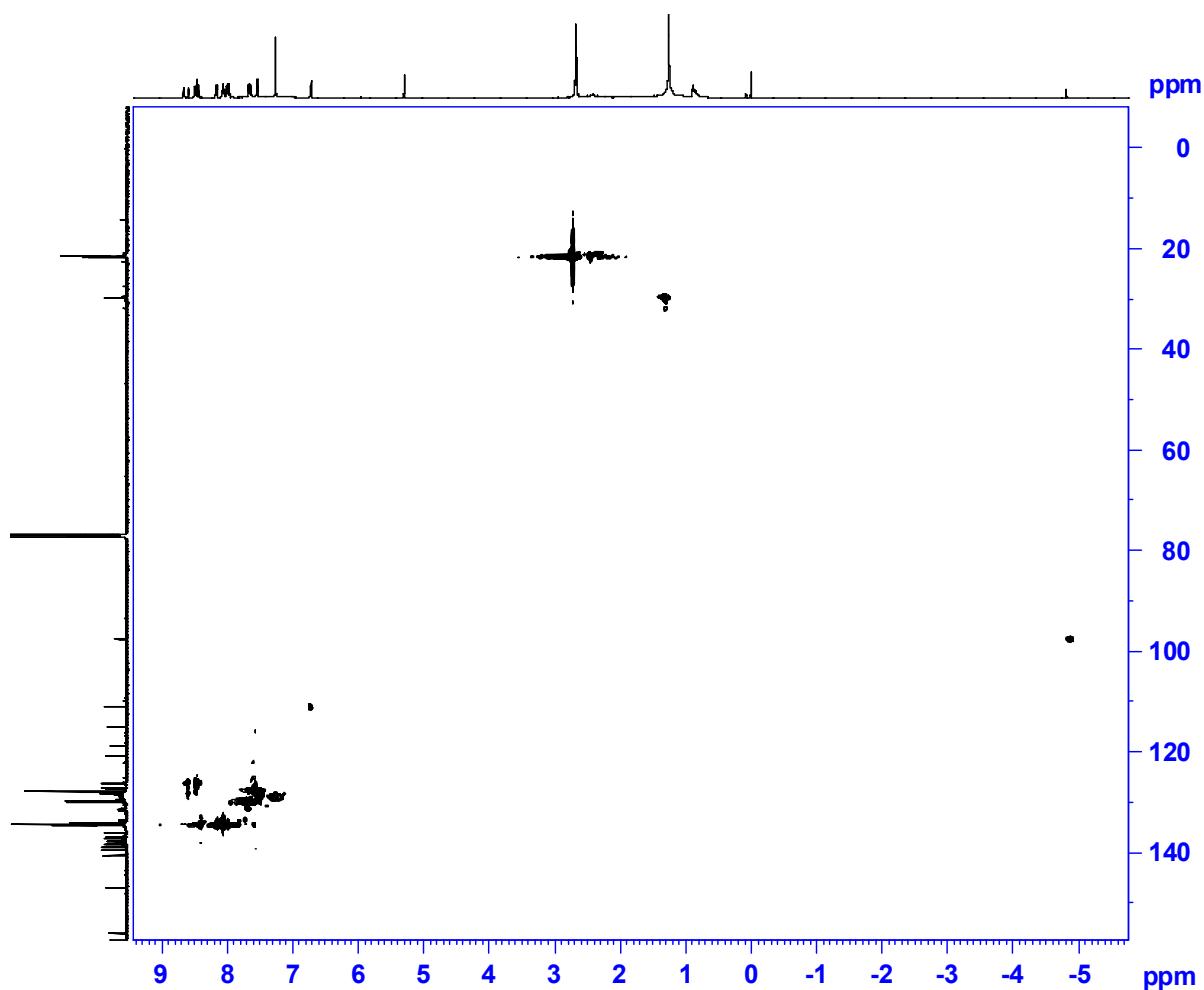


**Figure S19.** <sup>1</sup>H NMR spectrum of **3d** (298 K, CDCl<sub>3</sub>).

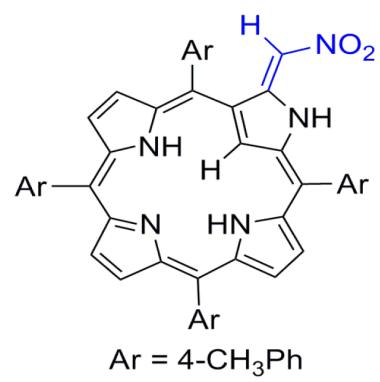


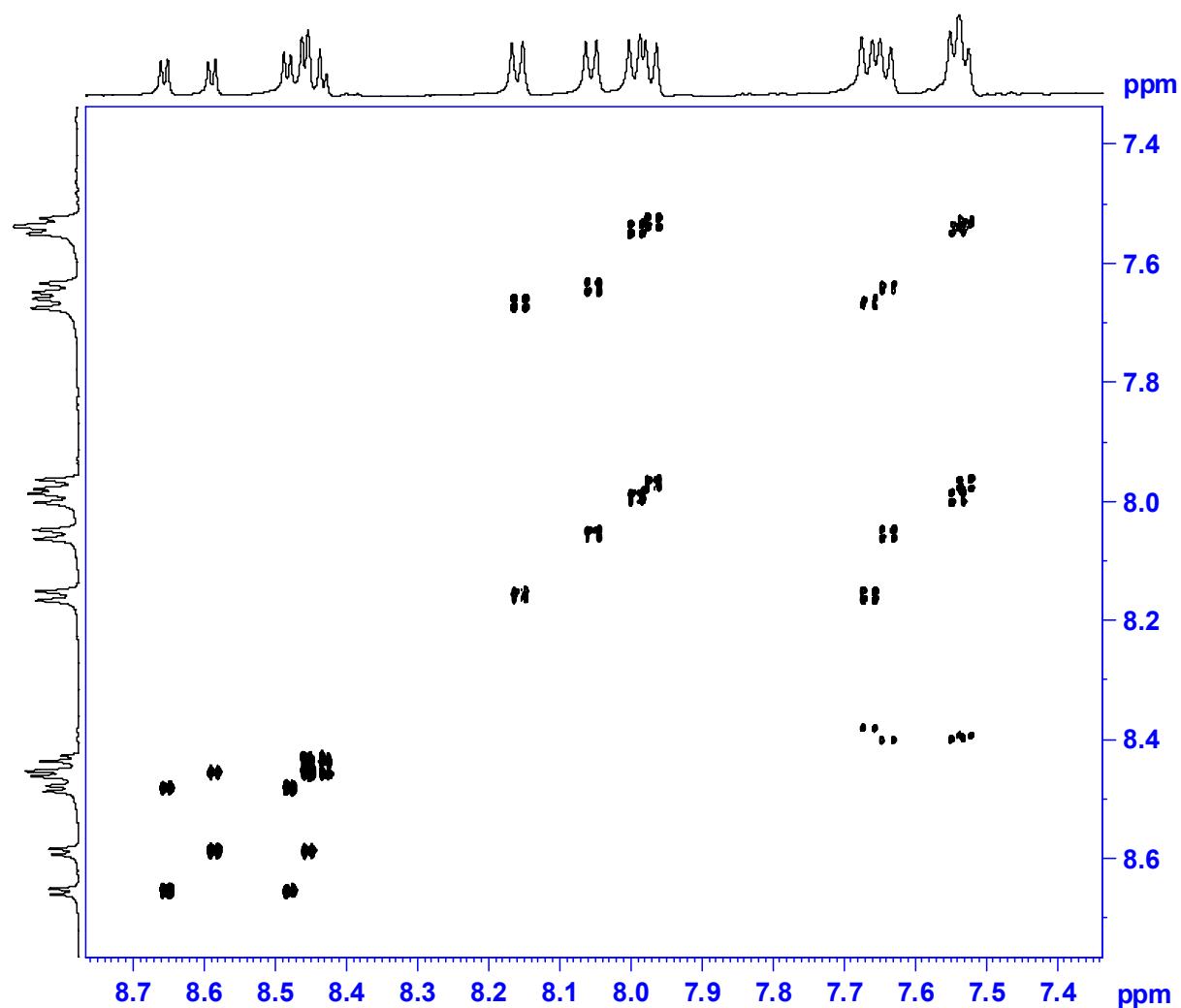
**Figure S20.** <sup>13</sup>C NMR spectrum of **3d** (298 K, CDCl<sub>3</sub>).



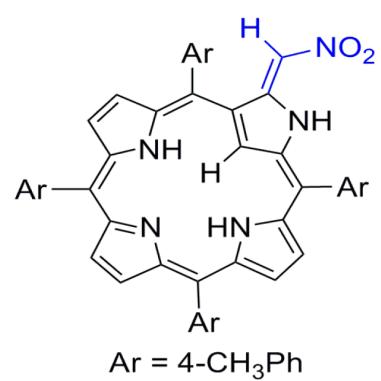


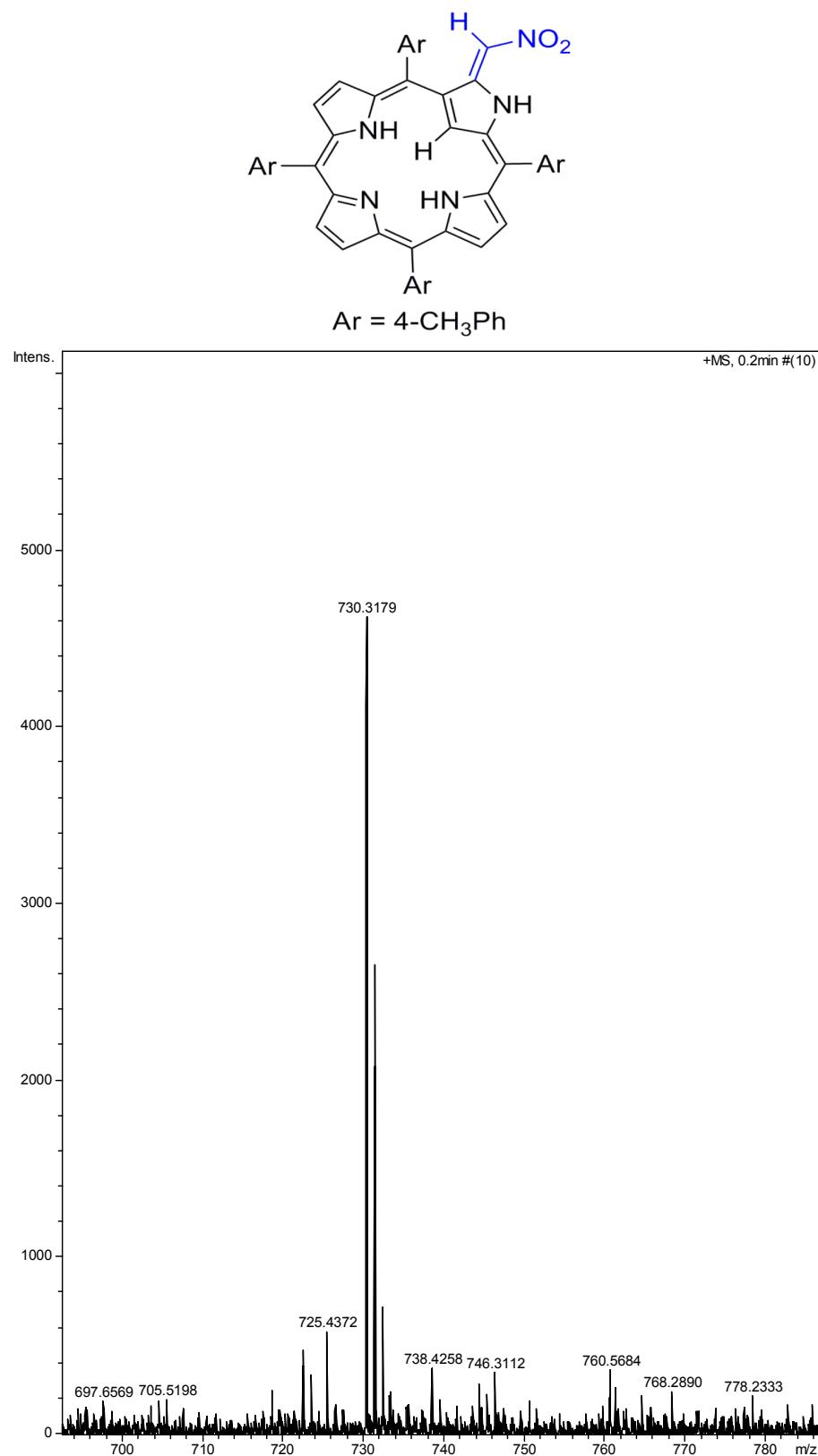
**Figure S21.** HSQC spectrum of **3d** ( $\text{CDCl}_3$ , 298 K).



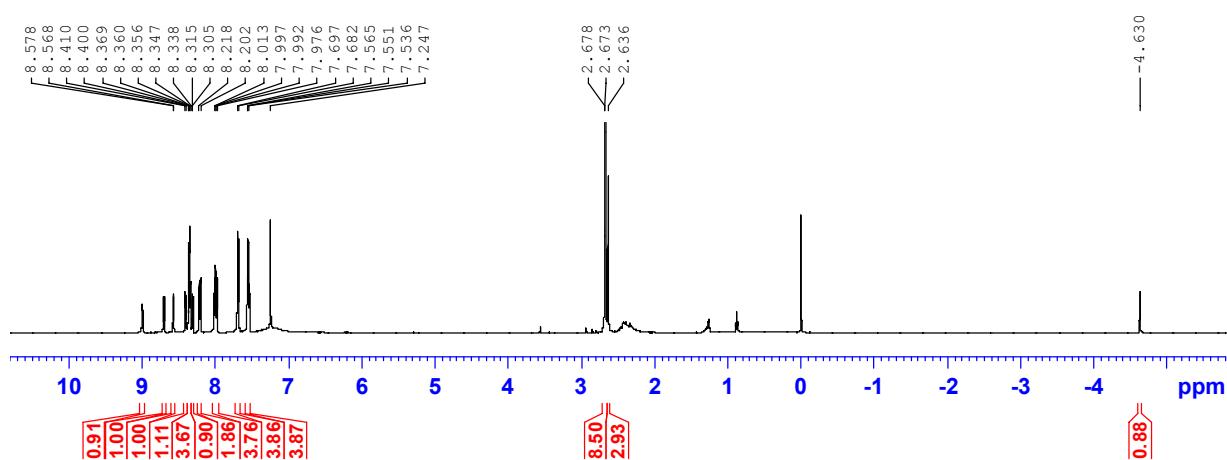


**Figure S22.** COSY spectrum of **3d** (low-field part).

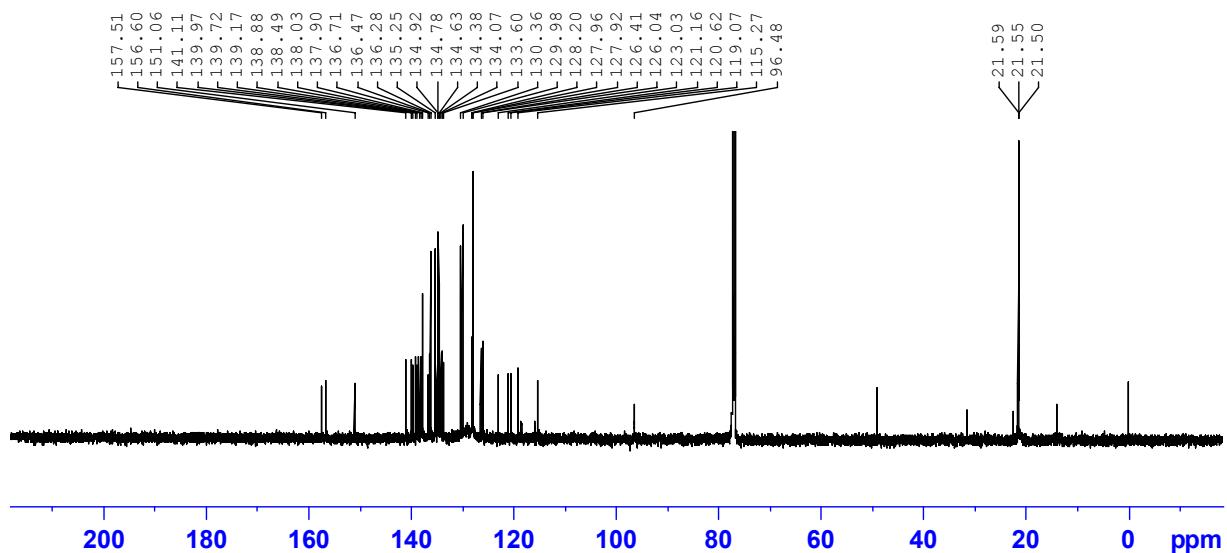




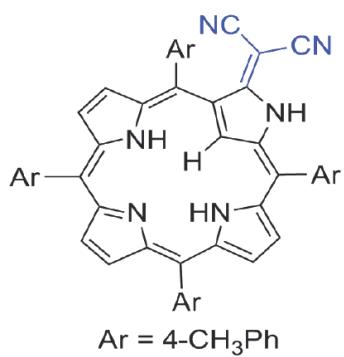
**Figure S23.** HRMS spectrum of **3d**.

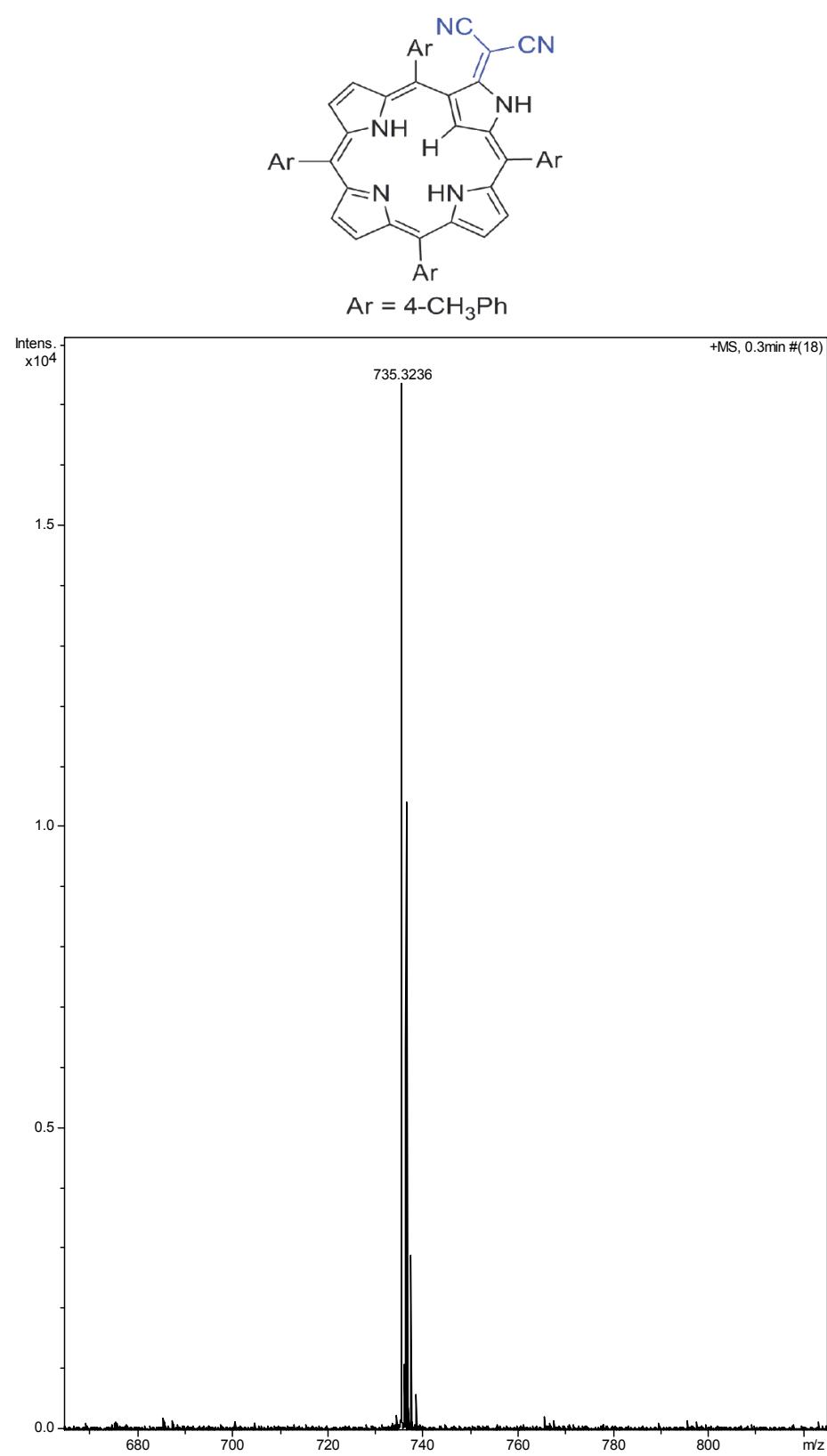


**Figure S24.** <sup>1</sup>H NMR spectrum of 3e (298 K, CDCl<sub>3</sub>).

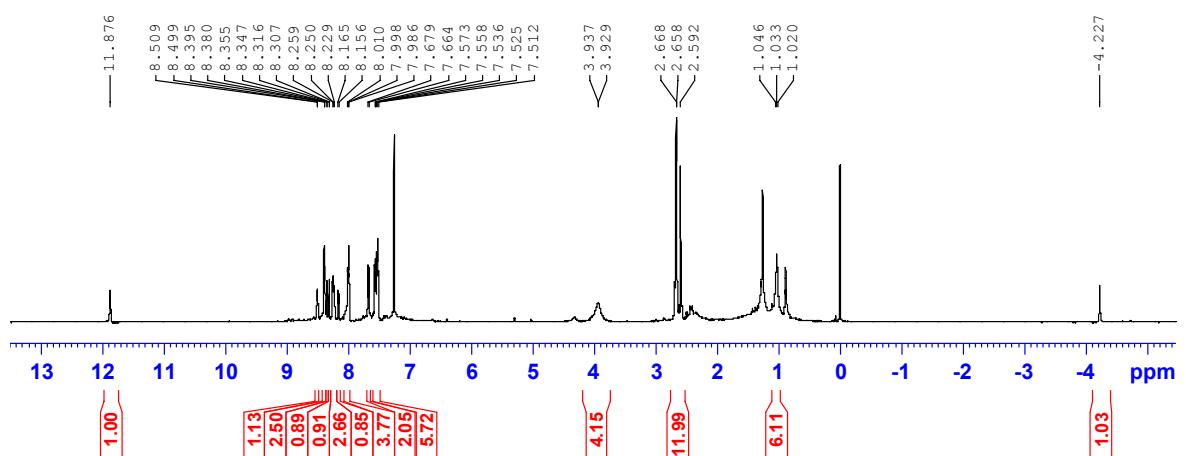


**Figure S25.** <sup>13</sup>C NMR spectrum of 3e (298 K, CDCl<sub>3</sub>).

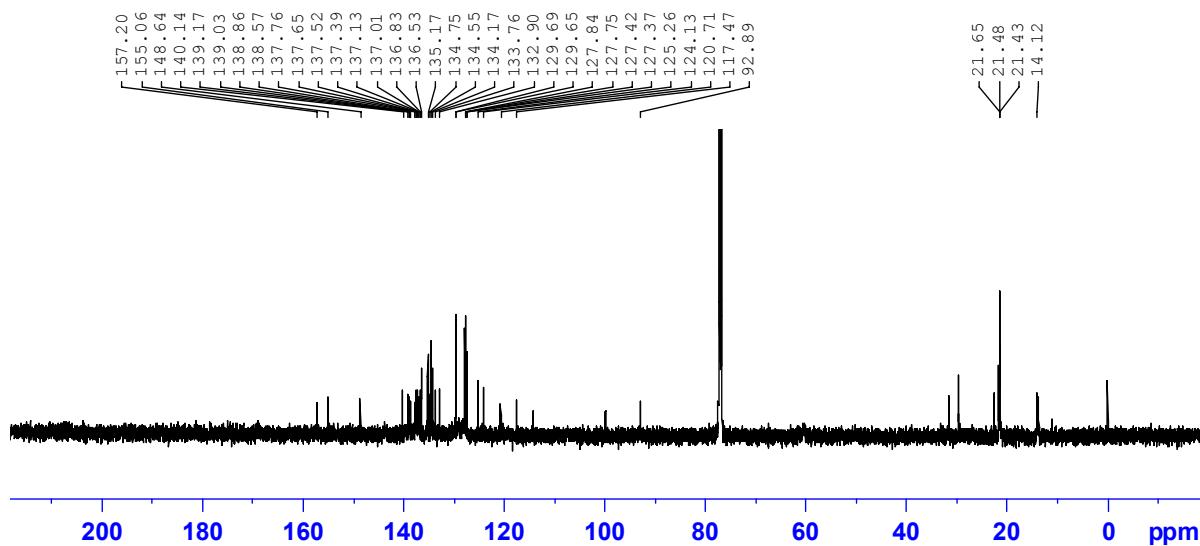




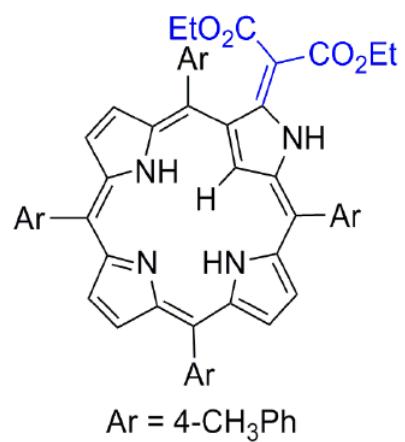
**Figure S26.** HRMS spectrum of 3e.

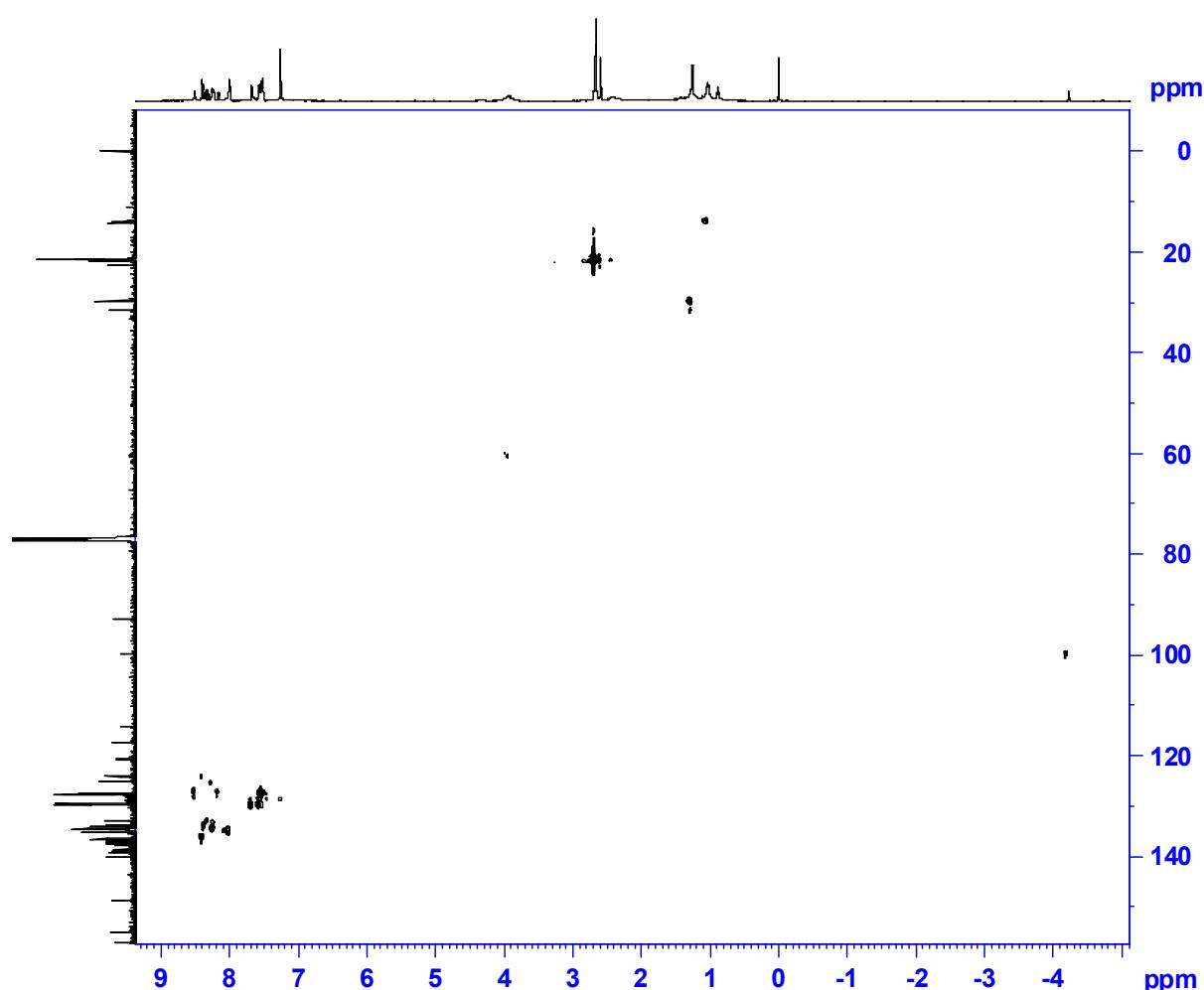


**Figure S27.** <sup>1</sup>H NMR spectrum of **3f** (298 K, CDCl<sub>3</sub>).

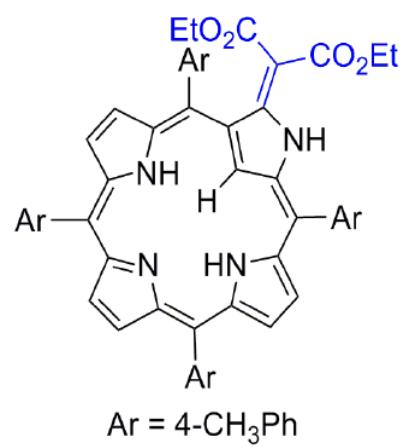


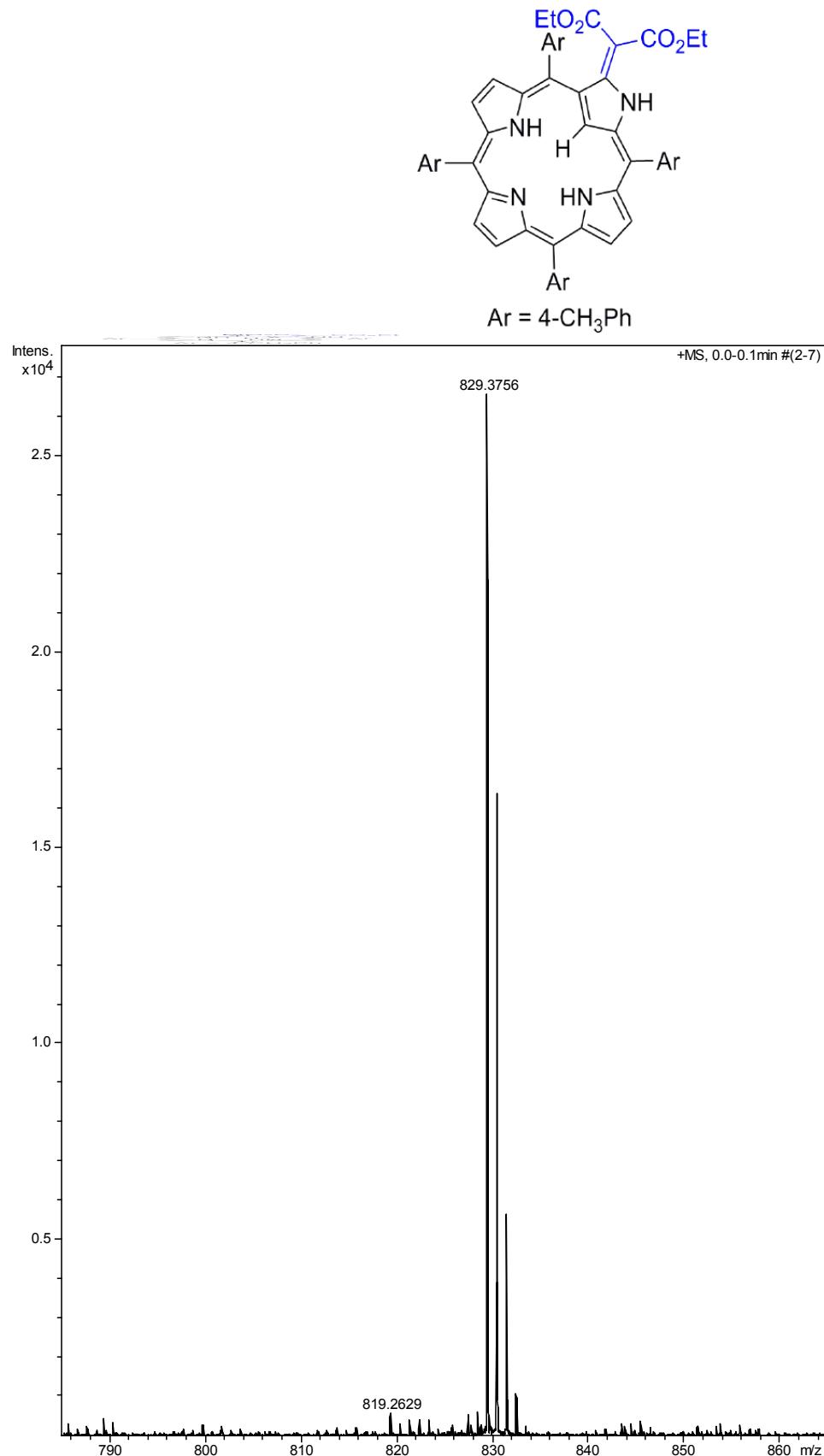
**Figure S28.** <sup>13</sup>C NMR spectrum of **3f** (298 K, CDCl<sub>3</sub>).



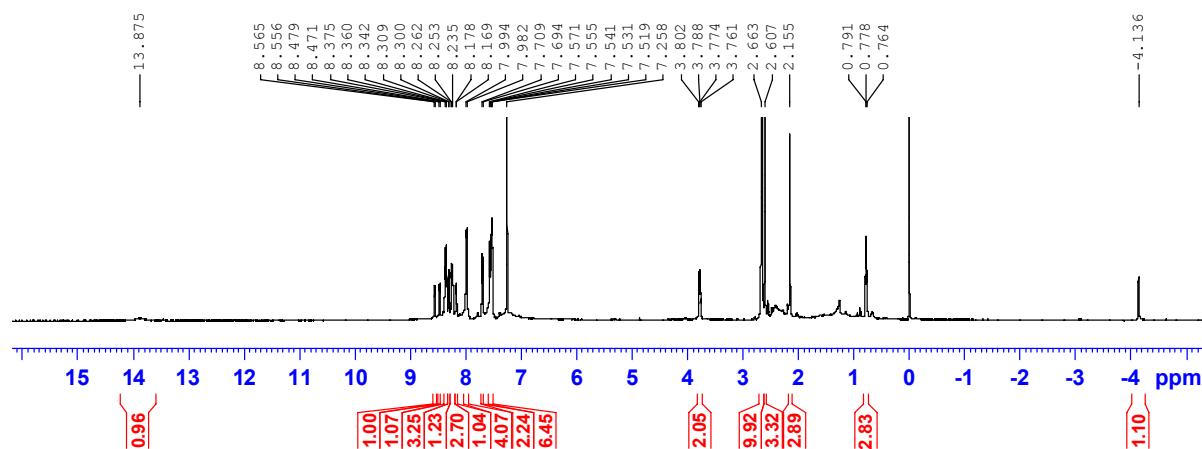


**Figure S29.** HSQC spectrum of **3f** ( $\text{CDCl}_3$ , 298 K).

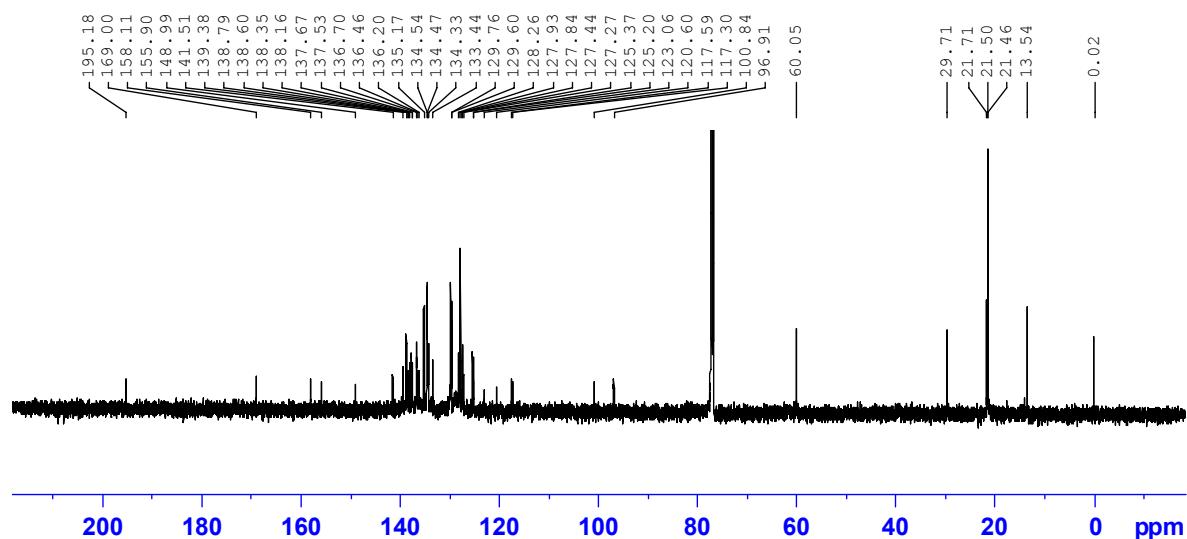




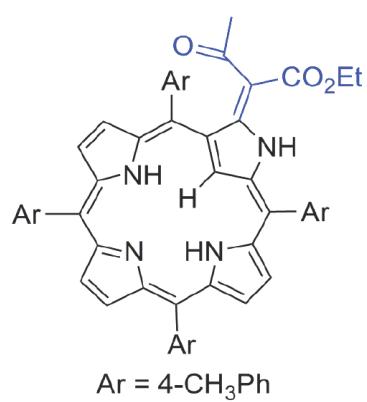
**Figure S30.** HRMS spectrum of **3f**.

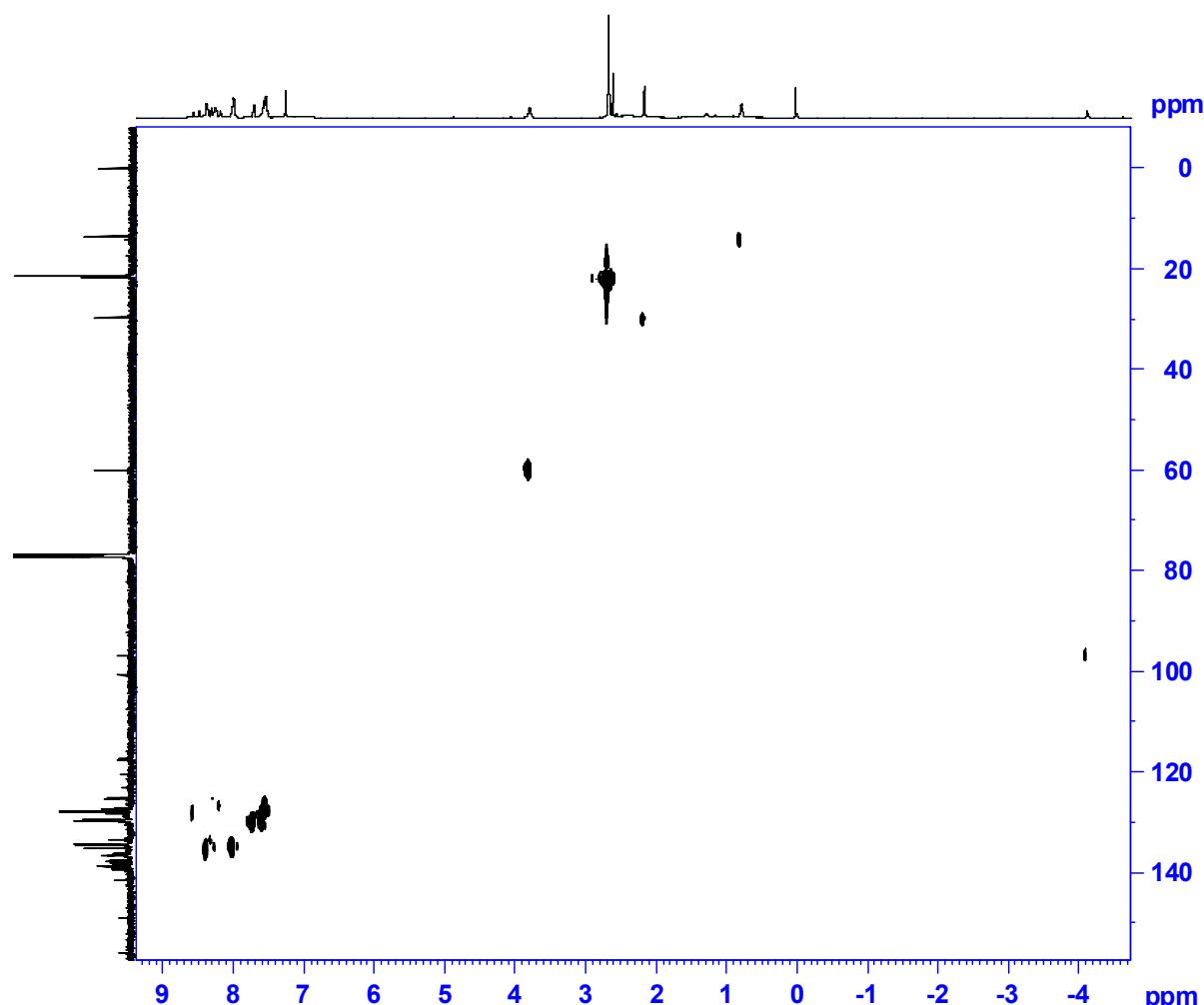


**Figure S31.** <sup>1</sup>H NMR spectrum of **3g** (298 K, CDCl<sub>3</sub>).

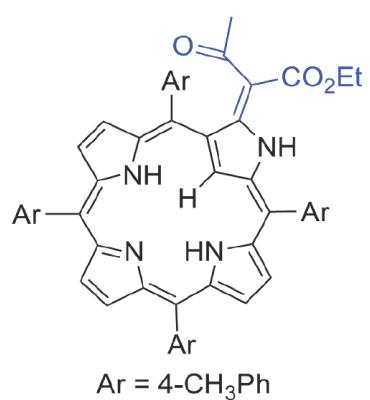


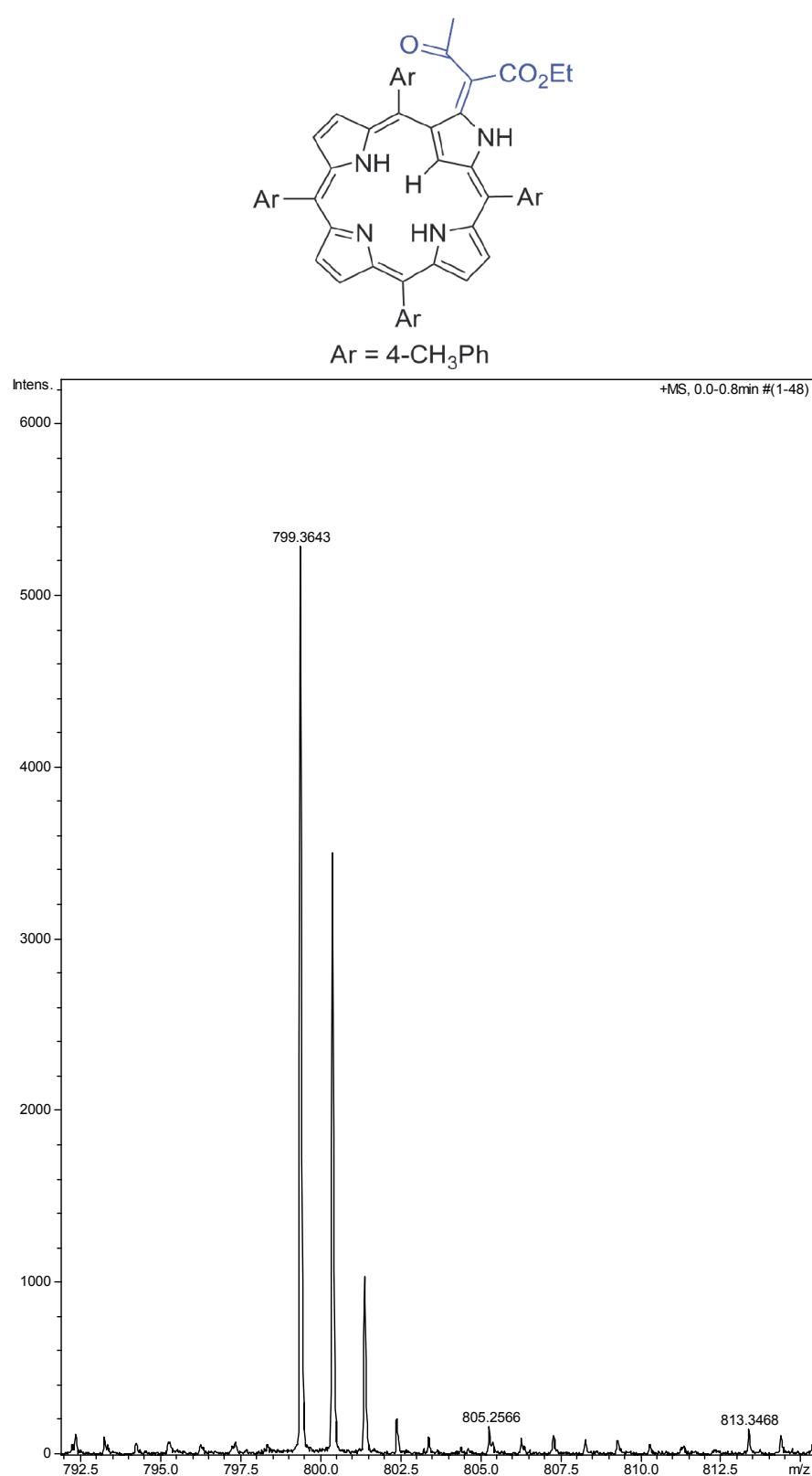
**Figure S32.** <sup>13</sup>C NMR spectrum of **3g** (298 K, CDCl<sub>3</sub>).



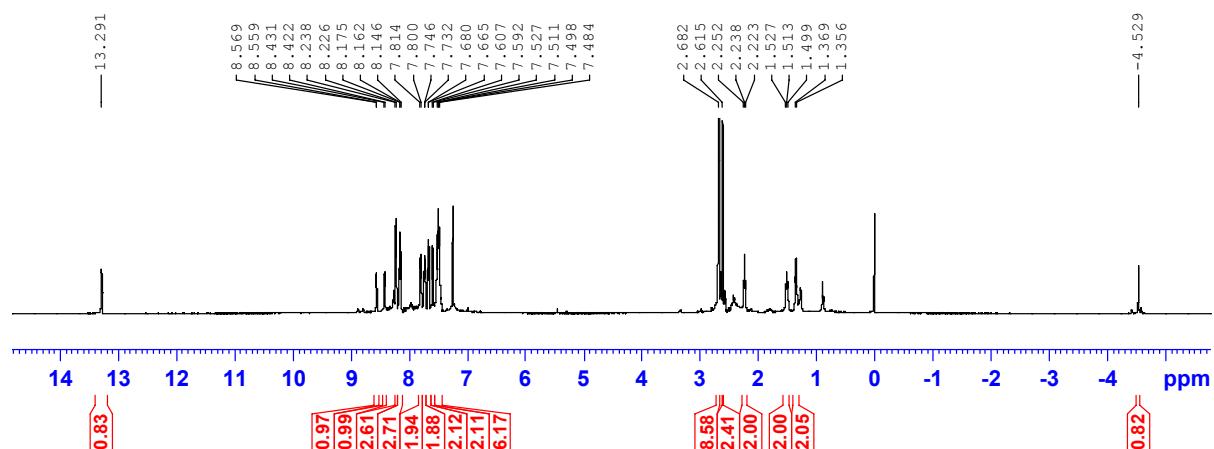


**Figure S33.** HSQC spectrum of **3g** ( $\text{CDCl}_3$ , 298 K).

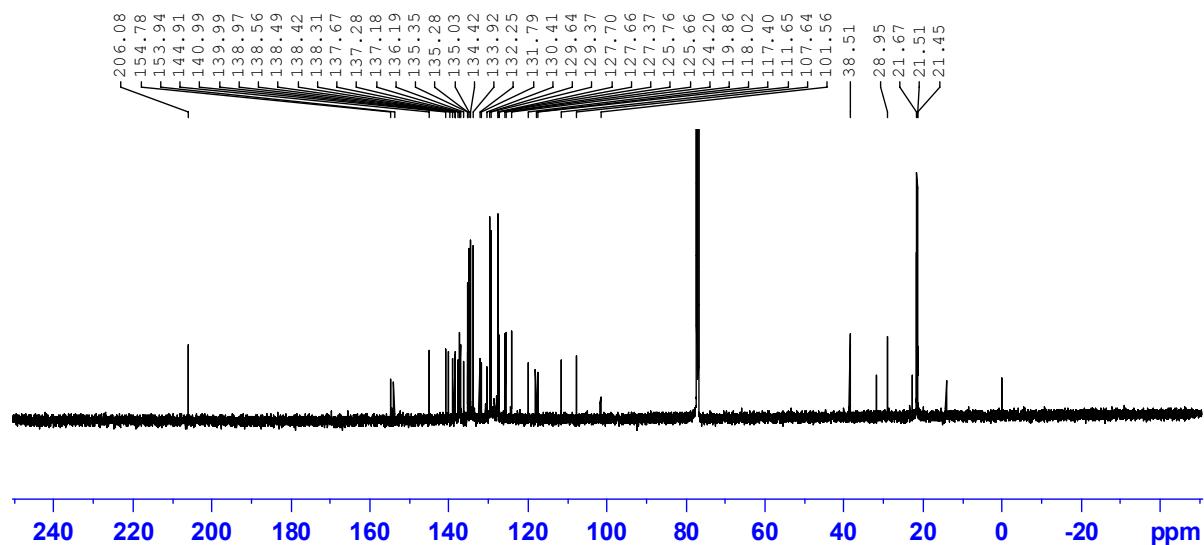




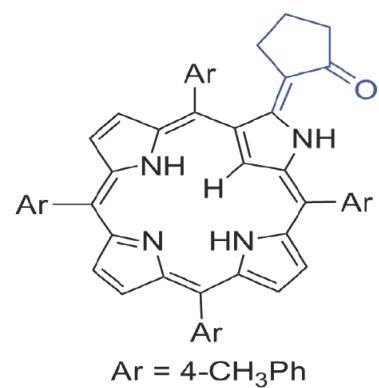
**Figure S34.** HRMS spectrum of **3g**.

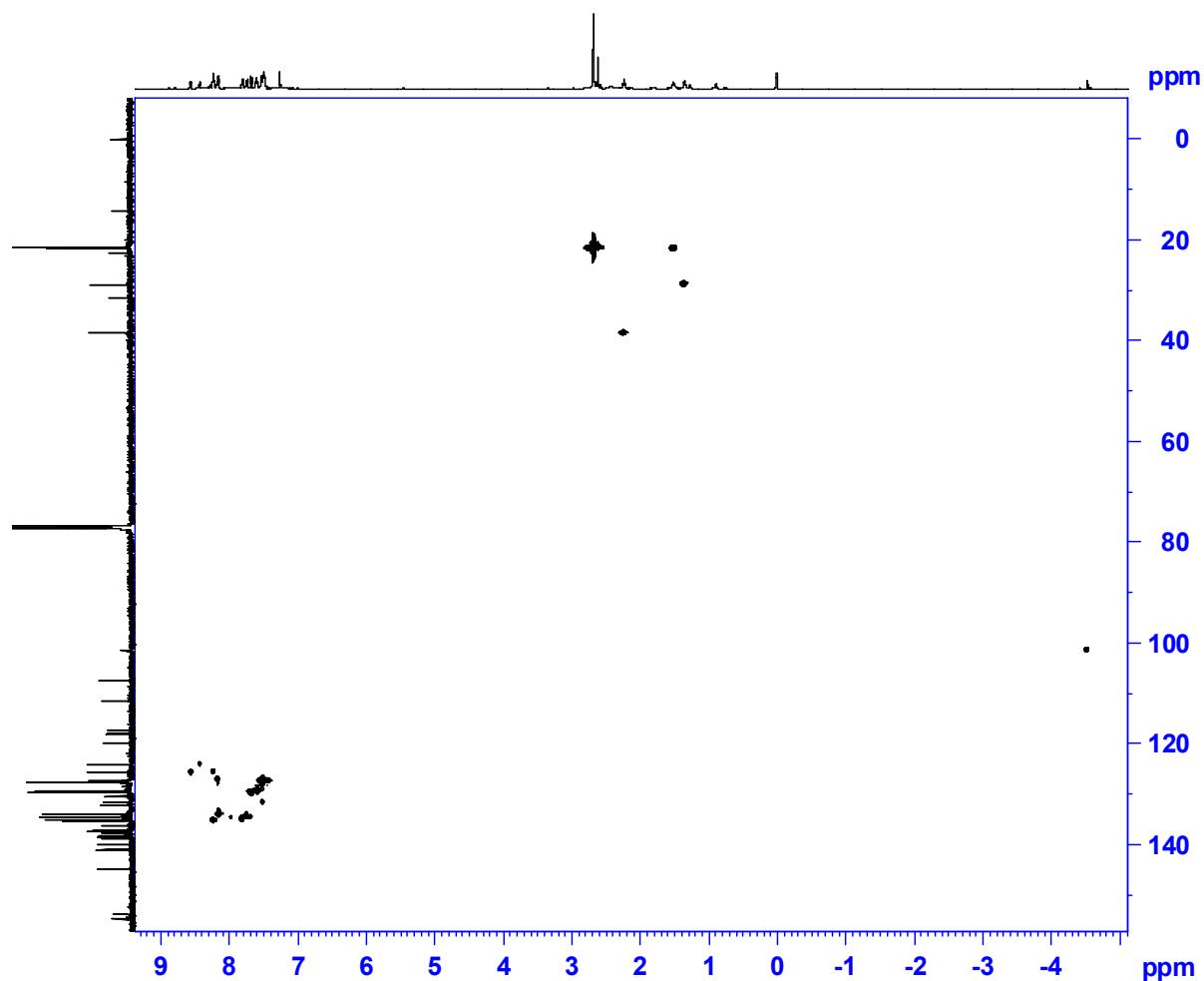


**Figure S35.** <sup>1</sup>H NMR spectrum of **3h** (298 K, CDCl<sub>3</sub>).

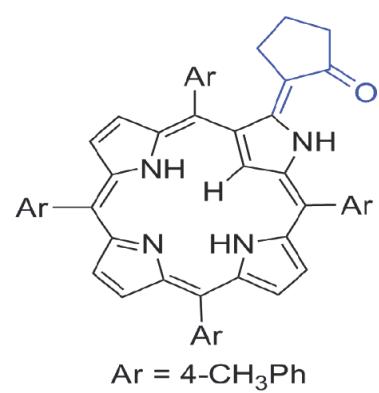


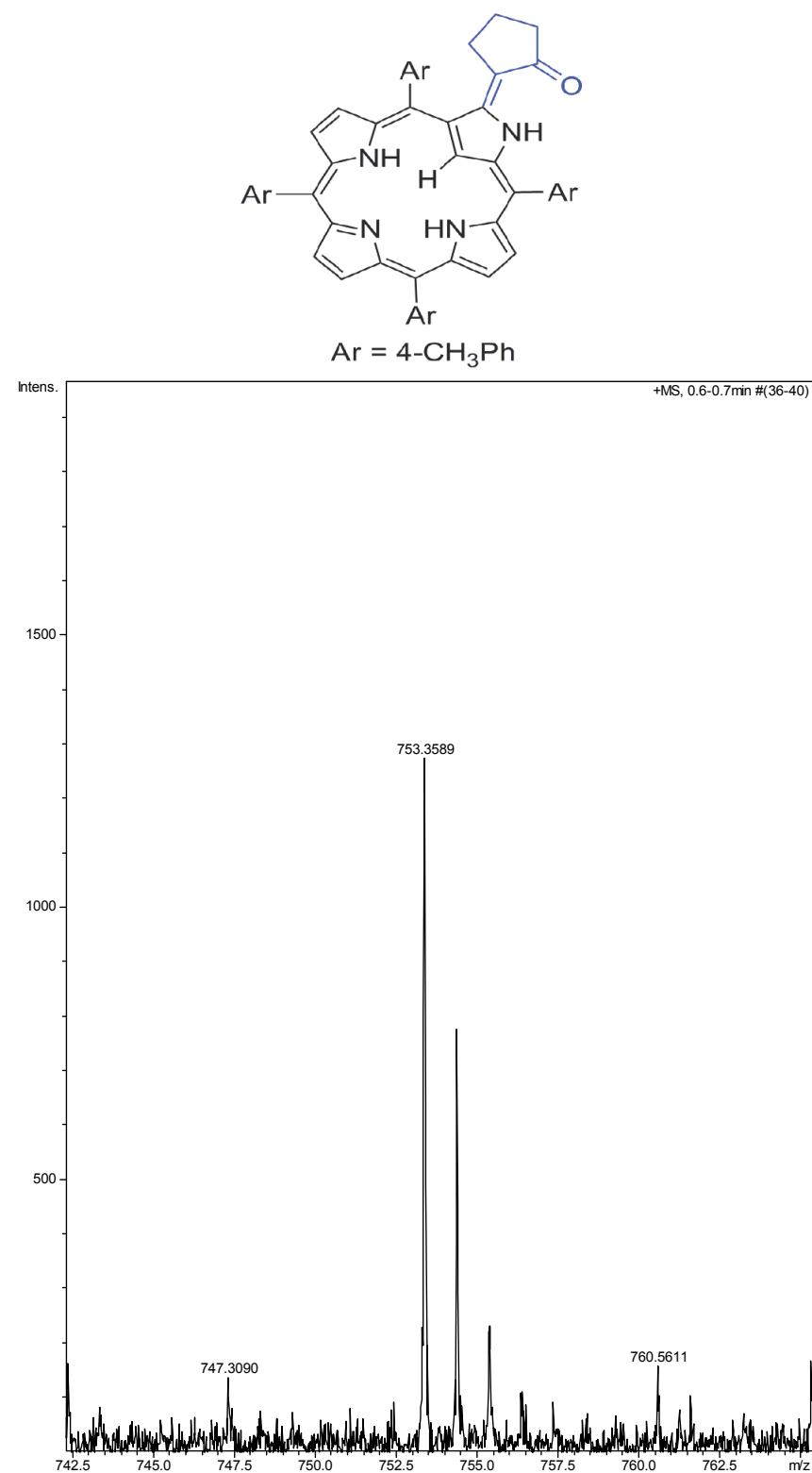
**Figure S36.** <sup>13</sup>C NMR spectrum of **3h** (298 K, CDCl<sub>3</sub>).



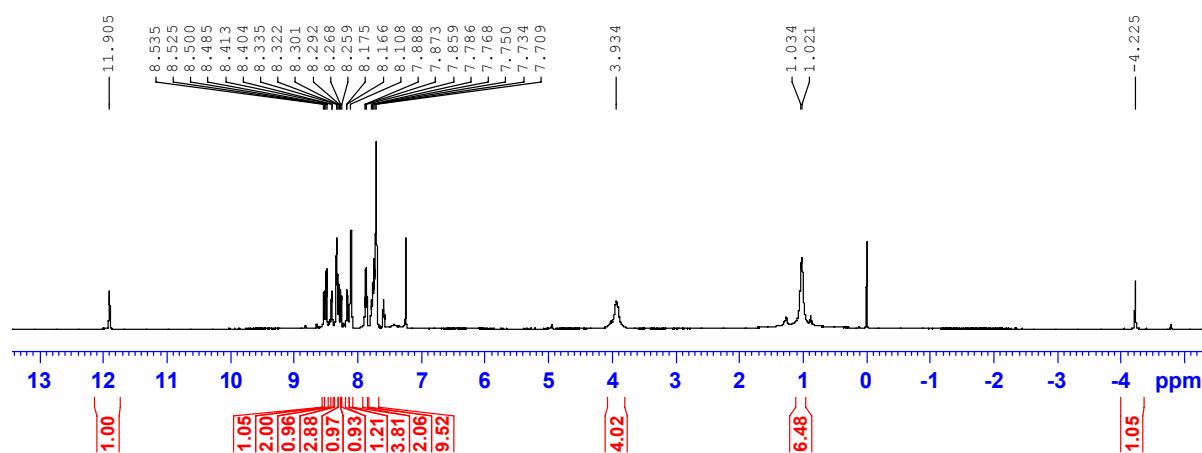


**Figure S37.** HSQC spectrum of **3h** ( $\text{CDCl}_3$ , 298 K).

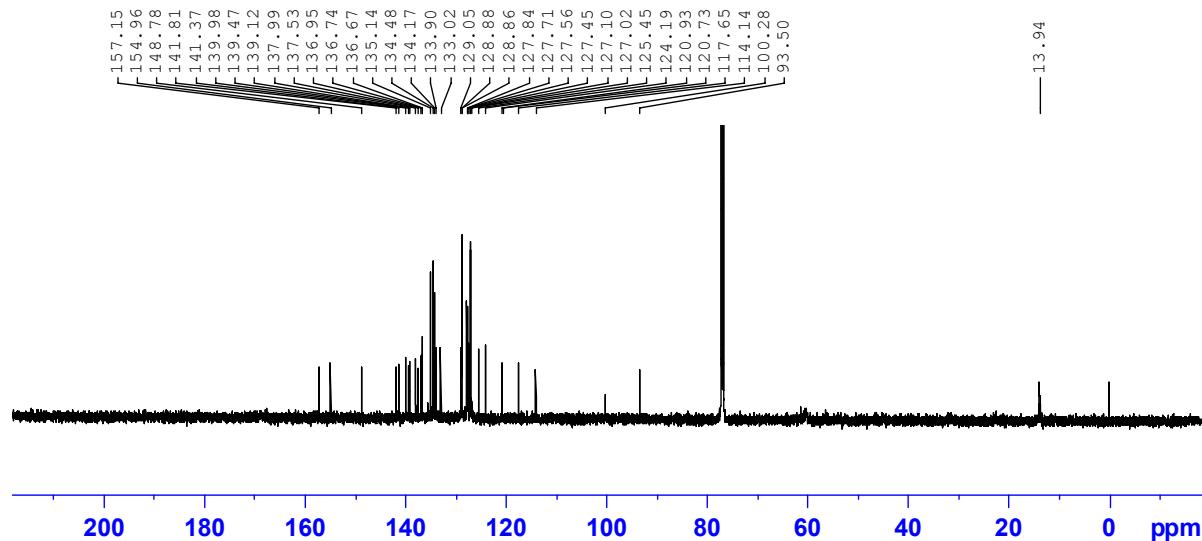




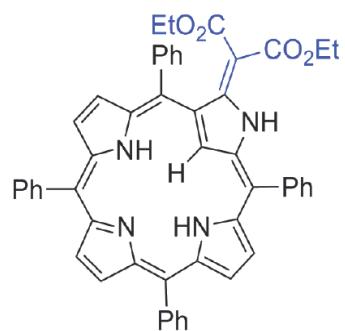
**Figure S38.** HRMS spectrum of **3h**.

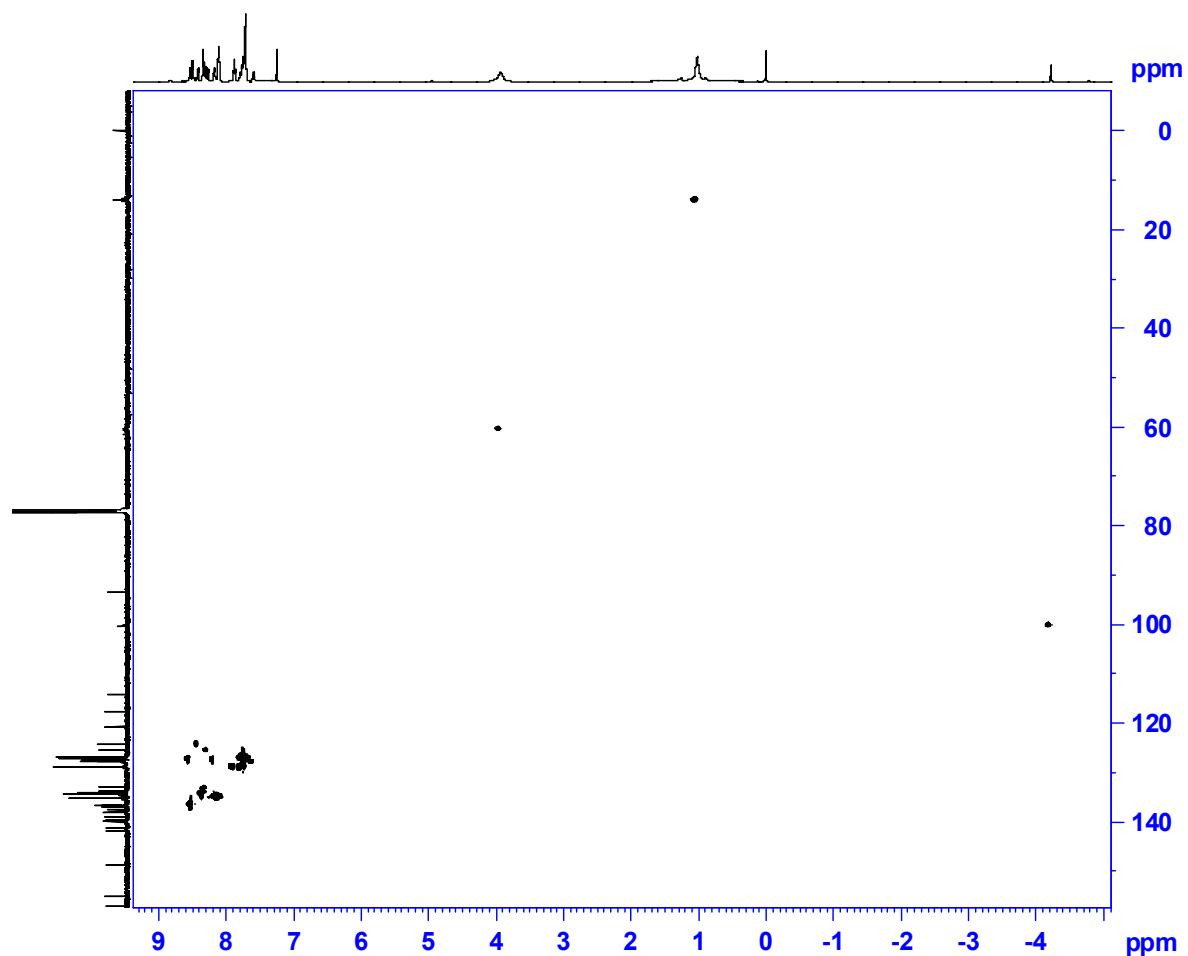


**Figure S39.** <sup>1</sup>H NMR spectrum of **3i** (298 K, CDCl<sub>3</sub>).

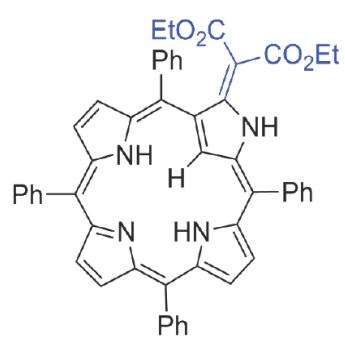


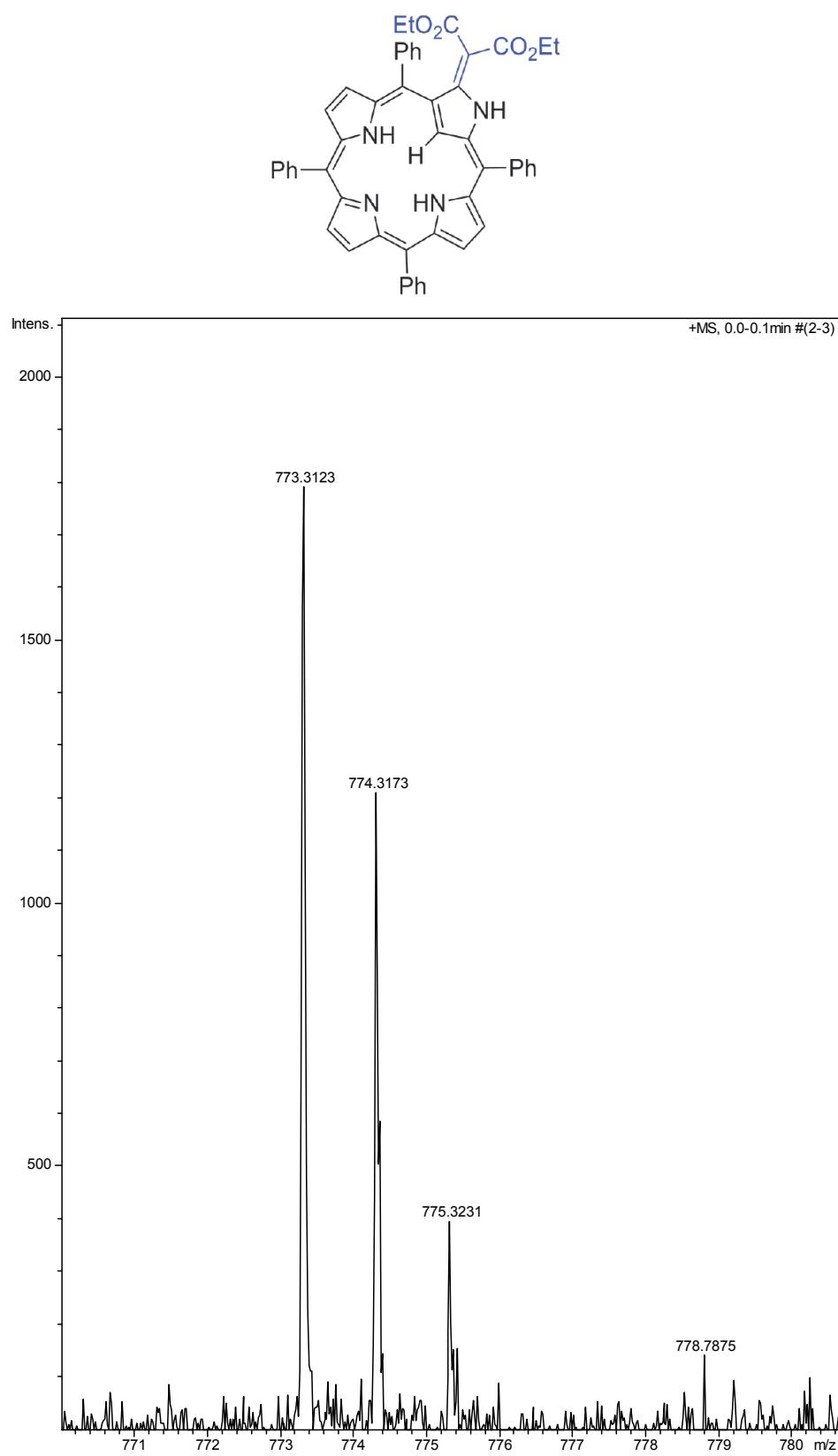
**Figure S40.** <sup>13</sup>C NMR spectrum of **3i** (298 K, CDCl<sub>3</sub>).



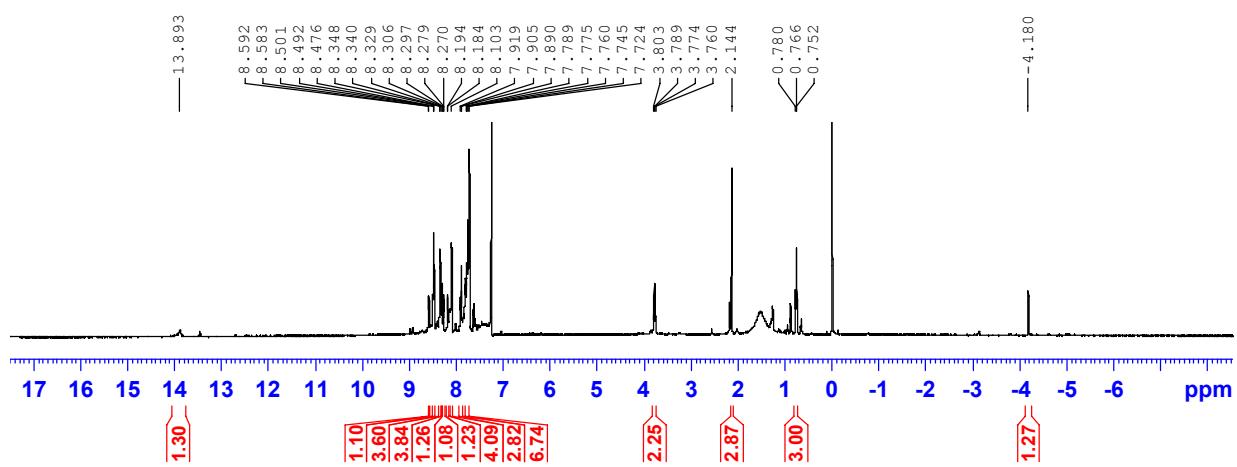


**Figure S41.** HSQC spectrum of **3i** ( $\text{CDCl}_3$ , 298 K).

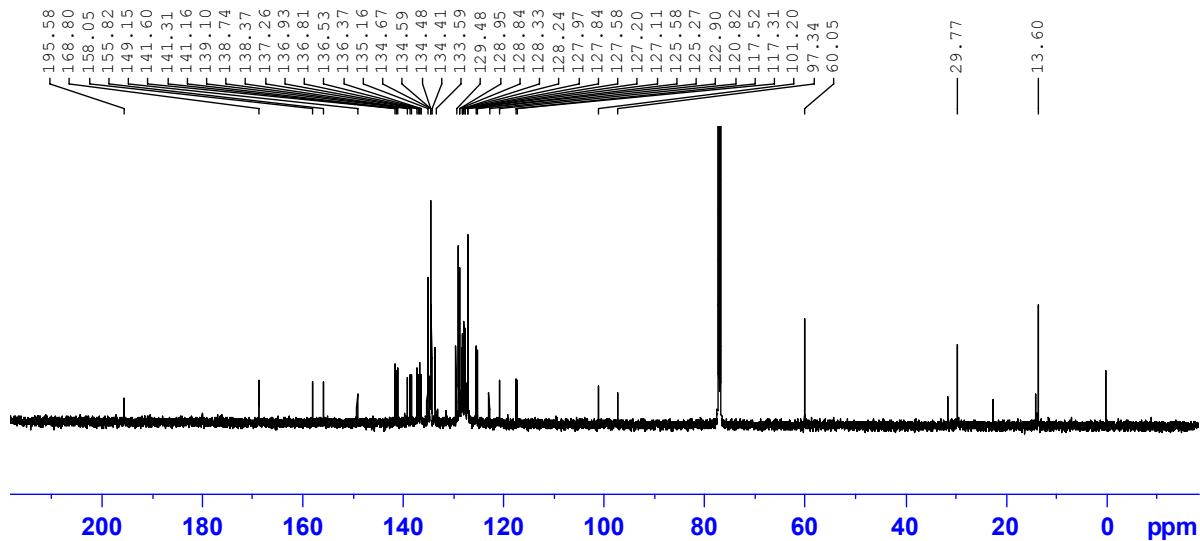




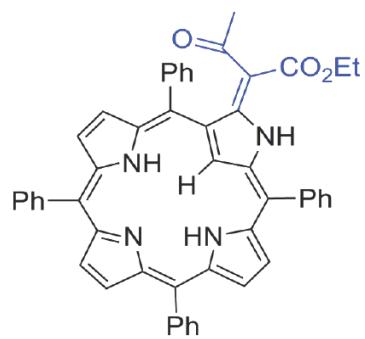
**Figure S42.** HRMS spectrum of **3i**.

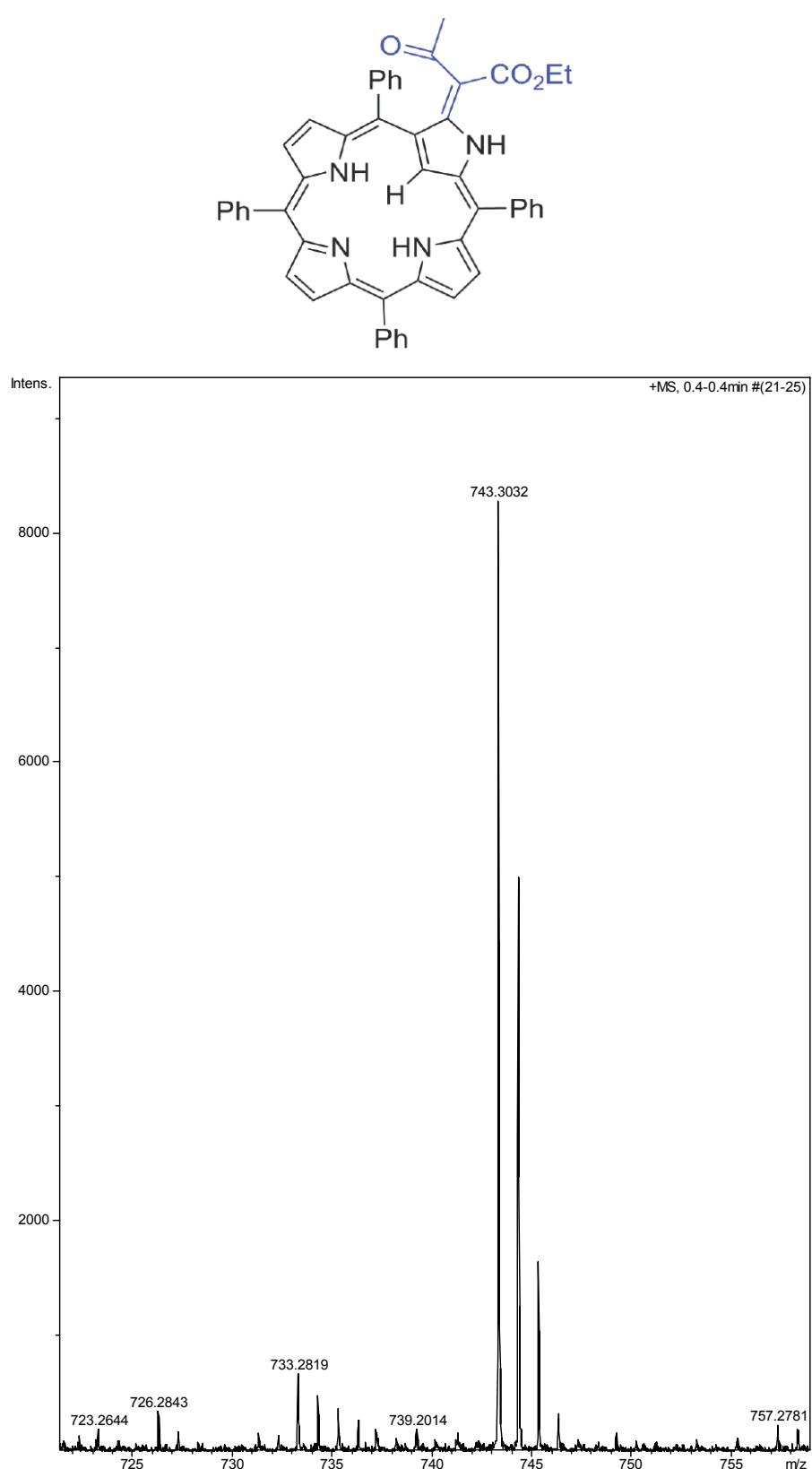


**Figure S43.** <sup>1</sup>H NMR spectrum of **3j** (298 K, CDCl<sub>3</sub>).

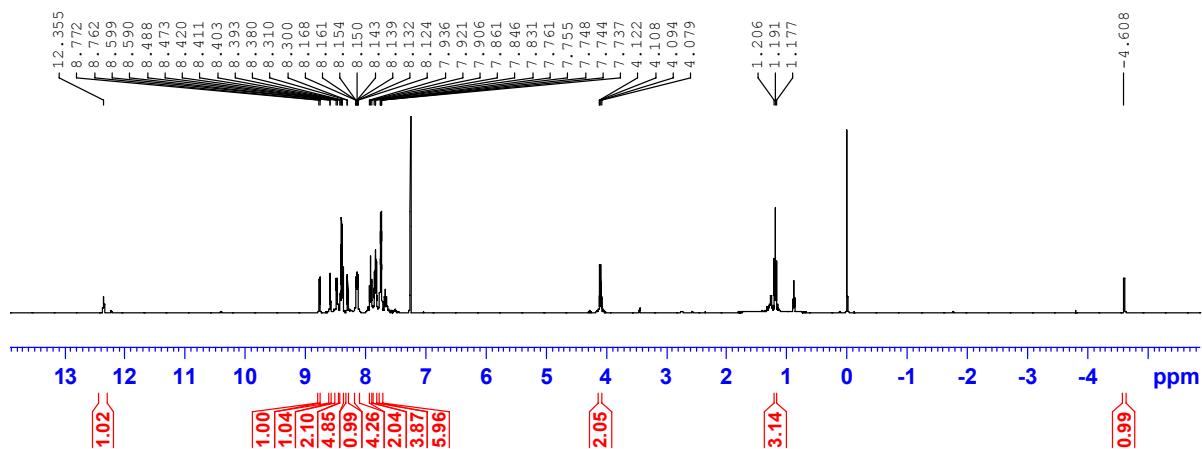


**Figure S44.** <sup>13</sup>C NMR spectrum of **3j** (298 K, CDCl<sub>3</sub>).

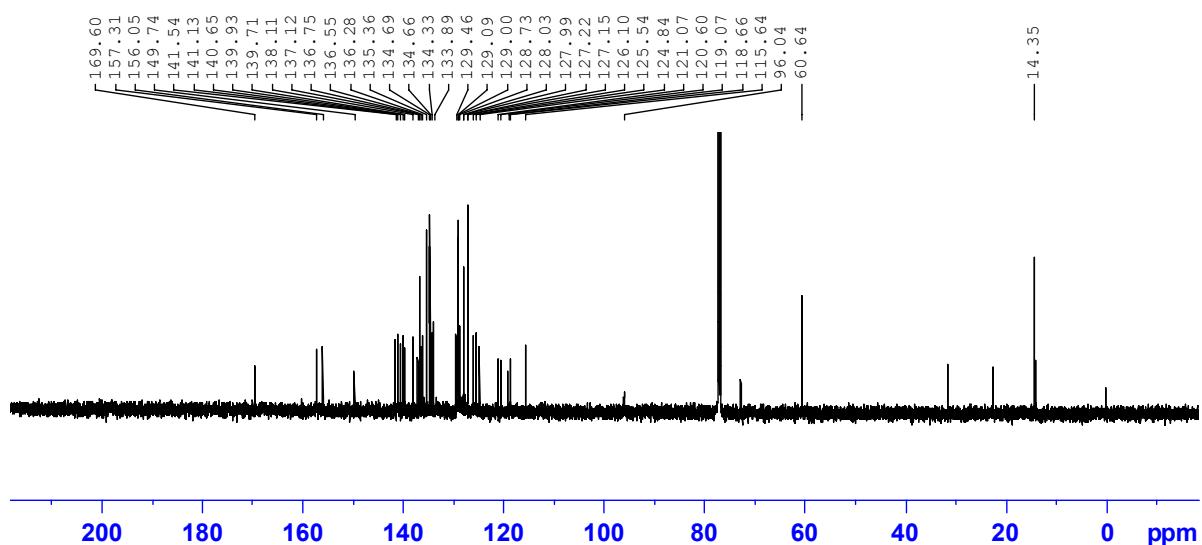




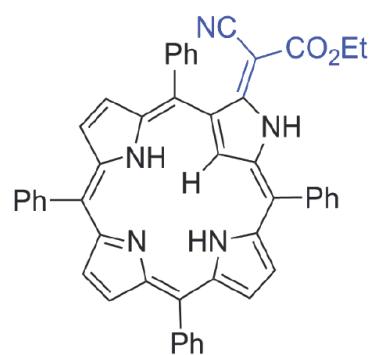
**Figure S45.** HRMS spectrum of 3j.

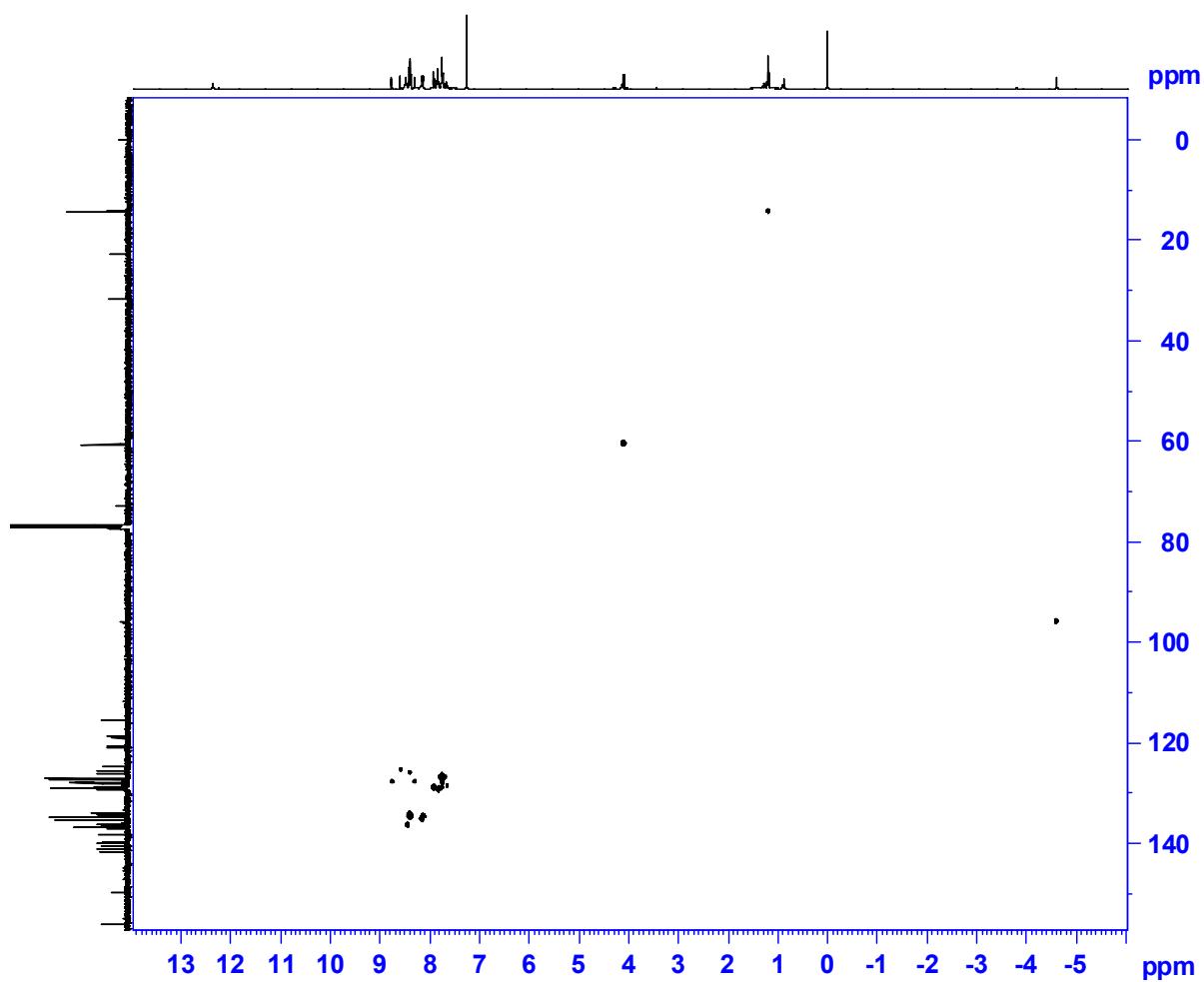


**Figure S46.**  $^1\text{H}$  NMR spectrum of **3k** (298 K,  $\text{CDCl}_3$ ).

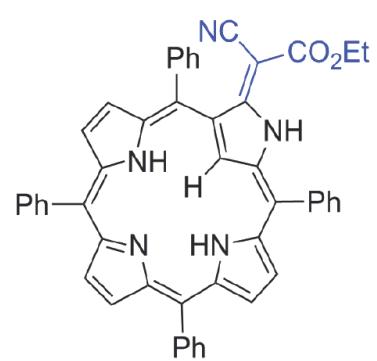


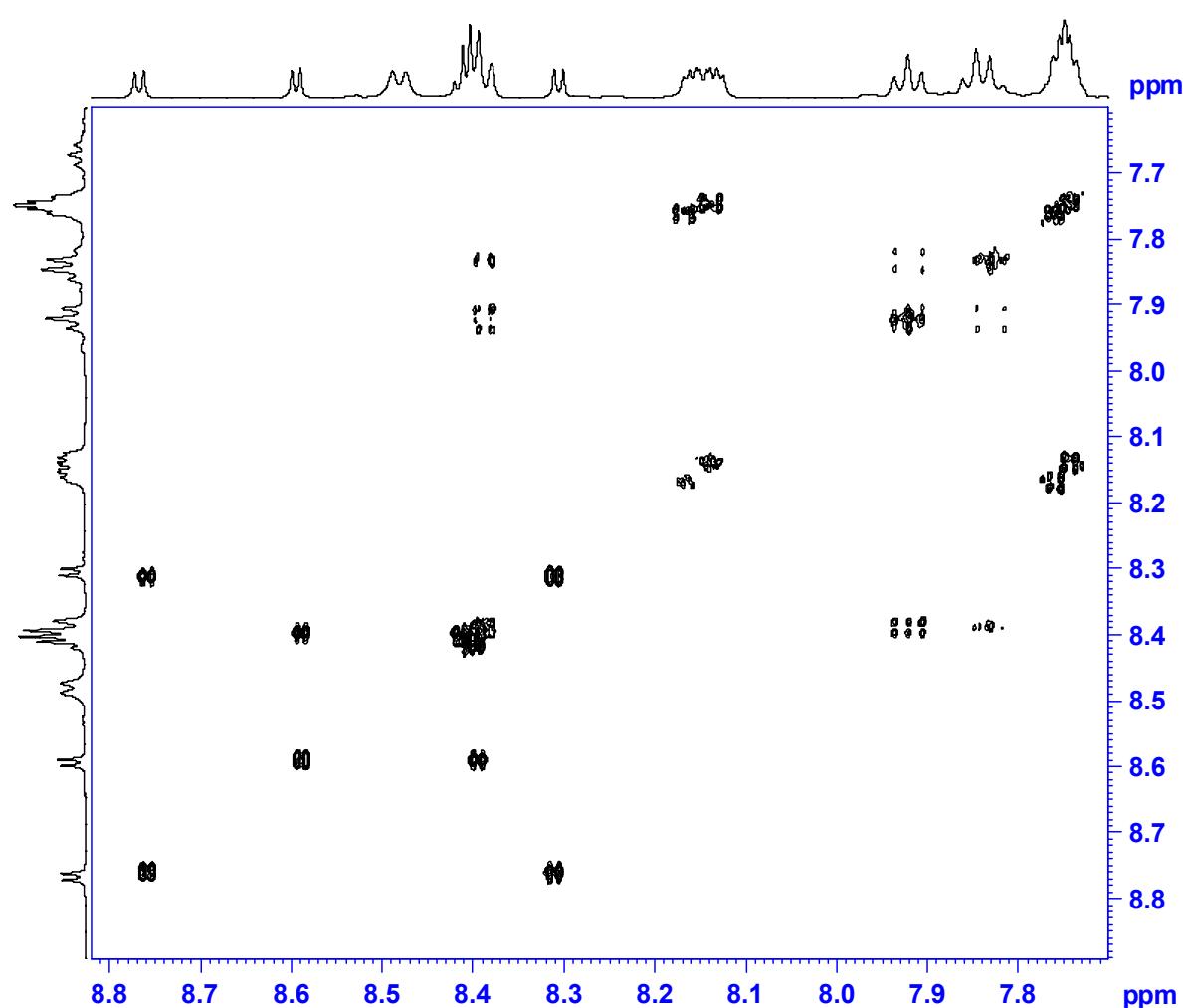
**Figure S47.**  $^{13}\text{C}$  NMR spectrum of **3k** (298 K,  $\text{CDCl}_3$ ).



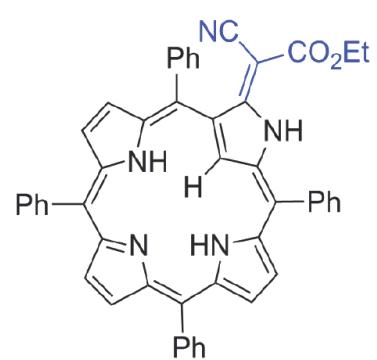


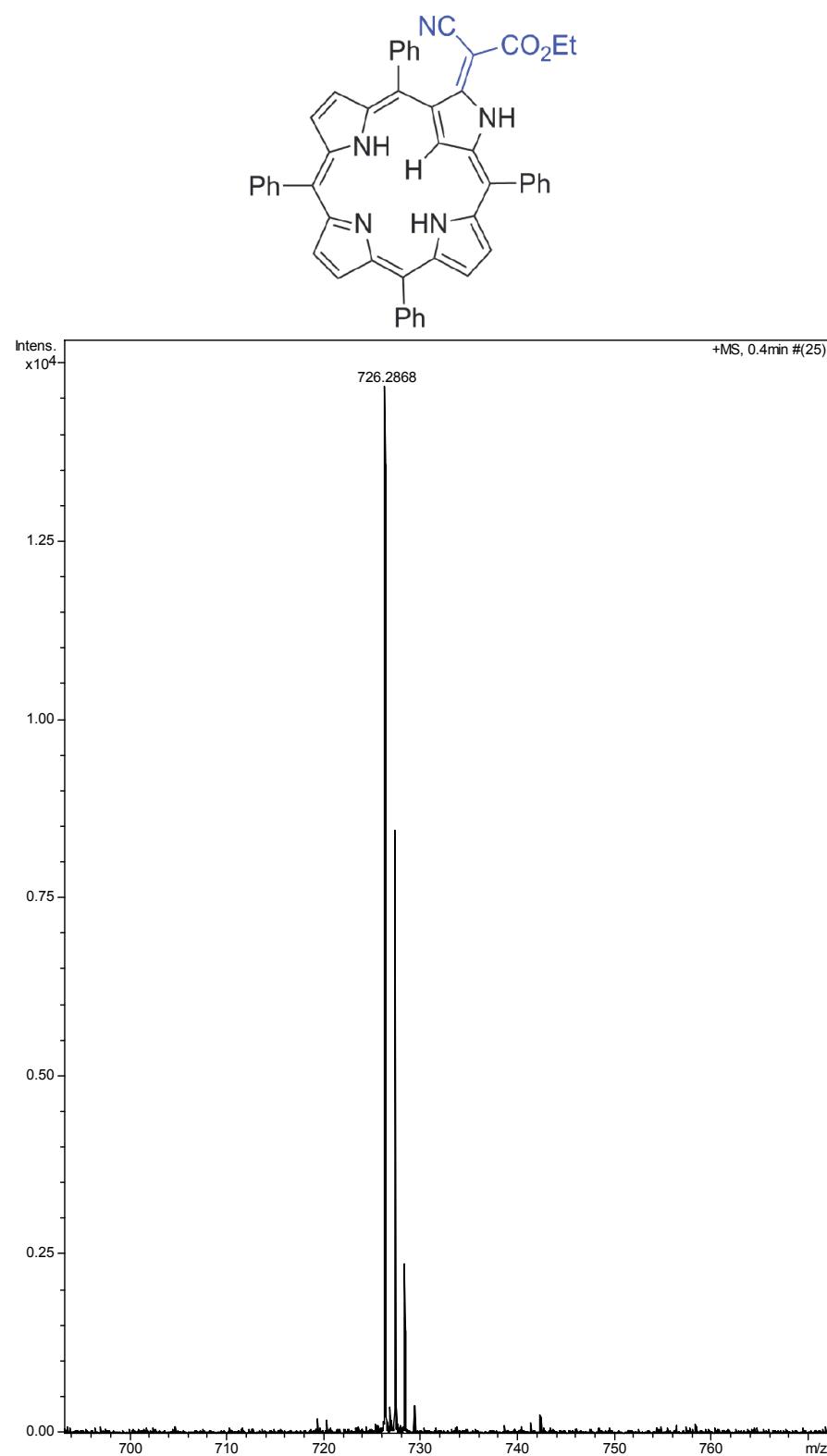
**Figure S48.** HSQC spectrum of **3k** ( $\text{CDCl}_3$ , 298 K).





**Figure S49.** COSY spectrum of **3k** (low-field part).





**Figure S50.** HRMS spectrum of **3k**.

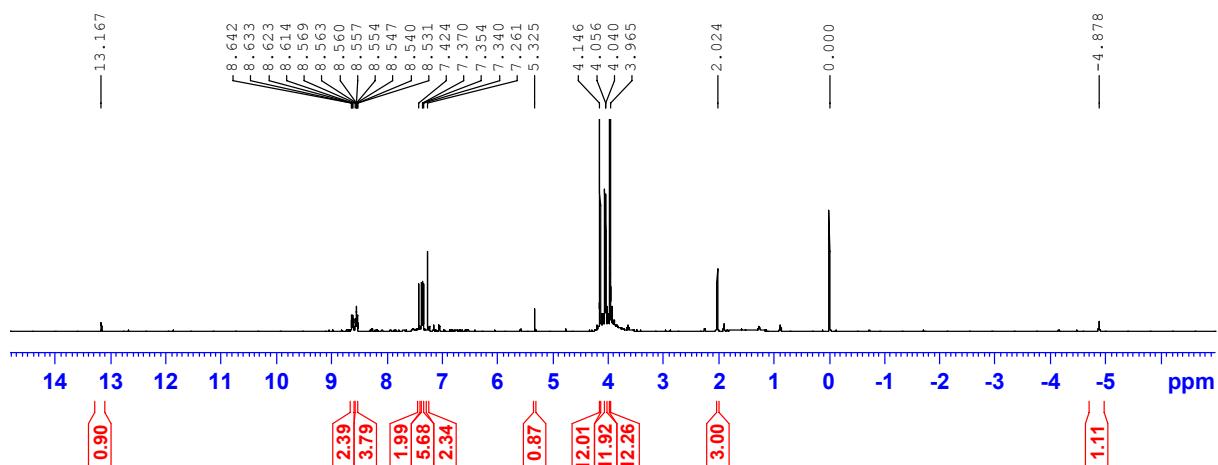


Figure S51. <sup>1</sup>H NMR spectrum of 3l.

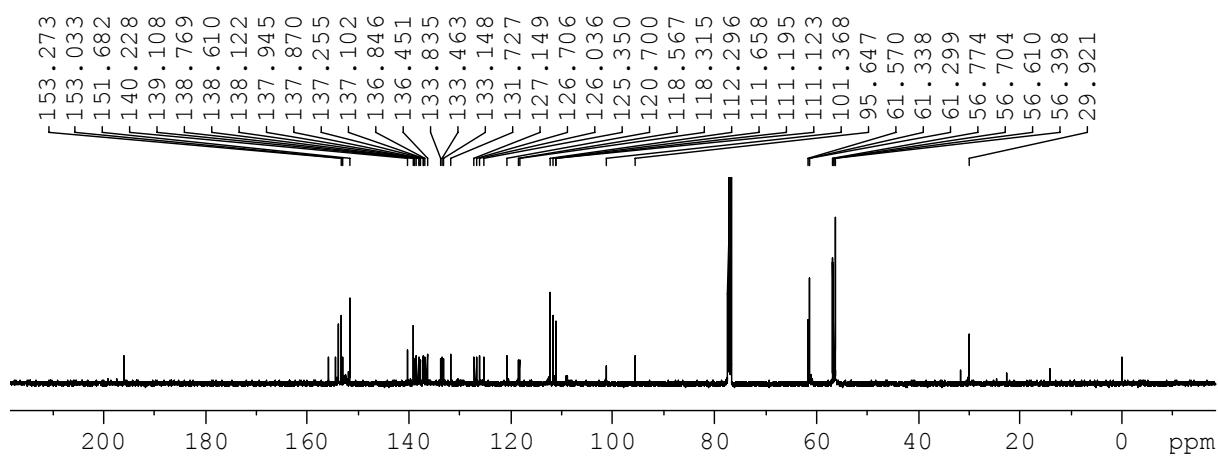
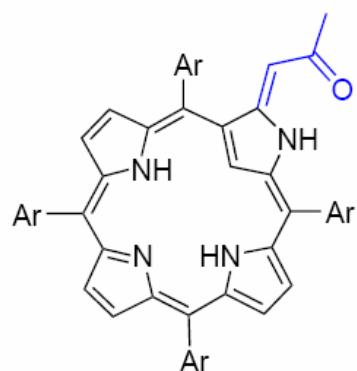
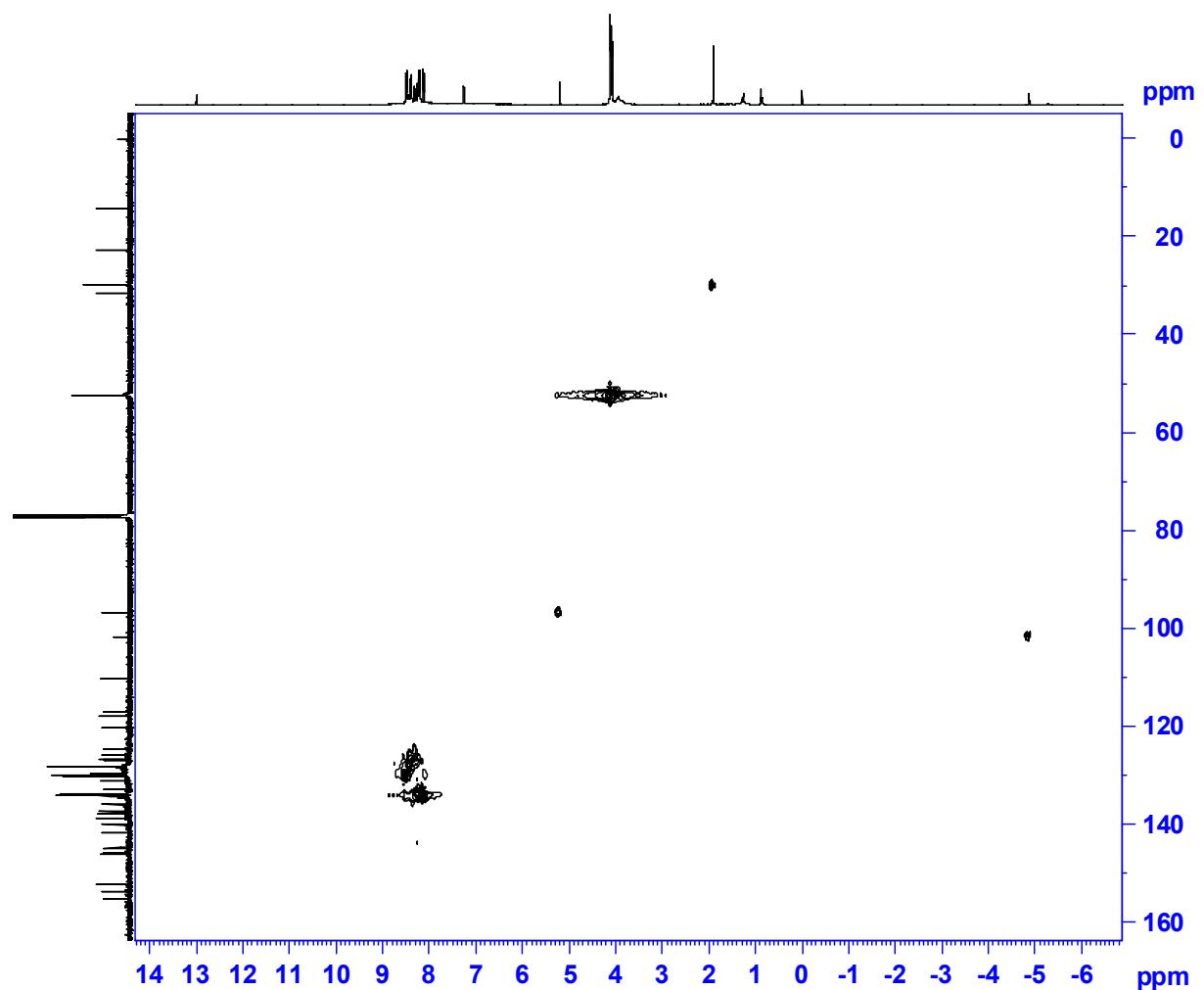


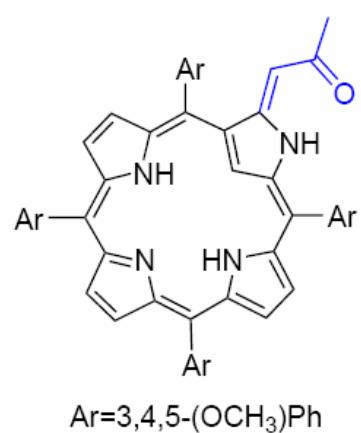
Figure S52. <sup>13</sup>C NMR spectrum of 3l.

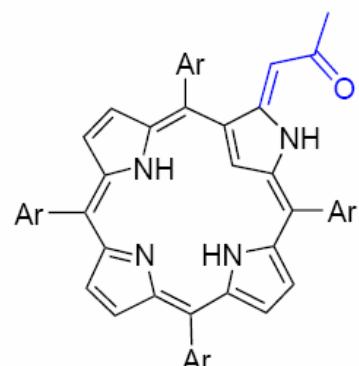


Ar=3,4,5-(OCH<sub>3</sub>)Ph

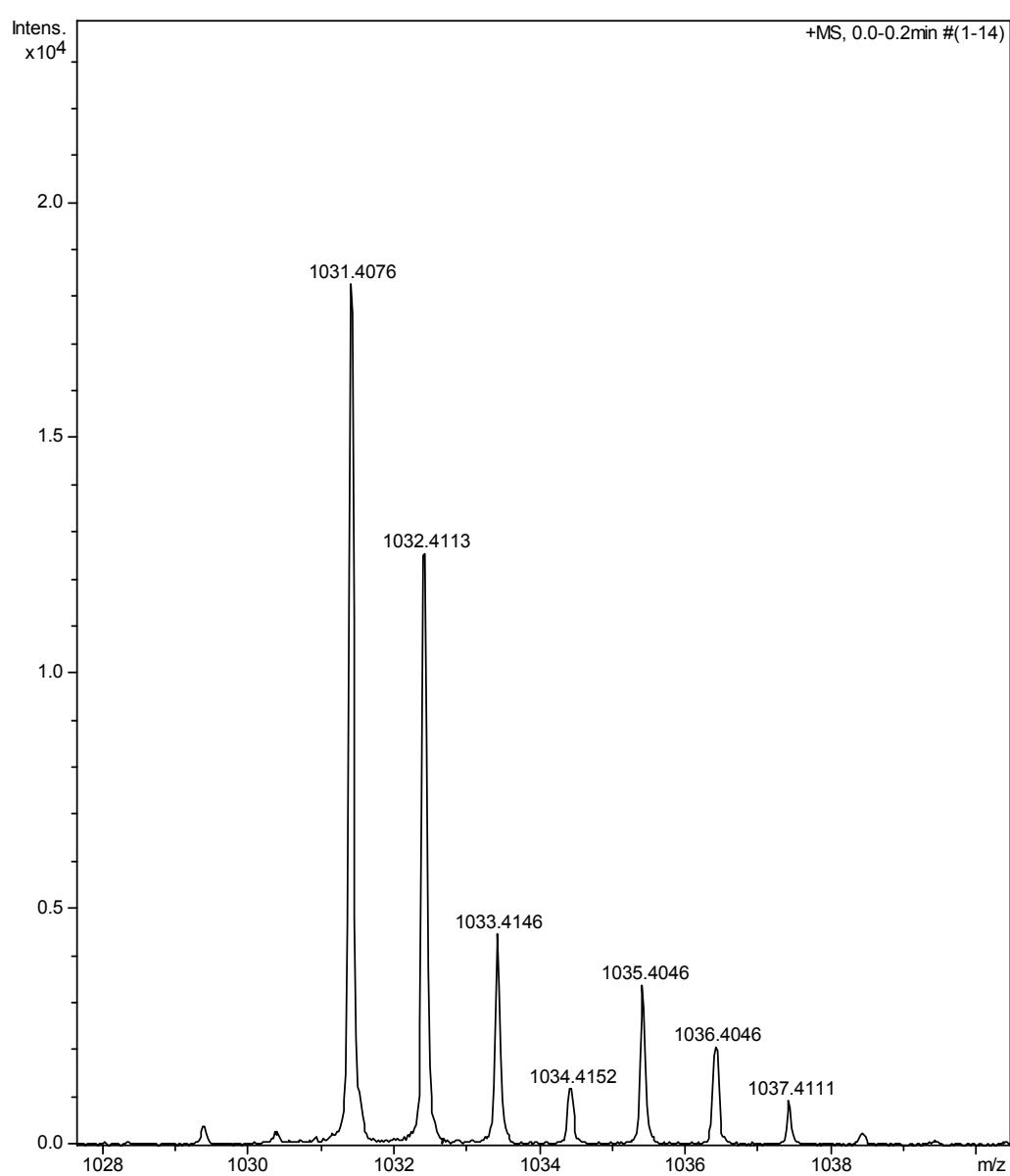


**Figure S53.** HSQC spectrum of **3l**.

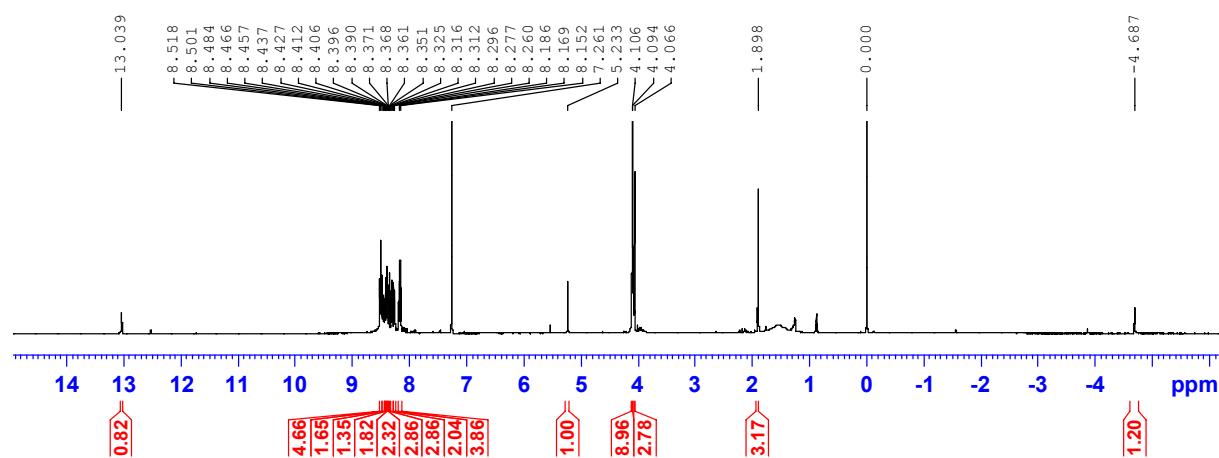




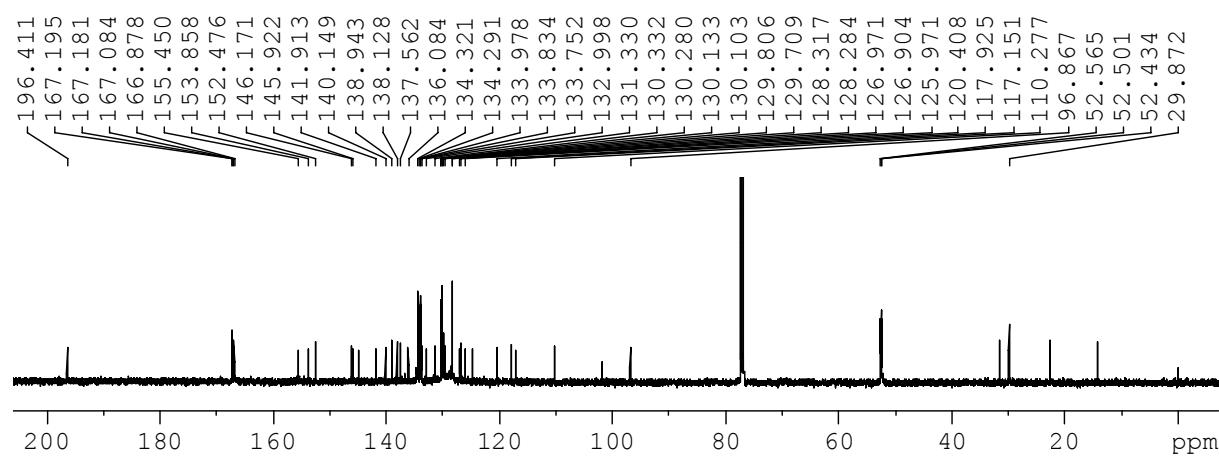
Ar=3,4,5-(OCH<sub>3</sub>)Ph



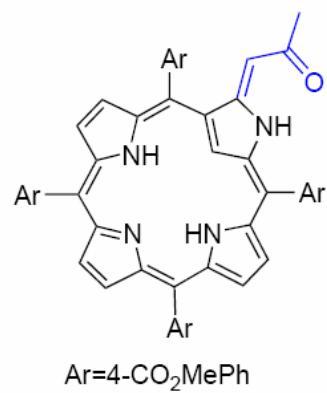
**Figure S54.** HRMS spectrum of **3l**.



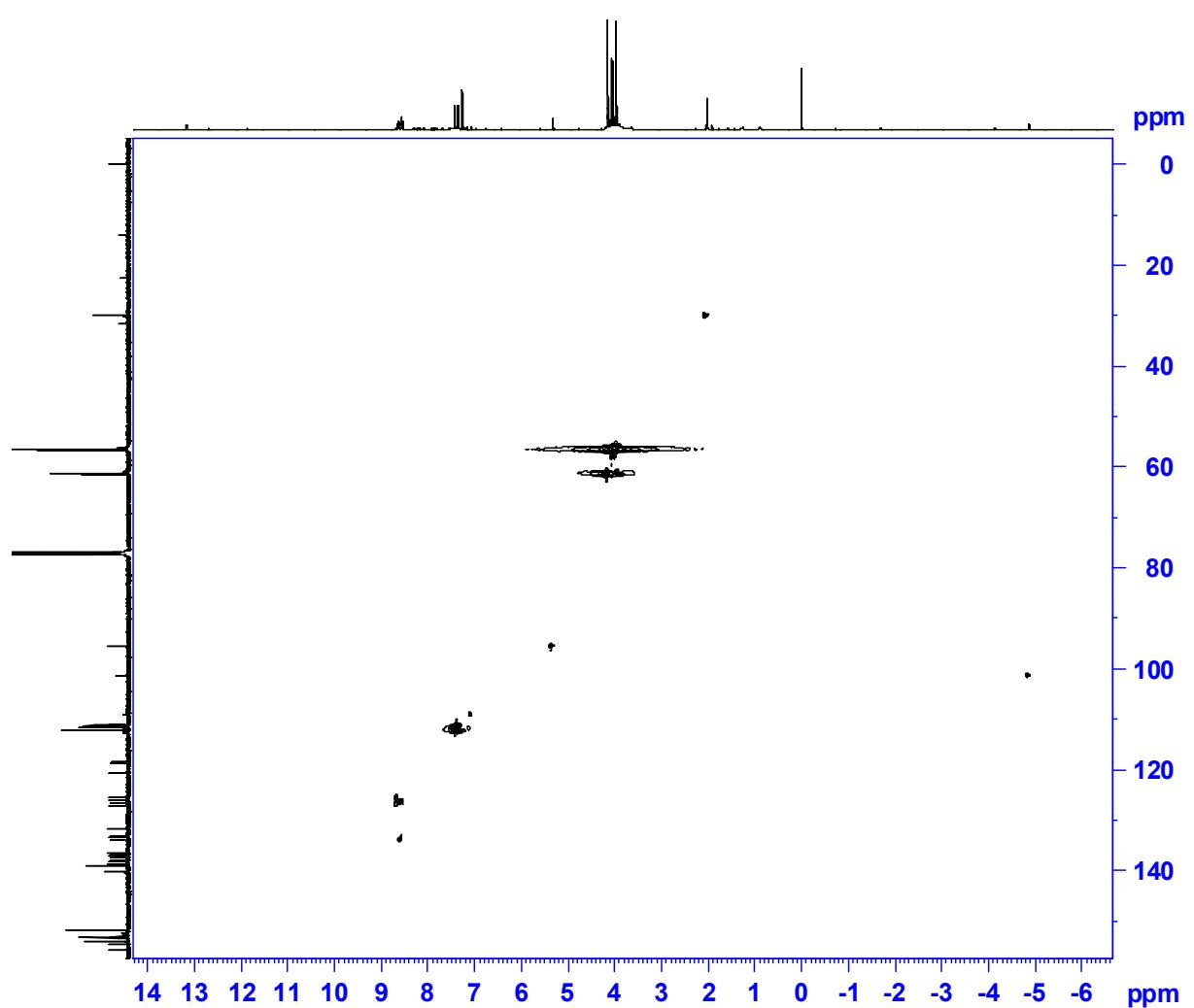
**Figure S55.**  $^1\text{H}$  NMR spectrum of **3m**.



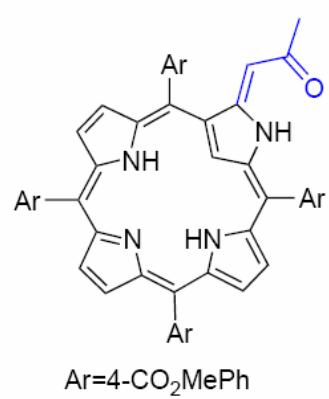
**Figure S56.**  $^{13}\text{C}$  NMR spectrum of **3m**.

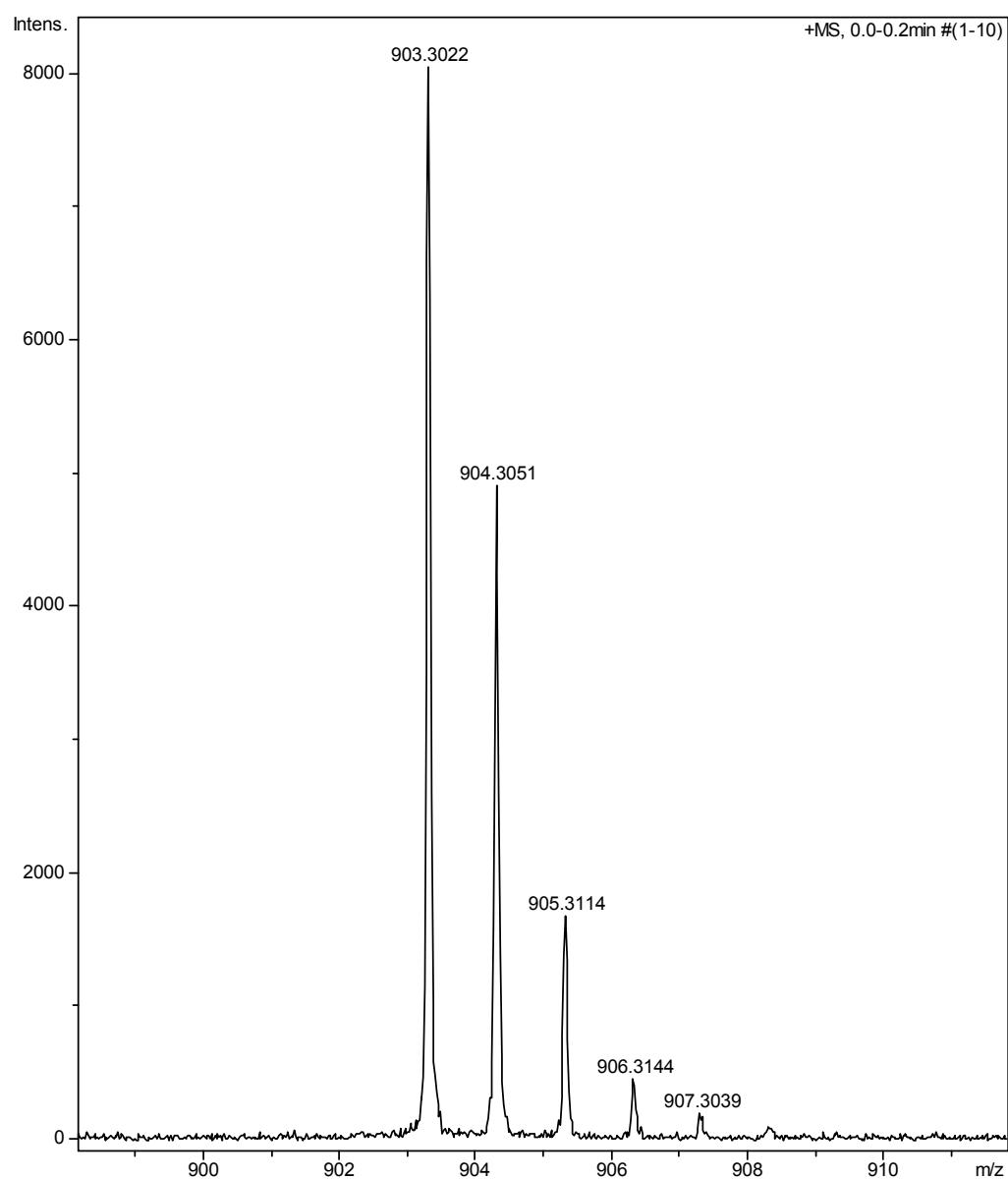
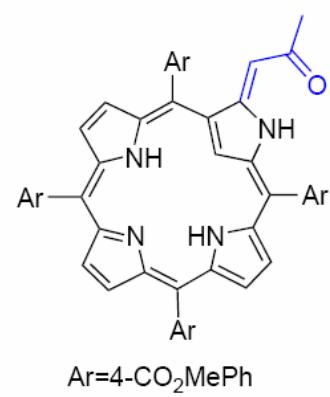


Ar=4-CO<sub>2</sub>MePh

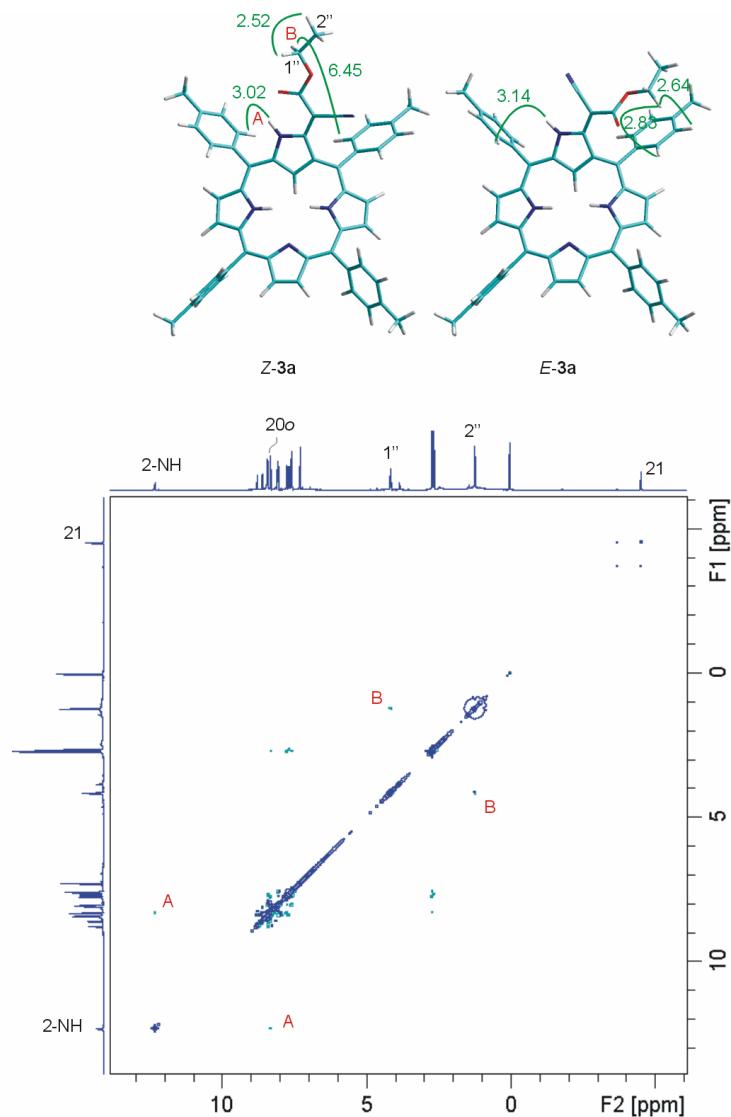


**Figure S57.** HSQC spectrum of **3m**.

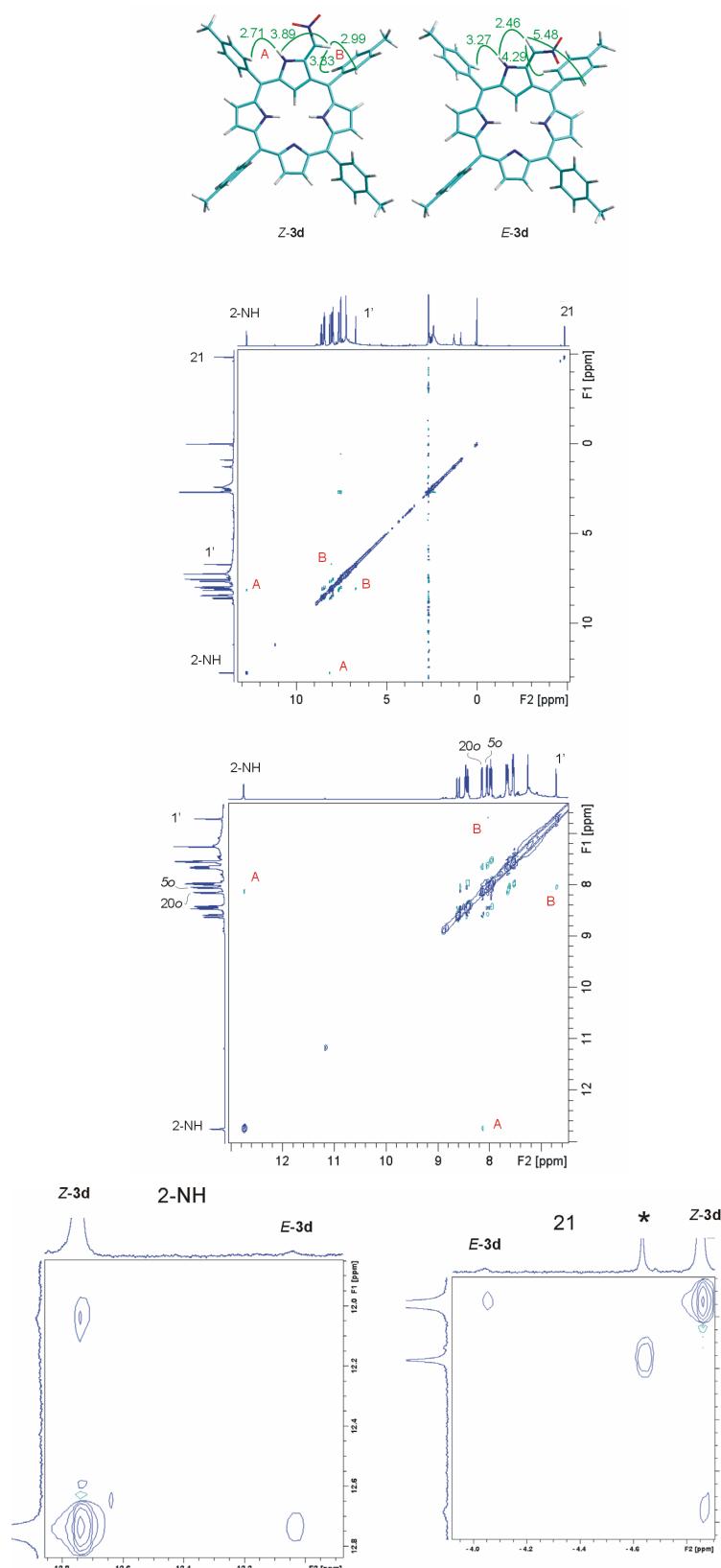




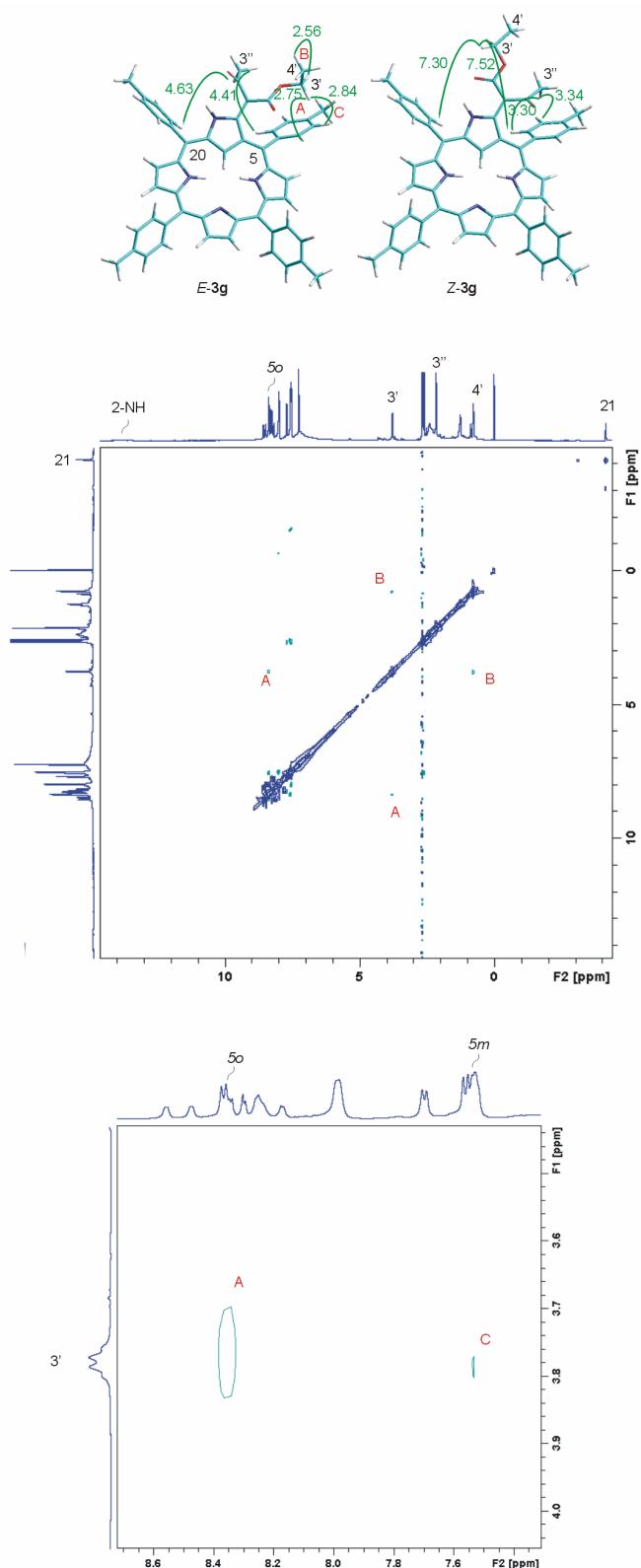
**Figure S58.** HRMS spectrum of **3m**.



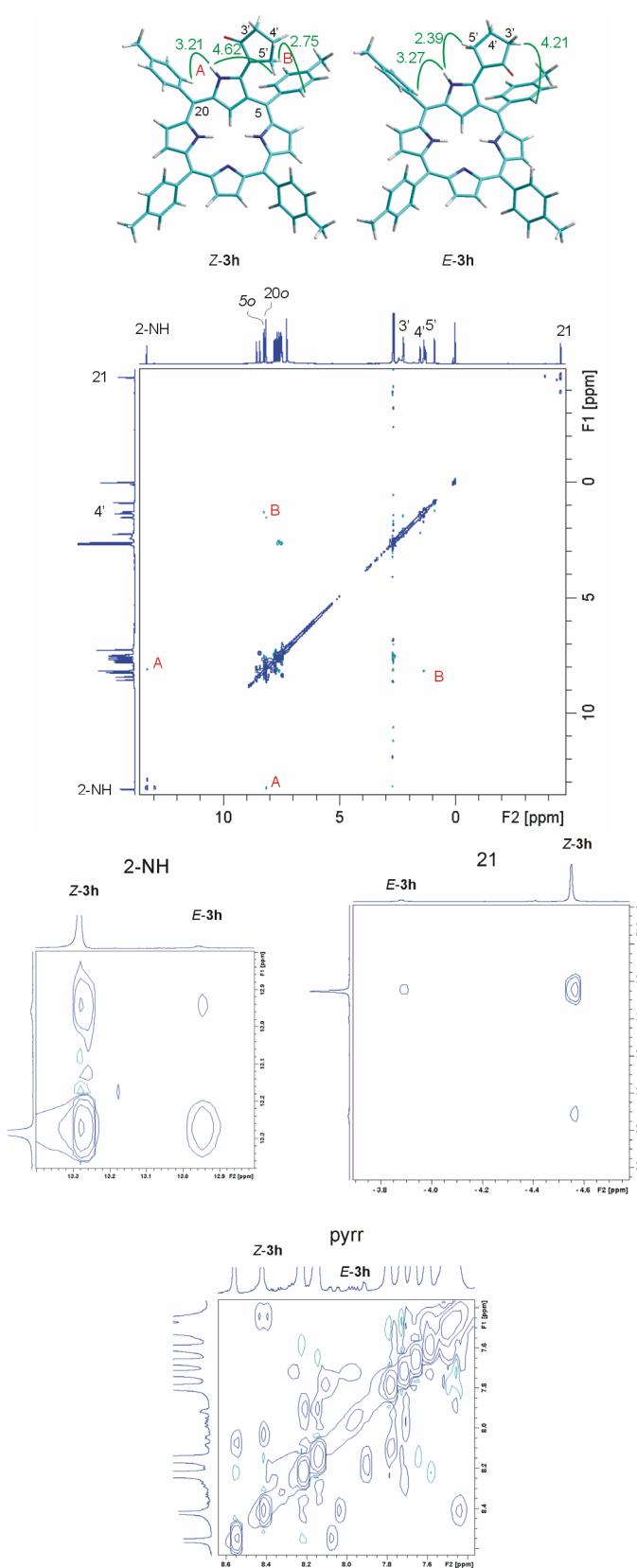
**Figure S59.** NOESY spectrum ( $\text{CDCl}_3$ , 300 K) and PM3 energy-optimized models of **3a**. The numbers associated with green curved lines are proton-proton distances measured for the models, while red letters denote NOE interactions observed in the NOESY map.



**Figure S60.** NOESY spectrum ( $\text{CDCl}_3$ , 300 K) and PM3 energy-optimized models of **3d**. The numbers associated with green curved lines are proton-proton distances measured for the models, while red letters denote NOE interactions observed in the NOESY map. The extended fragments of the map in the bottom row show chemical exchange (EXSY) correlations between stereoisomers. A signal of a by-product is denoted by asterisk.



**Figure S61.** NOESY spectrum ( $\text{CDCl}_3$ , 300 K) and PM3 energy-optimized models of **3g**. The numbers associated with green curved lines are proton-proton distances measured for the models, while red letters denote NOE interactions observed in the NOESY map.



**Figure S62.** NOESY spectrum ( $\text{CDCl}_3$ , 300 K) and PM3 energy-optimized models of **3h**. The numbers associated with green curved lines are proton-proton distances measured for the models, while red letters denote NOE interactions observed in the NOESY map. The extended fragments of the map in the bottom rows show chemical exchange (EXSY) correlations between stereoisomers (blue cross-peaks).