

# European Journal of Organic Chemistry

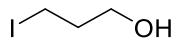
## Supporting Information

### Total Synthesis of Phenanthropiperidine Alkaloids by Sequential Alkylation of *N,N*-Dibenzylaminoacetonitrile

Christelle Bouvry, Milène Franzetti, Jean-François Cupif, and Jean-Pierre Hurvois\*

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**S2–S117** : Copies of the proton and carbon NMR spectra for the preparation of derivatives **1–19**.



3-iodopropan-1-ol

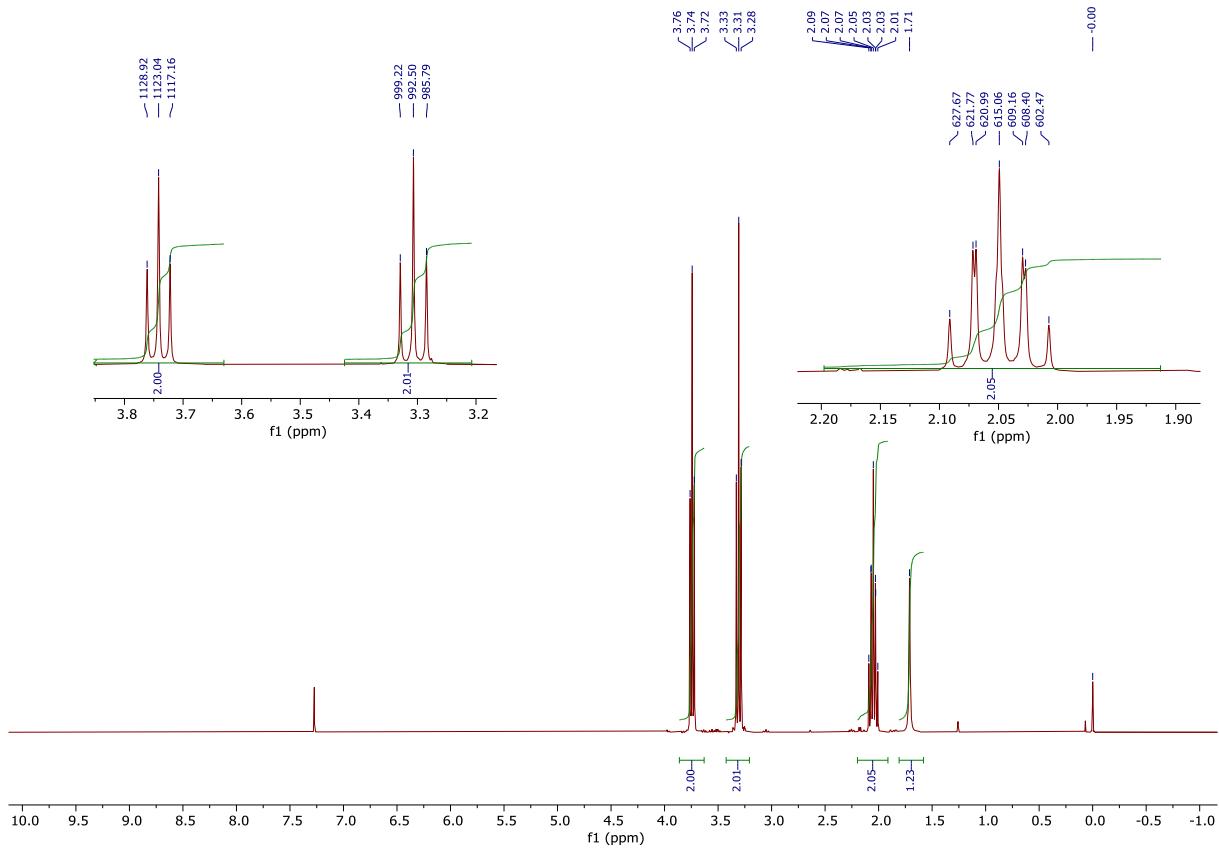


Figure S1. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 300 MHz) of 3-iodopropan-1-ol.

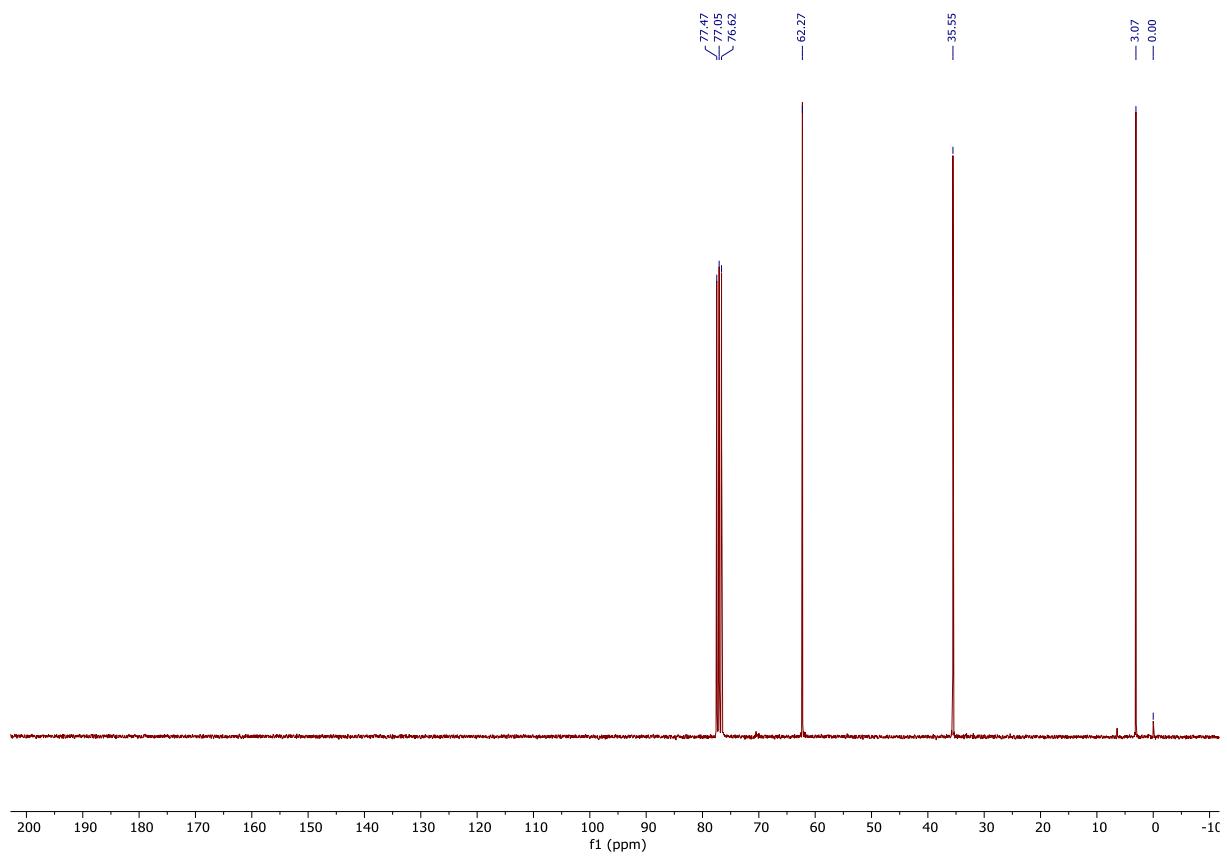


Figure S2.  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 75 MHz) of 3-iodopropan-1-ol.

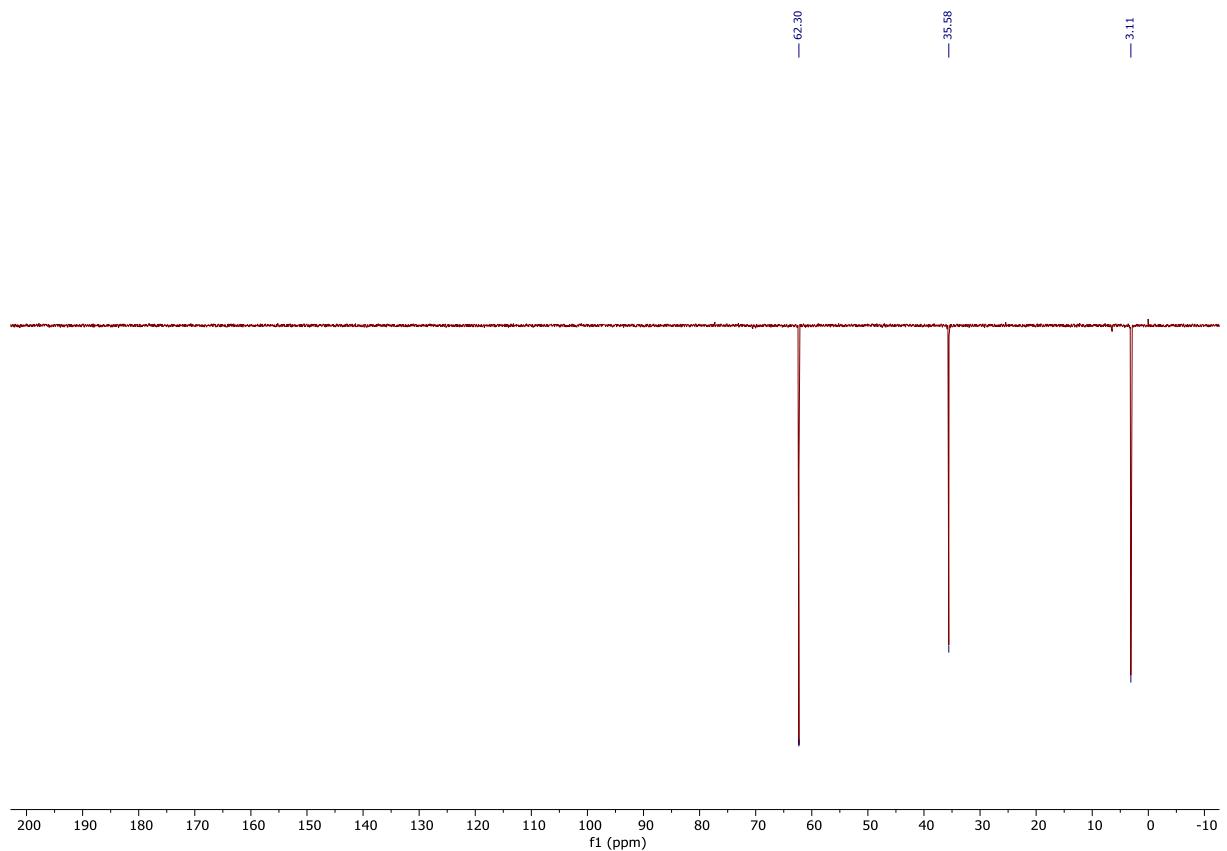


Figure S3. DEPT spectrum ( $\text{CDCl}_3$ , 75 MHz) of 3-iodopropan-1-ol.

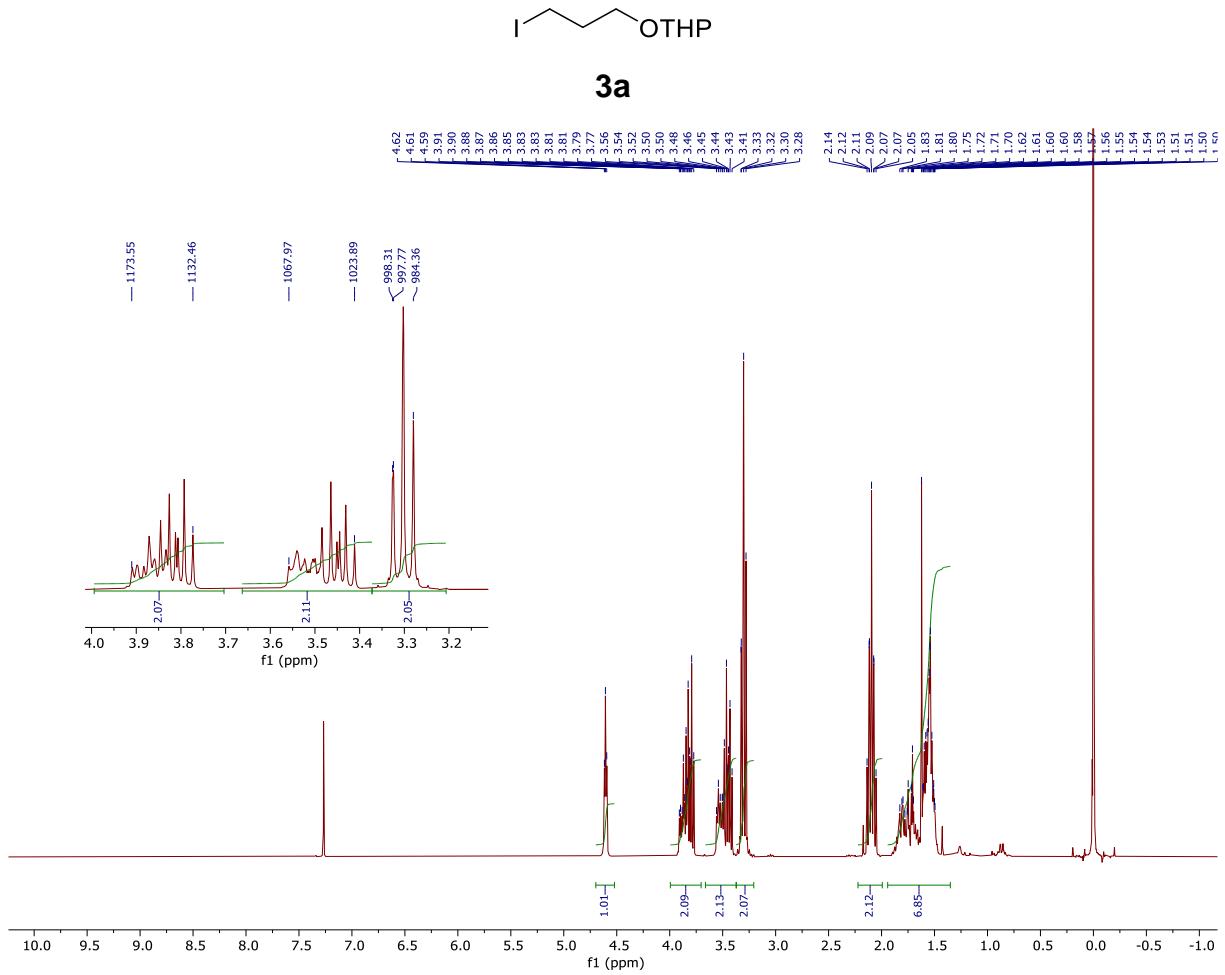


Figure S4. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 300 MHz) of derivative **3a**.

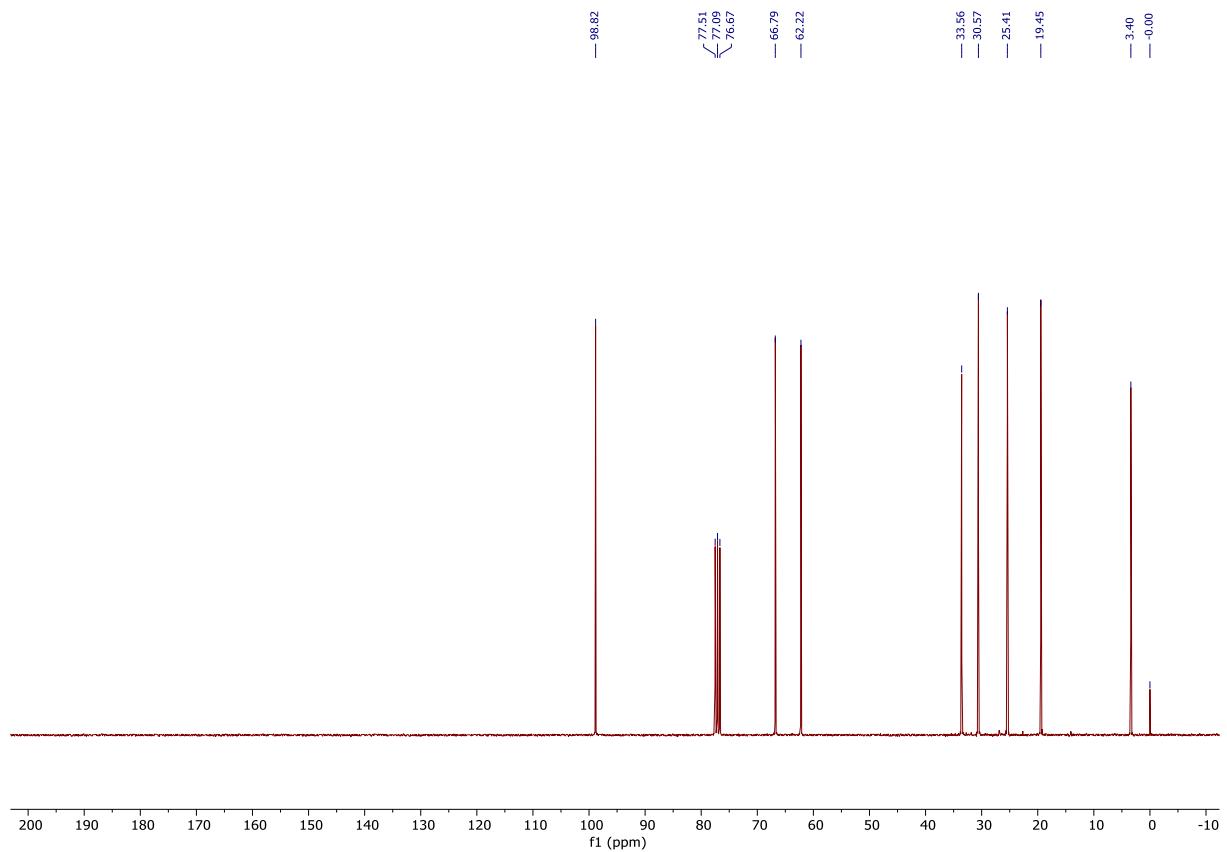


Figure S5.  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 75 MHz) of derivative **3a**.

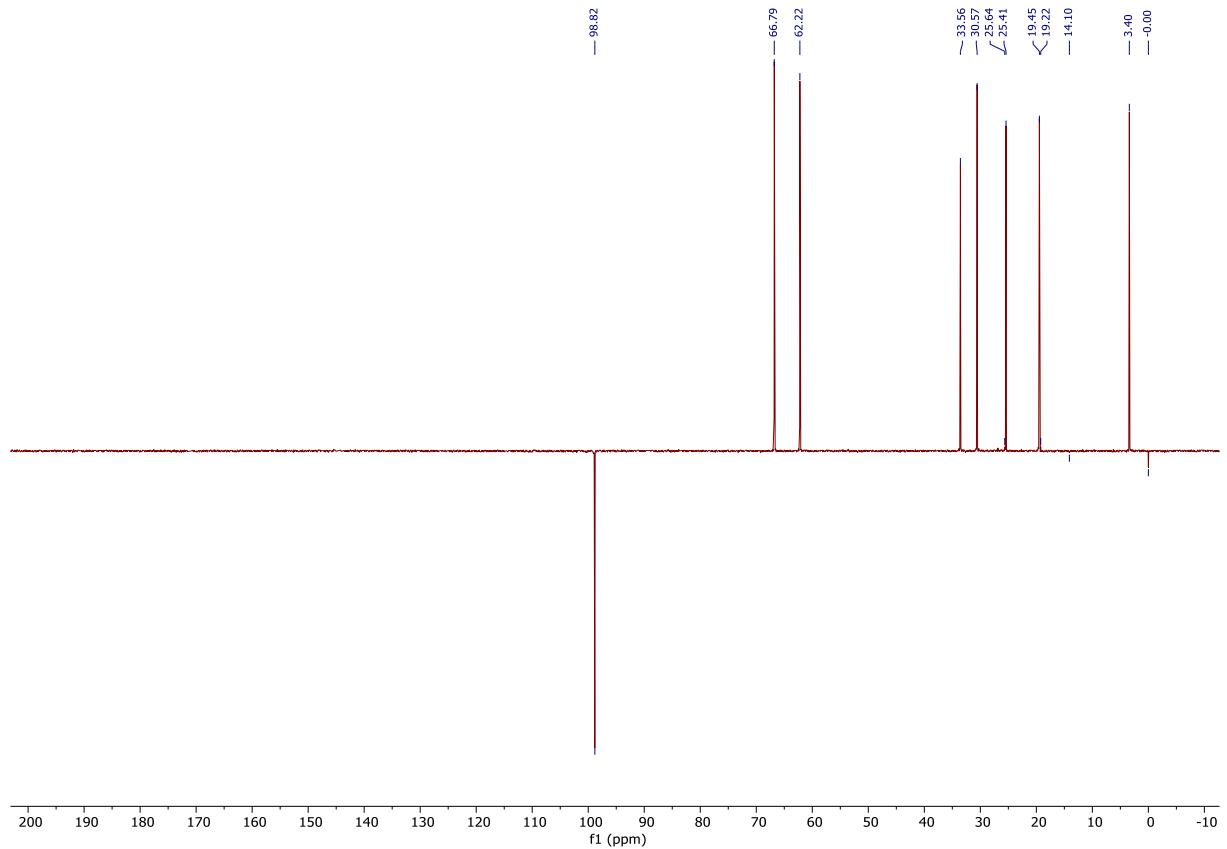


Figure S6. DEPT spectrum ( $\text{CDCl}_3$ , 75 MHz) of derivative **3a**.

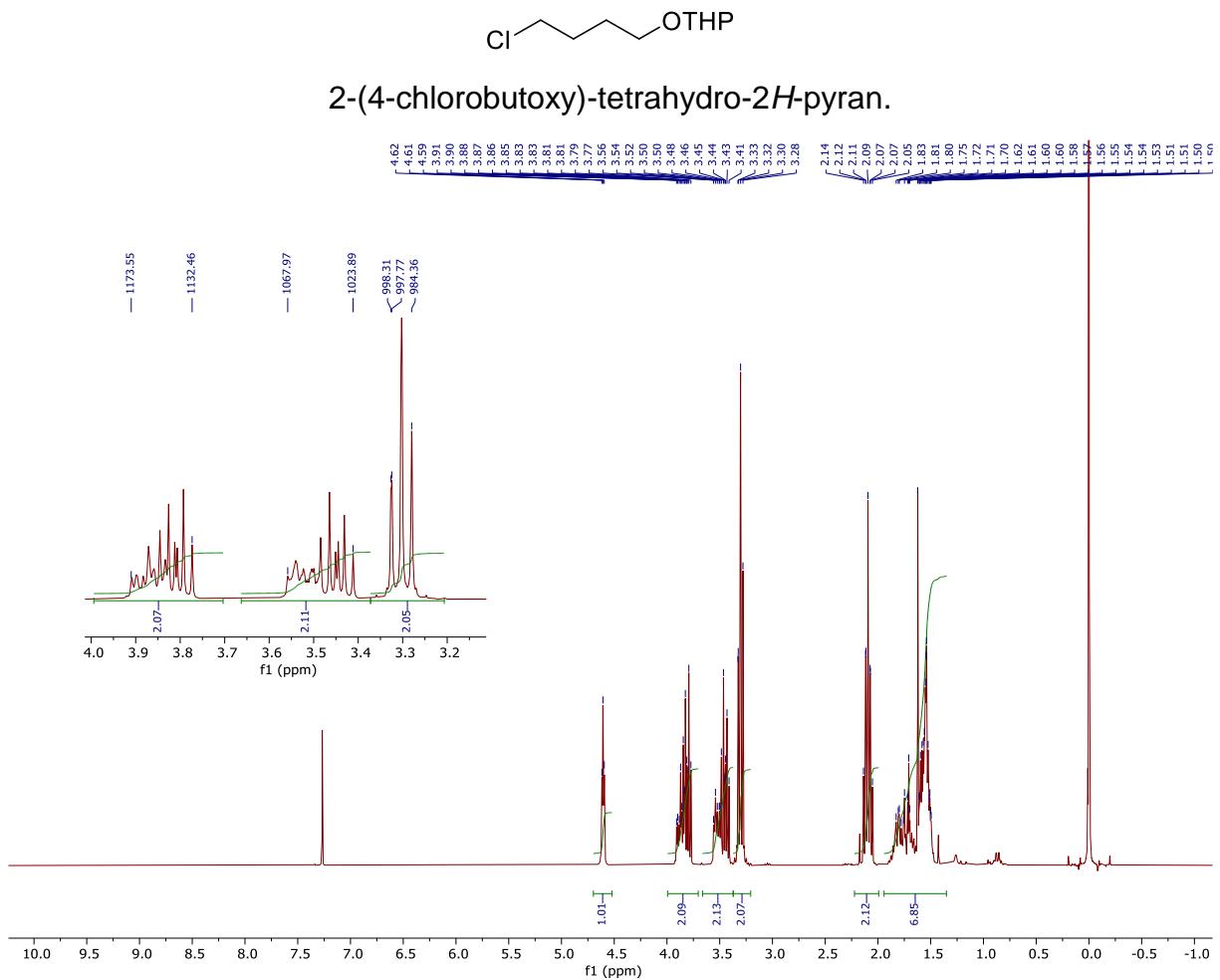


Figure S7. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 300 MHz) of 2-(4-chlorobutoxy)-tetrahydro-2*H*-pyran.

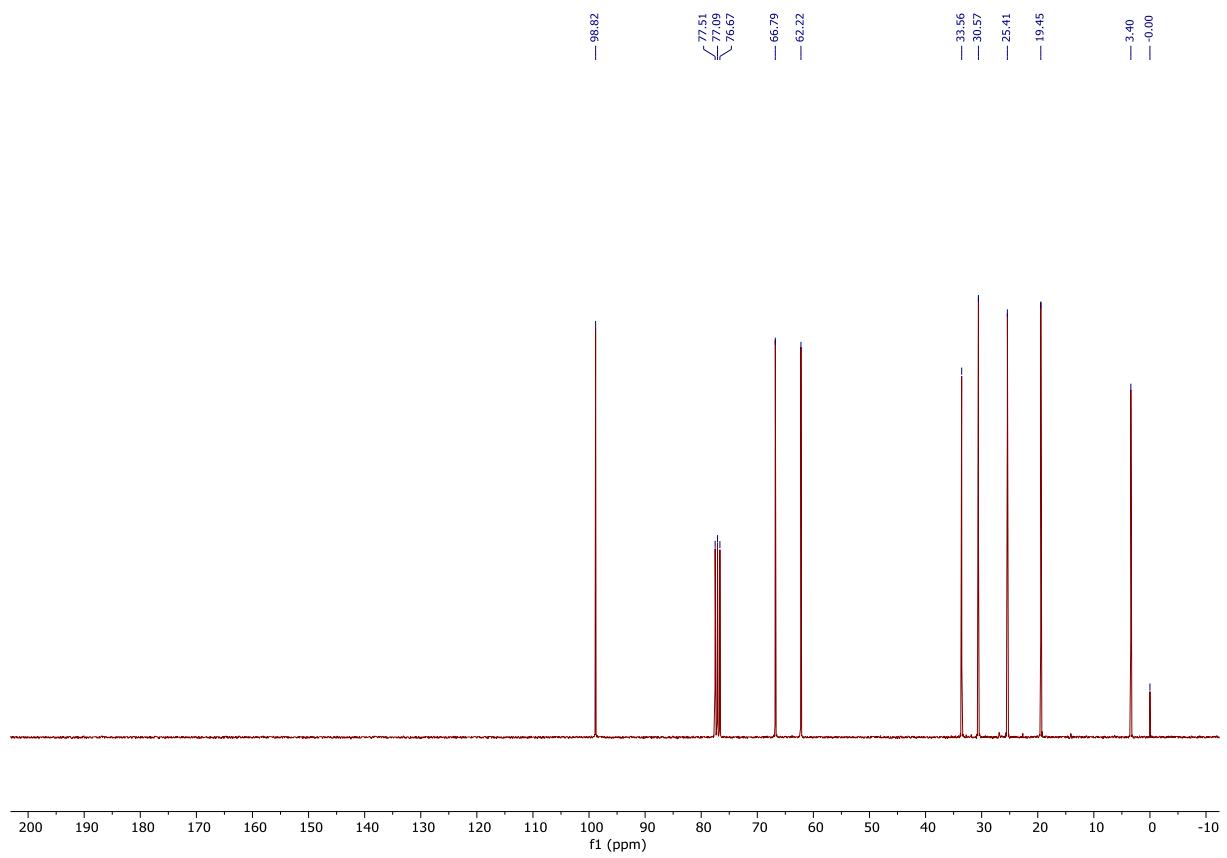
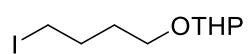


Figure S8.  $^{13}\text{C}$  NMR spectrum (CDCl<sub>3</sub>, 75 MHz) of 2-(4-chlorobutoxy)-tetrahydro-2*H*-pyran.



**3b**

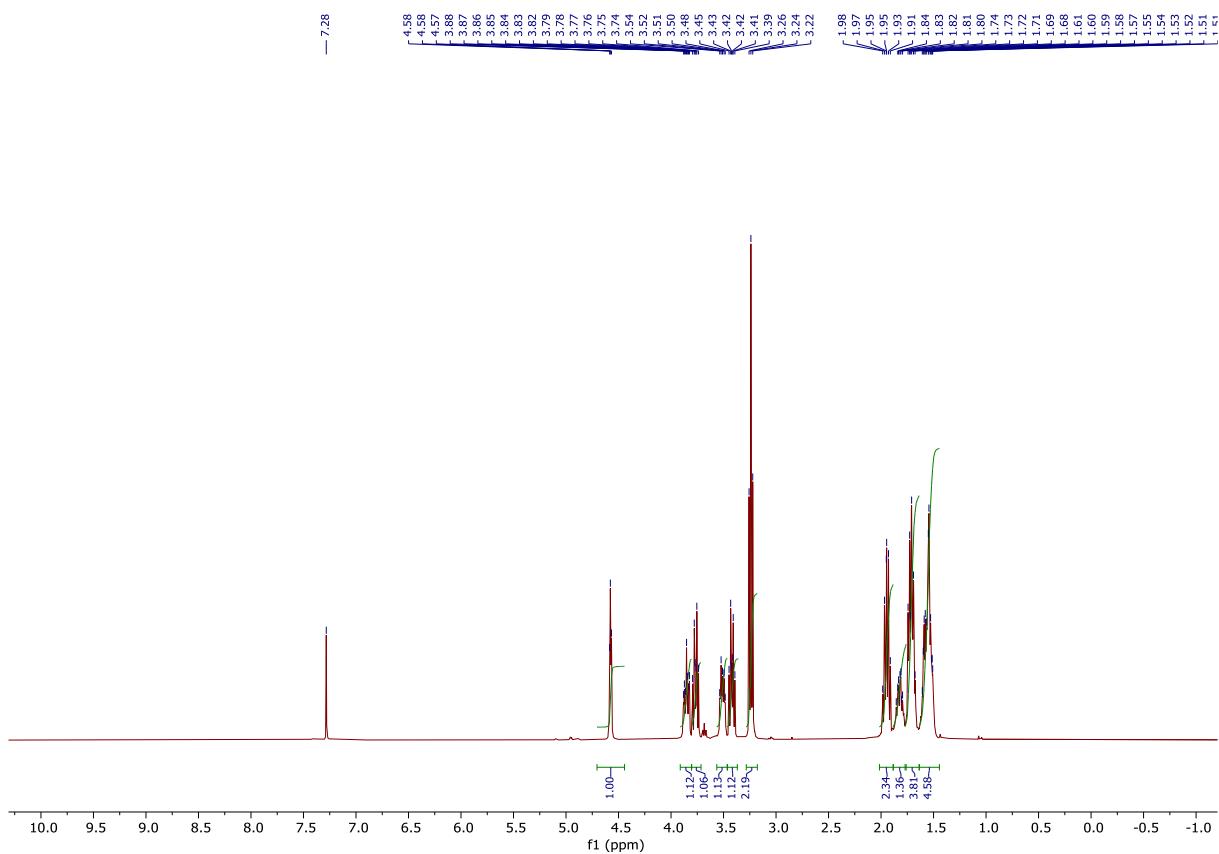


Figure S9. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of derivative **3b**.

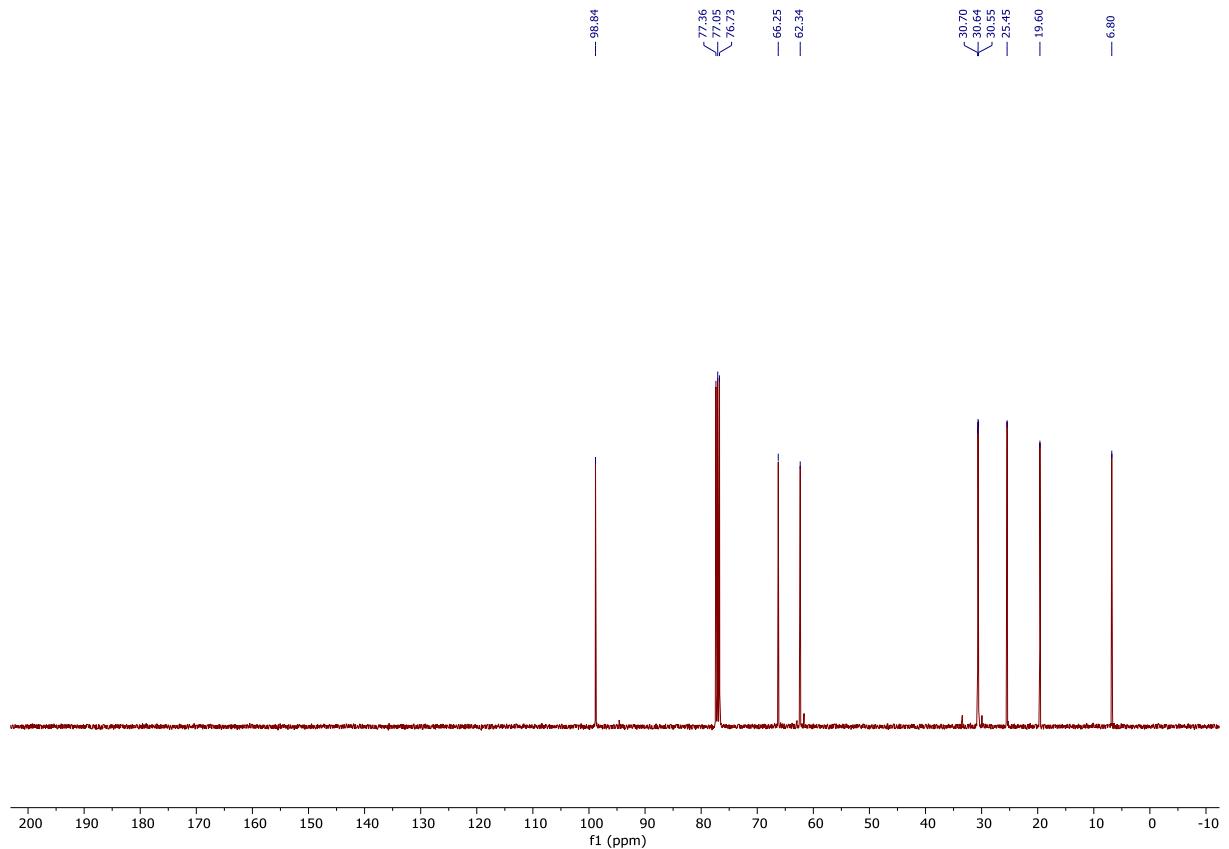


Figure S10. <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 100 MHz) of derivative **3b**.

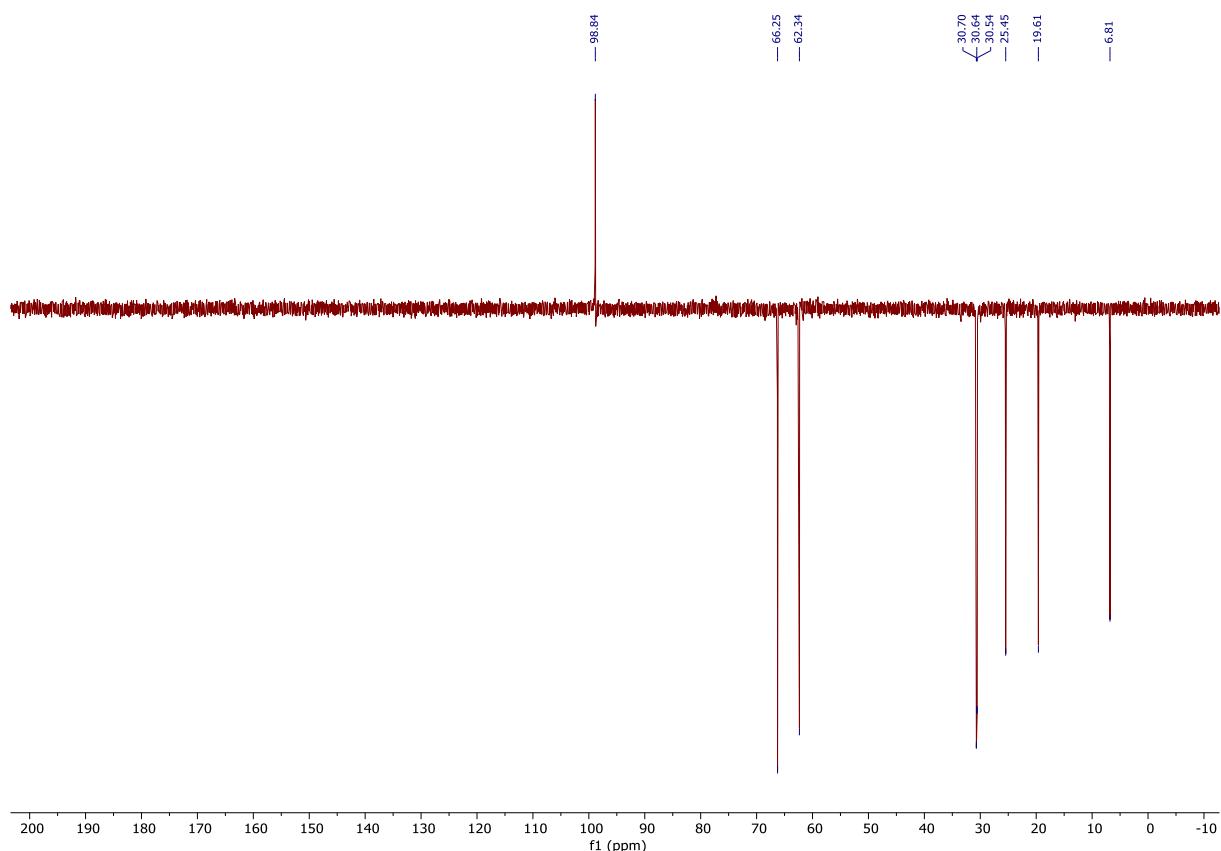
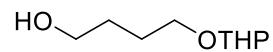


Figure S11. DEPT spectrum ( $\text{CDCl}_3$ , 100 MHz) of derivative **3b**.



4-((tetrahydro-2H-pyran-2-yl)oxy)butan-1-ol

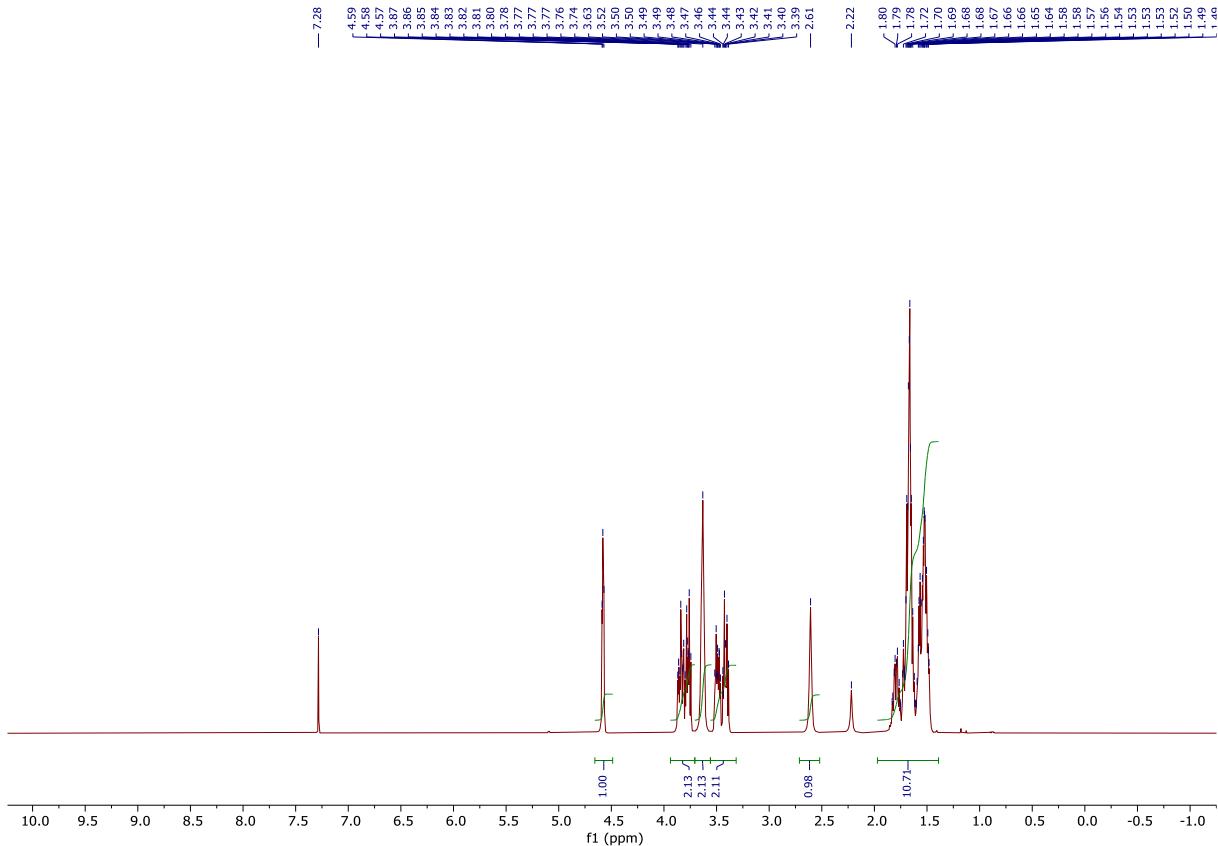


Figure S12.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 400 MHz) of 4-((tetrahydro-2H-pyran-2-yl)oxy)butan-1-ol.

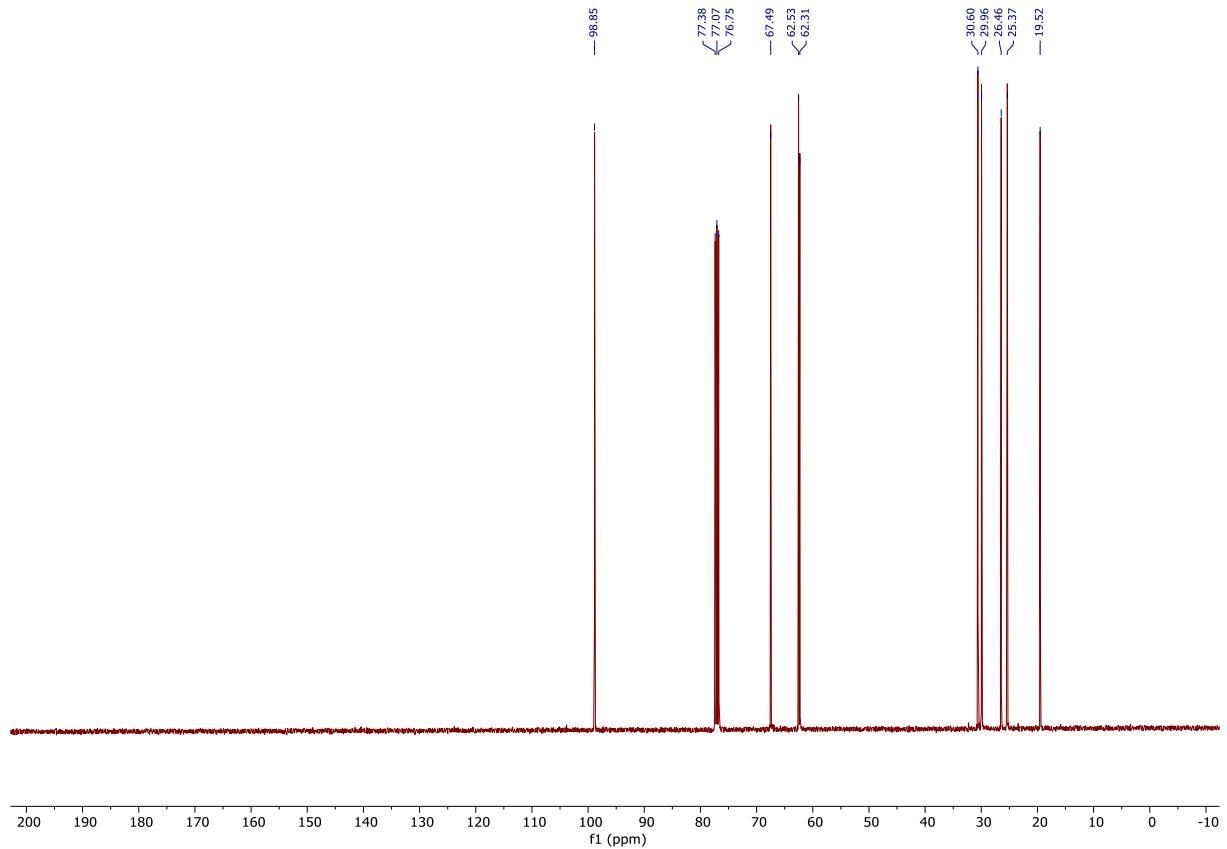


Figure S13.  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 100 MHz) of 4-((tetrahydro-2H-pyran-2-yl)oxy)butan-1-ol.

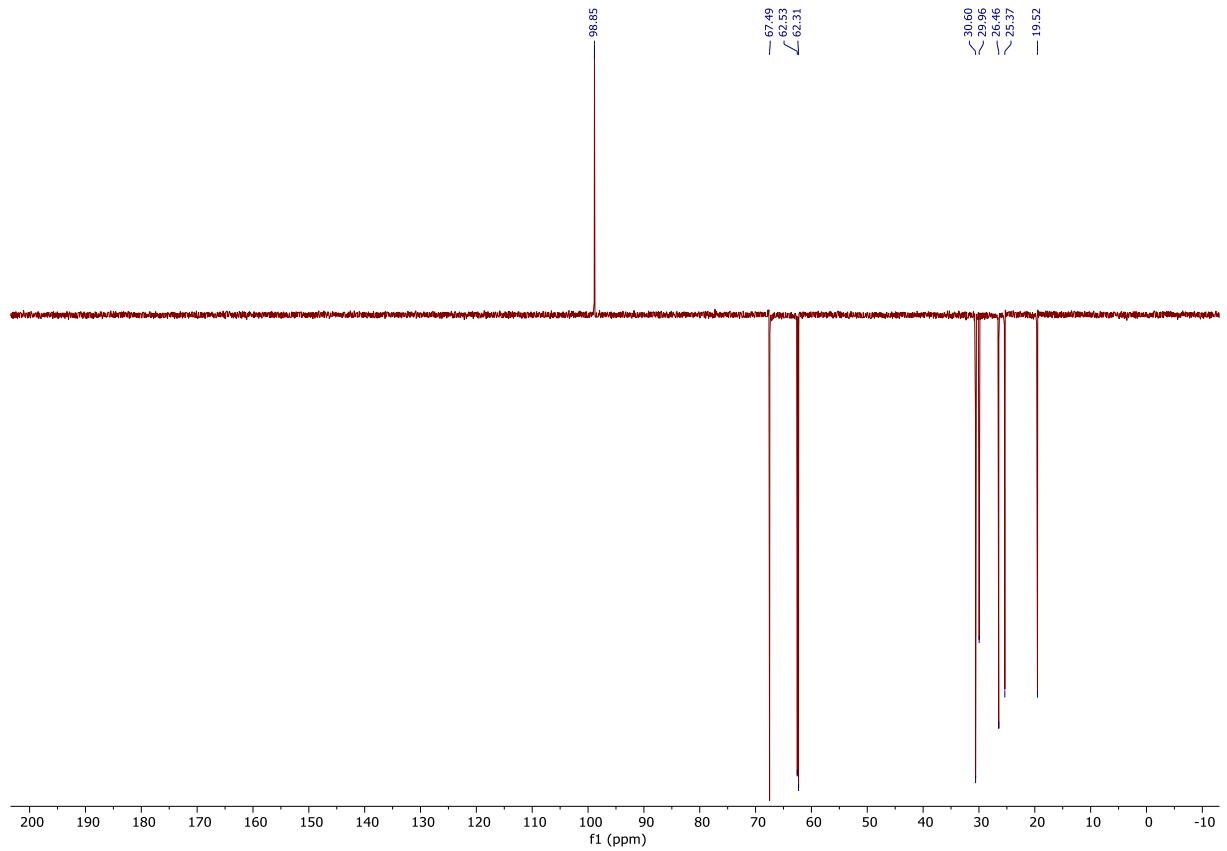
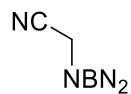


Figure S14. DEPT spectrum ( $\text{CDCl}_3$ , 100 MHz) of 4-((tetrahydro-2H-pyran-2-yl)oxy)butan-1-ol.



**4**

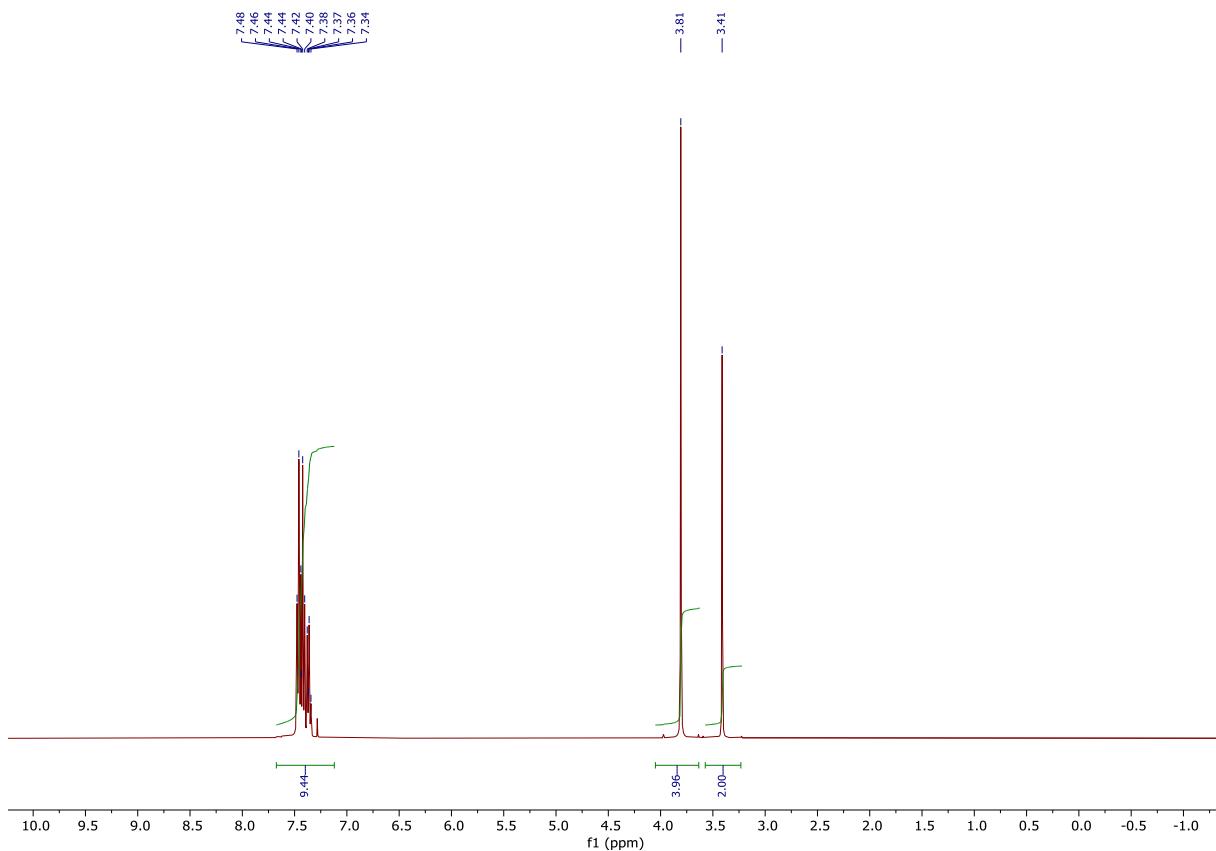


Figure S15. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of derivative **4**.

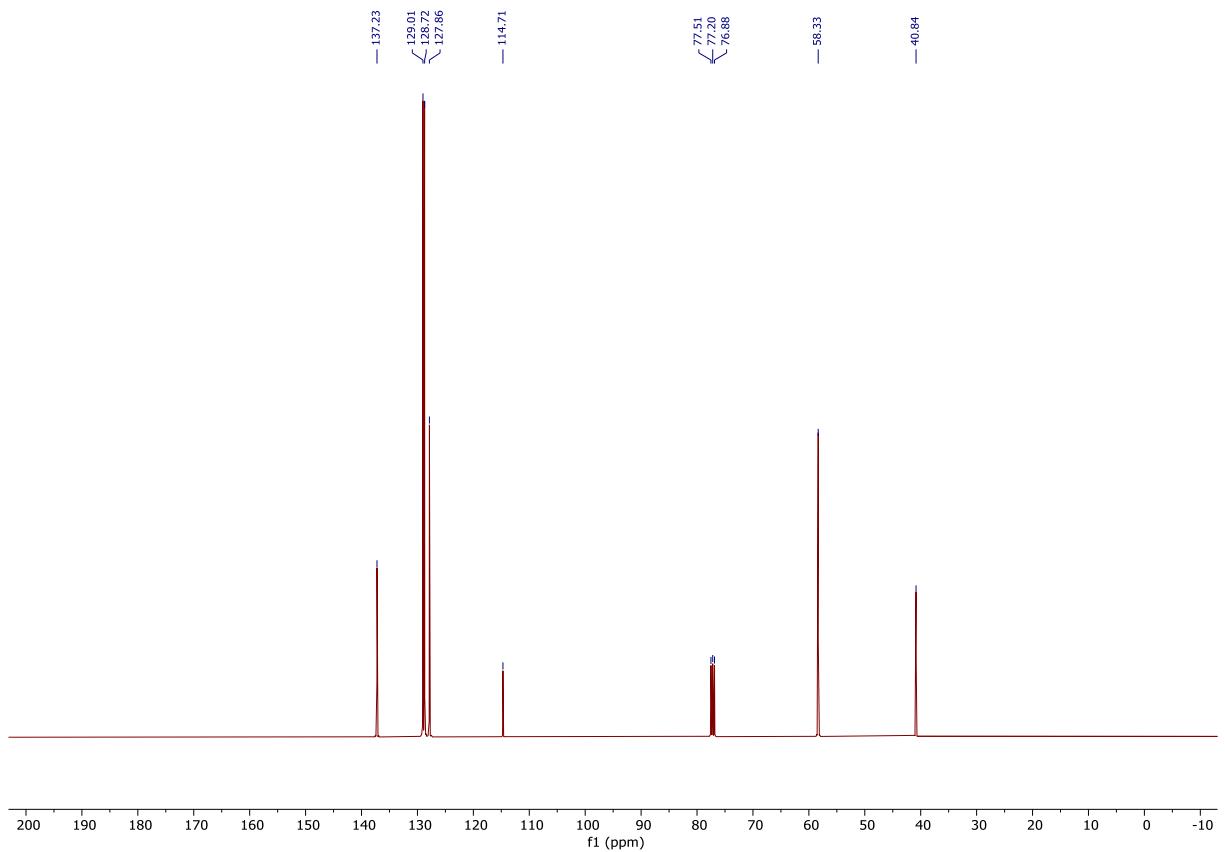


Figure S16.  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 100 MHz) of derivative **4**.

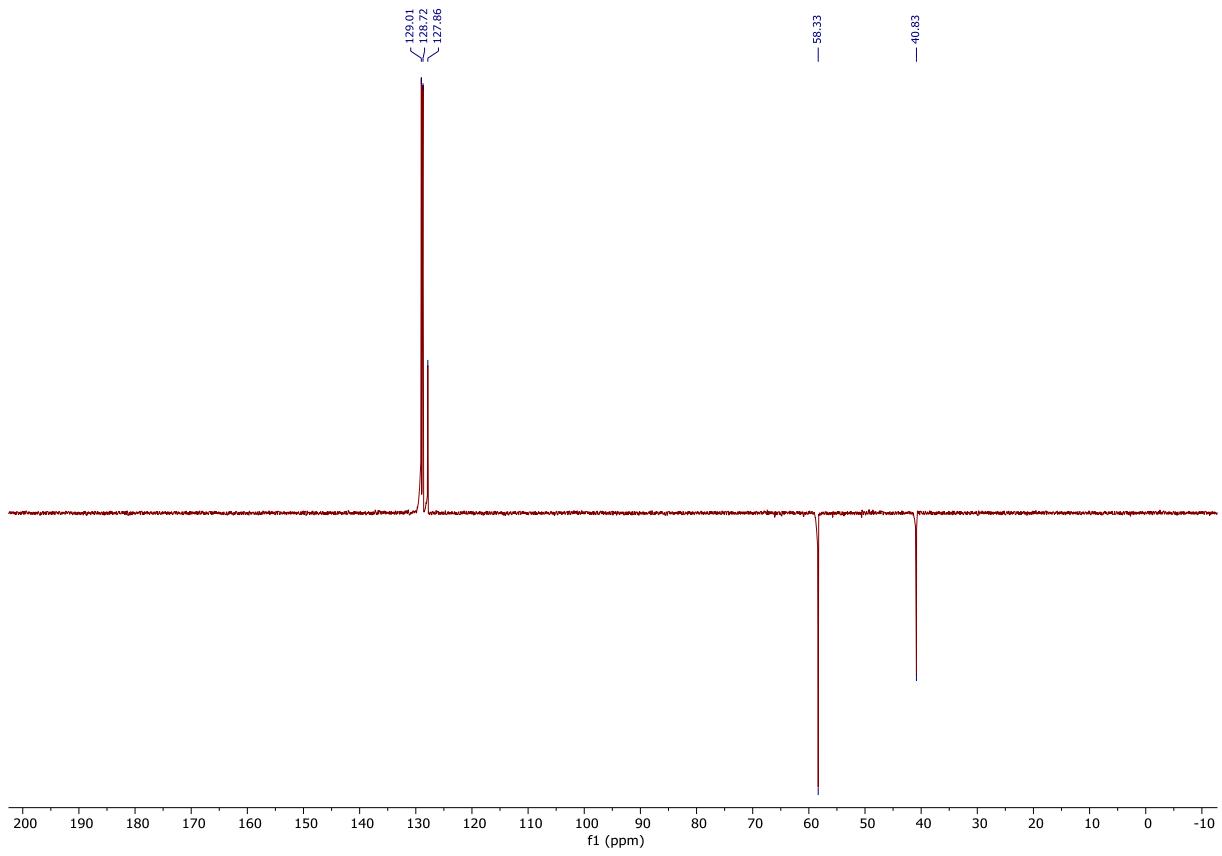


Figure S17. DEPT spectrum ( $\text{CDCl}_3$ , 100 MHz) of derivative 4.

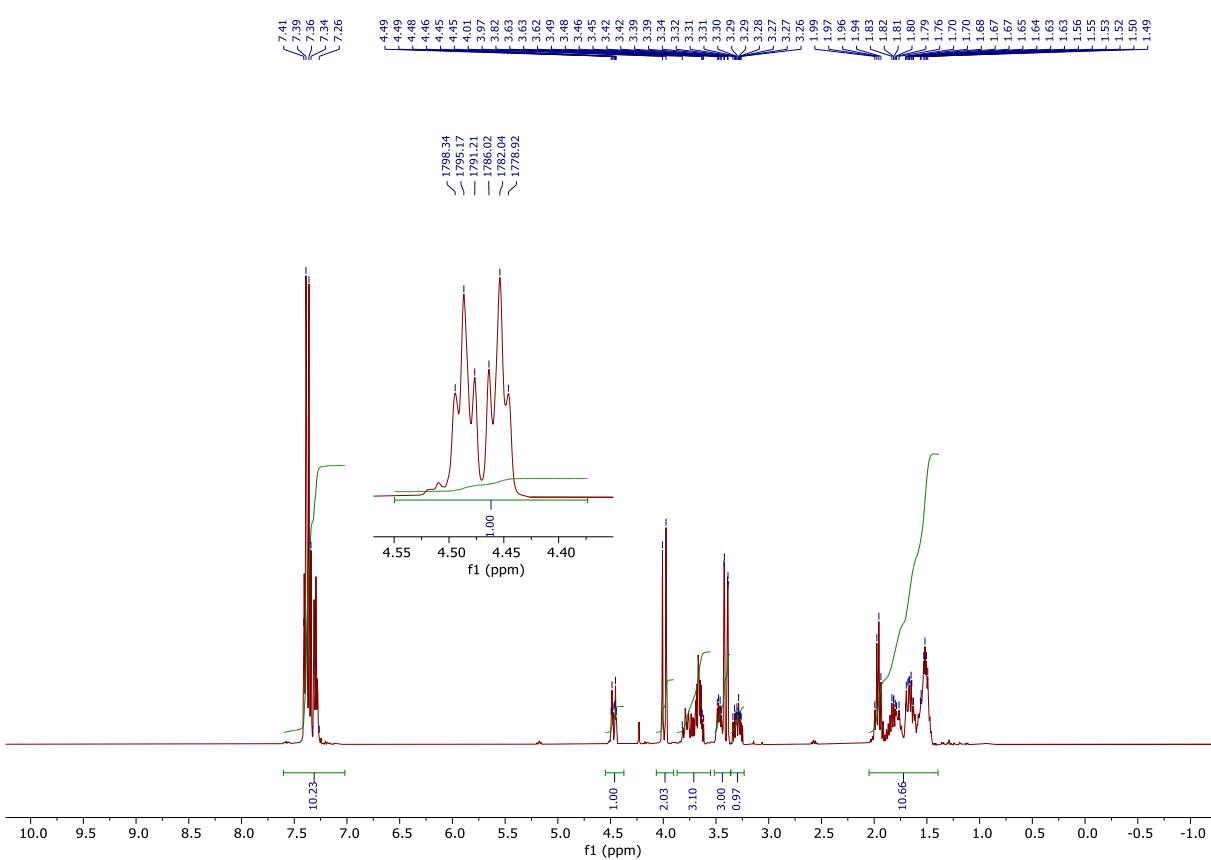
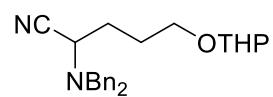


Figure S18.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 400 MHz) of derivative **5a**.

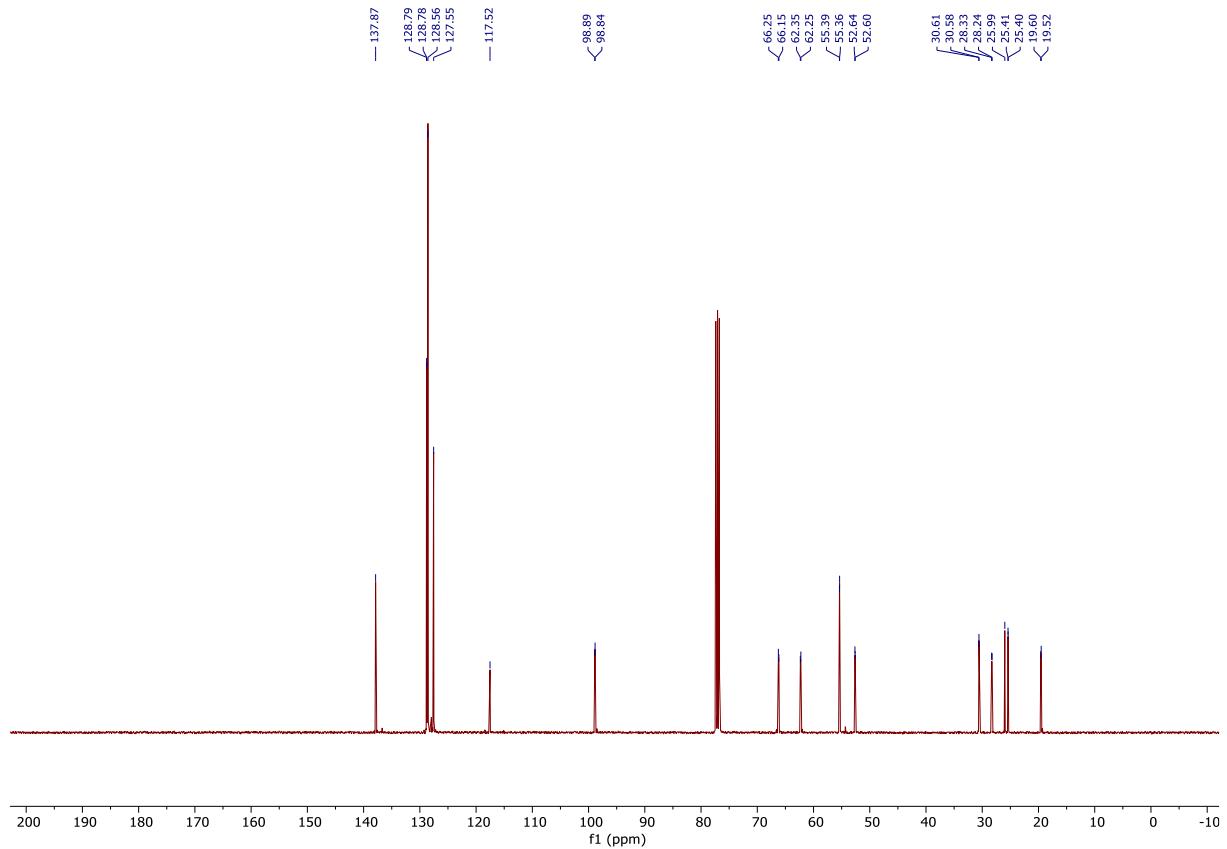


Figure S19.  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 100 MHz) of derivative **5a**.

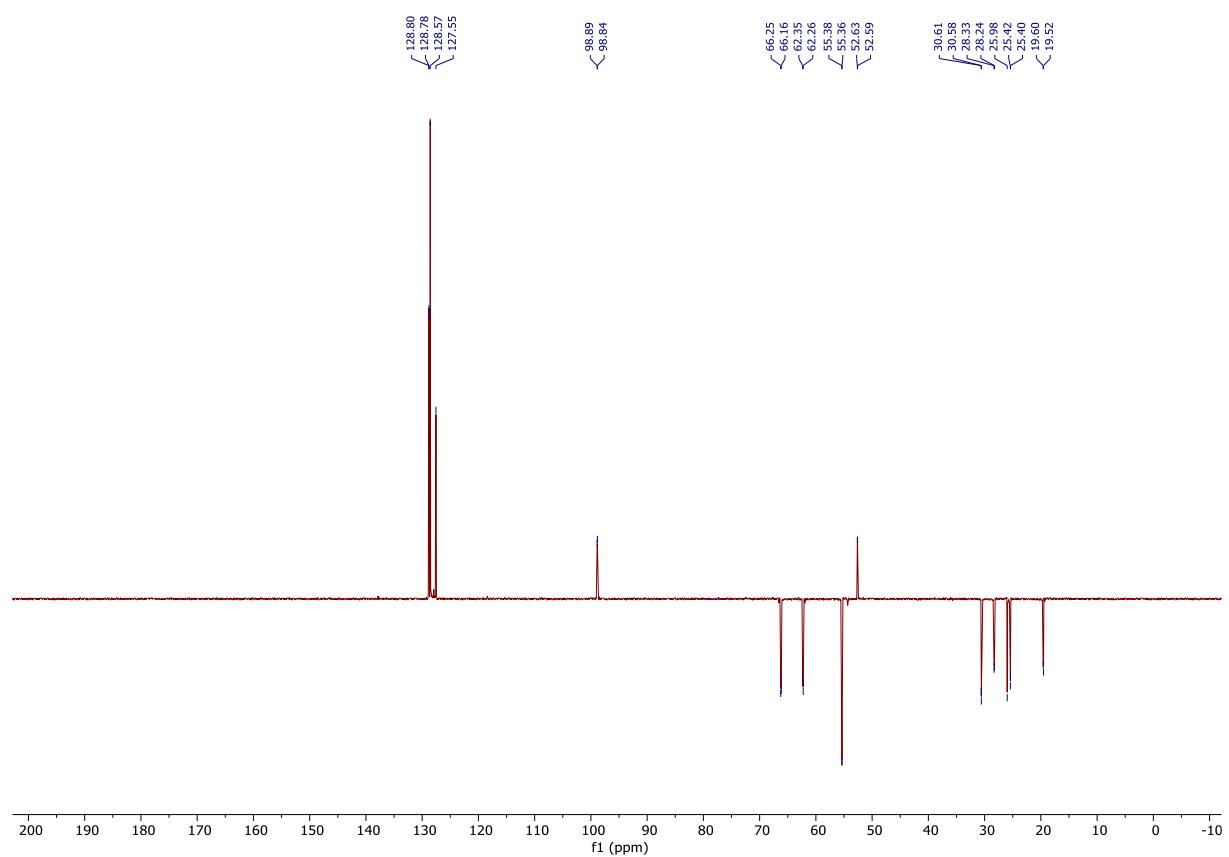


Figure S20. DEPT spectrum ( $\text{CDCl}_3$ , 100 MHz) of derivative **5a**.

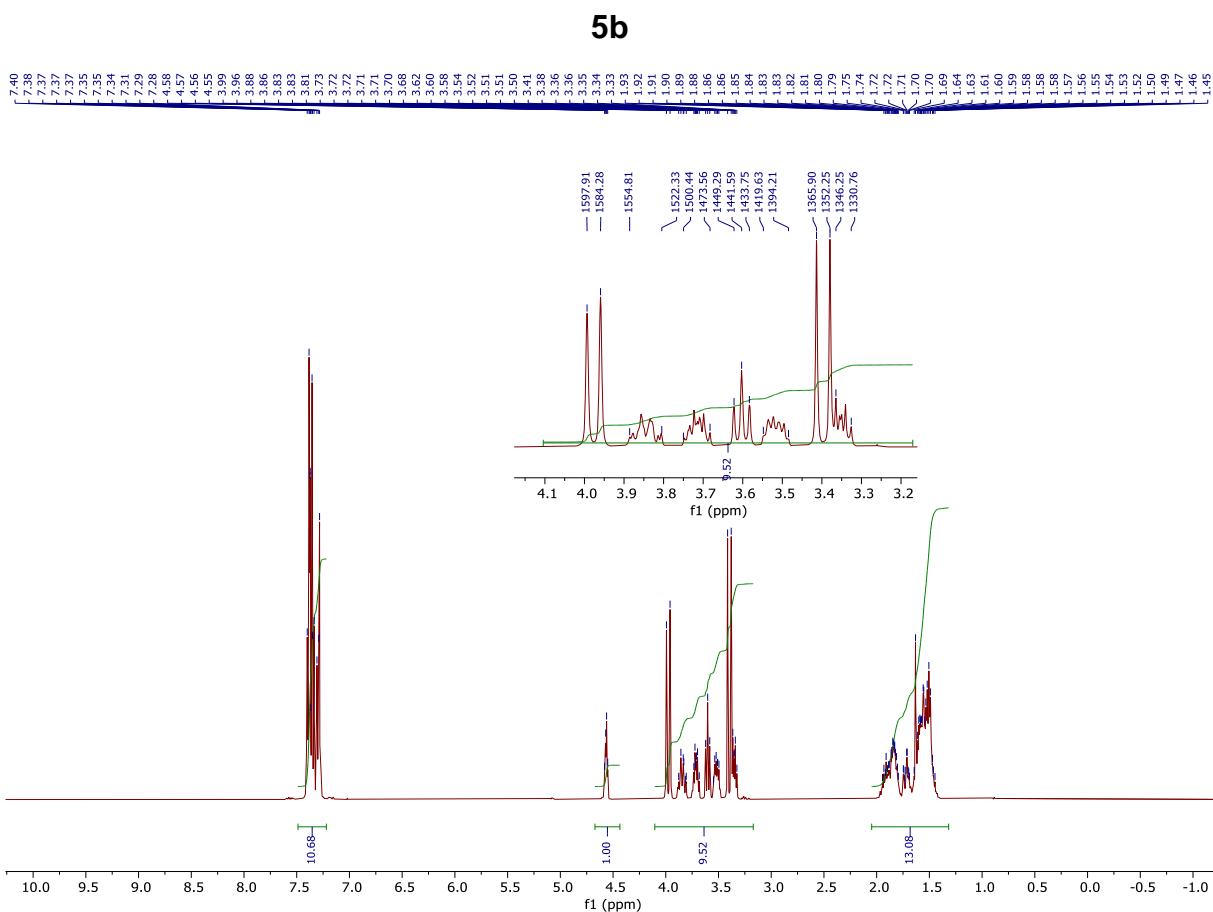
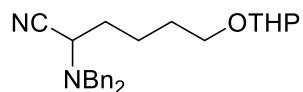


Figure S21.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 400 MHz) of derivative **5b**.

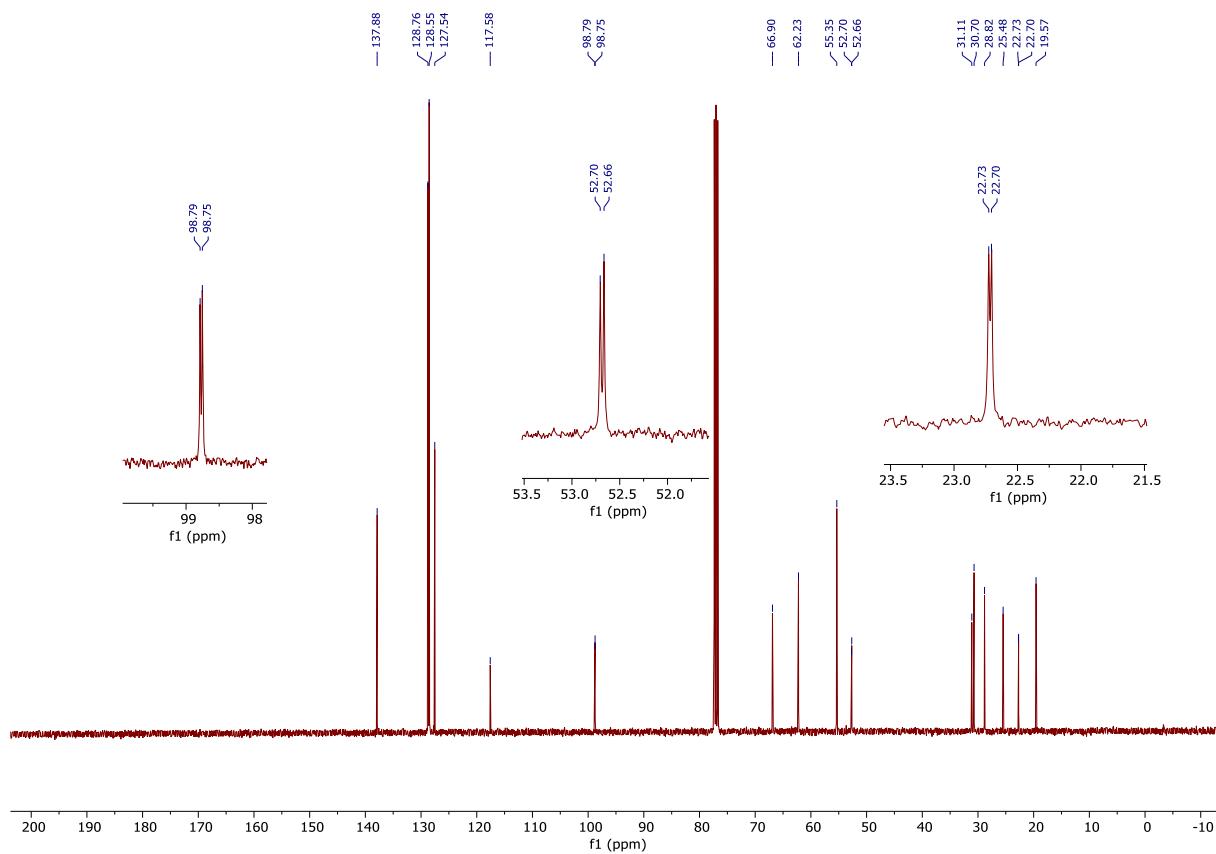


Figure S22.  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 100 MHz) of derivative **5b**.

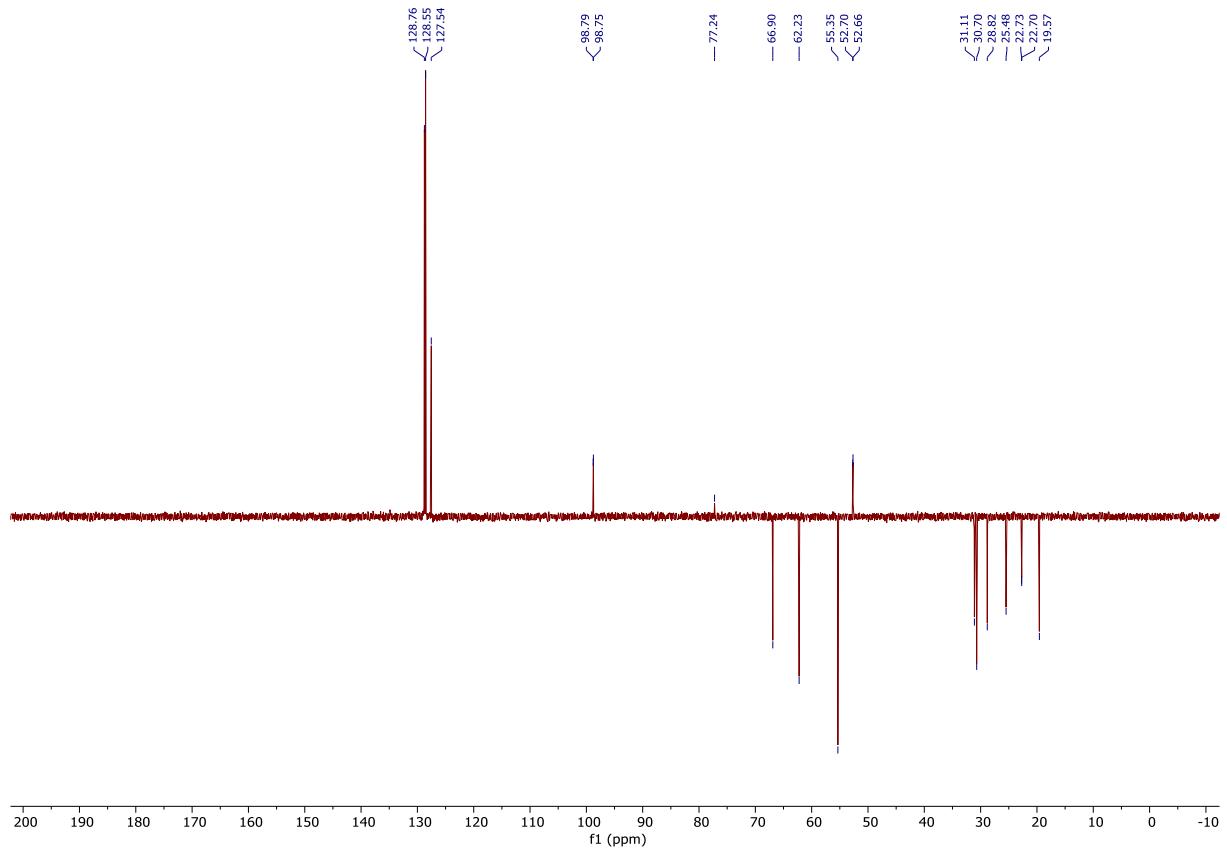
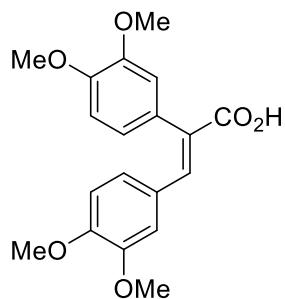


Figure S23. DEPT spectrum ( $\text{CDCl}_3$ , 100 MHz) of derivative **5b**.



**6a**

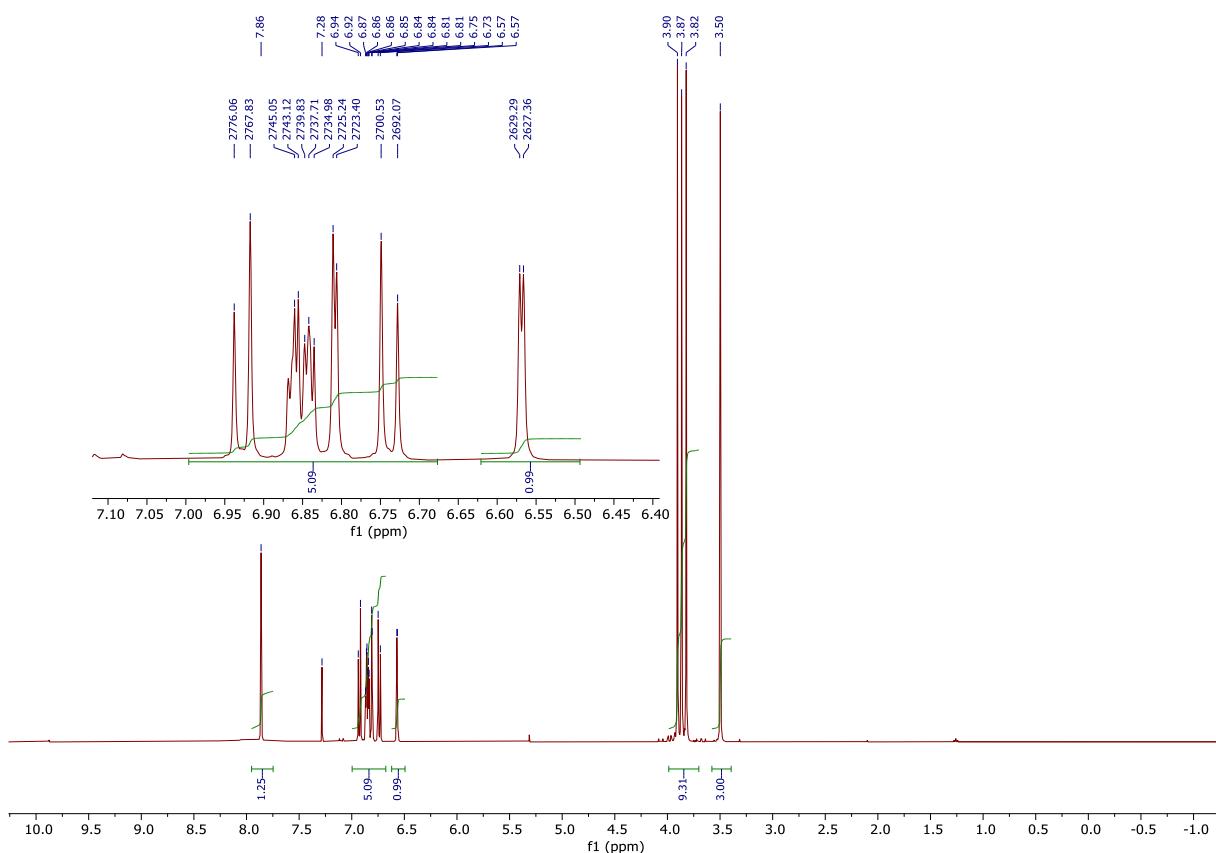


Figure S24.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 400 MHz) of derivative **6a**.

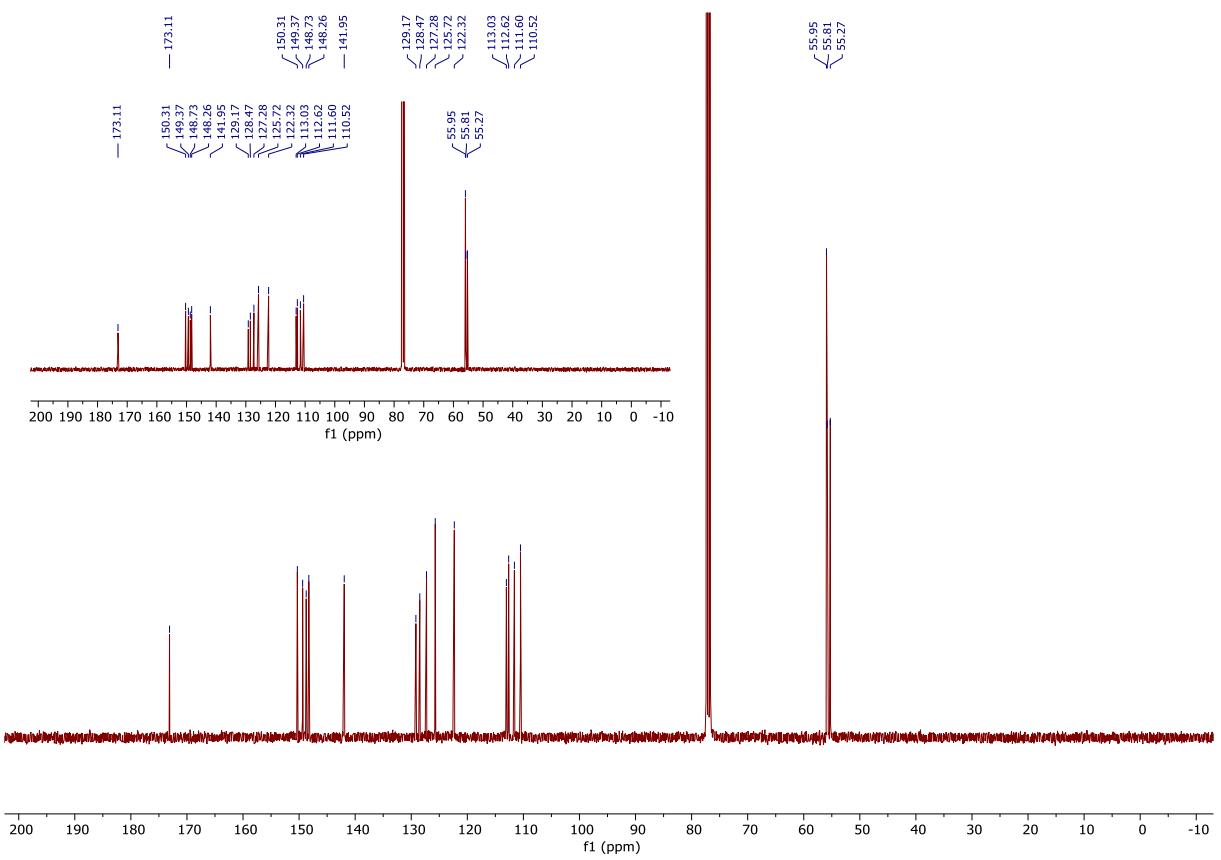


Figure S25.  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 100 MHz) of derivative **6a**.

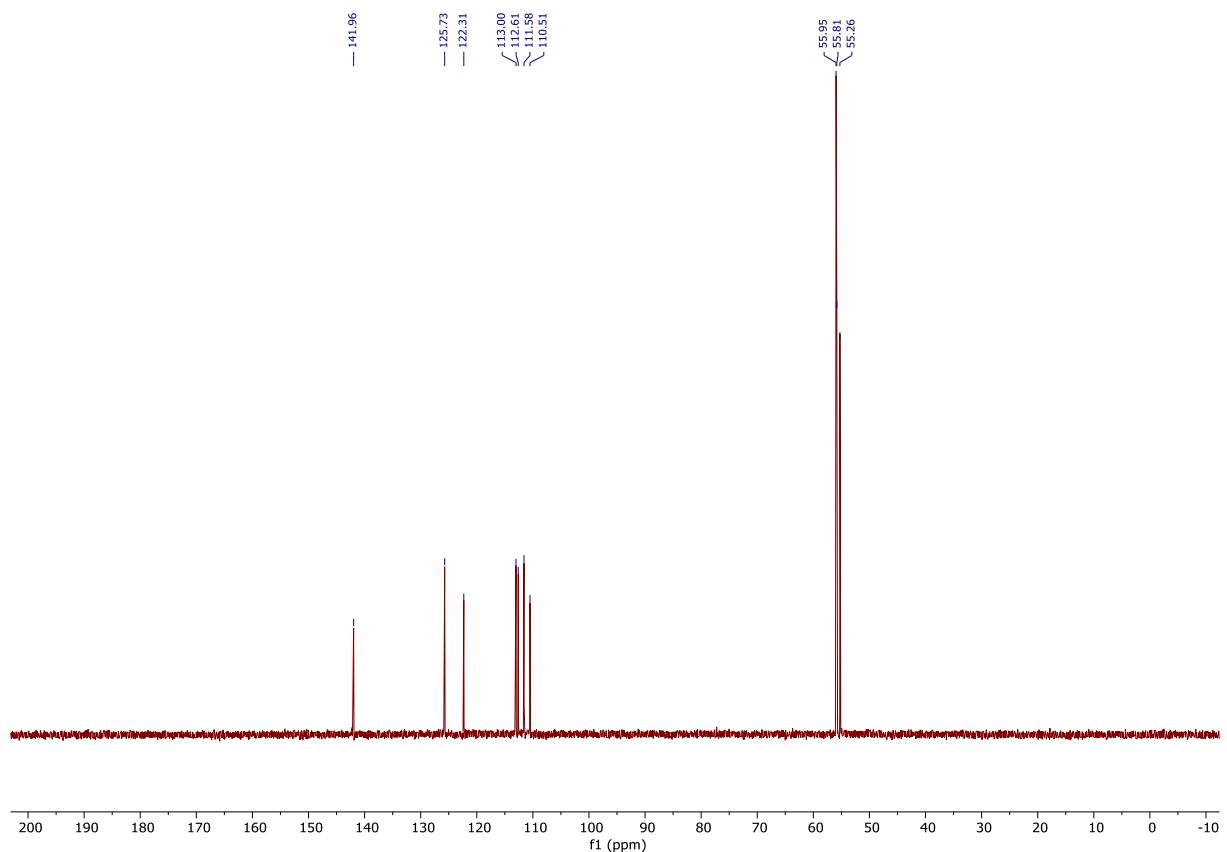


Figure S26. DEPT spectrum ( $\text{CDCl}_3$ , 100 MHz) of derivative **6a**.

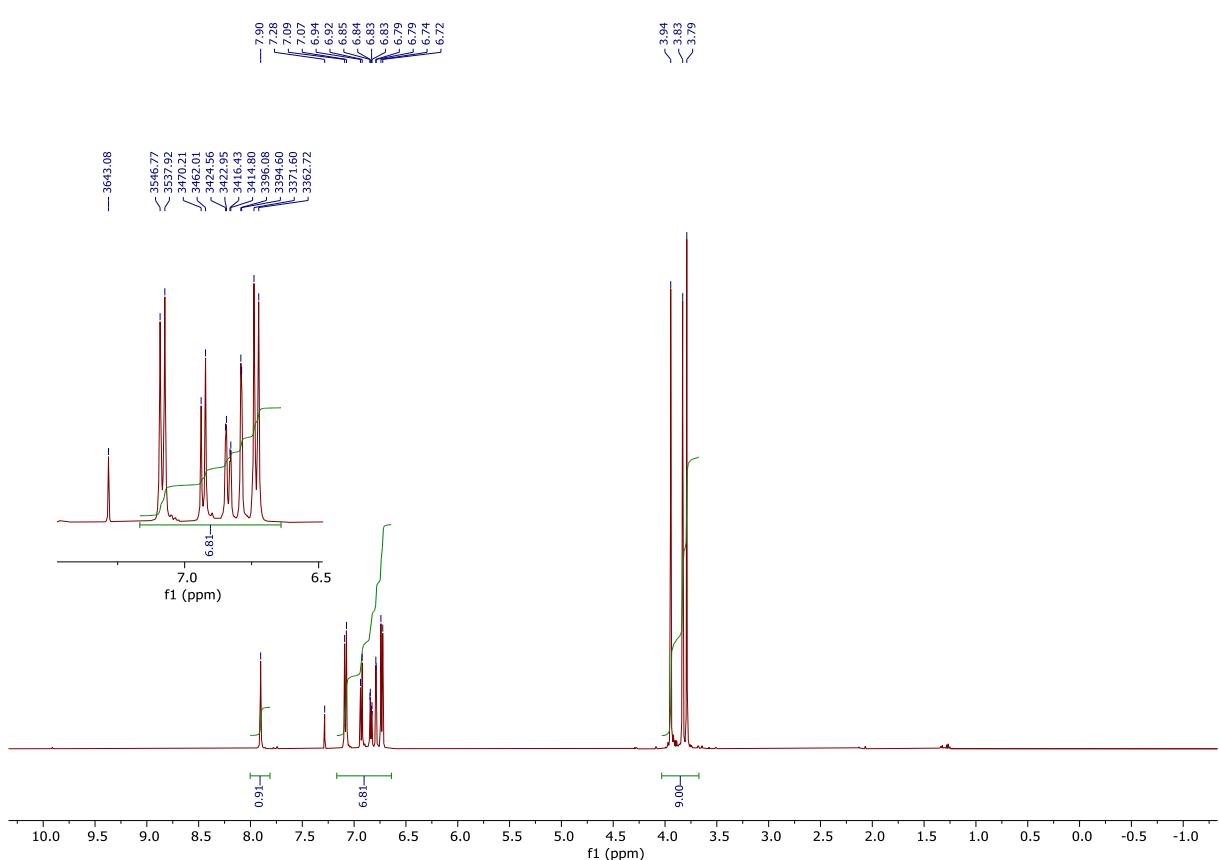
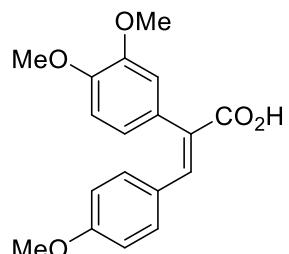


Figure S27. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 500 MHz) of derivative **6b**.

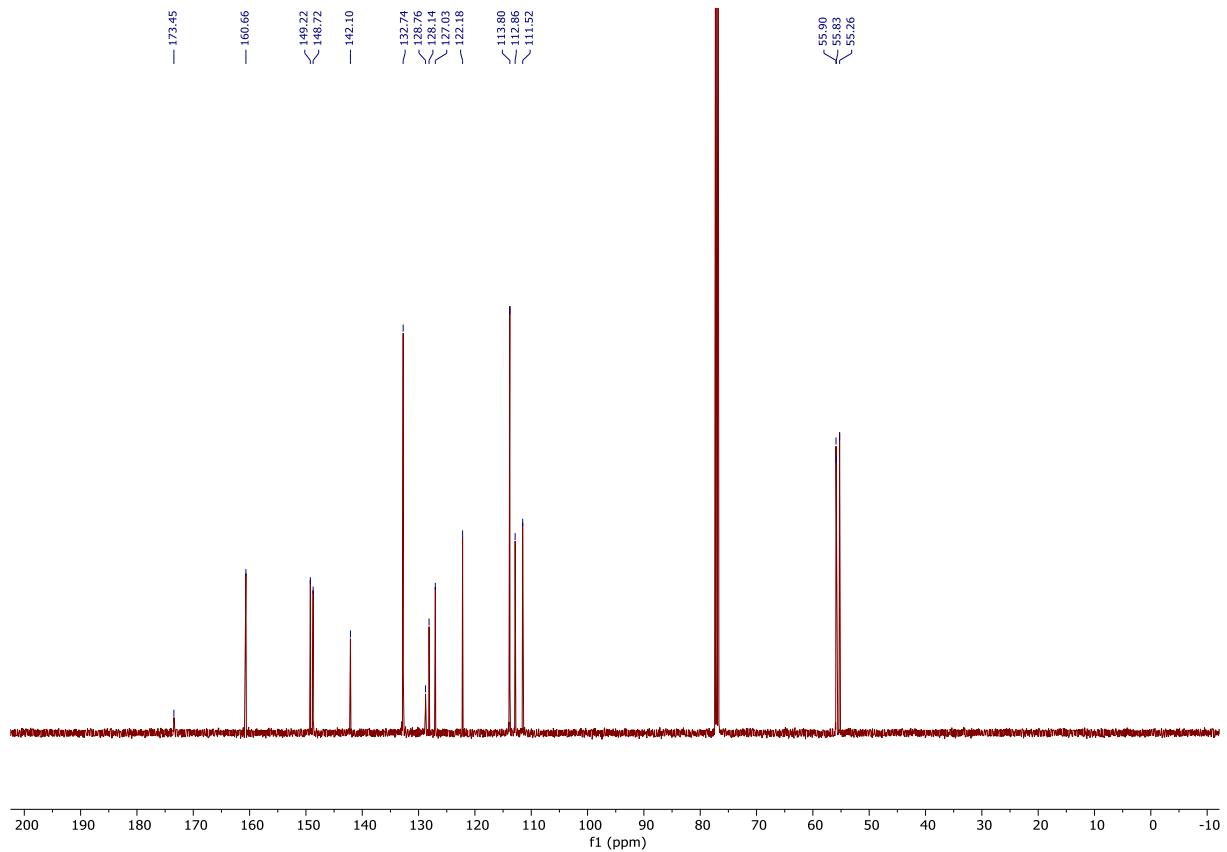


Figure S28.  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 125 MHz) of derivative **6b**.

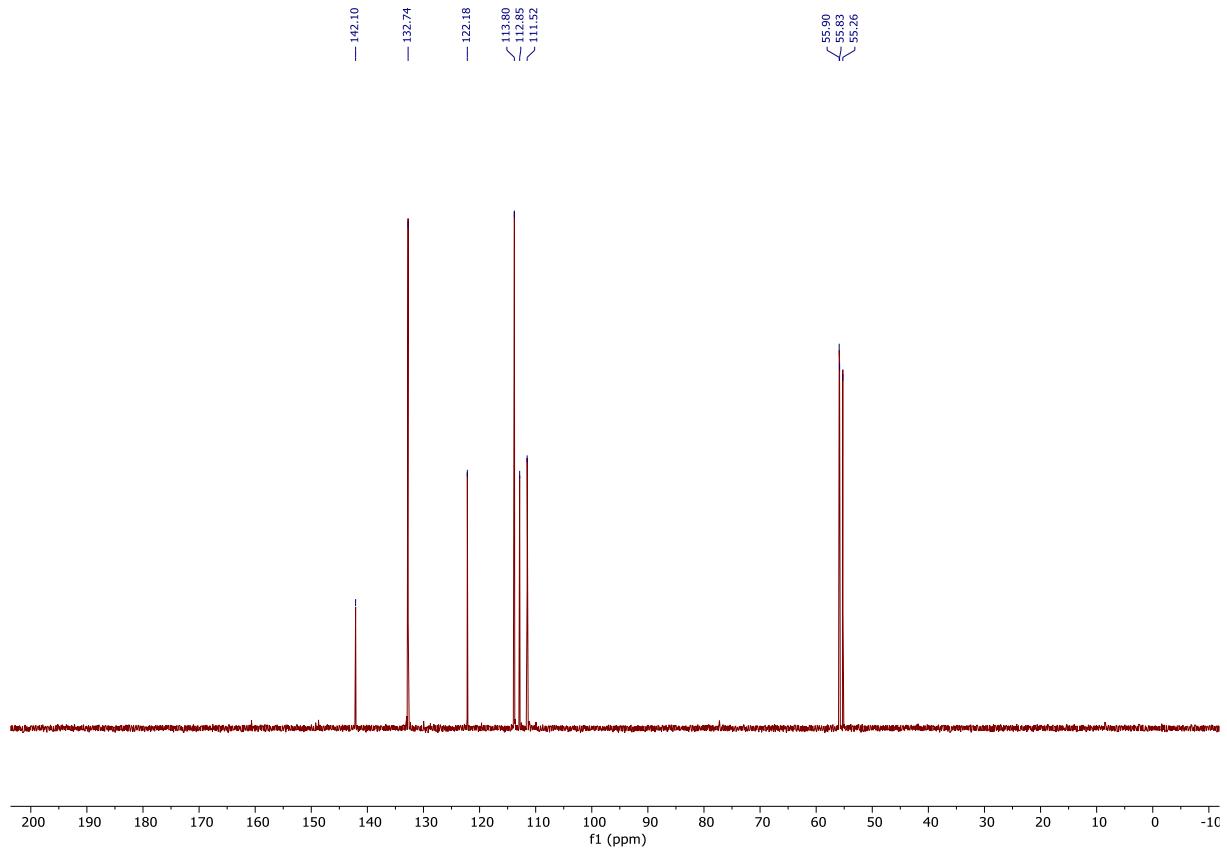
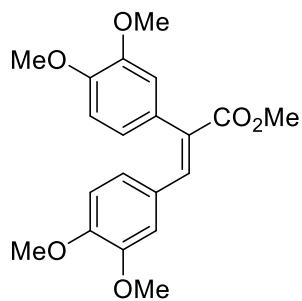


Figure S29. DEPT spectrum ( $\text{CDCl}_3$ , 125 MHz) of derivative **6b**.



**7a**

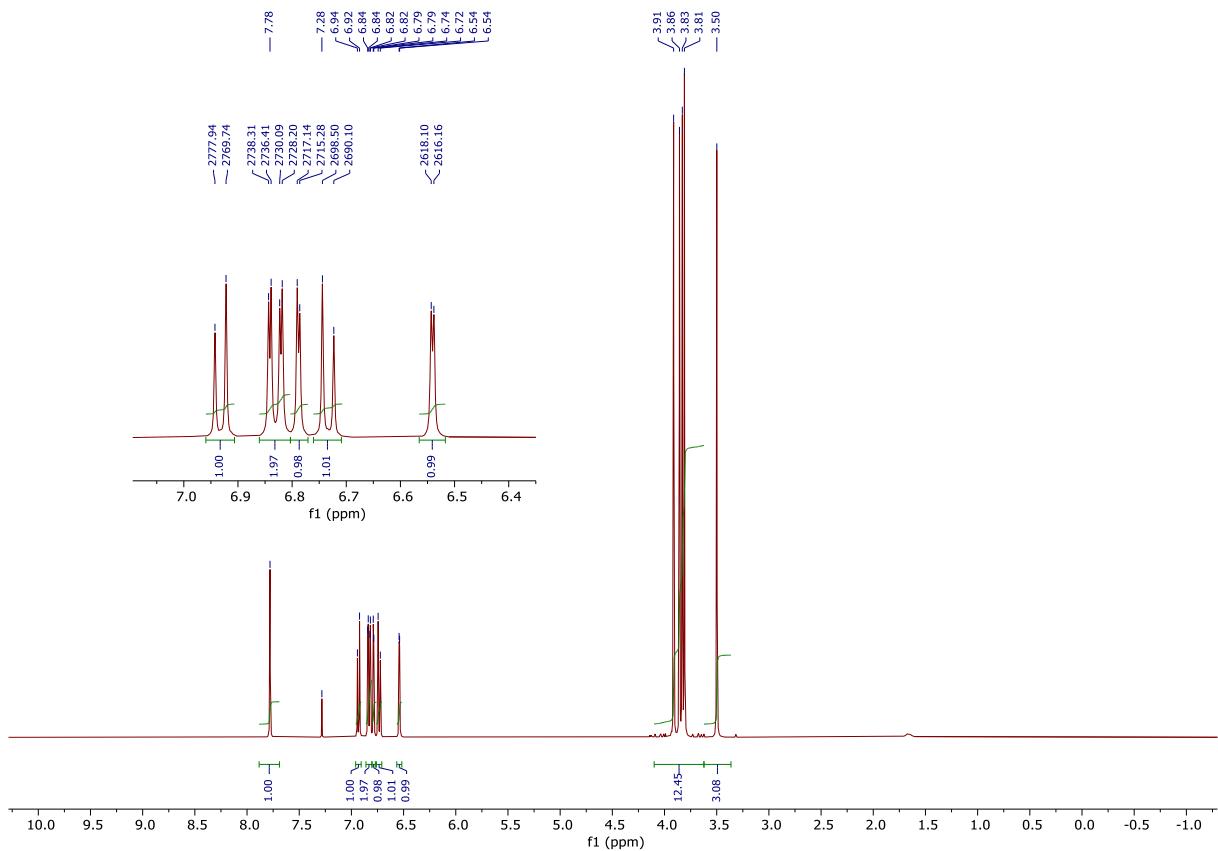


Figure S30.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 400 MHz) of derivative **7a**.

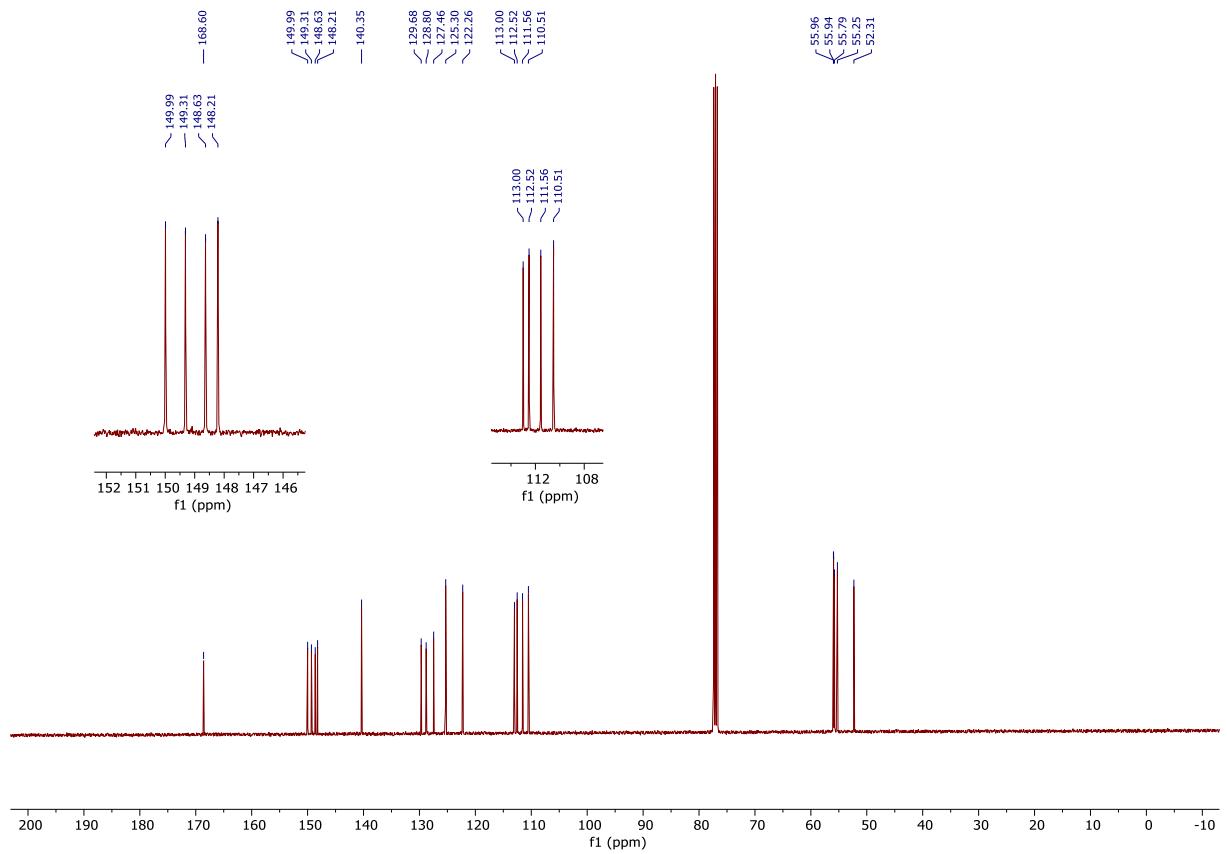


Figure S31.  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 100 MHz) of derivative **7a**.

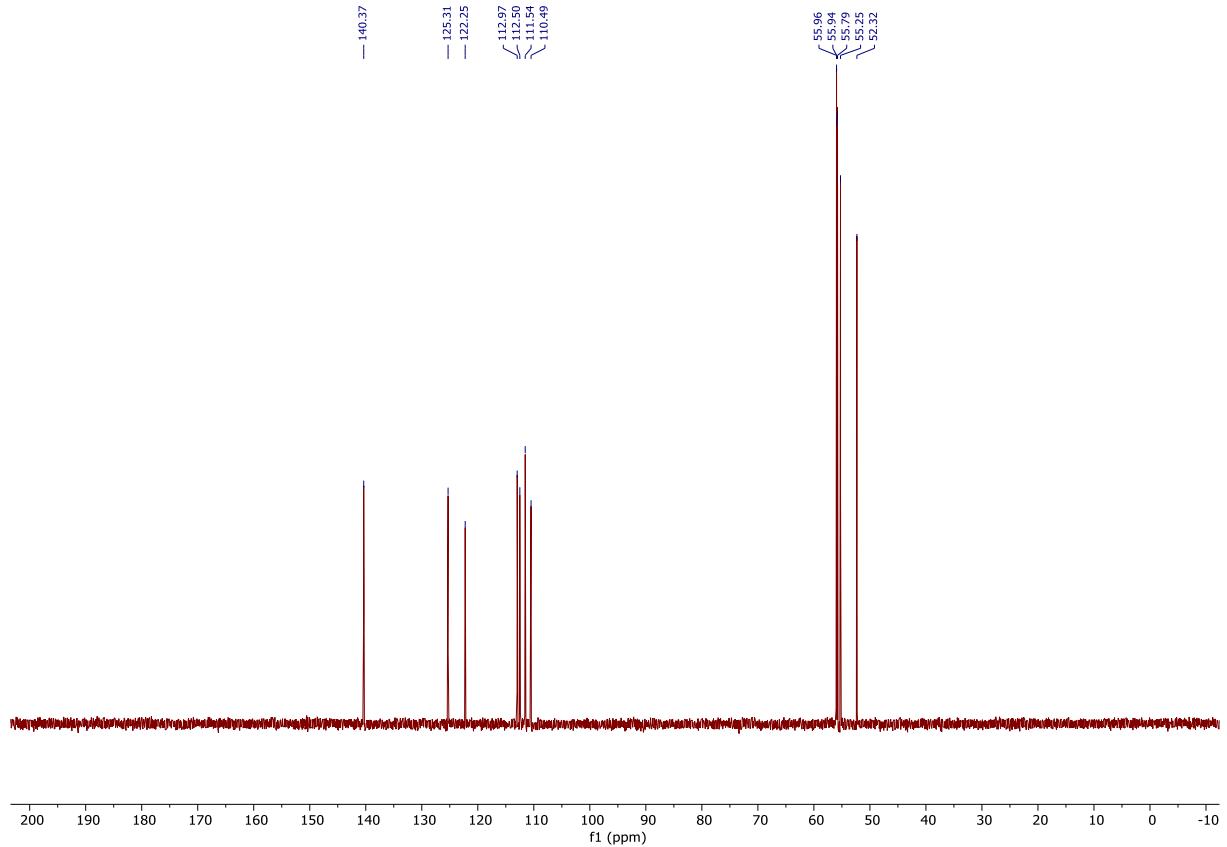
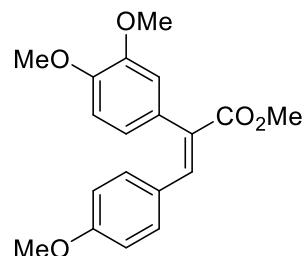


Figure S32. DEPT spectrum ( $\text{CDCl}_3$ , 100 MHz) of derivative **7a**.



**7b**

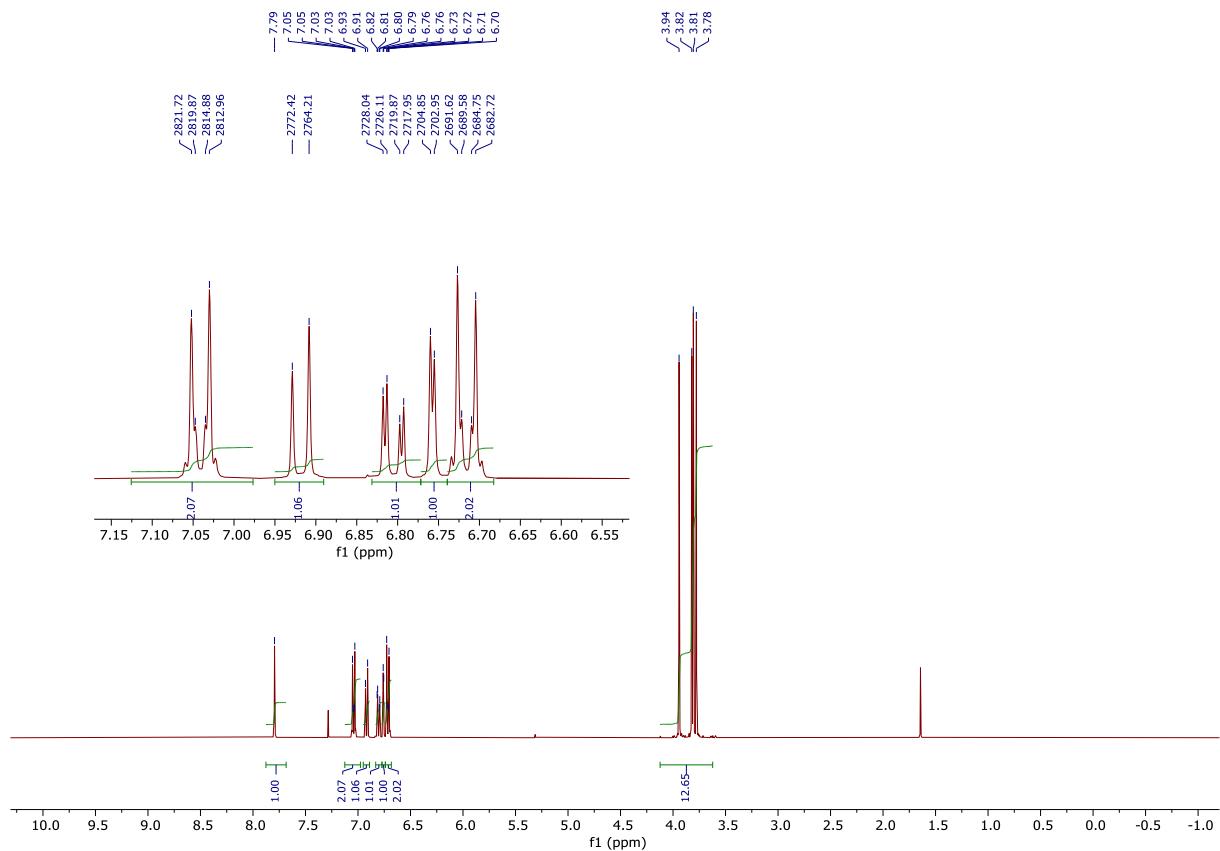


Figure S33.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 400 MHz) of derivative **7b**.

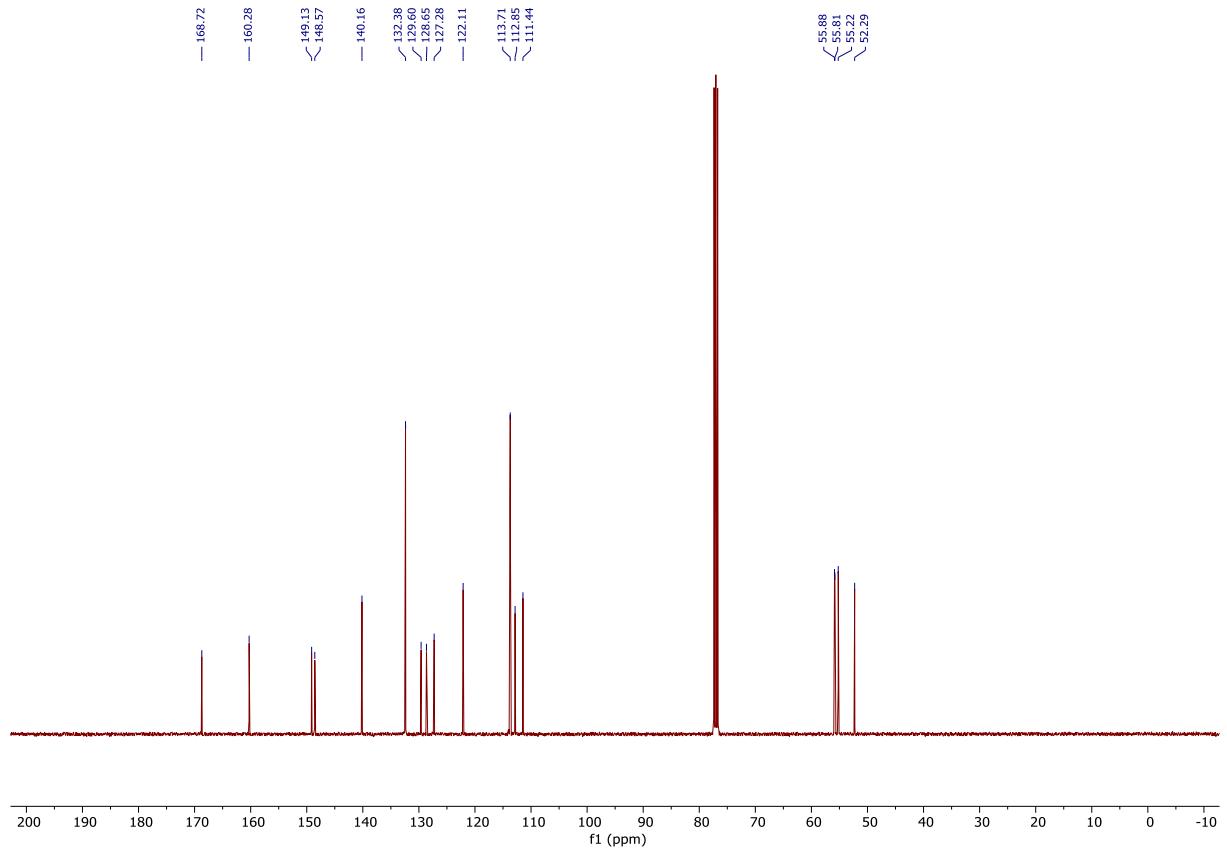


Figure S34.  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 100 MHz) of derivative **7b**.

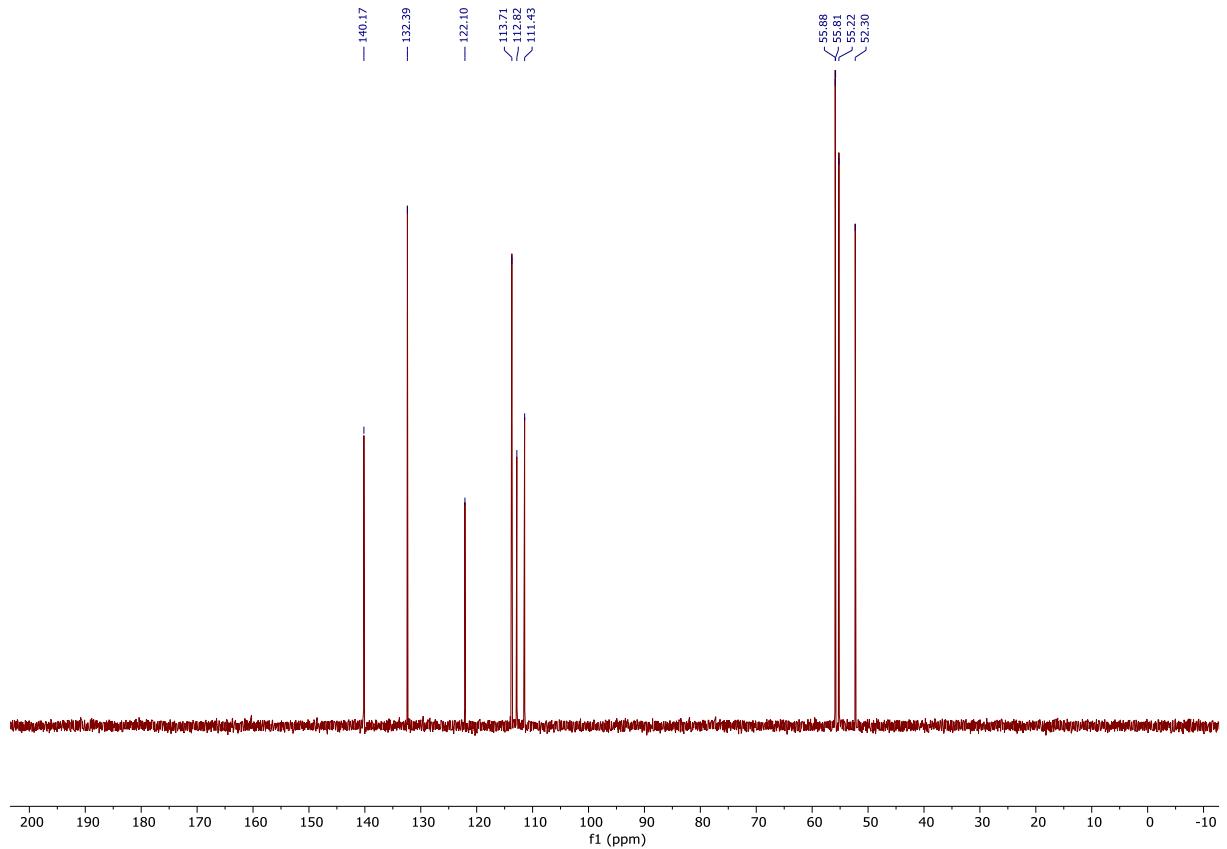


Figure S35. DEPT spectrum ( $\text{CDCl}_3$ , 100 MHz) of derivative **7b**.

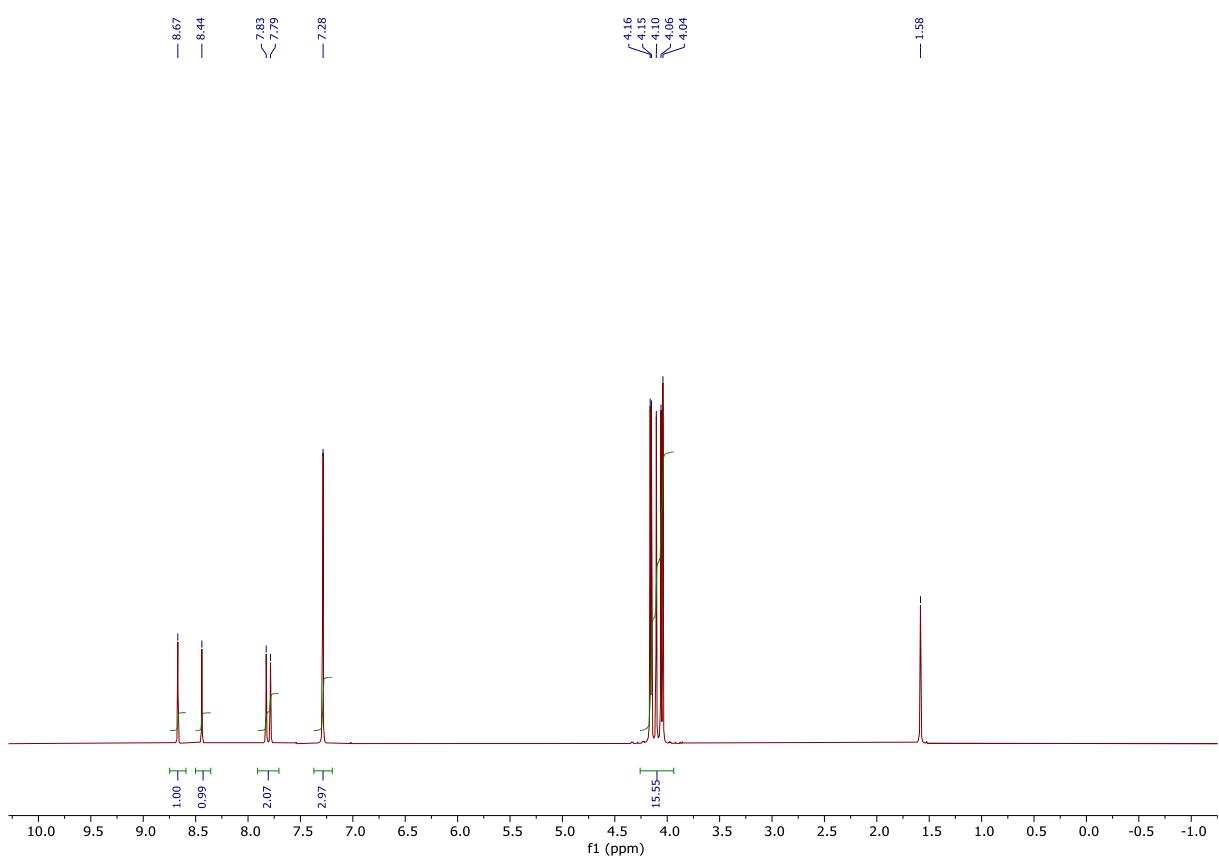
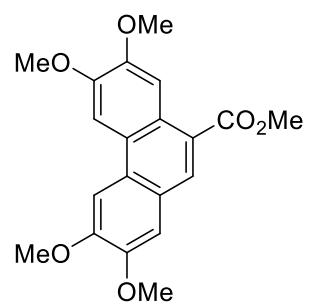


Figure S36. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of derivative **8a**.

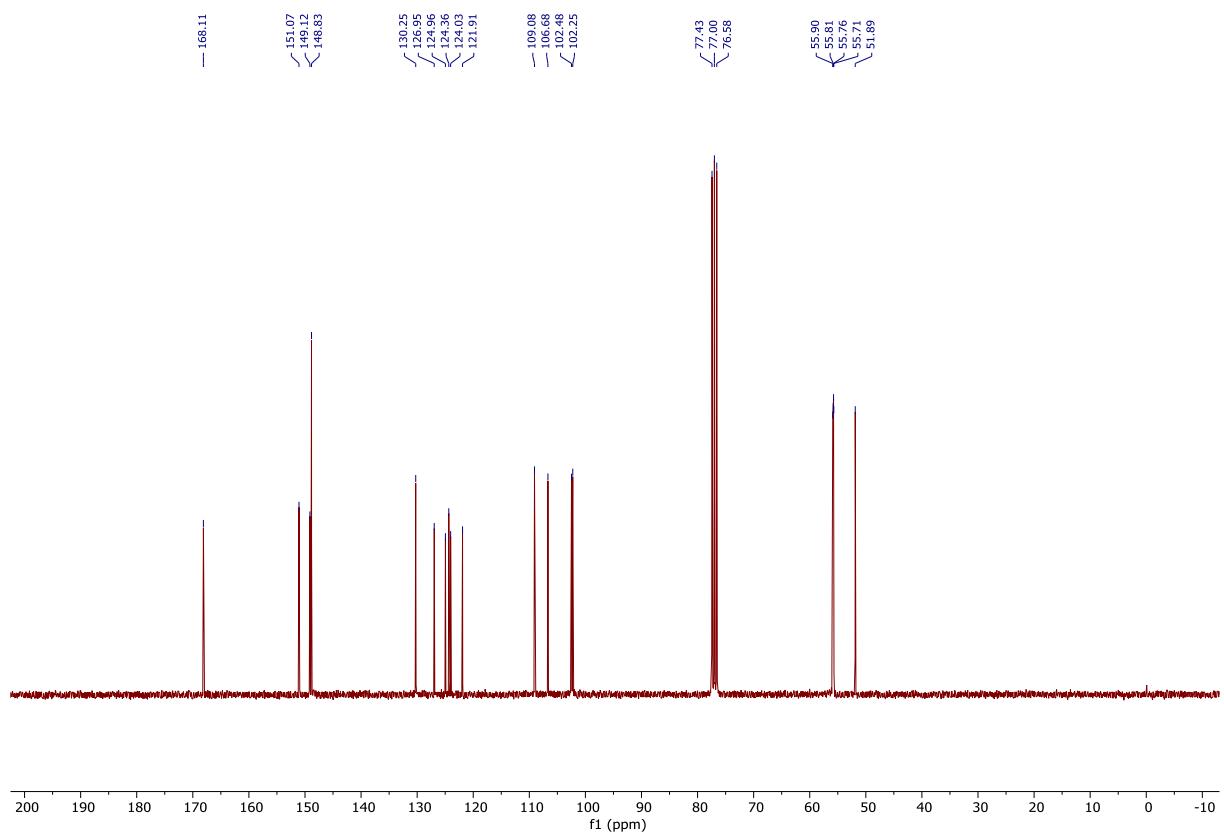


Figure S37.  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 100 MHz) of derivative **8a**.

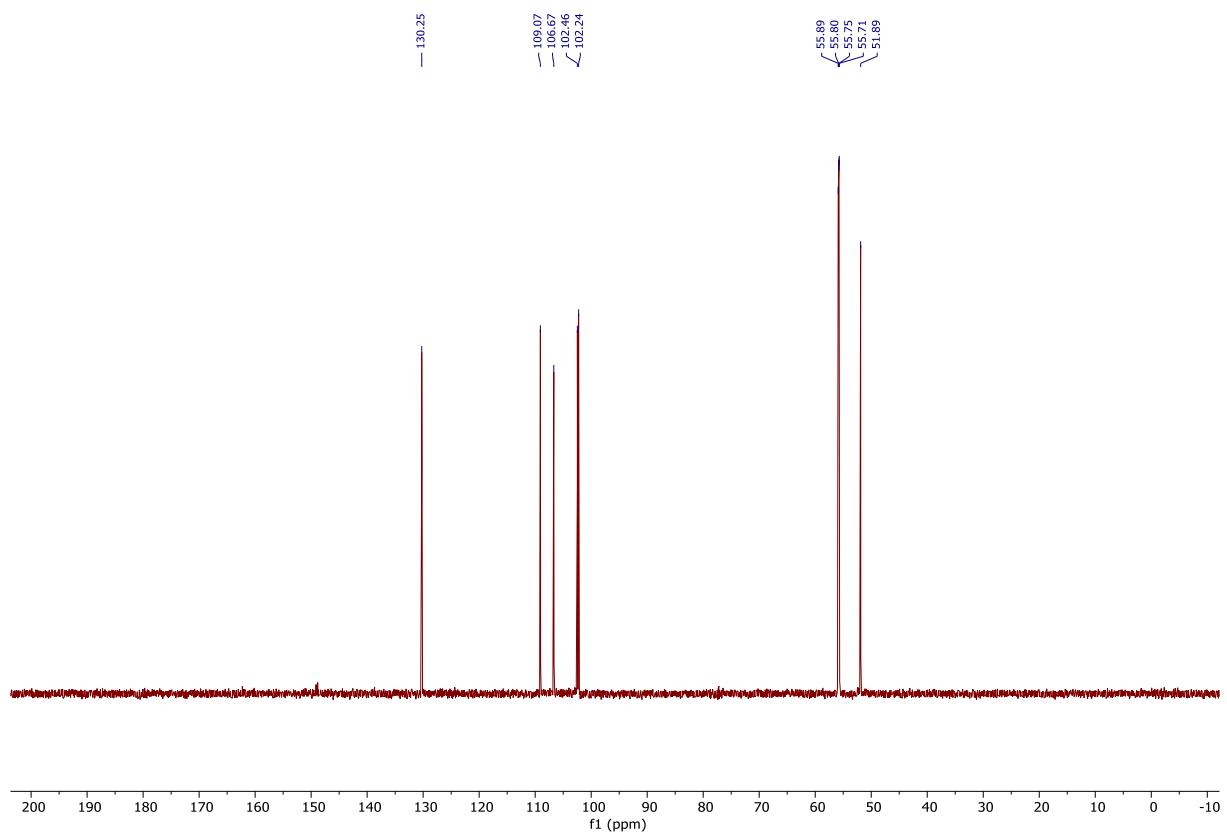


Figure S38. DEPT spectrum ( $\text{CDCl}_3$ , 100 MHz) of derivative **8a**.

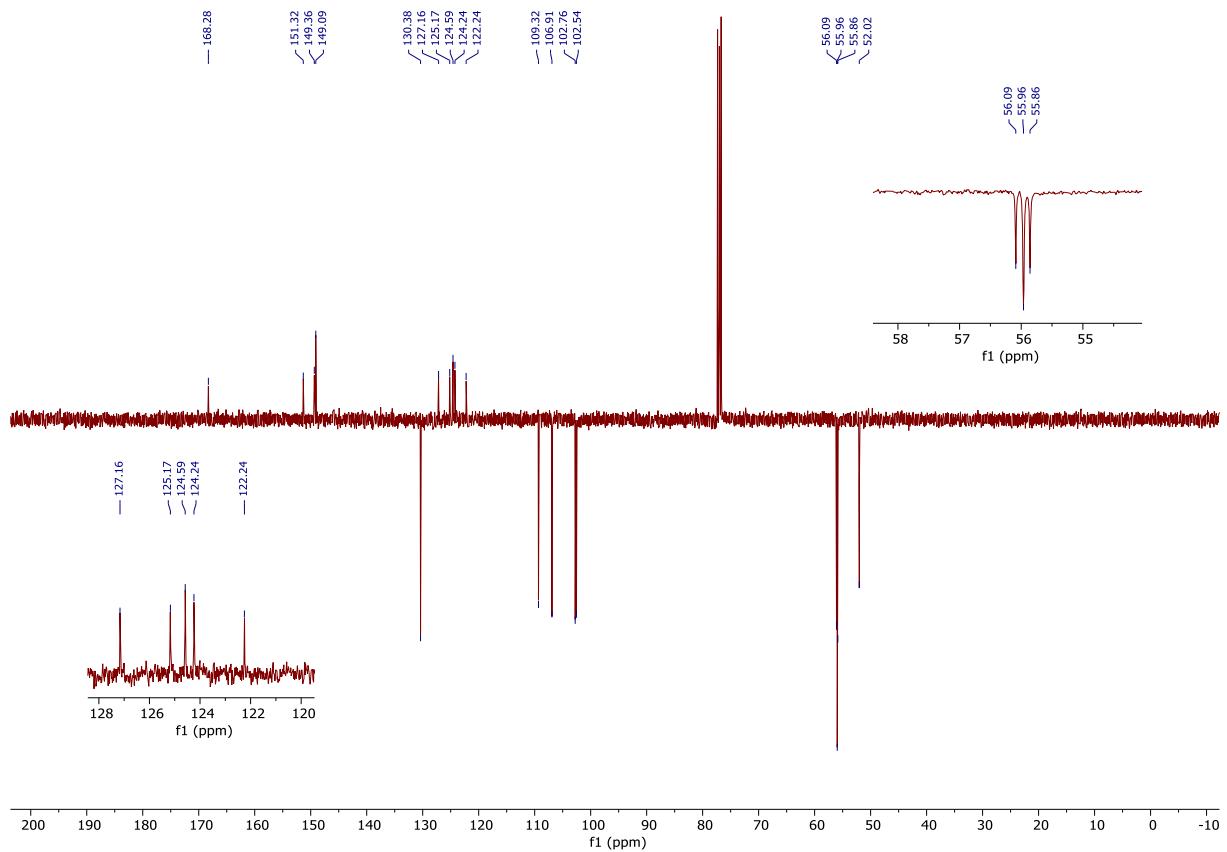


Figure S39. J-MOD NMR spectrum (CDCl<sub>3</sub>, 100 MHz) of derivative **8a**.

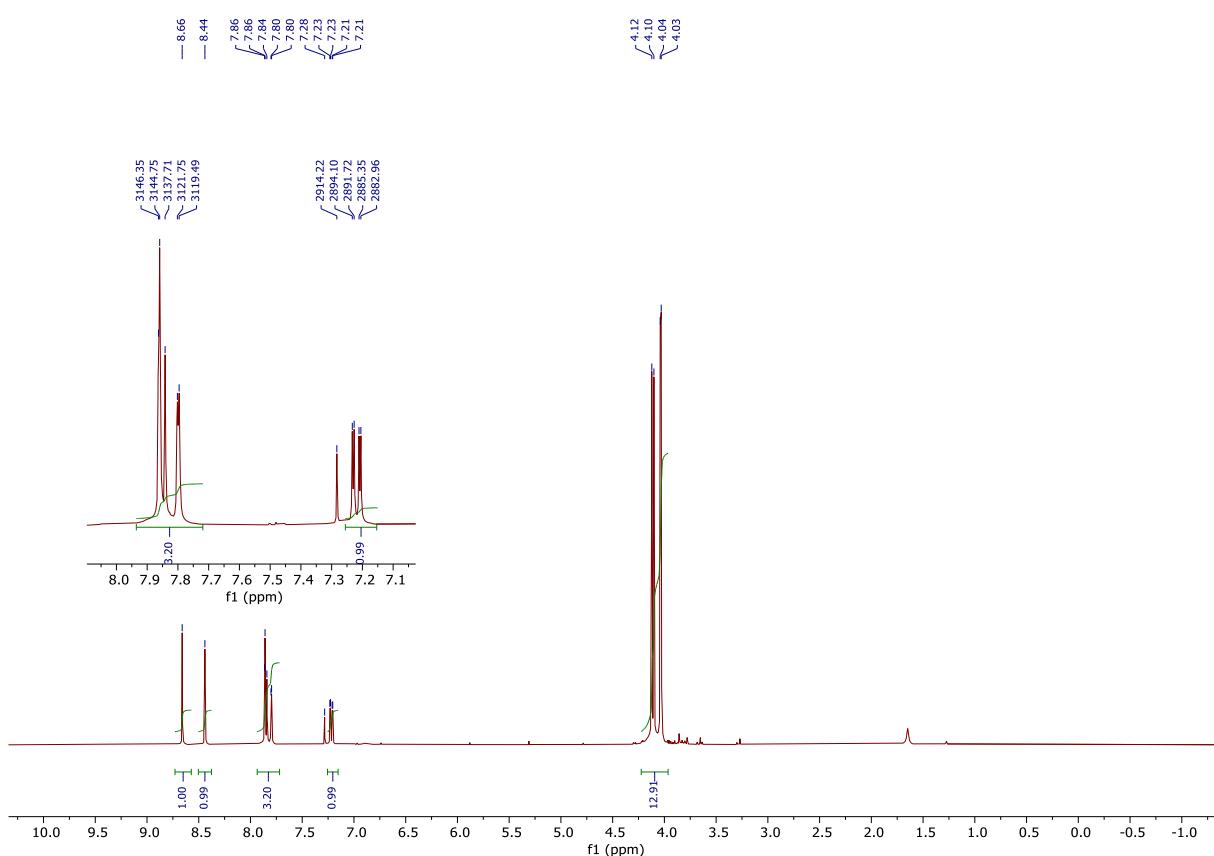
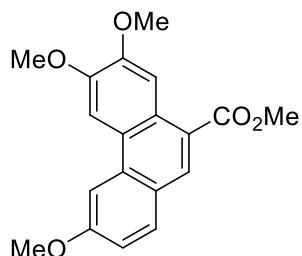


Figure S40. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of derivative **8b**.

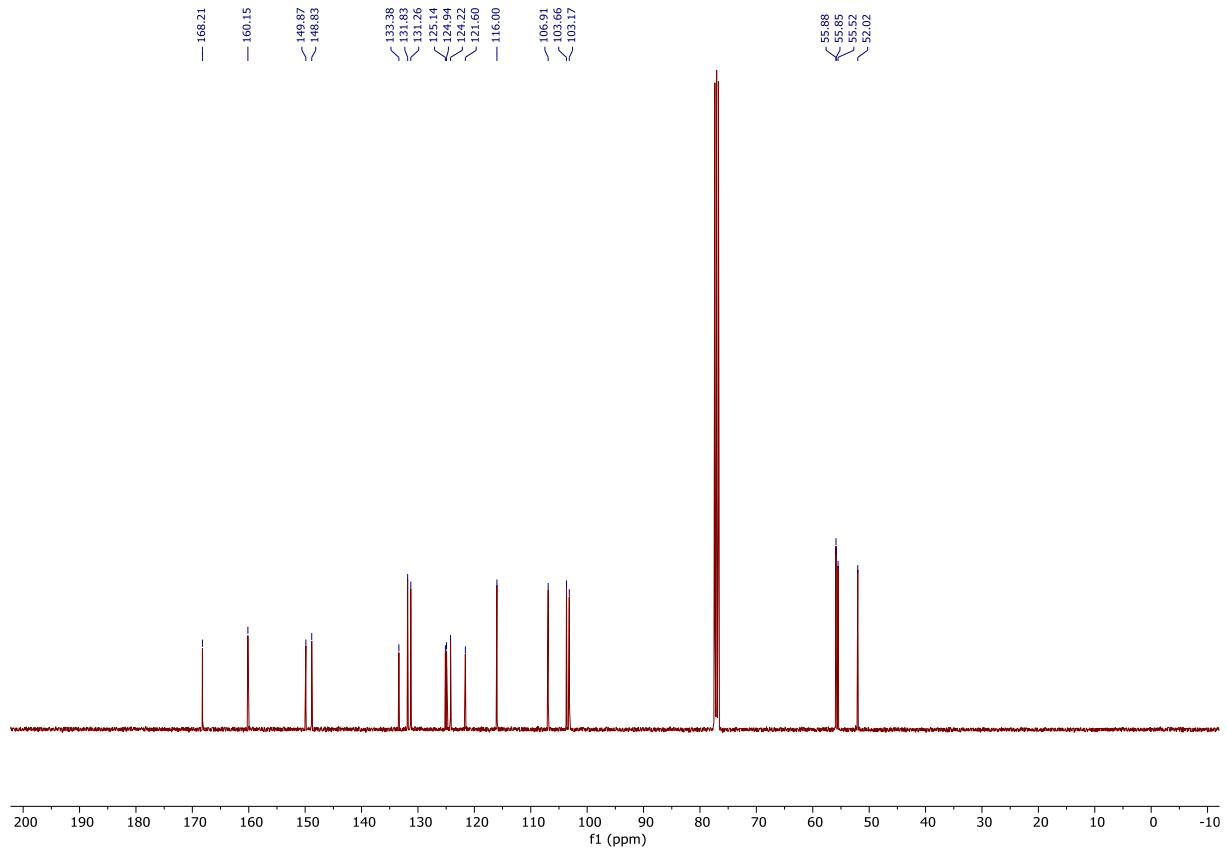


Figure S41.  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 100 MHz) of derivative **8b**.

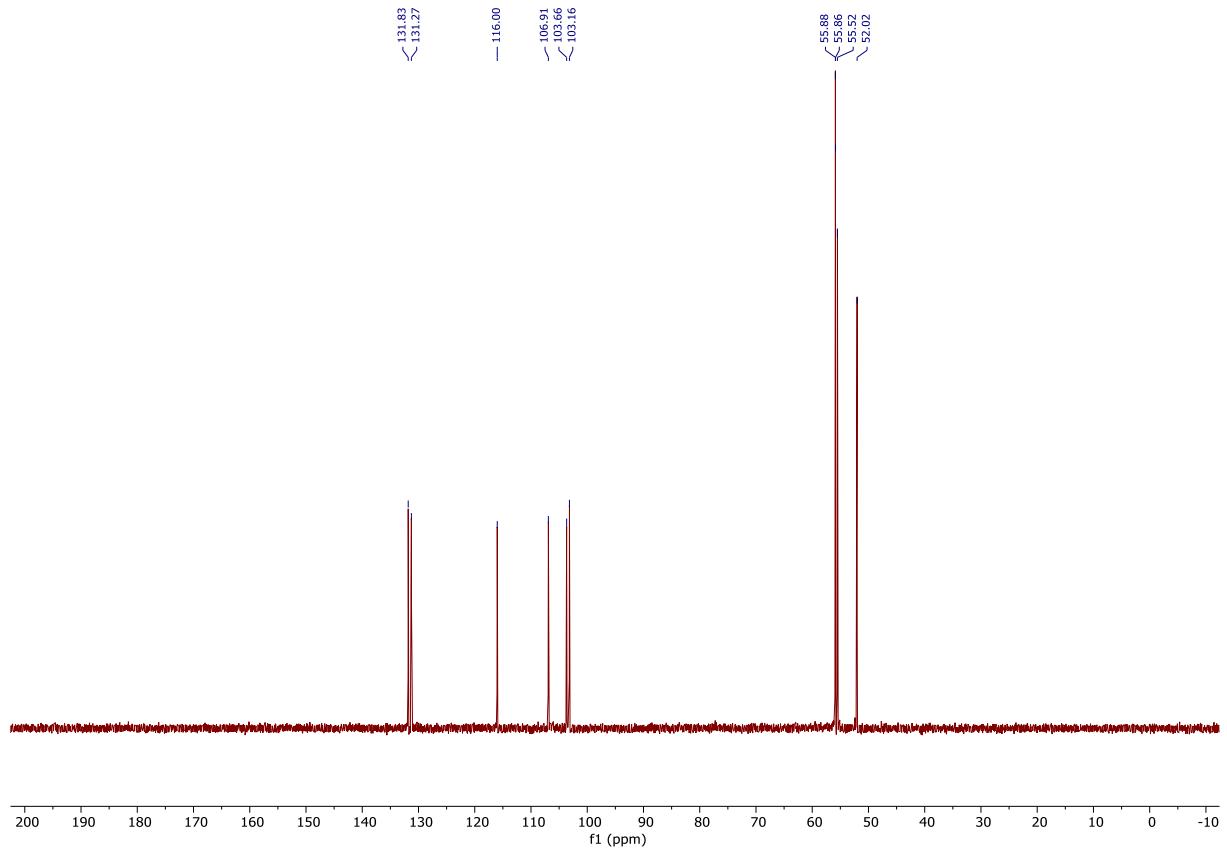


Figure S42. DEPT spectrum ( $\text{CDCl}_3$ , 100 MHz) of derivative **8b**.

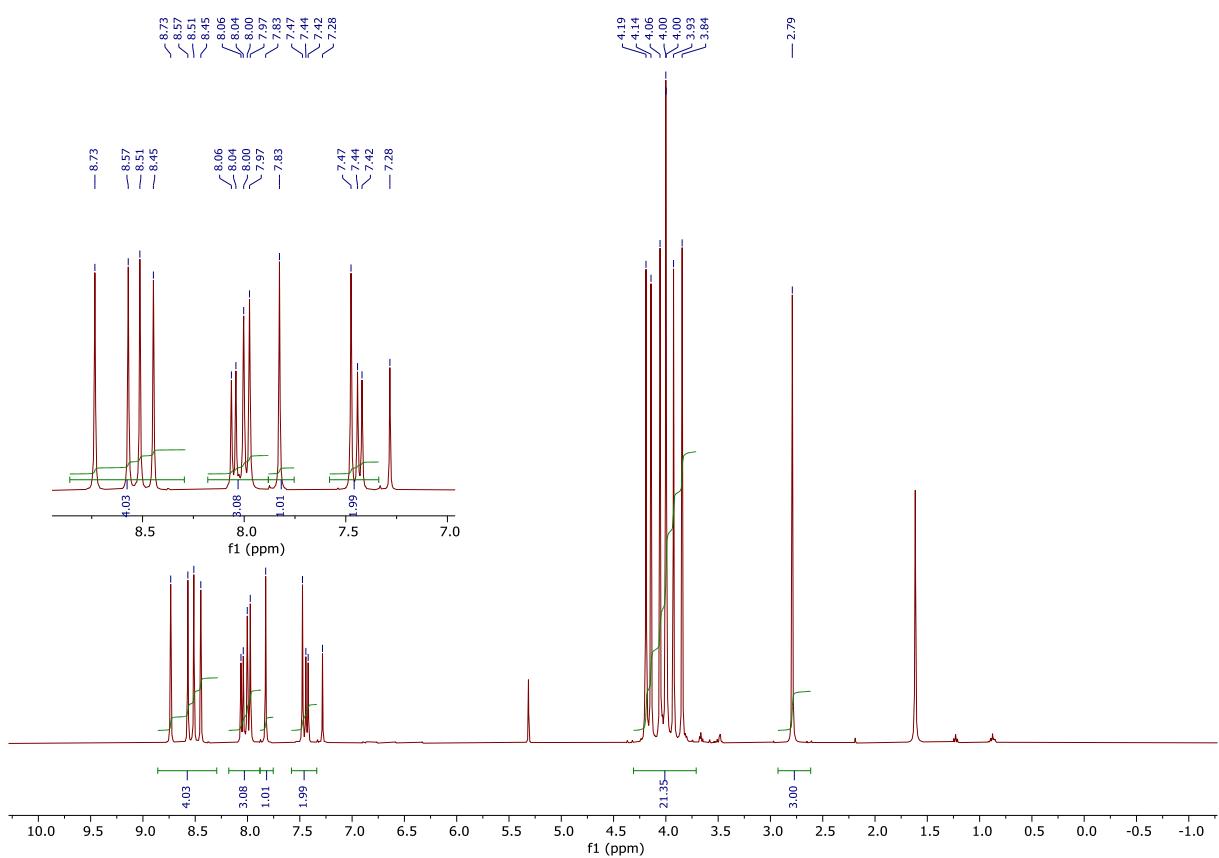
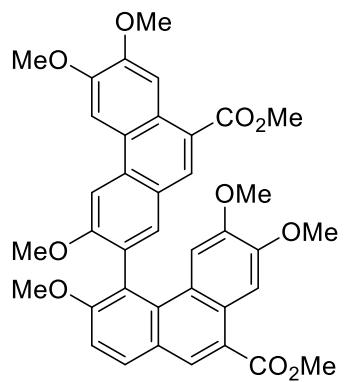


Figure S43.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 400 MHz) of derivative **9**.

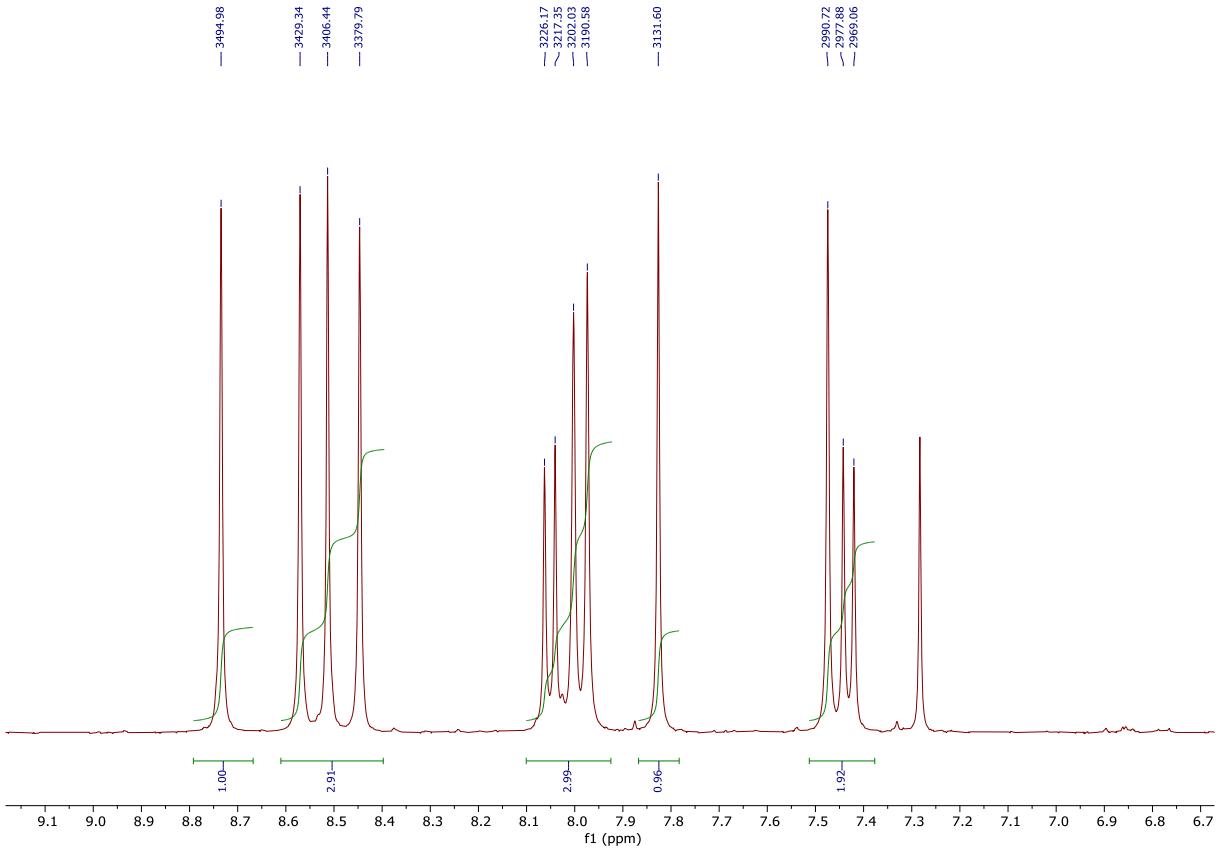


Figure S44.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 400 MHz) of derivative **9**.

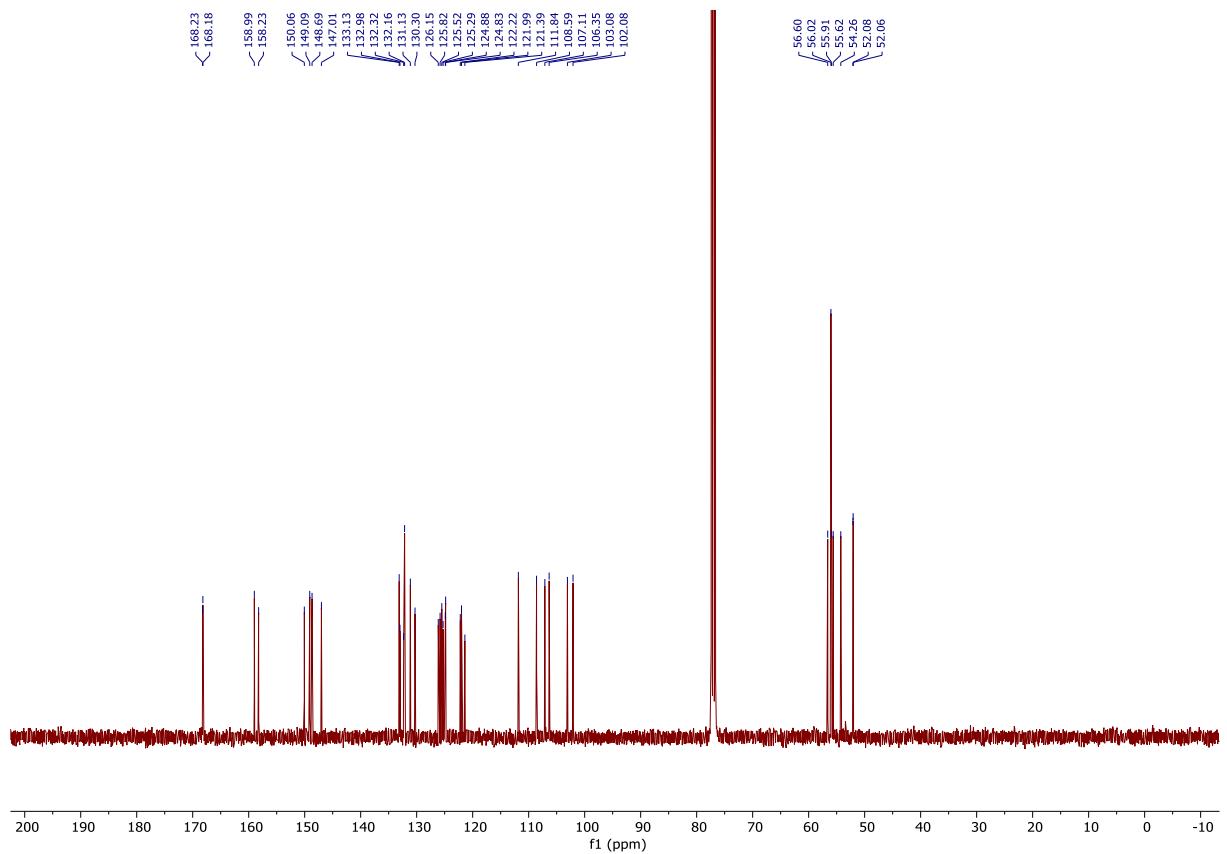


Figure S45.  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 100 MHz) of derivative **9**.

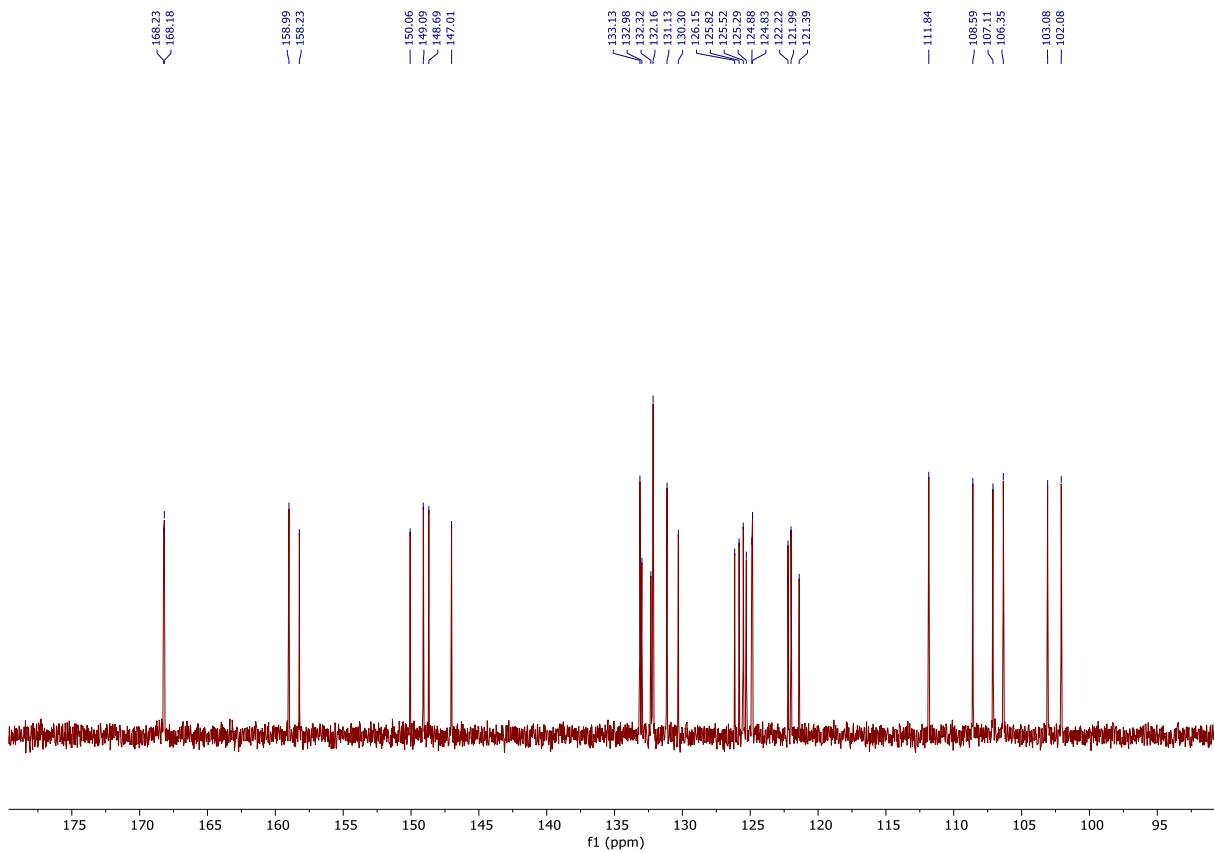


Figure S46.  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 100 MHz) of derivative **9**.

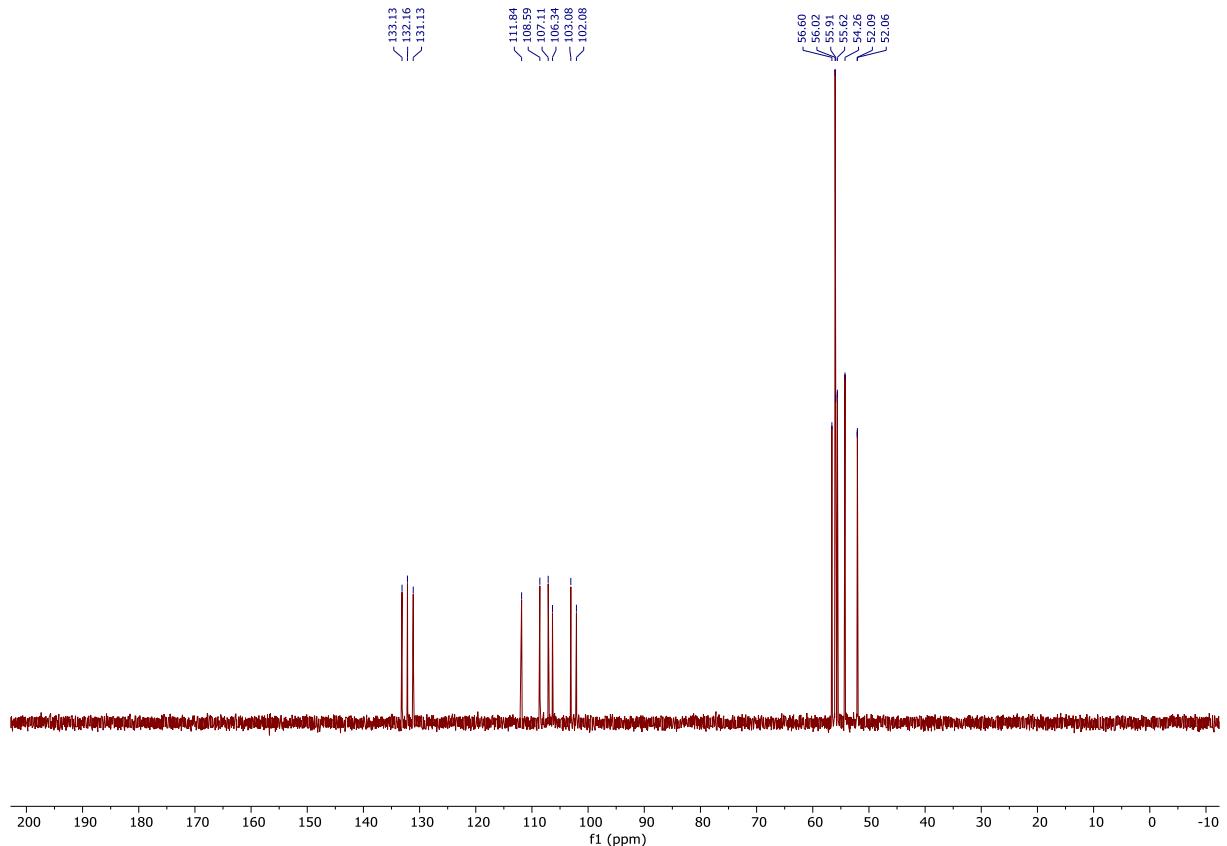


Figure S47. DEPT spectrum ( $\text{CDCl}_3$ , 100 MHz) of derivative **9**.

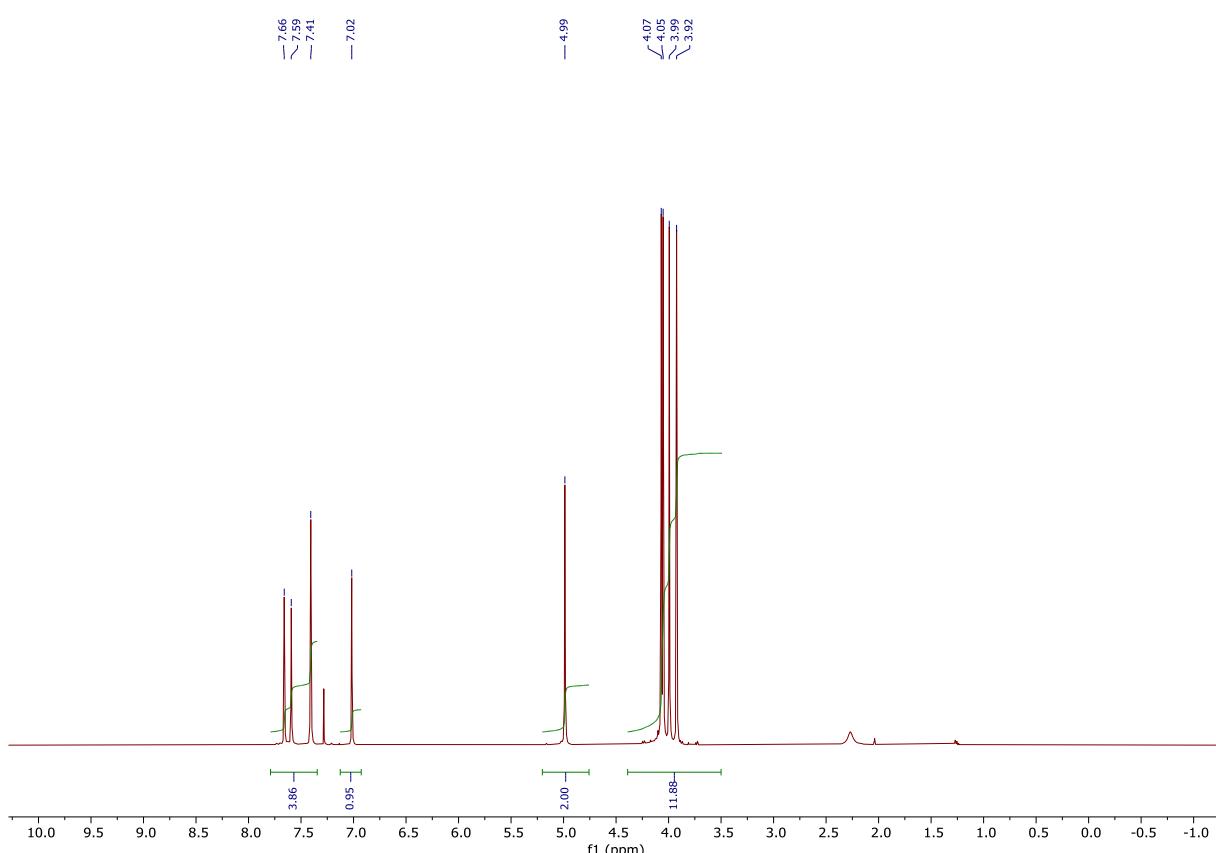
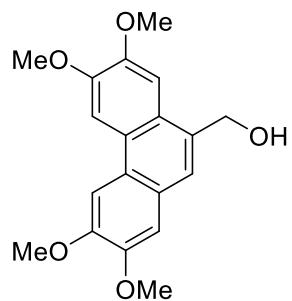


Figure S48. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of derivative **10a**.

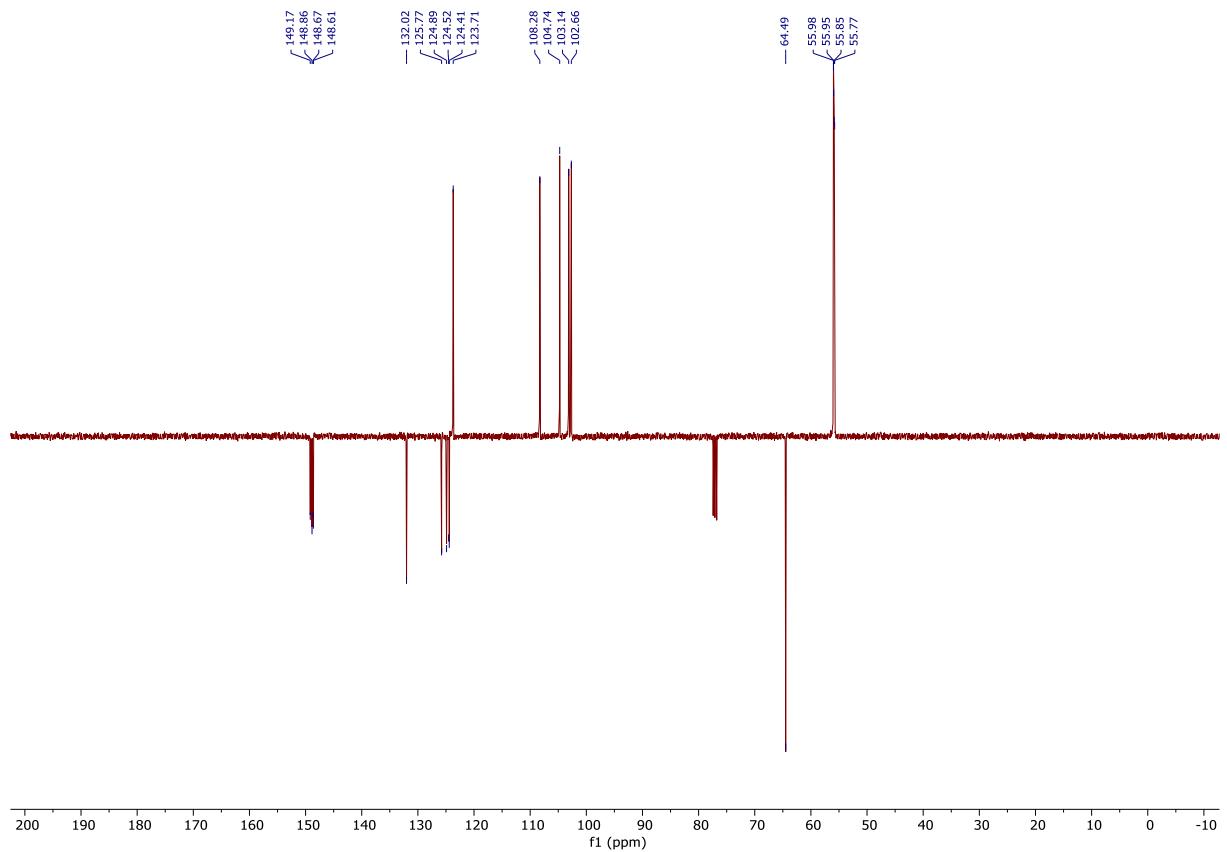
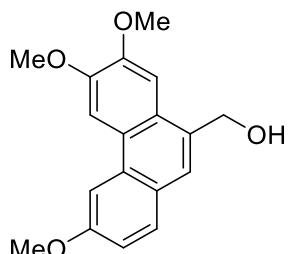


Figure S49. J-MOD NMR spectrum (CDCl<sub>3</sub>, 100 MHz) of derivative **10a**.



**10b**

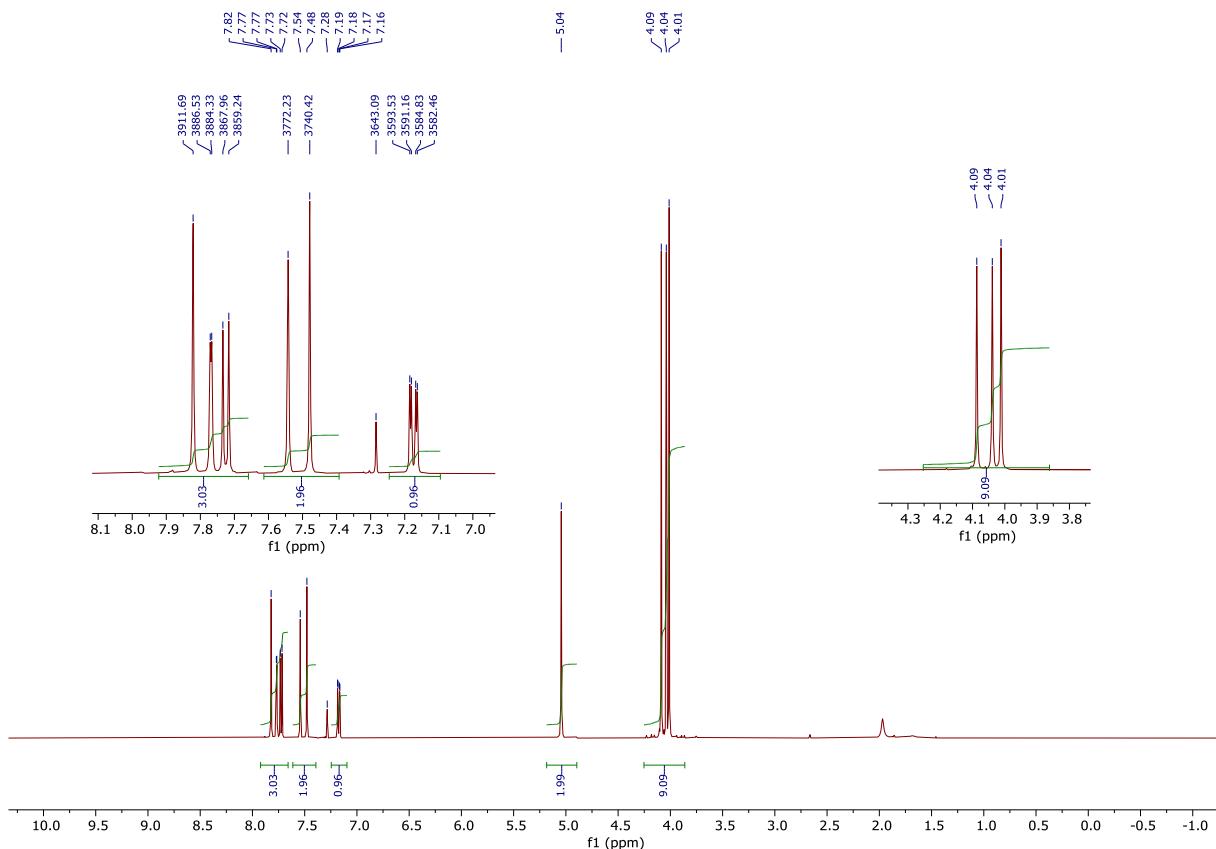


Figure S50.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 500 MHz) of derivative **10b**.

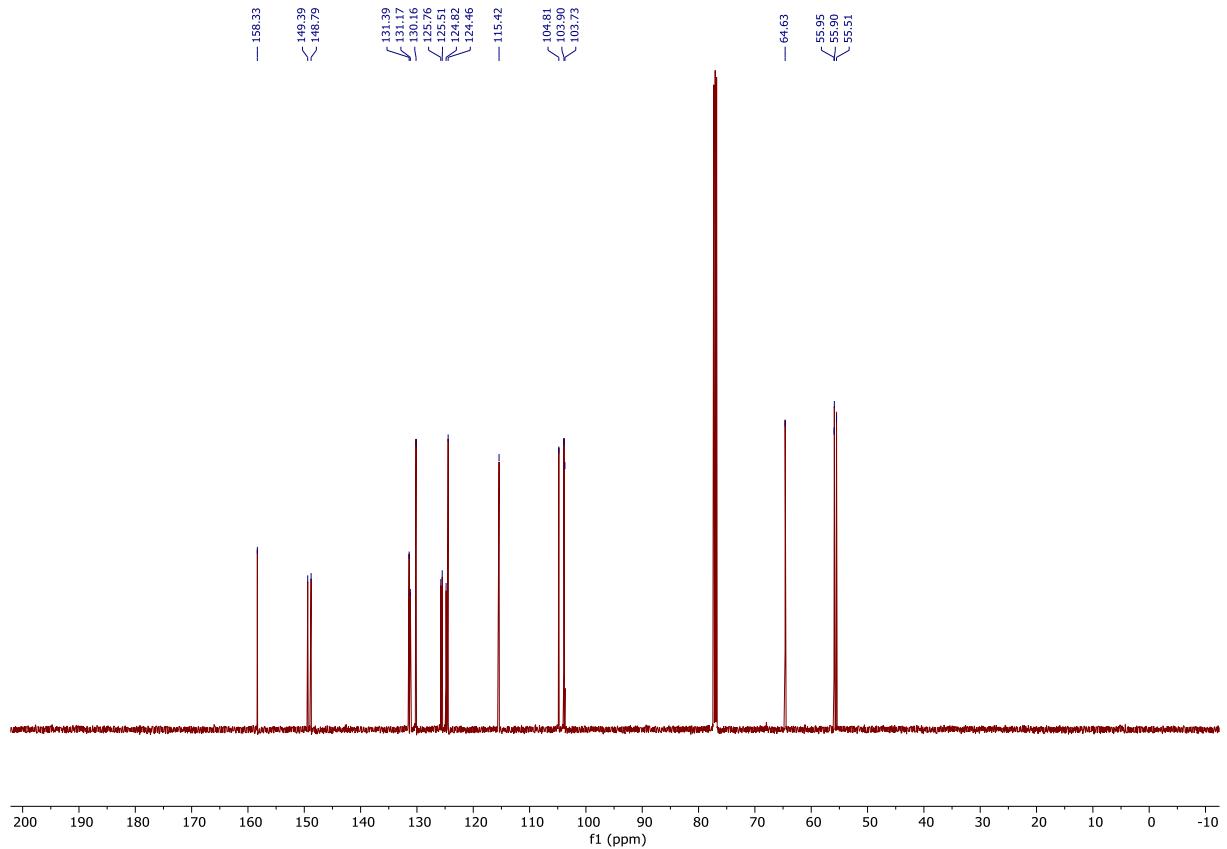


Figure S51.  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 125 MHz) of derivative **10b**.

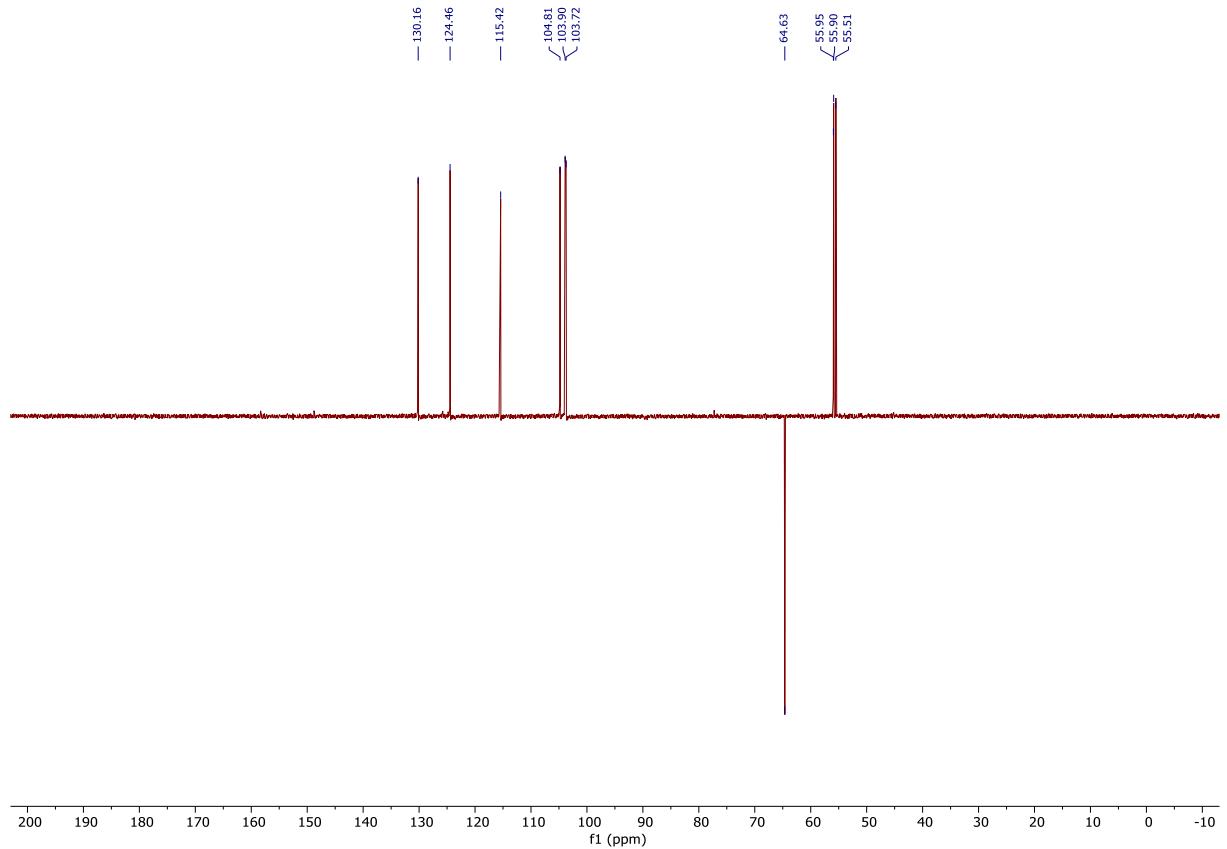


Figure S52. DEPT spectrum ( $\text{CDCl}_3$ , 125 MHz) of derivative **10b**.

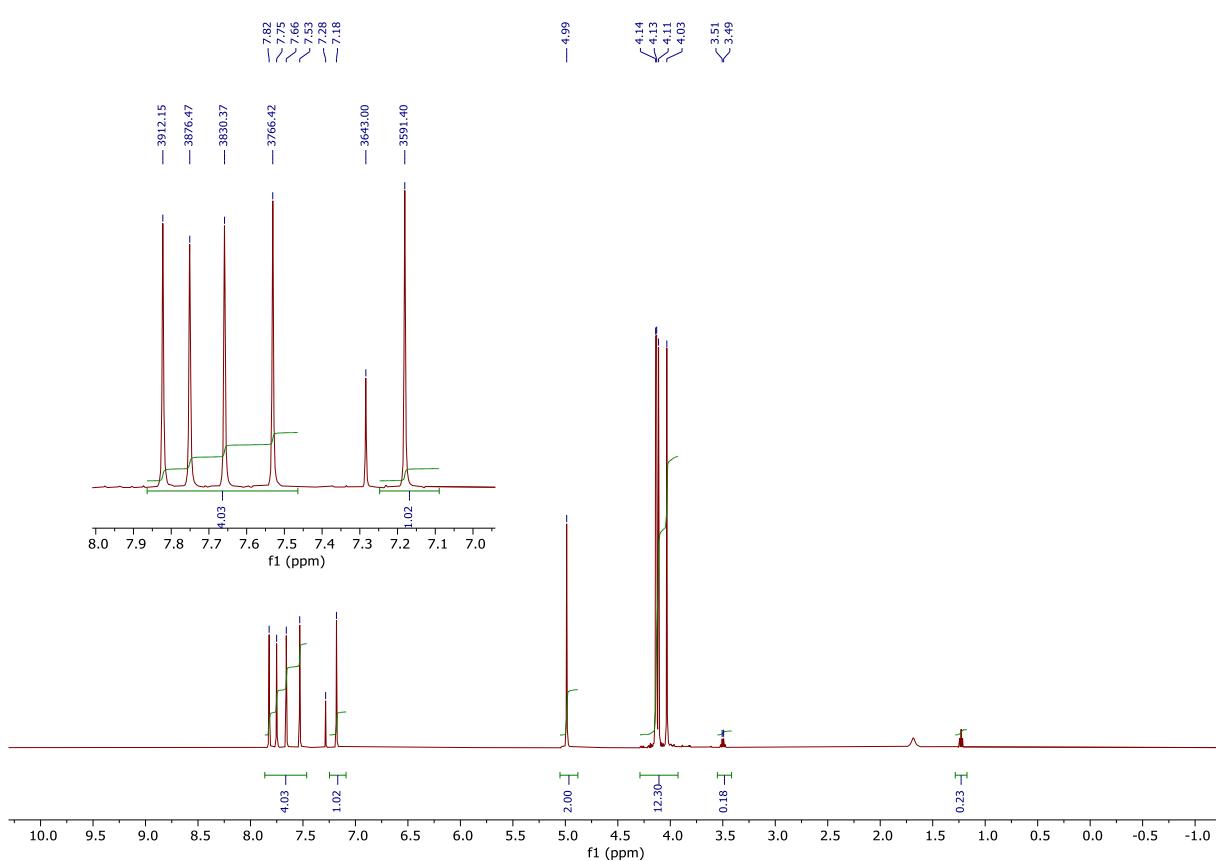
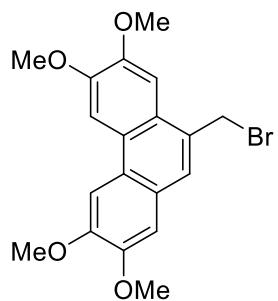


Figure S53.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 500 MHz) of derivative **11a**.

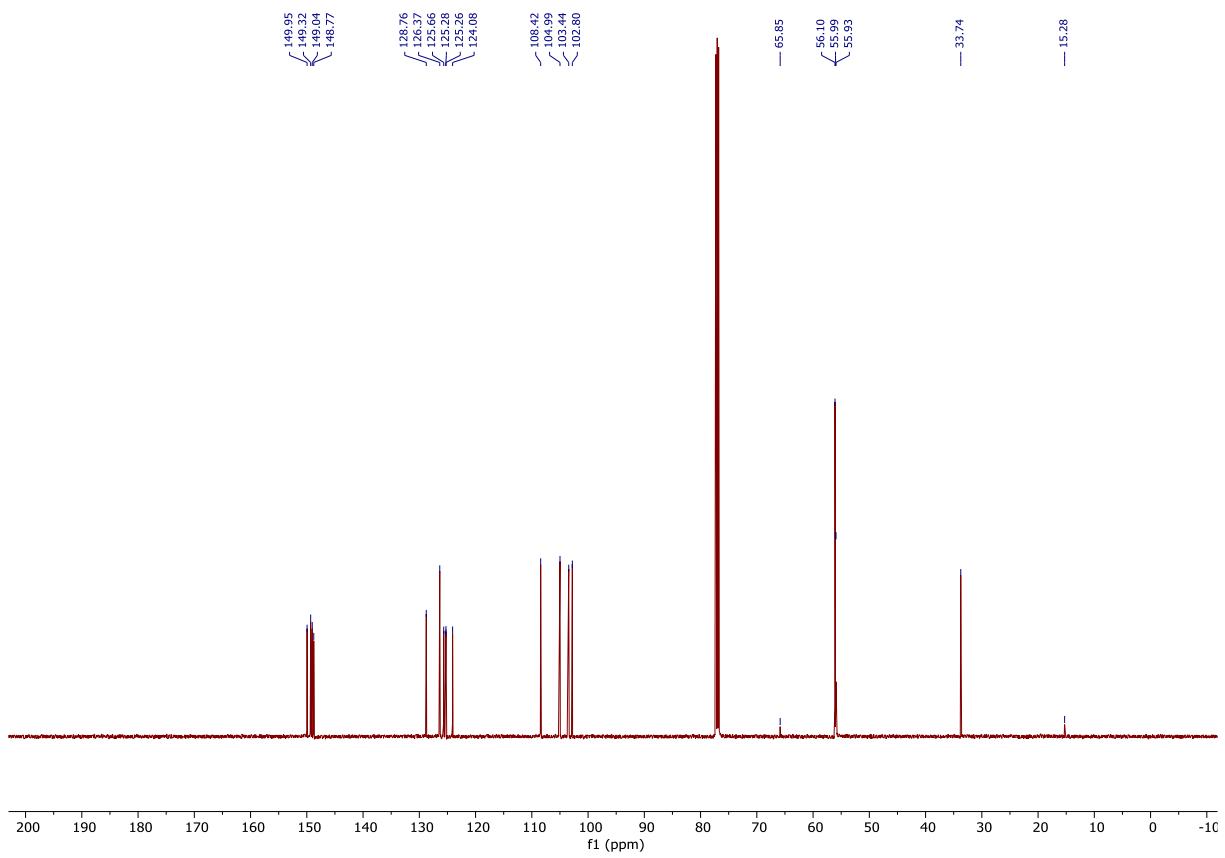


Figure S54.  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 125 MHz) of derivative **11a**.

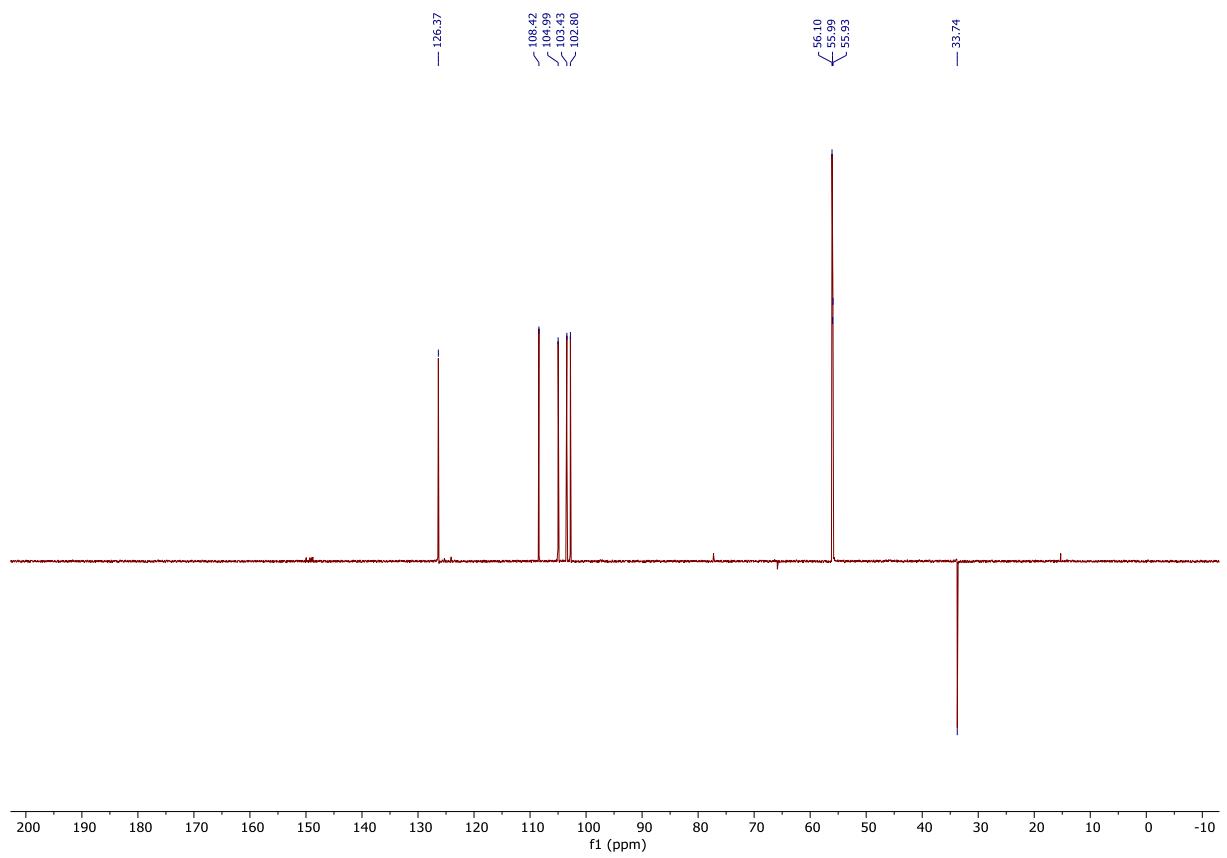
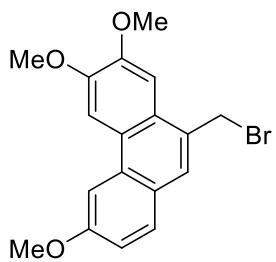


Figure S55. DEPT spectrum ( $\text{CDCl}_3$ , 125 MHz) of derivative **11a**.



11b

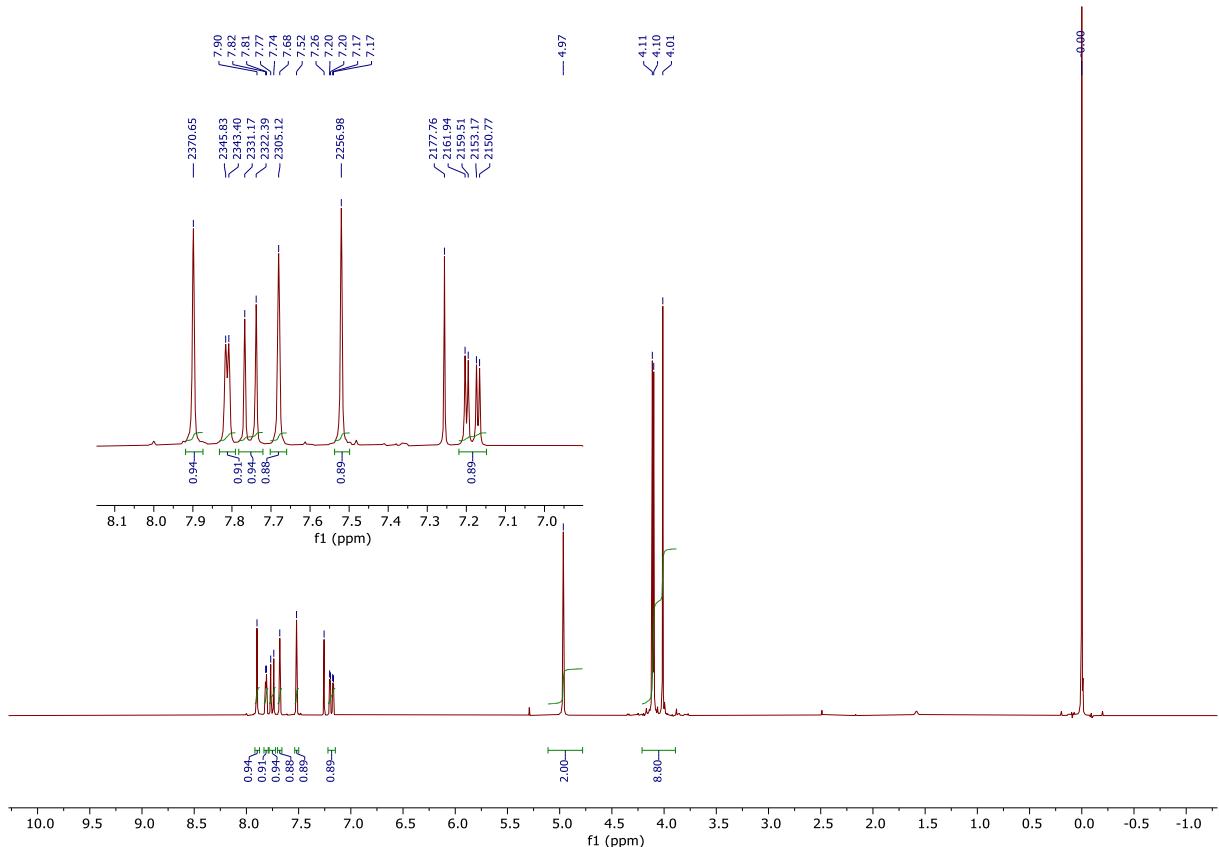


Figure S56.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 300 MHz) of derivative **11b**.

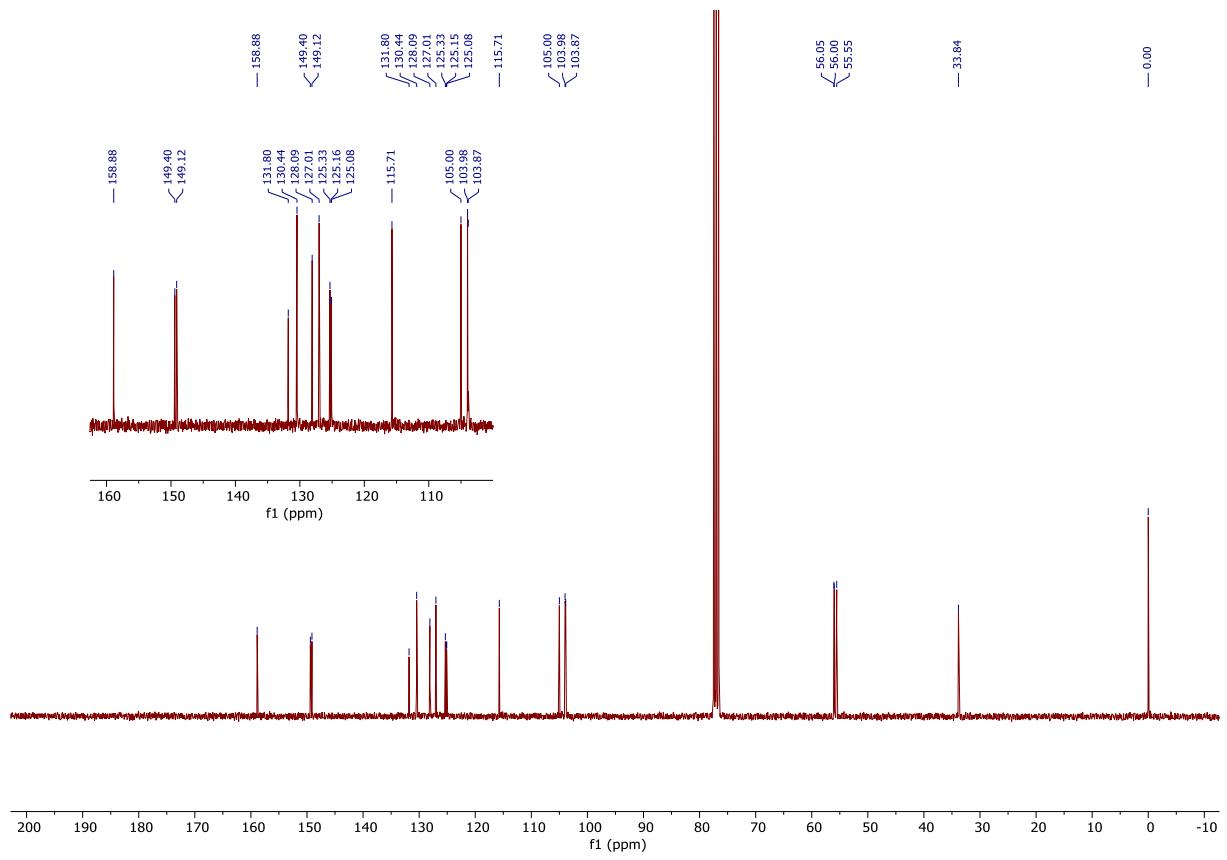


Figure S57.  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 75 MHz) of derivative **11b**.

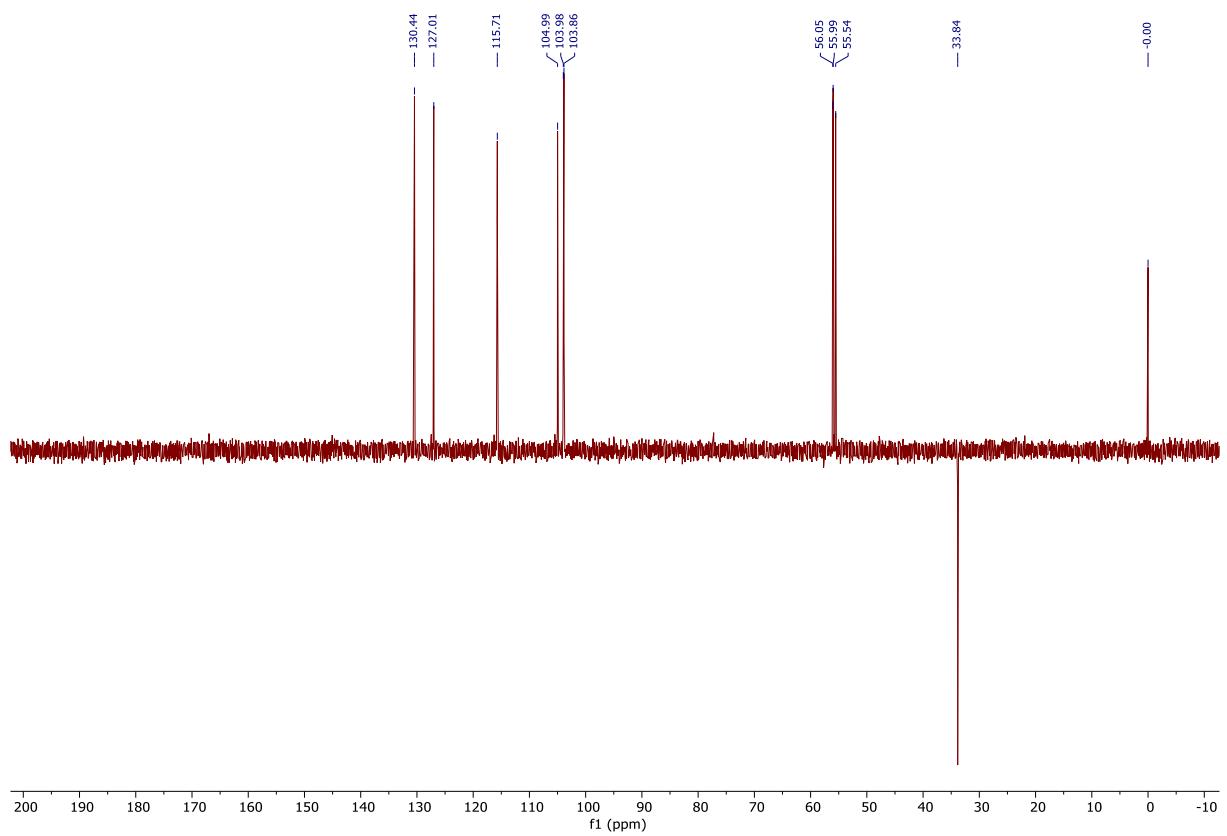
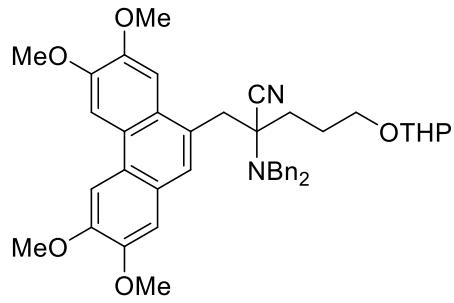


Figure S58. DEPT spectrum ( $\text{CDCl}_3$ , 75 MHz) of derivative **11b**.



12a

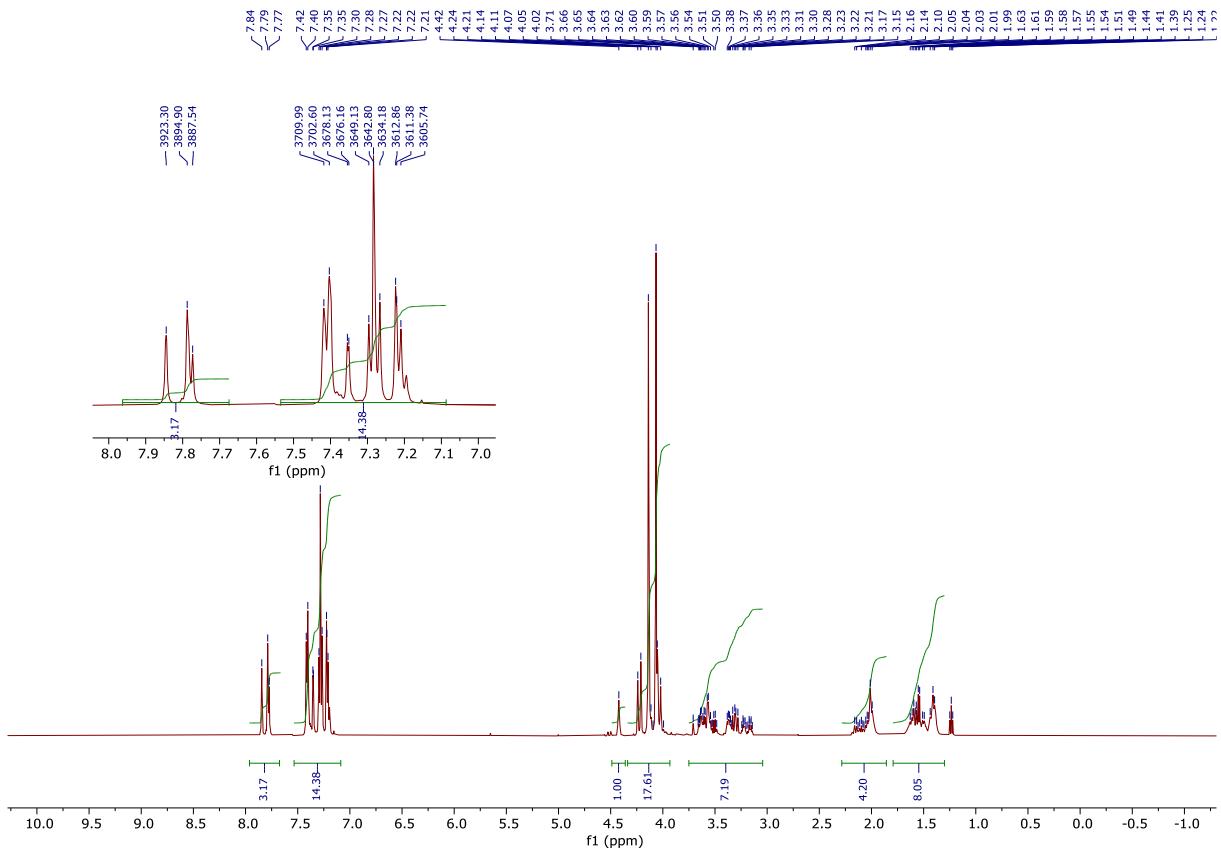


Figure S59.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 500 MHz) of derivative **12a**.

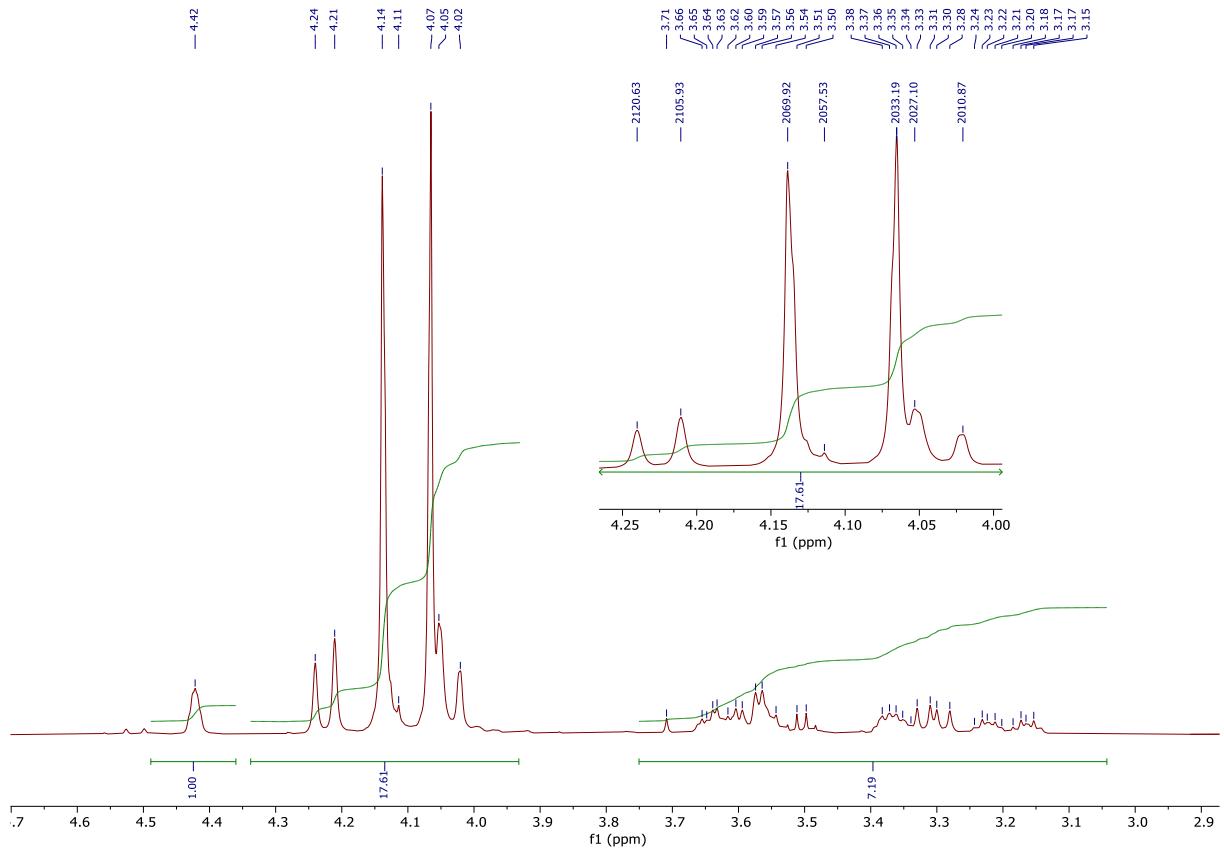


Figure S60.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 500 MHz) of derivative **12a**.

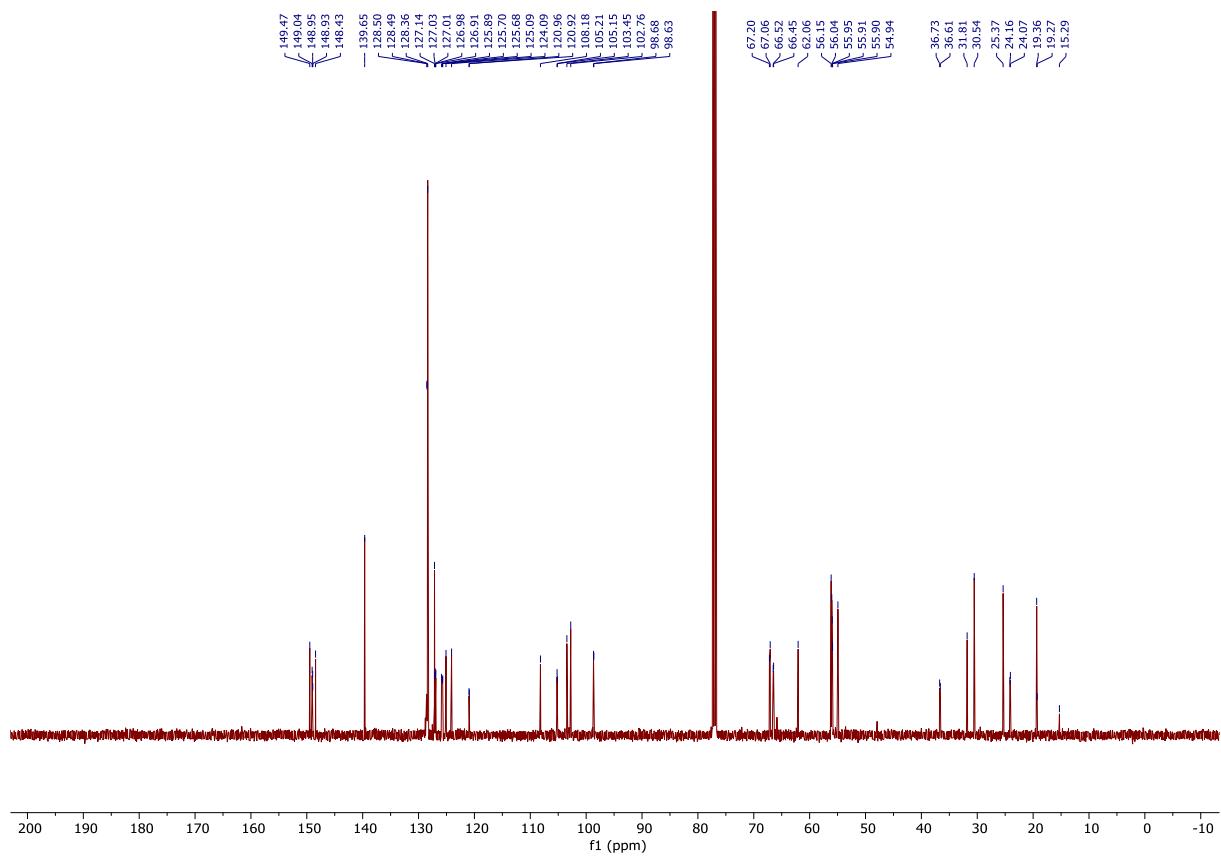


Figure S61.  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 125 MHz) of derivative **12a**.

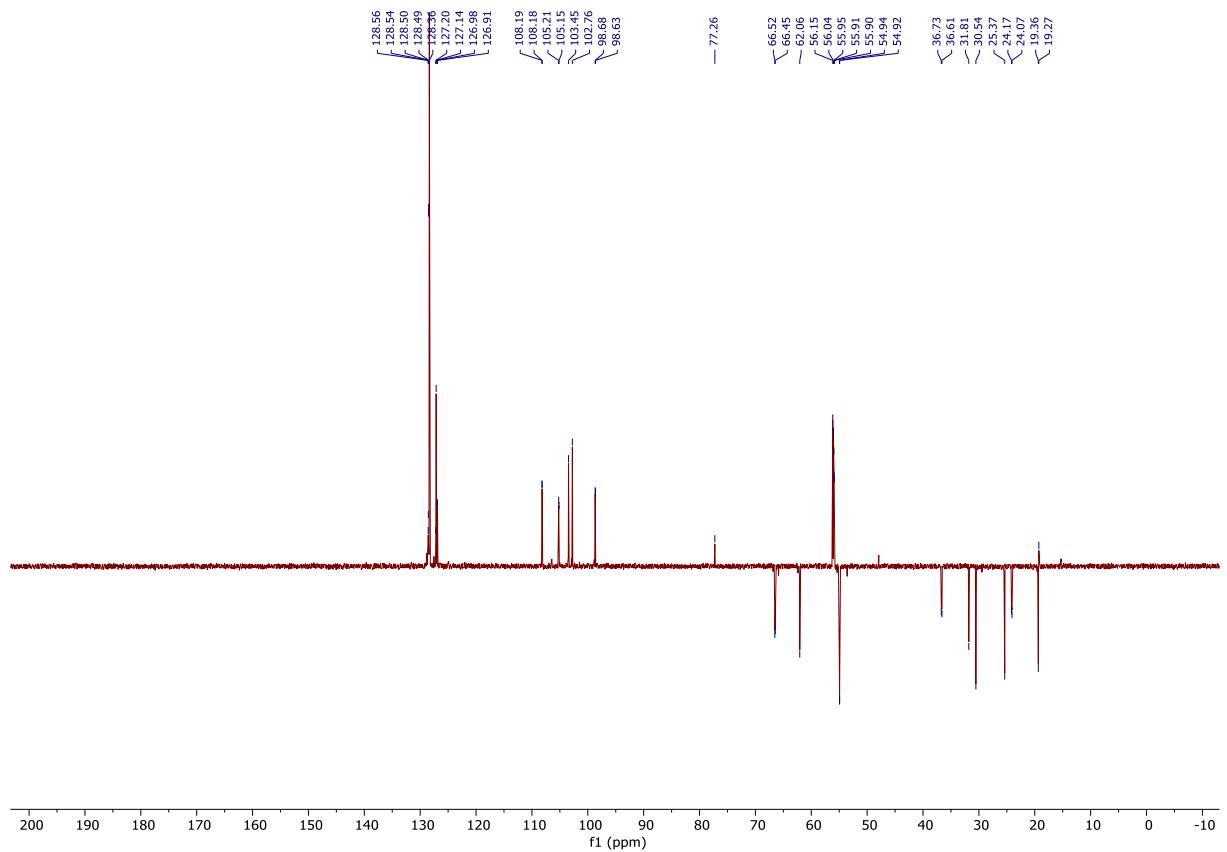


Figure S62. DEPT spectrum ( $\text{CDCl}_3$ , 125 MHz) of derivative **12a**.

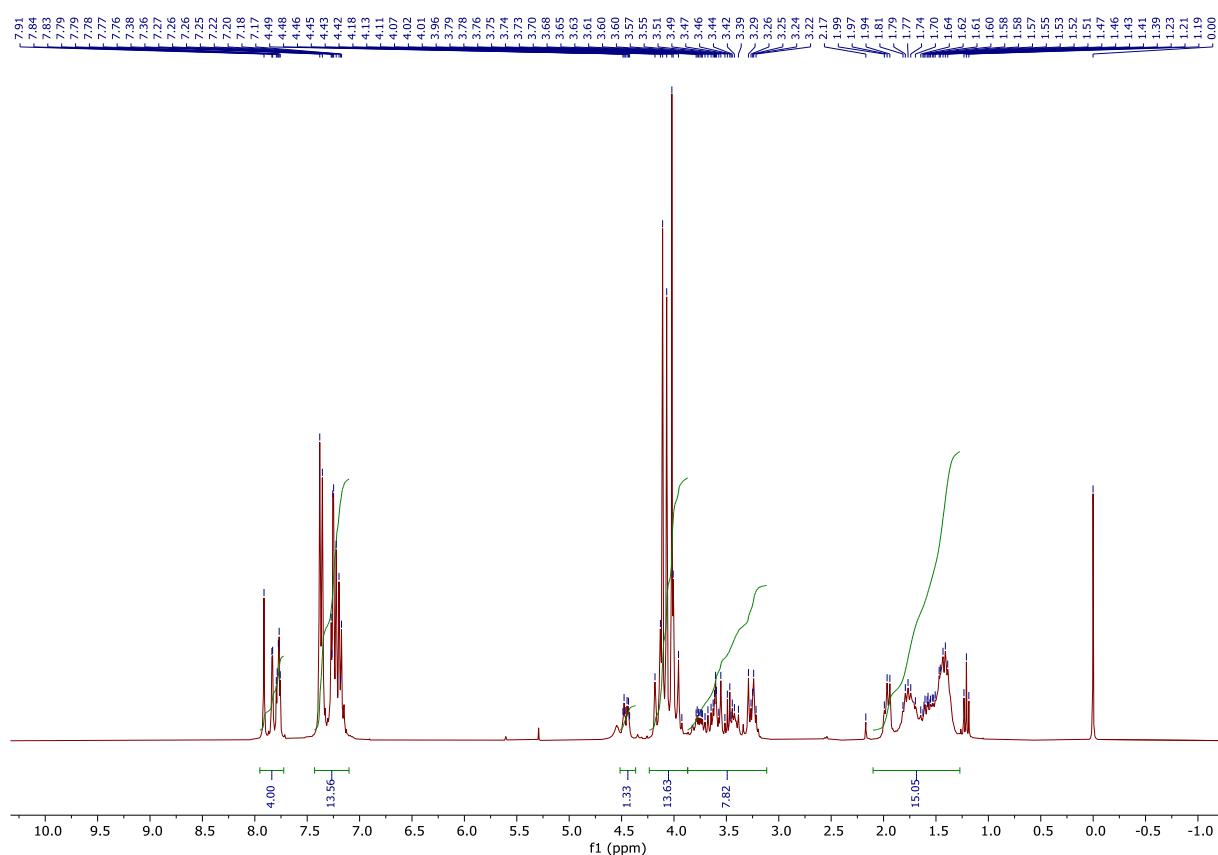
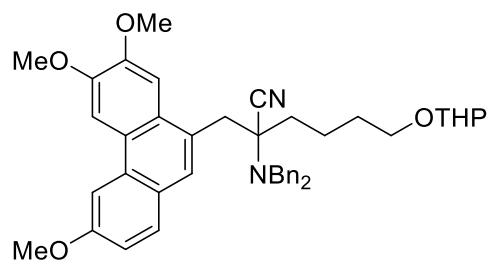


Figure S63.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 300 MHz) of derivative **12b**.

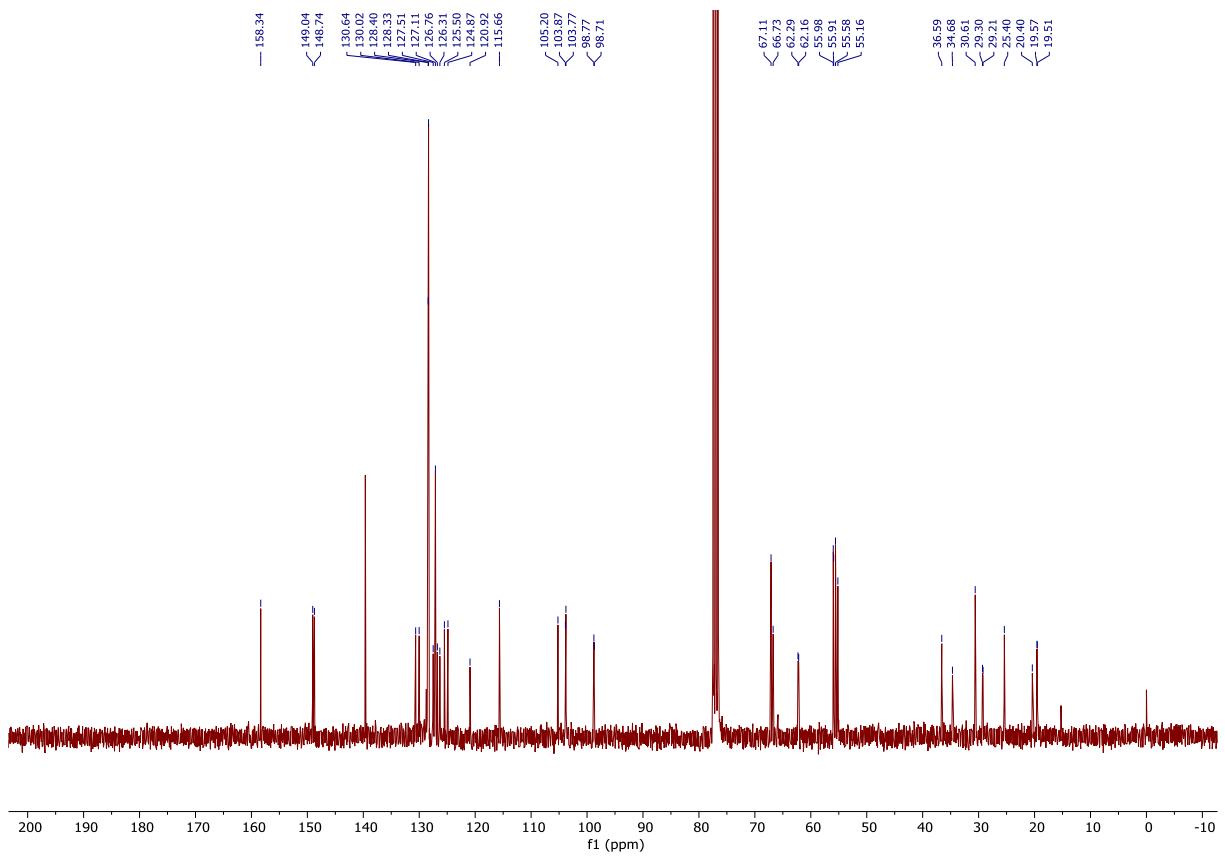


Figure S64.  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 75 MHz) of derivative **12b**.

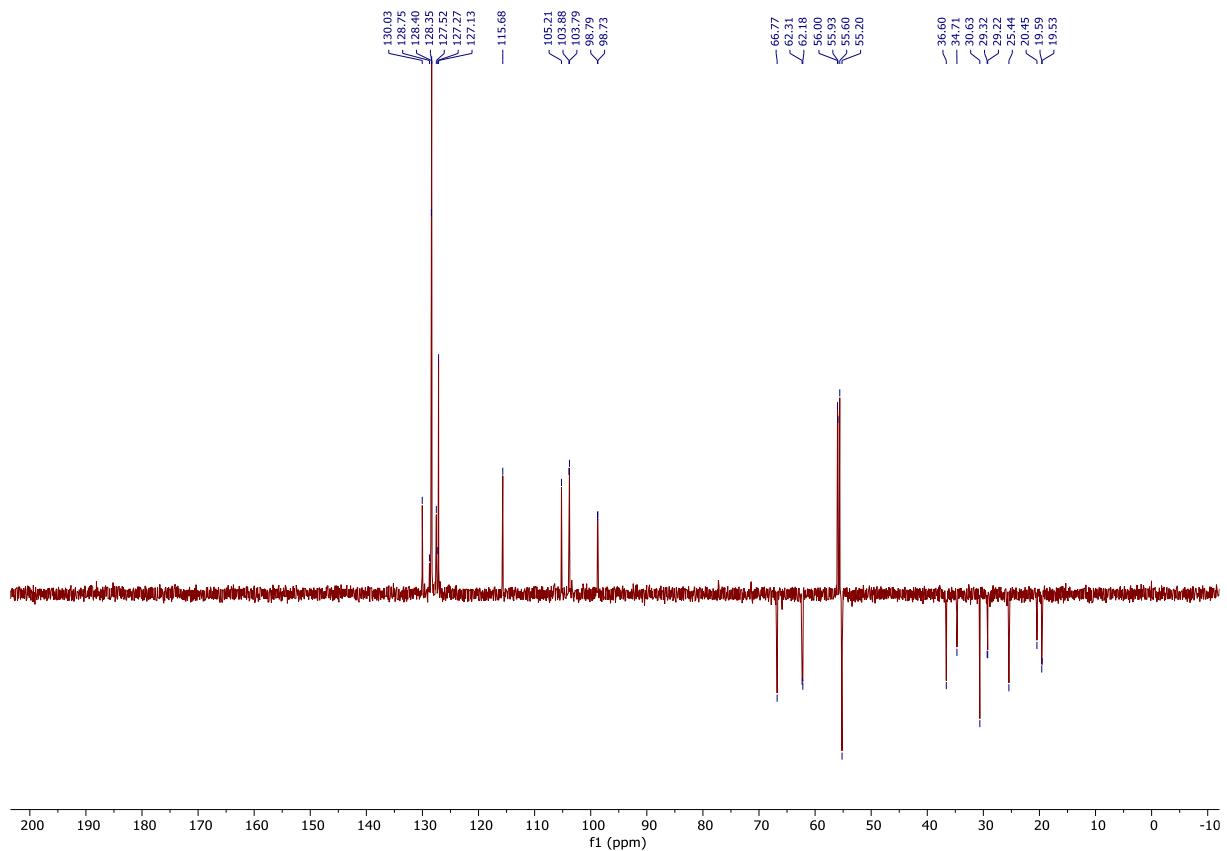
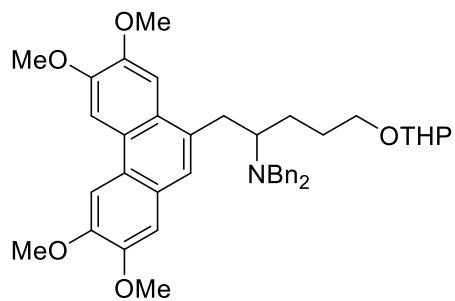


Figure S65. DEPT spectrum ( $\text{CDCl}_3$ , 75 MHz) of derivative **12b**.



**13a**

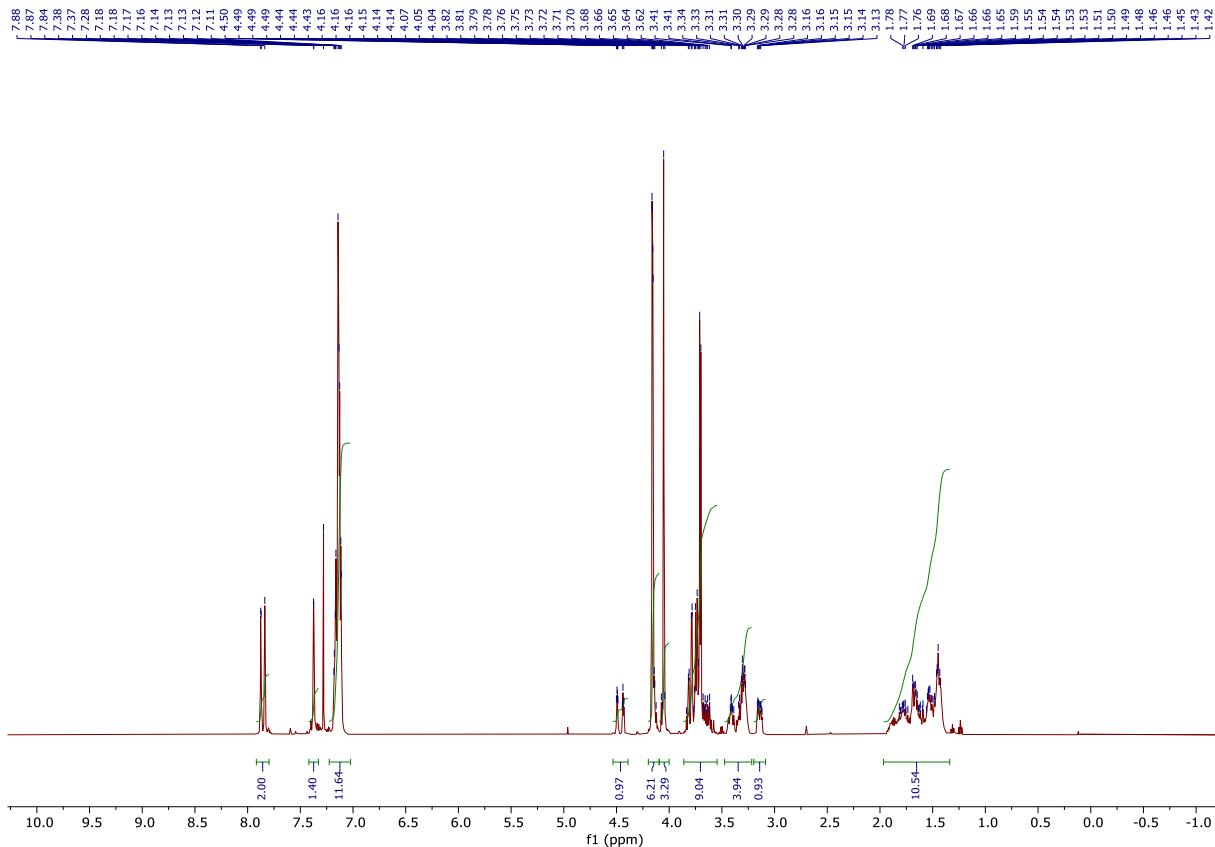


Figure S66.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 500 MHz) of derivative **13a**.

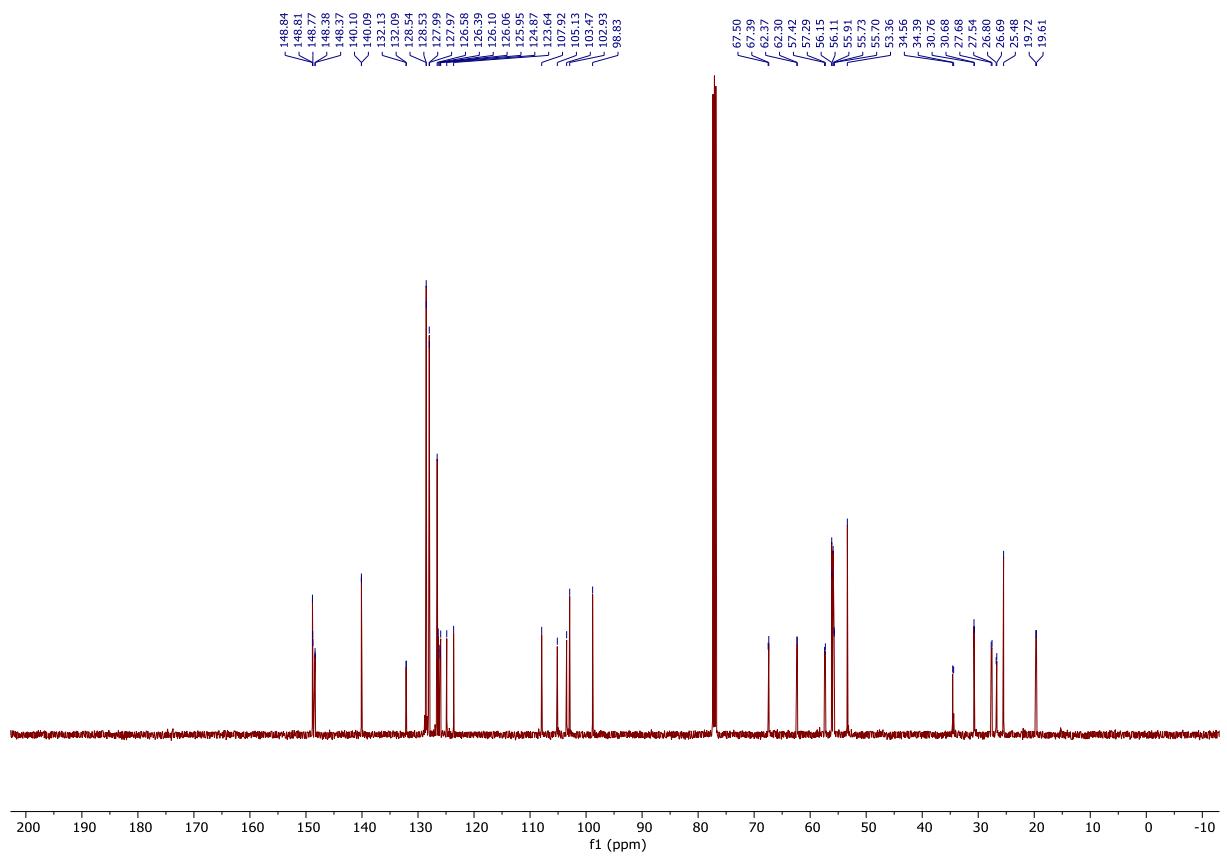


Figure S67. <sup>13</sup>C NMR spectrum ( $\text{CDCl}_3$ , 125 MHz) of derivative **13a**.

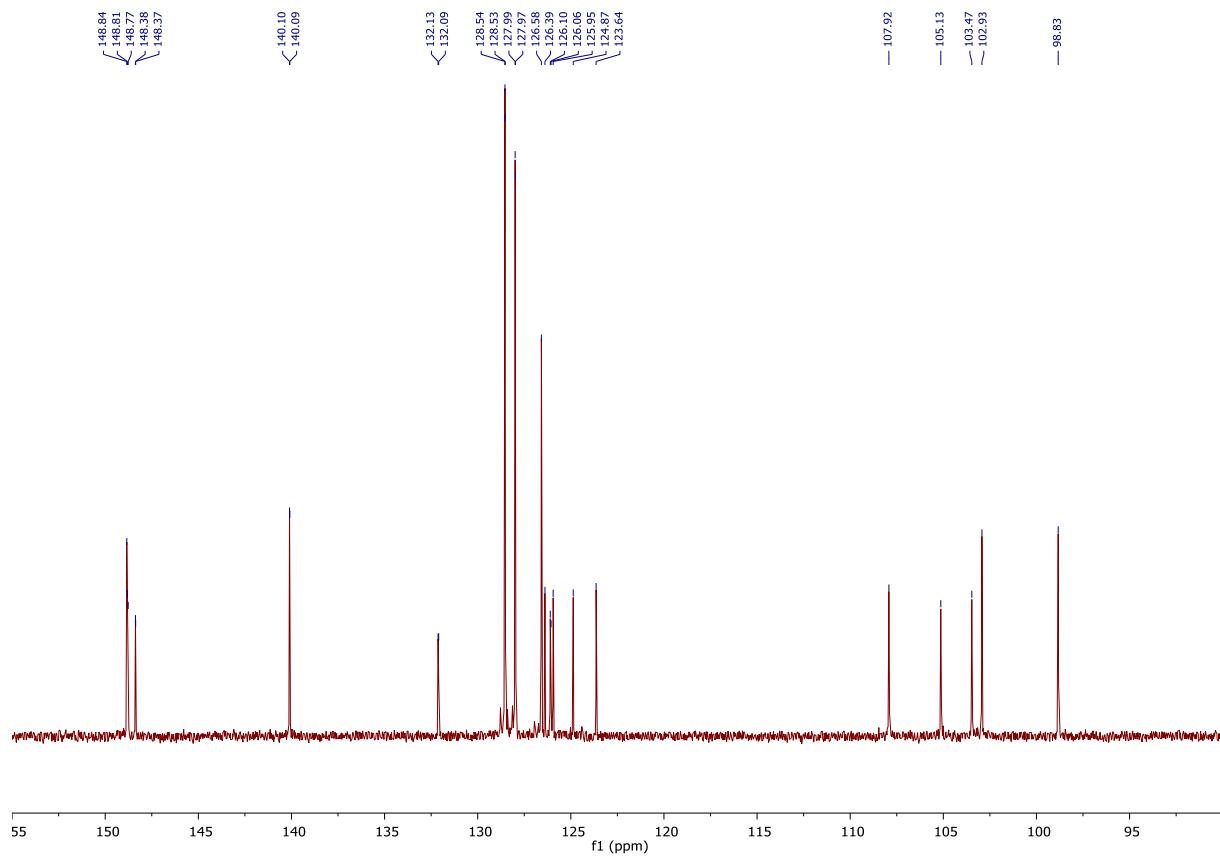


Figure S68.  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 125 MHz) of derivative **13a**.

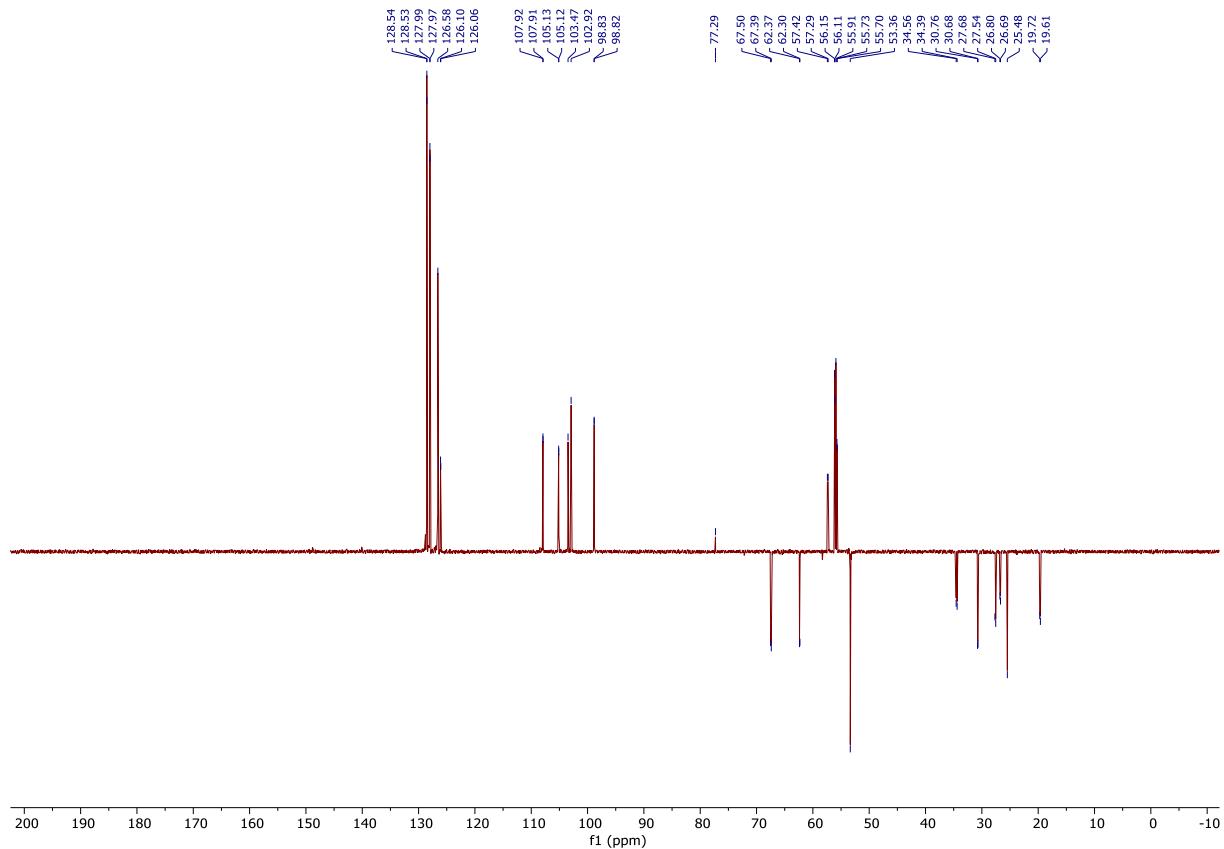


Figure S69. DEPT spectrum ( $\text{CDCl}_3$ , 125 MHz) of derivative **13a**.

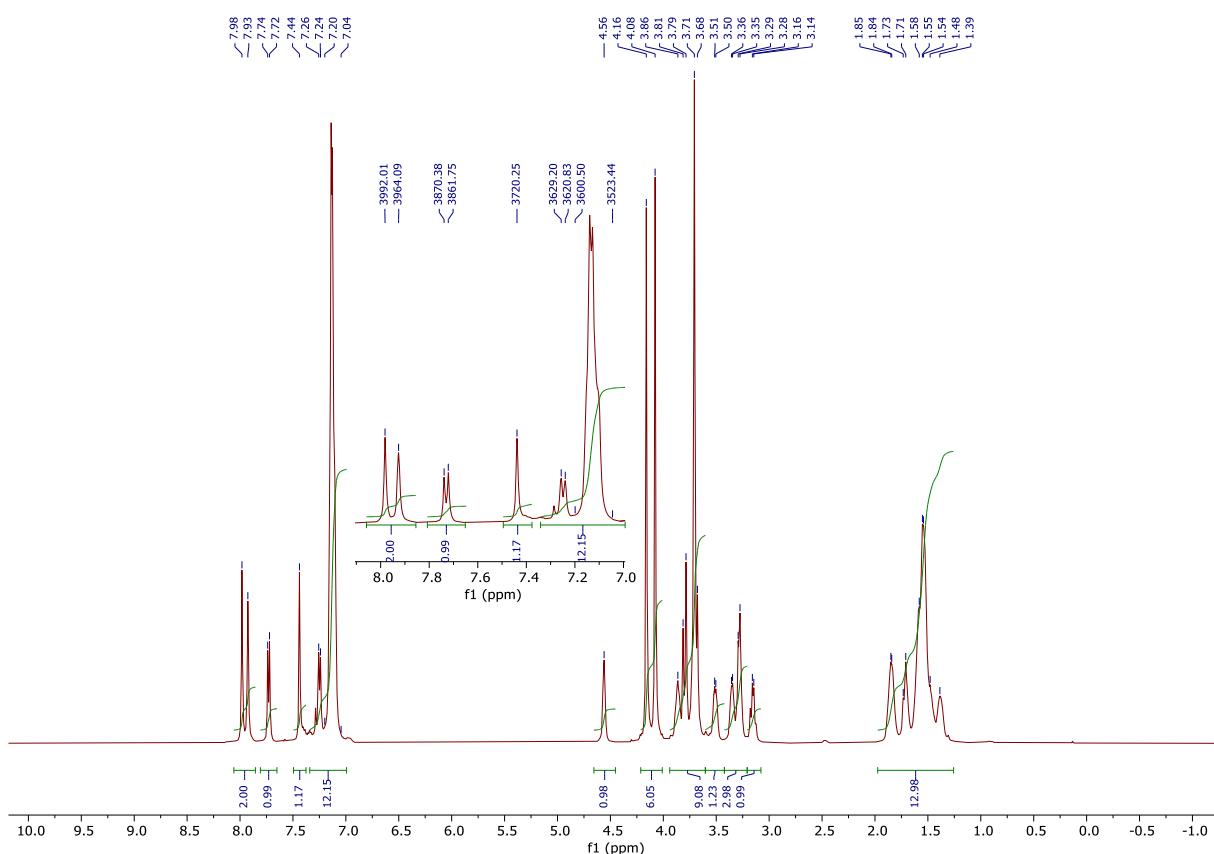
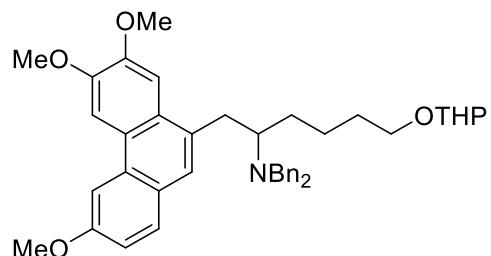


Figure S70.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 500 MHz) of derivative **13b**.

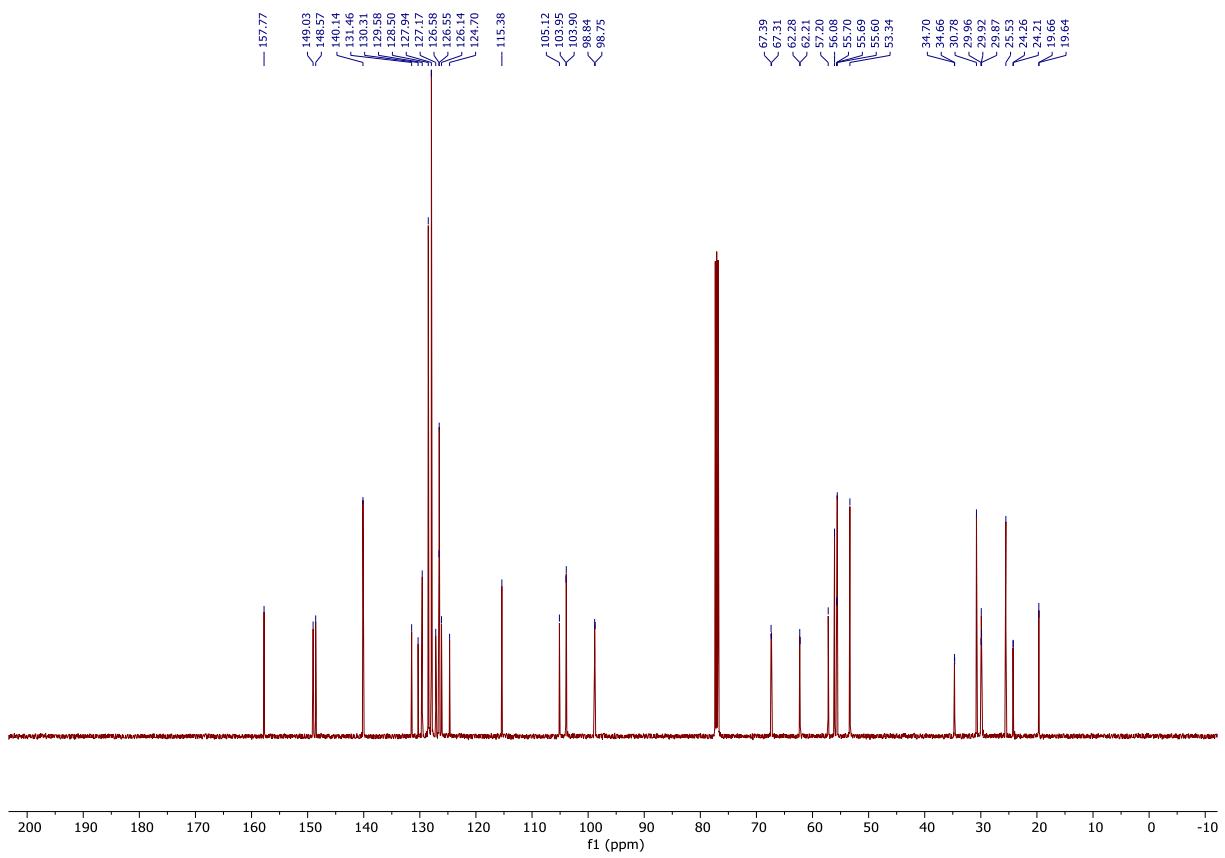


Figure S71.  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 125 MHz) of derivative **13b**.

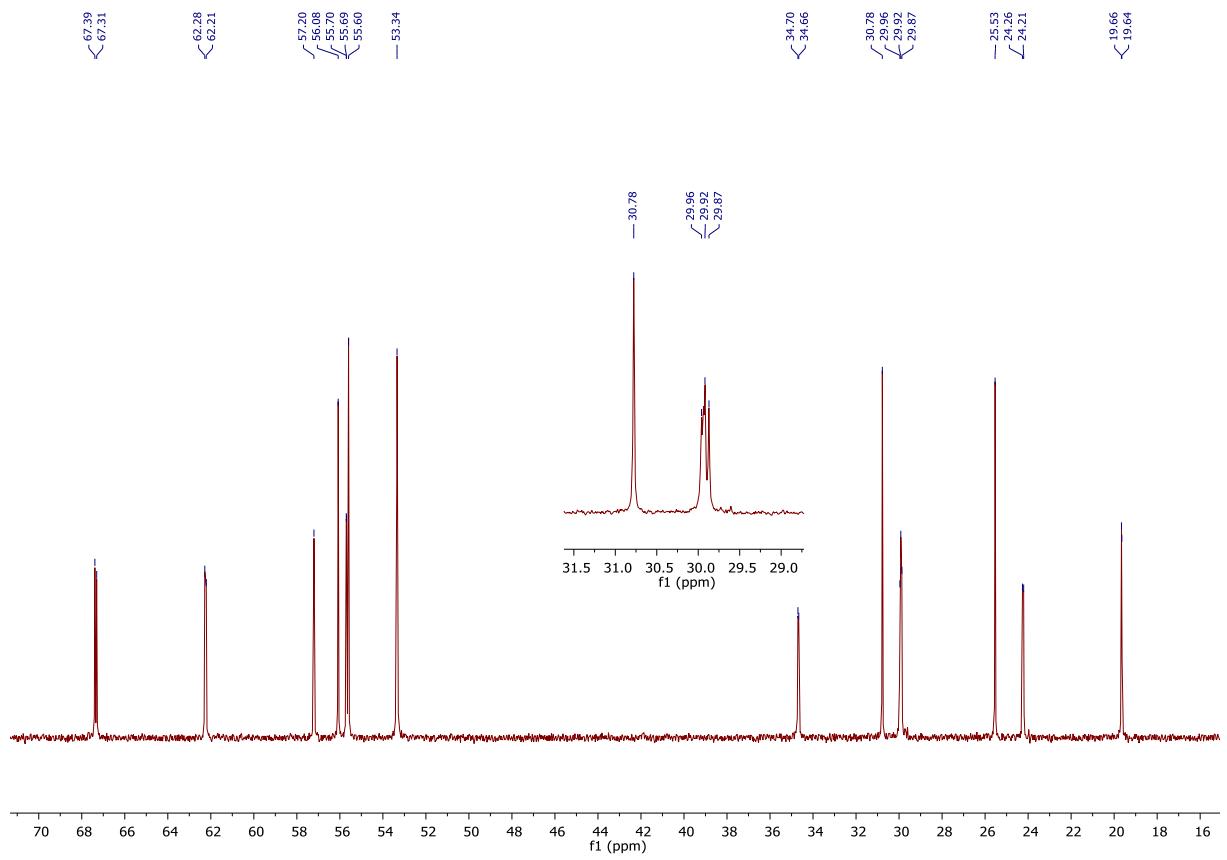


Figure S72.  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 125 MHz) of derivative **13b**.

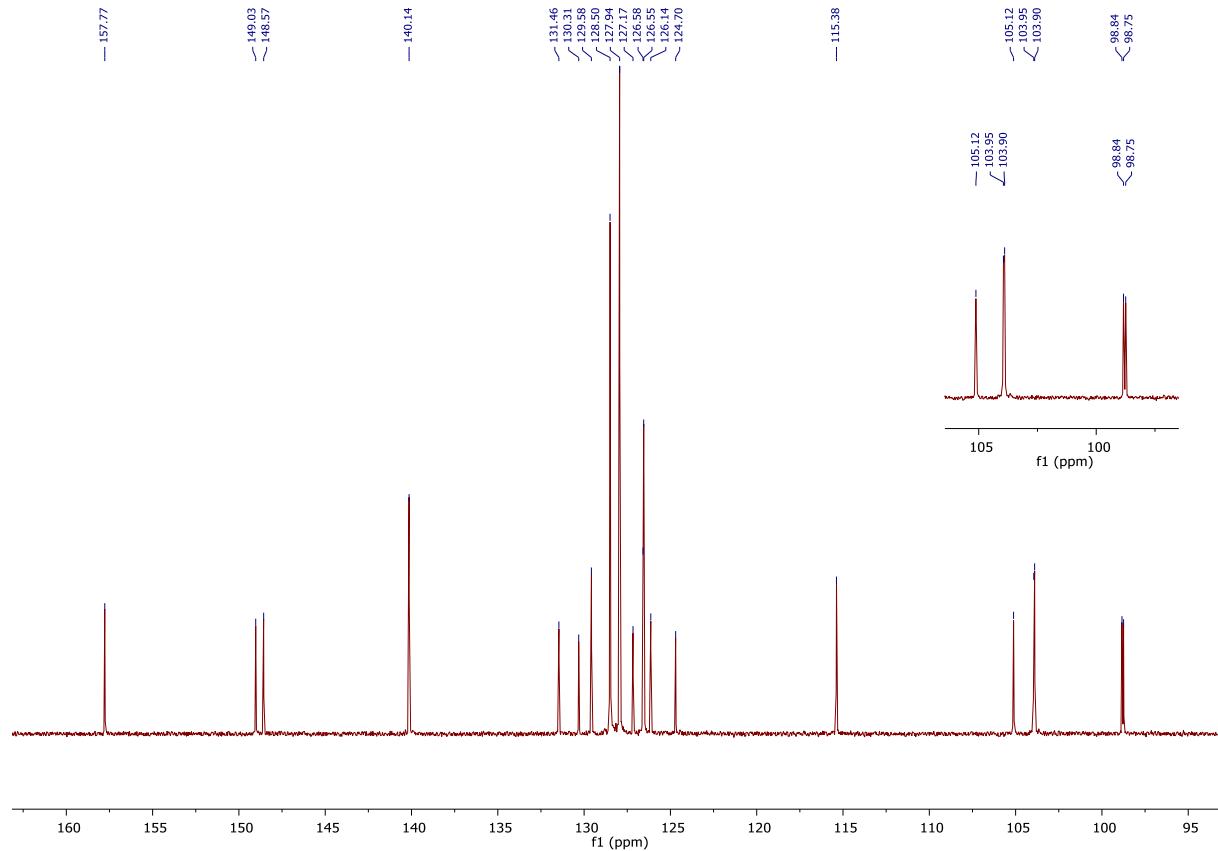


Figure S73. <sup>13</sup>C NMR spectrum ( $\text{CDCl}_3$ , 125 MHz) of derivative **13b**.

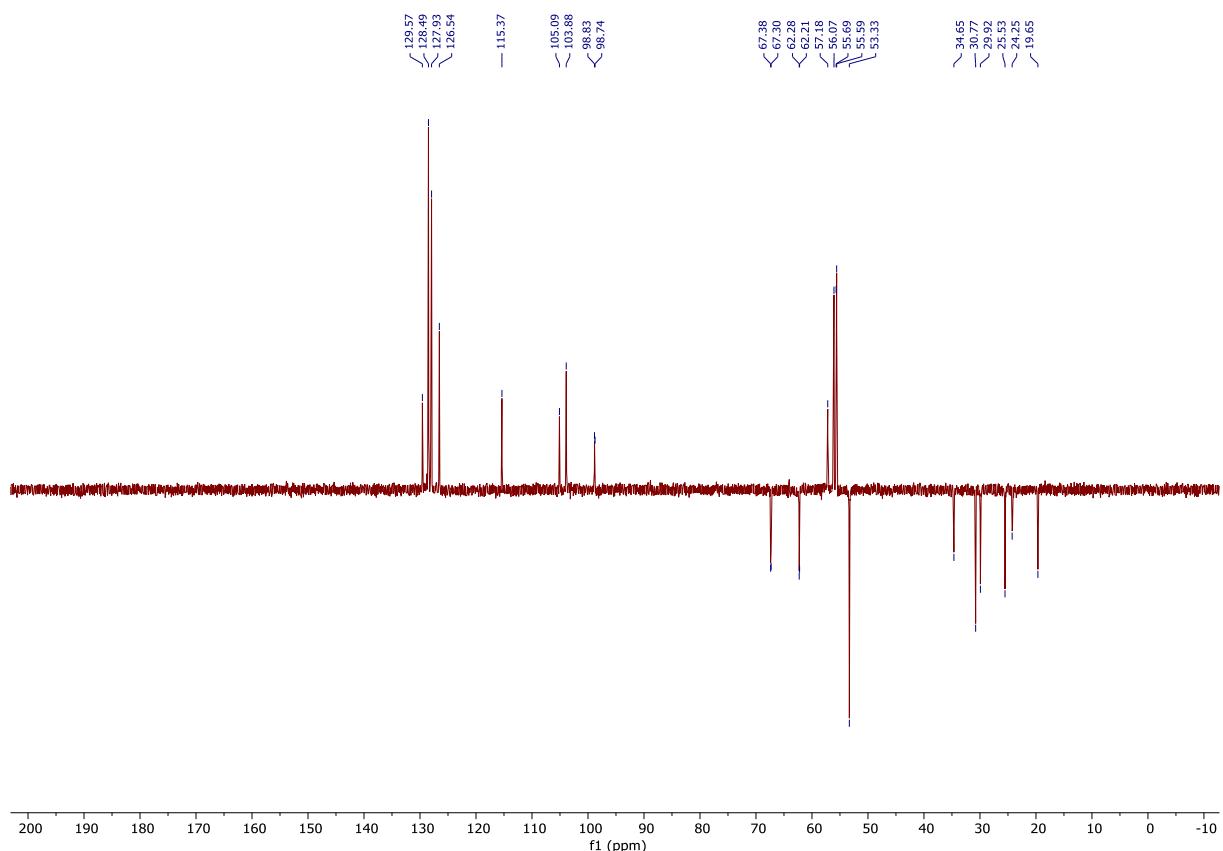


Figure S74. DEPT spectrum ( $\text{CDCl}_3$ , 125 MHz) of derivative **13b**.

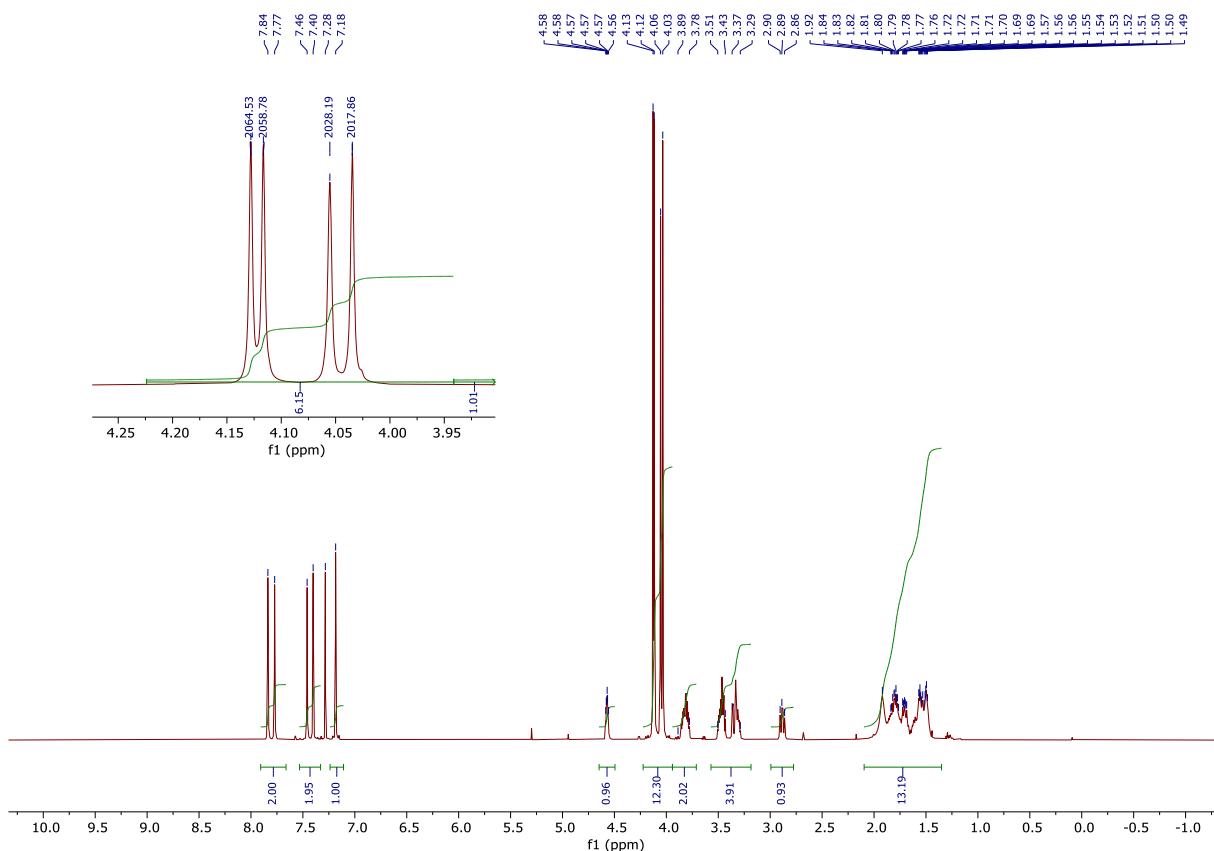
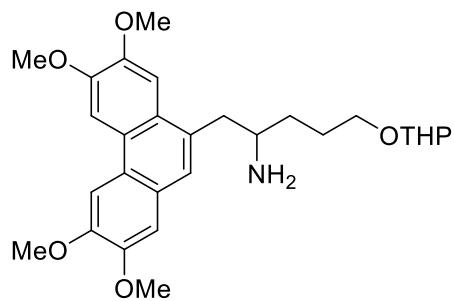


Figure S75.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 500 MHz) of derivative **14a**.

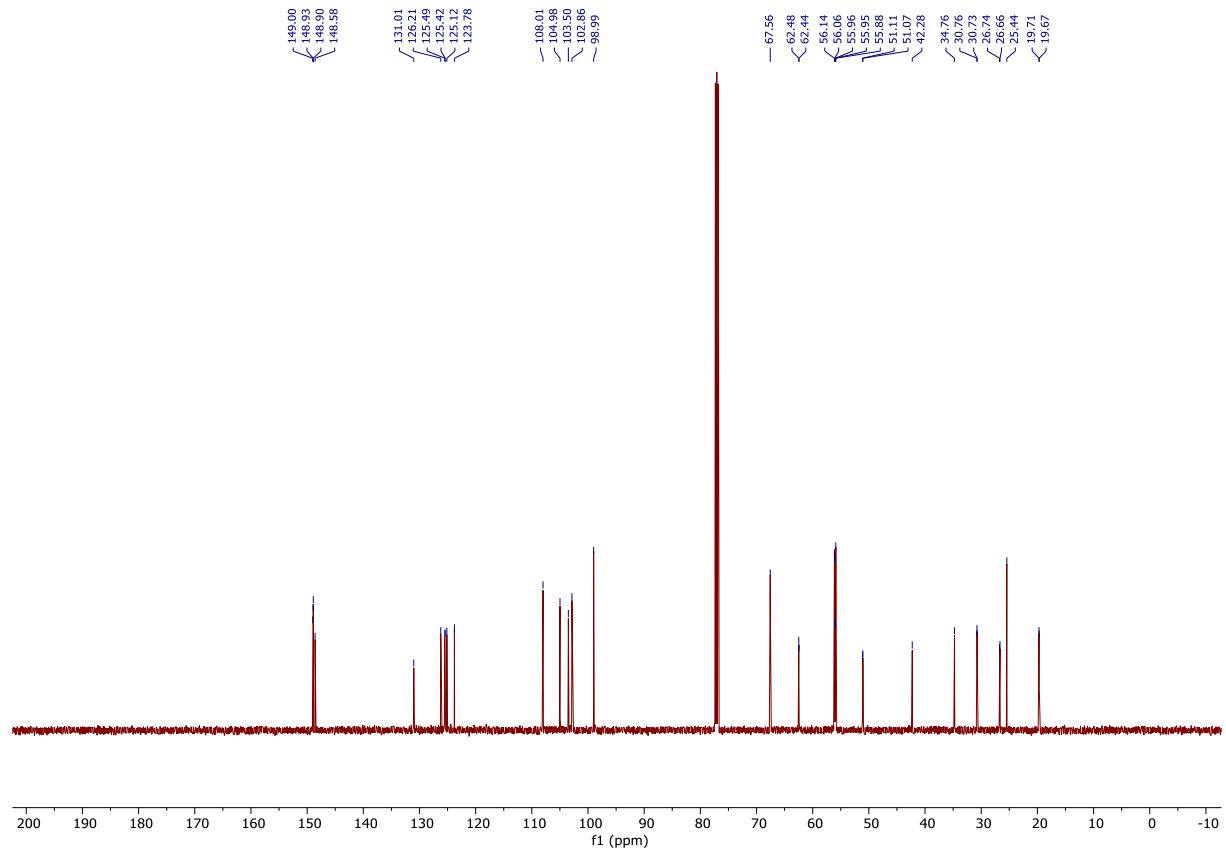


Figure S76.  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 125 MHz) of derivative **14a**.

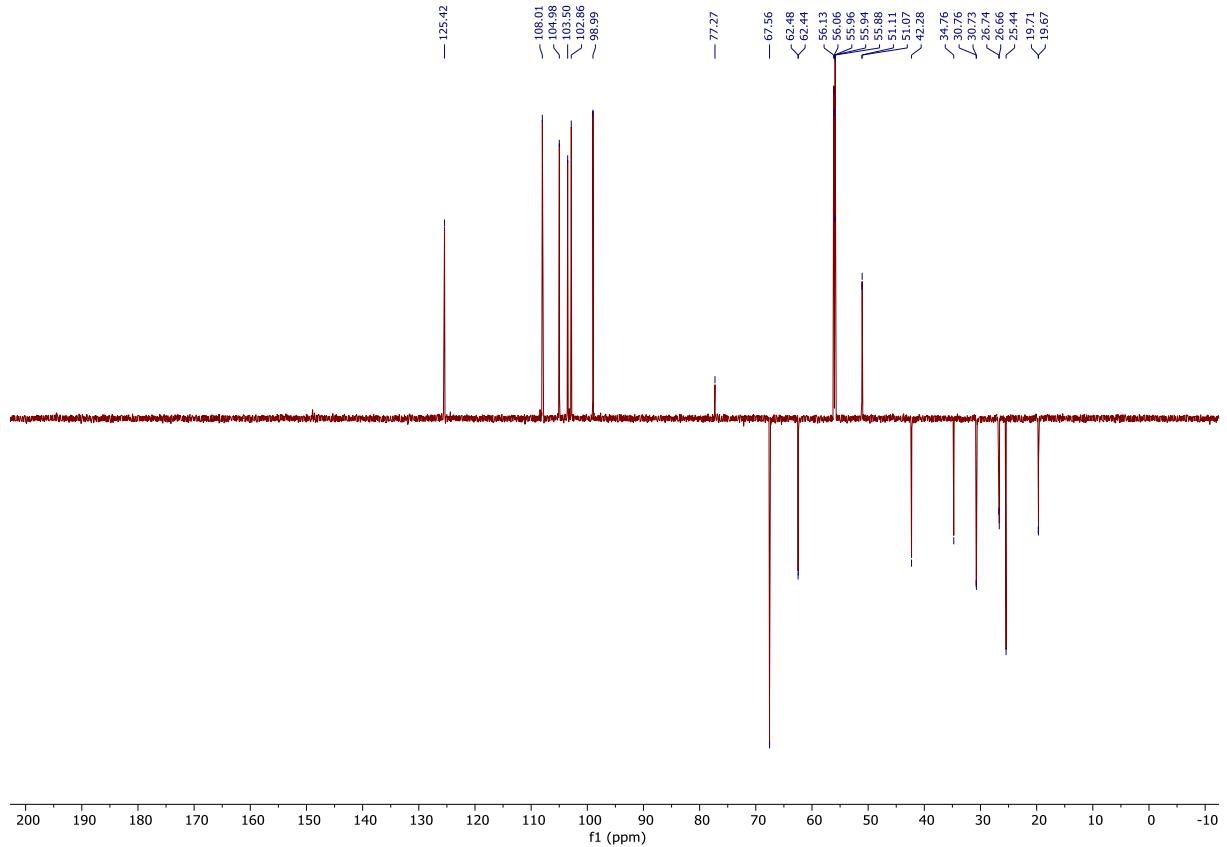
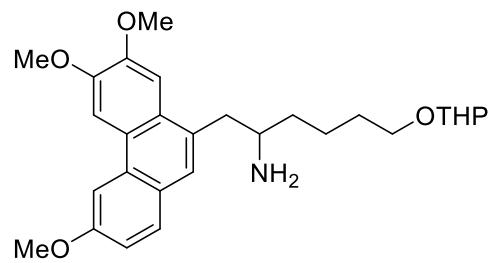


Figure S77. DEPT spectrum ( $\text{CDCl}_3$ , 125 MHz) of derivative **14a**.



14b

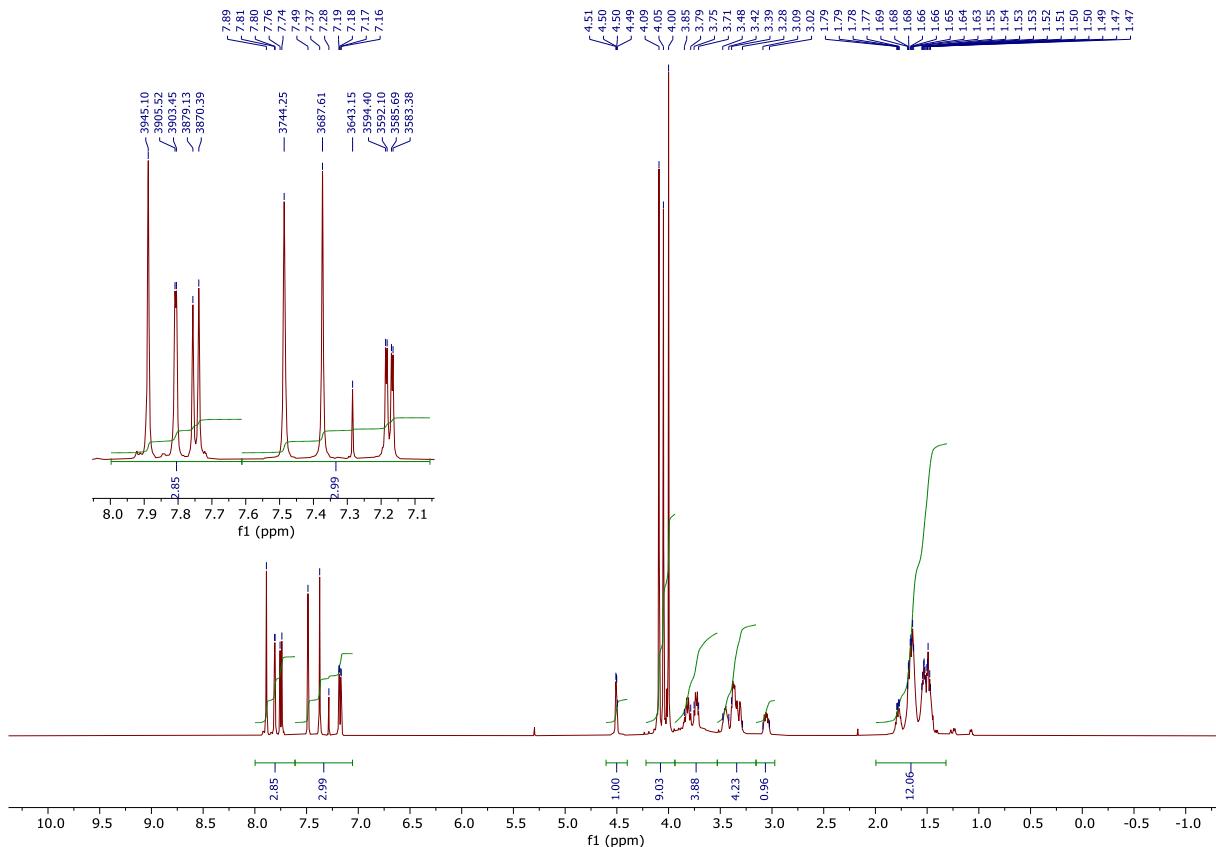


Figure S78.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 500 MHz) of derivative **14b**.

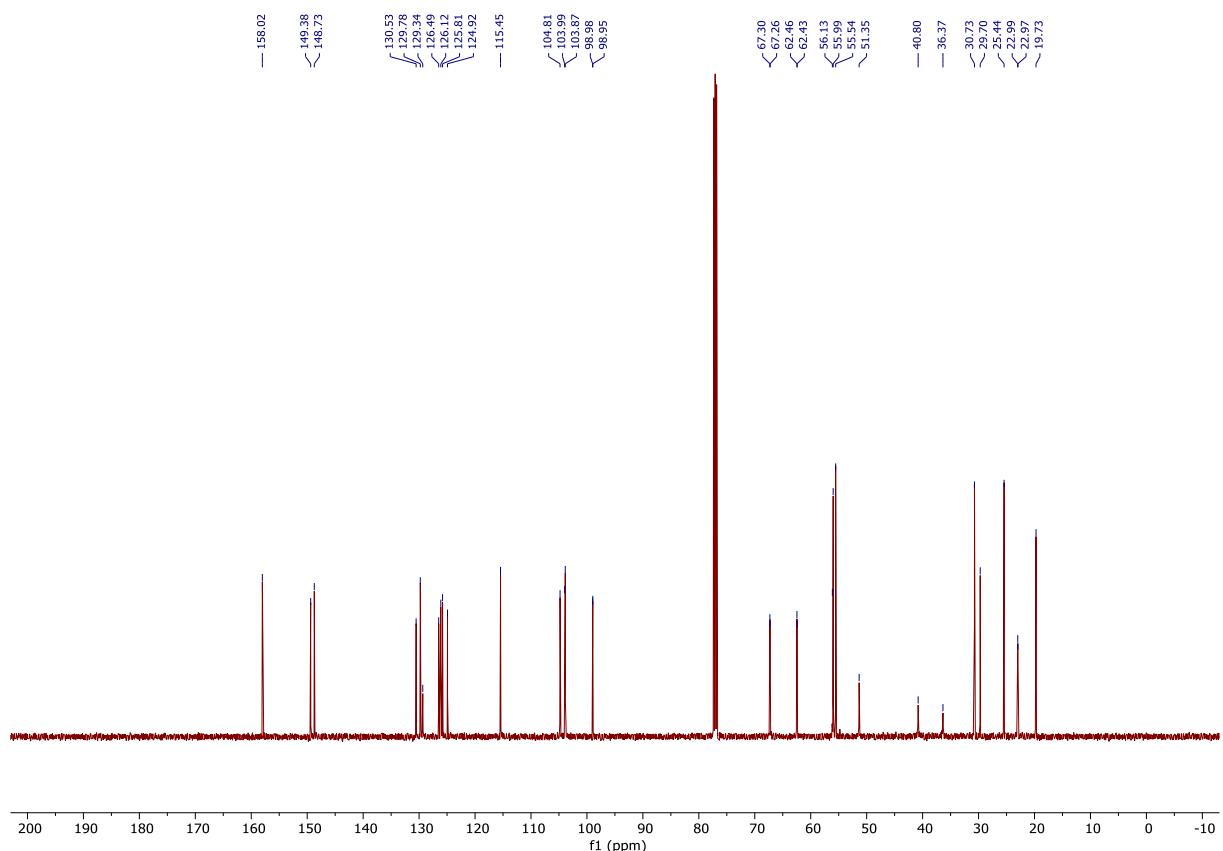


Figure S79.  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 125 MHz) of derivative **14b**.

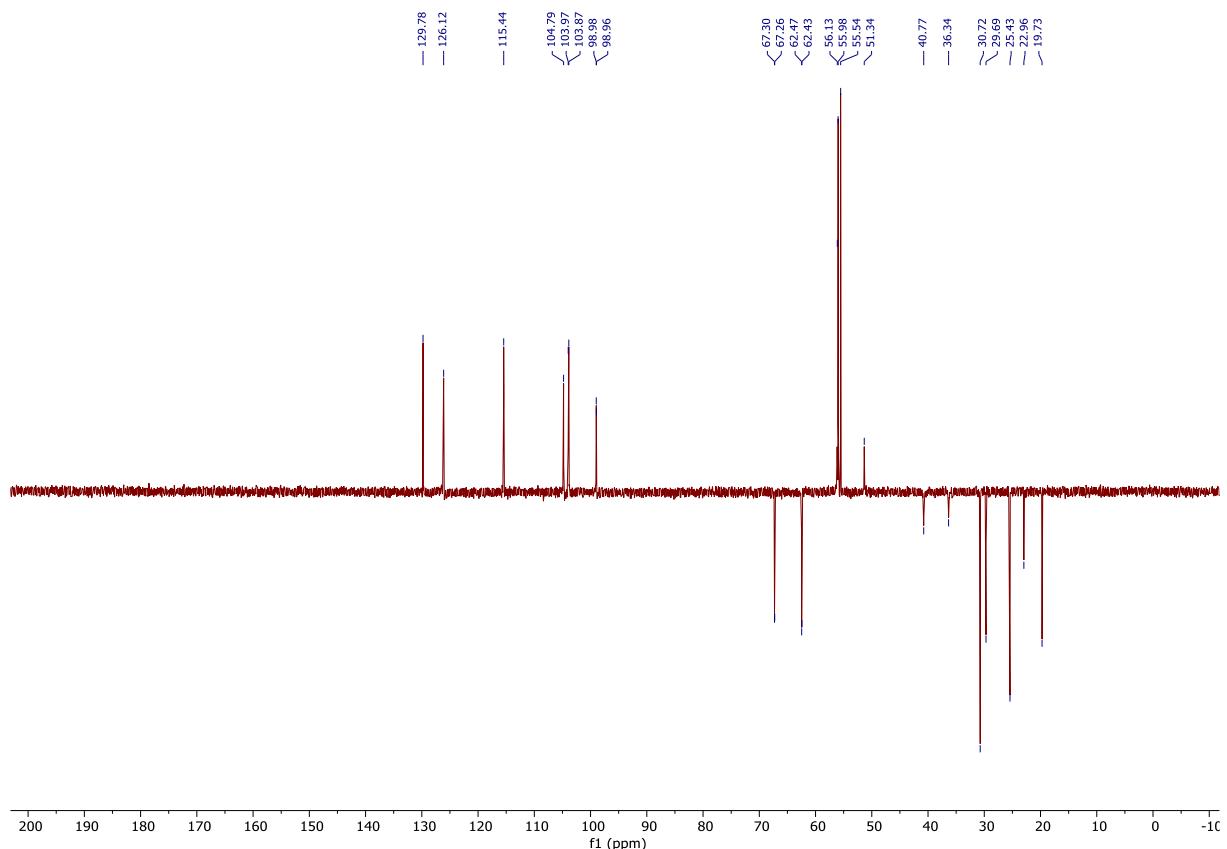


Figure S80. DEPT spectrum ( $\text{CDCl}_3$ , 125 MHz) of derivative **14b**.

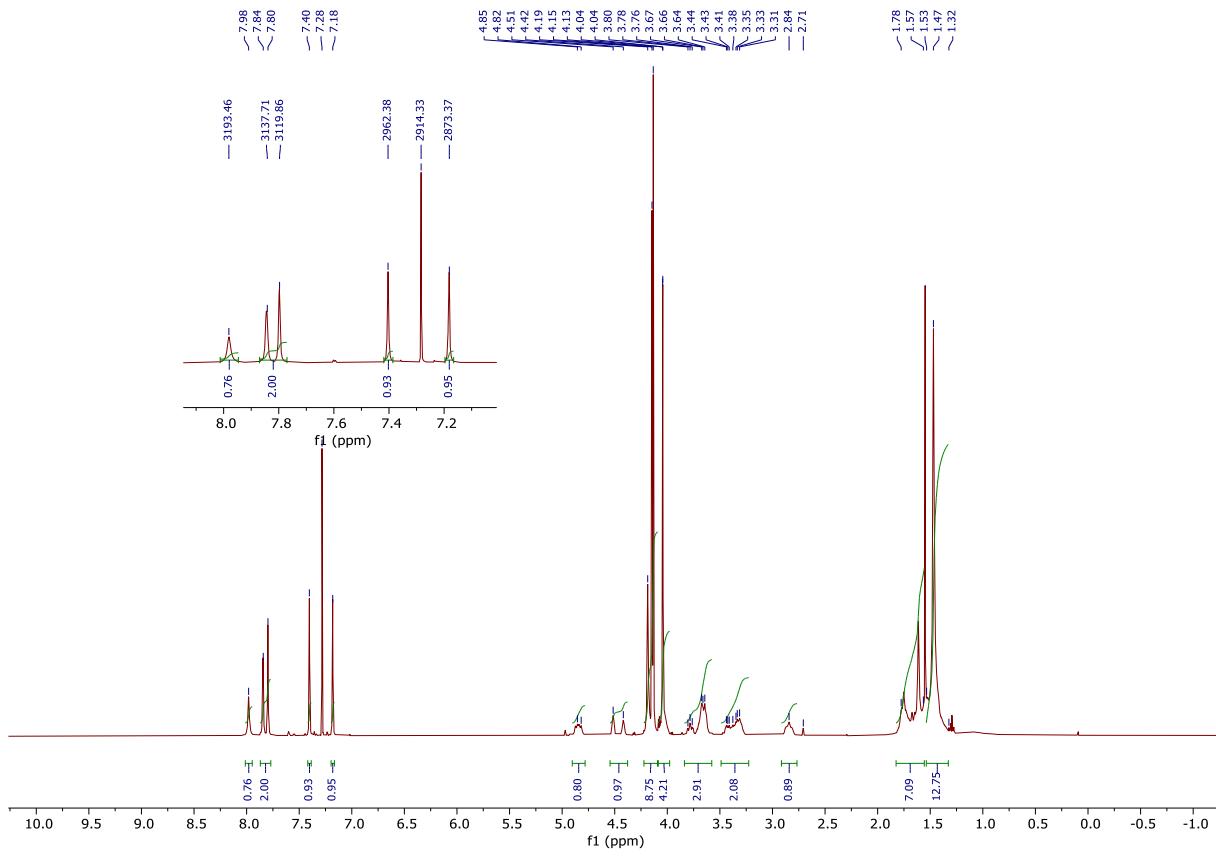
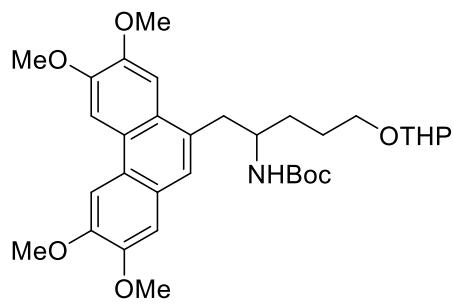


Figure S81.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 400 MHz) of derivative **15a**.

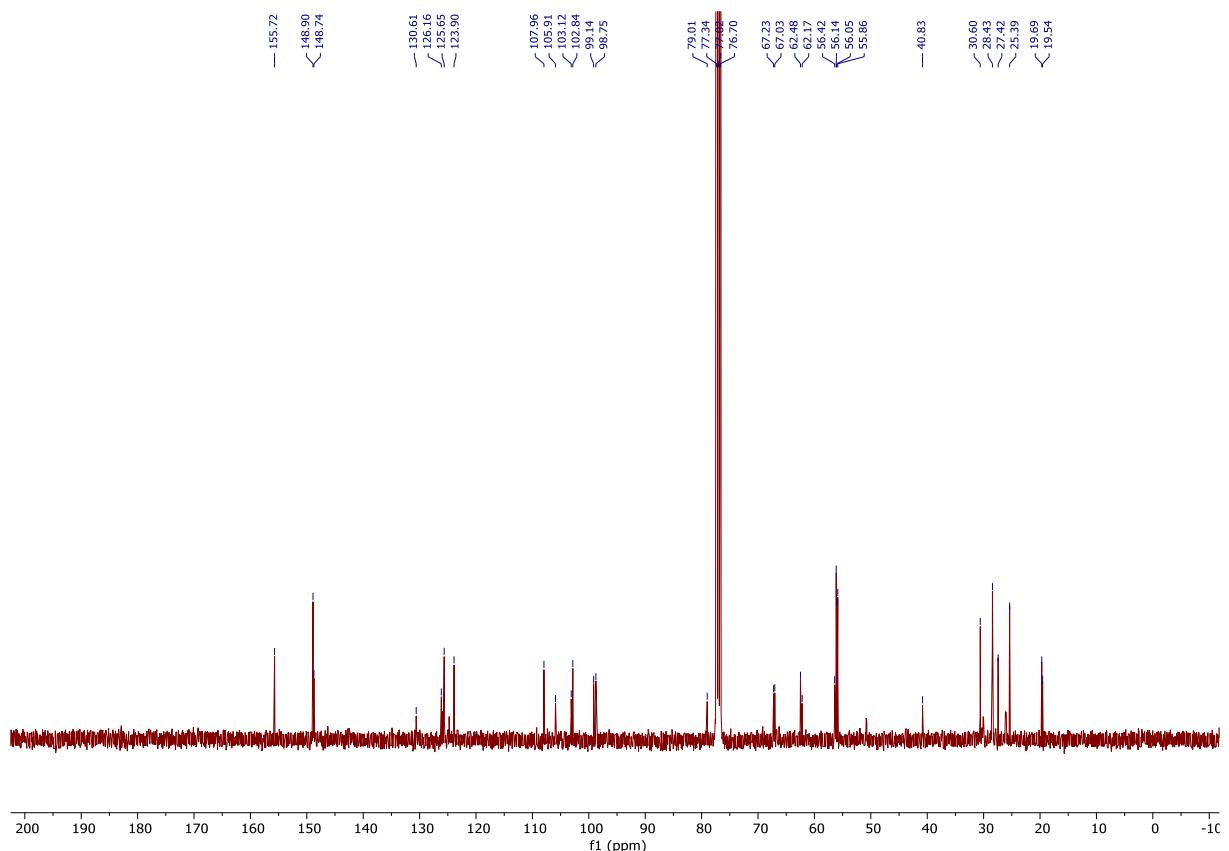


Figure S82. <sup>13</sup>C NMR spectrum ( $\text{CDCl}_3$ , 100 MHz) of derivative **15a**.

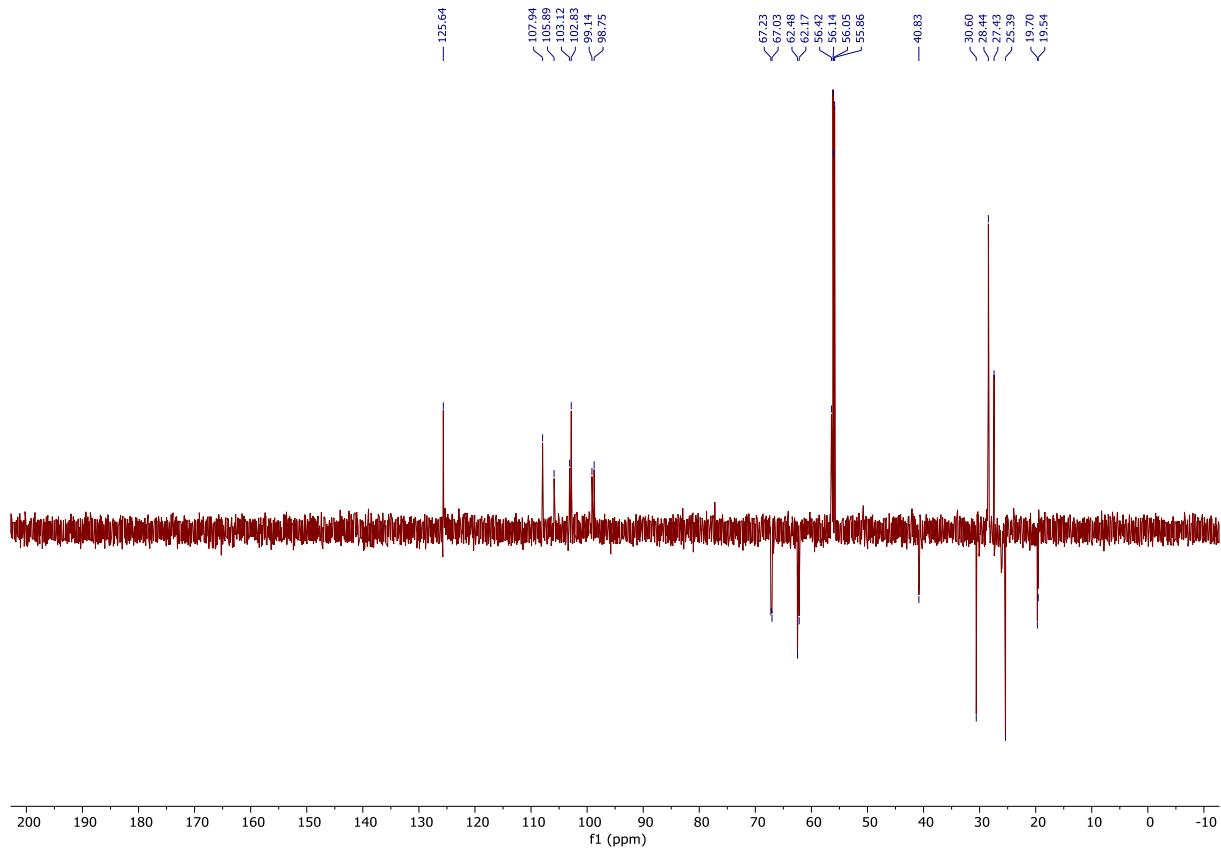


Figure S83. DEPT spectrum ( $\text{CDCl}_3$ , 125 MHz) of derivative **15a**.

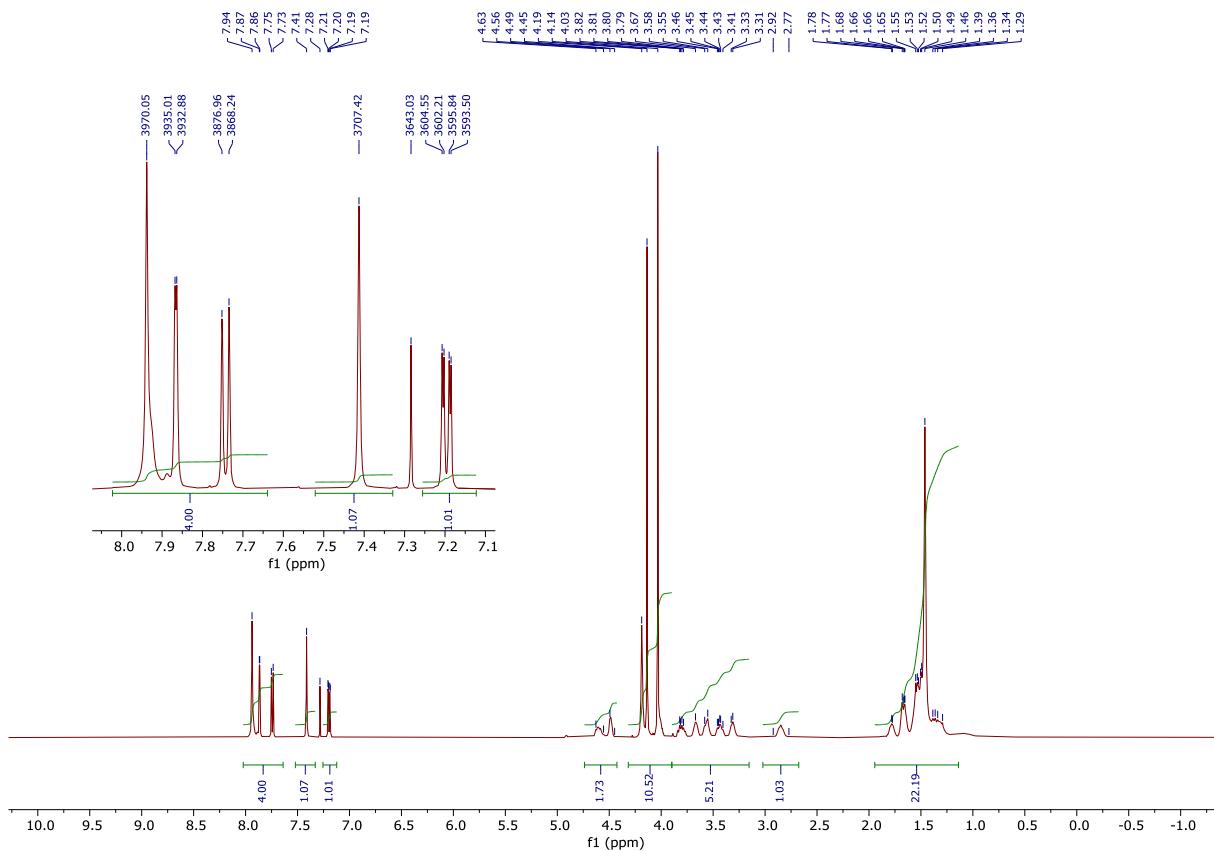
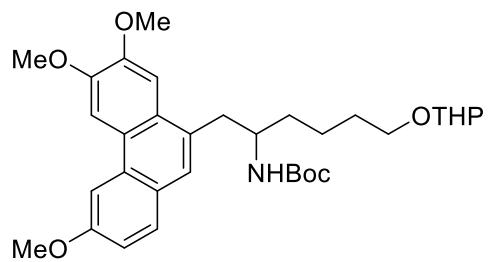


Figure S84. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 500 MHz) of derivative **15b**.

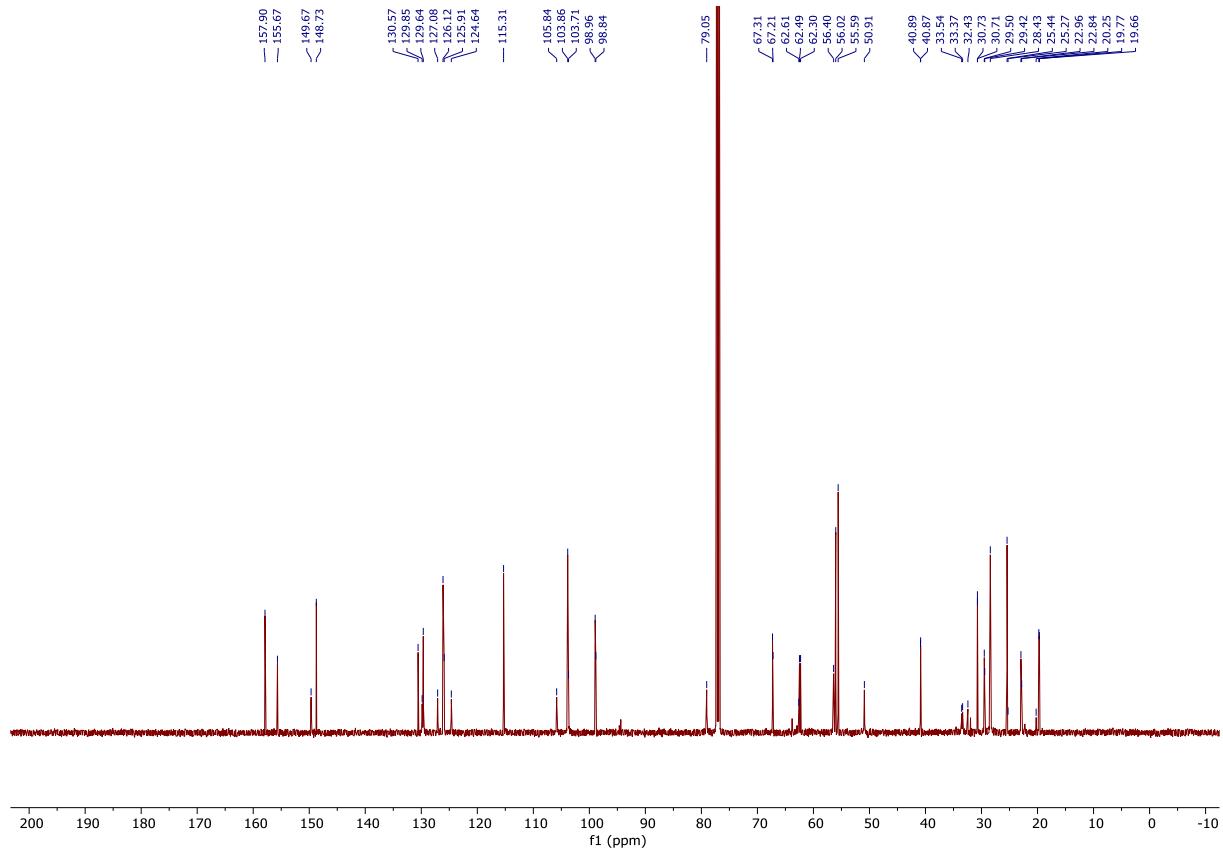


Figure S85. <sup>13</sup>C NMR spectrum ( $\text{CDCl}_3$ , 125 MHz) of derivative **15b**.

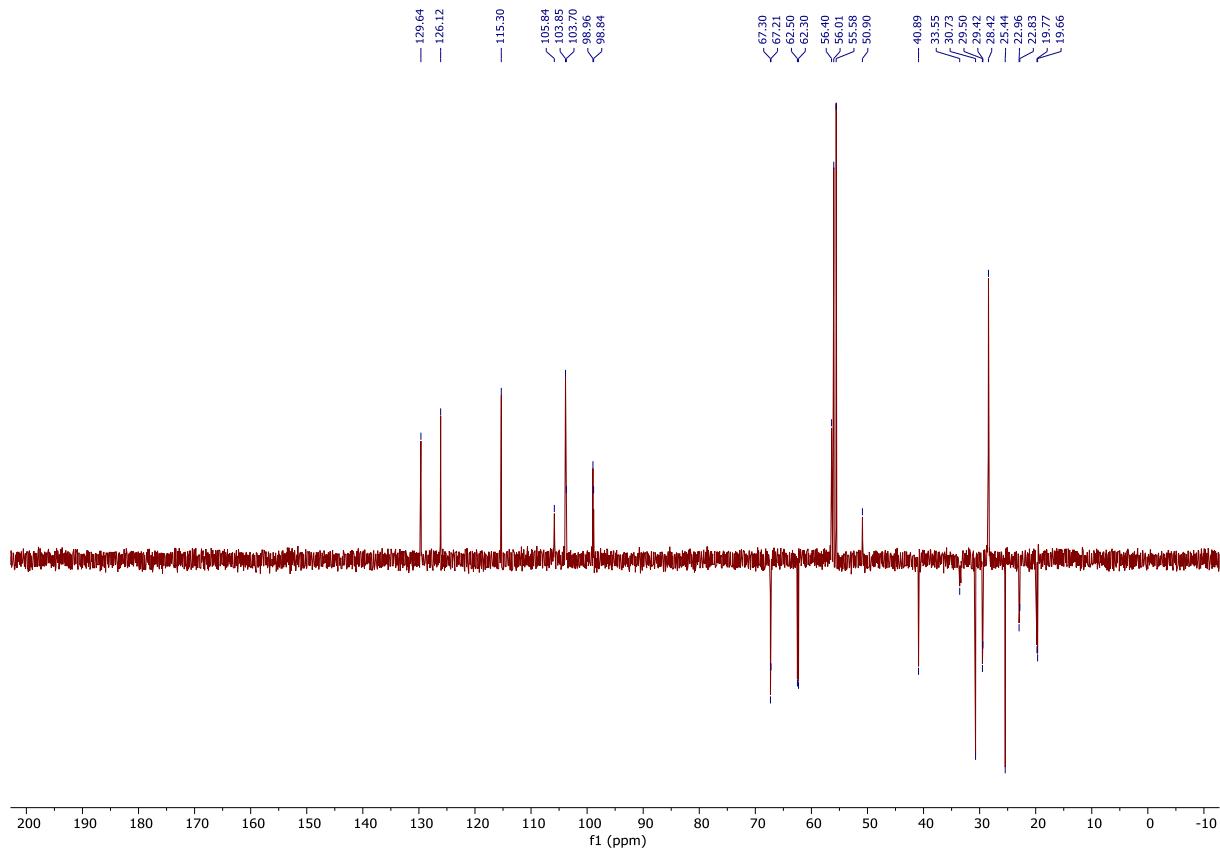


Figure S86. DEPT spectrum ( $\text{CDCl}_3$ , 125 MHz) of derivative **15b**.

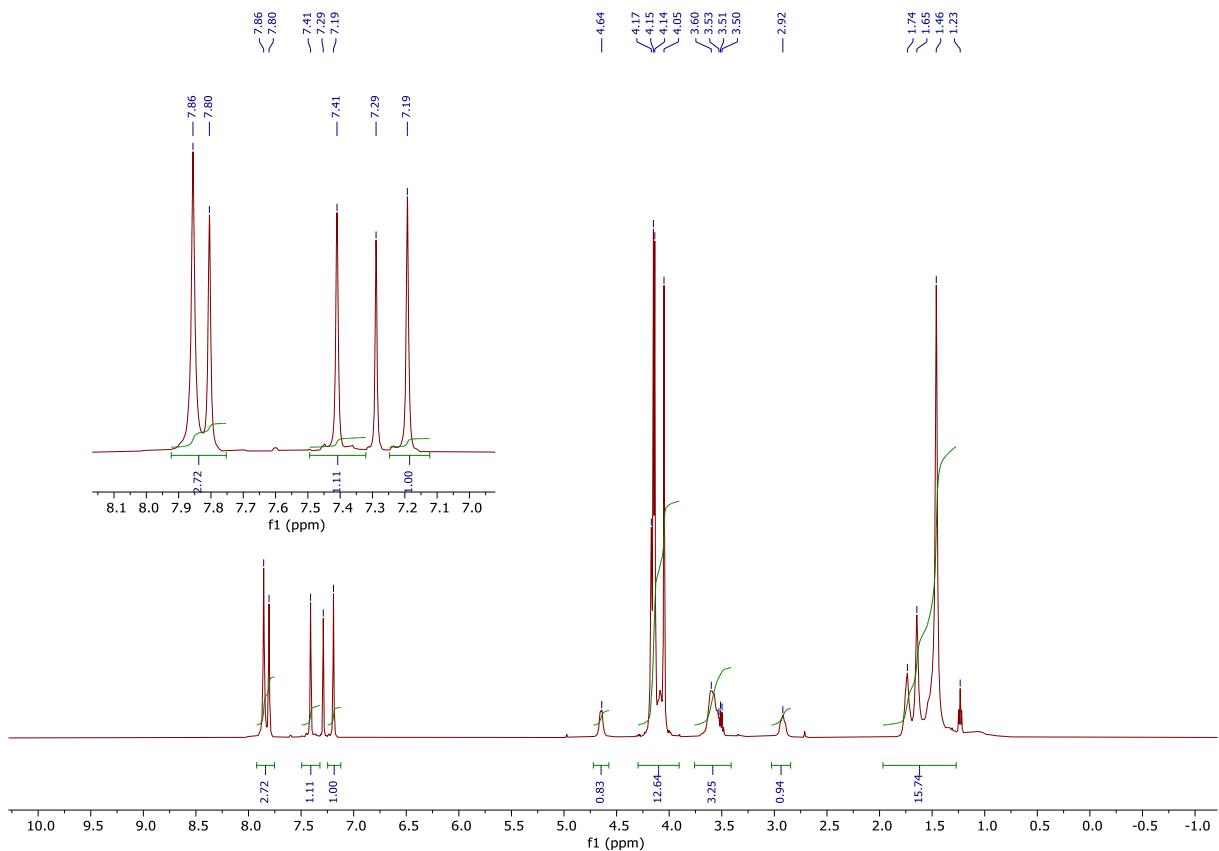
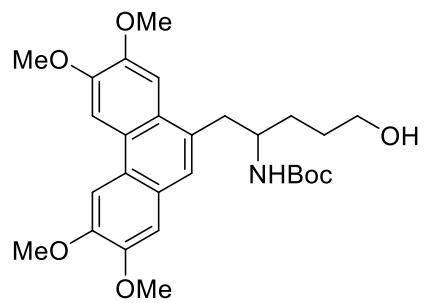


Figure S87. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of derivative **16a**.

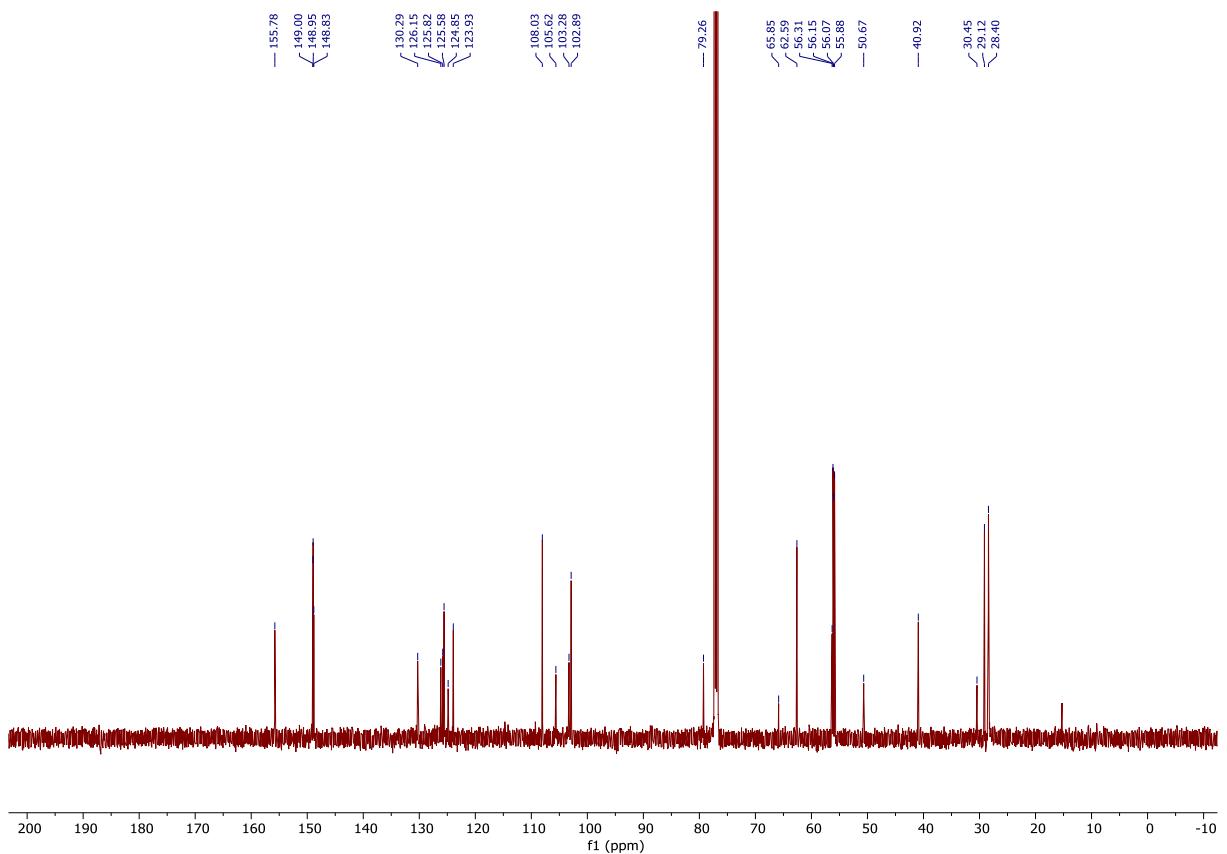


Figure S88. <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 100 MHz) of derivative **16a**.

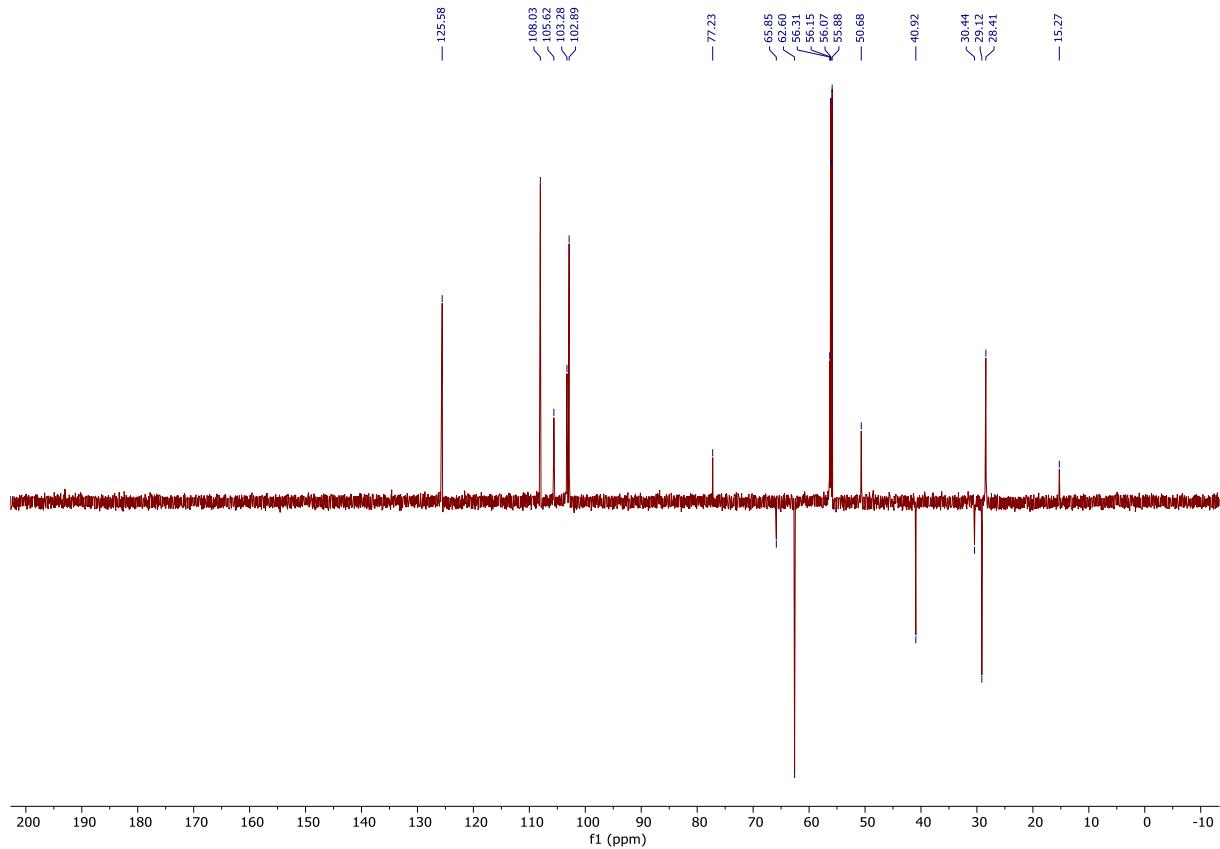


Figure S89. DEPT spectrum ( $\text{CDCl}_3$ , 100 MHz) of derivative **16a**.

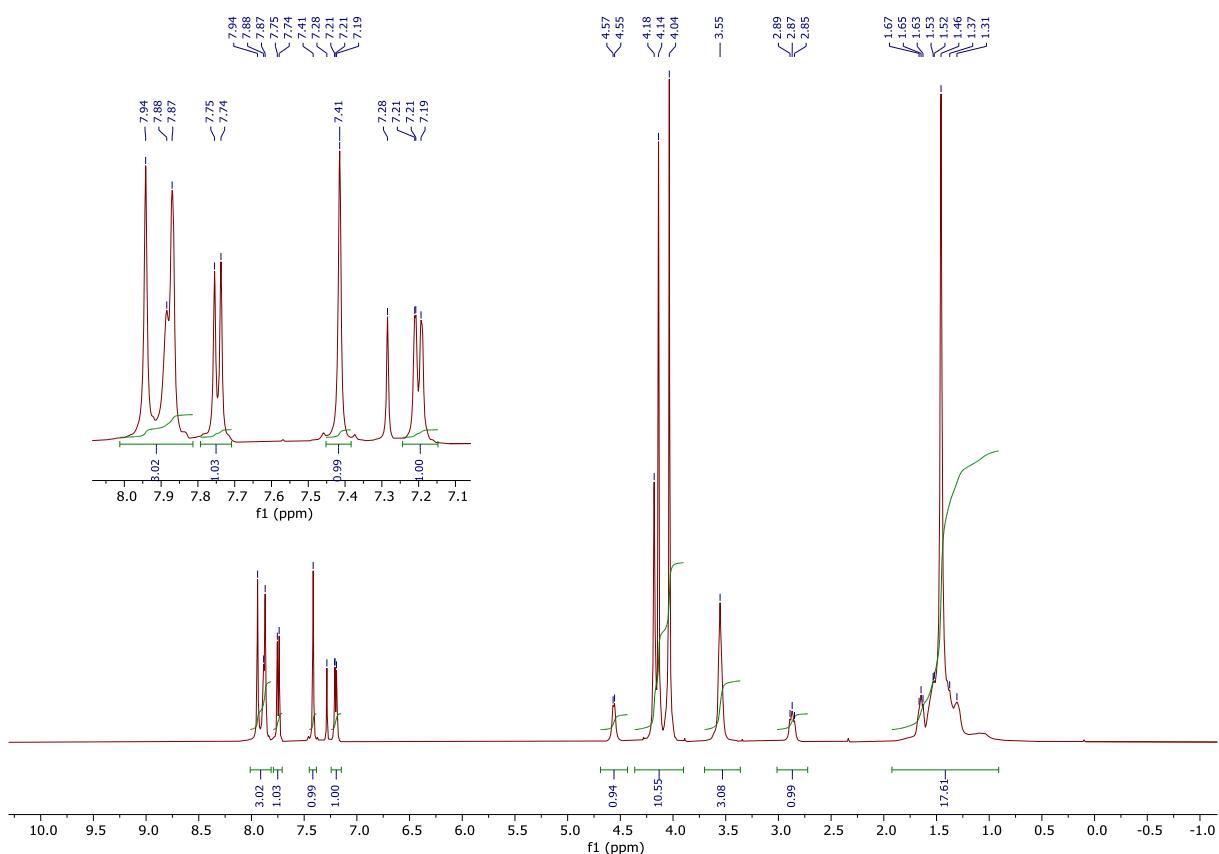
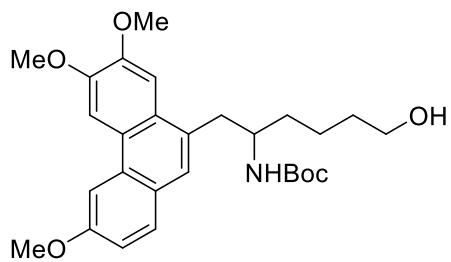


Figure S90.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 500 MHz) of derivative **16b**.

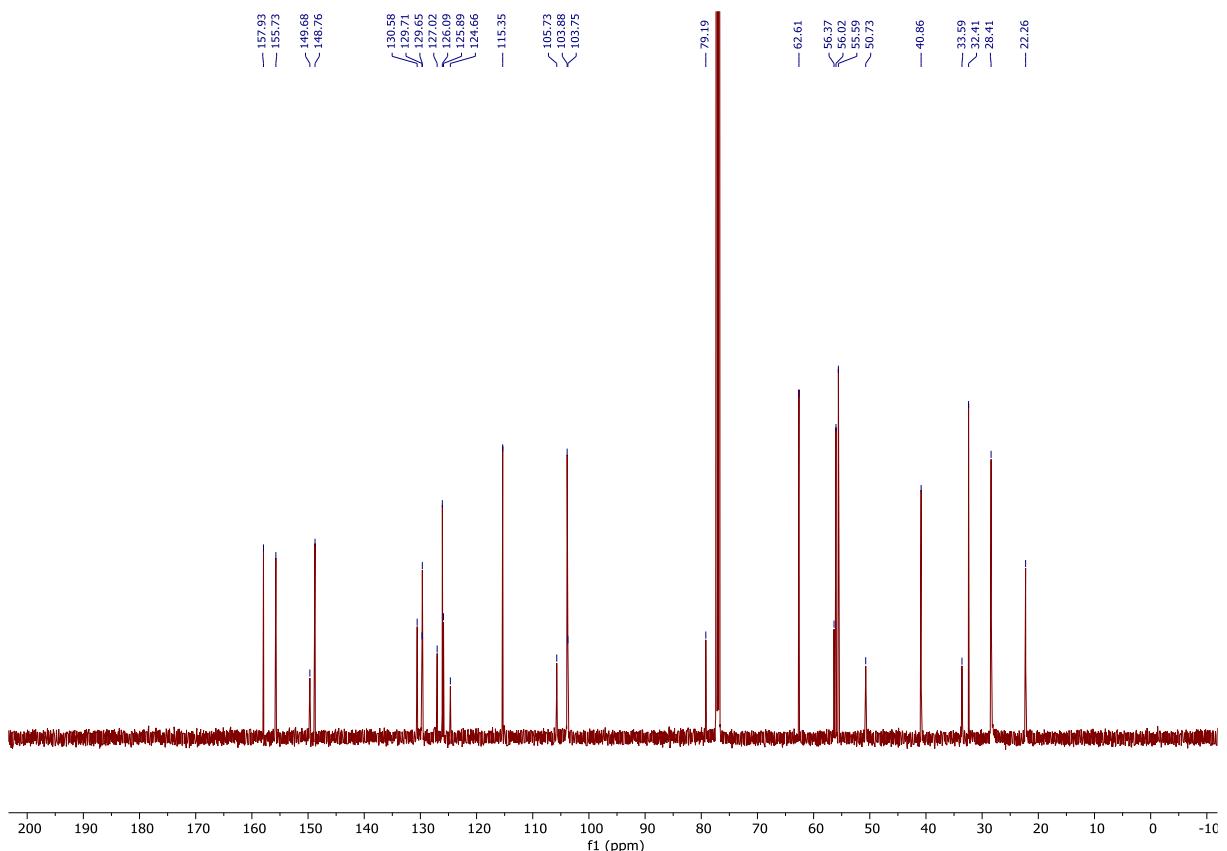


Figure S91. <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 125 MHz) of derivative **16b**.

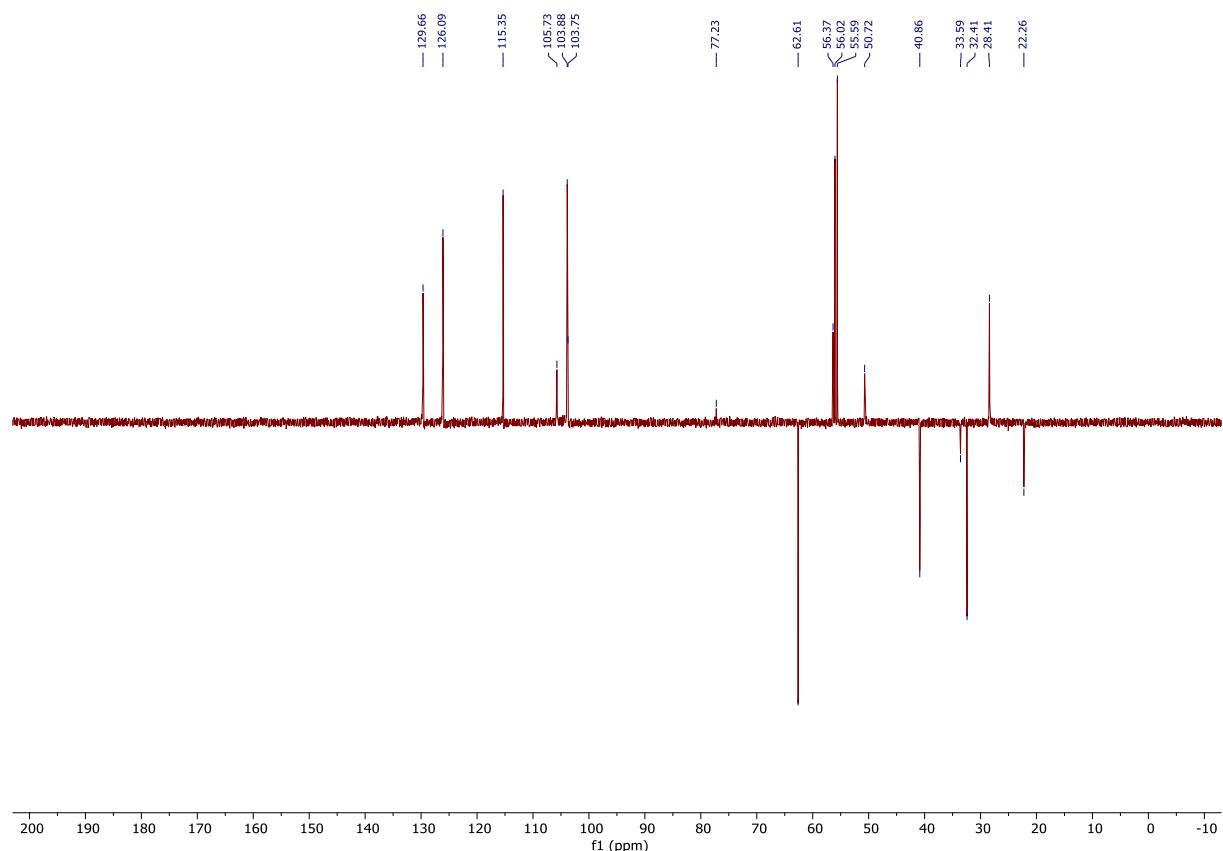


Figure S92. DEPT spectrum ( $\text{CDCl}_3$ , 125 MHz) of derivative **16b**.

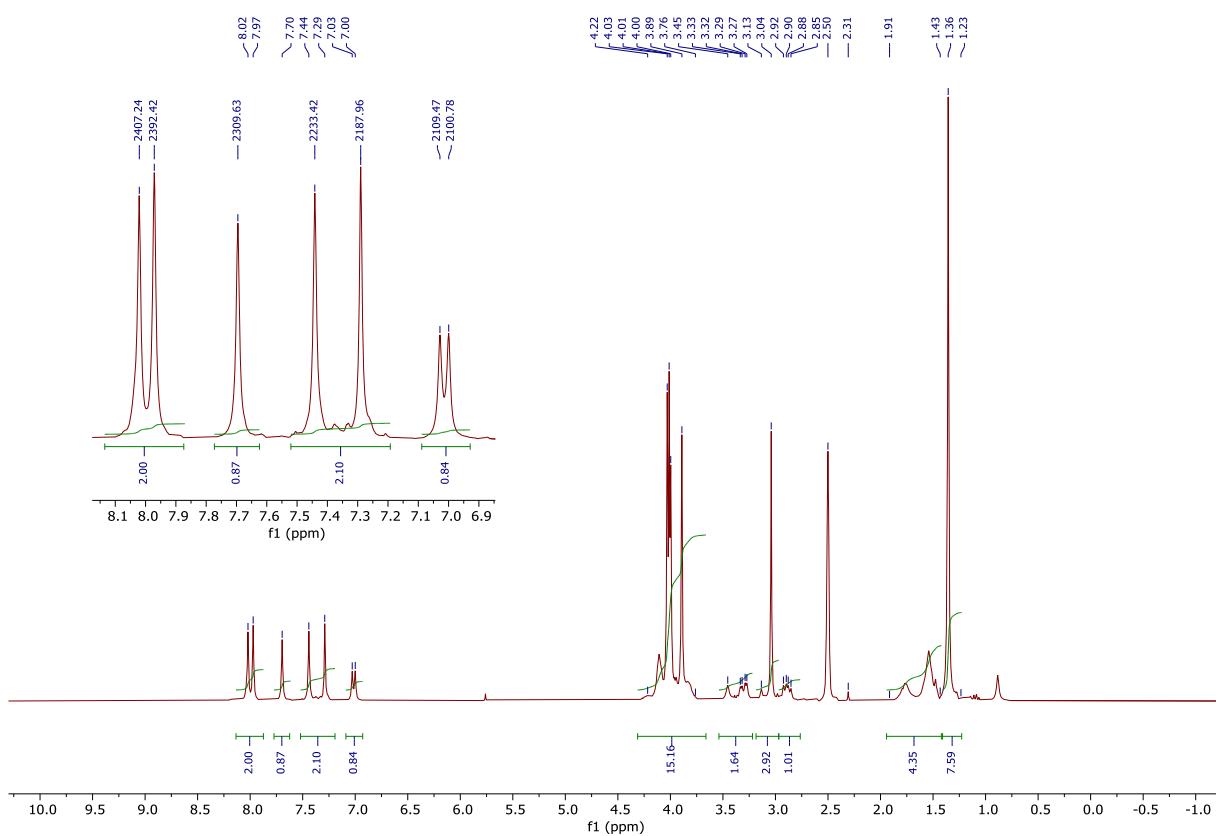
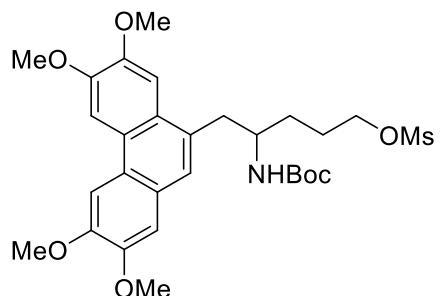


Figure S93.  $^1\text{H}$  NMR spectrum (DMSO- $\text{d}_6$ , 300 MHz) of derivative **17a**.

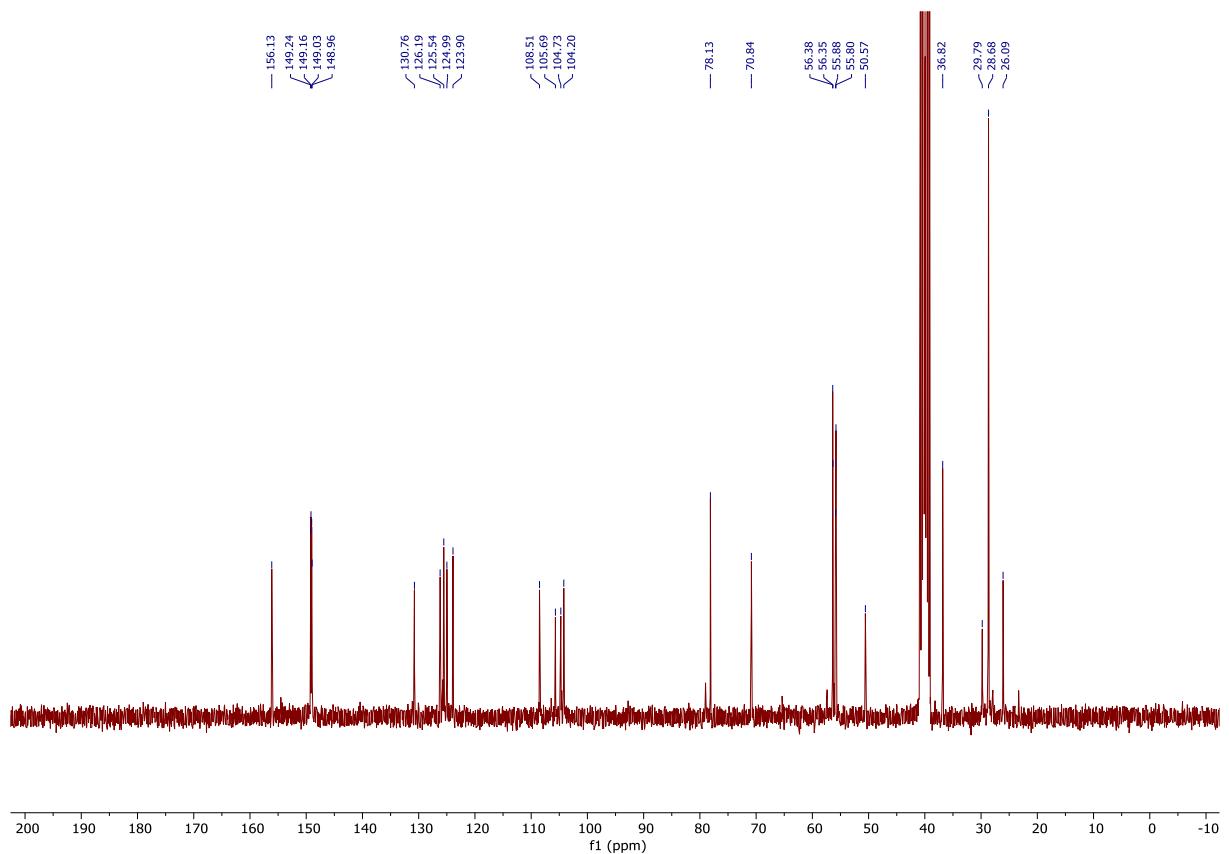


Figure S94.  $^{13}\text{C}$  NMR spectrum (DMSO-d<sub>6</sub>, 75 MHz) of derivative **17a**.

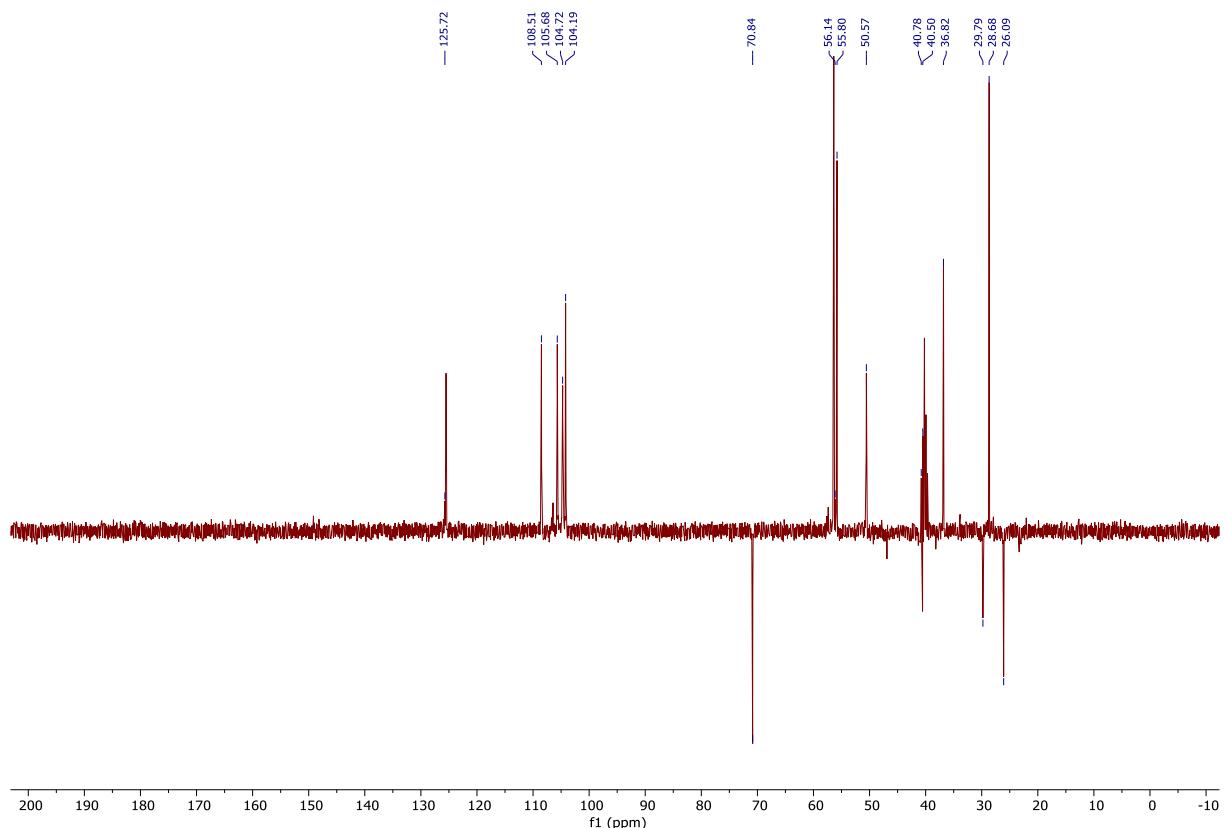


Figure S95. DEPT spectrum (DMSO-d<sub>6</sub>, 75 MHz) of derivative **17a**.

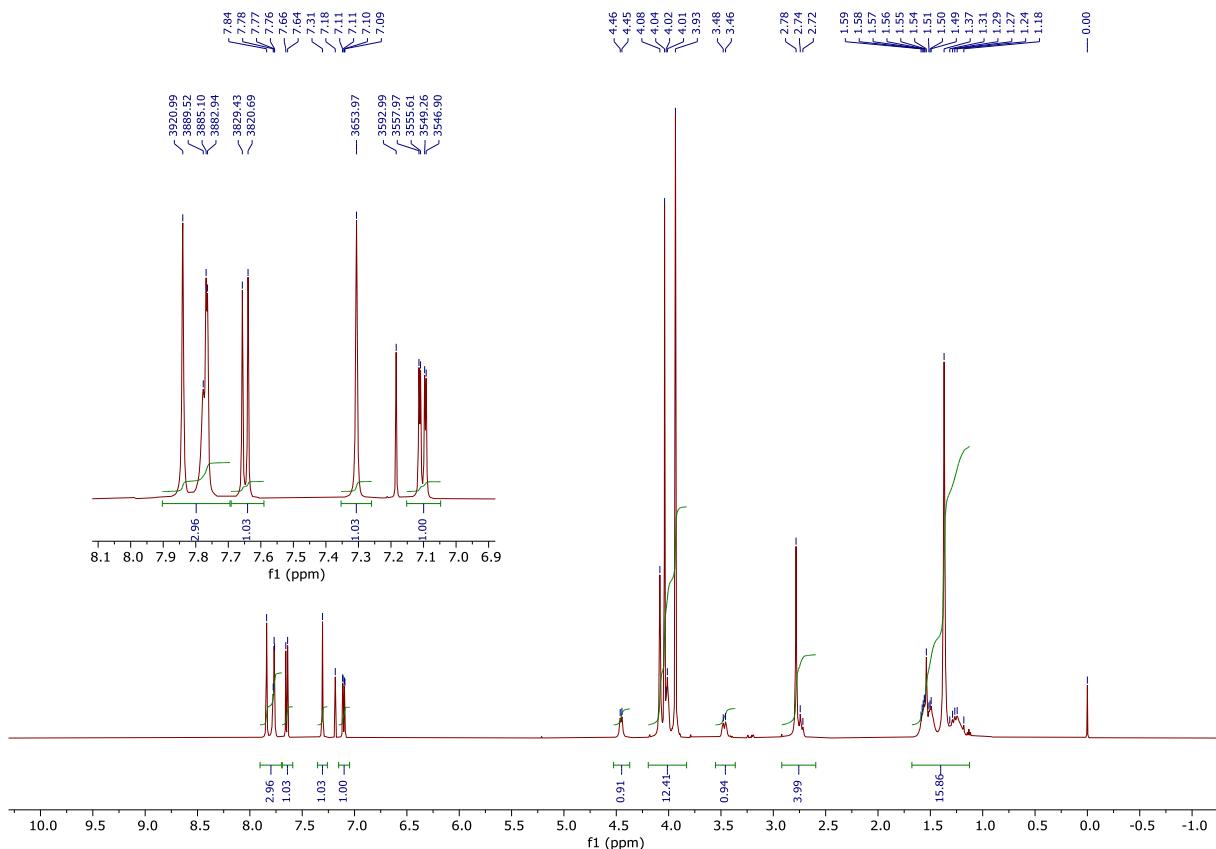
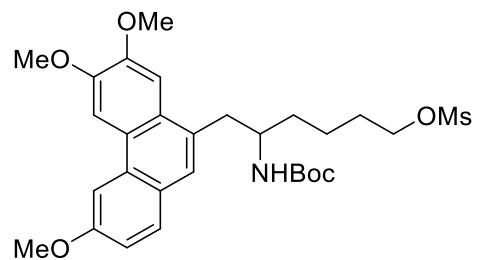


Figure S96.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 500 MHz) of derivative **17b**.

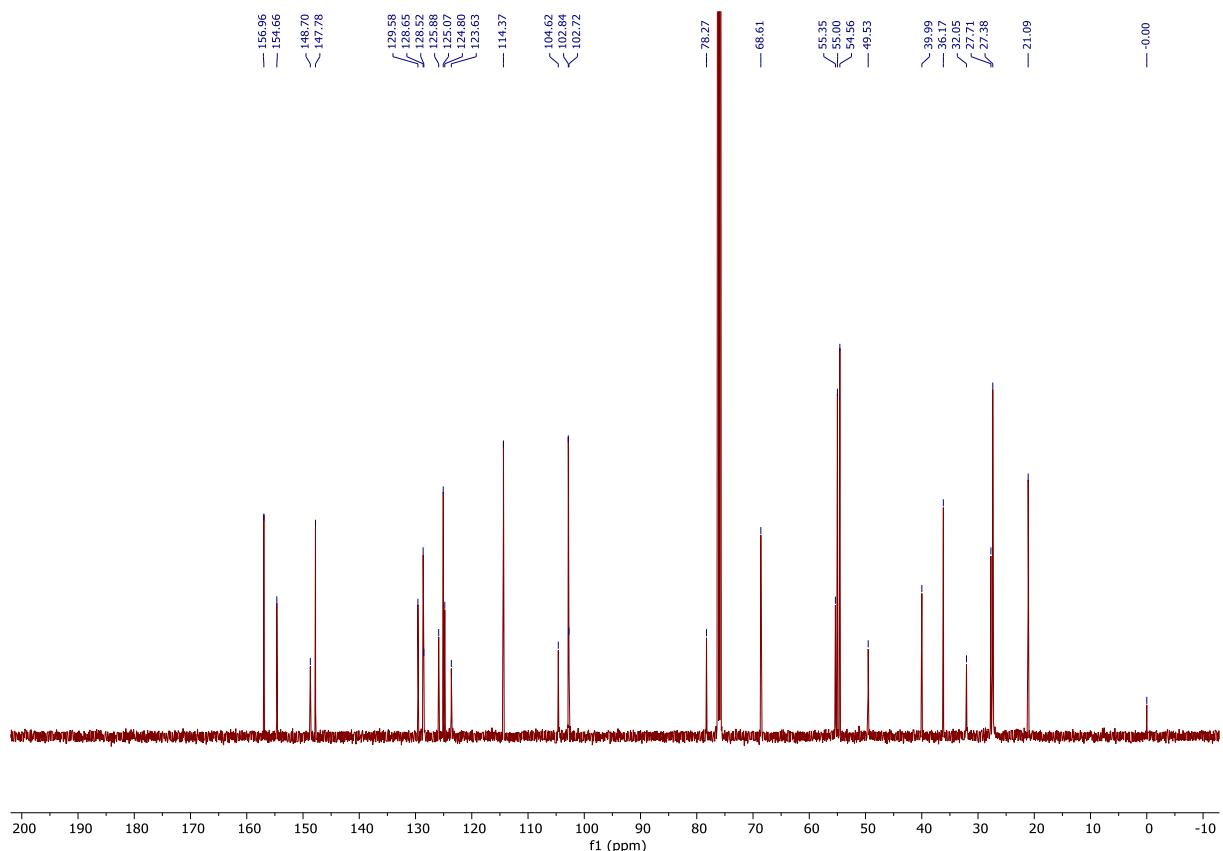


Figure S97.  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 125 MHz) of derivative **17b**.

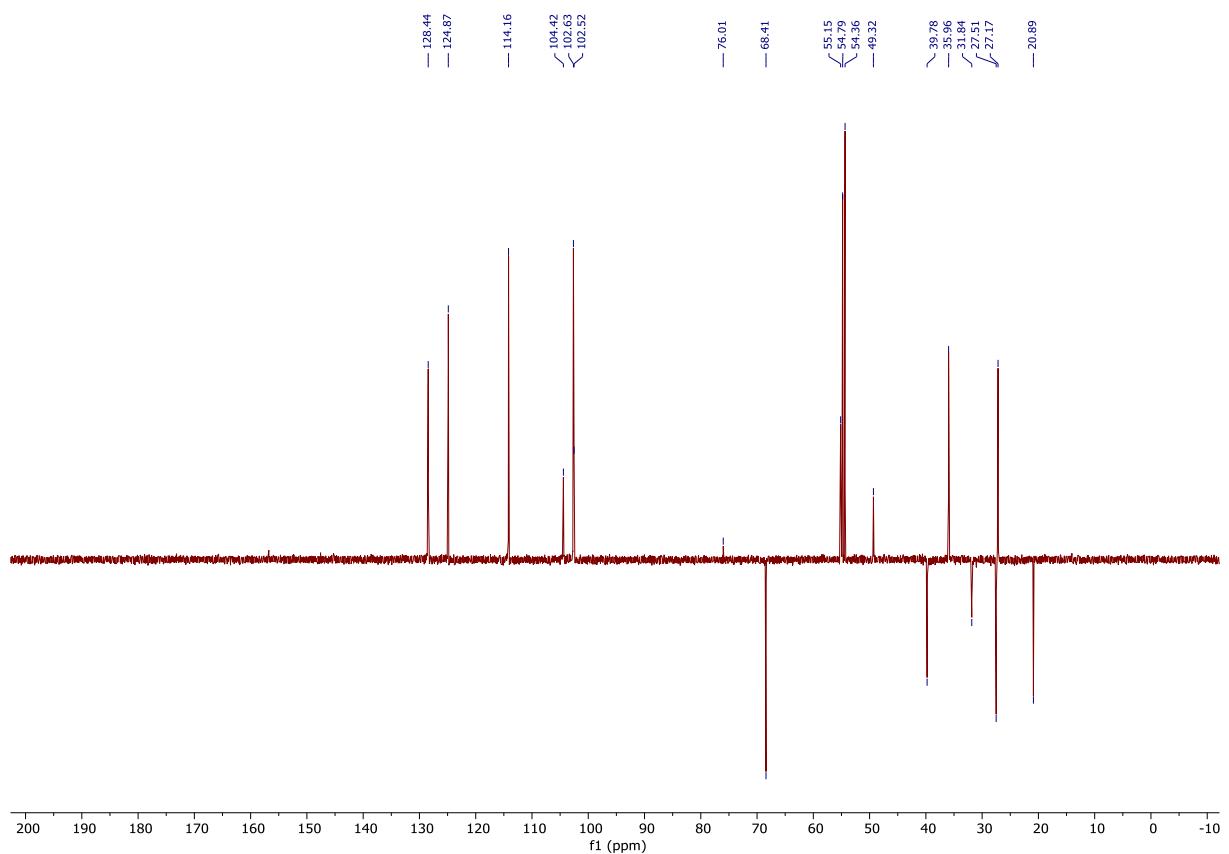


Figure S98. DEPT spectrum ( $\text{CDCl}_3$ , 125 MHz) of derivative **17b**.

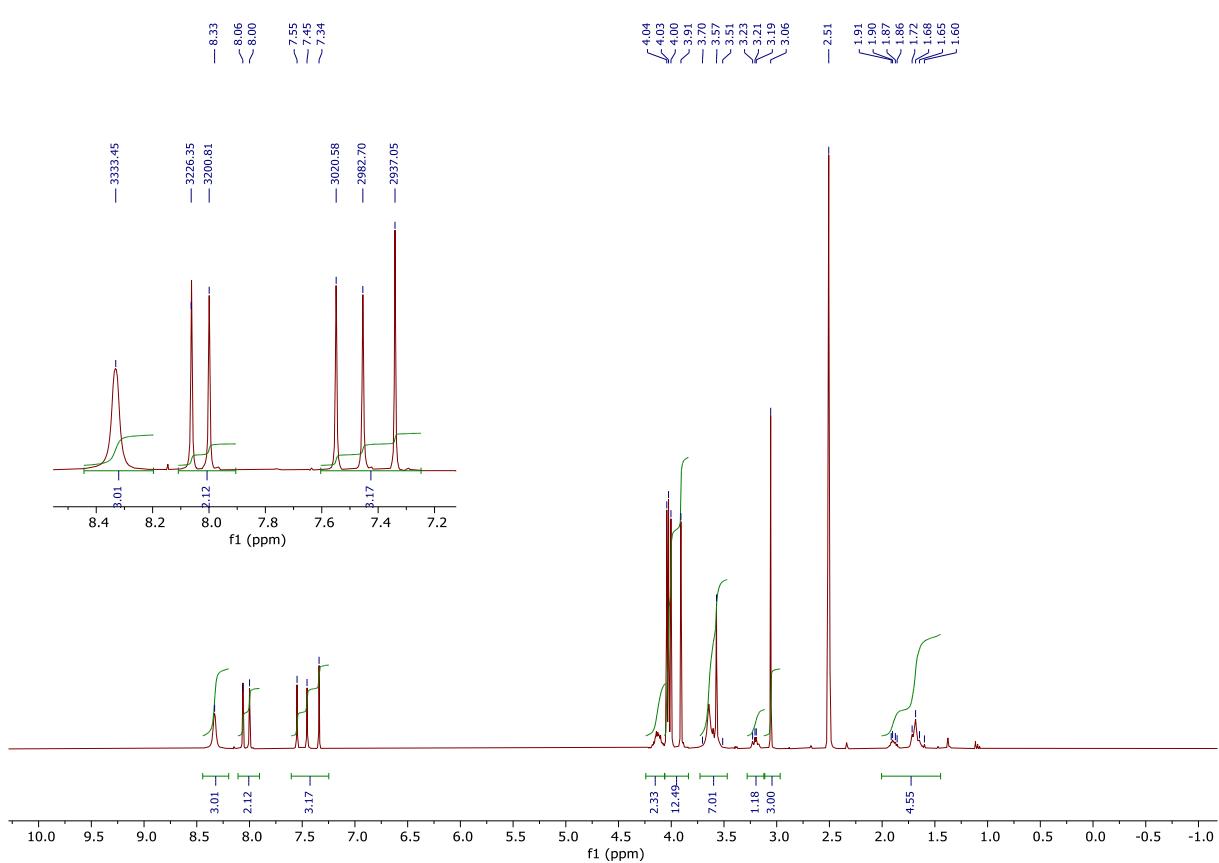
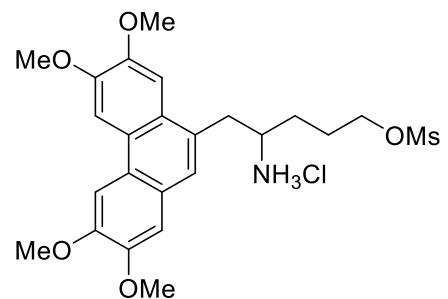


Figure S99.  $^1\text{H}$  NMR spectrum (DMSO-d<sub>6</sub>, 400 MHz) of derivative **18a**.

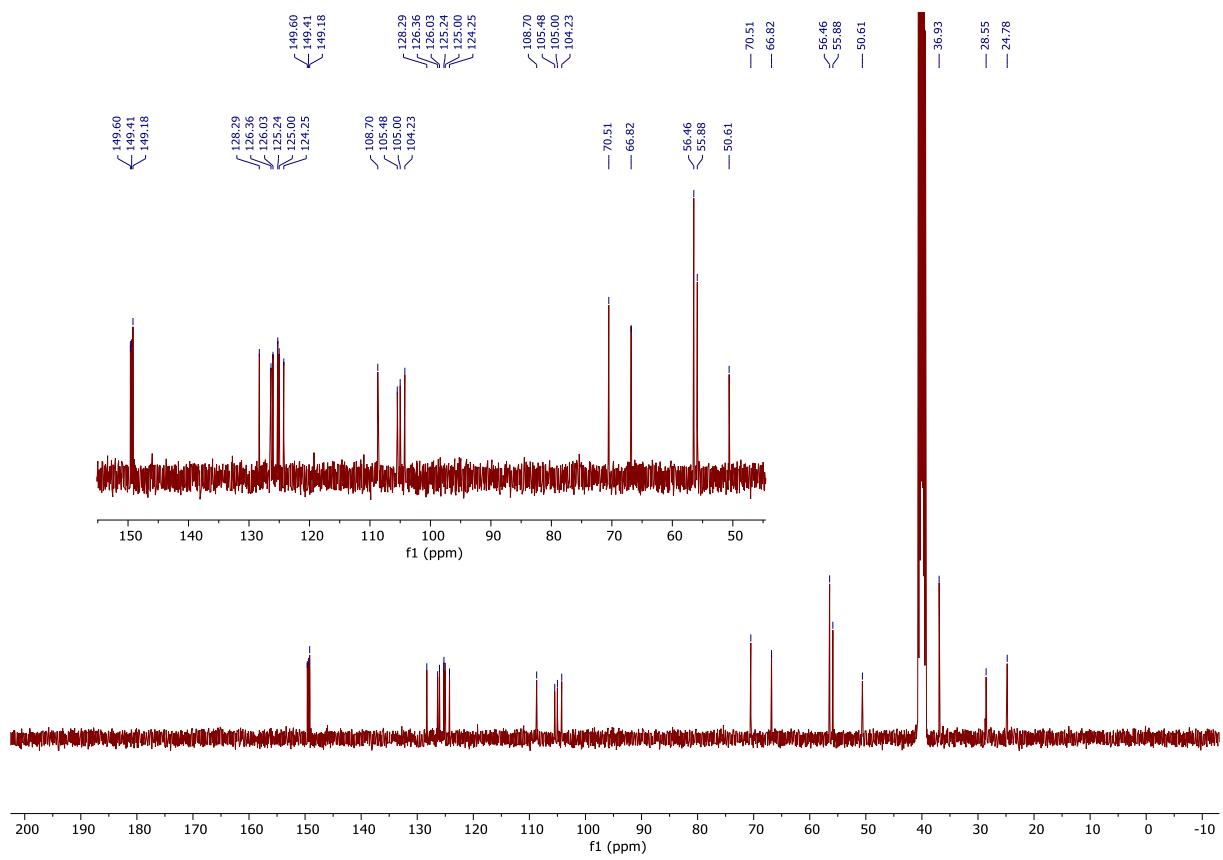


Figure S100.  $^{13}\text{C}$  NMR spectrum (DMSO-d<sub>6</sub>, 100 MHz) of derivative **18a**.

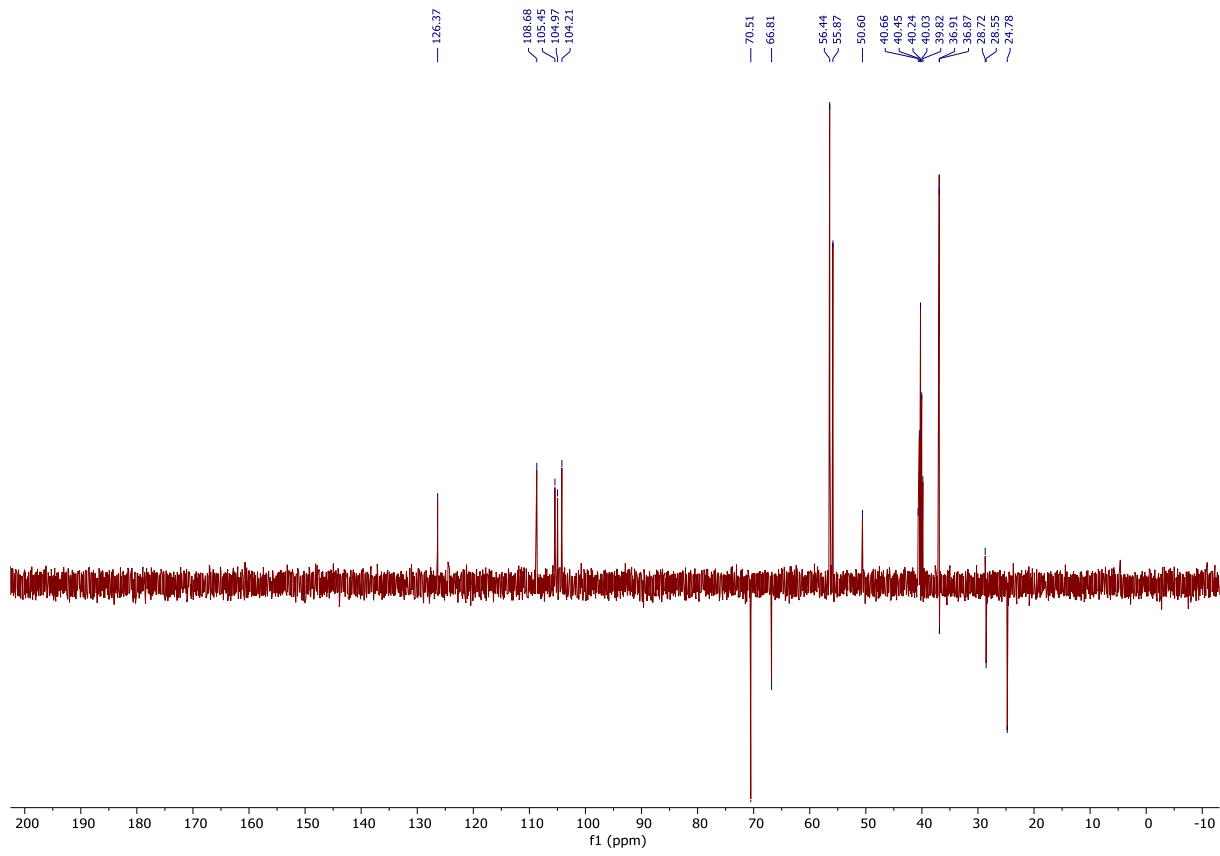


Figure S101. DEPT spectrum (DMSO-d<sub>6</sub>, 100 MHz) of derivative **18a**.

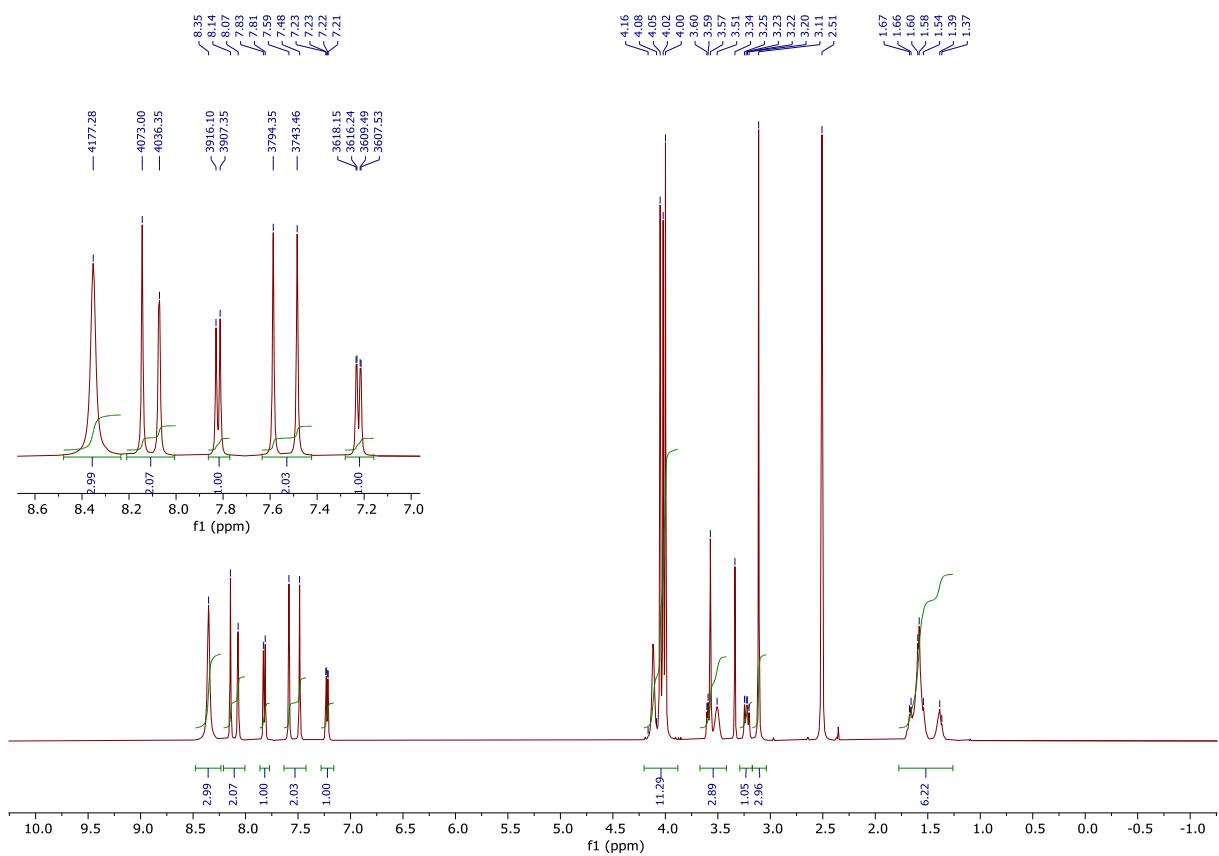
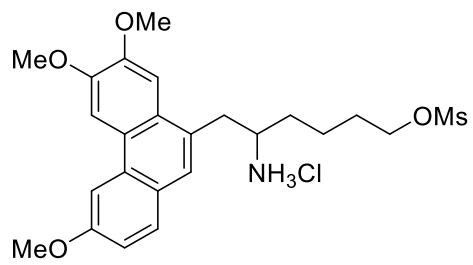


Figure S102. <sup>1</sup>H NMR spectrum (DMSO-d<sub>6</sub>, 500 MHz) of derivative **18b**.

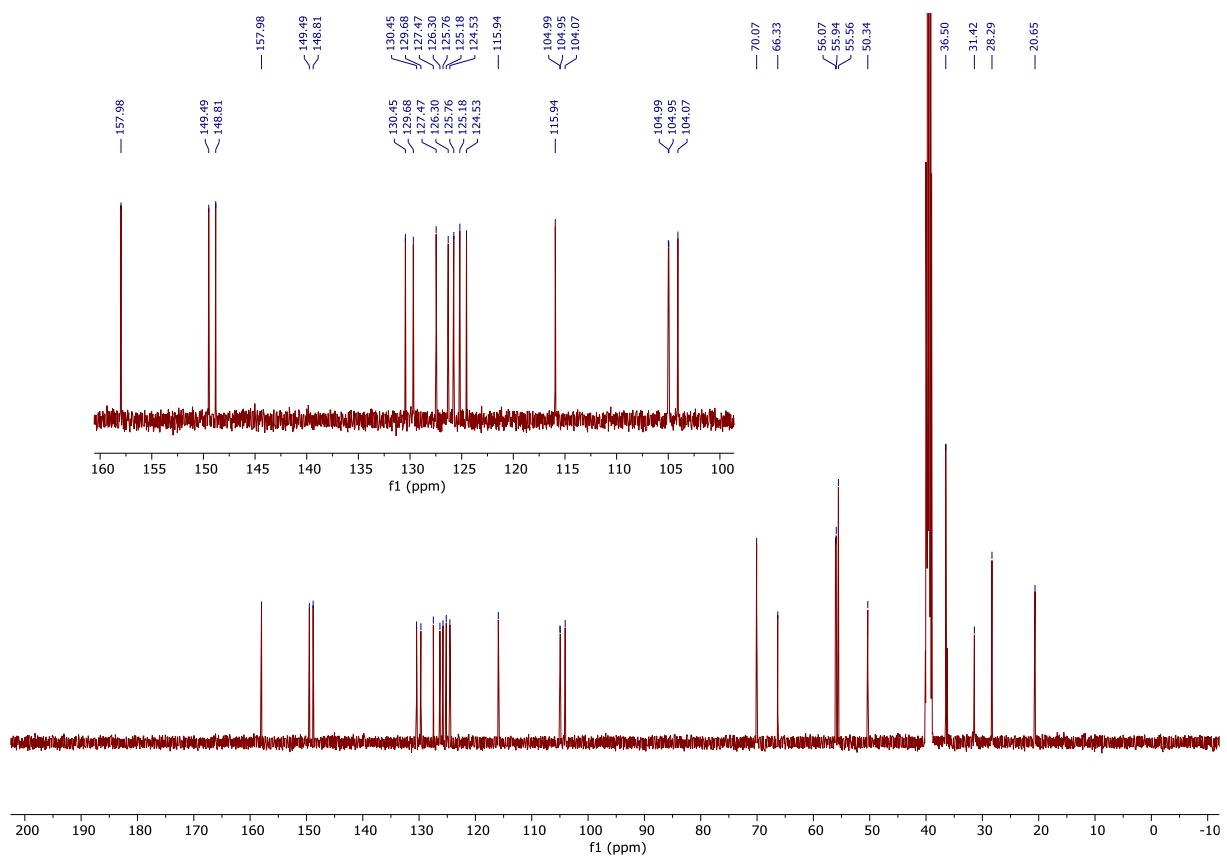


Figure S103. <sup>13</sup>C NMR spectrum (DMSO-d<sub>6</sub>, 125 MHz) of derivative **18b**.

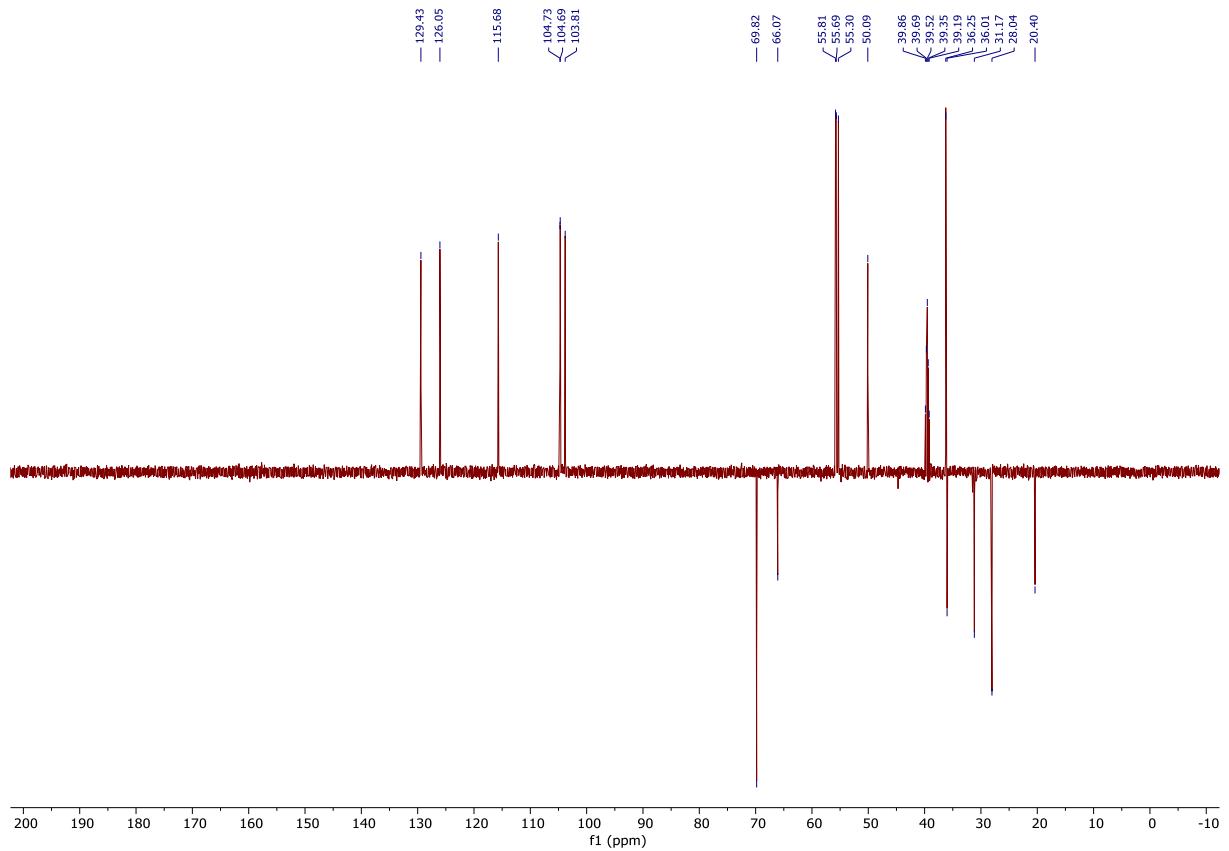
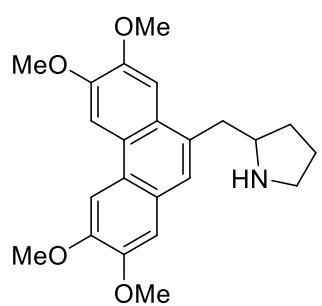


Figure S104. DEPT spectrum (DMSO-d<sub>6</sub>, 125 MHz) of derivative **18b**.



**19a**

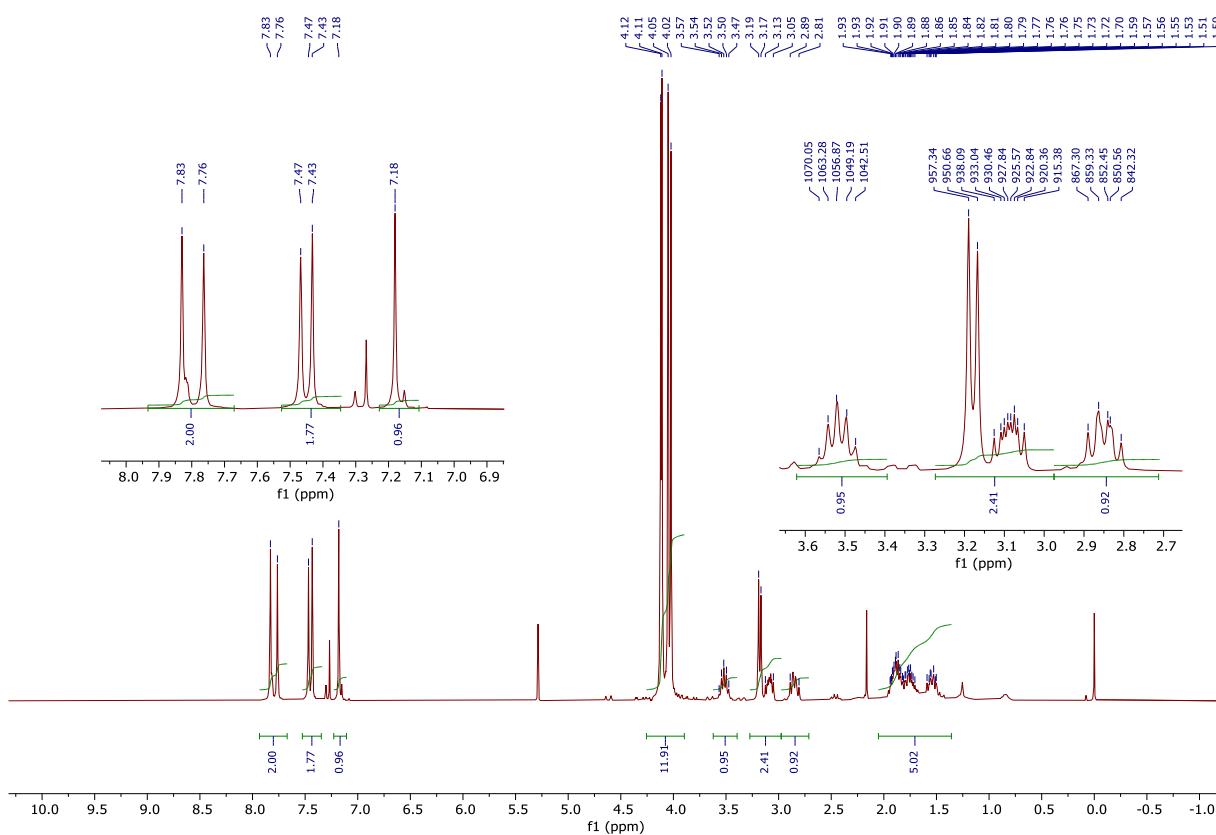


Figure S105.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 300 MHz) of derivative **19a**.

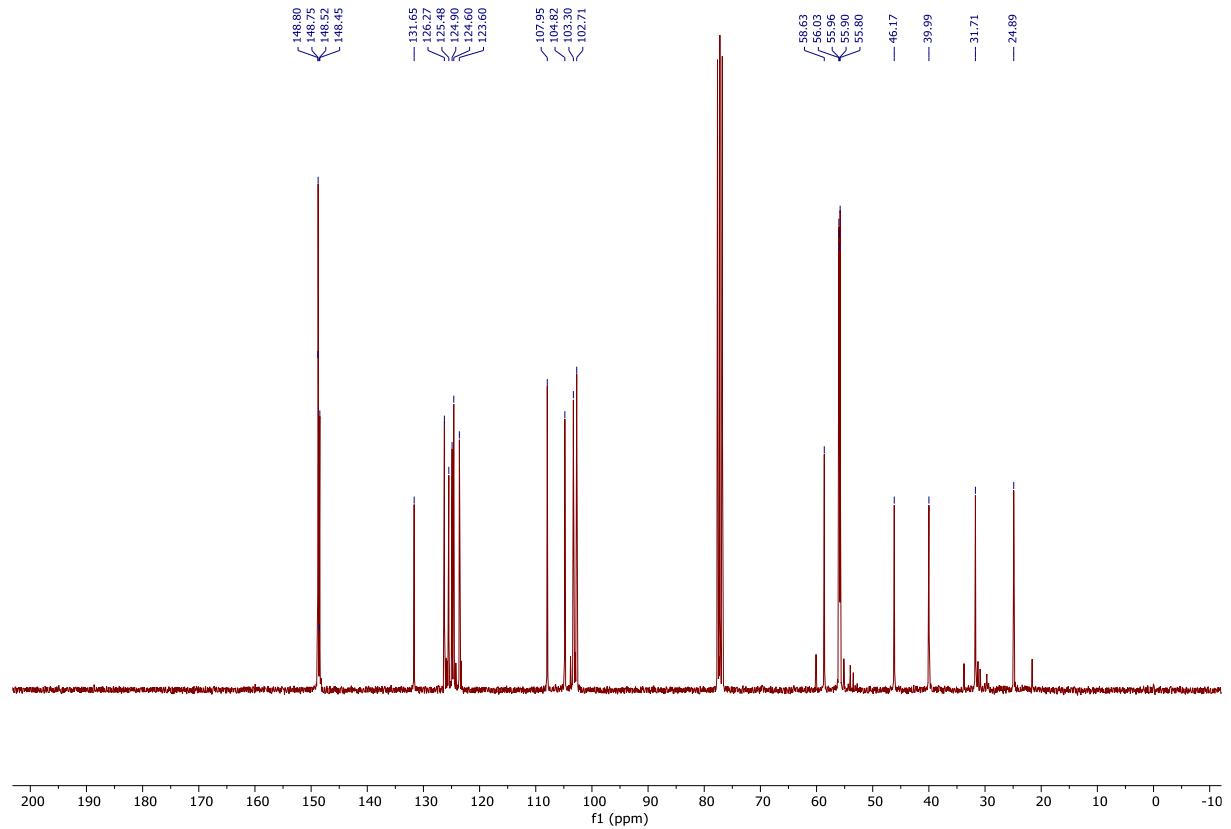


Figure S106.  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 75 MHz) of derivative **19a**.

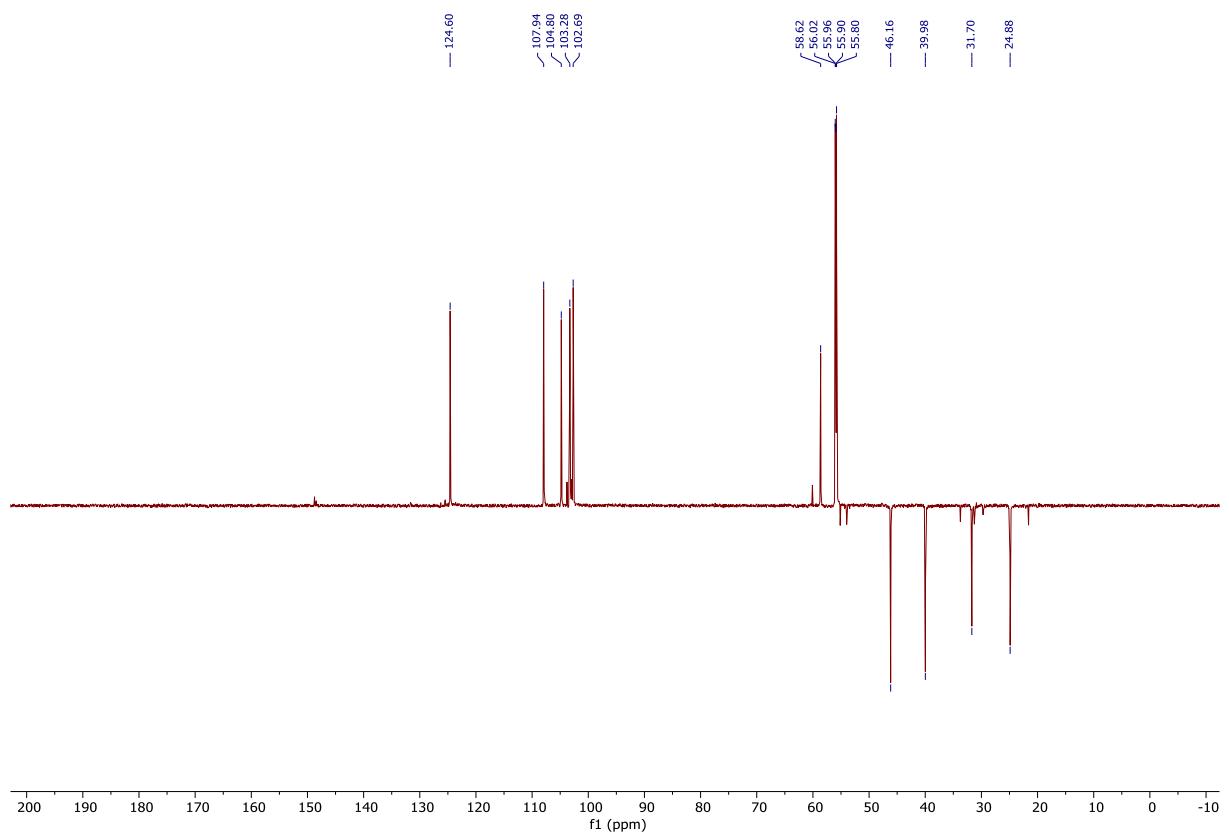
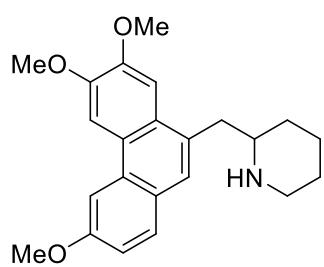


Figure S107. DEPT spectrum ( $\text{CDCl}_3$ , 75 MHz) of derivative **19a**.



**19b**

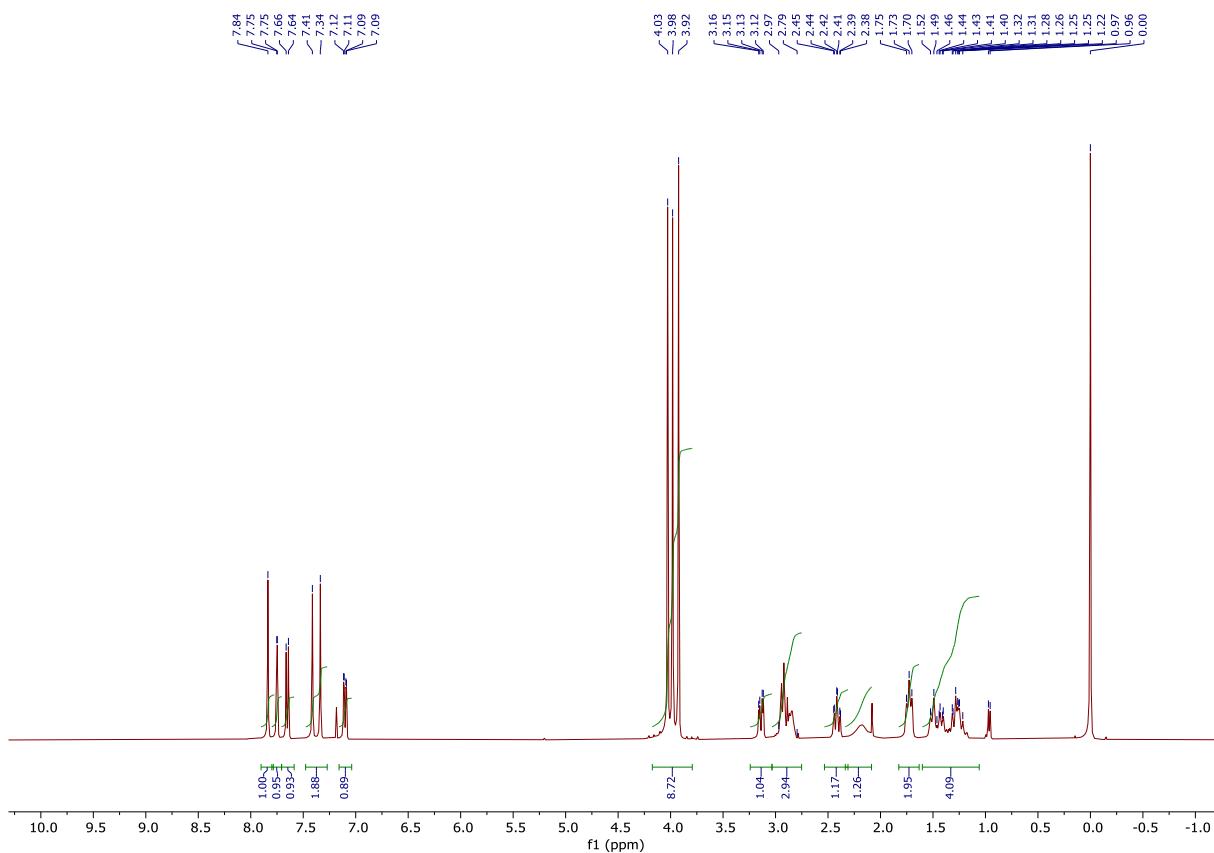


Figure S108.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 400 MHz) of derivative **19b**.

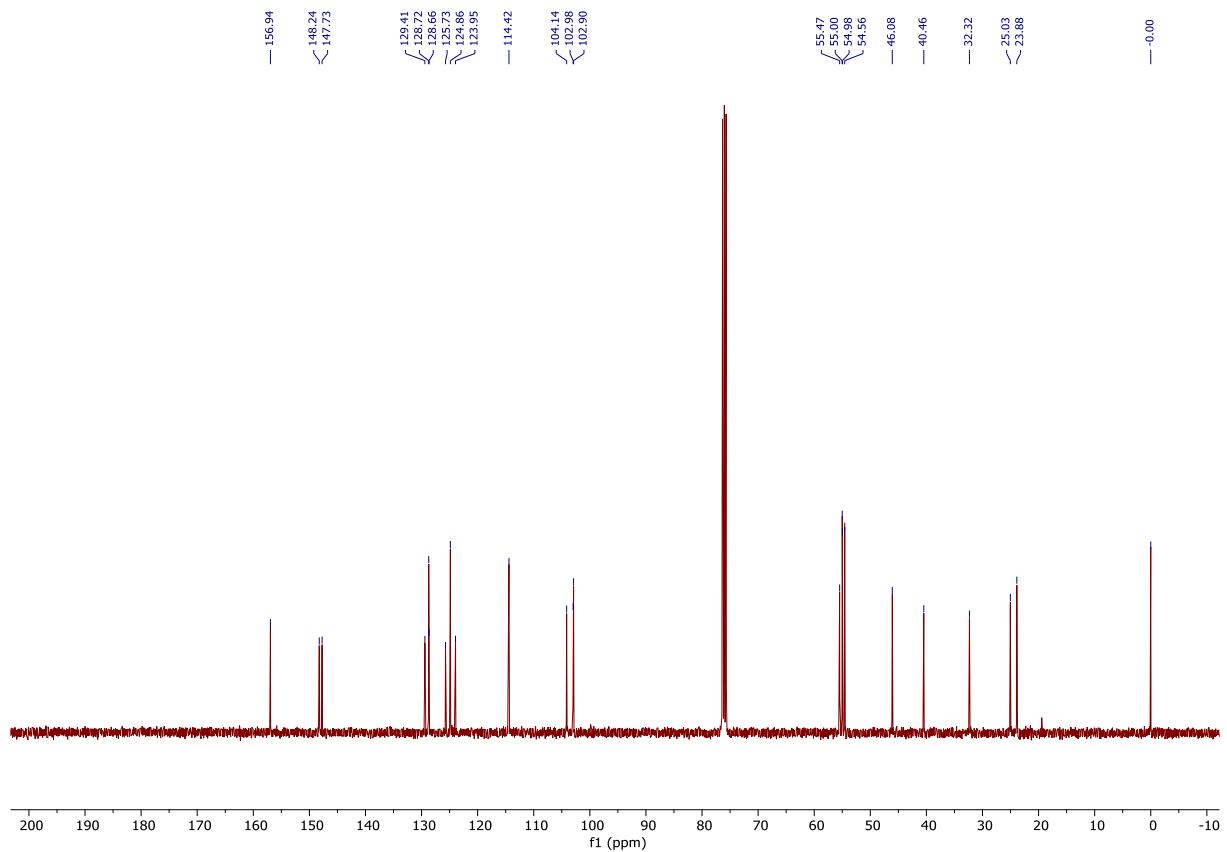


Figure S109.  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 100 MHz) of derivative **19b**.

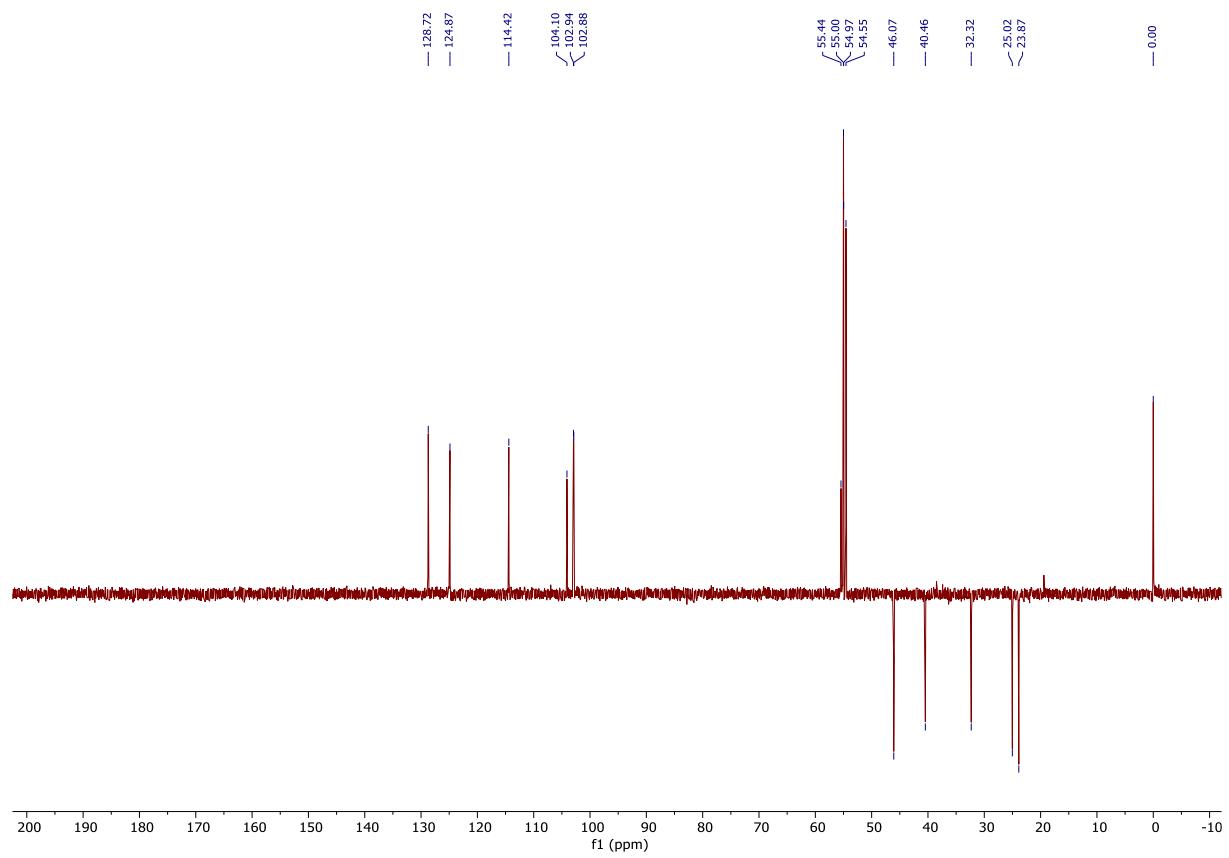
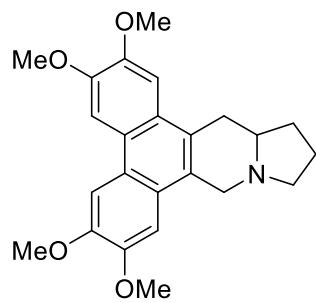


Figure S110. DEPT spectrum ( $\text{CDCl}_3$ , 100 MHz) of derivative **19b**.



Tylophorine (**1**)

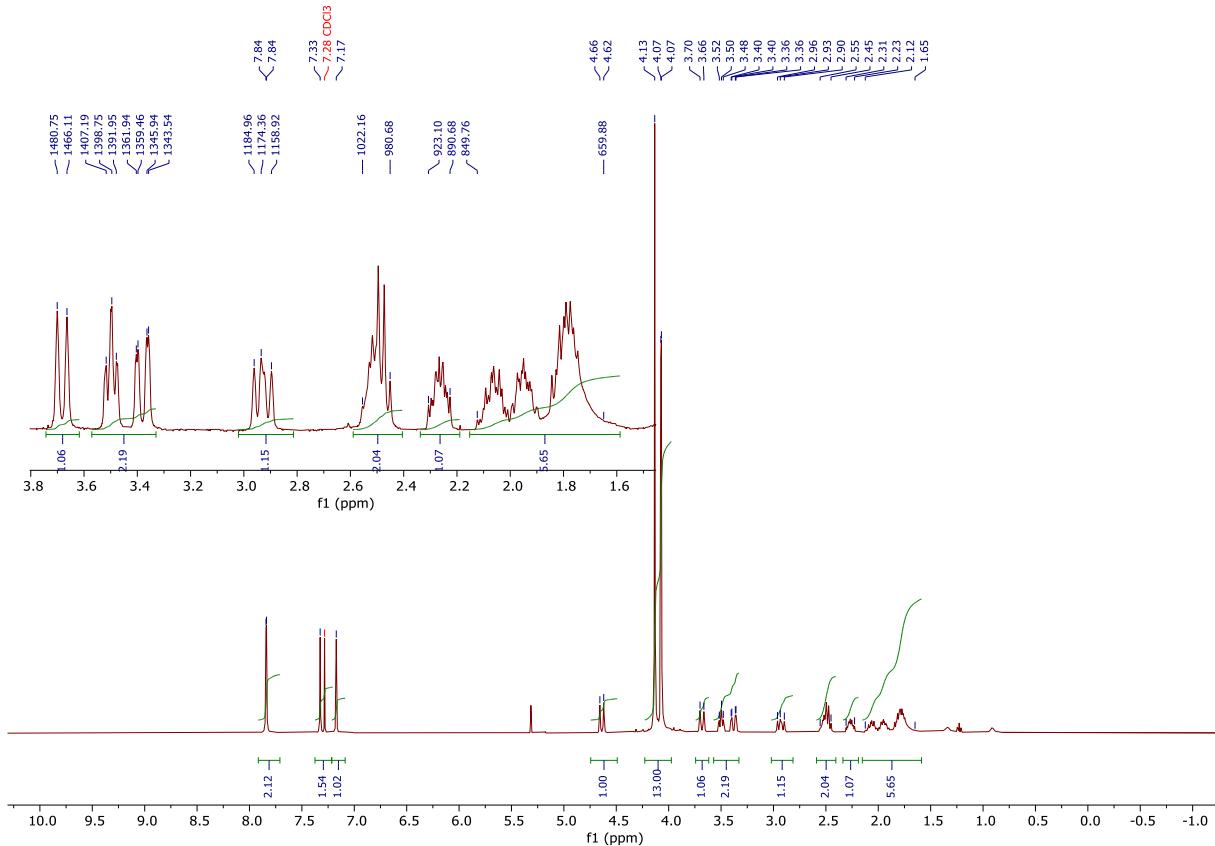


Figure S111. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of tylophorine (**1**).

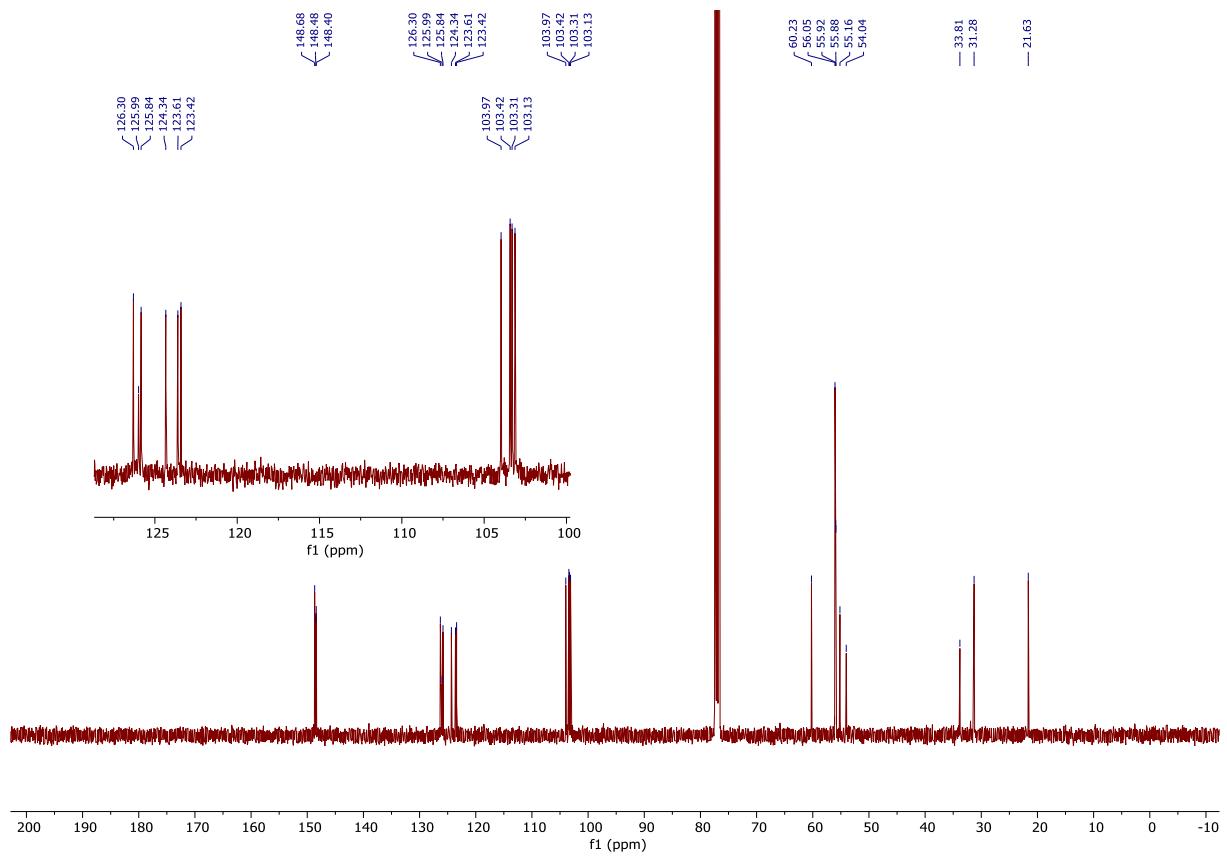


Figure S112.  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 100 MHz) of tylophorine (**1**).

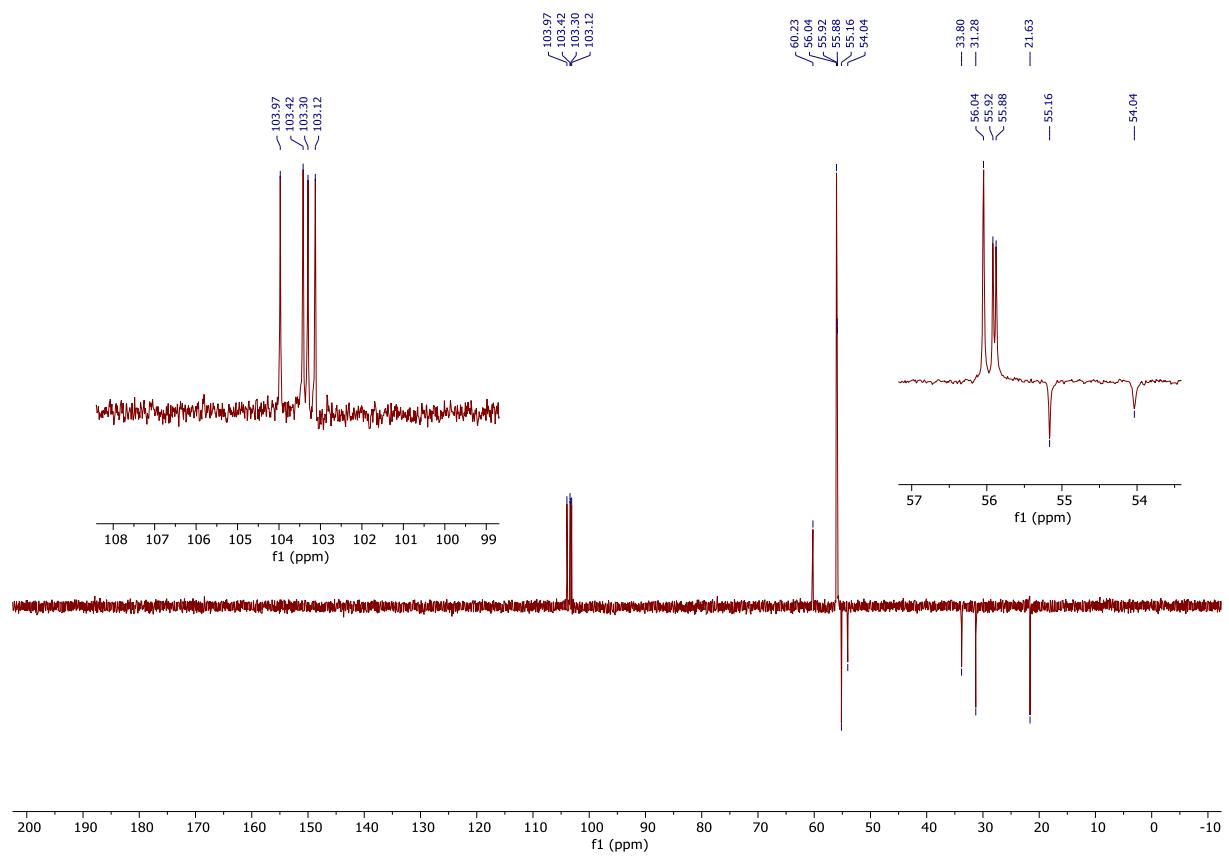
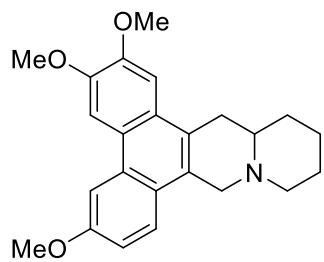


Figure S113. DEPT spectrum ( $\text{CDCl}_3$ , 100 MHz) of tylophorine (**1**).



**Cryptopleurine (2)**

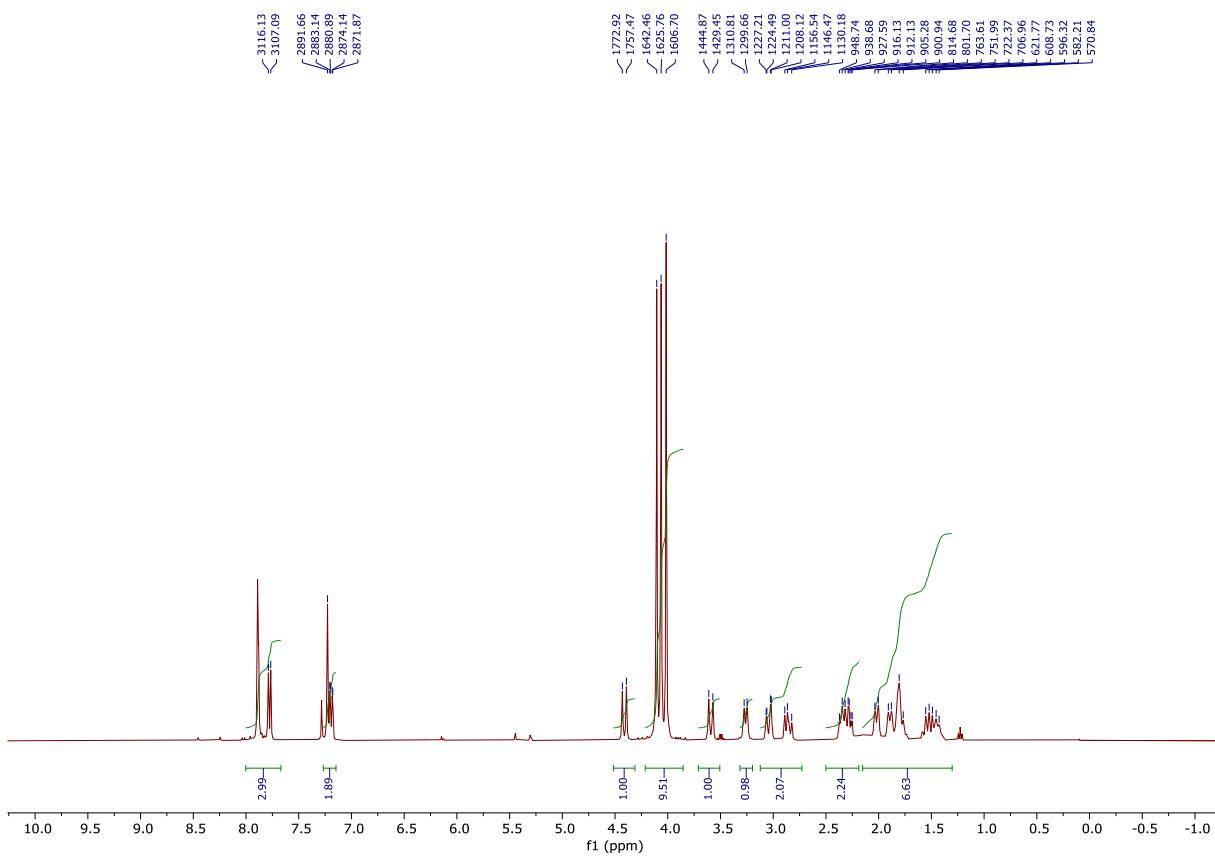


Figure S114.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 400 MHz) of cryptopleurine (2).

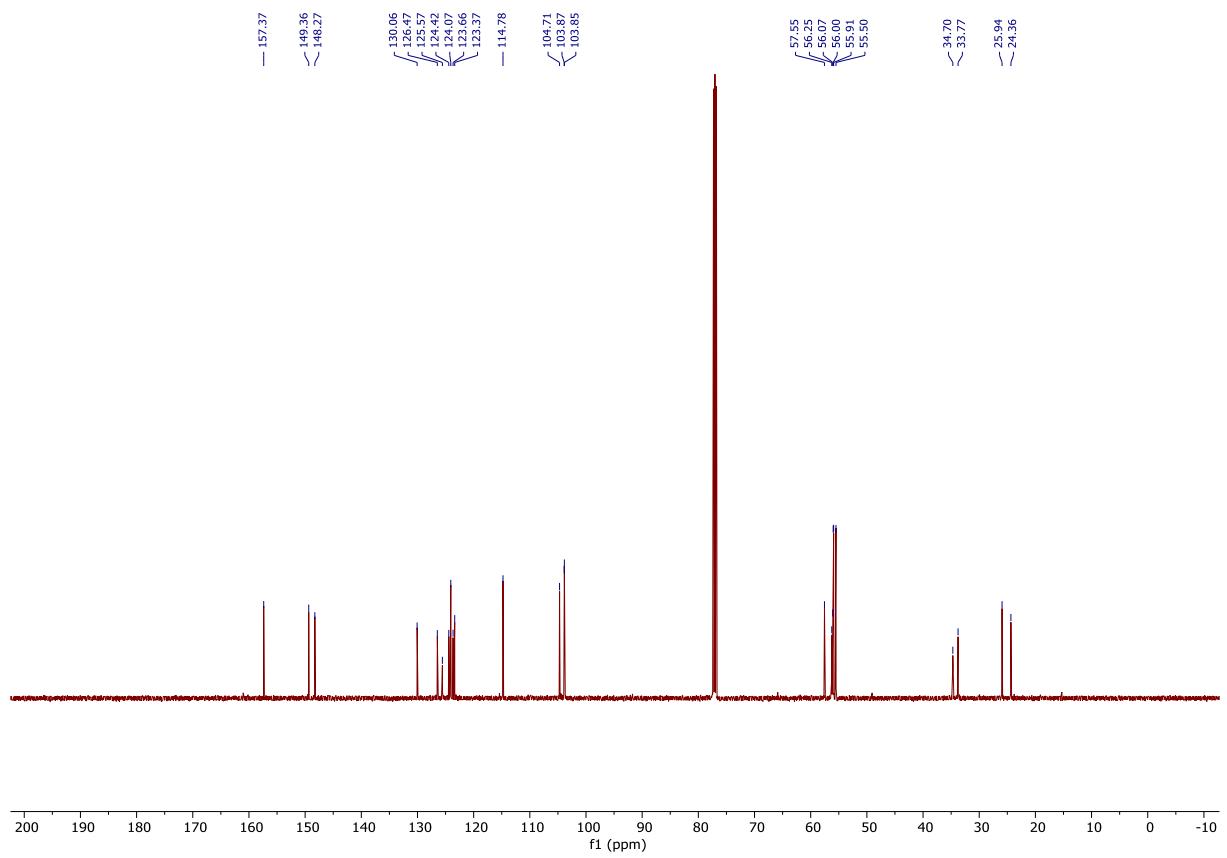


Figure S115. <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 100 MHz) of cryptopleurine (**2**).

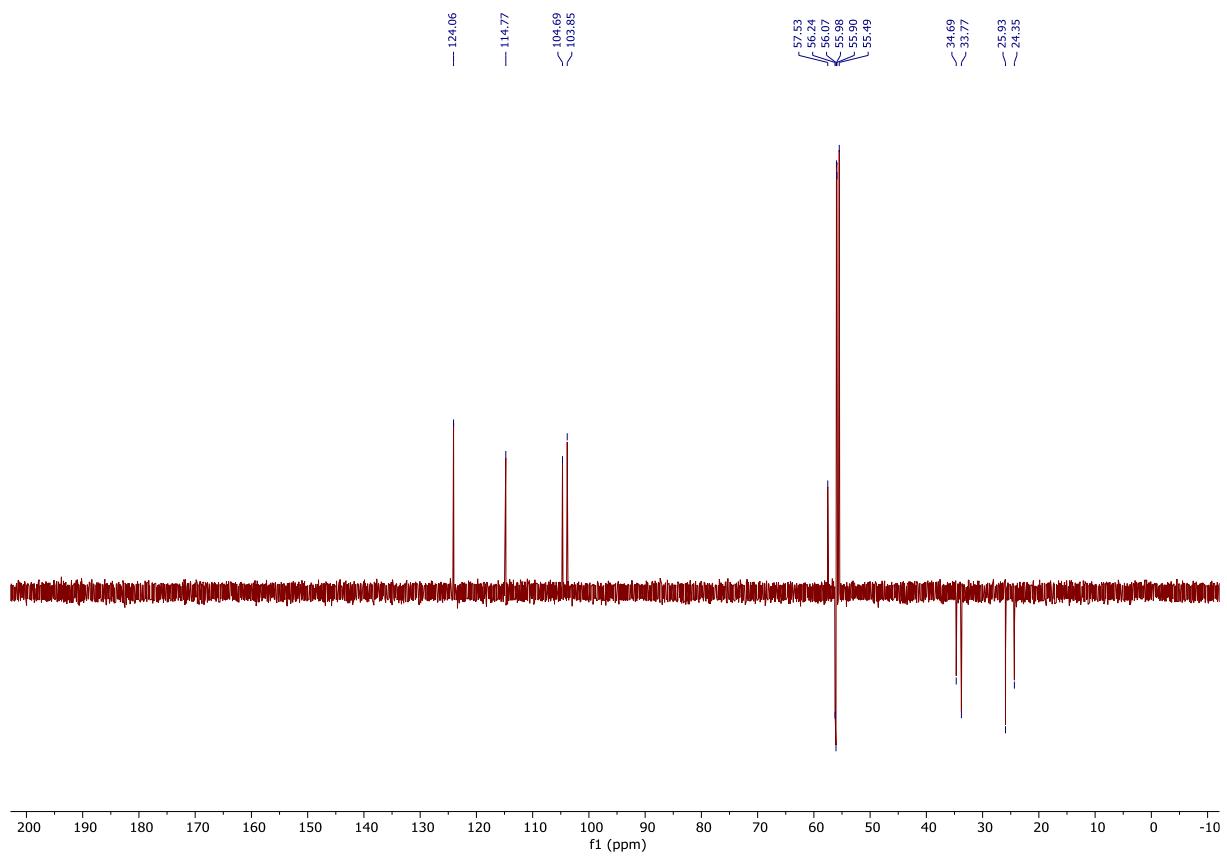


Figure S116. DEPT spectrum ( $\text{CDCl}_3$ , 100 MHz) of cryptoleurine (**2**).