Electronic Supplementary Material (ESI) for Dalton Transactions.

gem-DiBromovinyl Boron Dipyrrins: Synthesis, Spectral Properties and Crystal Structures

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Electronic Supplemental Information (ESI)

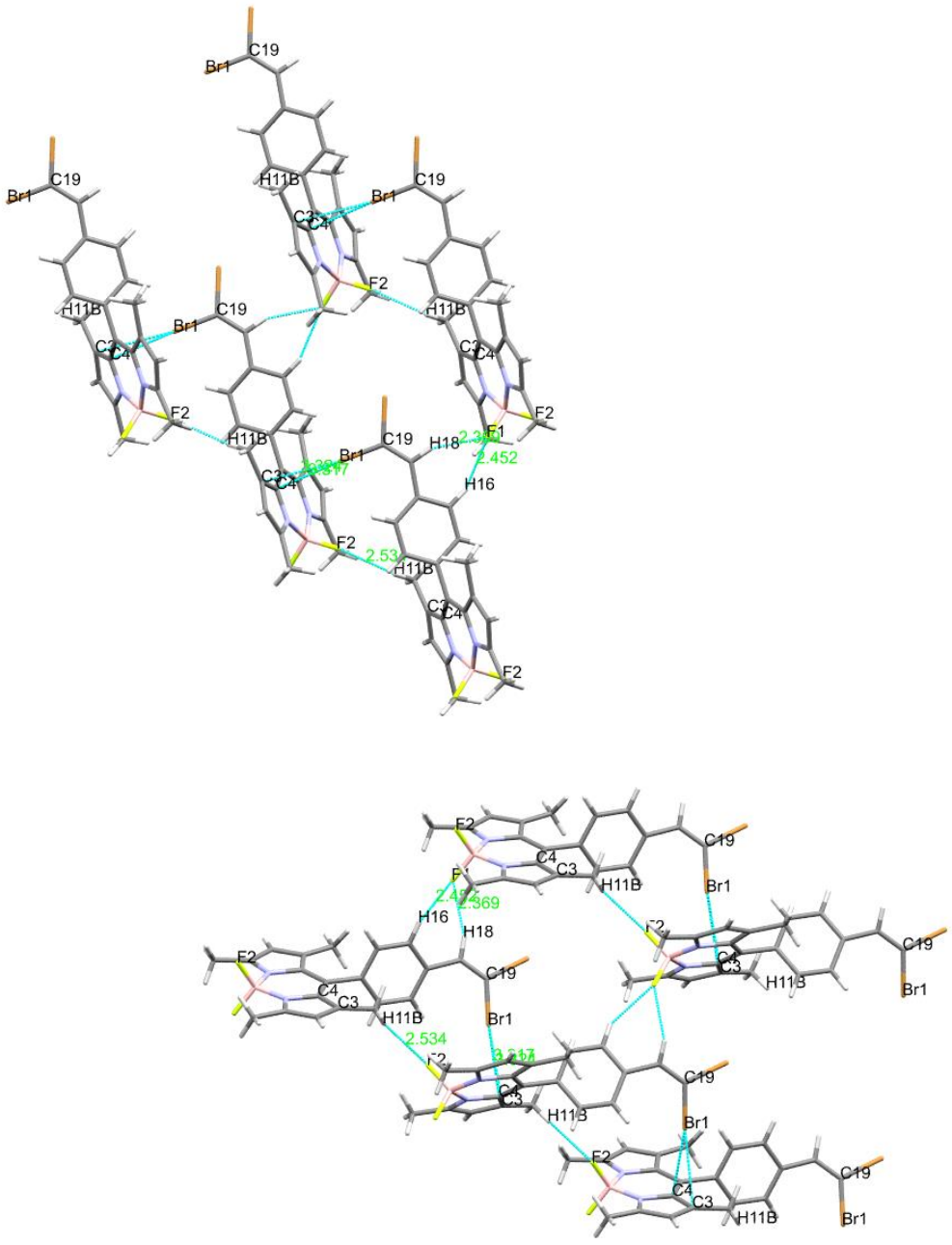


Fig. S1 Crystal structure packing of **2** (top) *b*-axis (bottom) *c*-axis

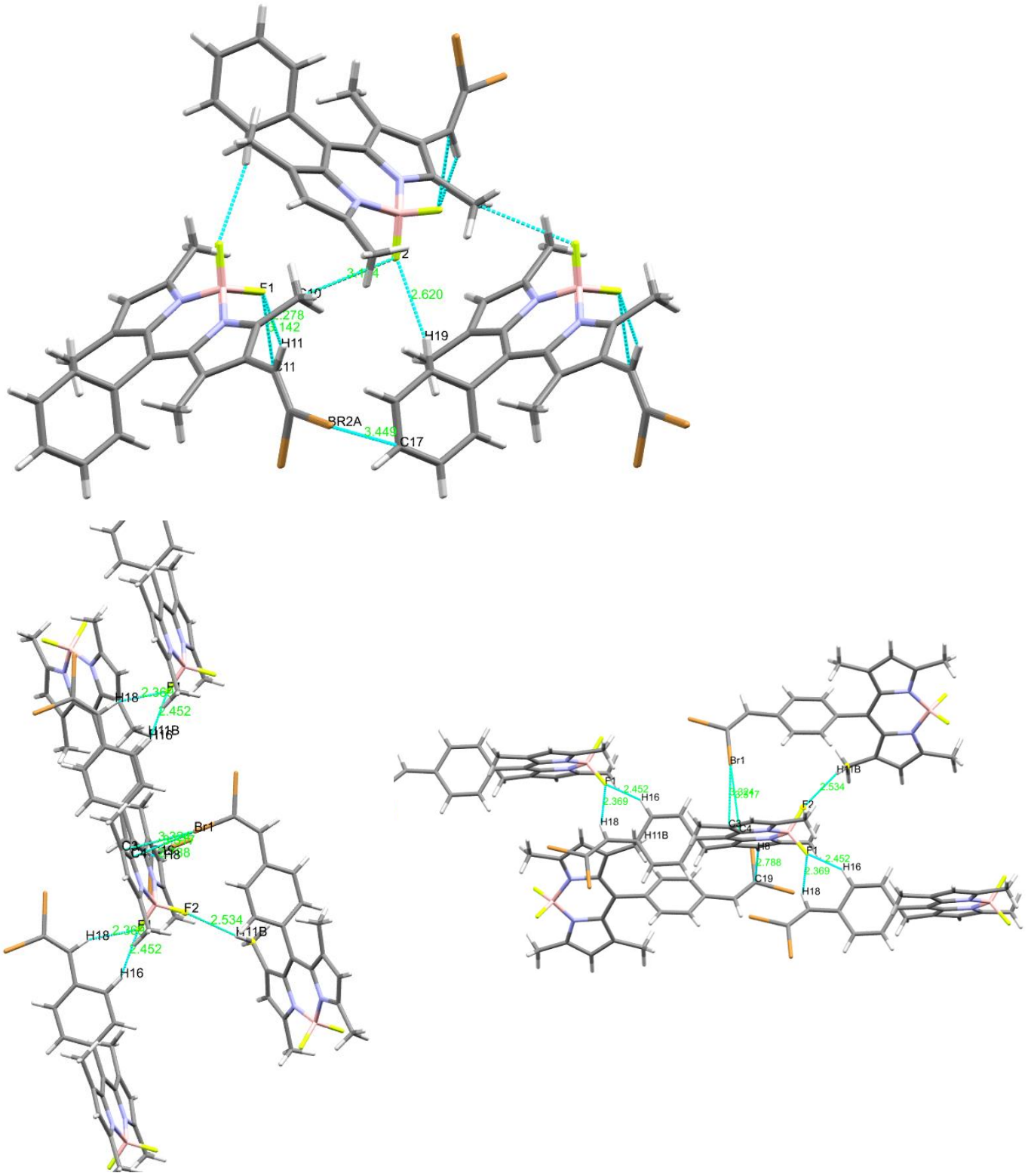


Fig. S2 Crystal structure packing **9.**

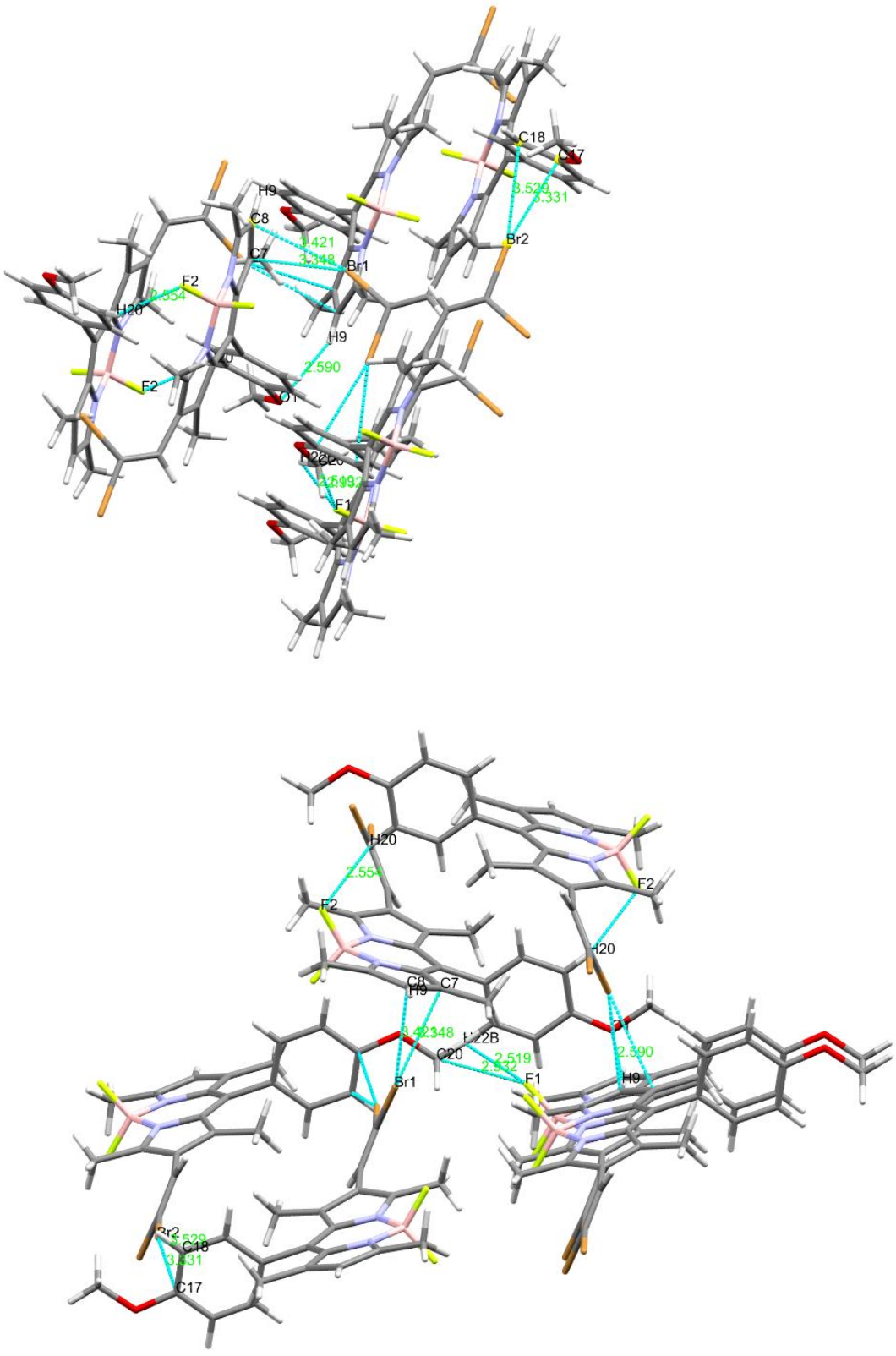


Fig. S3 Crystal structure packing of **10.**

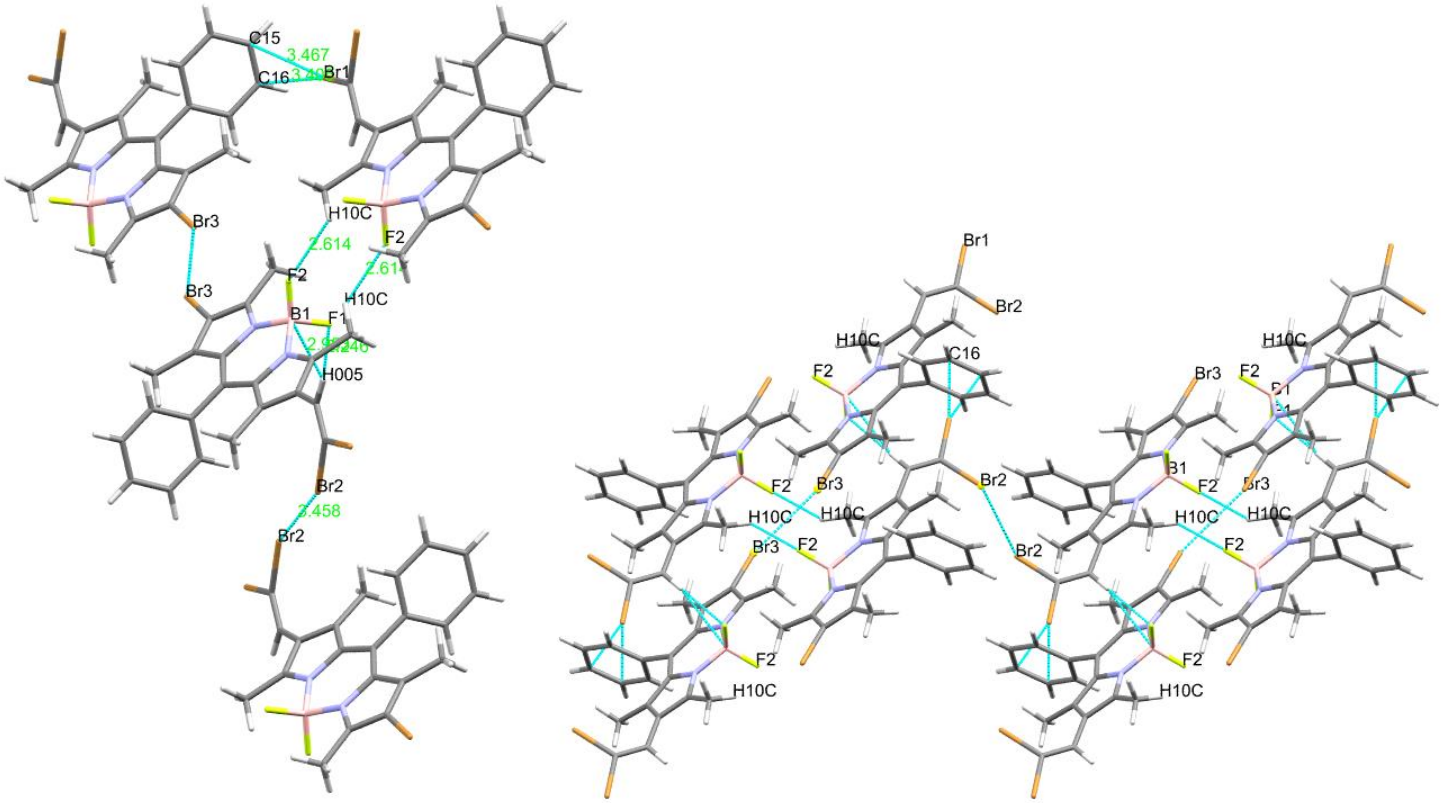


Fig. S4 Crystal structure packing of **12.**

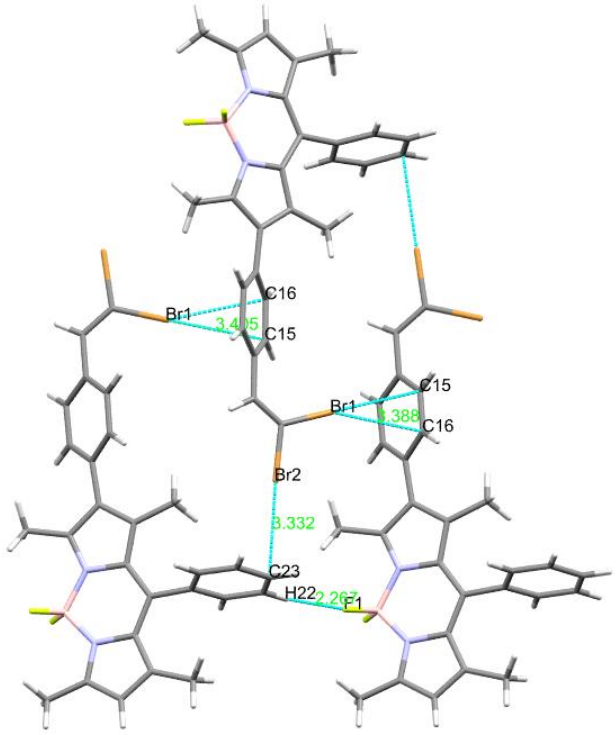


Fig. S5 Crystal structure packing of **16.**

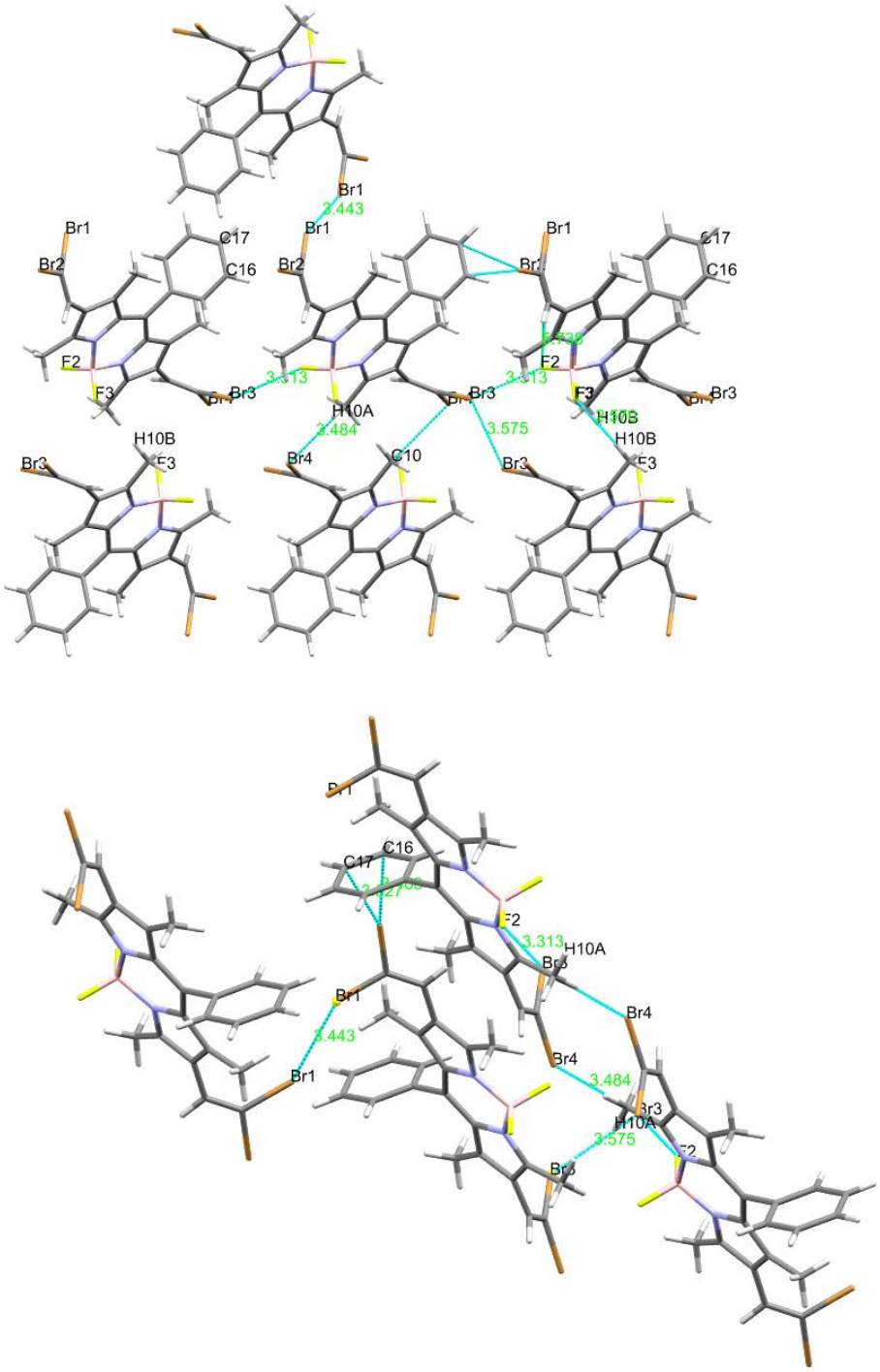


Fig. S6 Crystal structure packing of **19.**

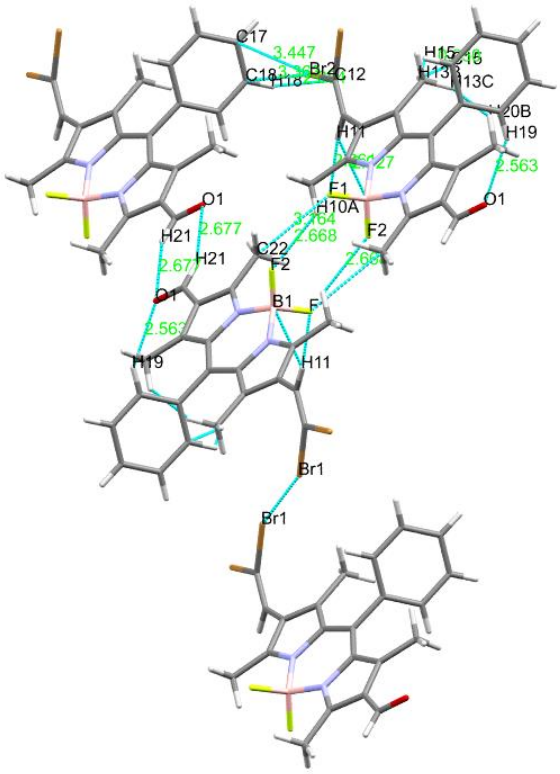


Fig. S7 Crystal structure packing of **20.**

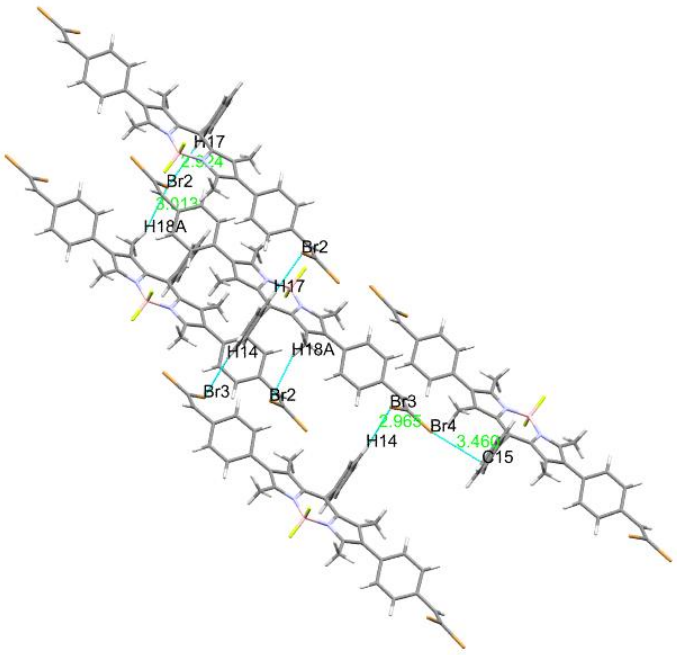


Fig. S8 Crystal structure packing of **23.**

Hirshfeld crystal surface analysis. Hirshfeld surfaces in the crystal structure and the associated 2D-fingerprint plots were calculated using the Crystal-Explorer17.5 program, which accepts CIF format file structure input. Hirshfeld surfaces and their associated two-dimensional fingerprint plots using **Crystal-Explorer (Version 3.1)**, [*S.K. Wolff, D.J. Grimwood, J.J. McKinnon, M.J. Turner, D. Jayatilaka, M.A. Spackman,. Eur. J. Inorg. Chem.*; 2012: 2653-2662], were employed to quantify the various intermolecular interactions. The Hirshfeld surface fingerprint plots of the molecules are mapped using the descriptor d_{norm}, which encompasses d_e (the distance of any surface point nearest to the internal atoms), d_i (the distance of the surface point nearest to the exterior atoms and also with the van der Waals radii of the atoms). These data were generated using this pair of coordinates. The Hirshfeld surfaces mapped over d_{norm} (range of -0.1-1.6 Å) are displayed in Fig S8. The value of d_{norm} is negative or positive depending on whether the intermolecular contacts are shorter or longer than the van der Waals separations.

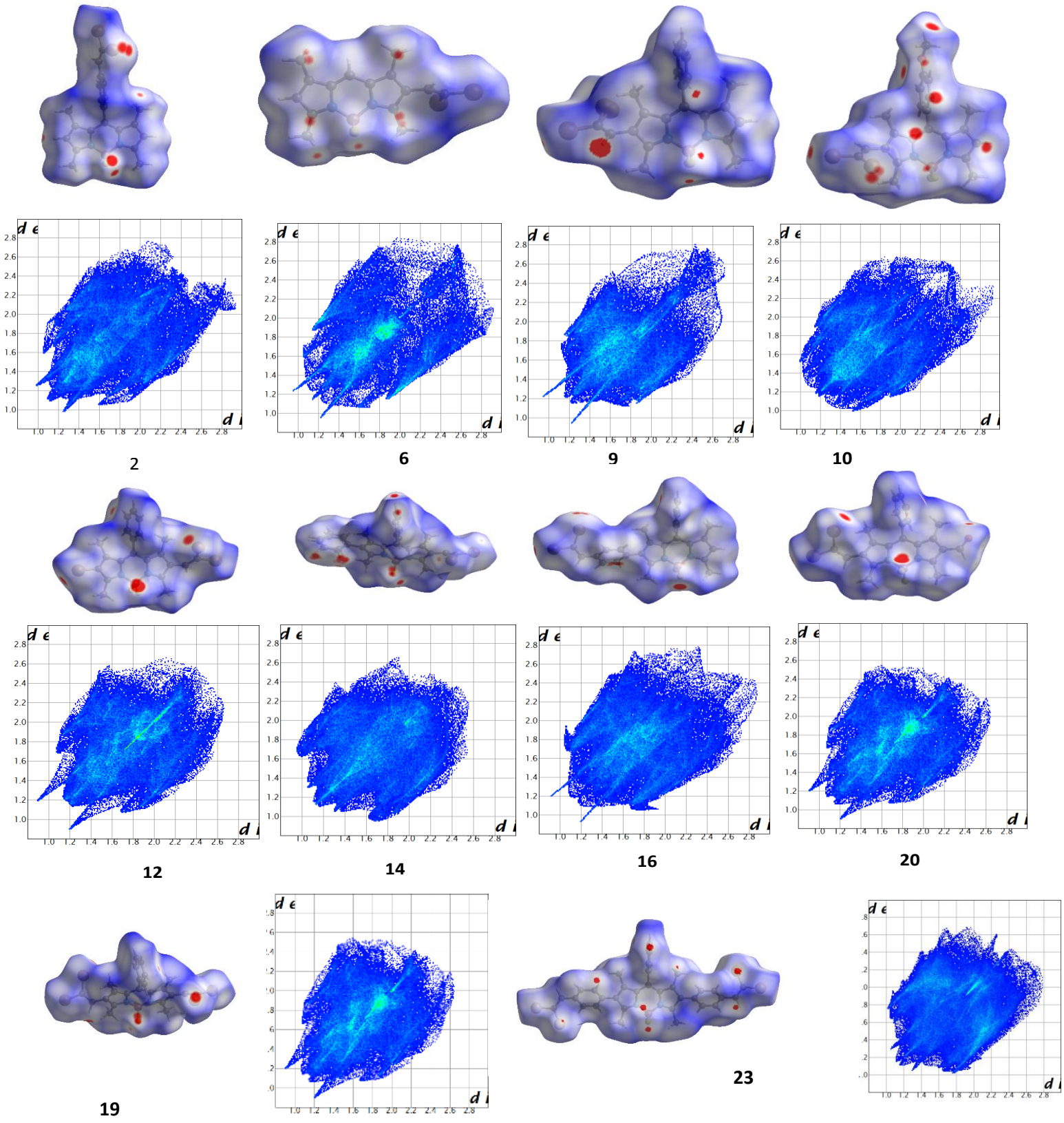


Fig. S9 Hirshfeld surfaces (HSs) and 2D fingerprint plots of *gem*-dibromovinyl BODIPYs

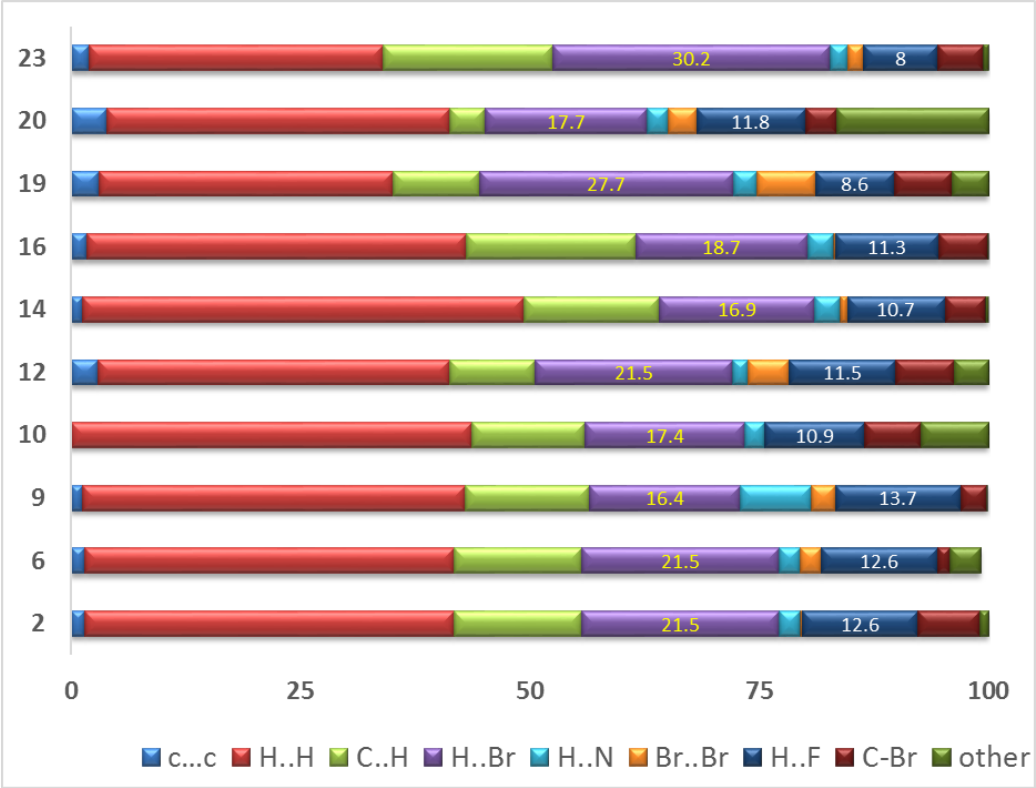


Fig. S10 Relative percentage contributions of various non-covalent intermolecular contacts on the basis of Hirshfeld surface in BODIPYs.

General method for the synthesis of *gem*-dibromovinyl boron dipyrrins.

For **1** or **5**: To a solution of BODIPY aldehyde (1 mmol) **7**, **8**, **11**, **13**, **15**, **17**, **18** and **22** in CH_2Cl_2 (4 mL) at 0 °C and CBr_4 (2 mmol) was added dropwise a solution of the corresponding phosphines, triphenyl phosphine (4 mmol) or P(Oi-Pr)$_3$ (3 mmol). After 30 min, the reaction was warmed to r.t. and extracted with CH_2Cl_2 (20-50 mL). After drying over $MgSO_4$, solvent was removed under vacuum and the product was purified over silica gel column. On elution using either a mixture of CH_2Cl_2-Hexane or EtOAc-hexane, bright coloured products were obtained. HPLC purification using a C_{18} reversed column in CH_3CN-H_2O furnished analytically pure products.

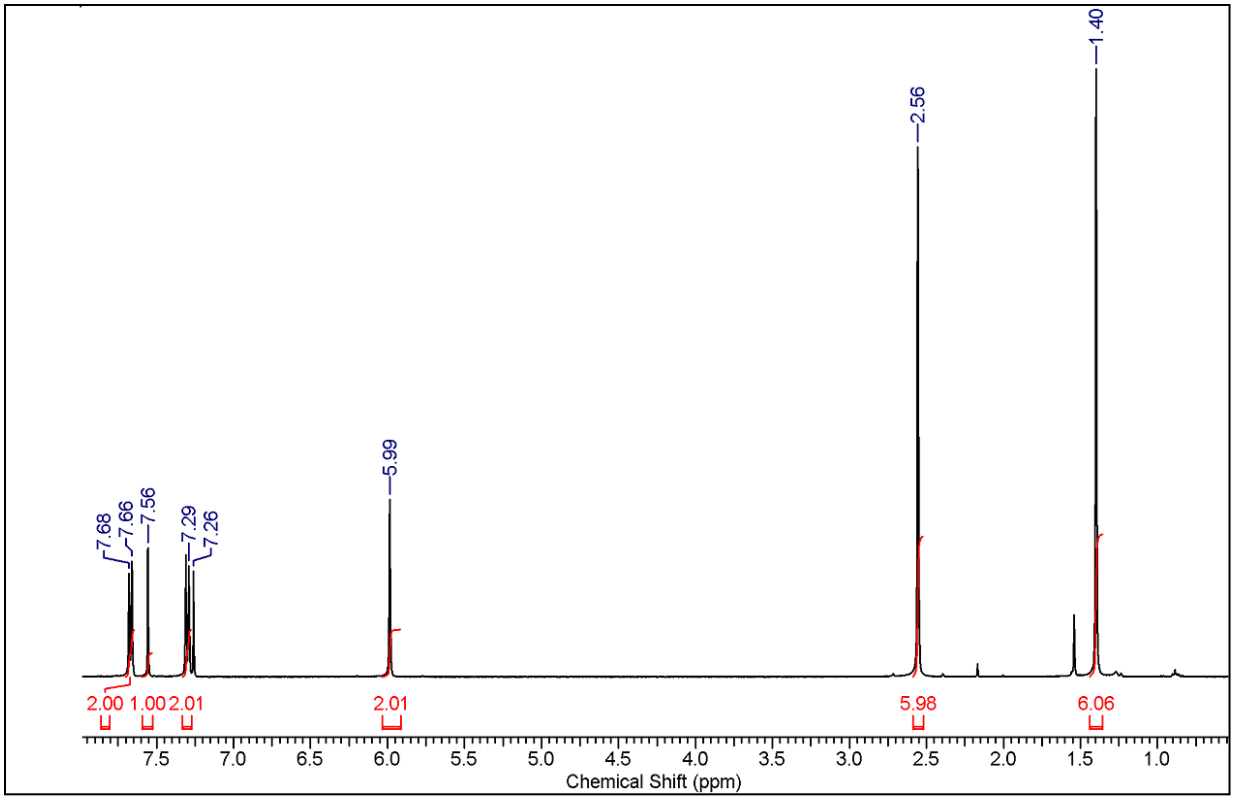


Fig S11. ^{1}H NMR spectrum of compound **2** in $CDCl_3$

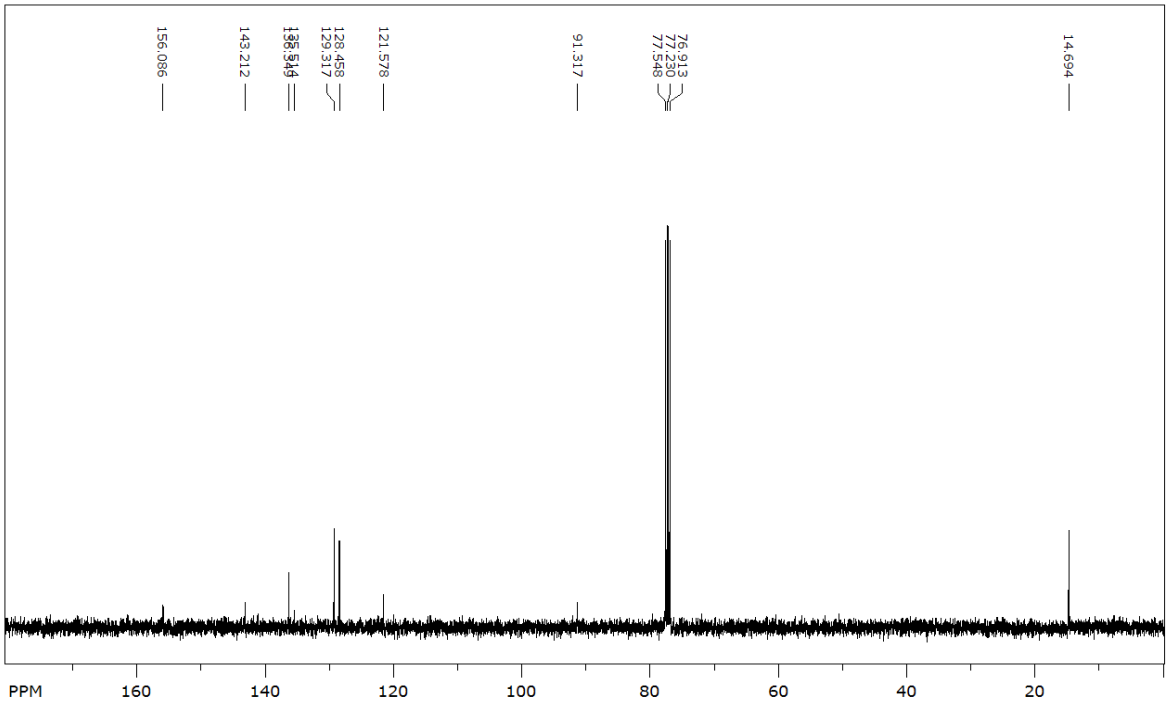


Fig S12. ^{13}C NMR spectrum of compound **2** in $CDCl_3$

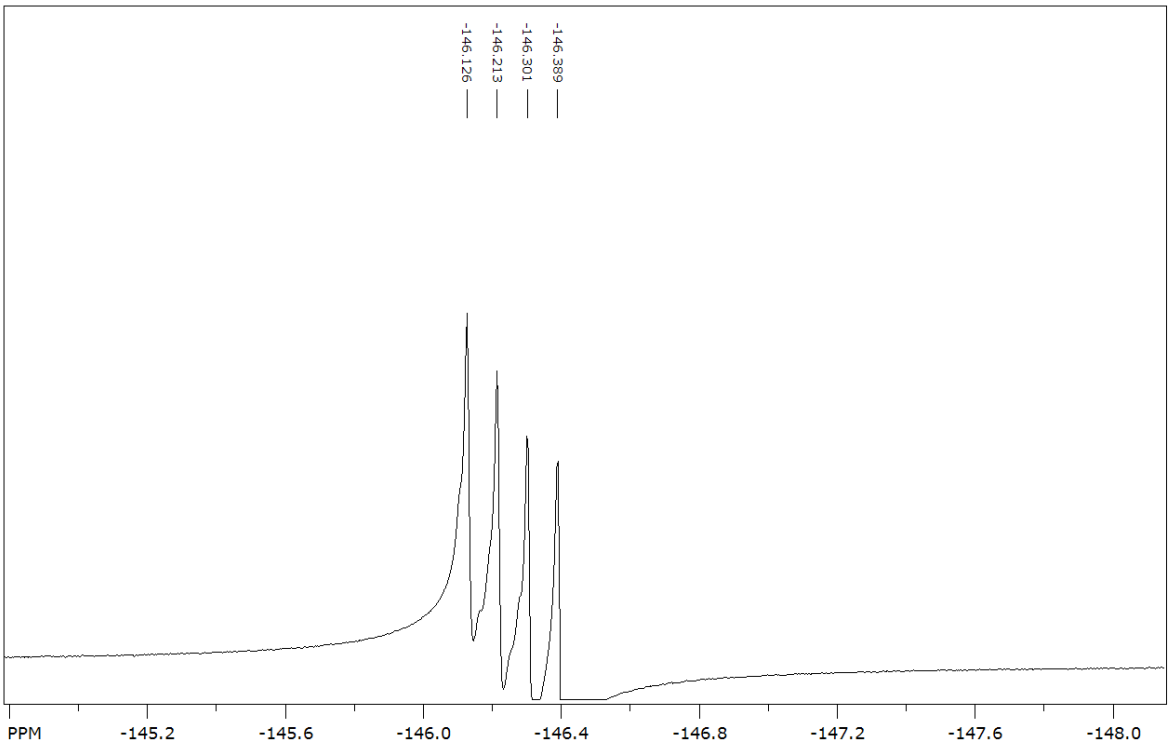


Fig S13. ^{19}F NMR spectrum of compound **2** in $CDCl_3$

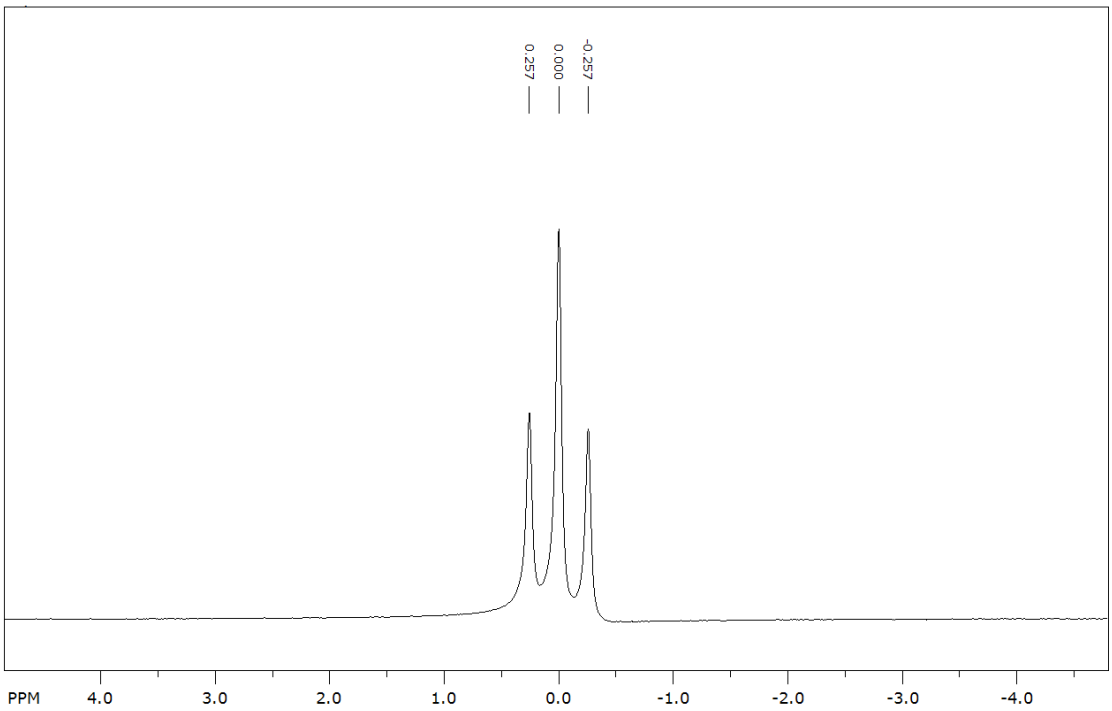


Fig S14. ^{11}B NMR spectrum of compound **2** in $CDCl_3$

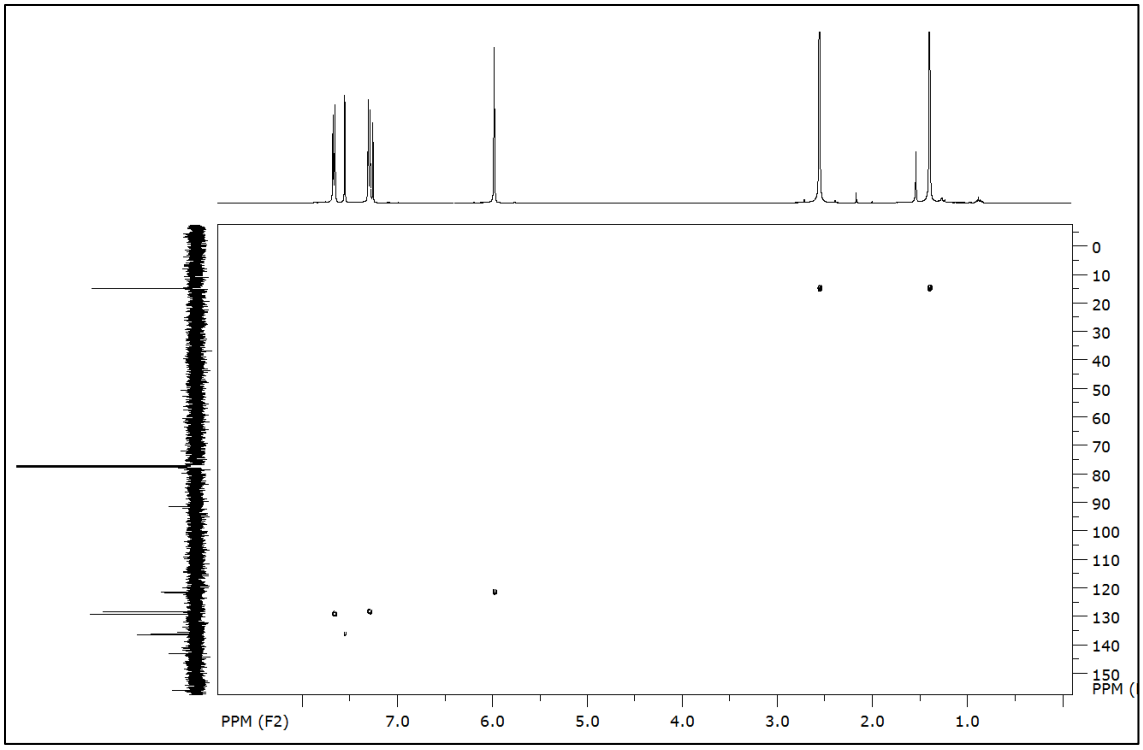


Fig S15. ^{1}H-^{13}C HSQC 2D NMR spectrum for compound **2** in $CDCl_3$

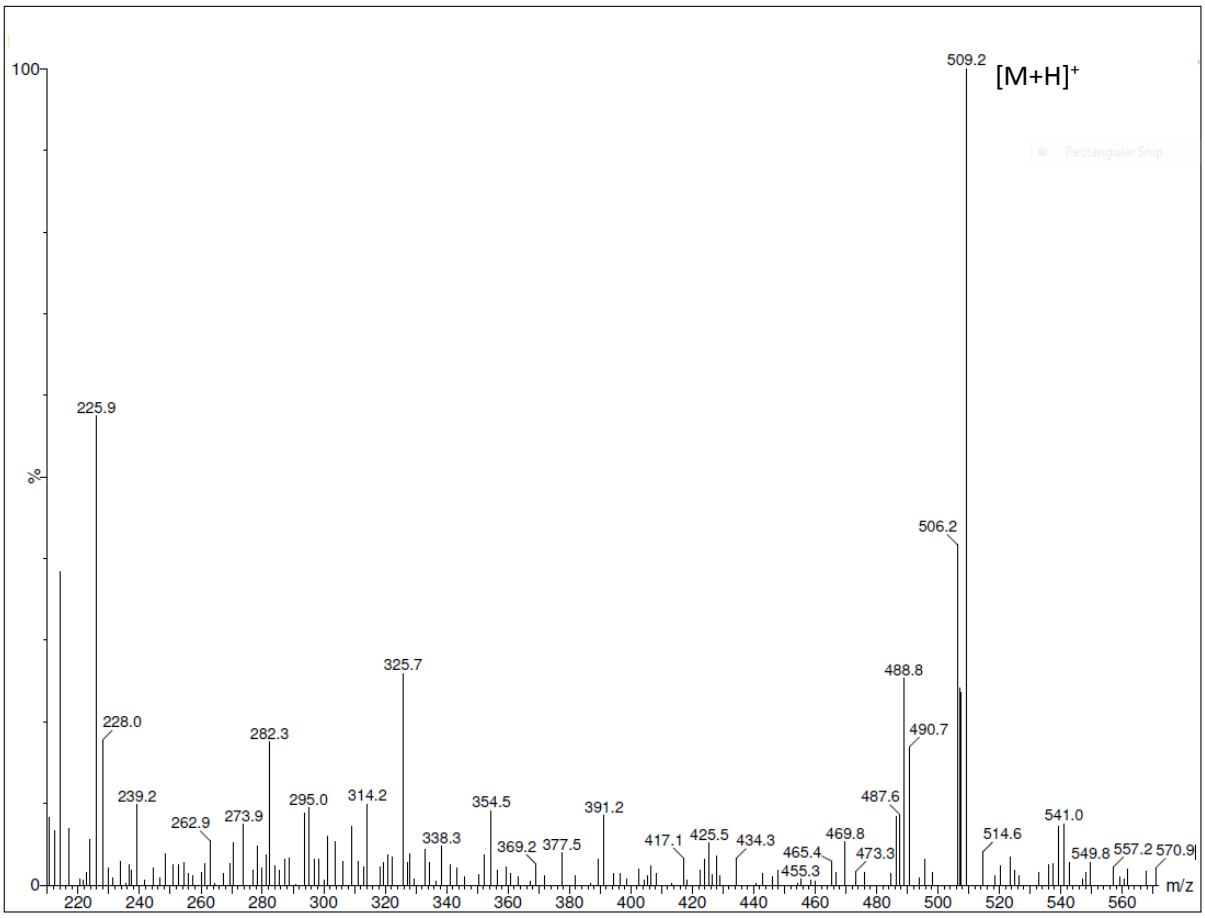


Fig S16. ESI-MS spectrum of compound **2**.

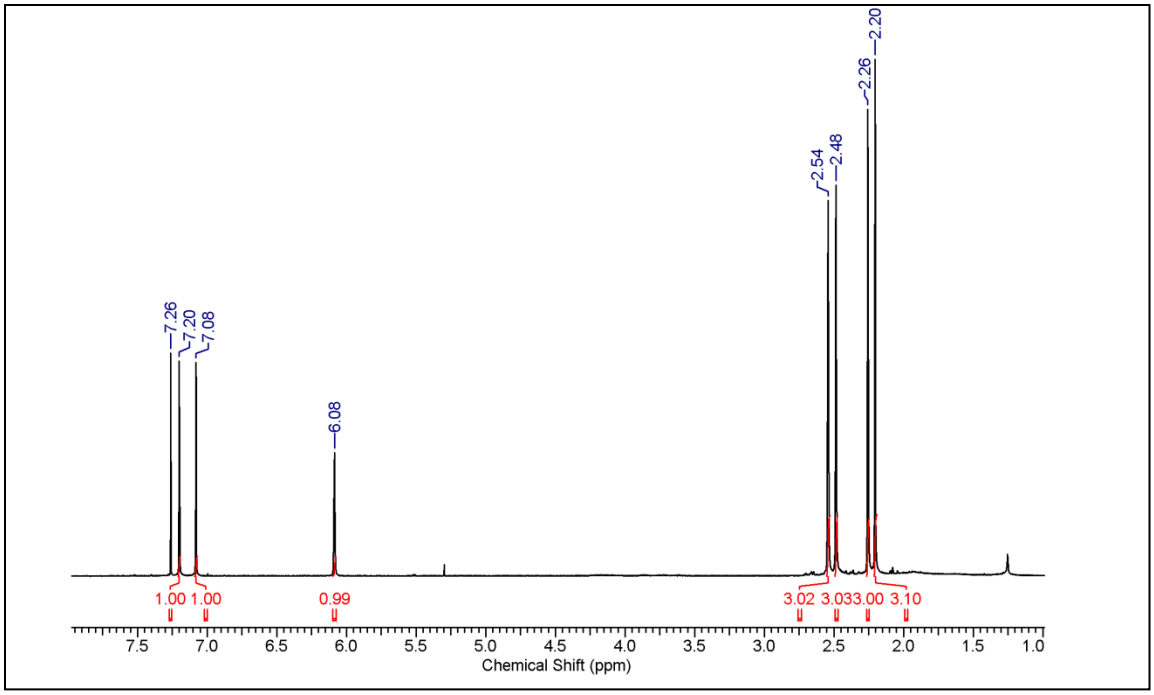


Fig S17. ^{1}H NMR spectrum of compound **6** in $CDCl_3$

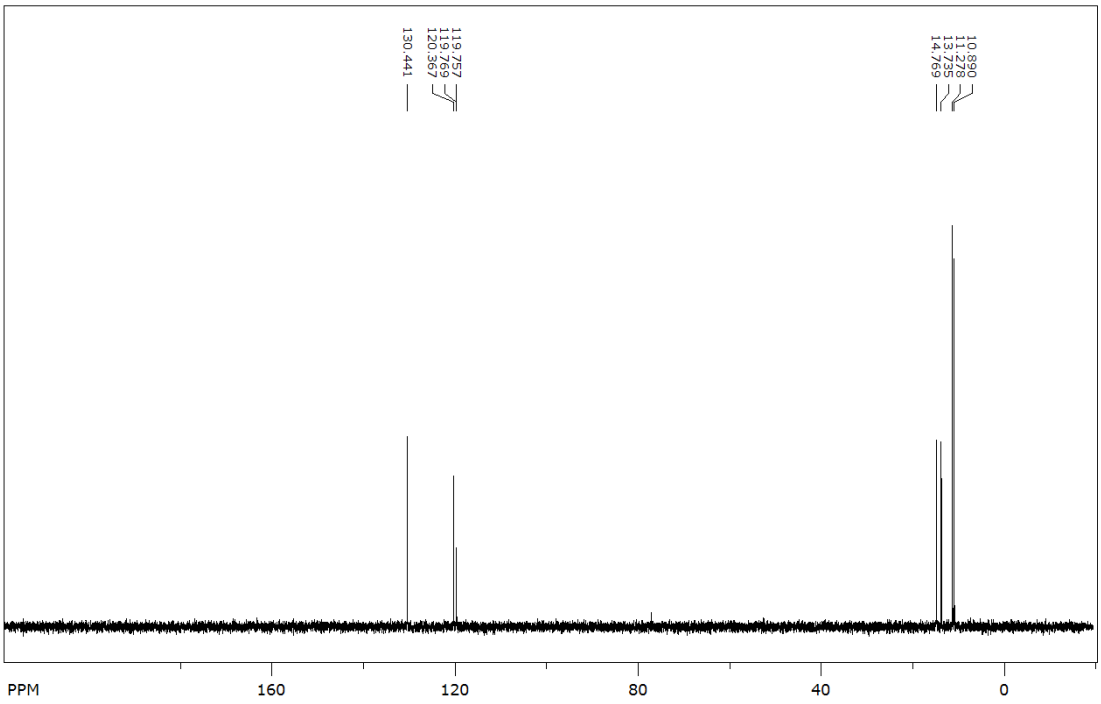


Fig S18. ^{13}C NMR spectrum of compound **6** in $CDCl_3$

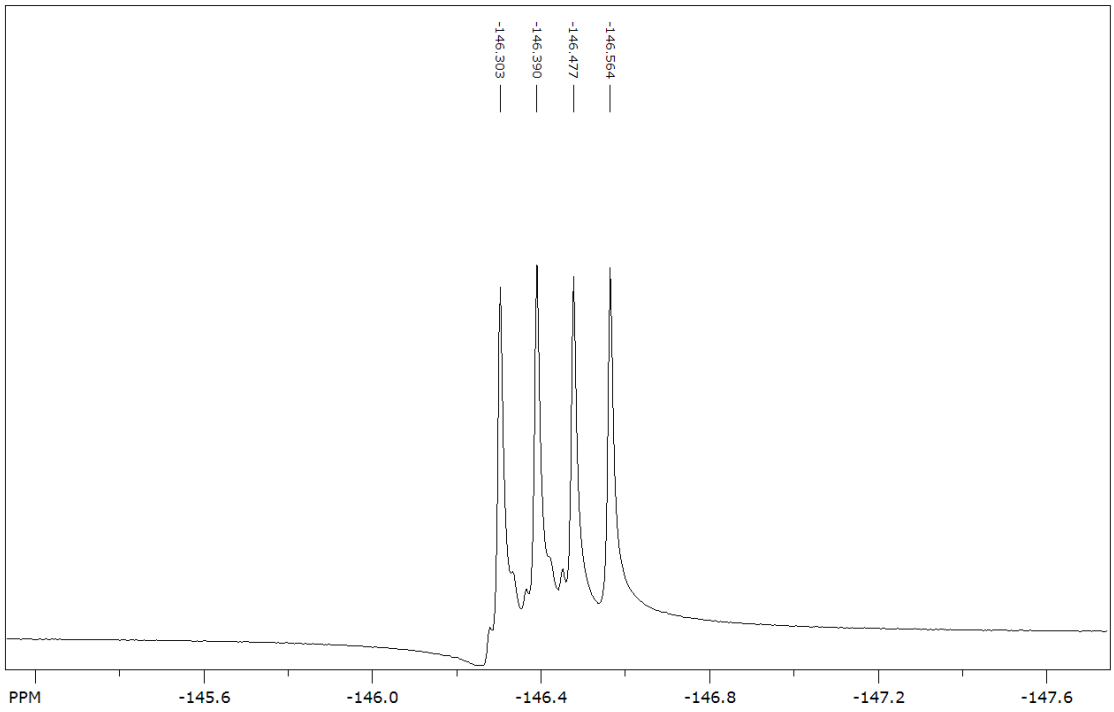


Fig S19. ^{19}F NMR spectrum of compound **6** in $CDCl_3$

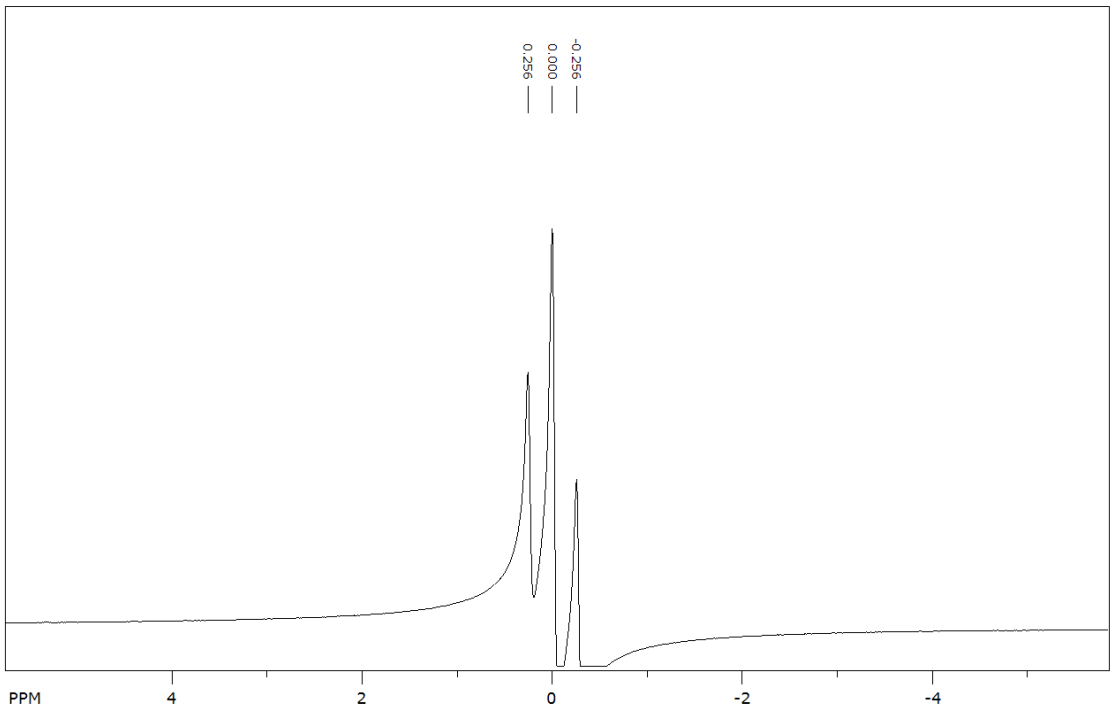


Fig S20. ^{11}B NMR spectrum of compound **6** in $CDCl_3$

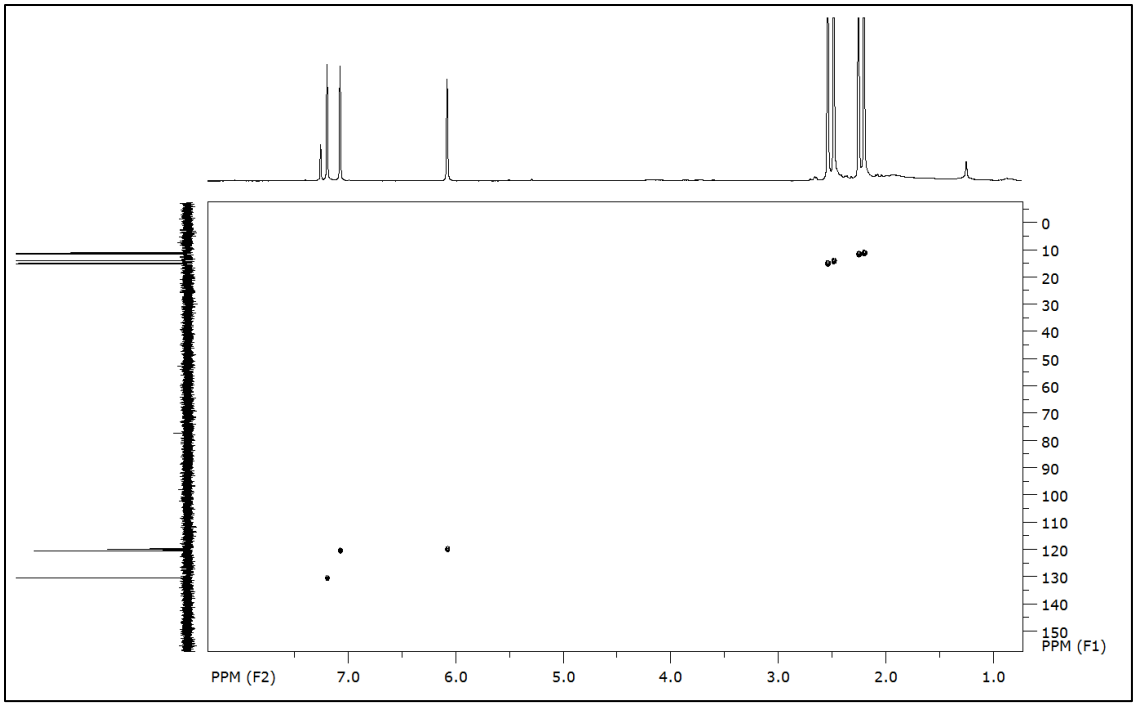


Fig S21. ^{1}H-^{13}C HSQC 2D NMR spectrum for compound **6** in $CDCl_3$

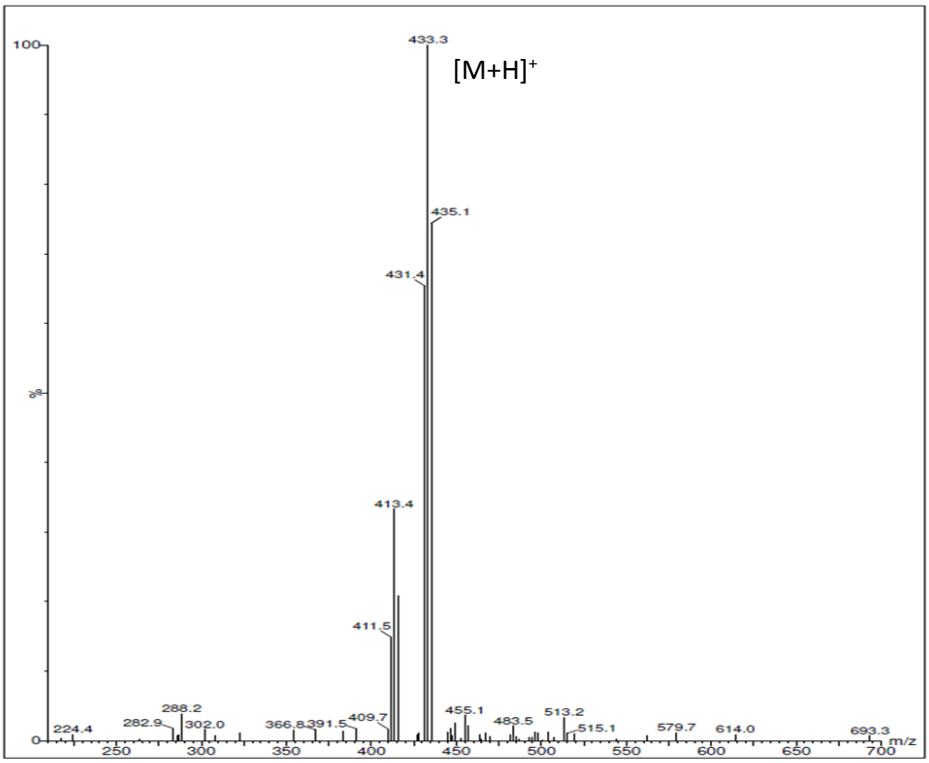


Fig S22. ESI-MS spectrum of compound **6**

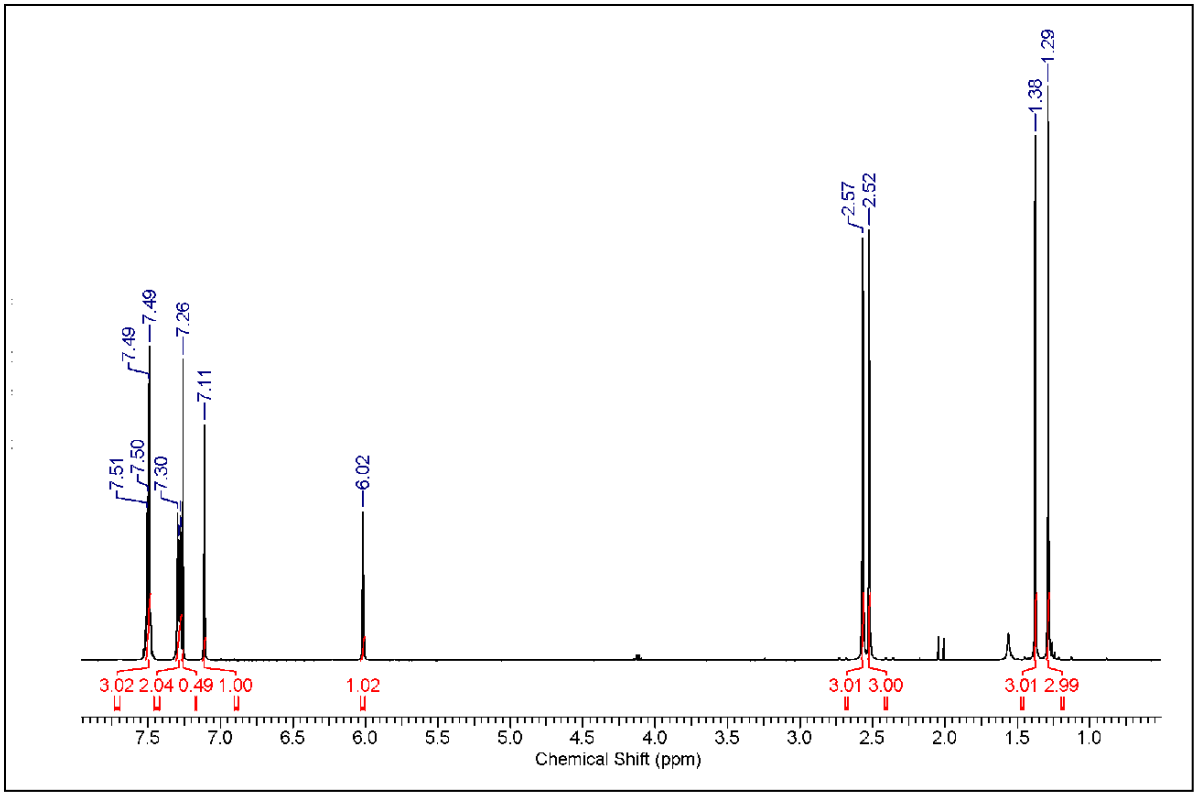


Fig S23. ^{1}H NMR spectrum of compound **9** in $CDCl_3$

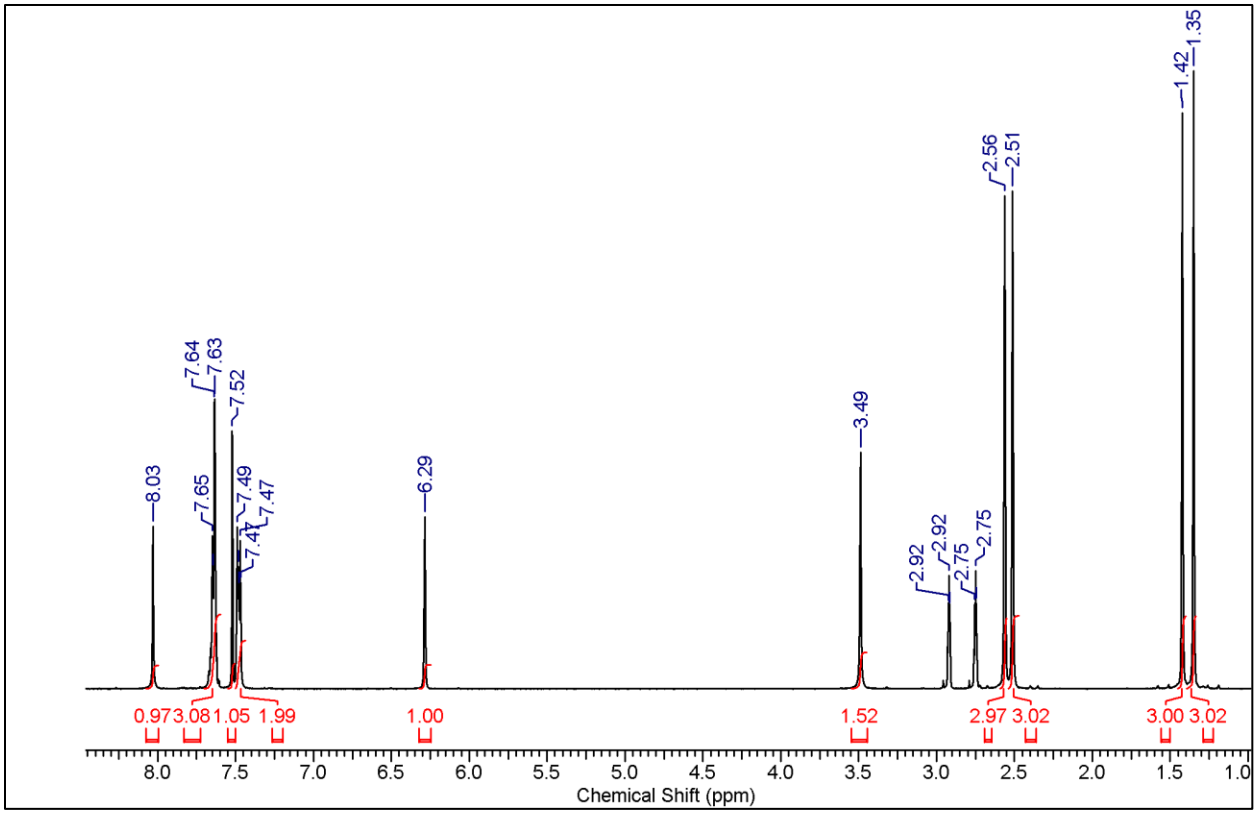


Fig S24. ^{1}H NMR spectrum of compound **9** in $DMFd_7$

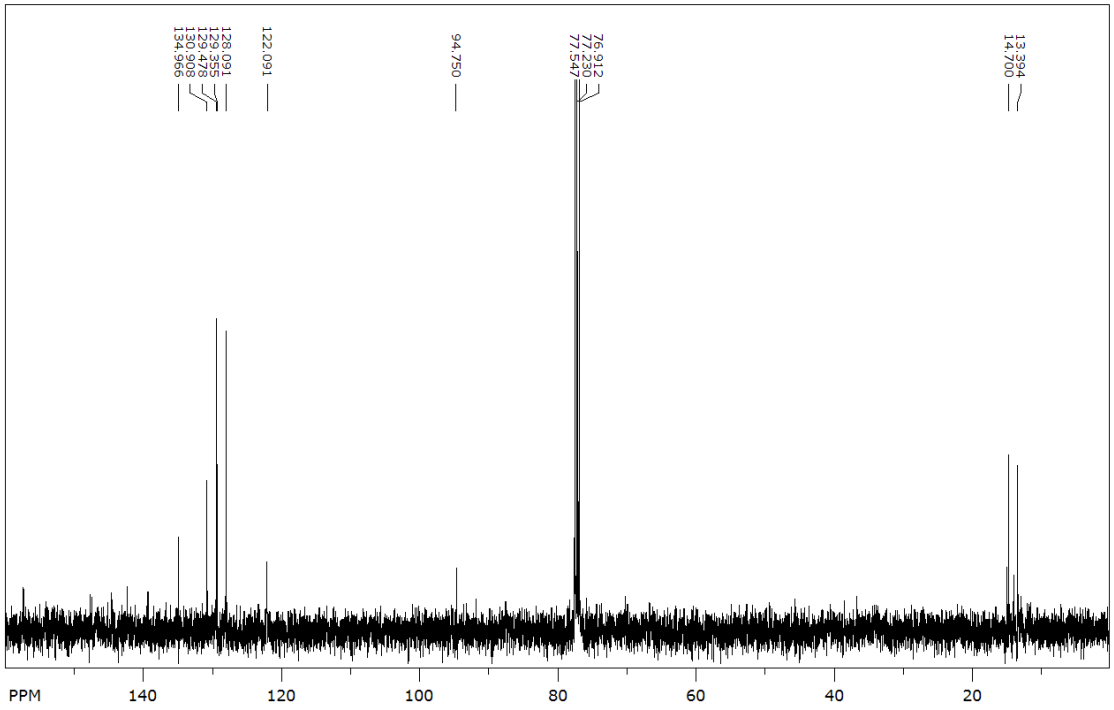


Fig S25. ^{13}C NMR spectrum of compound **9** in $CDCl_3$

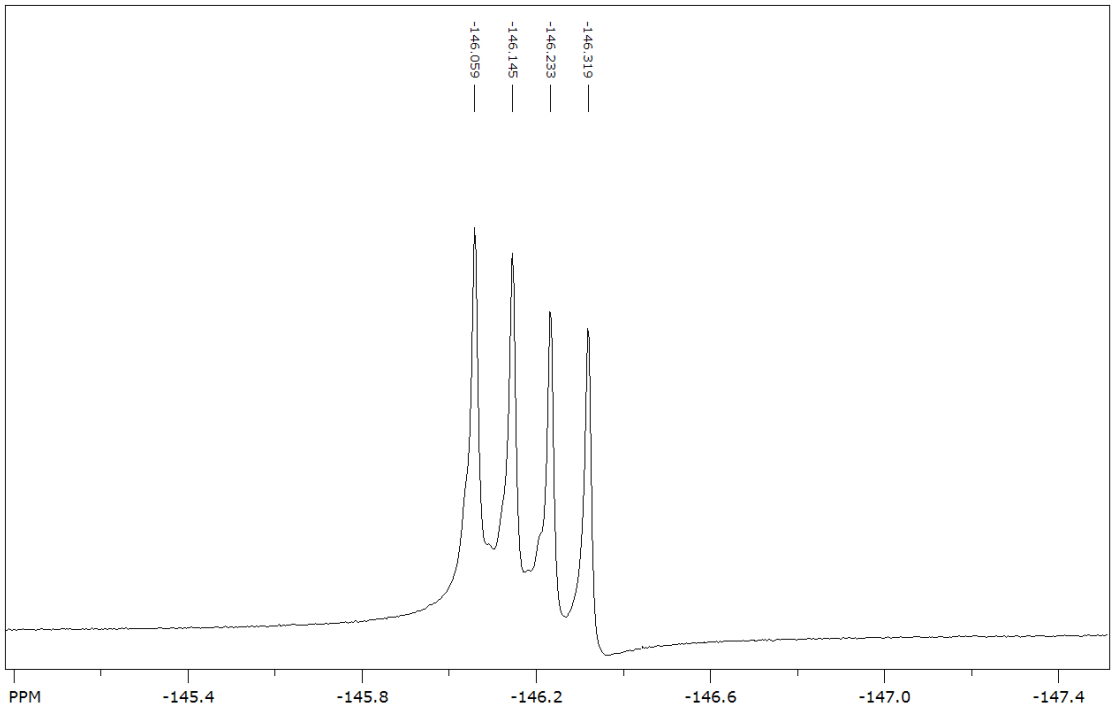


Fig S26. ^{19}F NMR spectrum of compound **9** in $CDCl_3$

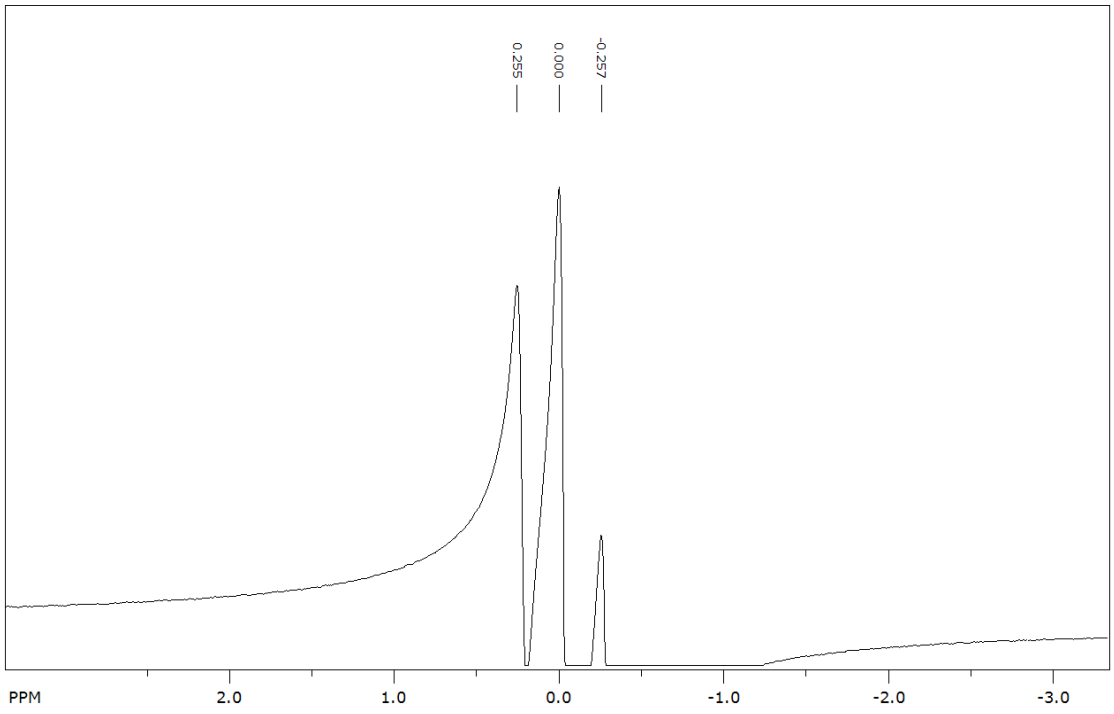


Fig S27. ^{11} B NMR spectrum of compound **9** in $CDCl_3$

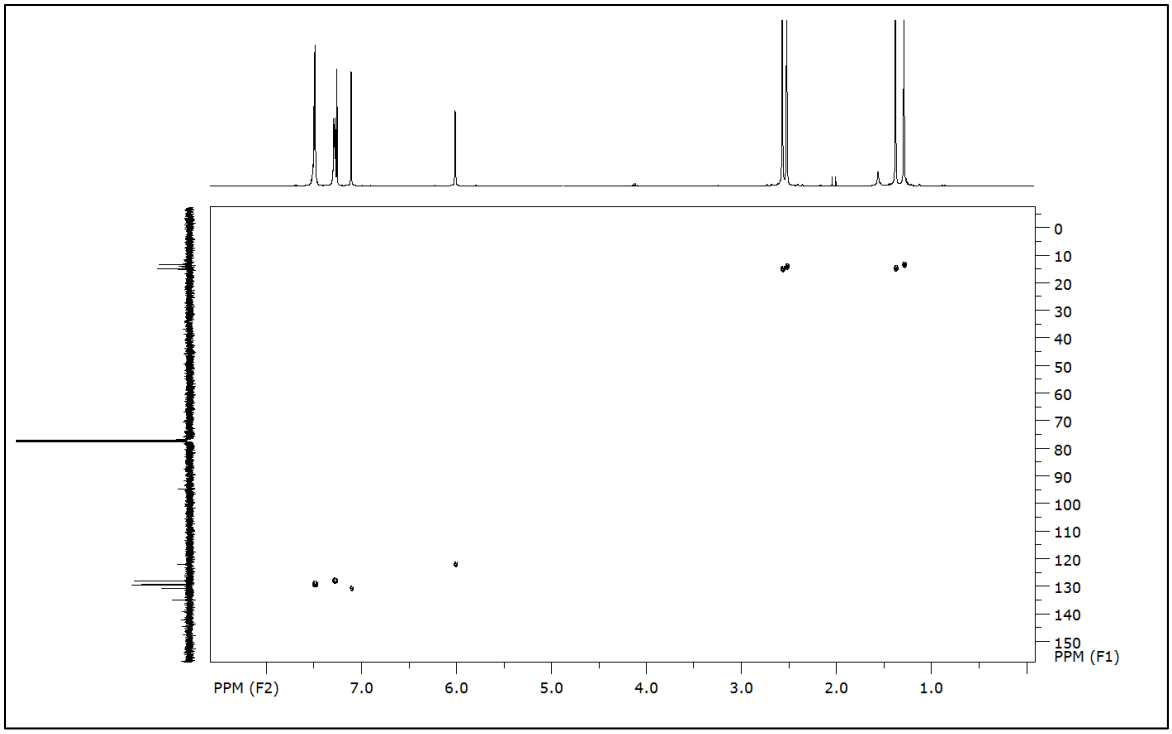
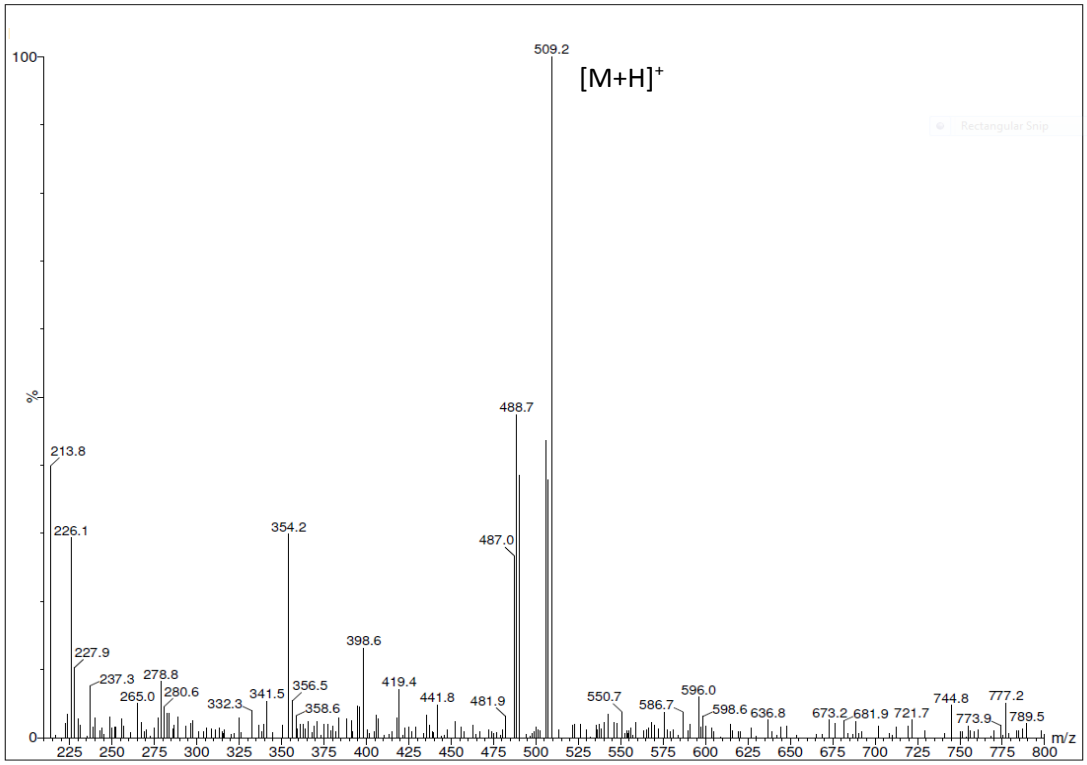


Fig S28. ^{1}H-^{13}C HSQC 2D NMR spectrum for compound **9** in $CDCl_3$



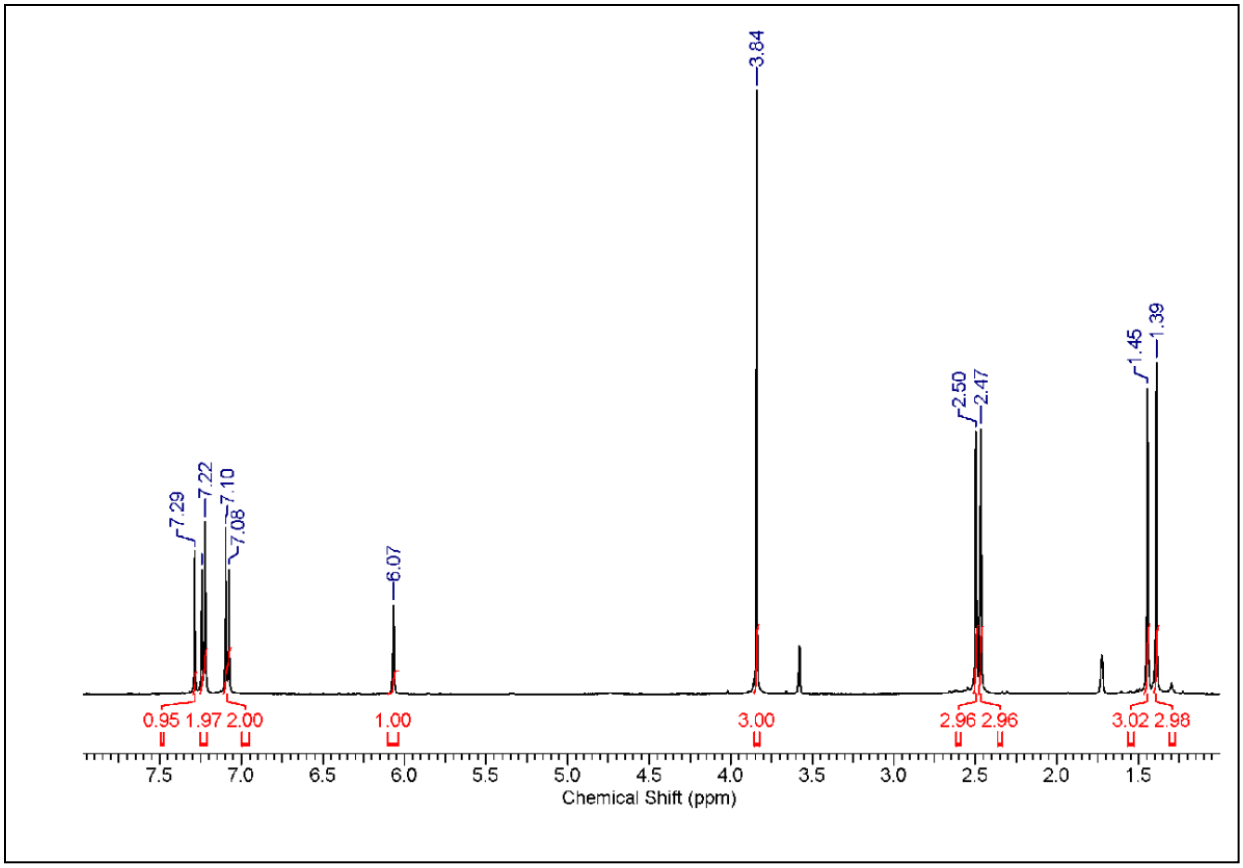


Fig S30. ^{1}H NMR spectrum of compound **10** in $CDCl_3$

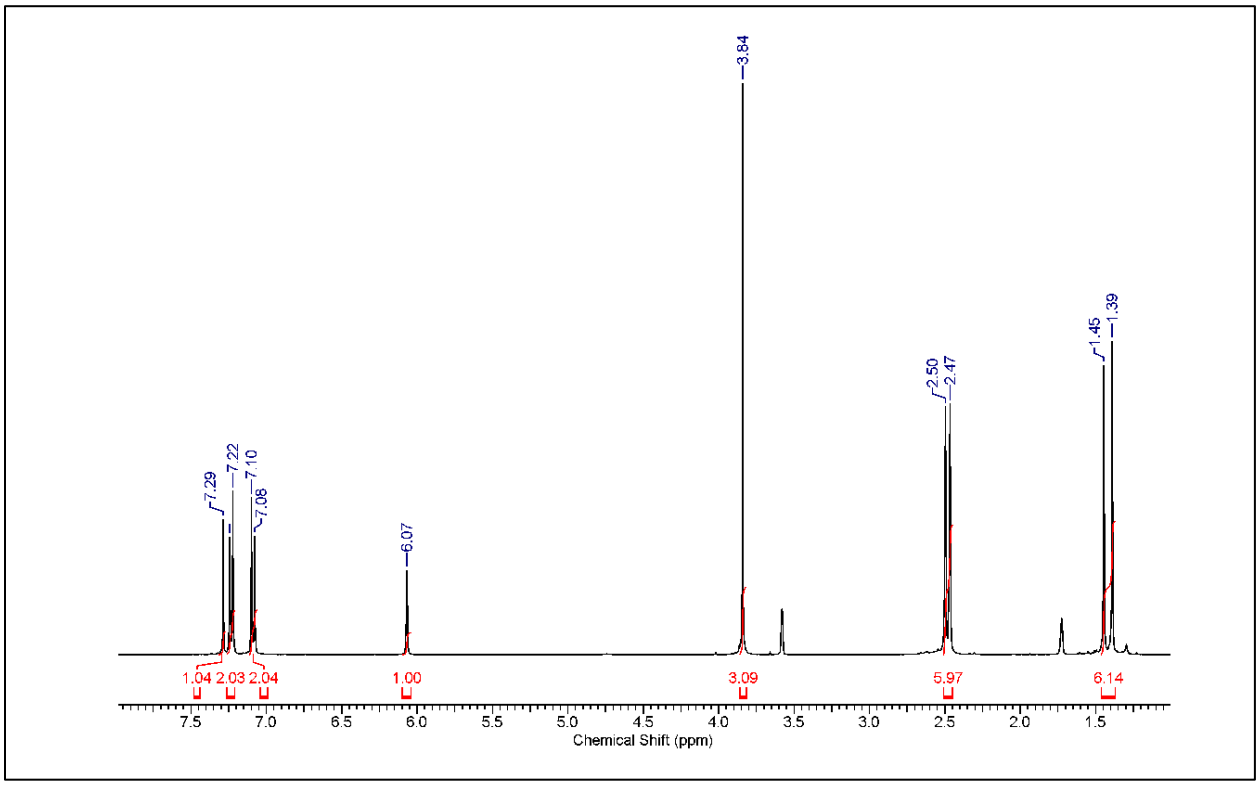


Fig S31. ^{1}H NMR spectrum of compound **10** in $THFd_4$

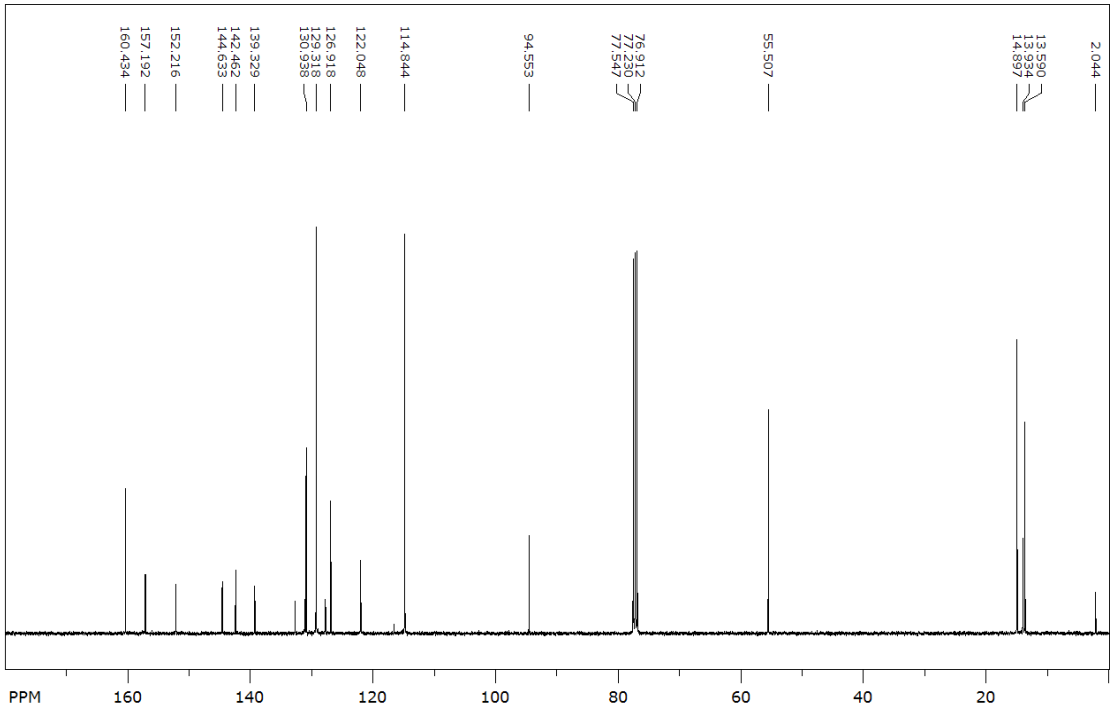


Fig S32. ^{13}C NMR spectrum of compound **10** in $CDCl_3$

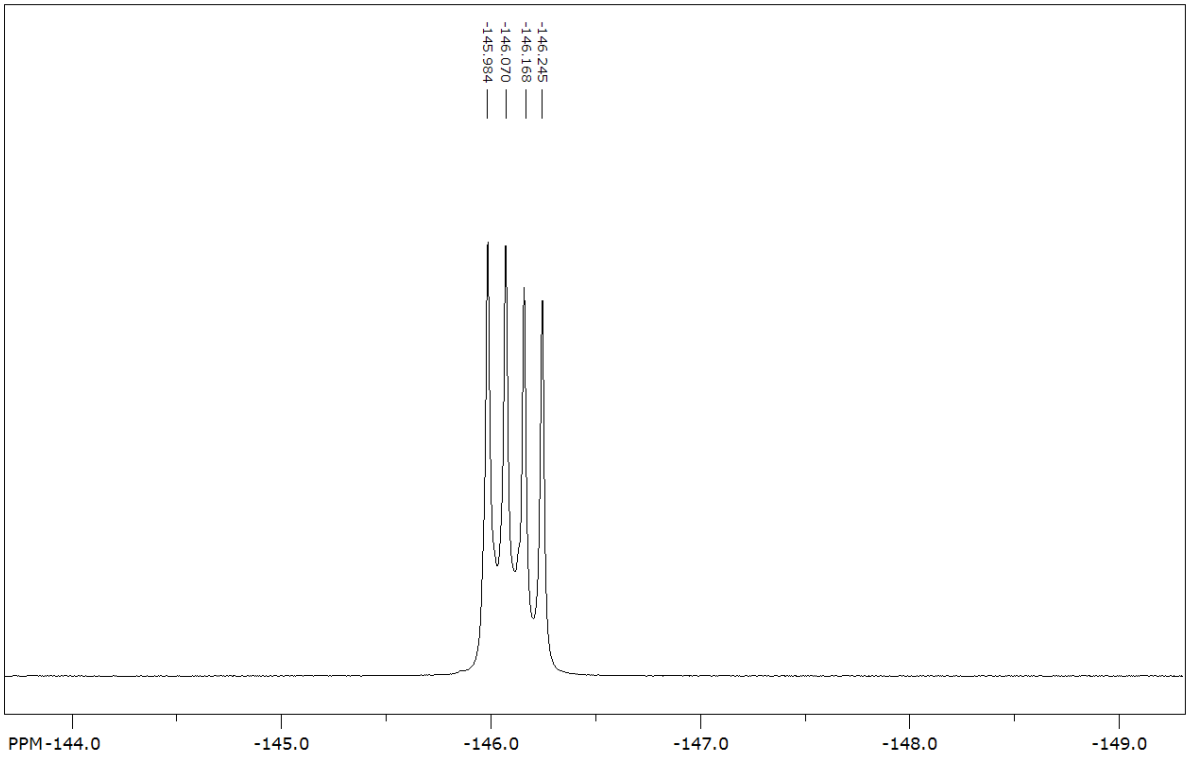


Fig S33. ^{19}F NMR spectrum of compound **10** in $CDCl_3$

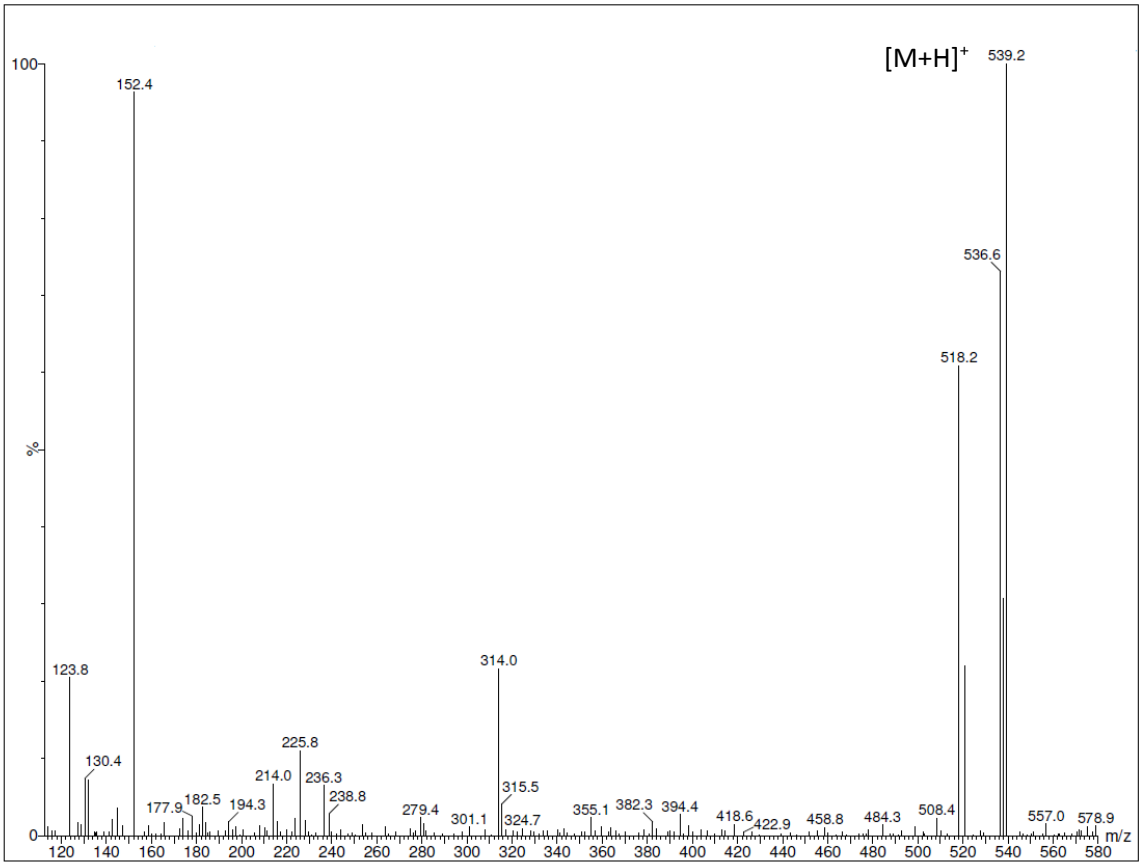


Fig S34. ESI-MS spectrum of compound **10**

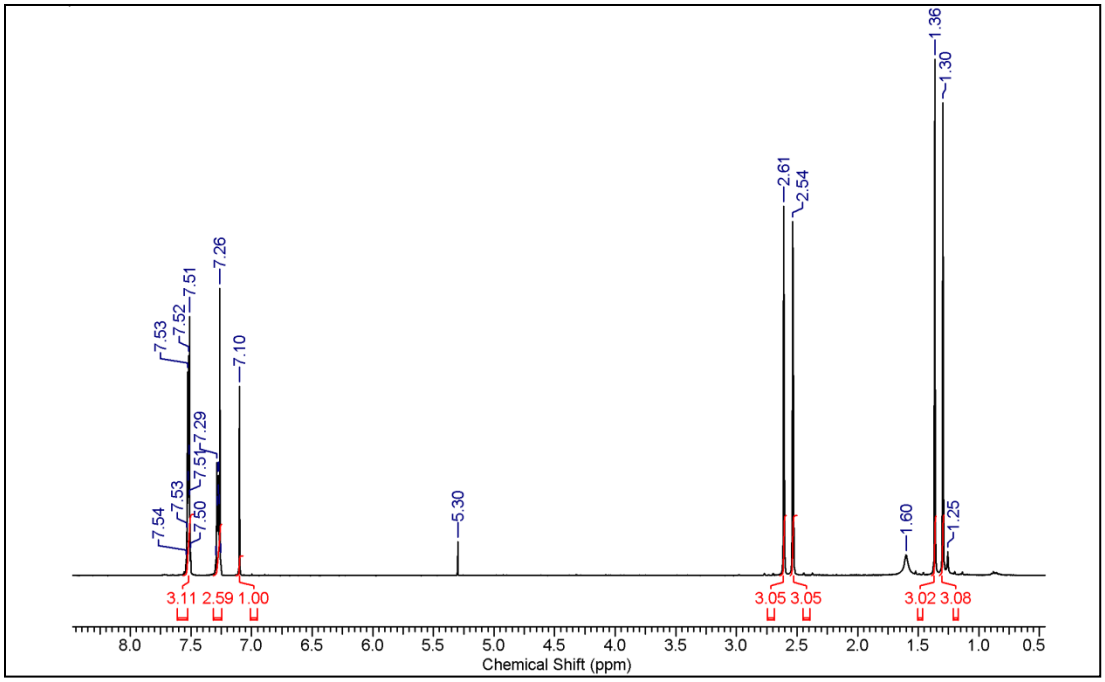


Fig S35. ^{1}H NMR spectrum of compound **12** in $CDCl_3$

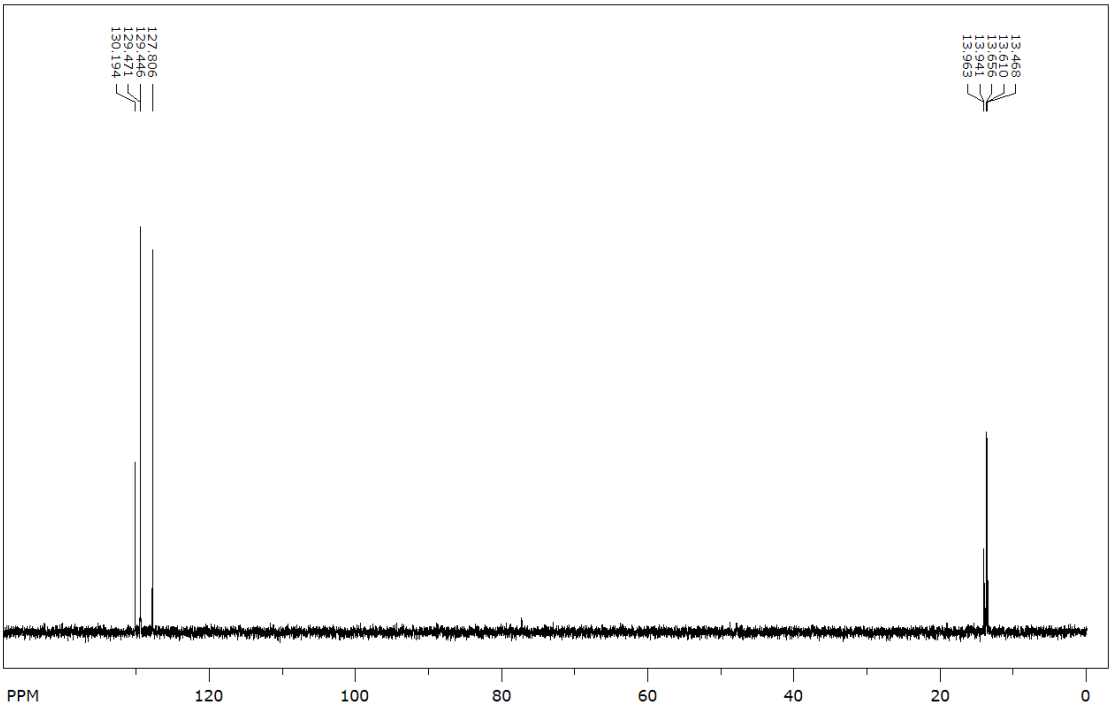


Fig S36. ^{13}CNMR spectrum of compound **12** in $CDCl_3$

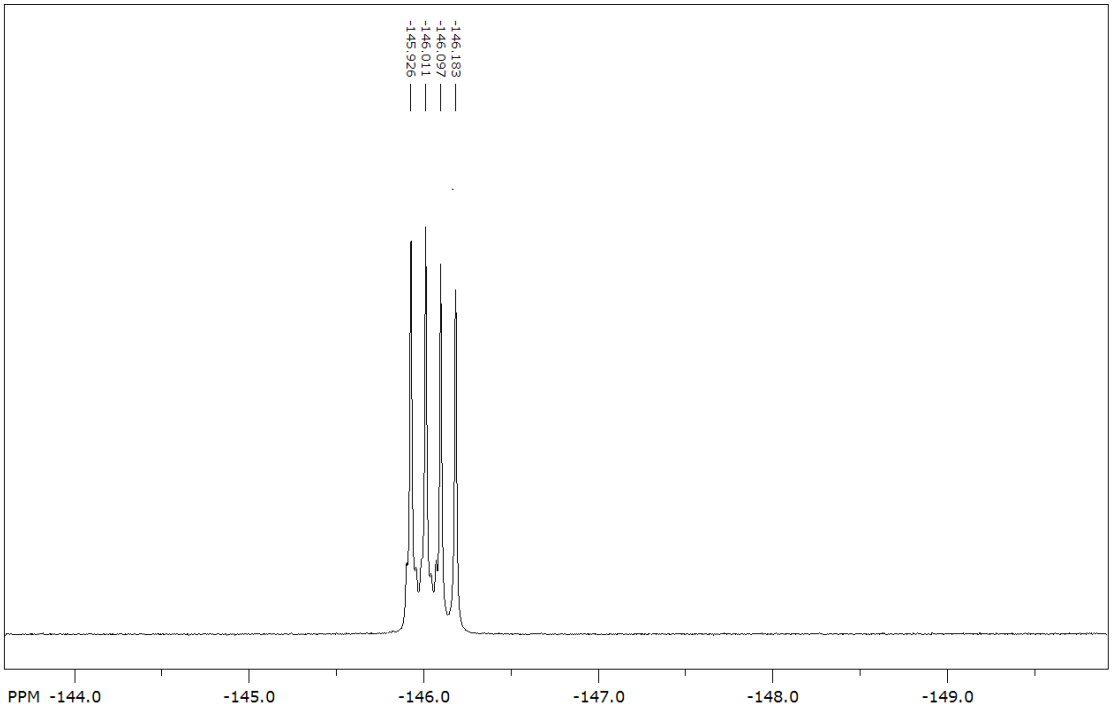


Fig S37. ^{19}F NMR spectrum of compound **12** in $CDCl_3$

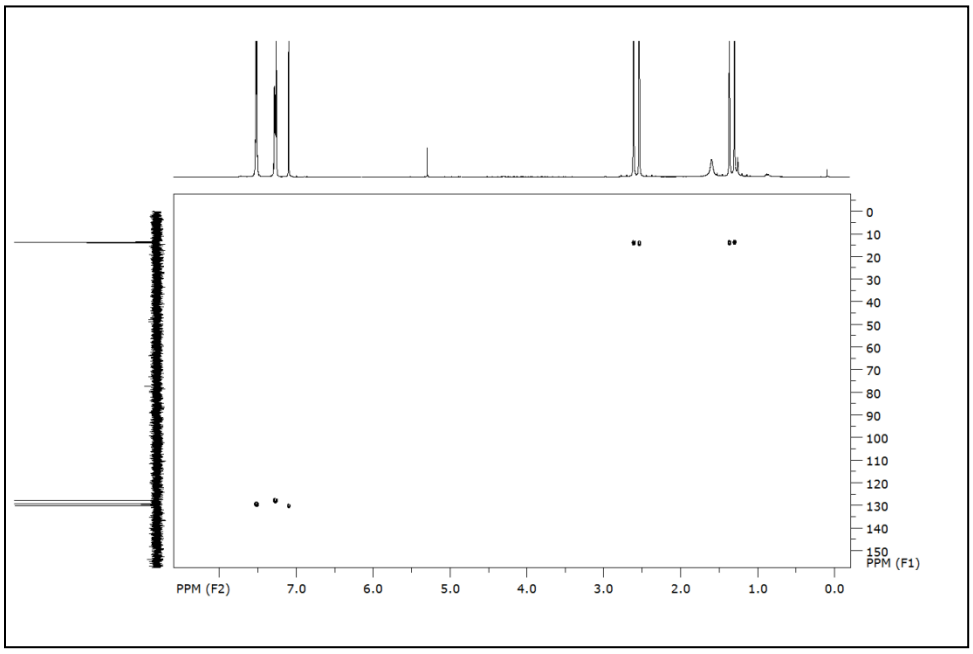


Fig S38. ^{1}H-^{13}C HSQC 2D NMR spectrum for compound **12** in $CDCl_3$

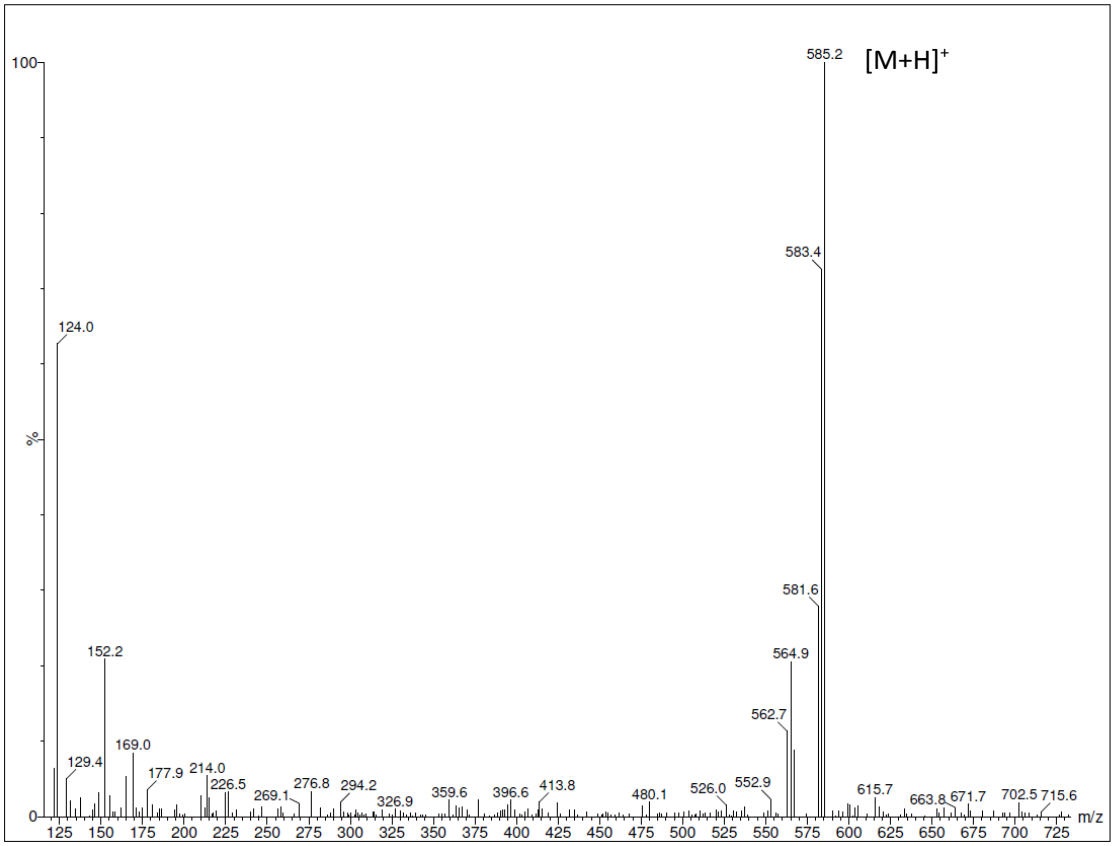


Fig S39. ESI-MS spectrum of compound **12**

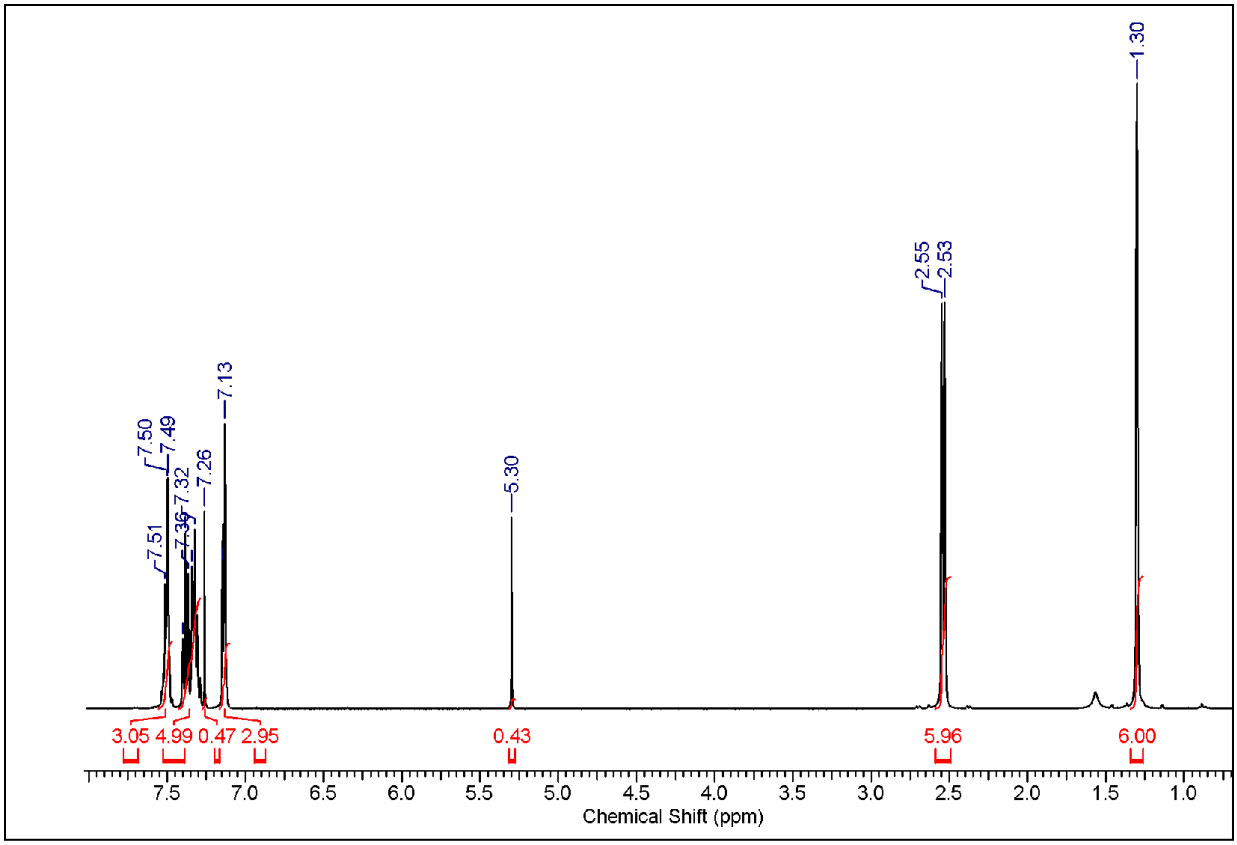


Fig S40. ^{1}H NMR spectrum of compound **14** in $CDCl_3$

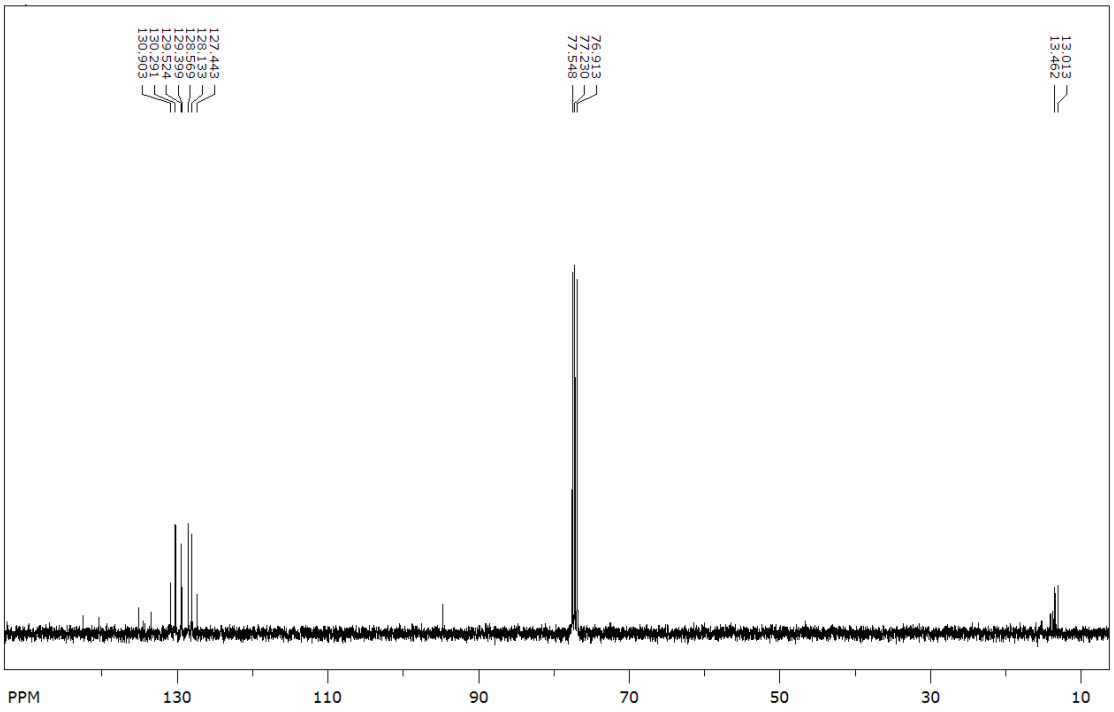


Fig S41. ^{13}C NMR spectrum of compound **14** in $CDCl_3$

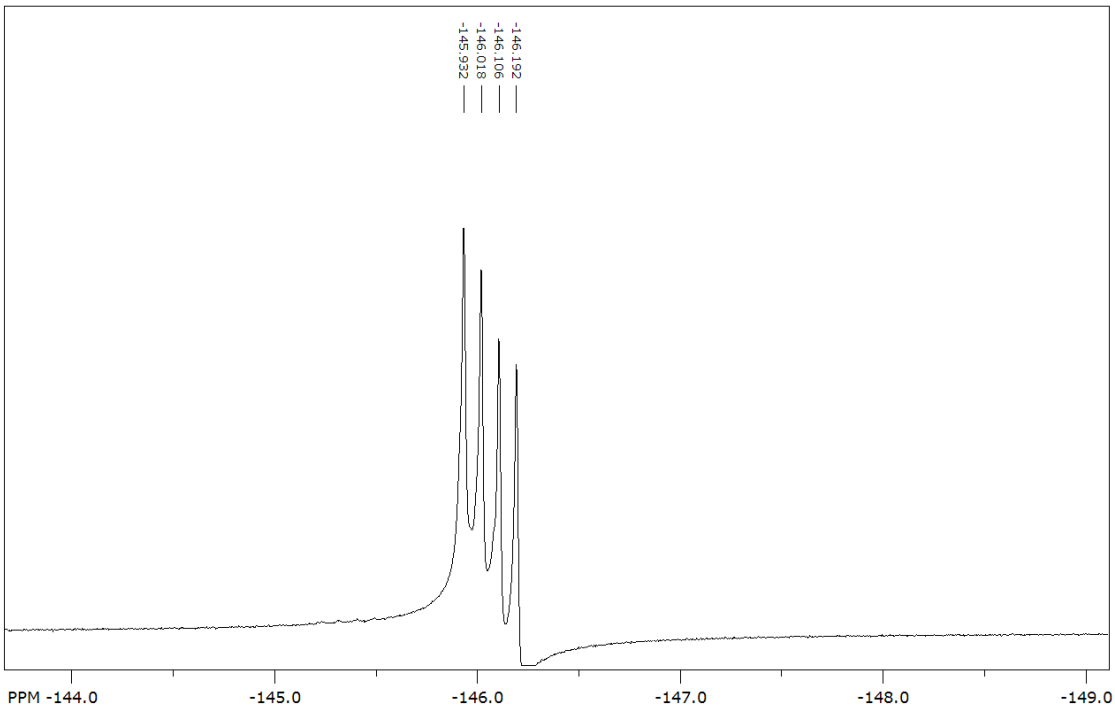


Fig S42. ^{19}F NMR spectrum of compound **14** in $CDCl_3$

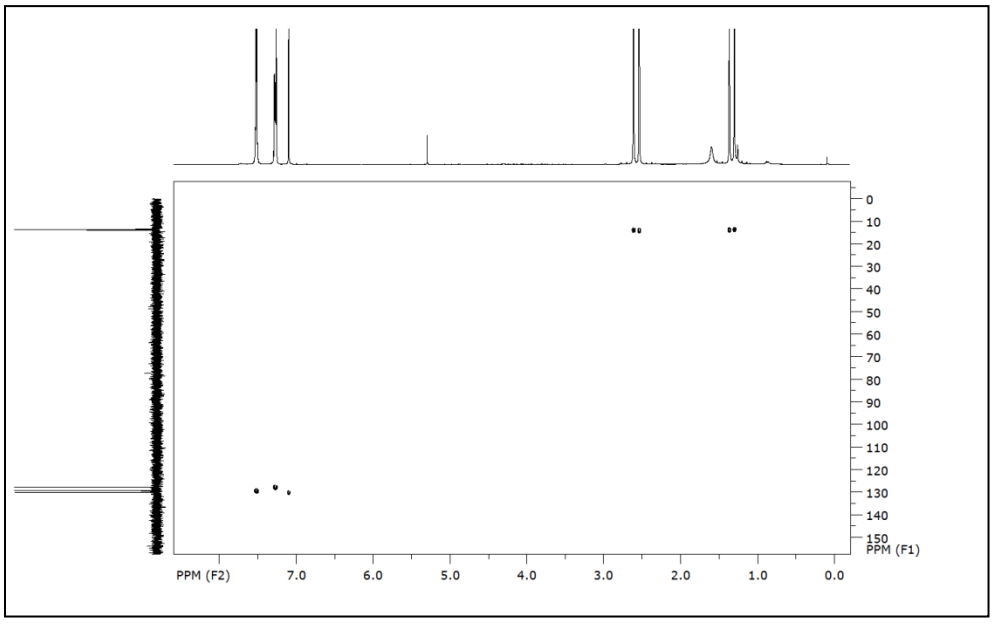
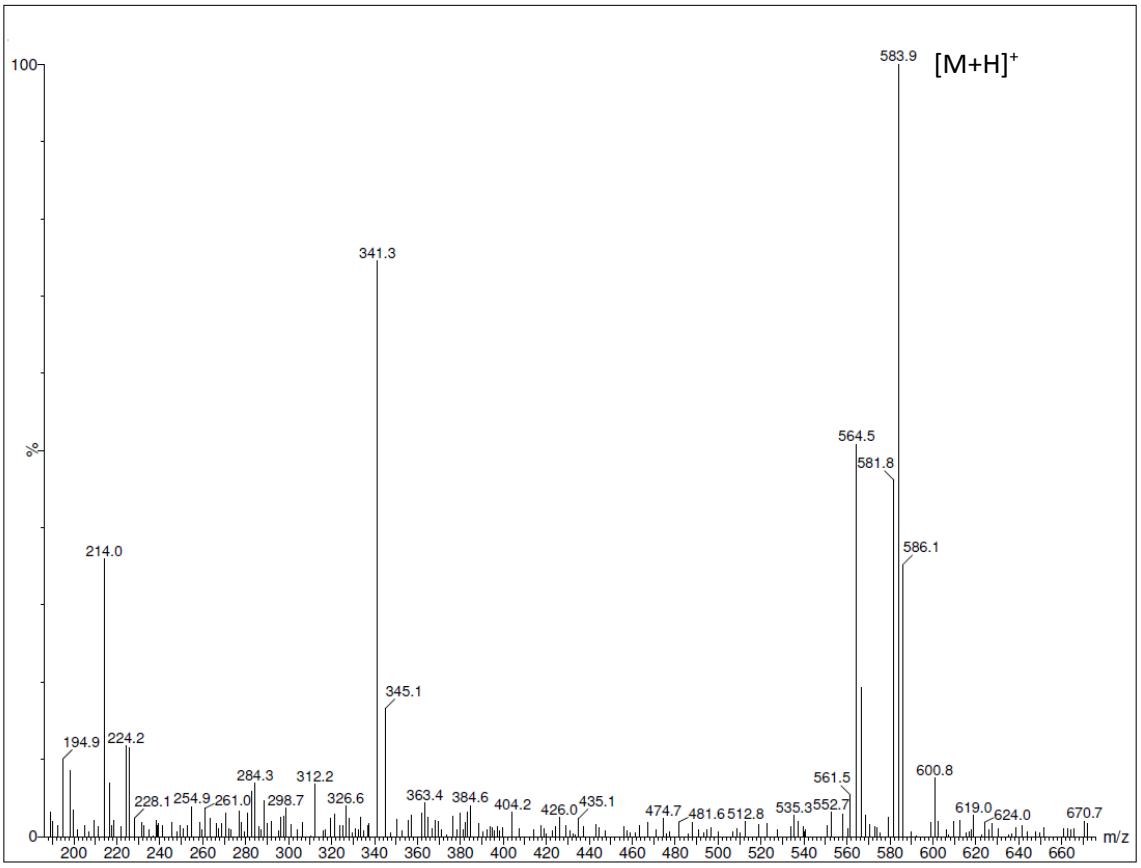


Fig S43. ^{1}H-^{13}C HSQC 2D NMR spectrum for compound **14** in $CDCl_3$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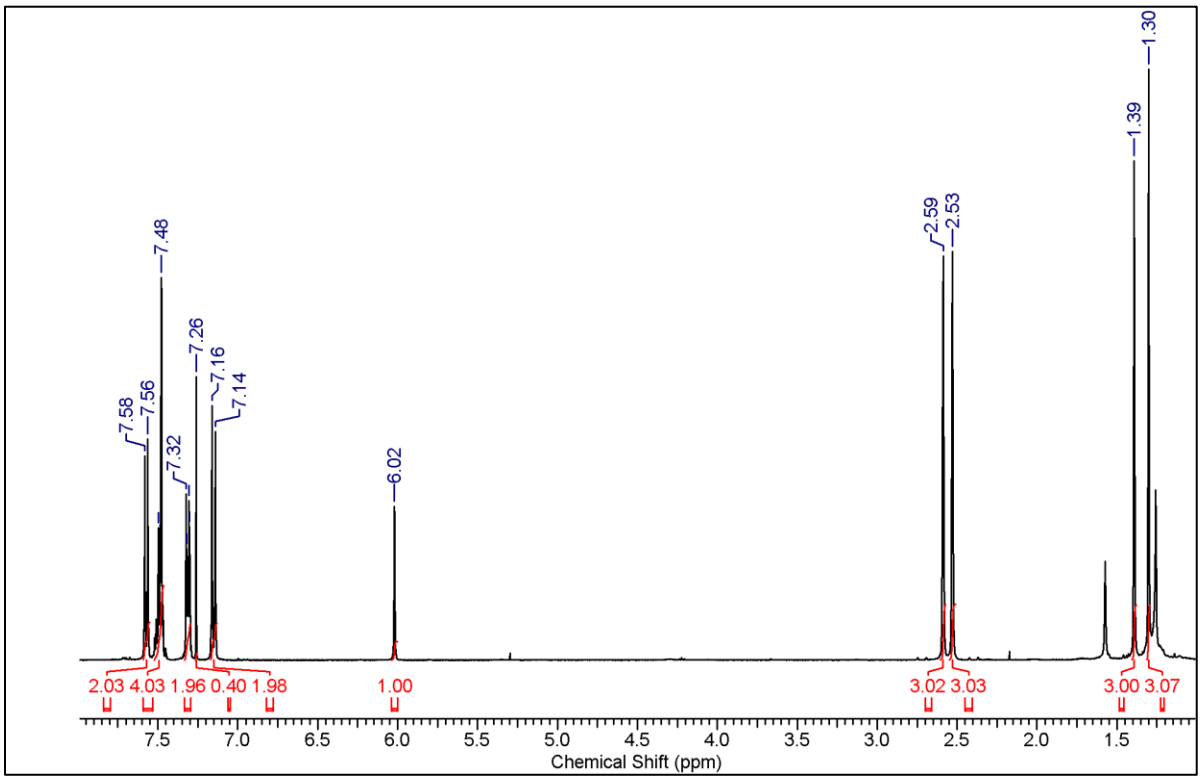
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1.00
3.02 3.03
3.00 3.07
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
Chemical Shift (ppm)

Fig S45. ^{1}H NMR spectrum of compound **16** in $CDCl_3$

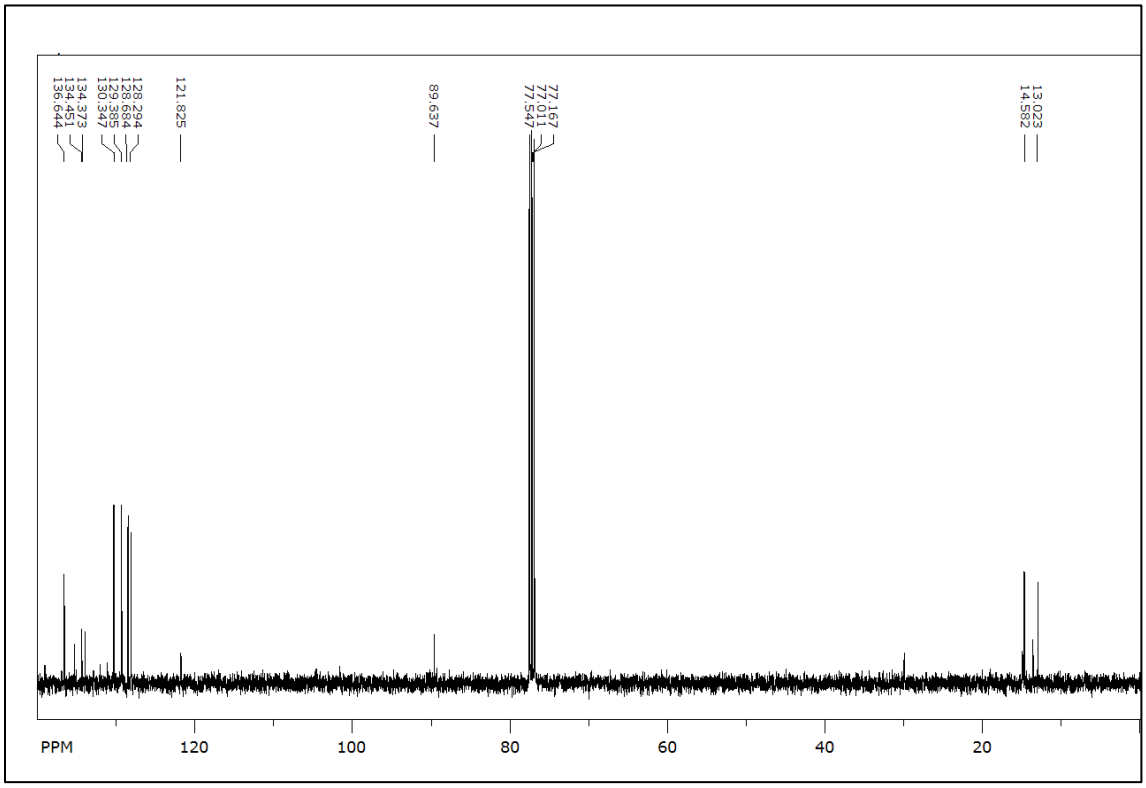

Fig S46. ^{13}C NMR spectrum of compound **16** in $CDCl_3$

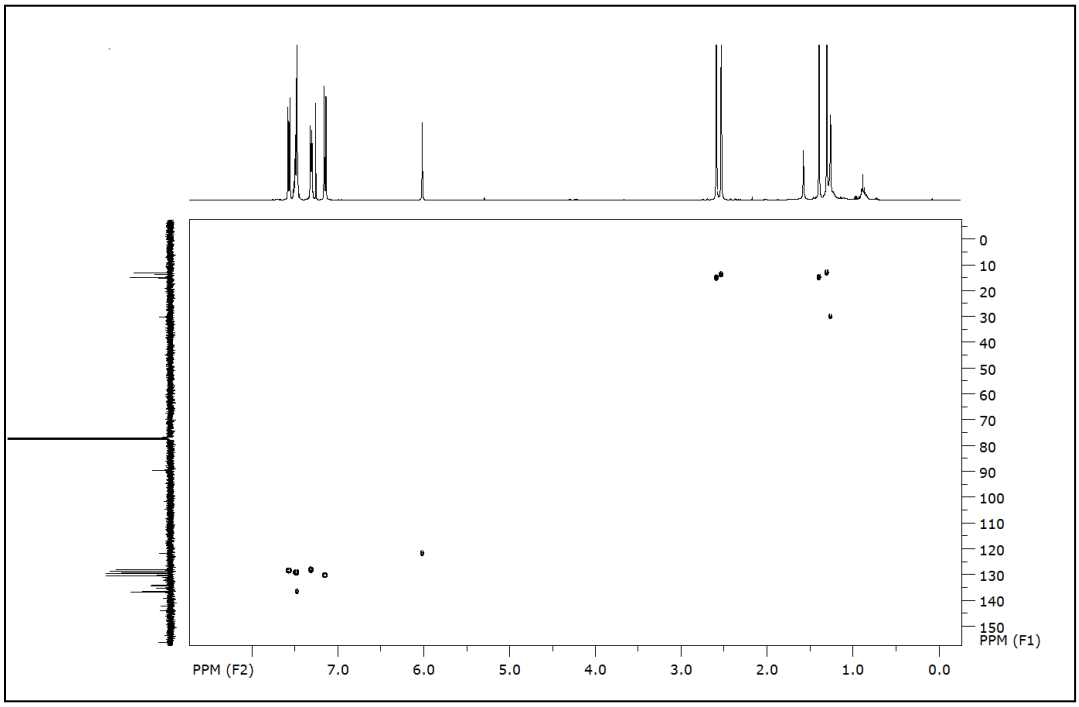

Fig S47. ^{1}H-^{13}C HSQC 2D NMR spectrum for compound **16** in $CDCl_3$

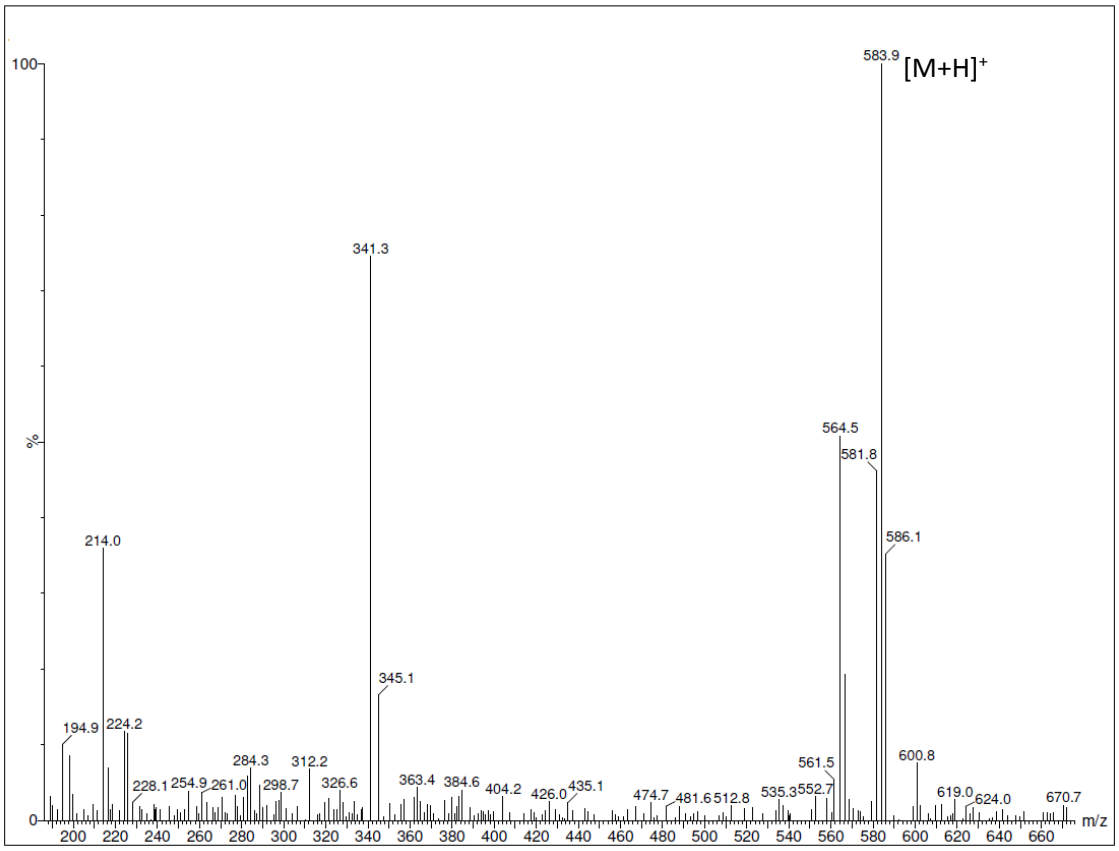

Fig S48. ESI-MS spectrum of compound **16**

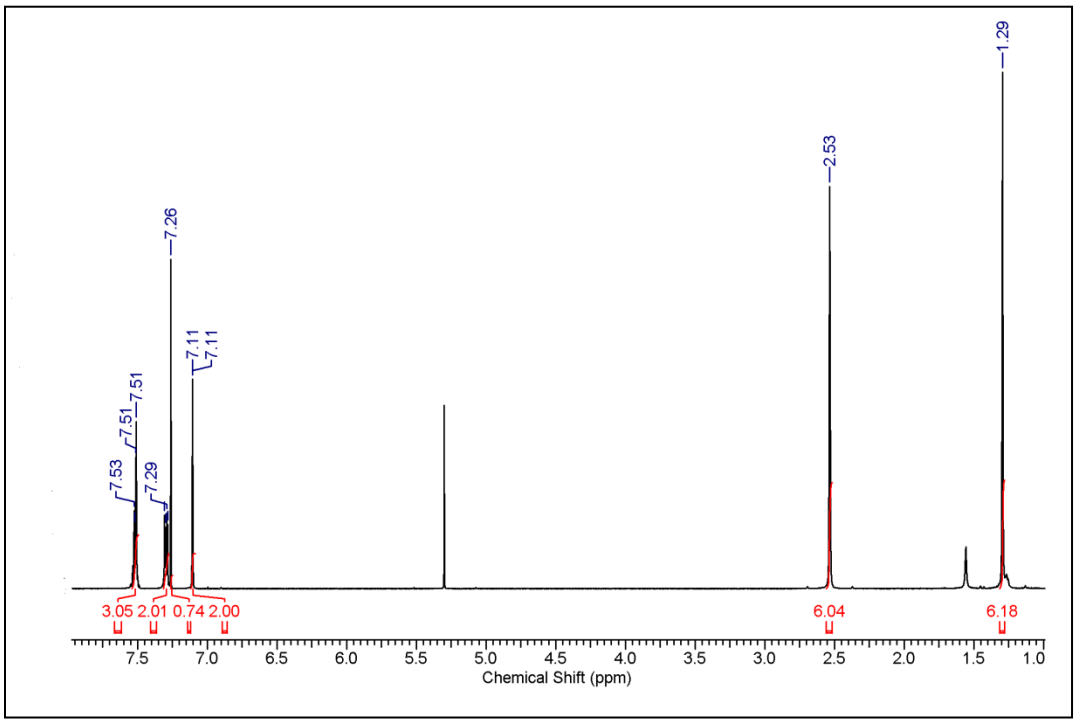

Fig S49. ^{1}H NMR spectrum of compound **19** in $CDCl_3$

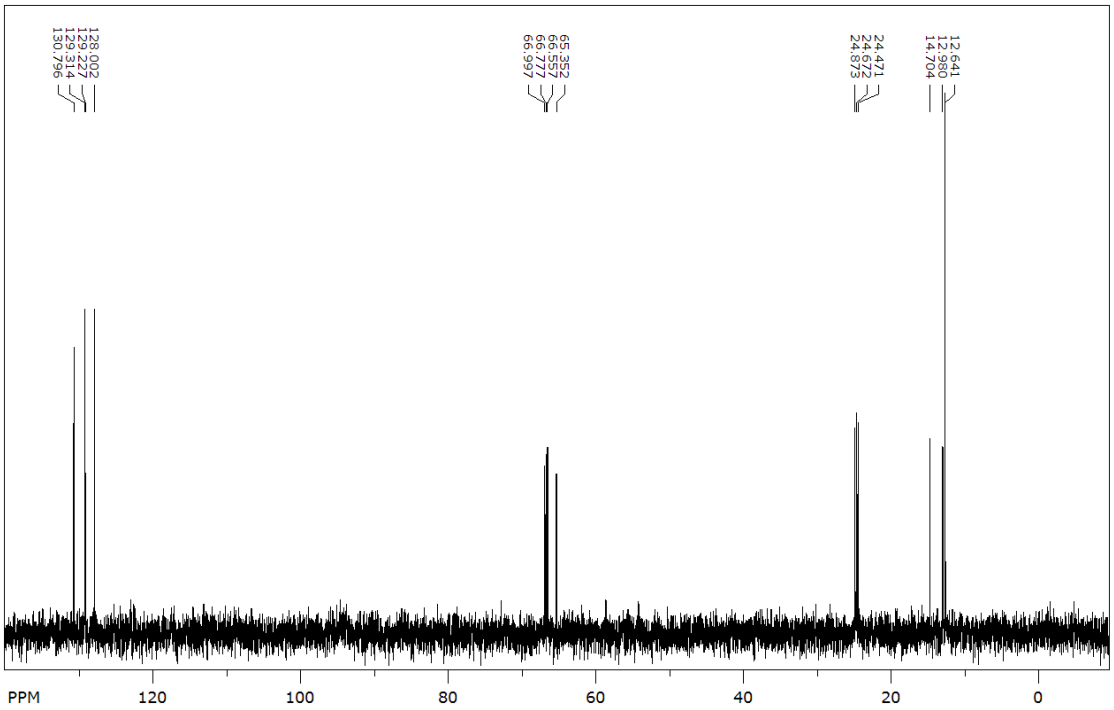

Fig S50. ^{13}C NMR spectrum of compound **19** in $CDCl_3$

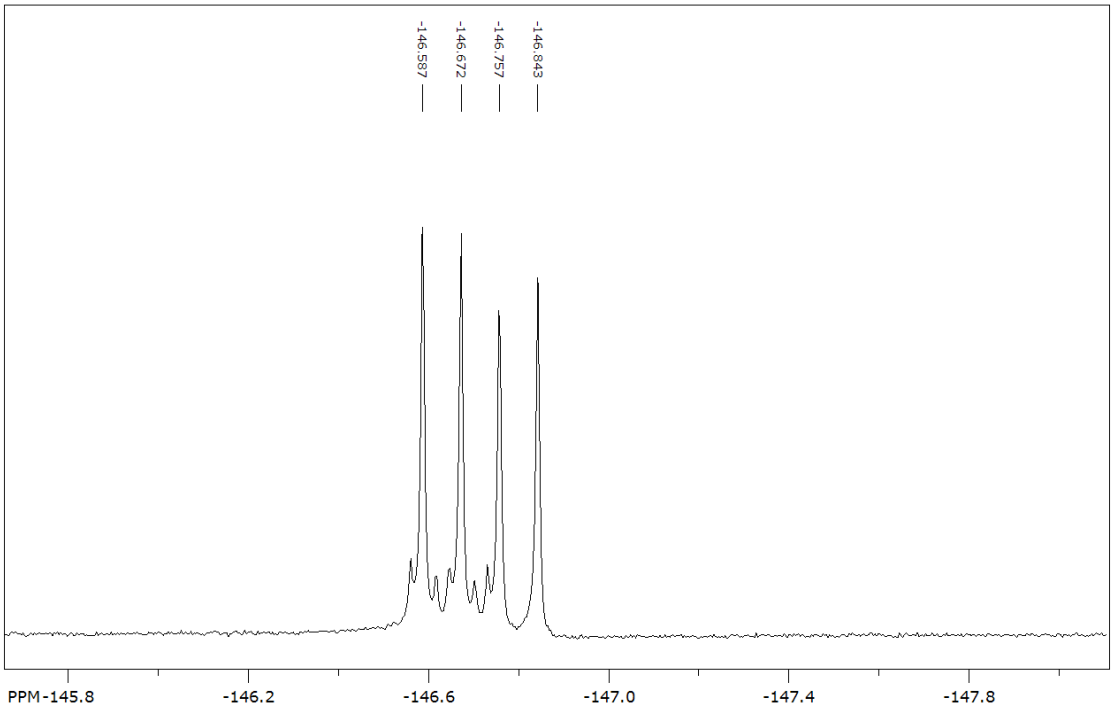

Fig S51. ^{19}F NMR spectrum of compound **19** in $CDCl_3$

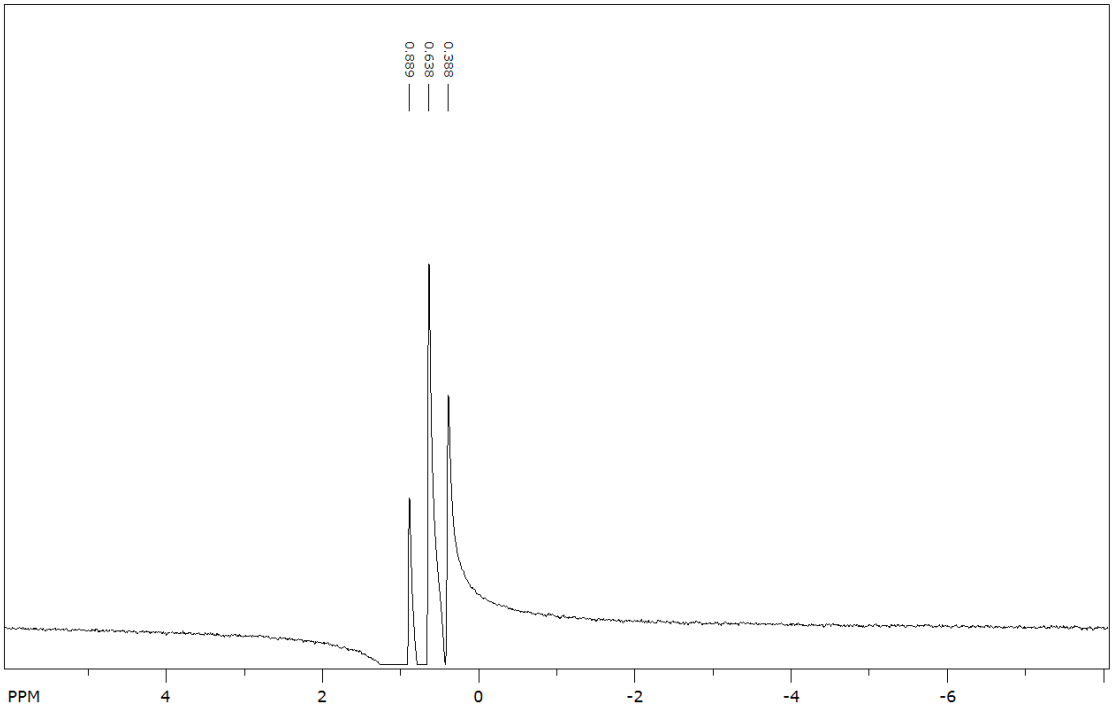

Fig S52. ^{11}B NMR spectrum of compound **19** in $CDCl_3$

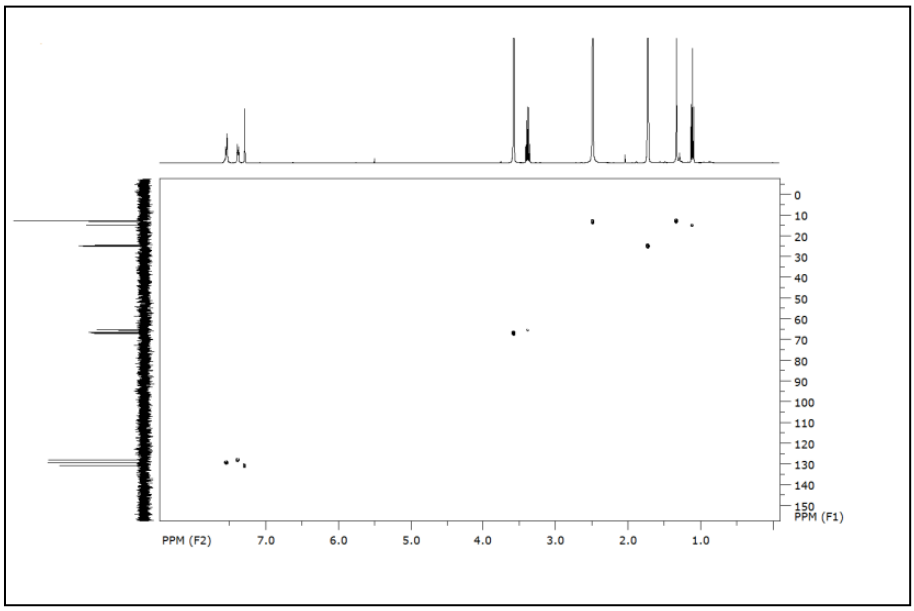

Fig S53. ^{1}H-^{13}C HSQC 2D NMR spectrum for compound **19** in THF

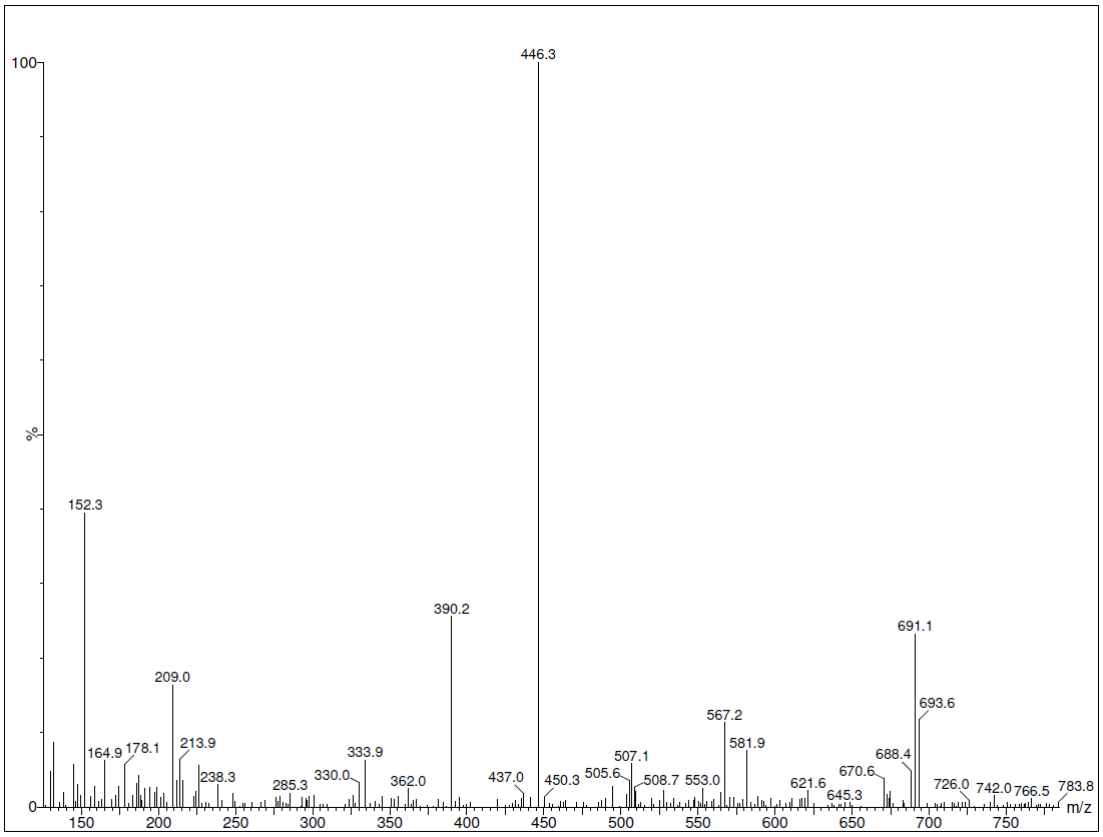

Fig S54. ESI-MS spectrum of compound **19**

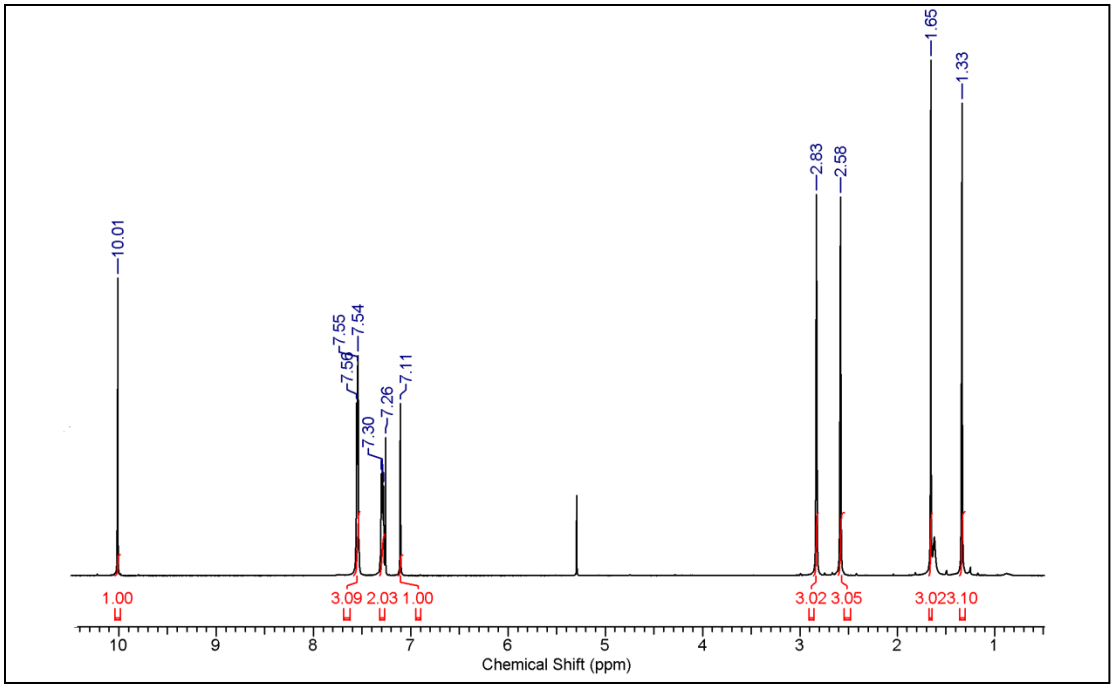

Fig S55. ^{1}H NMR spectrum of compound **20** in $CDCl_3$

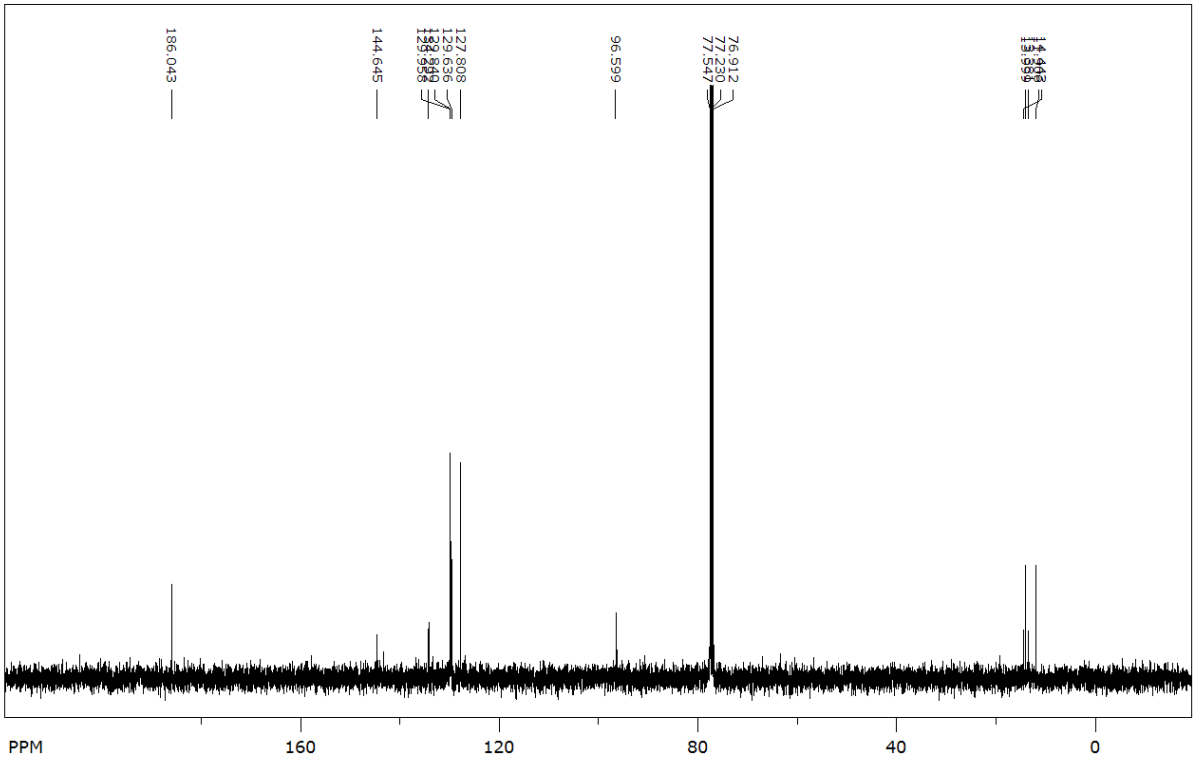

Fig S56. ^{13}C NMR spectrum of compound **20** in $CDCl_3$

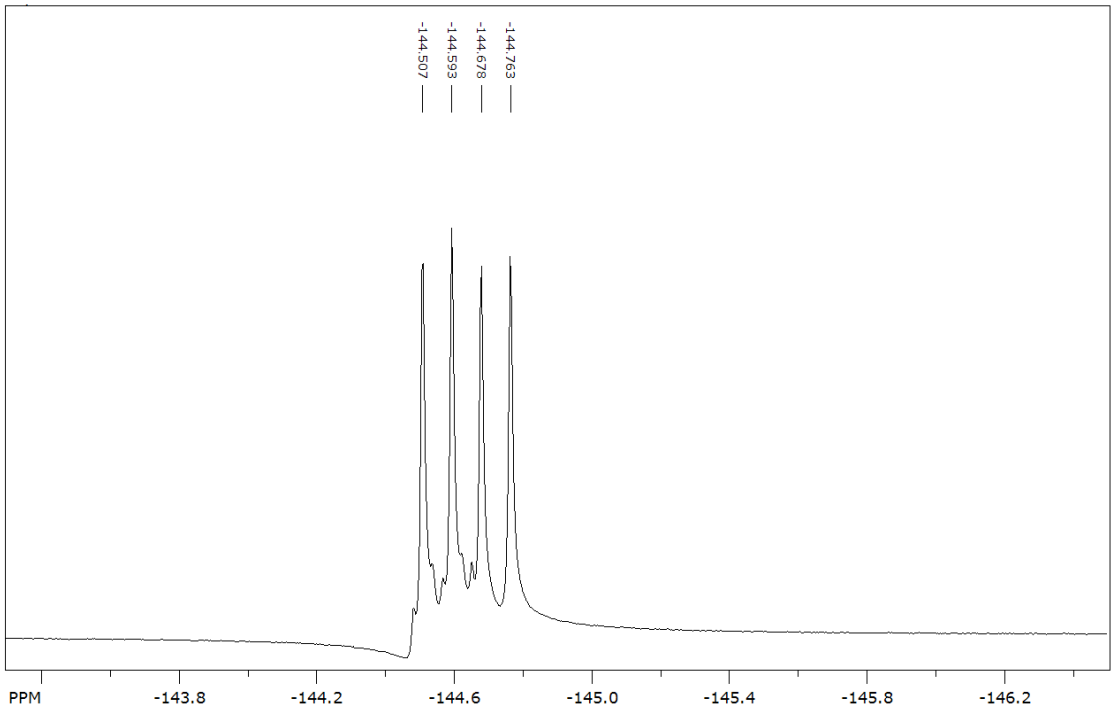

Fig S57. ^{11}B NMR spectrum of compound **20** in $CDCl_3$

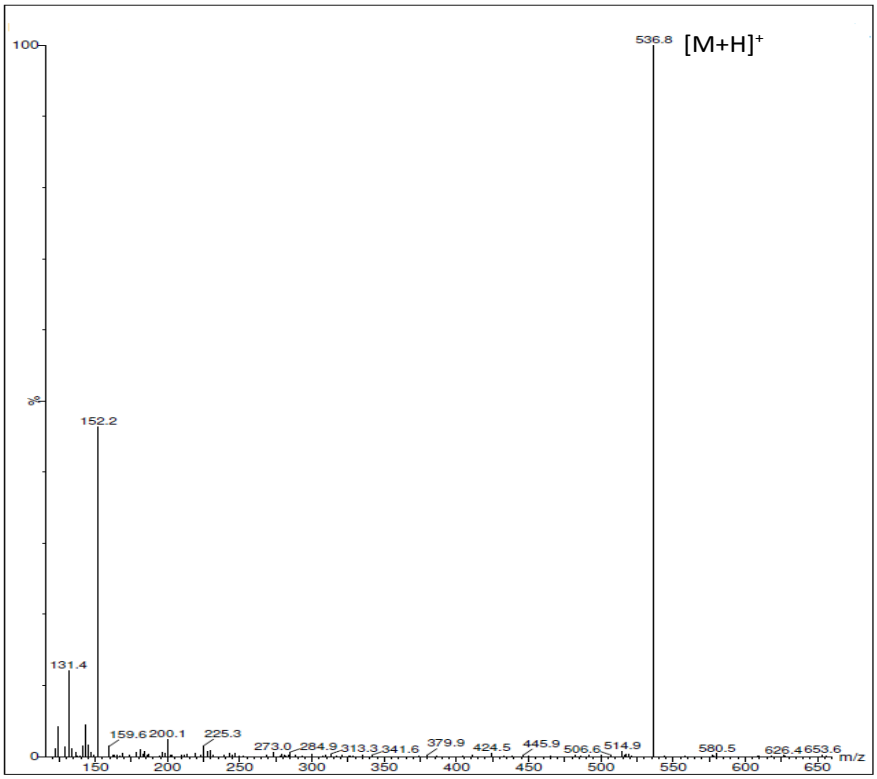

Fig S58. ESI-MS spectrum of compound **20**

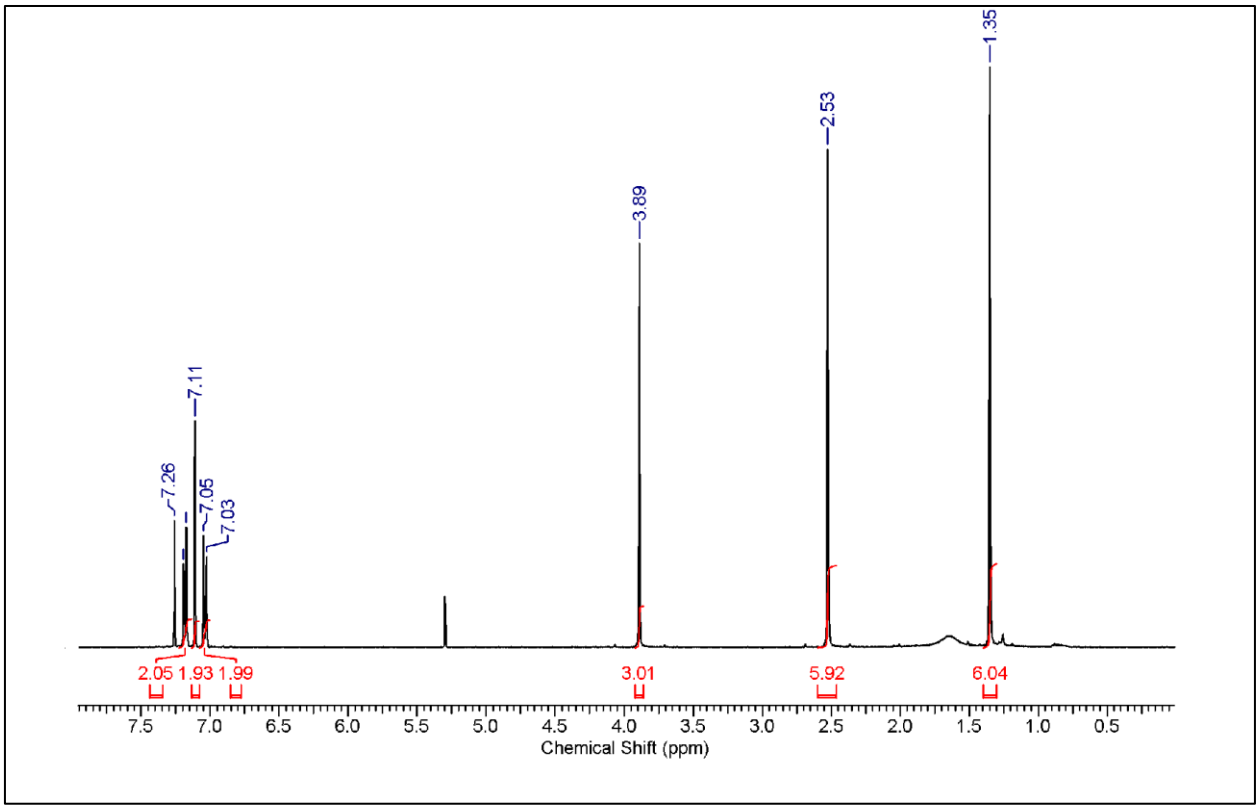

Fig S59. ^{1}H NMR spectrum of compound **21** in $CDCl_3$

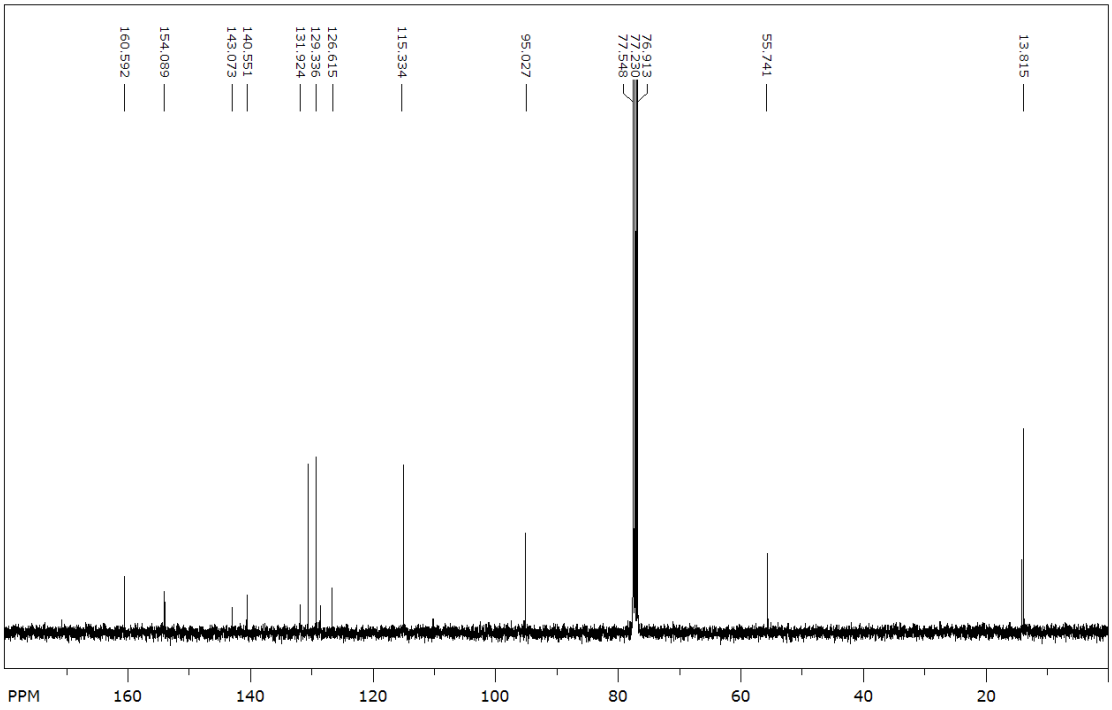

Fig S60. ^{13}C NMR spectrum of compound **21** in $CDCl_3$

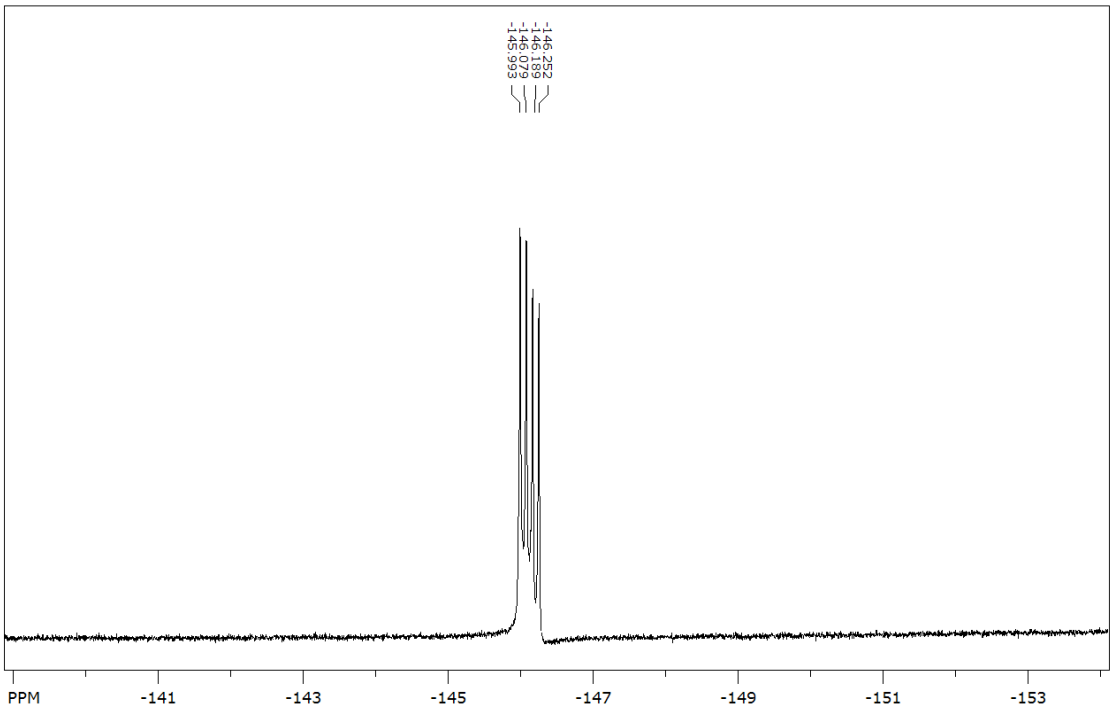

Fig S61. ^{19} F NMR spectrum of compound **21** in $CDCl_3$

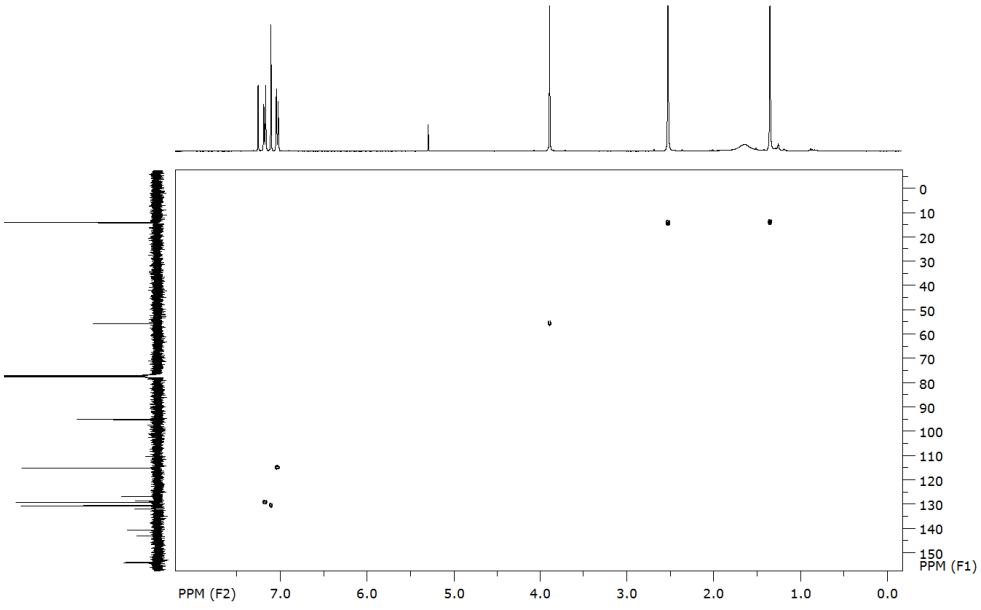

Fig S62. ^{1}H-^{13}C HSQC 2D NMR spectrum for compound **21** in $CDCl_3$

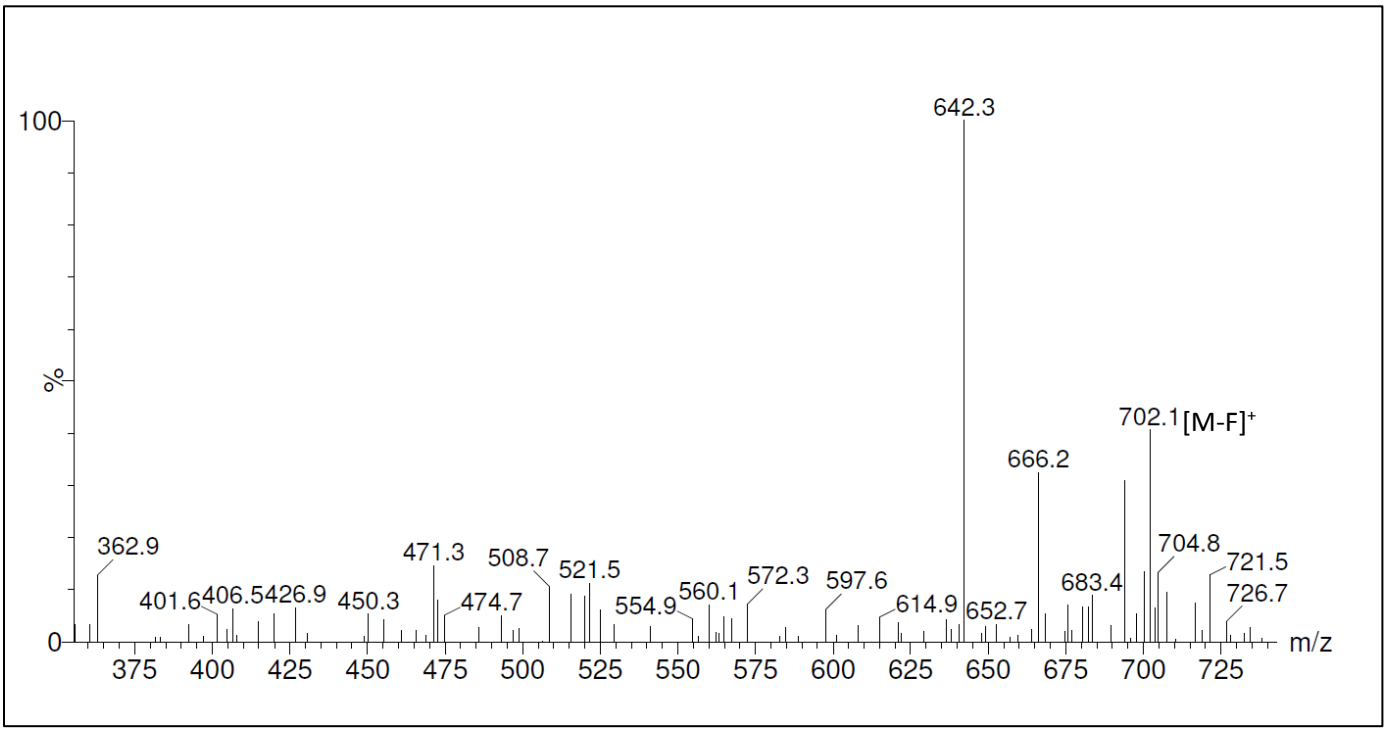

Fig S63. ESI-MS spectrum of compound **21**

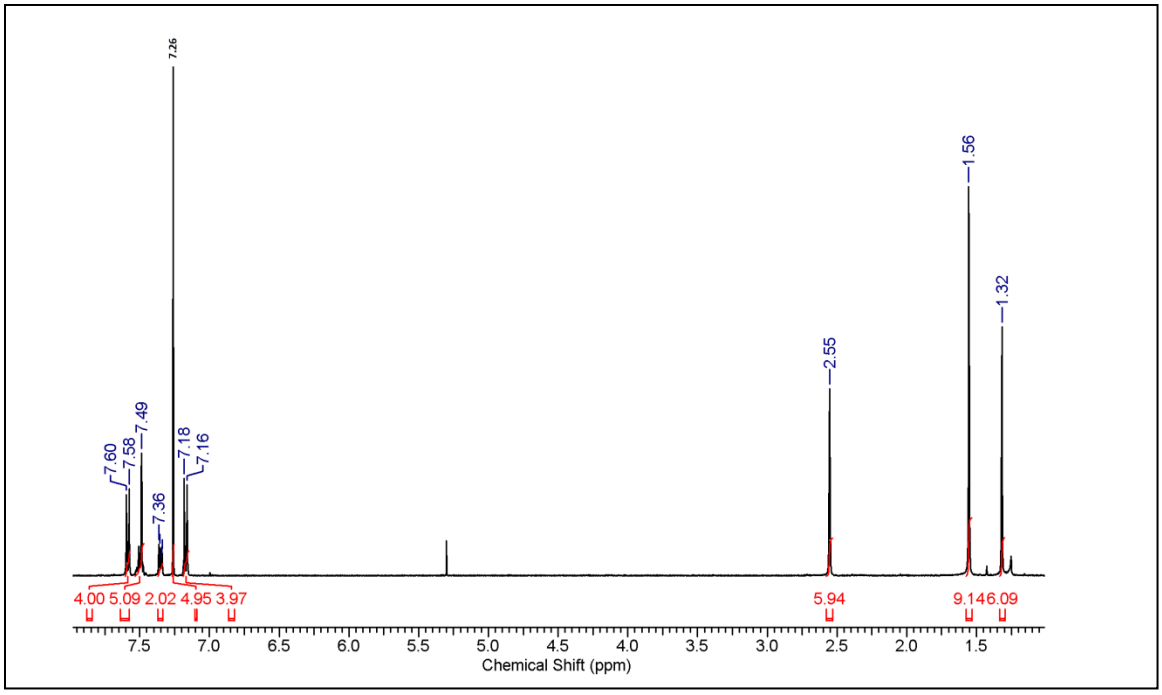

Fig S64. ^{1}H NMR spectrum of compound **23** in $CDCl_3$

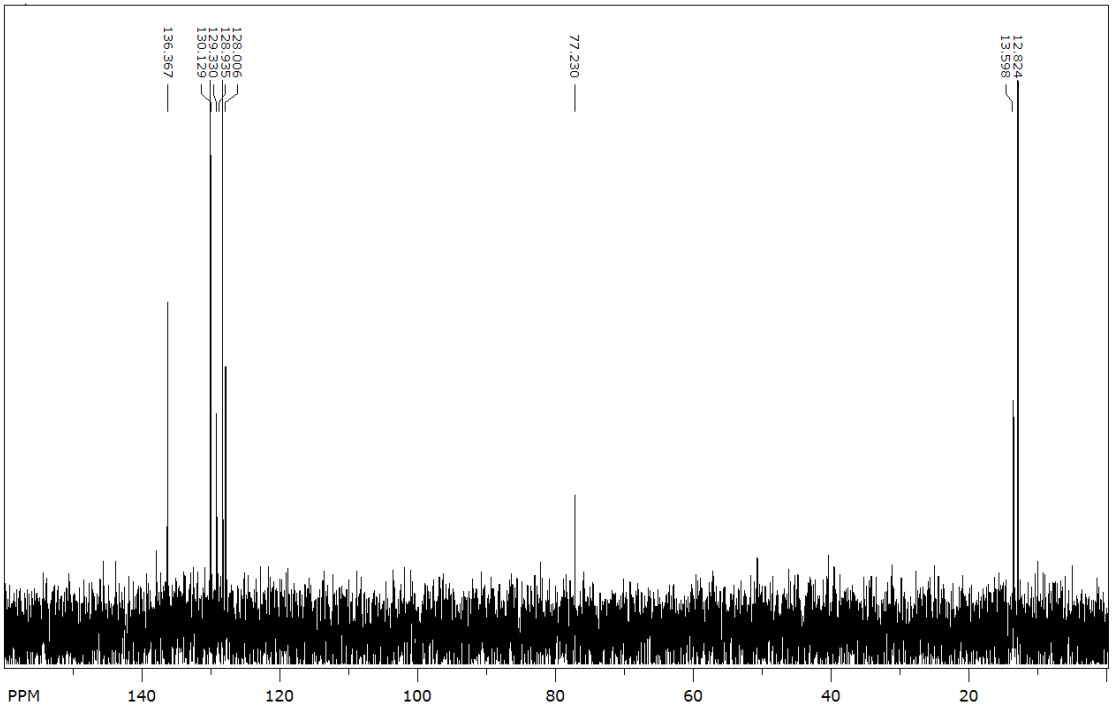

Fig S65. ^{13}C NMR spectrum of compound **23** in $CDCl_3$

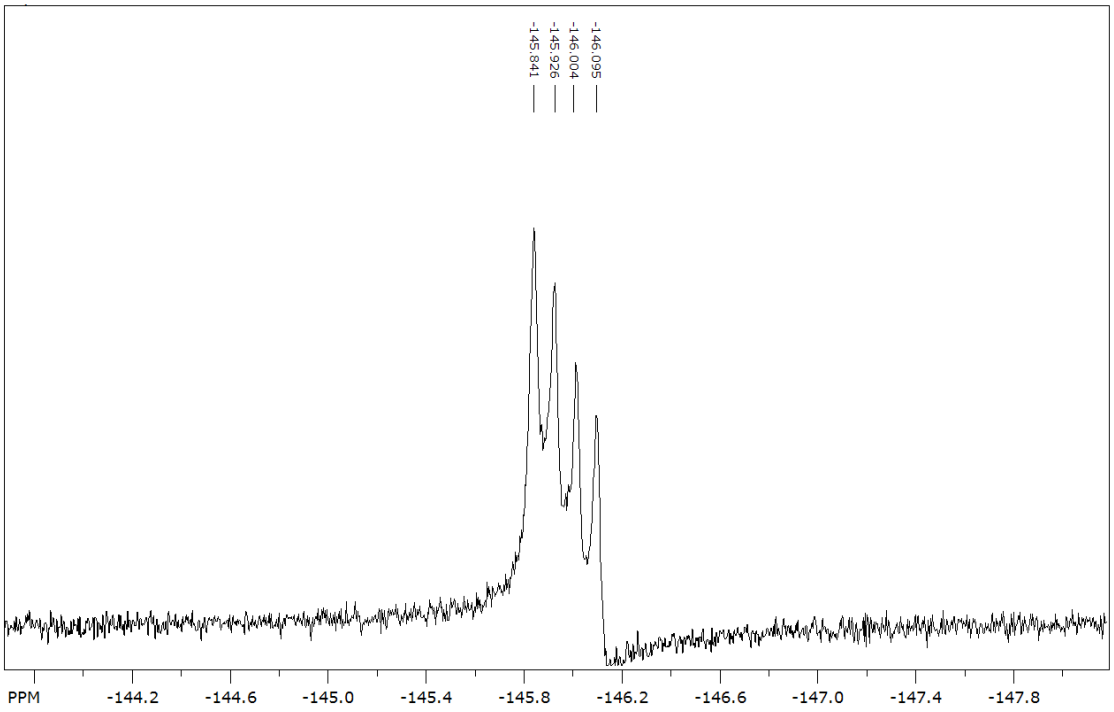

Fig S66. ^{19}F NMR spectrum of compound **23** in $CDCl_3$

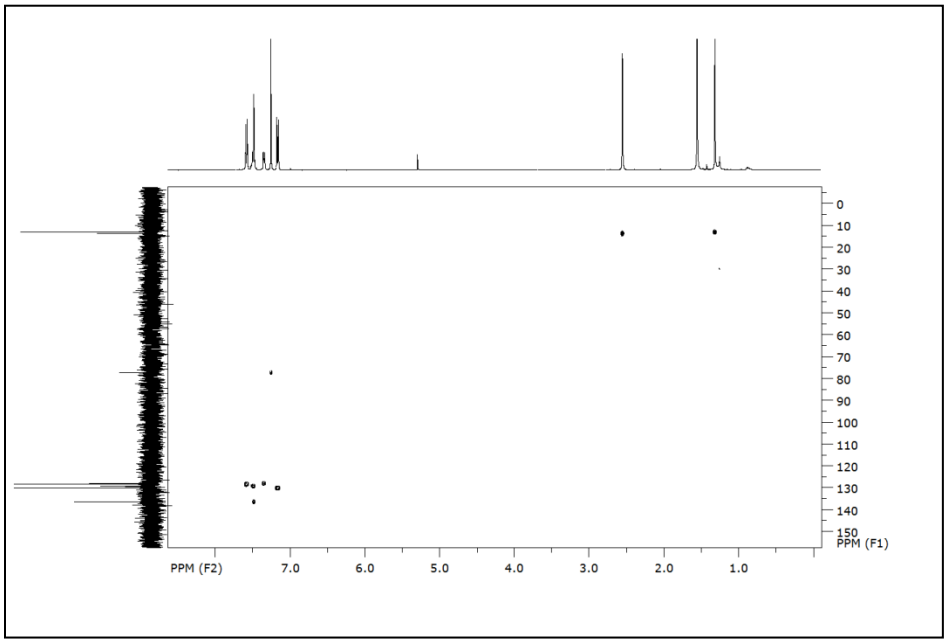

Fig S67. ^{1}H-^{13}C HSQC 2D NMR spectrum for compound **23** in $CDCl_3$