

Synthesis of maleimide-functionalized carboranes and their utility in Michael addition reactions

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1. The ^1H and ^{11}B NMR of *N*-(*o*-carboran-3-yl)maleimide (**6**)

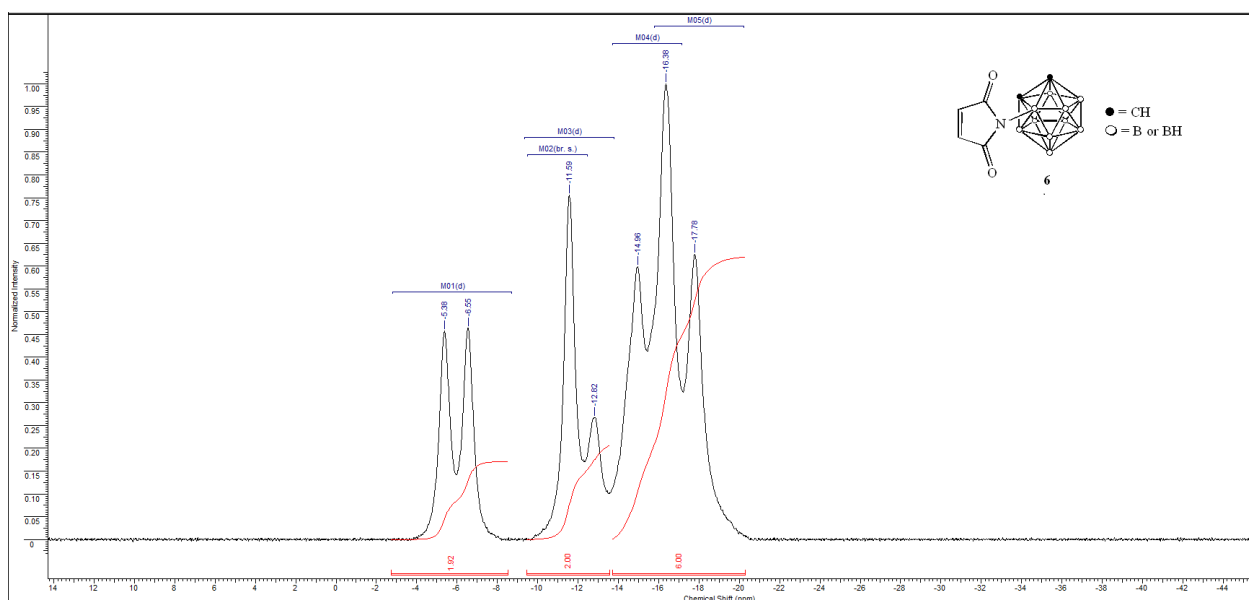
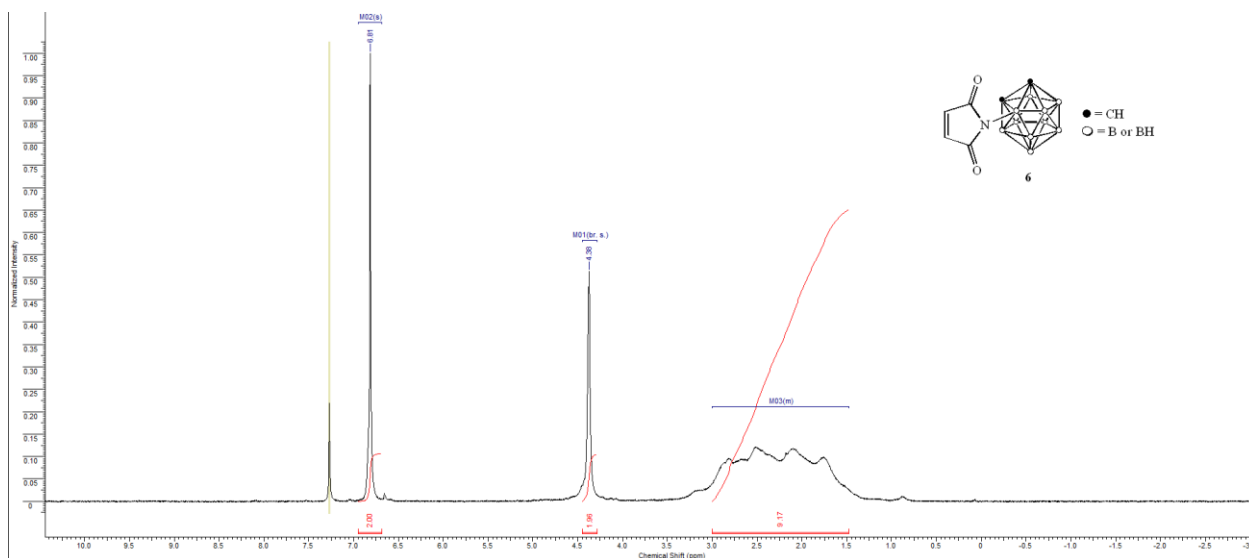
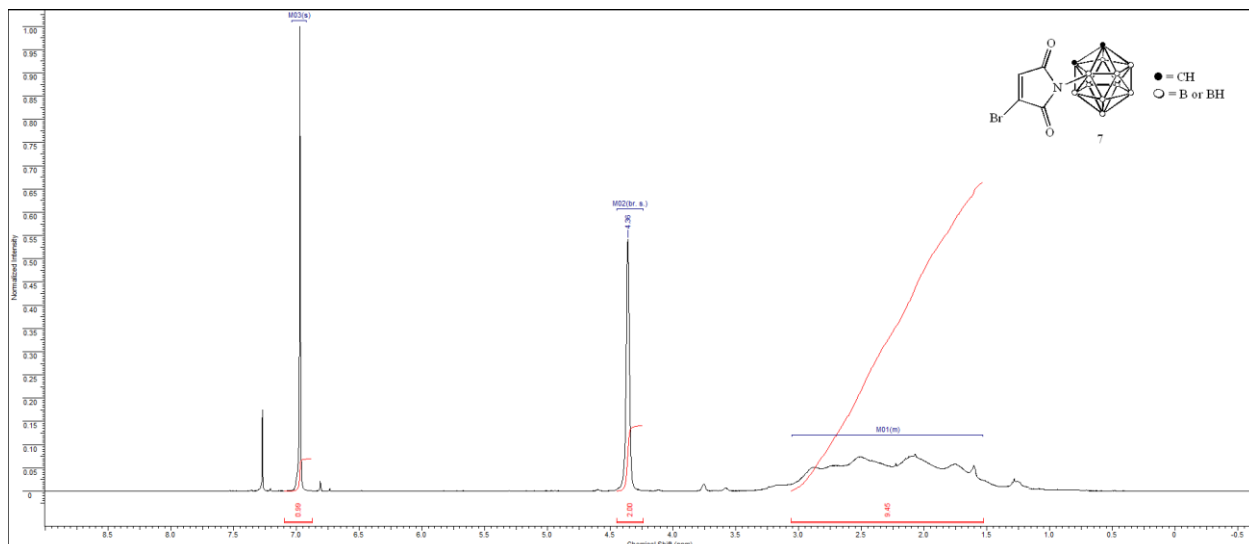


Figure S1. The ^1H , ^{11}B NMR spectra of **6** in CDCl_3 at 25 °C.

2. The ^1H and ^{11}B NMR spectra of 3-bromo-1-(*N*-(*o*-carborane-3'-yl))maleimide (**7**)



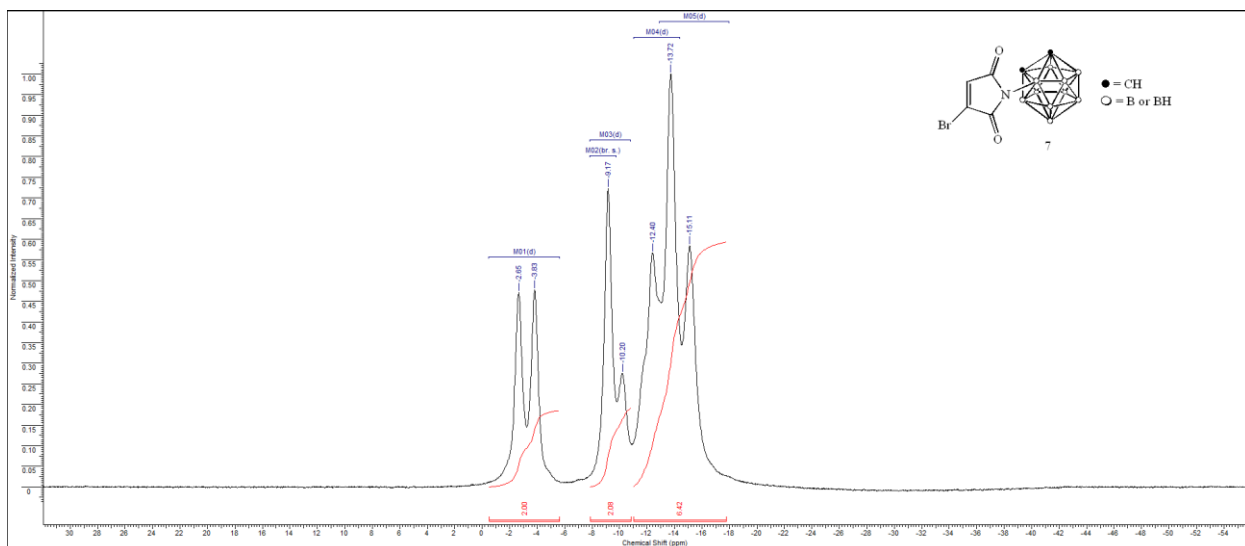
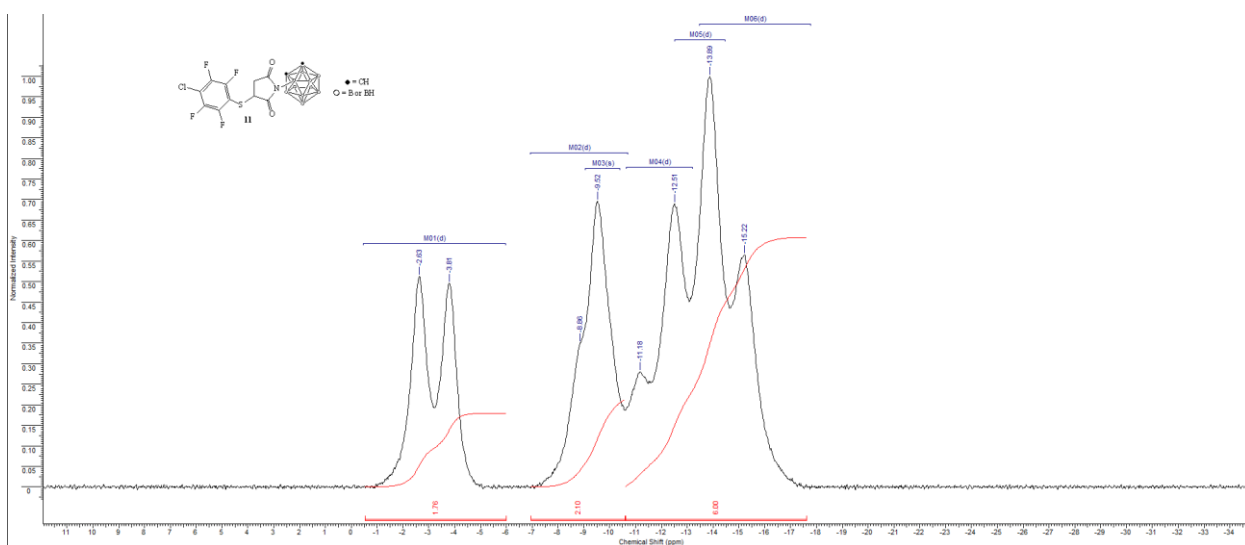
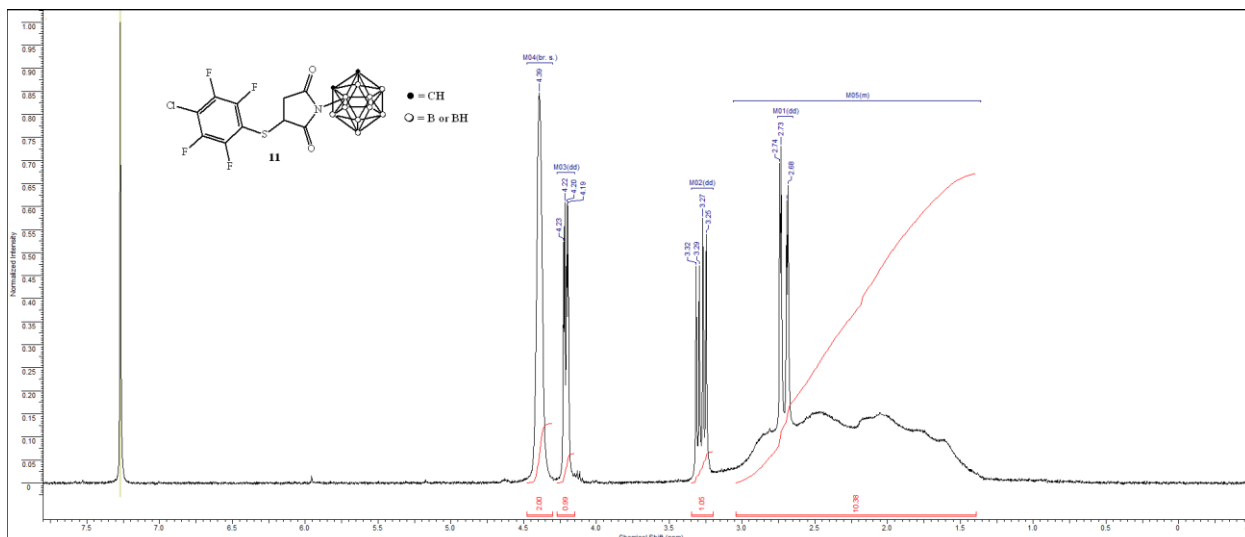


Figure S2. The ^1H , ^{11}B NMR spectra of **7** in CDCl_3 at 25°C .

3. The ^1H , ^{11}B and ^{19}F NMR spectra of [1-(*o*-carboran-3'-yl)-3-(4-chloro-2,3,5,6-tetrafluorophenyl)thio]-pyrrolidine-2,5-dione (**11**)



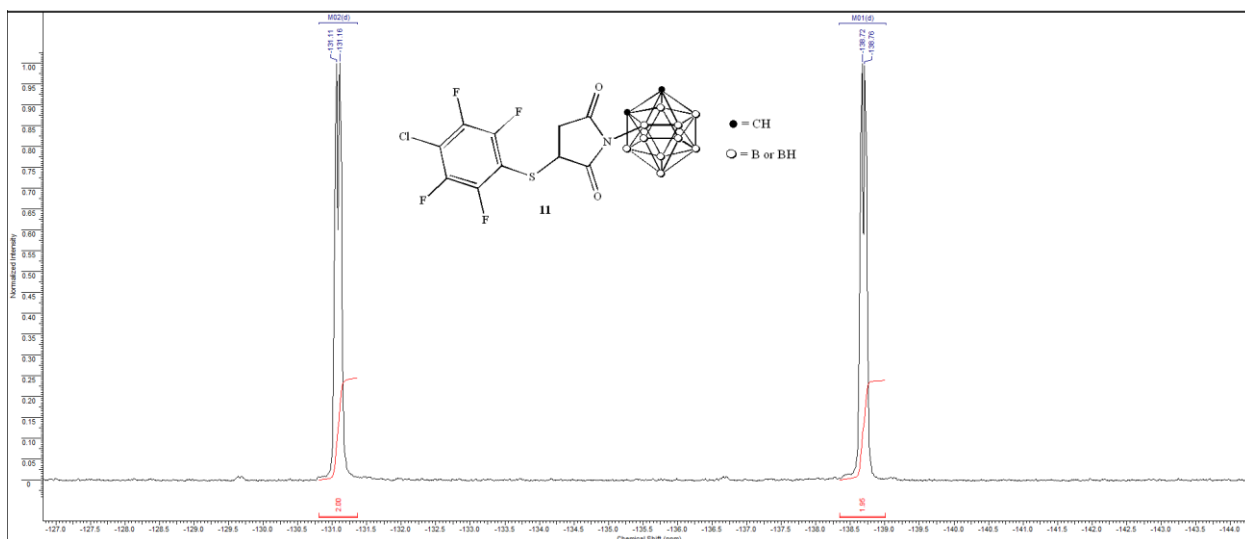


Figure S3. The ^1H , ^{11}B and ^{19}F NMR spectra of **11** in CDCl_3 at 25°C .

4. The ^1H and ^{11}B NMR spectra of [1-(*o*-carboran-3'-yl)-3-(*L*-S-ethoxycarbonylcysteinyl)-pyrrolidine-2,5-dione (**15**)]

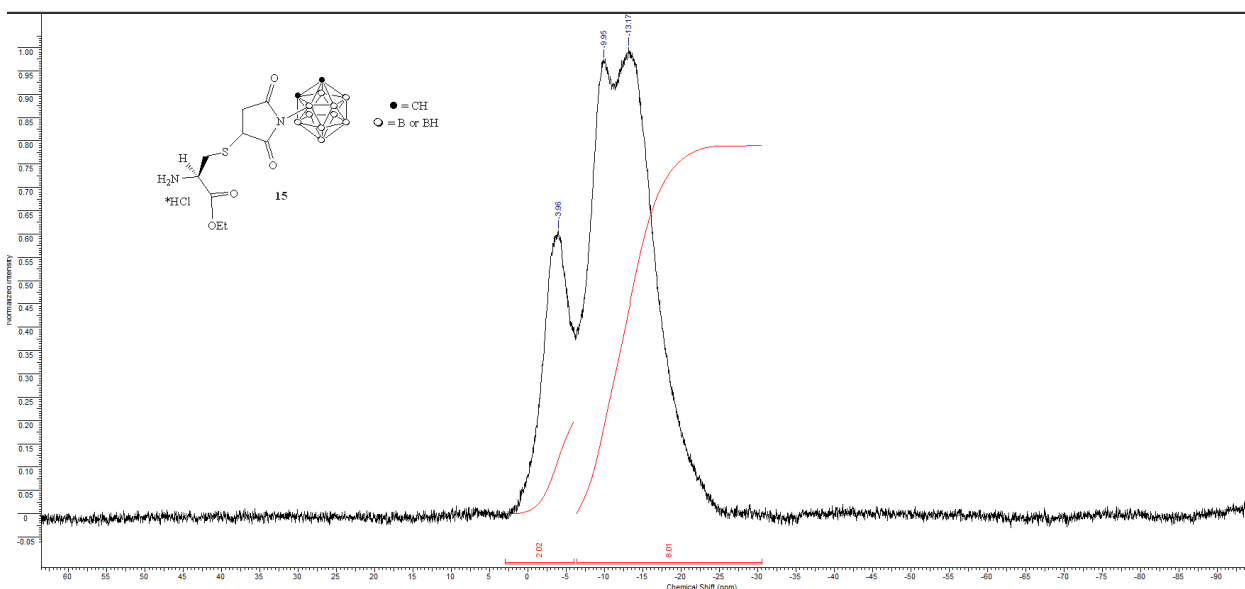
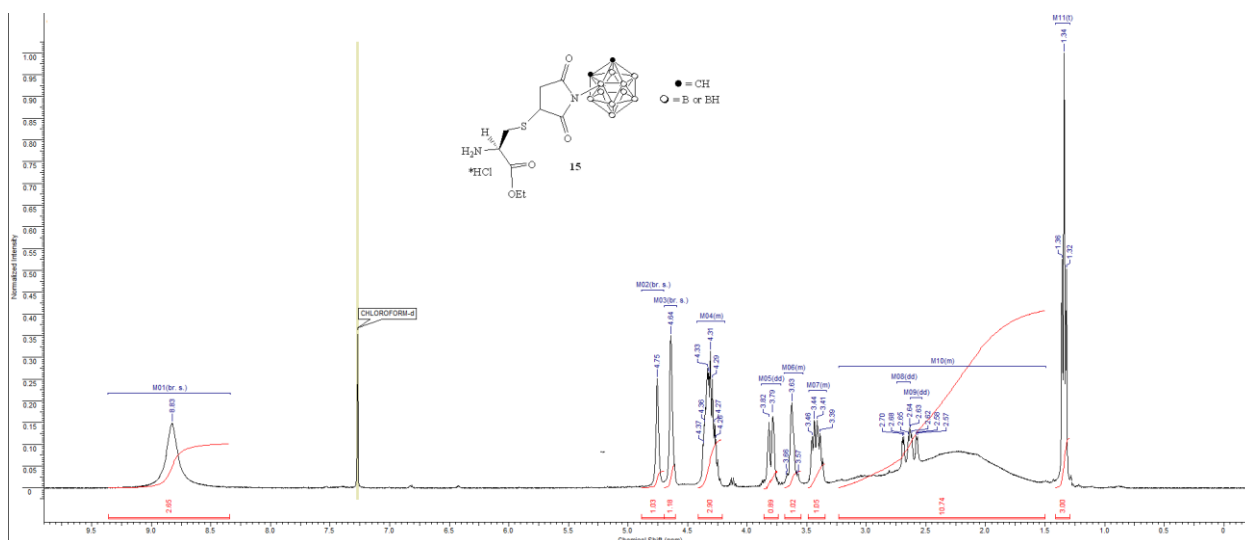


Figure S4. The ^1H , ^{11}B NMR spectra of **15** in CDCl_3 at 25°C .

5. The ^1H and ^{11}B NMR spectra of [1-(*o*-carborane-3'-yl)-3-(carboxymethenethio)]-pyrrol-2,5-dione (**20**)

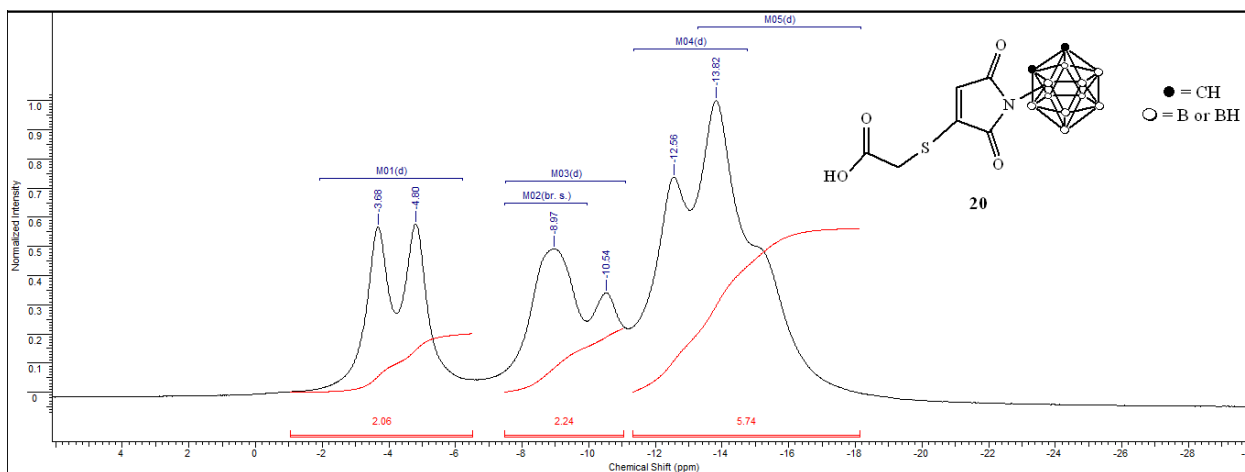
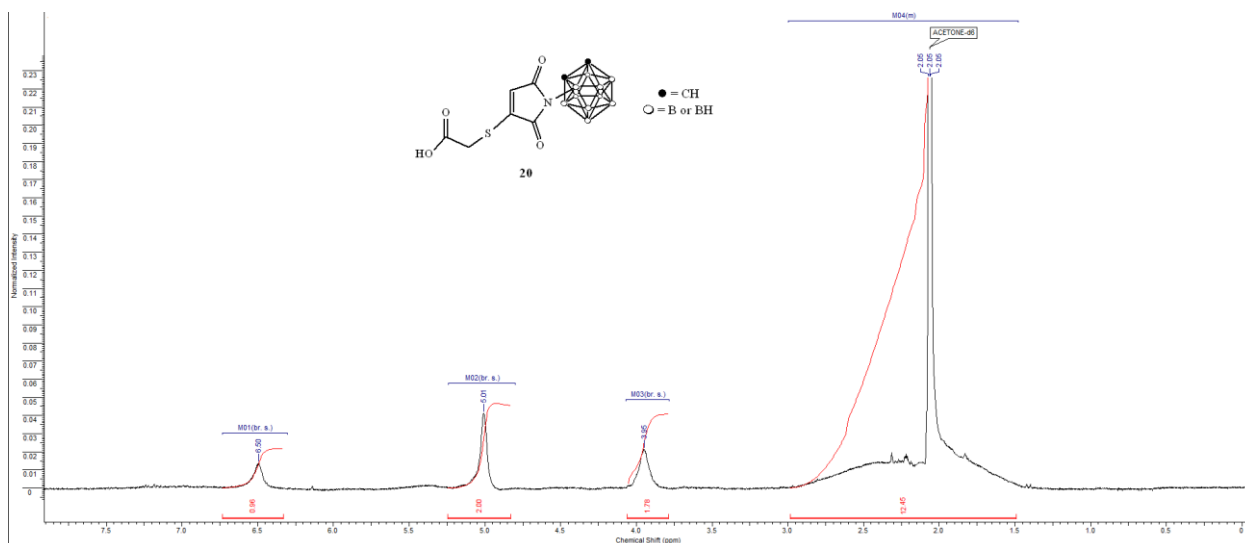
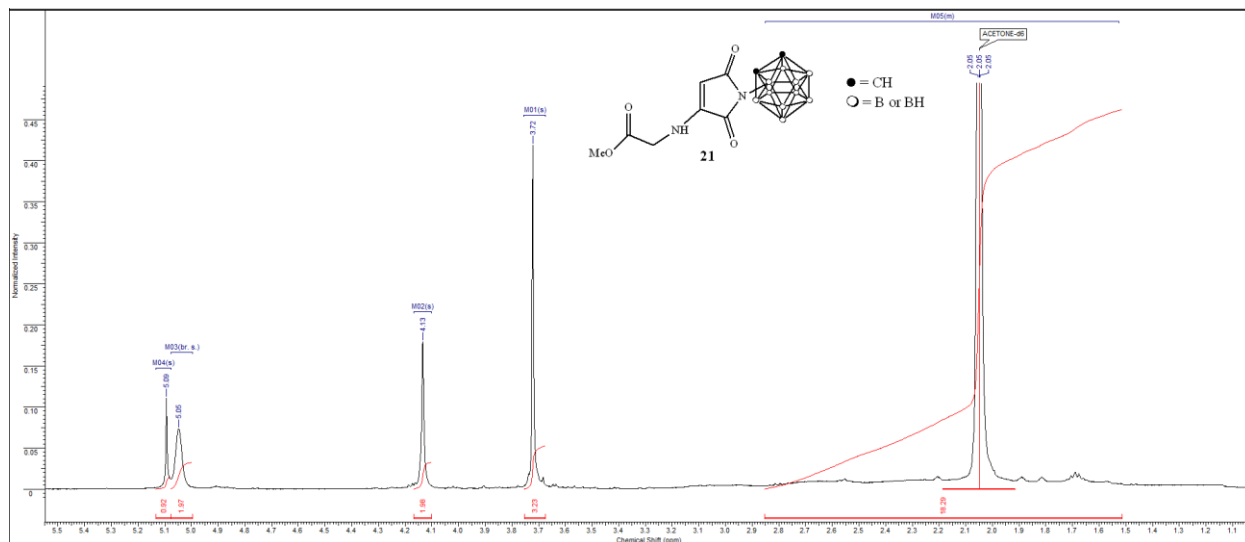


Figure S5. The ^1H and ^{11}B NMR spectra of **20** in $(\text{CD}_3)_2\text{CO}$ at 25 $^\circ\text{C}$.

6. The ^1H and ^{11}B NMR spectra of [1-(*o*-carborane-3'-yl)-3-(methoxycarbonylmethenamino)]-pyrrol-2,5-dione (**21**)



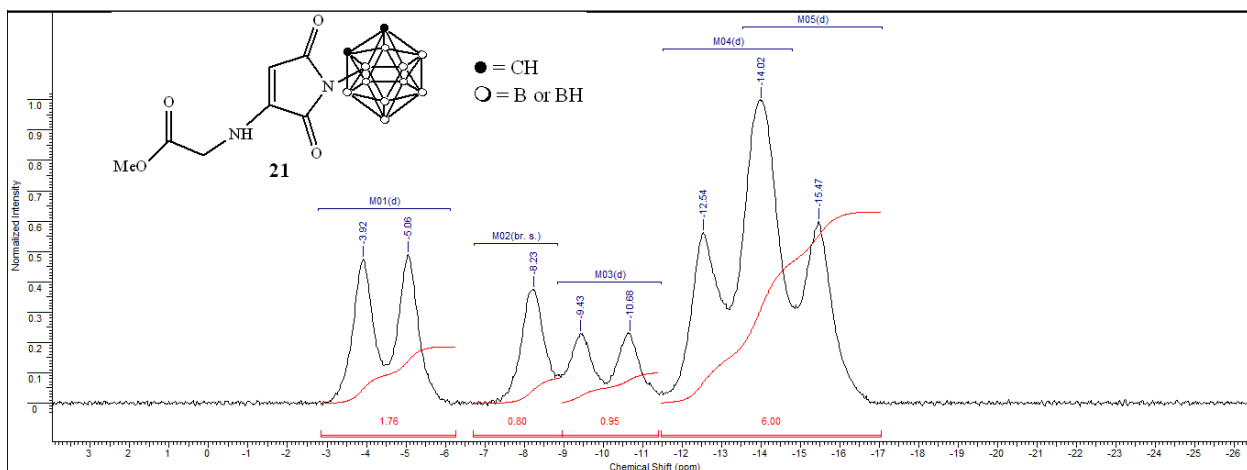


Figure S6. The ^1H and ^{11}B NMR spectra of **21** in $(\text{CD}_3)_2\text{CO}$ at 25°C .

7. The ^1H and ^{11}B NMR spectra of [1-(*o*-carborane-3'-yl)-3-(*N*-acetyl-*L*-S-cysteinyl)]-pyrrole-2,5-dione (**22**)

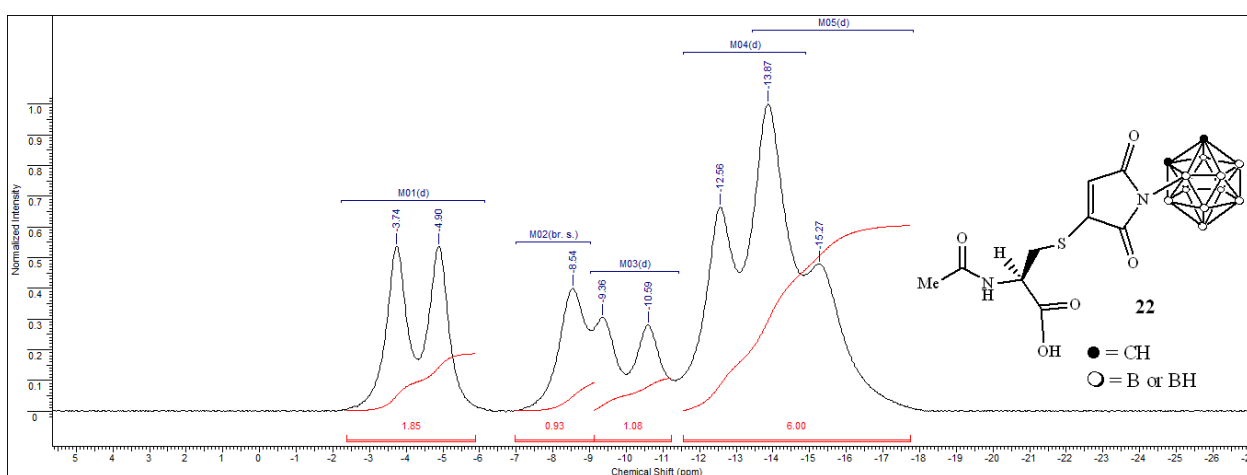
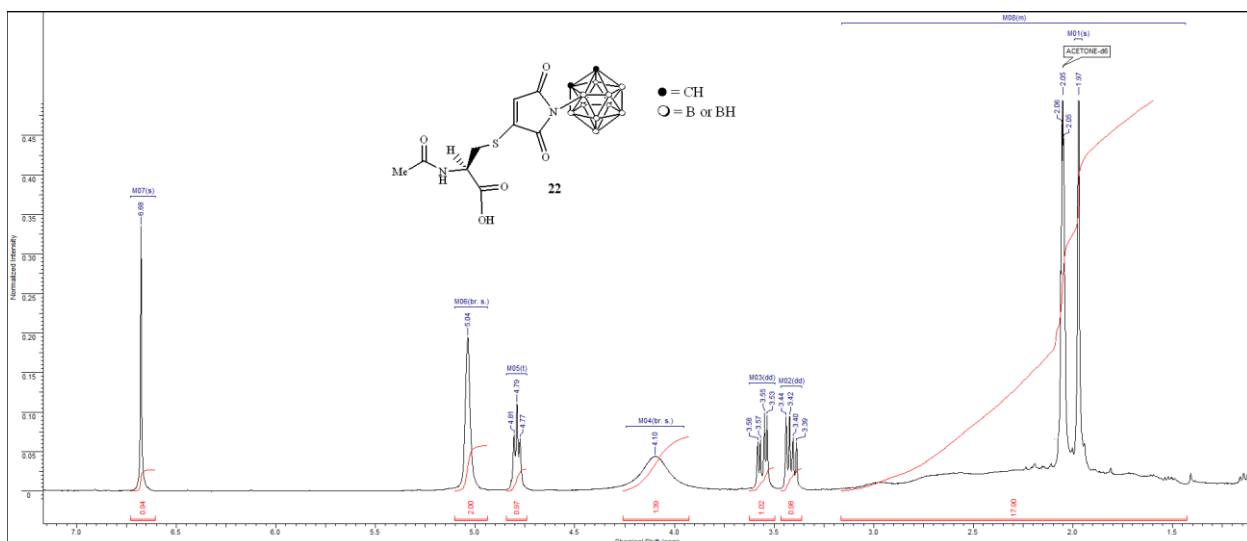


Figure S7. The ^1H and ^{11}B NMR spectra of **22** in $(\text{CD}_3)_2\text{CO}$ at 25°C .

8. The ^1H and ^{11}B NMR spectra of [1-(*o*-carborane-3'-yl)-3-(4,6-dimethylpyrimidin-2-yl)thio]pyrrole-2,5-dione (**23**)

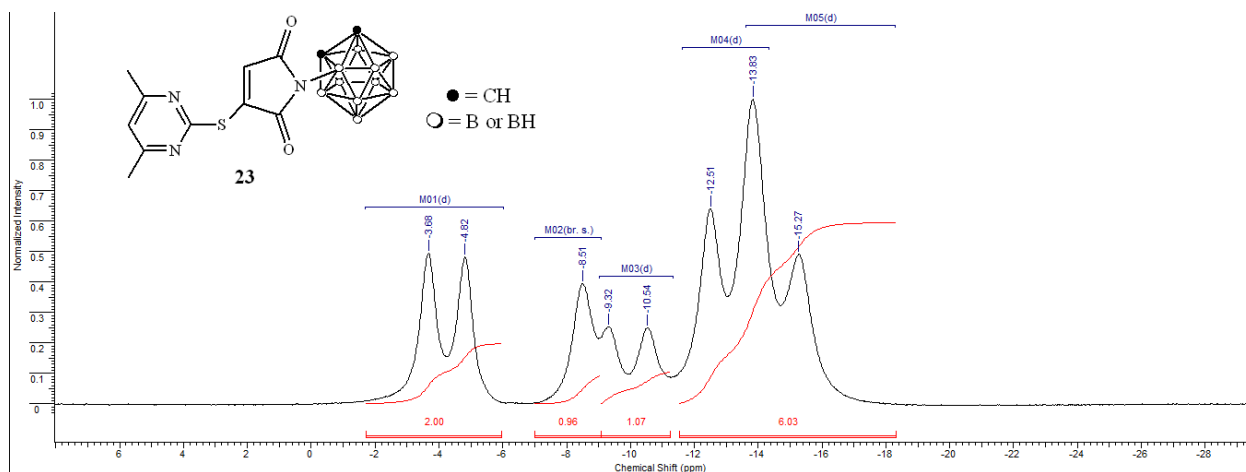
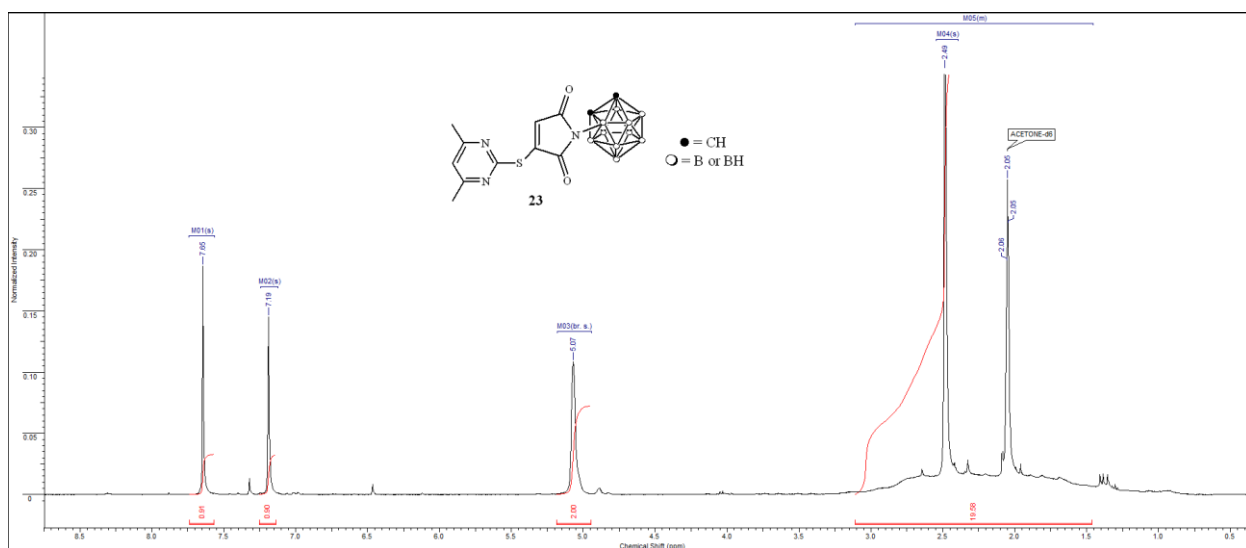
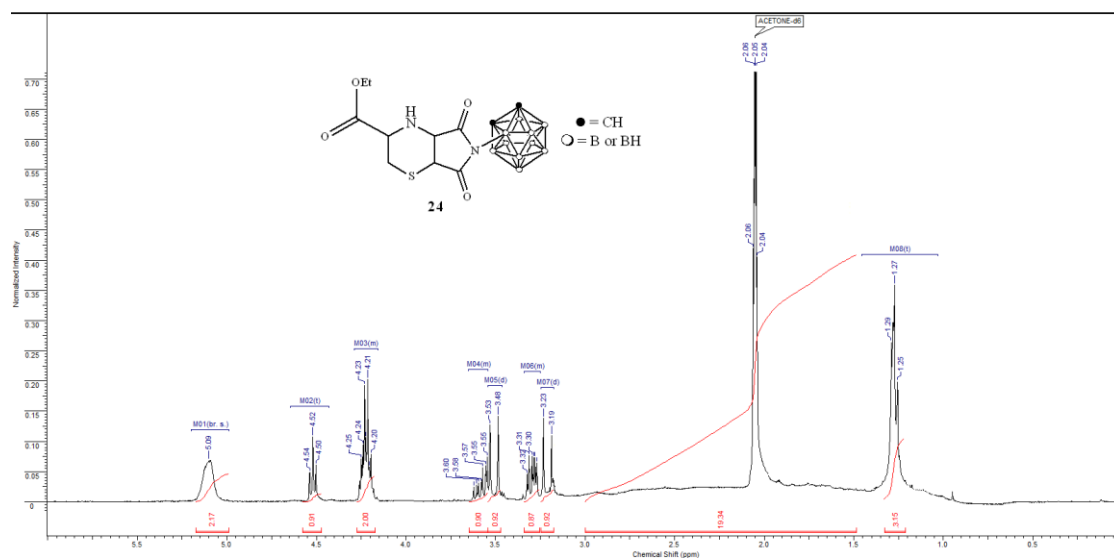


Figure S8. The ^1H and ^{11}B NMR spectra of **23** in $(\text{CD}_3)_2\text{CO}$ at 25 $^\circ\text{C}$.

9. The ^1H and ^{11}B NMR spectra of [6-(*o*-carboran-3'yl)-5,7-dioxo-3-ethoxycarbonyl]perhydropyrrolo[3,4-*b*]thiazine (**24**)



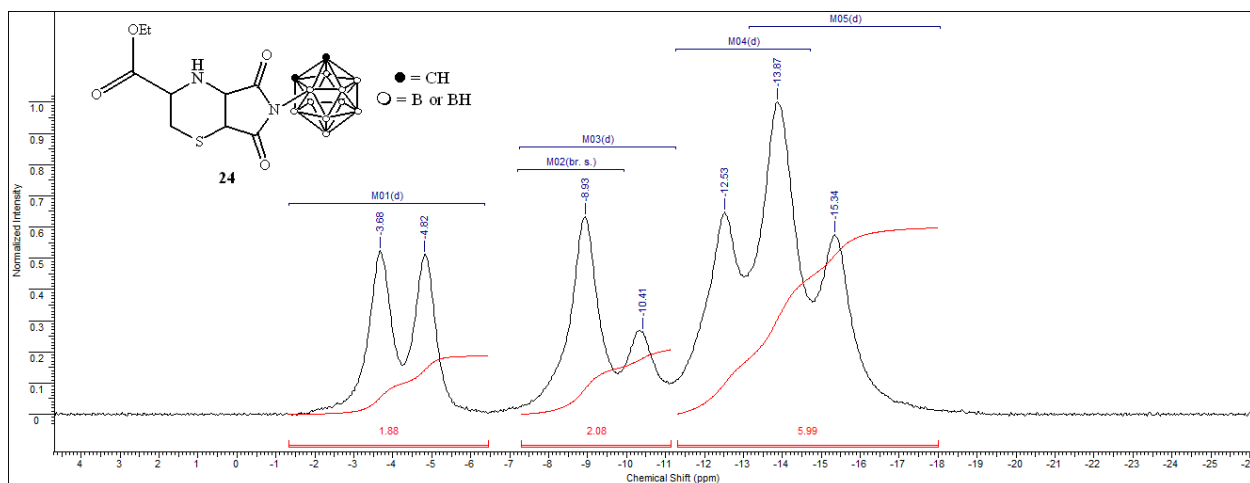


Figure S9. The ^1H and ^{11}B NMR spectra of **24** in $(\text{CD}_3)_2\text{CO}$ at 25°C .

10. The ^1H and ^{11}B NMR spectra of [1-(*o*-carborane-3'-yl)-3-(*m*-carborane-9'-yl)thio]-pyrrole-2,5-dione (28**)**

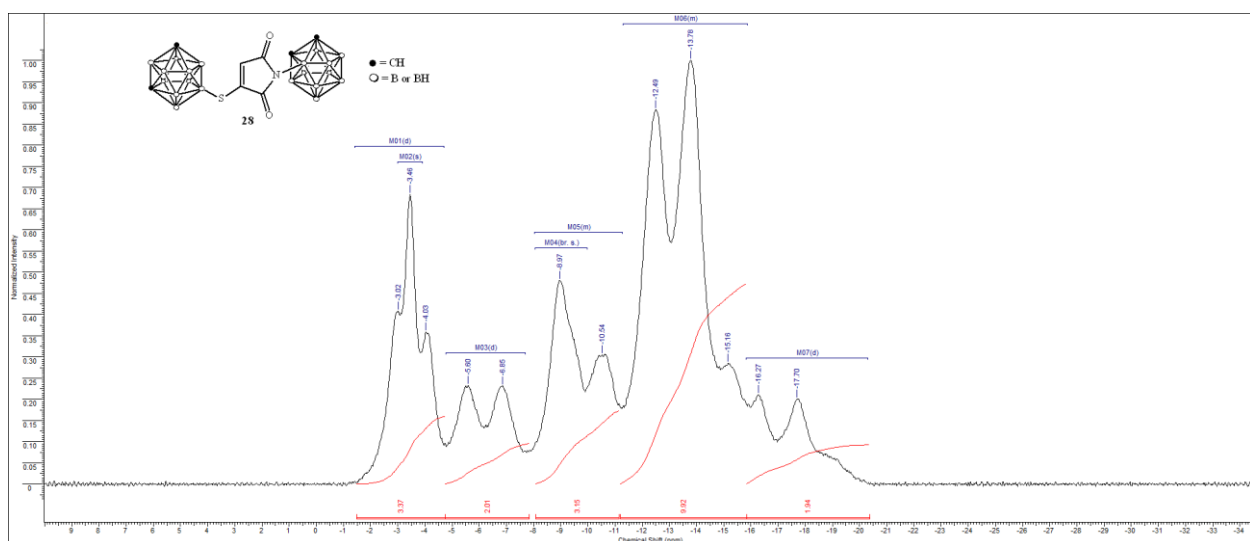
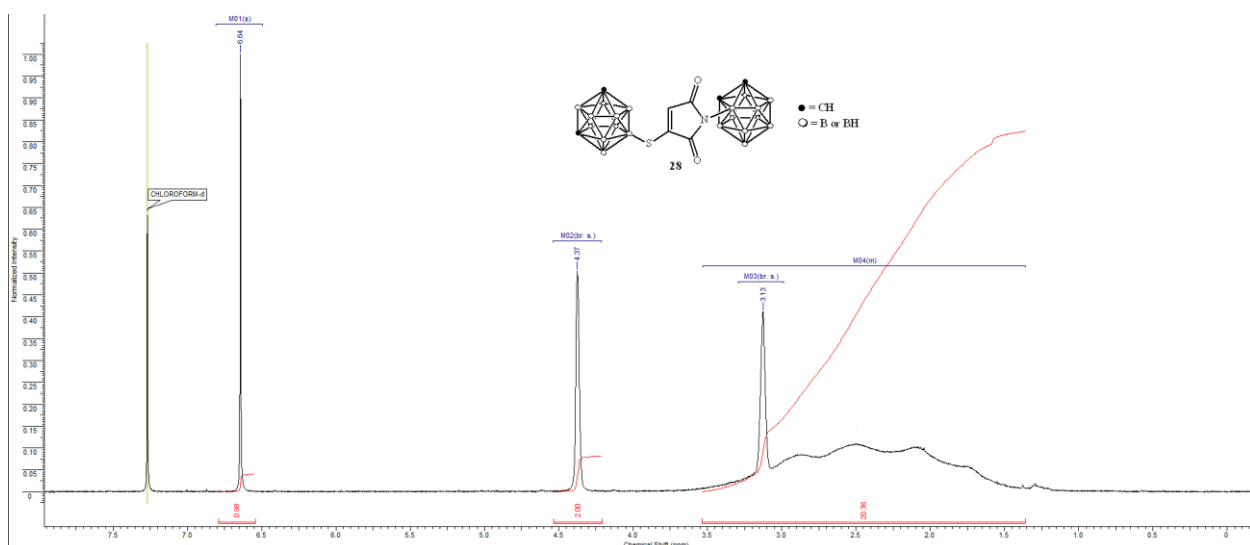


Figure S10. The ^1H , ^{11}B NMR spectra of **28** in CDCl_3 at 25°C .

11. The ^1H and ^{11}B NMR spectra of [1-(*o*-carborane-3'-yl)-3-(*o*-carborane-9'-yl)thio]-pyrrole-2,5-dione (29)

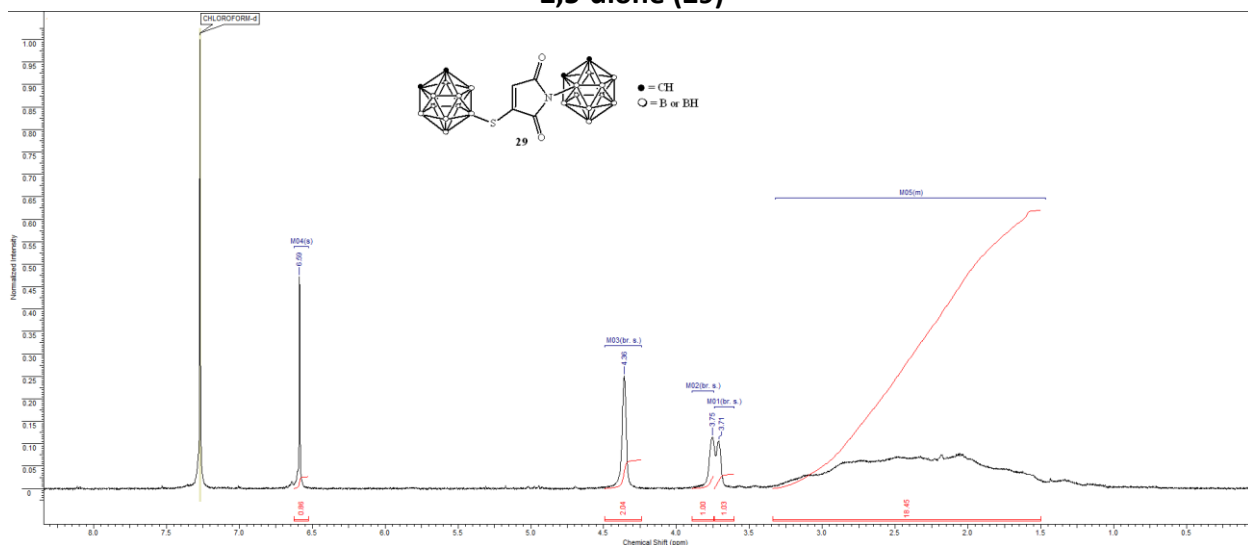
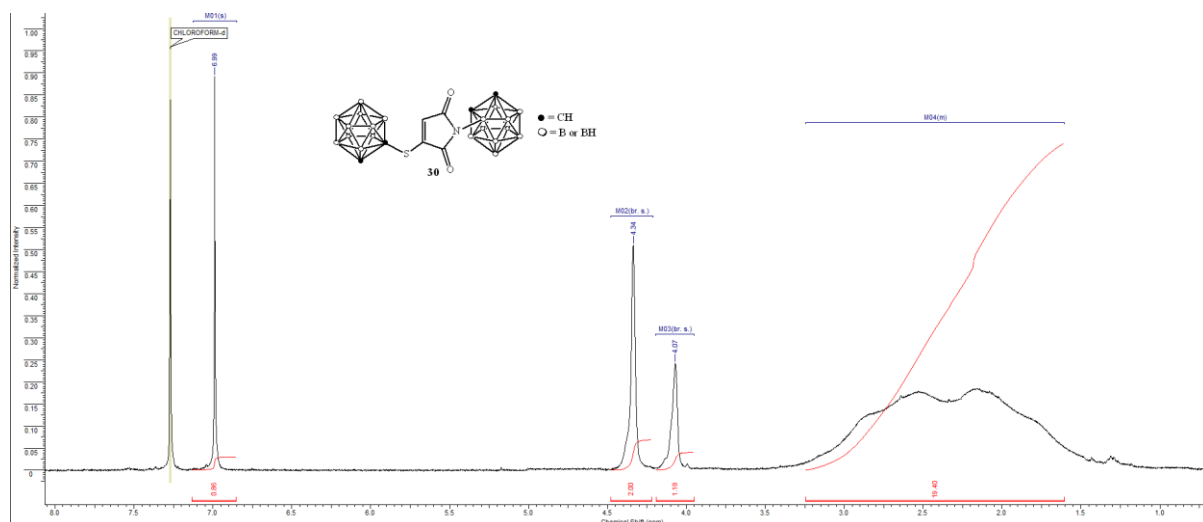


Figure S11. The ^1H , ^{11}B NMR spectra of 29 in CDCl_3 at 25 °C.

12. The ^1H and ^{11}B NMR spectra of [1-(*o*-carborane-3'-yl)-3-(*o*-carborane-1'-yl)thio]-pyrrole-2,5-dione (30)



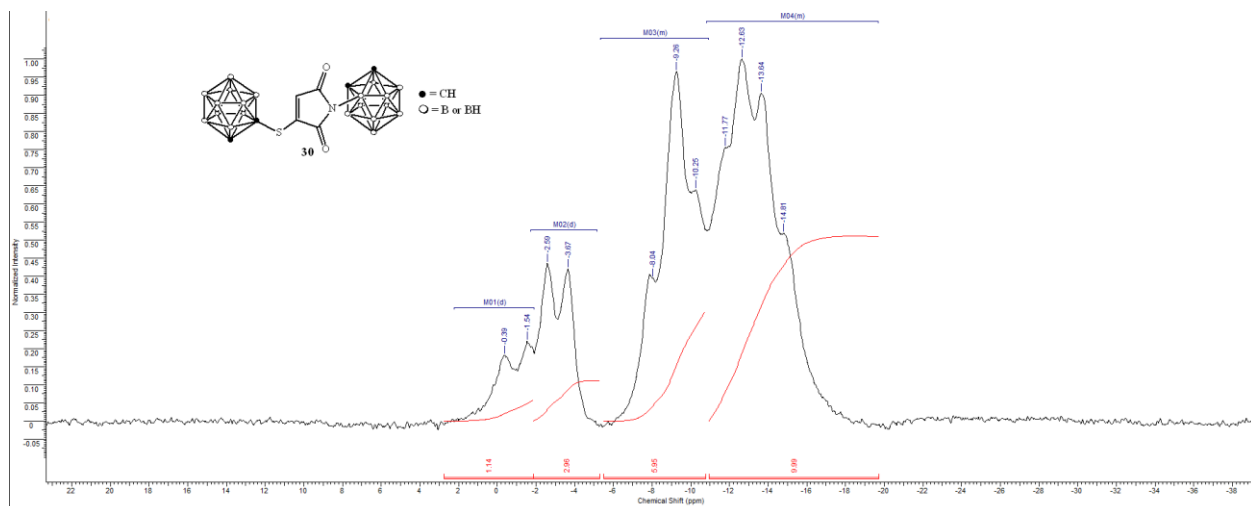


Figure S12. The ^1H , ^{11}B NMR spectra of **30** in CDCl_3 at 25°C .

13. The ^1H and ^{11}B NMR spectra of [1-(*o*-carboran-3'-yl)-3-S-glutathionyl]-pyrrolidine-2,5-dione (**32**)

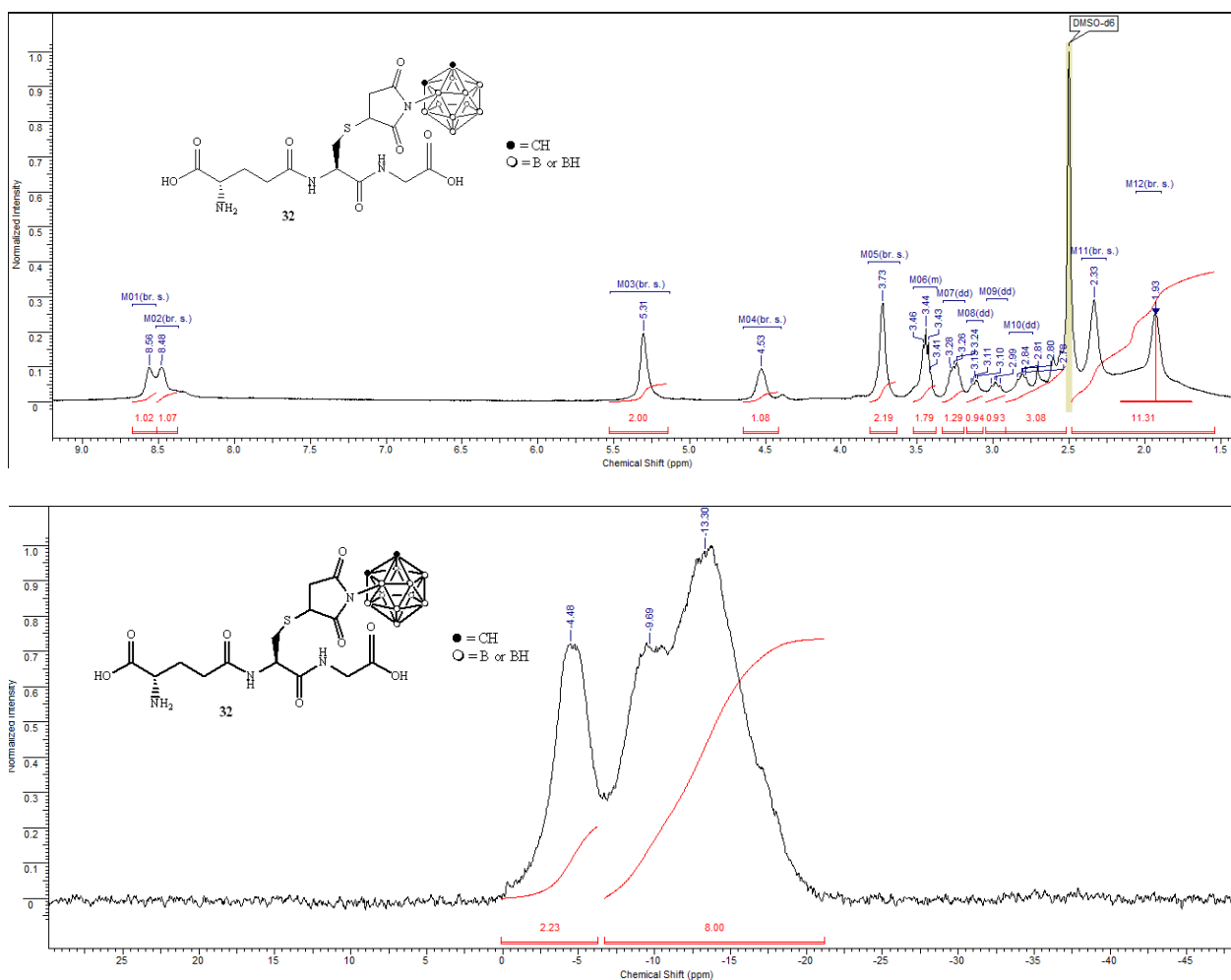


Figure S13. The ^1H and ^{11}B NMR spectra of **32** in $(\text{CD}_3)_2\text{SO}$ at 25°C .

14. The ^1H - ^1H COSY spectrum of [1-(*o*-carboran-3'-yl)-3-S-glutathionyl]-pyrrol-2,5-dione (**33**)

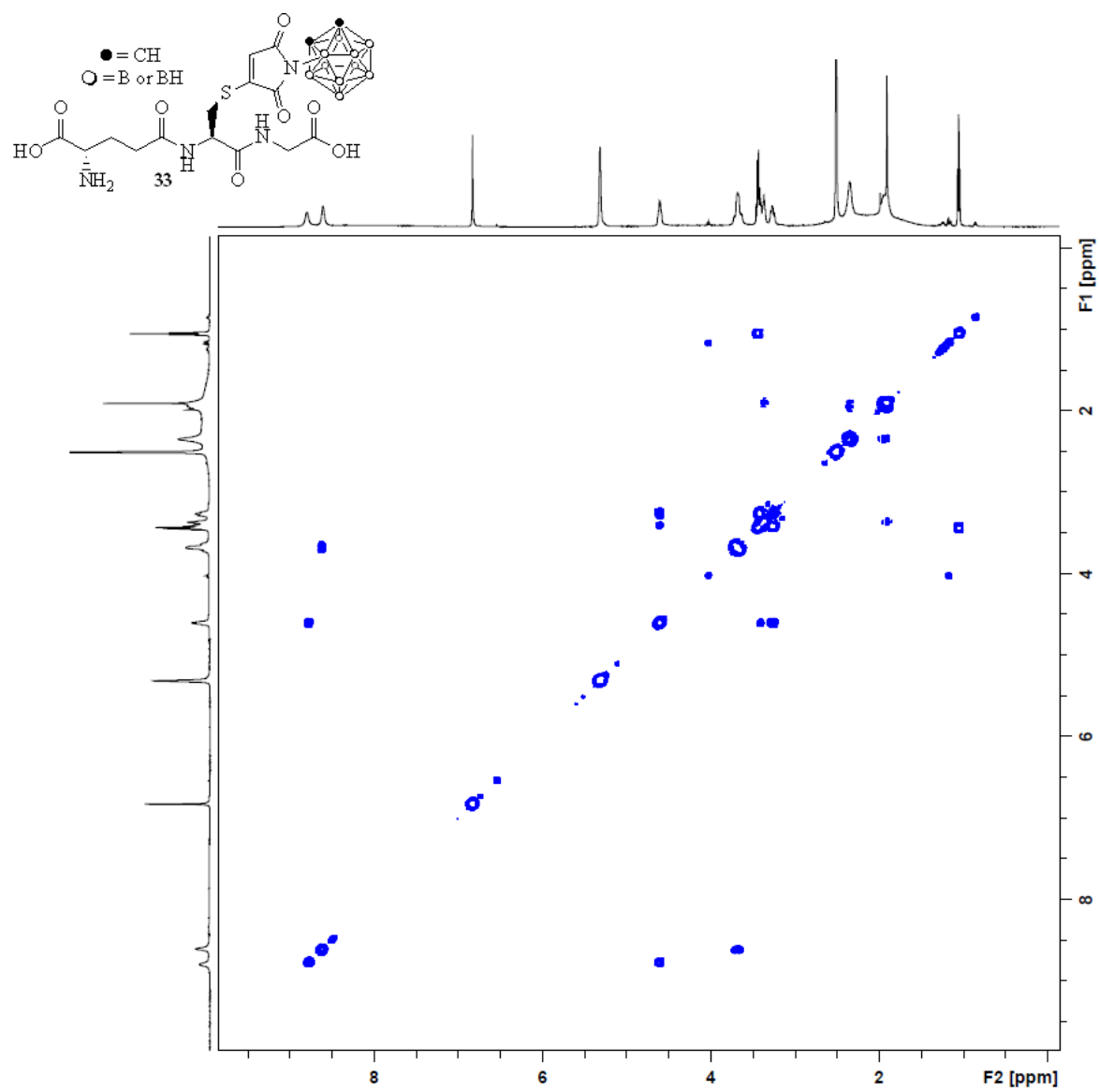


Figure S14. The ^1H - ^1H COSY spectrum of **33** in $(\text{CD}_3)_2\text{SO}$ at 25 °C.

15. The ^1H and $^1\text{H}\{^{11}\text{B}\}$ NMR spectra of [1-(*o*-carboran-3'-yl)-3-S-glutathionyl]-pyrrol-2,5-dione (**33**)

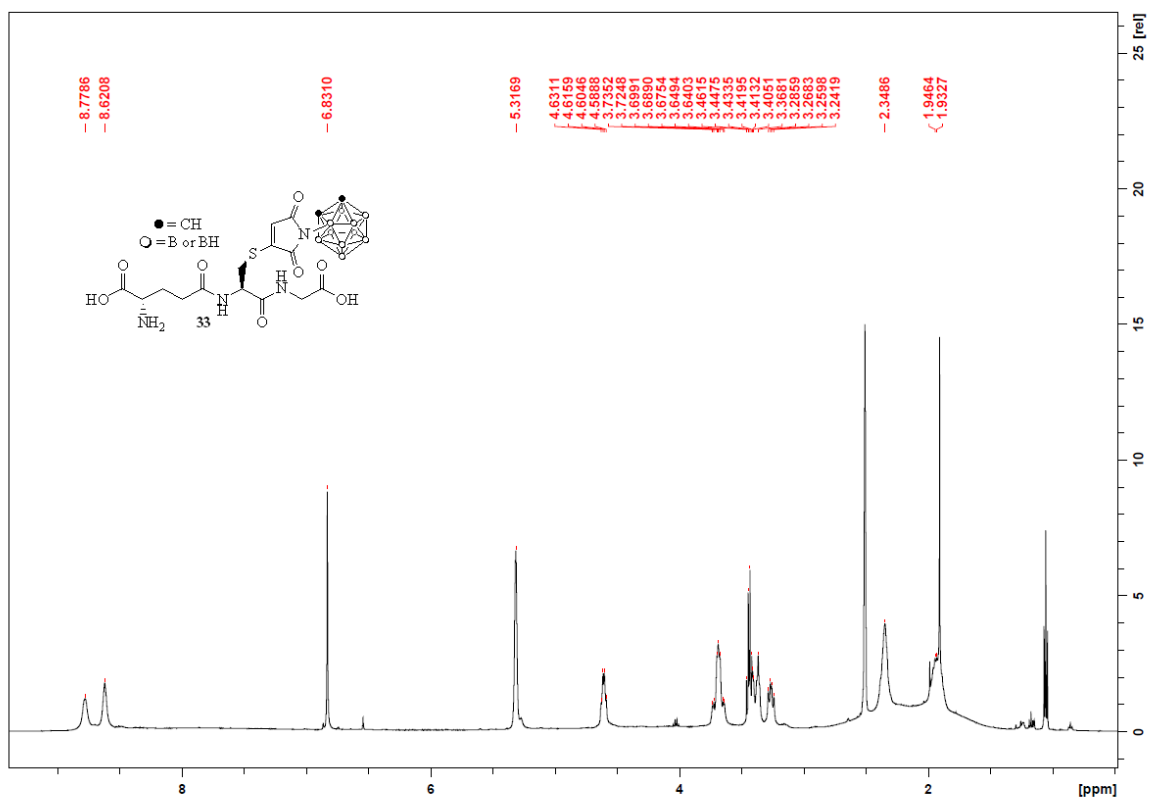
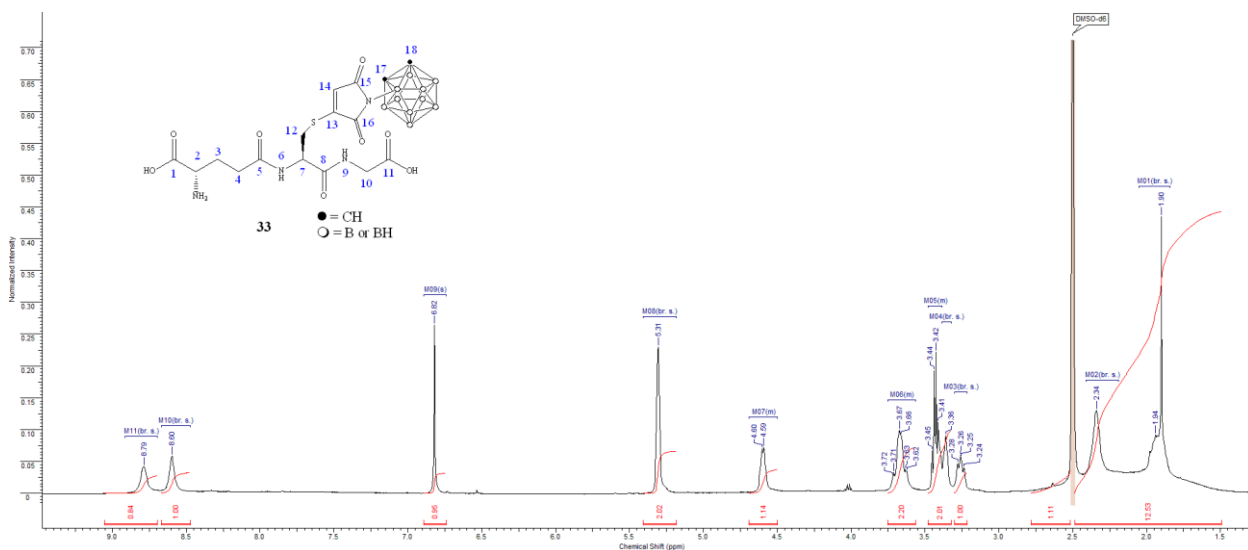


Figure S15. The ^1H and $^1\text{H}\{^{11}\text{B}\}$ NMR spectra of **33** in $(\text{CD}_3)_2\text{SO}$ at 25 °C.

16. The ^{11}B NMR and $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of [1-(*o*-carboran-3'-yl)-3-S-glutathionyl]-pyrrol-2,5-dione (**33**)

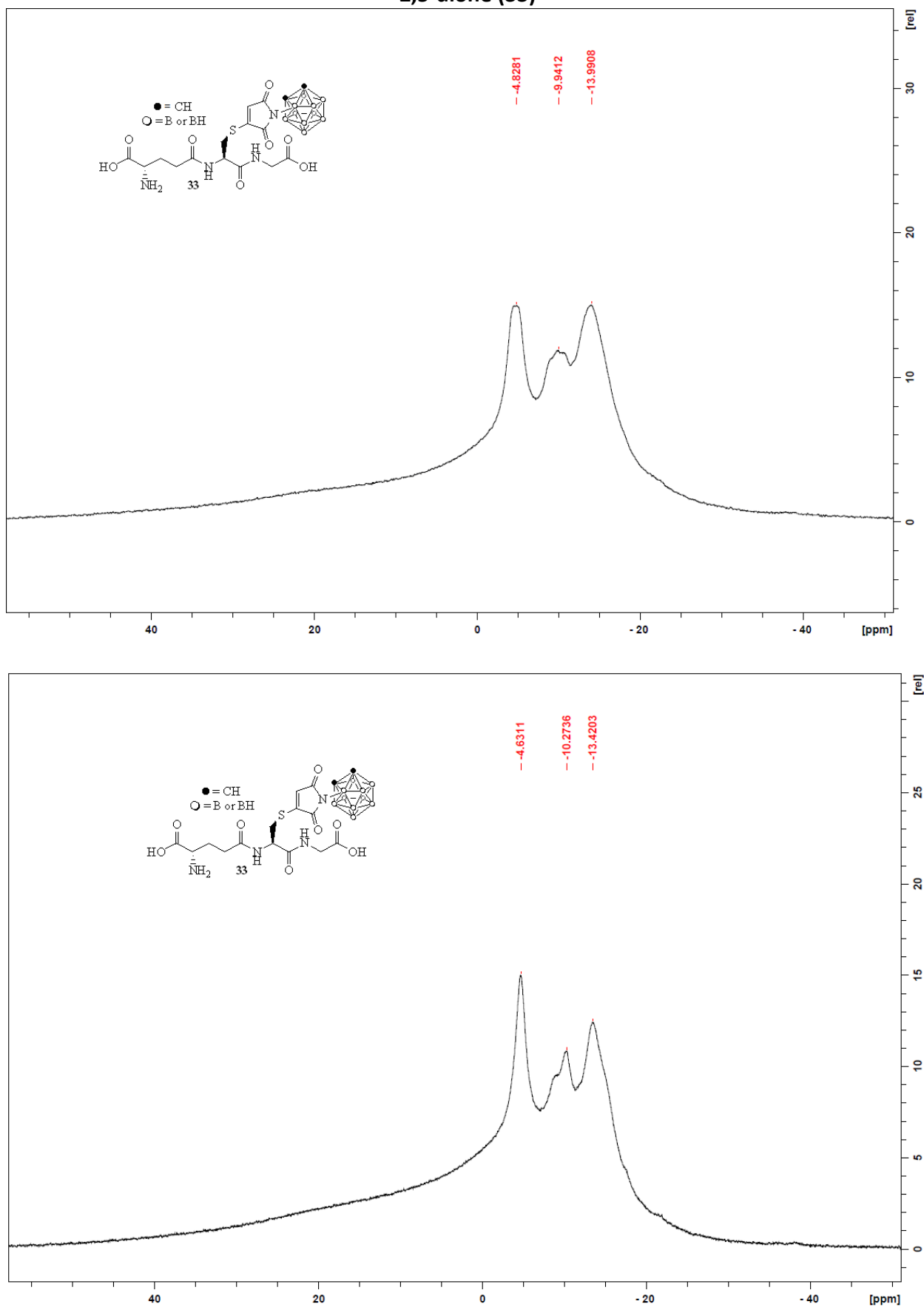


Figure S16. The ^{11}B NMR and $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of **33** in $(\text{CD}_3)_2\text{SO}$ at 25°C .

17. The ^{13}C NMR spectrum of [1-(*o*-carboran-3'-yl)-3-S-glutathionyl]-pyrrol-2,5-dione (**33**)

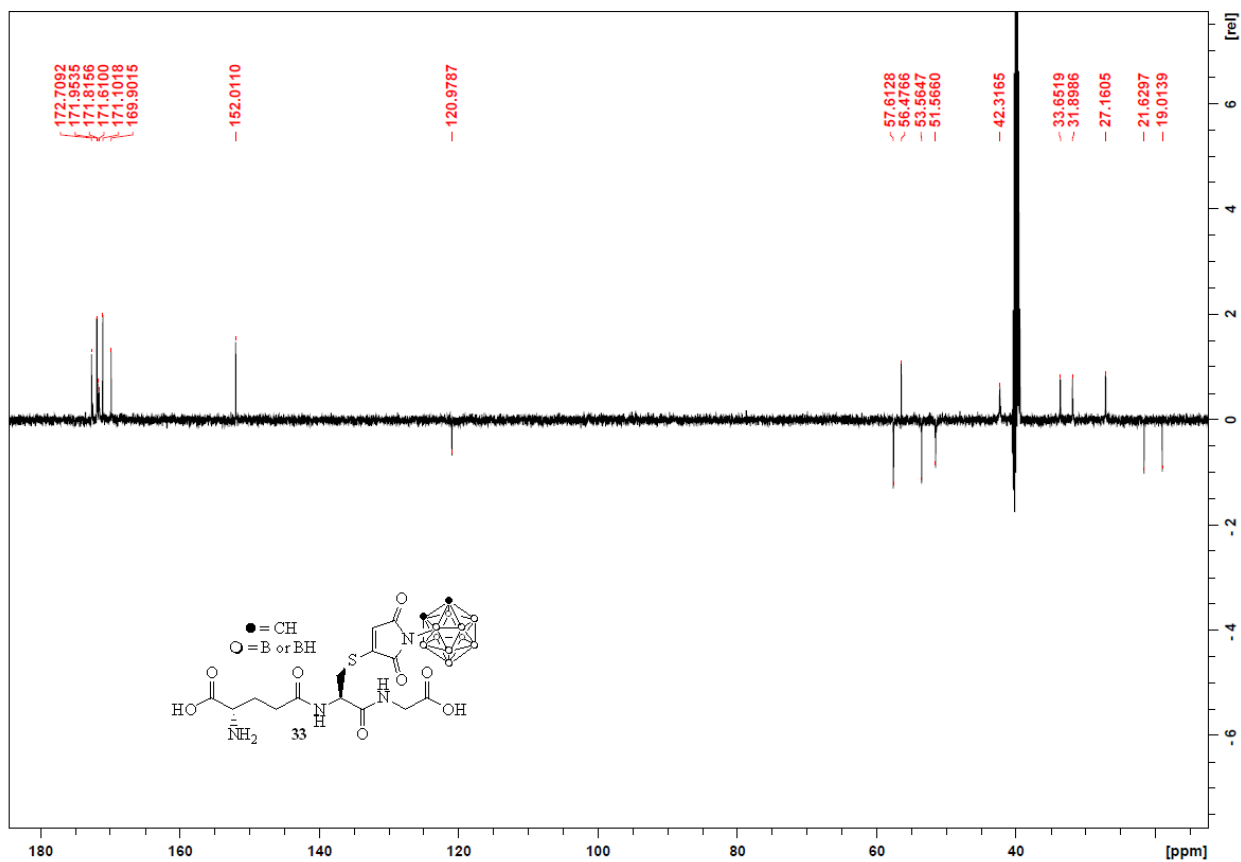


Figure S17. The ^{13}C NMR spectrum of **33** in $(\text{CD}_3)_2\text{SO}$ at 25°C .

18. The ^1H - ^{13}C HSQC spectrum of [1-(*o*-carboran-3'-yl)-3-S-glutathionyl]-pyrrol-2,5-dione (**33**)

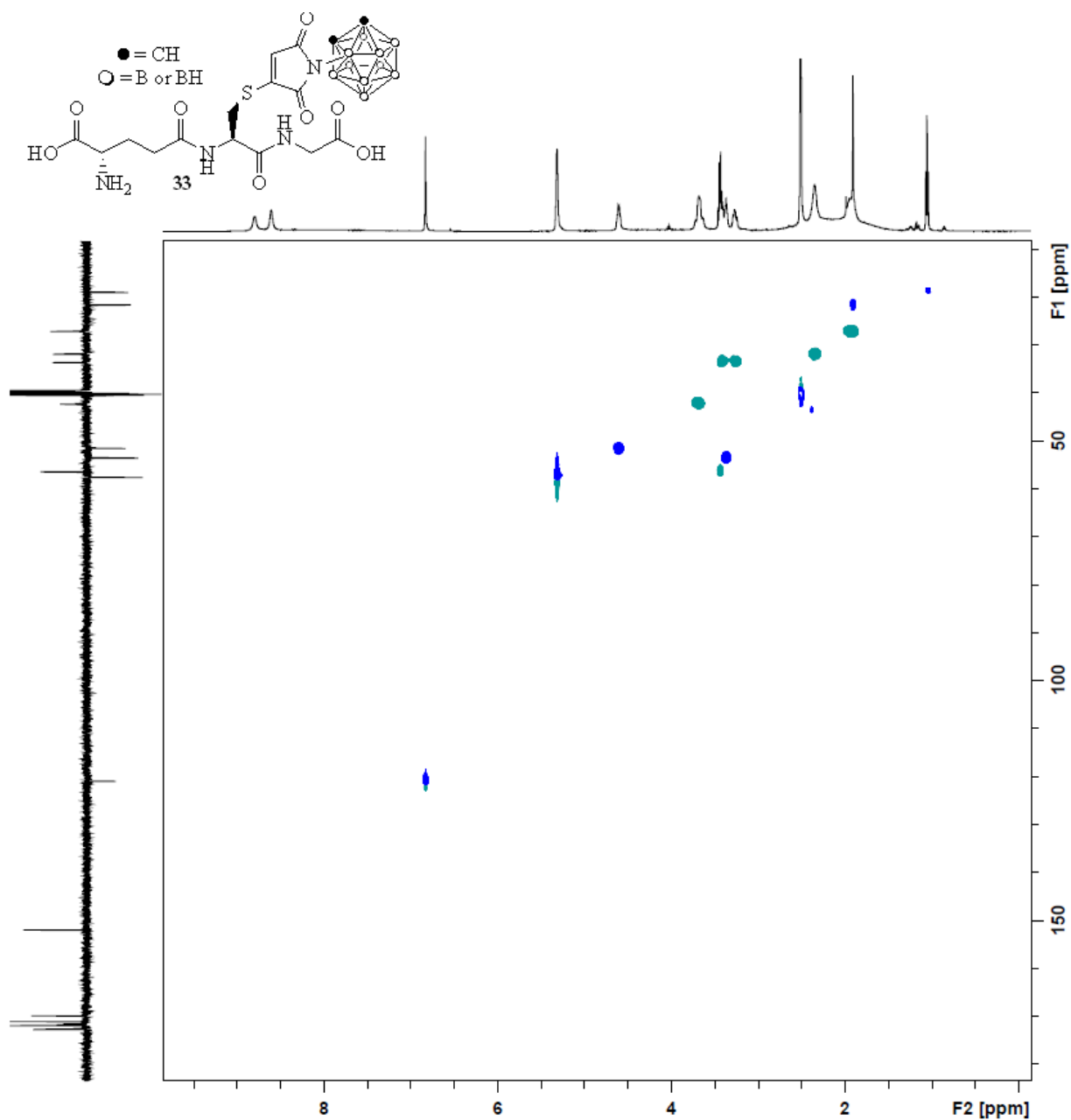


Figure S18. The ^1H - ^{13}C HSQC spectrum of **33** in $(\text{CD}_3)_2\text{SO}$ at 25 °C.

19. The ^1H - ^{13}C HMBC spectrum of [1-(*o*-carboran-3'-yl)-3-S-glutathionyl]-pyrrol-2,5-dione (**33**)

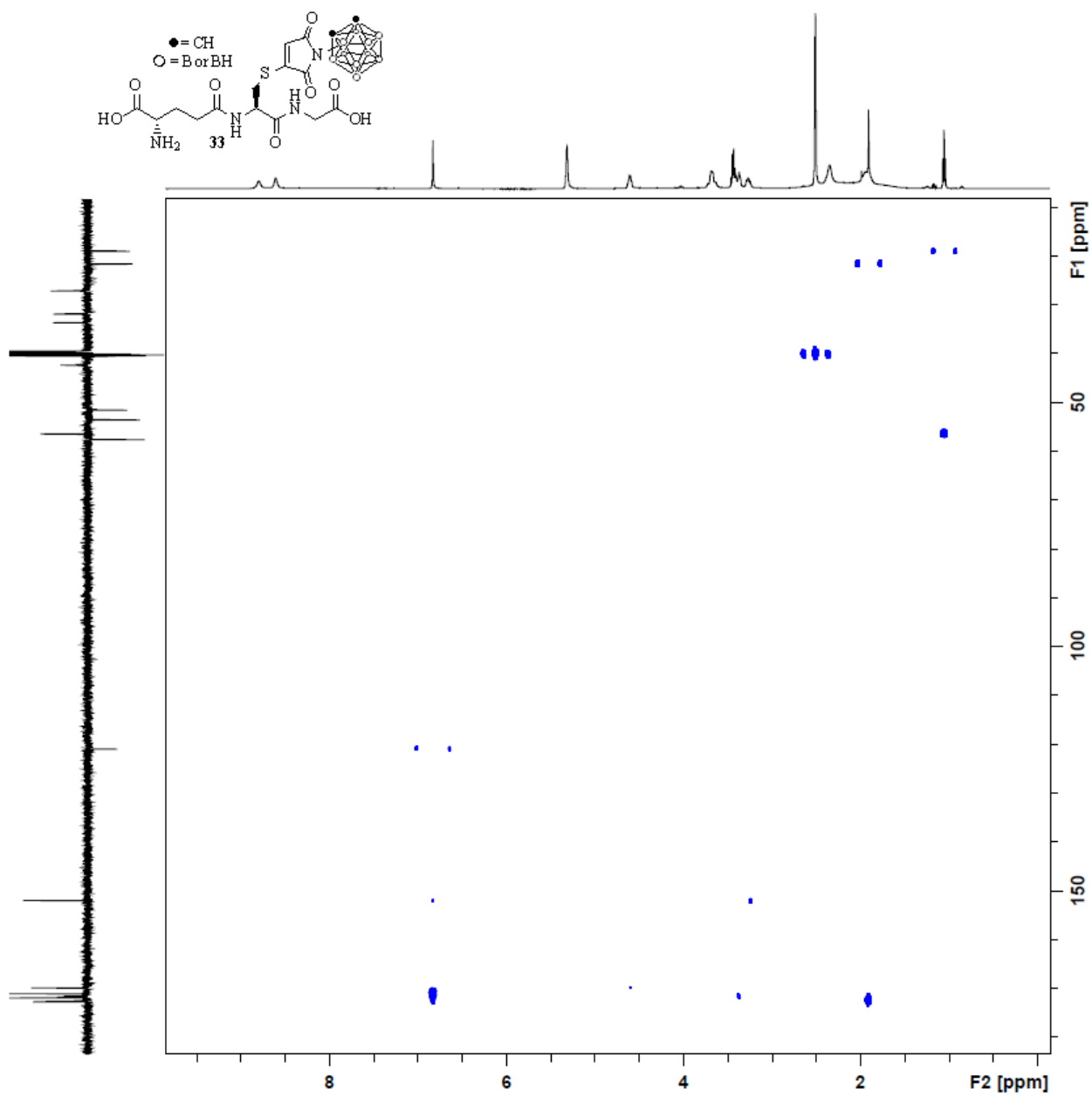


Figure S19. The ^1H - ^{13}C HMBC spectrum of **33** in $(\text{CD}_3)_2\text{SO}$ at 25 °C.