

Supplementary information

Part 1

Non-covalent Interactions in the Crystal Structures of Perbrominated Sulfonium Derivatives of the *closo*-Decaborate Anion

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Additional NMR and IR spectra

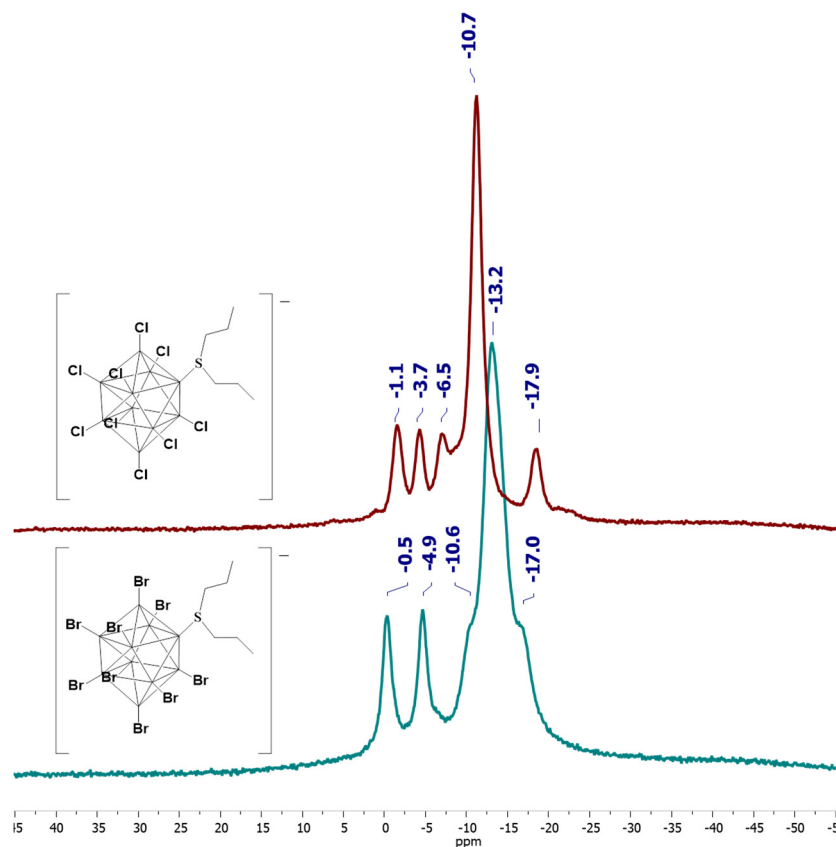


Figure S1. ^{11}B NMR spectra of perchlorinated sulfonium derivatives of the *closo*-decaborate anion

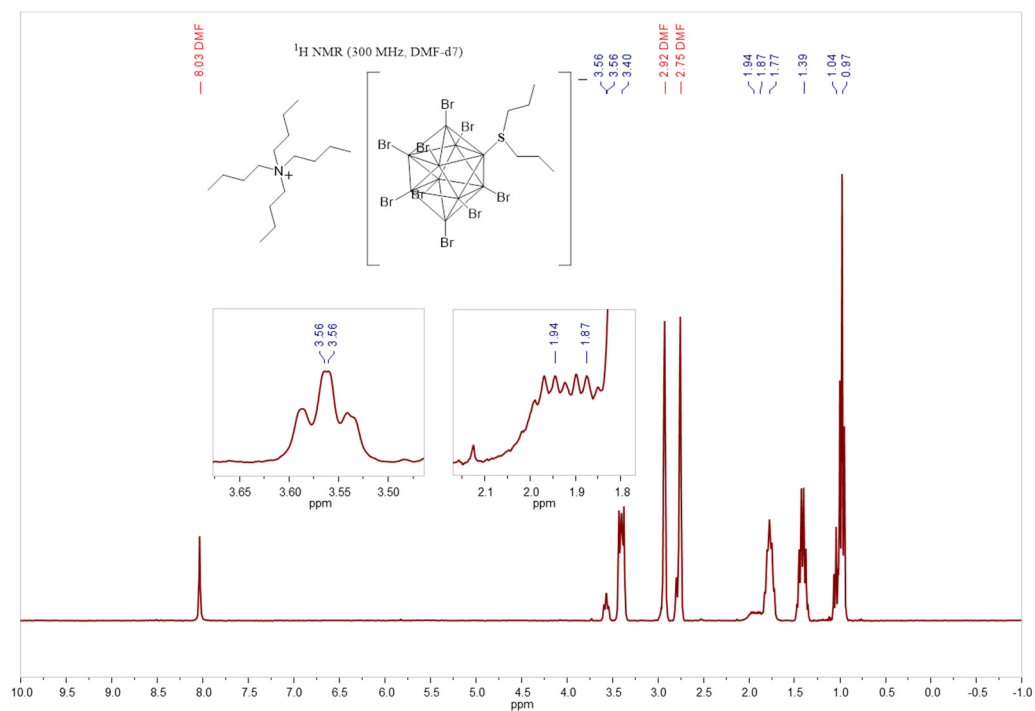


Figure S2. ^1H NMR spectrum of the compound **1** in DMF-d_7

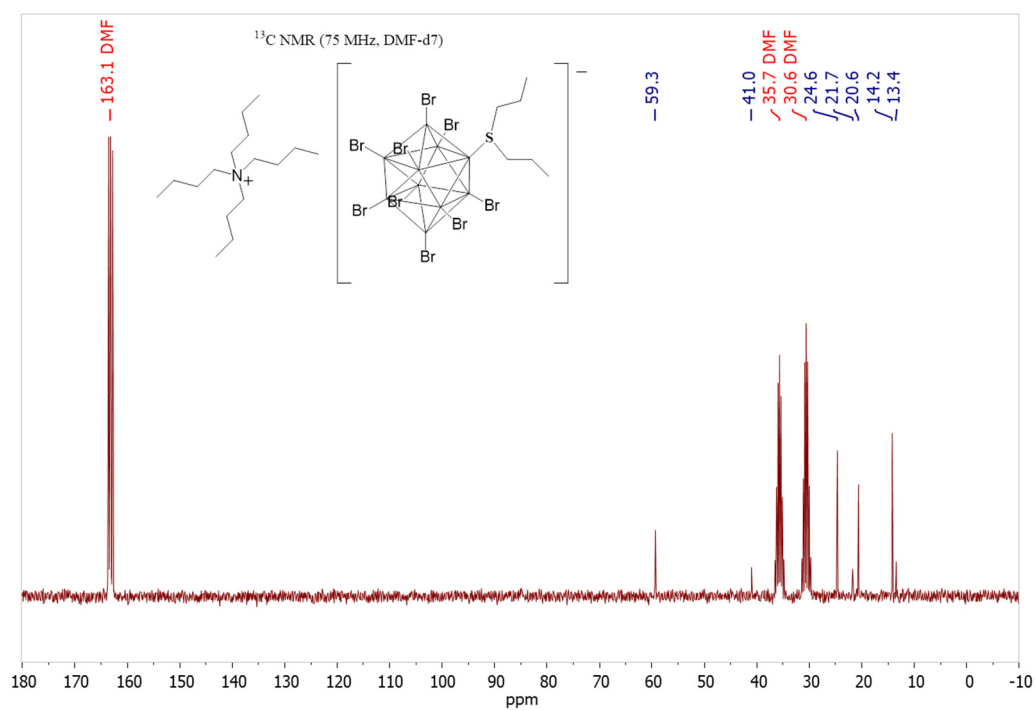


Figure S3. ^{13}C NMR spectrum of compound 1 in DMF- d_7

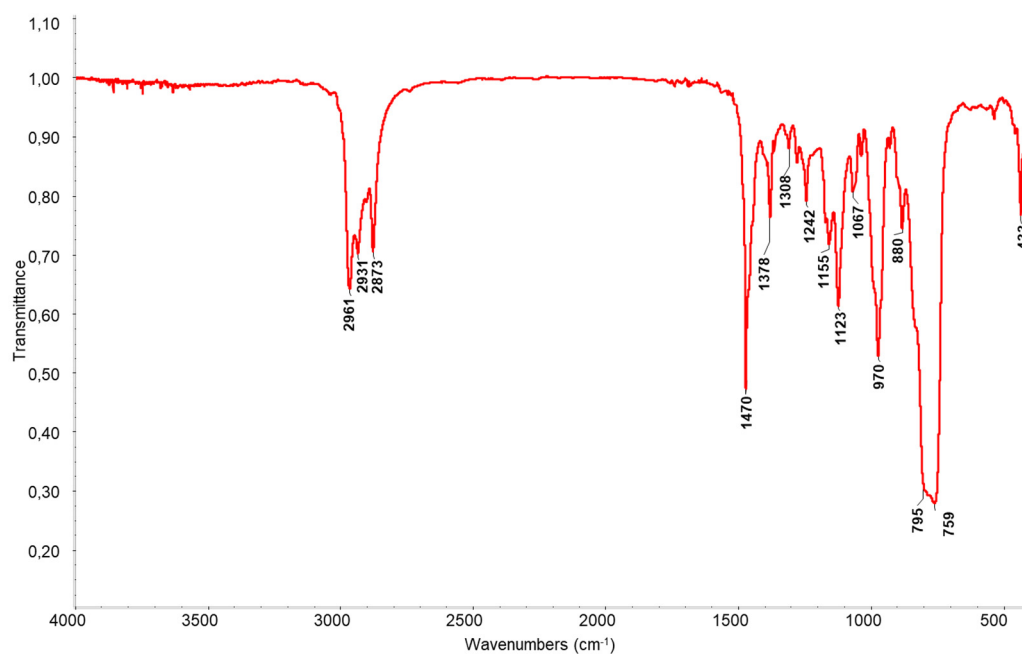


Figure S4. IR spectrum of the compound 1 in CCl_4

X-ray data

Table S1. Crystal data and structure refinement for compound **1**, **2**, **3**

Compound	(<i>n</i> -Bu ₄ N)[2-B ₁₀ Br ₉ S](<i>n</i> -Pr) ₂] (1)	(<i>n</i> -Bu ₄ N)[2-B ₁₀ Br ₉ S(<i>i</i> -Pr) ₂] (2)	(<i>n</i> -Bu ₄ N)[2-B ₁₀ Br ₉ S(<i>n</i> -Bu) ₂] (3)
Empirical formula	C ₂₂ H ₅₀ B ₁₀ Br ₉ NS	C ₂₂ H ₄₇ B ₁₀ Br ₉ NS	C ₂₄ H ₅₀ B ₁₀ Br ₉ SN _{0.5}
Formula weight	1187.98	1184.95	1204.99
Temperature/K	296	296	100
Crystal system	triclinic	triclinic	triclinic
Space group	P-1	P-1	P-1
a/Å	12.6658(3)	12.3314(8)	12.6289(8)
b/Å	12.8233(4)	12.8511(8)	12.7015(7)
c/Å	14.4929(4)	16.1993(10)	15.0571(9)
α/°	91.3600(10)	70.880(2)	90.755(2)
β/°	109.3590(10)	73.950(2)	111.322(2)
γ/°	107.6790(10)	62.054(2)	106.796(2)
Volume/Å ³	2095.57(10)	2119.3(2)	2134.9(2)
Z	2	2	2
ρ _{calc} /cm ³	1.883	1.857	1.874
μ/mm ⁻¹	8.676	8.578	8.517
F(000)	1140.0	1134.0	1157.0
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	4.82 to 55.64	3.69 to 50.63	4.468 to 55.992
Reflections collected	18556	15020	24397
Independent reflections	9649 [R _{int} = 0.0364, R _{sigma} = 0.0705]	7668 [R _{int} = 0.0366, R _{sigma} = 0.0714]	10176 [R _{int} = 0.0573, R _{sigma} = 0.0991]
Data/restraints/parameters	9649/0/394	7668/8/424	10176/0/412
Goodness-of-fit on F ²	0.964	1.037	0.954
Final R indexes [I>=2σ (I)]	R ₁ = 0.0408, wR ₂ = 0.0688	R ₁ = 0.0509, wR ₂ = 0.1158	R ₁ = 0.0485, wR ₂ = 0.0859
Final R indexes [all data]	R ₁ = 0.0879, wR ₂ = 0.0804	R ₁ = 0.1020, wR ₂ = 0.1331	R ₁ = 0.0937, wR ₂ = 0.0979
Largest diff. peak/hole / e Å ⁻³	0.61/-0.56	1.73/-1.44	1.15/-0.93

Table S1. Crystal data and structure refinement for compound **5**, **6**

Compound	(<i>n</i> -Bu ₄ N)[2-B ₁₀ Br ₉ S(<i>n</i> -C ₁₂ H ₂₅) ₂] (5)	(<i>n</i> -Bu ₄ N)[2-B ₁₀ Br ₉ S(<i>n</i> -C ₁₈ H ₃₇) ₂] (6)
Empirical formula	C ₄₀ H ₈₆ B ₁₀ Br ₉ NS	C ₅₂ H ₁₁₀ B ₁₀ Br ₉ NSO _{0.5}
Formula weight	1442.46	1616.75
Temperature/K	100	100
Crystal system	monoclinic	triclinic
Space group	P2 ₁ /c	P-1
a/Å	18.1779(6)	12.1587(3)
b/Å	12.7161(4)	12.3026(3)
c/Å	26.3463(10)	28.3917(7)
α/°	90.00	80.7610(10)
β/°	101.5690(10)	80.1370(10)
γ/°	90.00	62.6950(10)
Volume/Å³	5966.3(4)	3701.62(16)
Z	4	2
ρ_{calc}/cm³	1.606	1.451
μ/mm⁻¹	6.110	4.933
F(000)	2864.0	1628.0
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	3.58 to 52	3.742 to 52
Reflections collected	54265	31742
Independent reflections	11717 [R _{int} = 0.0649, R _{sigma} = 0.0665]	14366 [R _{int} = 0.0446, R _{sigma} = 0.0726]
Data/restraints/parameters	11717/0/556	14366/0/668
Goodness-of-fit on F²	1.014	1.030
Final R indexes [I>=2σ (I)]	R ₁ = 0.0447, wR ₂ = 0.0980	R ₁ = 0.0439, wR ₂ = 0.1099
Final R indexes [all data]	R ₁ = 0.0771, wR ₂ = 0.1108	R ₁ = 0.0688, wR ₂ = 0.1195
Largest diff. peak/hole / e Å⁻³	1.13/-0.84	1.13/-0.78

Powder XRD data

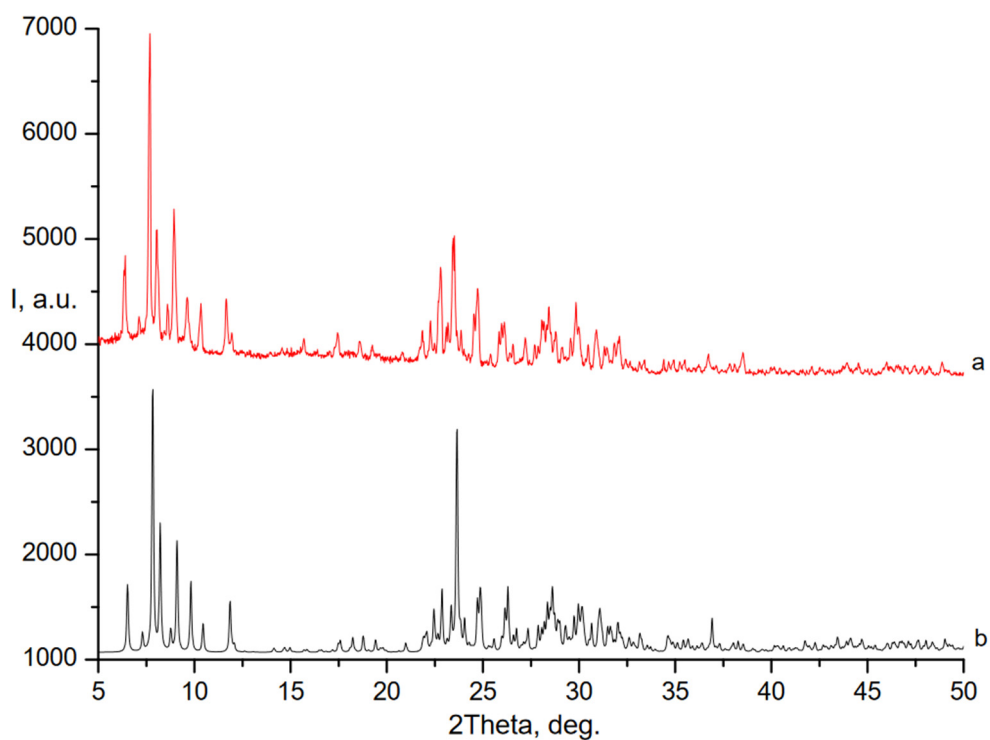


Figure S5. powder XRD data of the compound $(n\text{-Bu}_4\text{N})[2\text{-B}_{10}\text{Br}_9\text{S}(n\text{-Pr})_2]$.
a - experimental, b – theoretical

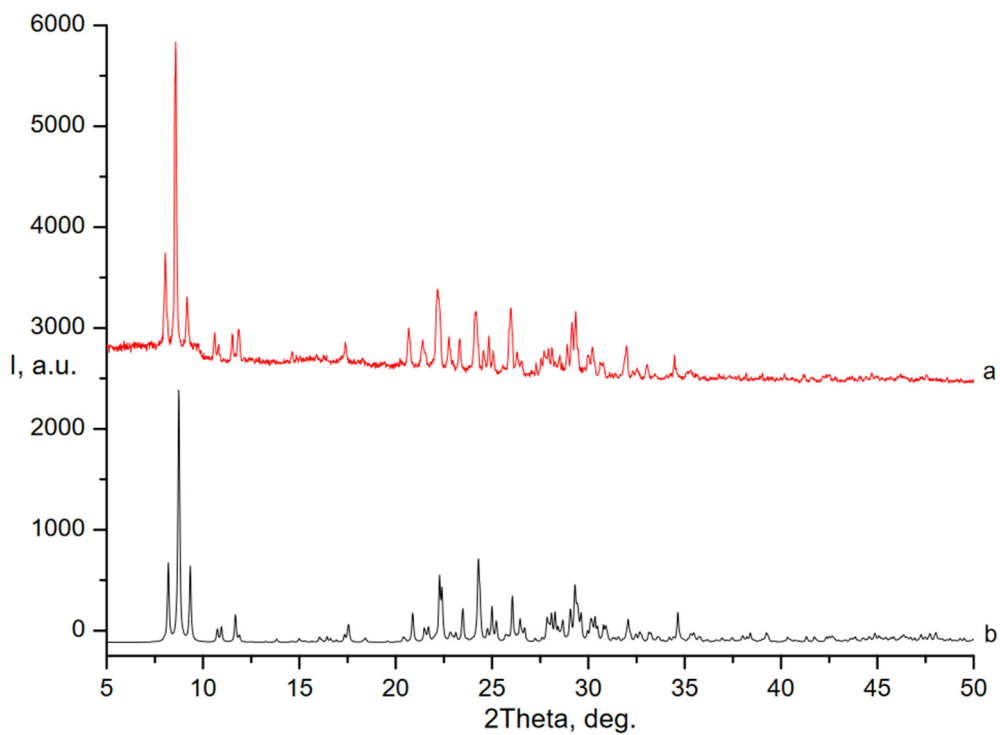


Figure S6. powder XRD data of the compound $(n\text{-Bu}_4\text{N})[2\text{-B}_{10}\text{Br}_9\text{S}(i\text{-Pr})_2]$.
a - experimental, b – theoretical

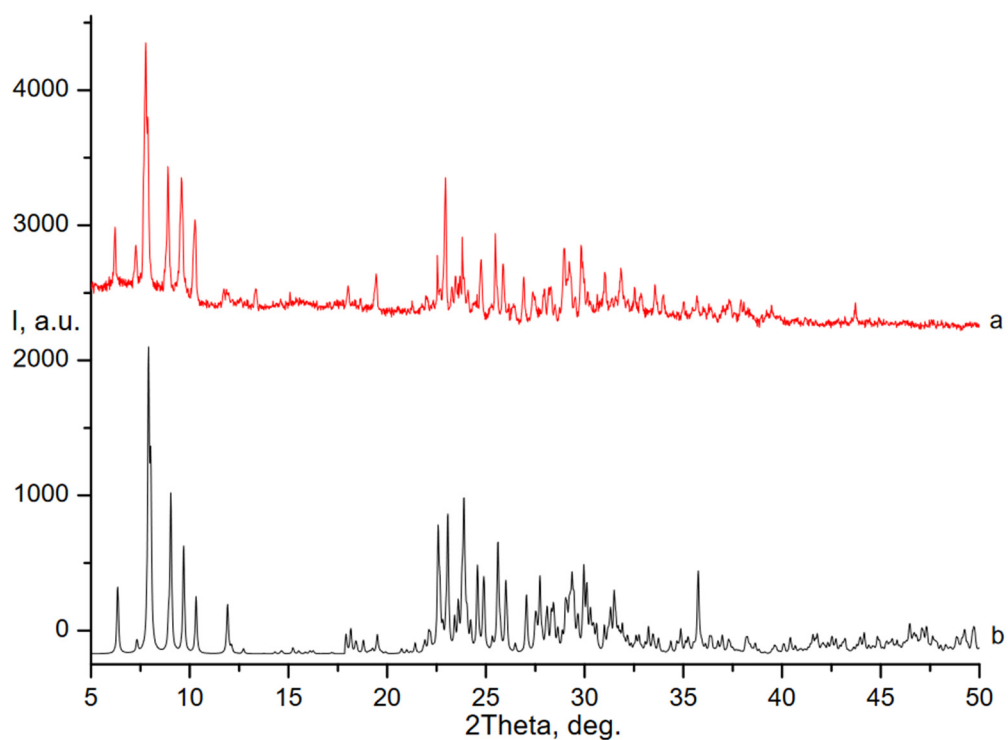


Figure S7. powder XRD data of the compound $(n\text{-Bu}_4\text{N})[2\text{-B}_{10}\text{Br}_9\text{S}(n\text{-Bu})_2]$.
a - experimental, b – theoretical

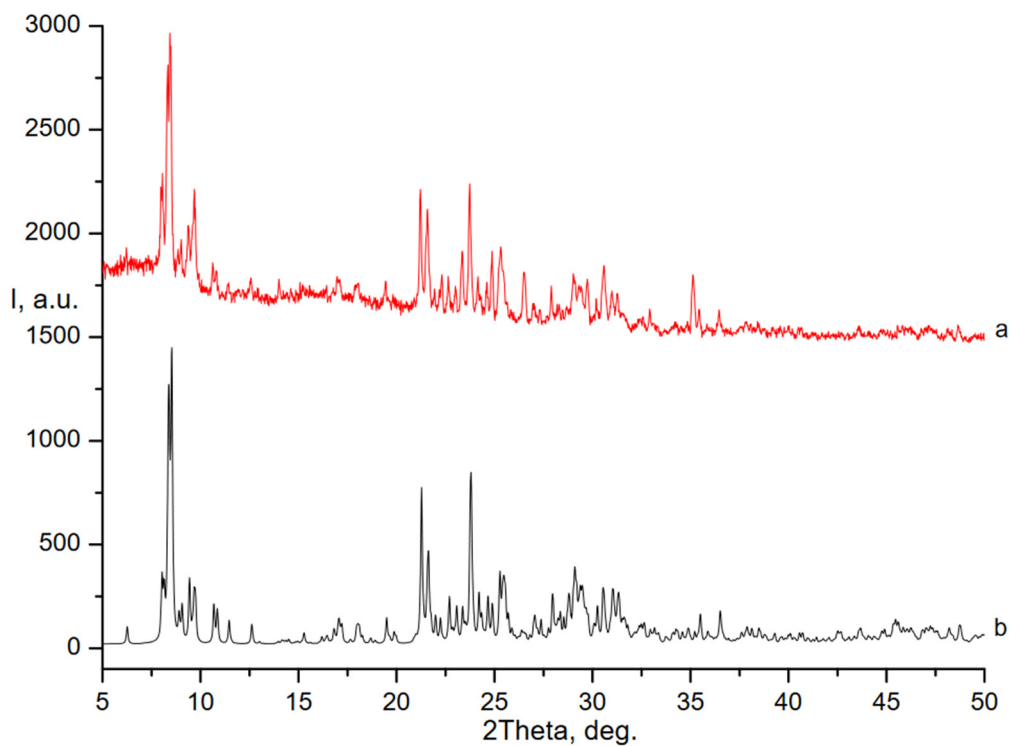


Figure S8. powder XRD data of the compound $(n\text{-Bu}_4\text{N})[2\text{-B}_{10}\text{Br}_9\text{S}(n\text{-C}_8\text{H}_{17})_2]$.
a - experimental, b – theoretical

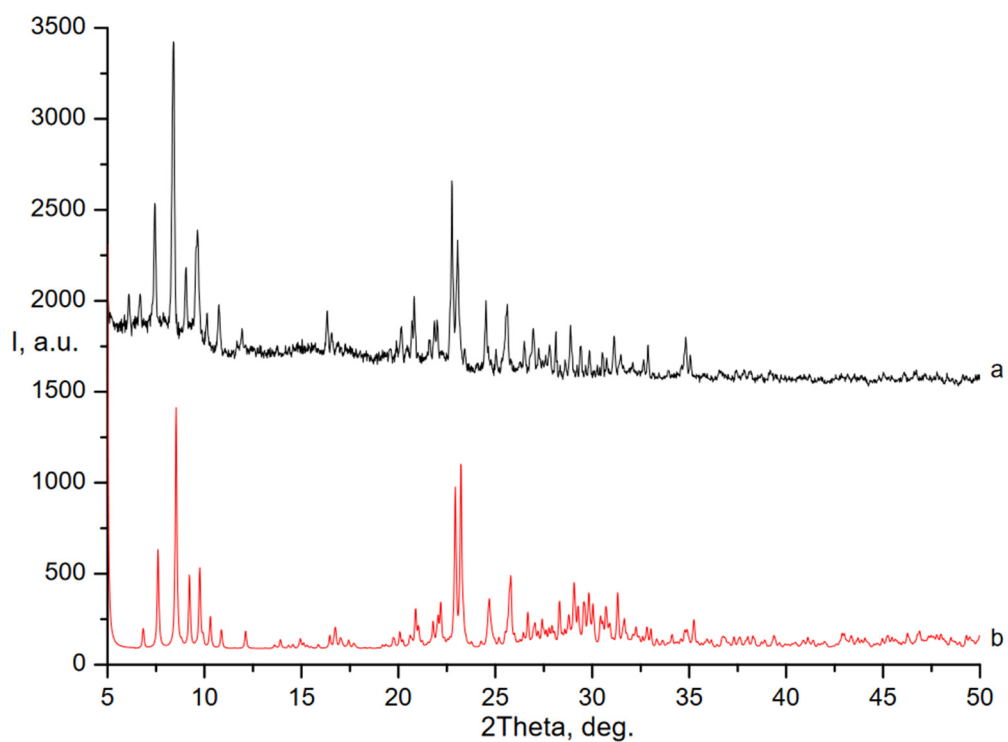


Figure S9. powder XRD data of the compound $(n\text{-Bu}_4\text{N})[2\text{-B}_{10}\text{Br}_9\text{S}(n\text{-C}_{12}\text{H}_{25})_2]$.
a - experimental, b – theoretical

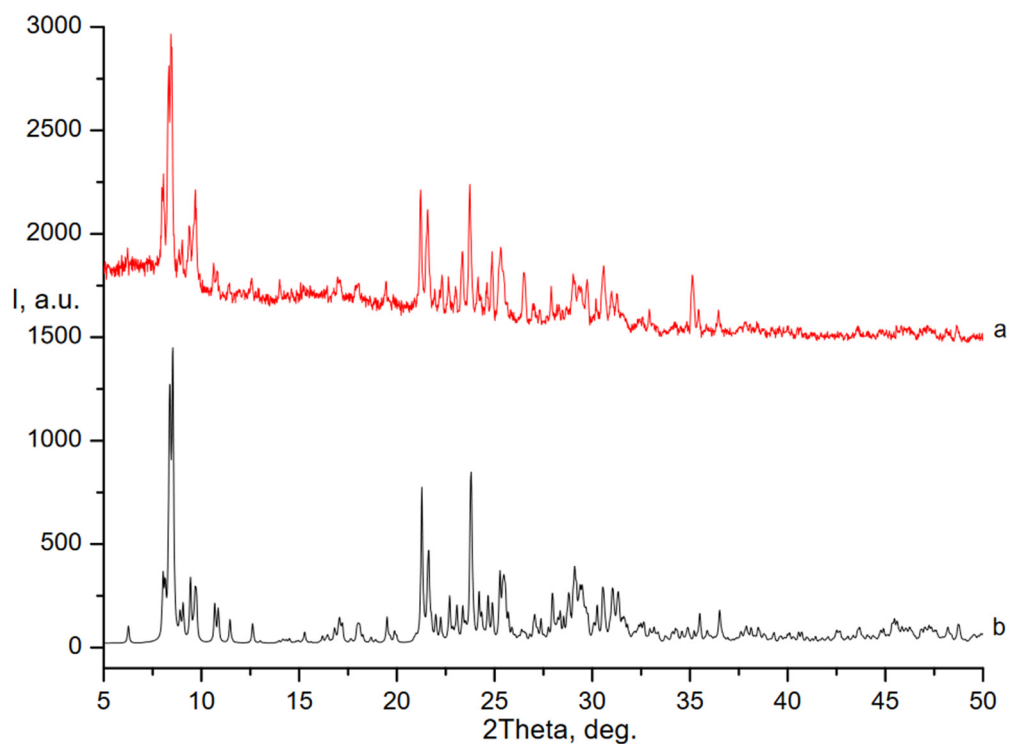


Figure S10. powder XRD data of the compound $(n\text{-Bu}_4\text{N})[2\text{-B}_{10}\text{Br}_9\text{S}(n\text{-C}_{18}\text{H}_{37})_2]$.
a - experimental, b – theoretical

NMR and IR spectra

$(n\text{-Bu}_4\text{N})[\text{B}_{10}\text{Br}_9\text{S}(i\text{-Pr})_2]$

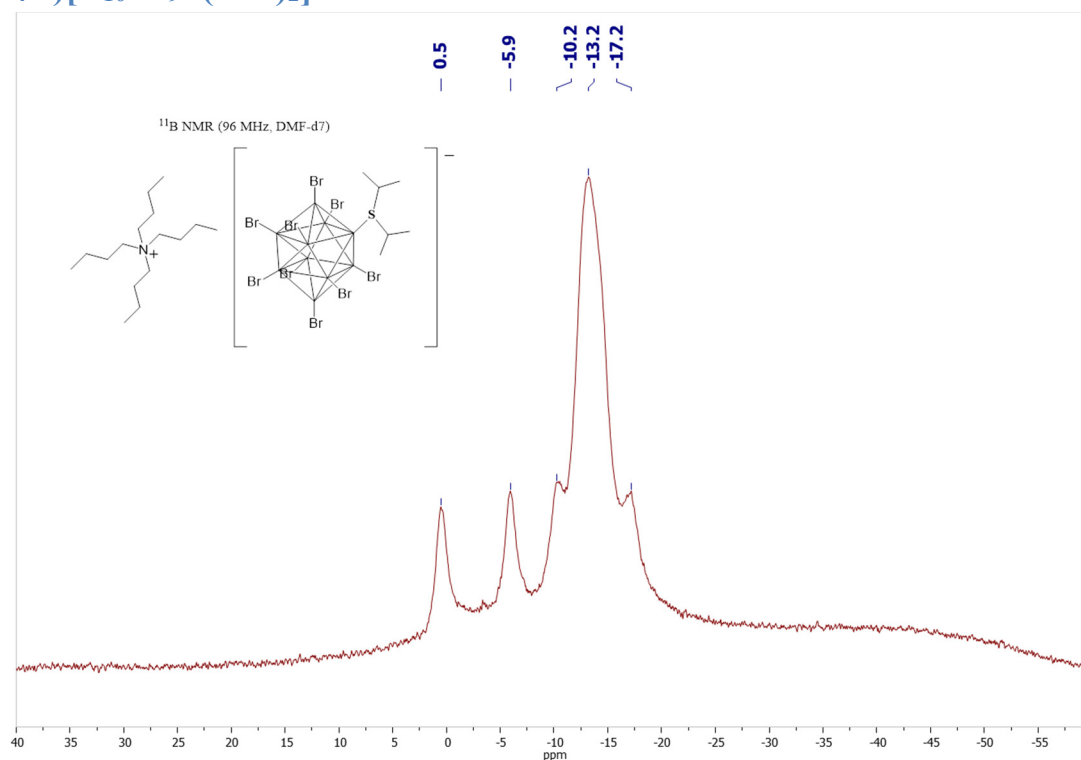


Figure S11. ^{11}B NMR spectrum (DMF- d_7 , 96.32 MHz) of $(\text{Bu}_4\text{N})[2\text{-B}_{10}\text{Br}_9\text{S}(i\text{-Pr})_2]$

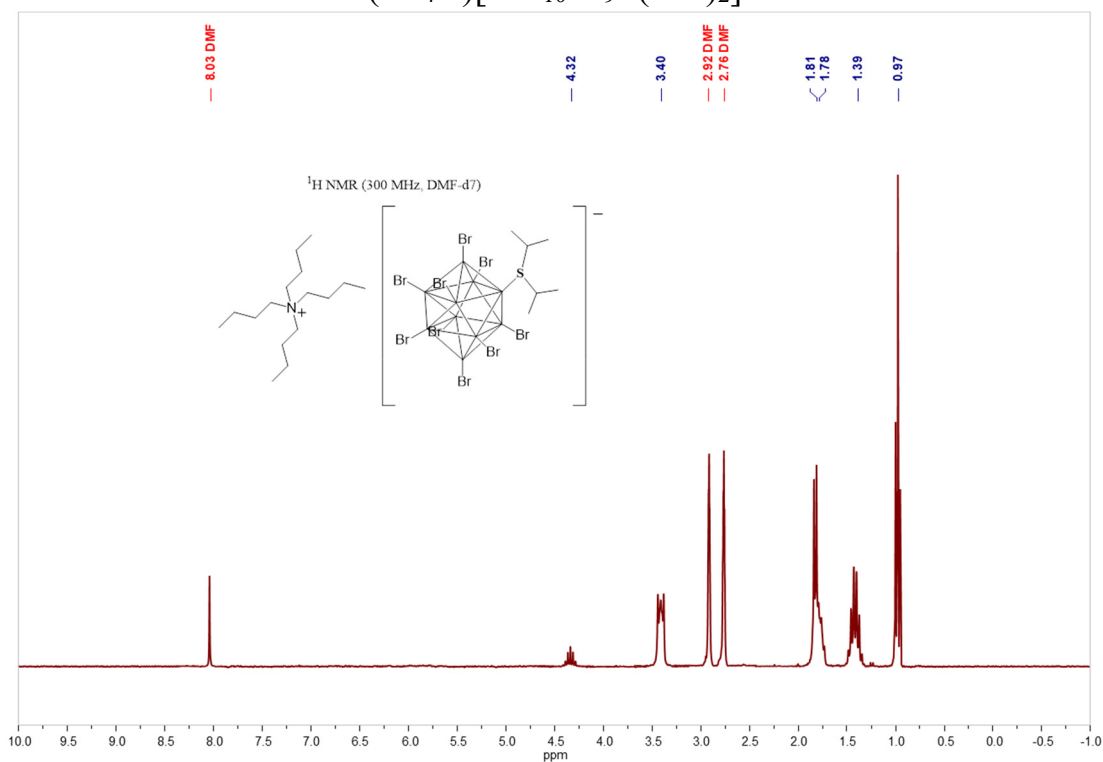


Figure S12. ^1H NMR spectrum (DMF- d_7 , 300.3 MHz) of $(n\text{-Bu}_4\text{N})[2\text{-B}_{10}\text{Br}_9\text{S}(i\text{-Pr})_2]$

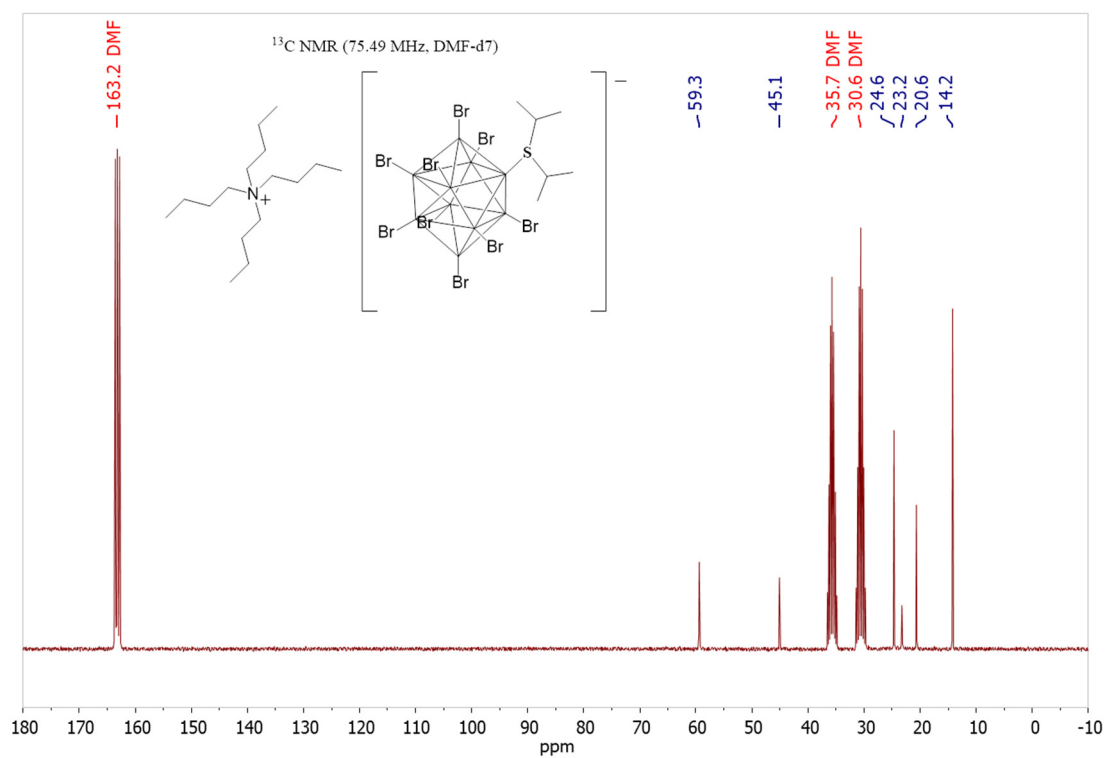


Figure S13. ¹³C NMR spectrum (DMF-d₇, 75.49 MHz) of $(n\text{-Bu}_4\text{N})[2\text{-B}_{10}\text{Br}_9\text{S}(i\text{-Pr})_2]$

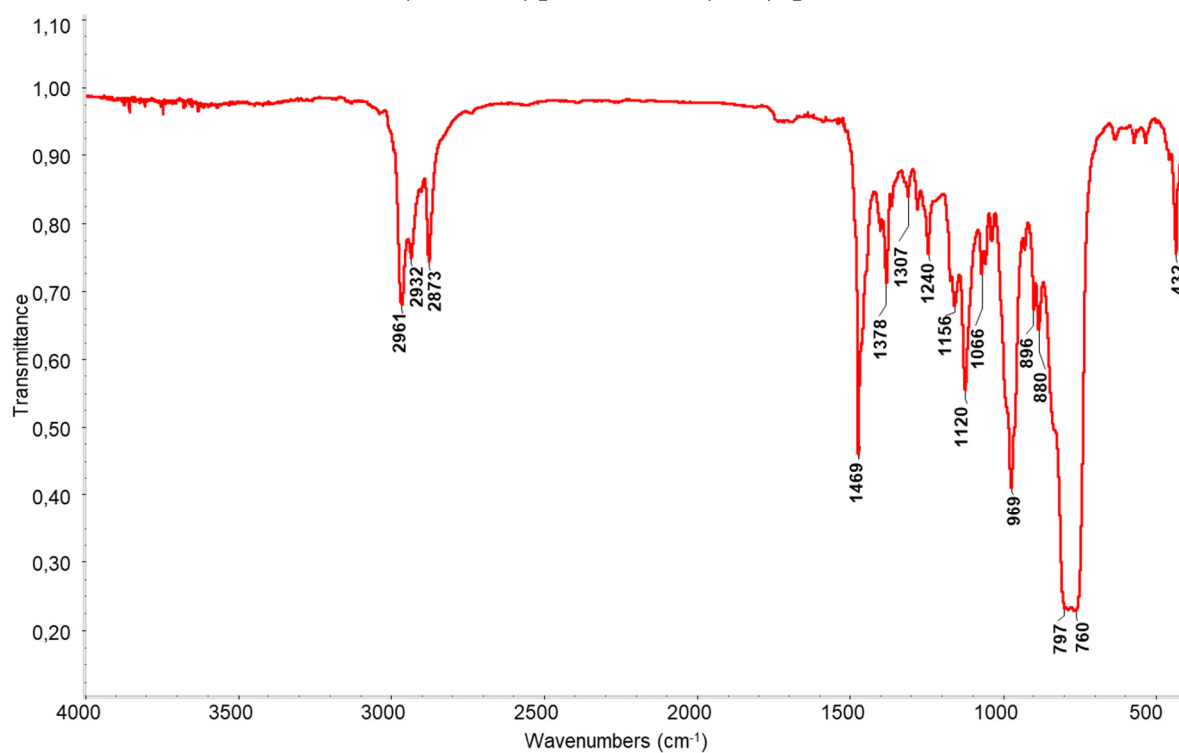


Figure S14. IR spectra (in CCl₄) of $(n\text{-Bu}_4\text{N})[2\text{-B}_{10}\text{Br}_9\text{S}(i\text{-Pr})_2]$

(*n*-Bu₄N)[2-B₁₀Br₉S(*n*-Pr)₂]

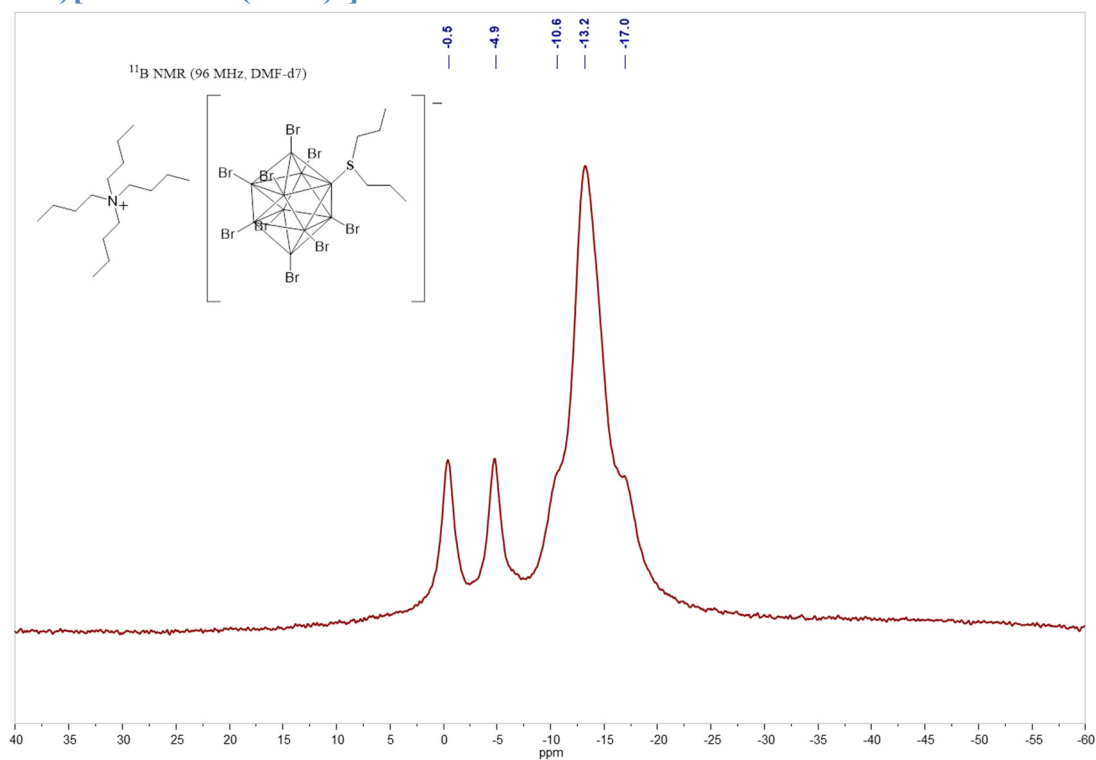


Figure S15. ^{11}B NMR spectrum (DMF- d_7 , 96.32 MHz) of $(n\text{-Bu}_4\text{N})[2\text{-B}_{10}\text{Br}_9\text{S}(n\text{-Pr})_2]$

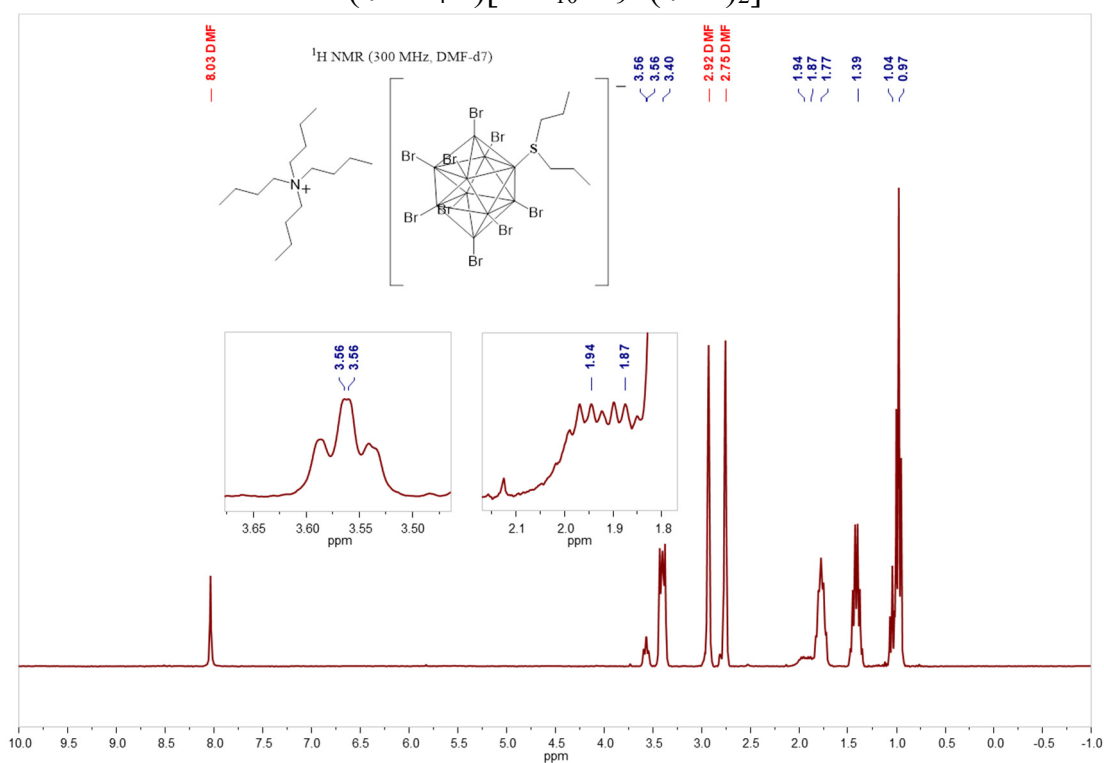


Figure S16. ^1H NMR spectrum (DMF- d_7 , 300.3 MHz) of $(n\text{-Bu}_4\text{N})[2\text{-B}_{10}\text{Br}_9\text{S}(n\text{-Pr})_2]$

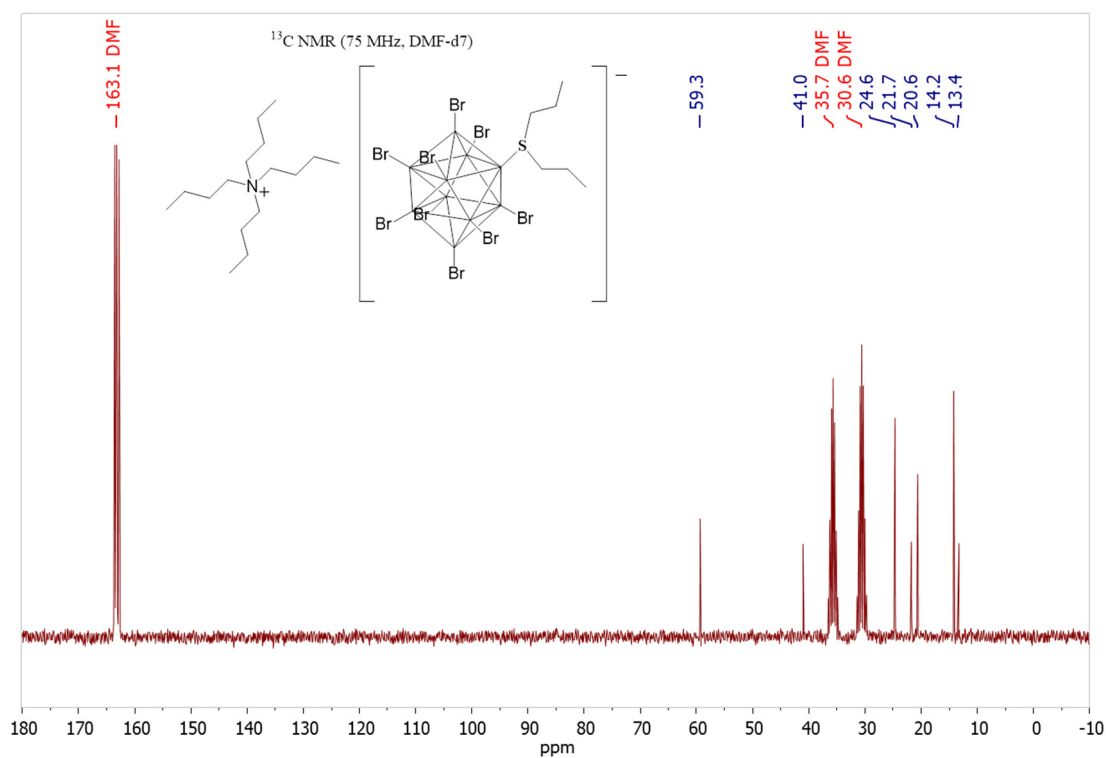


Figure S17. ¹³C NMR spectrum (DMF-d₇, 75.49 MHz) of $(n\text{-Bu}_4\text{N})[2\text{-B}_{10}\text{Br}_9\text{S}(n\text{-Pr})_2]$

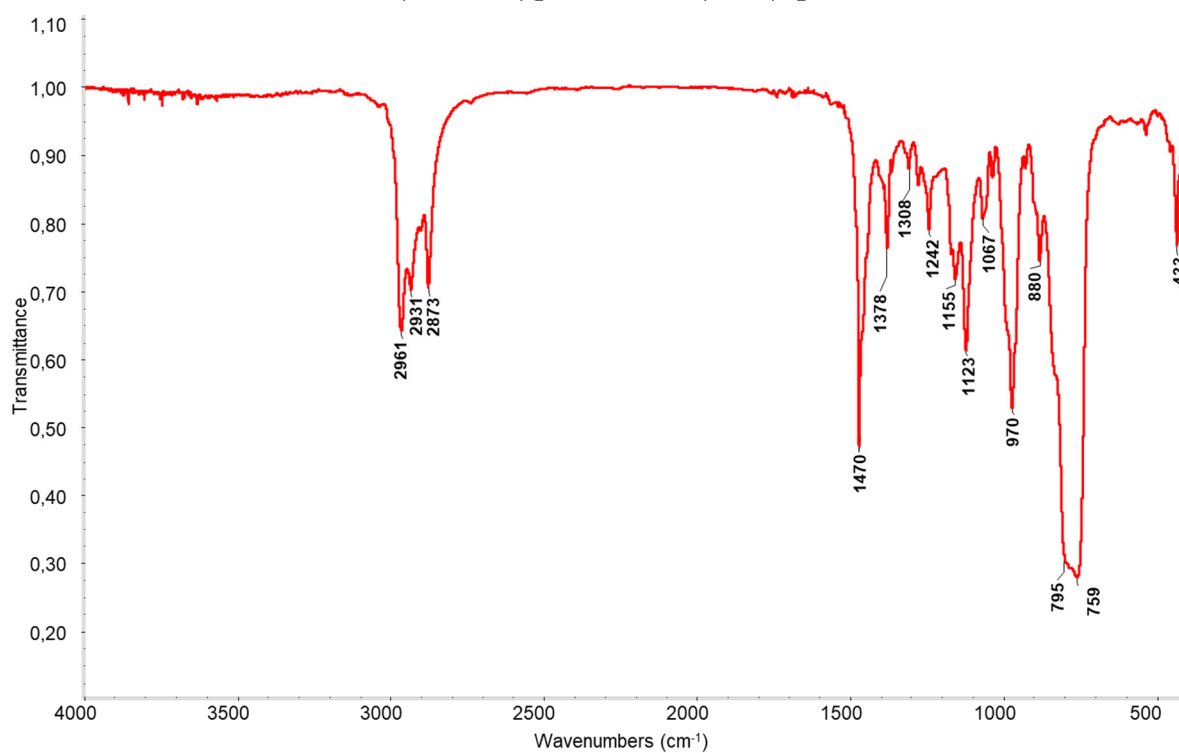


Figure S18. IR spectra (in CCl₄) of $(n\text{-Bu}_4\text{N})[2\text{-B}_{10}\text{Br}_9\text{S}(n\text{-Pr})_2]$

$(n\text{-Bu}_4\text{N})[2\text{-B}_{10}\text{Br}_9\text{S}(n\text{-Bu})_2]$

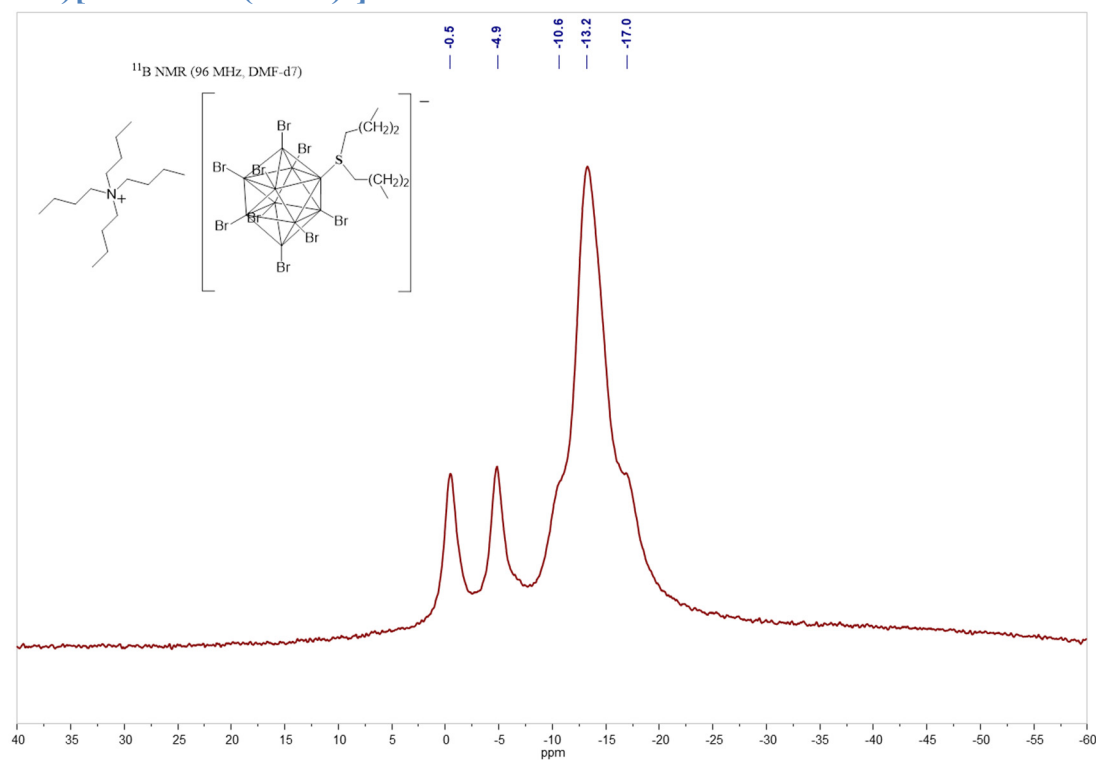


Figure S19. ^{11}B NMR spectrum (DMF- d_7 , 96.32 MHz) of $(n\text{-Bu}_4\text{N})[2\text{-B}_{10}\text{Br}_9\text{S}(n\text{-Bu})_2]$

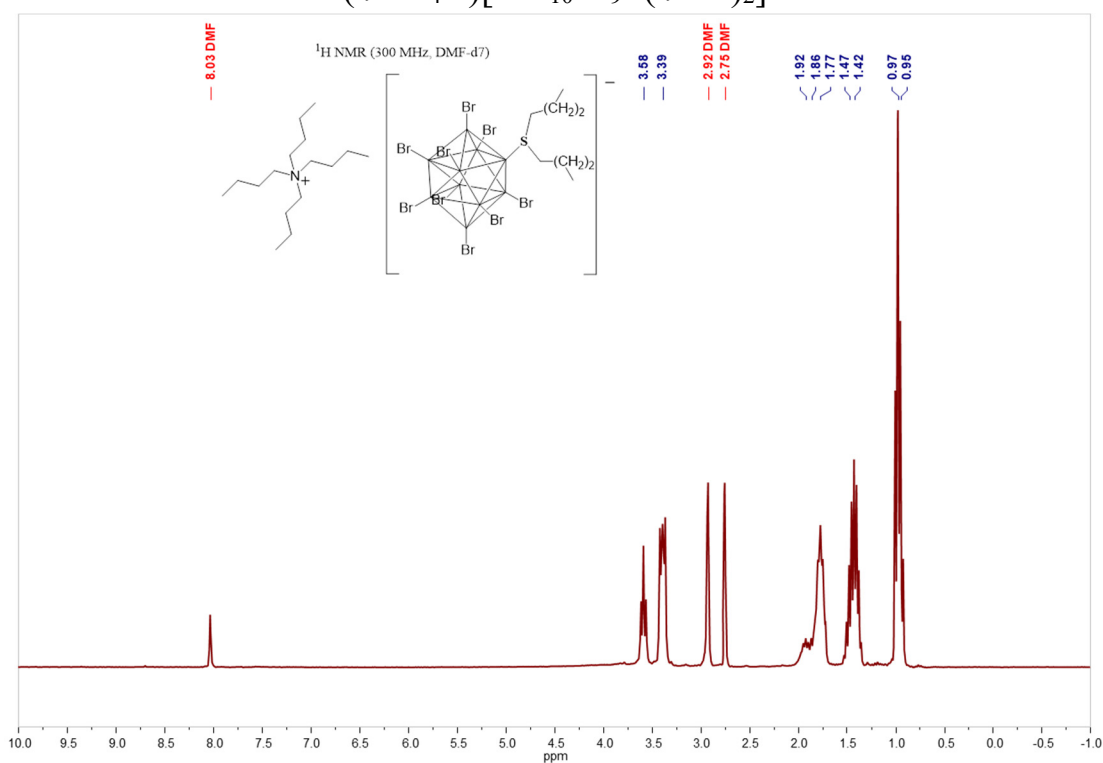


Figure S20. ^1H NMR spectrum (DMF- d_7 , 300.3 MHz) of $(n\text{-Bu}_4\text{N})[2\text{-B}_{10}\text{Br}_9\text{S}(n\text{-Bu})_2]$

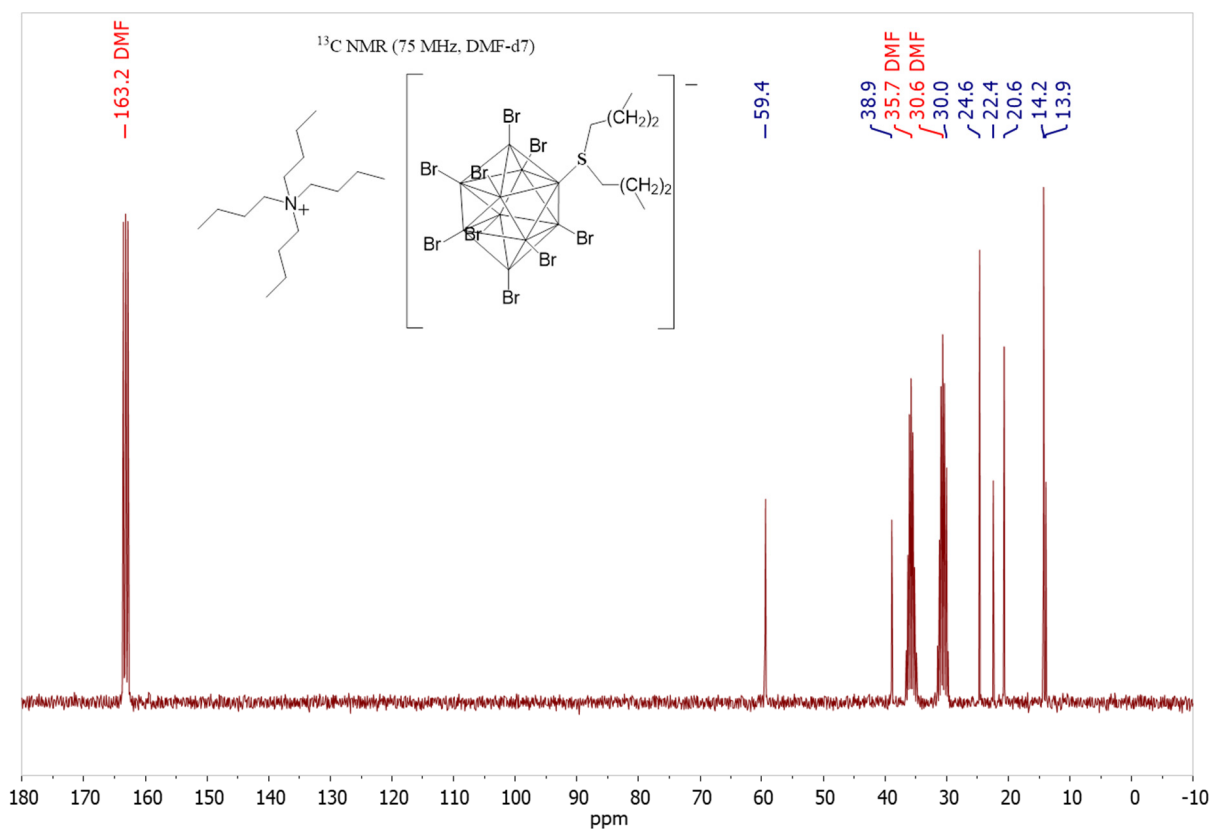


Figure S21. ¹³C NMR spectrum (DMF-d₇, 75.49 MHz) of $(n\text{-Bu}_4\text{N})[2\text{-B}_{10}\text{Br}_9\text{S}(n\text{-Bu})_2]$

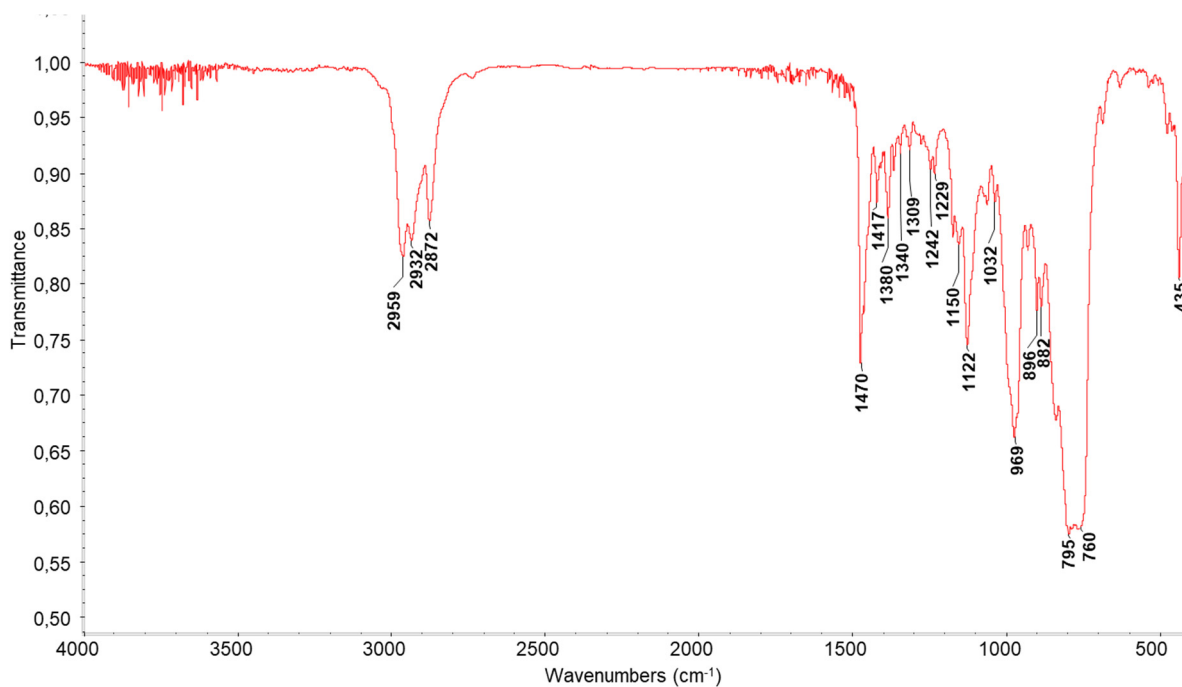


Figure S22. IR spectra (in CCl₄) of $(n\text{-Bu}_4\text{N})[2\text{-B}_{10}\text{Br}_9\text{S}(n\text{-Bu})_2]$

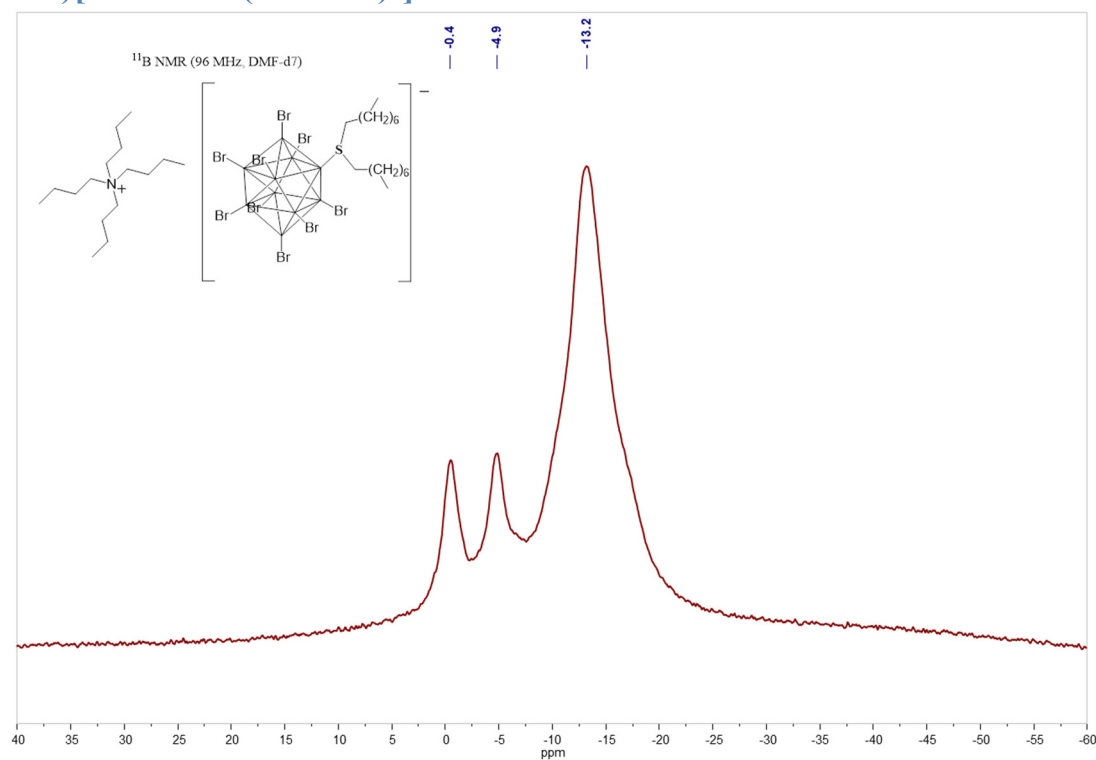


Figure S23. ^{11}B NMR spectrum (DMF- d_7 , 96.32 MHz) of $(n\text{-Bu}_4\text{N})[2\text{-B}_{10}\text{Br}_9\text{S}(n\text{-C}_8\text{H}_{17})_2]$

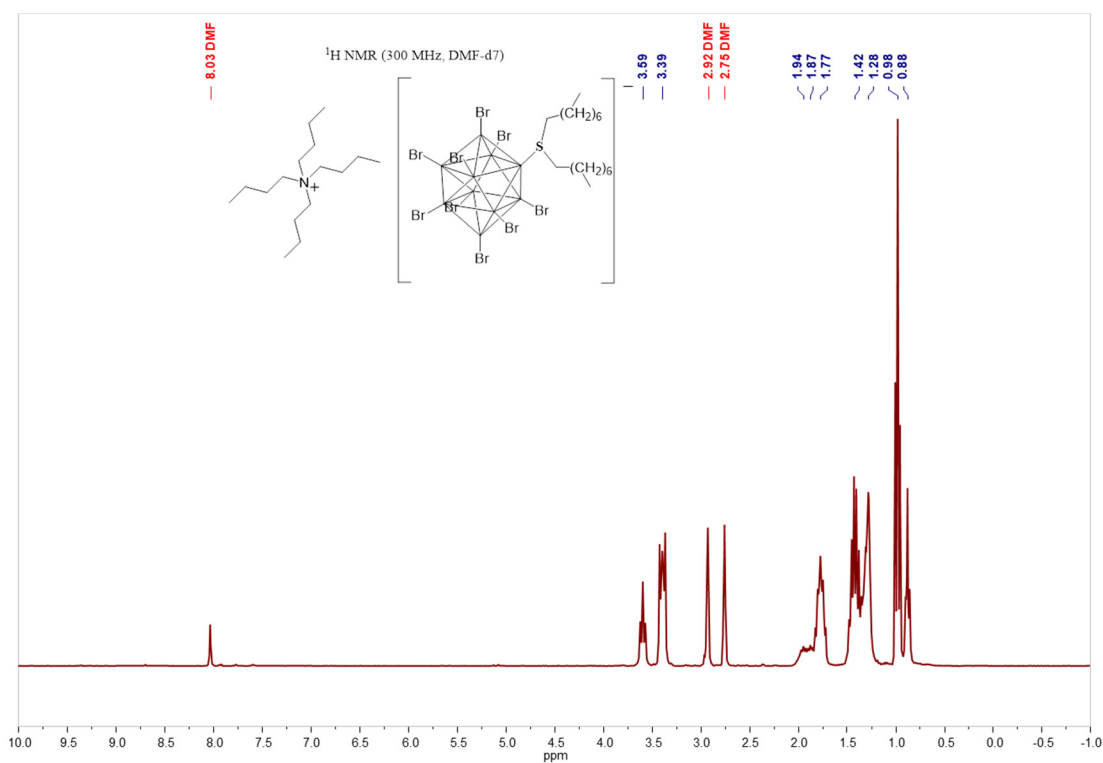


Figure S24. ^1H NMR spectrum (DMF- d_7 , 300.3 MHz) of $(n\text{-Bu}_4\text{N})[2\text{-B}_{10}\text{Br}_9\text{S}(n\text{-C}_8\text{H}_{17})_2]$

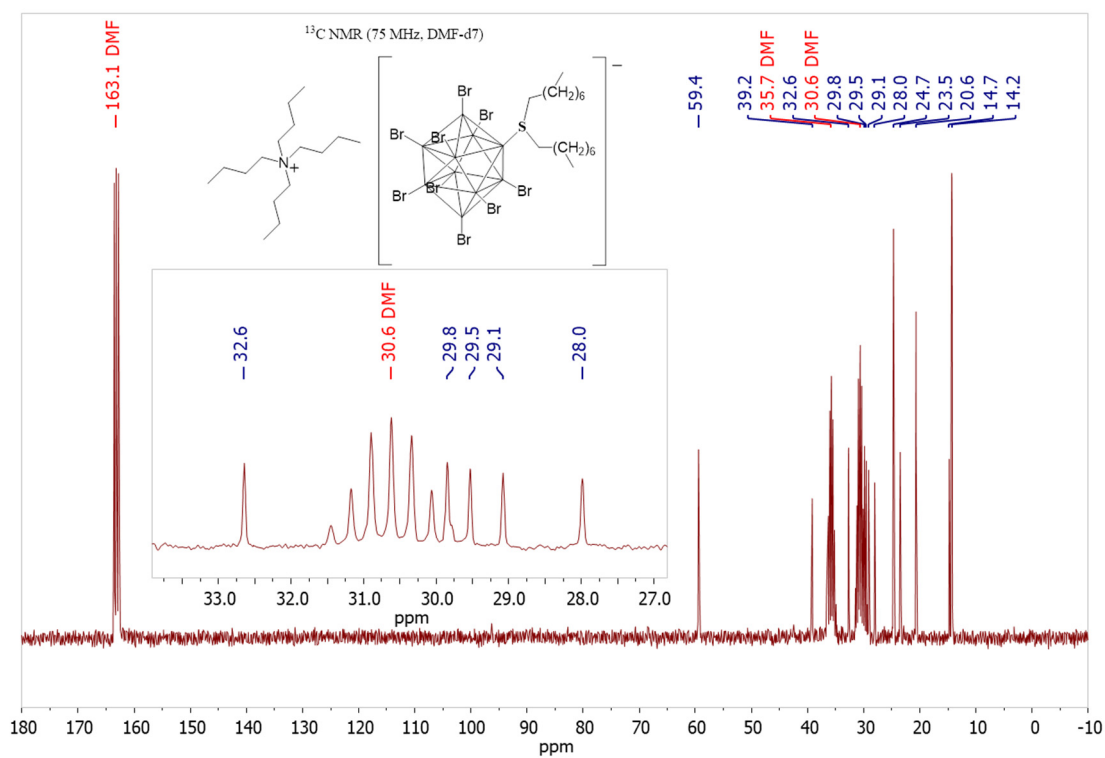


Figure S25. ¹³C NMR spectrum (DMF-d₇, 75.49 MHz) of $(n\text{-Bu}_4\text{N})[2\text{-B}_{10}\text{Br}_9\text{S}(\text{n-C}_8\text{H}_{17})_2]$

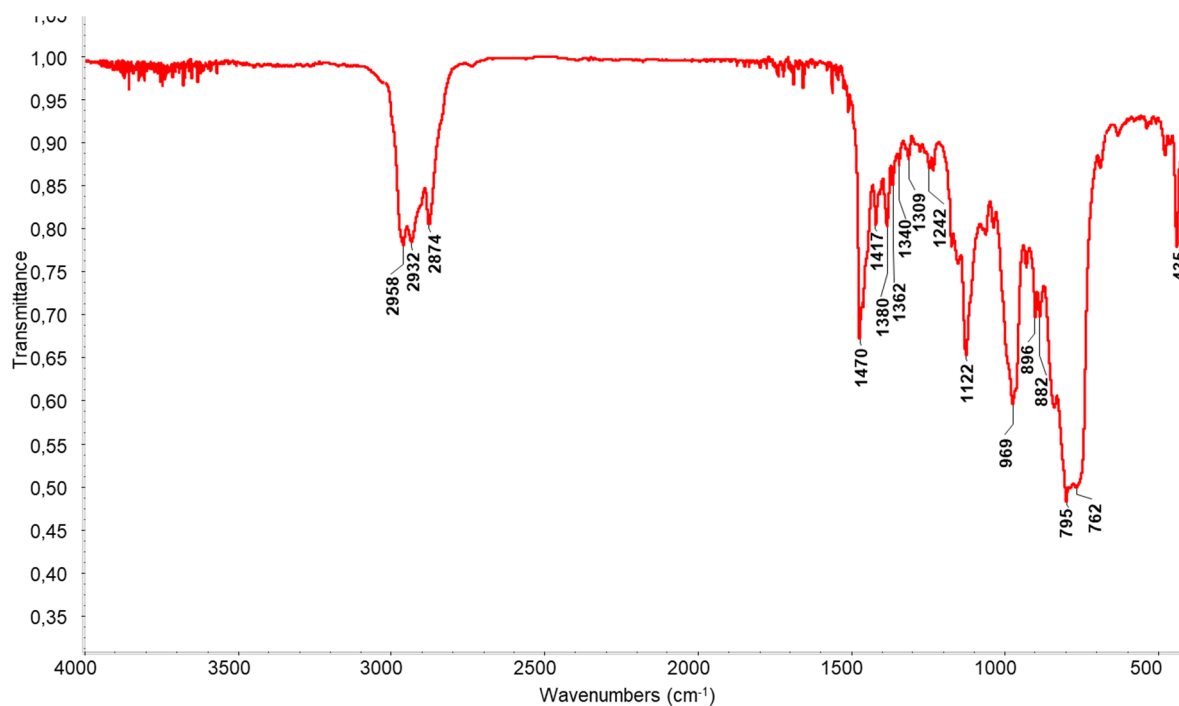


Figure S26. IR spectra (in CCl₄) of $(n\text{-Bu}_4\text{N})[2\text{-B}_{10}\text{Br}_9\text{S}(\text{n-C}_8\text{H}_{17})_2]$

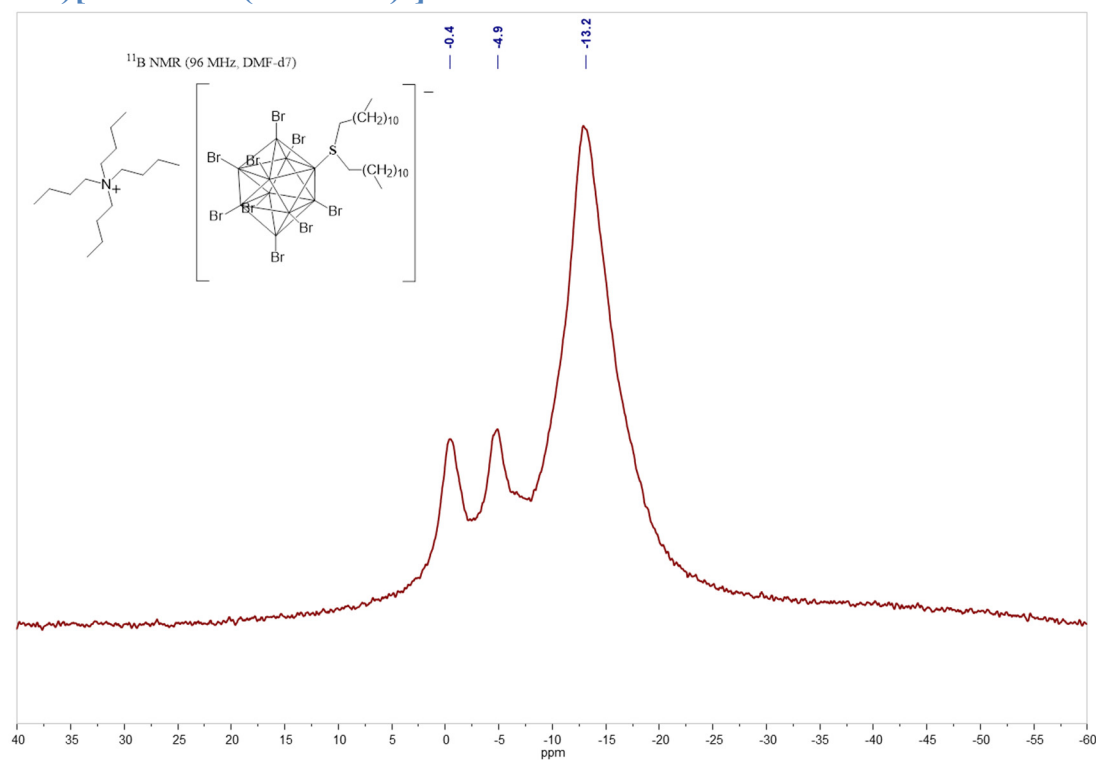


Figure S27. ^{11}B NMR spectrum (DMF- d_7 , 96.32 MHz) of $(n\text{-Bu}_4\text{N})[2\text{-B}_{10}\text{Br}_9\text{S}(n\text{-C}_{12}\text{H}_{25})_2]$

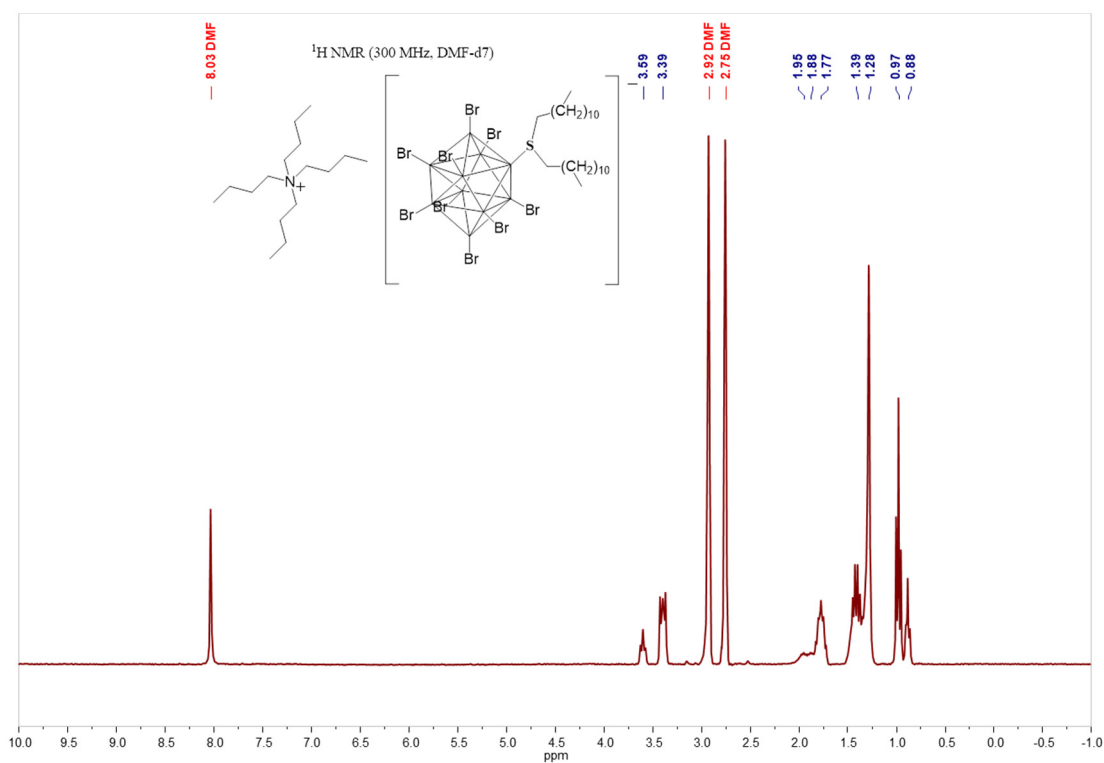


Figure S28. ^1H NMR spectrum (DMF- d_7 , 300.3 MHz) of $(n\text{-Bu}_4\text{N})[2\text{-B}_{10}\text{Br}_9\text{S}(n\text{-C}_{12}\text{H}_{25})_2]$

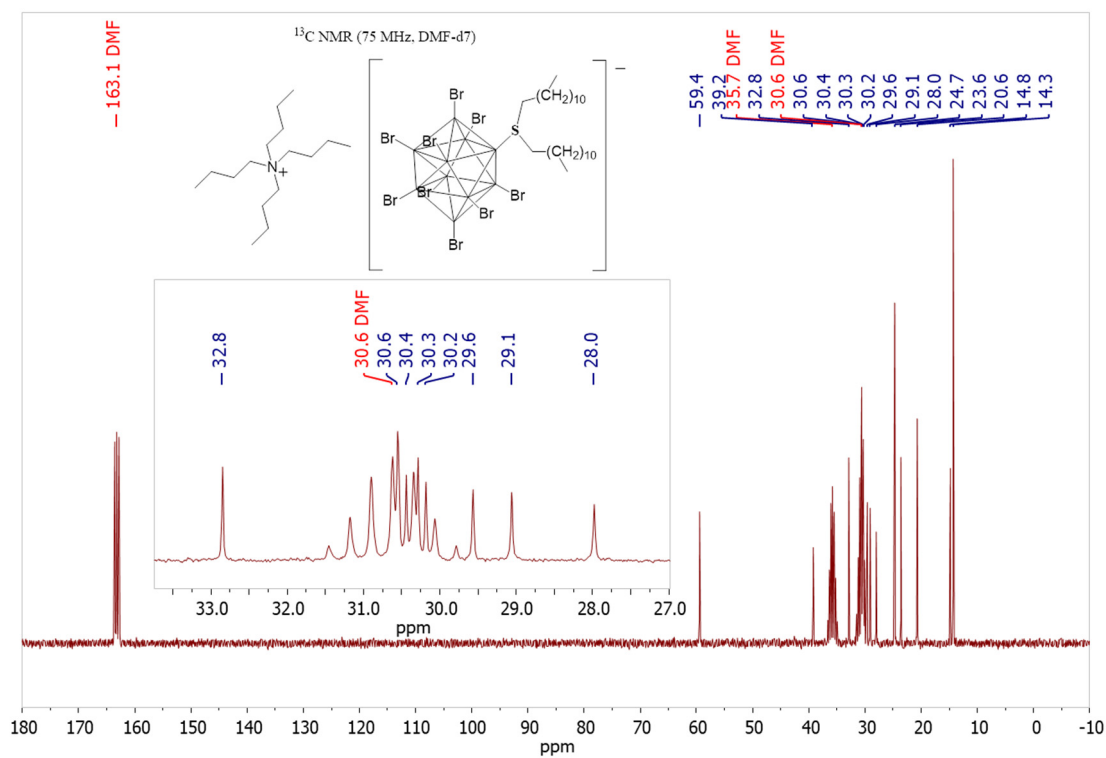


Figure S29. ¹³C NMR spectrum (DMF-d₇, 75.49 MHz) of (n-Bu₄N)[2-B₁₀Br₉S(n-C₁₂H₂₅)₂]

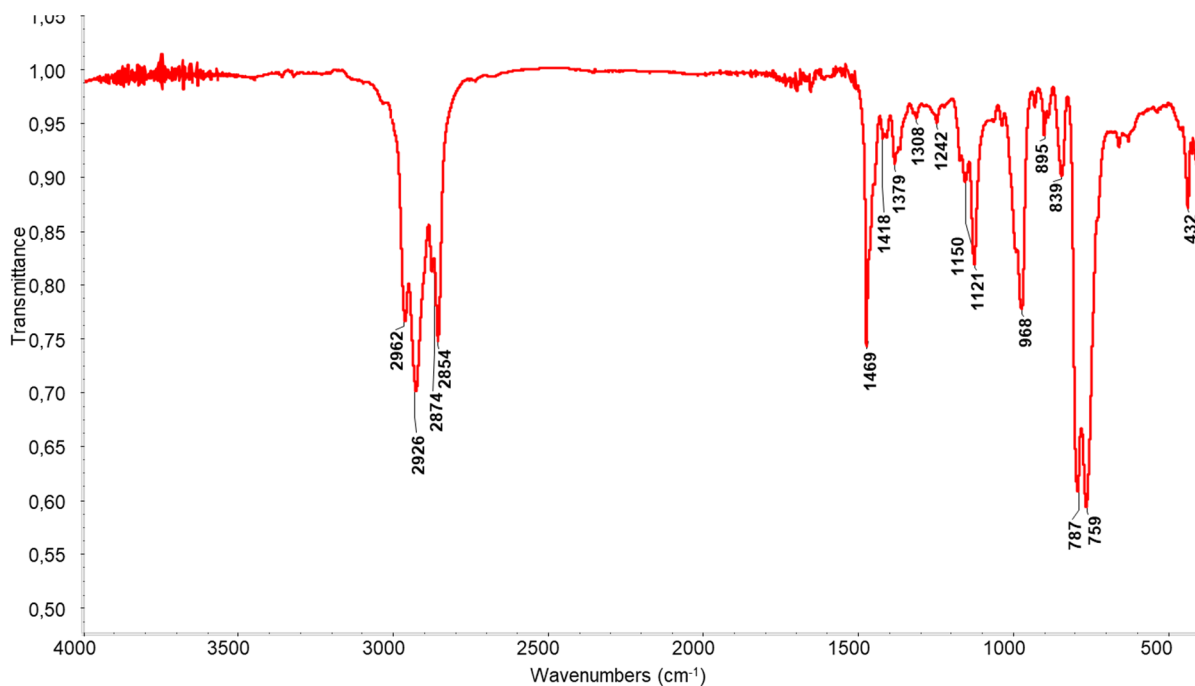


Figure S30. IR spectra (in CCl₄) of (n-Bu₄N)[2-B₁₀Br₉S(n-C₁₂H₂₅)₂]

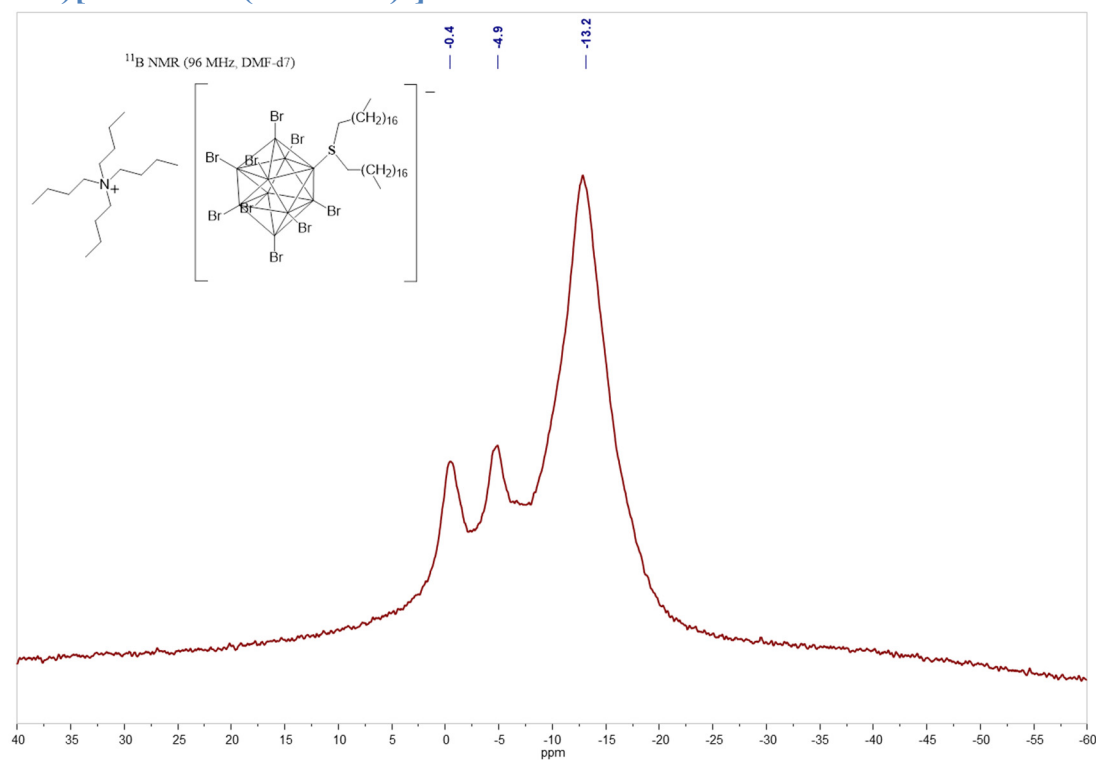


Figure S31. ^{11}B NMR spectrum (DMF- d_7 , 96.32 MHz) of $(n\text{-Bu}_4\text{N})[2\text{-B}_{10}\text{Br}_9\text{S}(n\text{-C}_{18}\text{H}_{37})_2]$

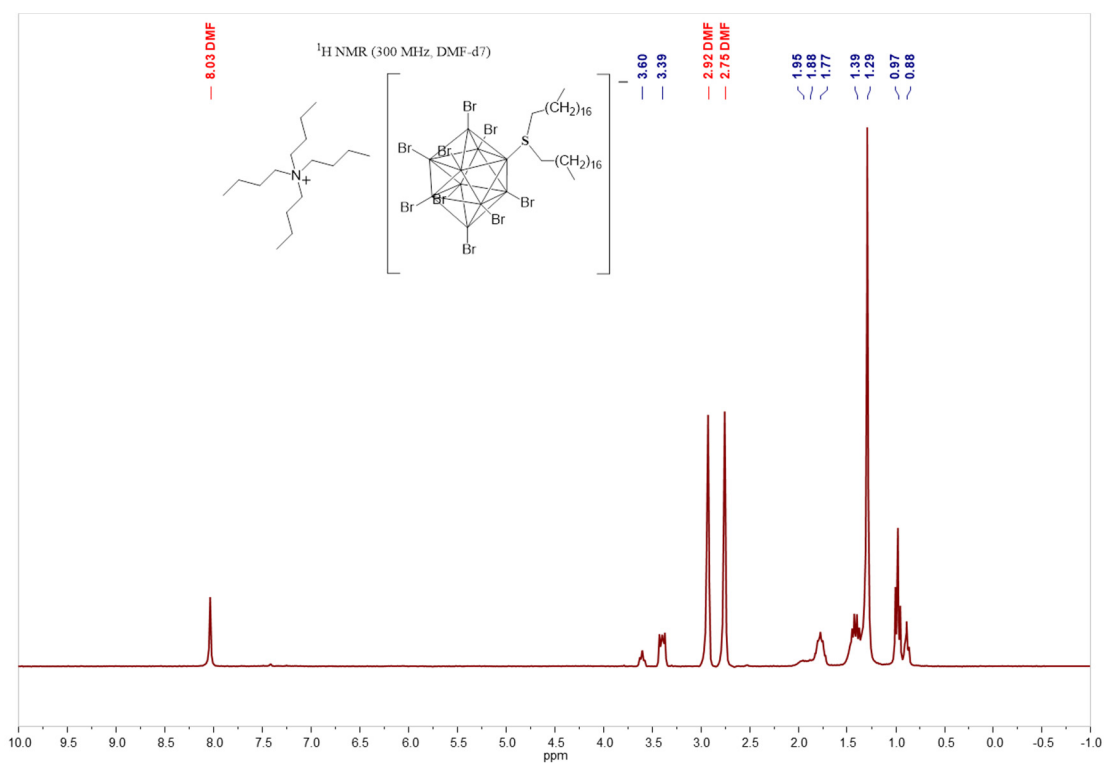


Figure S32. ^1H NMR spectrum (DMF- d_7 , 300.3 MHz) of $(n\text{-Bu}_4\text{N})[2\text{-B}_{10}\text{Br}_9\text{S}(n\text{-C}_{18}\text{H}_{37})_2]$

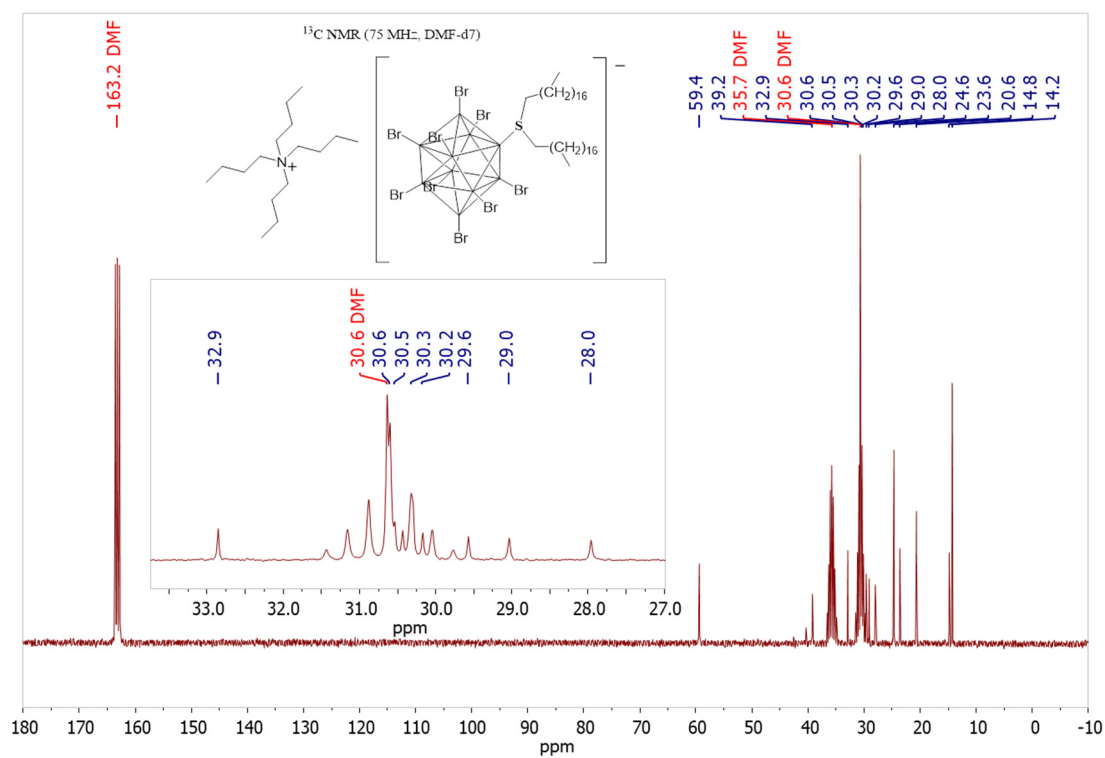


Figure S33. ¹³C NMR spectrum (DMF-d₇, 75.49 MHz) of $(n\text{-Bu}_4\text{N})[2\text{-B}_{10}\text{Br}_9\text{S}(n\text{-C}_{18}\text{H}_{37})_2]$

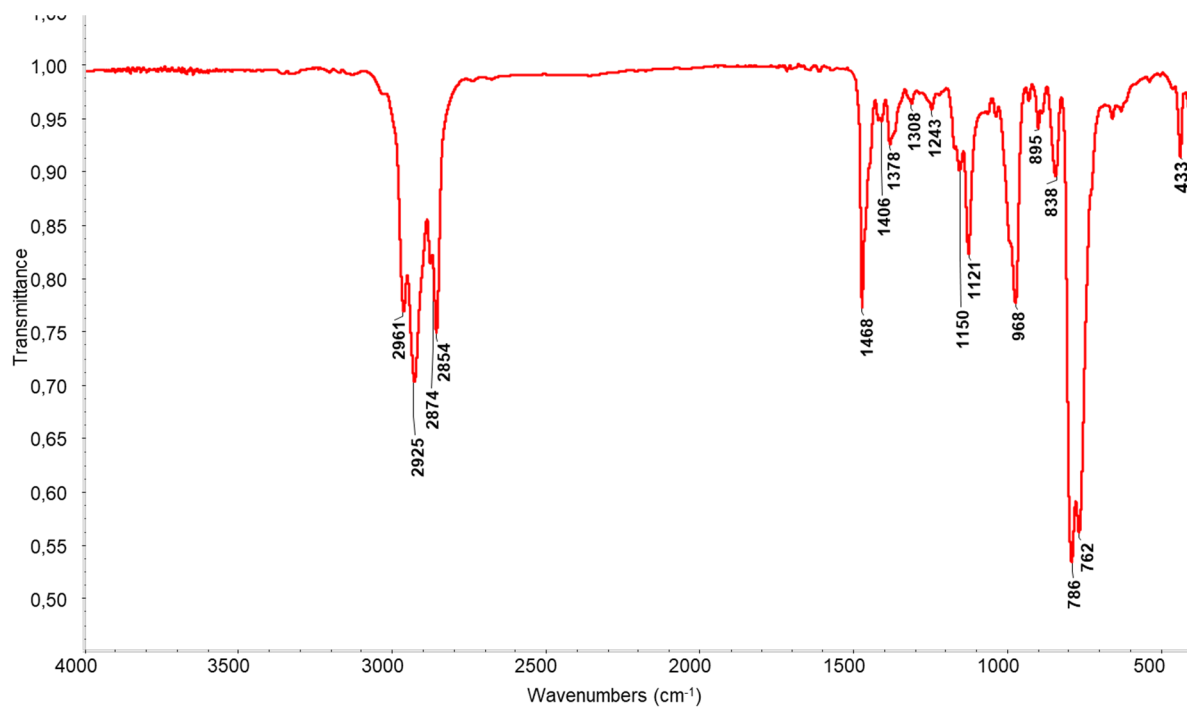


Figure S34. IR spectra (in CCl₄) of $(n\text{-Bu}_4\text{N})[2\text{-B}_{10}\text{Br}_9\text{S}(n\text{-C}_{18}\text{H}_{37})_2]$