Supporting information

Experimental Procedures

General Methods.

n-Heptane, toluene and deuterated solvents were dried with potassium and distilled. All synthetic work was carried out under an inert argon atmosphere using standard Schlenk and glove-box techniques.

Triphenylmethylium tetrafluoroborate and 1,4-bis(trimethylsilyl)butadiyne were purchased from TCI Deutschland GmbH.

NaO*t*Bu was sublimed before the use (10^{-2} mbar, 160°C).

^{1}H, ^{11}B, and ^{19}F NMR spectra were recorded on a Bruker AV 400 spectrometer, ^{13}C NMR spectra were recorded on a Bruker Avance III 600 spectrometer. All spectra were referenced to the resonances of the deuterated solvent used or to reference samples, respectively.

A single crystal of **2** for XRD analyses was mounted in inert oil under protective atmosphere. Data for X-ray crystal structure determination were obtained with a STOE STADIVARI using graphite-monochromated Mo−Kα radiation (λ=0.71073 Å). All structures were refined to convergence against F^2 using programs from the SHELX family.[1]

Infrared spectra were recorded on a Nicolet 5700 FT-IR spectrometer with nujol mulls between CsBr plates, and a Bruker Alpha FT-IR spectrometer with ATR unit containing a diamond crystal in the inert atmosphere of a glove box. Raman spectra were measured on a Nicolet 5700 FT-IR spectrometer combined with NXR 9650 FT-Raman Module equipped with a 1064 nm laser, a Microstage Microscope, and a NXR Genie Ge-detector using single crystals in glass capillaries under inert gas. Spectra are plotted with: Spectragryph, software for optical spectroscopy, V1.2.15 by Dr. F. Menges. Elemental analyses were performed with a varioELcube.

Synthesis of BF_4@1, BF_4@Na_{13}(O*t*Bu)$_{12}$: NaO*t*Bu (1.25 g, 13.0 mmol) was suspended in toluene (7 ml) and 0.33 g triphenylmethylium tetrafluoroborate [$Ph_3C(BF_4)$] (0.33 g, 1.0 mmol) was added slowly under stirring. The temperature of the greenish suspension was increased to 100°C and stirring was continued until the cloudy solution turned to a clear red–orange solution. This mixture was kept at 100°C for 10 h without stirring. After cooling slowly and storing for more than 24 h at room temperature afforded large colourless octahedral crystals (yield: 0.88 g, 0.70 mmol, 70%).

^{1}H NMR (400.13 MHz, [D6]benzene, TMS): δ = 1.36 ppm (s, 9H, O*t*Bu); ^{11}B NMR (128.43 MHz, [D6]benzene, $BF_3{\cdot}OEt_2$): δ = -2.61 ppm (quint, BF_4, $^1J_{B\text{-}F}$ = 12 Hz); ^{19}F NMR (376.61 MHz, [D6]benzene], $CFCl_3$): δ = -154.6 ppm (q, BF_4, $^1J_{F\text{-}B}$ = 12 Hz). Elemental analysis: Found: C, 42.40;[3] H, 8.51. Calc. for $C_{48}H_{108}BF_4Na_{13}O_{12}$: C, 45.64; H, 8.62%.

Synthesis of 2, Na_{13}(O*t*Bu)$_{11}$(C_4) · 0.5 *n*-heptane: NaO*t*Bu (1.34 g, 14.0 mmol) and 1,4-bis(trimethylsilyl)-butadiyne (0.194 g, 1.0 mmol) were suspended in *n*-heptane (10 ml). The suspension was heated to 100°C under stirring for 3 d. After cooling slowly and storing the mixture at room temperature afforded large pale brown crystals. Re-crystallisation after addition of more *n*-heptane (5 ml) afforded large colourless plates (yield: 0.81 g, 0.70 mmol, 70%).

^{1}H NMR (400.13 MHz, [D6]benzene, TMS): δ = 1.36 ppm (s, 9H, O*t*Bu); ^{1}H NMR (600.13 MHz, [D8]toluene, TMS): δ = 1.41 (s, 9H, O*t*Bu), 0.91 ppm (t, 3H, *n*-heptane); ^{13}C{^{1}H} NMR (150.92 MHz, [D8]toluene, TMS): δ = 66.5 (O*C*Me$_3$), 37.6 (OC*Me*$_3$), 32.3 (*n*-heptane), 27.0 (δ-C, *n*-heptane), 23.2 (*n*-heptane), 14.4 ppm (α-C *n*-heptane).

Elemental analysis: Found: C, 51.85; H, 8.33. Calc. for $C_{51.5}H_{107}BF_4Na_{13}O_{11}$: C, 51.49; H, 8.98%.

Table S1: Crystallographic data and refinement for compound **2**.

Compound	**2**
Formula	$C_{51.5}H_{107}Na_{13}O_{11}$
M_r [g mol^{-1}]	1201.23
Crystal size [mm^3]	0.65x0.59x0.55
Crystal system	orthorhombic
Space group	*Pbca*
a [Å]	19.484(4)
b [Å]	19.062(4)
c [Å]	38.558(8)
α [°]	90
β [°]	90
γ [°]	90
V [Å^3]	14321(5)
Z	8
ρ_{calcd} [g cm^{-3}]	1.114
μ(Mo$_{K\alpha}$) [mm^{-1}]	0.141
T [K]	120(2)
$2\theta_{\text{max}}$ [°]	29.21
measured refl.	155515
independent refl.	18586
R(int)	0.0299
refined parameters	782
$R1$ ($R1$ all data)	0.0312 (0.0844)
$wR2$ ($wR2$ all data)	0.0439 (0.0875)
max, min peaks [eÅ^{-3}]	0.319, -0.271
CCDC Number[2]	2161730

Figure S1-1: Thermal ellipsoid plot of the structure of **2** with 30% probability. Hydrogen atoms and selected sodium atoms, and co-crystallised *n*-heptane are omitted for clarity (red: oxygen; blue: sodium; gray: carbon).

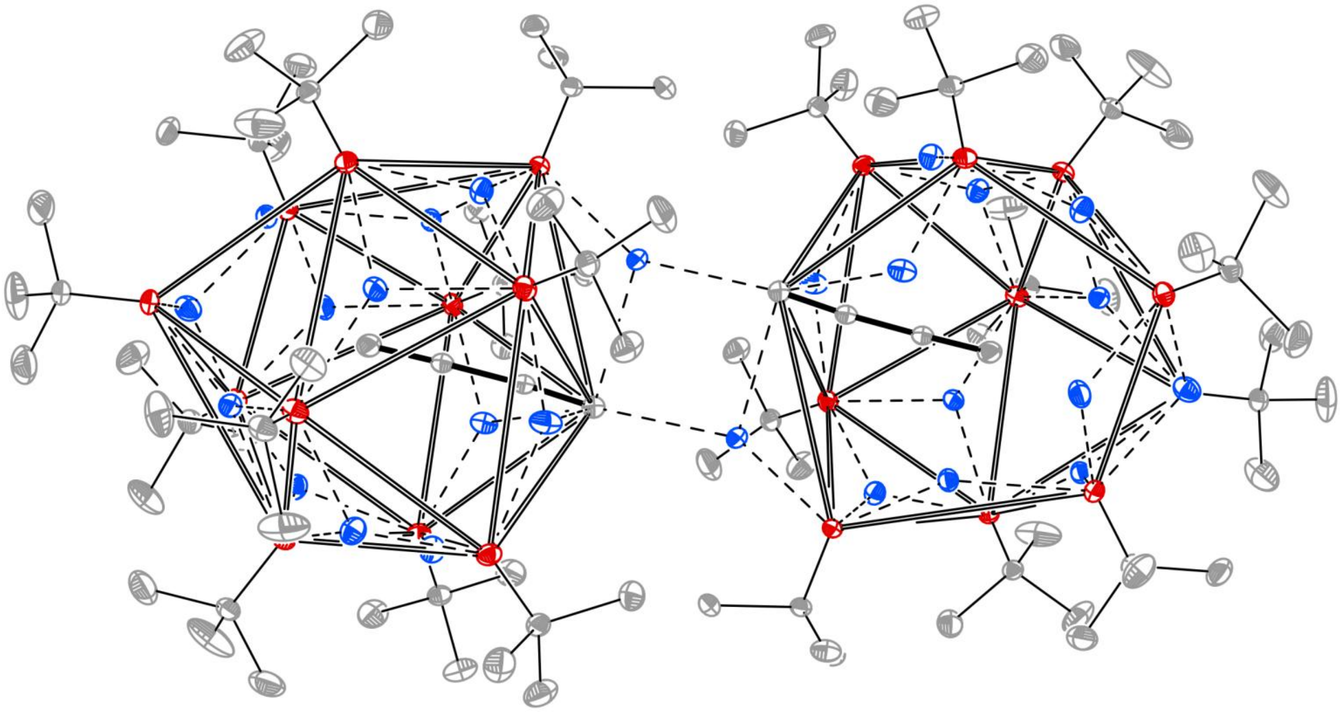


Figure S2-1: ^{1}H NMR of **BF$_4$@1** in [D$_6$]benzene:

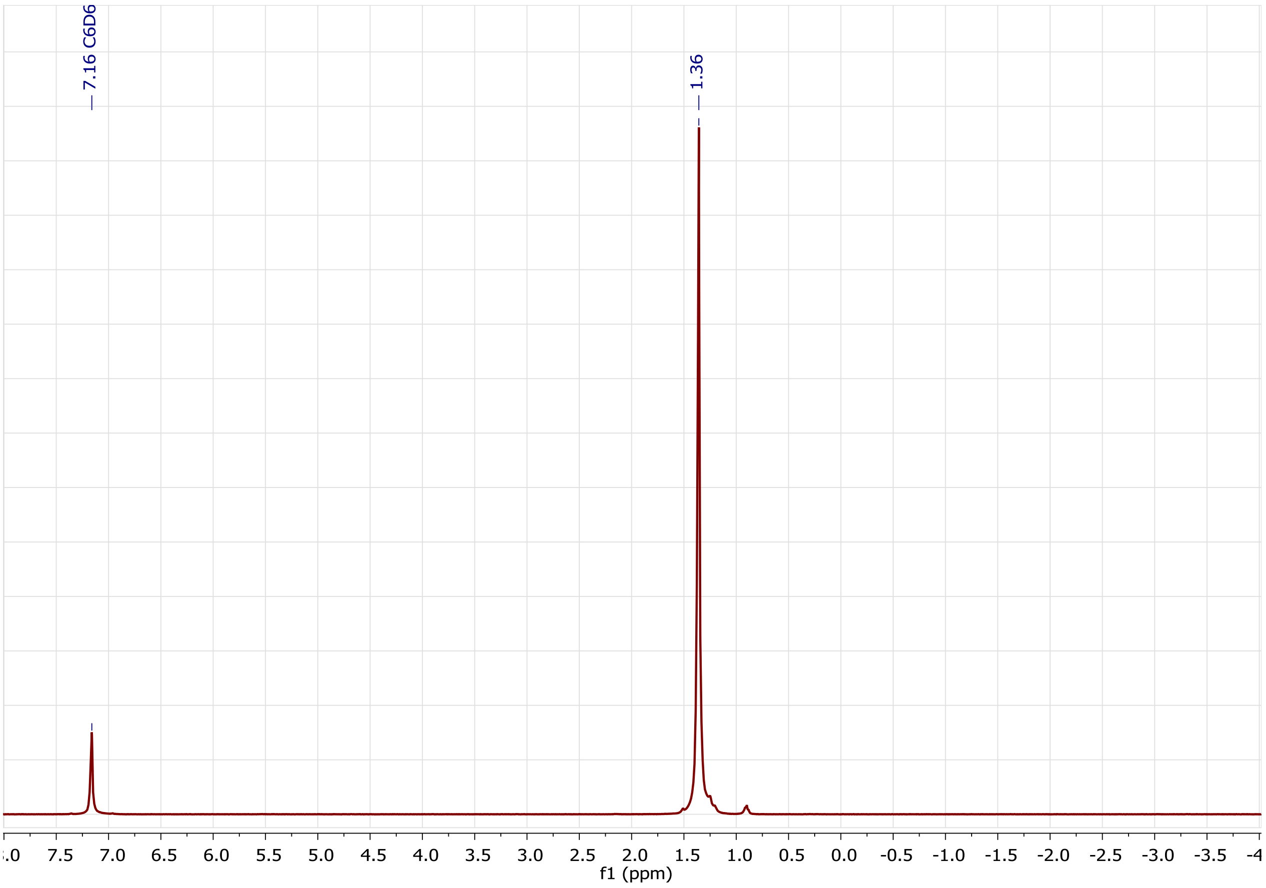


Figure S2-2: ^{11}B NMR of **BF$_4$@1** in [D$_6$]benzene:

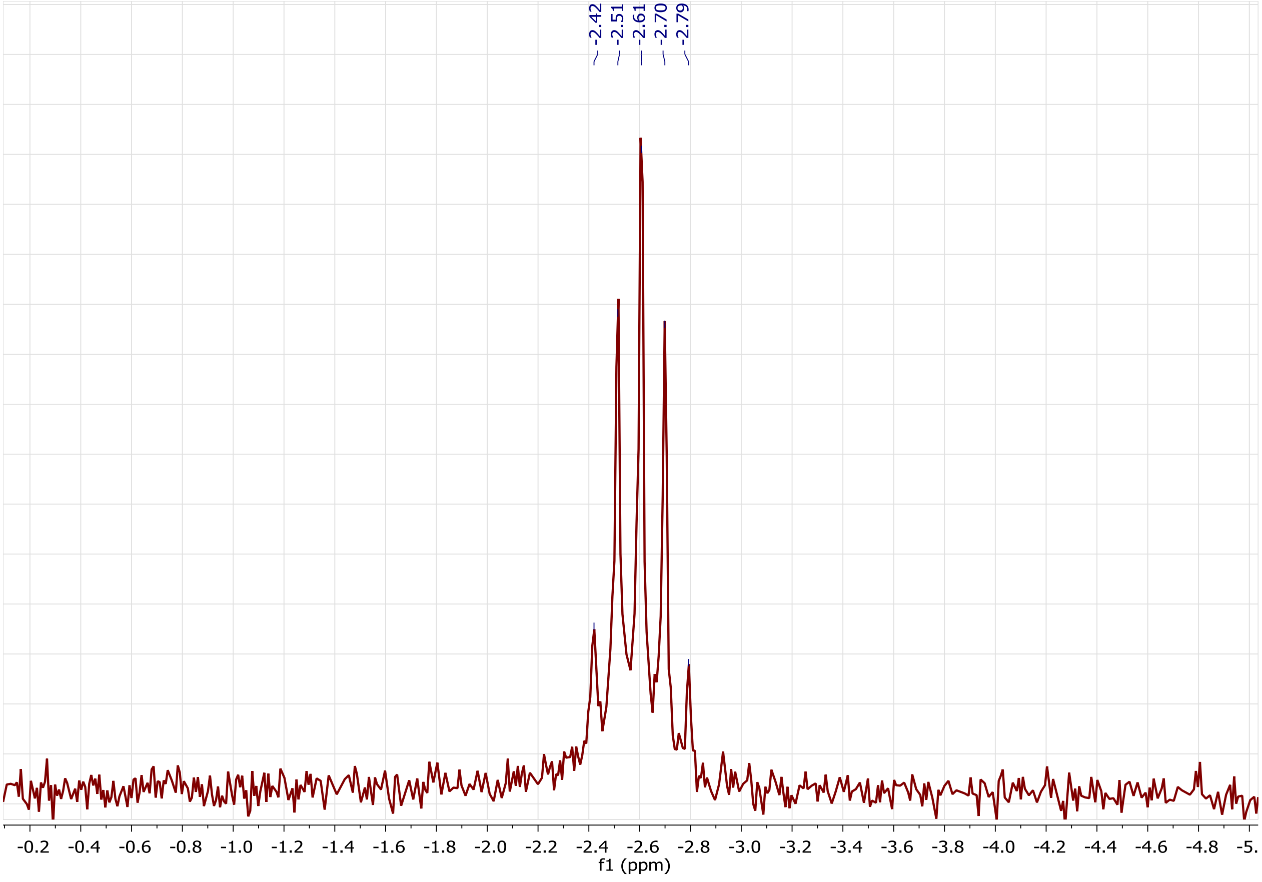


Figure S2-3: ^{19}F NMR of **BF$_4$@1** in [D$_6$]benzene:

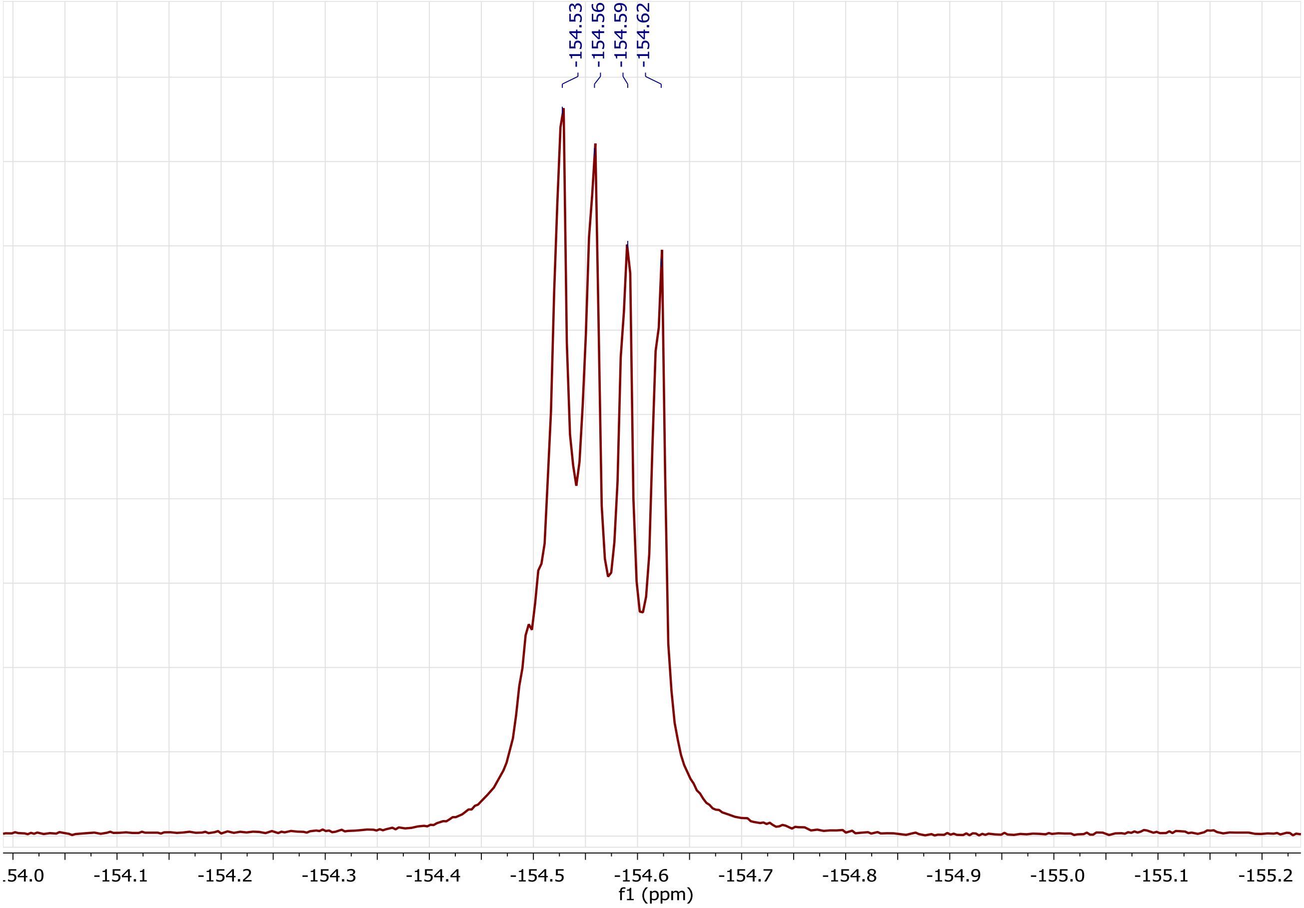


Figure S2-4: ^{19}F NMR of **BF$_4$@1** in [D$_6$]benzene (larger window):

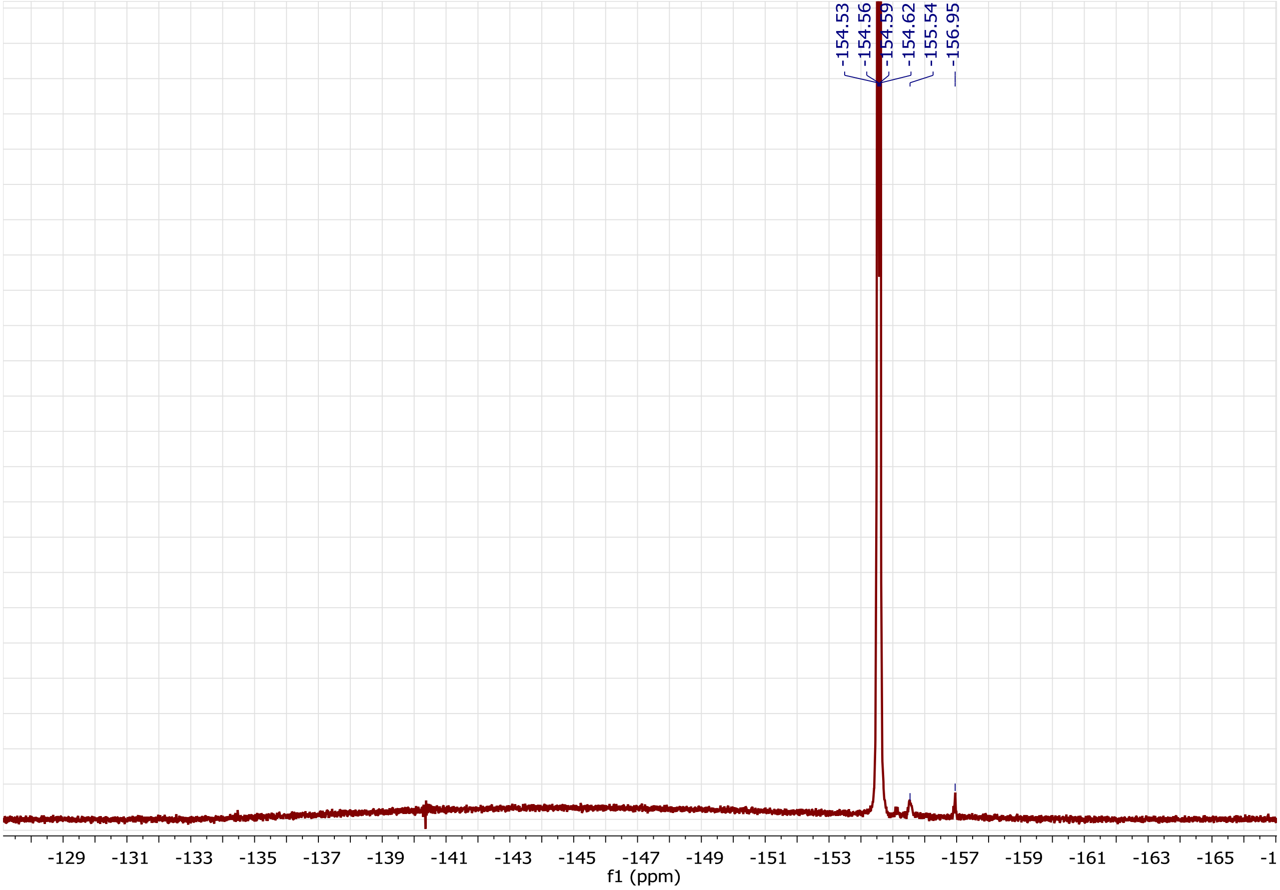


Figure S3-1: ^{1}H NMR of **2** in [D$_6$]benzene:

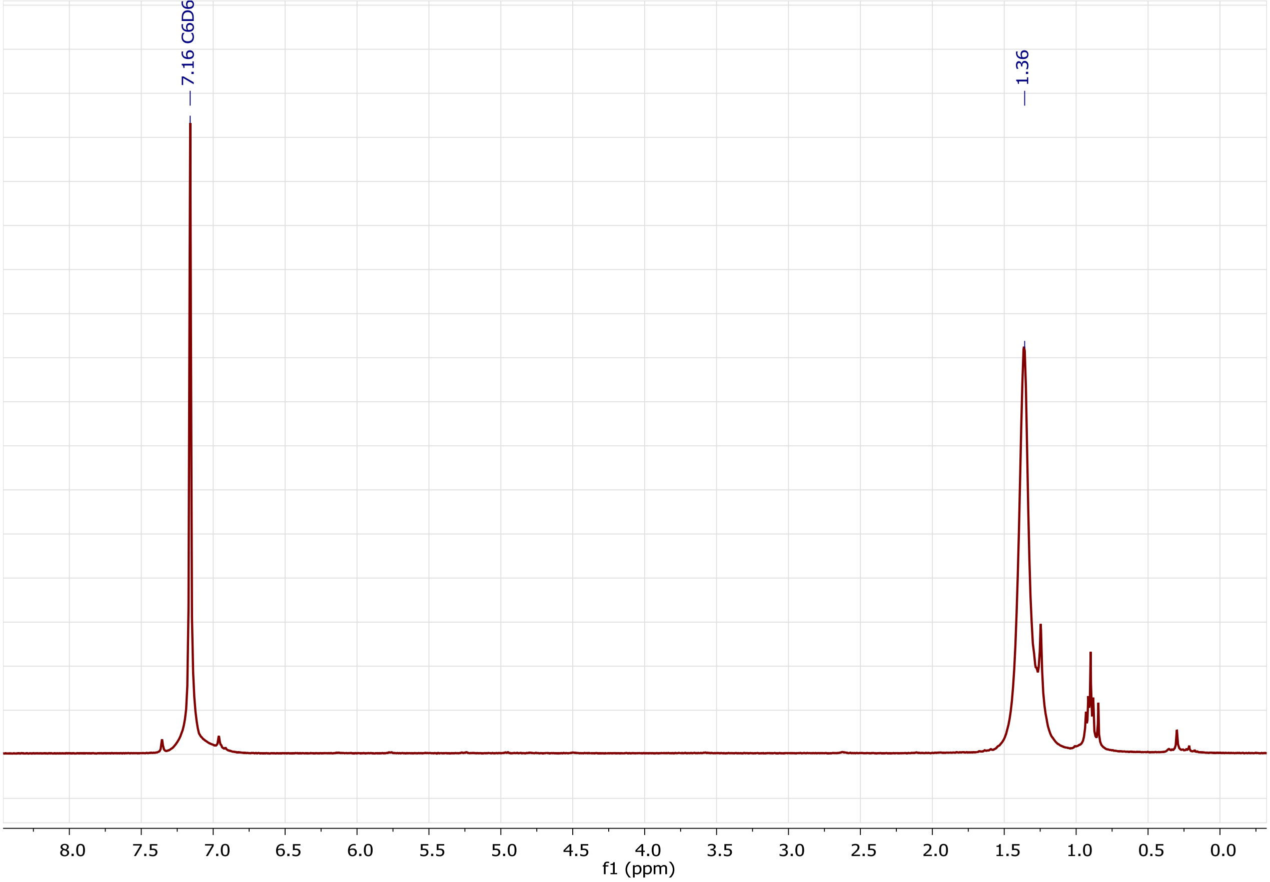


Figure S3-2: ^{1}H NMR of **2** in [D$_8$]toluene:

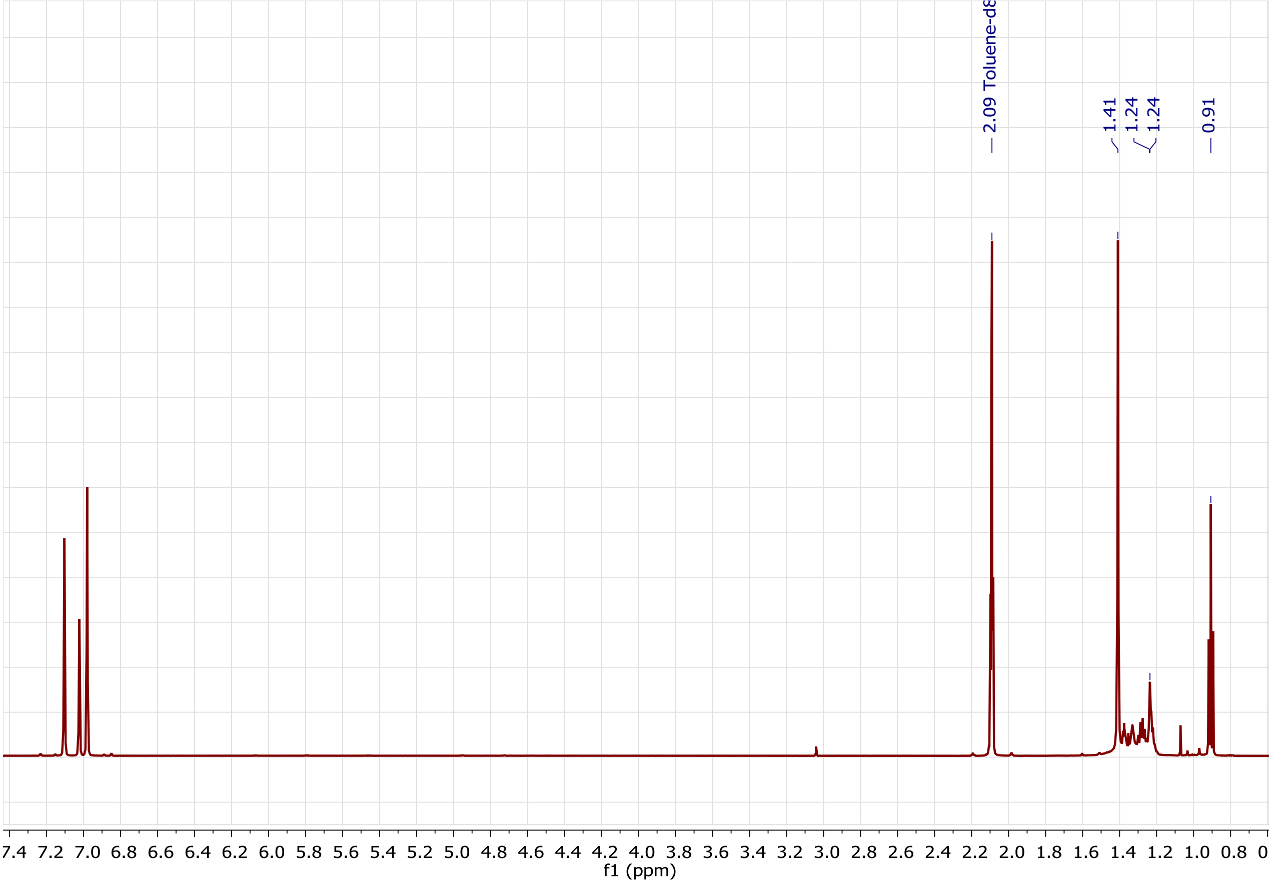


Figure S3-3: $^{13}C\{^{1}H\}$ NMR of **2** in [D$_8$]toluene:

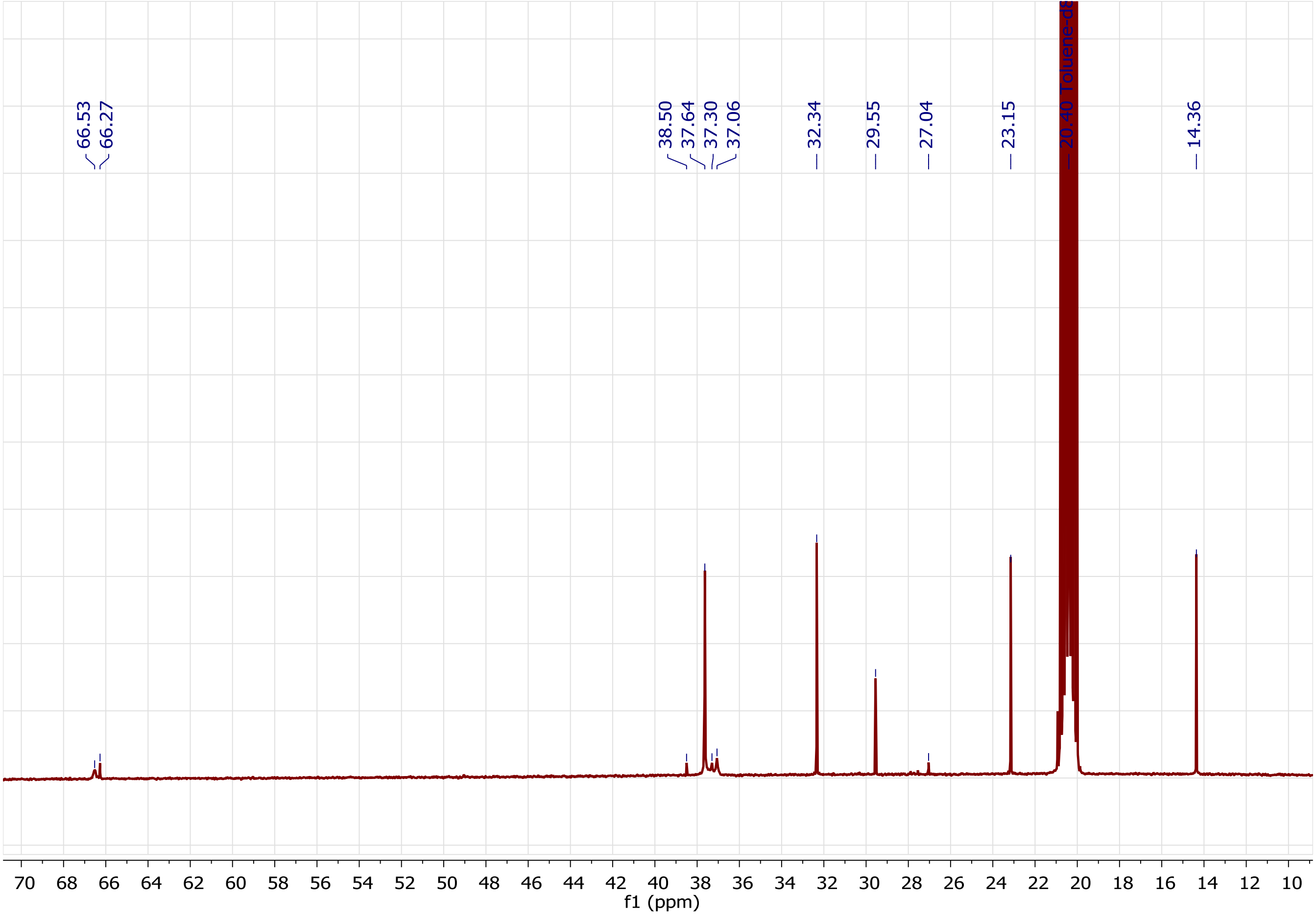


Figure S4-1: IR ATR-spectrum of **BF_4@1.**

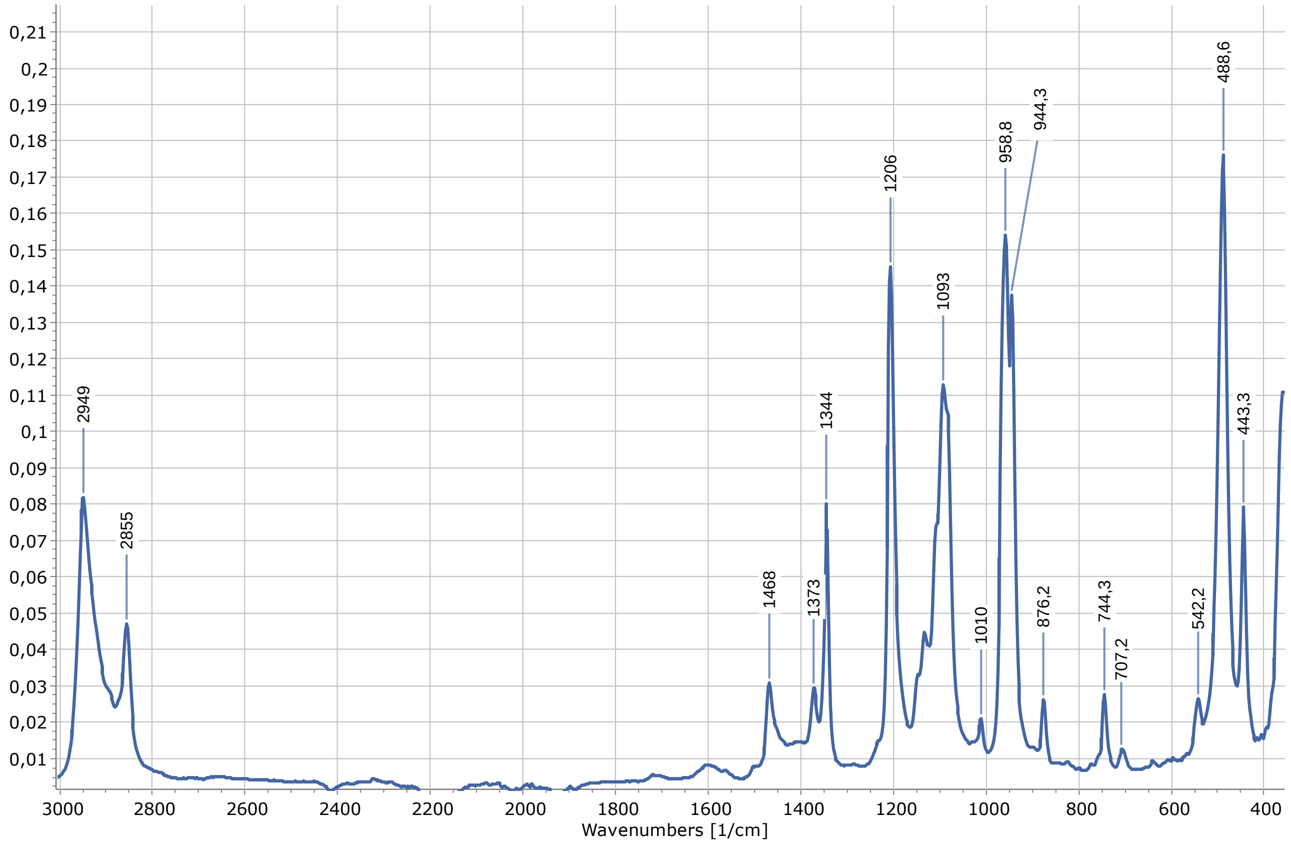


Figure S4-2: IR ATR-spectrum of **BF_4@1** (blue) combined with an IR-ATR-spectrum of **Br@1** (red).

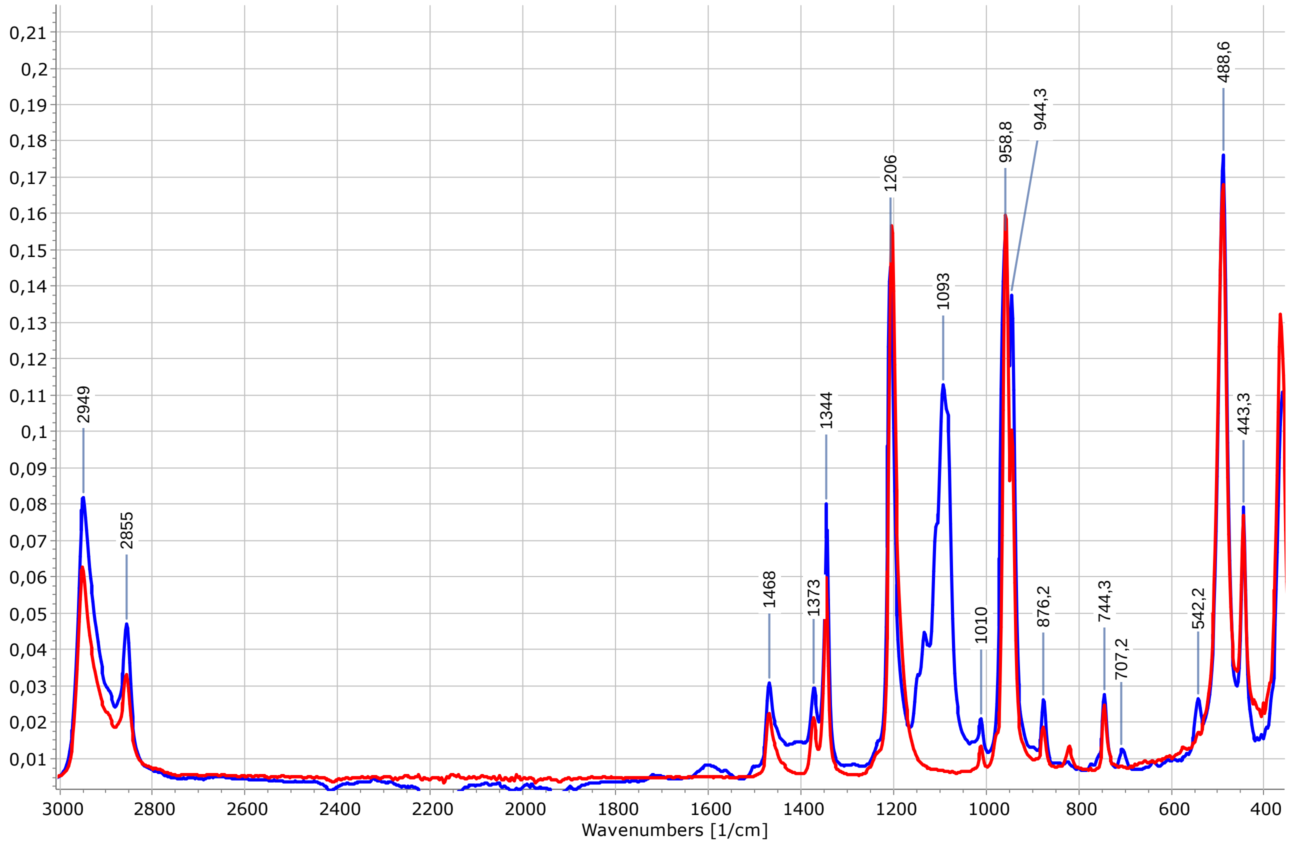


Figure S4-3: Raman spectrum of **BF_4@1.**

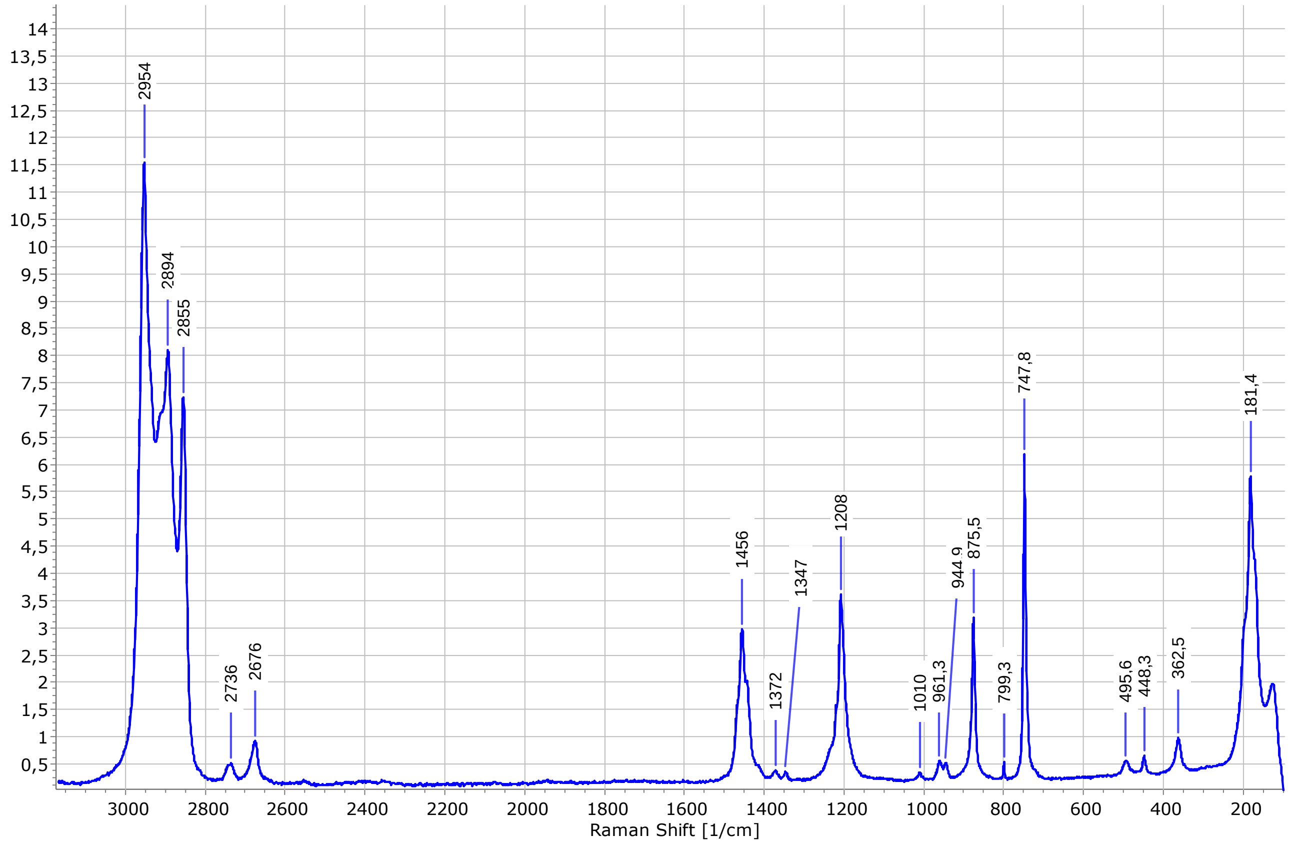


Figure S4-4: Raman spectrum of **BF_4@1** (blue) combined with a Raman spectrum of **Br@1** (red).

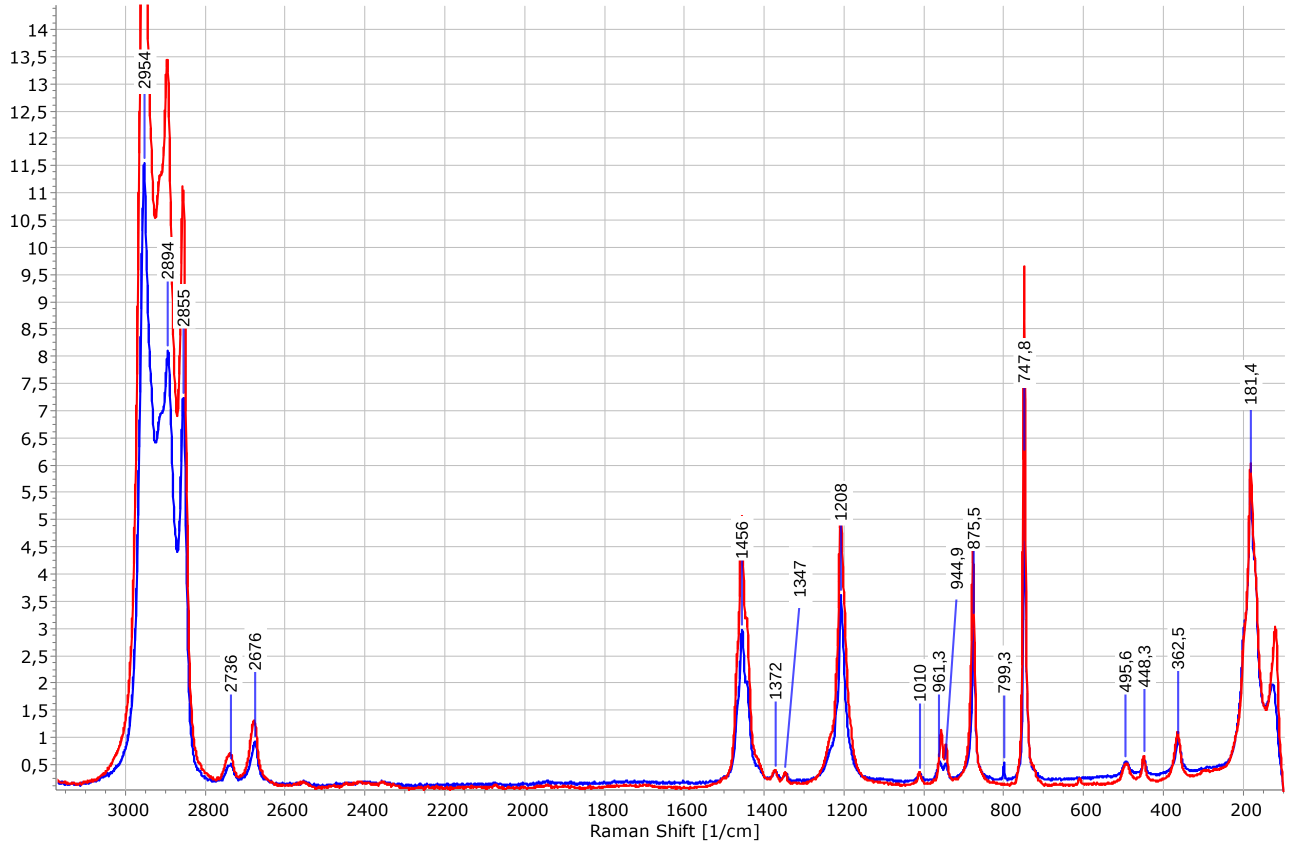


Figure S5-1: IR spectrum of **2** (blue, nujol mull between CsBr plates) combined with an IR spectrum of **Br@1** (red, nujol mull between CsBr plates).

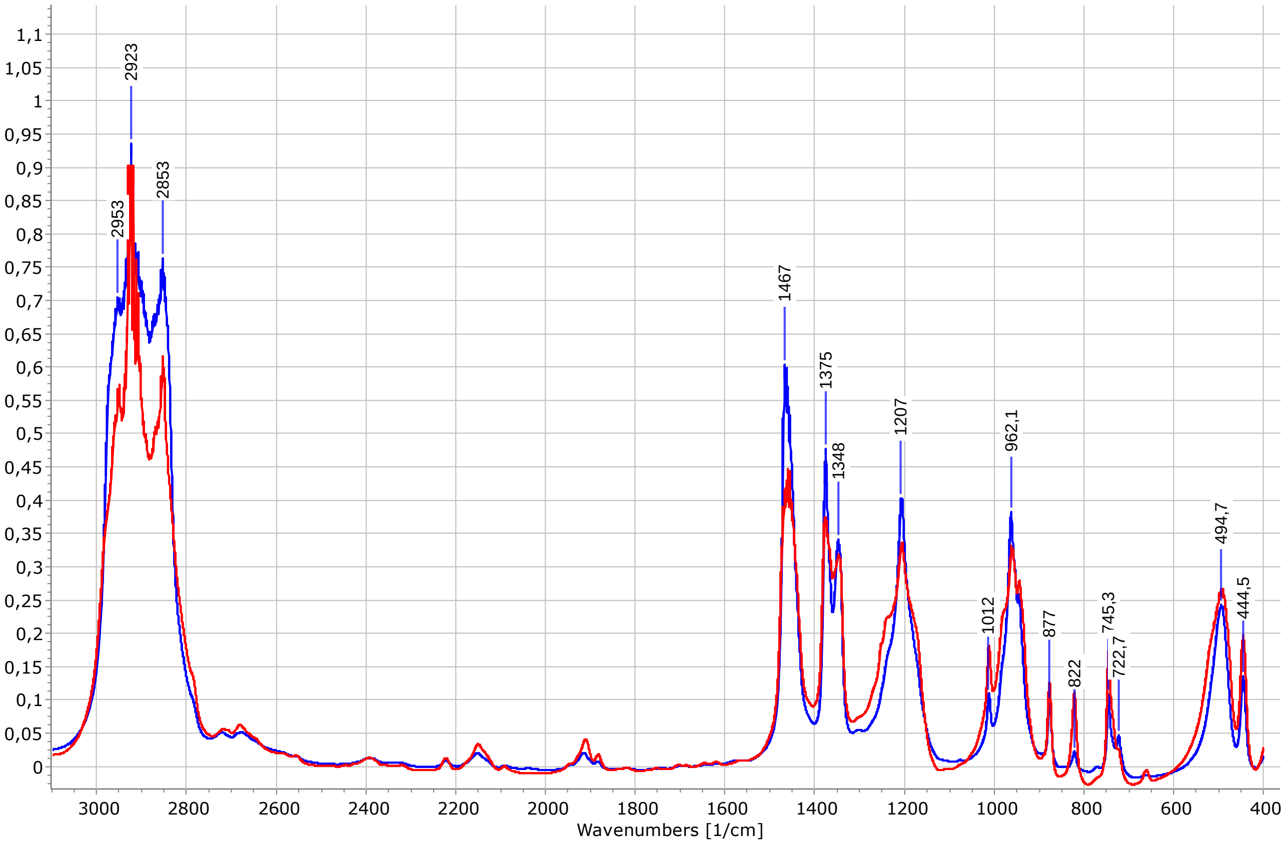


Figure S5-2: FIR spectrum of **2** (blue, nujol mull between CsBr plates) combined with a FIR spectrum of **Br@1** (red, nujol mull between CsBr plates).

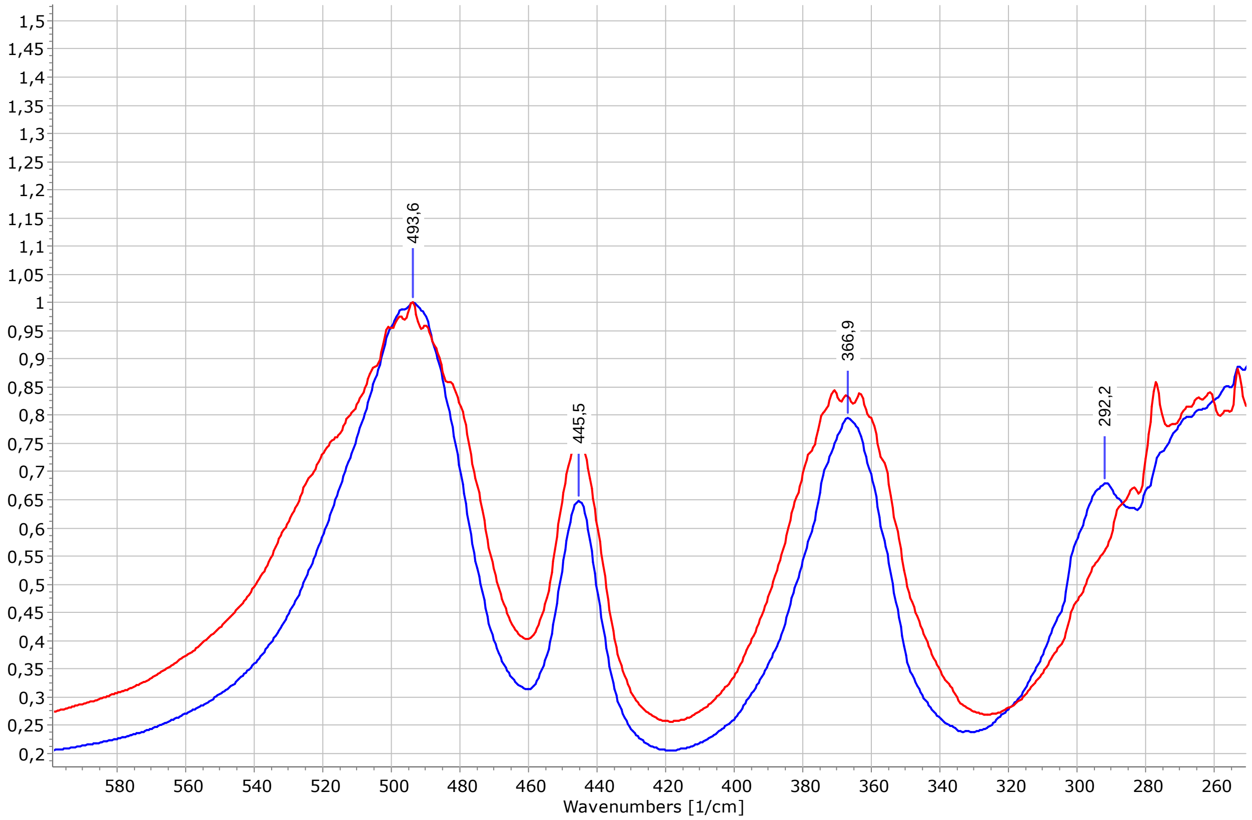


Figure S5-3: Raman spectrum of **2** (blue) combined with a Raman spectrum of **Br@1** (red).

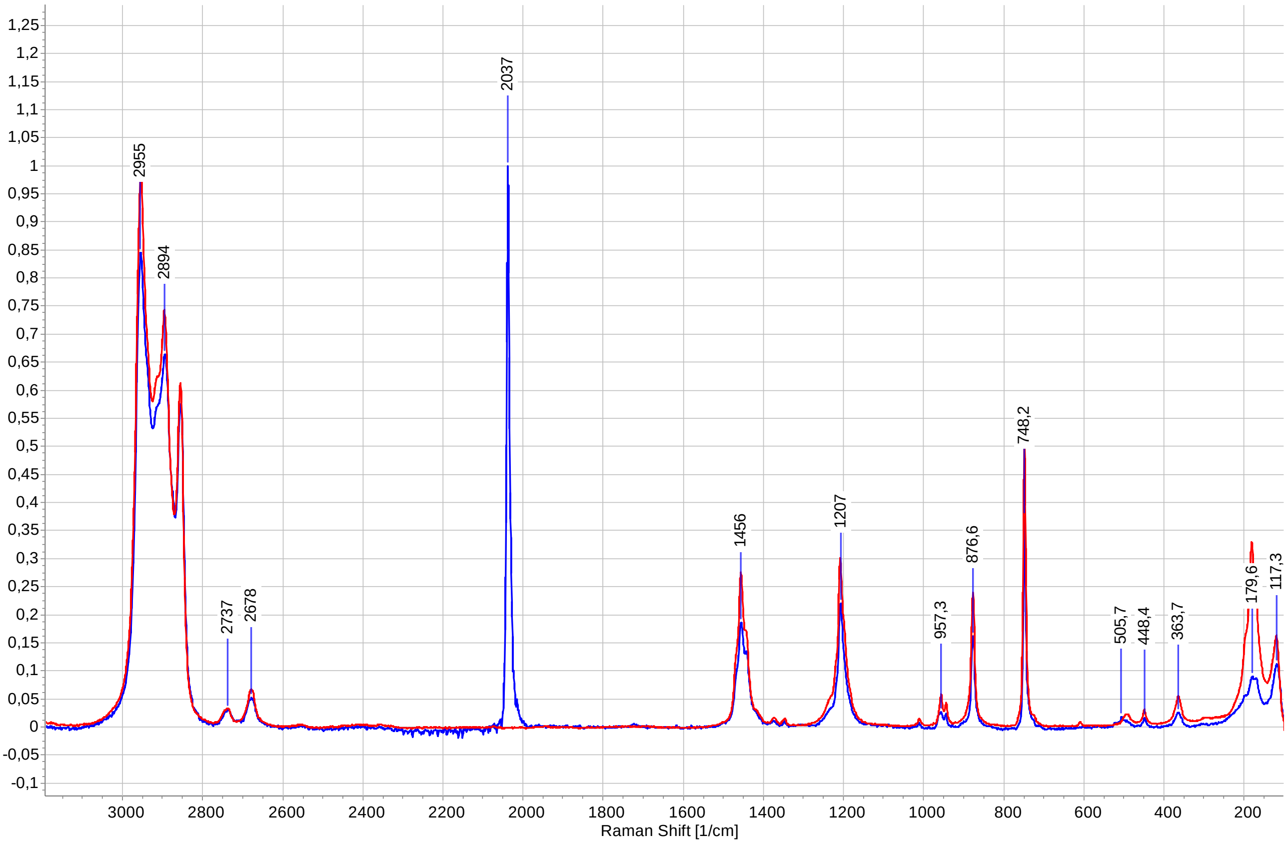
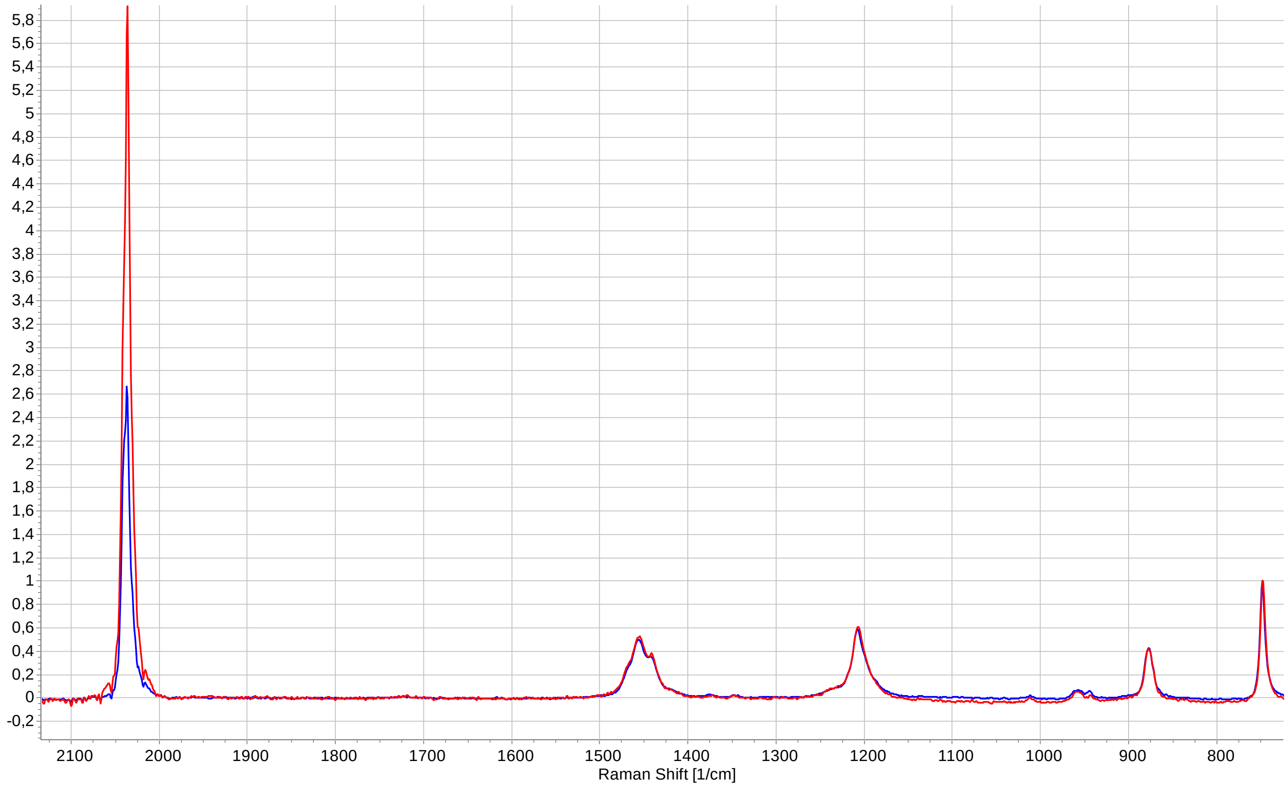


Figure S5-3: Raman spectra of **2** (blue and red) with changing orientation of the single crystal. The intensitiy of the band at 2037 cm-1 is affected by the orientation.



Author Contributions

J.K. conceived the project, wrote the manuscript, carried out spectroscopic studies and the crystallographic work. E.C. conceived experiments, performed experiments and carried out spectroscopic studies. S.S. performed experiments and carried out spectroscopic studies.

References

[1] a) P. Müller, *Crystal structure refinement*. *A crystallographer's guide to SHELXL*, Oxford Univ. Press, Oxford, **2010**; b) G. M. Sheldrick, *Acta crystallographica. Section A, Foundations of crystallography* **2008**, *64*, 112–122.

[2] CCDC 2161730 contains the supplementary crystallographic data for this publication. The data is provided free of charge by The Cambridge Crystallographic Data Centre.

[3] Elemental analyses of compounds containing tetrafluoroborate are shown to hinder the complete combustion of carbon in the samle. This produces systematically low values for the carbon content found in the sample: *Microchim. Acta* **2003**, *142*, 13–19.