

Electronic Supplementary Information

**Stabilization of a highly porous metal–organic framework utilizing a carborane-based
linker**

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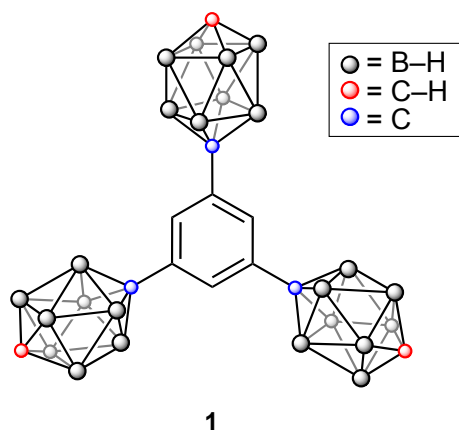
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1. Synthetic procedures and characterization

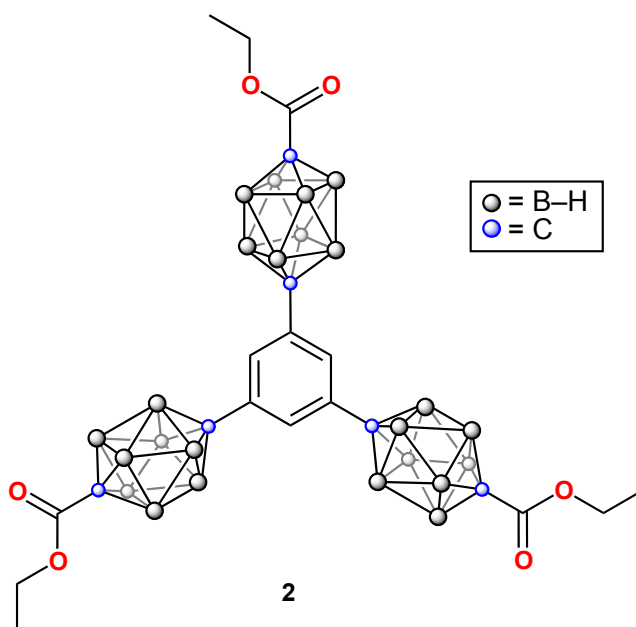
General considerations: 1,10-dicarbaborane (*p*-carborane) was purchased from Katchem (Czech Republic) and used as received. All other solvents and chemicals were obtained from Aldrich Chemical Co. (Milwaukee, USA). Deuterated solvents were purchased from Cambridge Isotope Laboratories and used as received. For all air-sensitive manipulations either a Vacuum Atmospheres Nexus II N₂-filled glove box or Schlenk techniques were employed. Analytical thin layer chromatography (TLC) was performed using plastic plates pre-coated with silica gel (0.25 mm, 60 Å pore size) with a fluorescent indicator (254 nm). Visualization was accomplished with UV light and/or palladium chloride (PdCl₂) in hydrochloric acid (0.6 M in EtOH) as a stain. All NMR spectra were recorded Bruker Avance 400 MHz equipped with a broadband probe at 300 K. ¹H and ¹H{¹¹B} NMR spectra were referenced internally to residual protons in the deuterated solvents (dichloromethane-*d*₂ = δ 5.32; DMSO-*d*₆ = δ 2.50). ¹³C{¹H} NMR spectra were referenced internally to carbons in the deuterated solvents (dichloromethane-*d*₂ = δ 53.84; DMSO-*d*₆ = δ 39.52). ¹¹B and ¹¹B{¹H} NMR spectra were referenced to a neat BF₃·Et₂O standard at 0.0 ppm. Electrospray ionization (ESI) and atmospheric pressure photoionization (APPI) mass spectra were recorded on an Agilent 6120A LC–TOF instrument in positive and negative ion mode. Elemental analyses (C, H, N) were performed by Quantitative Technologies (Intertek), Whitehouse, NJ.



Compound 1

Compound **1** was prepared following a procedure analogous to that reported by Schörbel et al.¹ To a solution of *p*-carborane (1.02 g, 8.4 mmol) in THF (50 mL) was added *n*-BuLi (1.6 M solution in hexane, 5.27 mL, 8.4 mmol) at -78 °C. After 1.5 hours of stirring at room temperature, CuCl (835 mg, 8.4 mmol) was added under nitrogen. The mixture was allowed to stir for 1 hour at room temperature, and then heated to 70 °C for 2 hours. A mixture of 1,3,5-tribromobenzene (758 mg, 2.41 mmol) and PdCl₂(PPh₃)₂ (295 mg, 0.42 mmol) in THF (20 mL) was then cannulated into the reaction. The mixture was stirred at 70 °C for 2 days, cooled, and the solvent was removed. Dichloromethane (120 mL) was then added to residue and stirred for 2 hours and subsequently filtered. The filtrate was then collected, solvent removed and the mixture was purified via column chromatography (hexanes), followed by precipitation with methanol: 822 mg (79 %). Single crystals suitable for X-ray diffractions studies were grown via slow evaporation from a concentrated sample in dichloromethane. ¹H NMR (400 MHz, CD₂Cl₂) δ 1.2–3.3 (m, 24 H, BH), 7.06 (s, 3 H, CH), 8.34 (s, 3 H, aromatic); ¹³C{¹H} NMR (100.6 MHz, CD₂Cl₂) δ 98.45 (C_{carborane}H), 123.59 (C_{carborane}C_{ar}), 129.98 (C_{ar}), 139.53 (C_{ar}C_{carborane}); ¹¹B NMR (128.4 MHz, CD₂Cl₂) δ -12.77 (d, ¹J_{B-H} = 166 Hz, 12 B), -10.18 (d, ¹J_{B-H} = 163 Hz, 12 B).

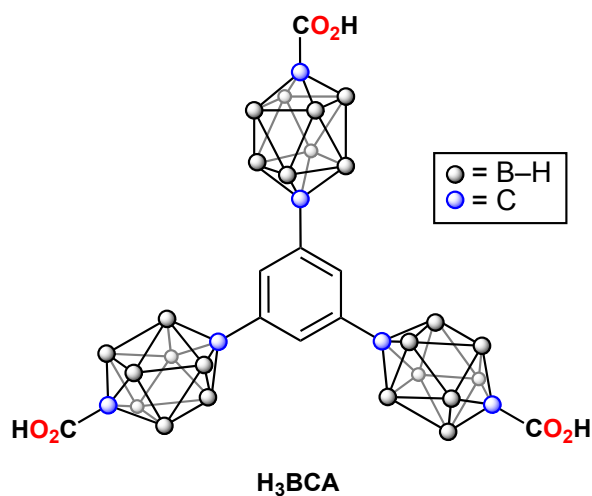
HRMS (APPI+): m/z calcd for $1+\text{H}^+$: 434.4841. Found: 434.4734. Anal. Calcd for **1**: C 33.22, H, 6.97. Found: C 32.52, H 7.14.



Compound 2

To a solution of **1** (623 mg, 1.44 mmol) in THF (100 mL) was added *n*-BuLi (1.6 M solution in hexane, 2.97 mL, 4.75 mmol) at room temperature, and the mixture was subsequently heated to 80 °C for 6 hours. After cooling the reaction to -78 °C, ethyl chloroformate (0.46 mL, 4.83 mmol) was slowly added and the reaction was allowed to warm to room temperature overnight. The solvent was removed under vacuum and the residue extracted with DCM and water. The organic layer was dried with MgSO₄, filtered, and the solvent removed. The resulting residue was then subjected to column chromatography (hexanes/ 10% diethyl ether) to yield **2**: 624 mg (68 %). ¹H NMR (400 MHz, CD₂Cl₂) δ 1.44 (t, 9 H, CH), 1.68–3.50 (bm, 24 B, BH), 4.50 (q, 6 H, CH), 8.31(s, 3 H, aromatic); ¹³C{¹H} NMR (100.6 MHz, CD₂Cl₂) δ 14.37 (CH₃-ester), 63.59 (CH₂-ester), 111.79 (C_{carborane}C_{ester}), 125.55 (C_{carborane}C_{ar}), 130.00 (C_{aryl}), 139.23 (C_{ar}C_{carborane}), 164.93 (COOEt); ¹¹B NMR (128.4 MHz, CD₂Cl₂) δ -10.14 (bm, 24 B). HRMS (ESI+): m/z calcd

for $2+\text{H}^+$: 651.4539. Found: 651.5459. Anal. Calcd for **2**: C 38.80, H 6.51. Found: C 39.48, H 6.38.



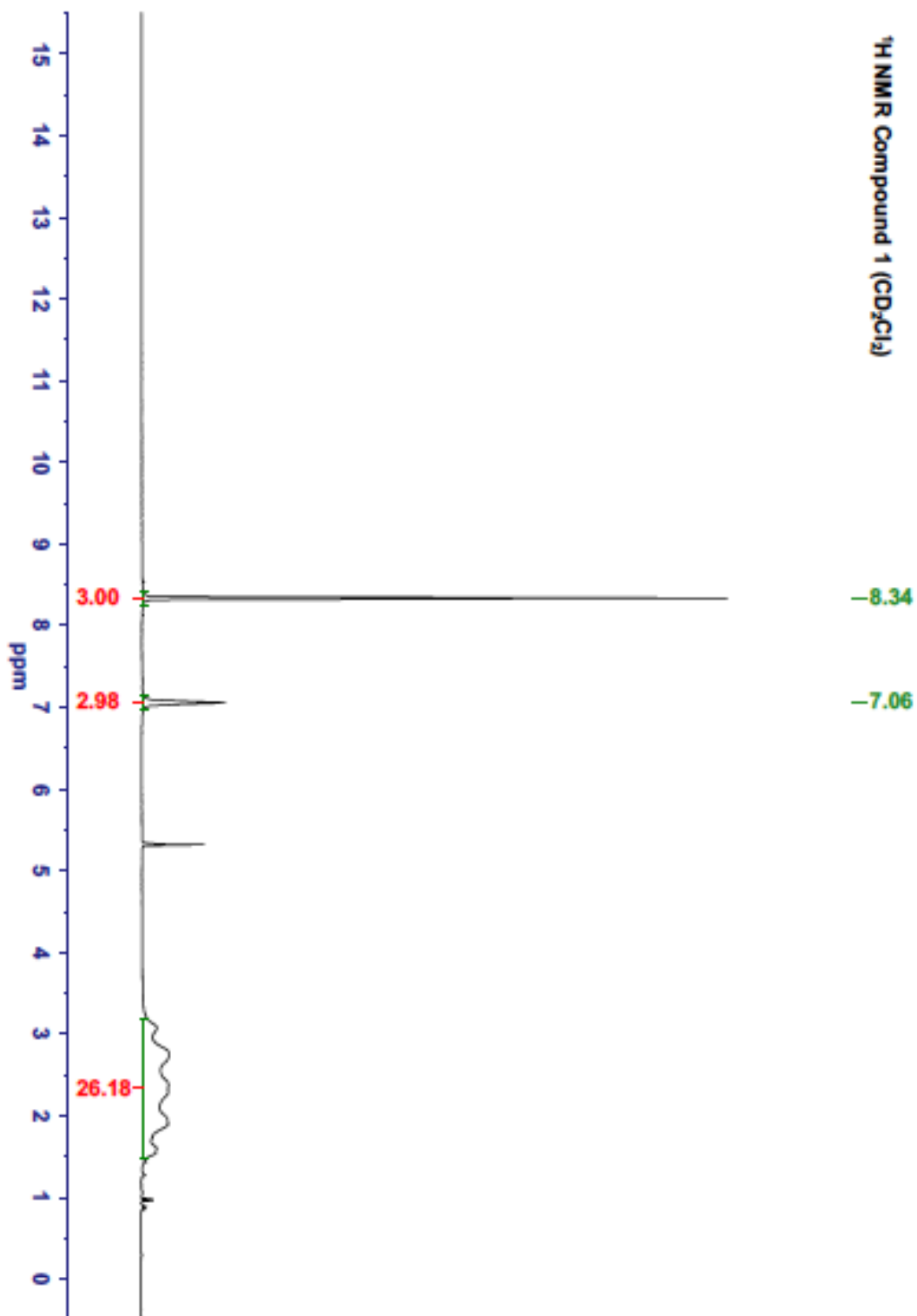
H₃BCA

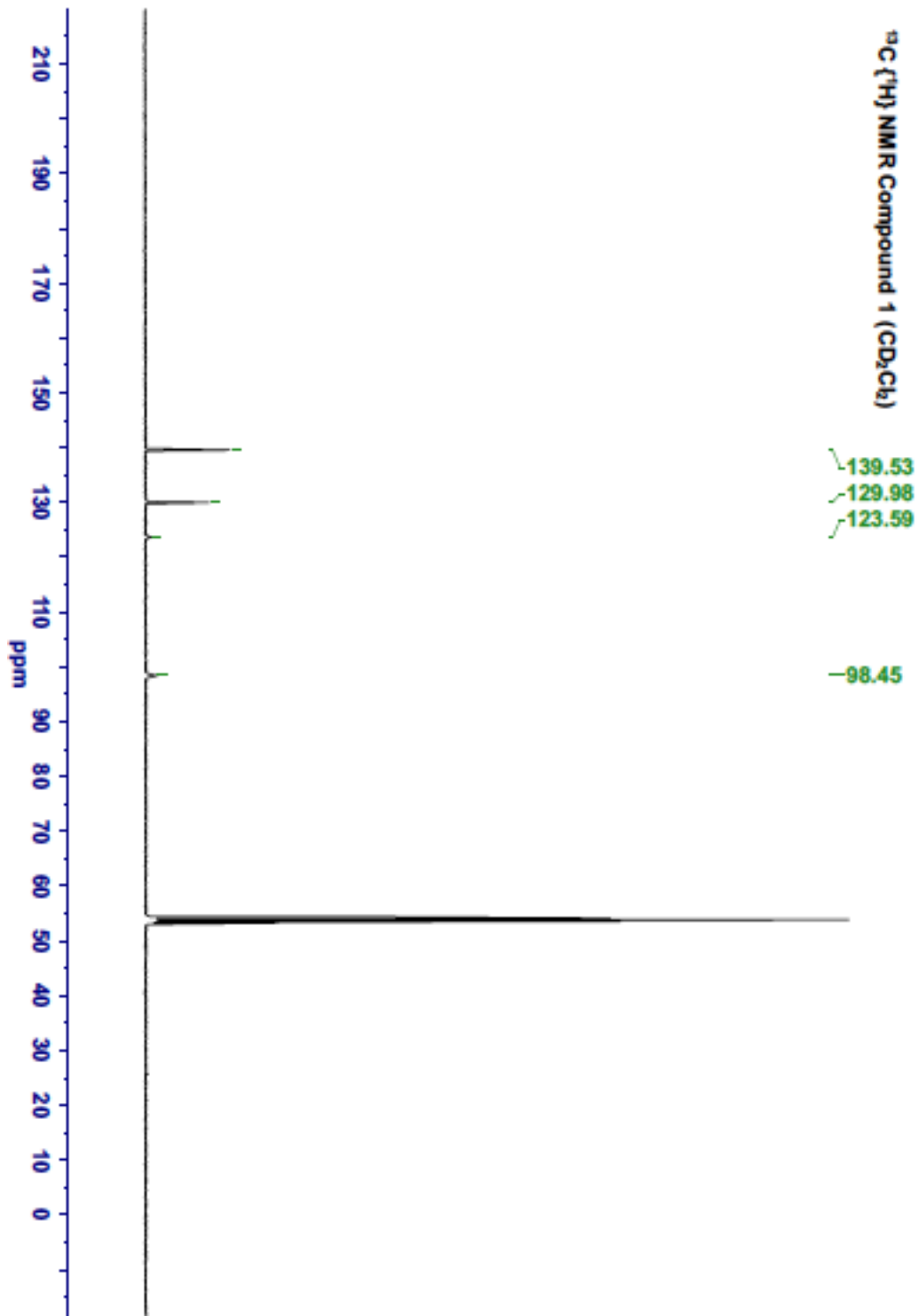
Compound **2** (533 mg, 0.82 mmol) was dissolved in a mixture of THF (12 mL), EtOH (8 mL), and H₂O (4 mL). To the solution was added LiOH (589 mg, 24.6 mmol) and the reaction was stirred overnight at room temperature. H₂O (20 mL) was then added to the reaction, and the mixture was subsequently acidified with concentrated hydrochloric acid. After acidifying, the organic solvents were removed under vacuum and the aqueous emulsion was then extracted with diethyl ether (3 x 20 mL). The organic layer was then dried with Mg₂SO₄, filtered, and dried under vacuum to yield **3**: 417 mg (90 %). ¹H NMR (400 MHz, DMSO-*d*₆) δ 1.60–3.50 (bm, 24 B, BH), 8.33 (s, 3 H, aromatic), 14.34 (bs, 3H, COOH); ¹³C{¹H} NMR (100.6 MHz, DMSO-*d*₆) δ 123.21 (*C*_{carborane}*C*_{ar}), 129.28 (*C*_{aryl}), 138.42 (*C*_{ar}*C*_{carborane}), 165.06 (COOH); ¹¹B NMR (128.4 MHz, DMSO-*d*₆) δ -10.36 (bm). HRMS (ESI⁻): *m/z* calcd for **H₂BCA⁻**: 564.4379. Found: 564.4395. Anal. Calcd for **2**: C 31.84, H, 5.34. Found: C 30.31, H 5.00.

NU-700

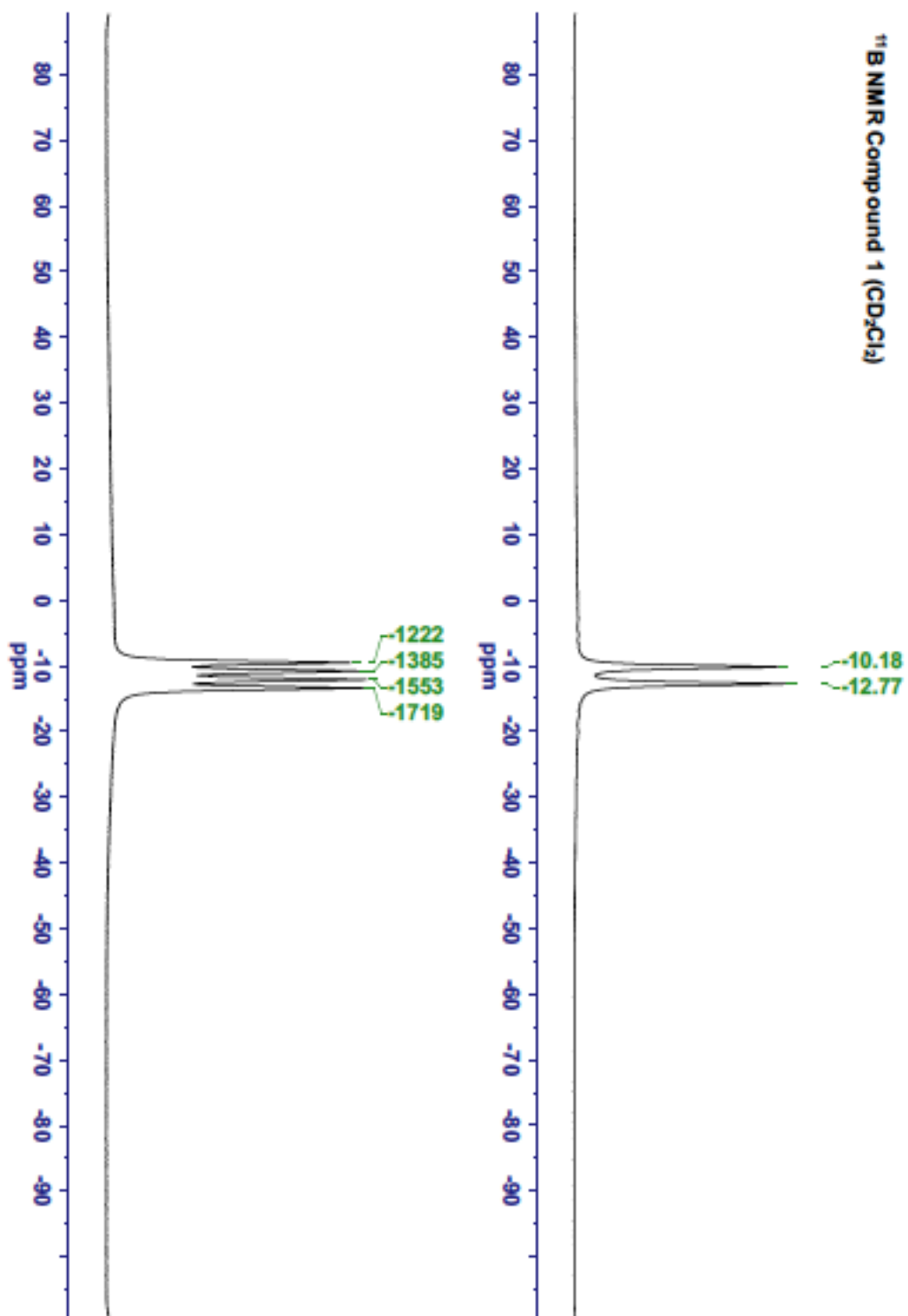
H₃BCA (26.1 mg, 0.05 mmol) and **Cu(NO₃)₂·2.5H₂O** (68.0 mg, 0.30 mmol) were dissolved in a 1:1 mixture of DMF and NMP (10 mL). Once the reactants had dissolved, the vial was placed in an oven at 90 °C for 48 h. After cooling, the mother liquor was decanted and replaced with fresh EtOH. This was repeated once a day for three days: , The solvent was removed using supercritical CO₂, and the crystals were further dried by heating under dynamic vacuum: 20.7 mg (16%). Anal. Calcd for **NU-700·3 H₂O**: C 26.29, H 4.41. Found: C 24.96, H 4.10. The water found in elemental analysis is most likely due to exposure of the material to ambient moisture during sample preparation.

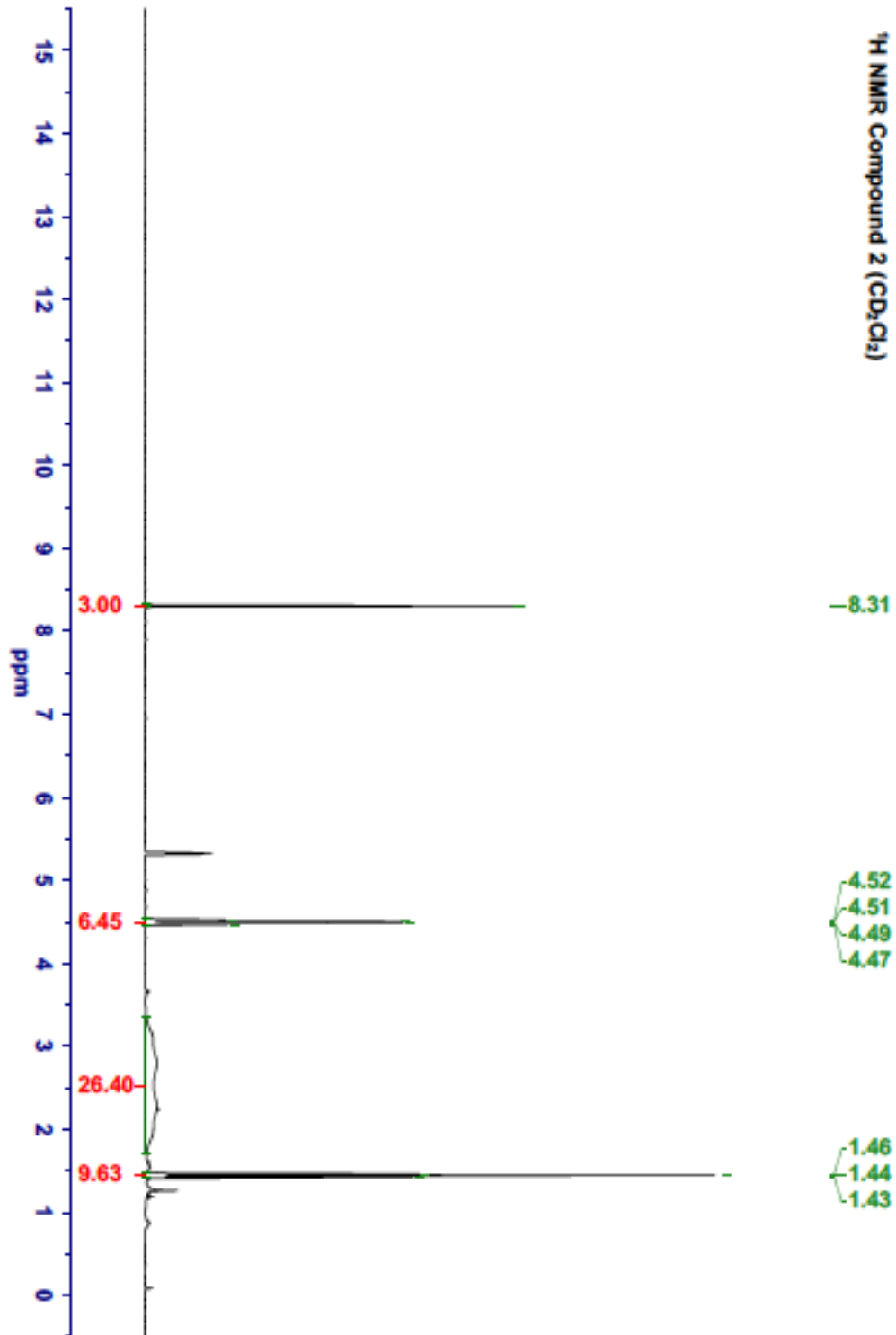
2. NMR Spectra for Compounds 1, 2, 3, and NU-700

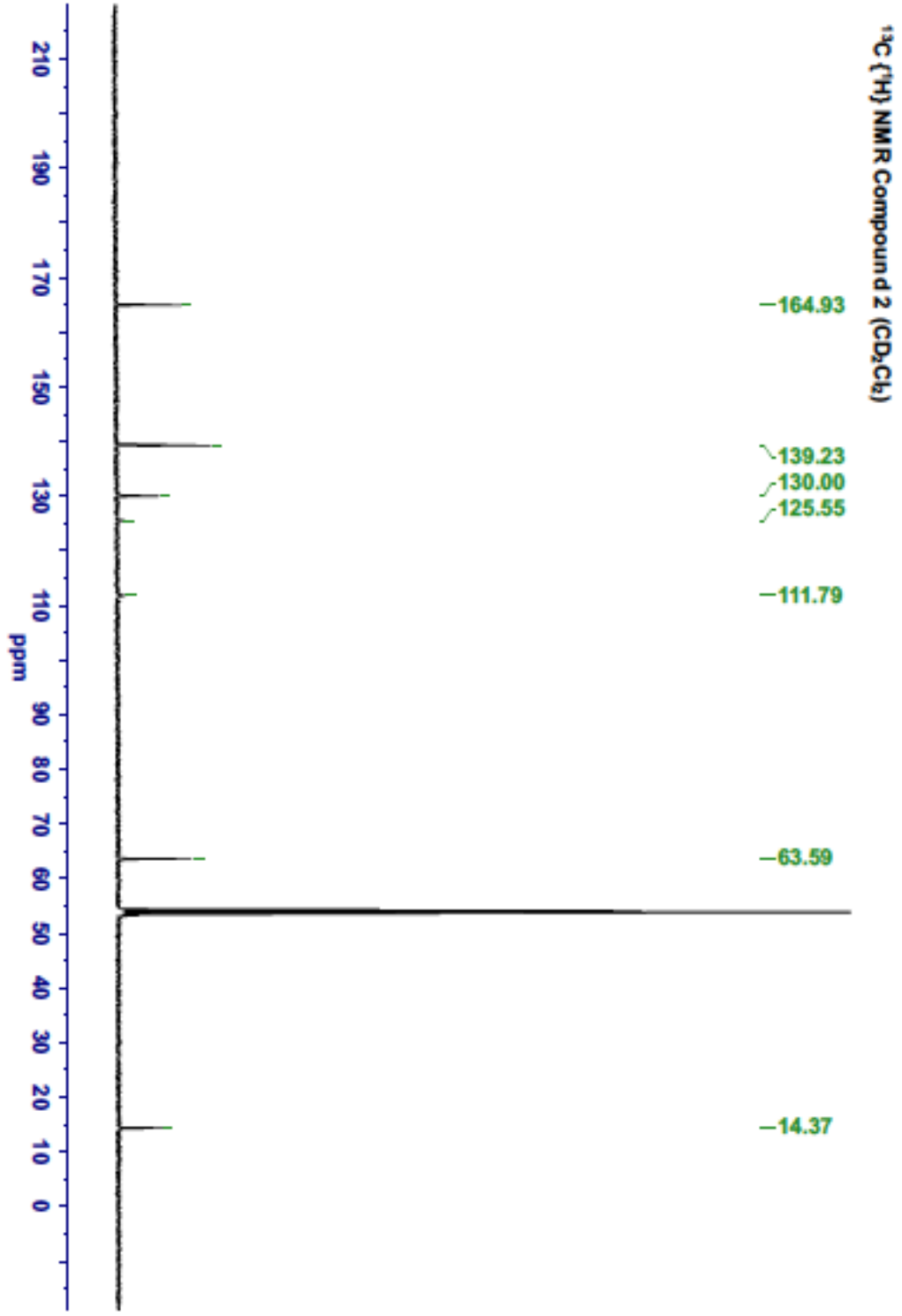




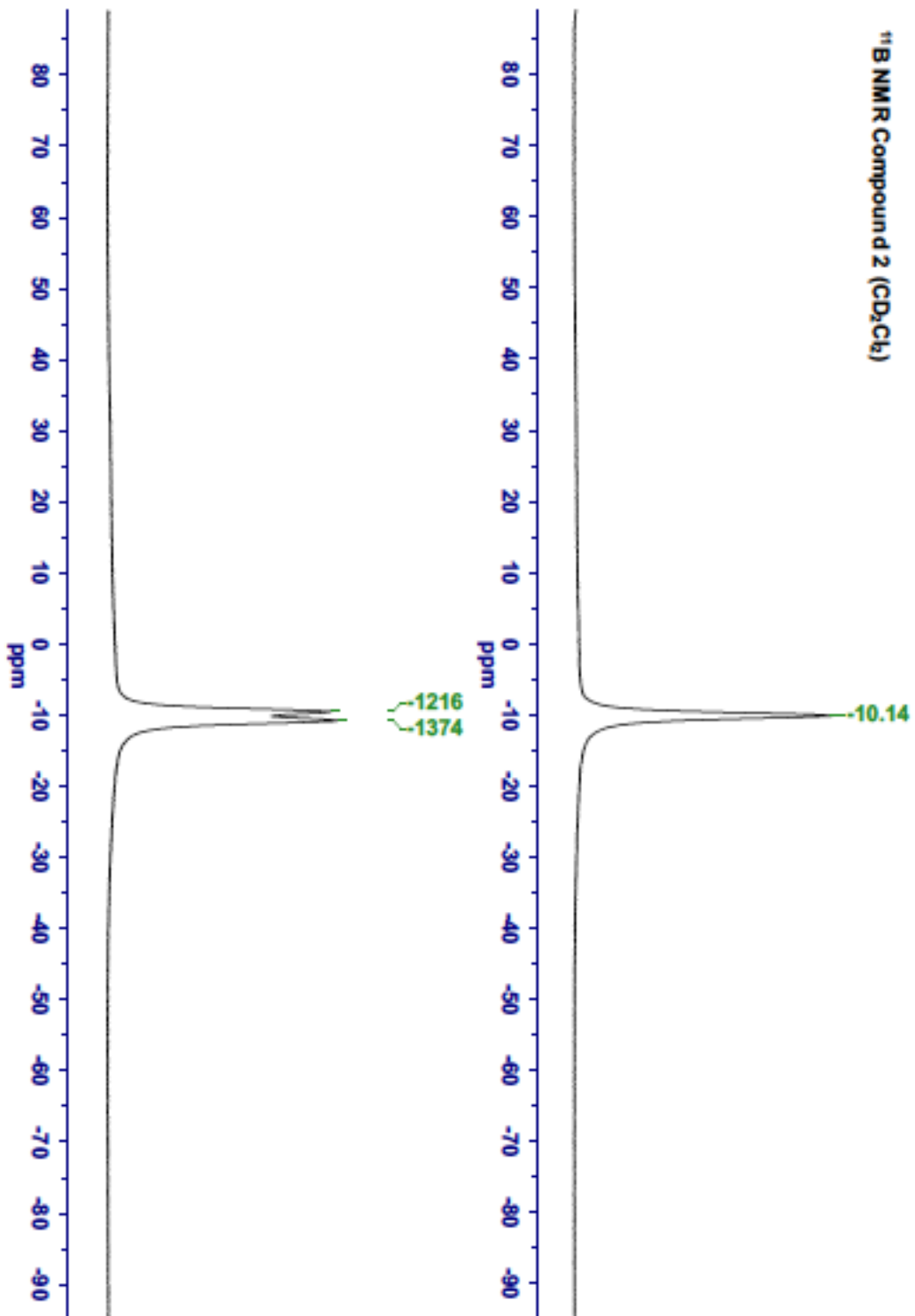
¹¹B NMR Compound 1 (CD₂Cl₂)



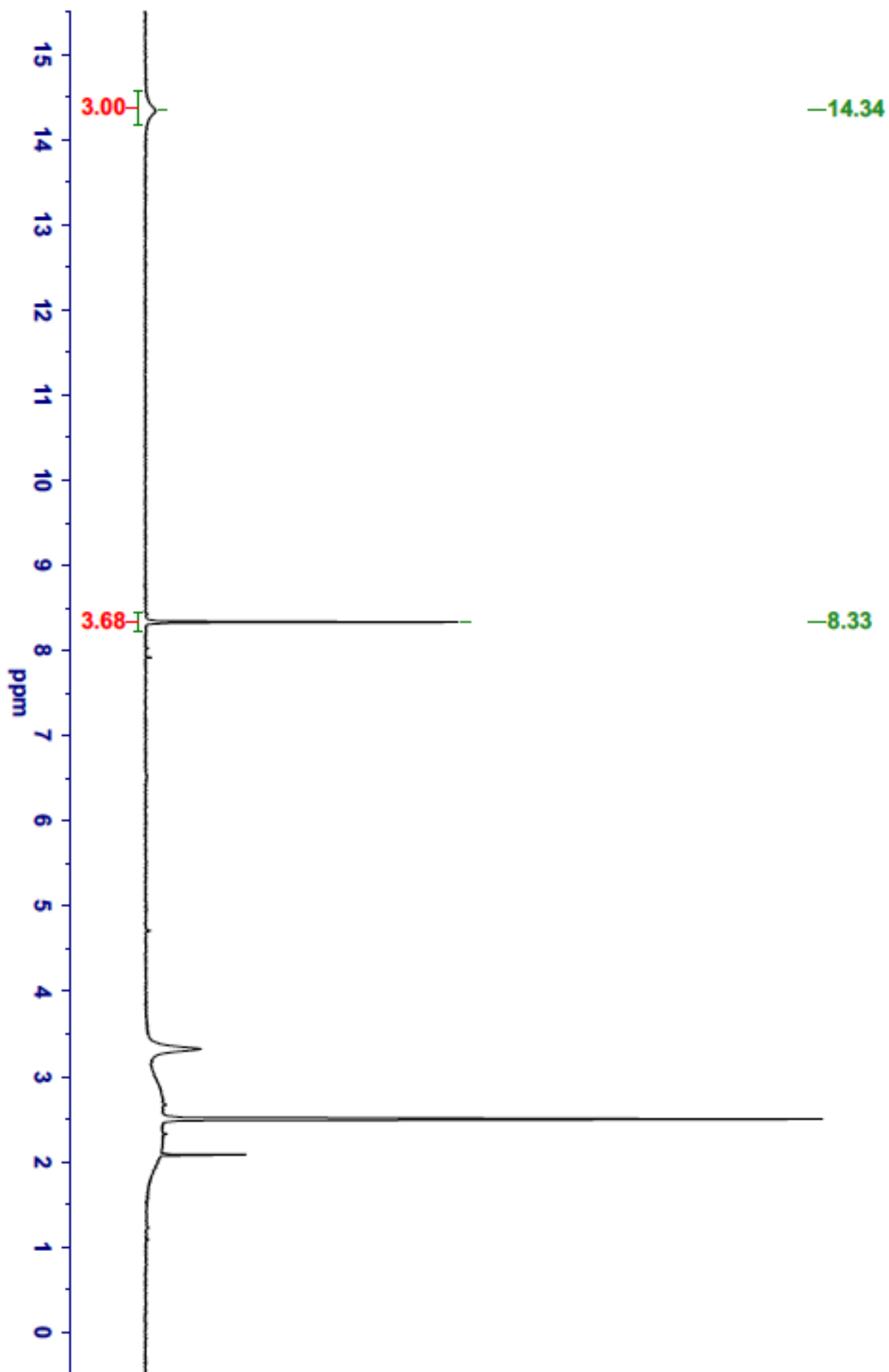




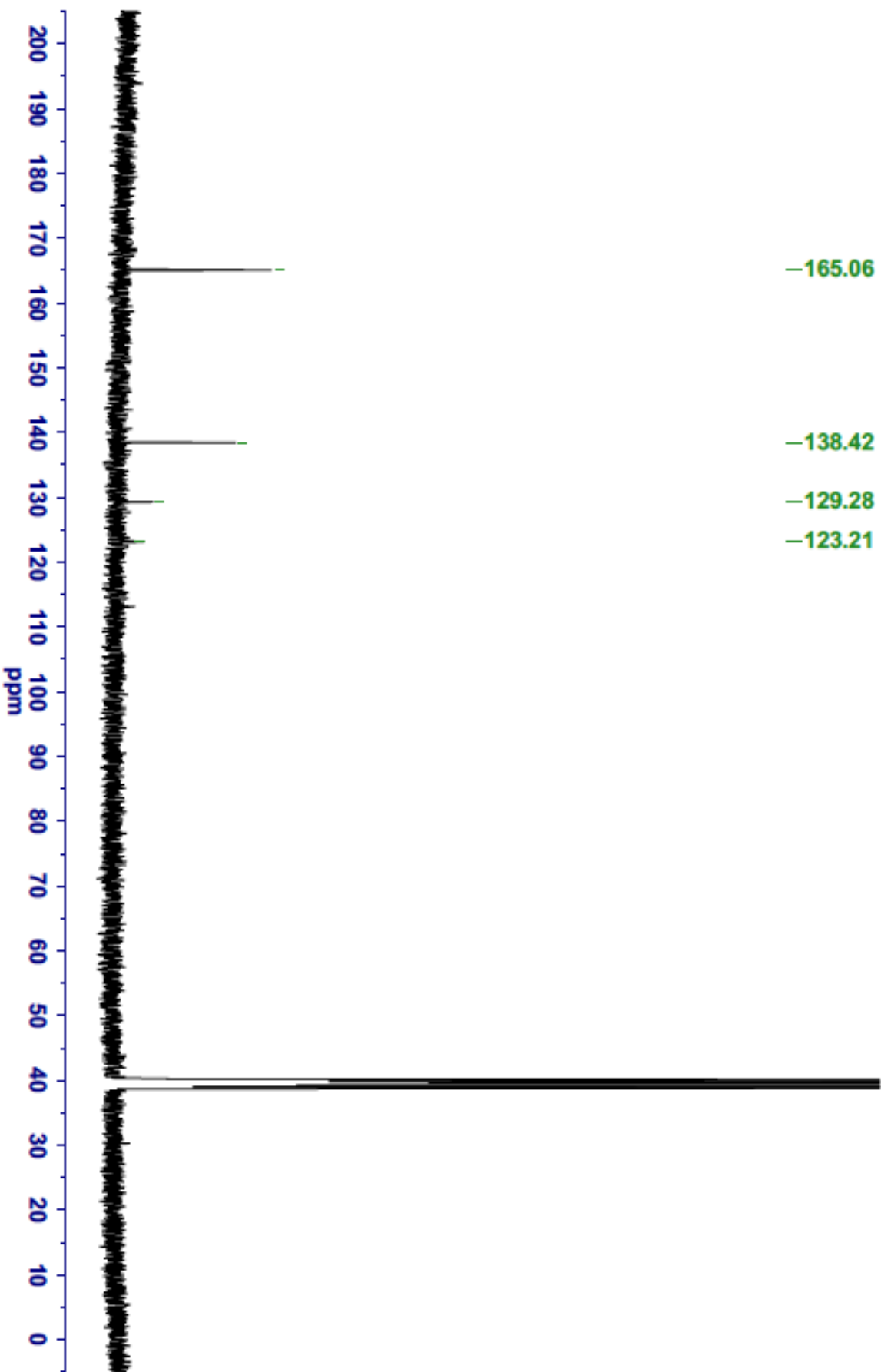
¹¹B NMR Compound 2 (CD₂Cl₂)



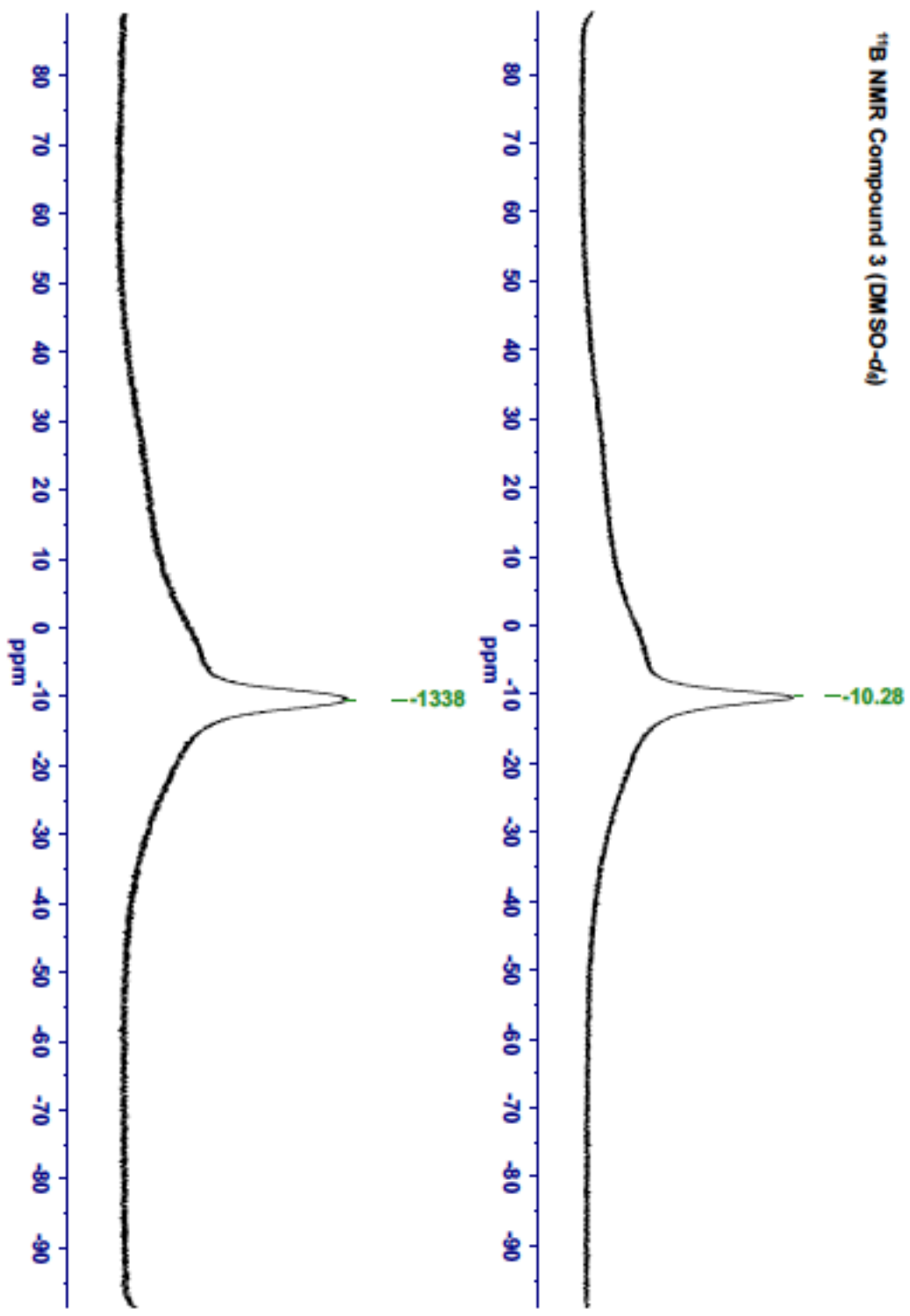
¹H NMR Compound 3 (DMSO-d₆)



¹³C {¹H} NMR Compound 3 (DMSO-*d*₆)



¹¹B NMR Compound 3 (DM SO-d₆)



3. Crystallographic Structure Determination and Refinement Details.

Single crystals of **1** were mounted in inert oil and transferred to the cold gas stream of a Bruker Kappa Apex2 diffractometer. The crystal was kept at 100(2) K during data collection. Using Olex2², the structure was solved with the ShelXD³ structure solution program using Dual Space and refined with the ShelXL⁴ refinement package using Least Squares minimization.

Table S1 Crystal data and structural refinement for **1**; for atomic coordinates, equivalent isotropic displacement parameters, bond lengths, angles, and anisotropic displacement parameters please see the CIF (CCDC code *1016256*)

Empirical formula	C ₁₂ H ₃₀ B ₂₄
Formula weight	433.80
Temperature (K)	100(2)
Crystal system	monoclinic
Space group	P2 ₁ /c
a (Å), b (Å), c (Å)	11.9932(7), 19.6594(10), 12.4615(6)
α (°), β (°), γ (°)	90, 118.684(3), 90
Volume (Å ³)	2577.6(2)
Z	4
ρ _{calc} (mg mm ⁻³)	1.118
μ (mm ⁻¹)	0.325
F(000)	888
Crystal size (mm ³)	0.414 × 0.137 × 0.034
2θ range for data collection	8.404 to 127.372°
Index ranges	-13 ≤ h ≤ 13, -22 ≤ k ≤ 22, -10 ≤ l ≤ 14
Reflections collected	11695
Independent reflections	4190[R(int) = 0.0214]
Data/restraints/parameters	4190/0/445
Goodness-of-fit on F ²	1.041

Final R indexes [$I > 2\sigma(I)$]	$R_1 = 0.0399$, $wR_2 = 0.1050$
Final R indexes [all data]	$R_1 = 0.0468$, $wR_2 = 0.1104$
Largest diff. peak/hole ($e \text{ \AA}^{-3}$)	0.203/-0.196

Single crystals of **NU-700** were mounted in inert oil and transferred to the cold gas stream of a Bruker Kappa Apex2 diffractometer. The crystal was kept at 250(2) K during data collection. Using Olex2², the structure was solved with the XT³ structure solution program using Direct Methods and refined with the ShelXL⁴ refinement package using Least Squares minimization. The enhanced rigid bond restraint (RIGU) was applied globally. The solvent masking procedure as implemented in Olex2 was used to remove the electronic contribution of solvent molecules from the refinement. As the exact solvent content is not known, only the atoms used in the refinement model are reported in the formula here. Total solvent accessible volume / cell = 19269.5 \AA^3 (79.2%)

Table S2 Crystal data and structural refinement for **NU-700**; for atomic coordinates, equivalent isotropic displacement parameters, bond lengths, angles, and anisotropic displacement parameters please see the CIF (CCDC code 1016255)

Empirical formula	$\text{C}_{10}\text{H}_{18}\text{B}_{16}\text{CuO}_5$
Formula weight	454.74
Temperature (K)	250(2)
Crystal system	cubic
Space group	$\text{Pm}\bar{3}\text{n}$
a (\AA), b (\AA), c (\AA)	28.973(2), 28.973(2), 28.973(2)
α ($^\circ$), β ($^\circ$), γ ($^\circ$)	90, 90, 90
Volume (\AA^3)	24322(5)
Z	12

ρ_{calc} (mg mm ⁻³)	0.373
μ (mm ⁻¹)	0.423
F(000)	2724
Crystal size (mm ³)	0.27 × 0.197 × 0.185
2 Θ range for data collection	4.312 to 88.922°
Index ranges	-26 ≤ h ≤ 26, -25 ≤ k ≤ 20, -23 ≤ l ≤ 25
Reflections collected	16503
Independent reflections	1700[R(int) = 0.0945]
Data/restraints/parameters	1700/84/79
Goodness-of-fit on F ²	2.359
Final R indexes [I > 2 σ (I)]	R ₁ = 0.1208, wR ₂ = 0.3451
Final R indexes [all data]	R ₁ = 0.1552, wR ₂ = 0.3726
Largest diff. peak/hole (e Å ⁻³)	0.580/-0.576

4. Powder X-ray Diffraction (PXRD)

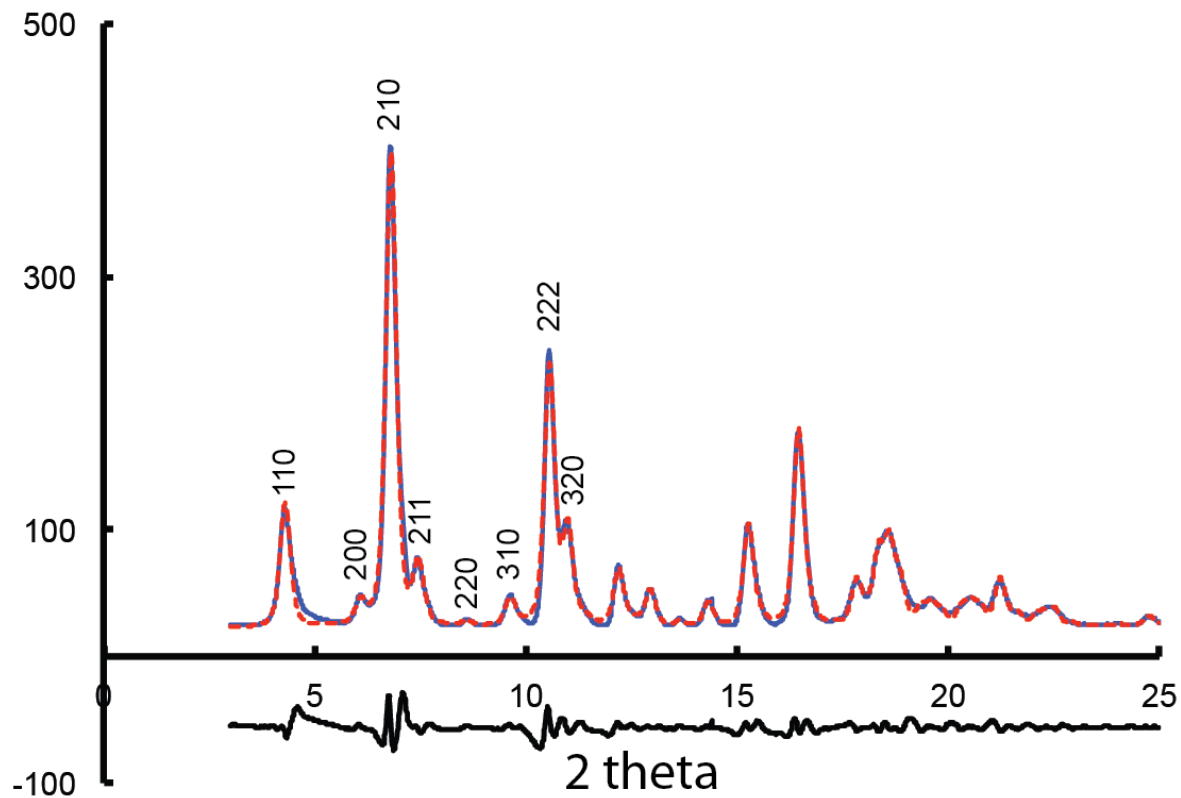


Figure S1. Pawley refinement of NU-700. Blue = experimental pattern from bulk single-crystal diffraction data; red = fit generated from single crystal symmetry and unit cell parameters; black = difference. Final statistics from Pawley refinement $R_p = 9.98\%$ and $R_{wp} = 8.12\%$.

5. Thermogravimetric Analysis (TGA)

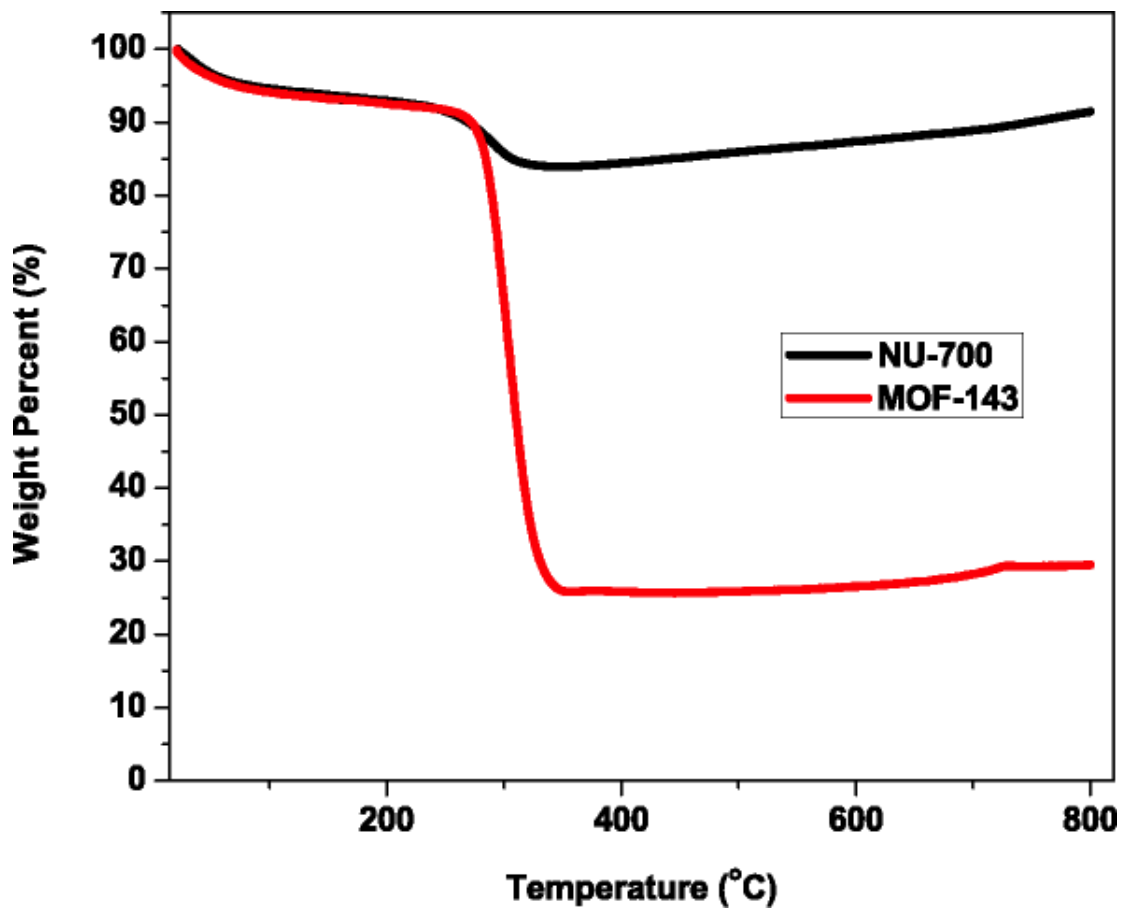


Figure S2. TGA curve of MOF-143 (red) and NU-700 (black).

6. Optical Microscopy of Single Crystals.

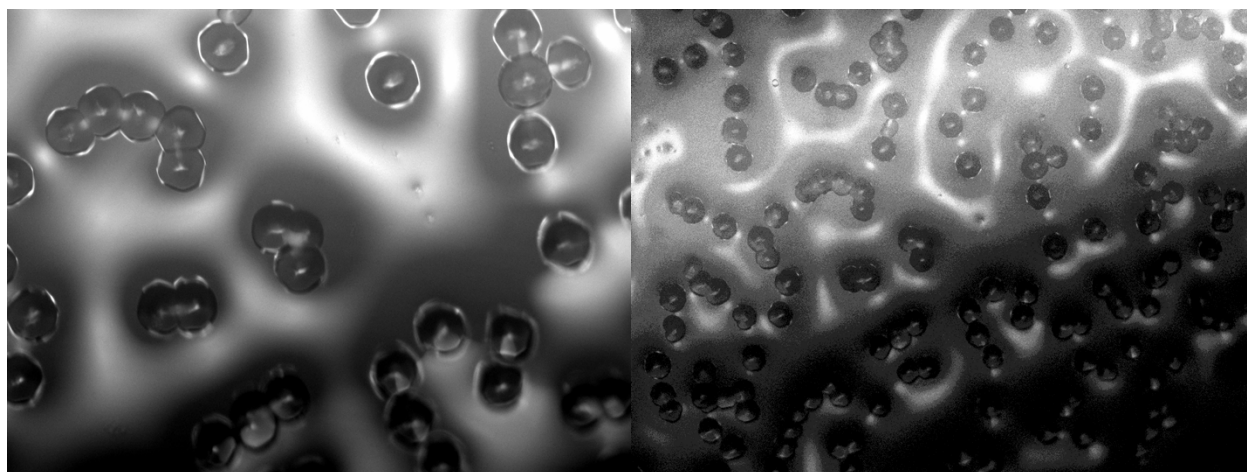


Figure S3: Optical microscopy of single crystals of NU-700

7. References

1. Schöberl, U.; Magnera, T. F.; Harrison, R. M.; Fleischer, F.; Pflug, J. L.; Schwab, P. F. H.; Meng, X.; Lipiak, D.; Noll, B. C.; Allured, V. S.; Rudalevige, T.; Lee, S.; Michl, J., Toward a Hexagonal Grid Polymer: Synthesis, Coupling, and Chemically Reversible Surface-Pinning of the Star Connectors, 1,3,5-C₆H₃(CB₁₀H₁₀CX)₃. *J. Am. Chem. Soc.* **1997**, *119*, 3907–3917.
2. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), *J. Appl. Cryst.* *42*, 339-341.
3. Sheldrick, G.M. (2008). *Acta Cryst. A* *64*, 112-122
4. Sheldrick, G.M. (2008). *Acta Cryst. A* *64*, 112-122