ChemComm

Dynamic covalent assembly of tribenzotriquinacenes into molecular cubes

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Supporting Information

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1 Materials and Chemicals

All chemicals were purchased from commercial suppliers ALFA AESAR, MERCK, ACROS and SIGMA ALDRICH and were used without further purification. The solvents were distilled prior to use. Dichloromethane and tetrahydrofuran were dried with the solvent purification system "PureSolv MD 5" from INNOVATIVE TECHNOLOGY.

Column chromatography: Glass-columns were individually packed with Silica gel (grain-size 4-63 μm, MERCK).

TLC-sheets: Silica gel 60 F_{254} TLC-aluminium foils (MERCK).

2 Technical Equipment

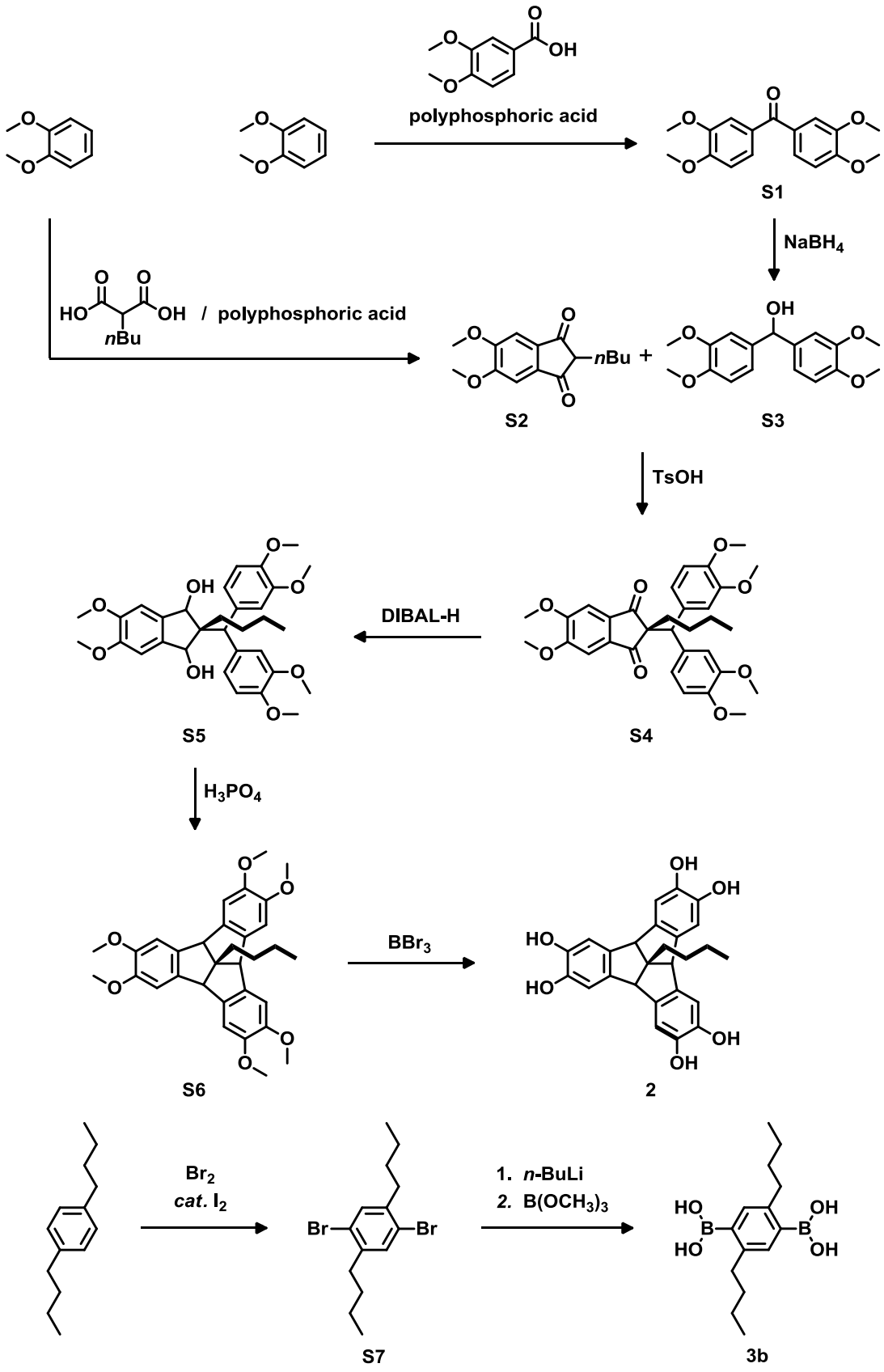
NMR spectroscopy: BRUKER AVANCE 400 and BRUKER AVANCE DMX 600. Chemical shifts are indicated in ppm in relation to the particular internal standard (^{1}H-NMR: 7.26 ppm for $CDCl_3$, 3.31 ppm for MeOD-d_4 and 3.58 ppm for THF-d_8; ^{13}C-NMR: 77.16 ppm for $CDCl_3$ and 49.00 ppm for MeOD). Signal multiplicities are denoted as s (singlet), d (dublet), t (triplet) and m (multiplet). Processing of the raw data was performed with the program Topspin 3.0.[S1]

IR spectroscopy: JASCO FT/IR-410 (ATR).

Mass spectroscopy (MALDI): autoflex II BRUKER, matrices: DCTB (*trans*-2-(3-(4-*t*-Butylphenyl)-2-methyl-2-propenylidene)malononitrile, TCNQ Tetracyanoquinodimethane.

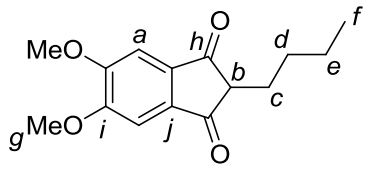
Elemental Analysis: Elementar CHNS 932 analyzer.

3 Synthetic procedures



S1[S2], **S3**[S2] and **S7**[S3] were synthesized according to literature procedures.

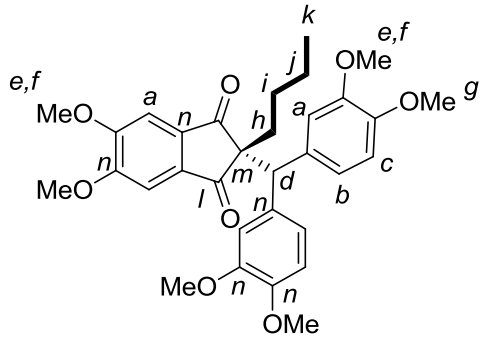
2-Butyl-5,6-dimethoxy-indene-1,3-dione S2



Butylmalonic acid (5.00 g, 31.2 mmol), veratrole (5.39 g, 39.0 mmol) and polyphosphoric acid (40 g) were mixed and heated at 80 °C for two hours.

Before cooling ice cooled water (200 ml) was added and the product was extracted with dichloromethane (2 x 200 ml). The organic solvent was removed and the solid was recrystallized from ethanol to give light orange solid **S2** (4.56 g, 17.4 mmol, 56%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.33 (s, 2H, H_a), 4.03 (s, 6H, H_g), 2.95 (t, 1H, J = 5.9 Hz, H_b), 1.96-1.90 (m, 2H, H_c), 1.38-1.28 (m, 4H, $H_{d,e}$), 0.87 (t, 3H, J = 7.1 Hz, H_f) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 200.33 (2C, C_h), 155.89 (2C, C_i), 137.53 (2C, C_j), 103.19 (2C, C_a), 56.67 (2C, C_g), 52.99 (1C, C_b), 28.36 (1C, C_d), 27.13 (1C, C_c), 22.80 (1C, C_e), 13.75 (1C, C_f) ppm. MS (MALDI, DCTB 1:3 in chloroform): *m/z* = 263.14 $[M]^+$. Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92; found: C, 68.75; H, 6.81.

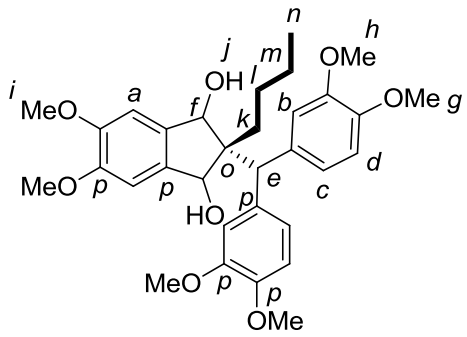
2-[Bis(dimethoxyphenyl)methyl]-2-butyl-5,6-dimethoxy-indene-1,3-dione S4



S2 (4.56 g, 17.4 mmol) was dissolved in toluene (200 ml). A spatula tip *para*-toluenesulfonic acid was added and the reaction mixture was heated to reflux. Within a period of two hours, a solution of **S3** (6.13 g, 20.1 mmol) in dichloroethane (100 ml) was added dropwise. The reaction mixture was refluxed for additional five hours, cooled to room temperature and then washed with 1M NaOH (2 x 200 ml) and H_2O (2 x 200 ml). The organic solvent was removed under reduced pressure and the residual solid was purified by coloumn chromatography on silica with

diethylether/hexane 8:1 as eluent to give the desired product **S4** (5.81 g, 10.6 mmol, 61%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.16 (m, 4H, H_a), 6.93 (dd, 2H, J = 8.3, 2.1 Hz, H_b), 6.66 (d, 2H, J = 8.3 Hz, H_c), 4.43 (s, 1H, H_d), 3.97 (s, 6H, $H_{e,f}$), 3.86 (s, 6H, $H_{e,f}$), 3.77 (s, 6H, H_g), 1.83-1.79 (m, 2H, H_h), 1.12-1.03 (m, 2H, H_i), 0.89-0.81 (m, 2H, H_j), 0.68 (t, 3H, J = 7.3 Hz, H_k) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 204.04 (2C, C_l), 155.99, 148.51, 147.68, 138.13, 133.15 (2C per peak, C_n), 122.06 (2C, C_b), 113.03 (2C, C_a), 110.99 (2C, C_c), 102.74 (2C, C_a), 62.96 (1C, C_m), 57.24 (1C, C_d), 56.72 (2C, $C_{e,f}$), 55.92 (2C, $C_{e,f}$), 55.84 (2C, C_g), 34.75 (1C, C_h), 27.43 (1C, C_i), 23.21 (1C, C_j), 13.80 (1C, C_k) ppm. MS (MALDI, DCTB 1:3 in chloroform): *m/z* = 548.20 $[M]^+$, 571.20 $[M+Na]^+$.

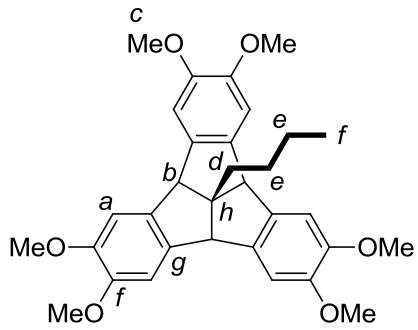
2-[Bis(dimethoxyphenyl)methyl]-2-butyl-5,6-dimethoxy-indene-1,3-diol S5



S4 (5.80 g, 10.6 mmol) was dissolved in dry dichloromethane (210 ml) and cooled to 0 °C under nitrogen atmosphere. A solution of 1.1 M DiBAl in cyclohexane (19.2 ml, 21.1 mmol) was added dropwise. The reaction mixture was stirred at room temperature overnight and subsequently quenched with H_2O (200 ml). The precipitate was filtrated and washed several times with dichloromethane. The organic layer was separated and the aqueous phase was extracted with dichloromethane (2 x 200ml). The combined organic layers were dried over sodium sulfate and the solvent was removed under reduced pressure to give a light yellow foam (5.58 g, 10.1 mmol, 95%) which was used in the next step without further purification. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.11 (d, 2H, J = 2.0 Hz, H_b), 7.08 (dd, 2H, J = 8.3, 1.9 Hz, H_c), 6.97 (s, 2H, H_a), 6.85 (d, 2H, J = 8.3 Hz, H_d), 5.15 (s, 1H, H_e), 4.68 (d, 2H, J = 7.0 Hz, H_f), 3.90 (s, 6H, H_i), 3.89 (s, 6H, H_h), 3.88 (s, 6H, H_g), 2.20 (d, 2H, J = 7.12 Hz, H_j), 1.50-1.45 (m, 2H, H_k), 0.90-0.81 (m, 2H, H_m), 0.55 (t, 3H, J = 7.3 Hz, H_n), 0.29-0.21 (m, 2H, H_l) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 150.40, 149.14, 147.84, 137.18,

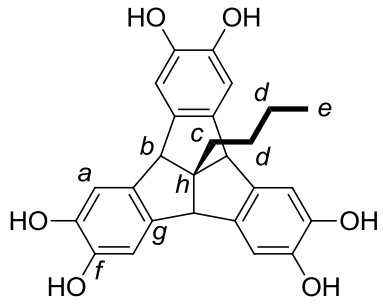
134.91 (2C per peak, C_p), 121.58 (C_c), 113.66 (C_b), 111.30 (C_d), 107.99 (C_a), 81.22 (C_f), 56.51 (C_o), 56.15, 56.08, 56.06 (2C per peak, $C_{g,h,i}$), 48.45 (C_e), 34.68 (C_k), 27.43 (C_l), 23.82 (C_m), 13.78 (C_n) ppm.

2,3,6,7,10,11-Hexamethoxy-12-butyltribenzotriquinacene S6



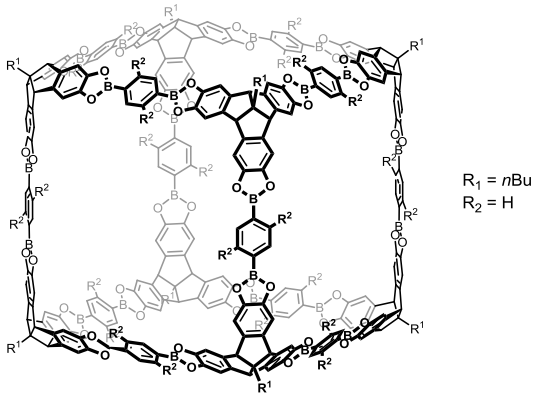
Orthophosphoric acid (85%, 1.68 ml) and chlorobenzene (85 ml) were heated to reflux for 30 minutes in a flask equipped with a soxhlet extractor containing molecular sieve 4 Å. Afterwards a solution of **S5** (5.58 g, 10.1 mmol) in chlorobenzene (50 ml) was added dropwise. After complete addition, the reaction mixture was heated for one hour. The mixture was cooled to room temperature and washed with 2 N KOH (2 x 200 ml) and H_2O (200 ml). The combined organic layers were dried over magnesium sulfate and the solvent was removed under reduced pressure. Coloumn chromatography on silica with hexane/ethyl acetate 1:1 as eluent furnished the desired product **S6** (2.55 g, 4.94 mmol, 49%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.88 (s, 6H, H_a), 4.40 (s, 3H, H_b), 3.86 (s, 18H, H_c), 1.97-1.93 (m, 2H, H_e), 1.44-1.32 (m, 4H, H_e), 0.90 (t, 3H, J = 7.1 Hz, H_f) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 149.31 (6C, C_f), 137.58 (6C, C_g), 107.52 (6C, C_a), 67.82 (1C, C_h), 60.87 (3C, C_b), 56.40 (6C, C_c), 39.93 (1C, C_d), 26.57, 23.56 (1C per peak, C_e), 14.25 (1C, C_f) ppm. MS (MALDI, DCTB 1:3 in chloroform): m/z = 516.21 $[M]^+$. Anal. Calcd for $C_{32}H_{36}O_6$: C, 74.39, H 7.02; found: C, 73.79, H, 7.30.

2,3,6,7,10,11-Hexahydroxy-12-butyltribenzotriquinacene 2



S6 (2.55 g, 4.94 mmol) was dissolved in dry dichloromethane (180 ml) and cooled to 0 °C. Under N_2 atmosphere, BBr_3 (5.69 g, 2.15 ml, 22.7 mmol) was added slowly over a period of 30 minutes. After stirring overnight at room temperature, the reaction mixture was quenched with H_2O (28 ml) and then stirred for several hours. The precipitate was filtrated under suction and washed several times with dichloromethane to yield the product **2** (2.13 g, 4.94 mmol, quantitative). ^{1}H-NMR (400 MHz, MeOD): δ = 6.77 (d, 6H, J = 0.5 Hz, H_a), 4.15 (s, 3H, H_b), 1.85-1.81 (m, 2H, H_c), 1.37-1.35 (m, 4H, H_d), 0.90 (t, 3H, H_e) ppm. ^{13}C-NMR (100 MHz, MeOD): δ = 145.78 (6C, C_f), 138.52 (6C, C_g), 111.58 (6C, C_a), 68.53 (1C, C_h), 61.60 (3C, C_b), 41.44 (1C, C_c), 27.72, 24.58 (1C per peak, C_d), 14.45 (1C, C_e) ppm. MS (MALDI, DCTB 1:3 in chloroform) *m/z* = 432.14 $[M]^+$. Anal. Calcd for $C_{26}H_{24}O_6 \cdot 0.5H_2O$: C, 70.74; H, 5.71; found: C, 70.31, H, 6.11.

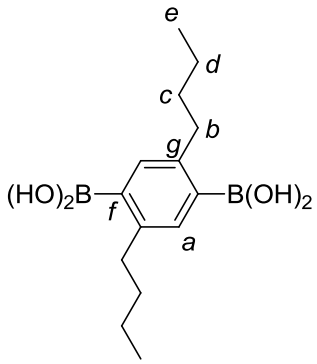
Cube 4a



2 (193 mg, 447 µmol) and **3a** (111 mg, 671 µmol) were dissolved in deuterated THF (15 ml). Molecular sieve 4 Å was added and precipitation of the product appeared after several days. The reaction mixture was filtrated, the molecular sieve was removed and the remaining solid was washed with dry THF to give the desired

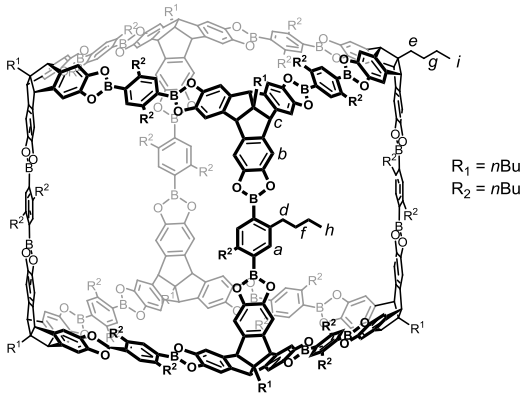
product **4a** (137 mg, 29.9 μmol, 53%). FT-IR: 3291, 2923, 1614, 1508, 1465, 1396, 1361, 1322, 1301, 1247, 1220, 1137, 1097, 1018, 896, 862, 815, 792, 775, 667. MS (MALDI, TCNQ molar ratio 1:500): *m/z* = 4584.49 $[M]^+$, 4528.86 $[M–C_4H_8]^+$. Anal. Calcd for $C_{32}H_{36}O_6 \cdot 18H_2O$: C, 68.52, H, 4.68; found: C, 68.43, H, 4.85.

2,5-Di-*n*-butyl-1,4-diboronic acid 3b



A solution of **S7** (3.88 g, 11.2 mmol) in 25 ml dry hexane was heated at 80 °C and *n*-Butyllithium (1.6 M in hexane, 18.8 ml, 30.1 mmol) was added slowly over a period of 30 minutes. The reaction mixture was heated to reflux overnight and subsequently cooled to –70 °C. Trimethylborate (9.73 g, 93.6 mmol, 10.6 ml) was added and the mixture stirred at room temperature for 12 h. After addition of 2 M HCl (3.5 ml) the resulting precipitate was filtrated, then suspended in water (30 ml), heated to reflux and again filtrated. The residue was washed with acetone to give **3b** (891 mg, 3.21 mmol, 29%). ^{1}H-NMR (400 MHz, MeOD): δ = 7.07 (s, 2H, H_a), 2.57 (t, 4H, J = 7.8 Hz, H_b), 1.58-1.49 (m, 4H, H_c), 1.39-1.30 (m, 4H, H_d), 0.93 (t, 6H, J = 7.32 Hz, H_e) ppm. ^{13}C-NMR (100 MHz, MeOD): δ = 142.79 (2C, C_f), 132.52 (4C, $C_{a,g}$), 36.64 (2C, C_b), 35.56 (2C, C_c), 23.54 (2C, C_d), 14.25 (2C, C_e) ppm. MS (MALDI, SDHB 1:3 in methanol): *m/z* = 279.19 $[M]^+$, 317.12 $[M+K]^+$. Anal. Calcd for $C_{14}H_{24}B_2O_4$: C, 60.49, H, 8.70; found: 61.65, H, 8.36.

Cube 4b



2 (20.5 mg, 47.5 µmol) and **3b** (19.8 mg, 71.3 µmol) were dissolved in 2.0 ml deuterated THF and molecular sieve 4 Å was added. After several days product was formed and hexane was added. The precipitate was filtered and washed with hexane and dissolved in $CDCl_3$ again and the solution was filtered to remove molecular sieve. The solvent was removed to give **4b** (33.2 mg, 5.6 µmol, 94%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.97 (s, 24H, H_a), 7.37 (s, 48H, H_b), 4.63 (s, 24H, H_c), 3.08-3.04 (m, 48H, H_d), 2.06-2.01 (m, 16H, H_e,), 1.65-1.41 (m, 128H, $H_{g,f}$), 0.97-0.91 (m, 96H, $H_{h,i}$) ppm. MS (MALDI, DCTB 1:1 in chloroform): *m/z* = 5933.01 $[M]^+$, 5955.71 $[M+Na]^+$, 5971.84 $[M+K]^+$. Anal Calcd for $C_{376}H_{384}B_{24}O_{48}\cdot 20CHCl_3\cdot 12C_6H_{14}$: C, 60.10, H, 6.16; found: C, 60.81, H, 7.07.

4 Analytical data

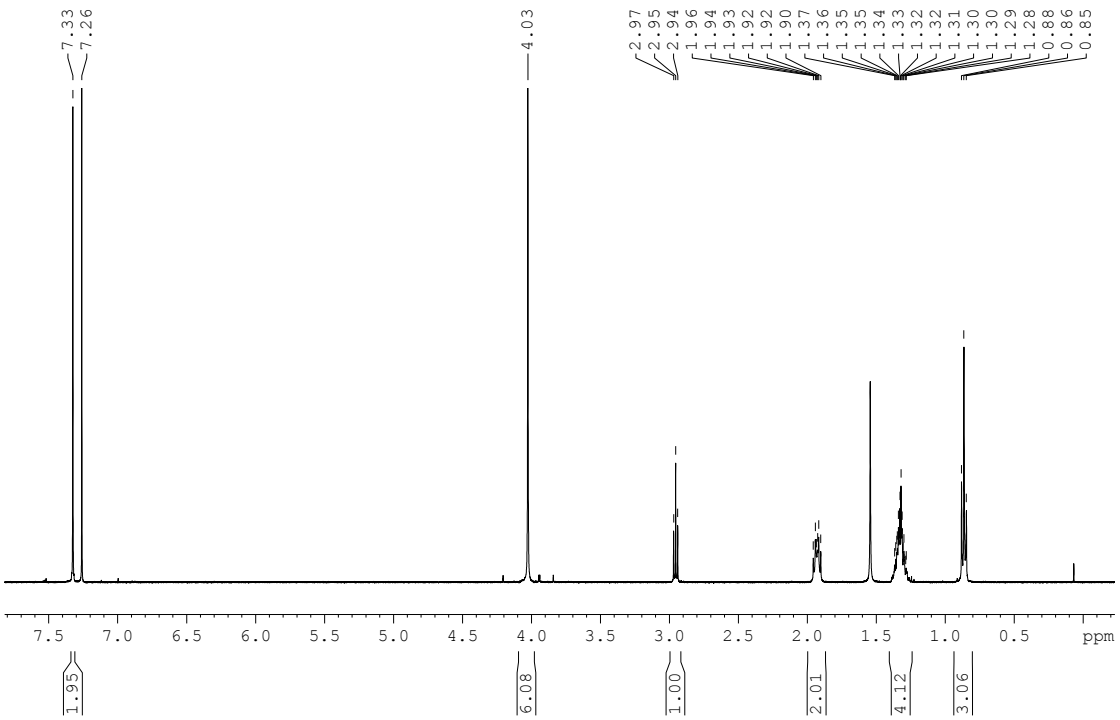


Figure S1. ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **S2**.

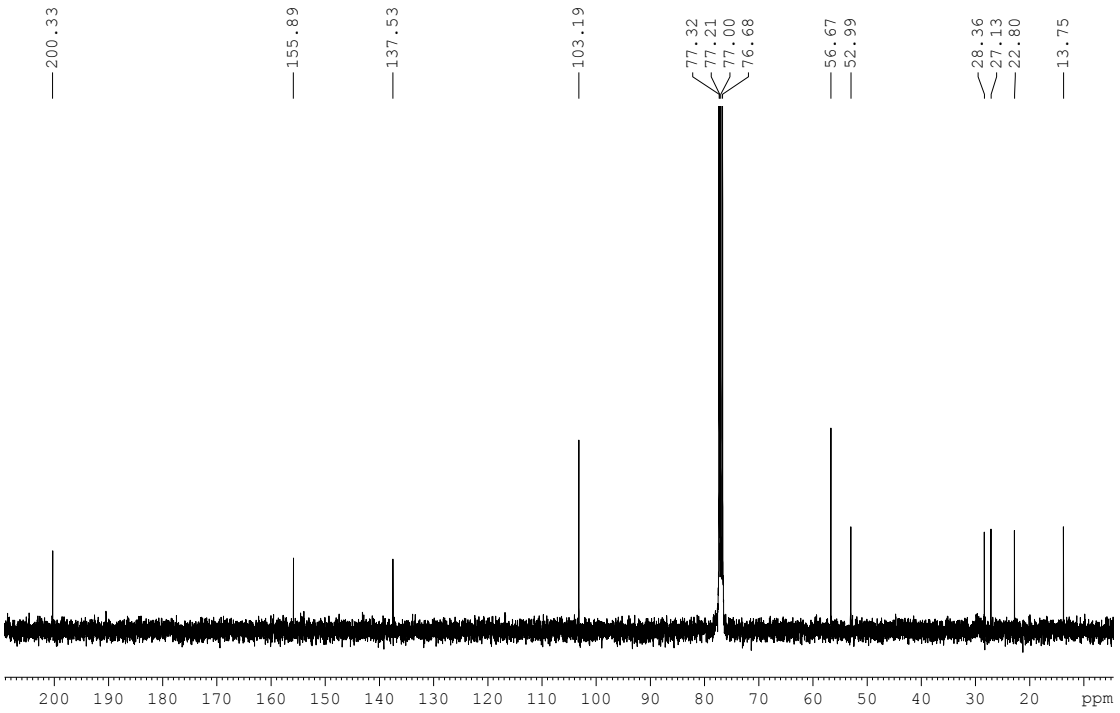


Figure S2. ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of **S2**.

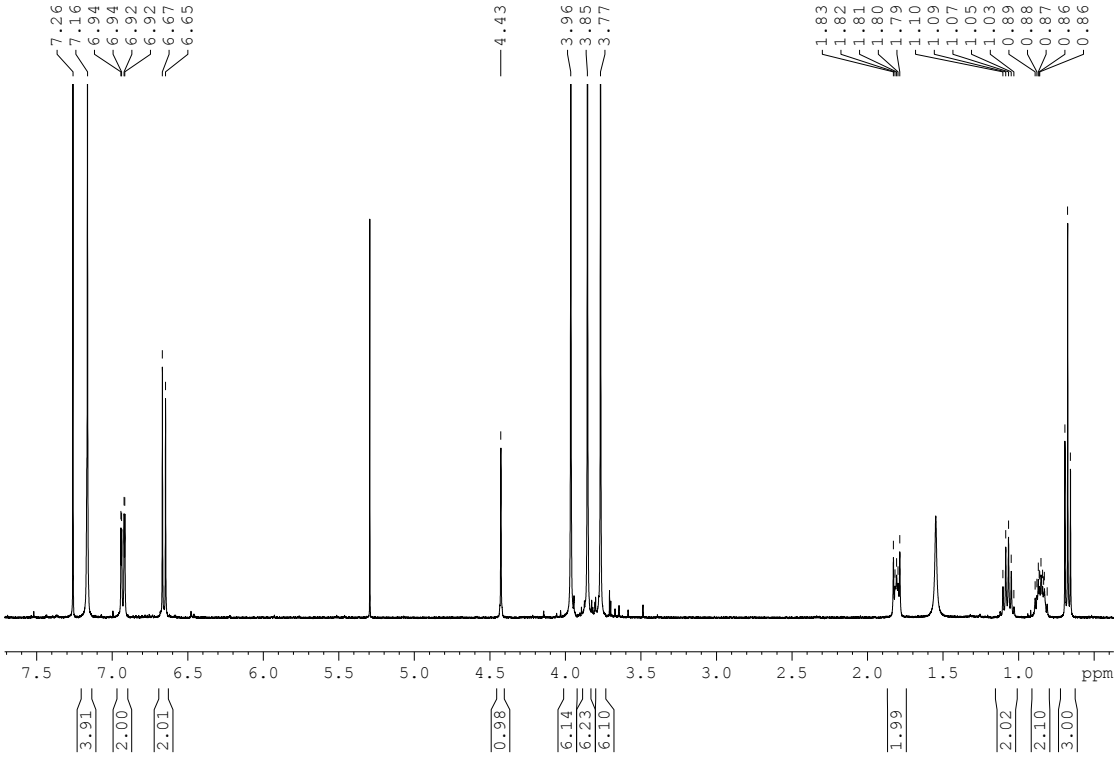


Figure S3. ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **S4**.

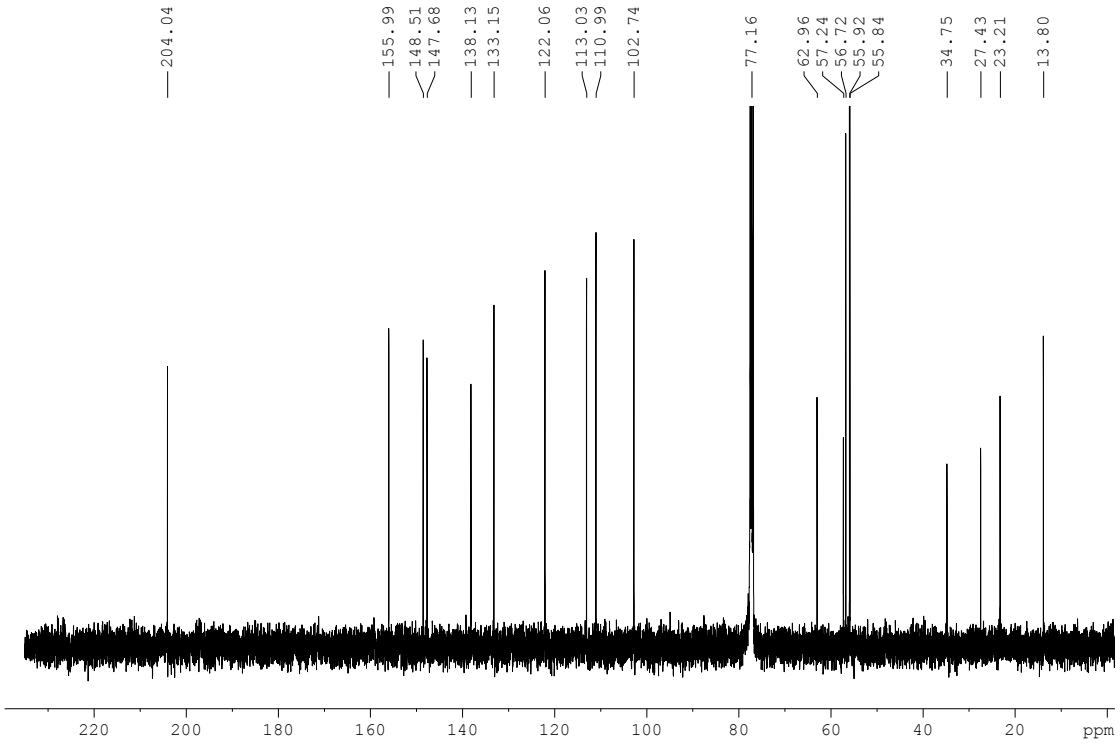


Figure S4. ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of **S4**.

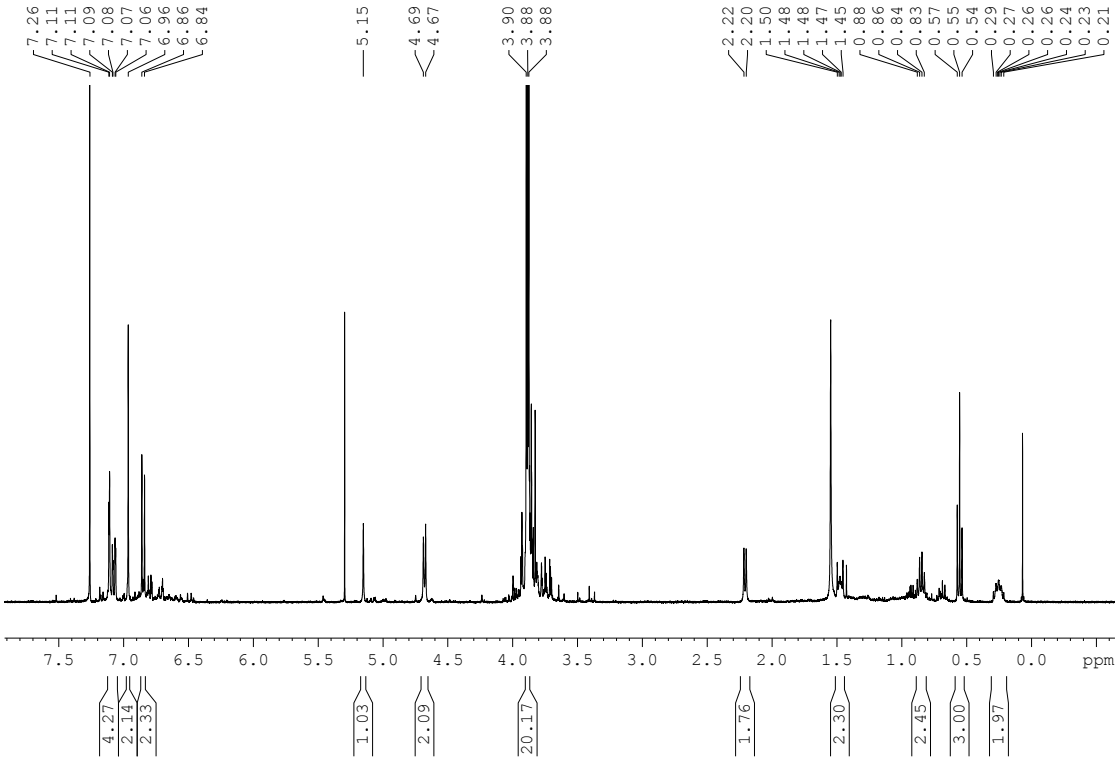


Figure S5. ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **S5**.

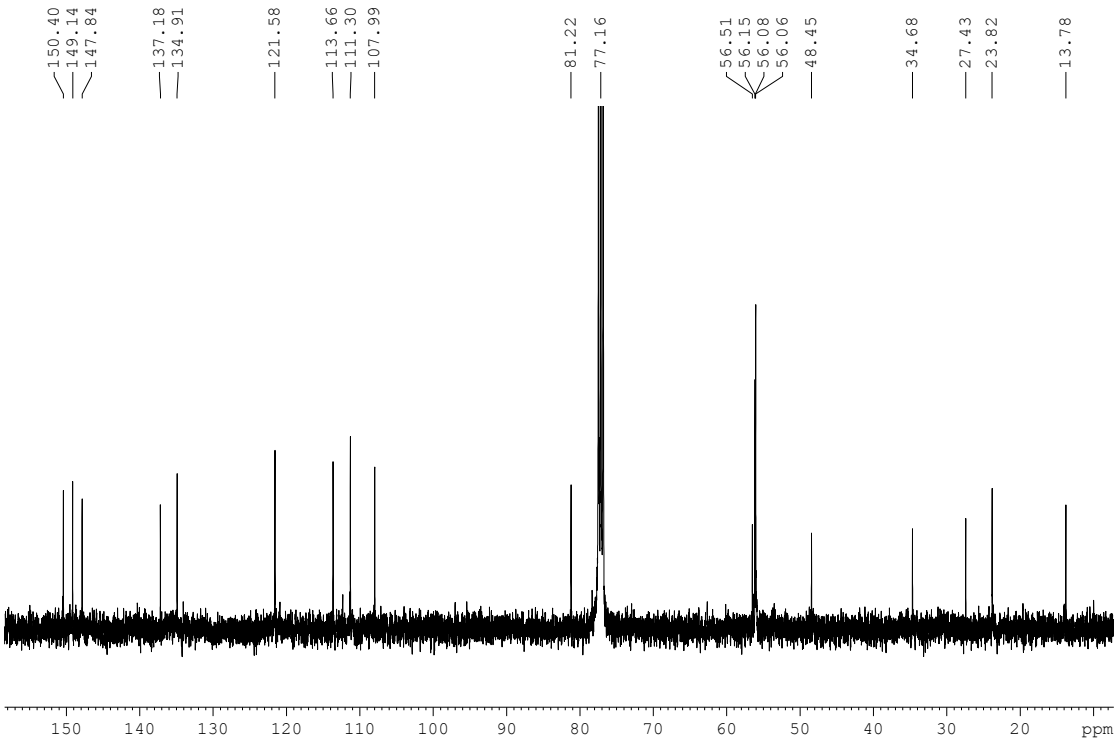


Figure S6. ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of **S5**.

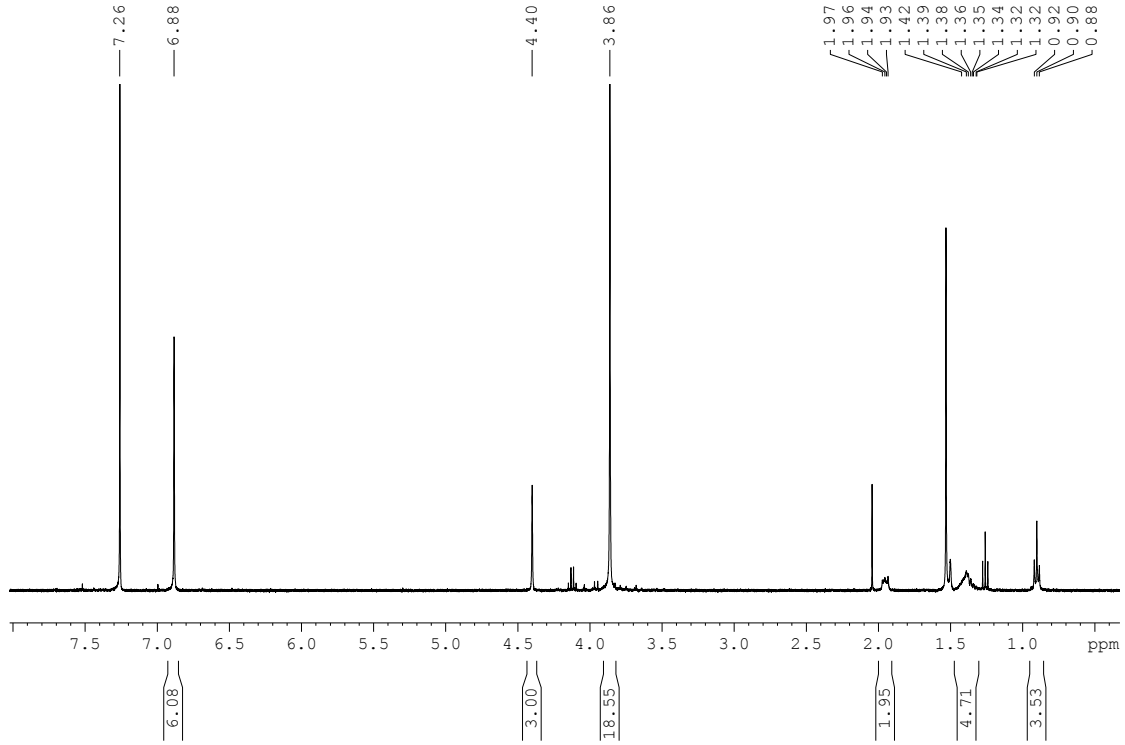


Figure S7. ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **S6**.

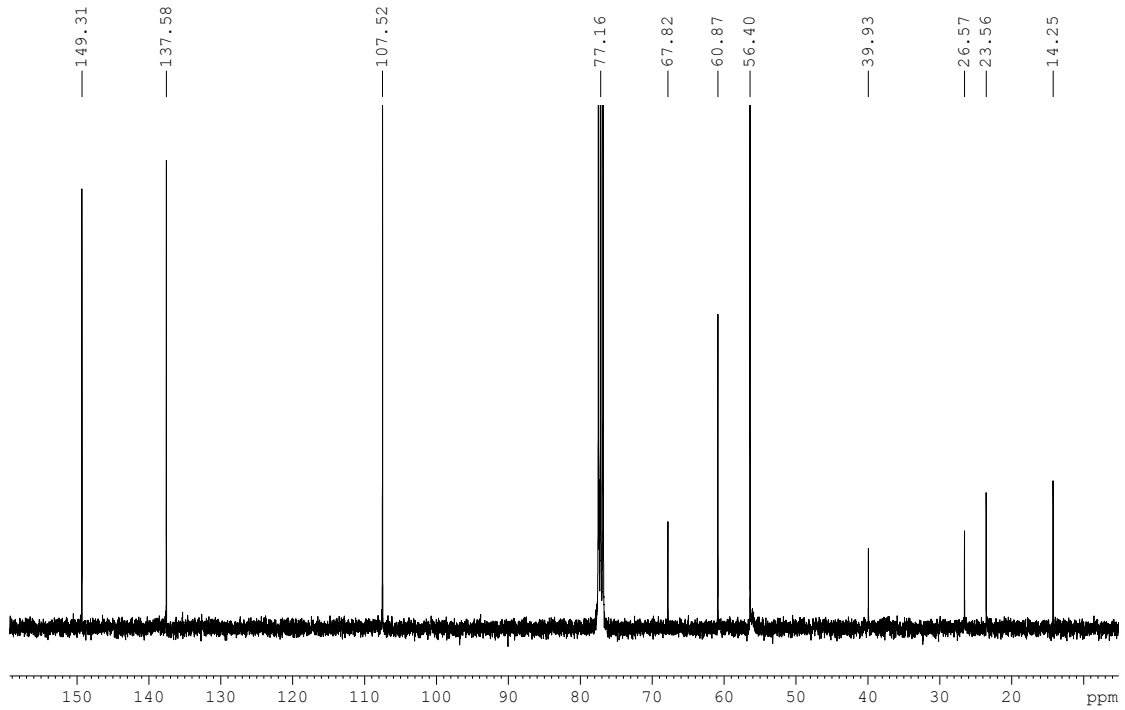


Figure S8. ^{13}C-NMR (100 MHz, MeOD) spectrum of **S6**.

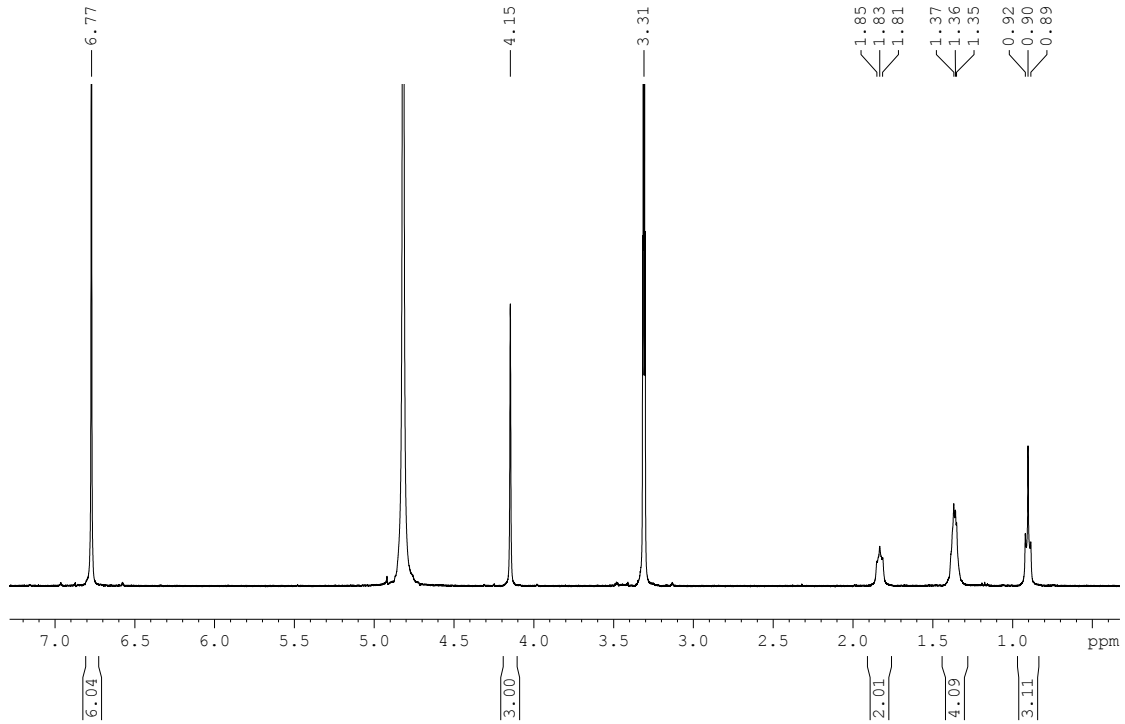


Figure S9. ^{1}H-NMR (400 MHz, MeOD) spectrum of **2**.

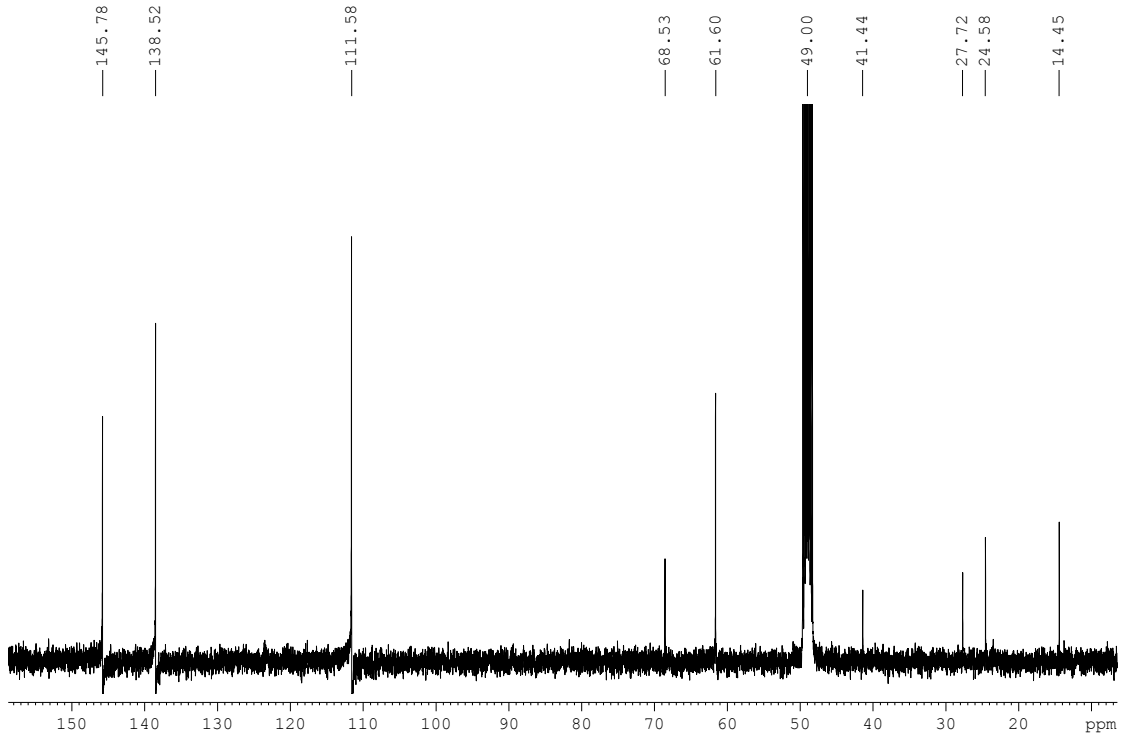


Figure S10. ^{13}C-NMR (400 MHz, MeOD) spectrum of **2**.

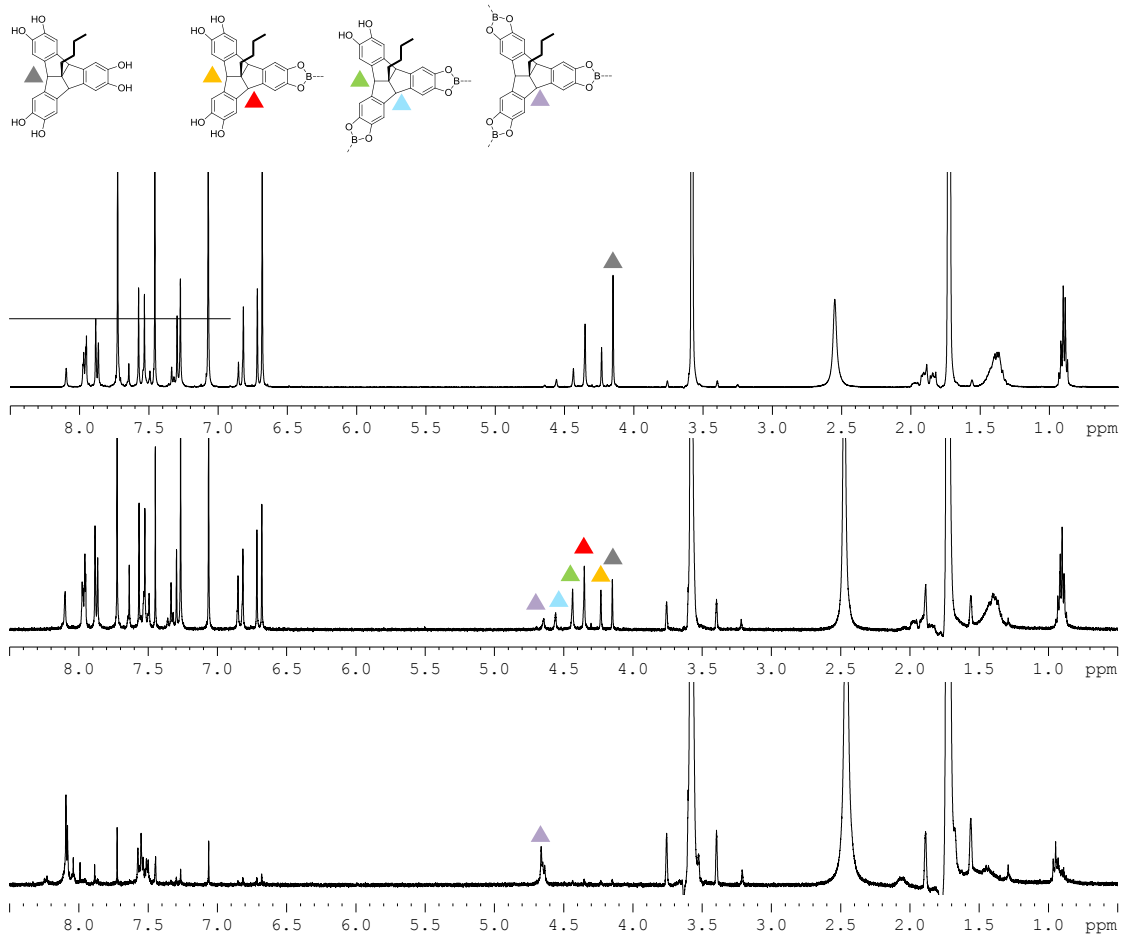


Figure S11. ^{1}H-NMR (400 MHz, THF-d^{8}) spectrum of reaction between **2** and **3a**. Top: start of reaction, middle: after addition of molecular sieve 4 Å, bottom: end of reaction.

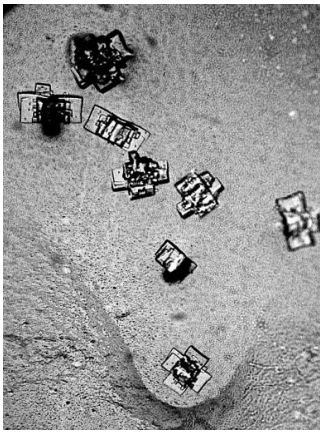


Figure S12. Crystalline precipitate of **4a**.

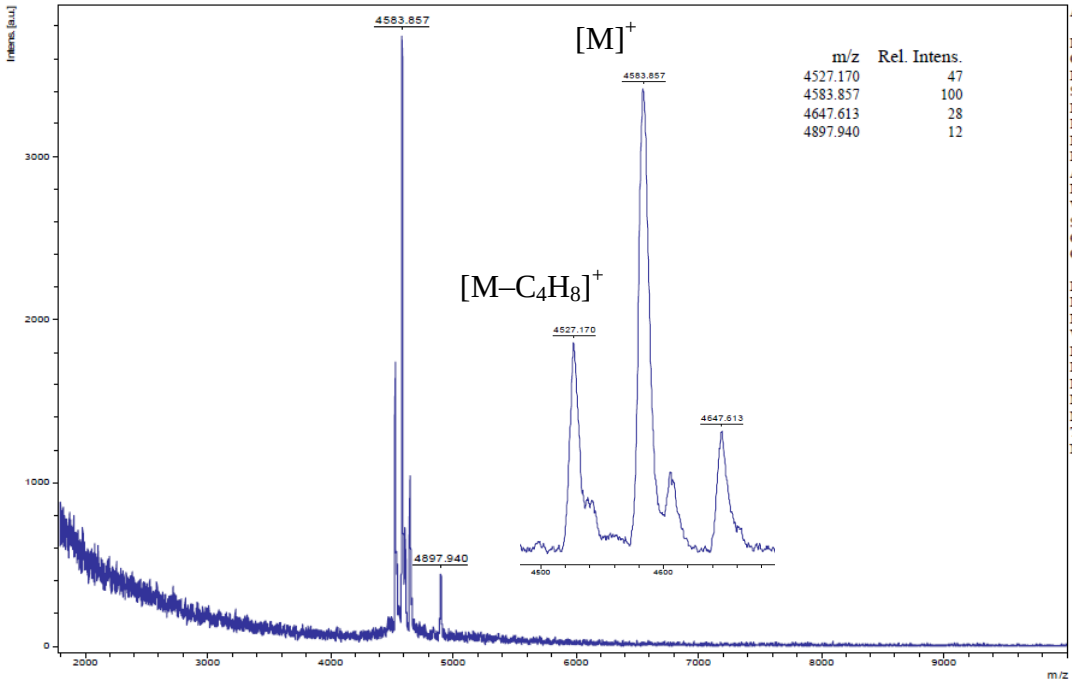


Figure S13. MALDI mass spectrum (DCTB) of the reaction mixture at the end of reaction between **2** and **3a**.

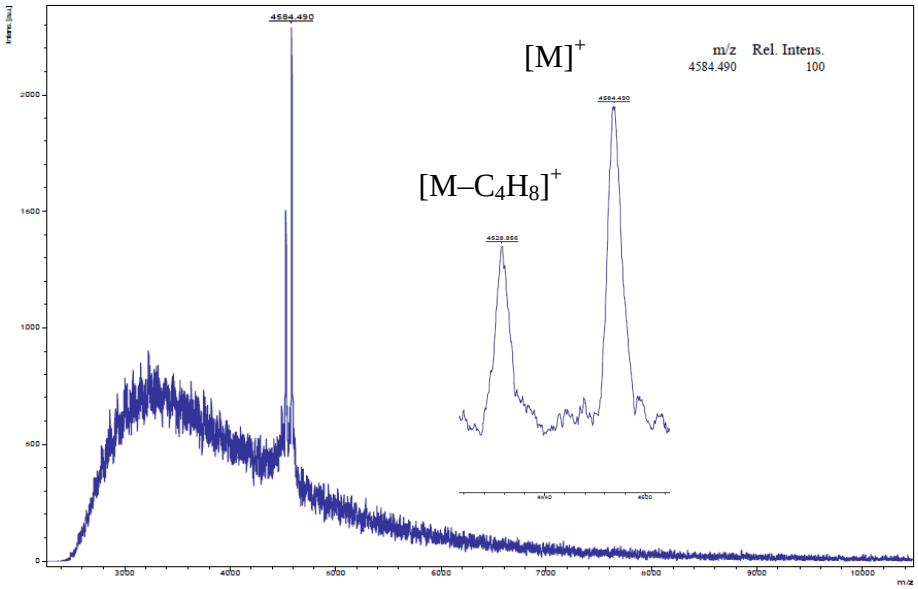


Figure S14. MALDI mass spectrum (TCNQ, solvent free, **4a**:matrix 1:500) of isolated cube **4a**.

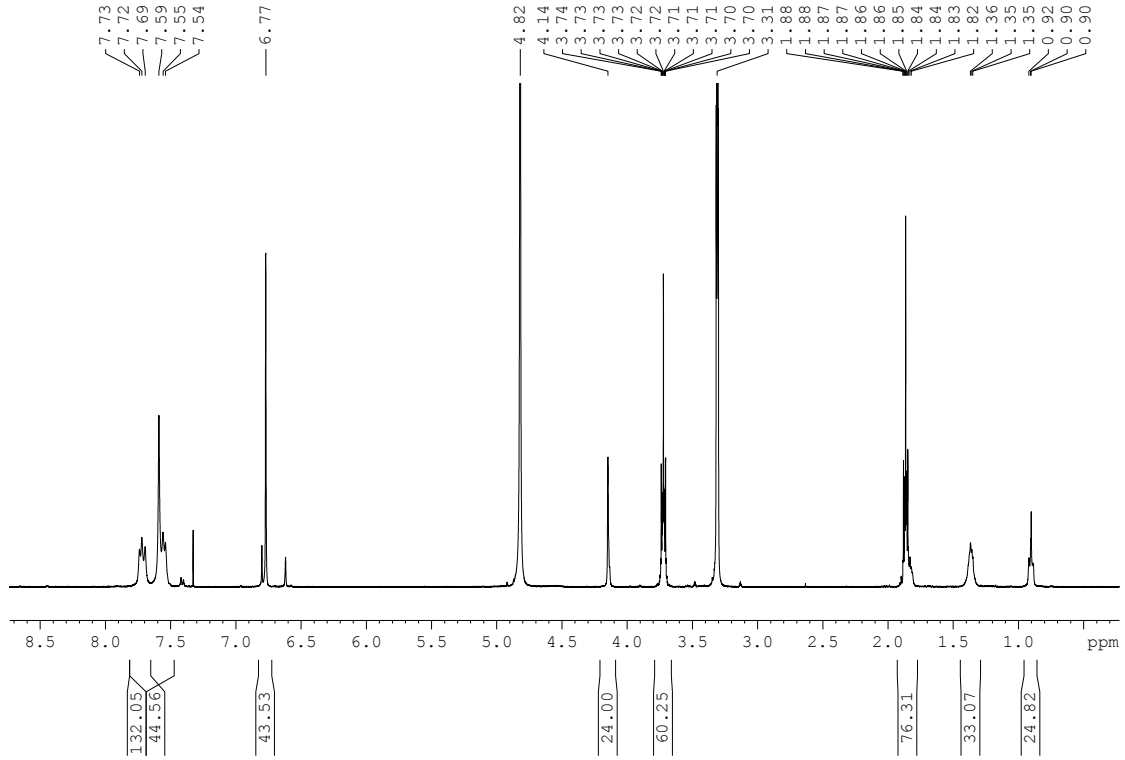


Figure S15. [1]H-NMR (400 MHz, MeOD) spectrum of isolated cube **4a** (Boronate ester bonds are cleaved in MeOD).

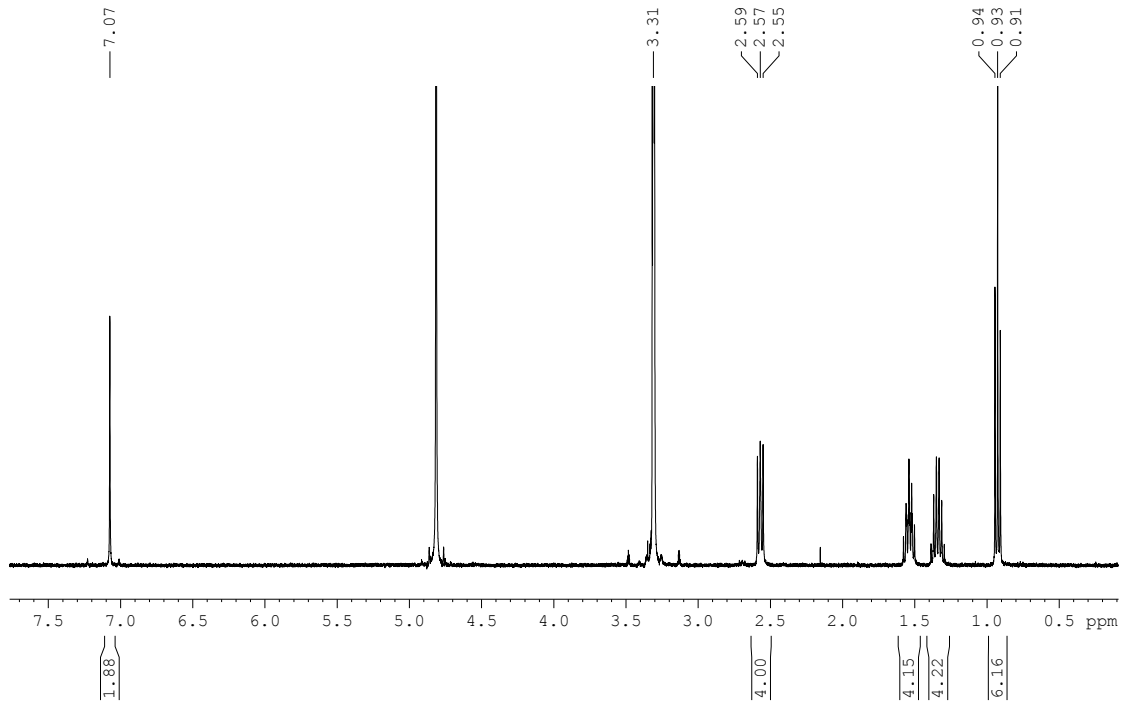


Figure S16. [1]H-NMR (400 MHz, MeOD) spectrum of **3b**.

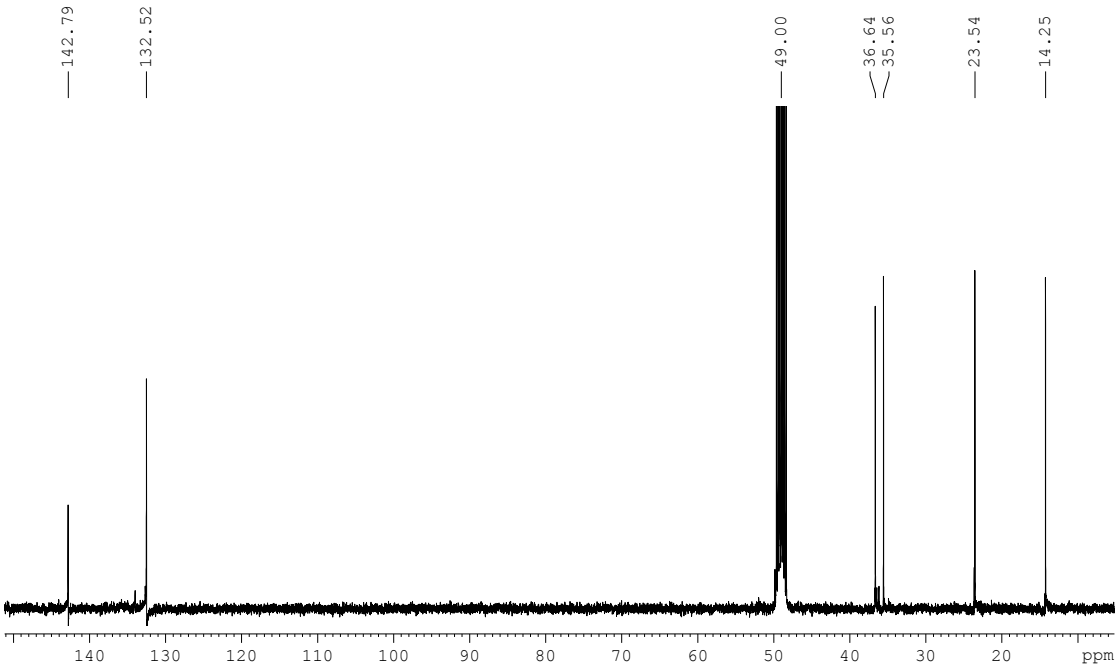


Figure S17. ^{13}C-NMR (400 MHz, MeOD) spectrum of **3b**.

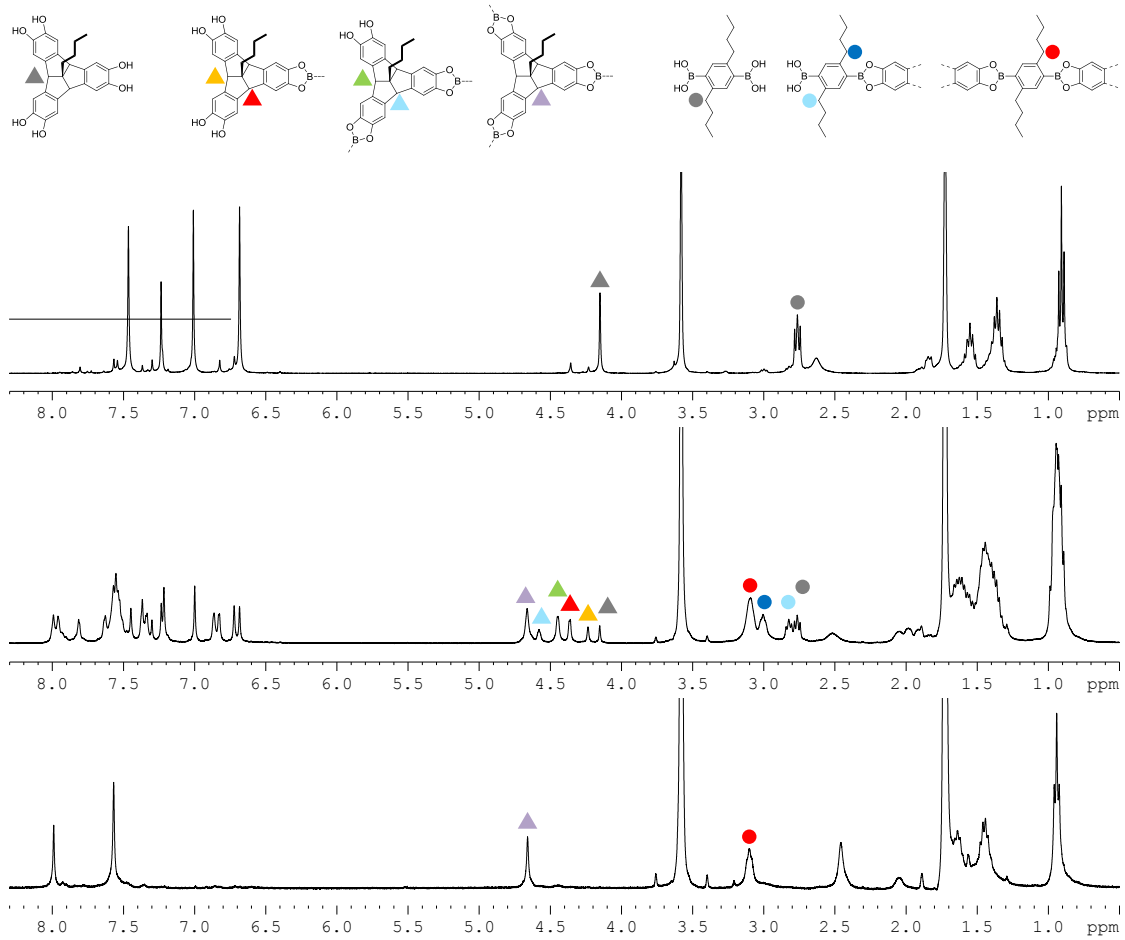


Figure S18. ^{1}H-NMR (400 MHz, THF-d^{8}) spectrum out of reaction between **2** and **3b** resulting cube **4b**. Top: start of reaction, middle: after addition of molecular sieve, bottom: end of reaction.

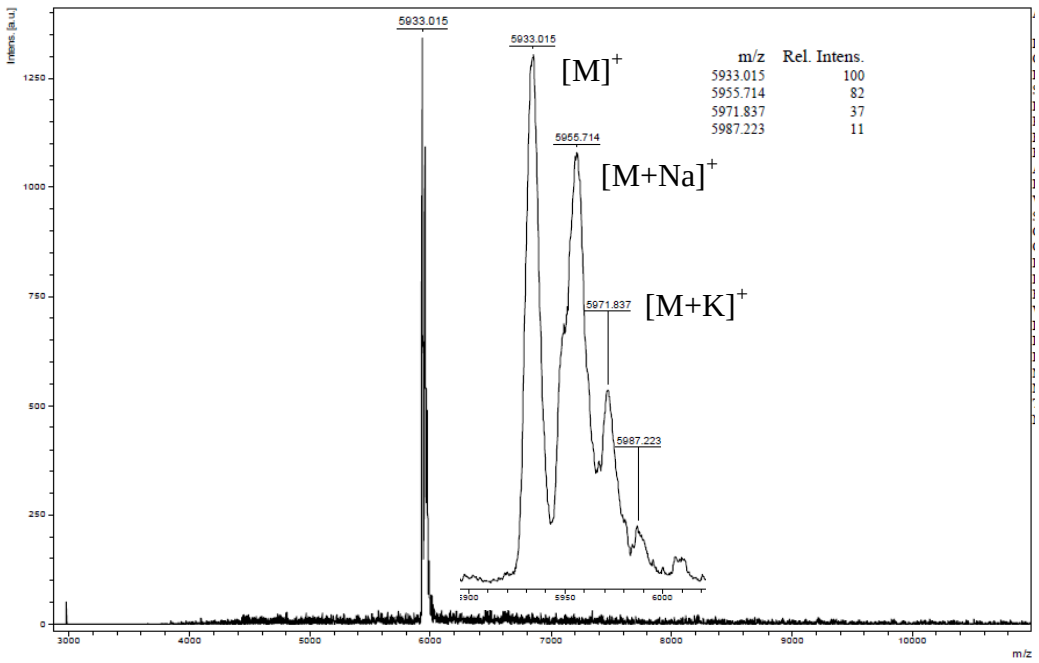


Figure S19. MALDI mass spectrum (DCTB, $CHCl_3$) of cube **4b**.

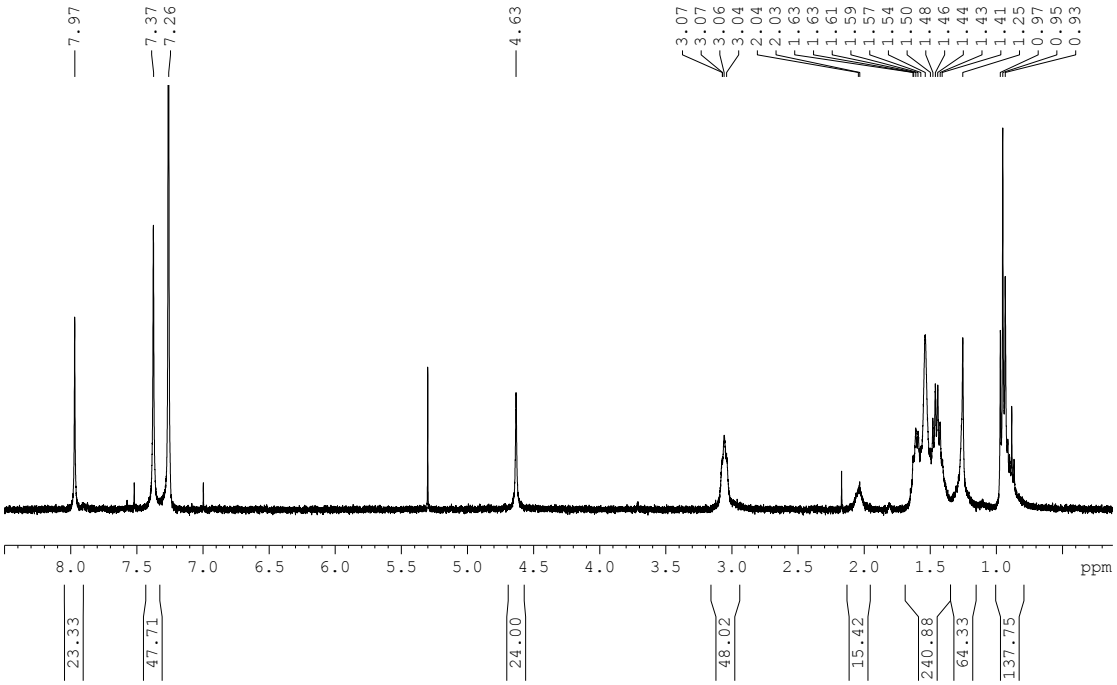


Figure S20. ^{1}H-NMR (400 MHz, $CDCl_3$) of cube **4b**.

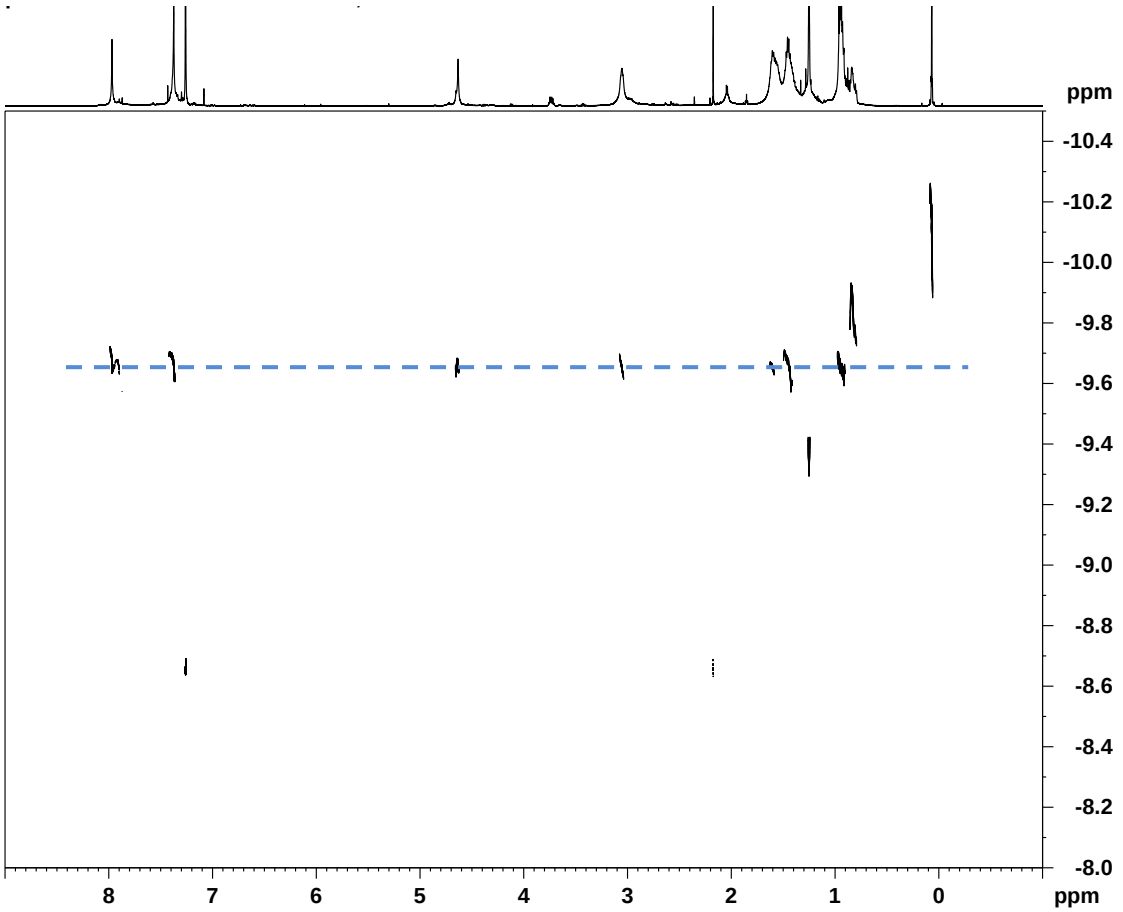


Figure S21. DOSY-NMR (600 MHz, $CDCl_3$) of cube **4b**.

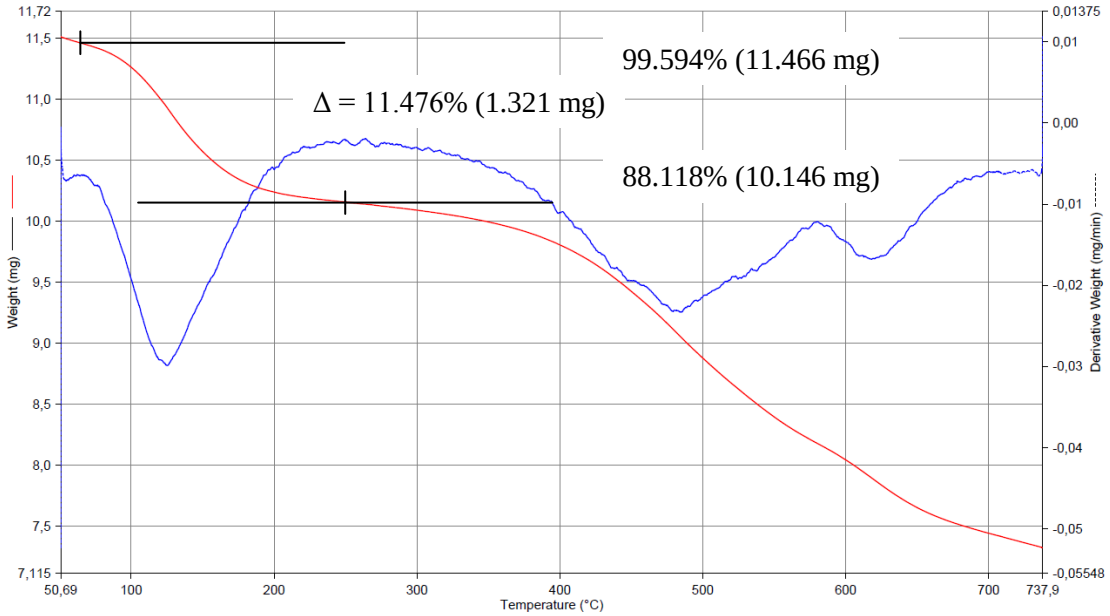


Figure S22. Thermogravimetric analysis of cube **4a**. Weight loss of 11.5% is attributed to removal of 8 equivalents of entrapped THF per cube molecule.

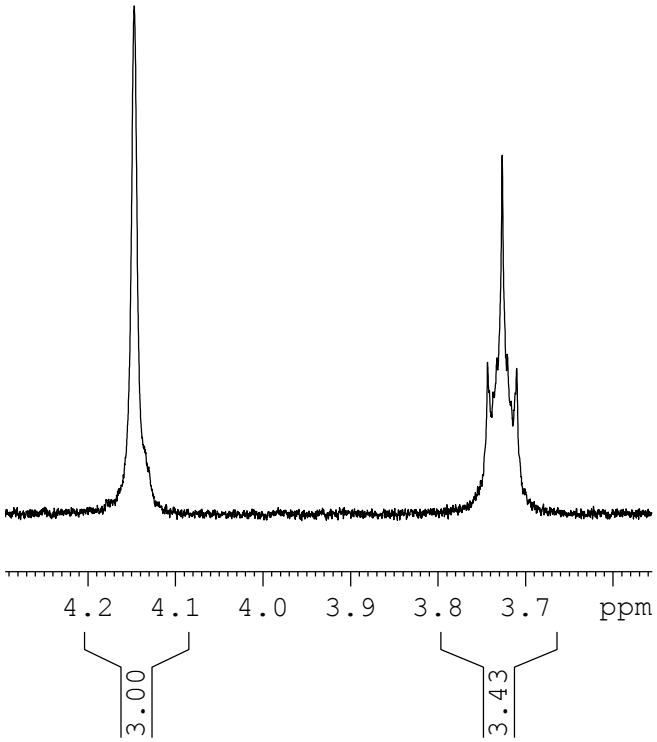


Figure S23. Cutout of ^{1}H-NMR (400 MHz, MeOD-d_4) of cube **4a** (dried at 50 °C, 1.0 x 10^{-3} mbar) showing methane protons of **2** and THF O-CH_2 protons. Boronate esters are cleaved. Ratio **2**:THF of about 1:0.9 is equivalent to roughly eight THF molecules per cube molecule.

5 References

[S1] Topspin 3.0, Bruker, http://www.bruker.com

[S2] J. Vile, M. Carta, C. G. Bezzu, N. B. McKeown, *Polym. Chem.* **2011**, *2*, 2257-2260.

[S3] E. Thorn-Csányi, P. Kraxner, *Macromol. Chem Phys.* **1997**, *198*, 3827-3843.