

Supplementary Information

Electro-Mechanically Switchable [8]Annulene Oligomers

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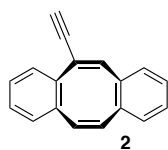
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I. General methods

Unless otherwise noted, air- and moisture-sensitive reactions were carried out in oven-dried (>110 °C) glassware capped with a rubber septum under a positive pressure of argon. Air- and moisture-sensitive reagents, solvents, and solutions were transferred via syringe or stainless-steel cannula under a dry argon atmosphere. Reactions were stirred using oven-dried Teflon®-coated magnetic stir bars. Room temperature indicates a temperature in the span 20 – 25 °C. Elevated temperatures were maintained using silicone oil baths actively controlled by thermostat devices. Commercial reagents and solvents were purchased from Fisher Scientific (Acros Organics and Alfa Aesar), Sigma-Aldrich, or VWR (TCI and Apollo Scientific) with a purity of 95% or higher and used as received unless otherwise noted. Commercial catalysts were stored and handled in an argon-filled glove box. CH₂Cl₂, Et₂O, THF, toluene, *n*-hexane, and acetonitrile were obtained from a dry solvent dispensing system. Analytical thin layer chromatography (TLC) was performed on silica-backed TLC plates (60 F₂₅₄ silica gel) and visualized by UV-light ($\lambda = 254$ nm) and/or treatment with either *p*-anisaldehyde stain, KMnO₄ stain, or phosphomolybdic acid (PMA) stain followed by gentle heating. Preparative column chromatography was performed according to the method of Still and co-workers¹ using silica gel 60 Å (40–60 μ m particle size) columns or a Biotage automatic flash purification system. NMR spectra were recorded on a 400 MHz (¹H at 400 MHz and ¹³C at 101 MHz) Bruker Avance II or a 500 MHz (¹H at 500 MHz and ¹³C at 126 MHz) Bruker Avance III HD spectrometer. Unless noted otherwise, the NMR spectra were recorded at $T = 298$ K. Spectra were processed using Mnova v10.0. ¹H NMR chemical shifts are referenced to the residual solvent peak as internal standard (CDCl₃ = 7.26 ppm; THF-d₈ = 3.58 and 1.73 ppm; DMSO-d₆ = 2.50 ppm) and are listed as follows: chemical shifts (δ , ppm), multiplicity, scalar coupling constant(s) in Hz, and integral values. NMR data for planar chiral structures are given for mixtures of interconverting stereoisomers. The multiplicity of signals from these compounds are reported based on the apparent shape of the respective peaks. ¹³C NMR chemical shifts are referenced to the residual solvent peak as internal standard (CDCl₃ = 77.16 ppm; THF-d₈ = 67.57 and 25.37 ppm; DMSO-d₆ = 39.62 ppm). Infrared spectra were recorded on a Bruker Alpha-P FT/IR instrument with a Diamond ATR sensor and are reported as follows: wavenumbers (cm⁻¹), description (w = weak, m = medium, s = strong, br = broad). Samples were prepared as a film for liquid or neat for solid substances. UV-VIS spectra for reduced oligomers were obtained by placing quartz Young's tube with samples directly in an Agilent Technologies Cary 60 UV-

VIS spectrophotometer. The homogeneity of the samples was confirmed by ^1H NMR spectroscopy prior to collection of UV-VIS data. Melting points were measured on a BÜCHI B-540 melting point apparatus and are uncorrected. High-resolution mass spectra (HRMS) were recorded on a Q-TOF, a LTQ Velos PRO Orbitrap ESI spectrometer, or a JEOL GCmate II spectrometer by direct probe using EI-ionization (70 eV).

II. Synthetic procedures and spectroscopic data for compounds 2, 3a/b, 4, S1, 5, dbCOT2, dbCOT3, S2, and dbCOT5



(5Z,11Z)-5-Ethynyldibenzo[*a,e*]cyclooctatetraene (2). To a stirred solution of triflate **1**² (0.63 g, 1.5 mmol), CuI (43 mg, 0.23 mmol), Et₃N (0.52 mL, 3.7 mmol), and ethynyltrimethylsilane (0.30 mL, 2.1 mmol) in THF (15 mL) was added Pd(dppf)Cl₂·CH₂Cl₂ (61 mg, 0.075 mmol) in one portion. After stirring at 50 °C overnight, the mixture was concentrated under reduced pressure, the residues re-dissolved in MeOH (15 mL), and then stirred. K₂CO₃ (0.30 g, 2.2 mmol) was added in one portion. After 2.5 h, the mixture was dry loaded onto silica and purified by flash chromatography (eluting with 17% CH₂Cl₂ in heptane) to afford alkyne **2**.

Yield: 0.19 g (56%), isolated as an orange oil, >95% pure by ^1H NMR spectroscopy and a single spot by TLC.

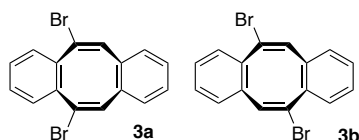
R_f: 0.42 (16:1 EtOAc/heptane).

^1H NMR (400 MHz, CDCl₃) δ : 7.39 – 7.34 (m, 1H), 7.28 (s, 1H), 7.23 – 7.14 (m, 4H), 7.10 – 7.02 (m, 3H), 6.82 (d, *J* = 11.8 Hz, 1H), 6.77 (d, *J* = 11.8 Hz, 1H), 2.98 (s, 1H) ppm.

^{13}C NMR (101 MHz, CDCl₃) δ : 140.5, 137.1, 136.91, 136.89, 136.0, 133.2, 133.0, 129.3, 129.0, 128.8, 128.7, 127.8, 127.6, 127.3, 127.0, 125.9, 86.0, 76.2 ppm.

FTIR (CH₂Cl₂ film): 3287 (m), 3013 (w), 1491 (m), 1413 (m), 1211 (s), 600 (s) cm⁻¹.

HRMS-ESI (m/z): [M + H]⁺ Calcd for C₁₈H₁₃ 229.1012; Found: 229.1018.



(5*E*,11*E*)-5,12-Dibromodibenzo[*a,e*]cyclooctatetraene (3a) and (5*E*,11*E*)-5,11-dibromodibenzo[*a,e*]cyclooctatetraene (3b). To a stirred solution of 5,6,11,12-tetrabromo-5,6,11,12-tetrahydrodibenzo[*a,e*][8]annulene (5.6 g, 11 mmol) in toluene (196 mL) heated to 120 °C was added 1,5-diazabicyclo[4.3.0]non-5-ene (7.0 mL, 56 mmol) dropwise via syringe. After 2 h, TLC indicated full conversion of the starting material. The reaction mixture was then cooled to room temperature, washed with 10% H₂SO₄ (150 mL) and then with water (150 mL). The organic layer was separated, passed through a phase separator, and concentrated under reduced pressure to furnish mixture of regioisomers (**3a to 3b** = 83:17 (¹³C NMR spectroscopy)) that was not readily separable by column chromatography.

Yield: 3.8 g (98%). Isolated as an off-white solid, >95% pure by ¹H NMR. Single spot by TLC (KMnO₄ stain).

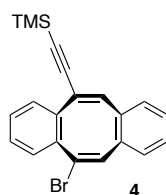
R_f: 0.71 (10:1 hexane/EtOAc).

¹H NMR (400 MHz, CDCl₃) δ: 7.41 – 7.35 (m, 2H), 7.34 – 7.30 (m, 2H), 7.26 – 7.15 (m, 4H), 7.10 – 7.03 (m, 2H) ppm.

¹³C NMR (101 MHz, CDCl₃) δ: major regioisomer **3a**: 137.5, 136.1, 134.9, 129.5, 128.8, 128.4, 127.7, 122.1 ppm; minor regioisomer **3b**: 138.1, 135.8, 133.9, 130.3, 128.7, 127.8, 127.8, 123.6 ppm.

FTIR (CH₂Cl₂ film): 3061 (w), 3021 (w), 1636 (m br), 1485 (m), 1430 (w), 1335 (w), 1164 (m br), 928 (m), 876 (s), 837 (m), 758 (s), 746 (s), 685 (s), 600 (m), 576 (m), 460 (w) cm⁻¹.

HRMS-APCI (m/z): [M + NH₄]⁺ Calcd for C₁₆H₁₄Br₂N 377.9493; Found: 377.9489.



(((5*E*,11*E*)-12-Bromodibenzo[*a,e*][8]annulen-5-yl)ethynyl)trimethylsilane (4). To a stirred solution of a 83 : 17 mixture of dibromides **3a** and **3b** (98 mg, 0.27 mmol), [Pd(PPh₃)₄] (6.0

mg, 5.2 μmol), CuI (4.0 mg, 21 μmol) and Et₃N (0.11 mL, 0.79 mmol) in benzene (2.7 mL) was added ethynyltrimethylsilane (81 μL , 0.59 mmol) in one portion, and the resulting mixture heated to 50 °C. After 90 min, TLC indicated complete conversion of the starting material. The reaction was then quenched by addition of ethylenediamine (20 μL), dry-loaded onto silica, and purified by flash chromatography (100% heptane) to afford alkyne **4**.

Yield: 46 mg (58% based on **3a**). Isolated as a pale-yellow oil, >95% pure in ¹H NMR. A single spot by TLC.

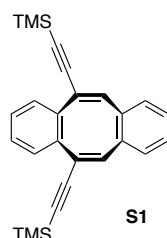
R_f: 0.26 (heptane).

¹H NMR (500 MHz, CDCl₃) δ : 7.40 – 7.36 (m, 1H), 7.34 – 7.31 (m, 1H), 7.27 – 7.25 (m, 2H; 2 singlets), 7.25 – 7.22 (m, 2H), 7.18 – 7.14 (m, 2H), 7.09 – 7.03 (m, 2H), 0.23 (s, 9H) ppm.

¹³C NMR (126 MHz, CDCl₃) δ : 139.8, 138.1, 136.4, 136.3, 135.9, 134.6, 129.8, 128.9, 128.8, 128.7, 128.3, 128.0, 127.6, 127.5, 126.5, 122.7, 106.3, 94.3, 0.1 ppm.

FTIR (CH₂Cl₂ film): 2959 (w), 2144 (w), 1487 (w), 1250 (w), 1061 (w), 917 (w), 840 (s), 759 (m), 691 (w) cm⁻¹.

HRMS-ESI (m/z): [M + H]⁺ Calcd for C₂₁H₂₀BrSi 379.0518; Found: 379.0515.



(5E,11E)-5,12-Bis(trimethylsilyl)ethynyl dibenzo[*a,e*][8]annulene (S1). To a stirred solution of bromide **4** (0.43 g, 1.1 mmol), [Pd(PPh₃)₄] (66 mg, 57 μmol), CuI (11 mg, 58 μmol), and Et₃N (1.3 mL, 9.3 mmol) in dry THF (25 mL) was added ethynyltrimethylsilane (0.35 mL, 2.5 mmol) in one portion. The resulting mixture was heated to 50 °C. After 20 h, TLC indicated complete conversion of the starting material. The reaction was then quenched by addition of ethylenediamine (0.20 mL). The resulting mixture was dry-loaded onto celite, and purified by an automated flash purification system (1% ethyl acetate in heptane) to afford di-yne **S1**.

Yield: 0.46 g, quant. Isolated as a colorless oil, >95% pure in ¹H NMR and a single spot by TLC.

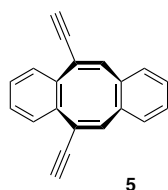
R_f: 0.37 (10:1 heptane/CH₂Cl₂).

¹H NMR (400 MHz, CDCl₃) δ: 7.36 – 7.31 (m, 2H), 7.25 – 7.20 (m, 4H), 7.17 – 7.12 (m, 2H), 7.07 – 7.02 (m, 2H), 0.22 (s, 18H) ppm.

¹³C NMR (101 MHz, CDCl₃) δ: 139.7, 136.7, 136.2, 129.2, 128.6, 127.9, 127.5, 126.9, 106.8, 93.8, 0.1 ppm.

FTIR (CH₂Cl₂ film): 2959 (w), 2141 (w), 1492 (w), 1249 (w), 1083 (w), 1050 (w), 905 (w), 842 (s), 757 (m) cm⁻¹.

HRMS-ESI (m/z): [M + H]⁺ Calcd for C₂₆H₂₉Si₂ 397.1808; Found: 397.1797.



(5Z,11Z)-5,12-Diethynyldibenzo[*a,e*]cyclooctatetraene (5). To a stirred solution of silyl protected di-yne **S1** (0.15 g, 0.37 mmol) in THF/MeOH 3:1 (16 mL), was added TBAF (1.8 mL, 1.8 mmol, 1.0 M in THF) dropwise over 30 seconds and the resulting mixture was heated to 35 °C. After stirring for 2.5 h, TLC indicated complete conversion of the starting material. The reaction mixture was evaporated, and the remaining residue dry-loaded onto celite. Purification by an automated flash purification system (10% to 15% toluene in heptane) afforded di-yne **5**.

Yield: 87 mg (98%). Isolated as a pale-yellow oil, >95% pure by ¹H NMR spectroscopy and a single spot by TLC.

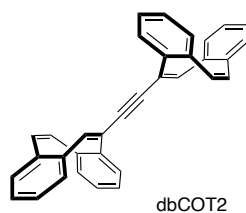
R_f: 0.17 (10:1 heptane/CH₂Cl₂).

¹H NMR (400 MHz, CDCl₃) δ: 7.38 – 7.31 (m, 2H), 7.28 – 7.26 (m, 2H), 7.25 – 7.22 (m, 2H), 7.20 – 7.16 (m, 2H), 7.10 – 7.04 (m, 2H), 3.03 (s, 2H) ppm.

¹³C NMR (101 MHz, CDCl₃) δ: 140.1, 136.5, 135.9, 129.0, 128.6, 128.1, 127.6, 125.7, 85.4, 77.0 ppm.

FTIR (CH₂Cl₂ film): 3284 (s), 3059 (w), 3018 (w), 1487 (w), 1430 (w), 1244 (w br), 1027 (w), 869 (m), 759 (m), 652 (m), 622 (m), 605 (m) cm⁻¹.

HRMS-ESI (m/z): [M + H]⁺ Calcd for C₂₀H₁₃ 253.1017; Found: 253.1019.



dbCOT2: 1,2-Bis((5Z,11Z)-dibenzo[*a,e*]cyclooctatetraen-5-yl)ethyne. Ethynyl-dbCOT **2** (0.11 g, 0.50 mmol), triflate **1** (0.18 g, 0.50 mmol), [Pd(PPh₃)₄] (29 mg, 25 μmol), CuI (10 mg, 53 μmol) and Et₃N (0.21 mL, 1.5 mmol) were charged in a round bottom flask and benzene (5.0 mL) was added. The resulting mixture was stirred at 50 °C overnight, then cooled down to room temperature, and concentrated under reduced pressure. The remaining crude mixture was dry-loaded onto silica and purified by flash chromatography (25% CH₂Cl₂ in heptane) to afford dbCOT2.

Yield: 0.14 g (64%). Isolated as an amorphous pale-yellow solid, >95% pure in ¹H NMR and a single spot by TLC.

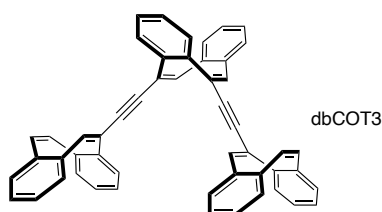
R_f: 0.46 (7:1 EtOAc/heptane).

¹H NMR (500 MHz, CDCl₃) δ: 7.41 – 7.35 (m, 2H), 7.22 – 7.15 (m, 10H), 7.07 – 7.05 (m, 6H), 6.85 – 6.76 (m, 4H) ppm.

¹³C NMR (126 MHz, CDCl₃) δ: 139.2, 139.0, 138.5, 137.4, 137.3, 137.12, 137.10, 136.8, 136.4, 133.2, 133.06, 133.04, 129.57, 129.54, 129.0, 128.84, 128.82, 128.7, 127.57, 127.4, 127.20, 127.18, 127.03, 126.99, 90.8, 90.7 ppm.

FTIR (CDCl₃ film): 3057 (m), 3012 (m), 1490 (s), 1427 (w), 1363 (w), 1213 (w), 908 (s), 860 (m), 771 (s), 752 (s), 733 (s), 600 (w), 516 (w), 454 (w) cm⁻¹.

HRMS-APCI (m/z): [M + H]⁺ Calcd for C₃₄H₂₃ 431.1800; Found: 431.1797.



dbCOT3: (5Z,11Z)-5,12-Bis(((5Z,11Z)-dibenzo[*a,e*]cyclooctatetraen-5-yl)ethynyl)dibenzo[*a,e*]cyclooctatetraene. Di-yne **5** (18 mg, 0.071 mmol), triflate **1** (54 mg, 0.15 mmol),

[Pd(PPh₃)₄] (4.0 mg, 3.5 μmol), CuI (1.0 mg, 5.3 μmol) and Et₃N (39 μL, 0.28 mmol) were dissolved in benzene (0.70 mL) and stirred at 50 °C for 6 hours after which TLC indicated complete conversion of **5**. The reaction mixture was then cooled to room temperature, dry-loaded onto silica, and purified by flash chromatography (14% to 25% benzene in heptane) to afford dbCOT3.

Yield: 31 mg (67%). Isolated as a pale-yellow solid, >95% pure in ¹H NMR and a single spot by TLC.

R_f: 0.48 (1:1 heptane/benzene).

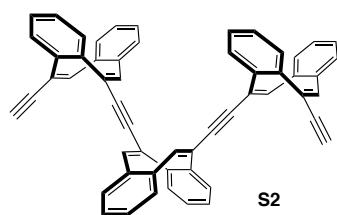
¹H NMR (400 MHz, CDCl₃) δ: 7.48–7.31 (m, 4H), 7.29–7.12 (m, 16H), 7.10–7.00 (m, 8H), 6.89–6.73 (m, 4H) ppm.

¹³C NMR (101 MHz, CDCl₃) δ: 139.4, 139.2, 138.96, 138.8, 137.4, 137.3, 137.14, 137.12, 136.9, 136.42, 136.37, 133.2, 133.1, 129.6, 129.2, 128.94, 128.87, 128.84, 128.74, 127.72, 127.89, 127.86, 127.6, 127.42, 127.38, 127.25, 127.22, 127.0, 126.86, 126.85, 91.5, 90.5 ppm.

FTIR (CH₂Cl₂ film): 3056 (w), 3013 (w), 1489 (m), 1428 (w), 1362 (w), 1264 (w), 859 (m), 754 (s) cm⁻¹.

HRMS-APCI (m/z): [M + H]⁺ Calcd for C₅₂H₃₃ 657.2582; Found: 657.2566.

mp: 140 °C (decomposition).



(5Z,11Z)-5,12-Bis(((5Z,11Z)-12-ethynyldibenzo[a,e]cyclooctatetraen-5-yl)ethynyl)

dibenzo[a,e]cyclooctatetraene (S2). A solution of bromide **4** (61 mg, 0.16 mmol), di-yne **5** (19 mg, 0.075 mmol), [Pd(PPh₃)₄] (4.0 mg, 3.5 μmol), CuI (1.0 mg, 5.3 μmol) and Et₃N (43 μL, 0.31 mmol) were dissolved in benzene (0.50 mL) and stirred at 50 °C for 18 h. The mixture was then cooled to room temperature, dry-loaded onto silica, and passed through a short column of silica (eluting with heptane/benzene 3:1). Fractions containing the major product (R_f = 0.35, heptane/benzene 2:1) were pooled and concentrated to yield 28 mg of an amorphous off-white oil. The crude product was re-dissolved in EtOH/THF 1:1 (1.0 mL). To this mixture was

added TBAF (0.16 mL, 0.16 mmol, 1.0 M in THF) dropwise. The resulting solution was heated to 40 °C and stirred overnight. The mixture was dry-loaded onto silica and purified by flash chromatography (eluting with 50% benzene in pentane) to afford di-yne **S2**.

Yield: 24 mg (44%). Isolated as a white amorphous solid, >95% pure in ¹H NMR spectroscopy and a single spot by TLC.

R_f: 0.45 (1:1 heptane/benzene).

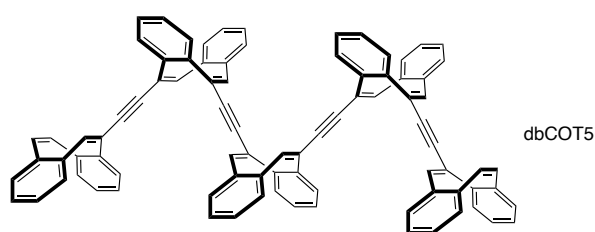
¹H NMR (500 MHz, CDCl₃) δ: 7.45 – 7.32 (m, 6H), 7.30 – 7.12 (m, 18H), 7.10 – 7.02 (m, 6H), 3.07 – 2.97 (m, 2H) ppm.

¹³C NMR (126 MHz, CDCl₃) δ: 140.29, 140.27, 140.24, 139.24, 139.22, 139.06, 139.01, 138.9, 138.82, 138.80, 137.03, 137.00, 136.89, 136.86, 136.83, 136.41, 136.39, 136.37, 136.34, 136.32, 136.30, 135.99, 135.95, 129.39, 129.37, 129.27, 129.11, 129.0, 128.77, 128.74, 128.72, 128.69, 128.5, 128.12, 128.07, 128.0, 127.94, 127.90, 127.6, 127.5, 126.79, 126.77, 125.8, 91.1, 90.9, 85.59, 85.57, 77.1, 76.9 ppm.

FTIR (CH₂Cl₂ film): 3287 (m), 3058 (w), 3017 (w), 1487 (m), 1429 (w), 1360 (m), 1287 (w), 908 (m), 866 (m), 756 (s), 732 (s), 697 (w), 650 (m), 603 (m) cm⁻¹.

HRMS-ESI (m/z): [M + H]⁺ Calcd for C₅₆H₃₃ 705.2582; Found: 705.2579.

mp: 125 °C (decomposition).



dbCOT5: (5Z,11Z)-5,12-Bis(((5Z,11Z)-12-(((5Z,11Z)-dibenzo[a,e]cyclooctatetraen-5-yl)ethynyl)dibenzo[a,e]cyclooctatetraen-5-yl)ethynyl)dibenzo[a,e]cyclooctatetraene. Tri-flate **1** (16 mg, 46 μmol), di-yne **S2** (16 mg, 23 μmol), [Pd(PPh₃)₄] (1.0 mg, 0.86 μmol), CuI (1.0 mg, 5.3 μmol) and Et₃N (12 μL, 86 μmol) were dissolved in benzene (0.70 mL) and stirred at 50 °C. After 60 min, the reaction showed complete consumption of starting materials (¹H NMR spectroscopy of an aliquot of the reaction mixture). The mixture was immediately cooled

to room temperature, dry-loaded onto silica, and purified via flash chromatography (eluting with 33% benzene in heptane) to afford dbCOT5.

Yield: 14 mg (58%). Isolated as a white solid, >95% pure by ^1H NMR spectroscopy and a single spot by TLC.

R_f: 0.27 (2:1 heptane/benzene).

^1H NMR (500 MHz, CDCl_3) δ : 7.48 – 7.32 (m, 8H), 7.26 – 6.97 (m, 40H), 6.87 – 6.70 (m, 4H) ppm.

^{13}C NMR (126 MHz, CDCl_3) δ : 139.40, 139.36, 139.27, 139.22, 139.19, 139.12, 139.10, 139.06, 139.04, 139.01, 138.98, 138.92, 138.89, 138.87, 138.82, 137.4, 137.3, 137.0, 136.9, 136.88, 136.86, 136.38, 136.36, 136.33, 136.2, 133.08, 133.07, 129.6, 129.38, 129.34, 129.31, 129.25, 128.88, 128.84, 128.7, 128.4, 128.0, 127.9, 127.69, 127.64, 127.58, 127.57, 127.4, 127.3, 127.24, 127.22, 127.02, 126.97, 126.87, 126.86, 126.84, 126.81, 91.56, 91.52, 91.47, 91.43, 91.2, 91.11, 91.09, 91.04, 91.01, 90.5, 90.4 ppm.

FTIR (CH_2Cl_2 film): 3058 (w), 3014 (w), 2955 (w), 2924 (w), 1721 (w), 1488 (m), 1428 (w), 1362 (w), 1286 (w), 906 (m), 864 (m br), 756 (s), 731 (s), 600 (w) cm^{-1} .

HRMS-APCI (m/z): $[\text{M} + \text{NH}_4]^+$ Calcd for $\text{C}_{88}\text{H}_{56}\text{N}$ 1126.4413; Found: 1126.4418.

mp: 130 °C (decomposition).

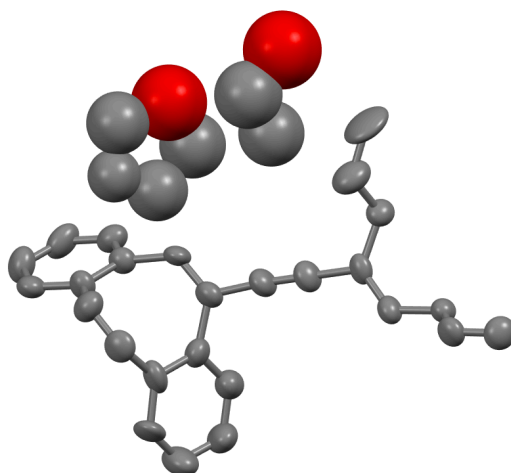
III. *Single crystal X-ray diffraction analysis of dbCOT3*

A sample of dbCOT3 in THF was gently warmed until all solids were completely dissolved. The resulting solution was stored in a sealed vial at room temperature for two weeks during which time crystals formed. Crystals were cut to size and mounted under a protective layer of parathion oil. Datasets were collected for several crystals from different batches but all gave very weak diffraction data (Supplementary Table 1, Supplementary Figure 1). Elevated R-values reflects poor crystal quality.

Supplementary Table 1. Crystal data for dbCOT3 [a]

Chemical formula	C ₅₂ H ₃₂ , 3(C ₄ H ₈ O)	
Formula Mass	873.09	
Crystal size /mm ³	0.1 x 0.05 x 0.05	
Crystal habit	colorless, rod	
Crystal system	monoclinic	
Unit cell dimensions:	$a = 8.6794 (19) \text{ \AA}$	$\alpha = 90^\circ$
	$b = 34.059 (7) \text{ \AA}$	$\beta = 109.96 (3)^\circ$
	$c = 9.0862 (18) \text{ \AA}$	$\gamma = 90^\circ$
Unit cell volume / \AA^3	2524.6 (10)	
Collection temperature/K	110 (2)	
Space group	$P 21/m$	
Number of formula units per cell, Z	2	
Radiation type	MoK α	
Absorption coefficient, μ/mm^{-1}	0.069	
No. reflections collected / unique	12705 / 5899 [$R_{(int)} = 0.1790$]	
Final R_I values ($I > 2\sigma(I)$)	$R_I = 0.1332$, $wR_2 = 0.1474$	
Final R_I values (<i>all data</i>)	$R_I = 0.4775$, $wR_2 = 0.2014$	
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.201	
Goodness of fit on F^2	1.095	
Largest diff. peak and hole / $e^-/\text{\AA}^3$	0.309 and -0.422	
CCDC	1957125	

[a] Both independent solvent molecules were modeled isotropically to obtain a stable refinement. Removal of the electron density originating from the THFs with SQUEEZE gave an unstable refinement.

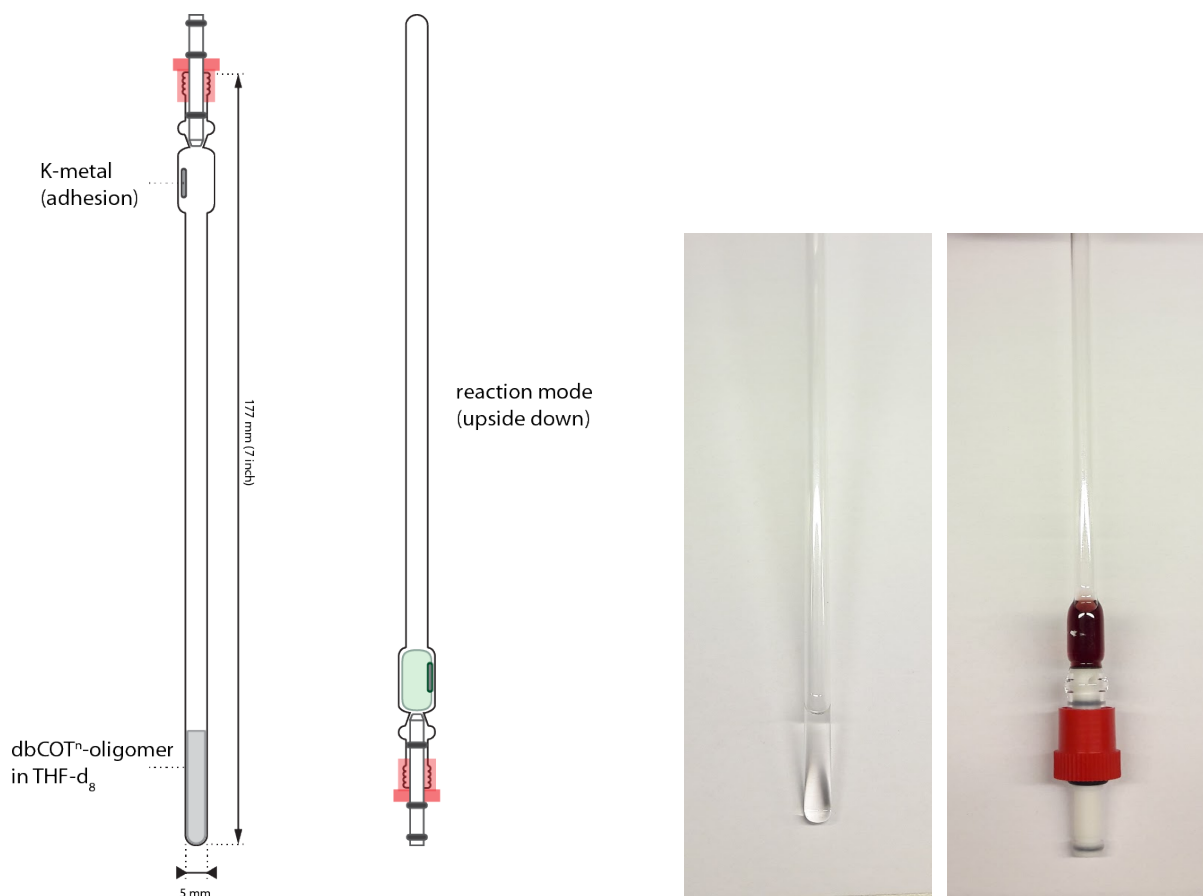


Supplementary Figure 1. The asymmetric unit of dbCOT3. Thermal ellipsoids are shown at 30% probability. Gray = carbon atom; red = oxygen atom. Hydrogen atoms are omitted for clarity.

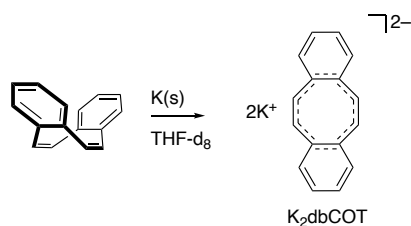
IV. Reduction of dbCOT, dbCOT2, dbCOT3, and dbCOT5 with potassium metal

General procedure. A sample of dbCOT or the respective oligomer was charged in an oven-dried J. Young NMR tube in an argon filled glovebox. A small piece of freshly cut potassium metal (excess) was adhesively deposited by pressing into a thin film on the glass surface of the broad top chamber of the tube (Supplementary Figure 2). Dry and oxygen-free THF- d_8 was introduced via a gas-tight syringe. The tube was then sealed, exported out of the glovebox, and sonicated in an upright position until the oligomer was fully dissolved (clear colorless solution).

Reduction was initiated by turning the tube upside down, thus exposing the liquid to the metal surface, followed by mild shaking. A color-change was indicative of the reduction proceeding. Returning the tube to an upright position ceased reduction immediately, and the samples could be stored for days without noticeable decomposition or further reduction. The degree of reduction was monitored by ^1H NMR spectroscopy. Unless otherwise noted, NMR spectra were obtained at ambient temperature.



Supplementary Figure 2. Left: Schematic representation of the experiment setup; Right: Images of a typical experiment (reduction of dbCOT) showing the tube in an upright and upside-down position.

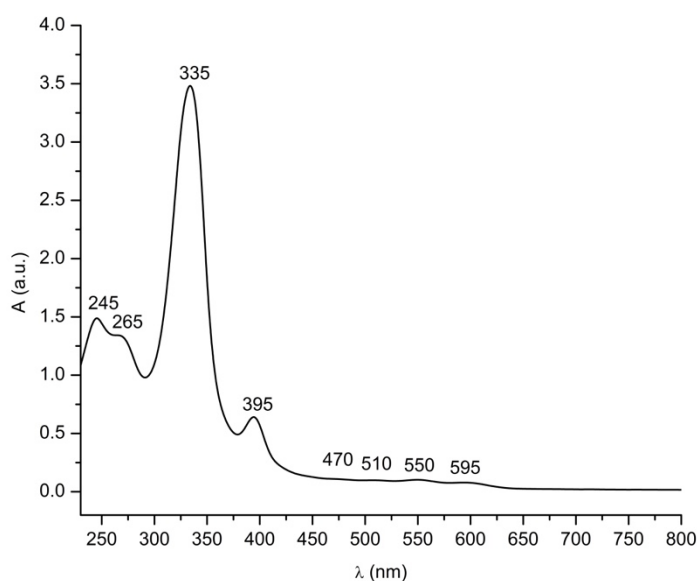


Reduction of dbCOT to K_2dbCOT .³ Following the general procedure, dbCOT (3.1 mg, 15 μmol) was dissolved in THF- d_8 (0.50 mL). Upon exposure of the resulting colorless solution to potassium metal (excess) the mixture gradually turned deep burgundy. The reaction was analyzed at regular intervals by ^1H NMR until a clean conversion into K_2dbCOT was achieved.

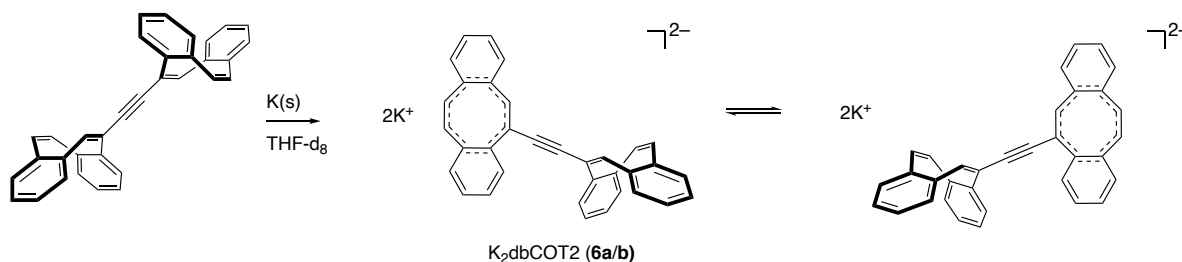
^1H NMR (500 MHz, THF- d_8) δ : 7.87 (dd, $J = 6.6, 3.4$ Hz, 4H), 7.17 (s, 4H), 6.19 (dd, $J = 6.7, 3.3$ Hz, 4H) ppm.

^{13}C NMR (126 MHz, THF- d_8) δ : 135.7, 109.4, 108.9, 95.8 ppm.

UV-VIS (λ -max in THF- d_8): 595, 550, 510, 470, 395, 335, 265, 245 nm.



Supplementary Figure 3. Left: UV-VIS spectrum of K_2dbCOT ; Right: Image of a dilute solution of K_2dbCOT in THF- d_8 .

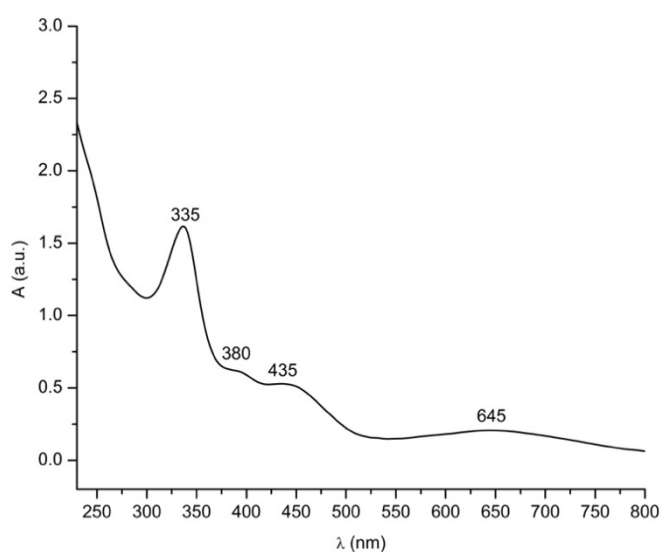


Reduction of dbCOT2 to $\text{K}_2\text{dbCOT2}$. Following the general procedure, dbCOT2 (0.58 mg, 1.3 μmol) was dissolved in THF- d_8 (0.50 mL). Upon exposure of the resulting colorless solution to potassium metal (excess) the mixture gradually turned deep green. The reaction was analyzed at regular intervals by ^1H NMR spectroscopy at 237.2 K until a clean formation of $\text{K}_2\text{dbCOT2}$ was achieved.

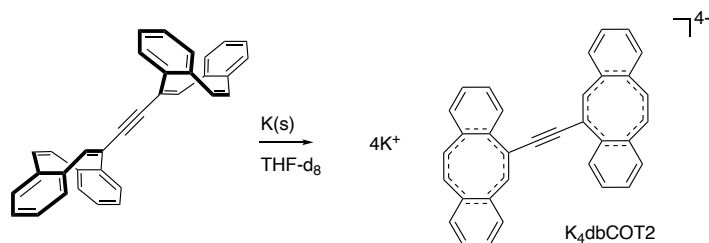
^1H NMR (500 MHz, THF- d_8 , at $T = 237.2$ K) δ : 9.09 – 9.00 (m, 1H), 7.91 – 7.83 (m, 1H), 7.76 (d, $J = 7.8$ Hz, 1H), 7.71 – 7.58 (m, 3H), 7.33 – 7.25 (m, 1H), 7.24 – 7.18 (m, 1H), 7.17 – 7.09 (m, 4H), 7.08 – 7.04 (m, 2H), 7.02 (d, $J = 7.7$ Hz, 1H), 6.89 (s, 1H), 6.85 (d, $J = 11.7$ Hz, 1H), 6.78 (d, $J = 11.7$ Hz, 1H), 6.43 – 6.34 (m, 2H), 6.22 (dd, $J = 8.4, 5.8$ Hz, 1H), 6.04 (dd, $J = 8.3, 5.8$ Hz, 1H) ppm.

^{13}C NMR (126 MHz, THF- d_8 , at $T = 237.2$ K) δ : 140.6, 138.7, 137.0, 136.3, 135.4 (2 signals overlapping), 134.3, 133.2, 133.1, 131.3, 130.6, 130.0, 129.1, 128.5, 128.1, 126.3, 126.2, 126.1, 125.3, 125.1, 112.3 (2 signals overlapping), 112.2, 111.9, 111.6, 110.3, 110.1, 106.6, 106.5, 102.5, 98.1, 97.2, 90.8, 82.0 ppm.

UV-VIS (λ -max in THF- d_8): 645, 435, 380, 335 nm.



Supplementary Figure 4. Left: UV-VIS spectrum of K₂dbCOT2; Right: Image of a dilute solution of K₂dbCOT2 in THF-d₈.

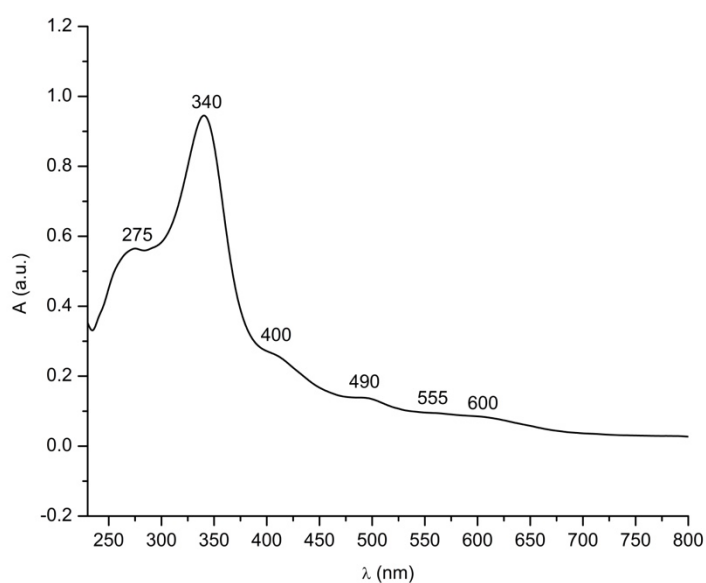


Reduction of dbCOT2 to K₄dbCOT2. Reduction of K₂dbCOT2 was continued following the general procedure. The reaction was analyzed at regular intervals by ¹H NMR spectroscopy until a clean formation of K₄dbCOT2 (deep green) was achieved.

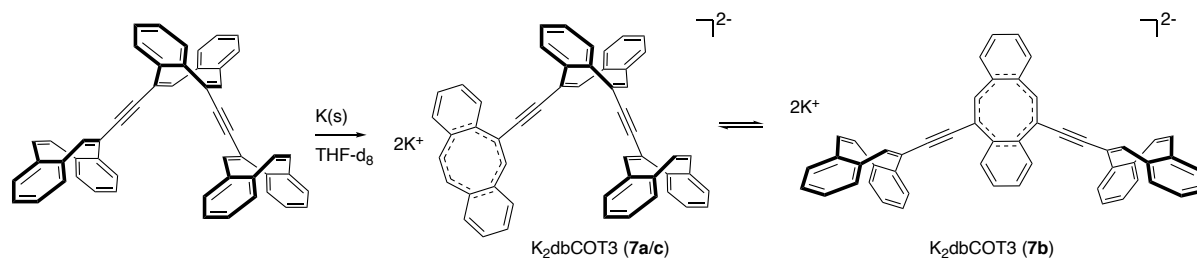
¹H NMR (500 MHz, THF-d₈) δ: 9.99 (d, *J* = 9.0 Hz, 2H), 8.48 (s, 2H), 8.08 – 7.97 (m, 4H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 13.0 Hz, 2H), 7.19 (d, *J* = 13.0 Hz, 2H), 6.55 (dd, *J* = 8.7, 5.7 Hz, 2H), 6.39 (dd, *J* = 8.3, 5.8 Hz, 2H), 6.26 (dd, *J* = 8.4, 5.8 Hz, 2H), 6.16 (dd, *J* = 8.3, 5.8 Hz, 2H) ppm.

¹³C NMR (126 MHz, THF-d₈) δ: 136.7, 136.4, 135.5, 134.2, 111.3, 111.2, 110.5, 110.3, 110.0, 109.5, 108.8, 108.3, 101.5, 100.3, 98.8, 97.4, 89.4 ppm.

UV-VIS (λ-max in THF-d₈): 600, 555, 490, 400, 340, 275 nm.



Supplementary Figure 5. Left: UV-VIS spectrum of $K_4dbCOT2$; Right: Image of a dilute solution of $K_4dbCOT2$ in THF- d_8 .

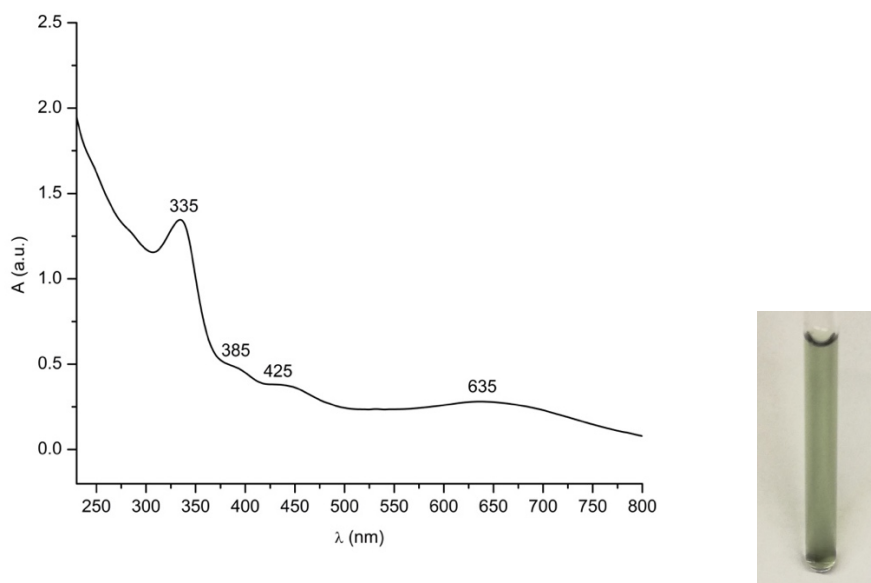


Reduction of dbCOT3 to $K_2dbCOT3$. Following the general procedure, dbCOT3 (0.34 mg, 0.52 μmol) was dissolved in THF- d_8 (0.45 mL). Upon exposure of the resulting colorless solution to potassium metal (excess), the mixture gradually turned deep green. The reaction was analyzed at regular intervals by ^1H NMR spectroscopy (223.2 K) until $\sim 75\%$ conversion into $K_2dbCOT2$ (mixture of regioisomers) was achieved. Further reduction gave formation also of $K_4dbCOT3$. Ratio of **7a/c** : **7b**: = 47:53.

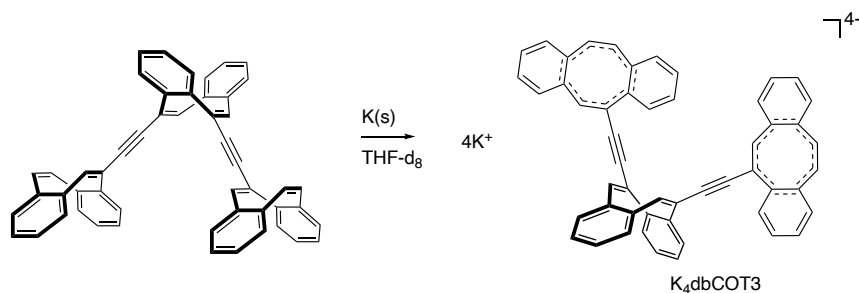
^1H NMR (500 MHz, THF- d_8 , at $T = 223.2$ K) δ : **7a**: 9.16 (dd, $J = 7.4$ Hz, 1H), **7b**: 9.08 (dd, $J = 8.7, 6.7, 3.6$ Hz, 2H), 7.92 – 7.88 (m, 1H), 7.79 (t, $J = 7.9$ Hz, 1H), 7.72 (s, 1H), 7.71 (s, 1H), 7.70 – 7.64 (m, 2H), 7.63 (d, $J = 3.8$ Hz, 1H), 7.53 – 7.50 (m, 2H), 7.49 – 6.66 (m, 25H), 6.54 – 6.48 (m, 2H), 6.48 – 6.40 (m, 2H), 6.27 – 6.22 (m, 1H), 6.08 – 6.00 (m, 3H) ppm. Mixture with 25% dbCOT3.

Selected ^{13}C chemical shifts by HSQC (126 MHz, THF- d_8 , at $T = 223.2$ K) δ : 135.9, 135.7, 135.4, 134.5, 134.2, 131.4 (two overlapping peaks), 130.2, 129.8, 112.2, 110.44, 110.36, 107.1, 106.5, 98.2, 97.6 ppm.

UV-VIS (λ -max in THF- d_8): 635, 425, 385, 335 nm.



Supplementary Figure 6. Left: UV-VIS spectrum of $K_2dbCOT3$; Right: Image of a dilute solution of $K_2dbCOT3$ in $THF-d_8$.

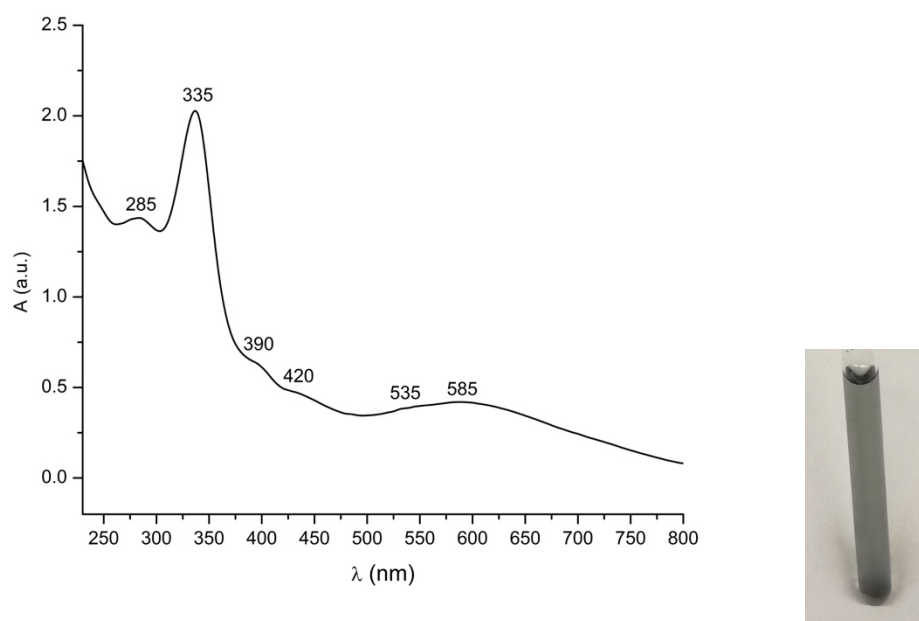


Reduction of dbCOT3 to $K_4dbCOT3$. Reduction of $K_2dbCOT3$ was continued following the general procedure. The reaction was analyzed at regular intervals by 1H NMR spectroscopy until a clean formation of $K_4dbCOT3$ (deep green) was achieved.

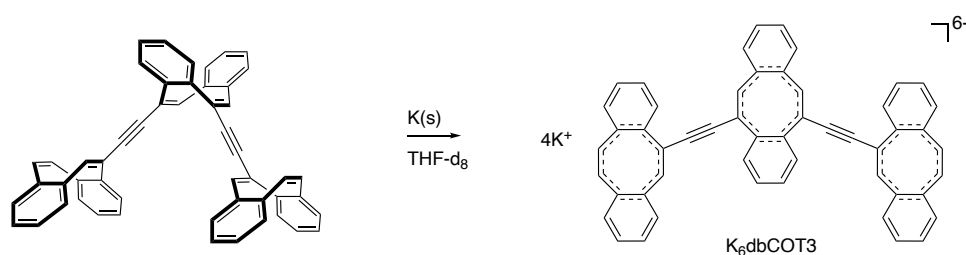
1H NMR (500 MHz, $THF-d_8$) δ : 9.16 (d, $J = 7.3$ Hz, 2H), 7.84 (d, $J = 8.5$ Hz, 2H), 7.80 (dd, $J = 5.8, 3.4$ Hz, 2H), 7.70–7.64 (m, 4H), 7.61 (d, $J = 8.5$ Hz, 2H), 7.33 (dd, $J = 5.8, 3.4$ Hz, 2H), 7.13–7.06 (m, 6H), 7.05–7.00 (m, 4H), 6.44 (dd, $J = 8.8, 5.8$ Hz, 2H), 6.36 (dd, $J = 8.4, 5.8$ Hz, 2H), 6.19 (dd, $J = 8.7, 5.8$ Hz, 2H), 6.02 (dd, $J = 8.5, 5.8$ Hz, 2H) ppm.

^{13}C NMR (126 MHz, $THF-d_8$) δ : 141.1, 139.9, 136.5, 136.4, 135.6, 132.5, 132.2, 130.7, 130.0, 128.4, 127.0, 126.2, 113.5, 113.3, 112.9, 112.7, 111.6, 111.2, 108.0, 107.9, 103.3, 99.3, 98.3, 91.9, 83.4 ppm. Two additional signals are overlapping.

UV-VIS (λ -max in $THF-d_8$): 585, 535, 420, 390, 335, 285 nm.



Supplementary Figure 7. Left: UV-VIS spectrum of $K_4dbCOT3$; Right: Image of a dilute solution of $K_4dbCOT3$ in $THF-d_8$.

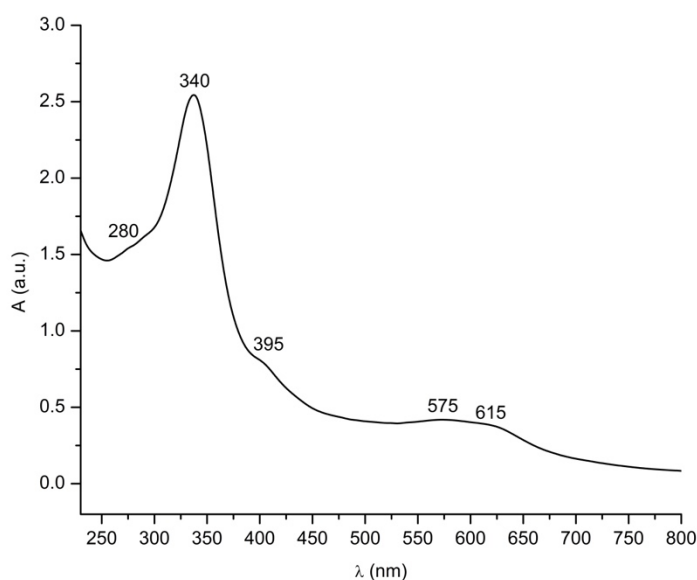


Exhaustive reductive extension of dbCOT3. Reduction of $K_4dbCOT3$ was continued following the general procedure. The reaction was analyzed at regular intervals by 1H NMR spectroscopy (268.2 K) until a clean formation of $K_6dbCOT3$ (deep green) was achieved.

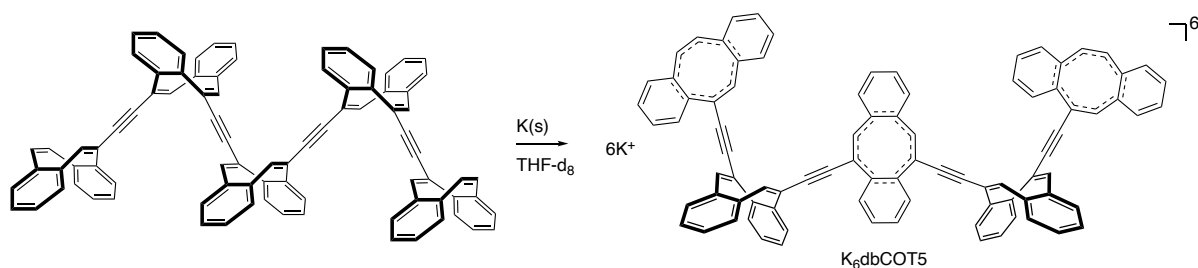
1H NMR (500 MHz, $THF-d_8$, at $T = 268.2$ K) δ : 10.27 (dd, $J = 7.0, 3.5$ Hz, 2H), 10.04 (d, $J = 9.0$ Hz, 2H), 8.56 (s, 2H), 8.55 (s, 2H), 8.08 (d, $J = 8.5$ Hz, 2H), 8.03 (d, $J = 8.5$ Hz, 2H), 8.00 (d, $J = 7.4$ Hz, 2H), 7.83 (d, $J = 8.5$ Hz, 2H), 7.32 (d, $J = 13.2$ Hz, 2H), 7.21 (d, $J = 13.2$ Hz, 2H), 6.79 (dd, $J = 7.1, 3.3$ Hz, 2H), 6.59 (dd, $J = 9.0, 5.6$ Hz, 2H), 6.41 (dd, $J = 8.5, 5.6$ Hz, 2H), 6.29 (dd, $J = 8.5, 5.7$ Hz, 2H), 6.26 (dd, $J = 6.7, 3.1$ Hz, 2H), 6.17 (dd, $J = 8.4, 5.7$ Hz, 2H) ppm.

^{13}C NMR (126 MHz, THF- d_8 , at $T = 268.2$ K) δ : 136.7, 136.45, 136.35, 135.5, 134.5, 134.2, 112.0, 111.2, 111.1, 110.5, 110.4, 110.3, 110.2, 110.0, 109.6, 109.5, 108.7, 108.2, 104.6, 101.5, 100.9, 100.3, 98.8, 97.4, 90.4, 89.4 ppm.

UV-VIS (λ -max THF- d_8): 615, 575, 395, 340, 280 nm.



Supplementary Figure 8. Left: UV-VIS spectrum of $\text{K}_6\text{dbCOT3}$; Right: Image of a dilute solution of $\text{K}_6\text{dbCOT3}$ in THF- d_8 .



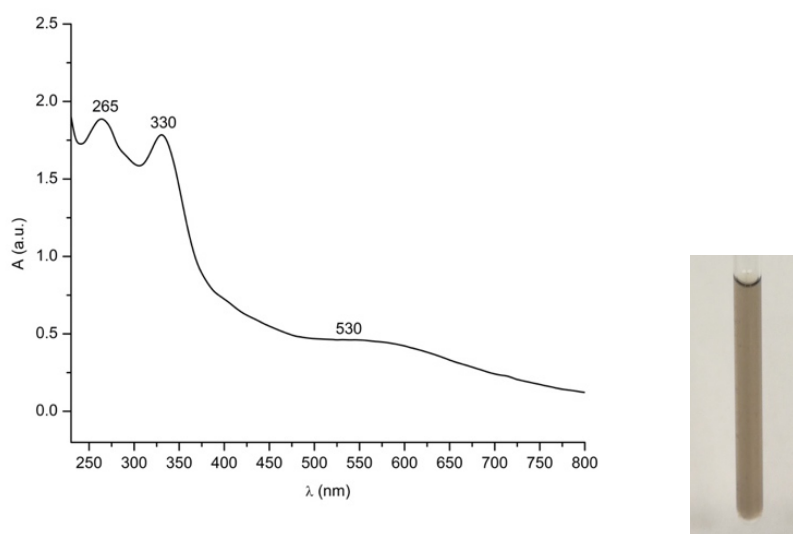
Reduction of dbCOT5 to $\text{K}_6\text{dbCOT5}$. Following the general procedure, dbCOT5 (0.60 mg, 0.52 μmol) was dissolved in THF- d_8 (0.50 mL). Upon exposure of the resulting colorless solution to potassium metal (excess) the mixture gradually turned deep green. The reaction was analyzed at regular intervals by ^1H NMR spectroscopy until a clean formation of $\text{K}_6\text{dbCOT5}$ (deep green) was achieved.

^1H NMR (500 MHz, THF- d_8 , at $T = 273.0$ K) δ : 9.27 – 9.22 (m, 1H), 9.22 (d, $J = 9.0$ Hz, 1H), 7.89 (d, $J = 7.6$ Hz, 1H), 7.83 (d, $J = 7.3$ Hz, 1H), 7.75 (d, $J = 7.3$ Hz, 1H), 7.70 (t, $J = 4.1$ Hz, 1H), 7.70 (d, $J = 4.0$ Hz, 1H), 7.66 (d, $J = 8.2$ Hz, 1H), 7.60 (d, $J = 4.9$ Hz, 1H), 7.42

(dt, $J = 5.9, 2.9$ Hz, 1H), 7.38 – 7.31 (m, 2H), 7.40 – 7.31 (m, 4H), 7.14 (s, 2H), 7.03 (d, $J = 1.7$ Hz, 1H), 6.99 (br s, 1H), 6.59 (dd, $J = 6.8, 3.5$ Hz, 1H), 6.50 – 6.44 (m, 1H), 6.43 – 6.38 (m, 1H), 6.26 – 6.21 (m, 1H), 6.08 – 6.04 (m, 1H), 6.00 (dt, $J = 6.4, 2.9$ Hz, 1H) ppm.

Selected ^{13}C chemical shifts by HSQC (126 MHz, THF- d_8 , at $T = 273.0$ K) δ : 135.4, 135.3, 135.1, 134.4, 131.6, 131.4, 129.6, 129.5, 128.9, 128.82, 127.9, 127.1, 126.0, 125.9, 125.2 (two signals overlapping), 111.9, 111.5, 110.37, 110.36, 110.1, 106.8, 106.3, 102.1, 98.2, 97.1 ppm.

UV-VIS (λ -max in THF- d_8): 530, 330, 265 nm.



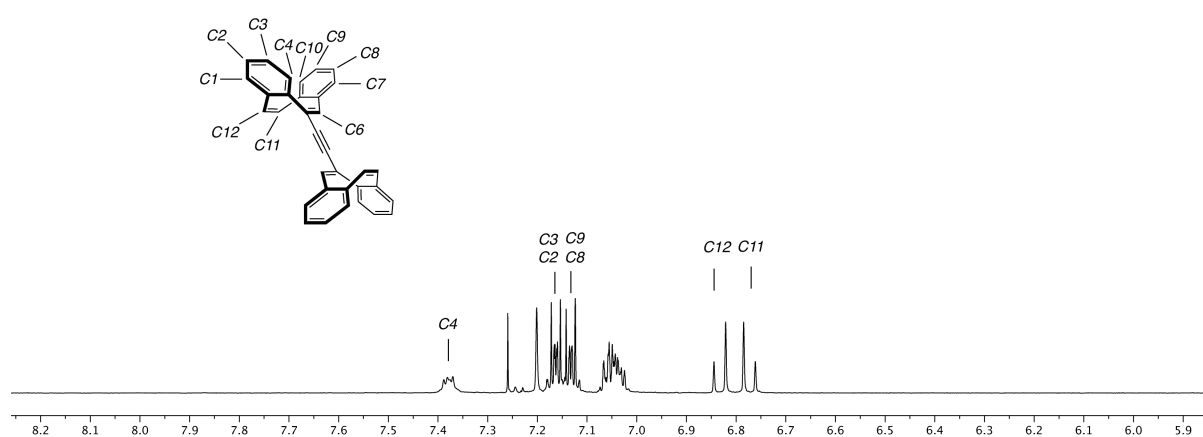
Supplementary Figure 9. Left: UV-VIS spectrum of $K_6\text{dbCOT5}$; Right: Image of a dilute solution of $K_6\text{dbCOT5}$ in THF- d_8 .

V. Structural and conformational assignment of dbCOT2, $K_2\text{dbCOT2}$, $K_4\text{dbCOT2}$, $K_2\text{dbCOT3}$, $K_4\text{dbCOT3}$, $K_6\text{dbCOT3}$, $K_6\text{dbCOT5}$

The ^1H NMR spectra of reduced derivatives of dbCOT2, dbCOT3, and dbCOT5 were assigned using a combination of one-dimensional (1D) and two-dimensional (2D) NMR experiments: COSY, ^1H - ^{13}C HMBC, ^1H - ^{13}C HSQC, and ROESY. For simplicity, the ^1H NMR peaks are labeled with the carbon to which the respective proton is attached (H(Cn)). From the left, as drawn, positions on a second dbCOT unit are designated Cn' and on a third unit Cn''. Where needed for clarity, unlabeled carbons are given the name of the closest carbon with a C–H bond that has the lowest number together with “adjacent” (e.g. C6'adjacent for the carbon between C6' and C7'). ^{13}C NMR chemical shifts needed for assignment are listed. Fluxionality refers to electron relay between adjacent dbCOT units in partially reduced structures.

Each dbCOT unit is stereogenic (planar chirality) and the stereoisomers rapidly interconvert at room temperature. Oligomers that exhibit diastereoisomerism are characterized as a mixture of diastereomers since the chemical shift differences between diastereomers are small. Structures where the planar chirality of non-reduced units breaks a symmetrical arrangement of reduced units into diastereomers (*e.g.*, K₂dbCOT3 b-series and K₆dbCOT5) are described as *pseudo*-symmetrical.

Assignment of dbCOT2.



Supplementary Figure 10. Selected assignments in the ¹H NMR spectrum (500 MHz) of K₂dbCOT2 in CDCl₃ at 373.0 K.

Supplementary Table 2. Assigned ¹H chemical shifts and relevant ¹³C chemical shifts for dbCOT2 in CDCl₃ at 373.1 K.

Proton	¹ H δ (ppm)	Carbon	¹³ C δ (ppm)	Proton	¹ H δ (ppm)	Carbon	¹³ C δ (ppm)
H(C1)	7.04	C1		H(C8)	7.13	C8	127.1/127.4
H(C2)	7.16	C2	127.7/127.2	H(C9)	7.13	C9	127.1/127.4
H(C3)	7.16	C3	127.7/127.2	H(C10)	7.06	C10	
H(C4)	7.38	C4		H(C11)	6.77	C11	
H(C6)	7.20	C6	91.3	H(C12)	6.83	C12	
H(C7)	7.06	C7	128.9				

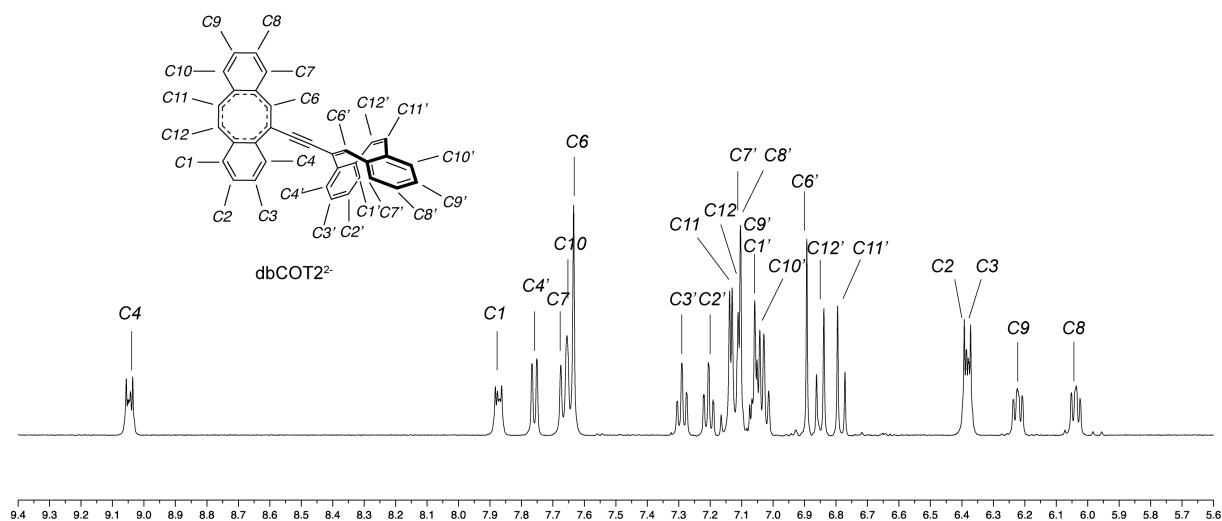
¹H NMR and selected ¹³C chemical shift assignment of dbCOT2. The NMR chemical shift assignment of dbCOT2 was first performed on a sample in CDCl₃ in a Young's NMR tube heated to 373K where the diastereomers are fast interconverting. The number of observed peaks in the ¹H and ¹³C spectra shows that there is a symmetry element (mirror plane/two-fold axis) at the center of the structure. The chemical shifts were referenced to the solvent peaks at 7.26/77.16 ppm.

The peak at $\delta = 7.20$ ppm is the only singlet and is assigned as H(C6). There is a $^3J_{CH}$ HMBC correlation from H(C6) to $\delta = 91.3$ ppm which can be assigned to the alkyne carbon. H(C6) has a $^3J_{CH}$ correlation to $\delta = 128.9$ ppm. $\delta = 128.9$ ppm shows an HSQC correlation to $\delta = 7.06$ ppm and can be assigned as H(C7)/C7. H(C7) has a COSY correlation to $\delta = 7.13$ ppm, which can be assigned to H(C8). The multiplet peak at $\delta = 7.13$ ppm integrates as 2H and shows two HSQC correlations at $\delta = 127.1$ ppm and 127.4 ppm. $\delta = 7.06$ ppm has another COSY correlation to $\delta = 6.77$ ppm, one part of a characteristic pattern of two strongly coupled vinylic protons. As there are no other COSY correlations from $\delta = 7.06$ ppm (besides a weak correlation to H(C6)), we can assign $\delta = 6.77$ ppm as H(C11) and H(C10) as having a chemical shift very close to H(C7). $\delta = 7.13$ ppm has no other COSY correlations, besides weak correlations to H(C6) and H(C11). From this it follows that H(C8) and H(C9) have very similar ¹H chemical shifts, $\delta = 7.13$ ppm, but slightly different ¹³C chemical shifts, $\delta = 127.1$ ppm and 127.4 ppm. They could, however, not be disambiguated. H(C11) has a COSY correlation to $\delta = 6.83$ ppm, the other part of the strongly coupled resonances which is assigned to H(C12). H(C12) has a COSY correlation to $\delta = 7.04$ ppm, assigned as H(C1). H(C1) has a COSY correlation to $\delta = 7.16$ ppm, assigned as H(C2). The multiplet peak at $\delta = 7.16$ ppm integrates as 2H and shows two HSQC correlations at $\delta = 127.2$ ppm and 127.7 ppm. From $\delta = 7.16$ ppm there is a COSY correlation to 7.38 ppm, which is assigned to H(C4). The proximity to the alkyne group causing a down-field shift change. As there are no other COSY correlations from $\delta = 7.16$ ppm, besides a weak correlation to H(C12), it follows that H(C2) and H(C3) have very similar ¹H chemical shifts, $\delta = 7.16$ ppm, but slightly different ¹³C chemical shifts, $\delta = 127.2$ ppm and 127.7 ppm. They could, however, not be disambiguated.

The ¹H and ¹³C resonance assignments of C2, C3, C8, and C9 of dbCOT2 in CDCl₃ at 373.1 K could then be transferred to spectra recorded in CDCl₃ at 295.0 K by direct comparison, and

further on to data acquired in THF- d_8 at 295.0 K: H(C2)/H(C3): $\delta = 7.16$ ppm; C2/C3: $\delta = 127.8/128.2$ ppm; H(C8)/H(C9): $\delta = 7.12$ ppm; C8/C9: $\delta = 127.7/128.1$ ppm.

Assignment of K₂dbCOT2.



Supplementary Figure 11. Assigned ¹H NMR spectrum (500 MHz) of K₂dbCOT2 in THF- d_8 . Spectrum recorded at $T = 237.2$ K.

Supplementary Table 3. Assigned ¹H chemical shifts and relevant ¹³C chemical shifts for K₂dbCOT2

Proton	¹ H δ (ppm)	Carbon	¹³ C δ (ppm)	Proton	¹ H δ (ppm)	Carbon	¹³ C δ (ppm)
H(C1)	7.87	C1	135.4	H(C1')	7.05	C1'	128.1
H(C2)	6.38	C2		H(C2')	7.20	C2'	126.1
H(C3)	6.38	C3		H(C3')	7.29	C3'	126.2
H(C4)	9.05	C4		H(C4')	7.76	C4'	130.0
H(C6)	7.63	C6	98.1	H(C6')	6.89	C6'	
H(C7)	7.66	C7	134.3	H(C7')	7.11	C7'	129.1
H(C8)	6.22	C8		H(C8')	7.05	C8'	125.3
H(C9)	6.04	C9	106.6	H(C9')	7.11	C9'	126.3
H(C10)	7.64	C10	135.4	H(C10')	7.02	C10'	128.5
H(C11)	7.13	C11	102.5	H(C11')	6.78	C11'	

H(C12)	7.11	C12	97.2	H(C12')	6.85	C12'
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¹H NMR chemical shift assignment of K₂dbCOT2. The number of signals in the ¹H NMR spectrum shows that there are no higher symmetry elements in the structure. Broad peaks in the room temperature ¹H NMR spectrum that sharpen upon cooling, together with the presence of exchange peaks in the 1D ROE and 2D ROESY experiments show that the structure is fluxional.

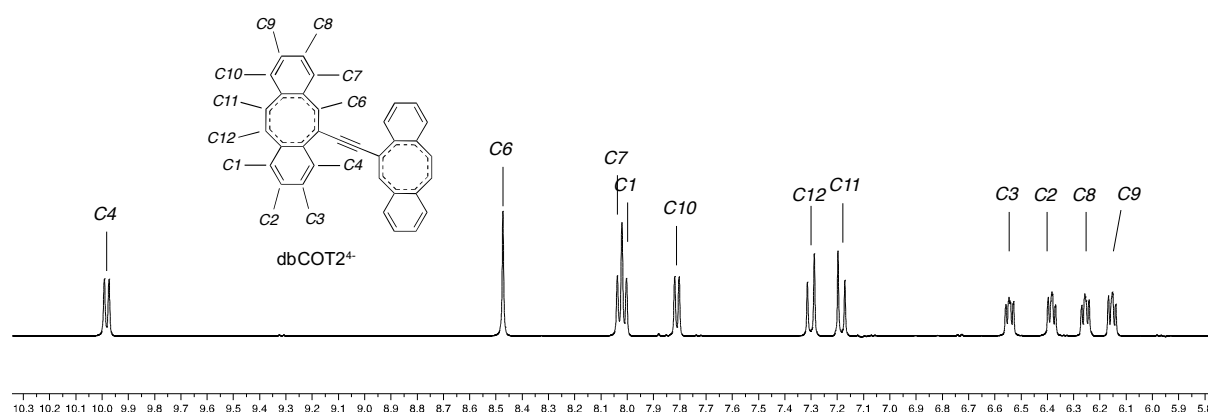
Each of the two dbCOT units has one proton without neighboring protons: H(C6) and H(C6'). These serve as starting point for the assignment. There are two singlets in the ¹H NMR spectrum: $\delta = 7.63$ ppm and $\delta = 6.89$ ppm. As protons on aromatic rings are deshielded, $\delta = 7.63$ ppm is assigned as H(C6), and $\delta = 6.89$ ppm as H(C6').

We then focus on the reduced dbCOT unit. H(C6) has a J_{CH} HSQC correlation to $\delta = 98.1$ ppm which is assigned to C6. H(C6) has a $^3J_{\text{CH}}$ HMBC correlation to $\delta = 134.3$ ppm. $\delta = 134.3$ ppm has an HSQC correlation to $\delta = 7.66$ ppm which is assigned as H(C7) on account of being the only proximal carbon to C6 that has a C–H bond (HSQC correlation). The assignment of C7 to $\delta = 134.3$ ppm follows. H(C7) has a $^3J_{\text{HH}}$ COSY correlation to $\delta = 6.22$ ppm which is assigned as H(C8). H(C8) has a COSY correlation to $\delta = 6.04$ ppm which is assigned as H(C9). The HSQC correlation at $\delta = 6.04/106.6$ ppm identifies C9. H(C9) has a COSY correlation to $\delta = 7.64$ ppm which is assigned as H(C10). H(C10) has an HSQC correlation to $\delta = 135.4$ ppm which is assigned as C10. H(C10) has $^2/3J_{\text{CH}}$ HMBC correlations to $\delta = 102.5$ ppm and to $\delta = 111.9$ ppm. Only the peak at $\delta = 102.5$ ppm has an HSQC correlation and is assigned to C11. C11 has an HSQC correlation to $\delta = 7.13$ and is assigned as H(C11). H(C11) has a $^2J_{\text{CH}}$ HMBC correlation to $\delta = 97.2$ ppm. The signal at $\delta = 97.2$ ppm has an HSQC correlation to $\delta = 7.11$ ppm and is assigned as H(C12). The assignment of C12 to $\delta = 97.2$ ppm follows. C12 has a $^3J_{\text{CH}}$ HMBC correlation to $\delta = 7.87$ which is assigned to H(C1). H(C1) has an HSQC correlation to $\delta = 135.4$ ppm which is assigned to C1. H(C1) has a COSY correlation to $\delta = 6.38$ ppm which is assigned as H(C2). H(C2) and H(C3) have very similar chemical shifts, and the integral of the resonance at $\delta = 6.38$ ppm shows that it corresponds to two protons. They also have very similar carbon chemical shifts, since there is only one HSQC correlation observed for $\delta = 6.38$ ppm. The slightly skewed HSQC peak shape also indicates two overlapping peaks. H(C3) has a COSY correlation to $\delta = 9.05$ ppm which is assigned as H(C4). H(C4) has a $^4J_{\text{CH}}$ HMBC

correlation to the alkyne carbon, corroborating the assignment. The extreme chemical shift of H(C4) is diagnostic of proximity to the alkyne moiety.

We then turn to the non-reduced dbCOT unit. First, we identify the roofed doublets at $\delta = 6.85$ ppm and $\delta = 6.78$ ppm in the ^1H NMR spectrum as characteristic of the two strongly coupled vinylic protons on the terminal non-reduced unit, H(C11') and H(C12'). The fluxional nature of K₂dbCOT2 is shown by selective inversion of H(C4) of the reduced dbCOT unit in a 1D NOESY experiment (see Figure 6A). This gives rise to an exchange peak with a proton chemical shift of 7.76 ppm within the non-reduced dbCOT unit and is assigned to H(C4'). There is a COSY correlation from H(C4') to $\delta = 7.29$ ppm which is assigned as H(C3'). There is a COSY correlation from H(C3') to $\delta = 7.20$ ppm which is assigned as H(C2'). There is a COSY correlation from H(C2') to $\delta = 7.05$ ppm which is assigned to H(C1'). Observed HSQC correlations at these ^1H chemical shifts identify the ^{13}C chemical shifts of C1' (128.1 ppm), C2' (126.1 ppm), C3' (126.2 ppm), and C4' (130.0 ppm). A $^3J_{\text{CH}}$ HMBC correlation from C1' to $\delta = 6.85$ ppm identifies this resonance (see above) as H(C12'). It then follows that the peak at $\delta = 6.78$ ppm can be assigned as H(C11'). A $^3J_{\text{CH}}$ HMBC correlation from H(C11') to $\delta = 128.5$ ppm identifies C10', and an HSQC correlation from C10' to 7.02 ppm identifies H(C10'). An HMBC correlation is observed from H(C6') at $\delta = 6.89$ ppm to $\delta = 129.1$ ppm, which is assigned as C7', and an HSQC correlation from C7' to $\delta = 7.11$ ppm identifies H(C7'). The two remaining correlations observed in the HSQC spectrum, at 7.05/125.3 ppm and 7.11/126.3 ppm, must correspond to the remaining unassigned C8' and C9'. To assign these, we start with a search for HMBC correlations to the carbons without C–H bonds (absence of HSQC correlations). The carbon located between C6' and C7', here called C6' adjacent, can be assigned as $\delta = 138.7$ ppm based on HMBC correlations from this signal to H(C6'), H(C7'), H(C7'), and H(C11'). An additional weak HMBC correlation to $\delta = 7.05$ ppm, can then be assigned to H(C8'). It follows that $\delta = 7.11$ ppm is assigned as H(C9') and concludes the assignment. Cross check of HMBC correlations corroborates the analysis.

Assignment of K₄dbCOT2.



Supplementary Figure 12. Assigned ^1H NMR spectrum (500 MHz) of K_4dbCOT_2 in THF-d_8 .

Supplementary Table 4. Assigned ^1H chemical shifts and relevant ^{13}C chemical shifts for K_4dbCOT_2

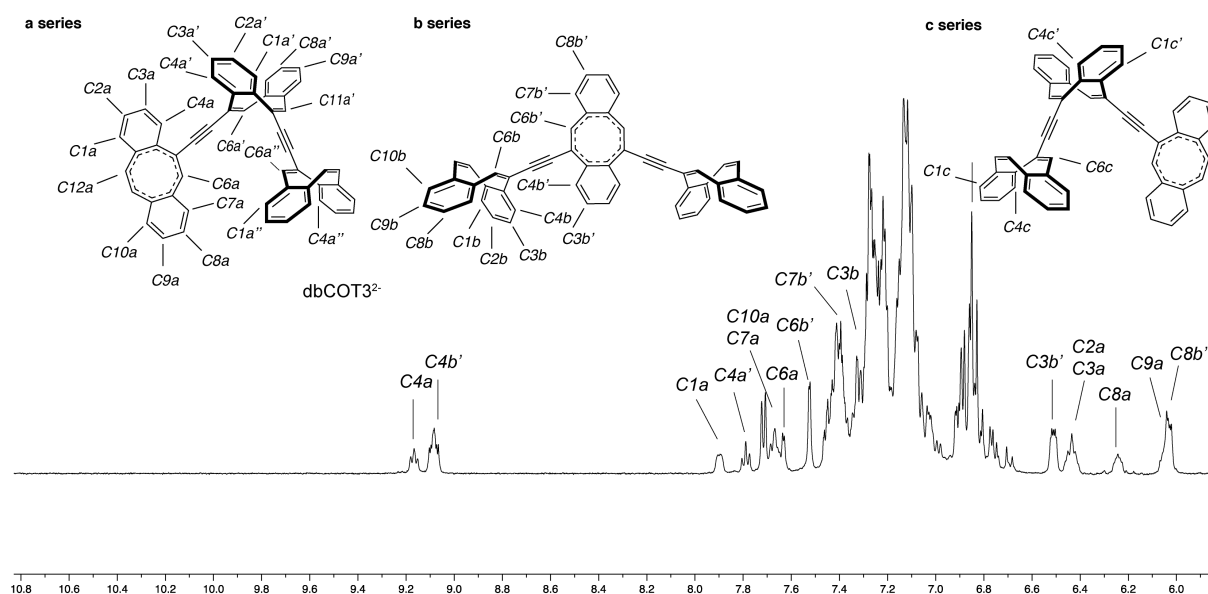
Proton	^1H δ (ppm)	Carbon	^{13}C δ (ppm)	Proton	^1H δ (ppm)	Carbon	^{13}C δ (ppm)
H(C1)	8.02	C1	136.7	H(C8)	6.26	C8	
H(C2)	6.39	C2		H(C9)	6.16	C9	
H(C3)	6.55	C3		H(C10)	7.81	C10	135.5
H(C4)	9.99	C4		H(C11)	7.19	C11	
H(C6)	8.48	C6		H(C12)	7.30	C12	
H(C7)	8.03	C7					

^1H NMR chemical shift assignment of K_4dbCOT_2 . A lack of broadening in the room temperature ^1H NMR spectrum show that there is no fluxionality in the structure. The number of peaks in the ^1H and ^{13}C spectra show that there is a symmetry element (mirror plane/two-fold axis) at the center of the structure.

The peak at $\delta = 8.48$ ppm is the only singlet and is assigned as H(C6). There is a $^3J_{\text{CH}}$ HMBC correlation from H(C6) to $\delta = 89.4$ ppm which can be assigned to the alkyne carbon. There is also a $^4J_{\text{CH}}$ HMBC correlation from this carbon to $\delta = 9.99$ ppm, which is assigned to H(C4). The extreme downfield chemical shift of H(C4) results from proximity to the alkyne and is diagnostic of H(C4). H(C4) has a $^3J_{\text{HH}}$ COSY correlation to $\delta = 6.55$ ppm which is assigned as H(C3). H(C3) has a COSY correlation to $\delta = 6.39$ ppm which is assigned as H(C2). H(C2) has a COSY correlation to $\delta = 8.02$ ppm which is assigned as H(C1). H(C1) has a J_{CH} HSQC

correlation to $\delta = 136.7$ ppm assigned to C1. There is a $^3J_{CH}$ HMBC correlation from C1 to $\delta = 7.30$ ppm which is assigned as H(C12). There is a COSY correlation from H(C12) to $\delta = 7.19$ ppm which is assigned as H(C11). There is a $^3J_{CH}$ HMBC correlation from H(C11) to $\delta = 135.5$ ppm which is assigned as C10. There is an HSQC correlation from C10 to $\delta = 7.81$ ppm which is assigned as H(C10). There is a COSY correlation from H(C10) to $\delta = 6.16$ ppm which is assigned as H(C9). There is a COSY correlation from H(C9) to $\delta = 6.26$ ppm which is assigned as H(C8). There is a COSY correlation from H(C8) to $\delta = 8.03$ ppm which is assigned to H(C7) and concludes the assignment.

Assignment of K₂dbCOT3.



Supplementary Figure 13. Selected assignments in the ¹H NMR spectrum (500 MHz) of K₂dbCOT3 in THF-d₈. Spectrum recorded at $T = 223.9$ K.

Supplementary Table 5. Assigned ¹H chemical shifts and relevant ¹³C chemical shifts for K₂dbCOT3.

Proton	¹ H δ (ppm)	Carbon	¹³ C δ (ppm)	Proton	¹ H δ (ppm)	Carbon	¹³ C δ (ppm)
a-series				b-series			
H(C1a)	7.89	C1a		H(C1b)	7.08	C1b	
H(C2a)	6.43	C2a		H(C2b)	7.32/7.25	C2b	
H(C3a)	6.45	C3a		H(C3b)	7.32/7.25	C3b	

H(C4a)	9.16	C4a		H(C4b)	7.71	C4b
H(C6a)	7.63	C6a	98.2	H(C6b)	6.85	C6b
H(C7a)	7.67	C7a	134.5	H(C8b)	7.14	C8b
H(C8a)	6.24	C8a		H(C9b)	7.13	C9b
H(C9a)	6.05	C9a		H(C10b)	7.38	C10b
H(C10a)	7.66	C10a		H(C3b')	6.51	C3a'
H(C12a)	7.14	C12a		H(C4b')	9.08	C4a'
H(C1a')	7.39	C1a'		H(C6b')	7.52	C6a'
H(C2a')	7.42/7.30	C2a'		H(C7b')	7.40	C7a'
H(C3a')	7.42/7.30	C3a'		H(C8b')	6.02	C8a'
H(C4a')	7.79	C4a'				
H(C6a')	7.25	C6a'		c-series		
H(C8a')	7.16/7.11	C8a'		H(C1c)	7.02	C1c
H(C9a')	7.16/7.11	C9a'		H(C4c)	7.38	C4c
H(C11a')	6.90	C11a'		H(C6c)	7.16	C6c
H(C1a'')	7.02	C1a''		H(C1c')	7.79	C1c'
H(C4a'')	7.38	C4a''		H(C4c')	7.39	C4c'
H(C6a'')	7.16	C6a''				

¹H NMR chemical shift assignment of K₂dbCOT3. Broad peaks in the room temperature ¹H NMR spectrum that sharpen upon cooling show that the structure is fluxional. The b-series structure has a *pseudo*-symmetry plane through the center unit whereas the a/c series are of C₁-symmetry.

The downfield chemical shifts of $\delta = 9.17$ ppm and $\delta = 9.08$ ppm are diagnostic of a proximity to the alkyne spacer why these are assigned as H(C4a)/H(C4b'). Selective excitation of $\delta = 9.16$ ppm in an 1D ROE experiment gives rise to only one exchange peak at $\delta = 7.71$ ppm, whereas selective excitation of $\delta = 9.08$ ppm gives rise to two exchange peaks at $\delta = 7.79$ ppm and $\delta = 7.39$ ppm. From symmetry, it follows that $\delta = 9.16$ ppm is H(C4a) and $\delta = 9.08$ ppm

is H(C4b'). Taking the inherent symmetry of the b-series into account, the integral of H(C4a) and H(C4b') gives a 47:53 ratio of concentrations for the a-series and b-series. Integration between $\delta = 7.50$ ppm and $\delta = 6.60$ ppm shows that the sample contains ~25% unreduced dbCOT3. The exchange experiments prove that the a-series, b-series, and c-series are fluxionally interconverting.

Nota bene: The a-series and c-series structures are identical by ^1H NMR spectroscopy. The protons on, for instance, the terminal units are however individual atoms. Magnetization from an individual proton on a terminal reduced unit in the a-series can therefore be transferred to two additional distinct states through rearrangement/electron relay: first to the equivalent position in the b-series, and then further on to the equivalent position on a non-reduced terminal unit in the a-series. This means that electron relay can be followed from **7a** through **7b** to **7c**.

Reduced dbCOT unit in the a-series: H(C4a) has a COSY correlation to $\delta = 6.45$ ppm which is assigned as H(C3a). H(C3a) has a poorly resolved COSY correlation to $\delta = 6.43$ ppm which is assigned as H(C2a). Integration of the signal at 6.43/6.45 ppm shows that it corresponds to two protons, and the HSQC spectrum has two cross peaks at this proton chemical shift. H(C2a) has a COSY correlation to $\delta = 7.89$ ppm which is assigned as H(C1a). Based on the chemical shift, integration (1H), and coupling pattern (*pseudo*-singlet), $\delta = 7.63$ ppm is assigned as H(C6a). H(C6a) has an HSQC correlation to $\delta = 98.2$ ppm which is assigned as C6a. C6a has a $^3J_{\text{CH}}$ HMBC correlation to a proton at 7.67 ppm, that in turn has an HSQC correlation to an appropriate chemical shift for C7a, $\delta = 134.5$ ppm. H(C7a) has a COSY correlation to $\delta = 6.24$ ppm which is assigned to H(C8a). H(C8a) has a COSY correlation to $\delta = 6.05$ ppm which is assigned to H(C9a). H(C9a) has a COSY correlation to $\delta = 7.66$ ppm which is assigned to H(C10a).

Reduced dbCOT unit in the b-series: H(C4b') has a COSY correlation to $\delta = 6.51$ ppm which is assigned as H(C3b'). Based on the chemical shift, integration (2H), and coupling pattern (*pseudo*-singlet), $\delta = 7.52$ ppm is assigned as H(C6b'). The assignment is corroborated by the absence of COSY correlations, and the fact that this peak shows exchange to two positions, $\delta = 7.25$ ppm and $\delta = 6.9$ ppm. It must thus originate from two symmetry related protons at the center unit which end up in different chemical environments upon electron relay. From assignment of K₂dbCOT2 and K₄dbCOT2 we know that chemical shifts below ~6.5 ppm are diagnostic of the distal positions on the benzene rings of reduced units. The only remaining signal

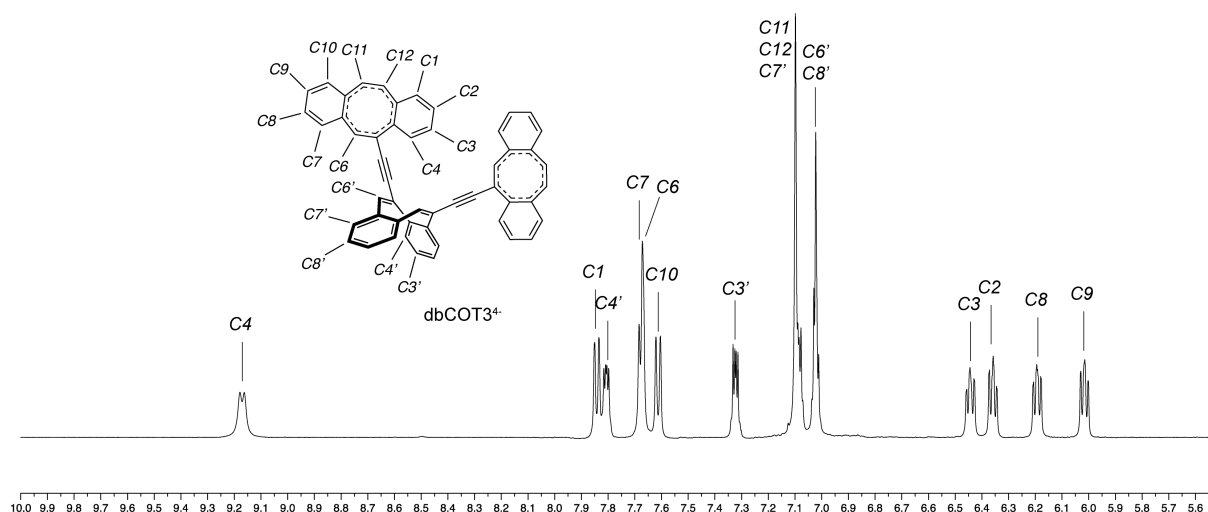
in this region (*vide supra*) is $\delta = 6.02$ ppm which is assigned to H(C8b'). H(C8b') has a COSY correlation to $\delta = 7.40$ ppm which is assigned to H(C7b').

a-series, assignments from exchange spectroscopy: In an 1D ROE experiment H(C3b') shows exchange to $\delta = 7.42$ ppm and $\delta = 7.30$ ppm due to a broken symmetry in the a-series structure. These peaks were assigned as H(C3a')/H(C2a') but were not disambiguated. H(C4b') has exchange to $\delta = 7.79$ ppm and to $\delta = 7.39$ ppm. $\delta = 7.79$ ppm was tentatively assigned to H(C4a') due to a higher shift from deshielding by proximity to the reduced unit (*cf.*, H(C4') vs H(C1') in K₂dbCOT2). This gives $\delta = 7.39$ ppm as H(C1a'). H(C6b') has exchange to $\delta = 7.25$ ppm and $\delta = 6.90$ ppm. $\delta = 7.25$ ppm was tentatively assigned to H(C6a') due to a higher shift from deshielding by proximity to the reduced unit. This gives $\delta = 6.90$ ppm as H(C11a'). H(C8b') has exchange to $\delta = 7.16$ ppm and $\delta = 7.11$ ppm due to a broken symmetry in the a-series structure. These were assigned as H(C8a')/H(C9a') but were not disambiguated. H(C1a) has a through space ROE correlation to 7.14 which is assigned as H(C12a). This correlation also corroborates the flat geometry of a terminal unit.

b-series, assignments from exchange spectroscopy: H(C1a) has exchange to $\delta = 7.08$ ppm which was assigned as H(C1b). H(C3a)/H(C2a) has exchange to $\delta = 7.32$ ppm and $\delta = 7.25$ ppm. These are assigned as H(C3b)/H(C2b) but were not further disambiguated. H(C4a) has exchange to $\delta = 7.71$ ppm which was assigned as H(C4b). H(C6a) has exchange to $\delta = 6.85$ ppm which was assigned to H(C6b). H(C8a) has exchange to $\delta = 7.14$ ppm which was assigned as H(C8b). H(C9a) has exchange to $\delta = 7.13$ ppm which was assigned as H(C9b). H(C10a) has exchange to $\delta = 7.38$ ppm which was assigned as H(C10b). H(C6b') has a through space ROE correlation to H(C7b') which corroborates the flat geometry of the center unit.

c-series, assignments from exchange spectroscopy: H(C1a) has a weak exchange peak to $\delta = 7.02$ ppm which is assigned as H(C1c). H(C1c) is chemically equivalent to H(C1a''). H(C4a) has a weak exchange peak to $\delta = 7.38$ ppm which was assigned as H(C4c). H(C4c) is chemically equivalent to H(C4a''). H(C6a) has a weak exchange peak to $\delta = 7.16$ ppm which is assigned as H(C6c). H(C6c) is chemically equivalent to H(C6a''). H(C1a') is chemically equivalent to H(C4c'). H(C4a') is chemically equivalent to H(C1c').

Assignment of K₄dbCOT3.



Supplementary Figure 14. Assigned ^1H NMR spectrum (500 MHz) of $\text{K}_4\text{dbCOT3}$ in THF-d_8 .

Supplementary Table 6. Assigned ^1H chemical shifts and relevant ^{13}C chemical shifts for $\text{K}_4\text{dbCOT3}$

Proton	^1H δ (ppm)	Carbon	^{13}C δ (ppm)	Proton	^1H δ (ppm)	Carbon	^{13}C δ (ppm)
H(C1)	7.84	C1		H(C10)	7.61	C10	
H(C2)	6.36	C2		H(C11)	7.02	C11	
H(C3)	6.44	C3		H(C12)	7.09	C12	98.3
H(C4)	9.16	C4		H(C3')	7.33	C3'	
H(C6)	7.66	C6	99.3	H(C4')	7.80	C4'	
H(C7)	7.68	C7		H(C6')	7.02	C6'	
H(C8)	6.19	C8		H(C7')	7.08	C7'	130.0
H(C9)	6.02	C9		H(C8')	7.02	C8'	

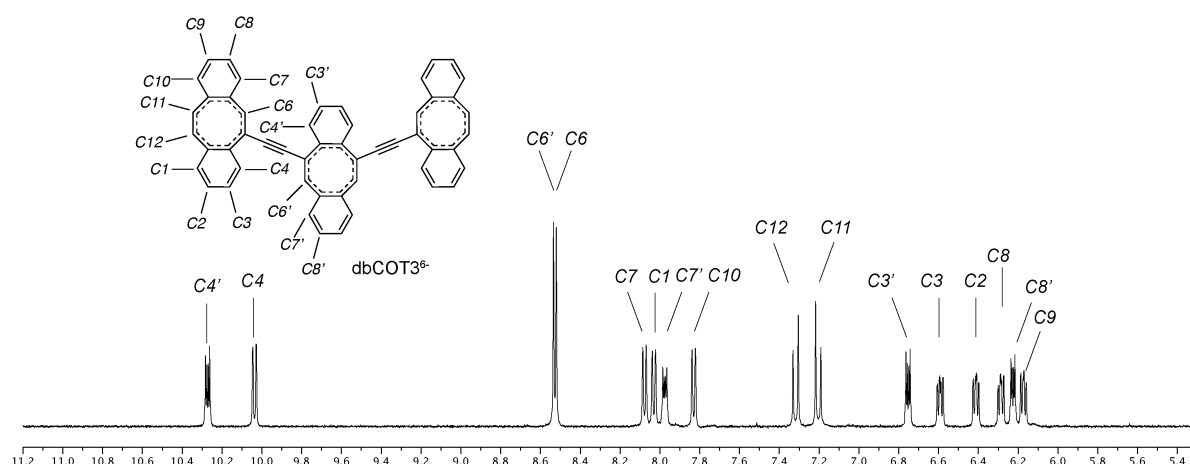
^1H NMR chemical shift assignment of $\text{K}_4\text{dbCOT3}$. A lack of significant broadening in the room temperature ^1H NMR spectrum shows that there is no fluxionality in the structure. The number of peaks in the ^1H and ^{13}C spectra shows that there is a *pseudo*-plane of symmetry at the center of the structure.

The extreme downfield chemical shift of $\delta = 9.16$ ppm is diagnostic of a proximity to the alkyne spacer in a planar structure and is assigned as H(C4). H(C4) has a COSY correlation to $\delta = 6.44$ ppm which was assigned as H(C3). H(C3) has a COSY correlation to $\delta = 6.36$ ppm which

was assigned to H(C2). H(C2) has a COSY correlation to $\delta = 7.84$ ppm which is assigned to H(C1). H(C1) has an $^3J_{\text{CH}}$ HMBC correlation to $\delta = 98.3$ ppm which is assigned as C12. C12 has an HSQC correlation to $\delta = 7.09$ ppm which was assigned to H(C12). H(C12) has a COSY correlation to $\delta = 7.02$ ppm which was assigned to H(C11). The singlet at $\delta = 7.66$ ppm was assigned as H(C6) due to a more downfield chemical shift than the singlet at $\delta = 7.02$ ppm. The singlet at $\delta = 7.02$ ppm was assigned as H(C6'). H(C6) has an HSQC correlation to $\delta = 99.3$ ppm which was assigned to C6. C6 has an $^3J_{\text{CH}}$ HMBC correlation to $\delta = 7.68$ ppm which was assigned to H(C7). H(C7) has a COSY correlation to $\delta = 6.19$ ppm which was assigned as H(C8). H(C8) has a COSY correlation to $\delta = 6.02$ ppm which was assigned to H(C9). H(C9) has a COSY correlation to $\delta = 7.61$ ppm which was assigned as H(C10).

H(C6') has an $^3J_{\text{CH}}$ HMBC correlation to $\delta = 130.0$. $\delta = 130.0$ ppm has an HSQC correlation from to $\delta = 7.08$ ppm which was assigned as H(C7'). H(C7') has a poorly resolved COSY correlation to $\delta = 7.02$ ppm which was assigned to H(C8'). There is a COSY correlation between $\delta = 7.80$ ppm and $\delta = 7.33$ ppm which are assigned to H(C3')/H(C4'). $\delta = 7.80$ ppm has $^{2/3}J_{\text{CH}}$ HMBC correlations to two carbons without C–H bond as seen by the absence of HSQC correlations ($\delta = 108.0$ ppm and $\delta = 111.2$ ppm), and $\delta = 7.33$ ppm has only one $^3J_{\text{CH}}$ HMBC correlation ($\delta = 108.0$ ppm), which is consistent with $\delta = 7.80$ ppm as H(C4') and $\delta = 7.33$ ppm as H(C3') and concludes the assignment.

Assignment of K₆dbCOT3.



Supplementary Figure 15. Assigned ^1H NMR spectrum (500 MHz) of K₆dbCOT3 in THF-*d*₈. Spectrum recorded at $T = 268.2$ K.

Supplementary Table 7. Assigned ^1H chemical shifts and relevant ^{13}C chemical shifts for K₆dbCOT3

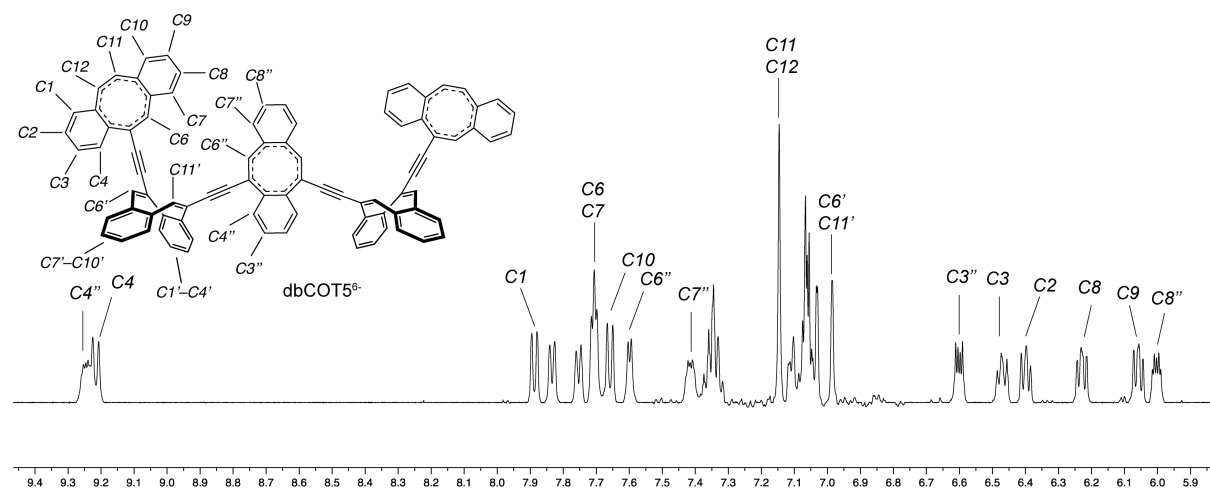
Proton	^1H δ (ppm)	Carbon	^{13}C δ (ppm)	Proton	^1H δ (ppm)	Carbon	^{13}C δ (ppm)
H(C1)	8.03	C1		H(C10)	7.83	C10	135.5
H(C2)	6.41	C2		H(C11)	7.21	C11	
H(C3)	6.59	C3		H(C12)	7.32	C12	97.4
H(C4)	10.04	C4		H(C3')	6.79	C3'	
H(C6)	8.55	C6	101.5	H(C4')	10.27	C4'	
H(C7)	8.08	C7	136.45	H(C6')	8.56	C6'	104.6
H(C8)	6.29	C8		H(C7')	8.00	C7'	136.35
H(C9)	6.17	C9		H(C8')	6.26	C8'	

^1H NMR chemical shift assignment of $\text{K}_6\text{dbCOT3}$. A lack of broadening in the room temperature ^1H NMR spectrum shows that there is no fluxionality in the structure. From the number of peaks in the ^1H and ^{13}C NMR spectra, there must be a symmetry element (plane/two-fold axis) through the center of the structure.

The extreme downfield shift of $\delta = 10.27$ ppm and $\delta = 10.04$ ppm are diagnostic of protons proximal to the alkyne in reduced structures. There is a COSY spin system from $\delta = 10.04$ ppm that connects four distinct signals (as opposed to two), why $\delta = 10.04$ ppm is assigned as H(C4). This assign $\delta = 10.27$ ppm to H(C4'). There is a COSY correlation from H(C4) to $\delta = 6.59$ which is assigned to H(C3). H(C3) has a COSY correlation to $\delta = 6.41$ ppm which is assigned to H(C2). H(C2) has a COSY correlation to $\delta = 8.03$ ppm which was assigned to H(C1). H(C1) has a $^3J_{\text{CH}}$ HMBC correlation to $\delta = 97.4$ ppm which is assigned to C12. C12 has an HSQC correlation to $\delta = 7.32$ ppm which is assigned to H(C12). H(C12) has a COSY correlation to $\delta = 7.21$ ppm which is assigned to H(C11). H(C11) has an $^3J_{\text{CH}}$ HMBC correlation to $\delta = 135.45$ ppm. $\delta = 135.45$ ppm has an HSQC correlation to $\delta = 7.83$ ppm which was assigned as H(C10). H(C10) has a COSY correlation to $\delta = 6.17$ ppm which was assigned to H(C9). H(C9) has a COSY correlation to $\delta = 6.29$ ppm which was assigned to H(C8). H(C8) has a COSY correlation to $\delta = 8.08$ ppm which was assigned to H(C7). H(C7) has one HMBC correlation to a carbon with an HSQC correlation, $\delta = 101.5$ ppm which was assigned as C6. C6 has an HSQC correlation to $\delta = 8.55$ ppm which was assigned as H(C6).

The only remaining singlet in the spectrum, $\delta = 8.56$ ppm, is assigned as H(C6'). H(C6') has an HSQC correlation to $\delta = 104.6$ ppm is assigned as C6'. H(C6') has a HMBC correlation to $\delta = 136.35$ ppm. $\delta = 136.35$ ppm has an HSQC correlation to $\delta = 8.00$ ppm which is assigned as H(C7') on account of being the only proximal carbon to H(C6') that has a C–H bond (HSQC correlation). H(C7') has a COSY correlation to $\delta = 6.26$ ppm which is assigned as H(C8'). H(C4') has a COSY correlation to $\delta = 6.79$ ppm which is assigned as H(C3') and concludes the assignment.

Assignment of K₆dbCOT5.



Supplementary Figure 16. Selected assignments in the ^1H NMR spectrum (500 MHz) of K₆dbCOT5 in THF-*d*₈. All Spectrum recorded at $T = 273.0$ K.

Supplementary Table 8. Assigned ^1H chemical shifts and relevant ^{13}C chemical shifts for K₆dbCOT5

Proton	^1H δ (ppm)	Carbon	^{13}C δ (ppm)	Proton	^1H δ (ppm)	Carbon	^{13}C δ (ppm)
H(C1)	7.89	C1		H(C3')	see text	C3'	
H(C2)	6.42	C2		H(C4')	see text	C4'	
H(C3)	6.46	C3		H(C6')	7.03/6.99	C6'	127.1/127.9
H(C4)	9.22	C4		H(C7')	see text	C7'	
H(C6)	7.70	C6	98.2	H(C8')	see text	C8'	
H(C7)	7.70	C7	135.5	H(C9')	see text	C9'	

H(C8)	6.23	C8		H(C10')	see text	C10'	
H(C9)	6.06	C9		H(C11')	7.03/6.99	C11'	127.1/127.9
H(C10)	7.66	C10	135.3	H(C3'')	6.60	C3''	
H(C11)	7.14	C11	102.1	H(C4'')	9.24	C4''	
H(C12)	7.14	C12	97.1	H(C6'')	7.59	C6''	
H(C1')	see text	C1'		H(C7'')	7.42	C7''	135.1
H(C2')	see text	C2'		H(C8'')	6.00	C8''	

¹H NMR chemical shift assignment of K₆dbCOT5. A lack of significant broadening in of signals in the ambient temperature ¹H NMR spectrum shows that there is no fluxionality in the structure. The number of peaks in the ¹H and ¹³C spectra shows that there is a *pseudo*-plane of symmetry at the center of the structure.

The extreme downfield shift of $\delta = 9.24$ ppm and $\delta = 9.22$ ppm are diagnostic of protons proximal to the alkyne. Of these $\delta = 9.22$ ppm, but not $\delta = 9.24$ ppm, is part of a COSY spin system that connects four peaks. $\delta = 9.22$ ppm is therefore assigned as H(C4) and $\delta = 9.24$ ppm as (HC4'').

Terminal reduced dbCOT unit. H(C4) has a COSY correlation to $\delta = 6.46$ ppm which is assigned as H(C3). H(C3) has a COSY correlation to $\delta = 6.42$ ppm and is assigned to H(C2). H(C2) has a COSY correlation to $\delta = 7.89$ which is assigned as H(C1). H(C1) has a ³J_{CH} HMBC correlation to $\delta = 97.1$ ppm which is assigned as C12. C12 has an HSQC correlation to $\delta = 7.14$ ppm which is assigned to H(C12). H(C12) has a ²J_{CH} HMBC correlation to $\delta = 102.1$ ppm which is assigned to C11. C11 has an HSQC correlation to $\delta = 7.14$ ppm which is assigned as H(C11). H(C11) and H(C12) thus overlaps, but C11 and C12 do not. H(C11) has a ³J_{CH} HMBC correlation to $\delta = 135.3$ ppm which, in turn, has an HSQC correlation to $\delta = 7.66$ ppm and is assigned to H(C10). H(C10) has a COSY correlation to $\delta = 6.06$ ppm which is assigned to H(C9). H(C9) has a COSY correlation to $\delta = 6.23$ ppm which is assigned as H(C8). H(C8) has a COSY correlation to $\delta = 7.70$ ppm which is assigned to H(C7). H(C7) has a ³J_{CH} HMBC correlation to $\delta = 98.2$ ppm and to $\delta = 135.5$ ppm. Both peaks have HSQC correlations to $\delta = 7.70$ ppm and H(C6) is assigned to $\delta = 7.70$ ppm (integral 2H). By analogy with chemical shifts in the K₂dbCOT3 a-series, $\delta = 98.2$ ppm is assigned to C6 and $\delta = 135.5$ ppm to C7.

Central reduced dbCOT unit. H(C4'') has a COSY correlation to $\delta = 6.60$ ppm which is assigned to H(C3''). $\delta = 6.00$ is assigned as H(C8'') being the only unaccounted signal with a diagnostic shielding. H(C8'') has a COSY correlation to $\delta = 7.42$ ppm which is assigned as H(C7''). H(C7'') has an HSQC correlation to $\delta = 135.1$ ppm which is assigned as C7''. C7'' has an $^3J_{\text{CH}}$ HMBC correlation to $\delta = 7.59$ ppm which is assigned as H(C6'').

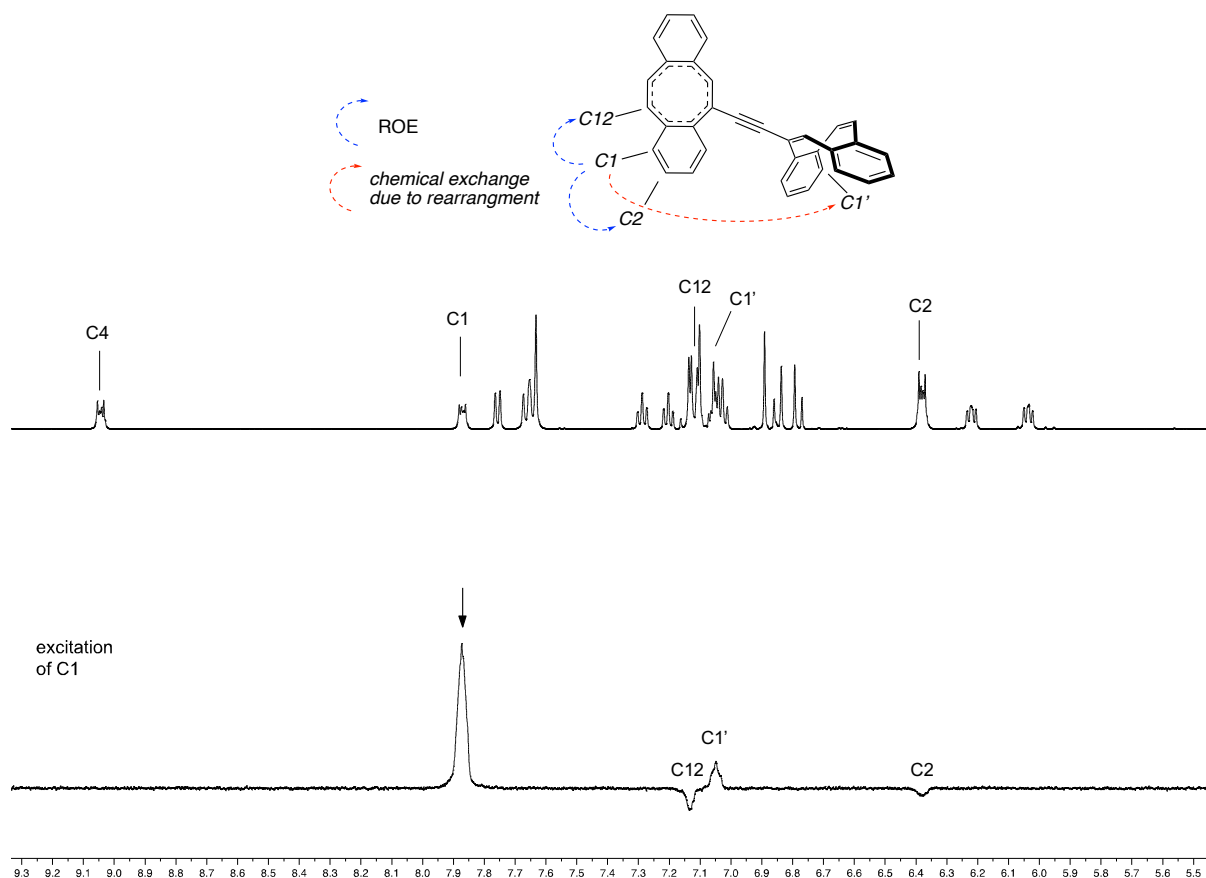
Non-reduced dbCOT unit. $\delta = 7.03$ ppm has an HSQC correlation to $\delta = 127.1$ ppm and $\delta = 6.99$ ppm has an HSQC correlation to $\delta = 127.9$ ppm. Based on the integrals, the chemical shifts and coupling patterns of these peaks are assigned as H(C6')/H(C11') but could not be disambiguated. $\delta = 7.03$ ppm has an $^3J_{\text{CH}}$ HMBC correlation to $\delta = 128.86$ ppm. $\delta = 128.86$ ppm has an HSQC correlation to $\delta = 7.10$ ppm. $\delta = 7.10$ ppm has an $^2J_{\text{CH}}$ HMBC correlation to $\delta = 125.2$ ppm. $\delta = 125.2$ ppm has an HSQC correlation to $\delta = 7.05$ ppm. $\delta = 6.99$ ppm has an $^3J_{\text{CH}}$ HMBC correlation to $\delta = 128.82$ ppm. $\delta = 128.82$ ppm has an HSQC correlation to $\delta = 7.06$ ppm. The integral between $\delta = 7.08$ ppm and $\delta = 7.04$ ppm reveals three protons. $\delta = 7.05/125.2$ ppm is therefore assigned as two CH groups on adjacent positions supported by the lack of clear COSY correlations. Starting from a vinylic proton following the carbon chain, this gives an order of $\delta = 7.03$ ppm \Rightarrow $\delta = 7.10$ ppm \Rightarrow $\delta = 7.05$ ppm \Rightarrow $\delta = 7.05$ ppm $\delta = 7.06$ ppm \Rightarrow $\delta = 6.99$ ppm corresponding to H(C6') \Rightarrow H(C7') \Rightarrow H(C8') \Rightarrow H(C9') \Rightarrow H(C10') \Rightarrow H(C11') or the reverse. This assignment is further corroborated by the chemical shifts which parallels those of equivalent positions in K₄dbCOT3.

There is a COSY correlation from $\delta = 7.75$ ppm to $\delta = 7.33$ ppm. There is a COSY correlation from $\delta = 7.33$ ppm to $\delta = 7.35$ ppm. There is a COSY correlation from $\delta = 7.35$ ppm to $\delta = 7.83$ ppm. There is an $^3J_{\text{CH}}$ HMBC correlation from $\delta = 7.03$ ppm to $\delta = 139.9$ ppm. There is an $^3J_{\text{CH}}$ HMBC correlation from $\delta = 7.35$ ppm to $\delta = 139.9$ ppm. $\delta = 139.9$ ppm does not have an HSQC correlation and is assigned as C1' adjacent or C4' adjacent. There is an $^3J_{\text{CH}}$ HMBC correlation from $\delta = 6.99$ ppm to $\delta = 139.5$ ppm. There is an $^3J_{\text{CH}}$ HMBC correlation from $\delta = 7.33$ ppm to $\delta = 139.5$ ppm. $\delta = 139.5$ ppm does not have an HSQC correlation and is assigned as C1' adjacent or C4' adjacent. From this, we assign $\delta = 7.35$ ppm to as proximal to $\delta = 7.03$ ppm and $\delta = 7.33$ ppm to as proximal to $\delta = 6.99$ ppm. Starting from a vinylic proton following the carbon chain, this gives an order of $\delta = 7.03$ ppm \Rightarrow $\delta = 7.83$ ppm \Rightarrow $\delta = 7.35$ ppm \Rightarrow $\delta = 7.33$ ppm $\delta = 7.75$ ppm \Rightarrow $\delta = 6.99$ ppm corresponding to H(C6') \Rightarrow H(C1') \Rightarrow H(C2') \Rightarrow

$H(C3') \Rightarrow H(C4') \Rightarrow H(C11')$ or the reverse. This assignment is supported by the chemical shifts which parallels those of equivalent positions in $K_4dbCOT3$.

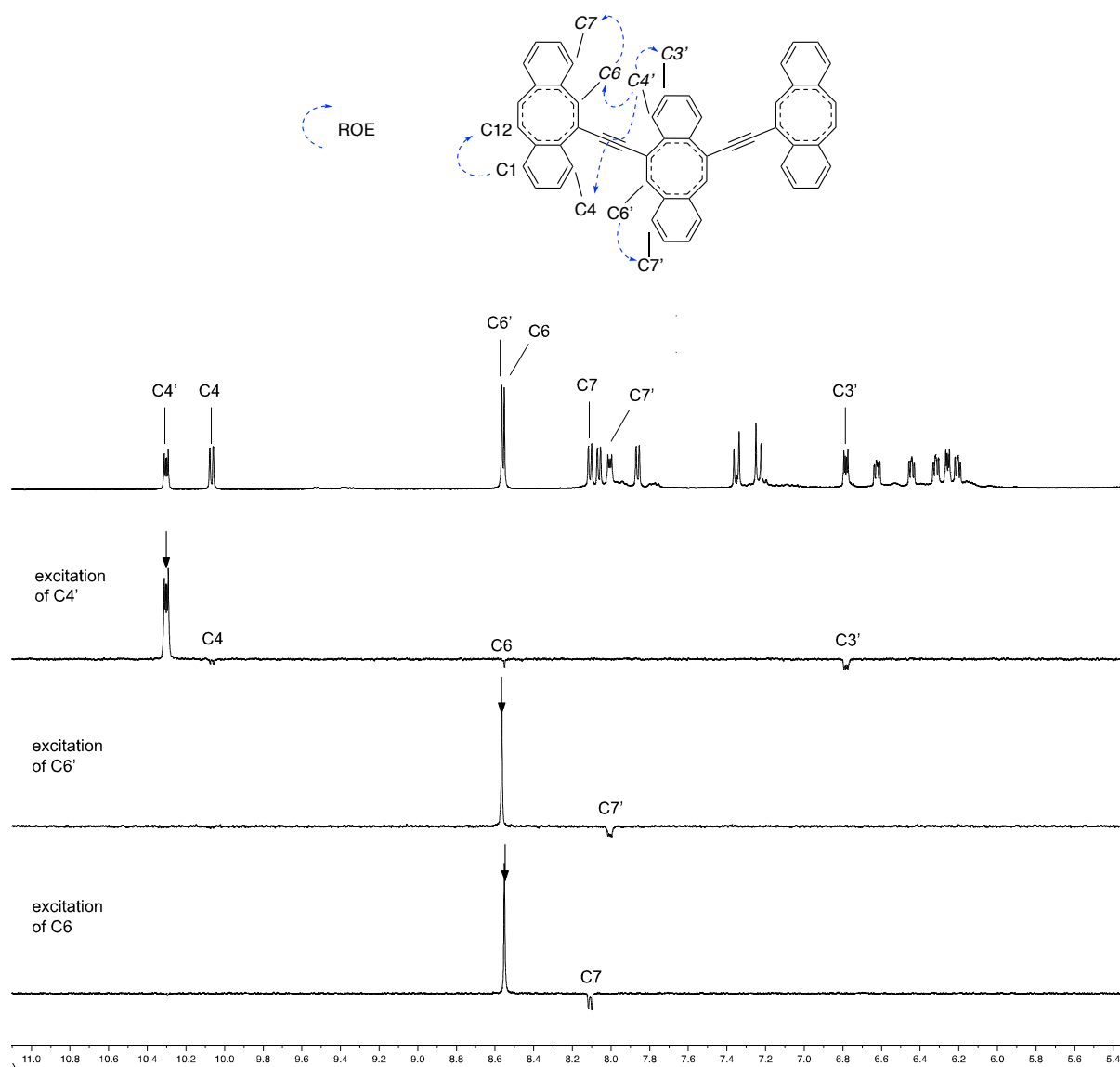
Confirmation of the planar conformation of reduced dbCOT units.

Partially reduced oligomers: The planar nature of one of the dbCOT units in $K_2dbCOT2$ was confirmed by a pronounced ROE between $H-(C1)$ and $H-(C12)$ in $K_2dbCOT2$ (Supplementary Figure 17). The extreme chemical shift of $H-(C4)$, which originates from being in close proximity to the alkyne, further strengthens this assignment. $K_2dbCOT3$, $K_4dbCOT3$, and $K_6dbCOT5$ were assigned by analogy.



Supplementary Figure 17. Diagnostic ROE observed in the reduced dbCOT unit of $K_2dbCOT2$. Spectra recorded at 500 MHz in THF- d_8 at $T = 248.0$ K, mixing time 200 ms. The arrow indicates selective excitation of $H-(C1)$ at 7.87 ppm.

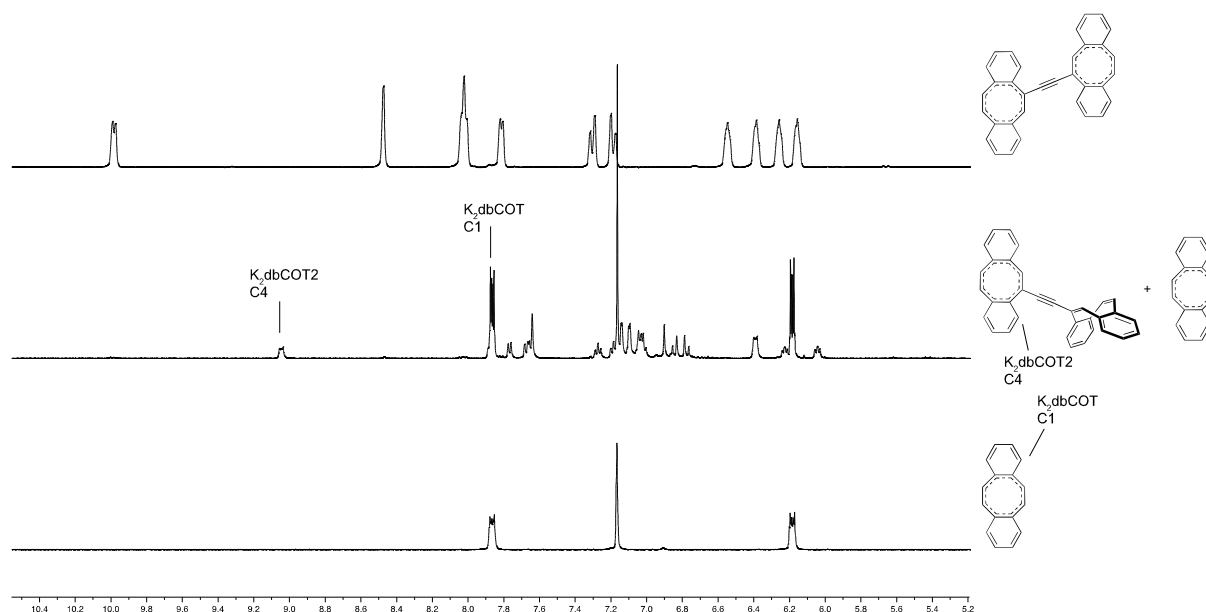
Fully reduced structures: The planar structure of the terminal dbCOT units in $K_6\text{dbCOT}_3$ was confirmed by a pronounced through-space ROE between $H-(C1)$ and $H-(C12)$ (Supplementary Figure 18). The same type of ROE was seen from $H-(C6)$ to $H-(C7)$. The ROEs between $H-C4'$ and $H-C4$, and $H-C4'$ and $C6$ indicate a propensity for adopting a globally planar structure wherein all dbCOT units are aligned in one plane and the π -system extends through the entirety of the structure. $K_4\text{dbCOT}_2$ was assigned similarly.



Supplementary Figure 18. Diagnostic ROE observed in $K_6\text{dbCOT}_3$. Spectra recorded at 500 MHz in THF-d_8 at $T = 268.2$ K, mixing time = 400 ms. Top: Selective excitation of $H-(C4')$ ($\delta = 10.31$ ppm); Middle: $H-(C6')$ ($\delta = 8.57$ ppm); Bottom: $H-(C6)$ ($\delta = 8.55$ ppm).

VI. Electron count in reduced oligomers

Titration of $K_4dbCOT2$ with $dbCOT$. A solution of $K_4dbCOT2$ was prepared following the standard procedure: $dbCOT2$ (1.5 mg, 3.5 μ mol) was dissolved in THF- d_8 (0.40 mL) in a Young's NMR tube and reduced. A solution of $dbCOT$ (0.69 mg, 3.4 μ mol) in THF- d_8 was then added in three 50 μ L portions (\sim 1.0 equiv.) under rigorous exclusion of air and moisture. The resulting mixture was analyzed by quantitative 1H NMR spectroscopy ($d1 = 30$ s; $T = 273.2$ K) and showed a clean conversion into $K_2dbCOT2$ and the known K_2dbCOT (Supplementary Figure 19). Integration of the resonances at 9.08 ppm ($H-(C4)$ in $K_2dbCOT2$) and 7.87 ppm (corresponding to 4H in K_2dbCOT) showed a ratio between the two species: $K_2dbCOT2$ to $K_2dbCOT = 48:52$. Formation of precisely one equivalent of K_2dbCOT confirms that $K_4dbCOT2$ is reduced with two electrons more than $K_2dbCOT2$.



Supplementary Figure 19. Titration of $K_4dbCOT2$ with $dbCOT$. Top: 1H NMR spectrum of $K_4dbCOT2$; Centre: quantitative 1H NMR spectrum after addition of 0.96 equiv. of $dbCOT$ to a solution of $K_4dbCOT2$; Bottom: 1H NMR spectrum of K_2dbCOT .

VII. Electron paramagnetic resonance (EPR) characterization

Samples were prepared following the standard stop-and-go method. Solution X-band EPR spectra were recorded on liquid samples at RT as prepared in Young-tubes. Data were acquired on a Bruker Elexsys E500 spectrometer equipped with a Bruker SUPER-X CW-EPR bridge, a

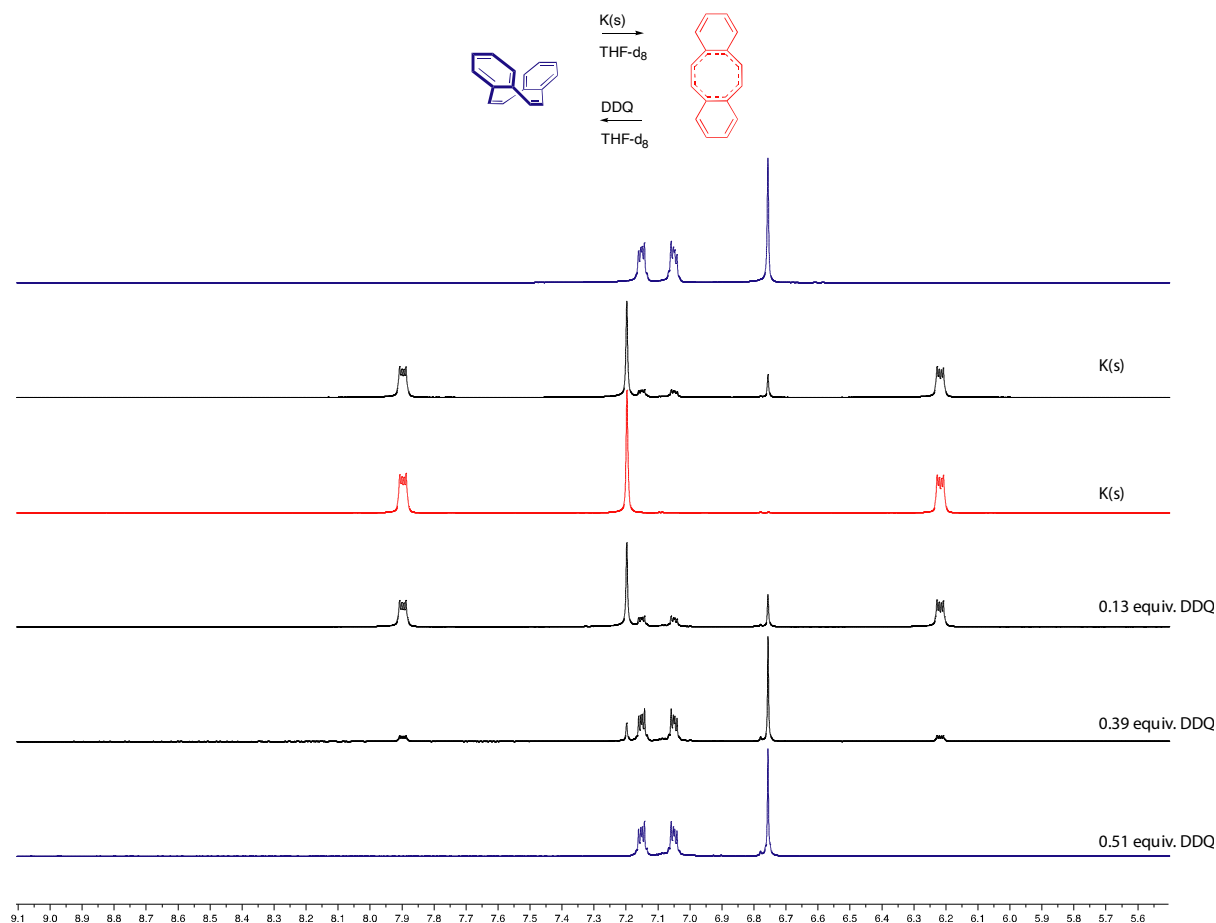
Bruker ER 4116 DM dual mode cavity, and an EIP 538B frequency counter at ambient temperature. Modulation amplitudes were tested in the range 0.1-8 G and microwave power was tested between 0.2 and 200 mW. All well-defined stages of reduction for dbCOT2 and dbCOT3 (confirmed by ^1H NMR spectroscopy), as well as stages between these were investigated, but all samples were EPR silent, putting an upper limit on the concentration of odd-electron species of approx. 0.1 μM .

The concentration of each oligomer respectively was: dbCOT2: 5.0 mM; dbCOT3: 1.5 mM.

VIII. Redox cycles of dbCOT, dbCOT2, and dbCOT3.

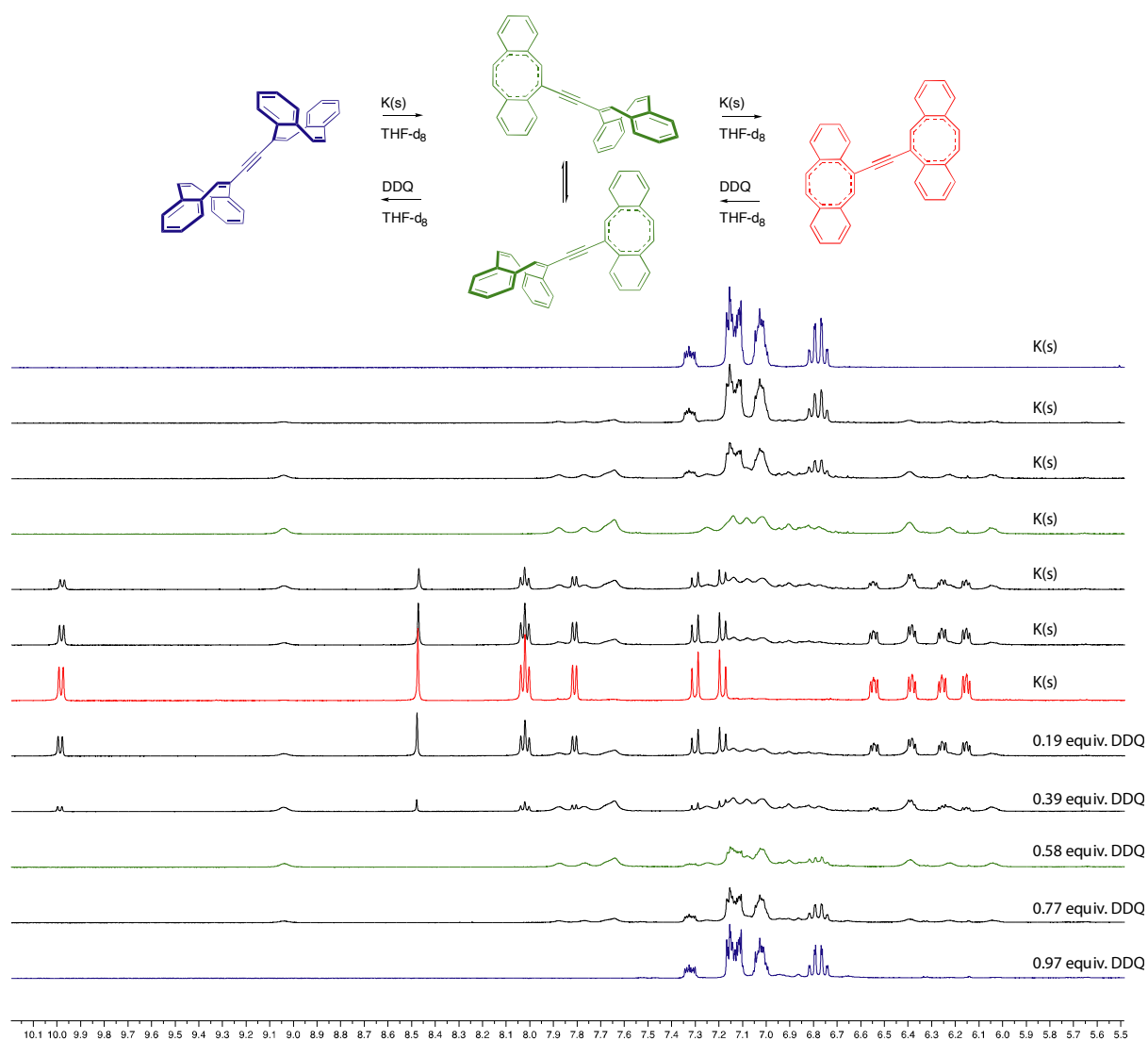
General method for oxidation/reduction cycles of dbCOT-oligomers with K/DDQ. Under argon atmosphere in a glovebox, solutions of reduced dbCOT-oligomers prepared according to the general reductive method was treated with a stock solution of DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) in dry and oxygen-free THF- d_8 via a gas-tight syringe. The solution was carefully vortexed (to prevent contact with the reactive metal) for 20 seconds, and exported out of the glovebox for NMR analysis. The procedure was iteratively repeated.

Titration of K_2dbCOT with DDQ. K_2dbCOT was prepared according to the general method by reacting dbCOT (0.55 mg, 2.7 μmol) with potassium metal (excess). The solution was treated stepwise with 20 μL aliquots of a stock solution of DDQ (1.2 mg, 5.2 μmol) in dry THF- d_8 (0.60 mL), until dbCOT was completely reformed as seen by ^1H NMR spectroscopy (Supplementary Figure 20).

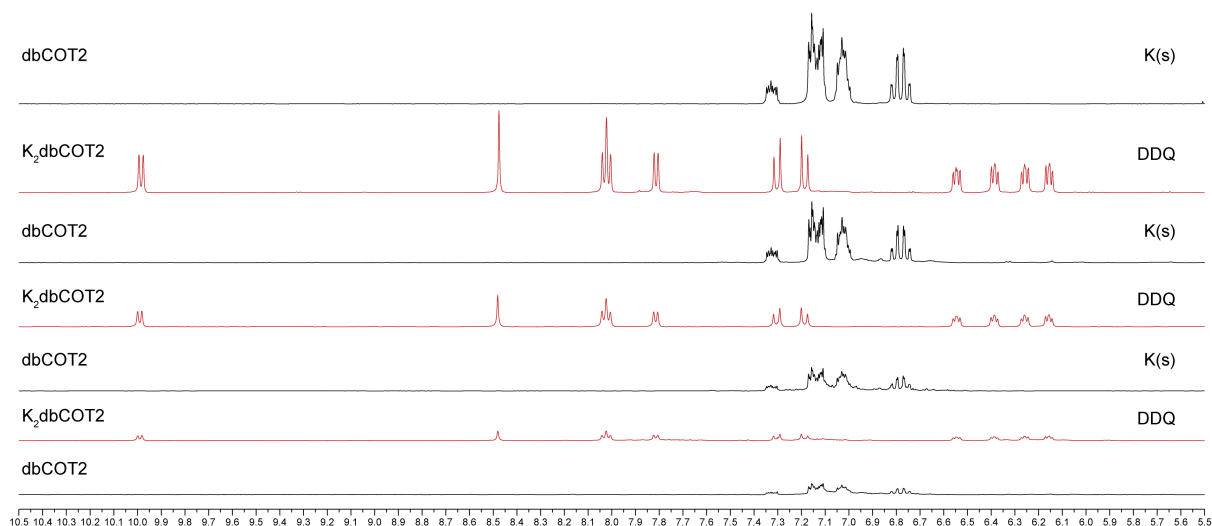


Supplementary Figure 20. Reduction-oxidation cycle of dbCOT. ^1H NMR spectra were recorded at $T = 273.0$ K.

Titration of K_4dbCOT_2 with DDQ. K_4dbCOT_2 was prepared according to the general method by reacting dbCOT2 (0.58 mg, 1.3 μmol) with potassium (excess) metal in THF- d_8 (0.45 mL). The solution was treated stepwise with 20 μL aliquots of a stock solution of DDQ (1.5 mg, 6.5 μmol) in dry THF- d_8 (0.50 mL), until dbCOT2 was completely reformed as seen by ^1H NMR spectroscopy (Supplementary Figure 21). The procedure could be repeated up to three cycles: Following the described cycle, K_2dbCOT_2 was reformed by re-exposing the mixture to the potassium metal followed by addition of DDQ (Supplementary Figure 22).

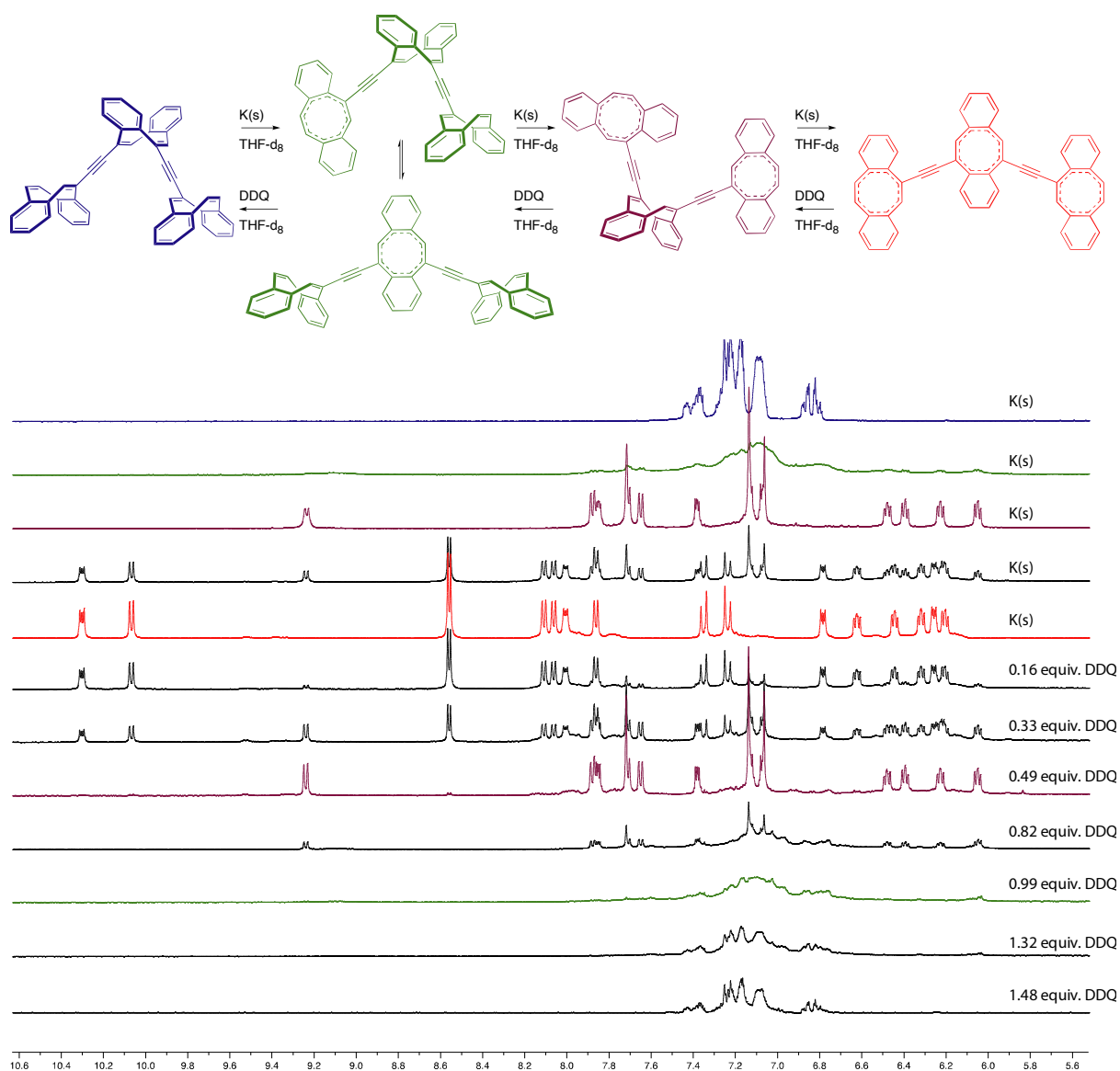


Supplementary Figure 21. Reduction-oxidation cycle of dbCOT2. Dilution of the sample reflects in reduced signal intensity.



Supplementary Figure 22. Three consecutive oxidation-reduction cycles of dbCOT2. Dilution of the sample reflects in reduced signal intensity.

Titration of $K_6dbCOT3$ with DDQ. $K_6dbCOT3$ was prepared according to the general method by reacting dbCOT3 (0.69 mg, 1.1 μmol) with potassium (excess) metal in THF- d_8 (0.45 mL). The solution was treated stepwise with 20 μL aliquots of a stock solution of DDQ (1.2 mg, 5.2 μmol) in dry THF- d_8 (0.60 mL), until dbCOT3 was completely reformed as seen by ^1H NMR spectroscopy (Supplementary Figure 23).



Supplementary Figure 23. Reduction-oxidation cycle of dbCOT3. ^1H NMR spectra were recorded at $T = 273.0$ K. Dilution of the sample reflects in reduced signal intensity.

IX. NMR characterization of intramolecular electron transfer.

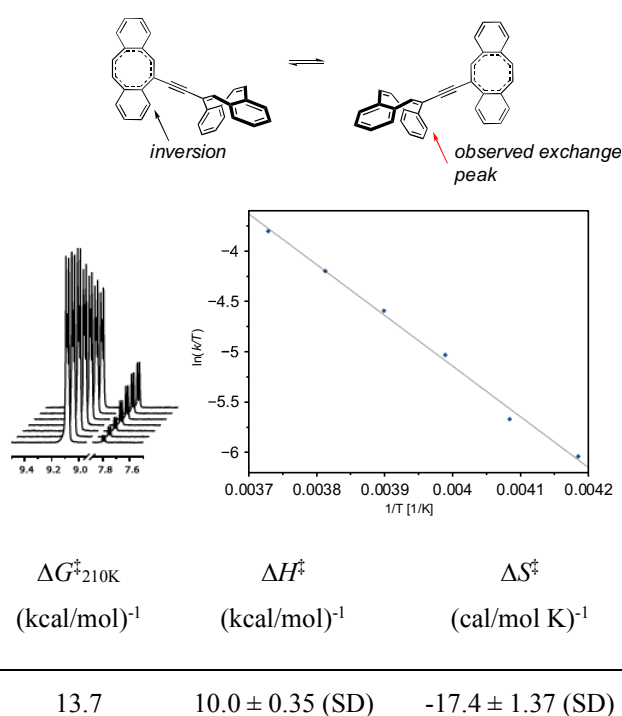
NMR characterization of electron transfer in $\text{K}_2\text{dbCOT2}$ and $\text{K}_2\text{dbCOT3}$.

General procedure for determination of rate constants. Samples of $\text{K}_2\text{dbCOT2}$ and $\text{K}_2\text{dbCOT3}$ in Young's NMR tubes were prepared following the general procedure. 1D chemical exchange NMR data were obtained with the Double Pulse Field Gradient Spin Echo Nuclear Overhauser Enhancement (DPFGSE NOE) experiment⁴ at variable mixing times from 25 – 200 ms, using a pulse sequence written in-house. The NMR spectrometer probe temperature was calibrated in the temperature range of 237.0 – 329.9 K using an NMR thermometer method based on

chemical shift difference in neat MeOH.⁵ The build-up curve for the exchange peak was determined by plotting the integral ratio of the exchange peak to the inverted peak, the so called PANIC approach.⁶ The rate constant of the exchange process is then given by the slope of the linear build-up curve, using only the data points for mixing times within the linear initial rate approximation.

Free energy barrier of charge transfer in K₂dbCOT2. Selective inversion of *H*-(C4) ($\delta = 9.08$ ppm) gave rise to an exchange peak at 7.80 ppm. Spectra with 50, 75, 100, 200 and 300 ms mixing time were collected at the following temperatures: 239.0, 244.9, 250.7, 256.5, 262.3, and 268.2 K. The rate constants of the exchange process at different temperatures were determined as described above. The thermodynamic parameters were determined from Eyring's equation, and by linear fitting of rate constants at different temperatures in an Eyring plot.

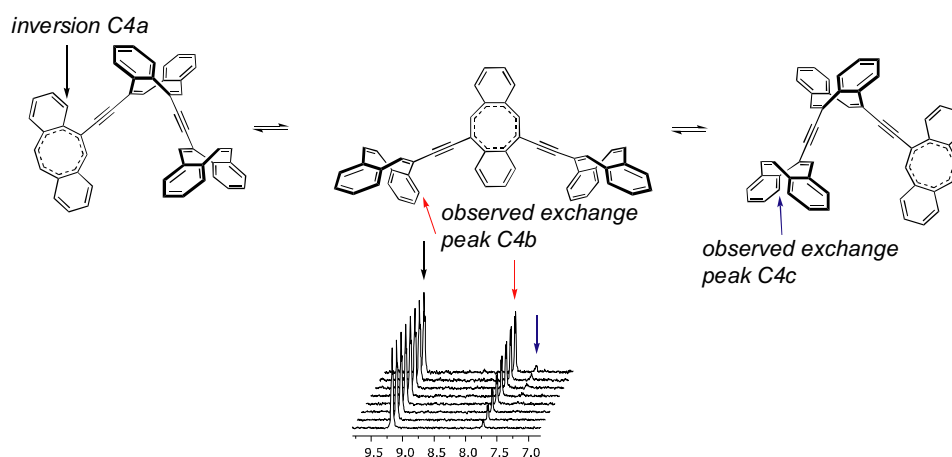
Supplementary Table 9. Free energy barrier of charge transfer within K₂dbCOT2^[a]



[a] Black arrow highlights the selectively inverted position. Red arrow indicates the position of the proton showing chemical exchange. Left: Representative stack of spectra with varying mixing times. Inversion at $\delta = 9.08$ ppm and $T = 268.2$ K. Right: Eyring plot.

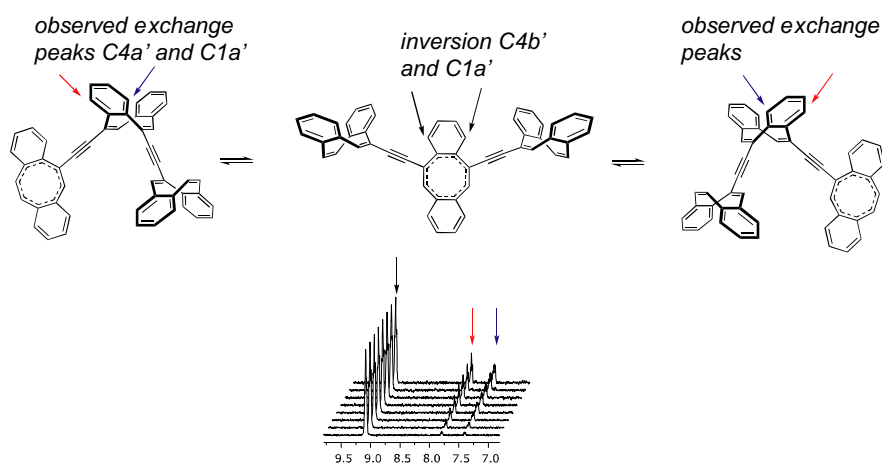
Free energy difference between isomers 7a/c and 7b of K₂dbCOT3 at 209.8 K. The relative concentrations of **7a/c** and **7b** at 209.8 K in THF-d₈ was measured by integration of the resonance from *H*-(C4)-**7a/c** ($\delta = 9.16$ ppm) and 2*H*-(C4')-**7b** ($\delta = 9.08$ ppm) in the ¹H NMR spectrum: **7a/c** to **7b** = 47:53.

Free energy barriers of charge transfer in K₂dbCOT3. Selective inversion of *H*-(C4a) ($\delta = 9.16$ ppm) at 209.8 K gave rise to a strong exchange peak at $\delta = 7.72$ ppm and a weak exchange peak at $\delta = 7.39$ ppm (Supplementary Figure 24). This can be understood as electron relay from a terminal dbCOT unit to the centre unit and further on to the second terminal unit. The free energy barrier of the exchange process was derived from the rate constant using the Eyring equation: $\Delta G^\ddagger_{209.8\text{K}} = 11.6 \pm 0.96$ kJ/mol⁻¹.



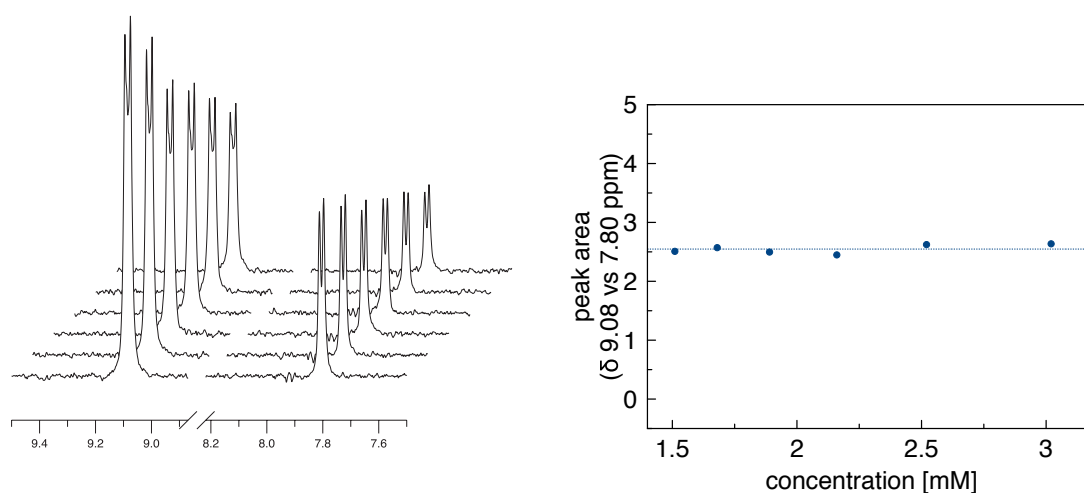
Supplementary Figure 24. Chemical exchange from the proton at C4a to C4b and to C4c in K₂dbCOT3.

Inversion of *2H*-(C4b'/C1a') ($\delta = 9.08$ ppm) at 209.8 K gave rise to a pair of resonances of equal size at $\delta = 7.79$ ppm and 7.40 ppm, respectively. This can be understood as electron relay from the centre dbCOT unit to either terminal group. Spectra were collected using 25, 50, 75, 100, 125, and 150 ms mixing time (Supplementary Figure 25). The free energy barrier of the exchange process was derived using the Eyring equation: $\Delta G^\ddagger_{209.8\text{K}} = 11.7 \pm 1.15$ (SD) kJ/mol⁻¹.



Supplementary Figure 25. Chemical exchange from the proton at C4b' to C4a' and C1b' to C1a' in K₂dbCOT3. C4b' and C1b' are pseudo-homotopic.

Concentration dependence of electron relay kinetics. $K_2dbCOT2$ (3.02 mM in 500 μ L THF- d_8) was prepared in a Young's NMR tube following the general procedure. A DPGSE NOE experiment with selective inversion at 9.08 ppm using 100 ms mixing time was performed at 268.0 K as described above. The sample was then diluted by addition of THF- d_8 in 100 μ L aliquots to a final concentration of 1.51 mM. The ratio of integrals at 9.08 ppm and 7.80 ppm was not influenced over this concentration range (mean integral ratio = 2.55 ± 0.075 (SD)) showing that the observed electron relay follows zero order kinetics in $K_2dbCOT2$ and thus that any intermolecular contribution is small (Supplementary Figure 26).



Supplementary Figure 26. Concentration dependence of charge relay in $K_2dbCOT2$. Left: Stack of chemical exchange spectra with concentrations from 3.02 mM to 1.51 mM; Right: Ratio between peak integrals as a function of concentration. Blue dotted line shows the average ratio of peak areas.

X. Cyclic voltammetry, differential pulse voltammetry, and anodic voltammetry stripping characterization

General: Cyclic voltammetry (CV), differential pulse voltammetry (DPV) and anodic stripping voltammetry (ASV) measurements were recorded using a three electrode potentiostat (Palm-sens4 (2018), PalmSens BV.). The experiments were performed in glass cells that were pre-dried at 135 °C overnight and cooled under a stream of argon. Experiments were performed in THF (dried over sodium-potassium alloy, vacuum distilled, and then purged with argon) under an argon atmosphere and at room temperature. The working electrode was mechanically polished using 0.05 μ m alumina powder on a soft lapping pad until a glossy finish was obtained.

The polished electrode was further washed and sonicated (10 s), first in ultrapure water, and then in dry CH_2Cl_2 , before drying in air.

Working electrode: Polycrystalline gold disc ($d = 2$ mm) from Palmsens BV (ItalSens).

Reference electrode: Silver wire pseudo-reference immersed in THF containing Bu_4NPF_6 (0.10 M) and AgNO_3 (sat.).

Counter electrode: Platinum wire.

Representative procedure for CV, DPV, and ASV measurements. To an electrochemical cell was added a solution of Bu_4NPF_6 (0.10 M) in THF (2.0 mL). Prior to each data collection, the cell was conditioned by four cycles of cyclic voltammetry (CV) at 0.40 V/s from 0.40 V to -3.00 V. The mixture was then gently vortexed and another four CV cycles were performed.

CV blank. CV data was recorded using the following parameters: $E(\text{begin}) = -2.00$ V; $E(\text{vertex1}) = -3.40$ V; $E(\text{vertex2}) = -2.00$ V; scan rate = 0.025 V/s; number of scans = 3.

DPV and ASV blank. DPV data was recorded from -2.00 V to -3.40 V using the following parameters: $E(\text{step}) = 0.005$ V; scan rate = -0.025 V/s; $E(\text{pulse}) = 0.025$ V; $t(\text{pulse}) = 0.07$ s. Electrochemical deposition prior to ASV measurements was performed at -3.40 V for 3 s followed by ASV and data was recorded from -3.40 V to -2.00 V using the following parameters: $E(\text{step}) = 0.005$ V; scan rate = 0.025 V/s; $E(\text{pulse}) = 0.025$ V; $t(\text{pulse}) = 0.07$ s.

Full CV. A solution of dbCOT (1.0 mL, 4.0 mM in THF), dbCOT2 (1.0 mL, 4.0 mM in THF), dbCOT3 (1.0 mL, 3.0 mM in THF), or dbCOT5 (1.0 mL, 1.8 mM in THF) was added to the cell. CV data was then recorded using the following parameters: $E(\text{begin}) = -2.00$ V; $E(\text{vertex1}) = -3.40$ V; $E(\text{vertex2}) = -2.00$ V; scan rate = 0.025 V/s; number of scans = 3.

Partial CV. CV data was then recorded over the first two redox processes using the following parameters: scan rate = 0.025 V/s; number of scans = 3. Potential windows:

- for dbCOT: $E(\text{begin}) = -2.30$ V; $E(\text{vertex1}) = -3.20$ V; $E(\text{vertex2}) = -2.30$ V;
- for dbCOT2: $E(\text{begin}) = -2.20$ V; $E(\text{vertex1}) = -2.90$ V; $E(\text{vertex2}) = -2.20$ V;
- for dbCOT3: $E(\text{begin}) = -2.20$ V; $E(\text{vertex1}) = -2.63$; $E(\text{vertex2}) = -2.20$ V;
- for dbCOT5: $E(\text{begin}) = -2.05$ V; $E(\text{vertex1}) = -2.65$; $E(\text{vertex2}) = -2.05$ V.

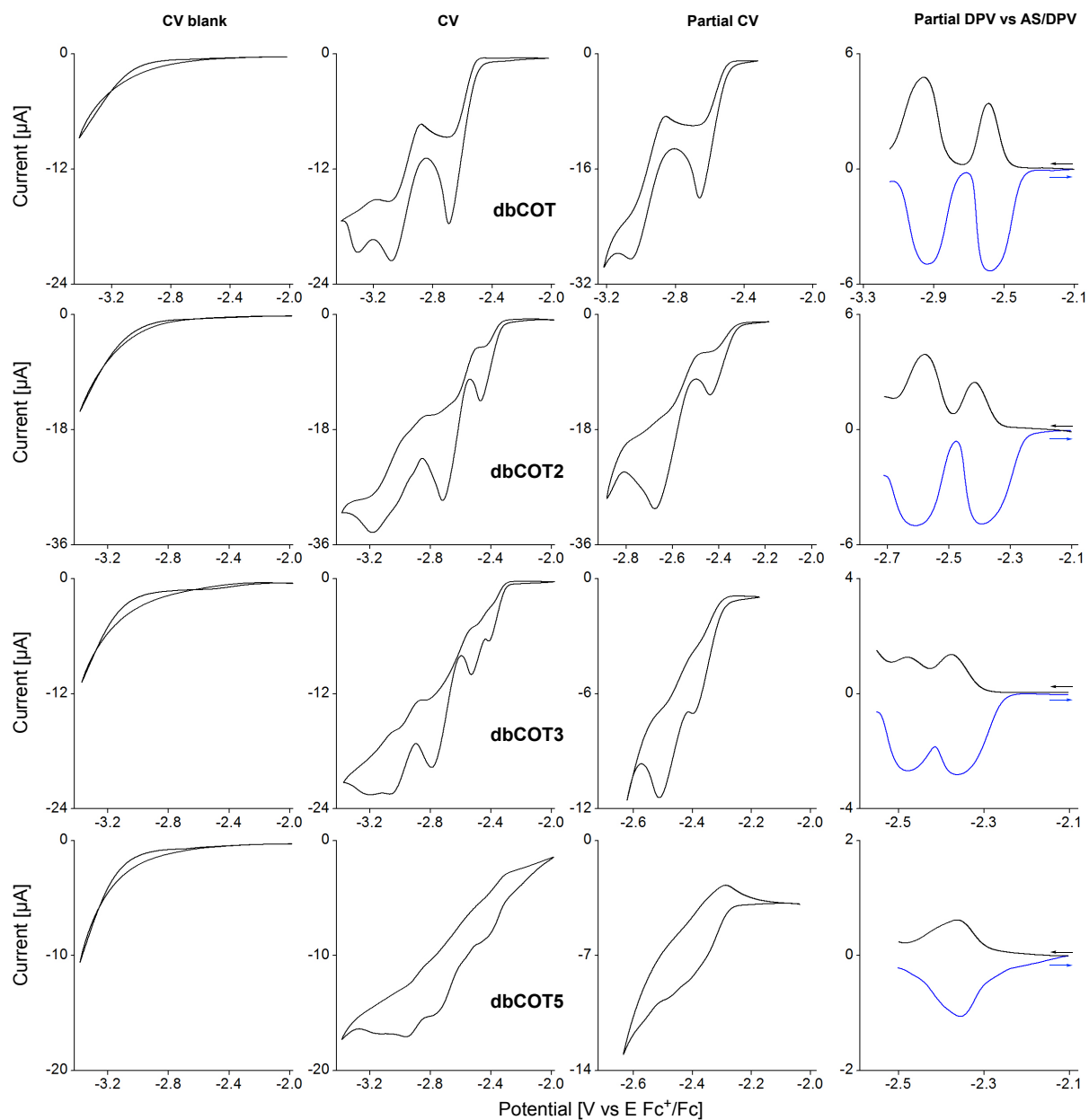
Partial DPV. DPV data was then recorded over the first two redox processes using the following parameters: $E(\text{step}) = 0.005$ V; scan rate = 0.025 V/s; $E(\text{pulse}) = 0.025$ V; $t(\text{pulse}) = 0.07$ s. Potential windows:

- for dbCOT: $E(\text{begin}) = -2.10 \text{ V}$; $E(\text{end}) = -3.15 \text{ V}$;
- for dbCOT2: $E(\text{begin}) = -2.10 \text{ V}$; $E(\text{end}) = -2.70 \text{ V}$;
- for dbCOT3: $E(\text{begin}) = -2.10 \text{ V}$; $E(\text{end}) = -2.55 \text{ V}$;
- for dbCOT5: $E(\text{begin}) = -2.10 \text{ V}$; $E(\text{end}) = -2.50 \text{ V}$.

Partial ASV. After collecting DPV data, electrochemical deposition was performed at $E(\text{begin})$ for 3 s followed by ASV and data was recorded using the following parameters: $E(\text{step}) = 0.005 \text{ V}$; scan rate = 0.025 V/s ; $E(\text{pulse}) = 0.025 \text{ V}$; $t(\text{pulse}) = 0.07 \text{ s}$. Potential windows:

- for dbCOT: $E(\text{begin}) = -3.15 \text{ V}$; $E(\text{end}) = -2.10 \text{ V}$;
- for dbCOT2: $E(\text{begin}) = -2.70 \text{ V}$; $E(\text{end}) = -2.10 \text{ V}$;
- for dbCOT3: $E(\text{begin}) = -2.55 \text{ V}$; $E(\text{end}) = -2.10 \text{ V}$;
- for dbCOT5: $E(\text{begin}) = -2.50 \text{ V}$; $E(\text{end}) = -2.10 \text{ V}$.

Reference to ferrocene. A solution of ferrocene (1.0 mL, 4.0 mM in THF) was added to the cell. CV data was then recorded using the following parameters: $E(\text{begin}) = -0.30 \text{ V}$; $E(\text{vertex1}) = +0.30 \text{ V}$; $E(\text{vertex2}) = -0.30 \text{ V}$; scan rate = 0.025 V/s ; number of scans = 3. DPV data was then recorded from $+0.30 \text{ V}$ to -0.30 V using the following parameters: $E(\text{step}) = 0.005 \text{ V}$; scan rate = 0.025 V/s ; $E(\text{pulse}) = 0.025 \text{ V}$; $t(\text{pulse}) = 0.07 \text{ s}$. Electrochemical deposition was performed at -0.30 V for 3 s followed by ASV and data was recorded from -0.30 V to $+0.30 \text{ V}$ using the following parameters: $E(\text{step}) = 0.005 \text{ V}$; scan rate = 0.025 V/s ; $E(\text{pulse}) = 0.025 \text{ V}$; $t(\text{pulse}) = 0.07 \text{ s}$.



Supplementary Figure 27. Cyclic voltammetry and differential pulse voltammetry characterization of dbCOT, dbCOT2, dbCOT3 and dbCOT5. Several experiments were performed for each and representative datasets are shown.

Supplementary Table 10. CV, DPV, and ASV peak potentials for the first two waves. ^[a]

	Method	Peak potentials (observed) (V)	Integral (μAV)
dbCOT	CV	-2.66, -3.06	0.968, 0.961
	DPV	-2.58, -2.94	
	ASV	-2.59, -2.95	
dbCOT2	CV	-2.44, -2.68	0.710, 1.47
	DPV	-2.40, -2.61	
	ASV	-2.42, -2.58	
dbCOT3	CV	-2.40, -2.51	0.166, 0.170
	DPV	-2.36, -2.48	
	ASV	-2.37, -2.48	
dbCOT5	CV	-2.40, -2.48	Insufficiently resolved.
	DPV	-2.36, -2.39 (partially resolved)	
	ASV	-2.36, br	

[a] Observed peak potentials listed. Potentials are referenced to the ferrocene peak potential (0.00 V). Experimentally, -0.14 V was measured versus the $\text{Ag} | \text{AgNO}_3$ pseudo-reference electrode. Integration was done using the integration function in PStTrace V5.8. The area under the wave is assumed to be proportional to the number of electrons.

XI. Spectroelectrochemical analysis

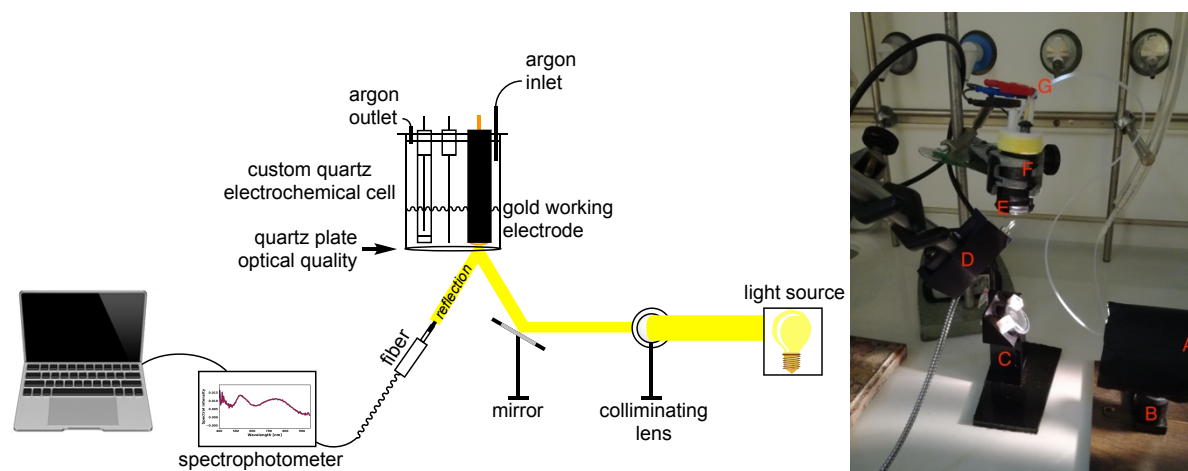
General: Spectroelectrochemical measurements were performed using a Palmsens4 (2018) Palmsens BV and custom-made quartz cells (Herasil®) that were pre-dried at 135 °C overnight and cooled under a stream of argon. Experiments were performed in dry THF (dried to a persistent blue color over sodium-potassium alloy and then vacuum distilled) under an argon atmosphere and at room temperature. The light from an incandescent lamp was collimated by a quartz lens and directed with a UV/enhanced aluminum mirror onto the polished working electrode (see Section *General*, Section X, for polishing procedure). The specular reflection from the gold working electrode was collected with a broadband hollow-core fiber and guided into an Avantes BV AvaSpec-3648 spectrophotometer. In this configuration, absorbance changes are recorded in reflective mode with the beam passing twice through the thin interaction region

at the gold working electrode (Supplementary Figure 28). The bottom of the custom-made quartz cell was made from a flat quartz plate with optical quality.

Working electrode: Polycrystalline gold disc ($d = 2$ mm) from Palmsens BV (ItalSens).

Reference electrode: Silver wire pseudo-reference immersed in THF containing Bu_4NPF_6 (0.10 M) and AgNO_3 (sat.).

Counter electrode: Platinum wire.



Supplementary Figure 28. Left: Schematic representation of the spectroelectrochemical setup; Right: Photograph of a typical experiment setup: A - light source; B - collimating lens; C – mirror; D - fiber connected to the spectrophotometer; E - gold working electrode; F - quartz electrochemical cell; G - argon inlet.

Representative procedure for spectroelectrochemical measurements. To an electrochemical cell was added a freshly prepared solution of Bu_4NPF_6 (0.10 M) in THF (2.0 mL). Prior to each data collection, the cell was conditioned by four cycles of cyclic voltammetry (CV) at 0.40 V/s from 0.40 V to -3.00 V. The mixture was then gently vortexed and another four CV cycles were performed. The light source and spectrophotometer were aligned and a blank UV-Vis spectrum recorded, after which the optical system was not altered. Appropriate scan widths were estimated from Supplementary Table 10.

CV blank. CV data was recorded using the following parameters: $E(\text{begin}) = -2.00$ V; $E(\text{vertex1}) = -3.40$ V; $E(\text{vertex2}) = -2.00$ V; scan rate = 0.025 V/s; number of scans = 4.

CV. A solution of dbCOT2 (1.0 mL, 4.0 mM in THF), dbCOT3 (1.0 mL, 3.0 mM in THF), or dbCOT5 (1.0 mL, 1.8 mM in THF) was added to the cell. The series of CV data was then recorded using the following parameters: scan rate = 0.025 V/s; number of scans = various.

During the CV measurements, the UV-Vis spectra was recorded in the reflective mode every 200 ms.

dbCOT2, scanning over the first two peaks: $E(\text{begin}) = -2.30 \text{ V}$; $E(\text{vertex1}) = -3.00 \text{ V}$; $E(\text{vertex2}) = -2.30 \text{ V}$.

dbCOT3, scanning over the first two peaks: $E(\text{begin}) = -2.20 \text{ V}$; $E(\text{vertex1}) = -2.80$; $E(\text{vertex2}) = -2.20 \text{ V}$.

dbCOT5, scanning over the first two peaks: $E(\text{begin}) = -2.25 \text{ V}$; $E(\text{vertex1}) = -2.65 \text{ V}$; $E(\text{vertex2}) = -2.25 \text{ V}$.

Reference to ferrocene. After the respective cycling experiment, a solution of ferrocene (1.0 mL, 4.0 mM in THF) was added to the cell. CV data was then recorded using the following parameters: $E(\text{begin}) = -0.30 \text{ V}$; $E(\text{vertex1}) = +0.30 \text{ V}$; $E(\text{vertex2}) = -0.30 \text{ V}$; scan rate = 0.025 V/s; number of scans = 3.

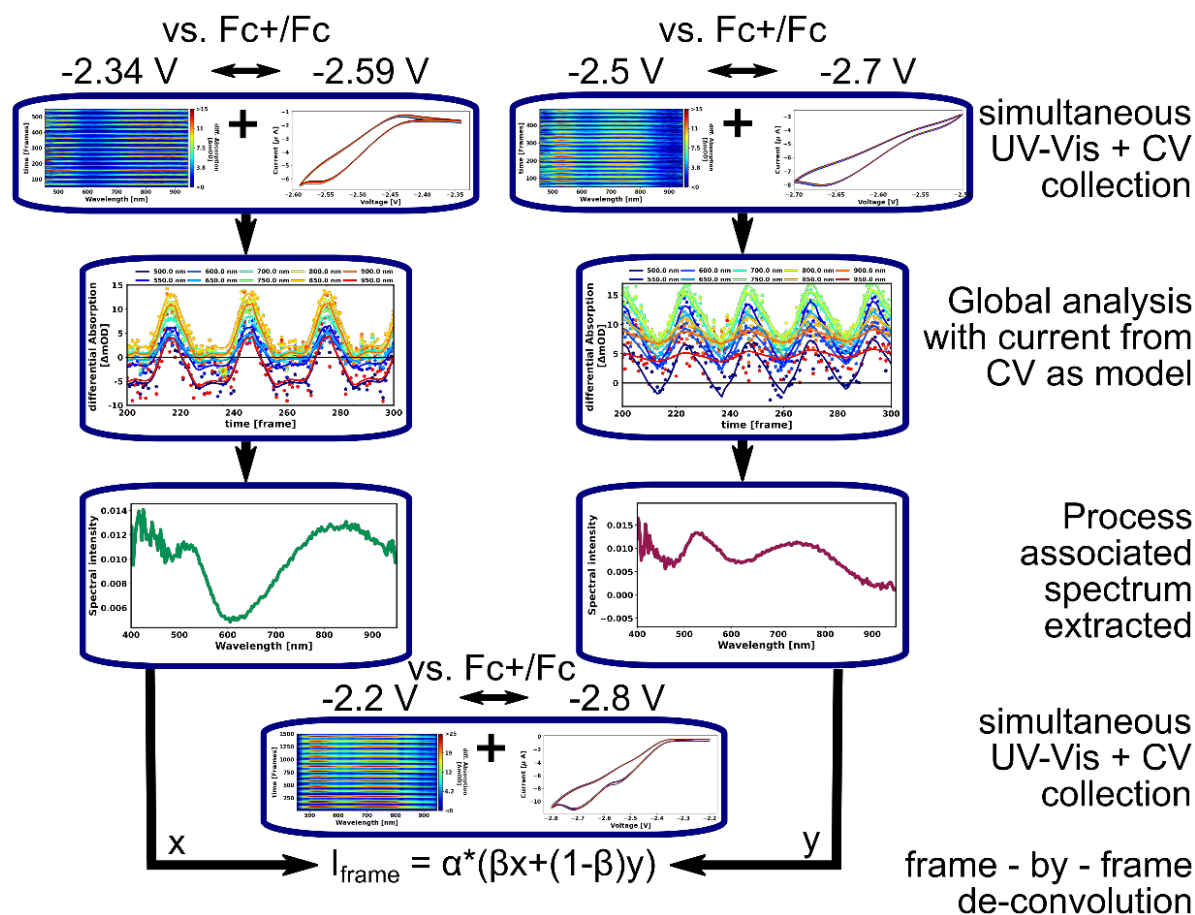
Data processing procedure for spectroelectrochemical measurements. After the respective measurement, both the electrochemical data and the collected absorbance frames were exported as asci-files for further processing in a custom developed python analysis package. The two datasets were correlated by relating the repeated pattern of the CV data to the repeating pattern of the optical variations as outlined below. The correlation requires only small adjustments. Typically, accumulation of the optical spectra was started a few seconds before the start of the first CV cycle and ended a few seconds after the finish of the last. The start and end time/points, as well as the actual time-period between each collected spectral frame were then adjusted to overlap both experiments. These three parameters were initially set manually and then optimized during a Global analysis outlined below and in Supplementary Figure 29.

The optical spectra were assembled into a 2D matrix with wavelength and frames as the axes. For Figure 4A-C, the spectral axis was re-binned into 10 nm bins, background-subtracted, and presented in the heat map. Selected spectral slices of 20 nm width are shown in the middle panel to emphasize the correlation to the CV data. The y-axis of the measured CV current in the left panel is adjusted to compensate for the difference in start and stop time of the measurements. A typical mismatch between the measurements is of the order of 2 s at the beginning and end for a typical total accumulation time of 500 s. The extracted spectrum above the heat map was generated by taking the mean of all spectra, in which the maximum observed difference spectrum reached 2/3 of the overall observed maximum change.

For de-convolution of the two components in Figure 4D, we followed the workflow illustrated in Supplementary Figure 29. First, the measurement for dbCOT3 was separated into two intervals. After each of the two measurements, a model was formed consisting of a modulating species and a background.

The modulating species was gained by using the integrated current of the CV curve (compensated for a linear ohmic fraction) and convoluting this current with an exponential decay. The concentration of the main component is thus the currently converted fraction of the molecules (the measured current). The experimentally found decay parameters are of the order of 1-2 frames (approximately 200 ms). The scale of the CV measurements and the measured spectral frames were correlated by estimating the different start and endpoints as well as the correlation between the measured CV data points, frames, and refining the parameter in a Global analysis scheme similar to transient optical absorption.^{7,8} In Global analysis, a parameter-based model, here created by shifting the time parameters of the measured current versus the frames of the spectra, is compared against the measured data and an optimum spectrum is extracted for each step of the optimization. The modeled matrix is then compared against the measured matrix and the parameters are chosen to minimize the difference. The extracted spectra represent the spectra associated with the process. As we measured the difference spectra while reducing and oxidizing dbCOT3 during the CV and used as the model a number representing the total amount of converted molecules (the measured current), the extracted spectrum represents the species formed during oxidation and reduction. Here the spectrum for the first and second reduction step, respectively, for the two voltage regions in which the scan was performed.

In a third and independent measurement, we again collected a CV with simultaneous UV-vis spectra over a wider range, encompassing both reduction steps. In the following analysis, we optimized each measured spectrum with a linear combination from the two spectra representing the first and second reduction steps. In this optimization, $\alpha\beta$ are fit-factors while the spectra denoted x and y are fixed. The pre-factor α is allowed to vary between 0 and 10, the ratio β are fit-factors and are allowed to vary between 0 and 1. The fractions presented in Figure 4D are the factors $\alpha\beta$ and $\alpha(1-\beta)$ respectively, representing the fractions of the first and second reduced spectra in the measured spectrum. As the total factor (α) was not limited to 1 a total fraction > 1 would have been possible but was not observed. This suggests that the combination of mass-transport and conversion ratio is comparable between the three independent experiments.



Supplementary Figure 29. Flow chart illustration the analysis procedure. Three independent data-sets are recorded. Two are modelled with Global analysis to extract Process associated spectra. The third data-set is then deconvoluted using these process associated spectra.

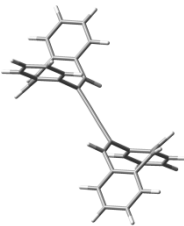
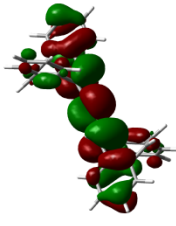
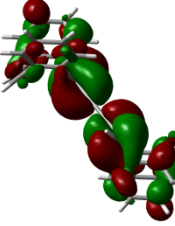
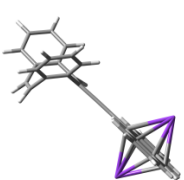
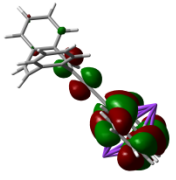
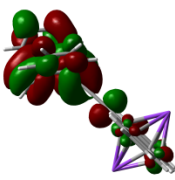
XII. Density functional theory calculations

Density functional theory (DFT) calculations were carried out using the standard B3LYP hybrid functional method⁹ together with standard 6-311+G(d,p) all-electron split-valence plus polarization functions basis sets¹⁰ and employing a polarizable continuum model (PCM) representation for a THF solvent environment throughout.¹¹ Subsequent frequency calculations were performed to validate the optimizations and provide free energies.

With formal full reduction/oxidation assignments, the investigated species can be described as K⁺_{2m}dbCOTn^{2m-} THF (PCM), where m corresponds to the specific number of 2e⁻/2K⁺ reductions, and n the number of dbCOT units in the oligomer. The pairs of explicit K⁺ counter ions included per doubly reduced dbCOT unit were in all cases located with one ion on each side of the plane of the dbCOT central ring. This was consistent with suggestions from initial testing

to identify suitable starting geometries. The optimized molecular species (neutral and reduced) were subsequently used to assess calculated structural parameters and to provide information about the calculated electronic structure properties at the same level of theory. All neutral and step-by-step doubly reduced dbCOT dimers (dbCOT2) and trimers (dbCOT3) structures with associated total energies and HOMO and LUMO orbitals from the B3LYP/6-311+G(d,p) calculations are presented in Supplementary Table 11. Optimized xyz-coordinates are listed as further supplementary information in the separate coordinate file. The quantum chemical calculations were performed using the Gaussian16¹² program.

Supplementary Table 11. Selected geometry optimizations and electronic structure calculations of dbCOT dimers and trimers in different reduction states from B3LYP/6-311+G(d,p) calculations with a self-consistent reaction field polarizable continuum model of the THF solvent. Energies in Hartree (H) and molecular orbitals displayed using a standard 0.02 isovalue.

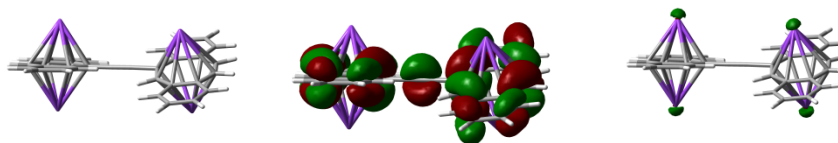
Description	Optimized geometry	HOMO	LUMO
dbCOT2			
Neutral dbCOT dimer.			
$E_{\text{tot}} = -1309.081330 \text{ H}$			
$G_{\text{tot}} = -1308.697892 \text{ H}$			
K₂dbCOT2			
Doubly reduced dbCOT dimer with potassium counter ions.			
$E_{\text{tot}} = -2509.052755 \text{ H}$			
$G_{\text{tot}} = -2508.678991 \text{ H}$			

K₄dbCOT2

Fully (four-fold) reduced
dbCOT dimer with potas-
sium counter ions.

$$E_{\text{tot}} = -3709.010668 \text{ H}$$

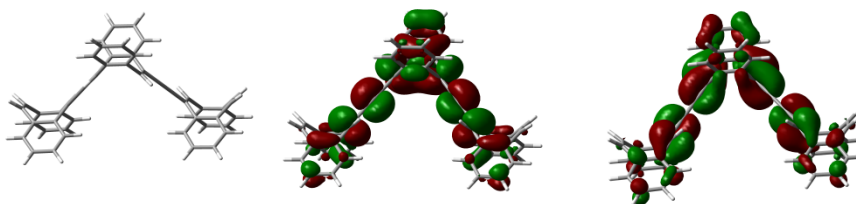
$$G_{\text{tot}} = -3708.643868 \text{ H}$$

**dbCOT3**

Neutral dbCOT trimer.

$$E_{\text{tot}} = -2001.109397 \text{ H}$$

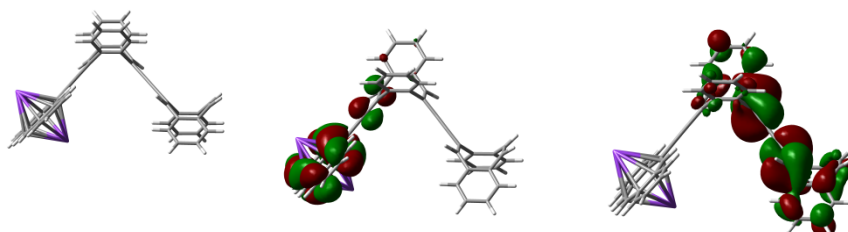
$$G_{\text{tot}} = -2000.530297 \text{ H}$$

**K₂dbCOT3(t)**

Doubly reduced dbCOT
trimer with potassium
counter ions on terminal
unit.

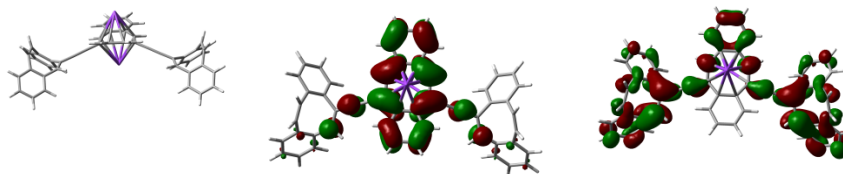
$$E_{\text{tot}} = -3201.081401 \text{ H}$$

$$G_{\text{tot}} = -3200.510903 \text{ H}$$



K₂dbCOT3(c)

Doubly reduced dbCOT trimer with potassium counter ions on central unit

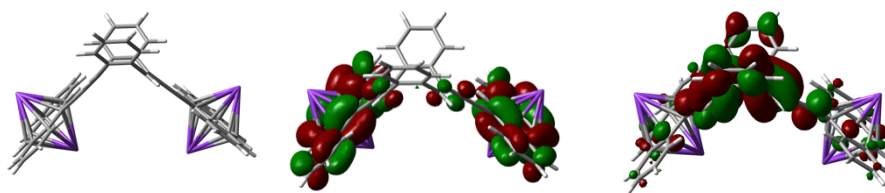


$$E_{\text{tot}} = -3201.078019 \text{ H}$$

$$G_{\text{tot}} = -3200.510564 \text{ H}$$

K₄dbCOT3

Fourfold reduced dbCOT trimer with potassium ions on the terminal units

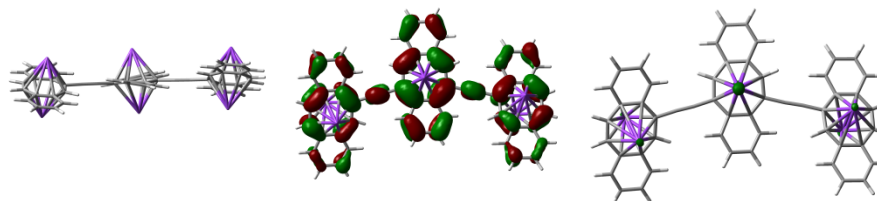


$$E_{\text{tot}} = -4401.05136998$$

$$G_{\text{tot}} = -4400.488721$$

K₆dbCOT3

Fully (six-fold) reduced dbCOT trimer with potassium counter ions

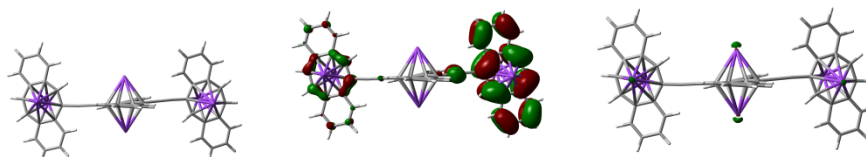


$$E_{\text{tot}} = -5600.994640 \text{ H}$$

$$G_{\text{tot}} = -5600.441630 \text{ H}$$

K₆dbCOT3(twist)

Fully (six-fold) reduced dbCOT trimer with potassium counter ions. Twisted dihedrals frozen in constrained optimization.



$$E_{\text{tot}} = -5600.992958 \text{ H}$$

Coordinates for optimized geometries:

dbcot_gs_b3lyp_6311+Gdp_thf_opt (ID: tetralith_16694860)

28

scf done: -617.053647

C	0.383916	-0.224942	-0.046566
C	1.772367	-0.388138	0.128152
C	0.923739	2.097669	-2.167818
C	2.731671	0.736854	0.210063
C	2.312213	1.934566	-1.993109
C	2.958119	1.710987	-0.679526
C	-0.440847	-1.363070	-0.018963
H	-1.512711	-1.232996	-0.126110
C	2.283033	-1.683182	0.323918
H	3.349031	-1.804326	0.485990
C	0.083311	-2.640091	0.139850
H	-0.575886	-3.500696	0.144027
C	1.458722	-2.801727	0.313008
H	1.882447	-3.789579	0.453700
H	3.393430	0.701129	1.073208
H	3.784941	2.385101	-0.464826
C	0.432627	2.394983	-3.451046
H	-0.633992	2.547727	-3.578630
C	3.156553	2.074859	-3.108316
H	4.227794	1.976158	-2.966960
C	1.276924	2.495274	-4.550074
H	0.868346	2.712813	-5.530352
C	2.652358	2.333512	-4.377037
H	3.326628	2.423597	-5.221103
C	-0.283356	1.091263	-0.169191
C	-0.056996	2.065357	-1.058862
H	-1.126212	1.232191	0.504554
H	-0.734722	2.916368	-1.033441

dbcot_red2_k2_b3lyp_6311+Gdp_thf (ID: tetralith_16694739)

30

scf done: -1817.024425

C	-1.803465	-0.737191	0.000882
C	-1.806819	0.728833	-0.010551
C	1.806885	-0.728860	0.010465
C	-0.710526	1.639585	-0.014752
C	1.803531	0.737165	-0.000964
C	0.703082	1.642846	-0.010992
C	-3.099331	-1.379889	0.002488
H	-3.100853	-2.467118	0.010964
C	-3.105611	1.365543	-0.018953
H	-3.112106	2.452754	-0.027442
C	-4.299153	-0.723607	-0.005802
H	-5.230399	-1.280663	-0.003898
C	-4.302418	0.703730	-0.016949
H	-5.236203	1.256482	-0.023732

H	-1.075119	2.664922	-0.023832
H	1.062983	2.669856	-0.018035
C	3.105677	-1.365570	0.018878
H	3.112172	-2.452780	0.027362
C	3.099397	1.379863	-0.002552
H	3.100919	2.467091	-0.011025
C	4.302484	-0.703757	0.016889
H	5.236269	-1.256508	0.023679
C	4.299219	0.723581	0.005747
H	5.230465	1.280636	0.003856
C	-0.703016	-1.642872	0.010903
C	0.710591	-1.639611	0.014658
H	1.075184	-2.664948	0.023736
H	-1.062917	-2.669882	0.017950
K	-0.006546	0.019575	2.462246
K	0.006661	-0.019556	-2.462340

dbcot2_gs_b3lyp_6311+Gdp_thf (ID: tetralith_16694810)

56

scf done: -1309.081330

C	4.188248	1.299239	0.199479
C	5.107065	0.740422	-0.713423
C	2.625139	-1.406656	0.286367
C	4.711837	-0.111268	-1.858859
C	3.524830	-1.972546	-0.633547
C	4.030936	-1.262983	-1.830251
C	4.663716	2.171591	1.194963
H	3.951415	2.623555	1.877019
C	6.467002	1.072744	-0.592525
H	7.169495	0.664451	-1.311499
C	6.016658	2.459079	1.323092
H	6.358004	3.122234	2.109702
C	6.926485	1.904896	0.421063
H	7.983524	2.132525	0.498359
H	5.103826	0.209508	-2.821698
H	3.917027	-1.798873	-2.769993
C	2.196043	-2.169350	1.383544
H	1.490074	-1.733485	2.081531
C	3.945634	-3.299636	-0.438339
H	4.618665	-3.745732	-1.162911
C	2.652317	-3.466381	1.584491
H	2.315838	-4.031688	2.446035
C	3.528668	-4.038947	0.661352
H	3.879109	-5.056031	0.795353
C	2.727643	1.114551	0.097191
C	2.028688	-0.042188	0.107744
H	2.148951	2.034619	0.071554
C	0.605793	0.000007	0.034366
C	-0.605673	0.000418	-0.033959
C	-2.727420	-1.114328	-0.096341
C	-4.663226	-2.172210	-1.193750
C	-5.106975	-0.740182	0.713902

C	-6.016101	-2.460021	-1.321842
H	-3.950791	-2.624369	-1.875537
C	-6.466840	-1.072847	0.593072
C	-6.926095	-1.905580	-0.420136
H	-6.357257	-3.123619	-2.108160
H	-7.169464	-0.664352	1.311803
H	-7.983085	-2.133458	-0.497372
C	-2.028591	0.042500	-0.107376
C	-4.712010	0.112144	1.858933
H	-5.104069	-0.208203	2.821890
C	-4.031233	1.263921	1.829846
H	-3.917465	1.800272	2.769337
C	-4.187987	-1.299280	-0.198660
C	-2.625217	1.406775	-0.286683
C	-2.196100	2.169004	-1.384184
C	-3.525146	1.972967	0.632809
C	-2.652611	3.465841	-1.585860
H	-1.489941	1.732926	-2.081844
C	-3.946213	3.299854	0.436851
C	-3.529233	4.038689	-0.663161
H	-2.316106	4.030790	-2.447629
H	-4.619445	3.746185	1.161091
H	-3.879876	5.055627	-0.797747
H	-2.148600	-2.034312	-0.070286

dbcot2_red2_k2_b3lyp_6311+Gdp_thf (ID: tetralith_16694839)

58

scf done: -2509.052755

C	-3.526002	4.047761	-0.514199
C	-2.766039	3.403776	-1.492060
C	-2.469119	2.053387	-1.351395
C	-2.944082	1.307058	-0.261079
C	-3.733164	1.947921	0.709785
C	-3.990794	3.323959	0.576634
C	-2.506958	-0.126637	-0.151541
C	-3.360730	-1.183412	-0.167871
C	-4.833630	-1.177553	-0.219648
C	-5.456165	-1.956733	-1.214751
C	-6.837456	-2.077624	-1.295898
C	-7.642581	-1.438646	-0.350735
C	-7.046043	-0.696151	0.661298
C	-5.651543	-0.539458	0.740673
C	-5.119809	0.210195	1.901713
C	-4.291410	1.261354	1.896496
C	-1.102058	-0.317546	-0.127822
C	0.110863	-0.455678	-0.089384
C	1.533185	-0.531998	-0.039762
C	2.063882	0.814424	-0.070949
C	3.265688	1.560854	-0.042887
C	4.657873	1.128736	0.053649
C	5.670784	2.156970	0.061881
C	5.417792	3.497919	-0.013458

C	4.059376	3.928771	-0.106425
C	3.060921	2.999106	-0.118537
C	5.163881	-0.195447	0.145977
C	4.698714	-1.516658	0.172882
C	3.486633	-2.284823	0.123146
C	2.086521	-1.878469	0.027238
C	1.126510	-2.955446	-0.004403
C	1.431417	-4.289987	0.049707
C	2.789776	-4.683702	0.146968
C	3.745013	-3.705921	0.180751
H	2.032038	3.340865	-0.188595
H	6.702175	1.821426	0.133782
H	3.819248	4.985409	-0.166590
H	6.229888	4.216643	-0.002177
H	6.249940	-0.186056	0.213034
H	5.548554	-2.189323	0.253605
H	0.083540	-2.681416	-0.078361
H	4.786545	-4.004405	0.254918
H	0.637187	-5.028484	0.018189
H	3.070422	-5.730510	0.193796
H	1.225666	1.499656	-0.136423
H	-4.830273	-2.470881	-1.936773
H	-7.284038	-2.674498	-2.083397
H	-7.666792	-0.224771	1.416506
H	-8.721829	-1.532042	-0.393276
H	-5.525968	-0.094224	2.864442
H	-4.082439	1.737986	2.852011
H	-1.850584	1.558148	-2.091270
H	-2.395500	3.953864	-2.349800
H	-4.576389	3.821794	1.342647
H	-3.750603	5.104958	-0.600231
H	-2.909055	-2.171328	-0.217786
K	3.477424	-0.445453	-2.464221
K	3.188934	-0.230054	2.559263

dbcot2_red4_k4_b3lyp_6311+Gdp_thf (ID: tetralith_16694939)

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scf done: -3709.010668

C	2.743042	-4.619874	-0.783228
C	1.441595	-4.051474	-0.732711
C	1.309314	-2.709822	-0.494875
C	2.399657	-1.782377	-0.280774
C	3.745176	-2.369427	-0.348812
C	3.815806	-3.793044	-0.598348
C	2.012938	-0.408554	-0.028290
C	2.705862	0.825227	0.238519
C	3.996418	1.406826	0.367529
C	3.966457	2.831244	0.645311
C	5.069946	3.621128	0.805239
C	6.366638	3.033583	0.699818
C	6.457294	1.693549	0.443360
C	5.327759	0.810722	0.266952

C	5.671349	-0.545068	0.019456
C	5.042930	-1.781127	-0.214502
C	0.590933	-0.150134	-0.036014
C	-0.590908	0.150287	-0.036053
C	-2.012924	0.408621	-0.028359
C	-2.705814	-0.825220	0.238251
C	-3.996356	-1.406874	0.367146
C	-5.327718	-0.810815	0.266550
C	-6.457226	-1.693705	0.442823
C	-6.366531	-3.033756	0.699180
C	-5.069821	-3.621256	0.804624
C	-3.966357	-2.831314	0.644815
C	-5.671358	0.544984	0.019167
C	-5.042972	1.781097	-0.214589
C	-3.745228	2.369469	-0.348693
C	-2.399690	1.782461	-0.280667
C	-1.309366	2.709969	-0.494584
C	-1.441679	4.051658	-0.732192
C	-2.743141	4.620029	-0.782650
C	-3.815889	3.793133	-0.597966
H	-2.984347	-3.289760	0.725096
H	-7.442739	-1.241388	0.363746
H	-4.957431	-4.681411	1.007483
H	-7.261360	-3.635045	0.820352
H	-6.752179	0.672273	0.010674
H	-5.804616	2.547285	-0.337123
H	-0.310074	2.298188	-0.459889
H	-4.812221	4.224412	-0.640428
H	-0.558996	4.666239	-0.877610
H	-2.888186	5.679765	-0.964890
H	-1.960976	-1.599652	0.386957
H	2.984461	3.289722	0.725575
H	4.957590	4.681272	1.008174
H	7.442793	1.241197	0.364303
H	7.261484	3.634827	0.821088
H	6.752165	-0.672409	0.011039
H	5.804553	-2.547331	-0.337069
H	0.310032	-2.298024	-0.460137
H	0.558899	-4.666005	-0.878260
H	4.812128	-4.224345	-0.640845
H	2.888062	-5.679580	-0.965659
H	1.961042	1.599664	0.387287
K	-3.887378	0.003875	-2.430312
K	-3.787523	0.947545	2.438501
K	3.887542	-0.003613	-2.430088
K	3.787311	-0.947848	2.438612

dbcot3_gs_b3lyp_6311+Gdp_thf (ID: tetralith_15602373)

84

scf done: -2001.109397

C	6.186830	-2.952322	-0.742421
C	4.777068	-2.921452	-0.780778

C	6.175029	-0.617116	1.360201
C	3.992949	-1.672639	-0.837037
C	4.769837	-0.608142	1.323666
C	3.988089	-0.648052	0.044409
C	6.837459	-4.196166	-0.806425
H	7.922182	-4.218166	-0.804468
C	4.072591	-4.134156	-0.886215
H	2.989781	-4.105734	-0.945816
C	6.126148	-5.388174	-0.870356
H	6.654883	-6.333893	-0.904520
C	4.731165	-5.356908	-0.910491
H	4.162940	-6.277695	-0.976063
H	3.289618	-1.608845	-1.663648
C	6.819730	-0.466665	2.600382
H	7.904137	-0.446517	2.626012
C	4.053466	-0.477876	2.523447
H	2.970024	-0.456451	2.487991
C	6.100382	-0.356358	3.783674
H	6.622667	-0.254875	4.728208
C	4.705268	-0.369913	3.745875
H	4.130142	-0.282238	4.660513
C	7.034731	-1.737956	-0.732589
C	7.027316	-0.736982	0.155619
H	7.806918	-1.715398	-1.498651
H	7.793077	0.028485	0.050989
C	3.117551	0.458650	-0.177003
C	2.390543	1.416599	-0.338104
C	1.513065	2.516464	-0.557765
C	0.701214	2.468206	-1.816605
C	1.515782	3.564353	0.295822
C	-0.701306	2.468251	-1.816566
C	1.384953	2.384518	-3.039353
C	0.706303	4.795915	0.211499
H	2.234055	3.535898	1.111328
C	-1.385108	2.384612	-3.039286
C	-1.513111	2.516548	-0.557694
H	2.469009	2.368304	-3.034574
C	0.697750	2.324687	-4.245293
C	-0.706221	4.795961	0.211531
C	1.384436	6.026674	0.250028
H	-2.469165	2.368469	-3.034453
C	-0.697967	2.324738	-4.245259
C	-1.515764	3.564447	0.295883
H	1.246255	2.272244	-5.178790
C	-1.384272	6.026764	0.250097
H	2.468770	6.024748	0.280117
C	0.698123	7.234562	0.245932
H	-1.246520	2.272334	-5.178730
H	-2.234018	3.536032	1.111407
H	-2.468605	6.024908	0.280237
C	-0.697880	7.234607	0.245967
H	1.246641	8.169393	0.259015

H	-1.246338	8.169473	0.259077
C	-2.390613	1.416709	-0.337999
C	-3.117607	0.458747	-0.176943
C	-3.988137	-0.647966	0.044447
C	-4.769888	-0.608116	1.323700
C	-3.992971	-1.672536	-0.837023
C	-6.175078	-0.617192	1.360220
C	-4.053534	-0.477811	2.523486
C	-4.777032	-2.921391	-0.780784
H	-3.289649	-1.608701	-1.663638
C	-6.819802	-0.466828	2.600402
C	-7.027357	-0.737061	0.155629
H	-2.970093	-0.456296	2.488035
C	-4.705353	-0.369922	3.745911
C	-6.186793	-2.952338	-0.742466
C	-4.072486	-4.134057	-0.886214
H	-7.904211	-0.446767	2.626025
C	-6.100470	-0.356489	3.783700
C	-7.034748	-1.738013	-0.732604
H	-7.793137	0.028391	0.051021
H	-4.130241	-0.282212	4.660554
C	-6.837353	-4.196215	-0.806523
H	-2.989675	-4.105575	-0.945779
C	-4.730995	-5.356843	-0.910539
H	-6.622768	-0.255073	4.728234
H	-7.806942	-1.715463	-1.498659
H	-7.922076	-4.218272	-0.804601
C	-6.125978	-5.388183	-0.870458
H	-4.162719	-6.277599	-0.976106
H	-6.654661	-6.333930	-0.904662

 dbcot3_red2_k2c_b3lyp_6311+Gdp_thf (ID: tetralith_15604809)

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scf done: -3201.078019

C	-9.113069	4.374748	-0.831381
C	-9.199035	3.265750	0.001692
C	-8.087265	2.445462	0.259819
C	-6.841846	2.774274	-0.323337
C	-6.767498	3.925204	-1.132994
C	-7.882406	4.708797	-1.400574
C	-5.585987	2.060241	-0.035102
C	-5.307200	0.737224	-0.180647
C	-6.260859	-0.261473	-0.773707
C	-7.484872	-0.606792	-0.175273
C	-8.253164	-1.638068	-0.744121
C	-7.853834	-2.284768	-1.906959
C	-6.652040	-1.920909	-2.516641
C	-5.863457	-0.931245	-1.941961
C	-8.007447	0.037110	1.050808
C	-8.274841	1.336980	1.223673
C	-4.026361	0.222488	0.136364
C	-2.932060	-0.234604	0.433069

C	-1.660038	-0.799478	0.716660
C	-1.638087	-2.190030	0.379078
C	-0.738592	-3.269025	0.272806
C	0.726186	-3.256317	0.226174
C	1.374535	-4.533848	-0.014516
C	0.717798	-5.718393	-0.164464
C	-0.712964	-5.732075	-0.109709
C	-1.379024	-4.559725	0.086520
C	1.615579	-2.165051	0.297648
C	1.647085	-0.784909	0.675325
C	0.722284	0.102307	1.394655
C	-0.724730	0.099173	1.407715
C	-1.360405	1.130535	2.175556
C	-0.697285	2.097576	2.892219
C	0.711004	2.097687	2.883971
C	1.366520	1.132620	2.157917
C	2.918440	-0.218439	0.389889
C	4.013122	0.239120	0.096161
C	5.298634	0.749133	-0.209862
C	6.246866	-0.249362	-0.812027
C	7.462958	-0.616042	-0.210174
C	8.224237	-1.647341	-0.788382
C	7.826286	-2.272945	-1.963173
C	6.632840	-1.887460	-2.575986
C	5.850608	-0.897805	-1.992598
C	7.983932	0.005254	1.028029
C	8.261037	1.300170	1.222106
C	8.089637	2.425047	0.274363
C	6.851644	2.774183	-0.312762
C	6.793597	3.938063	-1.105002
C	7.917437	4.715489	-1.352354
C	9.140747	4.361621	-0.779290
C	9.210585	3.239199	0.037094
C	5.587348	2.067451	-0.044126
H	10.151733	2.980054	0.511384
H	5.838866	4.225335	-1.533233
H	10.025243	4.963853	-0.953288
H	7.839448	5.597510	-1.978296
H	4.765319	2.708081	0.265944
H	9.148427	-1.947460	-0.305382
H	4.907576	-0.618456	-2.448742
H	8.438742	-3.055805	-2.396190
H	6.308340	-2.364621	-3.493960
H	8.748999	1.565655	2.158016
H	8.265600	-0.690018	1.816075
H	2.614538	-2.474547	0.003692
H	2.448297	1.136721	2.167090
H	-2.442037	1.131040	2.200159
H	1.276205	2.831652	3.448399
H	2.459573	-4.525289	-0.067026
H	-1.256129	2.830948	3.463664
H	-2.647530	-2.514906	0.142337

H	-2.464977	-4.570917	0.112353
H	1.271993	-6.635752	-0.331336
H	-1.260517	-6.660103	-0.234260
H	-4.760272	2.698223	0.270649
H	-4.914567	-0.668246	-2.395632
H	-9.183802	-1.921409	-0.263393
H	-8.298746	-0.644050	1.847627
H	-6.326221	-2.414702	-3.425309
H	-5.807119	4.197351	-1.558478
H	-8.471656	-3.067183	-2.333094
H	-8.765631	1.621074	2.152598
H	-10.145930	3.022355	0.472886
H	-7.791824	5.580321	-2.039402
H	-9.990786	4.982064	-1.021311
K	-0.083961	-1.027085	-1.994492
K	0.120769	-2.416051	3.142509

dbcot3_red2_k2t_b3lyp_6311+Gdp_thf (ID: tetralith_16694030)

86

scf done: -3201.081401

C	-5.958928	-5.709692	-0.507406
C	-6.768704	-4.584733	-0.605734
C	-6.229370	-3.287213	-0.618797
C	-4.828063	-3.134062	-0.565867
C	-4.020441	-4.284098	-0.507567
C	-4.572139	-5.557972	-0.458267
C	-4.147718	-1.830233	-0.688937
C	-4.292682	-0.734465	0.089169
C	-5.168757	-0.651154	1.303757
C	-6.567130	-0.782792	1.247072
C	-7.313334	-0.580602	2.421254
C	-6.696633	-0.300666	3.634118
C	-5.306353	-0.191394	3.691044
C	-4.558096	-0.349267	2.530874
C	-7.314156	-1.084394	0.004998
C	-7.172725	-2.157154	-0.782341
C	-3.504007	0.422363	-0.177653
C	-2.850860	1.424883	-0.380183
C	-2.060230	2.578476	-0.649667
C	-2.217656	3.693922	0.097380
C	-1.518453	4.984787	-0.046485
C	-0.111525	5.118710	0.035428
C	0.434315	6.417144	0.023762
C	-0.361694	7.547873	-0.105423
C	-1.748855	7.410638	-0.193328
C	-2.312102	6.141811	-0.142614
C	0.807256	3.989702	0.264274
C	0.958768	2.864604	-0.483327
C	0.224693	2.641717	-1.774114
C	-1.168497	2.501407	-1.851280
C	-1.767092	2.251716	-3.096547
C	-1.007723	2.166654	-4.256638

C	0.378713	2.311361	-4.183118
C	0.982178	2.534968	-2.951785
C	1.912747	1.872131	-0.151521
C	2.720150	0.996052	0.118227
C	3.640134	-0.064123	0.359523
C	4.441558	0.064482	1.570255
C	5.469845	-0.837750	2.082049
C	6.114241	-0.449850	3.316494
C	5.832124	0.680595	4.032405
C	4.829526	1.552956	3.539483
C	4.186870	1.237218	2.371426
C	5.982118	-2.080657	1.577009
C	5.829971	-2.981027	0.514782
C	5.057895	-3.141030	-0.666911
C	4.027211	-2.254269	-1.200873
C	3.406704	-2.692221	-2.441738
C	3.724417	-3.839958	-3.107444
C	4.734547	-4.700499	-2.579527
C	5.351858	-4.340156	-1.414621
C	3.519424	-1.026209	-0.715562
H	6.121455	-4.990197	-1.006350
H	2.636112	-2.047125	-2.854430
H	5.005796	-5.618288	-3.089659
H	3.211574	-4.093165	-4.029738
H	2.755389	-0.667552	-1.396611
H	6.880683	-1.120987	3.692650
H	3.425623	1.918014	2.017438
H	6.363875	0.897261	4.952756
H	4.567223	2.460124	4.073676
H	6.518018	-3.815018	0.637828
H	6.751553	-2.452431	2.248493
H	1.491095	4.118809	1.099602
H	2.060114	2.630116	-2.887785
H	-2.843109	2.126745	-3.145882
H	0.985196	2.243876	-5.079345
H	1.509883	6.526817	0.114918
H	-1.491718	1.985006	-5.209554
H	-2.987681	3.667313	0.864751
H	-3.391128	6.032300	-0.176272
H	0.094027	8.531566	-0.125958
H	-2.384038	8.284488	-0.282921
H	-3.393054	-1.777946	-1.469843
H	-3.480879	-0.231159	2.565592
H	-8.394520	-0.655302	2.371795
H	-8.129919	-0.401877	-0.223027
H	-4.810903	0.030747	4.629262
H	-2.942211	-4.164702	-0.499070
H	-7.294939	-0.162007	4.527449
H	-7.884160	-2.271695	-1.597433
H	-7.845065	-4.702762	-0.673694
H	-3.926646	-6.426794	-0.398359
H	-6.403874	-6.697959	-0.485700

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K      2.958061      -2.767641      1.724540
K      6.467528      -0.275906      -0.897258
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dbcot3_red4_k4tt_b3lyp_6311+Gdp_thf (ID: tetralith_17094502)
  88
scf done: -4401.05136998
6      -5.197259      -4.740951      -2.427235
6      -5.818796      -4.348632      -1.275014
6      -5.508109      -3.143101      -0.544077
6      -4.456297      -2.285038      -1.084497
6      -3.832109      -2.756722      -2.310798
6      -4.165070      -3.909822      -2.959734
6      -3.933703      -1.055004      -0.618769
6      -4.051866      -0.069293      0.433997
6      -4.839112      0.079372      1.650603
6      -5.881487      -0.800024      2.175933
6      -6.510392      -0.390778      3.411674
6      -6.199783      0.737268      4.119439
6      -5.180479      1.584674      3.616232
6      -4.552800      1.249656      2.445530
6      -6.422411      -2.034182      1.681028
6      -6.286545      -2.949283      0.628283
6      -3.147977      0.998065      0.154054
6      -2.366876      1.884349      -0.154782
6      -1.467547      2.906818      -0.551091
6      -1.425966      4.104065      0.088934
6      -0.596045      5.279854      -0.227674
6      0.820036      5.255119      -0.277937
6      1.507860      6.470237      -0.462589
6      0.840174      7.677400      -0.626334
6      -0.555587      7.702068      -0.575556
6      -1.251961      6.518964      -0.363317
6      1.626696      4.051426      -0.009188
6      1.588753      2.850370      -0.642242
6      0.720311      2.590991      -1.838699
6      -0.681895      2.623572      -1.798783
6      -1.402830      2.348187      -2.972757
6      -0.758962      2.064976      -4.170636
6      0.635990      2.029917      -4.209816
6      1.359492      2.280458      -3.050741
6      2.479303      1.804456      -0.288493
6      3.251055      0.904544      0.003408
6      4.119434      -0.190184      0.290391
6      5.121667      0.058763      1.318155
6      6.156889      -0.842497      1.821011
6      7.028517      -0.317267      2.848126
6      6.953875      0.940192      3.379710
6      5.945639      1.812571      2.897228
6      5.092406      1.370019      1.921214
6      6.486341      -2.197280      1.479538
6      6.089587      -3.245659      0.638339
6      5.116106      -3.524292      -0.357895

```

6	4.077007	-2.640493	-0.881279
6	3.223806	-3.217286	-1.908553
6	3.336333	-4.488944	-2.390128
6	4.354936	-5.346489	-1.873535
6	5.187652	-4.857883	-0.906204
6	3.750328	-1.301607	-0.559175
1	5.965691	-5.504656	-0.508809
1	2.444752	-2.575570	-2.310492
1	4.466407	-6.361226	-2.239774
1	2.656440	-4.841372	-3.159047
1	2.910613	-0.987426	-1.169387
1	7.798827	-0.988313	3.216595
1	4.333031	2.054520	1.570588
1	7.649468	1.255315	4.150192
1	5.843555	2.818811	3.289928
1	6.726625	-4.112183	0.804032
1	7.331364	-2.525305	2.079170
1	2.395455	4.178439	0.749558
1	2.442704	2.240281	-3.071659
1	-2.486163	2.359214	-2.932314
1	1.154358	1.804595	-5.135208
1	2.592966	6.453552	-0.474402
1	-1.339122	1.867438	-5.065184
1	-2.145195	4.254467	0.890640
1	-2.335069	6.540489	-0.297751
1	1.401465	8.592556	-0.779042
1	-1.093778	8.636714	-0.688142
1	-3.165121	-0.716745	-1.305222
1	-3.776625	1.910002	2.085096
1	-7.289169	-1.043001	3.795884
1	-7.202252	-2.381718	2.353580
1	-4.893102	2.487073	4.145618
1	-3.045507	-2.133577	-2.726976
1	-6.721297	0.970531	5.041628
1	-6.994965	-3.765317	0.756192
1	-6.605024	-4.976486	-0.863622
1	-3.648199	-4.189006	-3.872197
1	-5.481694	-5.661972	-2.924274
19	3.506249	-2.533444	2.216809
19	6.673986	-0.897892	-1.318357
19	-6.870213	-0.254689	-0.814583
19	-3.423780	-2.777869	1.836289

dbcot3_red6_k6_b3lyp_6311+Gdp_thf_ctd2 (ID: te-
tralith_15662248)

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scf done: -5600.994640

C	-8.167207	-4.950824	-1.244019
C	-8.809692	-3.830835	-0.794240
C	-8.159345	-2.581823	-0.472739
C	-6.707385	-2.526834	-0.636736
C	-6.084505	-3.745348	-1.121293

C	-6.750604	-4.901829	-1.414303
C	-5.785253	-1.470975	-0.403507
C	-5.675846	-0.108011	0.049832
C	-6.600810	0.916457	0.493828
C	-8.062901	0.851968	0.622629
C	-8.723968	2.056105	1.077331
C	-8.100480	3.228804	1.401333
C	-6.685132	3.288847	1.290233
C	-6.003042	2.182526	0.859983
C	-8.988912	-0.212727	0.381599
C	-9.037944	-1.553736	-0.038321
C	-4.282828	0.273057	0.041295
C	-3.087350	0.511981	0.013261
C	-1.695360	0.900938	-0.024061
C	-1.627454	2.325177	-0.162627
C	-0.722298	3.413038	-0.102561
C	0.722177	3.413010	0.102923
C	1.351320	4.711198	0.243953
C	0.700996	5.907911	0.134627
C	-0.701097	5.907934	-0.134053
C	-1.351429	4.711236	-0.243491
C	1.627350	2.325146	0.162885
C	1.695246	0.900875	0.024596
C	0.735592	-0.189473	-0.054408
C	-0.735755	-0.189409	0.055656
C	-1.339652	-1.491856	0.235675
C	-0.692016	-2.695015	0.149320
C	0.691785	-2.695135	-0.146422
C	1.339455	-1.492056	-0.233571
C	3.087221	0.511917	-0.013065
C	4.282700	0.273039	-0.041440
C	5.675708	-0.108058	-0.050265
C	6.600606	0.916426	-0.494372
C	8.062672	0.851930	-0.623467
C	8.723618	2.055954	-1.078655
C	8.100064	3.228628	-1.402617
C	6.684765	3.288768	-1.290946
C	6.002780	2.182521	-0.860347
C	8.988796	-0.212624	-0.382198
C	9.037968	-1.553457	0.038252
C	8.159419	-2.581556	0.472769
C	6.707386	-2.526823	0.636262
C	6.084516	-3.745550	1.120296
C	6.750736	-4.901851	1.413734
C	8.167473	-4.950433	1.244448
C	8.809922	-3.830315	0.794940
C	5.785182	-1.471042	0.402975
H	9.889073	-3.861828	0.666575
H	5.006010	-3.720686	1.251105
H	8.723835	-5.854645	1.467534
H	6.205795	-5.770374	1.769296
H	4.788221	-1.819629	0.650072

H	9.805343	2.006059	-1.167101
H	4.926326	2.249992	-0.781708
H	8.675585	4.085445	-1.737155
H	6.144004	4.196225	-1.540029
H	10.067689	-1.905707	0.030412
H	9.998370	0.126581	-0.600831
H	2.633243	2.705485	0.307391
H	2.403201	-1.506383	-0.424651
H	-2.403397	-1.506040	0.426774
H	1.240783	-3.621213	-0.284089
H	2.421864	4.714215	0.430851
H	-1.241040	-3.620981	0.287625
H	-2.633320	2.705468	-0.307442
H	-2.421970	4.714262	-0.430402
H	1.245747	6.840332	0.239938
H	-1.245835	6.840371	-0.239281
H	-4.788294	-1.819434	-0.650781
H	-4.926556	2.249935	0.781722
H	-9.805725	2.006259	1.165412
H	-9.998537	0.126473	0.600009
H	-6.144417	4.196291	1.539463
H	-5.006089	-3.720196	-1.252788
H	-8.676089	4.085697	1.735526
H	-10.067605	-1.906157	-0.030072
H	-9.888756	-3.862623	-0.665209
H	-6.205666	-5.770195	-1.770254
H	-8.723446	-5.855232	-1.466619
K	7.623968	-0.062085	2.347385
K	7.079719	-1.600128	-2.339456
K	-0.164897	1.624540	2.505408
K	0.165516	1.624331	-2.504906
K	-7.623818	-0.062533	-2.348052
K	-7.079513	-1.599627	2.339264

dbcot3_red6_k6_twisted_b3lyp_6311+Gdp_thf_ctd (ID: tetralith
166939759)

6	-9.200014	4.053040	-0.588087
6	-9.530286	2.756969	-0.871392
6	-8.616350	1.640477	-0.801934
6	-7.240794	1.931282	-0.400562
6	-6.952576	3.325076	-0.114266
6	-7.858669	4.344437	-0.194345
6	-6.117582	1.074822	-0.242940
6	-5.681928	-0.295078	-0.338374
6	-6.305474	-1.561198	-0.671935
6	-7.692967	-1.834114	-1.071698
6	-8.023702	-3.214236	-1.354992
6	-7.158148	-4.269282	-1.276833
6	-5.817515	-4.008312	-0.885005
6	-5.442811	-2.721310	-0.606453
6	-8.818190	-0.965698	-1.241406
6	-9.190067	0.386404	-1.140182

6	-4.275468	-0.361441	-0.003704
6	-3.086930	-0.337713	0.264626
6	-1.695288	-0.332719	0.667360
6	-1.634738	-0.534451	2.083871
6	-0.726372	-0.734357	3.150883
6	0.732237	-0.756177	3.143395
6	1.377300	-1.074473	4.402897
6	0.720862	-1.308287	5.577067
6	-0.706330	-1.240843	5.594299
6	-1.366800	-0.965728	4.431358
6	1.636679	-0.489229	2.087731
6	1.691837	-0.100822	0.709997
6	0.728701	0.087985	-0.367279
6	-0.733093	-0.110254	-0.404724
6	-1.330341	-0.050025	-1.722020
6	-0.689668	0.293735	-2.881425
6	0.682007	0.633247	-2.816642
6	1.323986	0.522359	-1.613154
6	3.079957	0.107868	0.351111
6	4.265740	0.278042	0.127162
6	5.671143	0.415348	-0.189594
6	6.233101	1.734690	0.027458
6	7.604036	2.208215	-0.208857
6	7.869773	3.597052	0.099678
6	6.958019	4.488704	0.591528
6	5.633228	4.031644	0.825760
6	5.319021	2.728037	0.549285
6	8.766415	1.535605	-0.704050
6	9.200394	0.277323	-1.156983
6	8.687824	-1.030679	-1.363502
6	7.330382	-1.521486	-1.130339
6	7.109121	-2.923093	-1.437760
6	8.060226	-3.779325	-1.915917
6	9.383342	-3.292536	-2.142704
6	9.651525	-1.979868	-1.870264
6	6.170134	-0.854518	-0.651974
1	10.657515	-1.604611	-2.041156
1	6.105099	-3.303995	-1.270602
1	10.159835	-3.948095	-2.522399
1	7.809233	-4.815098	-2.120624
1	5.348362	-1.561616	-0.627091
1	8.883718	3.943599	-0.079940
1	4.305438	2.399445	0.732984
1	7.244528	5.515125	0.795680
1	4.874239	4.701433	1.217553
1	10.252996	0.325390	-1.429348
1	9.600684	2.231794	-0.742923
1	2.652070	-0.575121	2.458681
1	2.377183	0.760598	-1.580571
1	-2.383320	-0.284784	-1.778900
1	1.225781	0.961709	-3.696803
1	2.463326	-1.114322	4.395010

1	-1.233843	0.313854	-3.820441
1	-2.648940	-0.589579	2.463922
1	-2.452762	-0.925809	4.444572
1	1.276056	-1.533546	6.481631
1	-1.258270	-1.411511	6.512693
1	-5.265404	1.672524	0.060860
1	-4.418513	-2.542905	-0.309494
1	-9.049696	-3.410857	-1.653473
1	-9.682439	-1.547059	-1.553216
1	-5.093863	-4.813407	-0.805436
1	-5.934237	3.558551	0.185058
1	-7.492152	-5.275465	-1.507776
1	-10.240770	0.501344	-1.399503
1	-10.550345	2.530245	-1.171567
1	-7.558705	5.361271	0.037590
1	-9.941784	4.841230	-0.661716
19	8.040202	-0.267001	1.660781
19	6.809410	0.956597	-2.992228
19	0.095406	-2.813615	0.865369
19	-0.095429	2.080311	1.883487
19	-8.039209	-0.311529	1.648385
19	-6.810398	0.397817	-3.109913

{Constraints: {D 7 8 19 20 F; D 27 28 37 52 F}}

dbcot_gs_b3lyp_6311+Gdp_thf_opt (ID: tetralith_16694860)

28

scf done: -617.053647

C	0.383916	-0.224942	-0.046566
C	1.772367	-0.388138	0.128152
C	0.923739	2.097669	-2.167818
C	2.731671	0.736854	0.210063
C	2.312213	1.934566	-1.993109
C	2.958119	1.710987	-0.679526
C	-0.440847	-1.363070	-0.018963
H	-1.512711	-1.232996	-0.126110
C	2.283033	-1.683182	0.323918
H	3.349031	-1.804326	0.485990
C	0.083311	-2.640091	0.139850
H	-0.575886	-3.500696	0.144027
C	1.458722	-2.801727	0.313008
H	1.882447	-3.789579	0.453700
H	3.393430	0.701129	1.073208
H	3.784941	2.385101	-0.464826
C	0.432627	2.394983	-3.451046
H	-0.633992	2.547727	-3.578630
C	3.156553	2.074859	-3.108316
H	4.227794	1.976158	-2.966960
C	1.276924	2.495274	-4.550074
H	0.868346	2.712813	-5.530352
C	2.652358	2.333512	-4.377037
H	3.326628	2.423597	-5.221103
C	-0.283356	1.091263	-0.169191

C	-0.056996	2.065357	-1.058862
H	-1.126212	1.232191	0.504554
H	-0.734722	2.916368	-1.033441

dbcot_red2_k2_b3lyp_6311+Gdp_thf (ID: tetralith_16694739)

30

scf done: -1817.024425

C	-1.803465	-0.737191	0.000882
C	-1.806819	0.728833	-0.010551
C	1.806885	-0.728860	0.010465
C	-0.710526	1.639585	-0.014752
C	1.803531	0.737165	-0.000964
C	0.703082	1.642846	-0.010992
C	-3.099331	-1.379889	0.002488
H	-3.100853	-2.467118	0.010964
C	-3.105611	1.365543	-0.018953
H	-3.112106	2.452754	-0.027442
C	-4.299153	-0.723607	-0.005802
H	-5.230399	-1.280663	-0.003898
C	-4.302418	0.703730	-0.016949
H	-5.236203	1.256482	-0.023732
H	-1.075119	2.664922	-0.023832
H	1.062983	2.669856	-0.018035
C	3.105677	-1.365570	0.018878
H	3.112172	-2.452780	0.027362
C	3.099397	1.379863	-0.002552
H	3.100919	2.467091	-0.011025
C	4.302484	-0.703757	0.016889
H	5.236269	-1.256508	0.023679
C	4.299219	0.723581	0.005747
H	5.230465	1.280636	0.003856
C	-0.703016	-1.642872	0.010903
C	0.710591	-1.639611	0.014658
H	1.075184	-2.664948	0.023736
H	-1.062917	-2.669882	0.017950
K	-0.006546	0.019575	2.462246
K	0.006661	-0.019556	-2.462340

dbcot2_gs_b3lyp_6311+Gdp_thf (ID: tetralith_16694810)

56

scf done: -1309.081330

C	4.188248	1.299239	0.199479
C	5.107065	0.740422	-0.713423
C	2.625139	-1.406656	0.286367
C	4.711837	-0.111268	-1.858859
C	3.524830	-1.972546	-0.633547
C	4.030936	-1.262983	-1.830251
C	4.663716	2.171591	1.194963
H	3.951415	2.623555	1.877019
C	6.467002	1.072744	-0.592525
H	7.169495	0.664451	-1.311499
C	6.016658	2.459079	1.323092

H	6.358004	3.122234	2.109702
C	6.926485	1.904896	0.421063
H	7.983524	2.132525	0.498359
H	5.103826	0.209508	-2.821698
H	3.917027	-1.798873	-2.769993
C	2.196043	-2.169350	1.383544
H	1.490074	-1.733485	2.081531
C	3.945634	-3.299636	-0.438339
H	4.618665	-3.745732	-1.162911
C	2.652317	-3.466381	1.584491
H	2.315838	-4.031688	2.446035
C	3.528668	-4.038947	0.661352
H	3.879109	-5.056031	0.795353
C	2.727643	1.114551	0.097191
C	2.028688	-0.042188	0.107744
H	2.148951	2.034619	0.071554
C	0.605793	0.000007	0.034366
C	-0.605673	0.000418	-0.033959
C	-2.727420	-1.114328	-0.096341
C	-4.663226	-2.172210	-1.193750
C	-5.106975	-0.740182	0.713902
C	-6.016101	-2.460021	-1.321842
H	-3.950791	-2.624369	-1.875537
C	-6.466840	-1.072847	0.593072
C	-6.926095	-1.905580	-0.420136
H	-6.357257	-3.123619	-2.108160
H	-7.169464	-0.664352	1.311803
H	-7.983085	-2.133458	-0.497372
C	-2.028591	0.042500	-0.107376
C	-4.712010	0.112144	1.858933
H	-5.104069	-0.208203	2.821890
C	-4.031233	1.263921	1.829846
H	-3.917465	1.800272	2.769337
C	-4.187987	-1.299280	-0.198660
C	-2.625217	1.406775	-0.286683
C	-2.196100	2.169004	-1.384184
C	-3.525146	1.972967	0.632809
C	-2.652611	3.465841	-1.585860
H	-1.489941	1.732926	-2.081844
C	-3.946213	3.299854	0.436851
C	-3.529233	4.038689	-0.663161
H	-2.316106	4.030790	-2.447629
H	-4.619445	3.746185	1.161091
H	-3.879876	5.055627	-0.797747
H	-2.148600	-2.034312	-0.070286

 dbcot2_red2_k2_b3lyp_6311+Gdp_thf (ID: tetralith_16694839)
 58

scf done: -2509.052755

C	-3.526002	4.047761	-0.514199
C	-2.766039	3.403776	-1.492060
C	-2.469119	2.053387	-1.351395

C	-2.944082	1.307058	-0.261079
C	-3.733164	1.947921	0.709785
C	-3.990794	3.323959	0.576634
C	-2.506958	-0.126637	-0.151541
C	-3.360730	-1.183412	-0.167871
C	-4.833630	-1.177553	-0.219648
C	-5.456165	-1.956733	-1.214751
C	-6.837456	-2.077624	-1.295898
C	-7.642581	-1.438646	-0.350735
C	-7.046043	-0.696151	0.661298
C	-5.651543	-0.539458	0.740673
C	-5.119809	0.210195	1.901713
C	-4.291410	1.261354	1.896496
C	-1.102058	-0.317546	-0.127822
C	0.110863	-0.455678	-0.089384
C	1.533185	-0.531998	-0.039762
C	2.063882	0.814424	-0.070949
C	3.265688	1.560854	-0.042887
C	4.657873	1.128736	0.053649
C	5.670784	2.156970	0.061881
C	5.417792	3.497919	-0.013458
C	4.059376	3.928771	-0.106425
C	3.060921	2.999106	-0.118537
C	5.163881	-0.195447	0.145977
C	4.698714	-1.516658	0.172882
C	3.486633	-2.284823	0.123146
C	2.086521	-1.878469	0.027238
C	1.126510	-2.955446	-0.004403
C	1.431417	-4.289987	0.049707
C	2.789776	-4.683702	0.146968
C	3.745013	-3.705921	0.180751
H	2.032038	3.340865	-0.188595
H	6.702175	1.821426	0.133782
H	3.819248	4.985409	-0.166590
H	6.229888	4.216643	-0.002177
H	6.249940	-0.186056	0.213034
H	5.548554	-2.189323	0.253605
H	0.083540	-2.681416	-0.078361
H	4.786545	-4.004405	0.254918
H	0.637187	-5.028484	0.018189
H	3.070422	-5.730510	0.193796
H	1.225666	1.499656	-0.136423
H	-4.830273	-2.470881	-1.936773
H	-7.284038	-2.674498	-2.083397
H	-7.666792	-0.224771	1.416506
H	-8.721829	-1.532042	-0.393276
H	-5.525968	-0.094224	2.864442
H	-4.082439	1.737986	2.852011
H	-1.850584	1.558148	-2.091270
H	-2.395500	3.953864	-2.349800
H	-4.576389	3.821794	1.342647
H	-3.750603	5.104958	-0.600231

H	-2.909055	-2.171328	-0.217786
K	3.477424	-0.445453	-2.464221
K	3.188934	-0.230054	2.559263

dbcot2_red4_k4_b3lyp_6311+Gdp_thf (ID: tetralith_16694939)

60

scf done: -3709.010668

C	2.743042	-4.619874	-0.783228
C	1.441595	-4.051474	-0.732711
C	1.309314	-2.709822	-0.494875
C	2.399657	-1.782377	-0.280774
C	3.745176	-2.369427	-0.348812
C	3.815806	-3.793044	-0.598348
C	2.012938	-0.408554	-0.028290
C	2.705862	0.825227	0.238519
C	3.996418	1.406826	0.367529
C	3.966457	2.831244	0.645311
C	5.069946	3.621128	0.805239
C	6.366638	3.033583	0.699818
C	6.457294	1.693549	0.443360
C	5.327759	0.810722	0.266952
C	5.671349	-0.545068	0.019456
C	5.042930	-1.781127	-0.214502
C	0.590933	-0.150134	-0.036014
C	-0.590908	0.150287	-0.036053
C	-2.012924	0.408621	-0.028359
C	-2.705814	-0.825220	0.238251
C	-3.996356	-1.406874	0.367146
C	-5.327718	-0.810815	0.266550
C	-6.457226	-1.693705	0.442823
C	-6.366531	-3.033756	0.699180
C	-5.069821	-3.621256	0.804624
C	-3.966357	-2.831314	0.644815
C	-5.671358	0.544984	0.019167
C	-5.042972	1.781097	-0.214589
C	-3.745228	2.369469	-0.348693
C	-2.399690	1.782461	-0.280667
C	-1.309366	2.709969	-0.494584
C	-1.441679	4.051658	-0.732192
C	-2.743141	4.620029	-0.782650
C	-3.815889	3.793133	-0.597966
H	-2.984347	-3.289760	0.725096
H	-7.442739	-1.241388	0.363746
H	-4.957431	-4.681411	1.007483
H	-7.261360	-3.635045	0.820352
H	-6.752179	0.672273	0.010674
H	-5.804616	2.547285	-0.337123
H	-0.310074	2.298188	-0.459889
H	-4.812221	4.224412	-0.640428
H	-0.558996	4.666239	-0.877610
H	-2.888186	5.679765	-0.964890
H	-1.960976	-1.599652	0.386957

H	2.984461	3.289722	0.725575
H	4.957590	4.681272	1.008174
H	7.442793	1.241197	0.364303
H	7.261484	3.634827	0.821088
H	6.752165	-0.672409	0.011039
H	5.804553	-2.547331	-0.337069
H	0.310032	-2.298024	-0.460137
H	0.558899	-4.666005	-0.878260
H	4.812128	-4.224345	-0.640845
H	2.888062	-5.679580	-0.965659
H	1.961042	1.599664	0.387287
K	-3.887378	0.003875	-2.430312
K	-3.787523	0.947545	2.438501
K	3.887542	-0.003613	-2.430088
K	3.787311	-0.947848	2.438612

dbcot3_gs_b3lyp_6311+Gdp_thf (ID: tetralith_15602373)

84

scf done: -2001.109397

C	6.186830	-2.952322	-0.742421
C	4.777068	-2.921452	-0.780778
C	6.175029	-0.617116	1.360201
C	3.992949	-1.672639	-0.837037
C	4.769837	-0.608142	1.323666
C	3.988089	-0.648052	0.044409
C	6.837459	-4.196166	-0.806425
H	7.922182	-4.218166	-0.804468
C	4.072591	-4.134156	-0.886215
H	2.989781	-4.105734	-0.945816
C	6.126148	-5.388174	-0.870356
H	6.654883	-6.333893	-0.904520
C	4.731165	-5.356908	-0.910491
H	4.162940	-6.277695	-0.976063
H	3.289618	-1.608845	-1.663648
C	6.819730	-0.466665	2.600382
H	7.904137	-0.446517	2.626012
C	4.053466	-0.477876	2.523447
H	2.970024	-0.456451	2.487991
C	6.100382	-0.356358	3.783674
H	6.622667	-0.254875	4.728208
C	4.705268	-0.369913	3.745875
H	4.130142	-0.282238	4.660513
C	7.034731	-1.737956	-0.732589
C	7.027316	-0.736982	0.155619
H	7.806918	-1.715398	-1.498651
H	7.793077	0.028485	0.050989
C	3.117551	0.458650	-0.177003
C	2.390543	1.416599	-0.338104
C	1.513065	2.516464	-0.557765
C	0.701214	2.468206	-1.816605
C	1.515782	3.564353	0.295822
C	-0.701306	2.468251	-1.816566

C	1.384953	2.384518	-3.039353
C	0.706303	4.795915	0.211499
H	2.234055	3.535898	1.111328
C	-1.385108	2.384612	-3.039286
C	-1.513111	2.516548	-0.557694
H	2.469009	2.368304	-3.034574
C	0.697750	2.324687	-4.245293
C	-0.706221	4.795961	0.211531
C	1.384436	6.026674	0.250028
H	-2.469165	2.368469	-3.034453
C	-0.697967	2.324738	-4.245259
C	-1.515764	3.564447	0.295883
H	1.246255	2.272244	-5.178790
C	-1.384272	6.026764	0.250097
H	2.468770	6.024748	0.280117
C	0.698123	7.234562	0.245932
H	-1.246520	2.272334	-5.178730
H	-2.234018	3.536032	1.111407
H	-2.468605	6.024908	0.280237
C	-0.697880	7.234607	0.245967
H	1.246641	8.169393	0.259015
H	-1.246338	8.169473	0.259077
C	-2.390613	1.416709	-0.337999
C	-3.117607	0.458747	-0.176943
C	-3.988137	-0.647966	0.044447
C	-4.769888	-0.608116	1.323700
C	-3.992971	-1.672536	-0.837023
C	-6.175078	-0.617192	1.360220
C	-4.053534	-0.477811	2.523486
C	-4.777032	-2.921391	-0.780784
H	-3.289649	-1.608701	-1.663638
C	-6.819802	-0.466828	2.600402
C	-7.027357	-0.737061	0.155629
H	-2.970093	-0.456296	2.488035
C	-4.705353	-0.369922	3.745911
C	-6.186793	-2.952338	-0.742466
C	-4.072486	-4.134057	-0.886214
H	-7.904211	-0.446767	2.626025
C	-6.100470	-0.356489	3.783700
C	-7.034748	-1.738013	-0.732604
H	-7.793137	0.028391	0.051021
H	-4.130241	-0.282212	4.660554
C	-6.837353	-4.196215	-0.806523
H	-2.989675	-4.105575	-0.945779
C	-4.730995	-5.356843	-0.910539
H	-6.622768	-0.255073	4.728234
H	-7.806942	-1.715463	-1.498659
H	-7.922076	-4.218272	-0.804601
C	-6.125978	-5.388183	-0.870458
H	-4.162719	-6.277599	-0.976106
H	-6.654661	-6.333930	-0.904662

dbcot3_red2_k2c_b3lyp_6311+Gdp_thf (ID: tetralith_15604809)

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scf done: -3201.078019

C	-9.113069	4.374748	-0.831381
C	-9.199035	3.265750	0.001692
C	-8.087265	2.445462	0.259819
C	-6.841846	2.774274	-0.323337
C	-6.767498	3.925204	-1.132994
C	-7.882406	4.708797	-1.400574
C	-5.585987	2.060241	-0.035102
C	-5.307200	0.737224	-0.180647
C	-6.260859	-0.261473	-0.773707
C	-7.484872	-0.606792	-0.175273
C	-8.253164	-1.638068	-0.744121
C	-7.853834	-2.284768	-1.906959
C	-6.652040	-1.920909	-2.516641
C	-5.863457	-0.931245	-1.941961
C	-8.007447	0.037110	1.050808
C	-8.274841	1.336980	1.223673
C	-4.026361	0.222488	0.136364
C	-2.932060	-0.234604	0.433069
C	-1.660038	-0.799478	0.716660
C	-1.638087	-2.190030	0.379078
C	-0.738592	-3.269025	0.272806
C	0.726186	-3.256317	0.226174
C	1.374535	-4.533848	-0.014516
C	0.717798	-5.718393	-0.164464
C	-0.712964	-5.732075	-0.109709
C	-1.379024	-4.559725	0.086520
C	1.615579	-2.165051	0.297648
C	1.647085	-0.784909	0.675325
C	0.722284	0.102307	1.394655
C	-0.724730	0.099173	1.407715
C	-1.360405	1.130535	2.175556
C	-0.697285	2.097576	2.892219
C	0.711004	2.097687	2.883971
C	1.366520	1.132620	2.157917
C	2.918440	-0.218439	0.389889
C	4.013122	0.239120	0.096161
C	5.298634	0.749133	-0.209862
C	6.246866	-0.249362	-0.812027
C	7.462958	-0.616042	-0.210174
C	8.224237	-1.647341	-0.788382
C	7.826286	-2.272945	-1.963173
C	6.632840	-1.887460	-2.575986
C	5.850608	-0.897805	-1.992598
C	7.983932	0.005254	1.028029
C	8.261037	1.300170	1.222106
C	8.089637	2.425047	0.274363
C	6.851644	2.774183	-0.312762
C	6.793597	3.938063	-1.105002
C	7.917437	4.715489	-1.352354

C	9.140747	4.361621	-0.779290
C	9.210585	3.239199	0.037094
C	5.587348	2.067451	-0.044126
H	10.151733	2.980054	0.511384
H	5.838866	4.225335	-1.533233
H	10.025243	4.963853	-0.953288
H	7.839448	5.597510	-1.978296
H	4.765319	2.708081	0.265944
H	9.148427	-1.947460	-0.305382
H	4.907576	-0.618456	-2.448742
H	8.438742	-3.055805	-2.396190
H	6.308340	-2.364621	-3.493960
H	8.748999	1.565655	2.158016
H	8.265600	-0.690018	1.816075
H	2.614538	-2.474547	0.003692
H	2.448297	1.136721	2.167090
H	-2.442037	1.131040	2.200159
H	1.276205	2.831652	3.448399
H	2.459573	-4.525289	-0.067026
H	-1.256129	2.830948	3.463664
H	-2.647530	-2.514906	0.142337
H	-2.464977	-4.570917	0.112353
H	1.271993	-6.635752	-0.331336
H	-1.260517	-6.660103	-0.234260
H	-4.760272	2.698223	0.270649
H	-4.914567	-0.668246	-2.395632
H	-9.183802	-1.921409	-0.263393
H	-8.298746	-0.644050	1.847627
H	-6.326221	-2.414702	-3.425309
H	-5.807119	4.197351	-1.558478
H	-8.471656	-3.067183	-2.333094
H	-8.765631	1.621074	2.152598
H	-10.145930	3.022355	0.472886
H	-7.791824	5.580321	-2.039402
H	-9.990786	4.982064	-1.021311
K	-0.083961	-1.027085	-1.994492
K	0.120769	-2.416051	3.142509

 dbcot3_red2_k2t_b3lyp_6311+Gdp_thf (ID: tetralith_16694030)
 86

scf done: -3201.081401

C	-5.958928	-5.709692	-0.507406
C	-6.768704	-4.584733	-0.605734
C	-6.229370	-3.287213	-0.618797
C	-4.828063	-3.134062	-0.565867
C	-4.020441	-4.284098	-0.507567
C	-4.572139	-5.557972	-0.458267
C	-4.147718	-1.830233	-0.688937
C	-4.292682	-0.734465	0.089169
C	-5.168757	-0.651154	1.303757
C	-6.567130	-0.782792	1.247072
C	-7.313334	-0.580602	2.421254

C	-6.696633	-0.300666	3.634118
C	-5.306353	-0.191394	3.691044
C	-4.558096	-0.349267	2.530874
C	-7.314156	-1.084394	0.004998
C	-7.172725	-2.157154	-0.782341
C	-3.504007	0.422363	-0.177653
C	-2.850860	1.424883	-0.380183
C	-2.060230	2.578476	-0.649667
C	-2.217656	3.693922	0.097380
C	-1.518453	4.984787	-0.046485
C	-0.111525	5.118710	0.035428
C	0.434315	6.417144	0.023762
C	-0.361694	7.547873	-0.105423
C	-1.748855	7.410638	-0.193328
C	-2.312102	6.141811	-0.142614
C	0.807256	3.989702	0.264274
C	0.958768	2.864604	-0.483327
C	0.224693	2.641717	-1.774114
C	-1.168497	2.501407	-1.851280
C	-1.767092	2.251716	-3.096547
C	-1.007723	2.166654	-4.256638
C	0.378713	2.311361	-4.183118
C	0.982178	2.534968	-2.951785
C	1.912747	1.872131	-0.151521
C	2.720150	0.996052	0.118227
C	3.640134	-0.064123	0.359523
C	4.441558	0.064482	1.570255
C	5.469845	-0.837750	2.082049
C	6.114241	-0.449850	3.316494
C	5.832124	0.680595	4.032405
C	4.829526	1.552956	3.539483
C	4.186870	1.237218	2.371426
C	5.982118	-2.080657	1.577009
C	5.829971	-2.981027	0.514782
C	5.057895	-3.141030	-0.666911
C	4.027211	-2.254269	-1.200873
C	3.406704	-2.692221	-2.441738
C	3.724417	-3.839958	-3.107444
C	4.734547	-4.700499	-2.579527
C	5.351858	-4.340156	-1.414621
C	3.519424	-1.026209	-0.715562
H	6.121455	-4.990197	-1.006350
H	2.636112	-2.047125	-2.854430
H	5.005796	-5.618288	-3.089659
H	3.211574	-4.093165	-4.029738
H	2.755389	-0.667552	-1.396611
H	6.880683	-1.120987	3.692650
H	3.425623	1.918014	2.017438
H	6.363875	0.897261	4.952756
H	4.567223	2.460124	4.073676
H	6.518018	-3.815018	0.637828
H	6.751553	-2.452431	2.248493

H	1.491095	4.118809	1.099602
H	2.060114	2.630116	-2.887785
H	-2.843109	2.126745	-3.145882
H	0.985196	2.243876	-5.079345
H	1.509883	6.526817	0.114918
H	-1.491718	1.985006	-5.209554
H	-2.987681	3.667313	0.864751
H	-3.391128	6.032300	-0.176272
H	0.094027	8.531566	-0.125958
H	-2.384038	8.284488	-0.282921
H	-3.393054	-1.777946	-1.469843
H	-3.480879	-0.231159	2.565592
H	-8.394520	-0.655302	2.371795
H	-8.129919	-0.401877	-0.223027
H	-4.810903	0.030747	4.629262
H	-2.942211	-4.164702	-0.499070
H	-7.294939	-0.162007	4.527449
H	-7.884160	-2.271695	-1.597433
H	-7.845065	-4.702762	-0.673694
H	-3.926646	-6.426794	-0.398359
H	-6.403874	-6.697959	-0.485700
K	2.958061	-2.767641	1.724540
K	6.467528	-0.275906	-0.897258

dbcot3_red4_k4tt_b3lyp_6311+Gdp_thf (ID: tetralith_17094502)

88

scf done: -4401.05136998

6	-5.197259	-4.740951	-2.427235
6	-5.818796	-4.348632	-1.275014
6	-5.508109	-3.143101	-0.544077
6	-4.456297	-2.285038	-1.084497
6	-3.832109	-2.756722	-2.310798
6	-4.165070	-3.909822	-2.959734
6	-3.933703	-1.055004	-0.618769
6	-4.051866	-0.069293	0.433997
6	-4.839112	0.079372	1.650603
6	-5.881487	-0.800024	2.175933
6	-6.510392	-0.390778	3.411674
6	-6.199783	0.737268	4.119439
6	-5.180479	1.584674	3.616232
6	-4.552800	1.249656	2.445530
6	-6.422411	-2.034182	1.681028
6	-6.286545	-2.949283	0.628283
6	-3.147977	0.998065	0.154054
6	-2.366876	1.884349	-0.154782
6	-1.467547	2.906818	-0.551091
6	-1.425966	4.104065	0.088934
6	-0.596045	5.279854	-0.227674
6	0.820036	5.255119	-0.277937
6	1.507860	6.470237	-0.462589
6	0.840174	7.677400	-0.626334
6	-0.555587	7.702068	-0.575556

6	-1.251961	6.518964	-0.363317
6	1.626696	4.051426	-0.009188
6	1.588753	2.850370	-0.642242
6	0.720311	2.590991	-1.838699
6	-0.681895	2.623572	-1.798783
6	-1.402830	2.348187	-2.972757
6	-0.758962	2.064976	-4.170636
6	0.635990	2.029917	-4.209816
6	1.359492	2.280458	-3.050741
6	2.479303	1.804456	-0.288493
6	3.251055	0.904544	0.003408
6	4.119434	-0.190184	0.290391
6	5.121667	0.058763	1.318155
6	6.156889	-0.842497	1.821011
6	7.028517	-0.317267	2.848126
6	6.953875	0.940192	3.379710
6	5.945639	1.812571	2.897228
6	5.092406	1.370019	1.921214
6	6.486341	-2.197280	1.479538
6	6.089587	-3.245659	0.638339
6	5.116106	-3.524292	-0.357895
6	4.077007	-2.640493	-0.881279
6	3.223806	-3.217286	-1.908553
6	3.336333	-4.488944	-2.390128
6	4.354936	-5.346489	-1.873535
6	5.187652	-4.857883	-0.906204
6	3.750328	-1.301607	-0.559175
1	5.965691	-5.504656	-0.508809
1	2.444752	-2.575570	-2.310492
1	4.466407	-6.361226	-2.239774
1	2.656440	-4.841372	-3.159047
1	2.910613	-0.987426	-1.169387
1	7.798827	-0.988313	3.216595
1	4.333031	2.054520	1.570588
1	7.649468	1.255315	4.150192
1	5.843555	2.818811	3.289928
1	6.726625	-4.112183	0.804032
1	7.331364	-2.525305	2.079170
1	2.395455	4.178439	0.749558
1	2.442704	2.240281	-3.071659
1	-2.486163	2.359214	-2.932314
1	1.154358	1.804595	-5.135208
1	2.592966	6.453552	-0.474402
1	-1.339122	1.867438	-5.065184
1	-2.145195	4.254467	0.890640
1	-2.335069	6.540489	-0.297751
1	1.401465	8.592556	-0.779042
1	-1.093778	8.636714	-0.688142
1	-3.165121	-0.716745	-1.305222
1	-3.776625	1.910002	2.085096
1	-7.289169	-1.043001	3.795884
1	-7.202252	-2.381718	2.353580

1	-4.893102	2.487073	4.145618
1	-3.045507	-2.133577	-2.726976
1	-6.721297	0.970531	5.041628
1	-6.994965	-3.765317	0.756192
1	-6.605024	-4.976486	-0.863622
1	-3.648199	-4.189006	-3.872197
1	-5.481694	-5.661972	-2.924274
19	3.506249	-2.533444	2.216809
19	6.673986	-0.897892	-1.318357
19	-6.870213	-0.254689	-0.814583
19	-3.423780	-2.777869	1.836289

dbcot3_red6_k6_b3lyp_6311+Gdp_thf_ctd2 (ID: te-
tralith_15662248)

90

scf done: -5600.994640

C	-8.167207	-4.950824	-1.244019
C	-8.809692	-3.830835	-0.794240
C	-8.159345	-2.581823	-0.472739
C	-6.707385	-2.526834	-0.636736
C	-6.084505	-3.745348	-1.121293
C	-6.750604	-4.901829	-1.414303
C	-5.785253	-1.470975	-0.403507
C	-5.675846	-0.108011	0.049832
C	-6.600810	0.916457	0.493828
C	-8.062901	0.851968	0.622629
C	-8.723968	2.056105	1.077331
C	-8.100480	3.228804	1.401333
C	-6.685132	3.288847	1.290233
C	-6.003042	2.182526	0.859983
C	-8.988912	-0.212727	0.381599
C	-9.037944	-1.553736	-0.038321
C	-4.282828	0.273057	0.041295
C	-3.087350	0.511981	0.013261
C	-1.695360	0.900938	-0.024061
C	-1.627454	2.325177	-0.162627
C	-0.722298	3.413038	-0.102561
C	0.722177	3.413010	0.102923
C	1.351320	4.711198	0.243953
C	0.700996	5.907911	0.134627
C	-0.701097	5.907934	-0.134053
C	-1.351429	4.711236	-0.243491
C	1.627350	2.325146	0.162885
C	1.695246	0.900875	0.024596
C	0.735592	-0.189473	-0.054408
C	-0.735755	-0.189409	0.055656
C	-1.339652	-1.491856	0.235675
C	-0.692016	-2.695015	0.149320
C	0.691785	-2.695135	-0.146422
C	1.339455	-1.492056	-0.233571
C	3.087221	0.511917	-0.013065
C	4.282700	0.273039	-0.041440

C	5.675708	-0.108058	-0.050265
C	6.600606	0.916426	-0.494372
C	8.062672	0.851930	-0.623467
C	8.723618	2.055954	-1.078655
C	8.100064	3.228628	-1.402617
C	6.684765	3.288768	-1.290946
C	6.002780	2.182521	-0.860347
C	8.988796	-0.212624	-0.382198
C	9.037968	-1.553457	0.038252
C	8.159419	-2.581556	0.472769
C	6.707386	-2.526823	0.636262
C	6.084516	-3.745550	1.120296
C	6.750736	-4.901851	1.413734
C	8.167473	-4.950433	1.244448
C	8.809922	-3.830315	0.794940
C	5.785182	-1.471042	0.402975
H	9.889073	-3.861828	0.666575
H	5.006010	-3.720686	1.251105
H	8.723835	-5.854645	1.467534
H	6.205795	-5.770374	1.769296
H	4.788221	-1.819629	0.650072
H	9.805343	2.006059	-1.167101
H	4.926326	2.249992	-0.781708
H	8.675585	4.085445	-1.737155
H	6.144004	4.196225	-1.540029
H	10.067689	-1.905707	0.030412
H	9.998370	0.126581	-0.600831
H	2.633243	2.705485	0.307391
H	2.403201	-1.506383	-0.424651
H	-2.403397	-1.506040	0.426774
H	1.240783	-3.621213	-0.284089
H	2.421864	4.714215	0.430851
H	-1.241040	-3.620981	0.287625
H	-2.633320	2.705468	-0.307442
H	-2.421970	4.714262	-0.430402
H	1.245747	6.840332	0.239938
H	-1.245835	6.840371	-0.239281
H	-4.788294	-1.819434	-0.650781
H	-4.926556	2.249935	0.781722
H	-9.805725	2.006259	1.165412
H	-9.998537	0.126473	0.600009
H	-6.144417	4.196291	1.539463
H	-5.006089	-3.720196	-1.252788
H	-8.676089	4.085697	1.735526
H	-10.067605	-1.906157	-0.030072
H	-9.888756	-3.862623	-0.665209
H	-6.205666	-5.770195	-1.770254
H	-8.723446	-5.855232	-1.466619
K	7.623968	-0.062085	2.347385
K	7.079719	-1.600128	-2.339456
K	-0.164897	1.624540	2.505408
K	0.165516	1.624331	-2.504906

K	-7.623818	-0.062533	-2.348052
K	-7.079513	-1.599627	2.339264

dbcot3_red6_k6_twisted_b3lyp_6311+Gdp_thf_ctd (ID: tetralith
166939759)

6	-9.200014	4.053040	-0.588087
6	-9.530286	2.756969	-0.871392
6	-8.616350	1.640477	-0.801934
6	-7.240794	1.931282	-0.400562
6	-6.952576	3.325076	-0.114266
6	-7.858669	4.344437	-0.194345
6	-6.117582	1.074822	-0.242940
6	-5.681928	-0.295078	-0.338374
6	-6.305474	-1.561198	-0.671935
6	-7.692967	-1.834114	-1.071698
6	-8.023702	-3.214236	-1.354992
6	-7.158148	-4.269282	-1.276833
6	-5.817515	-4.008312	-0.885005
6	-5.442811	-2.721310	-0.606453
6	-8.818190	-0.965698	-1.241406
6	-9.190067	0.386404	-1.140182
6	-4.275468	-0.361441	-0.003704
6	-3.086930	-0.337713	0.264626
6	-1.695288	-0.332719	0.667360
6	-1.634738	-0.534451	2.083871
6	-0.726372	-0.734357	3.150883
6	0.732237	-0.756177	3.143395
6	1.377300	-1.074473	4.402897
6	0.720862	-1.308287	5.577067
6	-0.706330	-1.240843	5.594299
6	-1.366800	-0.965728	4.431358
6	1.636679	-0.489229	2.087731
6	1.691837	-0.100822	0.709997
6	0.728701	0.087985	-0.367279
6	-0.733093	-0.110254	-0.404724
6	-1.330341	-0.050025	-1.722020
6	-0.689668	0.293735	-2.881425
6	0.682007	0.633247	-2.816642
6	1.323986	0.522359	-1.613154
6	3.079957	0.107868	0.351111
6	4.265740	0.278042	0.127162
6	5.671143	0.415348	-0.189594
6	6.233101	1.734690	0.027458
6	7.604036	2.208215	-0.208857
6	7.869773	3.597052	0.099678
6	6.958019	4.488704	0.591528
6	5.633228	4.031644	0.825760
6	5.319021	2.728037	0.549285
6	8.766415	1.535605	-0.704050
6	9.200394	0.277323	-1.156983
6	8.687824	-1.030679	-1.363502
6	7.330382	-1.521486	-1.130339

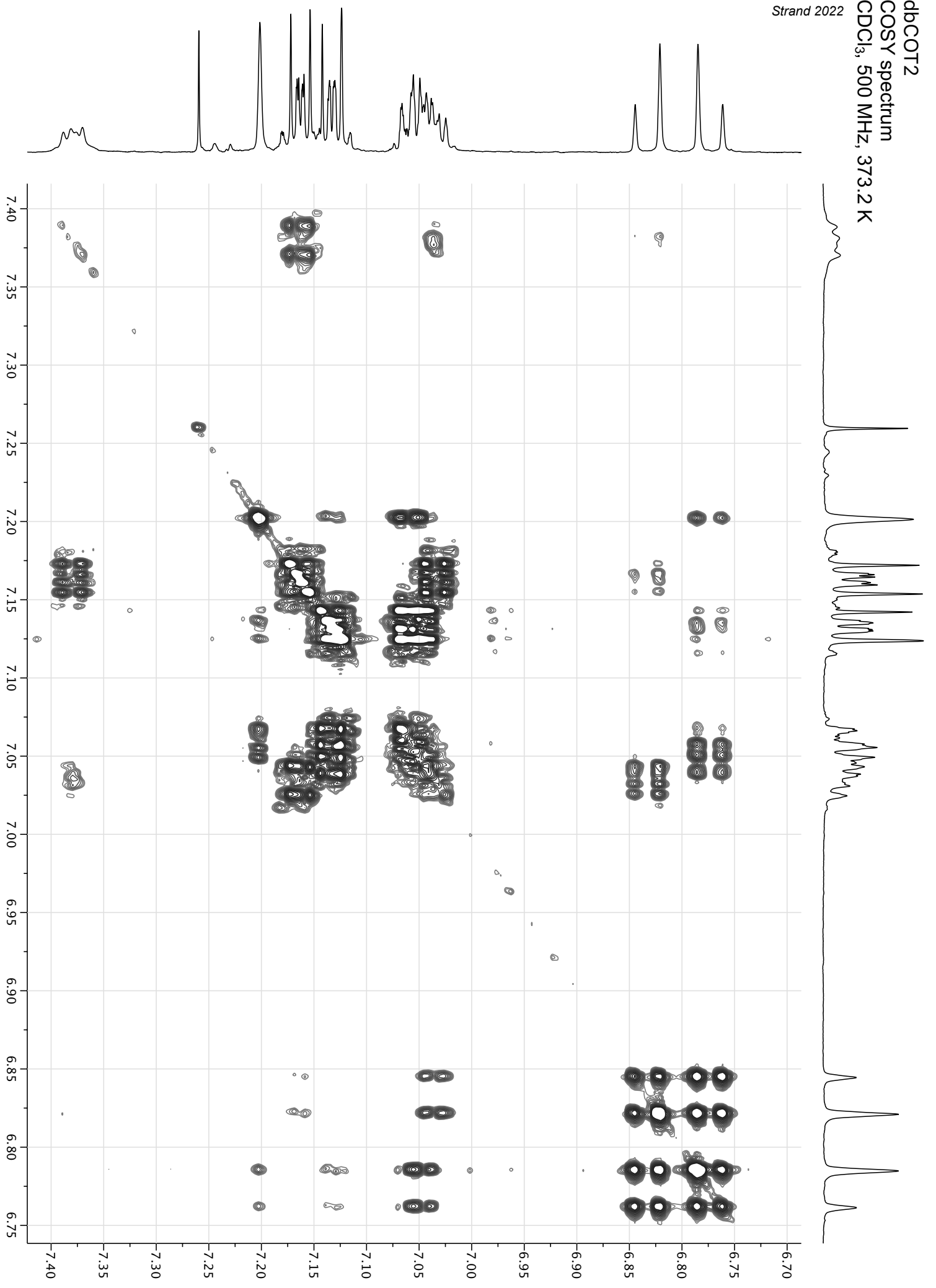
6	7.109121	-2.923093	-1.437760
6	8.060226	-3.779325	-1.915917
6	9.383342	-3.292536	-2.142704
6	9.651525	-1.979868	-1.870264
6	6.170134	-0.854518	-0.651974
1	10.657515	-1.604611	-2.041156
1	6.105099	-3.303995	-1.270602
1	10.159835	-3.948095	-2.522399
1	7.809233	-4.815098	-2.120624
1	5.348362	-1.561616	-0.627091
1	8.883718	3.943599	-0.079940
1	4.305438	2.399445	0.732984
1	7.244528	5.515125	0.795680
1	4.874239	4.701433	1.217553
1	10.252996	0.325390	-1.429348
1	9.600684	2.231794	-0.742923
1	2.652070	-0.575121	2.458681
1	2.377183	0.760598	-1.580571
1	-2.383320	-0.284784	-1.778900
1	1.225781	0.961709	-3.696803
1	2.463326	-1.114322	4.395010
1	-1.233843	0.313854	-3.820441
1	-2.648940	-0.589579	2.463922
1	-2.452762	-0.925809	4.444572
1	1.276056	-1.533546	6.481631
1	-1.258270	-1.411511	6.512693
1	-5.265404	1.672524	0.060860
1	-4.418513	-2.542905	-0.309494
1	-9.049696	-3.410857	-1.653473
1	-9.682439	-1.547059	-1.553216
1	-5.093863	-4.813407	-0.805436
1	-5.934237	3.558551	0.185058
1	-7.492152	-5.275465	-1.507776
1	-10.240770	0.501344	-1.399503
1	-10.550345	2.530245	-1.171567
1	-7.558705	5.361271	0.037590
1	-9.941784	4.841230	-0.661716
19	8.040202	-0.267001	1.660781
19	6.809410	0.956597	-2.992228
19	0.095406	-2.813615	0.865369
19	-0.095429	2.080311	1.883487
19	-8.039209	-0.311529	1.648385
19	-6.810398	0.397817	-3.109913

{Constraints: {D 7 8 19 20 F; D 27 28 37 52 F}}

XIII. Copies of COSY, ^{13}C -HSQC, and ^{13}C -HMBC for dbCOT2, $K_2\text{dbCOT2}$, $K_4\text{dbCOT2}$, $K_2\text{dbCOT3}$, $K_4\text{dbCOT3}$, $K_6\text{dbCOT3}$, and $K_6\text{dbCOT5}$. Excitation transfer spectra for $K_2\text{dbCOT3}$.

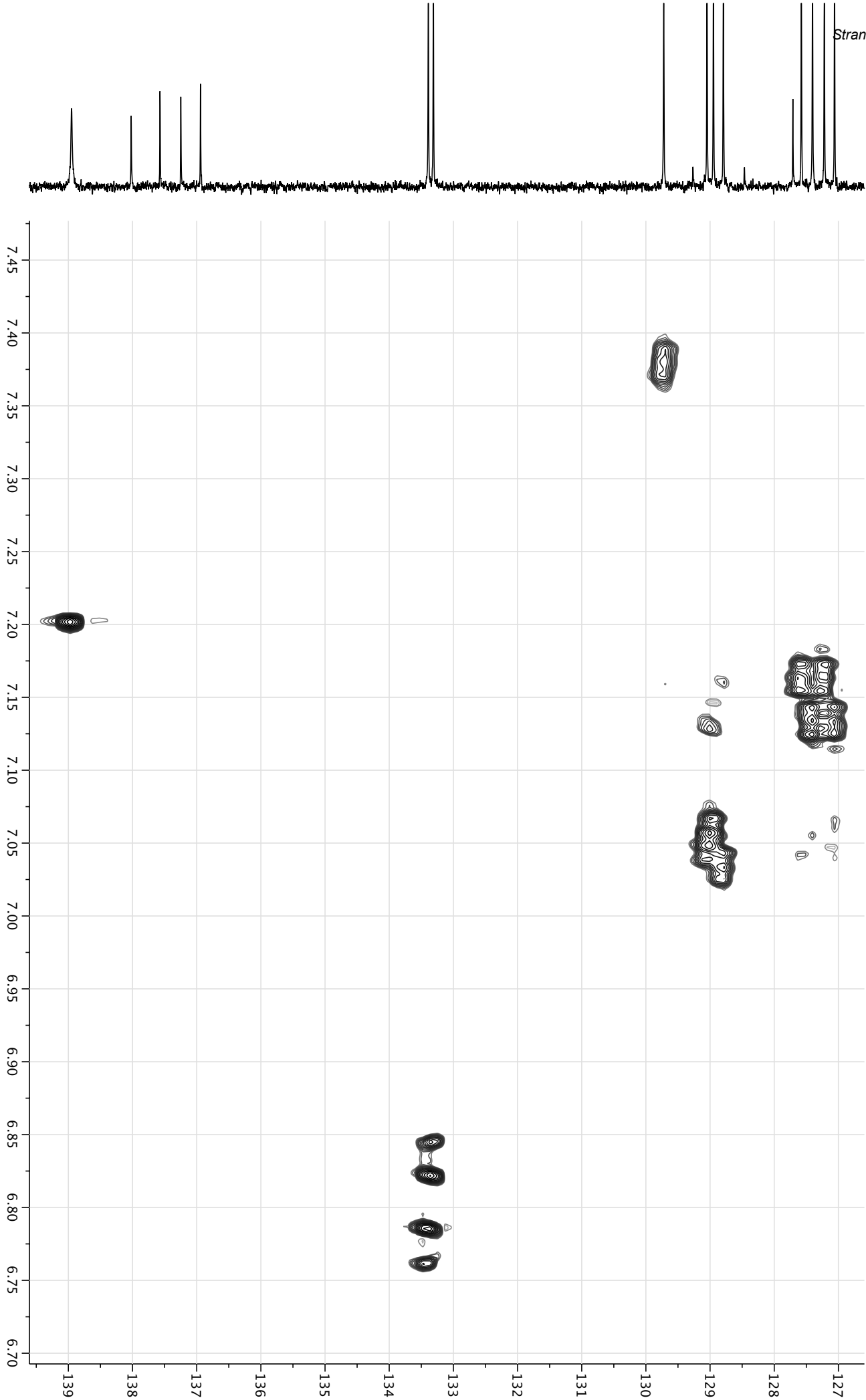
dbCOT2
COSY spectrum
CDCl₃, 500 MHz, 373.2 K

Strand 2022



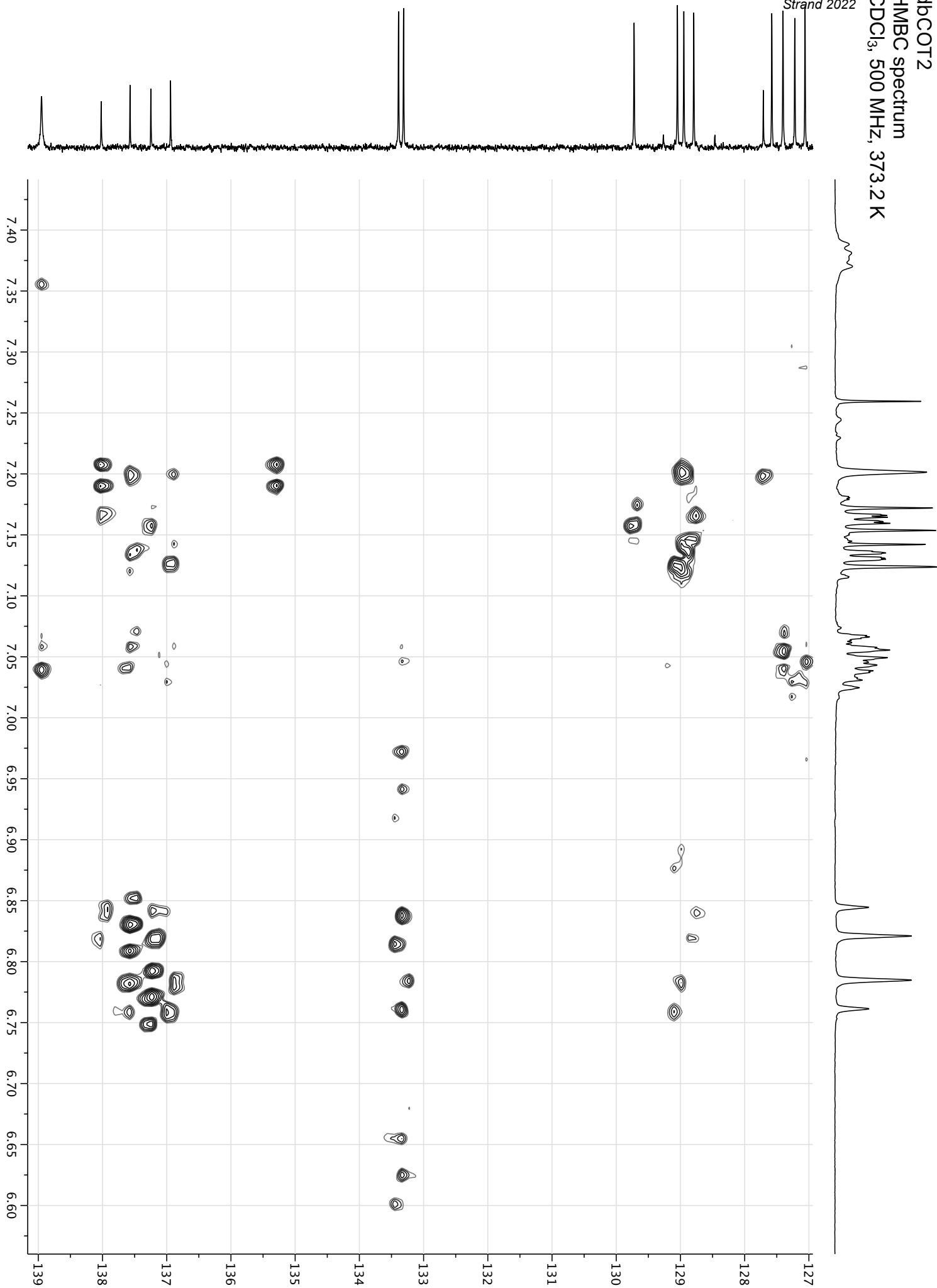
dbCOT2
HSQC spectrum
CDCl₃, 500 MHz, 373.2 K

Strand 2022



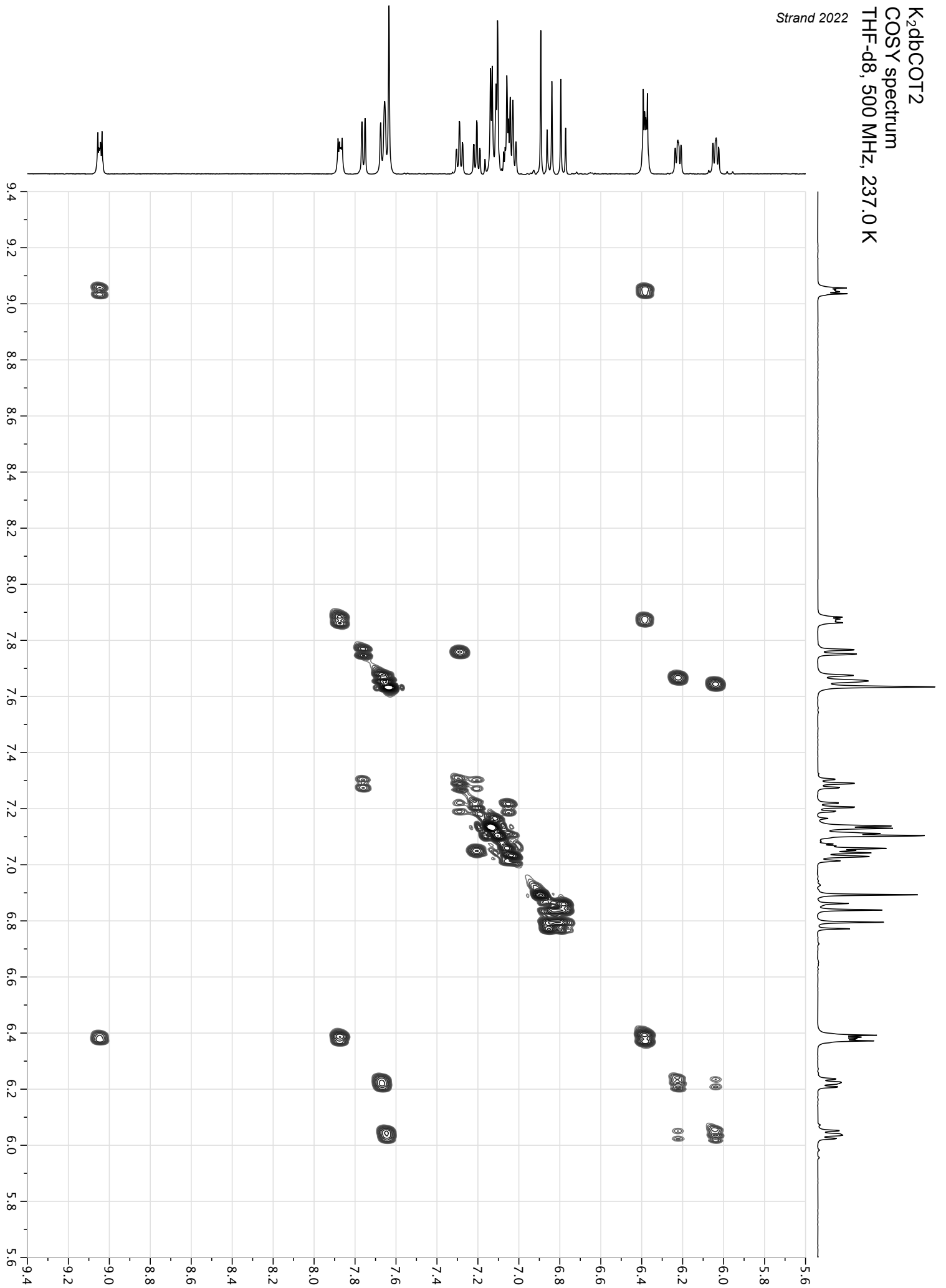
dbCOT2
HMBC spectrum
CDCl₃, 500 MHz, 373.2 K

Strand 2022



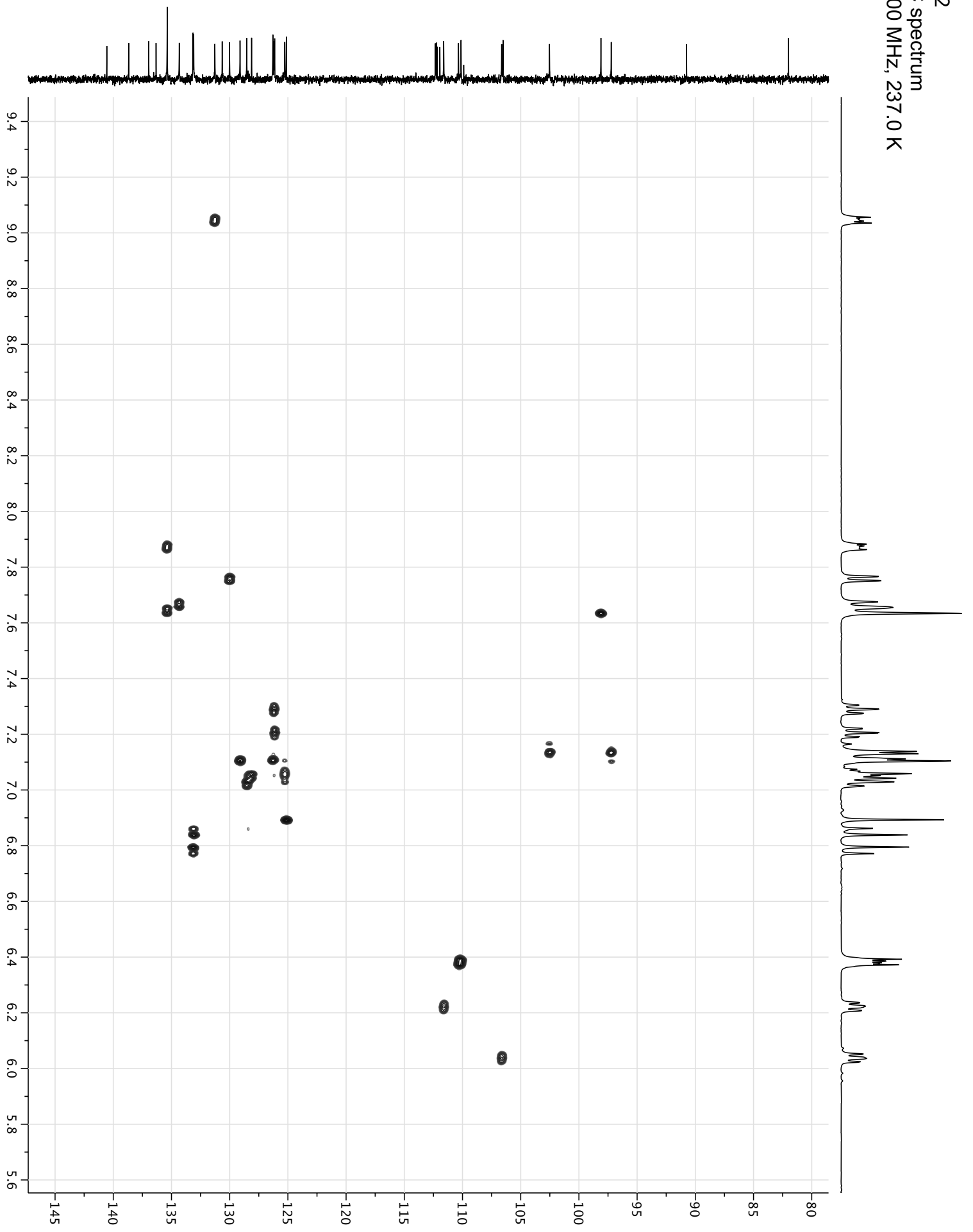
K₂dbCOT2
COSY spectrum
THF-d₈, 500 MHz, 237.0 K

Strand 2022

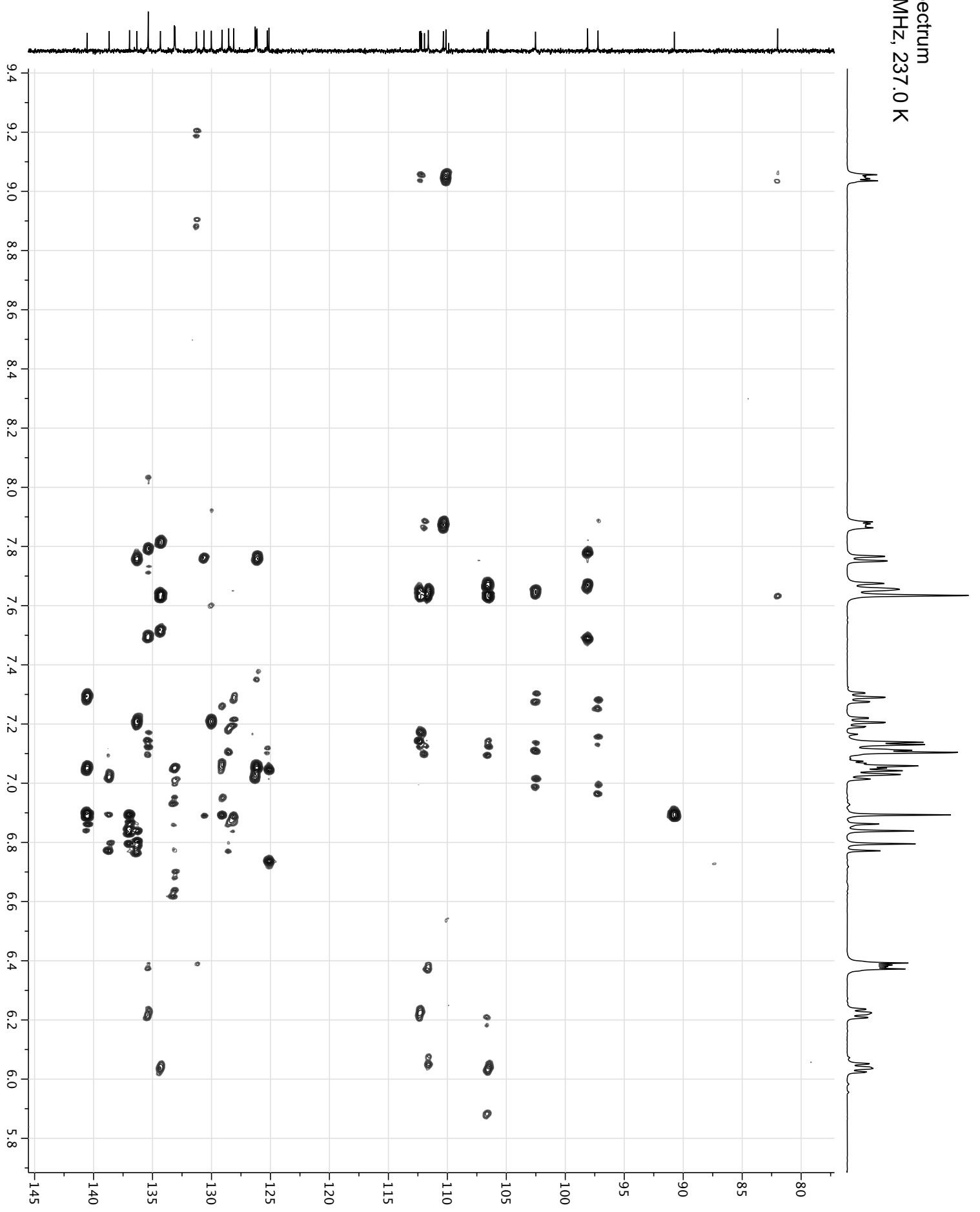


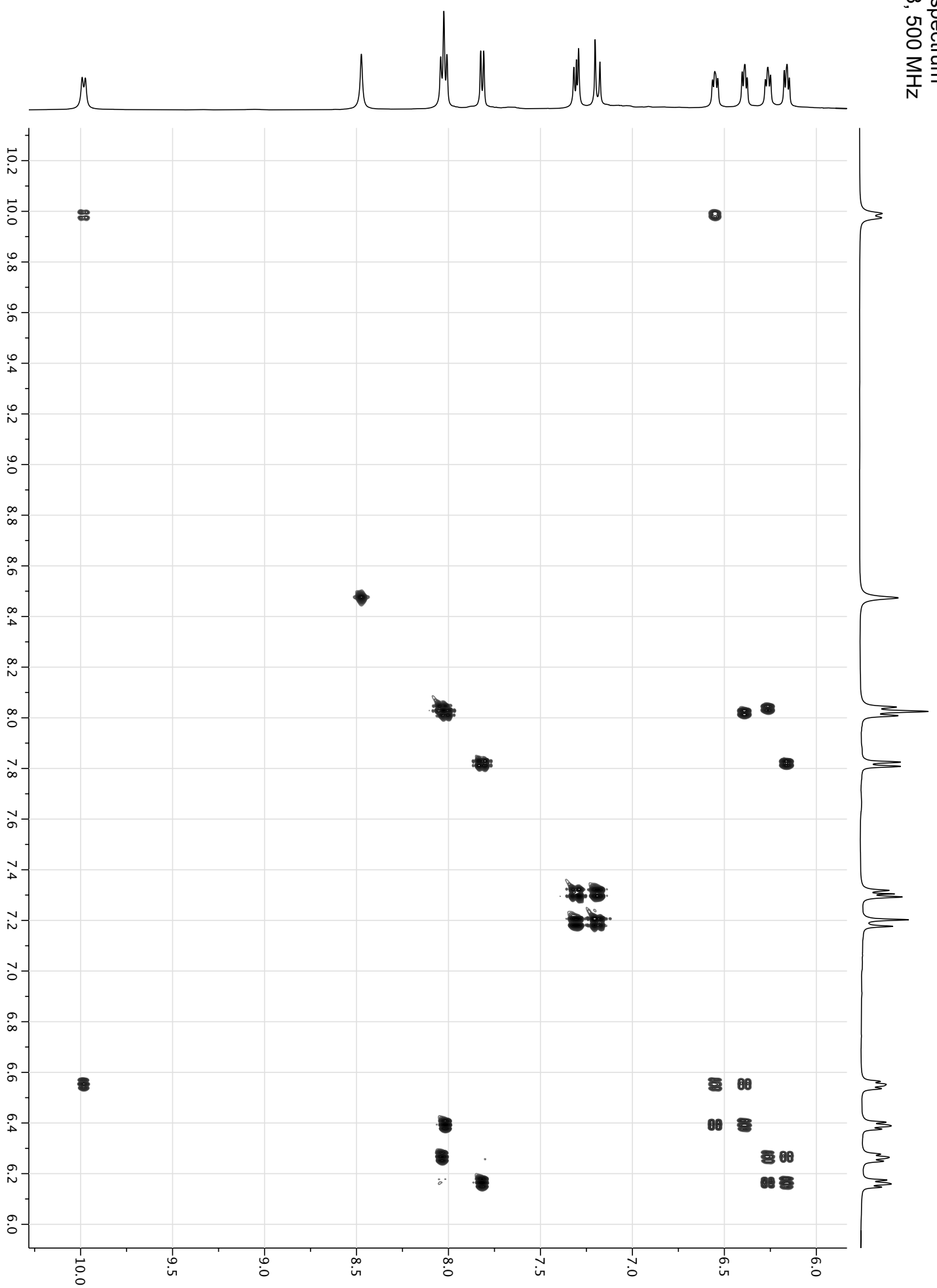
K₂dbccOT2
¹³C-HSQC spectrum
THF-d₈, 500 MHz, 237.0 K

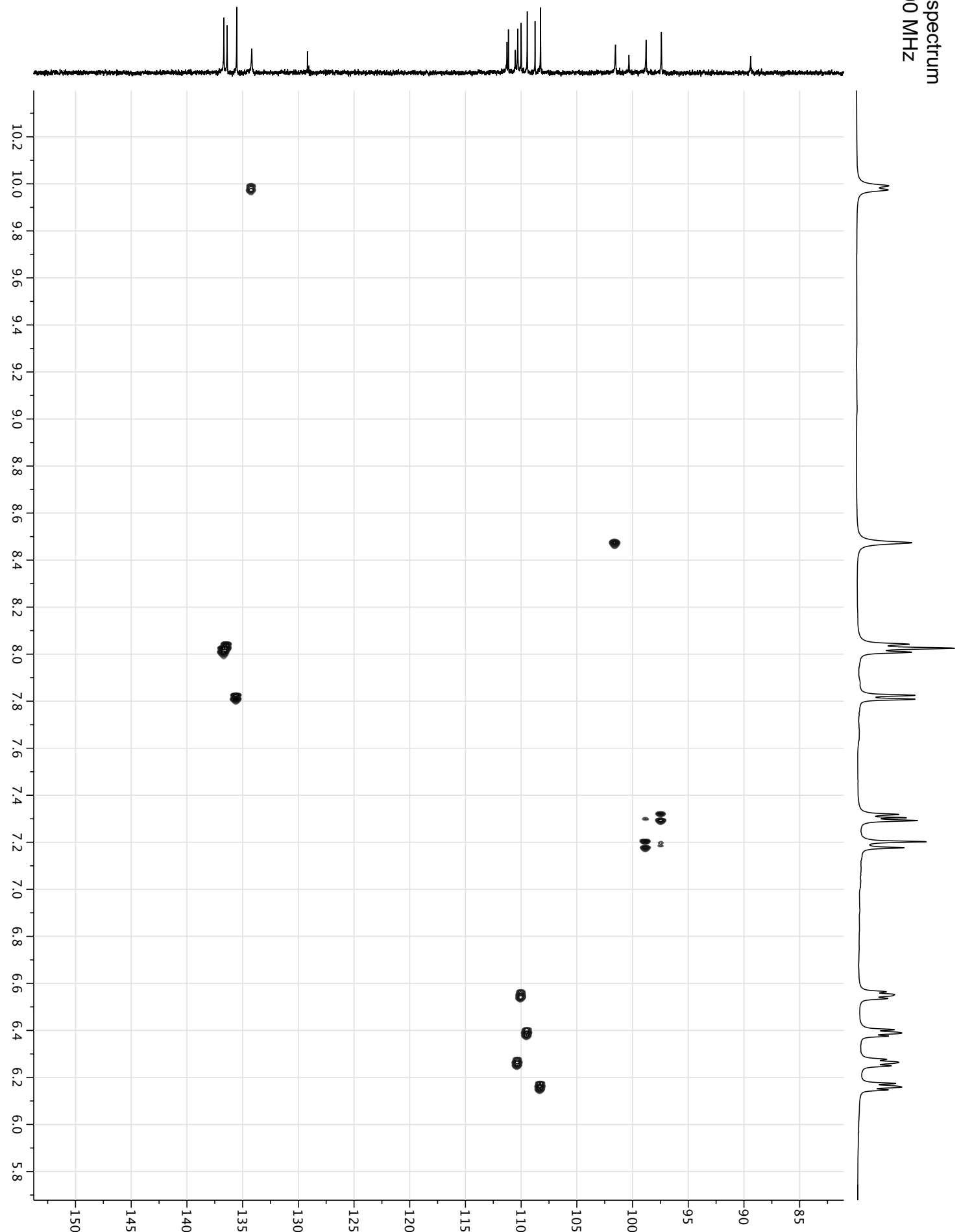
Strand 2022



K₂dbbCOT2
¹³C-HMBC spectrum
THF-d₈, 500 MHz, 237.0 K

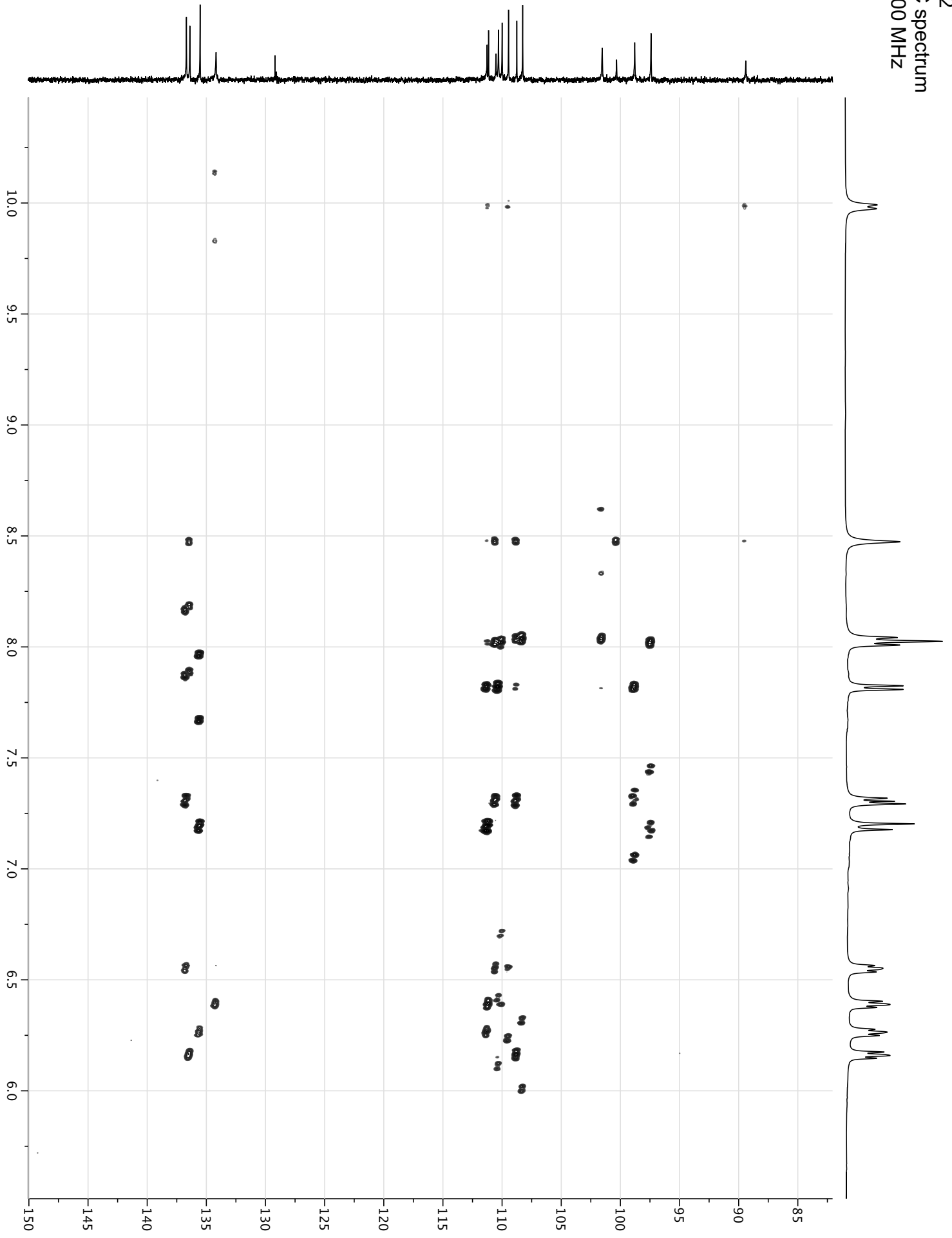






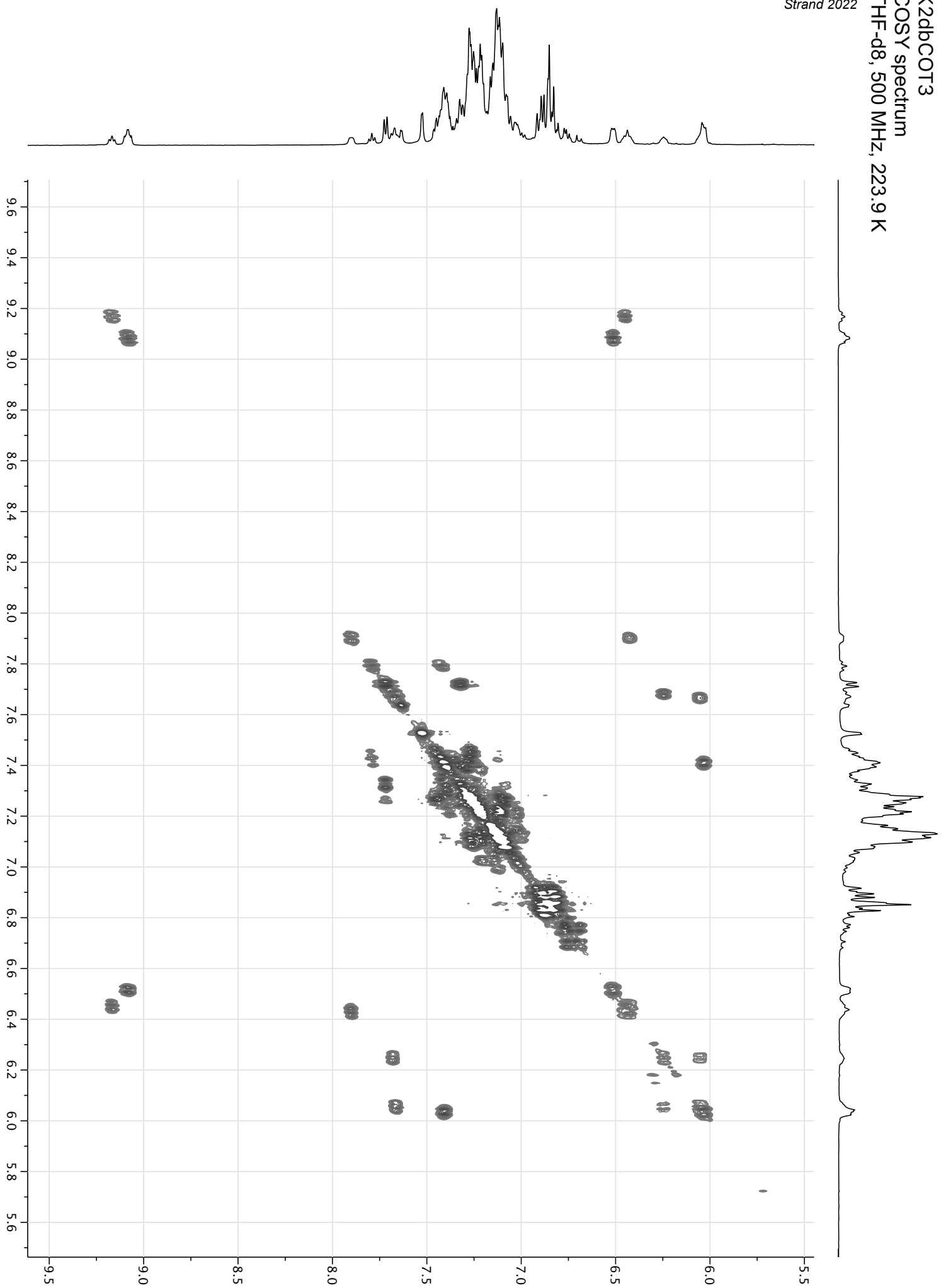
K₄dbbCOT2
¹³C-HMBC spectrum
THF-d₈, 500 MHz

Strand 2022



K2dbCOT3
COSY spectrum
THF-d8, 500 MHz, 223.9 K

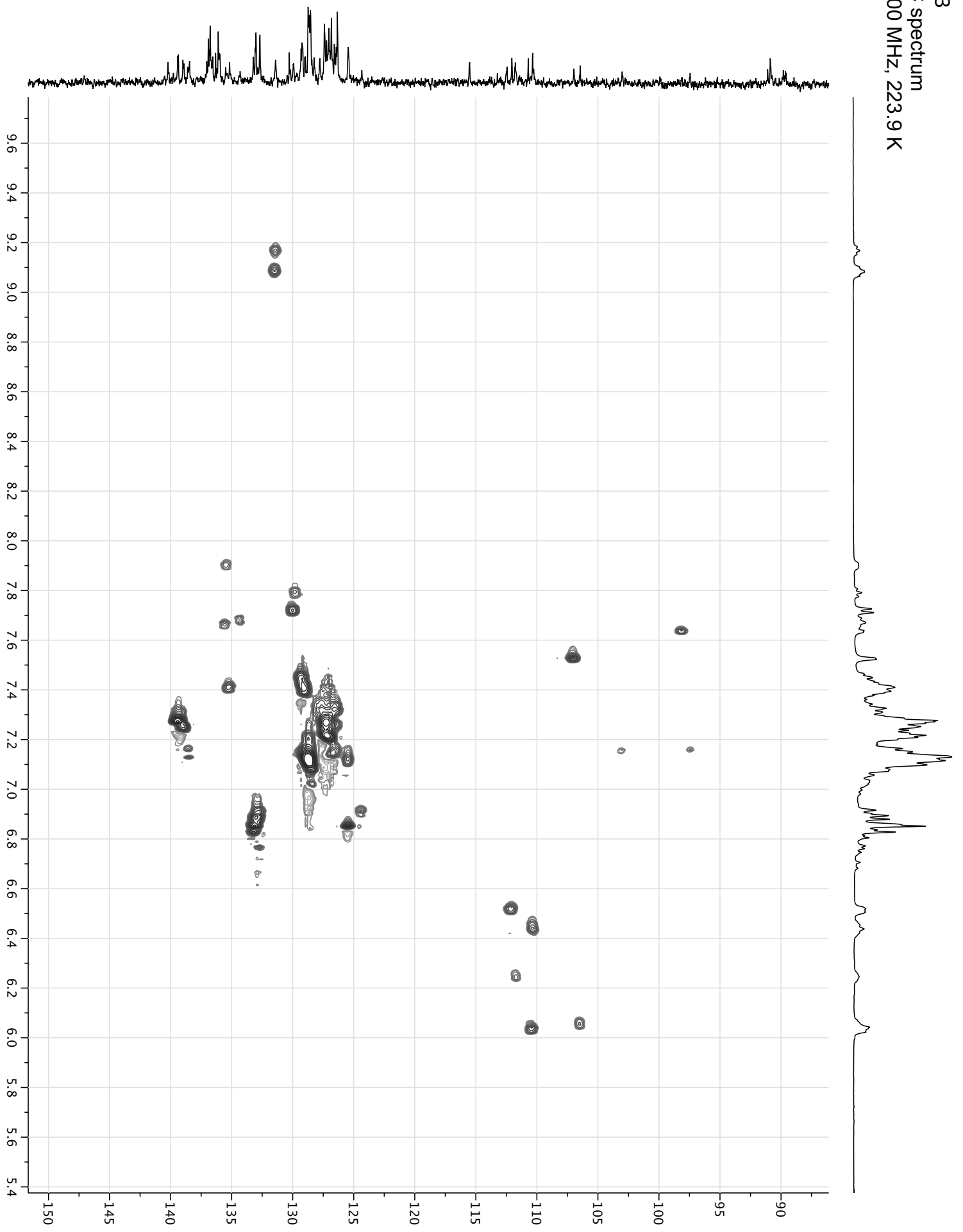
Strand 2022



f1 (ppm) - S101 -

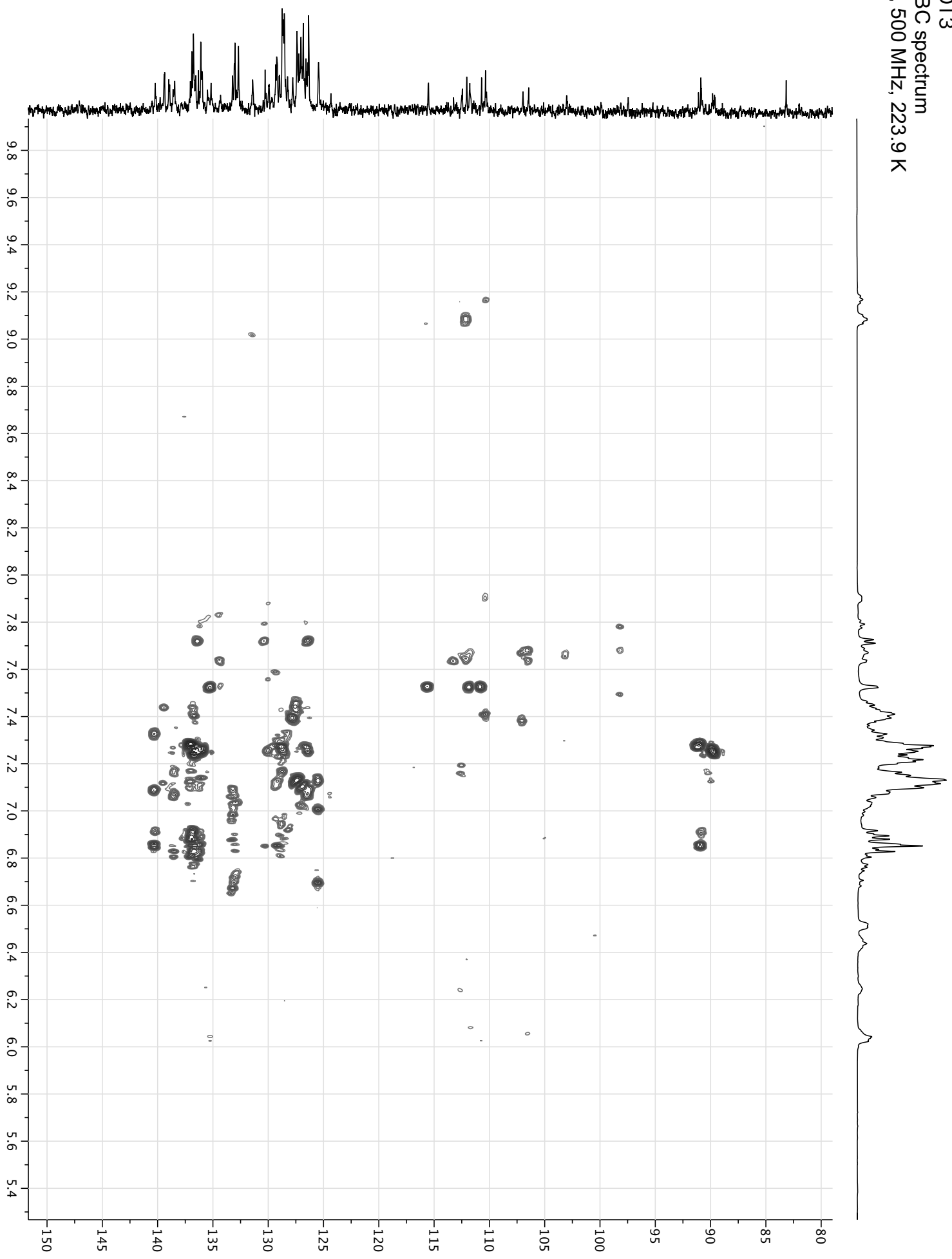
K₂dbccOT3
¹³C-HSQC spectrum
THF-d₈, 500 MHz, 223.9 K

Strand 2022

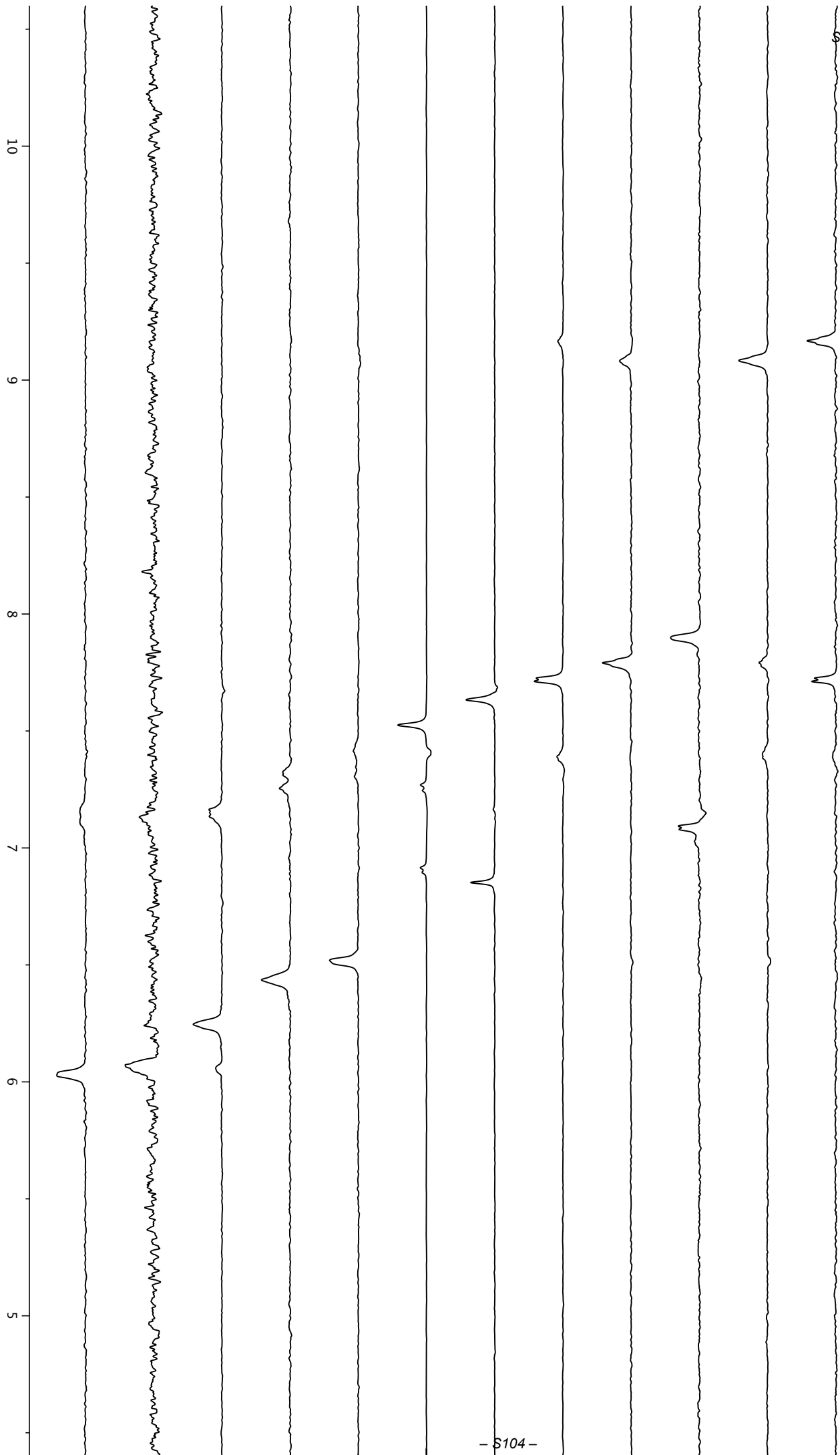


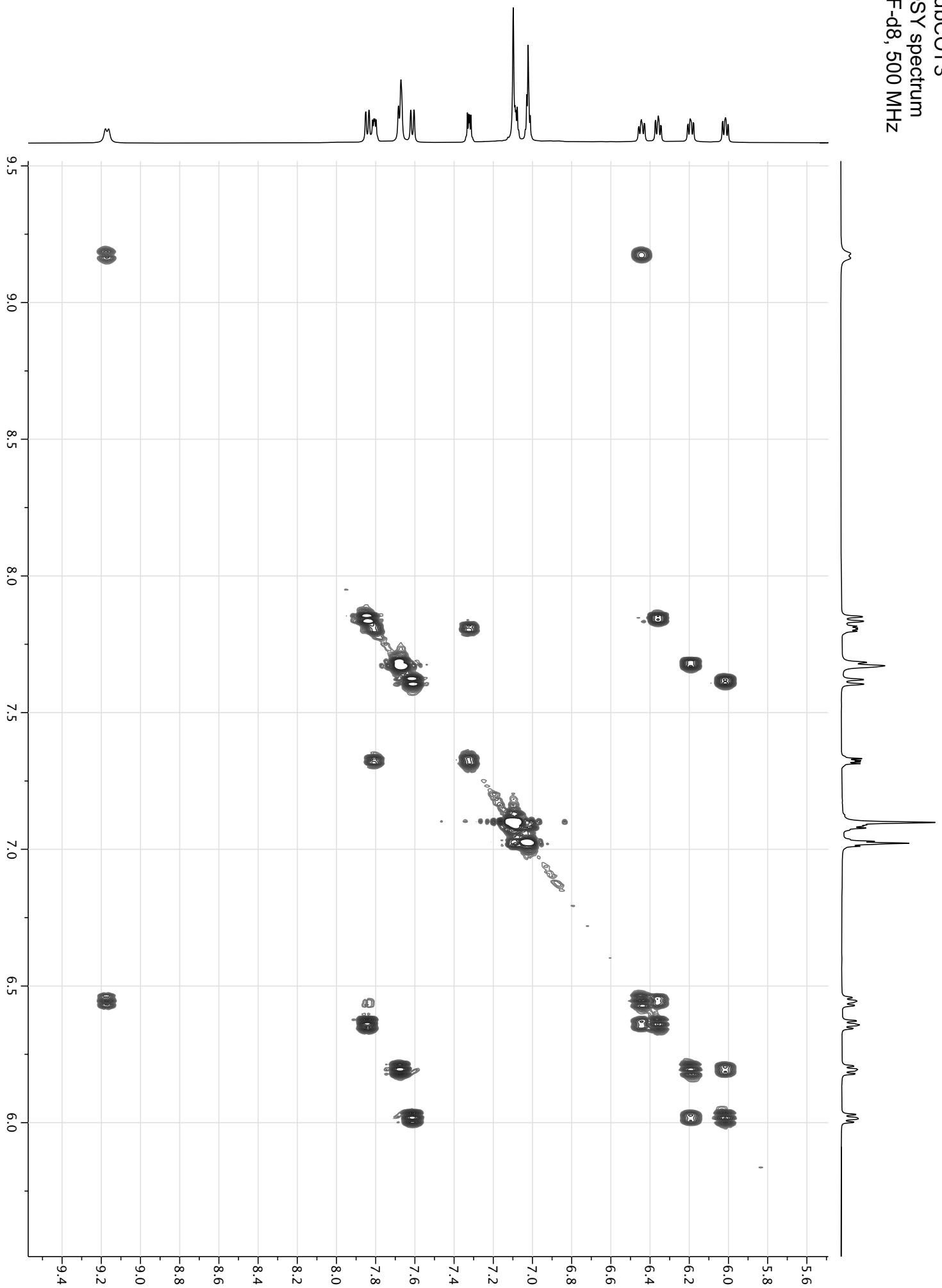
K₂dbccOT3
¹³C-HMBC spectrum
THF-d₈, 500 MHz, 223.9 K

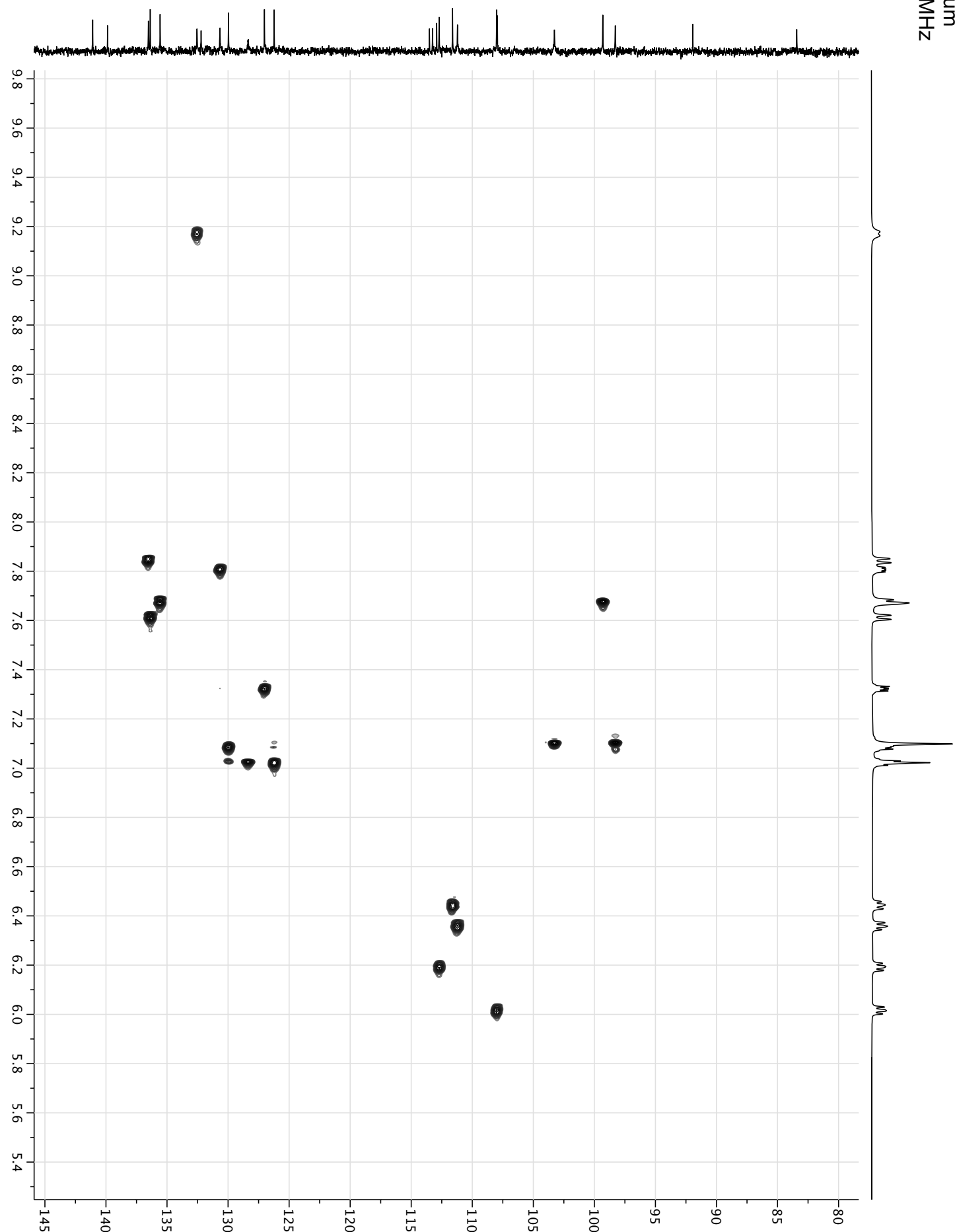
Strand 2022

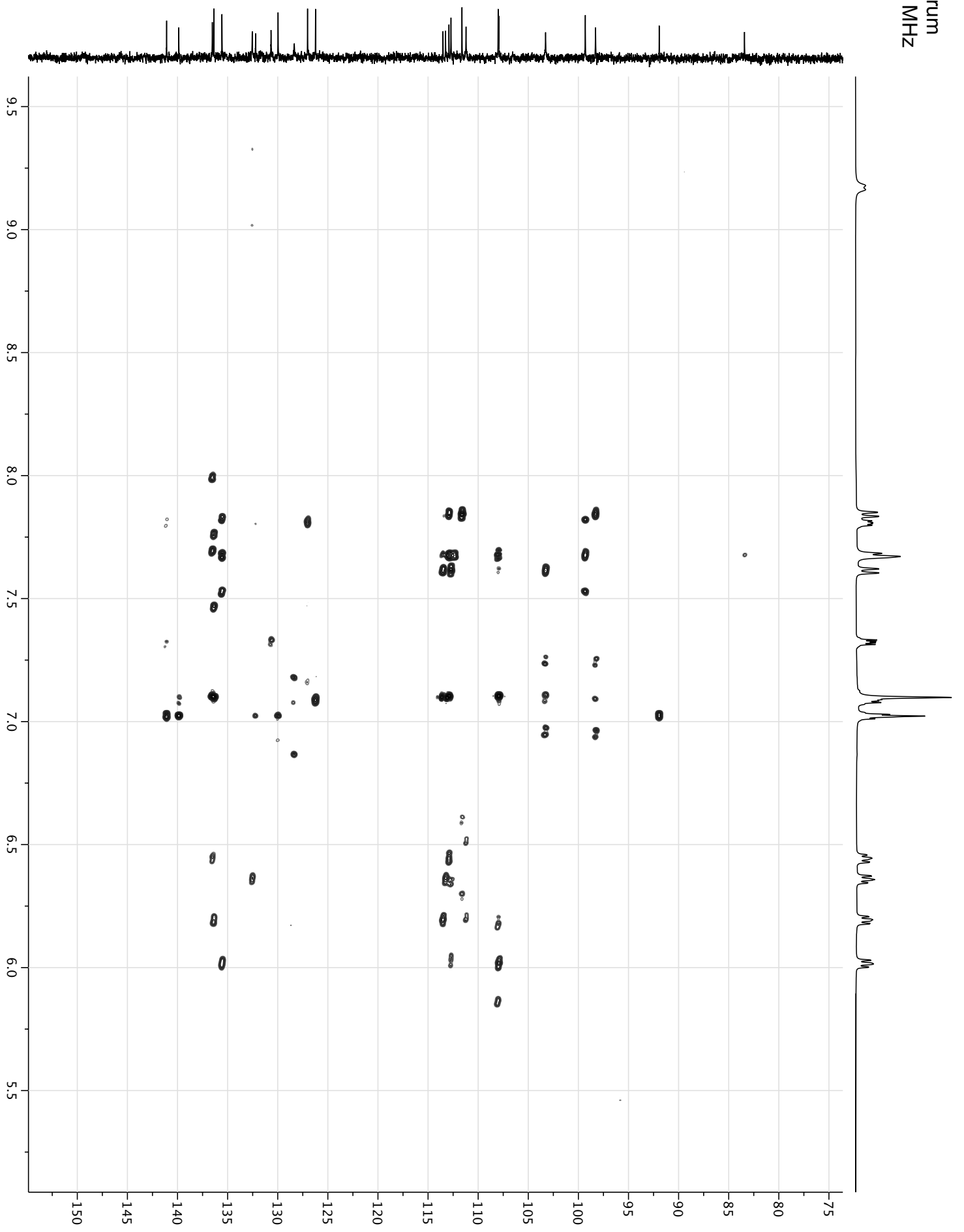


K₂dbcOT3
excitation transfer
THF-d8, 500 MHz, 223.9 K



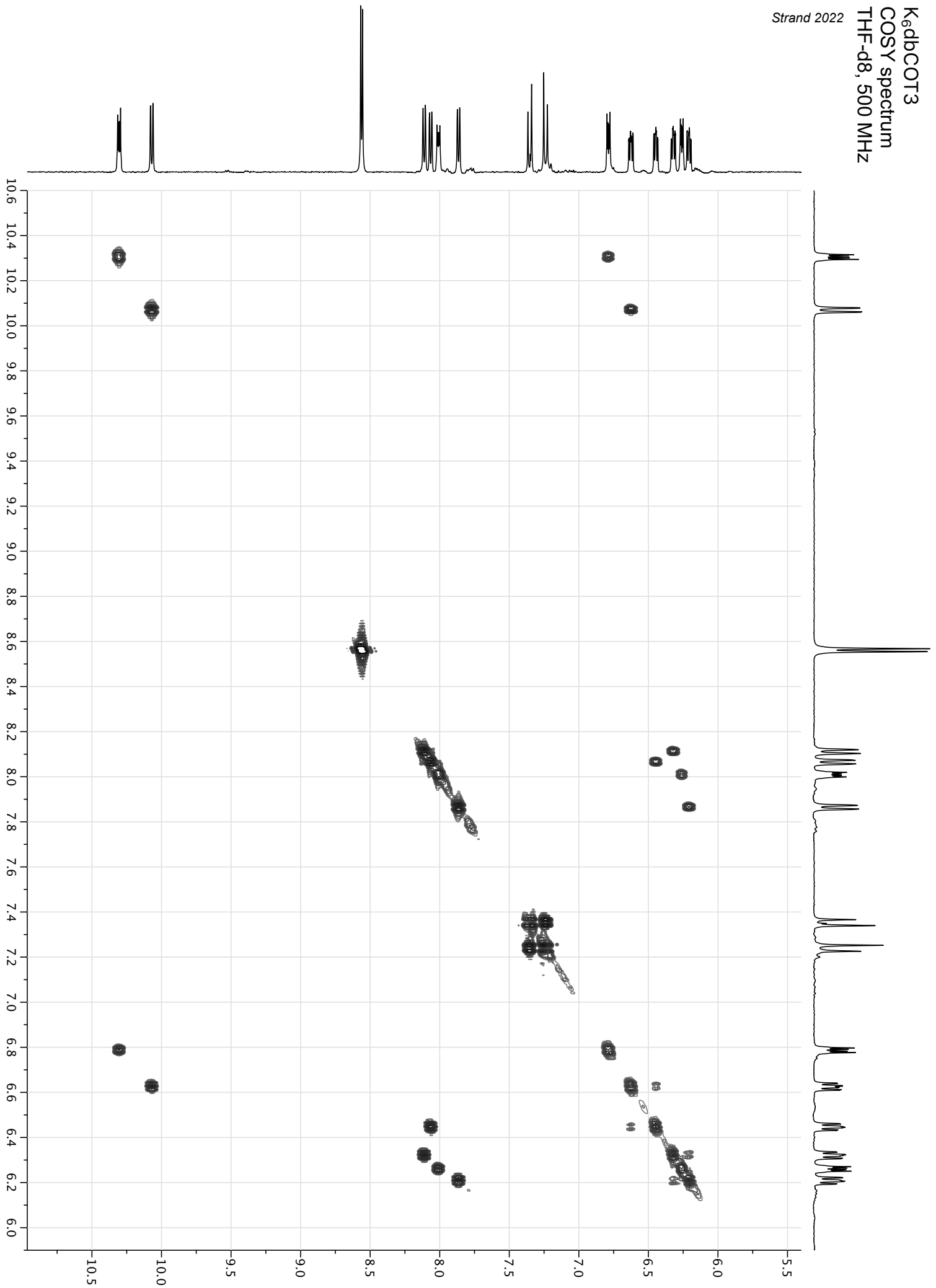






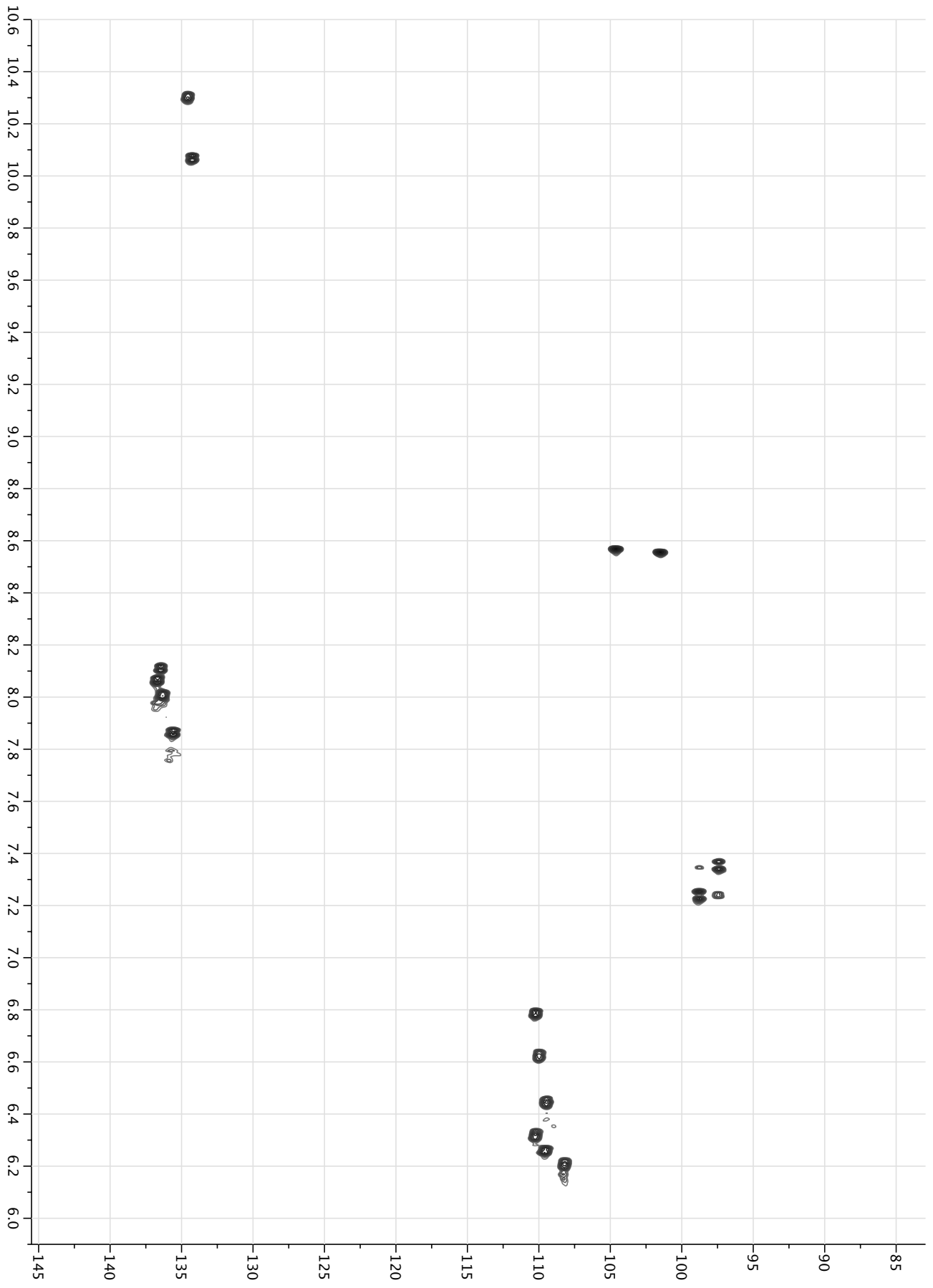
K₆dbCCOT3
COSY spectrum
THF-d₈, 500 MHz

Strand 2022



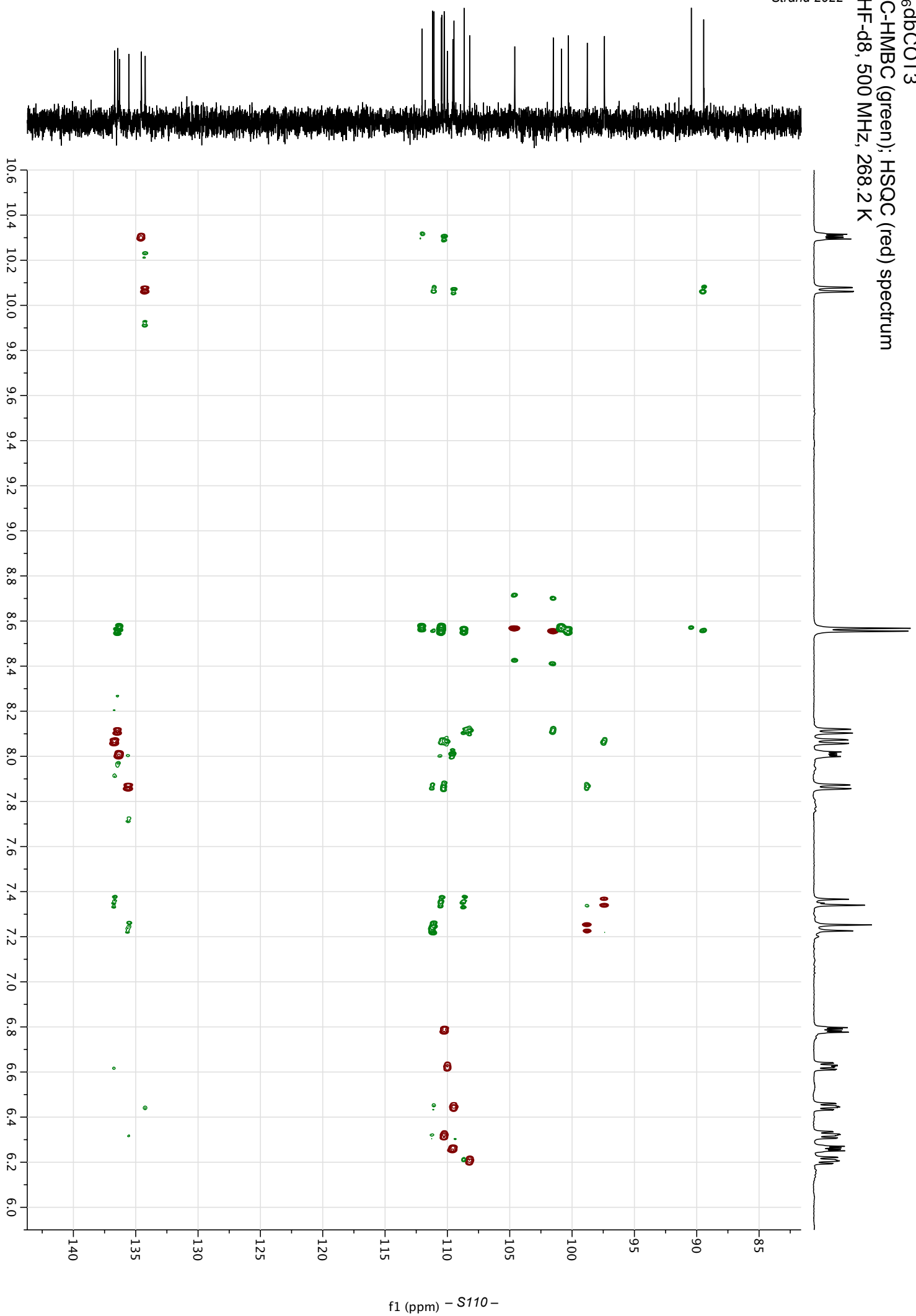
K₂dbbCOT₃
¹³C-HSQC spectrum
THF-d₈, 500 MHz, 268.2 K

Strand 2022

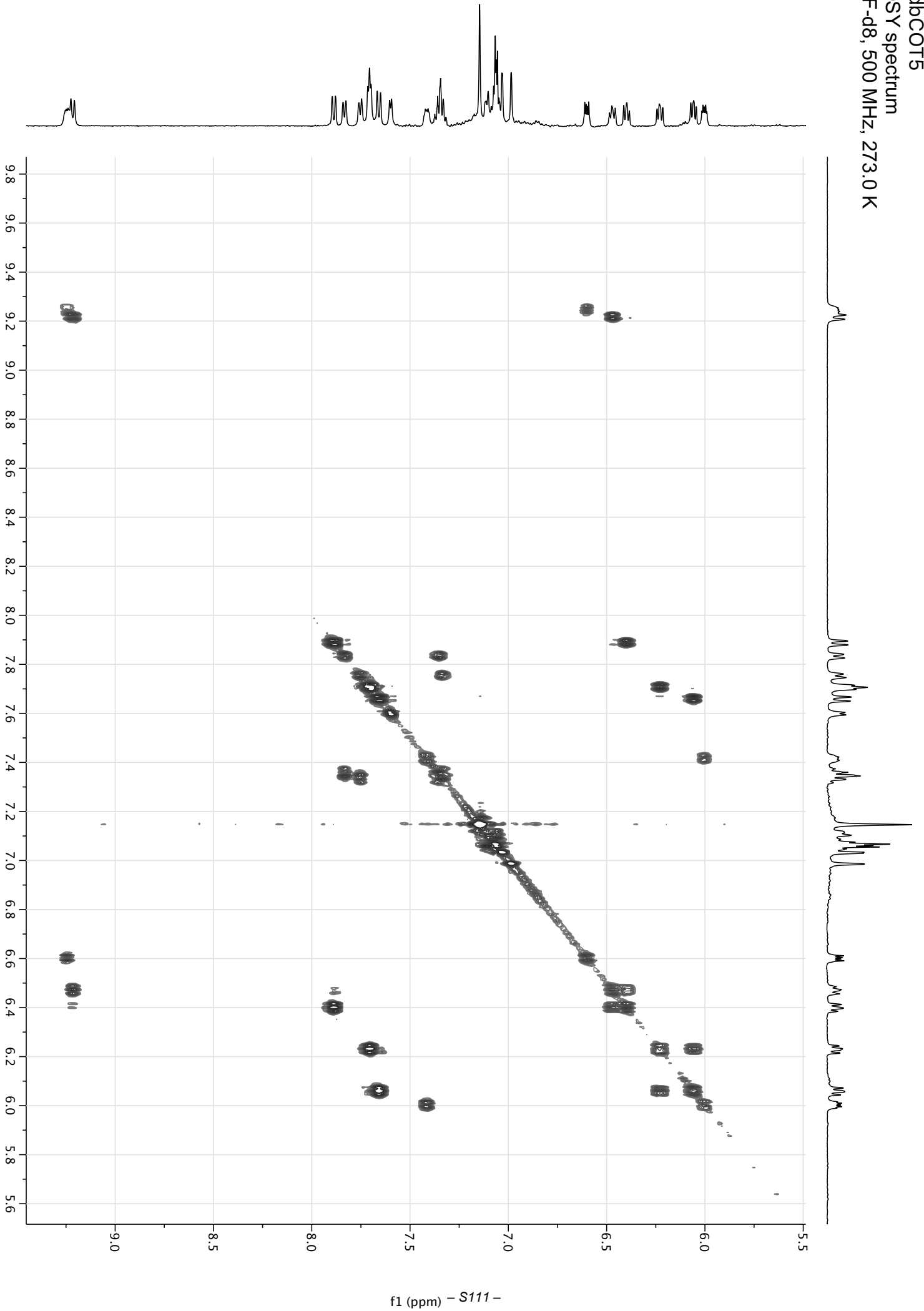


K₆dbccOT3
¹³C-HMBC (green); HSQC (red) spectrum
THF-d₈, 500 MHz, 268.2 K

Strand 2022

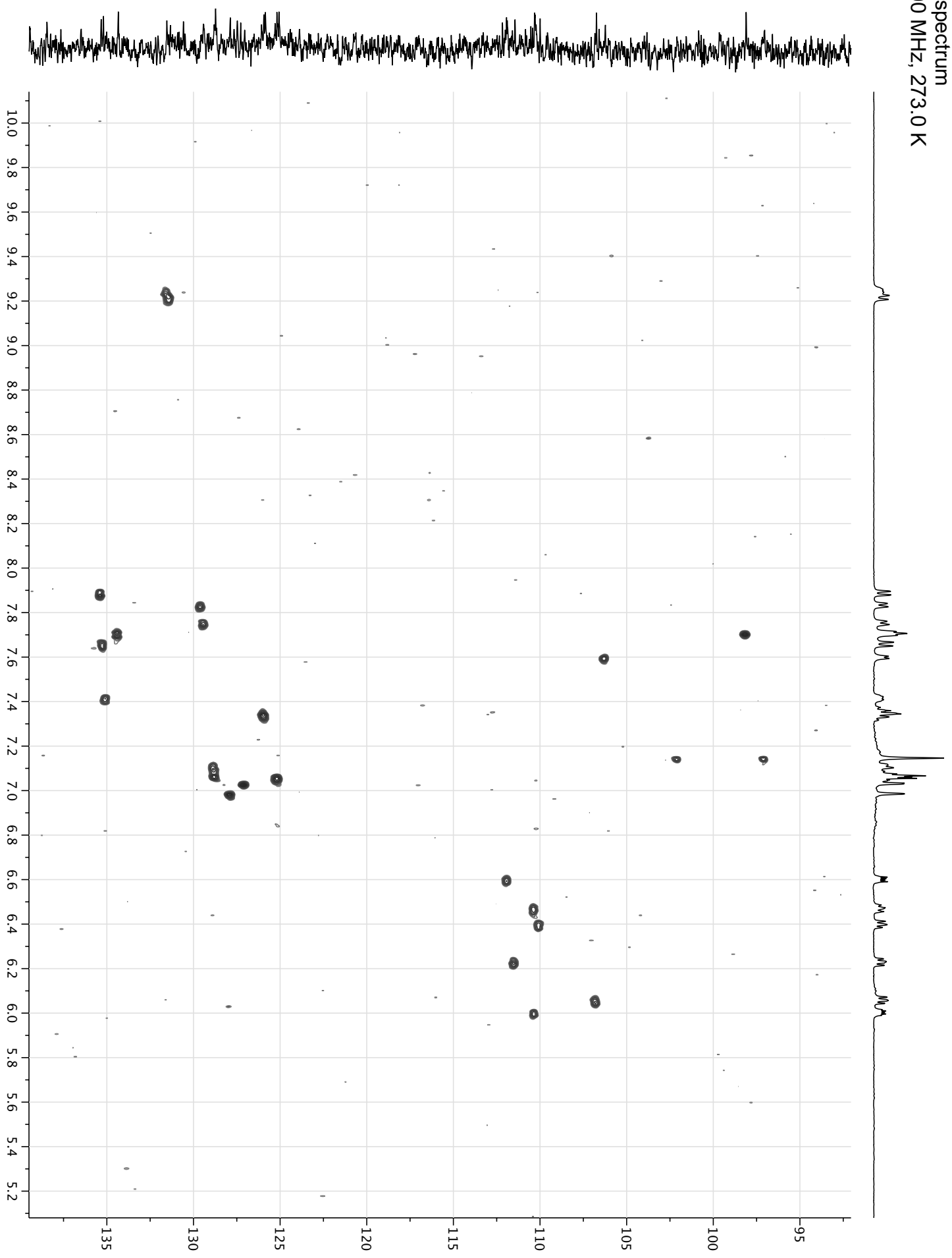


K₂O/COT5
COSY spectrum
THF-d₈, 500 MHz, 273.0 K



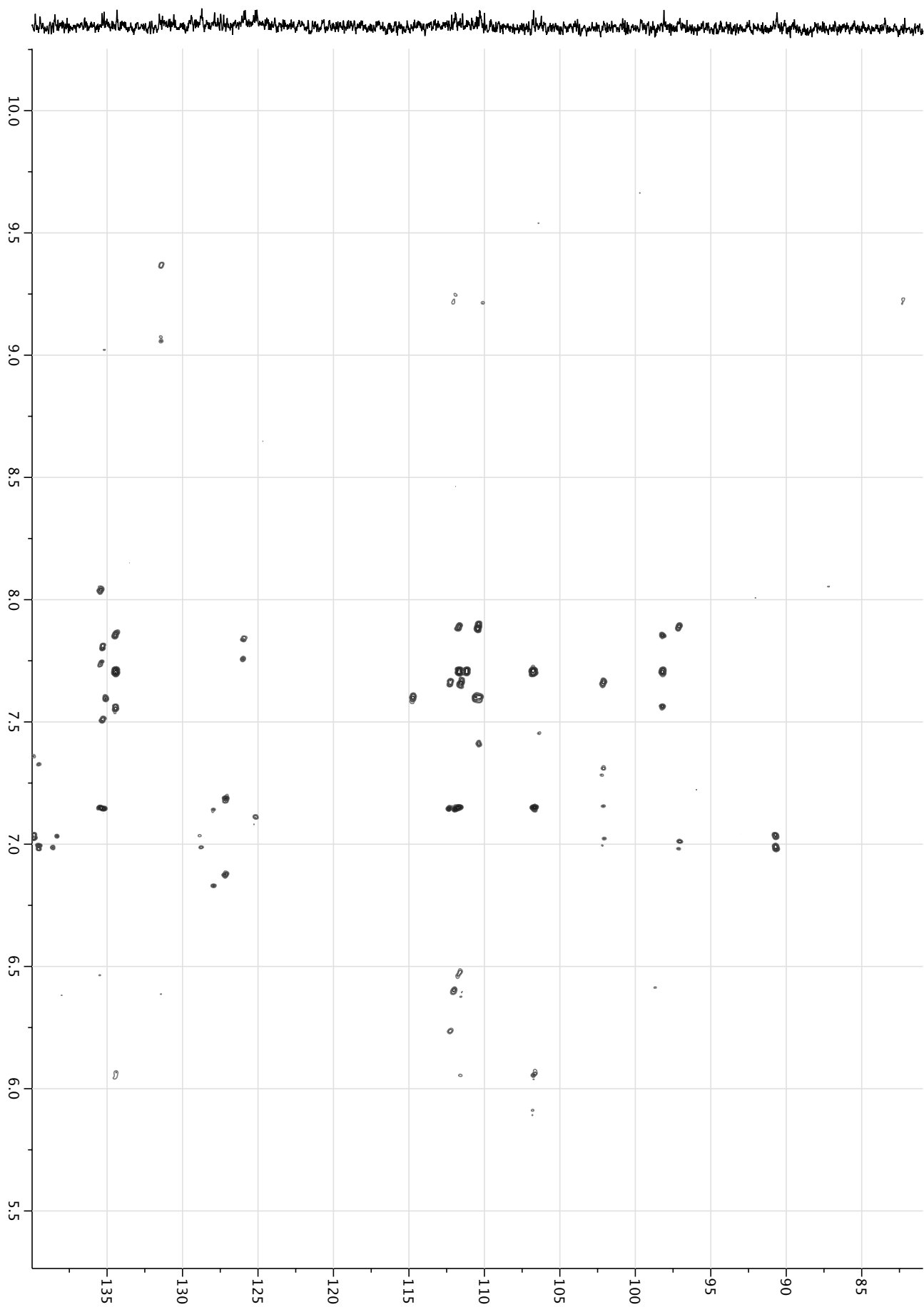
K₆dbCCOT5
¹³C-HSQC spectrum
THF-d₈, 500 MHz, 273.0 K

Strand 2022

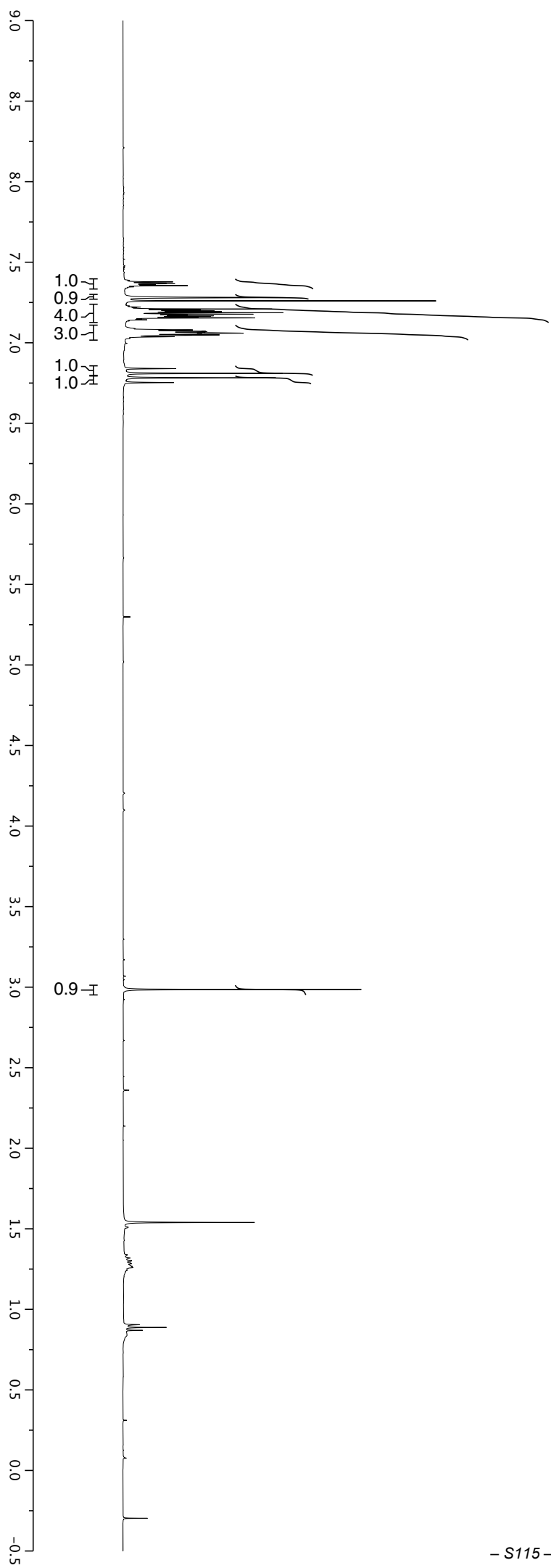
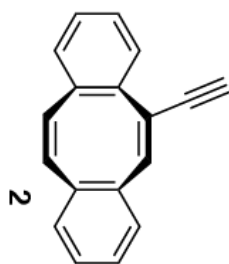


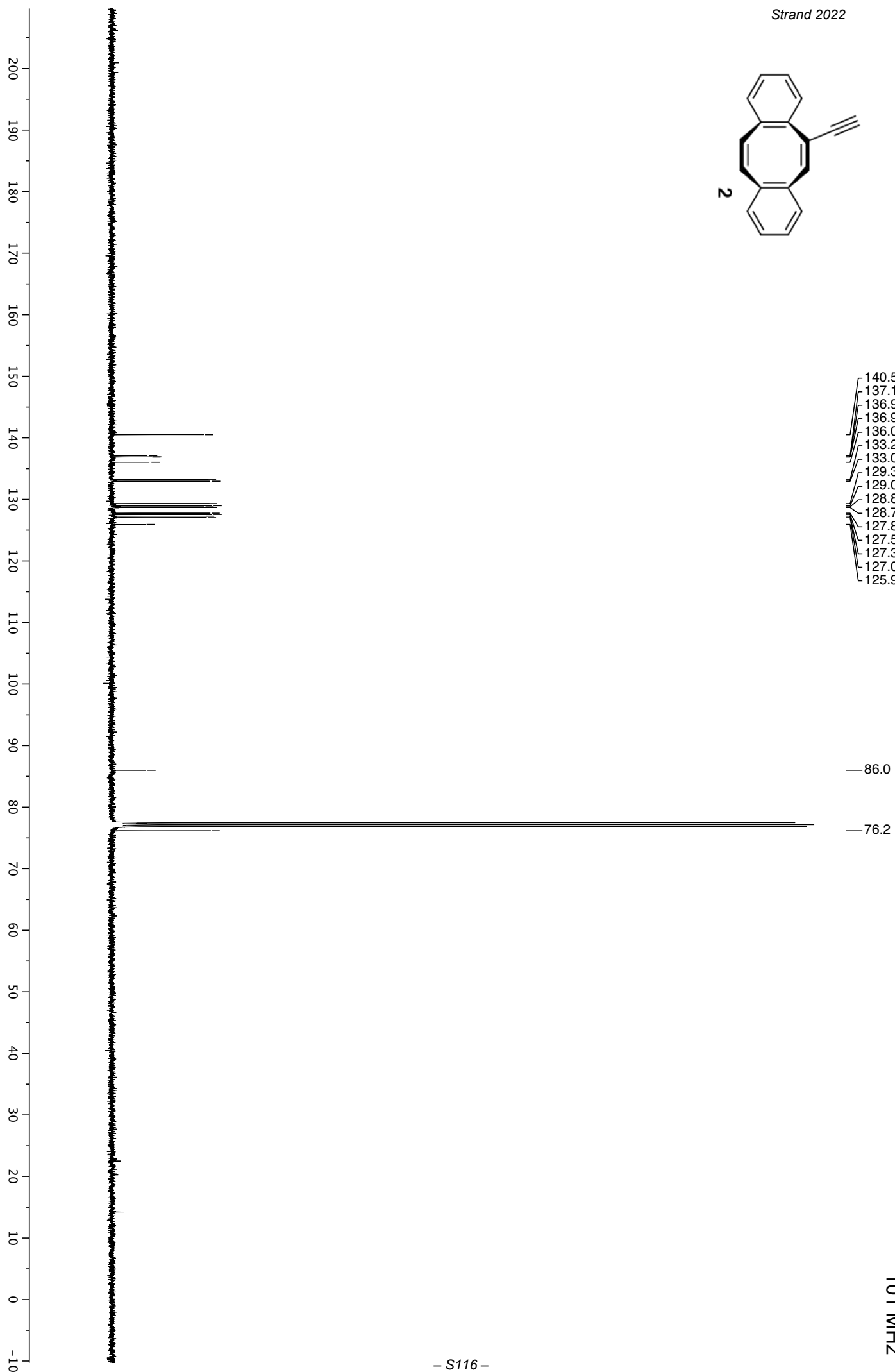
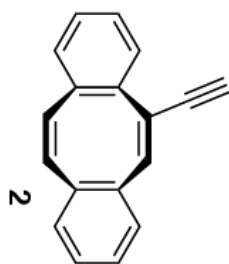
K₆dbCCOT5
¹³C-HMBC spectrum
THF-d₈, 500 MHz, 273.0 K

Strand 2022

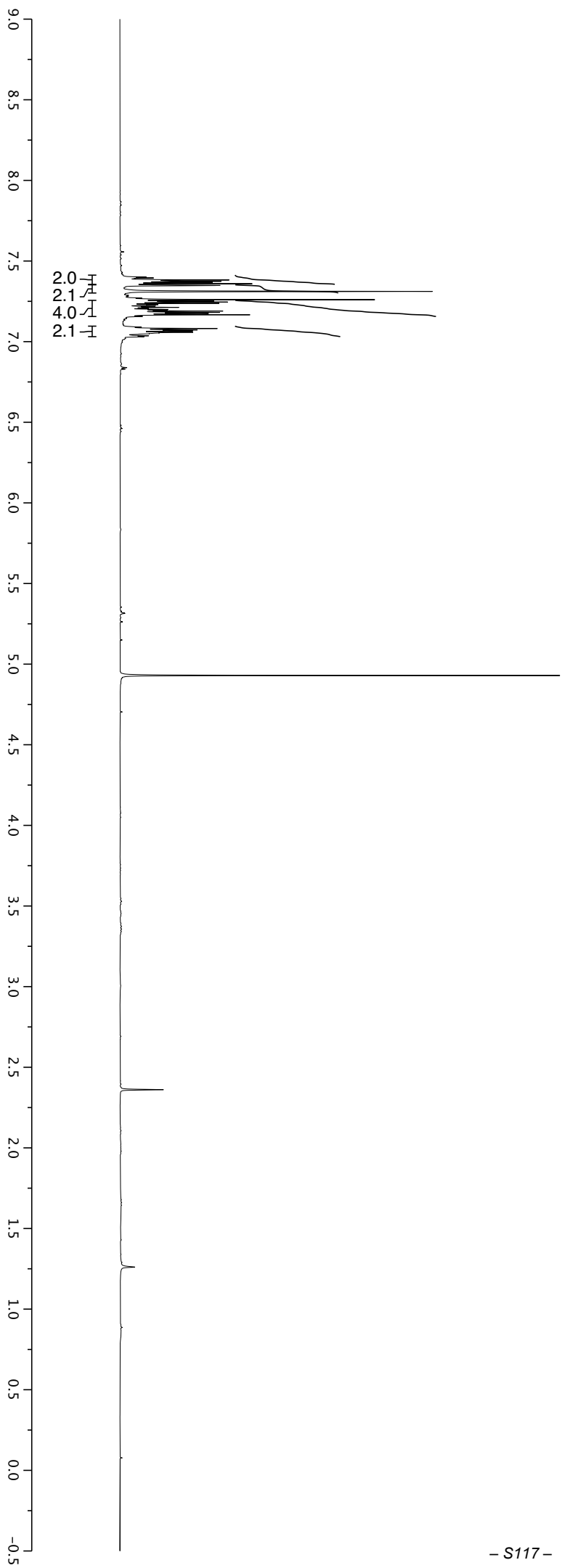
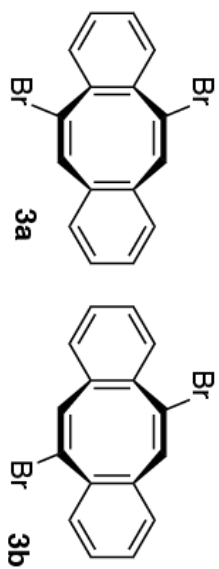


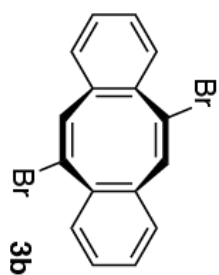
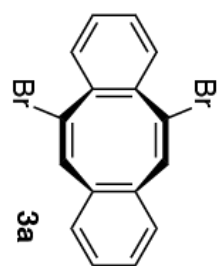
XIV. Copies of ^1H and ^{13}C NMR spectra



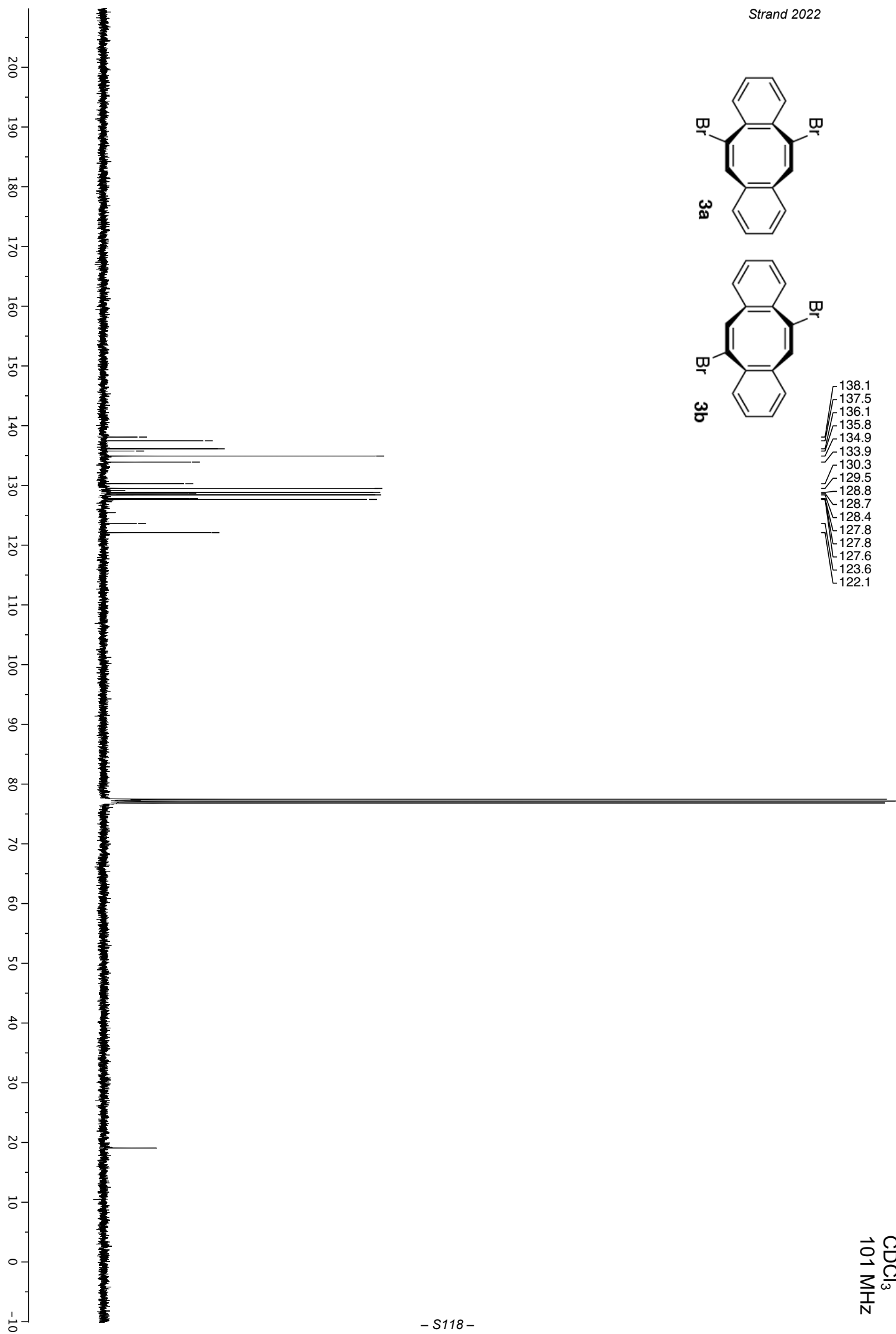


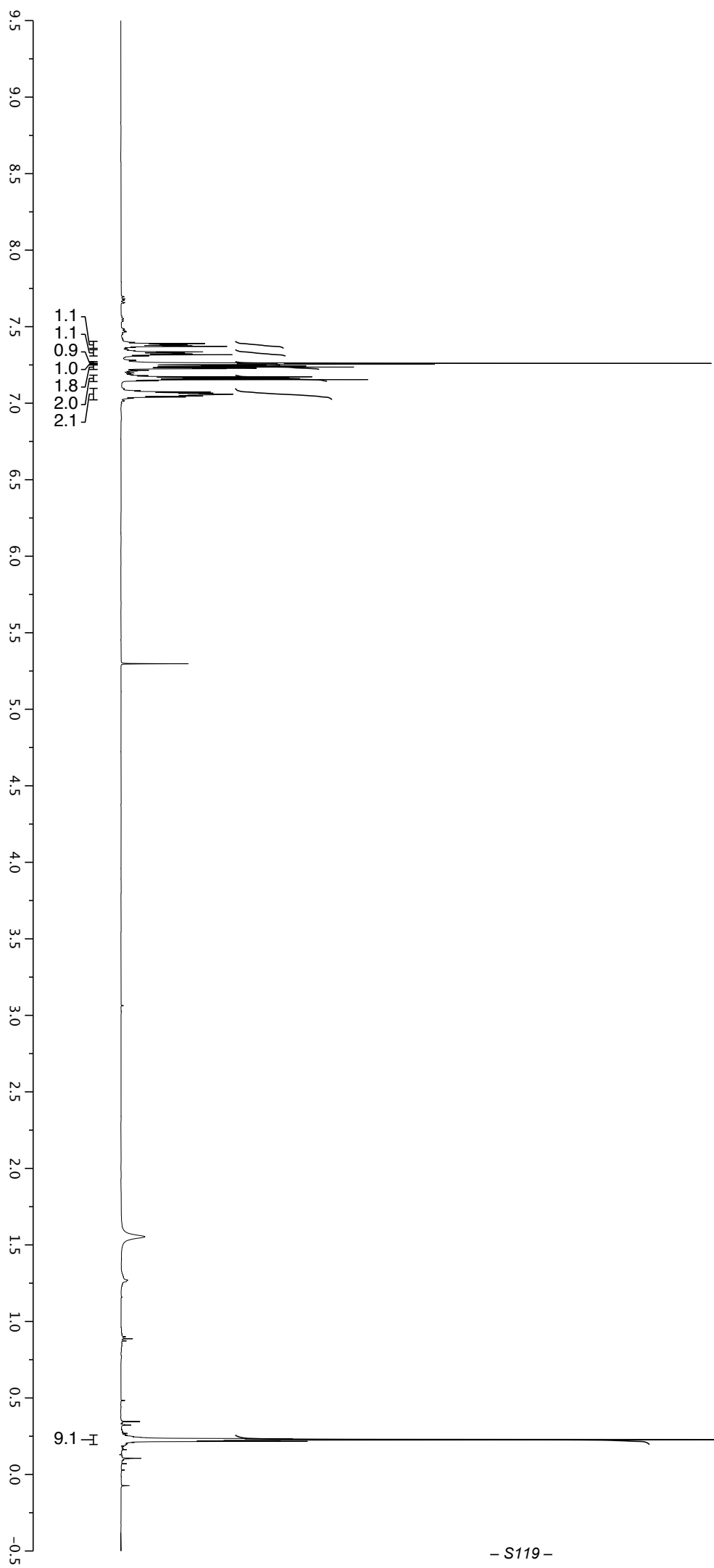
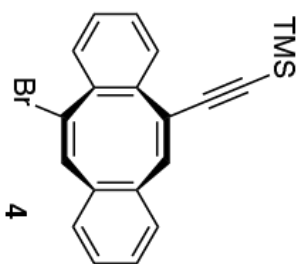
CDCl₃
101 MHz

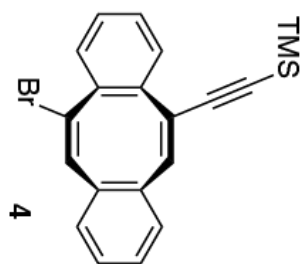




138.1
137.5
136.1
135.8
134.9
133.9
130.3
129.5
128.8
128.7
128.4
127.8
127.8
127.6
123.6
122.1





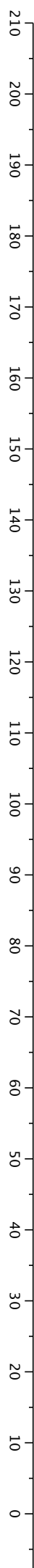


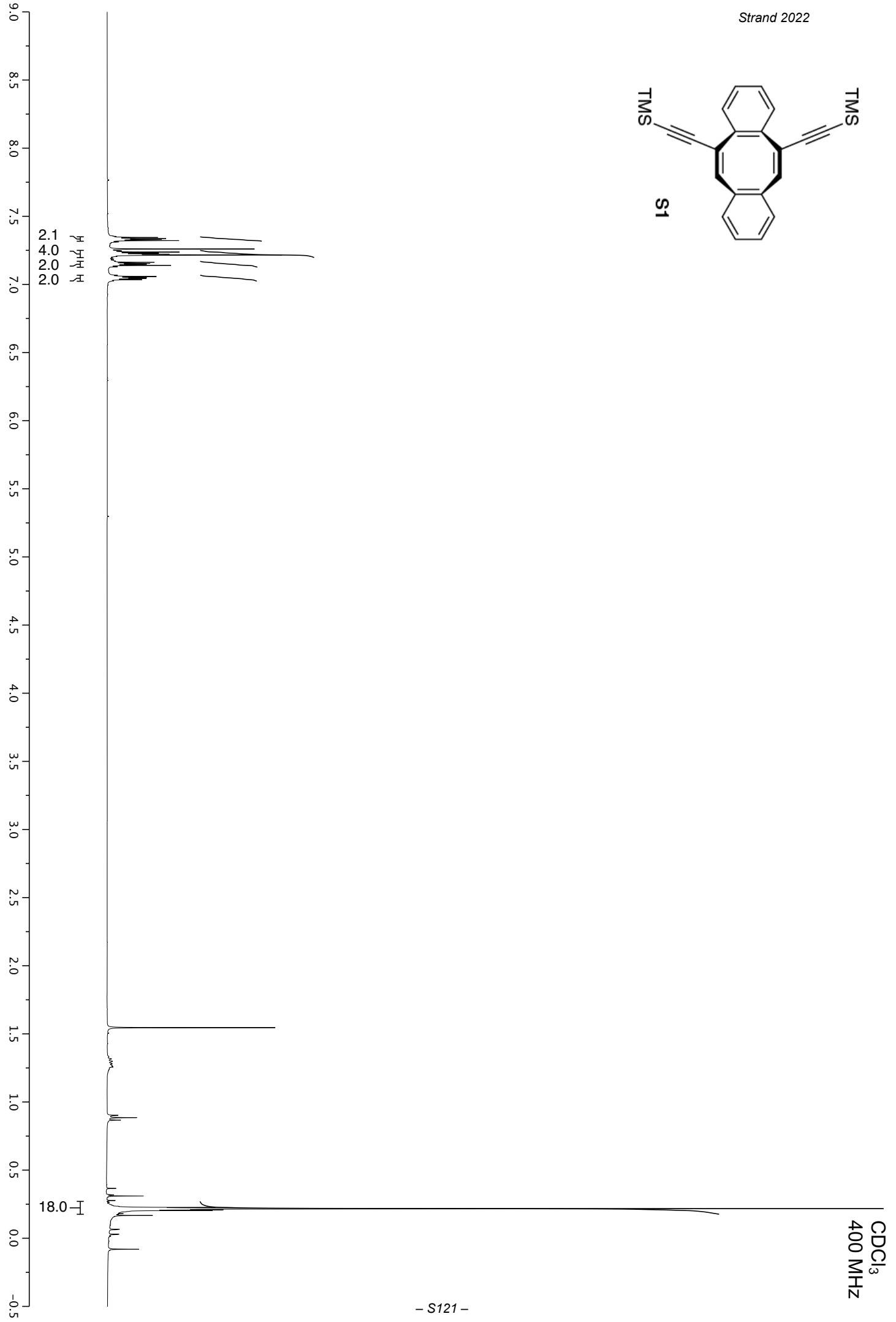
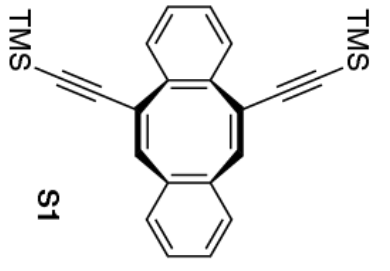
- 139.7
- 138.1
- 136.4
- 136.3
- 135.9
- 134.6
- 129.8
- 128.9
- 128.8
- 128.7
- 128.3
- 128.0
- 127.6
- 127.5
- 126.5
- 122.7

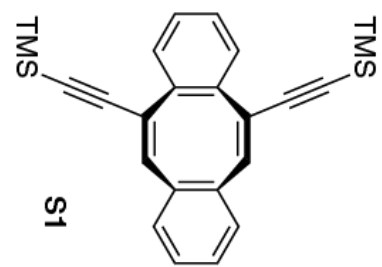
106.3

94.3

CDCl₃
126 MHz
0.1





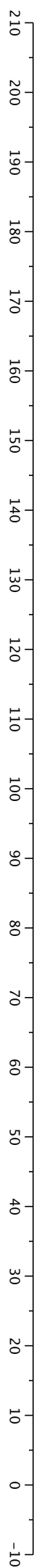


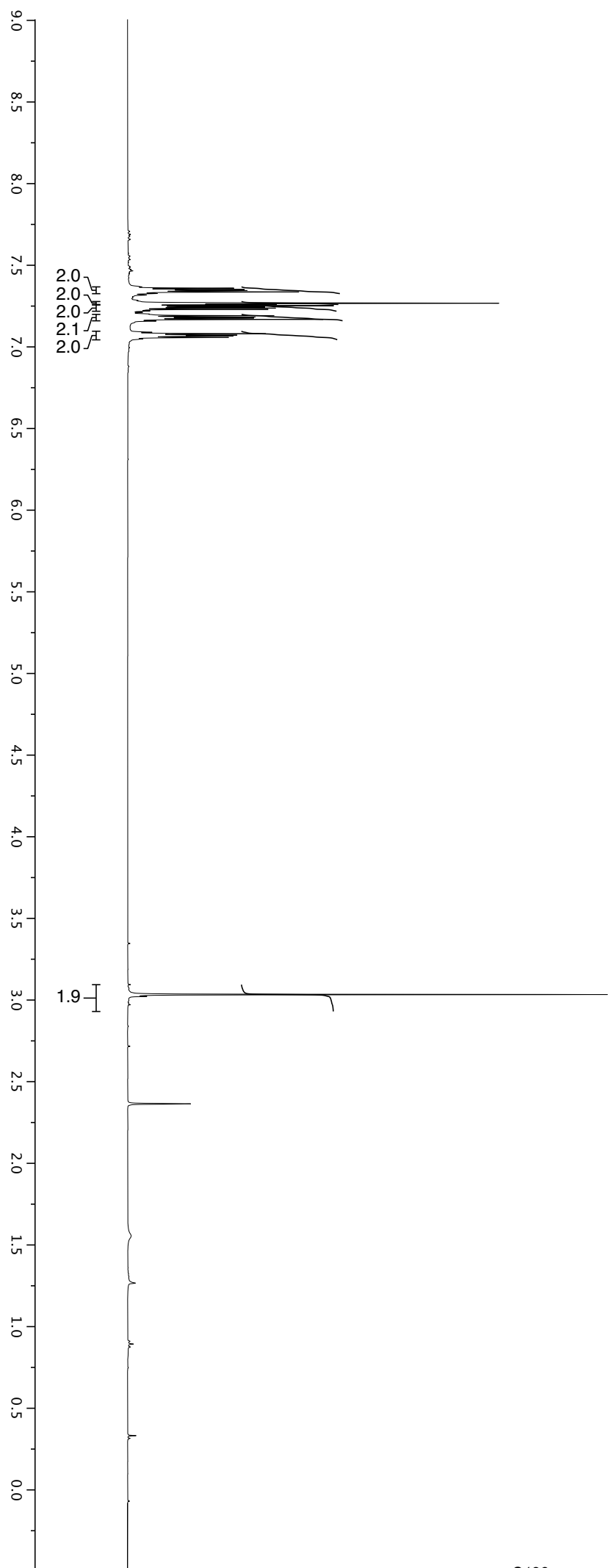
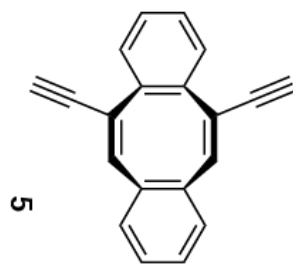
- 139.7
- 136.7
- 136.2
- 129.2
- 128.6
- 127.9
- 127.5
- 126.9

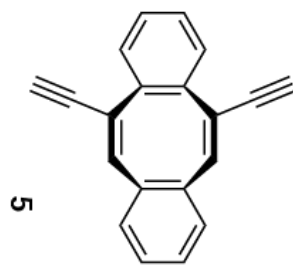
106.8

93.8

CDCl₃
101 MHz
0.1







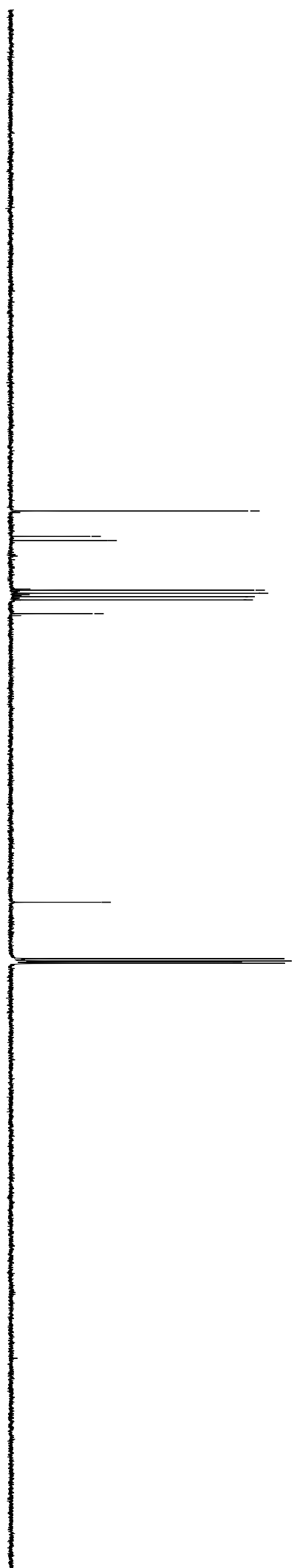
140.1
136.5
135.9
129.0
128.6
128.1
127.6
125.7

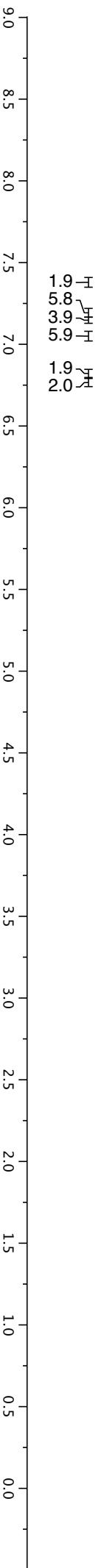
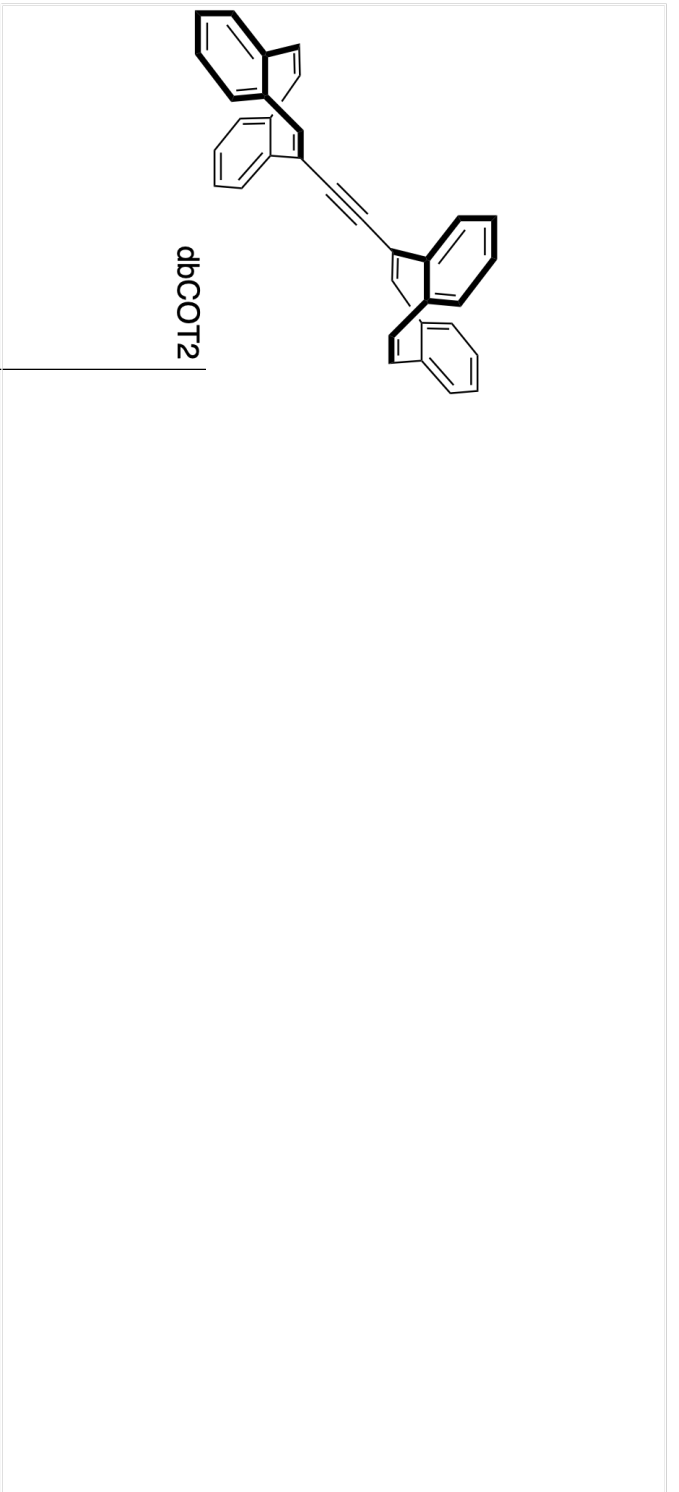
85.4

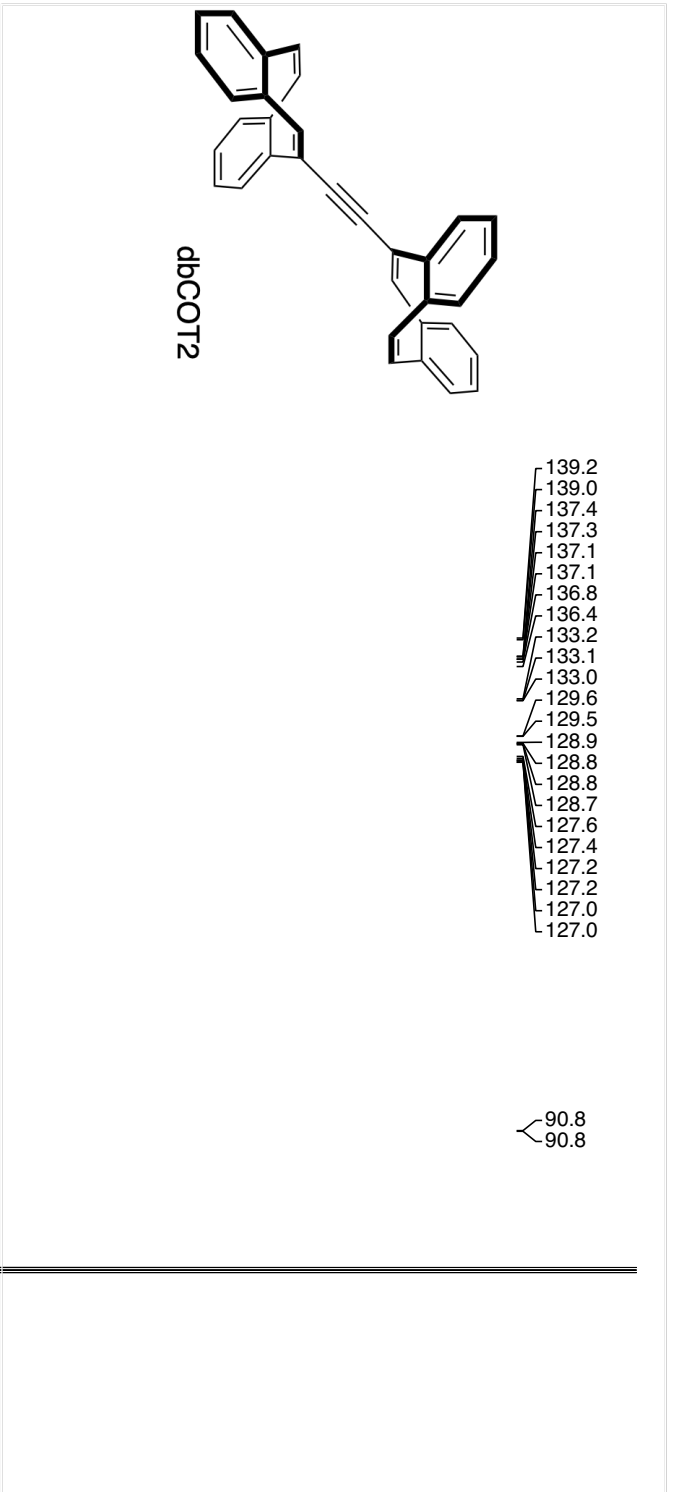
77.0

CDCl₃
101 MHz

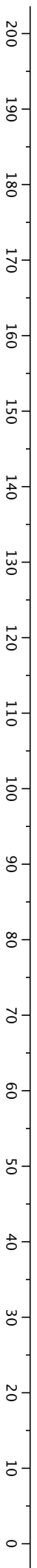
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

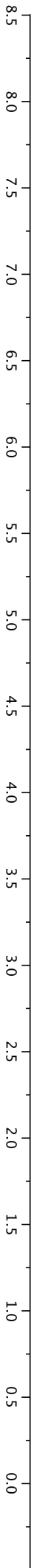
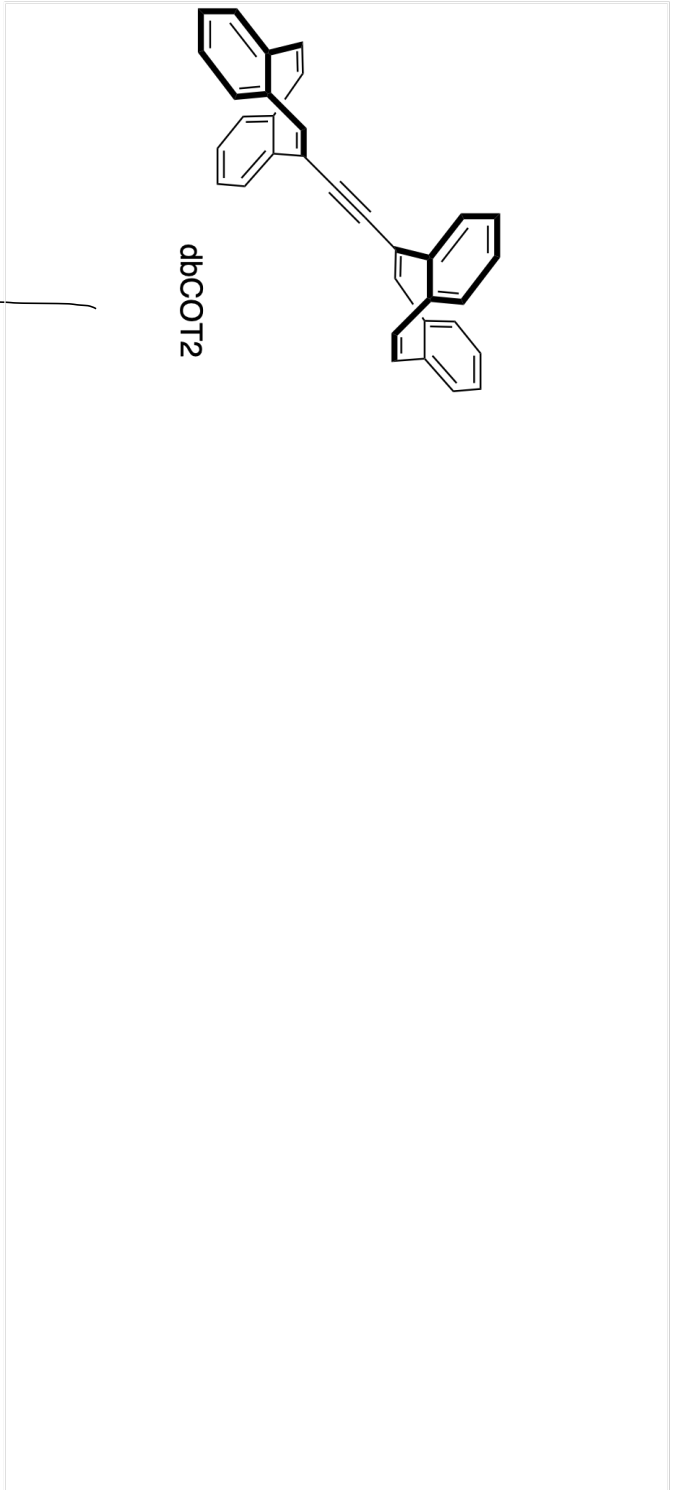


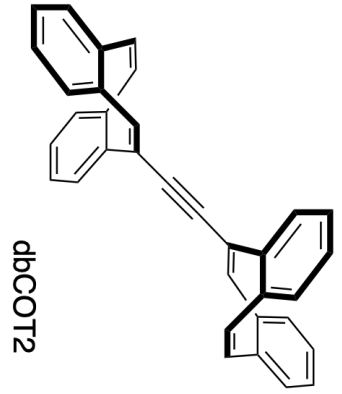




CDCl₃
126 MHz

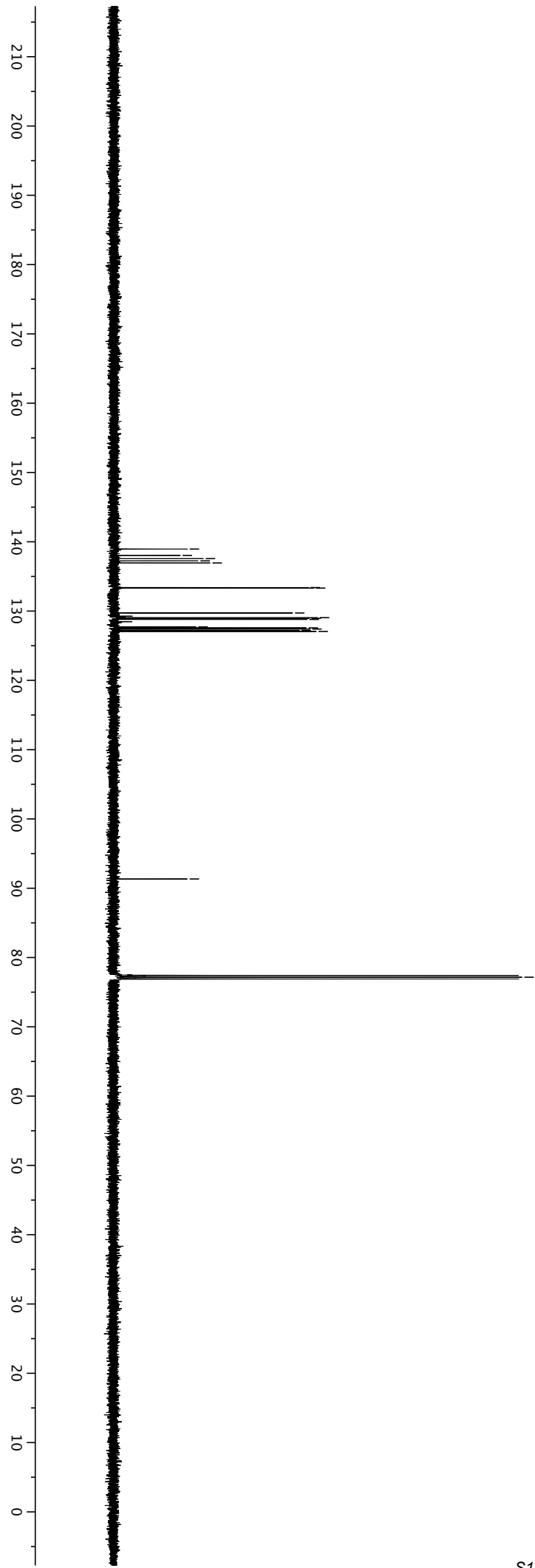




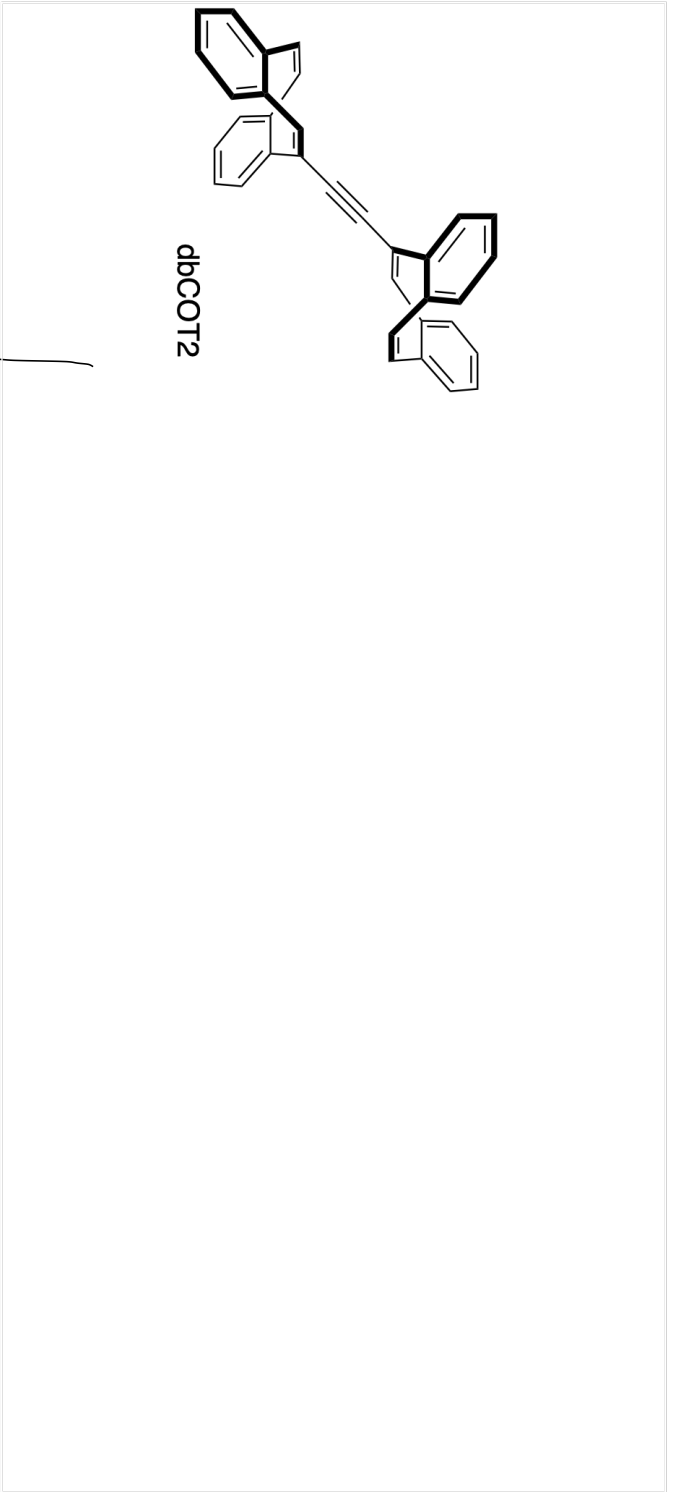


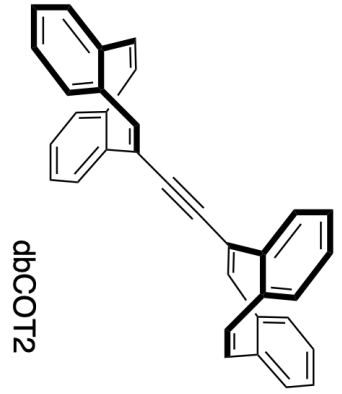
- 138.9
 - 138.0
 - 137.6
 - 137.2
 - 136.9
 - 133.4
 - 133.3
 - 129.7
 - 129.0
 - 128.9
 - 128.8
 - 127.7
 - 127.6
 - 127.4
 - 127.2
 - 127.1
- 91.3
- 77.2 CDCl₃

CDCl₃
126 MHz
373.2 K



THF-d8
500 MHz
295.0 K



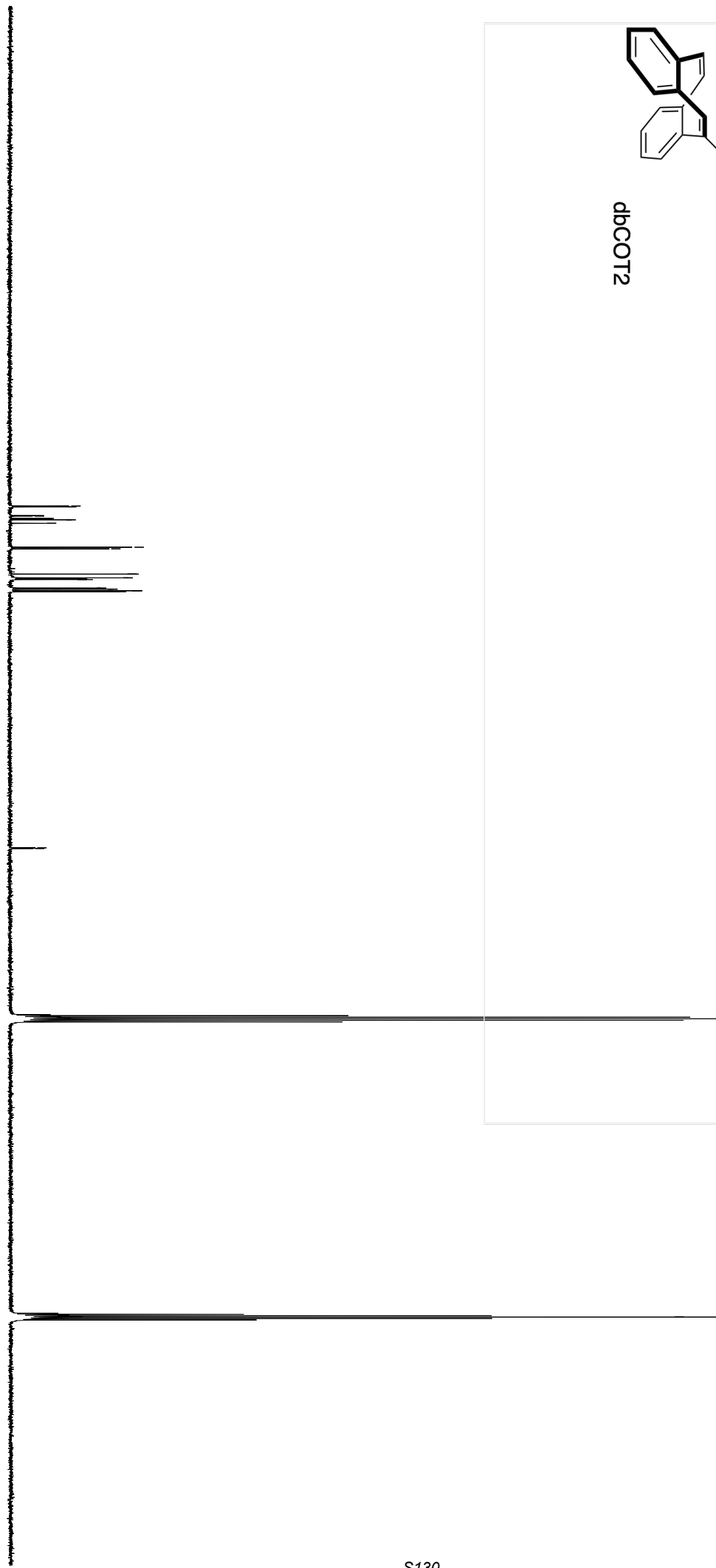
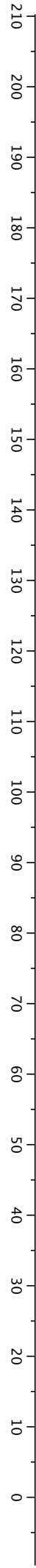


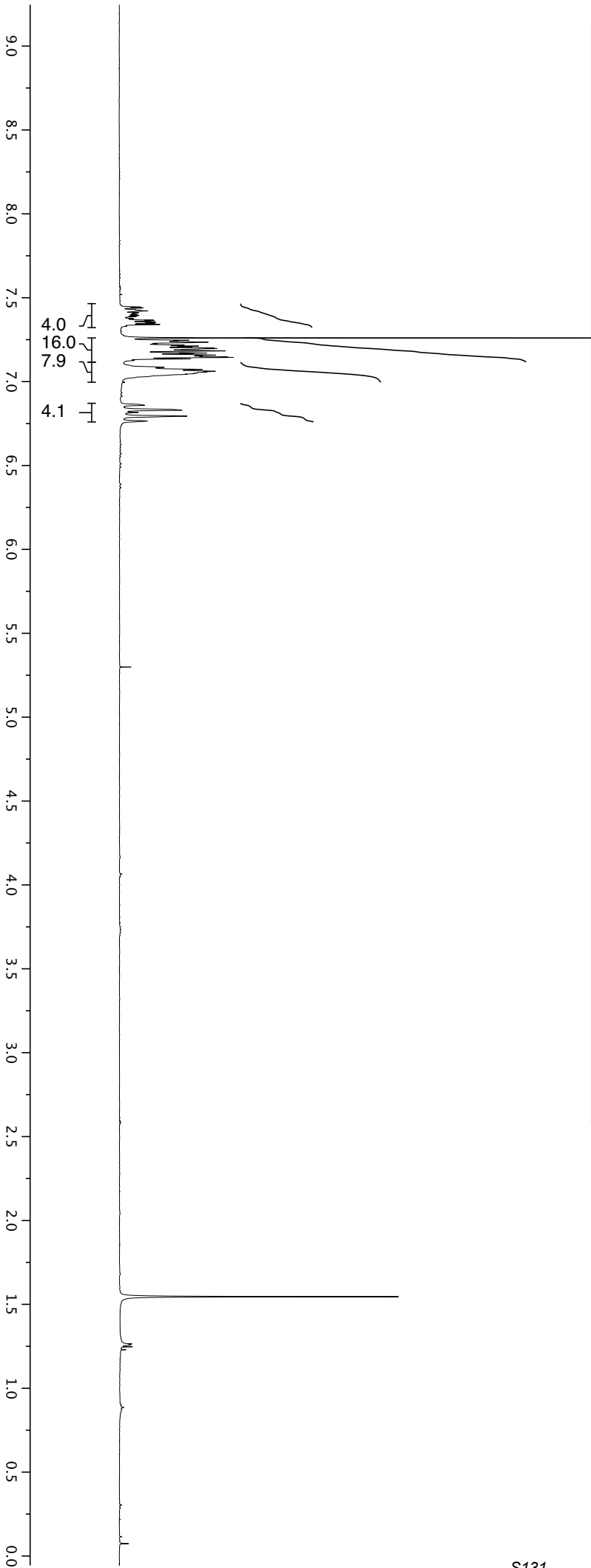
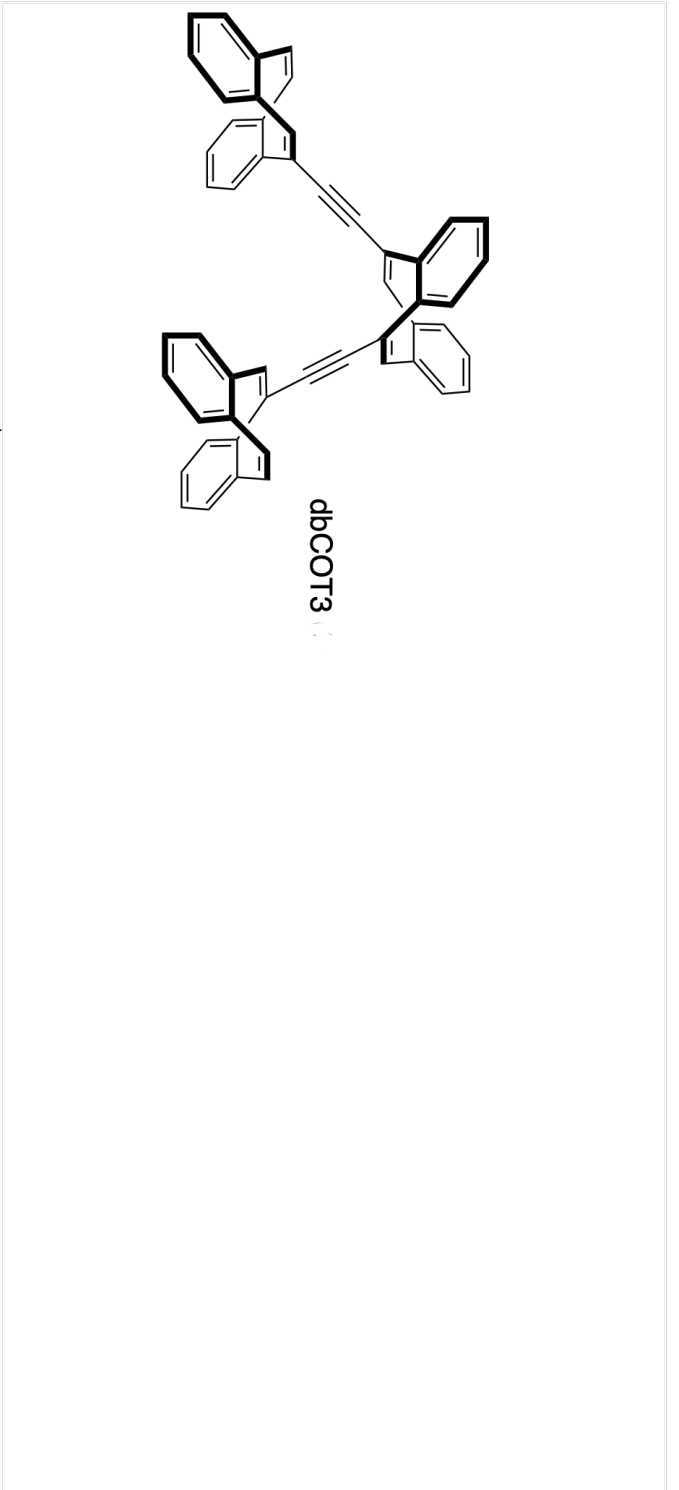
- 139.8
- 139.7
- 138.4
- 138.4
- 138.0
- 137.8
- 137.3
- 134.0
- 133.7
- 130.2
- 129.6
- 129.5
- 129.5
- 129.4
- 128.2
- 128.1
- 128.0
- 127.8
- 127.7

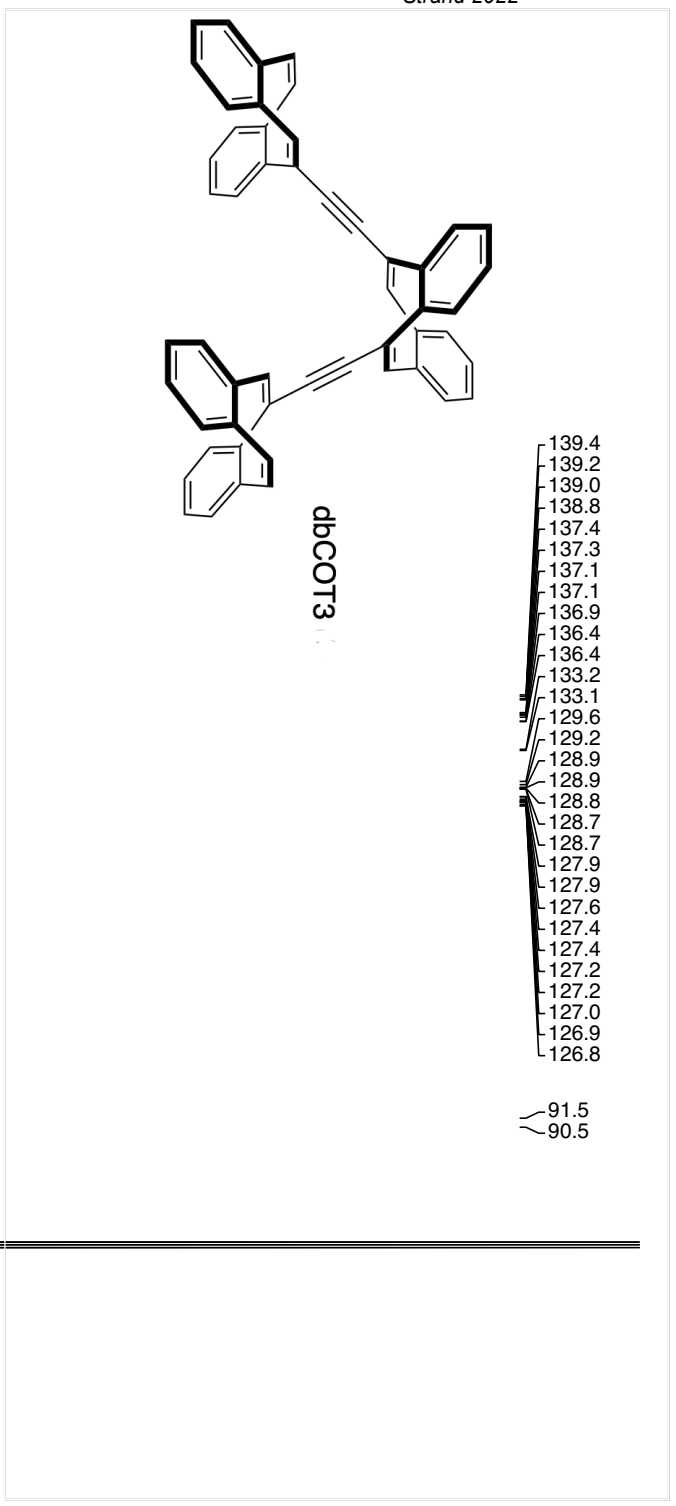
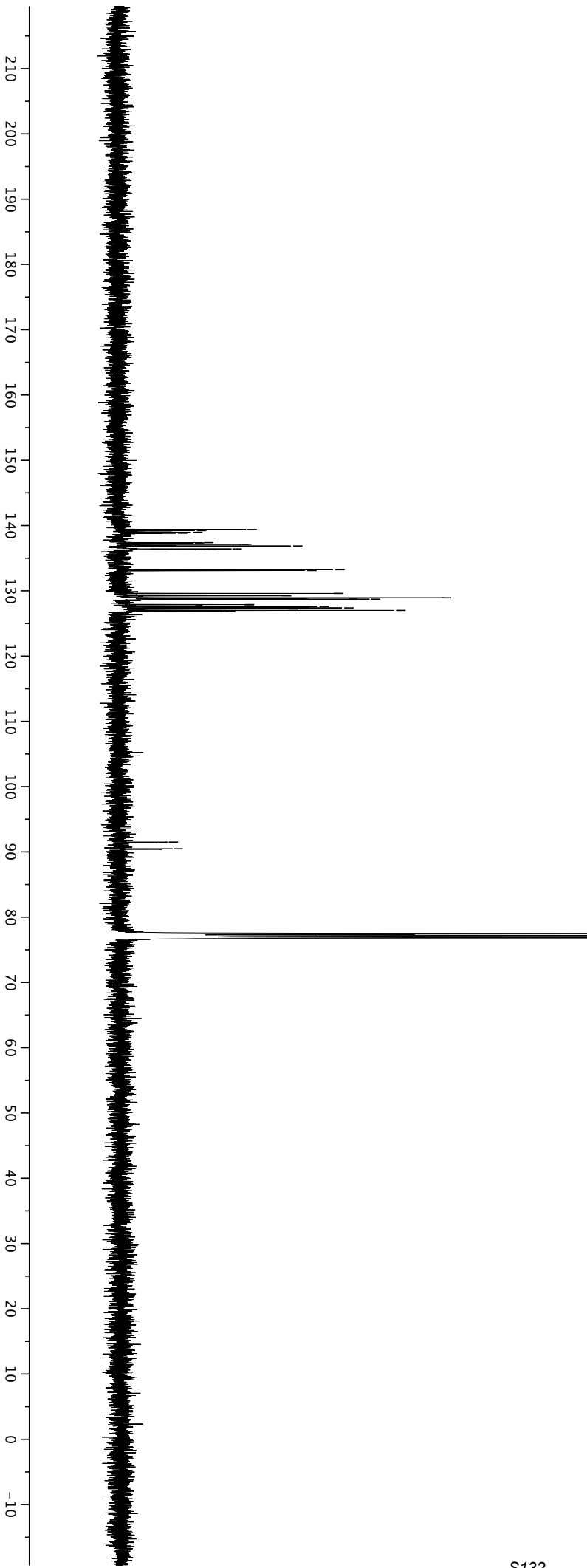
- 91.6
- 91.5

— 25.4 THF-d8

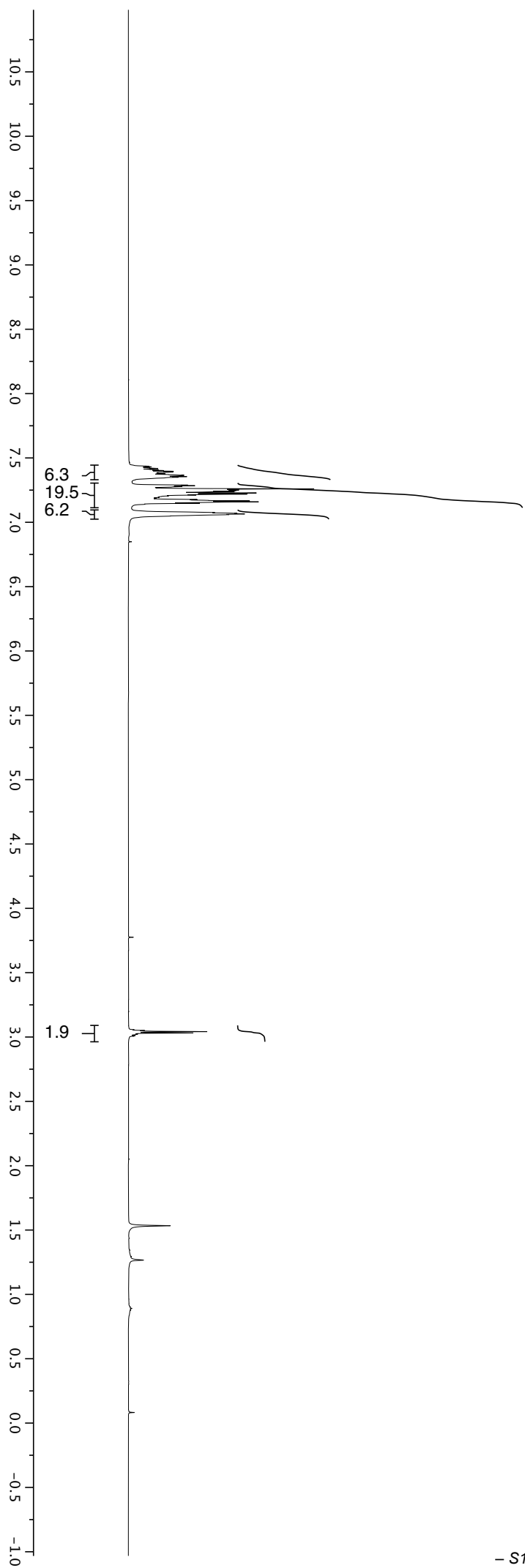
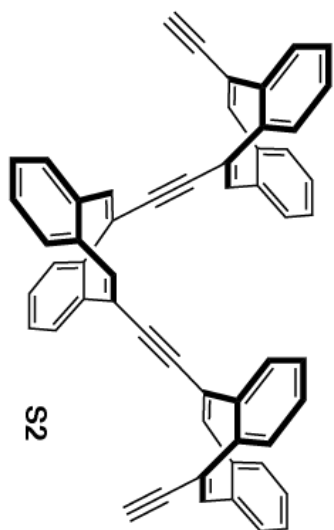
THF-d8
126 MHz
295.0 K

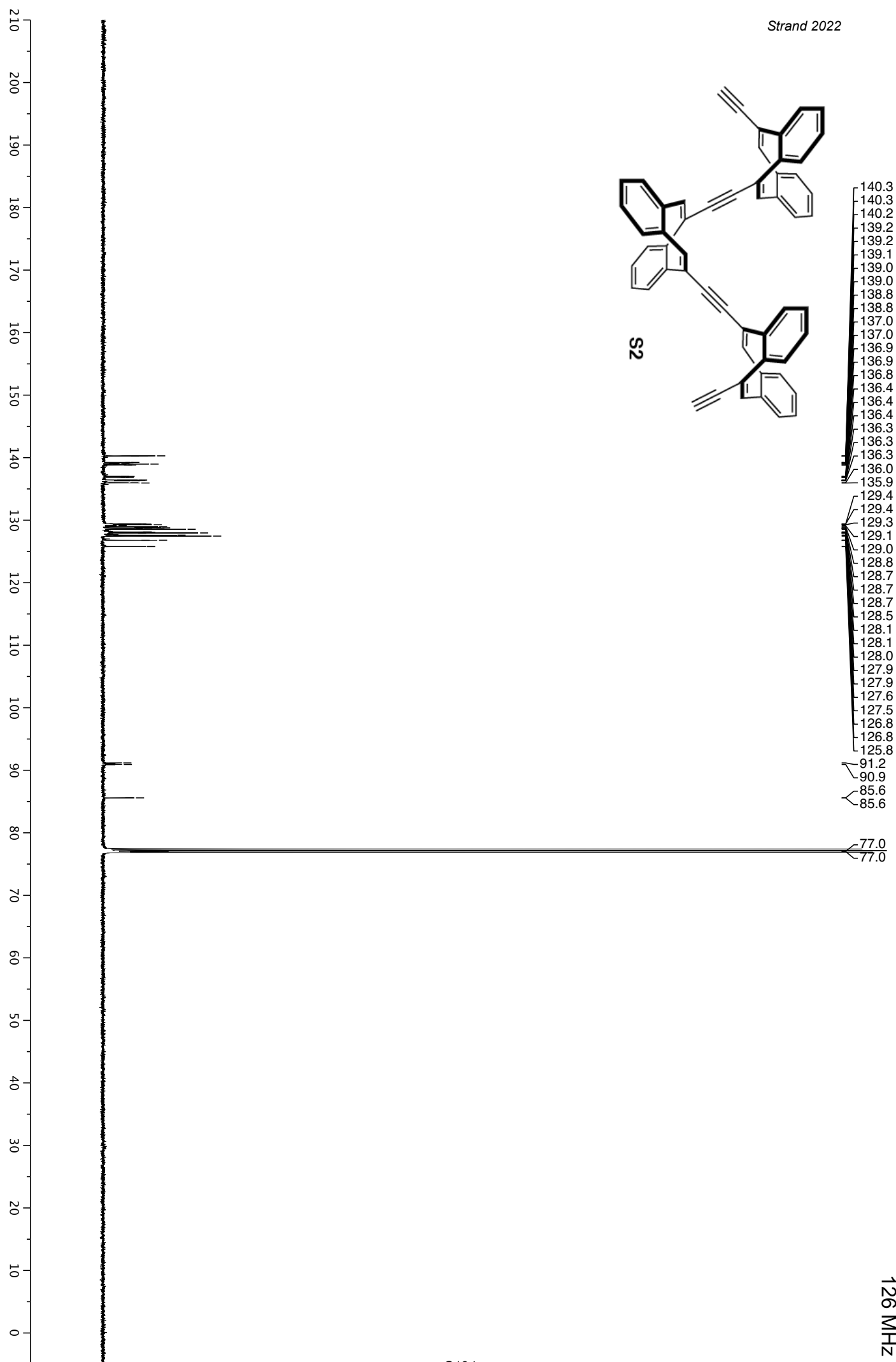


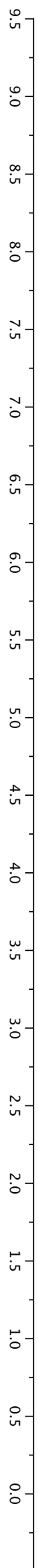
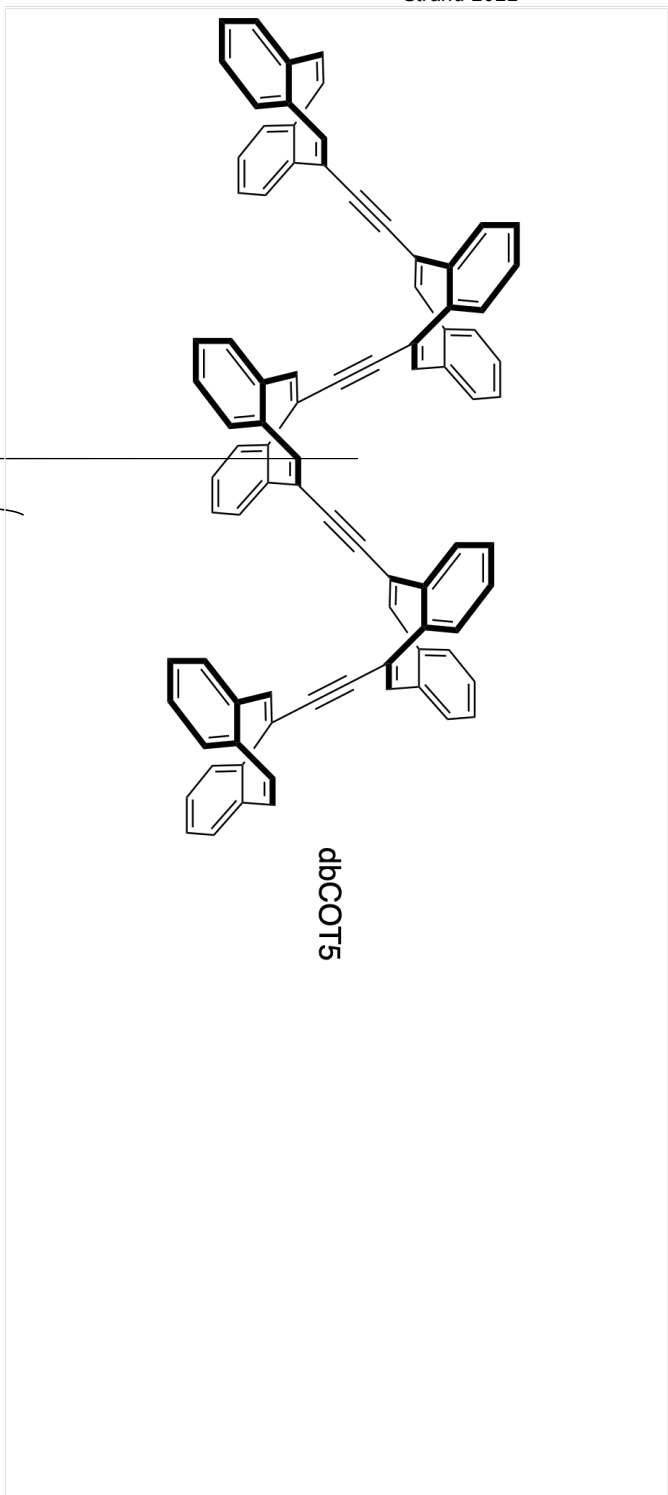




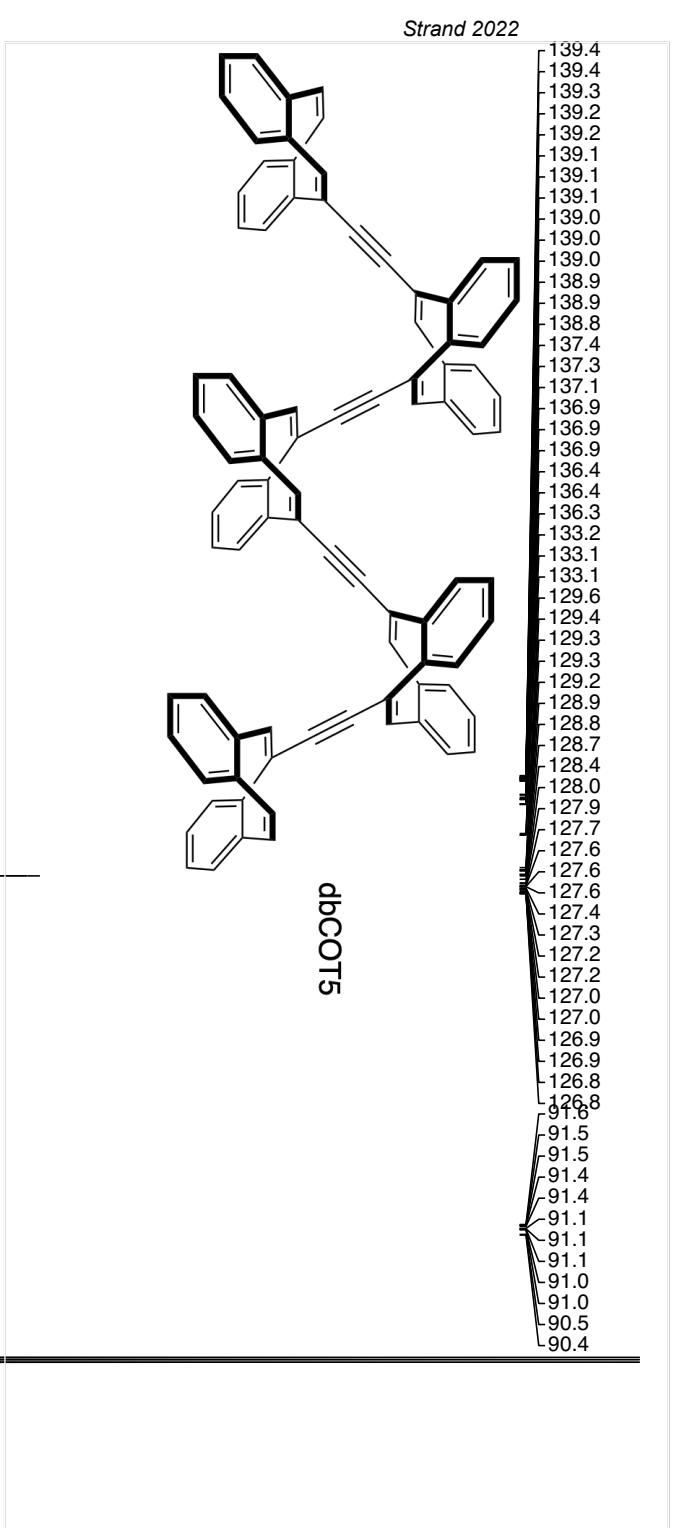
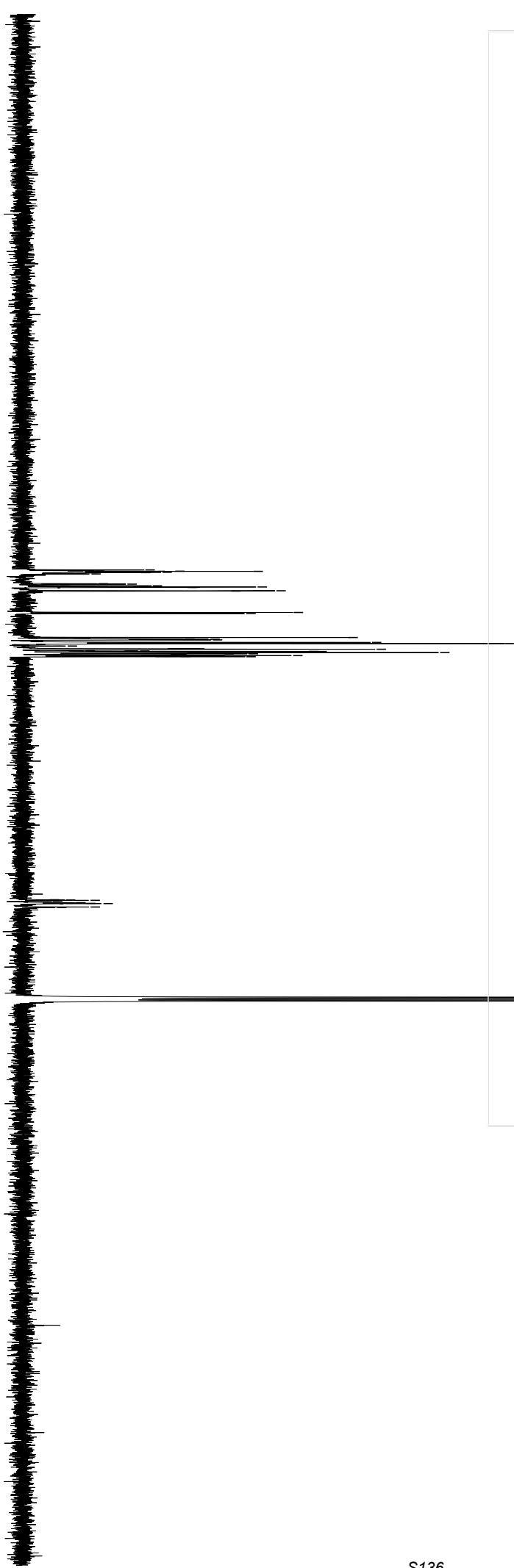
CDCl₃
101 MHz



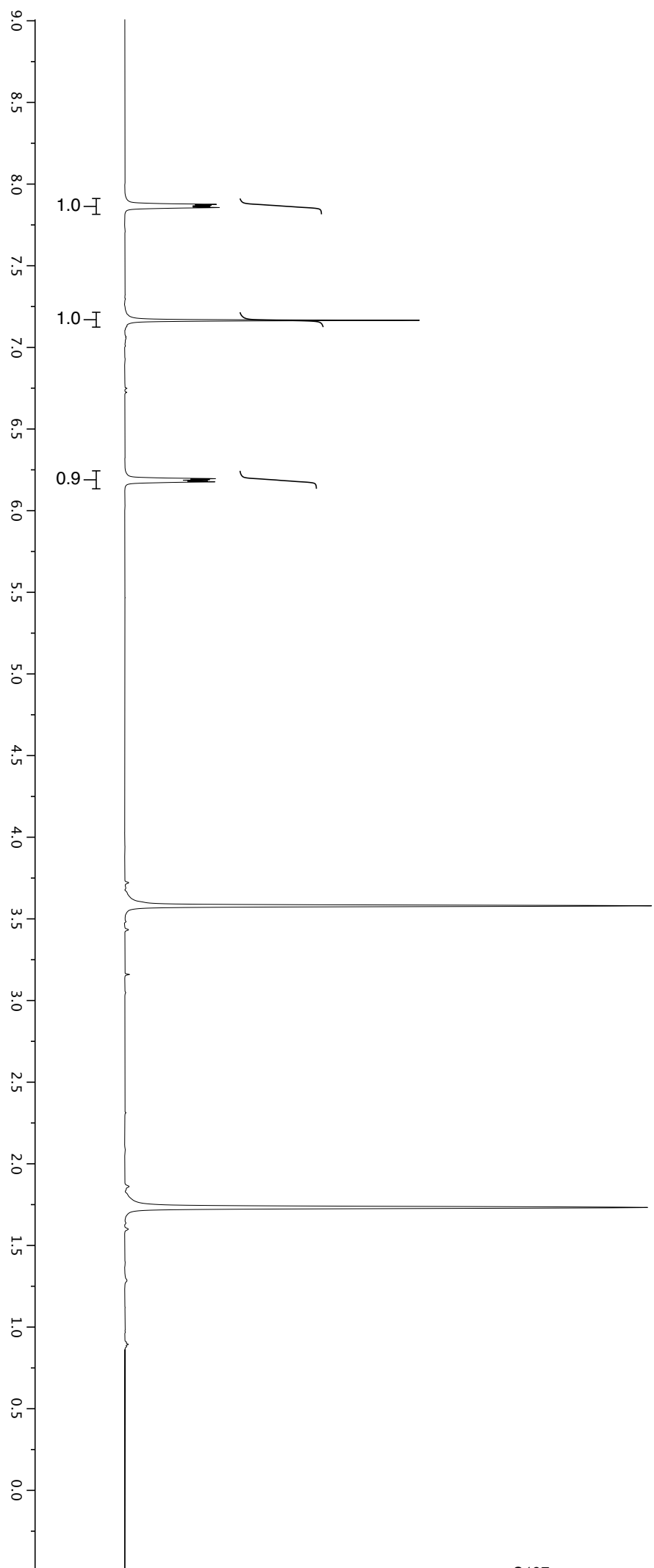
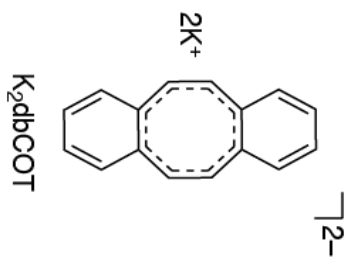




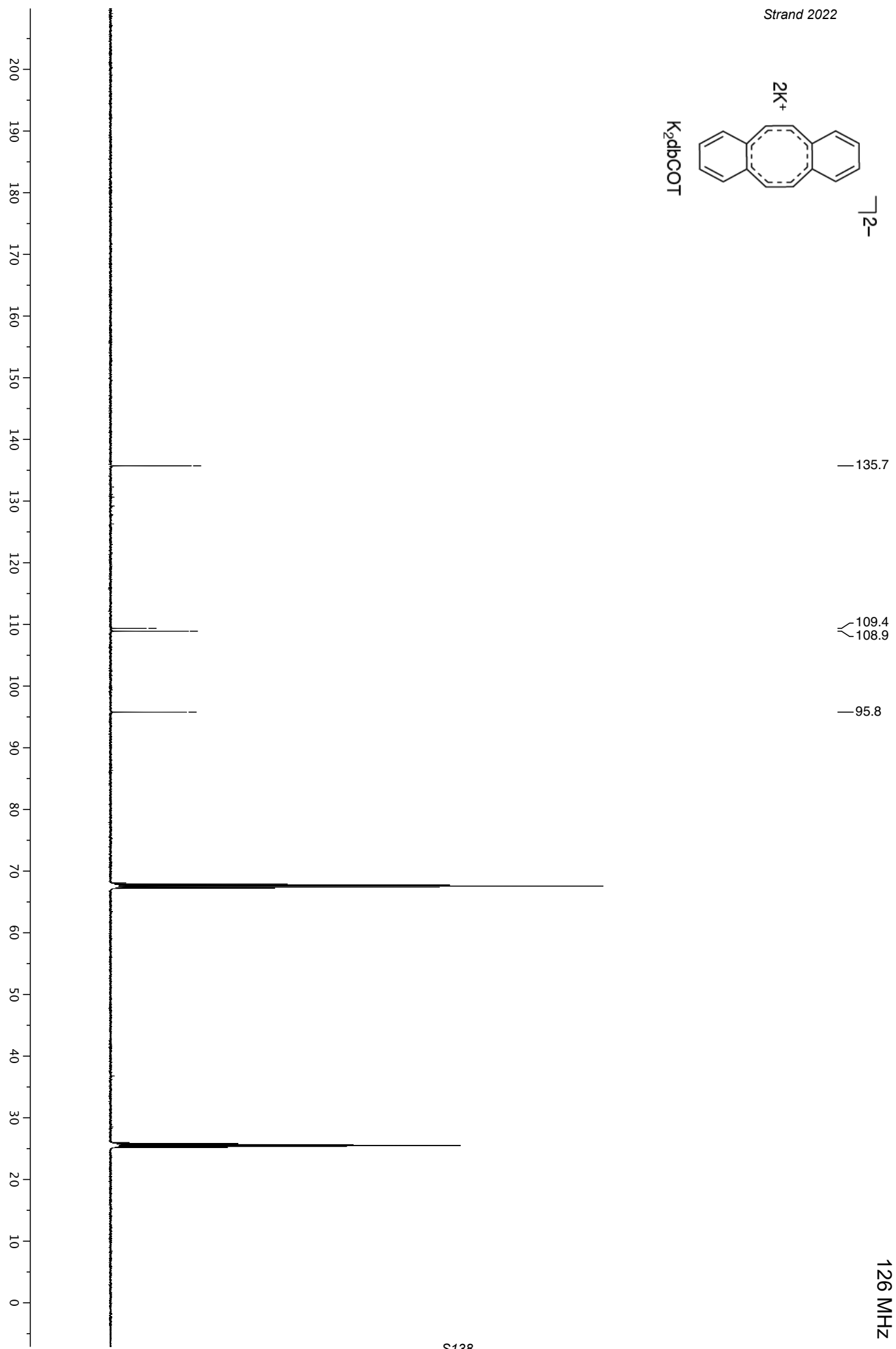
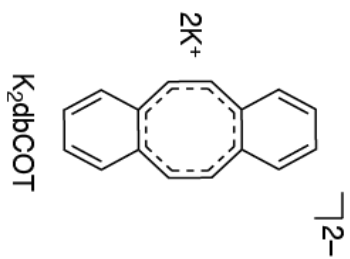
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

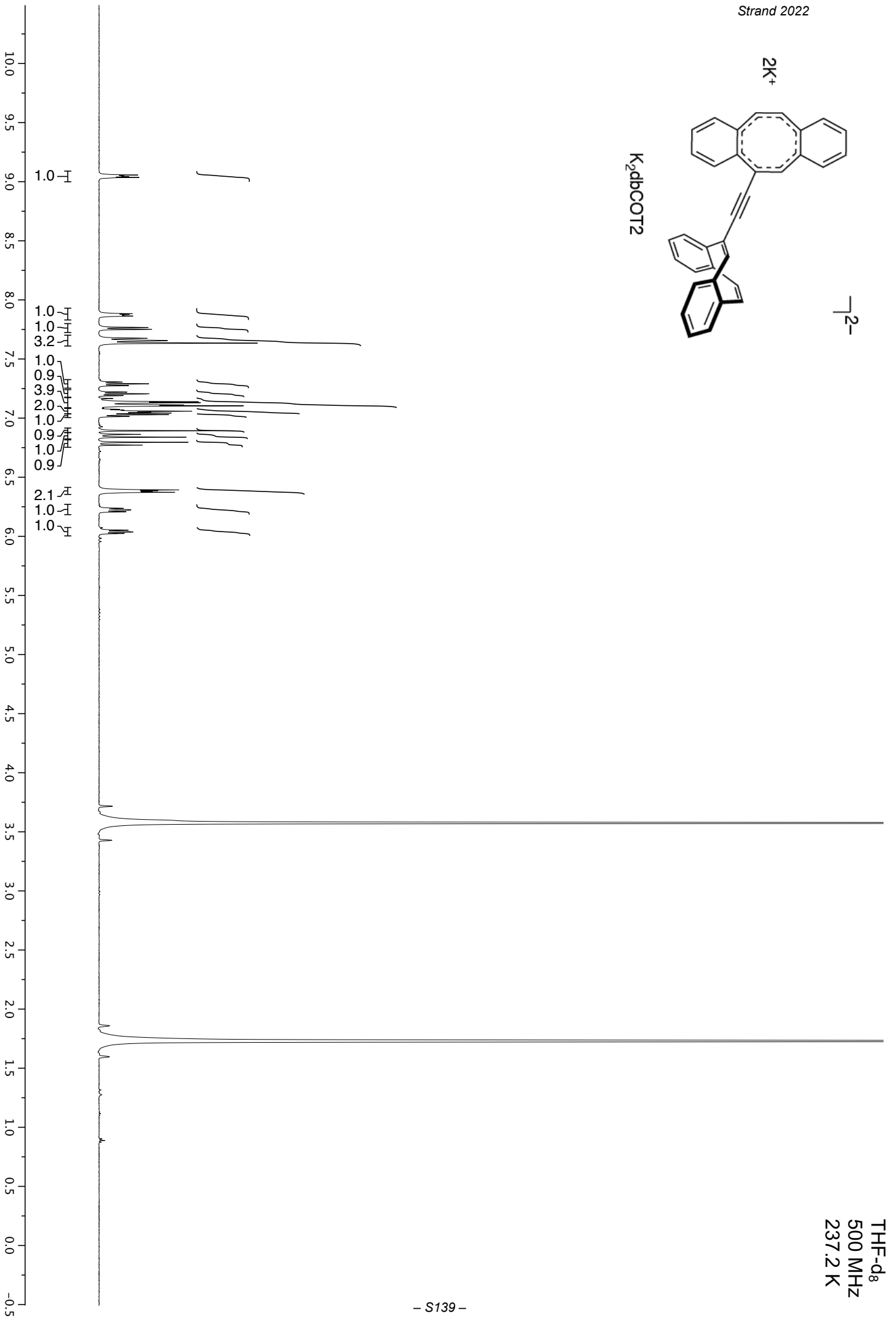
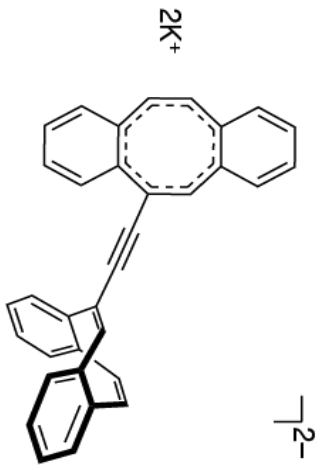


CDCl₃
126 MHz

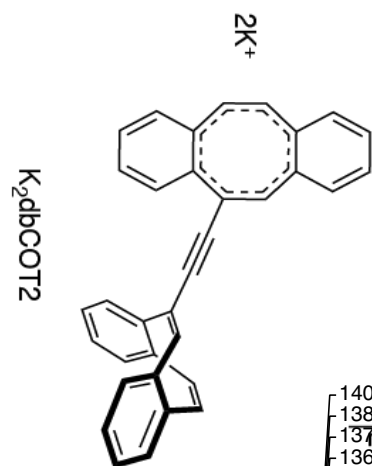


THF-d₈
500 MHz

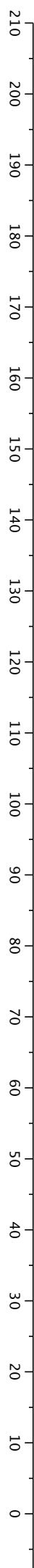


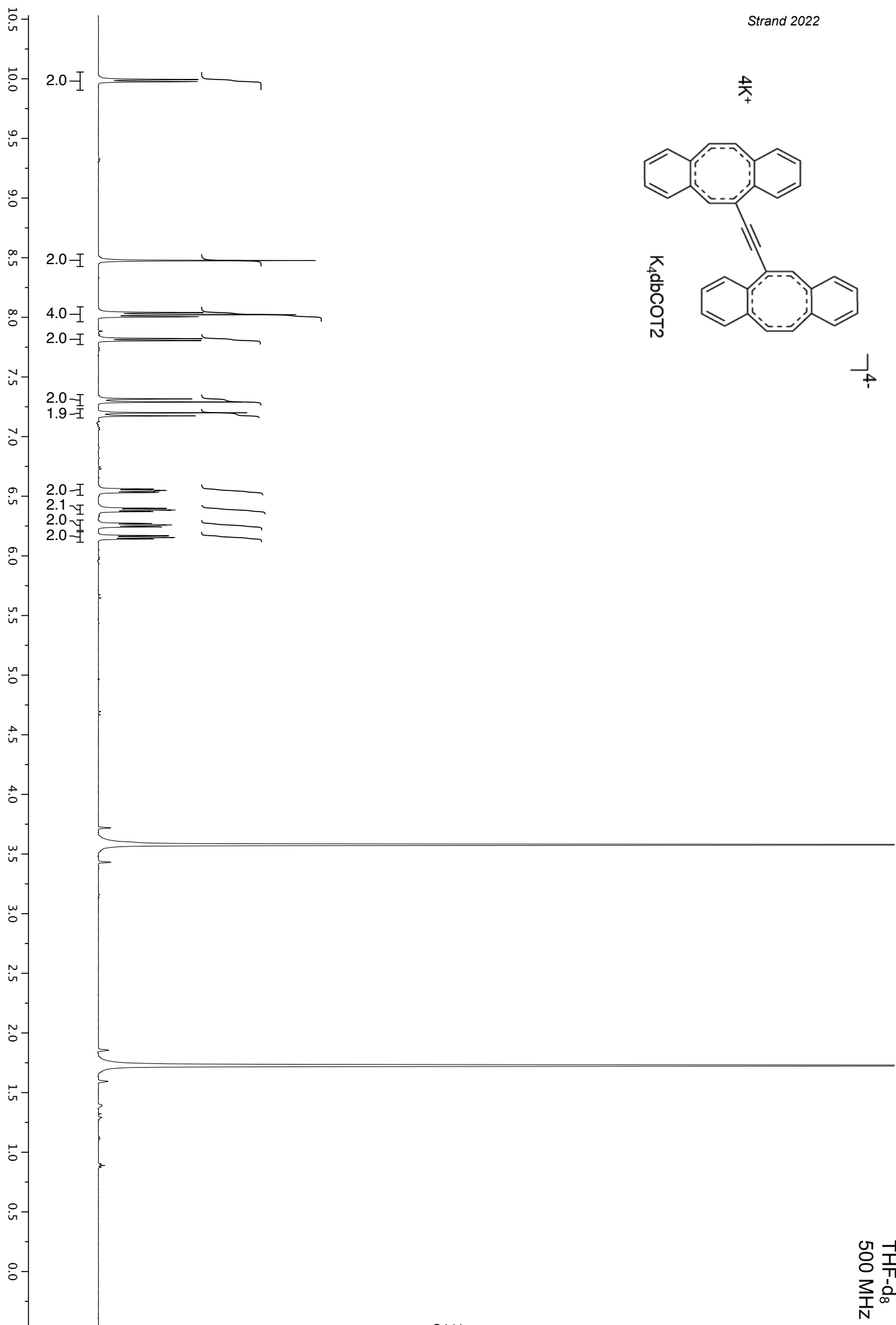
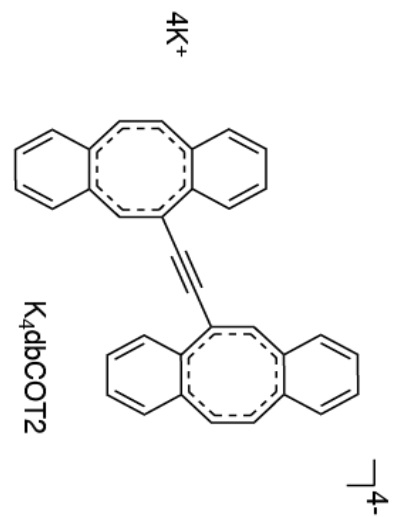


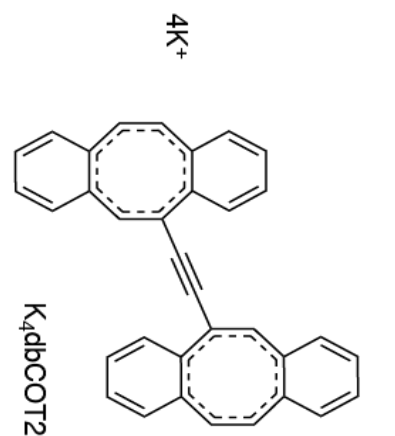
THF-d₈
126 MHz
237.2 K



- 140.6
- 138.7
- 137.9
- 136.3
- 135.4
- 134.3
- 133.1
- 133.1
- 131.3
- 130.6
- 130.0
- 129.1
- 128.5
- 128.1
- 126.3
- 126.2
- 126.1
- 125.3
- 125.1
- 112.3
- 112.3
- 112.2
- 111.9
- 111.6
- 110.3
- 110.1
- 106.6
- 106.5
- 102.5
- 98.1
- 97.2
- 90.8
- 82.0







4-

136.7
136.4
135.5
134.2

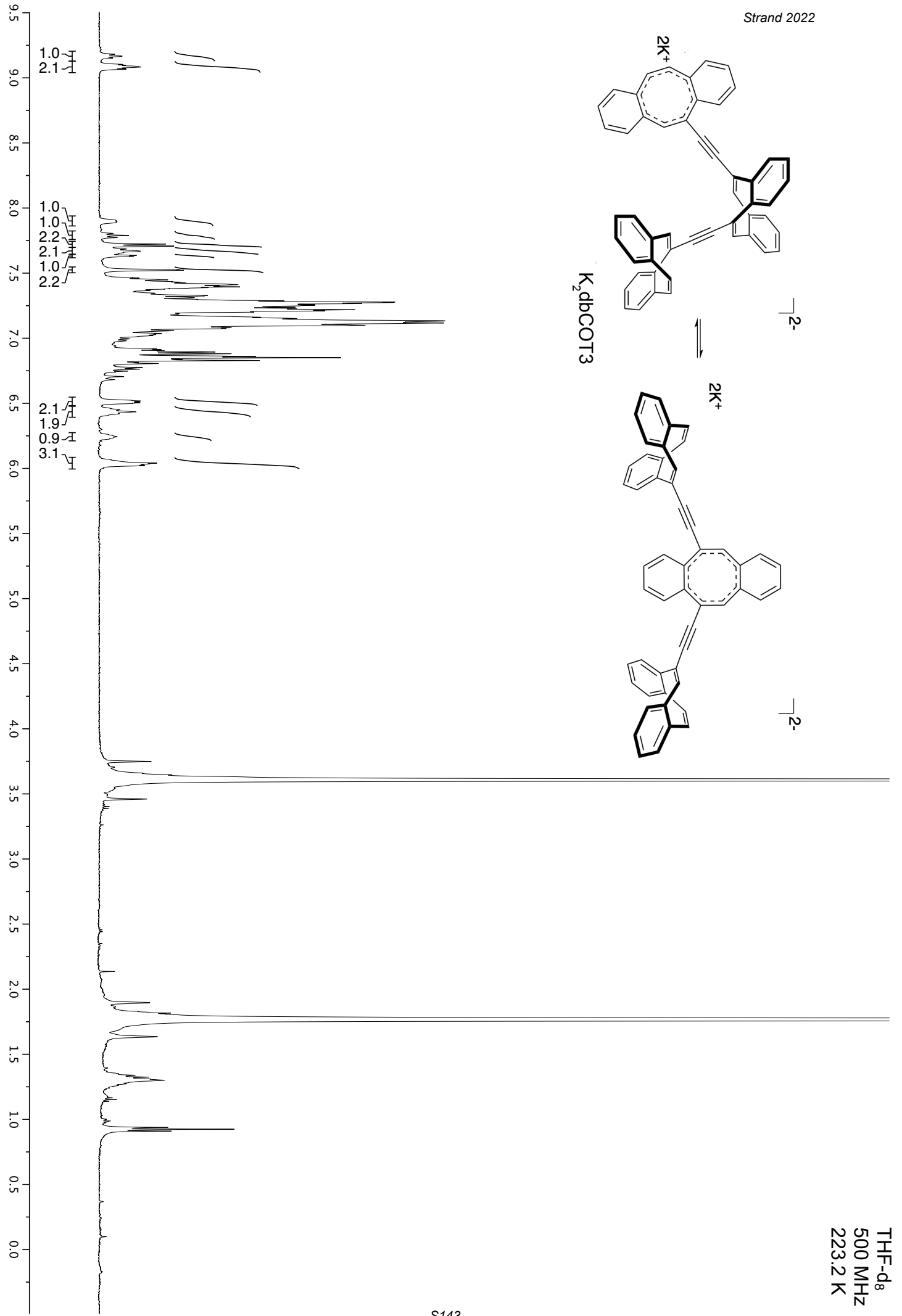
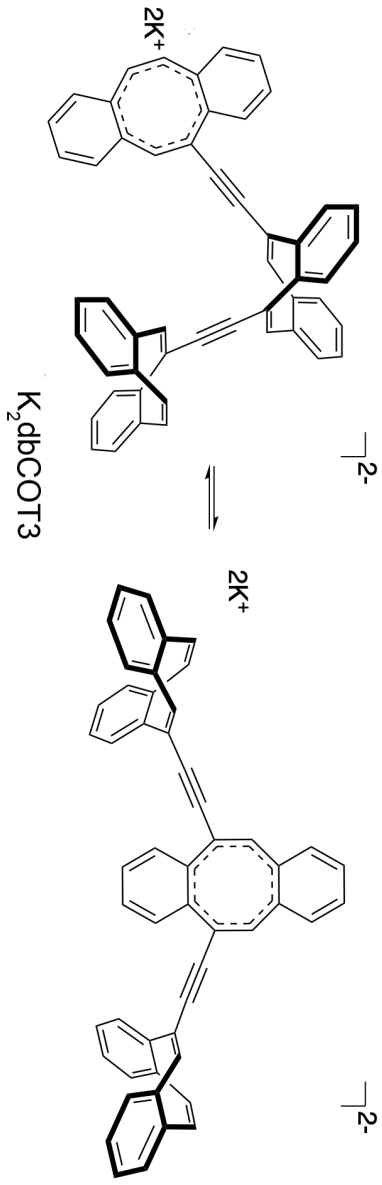
111.3
111.2
110.5
110.3
110.0
109.5
108.8
108.3
101.5
100.3
98.8
97.4

89.4

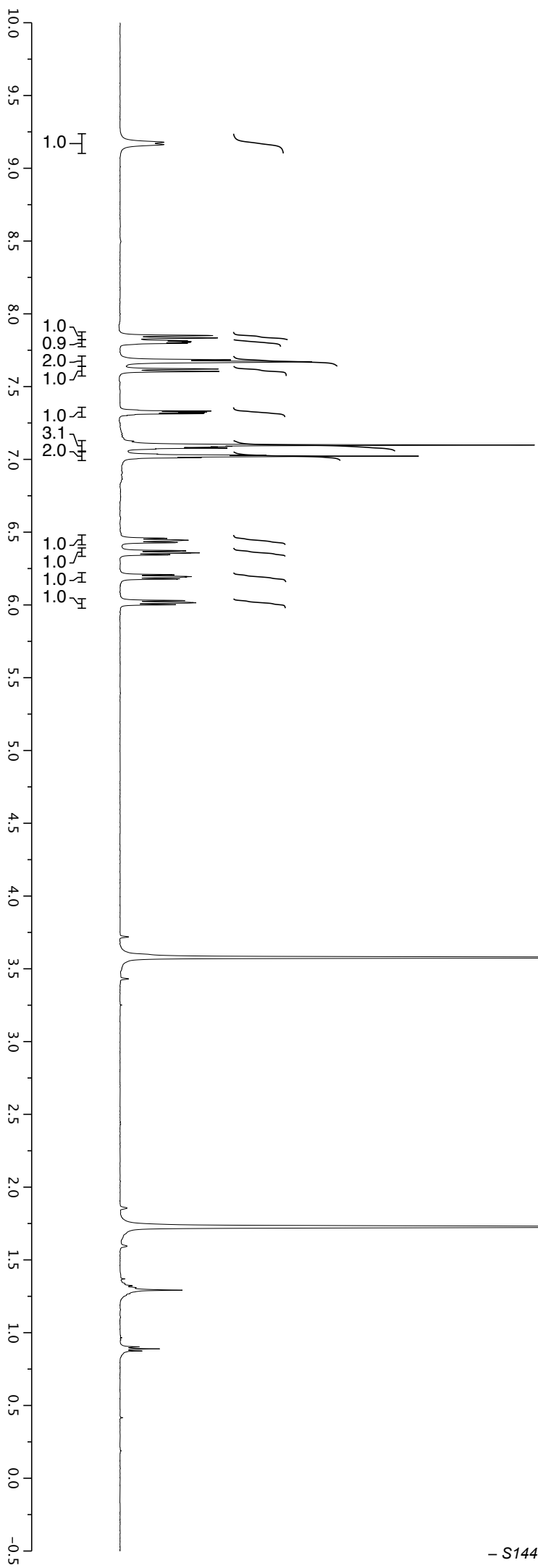
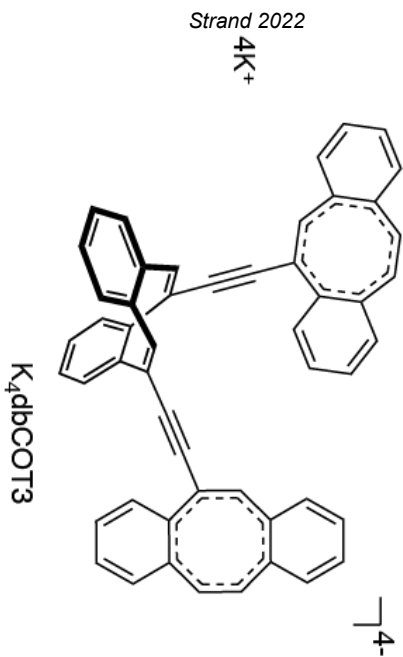
benzene

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

THF-d₈
126 MHz

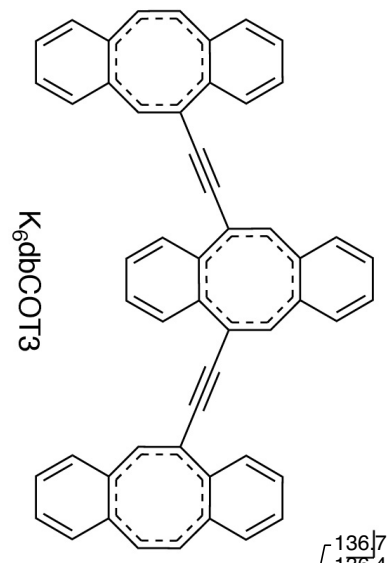


THF-d_8
500 MHz
223.2 K



Strand 2022

6K+

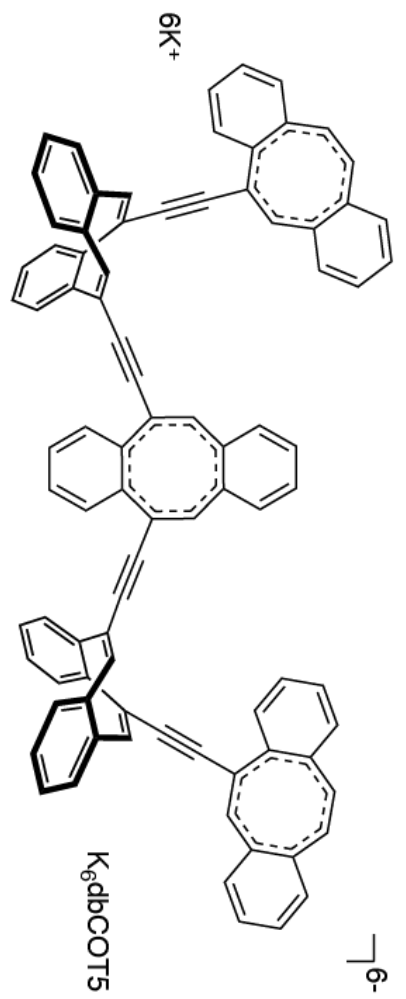


- 136.7
- 136.5
- 136.3
- 135.5
- 134.5
- 134.2
- 112.0
- 111.2
- 111.1
- 110.5
- 110.4
- 110.3
- 110.2
- 110.0
- 109.6
- 109.5
- 108.7
- 108.2
- 104.6
- 101.5
- 100.9
- 100.3
- 98.8
- 97.4
- 90.4
- 89.4

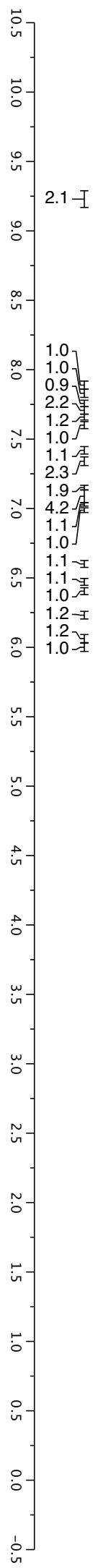
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



THF-d₈
126 MHz
268.2 K



THF-d₈
500 MHz
273.0 K



XV. *Supplementary references*

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