Supporting Information

Heteroatom-Substituted Expanded Radialenes: One-pot Synthesis and Characterization of Expanded 1,3-Dithiolane[n]radialenes

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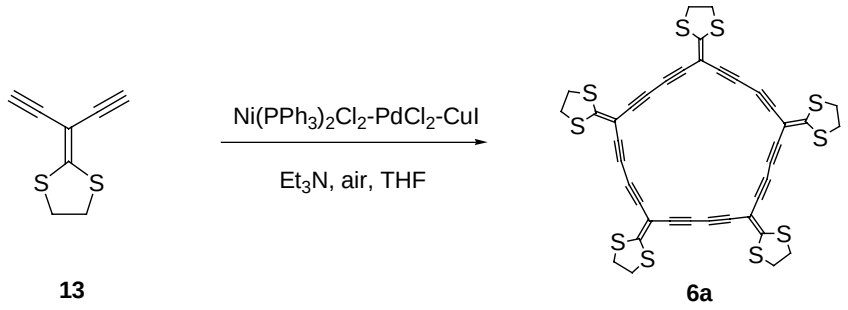
Experimental Section

General Information

All reagents were commercial and were used without further purification. Chromatography was carried on flash silica gel (300-400 mesh). All reactions were monitored by TLC, which was performed on pre-coated aluminum sheets of silica gel 60 (F_{254}). Melting points were uncorrected. The ^{1}H NMR spectra were determined on a 500 MHz spectrometer in $CDCl_3$ or DMSO-d_6 with TMS as internal standard, and ^{13}C NMR spectra were recorded at 125 MHz. All shifts are given in ppm. IR (KBr) spectra were measured using a IR spectrometer. Mass spectra were recorded on LCMsD or IonSpec 7.0T FT-ICRMs spectrometer. The compound **6a** with dimension 0.380 × 0.157 × 0.055 mm, was glued on a glass fiber. Data were collected on a CCD area detector with graphite monochromated Mo-Ka radiation (λ = 0.71073 Å) in the range of $3.27 < \theta < 26.08°$. The structure was solved by the direct method and refined by the Full-matrix least squares on F^2 using the SHELXTL-97 software. Crystal data for 6a: $C_{22.5}H_{12.5}OS_{5.5}$, Mr = 475.10, monoclinic space group P2(1)/m, a = 8.6162(10), b = 22.137(3), c = 12.4884(14) Å, α = 90, β = 93.563(2), γ = 90º, V = 2377.4(5) $Å^3$, Z = 4, ρ_{calcd} = 1.713, T = 293(2) K, 12272 reflections (4481 unique), 271 refined parameters, R = 0.0701 (4481 data with $I>2\sigma(I)$), $wR(F^2)$ = 0.1537, residual electron density= 0.949 to -0.349 e. $Å^{-3}$. The H atoms were revealed in the difference Fourier map and refined isotropically. CCDC 256440 (**6a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

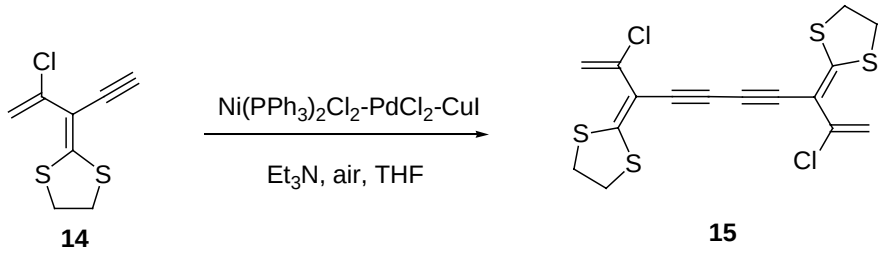
Procedure for expanded 1,3-dithiolan[5]radialene (6a). Under atmosphere, to a solution of $Ni(PPh_3)_2Cl_2$ (0.20 mmol, 130.8 mg), $PdCl_2$ (0.20 mmol, 35.4 mg), CuI (0.20 mmol, 38.1 mg) and triethylamine (6.0 mmol, 0.83 mL) in THF (180 mL), enediyne **13** (2.0 mmol, 332 mg in 20 mL THF was added dropwise over 2-3 h. Then the reaction mixture was stirred for 5-6 h at room temperature. After the starting material **13** was consumed (monitored by TLC), the reaction mixture was poured into water (400 mL) and stirred. The crude solid was filtered, washed with water, and chromatographed over silica gel using diethyl acetone-hexane-ethanol (1/1/0.1,v/v/v) as eluent to give compound **6a** 49.2 mg (15 % total yield).



Scheme 1 Synthesis of expanded radialene **6a**.

2-(6,11,16,21-tetra(1,3-dithiolan-2-ylidene)cyclopentacosa-2,4,7,9,12,14,17,19,22,24-decaynylidene)-1,3-dithiolane (Compound 6a): red solid; m. p. 260 ^{o}C (decomp); **^{1}H NMR** (DMSO-d_6, 500 MHz) δ: 3.34 (s, 20H); **^{13}C NMR** (DMSO-d_6, 125 MHz) δ: 31.2, 79.1, 81.7, 85.2, 172.4; **IR** (KBr, cm^{-1}): 1280, 1492, 1631, 2122; UV/vis (DMSO): λ_{max} (ε) = 288 nm (47789), 390 nm (111768), 403 nm (114612), 424 nm (85675), 443 nm (68548); **HRMS (EI)** calcd for $C_{40}H_{20}S_{10}$ 819.8772, found 819.8903.

Synthetic procedure for compound 15: To a solution of compound **14** (1.0 mmol, 202 mg), $Ni(PPh_3)_2Cl_2$ (0.050 mmol, 32.7 mg), $PdCl_2$ (0.050 mmol, 8.9 mg), CuI (0.050 mmol, 9.5 mg) and triethylamine (3.0 mmol, 0.42 mL) in THF (40 mL) was stirred for 8-10 h at room temperature. After the starting material **14** was consumed (monitored by TLC), the reaction mixture was poured into water (200 mL) and stirred. The crude solid was filtered, washed with water, and chromatographed using diethyl acetone-hexane = (1/2, v/v) as eluent to give a 80 % yield of compound **15** (0. 4 mmol, 161 mg).

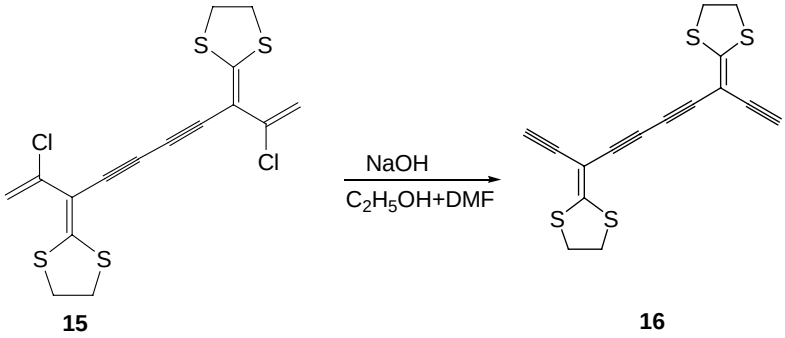


14 **15**

Scheme 2 Synthesis of compound **15**.

2-(2,9-dichloro-8-(1,3-dithiolan-2-ylidene)deca-1,9-dien-4,6-diyn-3-ylidene)-1,3-dithiolane (Compound 15): yellow solid; m. p. 183~185 ^{o}C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ: 3.47-3.52 (m, 8H), 5.48 (d, *J* = 1.5 Hz, 2H), 5.55 (d, *J* = 1.5 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ: 37.7, 39.7, 81.0, 82.3, 106.0, 116.8, 136.3, 159.3; **IR** (KBr, cm^{-1}): 665, 887, 1087, 1206, 1273, 1480, 1617, 1727, 2112, 2171, 2860, 2927; **MS:** m/z 403 [M^{+}+H]; **Anal**. Calcd (found) for: $C_{16}H_{12}Cl_2S_4$: C, 47.63 (47.70); H, 3.00 (3.09).

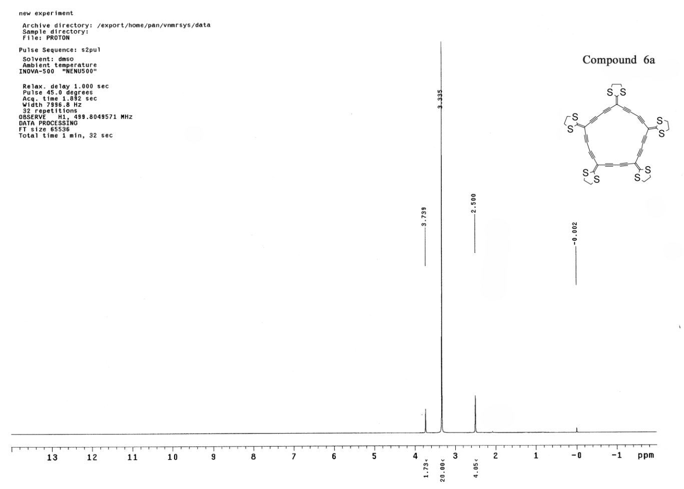
Synthetic Procedure for compound 16. To a solution of **15** (1.0 mmol, 403 mg) in DMF (3 mL) and C_2H_5OH (15 mL) was added NaOH (4.0 mmol, 160 mg) and H_2O (5 mL). Then the reaction mixture was refluxed for 10-12 h until compound **15** was consumed (monitored by TLC). Cooled down to room temperature, the reaction mixture was poured into water (80 mL), extracted with diethyl ether (3×10 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to yield the corresponding crude product, which was purified by column chromatography over silica gel using acetone-hexane (1/10, v/v) as eluent to give 132 mg (40%) of **16** as a light yellow solid.



15 **16**

Sheme3 Synthesis of compound **16**.

2-(8-(1,3-dithiolan-2-ylidene)deca-1,4,6,9-tetrayn-3-ylidene)-1,3-dithiolane (Compound 16): yellow solid; d. p. 146~148 ^oC; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ: 3.42 (s, 2H), 3.55 (s, 8H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ: 39.3, 39.4, 79.4, 79.7, 81.2, 82.7, 88.0, 167.5; **IR** (KBr, cm^{-1}): 581, 676, 887, 1281, 1457, 1640, 2126, 3280; **MS:** m/z 331 [M^++H]; **Anal.** Calcd (found) for $C_{16}H_{10}S_4$: C, 58.14 (58.19); H, 3.05 (3.11).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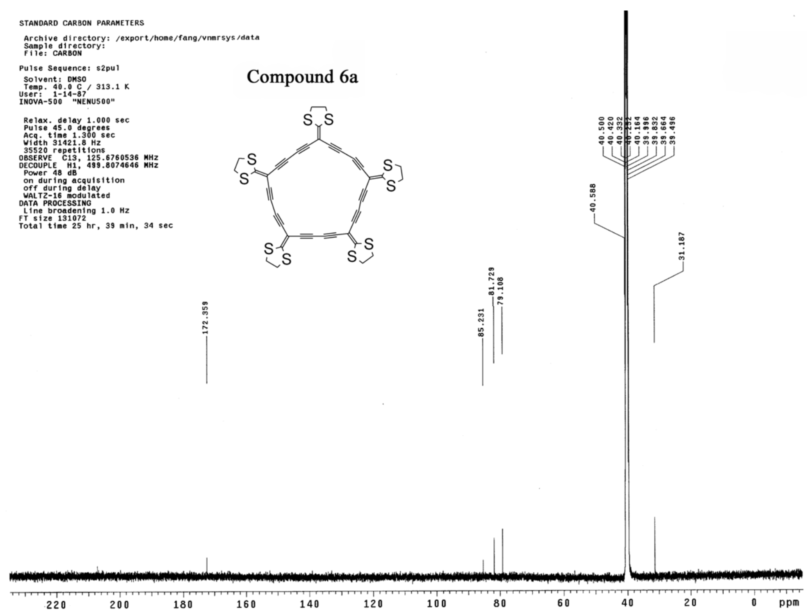
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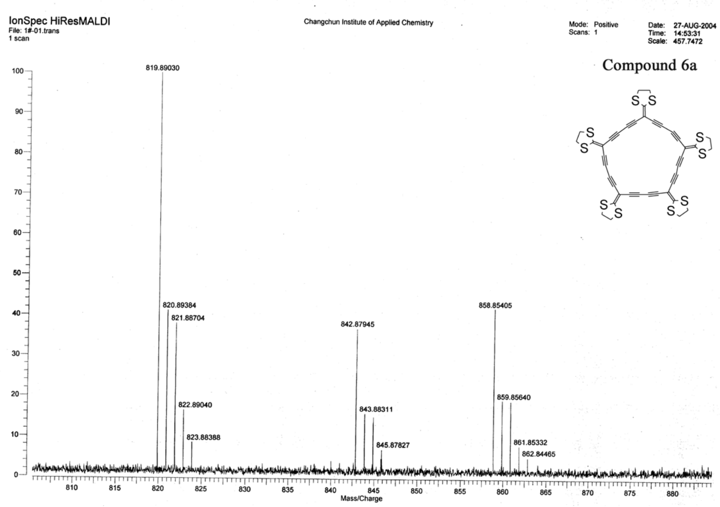
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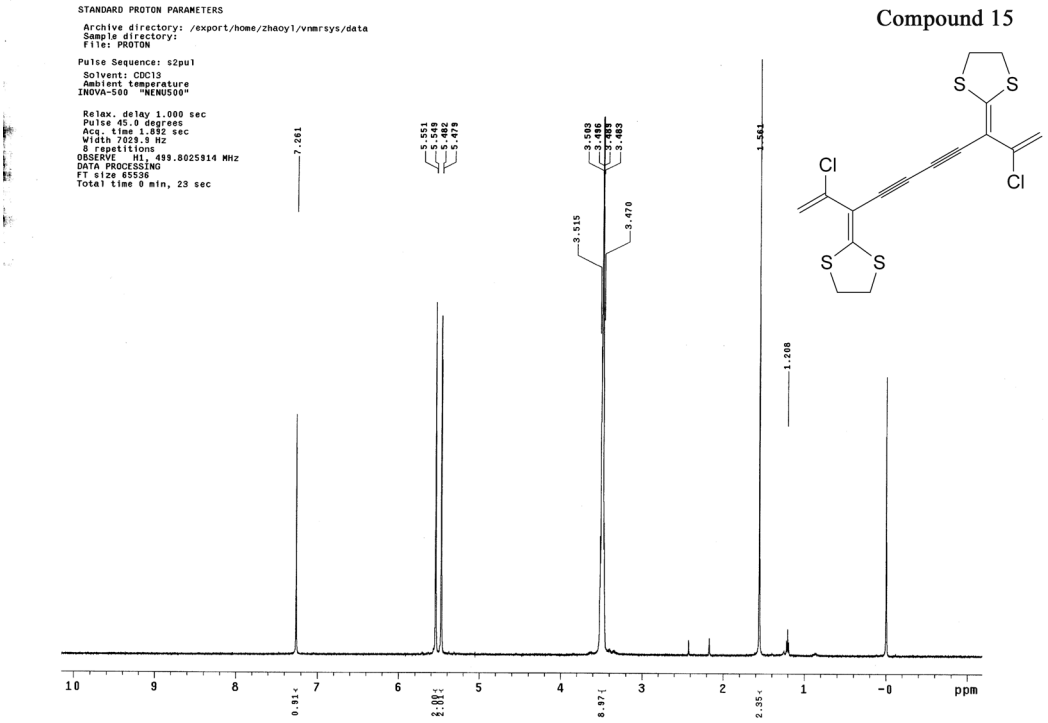
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3.470
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S
S
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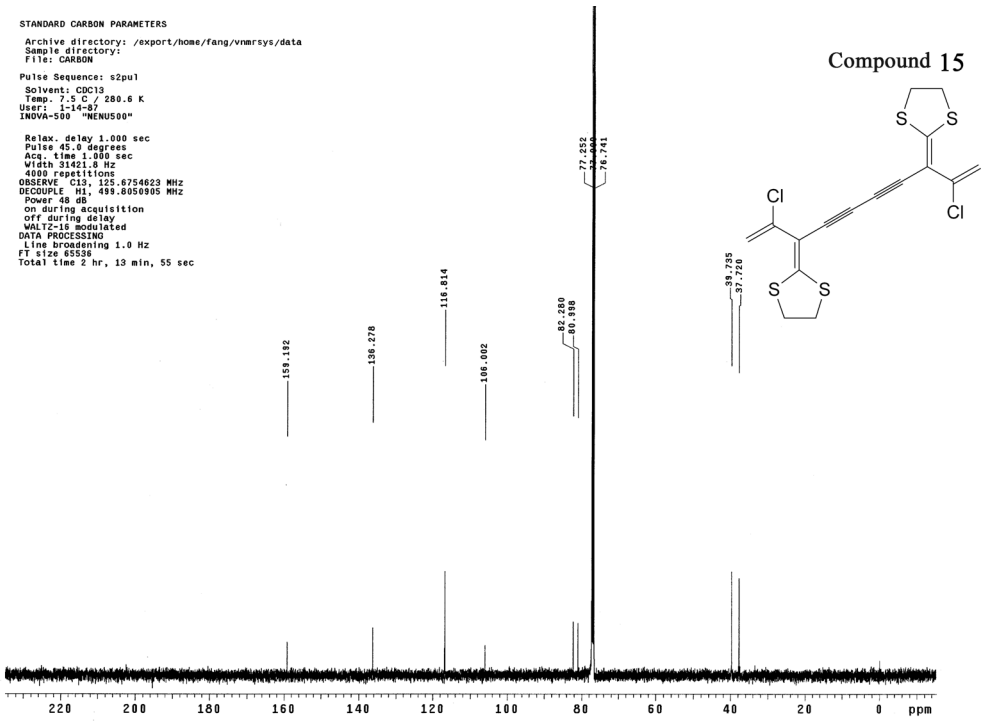
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off during delay
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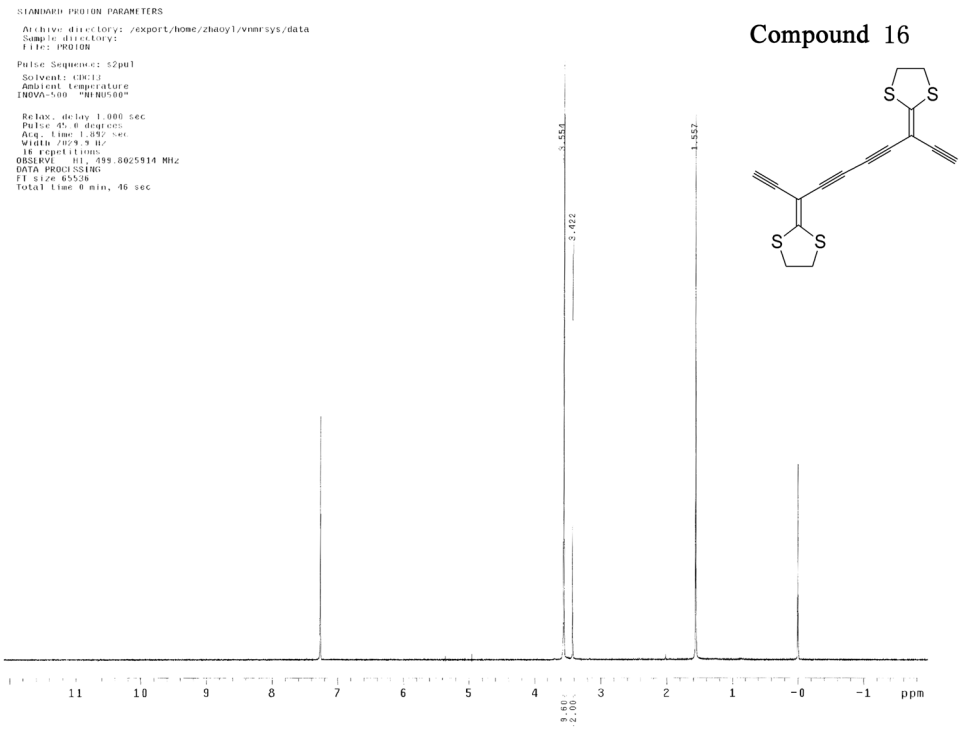
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Pulse 45.0 degrees
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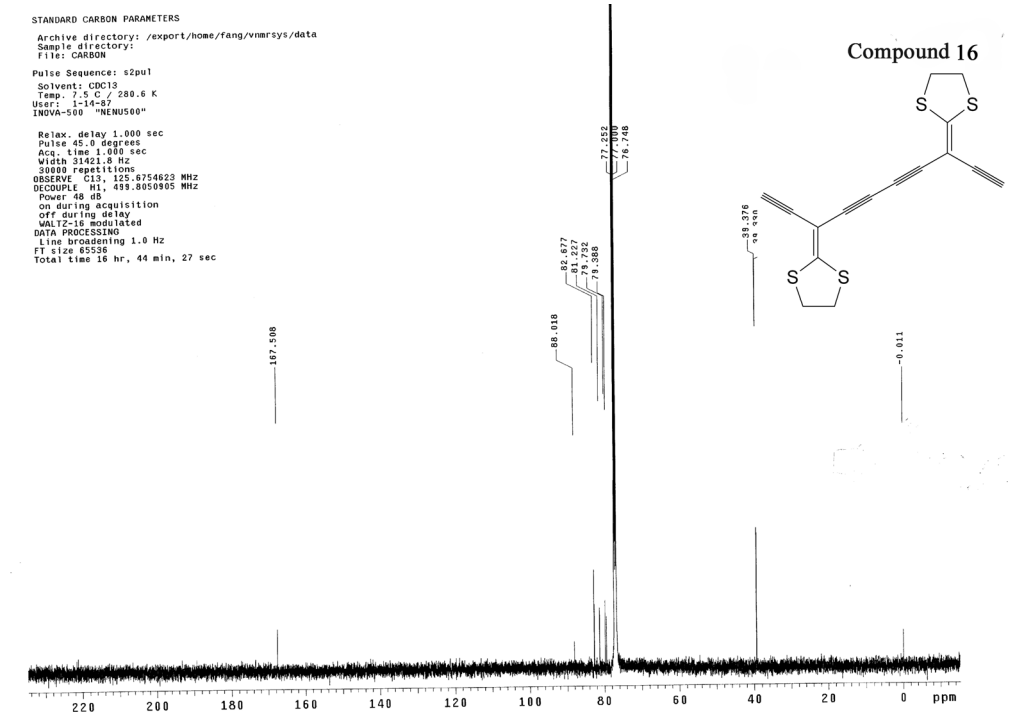
ppm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Pulse 45.0 degrees
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30000 repetitions
OBSERVE C13, 125.6754623 MHz
DECOUPLE H1, 499.8050905 MHz
Power 48 dB
on during acquisition
off during delay
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79.388
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220
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180
160
140
120
100
80
60
40
20
0
ppm