

**Unexpected Formation of Poly-Functionalized Fulvenes
by Reaction of a Tetraaryl[5]cumulene with Iodine**

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Table of Contents

General Information	S3
Experimental Procedures and Characterization	S3
Absorption Spectra	S7
References	S8
NMR Spectral Data	S9

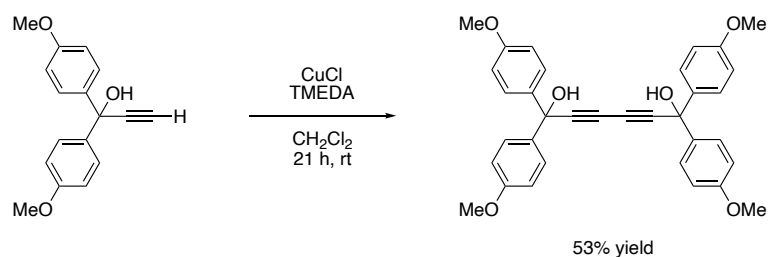
General Information

NMR spectra were recorded on a JEOL resonance JNM-ECZ-400 operating 400 MHz for ^1H - and 100 MHz for ^{13}C -NMR spectroscopy, respectively, in CDCl_3 or benzene- d_6 solutions. Chemical shifts are reported in parts per million (ppm) relative to TMS or residual solvent peaks as an internal standard. Melting points were measured on a Yanaco MP-J13 micro melting-point apparatus and uncorrected. High-resolution mass spectra (HRMS) were recorded on a ThermoFisher Exactive. X-ray single crystallographic analysis was conducted using a Rigaku R-Axis RAPID II or a Bruker APEX II Ultra. UV/vis spectra were recorded on a Shimadzu UV-1600.

Experimental Procedures and Characterization

Although a tetrakis(*p*-methoxyphenyl)[5]cumulene (**1**) is known,^{S1} we have synthesized the [5]cumulene **1** via Hay coupling of 1,1-bis(*p*-methoxyphenyl)prop-2-yn-1-ol followed by the reduction with SnCl_2 according to the literature.

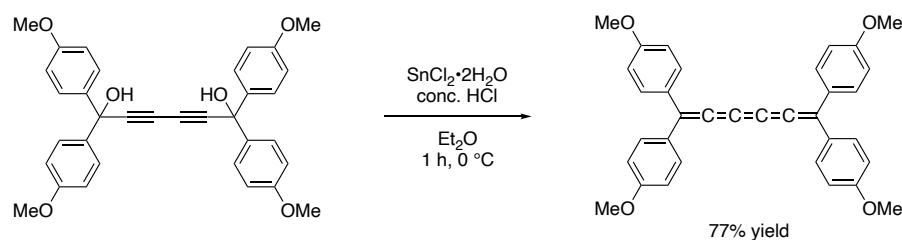
Preparation of 1,1,6,6-Tetrakis(*p*-methoxyphenyl)hexa-2,4-diyne-1,6-diol:



To a 40 mL dichloromethane solution containing 1,1-bis(*p*-methoxyphenyl)prop-2-yn-1-ol (8.82 mmol) were added CuCl (8.82 mmol) and tetramethylethylenediamine (TMEDA, 17.64 mmol), and the mixture was stirred for 21 hours at room temperature. After the reaction was quenched by addition of saturated NH_4Cl aq., the reaction mixture was extracted with dichloromethane. Then, the organic layer was dried over MgSO_4 and concentrated in *vacuo*. The residual mixture was subjected to chromatography on silica gel using mixtures of ethyl acetate and hexane as eluents, and 1,1,6,6-tetrakis(*p*-methoxyphenyl)hexa-2,4-diyne-1,6-diol (4.68 mmol) was isolated in 53% yield.

Yellow oil; ^1H NMR (CDCl_3) δ : 2.86 (s, 2H), 3.78 (s, 12H), 6.84 (d, $J = 9.1$ Hz, 8H), 7.44 (d, $J = 9.1$ Hz, 8H); ^{13}C NMR (CDCl_3) δ : 55.3, 70.9, 74.2, 83.0, 113.6, 127.4, 136.4, 159.2; HRMS (APCI) m/z calcd for $\text{C}_{34}\text{H}_{30}\text{O}_6\text{-OH}$ 517.2010, found 517.1998.

Preparation of Tetrakis(*p*-methoxyphenyl)[5]cumulene (**1**):



To a 11 mL diethyl ether solution containing 1,1,6,6-tetrakis(*p*-methoxyphenyl)hexa-2,4-diyne-1,6-diol (1.20 mmol)

were added $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (3.60 mmol) and conc. HCl aq. (3.4 mL), and the mixture was stirred for 1 hour at 0 °C. After the resulting red precipitate was collected and washed with water and ethanol, a tetrakis(*p*-methoxyphenyl)[5]cumulene (**1**, 0.92 mmol) was obtained in 77% yield without further purification. Because enough amount of cumulene **1** suitable for ^{13}C NMR measurement was not dissolved in any common organic solvents, the structure was determined by ^1H NMR, HRMS, and X-ray crystallographic analysis. The crystal structure of **1** is shown in **Fig. S1**.

Cumulene **1**: Red solid; mp 260.0–262.0 °C; ^1H NMR (CDCl_3) δ : 3.86 (s, 12H), 6.92 (d, $J = 9.2$ Hz, 8H), 7.51 (d, $J = 9.2$ Hz, 8H); HRMS (ESI) m/z calcd for $\text{C}_{34}\text{H}_{28}\text{O}_4$ 500.1982, found 500.1974.

Crystal data of **1**: $\text{C}_{34}\text{H}_{28}\text{O}_4$, $M_r = 500.56$, monoclinic space group $P2_1$, $a = 10.913(4)$ Å, $b = 7.442(3)$ Å, $c = 16.072(5)$ Å, $\beta = 101.62(3)^\circ$, $V = 1278.5(8)$ Å³, $Z = 2$, $\rho = 1.300$ Mg/m³, in the final least-squares refinement cycles on F^2 , the model converged at $R_1 = 0.1184$, $wR2 = 0.2748$, and GOF = 0.933 for 3532 reflections CCDC2089167-2089168.

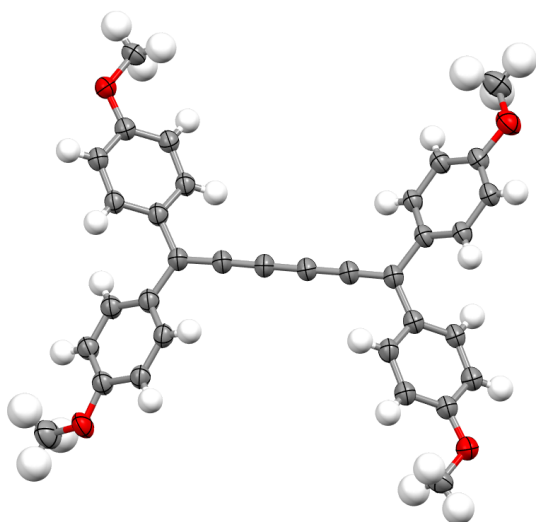


Fig. S1 ORTEP drawing of **1**.

General Procedure for Reaction of Tetrakis(*p*-methoxyphenyl)[5]cumulene (1**) with Iodine:**

To a 5 mL solution containing cumulene **1** (0.15 mmol) was added iodine (0.45 mmol), and the mixture was stirred for 30 min at room temperature. After the reaction was quenched by addition of saturated $\text{Na}_2\text{S}_2\text{O}_3$ aq., the reaction mixture was poured into water and extracted with ethyl acetate. Then, the organic layer was dried over MgSO_4 and concentrated in *vacuo*. The residual mixture was subjected to chromatography on silica gel using mixtures of ethyl acetate and hexane as eluents, and 2,3-diiodo-4,5,6,6-tetrakis(*p*-methoxyphenyl)fulvene (**2**) and 4-iodo-2,3,6,6-tetrakis(*p*-methoxyphenyl)fulvene (**3**) were separated. These results are shown in **Table 1**.

Fulvene **2**: Red solid; mp 100.0–101.0 °C; ¹H NMR (CDCl₃) δ: 3.57 (s, 3H), 3.65 (s, 3H), 3.76 (s, 3H), 3.91 (s, 3H), 6.26 (d, *J* = 8.8 Hz, 2H), 6.41 (d, *J* = 8.8 Hz, 2H), 6.52 (d, *J* = 8.8 Hz, 2H), 6.75 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 7.29 (d, *J* = 8.8 Hz, 2H); ¹³C NMR (CDCl₃) δ: 55.00, 55.01, 55.2, 55.5, 93.2, 112.5, 112.6, 112.8, 113.8, 115.8, 128.9, 129.8, 131.6, 132.0, 133.4, 134.2, 136.1, 136.2, 136.5, 143.1, 144.9, 156.7, 158.4, 158.5, 161.3, 162.2; HRMS (ESI) *m/z* calcd for C₃₄H₂₈O₄I₂+H 755.0150, found 755.0134.

Crystal data of **2**: C₃₄H₂₈I₂O₄, *Mr* = 754.40, monoclinic space group *P*2₁/*n*, *a* = 12.4916(3) Å, *b* = 14.1803(3) Å, *c* = 18.3463(5) Å, β = 103.830(7)°, *V* = 3155.55(17) Å³, *Z* = 4, ρ = 1.588 Mg/m³, in the final least-squares refinement cycles on *F*², the model converged at *R*₁ = 0.0705, *wR*₂ = 0.1979, and GOF = 1.128 for 5690 reflections CCDC2089131.

Fulvene **3**: Red solid; mp 135.0–136.0 °C; ¹H NMR (CDCl₃) δ: 3.61 (s, 3H), 3.65 (s, 3H), 3.78 (s, 3H), 3.89 (s, 3H), 6.30 (d, *J* = 8.6 Hz, 2H), 6.38 (d, *J* = 8.6 Hz, 2H), 6.54 (d, *J* = 8.6 Hz, 2H), 6.70 (s, 1H), 6.77 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 7.06 (d, *J* = 8.6 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H); ¹³C NMR (CDCl₃) δ: 55.00, 55.04, 55.1, 55.4, 95.1, 112.5, 112.6, 112.8, 113.2, 128.66, 128.74, 131.78, 131.84, 131.9, 132.3, 134.4, 134.5, 135.01, 135.05, 141.6, 143.3, 154.2, 156.8, 158.3, 160.3, 160.8; HRMS (ESI) *m/z* calcd for C₃₄H₂₉O₄I+H 629.1183, found 629.1170.

Crystal data of **3**: C₃₄H₂₉I₂O₄, *Mr* = 628.51, triclinic space group *P*-1, *a* = 10.24137(19) Å, *b* = 11.9283(2) Å, *c* = 13.3381(8) Å, α = 113.529(8)°, β = 109.913(8)°, γ = 93.193 (7)°, *V* = 1369.46(15) Å³, *Z* = 2, ρ = 1.524 Mg/m³, in the final least-squares refinement cycles on *F*², the model converged at *R*₁ = 0.0357, *wR*₂ = 0.0915, and GOF = 1.077 for 4921 reflections CCDC2089132.

Control Experiment Using **2** (Condition C):

To a 6 mL toluene solution containing fulvene **2** (0.03 mmol) was added hydroiodic acid (0.6 mmol), and the mixture was stirred for 30 min at room temperature. After the reaction was quenched by addition of saturated Na₂S₂O₃ aq., the reaction mixture was poured into water and extracted with ethyl acetate. Then, the organic layer was dried over MgSO₄ and concentrated in *vacuo*. The residual mixture was subjected to chromatography on silica gel using chloroform as an eluent, and 2,3,6,6-tetrakis(*p*-methoxyphenyl)fulvene (**4**) was separated in 85% yield. This result is shown in **Scheme 2**.

Fulvene **4**: brown solid; mp 175.0–176.0 °C; ¹H NMR (CDCl₃) δ: 3.667 (s, 3H), 3.670 (s, 3H), 3.76 (s, 3H), 3.87 (s, 3H), 6.31 (d, *J* = 5.4 Hz, 1H), 6.34–6.41 (m, 4H), 6.68 (d, *J* = 8.8 Hz, 2H), 6.71–6.73 (m, 3H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 8.8 Hz, 2H), 7.28 (d, *J* = 8.8 Hz, 2H); ¹³C NMR (CDCl₃) δ: 55.07, 55.09, 55.3, 112.3, 112.97, 113.03, 113.2, 127.5, 129.5, 129.9, 129.95, 129.98, 130.7, 131.9, 132.3, 134.0, 134.2, 135.6, 142.3, 142.9, 153.7, 156.9, 158.1, 159.7, 160.4; HRMS (ECI) *m/z* calcd for C₃₄H₃₀O₄+Na 525.2036, found 525.2037.

Control Experiment Using D₂O:

To a 0.5 mL benzene-*d*₆ solution containing cumulene **1** (0.03 mmol) were added iodine (0.09 mmol) and D₂O (0.66 mmol). After the mixture was stirred for 20 min at room temperature, ¹H NMR spectrum of the reaction mixture was measured without purification. This result is shown in **Fig. S2**.

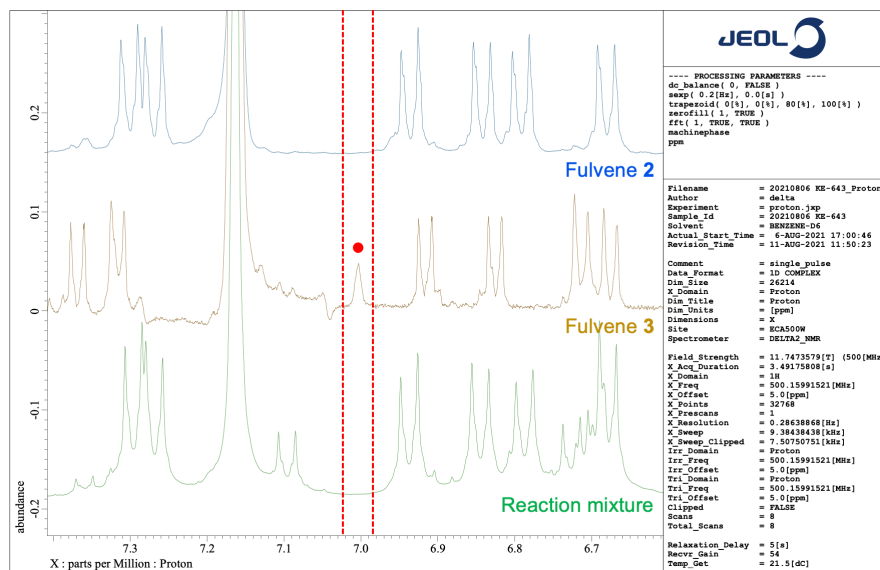
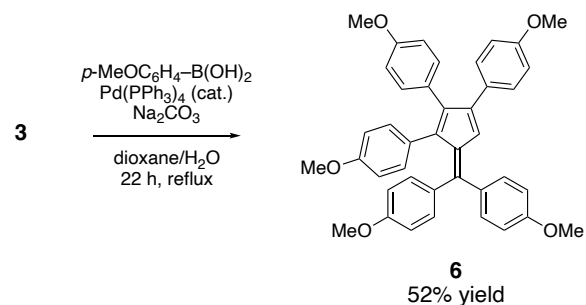


Fig. S2. ¹H NMR spectra of **2** (upper), **3** (middle) and the reaction mixture (lower) in benzene-*d*₆.

Suzuki–Miyaura Cross-coupling Reaction Using *p*-Methoxyphenylboronic Acid:

To a 21 mL mixed solution (1,4-dioxane/H₂O = 2/1) containing fulvene **2** (0.04 mmol) and *p*-methoxyphenylboronic acid (0.20 mmol) were added tetrakis(triphenylphosphine)palladium (5 mol%) and sodium carbonate (0.4 mmol), and the mixture was stirred for 22 hours under reflux. After the reaction mixture was poured into water and extracted with ethyl acetate, the organic layer was dried over MgSO₄ and concentrated in *vacuo*. Then, the residual mixture was subjected to chromatography on silica gel using mixtures of ethyl acetate and hexane as eluents, and the 2,3,4,5,6,6-hexakis(*p*-methoxyphenyl)fulvene (**5**) was separated in 81% yield. This result is shown in **Scheme 4**. The Suzuki–Miyaura cross coupling reaction of **3** with *p*-methoxyphenylboronic acid was also conducted in a similar way to give 2,3,4,6,6-pentakis(*p*-methoxyphenyl)fulvene (**6**) in 52% isolated yield and the result is shown in **Scheme S1**.



Scheme S1. Suzuki–Miyaura cross coupling reaction of **3** with *p*-methoxyphenylboronic acid.

Fulvene **5**: Brown solid; mp 224.0–225.0 °C; ¹H NMR (CDCl₃) δ: 3.63 (s, 6H), 3.66 (s, 6H), 3.71 (s, 6H), 6.30 (d, *J* =

8.8 Hz, 4H), 6.39 (d, $J = 8.6$ Hz, 4H), 6.53–6.63 (m, 12H), 6.94 (d, $J = 8.6$ Hz, 4H); ^{13}C NMR (CDCl_3) δ : 54.9, 55.0, 55.1, 112.29, 112.34, 112.6, 128.7, 130.5, 132.1, 132.3, 133.6, 134.6, 135.2, 141.9, 142.1, 154.8, 156.2, 157.3, 160.1; HRMS (APCI) m/z calcd for $\text{C}_{48}\text{H}_{42}\text{O}_6+\text{H}$ 715.3054, found 715.3040.

Crystal data of **5**: $\text{C}_{48}\text{H}_{42}\text{O}_6$, $M_r = 714.86$, monoclinic space group $C2/c$, $a = 23.5796(15)$ Å, $b = 15.5436(10)$ Å, $c = 11.2836(8)$ Å, $\beta = 102.796(7)^\circ$, $V = 4032.9(5)$ Å³, $Z = 4$, $\rho = 1.177$ Mg/m³, in the final least-squares refinement cycles on F^2 , the model converged at $R_1 = 0.1266$, $wR_2 = 0.3261$, and GOF = 1.261 for 1456 reflections CCDC2089134.

Fulvene **6**: Brown solid; mp 223.0–224.0 °C; ^1H NMR (CDCl_3) δ : 3.63 (s, 3H), 3.66 (s, 3H), 3.74 (s, 3H), 3.77 (s, 3H), 3.86 (s, 3H), 6.32 (d, $J = 8.9$ Hz, 2H), 6.36 (s, 1H), 6.38 (d, $J = 8.9$ Hz, 2H), 6.59 (d, $J = 8.9$ Hz, 2H), 6.65 (d, $J = 8.6$ Hz, 2H), 6.72 (d, $J = 8.9$ Hz, 2H), 6.82 (d, $J = 8.9$ Hz, 2H), 6.85 (d, $J = 8.6$ Hz, 2H), 6.90 (d, $J = 8.9$ Hz, 2H), 7.02 (d, $J = 8.9$ Hz, 2H), 7.33 (d, $J = 8.9$ Hz, 2H); ^{13}C NMR (CDCl_3) δ : 54.986, 54.990, 55.09, 55.13, 55.3, 112.2, 112.5, 112.7, 113.0, 113.1, 123.4, 128.8, 129.3, 129.5, 129.7, 131.8, 132.0, 132.6, 133.4, 134.0, 134.2, 135.7, 141.0, 143.1, 143.3, 152.9, 156.5, 157.8, 158.3, 159.7, 160.3; HRMS (APCI) m/z calcd for $\text{C}_{41}\text{H}_{36}\text{O}_5+\text{H}$ 609.2636, found 609.2617.

Absorption Spectra

The absorption spectra of **5** and **6** were measured in ethyl acetate. The absorption peaks were observed at 415 nm for **5** and 398 nm for **6**, respectively. These results are shown in Fig. S3.

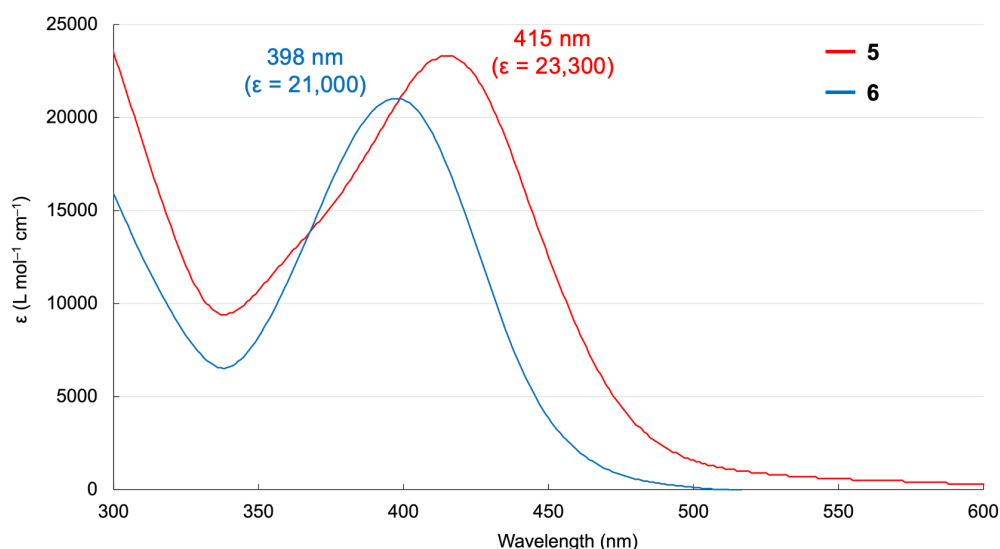


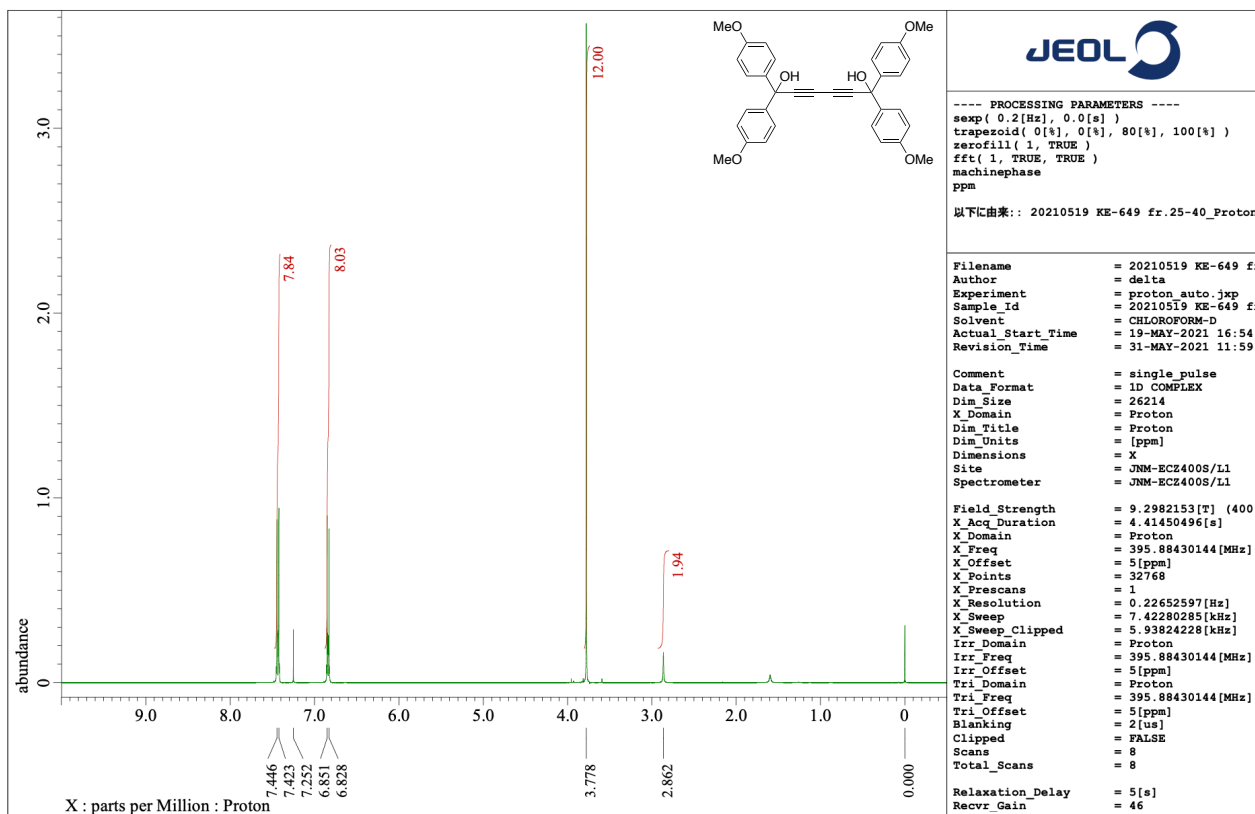
Fig. S3. Absorption spectra of **5** and **6** in ethyl acetate.

References

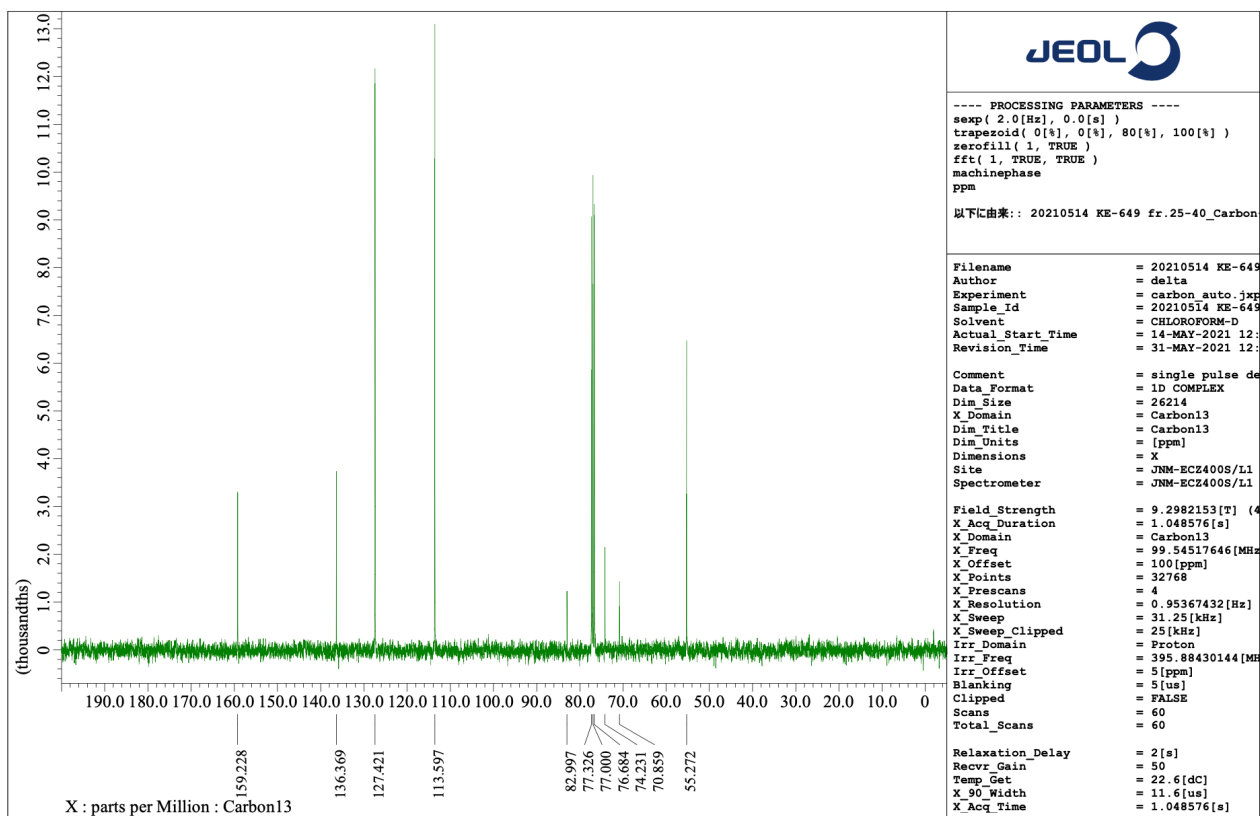
S1. P. Cadiot, *Ann. Chim.*, 1956, **13**, 214.

S2. J. A. Januszewski, D. Wendinger, C. D. Methfessel, F. Hampel and R. R. Tykwinski, *Angew. Chem. Int. Ed.*, 2013, **52**, 1817.

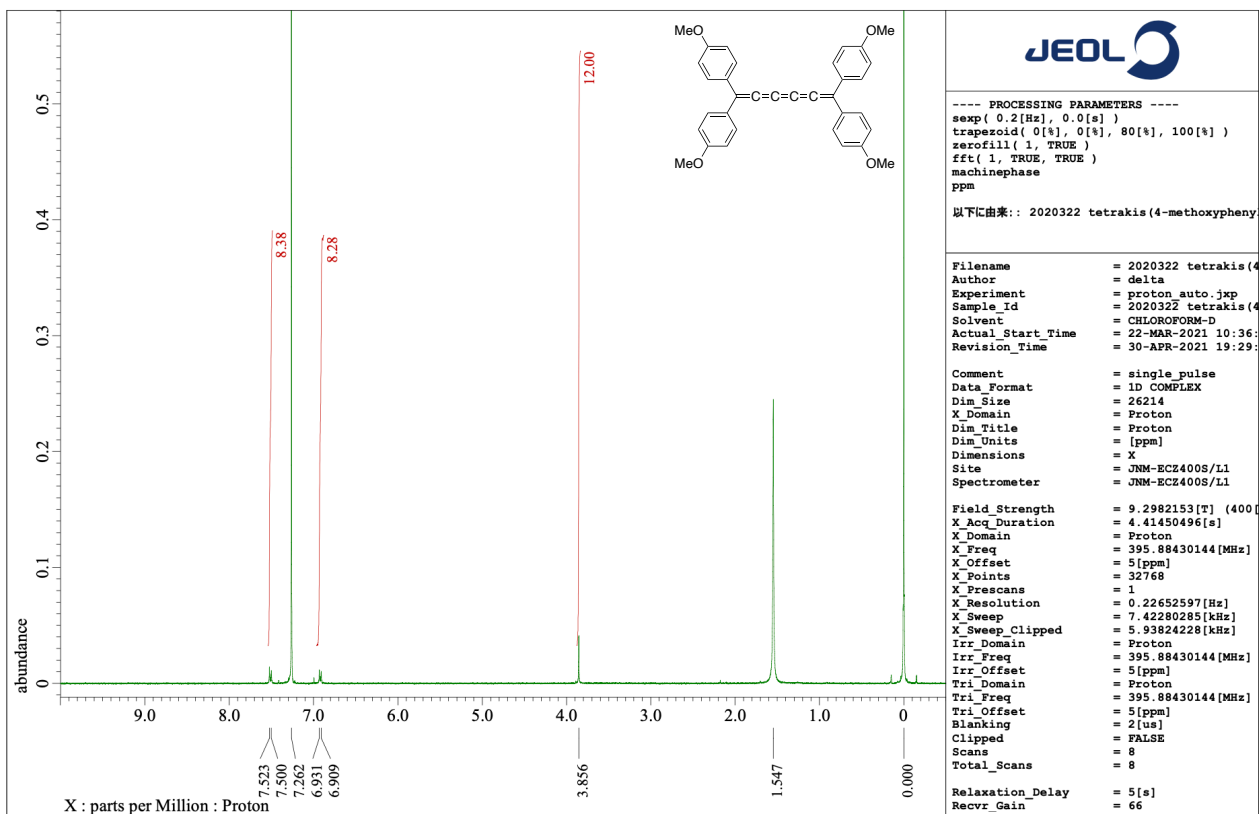
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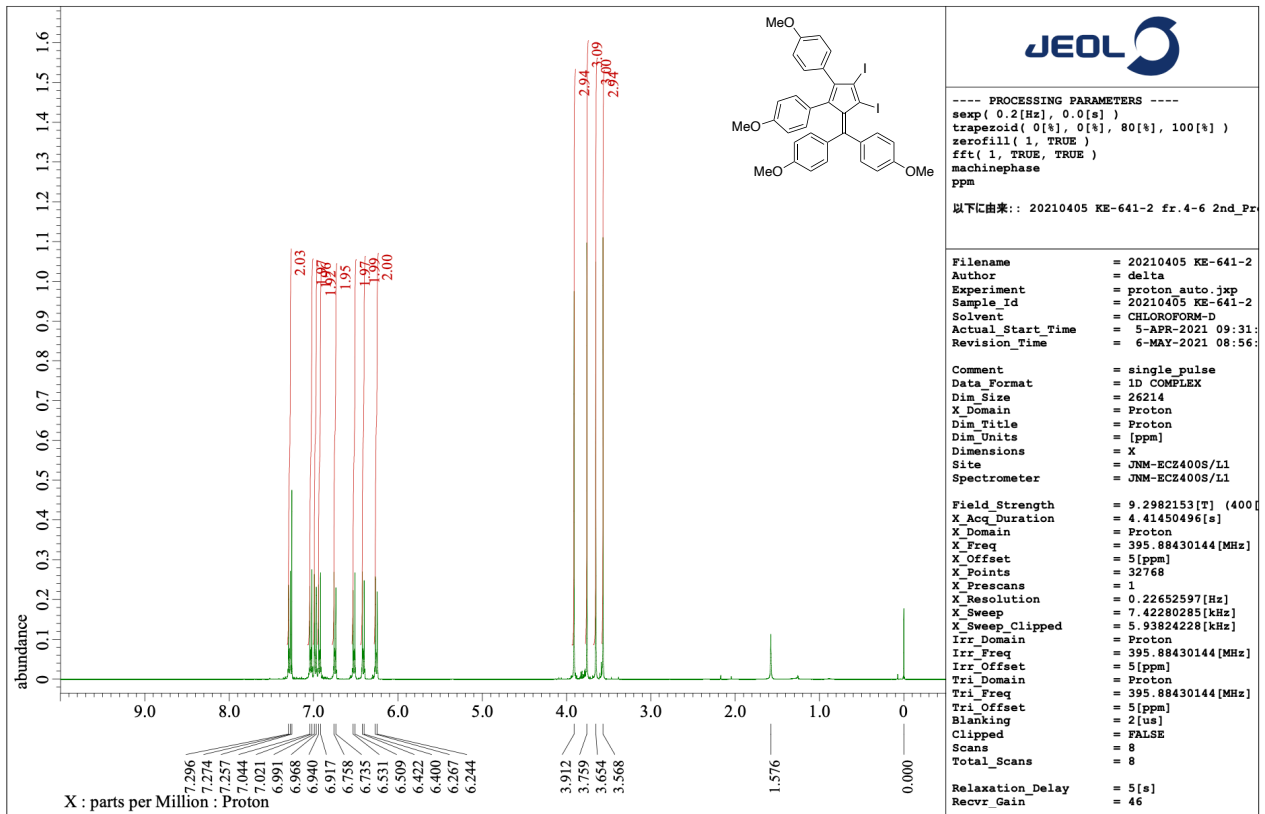
¹³C NMR spectrum of 1,1,6,6-tetrakis(*p*-methoxyphenyl)hexa-2,4-diyne-1,6-diol



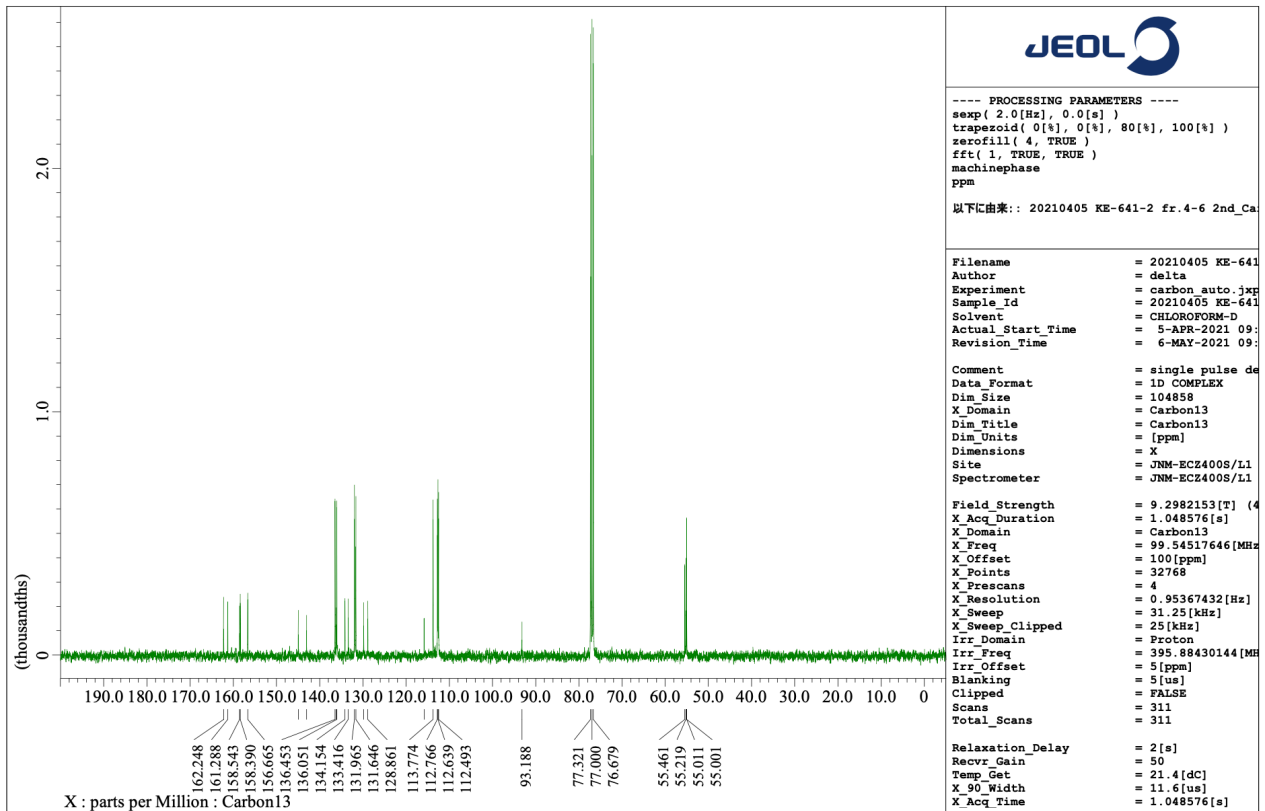
¹H NMR spectrum of 1



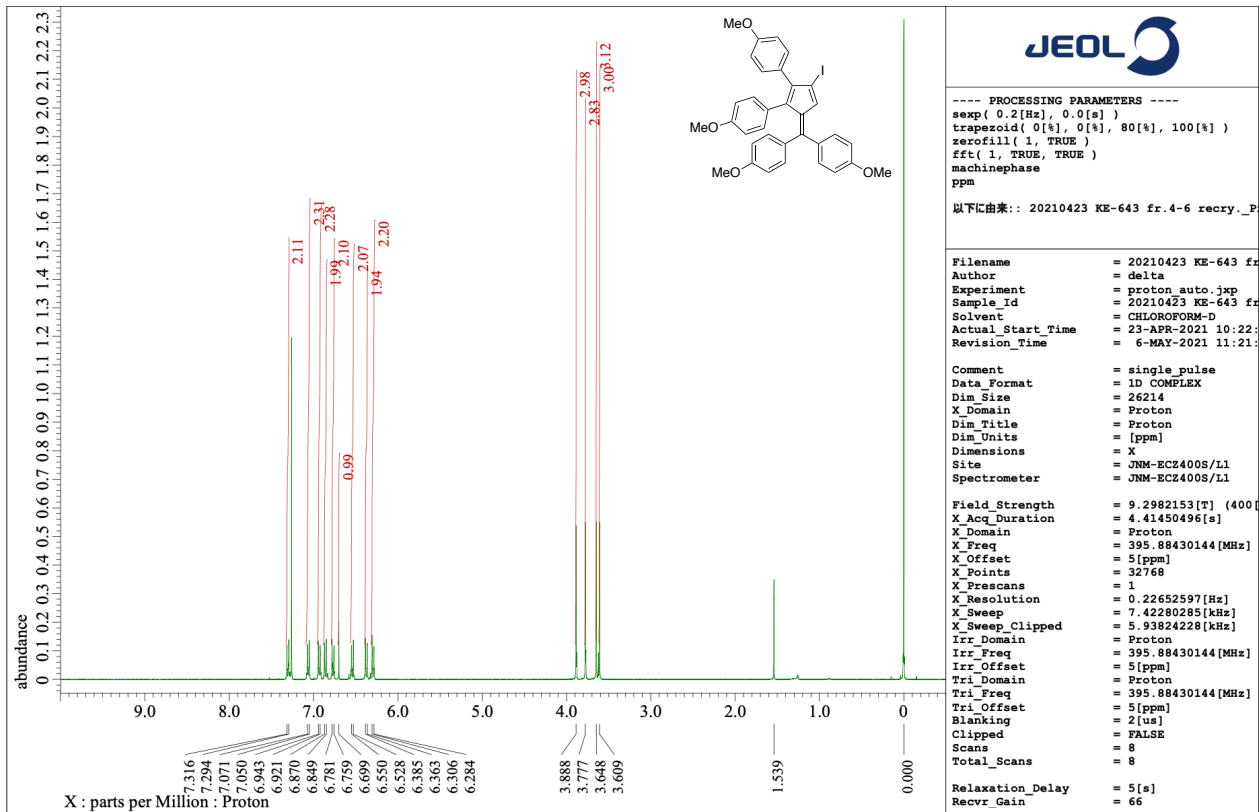
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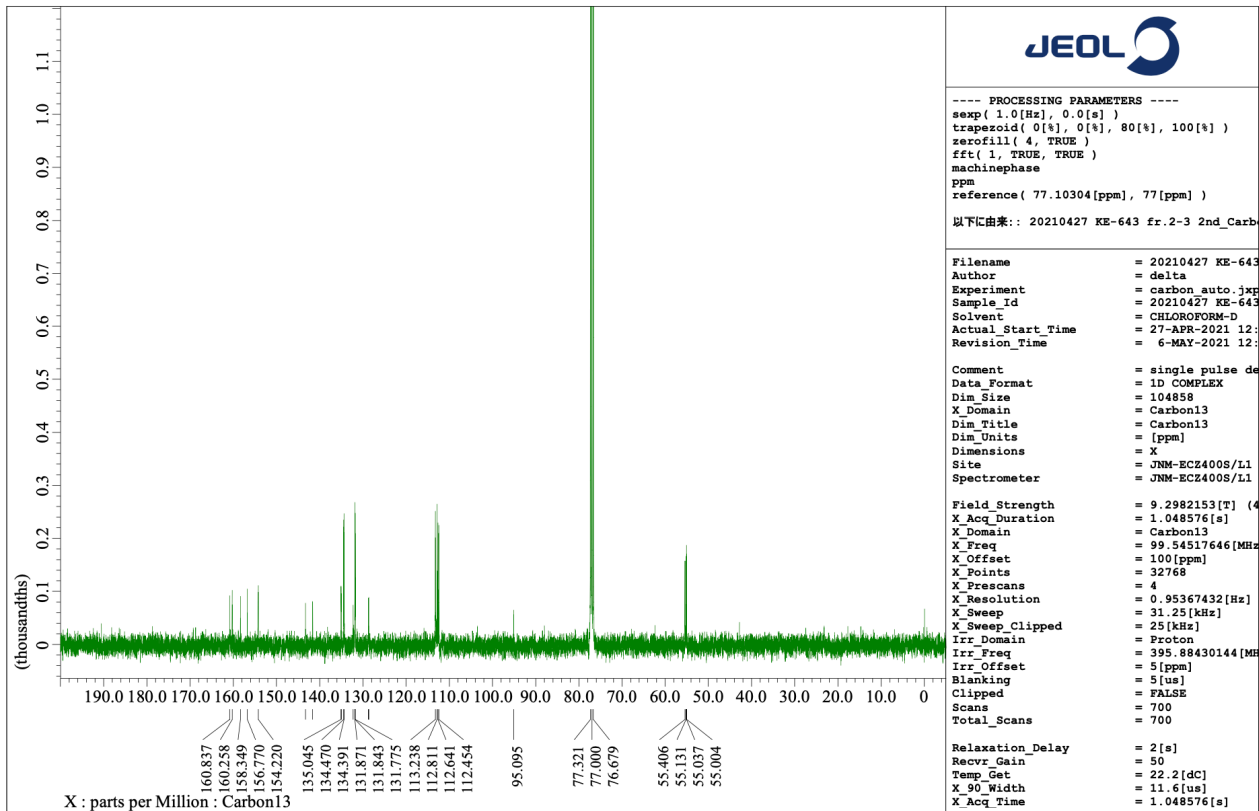
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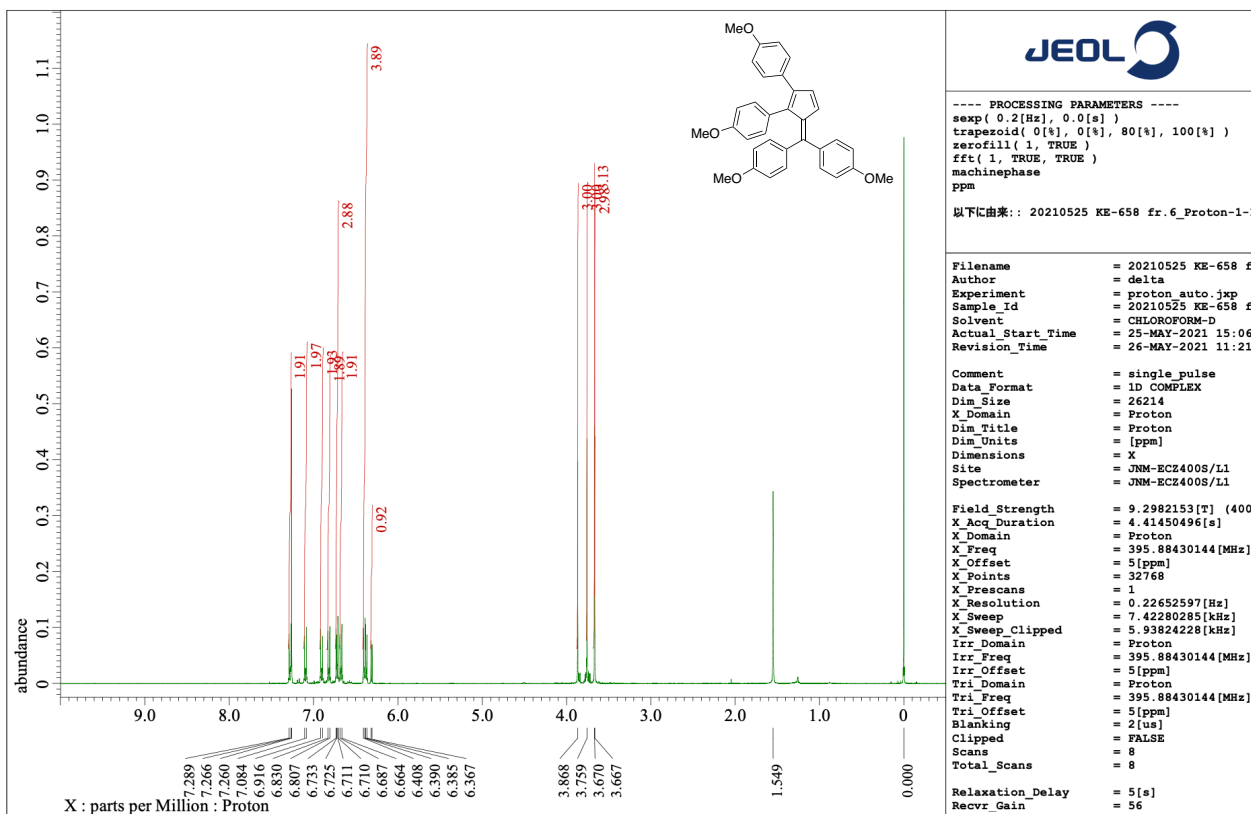
¹H NMR spectrum of 3



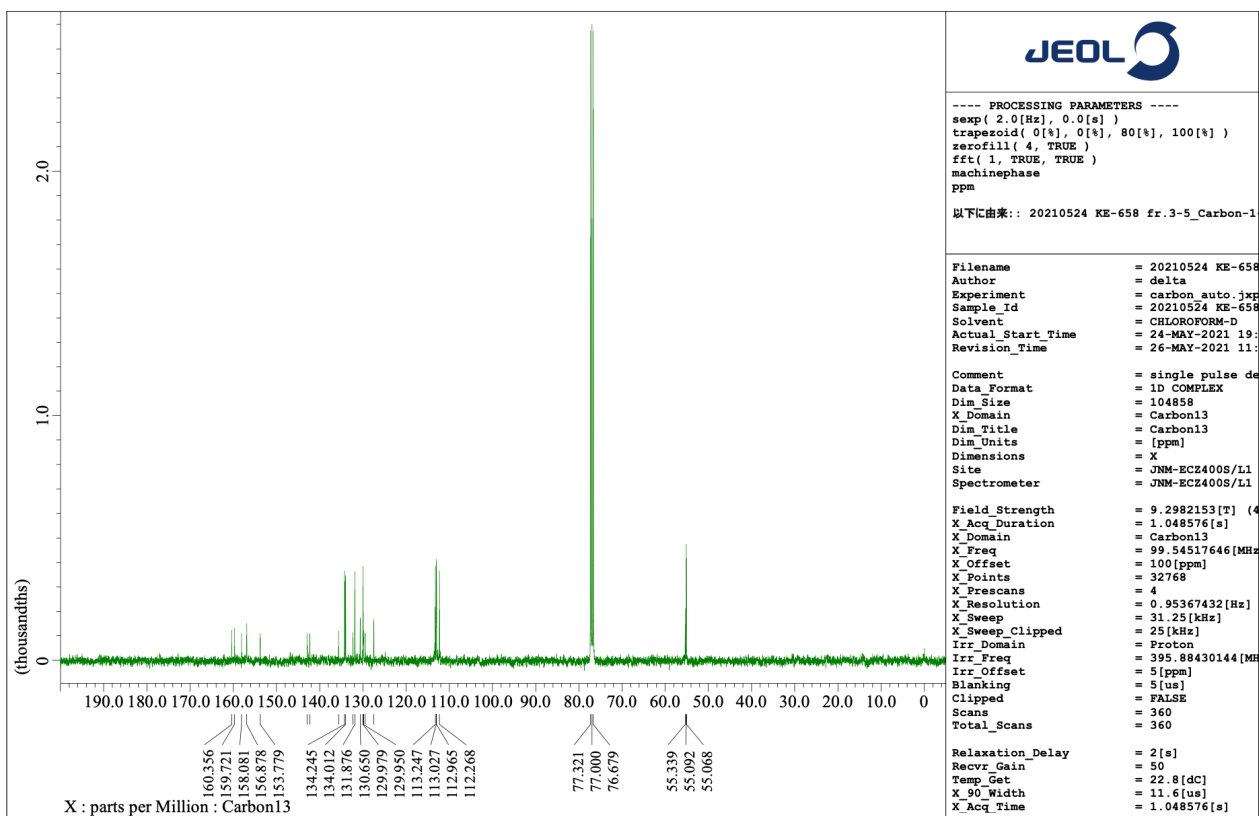
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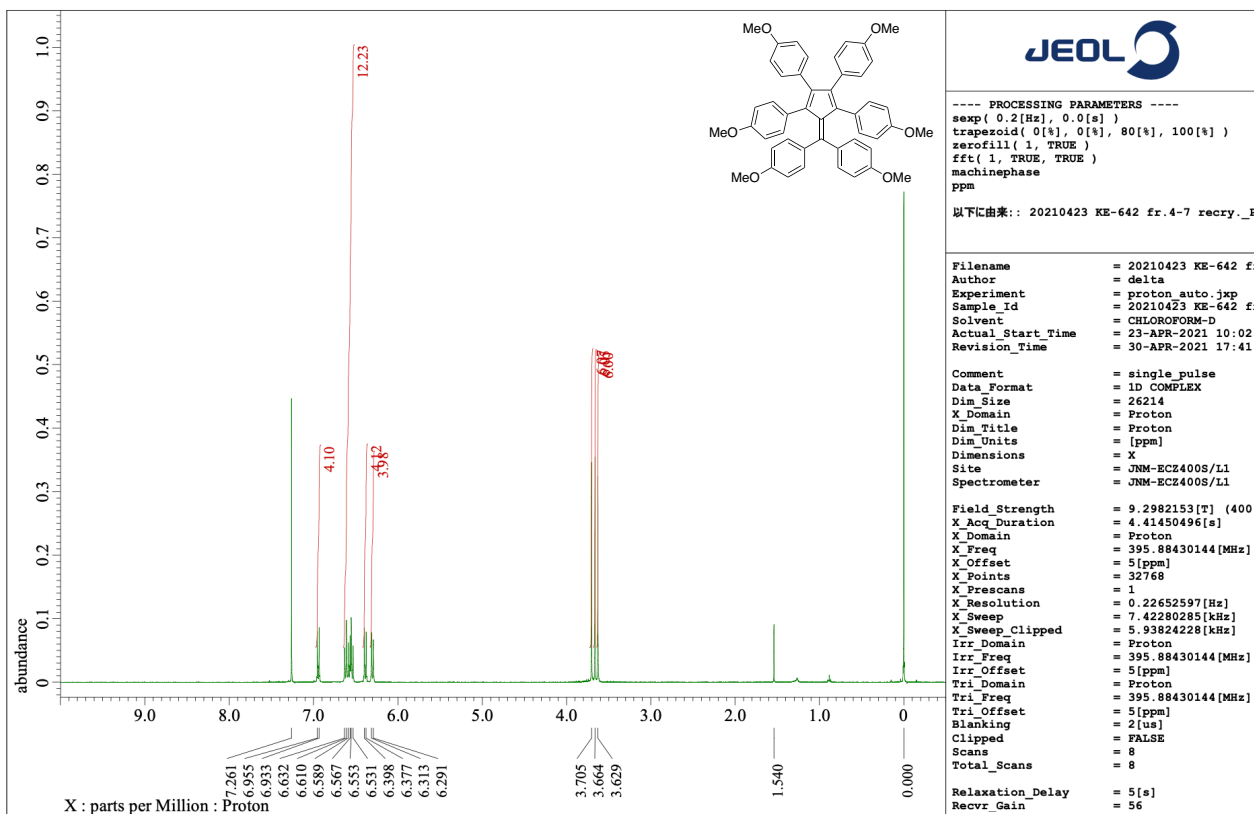
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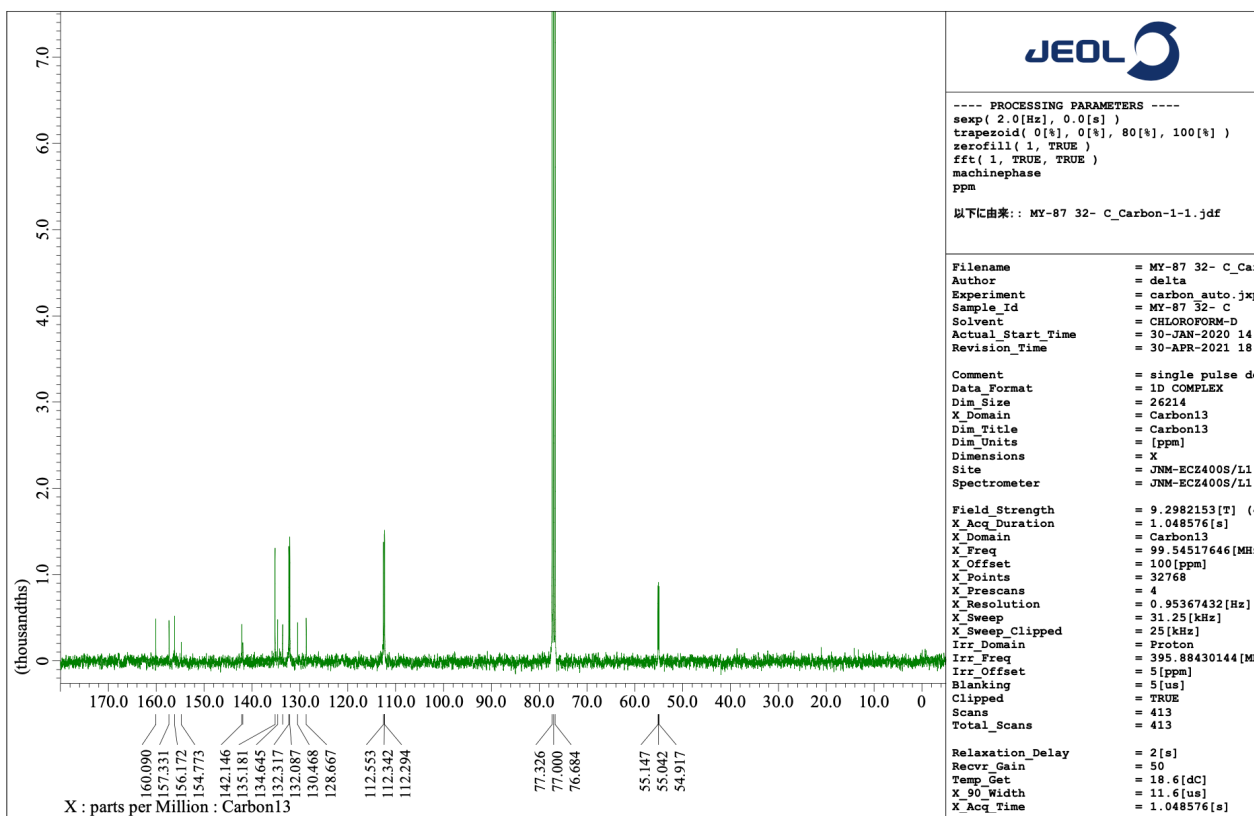
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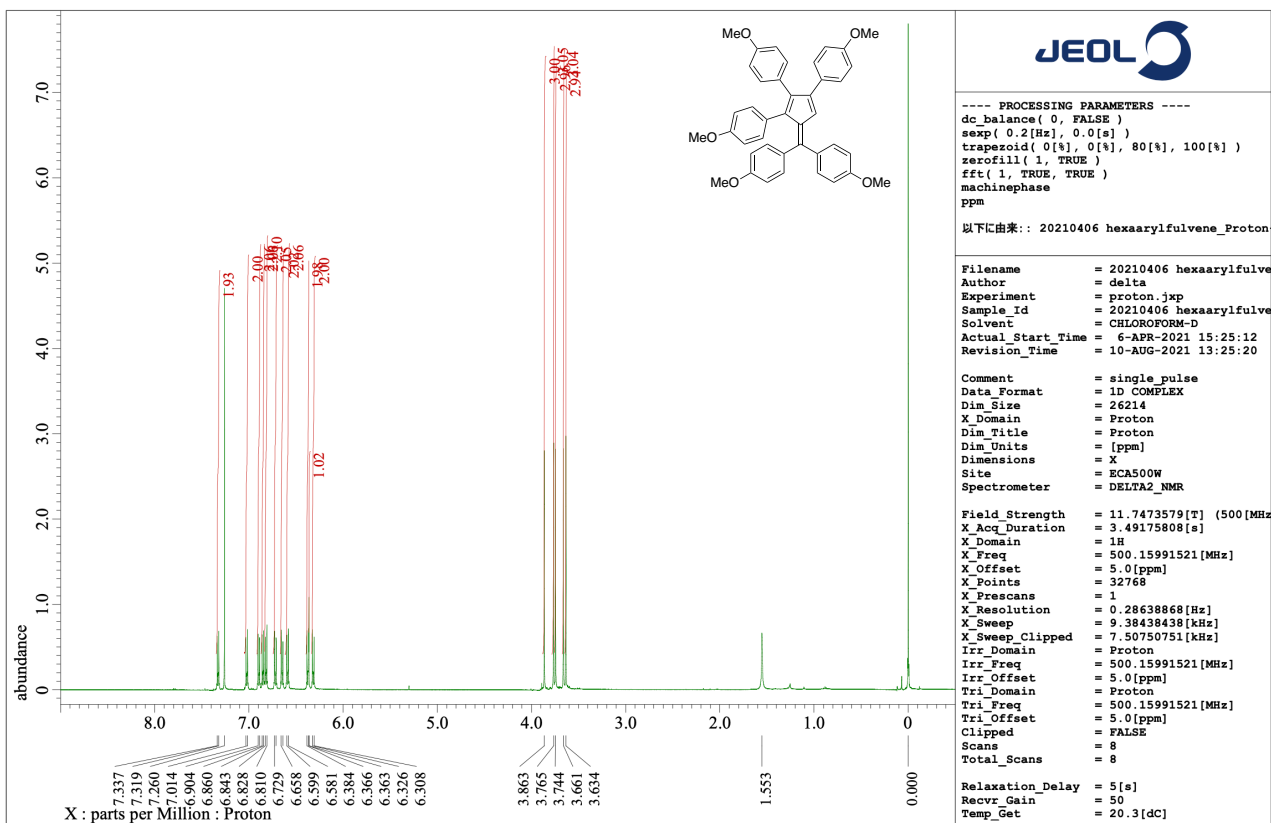
¹H NMR spectrum of 5



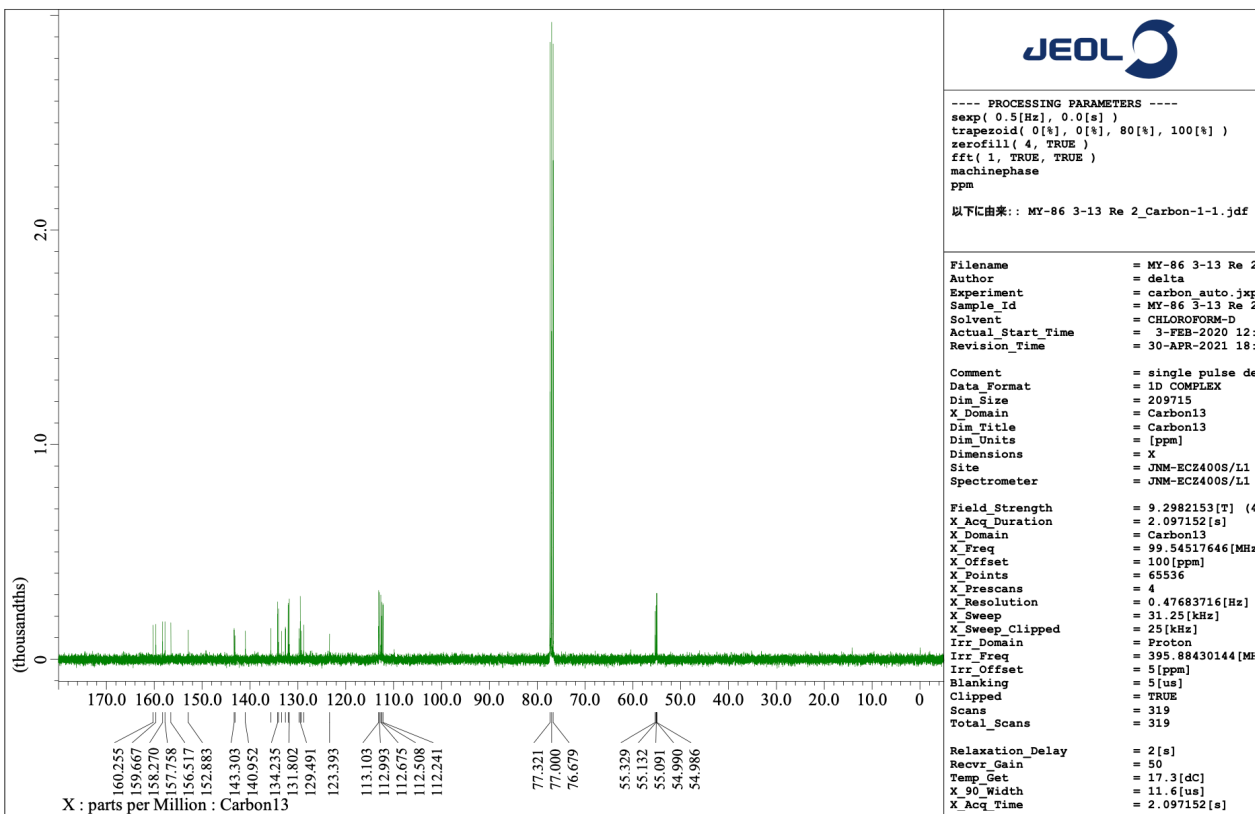
¹³C NMR spectrum of 5



¹H NMR spectrum of 6



¹³C NMR spectrum of 6



HMQC spectrum of 6

