

Supporting Information

Palladium-catalyzed carbopalladation and carbocyclization of arynes with aryl halides: a highly efficient route to functionalized triphenylenes

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Experimental Section

General: All reactions were conducted under nitrogen atmosphere on a dual-manifold Schlenk line unless otherwise mentioned and in oven-dried glass wares. Acetonitrile was dried with CaH₂ and distilled prior to use. Benzyne precursors **1a-c** were synthesized according to the literature procedures.¹ Pd(dba)₂ was prepared by reported procedure.² Other reagents were commercially available and used as purchased.

General Procedure for the Synthesis of Triphenylenes (3): To a solution of Pd(dba)₂ (0.0150 mmol), CsF (2.40 mmol), Tl(OAc) (0.36 mmol) and aryl iodide(**2**) (0.30 mmol) under one atmosphere of nitrogen was added benzyne precursor (**1**) (0.60 mmol) and CH₃CN (3.0 mL) via syringes. The reaction mixture was allowed to stir at 85 °C for 8 h. At the end of the reaction, the reaction mixture was diluted with CH₂Cl₂, filtered through Celite and silica gel. The filtrate was concentrated and the residue was purified through a silica gel column using hexane as eluent to give pure **3**.

Compounds **3a-h**, were prepared by following this procedure. Spectral data of **3a-h** are listed below:

References:

- 1 (a) Y. Himeshima, T. Sonoda and Kobayashi, H. *Chem. Lett.* 1983, 1211; (b) D. Peña, D. Pérez, E. Guitián. and L.Castedo, *J. Am. Chem. Soc.* 1999, **121**, 5827.
- 2 Y. Takahashi, T. Ito, S. Sakai and Y. Ishii, *J. Chem. Soc., Chem. Commun.* 1970, 1065.

1-(Triphenylen-6-yl)ethanone (3a): white solid, mp 152-153 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3): δ 2.70 (s, 3H), 7.59-7.63 (m, 4H), 8.01 (dd, $J = 8.5$, $J = 1.7$, 1H), 8.46-8.58 (m, 5H), 9.07 (s, 1H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ 26.7, 123.18, 123.20, 123.3, 123.4; 123.8, 123.9, 126.0, 127.3, 127.4, 127.6, 128.2, 128.7, 129.3, 129.3, 129.7, 130.5 133.1, 134.9, 197.9; **HRMS** calcd for $\text{C}_{20}\text{H}_{14}\text{O}$ 270.1045, found 270.1051. **Registry Number:** [74733-00-9]

Ethyl triphenylene-2-carboxylate (3b): white solid, mp 129-130 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 1.48 (t, $J = 7.2$ Hz, 3H), 4.48 (q, $J = 14.4$ Hz, $J = 7.2$ Hz, 2H), 7.64-7.70 (m, 4H), 8.23 (dd, $J = 8.8$ Hz, $J = 2.0$ Hz, 1H), 8.60-8.64 (m, 4H), 8.70-8.72 (m, 1H); 9.33 (s, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 14.4, 61.13, 123.2 (2C), 123.3(2C), 123.5, 125.3, 127.2, 127.3, 127.4, 127.6, 128.1, 128.7, 128.9, 129.4, 129.8, 130.6, 133.0, 166.7; **HRMS** calcd for $\text{C}_{21}\text{H}_{16}\text{O}_2$ 300.1150, found 300.1146. **Registry Number:** [34177-32-7]

2-Nitrotriphenylene (3c): yellow solid, mp 162-163 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.60 (m, 4H), 8.19 (d, $J = 6.3$ Hz, 1H), 8.39-8.43 (m, 3H), 8.50 (t, $J = 9.6$ Hz, 2H), 9.19 (s, 1H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ 118.8, 120.6, 123.2, 123.31, 123.32, 124.0, 124.1, 127.6, 127.7, 127.9, 128.3, 128.4, 129.0, 129.7, 129.9, 130.7, 134.0, 146.1; **HRMS** calcd for $\text{C}_{18}\text{H}_{11}\text{NO}_2$ 273.0790, found 273.0792. **Registry Number:** [81316-79-2]

1-(2,3,6,7-Tetramethyltriphenylen-11-yl)ethanone (3d): white solid, mp 236-237 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 2.76 (s, 3H), 2.50-2.49 (m, 12H), 8.07 (dd, $J = 8.8$ Hz, $J = 2.0$ Hz, 1H), 8.30-8.31 (m, 3H), 8.58 (d, $J = 4.0$ Hz, 2H), 9.16 (s, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 20.2, 20.26, 20.33, 26.8, 29.7, 123.2, 123.6, 123.7, (2C), 123.8, 124.5,

125.5, 126.7, 127.4, 127.9, 128.9, 129.1, 133.1, 134.7, 135.8, 136.0, 136.6, 137.4, 198.2;

HRMS calcd for C₂₄H₂₂O 326.1671, found 326.1675.

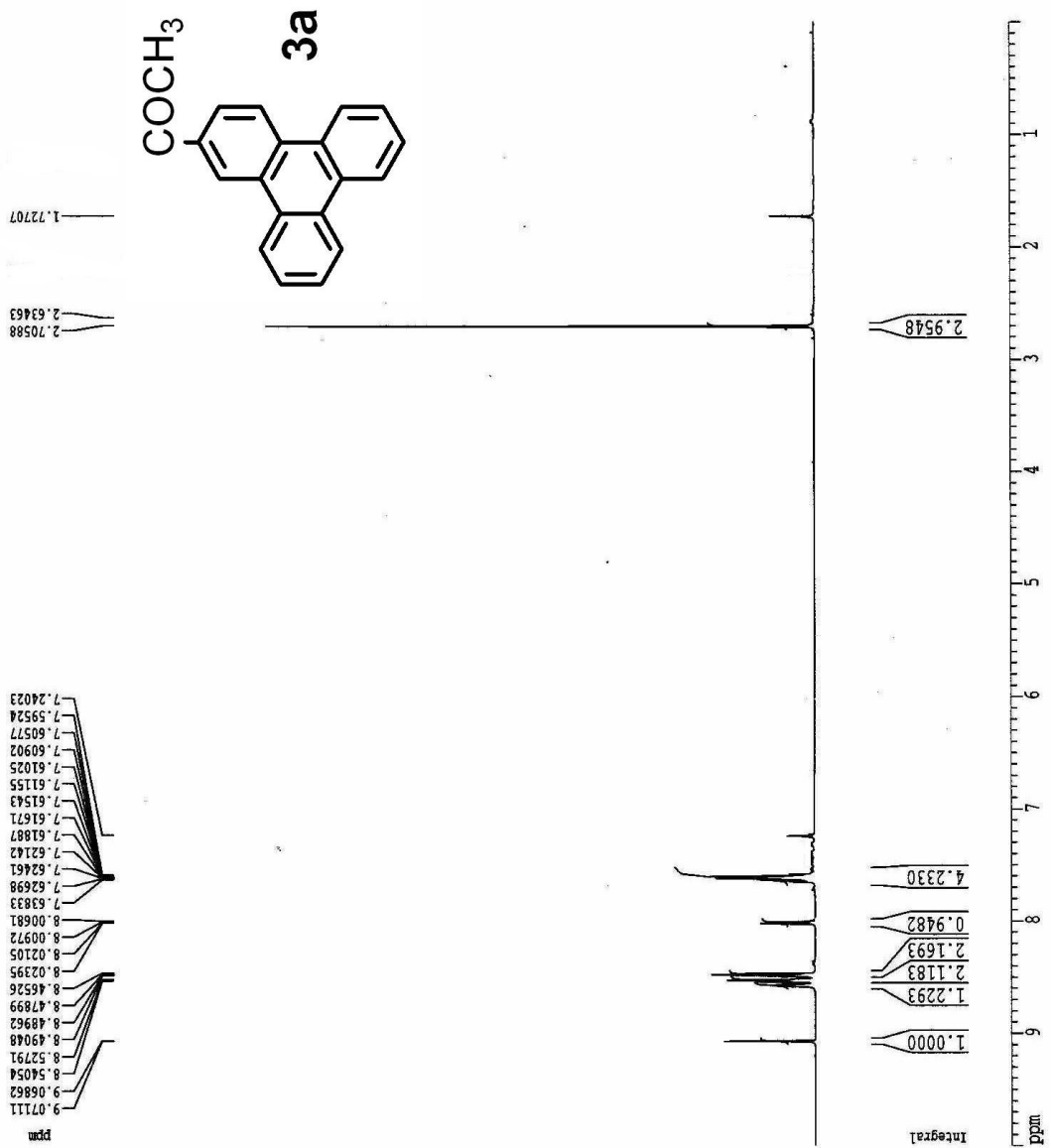
10-Fluoro-2,3,6,7-tetramethyltriphenylene (3e): white solid, mp 202-203 °C; **¹H NMR** (400 MHz, CDCl₃): δ 2.26 (s, 6H), 2.47 (s, 6H), 7.29-7.24 (m, 1H), 8.14-8.12 (m, 2H), 8.15 (s, 1H), 8.26 (s, 2H), 8.51-8.47 (m, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 20.2, 108.3 (d), 114.5 (d), 123.6 (2C), 123.9, 125.0, 125.1, 125.9, 126.8, 127.2, 127.3, 128.2, 131.3, 131.4, 135.6, 135.7, 136.6, 162.0 (d); **HRMS** calcd for C₂₂H₁₉F 302.1471, found 302.1468.

2,3,6,7-Tetramethyltriphenylene (3f): white solid, mp 199-200 °C; **¹H NMR** (600 MHz, CDCl₃): δ 2.49-2.50 (m, 12H), 7.57 - 7.59 (m, 2H), 8.34 (d, *J* = 10.2 Hz, 4H), 8.57 - 8.59 (m, 2H); **¹³C NMR** (100 MHz, CDCl₃): δ 20.2, 123.0, 123.6, 123.8, 126.4, 127.6, 127.9, 129.5, 135.5, 136.0; **HRMS** calcd for C₂₂H₂₀ 284.1565, found 284.1567.

1-(1,2,3,10,11,12-Hexahydrodicyclopenta[*b,h*]triphenylene-6-yl)-1-ethanone (3g): white solid, mp 281-282 °C; **¹H NMR** (400MHz, CDCl₃): δ 2.18-2.22 (m, 4H), 2.76 (s, 3H), 3.10-3.16 (m, 8H), 8.07 (d, *J* = 8.4Hz, 1H), 8.43 (s, 3H), 8.50 (s, 1H), 8.59 (d, *J* = 8.8 Hz, 1H), 9.12 (s, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 25.8 (2C), 26.8, 32.9, 33.0 (2C), 33.1, 118.3, 118.4, 118.5, 119.0, 123.4, 123.9, 125.5, 127.3, 127.9, 129.1, 129.5, 130.0, 133.5, 134.5, 143.8, 143.9, 144.7, 145.4, 198.2; **HRMS** calcd for C₂₆H₂₂O 350.1671, found 350.1677.

Ethyl 1,2,3,10,11,12-hexahydrodicyclopenta[*b,h*]triphenylene-6-carboxylate (3h): white solid, mp 253-255 °C; **¹H NMR** (400MHz, CDCl₃): δ 1.49 (t, *J* = 7.2 Hz, 3H), 2.15-2.26 (m, 4H), 3.06-3.13 (m, 8H), 4.49 (q, *J* = 14.4 Hz, *J* = 7.2 Hz, 2H), 8.12 (dd, *J* =

8.8 Hz, 1H), 8.33 (s, 3H), 8.44 (s, 1H), 8.50 (d, $J = 8.8$ Hz, 1H), 9.22 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 14.5, 25.7 (2C), 32.8, 32.88, 32.97, 33.0, 61.0, 118.1, 118.2, 118.4, 118.8, 123.0, 125.1, 126.3, 127.3, 127.7, 127.8, 128.9, 129.4, 129.8, 133.2, 143.5, 143.7, 144.3, 145.0, 167.0; **HRMS** calcd for $\text{C}_{27}\text{H}_{24}\text{O}_2$ 380.1776, found 380.1772.



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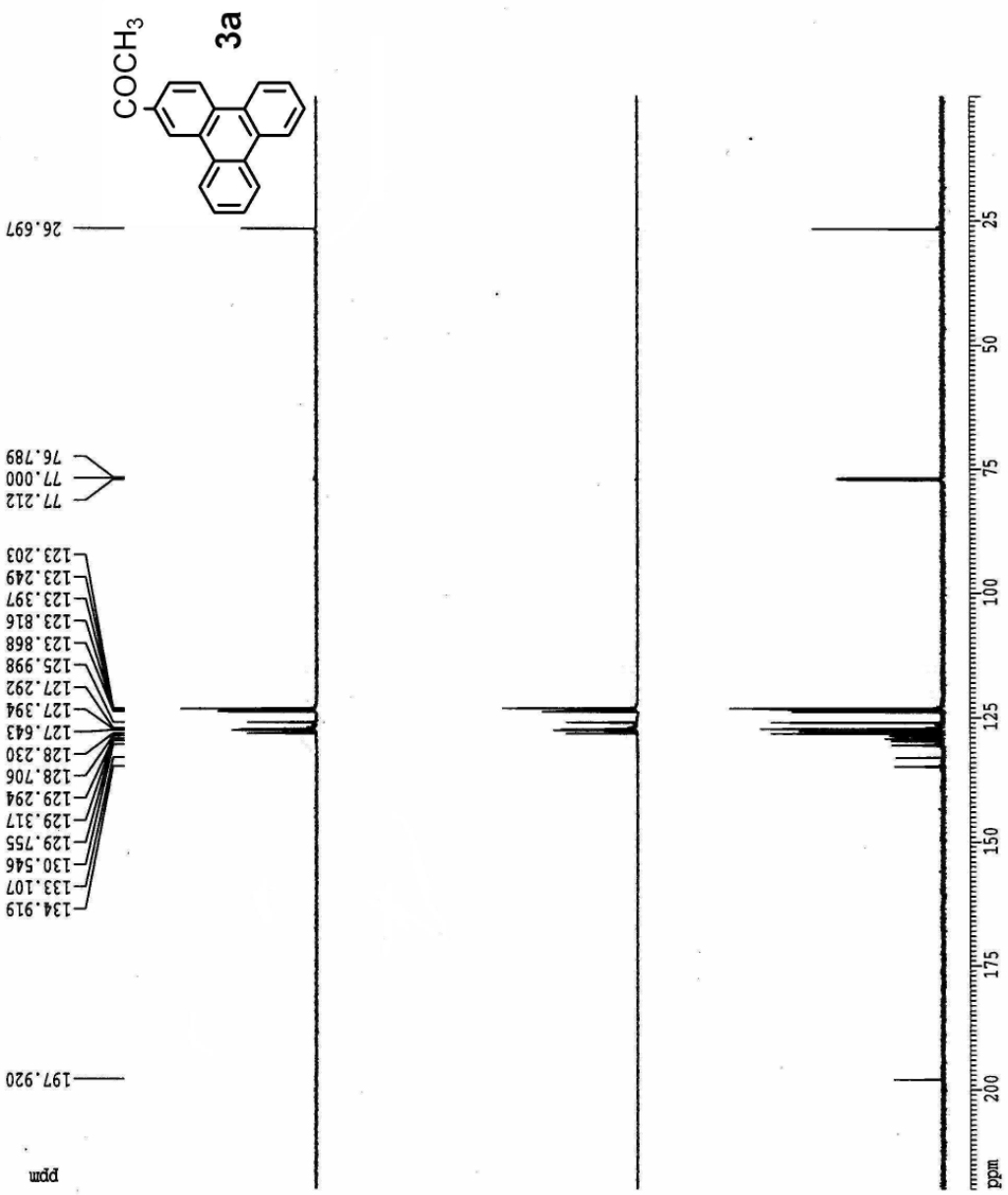
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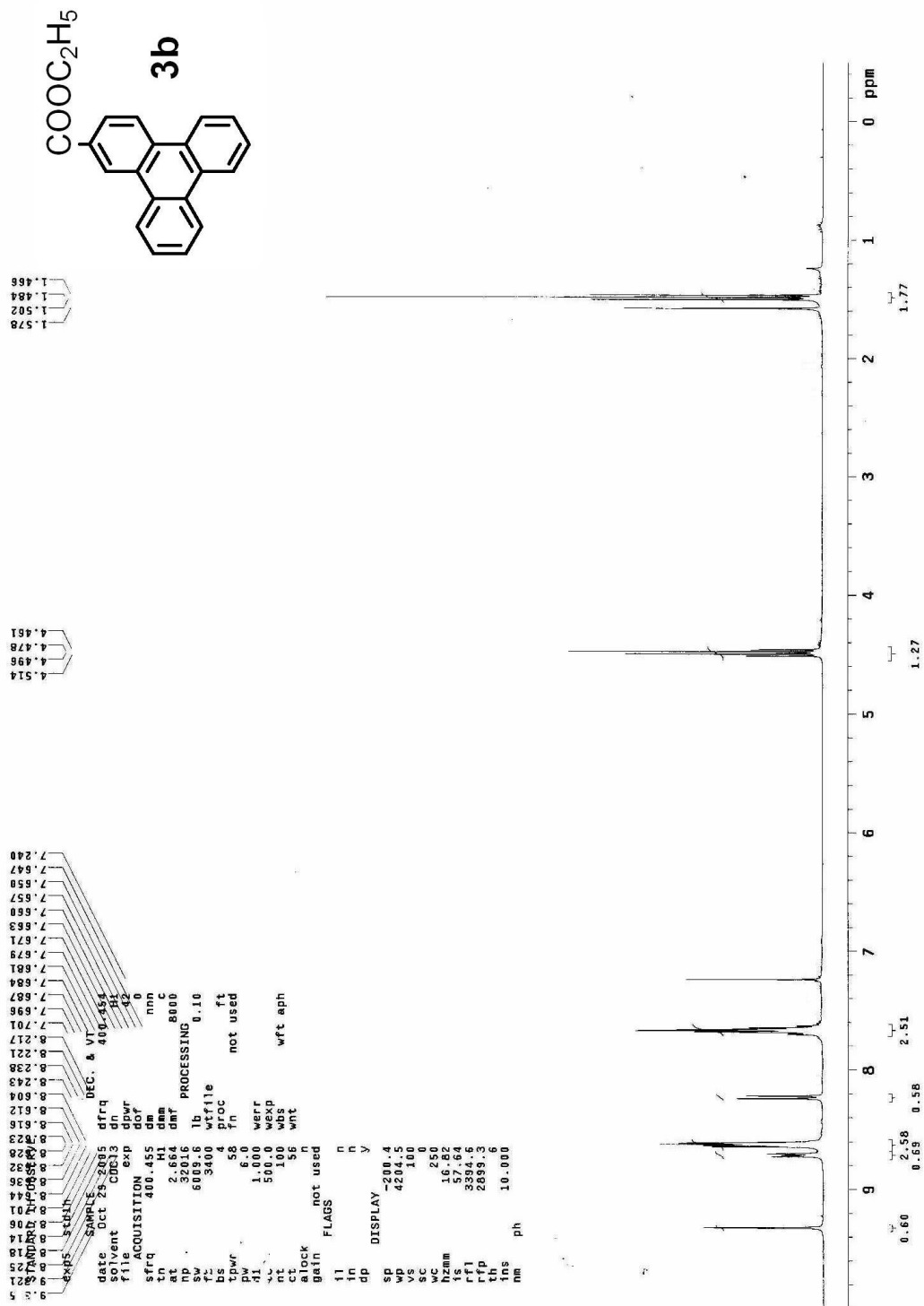
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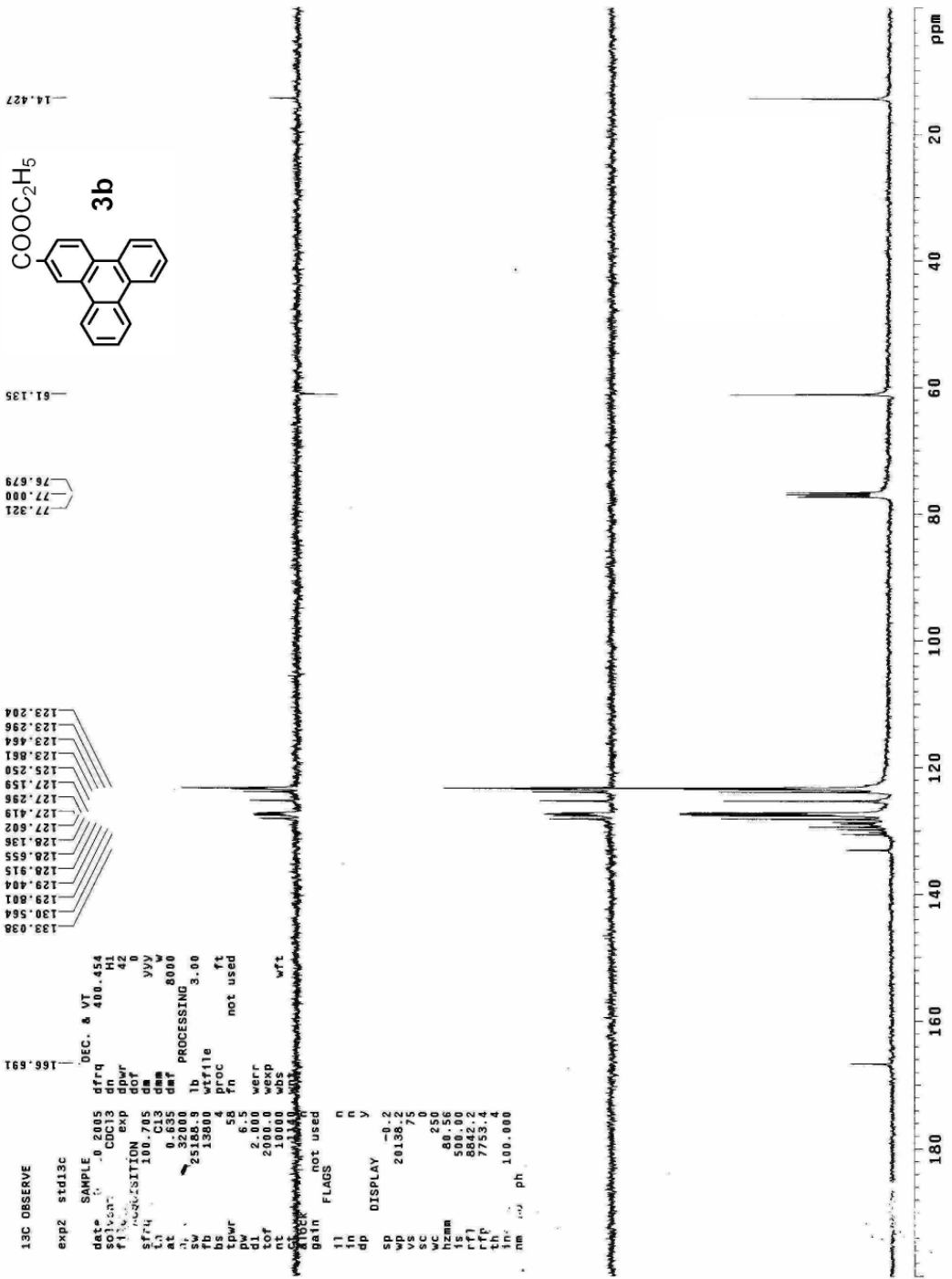
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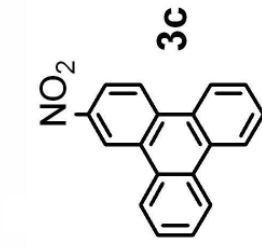
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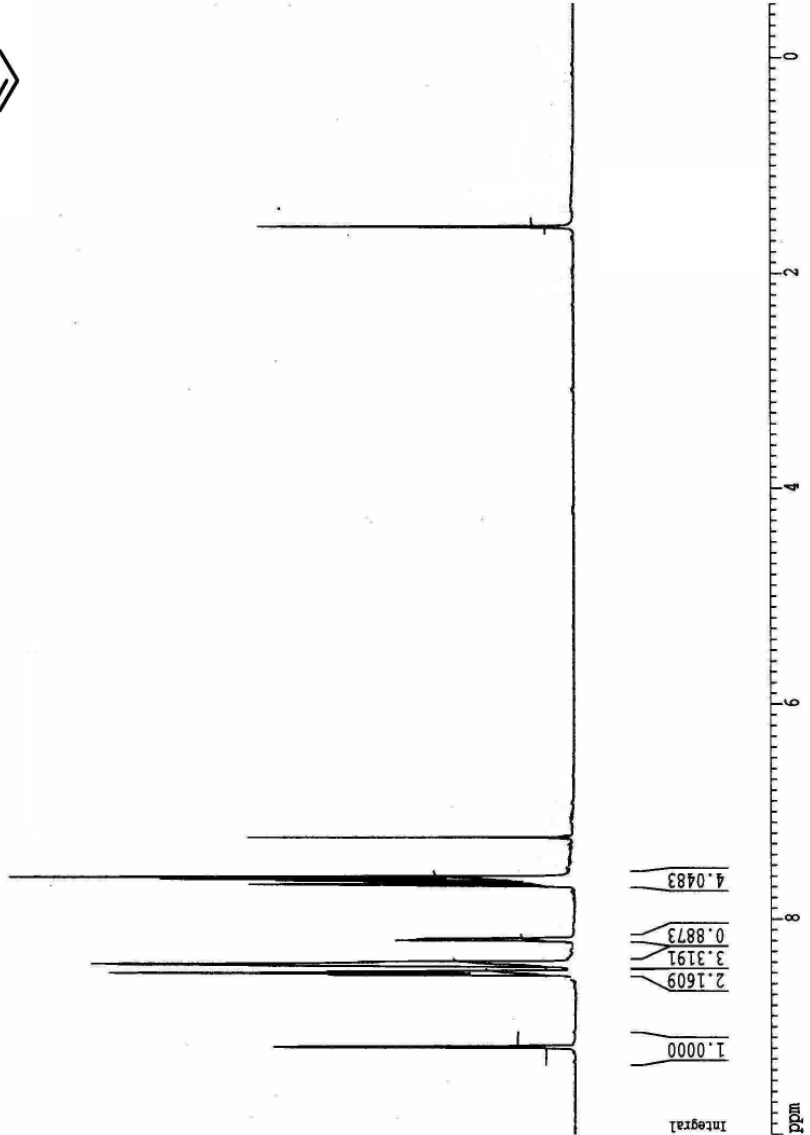
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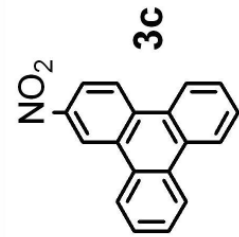
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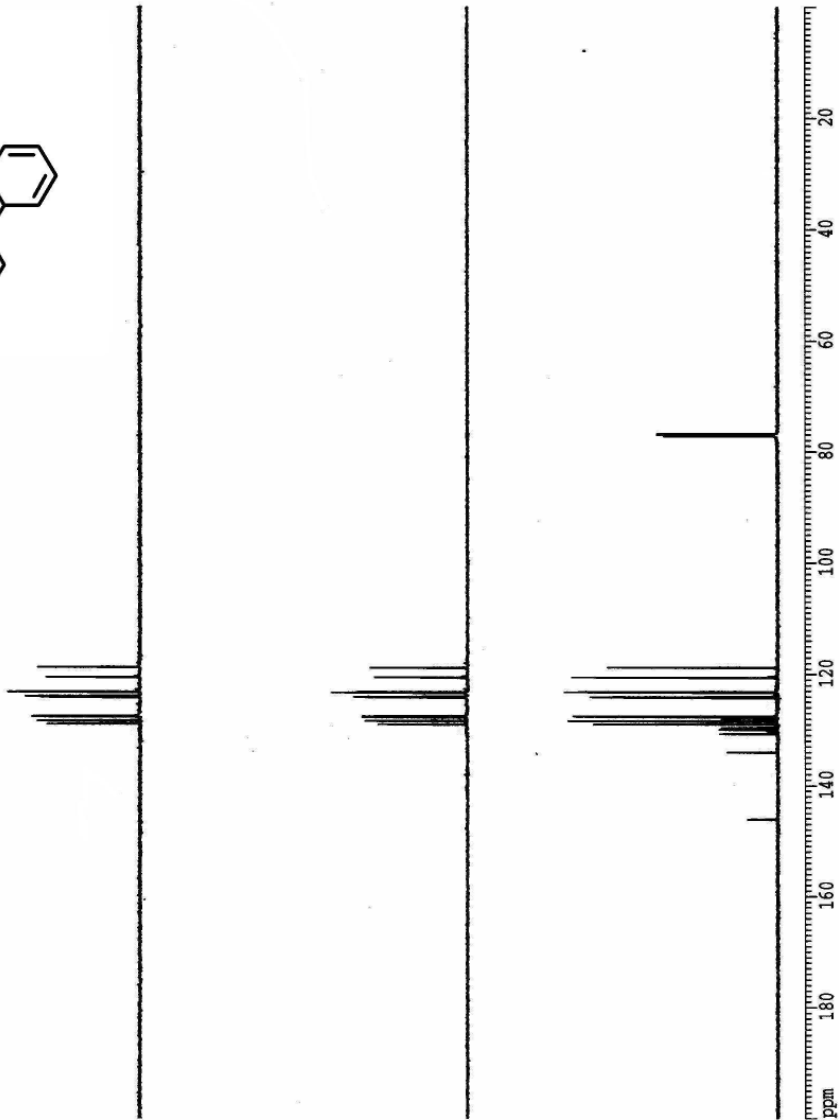
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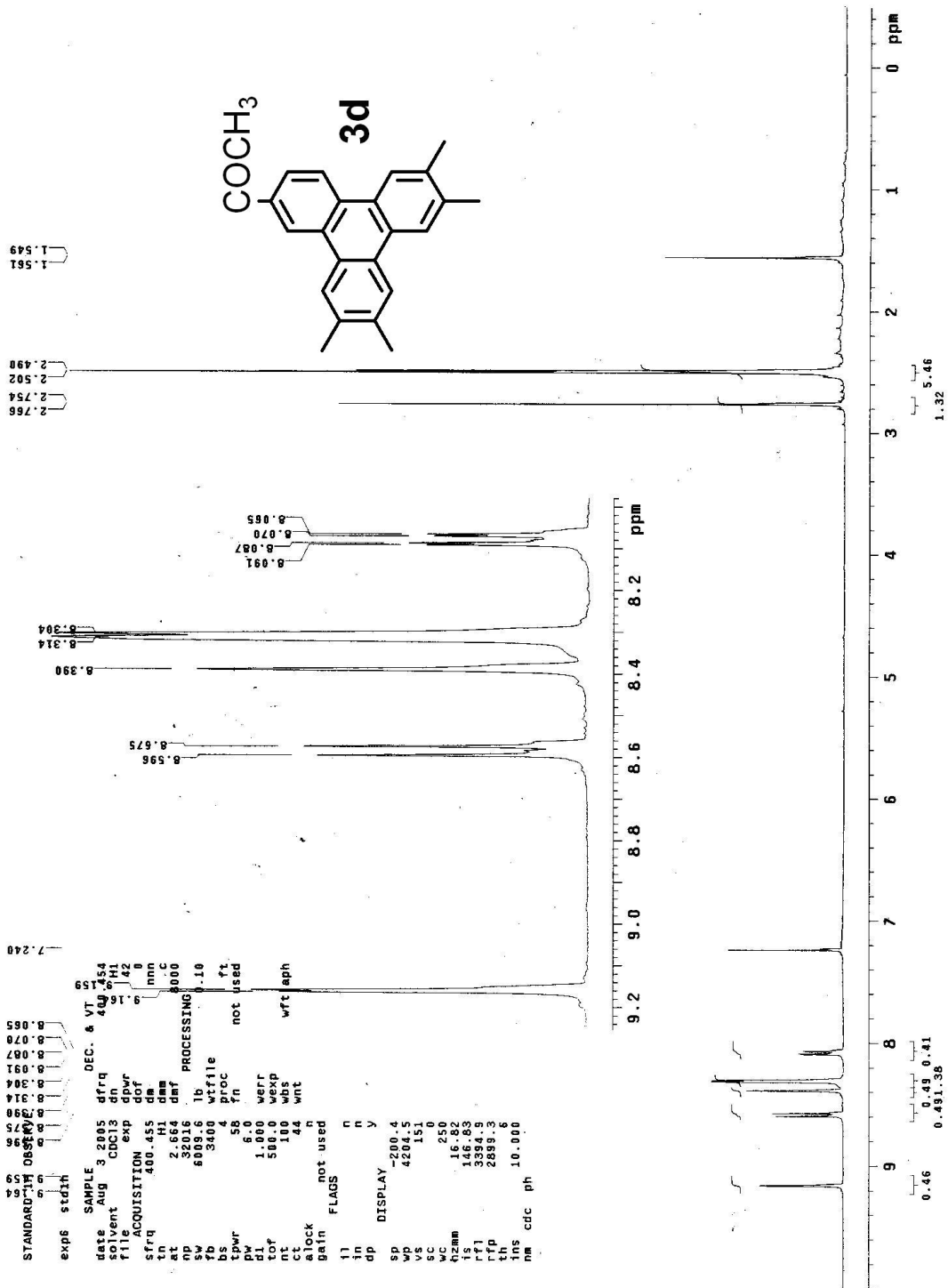
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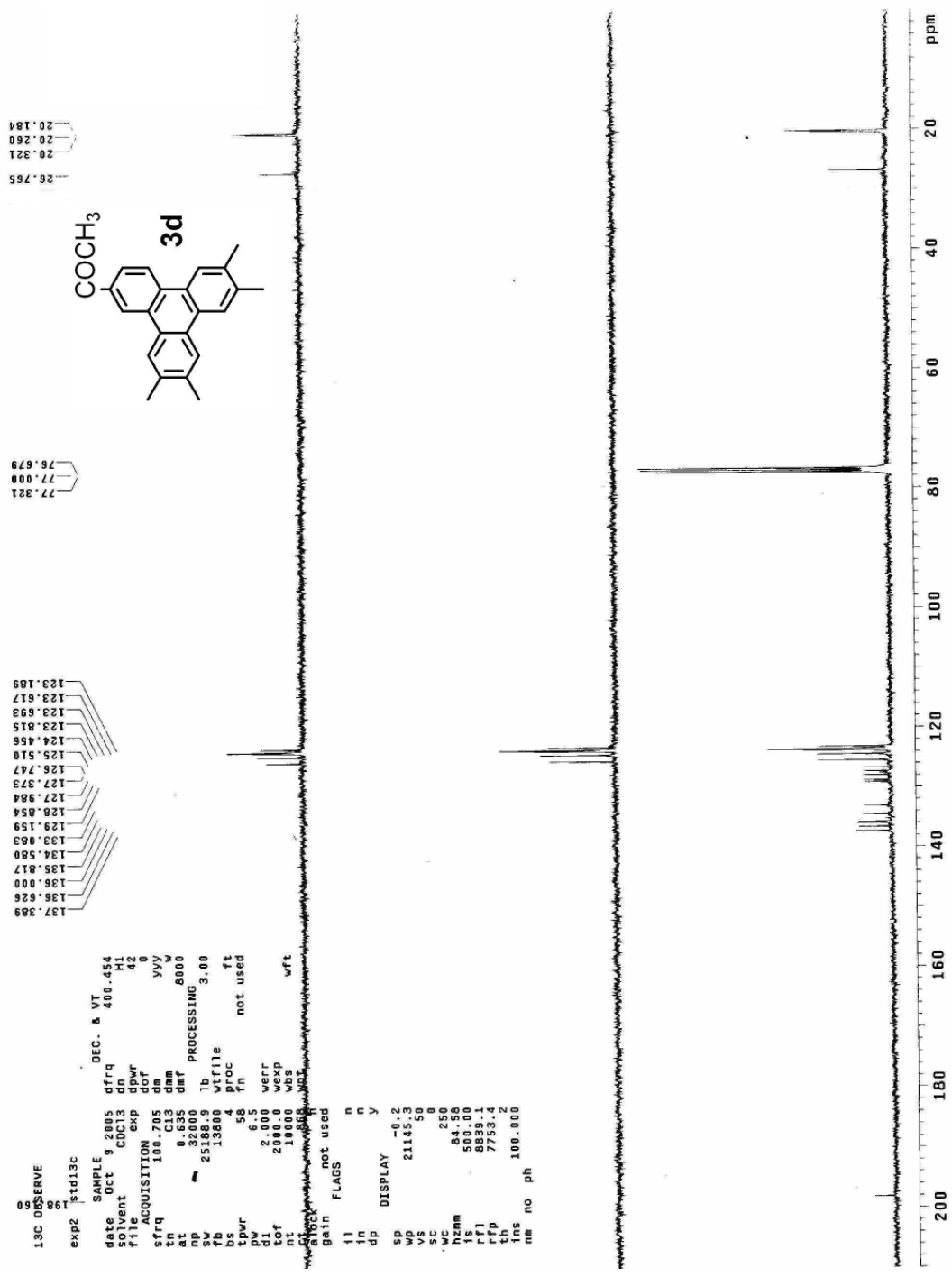


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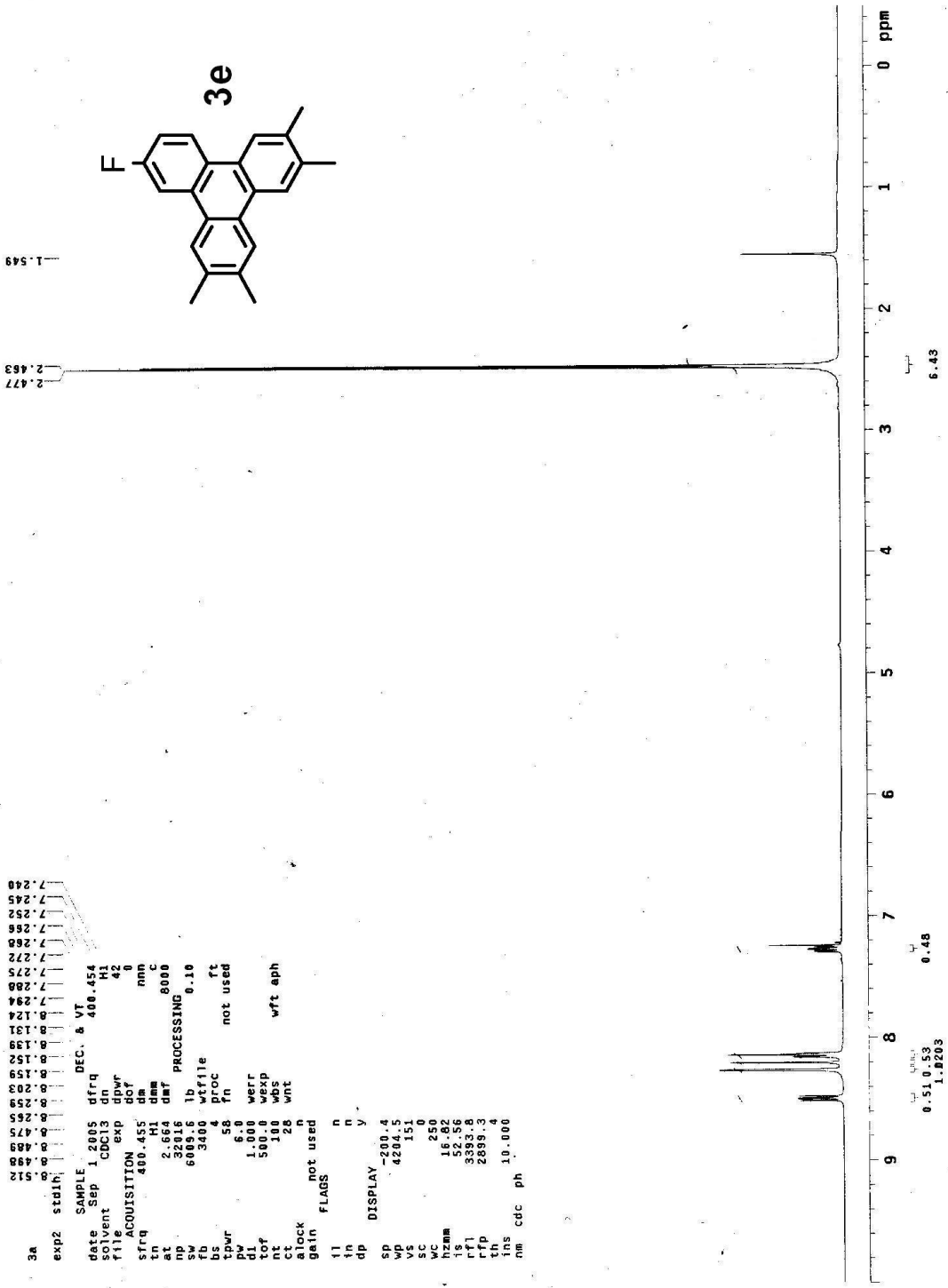


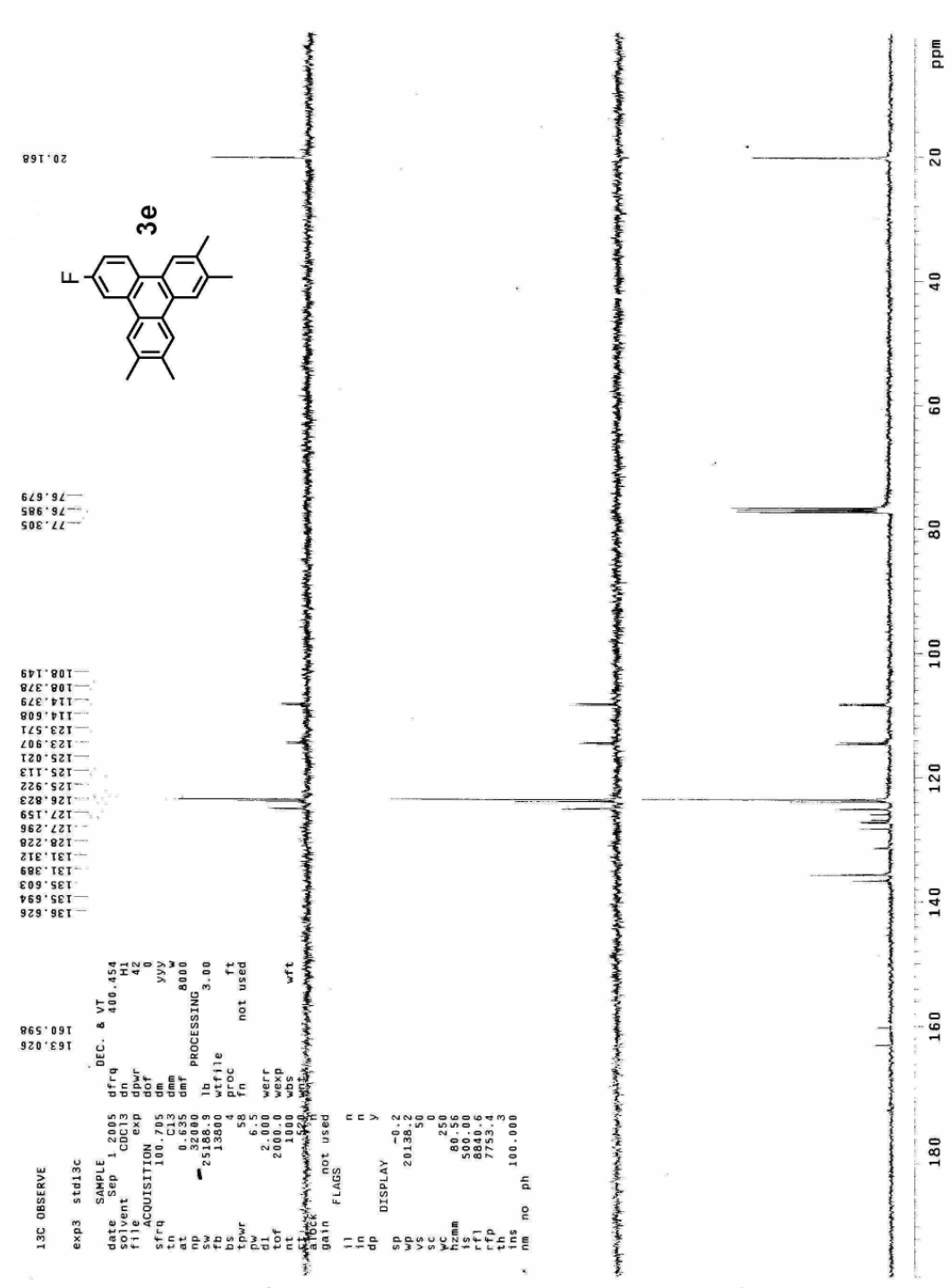


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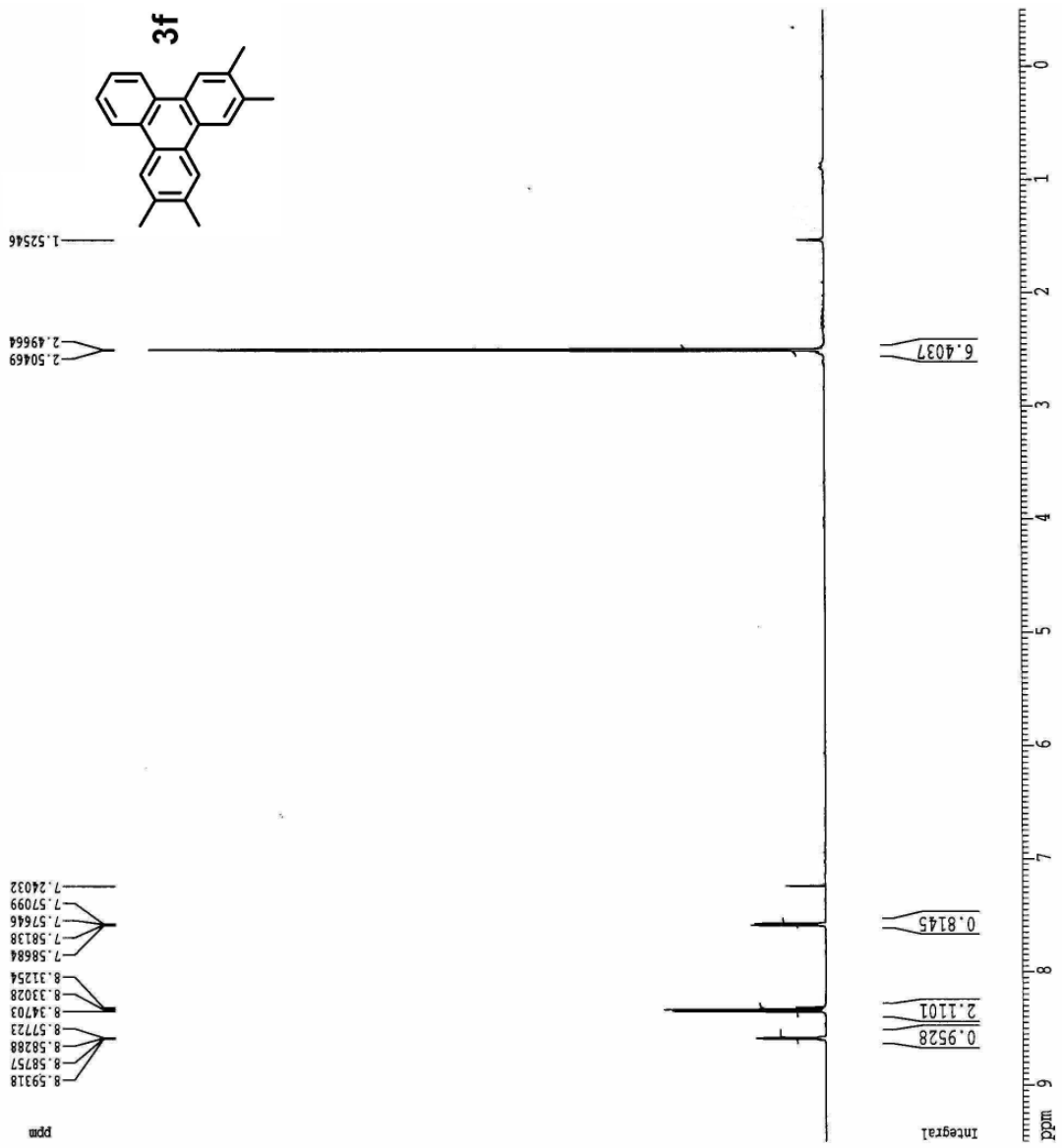
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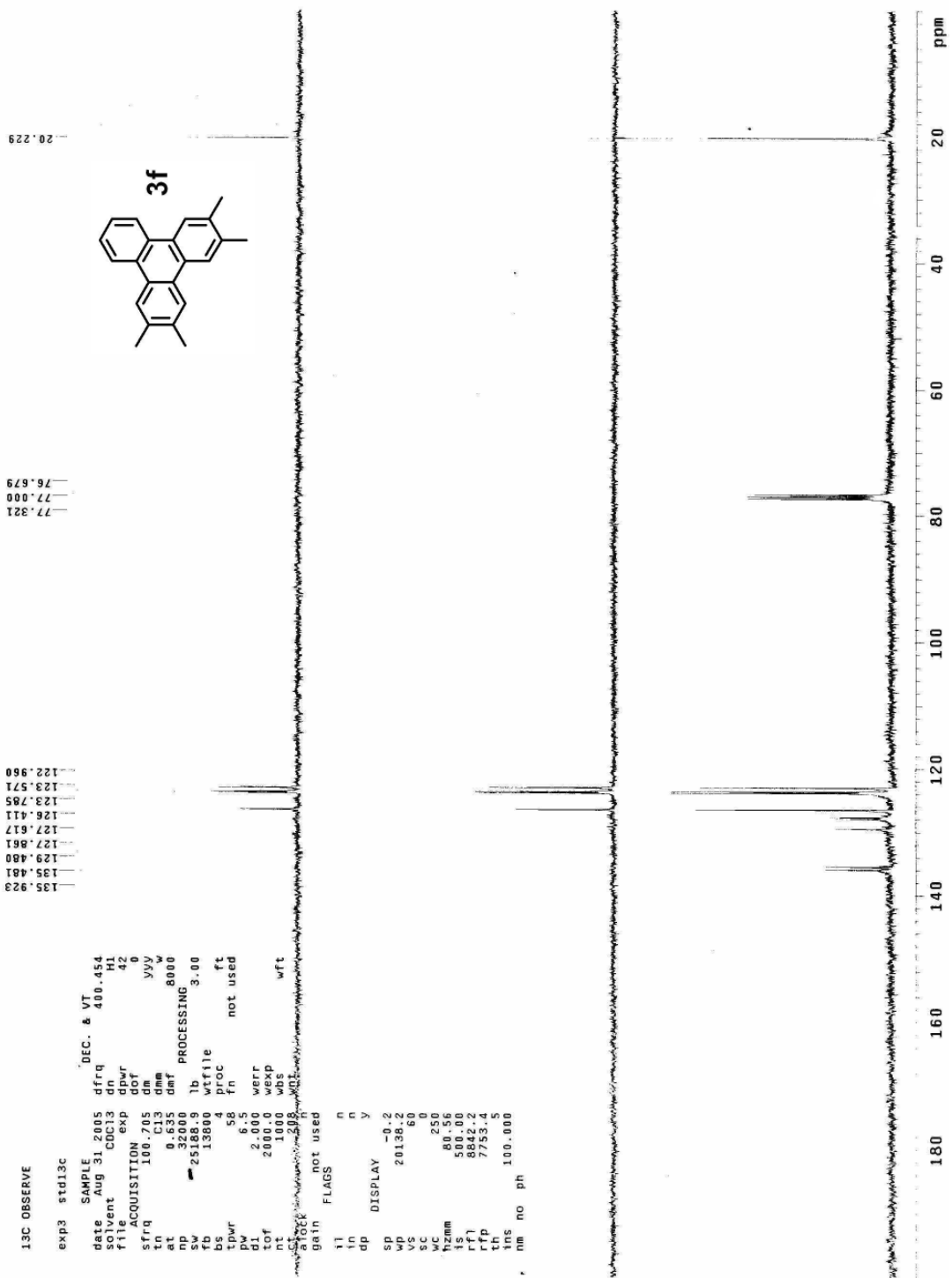
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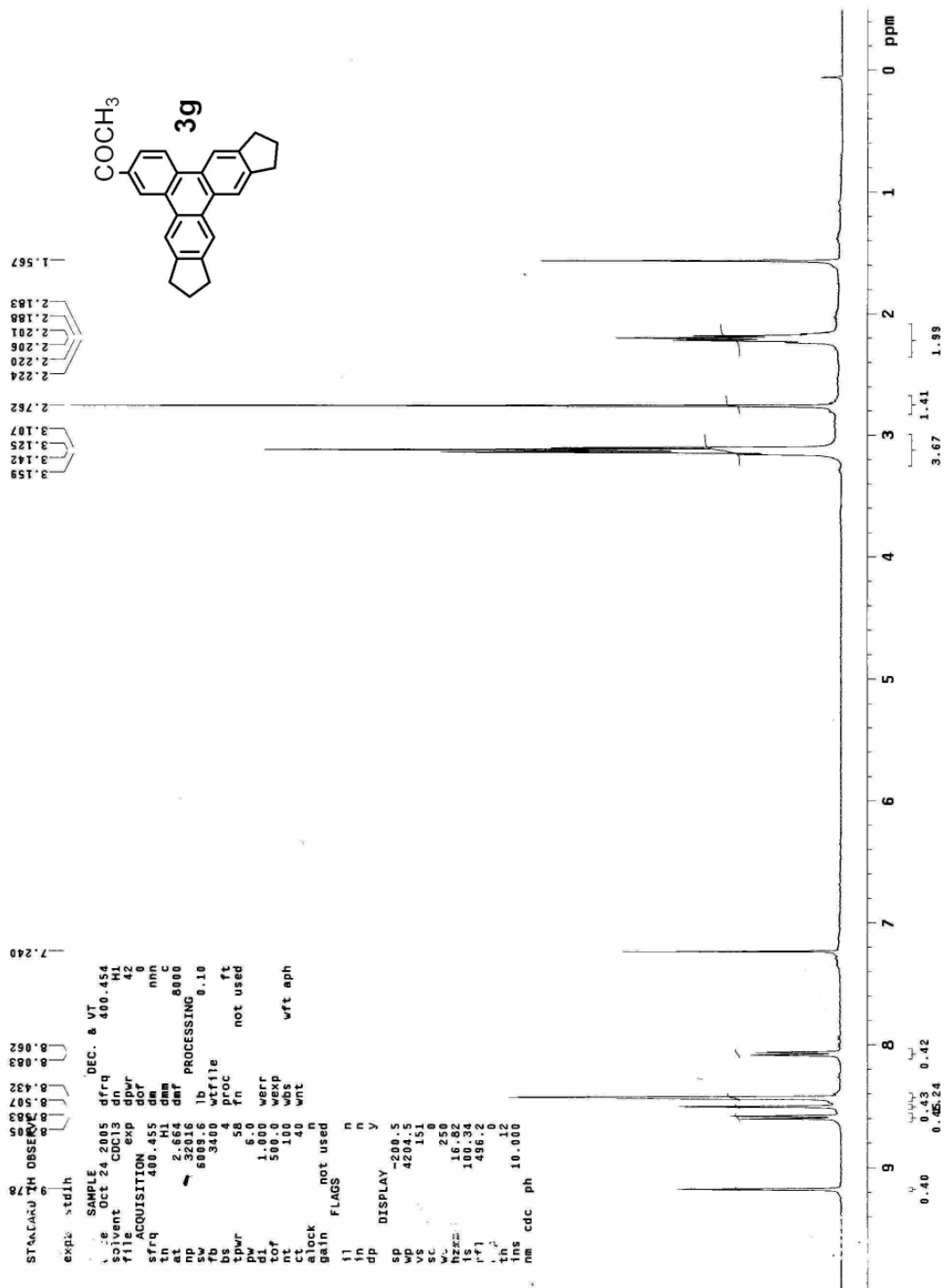
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